Supporting Information

Enantioselective Intermolecular All-Carbon [4+2] Annulation via N-Heterocyclic Carbene Organocatalysis

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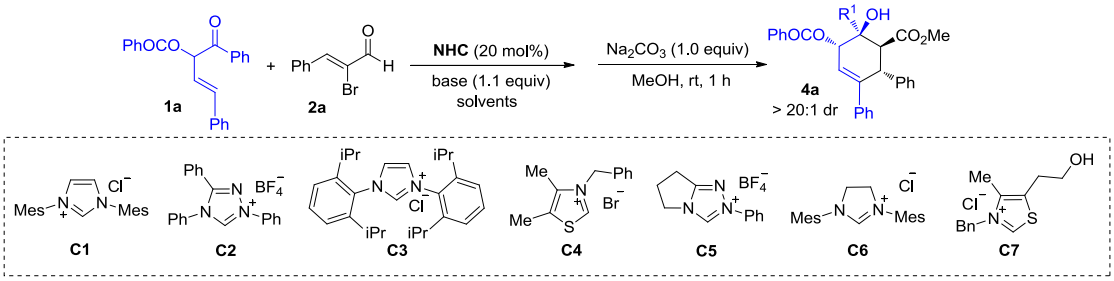
I. General Information.

Commercially available materials purchased from Aladdin, Beijing Ouhe, Meryer, BidePharmaTech, and Adamas were used as received, unless otherwise noted, all reactions and manipulations involving air- or moisture-sensitive compounds were performed using standard Schlenk technique. All solvents were purified and dried using standard procedures. ^{1}H NMR spectra were recorded on a Bruker AVANCE III HD400 (400 MHz) spectrometer. Chemical shifts were recorded in parts per million (ppm, δ) relative to tetramethylsilane (δ = 0.00 ppm) or chloroform (δ = 7.26 ppm). ^{1}H NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), dd (doublet of doublets), m (multiplet), and broad (br). ^{13}C NMR spectra were recorded on a Bruker AVANCE III HD400 (100 MHz) spectrometer. High resolution mass spectral analysis (HRMS) was performed on Thermo Fisher Scientific LTQ FT Ultra mass spectrometer. The determination of *ee* was performed using Shimadzu LC-20AD HPLC workstation. X-ray crystallography analysis was performed on Agilent SuperNova X-ray diffractionmeter. Optical rotations were measured using a 1 mL cell with a 5dm path length on an INESA SGW-1 polarimeter and are reported as follows: $[\alpha]^{rt}_{D}$ (c in g/100 mL solvent). Analytical thin-layer chromatography (TLC) was carried out on WFH-203 F254 pre-coated silica gel plate (0.2 mm thickness). Visualization was performed using a UV lamp, 2,4-Dinitrophenylhydrazine, or potassium permanganate stain.

II. Optimization of Reaction Conditions

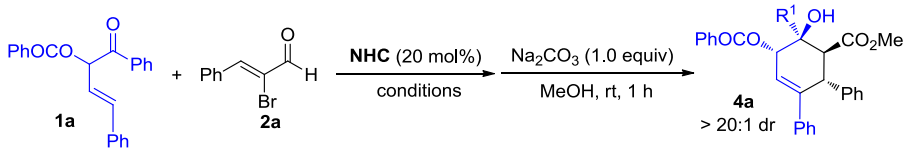
Table S1. Optimization of non-asymmetric all-carbon [4+2] annulation.

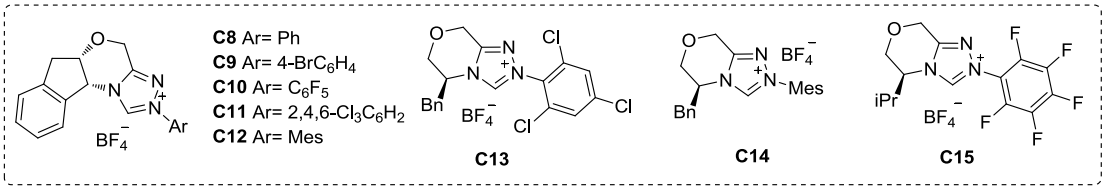


entry	conditons[a]	yield (%)[b]
1	**C2,** Cs_2CO_3, THF, 30 °C	0
2	**C3,** Cs_2CO_3, THF, 30 °C	0
3	**C4,** Cs_2CO_3, THF, 30 °C	0
4	**C5,** Cs_2CO_3, THF, 30 °C	0
5	**C6,** Cs_2CO_3, THF, 30 °C	0
6	**C7,** Cs_2CO_3, THF, 30 °C	0
7	**C1,** Cs_2CO_3, THF, 30 °C	74
8	**C1,** K_2CO_3, THF, 30 °C	82
9	**C1,** CsOAc, THF, 30 °C	27
10	**C1,** Et_3N, THF, 30 °C	53
11	**C1,** DBU, THF, 30 °C	0
12	**C1,** Na_2CO_3, THF, 30 °C	28
13	**C1,** $NaHCO_3$, THF, 30 °C	7
14	**C1,** $KHCO_3$, THF, 30 °C	46
15	**C1,** NaOAc, THF, 30 °C	8
16	**C1,** K_2CO_3, toluene, 30 °C	76
17	**C1,** K_2CO_3, CH_2Cl_2, 30 °C	55
18	**C1,** K_2CO_3, CH_3CN, 30 °C	41
19	**C1,** K_2CO_3, DMF, 30 °C	30

[a]Reaction conditions: **1a** (0.2 mmol), NHC (20 mol %), solvent (1 mL), base (0.22 mmol), **2a** (0.22 mmol), 6 h, argon protection. Diastereomeric ratio was determined via ^{1}H NMR analysis of the reaction mixture. [b]Isolated yields based on **1a**.

Table S2. Optimization of enantioselective all-carbon [4+2] annulation.[a]





entry	NHC	base (equiv)	**2a** (equiv)	solvent	additive	yield[b] (%)	ee[c] (%)
1	**C8**	Cs_2CO_3 (1.1)	1.1	THF	--	24	-53
2	**C9**	Cs_2CO_3 (1.1)	1.1	THF	--	trace	--
3	**C10**	Cs_2CO_3 (1.1)	1.1	THF	--	--	--
4	**C11**	Cs_2CO_3 (1.1)	1.1	THF	--	--	--
5	**C12**	Cs_2CO_3 (1.1)	1.1	THF	--	33	–55
6	**C13**	Cs_2CO_3 (1.1)	1.1	THF	--	--	--
7	**C14**	Cs_2CO_3 (1.1)	1.1	THF	--	36	89
8	**C15**	Cs_2CO_3 (1.1)	1.1	THF	--	--	--
9	**C14**	K_2CO_3 (1.1)	1.1	THF	--	--	--
10	**C14**	LiOH (1.1)	1.1	THF	--	--	--
11	**C14**	CsOAc (1.1)	1.1	THF	--	--	--
12	**C14**	^{t}BuOLi (1.1)	1.1	THF	--	--	--
13	**C14**	DBU (1.1)	1.1	THF	--	27	89
14	**C14**	Et_3N (1.1)	1.1	THF	--	trace	--

15	**C12**	Cs_2CO_3 (1.1)	1.1	THF	LiCl (1.0 equiv)	--	--
16	**C14**	Cs_2CO_3 (1.1)	1.1	THF	LiCl (1.0 equiv)	--	--
17	**C14**	^{t}BuOK (1.1)	1.1	THF	--	trace	--
18	**C14**	Rb_2CO_3 (1.1)	1.1	THF	--	--	--
19	**C14**	$(^t$BuO$)_2$Mg (1.1)	1.1	THF	--	--	--
20	**C14**	DABCO (1.1)	1.1	THF	--	--	--
21	**C12**	Cs_2CO_3 (1.1)	1.1	THF	4Å M.S. (100 mg)	33	–53
22	**C14**	Cs_2CO_3 (1.1)	1.1	THF	4Å M.S. (100 mg)	18	89
23	**C14**	Cs_2CO_3 (1.1)	1.1	THF	4Å M.S. (200 mg)	21	93
24	**C14**	Cs_2CO_3 (1.1)	1.1	THF	4Å M.S. (300 mg)	17	93
25	**C14**	Cs_2CO_3 (2.0)	2.0	THF	4Å M.S. (100 mg)	18	93
26	**C14**	Cs_2CO_3 (2.0)	2.0	THF	4Å M.S. (200 mg)	55	93
27	**C14**	Cs_2CO_3 (2.0)	2.0	CH_2Cl_2	4Å M.S. (200 mg)	24	93
28	**C14**	Cs_2CO_3 (2.0)	2.0	toluene	4Å M.S. (200 mg)	--	--
29	**C14**	Cs_2CO_3 (2.0)	2.0	DMF	4Å M.S. (200 mg)	58	66
30	**C14**	Cs_2CO_3 (2.0)	2.0	dioxane	4Å M.S. (200 mg)	25	75
31	**C14**	Cs_2CO_3 (2.0)	2.0	Et_2O	4Å M.S. (200 mg)	--	--
32	**C14**	Cs_2CO_3 (2.0)	2.0	CH_3CN	4Å M.S. (200 mg)	44	58

33	**C14**	Cs_2CO_3 (2.0)	2.0	MeOH	4Å M.S. (200 mg)	--	--
34	**C14**	Cs_2CO_3 (2.0)	2.0	MTBE	4Å M.S. (200 mg)	--	--
35	**C14**	Cs_2CO_3 (1.2)	1.5	THF	4Å M.S. (200 mg)	66	93
36	**C14**	Cs_2CO_3 (1.5)	1.5	THF	4Å M.S. (200 mg)	62	93
37	**C14**	Cs_2CO_3 (1.2)	2.0	THF	4Å M.S. (200 mg)	45	93
38	**C14**	Cs_2CO_3 (1.5)	2.0	THF	4Å M.S. (200 mg)	46	93
39	**C14**	Cs_2CO_3 (1.2)	1.1	THF	4Å M.S. (200 mg)	53	93
40	**C14**	Cs_2CO_3 (1.2)	1.2	THF	4Å M.S. (200 mg)	60	93
41	**C14**	Cs_2CO_3 (1.2)	1.3	THF	4Å M.S. (200 mg)	66	93
42	**C14**	Cs_2CO_3 (1.2)	1.4	THF	4Å M.S. (200 mg)	50	93
43	**C14**	Cs_2CO_3 (1.5)	1.3	THF	4Å M.S. (200 mg)	74	93
44	**C14**	Cs_2CO_3 (2.0)	1.5	THF	4Å M.S. (200 mg)	80	93

[a]Reaction conditions: **1a** (0.2 mmol), NHC (20 mol %), solvent (1 mL), argon protection. Diastereomeric ratio was determined via ^{1}H NMR analysis of the reaction mixtures. [b]Isolated yields based on **1a**. [c]Determined via HPLC analysis on a chiral stationary phase.

III. Single-Crystal X-Ray Crystallographic Analysis.

Method for single crystal cultivation: a solid sample of **4d** (10–20 mg) was dissolved in ethyl acetate (50–100 μL) in a vial at room temperature, and petroleum ether (2–8 mL) was added into the above solution slowly while keeping the sample all dissolved. Then the vial was sealed with a piece of parafilm and stayed quietly for several days to allow the slow evaporation of the solvents until a single crystal was obtained.

CCDC 1569976 (**4d**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Centre via www.ccdc.cam.ac.uk/data_request/cif.

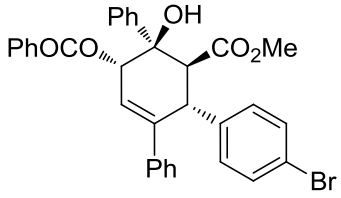
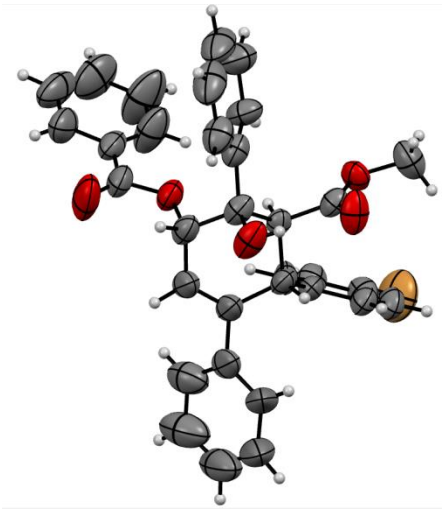
Compound 4d	X-ray structure
	

Table S3. Crystal data and structure refinement for data of compound 4d:

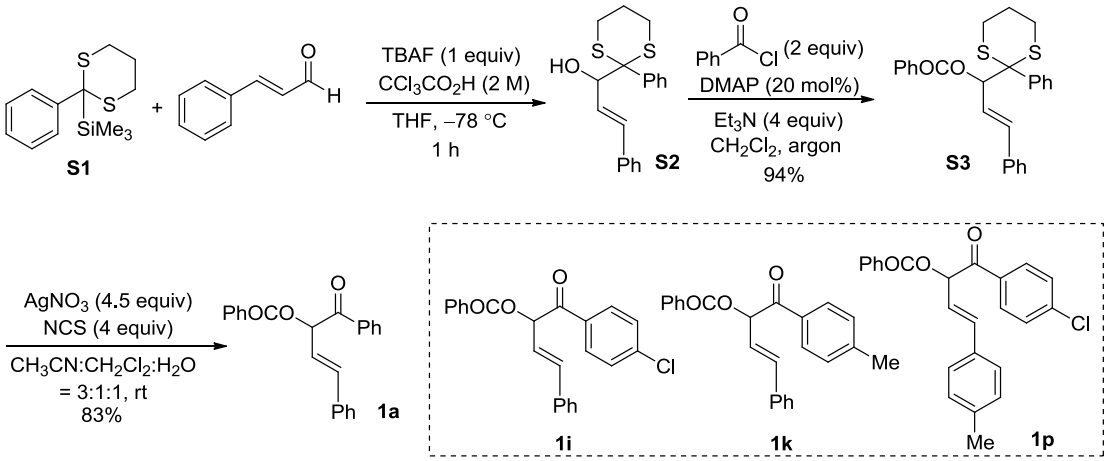
Identification code	Compound-4d	
Empirical formula	C33 H27 Br O5	
Formula weight	583.45	
Temperature	293.15 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 10.024(5) Å	a= 90 °.
	b = 11.074(5) Å	b= 92.686(9) °.
	c = 13.112(6) Å	g = 90 °.
Volume	1454.0(12) $Å^3$	
Z	2	
Density (calculated)	1.333 Mg/m^3	
Absorption coefficient	1.452 mm^{-1}	
F(000)	600	
Crystal size	0.800 x 0.400 x 0.300 mm^3	
Theta range for data collection	3.106 to 27.429 °.	
Index ranges	-11<=h<=12, -14<=k<=13, -16<=l<=16	
Reflections collected	12172	
Independent reflections	5835 [R(int) = 0.0435]	
Completeness to theta = 25.242 °	99.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.7225	
Refinement method	Full-matrix least-squares on F^2	

Data / restraints / parameters	5835 / 101 / 354
Goodness-of-fit on F^2	0.732
Final R indices [I>2sigma(I)]	R1 = 0.0477, wR2 = 0.1078
R indices (all data)	R1 = 0.0762, wR2 = 0.1157
Absolute structure parameter	0.255(12)
Extinction coefficient	n/a
Largest diff. peak and hole	0.179 and -0.356 e.Å^{-3}

IV.

1. General procedures for the preparation of substrates.

(1) Procedures for the synthesis of **1a**, **1i**, **1k**, and **1p**:



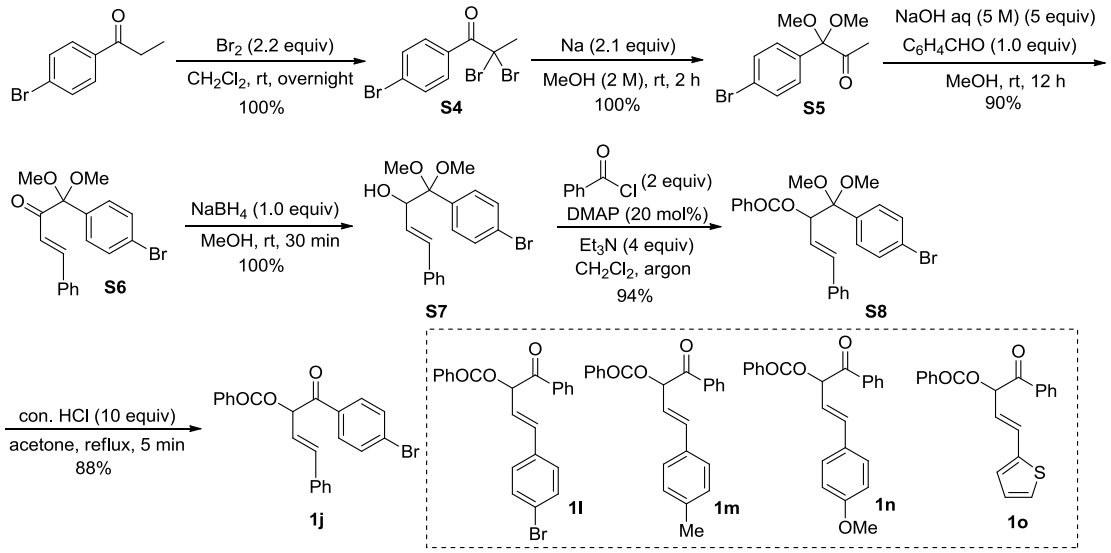
Typically, to a 50-mL round bottom flask with septum and stir bar was added **S1** (805.5 mg, 3.0 mmol, 1.5 equiv). The flask was evacuated and backfilled with argon twice, then *trans*-cinnamaldehyde (264 mg, 252 μL, 2.0 mmol, 1.0 equiv) and 20 mL of THF were added by syringe. The reaction was cooled to –78 ℃ and stirred under argon atmosphere. A freshly prepared solution of TBAF (1 equiv) in THF (0.2 M) was added dropwise to the reaction mixture and stirred at –78 ℃ for 1 hour. The reaction was quenched at –78 ℃ with 20 mL of 2.0 M Cl_3CCO_2H in THF. The cooling bath was then removed and the reaction was stirred at room temperature for 0.5 hour. To the reaction mixture was added 50 mL of Et_2O and transferred to a separatory funnel containing 50 mL of sat. $NaHCO_3$ aqueous solution. After work-up the ether layer was collected and washed with distilled water (2 × 20 mL) and saturated brine (1 × 20 mL). The organic phase was dried over anhydrous Na_2SO_4, and concentrated using

rotary evaporation. Purification of crude product through a silica gel column using a mixture of hexane and ethyl acetate (70:30 v/v) as eluent gave **S2** (520 mg, 79% yield).

To a solution of **S2** (1.6 mmol, 520 mg, 1.0 equiv) in 10 mL of CH_2Cl_2 under argon at 0 ^oC was added DMAP (0.32 mmol, 39 mg, 20 mol%) and 4 equiv of Et_3N. Then benzoyl chloride (2 equiv) was added dropwise to the stirred solution at 0 ^oC. The reaction mixture was slowly warmed to room temperature and stirred overnight. After the starting materials were consumed, the reaction mixture was extracted with dichloromethane (20 mL) and water. The organic layer was then separated, dried over anhydrous sodium sulfate and concentrated using rotary evaporation. Purification of crude product through a silica gel column using a mixture of hexane and ethyl acetate (80:20 v/v) as eluent gave **S3** (650 mg, 94% yield).

To the solution of **S3** (1.5 mmol, 1 equiv) in acetonitrile/dichloromethane/water (3:1:1) were added the mixture of *N*-chlorosuccinimide (4 equiv) and $AgNO_3$ (4.5 equiv) at room temperature. The mixture was stirred at room temperature for 20 minutes. After completion, aqueous $Na_2S_2O_3$ solution was added. Then the reaction mixture was extracted with CH_2Cl_2, dried over anhydrous Na_2SO_4, concentrated and purified by column chromatography using a mixture of petroleum ether and ethyl acetate (90:10 v/v) as eluent to give **1a** (426 mg, 83% yield).

(2) Procedures for the synthesis of **1j**, **1l**, **1m**, **1n**, and **1o**:



Typically, to a solution of 4-bromophenylactone (5.0 mmol, 1.0 equiv) in CH_2Cl_2 (50 mL) was added Br_2 (11.0 mmol, 2.2 equiv) dropwise at room temperature. The reaction mixture was stirred overnight. After full consumption of staring material, saturated $NaHCO_3$ aqueous solution and saturated $Na_2S_2O_3$ aqueous solution were added to the reaction mixture. After having been stirred for 5 minutes, the reaction mixture was extracted with dichloromethane (20 mL) and water. The organic layer was then separated, dried over anhydrous sodium sulfate and concentrated using rotary evaporation. Purification of crude product through a silica gel column using a mixture of hexane and ethyl acetate (10:1 v/v) as eluent gave **S4** (1.9 g, 100% yield).

Sodium turnings (5.0 mmol, 2.1 equiv) was added in portions to MeOH (2.0 M). After sodium was dissolved completely into MeOH, the starting material **S4** (2.4 mmol, 1.0 equiv) was added by syringe dropwise to the above solution. After 2h, the reaction mixture was checked by TLC, then added water and brine before the reaction mixture was extracted with dichloromethane (20 mL) and water. The organic layer was then separated, dried over anhydrous sodium sulfate and concentrated using rotary evaporation. Purification of crude product through a silica gel column using a mixture of hexane and ethyl acetate (10:1 v/v) as eluent gave **S5** (655 mg, 100% yield).

In a 100 mL round bottom flask was taken a mixture of benzaldehyde (5.0 mmol, 1 equiv) and **S5** (5.0 mmol, 1 equiv) in 10 mL of methanol. Then a 4.5 mL of 5 M aqueous sodium hydroxide solution (25 mmol) were added. The mixture was stirred for 12 h at room temperature. After the reaction was completed, methanol was removed under reduced pressure and the remaining aqueous phase was extracted with methylene chloride and the organic phase was washed with brine. After drying with anhydrous Na_2SO_4 and evaporation of the organic phase, purification of crude product through a silica gel column using a mixture of hexane and ethyl acetate (10:1 v/v) as eluent gave **S6** (1.7 g, 92% yield).

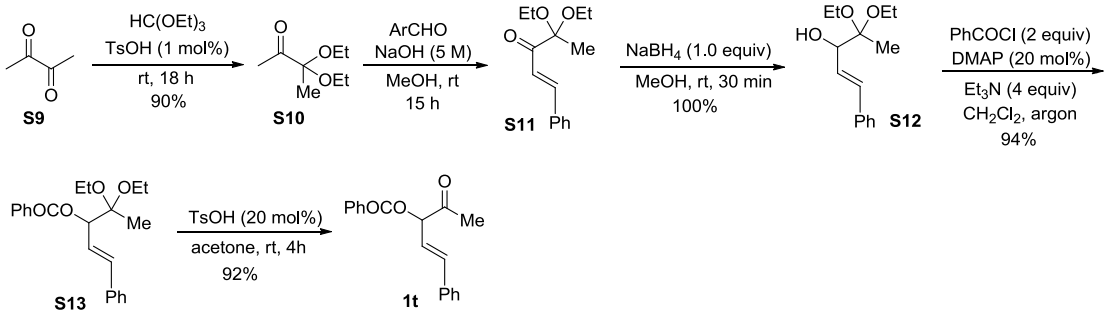
To a solution of **S6** (5 mmol, 1.0 equiv) in absolute MeOH (10 mL) was added $NaBH_4$ (5 mmol, 1.0 equiv) at room temperature. The mixture was stirred at room temperature for 30 minutes. After completion, H_2O and brine were added. Then the

reaction mixture was extracted with CH_2Cl_2, dried over anhydrous Na_2SO_4, concentrated and purified by column chromatography using a mixture of petroleum ether and ethyl acetate (90:10 v/v) as eluent to give **S7** (1.8 g, 100% yield).

To a solution of **S7** (5 mmol, 1.0 equiv) in 10 mL of CH_2Cl_2 under argon at 0 ^oC was added 20 mol% of DMAP and 4 equiv of Et_3N. Then benzoyl chloride (2 equiv) was added dropwise to the stirred solution at 0 ^oC. The reaction mixture was slowly warmed to room temperature and stirred overnight. After the starting materials were consumed, the reaction mixture was extracted with dichloromethane (20 mL) and water. The organic layer was then separated, dried over anhydrous sodium sulfate and concentrated using rotary evaporation. Purification of the crude product through a silica gel column using a mixture of hexane and ethyl acetate (80:20 v/v) as eluent gave **S8** (2.2 g, 94% yield).

To a solution of **S8** (5.0 mmol, 1.0 equiv) in acetone (20 mL) was added concentrated HCl (50 mmol, 10.0 equiv), and refluxed for 5 minutes until some precipitates were generated from the reaction mixture. After checked by TLC, the reaction mixture was cooled to room temperature. The solids were filtered and washed with a mixture of hexane and ethyl acetate (100:1 v/v). Collection of the solid by filtration afforded **1j** (1.9 g, 88% yield). Then the solid was further dried under vacuum and used for the NHC-catalyzed reactions.

(3) Procedures for the synthesis of **1t**:



The reaction of butane-2,3-dione **S9** with triethylorthoformate afforded 3,3-diethoxybutane-2-one **S10** in 90% yield according to the reported method (*J. Org. Chem.* **1995**, *60*, 8204; *Angew. Chem., Int. Ed.* **2016**, *55*, 1208). In a 100 mL round bottom flask was taken a mixture of aromatic aldehyde (5.0 mmol, 1 equiv) and

3,3-diethoxybutane-2-one **S10** (800.5 mg, 5.0 mmol, 1 equiv) in 10 mL of methanol. Then a 4.5 mL of 5M aqueous sodium hydroxide solution was added. The mixture was stirred for 15 h at room temperature. After the reaction was complete, methanol was removed under reduced pressure and the remaining aqueous phase was extracted with methylene chloride and the organic phase was washed with brine. After drying with anhydrous Na_2SO_4 and evaporation of the organic phase, product **S11** (721 mg, 90% yield) was pure enough and can be used in the next step.

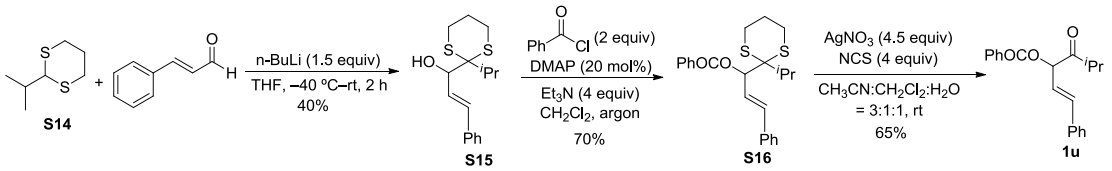
To a solution of **S11** (5 mmol, 1.0 equiv) in absolute MeOH (10 mL) was added $NaBH_4$ (5 mmol, 1.0 equiv) at room temperature. The mixture was stirred at room temperature for 30 minutes. After completion, H_2O and brine were added. Then the reaction mixture was extracted with CH_2Cl_2, dried over anhydrous Na_2SO_4, concentrated and purified by column chromatography using a mixture of petroleum ether and ethyl acetate (90:10 v/v) as eluent to give **S12** (1.3 g, 100% yield).

To the solution of **S12** (5 mmol) in 10 mL of CH_2Cl_2 under argon at 0 ^oC was added 20 mol% of DMAP and 4 equiv of Et_3N. Then benzoyl chloride (2 equiv) was added dropwise to the solution was stirred at 0 ^oC. The reaction mixture was slowly warmed to room temperature and stirred overnight. After the starting materials were consumed, the reaction mixture was extracted with dichloromethane (20 mL) and water. The organic layer was then separated, dried over anhydrous sodium sulfate and concentrated using rotary evaporation. Purification of the crude product through a silica gel column using a mixture of hexane and ethyl acetate (80:20 v/v) as eluent gave **S13** (1.7 g, 94% yield).

In a 50 mL round bottom flask, acetal **S13** (5 mmol) was dissolved in 20 mL of acetone. To this solution *p*-TSA (20 mol%) was added and the mixture was stirred for 3 h at room temperature. The solvent was evaporated under reduced pressure and the residue was dissolved in methylene chloride and washed with water. Drying of the organic phase with anhydrous Na_2SO_4 and the following evaporation gave the crude product as a yellowish solid. The yellow solid was kept for crystallization in petroleum ether/methylene chloride (4:1 v/v, 20 mL). After crystallization, the yellow

solid was filtered through a Büchner funnel to afford *α,β*-unsaturated compound **1t** (1.3 g, 92%).

(4) Procedures for the synthesis of **1u**:

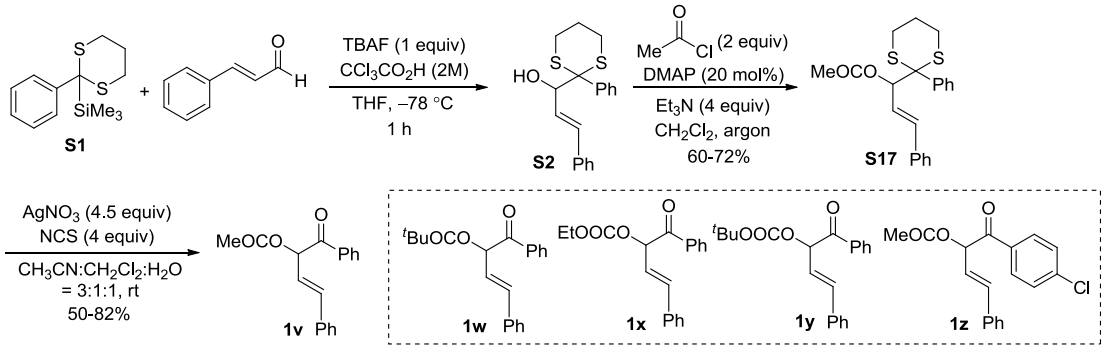


To a 50-mL round bottom flask with septum and stir bar was added **S14** (3.0 mmol, 1.0 equiv). The flask was evacuated and backfilled with argon twice before 20 mL of THF was added. *n*-Butylithium (4.5 mmol, 1.5 equiv) was subsequently added dropwise by syringe at –40 °C. The reaction mixture was stirred for 1h at –40 °C under argon atmosphere. Then cinnamaldehyde (3.0 mmol, 1.0 equiv) was added dropwise to the above reaction mixture at the same temperature. After cinnamaldehyde was consumed completely (about 1h), the reaction mixture was quenched with water at –40 °C and the ice bath was removed. After the reaction mixture was warmed to room temperature, the solvent was removed under vacuum and the crude product was extracted with CH_2Cl_2. The organic layers were collected and dried over anhydrous sodium sulfate before evaporation. The residue was purified by silica gel column chromatography using the mixture of hexanes/ethyl acetate (80:20 v/v) as eluent to give **S15** (353 mg, 40% yield).

To a solution of **S15** (5 mmol) in 10 mL of CH_2Cl_2 under argon at 0 ^oC was added 20 mol% of DMAP and 4 equiv of Et_3N. Then benzoyl chloride (2 equiv) was added dropwise to the stirred solution at 0 ^oC. The reaction mixture was slowly warmed to room temperature and stirred overnight. After the starting materials were consumed, the reaction mixture was extracted with dichloromethane (20 mL) and water. The organic layer was then separated, dried over anhydrous sodium sulfate and concentrated using rotary evaporation. Purification of the crude product through a silica gel column using a mixture of hexanes and ethyl acetate (80:20 v/v) as eluent gave **S16** (1.4 g, 70% yield).

To the solution of **S16** (5.0 mmol, 1 equiv) in acetonitrile/dichloromethane/water (3:1:1) was added the mixture of *N*-chlorosuccinimide (4 equiv) and $AgNO_3$ (4.5 equiv) at room temperature. The mixture was stirred at room temperature for 20 minutes. After completion, aqueous $Na_2S_2O_3$ solution was added. Then the reaction mixture was extracted with CH_2Cl_2, dried over anhydrous Na_2SO_4, concentrated and purified by column chromatography using a mixture of petroleum ether and ethyl acetate (90:10 v/v) as eluent to give **1u** (1.0 g, 65% yield).

(5) Procedures for the synthesis of **1v**, **1w**, **1x**, **1y**, and **1z**:



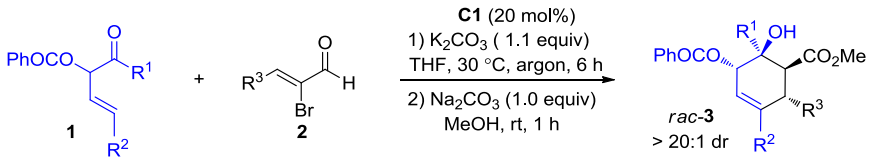
To a 50-mL round bottom flask with septum and stir bar was added **S1** (805.5 mg, 3.0 mmol, 1.5 equiv). The flask was evacuated and backfilled with argon twice, then *trans*-cinnamaldehyde (264 mg, 252 μL, 2.0 mmol, 1.0 equiv) and 20 mL of THF were added by syringe. The reaction was cooled to –78 ℃ and stirred under argon atmosphere. A freshly prepared solution of TBAF (1 equiv) in THF (0.2 M) was added dropwise to the reaction mixture and stirred at –78 ℃ for 1 hour. The reaction was quenched at –78 ℃ with 20 mL of 2.0 M Cl_3CCO_2H in. The cooling bath was then removed and the reaction was stirred at room temperature for 0.5 hour. The reaction mixture was added 50 mL of Et_2O and transferred to a separatory funnel containing 50 mL of sat. $NaHCO_3$ aq solution. After work-up the ether layer was separated and washed with distilled water (2 × 20 mL) and saturated brine (1 × 20 mL). The organic phase was dried over anhydrous Na_2SO_4, and concentrated using rotary evaporation. Purification of the crude product through a silica gel column using a mixture of hexane and ethyl acetate (70:30 v/v) as eluent gave **S2** (520 mg, 79% yield).

To a solution of **S2** (5 mmol) in 10 mL of CH_2Cl_2 under argon at 0 ^oC was added 20 mol% of DMAP and 4 equiv of Et_3N. Then acetyl chloride (2 equiv) was added dropwise to the stirred solution at 0 ^oC. The reaction mixture was warmed to room temperature and stirred overnight. After the starting materials were consumed, the reaction mixture was extracted with dichloromethane (20 mL) and water. The organic layer was then separated, dried over anhydrous sodium sulfate and concentrated using rotary evaporation. Purification of crude product through a silica gel column using a mixture of hexane and ethyl acetate (80:20 v/v) as eluent gave **S17**(1.1 g, 60%).

To the solution of **S17** (5.0 mmol, 1 equiv) in acetonitrile/dichloromethane/water (3:1:1) was added the mixture of *N*-chlorosuccinimide (4 equiv) and $AgNO_3$ (4.5 equiv) at room temperature. The mixture was stirred at room temperature for 20 minutes. After completion, aqueous $Na_2S_2O_3$ solution was added. Then the reaction mixture was extracted with CH_2Cl_2, dried over anhydrous Na_2SO_4, concentrated and purified by column chromatography using a mixture of petroleum ether and ethyl acetate (90:10 v/v) as eluent to give **1v** (700 mg, 50% yield).

2. General procedures for the annulation reactions.

(1) General procedure for the non-asymmetric all-carbon [4+2] annulation:

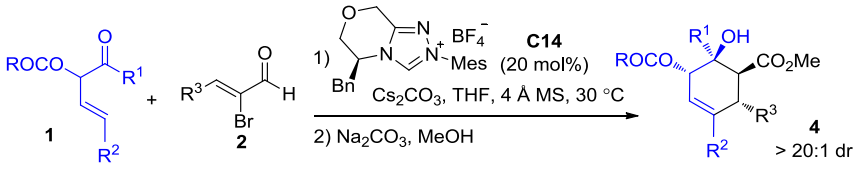


To a dried 10 mL Schlenk tube equipped with a tiny magnetic stir bar were added catalyst **C1** (13.6 mg, 20 mol %), K_2CO_3 (30.4 mg, 0.22 mmol, 1.1 equiv), **1a** (68.5 mg, 0.2 mmol, 1 equiv), and α-bromocinnamaldehyde **2a** (46.4 mg, 0.22 mmol, 1.1 equiv). After argon was backfilled twice, THF (1 mL) was added and the resulting solution was stirred for 6h at 30 ^oC. After completion of the reaction, solvent was evaporated and the resulting crude product was purified through a short column chromatography on silica gel with petroleum ether/ethyl acetate (4:1 v/v) as eluent to afford the cyclohexyl *β*-lactone product and it was used immediately for the next step.

To a solution of the cyclohexyl *β*-lactone (0.2 mmol, 1.0 equiv) in MeOH (1 mL) was added Na_2CO_3 (0.2 mmol, 1.0 equiv) at room temperature. After the completion

of reaction, water and brine were added, and the reaction mixture was extracted with CH_2Cl_2, dried over anhydrous Na_2SO_4, concentrated and purified by column chromatography using a mixture of petroleum ether and ethyl acetate (5:1 v/v) as eluent to give *rac*-**3a** (82 mg, 82% yield over two steps).

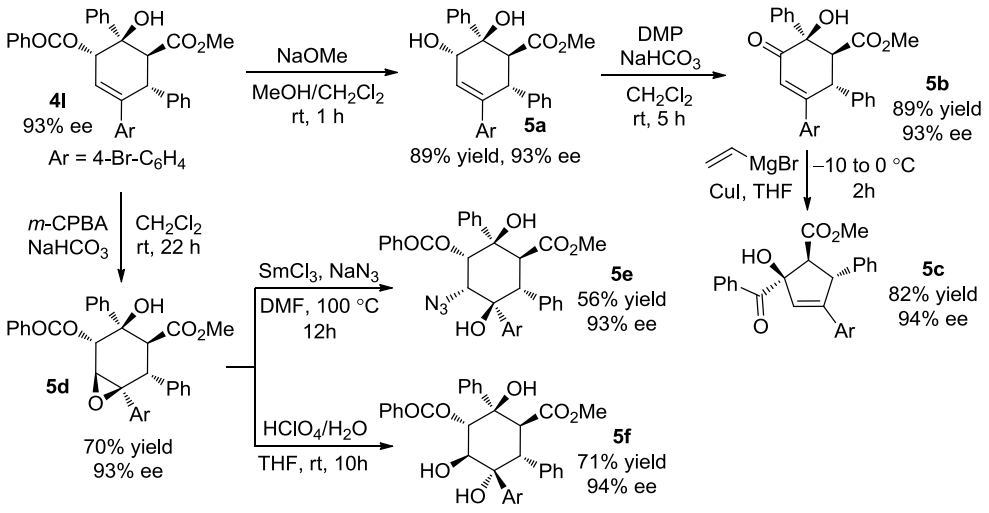
(2) General procedure for the asymmetric all-carbon [4+2] annulation:



To a dried 10 mL Schlenk tube equipped with a tiny magnetic stir bar were added catalyst **C10** (16.8 mg, 20 mol %), Cs_2CO_3 (130 mg, 0.4 mmol, 2.0 equiv), **1a** (68.5 mg, 0.2 mmol, 1 equiv), α-bromocinnamaldehyde **2a** (63.3 mg, 0.3 mmol, 1.5 equiv) and 4Å molecular seives (400 mg). The tube was backfilled with argon twice. THF (1 mL) was added and the resulting solution was stirred for 12 at 30 ℃. After completion of the reaction, solvent was evaporated after filtration through celite and the resulting crude product was purified through a short column chromatography on silica gel with petroleum ether/ethyl acetate (4:1 v/v) as eluent to afford the cyclohexyl *β*-lactone product and it was used immediately for the next step.

To a solution of the cyclohexyl *β*-lactone (0.2 mmol, 1.0 equiv) in MeOH (1 mL) was added Na_2CO_3 (0.2 mmol, 1.0 equiv) and stirred at room temperature. After the completion of the reaction, water and brine were added, and the reaction mixture was extracted with CH_2Cl_2, dried over anhydrous Na_2SO_4, concentrated and purified by column chromatography using a mixture of petroleum ether and ethyl acetate (5:1 v/v) as eluent to give **4a** (81 mg, 80% yield over two steps).

3. Procedures for products derivatizations.



Synthesis of compound 5a. To the solution of **4l** (467 mg, 0.8 mmol) in MeOH/CH_2Cl_2 (1:1 v/v, 8.0 mL) was added 4.0 mL solution of NaOMe (1.0 M in MeOH) at room temperature. The mixture was stirred at room temperature for 1 hour. After completion, the reaction mixture was diluted by water, extracted with CH_2Cl_2, dried over anhydrous Na_2SO_4, concentrated and purified by column chromatography using a mixture of petroleum ether and ethyl acetate (5:1 v/v) as eluent gave **5a** as a white solid in 89% yield (340.3 mg).

Synthesis of compound 5b. To a solution of **5a** (144 mg, 0.3 mmol) in 12 mL CH_2Cl_2 at room temperature, was added 3 equiv of $NaHCO_3$ (76 mg, 0.9 mmol) and 2 equiv of Dess-Martin periodinane (254 mg, 0.6 mmol). After having been stirred for 5 h, the reaction was quenched via addition of saturated aqueous $NaHCO_3$ (10 mL) and $Na_2S_2O_3$ (10 mL), and diluted with CH_2Cl_2 (10 mL). The biphasic mixture was vigorously stirred at room temperature for 15 min and then the aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic extracts were dried over Na_2SO_4, filtered and concentrated and the crude product was purified by column chromatography using a mixture of petroleum ether and ethyl acetate (4:1 v/v) as eluent to give **5b** as a white solid in 89% yield (127.1 mg).

Synthesis of compound 5c. To a solution of CuI (38 mg, 0.2 mmol) in 1.0 mL dry THF at -10 ℃, was added $CH_2CHMgBr$ solution (1.0 M in THF, 400 uL). After having been stirred for 10 mins, **5b** (48 mg, 0.1 mmol) was added, then the mixture was stirred at room temperature for 2h. The reaction was quenched with saturated

aqueous NH_4Cl/25% aqueous NH_3 (9:1 v/v, 10 mL), then the aqueous phase was extracted with CH_2Cl_2 (2 × 10 mL). The combined organic extracts were dried over Na_2SO_4, filtered and concentrated and the crude product was purified by column chromatography using a mixture of petroleum ether and ethyl acetate (10:1 v/v) as eluent to give **5c** as a white solid in 82% yield (39.0 mg).

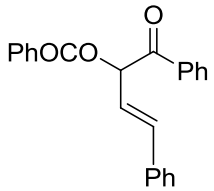
Synthesis of compound 5d. To a solution of **4l** (467 mg, 0.8 mmol) in dry CH_2Cl_2 (16 mL) at room temperature, was added *m*-chloroperoxybenzoic acid (413 mg, 2.4 mmol) and $NaHCO_3$ (202 mg, 2.4 mmol). The mixture was stirred at room temperature for 22 h, then the reaction was quenched via addition of saturated aqueous $NaHCO_3$ (10 mL) and $Na_2S_2O_3$ (10 mL) after completion, and diluted with CH_2Cl_2 (10 mL). The biphasic mixture was vigorously stirred at room temperature for 10 min and then the aqueous phase was extracted with CH_2Cl_2 (2 × 20 mL). The combined organic extracts were dried over Na_2SO_4, filtered and concentrated and the crude product was purified by column chromatography using a mixture of petroleum ether and ethyl acetate (10:1 v/v) as eluent to give **5d** as a white solid in 70% yield (334.9 mg).

Synthesis of compound 5e. To a solution of **5d** (100 mg, 0.167 mmol) in 1.67 mL dry DMF at room temperature, was added NaN_3 (108 mg, 1.67 mmol) and $SmCl_3$ (26 mg, 0.167 mmol). The mixture was stirred at 100 ℃ under argon atmosphere for 12 h. After cooled to room temperature, the mixture was diluted by ethyl acetate(20 mL), then washed by saturated aqueous NaCl (3 × 20 mL). The organic phase was dried over Na_2SO_4, filtered and concentrated and the crude product was purified by column chromatography using a mixture of petroleum ether and ethyl acetate (10:1 v/v) as eluent to give **5c** as a white solid in 56% yield (59.9 mg).

Synthesis of compound 5f. To a solution of **5d** (105 mg, 0.175 mmol) in 5 mL THF at room temperature, was added 5 drops $HClO_4$ (60% in water). After stirred at room temperature for 10 h, the reaction was quenched via addition of saturated aqueous $NaHCO_3$ (20 mL), then the aqueous phase was extracted with CH_2Cl_2 (2 × 20 mL). The combined organic extracts were dried over Na_2SO_4, filtered and concentrated and the crude product was purified by column chromatography using a mixture of

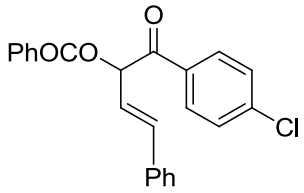
petroleum ether and ethyl acetate (5:1 v/v) as eluent to give **5f** as a white solid in 71% yield (76.5 mg).

V. Characterizations of New Compounds.



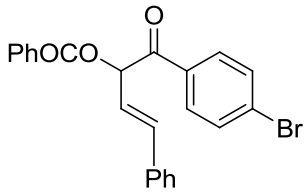
1a

(*E*)-1-oxo-1,4-diphenylbut-3-en-2-yl benzoate (1a): White solid, 141.9 mg, 83% yield. Mp 147–149 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15–8.07 (m, 4H), 7.59–7.55 (m, 2H), 7.49–7.39 (m, 6H), 7.32–7.23 (m, 3H), 6.95 (d, *J* = 15.9 Hz, 1H), 6.72 (d, *J* = 7.6 Hz, 1H), 6.46 (dd, *J* = 15.9 and 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.1, 166.0, 136.9, 135.7, 134.8, 133.8, 133.5, 130.1, 129.5, 128.93, 128.92, 128.83, 128.81, 128.6, 127.0, 121.5, 76.7; HRMS (ESI, m/z): calcd. for $C_{23}H_{19}O_3^+$ 343.1329, found 343.1329; IR (KBr thin film, cm^{-1}): ν 3062, 1718, 1698, 1271, 1109, 709.



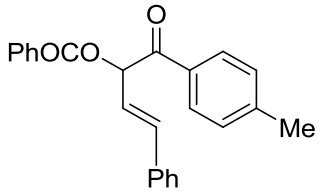
1i

(*E*)-1-(4-chlorophenyl)-1-oxo-4-phenylbut-3-en-2-yl benzoate (1i): White solid, 118.4 mg, 63% yield. Mp 142–143 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14–8.12 (m, 2H), 8.03–8.00 (m, 2H), 7.60–7.57 (m, 1H), 7.48–7.39 (m, 6H), 7.34–7.25 (m, 3H), 6.94 (d, *J* = 15.9 Hz, 1H), 6.64 (d, *J* = 7.7 Hz, 1H), 6.43 (dd, *J* = 15.9 and 7.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.1, 166.0, 140.3, 137.3, 135.5, 133.7, 133.1, 130.3, 130.1, 129.34, 129.30, 129.0, 128.9, 128.6, 127.0, 121.1, 76.8; HRMS (ESI, m/z): calcd. for $C_{23}H_{18}ClO_3^+$ 377.0939, found 377.0944; IR (KBr thin film, cm^{-1}): ν 3063, 1718, 1699, 1588, 1273, 1245, 1093, 709.



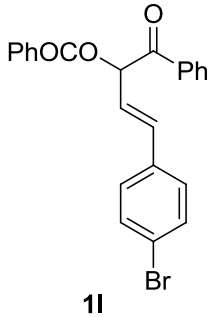
1j

(*E*)-1-(4-bromophenyl)-1-oxo-4-phenylbut-3-en-2-yl benzoate (1j): White solid, 184.8 mg, 88% yield. Mp 142–144 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13–8.11 (m, 2H), 7.94–7.92 (m, 2H), 7.63–7.57 (m, 3H), 7.48–7.39 (m, 4H), 7.34–7.25 (m, 3H), 6.94 (d, *J* = 15.9 Hz, 1H), 6.63 (d, *J* = 7.5 Hz, 1H), 6.43 (dd, *J* = 15.9 and 7.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.4, 166.0, 137.3, 135.6, 133.7, 133.6, 132.3, 130.4, 130.1, 129.4, 129.2, 129.0, 128.9, 128.7, 127.1, 121.1, 76.8; HRMS (ESI, m/z): calcd. for $C_{23}H_{18}BrO_3^+$ 421.0434, found 421.0435; IR (KBr thin film, cm^{-1}): ν3064, 1717, 1699, 1541, 1272, 713.



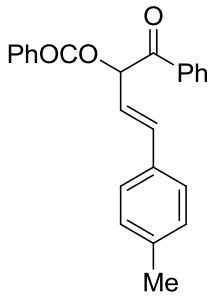
1k

(*E*)-1-oxo-4-phenyl-1-p-tolylbut-3-en-2-yl benzoate (1k): White solid, 124.6 mg, 70% yield. Mp 141–142 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15–8.13 (m, 2H), 7.99–7.97 (m, 2H), 7.58–7.55 (m, 1H), 7.46–7.38 (m, 4H), 7.32–7.24 (m, 5H), 6.94 (d, *J* = 16.0 Hz, 1H), 6.71 (d, *J* = 7.5 Hz, 1H), 6.46 (dd, *J* = 16.0 and 7.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.6, 165.9, 144.8, 136.7, 135.8, 133.5, 132.3, 130.1, 129.6, 129.1, 128.8, 128.6, 127.0, 121.7, 76.7, 21.9; HRMS (ESI, m/z): calcd. for $C_{24}H_{21}O_3^+$ 357.1485, found 357.1486; IR (KBr thin film, cm^{-1}): ν 3056, 1717, 1698, 1266, 739, 709.



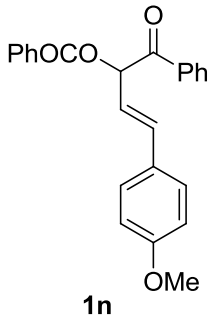
1l

(*E*)-4-(4-bromophenyl)-1-oxo-1-phenylbut-3-en-2-yl benzoate (1l): White solid, 184.8 mg, 88% yield. Mp 149–152 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14–8.12 (m, 2H), 8.07–8.05 (m, 2H), 7.61–7.57 (m, 2H), 7.51–7.43 (m, 6H), 7.27–7.25 (m, 2H), 6.88 (d, *J* = 16.0 Hz, 1H), 6.71 (d, *J* = 7.4 Hz, 1H), 6.45 (dd, *J* = 16.0 and 7.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.0, 165.9, 135.5, 134.8, 134.7, 134.0, 133.6, 132.0, 130.1, 129.5, 129.0, 128.9, 128.6, 128.5, 122.8, 122.3, 76.5; HRMS (ESI, m/z): calcd. for $C_{23}H_{18}BrO_3^+$ 421.0434, found 421.0435; IR (KBr thin film, cm^{-1}): ν 2922, 1718, 1699,1268, 1070, 709.



1m

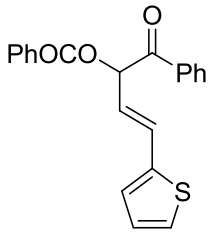
(*E*)-1-oxo-1-phenyl-4-p-tolylbut-3-en-2-yl benzoate (1m): White solid, 160.2 mg, 90% yield. Mp 154–156 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15–8.13 (m, 2H), 8.08–8.06 (m, 2H), 7.60–7.56 (m, 2H), 7.50–7.44 (m, 4H), 7.31–7.29 (m, 2H), 7.13–7.11 (m, 2H), 6.92 (d, *J* = 16.0 Hz, 1H), 6.70 (d, *J* = 7.6 Hz, 1H), 6.40 (dd, *J* = 16.0 and 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 166.0, 138.9, 137.0, 134.9, 133.8, 133.5, 133.0, 130.1, 129.6, 129.5, 128.90, 128.89, 128.5, 126.9, 120.3, 76.9, 21.4; HRMS (ESI, m/z): calcd. for $C_{24}H_{21}O_3^+$ 357.1485, found 357.1485; IR (KBr thin film, cm^{-1}): ν 3059, 1718, 1698, 1449, 1272,1109, 711.



1n

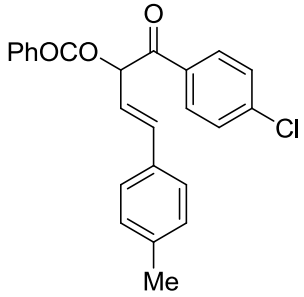
(*E*)-4-(4-methoxyphenyl)-1-oxo-1-phenylbut-3-en-2-yl benzoate (1n): White solid, 120.9 mg, 65% yield. Mp 116–117 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14–8.13 (m, 2H), 8.09–8.07 (m, 2H), 7.59–7.56 (m, 2H), 7.50–7.43 (m, 4H), 7.35–7.33 (m, 2H),

6.91–6.84 (m, 3H), 6.69 (d, *J* = 7.8 Hz, 1H), 6.31 (dd, *J* = 15.8 and 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 166.1, 160.2, 136.8, 134.9, 133.8, 133.5, 130.1, 129.6, 128.95, 128.92, 128.6, 128.5, 128.4, 119.1, 114.2, 77.0, 55.5; HRMS (ESI, m/z): calcd. for $C_{24}H_{21}O_4^+$ 373.1434, found 373.1433; IR (KBr thin film, cm^{-1}): ν 3064, 1718, 1698, 1511, 1274, 1252,710.



1o

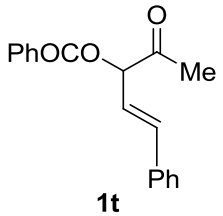
(*E*)-1-oxo-1-phenyl-4-(thiophen-2-yl)but-3-en-2-yl benzoate (1o): White solid, 132.2 mg, 76% yield. Mp 124–126 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14–8.12 (m, 2H), 8.07–8.05 (m, 2H), 7.56–7.53 (m, 2H), 7.47–7.41 (m, 4H), 7.18–7.17 (m, 1H), 7.08–7.01 (m, 2H), 6.93–6.92 (m, 1H), 6.68 (d, *J* = 7.6 Hz, 1H), 6.28 (dd, *J* = 15.7 and 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.8, 165.9, 140.6, 134.7, 133.8, 133.5, 130.0, 129.9, 129.4, 128.9, 128.8, 128.5, 127.7, 127.6, 125.9, 120.4, 76.3; HRMS (ESI, m/z): calcd. for $C_{21}H_{17}O_3S^+$ 349.0893, found 349.0895; IR (KBr thin film, cm^{-1}): ν 3066, 1719, 1698, 1450, 1275, 1109, 956, 708.



1p

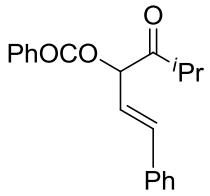
(*E*)-1-(4-chlorophenyl)-1-oxo-4-p-tolylbut-3-en-2-yl benzoate (1p): White solid, 152.1 mg, 78% yield. Mp 153–155 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13–8.11 (m, 2H), 8.02–8.00 (m, 2H), 7.60–7.56 (m, 1H), 7.47–7.43 (m, 4H), 7.30–7.29 (m, 2H), 7.13–7.12 (m, 2H), 6.90 (d, *J* = 15.9 Hz, 1H), 6.68 (d, *J* = 7.7 Hz, 1H), 6.37 (dd, *J* = 15.9 and 7.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.2, 166.0, 140.3, 139.1, 137.4, 133.6, 133.2, 132.8, 130.3, 130.1, 129.6, 129.4, 129.3, 128.6, 127.0, 120.0,

76.9, 21.4; HRMS (ESI, m/z): calcd. for $C_{24}H_{20}ClO_3^+$ 391.1096, found 391.1098; IR (KBr thin film, cm^{-1}): ν 3065, 1718, 1698, 1273, 1245, 1093,709.



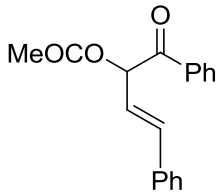
1t

(*E*)-1-(4-chlorophenyl)-1-oxo-4-p-tolylbut-3-en-2-yl benzoate (1t): White solid, 65.8 mg, 47% yield. Mp 43–45 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14–8.12 (m, 2H), 7.63–7.59 (m, 1H), 7.50–7.43 (m, 4H), 7.38–7.30 (m, 3H), 6.91 (d, *J* = 15.9 Hz, 1H), 6.31 (dd, *J* = 15.9 and 7.5 Hz, 1H), 5.86 (d, *J* = 7.5 Hz, 1H), 2.30 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.7, 165.9, 136.3, 135.7, 133.7, 130.1, 129.4, 128.91, 128.89, 128.7, 127.0, 120.8, 80.4, 26.3; HRMS (ESI, m/z): calcd. for $C_{18}H_{17}O_3^+$ 281.1172, found 281.1166; IR (KBr thin film, cm^{-1}): ν 1720, 1272, 1111, 746, 712, 693.



1u

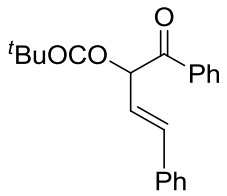
(*E*)-5-methyl-4-oxo-1-phenylhex-1-en-3-yl benzoate (1u): Yellow oil, 117.0 mg, 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14–8.11 (m, 2H), 7.60–7.56 (m, 1H), 7.48–7.42 (m, 4H), 7.37–7.30 (m, 3H), 6.91 (d, *J* = 15.9 Hz, 1H), 6.31 (dd, *J* = 15.9 and 7.8 Hz, 1H), 6.01 (dd, *J* = 7.8 and 1.1 Hz, 1H), 3.03–2.96 (m, 1H), 1.26 (d, *J* = 7.0 Hz, 3H), 1.11 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.4, 165.8, 136.5, 135.7, 133.5, 130.0, 129.6, 128.9, 128.8, 128.6, 127.0, 121.2, 79.0, 37.4, 19.1, 18.1; HRMS (ESI, m/z): calcd. for $C_{20}H_{21}O_3^+$ 309.1485, found 309.1488; IR (KBr thin film, cm^{-1}): ν 2926, 2854, 1718, 1456, 1269, 1108, 710.



1v

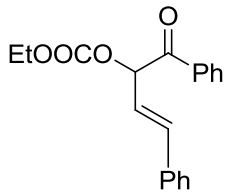
(*E*)-1-oxo-1,4-diphenylbut-3-en-2-yl acetate (1v): Yellow oil, 105.0 mg, 75% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02–8.00 (m, 2H), 7.59–7.55 (m, 1H), 7.49–7.44 (m, 2H), 7.37–7.24 (m, 5H), 6.86 (d, *J* = 15.9 Hz, 1H), 6.49 (d, *J* = 7.6 Hz, 1H), 6.31 (d, *J* = 15.9 and 7.6 Hz, 1H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 170.4, 136.8, 135.7, 134.8, 133.8, 128.91, 128.86, 128.82, 128.79, 127.0, 121.3, 76.3, 20.9; HRMS (ESI, m/z): calcd. for $C_{18}H_{17}O_3^+$ 281.1172, found 281.1171; IR (KBr thin film, cm^{-1}): ν 3064, 2926, 1735, 1699, 1450, 1230, 699.



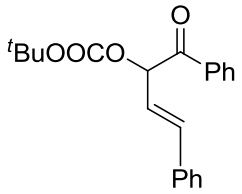
1w

(*E*)-1-oxo-1,4-diphenylbut-3-en-2-yl pivalate (1w): White solid, 112.7 mg, 70% yield. Mp 64–66 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00–8.00 (m, 2H), 7.59–7.55 (m, 1H), 7.48–7.44 (m, 2H), 7.38–7.36 (m, 2H), 7.33–7.27 (m, 3H), 6.84 (d, *J* = 15.7 Hz, 1H), 6.42 (d, *J* = 7.4 Hz, 1H), 6.33 (d, *J* = 15.7 and 7.4 Hz, 1H), 1.27 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.6, 177.9, 136.2, 135.9, 135.0, 133.7, 128.9, 128.8, 128.7, 127.0, 121.6, 76.3, 38.9, 27.2; HRMS (ESI, m/z): calcd. for $C_{21}H_{23}O_3^+$ 323.1642, found 323.1643; IR (KBr thin film, cm^{-1}): ν 2974, 1733, 1717, 1699, 1541, 1148.



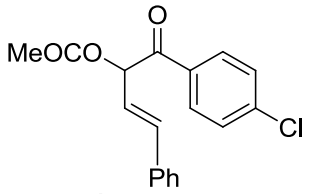
1x

(*E*)-ethyl 1-oxo-1,4-diphenylbut-3-en-2-yl carbonate (1x): White solid, 97.7 mg, 63% yield. Mp 68–70 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03–8.01 (m, 2H), 7.60–7.57 (m, 1H), 7.50–7.46 (m, 2H), 7.37–7.35 (m, 2H), 7.32–7.27 (m, 3H), 6.90 (d, *J* = 15.6 Hz, 1H), 6.39–6.28 (m, 2H), 4.23 (q, *J* = 7.1 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.9, 154.5, 137.1, 135.6, 134.6, 133.9, 129.0, 128.93, 128.90, 128.8, 127.0, 120.8, 79.0, 64.9, 14.3; HRMS (ESI, m/z): calcd. for $C_{19}H_{19}O_4^+$ 311.1278, found 311.1278; IR (KBr thin film, cm^{-1}): ν 2926, 1747, 1699, 1449, 1373, 1268, 699.



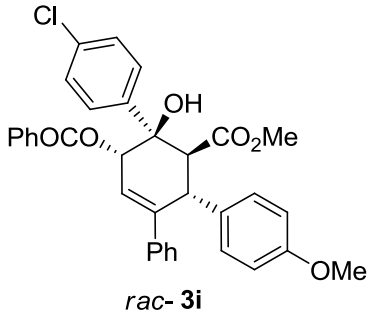
1y

(*E*)-tert-butyl 1-oxo-1,4-diphenylbut-3-en-2-yl carbonate (1y): Yellow oil, 82.8 mg, 49% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03–8.00 (m, 2H), 7.59–7.55 (m, 1H), 7.49–7.45 (m, 2H), 7.36–7.24 (m, 5H), 6.90–6.85 (m, 1H), 6.31–6.28 (m, 2H), 1.47 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.4, 152.8, 136.8, 135.7, 134.7, 133.8, 128.9, 128.8, 127.0, 121.0, 83.4, 78.6, 27.8; HRMS (ESI, m/z): calcd. for $C_{21}H_{23}O_4^+$ 339.1591, found 339.1596; IR (KBr thin film, cm^{-1}): ν 3064, 2925, 1717, 1698, 1685, 1596, 1559, 1450, 697.



1z

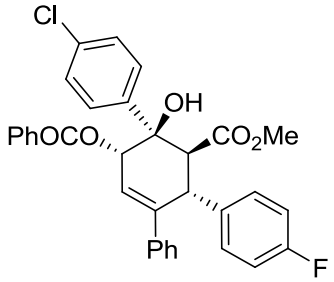
(*E*)-1-(4-chlorophenyl)-1-oxo-4-phenylbut-3-en-2-yl acetate (1z): Yellow oil, 128.7 mg, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.8 Hz, 2H), 7.45 (d, *J* = 7.9 Hz, 2H), 7.38–7.26 (m, 5H), 6.85 (d, *J* = 15.9 Hz, 1H), 6.41 (d, *J* = 7.7 Hz, 1H), 6.28 (dd, *J* = 15.9 and 7.7 Hz, 1H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.2, 170.4, 140.4, 137.2, 135.5, 133.1, 130.3, 129.3, 129.0, 128.9, 127.0, 120.9, 76.3, 20.9; HRMS (ESI, m/z): calcd. for $C_{16}H_{10}O_2H^+$ 235.0754, found 235.0754; IR (KBr thin film, cm^{-1}): ν 3064, 1735, 1698, 1684, 1229, 1092.



rac- **3i**

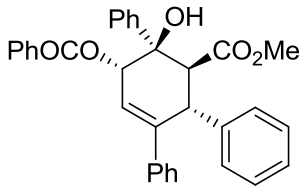
(1*S*,4*R*,5*S*,6*R*)-6-(4-chlorophenyl)-6-hydroxy-5-(methoxycarbonyl)-4-(4-methoxy phenyl)-3-phenylcyclohex-2-enyl benzoate (*rac*-3i): Yellow oil, 82.9 mg, 73% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92–7.90 (m, 2H), 7.58–7.56 (m, 3H), 7.46–7.42 (m, 2H), 7.21–7.08 (m, 7H), 7.02–6.99 (m, 2H), 6.72–6.70 (m, 2H), 6.37 (dd, *J* = 5.6 and 1.8 Hz, 1H), 5.47 (d, *J* = 5.7 Hz, 1H), 4.50 (d, *J* = 10.0 Hz, 1H), 4.30 (s, 1H), 3.77 (d, *J* = 10.2 Hz, 1H), 3.71 (s, 3H), 3.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.9, 164.8, 158.4, 145.1, 141.3, 139.9, 134.0, 133.3, 132.9, 129.8, 129.6, 129.5, 128.6, 128.2, 128.1, 128.0, 127.4, 127.2, 122.6, 114.1, 74.4, 71.4, 55.2, 53.5, 52.0, 45.9; HRMS (ESI, m/z): calcd. for $C_{34}H_{30}ClO_6^+$ 569.1725, found 569.1728; IR (KBr thin film, cm^{-1}): ν 3497, 2926, 1719, 1511, 1261, 1175, 1095, 710.



rac- **3j**

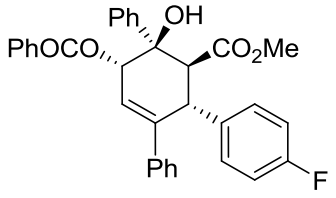
(1*S*,4*R*,5*S*,6*R*)-6-(4-chlorophenyl)-4-(4-fluorophenyl)-6-hydroxy-5-(methoxycarbonyl)-3-phenylcyclohex-2-enyl benzoate (*rac*-3j): Yellow oil, 81.2 mg, 73% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91–7.89 (m, 2H), 7.59–7.55 (m, 3H), 7.46–7.43 (m, 2H), 7.20–7.04 (m, 9H), 6.89–6.85 (m, 2H), 6.39 (dd, *J* = 5.7 and 2.1 Hz, 1H), 5.47 (d, *J* = 5.8 Hz, 1H), 4.55 (d, *J* = 10.1 Hz, 1H), 4.28 (s, 1H), 3.75 (d, *J* = 10.3 Hz, 1H), 3.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.6, 164.8, 161.6 (d, *J* = 244.1 Hz), 144.5, 141.1, 139.6, 136.7 (d, *J* = 3.3 Hz), 134.0, 133.4, 130.0 (d, *J* = 8.0 Hz), 129.7, 129.6, 128.6, 128.2, 128.1, 128.0, 127.6, 127.1, 122.9, 115.7 (d, *J* = 21.4 Hz), 74.4, 71.3, 53.4, 52.0, 46.0; HRMS (ESI, m/z): calcd. for $C_{33}H_{27}ClFO_5^+$ 557.1526, found 557.1524; IR (KBr thin film, cm^{-1}): ν 3504, 2927, 1720, 1509, 1262, 1095, 711.



4a

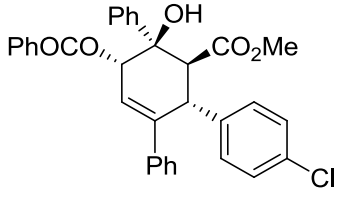
(1*S*,4*R*,5*S*,6*R*)-6-hydroxy-5-(methoxycarbonyl)-3,4,6-triphenylcyclohex-2-enyl benzoate (4a): Yellow oil, 80.6 mg, 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ

7.91–7.89 (m, 2H), 7.64–7.62 (m, 2H), 7.57–7.53 (m, 1H), 7.44–7.40 (m, 2H), 7.23–7.07 (m, 13H), 6.42 (dd, *J* = 5.7 and 2.0 Hz, 1H), 5.51 (d, *J* = 5.7 Hz, 1H), 4.57 (d, *J* = 10.2 Hz, 1H), 4.29 (s, 1H), 3.85 (d, *J* = 10.3 Hz, 1H), 3.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.0, 164.9, 144.8, 142.7, 141.2, 139.9, 133.2, 130.0, 129.7, 128.7, 128.6, 128.5, 128.1, 128.0, 127.4, 127.2, 127.0, 126.5, 123.0, 74.7, 71.7, 53.5, 51.8, 46.9; HRMS (ESI, m/z): calcd. for $C_{33}H_{29}O_5^+$ 505.2010, found 505.1995; IR (KBr thin film, cm^{-1}): ν 3503, 3060, 3028, 2952, 1720, 1264, 1172, 1105, 701; $[\alpha]^{29}_D$: 9.0 (*c* 0.7, $CHCl_3$); HPLC analysis: 93% ee (Chiralcel AD-H, 10:90 ^{i}PrOH/hexane, 1 mL/min, 254 nm), R_t (major) = 8.7 min, R_t (minor) = 18.8 min.



4b

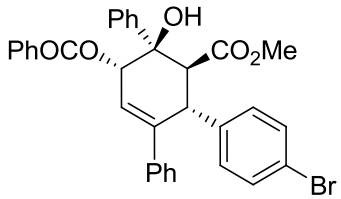
(1*S*,4*R*,5*S*,6*R*)-4-(4-fluorophenyl)-6-hydroxy-5-(methoxycarbonyl)-3,6-diphenylcyclohex-2-enyl benzoate (4b): Yellow oil, 66.8 mg, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90–7.88 (m, 2H), 7.63–7.53 (m, 3H), 7.44–7.39 (m, 2H), 7.22–7.05 (m, 10H), 6.89–6.85 (m, 2H), 6.41 (dd, *J* = 5.7 and 2.1 Hz, 1H), 5.50 (d, *J* = 5.7 Hz, 1H), 4.57 (d, *J* = 10.3 Hz, 1H), 4.24 (s, 1H), 3.85 (d, *J* = 10.4 Hz, 1H), 3.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.9, 164.9, 162.9, 160.4, 144.6, 142.5, 139.8, 137.0 (d, *J* = 3.2 Hz), 133.2, 130.1, 130.04, 129.97, 129.7, 128.5, 128.1, 127.5, 127.2, 126.5, 123.2, 115.7 (d, *J* = 21.3 Hz), 77.4, 73.1 (d, *J* = 306.7 Hz), 53.5, 51.9, 46.1; HRMS (ESI, m/z): calcd. for $C_{33}H_{27}FO_5Na+$ 545.1735, found 545.1734; IR (KBr thin film, cm^{-1}): ν 3502, 3061, 2954, 2926, 1720, 1509, 1264, 1096, 701; $[\alpha]^{31}_D$: 11.7 (*c* 1.2, $CHCl_3$); HPLC analysis: 89% ee (Chiralcel AD-H, 10:90 ^{i}PrOH/hexane, 1 mL/min, 254 nm), R_t (major) = 9.4 min, R_t (minor) = 12.7 min.



4c

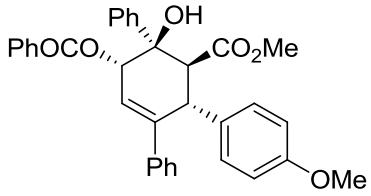
(1*S*,4*R*,5*S*,6*R*)-4-(4-chlorophenyl)-6-hydroxy-5-(methoxycarbonyl)-3,6-diphenylc

yclohex-2-enyl benzoate (4c): Yellow oil, 86.1 mg, 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83–7.81 (m, 2H), 7.56–7.47 (m, 3H), 7.37–7.33 (m, 2H), 7.19–6.96 (m, 12H), 6.35 (dd, *J* = 5.7 and 2.0 Hz, 1H), 5.42 (d, *J* = 5.6 Hz, 1H), 4.49 (d, *J* = 10.4 Hz, 1H), 4.16 (s, 1H), 3.72 (d, *J* = 10.3 Hz, 1H), 3.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.8, 164.9, 144.3, 142.4, 139.9, 139.7, 133.2, 132.7, 130.0, 129.9, 129.7, 129.0, 128.5, 128.2, 128.1, 127.6, 127.1, 126.5, 123.4, 74.6, 71.6, 53.4, 52.0 46.3; HRMS (ESI, m/z): calcd. for $C_{33}H_{27}ClO_5Na^+$ 561.1439, found 561.1440; IR (KBr thin film, cm^{-1}): ν 3503, 2925, 1719, 1262, 1094, 701; $[\alpha]^{32}_D$: 17.1 (*c* 1.9, $CHCl_3$); HPLC analysis: 91% ee (Chiralcel AD-H, 10:90 ^{i}PrOH/hexane, 1 mL/min, 254 nm), R_t (major) = 6.5 min, R_t (minor) = 7.4 min.



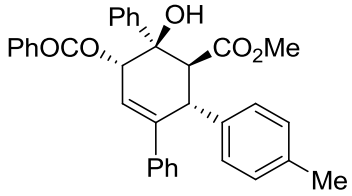
4d

(1*S*,4*R*,5*S*,6*R*)-4-(4-bromophenyl)-6-hydroxy-5-(methoxycarbonyl)-3,6-diphenylc yclohex-2-enyl benzoate (4d): Yellow solid, 74.5 mg, 64% yield. Mp 62–63 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90–7.88 (m, 2H), 7.63–7.53 (m, 3H), 7.44–7.36 (m, 2H), 7.31–7.29 (m, 2H), 7.25–7.12 (m, 8H), 7.00–6.84 (m, 2H), 6.42 (d, *J* = 4.5 Hz, 1H), 5.50 (d, *J* = 5.3 Hz, 1H), 4.55 (d, *J* = 9.5 Hz, 1H), 4.24 (s, 1H), 3.79 (d, *J* = 10.2 Hz, 1H), 3.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.8, 164.9, 144.1, 142.4, 140.4, 139.6, 133.2, 131.9, 130.3, 129.9, 129.7, 128.5, 128.2, 128.1, 127.6, 127.1, 126.4, 123.4, 120.8, 74.6, 71.5, 53.3, 52.0 46.3; HRMS (ESI, m/z): calcd. for $C_{33}H_{27}BrO_5Na^+$ 605.0934, found 605.0934; IR (KBr thin film, cm^{-1}): ν 2923, 2853, 1718, 1448, 1095, 1262, 700; $[\alpha]^{29}_D$: 8.7 (*c* 4.2, $CHCl_3$); HPLC analysis: 90% ee (Chiralcel AD-H, 10:90 ^{i}PrOH/hexane, 1 mL/min, 254 nm), R_t (major) = 6.7 min, R_t (minor) = 7.6 min.



4e

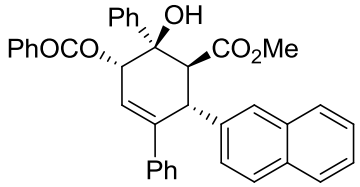
(1*S*,4*R*,5*S*,6*R*)-6-hydroxy-5-(methoxycarbonyl)-4-(4-methoxyphenyl)-3,6-dipheny lcyclohex-2-enyl benzoate (4e): Yellow oil, 64.1 mg, 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91–7.89 (m, 2H), 7.64–7.53 (m, 3H), 7.44–7.40 (m, 2H), 7.22–7.01 (m, 10H), 6.72–6.70 (m, 2H), 6.39 (dd, *J* = 5.6 and 2.0 Hz, 1H), 5.49 (d, *J* = 5.6 Hz, 1H), 4.52 (d, *J* = 10.1 Hz, 1H), 4.27 (s, 1H), 3.82 (d, *J* = 10.3 Hz, 1H), 3.71 (s, 3H), 3.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 164.9, 158.3, 145.1, 142.7, 140.0, 133.1, 130.0, 129.7, 129.5, 128.5, 128.1, 128.0, 127.3, 127.2, 126.5, 122.8, 114.1, 74.7, 71.7, 55.2, 53.6, 51.9 46.0; HRMS (ESI, m/z): calcd. for $C_{34}H_{30}O_6Na^+$ 557.1935, found 557.1935; IR (KBr thin film, cm^{-1}): ν 3502, 2928, 1719, 1511, 1261, 701; $[\alpha]^{31}_D$: 8.5 (*c* 2.5, $CHCl_3$); HPLC analysis: 97% ee (Chiralcel AD-H, 10:90 ^{i}PrOH/hexane, 1 mL/min, 254 nm), R_t (major) = 10.8 min, R_t (minor) = 14.3 min.



4f

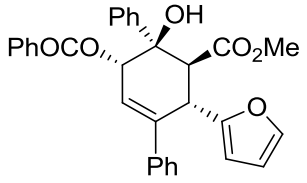
(1*S*,4*R*,5*S*,6*R*)-6-hydroxy-5-(methoxycarbonyl)-3,6-diphenyl-4-p-tolylcyclohex-2-enyl benzoate (4f): Yellow oil, 59.1 mg, 57% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84–7.82 (m, 2H), 7.56–7.46 (m, 3H), 7.36–7.32 (m, 2H), 7.18–6.99 (m, 8H), 6.93–6.89 (m, 4H), 6.34 (dd, *J* = 5.7 and 1.9 Hz, 1H), 5.42 (d, *J* = 5.7 Hz, 1H), 4.46 (d, *J* = 9.7 Hz, 1H), 4.21 (s, 1H), 3.76 (d, *J* = 10.2 Hz, 1H), 3.27 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 164.9, 145.0, 142.7, 140.0, 138.1, 136.4, 133.1, 130.1, 129.7, 129.5, 128.5, 128.4, 128.1, 128.0, 127.4, 127.2, 126.5, 122.9, 74.6, 71.7, 53.6, 51.9, 46.4, 21.2; HRMS (ESI, m/z): calcd. for $C_{34}H_{30}O_5Na^+$ 541.1986, found 541.1986; IR (KBr thin film, cm^{-1}): ν 2925, 1719, 1263, 1171, 1096, 752, 700; $[\alpha]^{30}_D$: 4.9 (*c* 1.4, $CHCl_3$); HPLC analysis: 97% ee (Chiralcel AD-H, 10:90 ^{i}PrOH/hexane, 1

mL/min, 254 nm), R_t (major) = 7.4 min, R_t (minor) = 10.8 min.



4g

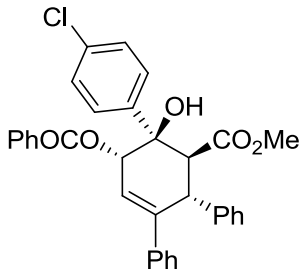
(1*S*,4*R*,5*S*,6*R*)-6-hydroxy-5-(methoxycarbonyl)-4-(naphthalen-2-yl)-3,6-diphenylcyclohex-2-enyl benzoate (4g): Yellow oil, 70.9 mg, 64% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94–7.92 (m, 2H), 7.71–7.63 (m, 5H), 7.58–7.54 (m, 2H), 7.45–7.39 (m, 4H), 7.28–7.15 (m, 6H), 7.09–7.00 (m, 3H), 6.48 (d, *J* = 4.0 Hz, 1H), 5.54 (d, *J* = 5.6 Hz, 1H), 4.76 (d, *J* = 10.1 Hz, 1H), 4.35 (s, 1H), 3.95 (d, *J* = 10.2 Hz, 1H), 3.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 165.0, 144.7, 142.6, 139.8, 138.7, 133.5, 133.2, 132.4, 130.0, 129.7, 129.3, 129.1, 128.8, 128.5, 128.1, 128.0, 127.8, 127.7, 127.4, 127.2, 126.5, 126.2, 126.0, 125.8, 123.2, 74.7, 71.7, 53.3, 51.9, 47.0; HRMS (ESI, m/z): calcd. for $C_{37}H_{30}O_5Na^+$ 577.1986, found 577.1981; IR (KBr thin film, cm^{-1}): ν 3504, 2925, 1719, 1263, 1096, 1068,752, 700; $[\alpha]^{30}_D$: -22.2 (*c* 2./1, $CHCl_3$); HPLC analysis: 99% ee (Chiralcel AD-H, 10:90 ^{i}PrOH/hexane, 1 mL/min, 254 nm), R_t (major) = 7.7 min, R_t (minor) = 10.1 min.



4h

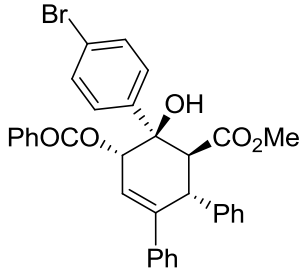
(1*S*,4*S*,5*S*,6*R*)-4-(furan-2-yl)-6-hydroxy-5-(methoxycarbonyl)-3,6-diphenylcyclohex-2-enyl benzoate (4h): Yellow oil, 42.5 mg, 43% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89–7.87 (m, 2H), 7.65–7.64 (m, 2H), 7.55–7.51 (m, 1H), 7.42–7.38 (m, 2H), 7.25–7.16 (m, 9H), 6.28 (dd, *J* = 5.4 and 2.3 Hz, 1H), 6.13 (s, 1H), 5.99 (d, *J* = 2.8 Hz, 1H), 5.47 (d, *J* = 5.4 Hz, 1H), 4.68 (d, *J* = 10.7 Hz, 1H), 4.25 (s, 1H), 4.09 (d, *J* = 10.7 Hz, 1H), 3.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.8, 164.9, 152.9, 142.9, 142.5, 142.1, 139.7, 133.1, 129.9, 129.7, 128.4, 128.12, 128.09, 128.0, 127.6, 126.9, 126.5, 122.7, 110.3, 108.6, 74.6, 71.4, 52.1, 50.0, 40.6; HRMS (ESI, m/z): calcd. for $C_{31}H_{26}O_6Na^+$ 517.1622, found 517.1627; IR (KBr thin film, cm^{-1}): ν 3503, 2926, 1719,

1262, 1096, 701; $[\alpha]^{29}_{D}$: 13.6 (*c* 1.0, $CHCl_3$); HPLC analysis: 73% ee (Chiralcel AD-H, 10:90 ^{i}PrOH/hexane, 1 mL/min, 254 nm), R_t (major) = 9.5 min, R_t (minor) = 21.0 min.



4i

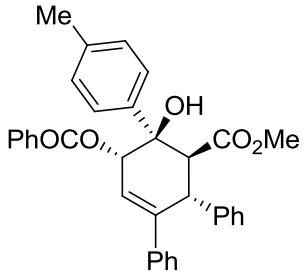
(1*S*,4*R*,5*S*,6*R*)-6-(4-chlorophenyl)-6-hydroxy-5-(methoxycarbonyl)-3,4-diphenylcyclohex-2-enyl benzoate (4i): Yellow oil, 81.8 mg, 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92–7.91 (m, 2H), 7.60–7.56 (m, 3H), 7.47–7.43 (m, 2H), 7.22–7.07 (m, 12H), 6.40 (dd, *J* = 5.7 and 2.0 Hz, 1H), 5.48 (d, *J* = 5.6 Hz, 1H), 4.55 (d, *J* = 10.0 Hz, 1H), 4.32 (s, 1H), 3.79 (d, *J* = 10.3 Hz, 1H), 3.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.9, 164.9, 144.8, 141.3, 141.0, 139.8, 134.0, 133.3, 129.8, 129.7, 128.8, 128.6, 128.5, 128.2, 128.1, 127.5, 127.2, 127.1, 122.7, 74.4, 71.4, 53.4, 52.0, 46.8; HRMS (ESI, m/z): calcd. for $C_{33}H_2ClO_5Na^+$ 561.1439, found 561.1443; IR (KBr thin film, cm^{-1}): ν 3497, 2924, 1721, 1262, 1095, 709; $[\alpha]^{31}_{D}$: 3.8 (*c* 2.1, $CHCl_3$); HPLC analysis: 81% ee (Chiralcel AD-H, 10:90 ^{i}PrOH/hexane, 1 mL/min, 254 nm), R_t (major) = 6.5 min, R_t (minor) = 15.3 min.



4j

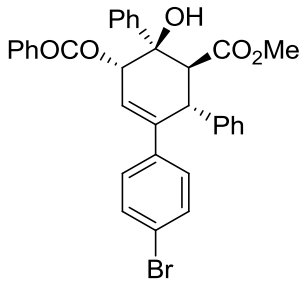
(1*S*,4*R*,5*S*,6*R*)-6-(4-bromophenyl)-6-hydroxy-5-(methoxycarbonyl)-3,4-diphenylcyclohex-2-enyl benzoate (4j): Yellow oil, 89.6 mg, 77% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92–7.90 (m, 2H), 7.59–7.50 (m, 3H), 7.46–7.42 (m, 2H), 7.34–7.32 (m, 2H), 7.22–7.06 (m, 10H), 6.40 (d, *J* = 5.4 Hz, 1H), 5.48 (d, *J* = 5.6 Hz, 1H), 4.54 (d, *J* = 10.1 Hz, 1H), 4.32 (s, 1H), 3.79 (d, *J* = 10.2 Hz, 1H), 3.33 (s, 3H); ^{13}C NMR (100

MHz, $CDCl_3$) δ 175.8, 164.8, 144.8, 141.9, 141.0, 139.8, 133.3, 131.2, 129.9, 129.6, 128.8, 128.6, 128.5, 128.4, 128.1, 127.5, 127.2, 127.1, 122.7, 122.3, 74.5, 71.4, 53.4, 52.0, 46.9; HRMS (ESI, m/z): calcd. for $C_{33}H_{27}BrO_5Na^+$ 605.0934, found 605.0935; IR (KBr thin film, cm^{-1}): ν 3497, 2954, 2927, 1720, 1262, 1095, 710; $[\alpha]^{30}_D$: 7.1 (*c* 2.5, $CHCl_3$); HPLC analysis: 83% ee (Chiralcel AD-H, 10:90 ^{i}PrOH/hexane, 1 mL/min, 254 nm), R_t (major) = 7.2 min, R_t (minor) = 17.6 min.



4k

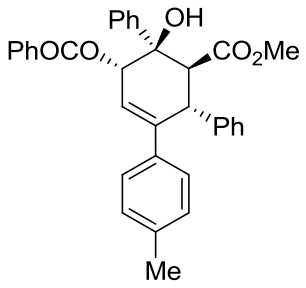
(1*S*,4*R*,5*S*,6*R*)-6-hydroxy-5-(methoxycarbonyl)-3,4-diphenyl-6-p-tolylcyclohex-2-enyl benzoate (4k): Yellow oil, 57.0 mg, 55% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93–7.91 (m, 2H), 7.57–7.49 (m, 3H), 7.44–7.41 (m, 2H), 7.22–7.00 (m, 12H), 6.42 (d, *J* = 5.2 Hz, 1H), 5.47 (d, *J* = 5.7 Hz, 1H), 4.55 (d, *J* = 10.1 Hz, 1H), 4.22 (s, 1H), 3.83 (d, *J* = 10.3 Hz, 1H), 3.33 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.0, 165.0, 144.8, 141.3, 140.0, 139.7, 137.6, 133.1, 130.2, 129.7, 128.8, 128.7, 128.6, 128.5, 128.0, 127.4, 127.2, 126.9, 126.4, 123.1, 74.5, 71.8, 53.6, 51.8, 47.0, 21.1; HRMS (ESI, m/z): calcd. for $C_{34}H_{31}O_5^+$ 519.2166, found 519.2177; IR (KBr thin film, cm^{-1}): ν 3504, 2925, 1719, 1264, 1106,711; $[\alpha]^{31}_D$: -8.5 (*c* 1.7, $CHCl_3$); HPLC analysis: 91% ee (Chiralcel AD-H, 10:90 ^{i}PrOH/hexane, 1 mL/min, 254 nm), R_t (major) = 6.2 min, R_t (minor) = 13.0 min.



4l

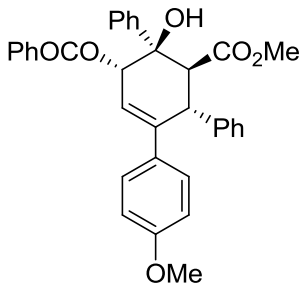
(1*S*,4*R*,5*S*,6*R*)-3-(4-bromophenyl)-6-hydroxy-5-(methoxycarbonyl)-4,6-diphenylc

yclohex-2-enyl benzoate (4l): Yellow oil, 89.6 mg, 77% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90–7.88 (m, 2H), 7.63–7.61 (m, 2H), 7.56–7.53 (m, 1H), 7.43–7.39 (m, 2H), 7.25–7.08 (m, 12H), 6.42 (d, *J* = 5.6 Hz, 1H), 5.48 (d, *J* = 5.7 Hz, 1H), 4.51 (d, *J* = 10.2 Hz, 1H), 4.28 (s, 1H), 3.84 (d, *J* = 10.3 Hz, 1H), 3.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.9, 164.9, 143.8, 142.5, 140.8, 138.9, 133.2, 131.2, 129.9, 129.7, 128.9, 128.8, 128.53, 128.50, 128.1, 127.2, 126.5, 123.6, 121.4, 74.6, 71.5, 53.4, 51.9, 46.8; HRMS (ESI, m/z): calcd. for $C_{33}H_{28}BrO_5^+$ 605.0934, found 605.0933; IR (KBr thin film, cm^{-1}): ν 3503, 3062, 3028, 2952, 1717, 1316, 1263, 704; $[\alpha]^{31}_D$: -28.2 (*c* 1.3, $CHCl_3$); HPLC analysis: 95% ee (Chiralcel AD-H, 10:90 ^{i}PrOH/hexane, 1 mL/min, 254 nm), R_t (major) = 11.2 min, R_t (minor) = 14.6 min.



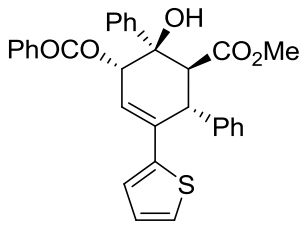
4m

(1*S*,4*R*,5*S*,6*R*)-6-hydroxy-5-(methoxycarbonyl)-4,6-diphenyl-3-p-tolylcyclohex-2-enyl benzoate (4m): Yellow oil, 76.7 mg, 74% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91–7.89 (m, 2H), 7.64–7.62 (m, 2H), 7.56–7.52 (m, 1H), 7.43–7.39 (m, 2H), 7.25–7.09 (m, 10H), 6.92–6.90 (m, 2H), 6.39 (dd, *J* = 7.8 and 2.1 Hz, 1H), 5.50 (d, *J* = 5.8 Hz, 1H), 4.55 (d, *J* = 10.3 Hz, 1H), 4.27 (s, 1H), 3.84 (d, *J* = 10.3 Hz, 1H), 3.32 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 164.9, 144.6, 142.7, 141.5, 137.1, 137.0, 133.1, 130.1, 129.7, 128.8, 128.7, 128.6, 128.5, 128.1, 128.0, 127.0, 126.9, 126.5, 122.3, 74.6, 71.8, 53.6, 51.8, 46.9, 21.2; HRMS (ESI, m/z): calcd. for $C_{34}H_{30}O_5Na^+$ 541.1986, found 541.1986; IR (KBr thin film, cm^{-1}): ν 3503, 3027, 2952, 1720, 1451, 1263, 1105, 703; $[\alpha]^{30}_D$: -13.7 (*c* 1.9, $CHCl_3$); HPLC analysis: 87% ee (Chiralcel AD-H, 10:90 ^{i}PrOH/hexane, 1 mL/min, 254 nm), R_t (major) = 9.1 min, R_t (minor) = 14.3 min.



4n

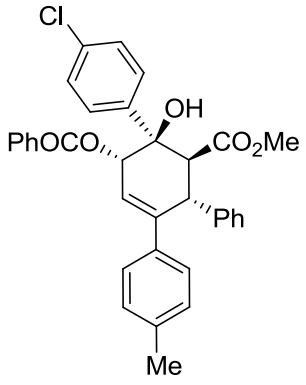
(1*S*,4*R*,5*S*,6*R*)-6-hydroxy-5-(methoxycarbonyl)-3-(4-methoxyphenyl)-4,6-dipheny lcyclohex-2-enyl benzoate (4n): Yellow oil, 70.5 mg, 66% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91–7.88 (m, 2H), 7.64–7.62 (m, 2H), 7.54–7.52 (m, 1H), 7.43–7.39 (m, 2H), 7.22–7.10 (m, 10H), 6.66–6.63 (m, 2H), 6.37 (dd, *J* = 5.8 and 2.1 Hz, 1H), 5.49 (d, *J* = 5.8 Hz, 1H), 4.52 (d, *J* = 10.2 Hz, 1H), 4.27 (s, 1H), 3.84 (d, *J* = 10.3 Hz, 1H), 3.68 (s, 3H), 3.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 165.0, 158.9, 144.2, 142.7, 141.6, 133.1, 132.4, 130.1, 129.7, 128.7, 128.6, 128.5, 128.3, 128.1, 128.0, 126.9, 126.5, 121.7, 113.4, 74.6, 71.8, 55.2, 53.6, 51.8, 46.9; HRMS (ESI, m/z): calcd. for $C_{34}H_{31}O_6^+$ 535.2115, found 535.2122; IR (KBr thin film, cm^{-1}): ν 3503, 2954, 1719, 1513, 1250, 1175, 703; $[\alpha]^{31}_D$: -21.7 (*c* 1.1, $CHCl_3$); HPLC analysis: 93% ee (Chiralcel AD-H, 10:90 ^{i}PrOH/hexane, 1 mL/min, 254 nm), R_t (major) = 11.3 min, R_t (minor) = 14.8 min.



4o

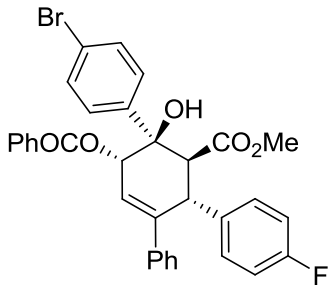
(1*S*,4*R*,5*S*,6*R*)-6-hydroxy-5-(methoxycarbonyl)-4,6-diphenyl-3-(thiophen-2-yl)cyc lohex-2-enyl benzoate (4o): Yellow oil, 85.7 mg, 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90–7.88 (m, 2H), 7.63–7.60 (m, 2H), 7.52–7.50 (m, 1H), 7.41–7.37 (m, 2H), 7.31–7.12 (m, 8H), 7.01–6.99 (m, 1H), 6.73–6.68 (m, 2H), 6.62 (dd, *J* = 6.0 and 1.9 Hz, 1H), 5.51 (d, *J* = 6.0 Hz, 1H), 4.40 (d, *J* = 10.1 Hz, 1H), 4.24 (s, 1H), 3.88 (d, *J* = 10.2 Hz, 1H), 3.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.7, 164.9, 142.7,

142.3, 141.8, 138.1, 133.1, 129.9, 129.6, 129.0, 128.5, 128.4, 128.0, 127.4, 127.0, 126.5, 126.3, 124.8, 121.8, 74.4, 71.8, 53.8, 51.8, 47.4; HRMS (ESI, m/z): calcd. for $C_{31}H_{26}O_5SNa^+$ 533.1393, found 533.1400; IR (KBr thin film, cm^{-1}): ν 3503, 3062, 2953, 1720, 1263, 1095, 702; $[\alpha]^{31}_D$: 8.2 (*c* 4.5, $CHCl_3$); HPLC analysis: 97% ee (Chiralcel AD-H, 10:90 ^{i}PrOH/hexane, 1 mL/min, 254 nm), R_t (major) = 10.9 min, R_t (minor) = 30.3 min.



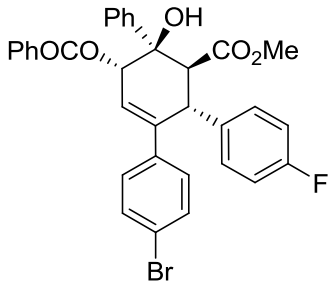
4p

(1*S*,4*R*,5*S*,6*R*)-6-(4-chlorophenyl)-6-hydroxy-5-(methoxycarbonyl)-4-phenyl-3-p-tolylcyclohex-2-enyl benzoate (4p): Yellow oil, 61.8 mg, 56% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92–7.90 (m, 2H), 7.58–7.54 (m, 3H), 7.48–7.41 (m, 2H), 7.20–7.09 (m, 9H), 6.92–6.90 (m, 2H), 6.38 (d, *J* = 5.8 Hz, 1H), 5.48 (d, *J* = 5.8 Hz, 1H), 4.53 (d, *J* = 10.2 Hz, 1H), 4.31 (s, 1H), 3.79 (d, *J* = 10.2 Hz, 1H), 3.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.9, 164.8, 144.6, 141.4, 141.3, 137.2, 136.8, 134.0, 133.3, 129.9, 129.6, 128.8, 128.6, 128.5, 128.2, 128.1, 127.0, 122.1, 74.4, 71.5, 53.5 51.9, 46.8, 21.2; HRMS (ESI, m/z): calcd. for $C_{34}H_{29}ClO_5Na^+$ 575.1596, found 575.1592; IR (KBr thin film, cm^{-1}): ν 3498, 3028, 2923, 1720, 1491, 1262, 1095, 710; $[\alpha]^{30}_D$: 2.2 (*c* 1.7, $CHCl_3$); HPLC analysis: 80% ee (Chiralcel AD-H, 10:90 ^{i}PrOH/hexane, 1 mL/min, 254 nm), R_t (major) = 5.7 min, R_t (minor) = 12.2 min.



4q

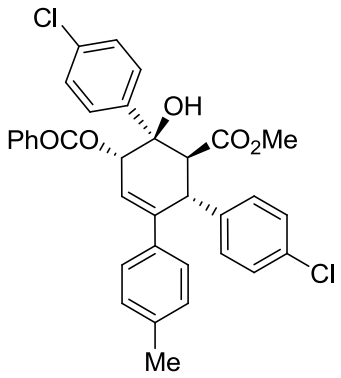
(1*S*,4*R*,5*S*,6*R*)-6-(4-bromophenyl)-4-(4-fluorophenyl)-6-hydroxy-5-(methoxycarbonyl)-3-phenylcyclohex-2-enyl benzoate (4q): Yellow oil, 78.0 mg, 65% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91–7.89 (m, 2H), 7.59–7.55 (m, 1H), 7.51–7.42 (m, 4H), 7.35–7.33 (m, 2H), 7.19–7.04 (m, 7H), 6.89–6.84 (m, 2H), 6.39 (dd, *J* = 5.7 and 2.2 Hz, 1H), 5.47 (d, *J* = 5.7 Hz, 1H), 4.54 (d, *J* = 10.2 Hz, 1H), 4.28 (s, 1H), 3.74 (d, *J* = 10.3 Hz, 1H), 3.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.7, 164.8, 161.7 (d, *J* = 244.2 Hz), 144.6, 140.7 (d, *J* = 211.3 Hz), 136.8 (d, *J* = 3.3 Hz), 134.0, 133.4, 131.2, 130.0 (d, *J* = 8.0 Hz), 129.8, 129.6, 128.6, 128.4, 128.2, 127.6, 127.2, 123.0, 122.4, 115.8 (d, *J* = 21.3 Hz), 74.5, 71.3, 53.4 52.1, 46.1; HRMS (ESI, m/z): calcd. for $C_{33}H_{26}BrFO_5Na^+$ 623.0840, found 623.0840; IR (KBr thin film, cm^{-1}): ν 3500, 3062, 2953, 1720, 1509, 1262, 1095, 711; $[\alpha]^{31}_{D}$: 5.4 (*c* 1.8, $CHCl_3$); HPLC analysis: 82% ee (Chiralcel AD-H, 10:90 ^{i}PrOH/hexane, 1 mL/min, 254 nm), R_t (major) = 7.5 min, R_t (minor) = 9.9 min.



4r

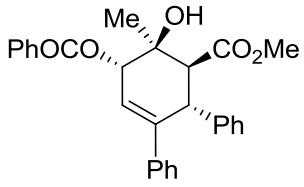
(1*S*,4*R*,5*S*,6*R*)-3-(4-bromophenyl)-4-(4-fluorophenyl)-6-hydroxy-5-(methoxycarbonyl)-6-phenylcyclohex-2-enyl benzoate (4r): Yellow oil, 66.0 g, 55% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89–7.87 (m, 2H), 7.63–7.61 (m, 2H), 7.56–7.52 (m, 1H), 7.43–7.39 (m, 2H), 7.23–7.14 (m, 5H), 7.07–7.04 (m, 4H), 6.90–6.86 (m, 2H), 6.41 (dd, *J* = 5.7 and 2.1 Hz, 1H), 5.48 (d, *J* = 5.7 Hz, 1H), 4.53 (d, *J* = 9.3 Hz, 1H), 4.25 (s,

1H), 3.79 (d, J = 10.3 Hz, 1H), 3.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.7, 164.9, 163.0, 160.5, 143.6, 142.3, 138.7, 136.6 (d, J = 3.2 Hz), 133.2, 131.3, 130.0 (d, J = 8.0 Hz), 129.8, 129.6, 128.8, 128.5, 128.2, 128.1, 126.4, 123.8, 121.5, 115.9 (d, J = 21.4 Hz), 74.6, 71.4, 53.4 51.9, 46.0; HRMS (ESI, m/z): calcd. for $C_{33}H_{26}BrFO_5Na^+$ 623.0840, found 623.0836; IR (KBr thin film, cm^{-1}): ν 3508, 3062, 2952, 1719, 1509, 1263, 1096, 710; $[\alpha]^{31}_D$: -18.9 (*c* 1.6, $CHCl_3$); HPLC analysis: 92% ee (Chiralcel AD-H, 10:90 ^{i}PrOH/hexane, 1 mL/min, 254 nm), R_t (major) = 8.1 min, R_t (minor) = 10.8 min.



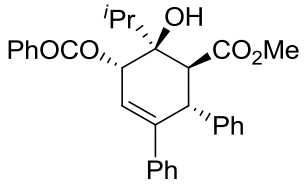
4s

(1*S*,4*R*,5*S*,6*R*)-4,6-bis(4-chlorophenyl)-6-hydroxy-5-(methoxycarbonyl)-3-p-tolylcyclohex-2-enyl benzoate (4s): Yellow oil, 82.0 mg, 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91–7.89 (m, 2H), 7.58–7.54 (m, 3H), 7.45–7.41 (m, 2H), 7.24–7.14 (m, 4H), 7.08–7.02 (m, 4H), 6.94–6.92 (m, 2H), 6.37 (dd, J = 5.8 and 2.0 Hz, 1H), 5.47 (d, J = 5.8 Hz, 1H), 4.53 (d, J = 10.2 Hz, 1H), 4.26 (s, 1H), 3.73 (d, J = 10.3 Hz, 1H), 3.35 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.6, 164.8, 141.1, 139.9, 137.4, 136.5, 134.1, 133.3, 132.7, 129.83, 129.81, 129.6, 129.0, 128.9, 128.6, 128.2, 128.0, 126.9, 122.4, 74.4, 71.4, 53.4, 52.0, 46.2, 21.2; HRMS (ESI, m/z): calcd. for $C_{34}H_{28}Cl_2O_5Na^+$ 609.1206, found 609.1206; IR (KBr thin film, cm^{-1}): ν 3456, 2960, 2927, 1729, 1489, 1250, 1093, 711; $[\alpha]^{27}_D$: -6.7 (*c* 1.8, $CHCl_3$); HPLC analysis: 85% ee (Chiralcel AD-H, 10:90 ^{i}PrOH/hexane, 1 mL/min, 254 nm), R_t (major) = 7.9 min, R_t (minor) = 9.9 min.



4t

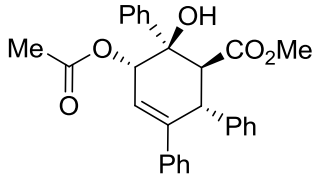
(1*S*,4*R*,5*S*,6*S*)-6-hydroxy-5-(methoxycarbonyl)-6-methyl-3,4-diphenylcyclohex-2-enyl benzoate (4t): Yellow oil, 35.4 mg, 40% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11–8.09 (m, 2H), 7.63–7.60 (m, 1H), 7.52–7.48 (m, 2H), 7.20–7.04 (m, 10H), 6.37 (d, *J* = 4.7 Hz, 1H), 5.45 (d, *J* = 5.7 Hz, 1H), 4.48 (d, *J* = 10.3 Hz, 1H), 3.58 (s, 3H), 3.32 (s, 1H), 3.13 (d, *J* = 10.4 Hz, 1H), 1.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.3, 165.6, 145.1, 141.4, 139.8, 133.5, 130.1, 129.9, 128.75, 128.68, 128.5, 128.0, 127.4, 127.1, 126.8, 122.4, 71.8, 70.9, 55.9, 52.0, 46.2, 25.1; HRMS (ESI, m/z): calcd. for $C_{28}H_{27}O_5^+$ 443.1853, found 443.1852; IR (KBr thin film, cm^{-1}): ν 3514, 2953, 1720, 1452, 1263, 1107, 700; $[\alpha]^{31}_D$: -7.6 (*c* 1.5, $CHCl_3$); HPLC analysis: 61% ee (Chiralcel AD-H, 10:90 ^{i}PrOH/hexane, 1 mL/min, 254 nm), R_t (minor) = 12.3 min, R_t (major) = 24.1 min.



4u

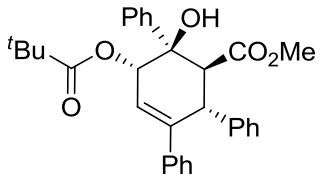
(1*S*,4*R*,5*S*,6*S*)-6-hydroxy-6-isopropyl-5-(methoxycarbonyl)-3,4-diphenylcyclohex-2-enyl benzoate (4u): Yellow oil, 14.1 mg, 15% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12–8.10 (m, 2H), 7.64–7.60 (m, 1H), 7.52–7.48 (m, 2H), 7.17–7.03 (m, 10H), 6.41 (dd, *J* = 6.0 and 1.9 Hz, 1H), 5.62 (d, *J* = 6.0 Hz, 1H), 4.44 (d, *J* = 10.1 Hz, 1H), 3.57 (s, 3H), 3.41 (d, *J* = 10.1 Hz, 1H), 3.29 (s, 1H), 1.94–1.87 (m, 1H), 1.09–1.06 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 165.2, 144.5, 141.5, 133.4, 130.1, 130.0, 128.8, 128.7, 128.5, 128.0, 127.4, 127.1, 126.8, 122.7, 69.2, 54.0, 51.9, 47.2, 37.4, 18.6, 16.7; HRMS (ESI, m/z): calcd. for $C_{30}H_{30}O_5Na^+$ 493.1986, found 493.1987; IR (KBr thin film, cm^{-1}): ν 2925, 2853, 1719, 1263, 1095, 711; $[\alpha]^{32}_D$: -16.9 (*c* 1.9, $CHCl_3$); HPLC analysis: 99% ee (Chiralcel AD-H, 10:90 ^{i}PrOH/hexane, 1 mL/min, 254 nm), R_t

(minor) = 6.8 min, R_t (major) = 12.9 min.



4v

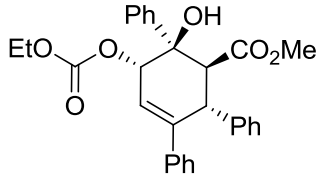
(1*S*,2*R*,5*S*,6*R*)-methyl 5-acetoxy-6-hydroxy-2,3,6-triphenylcyclohex-3-enecarboxylate (4v): Yellow oil, 36.2 mg, 41% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58–7.56 (m, 2H), 7.31–7.03 (m, 13H), 6.22 (dd, *J* = 5.6 and 1.6 Hz, 1H), 5.30 (d, *J* = 5.1 Hz, 1H), 4.51 (d, *J* = 10.4 Hz, 1H), 4.21 (s, 1H), 3.69 (d, *J* = 10.4 Hz, 1H), 3.25 (s, 3H), 1.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.0, 169.2, 144.5, 142.6, 141.1, 140.0, 128.62, 128.59, 128.0, 127.9, 127.3, 127.1, 126.9, 126.6, 123.0, 74.5, 70.7, 53.3, 51.7, 46.7, 20.9; HRMS (ESI, m/z): calcd. for $C_{28}H_{27}O_5^+$ 443.1853, found 443.1862; IR (KBr thin film, cm^{-1}): ν 3502, 3027, 2926, 1741, 1369, 1229, 700; $[\alpha]^{29}_D$: -14.5 (*c* 2.7, $CHCl_3$); HPLC analysis: 83% ee (Chiralcel AD-H, 10:90 ^{i}PrOH/hexane, 1 mL/min, 254 nm), R_t (major) = 7.5 min, R_t (minor) = 12.1 min.



4w

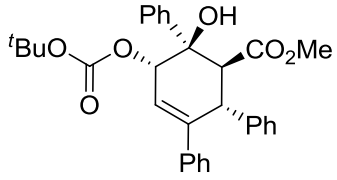
(1*S*,2*R*,5*S*,6*R*)-methyl 6-hydroxy-2,3,6-triphenyl-5-(pivaloyloxy)cyclohex-3-enecarboxylate (4w): Yellow oil, 54.2 mg, 56% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59–7.57 (m, 2H), 7.30–7.02 (m, 13H), 6.31 (d, *J* = 4.4 Hz, 1H), 5.21 (d, *J* = 5.6 Hz, 1H), 4.50 (d, *J* = 10.1 Hz, 1H), 4.28 (s, 1H), 3.72 (d, *J* = 10.3 Hz, 1H), 3.30 (s, 3H), 1.03 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.7, 176.1, 144.4, 143.0, 141.2, 140.0, 128.6, 128.5, 128.0, 127.94, 127.91, 127.3, 127.1, 126.9, 126.6, 123.0, 74.4, 71.3, 53.1, 51.7, 46.9, 38.7, 27.1; HRMS (ESI, m/z): calcd. for $C_{31}H_{32}O_5Na^+$ 507.2142, found 507.2140; IR (KBr thin film, cm^{-1}): ν 3504, 2972, 1731, 1145, 759, 700; $[\alpha]^{32}_D$: -30.1 (*c* 3.3, $CHCl_3$); HPLC analysis: 91% ee (Chiralcel AD-H, 10:90 ^{i}PrOH/hexane, 1 mL/min, 254 nm), R_t

(major) = 5.0 min, R_t (minor) = 6.5 min.



4x

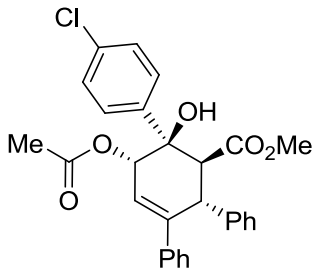
(1*S*,2*R*,5*S*,6*R*)-methyl 5-(ethoxycarbonyloxy)-6-hydroxy-2,3,6-triphenylcyclohex-3-enecarboxylate (4x): Yellow oil, 33.0 mg, 35% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62–7.60 (m, 2H), 7.32–7.05 (m, 13H), 6.24 (dd, *J* = 5.8 and 2.2 Hz, 1H), 5.16 (dd, *J* = 5.8 and 0.8 Hz, 1H), 4.49 (dd, *J* = 10.4 and 1.0 Hz, 1H), 4.24 (s, 1H), 3.97–3.89 (m, 2H), 3.71 (d, *J* = 10.4 Hz, 1H), 3.23 (s, 3H), 1.13 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 154.0, 145.3, 142.1, 140.8, 140.0, 128.8, 128.6, 128.03, 128.02, 128.00, 127.4, 127.2, 126.9, 126.8, 122.3, 74.5, 73.7, 64.2, 53.1, 51.7, 46.8, 14.3; HRMS (ESI, m/z): calcd. for $C_{29}H_{28}O_6Na^+$ 495.1778, found 495.1776; IR (KBr thin film, cm^{-1}): ν 3503, 2926, 1748, 1716, 1248, 699; $[\alpha]^{31}_D$: -25.2 (*c* 1.5, $CHCl_3$); HPLC analysis: 86% ee (Chiralcel AD-H, 10:90 ^{i}PrOH/hexane, 1 mL/min, 254 nm), R_t (major) = 6.5 min, R_t (minor) = 13.3 min.



4y

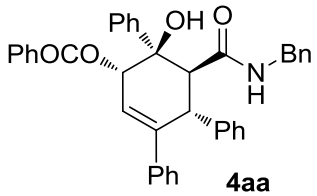
(1*S*,2*R*,5*S*,6*R*)-methyl 5-(tert-butoxycarbonyloxy)-6-hydroxy-2,3,6-triphenylcyclohex-3-enecarboxylate (4y): Yellow oil, 33.0 mg, 33% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62–7.60 (m, 2H), 7.31–7.27 (m, 2H), 7.24–7.20 (m, 3H), 7.15–7.03 (m, 8H), 6.20 (dd, *J* = 5.7 and 2.1 Hz, 1H), 5.19 (d, *J* = 5.2 Hz, 1H), 4.49 (d, *J* = 10.2 Hz, 1H), 4.23 (s, 1H), 3.71 (d, *J* = 10.5 Hz, 1H), 3.20 (s, 3H), 1.23 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 152.2, 144.7, 142.2, 140.9, 140.1, 128.8, 128.5, 127.98, 127.95, 127.8, 127.23, 127.16, 126.8, 122.7, 82.2, 74.7, 72.6, 53.2, 51.6, 46.7, 27.6; HRMS (ESI, m/z): calcd. for $C_{31}H_{33}O_6^+$ 501.2272, found 501.2279; IR (KBr thin film, cm^{-1}): ν 3503, 2980, 1745,

1271, 1168, 700; $[\alpha]^{28}_{D}$: -15.4 (*c* 2.2, $CHCl_3$); HPLC analysis: 81% ee (Chiralcel AD-H, 10:90 ^{i}PrOH/hexane, 1 mL/min, 254 nm), R_t (major) = 4.7 min, R_t (minor) = 9.5 min.



4z

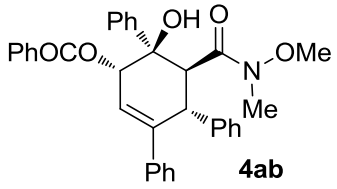
(1*S*,2*R*,5*S*,6*R*)-methyl 5-acetoxy-6-(4-chlorophenyl)-6-hydroxy-2,3-diphenylcyclohex-3-enecarboxylate (4z): Yellow oil, 39.0 mg, 41% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.51 (m, 2H), 7.28–7.25 (m, 2H), 7.21–7.06 (m, 10H), 6.22 (dd, *J* = 5.7 and 1.9 Hz, 1H), 5.26 (d, *J* = 5.7 Hz, 1H), 4.48 (d, *J* = 10.3 Hz, 1H), 4.24 (s, 1H), 3.64 (d, *J* = 10.4 Hz, 1H), 3.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.8, 169.1, 144.5, 141.3, 140.8, 139.8, 134.0, 128.7, 128.6, 128.2, 128.1, 128.0, 127.4, 127.1, 127.0, 122.8, 74.3, 70.5, 53.2, 51.9, 46.7, 20.9; HRMS (ESI, m/z): calcd. for $C_{28}H_{26}ClO_5^+$ 477.1463, found 477.1455; IR (KBr thin film, cm^{-1}): ν 3502, 2925, 2853, 1744, 1370, 1226, 1017, 699; $[\alpha]^{31}_{D}$: 4.3 (*c* 2.0, $CHCl_3$); HPLC analysis: 84% ee (Chiralcel AD-H, 10:90 ^{i}PrOH/hexane, 1 mL/min, 254 nm), R_t (major) = 7.4 min, R_t (minor) = 11.3 min.



4aa

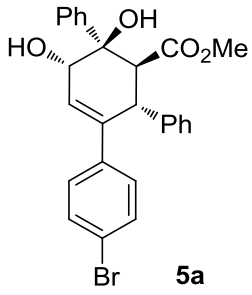
(1*S*,4*R*,5*S*,6*R*)-5-(benzylcarbamoyl)-6-hydroxy-3,4,6-triphenylcyclohex-2-enyl benzoate (4aa): Yellow oil, 30.1 mg, 52% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94–7.92 (m, 2H), 7.66–7.64 (m, 2H), 7.55–7.51 (m, 1H), 7.42–7.39 (m, 2H), 7.23–7.05 (m, 16H), 6.68–6.66 (m, 2H), 6.42 (dd, *J* = 5.8 and 1.8 Hz, 1H), 5.70 (s, 1H), 5.49 (d, *J* = 5.8 Hz, 1H), 5.28 (d, *J* = 5.3 Hz, 1H), 4.64 (d, *J* = 9.4 Hz, 1H), 4.24 (dd, *J* = 14.7 and 6.4 Hz, 1H), 3.83 (dd, *J* = 14.7 and 4.7 Hz, 1H), 3.44 (d, *J* = 9.9 Hz,

1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 164.9, 144.9, 143.0, 142.1, 140.1, 137.0, 133.1, 130.2, 129.6, 128.8, 128.6, 128.5, 128.0, 127.8, 127.7, 127.5, 127.3,127.2, 126.9, 126.7, 123.0, 74.5, 71.6, 54.2, 46.6, 43.3; HRMS (ESI, m/z): calcd. for $C_{39}H_{34}NO_4^+$ 580.2482, found 580.2488; IR (KBr thin film, cm^{-1}) ν 3356, 2921, 2852, 1718, 1641, 1262, 1094, 969, 702; $[\alpha]_D^{27.7}$ -4.073 (c 1.85, $CHCl_3$); HPLC analysis: 90% ee (Chiralcel AD-H, 30:70 ^{i}PrOH/hexane, 1 mL/min, 254 nm), R_t (major) = 3.7 min, R_t (minor) = 6.0 min.



4ab

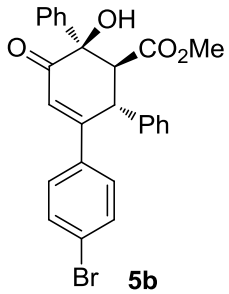
(1'R,4'S,5'R,6'S)-5'-hydroxy-6'-(methoxy(methyl)carbamoyl)-5'-phenyl-1',4',5',6'-tetrahydro-[1,1':2',1''-terphenyl]-4'-yl benzoate (4ab): Yellow oil, 68.2 mg, 64% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95–7.93 (m, 2H), 7.69–7.67 (m, 2H), 7.55–7.53 (m, 1H), 7.45–7.41 (m, 2H), 7.25–7.03 (m, 13H), 6.46 (dd, *J* = 5.8 and 2.0 Hz, 1H), 5.43–5.42 (m, 2H), 4.69 (d, *J* = 10.0 Hz, 1H), 4.46 (d, *J* = 10.1 Hz, 1H), 2.78 (s, 3H), 2.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.0, 165.1, 145.6, 143.1, 142.2, 140.4, 133.0, 130.4, 129.6, 129.5, 128.8, 128.4, 127.9, 127.8, 127.74, 127.67, 127.1, 126.8, 123.1, 75.9, 72.1, 60.3, 47.1, 46.6, 31.8; HRMS (ESI, m/z): calcd. for $C_{34}H_{32}NO_5^+$ 534.2275, found 534.2277; IR (KBr thin film, cm^{-1}): ν 3421, 2919, 2850, 1718, 1624, 1261, 1096, 701; $[\alpha]^{28}_D$: -9.1 (*c* 2.0, $CHCl_3$); HPLC analysis: 88% ee (Chiralcel AD-H, 30:70 ^{i}PrOH/hexane, 1 mL/min, 254 nm), R_t (major) = 3.8 min, R_t (minor) = 5.3 min.



5a

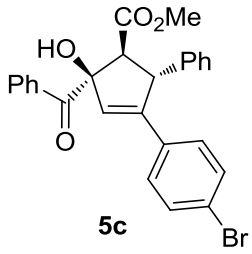
(2'R,3'S,4'R,5'S)-methyl 4-bromo-4',5'-dihydroxy-4'-phenyl-2',3',4',5'-tetrahydro-[1,1':2',1''-terphenyl]-3'

-carboxylate (5a): White solid, 340.3 mg, 89% yield . Mp 227–230 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61–7.59 (m, 2H), 7.39–7.29 (m, 3H), 7.26–7.24 (m, 2H), 7.18–7.06 (m, 7H), 6.27 (dd, *J* = 5.5 and 2.0 Hz, 1H), 4.41 (d, *J* = 10.1 Hz, 1H), 4.14 (s, 1H), 4.03 (s, 1H), 3.68 (d, *J* = 10.4 Hz, 1H), 3.25 (s, 3H), 1.63 (d, *J* = 3.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.3, 143.0, 142.1, 140.8, 139.4, 131.1, 128.8, 128.7, 128.64, 128.58, 128.3, 127.0, 126.6, 126.1, 121.1, 75.8, 70.2, 52.1, 51.7, 46.8; HRMS (ESI, m/z): calcd. for $C_{26}H_{23}BrO_4Na^+$ 501.0672, found 501.0664; IR (KBr thin film, cm^{-1}): ν 3450, 1701, 1045, 980, 806, 699; $[\alpha]^{27}_D$: -11.1 (*c* 0.3, $CHCl_3$); HPLC analysis: 93% ee (Chiralcel AD-H, 20:80 iPrOH/hexane, 1 mL/min, 254 nm), R_t (minor) = 6.1 min, R_t (major) = 7.2 min.



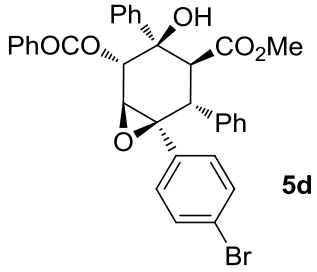
5b

(2'R,3'S,4'R)-methyl 4-bromo-4'-hydroxy-5'-oxo-4'-phenyl-2',3',4',5'-tetrahydro-[1,1':2',1''-terphenyl] -3'-carboxylate (5b): White solid, 127.1 mg, 89% yield. Mp 70–71 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.35 (m, 2H), 7.26–7.23 (m, 2H), 7.16 (s, 4H), 7.00–6.98 (m, 3H), 6.83–6.80 (m, 3H), 4.75 (dd, *J* = 5.7 and 1.3 Hz, 1H), 4.36 (s, 1H), 3.90 (d, *J* = 5.8 Hz, 1H), 3.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.3, 173.0, 157.4, 139.5, 138.7, 136.4, 131.9, 128.7, 128.6, 128.5, 128.2, 127.0, 126.54, 126.50, 124.3, 76.5, 59.7, 52.3, 45.8; HRMS (ESI, m/z): calcd. for $C_{26}H_{22}BrO_4^+$ 477.0696, found 477.0698; IR (KBr thin film, cm^{-1}): ν 3461, 2925, 1737,1679, 1167, 698; $[\alpha]^{27}_D$: -23.3 (*c* 0.1, $CHCl_3$); HPLC analysis: 94% ee (Chiralcel AD-H, 20:80 iPrOH/hexane, 1 mL/min, 254 nm), R_t (minor) = 15.5 min, R_t (major) = 20.9 min.



5c

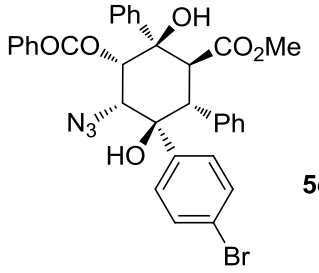
(1S,2R,5R)-methyl 2-benzoyl-4-(4-bromophenyl)-2-hydroxy-5-phenylcyclopent-3-enecarboxylate (5c): White solid, 39.0 mg, 82% yield. Mp 45–46 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21–8.19 (m, 2H), 7.62–7.58 (m, 1H), 7.51–7.48 (m, 2H), 7.37–7.34 (m, 2H), 7.23–7.12 (m, 7H), 6.36 (d, *J* = 1.9 Hz, 1H), 5.22 (dd, *J* = 5.7 and 1.9 Hz, 1H), 4.90 (s, 1H), 3.78 (d, *J* = 7.7 Hz, 1H), 3.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.9, 169.9, 149.9, 141.5, 133.9, 133.8, 133.1, 131.7, 129.9, 129.0, 128.84, 128.81, 128.4, 128.3, 127.1, 122.8, 87.8, 63.1, 52.2, 51.7; HRMS (ESI, m/z): calcd. for $C_{26}H_{22}BrO_4^+$ 477.0696, found 477.0693; IR (KBr thin film, cm^{-1}): ν 3433, 2951, 1745, 1677, 1488, 1232, 699; $[\alpha]^{27}_D$: -12.7 (*c* 0.3, $CHCl_3$); HPLC analysis: 94% ee (Chiralcel AS-H, 20:80 iPrOH/hexane, 1 mL/min, 254 nm), R_t (major) = 7.1 min, R_t (minor) = 8.8 min.



5d

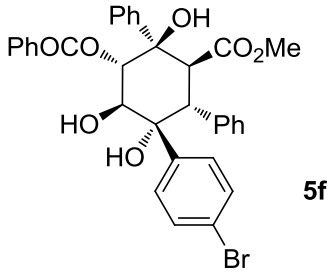
(1S,2R,3S,4R,5S,6S)-methyl 5-(benzoyloxy)-1-(4-bromophenyl)-4-hydroxy-2,4-diphenyl-7-oxabicyclo[4.1.0]heptane-3-carboxylate (5d): White solid, 334.9 mg, 70% yield. Mp 202–205 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06–8.04 (m, 2H), 7.68–7.64 (m, 3H), 7.56–7.52 (m, 2H), 7.21–7.01 (m, 12H), 5.63 (d, *J* = 2.7 Hz, 1H), 4.79 (s, 1H), 4.45 (d, *J* = 11.1 Hz, 1H), 3.99 (d, *J* = 11.1 Hz, 1H), 3.95 (dd, *J* = 2.6 and 0.8 Hz, 1H), 3.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 164.5, 140.3, 139.2, 136.9, 133.8, 131.1, 130.1, 129.8, 129.7, 129.2, 128.9, 128.7, 128.0, 127.7, 127.5, 126.9, 122.2, 74.9, 70.9, 64.7, 60.3, 52.2, 51.8, 46.6; HRMS (ESI, m/z): calcd. for $C_{33}H_{28}BrO_6^+$ 599.1064, found 599.1064;

IR (KBr thin film, cm^{-1}): ν 3458, 3062, 1734, 1255, 1093, 1070, 703; $[\alpha]^{27}_{D}$: 9.6 (*c* 0.1, $CHCl_3$); HPLC analysis: 93% ee (Chiralcel AD-H, 30:70 iPrOH/hexane, 1 mL/min, 220 nm), R_t (minor) = 15.8 min, R_t (major) = 27.3 min.



5e

(1S,2R,3S,4R,5S,6R)-6-azido-5-(4-bromophenyl)-2,5-dihydroxy-3-(methoxycarbonyl)-2,4-diphenylcyclohexyl benzoate (5e): White solid, 59.9 mg, 56% yield. Mp 223–225 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98–7.96 (m, 2H), 7.67–7.65 (m, 2H), 7.59–7.55 (m, 1H), 7.48–7.38 (m, 4H), 7.33–7.30 (m, 2H), 7.24–7.15 (m, 6H), 5.59 (s, 1H), 5.55 (d, *J* = 2.4 Hz, 1H), 5.32 (d, *J* = 10.0 Hz, 1H), 4.62 (d, *J* = 11.6 Hz, 1H), 4.33 (dd, *J* = 10.0 and 2.4 Hz, 1H), 4.12 (d, *J* = 11.6 Hz, 1H), 3.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.4, 164.4, 140.8, 138.2, 135.4, 133.5, 131.1, 129.9, 129.7, 129.2, 128.63, 128.58, 128.3, 127.9, 126.4, 122.2, 74.2, 72.9, 69.8, 52.0, 48.9, 45.9; HRMS (ESI, m/z): calcd. for $C_{33}H_{28}BrN_3O_6Na^+$ 664.1054, found 664.1054; IR (KBr thin film, cm^{-1}): ν 3433, 2106, 1729, 1265, 1094, 700; $[\alpha]^{27}_{D}$: 13.7 (*c* 0.1, $CHCl_3$); HPLC analysis: 93% ee (Chiralcel AD-H, 50:50 iPrOH/hexane, 1 mL/min, 220 nm), R_t (minor) = 6.5 min, R_t (major) = 10.5 min.

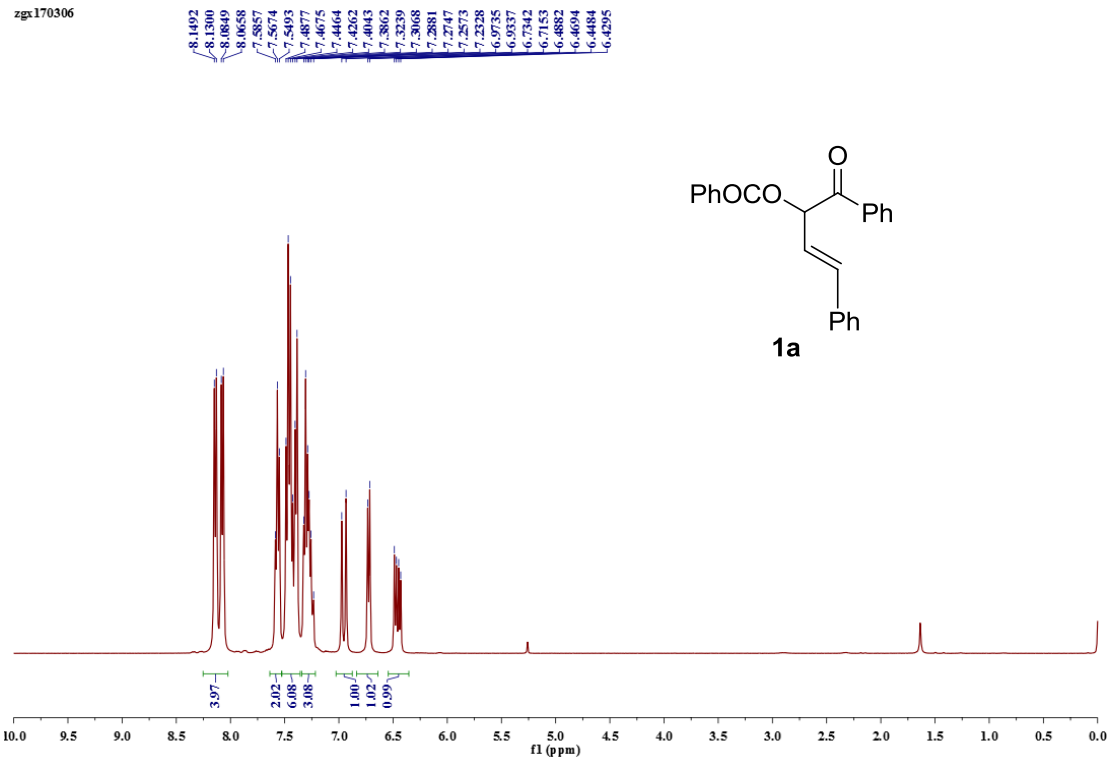


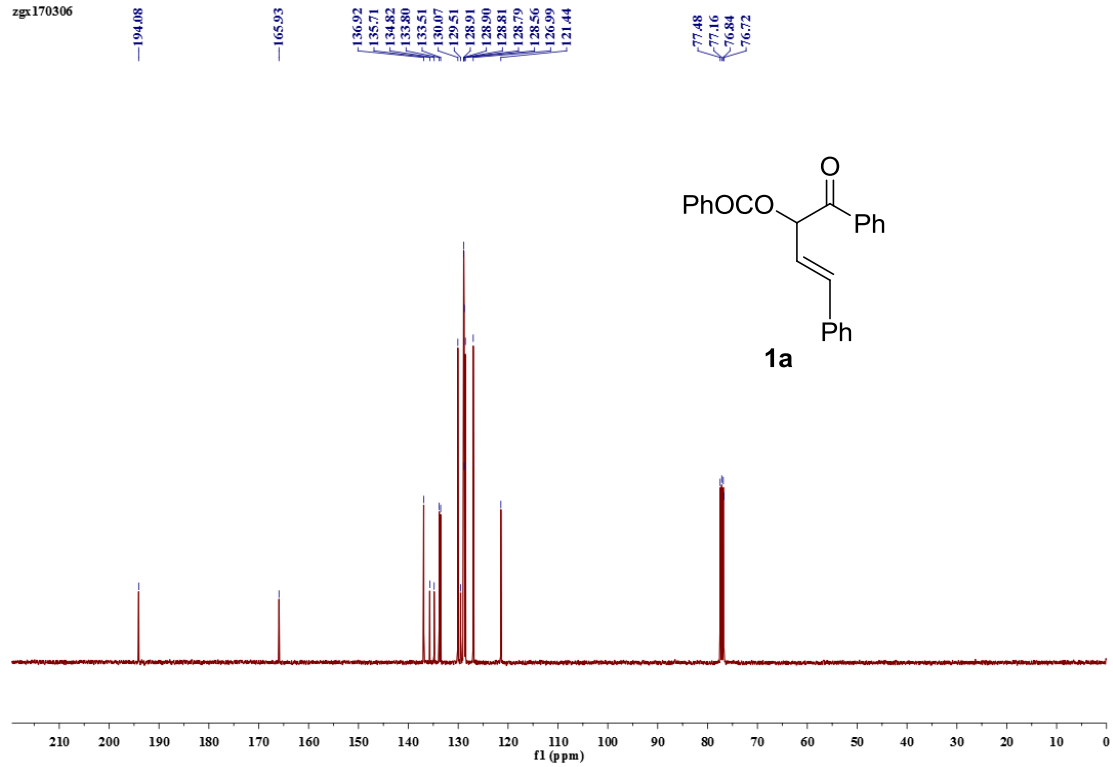
5f

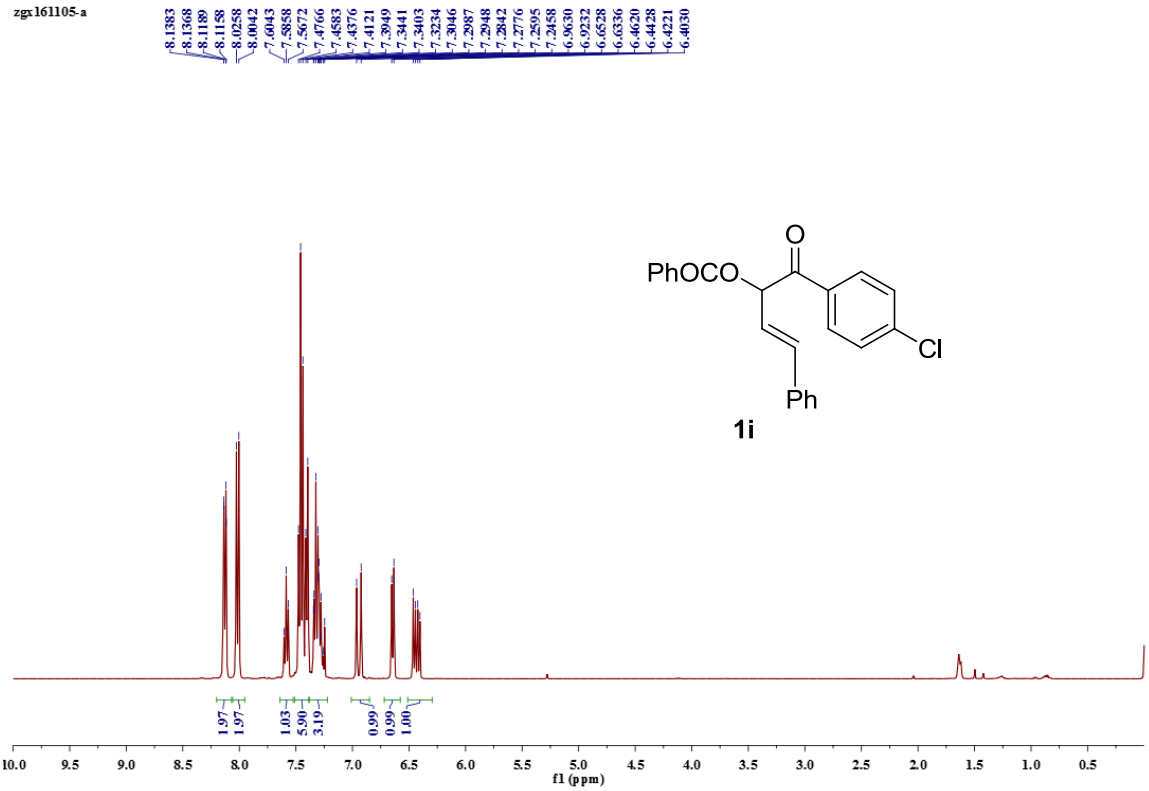
(1S,2R,3S,4R,5S,6R)-5-(4-bromophenyl)-2,5,6-trihydroxy-3-(methoxycarbonyl)-2,4-diphenylcyclohexyl benzoate (5f): White solid, 76.5 mg, 71% yield. Mp 234–236 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19–8.17 (m, 2H), 7.96 (brs, 1H), 7.68–7.55 (m, 5H), 7.41–7.30 (m, 6H), 7.14–7.10 (m, 3H), 6.98–6.95 (m, 1H), 6.45 (brs, 1H), 5.76 (d, *J* = 9.7 Hz, 1H), 5.65 (dd, *J* = 9.7 and 2.7 Hz, 1H), 5.56 (s, 1H),

4.82 (d, *J* = 11.9 Hz, 1H), 4.12 (d, *J* = 11.9 Hz, 1H), 4.02 (dd, *J* = 4.8 and 2.8 Hz, 1H), 3.09 (s, 3H), 1.54 (d, *J* = 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.6, 165.7, 141.6, 139.2, 135.6, 133.0, 131.8, 130.3, 129.7, 129.0, 128.74, 128.67, 128.6, 127.7, 127.4, 126.5, 121.3, 85.2, 78.5, 75.7, 70.6, 52.0, 48.4, 47.8; HRMS (ESI, m/z): calcd. for $C_{33}H_{29}BrO_7Na^+$ 639.0989, found 639.0995; IR (KBr thin film, cm^{-1}): ν 3431, 1722, 1271, 1246, 1108, 1067, 700; $[\alpha]^{27}_D$: -4.0 (*c* 0.2, $CHCl_3$); HPLC analysis: 94% ee (Chiralcel IC, 10:90 iPrOH/hexane, 1 mL/min, 220 nm), R_t (major) = 9.9 min, R_t (minor) = 12.7 min.

VI. ^{1}H NMR and ^{13}C NMR Spectra of Substrates and Products



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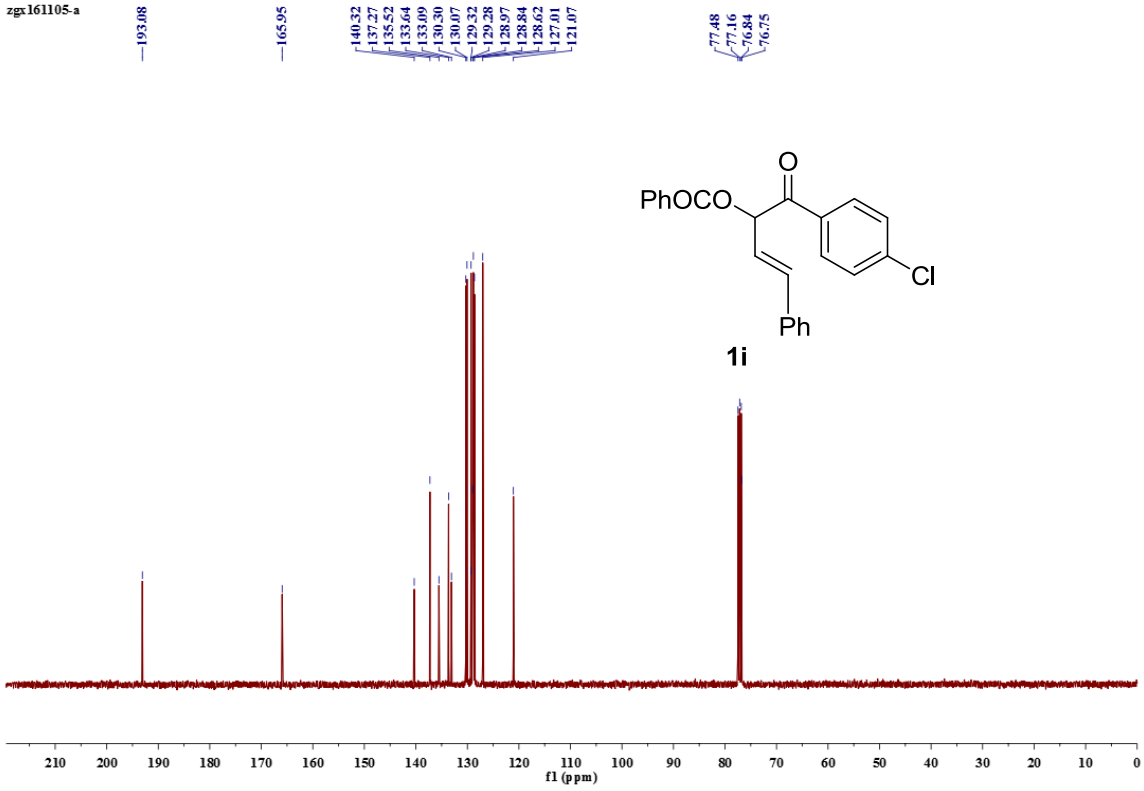
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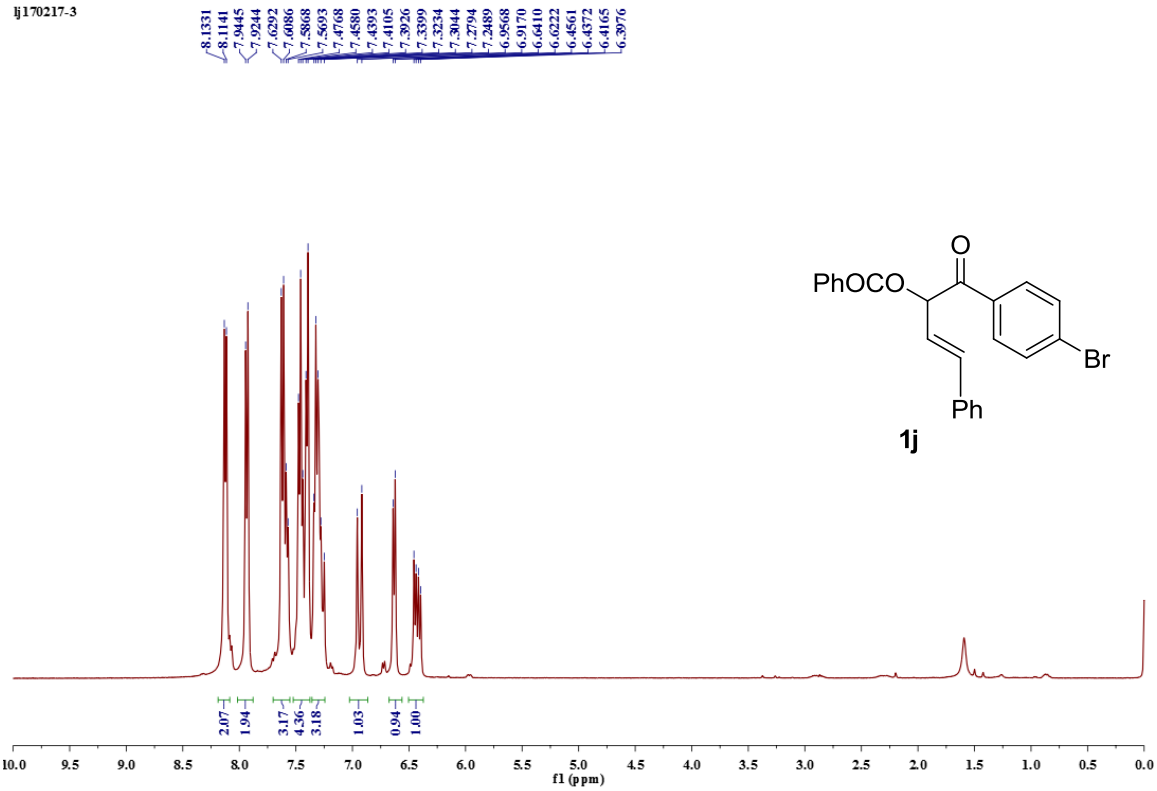
Ph
1i
f1 (ppm)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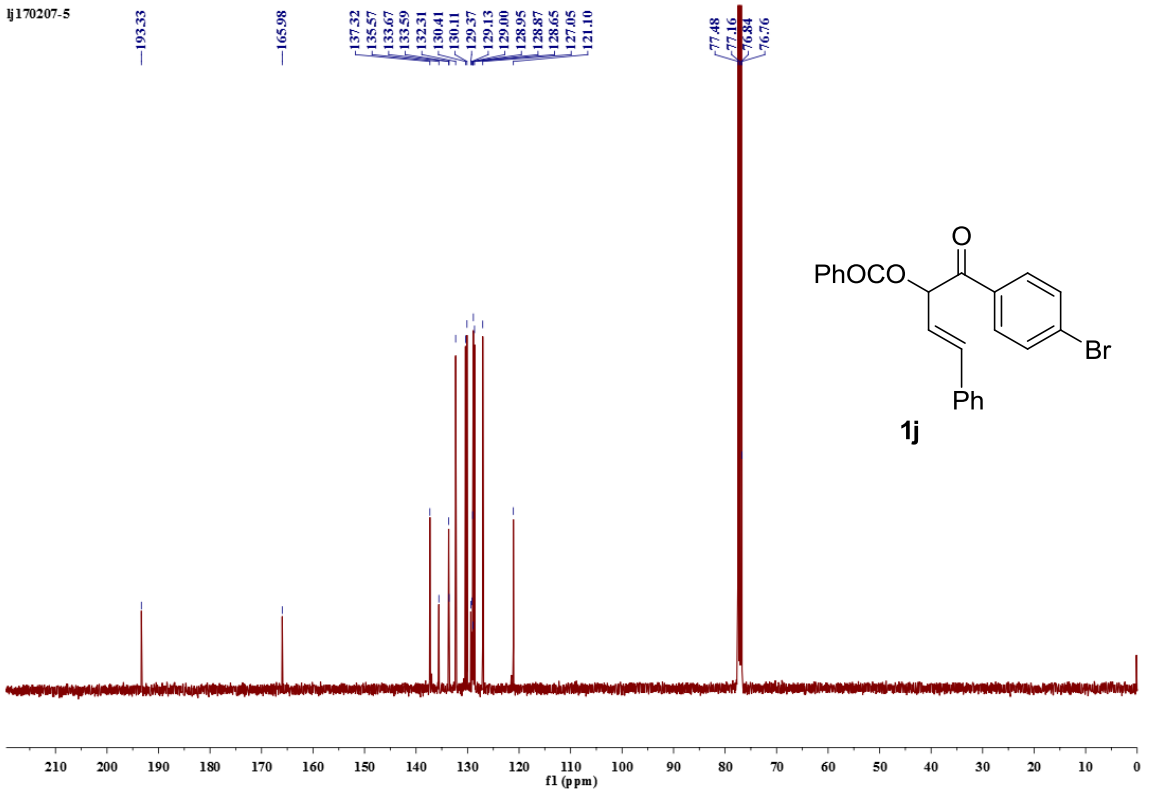
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Br
Ph
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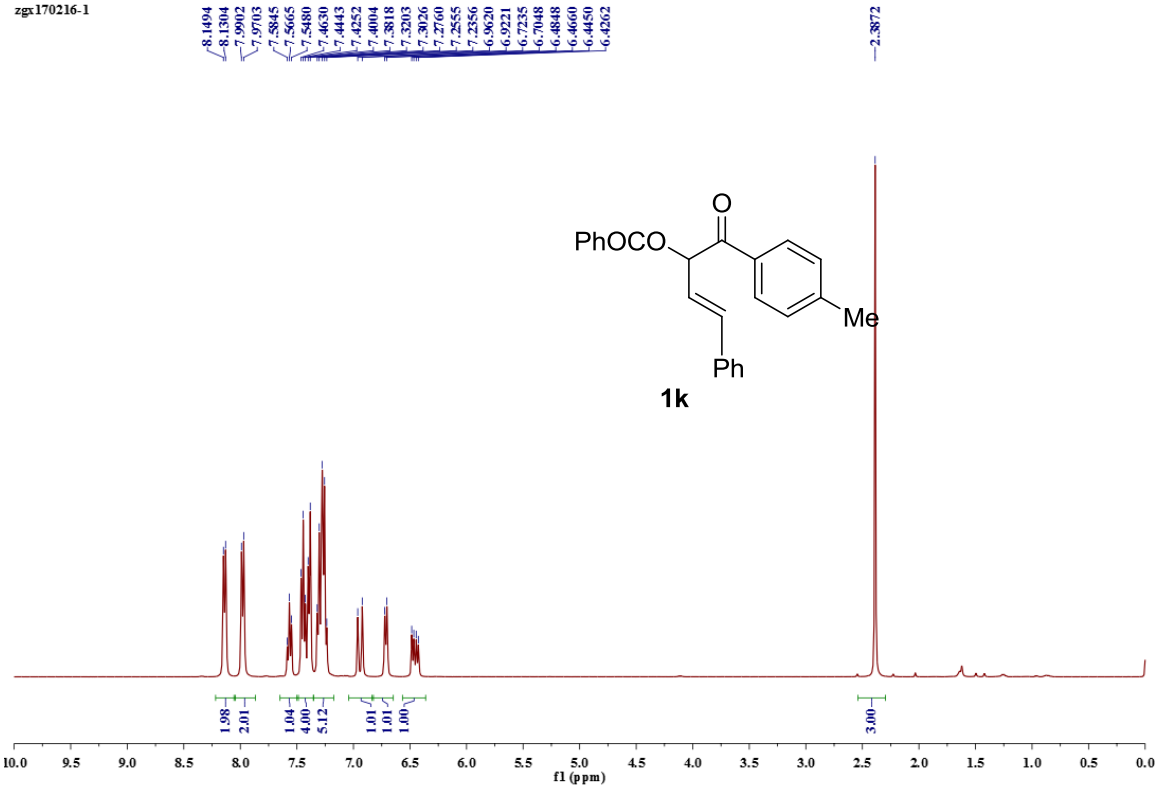
f1 (ppm)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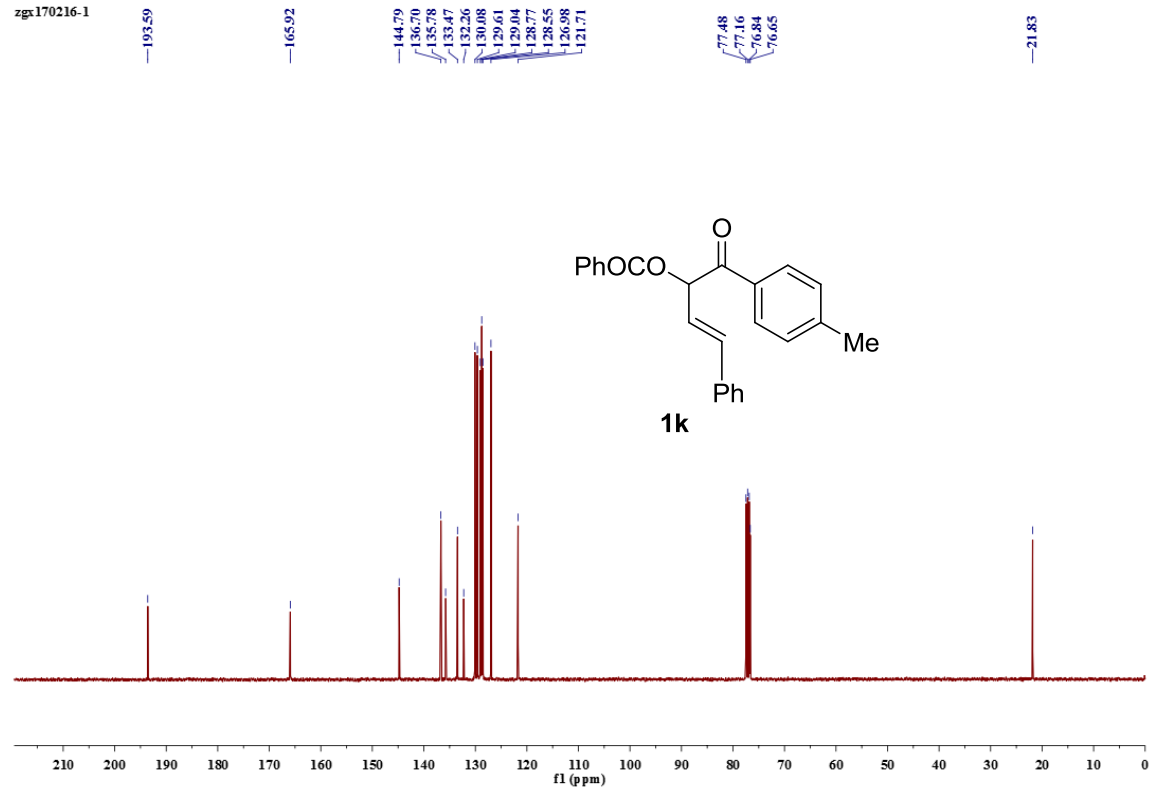
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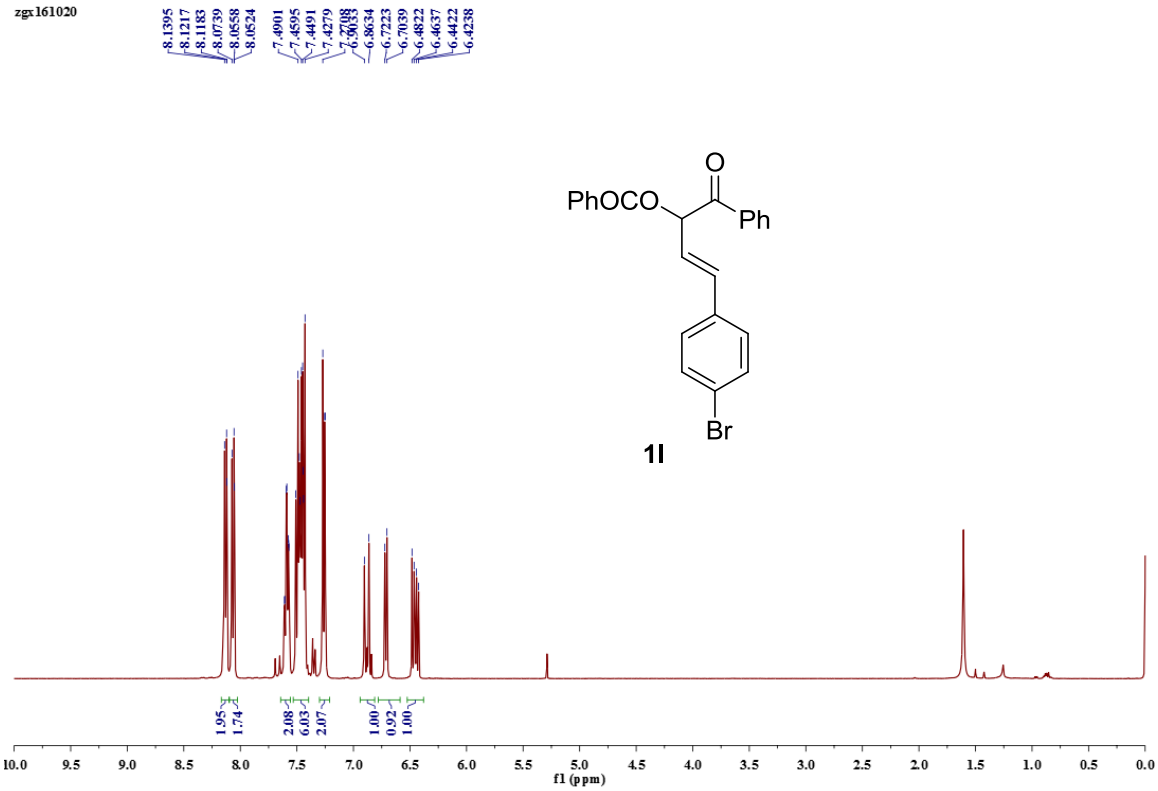
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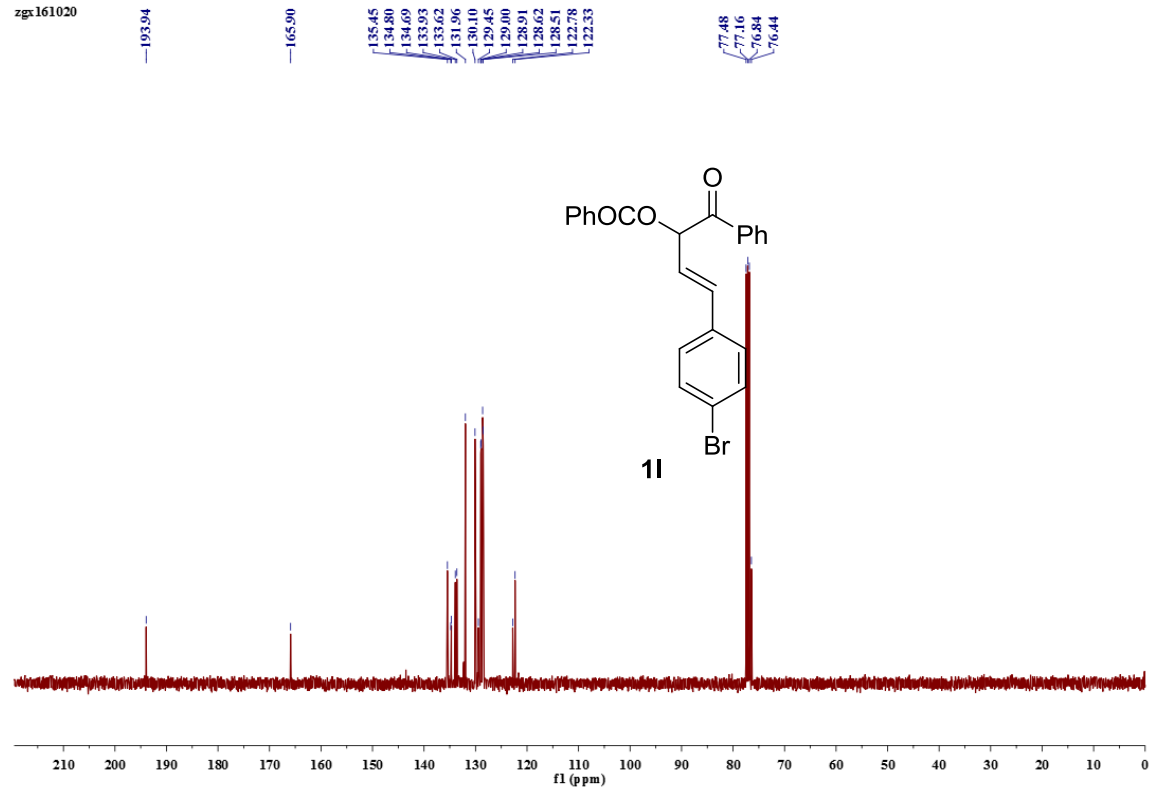
f1 (ppm)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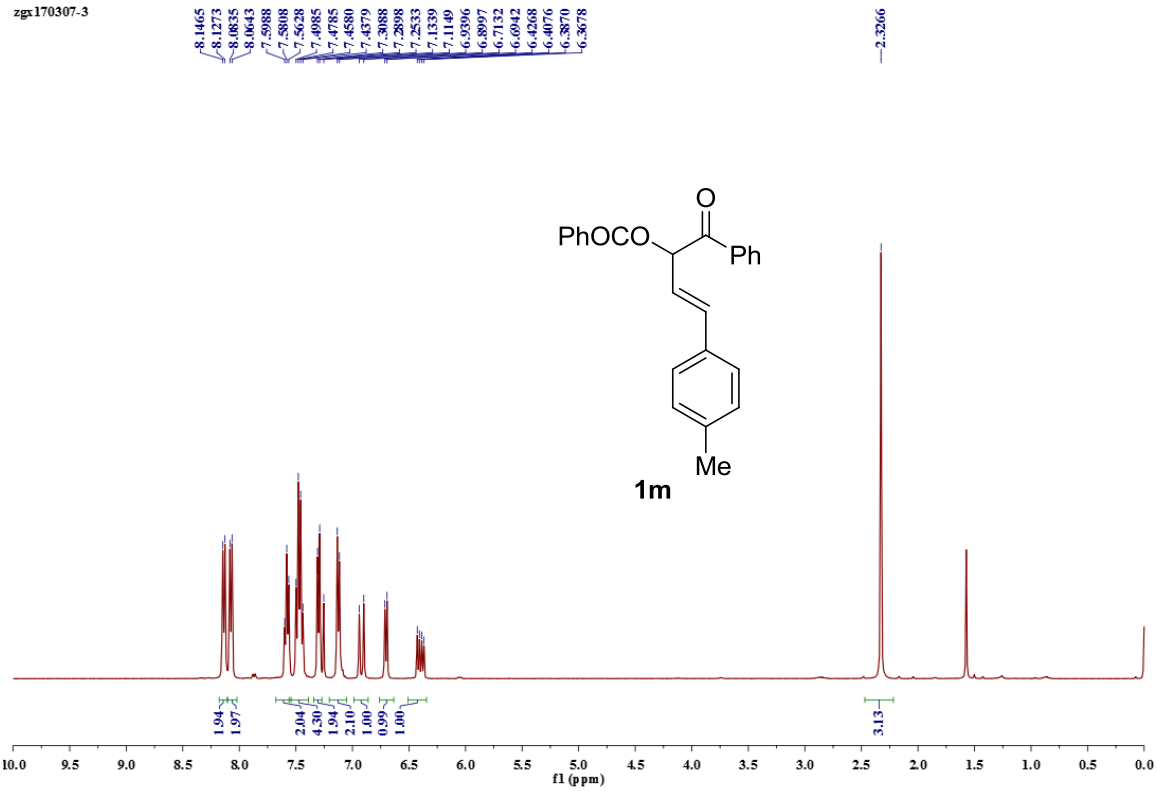
f1 (ppm)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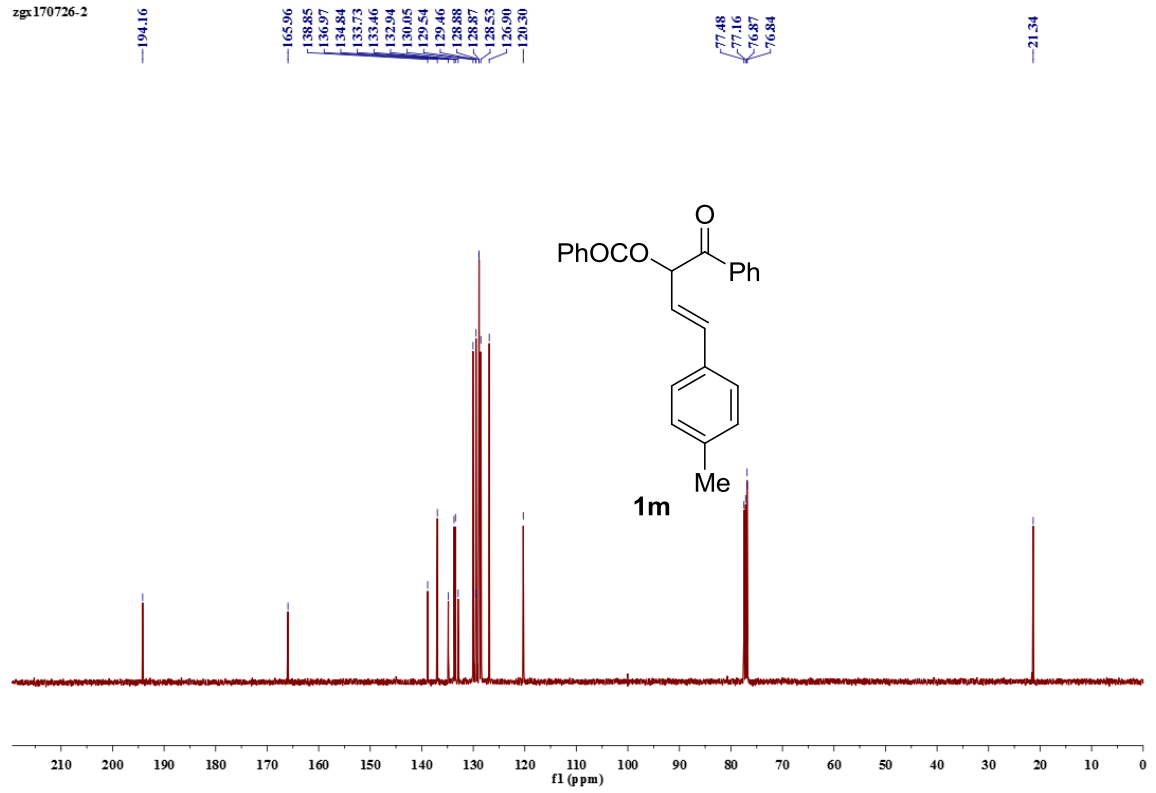
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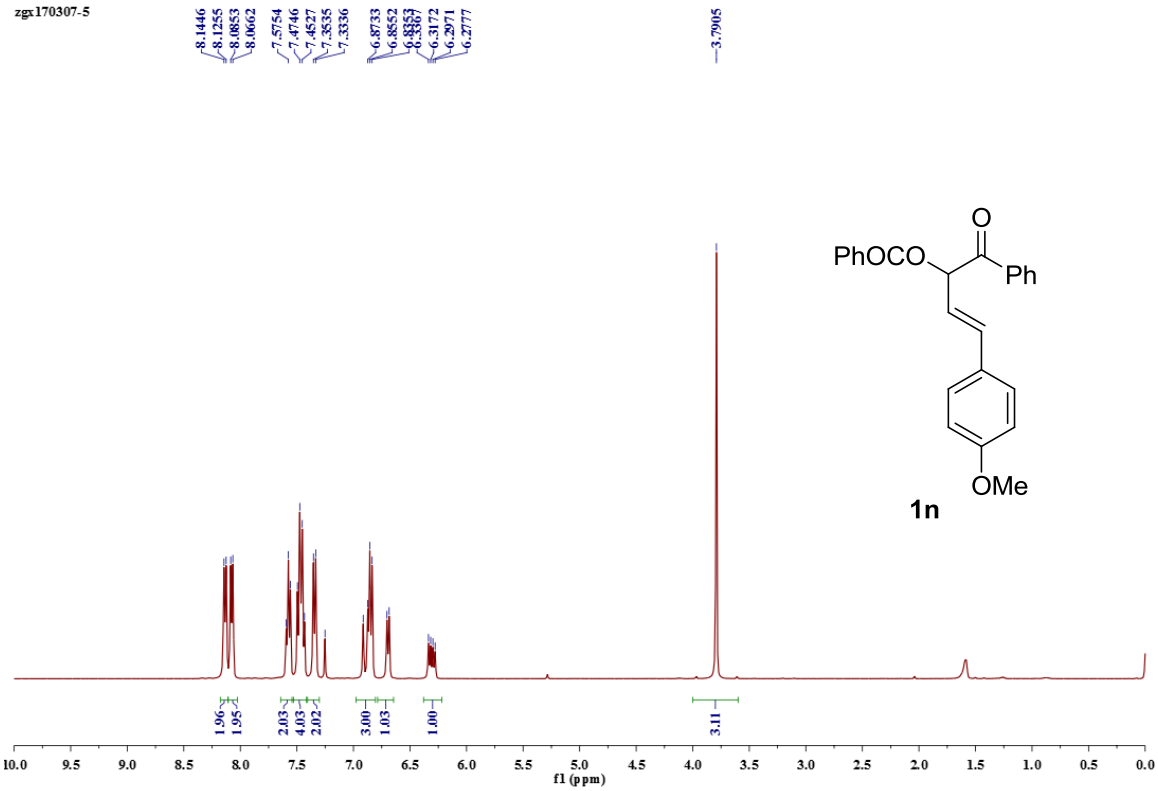
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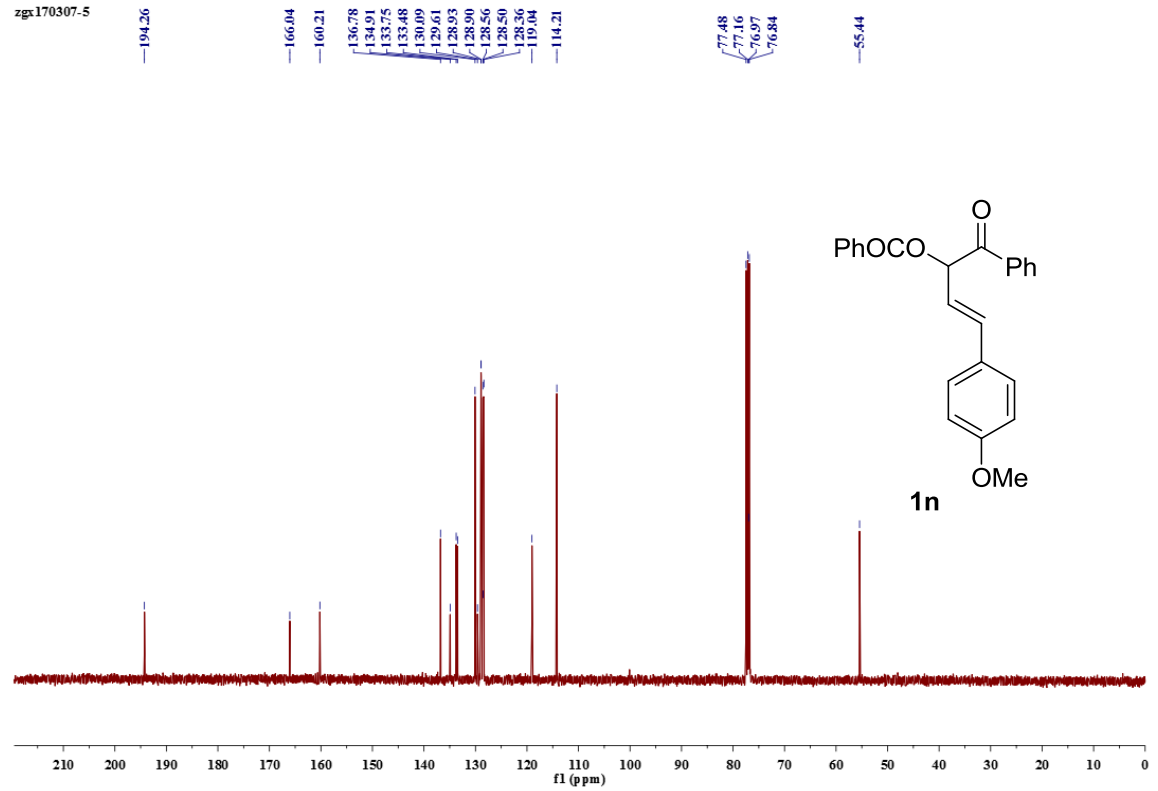
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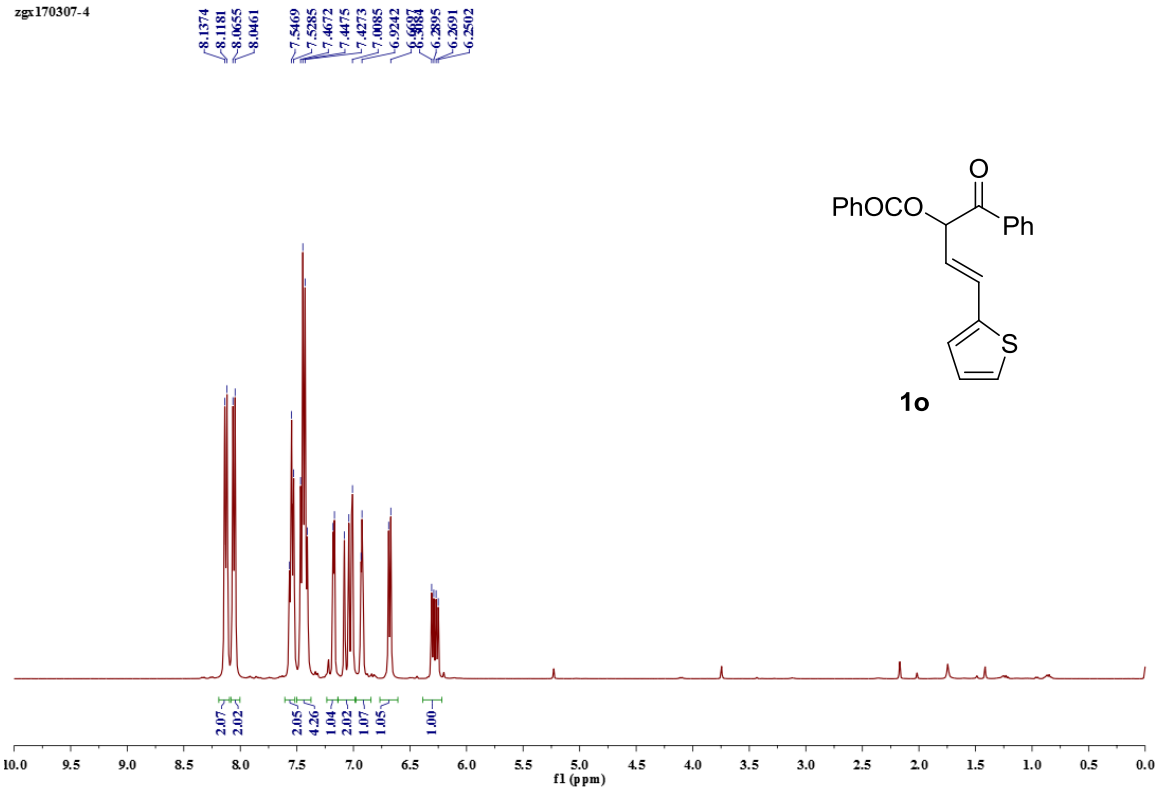
f1 (ppm)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1.04
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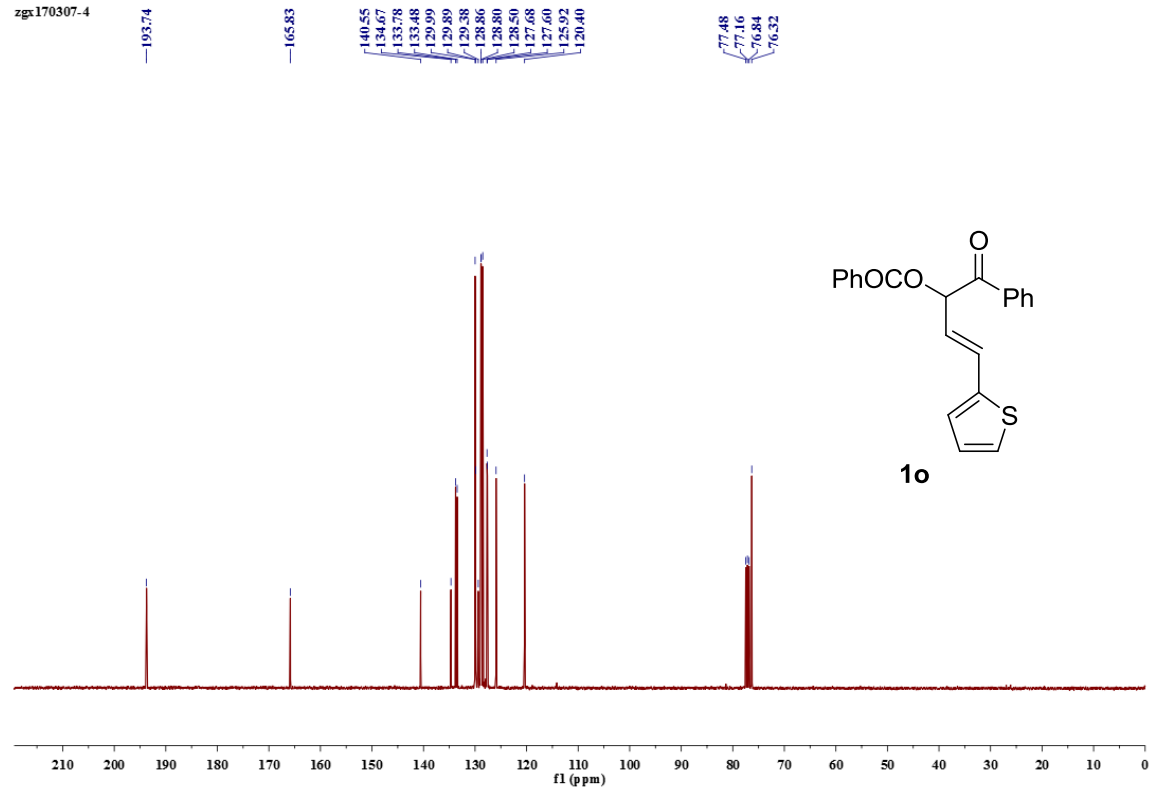
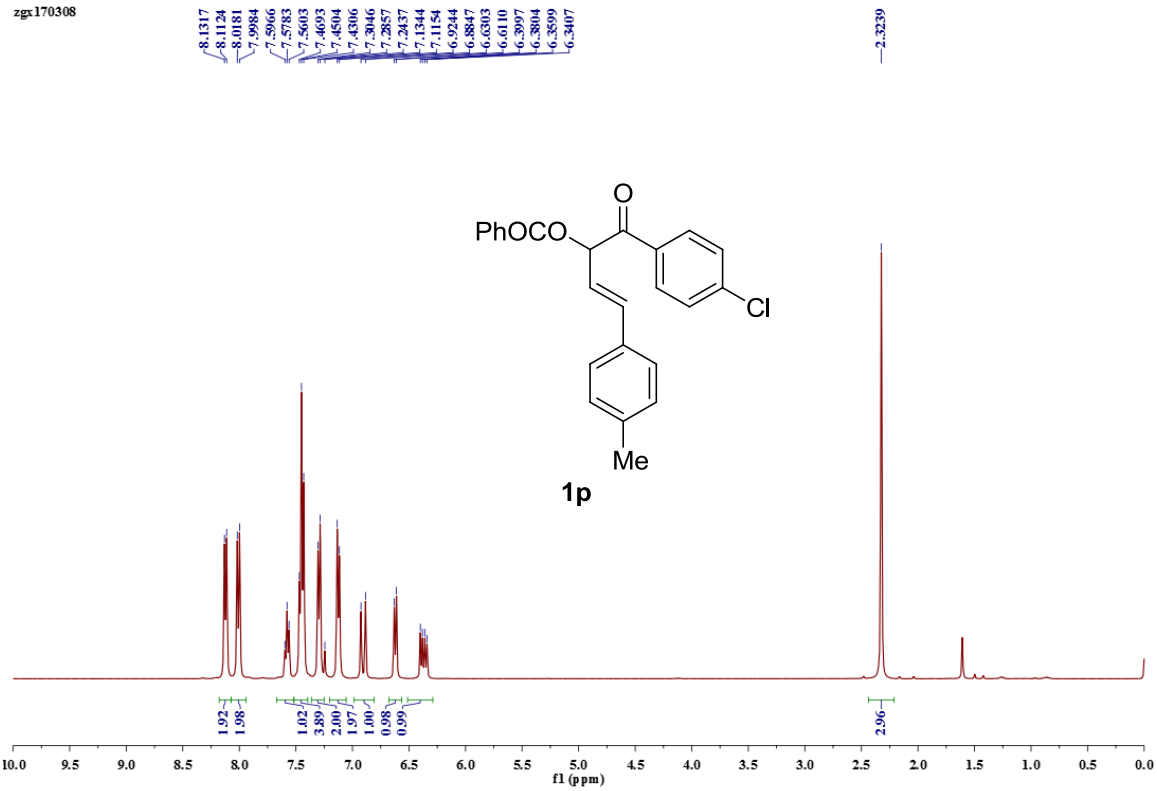
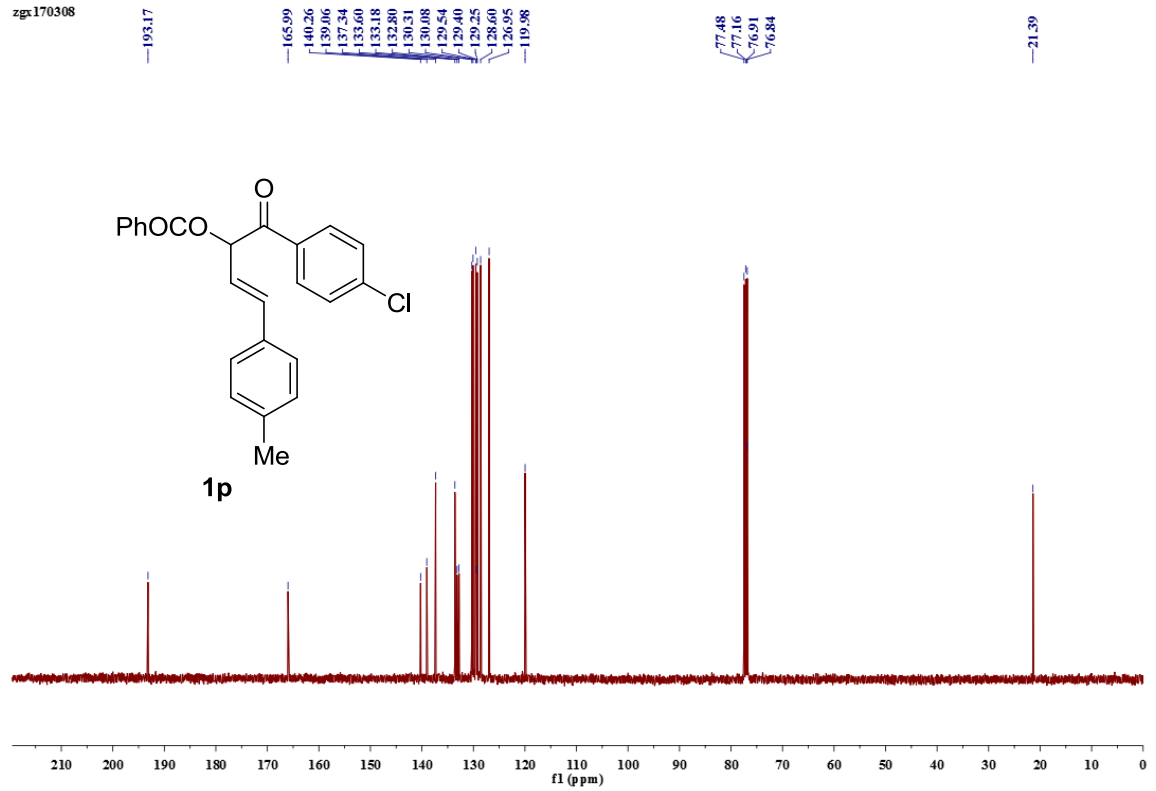
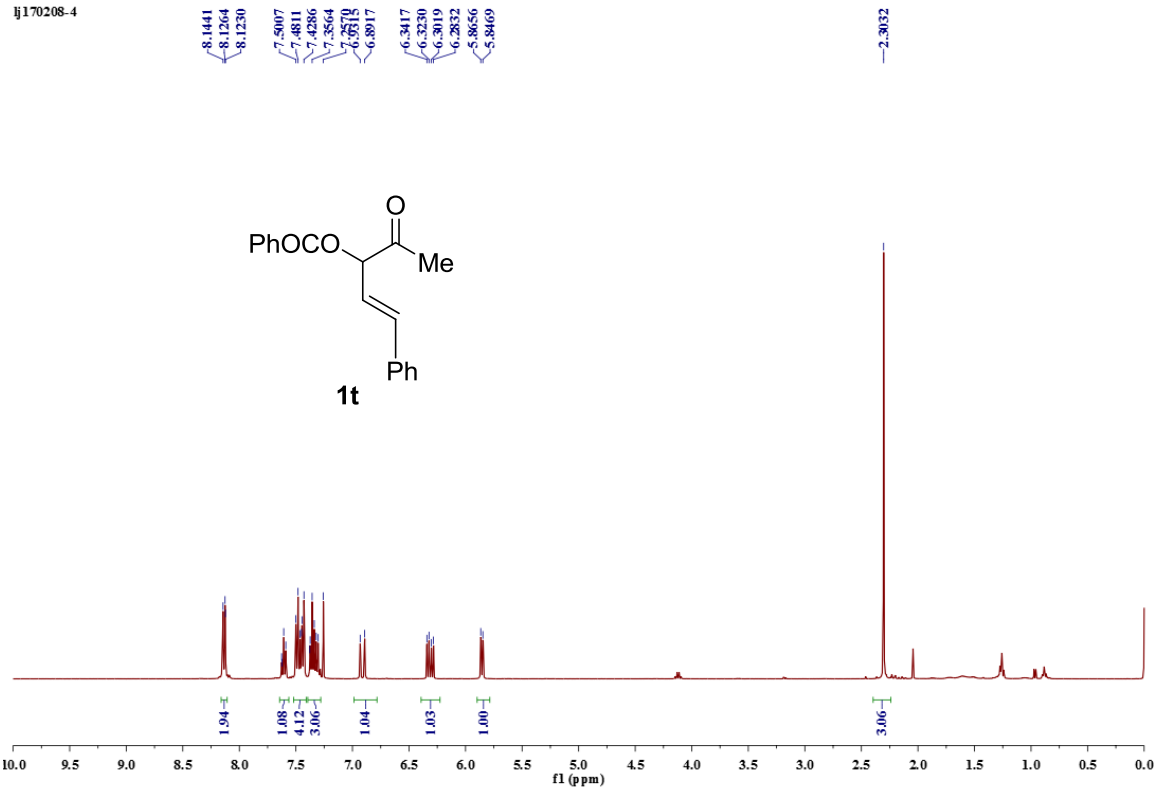
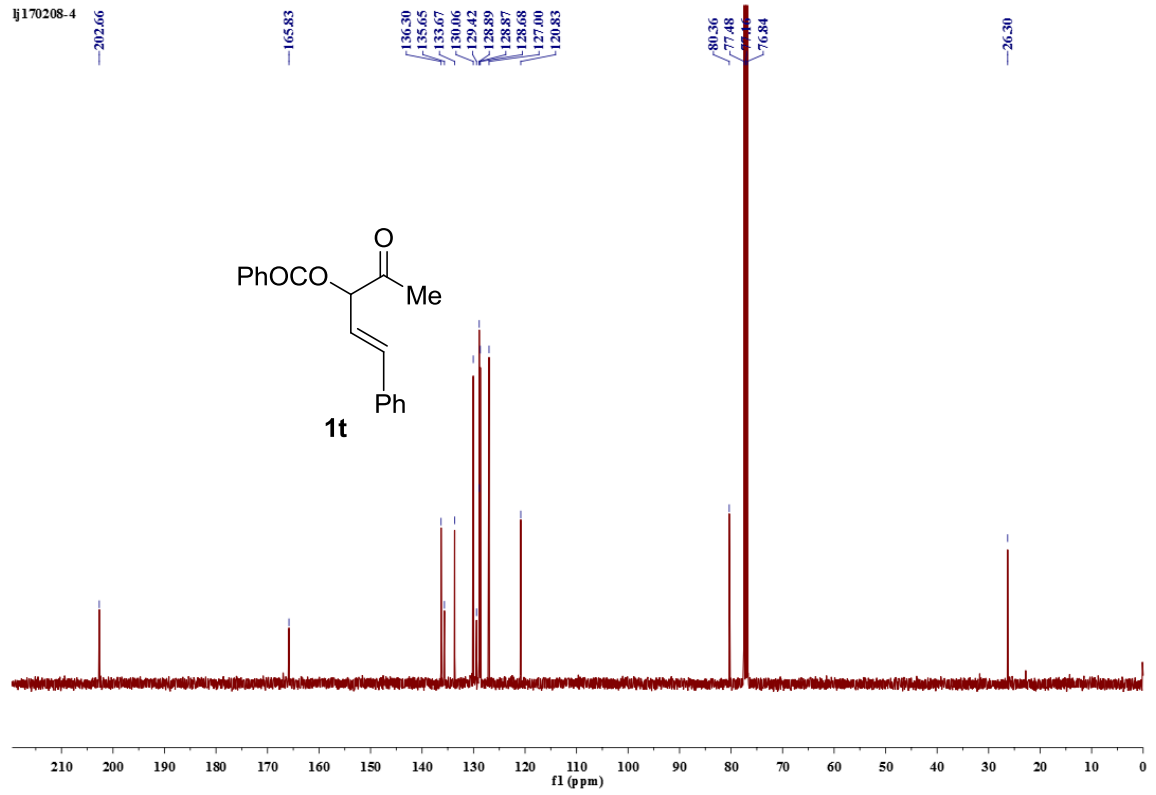
1.07
1.05
1.00
f1 (ppm)

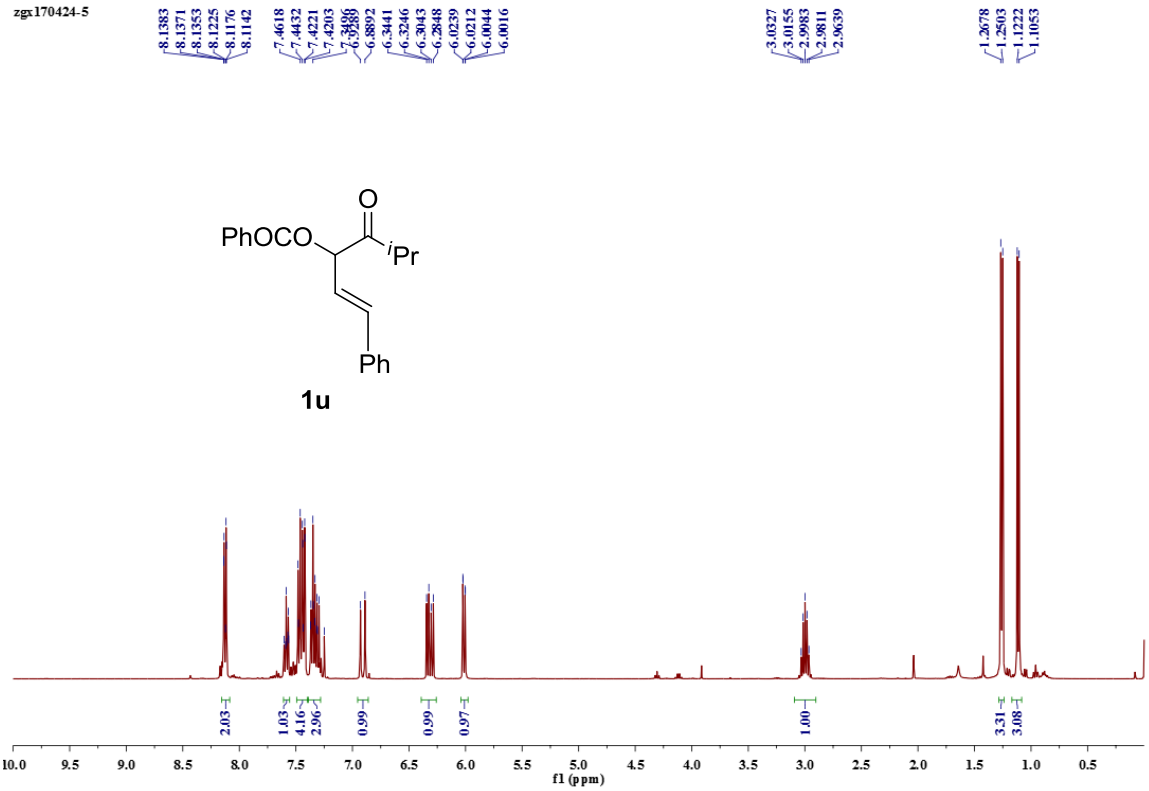

zgx170307-4
193.74
165.83
140.55
134.67
133.78
133.48
129.99
129.89
129.38
128.86
128.80
128.50
127.68
127.60
125.92
120.40
77.48
77.16
76.84
76.52
PhOCO
O
Ph
S
1o
f1 (ppm)

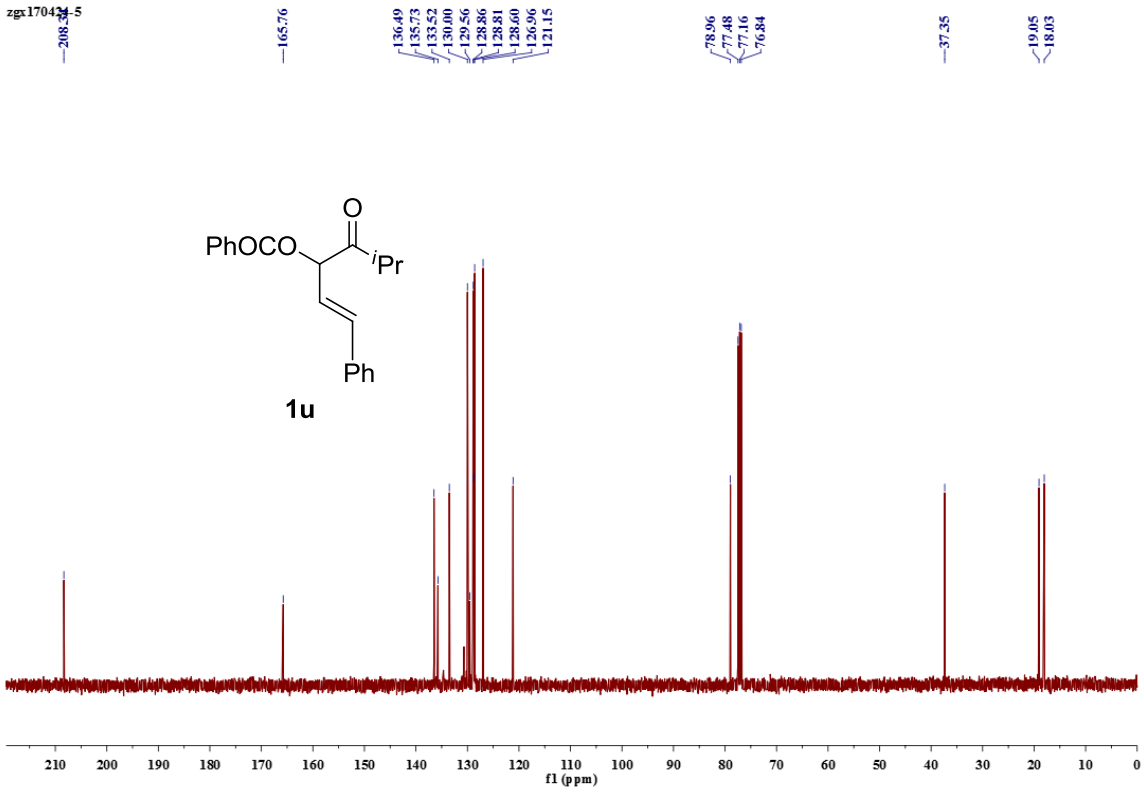

zgx170308
8.1317
8.1124
8.0181
7.9984
7.5966
7.5783
7.5603
7.4693
7.4504
7.4306
7.3046
7.2857
7.2437
7.1344
7.1154
6.9244
6.8847
6.6303
6.6110
6.3997
6.3804
6.3599
6.3407
2.3239
PhOCO
O
Cl
Me
1p
1.92
1.98
1.02
3.89
2.00
1.97
1.00
0.98
0.99
2.96
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

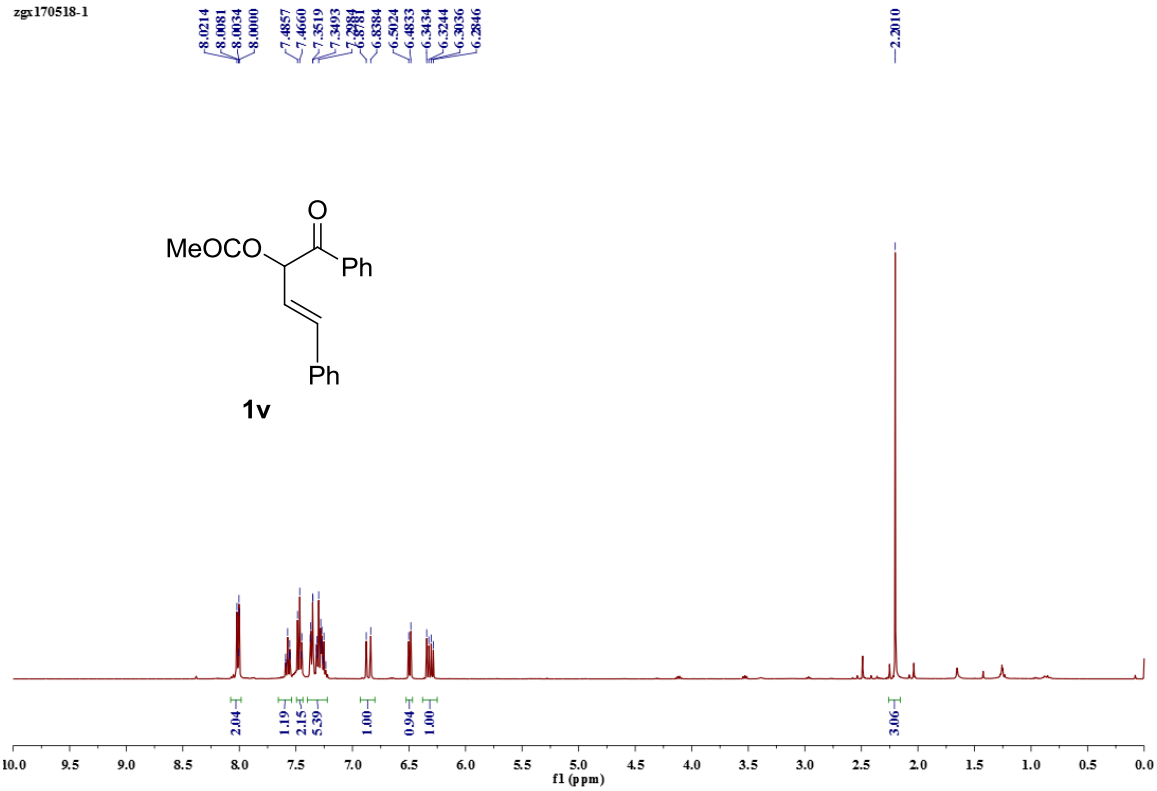

zgx170308
193.17
165.99
140.26
139.06
137.34
133.60
133.18
132.80
130.31
130.08
129.54
129.40
129.25
128.60
126.95
119.98
77.48
77.16
76.91
76.84
21.39
PhOCO
O
Cl
Me
1p
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

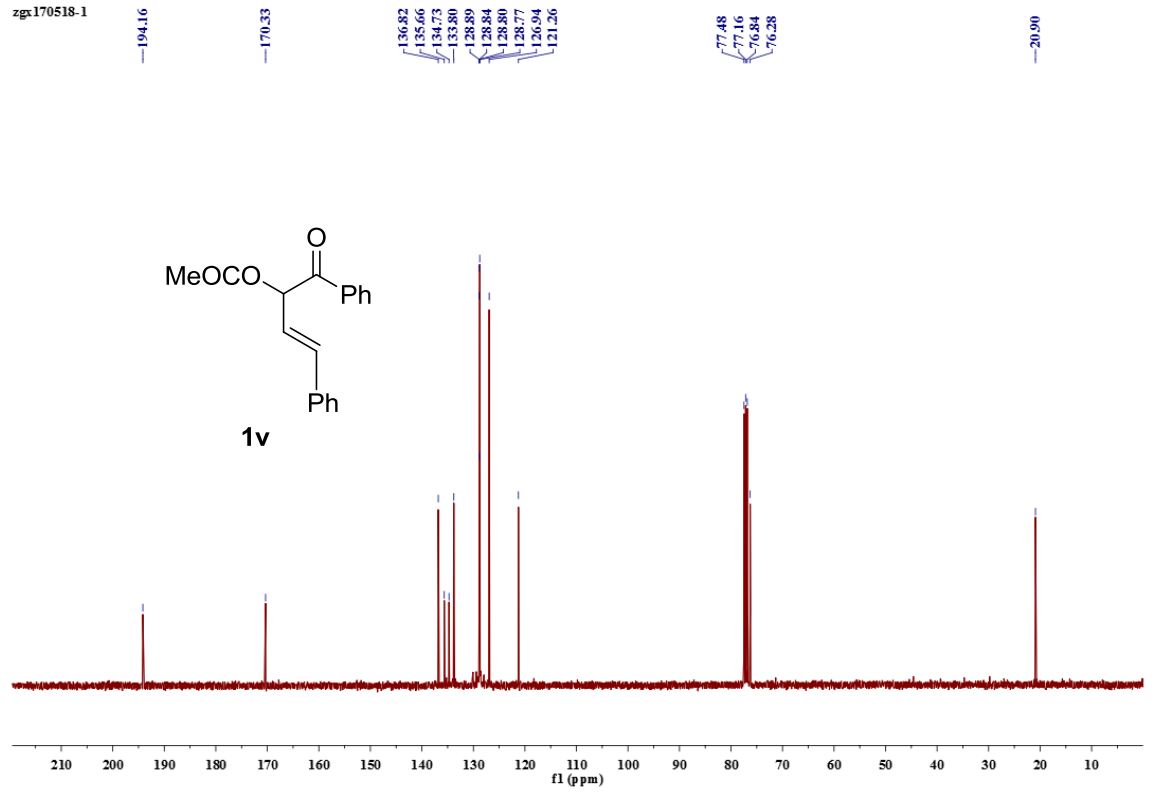

lj170208-4
8.1441
8.1264
8.1230
7.5007
7.4811
7.4286
7.3564
7.2570
6.9315
6.8917
6.3417
6.3230
6.3019
6.2832
5.8656
5.8469
2.3032
PhOCO
O
Me
Ph
1t
1.94
1.08
4.12
3.06
1.04
1.03
1.00
3.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

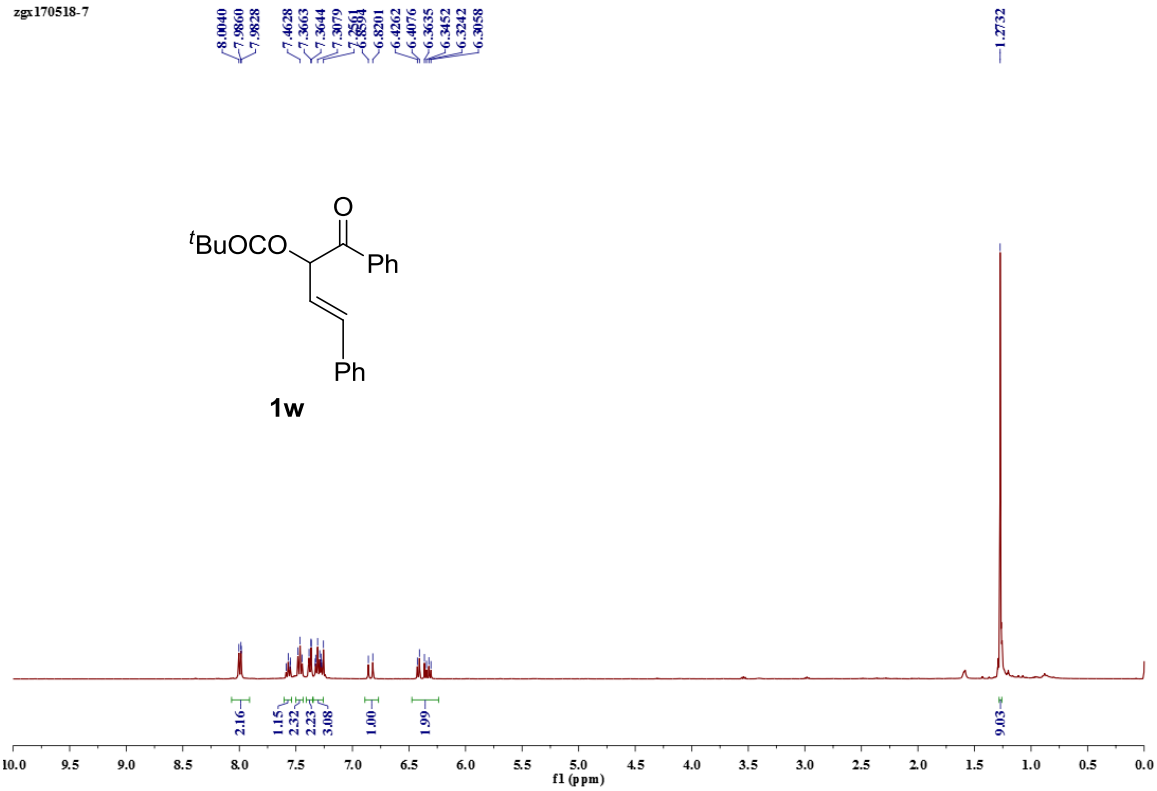

lj170208-4
202.66
165.83
136.30
135.65
133.67
130.06
129.42
128.89
128.87
128.68
127.00
120.83
80.36
77.48
76.84
26.30
PhOCO
O
Me
Ph
1t
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

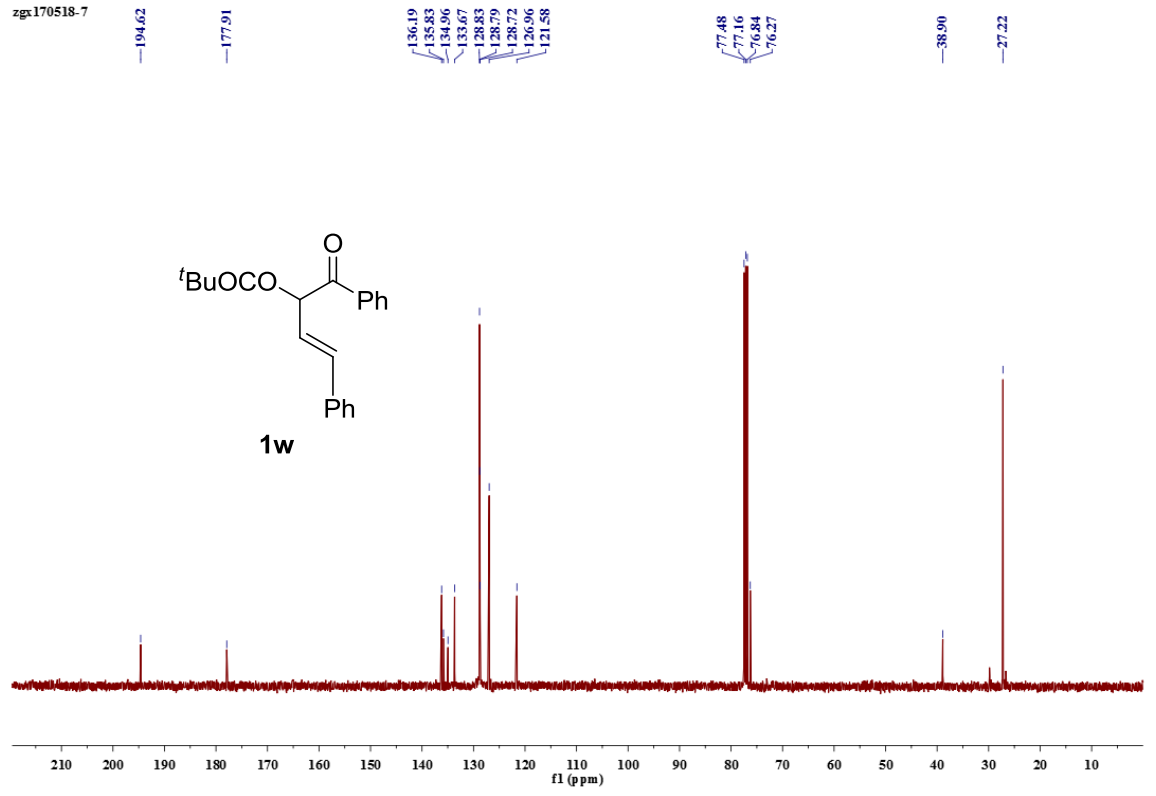

zgx170424-5
8.1383
8.1371
8.1353
8.1225
8.1176
8.1142
7.4618
7.4432
7.4221
7.4203
6.8892
6.3441
6.3246
6.3043
6.2848
6.0239
6.0212
6.0044
6.0016
3.0327
3.0155
2.9983
2.9811
2.9639
1.2678
1.2503
1.1222
1.1053
PhOCO
O
iPr
Ph
1u
2.03
1.03
4.16
2.96
0.99
0.99
0.97
1.00
3.31
3.08
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

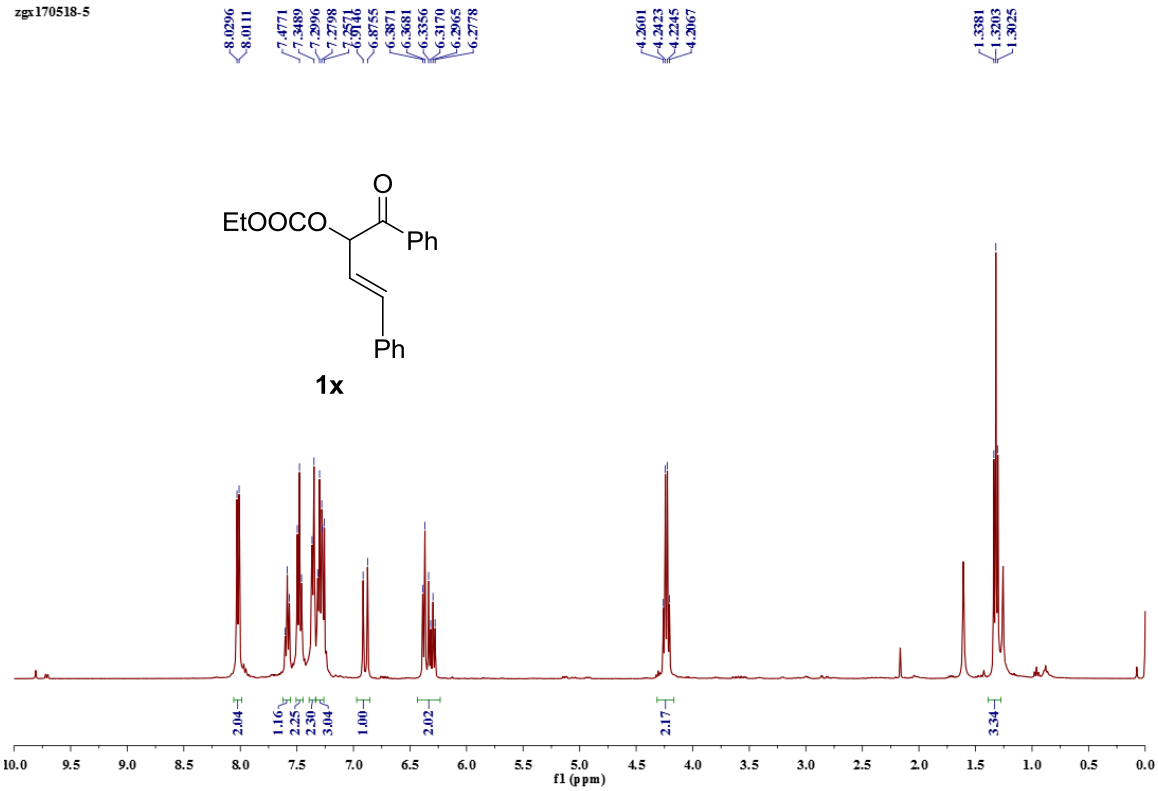

zgx170424-5
208.33
165.76
136.49
135.73
133.52
130.00
129.56
128.86
128.81
128.60
126.96
121.15
78.96
77.48
77.16
76.84
37.35
19.05
18.03
PhOCO
O
iPr
Ph
1u
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

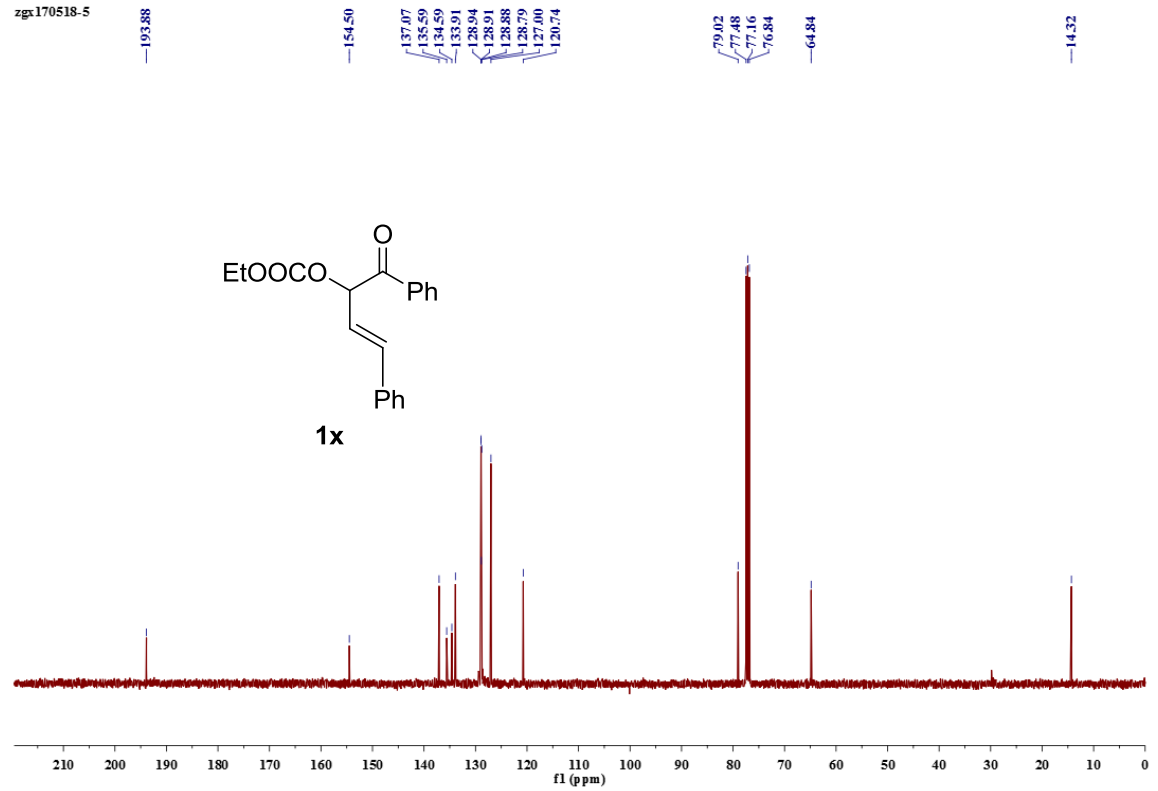

zgx170518-1
8.0214
8.0081
8.0034
8.0000
7.4857
7.4660
7.3519
7.3493
6.8384
6.5924
6.4833
6.3434
6.3244
6.3036
6.2846
2.2010
MeOCO
O
Ph
Ph
1v
2.04
1.19
2.15
5.39
1.00
0.94
1.00
3.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

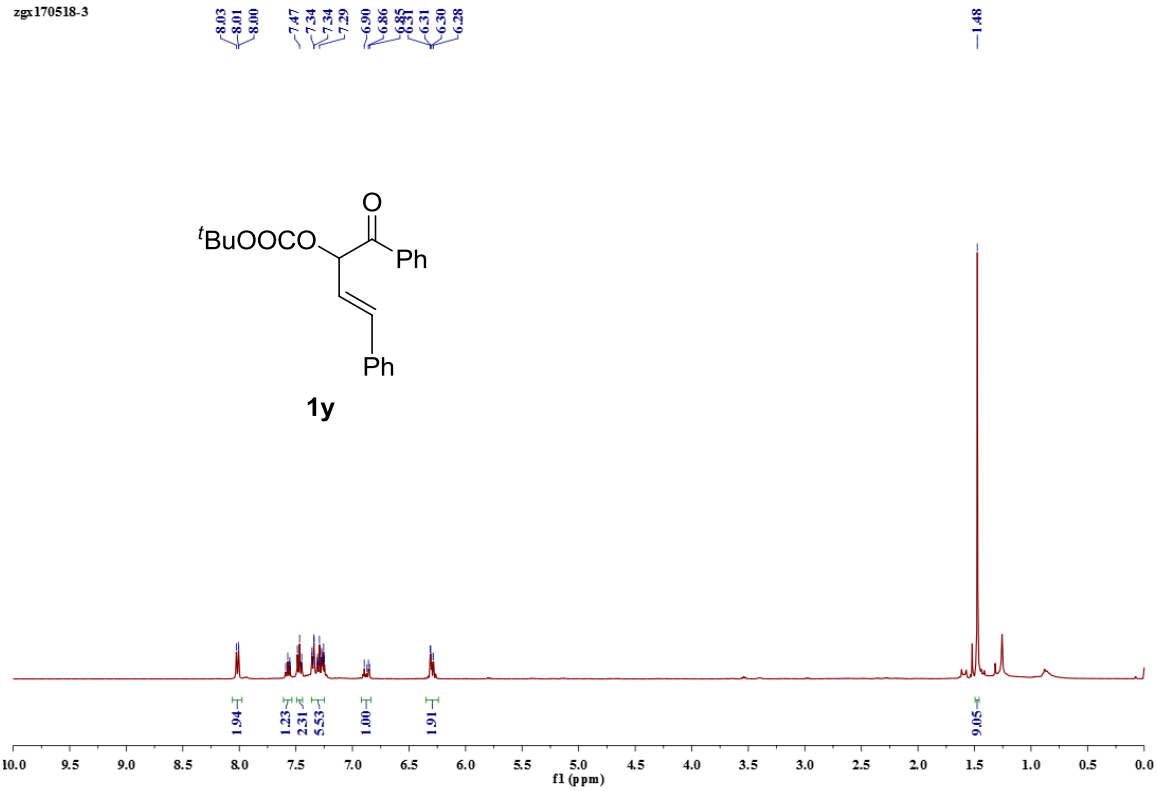

zgx170518-1
194.16
170.33
136.82
135.66
134.73
133.80
128.89
128.84
128.80
128.77
126.94
121.26
77.48
77.16
76.84
76.28
20.90
MeOCO
O
Ph
Ph
1v
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

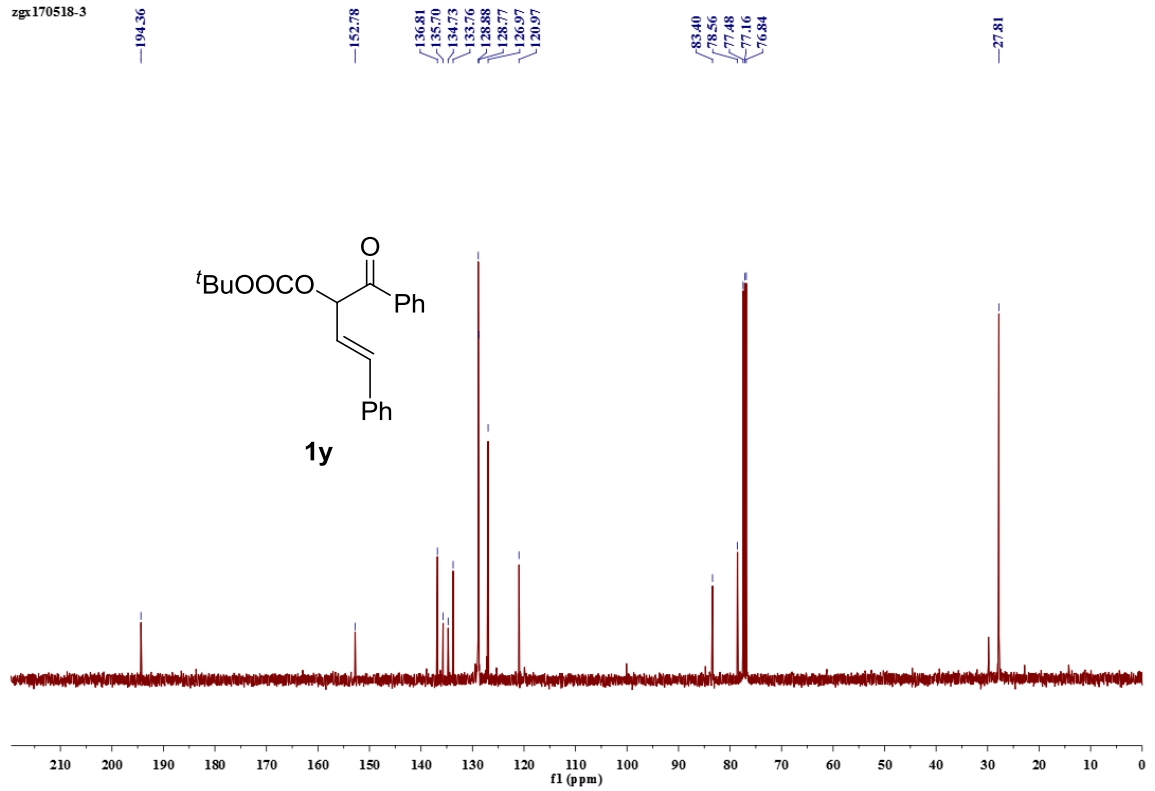

zgx170518-7
8.0040
7.9860
7.9828
7.4628
7.3663
7.3644
7.3079
6.8201
6.4262
6.4076
6.3635
6.3452
6.3242
6.3058
1.2732
O
tBuOCO
Ph
Ph
1w
2.16
1.15
2.32
2.23
3.08
1.00
1.99
9.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


zgx170518-7
194.62
177.91
136.19
135.83
134.96
133.67
128.83
128.79
128.72
126.96
121.58
77.48
77.16
76.84
76.27
38.90
27.22
O
tBuOCO
Ph
Ph
1w
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


zgx170518-5
8.0296
8.0111
7.4771
7.3489
7.2996
7.2798
7.2571
6.9146
6.8755
6.3871
6.3681
6.3356
6.3170
6.2965
6.2778
4.2601
4.2423
4.2245
4.2067
1.3381
1.3203
1.3025
EtOOCO
O
Ph
Ph
1x
2.04
1.16
2.25
2.30
3.04
1.00
2.02
2.17
3.34
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


zgx170518-5
193.88
154.50
137.07
135.59
134.59
133.91
128.94
128.91
128.88
128.79
127.00
120.74
79.02
77.48
77.16
76.84
64.84
14.32
EtOOCO
O
Ph
Ph
1x
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


zgx170518-3
8.03
8.01
8.00
7.47
7.34
7.34
7.29
6.90
6.86
6.31
6.30
6.28
1.48
O
tBuOOCO
Ph
Ph
1y
1.94
1.23
2.31
5.53
1.00
1.91
9.05
f1 (ppm)


zgx170518-3
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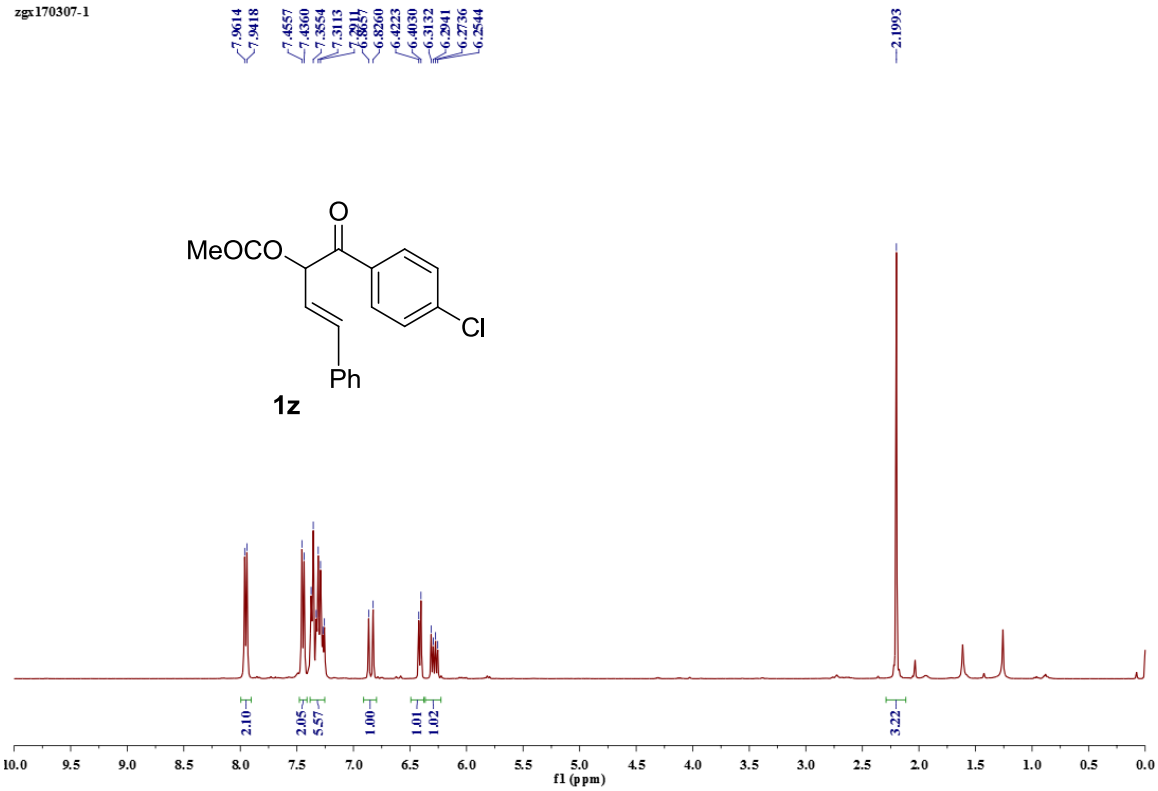
152.78
136.81
135.70
134.73
133.76
128.88
128.77
126.97
120.97
83.40
78.56
77.48
77.16
76.84
27.81
O
tBuOOCO
Ph
Ph
1y
f1 (ppm)


zgx170307-1
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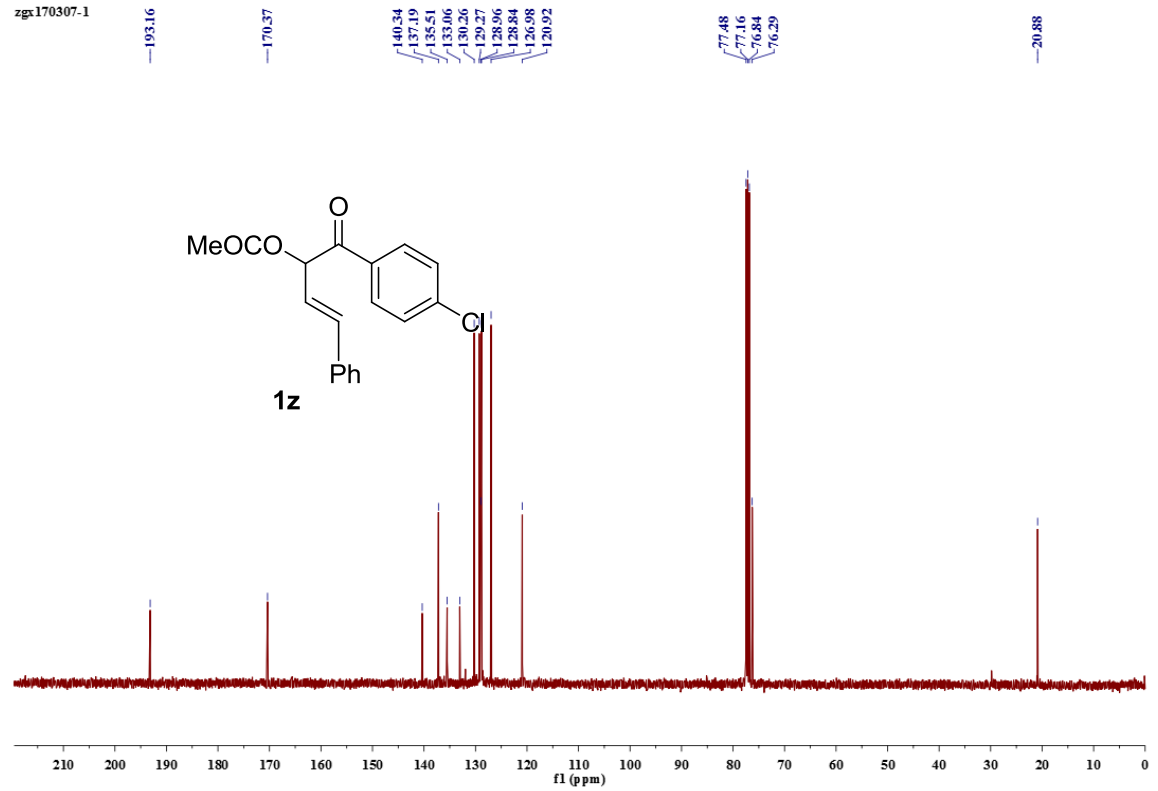
7.4557
7.4360
7.3554
7.3113
6.8260
6.4223
6.4030
6.3132
6.2941
6.2736
6.2544
2.1993
O
MeOCO
Cl
Ph
1z
2.10
2.05
5.57
1.00
1.01
1.02
3.22
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


zgx170307-1
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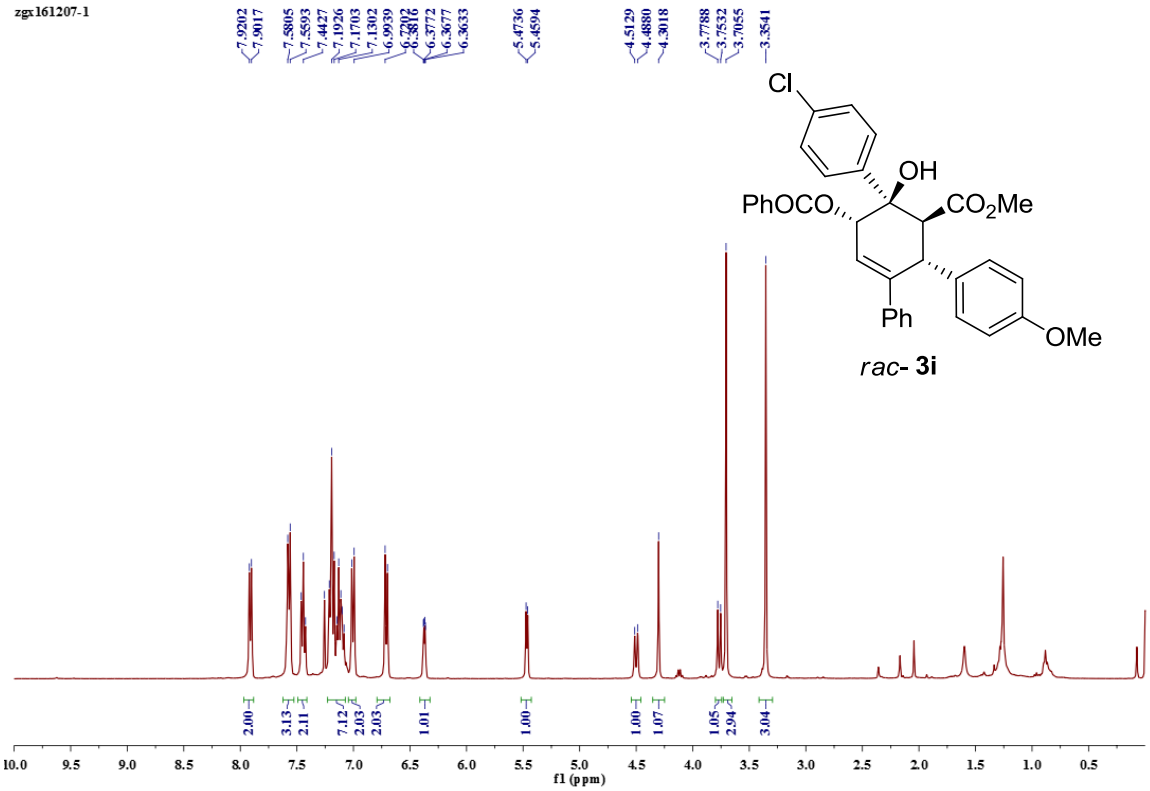
170.37
140.34
137.19
135.51
133.06
130.26
129.27
128.96
128.84
126.98
120.92
77.48
77.16
76.84
76.29
20.88
O
MeOCO
Cl
Ph
1z
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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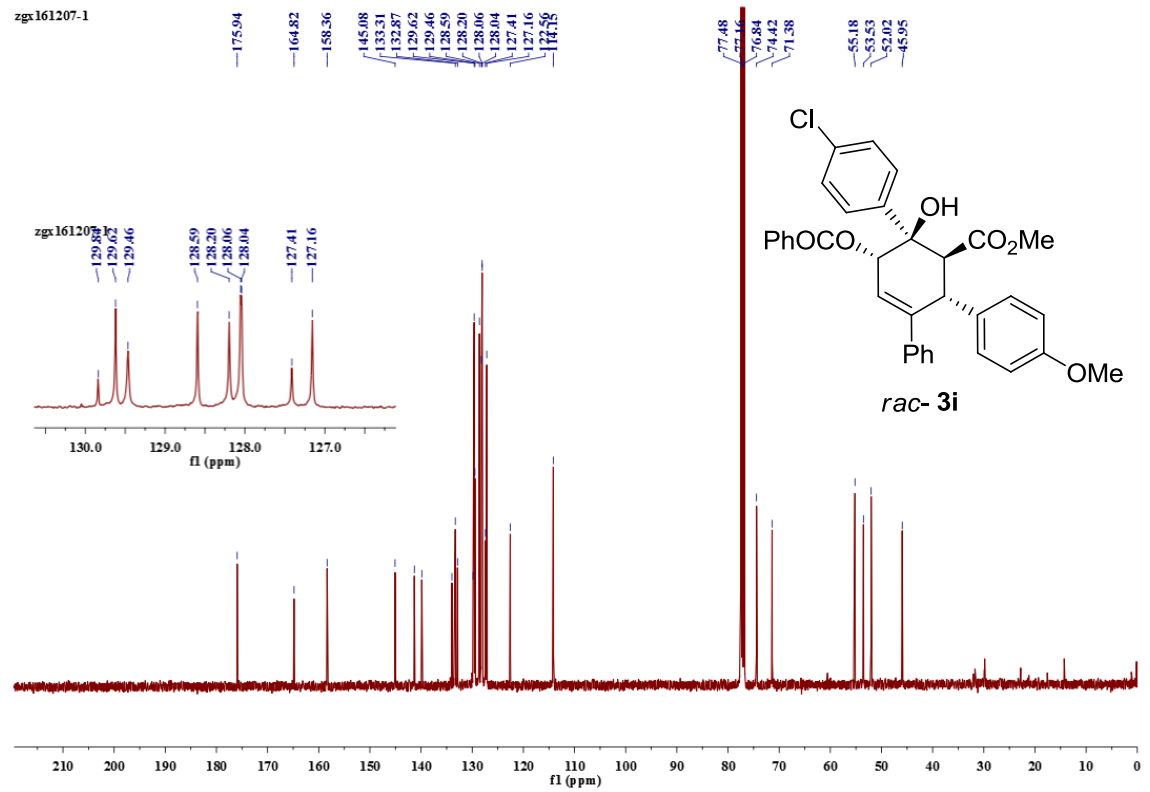
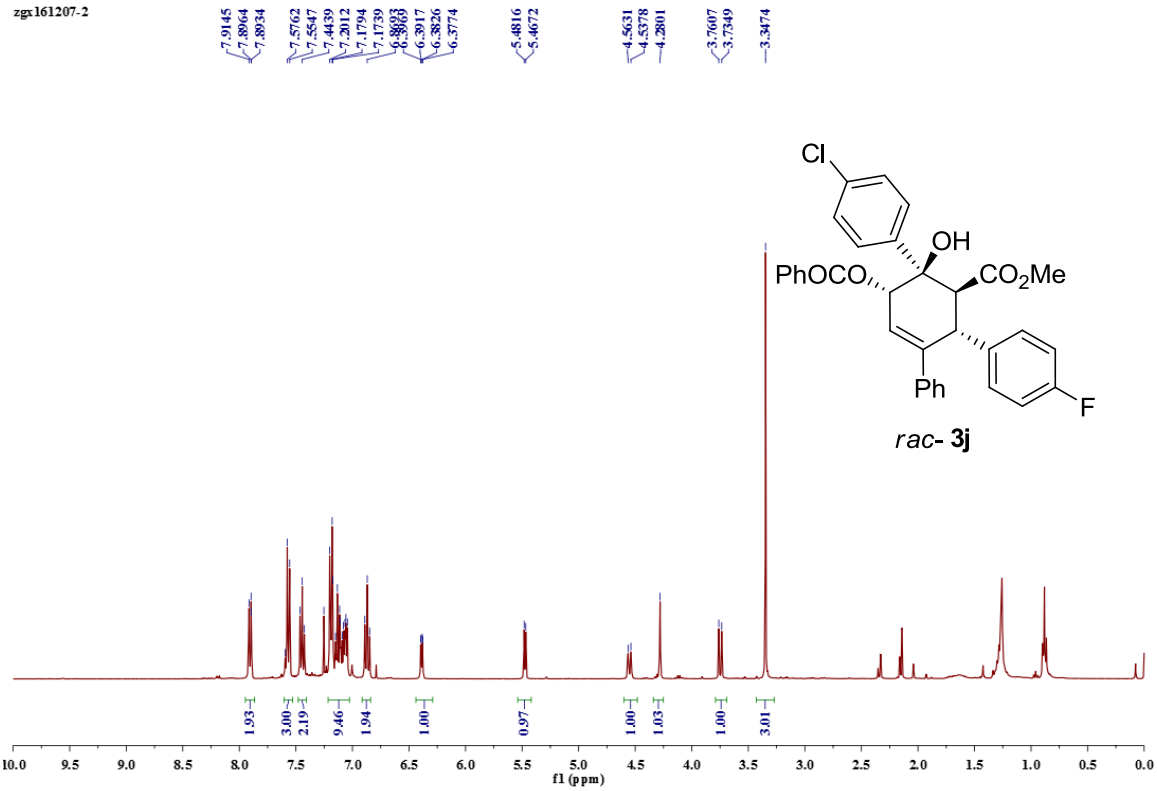
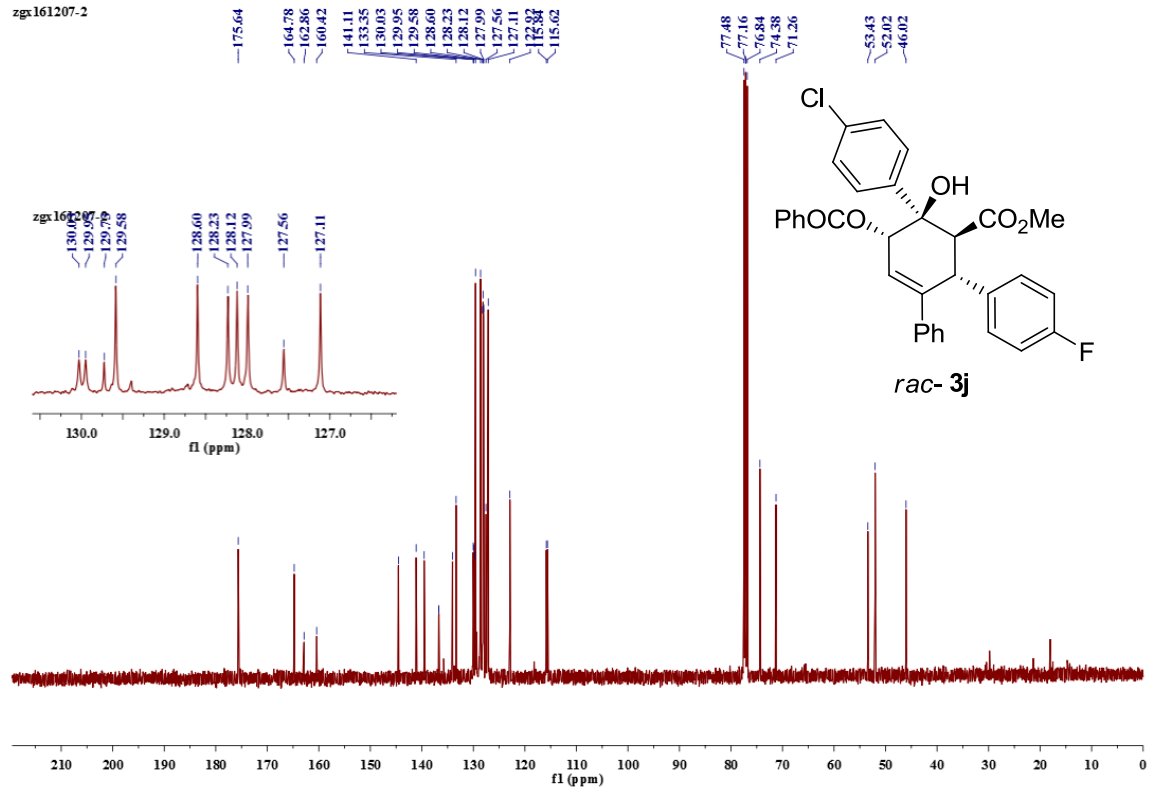
Cl
OH
PhOCO
CO2Me
Ph
OMe
rac- 3i
f1 (ppm)


zgx161207-1
Cl
OH
PhOCO
CO2Me
Ph
OMe
rac- 3i
f1 (ppm)


zgx161207-2
7.9145
7.8964
7.8934
7.5762
7.5547
7.4439
7.2012
7.1794
7.1739
6.3917
6.3826
6.3774
5.4816
5.4672
4.5631
4.5378
4.2801
3.7607
3.7349
3.3474
Cl
OH
PhOCO
CO2Me
Ph
F
rac- 3j
1.93
3.00
2.19
9.46
1.94
1.00
0.97
1.00
1.03
1.00
3.01
f1 (ppm)


zgx161207-2
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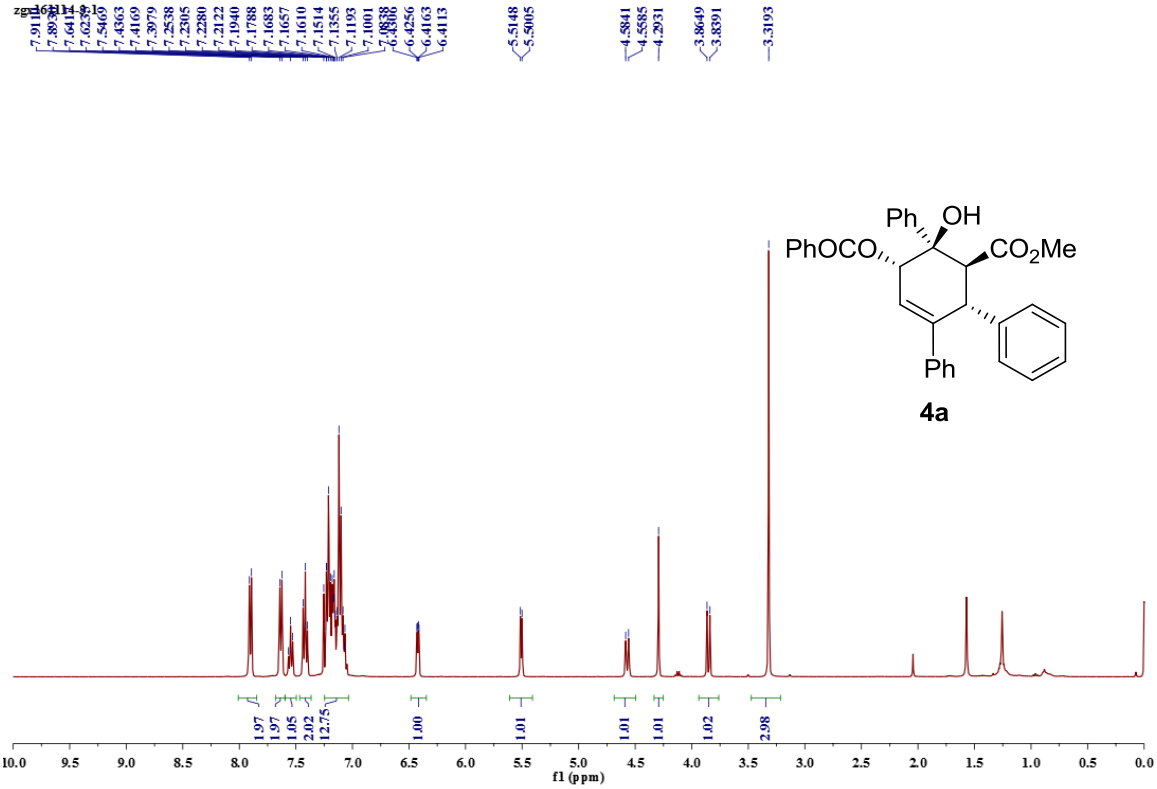
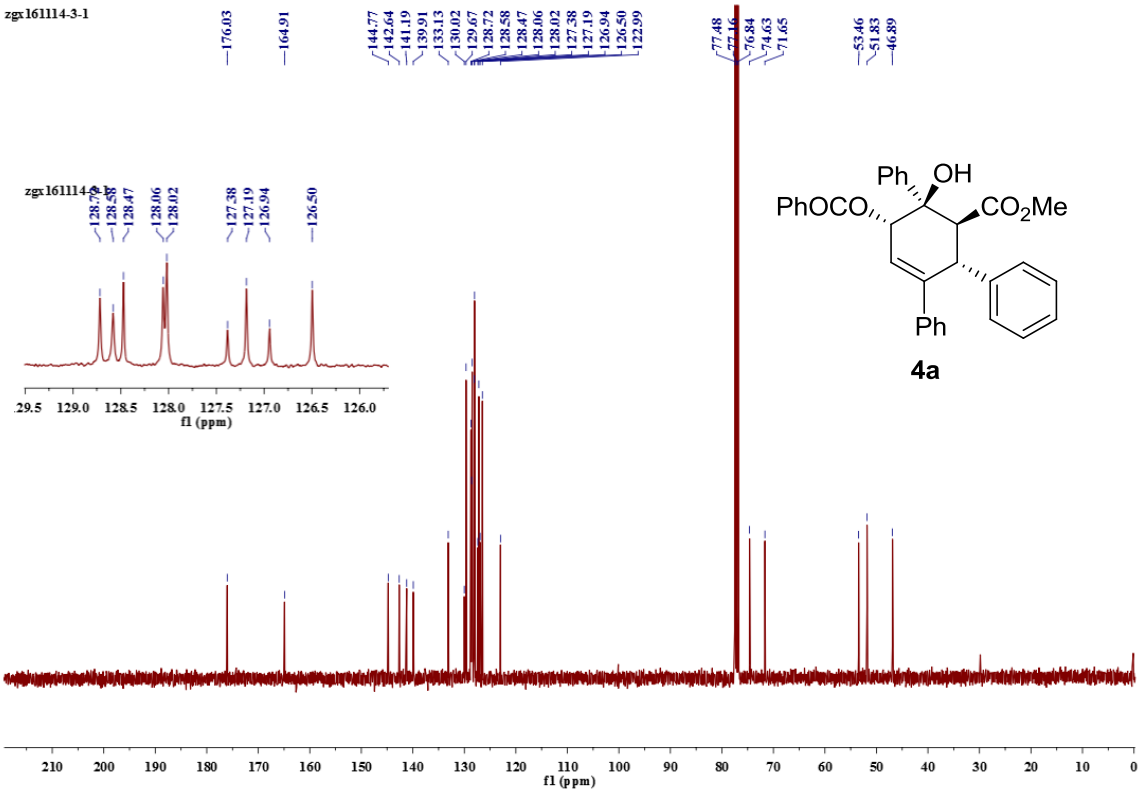
164.78
162.86
160.42
141.11
133.35
130.03
129.95
129.58
128.60
128.23
128.12
127.99
127.56
127.11
115.62
77.48
77.16
76.84
74.38
71.26
53.43
52.02
46.02
Cl
OH
PhOCO
CO2Me
Ph
F
rac- 3j
f1 (ppm)


Ph
OH
PhOCO
CO2Me
Ph
4a
fl (ppm)


zgx161114-3-1
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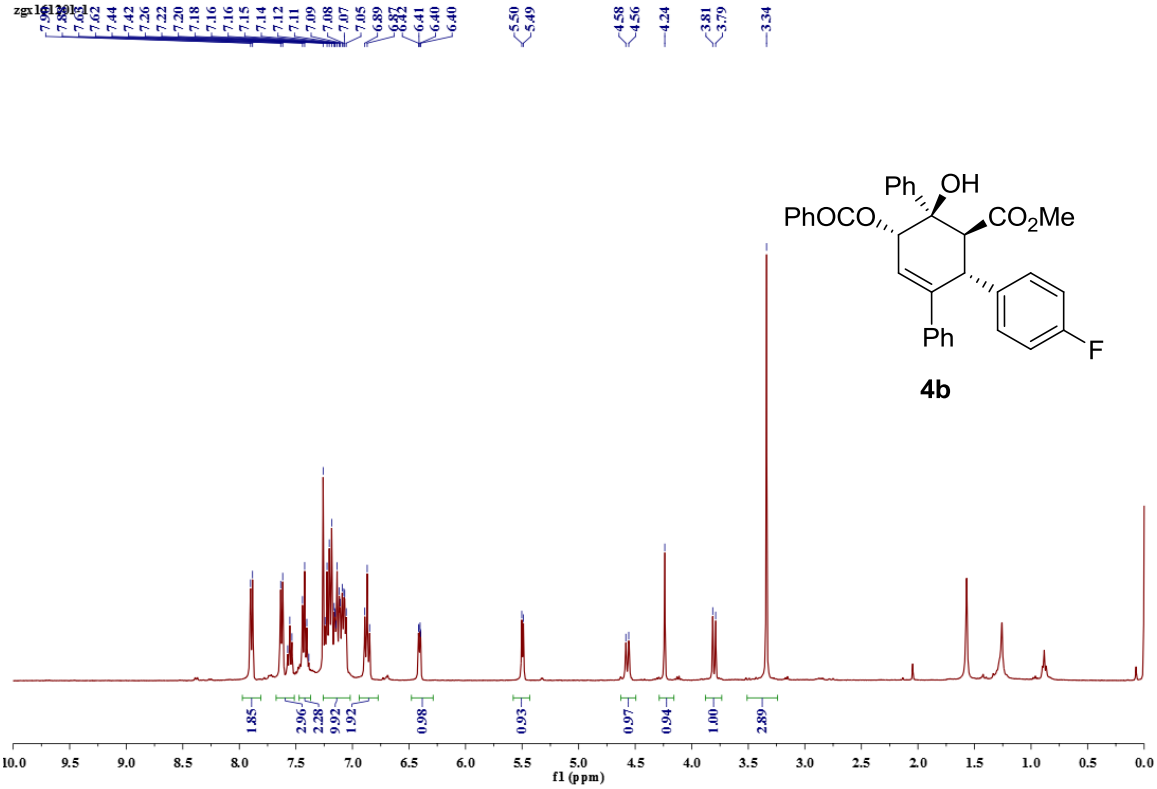
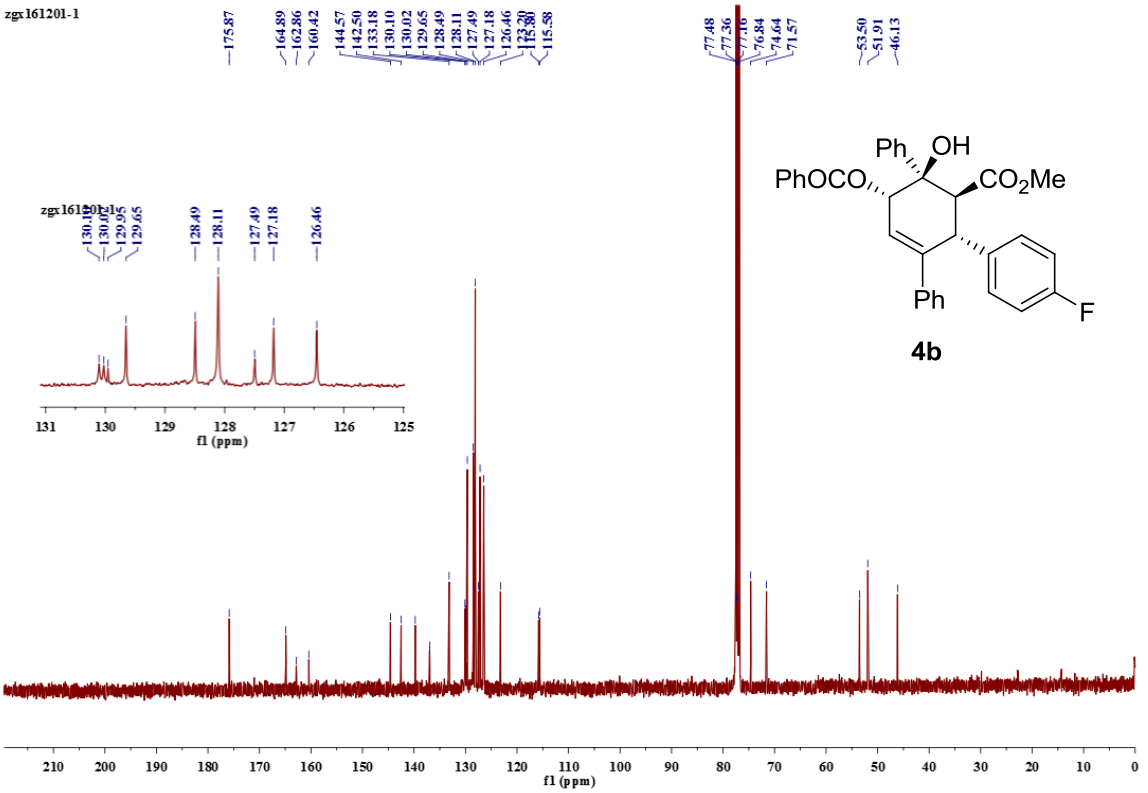
OH
PhOCO
CO2Me
Ph
4a
fl (ppm)


Ph
OH
PhOCO
CO2Me
Ph
F
4b
fl (ppm)


zgx161201-1
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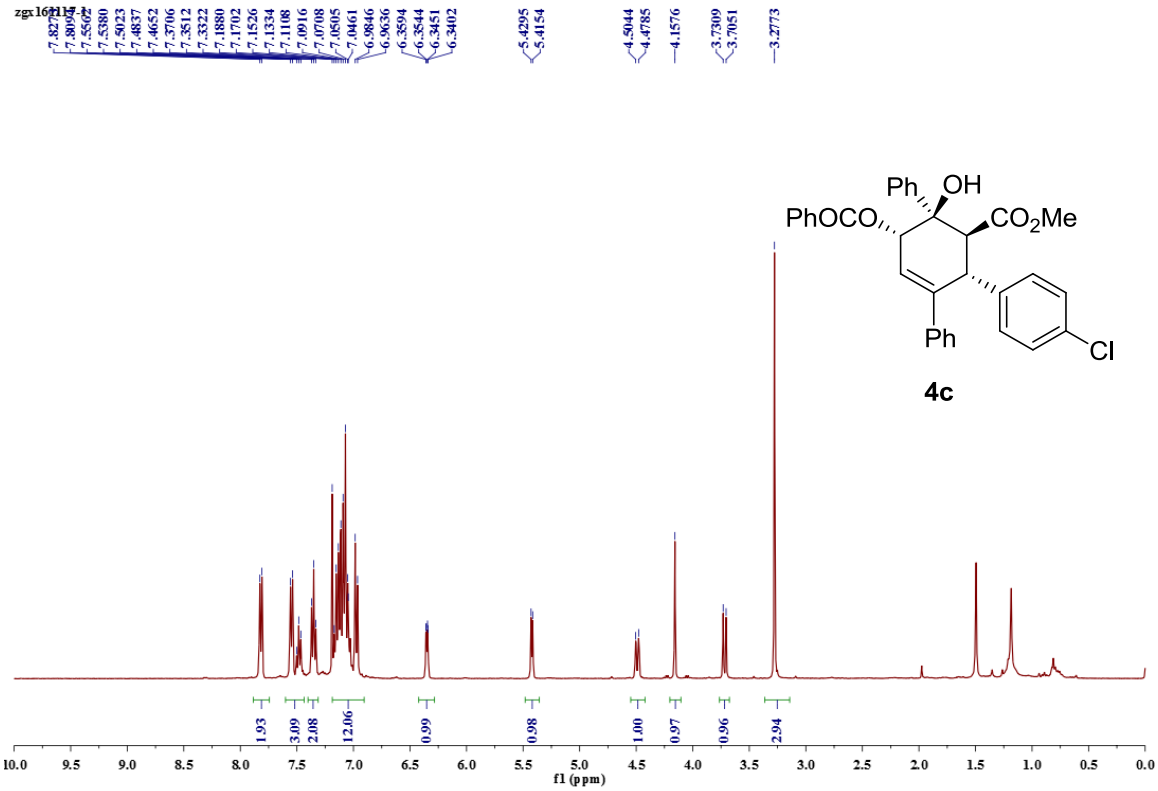
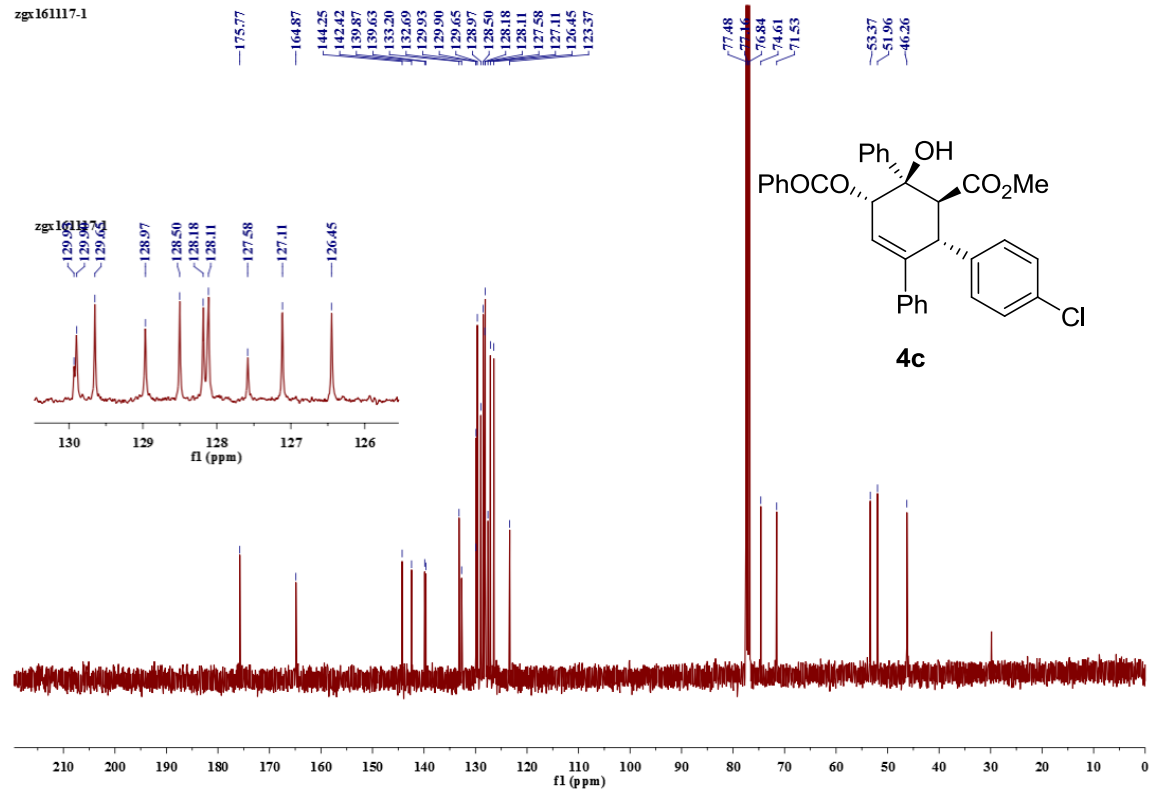
OH
PhOCO
CO2Me
Ph
F
4b
fl (ppm)


Ph
OH
PhOCO
CO2Me
Ph
Cl
4c
fl (ppm)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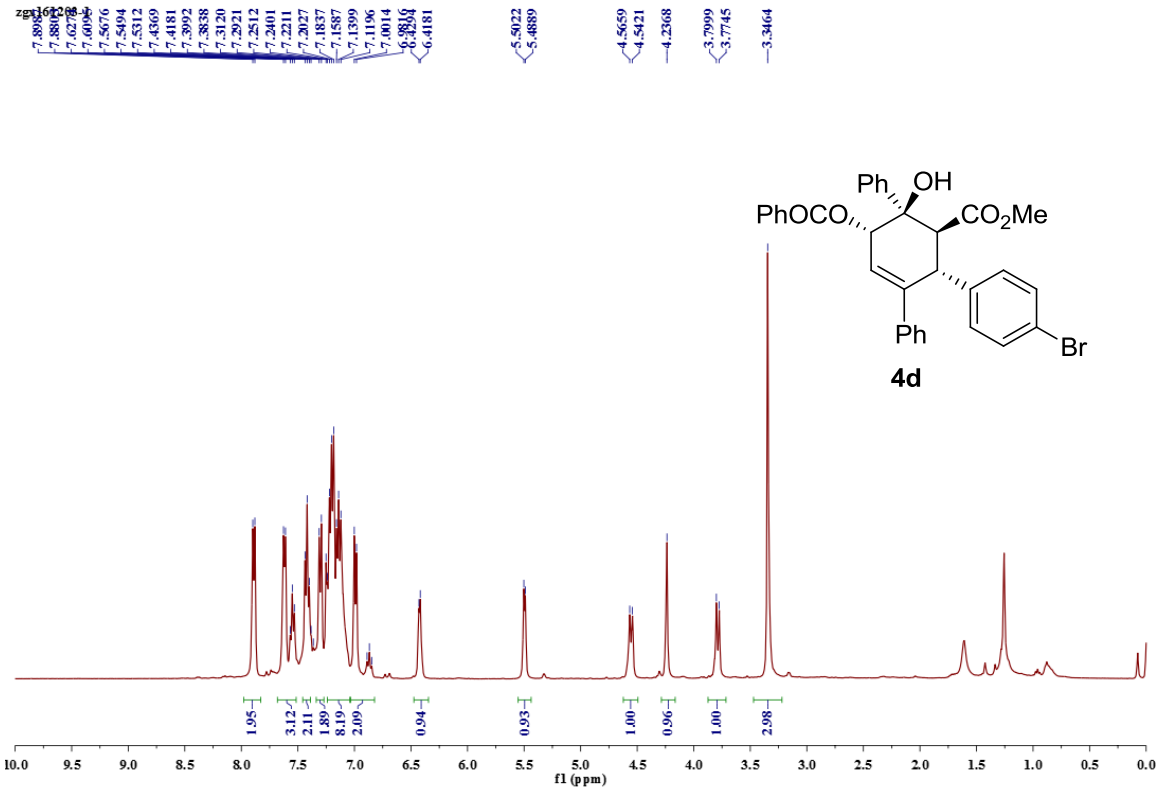
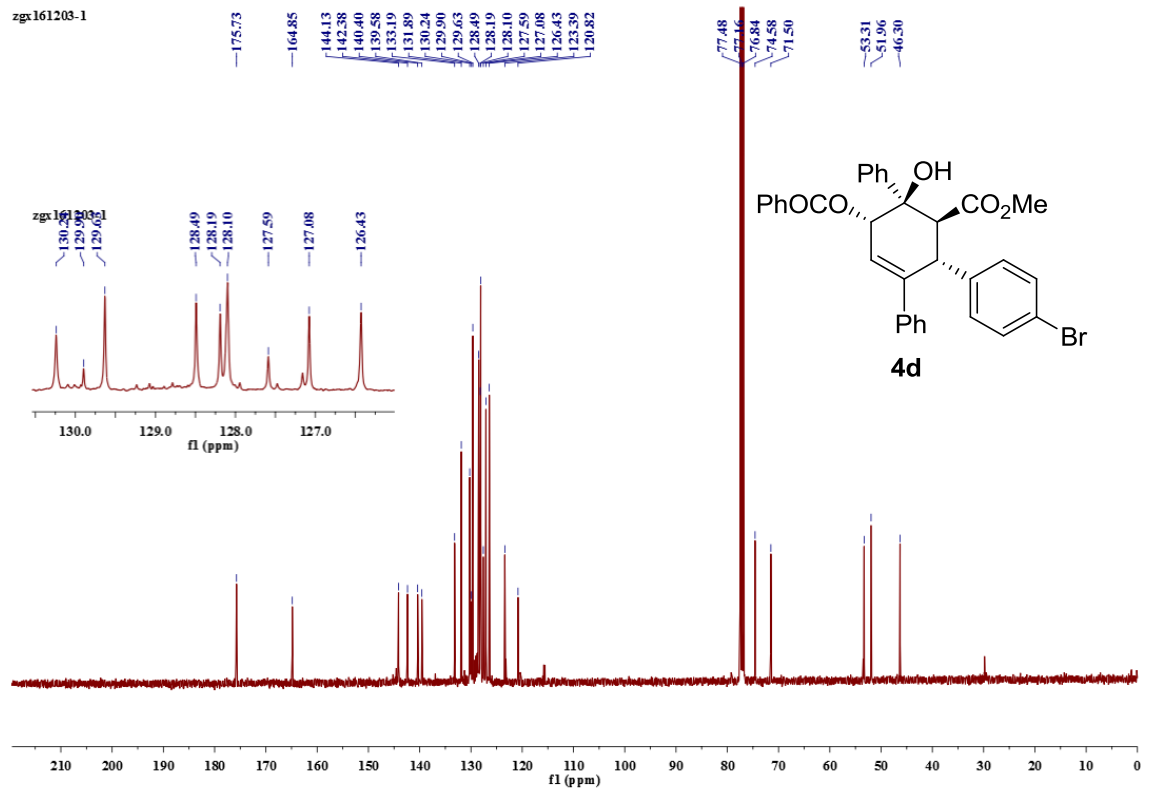
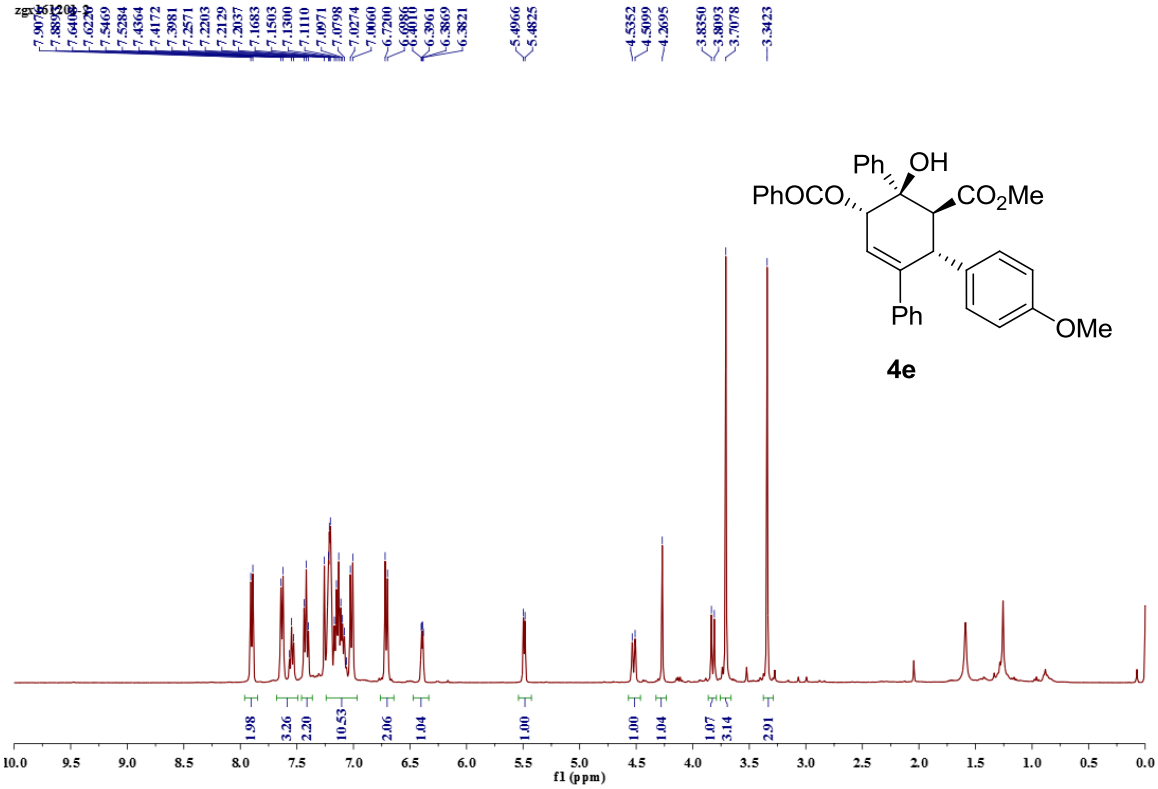
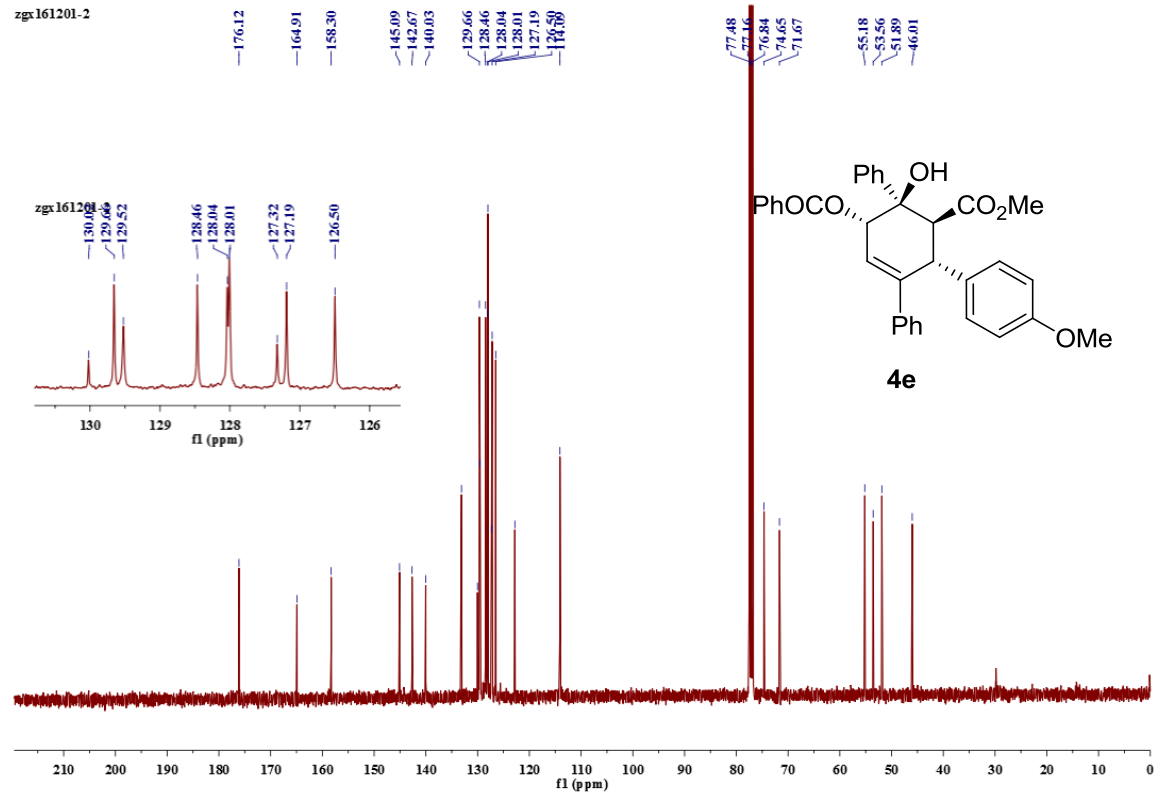
OH
PhOCO
CO2Me
Ph
Cl
4c
fl (ppm)


Ph
OH
PhOCO
CO2Me
Ph
Br
4d
1.95
3.12
2.11
1.89
8.19
2.09
0.94
0.93
1.00
0.96
1.00
2.98
f1 (ppm)


zgx161203-1
Ph
OH
PhOCO
CO2Me
Ph
Br
4d
f1 (ppm)


Ph
OH
PhOCO
CO2Me
Ph
OMe
4e
1.98
3.26
2.20
10.53
2.06
1.04
1.00
1.00
1.04
1.07
3.14
2.91
f1 (ppm)


zgx161201-2
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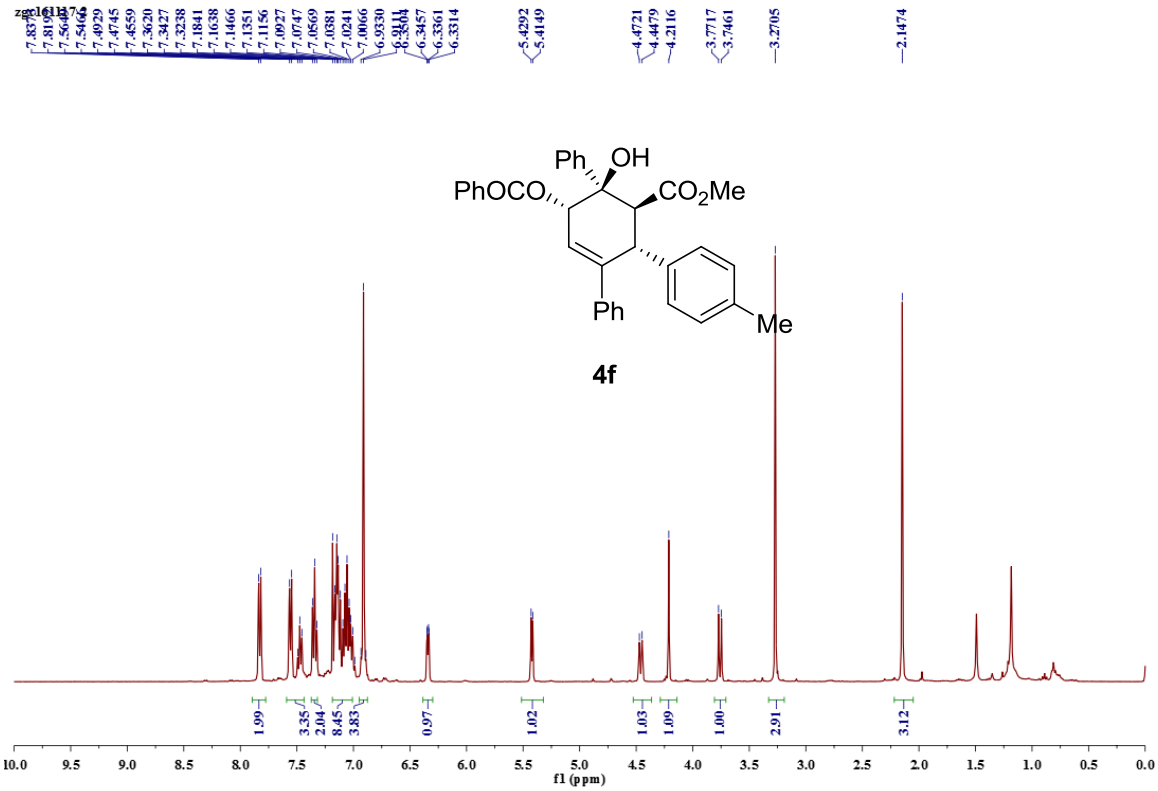
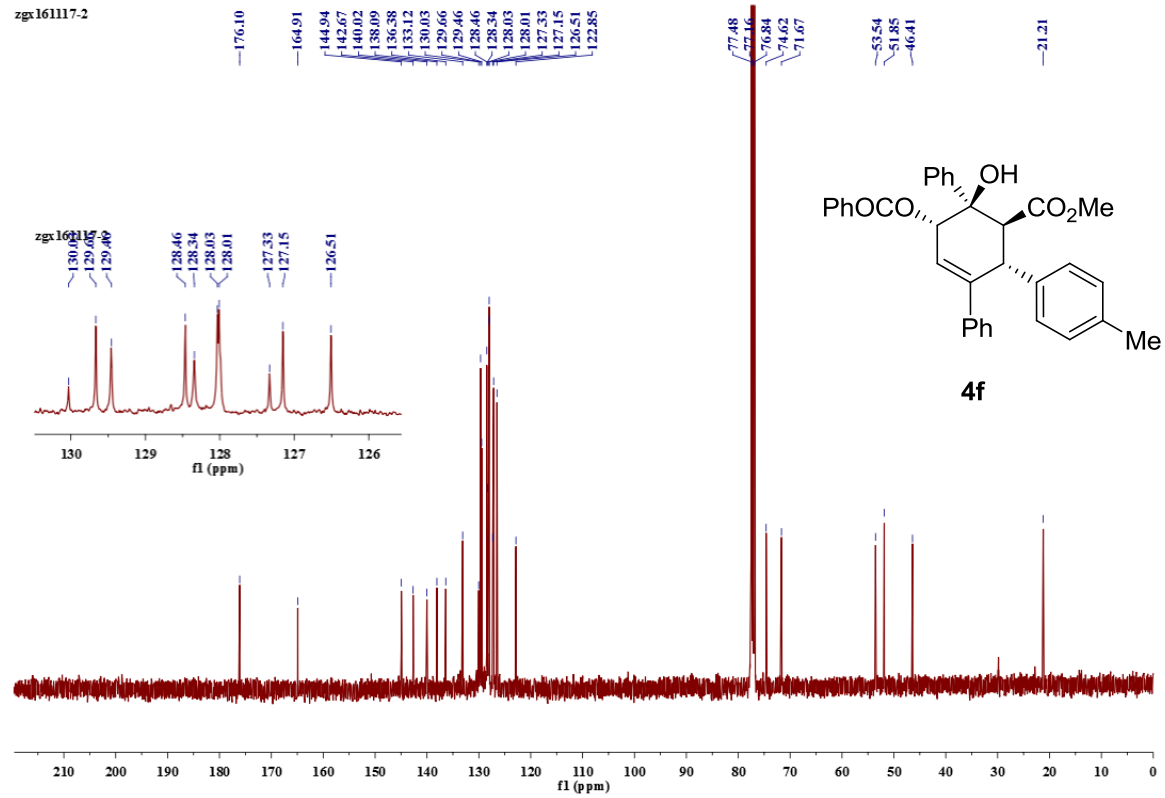
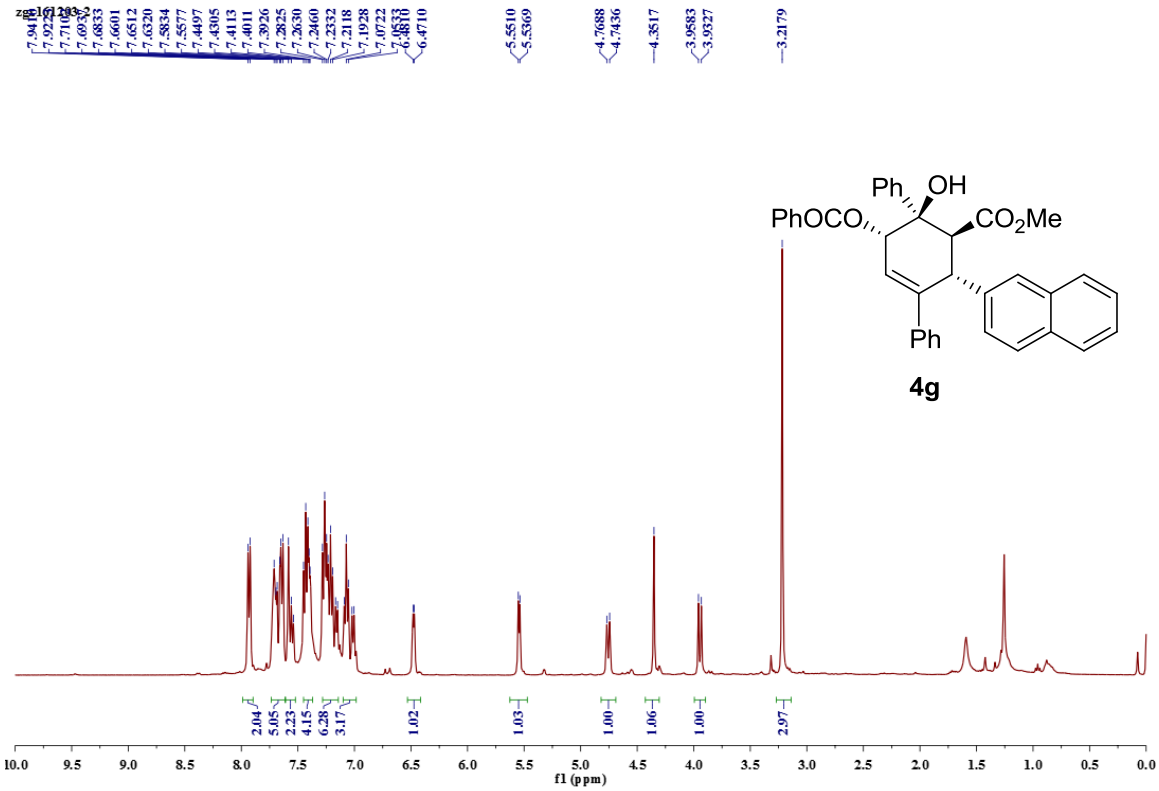
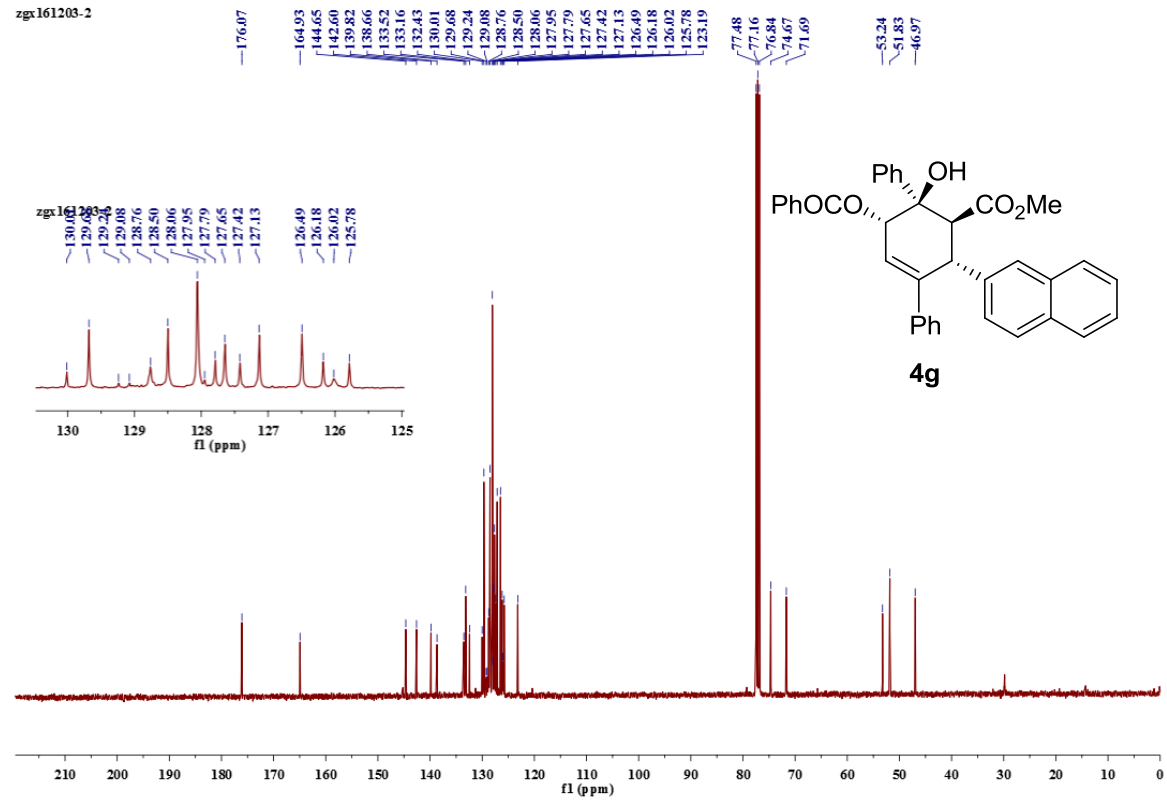
OH
PhOCO
CO2Me
Ph
OMe
4e
f1 (ppm)


Ph
OH
PhOCO
CO2Me
Ph
Me
4f
f1 (ppm)


zgx161117-2
Ph
OH
PhOCO
CO2Me
Ph
Me
4f
f1 (ppm)


Ph
OH
PhOCO
CO2Me
Ph
4g
f1 (ppm)


zgx161203-2
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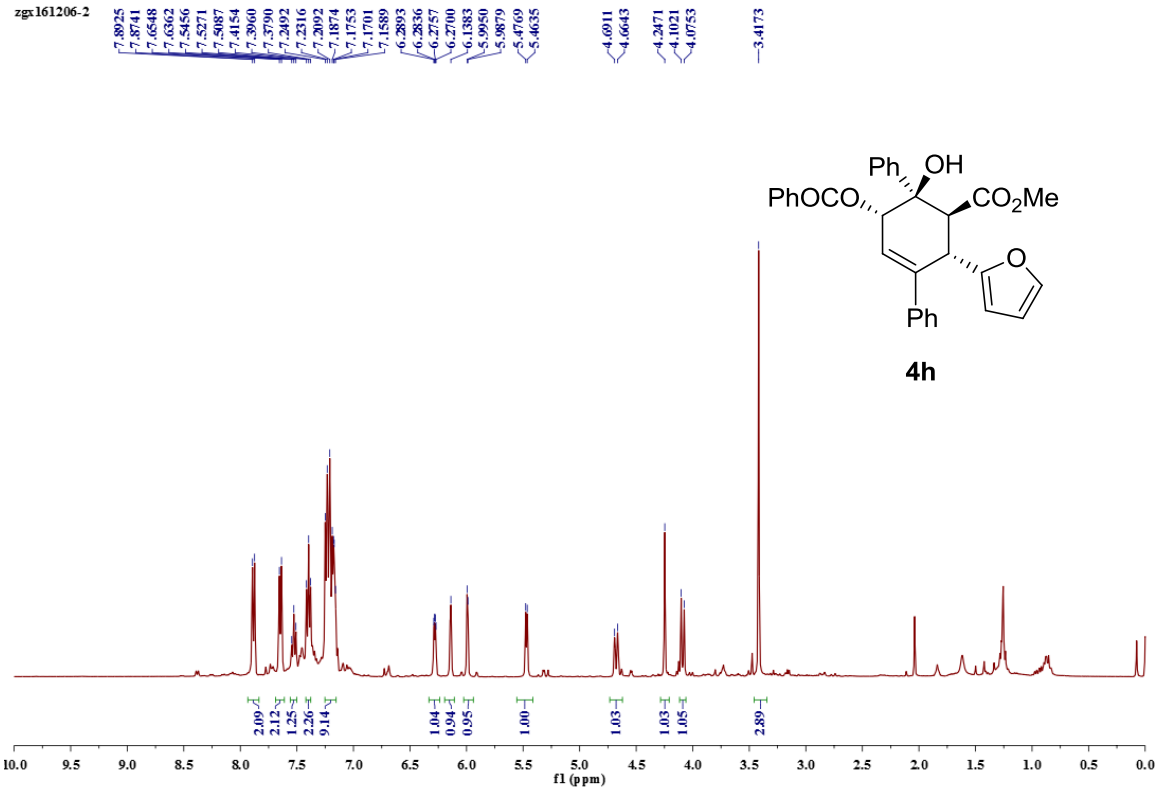
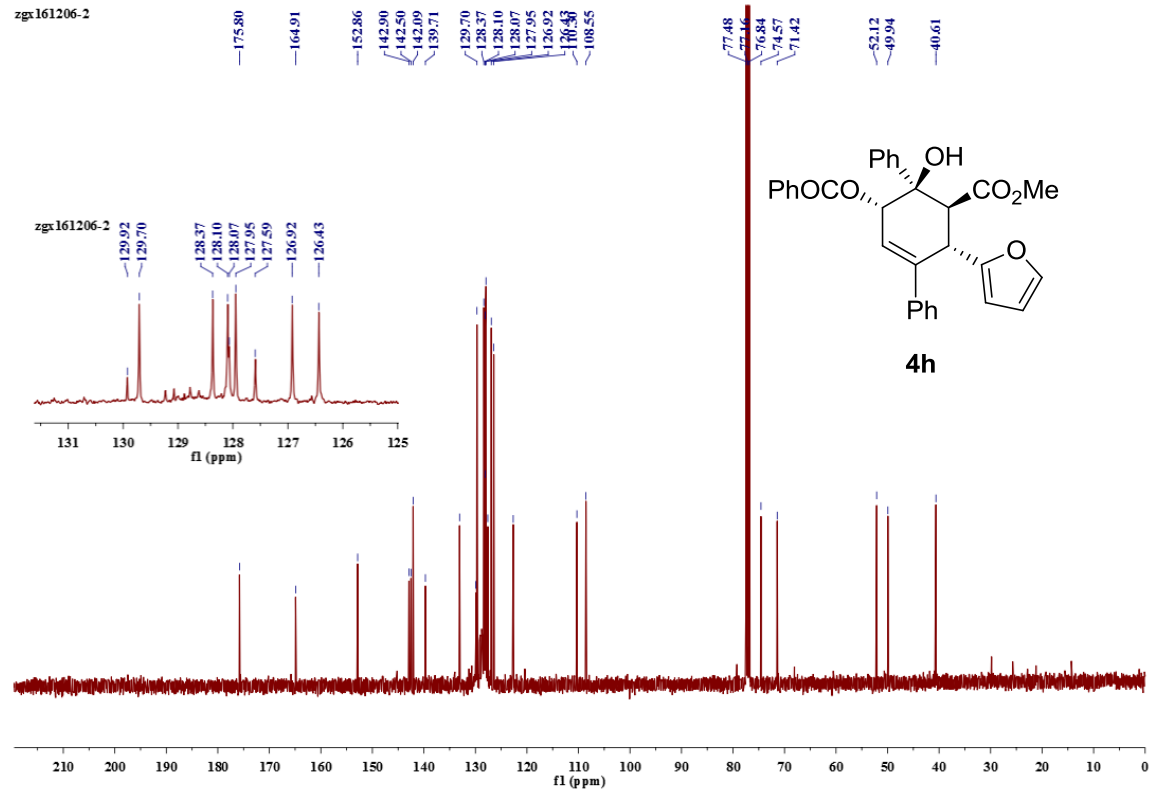
OH
PhOCO
CO2Me
Ph
4g
f1 (ppm)


zgx161206-2
7.8925
7.8741
7.6548
7.6362
7.5456
7.5271
7.5087
7.4154
7.3960
7.3790
7.2492
7.2316
7.2092
7.1874
7.1753
7.1701
7.1589
6.2893
6.2836
6.2757
6.2700
6.1383
5.9950
5.9879
5.4769
5.4635
4.6911
4.6643
4.2471
4.1021
4.0753
3.4173
Ph
OH
PhOCO
CO2Me
O
Ph
4h
2.09
2.12
1.25
2.26
9.14
1.04
0.94
0.95
1.00
1.03
1.03
1.05
2.89
f1 (ppm)


zgx161206-2
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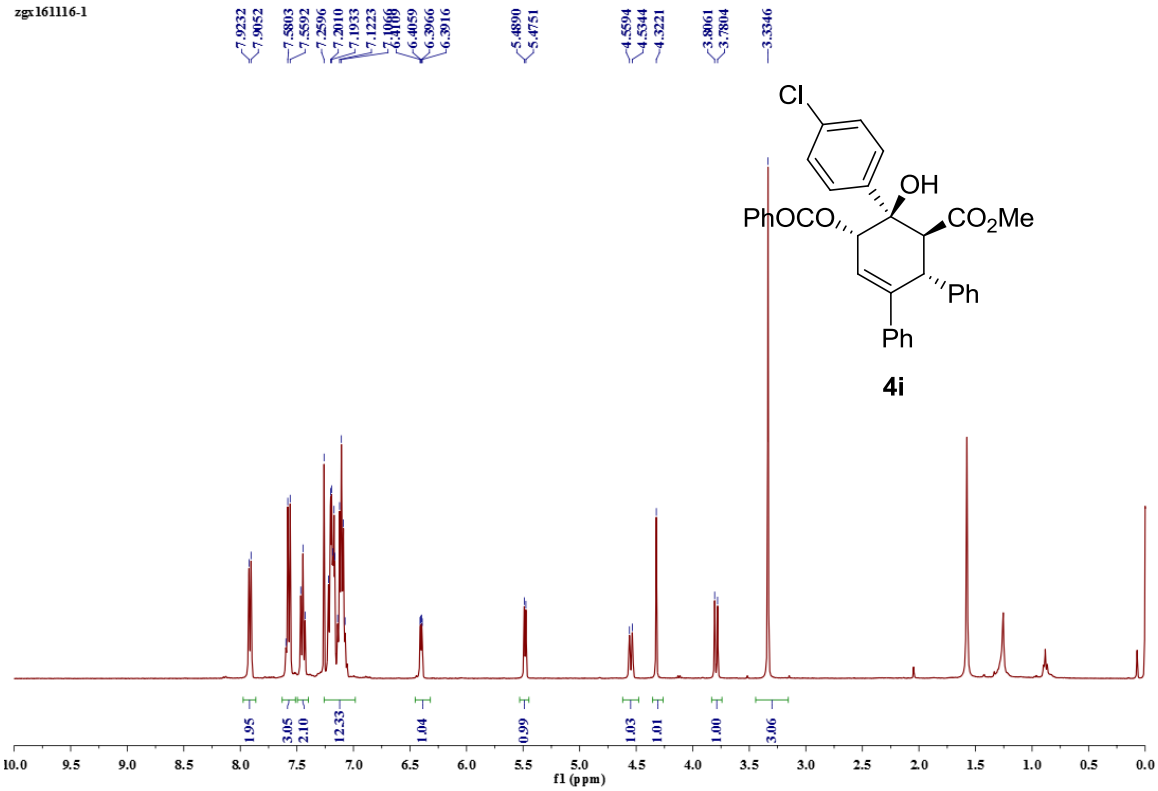
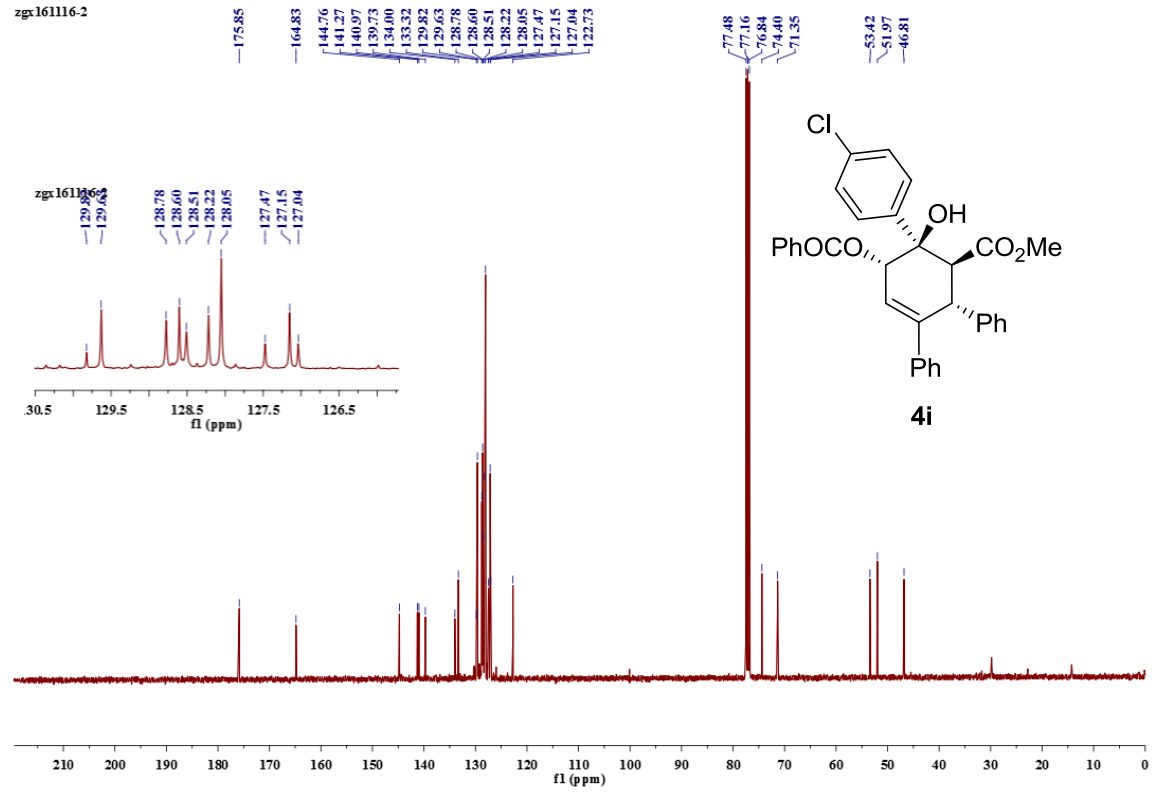
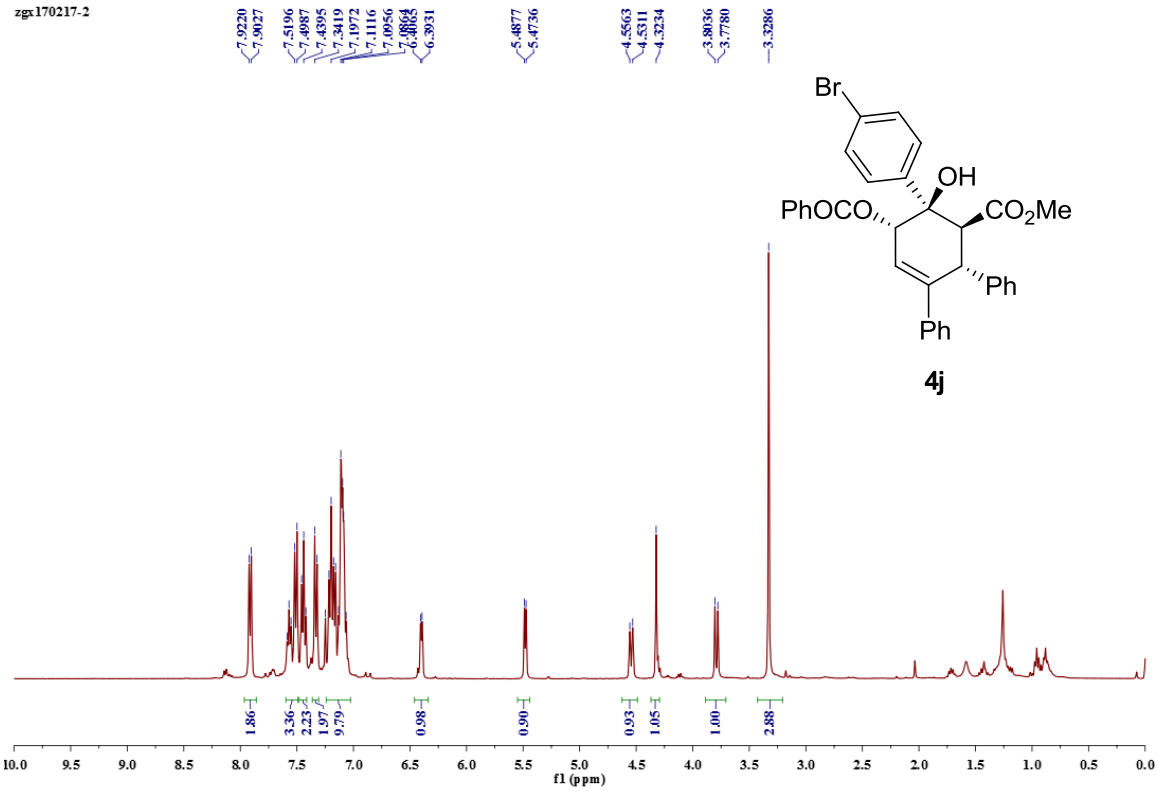
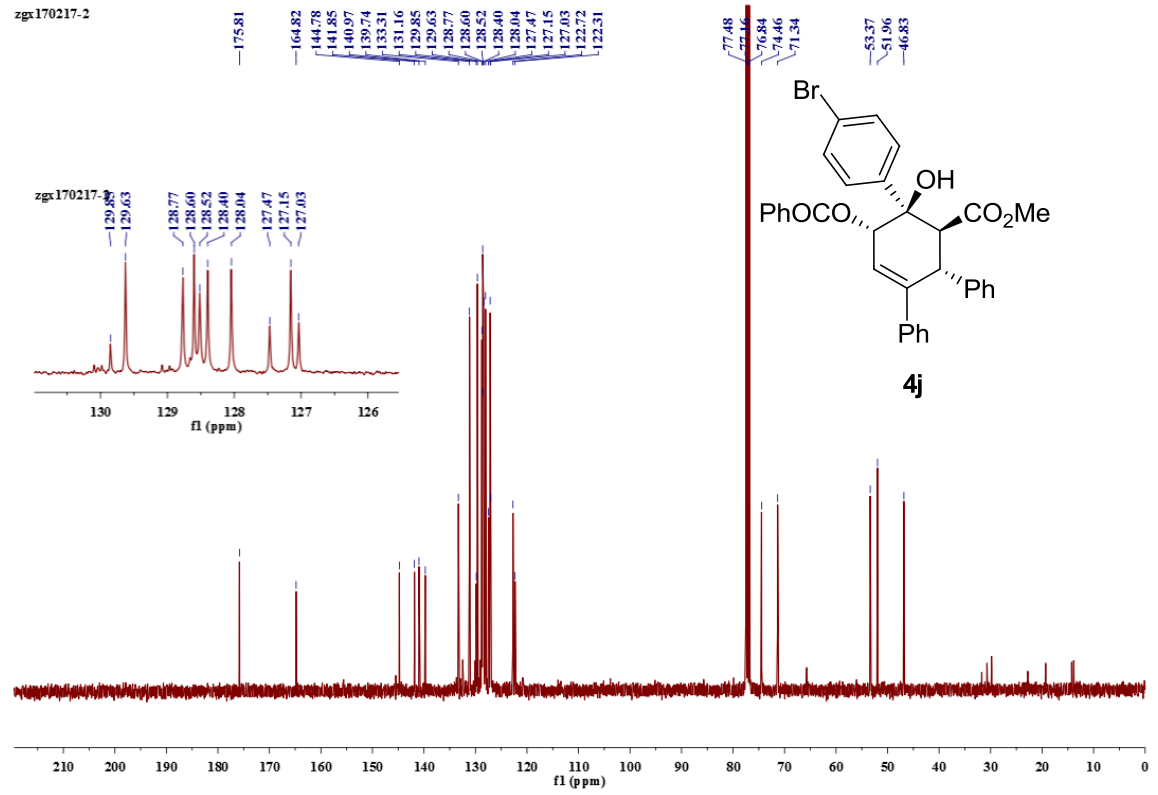
164.91
152.86
142.90
142.50
142.09
139.71
129.70
128.37
128.10
128.07
127.95
126.92
108.55
77.48
77.16
76.84
74.57
71.42
52.12
49.94
40.61
zgx161206-2
129.92
129.70
128.37
128.10
128.07
127.95
127.59
126.92
126.43
f1 (ppm)
Ph
OH
PhOCO
CO2Me
O
Ph
4h
f1 (ppm)


zgx161116-1
7.9232
7.9052
7.5803
7.5592
7.2596
7.2010
7.1933
7.1223
6.4059
6.3966
6.3916
5.4890
5.4751
4.5594
4.5344
4.3221
3.8061
3.7804
3.3346
Cl
OH
PhOCO
CO2Me
Ph
Ph
4i
1.95
3.05
2.10
12.33
1.04
0.99
1.03
1.01
1.00
3.06
f1 (ppm)


zgx161116-2
175.85
164.83
144.76
141.27
140.97
139.73
134.00
133.32
129.82
129.63
128.78
128.60
128.51
128.22
128.05
127.47
127.15
127.04
122.73
77.48
77.16
76.84
74.40
71.35
53.42
51.97
46.81
Cl
OH
PhOCO
CO2Me
Ph
Ph
4i
f1 (ppm)


zgx170217-2
7.9220
7.9027
7.5196
7.4987
7.4395
7.3419
7.1972
7.1116
7.0956
6.3931
5.4877
5.4736
4.5563
4.5311
4.3234
3.8036
3.7780
3.3286
Br
OH
PhOCO
CO2Me
Ph
Ph
4j
1.86
3.36
2.23
1.97
9.79
0.98
0.90
0.93
1.05
1.00
2.88
fl (ppm)


zgx170217-2
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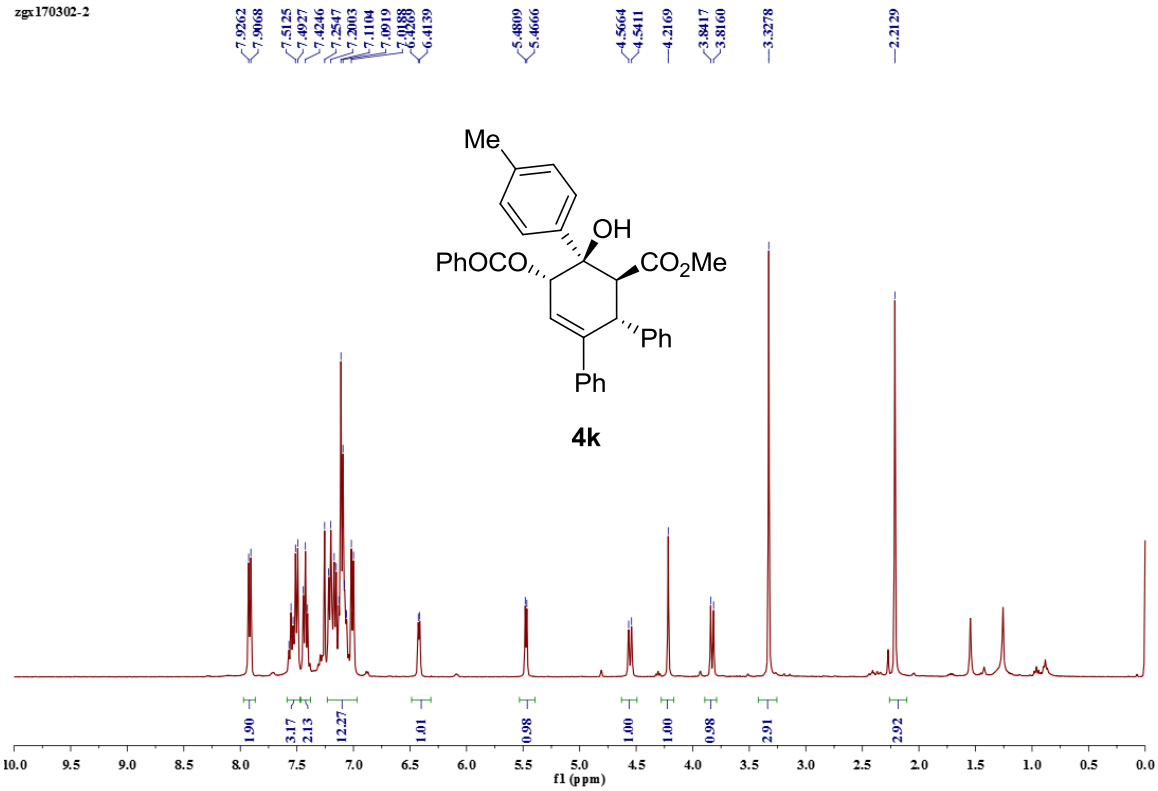
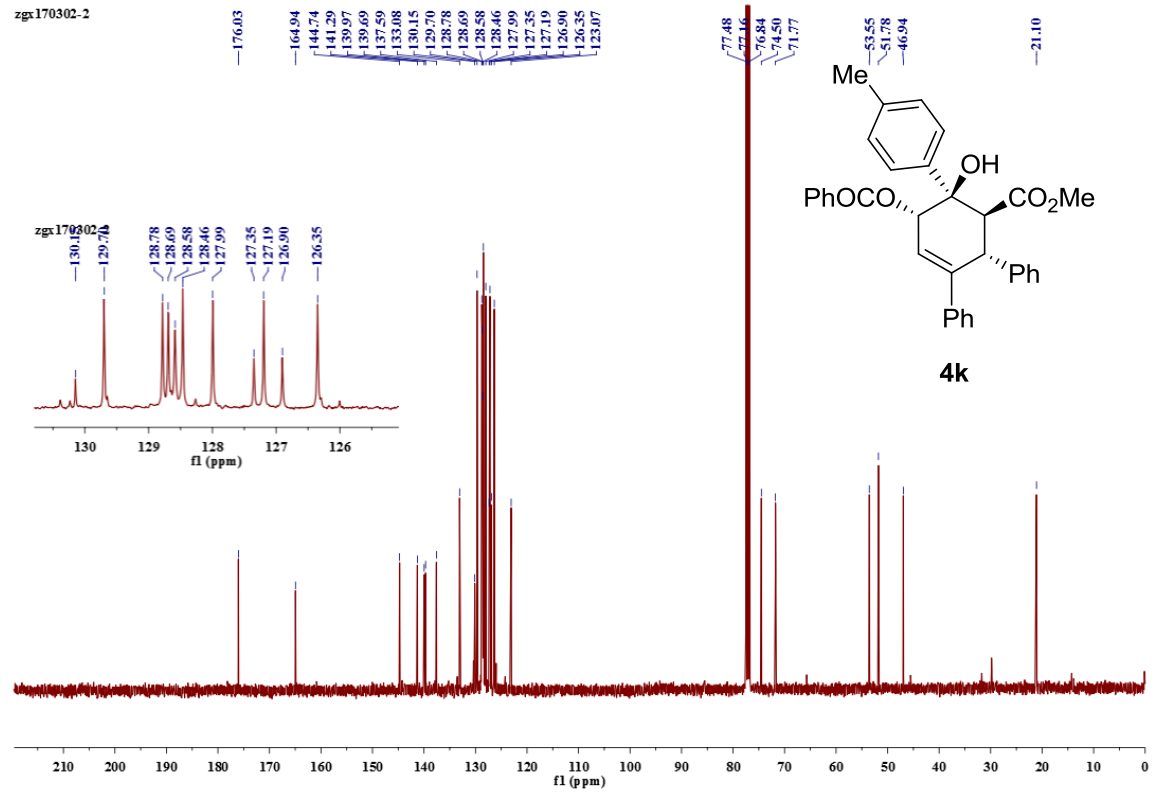
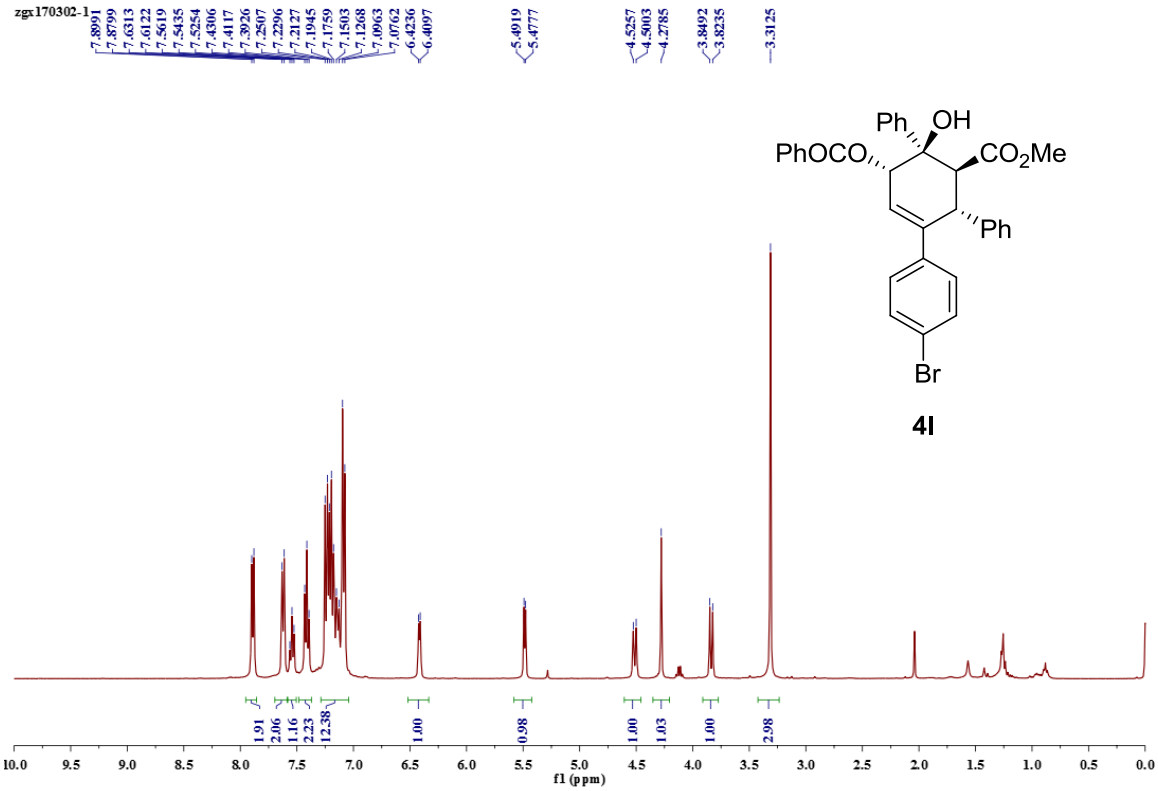
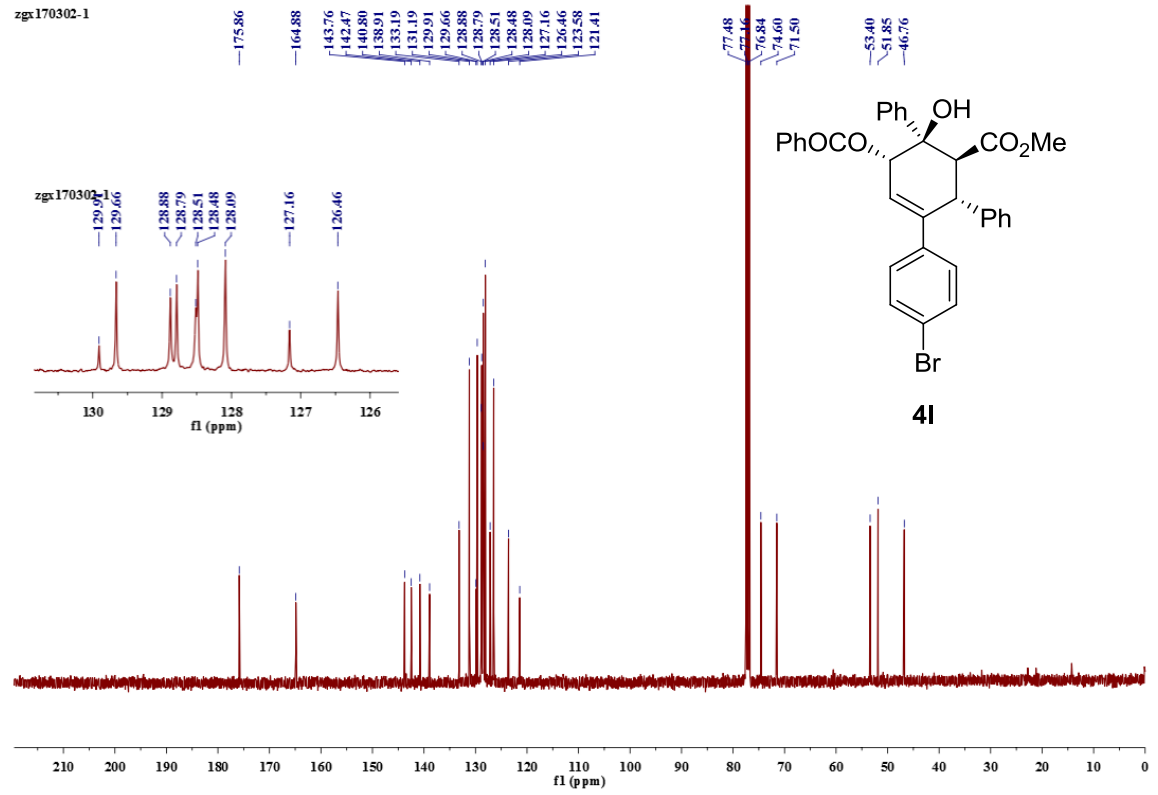
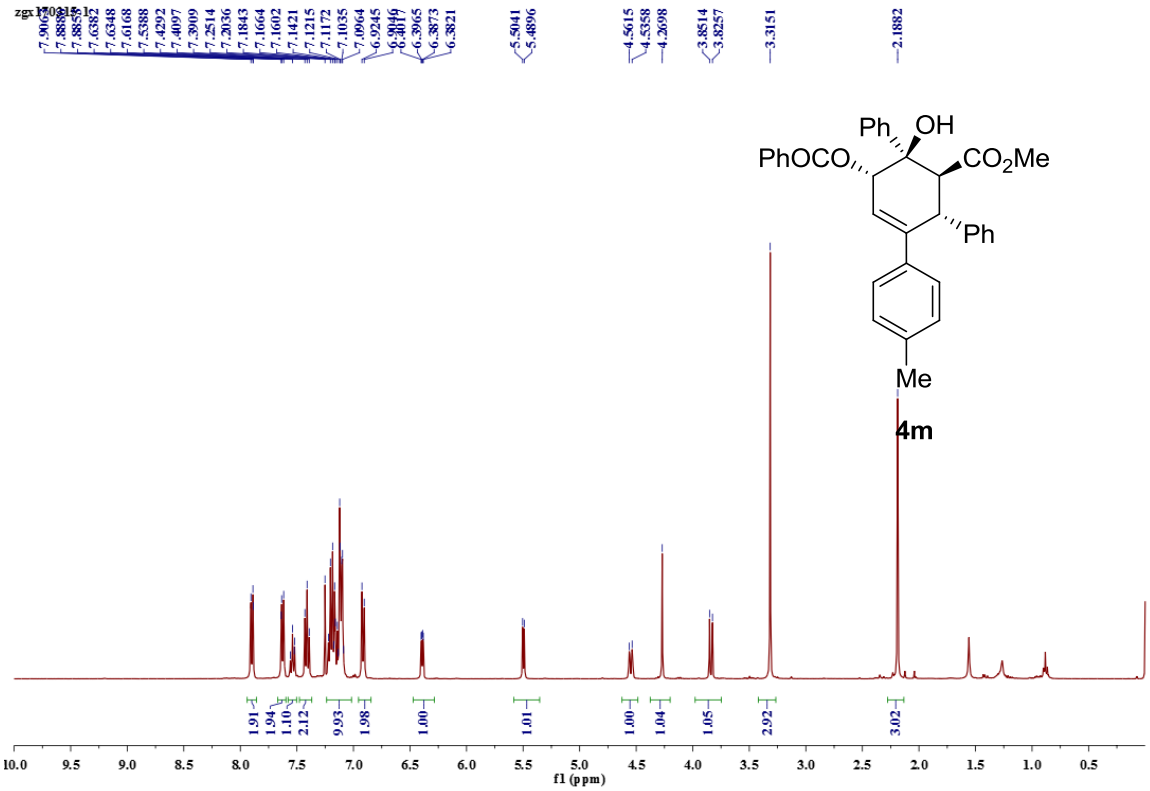
164.82
144.78
141.85
140.97
139.74
133.31
131.16
129.85
129.63
128.77
128.60
128.52
128.40
128.04
127.47
127.15
127.03
122.72
122.31
77.48
77.16
76.84
74.46
71.34
53.37
51.96
46.83
Br
OH
PhOCO
CO2Me
Ph
Ph
4j
fl (ppm)

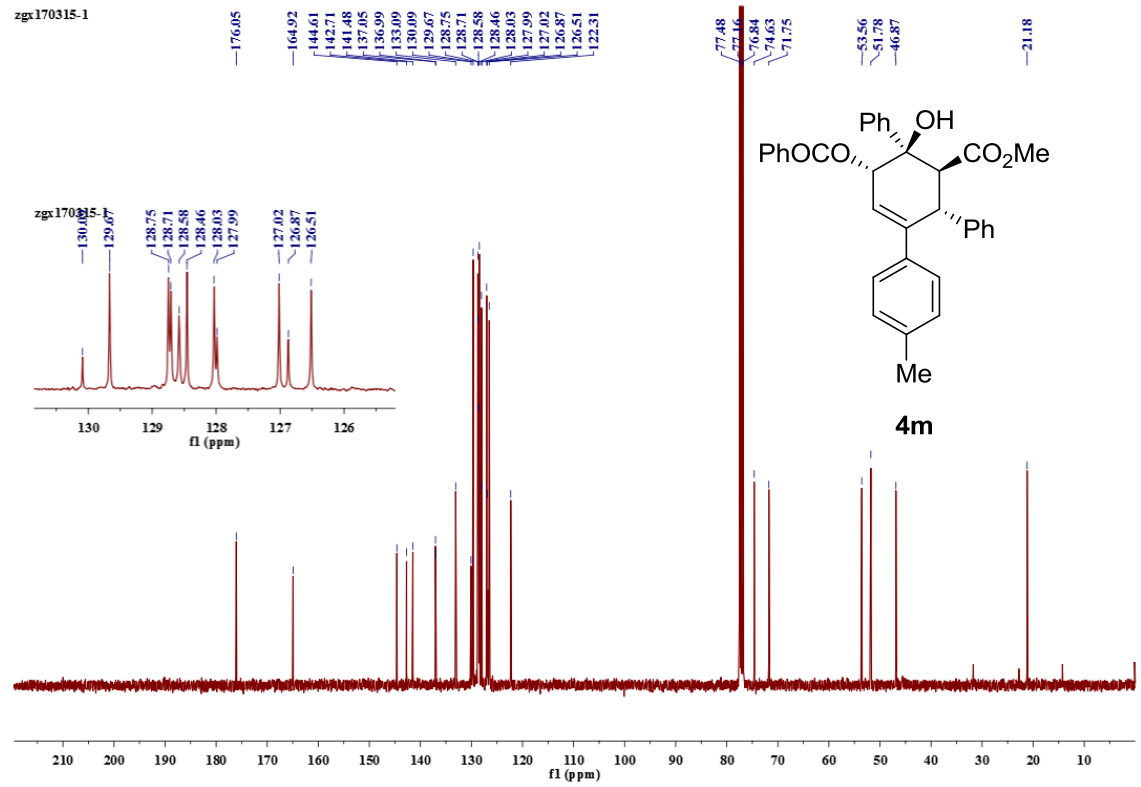

zgx170302-2
7.9262
7.9068
7.5125
7.4927
7.4246
7.2547
7.2003
7.1104
7.0919
7.0188
6.4288
6.4139
5.4809
5.4666
4.5664
4.5411
4.2169
3.8417
3.8160
3.3278
2.2129
Me
OH
PhOCO
CO2Me
Ph
Ph
4k
1.90
3.17
2.13
12.27
1.01
0.98
1.00
1.00
0.98
2.91
2.92
f1 (ppm)

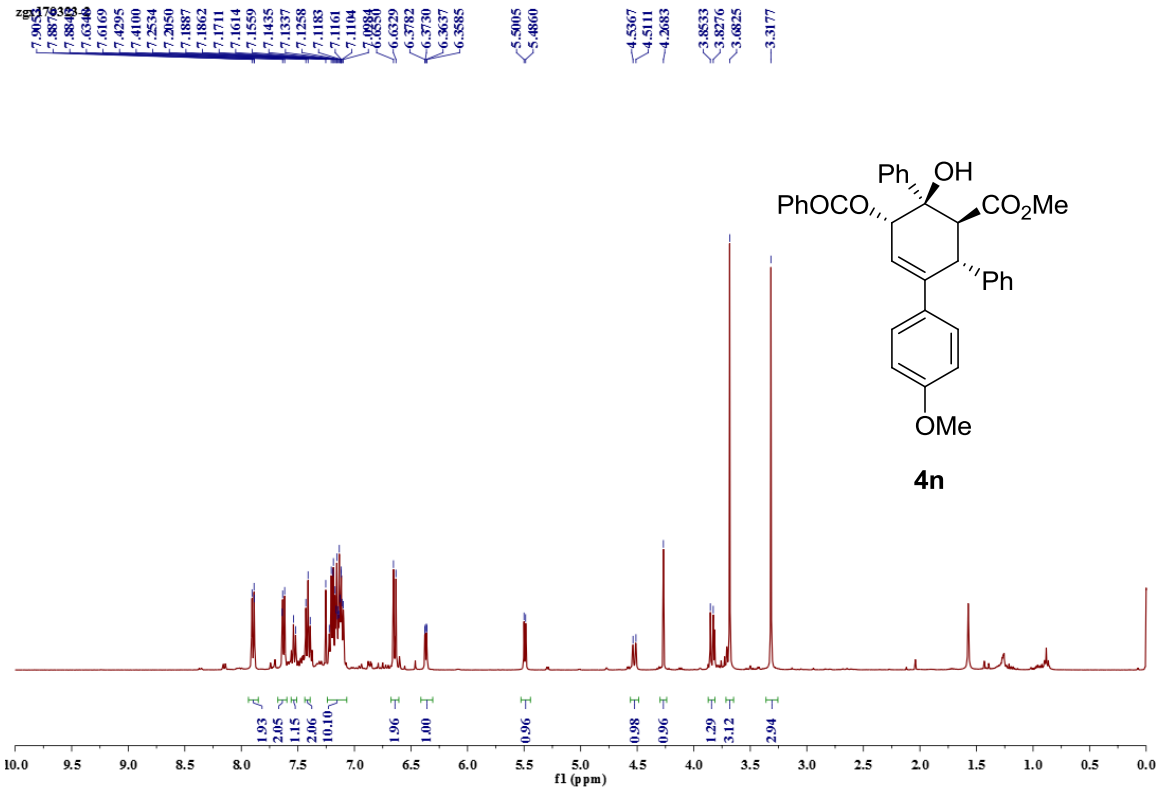

zgx170302-2
176.03
164.94
144.74
141.29
139.97
139.69
137.59
133.08
130.15
129.70
128.78
128.69
128.58
128.46
127.99
127.35
127.19
126.90
126.35
123.07
77.48
77.16
76.84
74.50
71.77
53.55
51.78
46.94
21.10
Me
OH
PhOCO
CO2Me
Ph
Ph
4k
f1 (ppm)

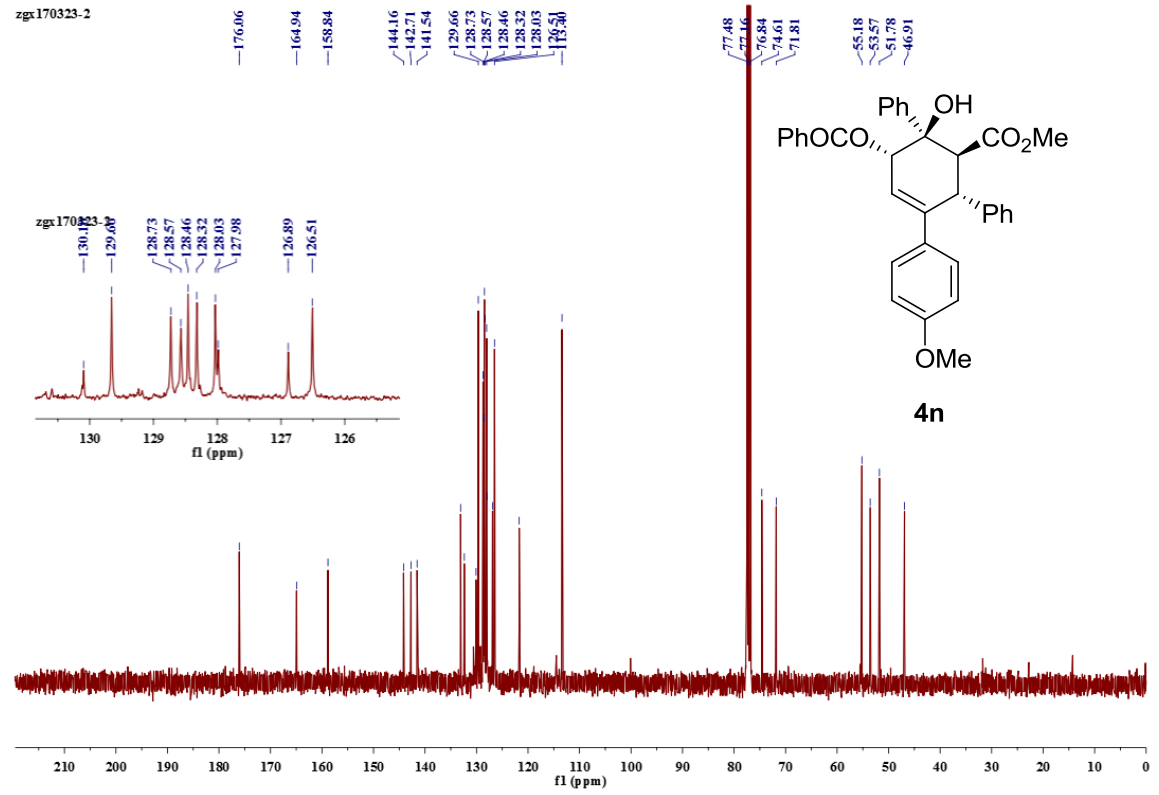

zgx170302-1
Ph
OH
PhOCO
CO2Me
Ph
Br
4l
fl (ppm)


zgx170302-1
zgx170302-1
Ph
OH
PhOCO
CO2Me
Ph
Br
4l
fl (ppm)
fl (ppm)


Ph
OH
PhOCO
CO2Me
Ph
Me
4m
f1 (ppm)


zgx170315-1
Ph
OH
PhOCO
CO2Me
Ph
Me
4m
f1 (ppm)


Ph
OH
PhOCO
CO2Me
Ph
OMe
4n
1.93
2.05
1.15
2.06
10.10
1.96
1.00
0.96
0.98
0.96
1.29
3.12
2.94
f1 (ppm)


zgx170323-2
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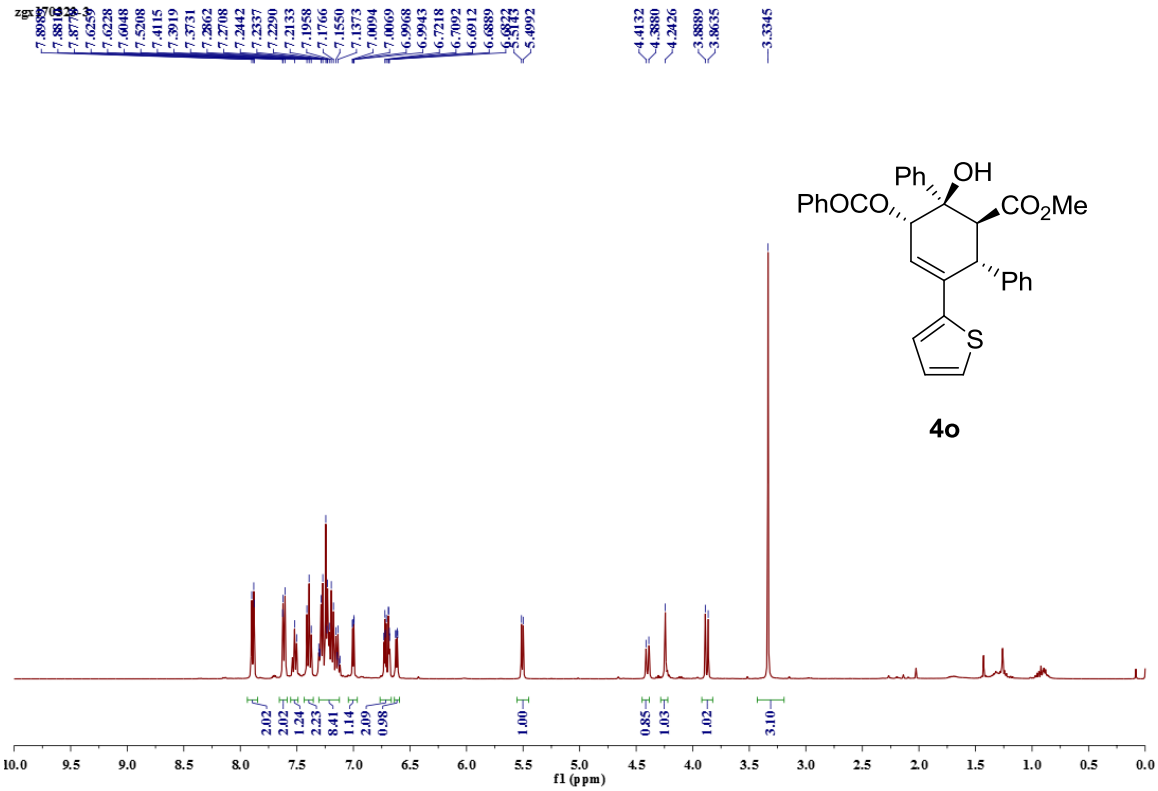
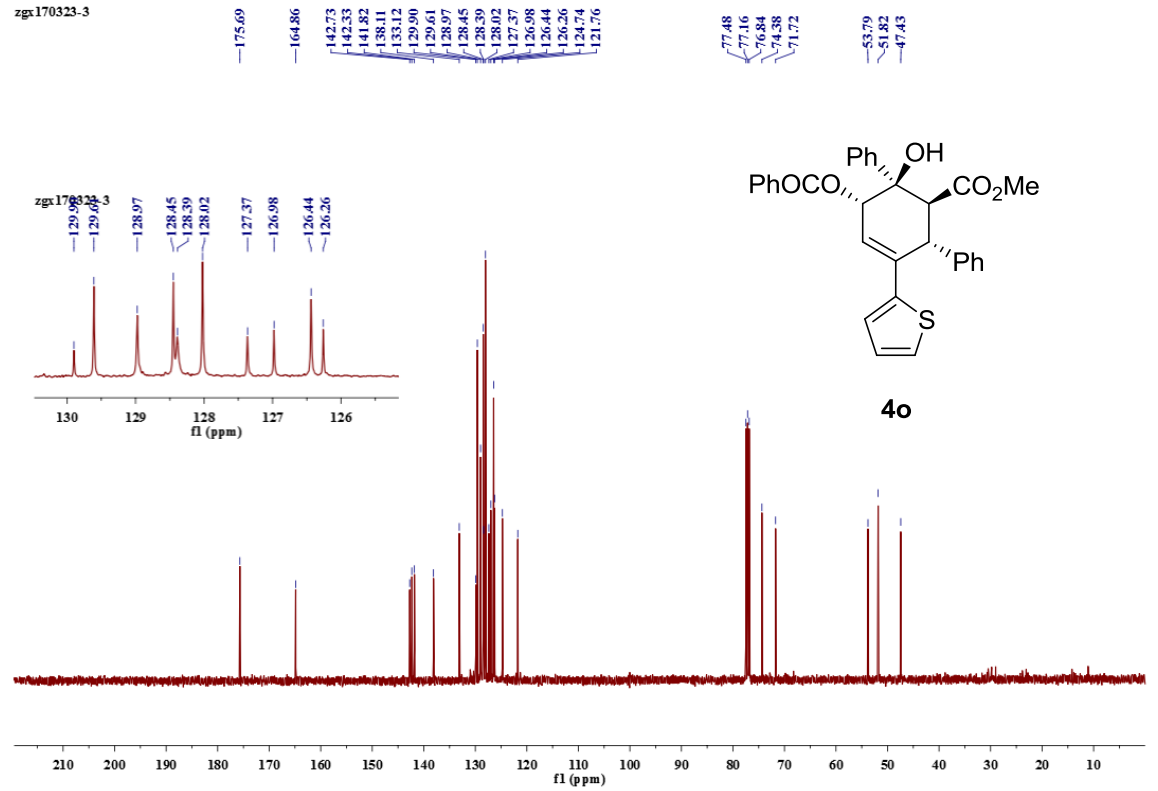
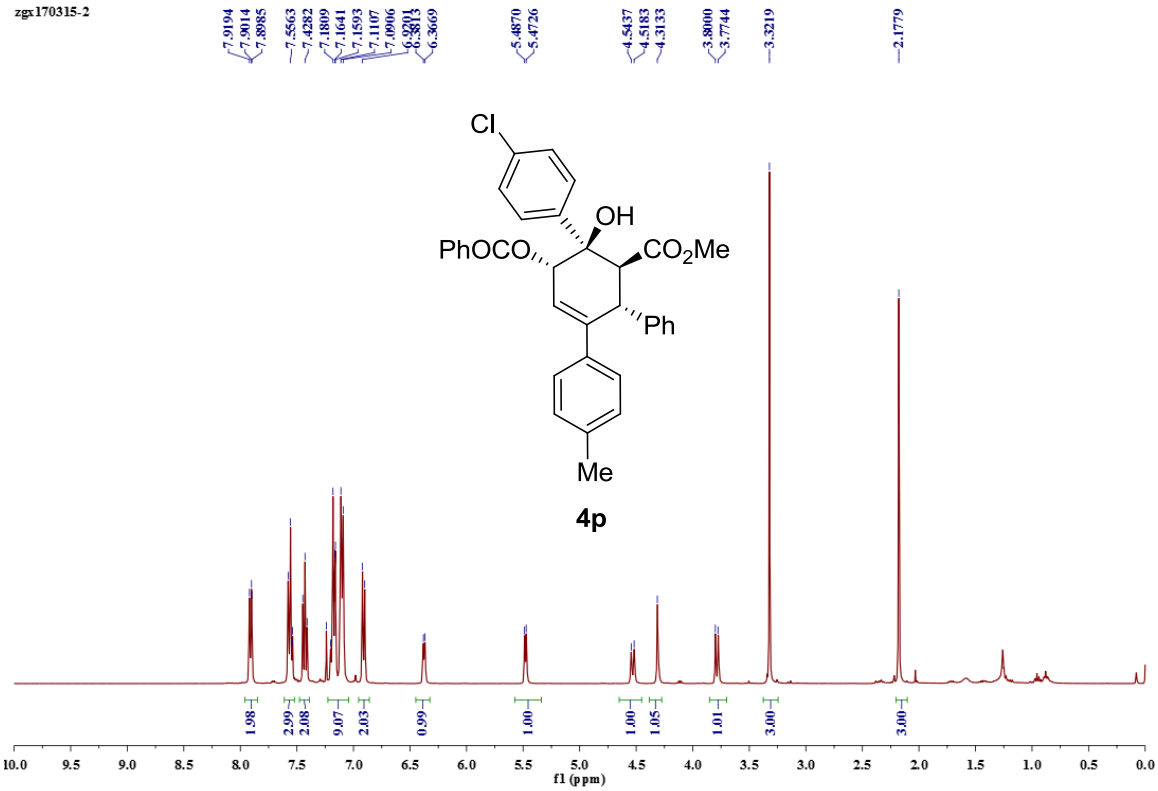
OH
PhOCO
CO2Me
Ph
OMe
4n
f1 (ppm)


Ph
OH
PhOCO
CO2Me
Ph
S
4o
fl (ppm)


zgx170323-3
Ph
OH
PhOCO
CO2Me
Ph
S
4o
fl (ppm)


zgx170315-2
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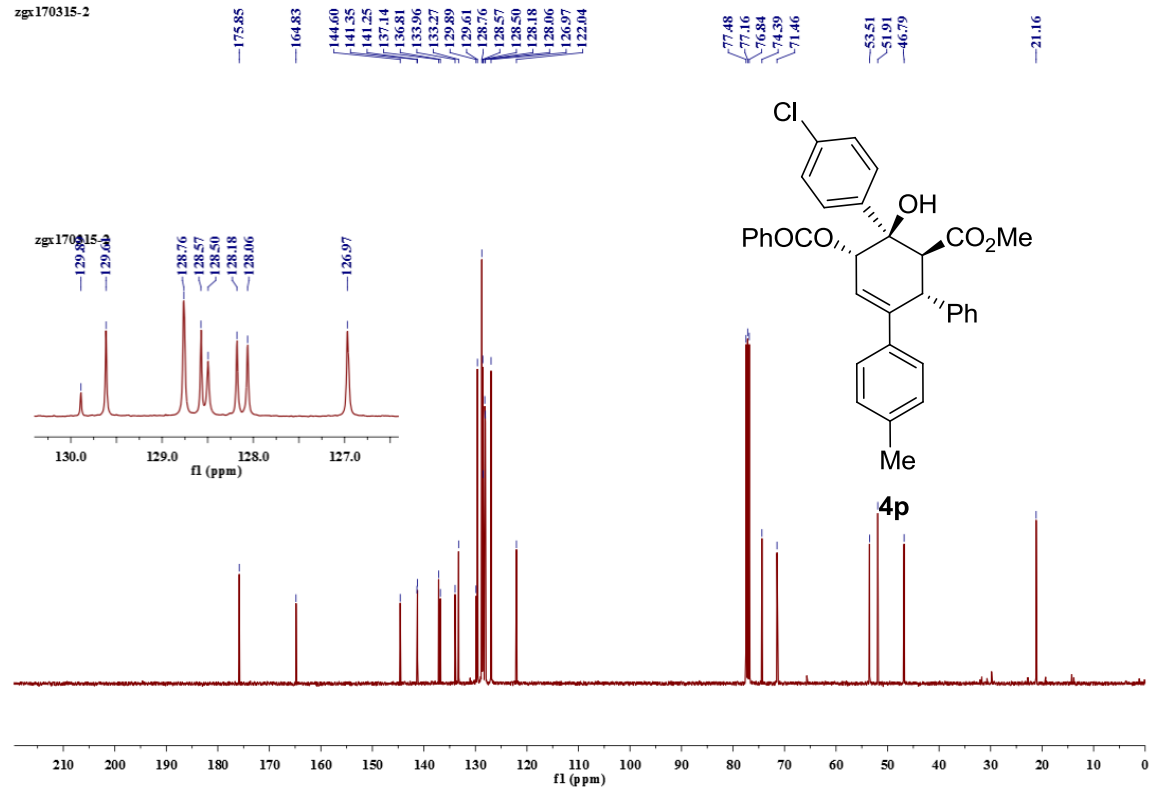
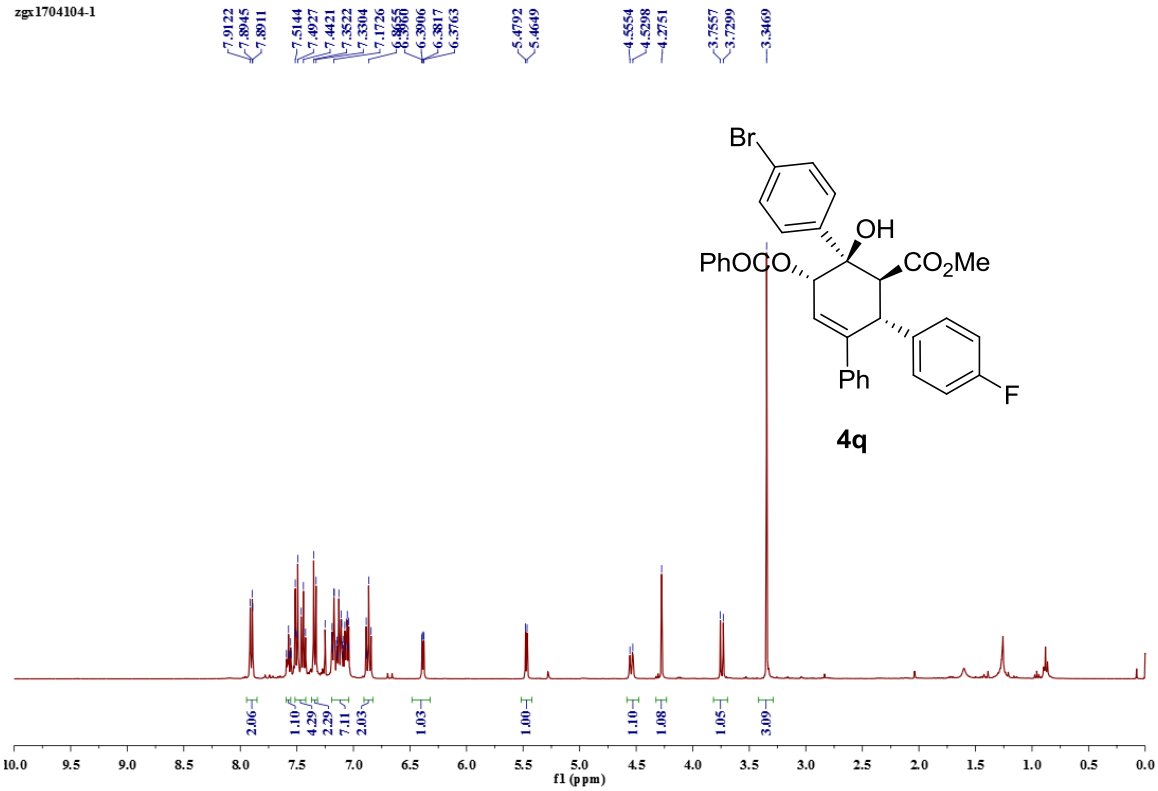
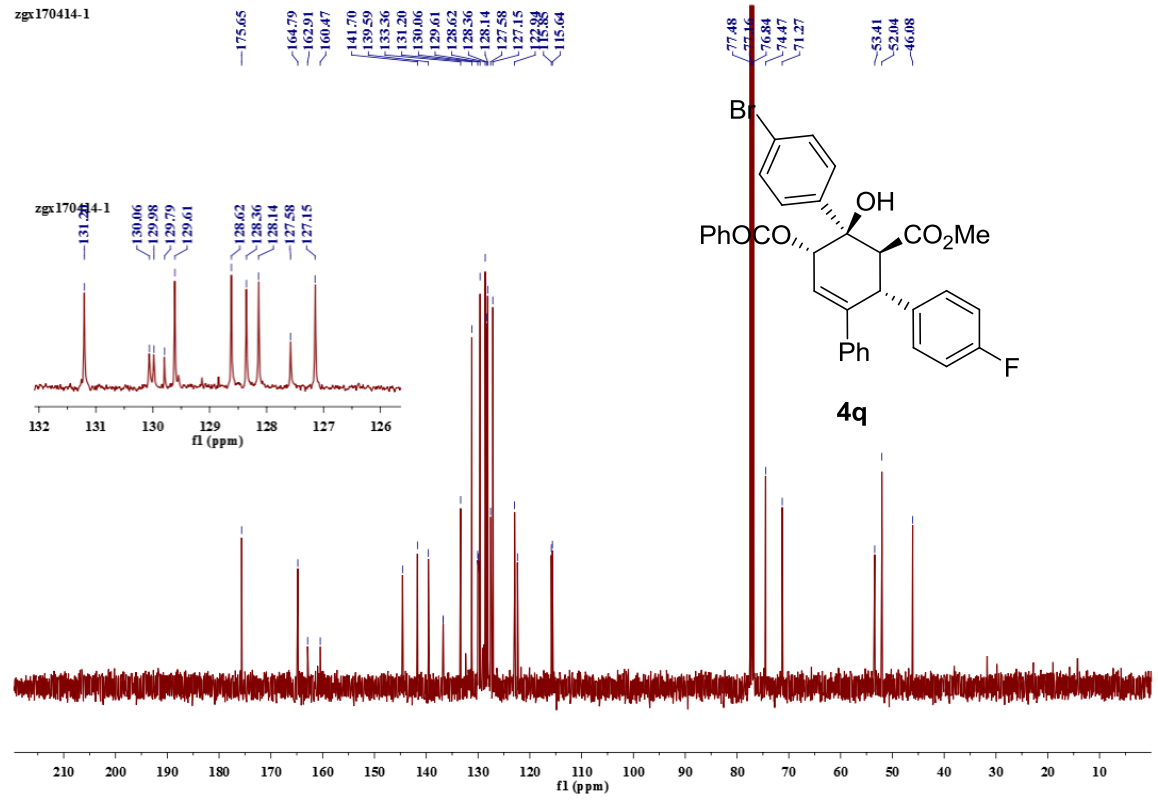
7.9014
7.8985
7.5563
7.4282
7.1809
7.1641
7.1593
7.1107
7.0906
6.3669
5.4870
5.4726
4.5437
4.5183
4.3133
3.8000
3.7744
3.3219
2.1779
Cl
OH
PhOCO
CO2Me
Ph
Me
4p
1.98
2.99
2.08
9.07
2.03
0.99
1.00
1.00
1.05
1.01
3.00
3.00
fl (ppm)


zgx170315-2
175.85
164.83
144.60
141.35
141.25
137.14
136.81
133.96
133.27
129.89
129.61
128.76
128.57
128.50
128.18
128.06
126.97
122.04
77.48
77.16
76.84
74.39
71.46
53.51
51.91
46.79
21.16
Cl
OH
PhOCO
CO2Me
Ph
Me
4p
fl (ppm)


zgx1704104-1
Br
OH
PhOCO
CO2Me
Ph
F
4q
fl (ppm)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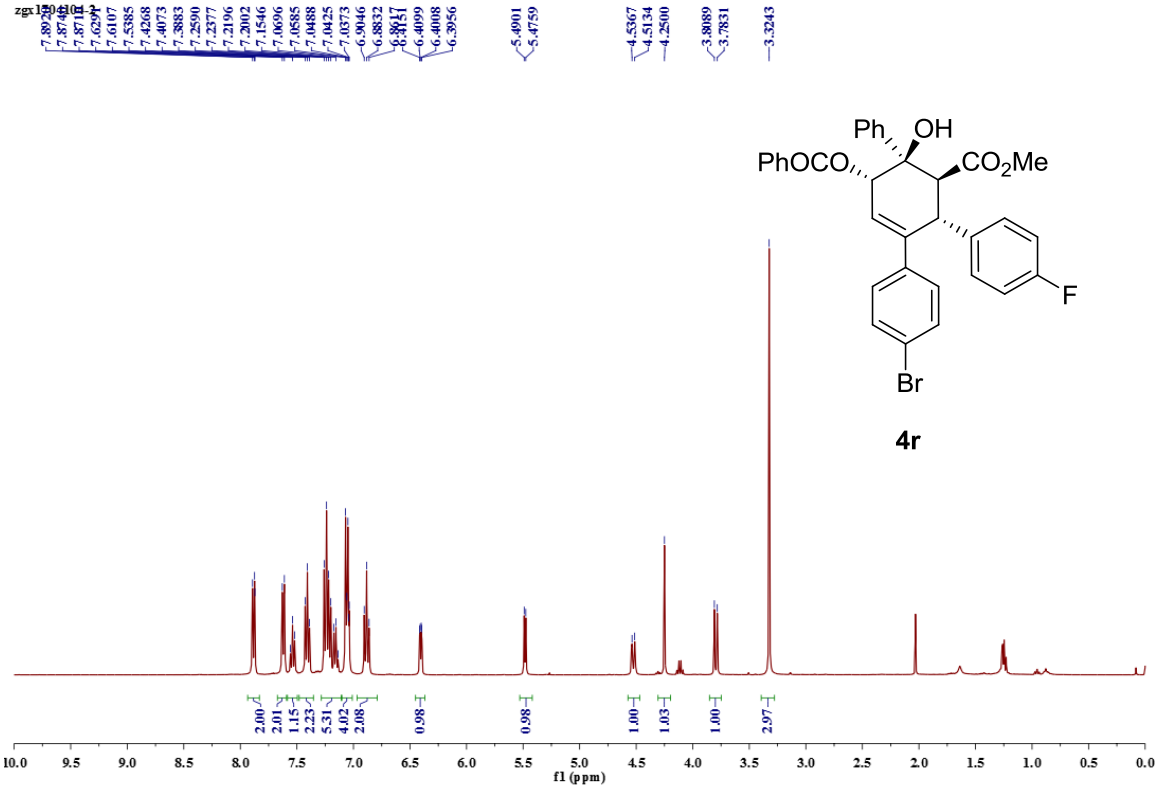
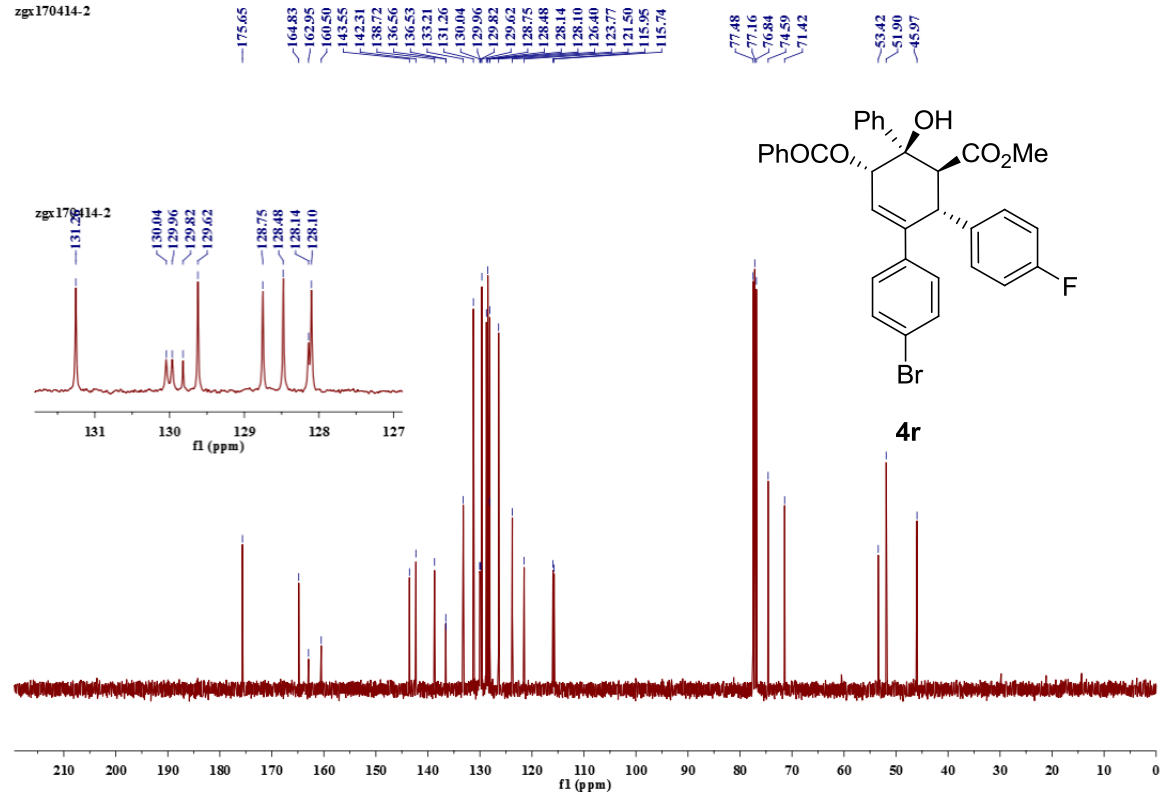
OH
PhOCO
CO2Me
Ph
F
4q
fl (ppm)


Ph
OH
PhOCO
CO2Me
F
Br
4r
f1 (ppm)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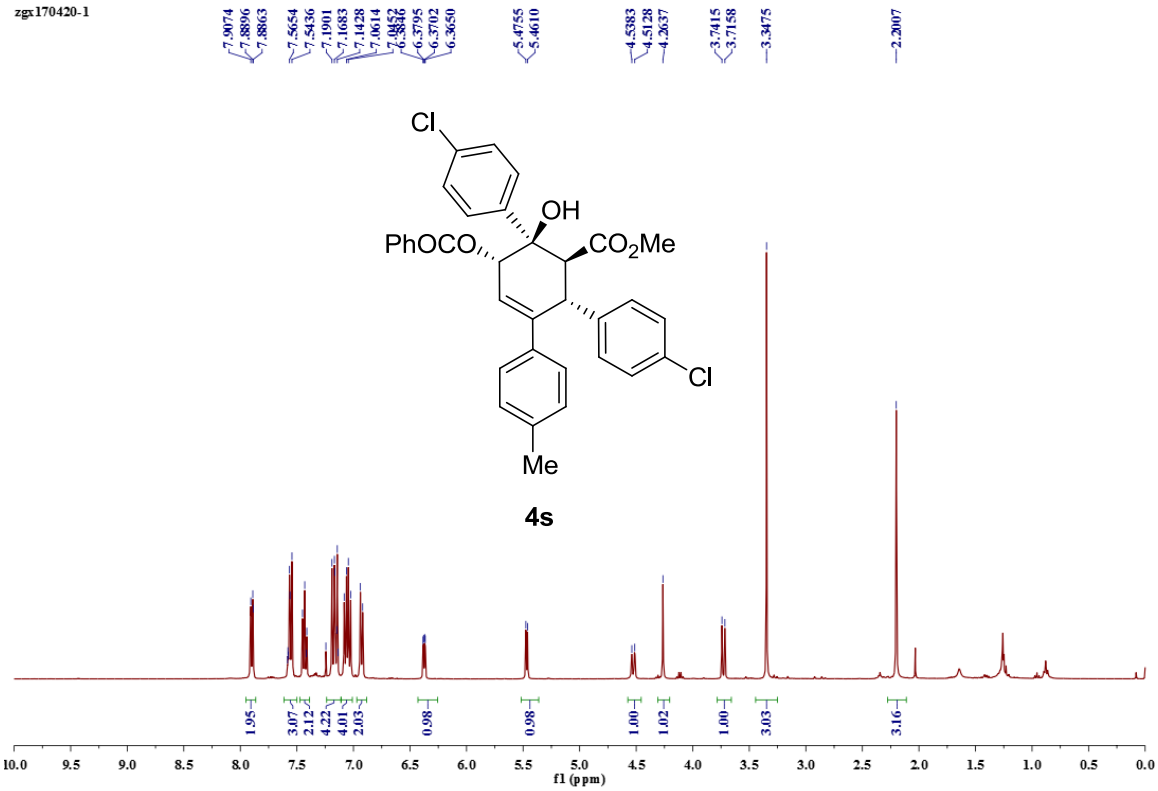
Ph
OH
PhOCO
CO2Me
F
Br
4r
f1 (ppm)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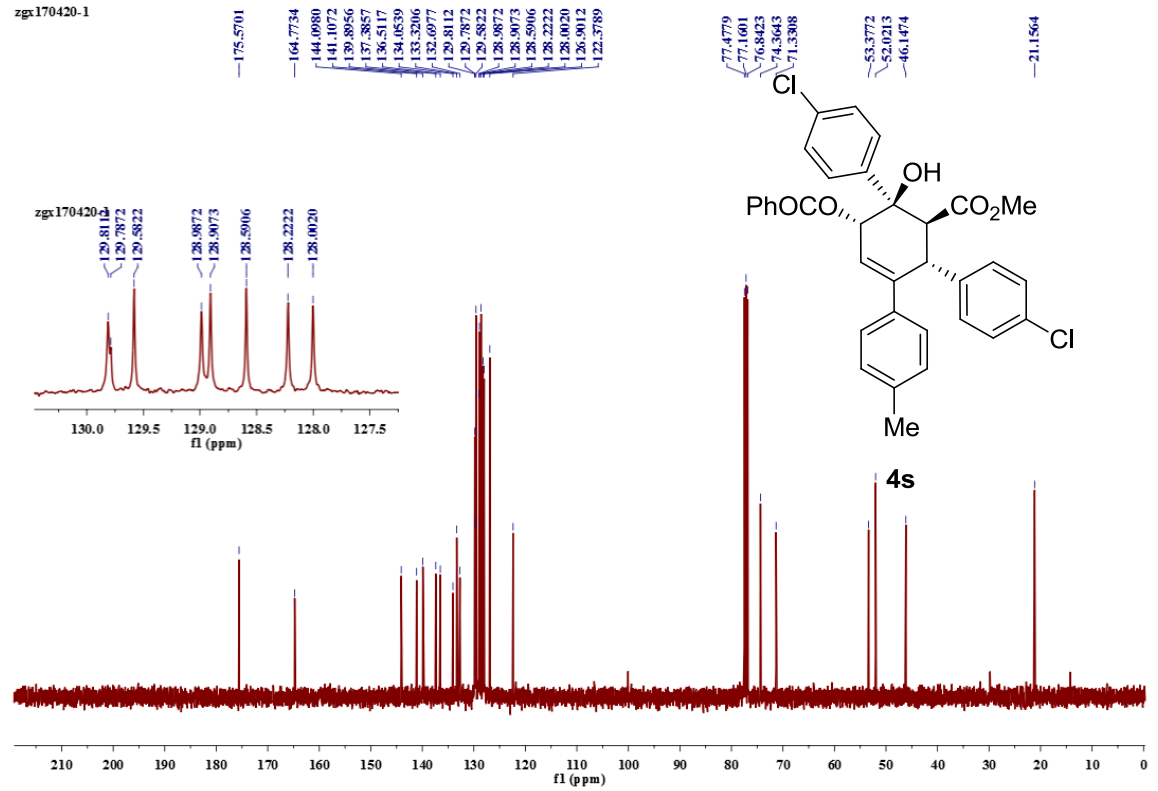
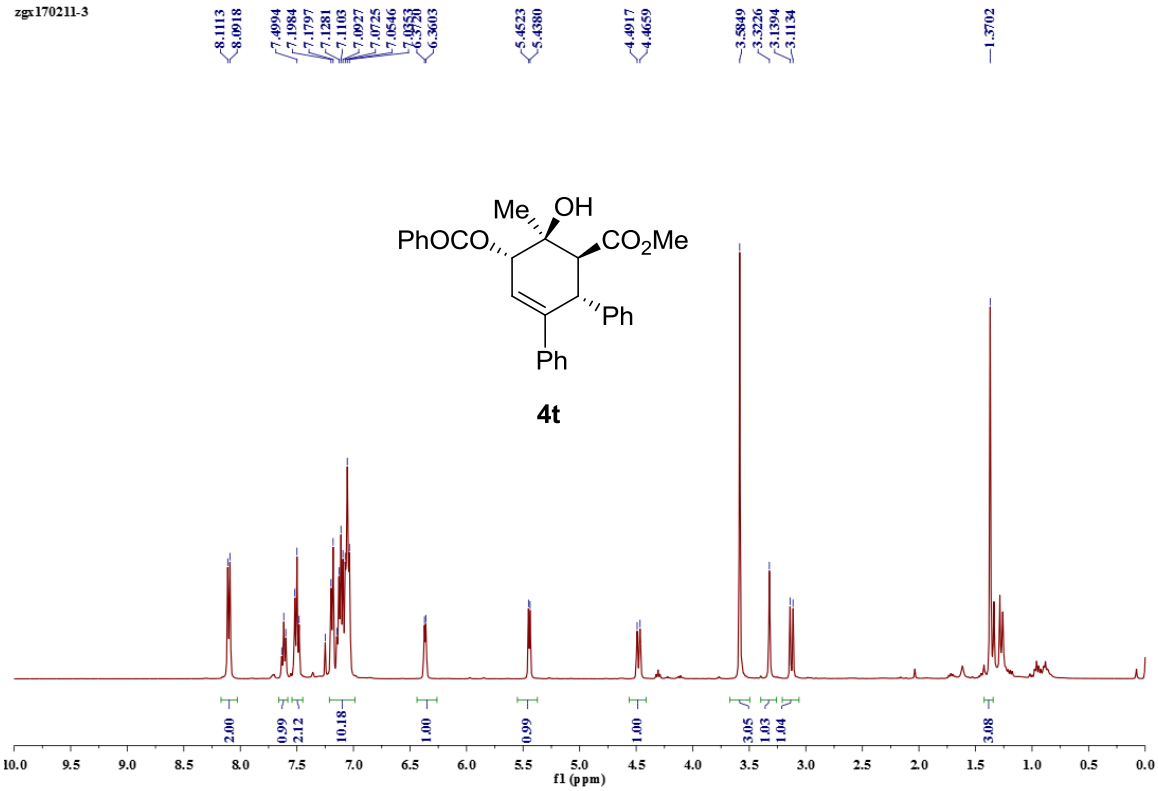
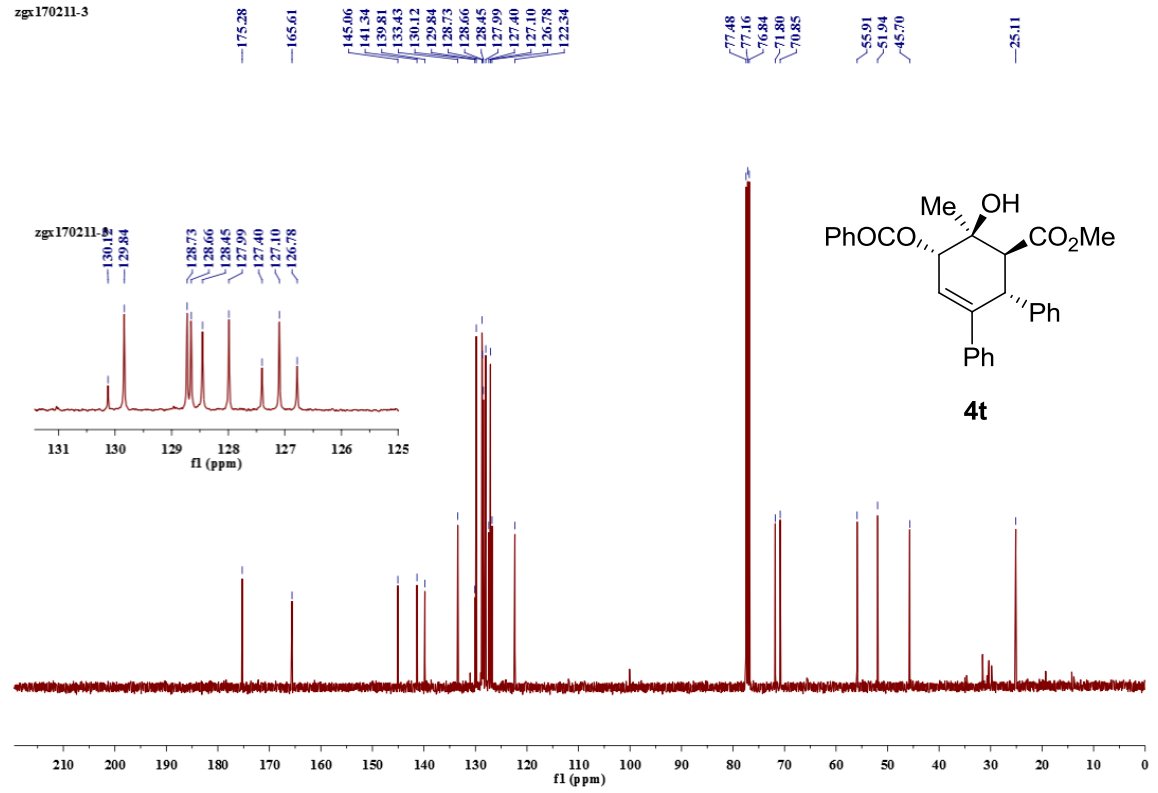
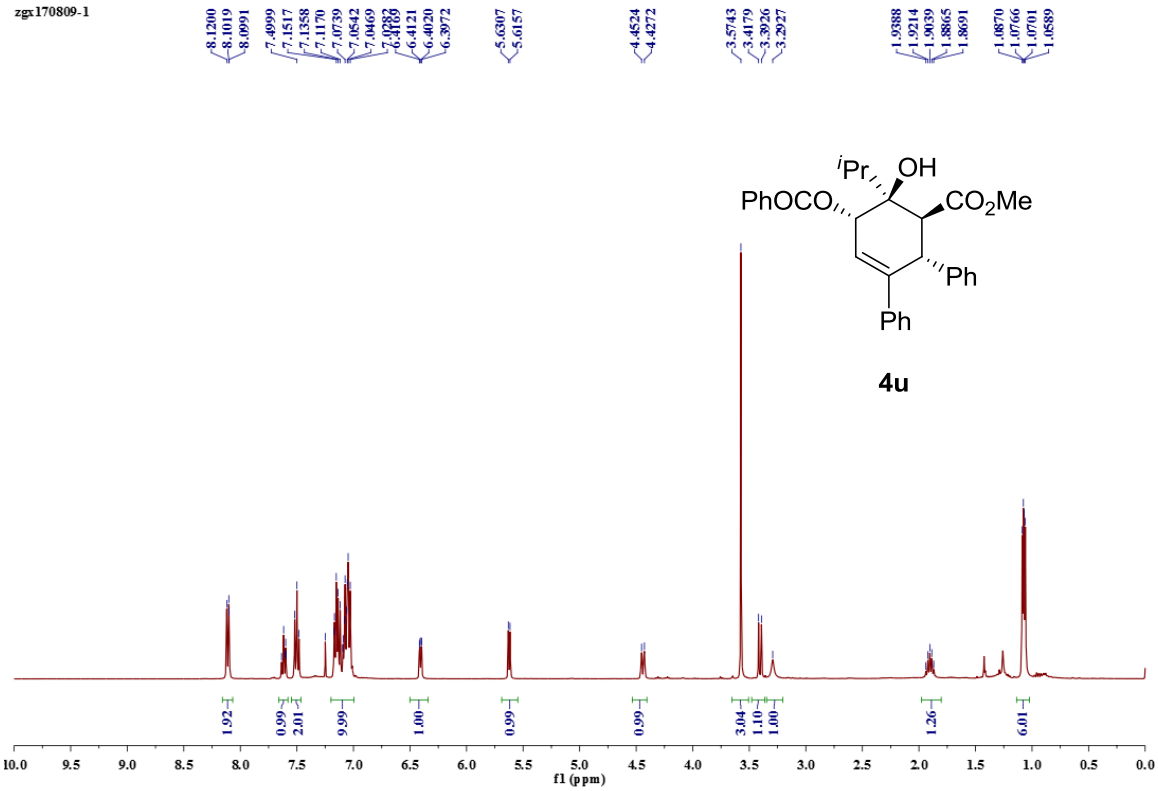
OH
PhOCO
CO2Me
Cl
Me
4s
fl (ppm)


zgx170420-1
Cl
OH
PhOCO
CO2Me
Cl
Me
4s
fl (ppm)


zgx170211-3
8.1113
8.0918
7.4994
7.1984
7.1797
7.1281
7.1103
7.0927
7.0725
7.0546
6.3603
5.4523
5.4380
4.4917
4.4659
3.5849
3.3226
3.1394
3.1134
1.3702
Me
OH
PhOCO
CO2Me
Ph
Ph
4t
2.00
0.99
2.12
10.18
1.00
0.99
1.00
3.05
1.03
1.04
3.08
f1 (ppm)


zgx170211-3
175.28
165.61
145.06
141.34
139.81
133.43
130.12
129.84
128.73
128.66
128.45
127.99
127.40
127.10
126.78
122.34
77.48
77.16
76.84
71.80
70.85
55.91
51.94
45.70
25.11
zgx170211-3
130.12
129.84
128.73
128.66
128.45
127.99
127.40
127.10
126.78
f1 (ppm)
Me
OH
PhOCO
CO2Me
Ph
Ph
4t
f1 (ppm)


zgx170809-1
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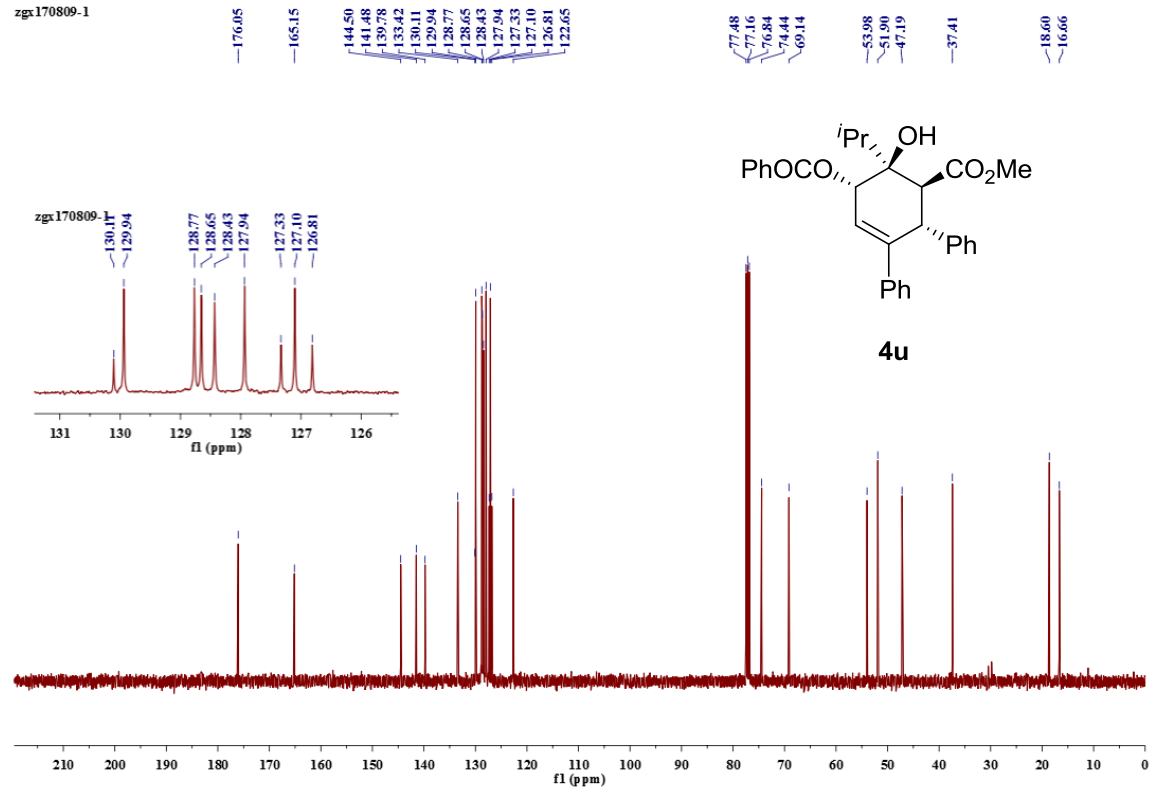
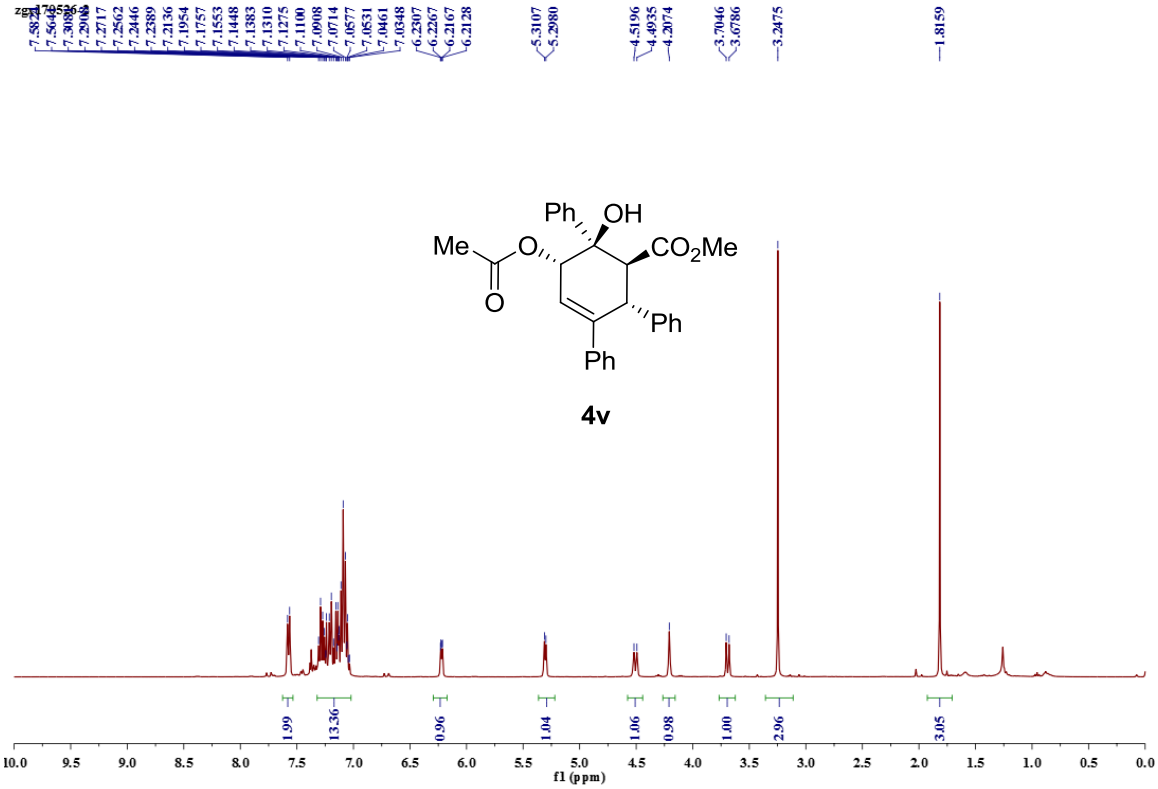
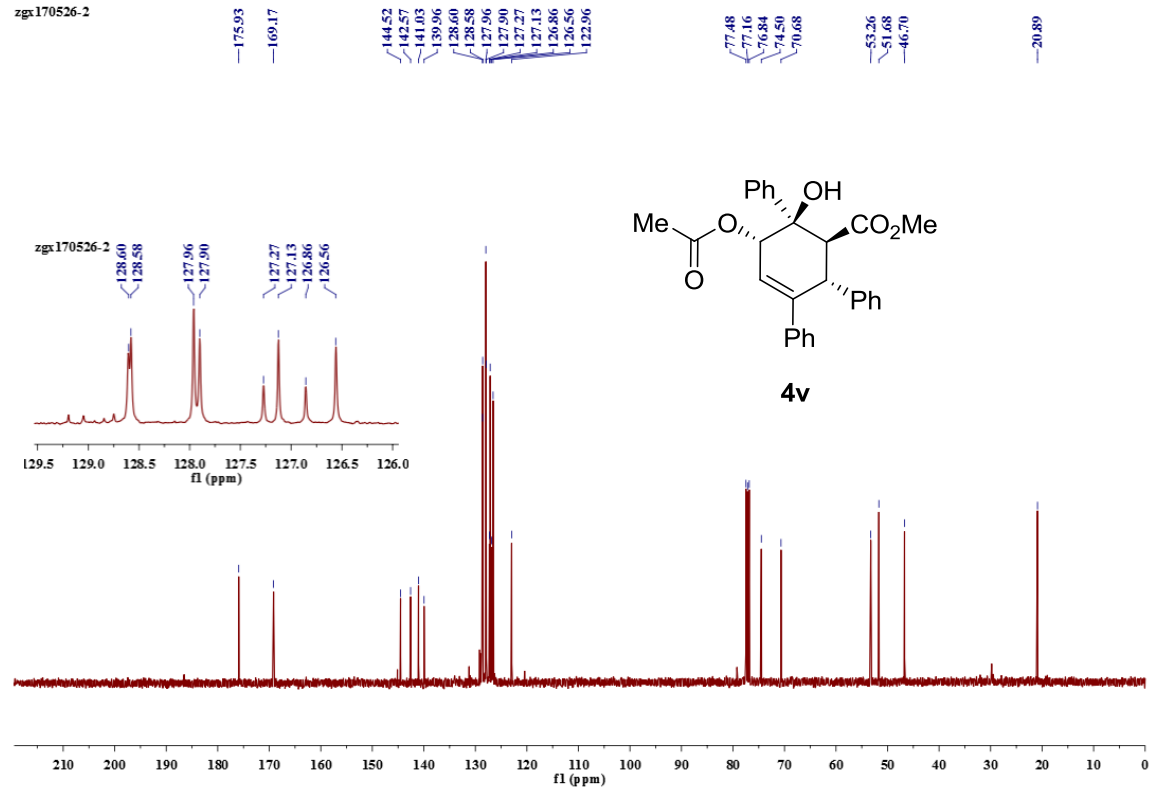
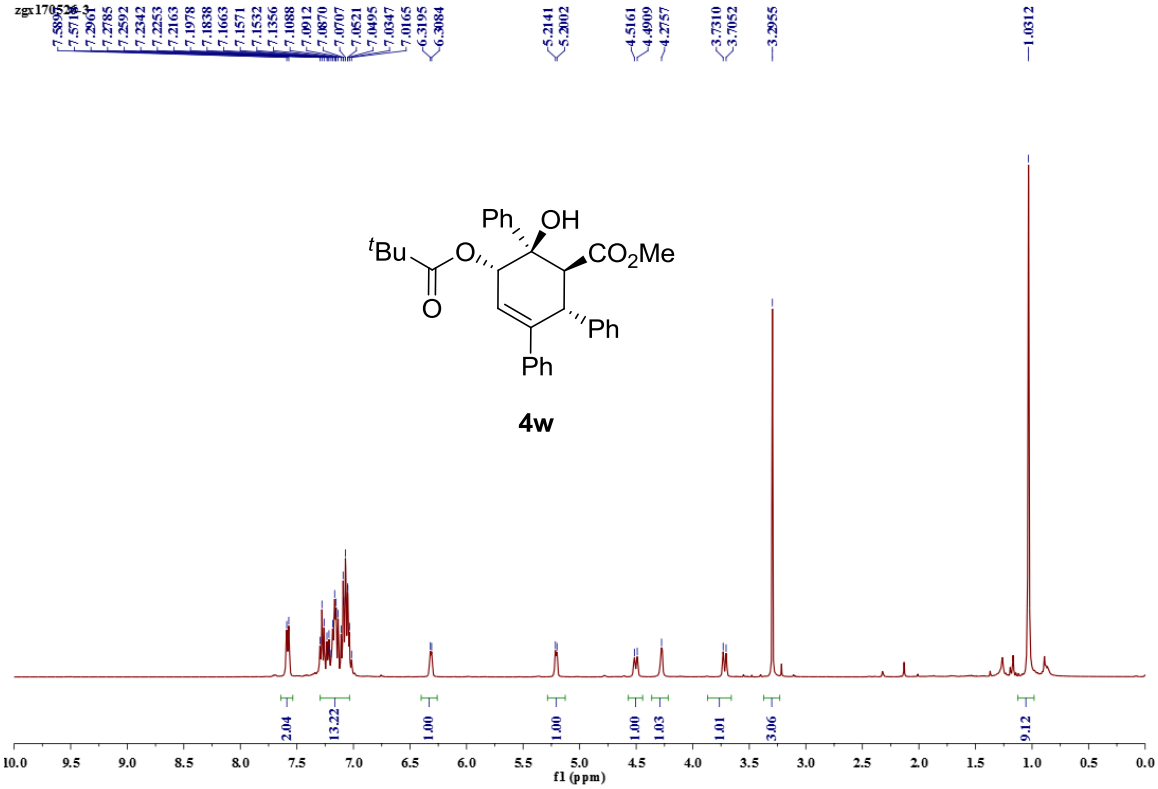
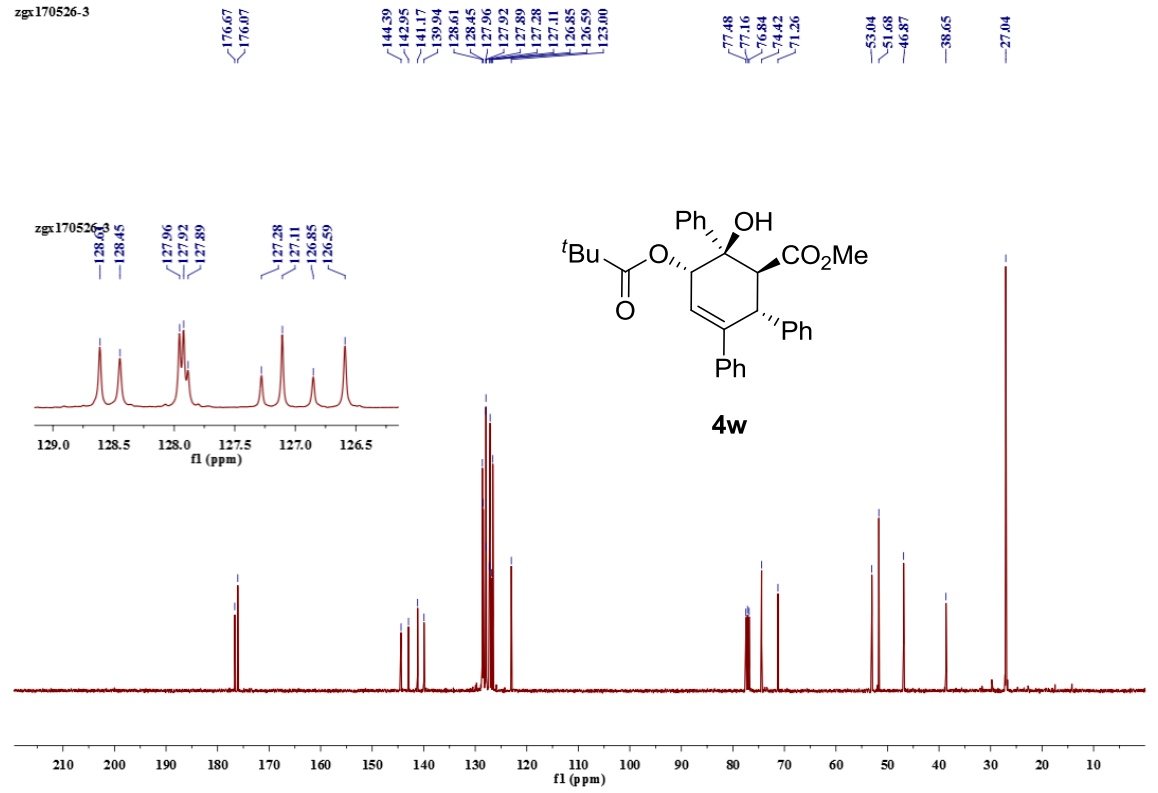
8.1019
8.0991
7.4999
7.1517
7.1358
7.1170
7.0739
7.0642
7.0469
6.4189
6.4121
6.4020
6.3972
5.6307
5.6157
4.4524
4.4272
3.5743
3.4179
3.3926
3.2927
1.9388
1.9214
1.9039
1.8865
1.8691
1.0870
1.0766
1.0701
1.0589
iPr
OH
PhOCO
CO2Me
Ph
Ph
4u
1.92
0.99
2.01
9.99
1.00
0.99
0.99
3.04
1.10
1.00
1.26
6.01
fl (ppm)

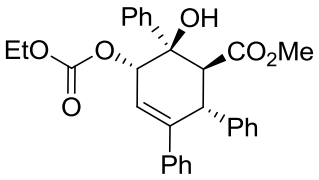

zgx170809-1
176.05
165.15
144.50
141.48
139.78
133.42
130.11
129.94
128.77
128.65
128.43
127.94
127.33
127.10
126.81
122.65
77.48
77.16
76.84
74.44
69.14
53.98
51.90
47.19
37.41
18.60
16.66
iPr
OH
PhOCO
CO2Me
Ph
Ph
4u
fl (ppm)


Ph
OH
Me
O
CO2Me
Ph
Ph
4v
fl (ppm)

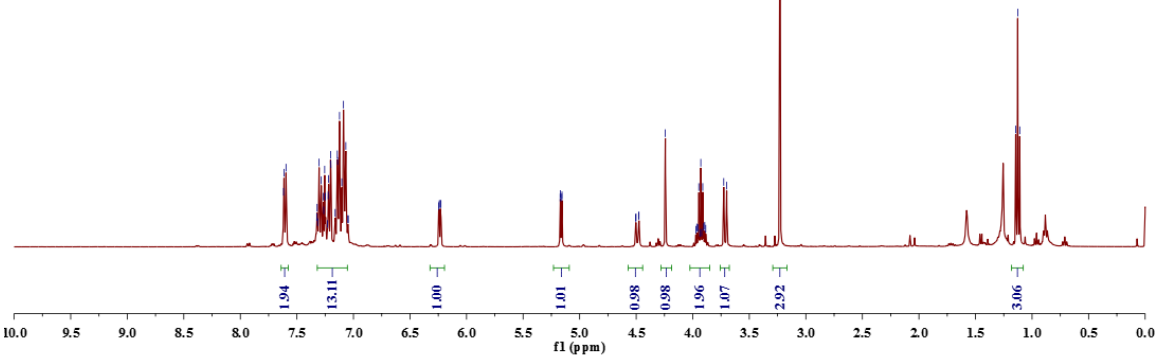

zgx170526-2
Ph
OH
Me
O
CO2Me
Ph
Ph
4v
fl (ppm)

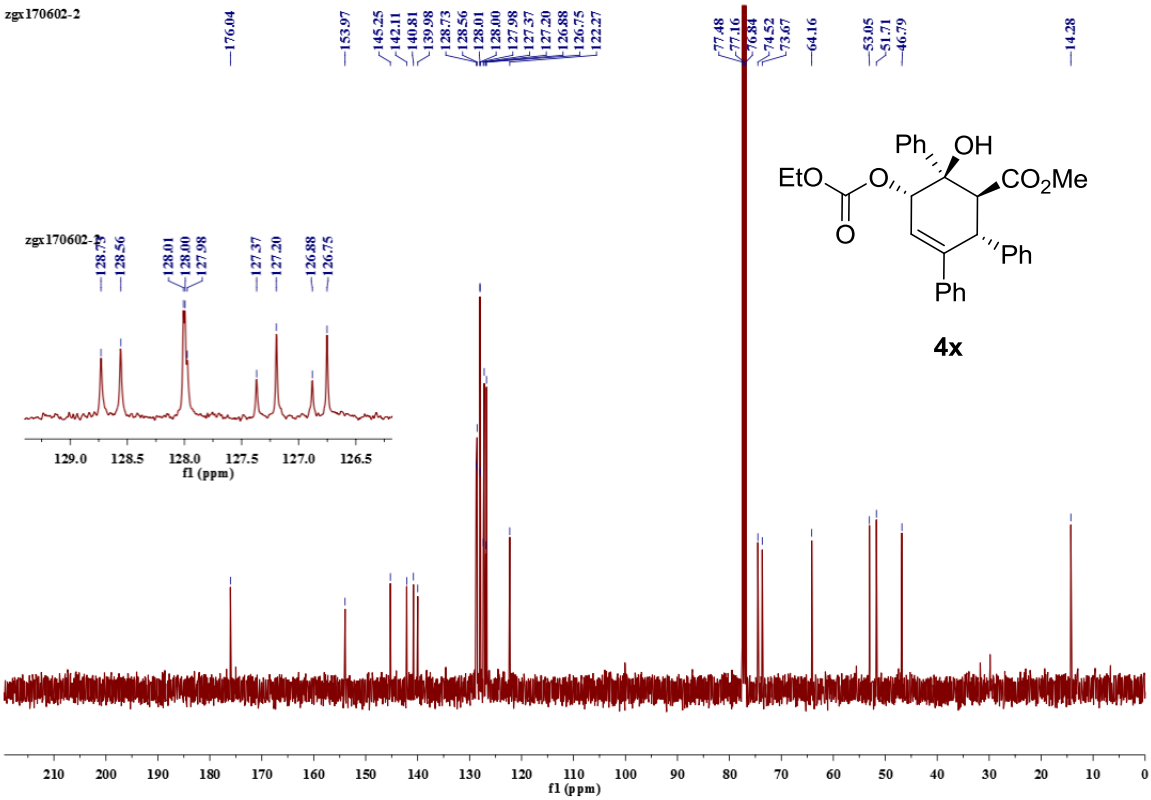

Ph
OH
tBu
O
O
CO2Me
Ph
Ph
4w
fl (ppm)


zgx170526-3
Ph
OH
tBu
O
O
CO2Me
Ph
Ph
4w
fl (ppm)

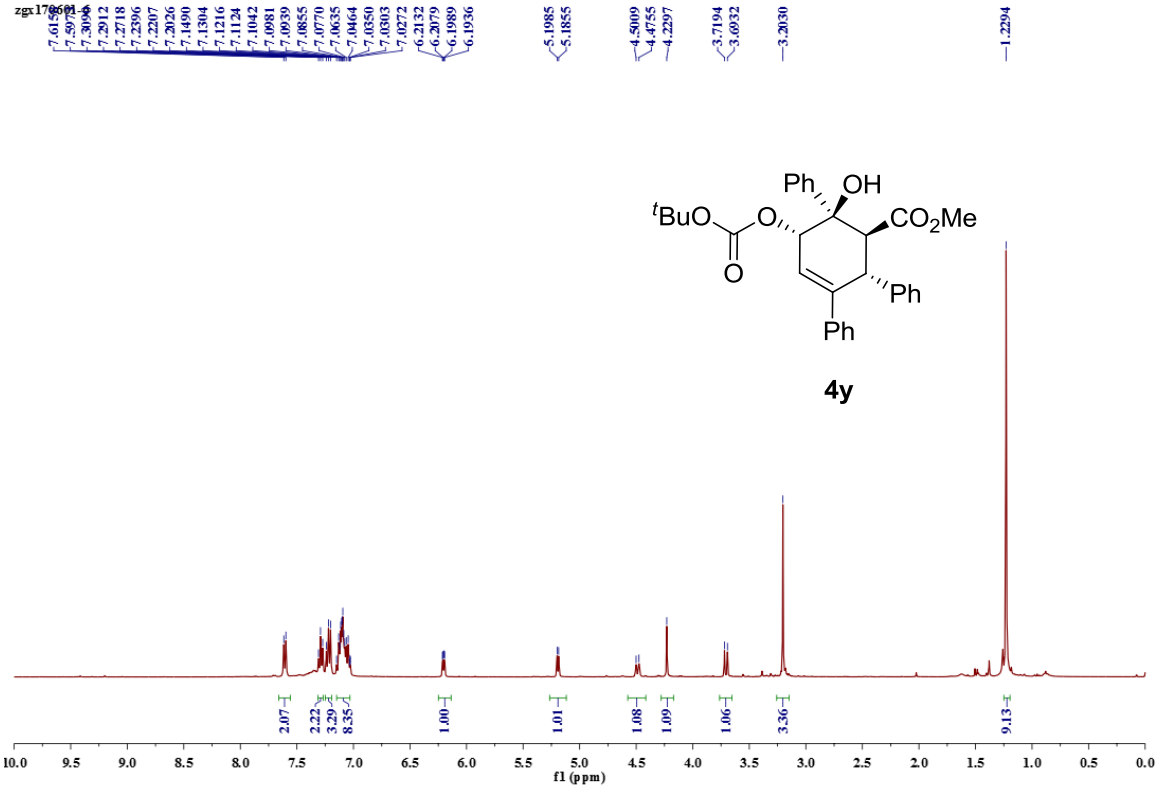

Ph
OH
EtO
O
O
CO2Me
Ph
Ph

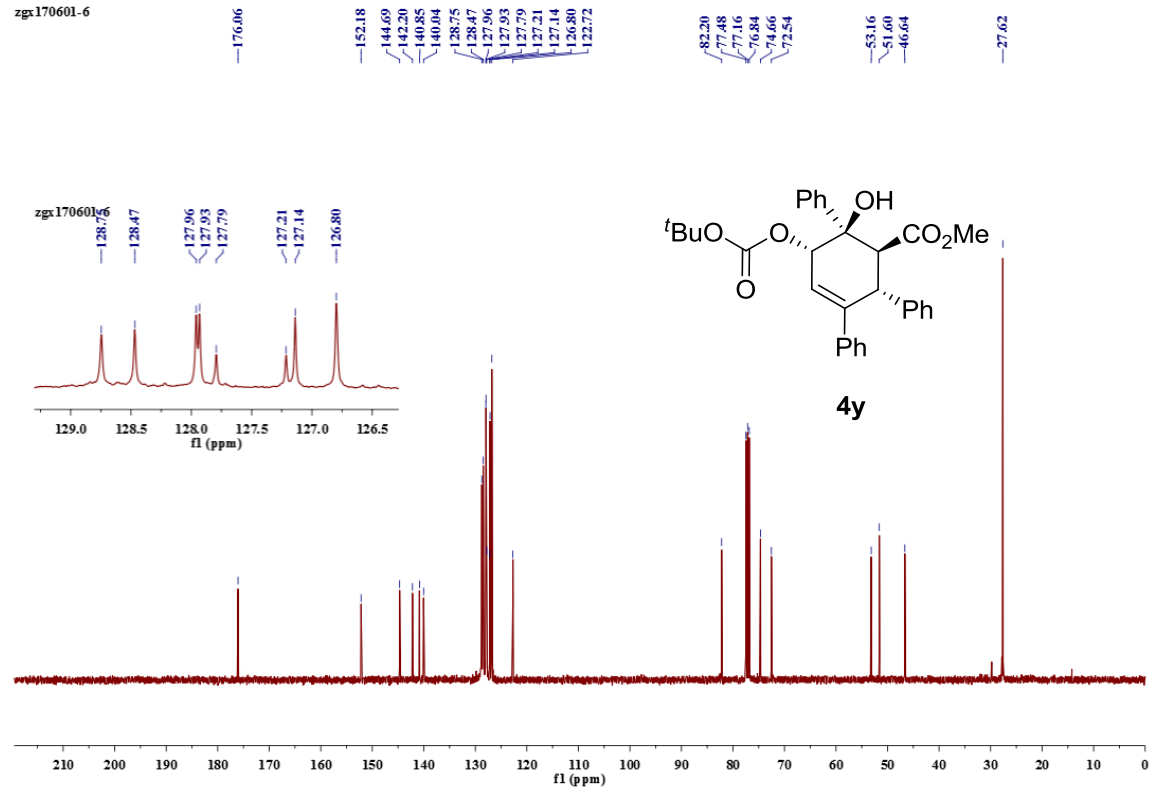
4x

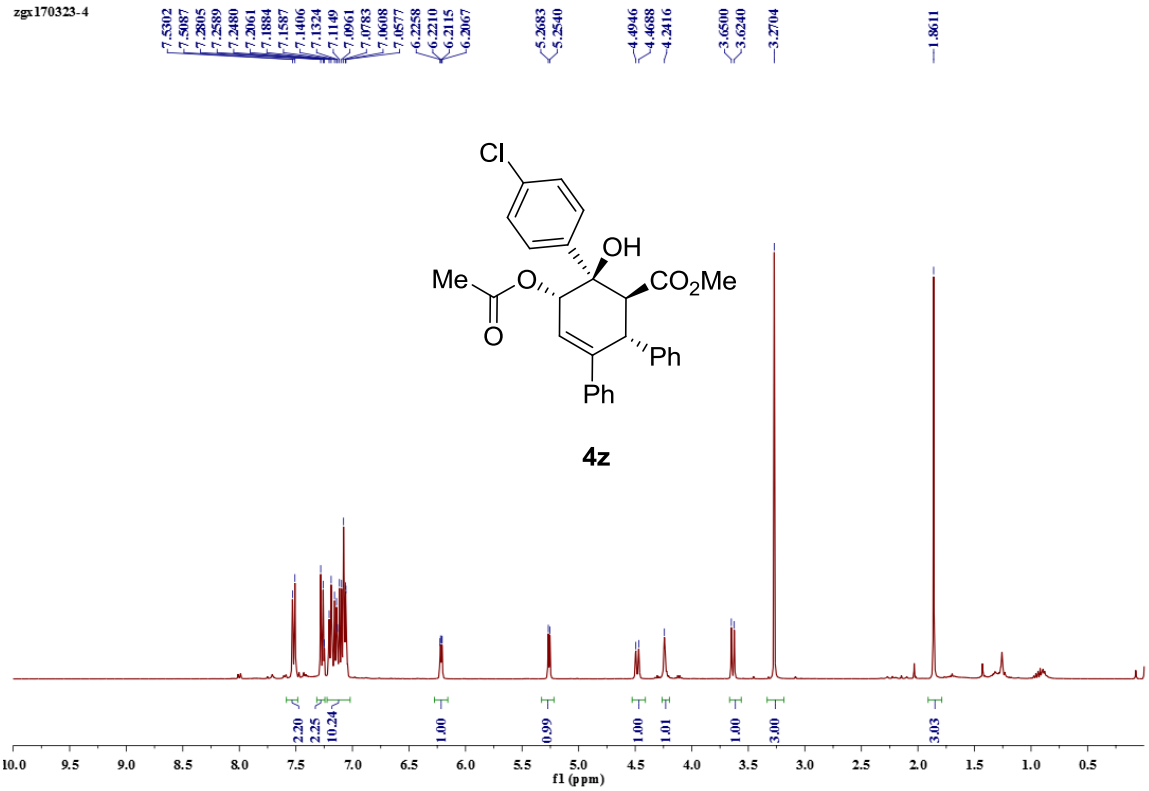

1.94
13.11
1.00
1.01
0.98
0.98
1.96
1.07
2.92
3.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

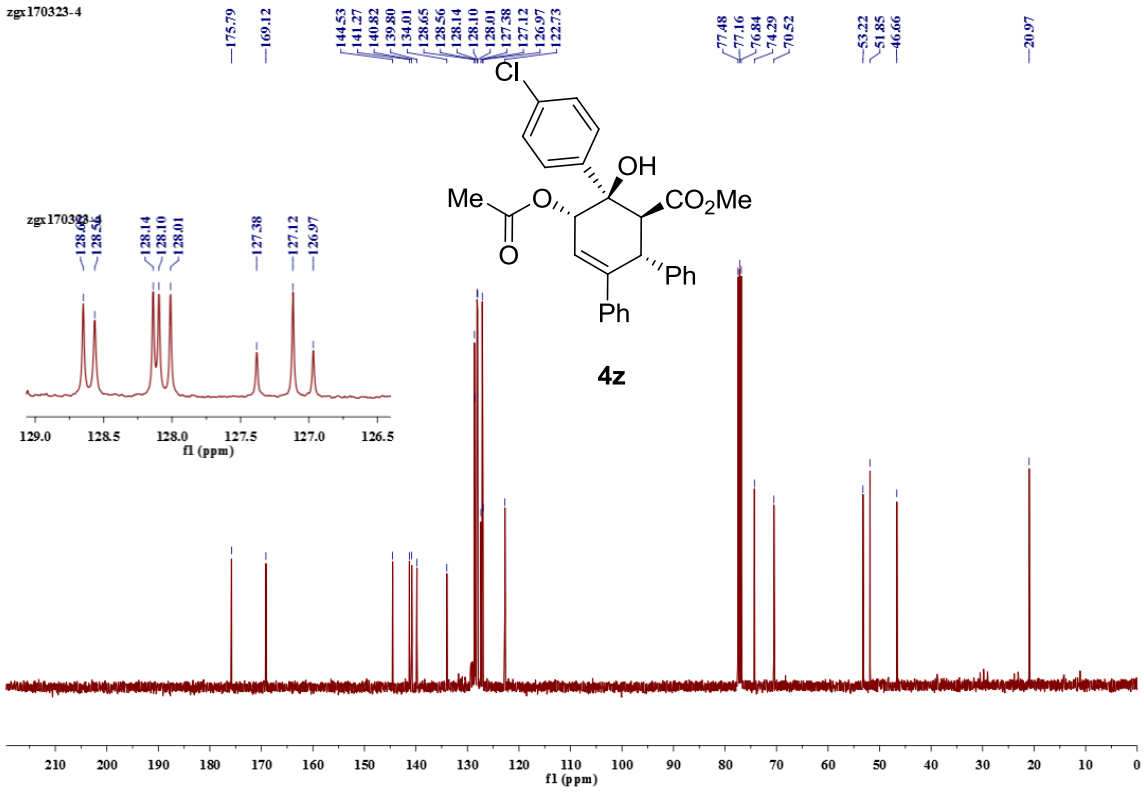

zgx170602-2
176.04
153.97
145.25
142.11
140.81
139.98
128.73
128.56
128.01
128.00
127.98
127.37
127.20
126.88
126.75
122.27
77.48
77.16
76.84
74.52
73.67
64.16
53.05
51.71
46.79
14.28
Ph
OH
EtO
O
O
CO2Me
Ph
Ph
zgx170602-2
128.72
128.56
128.01
128.00
127.98
127.37
127.20
126.88
126.75
129.0 128.5 128.0 127.5 127.0 126.5
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

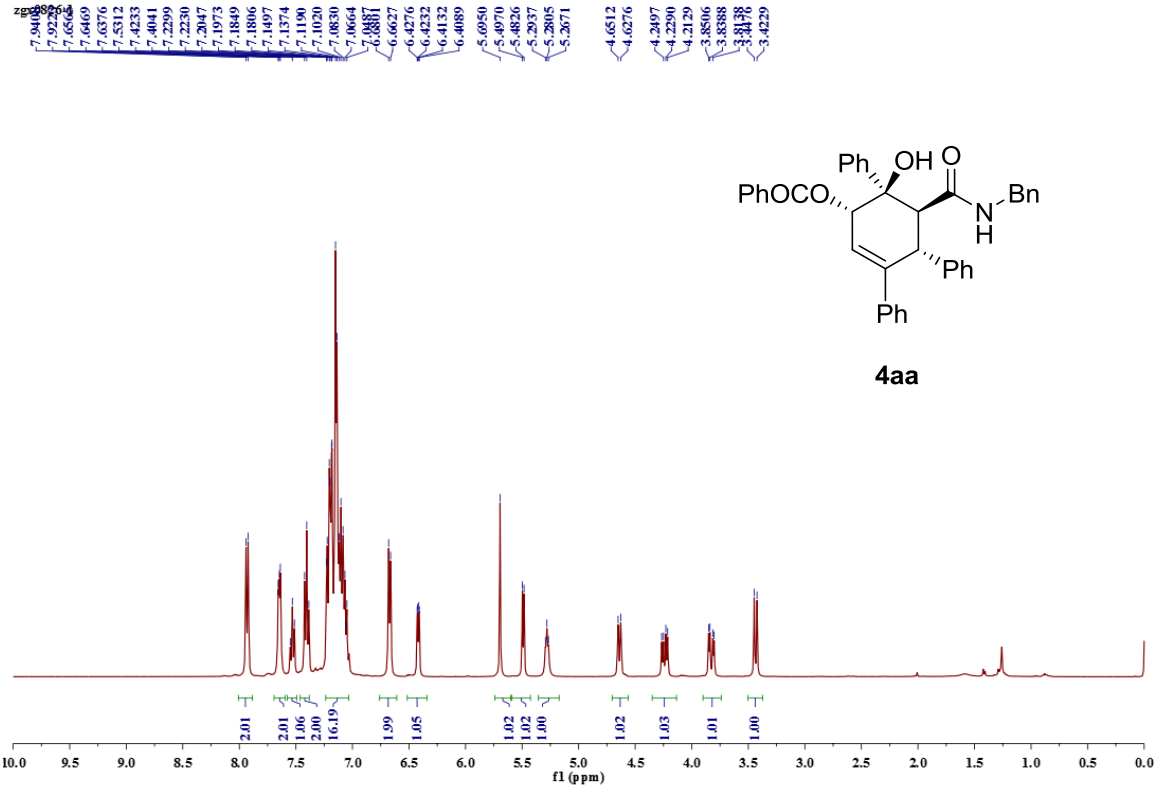
4x

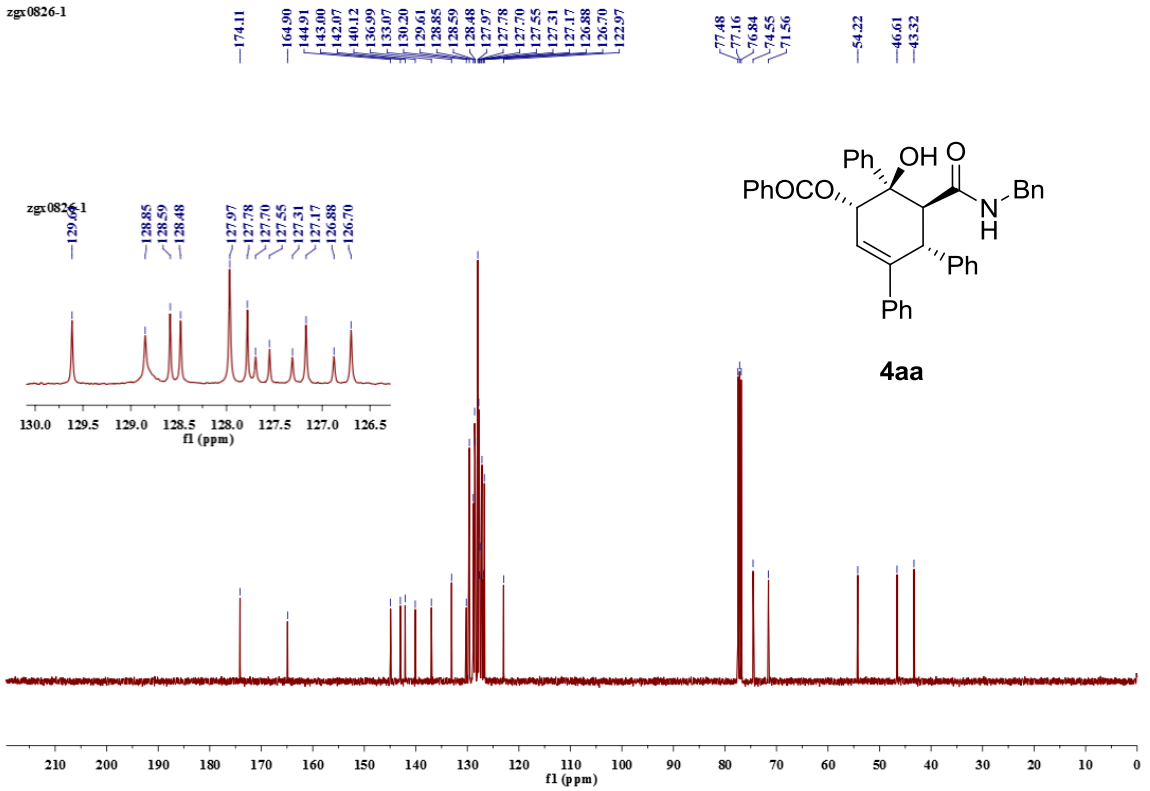

Ph
OH
tBuO
O
O
CO2Me
Ph
Ph
4y
fl (ppm)

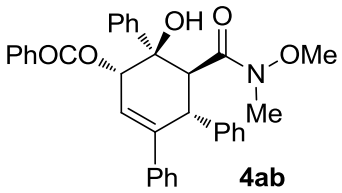

zgx170601-6
Ph
OH
tBuO
O
O
CO2Me
Ph
Ph
4y
fl (ppm)


zgx170323-4
7.5302
7.5087
7.2805
7.2589
7.2480
7.2061
7.1884
7.1587
7.1406
7.1324
7.1149
7.0961
7.0783
7.0608
7.0577
6.2258
6.2210
6.2115
6.2067
5.2683
5.2540
4.4946
4.4688
4.2416
3.6500
3.6240
3.2704
1.8611
Cl
OH
Me
O
CO2Me
O
Ph
Ph
4z
2.20
2.25
10.24
1.00
0.99
1.00
1.01
1.00
3.00
3.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

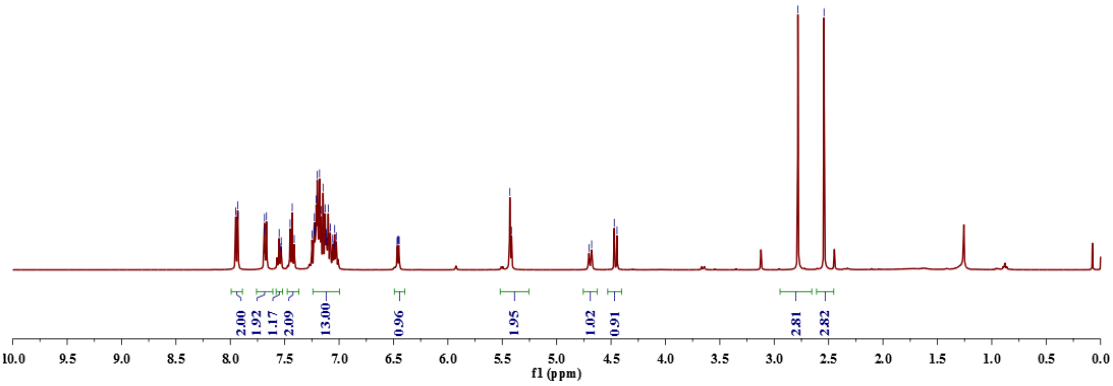

zgx170323-4
175.79
169.12
144.53
141.27
140.82
139.80
134.01
128.65
128.56
128.14
128.10
128.01
127.38
127.12
126.97
122.73
77.48
77.16
76.84
74.29
70.52
53.22
51.85
46.66
20.97
Cl
OH
Me
O
CO2Me
O
Ph
Ph
4z
zgx170323-4
128.65
128.56
128.14
128.10
128.01
127.38
127.12
126.97
129.0
128.5
128.0
127.5
127.0
126.5
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Ph
OH
O
PhOCO
N
Bn
H
Ph
Ph
4aa
2.01
2.01
1.06
2.00
16.19
1.99
1.05
1.02
1.02
1.00
1.02
1.03
1.01
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


zgx0826-1
174.11
164.90
144.91
143.00
142.07
140.12
136.99
133.07
130.20
129.61
128.85
128.59
128.48
127.97
127.78
127.70
127.55
127.31
127.17
126.88
126.70
122.97
77.48
77.16
76.84
74.55
71.56
54.22
46.61
43.32
Ph
OH
O
PhOCO
N
Bn
H
Ph
Ph
4aa
zgx0826-1
129.66
128.85
128.59
128.48
127.97
127.78
127.70
127.55
127.31
127.17
126.88
126.70
130.0
129.5
129.0
128.5
128.0
127.5
127.0
126.5
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

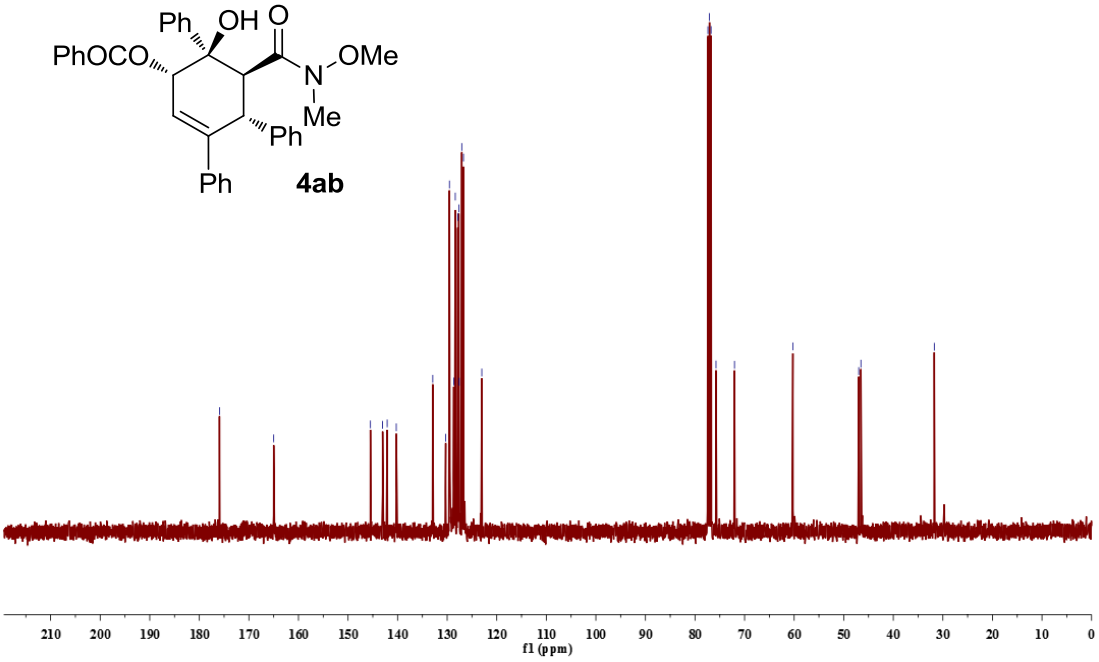

Ph
OH
O
PhOCO
OMe
N
Me
Ph
Ph

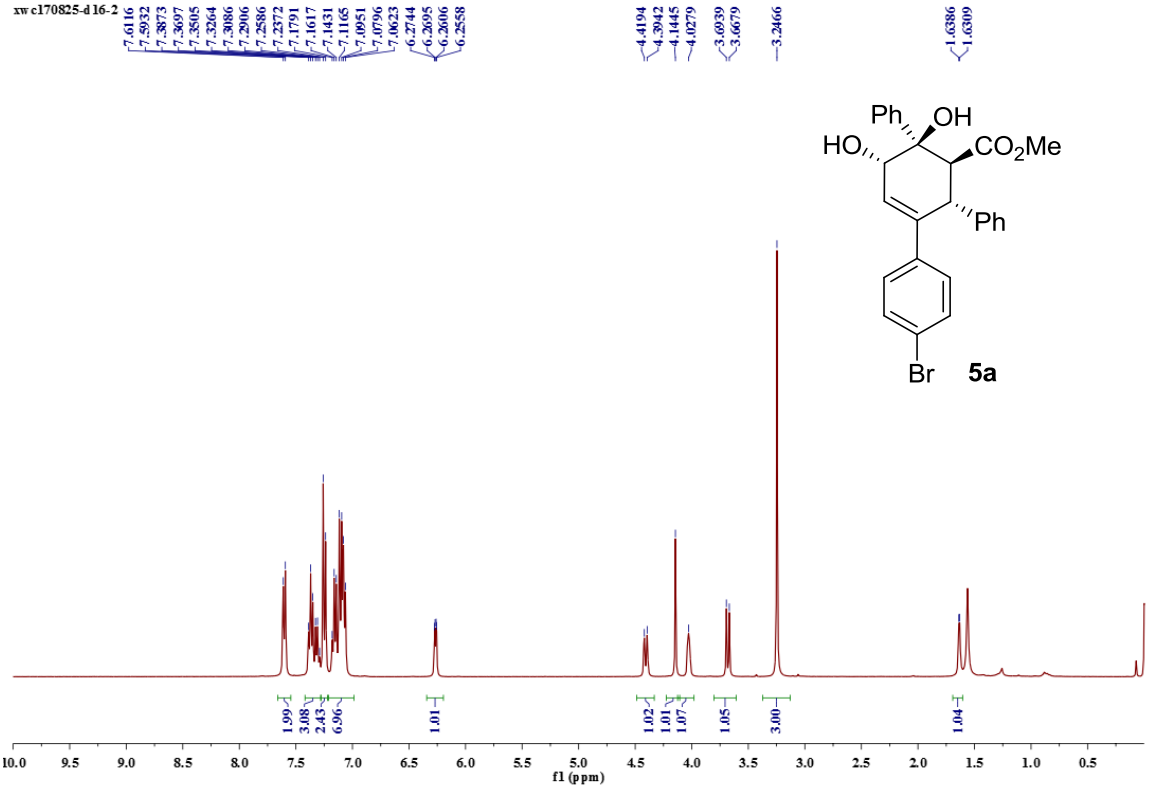
4ab

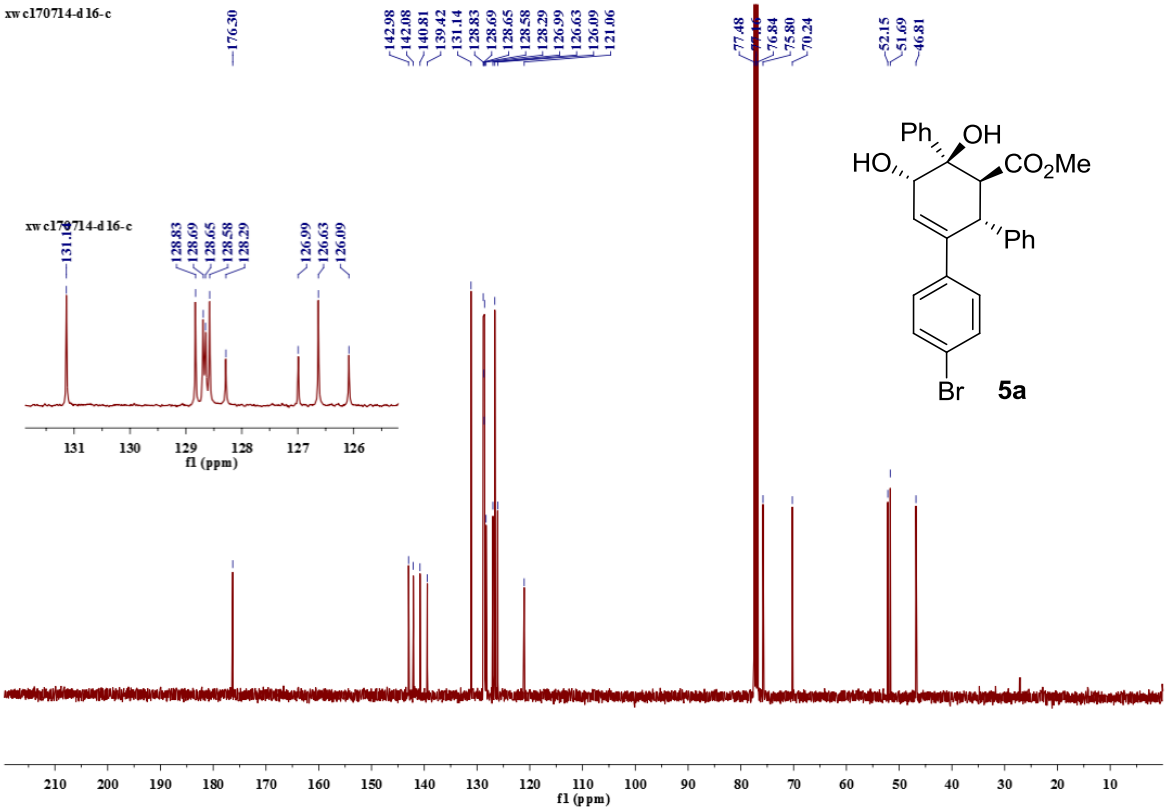

2.00
1.92
1.17
2.09
13.00
0.96
1.95
1.02
0.91
2.81
2.82
f1 (ppm)

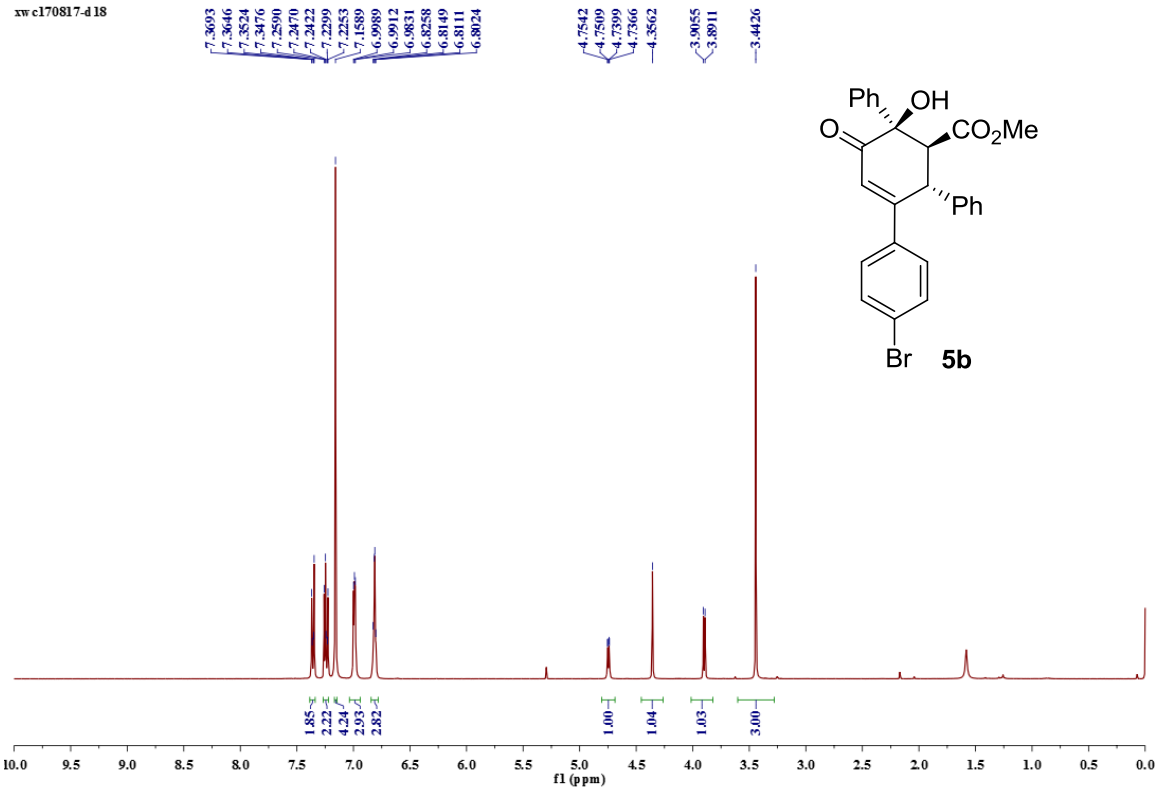
Ph
OH
O
PhOCO
OMe
N
Me
Ph
Ph

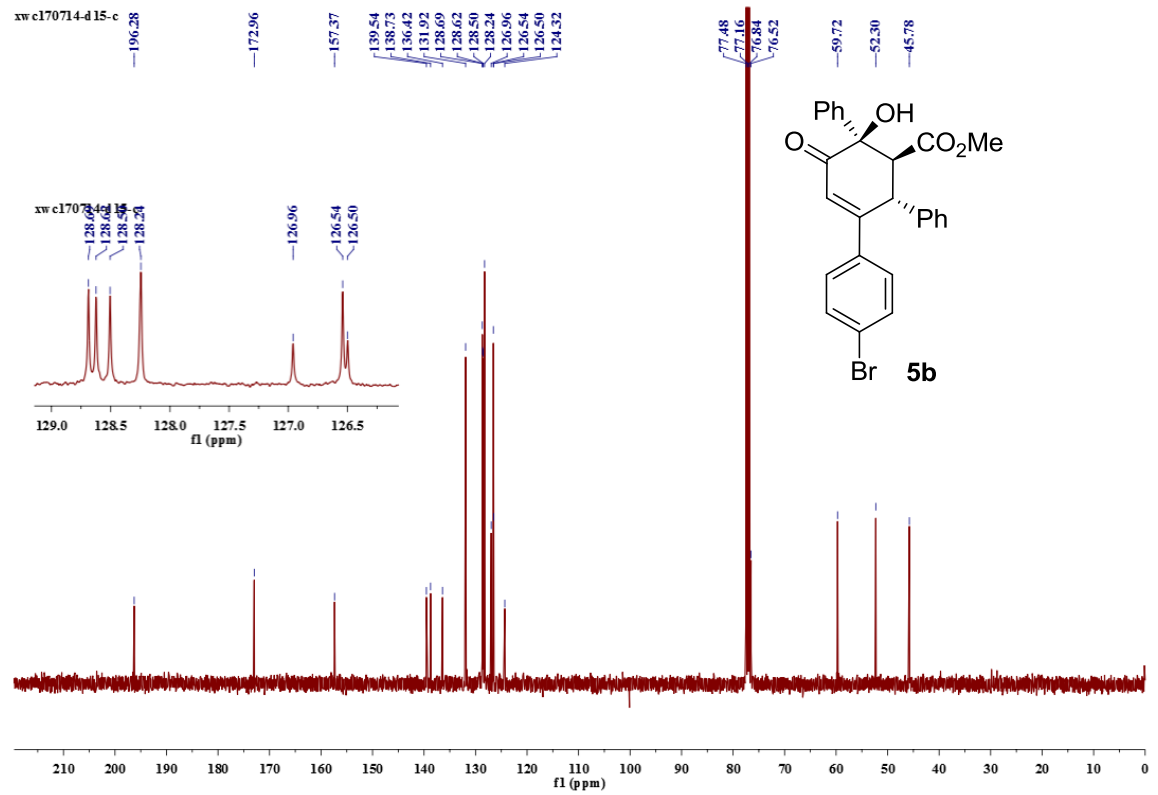
4ab

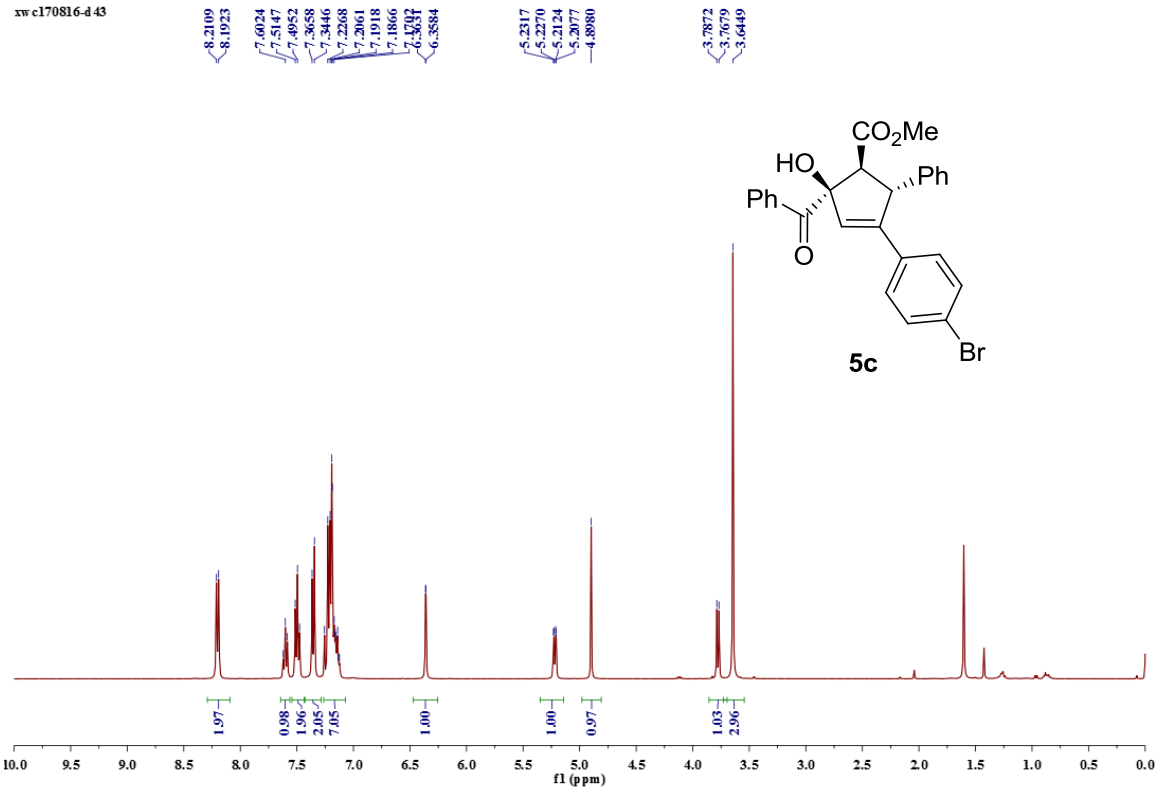

f1 (ppm)

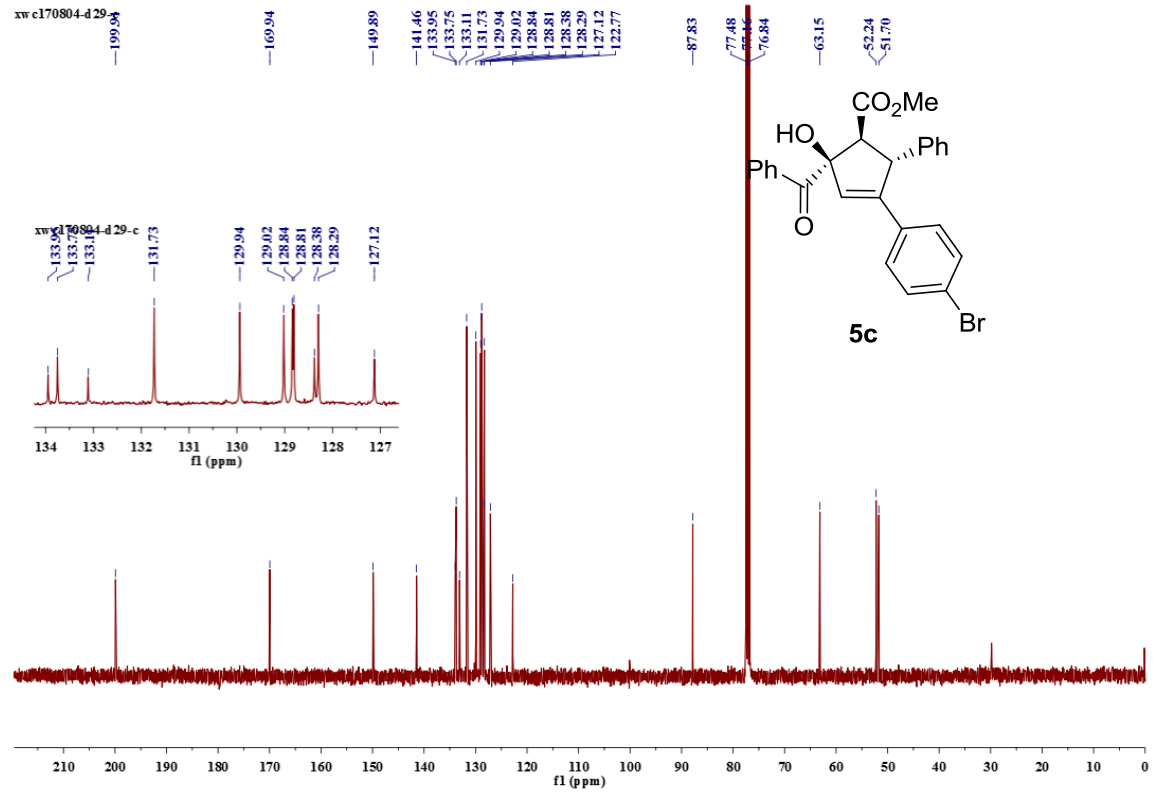

xw c170825-d 16-2
7.6116
7.5932
7.3873
7.3697
7.3505
7.3264
7.3086
7.2906
7.2586
7.2372
7.1791
7.1617
7.1431
7.1165
7.0951
7.0796
7.0623
6.2744
6.2695
6.2606
6.2558
4.4194
4.3942
4.1445
4.0279
3.6939
3.6679
3.2466
1.6386
1.6309
Ph
OH
HO
CO2Me
Ph
Br
5a
1.99
3.08
2.43
6.96
1.01
1.02
1.01
1.07
1.05
3.00
1.04
f1 (ppm)

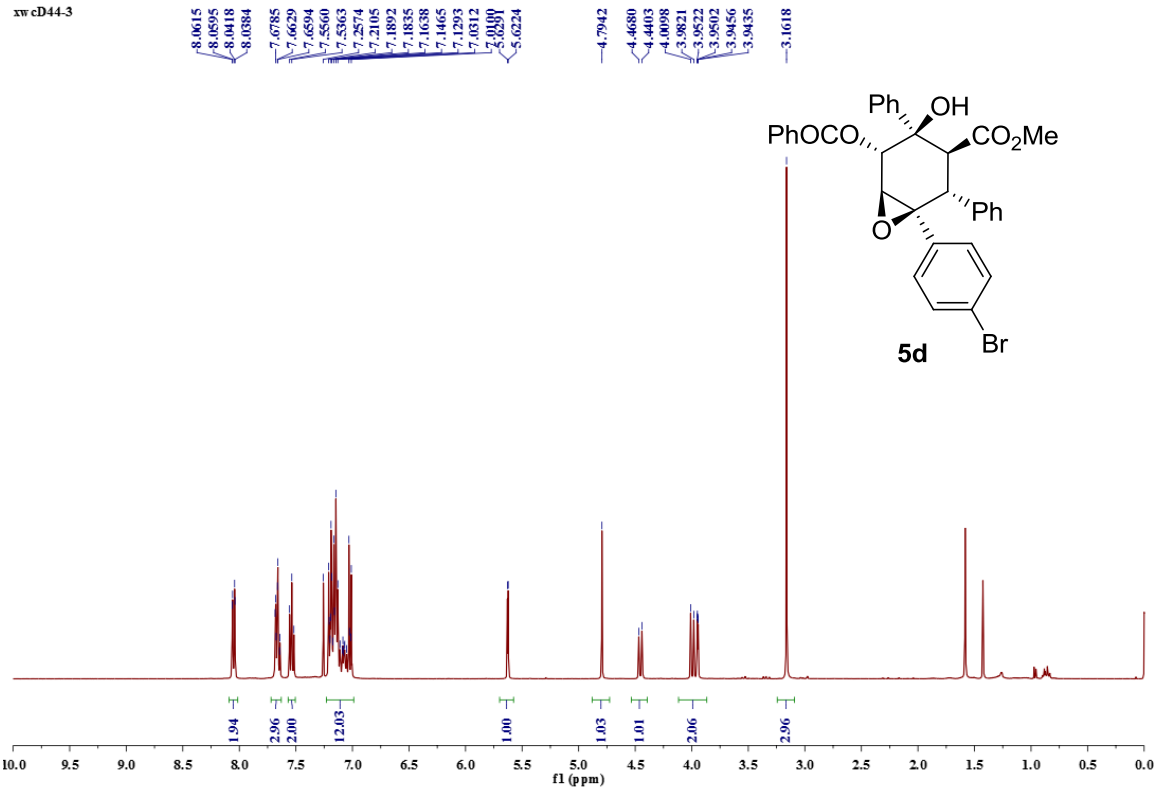

xw c170714-d 16-c
176.30
142.98
142.08
140.81
139.42
131.14
128.83
128.69
128.65
128.58
128.29
126.99
126.63
126.09
121.06
77.48
76.84
75.80
70.24
52.15
51.69
46.81
Ph
OH
HO
CO2Me
Ph
Br
5a
131.14
128.83
128.69
128.65
128.58
128.29
126.99
126.63
126.09
f1 (ppm)
f1 (ppm)

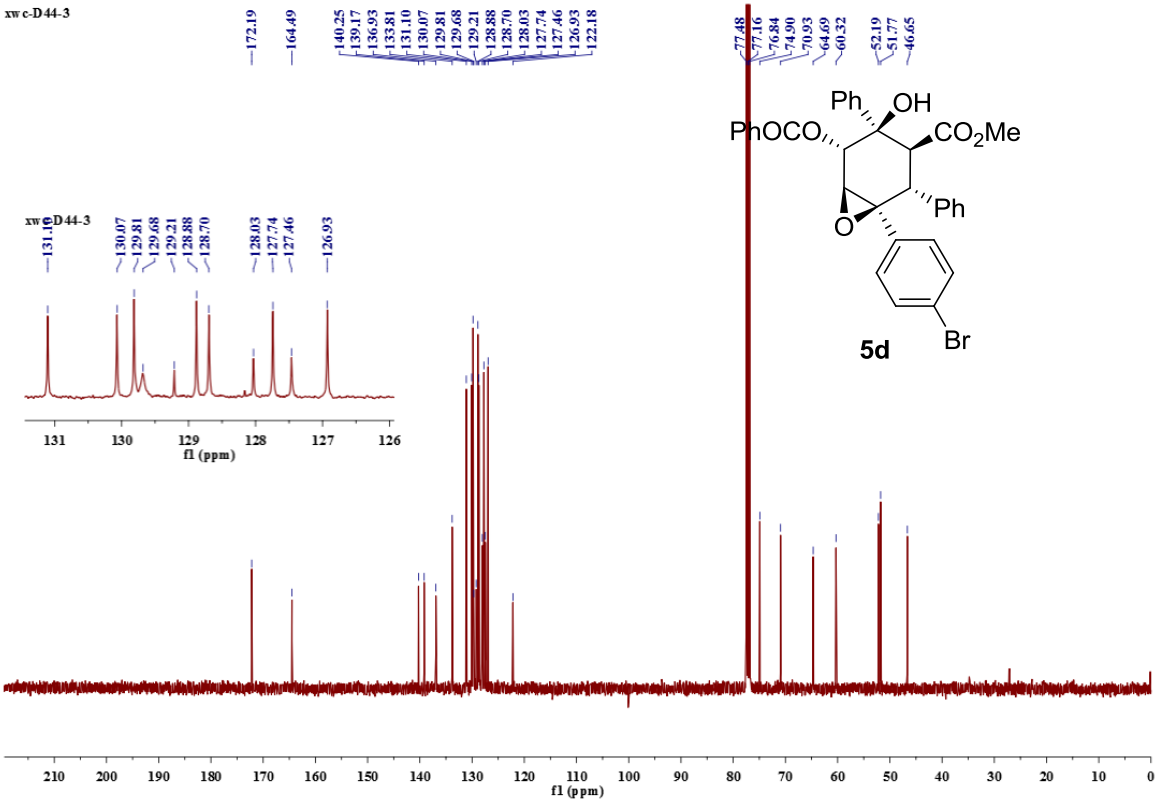

xwc170817-d18
7.3693
7.3646
7.3524
7.3476
7.2590
7.2470
7.2422
7.2299
7.2253
7.1589
6.9989
6.9912
6.9831
6.8258
6.8149
6.8111
6.8024
4.7542
4.7509
4.7399
4.7366
4.3562
3.9055
3.8911
3.4426
Ph
OH
O
CO2Me
Ph
Br
5b
1.85
2.22
4.24
2.93
2.82
1.00
1.04
1.03
3.00
f1 (ppm)

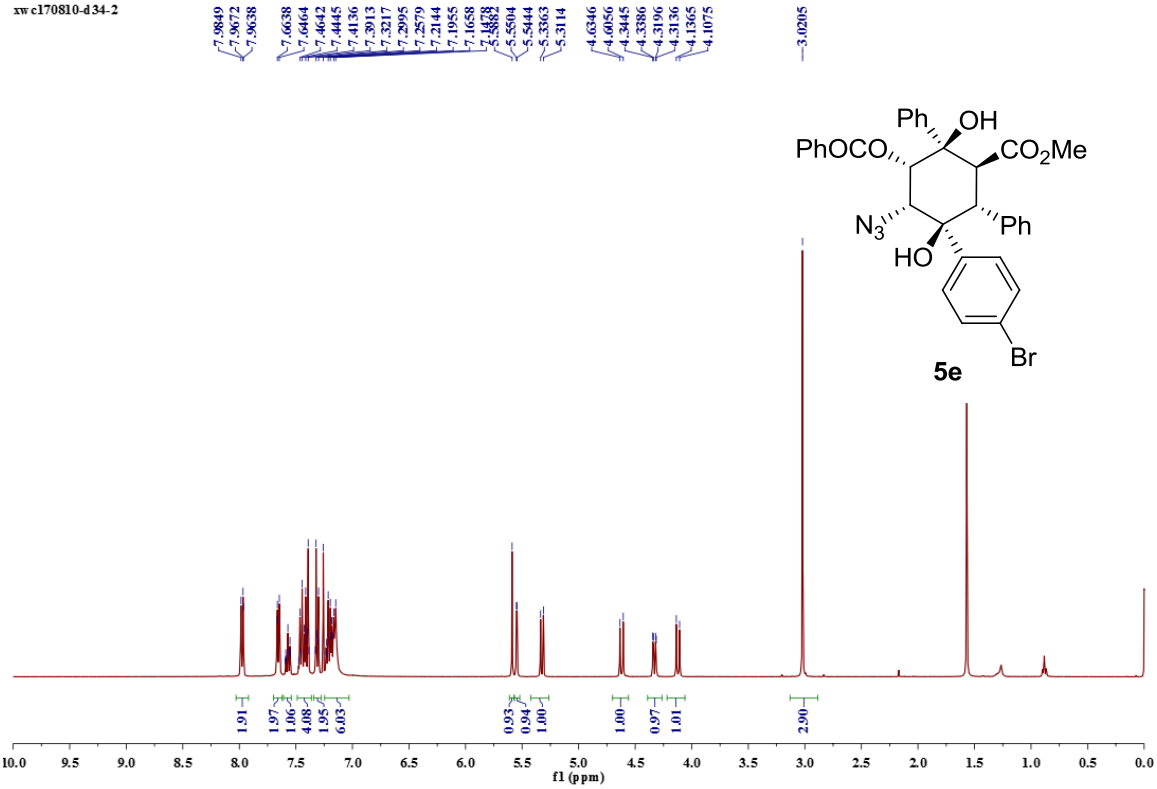

xwc170714-d15-c
196.28
172.96
157.37
139.54
138.73
136.42
131.92
128.69
128.62
128.50
128.24
126.96
126.54
126.50
124.32
77.48
77.16
76.84
76.52
59.72
52.30
45.78
Ph
OH
O
CO2Me
Ph
Br
5b
f1 (ppm)

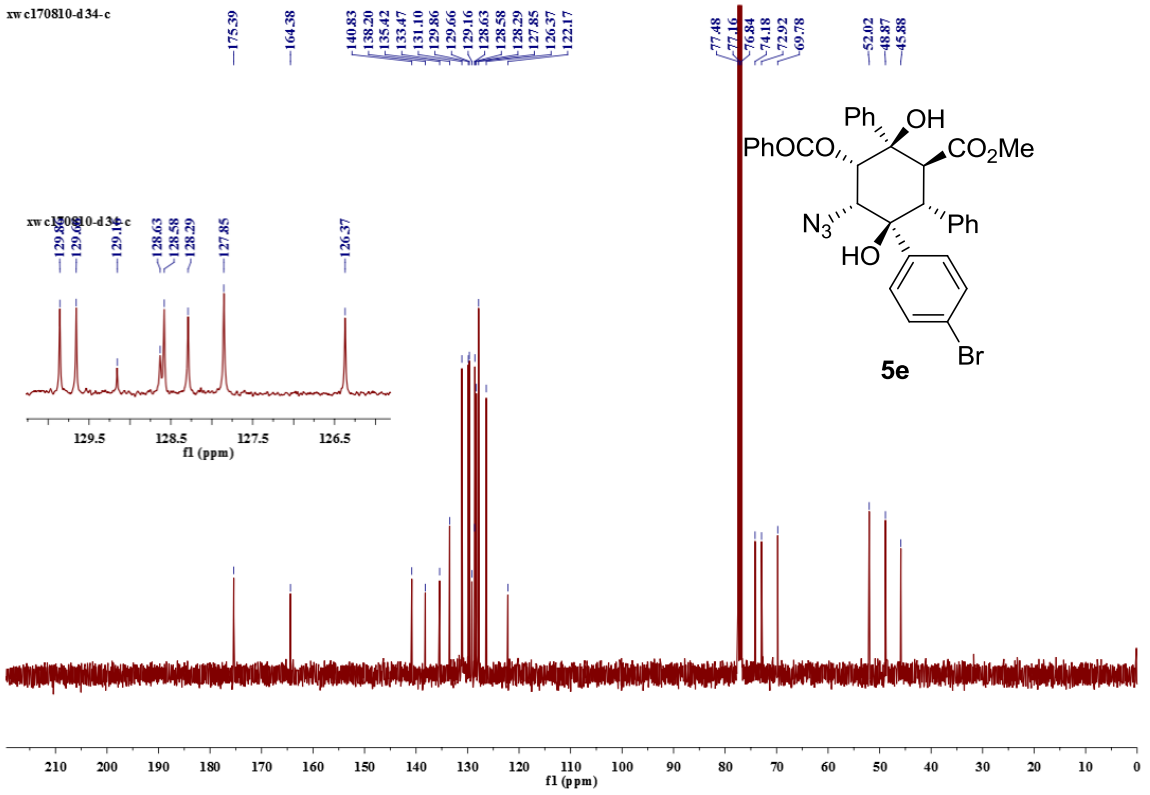

xwc170816-d 43
8.2109
8.1923
7.6024
7.5147
7.4952
7.3658
7.3446
7.2268
7.2061
7.1918
7.1866
6.3584
5.2317
5.2270
5.2124
5.2077
4.8980
3.7872
3.7679
3.6449
CO2Me
HO
Ph
Ph
O
Br
5c
1.97
0.98
1.96
2.05
7.05
1.00
1.00
0.97
1.03
2.96
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

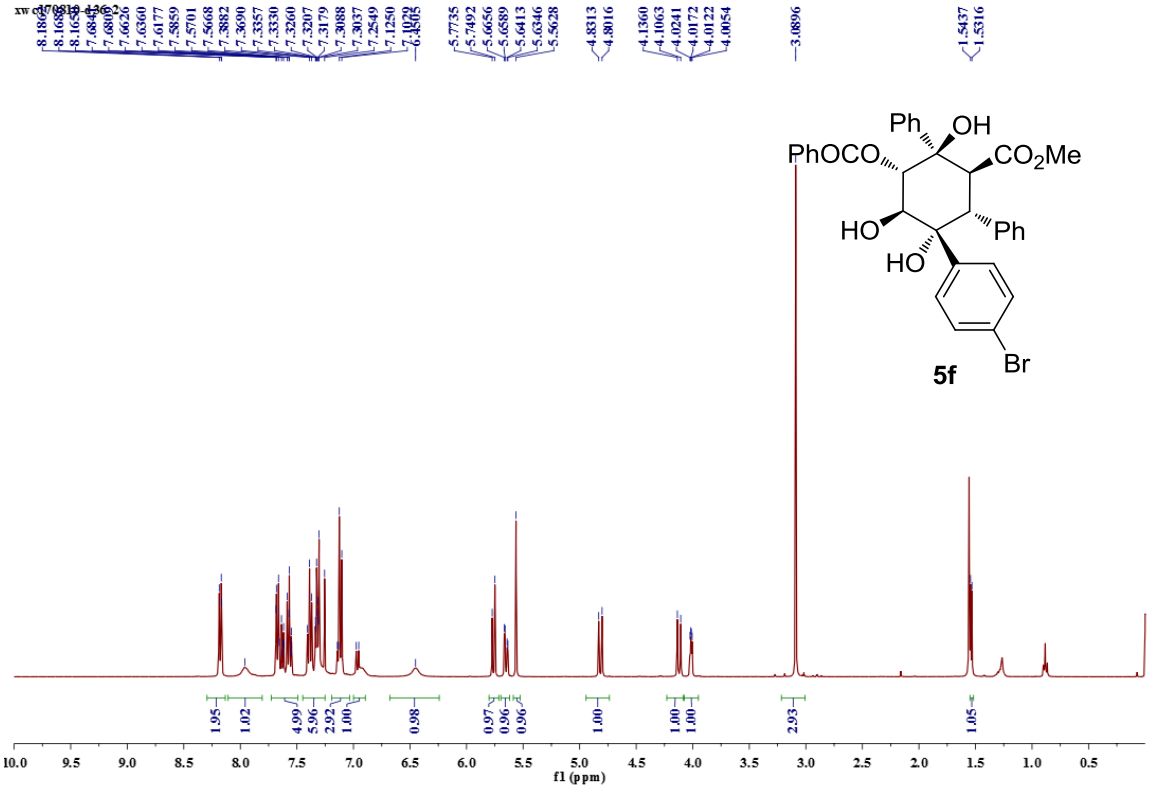

xwc170804-d29-c
199.34
169.94
149.89
141.46
133.95
133.75
133.11
131.73
129.94
129.02
128.84
128.81
128.38
128.29
127.12
122.77
87.83
77.48
76.84
63.15
52.24
51.70
CO2Me
HO
Ph
Ph
O
Br
5c
134
133
132
131
130
129
128
127
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

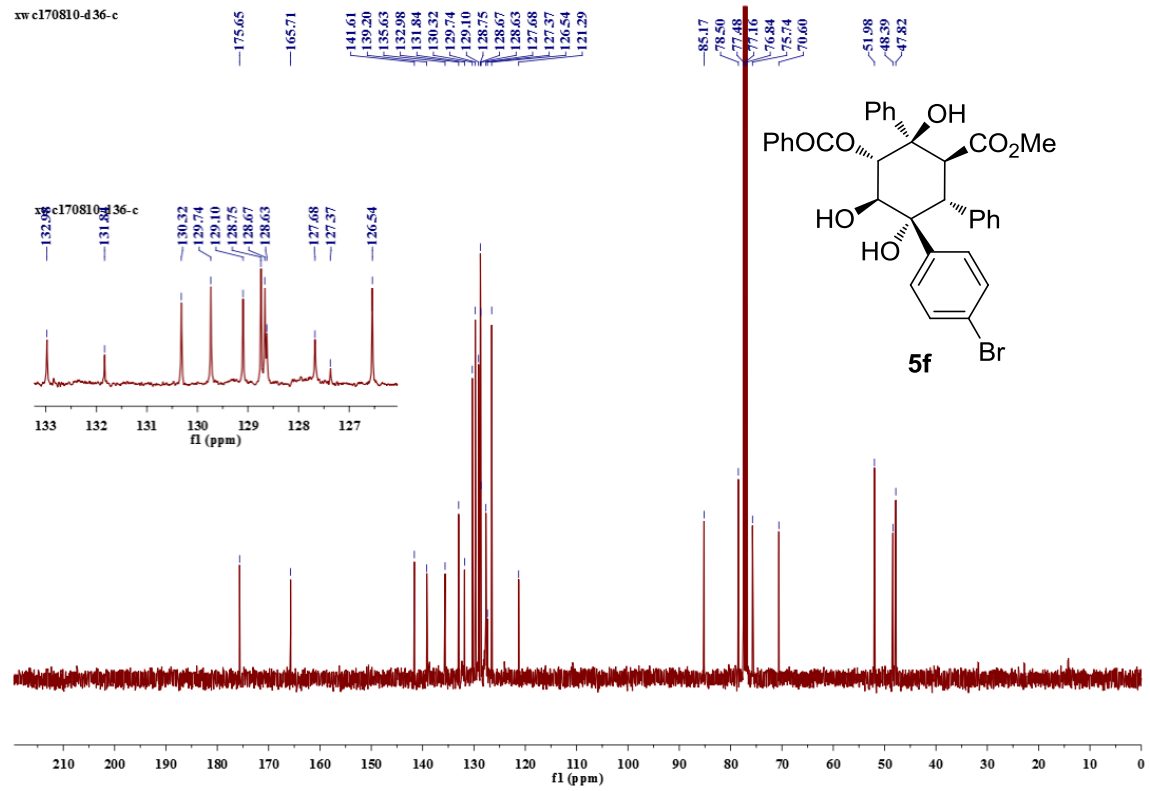

xw cD44-3
8.0615
8.0595
8.0418
8.0384
7.6785
7.6629
7.6594
7.5560
7.5363
7.2574
7.2105
7.1892
7.1835
7.1638
7.1465
7.1293
7.0312
5.6224
4.7942
4.4680
4.4403
4.0098
3.9821
3.9522
3.9502
3.9456
3.9435
3.1618
Ph
OH
PhOCO
CO2Me
Ph
O
Br
5d
1.94
2.96
2.00
12.03
1.00
1.03
1.01
2.06
2.96
f1 (ppm)


xw c-D44-3
172.19
164.49
140.25
139.17
136.93
133.81
131.10
130.07
129.81
129.68
129.21
128.88
128.70
128.03
127.74
127.46
126.93
122.18
77.48
77.16
76.84
74.90
70.93
64.69
60.32
52.19
51.77
46.65
Ph
OH
PhOCO
CO2Me
Ph
O
Br
5d
xw cD44-3
131.10
130.07
129.81
129.68
129.21
128.88
128.70
128.03
127.74
127.46
126.93
f1 (ppm)
f1 (ppm)

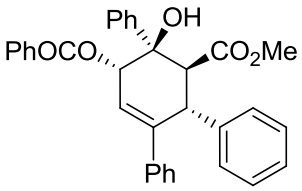

xwc170810-d34-2
7.9849
7.9672
7.9638
7.6638
7.6464
7.6442
7.4445
7.4136
7.3913
7.3217
7.2995
7.2579
7.2144
7.1955
7.1658
5.5504
5.5444
5.3363
5.3114
4.6346
4.6056
4.3445
4.3386
4.3196
4.3136
4.1365
4.1075
3.0205
Ph
OH
PhOCO
CO2Me
N3
Ph
HO
Br
5e
1.91
1.97
1.06
4.08
1.95
6.03
0.93
0.94
1.00
1.00
0.97
1.01
2.90
fl (ppm)


xwc170810-d34-c
175.39
164.38
140.83
138.20
135.42
133.47
131.10
129.86
129.66
129.16
128.63
128.58
128.29
127.85
126.37
122.17
77.48
77.16
76.84
74.18
72.92
69.78
52.02
48.87
45.88
Ph
OH
PhOCO
CO2Me
N3
Ph
HO
Br
5e
fl (ppm)


Ph
OH
PhOCO
CO2Me
HO
Ph
HO
Br
5f
f1 (ppm)


Ph
OH
PhOCO
CO2Me
HO
Ph
HO
Br
5f
f1 (ppm)

VII. HPLC Spectra for ee Determination.



4a

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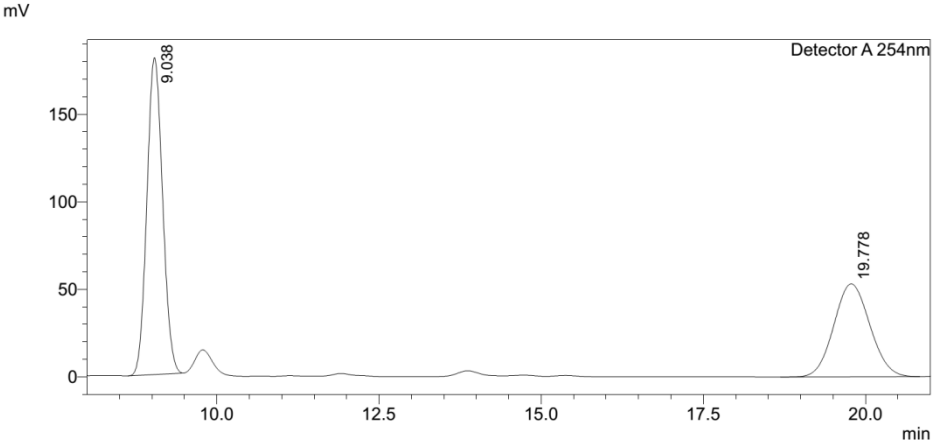
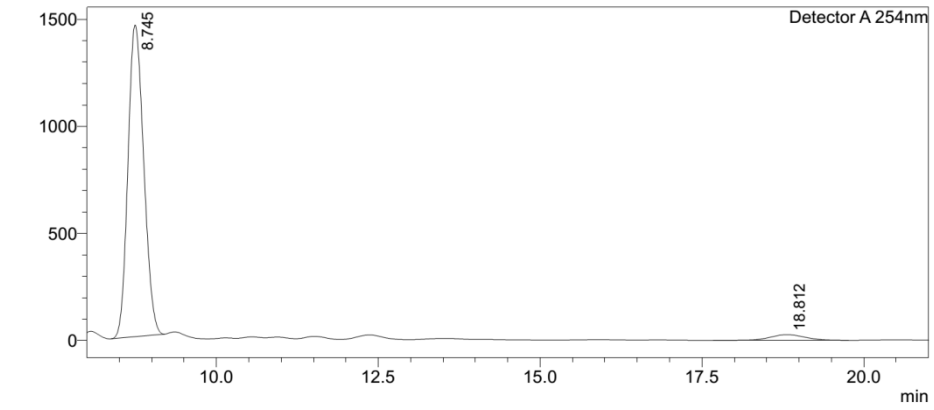


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.038	3053209	180957	59.779			
2	19.778	2054258	53057	40.221			
Total		5107467	234014				

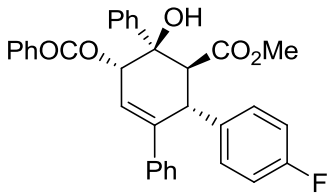
<Chromatogram>



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.745	24689773	1455745	96.241			
2	18.812	964419	25945	3.759			
Total		25654192	1481690				



4b

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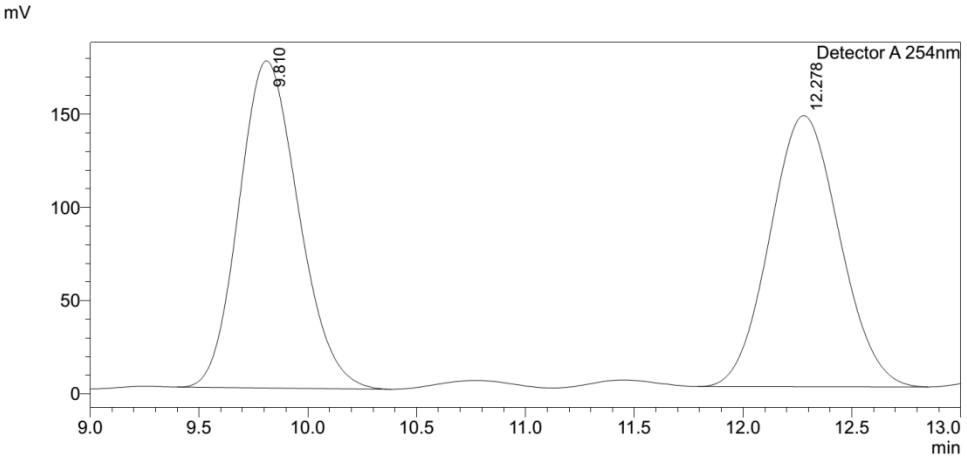
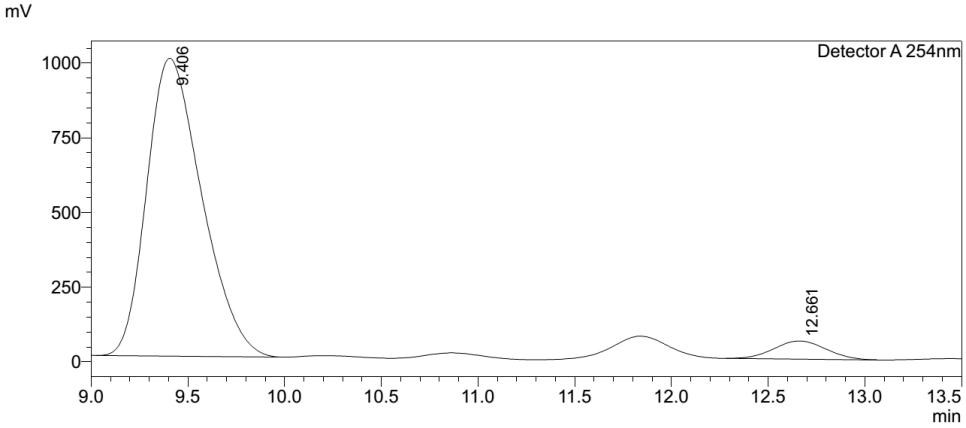


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.810	3352897	175603	50.822			
2	12.278	3244447	145494	49.178			
Total		6597344	321097				

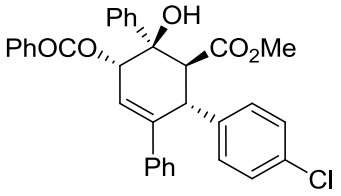
<Chromatogram>



<Peak Table>

Detector A 254nm

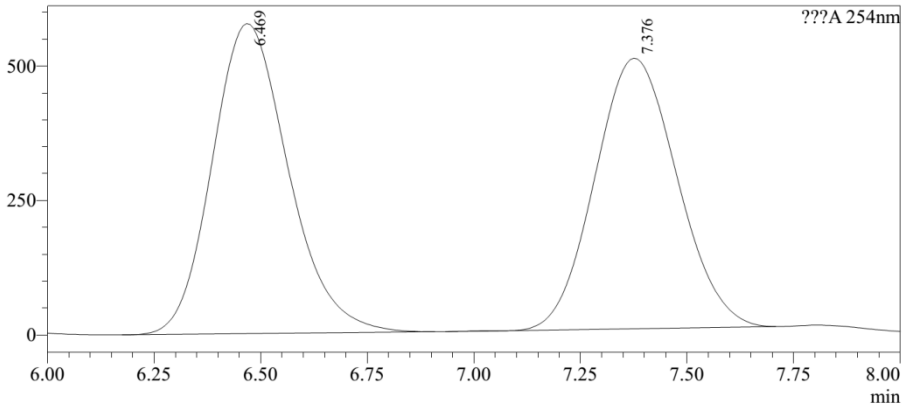
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.406	19775597	997273	94.526			
2	12.661	1145108	60966	5.474			
Total		20920705	1058239				



4c

<Chromatogram>

mV



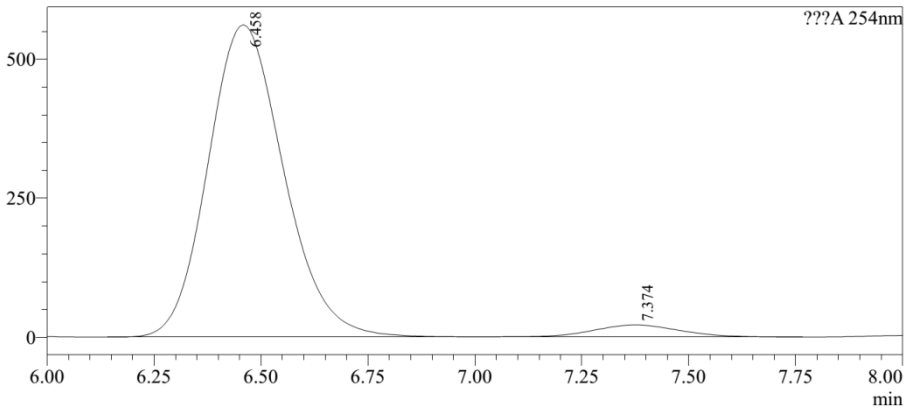
<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.469	7163572	576989	51.450			
2	7.376	6759884	503521	48.550			
Total		13923456	1080510				

<Chromatogram>

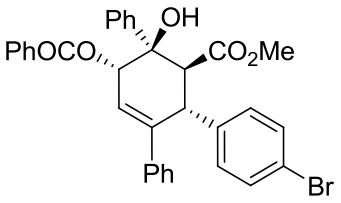
mV



<Peak Table>

???A 254nm

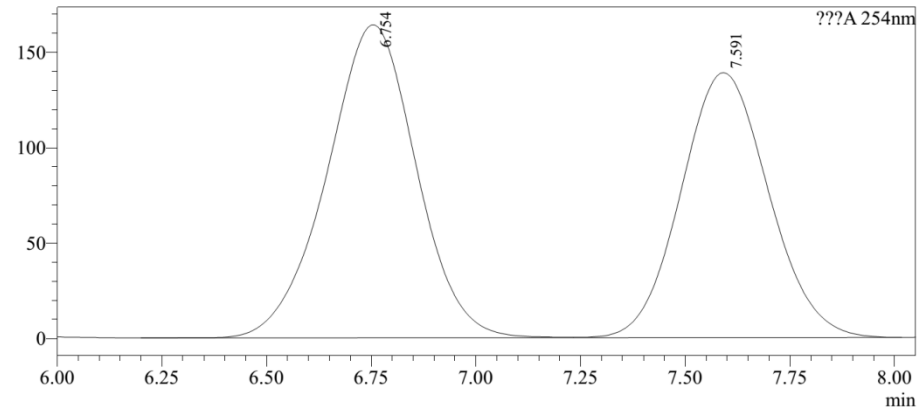
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.458	6917436	561570	95.639			
2	7.374	315417	21806	4.361		V	
Total		7232853	583376				



4d

<Chromatogram>

mV



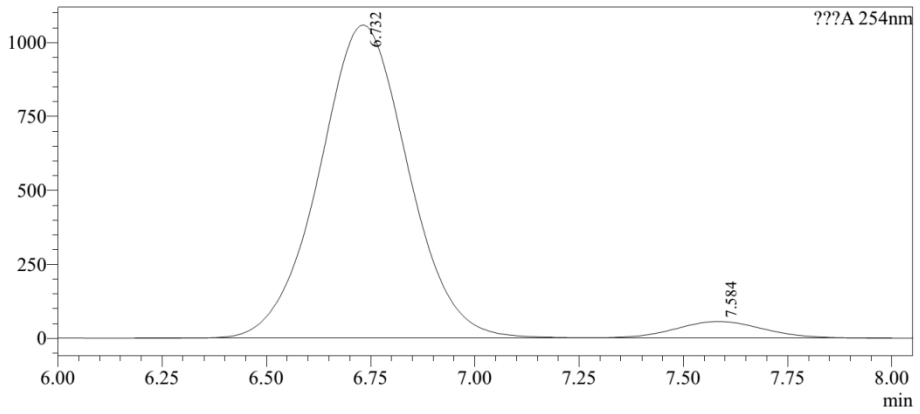
<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.754	2433275	164080	54.617			
2	7.591	2021865	138965	45.383		V	
Total		4455139	303045				

<Chromatogram>

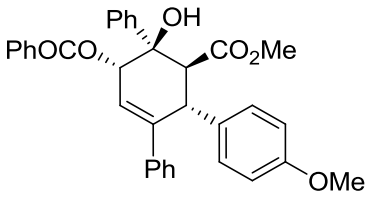
mV



<Peak Table>

???A 254nm

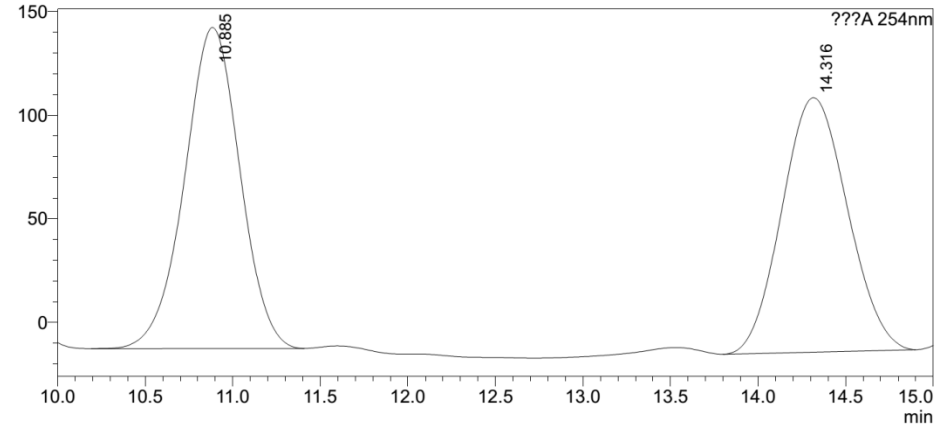
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.732	15727346	1059611	94.948			
2	7.584	836814	56396	5.052		V	
Total		16564160	1116007				



4e

<Chromatogram>

mV



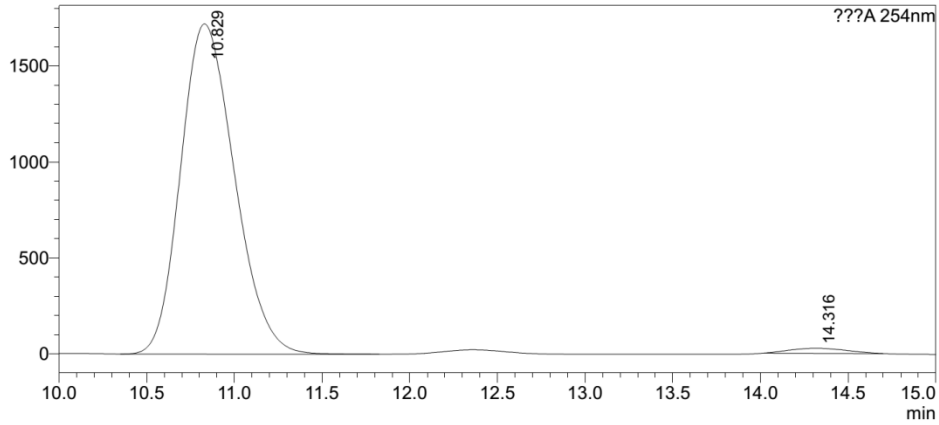
<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.885	3411542	154929	51.645			
2	14.316	3194237	122751	48.355			
Total		6605779	277680				

<Chromatogram>

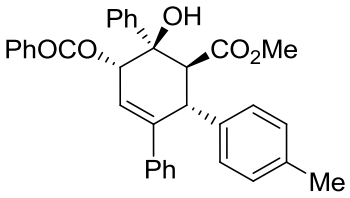
mV



<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.829	36761386	1719228	98.441			
2	14.316	582165	26029	1.559		M	
Total		37343552	1745256				



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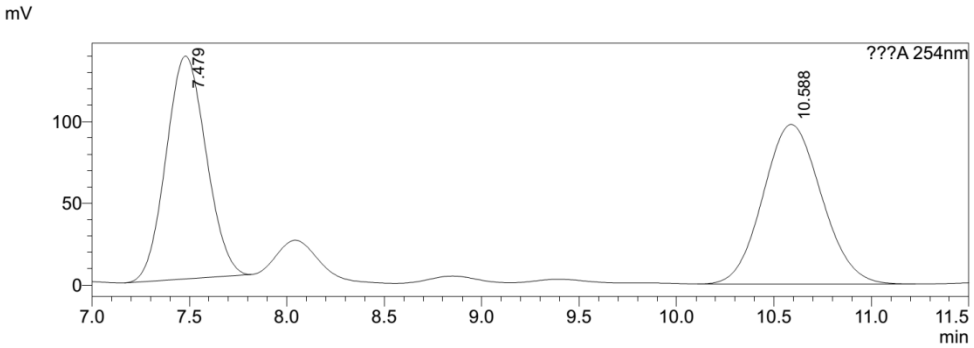
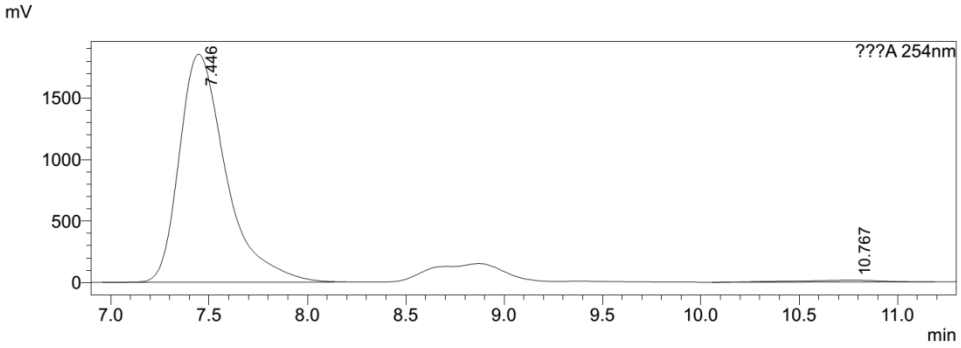


<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.479	1954330	136293	48.902			
2	10.588	2042129	97593	51.098			
Total		3996459	233886				

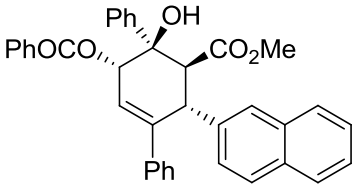
<Chromatogram>



<Peak Table>

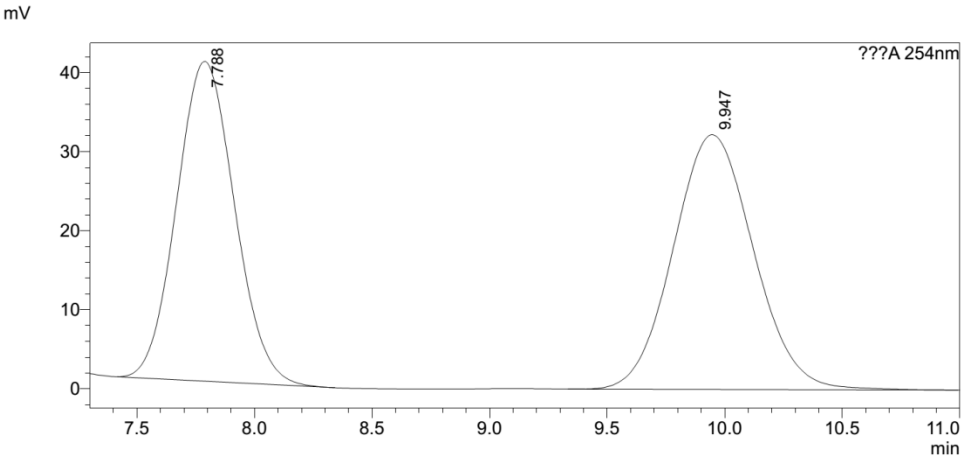
???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.446	30642298	1853182	98.543			
2	10.767	452933	14577	1.457			
Total		31095231	1867759				



4g

<Chromatogram>

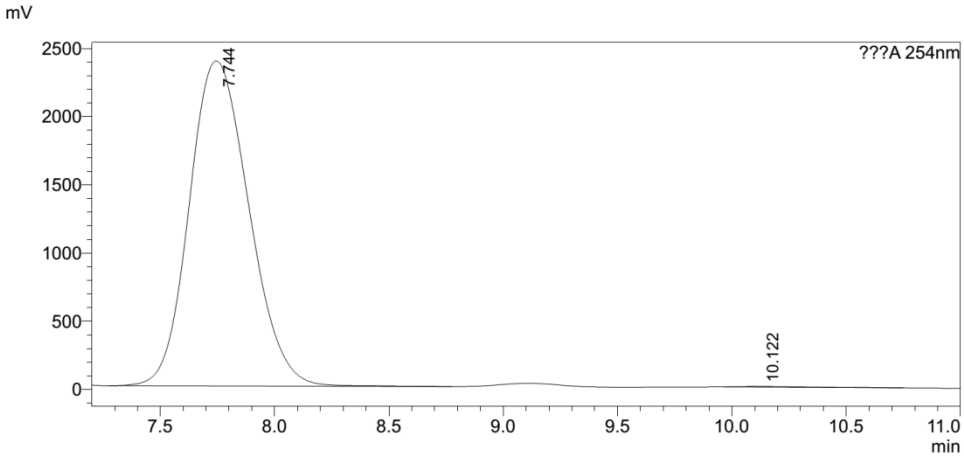


<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.788	694518	40426	47.559			
2	9.947	765797	32209	52.441			
Total		1460315	72635				

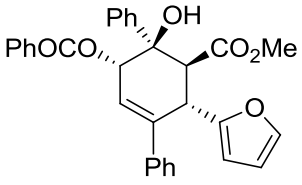
<Chromatogram>



<Peak Table>

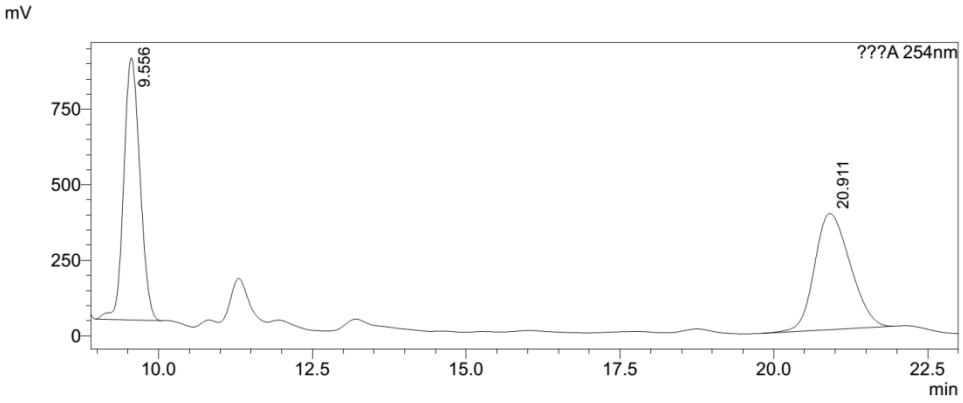
???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.744	43284870	2383657	99.688			
2	10.122	135364	5284	0.312		M	
Total		43420234	2388941				



4h

<Chromatogram>

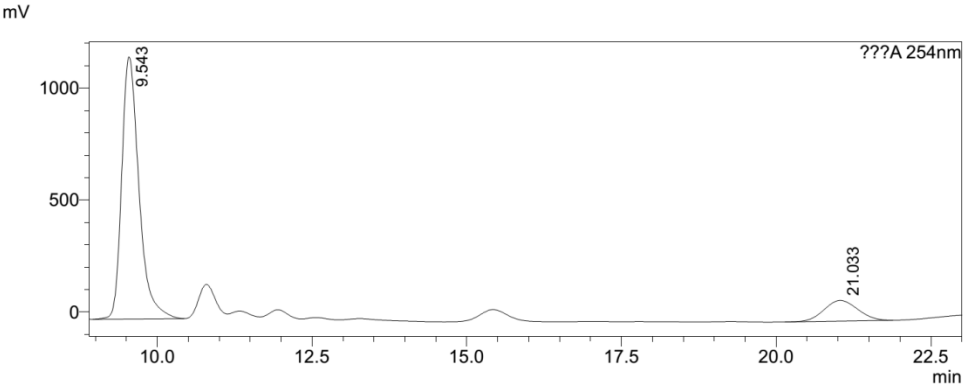


<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.556	15951277	868013	50.718			
2	20.911	15499589	384946	49.282			
Total		31450867	1252960				

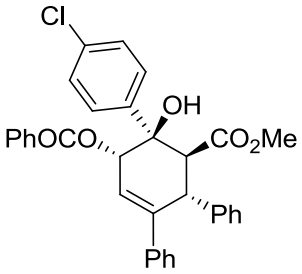
<Chromatogram>



<Peak Table>

???A 254nm

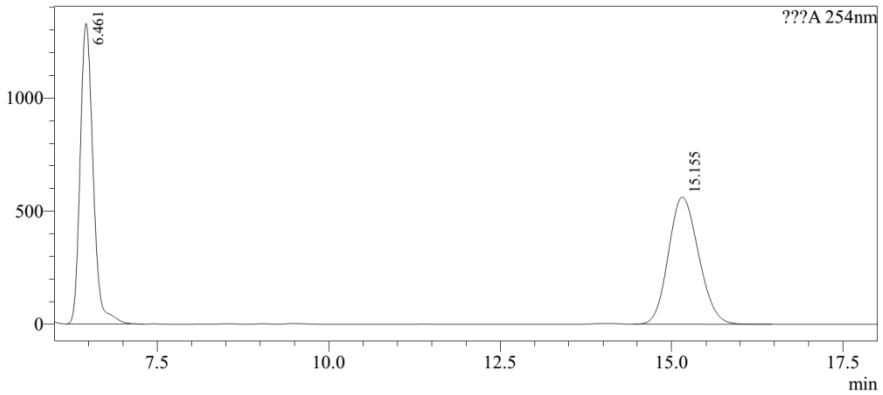
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.543	22745042	1171281	86.682			
2	21.033	3494455	92057	13.318			
Total		26239497	1263338				



4i

<Chromatogram>

mV



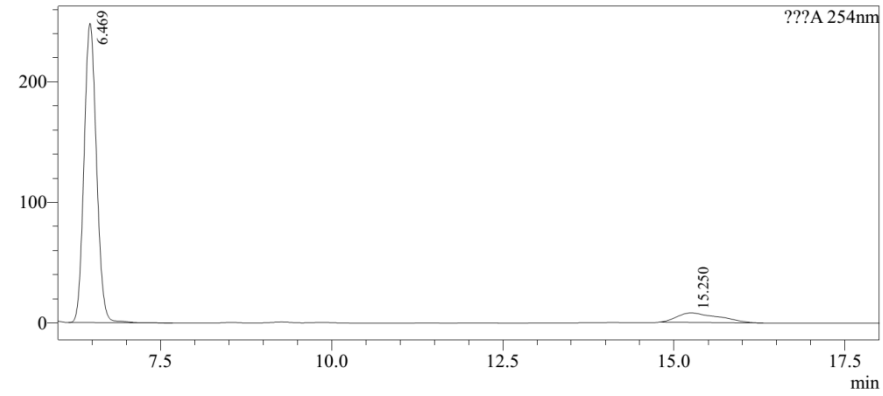
<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.461	17357676	1329588	50.274			
2	15.155	17168570	561866	49.726			
Total		34526246	1891455				

<Chromatogram>

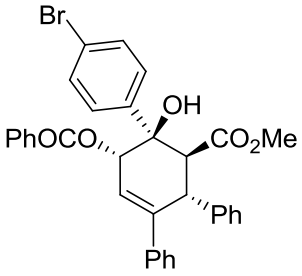
mV



<Peak Table>

???A 254nm

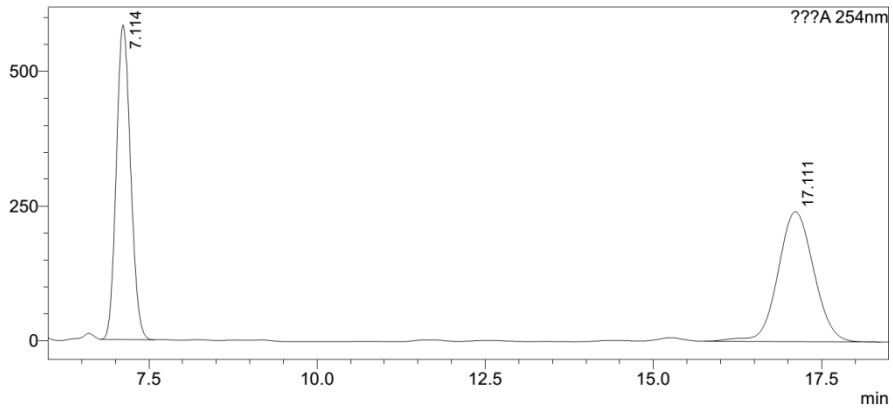
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.469	3135973	248392	90.357		S	
2	15.250	334693	7903	9.643		M	
Total		3470666	256295				



4j

<Chromatogram>

mV



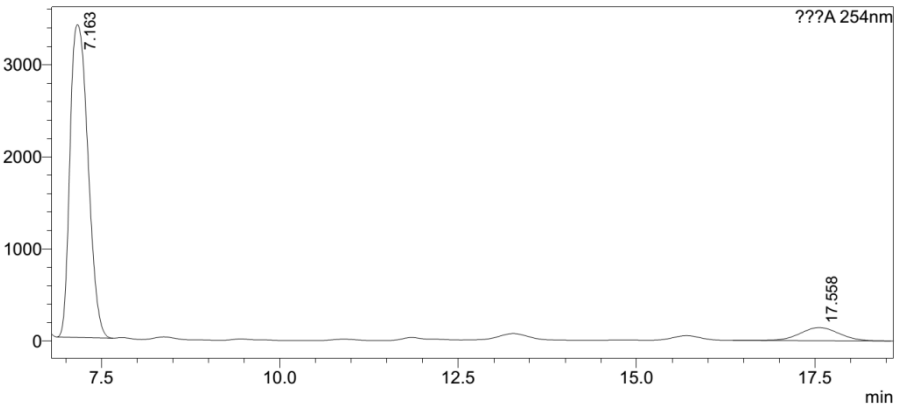
<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.114	8620216	583471	49.154			
2	17.111	8916880	241108	50.846			
Total		17537096	824579				

<Chromatogram>

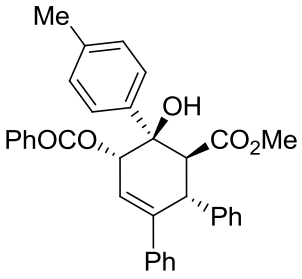
mV



<Peak Table>

???A 254nm

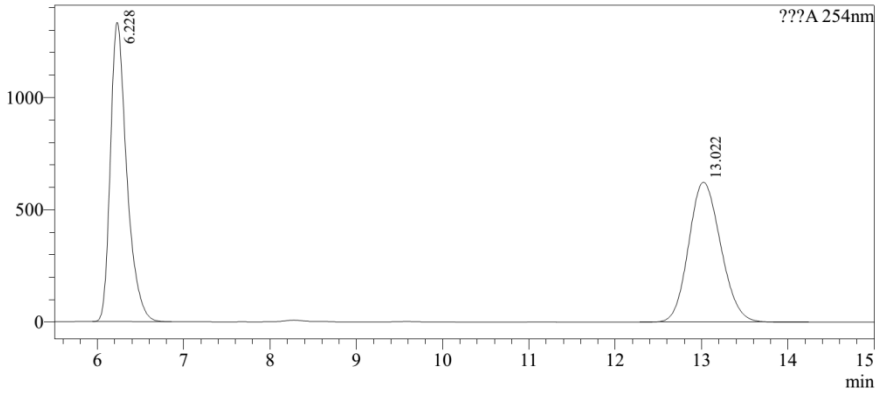
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.163	59557686	3396172	91.648			
2	17.558	5427227	142433	8.352			
Total		64984913	3538606				



4k

<Chromatogram>

mV



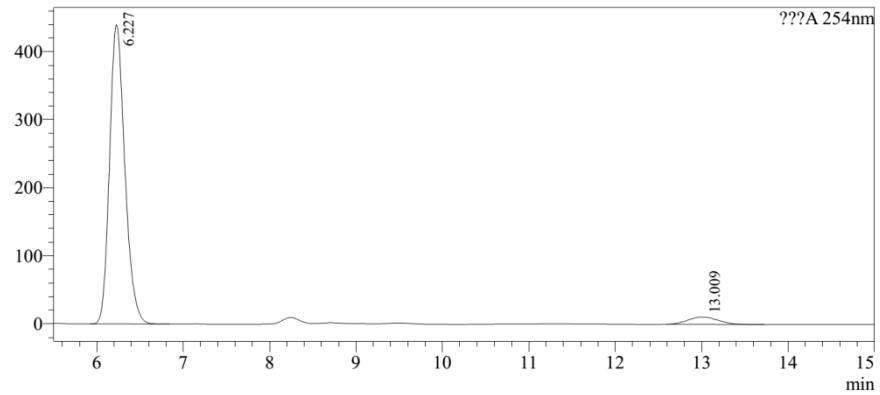
<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.228	17563599	1332319	52.167			
2	13.022	16104164	622888	47.833			
Total		33667763	1955207				

<Chromatogram>

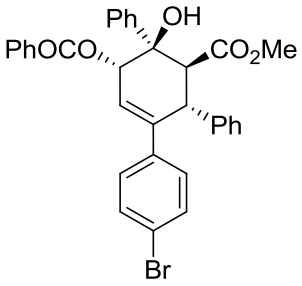
mV



<Peak Table>

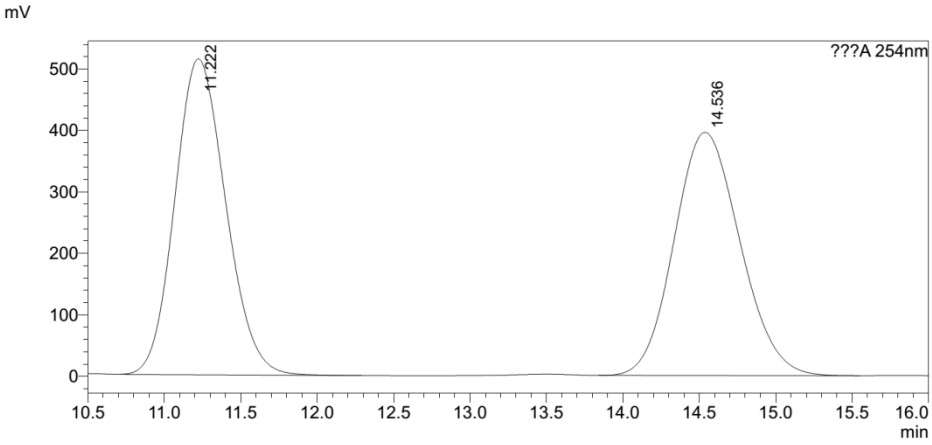
???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.227	5418917	440136	95.353			
2	13.009	264107	10839	4.647		M	
Total		5683023	450975				



4l

<Chromatogram>

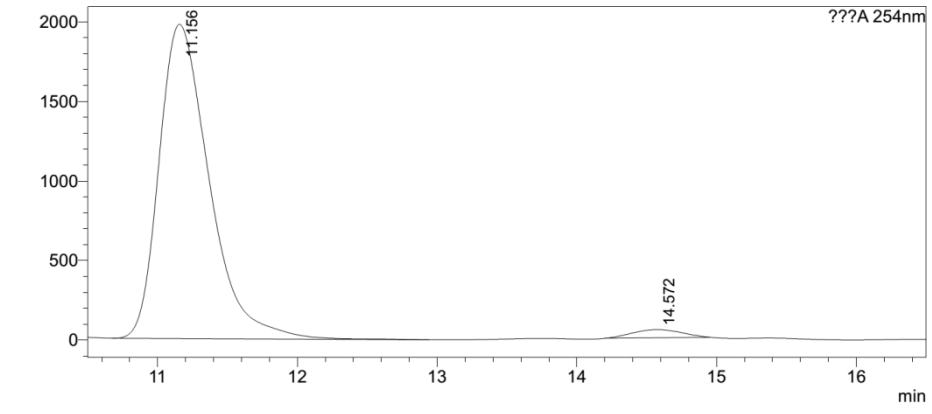


<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.222	11897415	513582	50.098			
2	14.536	11850704	395339	49.902			
Total		23748119	908921				

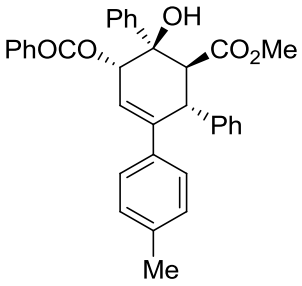
<Chromatogram>



<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.156	49282819	1974784	97.508			
2	14.572	1259504	51479	2.492		M	
Total		50542323	2026264				



4m

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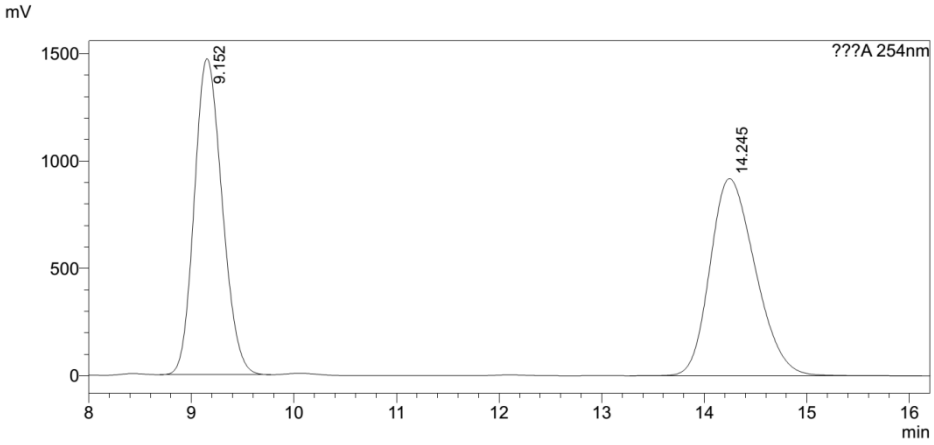
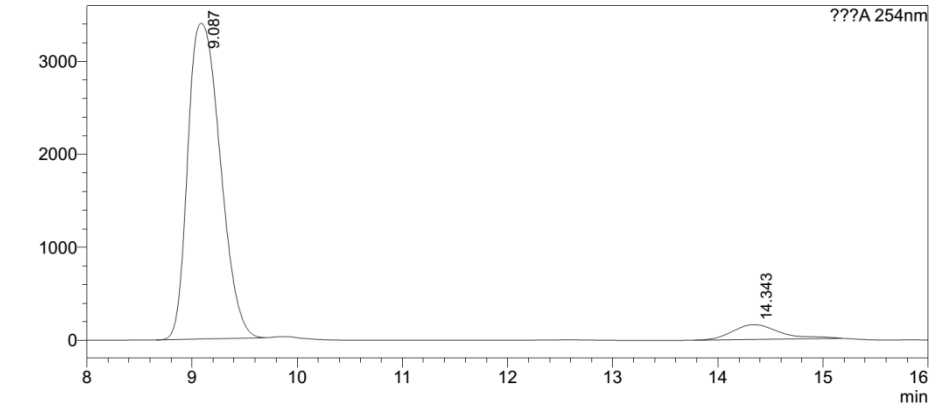


<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.152	27782848	1472000	49.659			
2	14.245	28164597	917943	50.341			
Total		55947445	2389943				

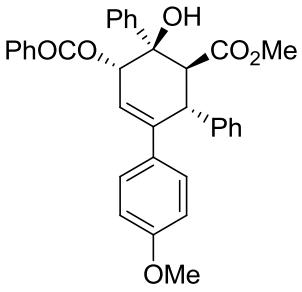
<Chromatogram>



<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.087	72711251	3392496	93.602			
2	14.343	4969691	159584	6.398		M	
Total		77680942	3552080				



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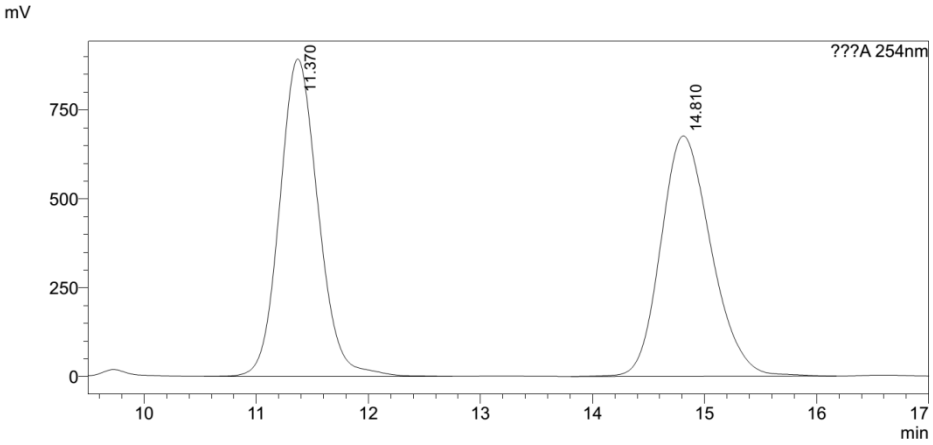
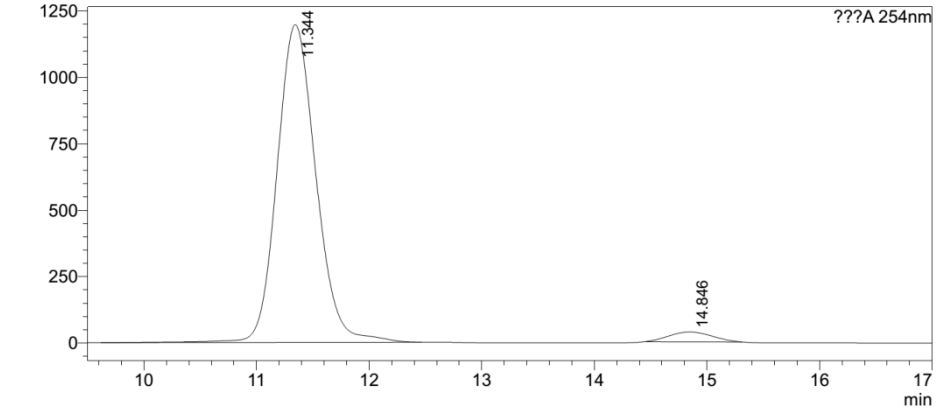


<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.370	21344935	891660	50.295			
2	14.810	21094669	675729	49.705			
Total		42439604	1567389				

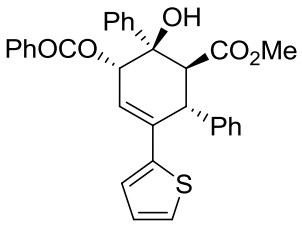
<Chromatogram>



<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.344	28715975	1196266	96.699			
2	14.846	980303	37024	3.301		M	
Total		29696278	1233290				



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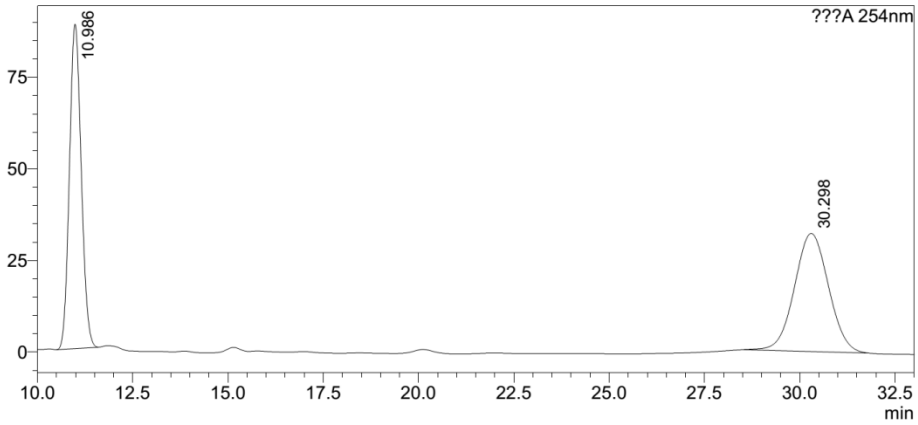
<Chromatogram>

mV



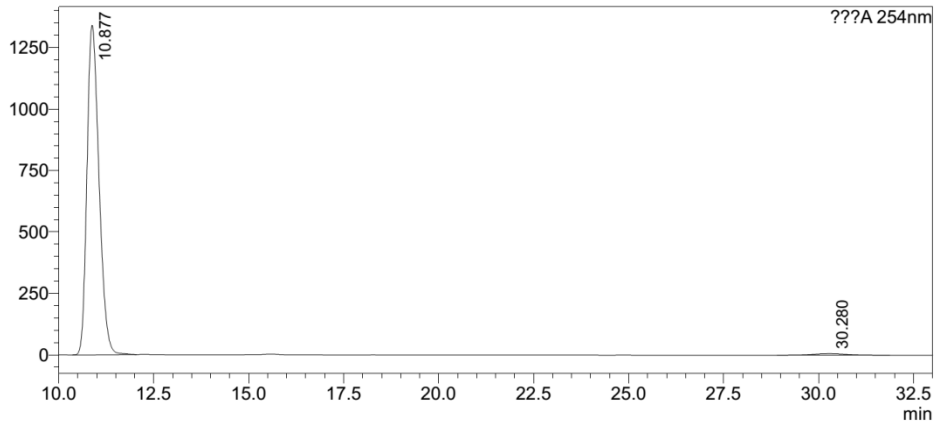
<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.986	1908655	88516	48.791			
2	30.298	2003215	32229	51.209		M	
Total		3911870	120744				

<Chromatogram>

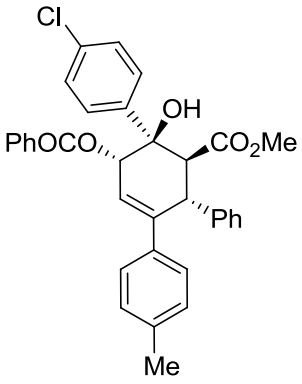
mV



<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.877	29541931	1340365	98.749			
2	30.280	374109	6141	1.251			
Total		29916040	1346506				



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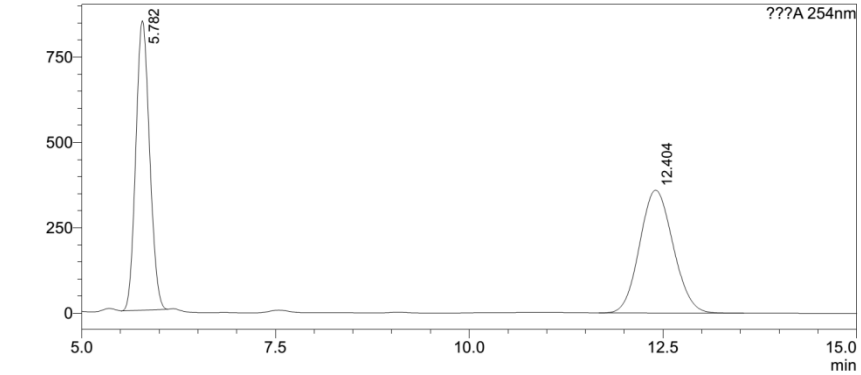
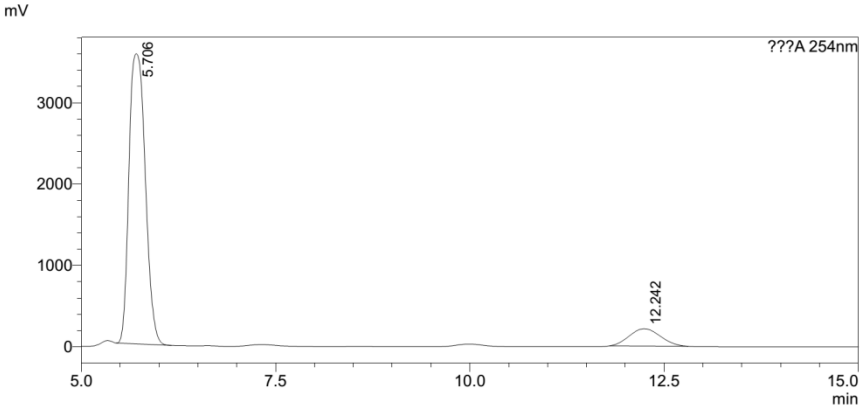


<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.782	10528318	848673	49.310			
2	12.404	10823118	360126	50.690			
Total		21351436	1208799				

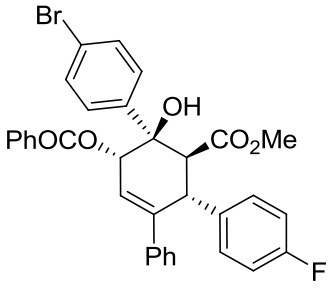
<Chromatogram>



<Peak Table>

???A 254nm

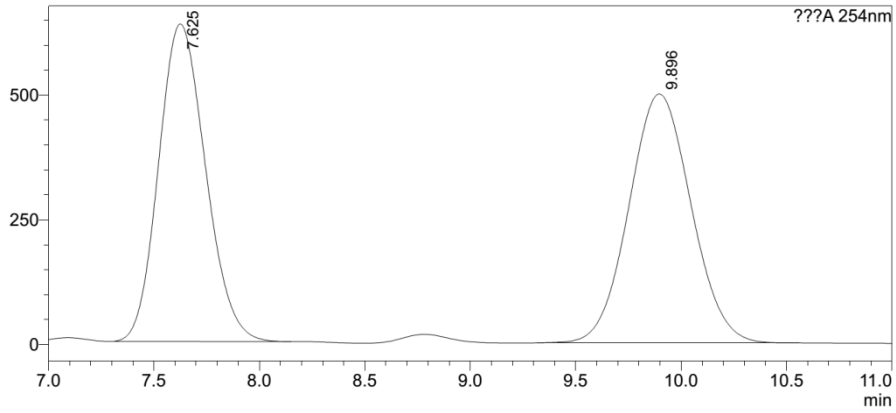
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.706	52391727	3566833	89.877			
2	12.242	5900900	212872	10.123		M	
Total		58292628	3779705				



4q

<Chromatogram>

mV



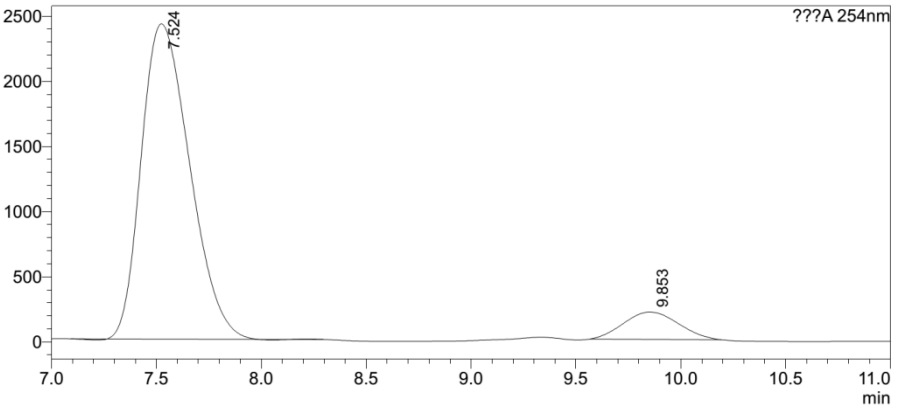
<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.625	9864701	636622	49.086			
2	9.896	10231964	498819	50.914		M	
Total		20096665	1135441				

<Chromatogram>

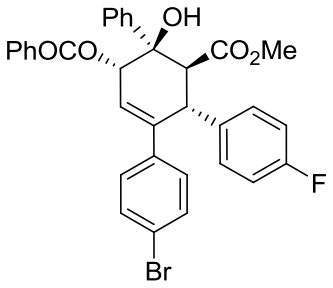
mV



<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.524	38825233	2419481	91.069		M	
2	9.853	3807656	209493	8.931		M	
Total		42632889	2628974				



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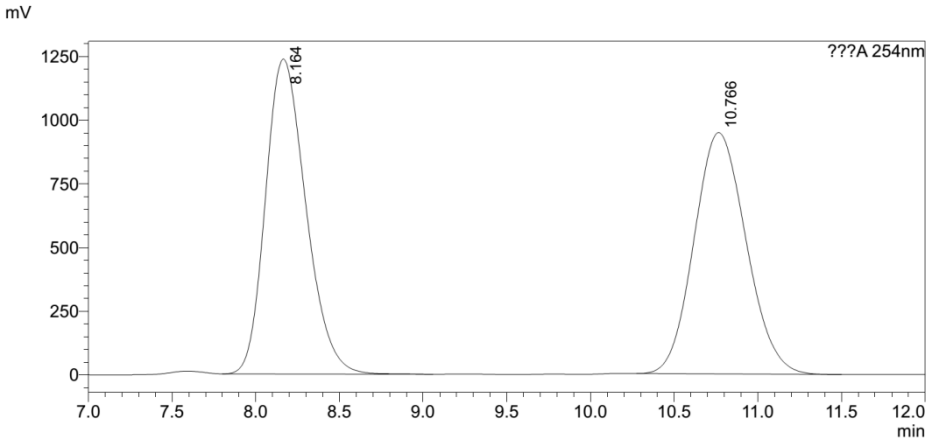
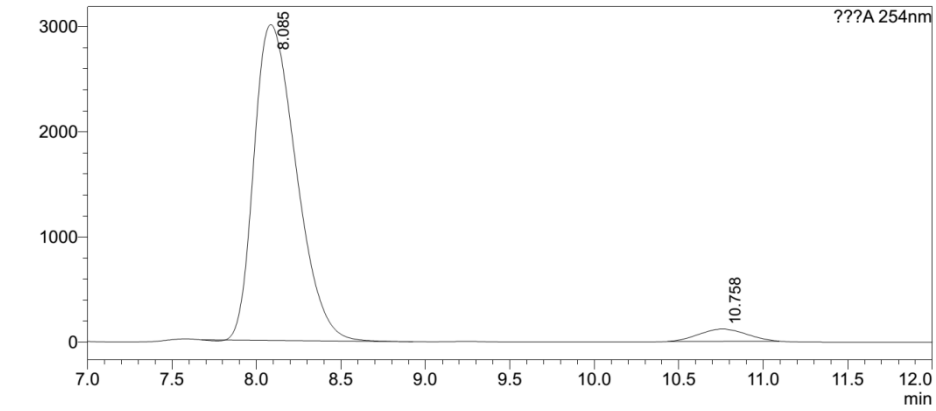


<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.164	20768938	1236230	50.327			
2	10.766	20498650	947504	49.673			
Total		41267588	2183734				

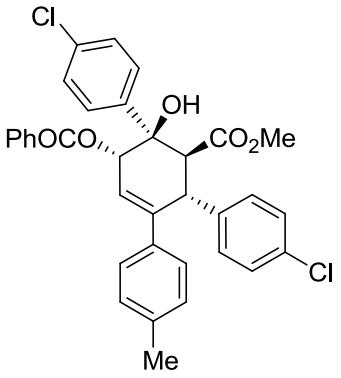
<Chromatogram>



<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.085	52184107	3002106	95.863		M	
2	10.758	2252036	115759	4.137		M	
Total		54436143	3117864				



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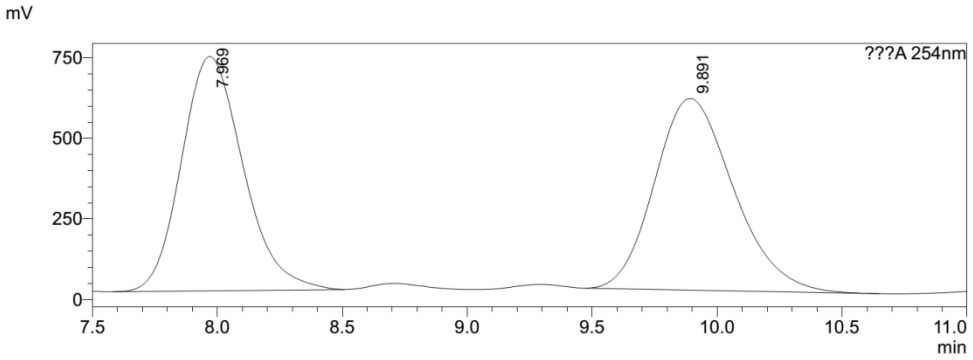
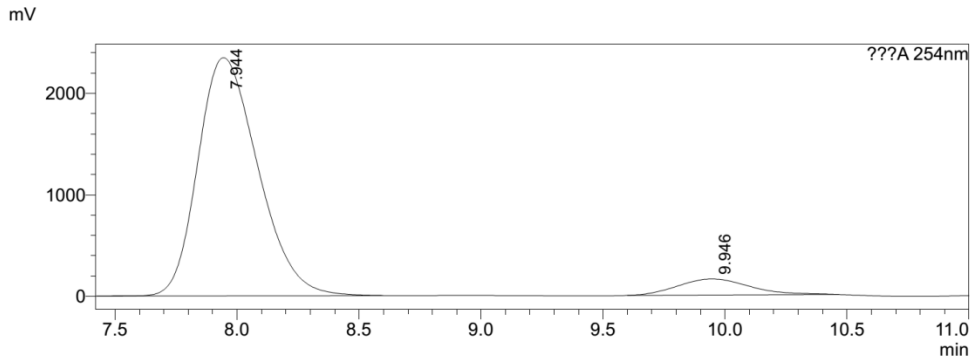


<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.969	12495109	726599	48.833			
2	9.891	13092431	594627	51.167			
Total		25587540	1321226				

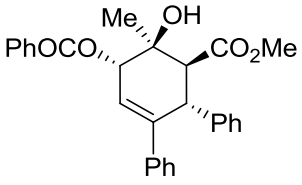
<Chromatogram>



<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.944	40280865	2348087	92.502			
2	9.946	3265300	158311	7.498		M	
Total		43546165	2506399				



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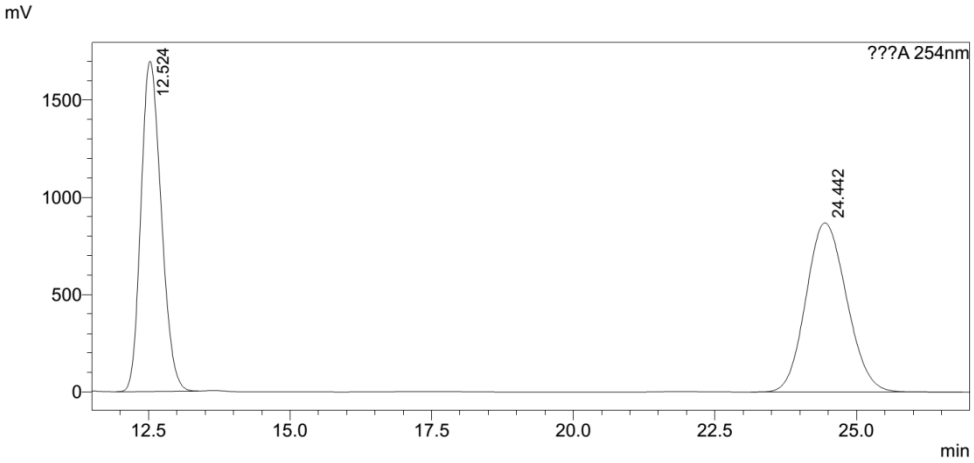
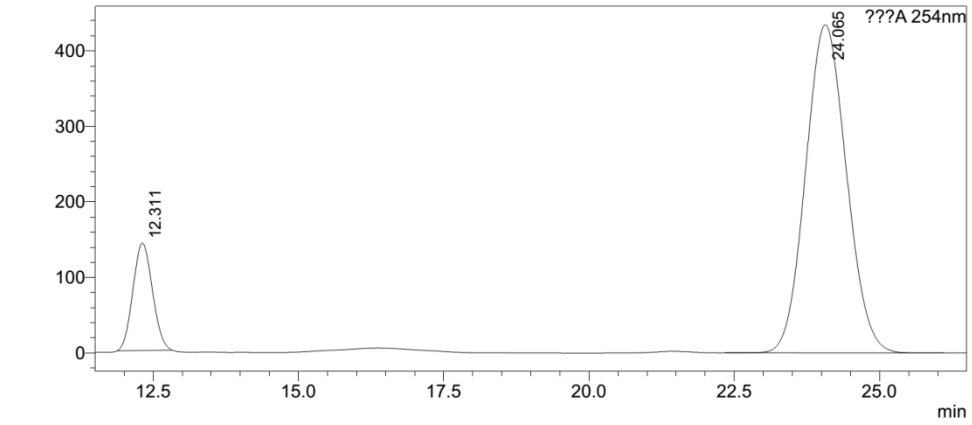


<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.524	42286392	1697968	49.325			
2	24.442	43443330	869408	50.675			
Total		85729722	2567377				

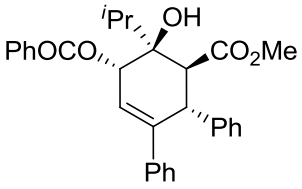
<Chromatogram>



<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.311	3318510	142326	13.508		M	
2	24.065	21248603	434423	86.492		M	
Total		24567113	576750				



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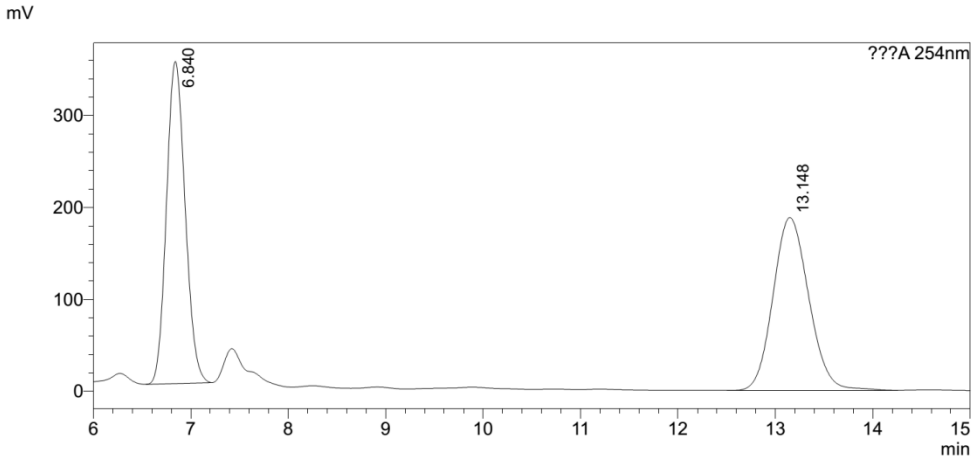
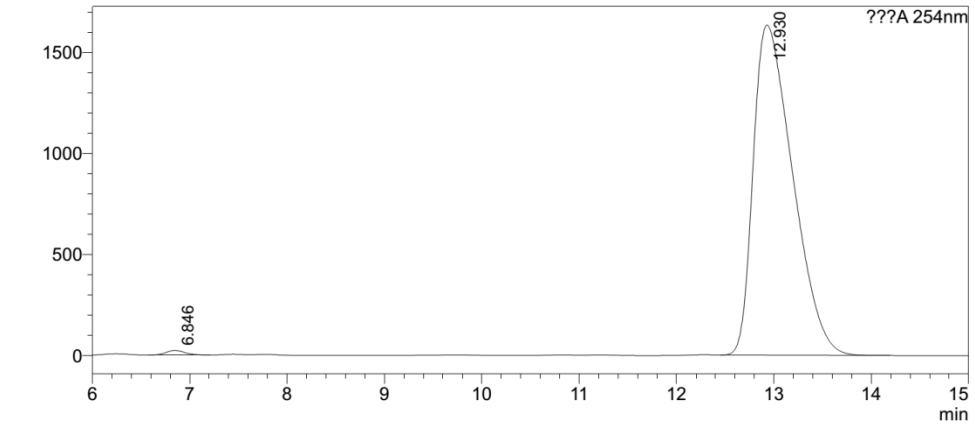


<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.840	4680892	350647	49.409			
2	13.148	4792929	188057	50.591			
Total		9473822	538704				

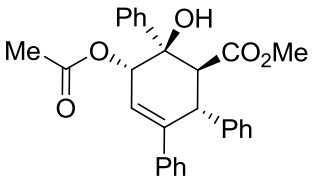
<Chromatogram>



<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.846	301299	22396	0.650			
2	12.930	46034411	1632546	99.350			
Total		46335710	1654942				



4v

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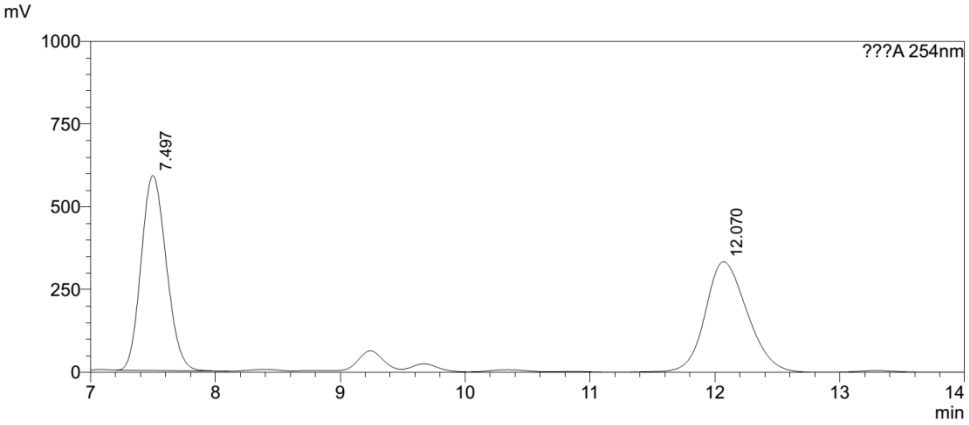
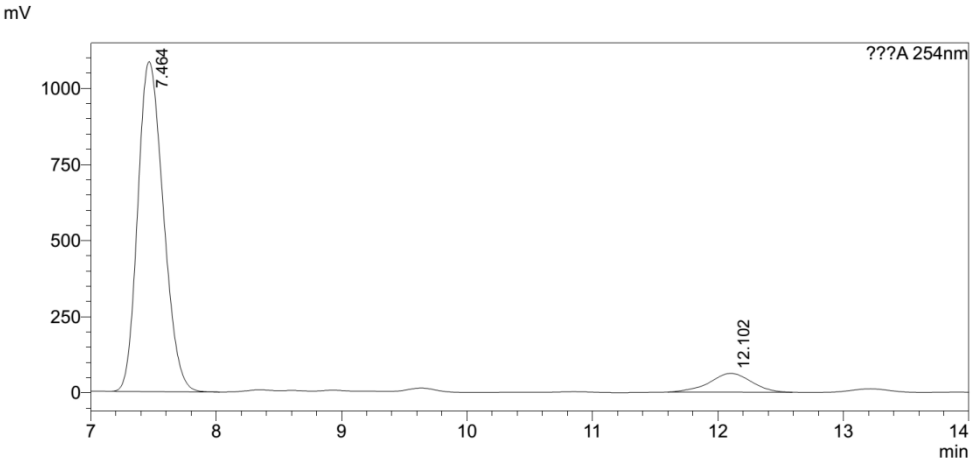


<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.497	8270916	589150	51.452			
2	12.070	7804101	333633	48.548			
Total		16075017	922783				

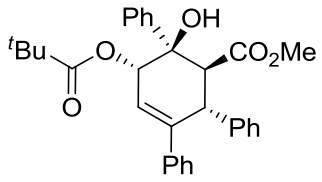
<Chromatogram>



<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.464	15371473	1083728	91.423			
2	12.102	1442175	61771	8.577		M	
Total		16813648	1145500				



4w

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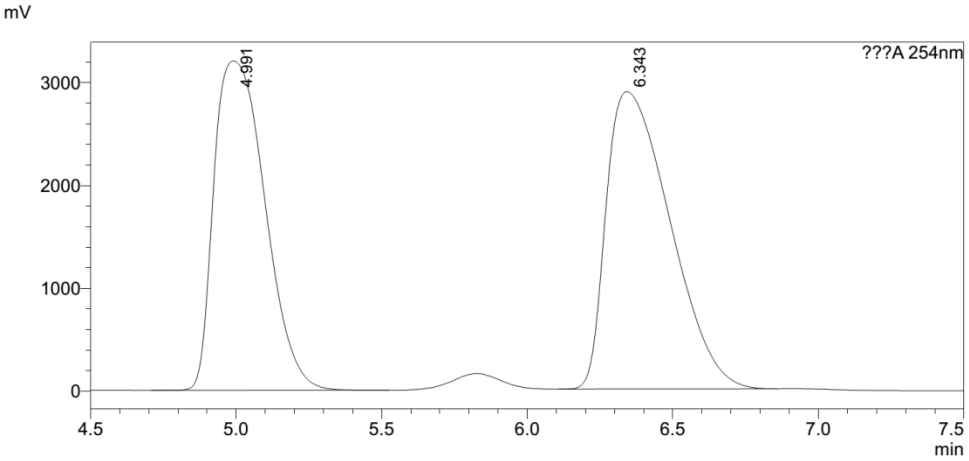
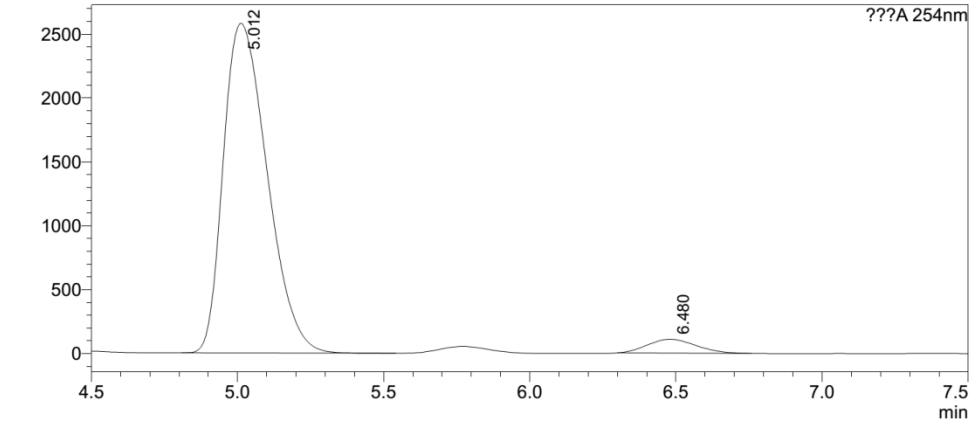


<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	4.991	39172094	3205366	47.008			
2	6.343	44159313	2894480	52.992			
Total		83331406	6099846				

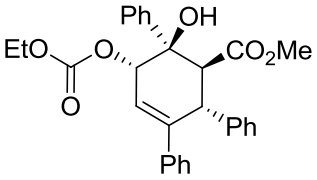
<Chromatogram>



<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.012	26948920	2579762	95.559		V	
2	6.480	1252428	108061	4.441		M	
Total		28201348	2687823				



4x

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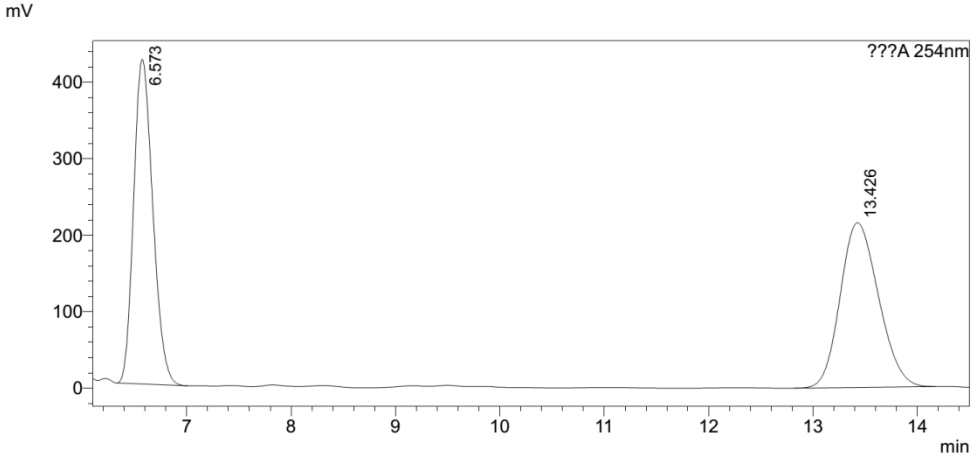

<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.573	5420582	424622	49.681			
2	13.426	5490131	215263	50.319			
Total		10910713	639885				

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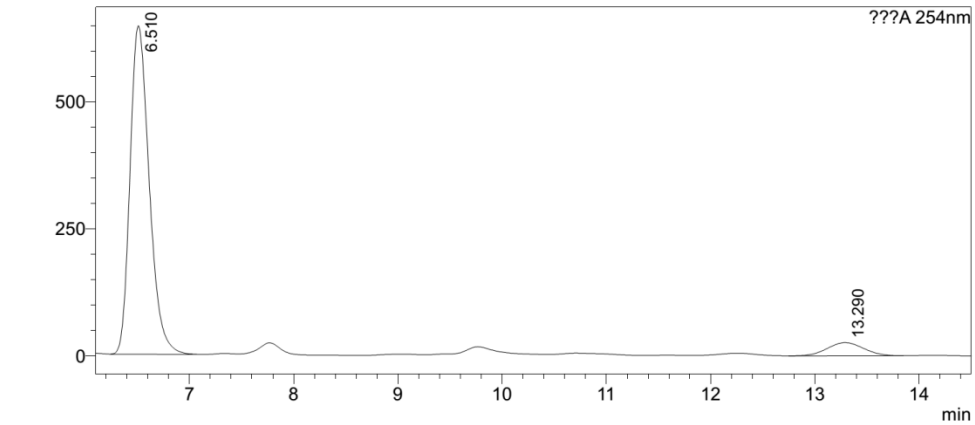
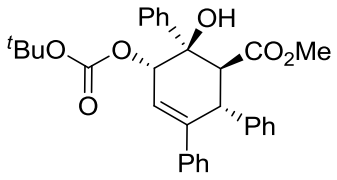


<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.510	8269243	646352	92.950			
2	13.290	627161	25889	7.050			
Total		8896404	672241				



4y

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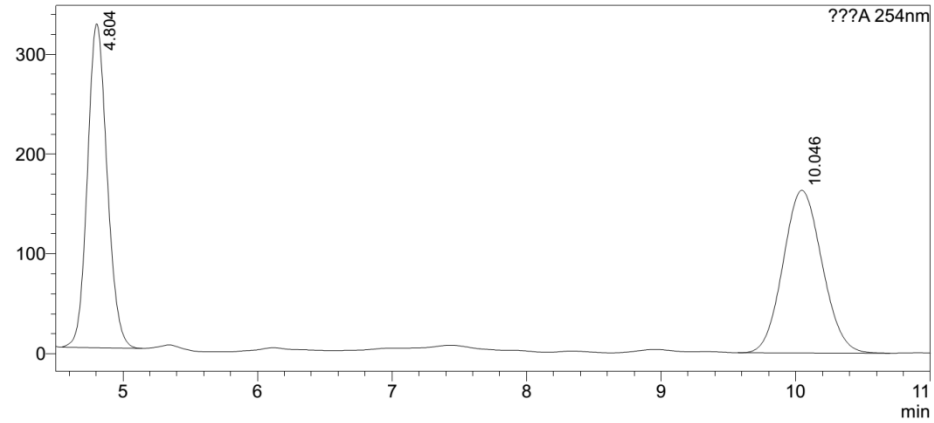
mV



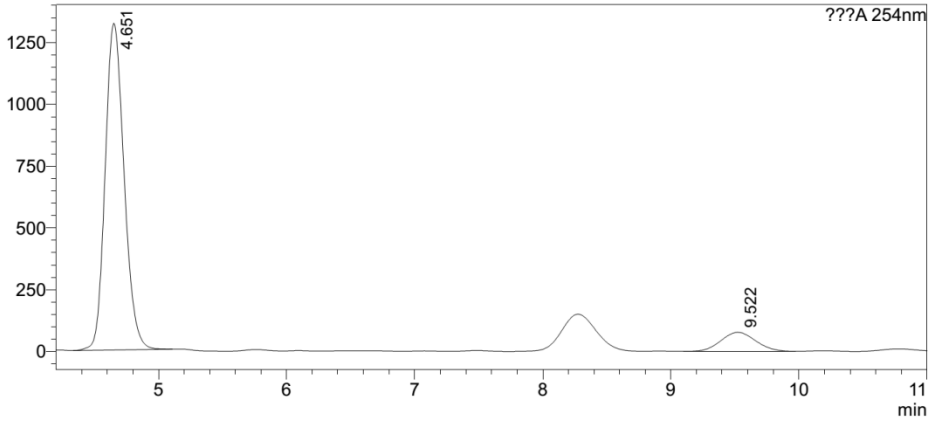
<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	4.804	3304418	324296	50.169			
2	10.046	3282143	162860	49.831			
Total		6586561	487156				

<Chromatogram>

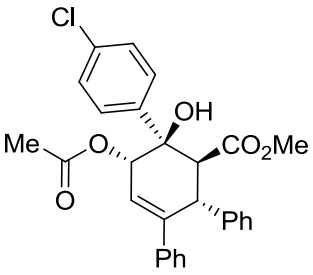
mV



<Peak Table>

???A 254nm

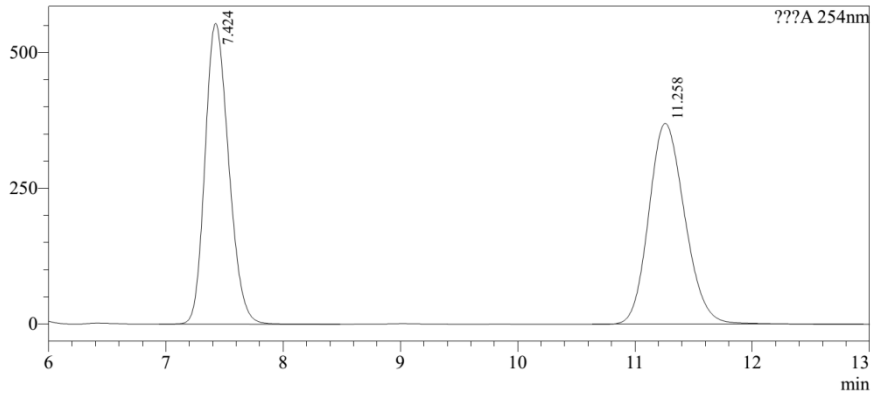
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	4.651	13591824	1322833	90.389			
2	9.522	1445198	76653	9.611			
Total		15037022	1399486				



4z

<Chromatogram>

mV



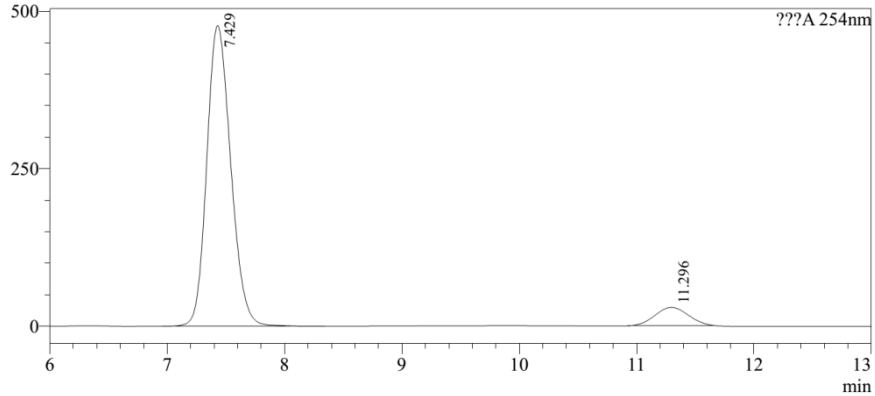
<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.424	7772533	555050	49.549			
2	11.258	7914028	370551	50.451			
Total		15686561	925600				

<Chromatogram>

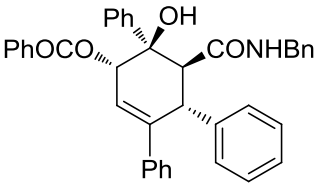
mV



<Peak Table>

???A 254nm

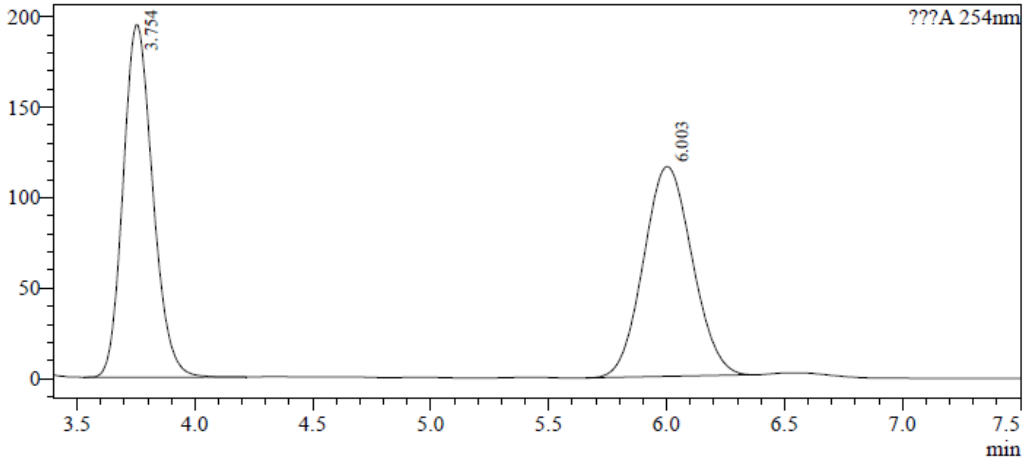
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.429	6790164	477069	92.092			
2	11.296	583041	29203	7.908		M	
Total		7373205	506273				



4aa

<Chromatogram>

mV



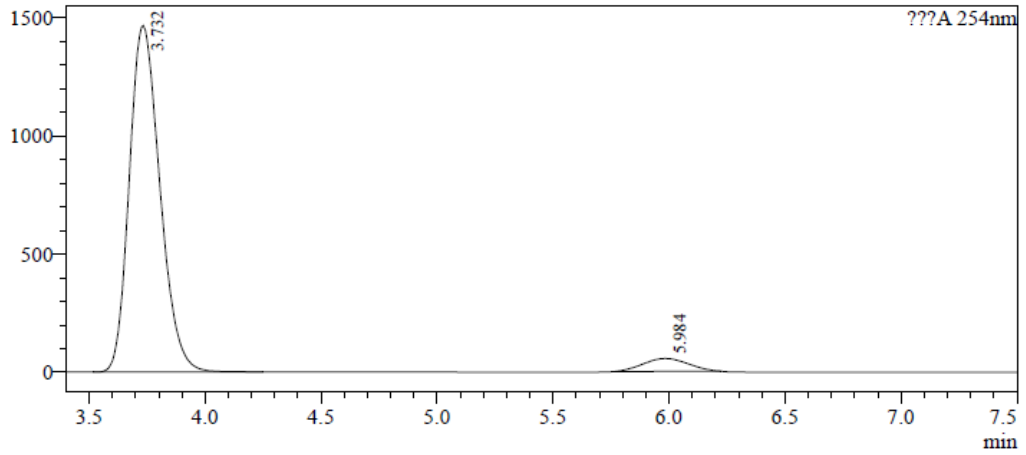
<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	3.754	1704254	194730	50.485		S	
2	6.003	1671540	115967	49.515			
Total		3375793	310697				

<Chromatogram>

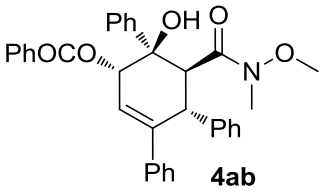
mV



<Peak Table>

???A 254nm

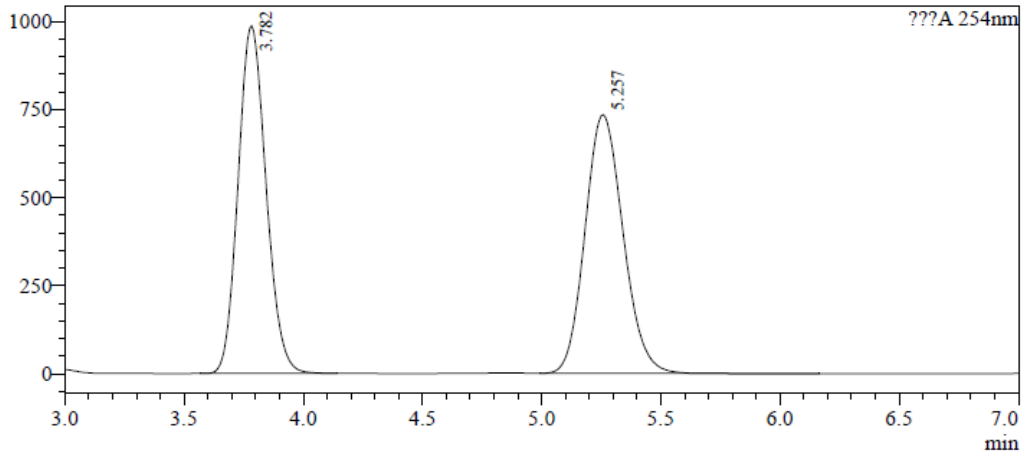
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	3.732	13446214	1465904	94.762			
2	5.984	743257	54813	5.238		M	
Total		14189472	1520717				



4ab

<Chromatogram>

mV



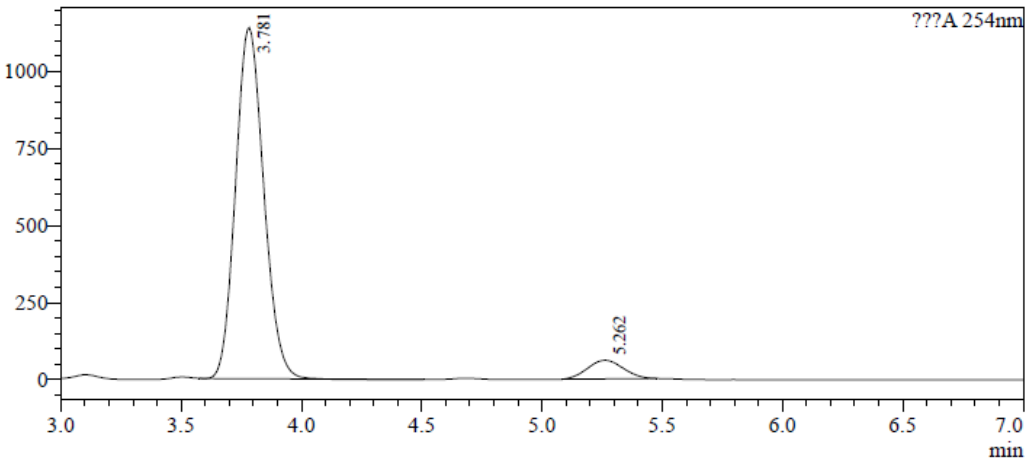
<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	3.782	8055804	986940	49.698			
2	5.257	8153677	734602	50.302		S	
Total		16209481	1721542				

<Chromatogram>

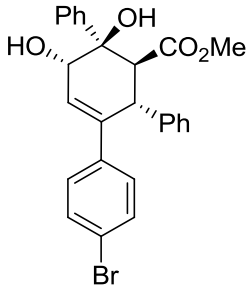
mV



<Peak Table>

???A 254nm

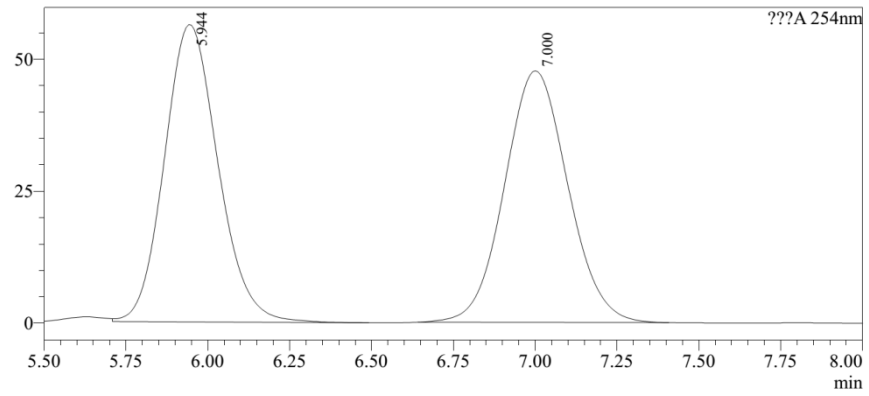
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	3.781	9279434	1139138	93.748		M	
2	5.262	618842	60227	6.252		M	
Total		9898275	1199366				



5a

<Chromatogram>

mV



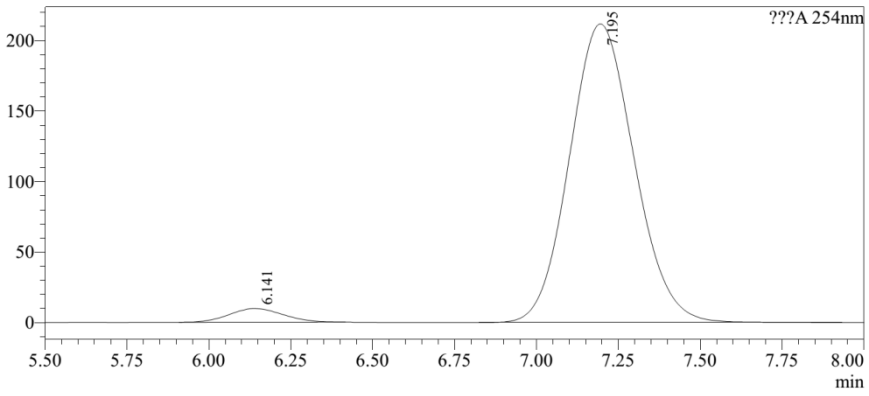
<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.944	642326	56339	50.052		M	
2	7.000	640985	47676	49.948		M	
Total		1283311	104014				

<Chromatogram>

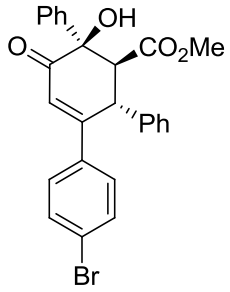
mV



<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.141	109450	9680	3.620		M	
2	7.195	2914409	211898	96.380		M	
Total		3023858	221578				



5b

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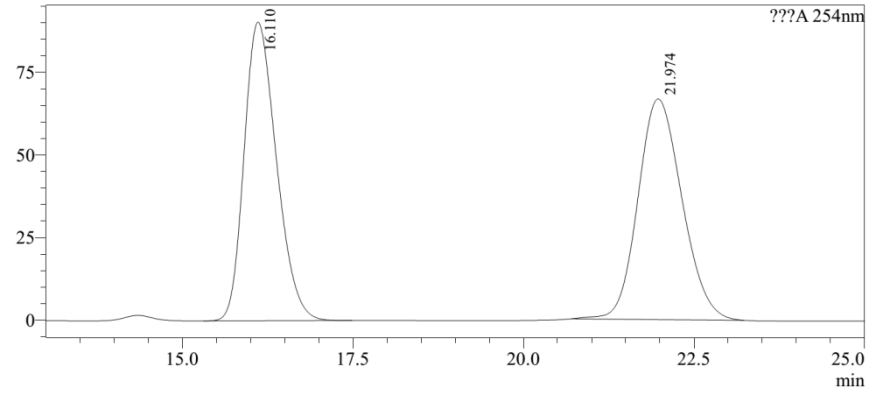
mV



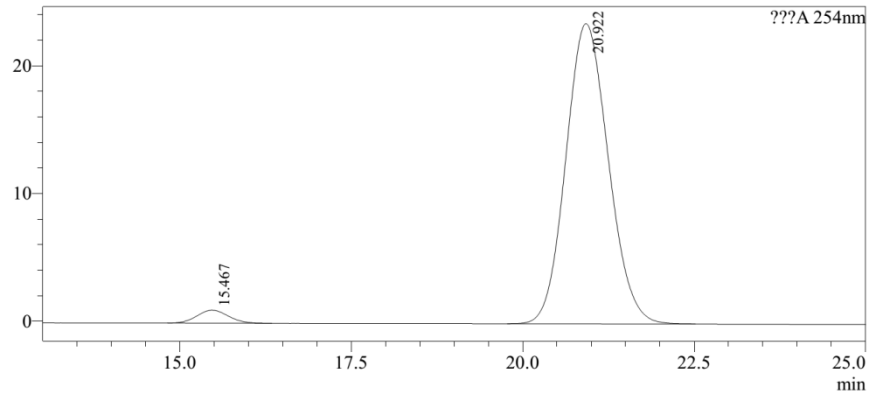
<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	16.110	2976889	90334	49.828			
2	21.974	2997443	66742	50.172		M	
Total		5974331	157075				

<Chromatogram>

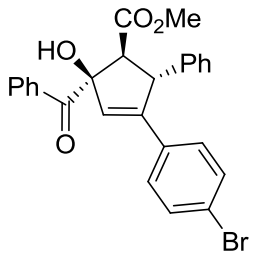
mV



<Peak Table>

???A 254nm

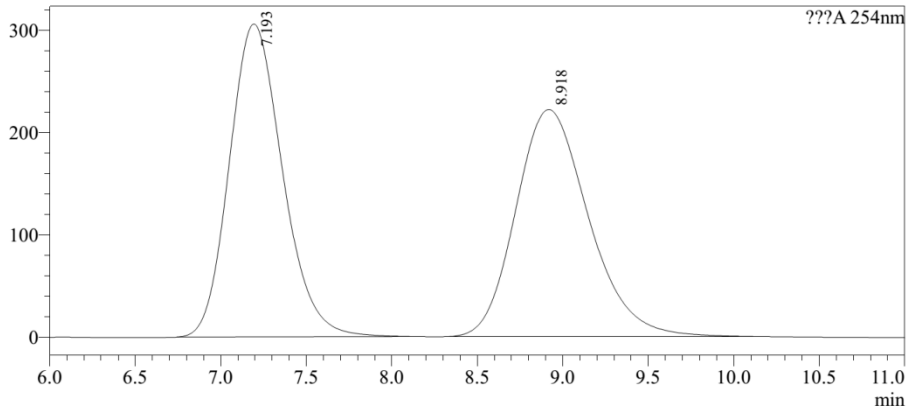
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.467	32456	1019	3.103			
2	20.922	1013503	23507	96.897			
Total		1045959	24526				



5c

<Chromatogram>

mV



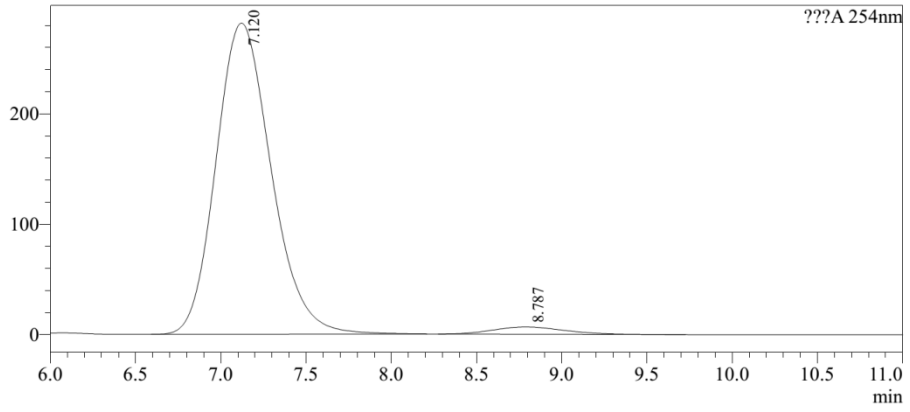
<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.193	6618941	306083	50.190		M	
2	8.918	6568872	222042	49.810		M	
Total		13187813	528125				

<Chromatogram>

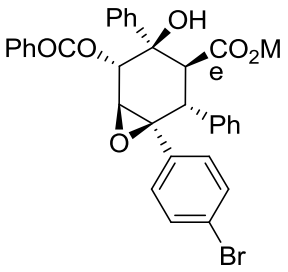
mV



<Peak Table>

???A 254nm

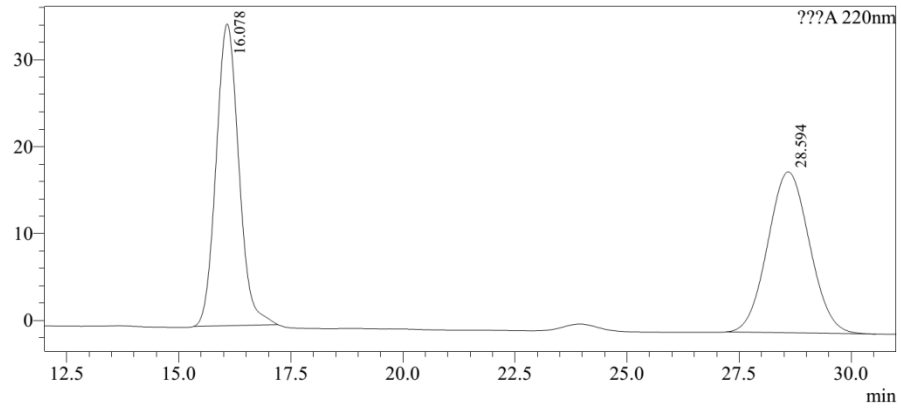
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.120	6342553	281556	97.086		M	
2	8.787	190384	6496	2.914		M	
Total		6532938	288052				



5d

<Chromatogram>

mV



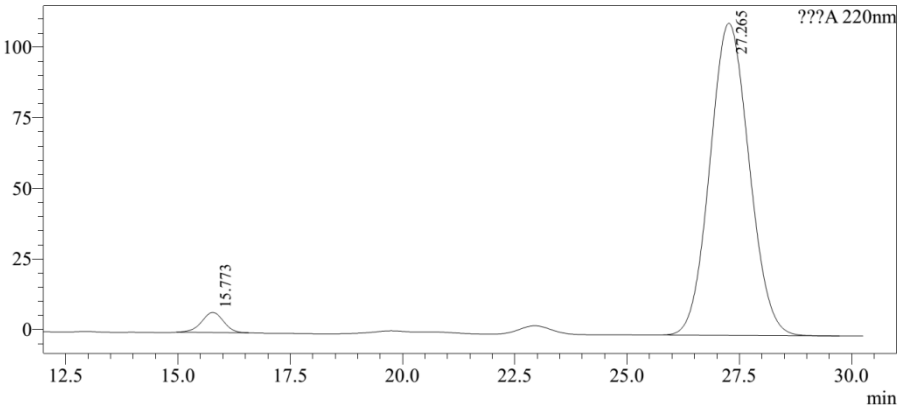
<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	16.078	1223907	34739	50.446		M	
2	28.594	1202268	18527	49.554		M	
Total		2426176	53266				

<Chromatogram>

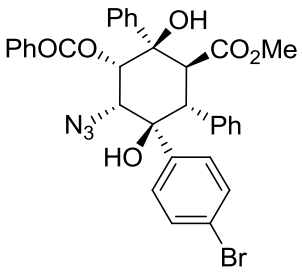
mV



<Peak Table>

???A 220nm

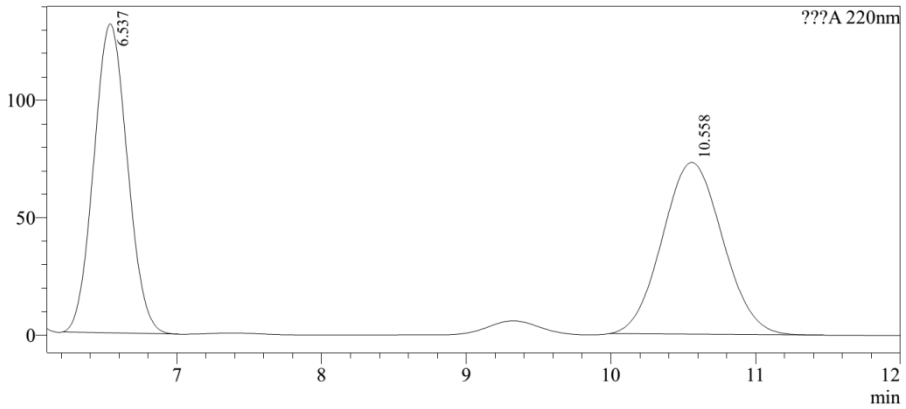
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.773	242982	7133	3.490		M	
2	27.265	6718930	110503	96.510		M	
Total		6961912	117635				



5e

<Chromatogram>

mV



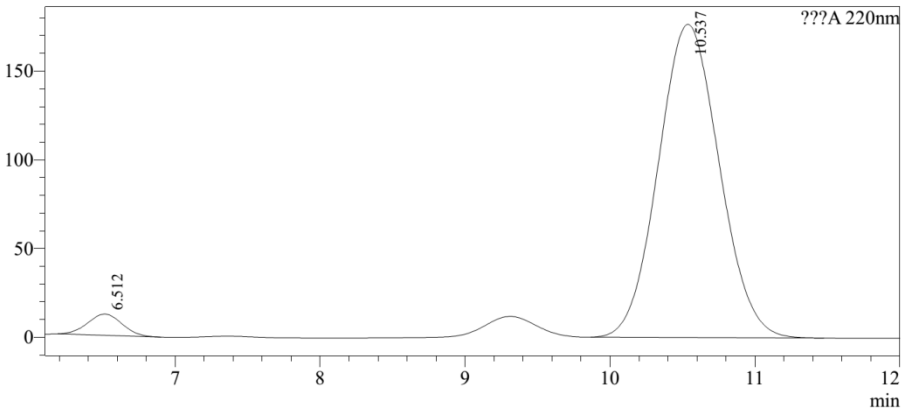
<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.537	2128445	131579	50.052		M	
2	10.558	2124041	73110	49.948		M	
Total		4252486	204689				

<Chromatogram>

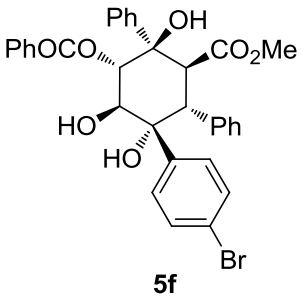
mV



<Peak Table>

???A 220nm

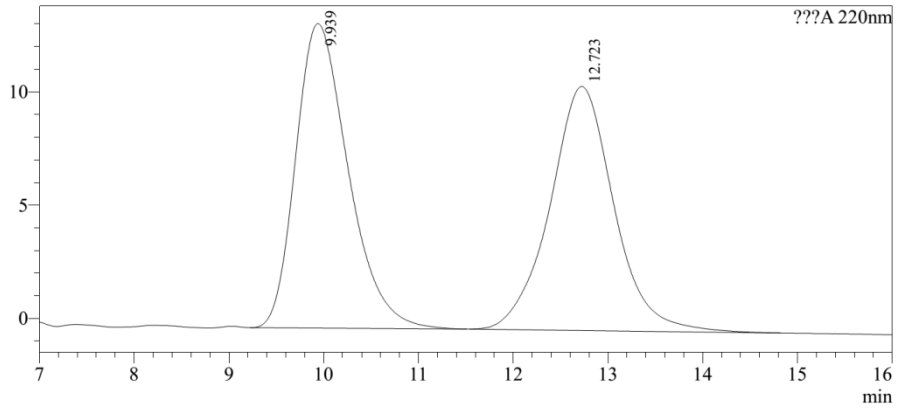
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.512	198948	11985	3.707		M	
2	10.537	5168416	176486	96.293		M	
Total		5367365	188470				



5f

<Chromatogram>

mV



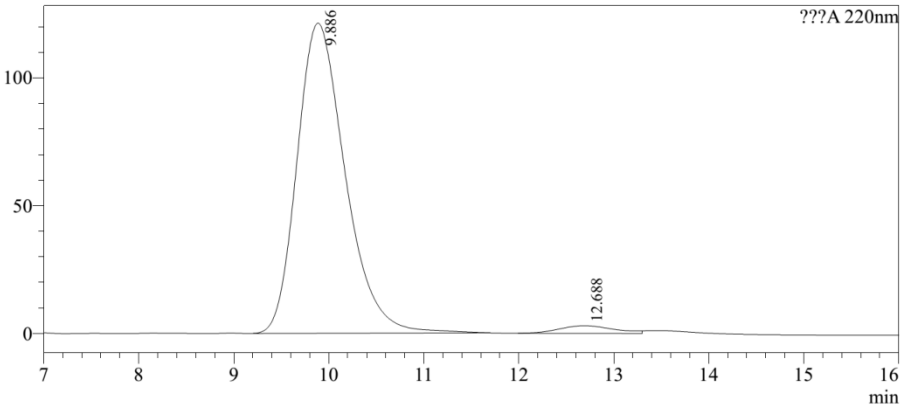
<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.939	517713	13445	50.588			
2	12.723	505681	10771	49.412			
Total		1023394	24216				

<Chromatogram>

mV



<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.886	4278927	121274	97.188		M	
2	12.688	123812	3044	2.812		M	
Total		4402739	124319				