Highly Stereoselective Cyclopropanation of Alkenes with Unsymmetrical Diazomalonates *via* Co(II)-Based Metalloradical Catalysis

by

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Department of Chemistry

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ABSTRACT

Highly Stereoselective Cyclopropanation of Alkenes with Unsymmetrical Diazomalonates *via* Co(II)-Based Metalloradical Catalysis

Jingyi Wang

Diazomalonates have been demonstrated, for the first time, as effective radical precursors for asymmetric radical cyclopropanation of alkenes *via* Co(II)-based metalloradical catalysis (MRC). With an optimized D_2-symmetric chiral amidoporphyrin as the supporting ligand, the Co(II)-based metalloradical system can efficiently activate unsymmetrical methyl phenyl diazomalonate (MPDM) for the asymmetric cyclopropanation of alkenes, enabling stereoselective construction of 1,1-cyclopropanediesters bearing two contiguous chiral centers, including at least one all-carbon quaternary stereogenic center. The Co(II)-catalyzed asymmetric cyclopropanation, which operates at room temperature without slow addition of the diazo compound, is generally applicable to a broad range of olefin substrates and tolerates various functionalities, providing a streamlined synthesis of chiral 1,1-cyclopropanediesters in high yields with high level of control in both diastereoselectivity and enantioselectivity. Mechanistic studies on the cyclopropanation reactions, including the use of (*E*)- and (*Z*)-β-deuterostyrenes, support the underlying stepwise radical pathway for the Co(II)-catalyzed cyclopropanation. In addition to functioning as effective 1,3-dipoles for stereospecific formation of five-membered ring structures, the resulting enantioenriched methyl phenyl (*E*)-1,1-cyclopropanediesters serve as useful building blocks for the synthesis of different 1,1-cyclopropanediesters, 1,1-cyclopropaneestercarboxylic acids and 1,1-cyclopropaneesteramides while maintaining the original stereochemistry. Additionally, the enantioenriched (*E*)-1,1-cyclopropanediesters can be converted to (*Z*)-diastereomers without affecting the high enantiopurity.

Keywords: Metalloradical Catalysis (MRC), Cobalt Catalyst, Asymmetric Cyclopropanation of Alkenes, Methyl Phenyl Diazomalonate (MPDM), Synthesis, Stereoselectivity

PhD Advisor: Prof. X. Peter Zhang

Committee Member: Prof. James P. Morken, Prof. Mark L. Snapper

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DEDICATION

I dedicate this dissertation to my parents. Without their continuous love, support and encouragement, it would not have been possible.

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Chapter 1 Developments of Cyclopropanation of Alkenes with Diazomalonates

1.1 Methodologies Developed for the Cyclopropanation of Alkenes with Diazomalonates

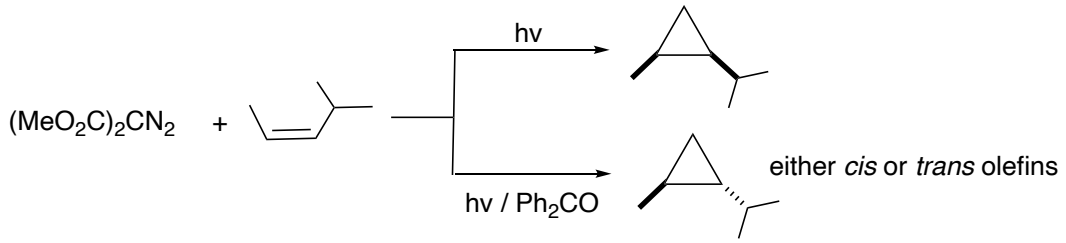
1.1.1 Introduction

The highly strained cyclopropanes moieties exhibit a remarkable reactivity, and have been caused to probe their applications in organic synthesis.[1,2] Since the late 1970s, there have been continuous effects on development of new methods for the installation of vicinal donor and acceptor substituents on the three-membered ring, which are referred to as donor−acceptor (D−A) cyclopropanes, to increase the reactivity of the C−C bond.[3] Different methods have been developed for the cyclopropanation of alkenes. This section we will introduce the methods developed for the cyclopropanation of alkenes with diazomalonates.

1.1.2 Irradiation Initiated Cyclopropanation of Alkenes with Diazomalonates

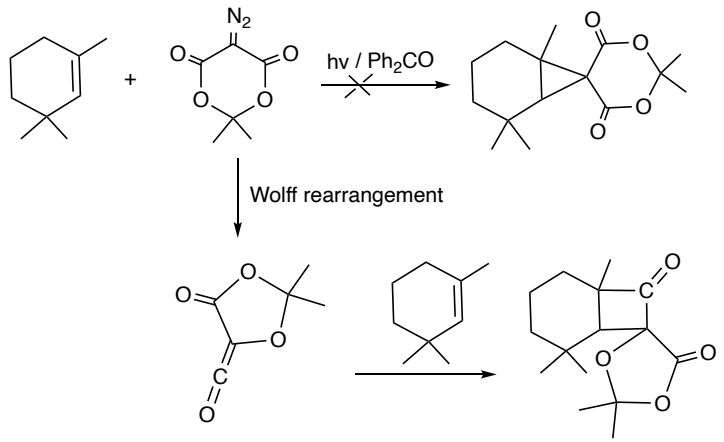
The singlet and triplet biscarbomethoxy carbene can be produced by direct and sensitized (with benzophenone) photo irradiation of methyl diazomalonate, the *in situ* produced carbenes can react with different alkenes including terminal and internal alkenes.[4] It was found that the *cis* adducts were predominately formed when *cis* olefins were used under direct irradiation condition. In contrast, major

trans adducts were isolated either *cis* olefins or *trans* ones were utilized under the sensitized (with benzophenone) irradiation (Scheme 1).



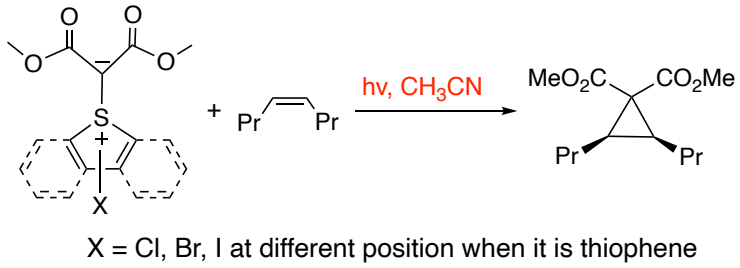
Scheme 1 Cyclopropanation of Olefins with Diazomalonate under Irradiation Condition

The spiro-activated cyclopropanes were originally reported being formed by direct irradiation of isopropylidene diazomalonate with alkenes.[5] In case of 4-tert-butyldimethylsilyloxy-1-cyclopentene, only 15% of the *cis* adduct was formed, whereas 3-*tert*-butyldimethylsilyloxy-1-cyclopentene or *cis*-3,4-methylenedioxy-l-cyclopentene the *trans* adduct was the exclusive produced. It was later proved that the corresponding fused-cyclobutanone (by single crystal X-Ray analysis and spectroscopic methods) was formed *via* a Wolff rearrangement of the initially formed carbene to afford ketene which underwent a remarkably regio- and stereospecific 2+2 cycloaddition with alkenes under the irradiation conditions (Scheme 2).[6]



Scheme 2 Irradiation of Isopropylidene Diazomalonate with Alkenes

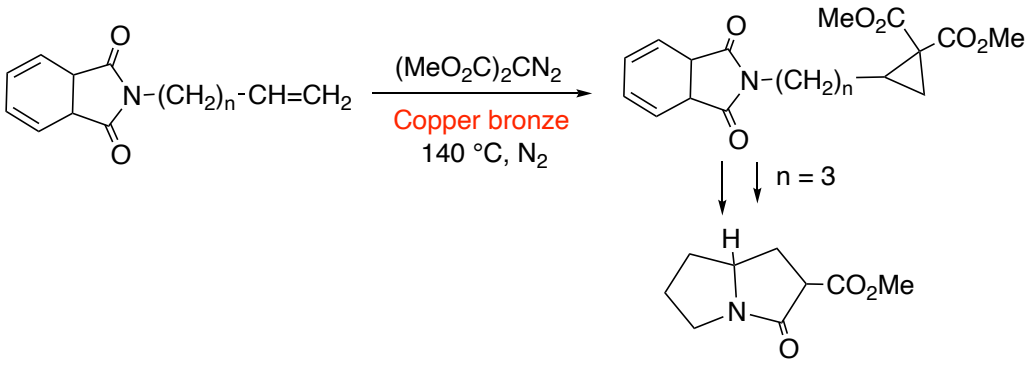
Dicarbomethoxy carbene can be generated by photolysis of S-C sulfonium ylides derived from thiophene or its derivatives, the reaction of the generated carbene with 10% *cis*-4-octene in acetonitrile was performed, the results indicated that the *cis*-product was predominantly generated (Scheme 3).[7]



Scheme 3 Cyclopropanation of Alkenes with Malonate Thiophene Derivative Ylides

1.1.3 Copper Complexes Catalyzed Cyclopropanation of Alkenes with Diazomalonates

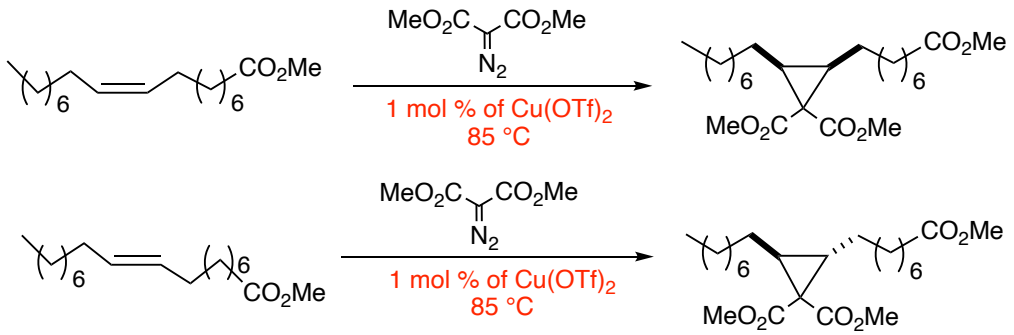
In 1974, Danishefsky and coworkers reported the preparation of the substituted cyclopropanes by cyclopropanation of phthalimido olefins with dimethyl diazomalonate upon heating the mixture of copper bronze at 140 °C under nitrogen. The products can be transferred into the corresponding fused cyclic compounds using appropriate work-up (Scheme 4).[8]



Scheme 4 Cyclopropanation of Phthalimido Olefins with Dimethyl Diazomalonate Catalyzed by Copper Bronze

In 2008, Tüzün and coworkers reported a DFT study on the mechanism of cyclopropanation via $Cu(acac)_2$-catalyzed siazo ester decomposition. They found that the diazo compound bears carbonyl group(s), the four-centered path, involving favorable interactions between copper and the carbonyl group, appears to be a more facile route, whereas the three-centered pathway via direct alkene addition is also a probable facile route for diazo compounds without a C=O group.[9]

The monounsaturated fatty esters with non-activated double bonds have been made to react with dimethyl diazomalonate (DDM) (Scheme 5), in copper catalyzed cyclopropanation reactions. Cyclopropanation reactions of methyl oleate and DDM catalyzed by $Cu(OTf)_2$ produced the product as high as 99% yield under the conditions of DDM:methyl oleate = 6:1 at 85 °C in 24 h.[10]

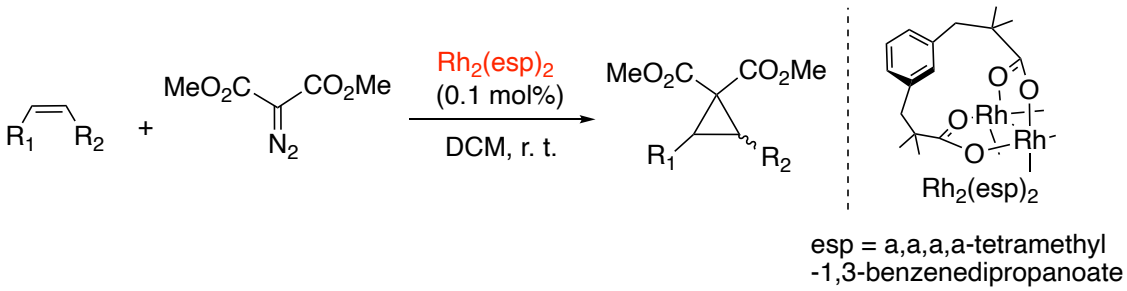


Scheme 5 Cyclopropanation of Monounsaturated Fatty Esters Bearing Non-activated Double Bonds with Dimethyl Diazomalonate Catalyzed by $Cu(OTf)_2$

1.1.4 Rhodium Catalyzed Cyclopropanation of Alkenes with Dimethyl Diazomalonates

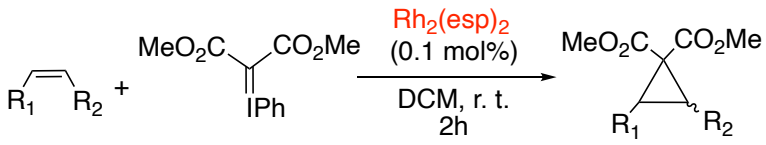
Dirhodium complex [$Rh_2(esp)_2$; esp = α, α, α, α-tetramethyl-1,3-benzenedipropanoate] was found to be outstanding catalyst for the cyclopropanation of a wide range of functionalized styrenes, aliphatic and cyclic alkenes with diazomalonate under mild reaction conditions producing the corresponding 1,1-

cyclopropane diesters (Scheme 6).[11] The terminal alkenes work more efficiently than the internal alkenes do in terms of yields under the same conditions.



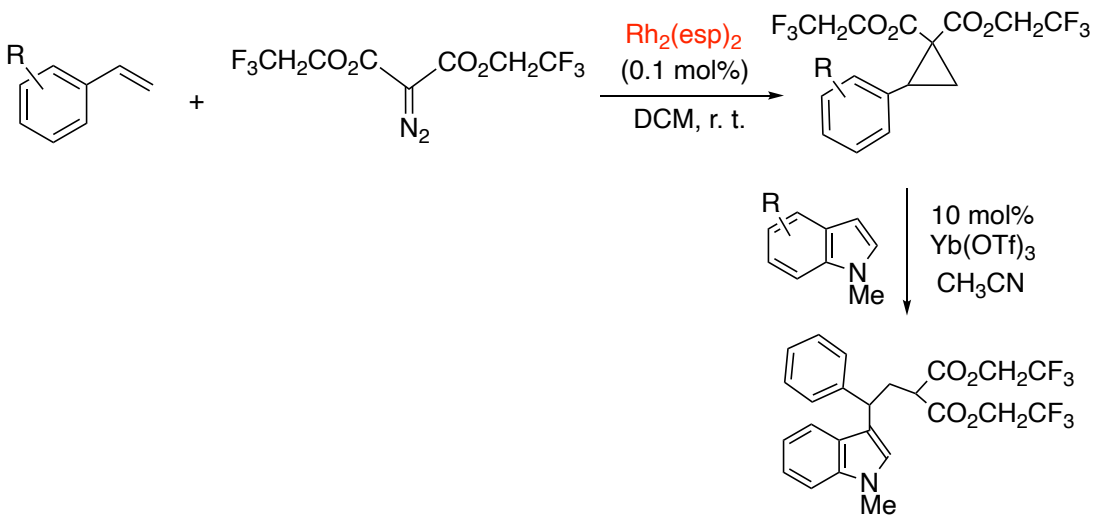
Scheme 6 Cyclopropanation of Alkenes with Diazomalonate Catalyzed by Dirhodium Catalysis

It is found that phenyliodonium ylides can be produced from the reactions of Malonate Esters with $PhI(OAc)_2$ using KOH as a base, the phenyliodonium ylides can be used as carbene equivalent for cyclopropanation of styrene to afford 1,1-cyclopropane diesters. $Rh_2(OAc)_4$ and CuOTf were effective for the cyclopropanation reaction, and $Rh_2(OAc)_4$ was found superior to CuOTf. Thus, various functionalized styrenes were cyclopropanated with phenyliodonium ylides in the presence of 0.1 mol% $Rh_2(esp)_2$ affording the corresponding 1,1-cyclopropane diesters (Scheme 7).[12]



Scheme 7 Cyclopropanation of Alkenes with Iodonium Ylide of Dimethyl Malonate Catalyzed by Dirhodium Complex

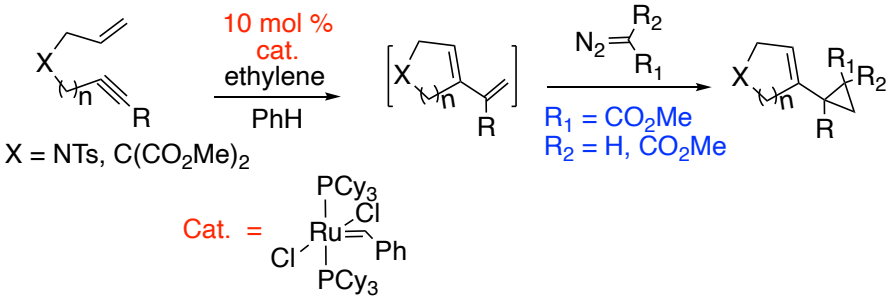
Bis(2,2,2-trifluoroethyl)cyclopropane-1,1-dicarboxylates were successfully prepared by treating diazo-bis-222-trifluoroethylmalonate with a variety of alkenes in the presence of 0.1 mol% rhodium catalysis $Rh_2(esp)_2$. The corresponding esters were reacted with *N*-methylindole under conditions of 10 mol% $Yb(OTf)_3$ in acetonitrile to produce the expected adducts in good to excellent yields, however the reaction times indicate a greatly enhanced reactivity of the fluorinated substrates (Scheme 8).[13]



Scheme 8 Cyclopropanation of Alkenes with Diazo-bis-222-trifluoroethylmalonate Catalyzed by Dirhodium Catalysis

1.1.5 Ruthenium(II) and Osmium(II) Catalyzed Cyclopropanation of Alkenes with Dimethyl Diazomalonates

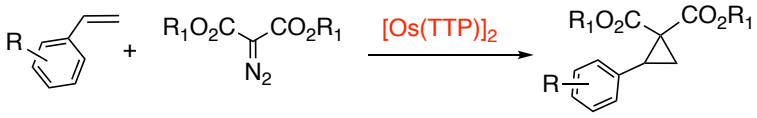
Alkenyl cyclopropanes were prepared by a tandem ring-closing enyne metathesis/ cyclopropanation by treatment of various diazo compounds with the *in situ* prepared 1,3-dienes using Grubbs I catalyst (Scheme 9).[14]



Scheme 9 Synthesis of Alkenyl Cyclopropanes by a Tandem Ring-closing Enyne Metathesis/ Cyclopropanation Catalyzed by Grubbs I Catalysis

The crystal structure of (5,10,15,20-tetraphenylporphyrinato)ruthenium(II) (diethoxycarbonyl)carbene(methanole) was determined, the complex was proved to be effective catalysis for cyclopropanation of styrene with EDA (ethyl diazoacetate).[15]

The (5,10,15,20-tetra-*p*-tolylporphyrinato)osmium(II) complex was also effective for the cyclopropanation of styrene with diazo reagents (carbene sources). The reaction was proved to proceed more slowly with diester diazo reagents than with monoester diazo reagents (Scheme 10).[16]



Scheme 10 Cyclopropanation of Styrenes with Diazomalonate Catalyzed by Osmium(II) Catalysis

1.2 Recent Developments of Transition Metal Catalyzed Enantioselective Cyclopropanation of Alkenes with Diazomalonates

1.2.1 Introduction

Catalytic cyclopropanation of alkenes with diazomalonates presents a potentially attractive approach for the synthesis of the highly valuable 1,1-cyclopropanediesters with a possibility of controlling stereoselectivity.[17] The application of 1,1-cyclopropanediesters in organic synthesis includes cycloaddition reaction,[18] ring opening reactions[19] and rearrangements.[20] Those further transformations are also utilized in various cases of total synthesis.[21] Compared with symmetrical diazomalonate, asymmetric cyclopropanation with unsymmetrical diazomalonates will create an extra chiral center to generate diastereomers so that the challenge and applications will also increase. To the best of our

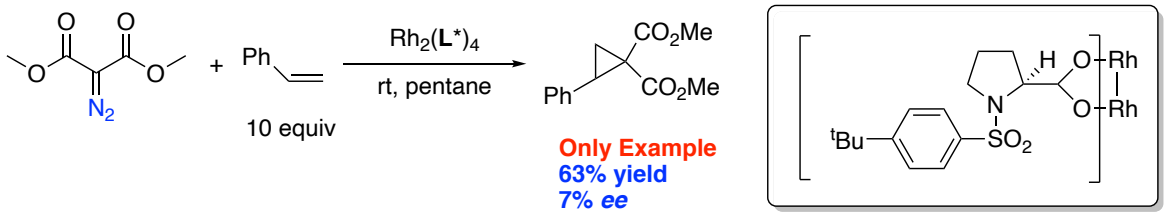
knowledge, unsymmetrical diazomalonates have not been previously employed for asymmetric olefin cyclopropanation.

1.2.2 Previous Report on Asymmetric Synthesis of 1,1-Diestercyclopropanes

1.2.2.1 Asymmetric Cyclopropanation with diazomalonates

Because of their low reactivity and inherent challenge of stereocontrol associated with the two similar electron-withdrawing ester groups, the use of diazomalonates as carbene precursors for asymmetric olefin cyclopropanation by existing catalytic systems has been limited with substrate scope and hampered by low enantioselectivity.

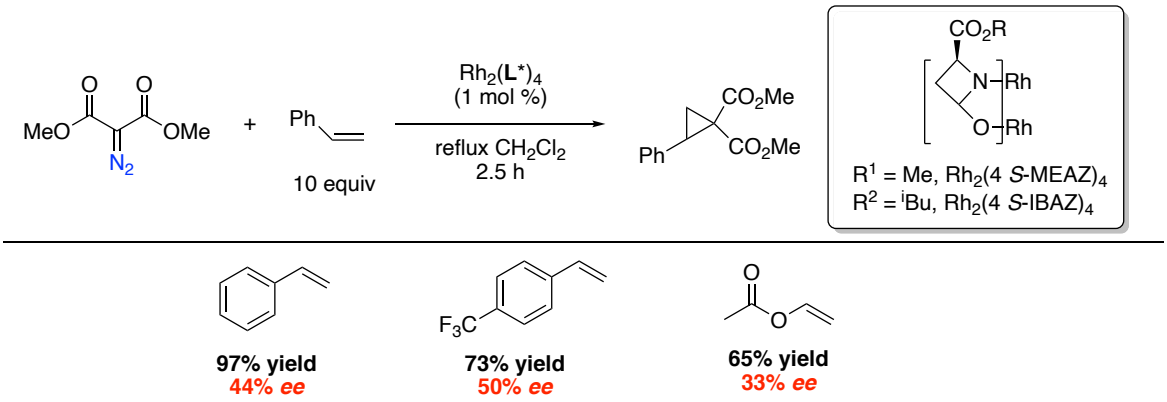
In 1996, Davies group reported the Rhodium(II) (*S*)-*N*-(arylsulfonyl)prolinate catalyzed cyclopropanation carbenoids containing two electron withdrawing groups resulted in cyclopropanation with low enantioselectivity as the first and only example of catalytic asymmetric cyclopropanation with diazomalonate (Scheme 11).[22] However, with good yield (63% yield), the enantioselectivity delivered only in a poor level (7%).



Scheme 11 Rhodium(II) (S)-N-(arylsulfonyl)prolinate Catalyzed Cyclopropanation of Diazomalonate with Styrene

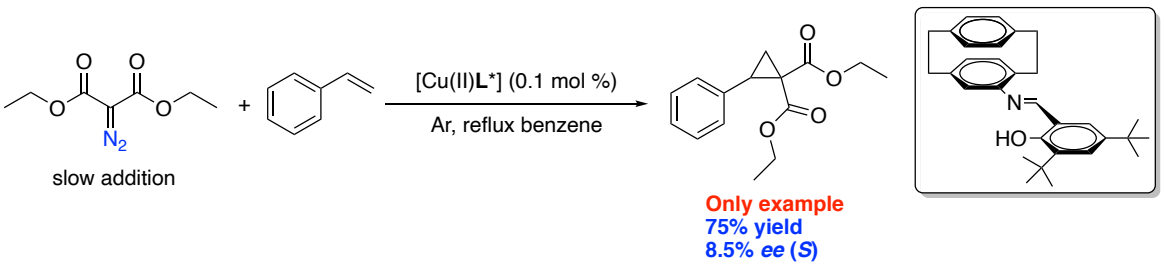
In the year of 2000, Doyle group reported a dirhodium catalyzed intramolecular cyclopropanation. In this study, they were surprised to discover that dirhodium(II) tetrakis[methyl 2-oxaazetidine-4(*S*)-carboxylate], Rh_2(4*S*-MEAZ)$_4$ was an effective catalyst for cyclopropanation reactions with dimethyl diazomalonate (Scheme 12).[23] The up to 50% enantioselectivity was the highest yet reported, and even

for cyclopropanation of the highly reactive and normally unselective vinyl acetate, the enantiometric excess of the cyclopropanation product was 33%.



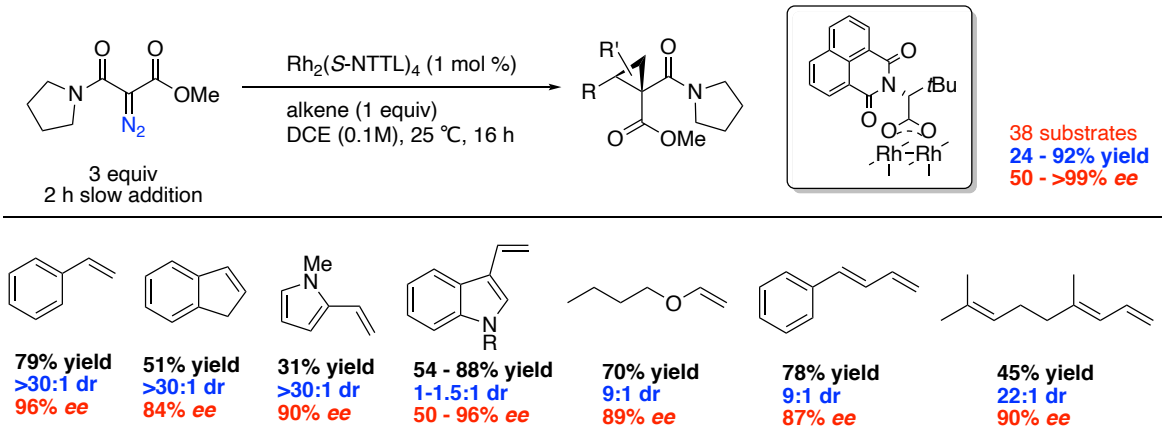
Scheme 12 Dirhodium(II) Tetrakis[methyl 2-oxaazetidine-4-carboxylate] Catalyzed Cyclopropanation of Diazomalonate with Styrene

Glatzhofer group, in the year of 2000, evaluated an asymmetric ligand for the copper-catalyzed cyclopropanation reaction using styrene (Scheme 13).[24] In an attempt to better understand the origin of the enantioselective induction of ligand, (*S*)-ligand was used as the ligand in the cyclopropanation of styrene with diethyldiazomalonate (DDM) synthesized from diethyl malonate using a diazo transfer reaction. The derivative of the 1,1-cyclopropanediester was subjected to polarimetry that revealed an enantioselectivity of 8.5% and the major product had the (*S)* absolute configuration.



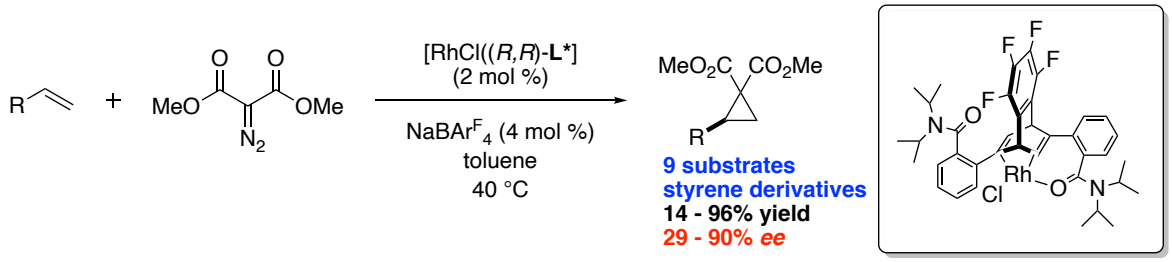
Scheme 13 N-(2',4'-Di-*tert*-butyl)salicylidene-4-amino[2.2]paracyclophane as an Asymmetric Ligand for the Enantioselective Cyclopropanation

In 2008, Charette group reported a novel stereoselective synthesis of cyclopropane bearing geminal dicarboxy groups with excellent enantio- and diastereocontrol utilizing the unprecedented *trans*-directing ability of an amide (Scheme 14).[25] [Rh_2(*S*-nttl)$_4$] was the most promising catalyst, giving >75% ee and >30:1 d.r. when using diazo reagent bearing pyrrolidine amide. The diazo reagent reacts with a variety of mono- and disubstituted alkenes in good to excellent yields.



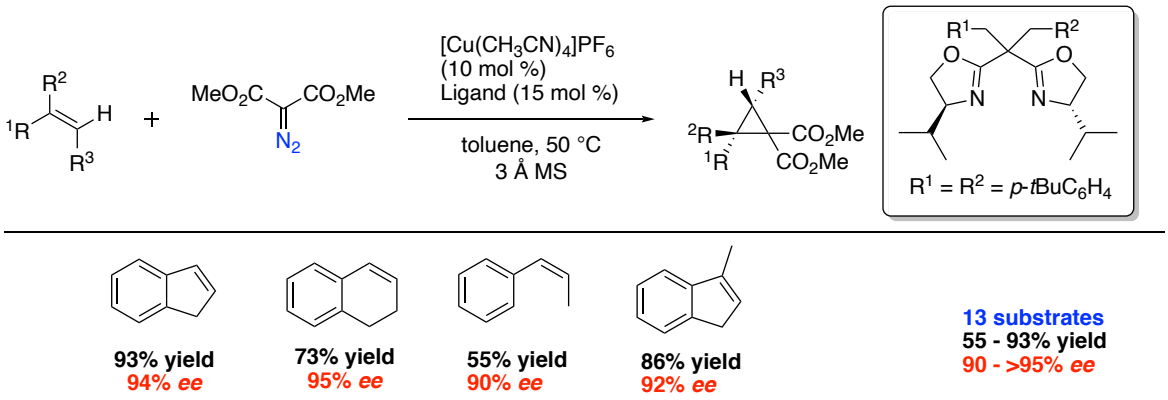
Scheme 14 *trans*-Directing Ability of Amide Groups Bearing Diazo Reagents in Cyclopropanation

In 2010, Hayashi group focused on a rhodium(I) catalyst bearing a single coordination site for the decomposition of dimethyl diazomalonate to generate the rhodiumcarbene in the asymmetric cyclopropanation of alkenes (Scheme 15).[26] The use of isolated monomeric rhodium–diene complex [RhCl((*R*,*R*)-**L***)] combined with $NaBArF_4$ led to high enantioselectivity. The cyclopropanation of styrene derivatives bearing a variety of substituents on the benzene rings gave the corresponding cyclopropane diesters in good yields, with enantioselectivities ranging from 80 to 90% ee. However, their substrate scope limited to only styrene derivatives and showed no functional group tolerance.



Scheme 15 Asymmetric Cyclopropanation of Alkenes with Dimethyl Diazomalonate Catalyzed by Chiral Diene–Rhodium Complexes

Recently, in 2017, Tang group reported the first enantioselective copper catalyzed cyclopropanation of internal olefins with diazomalonates. This process provided a new method for the synthesis of chiral 1,1-cyclopropane diesters (Scheme 16).[27] With a chiral bi-side arm bisoxazoline−copper(I) complex, the reaction performed well over a series of substrates, giving the desired products in good yields (up to 95%) and excellent enantioselectivities (90−95% ee).



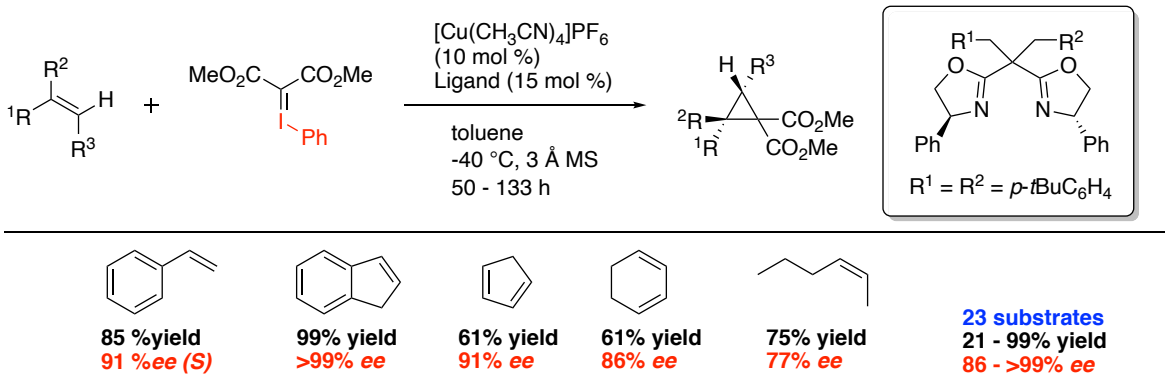
Scheme 16 Copper-Catalyzed Enantioselective Cyclopropanation of Internal Olefins with Diazomalonates

1.2.2.2 Phenyliodonium Ylides Utilized as Surrogates of Diazo Reagents

Because of diazomalonates' low reactivity and difficulties of stereocontrol due to the two similar electron-withdrawing ester groups, the corresponding phenyliodonium ylides, a class of alternative reagents that are more reactive but less stable and difficult to prepare, have been utilized as the surrogates

of diazomalonates for olefin cyclopropanation to synthesize 1,1-cyclopropanediesters with generation of stoichiometric amount of iodobenzene as a byproduct. But the underlying disadvantages involve with one more step of preparation, unstableness and one stoichiometric of byproduct.

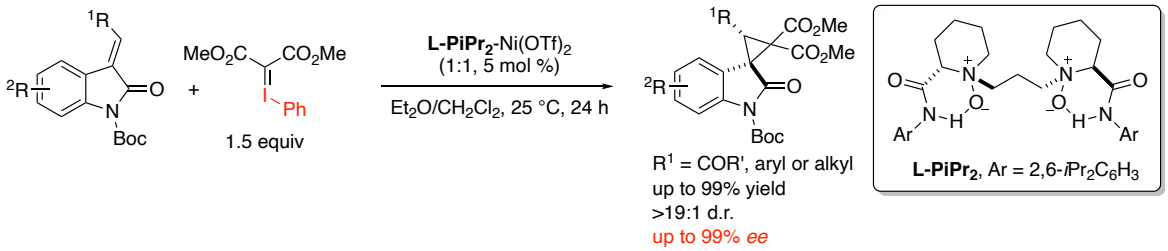
In 2012, Tang group developed a facile cagelike bisoxazoline–copper(I) complex chiral catalyst for the catalytic enantioselective cyclopropanation of multisubstituted olefins with phenyliodonium ylide malonate (Scheme 17).[28] The substrates include terminal, disubstituted, and trisubstituted olefins, giving the desired products in excellent yield (up to 99%) with enantioselectivity (up to >99% ee). This protocol provides an efficient method for the synthesis of chiral 1,1-cyclopropane diesters. However, this method was applied under low temperature as -40 °C and proceeded for time as long as 50-133 hours, which could be inconvenient practically.



Scheme 17 A Chiral Cagelike Copper(I) Catalyst for the Highly Enantioselective Synthesis of 1,1-Cyclopropane Diesters

Feng group, in 2016, reported phenyliodonium ylide as the carbene precursor to promote chiral Lewis acid-catalyzed enantioselective cyclopropanation of the activated alkenes (Scheme 18).[29] A variety of spirocyclopropane-oxindoles, which are versatile building blocks for the synthesis of natural products and pharmaceuticals, with contiguous tertiary and all carbon quaternary centers were obtained in excellent outcomes (up to 99% yield, >19 : 1 d.r., up to 99% ee). The chiral *N*,*N*'-dioxide/Ni(OTf)$_2$

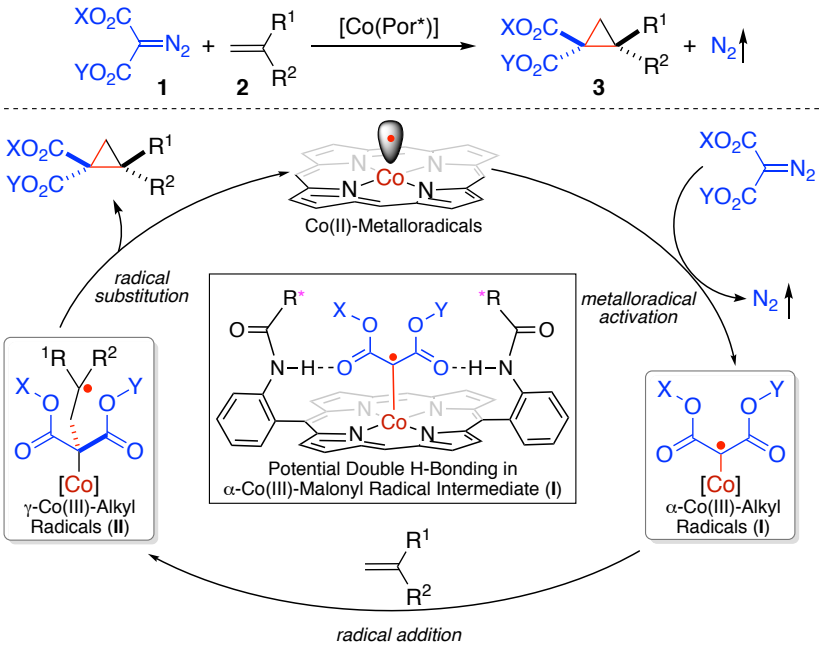
complex exhibited excellent performance in the reaction of 3-alkenyl-oxindoles with phenyliodonium ylide malonate under mild reaction conditions.



Scheme 18 Nickel(II)-Catalyzed Enantioselective Cyclopropanation of 3-alkenyl-oxindoles with Phenyliodonium Ylide via Free Carbene

1.3 Summary and Outlook

Given that asymmetric olefin cyclopropanation with diazomalonates is an important transformation with unaddressed issues, we were prompted to explore a potential solution via the Co(II)-MRC on the supposition that the generation and stabilization of the corresponding α-Co(III)-malonyl radicals I would be significantly facilitated by the double H-bonding interactions (Scheme 19).



Scheme 19 Working Proposal for Cyclopropanation of Alkenes with Diazomalonates via Co(II)-Based Metalloradical Catalysis

More challengingly, if unsymmetrical diazomalonates are used, could the stereochemistry of the two newly-formed chiral centers in the resulting 1,1-cyclopropanediesters be controlled? Considering that the two substituents in intermediate I are both ester groups, could the incoming olefin effectively differentiate the two pro-chiral faces of the Co-supported C-centered radical for enantioselective generation of the first stereocenter (Scheme 9)? For the same consideration, could the two similar ester substituents effectively discriminate the two pro-chiral faces of the *γ*-Co(III)-alkyl radical II during 3-exo-tet radical cyclization for diastereoselective C–C bond formation (Scheme 19)? If these challenges could be addressed through the use of proper [Co(D2-Por*)] catalyst, it would lead to the development of a new catalytic system for asymmetric cyclopropanation of alkenes with unsymmetrical diazomalonates to construct the optically active 1,1-cyclopropanediesters, which have been demonstrated as versatile building blocks for wide-ranging synthetic applications.

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Chapter 2 Highly Stereoselective Cyclopropanation of Alkenes with Unsymmetrical Diazomalonates via Co(II)-Based Metalloradical Catalysis

2.1 Introduction

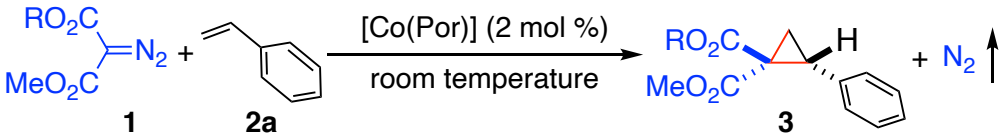
Here, we want to report the development of the first catalytic system via Co(II)-based MRC that is highly effective for asymmetric cyclopropanation of alkenes with unsymmetrical diazomalonates. We describe the significant ligand effects on the Co(II)-catalyzed cyclopropanation, leading to the identification of a suitable D2-symmetric chiral amidoporphyrin for the catalytic process. We show that the optimized catalytic system is remarkably general and can be efficiently applied to a broad range of alkenes, affording various 1,1-cyclopropanediesters in high yields with effective control in both diastereoselectivity and enantioselectivity of the two newly-constructed contiguous chiral centers. Among other attributes, the Co(II)-based metalloradical system is highlighted by a high degree of functional group tolerance. In addition to demonstrating synthetic utility of the enantioenriched 1,1-cyclopropanediester products, we present experimental evidence that agrees with the underlying stepwise radical mechanism for the new Co(II)-based catalytic system.

2.2 Results and Discussion

2.2.1 Condition Optimization of the Co(II)-Based Catalytic System for Enantioselective Cyclopropanation of Styrene with Diazomalonate

Our study began with the investigation of catalytic cyclopropanation reaction of styrene (**2a**) with the unsymmetrical benzyl methyl diazomalonate (**1a**) (Table 1).

Table 1 Ligand Effects on the Co(II)-Based Catalytic System for Cyclopropanation of Styrene with Unsymmetrical Diazomalonates[a]



1 **2a** **3**

entry	diazomalonate	[Co(Por)]	product	yield (%)[b]	(*E*):(*Z*)[c]	ee (%)[d]
1	**1a** (R = Bn)	[Co(TPP)]	(±)-**3a**	0	—	—
2	**1a** (R = Bn)	[Co(**P1**)]	(±)-**3a**	20	51:49	—
3	**1a** (R = Bn)	[Co(**P2**)]	(+)-**3a**	33	58:42	46
4	**1a** (R = Bn)	[Co(**P3**)]	(+)-**3a**	37	58:42	64
5	**1a** (R = Bn)	[Co(**P4**)]	(+)-**3a**	42	67:33	75
6	**1b** (R = ^{t}Bu)	[Co(**P4**)][e]	(+)-**3b**	56	88:12	87
7	**1c** (R = Ph)	[Co(**P4**)]	(+)-**3c**	**99**	**94:6**	**96**

[a] Carried out with diazomalonates **1** (0.10 mmol) and **2a** (0.12 mmol) in toluene at room temperature for 24 h in one-time fashion without slow addition using [Co(Por)] (2 mol %) under N_2. [b] Isolated yields. [c] Diastereomeric ratio (dr) determined by ^{1}H NMR. [d] Enantiomeric excess (ee) determined by chiral HPLC. [e] Using [Co(Por)] (5 mol %).

It was found that [Co(TPP)] (TPP = 5,10,15,20-tetraphenylporphyrin), the simple Co(II)-metalloradical catalyst, was inactive for the transformation, failing to provide any of the desired 1,1-cyclopropanediester **3a** (entry 1).

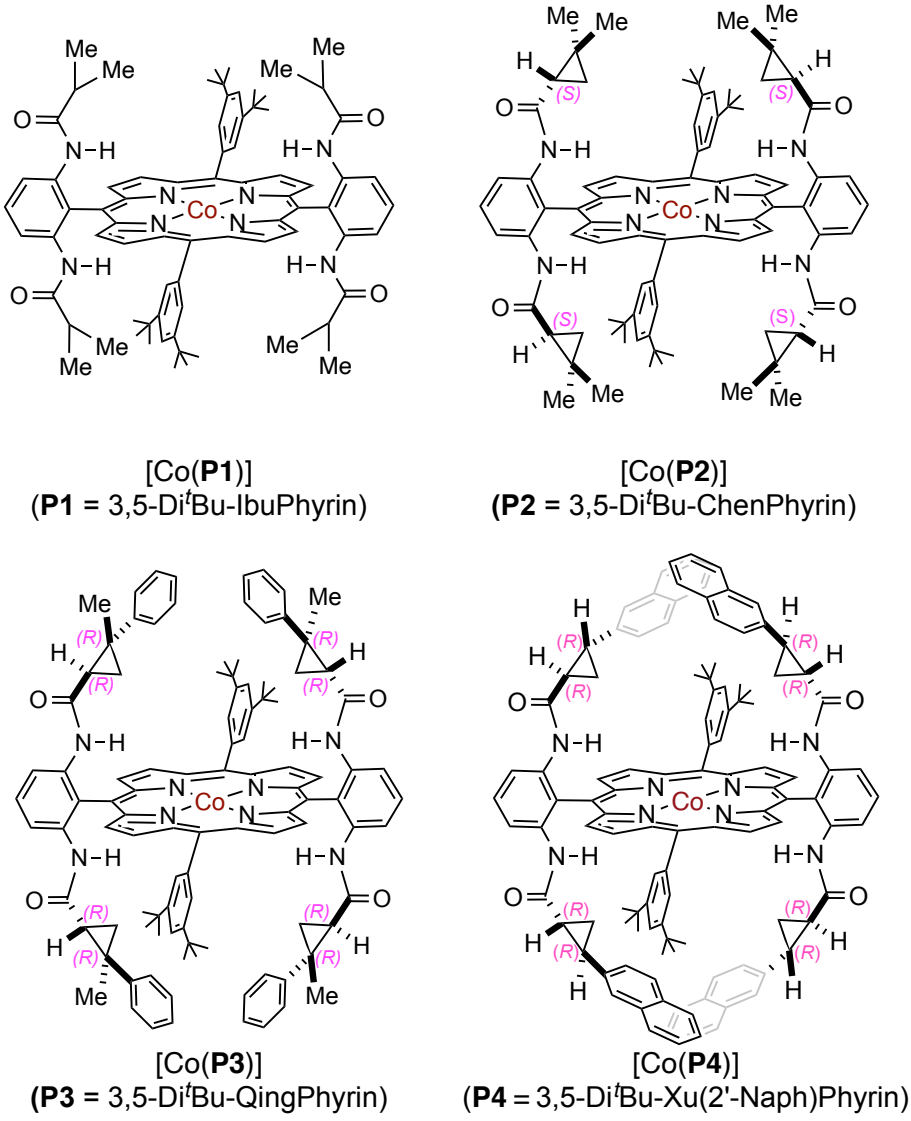


Figure 1 Achiral and Chiral Co(II)-Based Amidoporphyrin Catalyst Utilized in Condition Optimization for the Asymmetric Cyclopropanation of Styrene with Diazomalonate

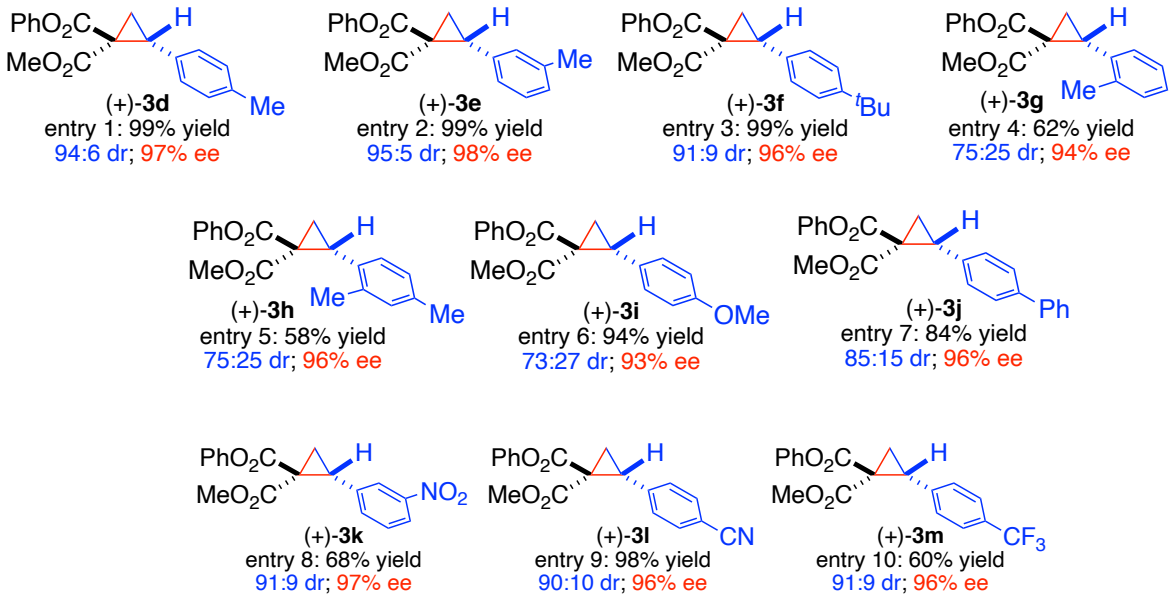
However, with the use of achiral amidoporphyrin catalyst [Co(**P1**)] (**P1** = 3,5-Di^{t}Bu-IbuPhyrin) (Figure 1), the reaction could proceed at room temperature and deliver the desired cyclopropane product **3a** in low but significant yield (Table 1, entry 2). The difference in catalytic activity between [Co(TPP)] and [Co(**P1**)] signifies the importance of the proposed double hydrogen-bonding interactions in activating and stabilizing the α-Co(III)-malonyl radical intermediate **I** (Scheme 19).

On the other hand, the formation of cyclopropane **3a** in almost equal ratio of (*E*)- and (*Z*)-diastereomers (Table 1, entry 2) clearly indicates the aforementioned challenge associated with the differentiation of the two similar ester groups during the catalytic process. When using the first-generation chiral metalloradical catalyst [Co(**P2**)] (**P2** = 3,5-Di^{t}Bu-ChenPhyrin), it delivered 1,1-cyclopropanediester **3a** in moderate enantioselectivity while improving both the yield and diastereoselectivity (Table 1, entry 3). When switching to the second-generation metalloradical catalyst [Co(**P3**)] (**P3** = 3,5-Di^{t}Bu-QingPhyrin), which differs from [Co(**P2**)] by replacing one of the two methyl groups in the chiral amides with a phenyl group for potential π-stacking interactions, it improved the enantioselectivity significantly without affecting the yield and diastereoselectivity (Table 1, entry 4). Further improvements in both stereoselectivities and reactivity were observed by using catalyst [Co(**P4**)] (**P4** = 3,5-Di^{t}Bu-Xu(2'-Naph)Phyrin) that bears naphthyl groups (Table 1, entry 5), indicating the possibility of enhanced π-stacking interactions. Replacement of diazomalonate **1a** by more sterically-hindered *tert*-butyl methyl diazomalonate (**1b**) afforded the corresponding 1,1-cyclopropanediester **3b** in higher yield as well as with better diastereoselectivity and enantioselectivity (Table 1, entry 6). To our delight, when methyl phenyl diazomalonate (MPDM; **1c**) was used as the radical precursor, the cyclopropanation of styrene by [Co(**P4**)] gave the corresponding 1,1-cyclopropanediester **3c** in almost quantitative yield with 96% ee and 94:6 dr (Table 1, entry 7).

2.2.2 Asymmetric Radical Cyclopropanation of Different Olefin Substrates

Under the optimized conditions, the scope of the [Co(**P4**)]-catalyzed asymmetric cyclopropanation with MPDM (**1c**) was investigated by using different types of alkenes as the substrates (Table 2).

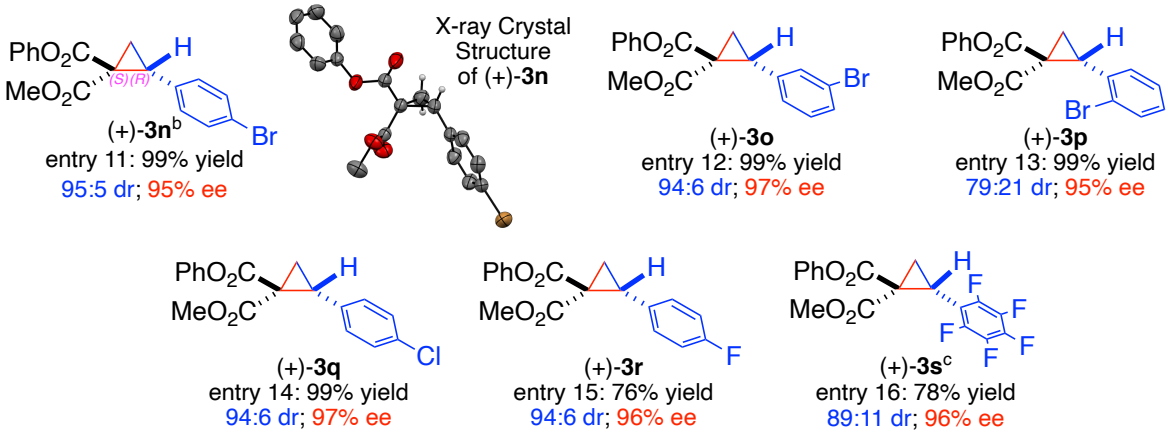
Table 2 [Co(P4)]-Catalyzed Asymmetric Radical Cyclopropanation of Alkenes with Methyl Phenyl Diazomalonate (MPDM)[a]



[a] Carried out with diazomalonate **1c** (0.10 mmol) and alkene **2** (0.12 mmol) in toluene at room temperature for 24 h in one-time fashion without slow addition using [Co(**P4**)] (2 mol %) under N_2; Isolated yields; Diastereomeric ratio (dr) determined by ^{1}H-NMR; Enantiomeric excesses (ee) determined by chiral HPLC.

Like styrene, styrene derivatives with alkyl substituents could be effectively cyclopropanated with MPDM by [Co(**P4**)], affording the corresponding 1,1-cyclopropanediesters **3d**–**3f** in almost quantitative yields with both excellent diastereoselectivities and enantioselectivities (Table 2, entries 1–3). The [Co(**P4**)]/MPDM-based system was able to cyclopropanate sterically encumbered 2-methylstyrene and 2,4-dimethylstyrene as well, forming the desired cyclopropanes **3g** and **3h** with high enantioselectivities despite in moderate yields and diastereoselectivities (Table 2, entries 4 and 5). Styrenes substituted with both electron-donating and electron-withdrawing groups were found to be also suitable substrates for the catalytic system as demonstrated with the formation of cyclopropanes **3i**–**3m** (Table 2, entries 6–10).

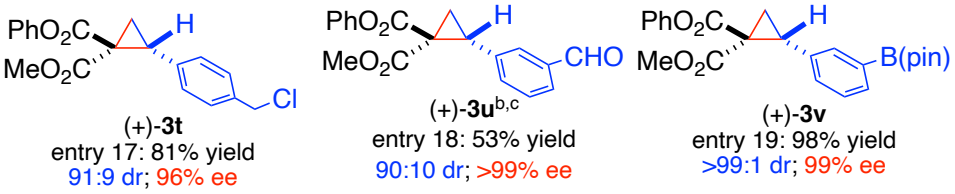
Table 3 [Co(P4)]-Catalyzed Asymmetric Radical Cyclopropanation of Halogenated Styrenes with Methyl Phenyl Diazomalonate (MPDM)[a]



[a] Carried out with diazomalonate **1c** (0.10 mmol) and alkene **2** (0.12 mmol) in toluene at room temperature for 24 h in one-time fashion without slow addition using [Co(**P4**)] (2 mol %) under N_2; Isolated yields; Diastereomeric ratio (dr) determined by ^{1}H NMR; Enantiomeric excesses (ee) determined by chiral HPLC. [b] Absolute configuration determined by X-ray crystallography. [c] With **2** (0.50 mmol).

Additionally, halogenated styrenes, including those substituted with Br, Cl and F atoms, could be catalytically transformed to the desired products **3n**–**3s** in high yields with excellent stereoselectivities (Table 3, entries 11–16). It is worthy of noting that even the highly electron-deficient pentafluorostyrene could be successfully cyclopropanated to produce the desired product **3s** (entry 16).

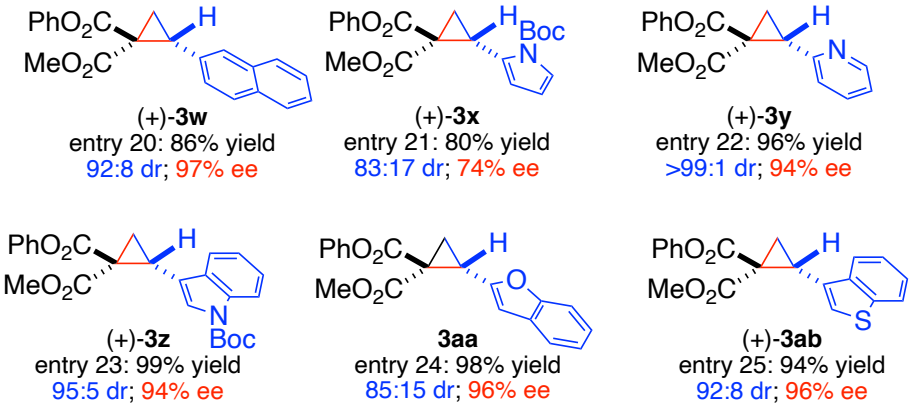
Table 4 [Co(P4)]-Catalyzed Asymmetric Radical Cyclopropanation of Styrenes with Aldehyde and Boron Functionality with Methyl Phenyl Diazomalonate (MPDM)[a]



[a] Carried out with diazomalonate **1c** (0.10 mmol) and alkene **2** (0.12 mmol) in toluene at room temperature for 24 h in one-time fashion without slow addition using [Co(**P4**)] (2 mol %) under N_2; Isolated yields; Diastereomeric ratio (dr) determined by ^{1}H NMR; Enantiomeric excesses (ee) determined by chiral HPLC. [b] With **2** (1.00 mmol). [c] Using [Co(**P4**)] (5 mol %).

The Co(II)-catalyzed asymmetric cyclopropanation was shown to tolerate additional functionalities such as chloromethyl, formyl and pinacolborane groups for the production of the functionalized cyclopropanes **3t**–**3v** (Table 4, entries 17–19).

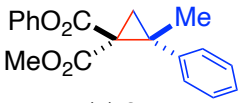
Table 5 [Co(P4)]-Catalyzed Asymmetric Radical Cyclopropanation of Naphthyl and Heteroaromatic Alkenes with Methyl Phenyl Diazomalonate (MPDM)[a]



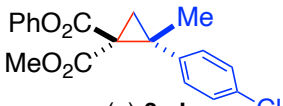
[a] Carried out with diazomalonate **1c** (0.10 mmol) and alkene **2** (0.12 mmol) in toluene at room temperature for 24 h in one-time fashion without slow addition using [Co(**P4**)] (2 mol %) under N_2; Isolated yields; Diastereomeric ratio (dr) determined by ^1H NMR; Enantiomeric excesses (ee) determined by chiral HPLC.

Furthermore, the metalloradical system was found to be compatible with polyaromatic and heteroaromatic olefins as exemplified by the stereoselective synthesis of cyclopropane derivatives **3w**–**3z** and **3aa**–**3ab** containing naphthalene, pyrrole, pyridine, indole, benzofuran and benzothiophene, affording the corresponding products very good yields with excellent enantioselectiviyt, respectively (Table 5, entries 20–25).

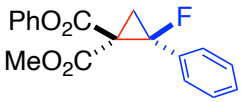
Table 6 [Co(P4)]-Catalyzed Asymmetric Radical Cyclopropanation of α-Substituted Styrenes with Methyl Phenyl Diazomalonate (MPDM)[a]



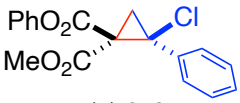
(+)-**3ac**
entry 26: 99% yield
89:11 dr; 97% ee



(+)-**3ad**
entry 27: 99% yield
87:13 dr; 98% ee



(+)-**3ae**
entry 28: 88% yield
92:8 dr; 94% ee

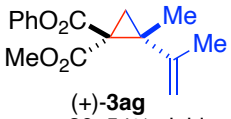


(+)-**3af**
entry 29: 78% yield
92:8 dr; 97% ee

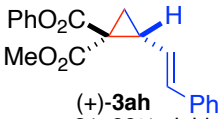
[a] Carried out with diazomalonate **1c** (0.10 mmol) and alkene **2** (0.12 mmol) in toluene at room temperature for 24 h in one-time fashion without slow addition using [Co(**P4**)] (2 mol %) under N_2; Isolated yields; Diastereomeric ratio (dr) determined by ^1H NMR; Enantiomeric excesses (ee) determined by chiral HPLC.

With the use of *α*-substituted styrenes as the substrates, the Co(**P4**)-based catalytic system could efficiently construct cyclopropane structures **3ac**–**3af** with effective control of the two contiguous quaternary stereocenters with excellent enantioselectivity (Table 6, entries 26–29).

Table 7 [Co(P4)]-Catalyzed Asymmetric Radical Cyclopropanation of Conjugated Dienes and Enynes with Methyl Phenyl Diazomalonate (MPDM)[a]



(+)-**3ag**
entry 30: 54% yield
60:40 dr; 87% ee



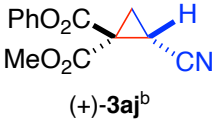
(+)-**3ah**
entry 31: 99% yield
68:32 dr; 83% ee

(+)-**3ai**
entry 32: 99% yield
74:26 dr; 82% ee

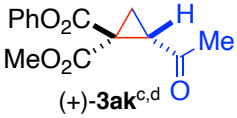
[a] Carried out with diazomalonate **1c** (0.10 mmol) and alkene **2** (0.12 mmol) in toluene at room temperature for 24 h in one-time fashion without slow addition using [Co(**P4**)] (2 mol %) under N_2; Isolated yields; Diastereomeric ratio (dr) determined by ^{1}H NMR; Enantiomeric excesses (ee) determined by chiral HPLC.

In addition to aromatic olefins, the [Co(**P4**)]/MPDM-based asymmetric system could be effectively applied to conjugated dienes and enynes, enabling chemoselective cyclopropanation of the terminal alkene units to form 2-alkenyl- and 2-alkynyl-1,1-cyclopropanediesters **3ag**–**3ai** with very high enantioselectivity (Table 7, entries 30–32).

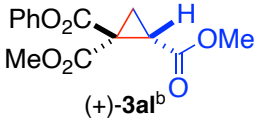
Table 8 [Co(P4)]-Catalyzed Asymmetric Radical Cyclopropanation of Electron-Deficient Alkenes with Methyl Phenyl Diazomalonate (MPDM)[a]



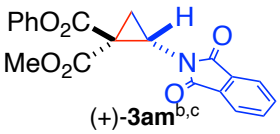
(+)-**3aj**[b]
entry 33: 73% yield
80:20 dr; 95% ee



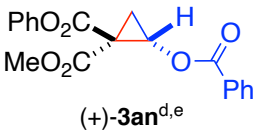
(+)-**3ak**[c,d]
entry 34: 72% yield
75:25 dr; 96% ee



(+)-**3al**[b]
entry 35: 85% yield
54:46 dr; 90% ee



(+)-**3am**[b,c]
entry 36: 77% yield
91:9 dr; 95% ee



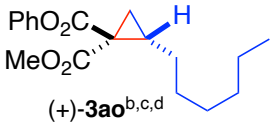
(+)-**3an**[d,e]
entry 37: 94% yield
75:25 dr; 71% ee

[a] Carried out with diazomalonate **1c** (0.10 mmol) and alkene **2** (0.12 mmol) in toluene at room temperature for 24 h in one-time fashion without slow addition using [Co(**P4**)] (2 mol %) under N_2; Isolated yields; Diastereomeric ratio (dr)

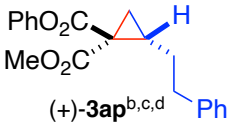
determined by ^{1}H NMR; Enantiomeric excesses (ee) determined by chiral HPLC. [b] With **2** (0.50 mmol). [c] With **2** (1.00 mmol). [d] Using [Co(**P4**)] (5 mol %). [e] With **2** (2.00 mmol).

Furthermore, electron-deficient alkenes such as acrylonitrile, methyl vinyl ketone and methyl acrylate, which are typically problematic substrates for existing catalytic systems involving electrophilic metallocarbene intermediates, could also be productively cyclopropanated with MPDM by [Co(**P4**)], providing the highly-electrophilic multi-functionalized cyclopropanes **3aj**–**3al** with excellent enantioselectivities albeit varied diastereoselectivities due to relatively smaller sizes compared with aromatic olefins (Table 8, entries 33–35). Electron-rich alkenes such as *N*-vinylphthalimide and vinyl benzoate could also serve as good substrates for the asymmetric cyclopropanation, affording the corresponding donor-acceptor cyclopropanes **3am** and **3an** stereoselectively (Table 8, entries 36 and 37).

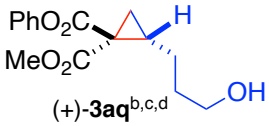
Table 9 [Co(P4)]-Catalyzed Asymmetric Radical Cyclopropanation of Aliphatic Alkenes with Methyl Phenyl Diazomalonate (MPDM)[a]



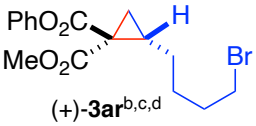
(+)-**3ao**[b,c,d]
entry 38: 74% yield
80:20 dr; 72% ee



(+)-**3ap**[b,c,d]
entry 39: 77% yield
83:17 dr; 80% ee



(+)-**3aq**[b,c,d]
entry 40: 99% yield
82:18 dr; 74% ee



(+)-**3ar**[b,c,d]
entry 41: 70% yield
80:20 dr; 63% ee

[a] Carried out with diazomalonate **1c** (0.10 mmol) and alkene **2** (0.12 mmol) in toluene at room temperature for 24 h in one-time fashion without slow addition using [Co(**P4**)] (2 mol %) under N_2; Isolated yields; Diastereomeric ratio (dr) determined by ^{1}H NMR; Enantiomeric excesses (ee) determined by chiral HPLC. [b] With **2** (1.00 mmol). [c] Using [Co(**P4**)] (5 mol %). [d] At 40 °C.

Moreover, aliphatic alkenes, which represent another class of challenging substrates for asymmetric cyclopropanation, could be cyclopropanated as well by the Co(II)-based metalloradical system as exemplified by the stereoselective formation of cyclopropanes **3ao**–**3ar** in good to excellent yields (Table 9, entries 38–41). It is worth to note the remarkable degree of functional

tolerance to the alkyl alcohol and alkyl bromide in the asymmetric formation of 1,1-cyclopropanediesters **3aq** and **3ar** (Table 9, entries 40 and 41).

Chapter 3 Mechanistic Insights for Radical Cyclopropanation and Further Transformation

3.1 Introdution

With the exploration of the optimized cyclopropanation reaction condition and the broad olefin scope applied into the Co(II)-based metalloradical catalysis (MRC), the next important investigation would be that to discover evidence of mechanistic studies of the stepwise radical pathway and the further transformation of the synthetically useful 1,1-diestercyclopropanes. Mechanistic studies could greatly facilitate the understanding of Co(II)-based metalloradical catalysis (MRC) and help the further design of new catalysts.

3.2 Mechanistic Insights for Radical Cyclopropanation

The profile of reactivity and selectivity displayed by the Co(II)-catalyzed olefin cyclopropanation is consistent with the proposed stepwise radical mechanism that involves key intermediacies of α-Co(III)-malonyl radical **I** and γ-Co(III)-alkyl radical **II** (Scheme 19). To obtain direct evidences for the proposed mechanism, several mechanistic experiments were conducted (Figures 2-3).

In an effort to directly detect the α-Co(III)-malonyl radical intermediates, the isotropic electron paramagnetic resonance (EPR) spectrum was recorded at room temperature for the reaction solution of [Co(**P1**)] with diazomalonate **1c** in benzene in the absence of alkenes (Figure 2). The spectrum displays strong well-resolved octet signals with observed isotropic g-value of ~2.00. The signals are

diagnostic of Co(III)-supported organic radicals, which is consistent with the formation of α-Co(III)-alkyl radical I[Co(**P1**)]/**1c** upon metalloradical activation of diazomalonate **1c** by [Co(**P1**)] with spin translocation from the Co(II)-center to the α-C-atom. The observed octet signals could be agreeably simulated on the basis of hyperfine coupling by ^{59}Co (I = 7/2) with g value of 2.00297 and $A_{(Co)}$ of 86.4 MHz (see Chapter 4 for experimental details).

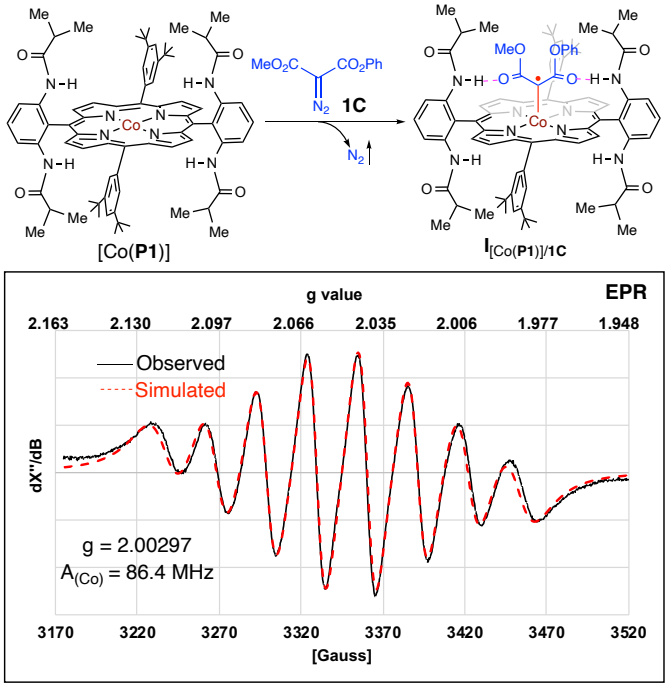


Figure 2 Detection of the α-Co(III)-Malonyl Radical Intermediates by EPR

Additionaly, α-Co(III)-alkyl radical $I_{[Co(\mathbf{P1})]/\mathbf{1c}}$ from the reaction mixture of [Co(**P1**)] with diazomalonate **1c** could also be detected by high-resolution mass spectrometry (HRMS) with ESI ionization in the absence of any additives as electron carriers (Figure 3). The obtained spectrum clearly revealed a signal corresponding to [(**P1**)Co(C(CO_2CH_3)($CO_2C_6H_5$))]+ (m/z = 1427.6666), which resulted from neutral *α*-Co(III)-malonyl radical intermediate $I_{[Co(\mathbf{P1})]/\mathbf{1c}}$ by the loss of one electron. Both the exact mass and the pattern of isotope distribution determined by ESI-HRMS

matched almost perfectly with those calculated from the formula [(**P1**)Co C(CO_2CH_3)($CO_2C_6H_5$)]$^+$ (see Chapter 4 for experimental details).

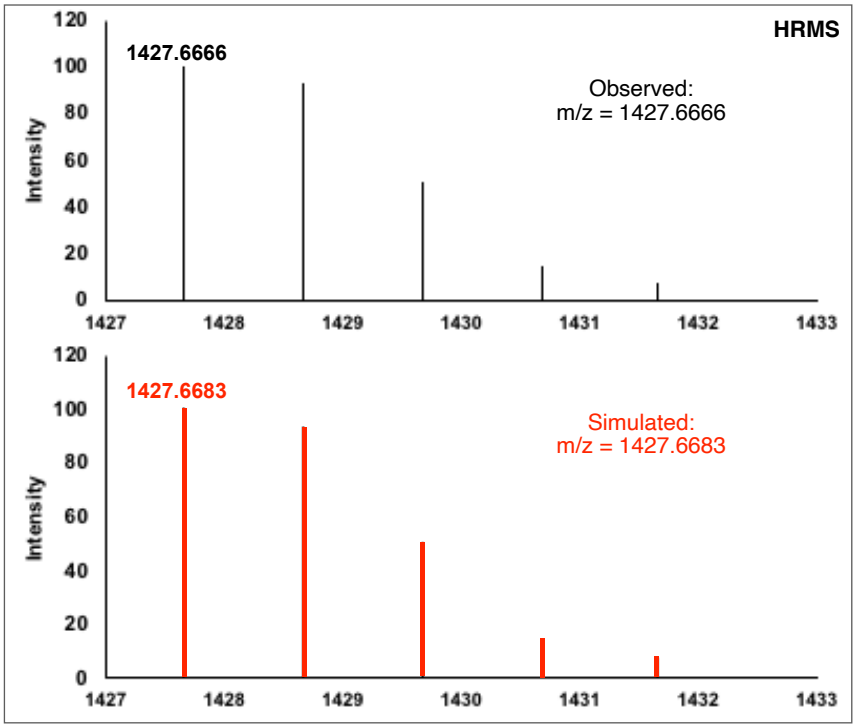


Figure 3 Detection of the α-Co(III)-Malonyl Radical Intermediates by HRMS

To probe the intermediacy of γ-Co(III)-alkyl radical **II** associated with subsequent steps of radical addition and radical cyclization in the proposed mechanism, both (*E*)- and (*Z*)-*β*-deuterostyrene ((*E*)-**2a$_D$** and (*Z*)-**2a$_D$**) were utilized as the substrates for the Co(II)-catalyzed cyclopropanation (Figure 4). Different from concerted mechanism that gives rise to stereospecific products, stepwise radical mechanism may generate four possible isotopomers of the cyclopropanes from the reaction of both (*E*)-**2a$_D$** and (*Z*)-**2a$_D$** due to potential rotation of the β-C–C bond in γ-Co(III)-alkyl radical intermediate **II** before the ring closure. To this end, unsymmetrical *tert*-butyl methyl diazomalonate (**1b**) was chosen as the radical precursor for the probing experiments because of its

noticeable slower reaction rate, which was expected to provide higher probability of the β-C–C bond rotation in the corresponding γ-Co(III)-alkyl radical intermediate **II**.

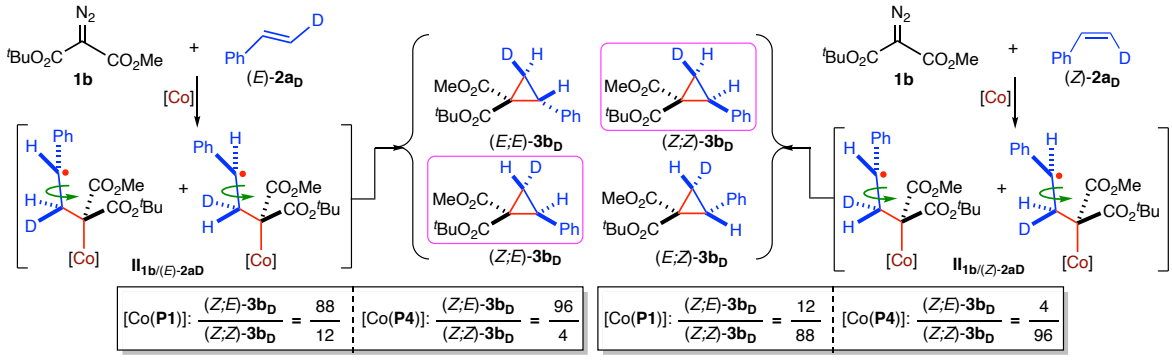


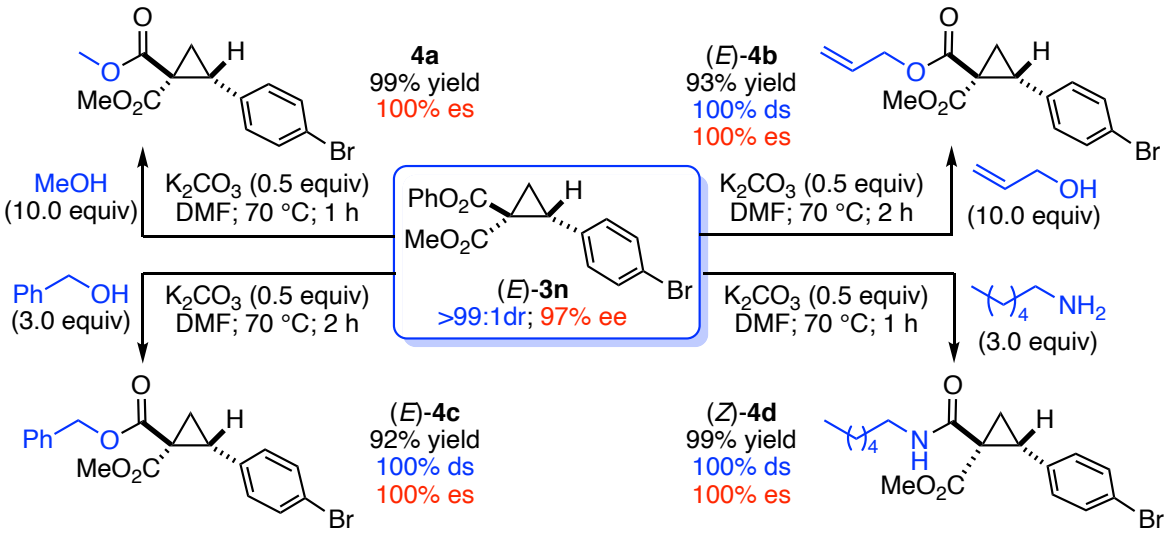
Figure 4 Probing of the γ-Co(III)-Alkyl Radical Intermediates by Reactions of β-Deuterostyrenes with Methyl tert-Butyl Diazomalonate

As expected, it was found that the Co(II)-catalyzed cyclopropanation reactions of both (*E*)-**2a$_D$** and (*Z*)-**2a$_D$** with **1b** generated the cyclopropane product as a mixture of four diastereomers: (*E*;*E*)-**3b$_D$**; (*Z*;*Z*)-**3b$_D$**; (*Z*;*E*)-**3b$_D$**; and (*E*;*Z*)-**3b$_D$** (Figure 4). Among the four isotopomers, the ratio of (*Z*;*E*)-**3b$_D$** to (*Z*;*Z*)-**3b$_D$** could be experimentally determined from analysis of the reaction mixtures by ^{1}H- and ^{2}H-NMR. When [Co(**P4**)] was used as the catalyst, cyclopropanation of (*E*)-**2a$_D$** with **1b** gave a 96:4 ratio of (*Z*;*E*)-**3b$_D$** to (*Z*;*Z*)-**3b$_D$** whereas the ration was switched to 4:96 for the cyclopropanation of (*Z*)-**2a$_D$** with **1b**. The observation of (*Z*;*Z*)-**3b$_D$** from (*E*)-**2a$_D$** and (*Z*;*E*)-**3b$_D$** from (*Z*)-**2a$_D$** is evidently a result of the rotation of the β-C−C bond in intermediates **II$_{1b/(E)\text{-}2aD}$** and **II$_{1b/(Z)\text{-}2aD}$**, respectively. When sterically less hindered [Co(**P1**)] was used as the catalyst, a significantly different isotopomeric ratio of (*Z*;*E*)-**3b$_D$** and (*Z*;*Z*)-**3b$_D$** (from 96:4 to 88:12) was observed for both reactions of (*E*)-**2a$_D$** (from 96:4 to 88:12) and (*Z*)-**2a$_D$** (from 4:96 to 12:88). The observed difference in the ratio of (*Z*;*E*)-**3b$_D$** to (*Z*;*Z*)-**3b$_D$** indicates that the less-crowded ligand environment of [Co(**P1**)] permitted relatively more facile rotation of the β-C−C bond in the γ-Co(III)-alkyl radical intermediates **II$_{1b/(E)\text{-}2aD}$** and **II$_{1b/(Z)\text{-}2aD}$**. Together with the direct observation of the α-Co(III)-alkyl radical intermediate **I** by EPR and HRMS, these results provided convincing evidence to support the

underlying stepwise radical mechanism for Co(II)-catalyzed olefin cyclopropanation with diazomalonates (see Chapter 4 for experimental details).

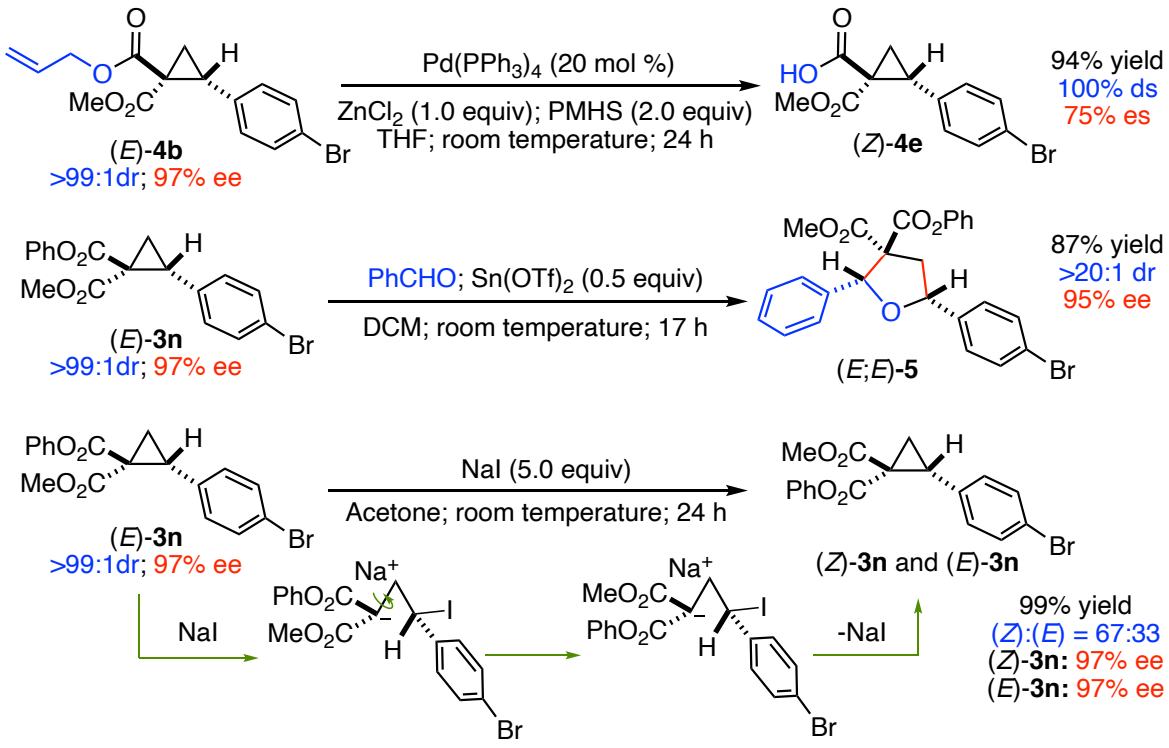
3.3 Further Transformations of 1,1-Cyclopropanediesters

In view of the difference in reactivity between methyl and phenyl esters, the resulting enantioenriched (*E*)-1,1-cyclopropanediesters from the Co(II)-catalyzed asymmetric cyclopropanation could be stereospecifically transformed to different chiral cyclopropane derivatives (Scheme 20). For example, the better leaving ability of phenoxy over methoxy group enabled selective transesterification of phenyl ester with various alcohols as exemplified with 1,1-cyclopropanediester (*E*)-**3n** for the acyl transfer reactions.[1] In the presence of K_2CO_3 as the base, the unsymmetrical methyl phenyl diester (*E*)-**3n** could readily react with methanol in DMF to form the symmetric bismethyl diester **4a** in near quantitative yield (99%) with full retention of the original high enantiopurity (100% es). Under the similar conditions, methyl phenyl diester (*E*)-**3n** underwent selective transesterification reactions with allylic alcohol and benzyl alcohol as well, producing methyl allyl diester (*E*)-**4b** and methyl benzyl diester (*E*)-**4c**, respectively, in high yields (93% and 92%) with full retention of the original high (*E*)-diastereomeric purity (100% ds) as well as enantiopurity (100% es). In addition to transesterification, (*E*)-**3n** could proceed selective amidation, as demonstrated with the stereospecific formation of 1,1-cyclopropaneesteramide (*Z*)-**4d** in near quantitative yield (99%) without diminishing the original high diastereomeric purity (100% ds) and enantiopurity (100% es) when reacting with *n*-hexylamine under the similar conditions.



Scheme 20 Transformations of the Optically Active Chiral 1,1-Cyclopropanediesters

Besides the transesterification and amidation reactions, the resulting enantioenriched 1,1-cyclopropanediesters from the catalytic process could be transformed to form other interesting compounds (Scheme 21). For example, the allylic group in the transesterification product (*E*)-**4b** was effectively removed by Pd-catalyzed hydrogenation reaction,[2] producing the corresponding 1,1-cyclopropaneester carboxylic acid (*Z*)-**4e** in high yield (94%) with retention of the original diastereomeric purity (100% ds) but some loss of the optical purity (75% es). As the donor-acceptor type of cyclopropanes, the resulting enantioenriched 1,1-cyclopropanediesters could function as effective 1,3-dipoles to undergo [3+2] cycloaddition as shown by the 1,3-dipolar cycloaddition of 1,1-cyclopropanediester (*E*)-**3n** with benzaldehyde under the catalysis of $Sn(OTf)_2$, affording multi-substituted tetrahydrofuran (*E*;*E*)-**5** containing three stereocenters in high yield (87%) with excellent diastereoselectivity (>20:1 dr) and high enantioselectivity (95% ee). While (*E*)-diastereomers were produced as the major diastereomers in [Co(**P4**)]-catalyzed olefin cyclopropanation with MPDM, the (*Z*)-diastereomers could be generated through an iodide-mediated stereospecific conversion. For example, when (*E*)-**3n** was treated with NaI (5.0 equiv) at room temperature, it resulted in the conversion to (*Z*)-**3n** as the major diastereomer without loss of the original optical purity (97% ee).



Scheme 21 Stereospecific Chemical Transformations of Optically Active Chiral 1,1-Cyclopropanediesters

3.4 Conclusion

In conclusion, we have found ligand effects on the cyclopropanation of olefins, the double hydrogen-bonding interactions play important role in activating and stabilizing the α-Co(III)-malonyl radical intermediate, and π-stacking between the substrates and catalysts also plays key roles in controlling both activity and enantioselectivity. We have developed the first catalytic system via Co(II)-based metalloradical catalysis (MRC) that is highly effective for asymmetric cyclopropanation of alkenes including various functionalized styrenes, conjugated dienes and enynes, heteroaromatic alkens, and aliphatic alkenes with methyl phenyl diazomalonate (MPDM), a common unsymmetrical diazomalonate, affording the corresponding 1,1-cyclopropanediesters with high diastereoselectivity and enantioselectivity. With D_2-symmetric chiral amidoporphyrin 3,5-Di^{t}Bu-

Xu(2'-Naph)Phyrin as the supporting ligand, the Co(II)-based metalloradical system can also efficaciously activate MPDM even at room temperature to cyclopropanate different α-substituted alkenes, affording 1,1-cyclopropanediesters bearing two contiguous stereogenic centers in high yields with a high level of control in both diastereoselectivity and enantioselectivity. Mechanistic studies on cyclopropanation reactions of (*E*)- and (*Z*)-β-deuterostyrenes, together with direct observation of α-Co(III)-malonyl radical intermediates, provide direct evidence in supporting the underlying stepwise radical pathway for the Co(II)-catalyzed process. The resulting enantioenriched (*E*)-1,1-cyclopropanediesters from the new catalytic radical process, as showcased in a number of stereospecific transformations including transesterification with different alcohols, transamination, and 1,3-dipole cycloaddition. The resultants should find useful synthetic applications.

3.5 Reference

(1) Watson, D. A.; Fan, X. X.; Buchwald, S. L. *J Org Chem* **2008**, *73*, 7096.

(2) Chandrasekhar, S.; Reddy, C. R.; Rao, R. J. *Tetrahedron* **2001**, *57*, 3435.

Chapter 4 Experimental Section

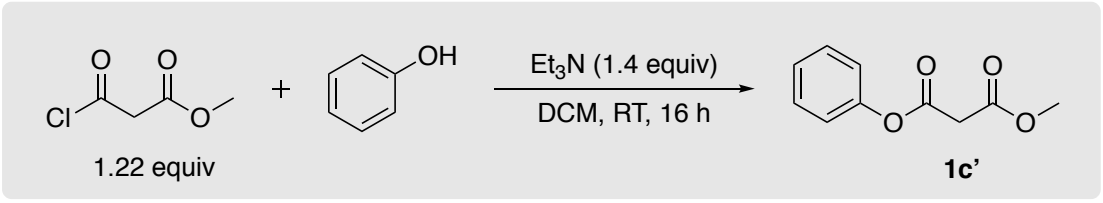
4.1 General Considerations

All cyclopropanation reactions were performed under an atmosphere of nitrogen in oven-dried Schlenk tubes using standard Schlenk techniques. Chemical reagents and anhydrous solvents are commercially available from Sigma-Aldrich, Oakwood Products Inc., Alfa Aesar, TCI, Acros, Strem, or Matrix Scientific and used as received unless otherwise stated. Thin layer chromatography (TLC) was performed on Merck TLC plates (silica gel 60 F254). Flash column chromatography was performed with ICN silica gel (60 Å, 230-400 mesh, 32-63 μm).

^{1}H NMR and ^{13}C NMR were recorded on a Varian600 (600 MHz), Varian500 (500 MHz) or a Varian Inova400 (400 MHz) instrument with chemical shifts reported relative to residual solvent. ^{19}F NMR were recorded on a Varian Inova400 (400 MHz) instrument. HPLC measurements were carried out on a Shimadzu HPLC system with Chiralcel OD-H, OJ-H, AD-H and Chiralpak IA, IB, IC, ID, IE, IF columns. Infrared spectra were measured with a Nicolet Avatar 320 spectrometer with a Smart Miracle accessory. Optical rotations were measured on a Rudolph Research Analytical AUTOPOL® IV digital polarimeter. HRMS data was obtained on an Agilent 6200 LC/MS ESI/TOF mass spectrometer and JEOL Accu TOF Dart mass spectrometer. HRMS data was obtained on an. X-ray diffraction data were collected using Bruker-AXS SMART-APEXII CCD diffractometer using Kα radiation (λ = 1.54178 Å).

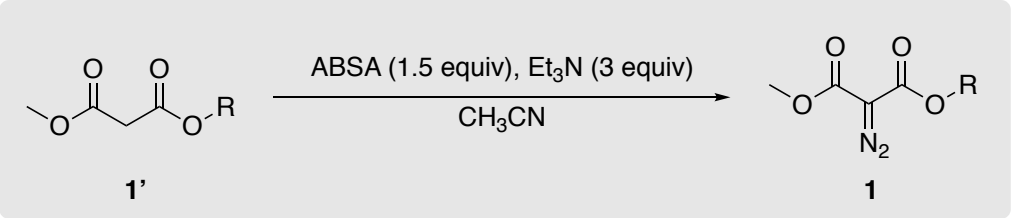
4.2 Procedure for Diazomalonte Synthesis

Benzyl methyl malonate (1a') Following a reported procedure,[1] to *N*,*N*-dimethylformamide (DMF) (15 mL) was added potassium methyl malonate (5.125 mmol, 1.025 equiv) with vigorous stirring and then benzyl bromide (5.0 mmol, 1.0 equiv). The reaction mixture was stirred for 16 h at room temperature. After the reaction finished, the mixture was diluted with ethyl acetate (25 mL), washed three times with water (3 × 30 mL), dried over sodium sulfate, and evaporated to give **1a'** as colorless oil (94%). TLC: Hexane:EtOAc = 8:1; R_f = 0.3. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36 (d, J = 3.4 Hz, 5H), 5.18 (s, 2H), 3.73 (s, 3H), 3.43 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.69, 166.17, 135.17, 128.45, 128.29, 128.12, 67.07, 52.34, 41.18. HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{11}H_{12}O_4Na^+$: 231.0628; Found: 231.0632. IR (neat, cm^{-1}): ν 2954, 1756, 1338, 1277, 1214, 1152, 1022.

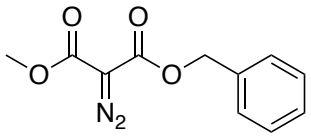


Methyl phenyl malonate (1c') Following a reported procedure on a similar reaction,[2] phenol (8.5 mmol, 1.0 equiv) was dissolved in anhydrous dichloromethane (50 mL) and then the solution was cooled to 0 °C. Methyl 3-chloro-3-oxopropanoate (10.4 mmol, 1.22 equiv) and triethylamine (11.9 mmol, 1.4 equiv) were slowly added. After 30 min, the reaction mixture was warmed up to room temperature and stirred for overnight. Solvent was evaporated under reduced pressure, water (50 mL) was added, and the mixture was extracted with ethyl acetate for three times (3 × 50 mL). The combined organic phases were washed with saturated aq. $NaHCO_3$ (2 × 30 mL) and brine (30 mL),

dried over sodium sulfate, and concentrated under reduced pressure. The yellow crude product was purified by column chromatography on silica gel (dichloromethane) to yield **1c'** as a colorless oil (93%). TLC: DCM; R_f = 0.7. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.38 (td, J = 7.6, 6.7, 1.2 Hz, 2H), 7.27 – 7.22 (m, 1H), 7.15 – 7.10 (m, 2H), 3.79 (s, 3H), 3.61 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.46, 164.84, 150.27, 129.34, 126.04, 121.19, 52.51, 41.19. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{10}H_{11}O_4^+$: 195.0652; Found: 195.0662. IR (neat, cm^{-1}): ν 2955, 2923, 2850, 1768, 1743, 1339, 1262, 1196, 1163, 1140.

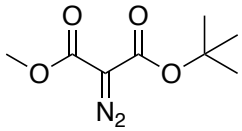


General procedure: Following a reported procedure on a similar reaction,[3] unsymmetrical malonate **1'** (8.3 mmol, 1.0 equiv) was dissolved in acetonitrile (45 mL) and then the stirred solution was cooled to 0 °C. Triethylamine (24.9 mmol, 3.0 equiv) and *p*-(acetamido)benzenesulfonyl azide (*p*-ABSA) (12.4 mmol, 1.5 equiv) were added to the reaction mixture. The reaction was gradually warmed up to room temperature and stirred for overnight. Then the suspension of the reaction mixture was filtered, washed with ether (50 mL), and the filtrate was then concentrated under reduced pressure. The yellow crude products were purified by column chromatography on silica gel (hexane/ethyl acetate) to afford pure products **1**.

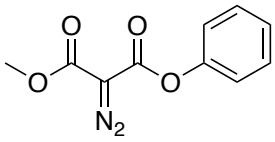


1-benzyl 3-methyl 2-diazomalonate (1a) Yield: 86%. Light yellow oil. TLC: Hexane:EtOAc = 3:1; R_f = 0.6. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43 – 7.27 (m, 5H), 5.26 (s, 2H), 3.82 (s, 3H). ^{13}C NMR (125 MHz,

$CDCl_3$): δ 161.23, 160.56, 135.17, 128.46, 128.29, 128.09, 66.83, 52.35. HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{11}H_{10}N_2O_4Na^+$: 257.0533; Found: 257.0533. IR (neat, cm^{-1}): ν 3034, 2957, 2139, 1762, 1739, 1695, 1438, 1383, 1331, 1273, 1104.

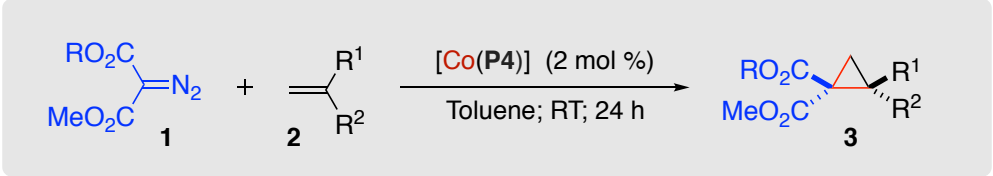


1-(*tert*-butyl) 3-methyl 2-diazomalonate (1b) Starting material *tert*-butyl methyl malonate is commercially available from Sigma-Aldrich. Yield: 88%. Light yellow oil . TLC: Hexane:EtOAc = 3:1; R_f = 0.6. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.83 (s, 3H), 1.51 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.04, 159.68, 83.08, 52.35, 28.14. HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_8H_{12}N_2O_4Na^+$: 223.0689; Found: 223.0695. IR (neat, cm^{-1}): ν 2980, 2138, 1763, 1694, 1438, 1371, 1342, 1105.

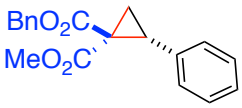


1-phenyl 3-methyl 2-diazomalonate (1c) Yield: 86%. Light yellow solid. TLC: Hexane:EtOAc = 4:1; R_f = 0.4. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 (t, J = 8.0 Hz, 2H), 7.26 (t, J = 7.4 Hz, 1H), 7.15 (d, J = 7.6 Hz, 2H), 3.89 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.17, 159.25, 149.84, 129.44, 126.18, 121.46, 52.70. HRMS (ESI) ([M+Na]$^+$) Calcd. for: $C_{10}H_8N_2O_4Na^+$: 243.0376; Found: 243.0361. IR (neat, cm^{-1}): ν 3464, 3041, 2959, 2161, 1727, 1685, 1334, 1260, 1189, 1160, 1053.

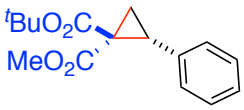
4.3 General Procedure for [Co(Por)]-Catalyzed Cyclopropanation



General procedure: Diazomalonate **1** (0.12 mmol, 1.2 equiv) and [Co(Por)] (2 mol %) was added to an oven-dried Schlenk tube. The Schlenk tube was then evacuated and back filled with nitrogen for 3 times. Olefin **2** (0.10 mmol, 1.0 equiv) and toluene (0.5 mL) were added *via* gas tight syringe. Teflon screw cap was used to close the Schlenk tube. The mixture was then stirred at room temperature for 24 h. Solvent was evaporated under reduced pressure. The crude products were purified by column chromatography on silica gel to afford pure products **3** as a mixture of *trans*/*cis* diastereomers.

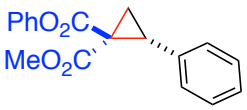


1-benzyl 1-methyl (1*S*,2*R*)-2-phenylcyclopropane-1,1-dicarboxylate (3a) Yield: 67%; 65:35 diastereomeric ratio. Colorless oil. TLC: Hexane:EtOAc = 8:1; R_f = 0.5. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.40 – 7.31 (m, 4H), 7.30 – 7.17 (m, 5H), 7.01 – 6.98 (m, 1H), 5.33 – 5.15 (m, 2H), 3.36 (s, 3H), 3.26 (ddd, J = 12.1, 9.1, 7.9 Hz, 1H), 2.22 (ddd, J = 8.1, 5.2, 1.2 Hz, 1H), 1.76 (dt, J = 9.2, 5.1 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 169.52, 166.93, 135.55, 134.51, 128.45, 128.30, 128.22, 128.13, 127.77, 127.37, 67.21, 52.14, 37.38, 32.52, 19.12. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{19}H_{19}O_4^+$: 311.1278; Found: 311.1290. IR (neat, cm^{-1}): ν3032, 2952, 2924, 1731, 1332, 1278, 1217, 1131. HPLC (chiral ID, 3% isopropanol-hexane, rate 0.8 ml/min): *trans*-isomer: t_{major} = 16.5 min, t_{minor} = 22.5 min, 75% *ee*. $[a]_D^{20}$ = +37.6° (c = 1, CH_2Cl_2).

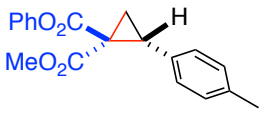


1-(*tert*-butyl) 1-methyl (1*S*,2*R*)-2-phenylcyclopropane-1,1-dicarboxylate (3b) Yield: 74%; 88:12 diastereomeric ratio. Colorless oil. TLC: Hexane:EtOAc = 8:1; R_f = 0.5. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.29 – 7.16 (m, 5H), 3.37 (s, 3H), 3.12 (dd, J = 9.1, 8.0 Hz, 1H), 2.09 (dd, J = 7.9, 5.1 Hz, 1H), 1.65 (dd, J = 9.2, 5.1 Hz, 1H), 1.48 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 168.62, 167.54, 135.04, 128.31, 128.08, 127.15, 82.02, 52.01,

38.50, 31.55, 27.98, 18.56. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{16}H_{21}O_4^+$: 277.1434; Found: 277.1441. IR (neat, cm^{-1}): ν 2979, 1724, 1456, 1369, 1333, 1295, 1218, 1172, 1134. HPLC (chiral IC, 2% isopropanol-hexane, rate 0.8 ml/min): *trans*-isomer: t_{major} = 11.3 min, t_{minor} = 12.3 min, 87% *ee*. $[a]_D^{20}$ = +65.9° (c = 1, CH_2Cl_2).

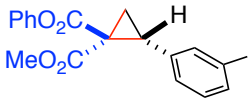


1-methyl 1-phenyl (1*S*,2*R*)-2-phenylcyclopropane-1,1-dicarboxylate (3c) Yield: 99%; 94:6 diastereomeric ratio. Colorless oil. TLC: Hexane:EtOAc = 8:1; R_f = 0.6. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 – 7.34 (m, 2H), 7.33 – 7.21 (m, 6H), 7.15 (d, J = 7.5 Hz, 2H), 3.42 (s, 3H), 3.37(t, J = 11.0, 1H), 2.34 (dd, J = 8.2, 5.2 Hz, 1H), 1.90 (dd, J = 9.3, 5.2 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.45, 166.74, 150.58, 134.24, 129.41, 128.52, 128.21, 127.54, 126.05, 121.36, 52.39, 37.35, 32.97, 19.69. HRMS (ESI) ([M+Na]$^+$) Calcd. for: $C_{18}H_{16}O_4Na^+$: 319.0941; Found: 319.0933. IR (neat, cm^{-1}): ν 3031, 2951, 1731, 1263, 1214, 1190, 1160, 1117. HPLC (chiral AD-H, 1.5% isopropanol-hexane, rate 1 ml/min): *trans*-isomer: t_{major} = 19.7 min, t_{minor} = 30.2 min, 96% *ee*. $[a]_D^{20}$ = +133.7° (c = 1, CH_2Cl_2).

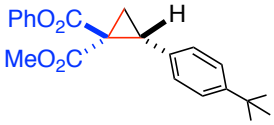


1-methyl 1-phenyl (1*S*,2*R*)-2-(*p*-tolyl)cyclopropane-1,1-dicarboxylate (3d) Yield: 99%; 94:6 diastereomeric ratio. Colorless oil. TLC: Hexane:EtOAc = 8:1; R_f = 0.6. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44 – 7.36 (m, 2H), 7.28 – 7.23 (m, 1H), 7.18 – 7.13 (m, 4H), 7.11 (d, J = 8.0 Hz, 2H), 3.46 (d, J = 0.6 Hz, 3H), 3.35 (t, J = 8.7 Hz, 1H), 2.40 – 2.27 (dd+s, 4H), 1.89 (dd, J = 9.3, 5.2 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.51, 166.83, 150.59, 137.20, 131.10, 129.38, 128.91, 128.38, 126.01, 121.37, 52.39, 37.25, 32.85, 21.08, 19.77. HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{19}H_{18}O_4Na^+$: 333.1097; Found: 333.1083. IR (neat, cm^{-1}): ν

2951, 1731, 1263, 1211, 1190, 1160, 1113. HPLC (chiral OJ-H, 35% isopropanol-hexane, rate 0.6 ml/min): *trans*-isomer: t_{major} = 61.1 min, t_{minor} = 78.7 min, 97% *ee*. $[a]_D^{20}$ = +113.2° (c = 1, CH_2Cl_2).

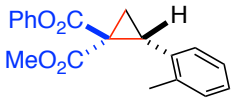


1-methyl 1-phenyl (1*S*,2*R*)-2-(*m*-tolyl)cyclopropane-1,1-dicarboxylate (3e) Yield: 99%; 95:5 diastereomeric ratio. Colorless oil. TLC: Hexane:EtOAc = 8:1; R_f = 0.6. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40 (dd, J = 8.5, 7.4 Hz, 2H), 7.29 – 7.23 (m, 1H), 7.20 (t, J = 7.5 Hz, 1H), 7.18 – 7.14 (m, 2H), 7.11 – 7.02 (m, 3H), 3.46 (s, 3H), 3.35 (t, J = 8.7 Hz, 1H), 2.34 (dd+s, J = 5.2 Hz, 4H), 1.90 (dd, J = 9.3, 5.2 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.51, 166.80, 150.60, 137.83, 134.18, 129.41, 129.38, 128.31, 128.08, 126.04, 125.36, 121.38, 52.39, 37.30, 33.02, 21.33, 19.80. HRMS (ESI) ($[M+H]^+$) Calcd. for: $C_{19}H_{19}O_4^+$: 311.1278; Found: 311.1279. IR (neat, cm^{-1}): ν 2951, 1732, 1329, 1265, 1204, 1190, 1160, 1117. HPLC (chiral OJ-H, 10% isopropanol-hexane, rate 0.8 ml/min): *trans*-isomer: t_{minor} = 53.2 min, t_{major} = 56.3 min, 98% *ee*. $[a]_D^{20}$ = +115.5° (c = 1, CH_2Cl_2).

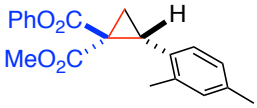


1-methyl 1-phenyl (1*S*,2*R*)-2-(4-(*tert*-butyl)phenyl)cyclopropane-1,1-dicarboxylate (3f) Yield: 99%; 91:9 diastereomeric ratio. White solid. TLC: Hexane:EtOAc = 8:1; R_f = 0.6. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40 (dd, J = 8.5, 7.4 Hz, 2H), 7.33 (d, J = 8.4 Hz, 2H), 7.25 (t, J = 7.3 Hz, 1H), 7.22 – 7.13 (m, 4H), 3.43 (s, 3H), 3.35 (t, J = 8.7 Hz, 1H), 2.34 (dd, J = 8.2, 5.2 Hz, 1H), 1.90 (dd, J = 9.3, 5.2 Hz, 1H), 1.31 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.54, 166.86, 150.60, 150.50, 131.12, 129.39, 128.16, 125.09, 121.38, 52.32, 37.31, 34.47, 32.80, 31.31, 31.26, 19.81. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{22}H_{24}O_4Na^+$: 375.1567; Found: 375.1563. IR (neat, cm^{-1}): ν 2952, 2867, 1737, 1721, 1266, 1190, 1121. HPLC (chiral OJ-H,

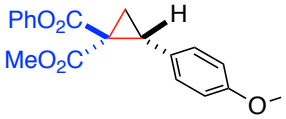
8% isopropanol-hexane, rate 0.8 ml/min): *trans*-isomer: t_{minor} = 23.7 min, t_{major} = 40.8 min, 96% *ee*. $[a]_D^{20}$ = +95.8° (c = 1, CH_2Cl_2).



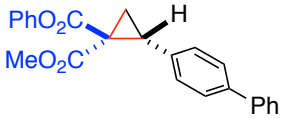
1-methyl 1-phenyl (1*S*,2*R*)-2-(*o*-tolyl)cyclopropane-1,1-dicarboxylate (3g) Yield: 62%; 75:25 diastereomeric ratio. Colorless oil. TLC: Hexane:EtOAc = 8:1; R_f = 0.6. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41 (dd, J = 8.5, 7.4 Hz, 2H), 7.29 – 7.22 (m, 1H), 7.20 – 7.07 (m, 6H), 3.37 (s, 3H), 3.31 (t, J = 8.7 Hz, 1H), 2.47 (dd, J = 8.4, 5.2 Hz, 1H), 2.43 (s, 3H), 1.92 (dd, J = 9.2, 5.2 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.59, 166.75, 150.66, 139.00, 132.35, 129.76, 129.44, 127.71, 127.36, 126.05, 125.55, 121.37, 52.26, 36.41, 32.14, 19.42, 19.17. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{19}H_{18}NaO_4^+$: 333.1097; Found: 333.1083. IR (neat, cm^{-1}): ν 2951, 1731, 1268, 1191, 1160, 1118, 1083, 1068. HPLC (chiral OJ-H, 35% isopropanol-hexane, rate 0.6 ml/min): *trans*-isomer: t_{minor} = 33.4 min, t_{major} = 47.3 min, 94% *ee*. $[a]_D^{20}$ = +29.3° (c = 1).



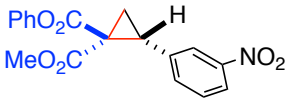
1-methyl 1-phenyl (1*S*,2*R*)-2-(2,4-dimethylphenyl)cyclopropane-1,1-dicarboxylate (3h) Yield: 58%; 75:25 diastereomeric ratio. Colorless oil. TLC: Hexane:EtOAc = 8:1; R_f = 0.5. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.41 (ddd, J = 8.5, 7.4, 0.9 Hz, 2H), 7.27 – 7.25 (m, 1H), 7.16 (dt, J = 8.6, 1.0 Hz, 2H), 7.01 – 6.95 (m, 3H), 3.40 (s, 3H), 3.28 (t, J = 8.9 Hz, 1H), 2.44 (ddd, J = 8.4, 5.1, 0.9 Hz, 1H), 2.39 (s, 3H), 2.30 (s, 3H), 1.90 (ddd, J = 9.2, 5.1, 0.9 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 168.64, 166.85, 150.68, 138.72, 137.33, 130.67, 129.42, 129.13, 127.32, 126.16, 126.01, 121.38, 52.27, 36.39, 32.05, 21.03, 19.31, 19.26. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{20}H_{21}O_4^+$: 325.1434; Found: 325.1446. IR (neat, cm^{-1}): ν 2951, 1730, 1268, 1190, 1113, 1081, 750, 687. HPLC (chiral IC, 4% isopropanol-hexane, rate 0.8 ml/min): *trans*-isomer: t_{minor} = 14.7 min, t_{major} = 17.3 min, 96% *ee*. $[a]_D^{20}$ = +88.6° (c = 1, CH_2Cl_2).



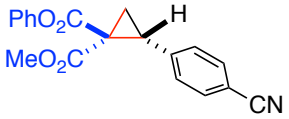
1-methyl 1-phenyl (1*S*,2*R*)-2-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate (3i) Yield: 94%; 73:27diastereomeric ratio. White solid. TLC: Hexane:EtOAc = 3:1; R_f = 0.4. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41 (t, J = 7.7 Hz, 2H), 7.31 – 7.14 (m, 5H), 6.87 – 6.81 (m, 2H), 3.87 (s, 1H), 3.81 (d, J = 5.2 Hz, 4H), 3.47 (s, 3H), 3.41 – 3.30 (m, 1H), 2.31 (ddd, J = 13.4, 8.1, 5.2 Hz, 2H), 1.90 (dd, J = 9.3, 5.1 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.52, 166.86, 158.98, 150.61, 129.70, 129.39, 126.11, 126.01, 121.38, 113.61, 55.19, 52.41, 37.20, 32.65, 19.86. HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{19}H_{18}O_5Na^+$: 349.1046; Found: 349.1051. IR (neat, cm^{-1}): ν 2956, 2838, 1727, 1249, 1214, 1192, 1182, 1168, 1109. HPLC (chiral OD-H, 2% isopropanol-hexane, rate 1 ml/min): *trans*-isomer: t_{major} = 16.7 min, t_{minor} = 27.2 min, 93% *ee*. [a]$_D^{20}$ = +73.1° (c = 1, CH_2Cl_2).



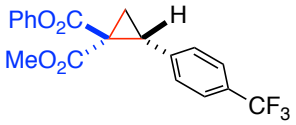
1-methyl 1-phenyl (1*S*,2*R*)-2-([1,1'-biphenyl]-4-yl)cyclopropane-1,1-dicarboxylate (3j) Yield: 84%; 85:15 diastereomeric ratio. White solid. TLC: Hexane:EtOAc = 8:1; R_f = 0.6. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63 – 7.54 (m, 4H), 7.48 – 7.32 (m, 7H), 7.30 – 7.25 (m, 1H), 7.21 – 7.16 (m, 2H), 3.48 (s, 3H), 3.42 (t, J = 8.8 Hz, 1H), 2.40 (dd, J = 8.1, 5.3 Hz, 1H), 1.95 (dd, J = 9.3, 5.3 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.42, 166.77, 150.60, 140.45, 140.31, 133.31, 129.43, 128.94, 128.76, 127.37, 126.95, 126.85, 126.07, 121.37, 52.49, 37.46, 32.74, 19.82. HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{24}H_{20}O_4Na^+$: 395.1254; Found: 395.1259. IR (neat, cm^{-1}): ν 2955, 2923, 2850, 1757, 1731, 1270, 1209, 1193, 1171, 1111. HPLC (chiral OJ-H, 35% isopropanol-hexane, rate 0.6 ml/min): *trans*-isomer: t_{minor} = 90.2 min, t_{major} = 266.7 min, 96% *ee*. [a]$_D^{20}$ = +127.8° (c = 1, CH_2Cl_2).



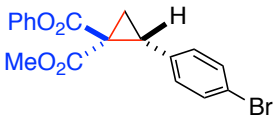
1-methyl 1-phenyl (1*S*,2*R*)-2-(3-nitrophenyl)cyclopropane-1,1-dicarboxylate (3k) Yield: 68%; 91:9 diastereomeric ratio. Colorless oil. TLC: Hexane:DCM = 1:1; R_f = 0.3. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.15 (dd, J = 9.2, 1.8 Hz, 2H), 7.62 (dd, J = 7.8, 1.6 Hz, 1H), 7.50 (t, J = 7.8 Hz, 1H), 7.45 – 7.38 (m, 2H), 7.30 – 7.24 (m, 1H), 7.19 – 7.13 (m, 2H), 3.50 (s, 3H), 3.43 (t, J = 8.7 Hz, 1H), 2.39 (dd, J = 8.1, 5.5 Hz, 1H), 1.99 (dd, J = 9.3, 5.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.84, 166.31, 150.47, 148.13, 136.69, 134.81, 129.51, 129.23, 126.27, 123.68, 122.66, 121.26, 52.73, 37.36, 31.72, 19.72. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{18}H_{15}NO_6Na^+$: 364.0792; Found: 364.0792. IR (neat, cm^{-1}): ν 2953, 1731, 1528, 1348, 1264, 1217, 1190, 1118. HPLC (chiral OJ-H, 40% isopropanol-hexane, rate 0.6 ml/min): *trans*-isomer: t_{minor} = 94.0 min, t_{major} = 100.3 min, 97% *ee*. $[a]_D^{20}$ = +109.4° (c = 1, CH_2Cl_2).



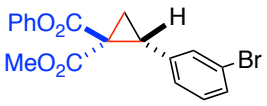
1-methyl 1-phenyl (1*S*,2*R*)-2-(4-cyanophenyl)cyclopropane-1,1-dicarboxylate (3l) Yield: 98%; 90:10 diastereomeric ratio. Light yellow oil. TLC: Hexane:EtOAc = 5:1; R_f = 0.6. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60 (d, J = 8.3 Hz, 2H), 7.44 – 7.34 (m, 4H), 7.27 (d, J = 7.5 Hz, 1H), 7.18 – 7.10 (m, 2H), 3.48 (s, 3H), 3.41 – 3.34 (m, 1H), 2.34 (dd, J = 8.1, 5.5 Hz, 1H), 1.96 (dd, J = 9.2, 5.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.81, 166.26, 150.48, 139.97, 131.99, 129.49, 129.34, 126.24, 121.22, 118.50, 111.48, 52.68, 37.71, 32.13, 19.59. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{19}H_{16}NO_4^+$: 322.1074; Found: 322.1075. IR (neat, cm^{-1}): ν2953, 2228, 1731, 1332, 1265, 1191, 1115, 848, 753. HPLC (chiral ID, 15% isopropanol-hexane, rate 0.8 ml/min): *trans*-isomer: t_{major} = 19.6 min, t_{minor} = 20.5 min, 97% *ee*. $[a]_D^{20}$ = +160.6° (c = 1, CH_2Cl_2).



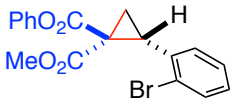
1-methyl 1-phenyl (1*S*,2*R*)-2-(4-(trifluoromethyl)phenyl)cyclopropane-1,1-dicarboxylate (3m) Yield: 60%; 91:9 diastereomeric ratio. White solid. TLC: Hexane:EtOAc = 3:1; R_f = 0.4. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.57 (d, J = 8.1 Hz, 2H), 7.40 (td, J = 8.8, 7.5 Hz, 4H), 7.27 (t, J = 7.4 Hz, 1H), 7.18 – 7.13 (m, 2H), 3.47 (s, 3H), 3.39 (t, J = 8.7 Hz, 1H), 2.36 (dd, J = 8.1, 5.4 Hz, 1H), 1.95 (dd, J = 9.3, 5.4 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.09, 166.44, 150.51, 138.49, 129.49, 128.96, 126.21, 125.19, 125.16, 121.29, 120.89, 52.62, 37.49, 32.16, 19.67. ^{19}F NMR (375 MHz, $CDCl_3$) δ -63.09 (s). HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{19}H_{15}F_3O_4Na^+$: 387.0815; Found: 387.0819. IR (neat, cm^{-1}): ν 2952, 1736, 1324, 1262, 1200, 1157, 1111, 1068, 1016. HPLC (chiral OJ-H, 25% isopropanol-hexane, rate 0.7 ml/min): *trans*-isomer: t_{minor} = 24.0 min, t_{major} = 133.3 min, 96% *ee*. [a]$_D^{20}$ = +64.4° (c = 1, CH_2Cl_2).



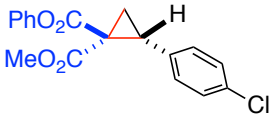
1-methyl 1-phenyl (1*S*,2*R*)-2-(4-bromophenyl)cyclopropane-1,1-dicarboxylate (3n) Yield: 99%; 95:5 diastereomeric ratio. White solid. TLC: Hexane:EtOAc = 4:1; R_f = 0.6. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43 (dd, J = 9.8, 3.3 Hz, 2H), 7.39 (d, J = 7.8 Hz, 2H), 7.26 (m, 1H), 7.18 – 7.09 (m, 4H), 3.48 (s, 3H), 3.31 (t, J = 8.7 Hz, 1H), 2.30 (dd, J = 8.1, 5.4 Hz, 1H), 1.90 (dd, J = 9.3, 5.3 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.19, 166.54, 150.52, 133.35, 131.36, 130.26, 129.44, 126.13, 121.61, 121.30, 52.59, 37.27, 32.17, 19.65. HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{18}H_{15}BrO_4Na^+$: 397.0046; Found: 397.0040. IR (neat, cm^{-1}): ν 2954, 1748, 1727, 1274, 1216, 1192, 1162, 1124. HPLC (chiral OJ-H, 38% isopropanol-hexane, rate 0.6 ml/min): *trans*-isomer: t_{minor} = 40.0 min, t_{major} = 190.1 min, 95% *ee*. [a]$_D^{20}$ = +115.4° (c = 1, CH_2Cl_2).



1-methyl 1-phenyl (1*S*,2*R*)-2-(3-bromophenyl)cyclopropane-1,1-dicarboxylate (3o) Yield: 99%; 94:6 diastereomeric ratio. Colorless oil. TLC: Hexane:EtOAc = 4:1; R_f = 0.6. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46 – 7.37 (m, 4H), 7.29 – 7.23 (m, 1H), 7.21 – 7.13 (m, 4H), 3.50 (s, 3H), 3.38 – 3.28 (m, 1H), 2.30 (dd, J = 8.2, 5.4 Hz, 1H), 1.90 (dd, J = 9.2, 5.3 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.15, 166.47, 150.52, 136.73, 131.78, 130.71, 129.74, 129.45, 127.16, 126.15, 122.25, 121.31, 52.58, 37.31, 32.12, 19.67. HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{18}H_{15}BrO_4Na^+$: 397.0046; Found: 397.0022. IR (neat, cm^{-1}): ν 2951, 1731, 1262, 1213, 1190, 1160, 1117. HPLC (chiral AD-H, 1.3% isopropanol-hexane, rate 1 ml/min): *trans*-isomer: t_{major} = 20.0 min, t_{minor} = 30.8 min, 97% *ee*. $[a]_D^{20}$ = +86.9° (c = 1, CH_2Cl_2).

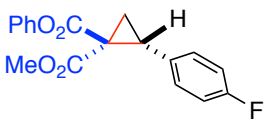


1-methyl 1-phenyl (1*S*,2*S*)-2-(2-bromophenyl)cyclopropane-1,1-dicarboxylate (3p) Yield: 99%; 79:21 diastereomeric ratio. Colorless oil. TLC: Hexane:EtOAc = 4:1; R_f = 0.6. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59 (dd, J = 8.3, 1.2 Hz, 1H), 7.45 – 7.37 (m, 2H), 7.31 – 7.09 (m, 6H), 3.47 (t, J = 8.9 Hz, 1H), 3.44 (s, 3H), 2.41 (dd, J = 8.4, 5.3 Hz, 1H), 2.00 (dd, J = 9.2, 5.3 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.98, 166.66, 150.65, 134.09, 132.50, 129.42, 129.17, 129.11, 127.00, 126.03, 121.41, 121.05, 52.40, 36.56, 34.57, 19.66. HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{18}H_{15}BrO_4Na^+$: 397.0046; Found: 397.0034. IR (neat, cm^{-1}): ν 2951, 1730, 1279, 1264, 1213, 1190, 1160, 1113, 1083, 1066. HPLC (chiral OJ-H, 15% isopropanol-hexane, rate 0.8 ml/min): *trans*-isomer: t_{major} = 48.1 min, t_{minor} = 73.8 min, 95% *ee*. $[a]_D^{20}$ = +11.9° (c = 1, CH_2Cl_2).

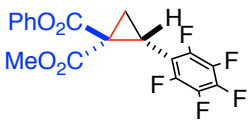


1-methyl 1-phenyl (1*S*,2*R*)-2-(4-chlorophenyl)cyclopropane-1,1-dicarboxylate (3q) Yield: 99%; 94:6 diastereomeric ratio. White solid.

TLC: Hexane:EtOAc = 5:1; R_f = 0.6. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41 (t, J = 7.9 Hz, 2H), 7.28 (q, J = 8.4 Hz, 3H), 7.21 (d, J = 8.5 Hz, 2H), 7.18 – 7.13 (m, 2H), 3.49 (s, 3H), 3.34 (t, J = 8.7 Hz, 1H), 2.31 (dd, J = 8.1, 5.3 Hz, 1H), 1.91 (dd, J = 9.3, 5.3 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.22, 166.57, 150.53, 133.47, 132.81, 129.93, 129.44, 128.41, 126.13, 121.31, 52.57, 37.31, 32.13, 19.70. HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{18}H_{16}ClO_4^+$: 331.0732; Found: 331.0735. IR (neat, cm^{-1}): ν 2950, 1740, 1720, 1263, 1215, 1193, 1127, 1014. HPLC (chiral OJ-H, 35% isopropanol-hexane, rate 0.6 ml/min): *trans*-isomer: t_{minor} = 45.8 min, t_{major} = 185.9 min, 97% *ee*. $[a]_D^{20}$ = +111.0° (c = 1, CH_2Cl_2).

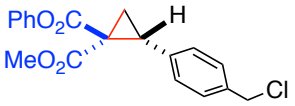


1-methyl 1-phenyl (1*S*,2*R*)-2-(4-fluorophenyl)cyclopropane-1,1-dicarboxylate (3r) Yield: 76%; 94:6 diastereomeric ratio. Colorless oil. TLC: Hexane:EtOAc = 5:1; R_f = 0.6. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45 – 7.36 (m, 2H), 7.29 – 7.20 (m, 3H), 7.18 – 7.12 (m, 2H), 7.03 – 6.96 (m, 2H), 3.47 (s, 3H), 3.35 (t, J = 8.7 Hz, 1H), 2.31 (dd, J = 8.1, 5.3 Hz, 1H), 1.91 (dd, J = 9.3, 5.3 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.30, 166.65, 162.18 (d, J = 246.8 Hz), 150.54, 130.25 (d, J = 9.2 Hz), 129.96 (d, J = 4.1 Hz), 129.43, 126.10, 121.32, 115.16 (d, J = 22.2 Hz), 52.48, 37.20, 32.13, 19.79. ^{19}F NMR (375 MHz, $CDCl_3$): δ -115.03 (tt, J = 8.6, 5.3 Hz). HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{18}H_{15}FO_4Na^+$: 337.0847; Found: 337.0849. IR (neat, cm^{-1}): ν 2953, 1731, 1513, 1264, 1213, 1190, 1159, 1118. HPLC (chiral OJ-H, 20% isopropanol-hexane, rate 0.8 ml/min): *trans*-isomer: t_{minor} = 40.4 min, t_{major} = 108.1 min, 96% *ee*. $[a]_D^{20}$ = +111.7° (c = 1, CH_2Cl_2).

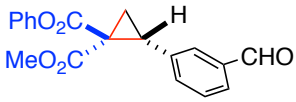


1-methyl 1-phenyl (1*S*,2*S*)-2-(perfluorophenyl)cyclopropane-1,1-dicarboxylate (3s) Yield: 78%; 89:11 diastereomeric ratio. White solid. TLC:

Hexane:EtOAc = 3:1; R_f = 0.4. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42 (dd, J = 8.5, 7.4 Hz, 2H), 7.30 – 7.25 (m, 1H), 7.18 – 7.14 (m, 2H), 3.70 (s, 3H), 3.03 (t, J = 9.0 Hz, 1H), 2.37 (dd, J = 8.3, 5.6 Hz, 1H), 2.12 (dd, J = 9.6, 5.6 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.27, 167.23, 150.53, 146.40 (d, J = 249.5 Hz), 140.69 (d, J = 255.3 Hz), 137.37 (dt, J = 251.5, 18.4 Hz), 129.51, 126.25, 121.18, 109.13 (td, J = 16.2, 4.8 Hz), 53.05, 34.38, 21.70, 20.54 (t, J = 4.4 Hz). ^{19}F NMR (375 MHz, $CDCl_3$): δ -141.56 (dd, J = 21.9, 7.9 Hz), -154.87 (t, J = 20.3 Hz), -162.88 (td, J = 21.8, 8.0 Hz). HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{18}H_{11}F_5O_4Na^+$: 409.0470; Found: 409.0469. IR (neat, cm^{-1}): ν 2960, 1757, 1728, 1497, 1487, 1210, 1190. HPLC (chiral OD-H, 1% isopropanol-hexane, rate 0.8 ml/min): *trans*-isomer: t_{major} = 23.7 min, t_{minor} = 27.6 min, 96% *ee*. $[a]_D^{20}$ = +71.2° (c = 1, CH_2Cl_2).

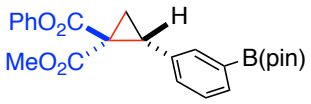


1-methyl 1-phenyl (1*S*,2*R*)-2-(4-(chloromethyl)phenyl)cyclopropane-1,1-dicarboxylate (3t) Yield: 81%; 91:9 diastereomeric ratio. Colorless oil. TLC: Hexane:EtOAc = 4:1; R_f = 0.4. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43 – 7.38 (m, 2H), 7.33 (d, J = 8.2 Hz, 2H), 7.28 – 7.23 (m, 3H), 7.18 – 7.13 (m, 2H), 4.57 (s, 2H), 3.45 (s, 3H), 3.36 (t, J = 8.7 Hz, 1H), 2.34 (dd, J = 8.2, 5.3 Hz, 1H), 1.91 (dd, J = 9.3, 5.3 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.32, 166.66, 150.55, 136.79, 134.62, 129.44, 128.92, 128.47, 126.11, 121.34, 52.50, 45.81, 37.38, 32.54, 19.75. HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{19}H_{17}ClO_4Na^+$: 367.0708; Found: 367.0694. IR (neat, cm^{-1}): ν 3101, 2951, 1750, 1730, 1264, 1211, 1191, 1169, 1158, 1114. HPLC (chiral AD-H, 2% isopropanol-hexane, rate 1 ml/min): *trans*-isomer: t_{major} = 23.2 min, t_{minor} = 45.2 min, 96% *ee*. $[a]_D^{20}$ = +82.9° (c = 1, CH_2Cl_2).

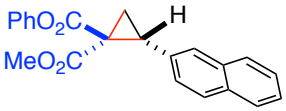


1-methyl 1-phenyl (1*S*,2*R*)-2-(3-formylphenyl)cyclopropane-1,1-dicarboxylate (3u) Yield: 53%; 90:10 diastereomeric ratio. Colorless oil.

TLC: Hexane:EtOAc = 3:1; R_f = 0.3. ^{1}H NMR (600 MHz, $CDCl_3$): δ 10.02 (s, 1H), 7.79 (d, *J* = 2.0 Hz, 2H), 7.57 – 7.53 (m, 1H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.44 – 7.38 (m, 2H), 7.28 – 7.25 (m, 1H), 7.18 – 7.13 (m, 2H), 3.45 (s, 3H), 3.42 (d, *J* = 8.8 Hz, 1H), 2.40 (dd, *J* = 8.1, 5.4 Hz, 1H), 1.96 (dd, *J* = 9.2, 5.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): *δ* 191.93, 168.10, 166.49, 150.55, 136.42, 135.71, 134.67, 129.78, 129.48, 129.01, 128.99, 126.19, 121.31, 52.56, 37.34, 32.17, 19.64. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{19}H_{17}O_5^+$: 325.1071; Found: 325.1072. IR (neat, cm^{-1}): *ν* 2951, 2874, 1731, 1697, 1331, 1267, 1191, 1119, 752, 690. HPLC (chiral OJ-H, 40% isopropanol-hexane, rate 0.8 ml/min): *trans*-isomer: t_{major} = 78.4 min, >99% *ee*. $[a]_D^{20}$ = +79.2° (c = 1, CH_2Cl_2).

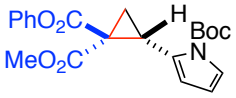


1-methyl 1-phenyl (1*S*,2*R*)-2-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)cyclopropane-1,1-dicarboxylate (3v) Yield: 98%; >99:1 diastereomeric ratio. White solid. TLC: Hexane:EtOAc = 8:1; R_f = 0.3. ^{1}H NMR (600 MHz, $CDCl_3$): *δ* 7.74 (d, *J* = 0.9 Hz, 1H), 7.72 – 7.68 (m, 1H), 7.40 (tt, *J* = 7.4, 1.0 Hz, 2H), 7.34 – 7.29 (m, 2H), 7.26 – 7.23 (m, 1H), 7.16 (dt, *J* = 8.6, 1.1 Hz, 2H), 3.44 (s, 3H), 3.42 – 3.36 (m, 1H), 2.38 (ddd, *J* = 8.2, 5.2, 0.9 Hz, 1H), 1.91 (ddd, *J* = 9.3, 5.2, 1.0 Hz, 1H), 1.36 (s, 12H). ^{13}C NMR (150 MHz, $CDCl_3$): *δ* 168.44, 166.75, 150.62, 135.34, 133.97, 133.64, 131.03, 129.41, 127.62, 126.02, 121.41, 83.87, 52.34, 37.21, 33.00, 24.88, 24.86, 19.82. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{24}H_{28}O_6B^+$: 423.1973; Found: 423.1999. IR (neat, cm^{-1}): *ν* 2978, 1735, 1350, 1318, 1269, 1214, 1194, 1144, 1119. HPLC (chiral IA, 0.7% isopropanol-hexane, rate 0.8 ml/min): *trans*-isomer: t_{major} = 11.7 min, t_{minor} = 16.8 min, 99% *ee*. $[a]_D^{20}$ = +123.2° (c = 1, CH_2Cl_2).

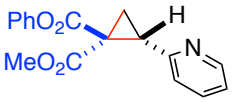


1-methyl 1-phenyl (1*S*,2*R*)-2-(naphthalen-2-yl)cyclopropane-1,1-dicarboxylate (3w) Yield: 86%; 92:8 diastereomeric ratio. White solid.

TLC: Hexane:EtOAc = 8:1; R_f = 0.6. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85 – 7.76 (m, 3H), 7.71 (d, J = 1.7 Hz, 1H), 7.51 – 7.44 (m, 2H), 7.44 – 7.38 (m, 3H), 7.29 – 7.24 (m, 1H), 7.18 (dd, J = 7.8, 1.2 Hz, 2H), 3.53 (t, J = 8.6 Hz, 1H), 3.37 (s, 3H), 2.49 (dd, J = 8.1, 5.3 Hz, 1H), 1.99 (dd, J = 9.2, 5.2 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.46, 166.75, 150.61, 133.09, 132.71, 131.79, 129.43, 127.86, 127.79, 127.58, 127.32, 126.61, 126.19, 126.08, 126.00, 121.38, 52.45, 37.51, 33.17, 19.88. HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{22}H_{18}O_4Na^+$: 369.1097; Found: 369.1097. IR (neat, cm^{-1}): ν 3006, 2957, 1747, 1727, 1216, 1185, 1120. HPLC (chiral AD-H, 2% isopropanol-hexane, rate 1 ml/min): *trans*-isomer: t_{major} = 19.2 min, t_{minor} = 21.9 min, 97% *ee*. $[a]_D^{20}$ = +178.5° (c = 1, CH_2Cl_2).

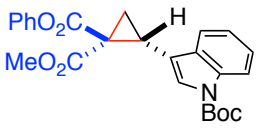


1-methyl 1-phenyl (1*S*,2*S*)-2-(1-(*tert*-butoxycarbonyl)-1*H*-pyrrol-2-yl)cyclopropane-1,1-dicarboxylate (3x) Yield: 80%; 83:17 diastereomeric ratio. Colorless oil. TLC: Hexane:EtOAc = 10:1; R_f = 0.4. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 (dd, J = 8.5, 7.4 Hz, 2H), 7.28 – 7.22 (m, 2H), 7.15 (dd, J = 8.7, 1.2 Hz, 2H), 6.06 (t, J = 3.3 Hz, 1H), 6.03 (dt, J = 3.2, 1.5 Hz, 1H), 3.58 (t, J = 8.5 Hz, 1H), 3.48 (s, 3H), 2.16 (dd, J = 8.0, 5.0 Hz, 1H), 1.98 (dd, J = 9.0, 5.0 Hz, 1H), 1.62 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.44, 166.92, 150.69, 149.12, 129.38, 125.93, 122.72, 121.40, 113.04, 109.61, 83.85, 52.37, 36.36, 27.98, 27.81, 20.32. HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{21}H_{23}NO_6Na^+$: 408.1418; Found: 408.1400. IR (neat, cm^{-1}): ν 2979, 1733, 1327, 1303, 1261, 1191, 1160, 1125, 1091. HPLC (chiral IC, 4% isopropanol-hexane, rate 0.8 ml/min): *trans*-isomer: t_{major} = 13.1 min, t_{minor} = 17.2 min, 74% *ee*. $[a]_D^{20}$ = +2.6° (c = 1, CH_2Cl_2).

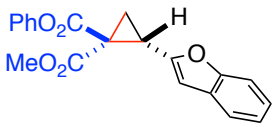


1-methyl 1-phenyl (1*S*,2*S*)-2-(pyridin-2-yl)cyclopropane-1,1-dicarboxylate (3y) Yield: 96%; > 99:1 diastereomeric ratio. Colorless oil.

TLC: Hexane:EtOAc = 3:1; R_f = 0.4. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.47 (dt, J = 4.6, 1.4 Hz, 1H), 7.63 (td, J = 7.7, 1.9 Hz, 1H), 7.42 – 7.31 (m, 3H), 7.28 – 7.21 (m, 1H), 7.18 – 7.08 (m, 3H), 3.55 (s, 3H), 3.26 (dd, J = 9.1, 7.5 Hz, 1H), 2.50 (dd, J = 7.5, 4.6 Hz, 1H), 1.98 (dd, J = 9.1, 4.6 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.45, 166.89, 155.05, 150.48, 148.99, 136.24, 129.37, 126.07, 123.92, 122.01, 121.36, 52.44, 37.90, 33.43, 20.94. HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{17}H_{15}NO_4Na^+$: 320.0893; Found: 320.0900. IR (neat, cm^{-1}): ν 2950, 1735, 1260, 1189, 1160, 1121. HPLC (chiral AD-H, 2.5% isopropanol-hexane, rate 1 ml/min): *trans*-isomer: t_{major} = 26.7 min, t_{minor} = 47.0 min, 94% *ee*. $[a]_D^{20}$ = +153.2° (c = 1, CH_2Cl_2).

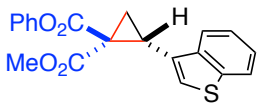


1-methyl 1-phenyl (1*S*,2*R*)-2-(1-(*tert*-butoxycarbonyl)-1*H*-indol-3-yl)cyclopropane-1,1-dicarboxylate (3z) Yield: 99%; 95:5 diastereomeric ratio. Colorless oil. TLC: Hexane:EtOAc = 10:1; R_f = 0.4. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.12 (d, J = 7.8 Hz, 1H), 7.71 – 7.65 (m, 1H), 7.46 – 7.39 (m, 3H), 7.37 – 7.31 (m, 1H), 7.27 (dd, J = 8.0, 6.8 Hz, 2H), 7.22 – 7.17 (m, 2H), 3.41 (s, 3H), 3.32 (ddd, J = 9.2, 7.9, 1.4 Hz, 1H), 2.27 (dd, J = 8.0, 4.9 Hz, 1H), 1.97 (dd, J = 9.2, 4.9 Hz, 1H), 1.68 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.48, 166.97, 150.61, 149.42, 135.34, 130.25, 129.44, 126.09, 124.67, 124.18, 122.59, 121.34, 119.18, 115.14, 114.96, 83.84, 52.42, 36.18, 28.16, 23.94, 19.70. HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{25}H_{25}NO_6Na^+$: 458.1574; Found: 458.1569. IR (neat, cm^{-1}): ν 2989, 1757, 1725, 1370, 1258, 1151. HPLC (chiral IF, 2% isopropanol-hexane, rate 0.8 ml/min): *trans*-isomer: t_{major} = 13.9 min, t_{minor} = 17.5 min, 94% *ee*. $[a]_D^{20}$ = +68.3° (c = 1, CH_2Cl_2).

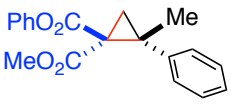


1-methyl 1-phenyl (1*S*,2*S*)-2-(benzofuran-2-yl)cyclopropane-1,1-dicarboxylate (3aa) Yield: 98%; 85:15 diastereomeric ratio. Colorless oil.

TLC: Hexane: EtOAc = 5:1; R_f = 0.4. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.54 – 7.49 (m, 1H), 7.45 – 7.37 (m, 3H), 7.26 (d, J = 2.7 Hz, 2H), 7.23 – 7.19 (m, 1H), 7.18 – 7.14 (m, 2H), 6.60 (s, 1H), 3.88 (s, 1H), 3.57 (s, 3H), 3.37 (dd, J = 9.4, 7.9 Hz, 1H), 2.37 (dd, J = 7.8, 5.2 Hz, 1H), 2.04 (dd, J = 9.5, 5.2 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.72, 166.50, 154.85, 152.21, 150.47, 129.46, 128.17, 126.21, 124.19, 122.86, 121.31, 120.78, 110.85, 104.85, 52.88, 37.00, 26.13, 19.63. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{20}H_{17}O_5^+$: 337.1071; Found: 337.1067. IR (neat, cm^{-1}): ν 2951, 1735, 1454, 1330, 1255, 1207, 1190, 1118, 750. HPLC (chiral WHELK, 20% isopropanol-hexane, rate 0.8 ml/min): *trans*-isomer: t_{minor} = 17.3 min, t_{major} = 19.2 min, 96% *ee*. $[a]_D^{20}$ = +137.2° (c = 0.5, CH_2Cl_2).

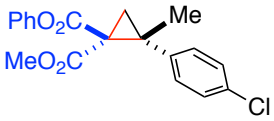


1-methyl 1-phenyl (1*S*,2*S*)-2-(benzo[*b*]thiophen-3-yl)cyclopropane-1,1-dicarboxylate (3ab) Yield: 94%; 92:8 diastereomeric ratio. Colorless oil. TLC: Hexane: EtOAc = 5:1; R_f = 0.4. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.94 (dd, J = 7.9, 1.0 Hz, 1H), 7.84 (dd, J = 8.0, 1.0 Hz, 1H), 7.46 – 7.41 (m, 3H), 7.38 (t, J = 7.5 Hz, 1H), 7.28 (td, J = 7.6, 1.1 Hz, 1H), 7.23 – 7.21 (m, 1H), 7.20 (d, J = 4.3 Hz, 2H), 3.50 – 3.45 (m, 1H), 3.31 (s, 3H), 2.40 (dd, J = 8.0, 5.1 Hz, 1H), 2.02 (dd, J = 9.2, 5.1 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.35, 166.74, 150.65, 140.06, 138.95, 129.74, 129.47, 126.13, 124.64, 124.20, 123.96, 122.69, 121.95, 121.34, 52.37, 36.48, 26.50, 19.59. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{20}H_{17}O_4S^+$: 353.0842; Found: 353.0828. IR (neat, cm^{-1}): ν 2950, 1732, 1313, 1269, 1209, 1191, 1118, 759, 710. HPLC (chiral ID, 10% isopropanol-hexane, rate 0.8 ml/min): *trans*-isomer: t_{major} = 11.3 min, t_{minor} = 13.9 min, 96% *ee*. $[a]_D^{20}$ = +20.4° (c = 1, CH_2Cl_2).

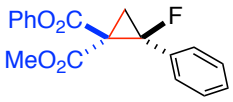


1-methyl 1-phenyl (1*S*,2*R*)-2-methyl-2-phenylcyclopropane-1,1-dicarboxylate (3ac) Yield: 99%; 89:11 diastereomeric ratio. Colorless oil.

TLC: Hexane:EtOAc = 8:1; R_f = 0.6. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43 (dd, J = 8.5, 7.4 Hz, 2H), 7.38 – 7.23 (m, 6H), 7.21 – 7.16 (m, 2H), 3.45 (s, 3H), 2.31 (d, J = 5.3 Hz, 1H), 1.83 (d, J = 5.3 Hz, 1H), 1.69 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.83, 167.08, 150.83, 140.88, 129.48, 128.28, 128.23, 127.18, 126.05, 121.43, 52.30, 40.46, 38.47, 25.21, 24.77. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{19}H_{18}O_4Na^+$: 333.1097; Found: 333.1089. IR (neat, cm^{-1}): ν2952, 1733, 1221, 1190, 1092, 1074. HPLC (chiral IC, 8% isopropanol-hexane, rate 0.8 ml/min): *trans*-isomer: t_{minor} = 13.8 min, t_{major} = 20.2 min, 97% *ee*. $[a]_D^{20}$ = +41.8° (c = 1, CH_2Cl_2).

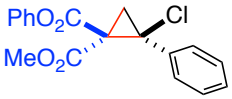


1-methyl 1-phenyl (1*S*,2*R*)-2-(4-chlorophenyl)-2-methylcyclopropane-1,1-dicarboxylate (3ad) Yield: 99%; 87:13 diastereomeric ratio. Colorless oil. TLC: Hexane:EtOAc = 8:1; R_f = 0.4. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.45 – 7.40 (m, 2H), 7.36 – 7.22 (m, 5H), 7.18 (dd, J = 7.7, 1.1 Hz, 2H), 3.51 (s, 3H), 2.26 (d, J = 5.4 Hz, 1H), 1.83 (d, J = 5.4 Hz, 1H), 1.66 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 167.70, 166.78, 150.77, 139.45, 132.96, 129.64, 129.50, 128.51, 126.11, 121.35, 52.46, 40.43, 37.58, 25.25, 24.71. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{19}H_{18}ClO_4^+$: 345.0888; Found: 345.0895. IR (neat, cm^{-1}): ν2967, 1738, 1493, 1230, 1194, 1090. HPLC (chiral IC, 5% isopropanol-hexane, rate 0.8 ml/min): *trans*-isomer: t_{minor} = 13.1 min, t_{major} = 19.6 min, 98% *ee*. $[a]_D^{20}$ = +72.0° (c = 1, CH_2Cl_2).

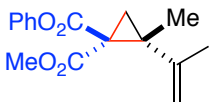


1-methyl 1-phenyl (1*S*,2*S*)-2-fluoro-2-phenylcyclopropane-1,1-dicarboxylate (3ae) Yield: 88%; 92:8 diastereomeric ratio. Colorless oil. TLC: Hexane:EtOAc = 5:1; R_f = 0.6. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.57 (ddd, J = 6.5, 2.7, 1.6 Hz, 2H), 7.48 – 7.39 (m, 5H), 7.31 – 7.25 (m, 1H), 7.24 – 7.18 (m, 2H), 3.55 (s, 3H), 2.58 (dd, J = 20.4, 7.8 Hz, 1H), 2.49 (dd, J = 14.1, 7.9 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.12, 163.84 (d, J = 2.9

Hz), 150.84, 131.81 (d, J = 21.0 Hz), 129.94 (d, J = 2.7 Hz), 129.48, 128.40 (d, J = 4.4 Hz), 128.37, 126.18, 121.45, 84.84 (d, J = 228.9 Hz), 52.77, 40.97 (d, J = 15.3 Hz), 21.76 (d, J = 10.5 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -158.08 (dd, J = 20.5, 14.1 Hz). HRMS (DART) ($[M+H]^+$) Calcd. for $C_{18}H_{16}FO_4^+$: 315.1027; Found: 315.1013. IR (neat, cm^{-1}): ν 2954, 1763, 1738, 1685, 1191, 1159, 1135, 751, 688. HPLC (chiral OJ-H, 50% isopropanol-hexane, rate 0.4 ml/min): *trans*-isomer: t_{minor} = 79.4 min, t_{major} = 193.5 min, 94% *ee*. $[a]_D^{20}$ = +0.4° (c = 1, CH_2Cl_2).

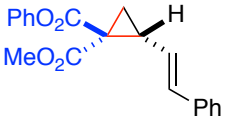


1-methyl 1-phenyl (1*S*,2*S*)-2-chloro-2-phenylcyclopropane-1,1-dicarboxylate (3af) Yield: 78%; 92:8 diastereomeric ratio. Light yellow oil. TLC: Hexane:EtOAc = 5:1; R_f = 0.6. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52 (dd, J = 8.1, 1.5 Hz, 2H), 7.46 – 7.41 (m, 2H), 7.40 – 7.34 (m, 3H), 7.31 – 7.27 (m, 1H), 7.27 – 7.23 (m, 2H), 3.53 (s, 3H), 2.62 (d, J = 7.1 Hz, 1H), 2.46 (d, J = 7.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.99, 164.33, 150.90, 136.96, 129.49, 129.10, 128.72, 128.51, 126.23, 121.47, 52.89, 52.68, 42.33, 26.31. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{18}H_{16}ClO_4^+$: 331.0732; Found: 331.0724. IR (neat, cm^{-1}): ν 3030, 2952, 1736, 1249, 1191, 1109, 738, 697. HPLC (chiral OD-H, 2.5% isopropanol-hexane, rate 0.8 ml/min): *trans*-isomer: t_{minor} = 27.3 min, t_{major} = 32.7 min, 98% *ee*. $[a]_D^{20}$ = +72.0° (c = 1, CH_2Cl_2).

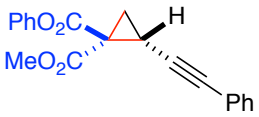


1-methyl 1-phenyl (1*S*,2*R*)-2-methyl-2-(prop-1-en-2-yl)cyclopropane-1,1-dicarboxylate (3ag) Yield: 54%; 60:40 diastereomeric ratio. Colorless oil. TLC: Hexane:EtOAc = 6:1; R_f = 0.6. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40 (dd, J = 8.5, 7.4 Hz, 2H), 7.27 – 7.23 (m, 1H), 7.15 – 7.10 (m, 2H), 5.02 – 4.89 (m, 2H), 3.74 (s, 3H), 2.02 (d, J = 5.2 Hz, 1H), 1.83 (s, 3H), 1.63 (t, J = 4.8 Hz, 1H), 1.48 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.19, 167.10, 150.80, 144.00, 129.42, 125.98, 121.39, 113.66, 52.52, 40.01, 39.42, 25.89, 21.27, 20.42. HRMS (ESI)

([M+Na]$^+$) Calcd. for $C_{16}H_{18}O_4Na^+$: 297.1097; Found: 297.1106. IR (neat, cm^{-1}): ν2952, 1732, 1262, 1220, 1190, 1069. HPLC (chiral IC, 5% isopropanol-hexane, rate 0.8 ml/min): *trans*-isomer: t_{minor} = 12.1 min, t_{major} = 24.7 min, 87% *ee*. [a]$_D^{20}$ = +10.3° (c = 1, CH_2Cl_2).

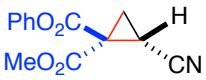


1-methyl 1-phenyl (1*S*,2*R*)-2-((*E*)-styryl)cyclopropane-1,1-dicarboxylate (3ah) Yield: 99%; 68:32 diastereomeric ratio. Colorless oil. TLC: Hexane:EtOAc = 8:1; R_f = 0.3. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40 (dd, J = 8.5, 7.4 Hz, 2H), 7.37 – 7.29 (m, 4H), 7.28 – 7.19 (m, 2H), 7.16 – 7.11 (m, 2H), 6.72 (d, J = 15.8 Hz, 1H), 5.90 (dd, J = 15.8, 8.8 Hz, 1H), 3.80 (s, 3H), 2.96 – 2.86 (m, 1H), 2.01 (dd, J = 7.7, 5.1 Hz, 1H), 1.87 (dd, J = 9.0, 5.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.17, 167.71, 150.57, 136.57, 134.23, 129.43, 128.58, 127.70, 126.18, 126.06, 124.12, 121.34, 52.86, 36.17, 32.14, 21.88. HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{20}H_{18}O_4Na^+$: 345.1097; Found: 345.1102. IR (neat, cm^{-1}): ν3026, 2952, 1728, 1277, 1191, 1114. HPLC (chiral OD-H, 2% isopropanol-hexane, rate 1 ml/min): *trans*-isomer: t_{minor} = 21.6 min, t_{major} = 44.5 min, 82% *ee*; *cis*-isomer: t_{major} = 13.3 min, $_{minor}$ = 25.9 min, 83% *ee*. [a]$_D^{20}$ = +65.3° (c = 1, CH_2Cl_2).

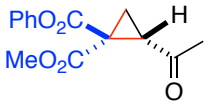


1-methyl 1-phenyl (1*S*,2*R*)-2-(phenylethynyl)cyclopropane-1,1-dicarboxylate (3ai) Yield: 81%; 74:26 diastereomeric ratio. Light yellow oil. TLC: Hexane: EtOAc = 5:1; R_f = 0.3. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 (dd, J = 7.6, 2.2 Hz, 3H), 7.33 – 7.23 (m, 5H), 7.16 – 7.11 (m, 2H), 3.87 (s, 3H), 2.82 (dd, J = 9.2, 7.3 Hz, 1H), 2.12 (dd, J = 7.4, 4.7 Hz, 1H), 1.86 (dd, J = 9.2, 4.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.36, 166.59, 150.46, 131.74, 129.49, 128.35, 128.28, 126.23, 122.57, 121.28, 84.92, 80.84, 53.05, 36.59, 22.93, 18.20. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{20}H_{17}O_4^+$: 321.1121; Found: 321.1118. IR (neat, cm^{-1}):

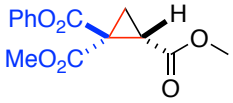
ν 2952, 1734, 1491, 1329, 1274, 1191, 1116, 755, 700. HPLC (chiral ID, 10% isopropanol-hexane, rate 0.8 ml/min): *trans*-isomer: t_{major} = 16.1 min, t_{minor} = 20.9 min, 82% *ee*. $[a]_D^{20}$ = +149.2° (c = 1, CH_2Cl_2).



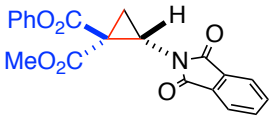
1-methyl 1-phenyl (1*S*,2*S*)-2-cyanocyclopropane-1,1-dicarboxylate (3aj) Yield: 73%; 80:20 diastereomeric ratio. Colorless oil. TLC: Hexane:EtOAc = 4:1; R_f = 0.4. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41 (dd, J = 8.5, 7.4 Hz, 2H), 7.31 – 7.26 (m, 1H), 7.11 (dd, J = 8.6, 1.2 Hz, 2H), 3.94 (s, 3H), 2.63 (dd, J = 9.5, 7.2 Hz, 1H), 2.24 (dd, J = 7.3, 5.4 Hz, 1H), 1.90 (dd, J = 9.5, 5.4 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.45, 165.10, 150.12, 129.63, 126.64, 120.95, 116.01, 53.83, 34.90, 20.23, 12.61. HRMS (ESI) ($[M-CN+2H]^+$) Calcd. for $C_{12}H_{13}O_4^+$: 221.0808; Found: 221.0844. IR (neat, cm^{-1}): ν 3044, 2957, 1736, 1265, 1209, 1189, 1160, 1120. HPLC (chiral OD-H, 8% isopropanol-hexane, rate 0.8 ml/min): *trans*-isomer: t_{major} = 22.1 min, t_{minor} = 33.1 min, 95% *ee*. $[a]_D^{20}$ = +80.0° (c = 1, CH_2Cl_2).



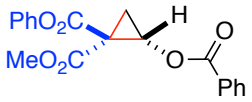
1-methyl 1-phenyl (1*S*,2*S*)-2-acetylcyclopropane-1,1-dicarboxylate (3ak) Yield: 72%; 75:25 diastereomeric ratio. Colorless oil. TLC: Hexane:EtOAc = 4:1; R_f = 0.3. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38 (dd, J = 8.5, 7.4 Hz, 2H), 7.28 – 7.23 (m, 1H), 7.11 (dd, J = 8.6, 1.2 Hz, 2H), 3.78 (s, 3H), 2.99 (dd, J = 8.6, 6.9 Hz, 1H), 2.41 (s, 3H), 2.12 (dd, J = 6.9, 4.4 Hz, 1H), 1.78 (dd, J = 8.6, 4.4 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 202.88, 167.64, 166.04, 150.25, 129.48, 126.36, 121.19, 53.08, 38.77, 34.48, 31.63, 21.33. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{14}H_{14}O_5Na^+$: 285.0733; Found: 285.0732. IR (neat, cm^{-1}): ν 2954, 1739, 1709, 1259, 1208, 1190, 1171, 1161, 1119. HPLC (chiral IC, 20% isopropanol-hexane, rate 0.8 ml/min): *trans*-isomer: t_{minor} = 18.4 min, t_{major} = 31.3 min, 96% *ee*. $[a]_D^{20}$ = +93.9° (c = 1, CH_2Cl_2).



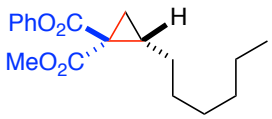
1,2-dimethyl 1-phenyl (1*S*,2*S*)-cyclopropane-1,1,2-tricarboxylate (3al) Yield: 85%; 54:46 diastereomeric ratio. Colorless oil. TLC: Hexane:EtOAc = 4:1; R_f = 0.5. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38 (ddd, J = 8.5, 7.5, 5.6 Hz, 2H), 7.27 – 7.22 (m, 1H), 7.16 – 7.08 (m, 2H), 3.81 (s, 3H), 3.75 (s, 3H), 2.74 (dt, J = 8.8, 6.7 Hz, 1H), 2.12 (ddd, J = 7.0, 4.8, 1.4 Hz, 1H), 1.82 (ddd, J = 16.3, 8.8, 4.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.62, 167.32, 166.02, 150.23, 129.48, 126.36, 121.19, 53.13, 52.58, 36.67, 28.20, 20.37. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{14}H_{14}O_6Na^+$: 301.0683; Found: 301.0673. IR (neat, cm^{-1}): ν 2955, 2917, 2849, 1730, 1264, 1223, 1190, 1162, 1118. HPLC (chiral IF, 3% isopropanol-hexane, rate 0.8 ml/min): *trans*-isomer: t_{minor} = 20.0 min, t_{major} = 26.4 min, 90% *ee*. $[a]_D^{20}$ = +27.6° (c = 1, CH_2Cl_2).



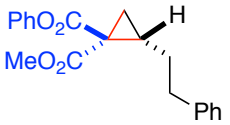
1-methyl 1-phenyl (1*S*,2*S*)-2-(1,3-dioxoisoindolin-2-yl)cyclopropane-1,1-dicarboxylate (3am) Yield: 77%; 91:9 diastereomeric ratio. Colorless oil. TLC: Hexane:EtOAc = 3:1; R_f = 0.3. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86 (dd, J = 5.5, 3.1 Hz, 2H), 7.74 (dd, J = 5.5, 3.0 Hz, 2H), 7.41 (dd, J = 8.5, 7.4 Hz, 2H), 7.29 – 7.23 (m, 1H), 7.21 – 7.16 (m, 2H), 3.82 (dd, J = 8.5, 6.7 Hz, 1H), 3.69 (s, 3H), 2.83 (t, J = 6.6 Hz, 1H), 2.20 (dd, J = 8.6, 6.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.76, 166.76, 166.66, 150.52, 134.32, 131.43, 129.45, 126.16, 123.50, 121.29, 53.07, 35.13, 33.34, 20.06. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{20}H_{16}NO_6^+$: 366.0972; Found: 366.0974. IR (neat, cm^{-1}): ν 2954, 1780, 1714, 1392, 1323, 1214, 1189, 1161, 1109, 1088. HPLC (chiral IC, 20% isopropanol-hexane, rate 0.8 ml/min): *trans*-isomer: t_{major} = 38.5 min, t_{minor} = 51.7 min, 95% *ee*. $[a]_D^{20}$ = +75.3° (c = 1, CH_2Cl_2).



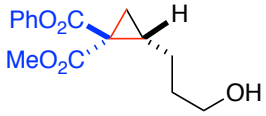
1-methyl 1-phenyl (1*S*,2*S*)-2-(benzoyloxy)cyclopropane-1,1-dicarboxylate (3an) Yield: 94%; 75:25 diastereomeric ratio. Colorless oil. TLC: Hexane:EtOAc = 5:1; R_f = 0.3. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.97 (dt, J = 8.4, 1.6 Hz, 1H), 7.59 (ddt, J = 7.3, 6.2, 1.3 Hz, 1H), 7.48 – 7.42 (m, 2H), 7.41 – 7.37 (m, 2H), 7.30 – 7.23 (m, 2H), 7.16 – 7.12 (m, 2H), 5.27 – 5.18 (m, 1H), 3.74 (s, 3H), 2.30 (dd, J = 6.8, 5.2 Hz, 1H), 2.01 (t, J = 6.9 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.69, 165.92, 165.62, 150.27, 133.64, 129.62, 129.45, 128.54, 126.21, 121.29, 57.53, 53.04, 34.55, 20.29. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{19}H_{16}O_6Na^+$: 363.0839; Found: 363.0842. IR (neat, cm^{-1}): ν 2953, 1732, 1261, 1213, 1189, 1161, 1091, 1023. HPLC (chiral OD-H, 3% isopropanol-hexane, rate 0.8 ml/min): *trans*-isomer: t_{major} = 18.9 min, t_{minor} = 30.3 min, 71% *ee*; *cis*-isomer: t_{minor} = 16.2 min, t_{major} = 17.4 min, 65% *ee*. $[a]_D^{20}$ = +44.4° (c = 1, CH_2Cl_2).



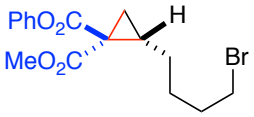
1-methyl 1-phenyl (1*S*,2*S*)-2-hexylcyclopropane-1,1-dicarboxylate (3ao) Yield: 74%; 80:20 diastereomeric ratio. Colorless oil. TLC: Hexane:EtOAc = 4:1; R_f = 0.8. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.43 – 7.34 (m, 2H), 7.28 – 7.20 (m, 1H), 7.10 (m, 2H), 3.81 (s, 3H), 2.06 (m, 1H), 1.61 – 1.41 (m, 5H), 1.40 – 1.20 (m, 7H), 0.95 – 0.84 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 169.13, 168.46, 150.64, 129.35, 125.91, 121.38, 52.57, 34.06, 31.67, 29.36, 28.91, 28.79, 28.52, 22.55, 22.02, 14.03. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{18}H_{25}O_4^+$: 305.1747; Found: 305.1754. IR (neat, cm^{-1}): ν2954, 2926, 2854, 2359, 1737, 1593, 1493, 1457, 1437, 1336, 1277, 1211, 1162, 1122, 1070. HPLC (chiral IB, 0.1% isopropanol-hexane, rate 0.8 ml/min): *trans*-isomer: t_{major} = 29.1 min, t_{minor} = 38.2 min, 72% *ee*. $[a]_D^{20}$ = +29.8° (c = 1).



1-methyl 1-phenyl (1*S*,2*S*)-2-phenethylcyclopropane-1,1-dicarboxylate (3ap) Yield: 77%; 83:17 diastereomeric ratio. Colorless oil. TLC: Hexane:EtOAc = 4:1; R_f = 0.8. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.41 – 7.35 (m, 2H), 7.30 (td, J = 7.7, 1.9 Hz, 2H), 7.26 – 7.18 (m, 4H), 7.12 – 7.07 (m, 2H), 3.82 (s, 3H), 2.83 – 2.70 (m, 2H), 2.10 (dtd, J = 9.0, 7.7, 6.7 Hz, 1H), 1.86 (ddt, J = 13.2, 8.9, 6.4 Hz, 1H), 1.68 – 1.61 (m, 1H), 1.59 (dd, J = 9.1, 4.7 Hz, 1H), 1.55 (dd, J = 7.9, 4.7 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 168.93, 168.37, 150.60, 141.18, 129.38, 128.44, 128.42, 126.04, 125.95, 121.35, 52.69, 35.12, 34.06, 30.58, 28.78, 21.81. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{20}H_{21}O_4^+$: 325.1434; Found: 325.1451. IR (neat, cm^{-1}): ν3026, 2926, 2859, 1811, 1736, 1593, 1494, 1455, 1437, 1392, 1336, 1277, 1212, 1162, 1123, 1069, 1052, 1029, 920. HPLC (chiral IB, 0.8% isopropanol-hexane, rate 0.8 ml/min): *trans*-isomer: t_{major} = 14.5 min, t_{minor} = 15.9 min, 80% *ee.* $[a]_D^{20}$ = +34.8° (c = 1, CH_2Cl_2).

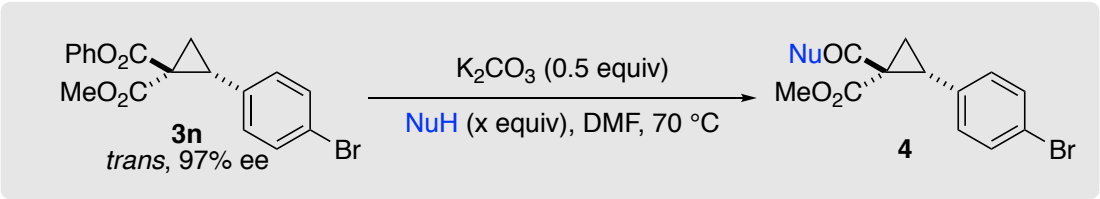


1-methyl 1-phenyl (1*S*,2*S*)-2-(3-hydroxypropyl)cyclopropane-1,1-dicarboxylate (3aq) Yield: 99%; 82:18 diastereomeric ratio. Colorless oil. TLC: Hexane:EtOAc = 1:1; R_f = 0.3. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.37 (ddd, J = 10.8, 5.8, 2.1 Hz, 2H), 7.25 – 7.21 (m, 1H), 7.14 – 7.06 (m, 2H), 3.81 (s, 3H), 3.67 (ddt, J = 12.8, 6.5, 2.9 Hz, 2H), 2.05 (dtd, J = 9.0, 7.7, 6.6 Hz, 1H), 1.72 (p, J = 6.9 Hz, 2H), 1.66 – 1.57 (m, 2H), 1.57 – 1.35 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 168.98, 168.41, 150.58, 129.38, 125.97, 121.34, 62.07, 52.69, 34.12, 31.79, 28.84, 24.82, 21.84. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{15}H_{19}O_5^+$: 279.1227; Found: 279.1230. IR (neat, cm^{-1}): ν3360, 2951, 1731, 1271, 1162, 1121. HPLC (chiral IE, 12% isopropanol-hexane, rate 0.8 ml/min): *trans*-isomer: t_{minor} = 17.1 min, t_{major} = 23.5 min, 74% *ee.* $[a]_D^{20}$ = +29.3° (c = 1, CH_2Cl_2).



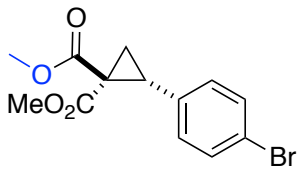
1-methyl 1-phenyl (1*S*,2*S*)-2-(4-bromobutyl)cyclopropane-1,1-dicarboxylate (3ar) Yield: 70%; 79:21 diastereomeric ratio. Colorless oil. TLC: Hexane:EtOAc = 4:1; R_f = 0.6. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.42 – 7.34 (m, 2H), 7.26 – 7.21 (m, 1H), 7.13 – 7.07 (m, 2H), 3.83 (s, 3H), 3.42 (td, J = 6.7, 1.9 Hz, 2H), 2.05 (m, 1H), 1.98 – 1.83 (m, 2H), 1.74 – 1.47 (m, 5H), 1.44 – 1.28 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 168.92, 168.34, 150.59, 129.38, 125.97, 121.34, 52.72, 34.02, 33.41, 32.27, 28.79, 27.67, 27.39, 21.83. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{16}H_{20}BrO_4^+$: 355.0539; Found: 355.0545. IR (neat, cm^{-1}): ν 2920, 2849, 1811, 1732, 1593, 1492, 1457, 1436, 1333, 1276, 1257, 1210, 1162, 1123, 1069, 922. HPLC (chiral IA, 0.6% isopropanol-hexane, rate 0.8 ml/min): *trans*-isomer: t_{major} = 17.1 min, t_{minor} = 20.5 min, 63% *ee*. $[a]_D^{20}$ = +23.2° (c = 1).

4.4 General Procedure for Ester Transformations

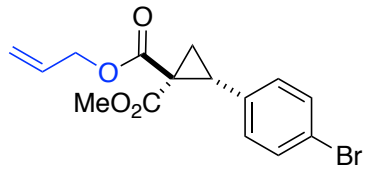


General procedure: Following a reported procedure,[4] to an oven-dried 10 mL Schlenk tube was added potassium carbonate (0.05 mmol, 0.5 equiv) and 1-methyl 1-phenyl (1*S*,2*R*)-2-(4-bromophenyl)cyclopropane-1,1-dicarboxylate **3n** (0.1 mmol, 1.0 equiv). Then, the nucleophile (0.3 or 1.0 mmol, 3.0 or 10.0 equiv) and *N*,*N*-dimethylformamide (DMF) (1 mL) were added to the tube *via* syringe. A Teflon screw cap was capped and the Schlenk tube was placed in 70 °C oil bath and stirred for 1 or 2 hours. The tube was cooled to room temperature after reaction. The reaction mixture was washed with water (10 mL) and extracted with diethyl ether for three times (3 × 10 mL). The combined organic phases were dried over sodium sulfate and concentrated under reduced

pressure. The light yellow crude product was purified by column chromatography on silica gel (hexane/ethyl acetate) to afford pure products **4**.

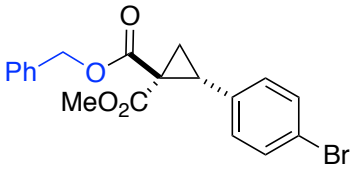


Dimethyl (*R*)-2-(4-bromophenyl)cyclopropane-1,1-dicarboxylate (4a) Yield: 99%. Colorless oil. TLC: Hexane:EtOAc = 5:1; R_f = 0.4. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.41 – 7.37 (m, 2H), 7.09 – 7.04 (m, 2H), 3.78 (s, 3H), 3.41 (s, 3H), 3.16 (dd, J = 9.1, 8.1 Hz, 1H), 2.14 (dd, J = 8.0, 5.3 Hz, 1H), 1.74 (dd, J = 9.2, 5.3 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 169.93, 166.80, 133.67, 131.29, 130.15, 121.43, 52.86, 52.37, 37.14, 31.77, 19.07. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{13}H_{14}BrO_4^+$: 313.0070; Found: 313.0082. IR (neat, cm^{-1}): ν 2952, 1726, 1436, 1281, 1217, 1131. HPLC (chiral ID, 2% isopropanol-hexane, rate 0.8 ml/min): t_{major} = 12.4 min, t_{minor} = 15.7 min, 97% *ee*. $[a]_D^{20}$ = +89.0° (c = 1, CH_2Cl_2).

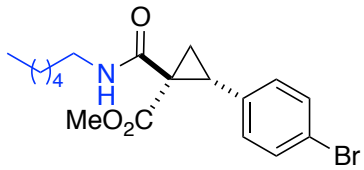


1-allyl 1-methyl (1*S*,2*R*)-2-(4-bromophenyl)cyclopropane-1,1-dicarboxylate (4b) Yield: 93%. White solid. TLC: Hexane:EtOAc = 5:1; R_f = 0.6. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.42 – 7.37 (m, 2H), 7.09 – 7.05 (m, 2H), 5.92 (ddt, J = 17.1, 10.8, 5.5 Hz, 1H), 5.35 (dq, J = 17.2, 1.6 Hz, 1H), 5.25 (dq, J = 10.5, 1.3 Hz, 1H), 4.72 (ddt, J = 13.4, 5.5, 1.5 Hz, 1H), 4.65 (ddt, J = 13.5, 5.6, 1.5 Hz, 1H), 3.42 (s, 3H), 3.17 (dd, J = 9.2, 8.0 Hz, 1H), 2.15 (dd, J = 8.0, 5.3 Hz, 1H), 1.74 (dd, J = 9.2, 5.3 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 169.11, 166.76, 133.66, 131.53, 131.28, 130.17, 121.42, 118.30, 66.19, 52.34, 37.25, 31.72, 19.09. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{15}H_{16}BrO_4^+$: 339.0226; Found: 339.0233. IR (neat, cm^{-1}): ν 2956, 1734, 1710, 1435, 1323, 1267, 1212, 1193, 1179, 1134,

1007, 932, 904. HPLC (chiral ID, 2% isopropanol-hexane, rate 0.8 ml/min): *trans*-isomer: t_{major} = 10.7 min, t_{minor} = 13.2 min, 97% *ee.* $[a]_D^{20}$ = +95.4° (c = 1, CH_2Cl_2).



1-benzyl 1-methyl (1*S*,2*R*)-2-(4-bromophenyl)cyclopropane-1,1-dicarboxylate (4c) Yield: 92%. Colorless oil. TLC: Hexane:EtOAc = 5:1; R_f = 0.6. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.42 – 7.31 (m, 6H), 7.10 – 7.05 (m, 2H), 5.28 (d, J = 12.5 Hz, 1H), 5.18 (d, J = 12.5 Hz, 1H), 3.41 (s, 3H), 3.20 (dd, J = 9.1, 8.1 Hz, 1H), 2.16 (dd, J = 8.0, 5.3 Hz, 1H), 1.76 (dd, J = 9.2, 5.3 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 169.25, 166.74, 135.42, 133.63, 131.28, 130.20, 128.54, 128.26, 127.81, 121.43, 67.34, 52.33, 37.31, 31.75, 19.10. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{19}H_{18}BrO_4^+$: 389.0383; Found: 389.0401. IR (neat, cm^{-1}): ν 2950, 1724, 1436, 1330, 1273, 1215, 1177, 1128, 1073, 1011. HPLC (chiral ID, 3% isopropanol-hexane, rate 0.8 ml/min): *trans*-isomer: t_{major} = 12.5 min, t_{minor} = 14.9 min, 97% *ee.* $[a]_D^{20}$ = +89.2° (c = 1, CH_2Cl_2).

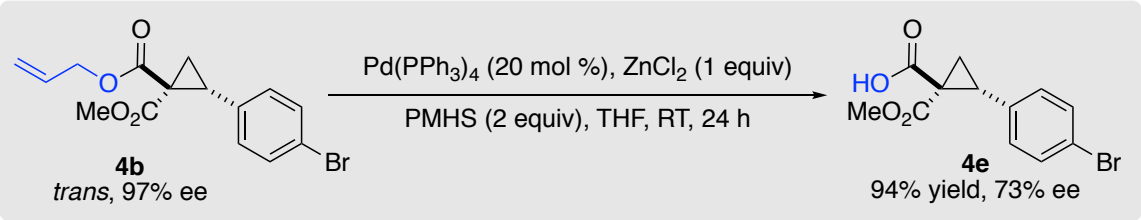


Methyl (1*R*,2*R*)-2-(4-bromophenyl)-1-(hexylcarbamoyl)cyclopropane-1-carboxylate (4d) Yield: 99%. Colorless oil. TLC: Hexane:EtOAc = 5:1; R_f = 0.4. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.37 (t, J = 5.6 Hz, 1H), 7.41 – 7.37 (m, 2H), 7.11 – 7.07 (m, 2H), 3.39 – 3.25 (m, 2H), 3.21 (s, 3H), 3.11 (dd, J = 9.2, 8.2 Hz, 1H), 2.22 – 2.15 (m, 2H), 1.60 – 1.52 (m, 2H), 1.40 – 1.26 (m, 6H), 0.92 – 0.85 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 171.10, 167.54, 134.61, 131.11, 130.80, 121.16, 51.51, 40.03, 36.43, 35.00, 31.44, 29.34, 26.64, 22.51, 18.98, 13.99. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{18}H_{25}BrNO_3^+$: 382.1012; Found: 382.1019. IR (neat, cm^{-1}): ν3363, 2952, 2927,

2856, 1709, 1659, 1537, 1144. HPLC (chiral ID, 5% isopropanol-hexane, rate 0.8 ml/min): *trans*-isomer: t_{major} = 12.8 min, t_{minor} = 14.5 min, 97% *ee*. $[a]_D^{20}$ = +94.4° (c = 1, CH_2Cl_2).

4.5 Procedure for Further Transformations

4.5.1 Selective Hydrogenation of Allyl Ester

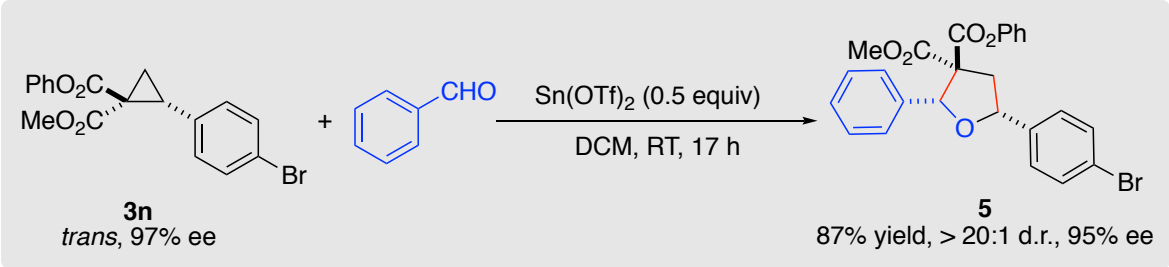


(1*R*,2*R*)-2-(4-bromophenyl)-1-(methoxycarbonyl)cyclopropane-1-carboxylic acid (4e)

Following a reported procedure,[5] to a THF (1 mL) solution of 1-allyl 1-methyl (1*S*,2*R*)-2-(4-bromophenyl)cyclopropane-1,1-dicarboxylate **4b** (0.1 mmol, 1.0 equiv) was added polymethylhydrosiloxane (PMHS) (0.2 mmol, 2.0 equiv), tetrakis(triphenylphosphine)palladium [$Pd(PPh_3)_4$] (20 mol %) and $ZnCl_2$ (0.1 mmol, 1.0 equiv). The reaction was conducted at room temperature with rigorous stirring. Upon completion of the reaction (monitored by TLC), the reaction mixture was washed with water (10 mL) and extracted with diethyl ether for three times (3 × 10 mL). The combined organic phases were dried over sodium sulfate and concentrated under reduced pressure. The light yellow crude product was purified by column chromatography on silica gel (hexane/ethyl acetate) to afford pure products **4e**. Yield: 94%. White solid. TLC: Hexane:EtOAc = 1:1; R_f = 0.1. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.47 – 7.40 (m, 2H), 7.14 – 7.09 (m, 2H), 3.34 (s+t, 4H), 2.35 (dd, J = 8.5, 4.9 Hz, 1H), 2.27 (dd, J = 9.4, 4.9 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 172.74, 170.44, 133.10, 131.43, 130.76, 121.94, 52.70, 39.24, 33.73, 21.23. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{12}H_{12}BrO_4^+$: 298.9913; Found: 298.9924. IR (neat, cm^{-1}): ν 2954, 2918, 2849,

2576, 1733, 1693, 1492, 1434, 1409, 1376, 1314, 1218, 1192, 1146, 1096, 1071, 1009, 973, 945, 925, 901. HPLC (chiral IA, 20% isopropanol-hexane, rate 0.8 ml/min): *trans*-isomer: t_{major} = 12.7 min, t_{minor} = 13.7 min, 73% *ee*. $[a]_D^{20}$ = +95.837° (c = 1, CH_2Cl_2).

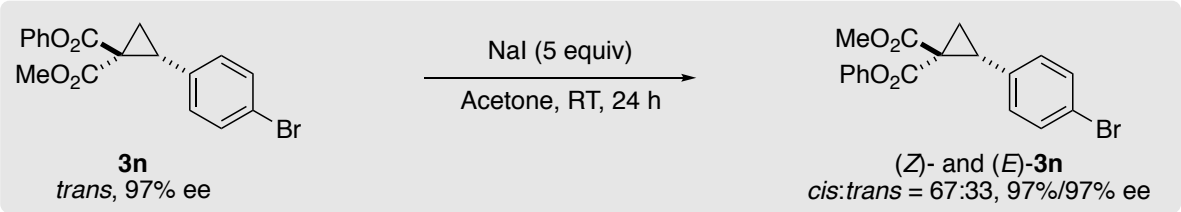
4.5.2 Application for Synthesis of Polysubstituted Tetrahydrofuran *via* 1,3-Dipole [3+2] Cycloaddition



3-methyl 3-phenyl (2*R*,3*S*,5*R*)-5-(4-bromophenyl)-2-phenyldihydrofuran-3,3(2*H*)-dicarboxylate (5) Following a reported procedure,[6] to a small vial was added 1-methyl 1-phenyl (1*S*,2*R*)-2-(4-bromophenyl)cyclopropane-1,1-dicarboxylate **3n** (0.1 mmol, 1.0 equiv) and $Sn(OTf)_2$ (0.05 mmol. 0.5 equiv). Then, dichloromethane (1 mL) and benzaldehyde (0.3 mmol, 3.0 equiv) were added to the vial *via* syringe. Reaction was monitored by TLC. Upon completion of the reaction, the reaction mixture was filtered through a plug of Celite with 10 mL of diethyl ether. The organic mixture was concentrated under reduced pressure. The light yellow crude product was purified by column chromatography on silica gel (hexane/ethyl acetate) to afford pure products **5**. Yield: 87%; > 20:1 diastereomeric ratio. White solid. TLC: Hexane:EtOAc = 5:1; R_f = 0.4. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.65 – 7.60 (m, 2H), 7.55 – 7.51 (m, 2H), 7.47 – 7.43 (m, 2H), 7.41 – 7.37 (m, 3H), 7.20 – 7.15 (m, 2H), 7.13 – 7.09 (m, 1H), 6.23 – 6.19 (m, 2H), 5.92 (s, 1H), 5.00 (dd, J = 10.3, 6.3 Hz, 1H), 3.93 (s, 3H), 3.05 (dd, J = 13.6, 10.3 Hz, 1H), 2.84 (dd, J = 13.6, 6.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.99, 167.76, 149.85, 138.82, 137.26, 131.66, 129.11, 128.49, 128.31, 128.27,

127.49, 126.03, 122.05, 120.84, 84.55, 79.06, 65.86, 53.20, 43.42. HRMS (DART) ([M+NH_4]$^+$) Calcd. for $C_{25}H_{25}BrNO_5^+$: 498.0911; Found: 498.0929. IR (neat, cm^{-1}): ν 2952, 1733, 1592, 1488, 1455, 1434, 1354, 1259, 1223, 1188, 1161, 1110, 1067, 1046, 1027, 1009, 974, 919. HPLC (chiral IB, 3% isopropanol-hexane, rate 0.8 ml/min): *trans*-isomer: t_{minor} = 12.4 min, t_{major} = 14.2 min, 95% *ee.* [a]$_D^{20}$ = -50.6° (c = 1, CH_2Cl_2).

4.5.3 Stereospecific Conversion of Quatary Carbon with NaI



1-methyl 1-phenyl (1*R*,2*R*)-2-(4-bromophenyl)cyclopropane-1,1-dicarboxylate (3n) Following a reported procedure,[3] 1-methyl 1-phenyl (1*S*,2*R*)-2-(4-bromophenyl)cyclopropane-1,1-dicarboxylate **3n** (0.1 mmol, 1.0 equiv) was dissolved into 1 mL of acetone. Then sodium iodide (NaI) (0.5 mmol, 5.0 equiv) was added to the vial. Reaction was stirred at room temperature for 24 h. Upon completion of the reaction, the reaction mixture was filtered through a plug of Celite with 10 mL of diethyl ether. The filtrate was concentrated under reduced pressure affording products **7**. Yield: 99%; 67:33 *cis*:*trans* diastereomeric ratio. White solid. TLC: Hexane:EtOAc = 5:1; R_f = 0.6. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.47 (d, J = 8.4 Hz, 2H), 7.28 – 7.23 (m, 2H), 7.19 (d, J = 8.5 Hz, 2H), 7.15 – 7.14 (m, 1H), 6.52 – 6.45 (m, 2H), 3.87 (s, 3H), 3.33 (t, J = 8.7 Hz, 1H), 2.27 (dd, J = 8.0, 5.5 Hz, 1H), 1.86 (dd, J = 9.2, 5.5 Hz, 1H) (*trans* diastereomer see **3n**). ^{13}C NMR (150 MHz, $CDCl_3$): δ 169.72, 165.16, 150.29, 133.33, 131.52, 130.47, 129.33, 125.99, 121.72, 121.04, 53.05, 37.35, 32.21, 18.98 (*trans* diastereomer see **3n**). HRMS (ESI) ([M+Na]$^+$) Calcd. for: $C_{18}H_{15}BrO_4Na^+$: 397.0046; Found: 397.0040. IR (neat, cm^{-1}): ν 2951, 1732, 1491, 1436, 1325, 1283, 1210, 1119. HPLC (chiral IC, 8%

isopropanol-hexane, rate 0.8 ml/min): *cis*-isomer: t_{major} = 14.8 min, t_{minor} = 15.5 min, 97% *ee*, *trans*-isomer: t_{minor} = 17.0 min, t_{major} = 17.6 min, 97% *ee.* $[a]_D^{20}$ = 119.6° (c = 1, CH_2Cl_2).

4.6 X Ray Crystallography

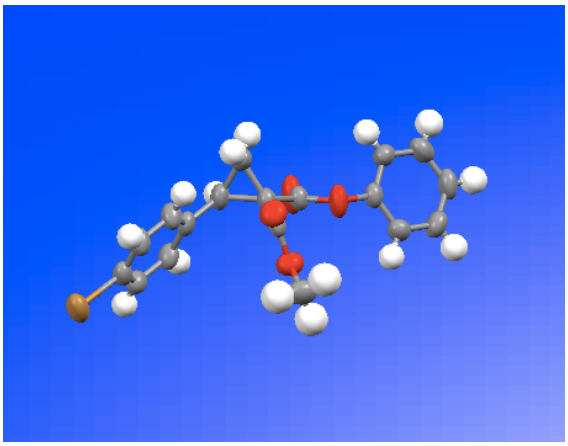


Figure 5 Single-Crystal X-Ray Structure of 3n

X-ray diffraction data for **3n** were collected using Bruker-AXS SMART-APEXII CCD diffractometer using Kα radiation (λ = 1.54178 Å). Indexing was performed using *APEX2* (Difference Vectors method).[7] Data integration and reduction were performed using SaintPlus 6.01. Absorption correction was performed by multi-scan method implemented in SADABS.[8] Space groups were determined using XPREP implemented in APEX2.[7] The structure was solved using SHELXS-97 (direct methods) and refined using SHELXL-2013[9] (full-matrix least-squares on F^2) contained in APEX2,[7] WinGX v1.70.01[10,11,12] and OLEX2[13,14]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of -CH, $-CH_2$ and $-CH_3$ groups were placed in geometrically calculated positions and included in the refinement process using riding model with isotropic thermal parameters: Uiso(H) = 1.2, Ueq(-CH,-CH_2[-CH_3]). Crystal data and refinement conditions are shown in **Table 10**. Ellipsoid plot of asymmetric unit and numbering scheme are shown on **Figure 6**.

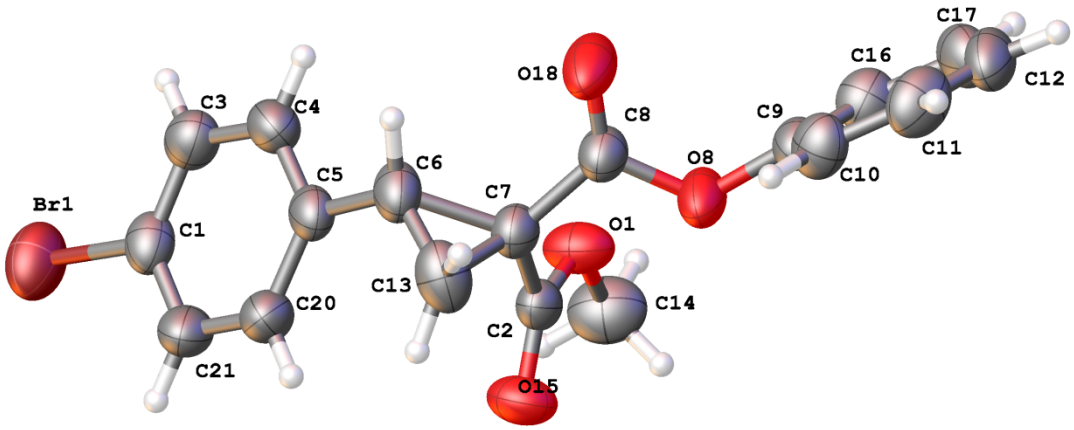


Figure 6 Asymmetric Unit and Numbering Scheme of 3n. Atomic Displacement Parameters Was Drawn at 50% Probability

Table 10 Crystal Data and Structure Refinement for 3n

Identification code	**3n**
Empirical formula	$C_{18}H_{15}BrO_4$
Formula weight	375.21
Temperature/K	296.15
Crystal system	monoclinic
Space group	$P2_1$
a/Å	7.9944(2)
b/Å	5.67570(10)
c/Å	18.9770(4)

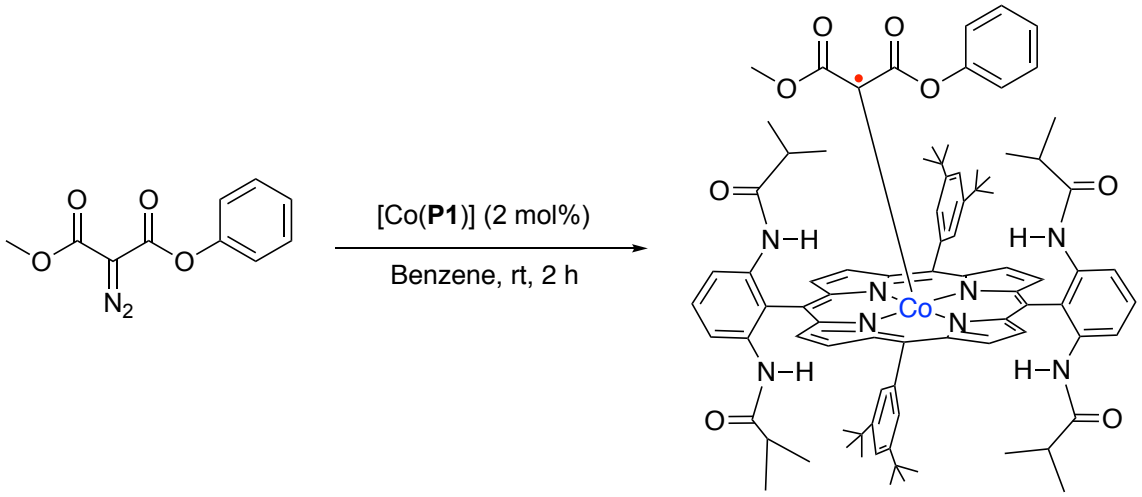
α/°	90
β/°	95.7430(10)
γ/°	90
Volume/Å^3	856.74(3)
Z	2
ρ_{calc}g/cm^3	1.454
μ/mm^{-1}	3.419
F(000)	380.0
Crystal size/mm^3	0.25 × 0.11 × 0.02
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	4.68 to 142.404
Index ranges	$-9 \leq h \leq 9$, $-6 \leq k \leq 6$, $-22 \leq l \leq 23$
Reflections collected	10466
Independent reflections	3101 [R_{int} = 0.0428, R_{sigma} = 0.0441]
Data/restraints/parameters	3101/1/209
Goodness-of-fit on F^2	1.077
Final R indexes [I>=2σ (I)]	R_1 = 0.0358, wR_2 = 0.0981

Final R indexes [all data]	R_1 = 0.0382, wR_2 = 0.1003
Largest diff. peak/hole / e Å^{-3}	0.53/-0.27
Flack parameter	0.003(12)

4.7 Experimental Study of Stepwise Radical Mechanism

4.7.1 EPR Experiment

Characterization of the α-Co(III)-Akyl Radical I by EPR.



Scheme 22 Detection of Radical Intermediate I by EPR

Procedure for EPR Experiment: To an over-dried Schlenk tube, [Co(**P1**)] (2 mol %) was added. The Schlenk tube was then evacuated and backfilled with nitrogen for 3 times. The Teflon screw cap was replaced with a rubber septum, and $TrocN_3$ (0.1mmol) and Benzene (0.5 mL) were added via a gas-tight syringe. The mixture was then stirred at room temperature for 2h and transferred into a

degassed EPR tube (filled with argon) through a gas tight syringe. The sample was then carried out for EPR experiment at room temperature (EPR settings: T = 298 K; microwave frequency: 9.37762 GHz; power: 20 mW; modulation amplitude: 1.0 G).

X-band EPR spectra were recorded on a Bruker EMX-Plus spectrometer (Bruker BioSpin). Simulations of the EPR spectra were performed by iteration of the isotropic g-values and line widths using the EPR simulation program SpinFit in Xenon.

EPR Simulation Details:

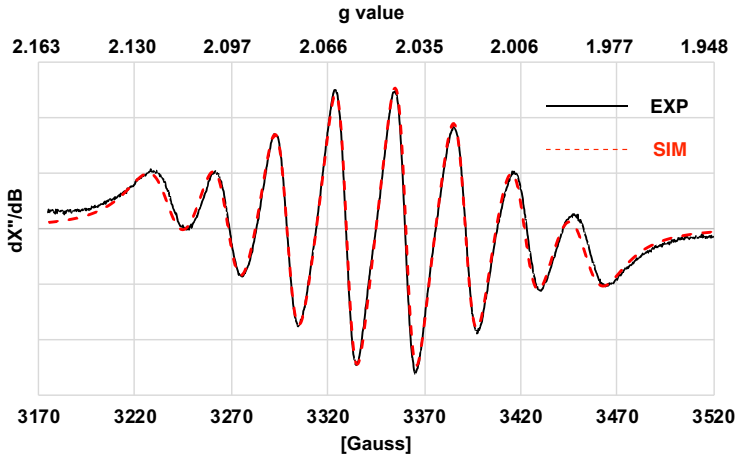


Figure 7 Experimental and Theorectical Simulation of EPR Result

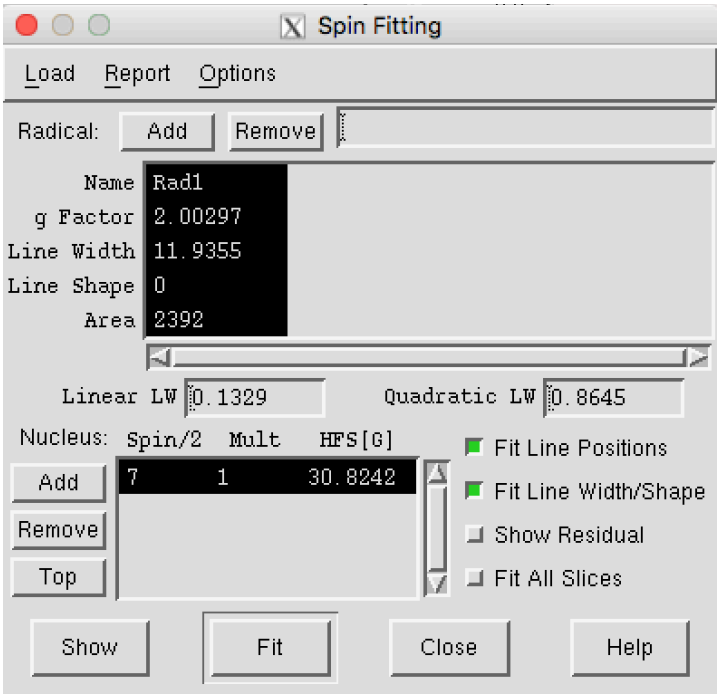


Figure 8 EPR Report

g = 2.00297

$A_{(Co)}$ = 30.8242 x 2.00236 x1.399611451 = 86.38 MHz

4.7.2 HRMS Experiment

Radical intermediate detected by HRMS

Chemical Formular: $C_{86}H_{96}CoN_8O_8$•
Calculated Mass: 1427.6683
Found Mass: 1427.6666

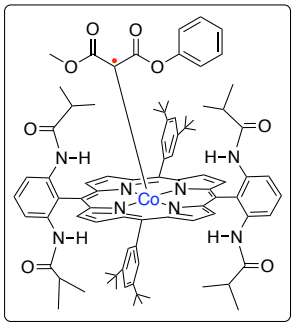


Figure 9 Radical Intermediate Detected by HRMS

Procedure for HRMS Experiment: Diazo **1a** was dissolved in 0.5mL of acetonitrile and added in a HPLC vial (vial A, degassed and backfilled with argon). At the same time, [Co(**P1**)] (2 mol %) was charged into another HPLC vial (vial B, degassed and backfilled with argon) and dissolved in acetonitrile (0.5 mL). After mixing equal amount of solutions from vial A (0.1 mL) and vial B (0.1 mL), the sample was further diluted with CH_3CN and immediately injected into HRMS instrument. The HRMS experiment was carried out in the absence of any additives such as formic acid, which commonly act as electron carriers for ionization, allowing for the detection of the molecular ion signals corresponding to Co(III)-alkyl radical ($C_{86}H_{96}CoN_8O_8$·) by the loss of one electron.

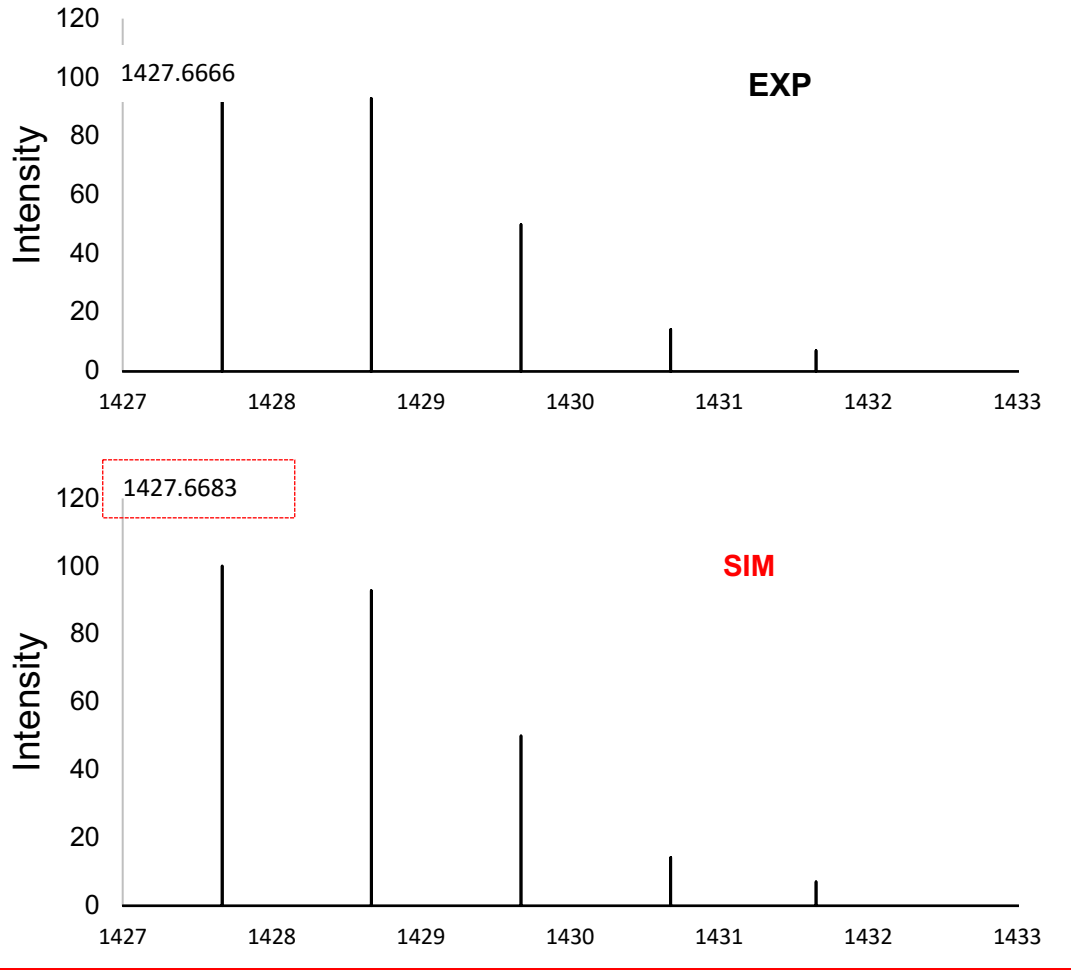


Figure 10 Experiment and Theorectial Simulation of HRMS

4.7.3 Probing of the γ-Co(III)-Alkyl Radical Intermediates by Reactions of β-Deuterostyrenes

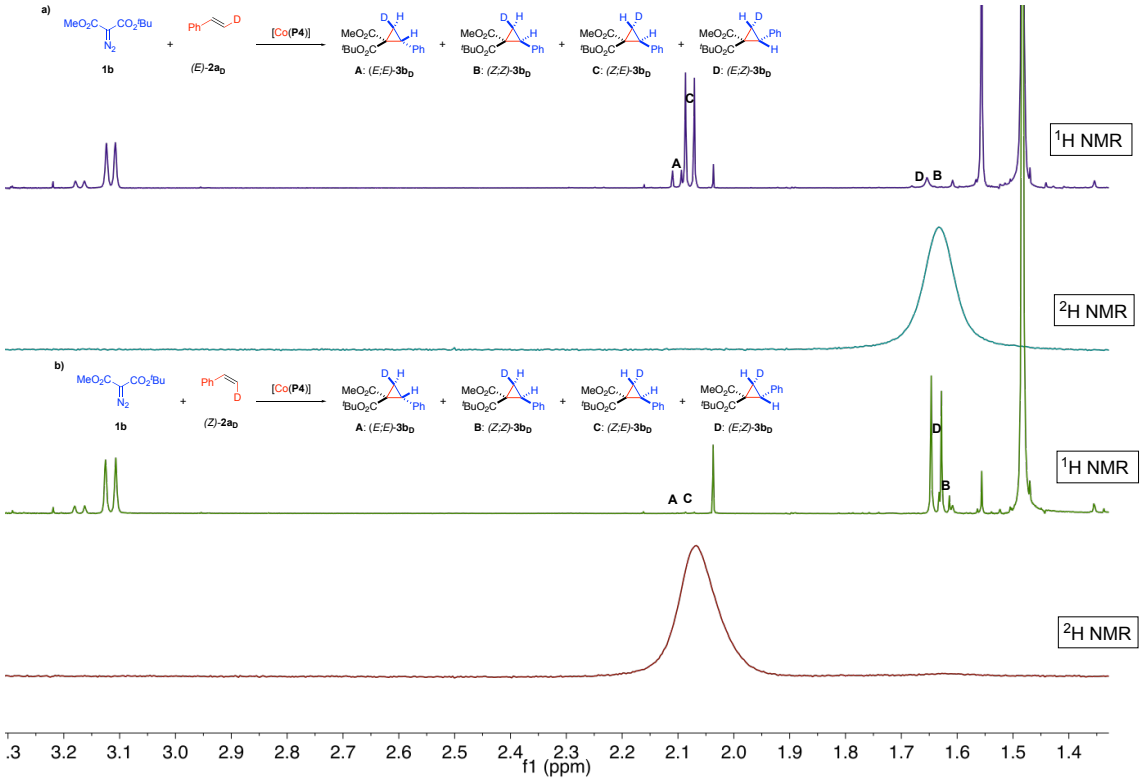


Figure 11 Upfield ^{2}H NMR and ^{1}H NMR for Cyclopropane Isomers 3b from [Co(P4)]-Catalyzed Cyclopropanation between: a) *tert*-Butyl Methyl Diazomalonate (1b) and (*E*)-β-Deuterostyrene ((*E*)-2a$_D$); b) *tert*-Butyl Methyl Diazomalonate (1b) and (*Z*)-β-Deuterostyrene ((*Z*)-2a$_D$)

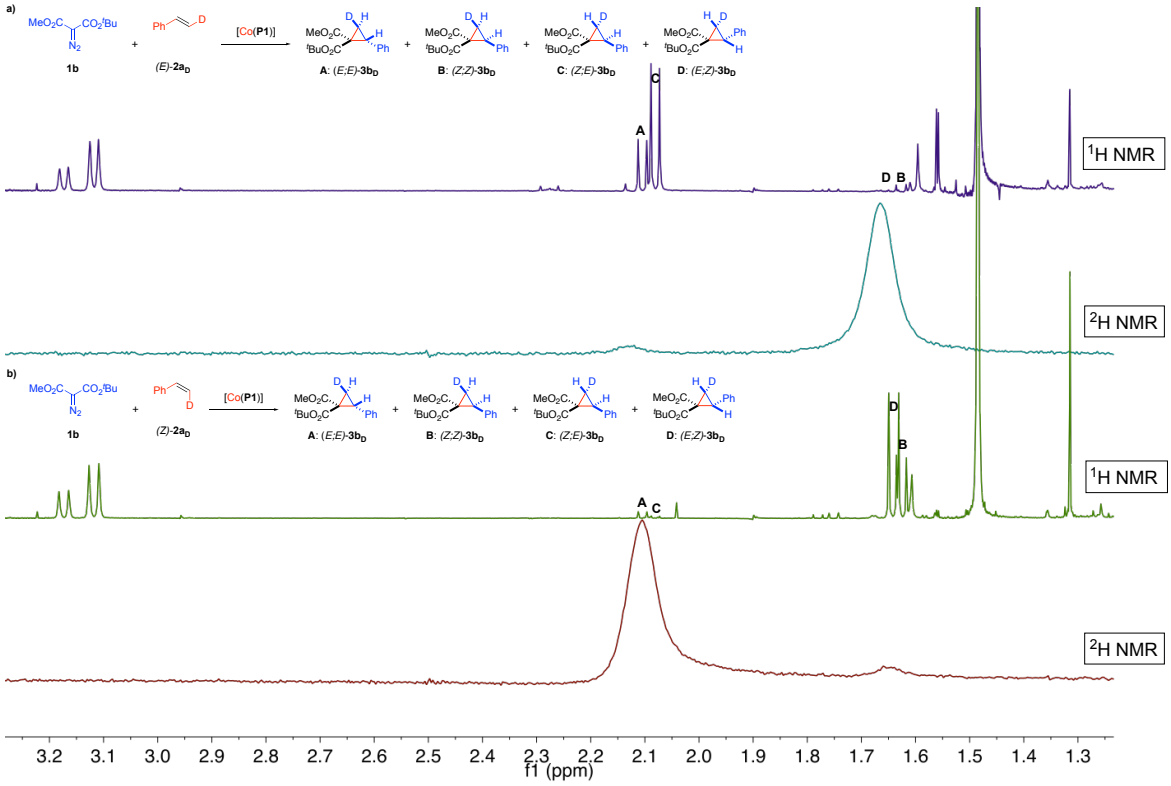


Figure 12 Upfield ^{2}H NMR and ^{1}H NMR for Cyclopropane Isomers 3b from [Co(P1)]-Catalyzed Cyclopropanation between: a) *tert*-Butyl Methyl Diazomalonate (1b) and (*E*)-β-Deuterostyrene ((*E*)-2a$_D$); b) *tert*-Butyl Methyl Diazomalonate (1b) and (*Z*)-β-Deuterostyrene ((Z)-2a$_D$)

4.8 References

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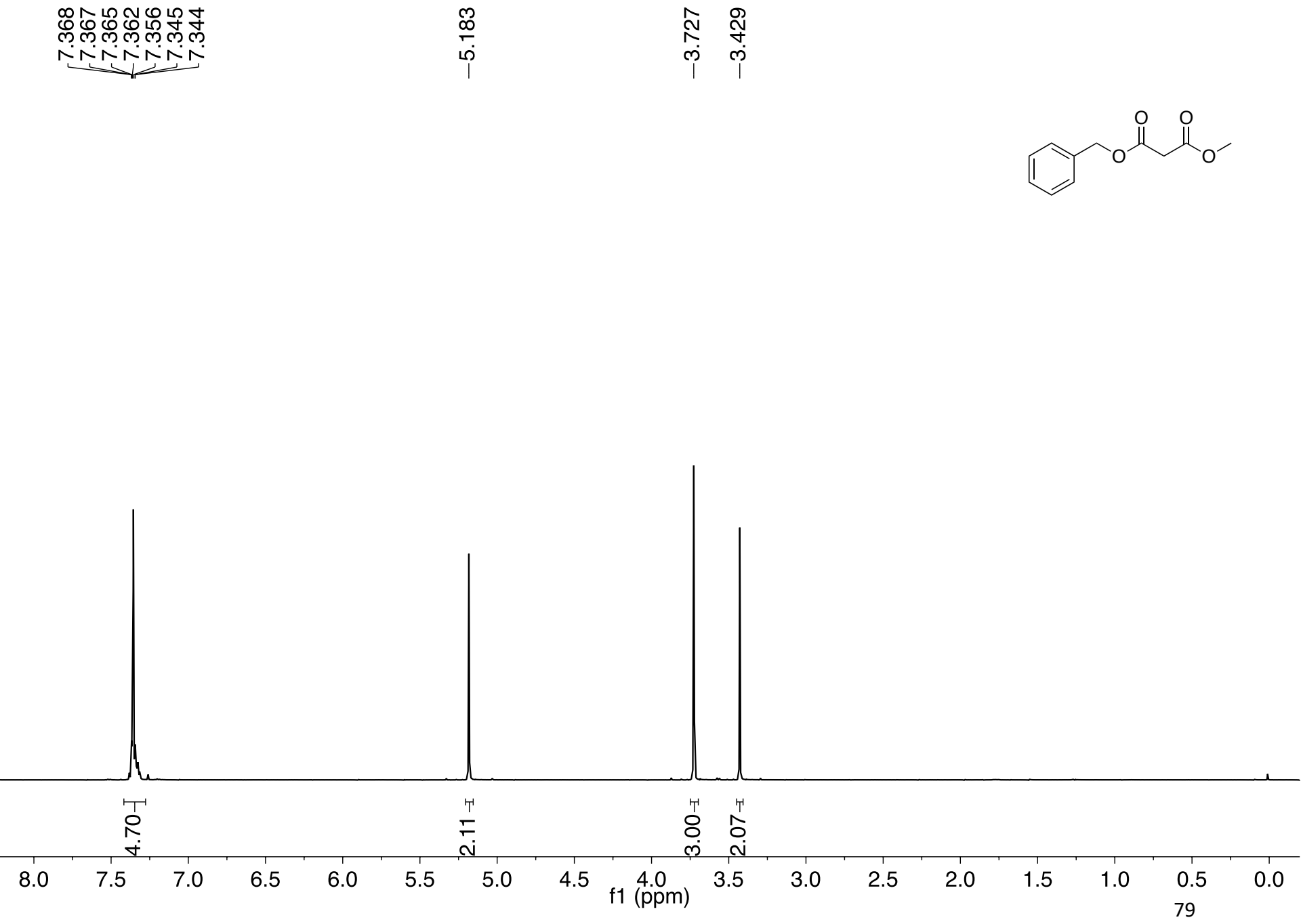
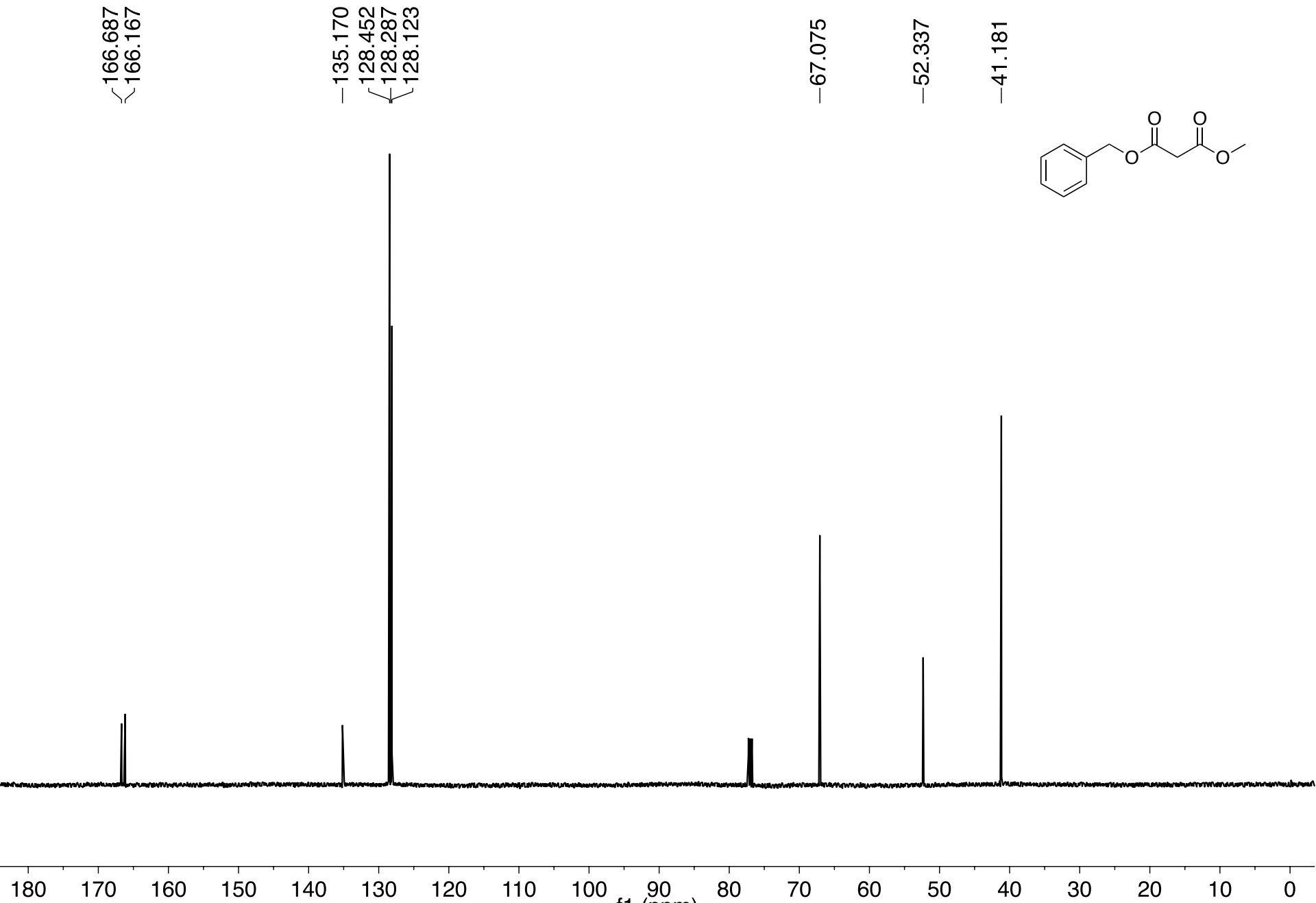
Chapter 5 Spectral Data

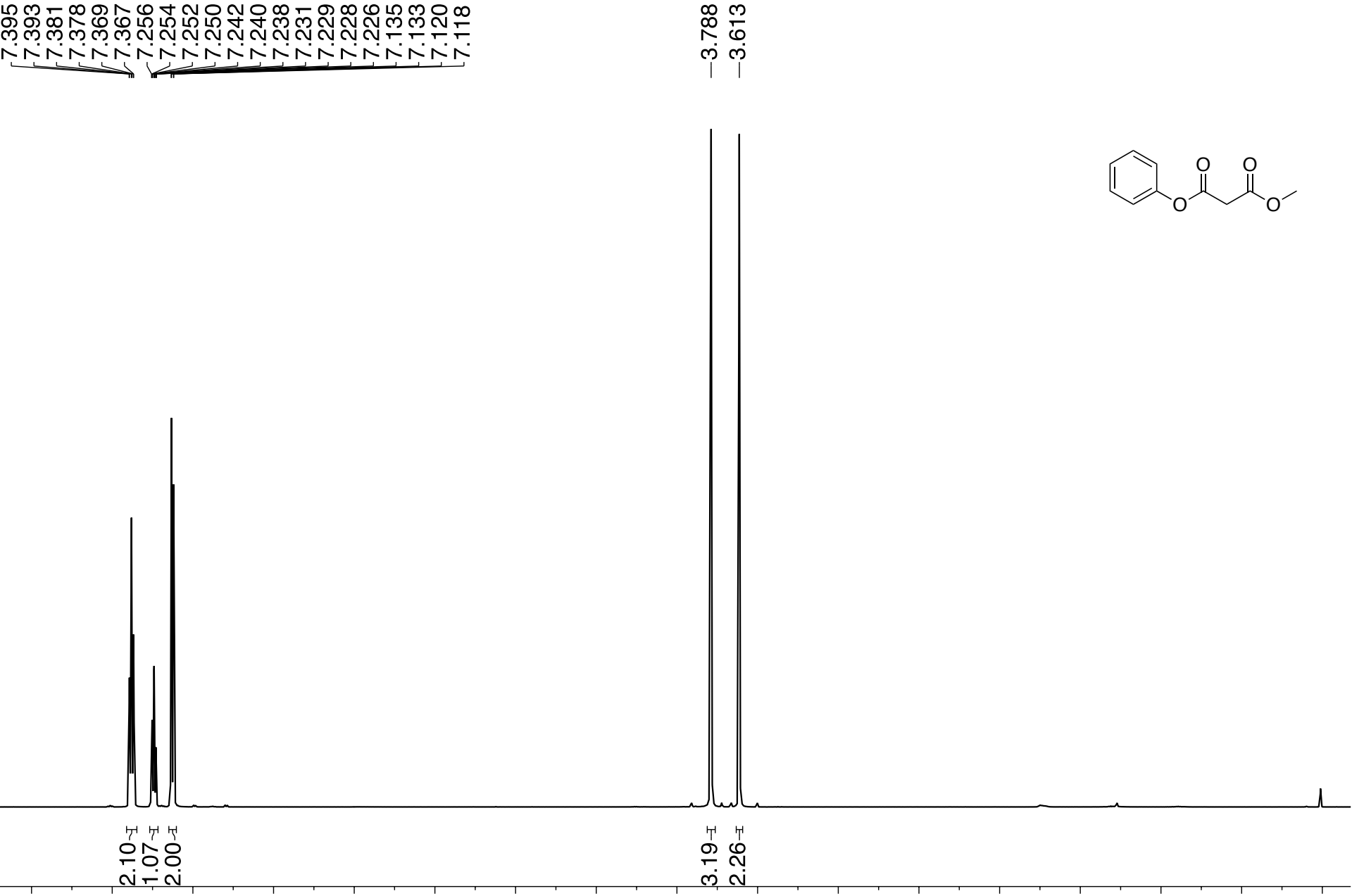
benzyl methyl malonate



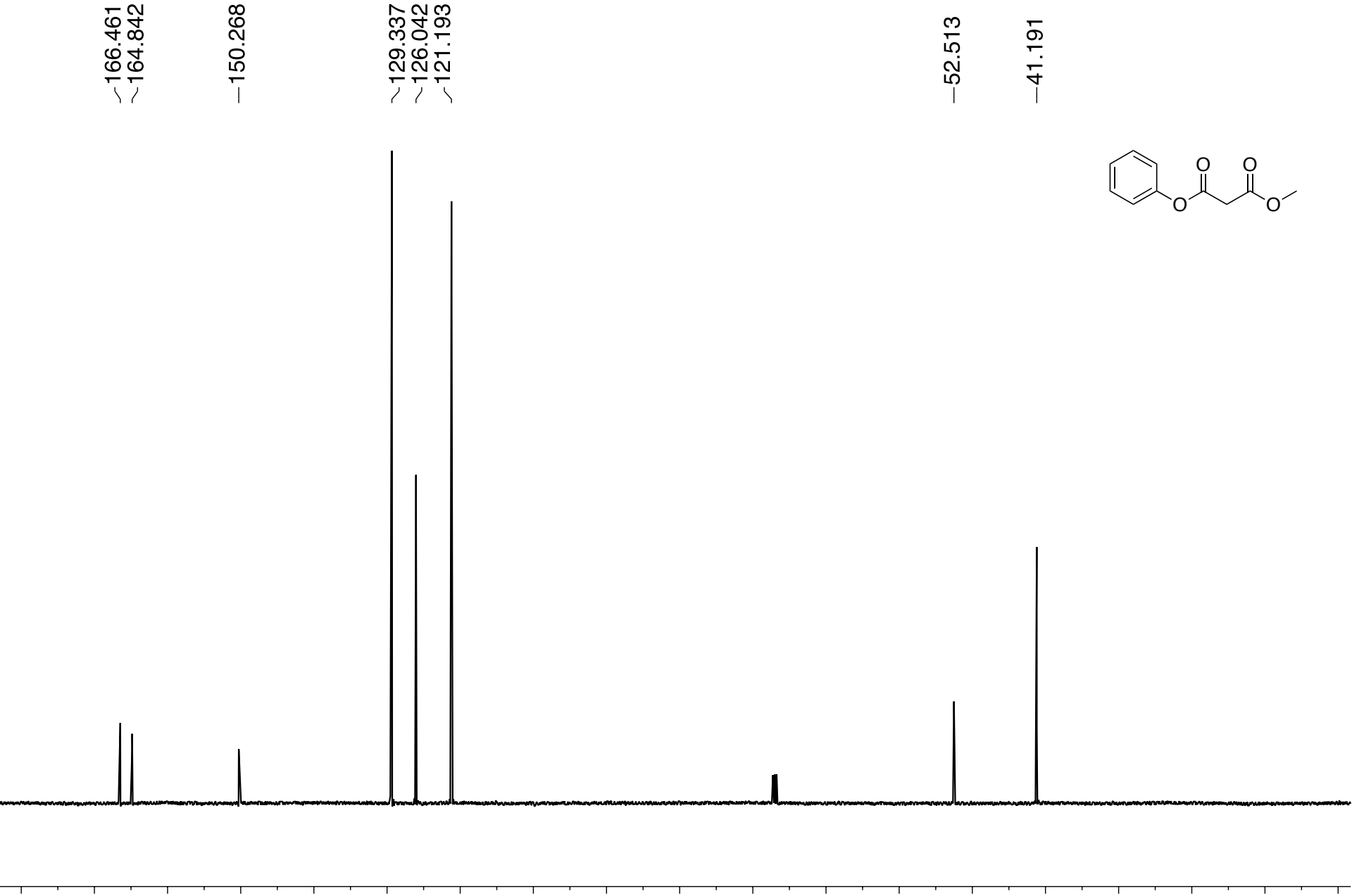
benzyl methyl malonate



methyl phenyl malonate



methyl phenyl malonate



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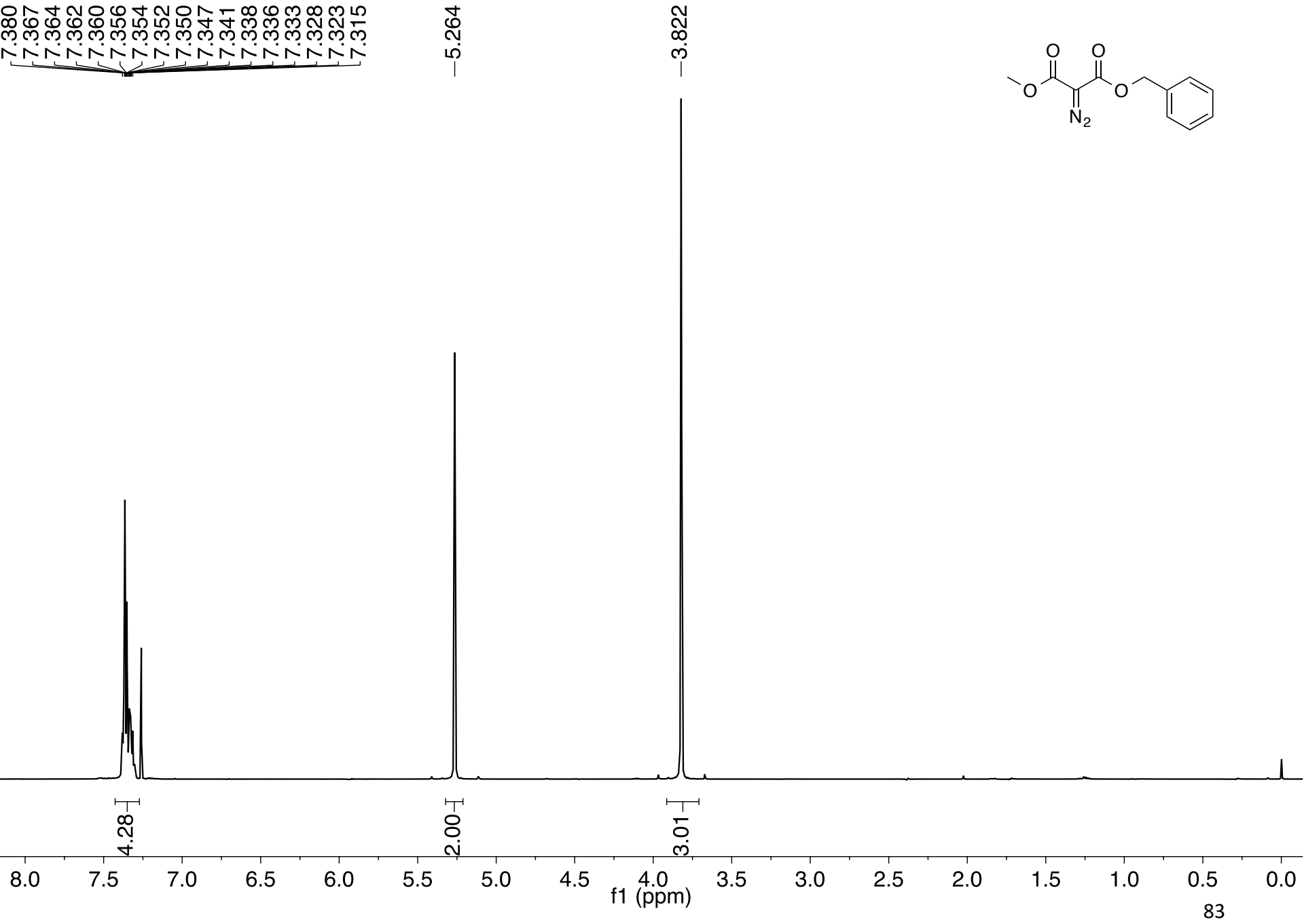

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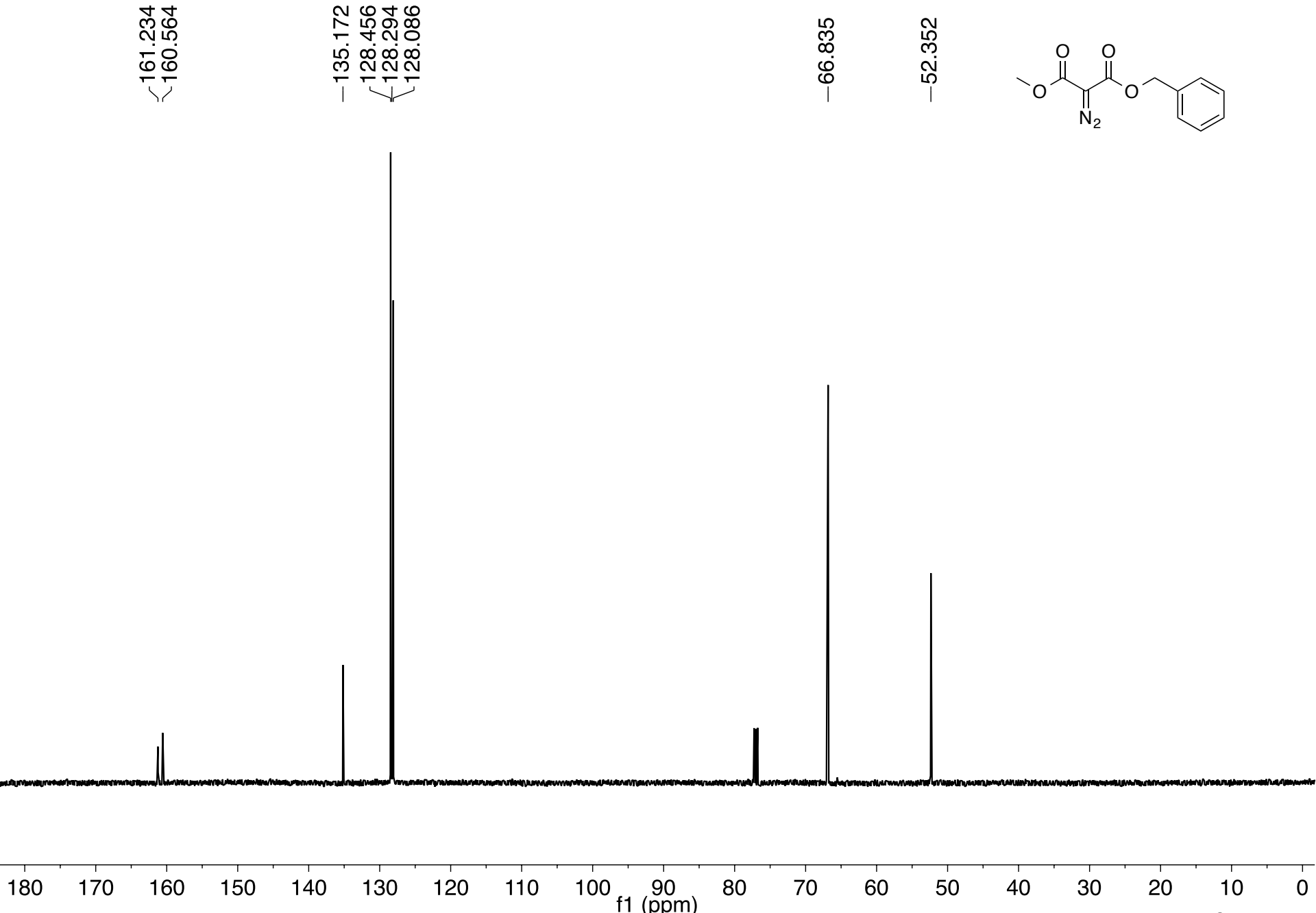

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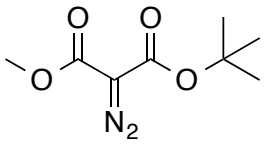

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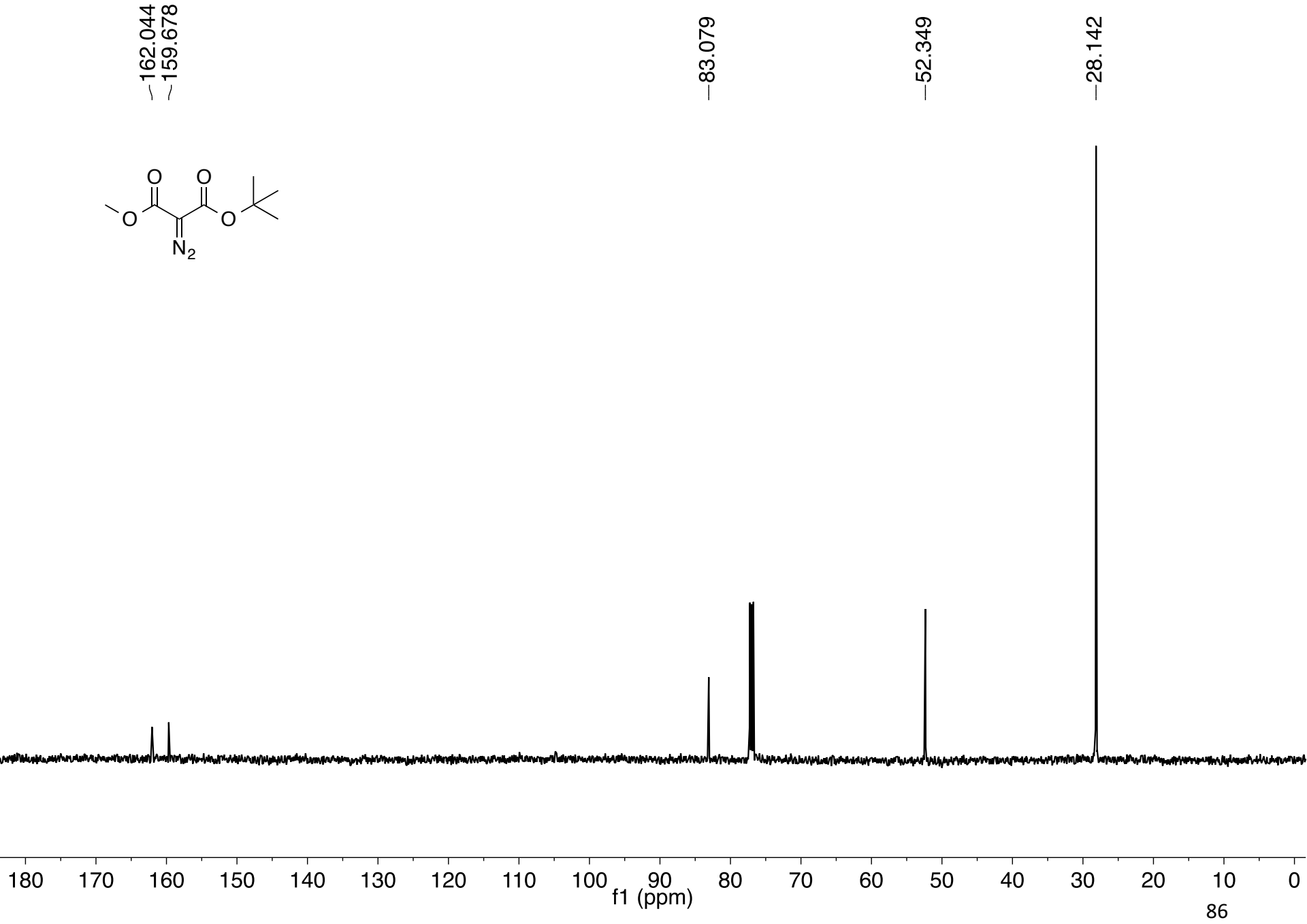

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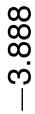

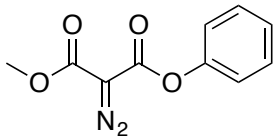

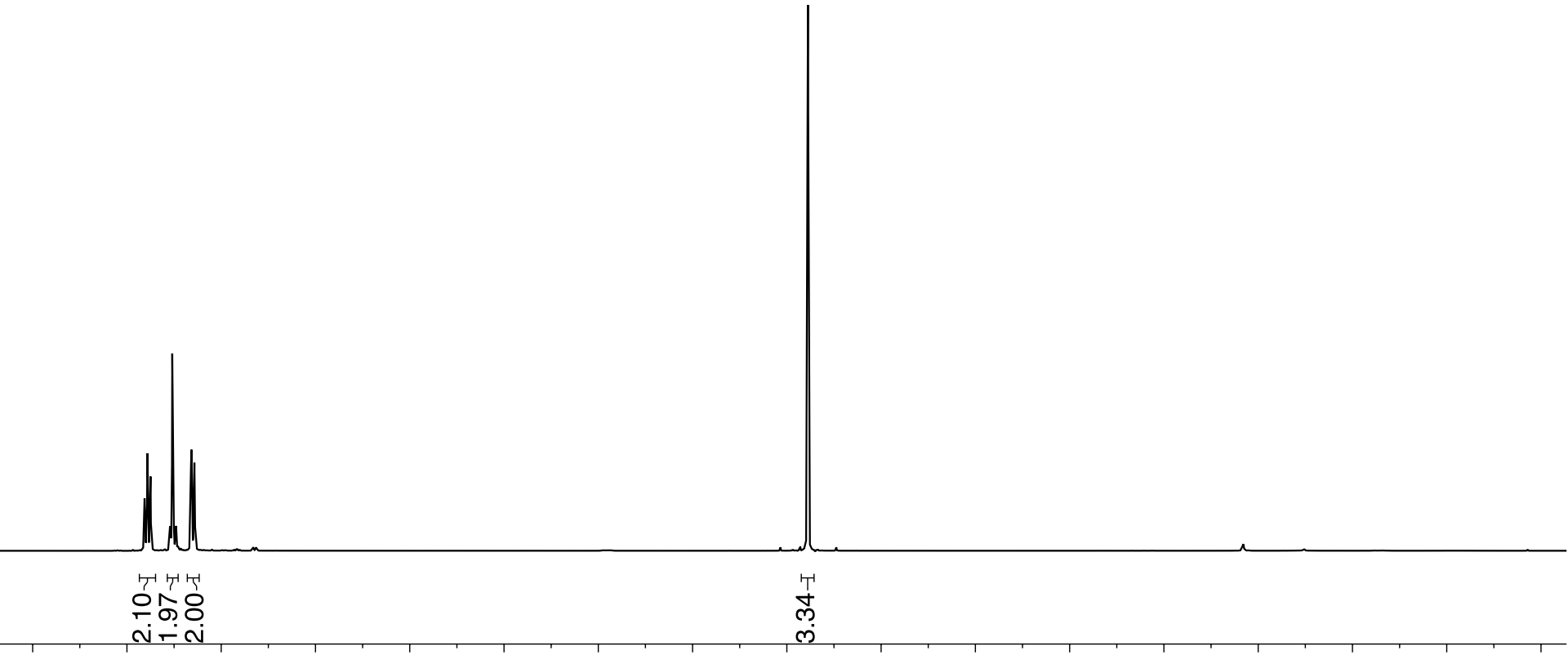

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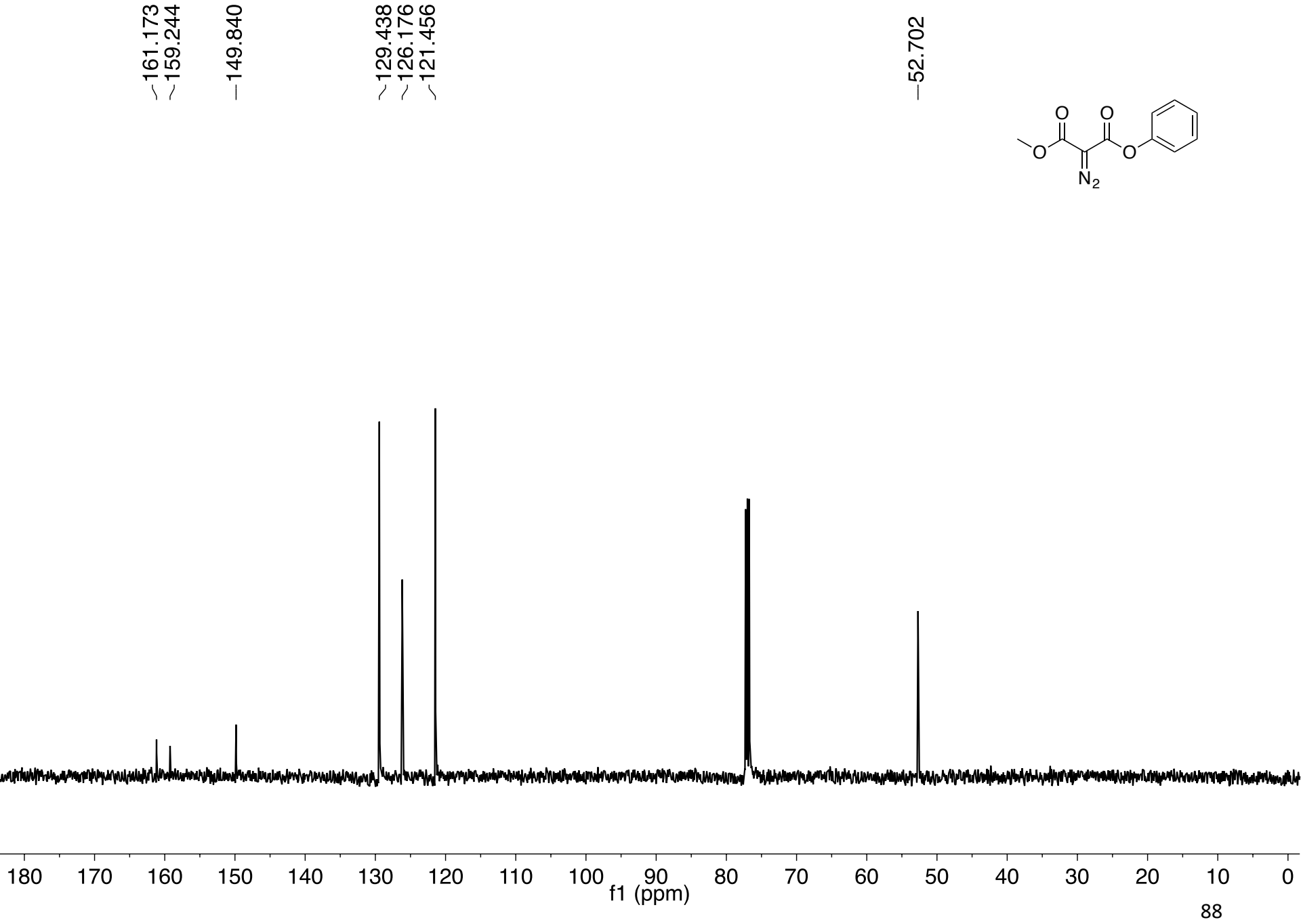

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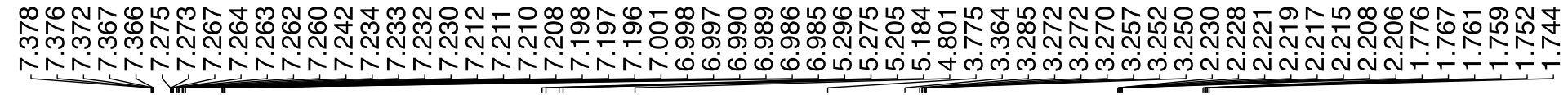

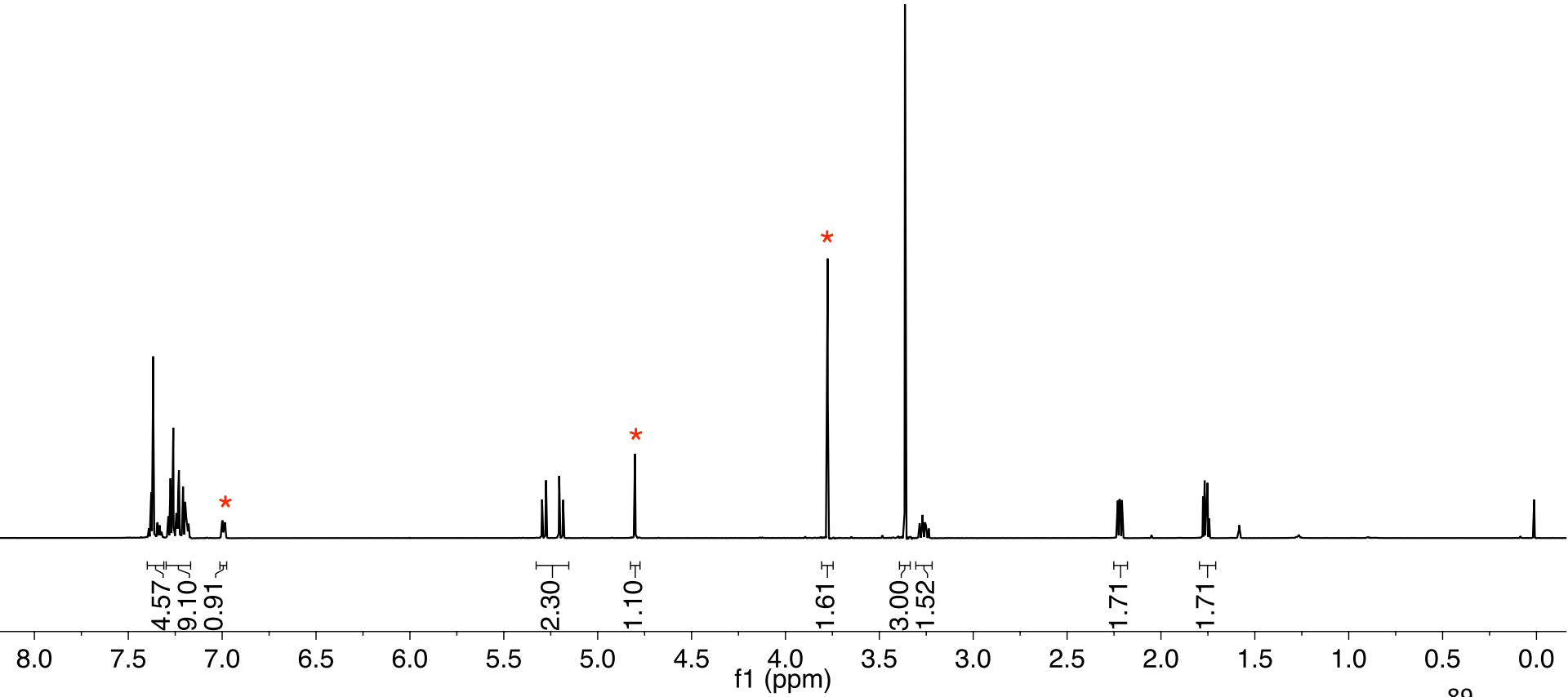

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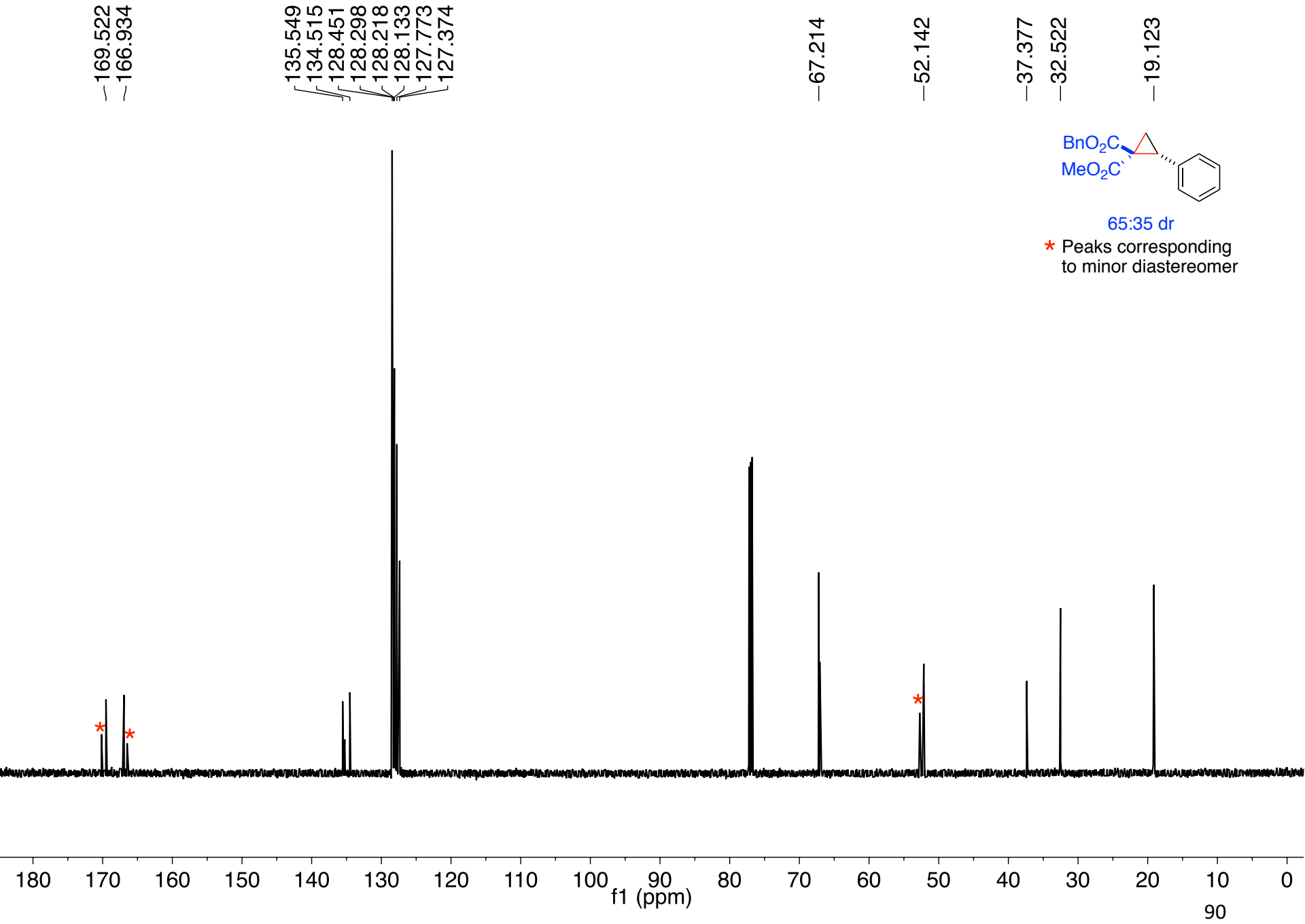

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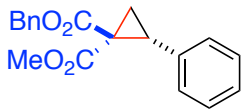

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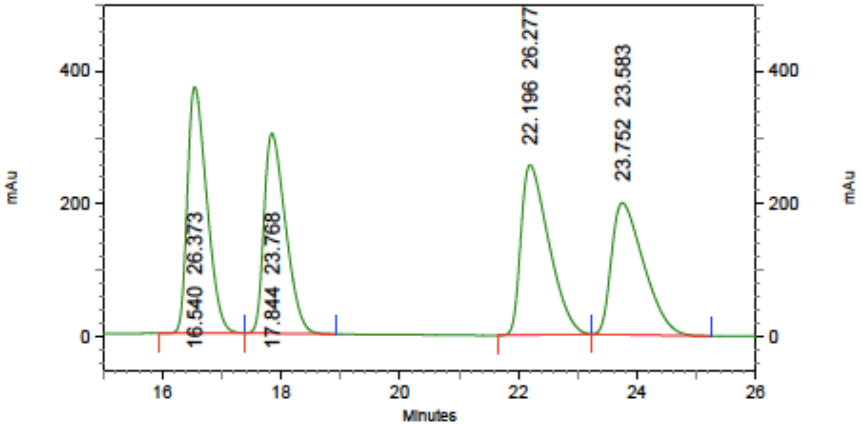
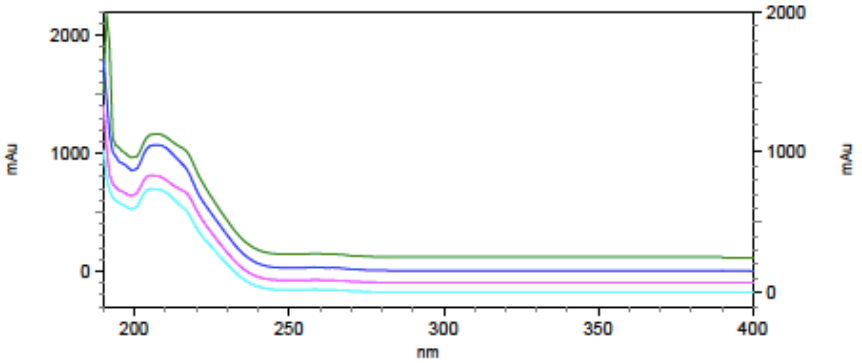
75% ee





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nm Results

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2	17.844	23.768
3	22.196	26.277
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1-benzyl 1-methyl (1*S*,2*R*)-2-phenylcyclopropane-1,1-dicarboxylate

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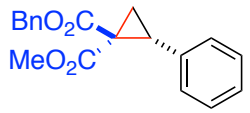

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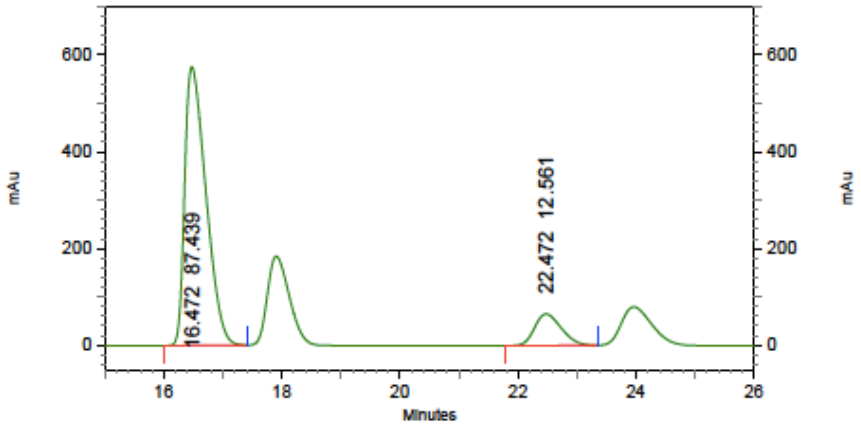
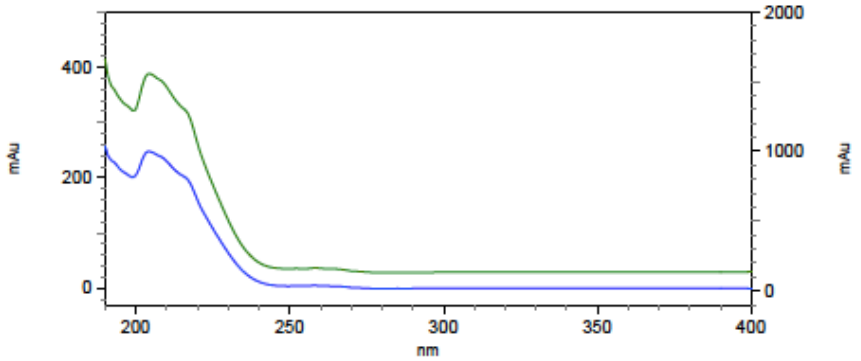
75% ee





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nm Results

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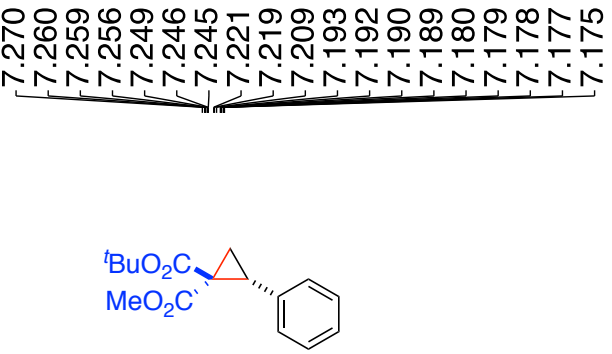
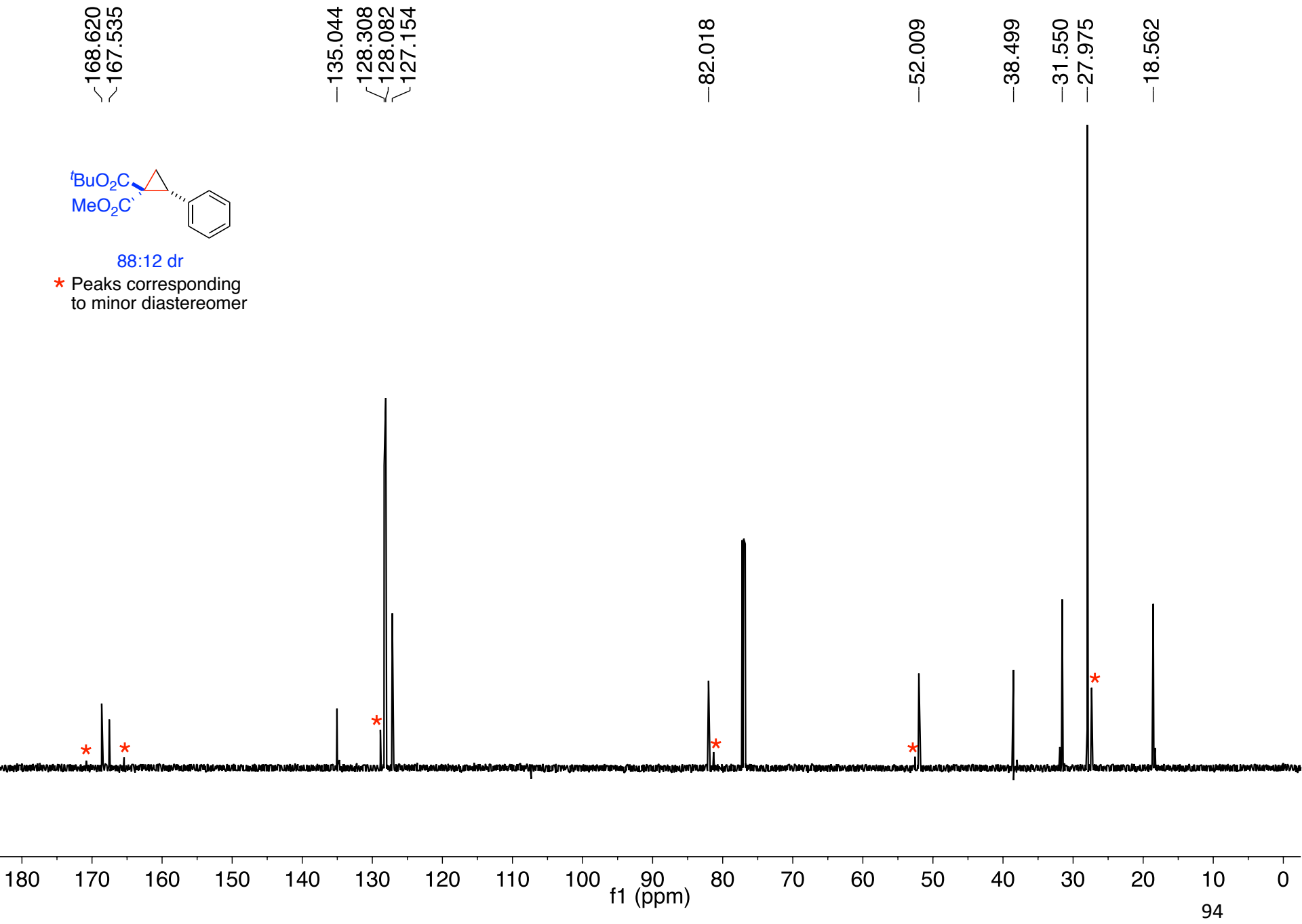
1-(*tert*-butyl) 1-methyl (1*S*,2*R*)-2-phenylcyclopropane-1,1-dicarboxylate



1-(*tert*-butyl) 1-methyl (1*S*,2*R*)-2-phenylcyclopropane-1,1-dicarboxylate



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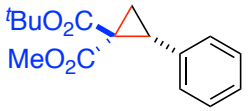

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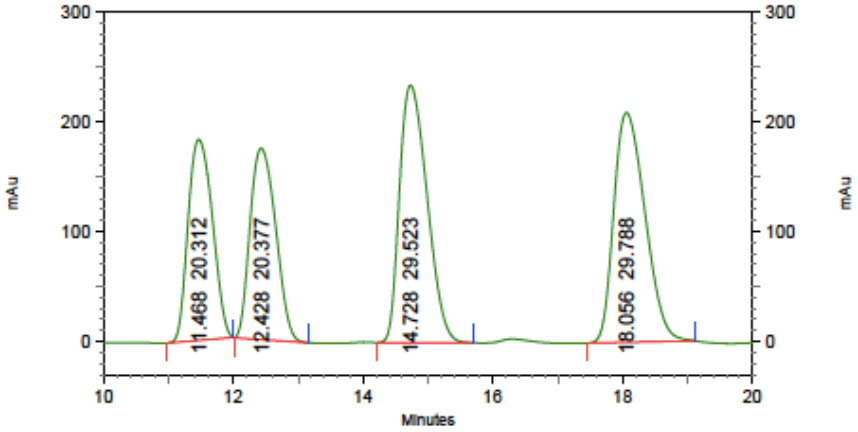
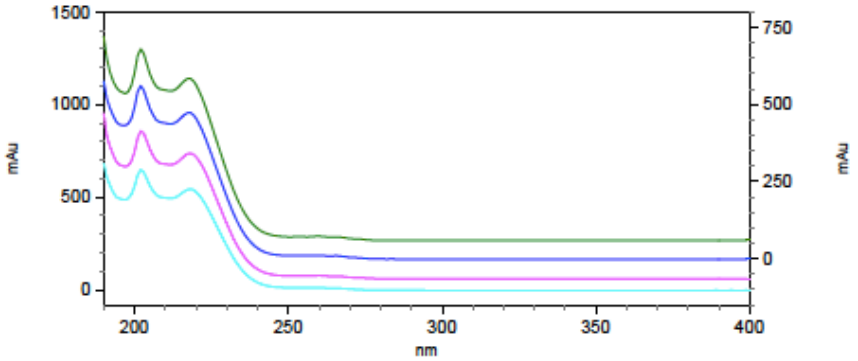
87% ee





3: 231 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	11.468	20.312
2	12.428	20.377
3	14.728	29.523
4	18.056	29.788
Totals		100.000

1-(*tert*-butyl) 1-methyl (1*S*,2*R*)-2-phenylcyclopropane-1,1-dicarboxylate

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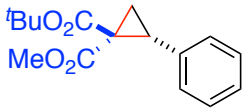
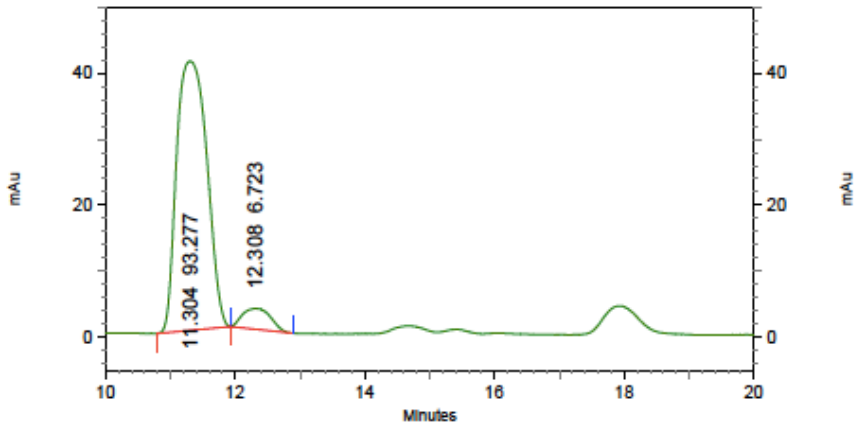
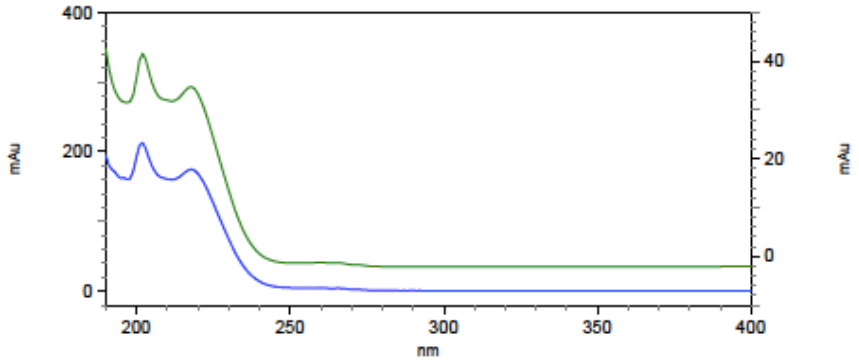


88:12 dr
87% ee

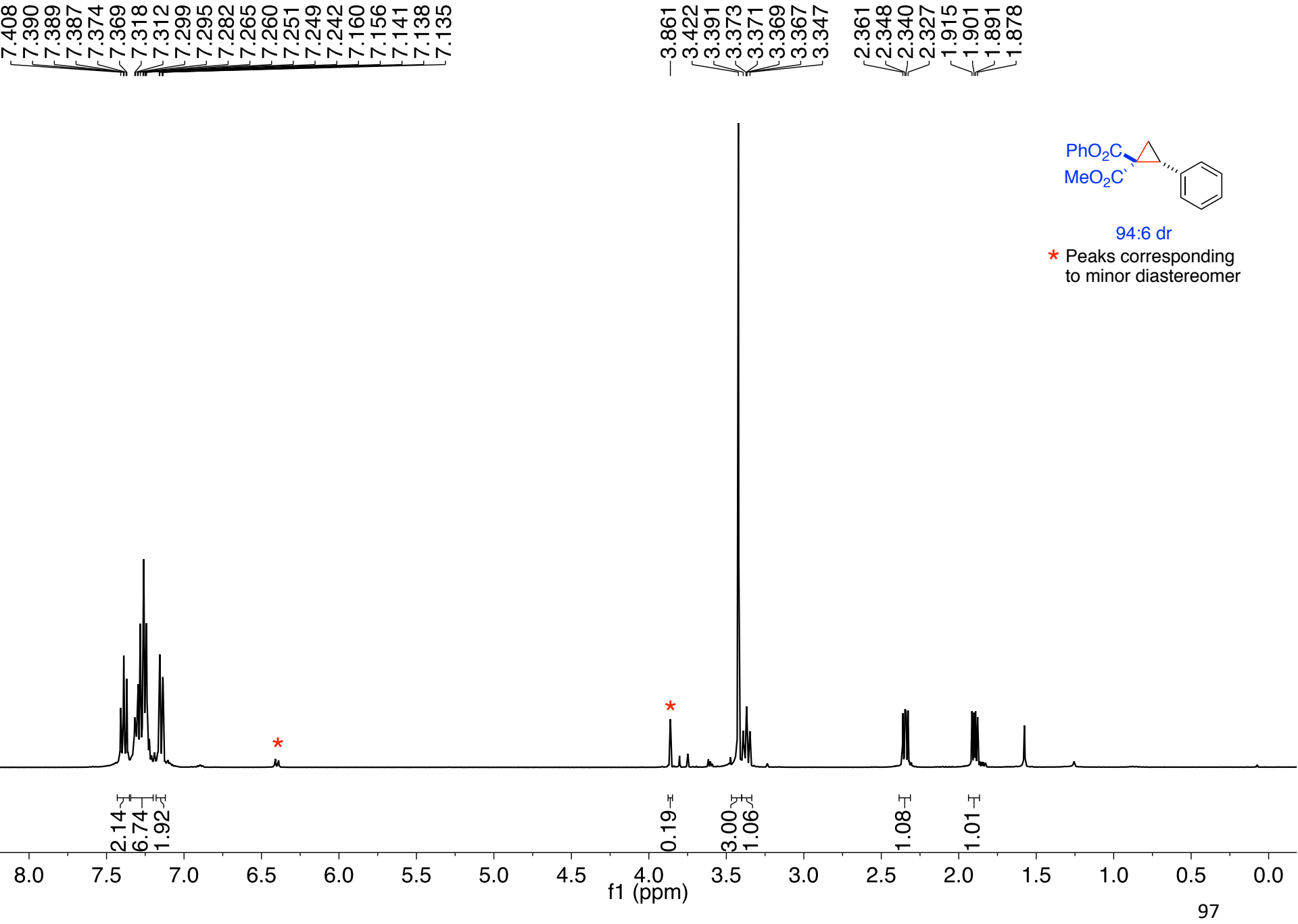




3: 255 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	11.304	93.277
2	12.308	6.723
Totals		100.000

1-methyl 1-phenyl (1*S*,2*R*)-2-phenylcyclopropane-1,1-dicarboxylate



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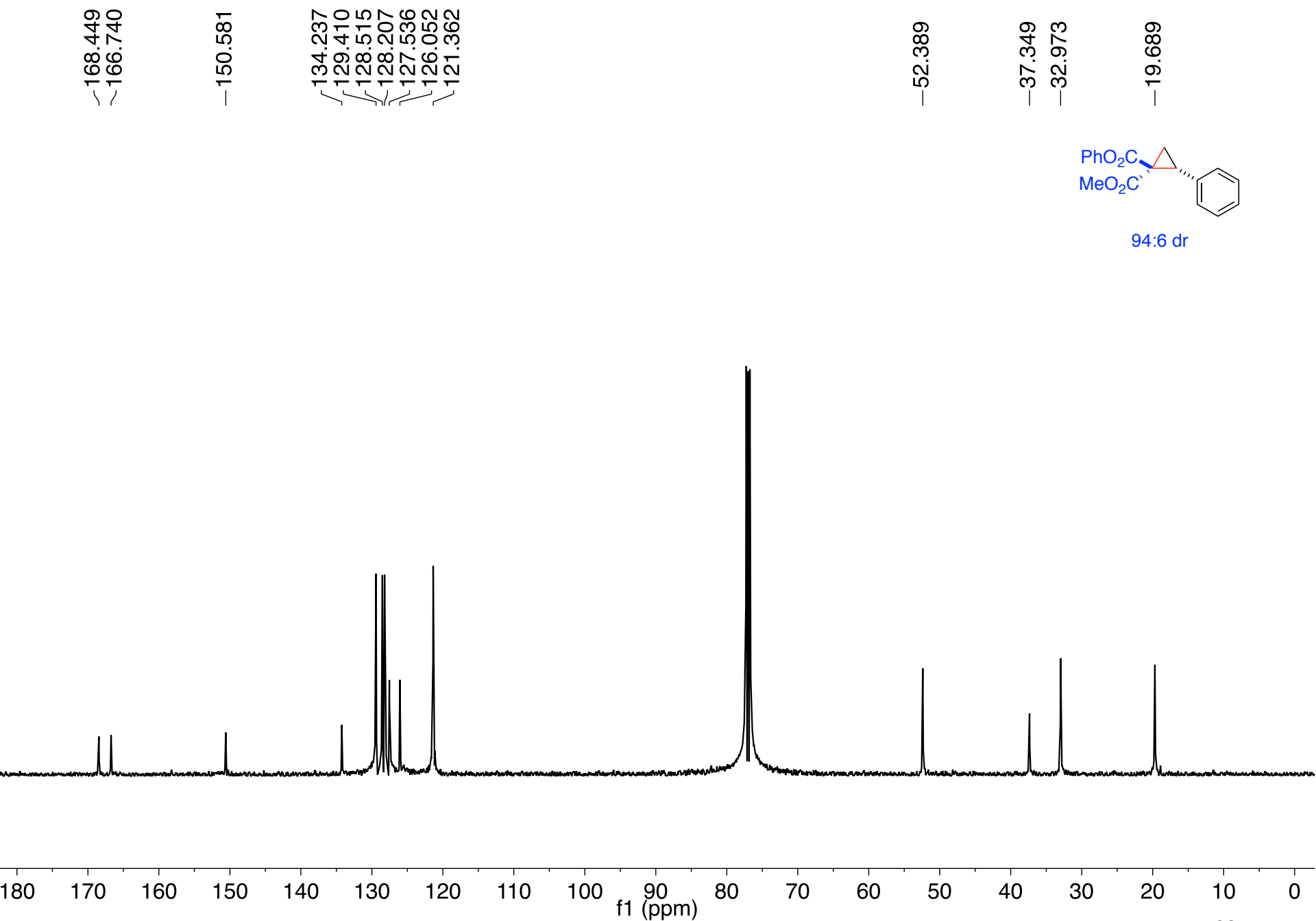

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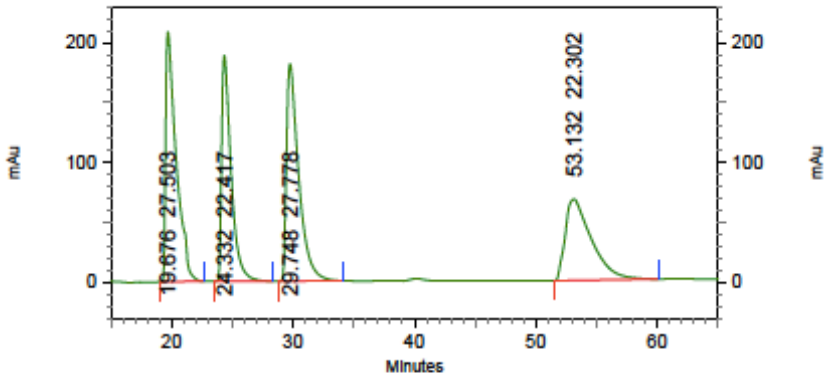

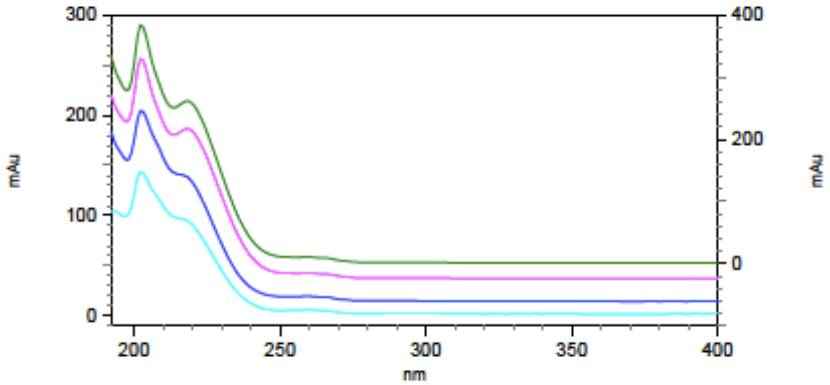

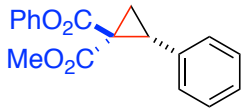

94:6 dr
96% ee

6: 225 nm, 4 nm
Results

Name	Retention Time	Area Percent	Pk #
	19.676	27.503	1
	24.332	22.417	2
	29.748	27.778	3
	53.132	22.302	4

Totals	
	100.000

1-methyl 1-phenyl (1*S*,2*R*)-2-phenylcyclopropane-1,1-dicarboxylate

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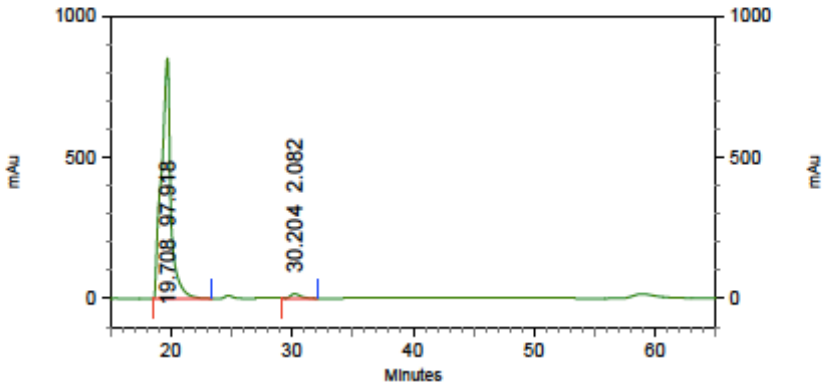

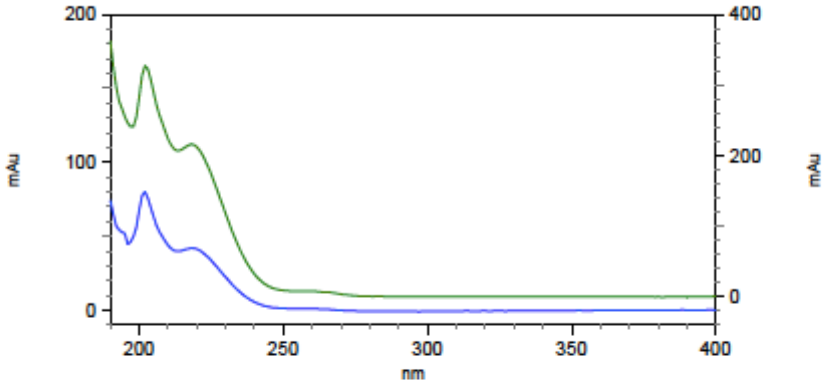

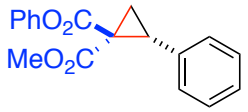

94:6 dr
96% ee

6: 225 nm, 4 nm
Results

Name	Retention Time	Area Percent	Pk #
	19.708	97.918	1
	30.204	2.082	2

Totals	
	100.000

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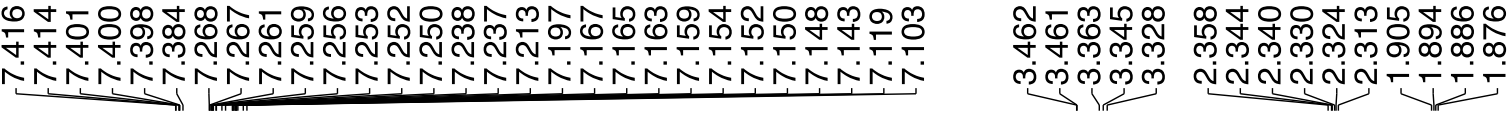
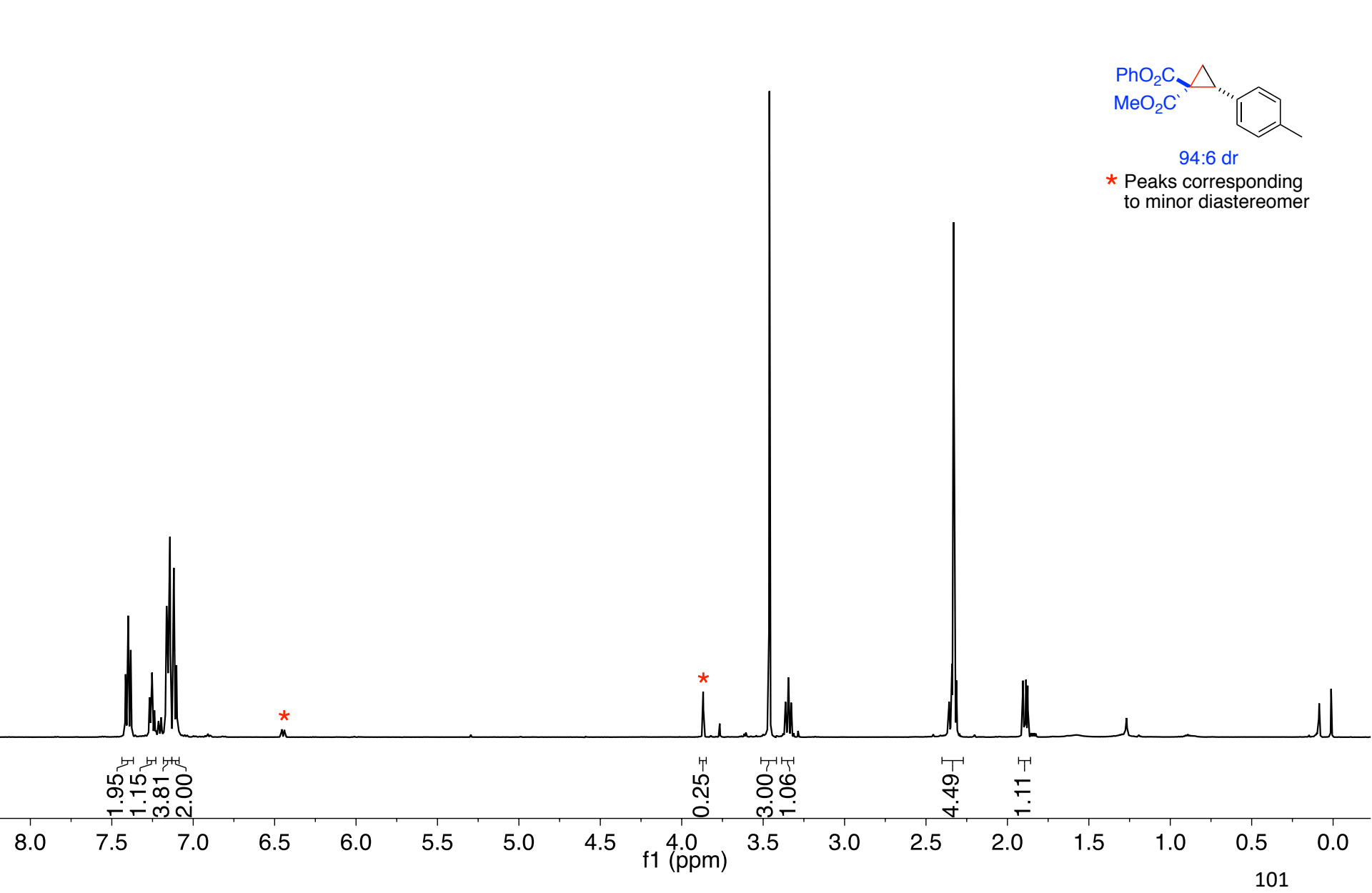
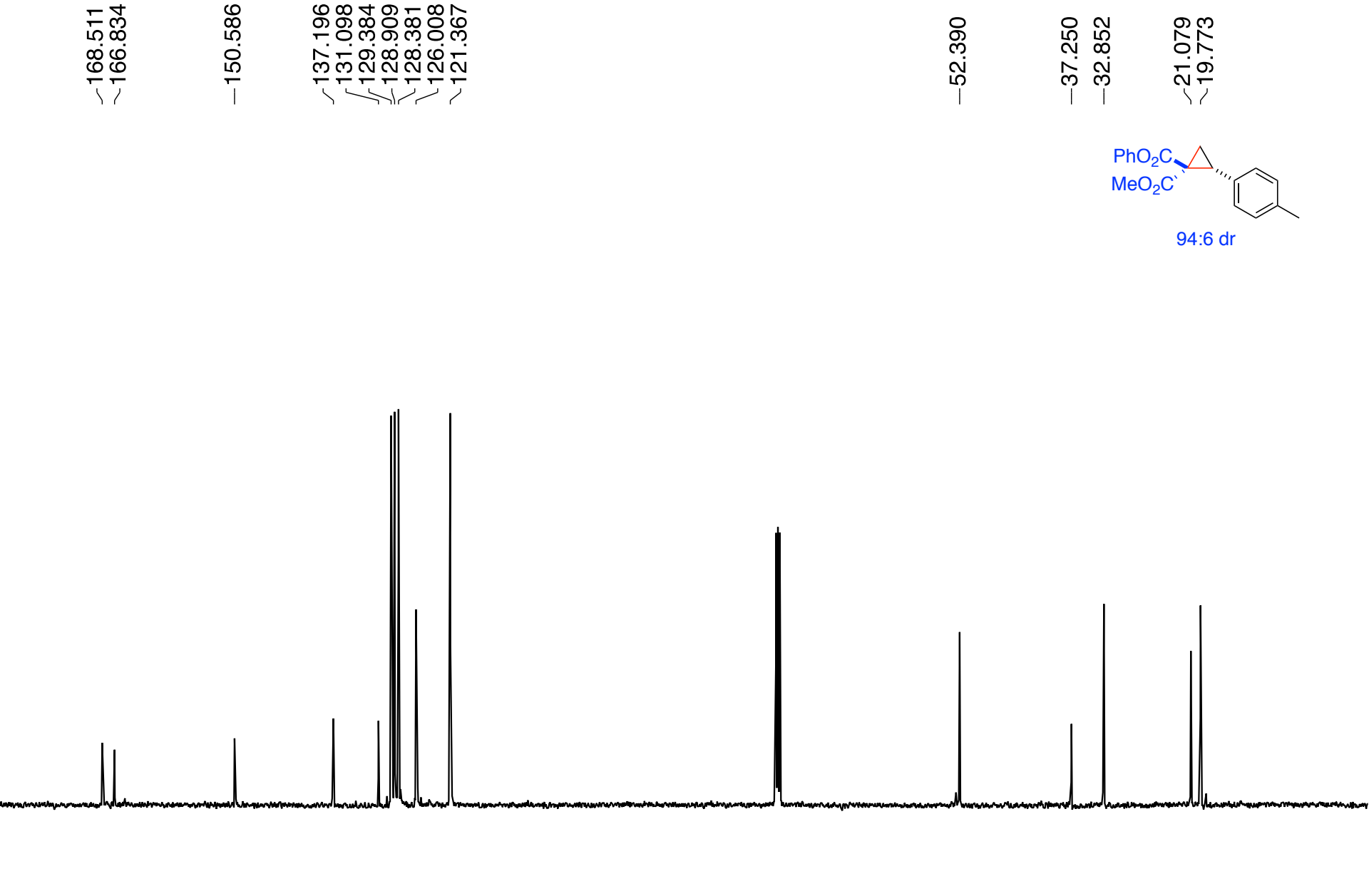
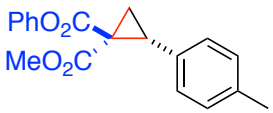




1-methyl 1-phenyl (1*S*,2*R*)-2-(*p*-tolyl)cyclopropane-1,1-dicarboxylate



1-methyl 1-phenyl (1*S*,2*R*)-2-(*p*-tolyl)cyclopropane-1,1-dicarboxylate

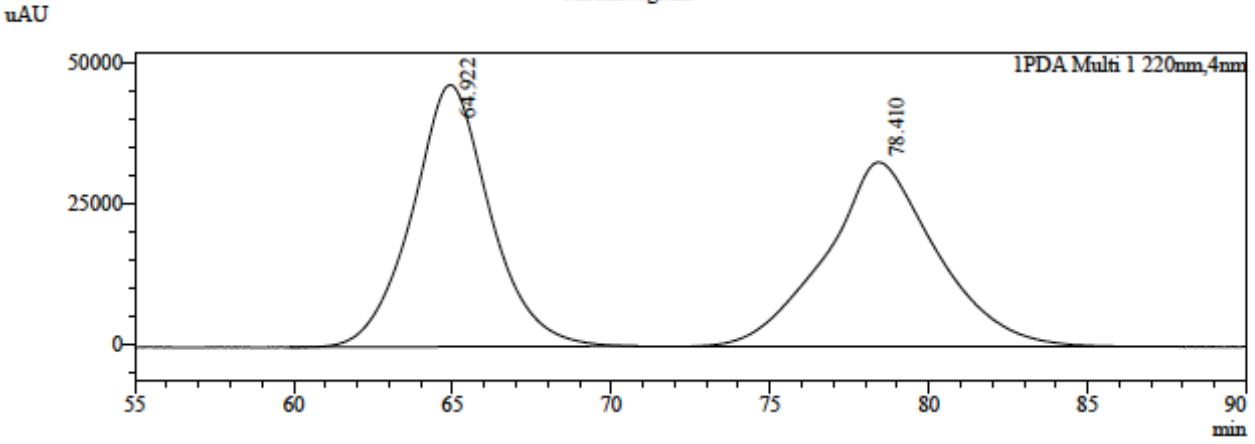


94:6 dr
97% ee

Sample Information

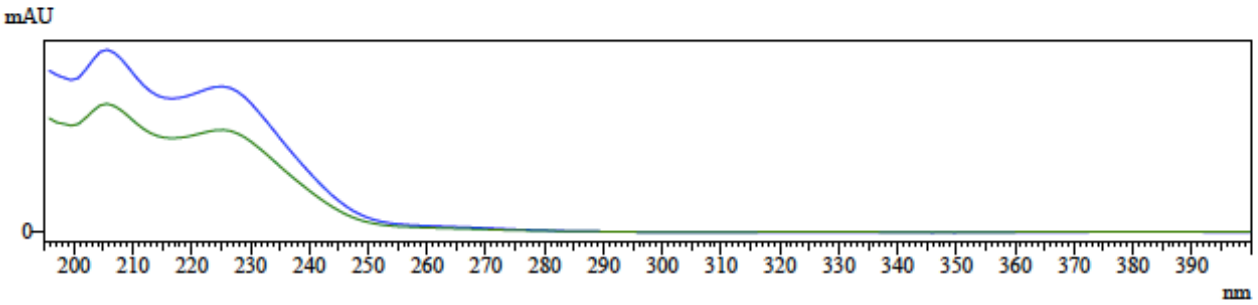
Sample Name	: JYW-II-98
Sample ID	: JYW-II-98-OJH-35%-0.6mlre2
Data File	: JYW-II-98-OJH-35%-0.6mlre2.lcd
Method File	: JYW-method.lcm
Date Acquired	: 10/14/2015 11:50:08 AM

Chromatogram



UV Spectrum

JYW-II-98-OJH-35%-0.6mlre2.lcd

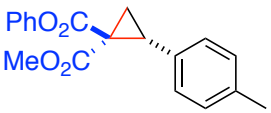


Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	64.922	7949939	49.903
2	78.410	7980734	50.097
Total		15930673	100.000

1-methyl 1-phenyl (1*S*,2*R*)-2-(*p*-tolyl)cyclopropane-1,1-dicarboxylate

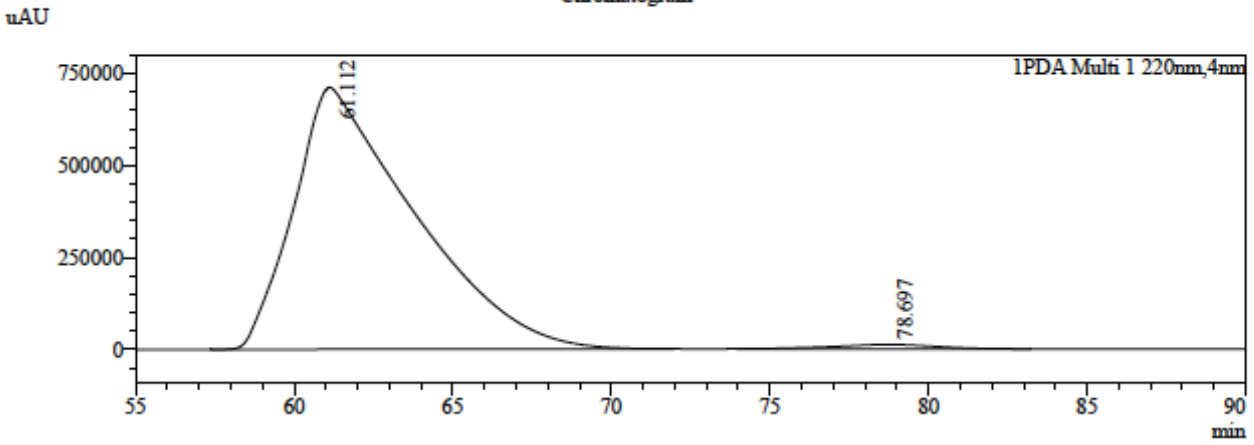


94:6 dr
97% ee

Sample Information

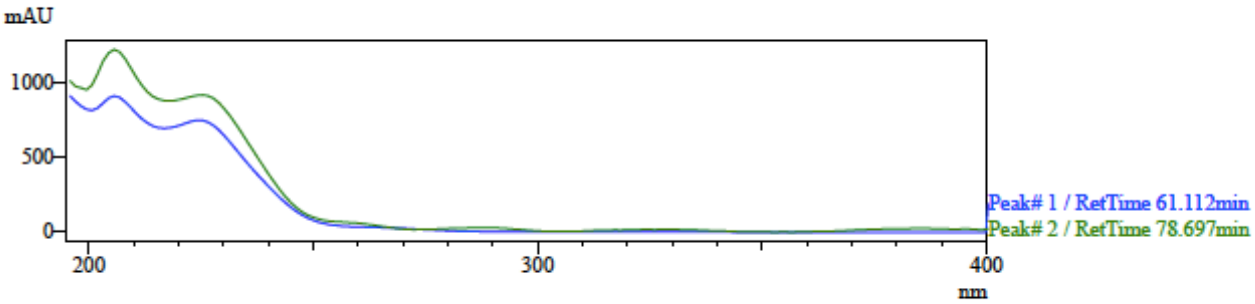
Sample Name	: JYW-II-103
Sample ID	: JYW-II-102-OJH-35%-0.6ml
Data File	: JYW-II-103-OJH-35%-0.6ml.lcd
Method File	: JYW-method.lcm
Date Acquired	: 10/14/2015 1:20:45 PM

Chromatogram



UV Spectrum

JYW-II-103-OJH-35%-0.6ml.lcd

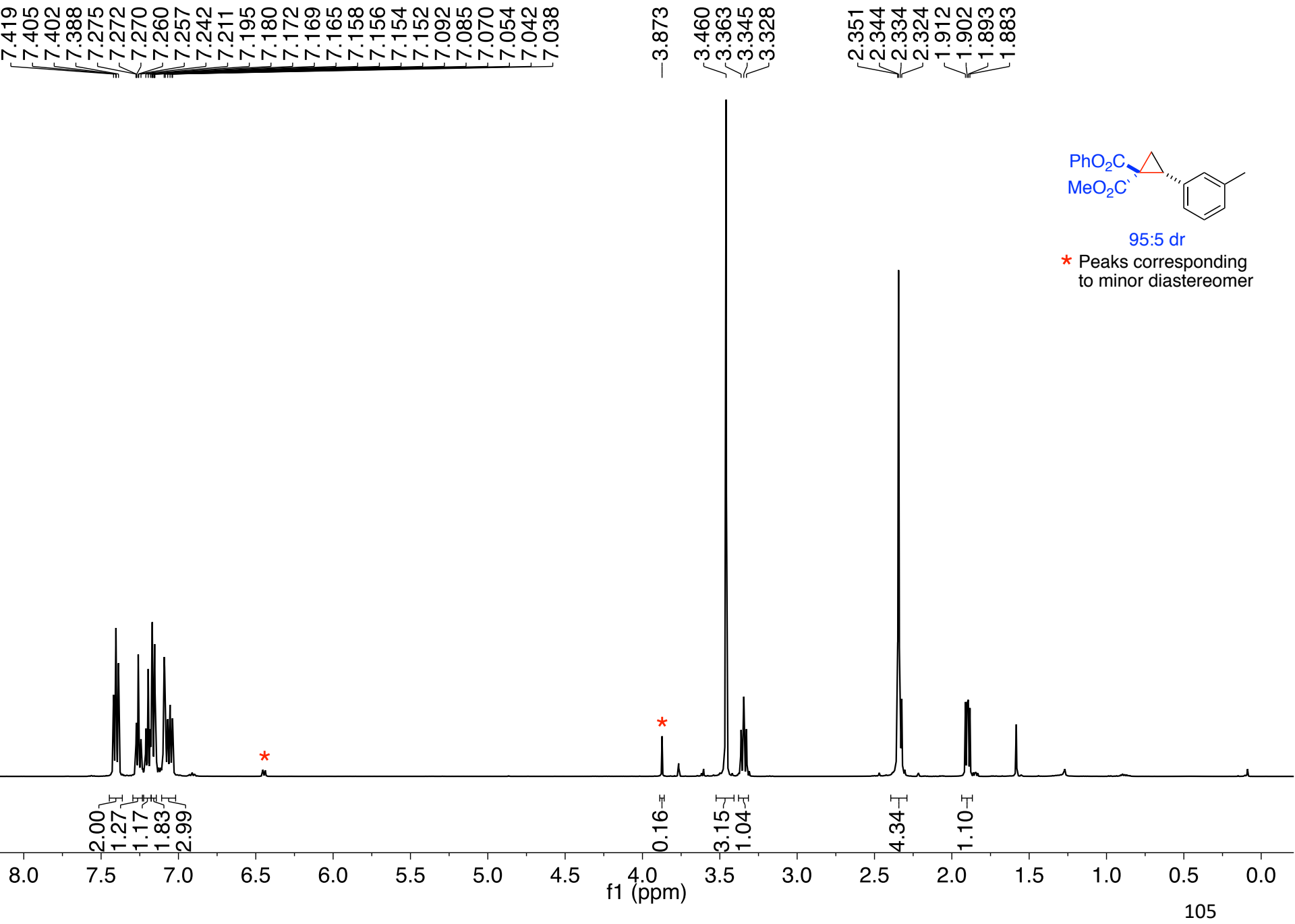


Peak Table

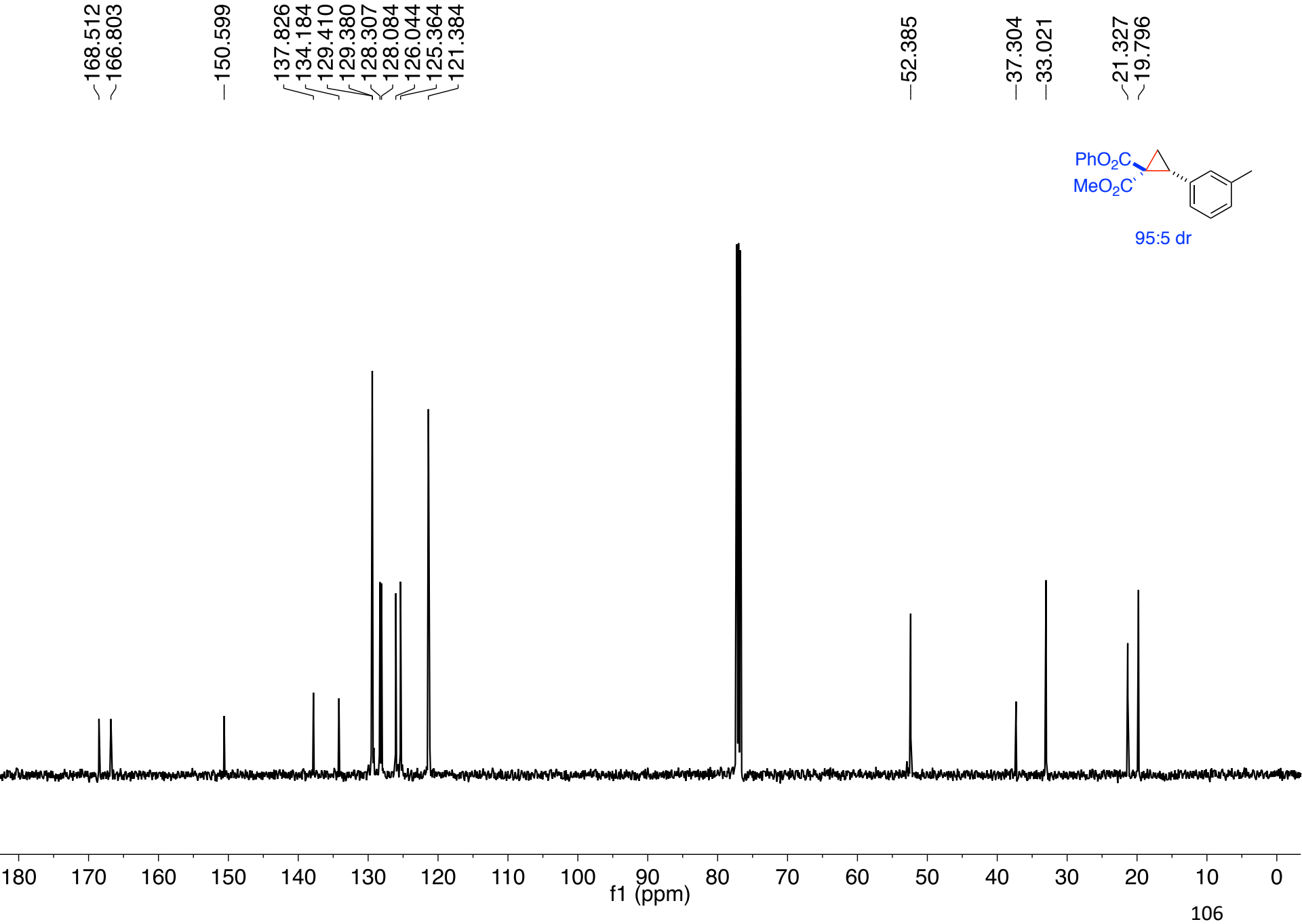
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	61.112	188458184	98.511
2	78.697	2847759	1.489
Total		191305943	100.000

1-methyl 1-phenyl (1*S*,2*R*)-2-(*m*-tolyl)cyclopropane-1,1-dicarboxylate

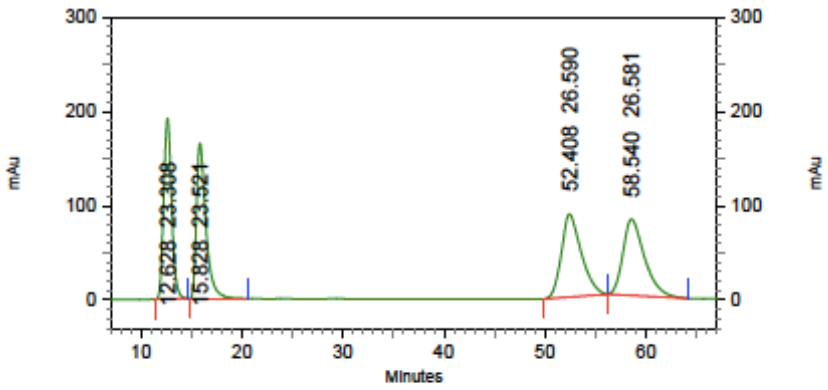


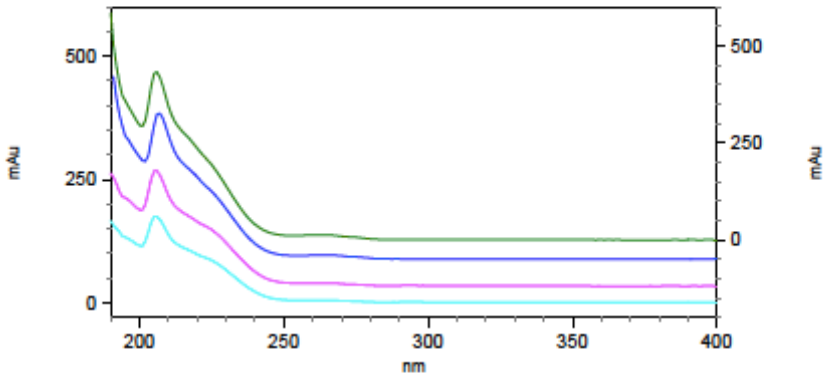
1-methyl 1-phenyl (1*S*,2*R*)-2-(*m*-tolyl)cyclopropane-1,1-dicarboxylate

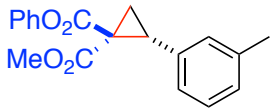


1-methyl 1-phenyl (1*S*,2*R*)-2-(*m*-tolyl)cyclopropane-1,1-dicarboxylate

JYW-II-110A-OJH-10%-0.8mlre
C:\EZStart\Projects\Default\Method\LK0.8-3%.met
C:\EZStart\Projects\Default\Data\JYW-II-110A-OJH-10%-0.8mlre







95:5 dr
98% ee

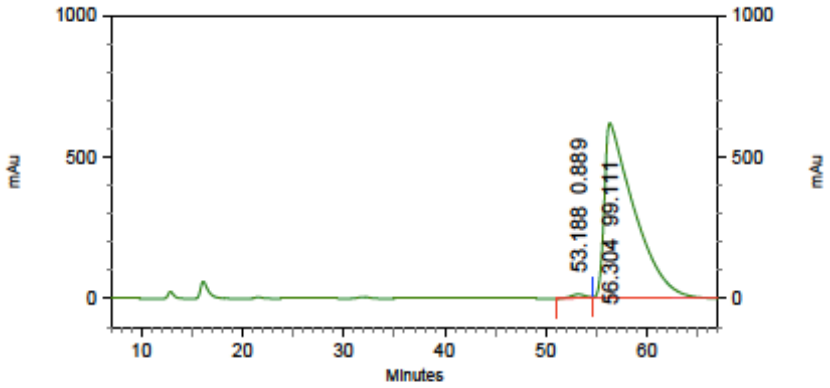
3: 225 nm, 4 nm
Results

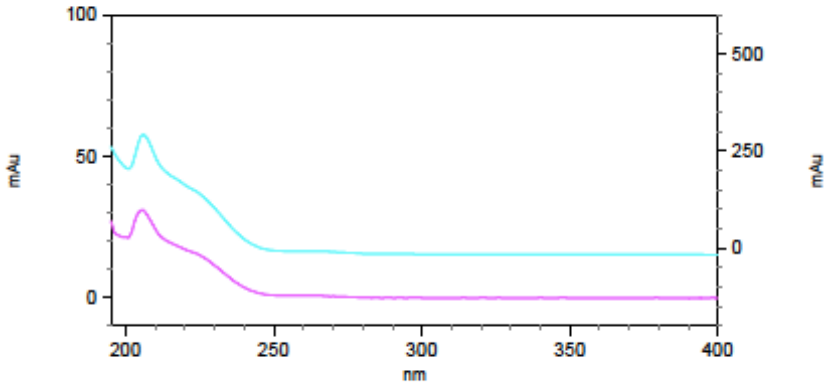
Name	Retention Time	Area Percent	Pk #
	12.628	23.308	1
	15.828	23.521	2
	52.408	26.590	3
	58.540	26.581	4

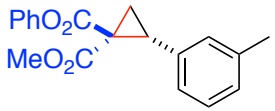
Totals	
	100.000

1-methyl 1-phenyl (1*S*,2*R*)-2-(*m*-tolyl)cyclopropane-1,1-dicarboxylate

JYW-II-110B-OJH-10%-0.8mlre
C:\EZStart\Projects\Default\Method\LK0.8-3%.met
C:\EZStart\Projects\Default\Data\JYW-II-110B-OJH-10%-0.8mlre







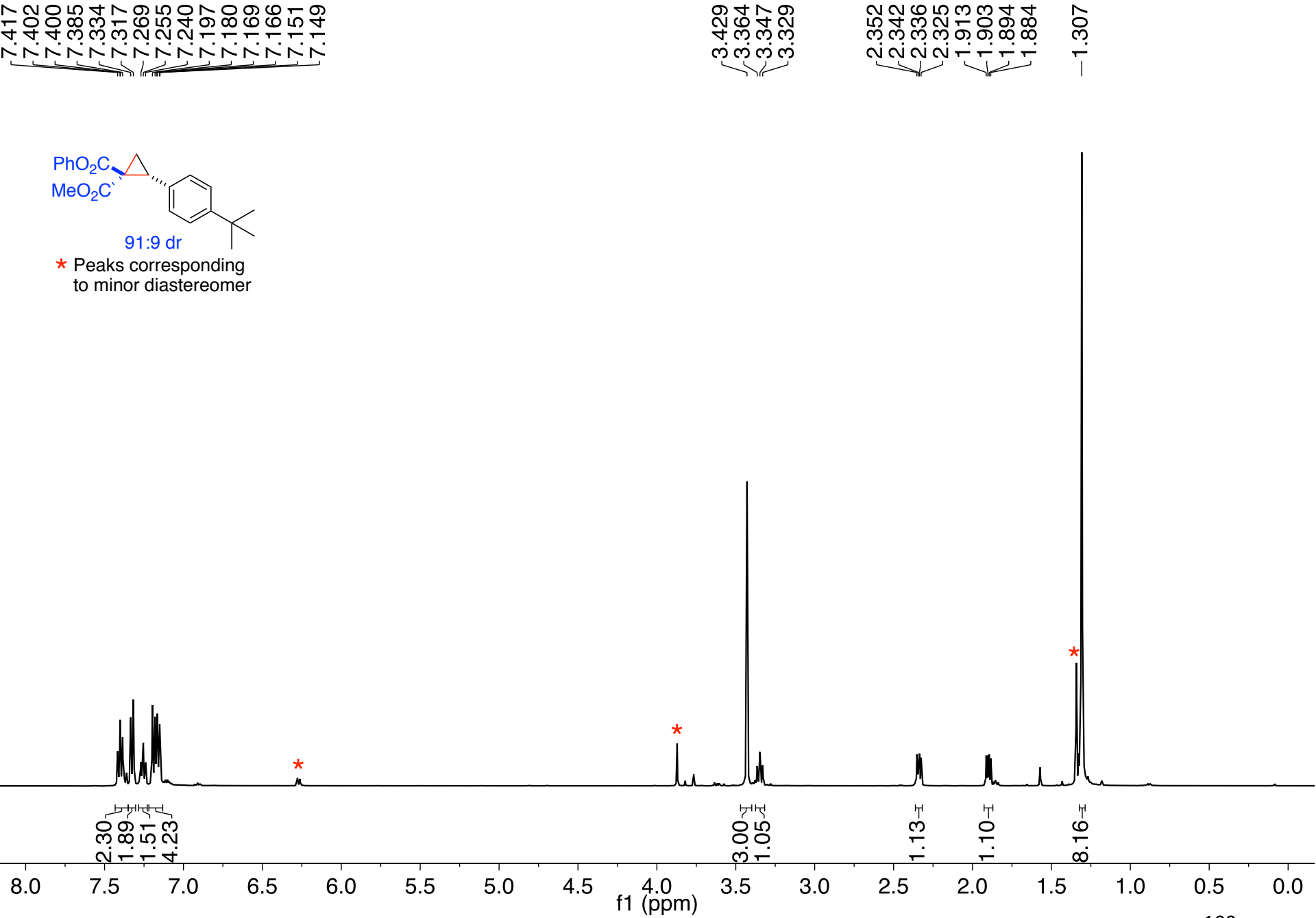
95:5 dr
98% ee

3: 225 nm, 4 nm
Results

Name	Retention Time	Area Percent	Pk #
	53.188	0.889	1
	56.304	99.111	2

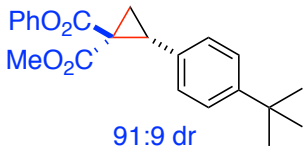
Totals	
	100.000

1-methyl 1-phenyl (1*S*,2*R*)-2-(4-(*tert*-butyl)phenyl)cyclopropane-1,1-dicarboxylate



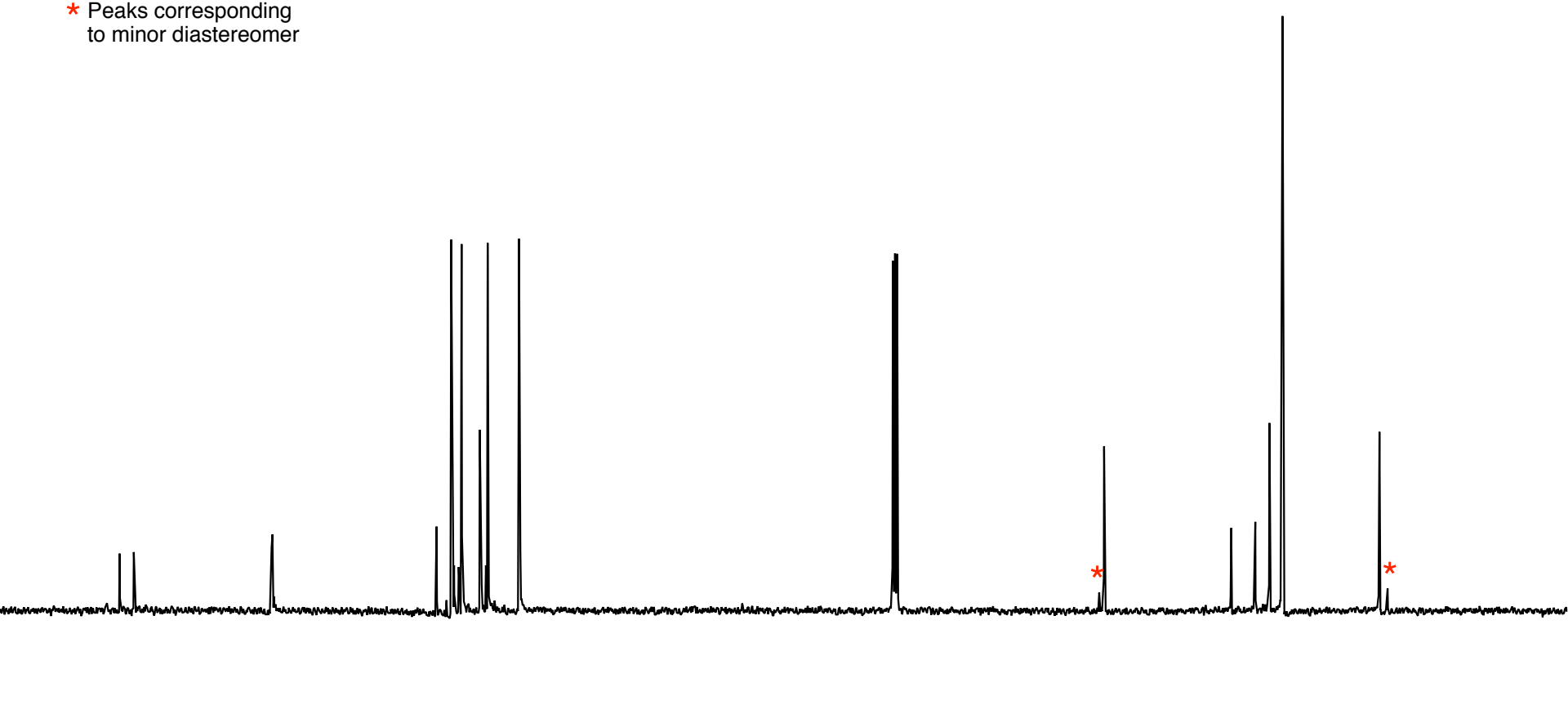
1-methyl 1-phenyl (1*S*,2*R*)-2-(4-(*tert*-butyl)phenyl)cyclopropane-1,1-dicarboxylate

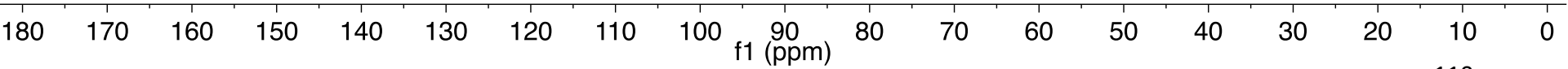
168.537
166.862
150.596
150.495
131.120
129.393
128.165
125.088
121.384
52.323
37.307
34.470
32.797
31.312
31.258
19.812



91:9 dr

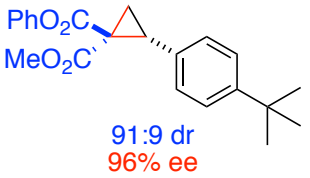
* Peaks corresponding to minor diastereomer



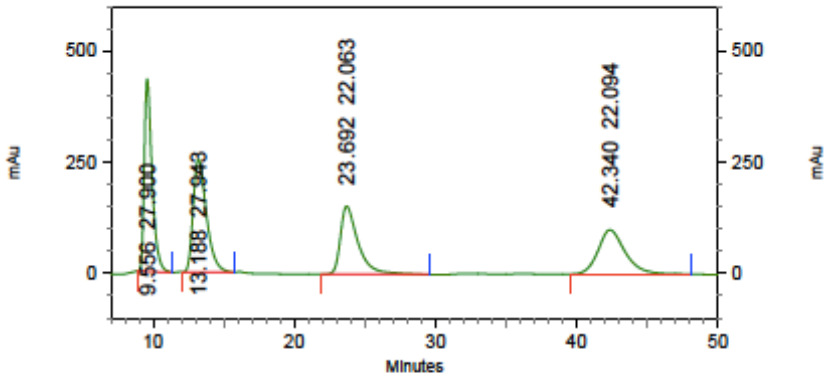


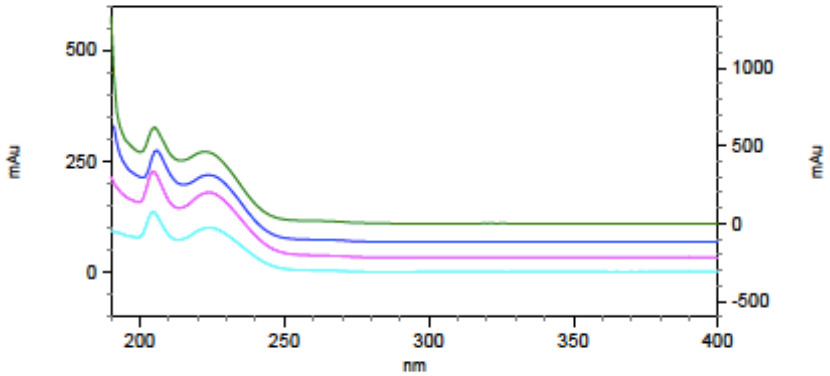
1-methyl 1-phenyl (1*S*,2*R*)-2-(4-(*tert*-butyl)phenyl)cyclopropane-1,1-dicarboxylate

JYW-II-111A-OJH-8%-0.8ml
C:\EZStart\Projects\Default\Method\LK0.8-3%.met
C:\EZStart\Projects\Default\Data\JYW-II-111A-OJH-8%-0.8ml



91:9 dr
96% ee





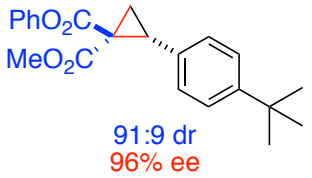
3: 226 nm, 4 nm
Results

Name	Retention Time	Area Percent	Pk #
	9.556	27.900	1
	13.188	27.943	2
	23.692	22.063	3
	42.340	22.094	4

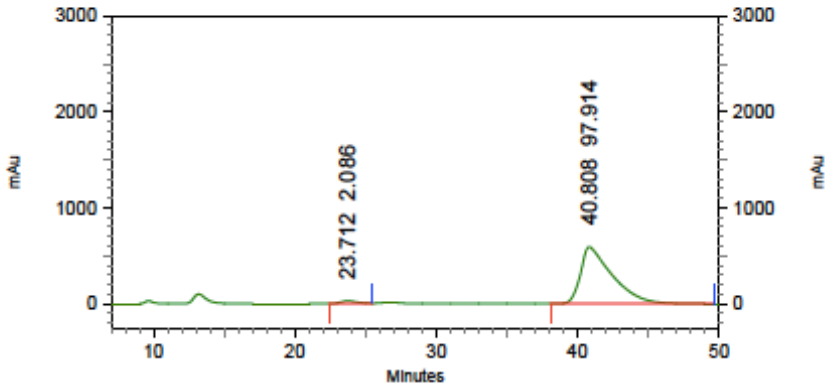
Totals	
	100.000

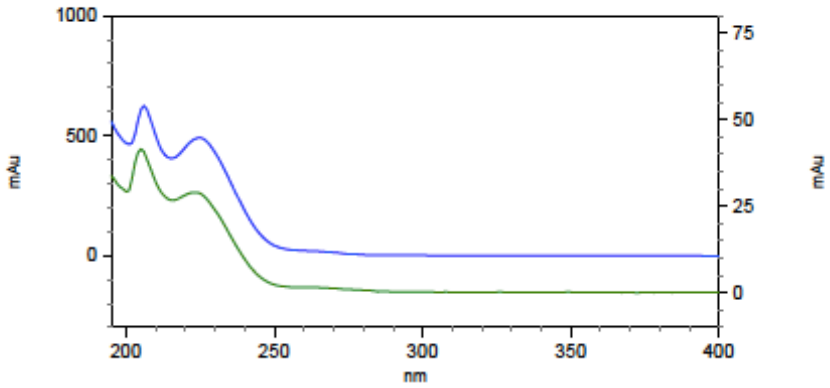
1-methyl 1-phenyl (1*S*,2*R*)-2-(4-(*tert*-butyl)phenyl)cyclopropane-1,1-dicarboxylate

JYW-II-111B-OJH-8%-0.8ml
C:\EZStart\Projects\Default\Method\LK0.8-3%.met
C:\EZStart\Projects\Default\Data\JYW-II-111B-OJH-8%-0.8ml



91:9 dr
96% ee



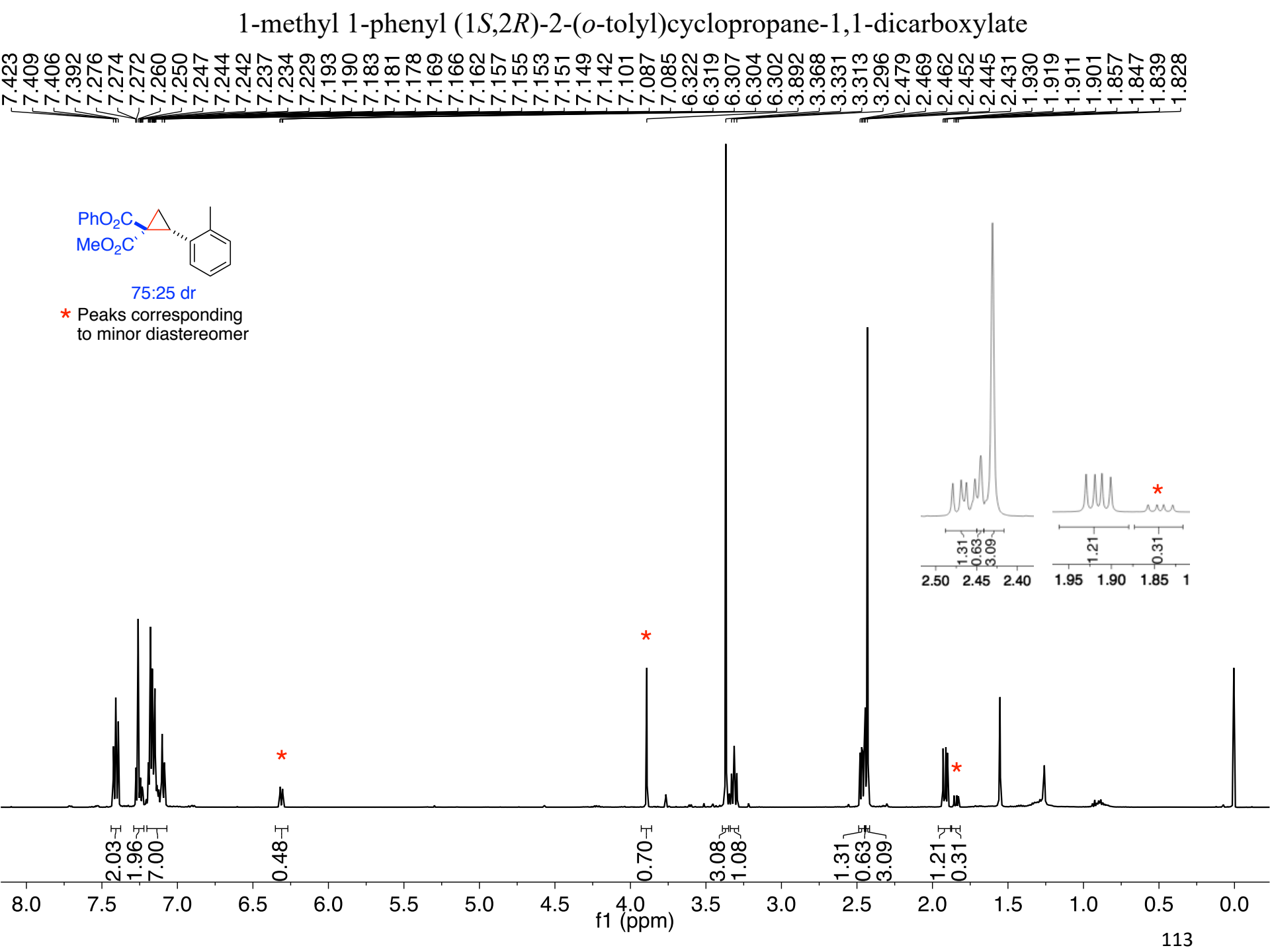


3: 226 nm, 4 nm
Results

Name	Retention Time	Area Percent	Pk #
	23.712	2.086	1
	40.808	97.914	2

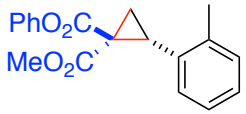
Totals	
	100.000

1-methyl 1-phenyl (1*S*,2*R*)-2-(*o*-tolyl)cyclopropane-1,1-dicarboxylate



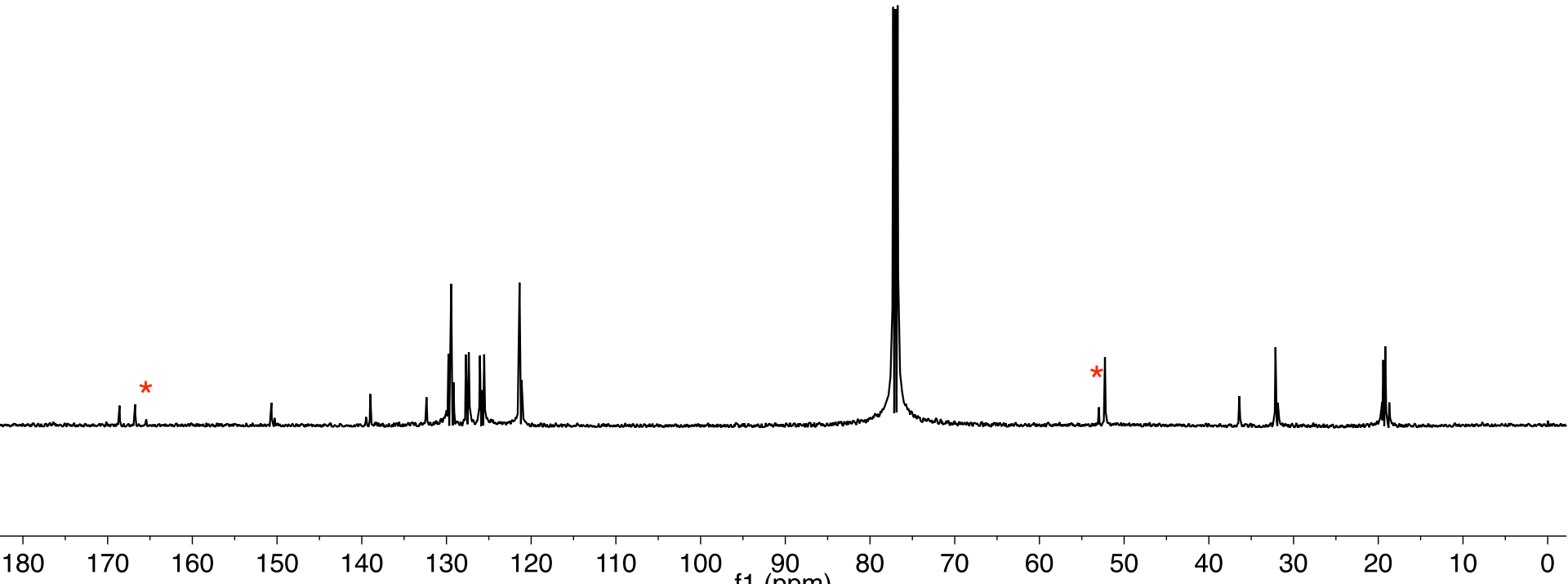
1-methyl 1-phenyl (1*S*,2*R*)-2-(*o*-tolyl)cyclopropane-1,1-dicarboxylate

168.585
166.755
150.657
138.995
132.354
129.763
129.436
127.709
127.361
126.052
125.547
121.368
52.264
36.408
32.135
19.417
19.174



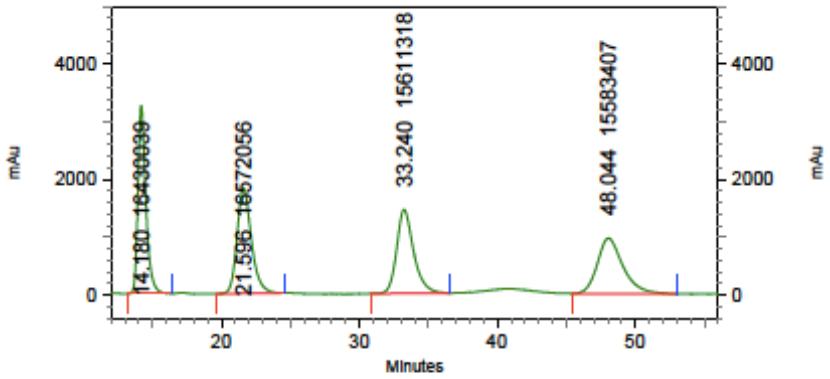
75:25 dr

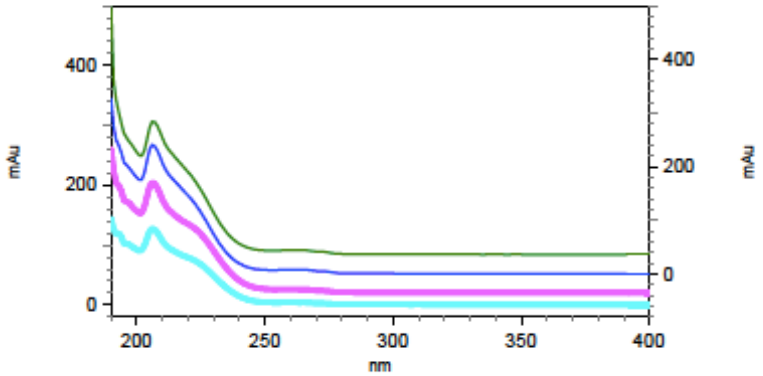
* Peaks corresponding to minor diastereomer

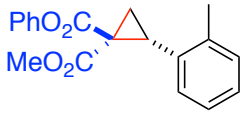


1-methyl 1-phenyl (1*S*,2*R*)-2-(*o*-tolyl)cyclopropane-1,1-dicarboxylate

JYW-II-116A-OJH-35%-0.6mlre
C:\EZStart\Projects\Default\Method\ywang1.0.met
C:\EZStart\Projects\Default\Data\JYW-II-116A-OJH-35%-0.6mlre







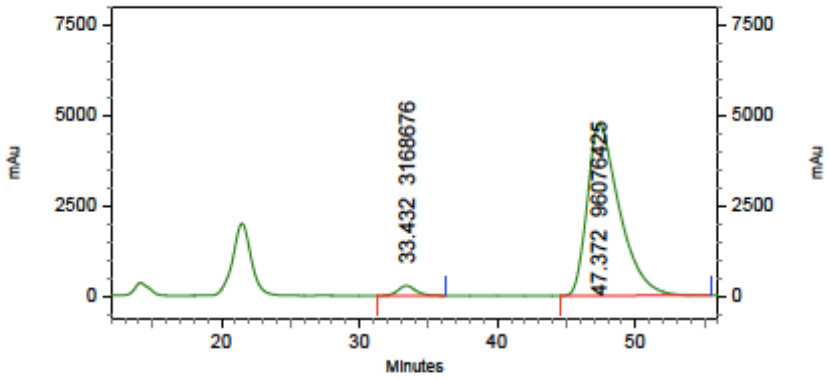
75:25 dr
94% ee

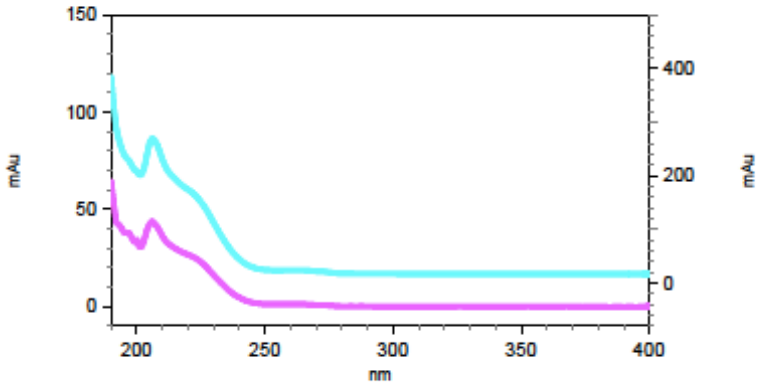
3: 206 nm, 4 nm
Results

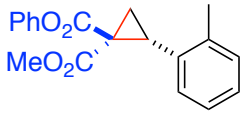
Pk #	Name	Retention Time	Area Percent
1		14.180	25.593
2		21.596	25.814
3		33.240	24.318
4		48.044	24.274
Totals			100.000

1-methyl 1-phenyl (1*S*,2*R*)-2-(*o*-tolyl)cyclopropane-1,1-dicarboxylate

JYW-II-127-OJH-35%-0.6ml
C:\EZStart\Projects\Default\Method\ywang1.0.met
C:\EZStart\Projects\Default\Data\JYW-II-127-OJH-35%-0.6ml





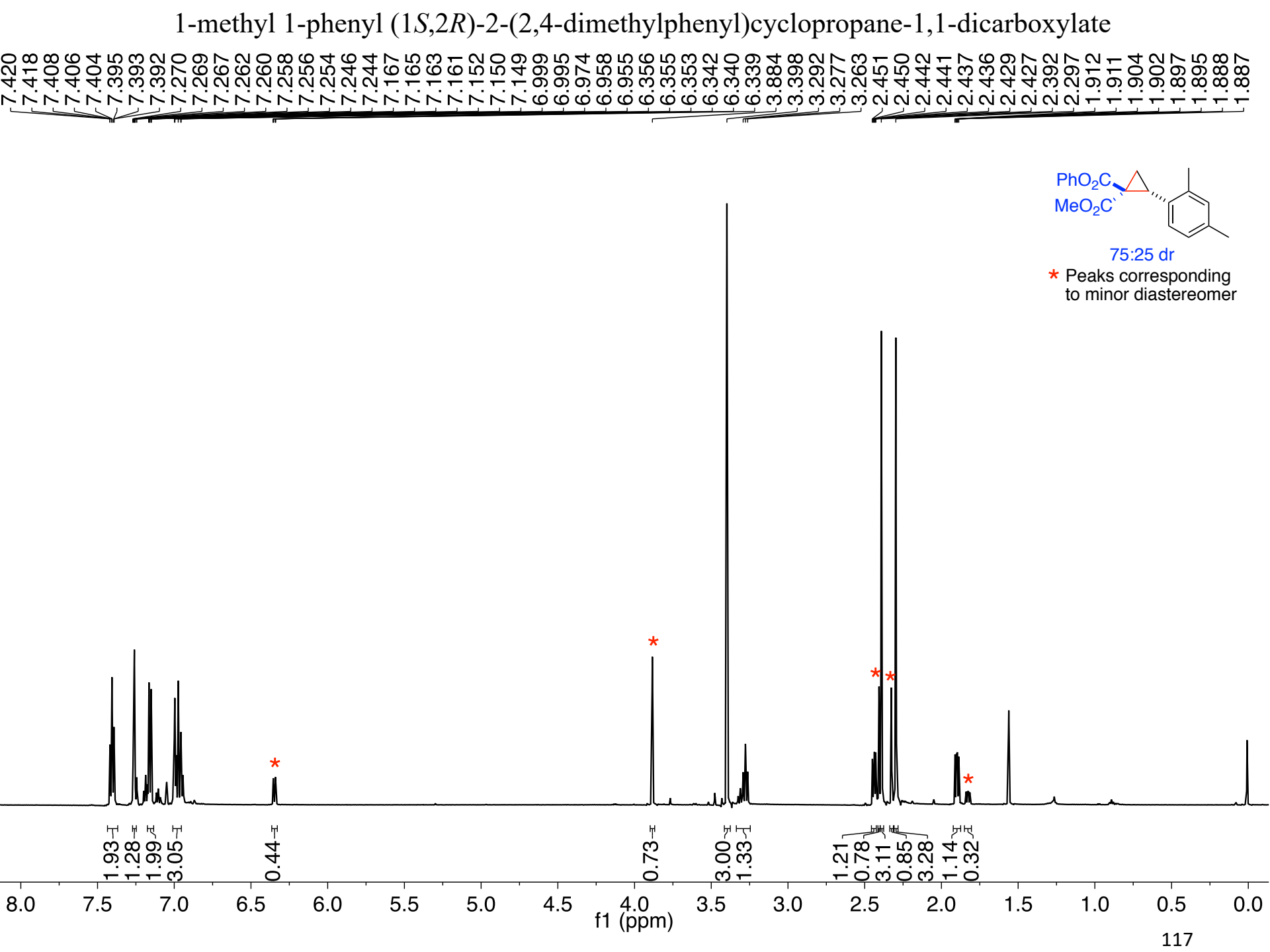


75:25 dr
94% ee

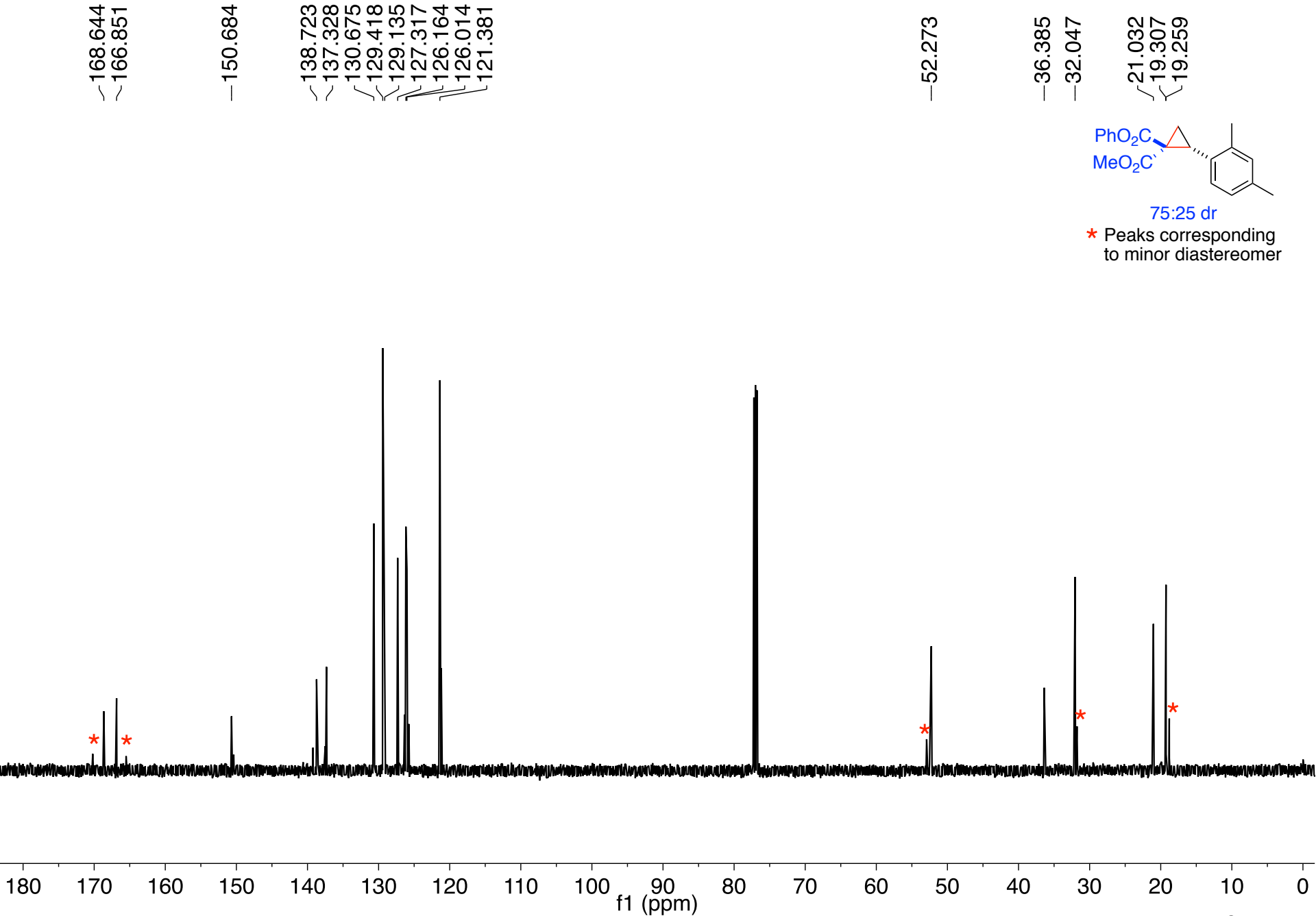
3: 206 nm, 4 nm
Results

Pk #	Name	Retention Time	Area Percent
1		33.432	3.193
2		47.372	96.807
Totals			100.000

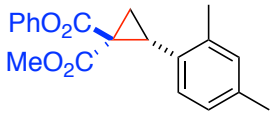
1-methyl 1-phenyl (1*S*,2*R*)-2-(2,4-dimethylphenyl)cyclopropane-1,1-dicarboxylate



1-methyl 1-phenyl (1*S*,2*R*)-2-(2,4-dimethylphenyl)cyclopropane-1,1-dicarboxylate



1-methyl 1-phenyl (1*S*,2*R*)-2-(2,4-dimethylphenyl)cyclopropane-1,1-dicarboxylate

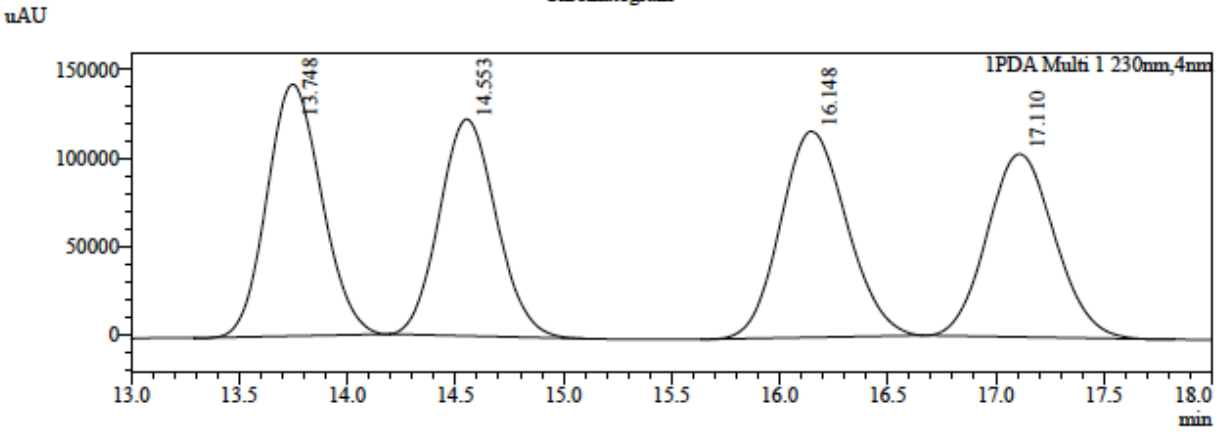


75:25 dr
96% ee

Sample Information

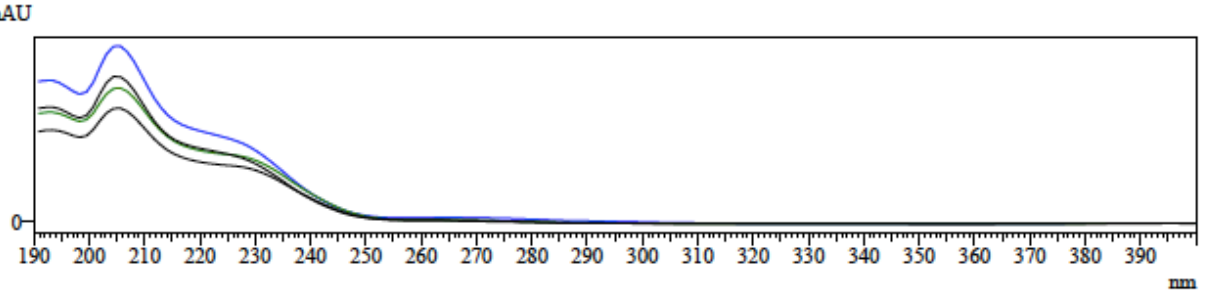
Sample Name	: JYW-0376
Sample ID	: JYW-0376-IC-4%-0.8ml-2
Data File	: JYW-0376-IC-4%-0.8ml-2.lcd
Method File	: JYW-method.lcm
Date Acquired	: 6/24/2017 3:52:49 PM

Chromatogram



UV Spectrum

JYW-0376-IC-4%-0.8ml-2.lcd

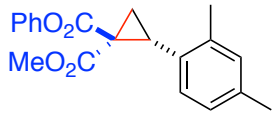


Peak Table

PDA Ch1 230nm

Peak#	Ret. Time	Area	Area%
1	13.748	2498869	26.389
2	14.553	2243244	23.690
3	16.148	2479598	26.186
4	17.110	2247559	23.735
Total		9469270	100.000

1-methyl 1-phenyl (1*S*,2*R*)-2-(2,4-dimethylphenyl)cyclopropane-1,1-dicarboxylate

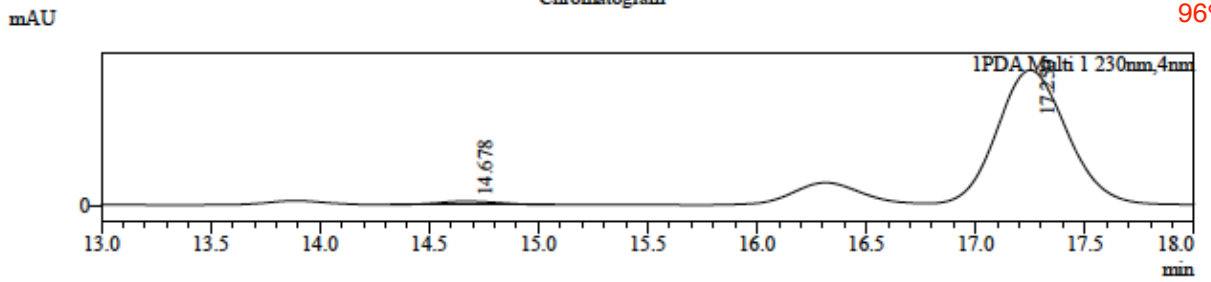


75:25 dr
96% ee

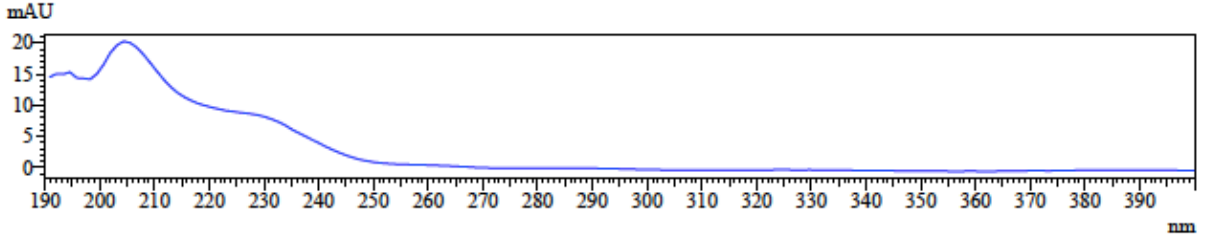
Sample Information

Sample Name	: JYW-0378
Sample ID	: JYW-0378-IC-4%-0.8ml-2
Data File	: JYW-0378-IC-4%-0.8ml-2.lcd
Method File	: JYW-method.lcm

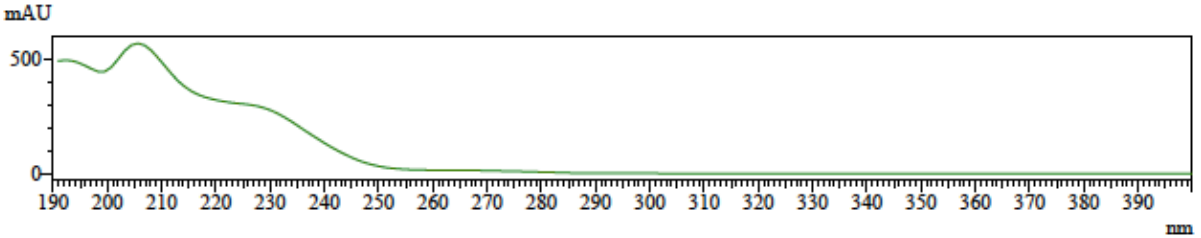
Chromatogram



UV Spectrum
Retention time = 14.678



UV Spectrum
Retention time = 17.250

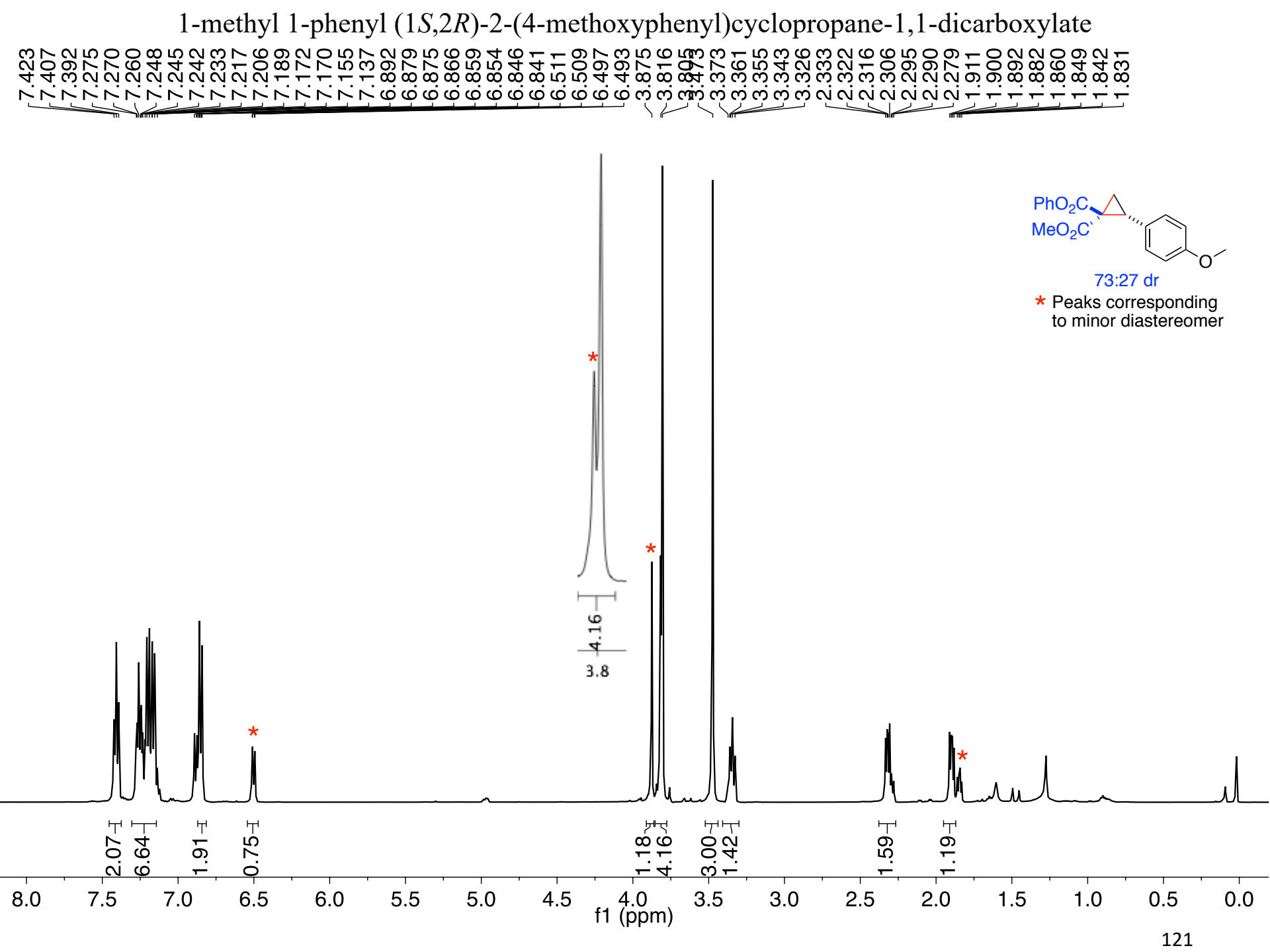


Peak Table

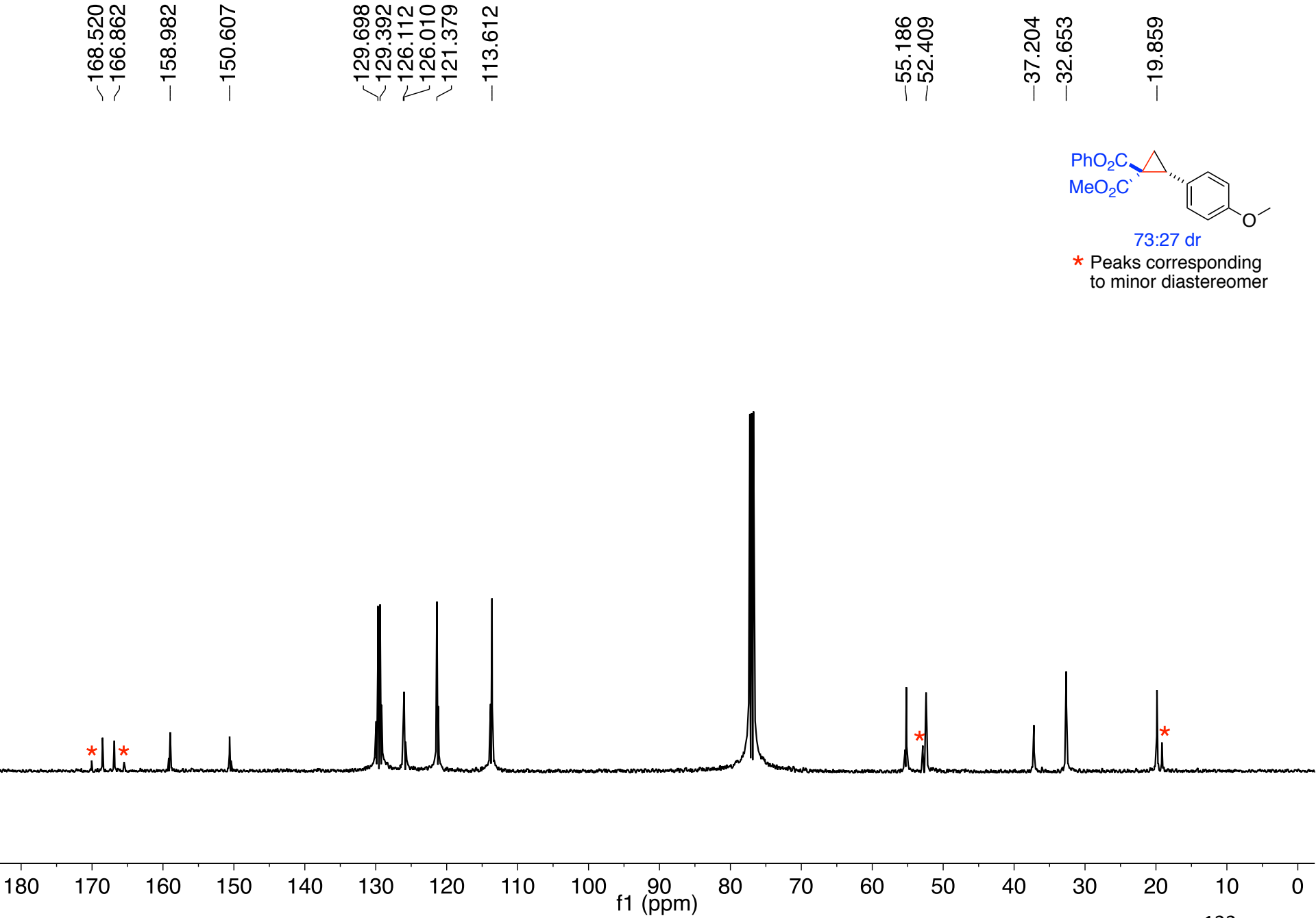
PDA Ch1 230nm

Peak#	Ret. Time	Area	Area%
1	14.678	126167	2.098
2	17.250	5886232	97.902
Total		6012398	100.000

1-methyl 1-phenyl (1*S*,2*R*)-2-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate



1-methyl 1-phenyl (1*S*,2*R*)-2-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate



1-methyl 1-phenyl (1*S*,2*R*)-2-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate

JYW-II-121-ODH-2%-1mlRE
C:\EZStart\Projects\Default\Method\ywang0.8-1.0%.met
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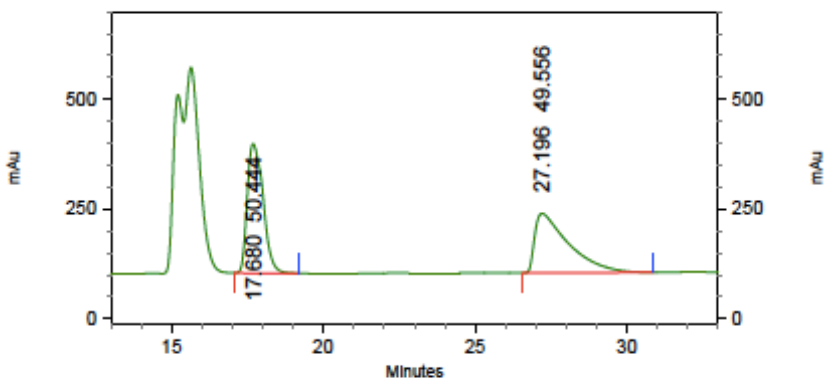
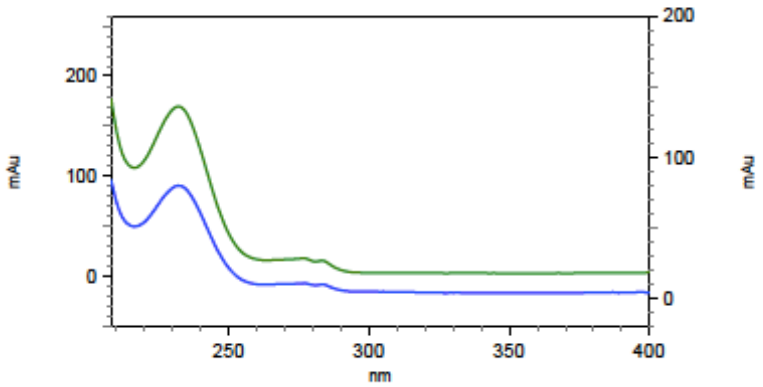
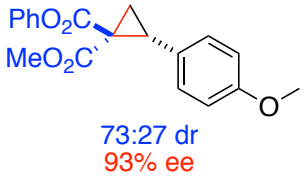






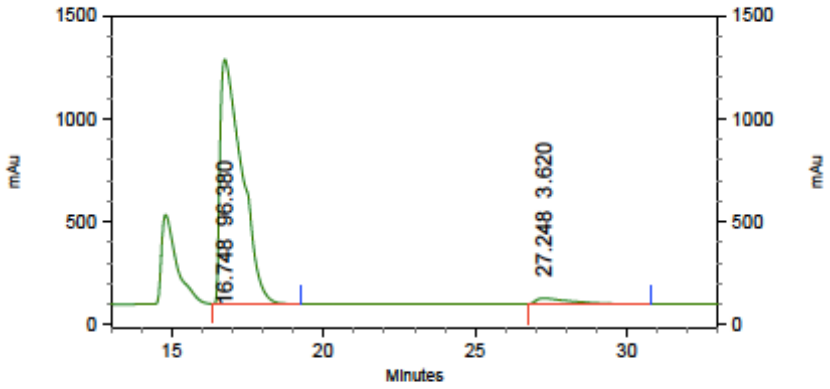
73:27 dr
93% ee

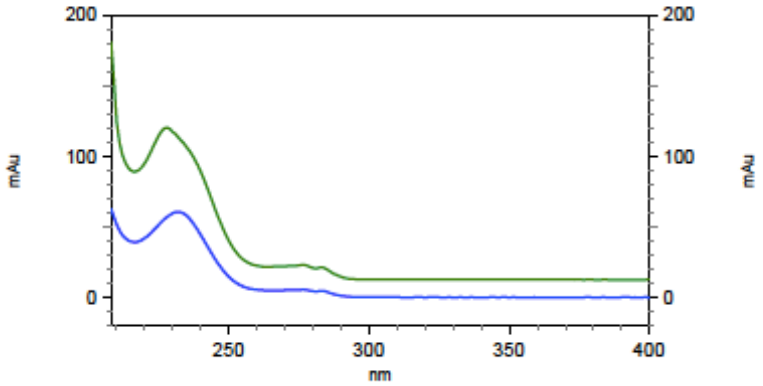
4: 226 nm, 4 nm
Results

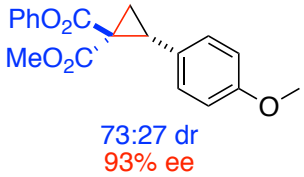
Pk #	Name	Retention Time	Area Percent
1		17.680	50.444
2		27.196	49.556
Totals			100.000

1-methyl 1-phenyl (1*S*,2*R*)-2-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate

JYW-II-125-ODH-2%-1ml
C:\EZStart\Projects\Default\Method\ywang0.8-1.0%.met
C:\EZStart\Projects\Default\Data\JYW-II-125-ODH-2%-1ml





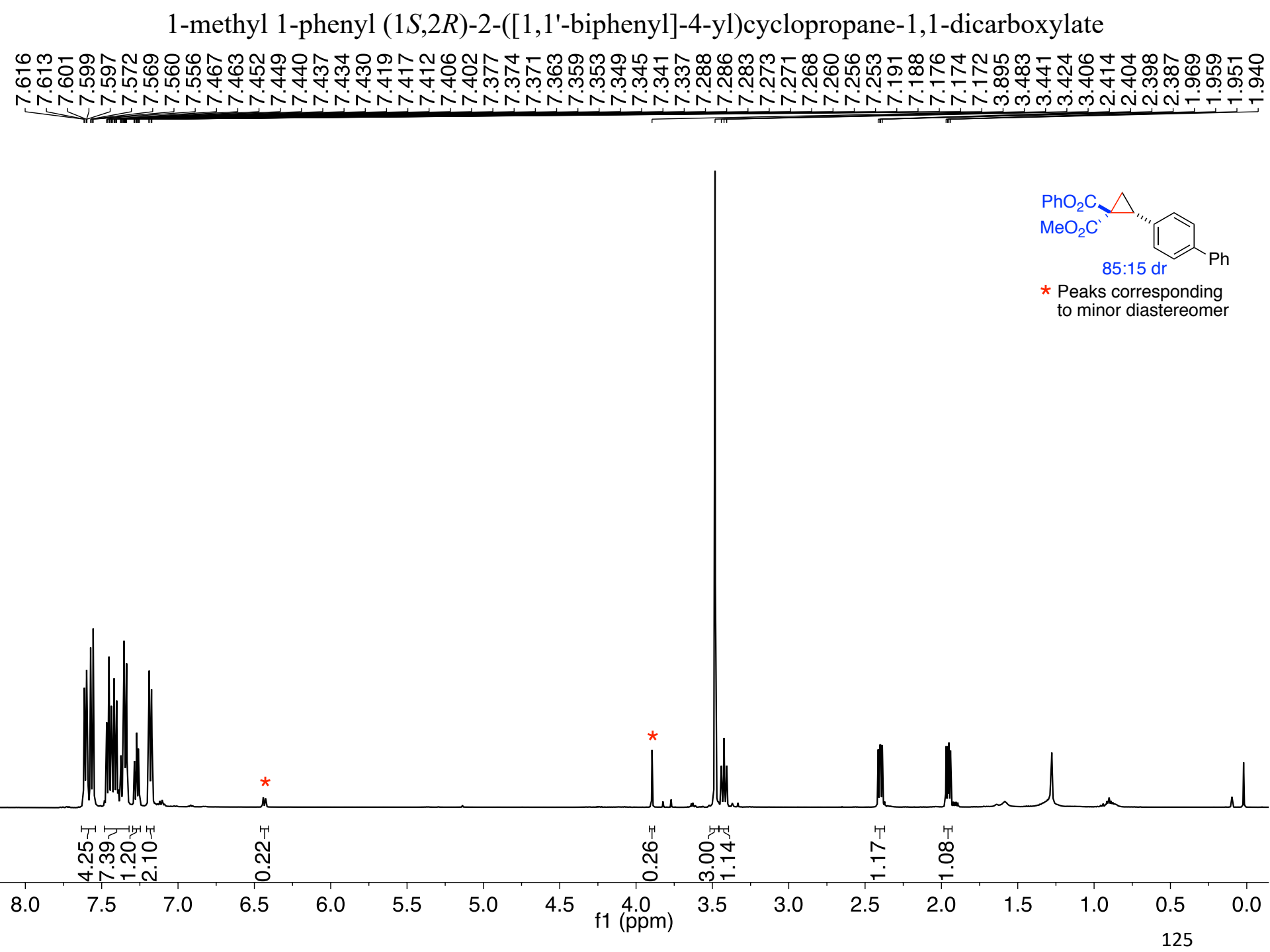


73:27 dr
93% ee

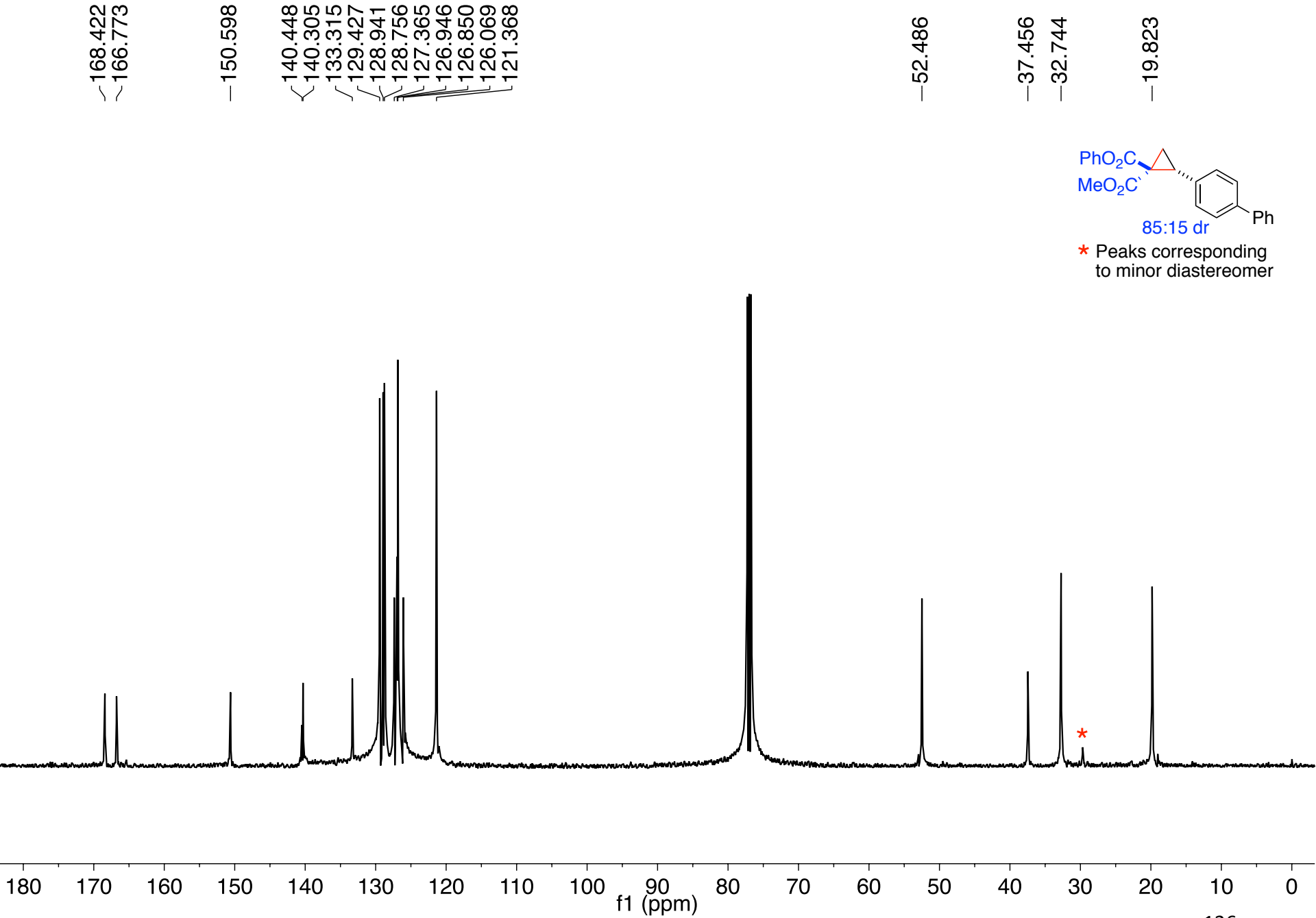
4: 250 nm, 4 nm
Results

Pk #	Name	Retention Time	Area Percent
1		16.748	96.380
2		27.248	3.620
Totals			100.000

1-methyl 1-phenyl (1*S*,2*R*)-2-([1,1'-biphenyl]-4-yl)cyclopropane-1,1-dicarboxylate

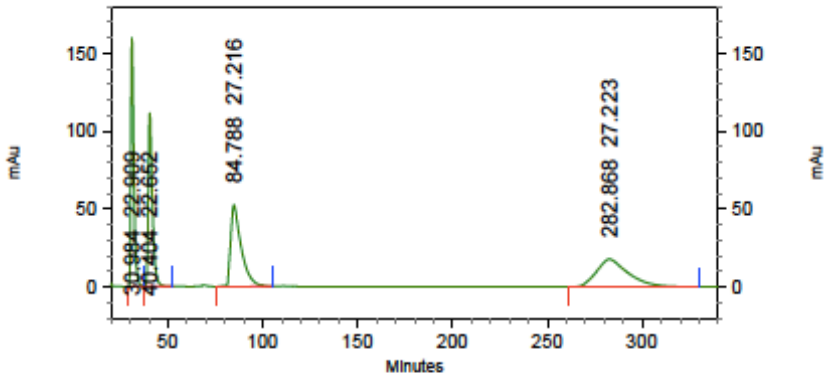


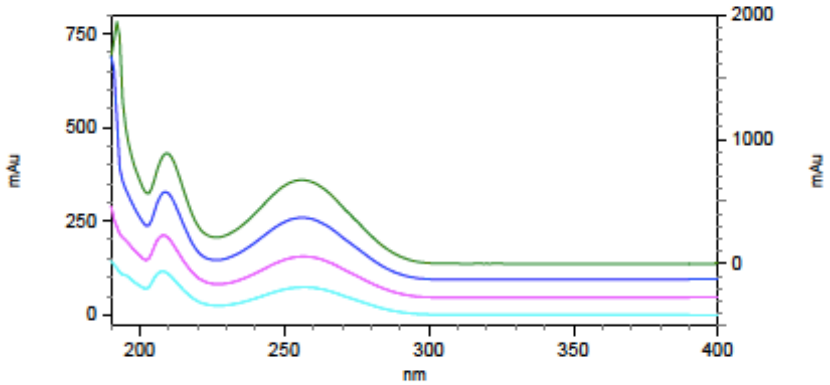
1-methyl 1-phenyl (1*S*,2*R*)-2-([1,1'-biphenyl]-4-yl)cyclopropane-1,1-dicarboxylate

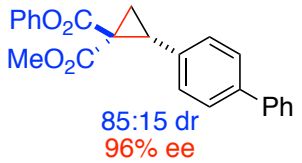


1-methyl 1-phenyl (1*S*,2*R*)-2-([1,1'-biphenyl]-4-yl)cyclopropane-1,1-dicarboxylate

JYW-II-222-OJH-35%-0.6ml
C:\EZStart\Projects\Default\Method\PS-2-37-2ODH2%1.met
C:\EZStart\Projects\Default\Data\JYW-II-222-OJH-35%-0.6ml







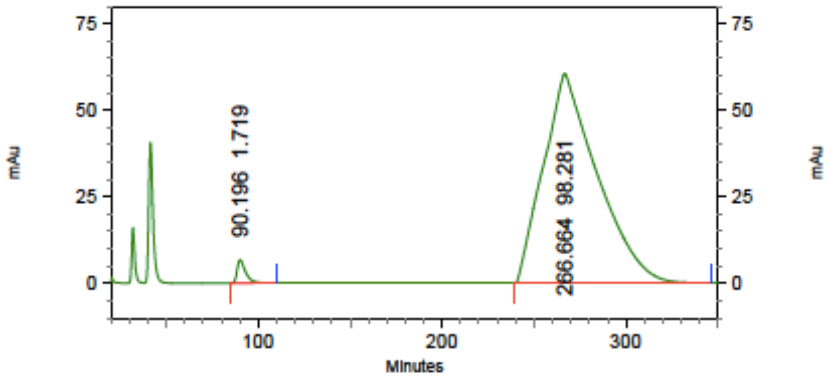
3: 261 nm, 4 nm
Results

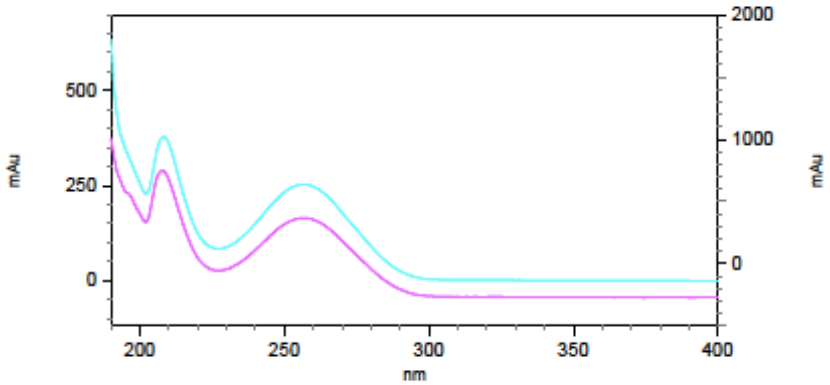
Name	Retention Time	Area Percent	Pk #
	30.984	22.909	1
	40.404	22.652	2
	84.788	27.216	3
	282.868	27.223	4

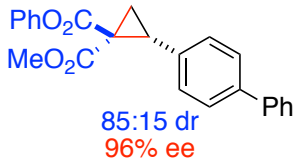
Totals	100.000

1-methyl 1-phenyl (1*S*,2*R*)-2-([1,1'-biphenyl]-4-yl)cyclopropane-1,1-dicarboxylate

JYW-II-231-OJH-35%-0.6ml
C:\EZStart\Projects\Default\Method\PS-2-37-2ODH2%1.met
C:\EZStart\Projects\Default\Data\JYW-II-231-OJH-35%-0.6ml





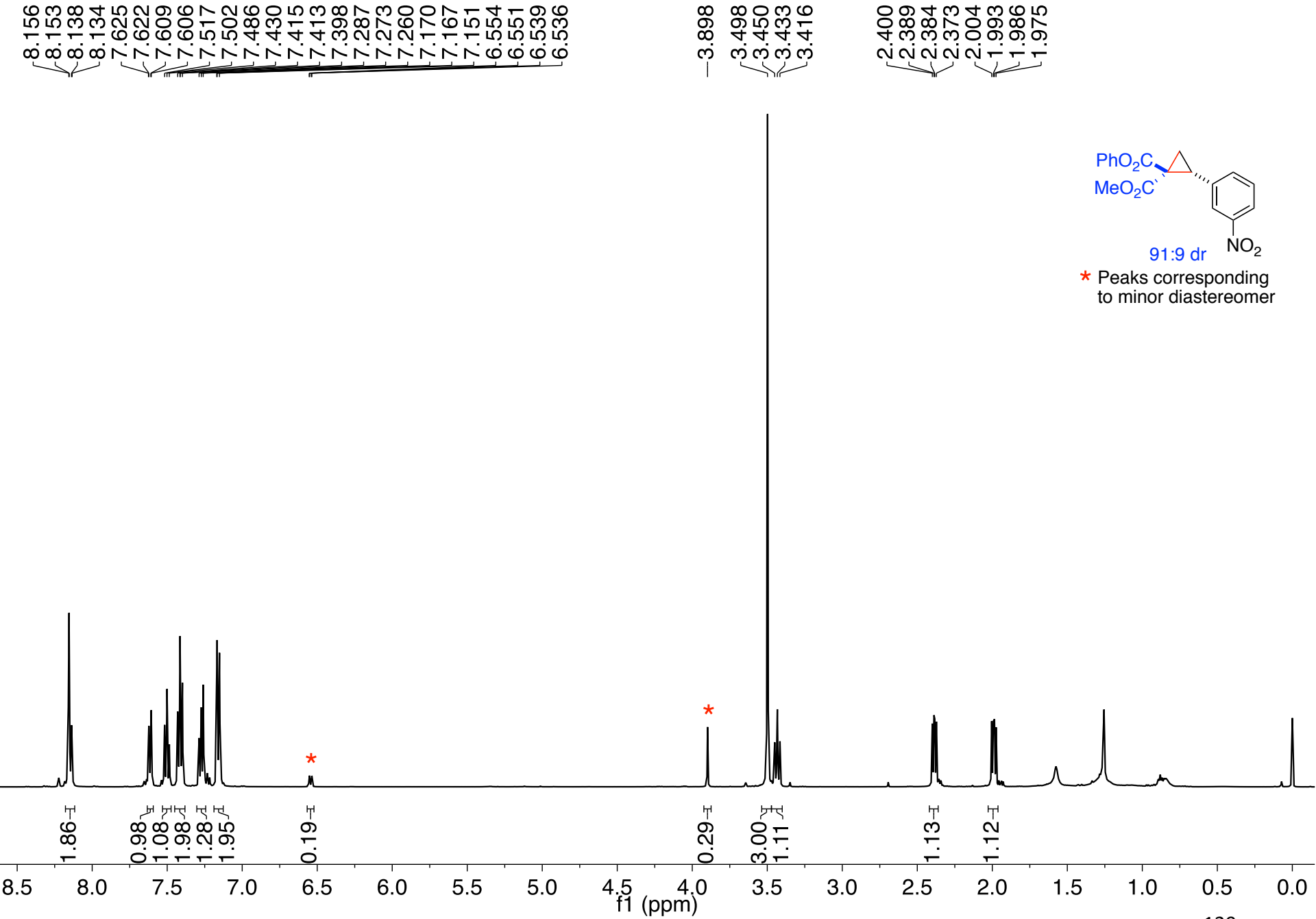


3: 261 nm, 4 nm
Results

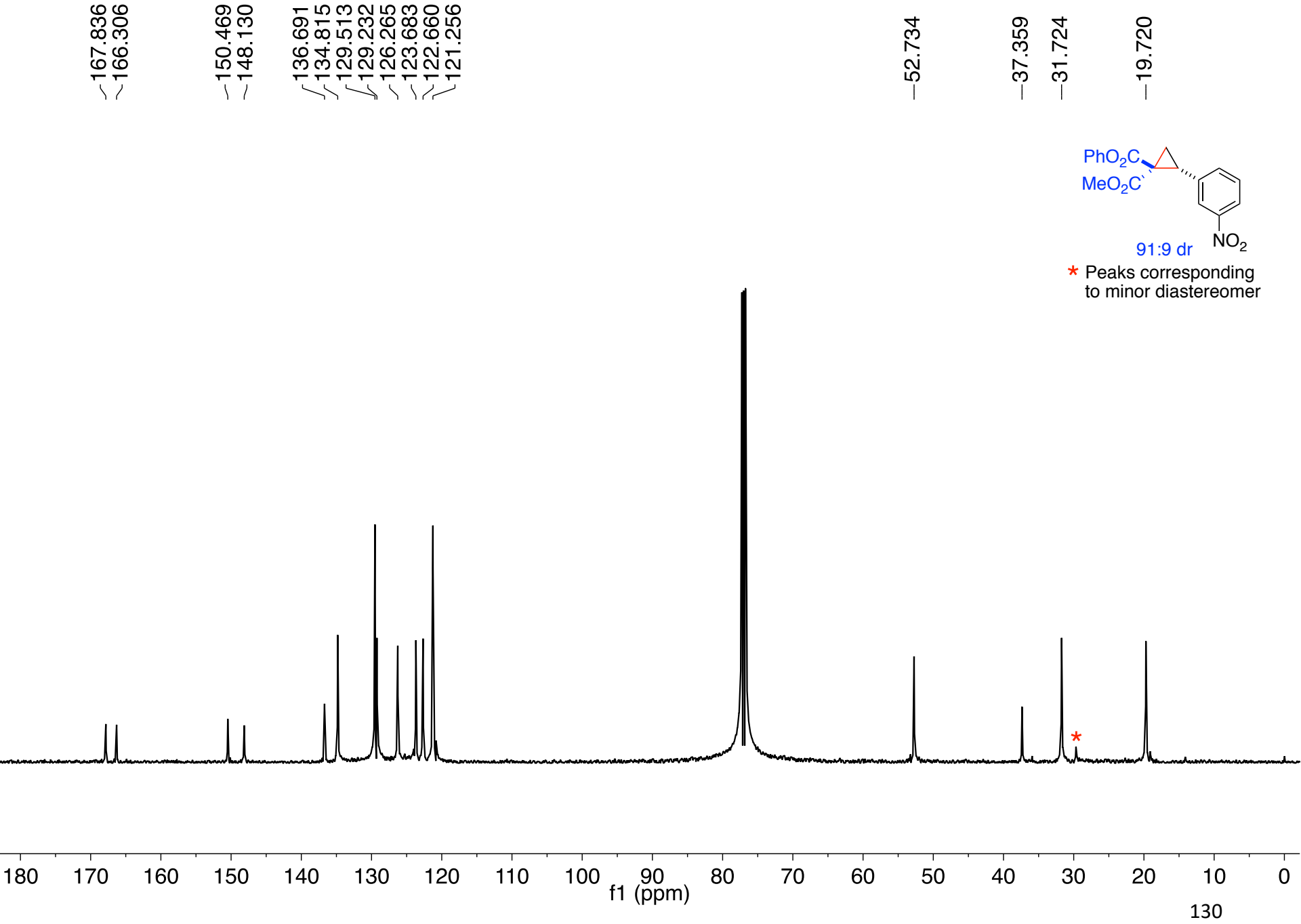
Name	Retention Time	Area Percent	Pk #
	90.196	1.719	1
	266.664	98.281	2

Totals	
	100.000

1-methyl 1-phenyl (1*S*,2*R*)-2-(3-nitrophenyl)cyclopropane-1,1-dicarboxylate



1-methyl 1-phenyl (1*S*,2*R*)-2-(3-nitrophenyl)cyclopropane-1,1-dicarboxylate



1-methyl 1-phenyl (1*S*,2*R*)-2-(3-nitrophenyl)cyclopropane-1,1-dicarboxylate

JYW-II-193A-OJH-40%-0.6ml
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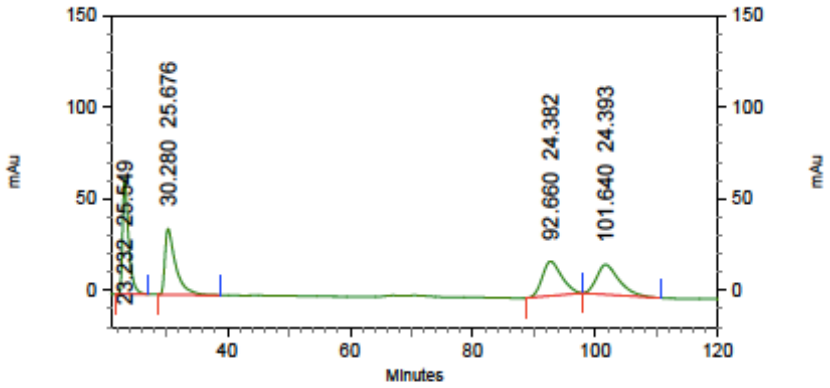
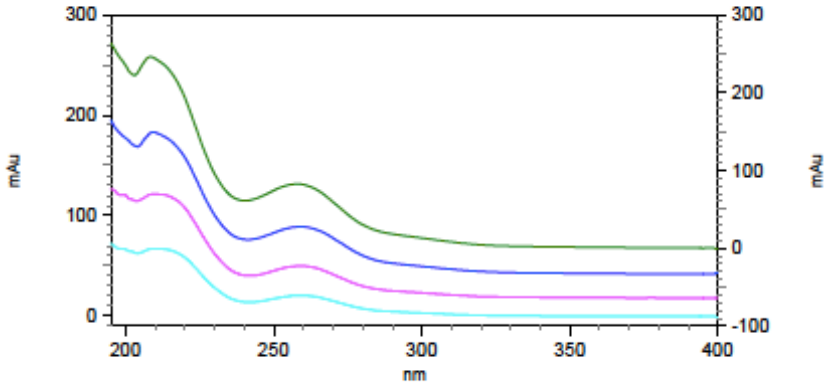
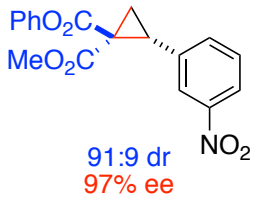
C:\EZStart\Projects\Default\Data\JYW-II-193A-OJH-40%-0.6ml







91:9 dr
97% ee

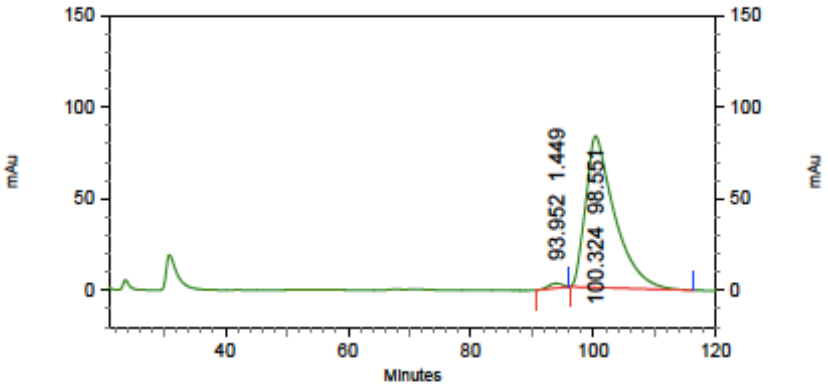
4: 241 nm, 4 nm
Results

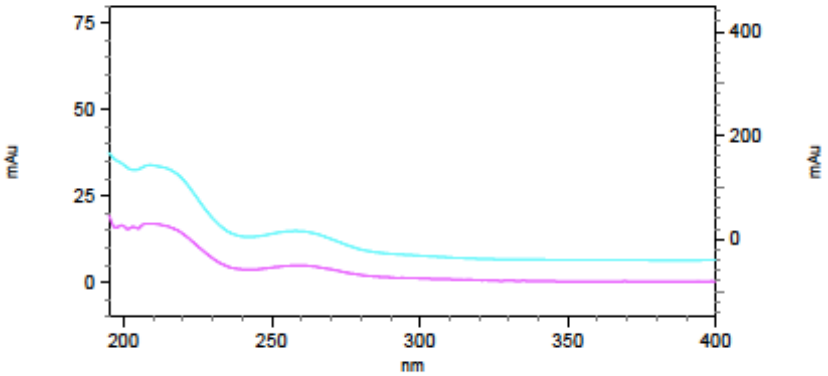
Name	Retention Time	Area Percent	Pk #
	23.232	25.549	1
	30.280	25.676	2
	92.660	24.382	3
	101.640	24.393	4

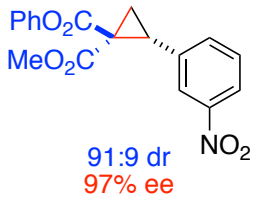
Totals	
	100.000

1-methyl 1-phenyl (1*S*,2*R*)-2-(3-nitrophenyl)cyclopropane-1,1-dicarboxylate

JYW-II-214-OJH-40%-0.6ml
C:\EZStart\Projects\Default\Method\LK0.8-3%.met
C:\EZStart\Projects\Default\Data\JYW-II-214-OJH-40%-0.6ml







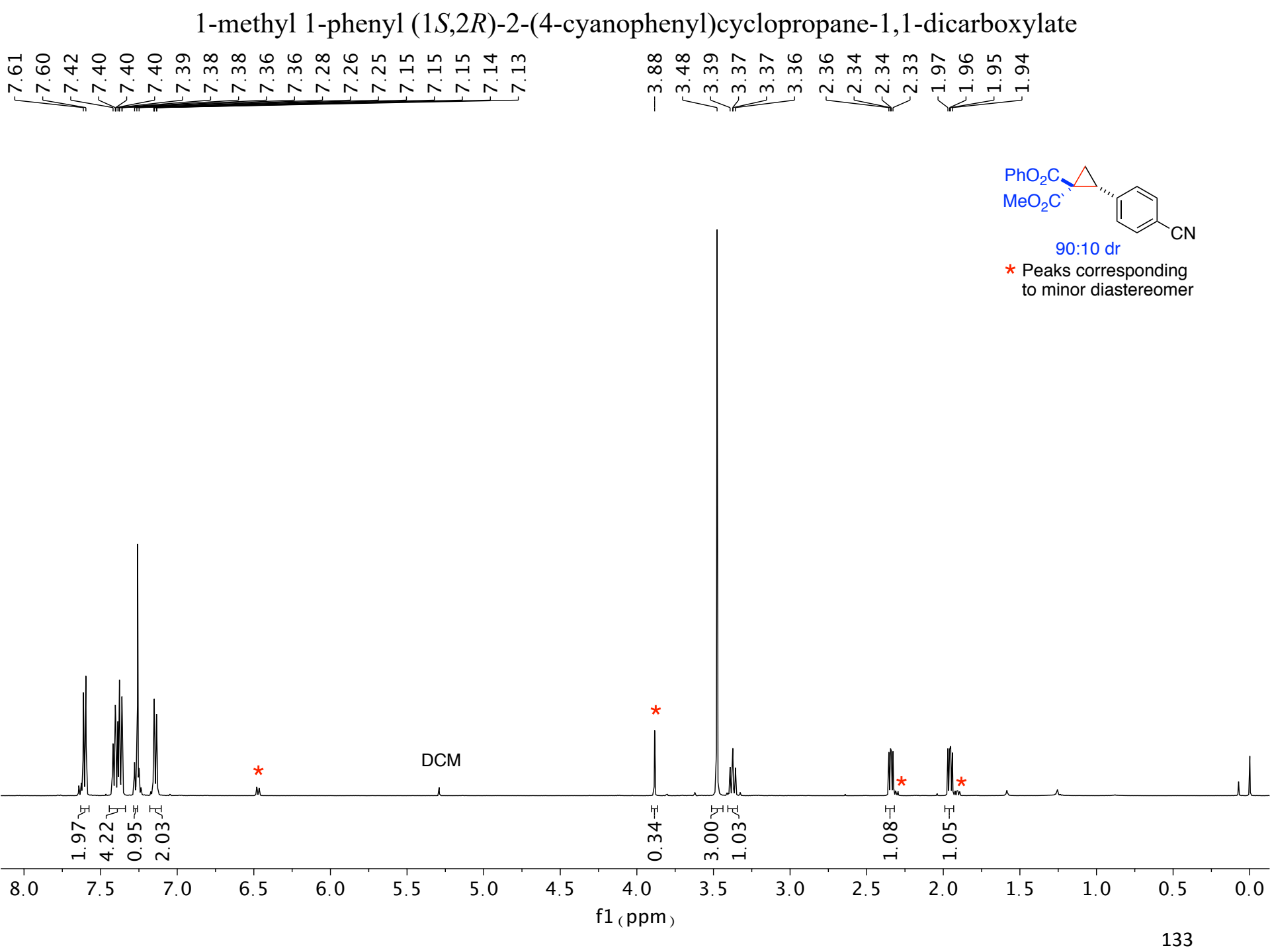
91:9 dr
97% ee

4: 241 nm, 4 nm
Results

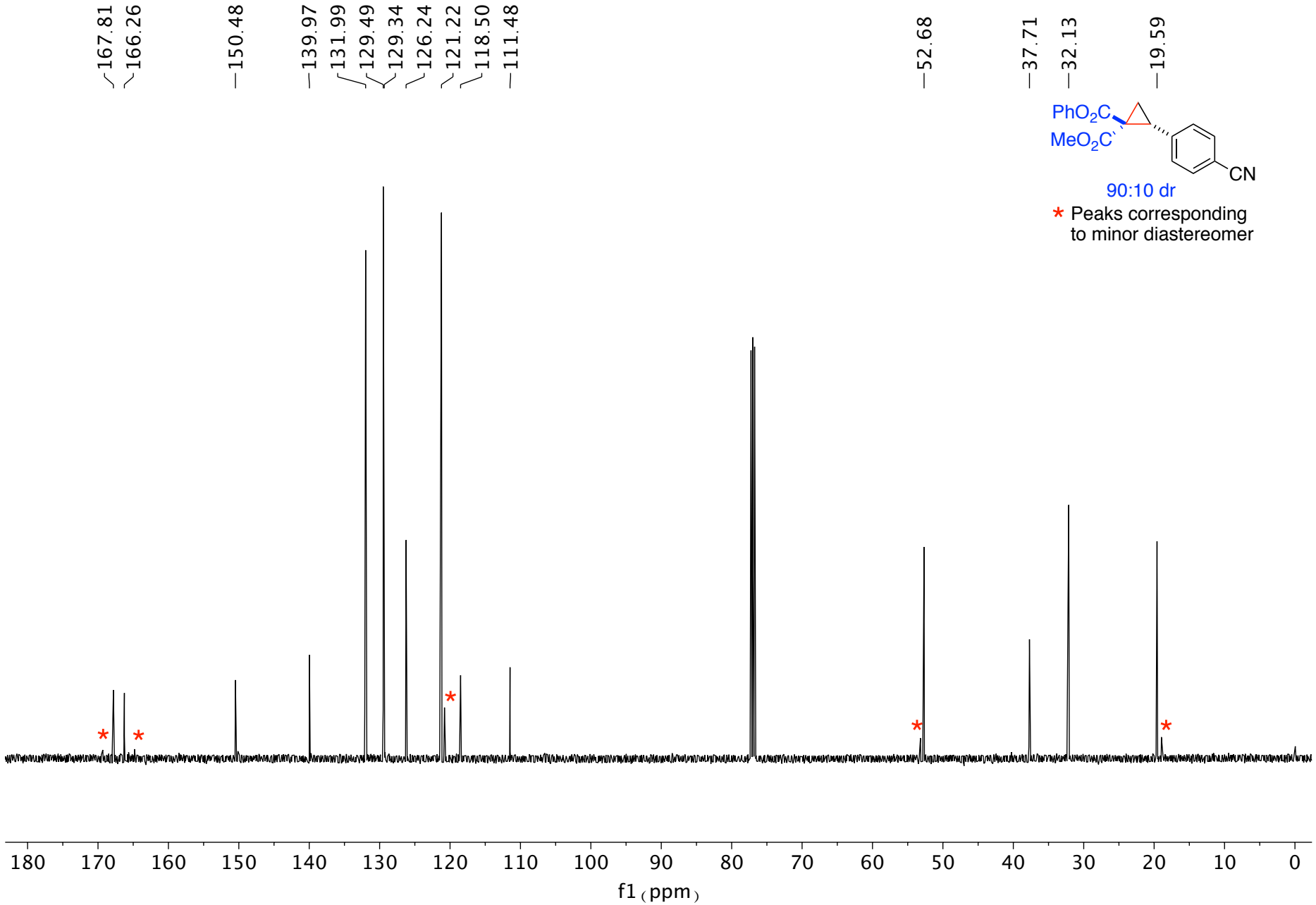
Name	Retention Time	Area Percent	Pk #
	93.952	1.449	1
	100.324	98.551	2

Totals	
	100.000

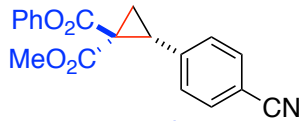
1-methyl 1-phenyl (1*S*,2*R*)-2-(4-cyanophenyl)cyclopropane-1,1-dicarboxylate



1-methyl 1-phenyl (1*S*,2*R*)-2-(4-cyanophenyl)cyclopropane-1,1-dicarboxylate



1-methyl 1-phenyl (1*S*,2*R*)-2-(4-cyanophenyl)cyclopropane-1,1-dicarboxylate

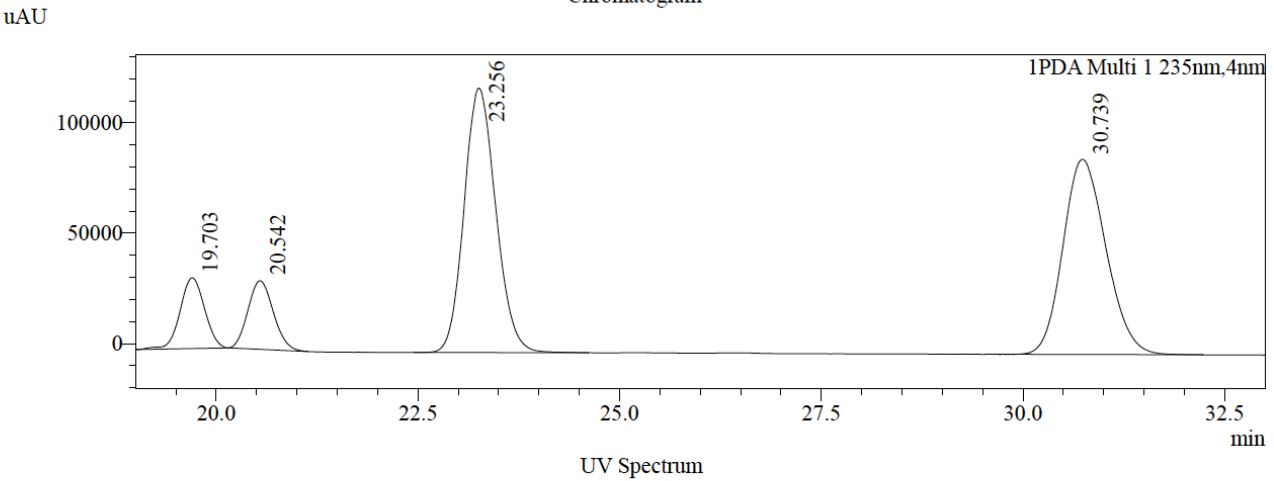


90:10 dr
97% ee

Sample Information

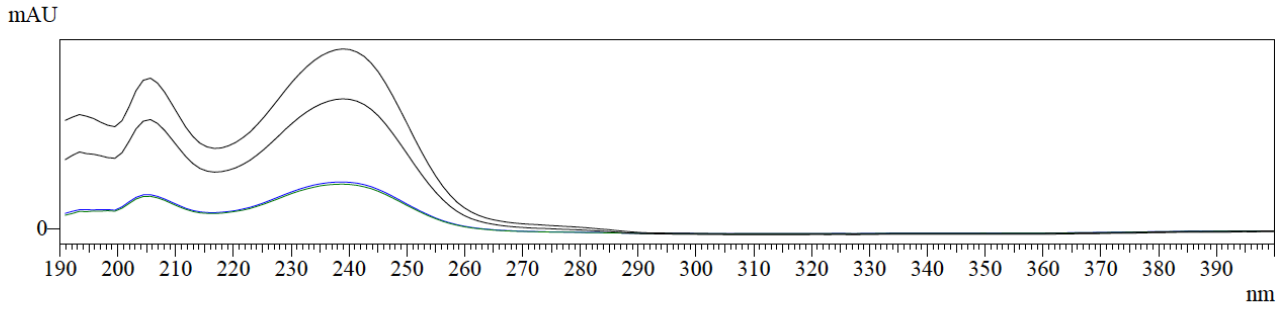
Sample Name	: JYW-0889-ID-15%-0.8ml2
Sample ID	: JYW-0889-ID-15%-0.8ml2
Data File	: JYW-0889-ID-15%-0.8ml2.lcd
Method File	: JYW-method.lcm
Date Acquired	: 1/30/2019 7:47:44 PM

Chromatogram



UV Spectrum

JYW-0889-ID-15%-0.8ml2.lcd

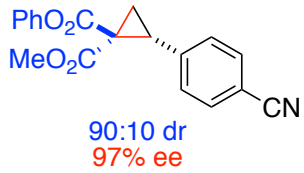


Peak Table

PDA Ch1 235nm

Peak#	Ret. Time	Area	Area%
1	19.703	677399	8.557
2	20.542	677559	8.559
3	23.256	3282947	41.473
4	30.739	3278000	41.410
Total		7915904	100.000

1-methyl 1-phenyl (1*S*,2*R*)-2-(4-cyanophenyl)cyclopropane-1,1-dicarboxylate

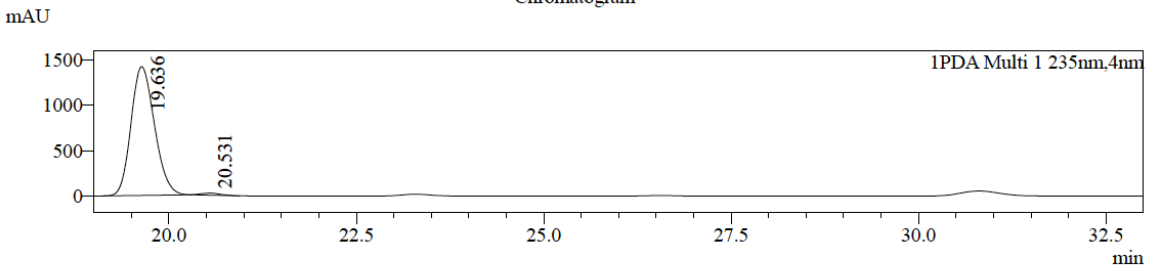


90:10 dr
97% ee

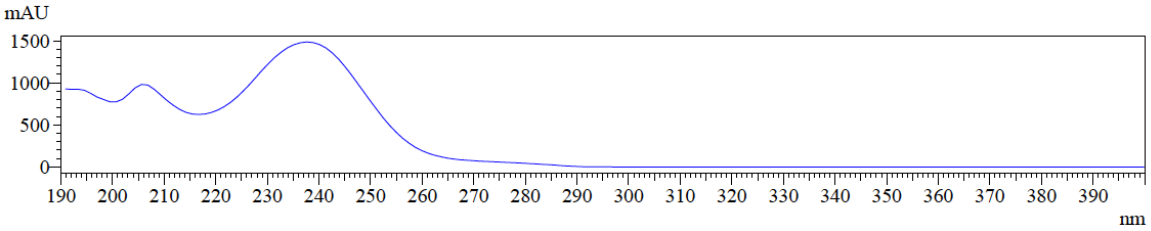
Sample Information

Sample Name	: JYW-0898-ID-15%-0.8ml
Sample ID	: JYW-0898-ID-15%-0.8ml
Data File	: JYW-0898-ID-15%-0.8ml.lcd
Method File	: JYW-method.lcm

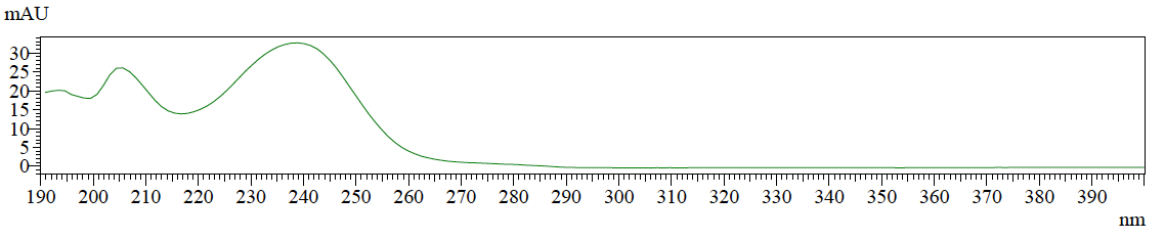
Chromatogram



UV Spectrum
Retention time = 19.636



UV Spectrum
Retention time = 20.531

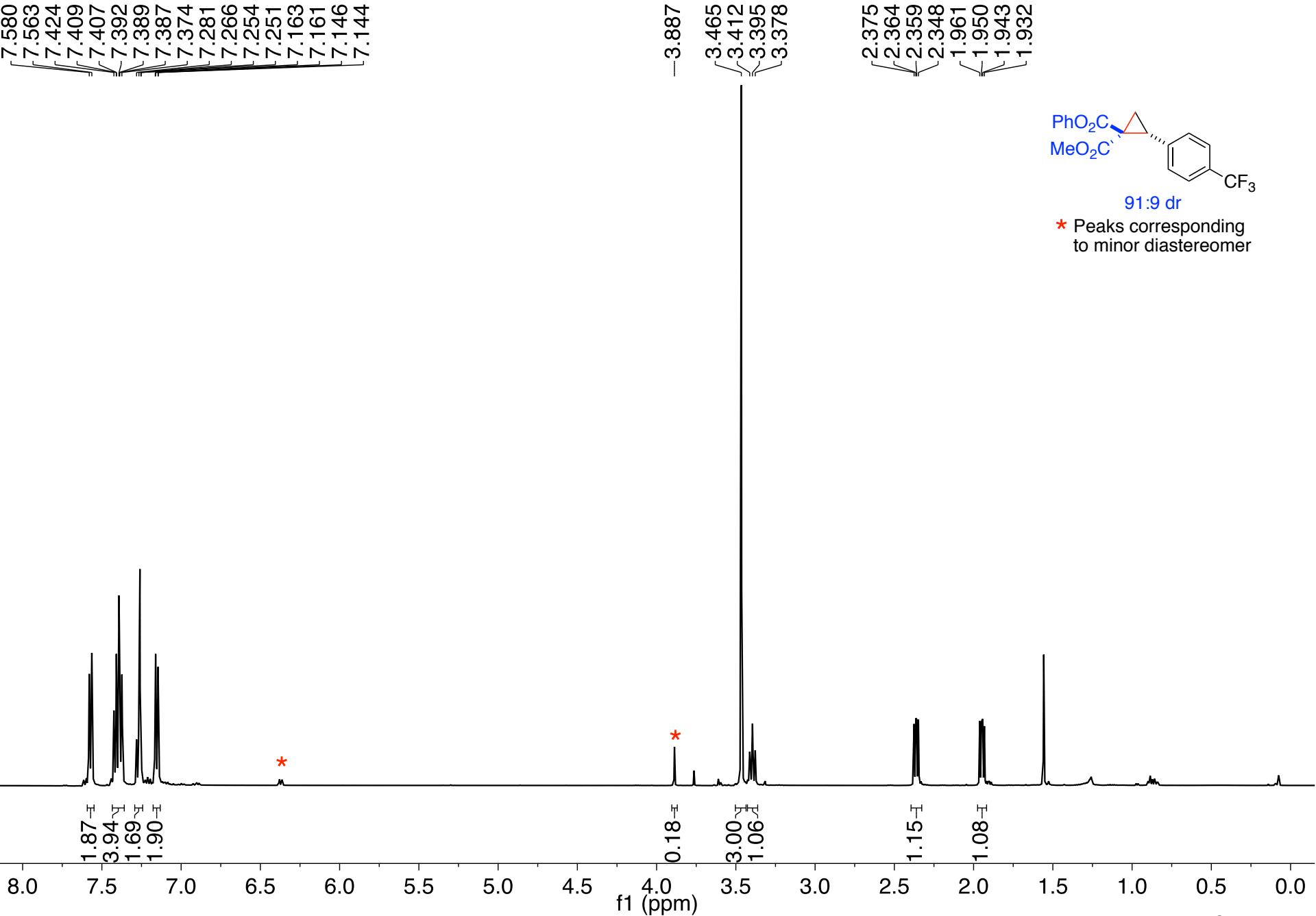


Peak Table

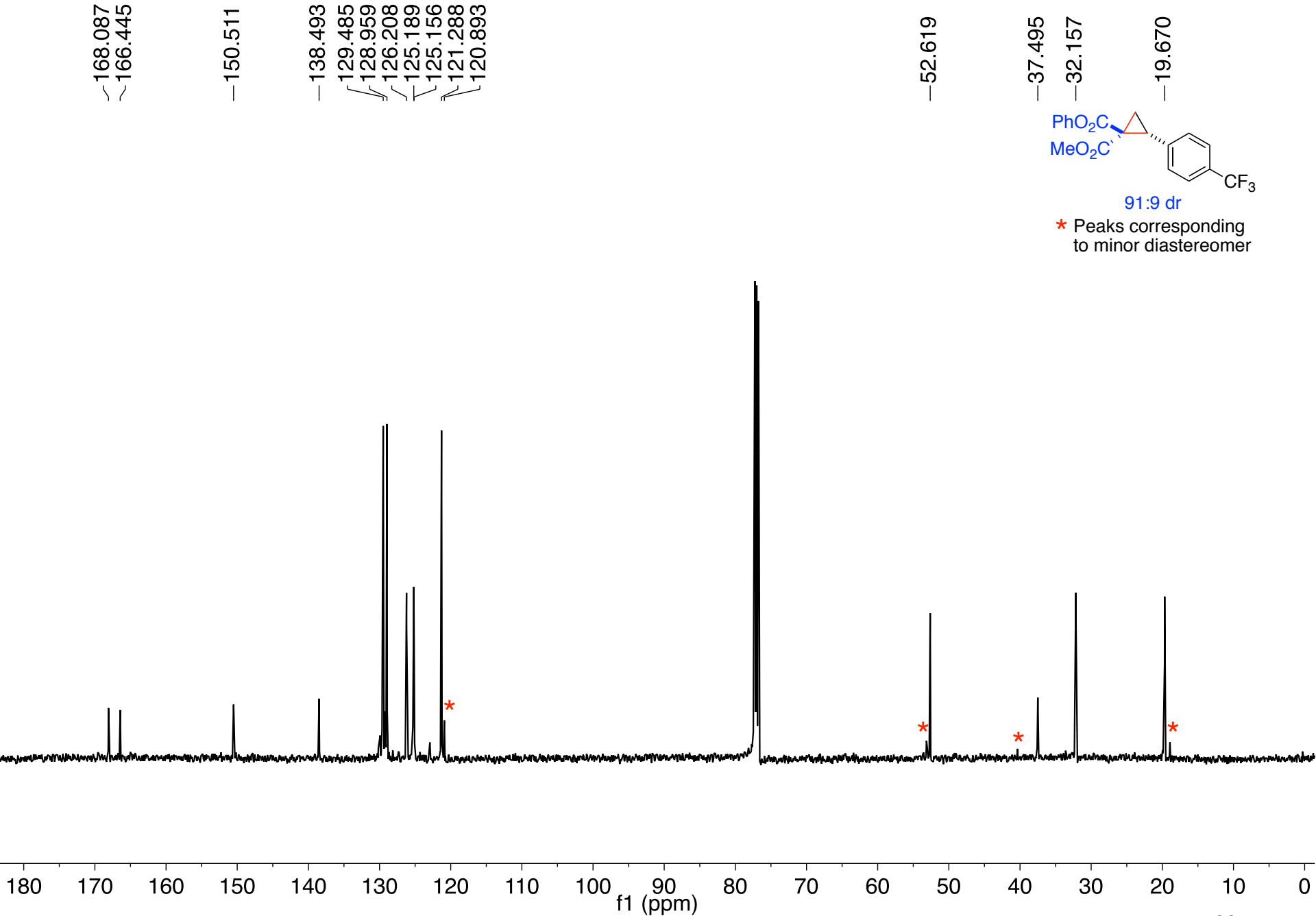
PDA Ch1 235nm

Peak#	Ret. Time	Area	Area%
1	19.636	30910384	98.734
2	20.531	396194	1.266
Total		31306578	100.000

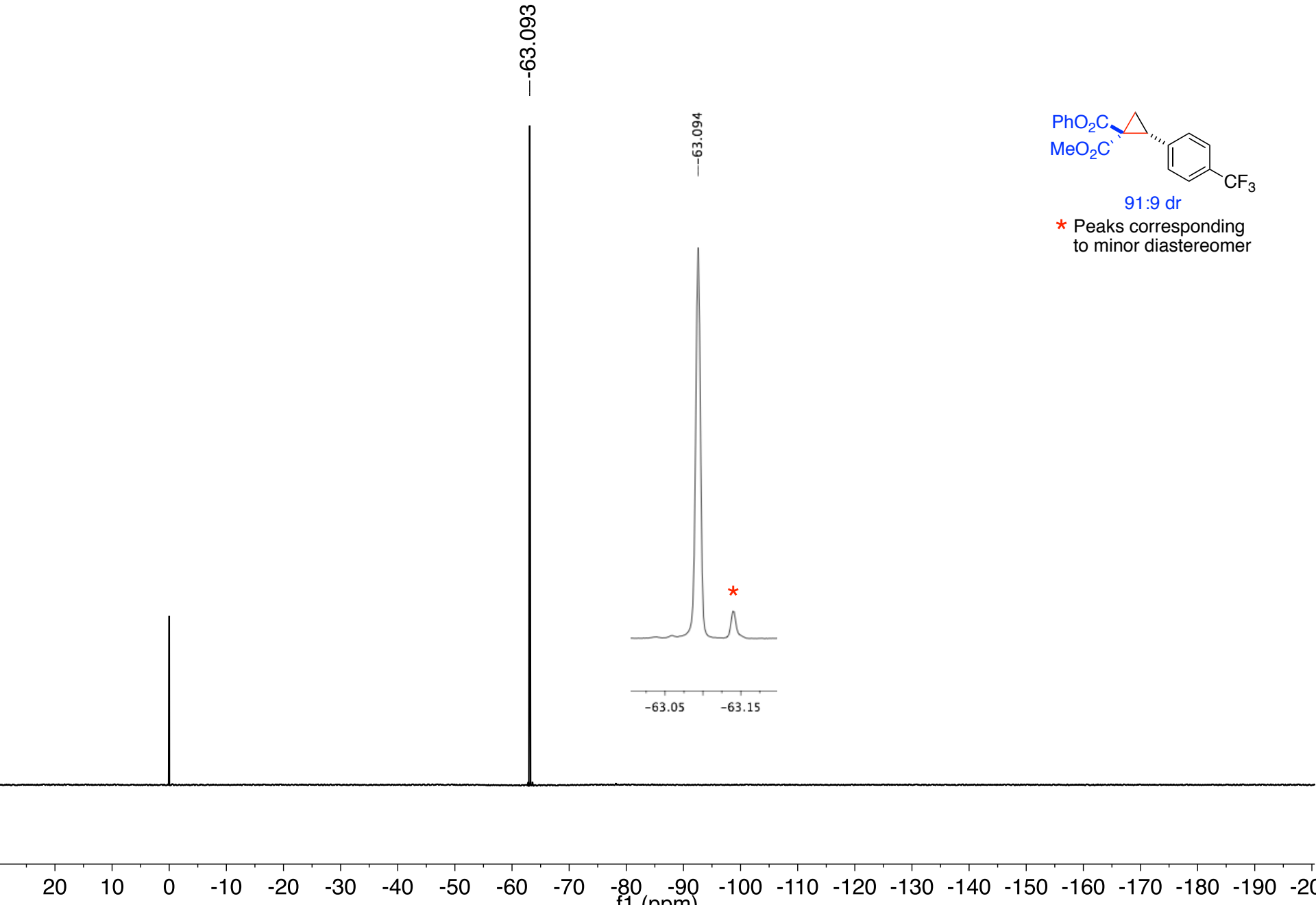
1-methyl 1-phenyl (1*S*,2*R*)-2-(4-(trifluoromethyl)phenyl)cyclopropane-1,1-dicarboxylate



1-methyl 1-phenyl (1*S*,2*R*)-2-(4-(trifluoromethyl)phenyl)cyclopropane-1,1-dicarboxylate

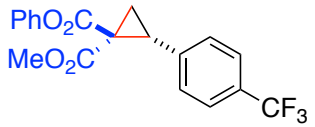


1-methyl 1-phenyl (1*S*,2*R*)-2-(4-(trifluoromethyl)phenyl)cyclopropane-1,1-dicarboxylate

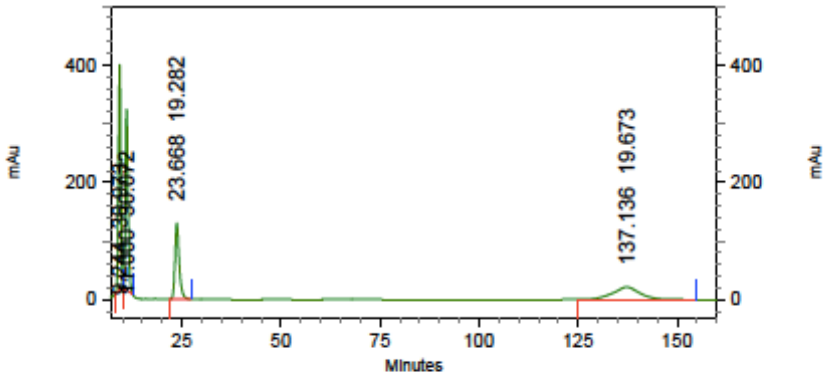


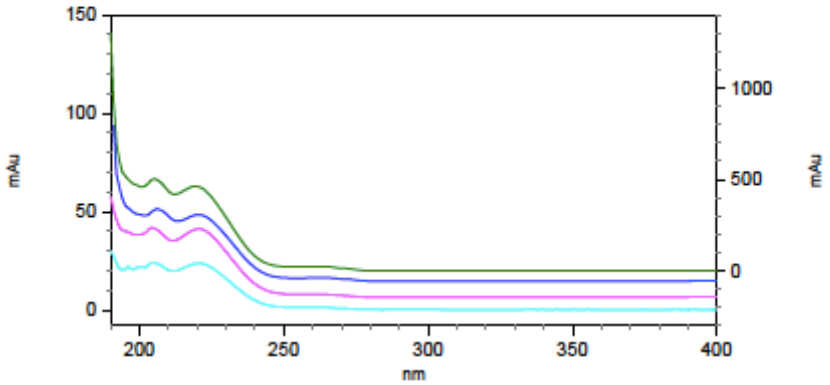
1-methyl 1-phenyl (1*S*,2*R*)-2-(4-(trifluoromethyl)phenyl)cyclopropane-1,1-dicarboxylate

JYW-II-105-ojh-25%-0.7ml
C:\EZStart\Projects\Default\Method\LK0.8-3%.met
C:\EZStart\Projects\Default\Data\JYW-II-105-ojh-25%-0.7ml



91:9 dr
96% ee





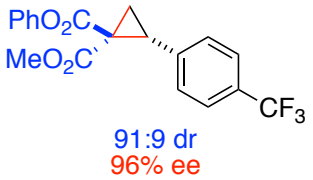
3: 225 nm, 4 nm
Results

Name	Retention Time	Area Percent	Pk #
	9.244	30.973	1
	11.000	30.072	2
	23.668	19.282	3
	137.136	19.673	4

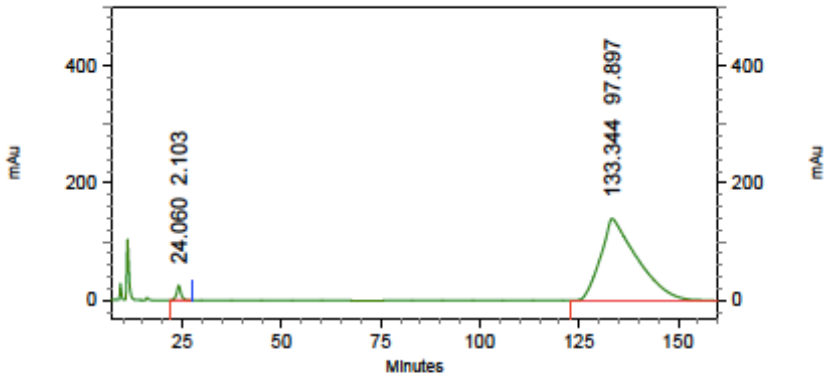
Totals	
	100.000

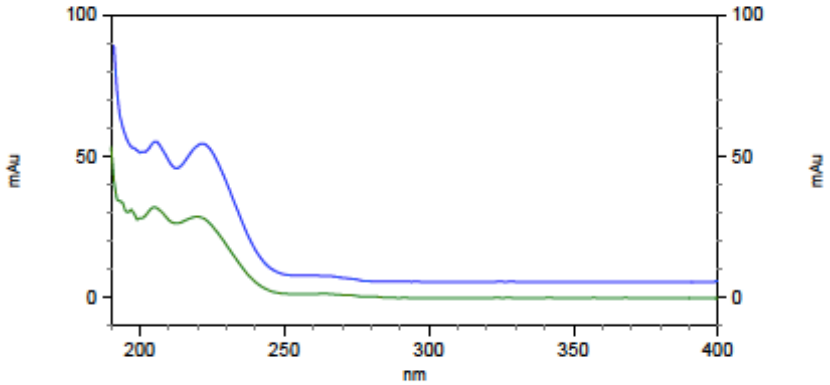
1-methyl 1-phenyl (1*S*,2*R*)-2-(4-(trifluoromethyl)phenyl)cyclopropane-1,1-dicarboxylate

JYW-II-106-ojh-25%-0.7ml
C:\EZStart\Projects\Default\Method\LK0.8-3%.met
C:\EZStart\Projects\Default\Data\JYW-II-106-ojh-25%-0.7ml



91:9 dr
96% ee



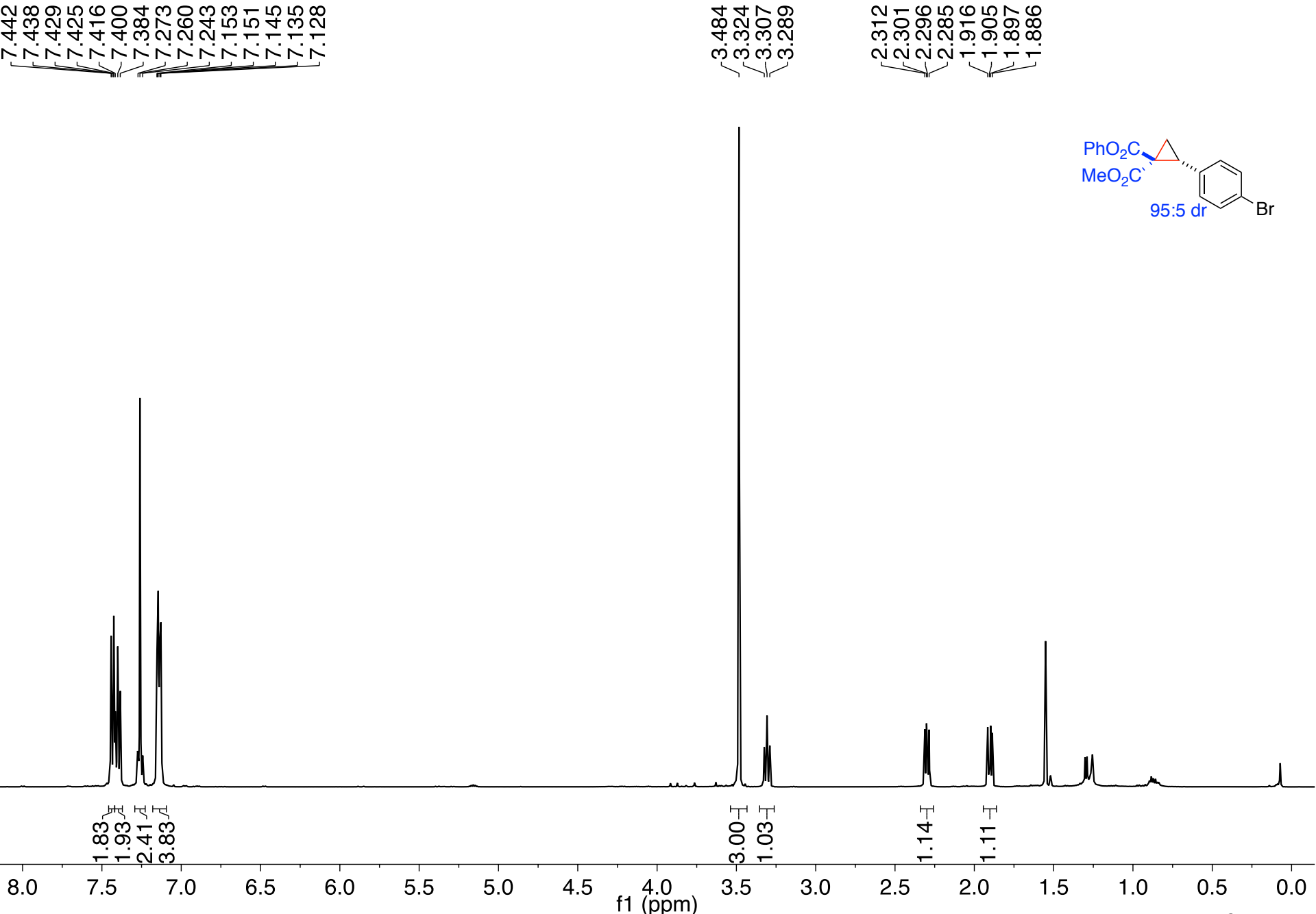


3: 225 nm, 4 nm
Results

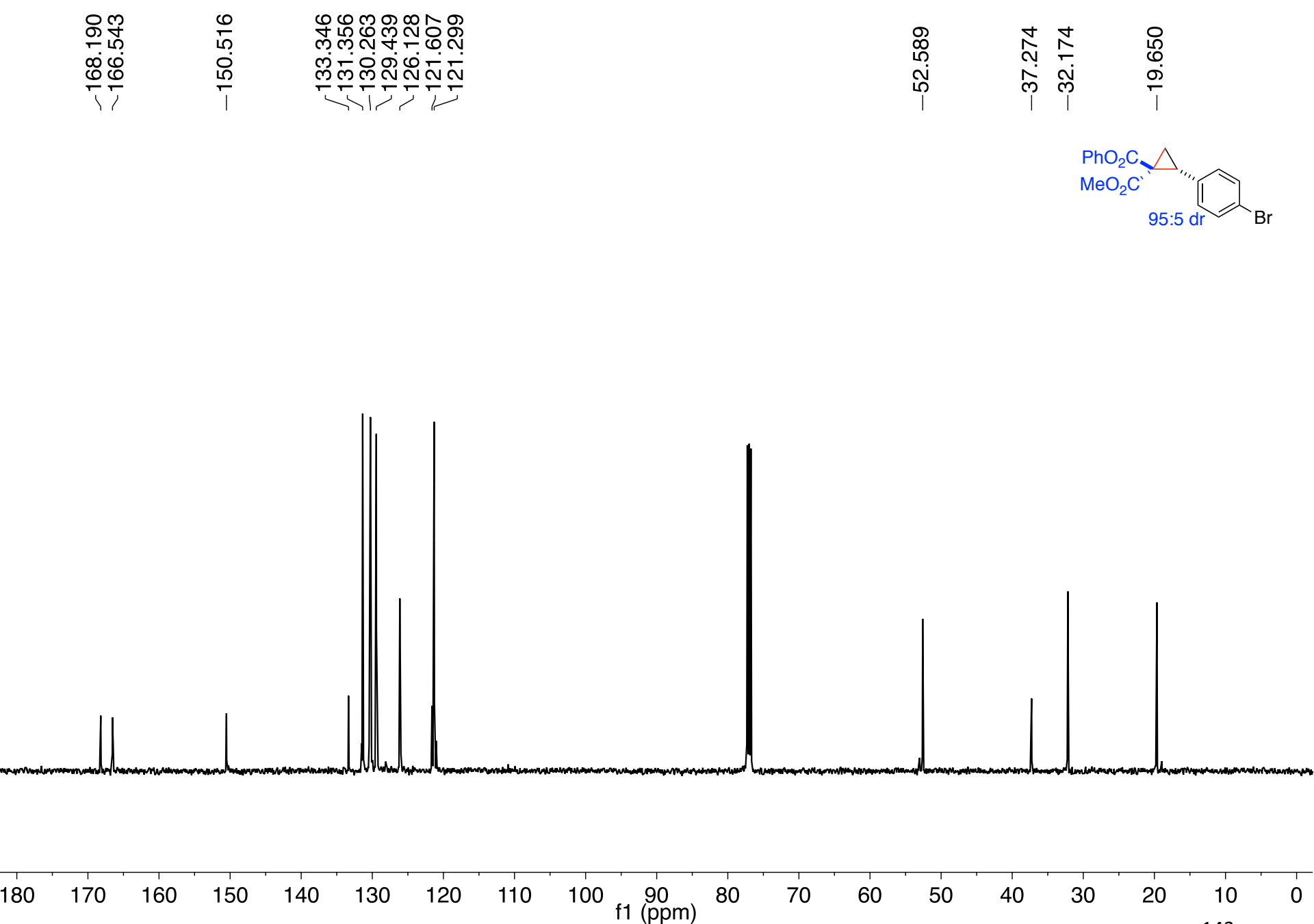
Name	Retention Time	Area Percent	Pk #
	24.060	2.103	1
	133.344	97.897	2

Totals	
	100.000

1-methyl 1-phenyl (1*S*,2*R*)-2-(4-bromophenyl)cyclopropane-1,1-dicarboxylate



1-methyl 1-phenyl (1*S*,2*R*)-2-(4-bromophenyl)cyclopropane-1,1-dicarboxylate



1-methyl 1-phenyl (1*S*,2*R*)-2-(4-bromophenyl)cyclopropane-1,1-dicarboxylate

JYW-II-100-OJH-38%-0.6ml
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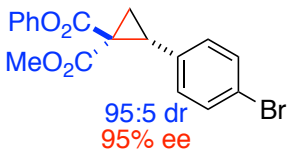
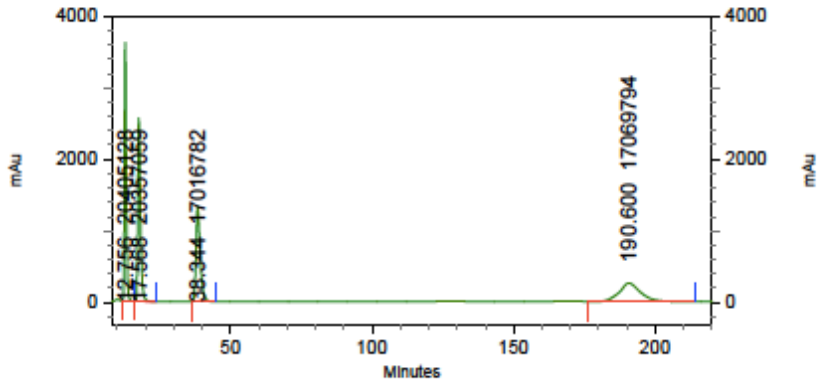
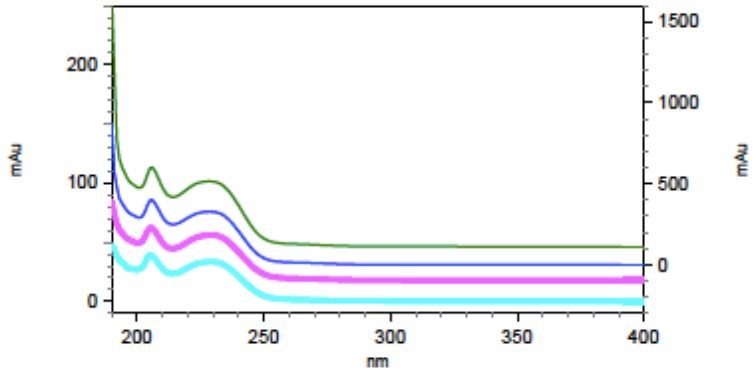
C:\EZStart\Projects\Default\Data\JYW-II-100-OJH-38%-0.6ml





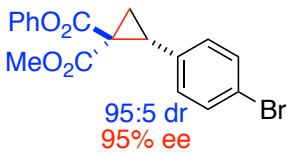


4: 225 nm, 4 nm
Results

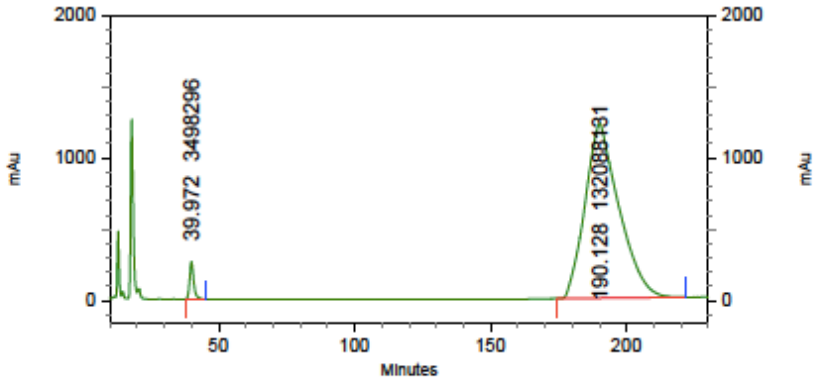
Pk #	Name	Retention Time	Area Percent
1		12.756	27.262
2		17.568	27.198
3		38.344	22.735
4		190.600	22.806
Totals			100.000

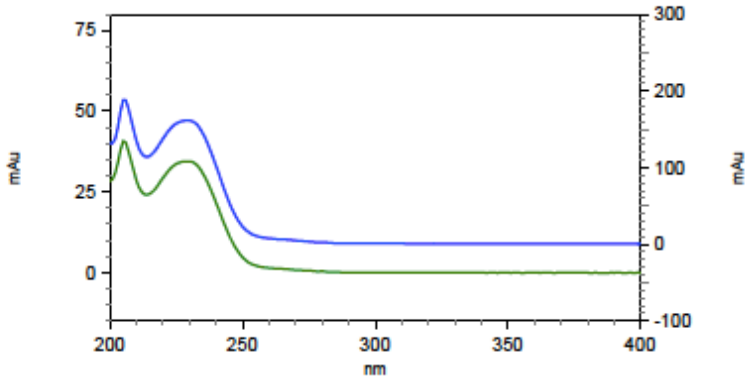
1-methyl 1-phenyl (1*S*,2*R*)-2-(4-bromophenyl)cyclopropane-1,1-dicarboxylate

JYW-II-101-OJH-38%-0.6ml
C:\EZStart\Projects\Default\Method\ywang1.0.met
C:\EZStart\Projects\Default\Data\JYW-II-101-OJH-38%-0.6ml



95:5 dr
95% ee

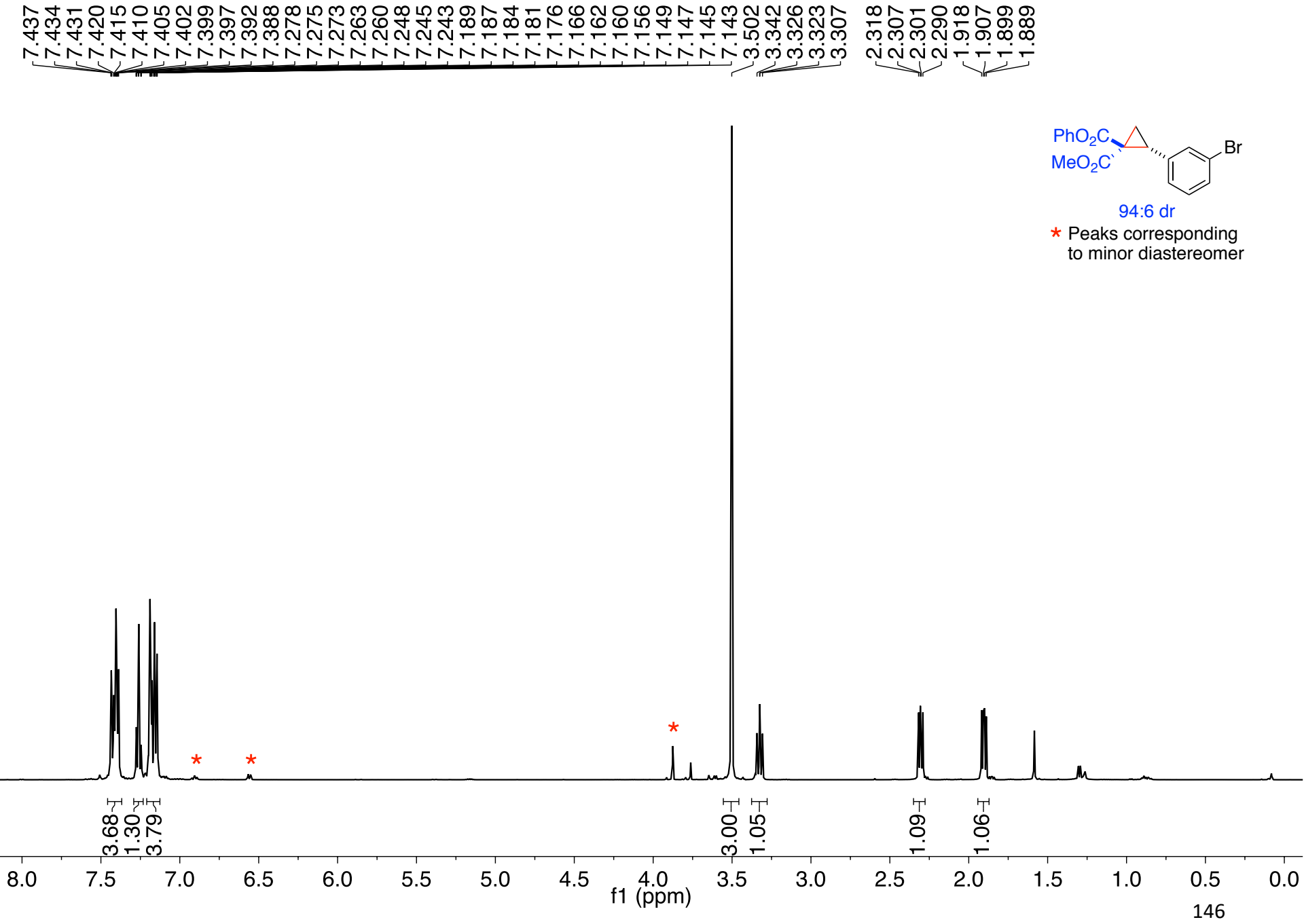




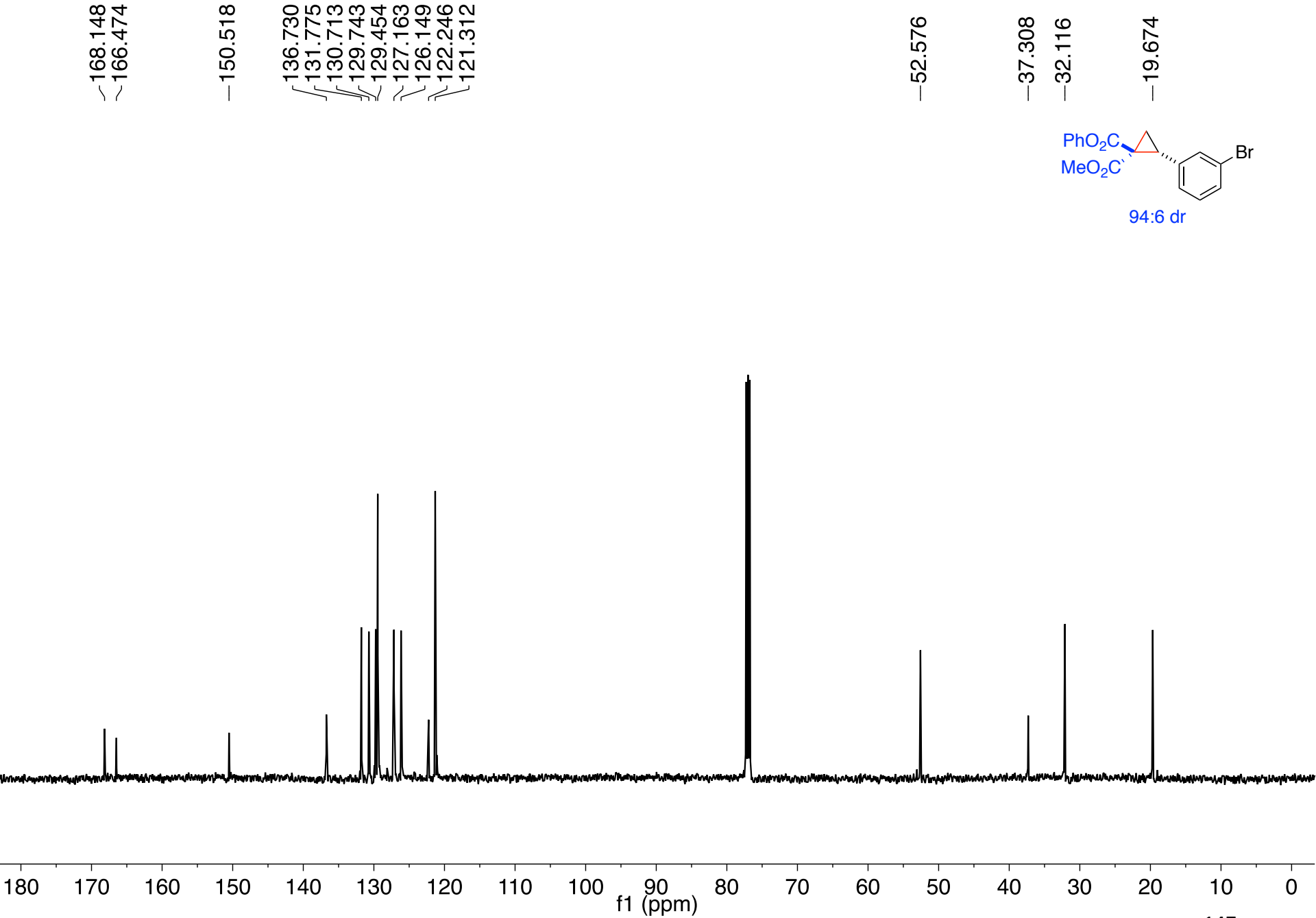
4: 233 nm, 4 nm
Results

Pk #	Name	Retention Time	Area Percent
1		39.972	2.580
2		190.128	97.420
Totals			100.000

1-methyl 1-phenyl (1*S*,2*R*)-2-(3-bromophenyl)cyclopropane-1,1-dicarboxylate

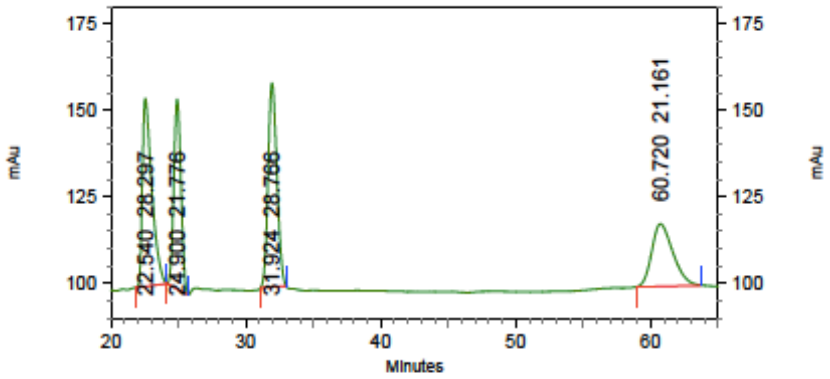


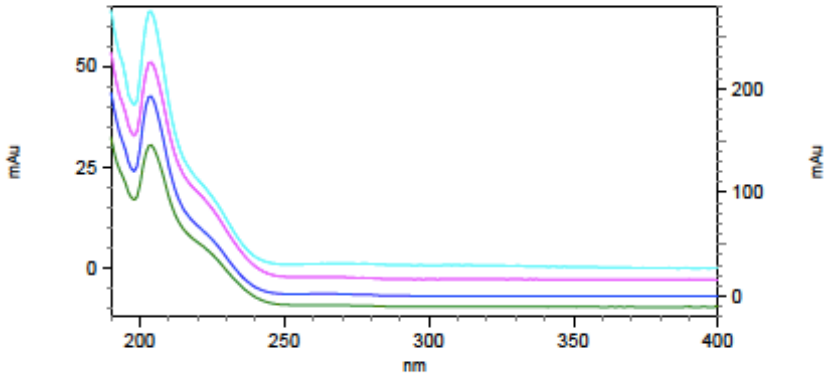
1-methyl 1-phenyl (1*S*,2*R*)-2-(3-bromophenyl)cyclopropane-1,1-dicarboxylate

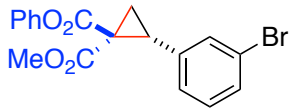


1-methyl 1-phenyl (1*S*,2*R*)-2-(3-bromophenyl)cyclopropane-1,1-dicarboxylate

JYW-II-109A-newADH-1.3%-1ml
C:\EZStart\Projects\Default\Method\XC-5%-ADH0.8ml.met
C:\EZStart\Projects\Default\Data\JYW-II-109A-newADH-1.3%-1ml







94:6 dr
97% ee

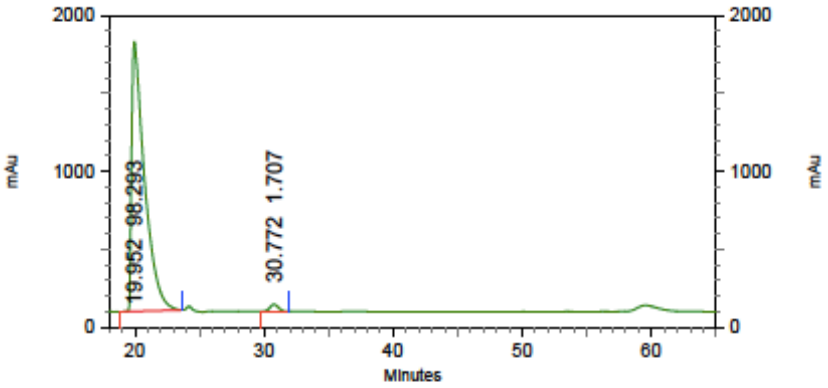
6: 233 nm, 4 nm
Results

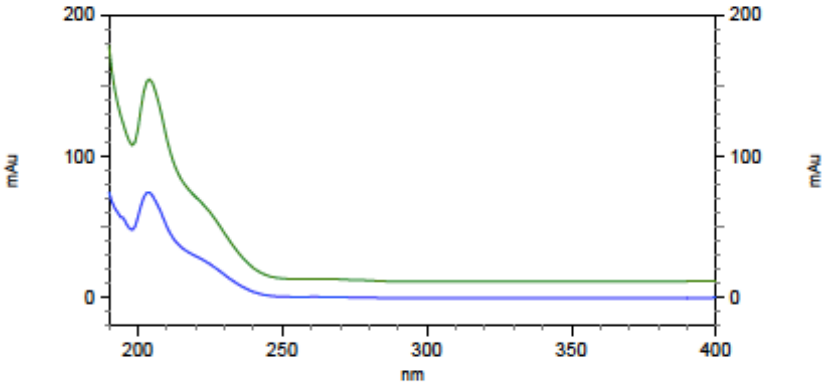
Name	Retention Time	Area Percent	Pk #
	22.540	28.297	1
	24.900	21.776	2
	31.924	28.766	3
	60.720	21.161	4

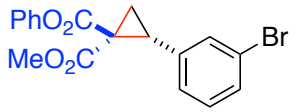
Totals	100.000

1-methyl 1-phenyl (1*S*,2*R*)-2-(3-bromophenyl)cyclopropane-1,1-dicarboxylate

JYW-II-109B-newADH-1.3%-1ml
C:\EZStart\Projects\Default\Method\XC-5%-ADH0.8ml.met
C:\EZStart\Projects\Default\Data\JYW-II-109B-newADH-1.3%-1ml







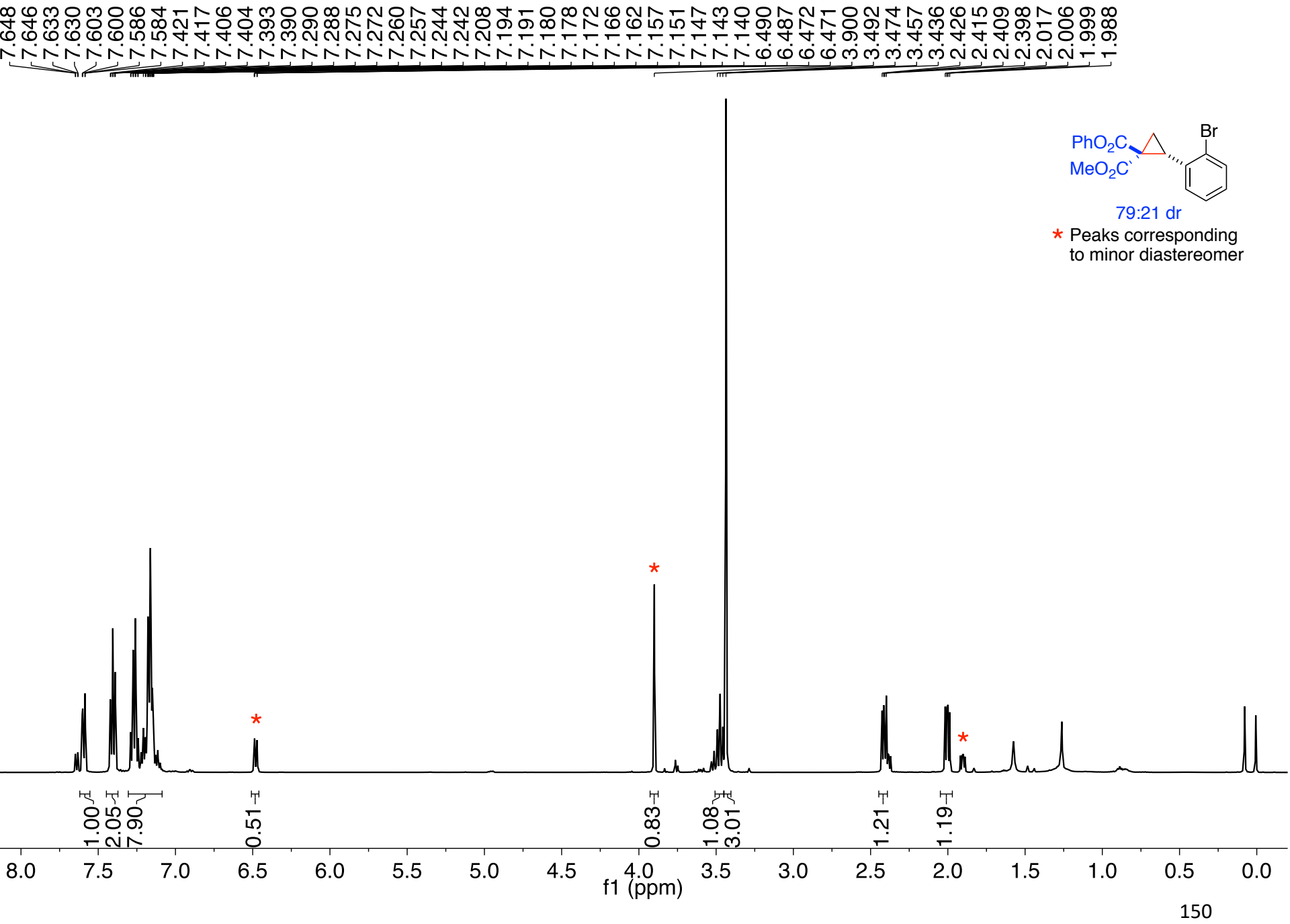
94:6 dr
97% ee

6: 226 nm, 4 nm
Results

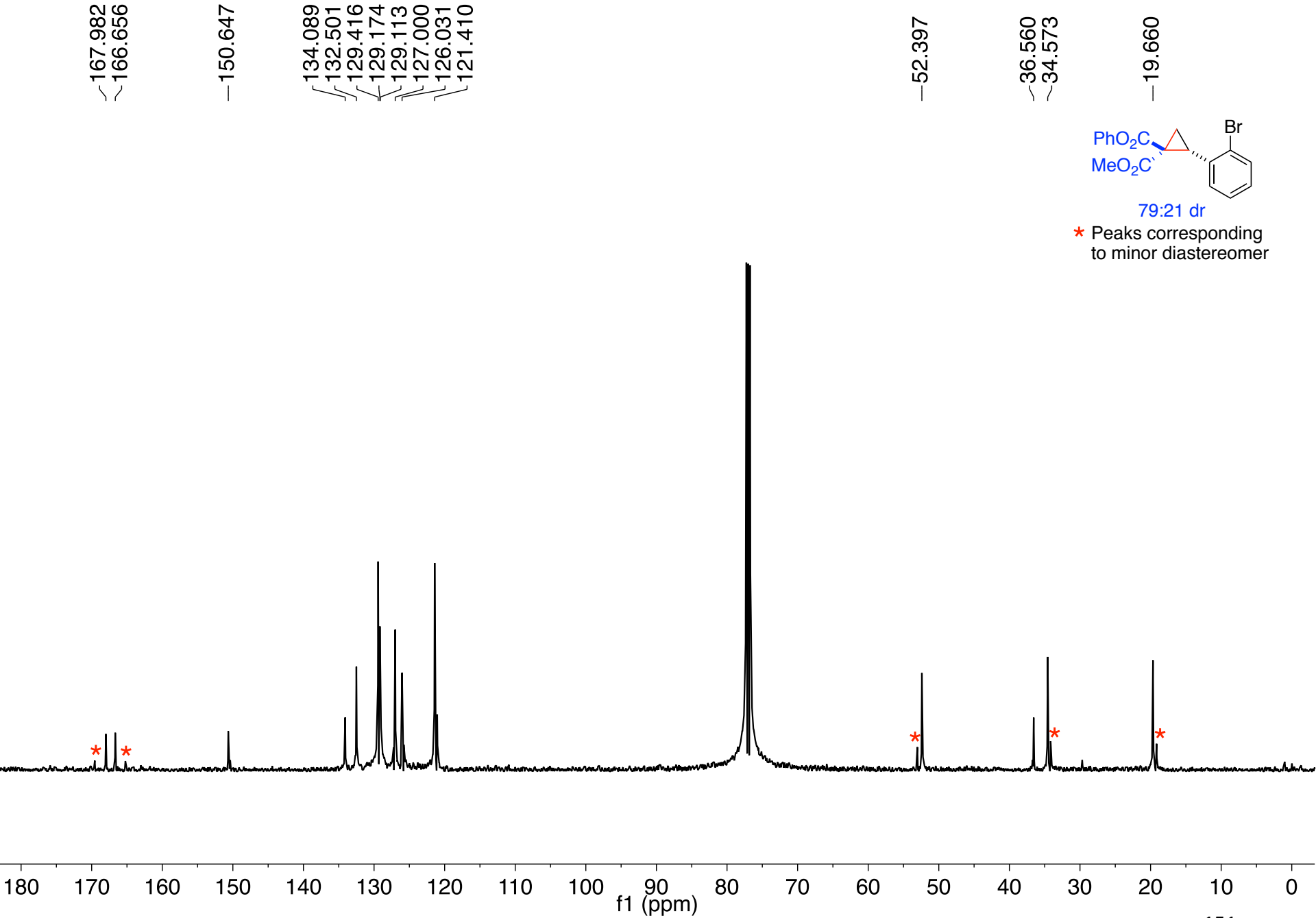
Name	Retention Time	Area Percent	Pk #
	19.952	98.293	1
	30.772	1.707	2

Totals	
	100.000

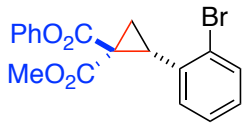
1-methyl 1-phenyl (1*S*,2*S*)-2-(2-bromophenyl)cyclopropane-1,1-dicarboxylate



1-methyl 1-phenyl (1*S*,2*S*)-2-(2-bromophenyl)cyclopropane-1,1-dicarboxylate



1-methyl 1-phenyl (1*S*,2*S*)-2-(2-bromophenyl)cyclopropane-1,1-dicarboxylate

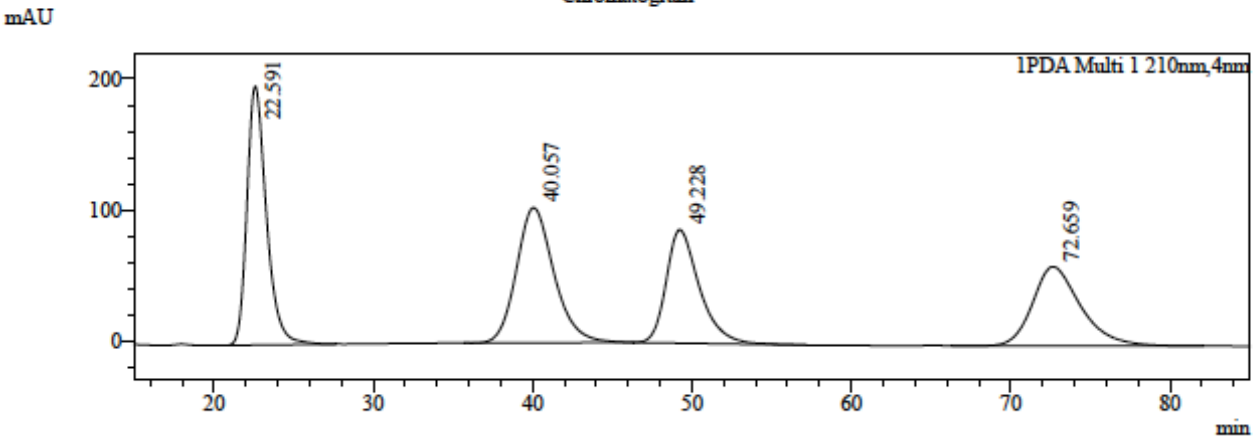


79:21 dr
95% ee

Sample Information

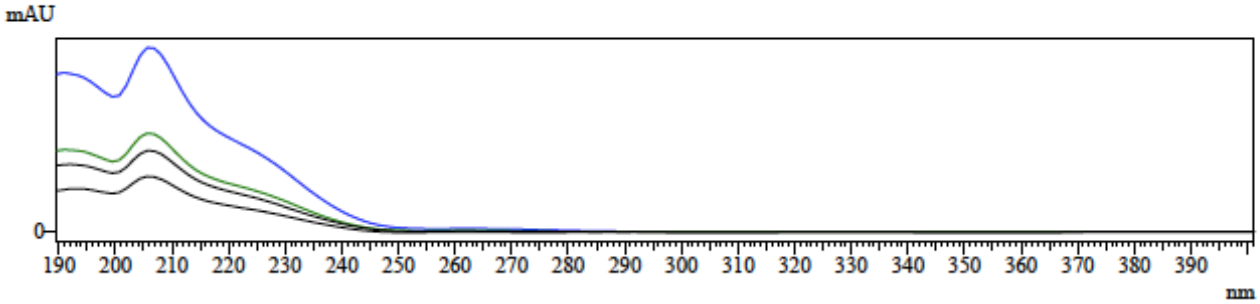
Sample Name	:
Sample ID	: JYW-II-166-OJH-15%-0.8ml
Data File	: JYW-II-166-OJH-15%-0.8ml.lcd
Method File	: JYW-method.lcm
Date Acquired	: 9/29/2015 12:04:47 PM

Chromatogram



UV Spectrum

JYW-II-166-OJH-15%-0.8ml.lcd

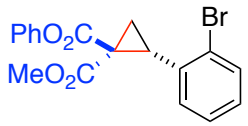


Peak Table

PDA Ch1 210nm

Peak#	Ret. Time	Area	Area%
1	22.591	16725852	28.442
2	40.057	16824867	28.610
3	49.228	12556413	21.352
4	72.659	12699893	21.596
Total		58807026	100.000

1-methyl 1-phenyl (1*S*,2*S*)-2-(2-bromophenyl)cyclopropane-1,1-dicarboxylate

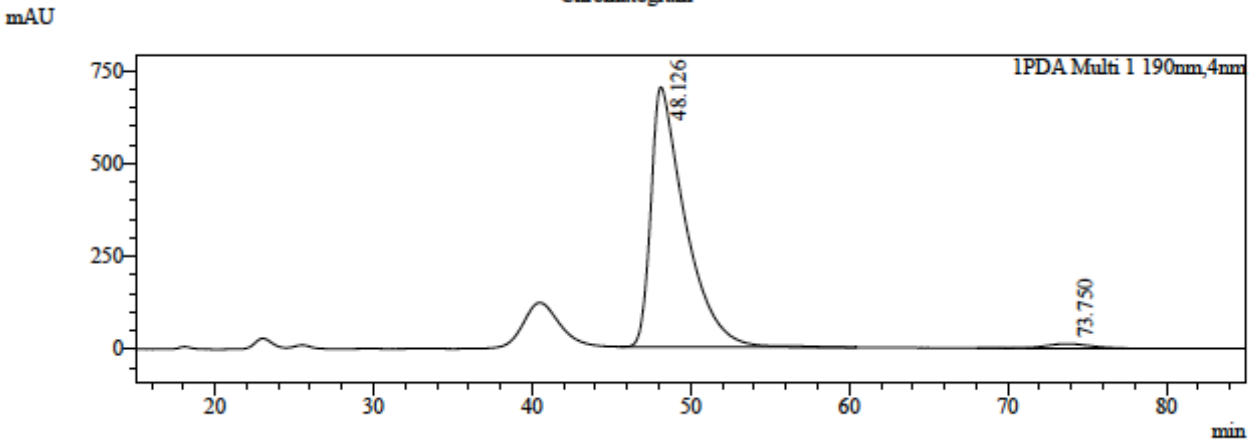


79:21 dr
95% ee

Sample Information

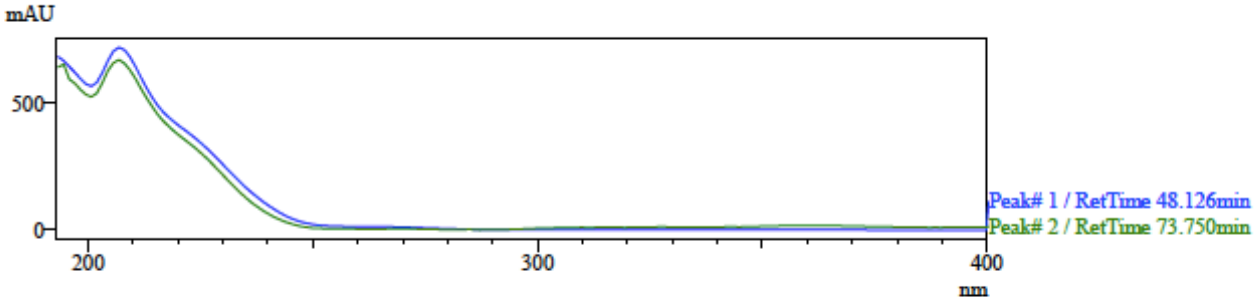
Sample Name	:
Sample ID	: JYW-II-152-OJH-15%-0.8ml
Data File	: JYW-II-152-OJH-15%-0.8ml.lcd
Method File	: JYW-method.lcm
Date Acquired	: 9/29/2015 2:05:25 PM

Chromatogram



UV Spectrum

JYW-II-152-OJH-15%-0.8ml.lcd

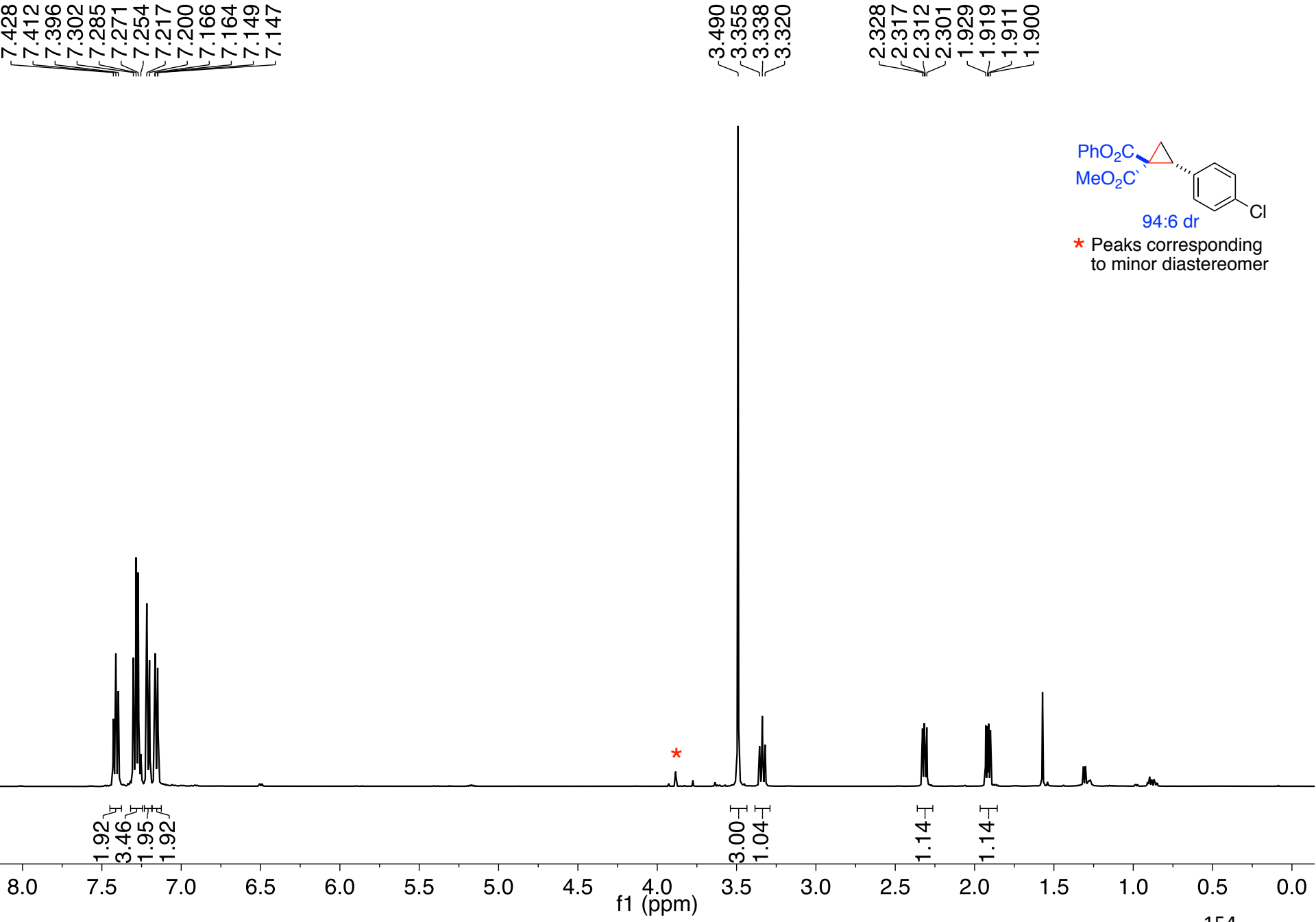


Peak Table

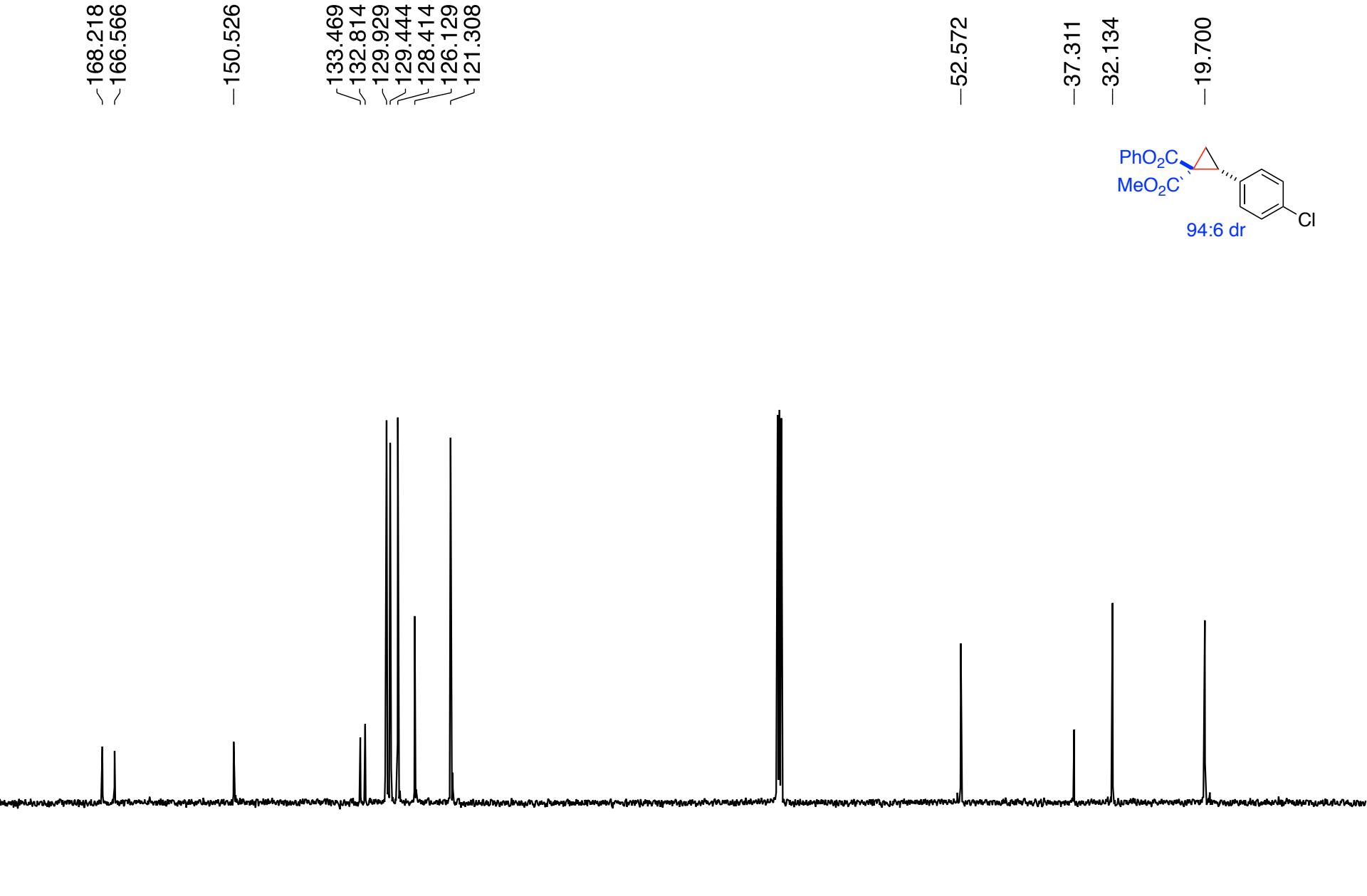
PDA Ch1 190nm

Peak#	Ret. Time	Area	Area%
1	48.126	105573494	97.745
2	73.750	2435808	2.255
Total		108009302	100.000

1-methyl 1-phenyl (1*S*,2*R*)-2-(4-chlorophenyl)cyclopropane-1,1-dicarboxylate

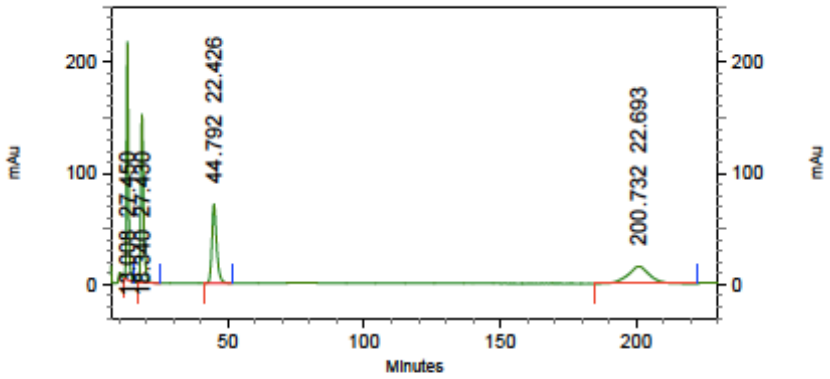


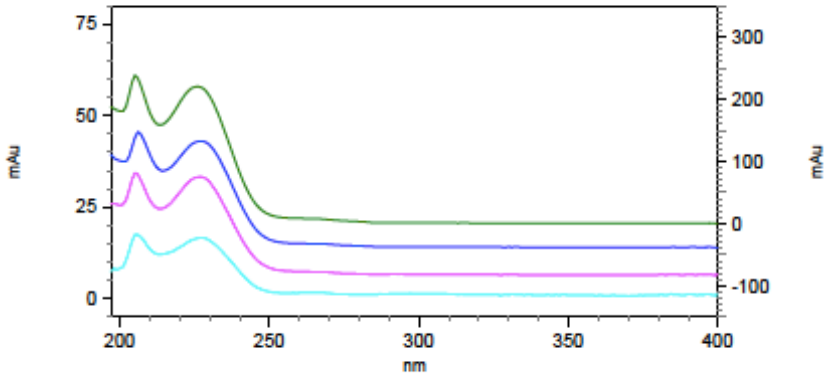
1-methyl 1-phenyl (1*S*,2*R*)-2-(4-chlorophenyl)cyclopropane-1,1-dicarboxylate

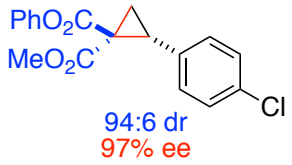


1-methyl 1-phenyl (1*S*,2*R*)-2-(4-chlorophenyl)cyclopropane-1,1-dicarboxylate

JYW-II-99-OJH-35%-0.6ml
C:\EZStart\Projects\Default\Method\LK0.8-3%.met
C:\EZStart\Projects\Default\Data\JYW-II-99-OJH-35%-0.6ml







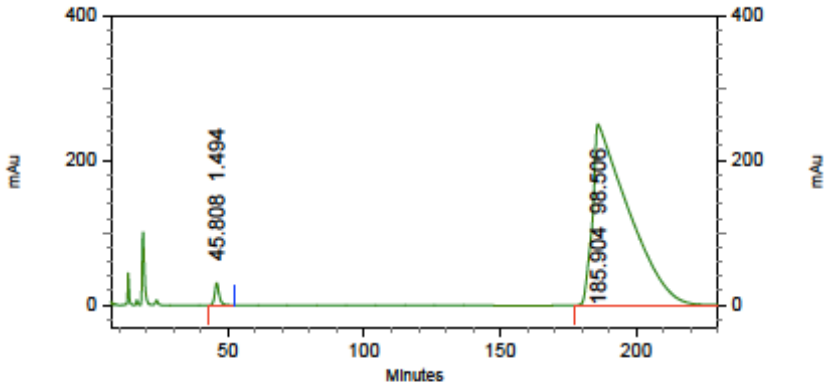
3: 225 nm, 4 nm
Results

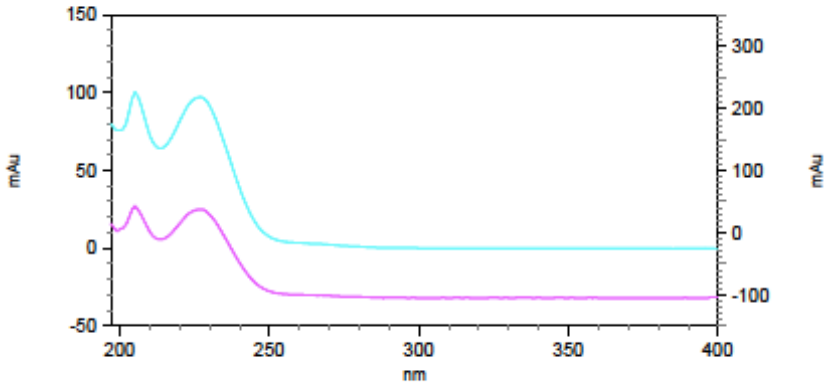
Name	Retention Time	Area Percent	Pk #
	13.008	27.450	1
	18.340	27.430	2
	44.792	22.426	3
	200.732	22.693	4

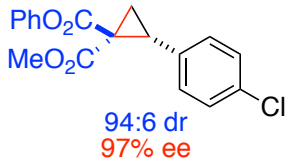
Totals	100.000

1-methyl 1-phenyl (1*S*,2*R*)-2-(4-chlorophenyl)cyclopropane-1,1-dicarboxylate

JYW-II-102-OJH-35%-0.6ml
C:\EZStart\Projects\Default\Method\LK0.8-3%.met
C:\EZStart\Projects\Default\Data\JYW-II-102-OJH-35%-0.6ml







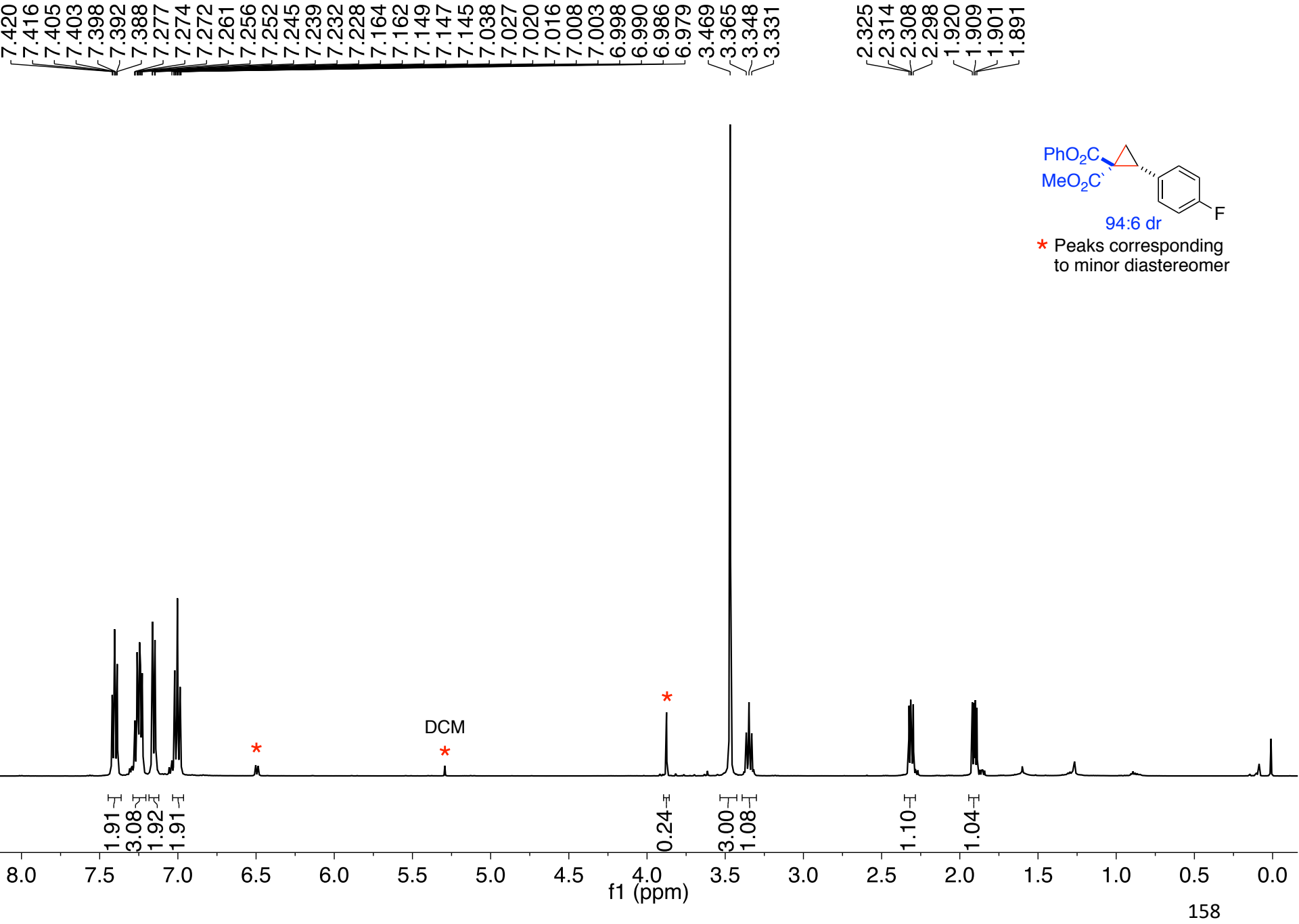
94:6 dr
97% ee

3: 225 nm, 4 nm
Results

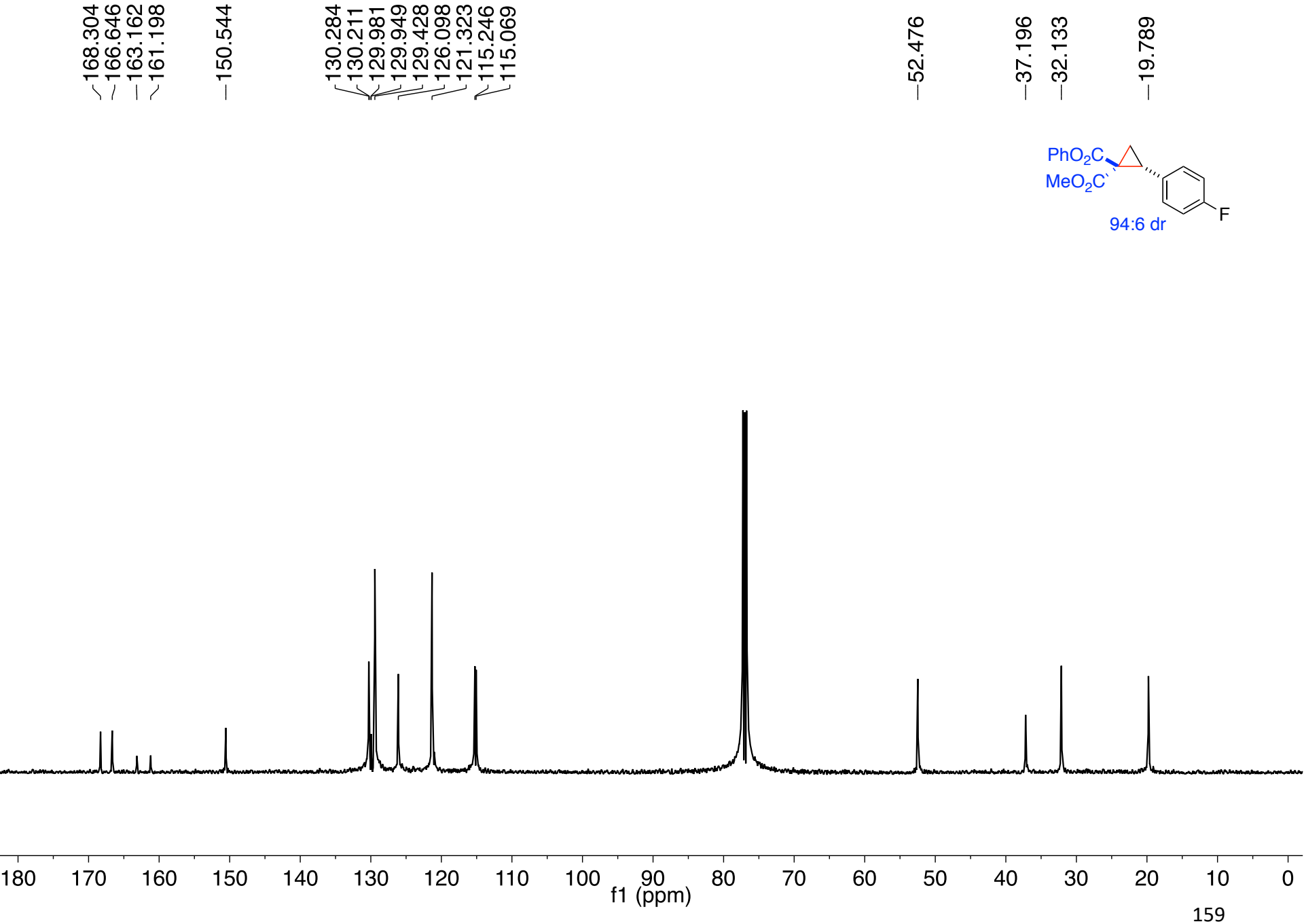
Name	Retention Time	Area Percent	Pk #
	45.808	1.494	1
	185.904	98.506	2

Totals	
	100.000

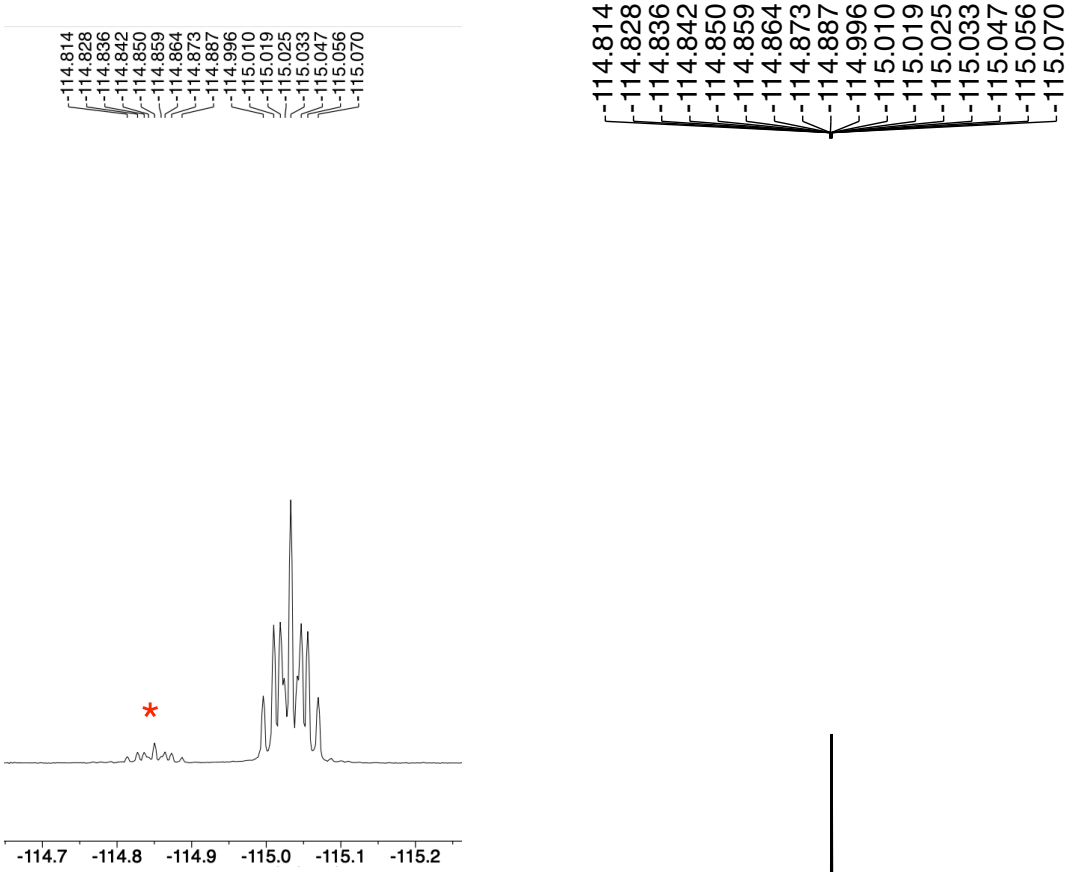
1-methyl 1-phenyl (1*S*,2*R*)-2-(4-fluorophenyl)cyclopropane-1,1-dicarboxylate

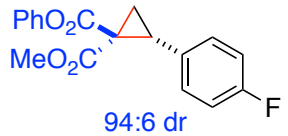


1-methyl 1-phenyl (1*S*,2*R*)-2-(4-fluorophenyl)cyclopropane-1,1-dicarboxylate



1-methyl 1-phenyl (1*S*,2*R*)-2-(4-fluorophenyl)cyclopropane-1,1-dicarboxylate



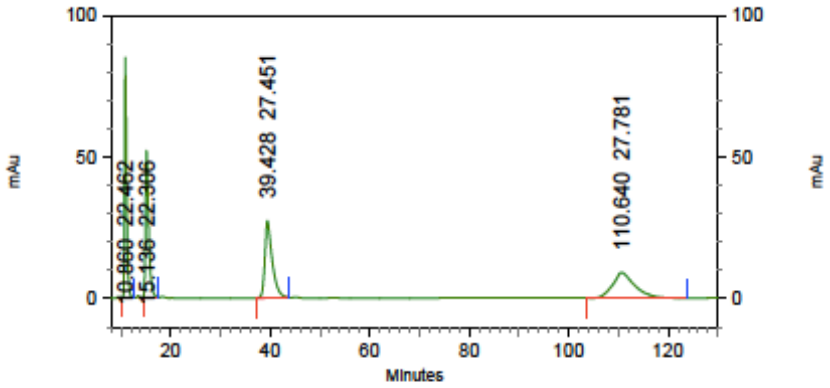


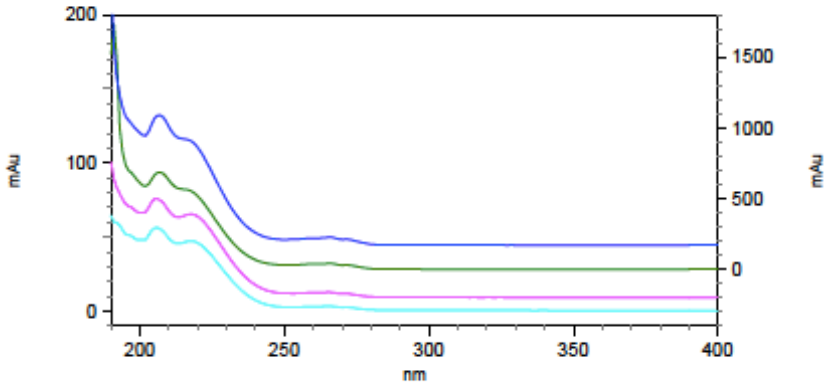
94:6 dr

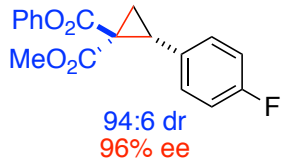
* Peaks corresponding to minor diastereomer

1-methyl 1-phenyl (1*S*,2*R*)-2-(4-fluorophenyl)cyclopropane-1,1-dicarboxylate

JYW-II-191A-OJH-20%-0.8mlrere
C:\EZStart\Projects\Default\Method\LK-10%-0.8-90min.met
C:\EZStart\Projects\Default\Data\JYW-II-191A-OJH-20%-0.8mlrere







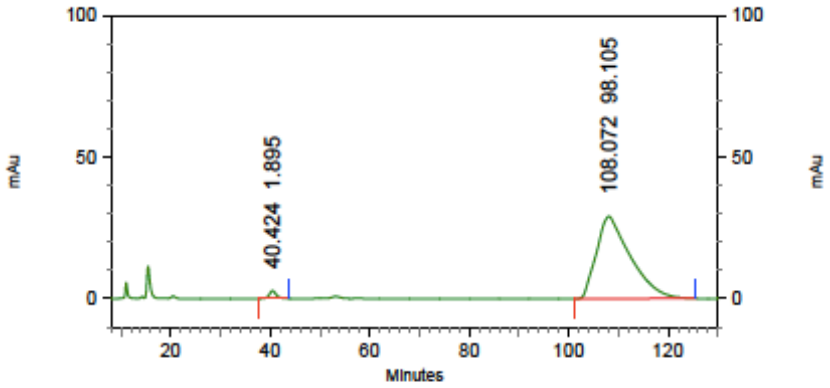
6: 225 nm, 4 nm
Results

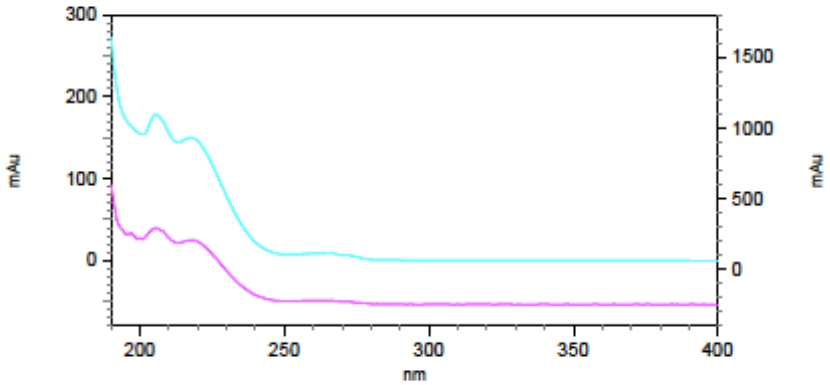
Name	Retention Time	Area Percent	Pk #
	10.860	22.462	1
	15.136	22.306	2
	39.428	27.451	3
	110.640	27.781	4

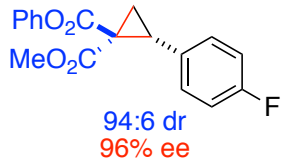
Totals	100.000

1-methyl 1-phenyl (1*S*,2*R*)-2-(4-fluorophenyl)cyclopropane-1,1-dicarboxylate

JYW-II-215A-OJH-20%-0.8ml
C:\EZStart\Projects\Default\Method\LK-10%-0.8-90min.met
C:\EZStart\Projects\Default\Data\JYW-II-215A-OJH-20%-0.8ml



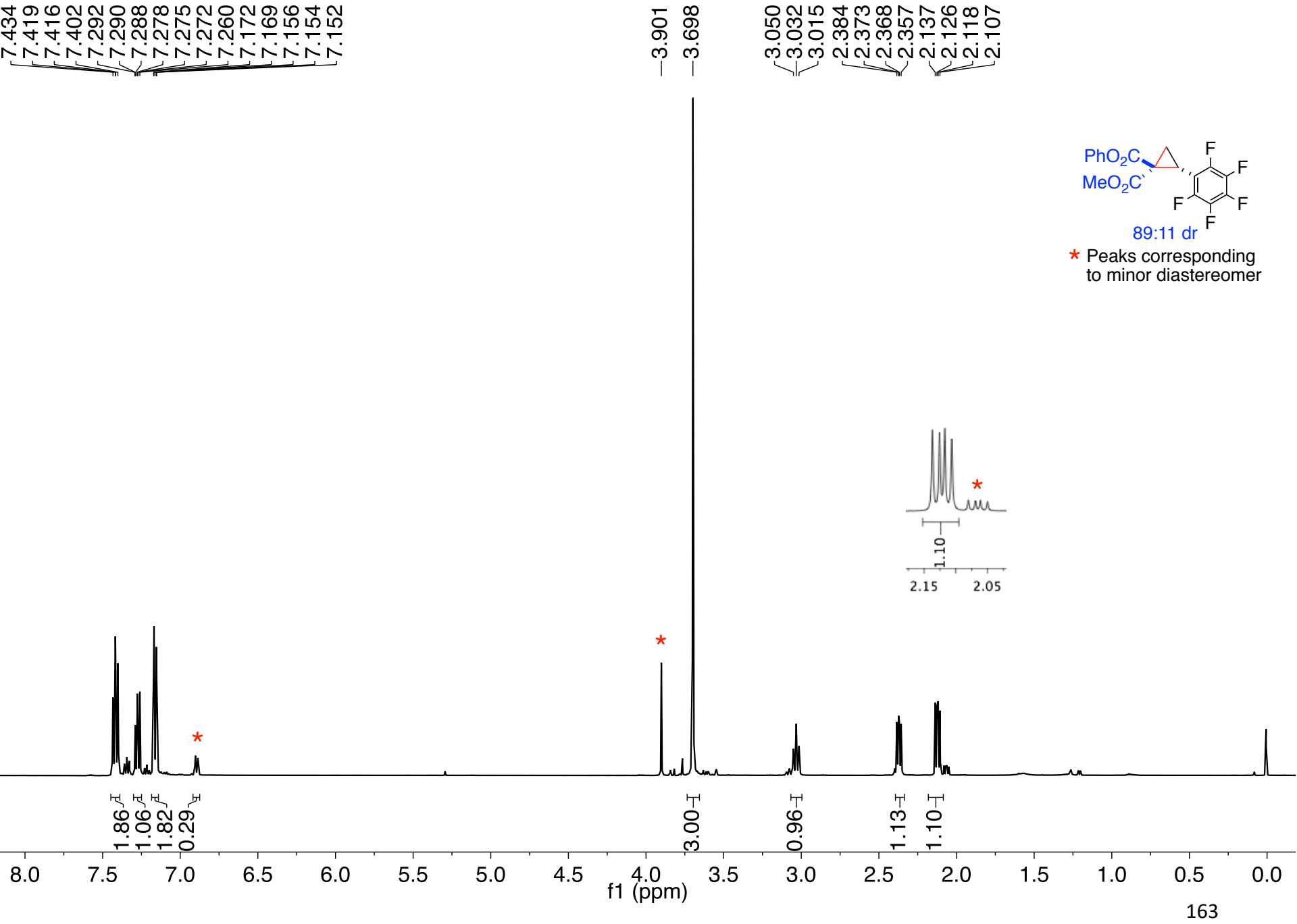




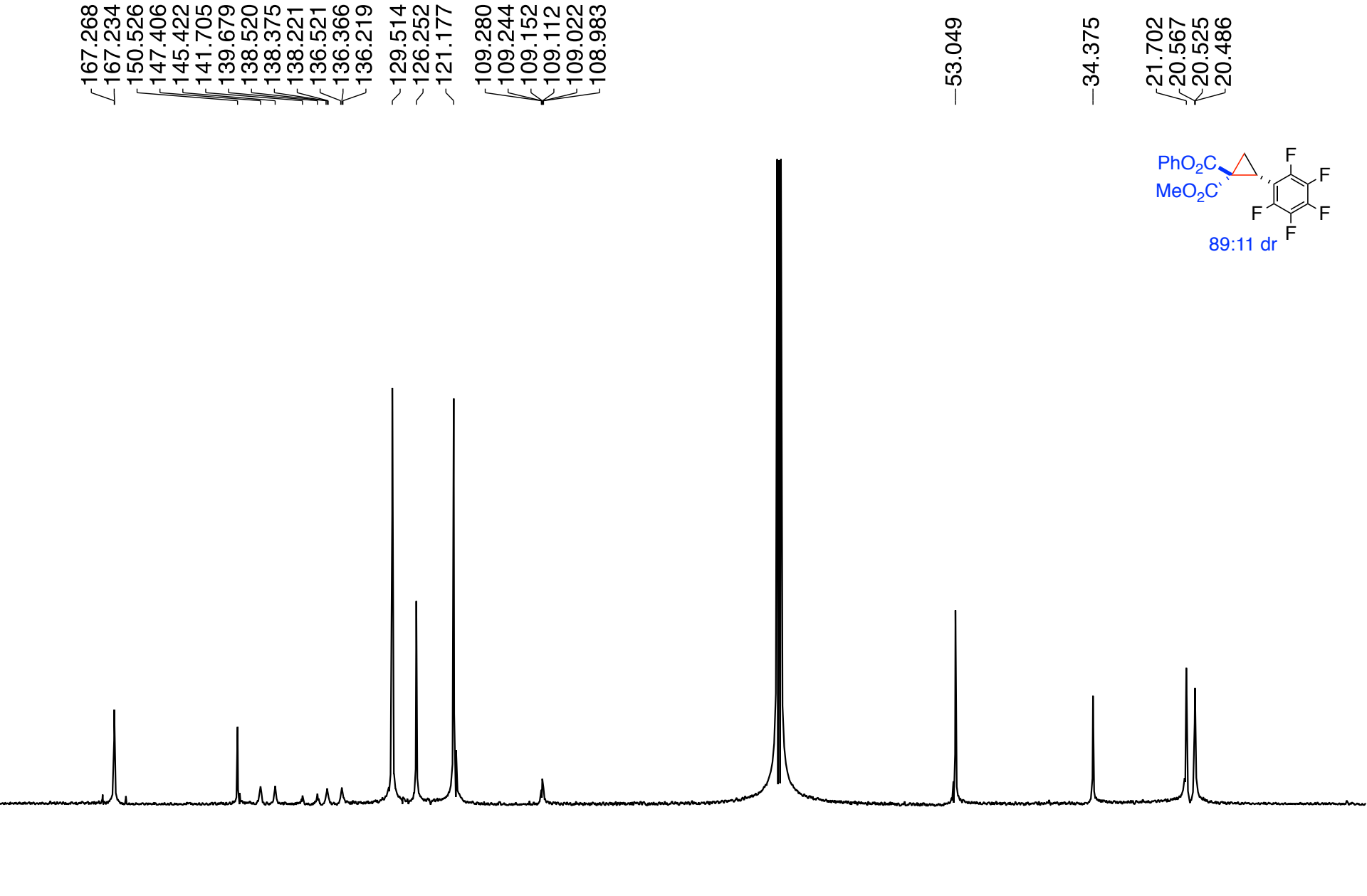
6: 225 nm, 4 nm
Results

Name	Retention Time	Area Percent	Pk #
	40.424	1.895	1
	108.072	98.105	2
Totals		100.000	

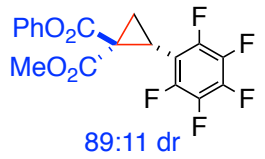
1-methyl 1-phenyl (1*S*,2*S*)-2-(perfluorophenyl)cyclopropane-1,1-dicarboxylate



1-methyl 1-phenyl (1*S*,2*S*)-2-(perfluorophenyl)cyclopropane-1,1-dicarboxylate



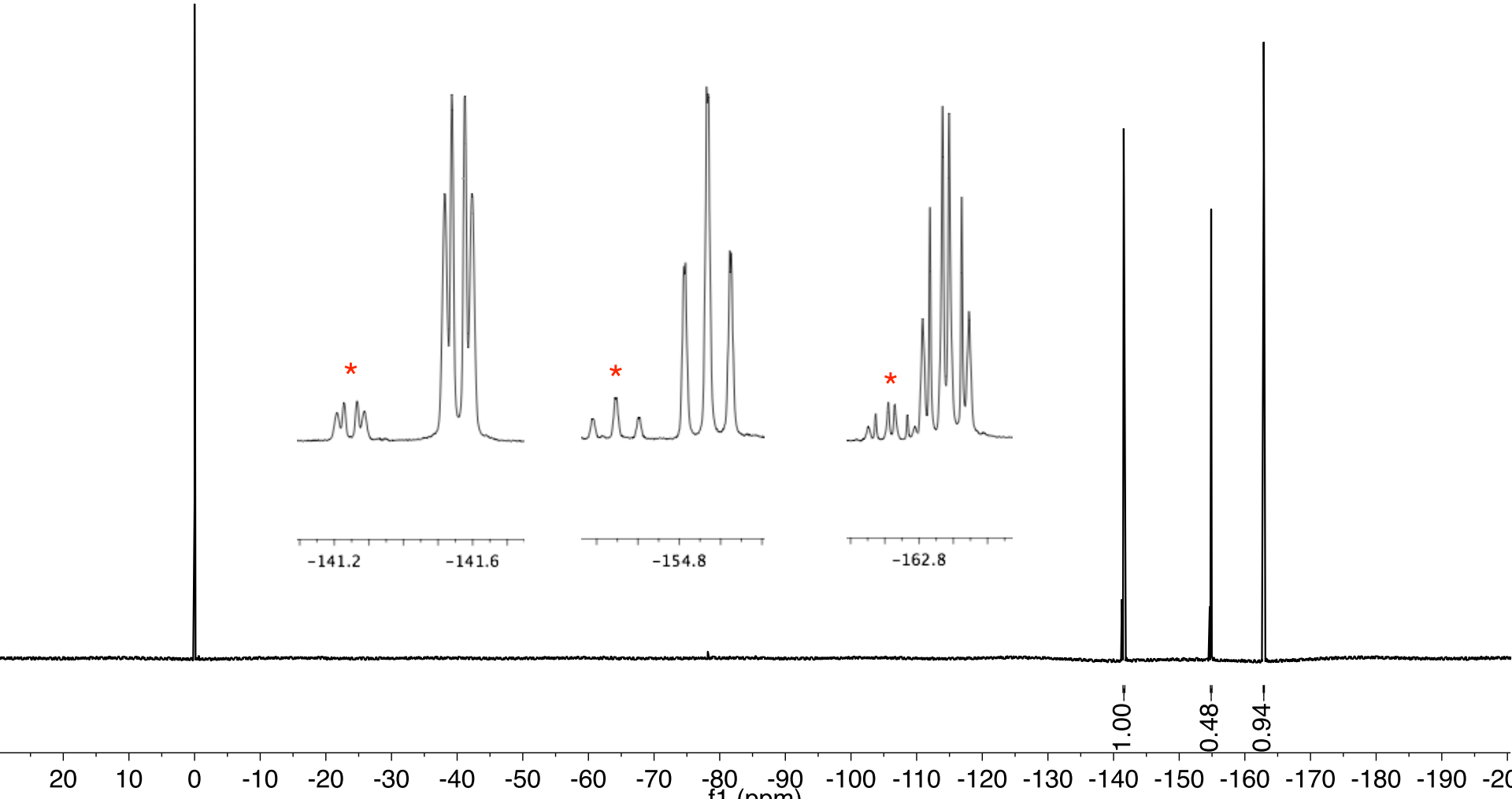
1-methyl 1-phenyl (1*S*,2*S*)-2-(perfluorophenyl)cyclopropane-1,1-dicarboxylate



89:11 dr

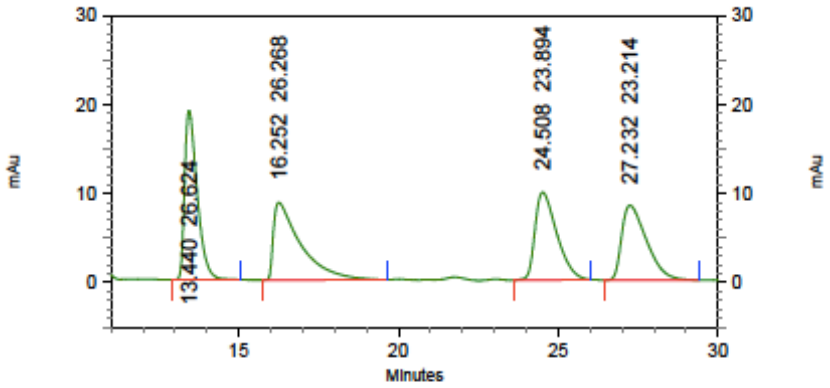
* Peaks corresponding to minor diastereomer

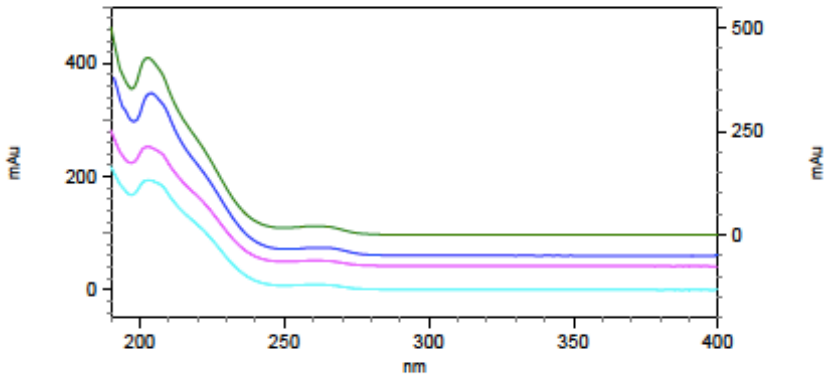
-141.524
-141.545
-141.582
-141.603
-154.817
-154.872
-154.928
-162.815
-162.836
-162.873
-162.892
-162.929
-162.950

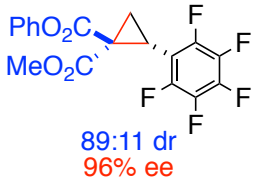


1-methyl 1-phenyl (1*S*,2*S*)-2-(perfluorophenyl)cyclopropane-1,1-dicarboxylate

JYW-II-155A-ODH-1%-0.8ml
C:\EZStart\Projects\Default\Method\LK0.8-3%.met
C:\EZStart\Projects\Default\Data\JYW-II-155A-ODH-1%-0.8ml







89:11 dr
96% ee

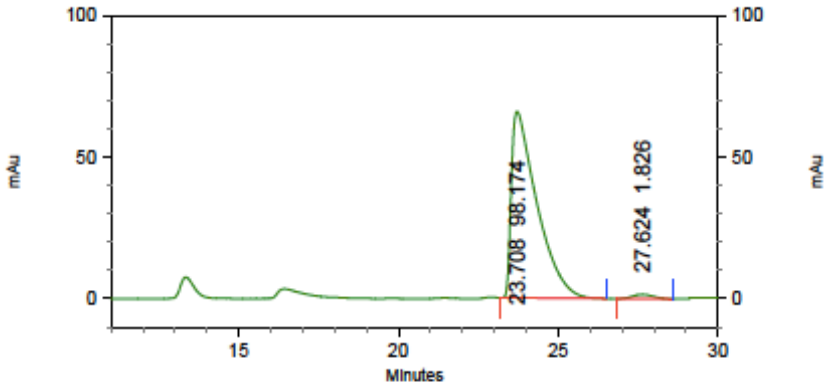
4: 246 nm, 4 nm
Results

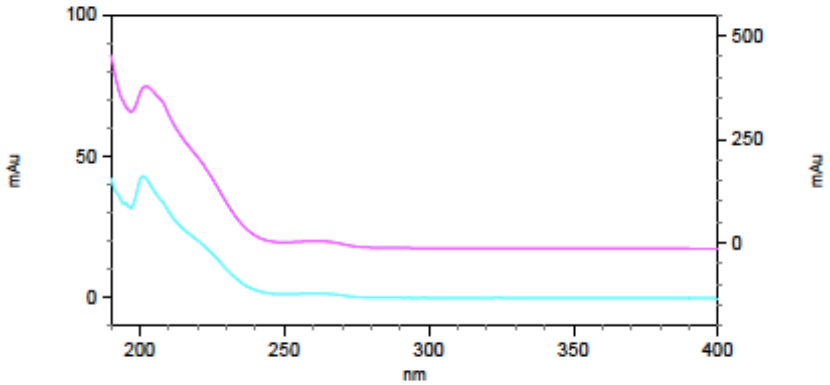
Name	Retention Time	Area Percent	Pk #
	13.440	26.624	1
	16.252	26.268	2
	24.508	23.894	3
	27.232	23.214	4

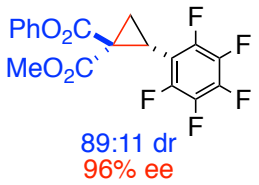
Totals	100.000

1-methyl 1-phenyl (1*S*,2*S*)-2-(perfluorophenyl)cyclopropane-1,1-dicarboxylate

JYW-II-216A-ODH-1%-0.8ml
C:\EZStart\Projects\Default\Method\LK0.8-3%.met
C:\EZStart\Projects\Default\Data\JYW-II-216A-ODH-1%-0.8ml







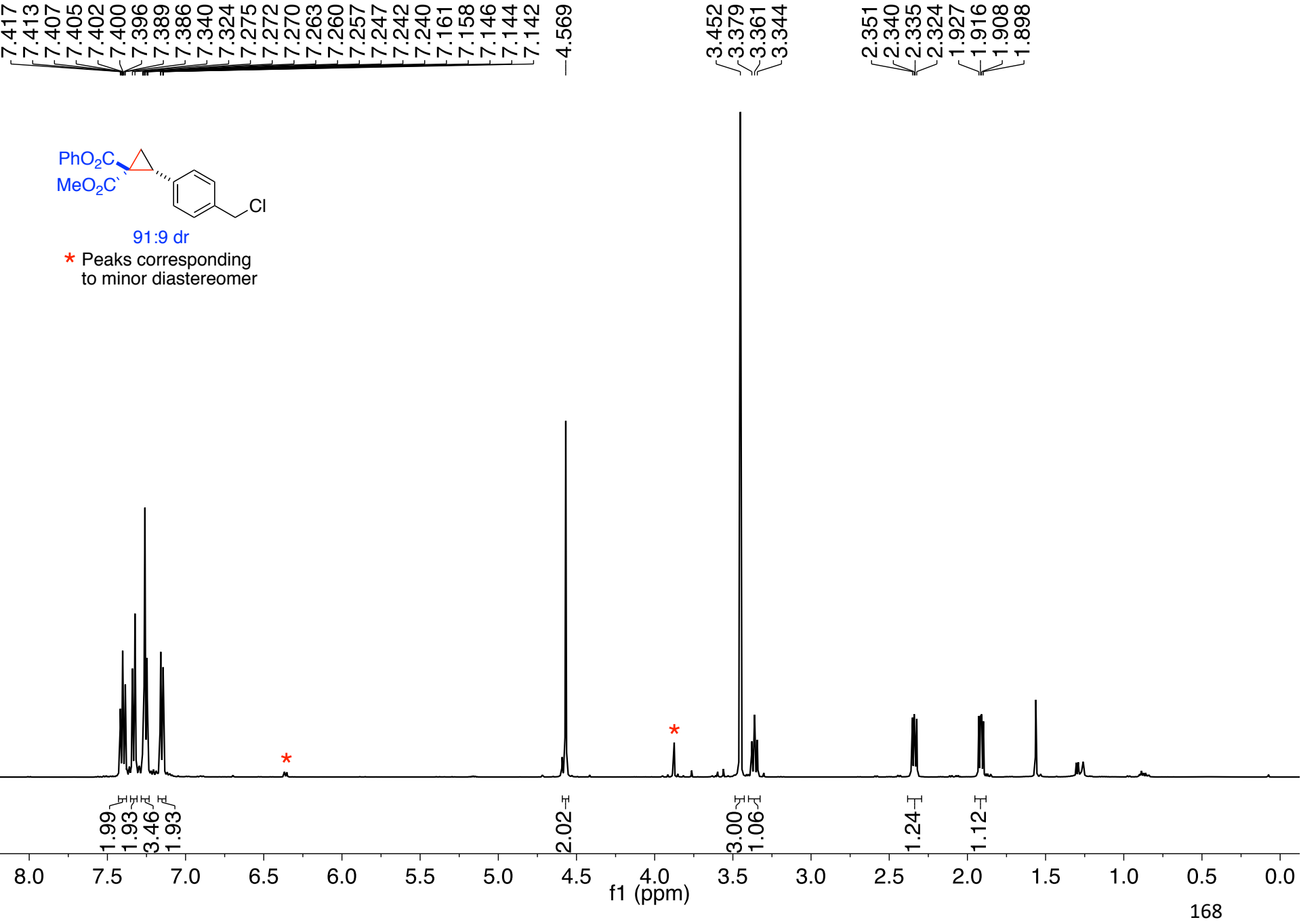
89:11 dr
96% ee

4: 246 nm, 4 nm
Results

Name	Retention Time	Area Percent	Pk #
	23.708	98.174	1
	27.624	1.826	2

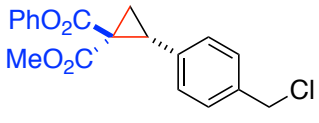
Totals	
	100.000

1-methyl 1-phenyl (1*S*,2*R*)-2-(4-(chloromethyl)phenyl)cyclopropane-1,1-dicarboxylate



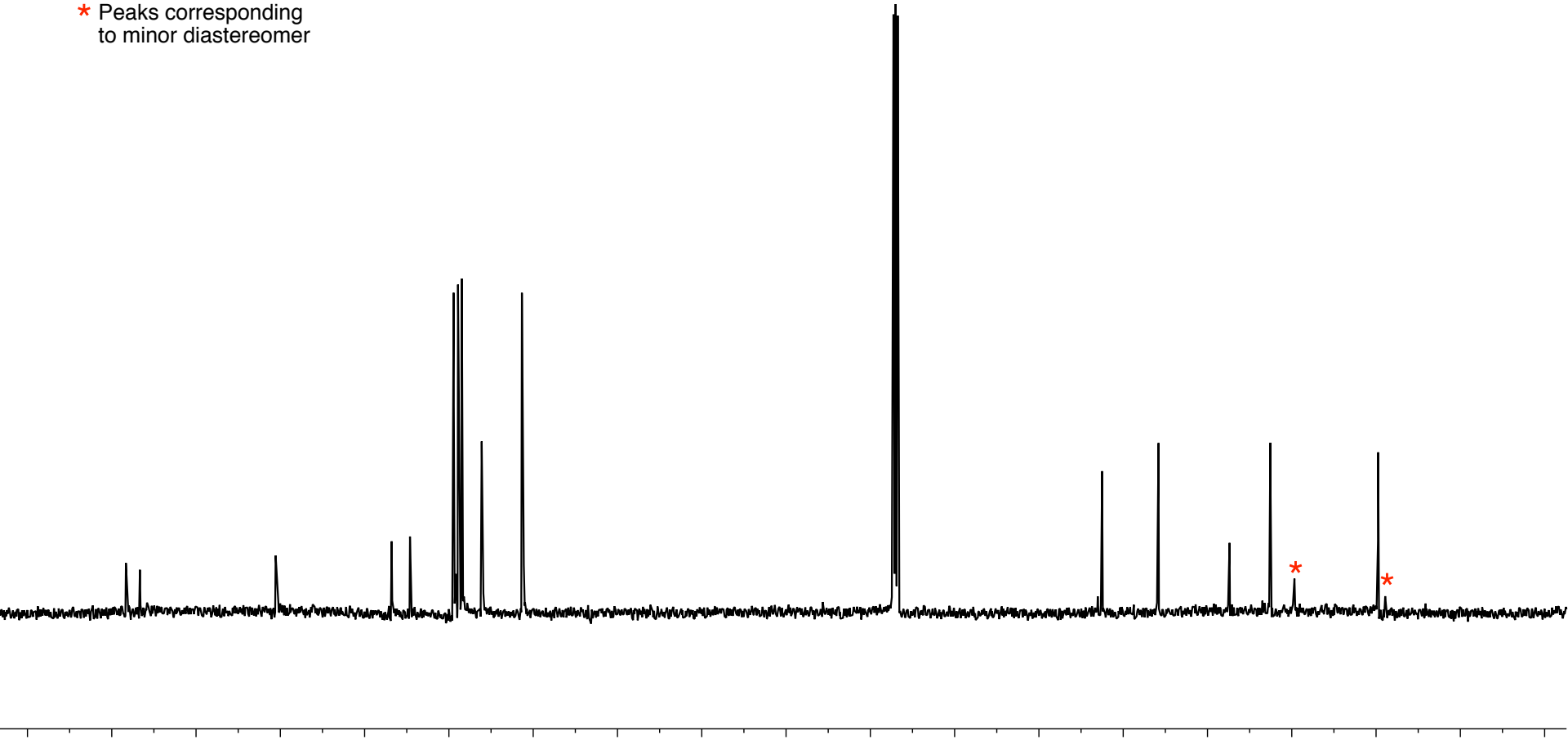
1-methyl 1-phenyl (1*S*,2*R*)-2-(4-(chloromethyl)phenyl)cyclopropane-1,1-dicarboxylate

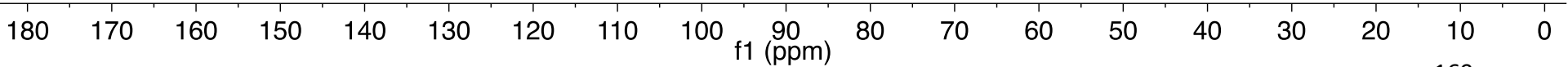
168.321
166.660
150.554
136.791
134.616
129.438
128.920
128.468
126.108
121.338
52.503
45.813
37.385
32.544
19.751



91:9 dr

* Peaks corresponding to minor diastereomer





1-methyl 1-phenyl (1*S*,2*R*)-2-(4-(chloromethyl)phenyl)cyclopropane-1,1-dicarboxylate

JYW-II-143-newADH-2%-1ml
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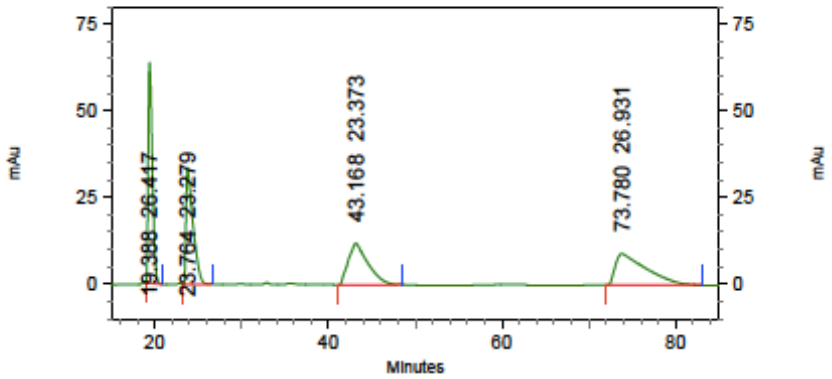
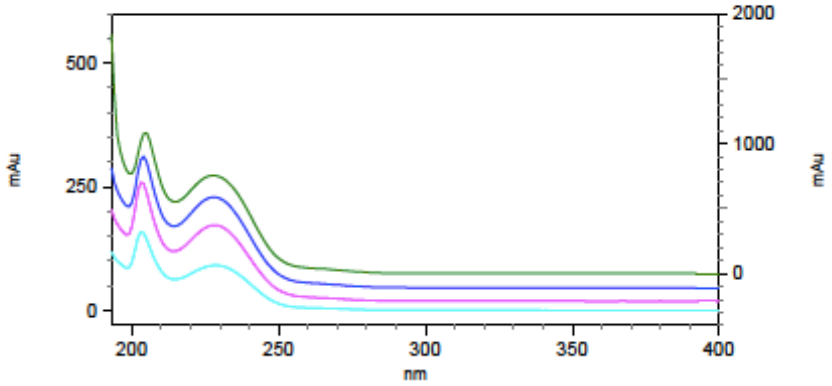
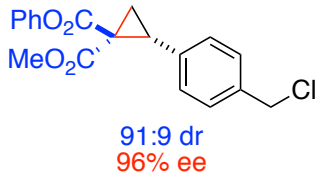
C:\EZStart\Projects\Default\Data\JYW-II-143-newADH-2%-1ml







91:9 dr
96% ee

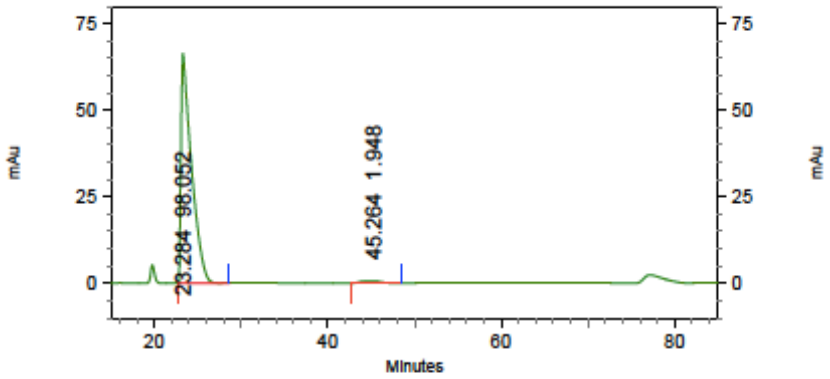
4: 237 nm, 4 nm
Results

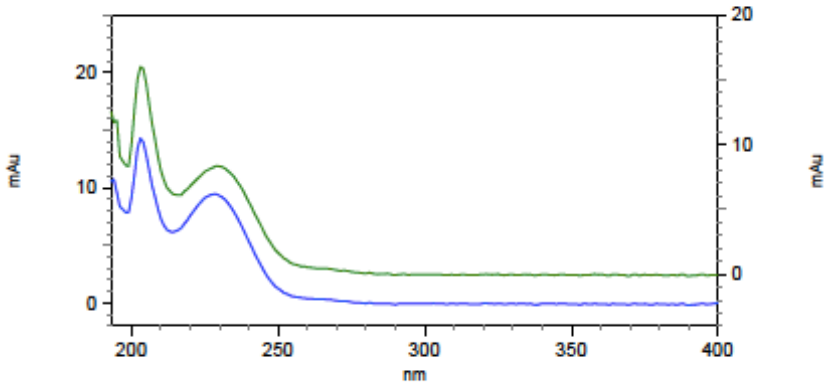
Name	Retention Time	Area Percent	Pk #
	19.388	26.417	1
	23.764	23.279	2
	43.168	23.373	3
	73.780	26.931	4

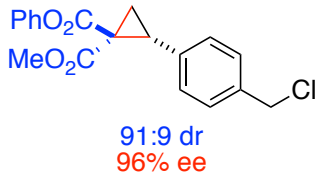
Totals	100.000

1-methyl 1-phenyl (1*S*,2*R*)-2-(4-(chloromethyl)phenyl)cyclopropane-1,1-dicarboxylate

JYW-II-107B-newADH-2%-1ml
C:\EZStart\Projects\Default\Method\LK-10%-0.8-90min.met
C:\EZStart\Projects\Default\Data\JYW-II-107B-newADH-2%-1ml







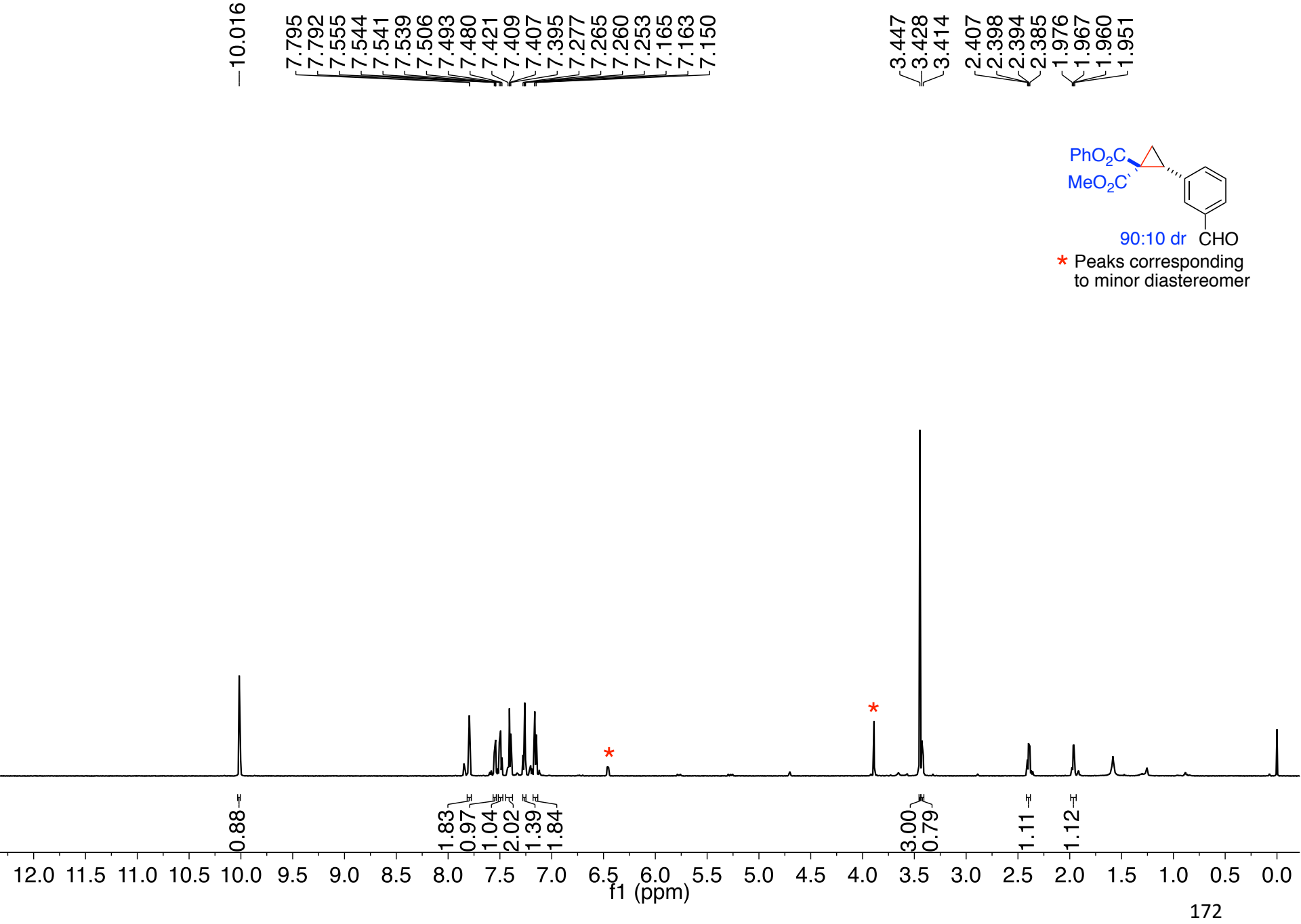
91:9 dr
96% ee

4: 240 nm, 4 nm
Results

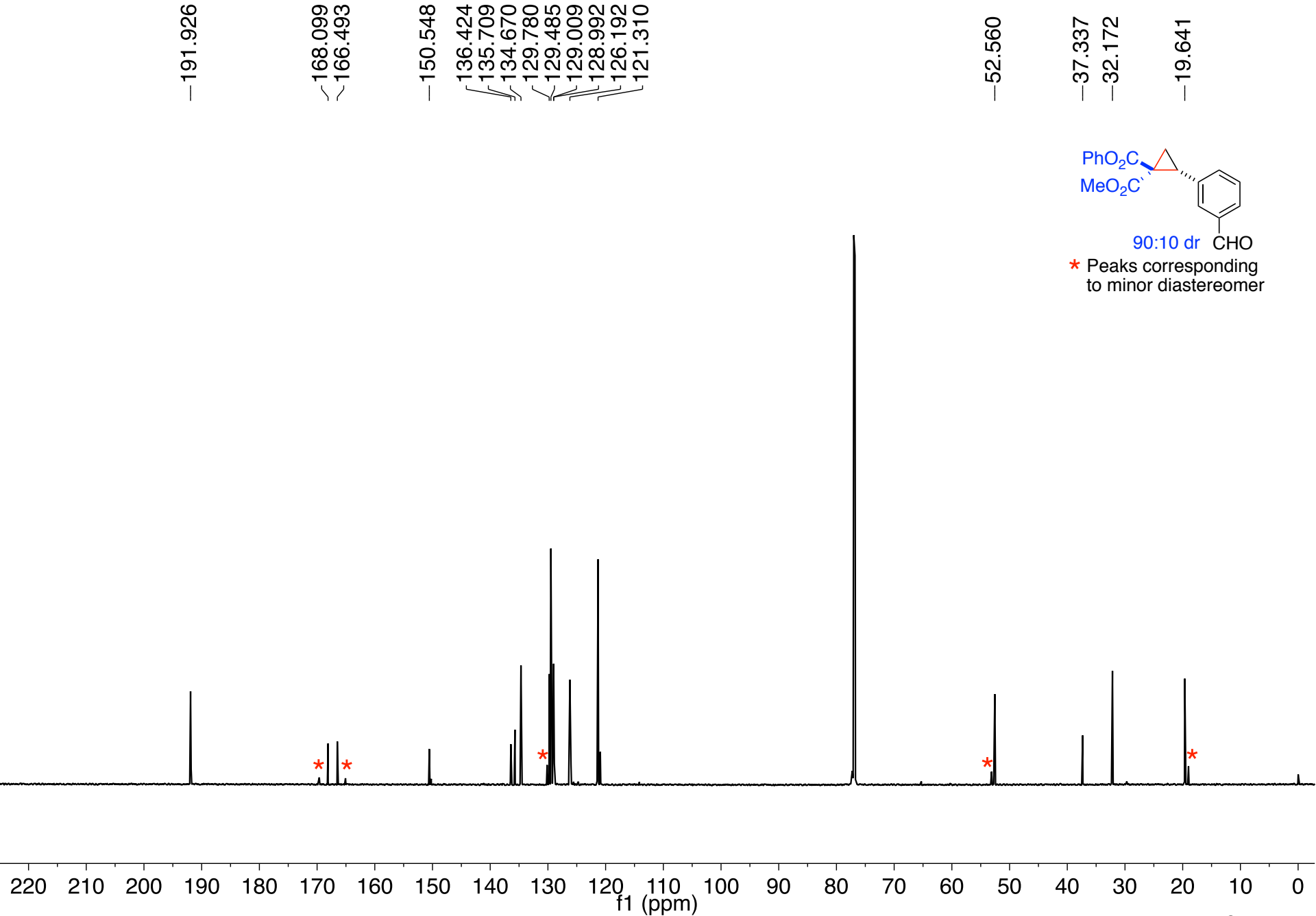
Name	Retention Time	Area Percent	Pk #
	23.284	98.052	1
	45.264	1.948	2

Totals	
	100.000

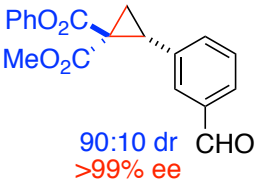
1-methyl 1-phenyl (1*S*,2*R*)-2-(3-formylphenyl)cyclopropane-1,1-dicarboxylate



1-methyl 1-phenyl (1*S*,2*R*)-2-(3-formylphenyl)cyclopropane-1,1-dicarboxylate



1-methyl 1-phenyl (1*S*,2*R*)-2-(3-formylphenyl)cyclopropane-1,1-dicarboxylate

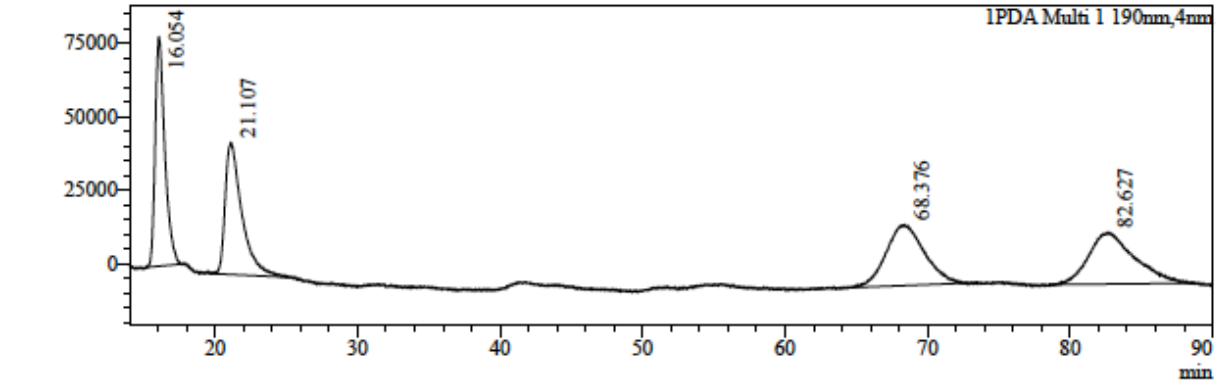


90:10 dr
>99% ee

Sample Information

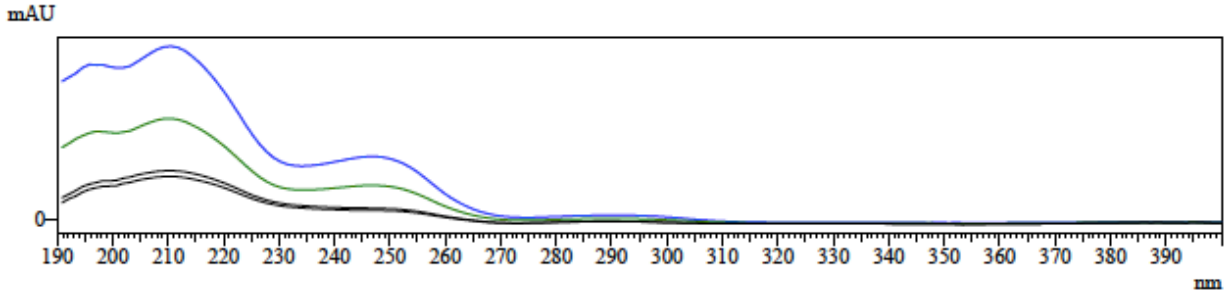
Sample Name	: JYW-0380
Sample ID	: JYW-0380-OJH-40%-0.8ml002
Data File	: JYW-0380-OJH-40%-0.8ml002.lcd
Method File	: JYW-method.lcm
Date Acquired	: 7/11/2017 2:45:29 PM

Chromatogram



UV Spectrum

JYW-0380-OJH-40%-0.8ml002.lcd

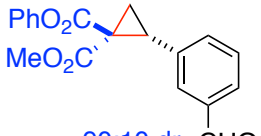


Peak Table

PDA Ch1 190nm

Peak#	Ret. Time	Area	Area%
1	16.054	3671799	24.285
2	21.107	3665083	24.241
3	68.376	3853197	25.485
4	82.627	3929454	25.989
Total		15119532	100.000

1-methyl 1-phenyl (1*S*,2*R*)-2-(3-formylphenyl)cyclopropane-1,1-dicarboxylate

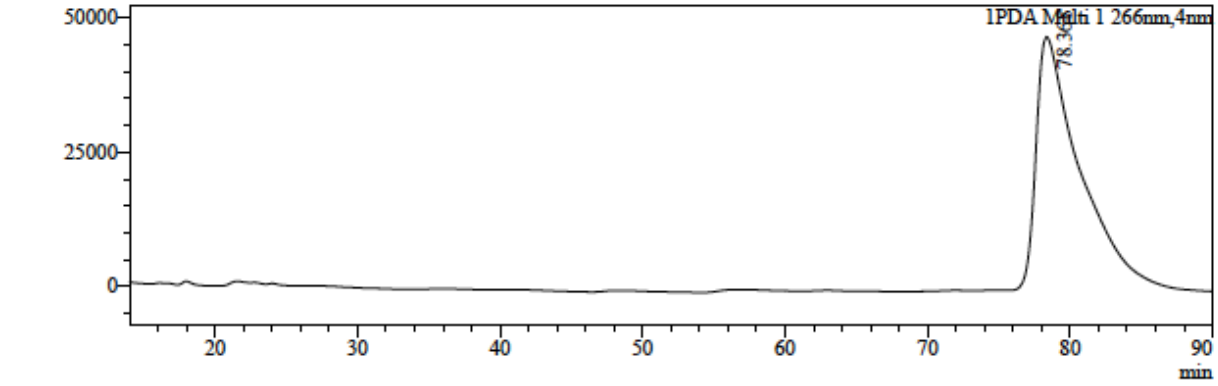


90:10 dr
>99% ee

Sample Information

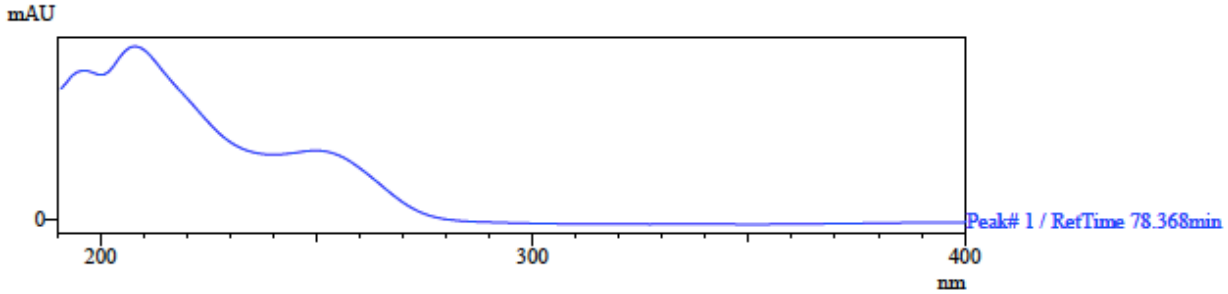
Sample Name	: JYW-0381
Sample ID	: JYW-0381-OJH-40%-0.8ml001
Data File	: JYW-0381-OJH-40%-0.8ml001.lcd
Method File	: JYW-method.lcm
Date Acquired	: 7/11/2017 4:45:26 PM

Chromatogram



UV Spectrum

JYW-0381-OJH-40%-0.8ml001.lcd

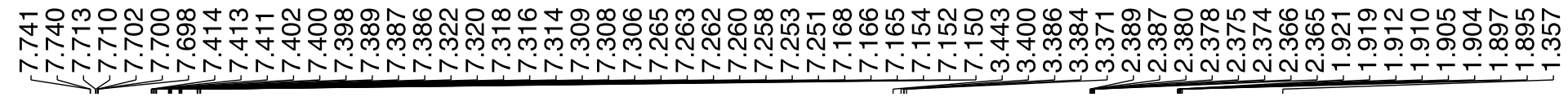


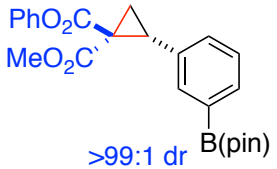
Peak Table

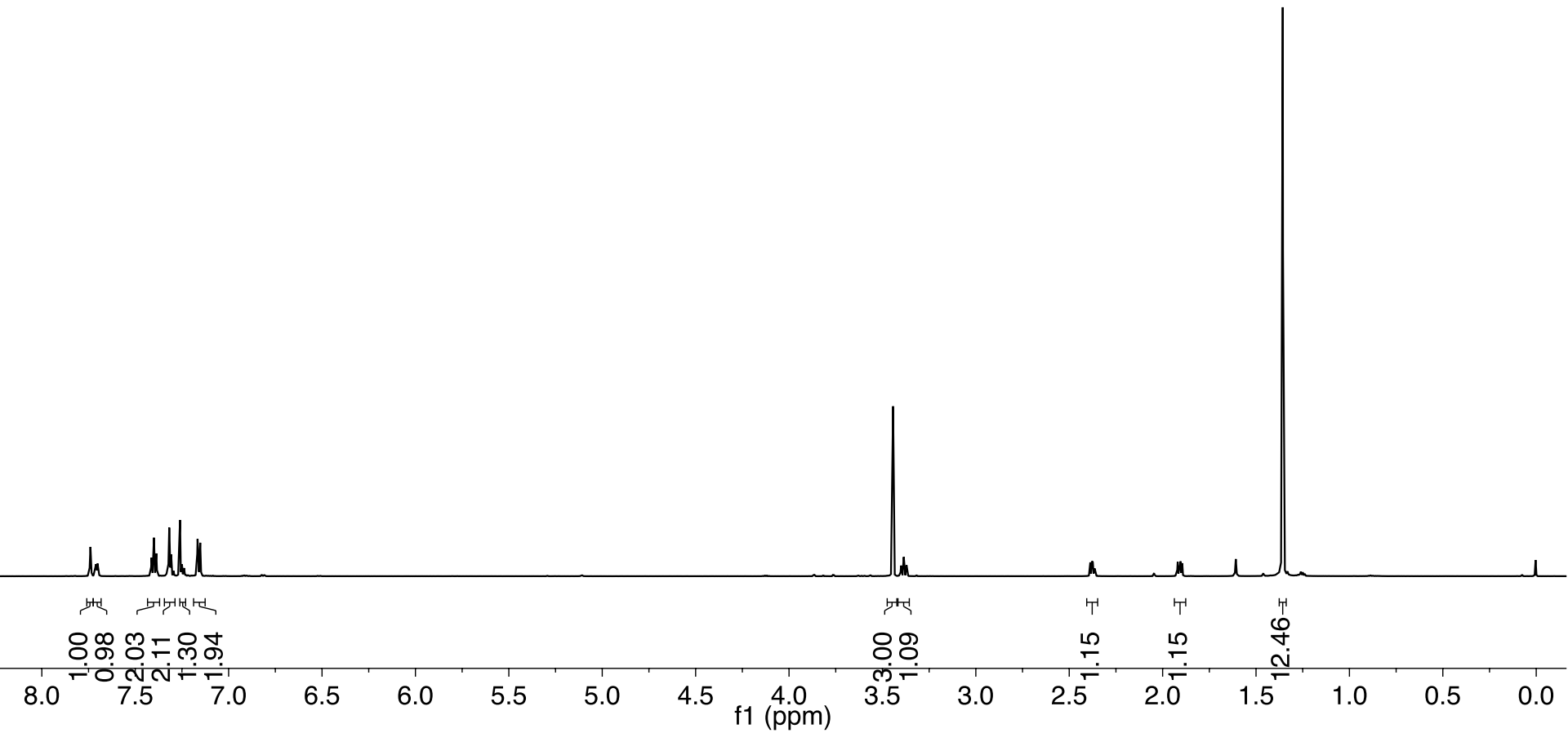
PDA Ch1 266nm

Peak#	Ret. Time	Area	Area%
1	78.368	10265090	100.000
Total		10265090	100.000

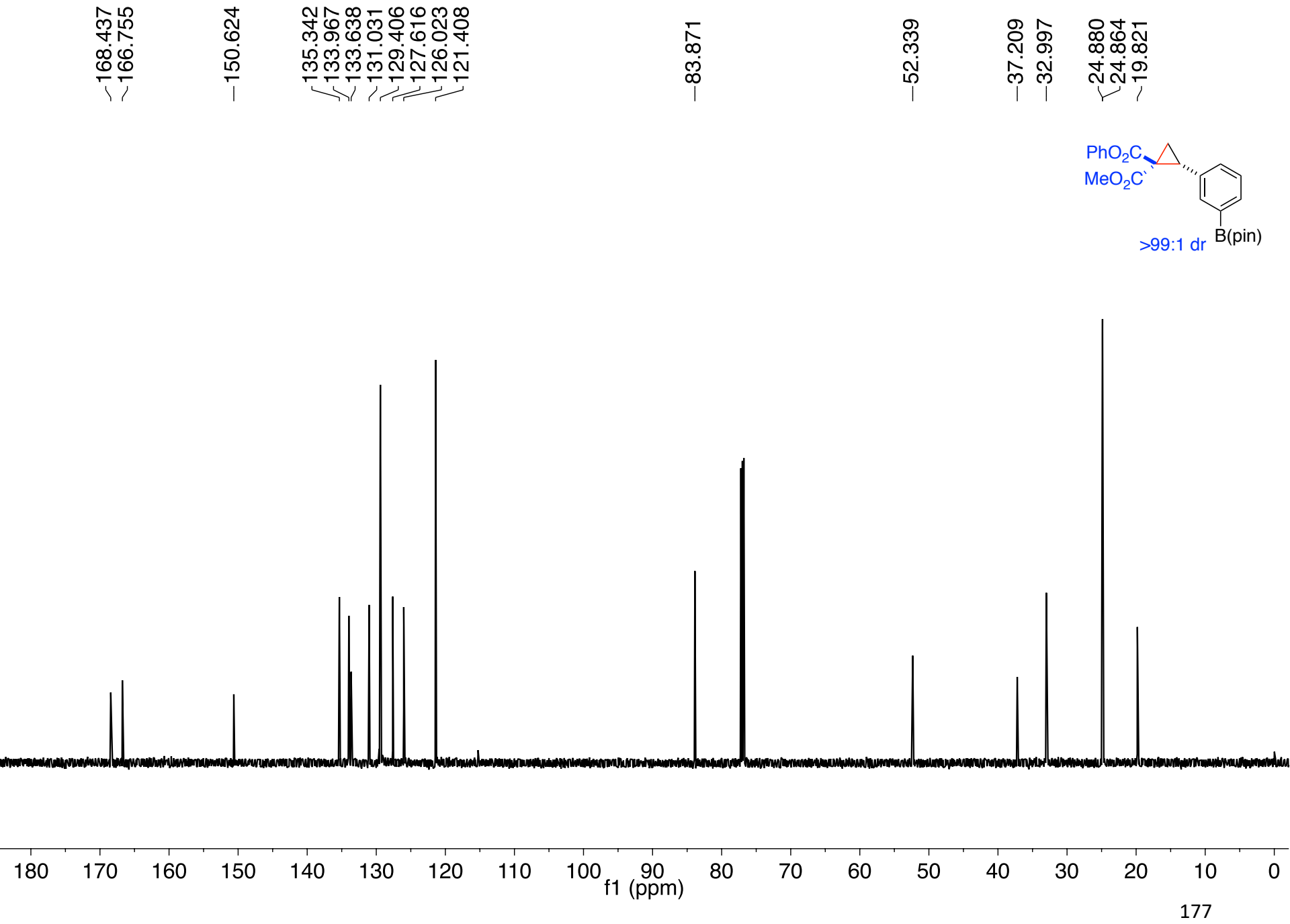
1-methyl 1-phenyl (1*S*,2*R*)-2-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)cyclopropane-1,1-dicarboxylate



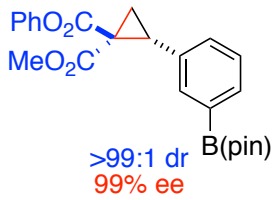




1-methyl 1-phenyl (1*S*,2*R*)-2-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)cyclopropane-1,1-dicarboxylate



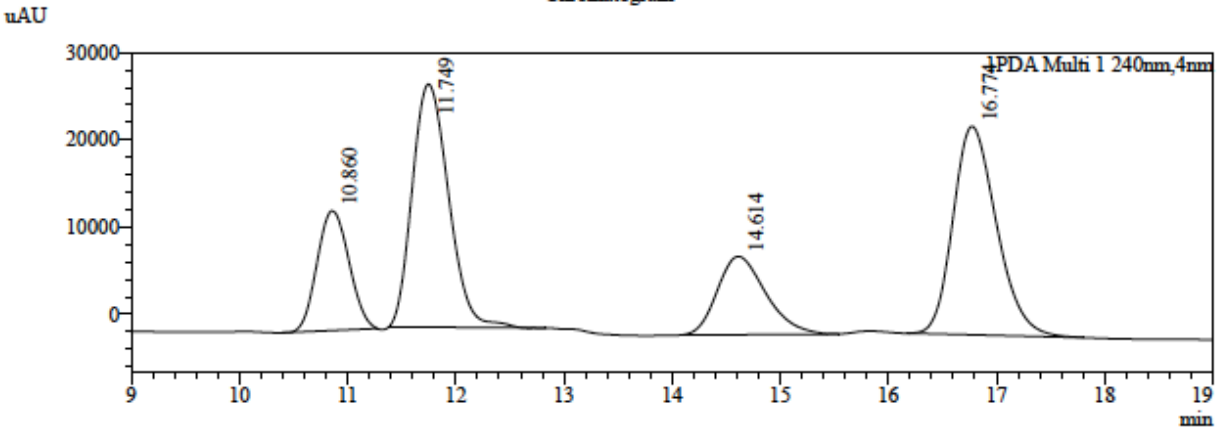
1-methyl 1-phenyl (1*S*,2*R*)-2-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)cyclopropane-1,1-dicarboxylate



Sample Information

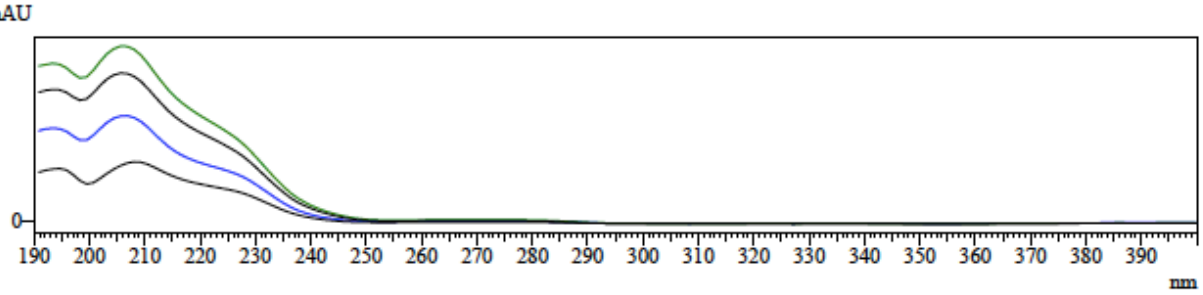
Sample Name	: JYW-0398
Sample ID	: JYW-0398-IA-0.7%-0.8ml
Data File	: JYW-0398-IA-0.7%-0.8ml.lcd
Method File	: JYW-method.lcm
Date Acquired	: 7/18/2017 7:21:12 PM

Chromatogram



UV Spectrum

JYW-0398-IA-0.7%-0.8ml.lcd

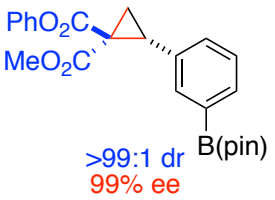


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time	Area	Area%
1	10.860	281739	14.976
2	11.749	651161	34.614
3	14.614	279195	14.841
4	16.774	669136	35.569
Total		1881232	100.000

1-methyl 1-phenyl (1*S*,2*R*)-2-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)cyclopropane-1,1-dicarboxylate

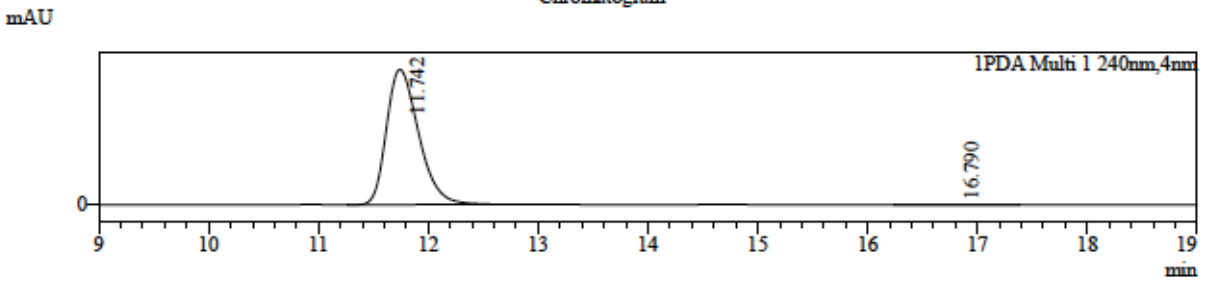


>99:1 dr
99% ee

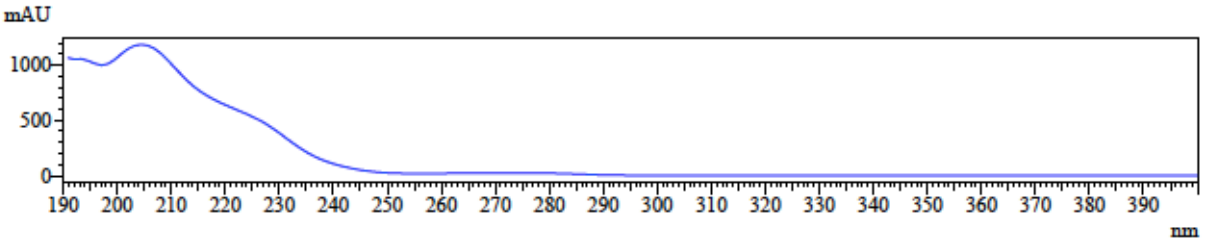
Sample Information

Sample Name	: JYW-0399
Sample ID	: JYW-0399-IA-0.7%-0.8ml
Data File	: JYW-0399-IA-0.7%-0.8ml.lcd
Method File	: JYW-method.lcm

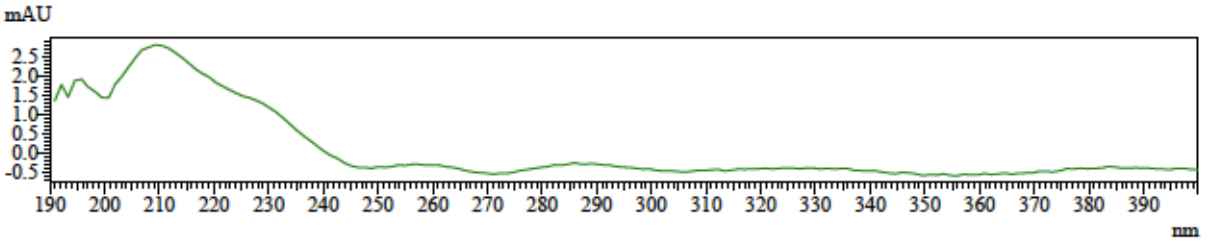
Chromatogram



UV Spectrum
Retention time = 11.742



UV Spectrum
Retention time = 16.790

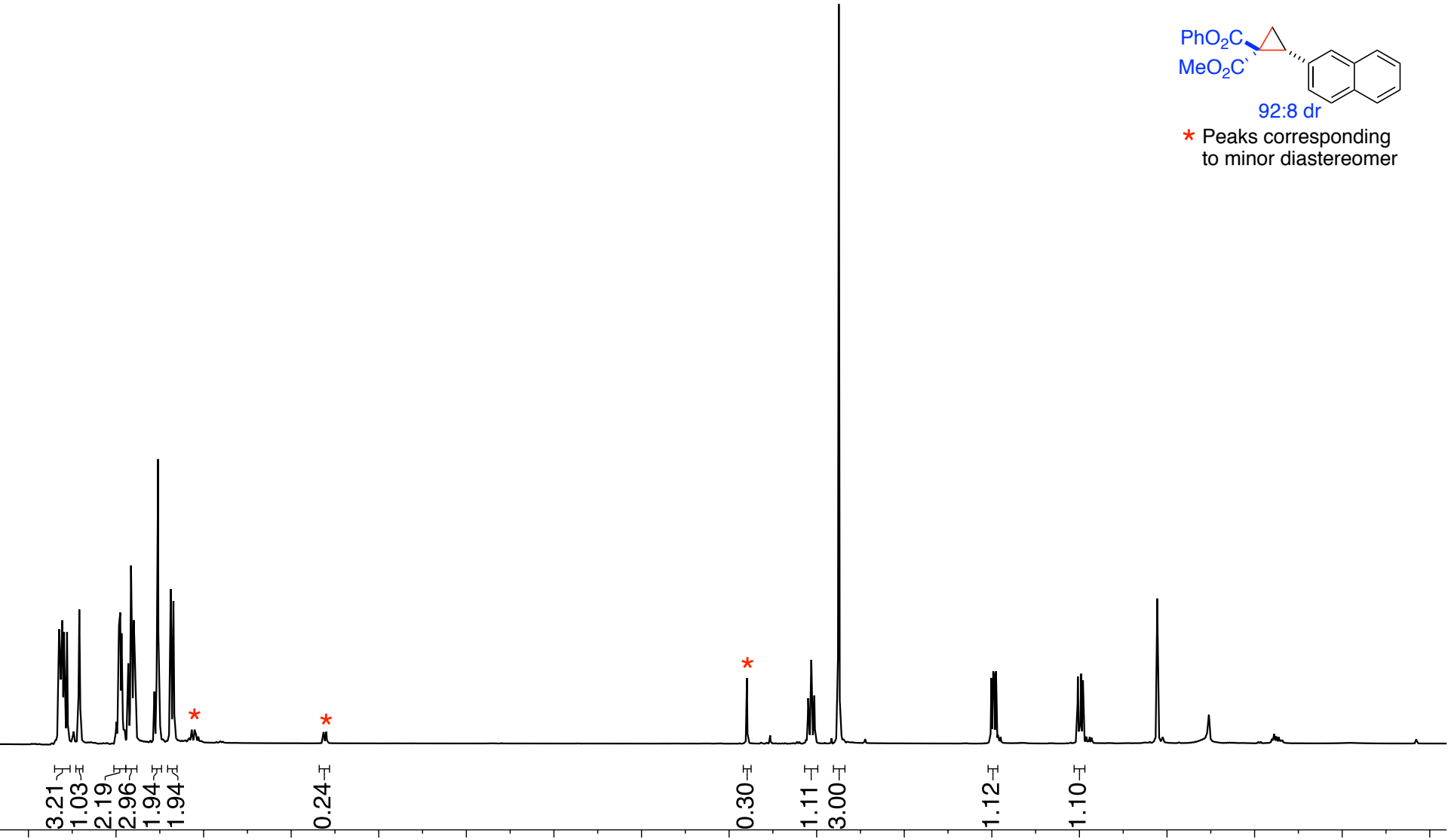


Peak Table

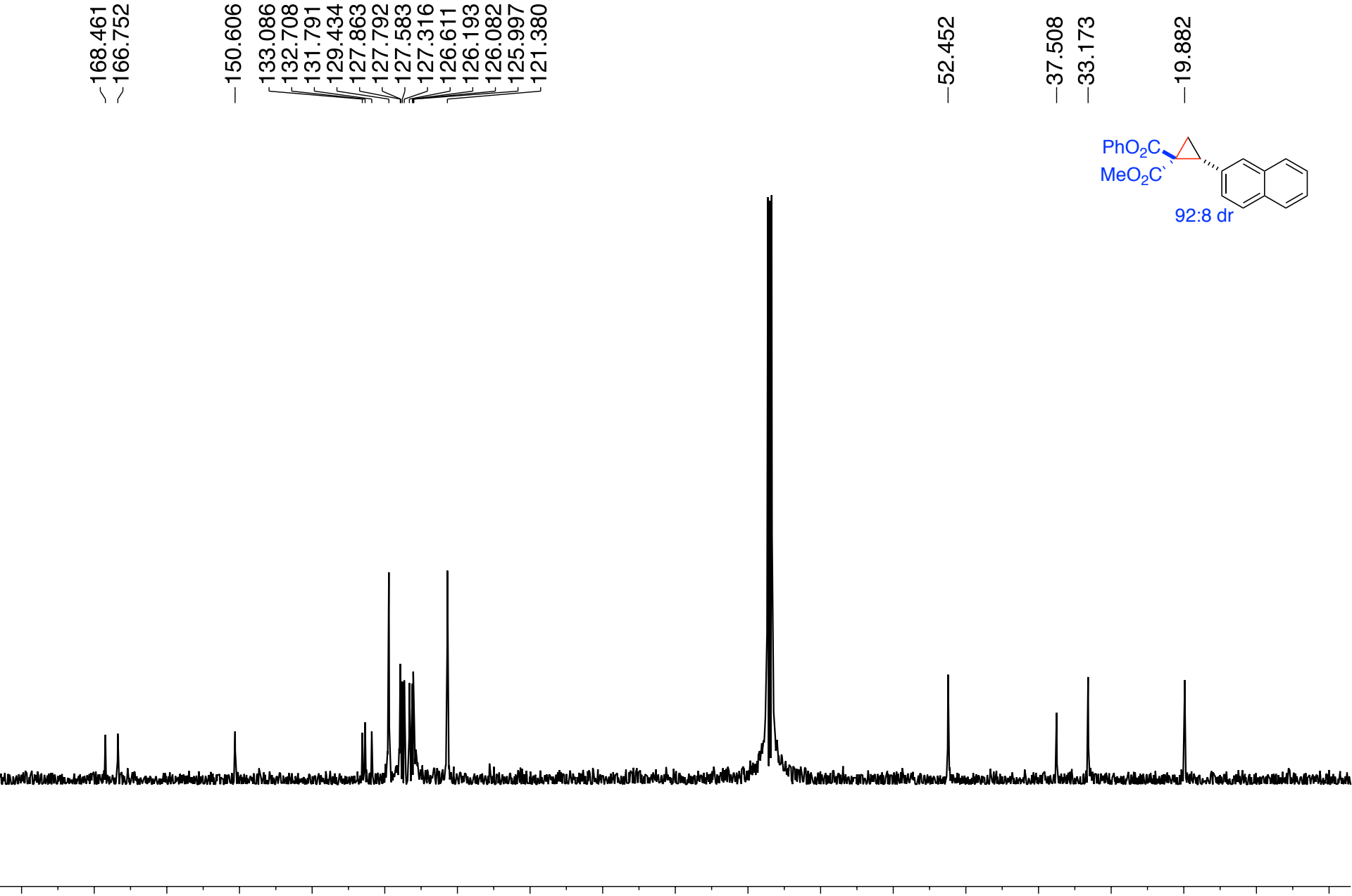
PDA Ch1 240nm

Peak#	Ret. Time	Area	Area%
1	11.742	2252112	99.527
2	16.790	10695	0.473
Total		2262807	100.000

1-methyl 1-phenyl (1*S*,2*R*)-2-(naphthalen-2-yl)cyclopropane-1,1-dicarboxylate

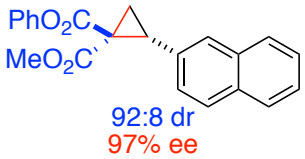


1-methyl 1-phenyl (1*S*,2*R*)-2-(naphthalen-2-yl)cyclopropane-1,1-dicarboxylate

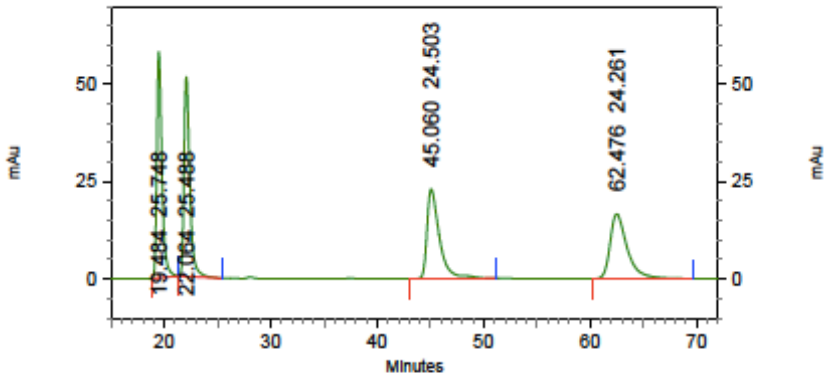


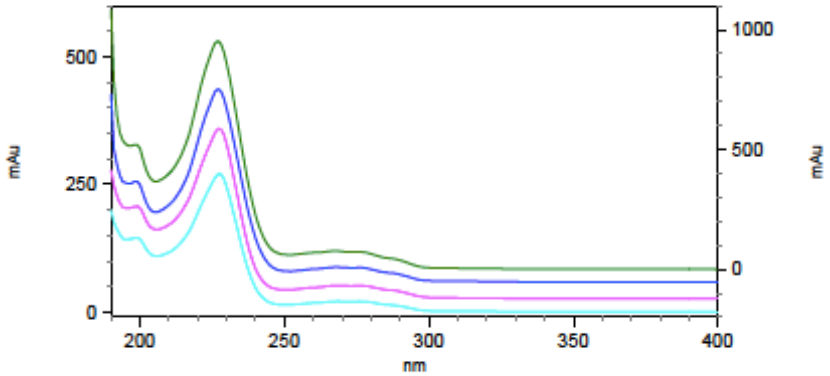
1-methyl 1-phenyl (1*S*,2*R*)-2-(naphthalen-2-yl)cyclopropane-1,1-dicarboxylate

JYW-II-142A-newADH-2%-1ml
C:\EZStart\Projects\Default\Method\LK-10%-0.8-90min.met
C:\EZStart\Projects\Default\Data\JYW-II-142A-newADH-2%-1ml



92:8 dr
97% ee





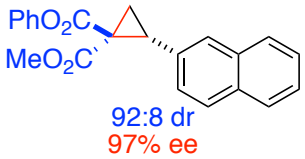
4: 235 nm, 4 nm
Results

Name	Retention Time	Area Percent	Pk #
	19.484	25.748	1
	22.064	25.488	2
	45.060	24.503	3
	62.476	24.261	4

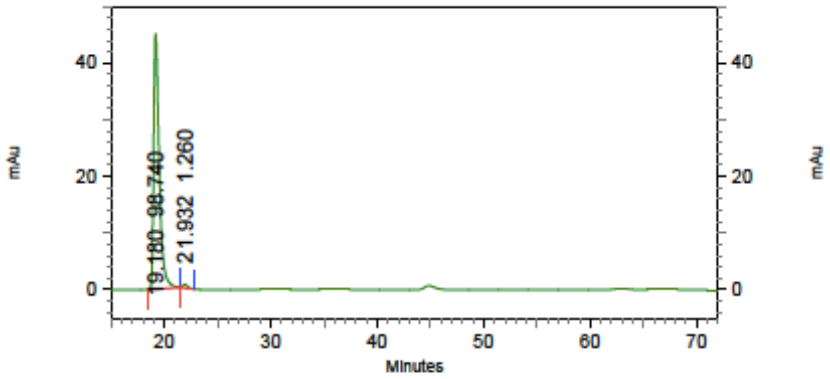
Totals	100.000

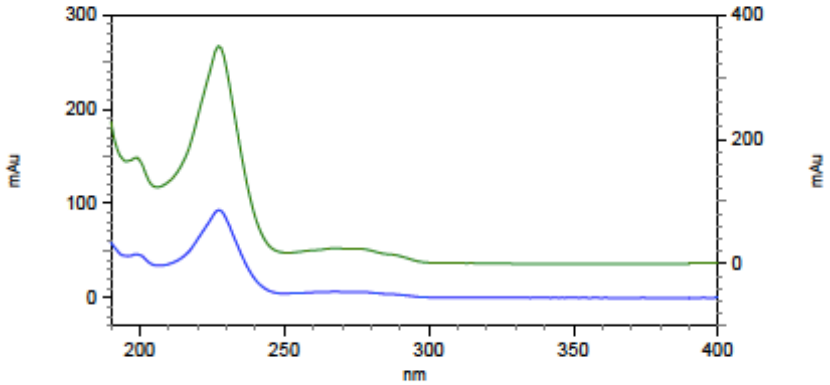
1-methyl 1-phenyl (1*S*,2*R*)-2-(naphthalen-2-yl)cyclopropane-1,1-dicarboxylate

JYW-II-142B-newADH-2%-1ml
C:\EZStart\Projects\Default\Method\LK-10%-0.8-90min.met
C:\EZStart\Projects\Default\Data\JYW-II-142B-newADH-2%-1ml



92:8 dr
97% ee



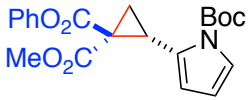


4: 245 nm, 4 nm
Results

Name	Retention Time	Area Percent	Pk #
	19.180	98.740	1
	21.932	1.260	2

Totals	
	100.000

1-methyl 1-phenyl (1*S*,2*S*)-2-(1-(*tert*-butoxycarbonyl)-1*H*-pyrrol-2-yl)cyclopropane-1,1-dicarboxylate

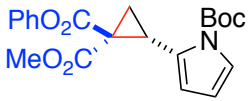


83:17 dr

* Peaks corresponding to minor diastereomer

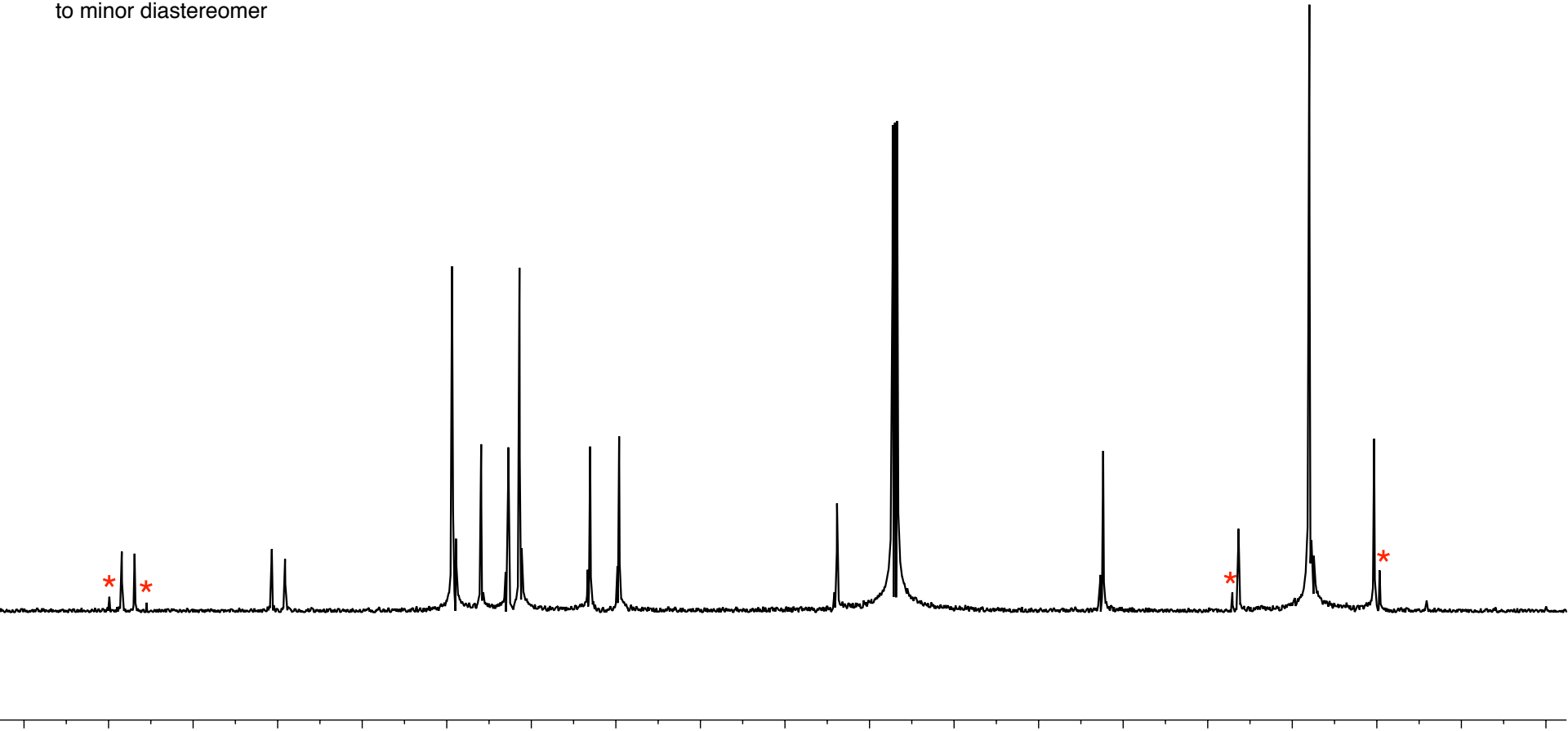
1-methyl 1-phenyl (1*S*,2*S*)-2-(1-(*tert*-butoxycarbonyl)-1*H*-pyrrol-2-yl)cyclopropane-1,1-dicarboxylate

168.435
166.923
150.689
149.122
129.377
125.930
122.720
121.397
113.039
109.613
83.846
52.369
36.362
27.978
27.813
20.321



83:17 dr

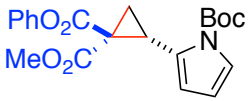
* Peaks corresponding to minor diastereomer



1-methyl 1-phenyl (1*S*,2*S*)-2-(1-(*tert*-butoxycarbonyl)-1*H*-pyrrol-2-yl)cyclopropane-1,1-dicarboxylate

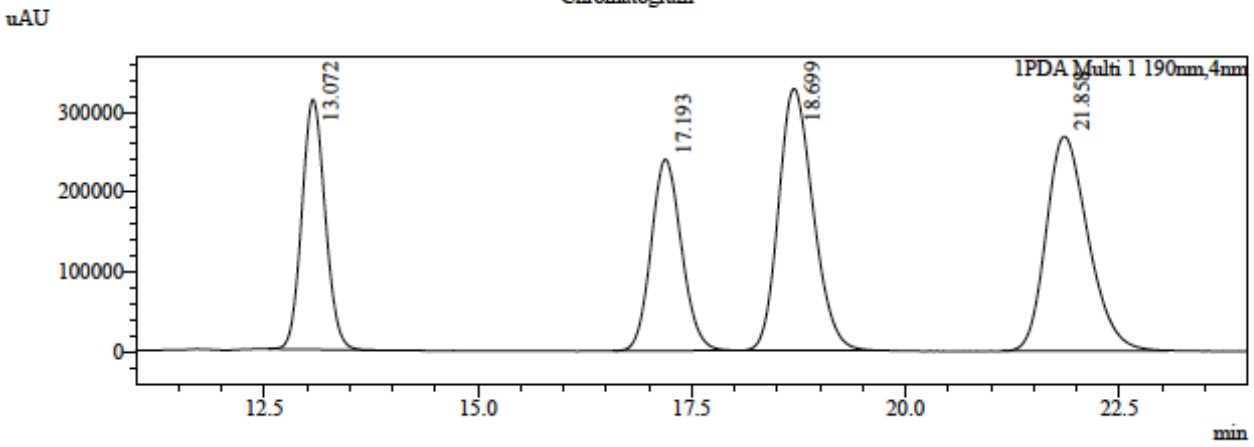
Sample Information

Sample Name	:
Sample ID	: JYW-II-134-IC-4%-0.8ml
Data File	: JYW-II-134-IC-4%-0.8ml.lcd
Method File	: JYW-method.lcm
Date Acquired	: 9/30/2015 8:48:20 PM



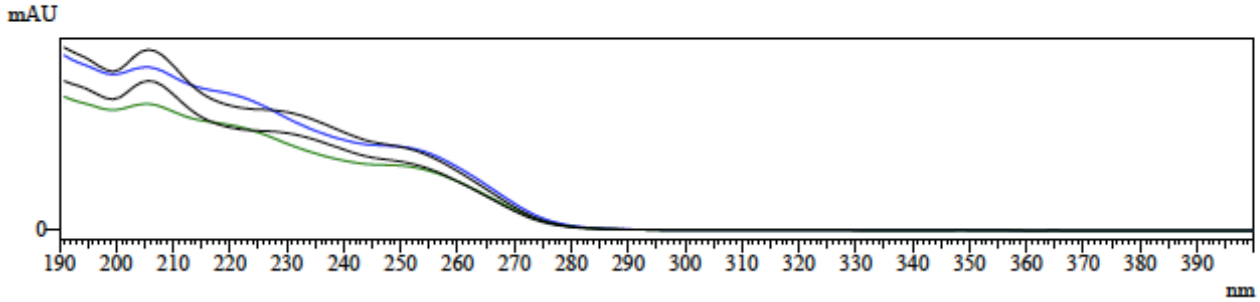
83:17 dr
74% ee

Chromatogram



UV Spectrum

JYW-II-134-IC-4%-0.8ml.lcd

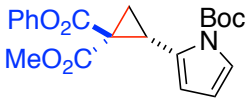


Peak Table

PDA Ch1 190nm

Peak#	Ret. Time	Area	Area%
1	13.072	5923851	19.609
2	17.193	5922288	19.604
3	18.699	9204952	30.471
4	21.858	9158044	30.315
Total		30209137	100.000

1-methyl 1-phenyl (1*S*,2*S*)-2-(1-(*tert*-butoxycarbonyl)-1*H*-pyrrol-2-yl)cyclopropane-1,1-dicarboxylate

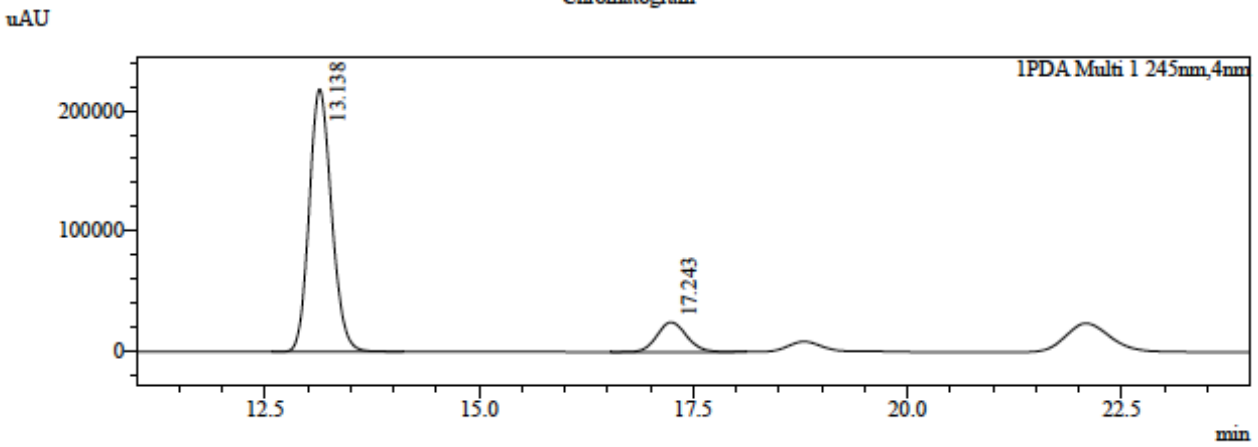


83:17 dr
74% ee

Sample Information

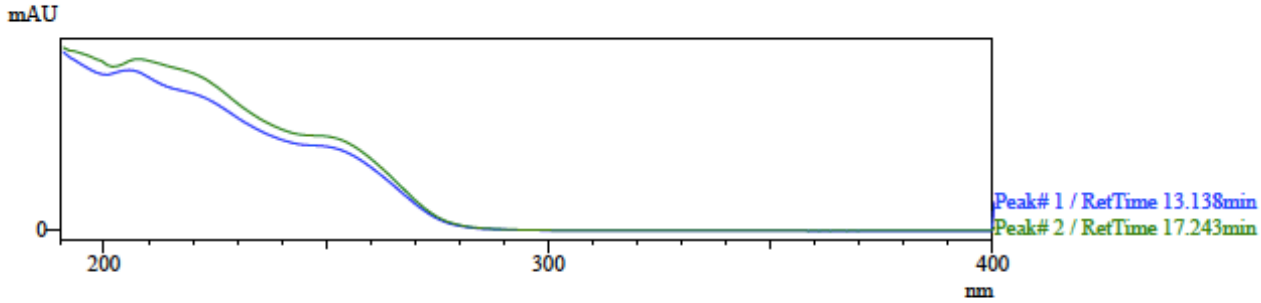
Sample Name	:
Sample ID	: JYW-II-242-IC-4%-0.8mlre1
Data File	: JYW-II-242-IC-4%-0.8mlre1.lcd
Method File	: JYW-method.lcm
Date Acquired	: 10/1/2015 4:09:35 PM

Chromatogram



UV Spectrum

JYW-II-242-IC-4%-0.8mlre1.lcd



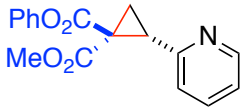
Peak Table

PDA Ch1 245nm

Peak#	Ret. Time	Area	Area%
1	13.138	3966636	86.935
2	17.243	596146	13.065
Total		4562782	100.000

1-methyl 1-phenyl (1*S*,2*S*)-2-(pyridin-2-yl)cyclopropane-1,1-dicarboxylate

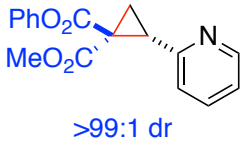
8.482 8.479 8.477 8.473 8.470 8.467 7.645 7.641 7.629 7.626 7.614 7.610 7.395 7.380 7.378 7.367 7.364 7.358 7.356 7.343 7.340 7.256 7.253 7.251 7.238 7.223 7.154 7.152 7.144 7.141 7.137 7.129 7.126 7.124 3.552 3.281 3.266 3.263 3.248 2.514 2.504 2.498 2.489 1.992 1.982 1.973 1.964



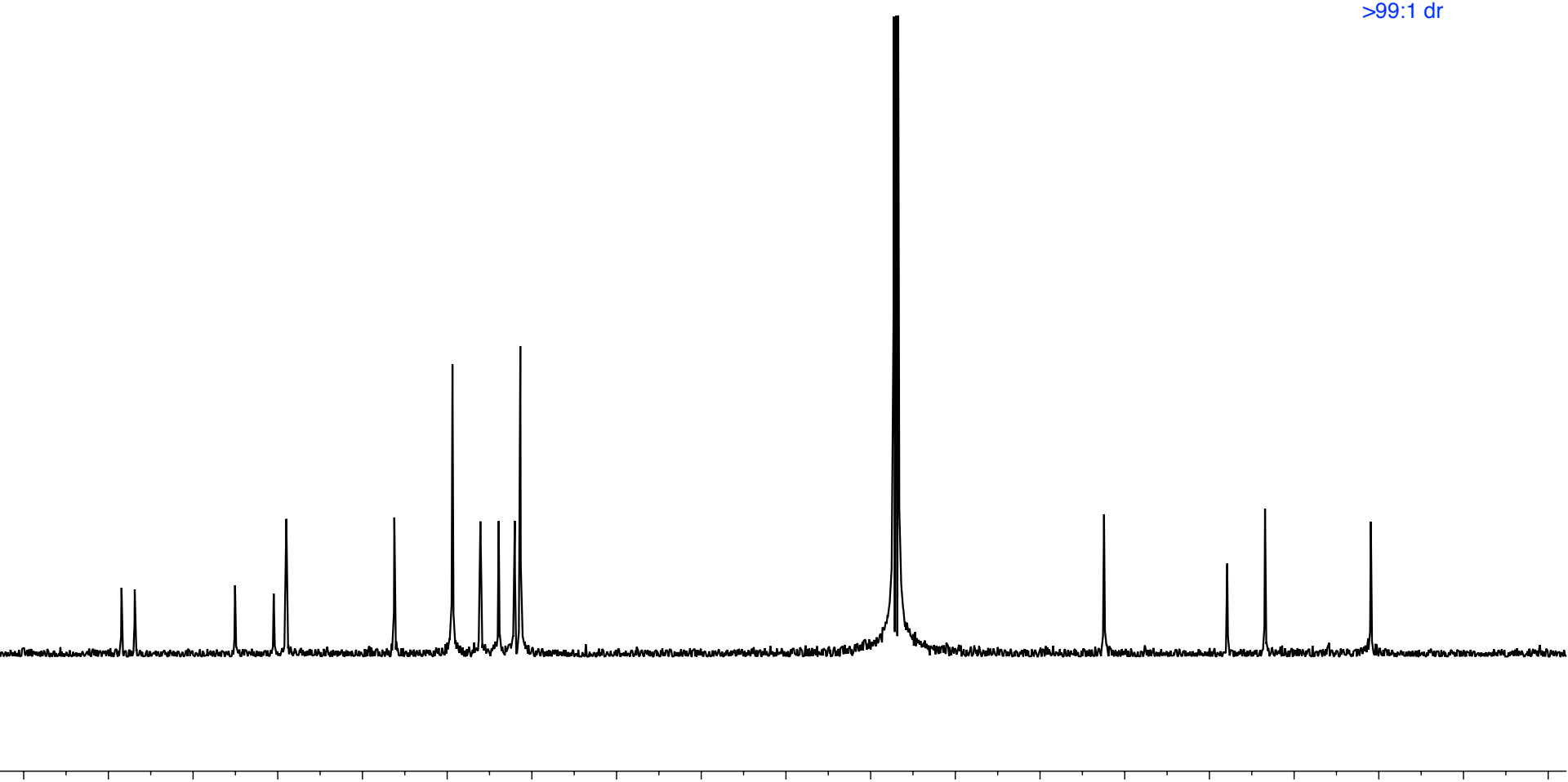
>99:1 dr

1-methyl 1-phenyl (1*S*,2*S*)-2-(pyridin-2-yl)cyclopropane-1,1-dicarboxylate

168.450
166.888
155.046
150.480
148.989
136.236
129.373
126.074
123.916
122.009
121.358
52.445
37.898
33.433
20.937



>99:1 dr

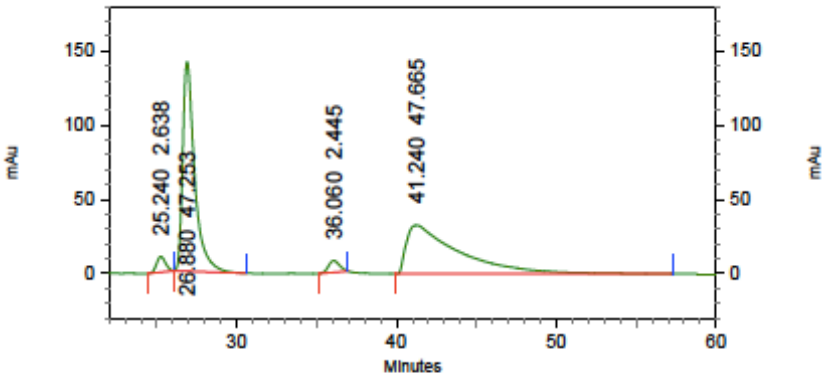


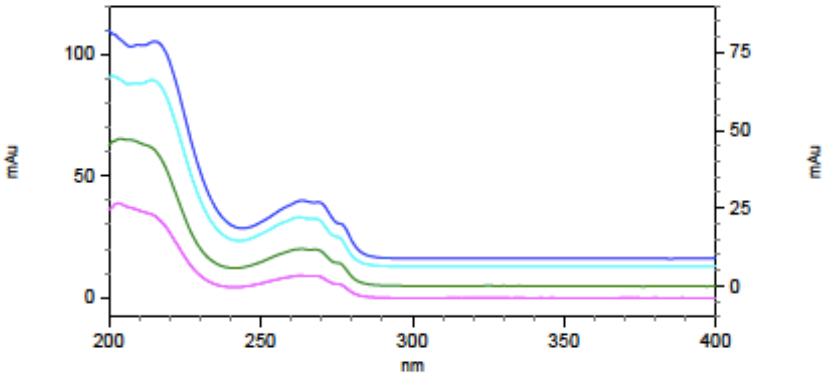
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

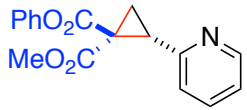
f1 (ppm)

1-methyl 1-phenyl (1*S*,2*S*)-2-(pyridin-2-yl)cyclopropane-1,1-dicarboxylate

JYW-II-202-ADH-2.5%-1ml
C:\EZStart\Projects\Default\Method\LK0.8-3%.met
C:\EZStart\Projects\Default\Data\JYW-II-202-ADH-2.5%-1ml







>99:1 dr
94% ee

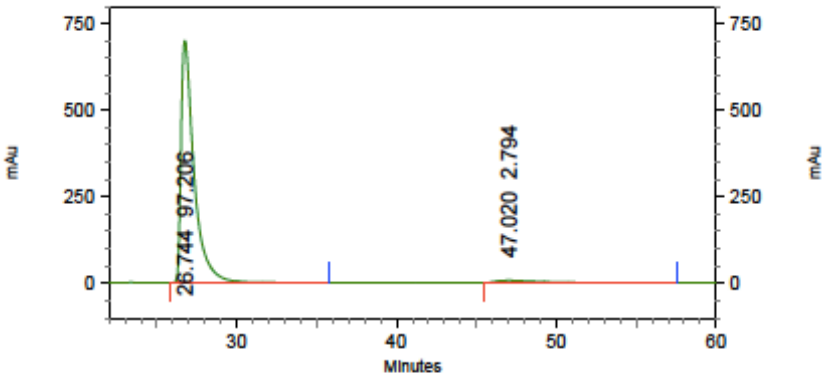
3: 260 nm, 4 nm
Results

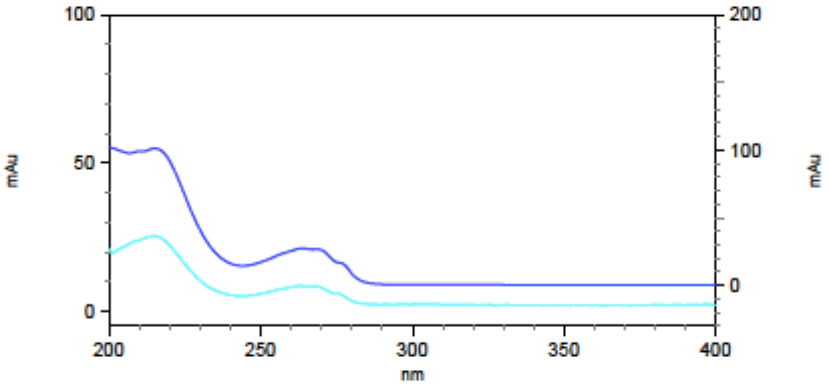
Name	Retention Time	Area Percent	Pk #
	25.240	2.638	1
	26.880	47.253	2
	36.060	2.445	3
	41.240	47.665	4

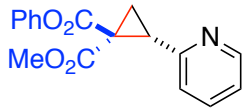
Totals	100.000

1-methyl 1-phenyl (1*S*,2*S*)-2-(pyridin-2-yl)cyclopropane-1,1-dicarboxylate

JYW-II-151-ADH-2.5%-1ml
C:\EZStart\Projects\Default\Method\LK0.8-3%.met
C:\EZStart\Projects\Default\Data\JYW-II-151-ADH-2.5%-1ml







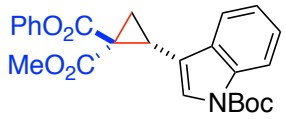
>99:1 dr
94% ee

3: 265 nm, 4 nm
Results

Name	Retention Time	Area Percent	Pk #
	26.744	97.206	1
	47.020	2.794	2

Totals	
	100.000

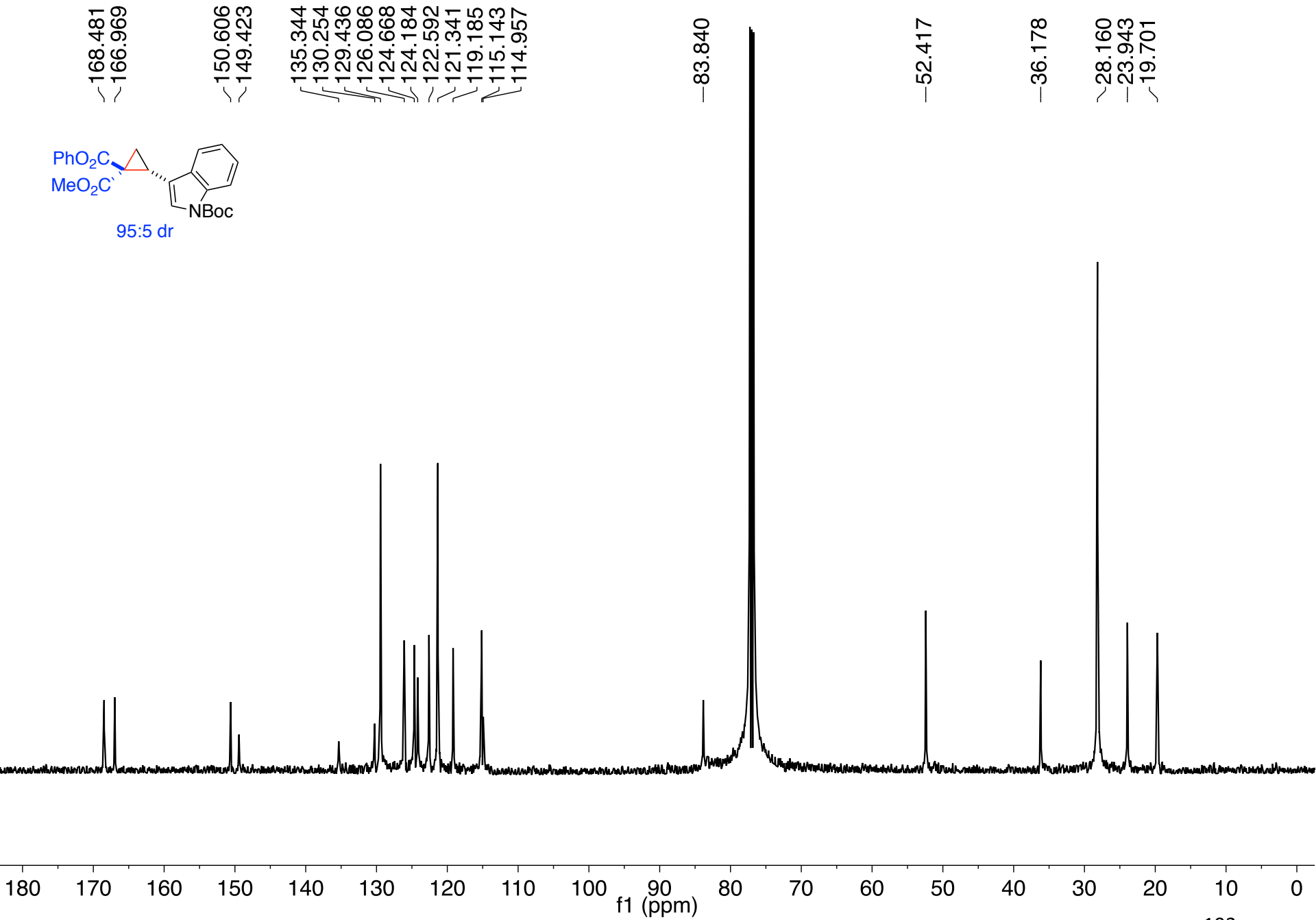
1-methyl 1-phenyl (1*S*,2*R*)-2-(1-(*tert*-butoxycarbonyl)-1*H*-indol-3-yl)cyclopropane-1,1-dicarboxylate



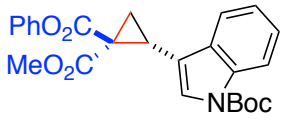
95:5 dr

* Peaks corresponding to minor diastereomer

1-methyl 1-phenyl (1*S*,2*R*)-2-(1-(*tert*-butoxycarbonyl)-1*H*-indol-3-yl)cyclopropane-1,1-dicarboxylate



1-methyl 1-phenyl (1*S*,2*R*)-2-(1-(*tert*-butoxycarbonyl)-1*H*-indol-3-yl)cyclopropane-1,1-dicarboxylate

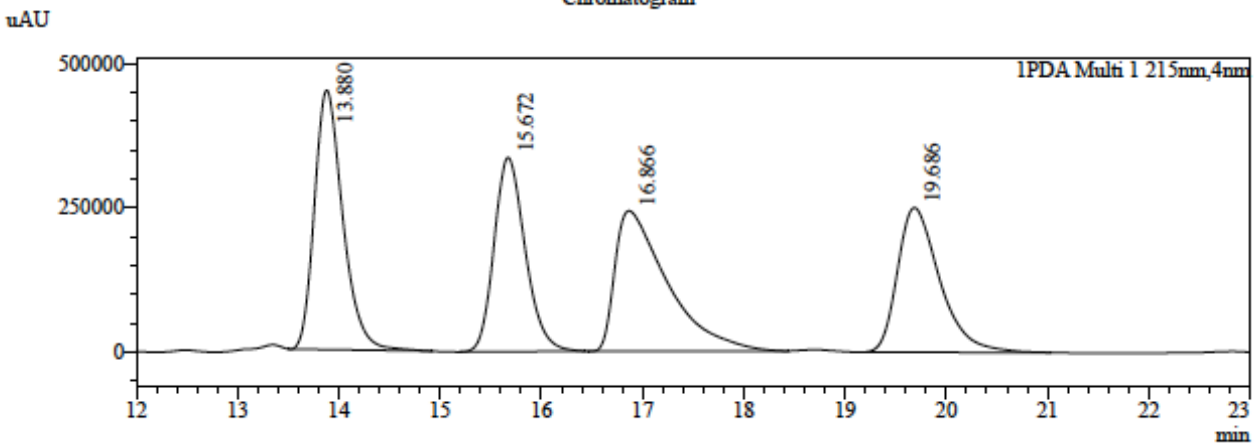


95:5 dr
94% ee

Sample Information

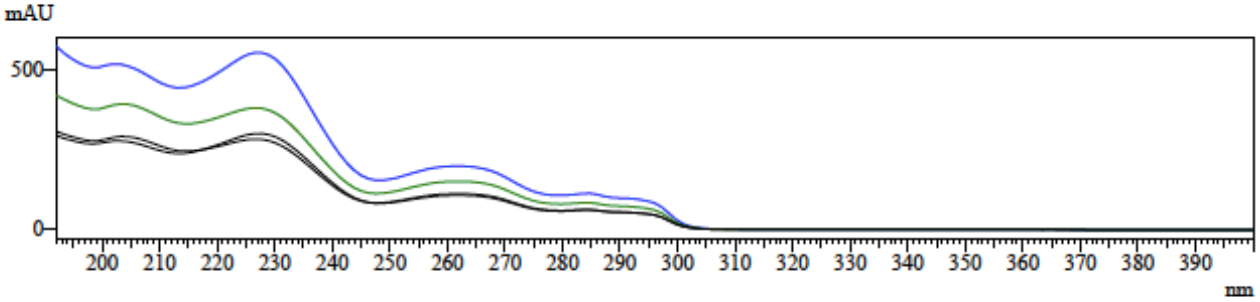
Sample Name	:
Sample ID	: JYW-II-243A-IF-2%-0.8mlre
Data File	: JYW-II-243A-IF-2%-0.8mlre.lcd
Method File	: JYW-method.lcm
Date Acquired	: 10/5/2015 8:52:07 PM

Chromatogram



UV Spectrum

JYW-II-243A-IF-2%-0.8mlre.lcd

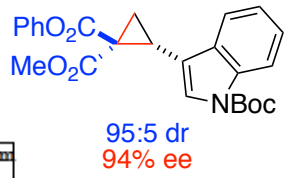


Peak Table

PDA Ch1 215nm

Peak#	Ret. Time	Area	Area%
1	13.880	8783285	27.437
2	15.672	7209545	22.521
3	16.866	8731120	27.274
4	19.686	7288469	22.768
Total		32012420	100.000

1-methyl 1-phenyl (1*S*,2*R*)-2-(1-(*tert*-butoxycarbonyl)-1*H*-indol-3-yl)cyclopropane-1,1-dicarboxylate

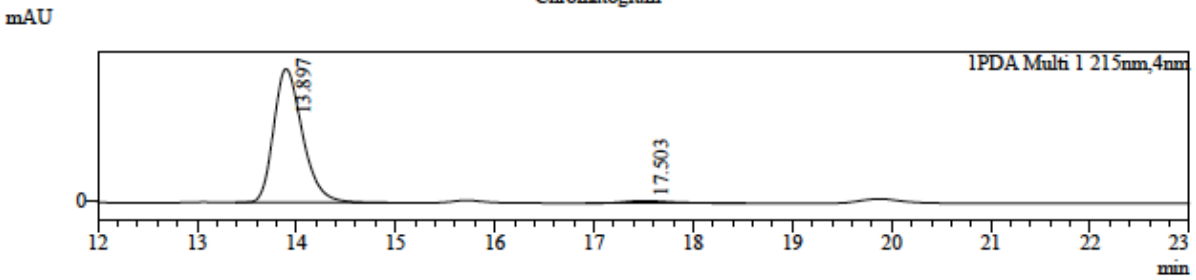


95:5 dr
94% ee

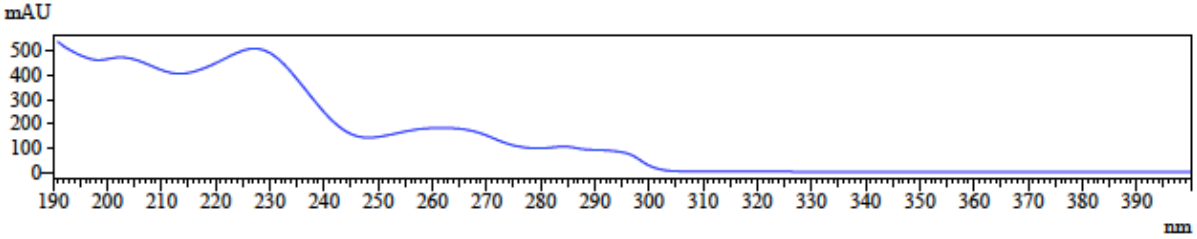
Sample Information

Sample Name :
Sample ID : JYW-II-243B-IF-2%-0.8ml
Data File : JYW-II-243B-IF-2%-0.8ml.lcd
Method File : JYW-method.lcm

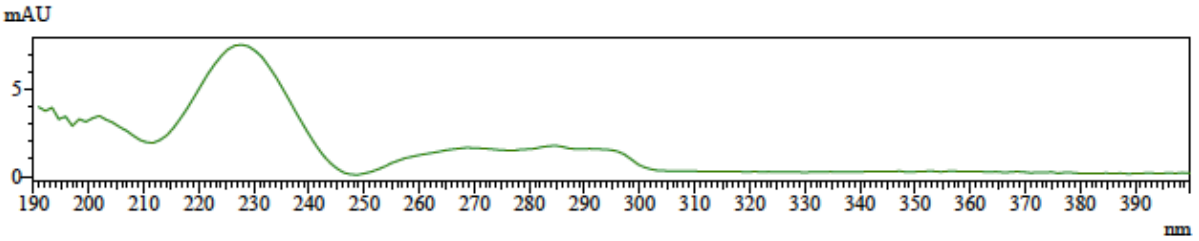
Chromatogram



UV Spectrum
Retention time = 13.897



UV Spectrum
Retention time = 17.503

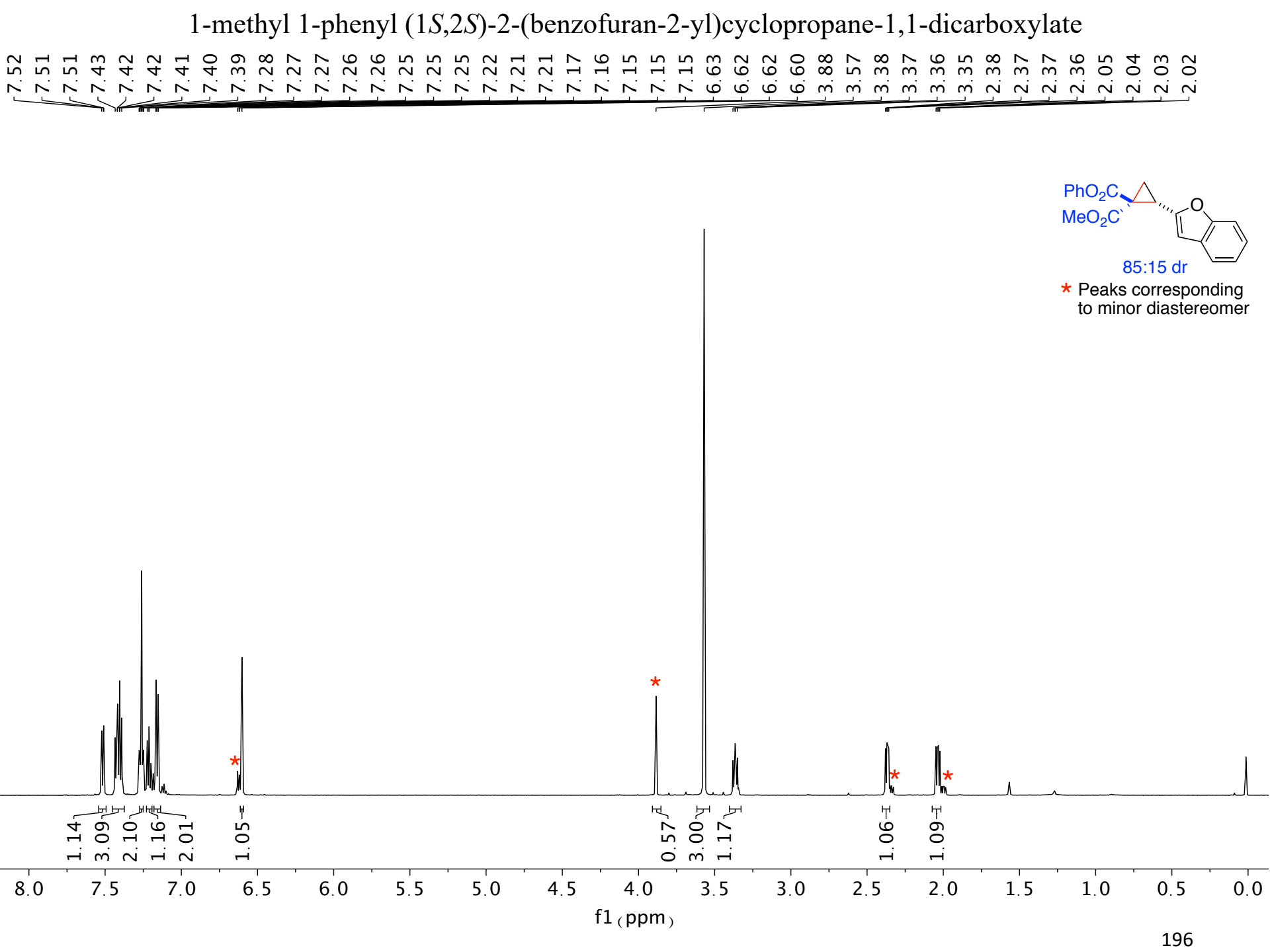


Peak Table

PDA Ch1 215nm

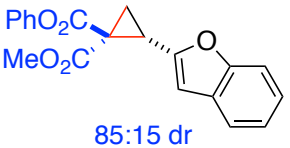
Peak#	Ret. Time	Area	Area%
1	13.897	8445249	97.088
2	17.503	253269	2.912
Total		8698518	100.000

1-methyl 1-phenyl (1*S*,2*S*)-2-(benzofuran-2-yl)cyclopropane-1,1-dicarboxylate



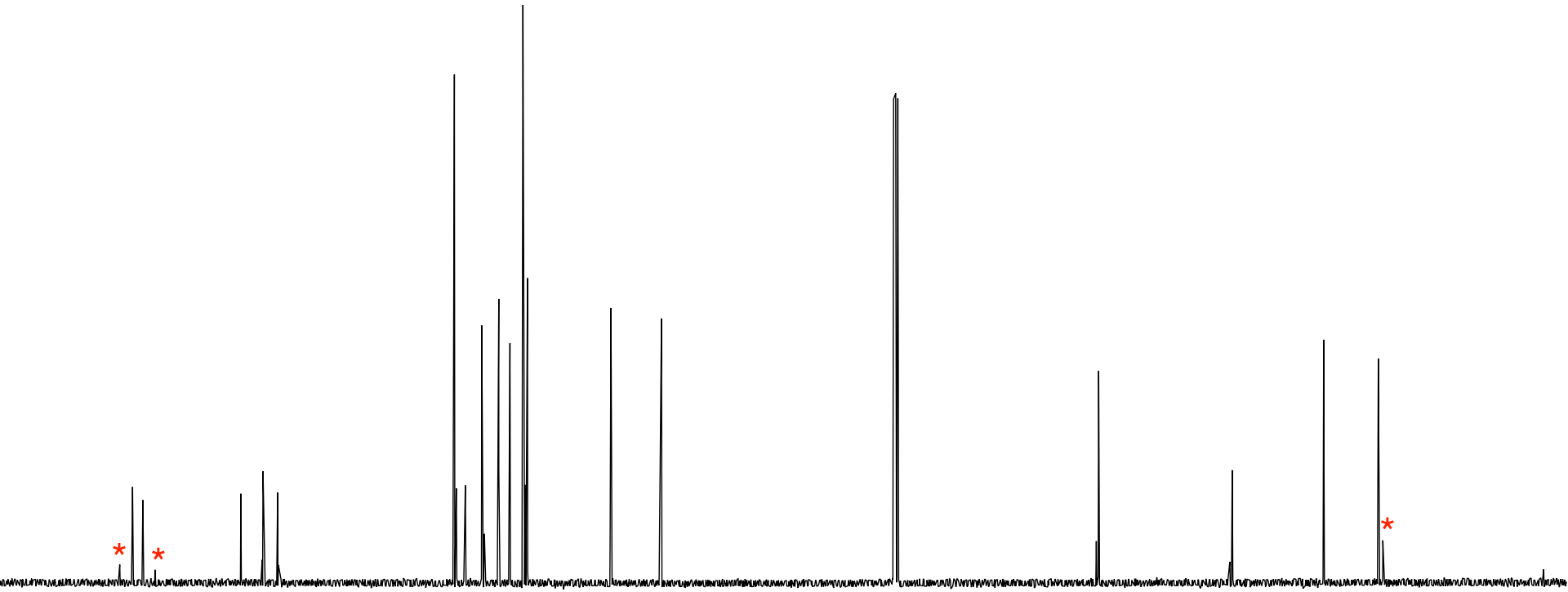
1-methyl 1-phenyl (1*S*,2*S*)-2-(benzofuran-2-yl)cyclopropane-1,1-dicarboxylate

167.72
166.50
154.85
152.21
150.47
129.46
128.17
126.21
124.19
122.86
121.31
120.78
110.85
104.85
52.88
37.00
26.13
19.63



85:15 dr

* Peaks corresponding to minor diastereomer

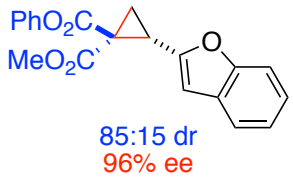


180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

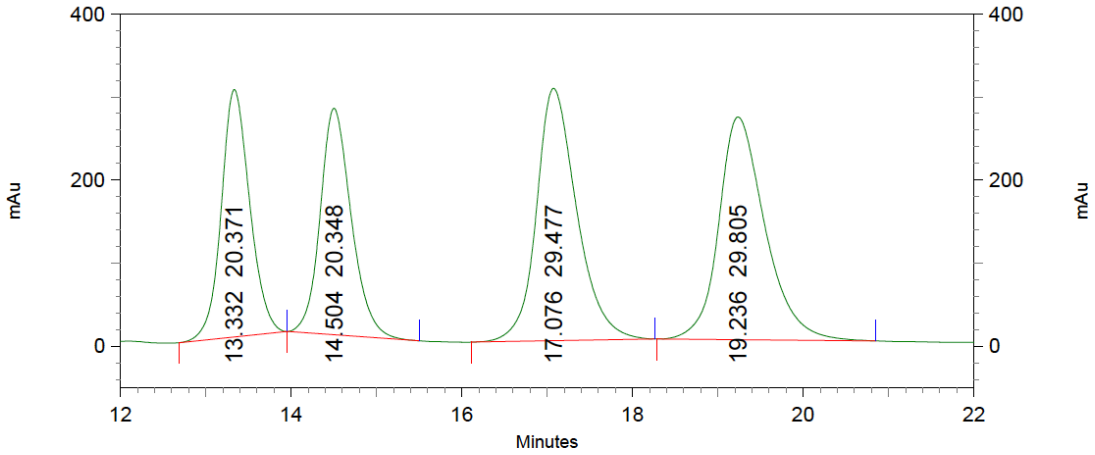
f1 (ppm)

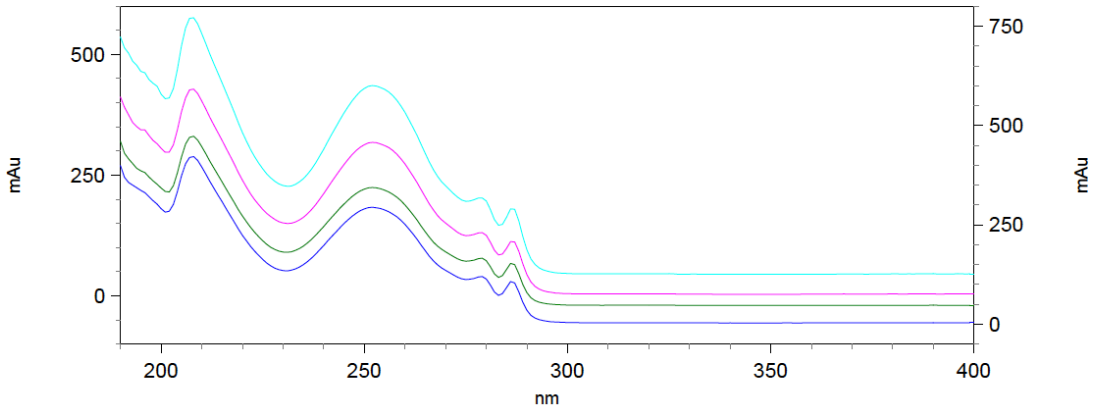
1-methyl 1-phenyl (1*S*,2*S*)-2-(benzofuran-2-yl)cyclopropane-1,1-dicarboxylate

C:\EZStart\Projects\Default\Data\JYW-0877-whelk-20%-0.8ml3
C:\EZStart\Projects\Default\Method\report-SMG.met



85:15 dr
96% ee





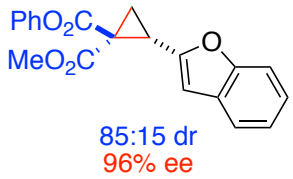
2: 255 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	13.332	20.371
2	14.504	20.348
3	17.076	29.477
4	19.236	29.805

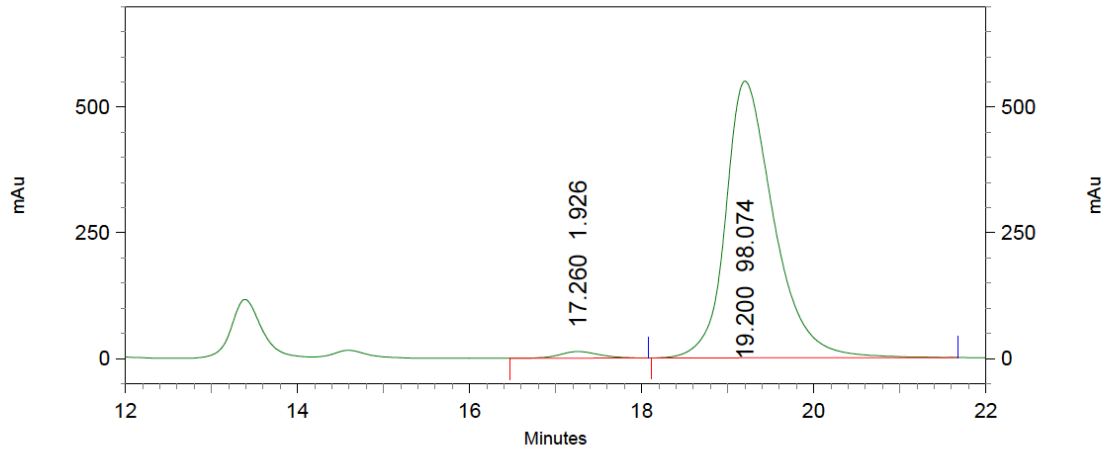
Totals		100.000

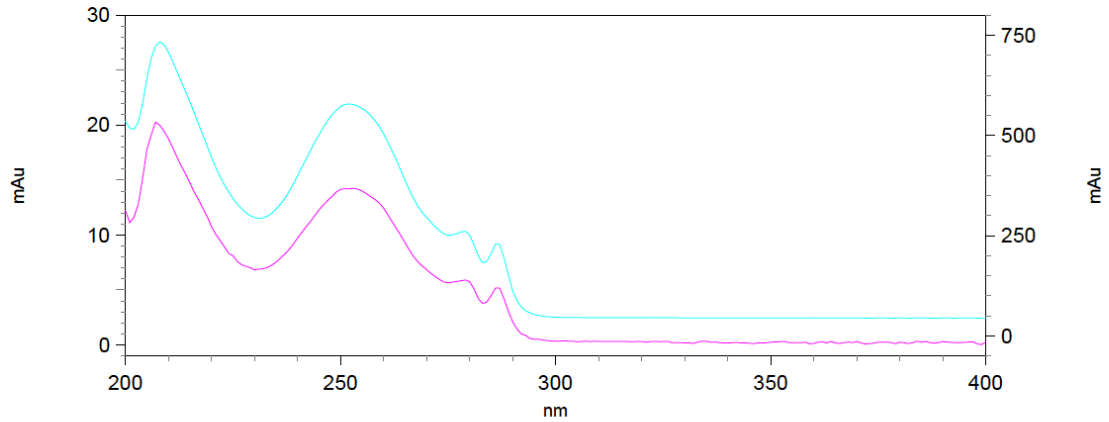
1-methyl 1-phenyl (1*S*,2*S*)-2-(benzofuran-2-yl)cyclopropane-1,1-dicarboxylate

C:\EZStart\Projects\Default\Data\JYW-0872-whelk-20%-0.8ml2
C:\EZStart\Projects\Default\Method\report-SMG.met



85:15 dr
96% ee



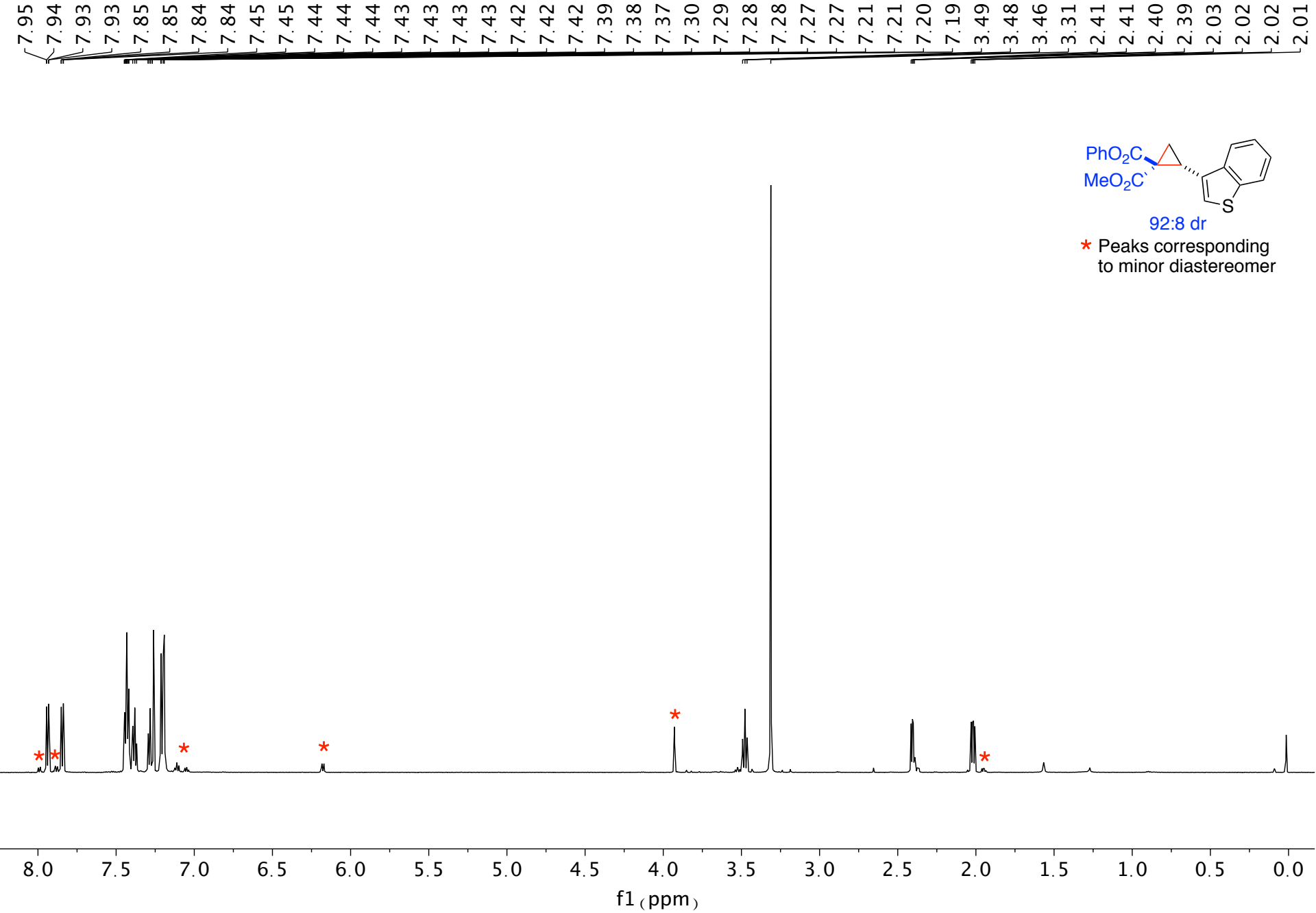


2: 255 nm, 4
nm Results

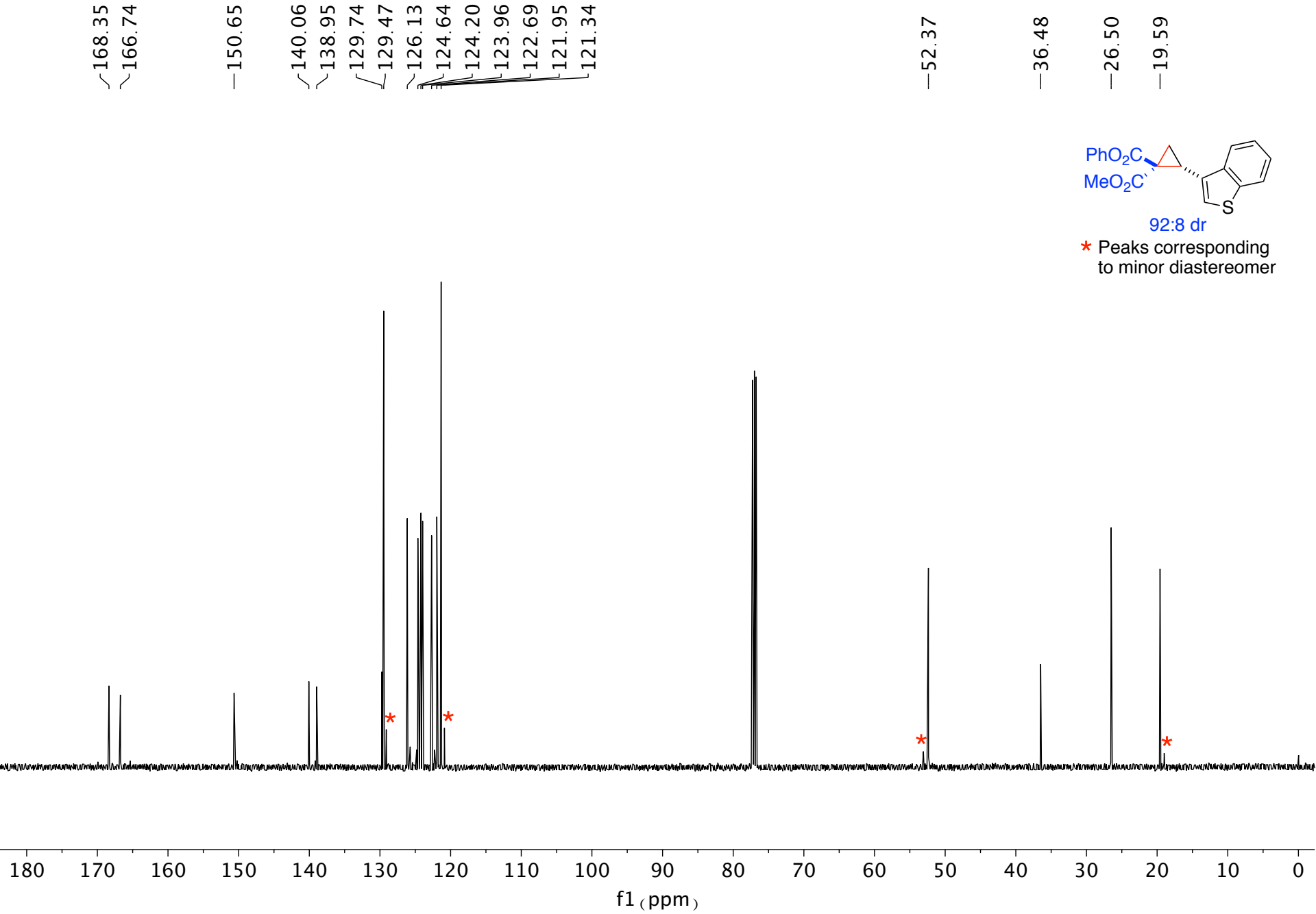
Pk #	Retention Time	Area Percent
1	17.260	1.926
2	19.200	98.074

Totals		100.000

1-methyl 1-phenyl (1*S*,2*S*)-2-(benzo[*b*]thiophen-3-yl)cyclopropane-1,1-dicarboxylate

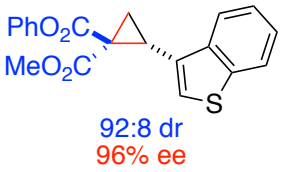


1-methyl 1-phenyl (1*S*,2*S*)-2-(benzo[*b*]thiophen-3-yl)cyclopropane-1,1-dicarboxylate

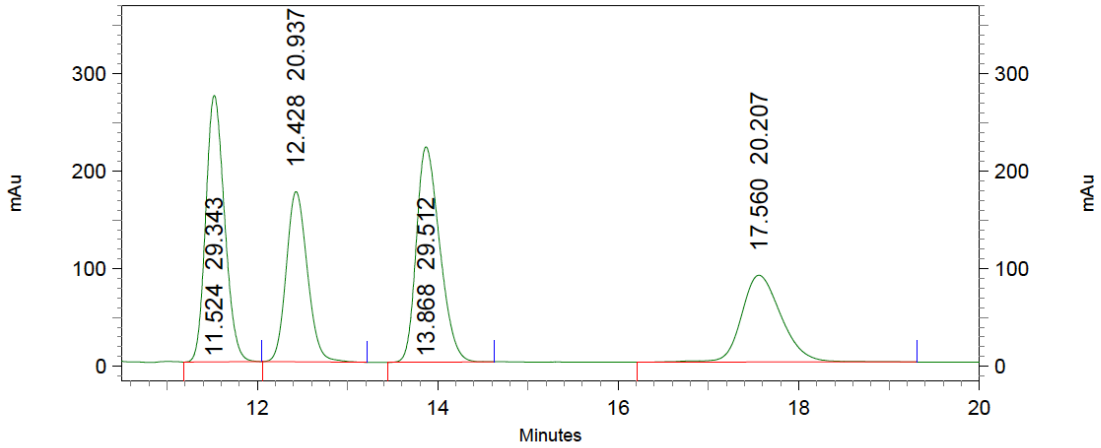


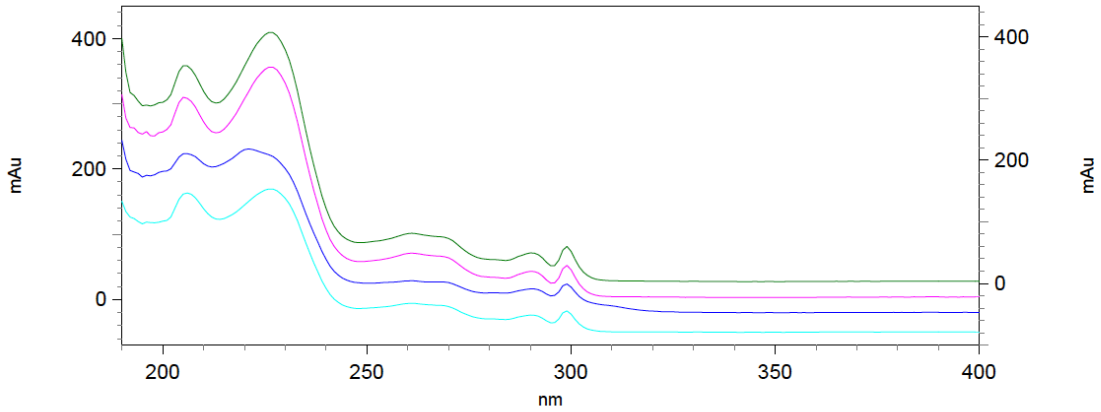
1-methyl 1-phenyl (1*S*,2*S*)-2-(benzo[*b*]thiophen-3-yl)cyclopropane-1,1-dicarboxylate

C:\EZStart\Projects\Default\Data\JYW-0869-ID-10%-0.8ml2
C:\EZStart\Projects\Default\Method\report-SMG.met



92:8 dr
96% ee



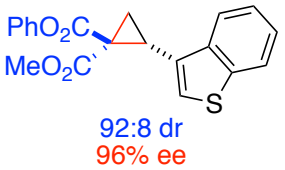


3: 268 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	11.524	29.343
2	12.428	20.937
3	13.868	29.512
4	17.560	20.207

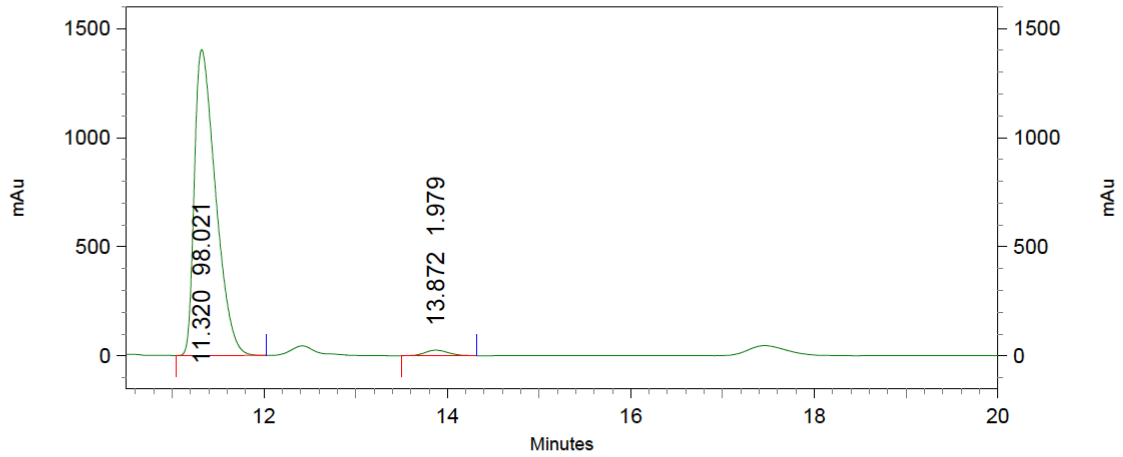
Totals		100.000

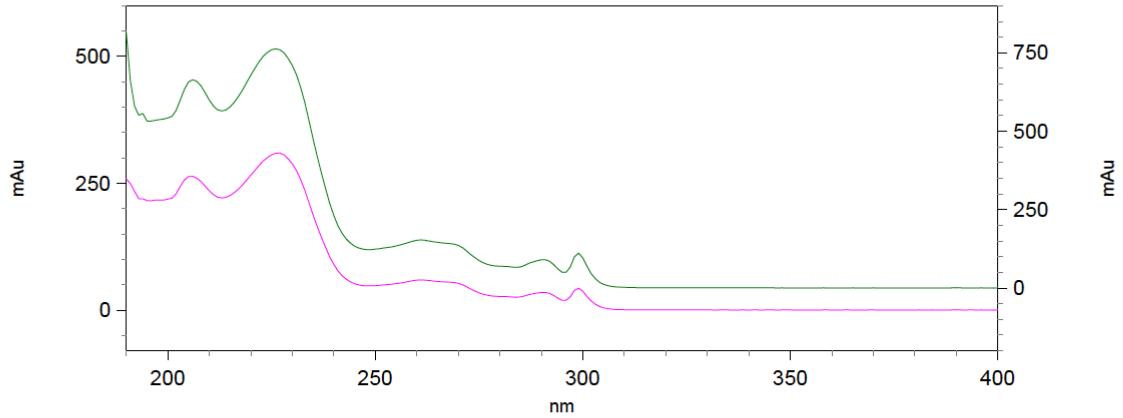
1-methyl 1-phenyl (1*S*,2*S*)-2-(benzo[*b*]thiophen-3-yl)cyclopropane-1,1-dicarboxylate



92:8 dr
96% ee

C:\EZStart\Projects\Default\Data\JYW-0870-ID-10%-0.8ml
C:\EZStart\Projects\Default\Method\report-SMG.met



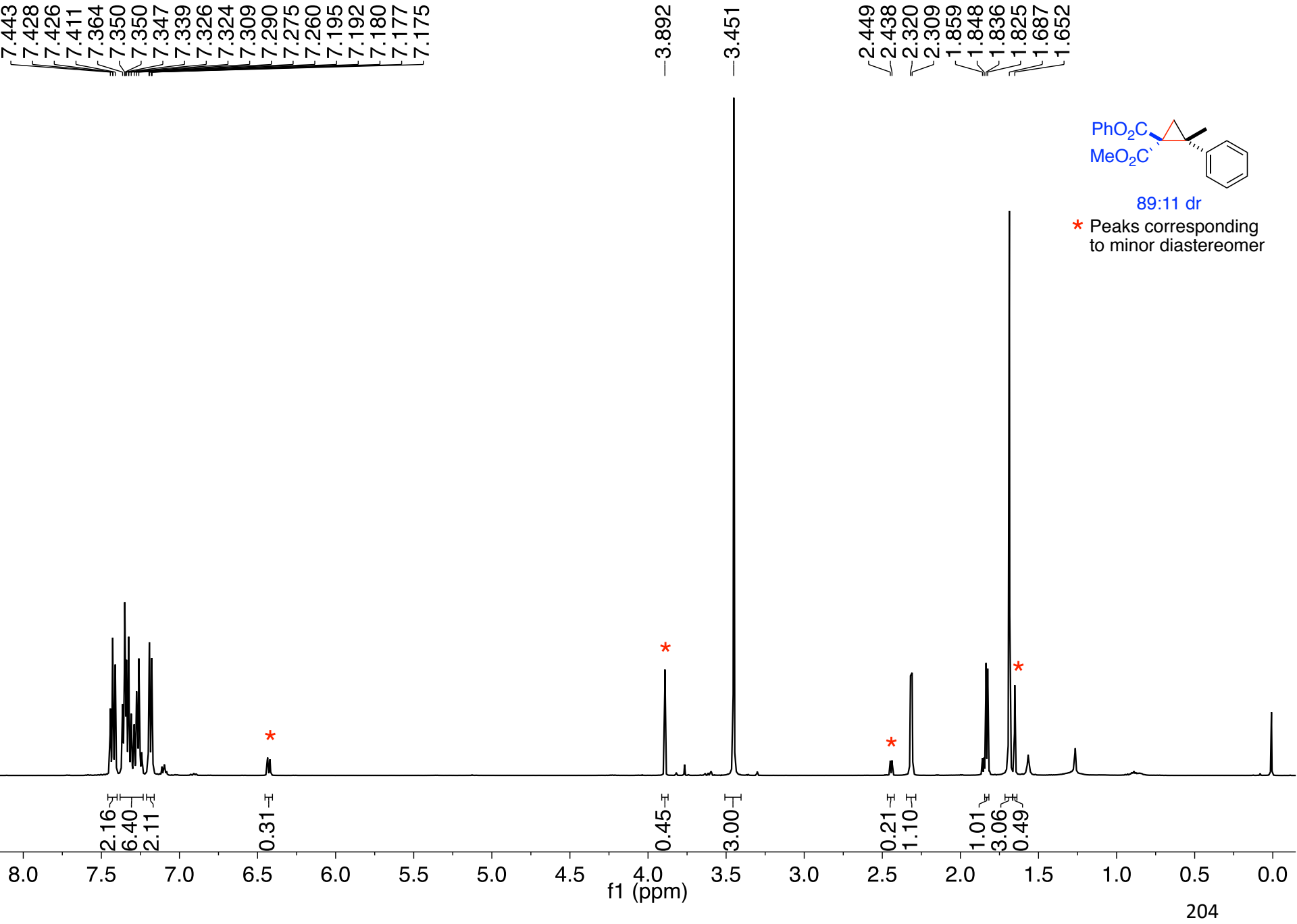


3: 282 nm, 4
nm Results

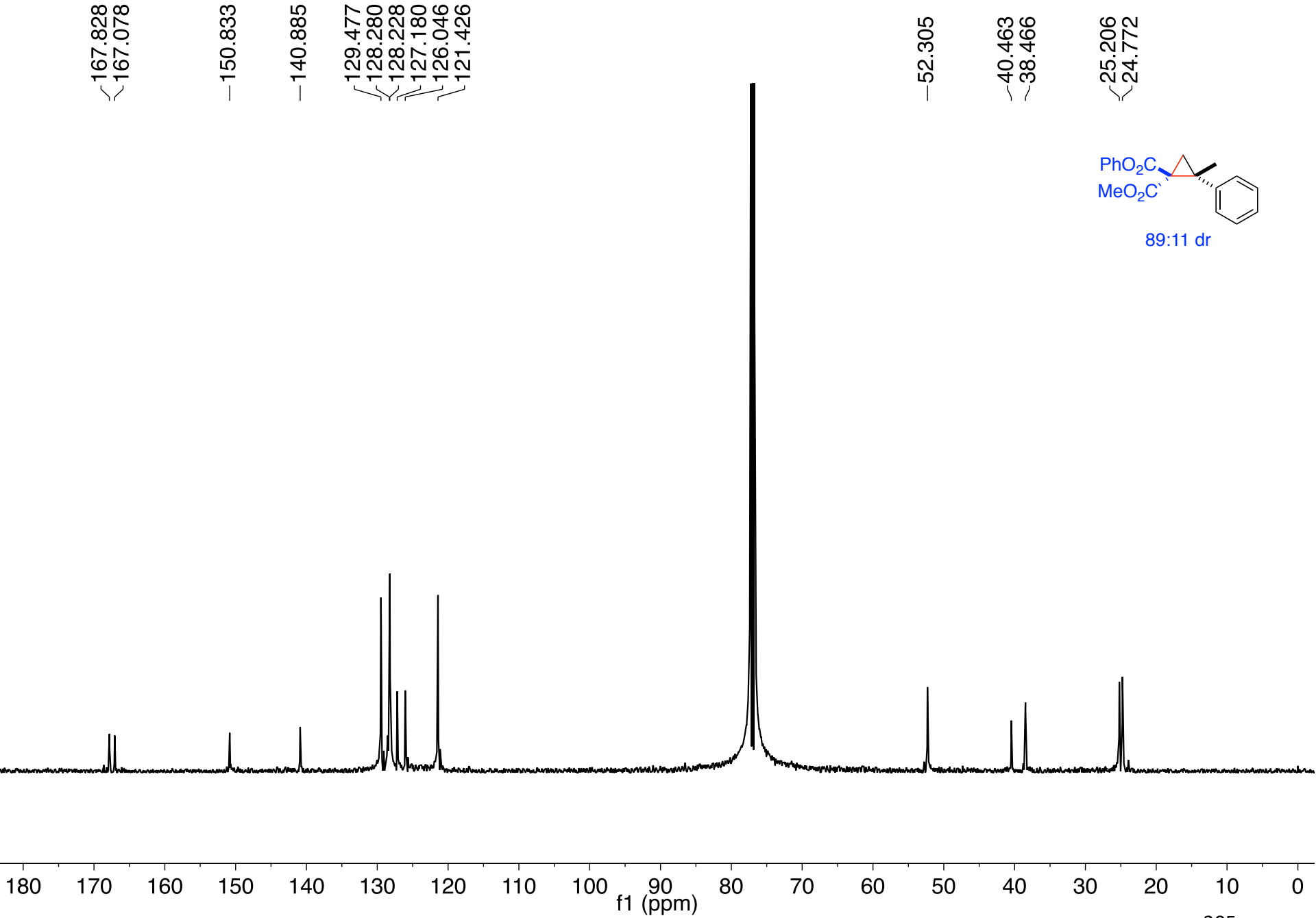
Pk #	Retention Time	Area Percent
1	11.320	98.021
2	13.872	1.979

Totals		100.000

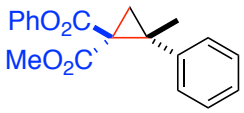
1-methyl 1-phenyl (1*S*,2*R*)-2-methyl-2-phenylcyclopropane-1,1-dicarboxylate



1-methyl 1-phenyl (1*S*,2*R*)-2-methyl-2-phenylcyclopropane-1,1-dicarboxylate



1-methyl 1-phenyl (1*S*,2*R*)-2-methyl-2-phenylcyclopropane-1,1-dicarboxylate

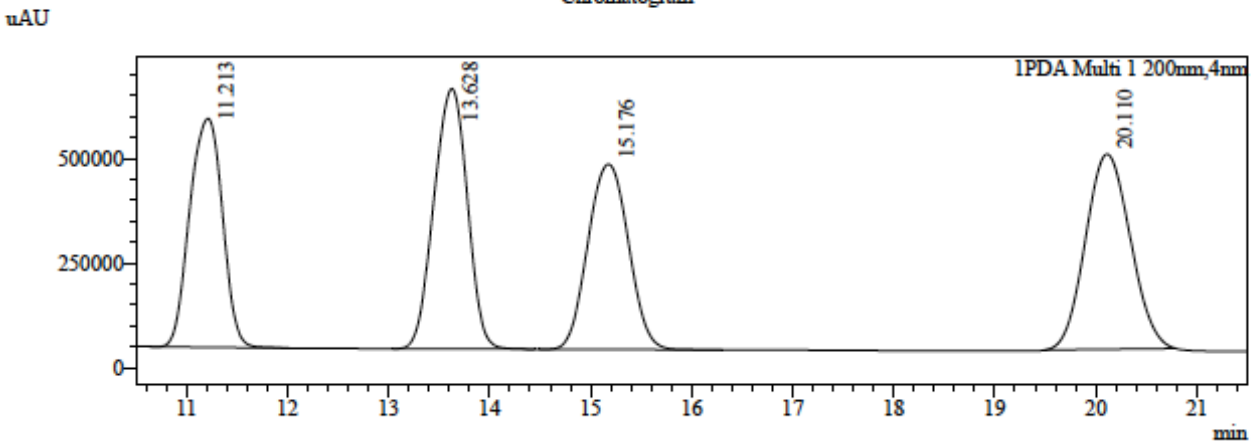


89:11 dr
97% ee

Sample Information

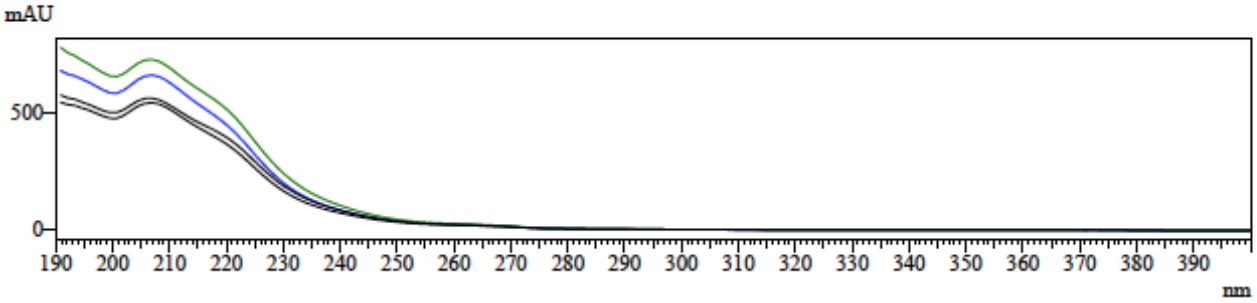
Sample Name	: JYW-II-165
Sample ID	: JYW-II-165-IC-8%-0.8mlre
Data File	: JYW-II-165-IC-8%-0.8mlre.lcd
Method File	: JYW-method.lcm
Date Acquired	: 10/10/2015 12:28:11 PM

Chromatogram



UV Spectrum

JYW-II-165-IC-8%-0.8mlre.lcd

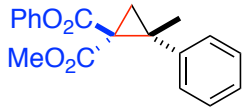


Peak Table

PDA Ch1 200nm

Peak#	Ret. Time	Area	Area%
1	11.213	12375109	23.128
2	13.628	14353166	26.825
3	15.176	12376432	23.131
4	20.110	14402228	26.917
Total		53506935	100.000

1-methyl 1-phenyl (1*S*,2*R*)-2-methyl-2-phenylcyclopropane-1,1-dicarboxylate

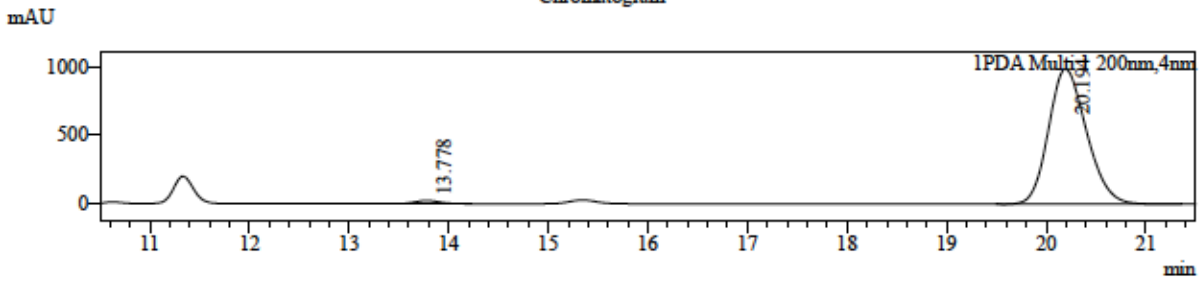


89:11 dr
97% ee

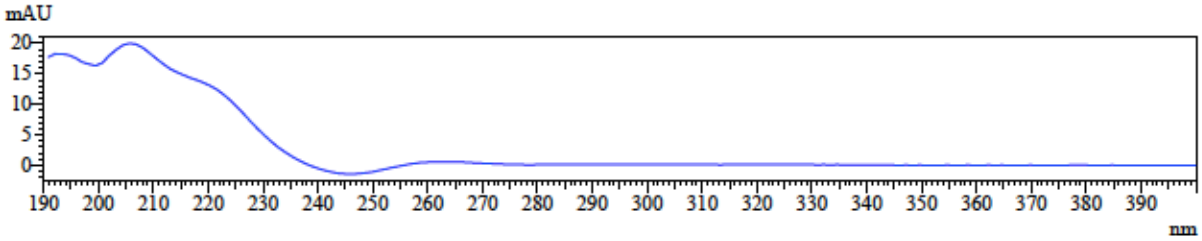
Sample Information

Sample Name : JYW-III-79
Sample ID : JYW-III-79-IC-8%-0.8mlre
Data File : JYW-III-79-IC-8%-0.8mlre.lcd
Method File : JYW-method.lcm

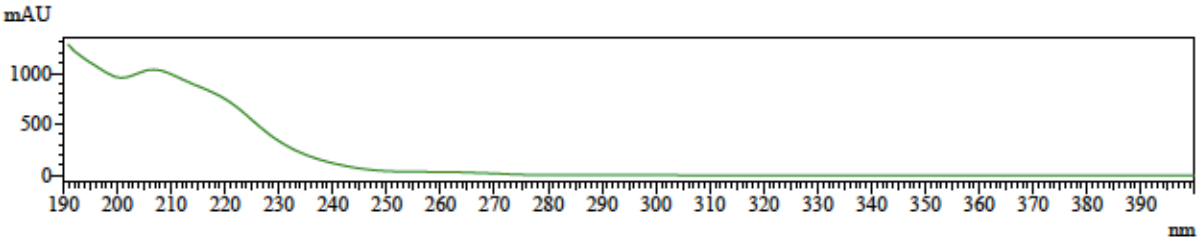
Chromatogram



UV Spectrum
Retention time = 13.778



UV Spectrum
Retention time = 20.194

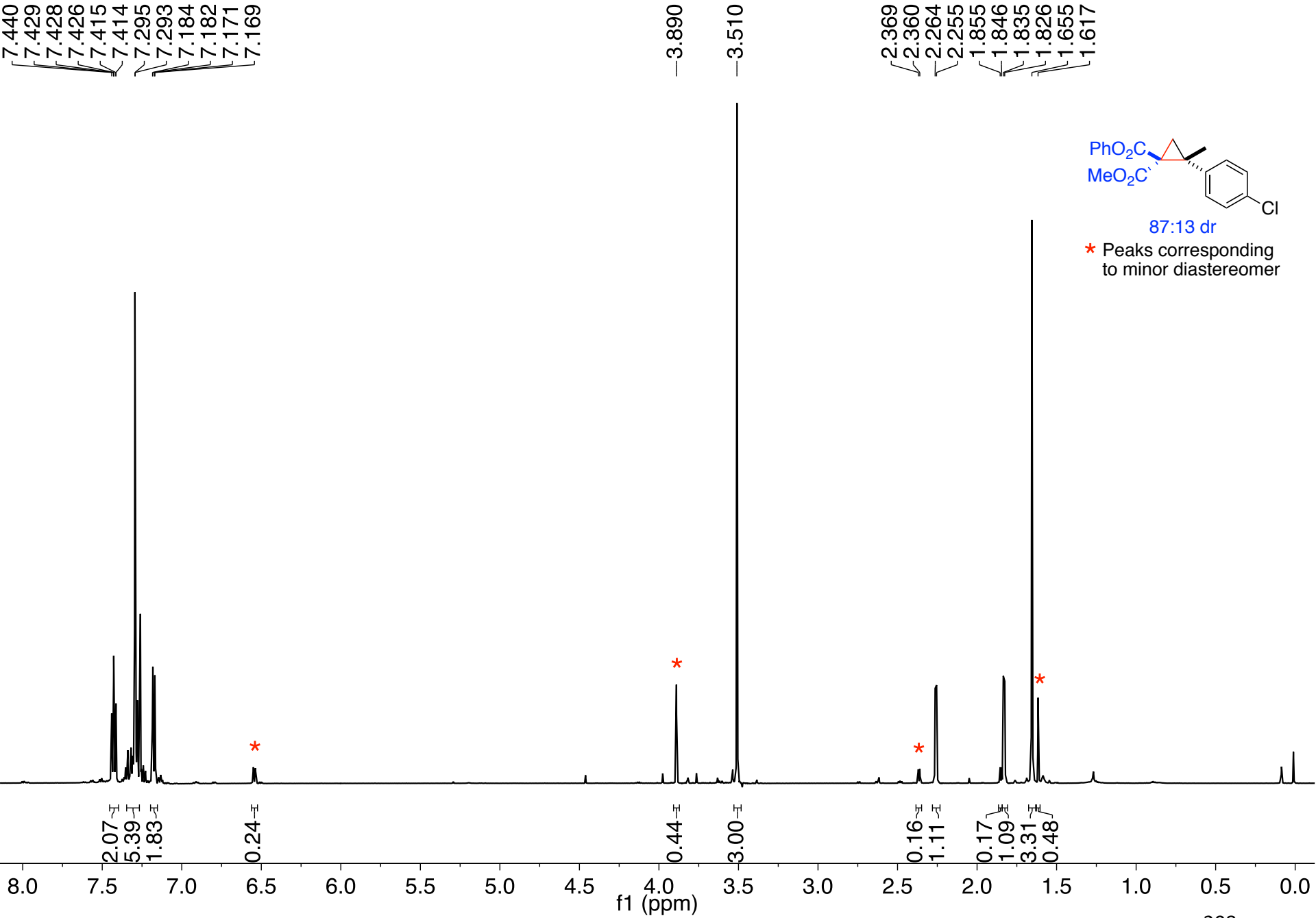


Peak Table

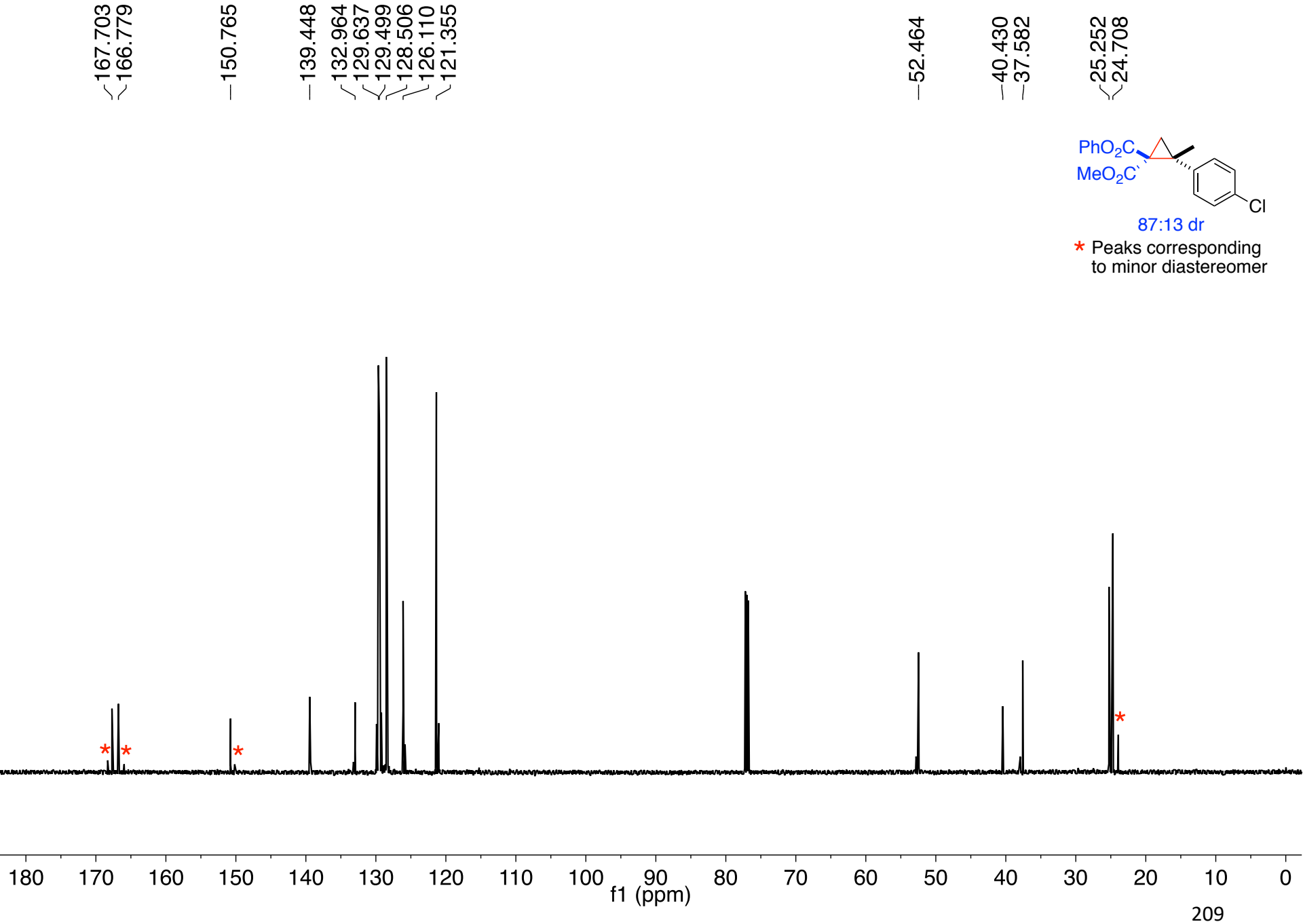
PDA Ch1 200nm

Peak#	Ret. Time	Area	Area%
1	13.778	393540	1.473
2	20.194	26318698	98.527
Total		26712238	100.000

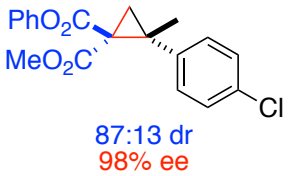
1-methyl 1-phenyl (1*S*,2*R*)-2-(4-chlorophenyl)-2-methylcyclopropane-1,1-dicarboxylate



1-methyl 1-phenyl (1*S*,2*R*)-2-(4-chlorophenyl)-2-methylcyclopropane-1,1-dicarboxylate



1-methyl 1-phenyl (1*S*,2*R*)-2-(4-chlorophenyl)-2-methylcyclopropane-1,1-dicarboxylate

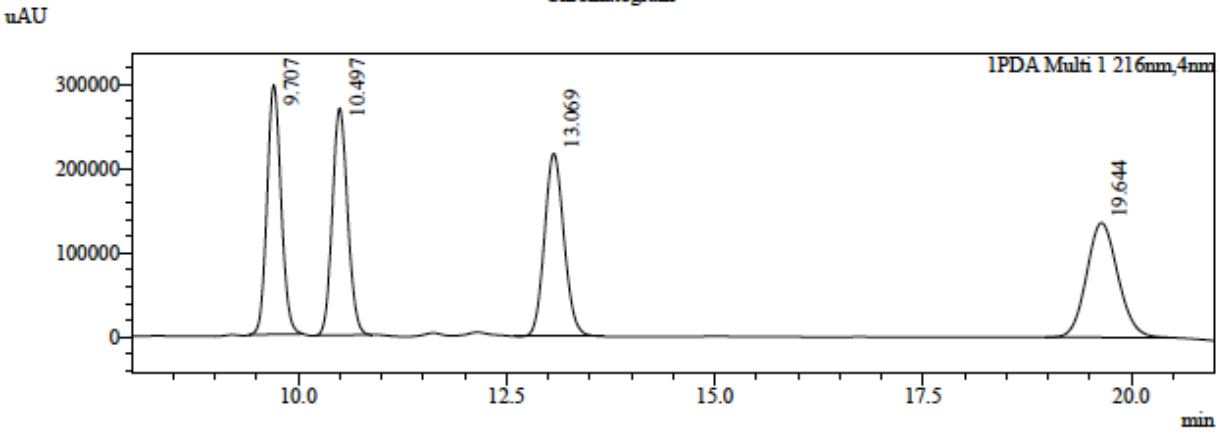


87:13 dr
98% ee

Sample Information

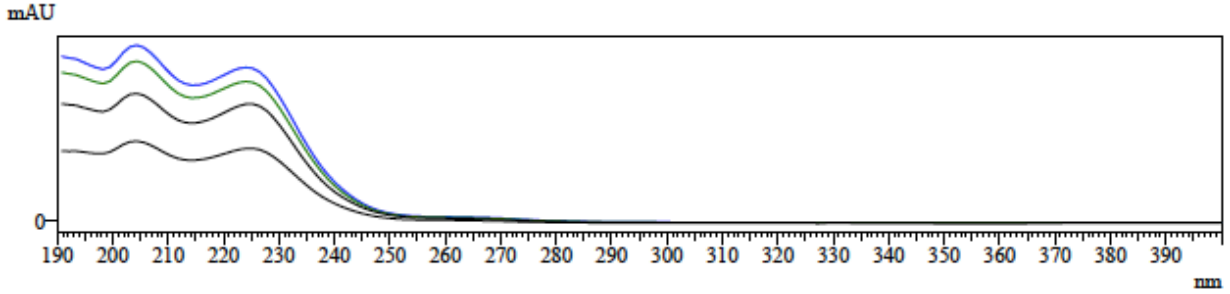
Sample Name	: JYW-0370
Sample ID	: JYW-0370-IC-5%-0.8ml-3
Data File	: JYW-0370-IC-5%-0.8ml-3.lcd
Method File	: JYW-method.lcm
Date Acquired	: 6/21/2017 5:28:41 PM

Chromatogram



UV Spectrum

JYW-0370-IC-5%-0.8ml-3.lcd



Peak Table

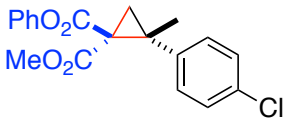
PDA Ch1 216nm

Peak#	Ret. Time	Area	Area%
1	9.707	3480281	24.801
2	10.497	3445988	24.556
3	13.069	3540085	25.227
4	19.644	3566620	25.416
Total		14032975	100.000

1-methyl 1-phenyl (1*S*,2*R*)-2-(4-chlorophenyl)-2-methylcyclopropane-1,1-dicarboxylate

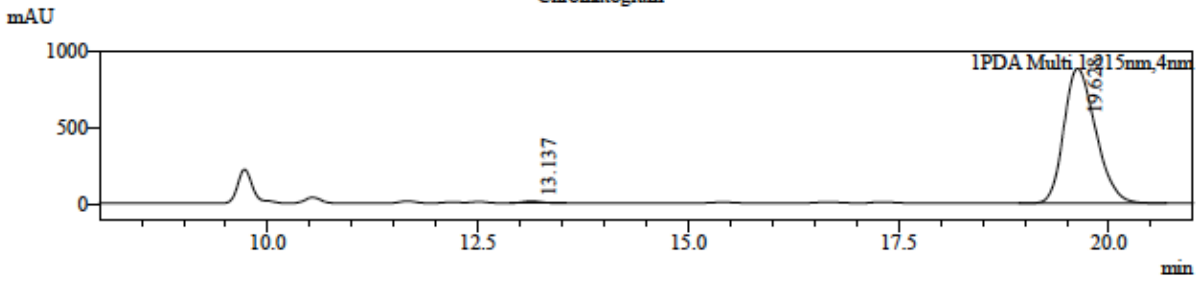
Sample Information

Sample Name	: JYW-0371
Sample ID	: JYW-0371-IC-5%-0.8ml
Data File	: JYW-0371-IC-5%-0.8ml.lcd
Method File	: JYW-method.lcm

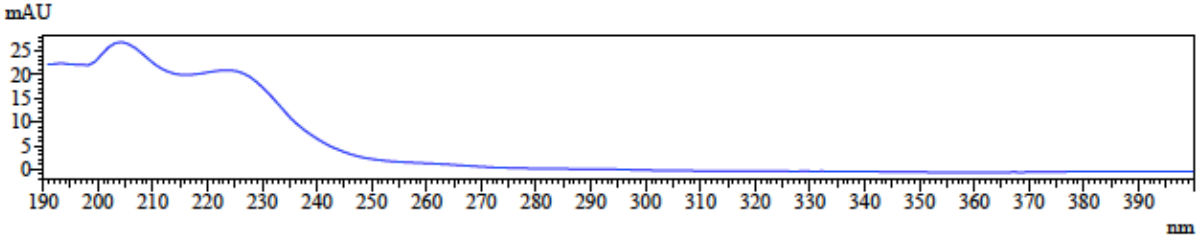


87:13 dr
98% ee

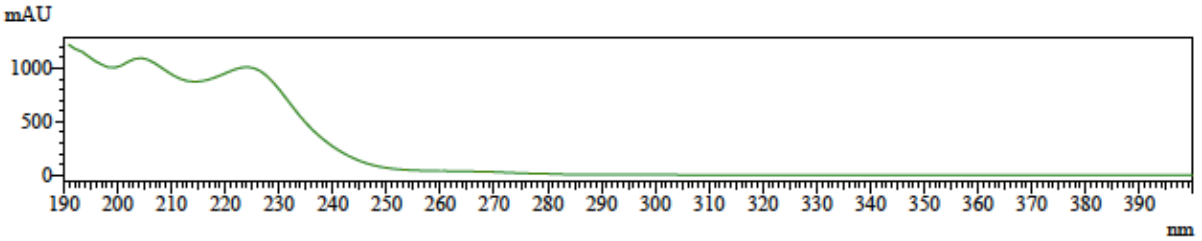
Chromatogram



UV Spectrum
Retention time = 13.137



UV Spectrum
Retention time = 19.628

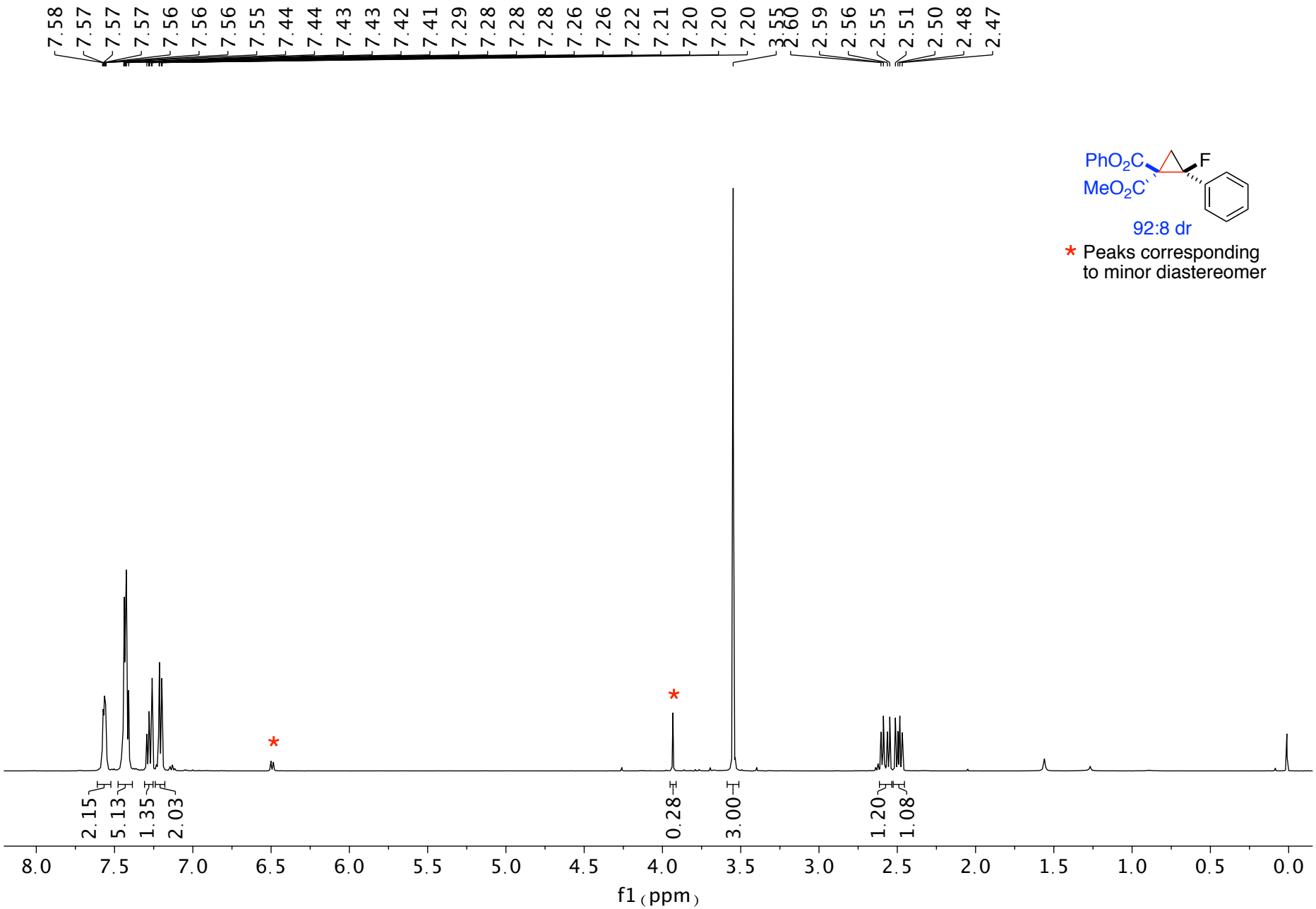


Peak Table

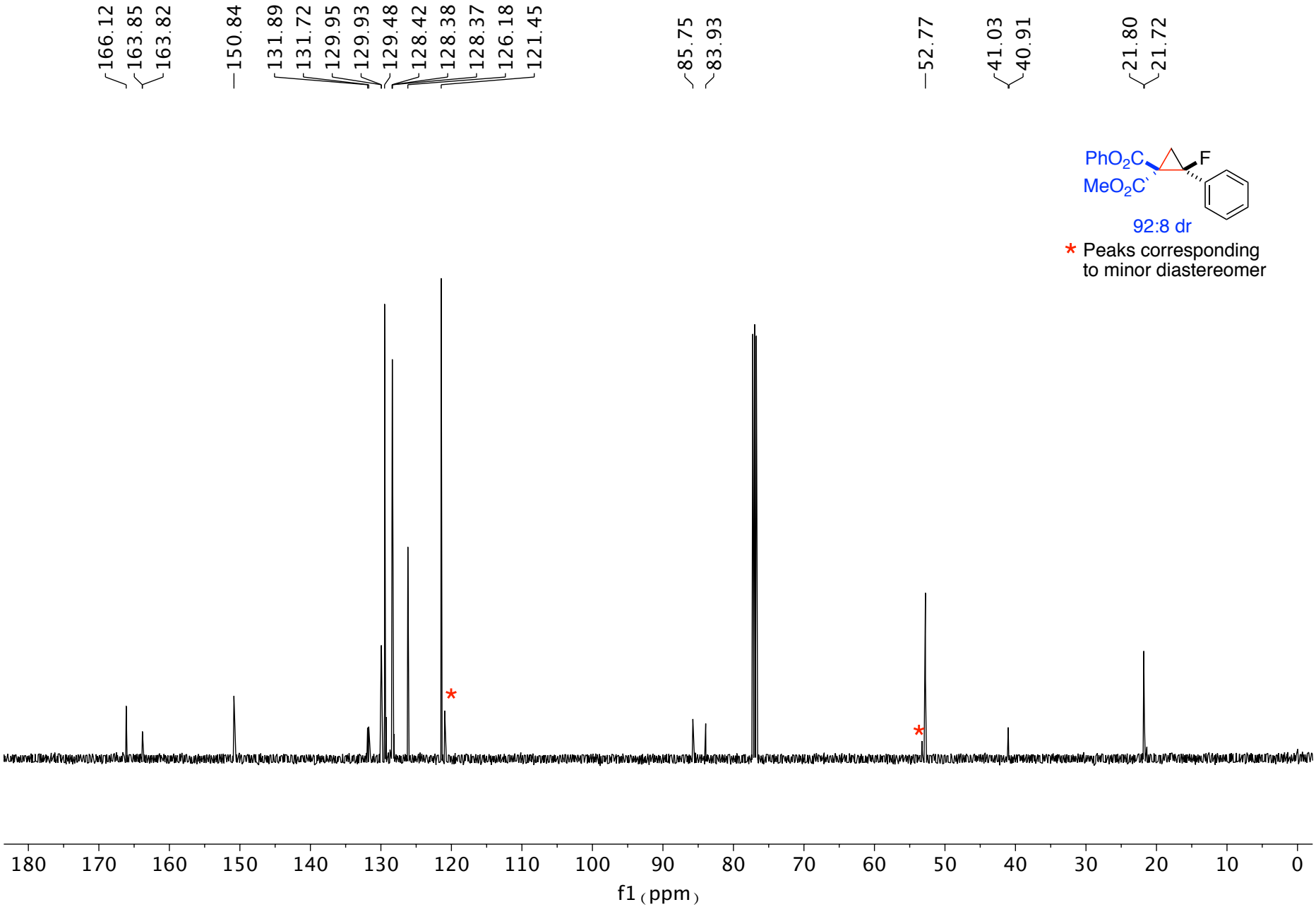
PDA Ch1 215nm

Peak#	Ret. Time	Area	Area%
1	13.137	209864	0.893
2	19.628	23278892	99.107
Total		23488756	100.000

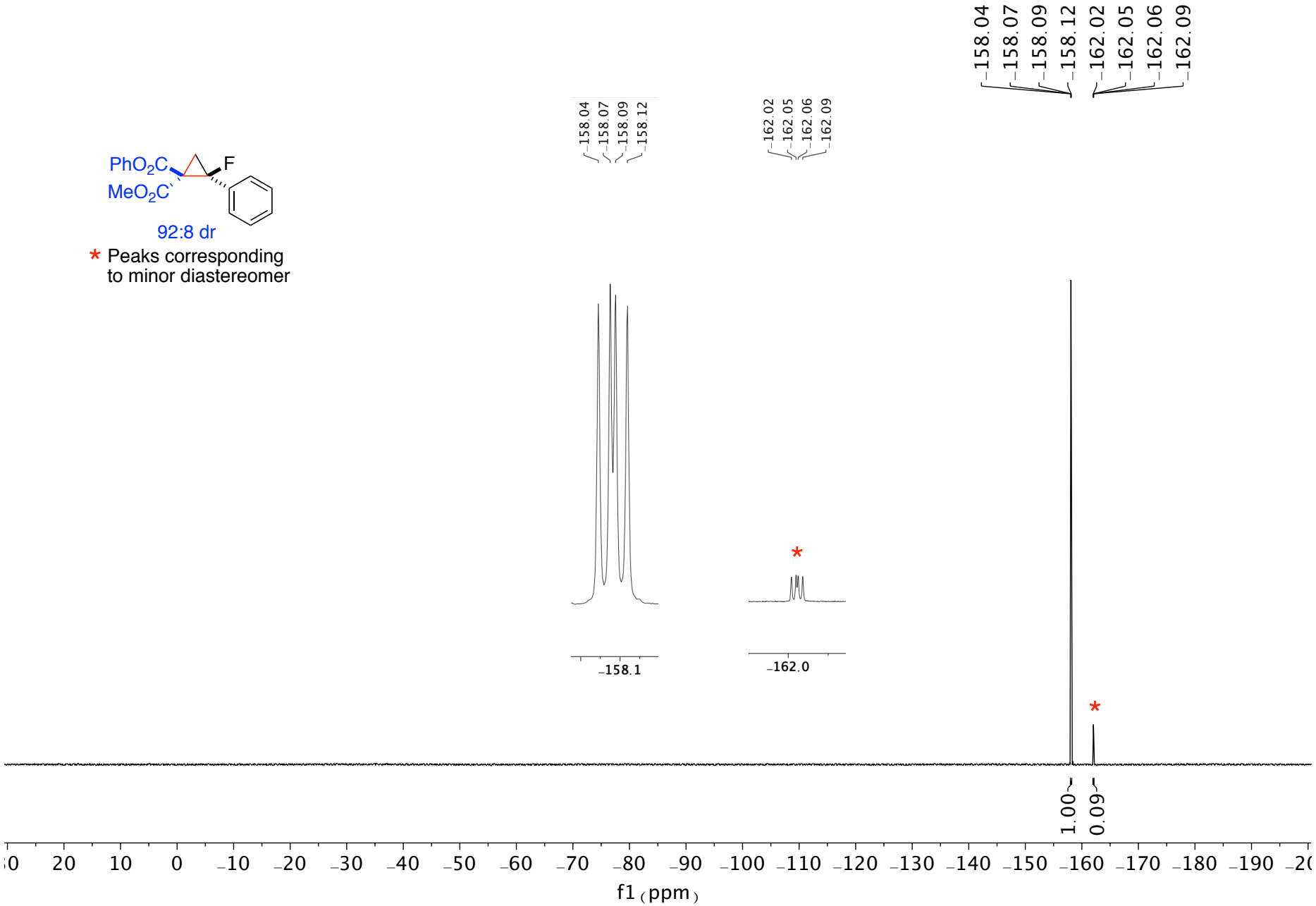
1-methyl 1-phenyl (1*S*,2*S*)-2-fluoro-2-phenylcyclopropane-1,1-dicarboxylate



1-methyl 1-phenyl (1*S*,2*S*)-2-fluoro-2-phenylcyclopropane-1,1-dicarboxylate

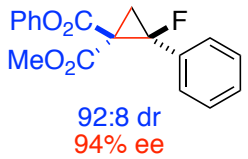


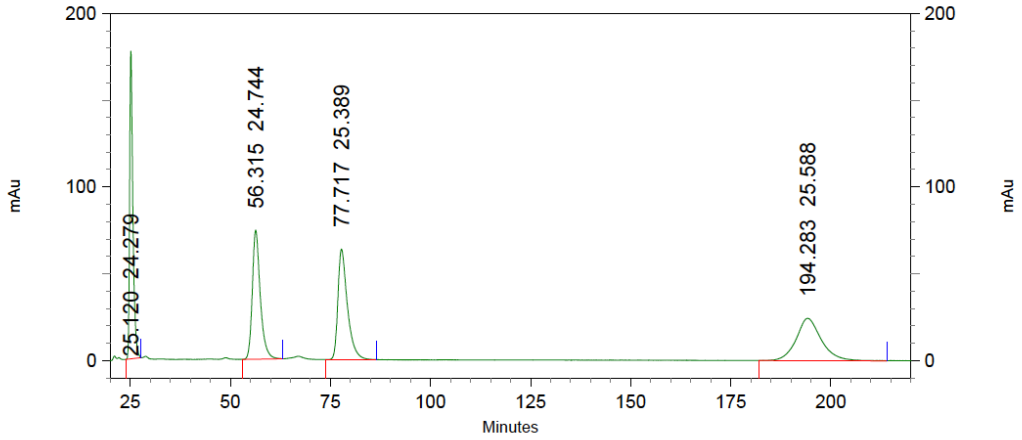
1-methyl 1-phenyl (1*S*,2*S*)-2-fluoro-2-phenylcyclopropane-1,1-dicarboxylate

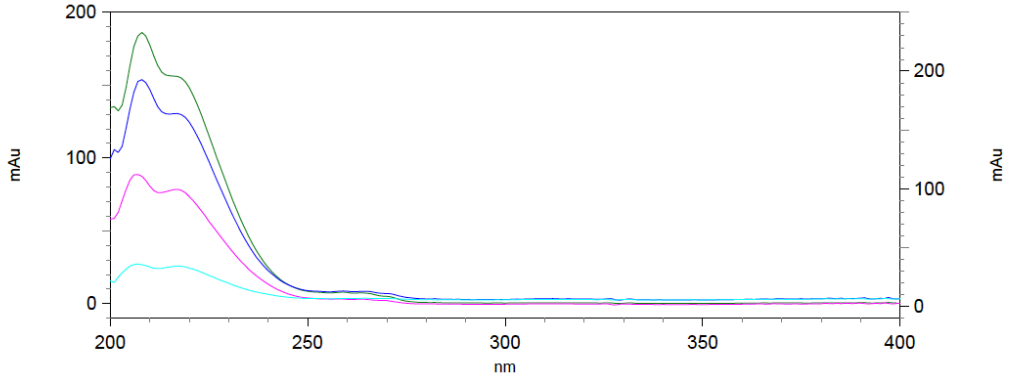


1-methyl 1-phenyl (1*S*,2*S*)-2-fluoro-2-phenylcyclopropane-1,1-dicarboxylate

JYW-0912-50%-0.4mL
C:\Documents and Settings\zhang\Desktop\Lucas\LSP-HEX-0.8mL.met
C:\EZStart\Projects\Default\Data\JYW-0912-50%-0.4mL







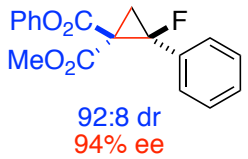
6: 220 nm, 4 nm
Results

Name	Retention Time	Area Percent	Pk #
	25.120	24.279	1
	56.315	24.744	2
	77.717	25.389	3
	194.283	25.588	4

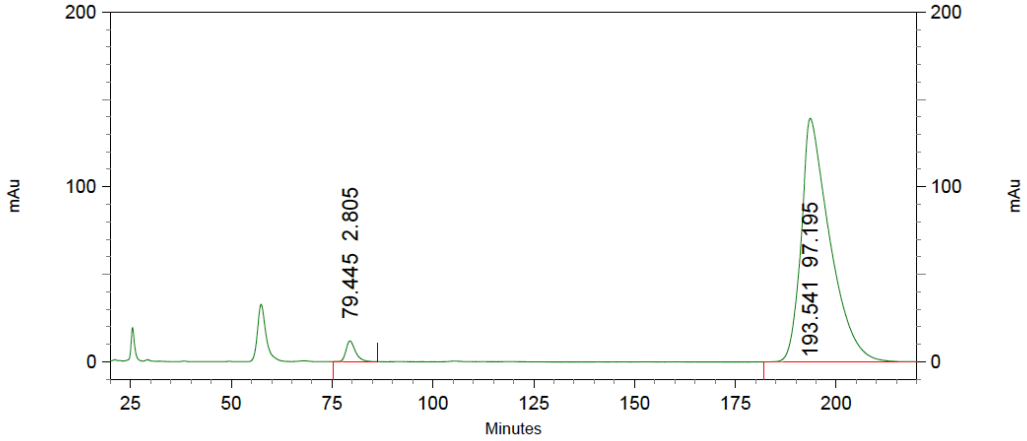
Totals		
	100.000	

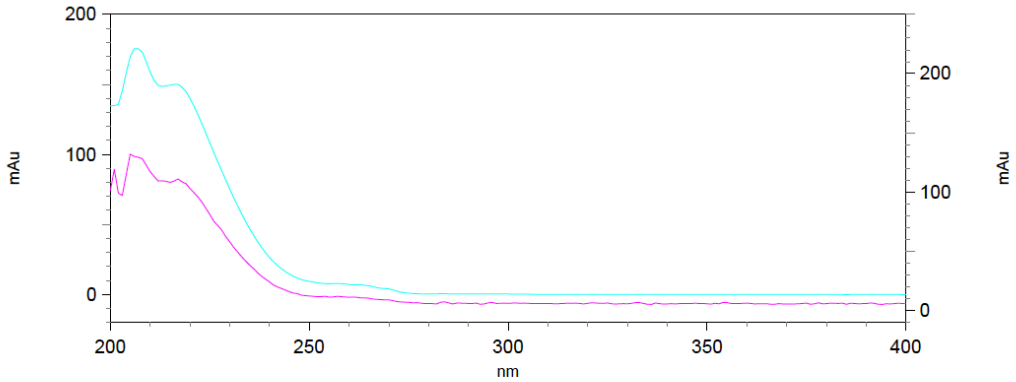
1-methyl 1-phenyl (1*S*,2*S*)-2-fluoro-2-phenylcyclopropane-1,1-dicarboxylate

JYW-0913-50%-0.4mL
C:\Documents and Settings\zhang\Desktop\Lucas\LSP-HEX-0.8mL.met
C:\EZStart\Projects\Default\Data\JYW-0913-50%-0.4mL



92:8 dr
94% ee



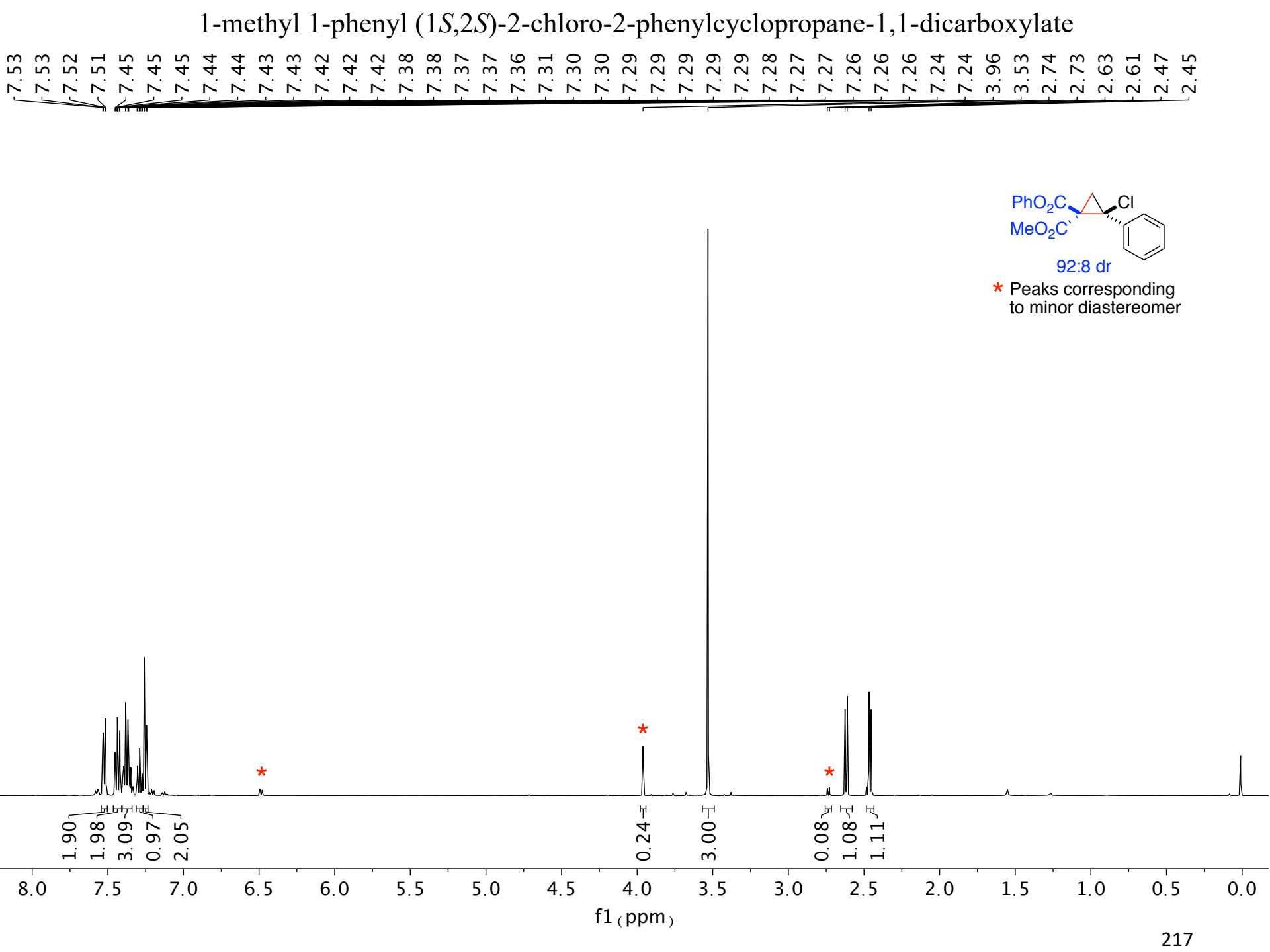


6: 220 nm, 4 nm
Results

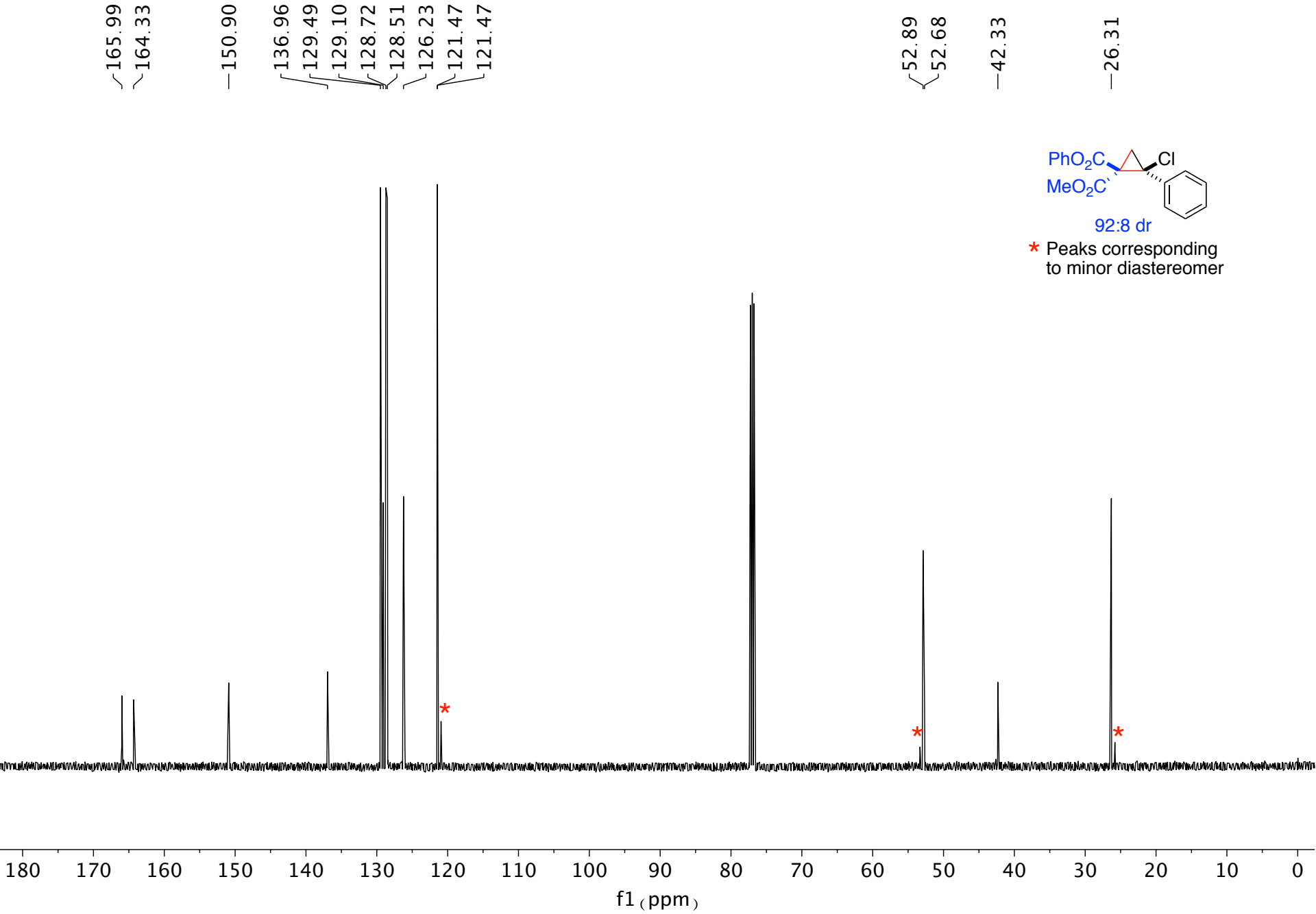
Name	Retention Time	Area Percent	Pk #
	79.445	2.805	1
	193.541	97.195	2

Totals		
	100.000	

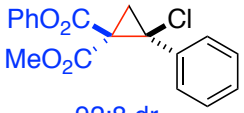
1-methyl 1-phenyl (1*S*,2*S*)-2-chloro-2-phenylcyclopropane-1,1-dicarboxylate



1-methyl 1-phenyl (1*S*,2*S*)-2-chloro-2-phenylcyclopropane-1,1-dicarboxylate



1-methyl 1-phenyl (1*S*,2*S*)-2-chloro-2-phenylcyclopropane-1,1-dicarboxylate

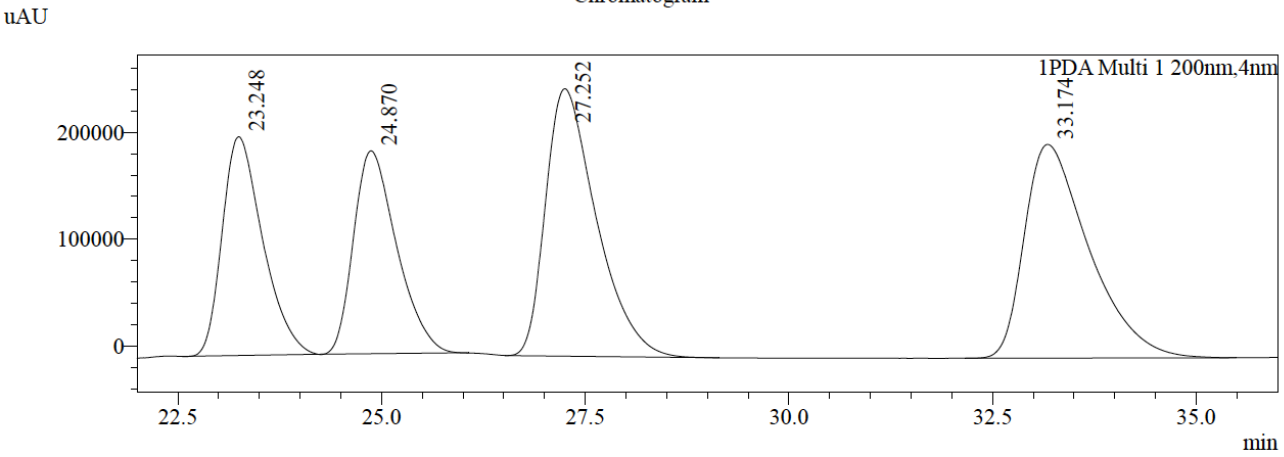


92:8 dr
98% ee

Sample Information

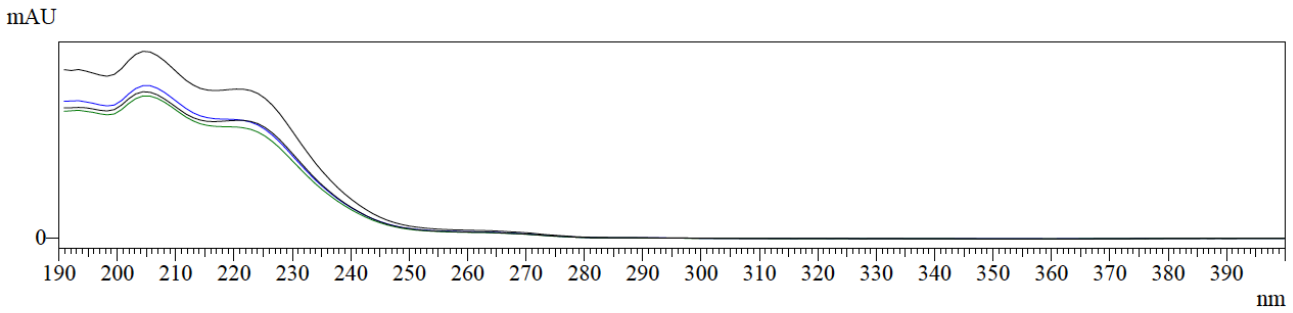
Sample Name	: JYW-0888-ODH-2.5%-0.8ml
Sample ID	: JYW-0888-ODH-2.5%-0.8ml
Data File	: JYW-0888-ODH-2.5%-0.8ml.lcd
Method File	: JYW-method.lcm
Date Acquired	: 1/25/2019 2:21:56 PM

Chromatogram



UV Spectrum

JYW-0888-ODH-2.5%-0.8ml.lcd

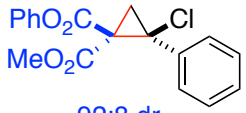


Peak Table

PDA Ch1 200nm

Peak#	Ret. Time	Area	Area%
1	23.248	7078731	19.682
2	24.870	6994895	19.449
3	27.252	10853149	30.177
4	33.174	11038416	30.692
Total		35965191	100.000

1-methyl 1-phenyl (1*S*,2*S*)-2-chloro-2-phenylcyclopropane-1,1-dicarboxylate

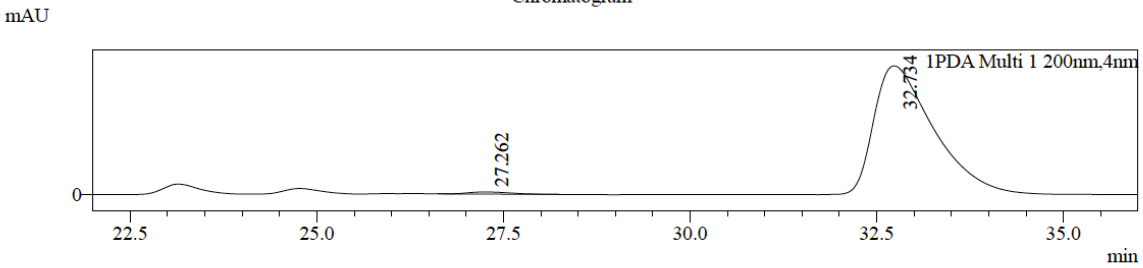


92:8 dr
98% ee

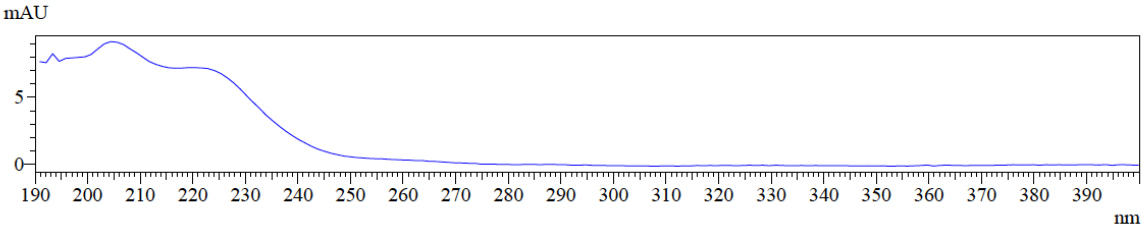
Sample Information

Sample Name	: JYW-0904-ODH-2.5%-0.8ml
Sample ID	: JYW-0904-ODH-2.5%-0.8ml
Data File	: JYW-0904-ODH-2.5%-0.8ml.lcd
Method File	: JYW-method.lcm

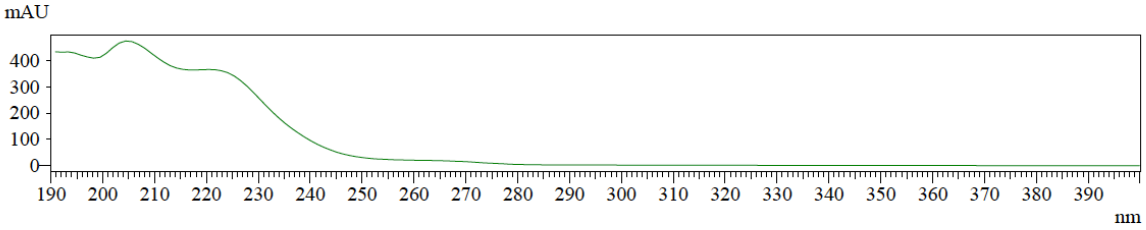
Chromatogram



UV Spectrum
Retention time = 27.262



UV Spectrum
Retention time = 32.734

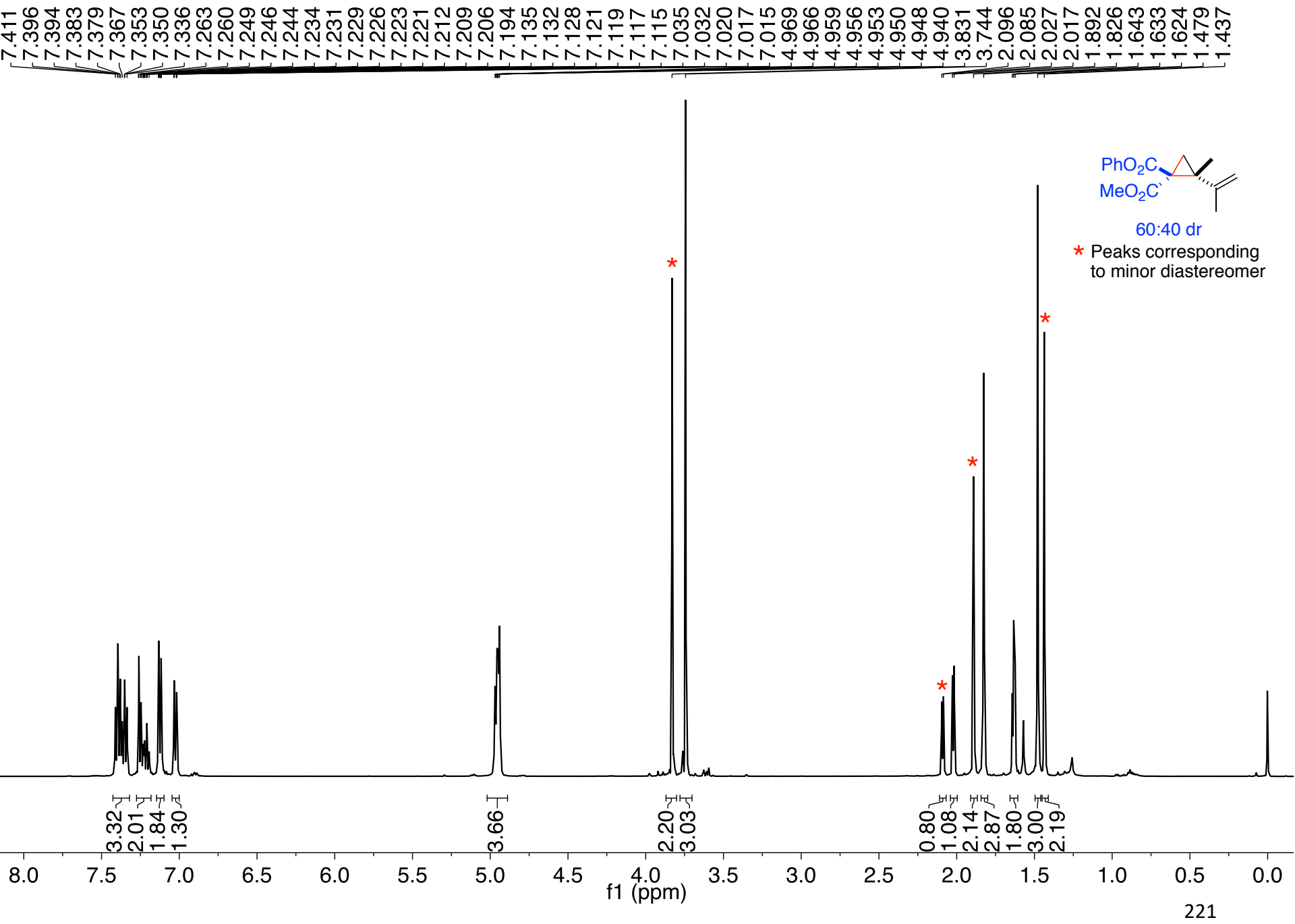


Peak Table

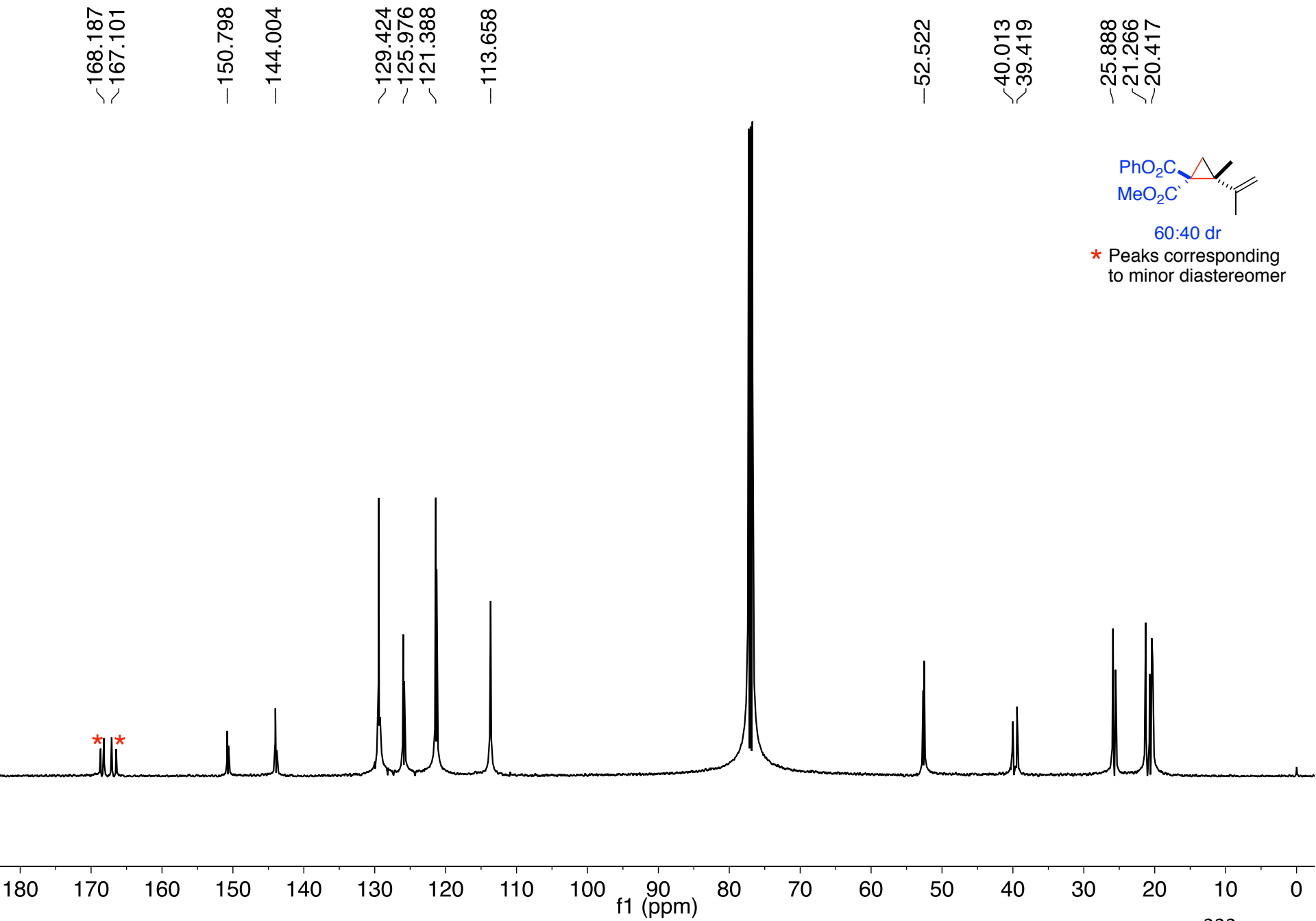
PDA Ch1 200nm

Peak#	Ret. Time	Area	Area%
1	27.262	274898	1.135
2	32.734	23941298	98.865
Total		24216196	100.000

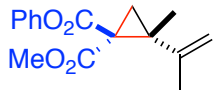
1-methyl 1-phenyl (1*S*,2*R*)-2-methyl-2-(prop-1-en-2-yl)cyclopropane-1,1-dicarboxylate



1-methyl 1-phenyl (1*S*,2*R*)-2-methyl-2-(prop-1-en-2-yl)cyclopropane-1,1-dicarboxylate



1-methyl 1-phenyl (1*S*,2*R*)-2-methyl-2-(prop-1-en-2-yl)cyclopropane-1,1-dicarboxylate

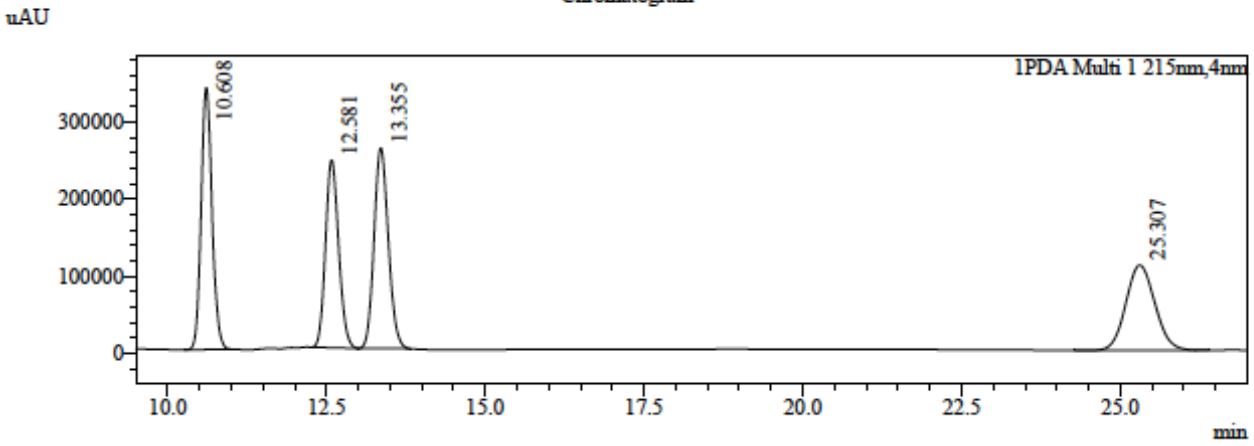


60:40 dr
87% ee

Sample Information

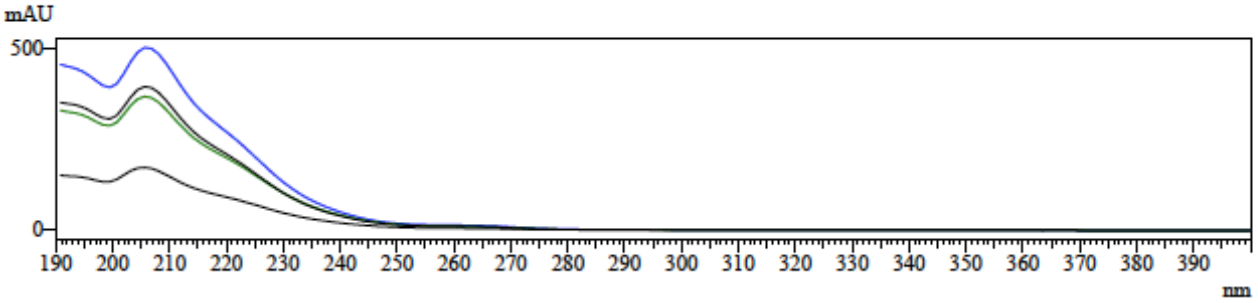
Sample Name	:
Sample ID	: JYW-II-248-IC-5%-0.8ml
Data File	: JYW-II-248-IC-5%-0.8ml.lcd
Method File	: JYW-method.lcm
Date Acquired	: 10/1/2015 6:13:34 PM

Chromatogram



UV Spectrum

JYW-II-248-IC-5%-0.8ml.lcd

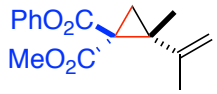


Peak Table

PDA Ch1 215nm

Peak#	Ret. Time	Area	Area%
1	10.608	4032660	26.731
2	12.581	3502609	23.217
3	13.355	4063189	26.933
4	25.307	3487625	23.118
Total		15086082	100.000

1-methyl 1-phenyl (1*S*,2*R*)-2-methyl-2-(prop-1-en-2-yl)cyclopropane-1,1-dicarboxylate

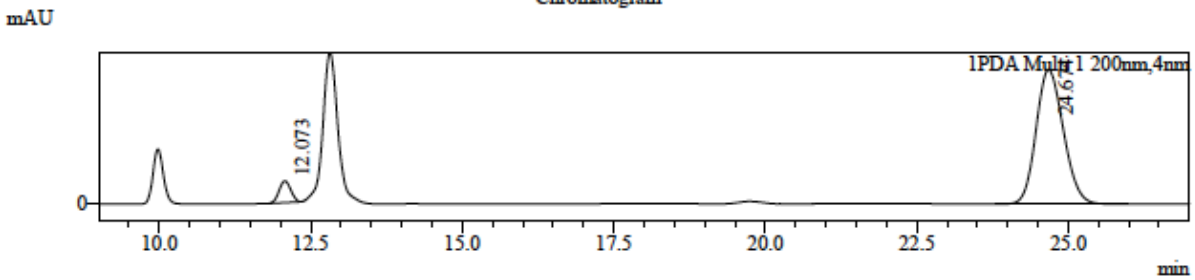


60:40 dr
87% ee

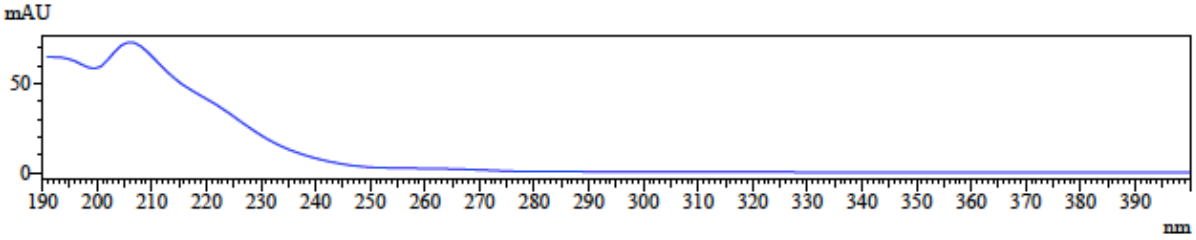
Sample Information

Sample Name :
Sample ID : JYW-III-78-IC-5%-0.8ml
Data File : JYW-III-78-IC-5%-0.8ml.lcd
Method File : JYW-method.lcm

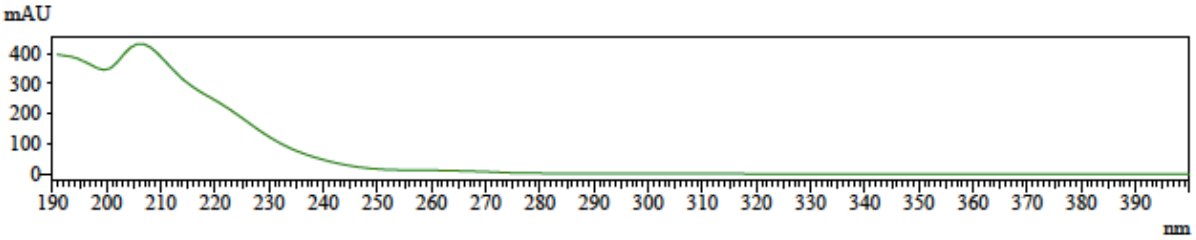
Chromatogram



UV Spectrum
Retention time = 12.073



UV Spectrum
Retention time = 24.674

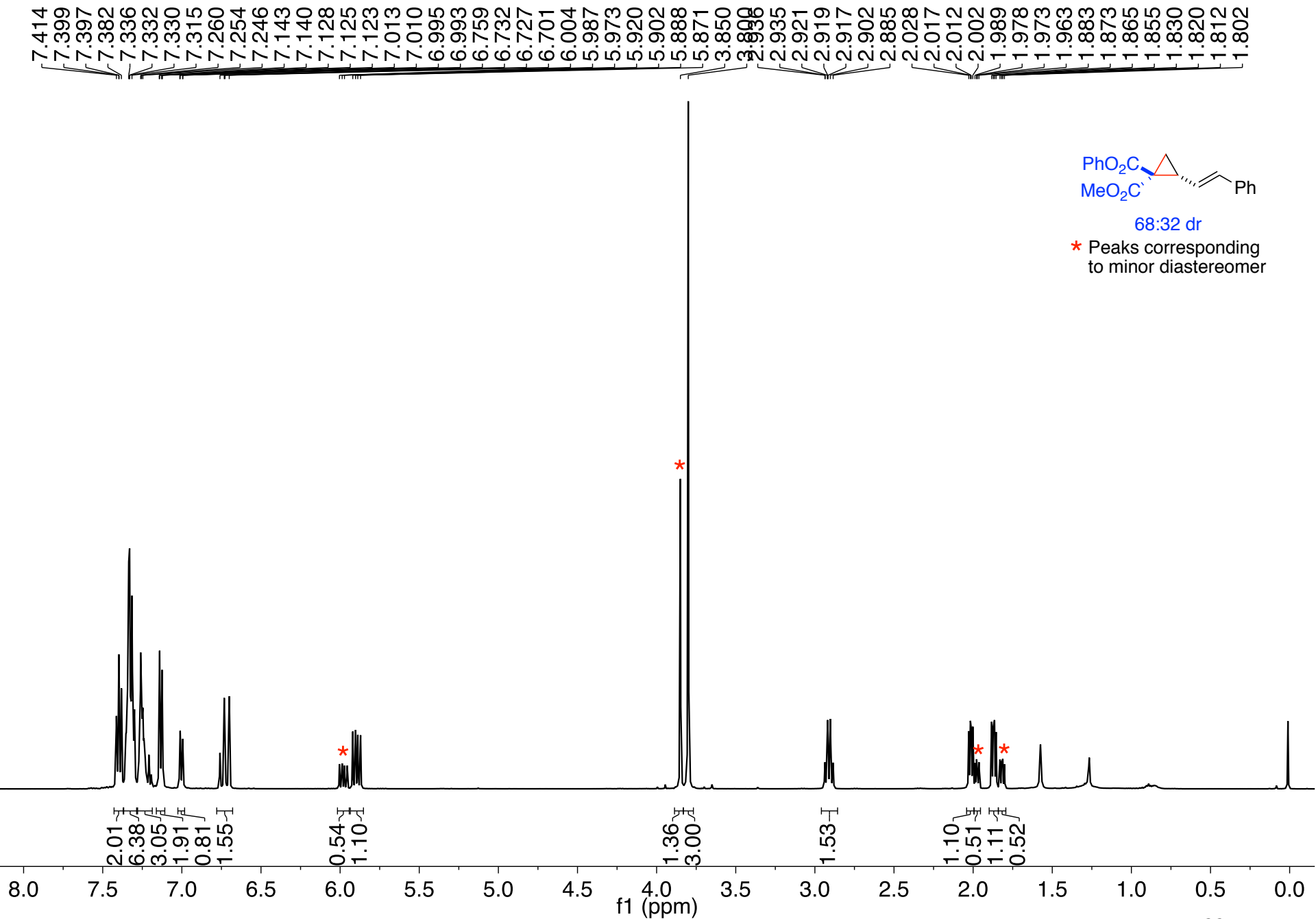


Peak Table

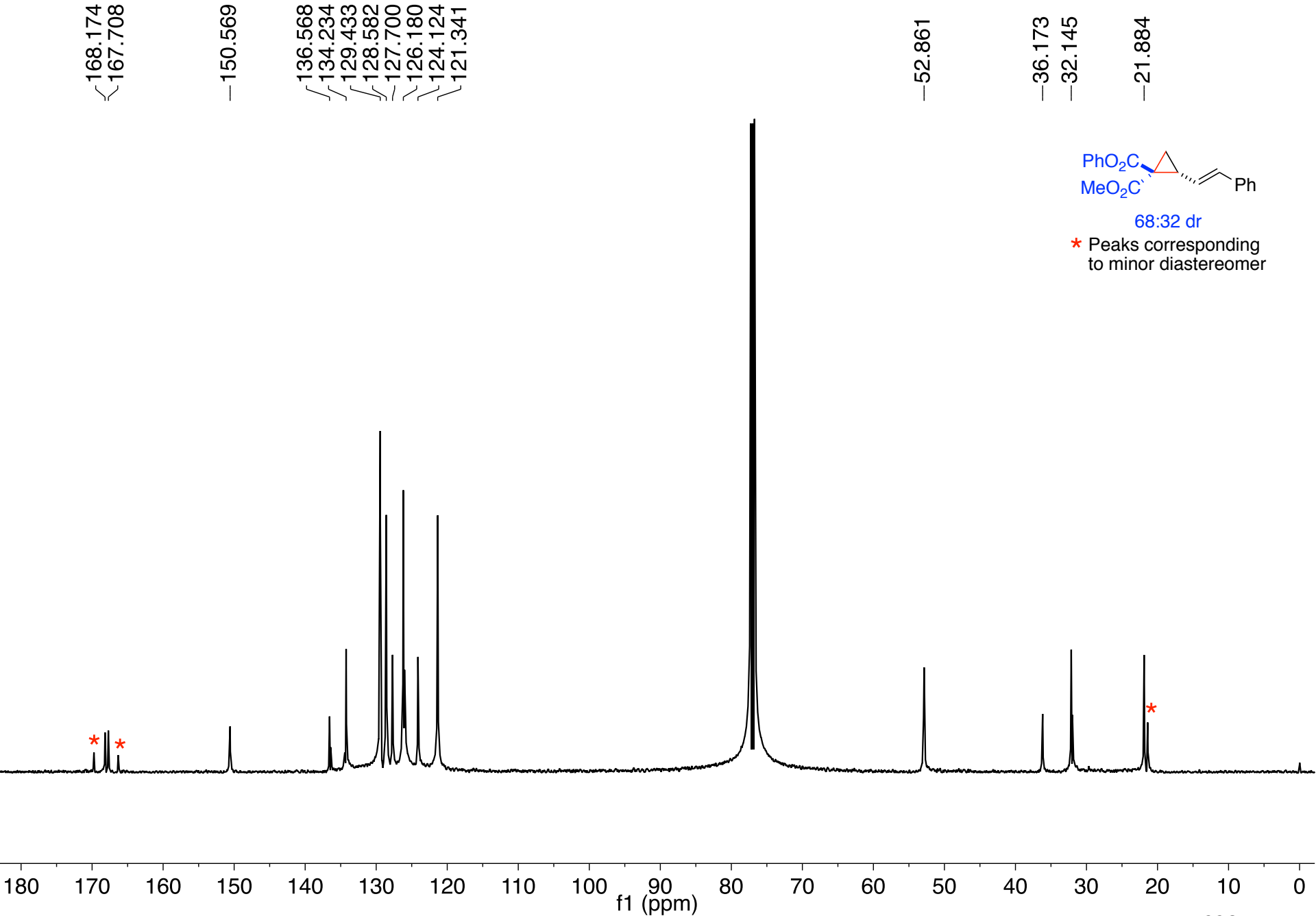
PDA Ch1 200nm

Peak#	Ret. Time	Area	Area%
1	12.073	794735	6.494
2	24.674	11443173	93.506
Total		12237908	100.000

1-methyl 1-phenyl (1*S*,2*R*)-2-((*E*)-styryl)cyclopropane-1,1-dicarboxylate

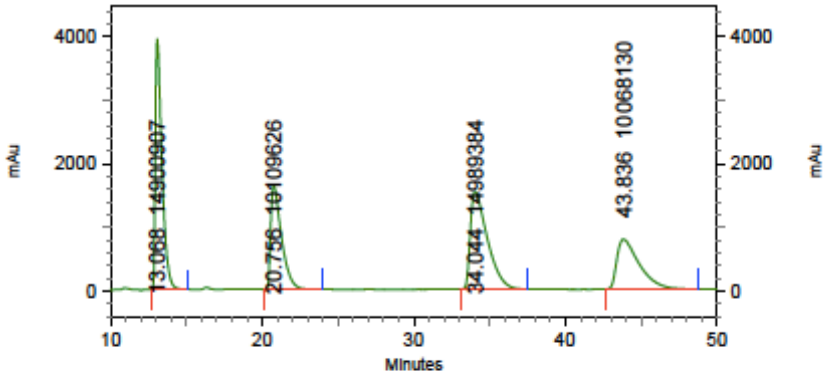


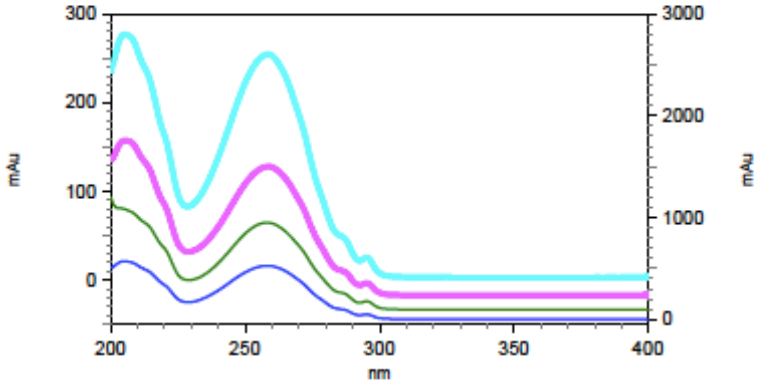
1-methyl 1-phenyl (1*S*,2*R*)-2-((*E*)-styryl)cyclopropane-1,1-dicarboxylate



1-methyl 1-phenyl (1*S*,2*R*)-2-((*E*)-styryl)cyclopropane-1,1-dicarboxylate

JYW-II-183A-ODH-2%-1ml
C:\EZStart\Projects\Default\Method\ywang0.8.met
C:\EZStart\Projects\Default\Data\JYW-II-183A-ODH-2%-1ml





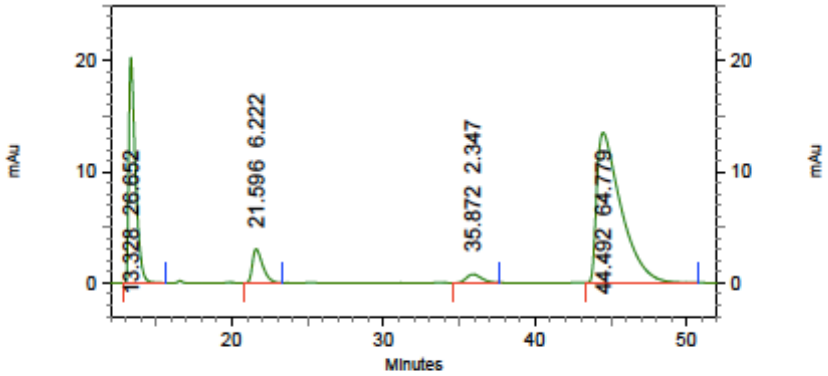
68:32 dr
83% ee

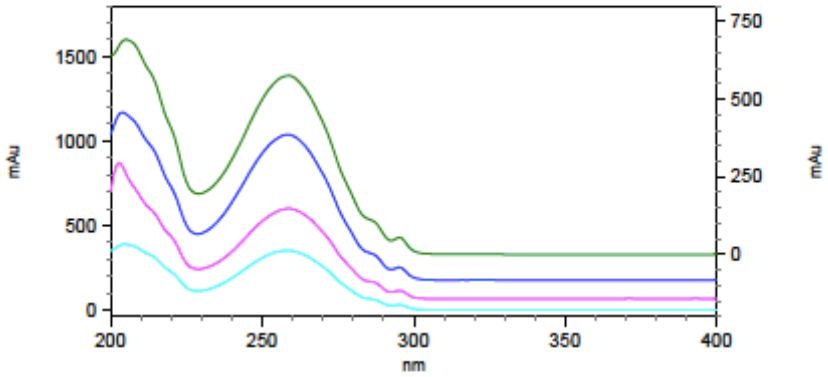
4: 225 nm, 4 nm
Results

Pk #	Name	Retention Time	Area Percent
1		13.068	29.761
2		20.756	20.192
3		34.044	29.938
4		43.836	20.109
Totals			100.000

1-methyl 1-phenyl (1*S*,2*R*)-2-((*E*)-styryl)cyclopropane-1,1-dicarboxylate

JYW-II-183B-ODH-2%-1ml
C:\EZStart\Projects\Default\Method\LK-10%-0.8-90min.met
C:\EZStart\Projects\Default\Data\JYW-II-183B-ODH-2%-1ml





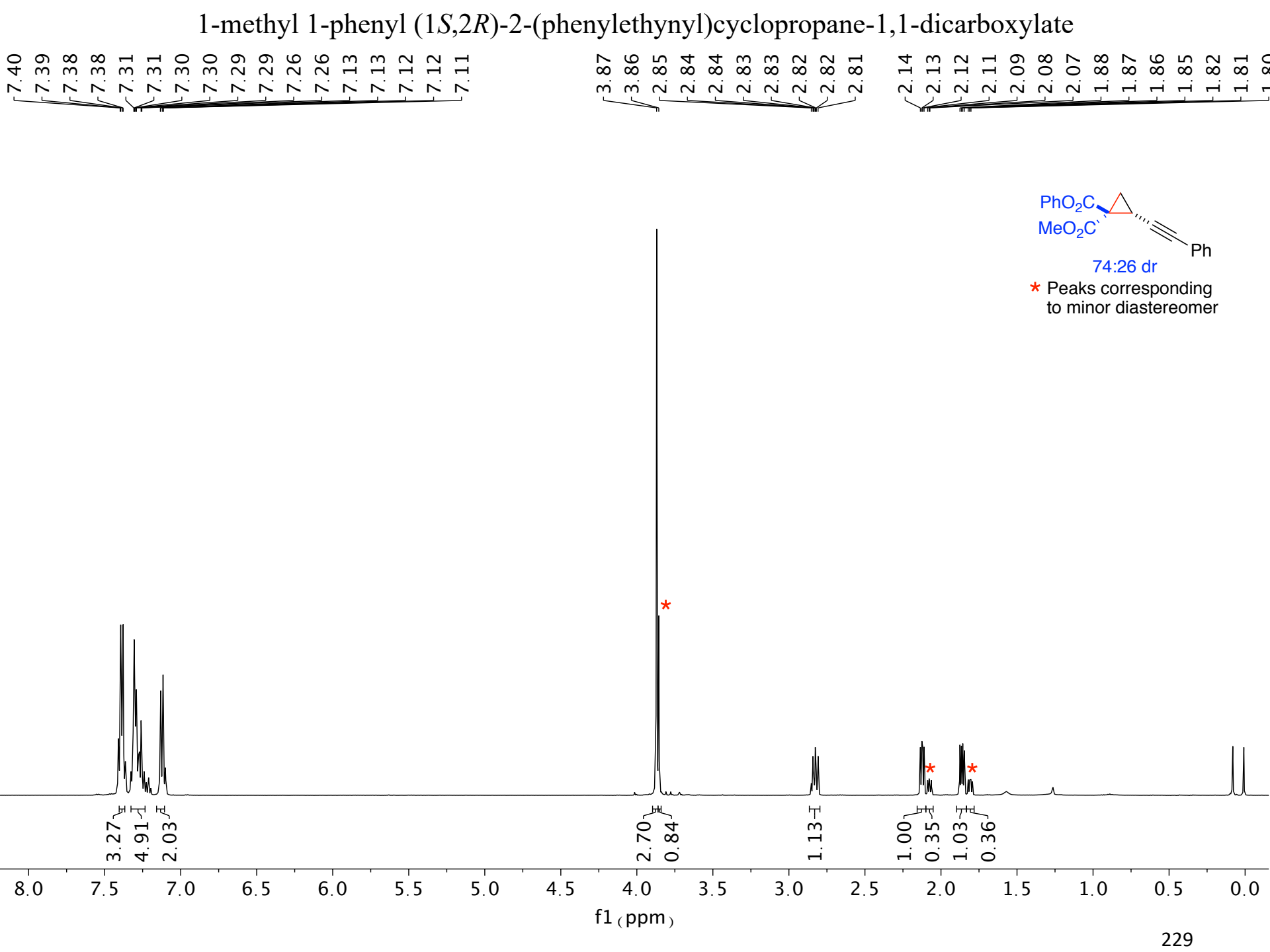
68:32 dr
83% ee

4: 280 nm, 4 nm
Results

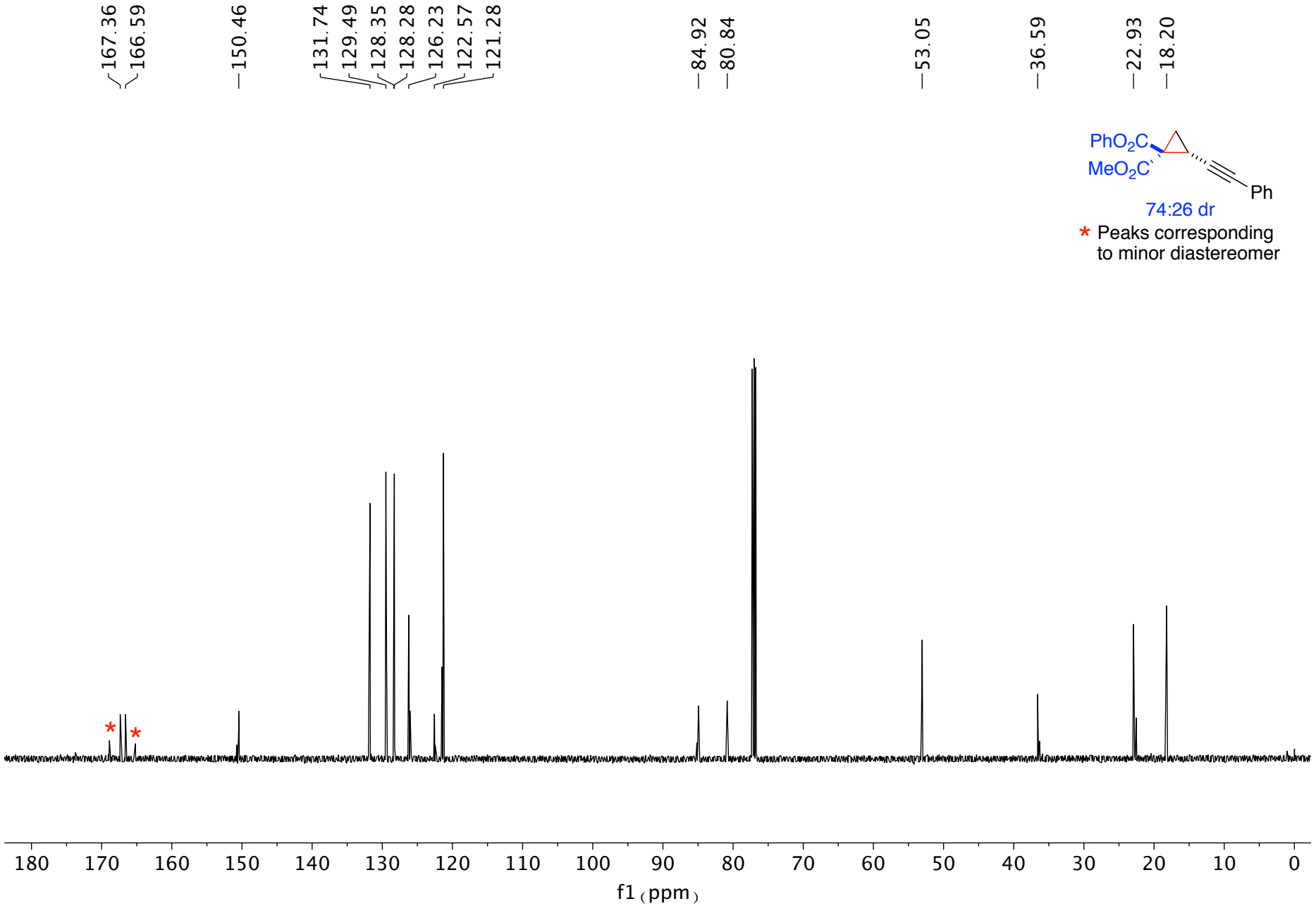
Name	Retention Time	Area Percent	Pk #
	13.328	26.652	1
	21.596	6.222	2
	35.872	2.347	3
	44.492	64.779	4

Totals	
	100.000

1-methyl 1-phenyl (1*S*,2*R*)-2-(phenylethynyl)cyclopropane-1,1-dicarboxylate



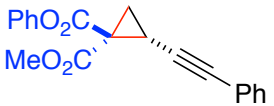
1-methyl 1-phenyl (1*S*,2*R*)-2-(phenylethynyl)cyclopropane-1,1-dicarboxylate



1-methyl 1-phenyl (1*S*,2*R*)-2-(phenylethynyl)cyclopropane-1,1-dicarboxylate

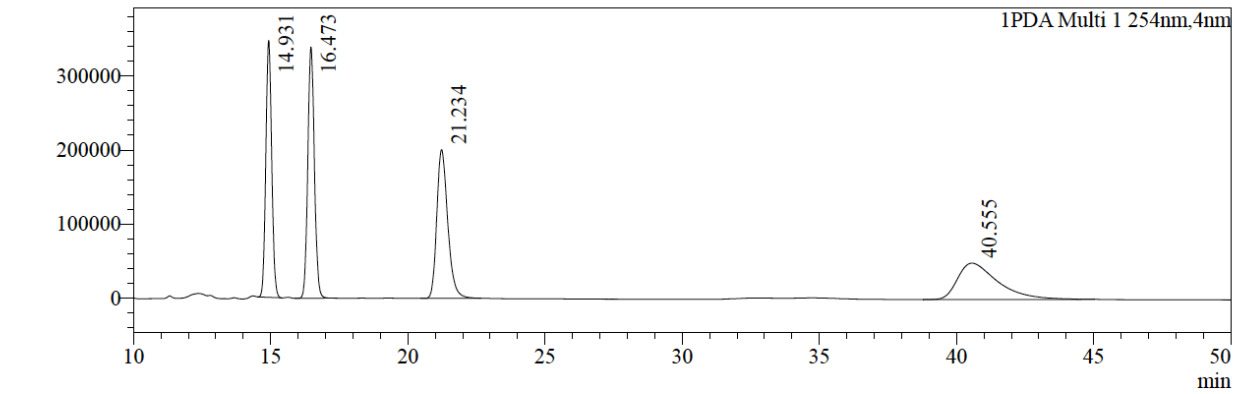
Sample Information

Sample Name	: JYW-0845
Sample ID	: JYW-0845-ID-10%-0.8ml3
Data File	: JYW-0845-ID-10%-0.8ml3.lcd
Method File	: JYW-method.lcm
Date Acquired	: 12/17/2018 9:23:48 PM



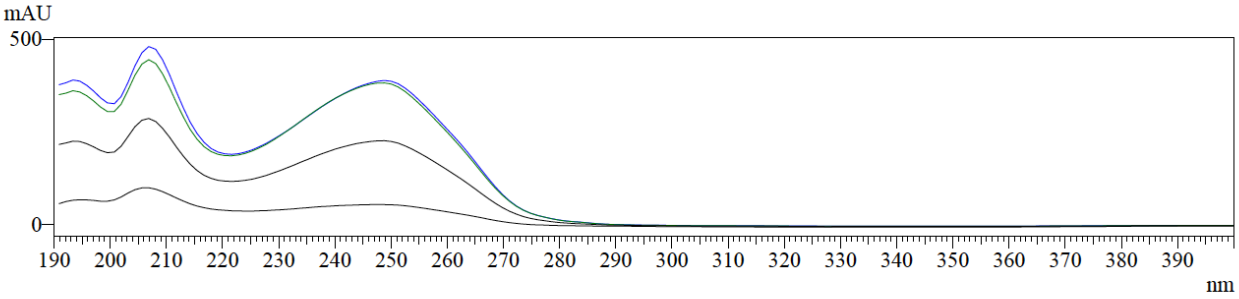
74:26 dr
82% ee

Chromatogram



UV Spectrum

JYW-0845-ID-10%-0.8ml3.lcd



Peak Table

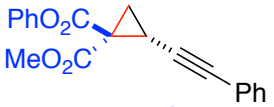
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	14.931	5164555	24.085
2	16.473	5673370	26.457
3	21.234	5577688	26.011
4	40.555	5027850	23.447
Total		21443464	100.000

1-methyl 1-phenyl (1*S*,2*R*)-2-(phenylethynyl)cyclopropane-1,1-dicarboxylate

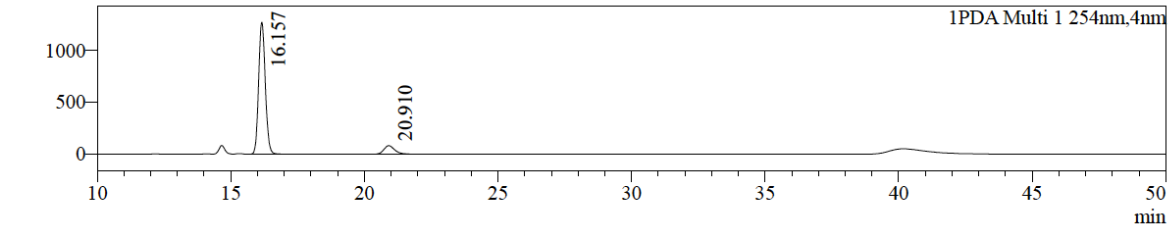
Sample Information

Sample Name : JYW-0846
Sample ID : JYW-0846-ID-10%-0.8ml3
Data File : JYW-0846-ID-10%-0.8ml3.lcd
Method File : JYW-method.lcm

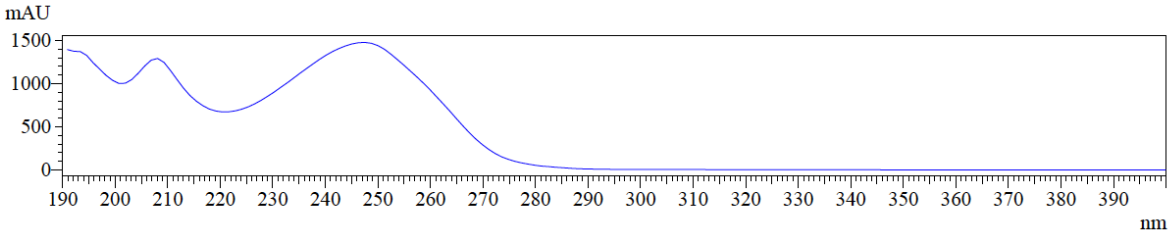


74:26 dr
82% ee

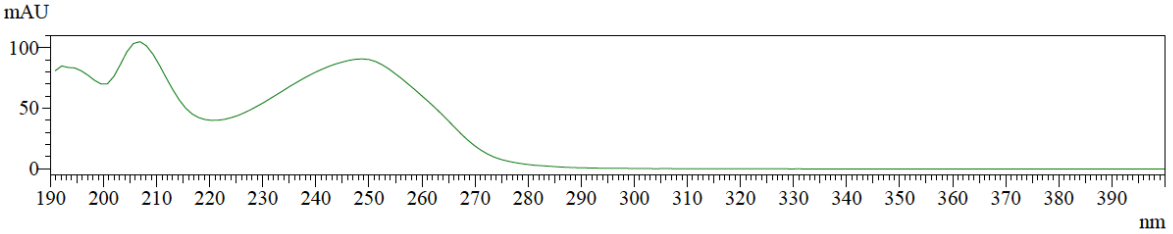
Chromatogram



UV Spectrum
Retention time = 16.157



UV Spectrum
Retention time = 20.910

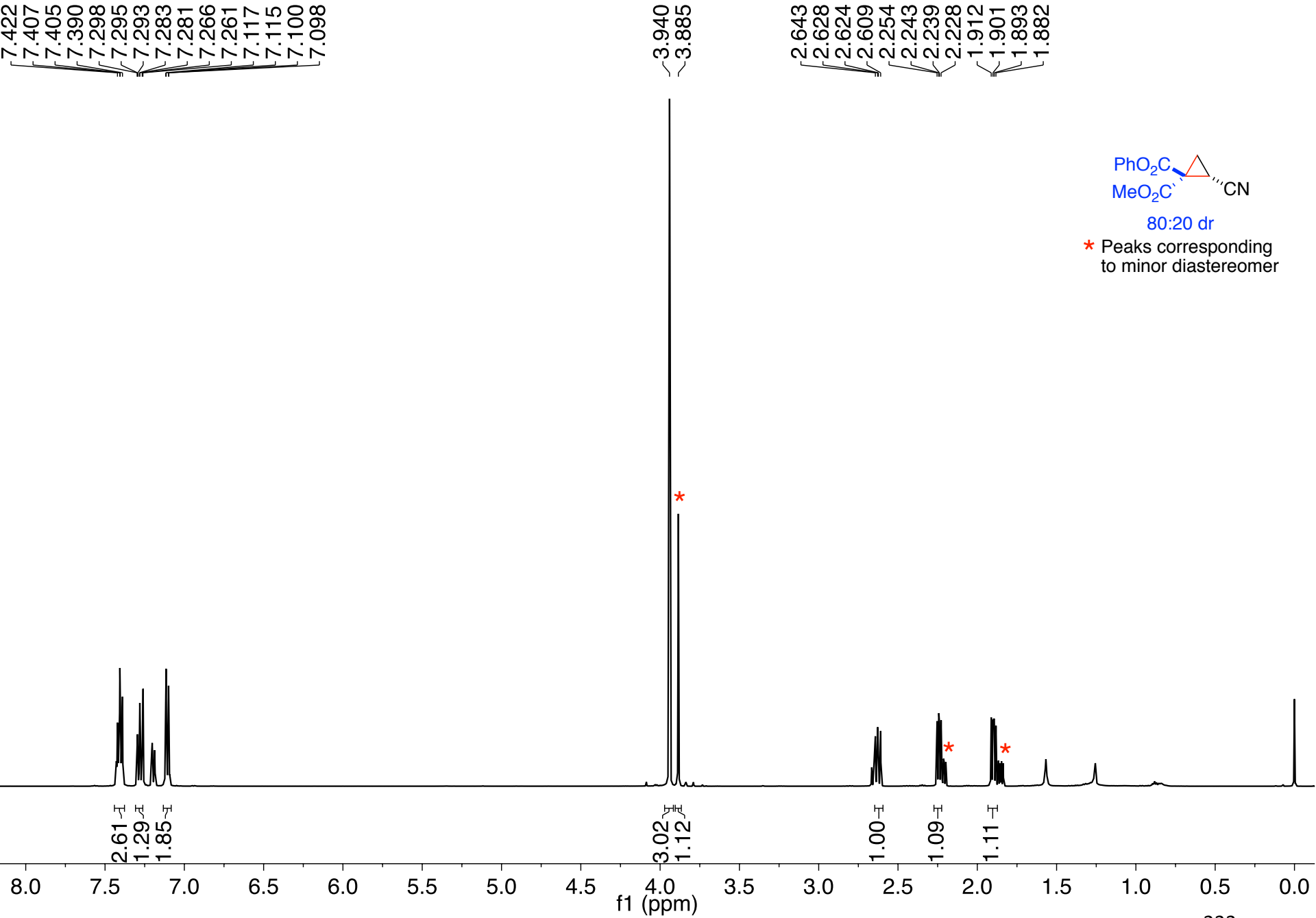


Peak Table

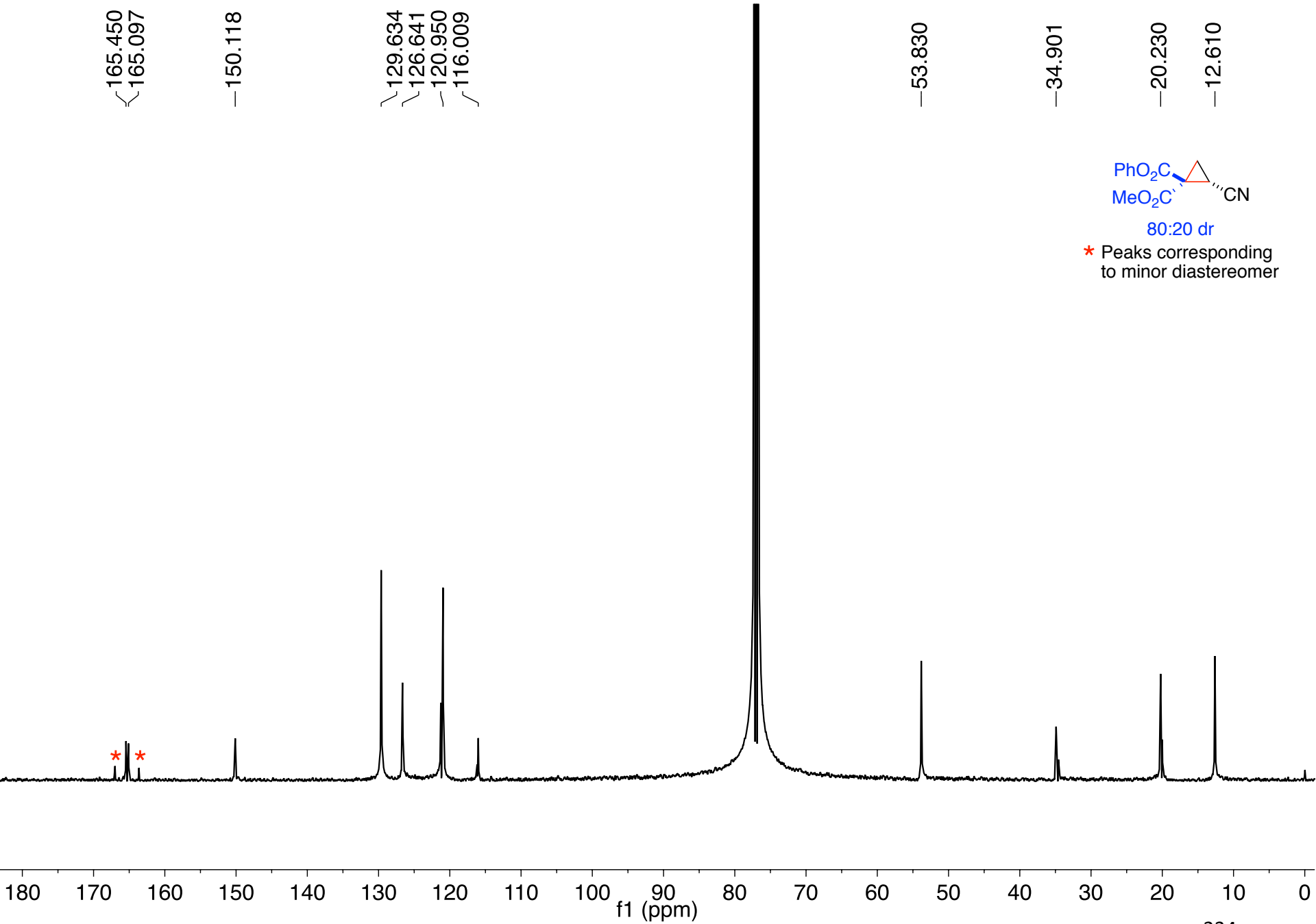
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	16.157	22040458	90.758
2	20.910	2244376	9.242
Total		24284833	100.000

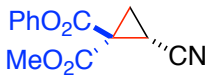
1-methyl 1-phenyl (1*S*,2*S*)-2-cyanocyclopropane-1,1-dicarboxylate



1-methyl 1-phenyl (1*S*,2*S*)-2-cyanocyclopropane-1,1-dicarboxylate



1-methyl 1-phenyl (1*S*,2*S*)-2-cyanocyclopropane-1,1-dicarboxylate

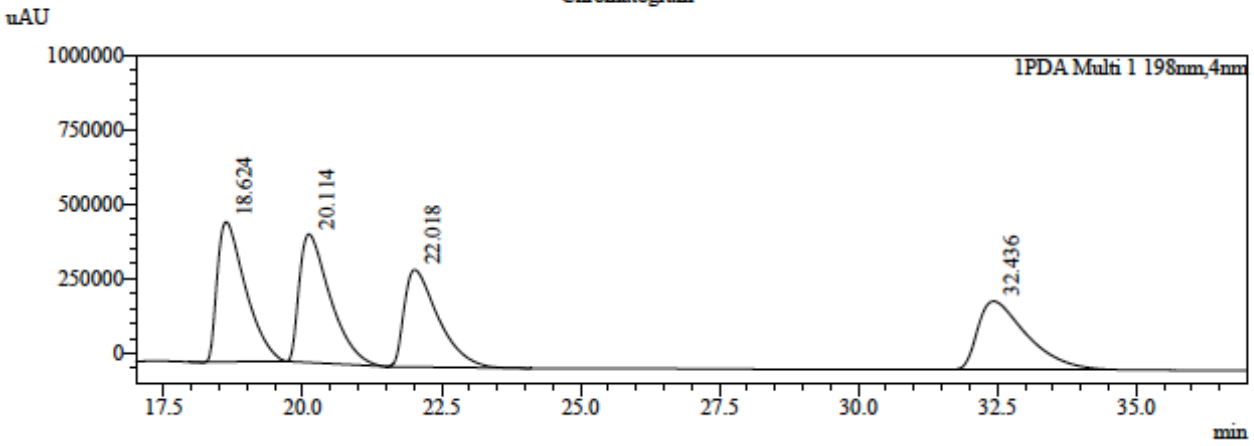


80:20 dr
95% ee

Sample Information

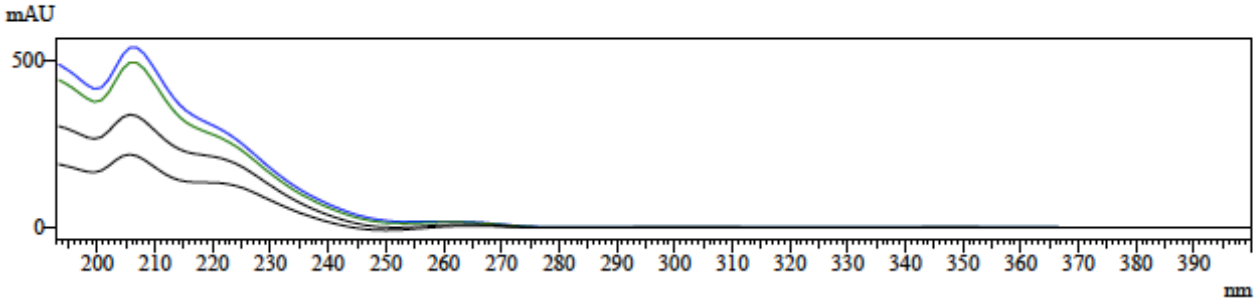
Sample Name	:
Sample ID	: JYW-III-113-ODH-8%-0.8ml
Data File	: JYW-III-113-ODH-8%-0.8ml.lcd
Method File	: JYW-method.lcm
Date Acquired	: 9/29/2015 8:53:28 PM

Chromatogram



UV Spectrum

JYW-III-113-ODH-8%-0.8ml.lcd

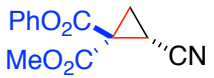


Peak Table

PDA Ch1 198nm

Peak#	Ret. Time	Area	Area%
1	18.624	16566434	27.108
2	20.114	16685250	27.303
3	22.018	13888347	22.726
4	32.436	13971672	22.863
Total		61111703	100.000

1-methyl 1-phenyl (1*S*,2*S*)-2-cyanocyclopropane-1,1-dicarboxylate

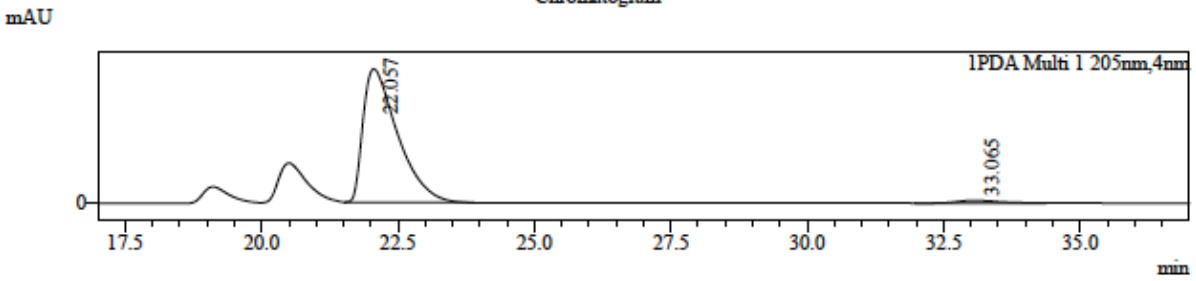


80:20 dr
95% ee

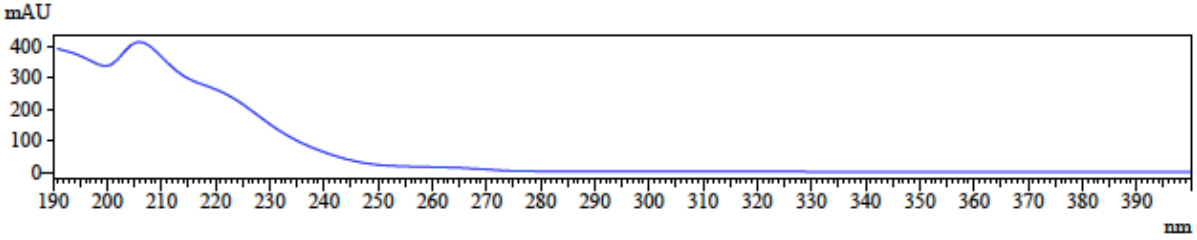
Sample Information

Sample Name :
Sample ID : JYW-III-111-ODH-8%-0.8ml
Data File : JYW-III-111-ODH-8%-0.8ml.lcd
Method File : JYW-method.lcm

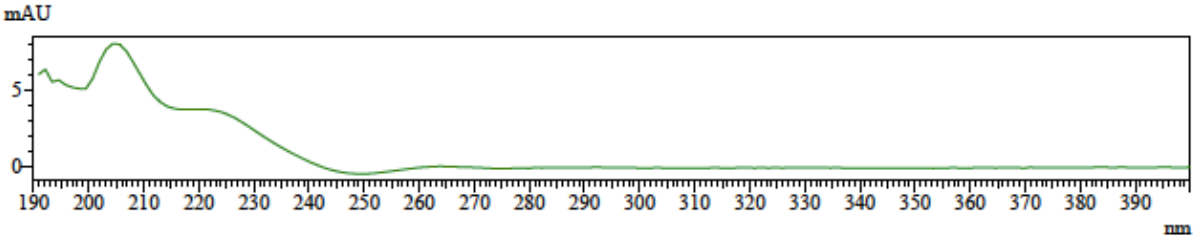
Chromatogram



UV Spectrum
Retention time = 22.057



UV Spectrum
Retention time = 33.065

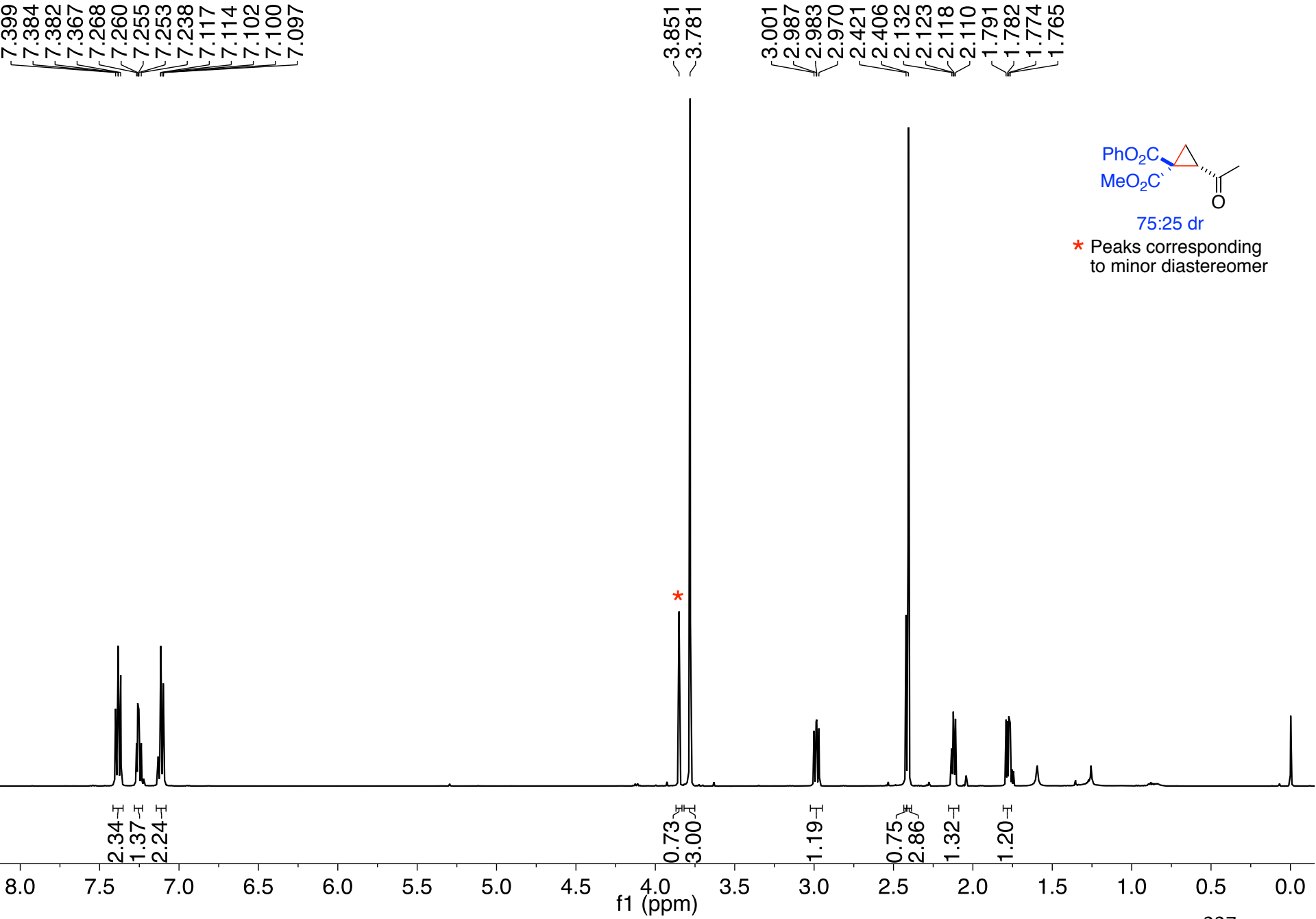


Peak Table

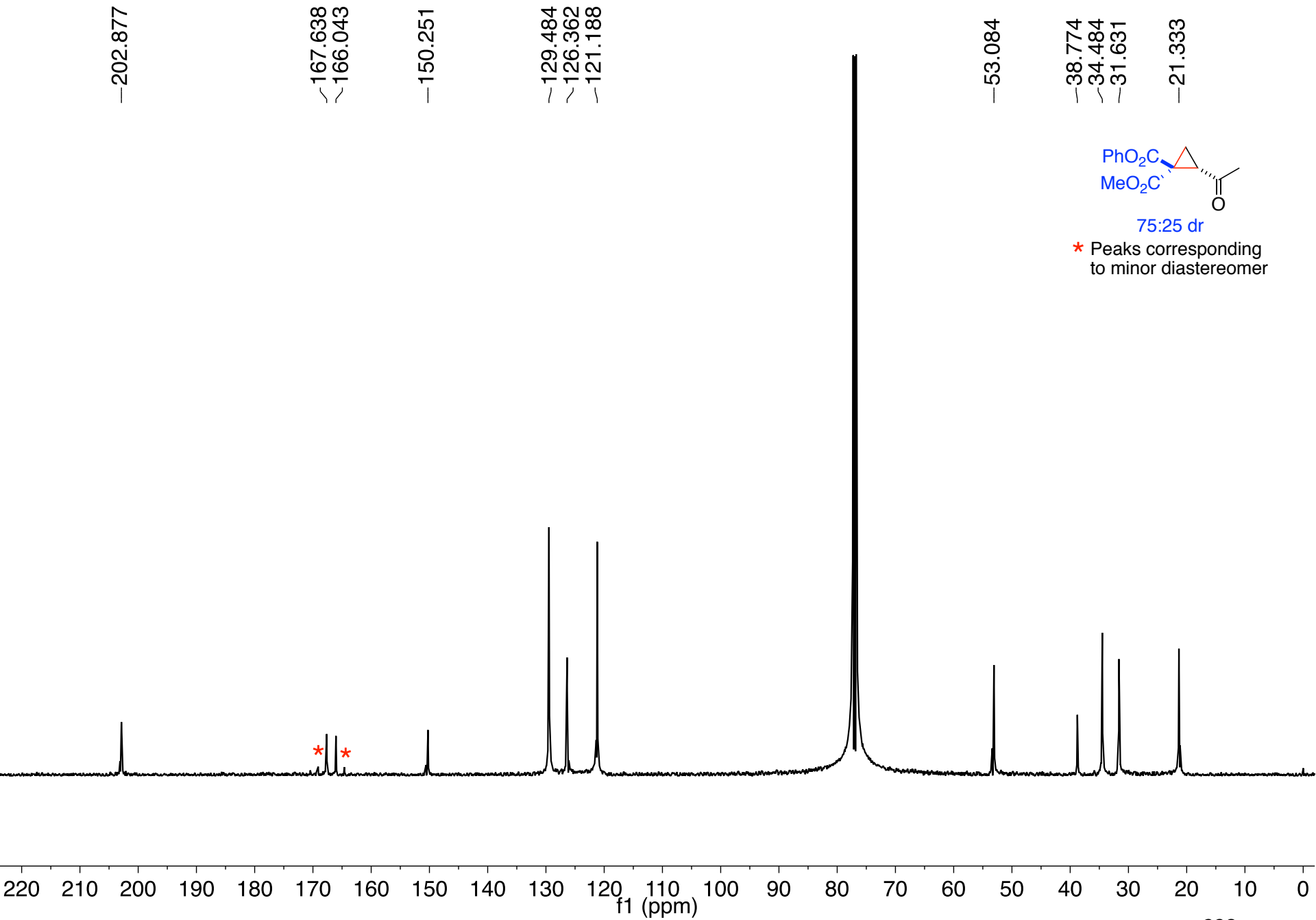
PDA Ch1 205nm

Peak#	Ret. Time	Area	Area%
1	22.057	17413507	97.496
2	33.065	447178	2.504
Total		17860685	100.000

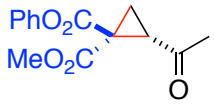
1-methyl 1-phenyl (1*S*,2*S*)-2-acetylcyclopropane-1,1-dicarboxylate



1-methyl 1-phenyl (1*S*,2*S*)-2-acetylcyclopropane-1,1-dicarboxylate



1-methyl 1-phenyl (1*S*,2*S*)-2-acetylcyclopropane-1,1-dicarboxylate

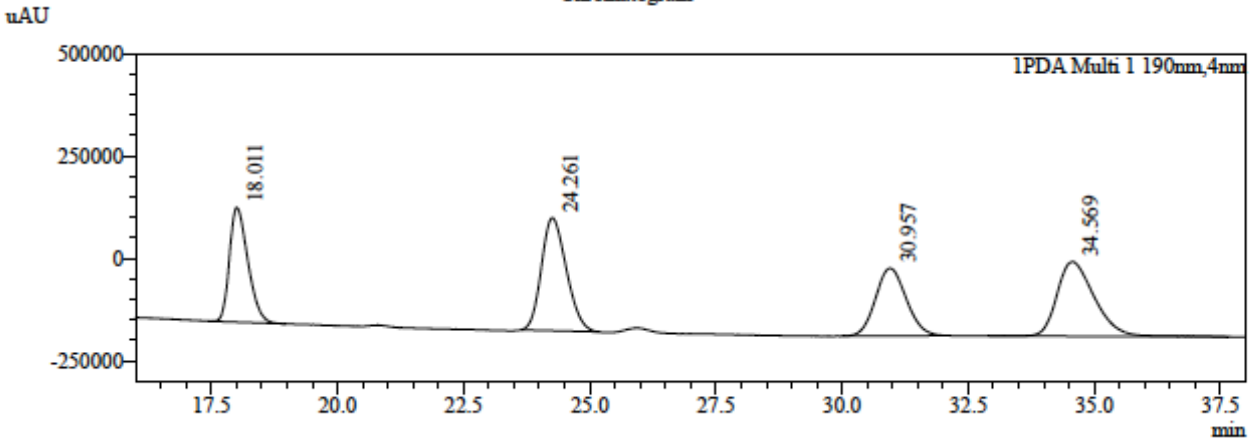


75:25 dr
96% ee

Sample Information

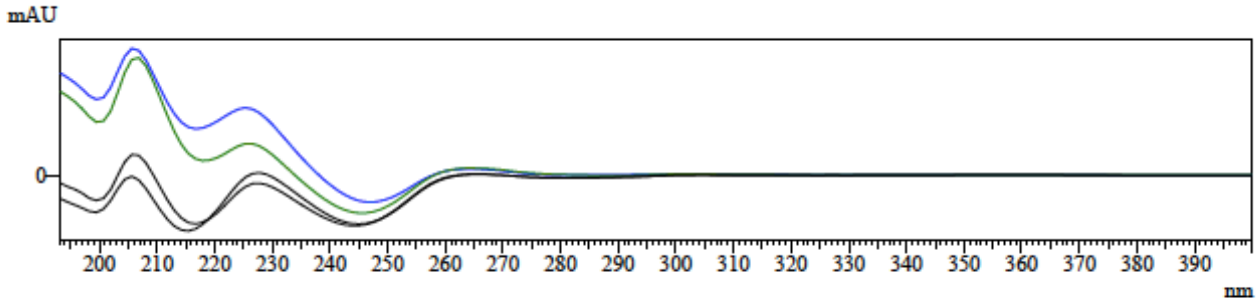
Sample Name	:
Sample ID	: JYW-III-118-IC-20%-0.8ml
Data File	: JYW-III-118-IC-20%-0.8ml.lcd
Method File	: JYW-method.lcm
Date Acquired	: 9/30/2015 3:11:48 PM

Chromatogram



UV Spectrum

JYW-III-118-IC-20%-0.8ml.lcd

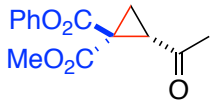


Peak Table

PDA Ch1 190nm

Peak#	Ret. Time	Area	Area%
1	18.011	7110667	21.593
2	24.261	9455803	28.714
3	30.957	7004693	21.271
4	34.569	9359414	28.422
Total		32930578	100.000

1-methyl 1-phenyl (1*S*,2*S*)-2-acetylcyclopropane-1,1-dicarboxylate

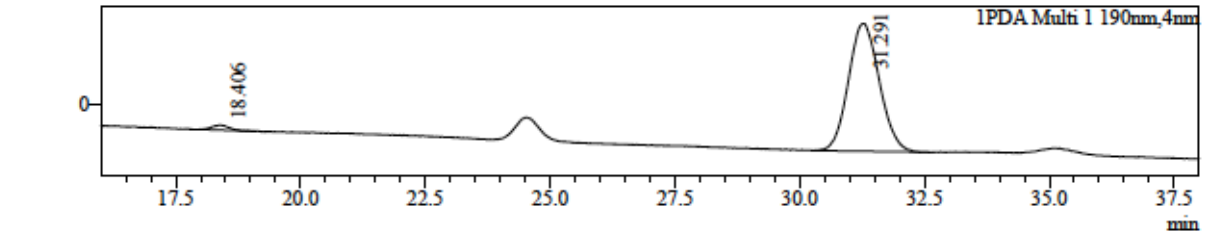


75:25 dr
96% ee

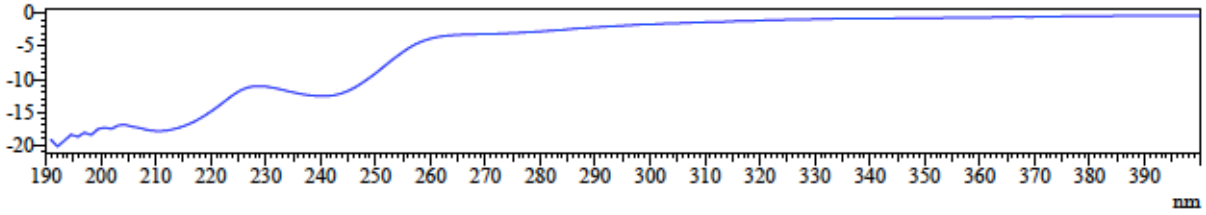
Sample Information

Sample Name	:
Sample ID	: JYW-III-117-IC-20%-0.8ml
Data File	: JYW-III-117-IC-20%-0.8ml.lcd
Method File	: JYW-method.lcm

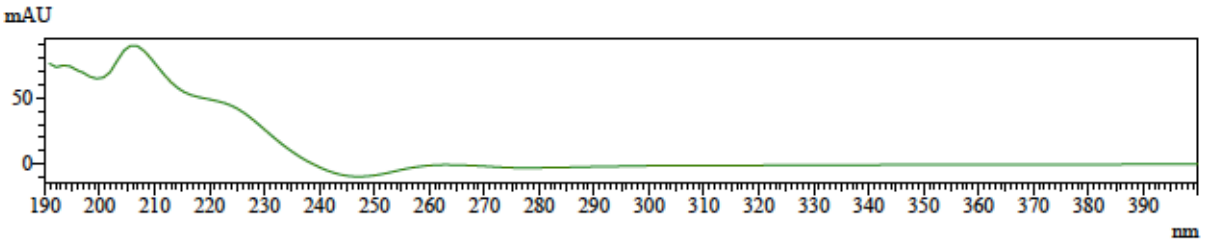
Chromatogram



UV Spectrum
Retention time = 18.406



UV Spectrum
Retention time = 31.291

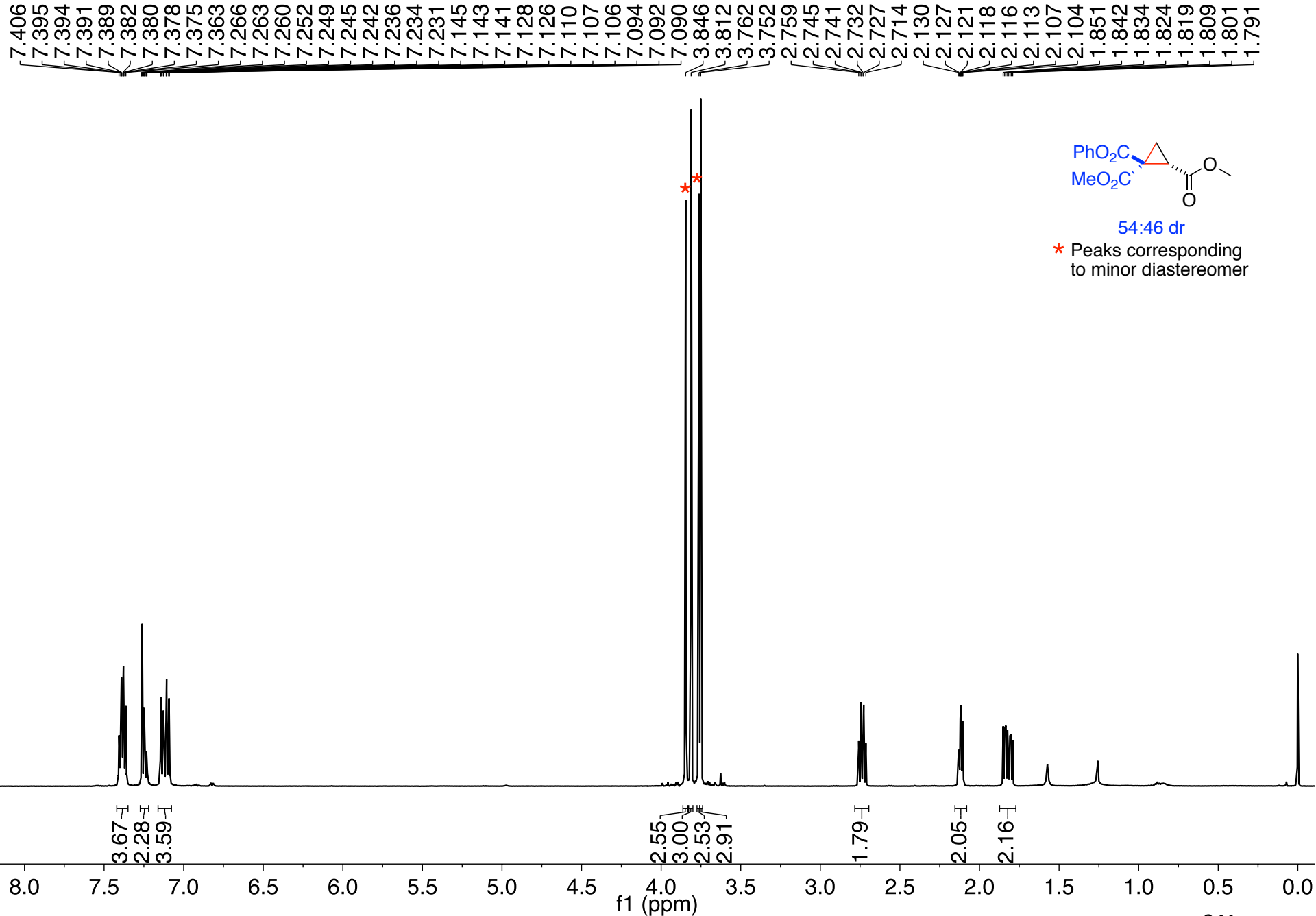


Peak Table

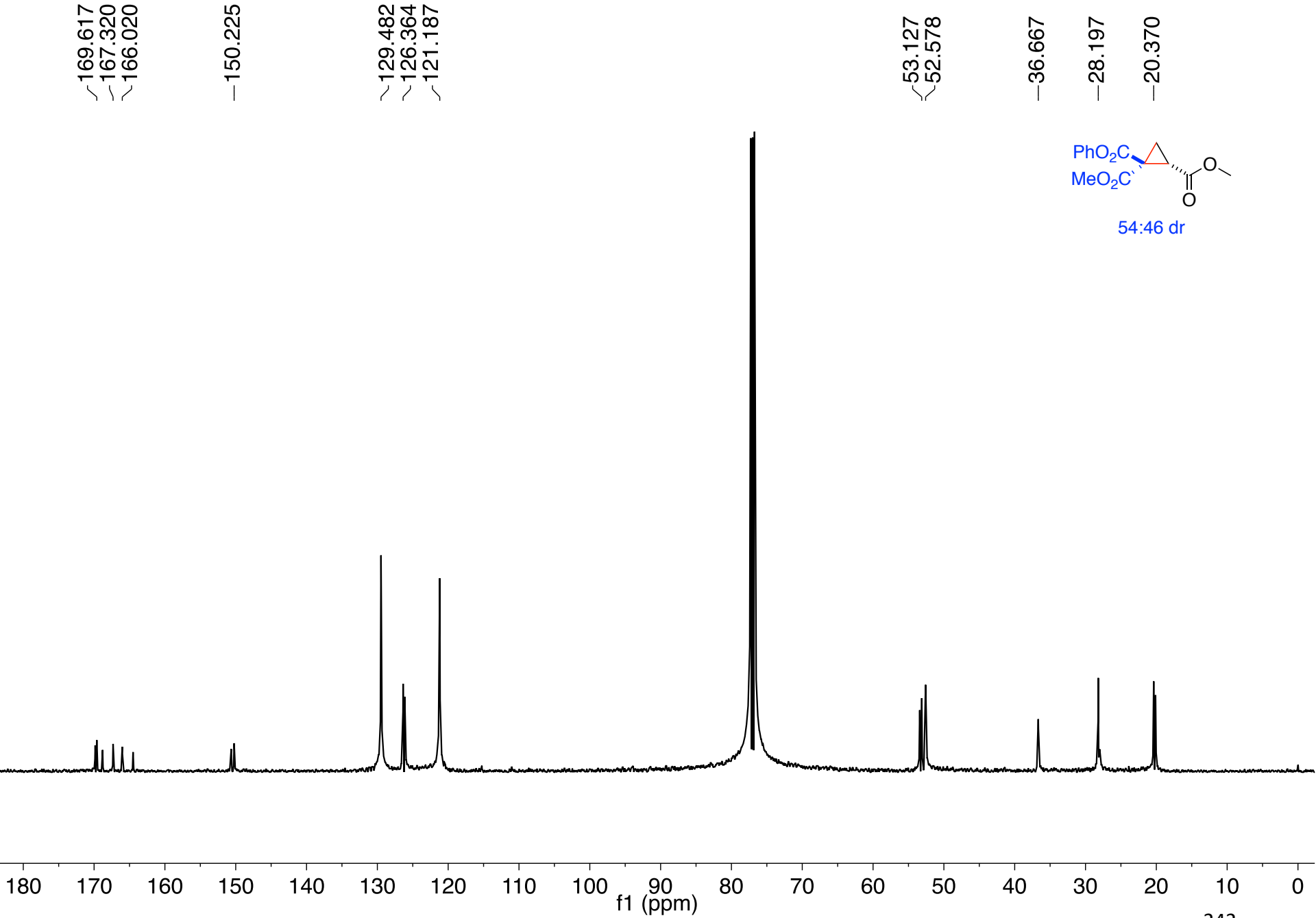
PDA Ch1 190nm

Peak#	Ret. Time	Area	Area%
1	18.406	109744	2.102
2	31.291	5112133	97.898
Total		5221877	100.000

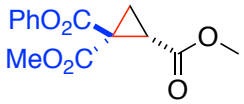
1,2-dimethyl 1-phenyl (1*S*,2*S*)-cyclopropane-1,1,2-tricarboxylate



1,2-dimethyl 1-phenyl (1*S*,2*S*)-cyclopropane-1,1,2-tricarboxylate



1,2-dimethyl 1-phenyl (1*S*,2*S*)-cyclopropane-1,1,2-tricarboxylate

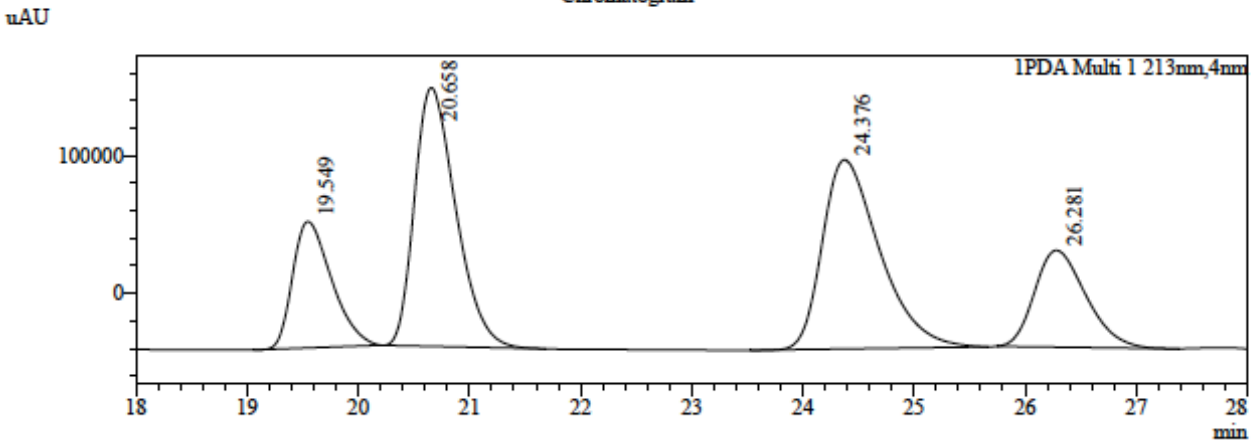


54:46 dr
90% ee

Sample Information

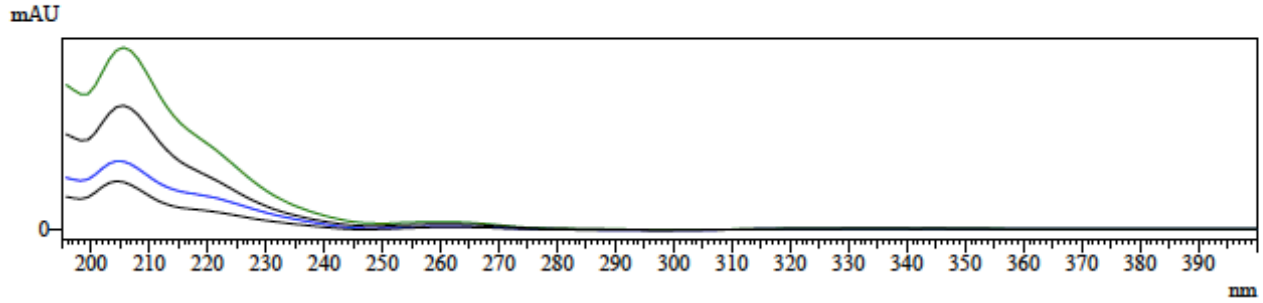
Sample Name	: JYW-III-231
Sample ID	: JYW-III-231-IF-3%-0.8ml
Data File	: JYW-III-231-IF-3%-0.8ml.lcd
Method File	: JYW-method.lcm
Date Acquired	: 10/17/2015 4:58:51 PM

Chromatogram



UV Spectrum

JYW-III-231-IF-3%-0.8ml.lcd

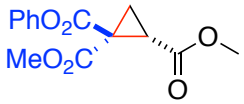


Peak Table

PDA Ch1 213nm

Peak#	Ret. Time	Area	Area%
1	19.549	2237481	15.628
2	20.658	4868574	34.006
3	24.376	4946766	34.552
4	26.281	2263907	15.813
Total		14316728	100.000

1,2-dimethyl 1-phenyl (1*S*,2*S*)-cyclopropane-1,1,2-tricarboxylate

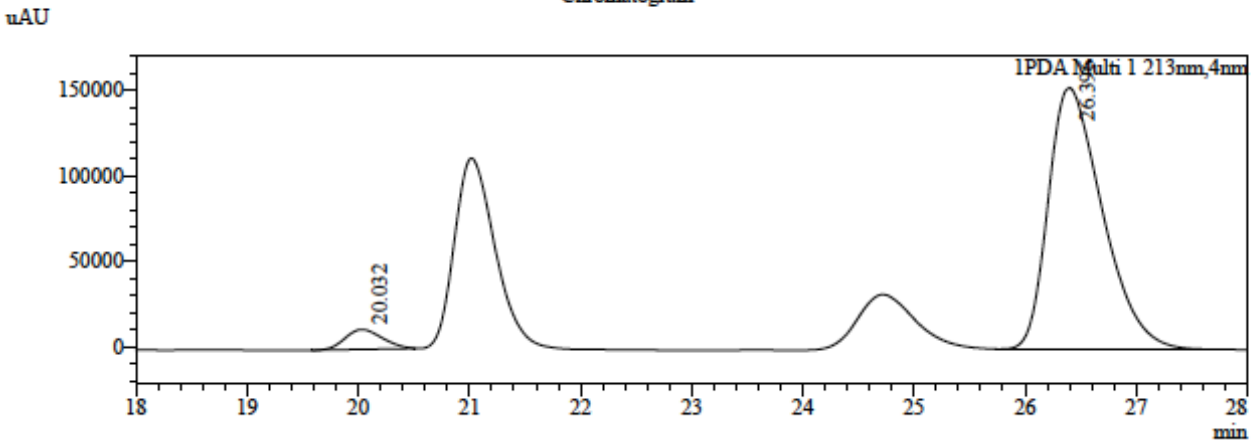


54:46 dr
90% ee

Sample Information

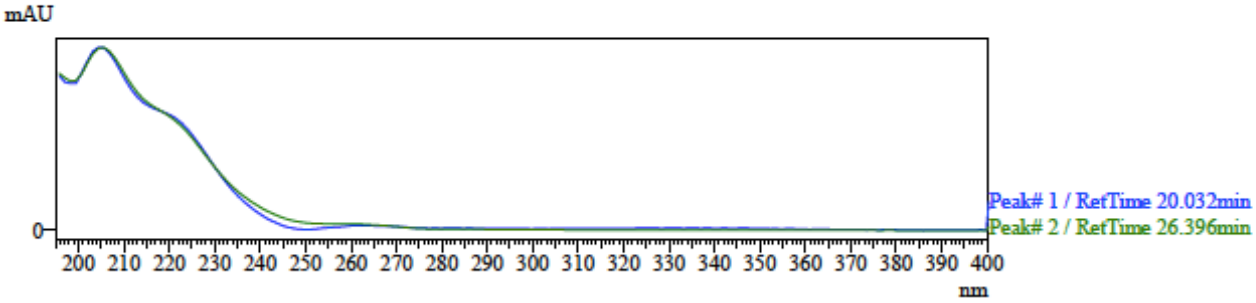
Sample Name	: JYW-III-123
Sample ID	: JYW-III-123-IF-3%-0.8mlre
Data File	: JYW-III-123-IF-3%-0.8mlre.lcd
Method File	: JYW-method.lcm
Date Acquired	: 10/17/2015 5:34:28 PM

Chromatogram



UV Spectrum

JYW-III-123-IF-3%-0.8mlre.lcd

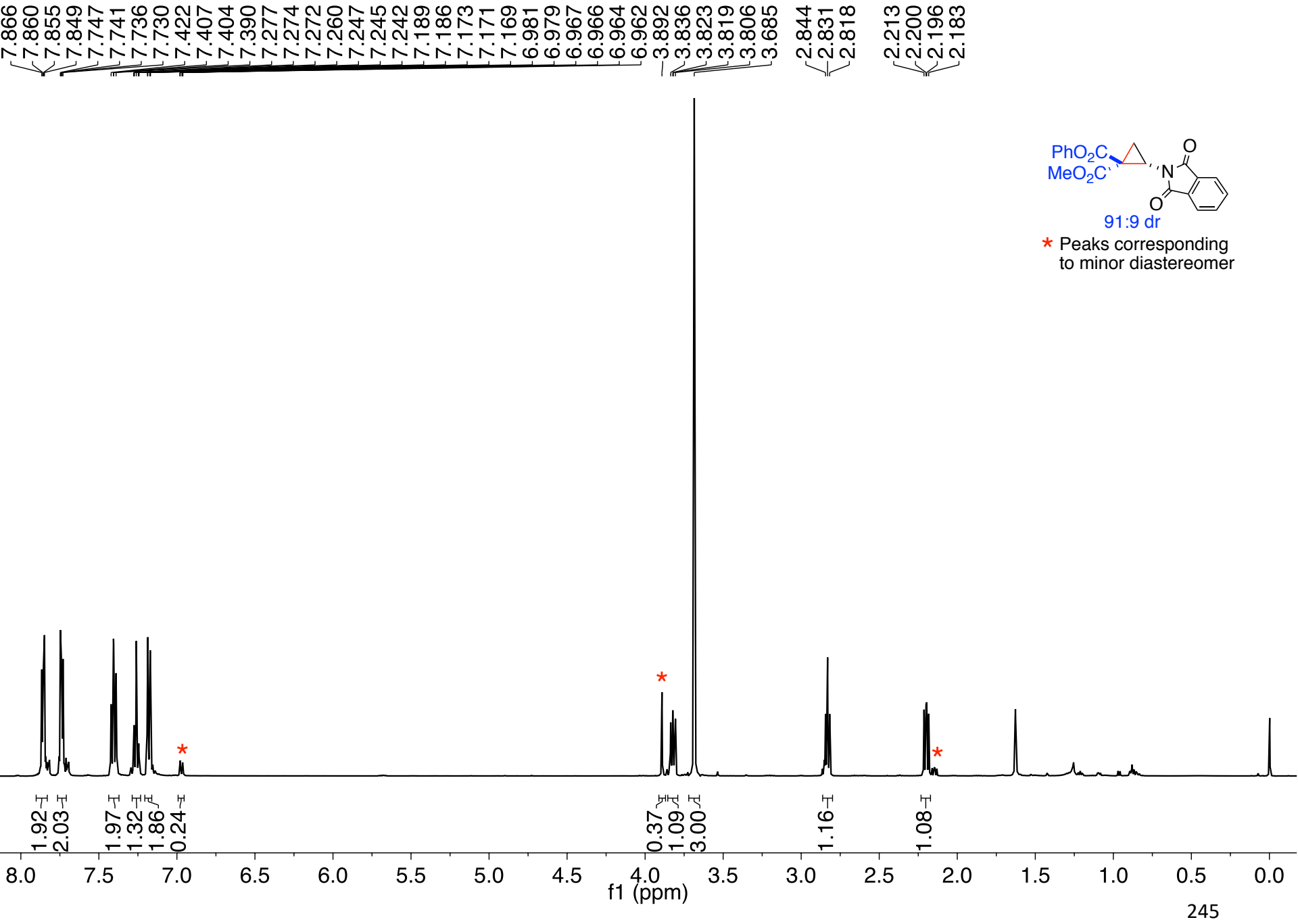


Peak Table

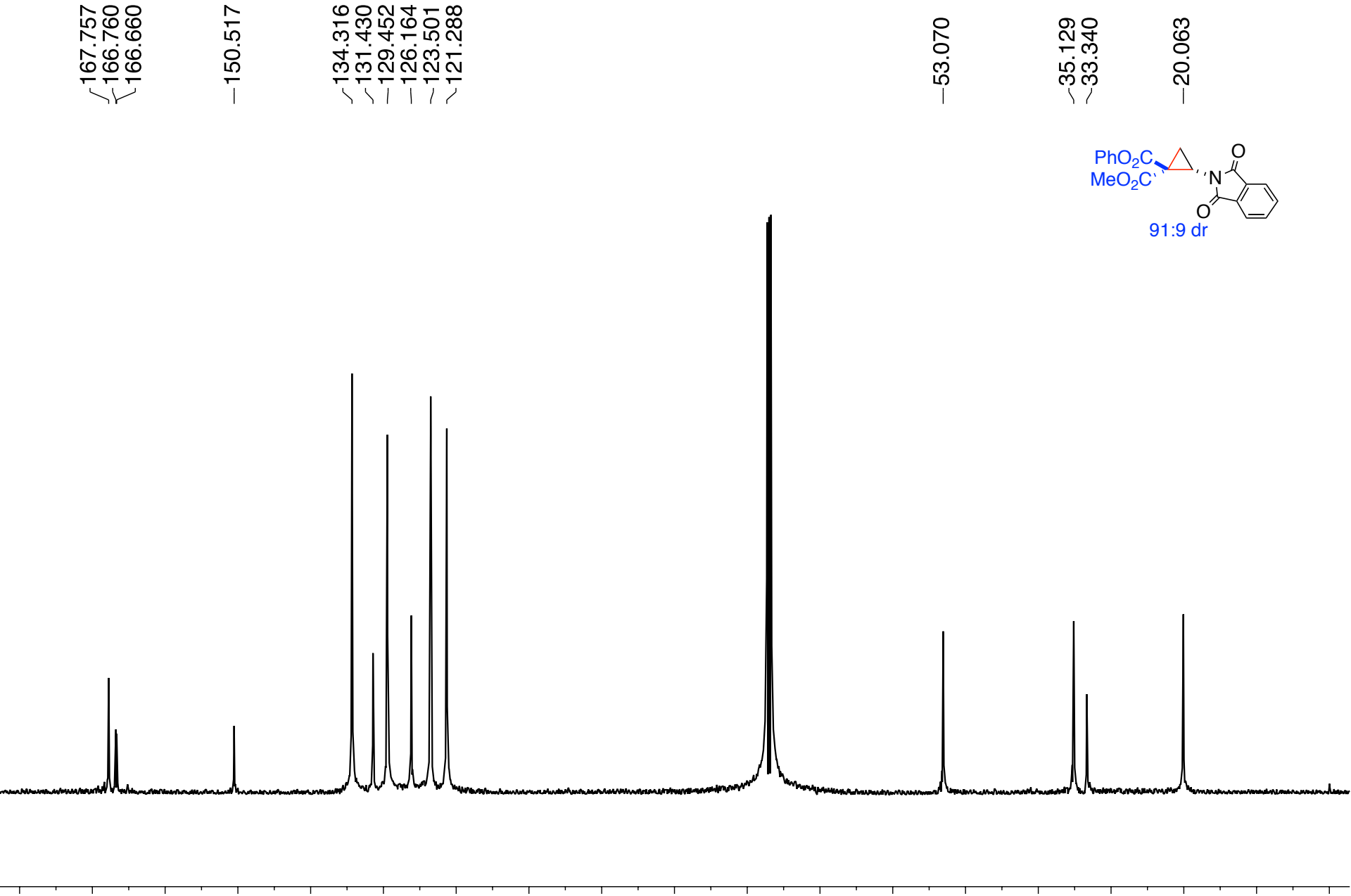
PDA Ch1 213nm

Peak#	Ret. Time	Area	Area%
1	20.032	269074	4.945
2	26.396	5172315	95.055
Total		5441389	100.000

1-methyl 1-phenyl (1*S*,2*S*)-2-(1,3-dioxoisoindolin-2-yl)cyclopropane-1,1-dicarboxylate



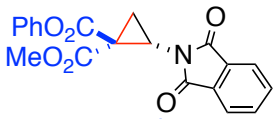
1-methyl 1-phenyl (1*S*,2*S*)-2-(1,3-dioxoisoindolin-2-yl)cyclopropane-1,1-dicarboxylate



1-methyl 1-phenyl (1*S*,2*S*)-2-(1,3-dioxoisoindolin-2-yl)cyclopropane-1,1-dicarboxylate

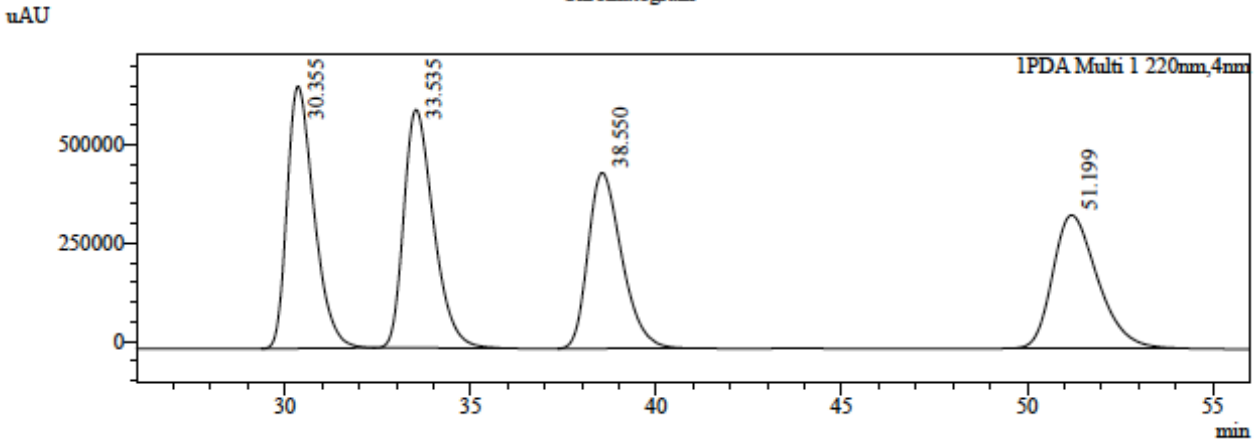
Sample Information

Sample Name	: JYW-III-232
Sample ID	: JYW-III-232-IC-20%-0.8ml
Data File	: JYW-III-232-IC-20%-0.8ml.lcd
Method File	: JYW-method.lcm
Date Acquired	: 10/19/2015 3:23:59 PM



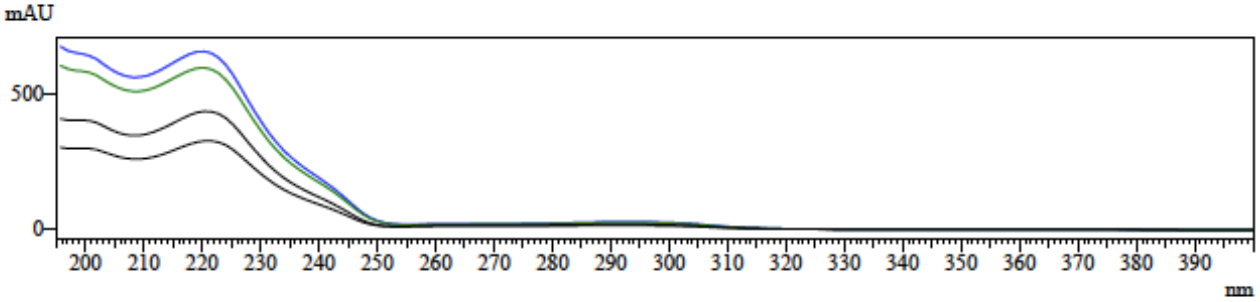
91:9 dr
95% ee

Chromatogram



UV Spectrum

JYW-III-232-IC-20%-0.8ml.lcd



Peak Table

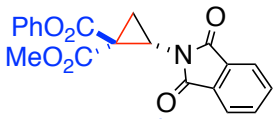
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	30.355	33707299	27.157
2	33.535	33827736	27.254
3	38.550	28080462	22.623
4	51.199	28506884	22.967
Total		124122380	100.000

1-methyl 1-phenyl (1*S*,2*S*)-2-(1,3-dioxoisoindolin-2-yl)cyclopropane-1,1-dicarboxylate

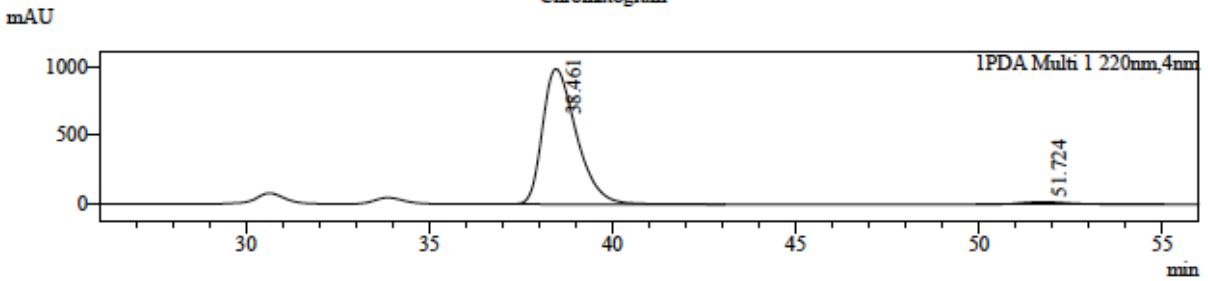
Sample Information

Sample Name : JYW-II-213
Sample ID : JYW-II-213-IC-20%-0.8ml
Data File : JYW-II-213-IC-20%-0.8ml.lcd
Method File : JYW-method.lcm

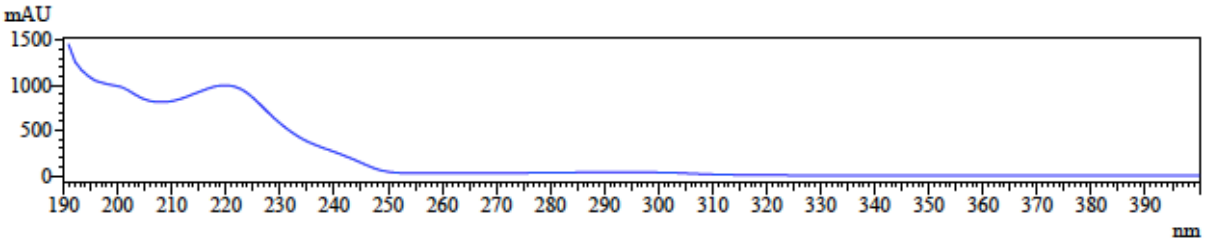


91:9 dr
95% ee

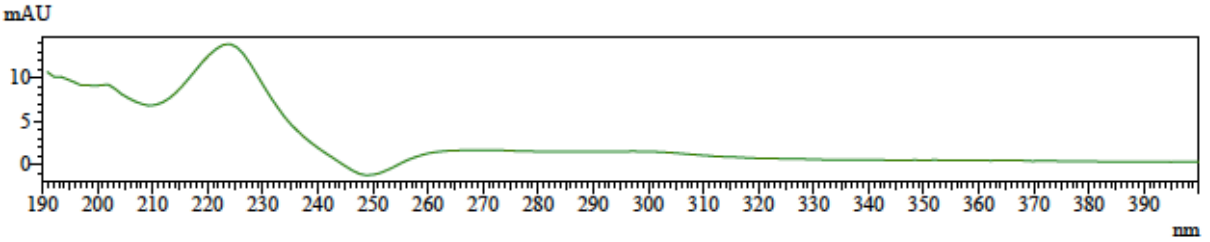
Chromatogram



UV Spectrum
Retention time = 38.461



UV Spectrum
Retention time = 51.724

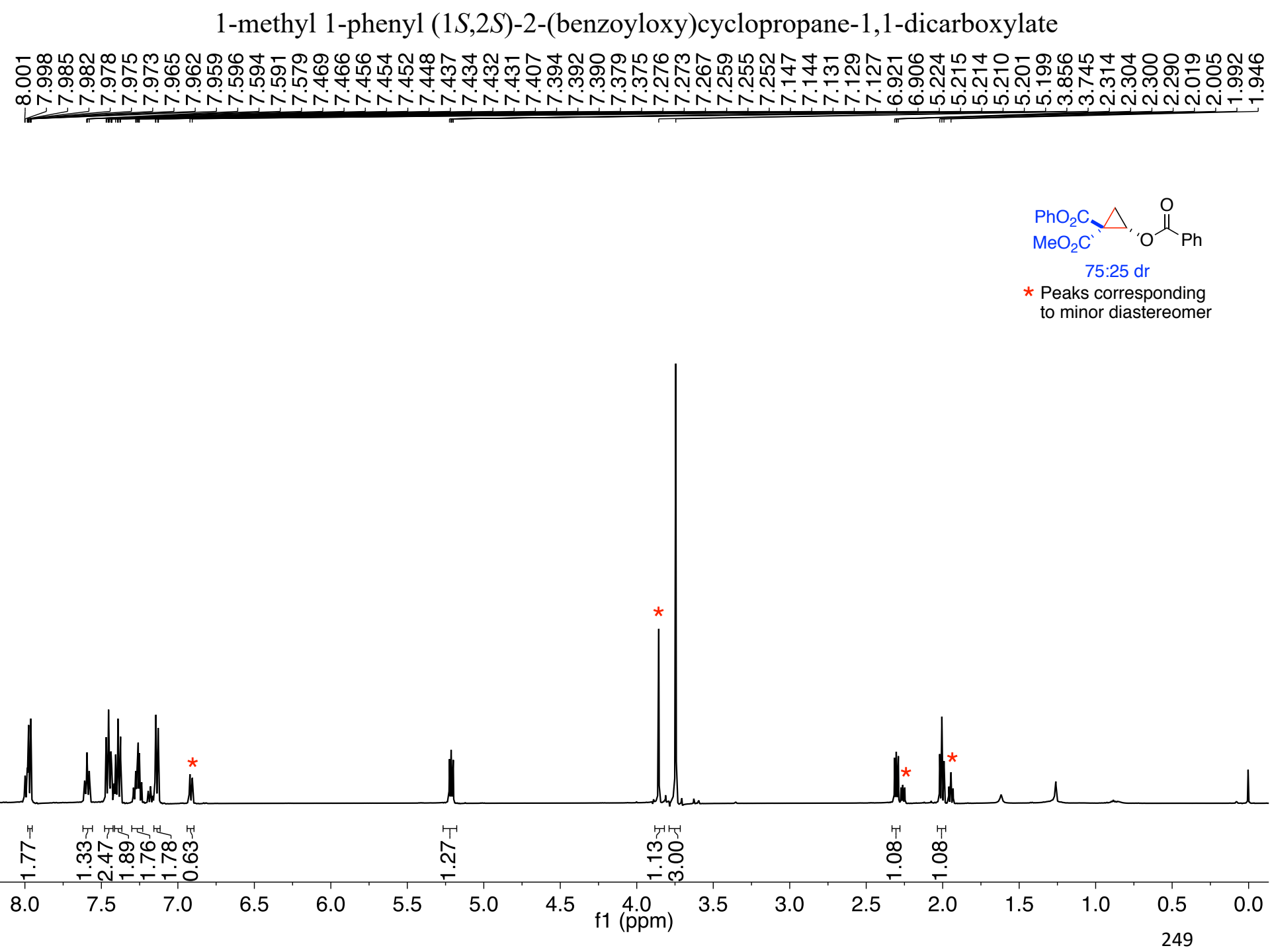


Peak Table

PDA Ch1 220nm

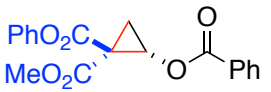
Peak#	Ret. Time	Area	Area%
1	38.461	63522341	97.251
2	51.724	1795600	2.749
Total		65317941	100.000

1-methyl 1-phenyl (1*S*,2*S*)-2-(benzoyloxy)cyclopropane-1,1-dicarboxylate



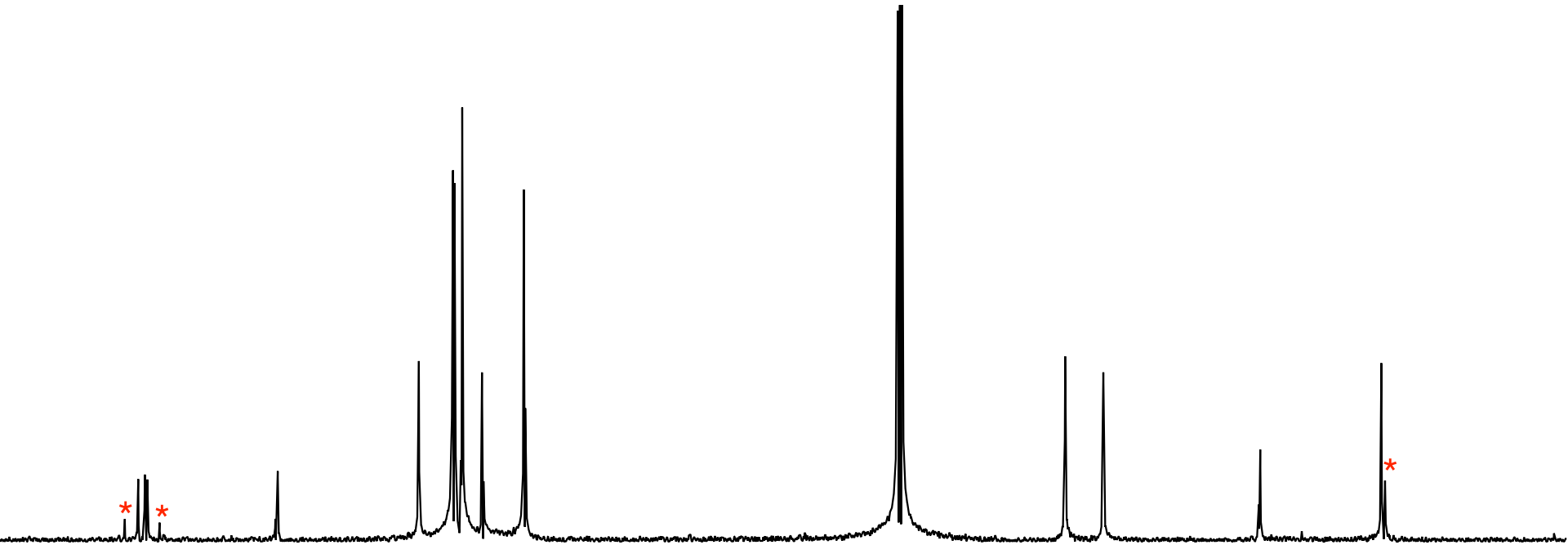
1-methyl 1-phenyl (1*S*,2*S*)-2-(benzoyloxy)cyclopropane-1,1-dicarboxylate

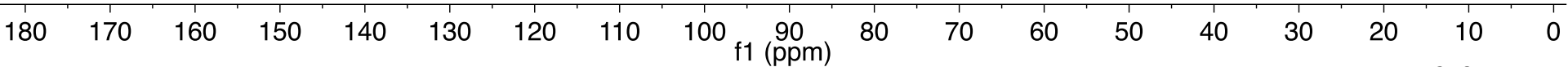
166.692
165.921
165.623
150.265
133.641
129.624
129.446
128.537
126.212
121.289
57.526
53.037
34.553
20.292



75:25 dr

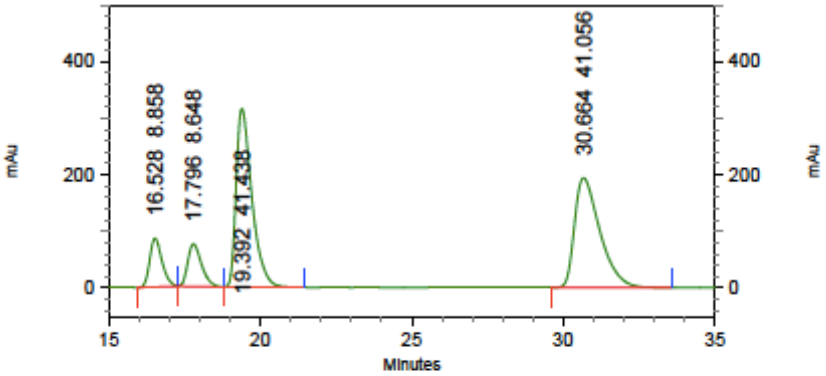
* Peaks corresponding to minor diastereomer

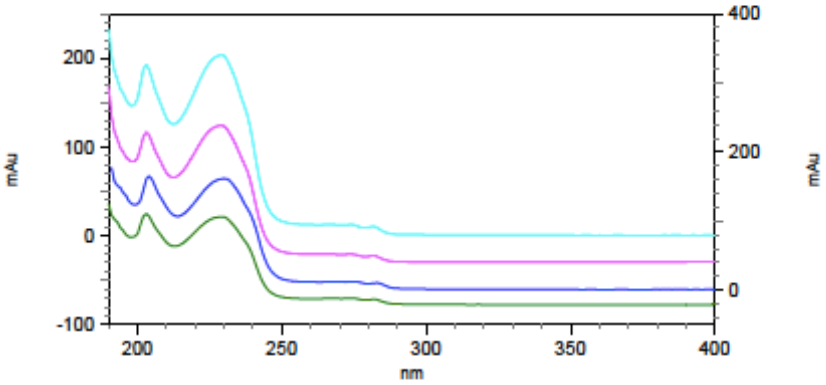


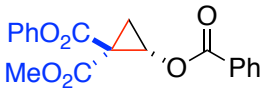


1-methyl 1-phenyl (1*S*,2*S*)-2-(benzoyloxy)cyclopropane-1,1-dicarboxylate

JYW-II-273-ODH-3%-0.8ml
C:\EZStart\Projects\Default\Method\lk-5%0.8.met
C:\EZStart\Projects\Default\Data\JYW-II-273-ODH-3%-0.8ml







75:25 dr
71% ee

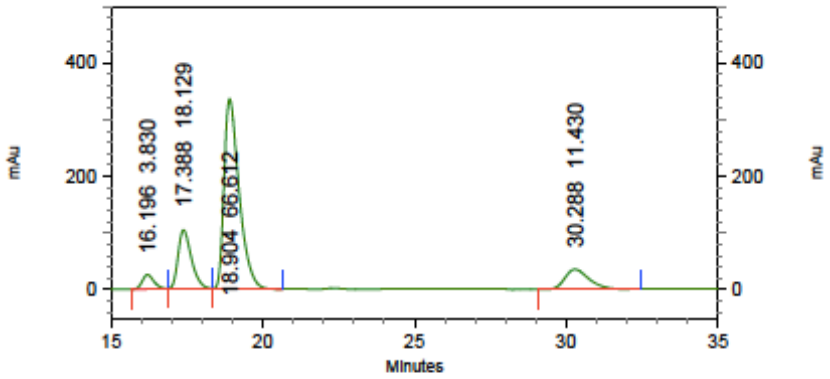
6: 225 nm, 4 nm
Results

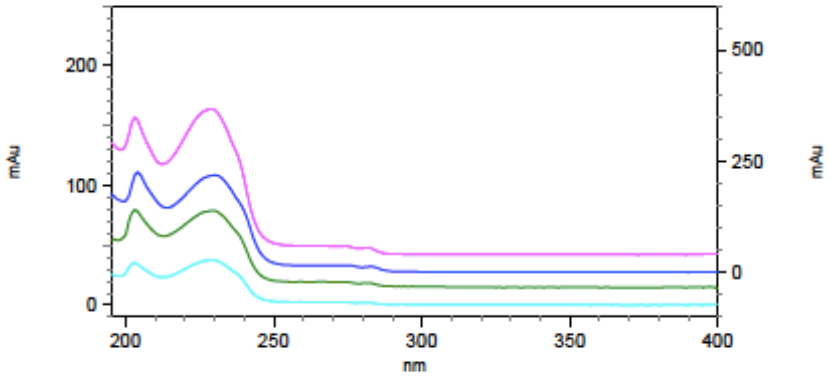
Name	Retention Time	Area Percent	Pk #
	16.528	8.858	1
	17.796	8.648	2
	19.392	41.438	3
	30.664	41.056	4

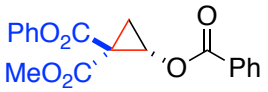
Totals	
	100.000

1-methyl 1-phenyl (1*S*,2*S*)-2-(benzoyloxy)cyclopropane-1,1-dicarboxylate

JYW-III-88-ODH-3%-0.8ml
C:\EZStart\Projects\Default\Method\lk-5%0.8.met
C:\EZStart\Projects\Default\Data\JYW-III-88-ODH-3%-0.8ml







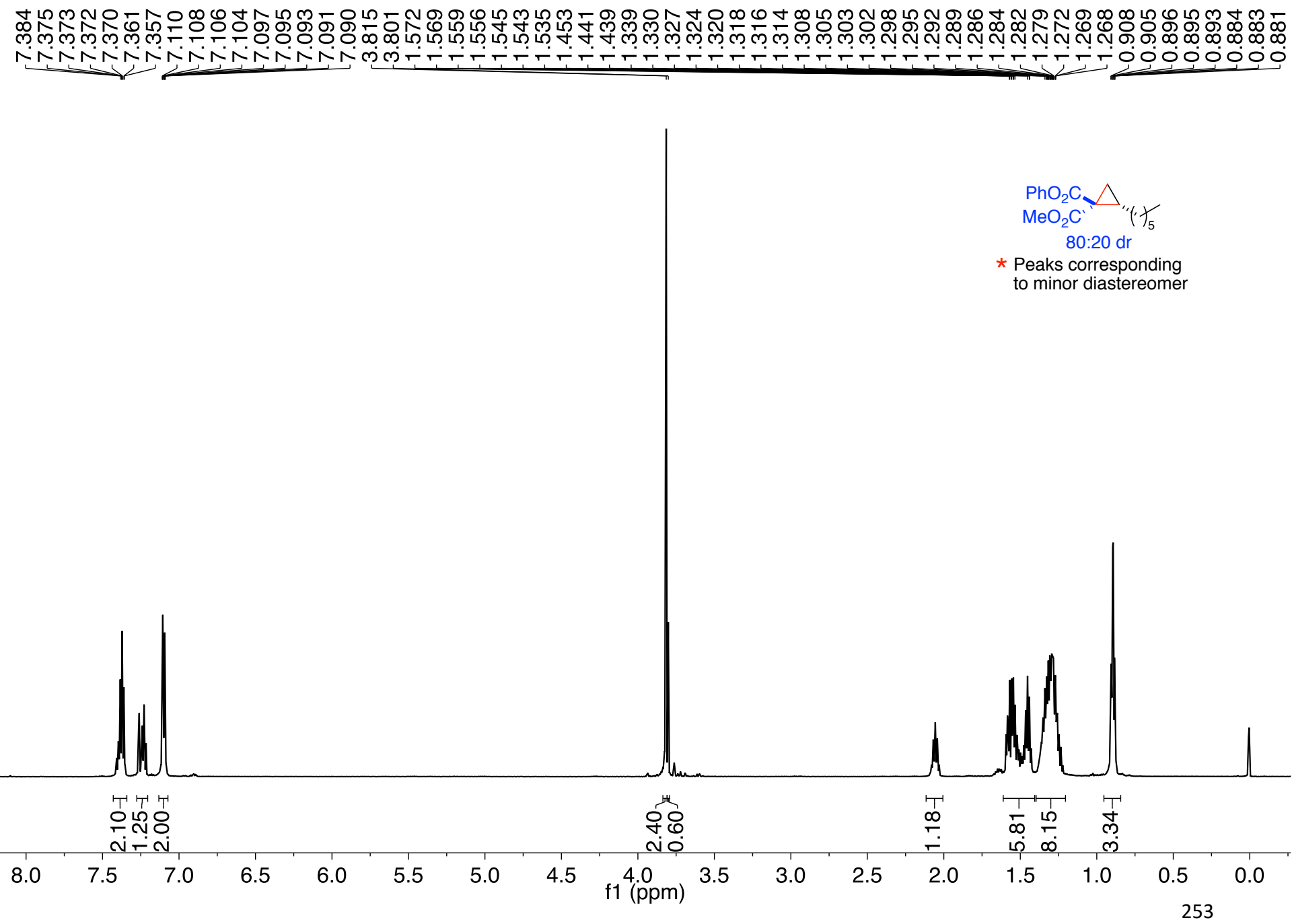
75:25 dr
71% ee

6: 225 nm, 4 nm
Results

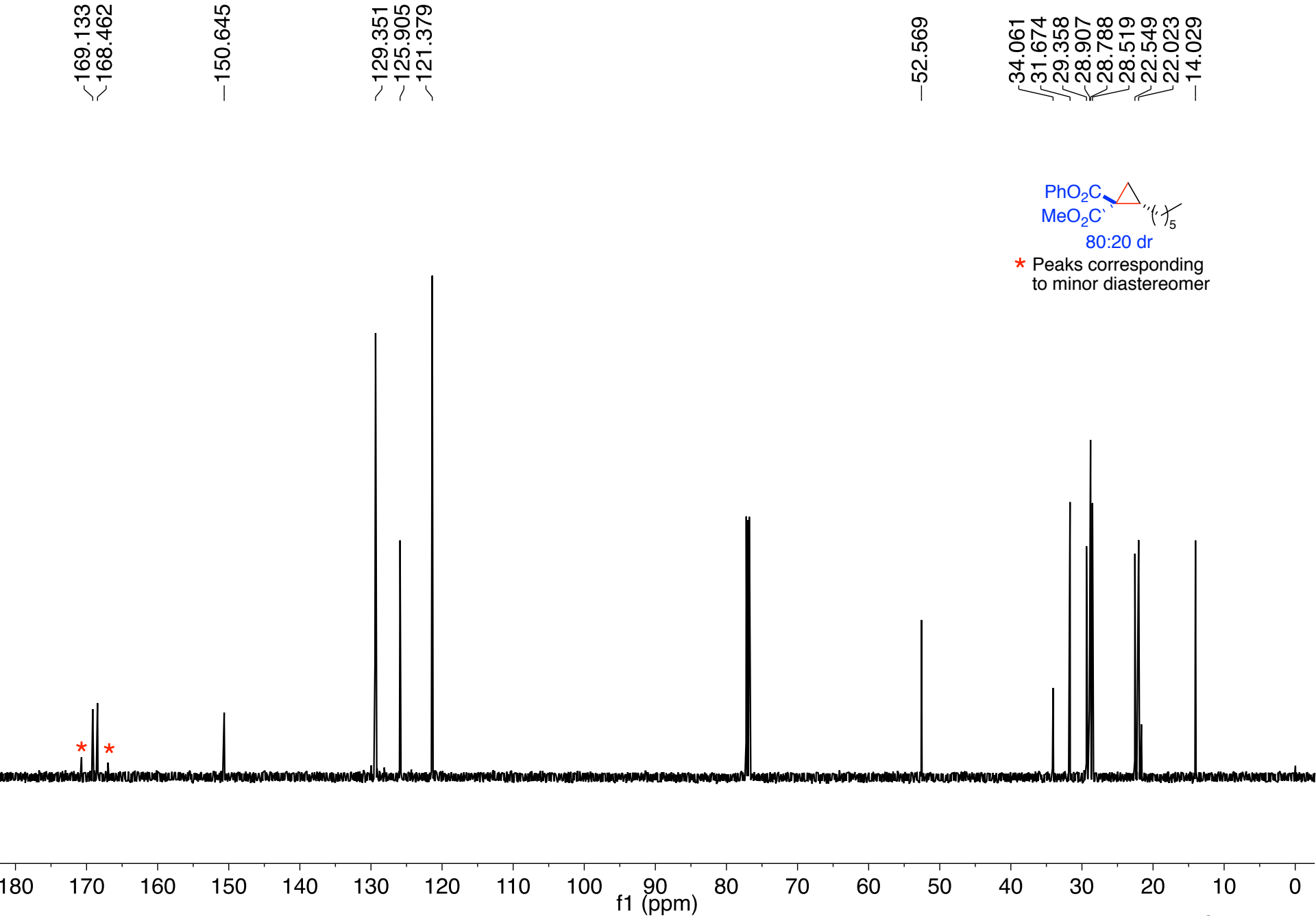
Name	Retention Time	Area Percent	Pk #
	16.196	3.830	1
	17.388	18.129	2
	18.904	66.612	3
	30.288	11.430	4

Totals	
	100.000

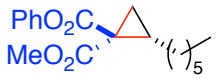
1-methyl 1-phenyl (1*S*,2*S*)-2-hexylcyclopropane-1,1-dicarboxylate



1-methyl 1-phenyl (1*S*,2*S*)-2-hexylcyclopropane-1,1-dicarboxylate



1-methyl 1-phenyl (1*S*,2*S*)-2-hexylcyclopropane-1,1-dicarboxylate

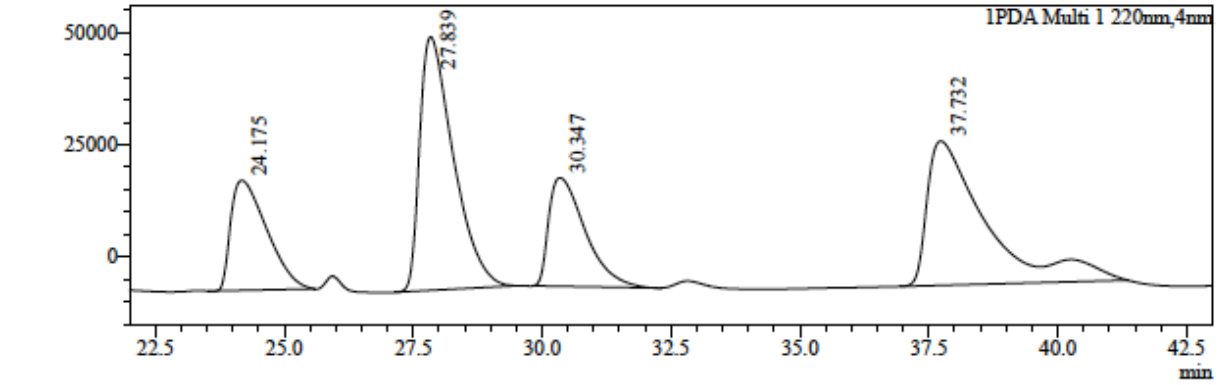


80:20 dr
72% ee

Sample Information

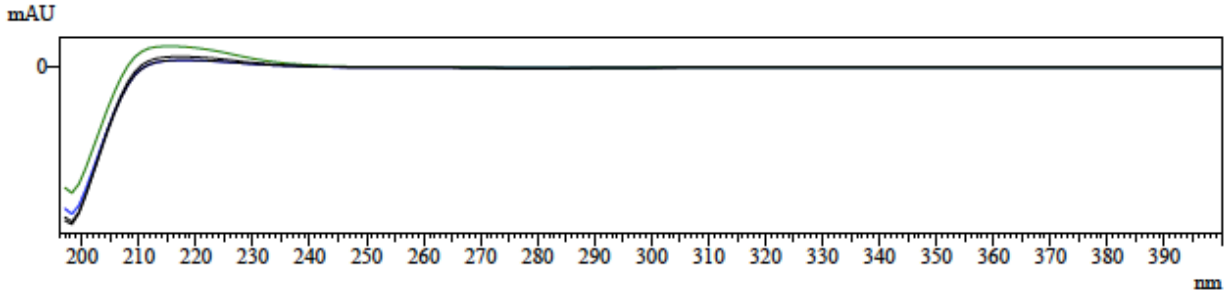
Sample Name	: JYW-III-281B
Sample ID	: JYW-III-281B-IB-0.1%-0.8ml
Data File	: JYW-III-281B-IB-0.1%-0.8ml.lcd
Method File	: JYW-method.lcm
Date Acquired	: 12/4/2015 10:31:50 AM

Chromatogram



UV Spectrum

JYW-III-281B-IB-0.1%-0.8ml.lcd

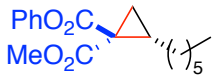


Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	24.175	1188409	15.806
2	27.839	2568482	34.162
3	30.347	1184503	15.754
4	37.732	2577118	34.277
Total		7518513	100.000

1-methyl 1-phenyl (1*S*,2*S*)-2-hexylcyclopropane-1,1-dicarboxylate

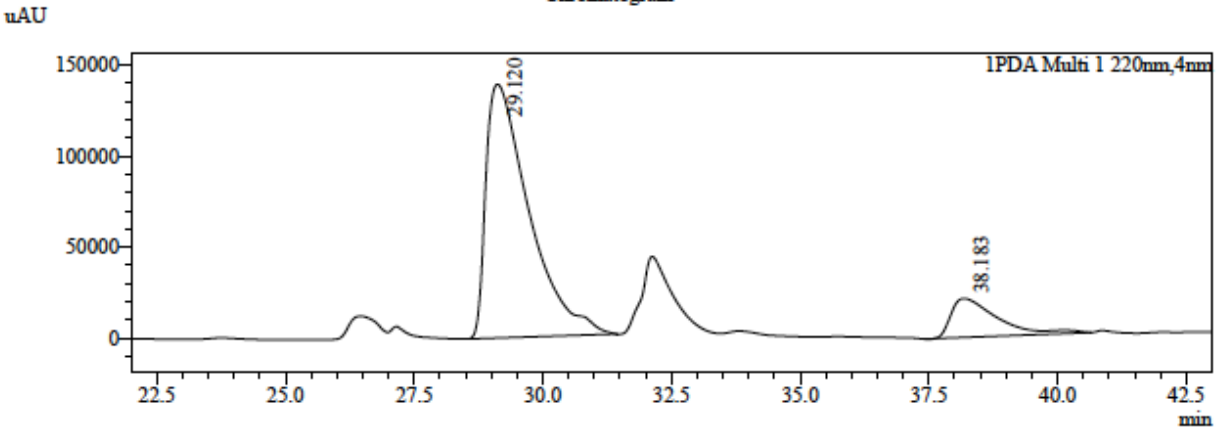


80:20 dr
72% ee

Sample Information

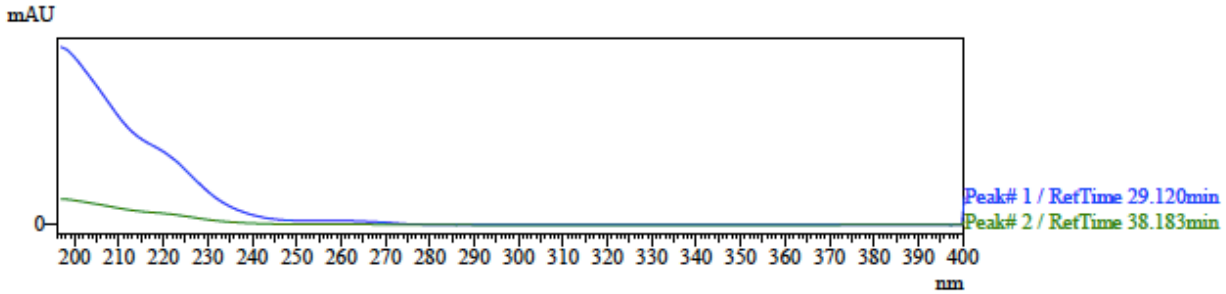
Sample Name	: JYW-III-288
Sample ID	: JYW-III-288-IB-0.1%-0.8ml
Data File	: JYW-III-288-IB-0.1%-0.8ml.lcd
Method File	: JYW-method.lcm
Date Acquired	: 12/4/2015 12:14:54 PM

Chromatogram



UV Spectrum

JYW-III-288-IB-0.1%-0.8ml.lcd

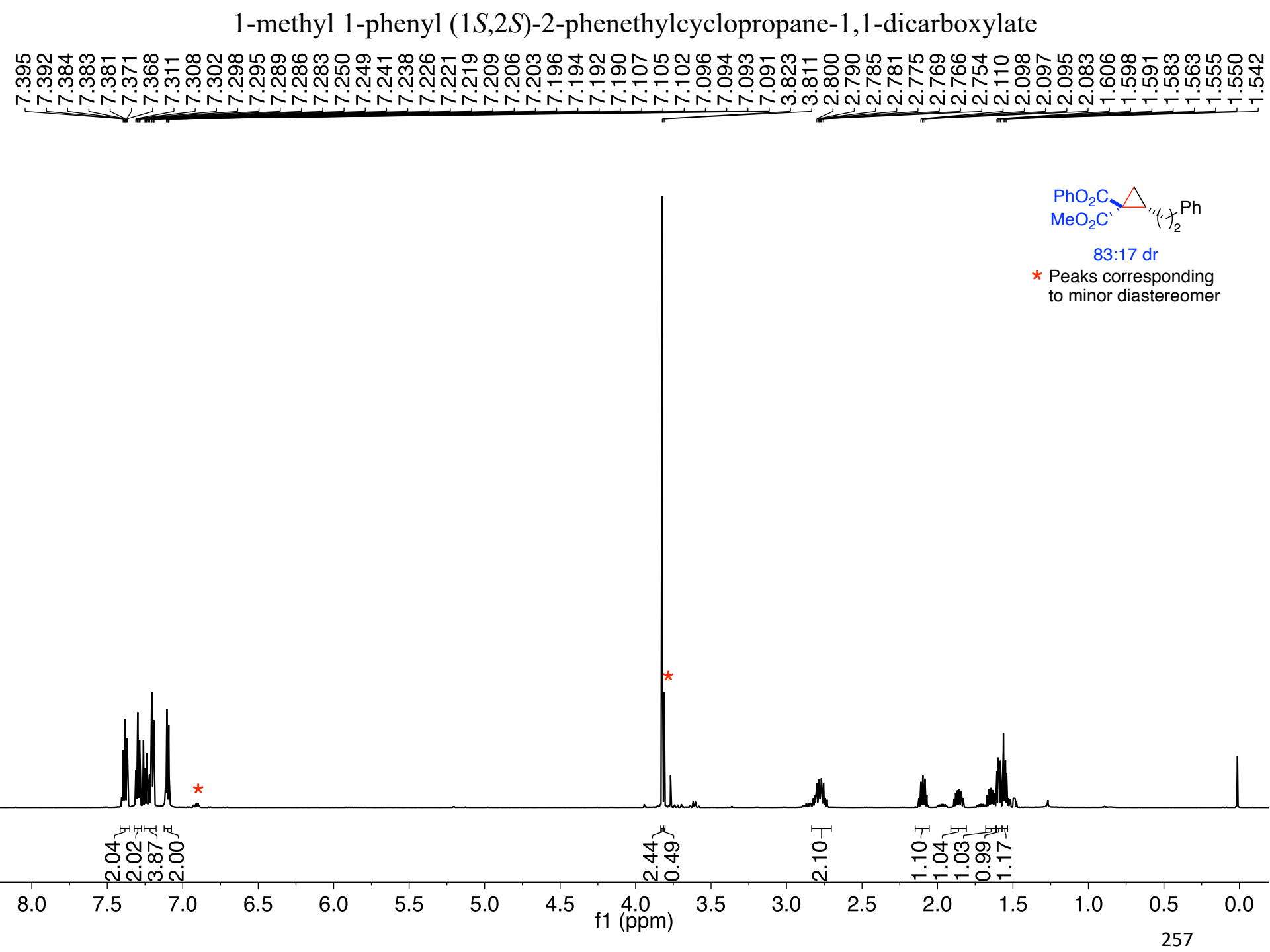


Peak Table

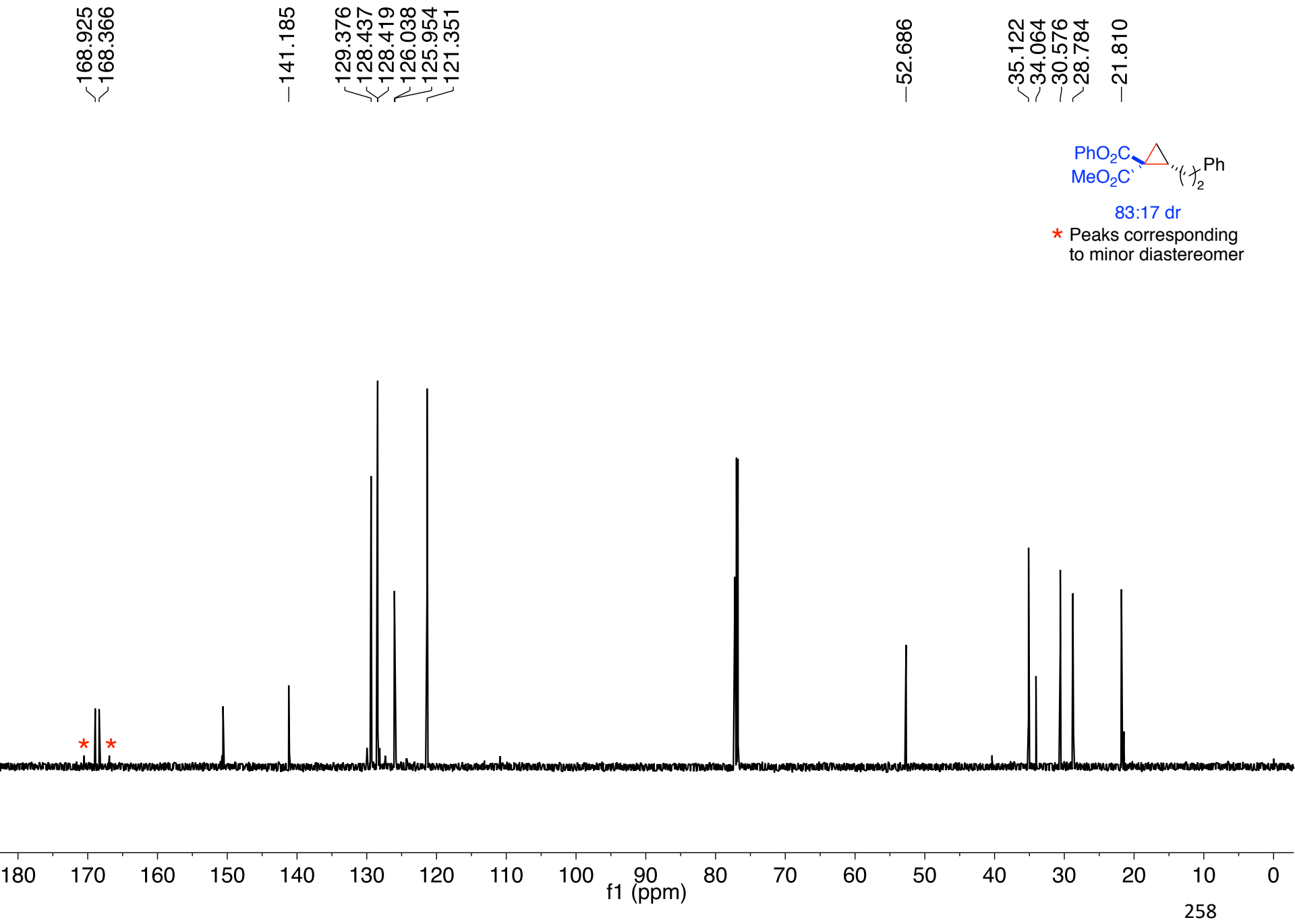
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	29.120	8119675	85.902
2	38.183	1332540	14.098
Total		9452215	100.000

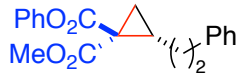
1-methyl 1-phenyl (1*S*,2*S*)-2-phenethylcyclopropane-1,1-dicarboxylate



1-methyl 1-phenyl (1*S*,2*S*)-2-phenethylcyclopropane-1,1-dicarboxylate



1-methyl 1-phenyl (1*S*,2*S*)-2-phenethylcyclopropane-1,1-dicarboxylate

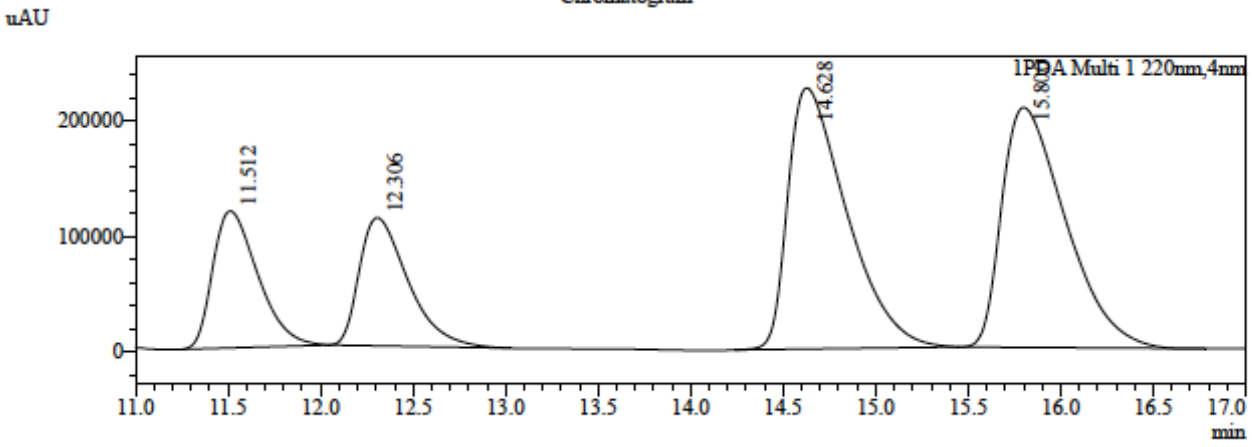


83:17 dr
80% ee

Sample Information

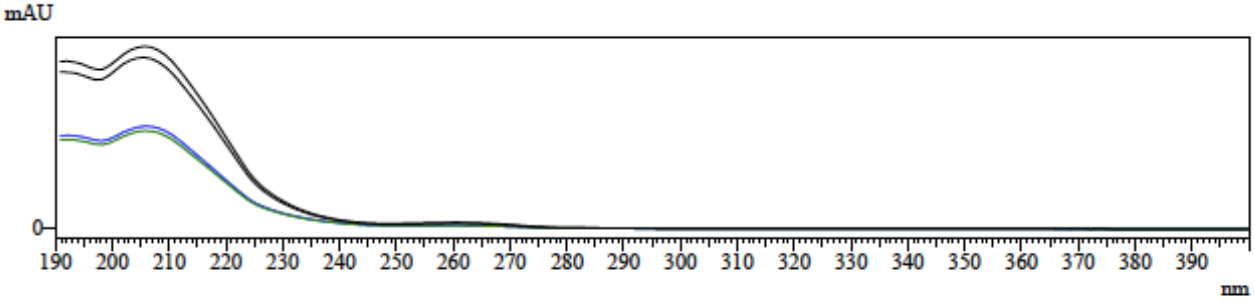
Sample Name	: JYW-III-283B
Sample ID	: JYW-III-283B-IB-0.8%-0.8ml
Data File	: JYW-III-283B-IB-0.8%-0.8ml.lcd
Method File	: JYW-method.lcm
Date Acquired	: 12/3/2015 5:25:52 PM

Chromatogram



UV Spectrum

JYW-III-283B-IB-0.8%-0.8ml.lcd



Peak Table

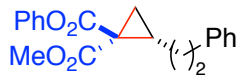
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	11.512	2003845	14.316
2	12.306	2027166	14.483
3	14.628	4992747	35.670
4	15.800	4973469	35.532
Total		13997226	100.000

1-methyl 1-phenyl (1*S*,2*S*)-2-phenethylcyclopropane-1,1-dicarboxylate

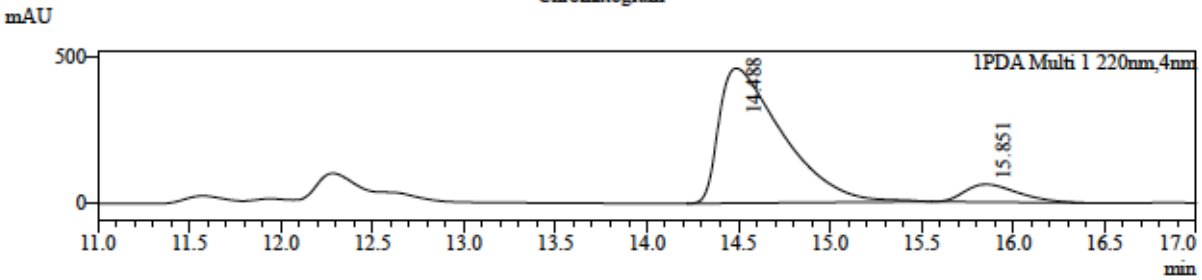
Sample Information

Sample Name : JYW-III-290
Sample ID : JYW-III-290-IB-0.8%-0.8ml
Data File : JYW-III-290-IB-0.8%-0.8ml.lcd
Method File : JYW-method.lcm

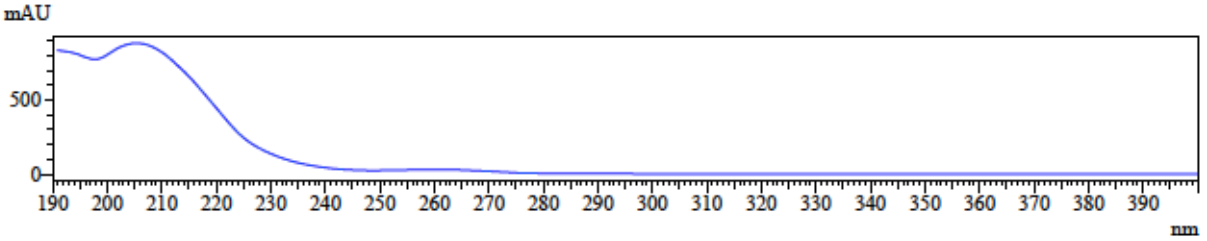


83:17 dr
80% ee

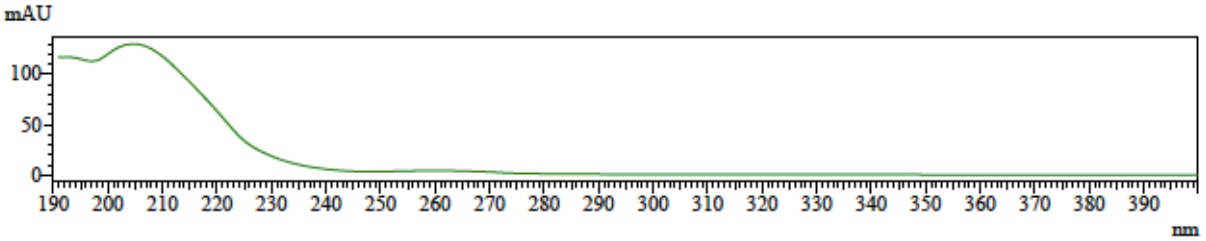
Chromatogram



UV Spectrum
Retention time = 14.488



UV Spectrum
Retention time = 15.851

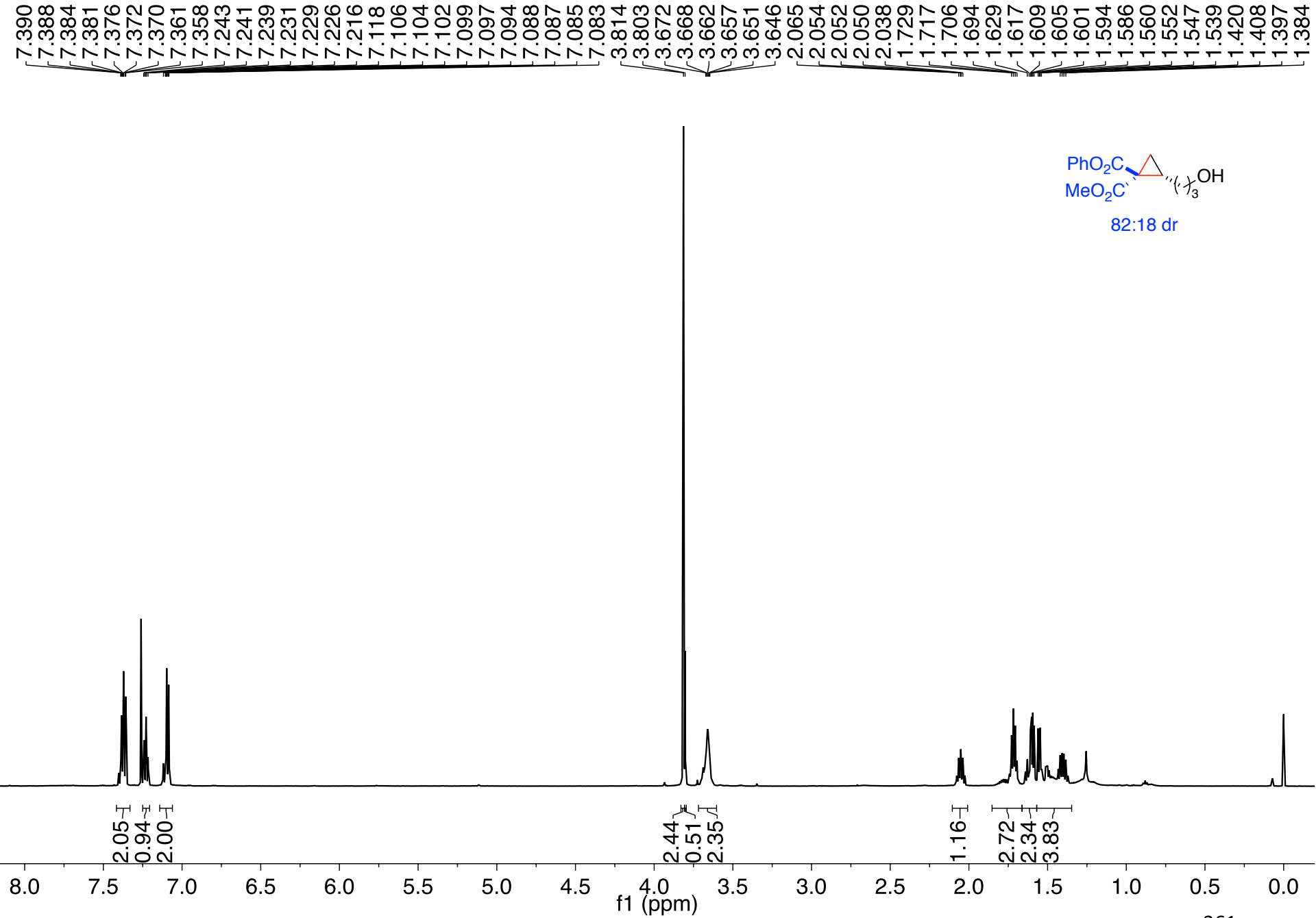


Peak Table

PDA Ch1 220nm

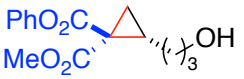
Peak#	Ret. Time	Area	Area%
1	14.488	11079412	90.007
2	15.851	1230143	9.993
Total		12309555	100.000

1-methyl 1-phenyl (1*S*,2*S*)-2-(3-hydroxypropyl)cyclopropane-1,1-dicarboxylate



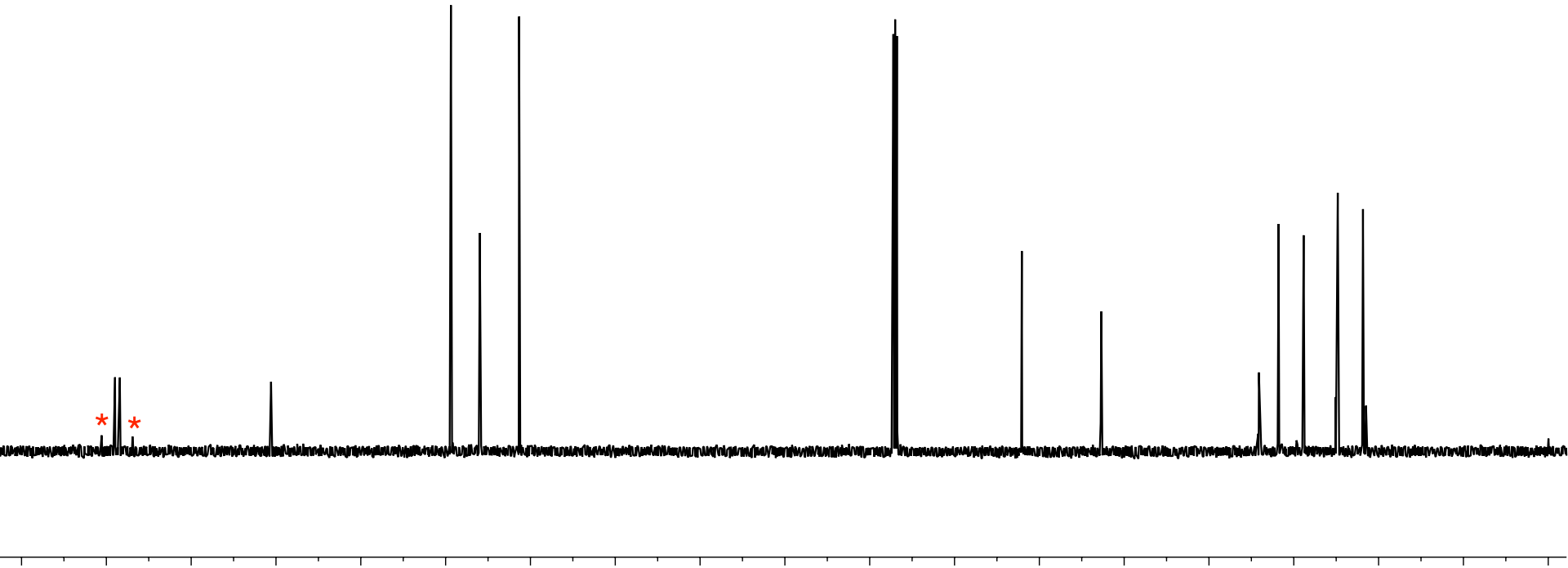
1-methyl 1-phenyl (1*S*,2*S*)-2-(3-hydroxypropyl)cyclopropane-1,1-dicarboxylate

168.978
168.411
150.582
129.376
125.970
121.335
62.066
52.690
34.115
31.794
28.837
24.816
21.842



82:18 dr

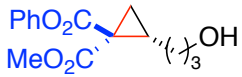
* Peaks corresponding to minor diastereomer



180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

1-methyl 1-phenyl (1*S*,2*S*)-2-(3-hydroxypropyl)cyclopropane-1,1-dicarboxylate

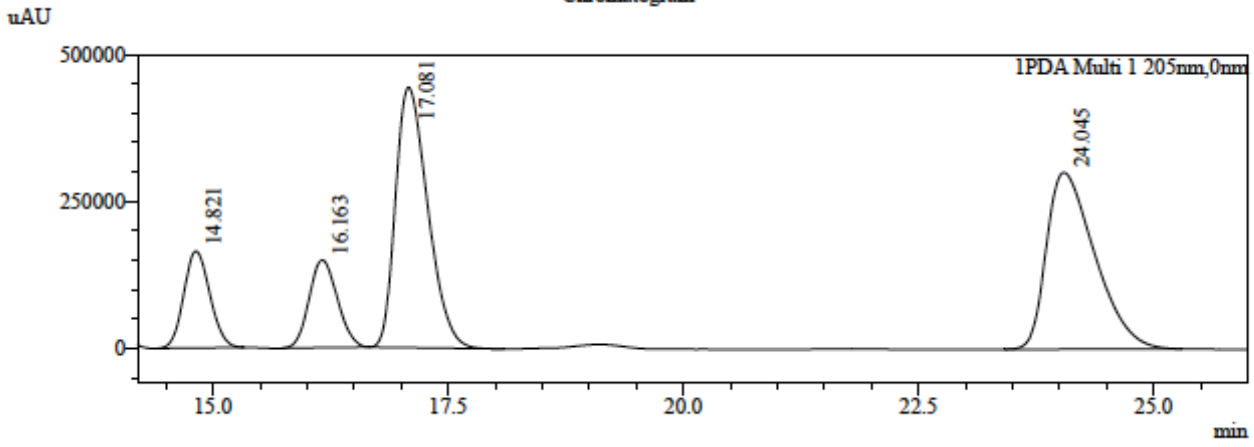


82:18 dr
74% ee

Sample Information

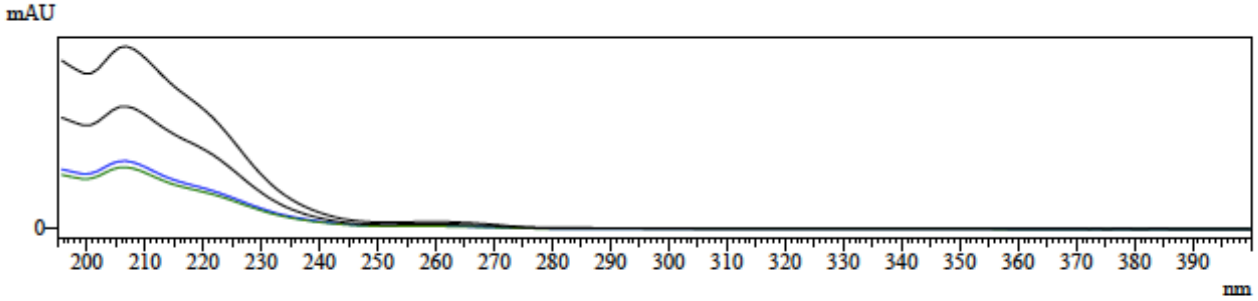
Sample Name	: JYW-III-293A
Sample ID	: JYW-III-293A-IE-12%-0.8ml-2
Data File	: JYW-III-293A-IE-12%-0.8ml-2.lcd
Method File	: JYW-method.lcm
Date Acquired	: 12/2/2015 11:55:16 AM

Chromatogram



UV Spectrum

JYW-III-293A-IE-12%-0.8ml-2.lcd



Peak Table

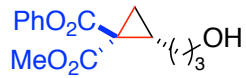
PDA Ch1 205nm

Peak#	Ret. Time	Area	Area%
1	14.821	3181113	11.509
2	16.163	3116582	11.276
3	17.081	10576011	38.263
4	24.045	10766576	38.952
Total		27640283	100.000

1-methyl 1-phenyl (1*S*,2*S*)-2-(3-hydroxypropyl)cyclopropane-1,1-dicarboxylate

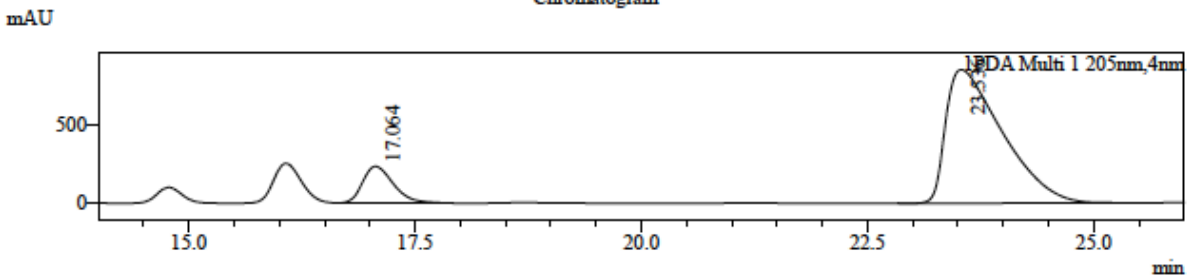
Sample Information

Sample Name	: JYW-III-293B
Sample ID	: JYW-III-293B-IE-12%-0.8ml
Data File	: JYW-III-293B-IE-12%-0.8ml.lcd
Method File	: JYW-method.lcm

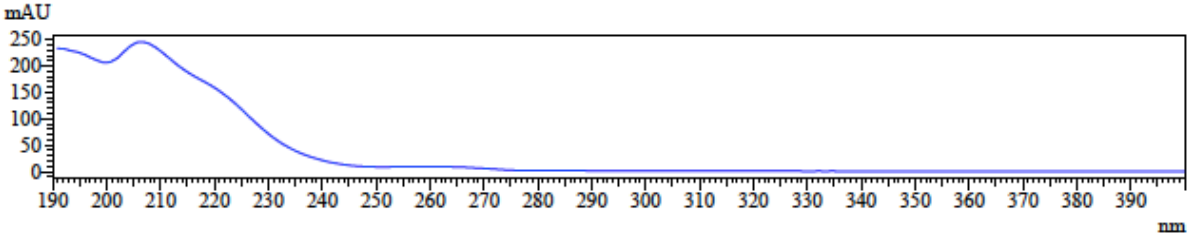


82:18 dr
74% ee

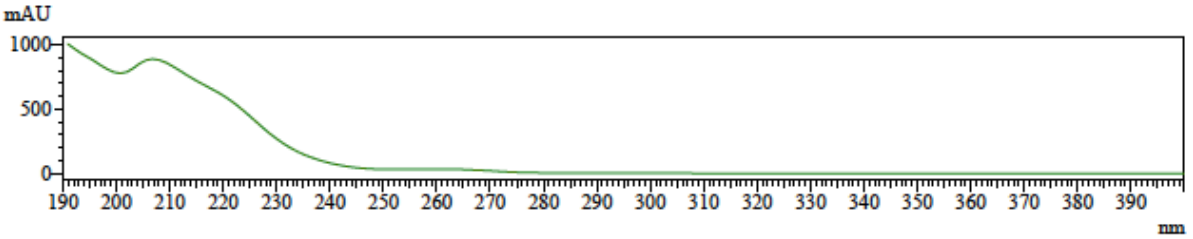
Chromatogram



UV Spectrum
Retention time = 17.064



UV Spectrum
Retention time = 23.536

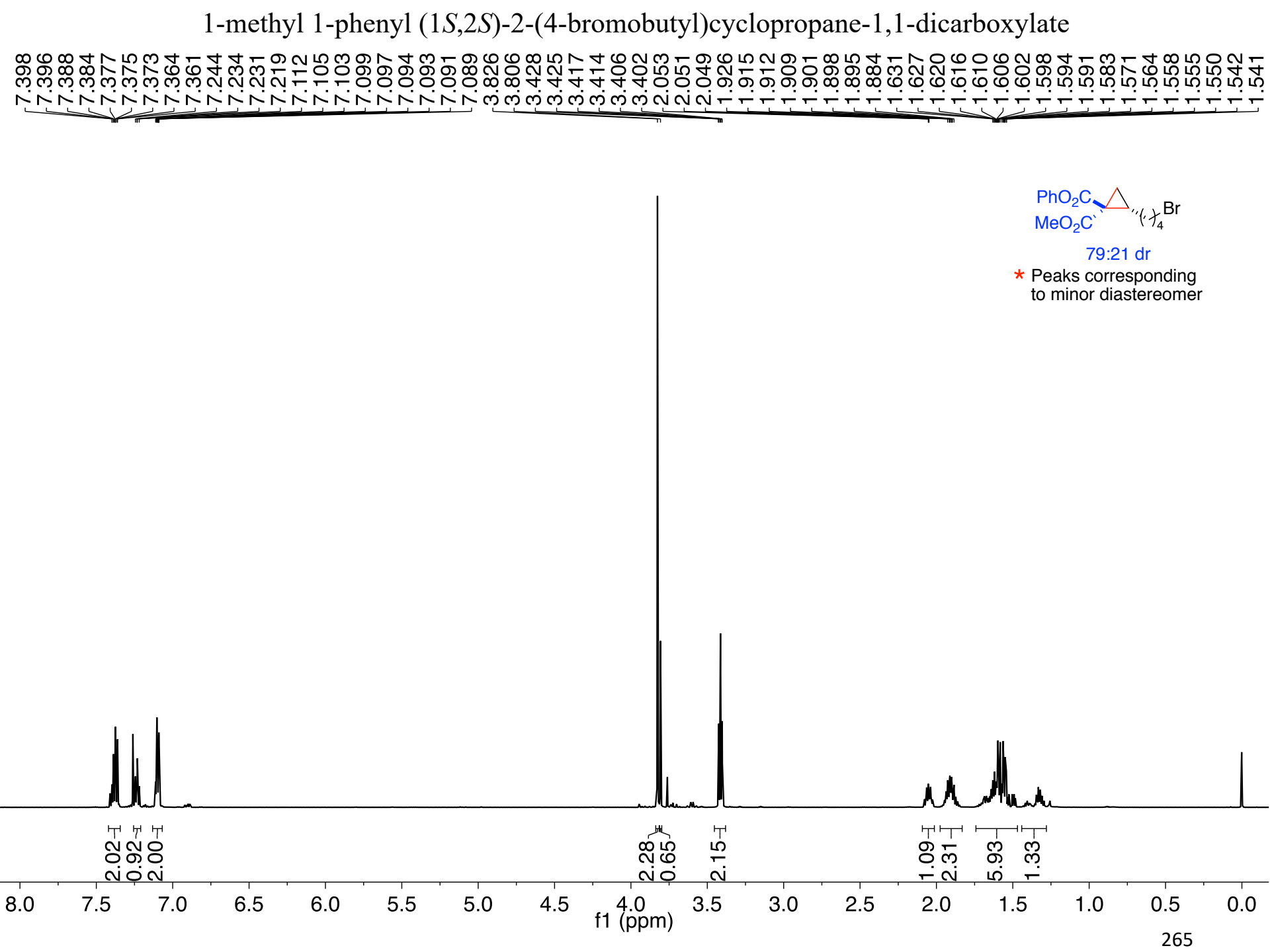


Peak Table

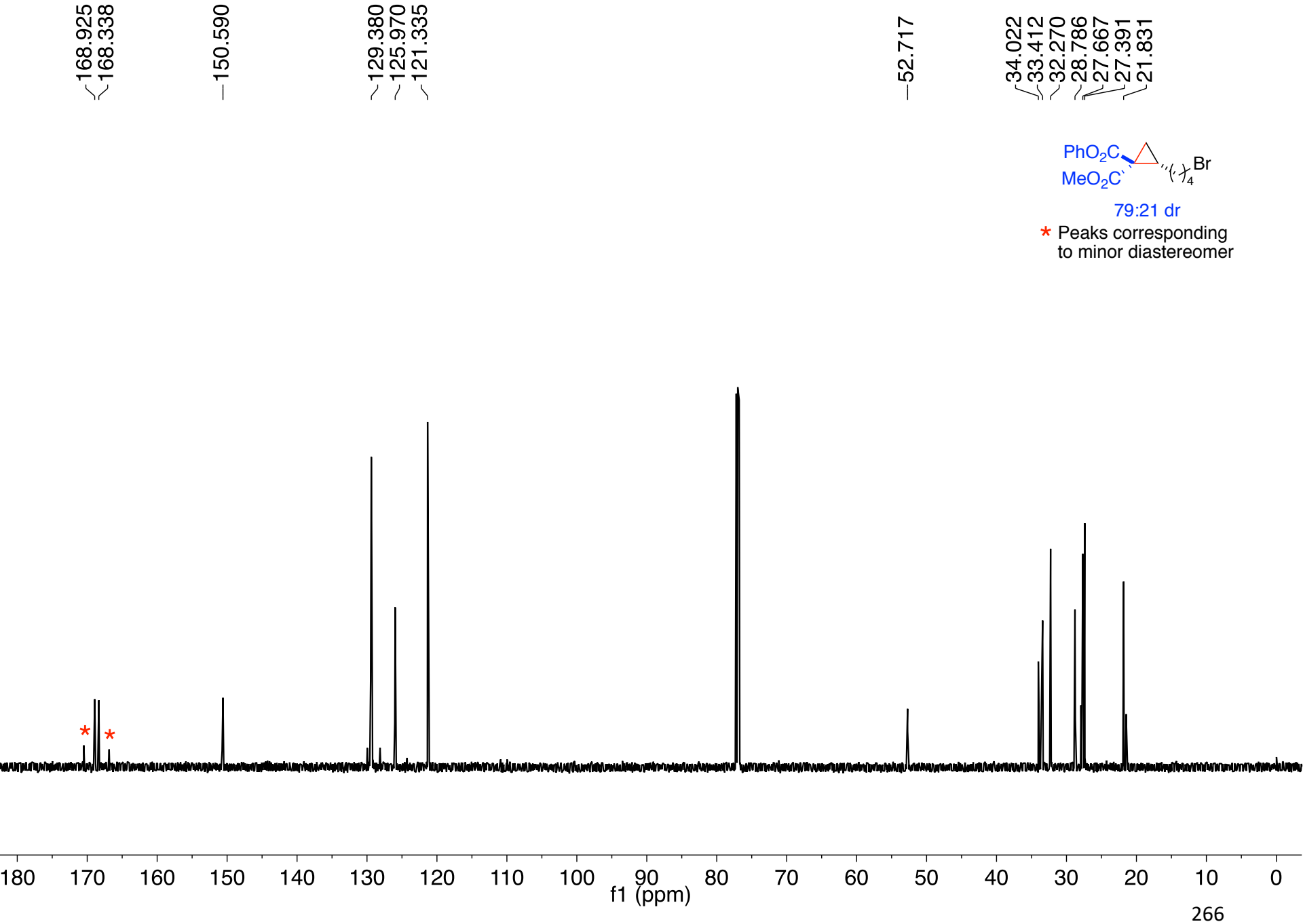
PDA Ch1 205nm

Peak#	Ret. Time	Area	Area%
1	17.064	5543080	13.006
2	23.536	37074751	86.994
Total		42617831	100.000

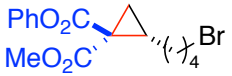
1-methyl 1-phenyl (1*S*,2*S*)-2-(4-bromobutyl)cyclopropane-1,1-dicarboxylate



1-methyl 1-phenyl (1*S*,2*S*)-2-(4-bromobutyl)cyclopropane-1,1-dicarboxylate



1-methyl 1-phenyl (1*S*,2*S*)-2-(4-bromobutyl)cyclopropane-1,1-dicarboxylate

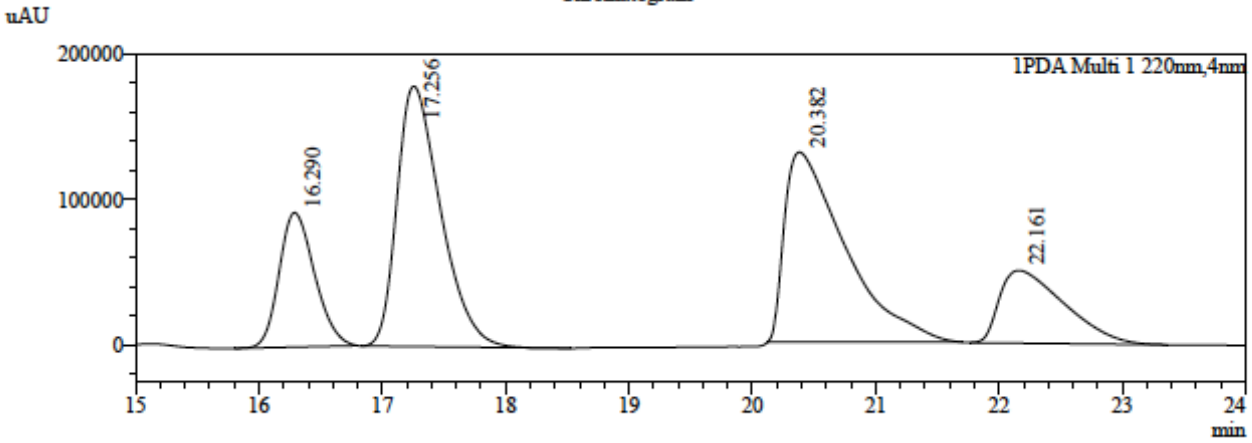


79:21 dr
63% ee

Sample Information

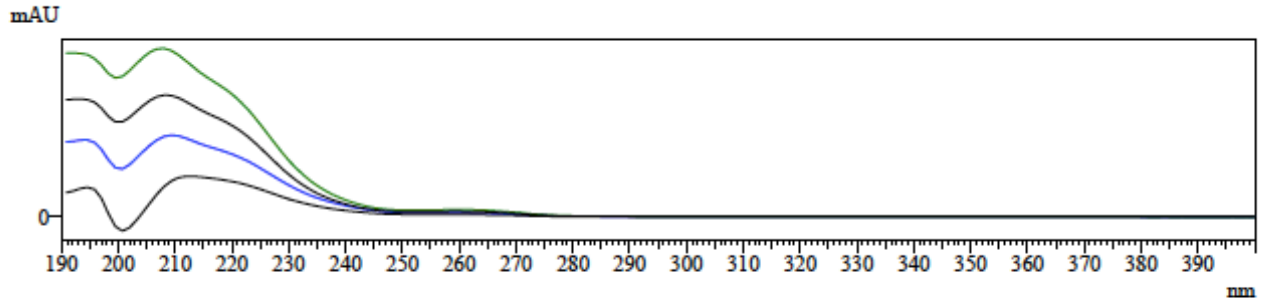
Sample Name	: JYW-III-282B
Sample ID	: JYW-III-282B-IA-0.6%-0.8ml-1
Data File	: JYW-III-282B-IA-0.6%-0.8ml-1.lcd
Method File	: JYW-method.lcm
Date Acquired	: 12/3/2015 12:46:14 PM

Chromatogram



UV Spectrum

JYW-III-282B-IA-0.6%-0.8ml-1.lcd

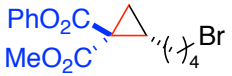


Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	16.290	1842990	14.699
2	17.256	4405685	35.138
3	20.382	4470254	35.653
4	22.161	1819321	14.510
Total		12538251	100.000

1-methyl 1-phenyl (1*S*,2*S*)-2-(4-bromobutyl)cyclopropane-1,1-dicarboxylate

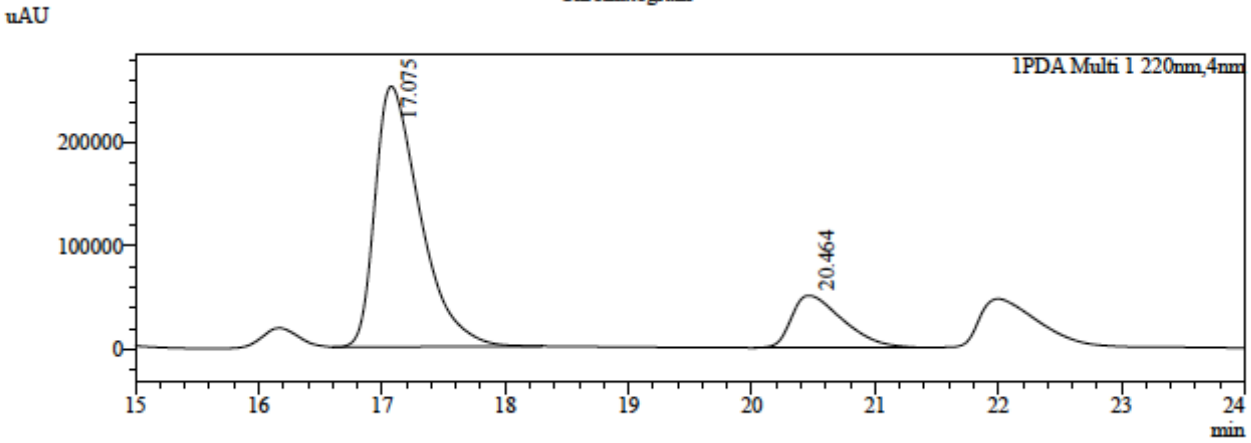


79:21 dr
63% ee

Sample Information

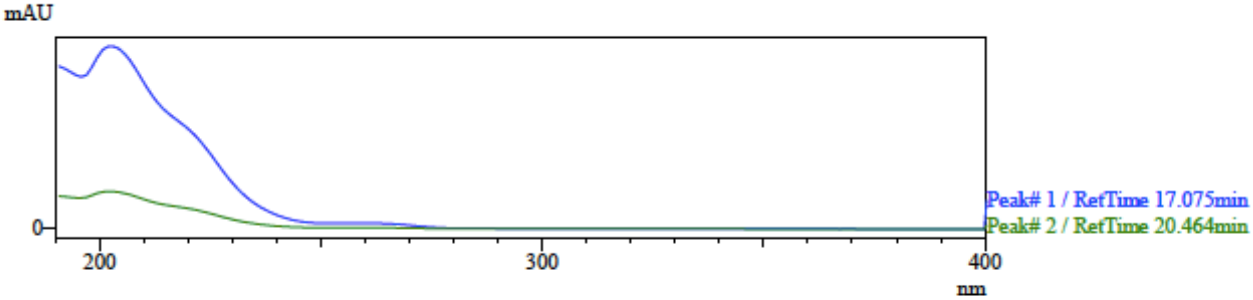
Sample Name	: JYW-III-289
Sample ID	: JYW-III-289-IA-0.6%-0.8ml
Data File	: JYW-III-289-IA-0.6%-0.8ml.lcd
Method File	: JYW-method.lcm
Date Acquired	: 12/3/2015 1:16:51 PM

Chromatogram



UV Spectrum

JYW-III-289-IA-0.6%-0.8ml.lcd

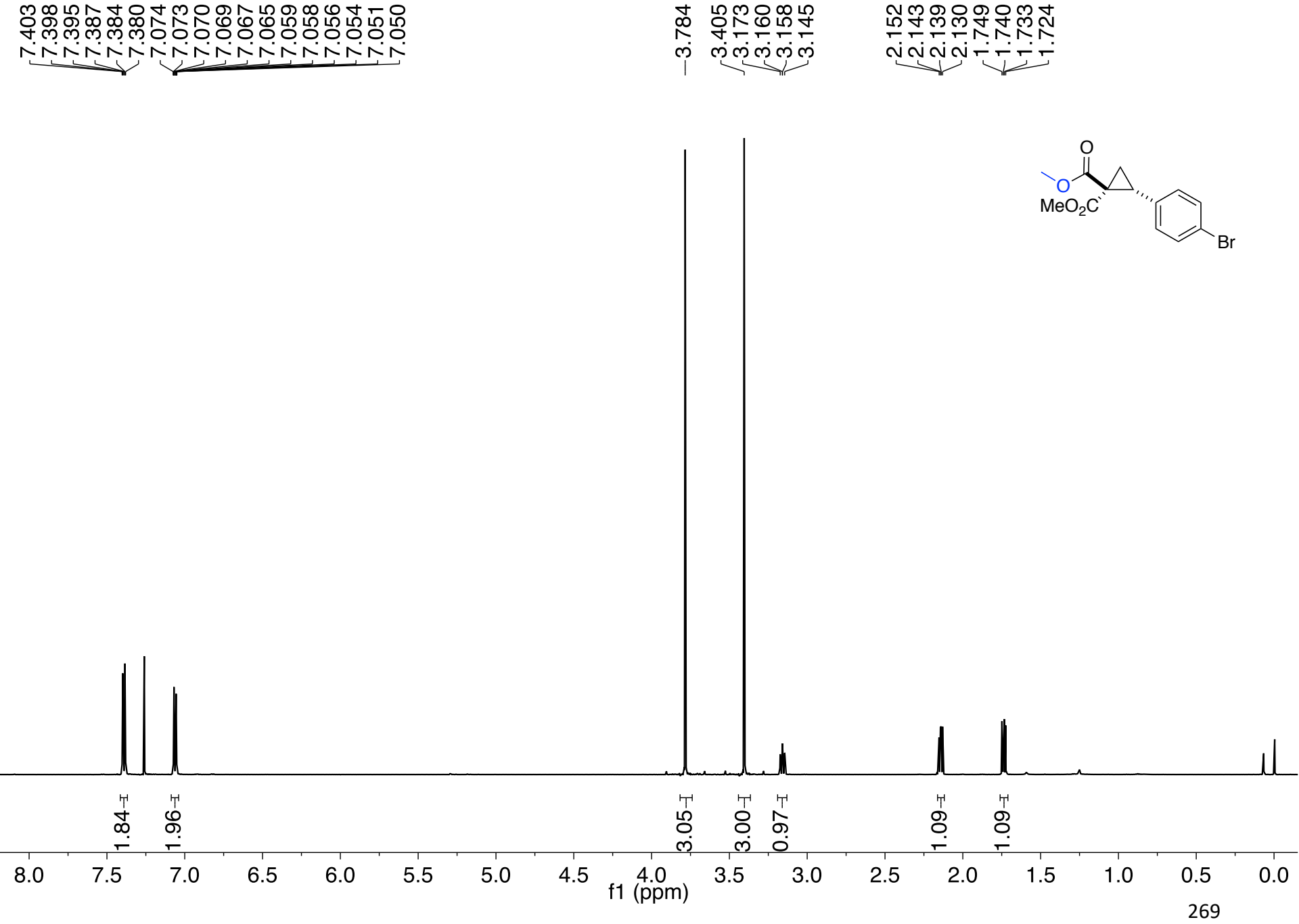


Peak Table

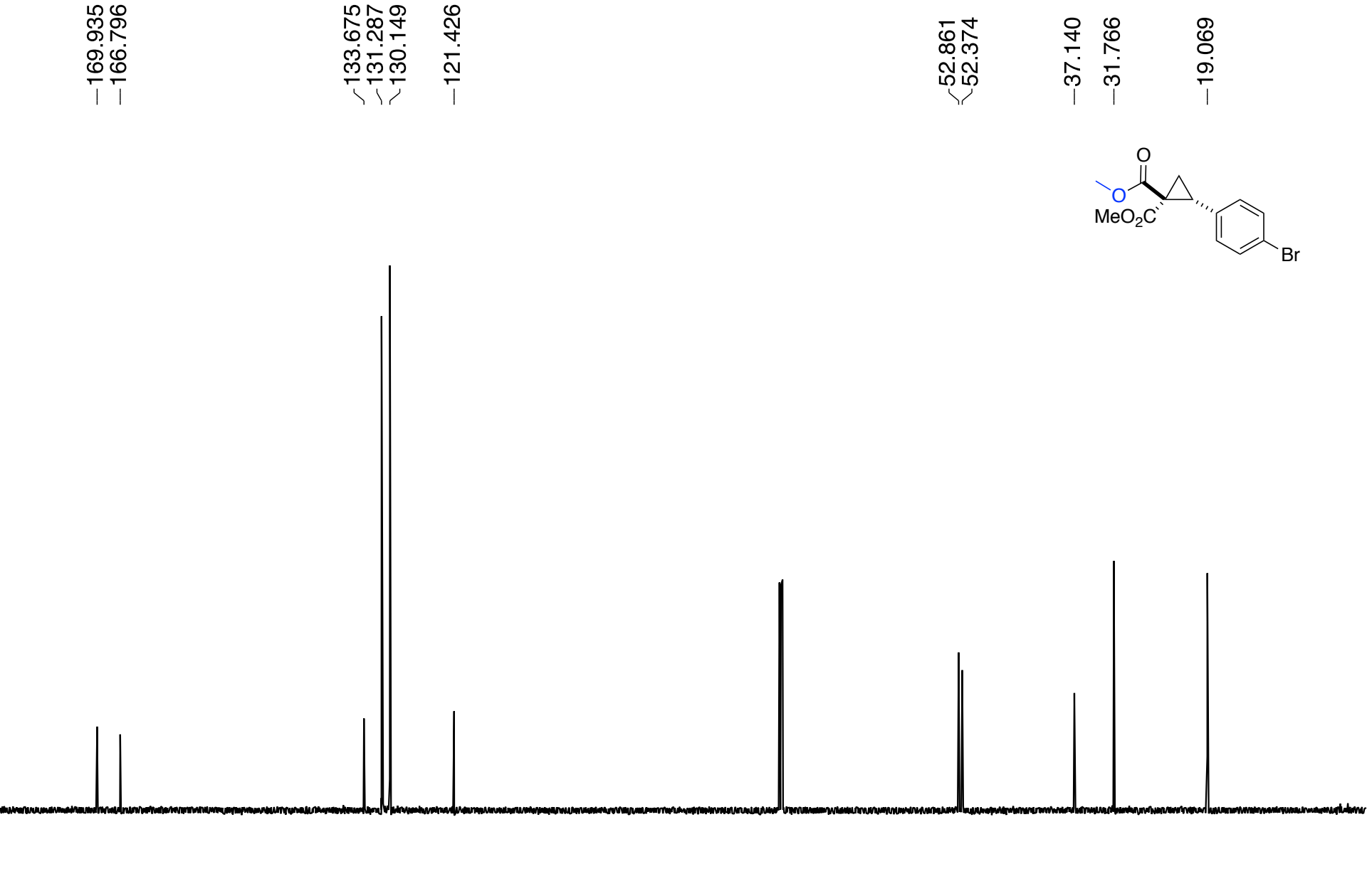
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	17.075	6444153	81.518
2	20.464	1461059	18.482
Total		7905211	100.000

dimethyl (*R*)-2-(4-bromophenyl)cyclopropane-1,1-dicarboxylate

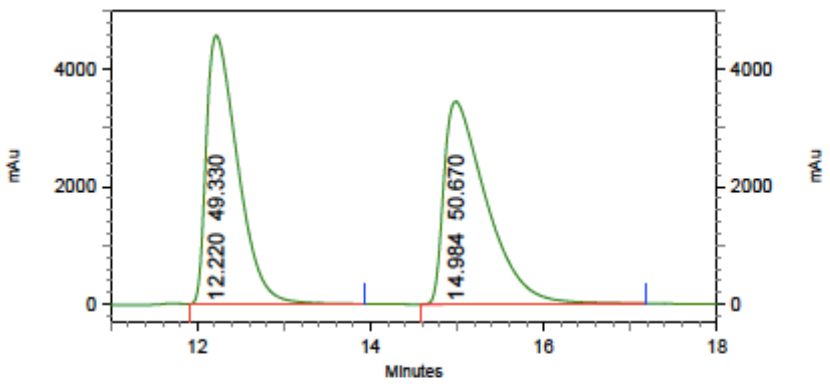


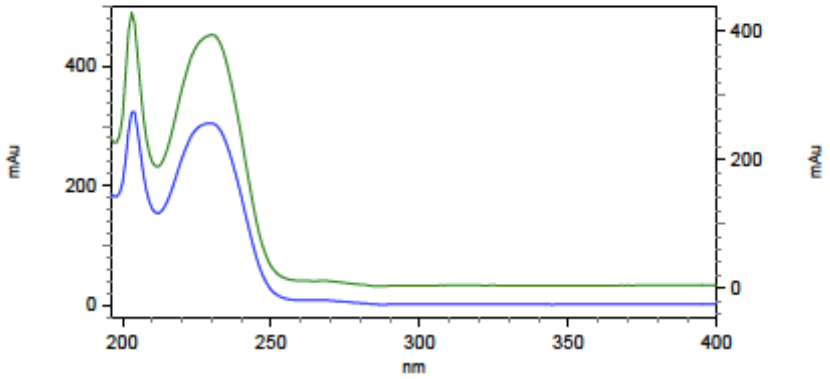
dimethyl (*R*)-2-(4-bromophenyl)cyclopropane-1,1-dicarboxylate

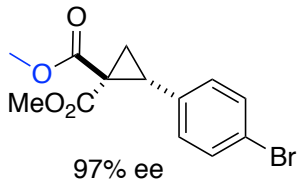


dimethyl (*R*)-2-(4-bromophenyl)cyclopropane-1,1-dicarboxylate

JYW-IV-149-ID-2%-0.8ml2
C:\EZStart\Projects\Default\Data\JYW-IV-149-ID-2%-0.8ml2







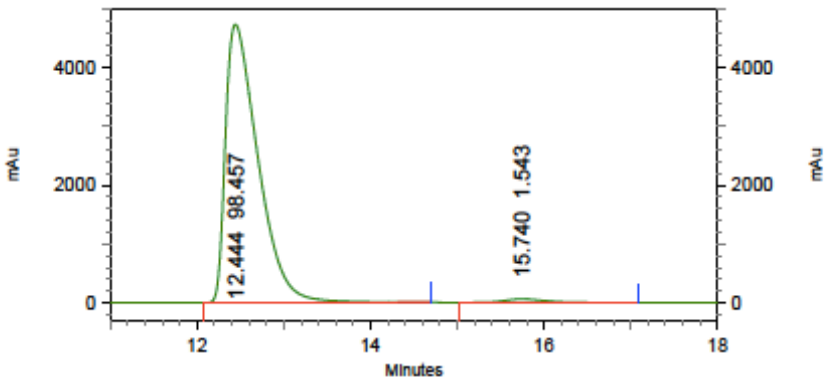
97% ee

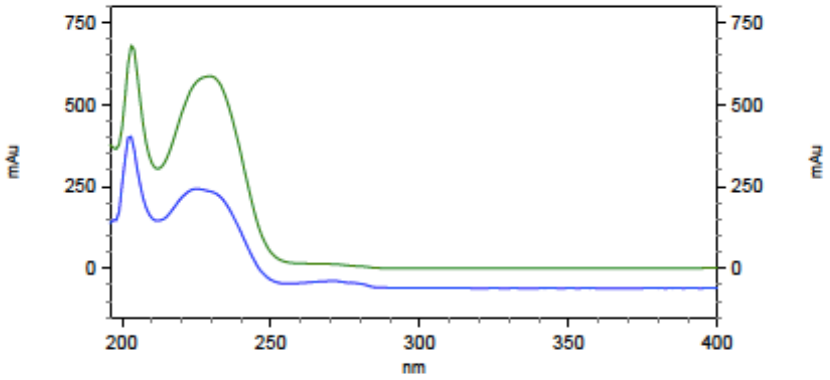
3: 248 nm, 4 nm
Results

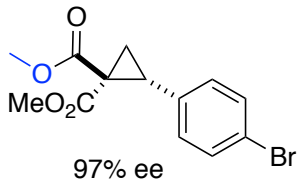
Name	Retention Time	Area Percent	Pk #
	12.220	49.330	1
	14.984	50.670	2
Totals		100.000	

dimethyl (*R*)-2-(4-bromophenyl)cyclopropane-1,1-dicarboxylate

JYW-IV-157-ID-2%-0.8ml
C:\EZStart\Projects\Default\Data\JYW-IV-157-ID-2%-0.8ml





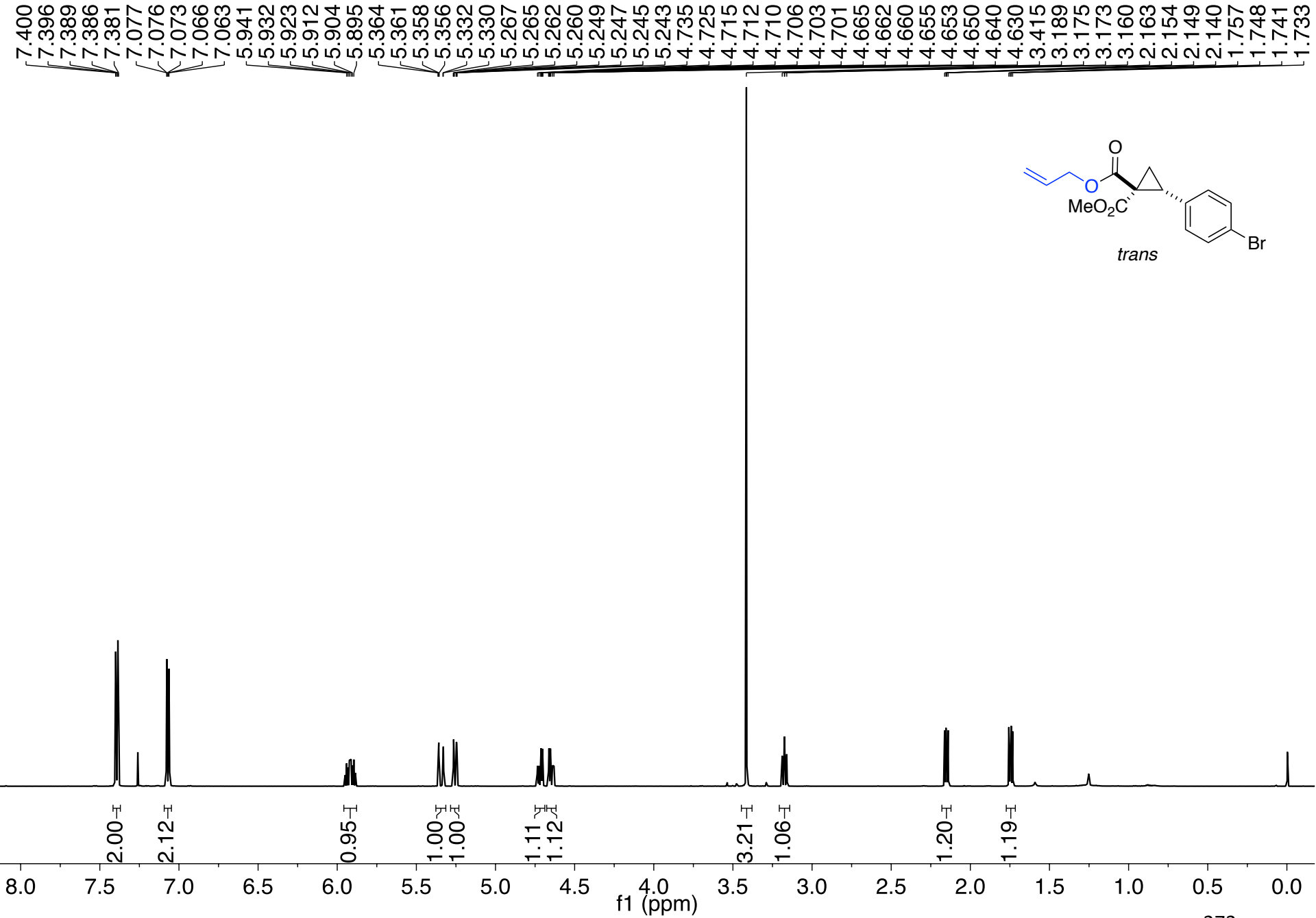


97% ee

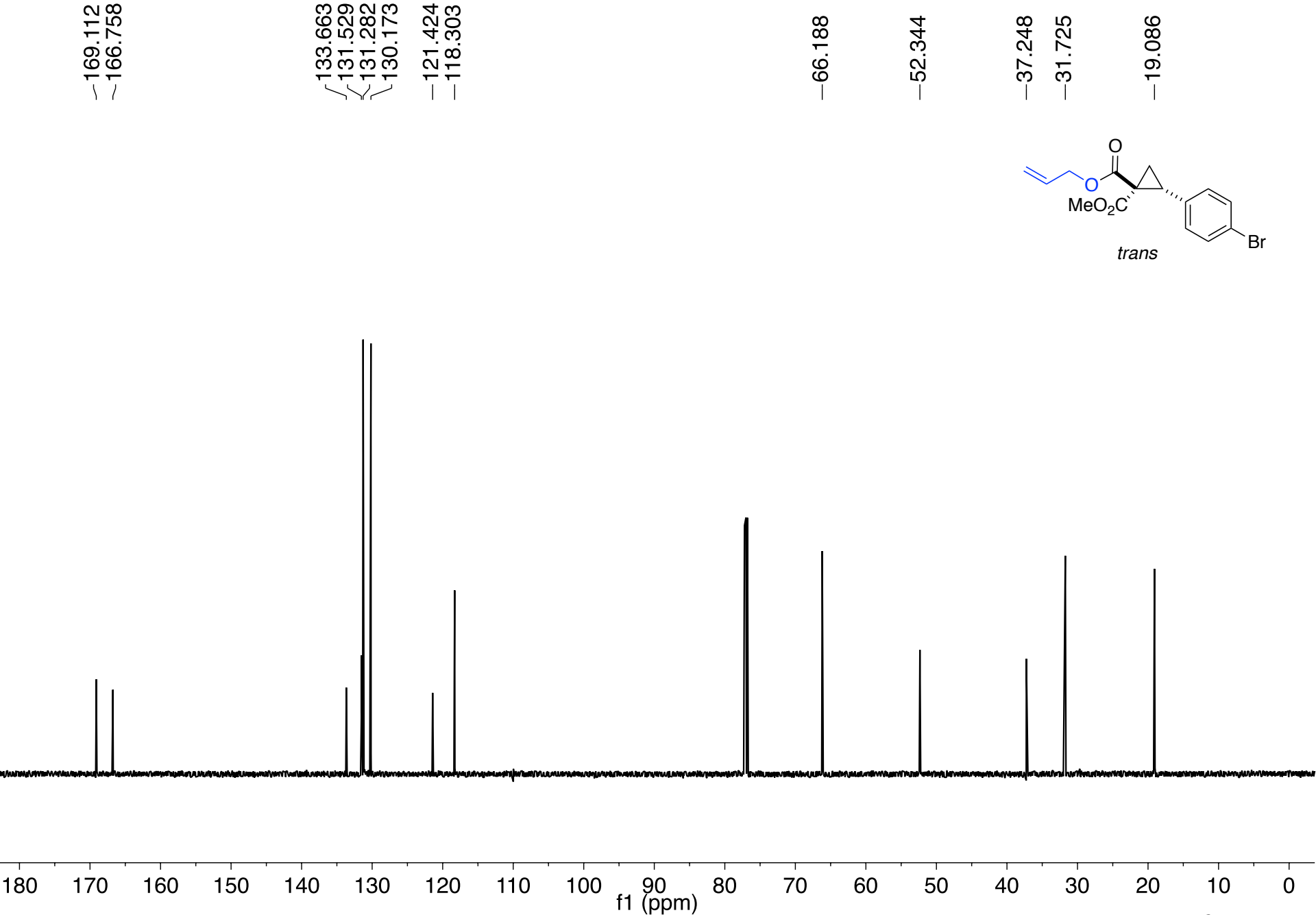
3: 248 nm, 4 nm
Results

Name	Retention Time	Area Percent	Pk #
	12.444	98.457	1
	15.740	1.543	2
Totals		100.000	

1-allyl 1-methyl (1*S*,2*R*)-2-(4-bromophenyl)cyclopropane-1,1-dicarboxylate

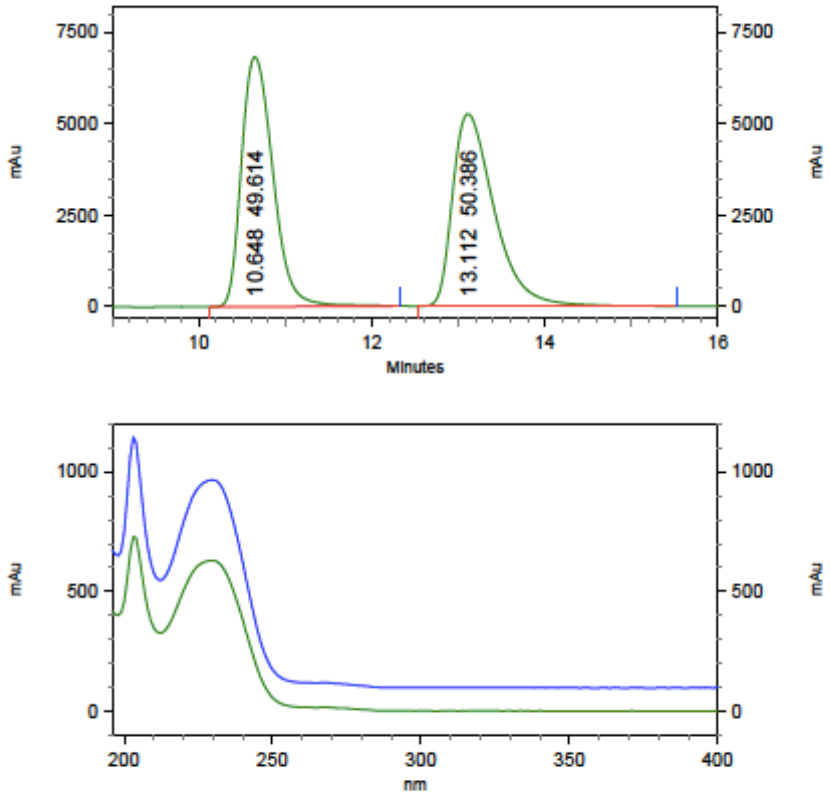


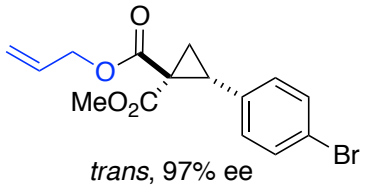
1-allyl 1-methyl (1*S*,2*R*)-2-(4-bromophenyl)cyclopropane-1,1-dicarboxylate



1-allyl 1-methyl (1*S*,2*R*)-2-(4-bromophenyl)cyclopropane-1,1-dicarboxylate

JYW-IV-147A-ID-2%-0.8ml2
C:\EZStart\Projects\Default\Data\JYW-IV-147A-ID-2%-0.8ml2





trans, 97% ee

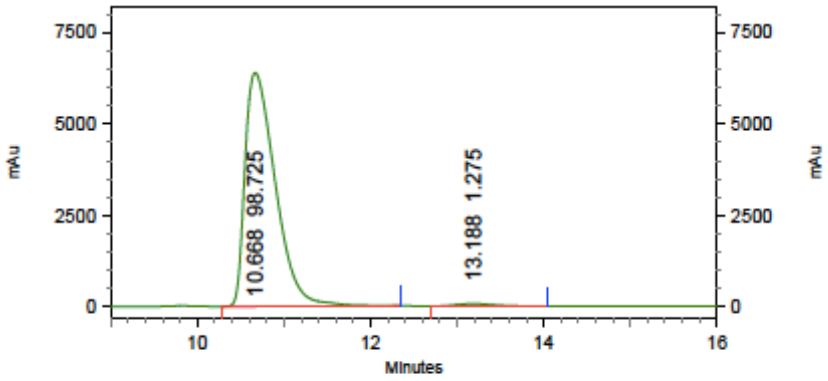
3: 230 nm, 4 nm
Results

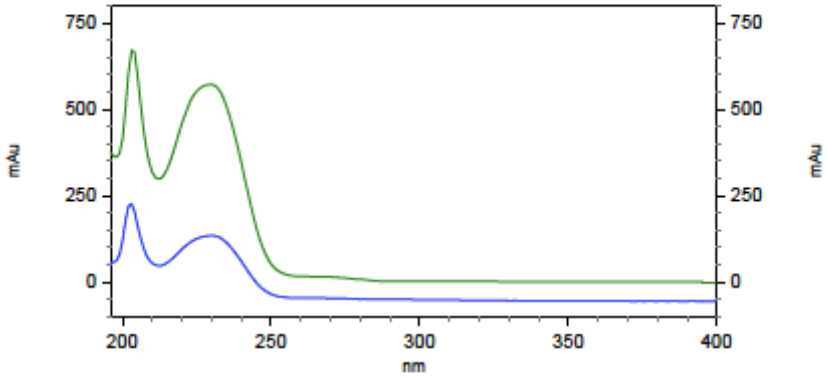
Name	Retention Time	Area Percent	Pk #
	10.648	49.614	1
	13.112	50.386	2

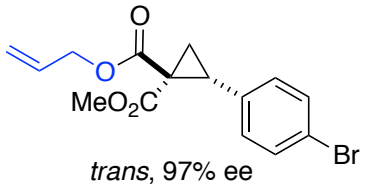
Totals	
	100.000

1-allyl 1-methyl (1*S*,2*R*)-2-(4-bromophenyl)cyclopropane-1,1-dicarboxylate

JYW-IV-158-ID-2%-0.8ml
C:\EZStart\Projects\Default\Data\JYW-IV-158-ID-2%-0.8ml







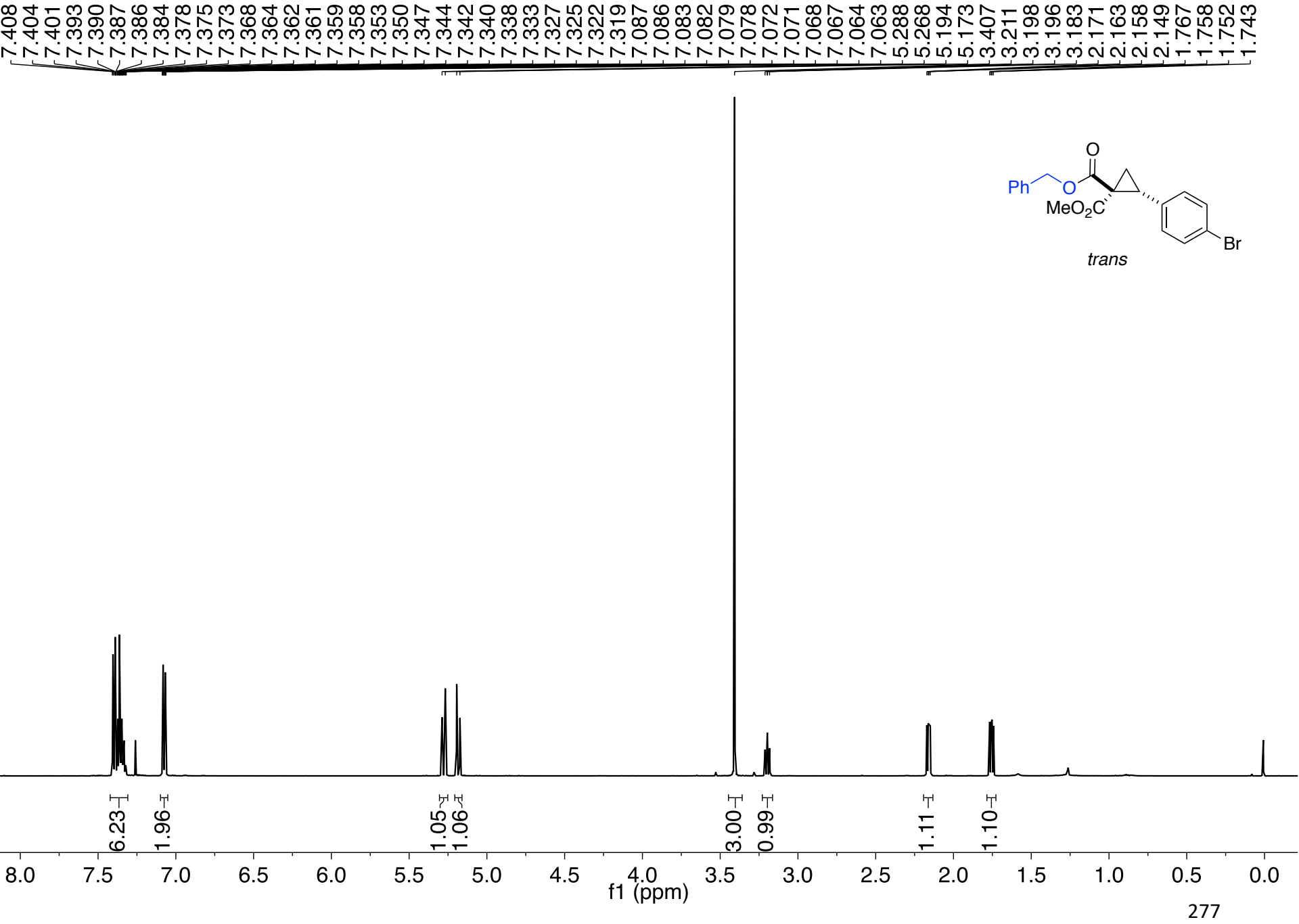
trans, 97% ee

3: 248 nm, 4 nm
Results

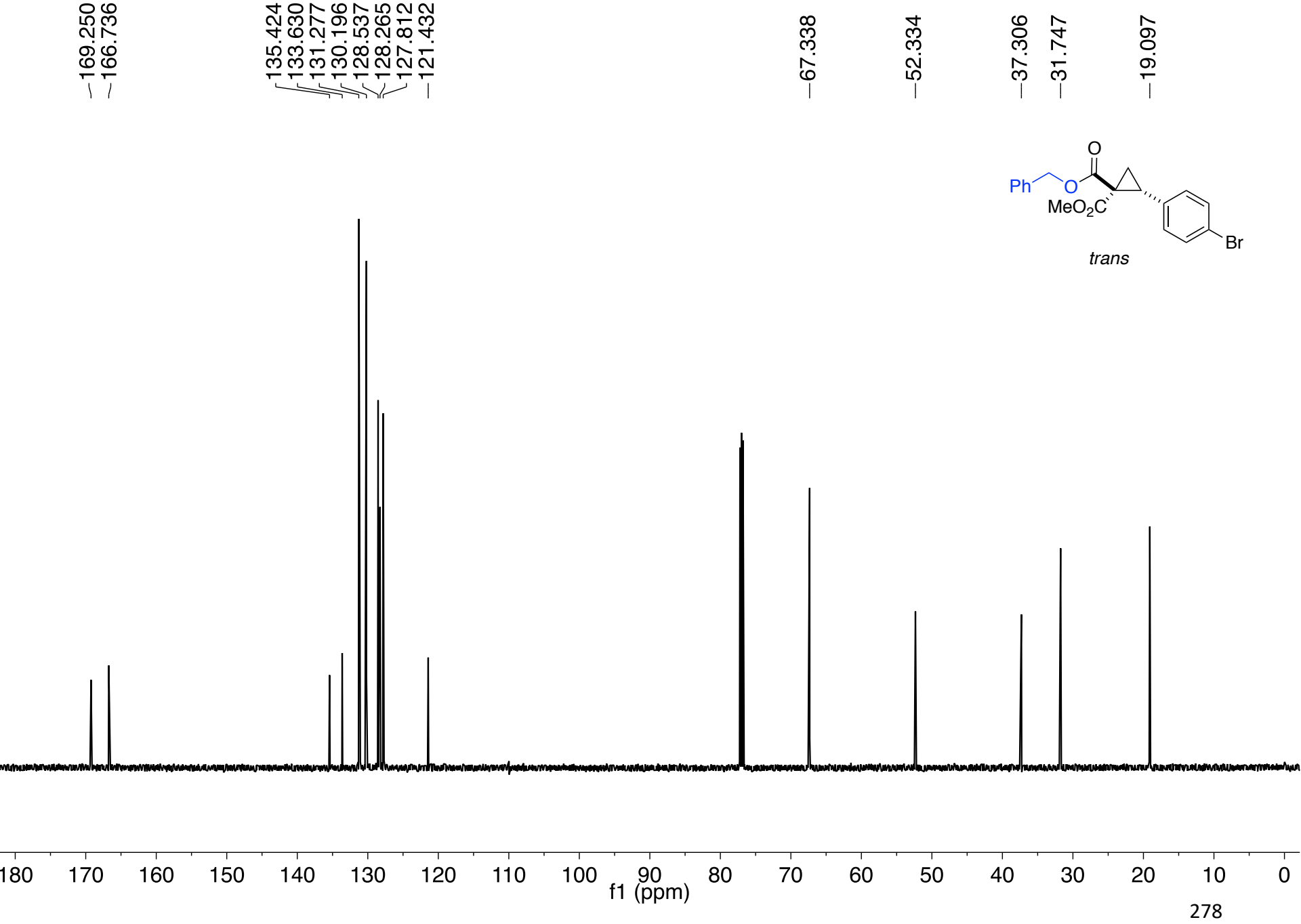
Name	Retention Time	Area Percent	Pk #
	10.668	98.725	1
	13.188	1.275	2

Totals	
	100.000

1-benzyl 1-methyl (1*S*,2*R*)-2-(4-bromophenyl)cyclopropane-1,1-dicarboxylate

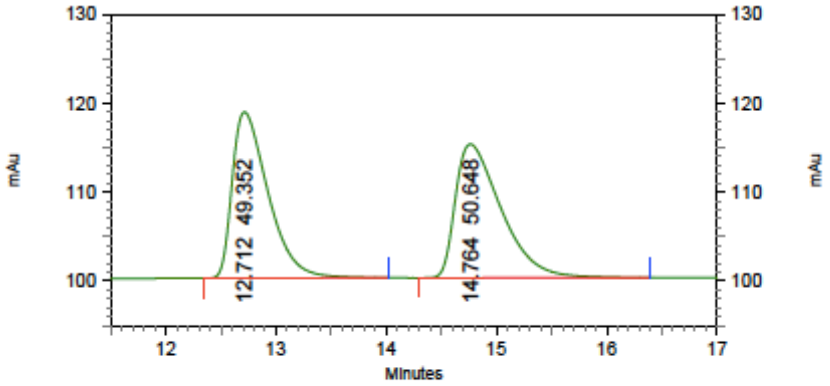


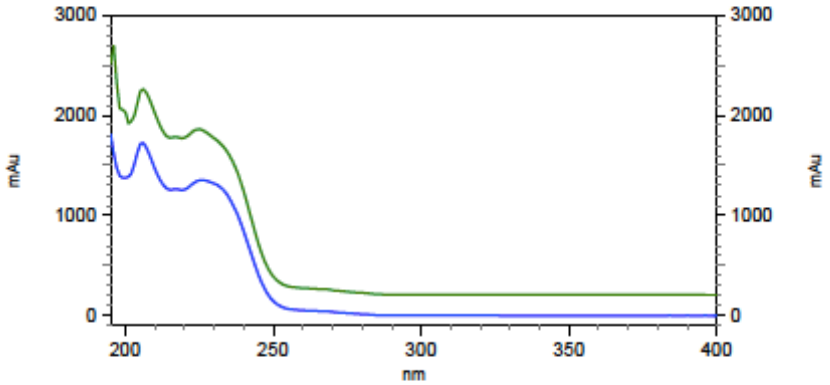
1-benzyl 1-methyl (1*S*,2*R*)-2-(4-bromophenyl)cyclopropane-1,1-dicarboxylate

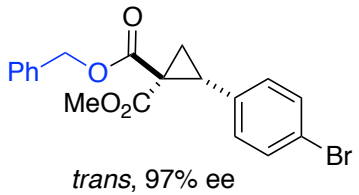


1-benzyl 1-methyl (1*S*,2*R*)-2-(4-bromophenyl)cyclopropane-1,1-dicarboxylate

JYW-IV-148A-ID-3%-0.8ml5
C:\EZStart\Projects\Default\Method\untitled.met
C:\EZStart\Projects\Default\Data\JYW-IV-148A-ID-3%-0.8ml5







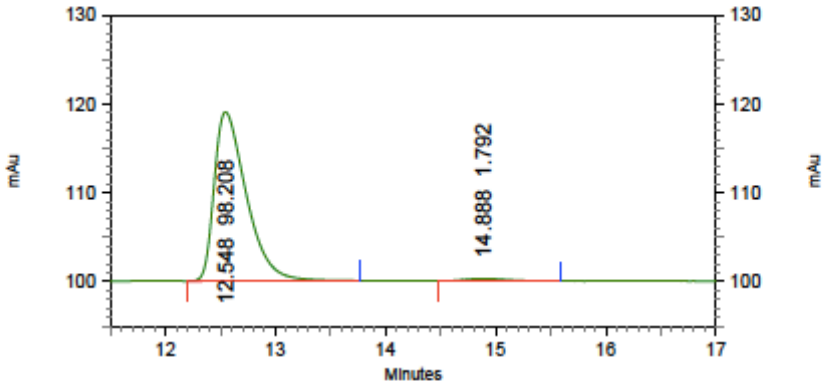
trans, 97% ee

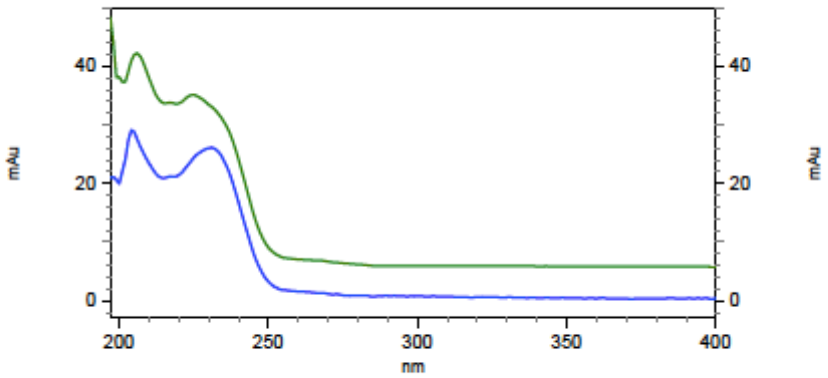
3: 250 nm, 4 nm
Results

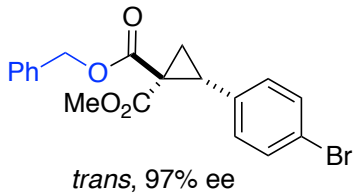
Pk #	Name	Retention Time	Area Percent
1		12.712	49.352
2		14.764	50.648
Totals			100.000

1-benzyl 1-methyl (1*S*,2*R*)-2-(4-bromophenyl)cyclopropane-1,1-dicarboxylate

JYW-IV-181-ID-3%-0.8ml
C:\EZStart\Projects\Default\Method\untitled.met
C:\EZStart\Projects\Default\Data\JYW-IV-181-ID-3%-0.8ml





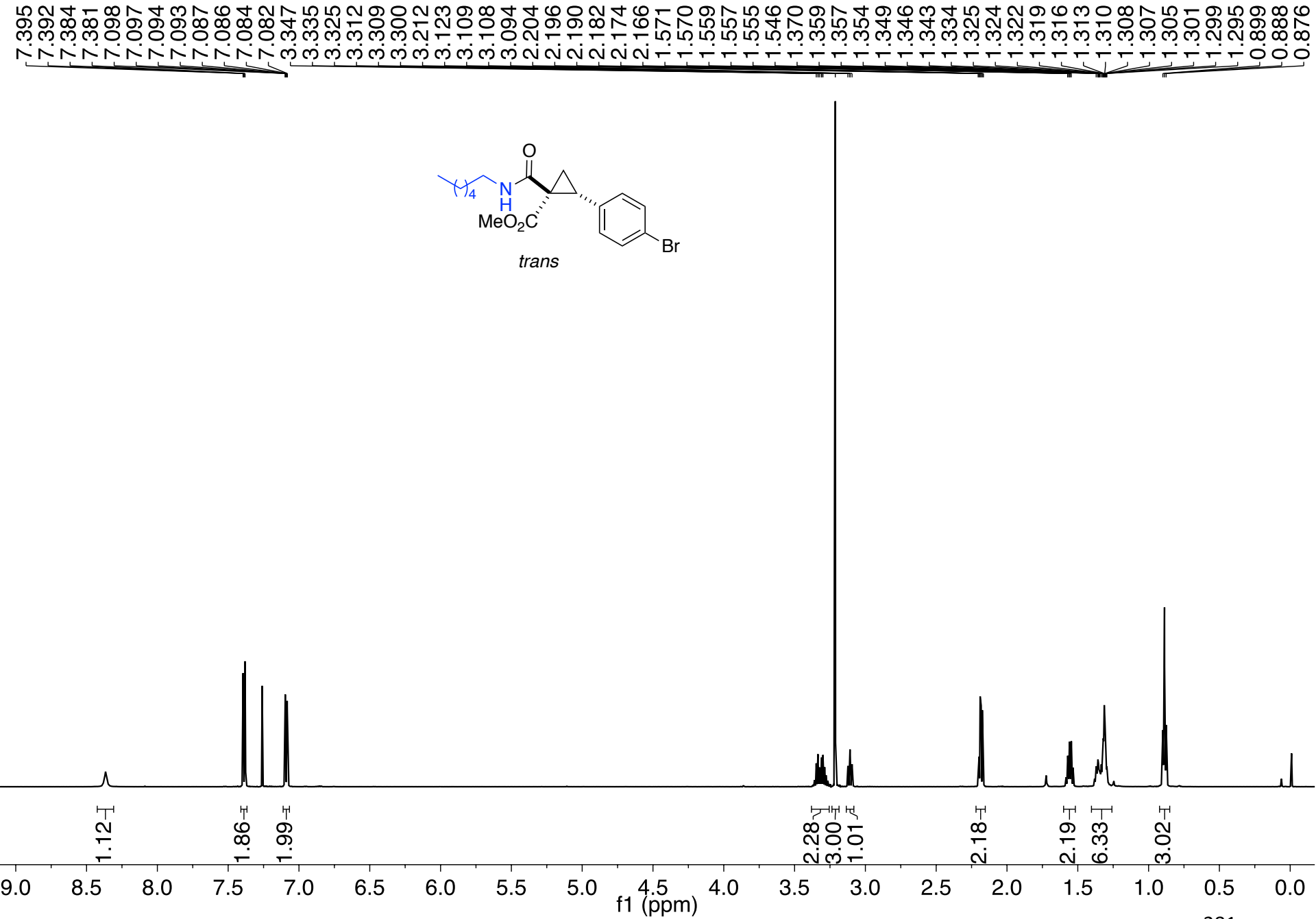


trans, 97% ee

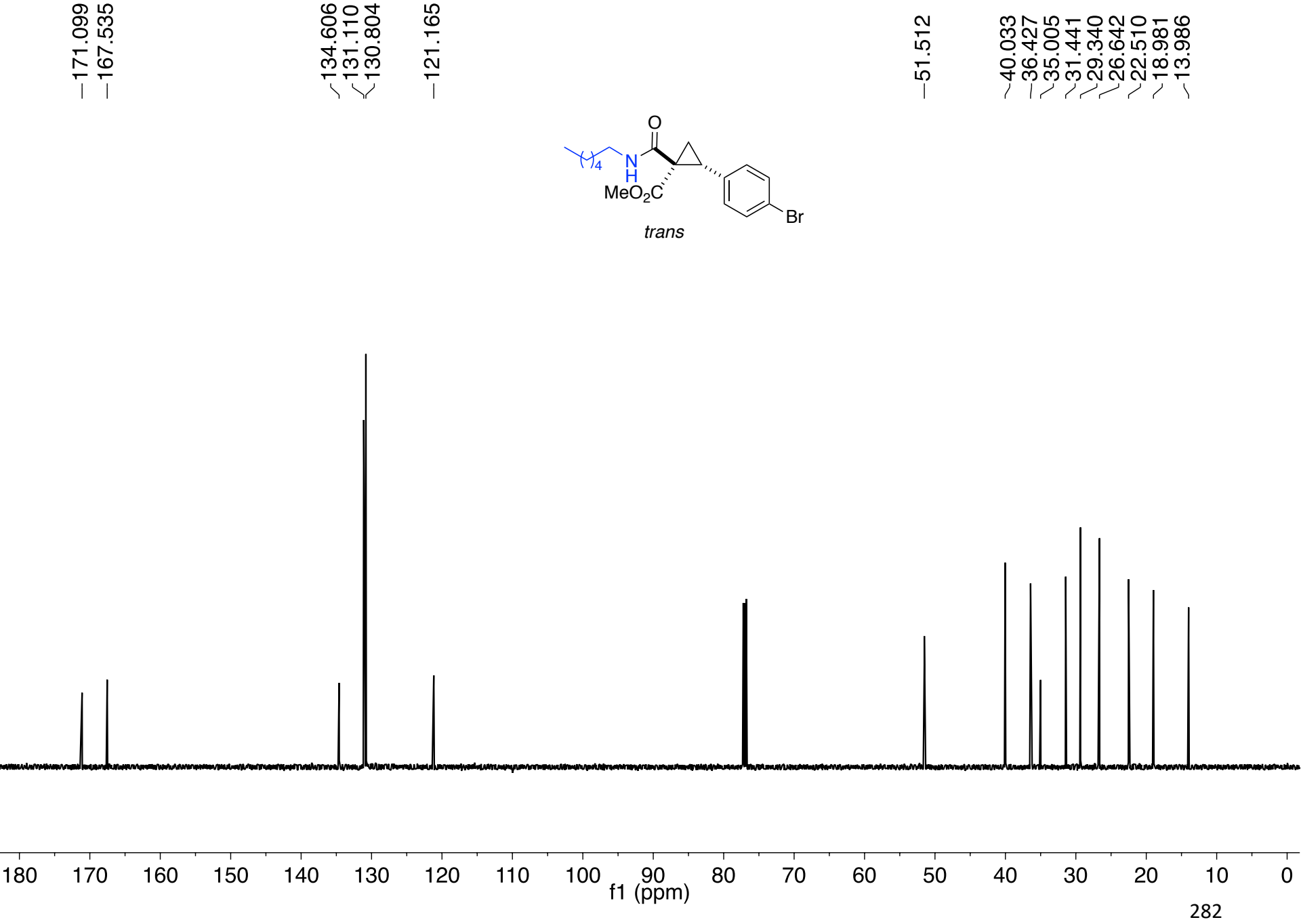
3: 250 nm, 4 nm
Results

Pk #	Name	Retention Time	Area Percent
1		12.548	98.208
2		14.888	1.792
Totals			100.000

methyl (1*R*,2*R*)-2-(4-bromophenyl)-1-(hexylcarbamoyl)cyclopropane-1-carboxylate

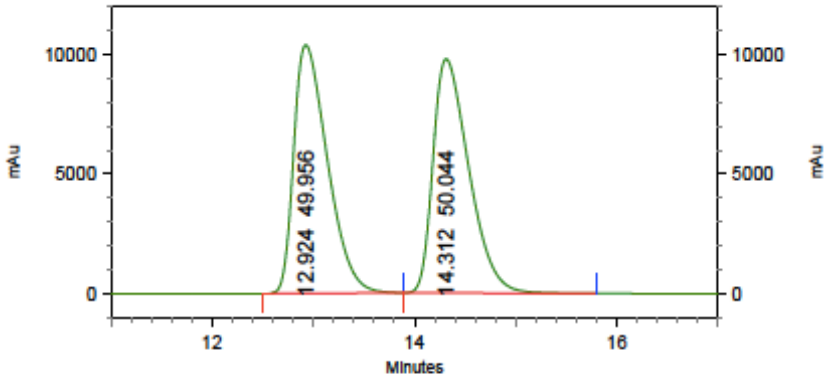


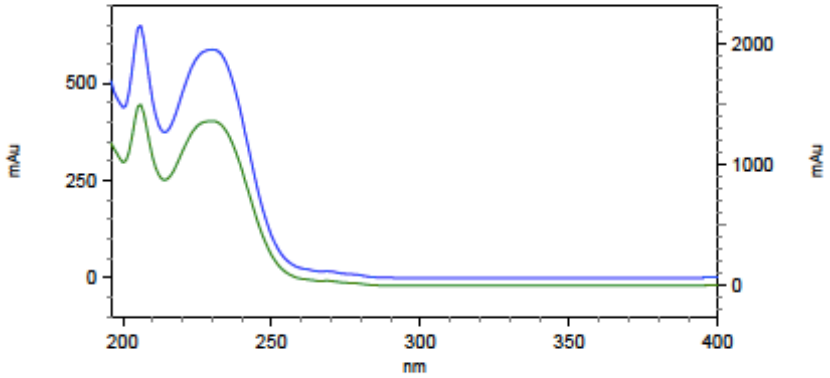
methyl (1*R*,2*R*)-2-(4-bromophenyl)-1-(hexylcarbamoyl)cyclopropane-1-carboxylate

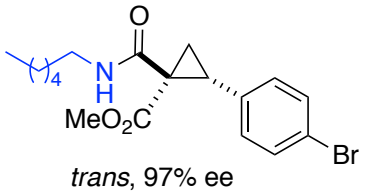


methyl (1*R*,2*R*)-2-(4-bromophenyl)-1-(hexylcarbamoyl)cyclopropane-1-carboxylate

JYW-IV-161-ID-5%-0.8ml2
C:\EZStart\Projects\Default\Data\JYW-IV-161-ID-5%-0.8ml2







trans, 97% ee

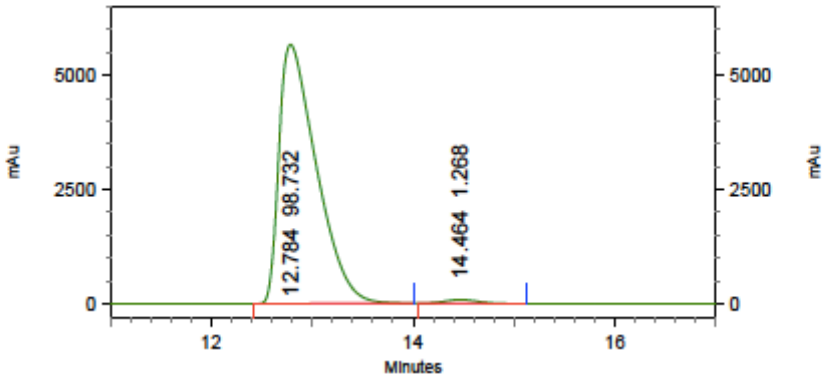
3: 240 nm, 4 nm
Results

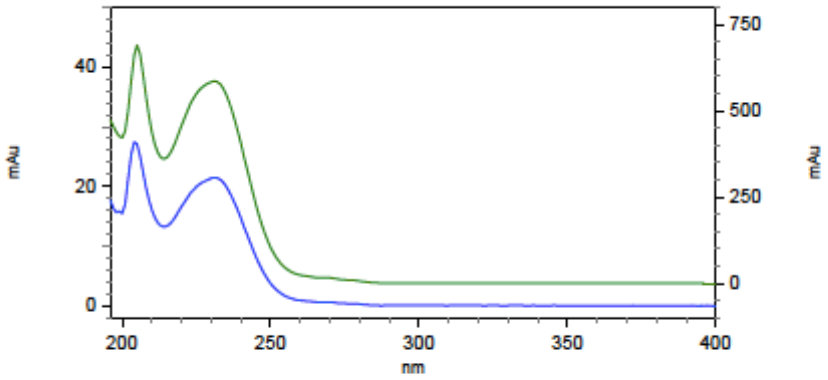
Name	Retention Time	Area Percent	Pk #
	12.924	49.956	1
	14.312	50.044	2

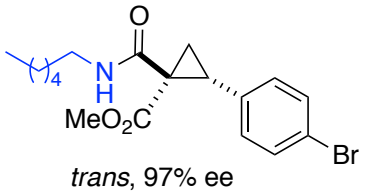
Totals	
	100.000

methyl (1*R*,2*R*)-2-(4-bromophenyl)-1-(hexylcarbamoyl)cyclopropane-1-carboxylate

JYW-IV-165-ID-5%-0.8ml
C:\EZStart\Projects\Default\Data\JYW-IV-165-ID-5%-0.8ml







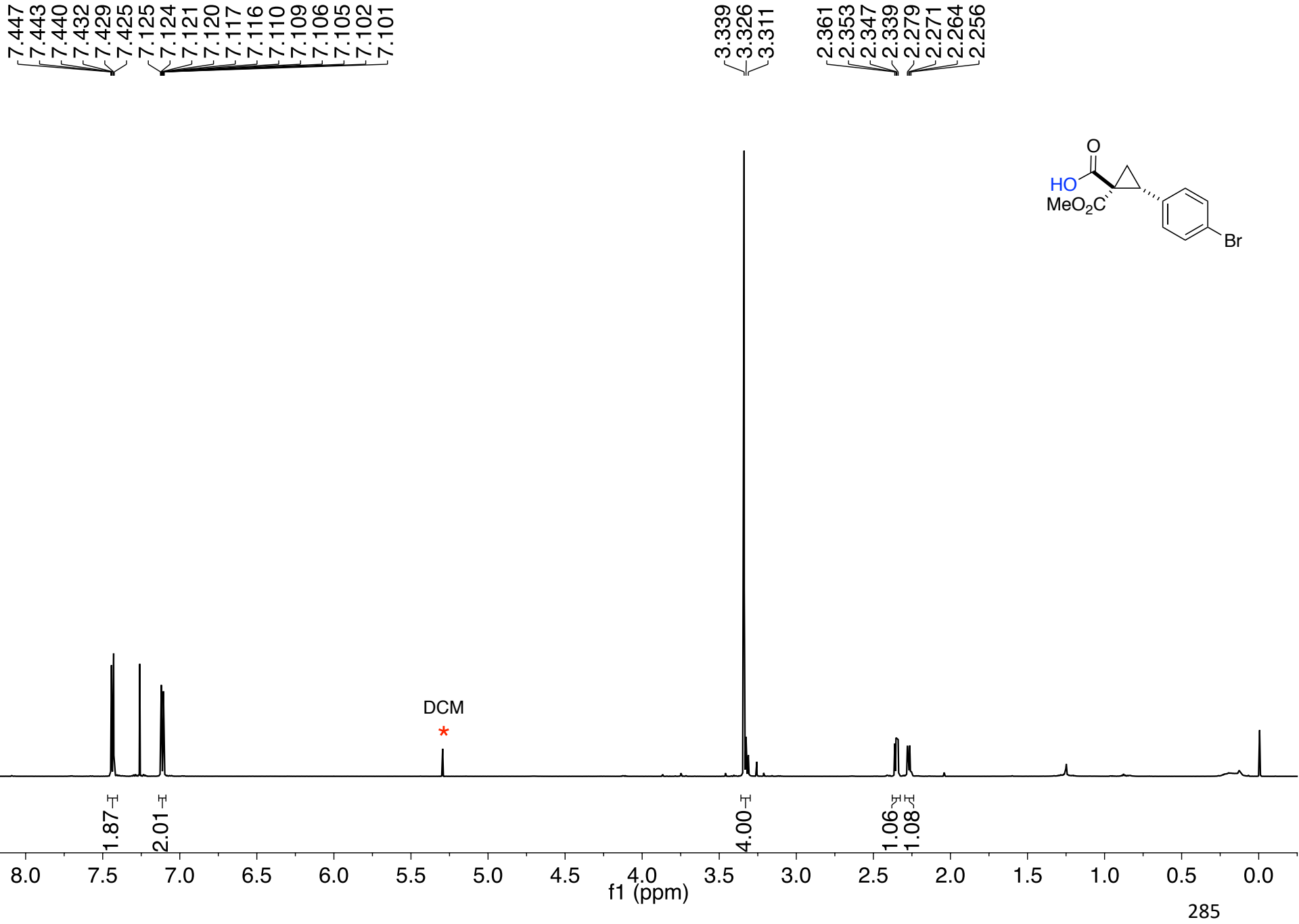
trans, 97% ee

3: 250 nm, 4 nm
Results

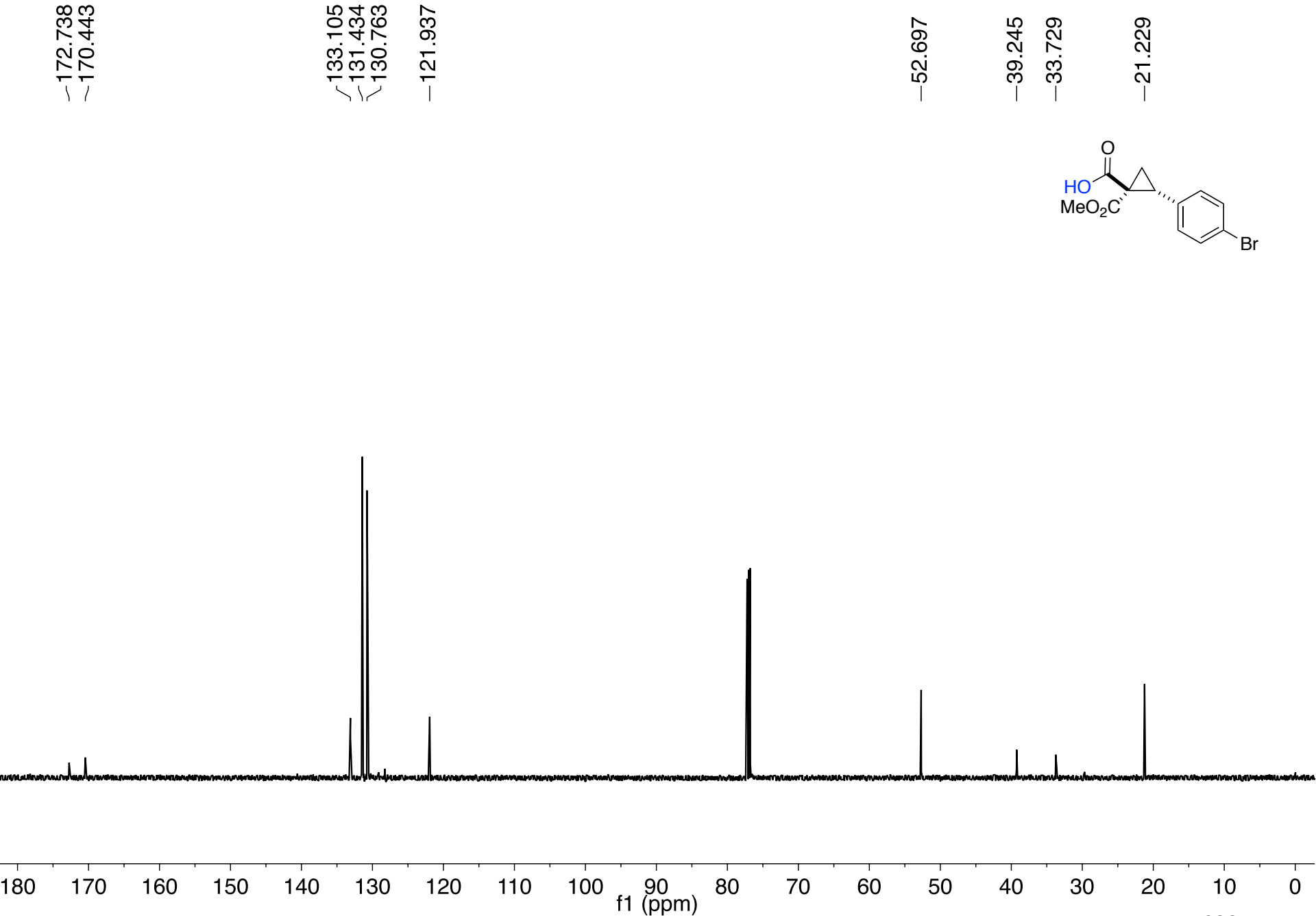
Name	Retention Time	Area Percent	Pk #
	12.784	98.732	1
	14.464	1.268	2

Totals	
	100.000

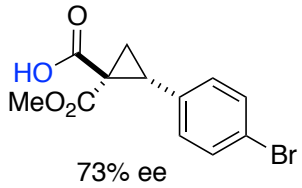
(1*R*,2*R*)-2-(4-bromophenyl)-1-(methoxycarbonyl)cyclopropane-1-carboxylic acid



(1*R*,2*R*)-2-(4-bromophenyl)-1-(methoxycarbonyl)cyclopropane-1-carboxylic acid



(1*R*,2*R*)-2-(4-bromophenyl)-1-(methoxycarbonyl)cyclopropane-1-carboxylic acid



73% ee

JYW-IV-177-IA-20%-0.8ml2
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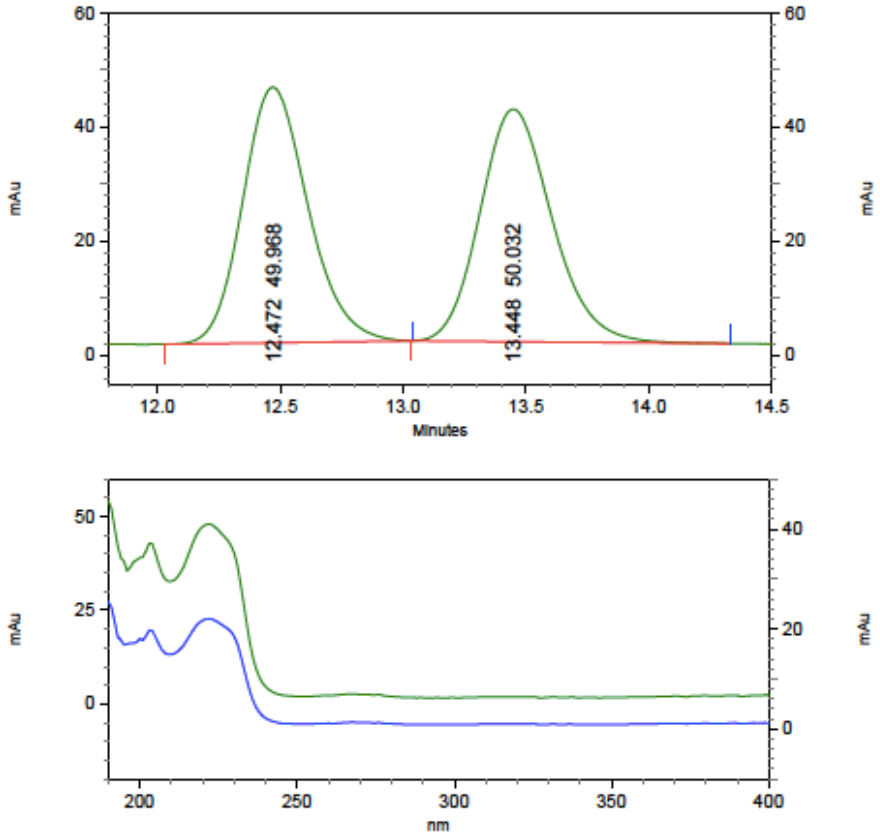
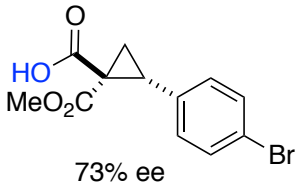
C:\Documents and Settings\zhang\Desktop\DSW\Report-1120.met



3: 220 nm, 4
nm Results

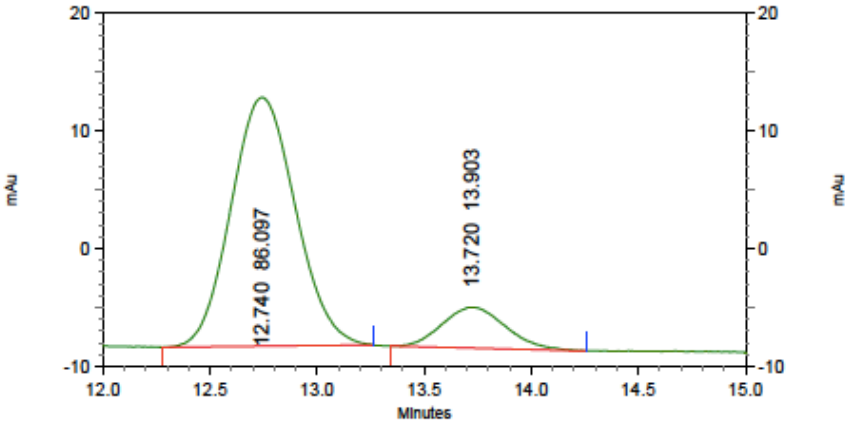
Pk #	Retention Time	Area Percent
1	12.472	49.968
2	13.448	50.032
Totals		100.000

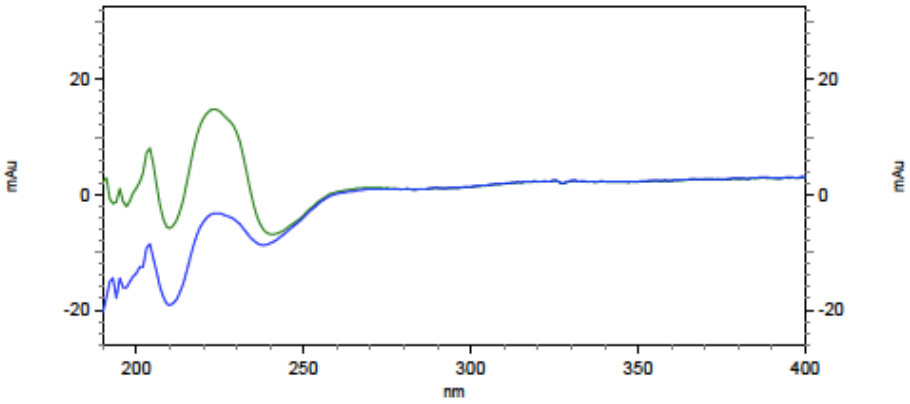
(1*R*,2*R*)-2-(4-bromophenyl)-1-(methoxycarbonyl)cyclopropane-1-carboxylic acid



73% ee

JYW-0235-IA-20%-0.8ml
C:\EZStart\Projects\Default\Data\JYW-0235-IA-20%-0.8ml
C:\Documents and Settings\zhang\Desktop\DSW\0404.met

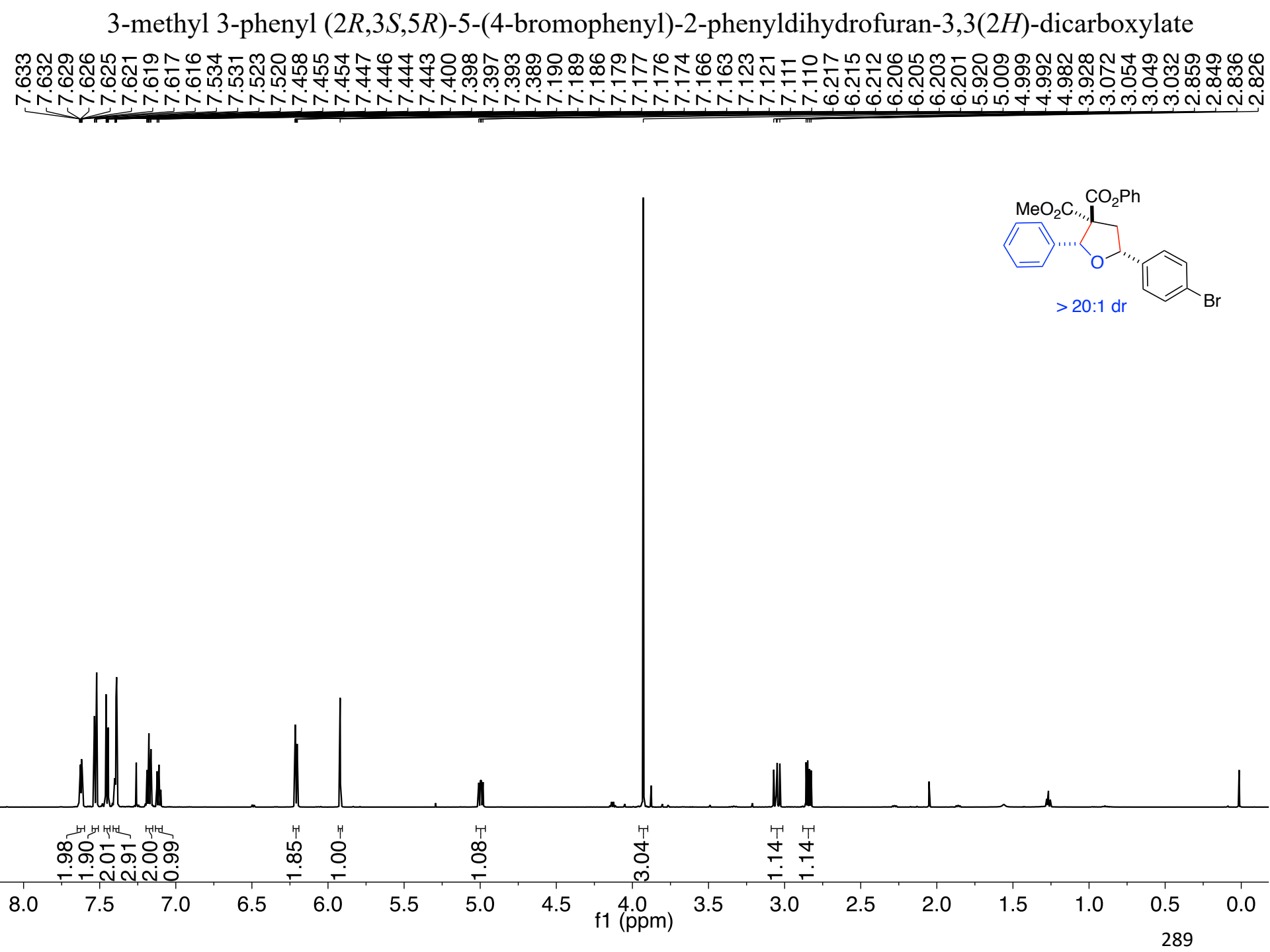




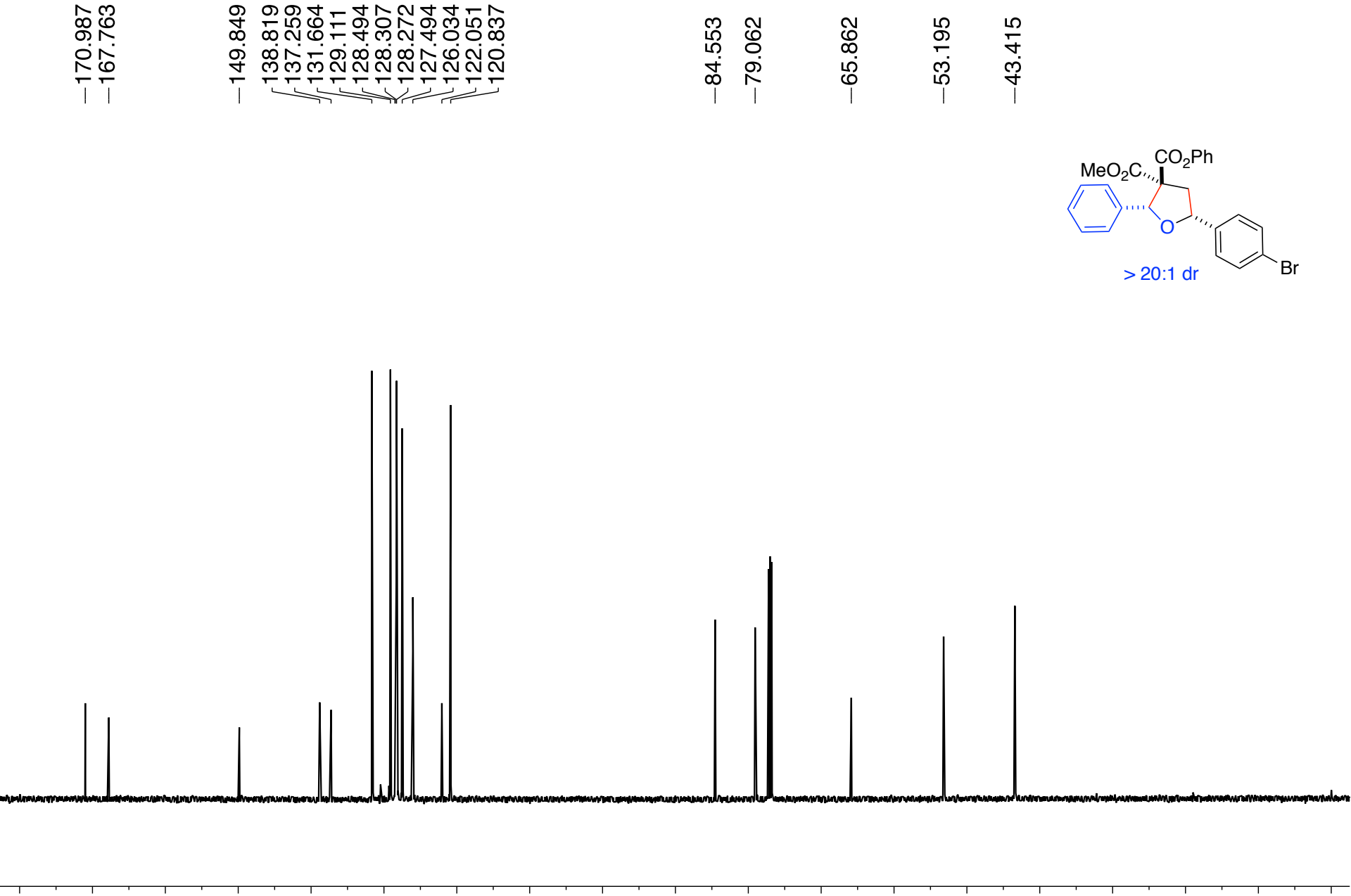
3: 220 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	12.740	86.097
2	13.720	13.903
Totals		100.000

3-methyl 3-phenyl (2*R*,3*S*,5*R*)-5-(4-bromophenyl)-2-phenyldihydrofuran-3,3(2*H*)-dicarboxylate



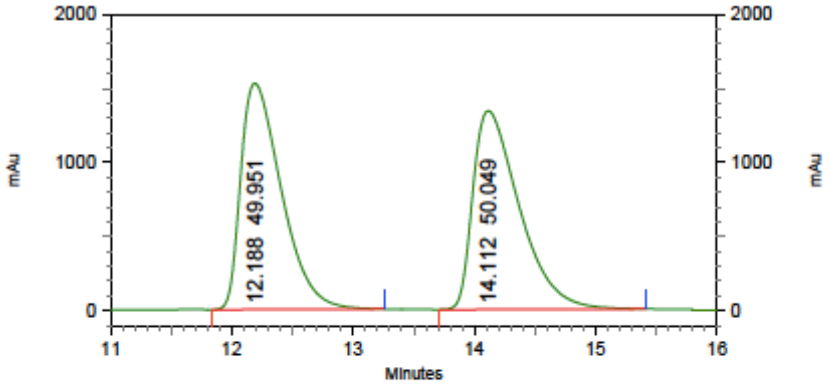
3-methyl 3-phenyl (2*R*,3*S*,5*R*)-5-(4-bromophenyl)-2-phenyldihydrofuran-3,3(2*H*)-dicarboxylate

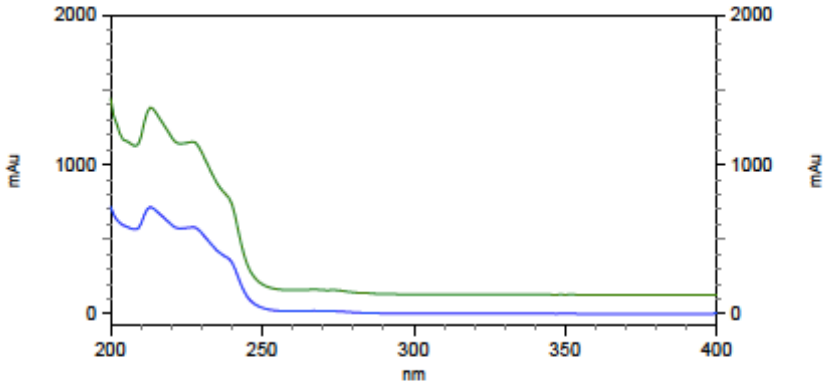


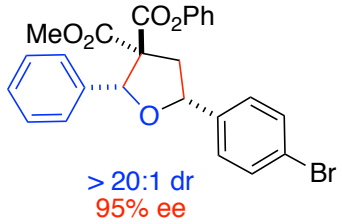
3-methyl 3-phenyl (2*R*,3*S*,5*R*)-5-(4-bromophenyl)-2-phenyldihydrofuran-3,3(2*H*)-dicarboxylate

JYW-IV-199-2-IB-3%-0.8ml2

C:\EZStart\Projects\Default\Data\JYW-IV-199-2-IB-3%-0.8ml2







> 20:1 dr
95% ee

5: 223 nm, 4 nm

Results

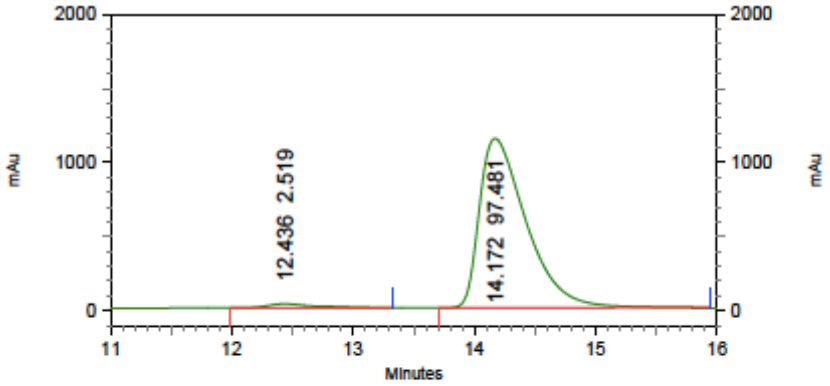
Name	Retention Time	Area Percent	Pk #
	12.188	49.951	1
	14.112	50.049	2

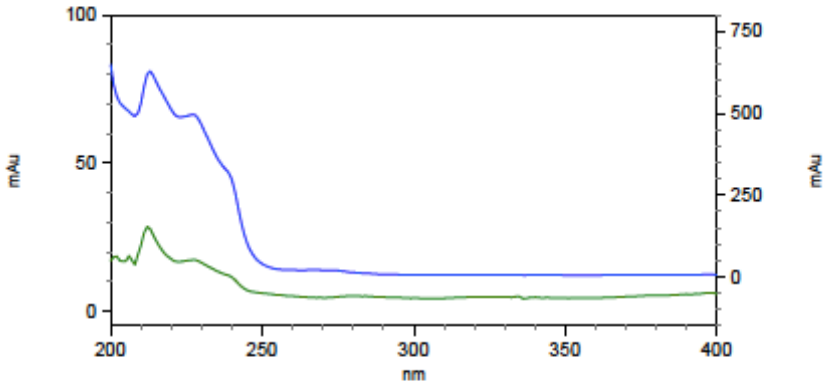
Totals	
	100.000

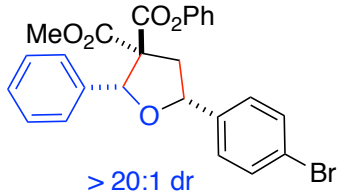
3-methyl 3-phenyl (2*R*,3*S*,5*R*)-5-(4-bromophenyl)-2-phenyldihydrofuran-3,3(2*H*)-dicarboxylate

JYW-IV-198-IB-3%-0.8ml

C:\EZStart\Projects\Default\Data\JYW-IV-198-IB-3%-0.8ml







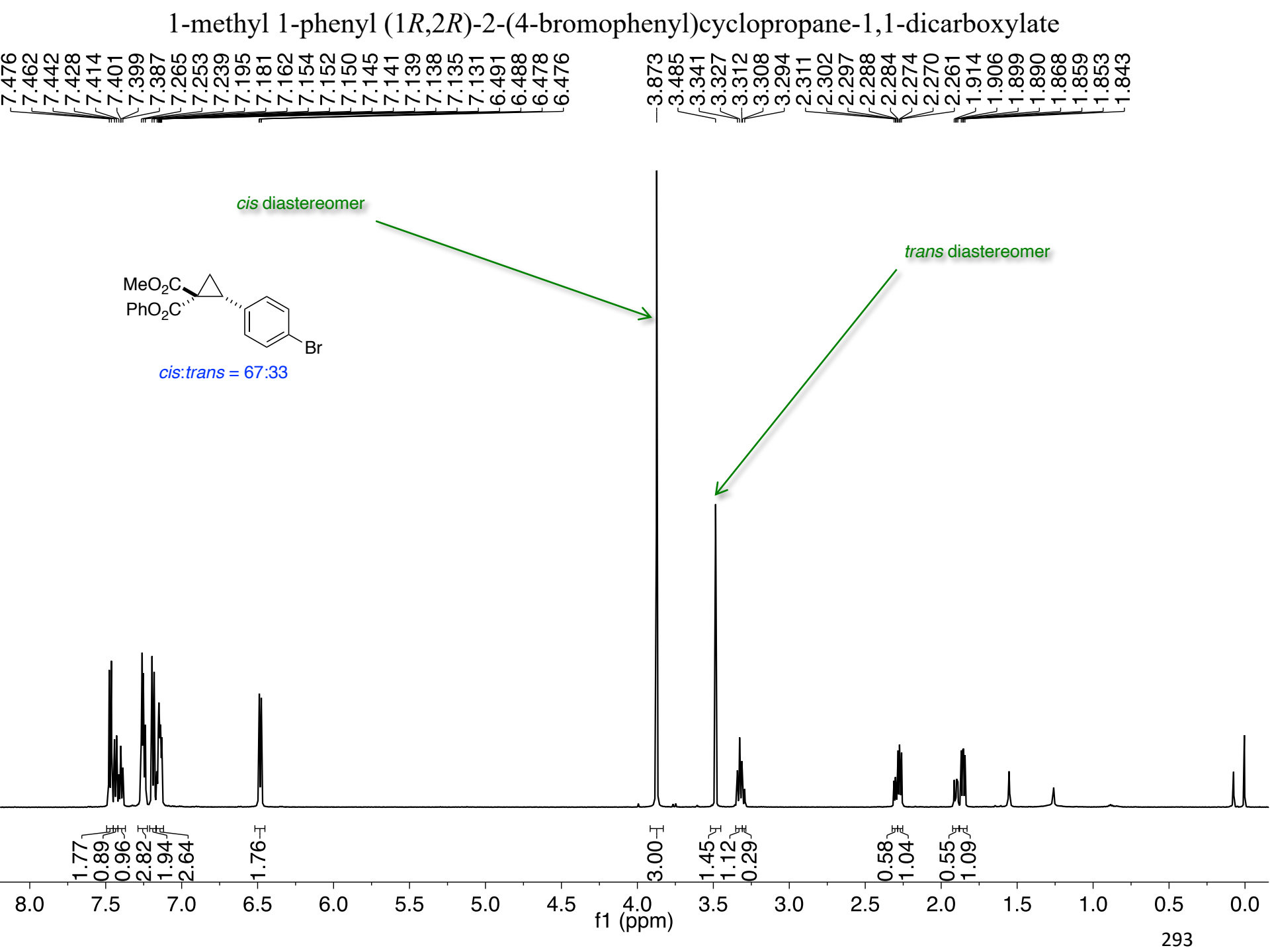
> 20:1 dr
95% ee

5: 223 nm, 4 nm

Results

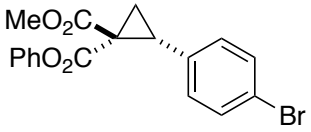
Name	Retention Time	Area Percent	Pk #
	12.436	2.519	1
	14.172	97.481	2
Totals		100.000	

1-methyl 1-phenyl (1*R*,2*R*)-2-(4-bromophenyl)cyclopropane-1,1-dicarboxylate

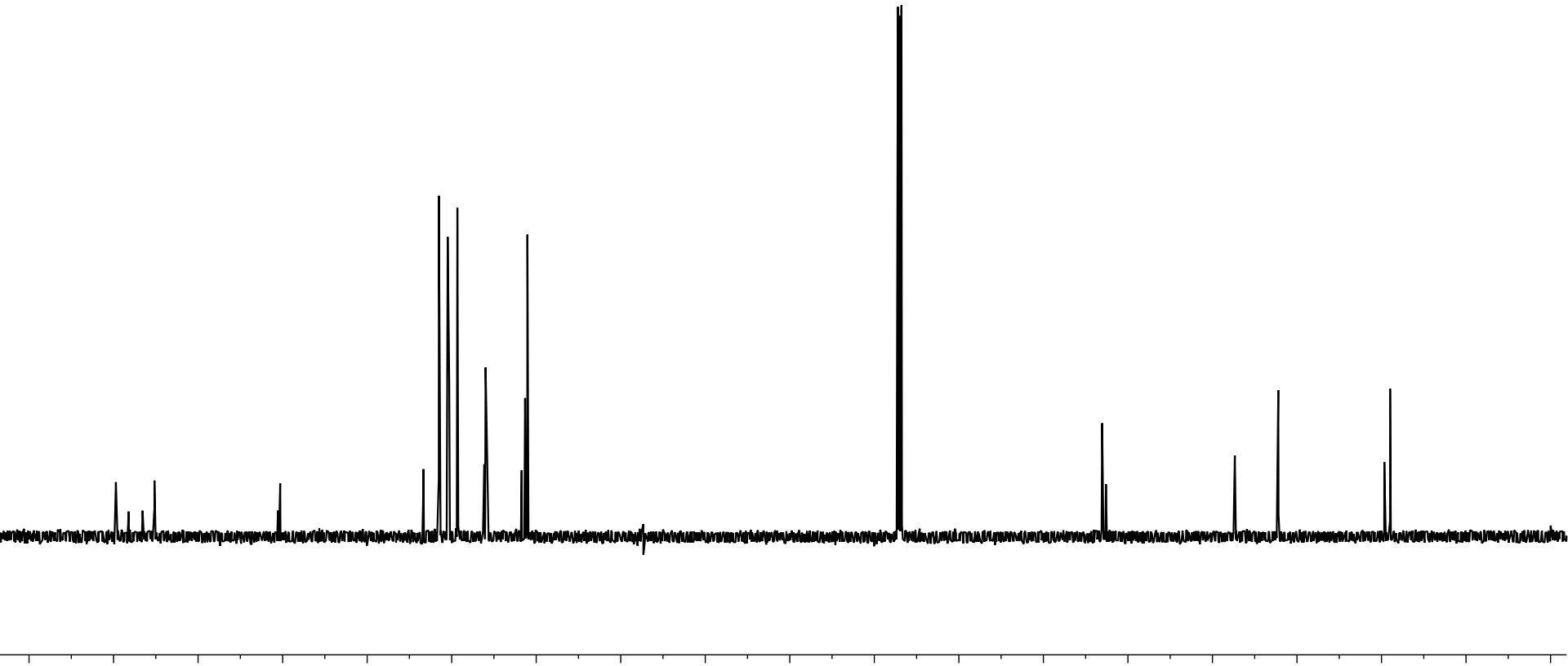


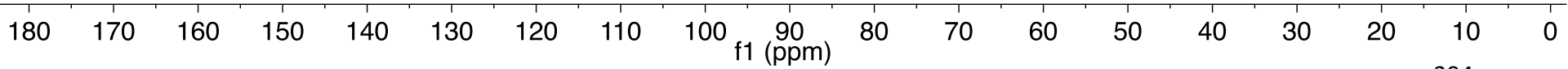
1-methyl 1-phenyl (1*R*,2*R*)-2-(4-bromophenyl)cyclopropane-1,1-dicarboxylate

169.724
168.206
166.563
165.163
150.557
150.285
133.380
133.329
131.517
131.383
130.474
130.287
129.456
129.326
126.143
125.987
121.721
121.632
121.318
121.040
53.045
52.597
37.350
37.297
32.210
32.191
19.662
18.980

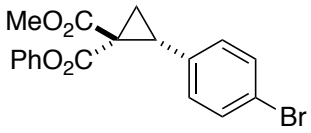


cis:*trans* = 67:33





1-methyl 1-phenyl (1*R*,2*R*)-2-(4-bromophenyl)cyclopropane-1,1-dicarboxylate

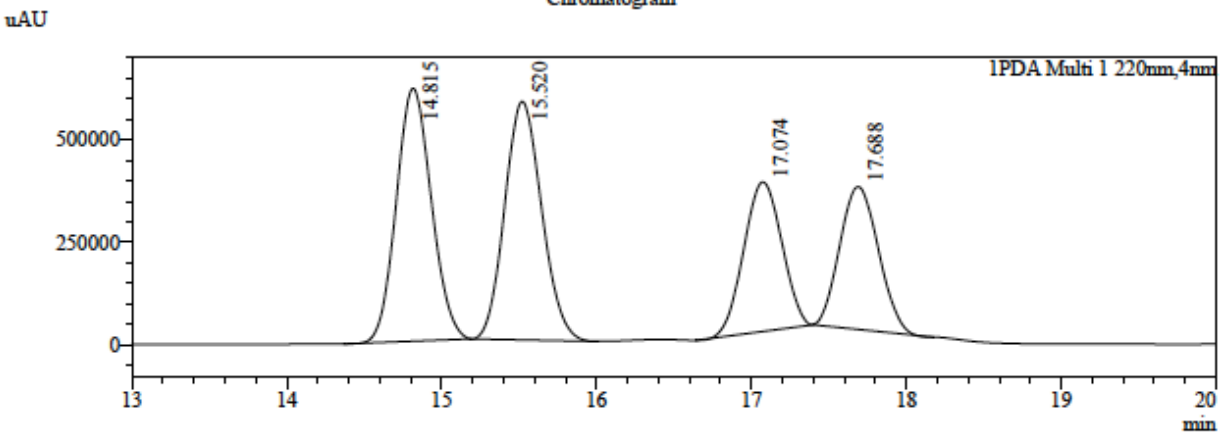


cis:*trans* = 67:33
97%/97% ee

Sample Information

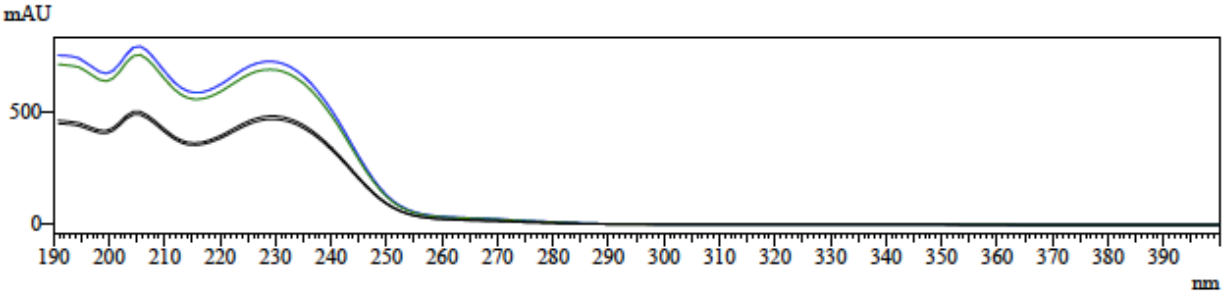
Sample Name	: JYW-II-100
Sample ID	: JYW-II-100-IC-8%-0.8ml2
Data File	: JYW-II-100-IC-8%-0.8ml2.lcd
Method File	: JYW-method.lcm
Date Acquired	: 3/29/2018 7:19:47 PM

Chromatogram



UV Spectrum

JYW-II-100-IC-8%-0.8ml2.lcd



Peak Table

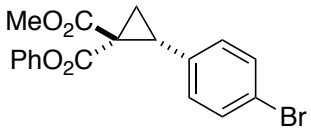
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	14.815	9736587	30.711
2	15.520	9678428	30.527
3	17.074	6243444	19.693
4	17.688	6045894	19.070
Total		31704354	100.000

1-methyl 1-phenyl (1*R*,2*R*)-2-(4-bromophenyl)cyclopropane-1,1-dicarboxylate

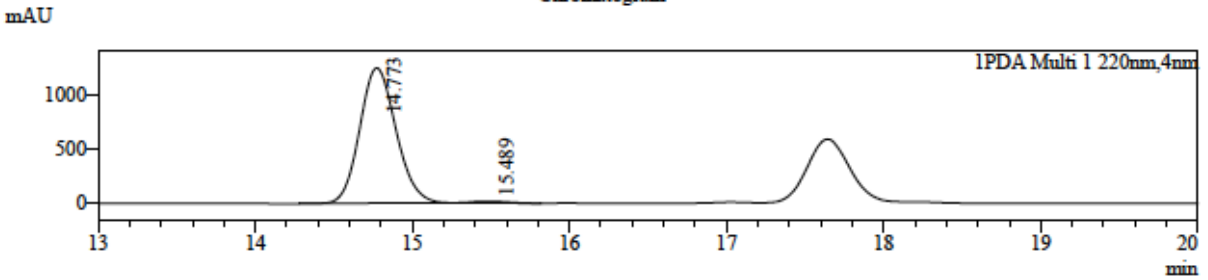
Sample Information

Sample Name	: JYW-0645
Sample ID	: JYW-0645-IC-8%-0.8ml
Data File	: JYW-0645-IC-8%-0.8ml.lcd
Method File	: JYW-method.lcm

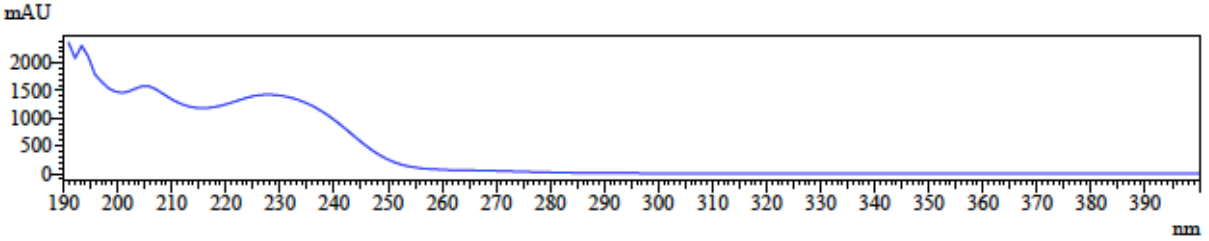


cis:*trans* = 67:33
97%/97% ee

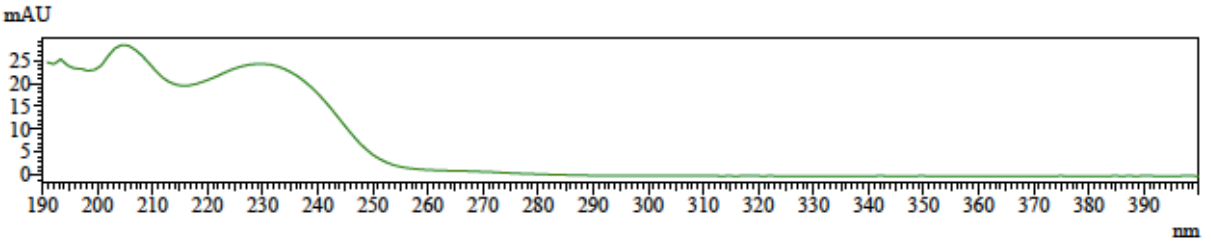
Chromatogram



UV Spectrum
Retention time = 14.773



UV Spectrum
Retention time = 15.489

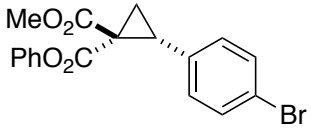


Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	14.773	20075490	98.800
2	15.489	243823	1.200
Total		20319313	100.000

1-methyl 1-phenyl (1*R*,2*R*)-2-(4-bromophenyl)cyclopropane-1,1-dicarboxylate

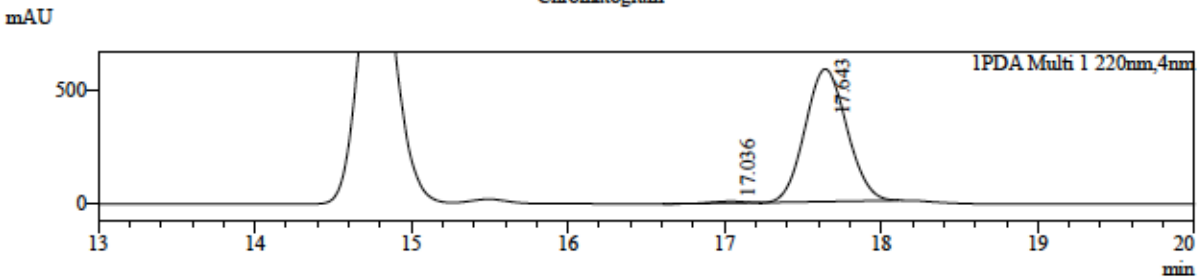


cis:*trans* = 67:33
97%/97% ee

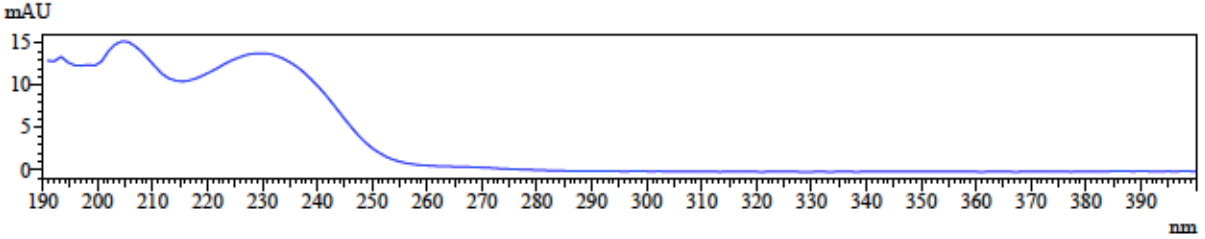
Sample Information

Sample Name	: JYW-0645
Sample ID	: JYW-0645-IC-8%-0.8ml
Data File	: JYW-0645-IC-8%-0.8ml.lcd
Method File	: JYW-method.lcm

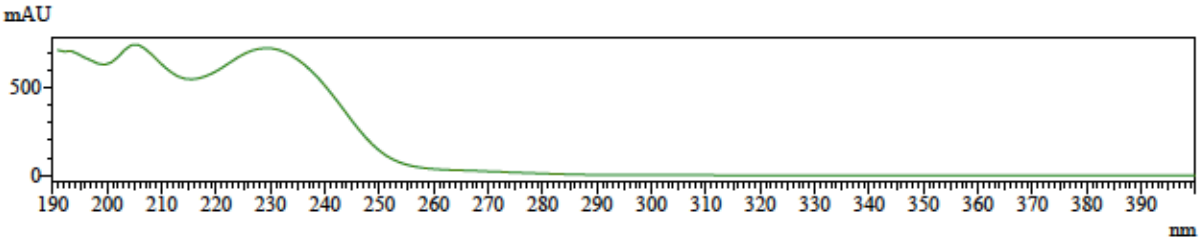
Chromatogram



UV Spectrum
Retention time = 17.036



UV Spectrum
Retention time = 17.643



Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	17.036	111008	1.012
2	17.643	10863003	98.988
Total		10974011	100.000