Supporting Information

Rh(I)-catalyzed enantioselective and scalable [4+2] cycloaddition of 1,3-dienes with dialkyl acetylenedicarboxylates

Robert Li-Yuan Bao,[ac] Junjie Yin,[ac] Lei Shi[ab]* and Limin Zheng[a]

[a] School of Science, Harbin Institute of Technology, Shenzhen, 518055, China
[b] Beijing National Laboratory for Molecular Sciences, Beijing 100190, China
[c] These authors contribute equally.
E-mail: lshi@hit.edu.cn Homepage: http://homepage.hit.edu.cn/shilei.

Contents

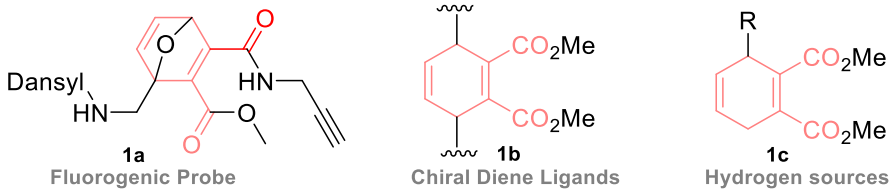
1. General Information

Unless otherwise noted, all materials obtained from commercial suppliers were used directly without further purification. Tetrahydrofuran (THF) and toluene were freshly distilled from sodium prior to use. All reactions were monitored by TLC and visualized by UV lamp (254 nm), or stained with potassium permanganate. Column chromatography was performed using 200-300 mesh silica gel.

^{1}H NMR spectra and ^{13}C NMR spectra were recorded on a Bruker 400 MHz or 600 MHz spectrometer in chloroform-d. Chemical shifts (in ppm) were referenced to tetramethylsilane (0 ppm) in $CDCl_3$ as an internal standard. ^{13}C-NMR spectra were obtained by using NMR spectrometers and were calibrated with $CDCl_3$ (77.00 ppm). The data is being reported as (s = singlet, d = doublet, dd = doublet of doublet, t = triplet, m = multiplet or unresolved, br = broad signal, coupling constant(s) in Hz, integration). HRMS (ESI) was recorded using Agilent 6520 accurate - Mass Q-TOF LC/MS system (1200-6520/Agilent). Optical rotations were measured on an Anton Paar MCP 500 Polarimeter in a 1dm cell. The enantiomeric excesses were determined by HPLC analysis using an Agilent 1260 Infinity II LC system (column Daicel Co. CHIRALCEL OD-H, OJ-H, AD-H, AS-H; eluent: hexane/2-propanol). The chiral HPLC methods were calibrated with the corresponding racemic mixtures. Chemical yields refer to pure isolated substances.

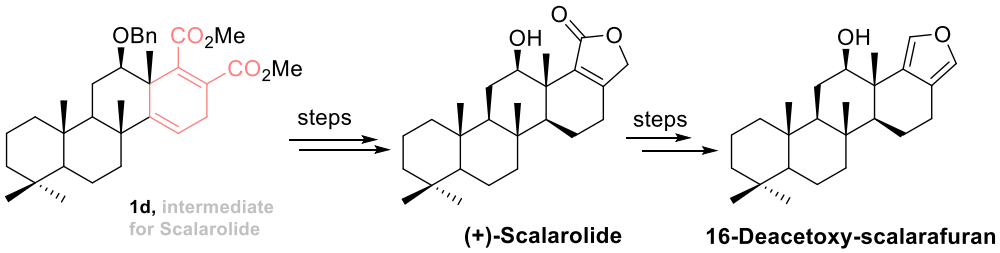
2. Representative compounds containing substituted cyclohexa-1,4-dienes

2.1 Versatile functional units.[1-3]

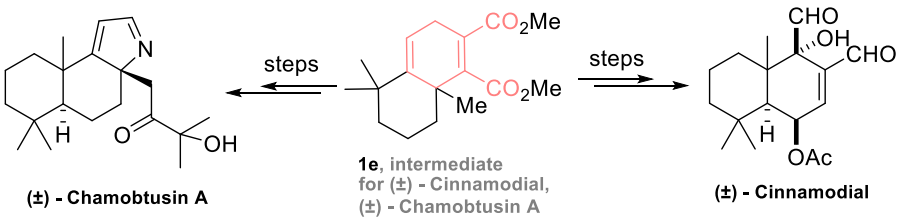


2.2 Intermediates towards the synthesis of natural products.

Intermediate for (+)-Scalarolide and 16-Deacetoxy-scalarafuran.[4]



Intermediate for (±)-Cinnamodial[5] and (±)-Chamobtusin A [6] :

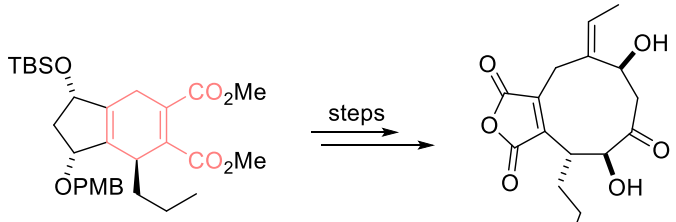


(±) - Chamobtusin A

1e, intermediate for (±) - Cinnamodial, (±) - Chamobtusin A

(±) - Cinnamodial

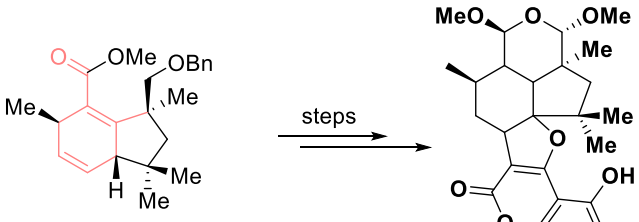
Intermediate for Cornexistin:[7]



1f, intermediate for Cornexistin

Cornexistin

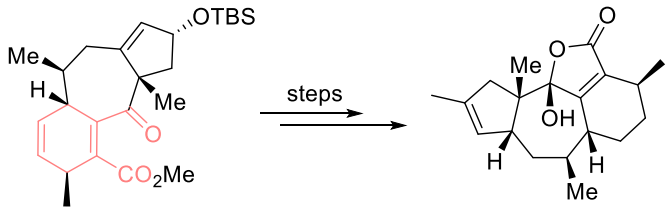
Intermediate for Hypocrolide A:[8]



1g, intermediate for Hypocrolide A

Hypocrolide A

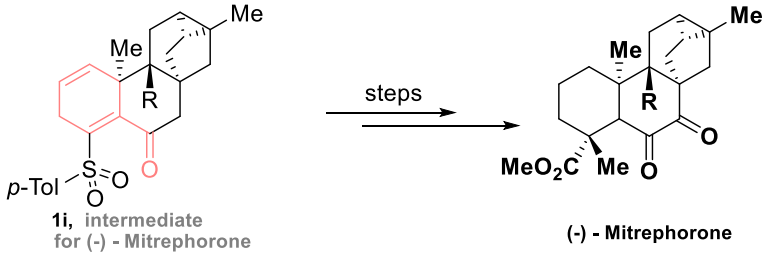
Intermediate for Caribenol: [9]



1h, intermediate for Caribenol A

Caribenol A

Intermediate for (-)-Mitrephorone:[10]



1i, intermediate for (-) - Mitrephorone

(-) - Mitrephorone

3. Procedures for the preparation of the ligands and the starting materials

3.1 Procedures for the preparation of the ligands

The ligand **L1** was purchased from Energy Chemical. The ligand **L2**, **L6** and **L7** were purchased from Daicel Chiral Technologies (China) Co., LTD.

The ligand **L3** was synthesized according to a reported procedure:[11]

To a solution of dicyclohexylamine (1.20 mL, 6.00 mmol) in tetrahydrofuran (30 mL) was added dropwise n-butyllithium (2.5 M in hexanes) (2.40 mL, 6.00 mmol) at -78 ℃, and the mixture was stirred for 40 min. Phosphorus trichloride (5.24 mL, 60 mmol) was added and the mixture was stirred at room temperature overnight. The reaction mixture was concentrated and the residue was suspended in toluene. Insoluble material was removed by filtration and the filtrate was concentrated. To the residue was added toluene (30 mL), (*S*)-(-)-1,1′-bi-2-naphthol (1.58 g, 6.00 mmol), and triethylamine (4.2 mL, 30.0 mmol), and the mixture was stirred at room temperature. After 16 h, the mixture was diluted with diethyl ether, insoluble material was removed by filtration, and the filtrate was concentrated. The residue was purified by silica gel column chromatography.

The ligand **L4** was synthesized according to a reported procedure:[12]

A flame-dried 250 mL, two-necked flask was equipped with vacuum/argon stopcock and a magnetic stirring bar. The flask was charged with toluene (50 mL) and PCl_3 (0.67 mL, 7.7 mmol), and then cooled to 0 °C. Another flame-dried, 25 mL flask was charged with 1,2,3,4-tetrahydroquinoline (1.02 g, 7.7 mmol), toluene (8 mL), and Et_3N (1.8 mL, 12.9 mmol). This mixture was added dropwise to the above mentioned PCl_3 solution at 0 °C. After the addition was complete, the reaction mixture was heated at 80 °C for 6 h, and then was cooled to -78 °C slowly. To this flask at -78 °C, a solution of (*S*)-(-)-1,1′-bi-2-naphthol (2.0 g, 7.0 mmol) and Et_3N (3.5 mL, 25.2 mmol) in toluene (30 mL) and THF (6 mL) was added slowly. The resulting mixture was stirred at room temperature overnight, then filtered through celite, and washed with Et_2O. The organic phase was concentrated in vacuo. The product was purified by column chromatography.

The ligand **L5** was synthesized according to a reported procedure:[13]

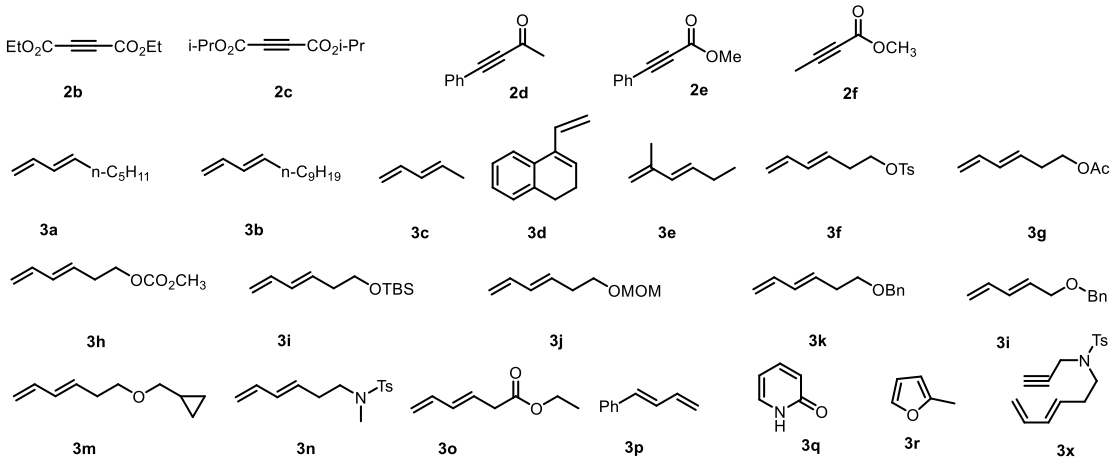
(*S*)-(-)-1,1′-bi-2-naphthol (1.00 g, 3.50 mmol) in 4 ml of PCl_3 was heated under reflux for 8 h. Excess of PCl_3 was removed by distillation in vacuo (20 mbar). The residual solid was subjected to azeotropic distillation with toluene (2x 10 ml) and dried in vacuo until a white foam resulted. The residue was dissolved in toluene to afford 5 ml of a chlorophosphite stock solution. A 2 ml aliquot of the above prepared chlorophosphite stock solution was added at 0 ℃ to a solution of 1.07 ml (7.70 mmol, 2.2 equiv.) of triethylamine and 3.85 mmol (1.1 equiv.) of the 1,2,3,4-tetrahydro-isoquinolin in 1.5 ml of dry THF. The reaction mixture was allowed to warm to 25 °C and stirred overnight. The mixture was diluted with diethyl ether (10 ml) and filtered over a plug of silica, washed with 10 ml of diethyl ether, and the solvent was removed in vacuo. The product was purified by column chromatography.

The ligand **L8** was synthesized according to a reported procedure:[14]

An oven-dried 100 mL Schlenk flask, fitted with a rubber septum, was charged with a stir bar and (S)-1,1-bi(2-naphthol) (1.15 g, 4.0 mmol, 1.0 equiv). The flask was evacuated and refilled with nitrogen 3 times. Phosphorus trichloride (5.25 mL, 15 equiv.) and anhydrous *N, N*-dimethylformamide (19 μL, 18 mg, 0.24 mmol, 0.06 equiv.) were added by syringes through the septum. The reaction mixture was stirred at 50 °C for 4 h. Excess phosphorus trichloride was removed via vacuum distillation and azeotropic removal with toluene (2 x 3 mL) under high vacuum to afford the phosphochloridite as an oily foam.

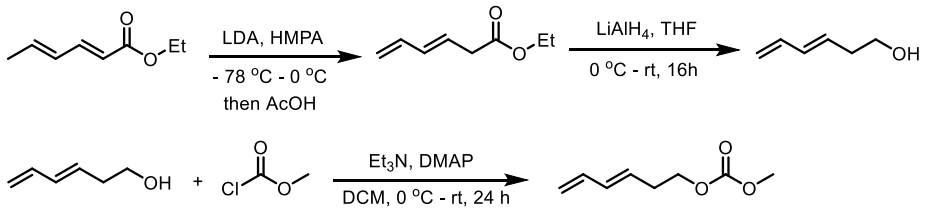
A separate oven-dried 250 mL round-bottomed flask was charged with a stir bar and 5*H*-dibenz[*b,f*]azepine (0.85 g, 4.40 mmol, 1.1 equiv). The flask was fitted with a rubber septum with a nitrogen line inlet and flushed with nitrogen. Anhydrous THF (24 mL) was added by syringe, and the orange solution was stirred at -78 °C. *n*-Butyllithium (2.75 mL, 4.40 mmol, 1.1 equiv) was added dropwise and the resulting dark blue solution was stirred at -78 °C for 1 h. The phosphochloridite prepared as above was dissolved in anhydrous THF (19 mL) and added to the deprotonated 5*H*-dibenz[*b,f*]azepine solution at -78 °C dropwise via a cannula over 20 min. The dark blue solution was stirred for 12 h while being gradually warmed to ambient temperature. Silica gel (10 g) was added to the orange reaction mixture, and the resulting slurry was carefully concentrated by rotary evaporation at room temperature. The product was purified by column chromatography and a white solid **L8** was obtained.

3.2 Procedures for the preparation of the starting materials



The starting materials **2b**, **2d**, **2e**, **2f** and **3r** were purchased from the Energy Chemical. The starting material **3p** was purchased from Sigma-Aladdin. The starting material **3q** was purchased from Aladdin. The starting materials **2c**,[15] **3a**,[16] **3b**,[17] **3c**,[18]] **3e**,[19] **3d**,[20] **3f**,[21] **3g**,[22] **3i**,[23] **3k**,[24] **3i**,[25] **3o**,[21] and **3x**[26] were prepared using the reported procedures. The **3h**, **3j**, **3m**, and **3n** were prepared and characterized as follows.

Procedure for the preparation of **3h**:

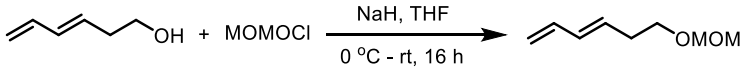


To a solution of diisopropylamine (2.9 g, 28.5 mmol) in anhydrous THF (28 mL) was added n-BuLi (12.0 mL, 2.5 M in hexane, 30.0 mmol) slowly at -78 ℃. After stirring at -78 ℃ for 45 min, HMPA (6.4 mL) was added and the reaction mixture was stirred at -78 ℃ for 30 min. Ethyl sorbate (2.0 g, 14.0 mmol) in THF (10 mL) was added dropwise over 15 min at -78 ℃. After stirring at 0 ℃ for 2 h, the reaction mixture was quenched with ice water (50 mL) containing glacial acetic acid (5 mL) and then partitioned between hexane (30 mL) and sequentially, saturated aqueous $NaHCO_3$ (15 mL) and brine (15 mL). The organic layer was dried over anhydrous sodium sulfate. The crude product was purified by silica gel column chromatography using petroleum ether/ethyl acetate (10:1) as eluent to yield a brown liquid, 1.9 g, 95% yield.

To a solution of $LiAlH_4$ (1.1 g, 29.9 mmol) in THF (90 mL) at 0 ℃ was added ester (1.9, 13.6 mmol). The reaction mixture was allowed to stir at room temperature for 12 h. The reaction was quenched with water (1 mL) at 0 ℃, followed by 15% aqueous NaOH (1 mL) and then water (3 mL). While the mixture was allowed to stir for 1 h, a white granular salt formed. The precipitate was filtered off and rinsed with THF. The combined filtrates were dried over anhydrous magnesium sulfate and the solvent was evaporated to near dryness at *20 ℃*. The crude product was purified by silica gel column chromatography using petroleum ether/ethyl acetate (5:1) as eluent to yield a clear oil, 1 g, 76% yield.

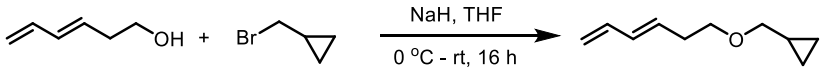
To a solution of (*E*)-hexa-3,5-dien-1-ol (735 mg, 5.0 mmol), triethylamine (1.4 mL, 10.0 mmol), and DMAP (61 mg, 0.5 mmol) in dichloromethane (10 mL) at 0 ℃ was added methyl chloroformate (567 mg, 6.0 mmol). The reaction mixture was allowed to warm to room temperature and stir for 12 h. The reaction was quenched with saturated NH_4Cl. The aqueous layer was extracted with dichloromethane and the combined organic layers was dried over sodium sulfate followed by filtration and concentration under reduced pressure. The crude product was purified with column chromatography on silica gel. Colorless liquid, 230 mg, 30% yield. ^{1}H NMR (600 MHz, Chloroform-d) δ 6.31 (dt, J = 16.9, 10.3 Hz, 1H), 6.14 (dd, J = 15.3, 10.4 Hz, 1H), 5.66 (m, J = 14.7, 7.1 Hz, 1H), 5.18 - 5.11 (m, 1H), 5.03 (d, J = 9.8 Hz, 1H), 4.25 - 4.16 (m, 2H), 3.78 (s, 3H), 2.46 (q, J = 6.8 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-d) δ 155.74, 136.69, 133.72, 129.07, 116.28, 67.11, 54.74, 31.91. HRMS (ESI) m/z Calcd. for $C_8H_{12}O_3$ $[M+H]^+$: 157.0859, found: 157.0864.

Procedure for the preparation of **3j**:



To a flame-dried 50 mL round-bottom flask equipped with a stir bar was charged with sodium hydride (240 mg, 6.0 mmol). The flask was sealed with a rubber septum, and placed under an atmosphere of nitrogen. Then 5 mL of anhydrous THF was added to the bottom flask via syringe at 0 ℃. After stirring at 0 ℃ for 10 min, (*E*)-hexa-3,5-dien-1-ol (735 mg, 5.0 mmol) was added dropwise to the bottom flask via syringe. The reaction was allowed to warm to room temperature slowly and stirred for 1h. Chloromethyl methyl ether (483 mg, 6.0 mmol) was added dropwise to the reaction flask at 0 ℃ *via* syringe. The resulting slurry was allowed to warm to room temperature and stir for 16 hours at ambient temperature. The reaction was quenched with saturated NH_4Cl. The aqueous layer was extracted with EA and the combined organic layers was dried over sodium sulfate followed by filtration and concentration under reduced pressure. The crude product was purified with column chromatography on silica gel (eluent: petroleum ether). Colorless liquid, 241 mg, 34% yield. ^{1}H NMR (600 MHz, Chloroform-d) δ 6.31 (dd, J = 17.0, 10.3 Hz, 1H), 6.14 (dd, J = 15.4, 10.3 Hz, 1H), 5.72 (dd, J = 14.9, 7.3 Hz, 1H), 5.19 - 5.08 (m, 1H), 5.07 - 4.95 (m, 1H), 4.63 (s, 2H), 3.59 (s, 2H), 3.36 (s, 3H), 2.40 (pd, J = 7.3, 6.8, 1.4 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-d) δ 137.01, 132.81, 131.12, 115.60, 96.40, 67.07, 55.20, 33.00. HRMS (ESI) m/z Calcd. for $C_8H_{14}O_2$ $[M+Na]^+$: 165.0886, found: 165.0883.

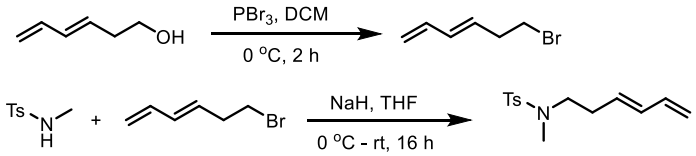
Procedure for the preparation of **3m**:



To a flame-dried 50 mL round-bottom flask equipped with a stir bar was charged with sodium hydride (480 mg, 12.0 mmol). The flask was sealed with a rubber septum, and placed under an atmosphere of nitrogen. Then 10 mL of anhydrous THF was added to the bottom flask *via* syringe at 0 ℃. After stirring at 0 ℃ for 10 min, (*E*)-hexa-3,5-dien-1-ol (981 mg, 10.0 mmol) was added dropwise to the bottom flask *via* syringe. The reaction was allowed to warm to room temperature slowly and stirred for 1h. (Bromomethyl)cyclopropane (2.0 g, 15.0 mmol) was added dropwise to the reaction flask at 0 ℃ *via* syringe. The resulting slurry was allowed to warm to room temperature and stir for 16 hours at ambient temperature.

The reaction was quenched with saturated NH_4Cl aqueous solution. The aqueous layer was extracted with EA and the combined organic layers was dried over sodium sulfate followed by filtration and concentration under reduced pressure. The crude product was purified with column chromatography on silica gel (eluent: petroleum ether). Colorless liquid, 685 mg, 45% yield. ^{1}H NMR (600 MHz, Chloroform-d) δ 6.24 (dt, J = 16.9, 10.2 Hz, 1H), 6.05 (dd, J = 15.3, 10.4 Hz, 1H), 5.76 - 5.58 (m, 1H), 5.13 - 5.00 (m, 1H), 4.99 - 4.87 (m, 1H), 3.42 (t, J = 6.9 Hz, 2H), 3.20 (d, J = 6.9 Hz, 2H), 2.32 (m, J = 6.9, 1.3 Hz, 2H), 1.02 - 0.96 (m, 1H), 0.48 - 0.44 (m, 2H), 0.13 (dd, J = 4.7, 1.5 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-d) δ 136.08, 131.57, 130.24, 114.37, 74.60, 68.92, 32.02, 1.97. HRMS (ESI) m/z Calcd. for $C_{10}H_{16}O$ $[M+H]^+$: 153.1274, found: 153.1269.

Procedure for the preparation of **3n**:

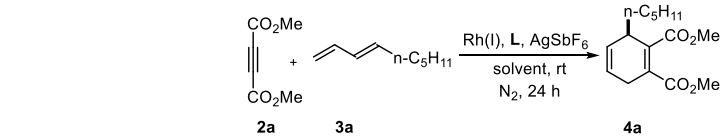


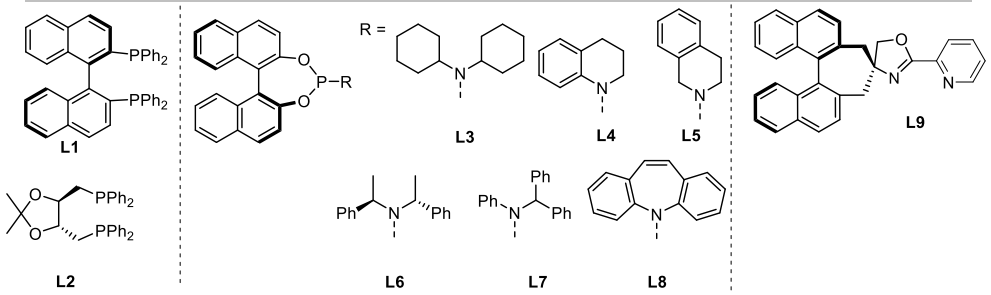
To a solution of (*E*)-hexa-3,5-dien-1-ol in anhydrous dichloromethane (10 mL) at 0 ℃ was added phosphorus tribromide (2.8 g, 10.3 mmol). The reaction mixture was allowed to stir at 0 ℃ for 2 h before addition of water. The mixture was extracted with diethyl ether, and the organic layer was washed with brine and dried over anhydrous magnesium sulfate before evaporation of the solvent in vacuo at 20 ℃. The crude product was used without further purification, yellow oil, 1.4 g, 90% yield.

To a flame-dried 50 mL round-bottom flask equipped with a stir bar was charged with sodium hydride (360 mg, 9.0 mmol). The flask was sealed with a rubber septum, and placed under an atmosphere of nitrogen. Then 8 mL of anhydrous THF was added to the bottom flask via syringe at 0 ℃. After stirring at 0 ℃ for 10 min, N,4-dimethylbenzene-1-sulfonamide (1.9 g, 8 mmol) was added dropwise to the bottom flask via syringe. The reaction was allowed to warm to room temperature slowly and stirred for 1h. (E)-6-bromohexa-1,3-diene (1.4 g, 9.0 mmol) was added dropwise to the reaction flask at 0 ℃ *via* syringe. The resulting slurry was allowed to warm to room temperature and stir for 16 hours at ambient temperature.

The reaction was quenched with saturated NH_4Cl aqueous solution. The aqueous layer was extracted with EtOAc and the combined organic layers was dried over sodium sulfate followed by filtration and concentration under reduced pressure. The crude product was purified with column chromatography on silica gel, yellow oil, 390 mg, 18% yield. ^{1}H NMR (600 MHz, Chloroform-d) δ 7.66 (d, J = 8.3 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 6.28 (dt, J = 17.0, 10.3 Hz, 1H), 6.08 (dd, J = 15.2, 10.4 Hz, 1H), 5.61 (m, J = 14.7, 7.1 Hz, 1H), 5.11 (d, J = 16.9 Hz, 1H), 5.01 (d, J = 10.2 Hz, 1H), 3.10 – 3.02 (m, 2H), 2.73 (s, 3H), 2.42 (s, 3H), 2.33 (q, J = 7.1 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-d) δ 143.32, 136.74, 134.62, 133.27, 130.31, 129.69, 127.40, 116.11, 34.86, 31.20, 21.52. HRMS (ESI) m/z Calcd. for $C_{18}H_{27}NO_2S$ $[M+Na]^+$: 288.1029, found: 288.1024.

4. Optimization of reaction conditions [a]

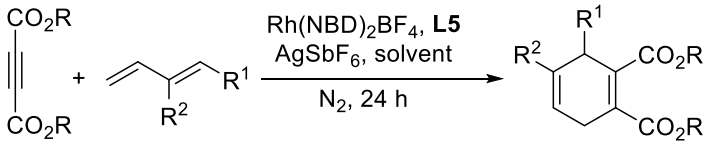




Entry	M	**L**	Solvent	Yield[b] %	Ee[c] %
1	$[Rh(COD)Cl]_2$	**L1**	Toluene	trace	--
2	$[Rh(COD)Cl]_2$	**L2**	Toluene	N.R.	--
3	$[Rh(COD)Cl]_2$	**L3**	Toluene	16	2
4	$[Rh(COD)Cl]_2$	**L4**	Toluene	15	0
5	$[Rh(COD)Cl]_2$	**L5**	Toluene	77	98
6	$[Rh(COD)Cl]_2$	**L6**	Toluene	N.R.	--
7	$[Rh(COD)Cl]_2$	**L7**	Toluene	N.R.	--
8	$[Rh(COD)Cl]_2$	**L8**	Toluene	67	54
9	$Rh(COD)_2BF_4$	**L5**	Toluene	82	96
10	$[Rh(COE)Cl]_2$	**L5**	Toluene	71	98
11	$[Rh(NBD)Cl]_2$	**L5**	Toluene	30	98
12	$Rh(NBD)_2BF_4$	**L5**	Toluene	96	99
13	No Rh(I)	**L5**	Toluene	trace	--
14[d]	$Rh(NBD)_2BF_4$	**L5**	Toluene	59	99
15[e]	$Rh(NBD)_2BF_4$	**L5**	Toluene	3	85
16[f]	$Rh(NBD)_2BF$	**L5**	Toluene	12	13
17	$Rh(NBD)_2BF$	**L5**	DCE	89	95
18	$Rh(NBD)_2BF$	**L5**	Et_2O	7	87
19	$Rh(NBD)_2BF$	**L5**	THF	N.R.	--
20	$Rh(NBD)_2BF$	**L5**	CH_3CN	N.R.	--
21	$Cu(OTf)_2$	**L9**	DCE	26	0
22	$Co(OAc)_2$	**L9**	DCE	16	0
23	$Ni(OTf)_2$	**L9**	DCE	31	0

[a] Reaction conditions: **2a** (0.2 mmol), **3a** (0.6 mmol), Rh(I) (10 mol%), **L** (12 mmol%) and $AgSbF_6$ (20 mol%) in solvent (3 mL) under N_2 at 25 °C. [b] Isolated yields. [c] Determined by HPLC. [d] Open to air. [e] H_2O (5 μL) was added. [f] No $AgSbF_6$. Rh(I) = rhodium complexes. DCE = 1,2-Dichloroethane. Et_2O = Diethyl ether. THF = Tetrahydrofuran.

5. Procedure for Rhodium-catalyzed [4+2] cycloaddition reactions



2 **3** **4**

General procedure A: (**4a**, **4b**, **4c**, **4d**, **4i**, **4m**, **4p**, **4v**, **4w**, and **4x**)

A Schlenk tube equipped with a stir bar was charged with $Rh(NBD)_2BF_4$ (3.73 mg, 0.02 mmol), **L5** (10.7 mg, 0.024 mmol) and $AgSbF_6$ (13.7 mg, 0.04 mmol) under nitrogen atmosphere. Then toluene (3 mL) was added via syringe and the resulting mixture was stirred at 25 ℃ for 1 h. The reaction was started by addition of the 1,3-dienes (0.6 mmol) and substituted alkynes (0.2 mmol) separately *via* syringe. The reaction was allowed to stir at 25 °C for 24 h. When the reaction was completed, the solvent was evaporated to give a crude product, which was purified with column chromatography on silica gel or prepared TLC.

General procedure B: (**4e**, **4q** and **4u**)

A Schlenk tube equipped with a stir bar was charged with $Rh(NBD)_2BF_4$ (3.73 mg, 0.02 mmol), **L5** (10.7 mg, 0.024 mmol) and $AgSbF_6$ (13.7 mg, 0.04 mmol) under nitrogen atmosphere. Then 1,2-dichloroethane (3 mL) were added via syringe and the resulting mixture was stirred at 25 ℃ for 1 h. The reaction was started by addition of the 1,3-dienes (0.6 mmol) and dialkyl acetylenedicarboxylates (0.2 mmol) separately *via* syringe. The reaction was allowed to stir at 25 °C for 72 h. When the reaction was completed, the solvent was evaporated to give a crude product, which was purified with column chromatography on silica gel or prepared TLC.

General procedure C: (**4f**, **4g**, **4h**, **4n**, and **4s**)

A Schlenk tube equipped with a stir bar was charged with $Rh(NBD)_2BF_4$ (3.73 mg, 0.02 mmol), **L5** (10.7 mg, 0.024 mmol) and $AgSbF_6$ (13.7 mg, 0.04 mmol) under nitrogen atmosphere. Then toluene (2 mL) and 1,2-dichloroethane (1 mL) were added via syringe and the resulting mixture was stirred at 25 ℃ for 1 h. The reaction was started by addition of the 1,3-dienes (0.6 mmol) and dialkyl acetylenedicarboxylates (0.2 mmol) separately *via* syringe. The reaction was allowed to stir at 25 °C for 72 h. When the reaction was completed, the solvent was evaporated to give a crude product, which was purified with column chromatography on silica gel or prepared TLC.

General procedure D: (**4j** and **4t**)

A Schlenk tube equipped with a stir bar was charged with $Rh(NBD)_2BF_4$ (3.73 mg, 0.02 mmol), **L5** (10.7 mg, 0.024 mmol) and $AgSbF_6$ (13.7 mg, 0.04 mmol) under

nitrogen atmosphere. Then toluene (2 mL) and 1,2-dichloroethane (1 mL) were added via syringe and the resulting mixture was stirred at 25 ℃ for 1 h. The reaction was started by addition of the 1,3-dienes (0.6 mmol) and dialkyl acetylenedicarboxylates (0.2 mmol) separately *via* syringe. The reaction was allowed to stir at 50 °C for 72 h. When the reaction was completed, the solvent was evaporated to give a crude product, which was purified with column chromatography on silica gel or prepared TLC.

General procedure E: (**4k** and **4l**)

A Schlenk tube equipped with a stir bar was charged with $Rh(NBD)_2BF_4$ (3.73 mg, 0.02 mmol), **L5** (10.7 mg, 0.024 mmol) and $AgSbF_6$ (13.7 mg, 0.04 mmol) under nitrogen atmosphere. Then toluene (3 mL) was added via syringe and the resulting mixture was stirred at 25 ℃ for 1 h. The reaction was started by addition of the 1,3-dienes (0.6 mmol) and dialkyl acetylenedicarboxylates (0.2 mmol) separately *via* syringe. The reaction was allowed to stir at 50 °C for 24 h. When the reaction was completed, the solvent was evaporated to give a crude product, which was purified with column chromatography on silica gel or prepared TLC.

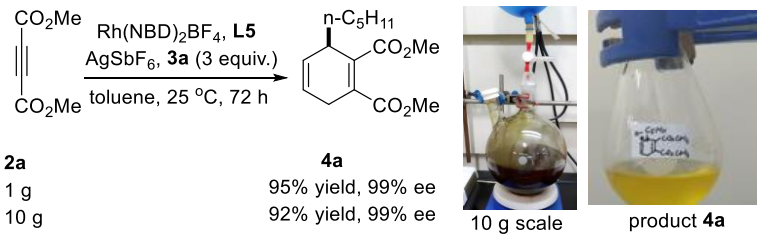
General procedure F: (**4o**)

A Schlenk tube equipped with a stir bar was charged with $Rh(NBD)_2BF_4$ (3.73 mg, 0.02 mmol), **L5** (10.7 mg, 0.024 mmol) and $AgSbF_6$ (13.7 mg, 0.04 mmol) under nitrogen atmosphere. Then toluene (3 mL) was added via syringe and the resulting mixture was stirred at 25 ℃ for 1 h. The reaction was started by addition of the 1,3-dienes (0.6 mmol) and dialkyl acetylenedicarboxylates (0.2 mmol) separately *via* syringe. The reaction was allowed to stir at 110 °C for 72 h. When the reaction was completed, the solvent was evaporated to give a crude product, which was purified with column chromatography on silica gel.

General procedure for the racemic reaction:

A racemic ligand was prepared according to synthetic procedure of **L5** when the racemic 1,1′-bi-2-naphthol was subjected the method. Then the racemic reactions were performed in the presence of the racemic ligand according the general procedures for the rhodium-catalyzed asymmetric [4+2] cycloaddition reactions.

General procedures for scale-up reactions:



Procedure for the [4+2] cycloaddition on 10 g scale:

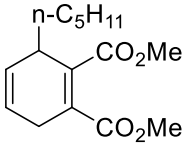
To a flame-dried 2 L two-necked flask equipped with a stir bar was charged with

the chiral phosphoramidite **L5** (3.78 g, 8.44 mmol), $Rh(NBD)_2BF_4$ (2.63 g, 7.03 mmol) and $AgSbF_6$ (4.83 g, 14.07 mmol) under N_2 . After addition of the anhydrous toluene (50 mL) to the flask, the resulting mixture was stirred for 4 h at 25 ℃ and then another 950 mL of anhydrous toluene was added to the flask. The reaction system was cooled to 0 ℃, then the (*E*)-1,3-nonadiene (26.20 g, 211.11 mmol) and dimethyl acetylenedicarboxylate (10 g, 70.37 mmol) were added to the flask via syringe, respectively. The reaction system was allowed to warm to 25 ℃ and stir at 25 ℃ for 72 h. After the completion of reaction, the reaction was quenched with water. The aqueous layer was extracted with ethyl acetate and the combined organic layers was dried over sodium sulfate followed by filtration and concentration under reduced pressure. The crude product was purified with column chromatography on silica gel using petroleum ether/ethyl acetate (20:1) as eluent to yield a light brown liquid. 17.2 g, 92% yield, 99% ee.

Procedure for the [4+2] cycloaddition on 1 g scale was similar to the reaction on 10 g scale.

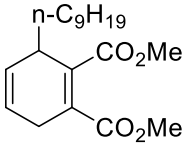
6. Characterizations of the products

Dimethyl 3-pentylcyclohexa-1,4-diene-1,2-dicarboxylate (4a)



General procedure A: yellow oil, 51.1mg, 96% yield, 99% ee. General procedure scale-up experiments (1 g scale): yellow oil,1.76 g, 95% yield, 99% ee. General procedure scale-up experiments (10 g scale): yellow oil, 17.2 g, 92% yield, 99% ee. [Daicel Chiralcel OD-H column (25 cm x 0.46 cm ID), *n*-hexane/*i*-PrOH = 99.5/0.5, 0.6 mL/min, 254 nm; t_{minor} =10.6 min, t_{major} = 11.4 min]. $[\alpha]_D^{20}$ = -52.45 (c = 1.0, $CHCl_3$). ^1H NMR (400 MHz, Chloroform-*d*) δ 5.79 - 5.71 (m, 1H), 5.71 - 5.64 (m, 1H), 3.79 (s, 3H), 3.75 (s, 3H), 3.30 - 3.16 (m, 1H), 3.08 - 2.95 (m, 1H), 2.89 (m, *J* = 23.0, 7.0, 3.9, 1.4 Hz, 1H), 1.56 - 1.39 (m, 2H), 1.33 - 1.20 (m, 6H), 0.87 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.34, 167.60, 139.80, 130.04, 127.27, 122.52, 77.33, 77.01, 76.69, 52.12, 52.07, 37.58, 33.89, 31.89, 27.22, 24.86, 22.47, 14.02. HRMS (ESI) m/z Calcd. for $C_{15}H_{22}O_4$ $[M+K]^+$: 305.1150, found: 305.1143.

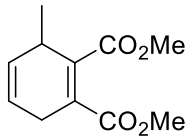
Dimethyl 3-decylcyclohexa-1,4-diene-1,2-dicarboxylate (4b)



General procedure A: yellow oil, 26.0 mg, 40% yield, 95% ee. [Daicel Chiralcel OD-H column (25 cm x 0.46 cm ID), *n*-hexane/*i*-PrOH = 99.5/0.5, 0.6 mL/min, 254 nm; t_{minor} =9.1 min, t_{major} = 9.8 min]. $[\alpha]_D^{20}$ = -24.1 (c = 0.2, $CHCl_3$). ^1H NMR (400 MHz, Chloroform-*d*) δ 5.78

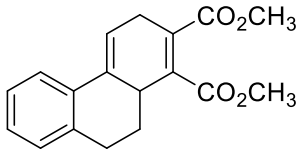
- 5.70 (m, 1H), 5.69 - 5.61 (m, 1H), 3.76 (d, *J* = 14.6 Hz, 6H), 3.22 (m, *J* = 7.6, 3.9 Hz, 1H), 3.05 - 2.78 (m, 2H), 1.51 (d, *J* = 10.4 Hz, 2H), 1.23 (m, 14H), 0.86 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.28, 167.53, 139.76, 129.98, 127.22, 122.47, 77.32, 77.00, 76.68, 52.06, 52.01, 37.53, 33.88, 31.83, 29.65, 29.51, 29.43, 29.24, 27.16, 25.16, 22.62, 14.04. HRMS (ESI) m/z Calcd. for $C_{10}H_{11}O_4$ $[M+H]^+$: 323.2217, found: 323.2219.

Dimethyl 3-methylcyclohexa-1,4-diene-1,2-dicarboxylate (4c)



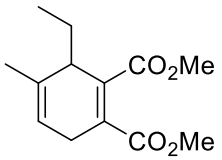
A known compound.[28] General procedure A: yellow oil, 35.4 mg, 84% yield, 99% ee. [Daicel Chiralcel AS-H column (25 cm x 0.46 cm ID), *n*-hexane/*i*-PrOH = 99/1, 1 mL/min, 254 nm; t_{major} =9.6 min, t_{minor} = 11.6 min]. $[\alpha]_D^{20}$ = 54.6 (c = 1.0, $CHCl_3$).^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.73 - 5.60 (m, 2H), 3.80 (d, *J* = 1.3 Hz, 3H), 3.76 (d, *J* = 1.4 Hz, 3H), 3.28 - 3.12 (m, 1H), 3.09 - 2.98 (m, 1H), 2.95 - 2.83 (m, 1H), 1.15 (dd, *J* = 7.1, 1.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.23, 167.73, 140.27, 129.42, 128.90, 121.31, 77.26, 77.05, 76.83, 52.21, 52.16, 32.45, 27.04, 20.50.

Dimethyl 3,9,10,10a-tetrahydrophenanthrene-1,2-dicarboxylate (4d)



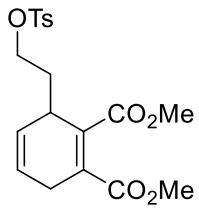
General procedure A: white solid, 35.4 mg, 84% yield, 8% ee. [Daicel Chiralcel AS-H column (25 cm x 0.46 cm ID), *n*-hexane/*i*-PrOH = 95/5, 1 mL/min, 254 nm; t_{minor} = 8.1 min, t_{major} = 11.1 min]. $[\alpha]_D^{20}$ = -2.6 (c = 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.60 - 7.42 (m, 1H), 7.22 - 7.12 (m, 2H), 7.12 - 7.05 (m, 1H), 6.12 (m, *J* = 3.7, 1.9 Hz, 1H), 3.84 (s, 3H), 3.78 (s, 3H), 3.40 - 3.24 (m, 2H), 3.16 - 2.98 (m, 2H), 2.92 (m, *J* = 17.1, 5.6, 1.8 Hz, 1H), 2.23 - 2.09 (m, 1H), 1.72 (m, *J* = 12.5, 5.5 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.36, 167.36, 139.70, 135.64, 134.57, 133.39, 129.11, 128.54, 127.53, 126.11, 124.01, 115.53, 52.31, 52.28, 37.59, 29.79, 29.35, 28.05. HRMS (ESI) m/z Calcd. for $C_{18}H_{18}O_4$ $[M+H]^+$: 299.1278, found: 299.1277.

Dimethyl 3-ethyl-4-methylcyclohexa-1,4-diene-1,2-dicarboxylate (4e)



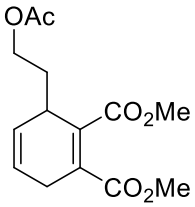
General procedure B: yellow oil, 29.9 mg, 62 % yield, 70% ee. [Daicel Chiralcel OD-H column (25 cm x 0.46 cm ID), *n*-hexane/*i*-PrOH = 99.5/0.5, 0.6 mL/min, 254 nm; t_{minor} =10.6 min, t_{major} = 11.4 min]. $[\alpha]_D^{20}$ = 18.7 (c = 0.5, $CHCl_3$). ^{1}H NMR (600 MHz, Chloroform-d) δ 5.57 - 5.48 (t, 1H), 3.77 (s, 3H), 3.74 (s, 3H), 3.17 (m, J = 4.6 Hz, 1H), 2.96 (m, J = 22.8, 4.6, 2.3 Hz, 1H), 2.90 - 2.80 (m, 1H), 1.74 (m, J = 14.4, 7.3, 4.5 Hz, 1H), 1.68 (s, J = 1.8 Hz, 3H), 1.58 (m, J = 14.7, 7.4, 3.7 Hz, 1H), 0.71 (t, J = 7.5 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.36, 167.82, 138.84, 132.35, 131.54, 119.11, 52.16, 52.14, 42.29, 28.08, 23.33, 20.88, 7.86. HRMS (ESI) m/z Calcd. for $C_{13}H_{18}O_4$ $[M+H]^+$: 239.1283, found: 239.1289.

Dimethyl 3-(2-(tosyloxy)ethyl)cyclohexa-1,4-diene-1,2-dicarboxylate (4f)



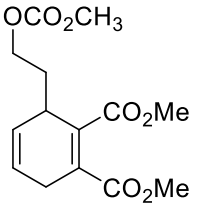
General procedure C: yellow semisolid, 42.8 mg, 54% yield, 98% ee. [Daicel Chiralcel AS-H column (25 cm x 0.46 cm ID), *n*-hexane/*i*-PrOH = 82/18, 1 mL/min, 254 nm; t_{major} = 26.9 min, t_{minor} = 29.9 min]. $[\alpha]_D^{20}$ = -53.2 (c = 1.0, $CHCl_3$).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 7.9 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 5.84 - 5.70 (m, 1H), 5.65 - 5.47 (m, 1H), 4.07 (t, *J* = 6.8 Hz, 2H), 3.75 (s, 6H), 3.41 - 3.21 (m, 1H), 2.92 (d, *J* = 4.4 Hz, 2H), 2.45 (s, 3H), 2.09 -1.91 (m, 1H), 1.88 - 1.72 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.42, 167.47, 144.82, 137.01, 132.99, 132.01, 129.86, 127.91, 125.65, 123.71, 77.29, 77.08, 76.87, 67.40, 52.34, 52.31, 34.28, 33.02, 27.24, 21.67. HRMS (ESI) m/z Calcd. for $C_{19}H_{22}O_7S$ $[M+H]^+$: 395.1164, found: 395.1161.

Dimethyl 3-(2-acetoxyethyl)cyclohexa-1,4-diene-1,2-dicarboxylate (4g)



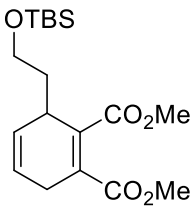
General procedure C: yellow oil, 30.9 mg, 55 % yield, 99% ee. [Daicel Chiralcel AS-H column (25 cm x 0.46 cm ID), *n*-hexane/*i*-PrOH = 99.5/0.5, 1.0 mL/min, 254 nm; t_{major} =16.9 min, t_{minor} = 18.7 min]. $[\alpha]_D^{20}$ = 39.0 (c = 1.0, $CHCl_3$). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 5.78 (d, *J* = 10.1 Hz, 1H), 5.66 (d, *J* = 10.2 Hz, 1H), 4.07 (td, *J* = 6.8, 2.7 Hz, 2H), 3.77 (s, 3H), 3.73 (s, 3H), 3.41 - 3.28 (m, 1H), 3.00 (dd, *J* = 23.1, 7.6 Hz, 1H), 2.95 - 2.84 (m, 1H), 1.99 (s, 3H), 1.91 -1.80 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.97, 168.38, 167.76, 136.89, 132.06, 126.17, 123.27, 77.21, 77.00, 76.79, 61.22, 52.14, 34.60, 32.35, 27.34, 20.82. HRMS (ESI) m/z Calcd. for $C_{14}H_{18}O_6$ $[M+H]^+$: 283.1176, found: 283.1171.

Dimethyl 3-(2-((methoxycarbonyl)oxy)ethyl)cyclohexa-1,4-diene-1,2 dicarboxylate (4h)



General procedure C: yellow oil, 16.5 mg, 32% yield, 99% ee. [Daicel Chiralcel AD-H column (25 cm x 0.46 cm ID), *n*-hexane/*i*-PrOH = 90/10, 1 mL/min, 254 nm; t_{minor} =9.7 min, t_{major} = 12.4 min]. $[\alpha]_D^{20}$ = -20.4 (c = 0.2, $CHCl_3$). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 5.84 - 5.77 (m, 1H), 5.76 - 5.67 (m, 1H), 4.17 (t, *J* = 7.1 Hz, 2H), 3.85 - 3.68 (m, 9H), 3.37 (m, *J* = 4.9, 2.0, 1.3 Hz, 1H), 3.11 - 2.87 (m, 2H), 2.05 - 1.95 (m, 1H), 1.85 (dd, *J* = 13.9, 7.0 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.59, 167.59, 155.66, 137.35, 131.84, 126.09, 123.44, 77.25, 77.04, 76.82, 65.07, 54.77, 52.32, 52.28, 34.54, 32.65, 27.30. HRMS (ESI) m/z Calcd. for $C_{14}H_{18}O_7$ $[M+Na]^+$: 305.0996, found: 305.0997.

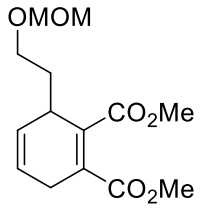
Dimethyl 3-(2-((tert-butyldimethylsilyl)oxy)- ethyl)cyclohexa-1,4-diene-1,2-dicarboxylate (4i)



A known compound.[28] General procedure A: yellow oil, 20.0 mg, 28% yield, 98% ee. [Daicel Chiralcel AS-H column (25 cm x 0.46 cm ID), n-hexane/i-PrOH = 99.5/0.5, 0.5 mL/min, 254 nm; t_{major} = 8.4 min, t_{minor} = 9.4 min]. $[\alpha]_D^{20}$ = 47.9 (c = 1.0, $CHCl_3$). 1H NMR (400 MHz, Chloroform-d) δ 5.74 (s, 2H), 3.76 (d, J = 13.6 Hz, 6H),

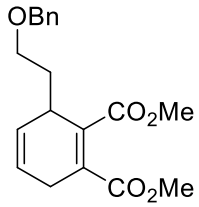
3.70 - 3.55 (m, 2H), 3.33 (dd, J = 7.8, 3.7 Hz, 1H), 3.05 - 2.83 (m, 2H), 1.91 - 1.79 (m, 1H), 1.65 - 1.54 (m, 1H), 0.87 (s, 9H), 0.03 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.03, 167.62, 139.38, 130.22, 126.91, 122.39, 77.28, 77.07, 76.85, 59.97, 52.16, 37.11, 34.67, 27.14, 25.88, 25.86, 25.65, 18.23, -3.58, -5.32, -5.39.

Dimethyl 3-(2-(methoxymethoxy)ethyl)cyclohexa-1,4-diene-1,2-dicarboxylate (4j)



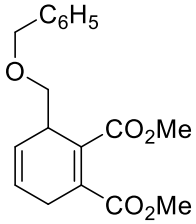
General procedure B: 50 ℃, yellow oil, 20.0 mg, 44% yield, 92% ee. [Daicel Chiralcel AS-H column (25 cm x 0.46 cm ID), *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, 254 nm; t_{major} = 6.8 min, t_{minor} = 8.2 min]. $[\alpha]_D^{20}$ = 73.8 (c = 1.0, $CHCl_3$). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 5.92 - 5.60 (m, 2H), 4.59 (s, 2H), 3.80 (s, 3H), 3.76 (s, 3H), 3.56 (t, *J* = 7.0 Hz, 2H), 3.35 (s, 4H), 3.07 -2.98 (m, 1H), 2.92 (m, *J* = 23.2, 7.0, 3.5 Hz, 1H), 1.95 (m, *J* = 11.1, 4.1 Hz, 1H), 1.73 (dd, *J* = 13.8, 6.9 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.96, 167.63, 138.69, 130.74, 126.64, 122.82, 96.47, 77.26, 77.05, 76.84, 64.65, 55.23, 52.24, 34.87, 33.92, 27.20. HRMS (ESI) m/z Calcd. for $C_{14}H_{20}O_6$ $[M+Na]^+$: 294.1079, found: 294.1070.

Dimethyl 3-(2-(benzyloxy)ethyl)cyclohexa-1,4-diene-1,2-dicarboxylate (4k)



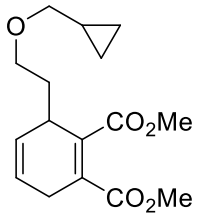
A known compound.[28] General procedure A: 50 ℃, yellow oil, 48.0 mg, 73% yield, 97% ee. [Daicel Chiralcel OJ-H column (25 cm x 0.46 cm ID), *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, 254 nm; t_{minor} = 25.7 min, t_{major} = 11.4 min]. $[\alpha]_D^{20}$ = -87.1 (c = 1.0, $CHCl_3$). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.36 - 7.25 (m, 5H), 6.04 - 5.53 (m, 2H), 4.50 (d, *J* = 11.8 Hz, 1H), 4.45 (d, *J* = 11.9 Hz, 1H), 3.77 (s, 3H), 3.75 (s, 3H), 3.52 (t, *J* = 6.9 Hz, 2H), 3.41 – 3.34 (m, 1H), 3.05 - 2.94 (m, 1H), 2.96 - 2.80 (m, 1H), 1.97 (m, *J* = 10.3, 3.6 Hz, 1H), 1.81 -1.70 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.95, 167.74, 138.73, 138.41, 130.83, 128.37, 127.63, 127.56, 126.89, 122.62, 77.28, 77.07, 76.85, 72.95, 67.25, 34.93, 33.96, 27.25, 0.02.

Dimethyl 3-((benzyloxy)methyl)cyclohexa-1,4-diene-1,2-dicarboxylate (4l)



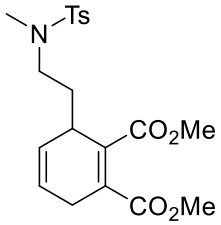
General procedure A: 50 ℃, yellow oil, 36.0 mg, 57 % yield, 94% ee. [Daicel Chiralcel OD-H column (25 cm x 0.46 cm ID), *n*-hexane/*i*-PrOH = 99/5, 0.7 mL/min, 254 nm; t_{major} =14.6 min, t_{minor} = 16.0 min]. $[\alpha]_D^{20}$ = 55.6 (c = 1.0, $CHCl_3$). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.35 - 7.29 (m, 4H), 7.29 - 7.25 (m, 2H), 5.85 -5.80 (m, 1H), 5.80 - 5.76 (m, 1H), 4.53 - 4.44 (m, 2H), 3.76 (s, 3H), 3.69 (s, 3H), 3.56 - 3.46 (m, 3H), 3.12 - 3.03 (m, 1H), 2.97 - 2.84 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.77, 167.83, 138.10, 135.98, 132.39, 128.32, 127.64, 127.58, 125.21, 123.63, 77.28, 77.07, 76.86, 73.18, 72.68, 52.25, 52.14, 38.73, 27.61, 0.02. HRMS (ESI) m/z Calcd. for $C_{18}H_{20}O_5$ $[M+H]^+$: 317.1384, found: 317.1382.

Dimethyl 3-(2-(cyclopropylmethoxy)ethyl)cyclohexa-1,4-diene-1,2-dicarboxylate (4m)



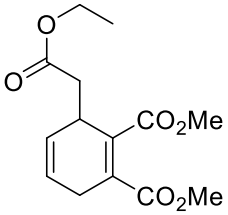
General procedure A: yellow oil, 30.0 mg, 51% yield, 96% ee. [Daicel Chiralcel AS-H column (25 cm x 0.46 cm ID), *n*-hexane/*i*-PrOH = 95/5, 1 mL/min, 254 nm; t_{major} = 7.0 min, t_{minor} = 11.8 min]. $[\alpha]_D^{20}$ = -11.2 (c = 1.0, $CHCl_3$). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 5.81 - 5.70 (m, 2H), 3.79 (s, 3H), 3.75 (s, 3H), 3.49 - 3.42 (m, 2H), 3.35 (m, *J* = 6.9, 3.3 Hz, 1H), 3.26 - 3.17 (m, 2H), 3.04 - 2.96 (m, 1H), 2.94 - 2.86 (m, 1H), 1.92 (m, *J* = 13.7, 8.1, 6.9, 4.1 Hz, 1H), 1.73 (d, *J* = 7.8 Hz, 1H), 1.02 (m, *J* = 10.9, 8.1, 4.8, 1.1 Hz, 1H), 0.55 - 0.47 (m, 2H), 0.18 (m, *J* = 4.9, 1.2 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.93, 167.73, 138.67, 130.80, 126.95, 122.56, 77.25, 77.03, 76.82, 75.58, 67.35, 52.23, 52.22, 34.94, 33.78, 27.24, 10.59, 3.00, 2.92, 2.92, 0.00. HRMS (ESI) m/z Calcd. for $C_{16}H_{22}O_5$ $[M+H]^+$: 295.1540, found: 295.1538.

Dimethyl 3-(2-((N,4-dimethylphenyl)sulfonamido)ethyl)cyclohexa-1,4-diene-1,2-dicarboxylate (4n)



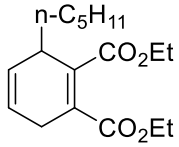
A known compound.[28] General procedure C: yellow semisolid, 59.3 mg, 73 % yield, 98% ee. [Daicel Chiralcel OD-H column (25 cm x 0.46 cm ID), *n*-hexane/*i*-PrOH = 95/5, 1.0 mL/min, 254 nm; t_{major} =34.7 min, t_{minor} = 39.6 min]. $[\alpha]_D^{20}$ = 69.0 (c = 0.3, $CHCl_3$). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 8.3 Hz, 2H), 7.33 - 7.29 (m, 2H), 5.79 (d, *J* = 1.1 Hz, 2H), 3.77 (d, *J* = 18.4 Hz, 6H), 3.35 - 3.25 (m, 2H), 3.01 - 2.90 (m, 2H), 2.75 (dd, *J* = 8.7, 4.6 Hz, 1H), 2.68 (s, 3H), 2.42 (s, 3H), 1.91 - 1.83 (m, 1H), 1.67 - 1.63 (m, 1H). Data were matched with the reported literature.[17]

Dimethyl 3-(2-ethoxy-2-oxoethyl)cyclohexa-1,4-diene-1,2-dicarboxylate (4o)



General procedure D: yellow oil, 12.7 mg, 23% yield, 18% ee. [Daicel Chiralcel AS-H column (25 cm x 0.46 cm ID), *n*-hexane/*i*-PrOH = 95/5, 0.7 mL/min, 254 nm; t_{major} = 20.8 min, t_{minor} = 22.5 min]. $[\alpha]_D^{20}$ = 7.6 (c = 1.0, $CHCl_3$). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 5.78 (t, *J* = 1.3 Hz, 2H), 4.14 (m, *J* = 7.1, 1.2 Hz, 2H), 3.79 (s, 3H), 3.77 (s, 3H), 3.67 - 3.57 (m, 1H), 3.07 - 2.98 (m, 1H), 2.98 - 2.90 (m, 1H), 2.69 (dd, *J* = 15.8, 4.3 Hz, 1H), 2.35 (dd, *J* = 15.8, 9.0 Hz, 1H), 1.26 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.18, 168.22, 136.18, 132.79, 126.25, 123.09, 77.28, 77.07, 76.85, 60.66, 52.33, 52.31, 39.48, 33.91, 27.47, 14.18. HRMS (ESI) m/z Calcd. for $C_{14}H_{18}O_6$ $[M+Na]^+$: 305.0996, found: 305.0997.

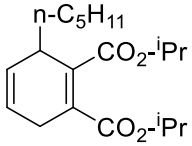
diethyl 3-pentylcyclohexa-1,4-diene-1,2-dicarboxylate (4s)



General procedure C: yellow oil, 44.9 mg, 73% yield, 97% ee. [Daicel Chiralcel OD-H column (25 cm x 0.46 cm ID), *n*-hexane/*i*-PrOH = 99.5/0.5, 0.6 mL/min, 254 nm; t_{minor} = 11.1 min, t_{major}= 12.0 min]. $[\alpha]_D^{20}$ = -57.8 (c = 1.0, $CHCl_3$). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 5.82 - 5.71 (m, 1H), 5.71 - 5.54 (m, 1H), 4.32 - 4.10 (m, 4H), 3.23 (m, *J* = 5.1, 1.3 Hz,

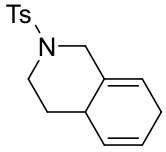
1H), 2.98 (d, *J* = 7.7 Hz, 1H), 2.97 - 2.78 (m, 1H), 1.5 - 1.39 (m, 2H), 1.34 - 1.21 (m, 12H), 0.85 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.86, 167.14, 139.55, 129.88, 127.25, 122.54, 77.21, 77.00, 76.79, 60.98, 60.94, 37.56, 33.80, 31.88, 27.20, 24.82, 22.46, 14.02. HRMS (ESI) m/z Calcd. for $C_{17}H_{26}O_4$ $[M+Na]^+$: 317.1723, found: 317.1714.

Diisopropyl 3-pentylcyclohexa-1,4-diene-1,2-dicarboxylate (4t)



General procedure C: yellow oil, 18.0 mg, 28% yield, 91% ee. [Daicel Chiralcel AD-H column (25 cm x 0.46 cm ID), *n*-hexane/*i*-PrOH = 99.5/0.5, 0.6 mL/min, 254 nm; t_{minor} =9.0 min, t_{major} = 10.3 min]. $[\alpha]_D^{20}$ = 59.8 (c = 1.0, $CHCl_3$). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 5.74 (m, *J* = 10.2, 4.1, 2.8, 1.4 Hz, 1H), 5.66 (m, *J* = 10.1, 3.8, 1.7 Hz, 1H), 5.20 - 5.10 (m, 1H), 5.10 - 4.99 (m, 1H), 3.23 (m, *J* = 7.4, 3.6, 1.3 Hz, 1H), 3.00 (m, *J* = 22.9, 7.8, 2.7 Hz, 1H), 2.86 (m, *J* = 22.9, 7.0, 3.9, 1.5 Hz, 1H), 1.58 - 1.50 (m, 1H), 1.47 (dd, *J* = 7.0, 3.9 Hz, 1H), 1.28 (m, *J* = 17.3, 6.7 Hz, 18H), 0.87 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.37, 166.66, 139.58, 129.96, 127.33, 122.61, 77.26, 77.04, 76.83, 68.50, 68.43, 37.62, 33.83, 31.96, 27.27, 24.93, 22.52, 21.82, 21.79, 21.62, 21.55, 14.09. HRMS (ESI) m/z Calcd. for $C_{19}H_{30}O_4$ $[M+Na]^+$: 345.2036, found: 345.2027.

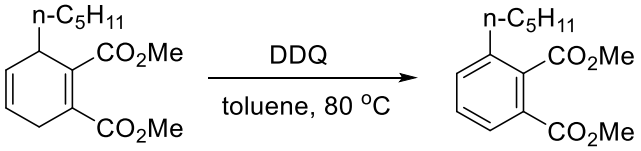
2-tosyl-1,2,3,4,4a,7-hexahydroisoquinoline (4x)



General procedure C: yellow solid, 24.3 mg, 84 % yield, 7% ee. [Daicel Chiralcel AS-H column (25 cm x 0.46 cm ID), *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm; t_{minor} =15.0 min, t_{major} = 17.5 min]. $[\alpha]_D^{20}$ = 4.6 (c = 1.0, $CHCl_3$). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 5.83 - 5.56 (m, 2H), 5.49 (dd, *J* = 9.9, 2.6 Hz, 1H), 4.11 (dd, *J* = 12.1, 1.9 Hz, 1H), 3.87 (d, *J* = 11.7 Hz, 1H), 2.83 (d, *J* = 11.9 Hz, 1H), 2.77 - 2.56 (m, 2H), 2.44 (s, 5H), 1.88 - 1.73 (m, 1H), 1.47 (qd, *J* = 12.7, 4.2 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.51, 133.11, 130.87, 129.61, 127.87, 127.18, 124.04, 120.97, 52.82, 46.88, 35.42, 32.80, 26.58, 21.56. HRMS (ESI) m/z Calcd. for $C_{16}H_{19}NO_2S$ $[M+Na]^+$: 290.1209, found: 290.1203.

7. Derivatizations

Oxidation of **4a**:

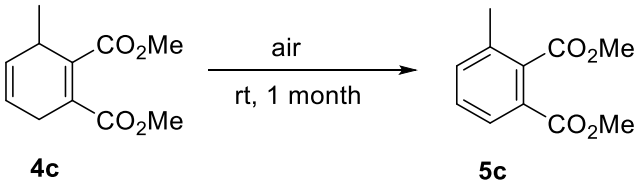


4a **5a**

The oxidation was performed according the reported literature.[29] A mixture of compound **4a** (53.2 mg, 0.2 mmol) and DDQ (7 mg, 0.2 mmol) in degassed toluene (10 mL) was heated under N_2 at 80 ℃ for 12 h. The toluene was removed under vacuum, and the crude product was purified by flash chromatography. yellow oil, 22.1 mg, 42%

yield. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.76 (dd, J = 7.4, 1.6 Hz, 1H), 7.40 - 7.26 (m, 2H), 3.84 (d, J = 21.6 Hz, 6H), 2.63 - 2.46 (m, 2H), 1.58 - 1.49 (m, 2H), 1.29 - 1.18 (m, 4H), 0.88 - 0.74 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 168.81, 165.34, 139.47, 133.89, 132.69, 128.04, 126.73, 126.56, 51.43, 51.40, 32.17, 30.58, 29.91, 21.38, 12.93.

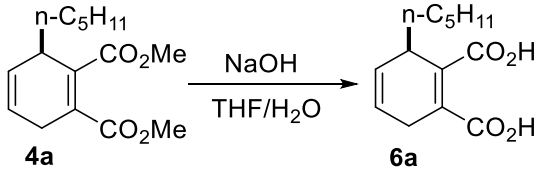
Oxidation of **4c**:



4c **5c**

The compound **4c** (63.1 mg, 0.3 mmol) was placed at room temperature under air for 1 moth, then **4c** was converted to **5c**. The crude product was purified by flash chromatography. Yellow oil, 38.1 mg, 61% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.44 - 7.31 (m, 2H), 3.94 (s, 3H), 3.89 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.89, 166.32, 135.56, 135.31, 134.50, 129.06, 127.69, 127.46, 77.29, 77.08, 76.87, 52.53, 52.49, 19.05. A known compound.[30]

Hydrolysis of **4a**:



4a **6a**

A solution of **4a** (53.2 mg, 0.2 mmol) in THF (1 mL) and water (1 mL) was added NaOH (80 mg, 2.0 mmol) and the mixture was heated at reflux overnight. After completion of the reaction it was cooled to 0 ℃ and acidified with 1 N HCl to pH 2. The product was extracted with CH_2Cl_2, washed with water, dried over Na_2SO_4. The solvent was removed under vacuum, and the crude product was purified by flash chromatography. Yellow semi-solid, 46.2 mg, 97% yield, 99% *ee*. The enantiomeric excess of **6a** was determined by HPLC after methylation of the **6a**. ^{1}H NMR (600 MHz, Chloroform-d) δ 11.27 (br, 2H), 6.23 (dd, J = 9.5, 5.8 Hz, 1H), 6.09 (dd, J = 9.6, 5.6 Hz, 1H), 3.63 (s, 1H), 2.94 (d, J = 6.5 Hz, 1H), 1.65 - 1.10 (m, 9H), 0.88 (t, J = 6.9 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 179.54, 172.67, 138.66, 135.94, 122.53, 122.12, 41.47, 36.38, 32.77, 31.66, 26.18, 22.51, 14.03. $[\alpha]_D^{20}$ = -620 (c = 1.0, $CHCl_3$). HRMS (ESI) m/z Calcd. for $C_{13}H_{18}O_4$ $[M+Na]^+$: 261.1097, found: 261.1089.

8. References

[1] Vu Hong, A. A. Kislukhin, and M. G. Finn, *J. Am. Chem. Soc.*, 2009, **131**, 9986.

[2] For a review, see: (a) C. Defieber, H. Grützmacher, and E. M. Carreira, *Angew. Chem. Int. Ed.*, 2008, **47**, 4482; (b) F. R. Hartlley, *Chem Rev.*, 1973, **73**, 163.

[3] N. Yasukawa, H. Yokoyama, M. Masuda, Y Monguchi, H. Sajiki, and Y. Sawama, *Green Chem.*, 2018, **20**,1213.

[4] (a) X.-J. Meng, Y. Liu, W.-Y. Fan, B. Hu, W. Du, and W.-P. Deng, *Tetrahedron Lett.*, 2009, **50**, 4983; (b) W.-Y. Fan, Z.-L. Wang, Z.-G. Zhang, H.-C. Li, and W.-P. Deng, *Tetrahedron*, 2011, **67**, 5596.

[5] L. P. J. Burton, and J. D. White, *J. Am. Chem. Soc.*, 1981, **103**, 3226.

[6] K. Kuzuya, N. Mori, and H. Watanabe, *Org. Lett.*, 2010, **12**, 4709.

[7] J. C. Tung, W. Chen, B. C. Noll, R. E. Taylor, S. C. Fields, W. H. Dent III, and F. R. Green III, *Synthesis*, 2007, **15**, 2388.

[8] C. Qiao, W. Zhang, J.-C. Han, W.-M. Dai, and C.-C Li, *Tetrahedron*, 2019, **75**, 1739.

[9] (a) L.-Z. Liu, J.-C. Han, G.-Z. Yue, C.-C. Li, and Z. Yang, *J. Am. Chem. Soc.*, 2010, **132**, 13608; (b) J.-C. Han, L.-Z. Liu, Y.-Y Chang, G.-Z. Yue, J. Guo, L.-Y. Zhou, C.-C. Li, and Z. Yang, *J. Org. Chem.*, 2013, **78**, 5492.

[10] M. J. R. Richter, M. Schneider, M. Brandstätter, S. Krautwald, and E. M. Carreira, *J. Am. Chem. Soc.*, 2018, **140**, 16704.

[11] H. Harada, R. K. Thalji, R. G. Bergman, and J. A. Ellman, *J. Org. Chem*., 2008, **73**, 6772.

[12] W.-B. Liu, C. Zheng, C.-X. Zhuo, L.-X. Dai, and S.-L. You, *J. Am. Chem. Soc.*, 2012, **134**, 4812.

[13] H. Bernsmann, M. van den Berg, R. Hoen, A. J. Minnaard, G. Mehler, M. T. Reetz, J. G. De Vries, and B. L. Feringa, *J. Org. Chem.*, 2005, **70**, 943.

[14] J. Y. Hamilton, D. Sarlah, and E. M. Carreira, *Org. Synth.*, 2015, **92**, 1.

[15] (a) J. L. Charlton, and G. Chee, *Tetrahedron Lett.*, 1994, **35**, 6243; b) J. L. Charlton, G. Chee, and H. McColeman, *Can. J. Chem.*, 1995, **73**, 1454.

[16] B. T. Sargent, and E. J. Alexanian, *J. Am. Chem. Soc.*, 2017, **139**, 12438.

[17] L. T. Kliman, S. N. Mlynarski, G. E. Ferris, and J. P. Morken, *Angew. Chem. Int. Ed.*, 2012, **51**, 521.

[18] E. M. Townsend, R. R. Schrock, and A. H. Hoveyda, *J. Am. Chem. Soc.*, 2012, **134**, 11334.

[19] D. Fiorito, S. Folliet, Y. Liu, and C. Mazet, *ACS Catal.*, 2018, **8**, 1392.

[20] A. S. Kende, J. S. Mendoza, and Y. Fujii, *Tetrahedron*, 1993, **49**, 8015.

[21] V. Polic, K. J. Cheong, F. Hammerer, and K. Auclair, *Adv. Synth. Catal.*, 2017, **359**, 3983.

[22] E. M. Stang M. C. White, *J. Am. Chem. Soc.*, 2011, **133**, 14892.

[23] G. Galvani, R. Lett, and C. Kouklovsky, *Chem. Eur. J.*, 2013, **19**, 15604.

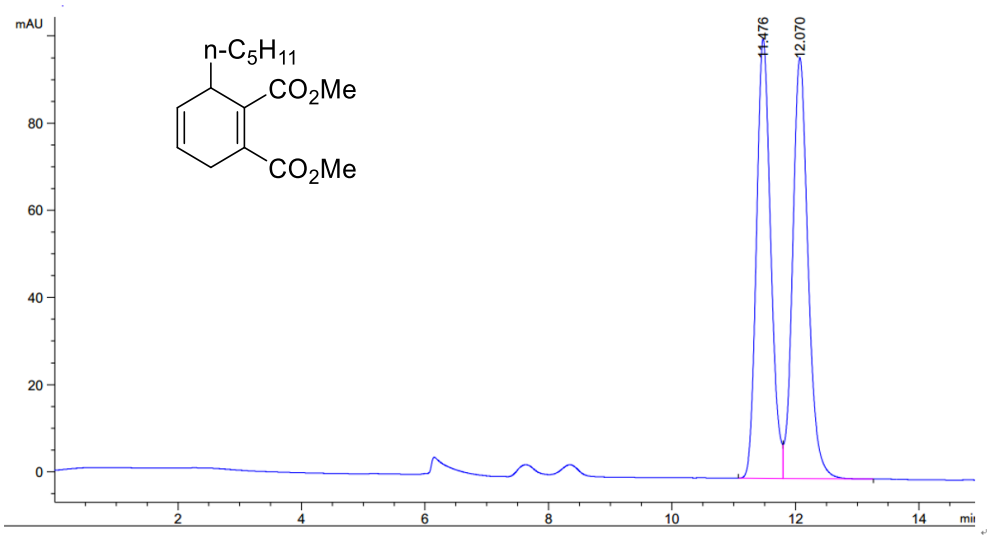
[24] R. E. Kyne, M. C. Ryan, L. T. Kliman, and J. P. Morken, *Org. Lett.*, 2010, **12**, 3796.

[25] M. G. Constantino, K. T. de Oliveira, E. C. Polo, G. J. da Silva, and T. J. Brocksom, *J. Org. Chem.*, 2006, **71**, 9880.

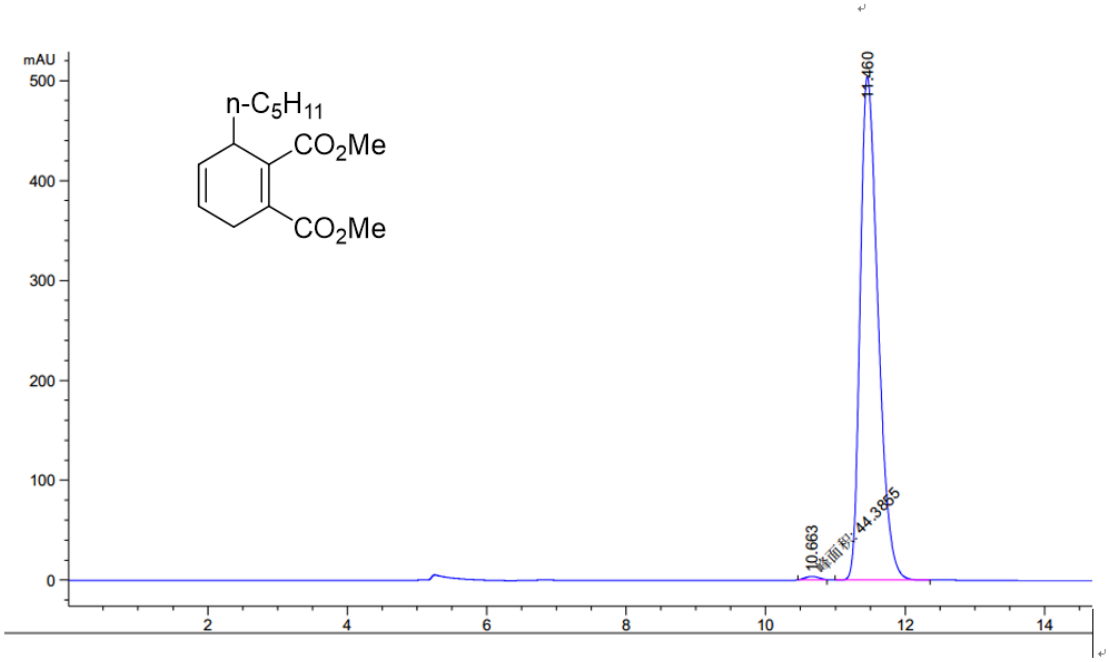
[26] S. M. Kim, J. H. Park, and Y. K. Chuang, *Chem. Comm.*, 2011, **47**, 6719.

[27] K. Shibatomi, T. Muto, Y. Sumikawa, A. Narayama, S. Iwasa, *Synlett*, **2009**, *2*, 241.
[28] T. Shibata, D. Fujiwara and K. Endo, *Org. Biomol. Chem.*, 2008, **6**, 464.
[29] S.-S Chou, C.-W. Huang, and C.-C. Chang, *Tetrahedron*, 2011, **67**, 4505.
[30] B. Thangavelu, V. Muttamsetty, Q. Wang, and R. E. Viola, *Bioorg. Med. Chem.*, 2017, **25**, 870.

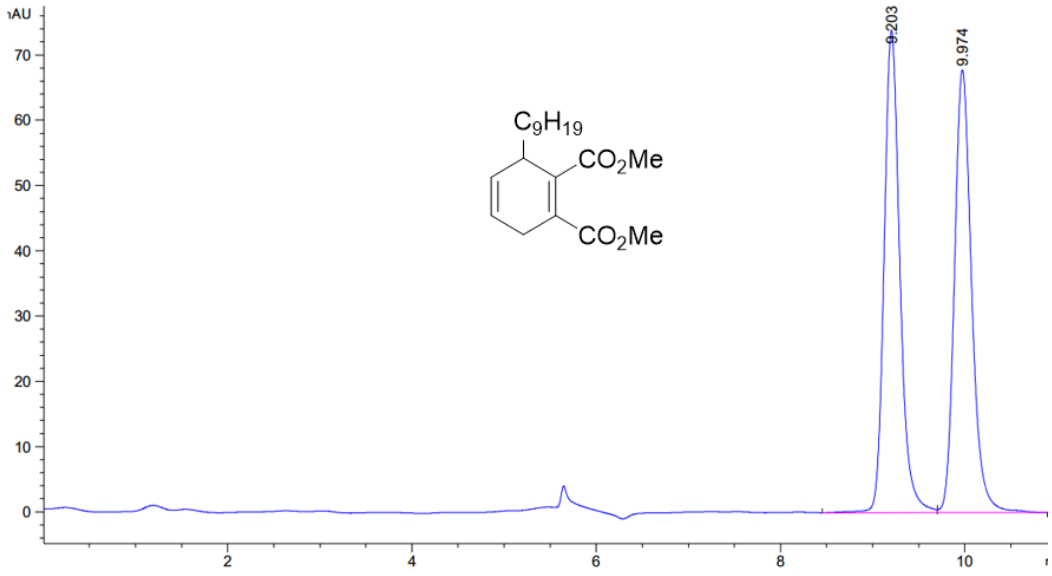
9. Copies of HPLC reports for racemic and chiral compounds



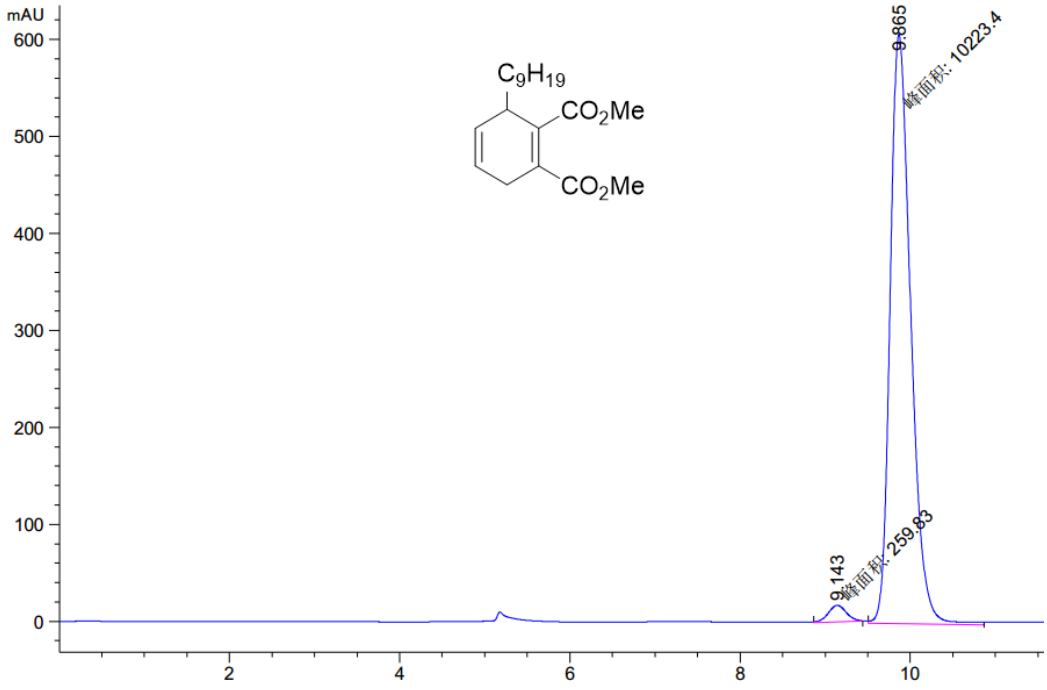
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	11.476	BV	0.2480	1616.92065	100.85087	49.1182
2	12.070	VB	0.2663	1674.97400	96.59215	50.8818



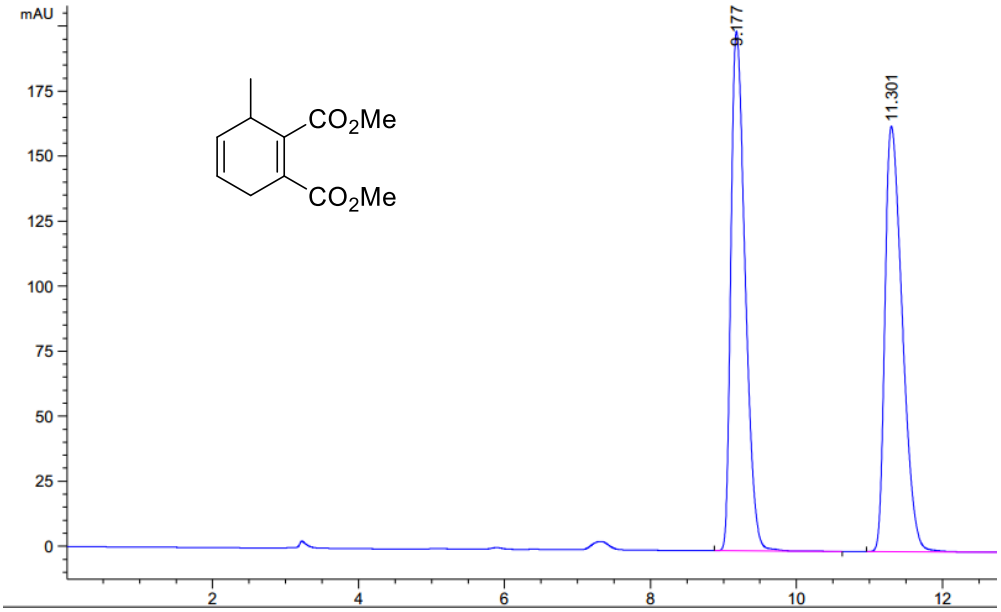
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	10.663	MM	0.2187	44.38552	3.38322	0.4922
2	11.460	BB	0.2768	8973.76465	503.93793	99.5078



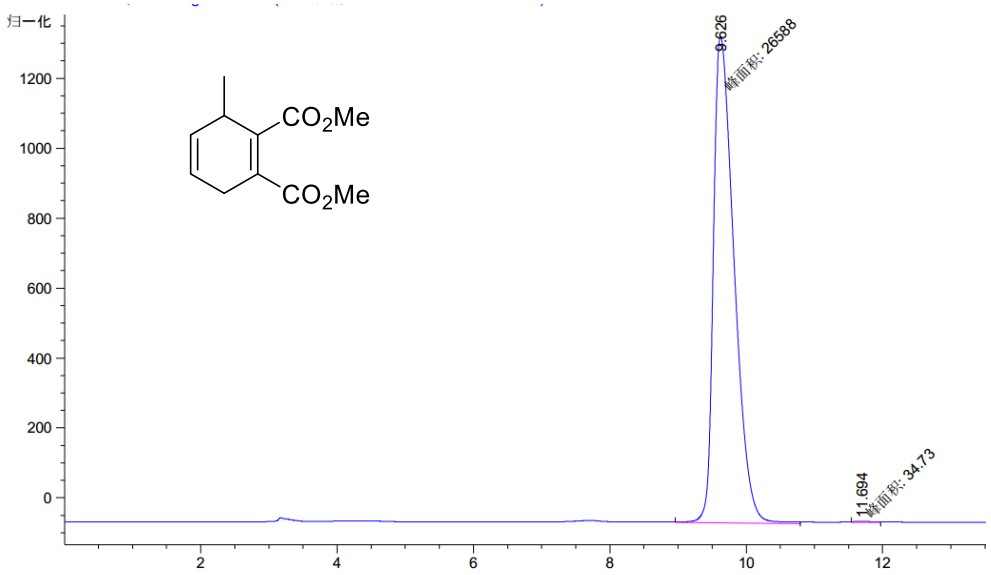
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.203	BV	0.1819	879.87848	73.91919	50.0884
2	9.974	VB	0.1977	876.77179	67.85698	49.9116



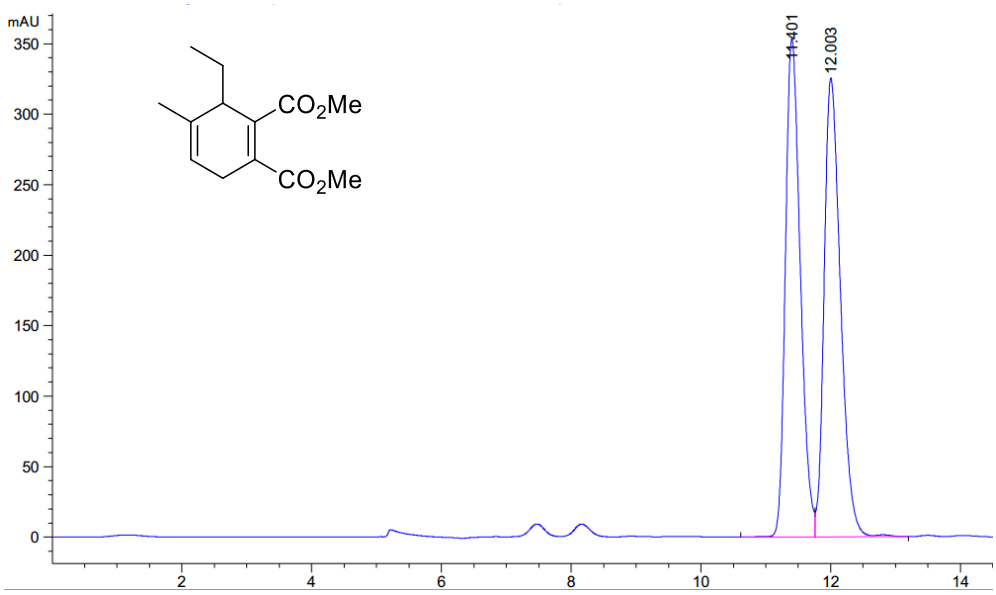
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.143	MM	0.2526	259.83020	17.14449	2.4785
2	9.865	MM	0.2805	1.02234e4	607.52887	97.5215



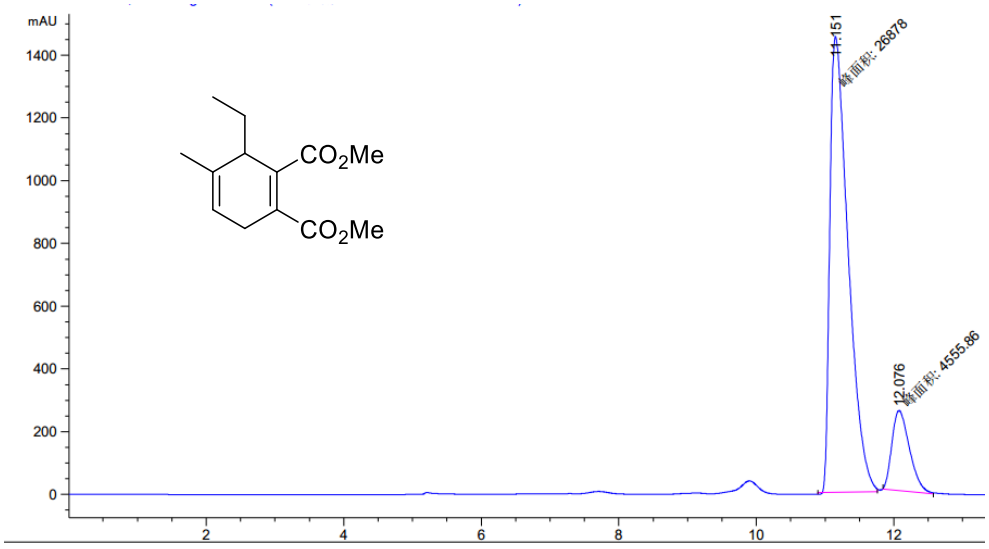
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.177	BB	0.2107	2700.37598	199.75156	49.8998
2	11.301	BB	0.2593	2711.22363	163.62531	50.1002



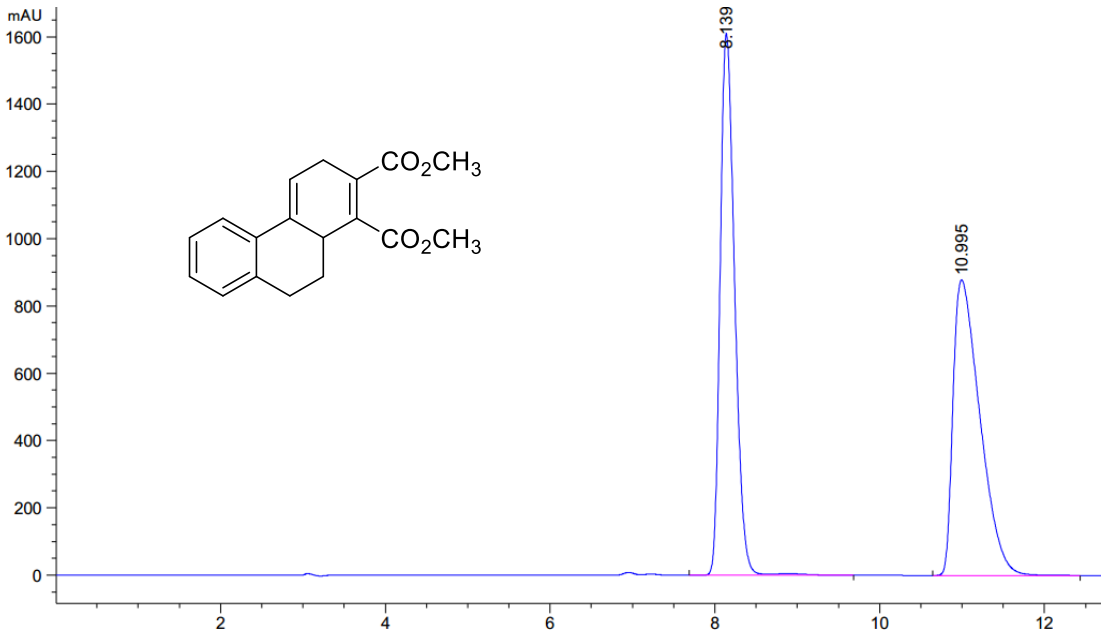
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.626	MM	0.3531	2.65880e4	1254.85815	99.8695
2	11.694	MM	0.2793	34.72997	2.07276	0.1305



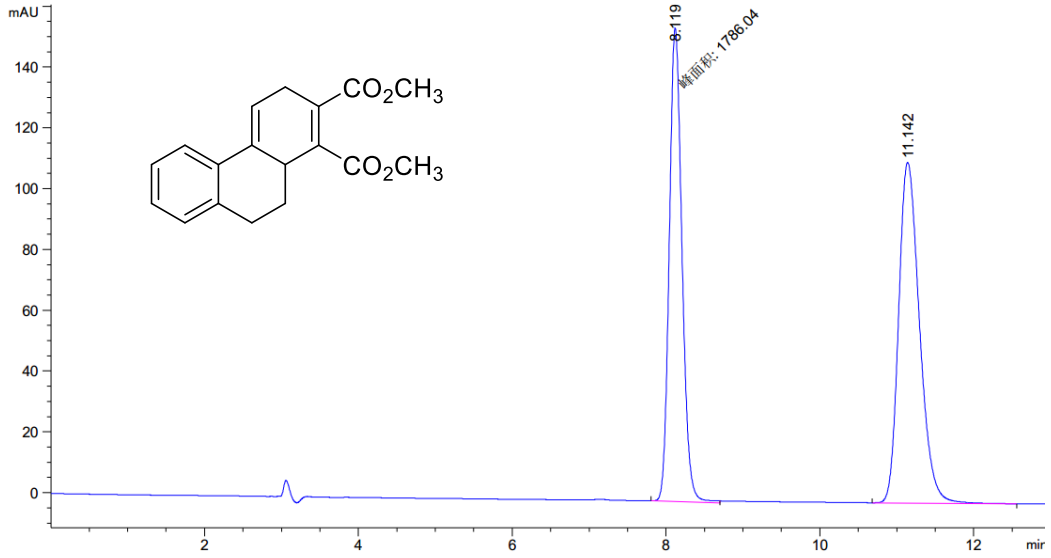
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	11.401	BV	0.2470	5638.48535	353.69412	49.6543
2	12.003	VV R	0.2710	5717.00537	325.37659	50.3457



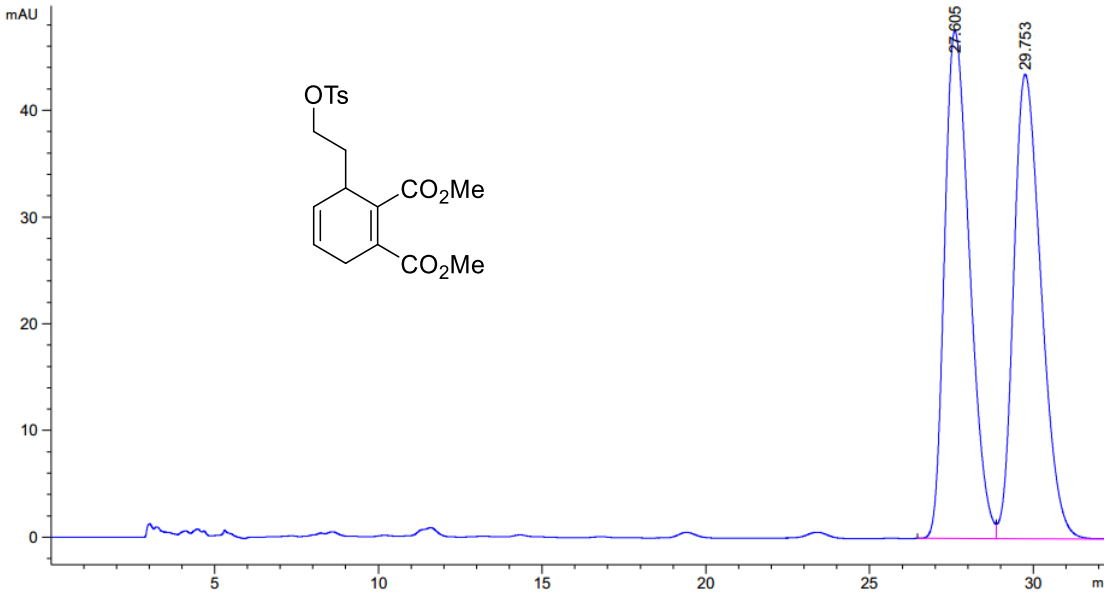
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	11.151	MM	0.3084	2.68780e4	1452.62573	85.5065
2	12.076	MM	0.2974	4555.85791	255.32018	14.4935



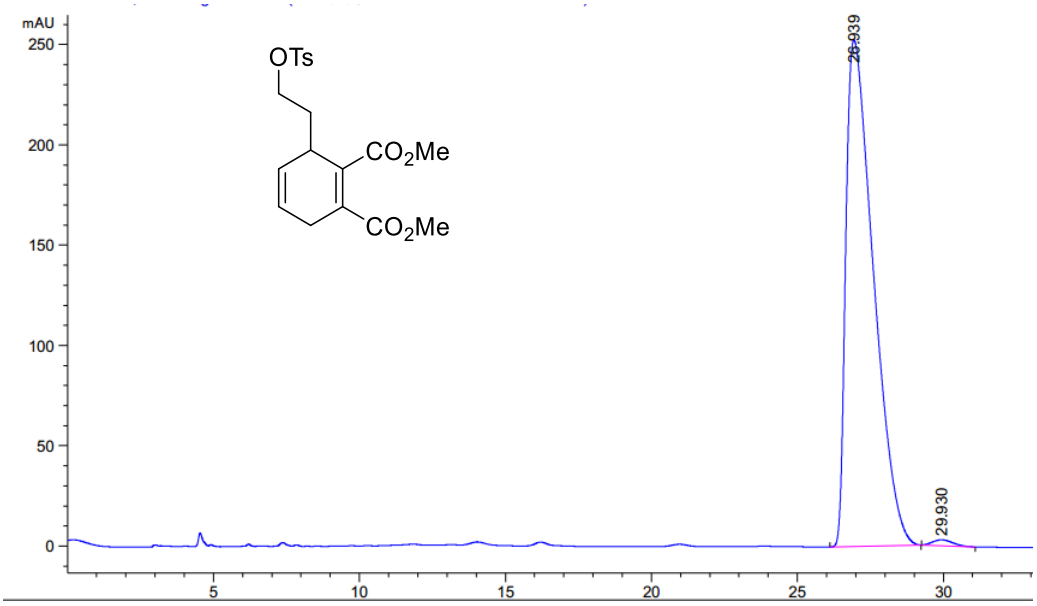
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.139	BV R	0.1899	1.97472e4	1610.11877	49.7904
2	10.995	BB	0.3504	1.99135e4	878.57147	50.2096



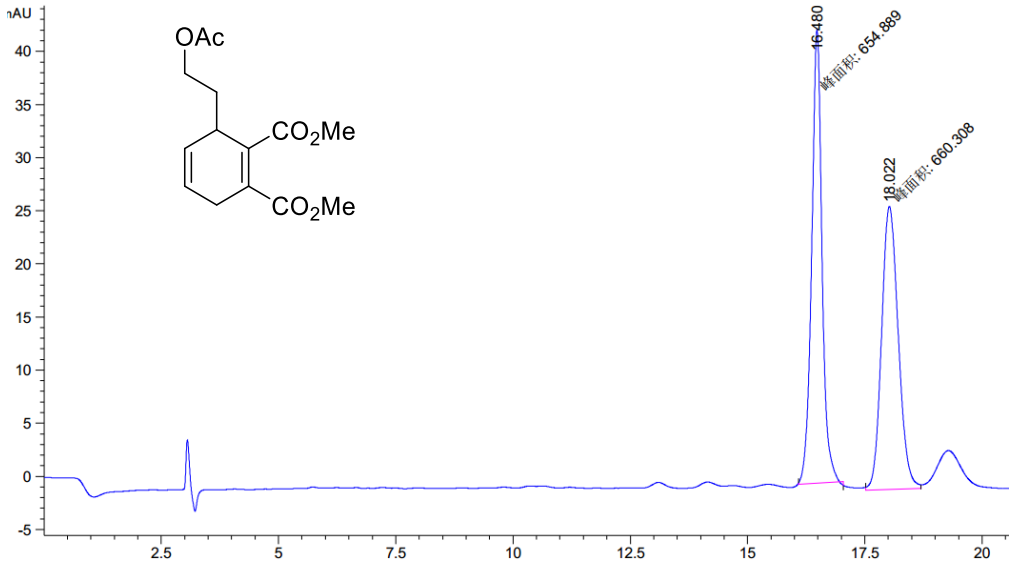
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.119	MM	0.1912	1786.03540	155.69818	45.8810
2	11.142	BB	0.2913	2106.71826	112.08398	54.1190



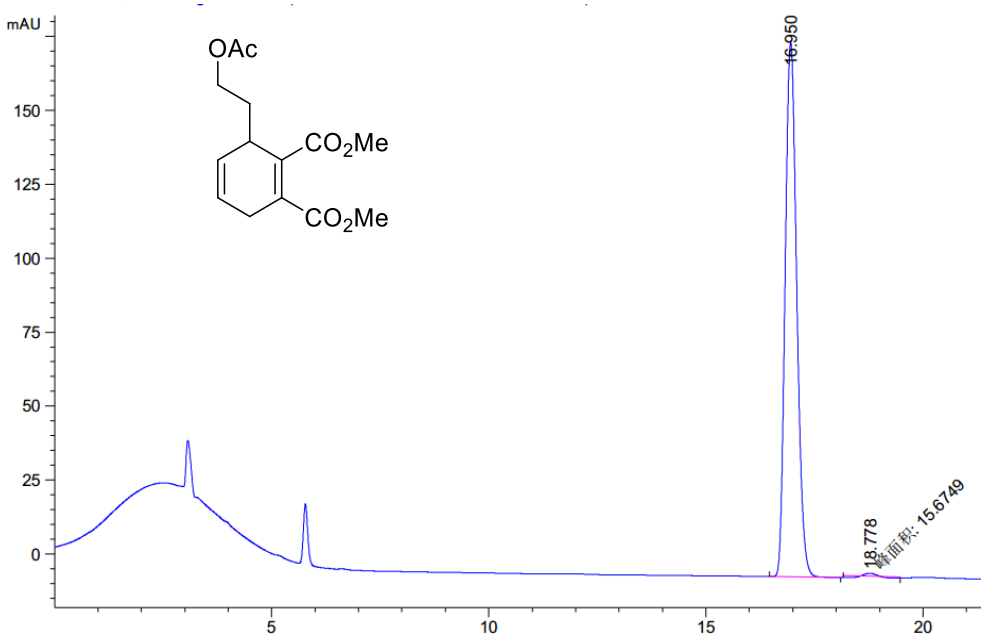
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	27.605	BV	0.8281	2528.44873	47.56778	49.8708
2	29.753	VB	0.9043	2541.55029	43.52422	50.1292



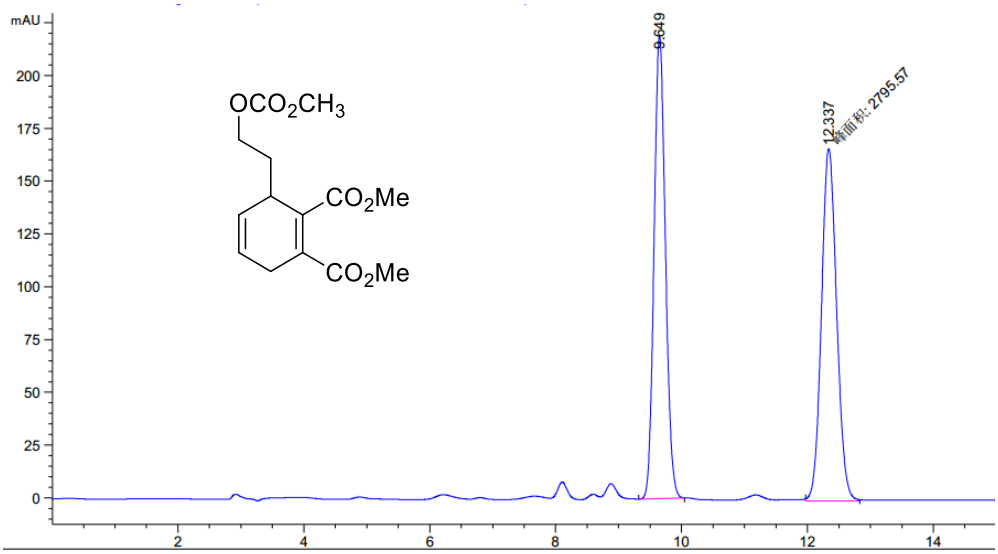
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	26.939	BB	1.0108	1.65248e4	252.39413	99.1592
2	29.930	BB	0.7078	140.11673	2.92019	0.8408



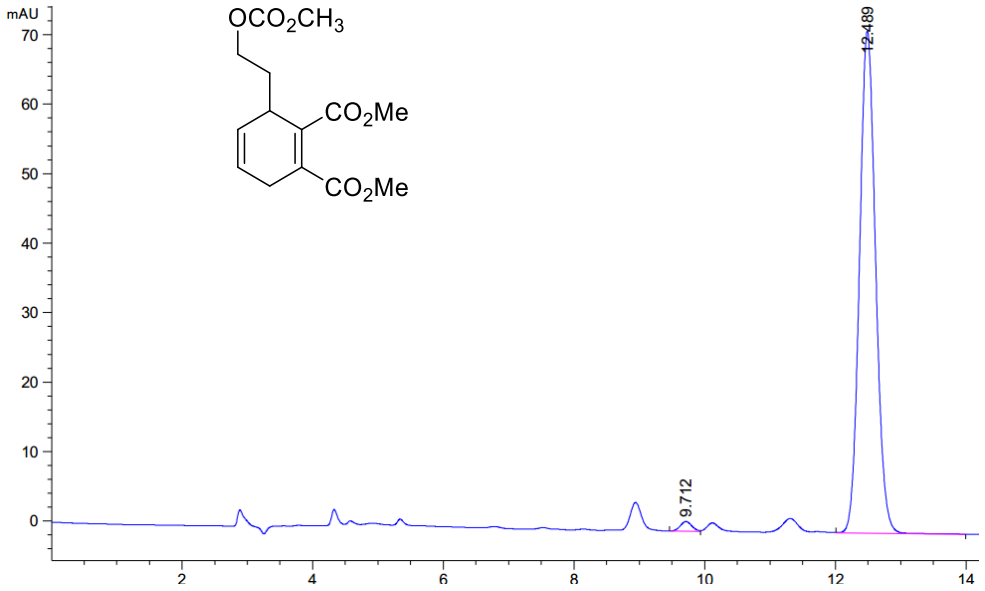
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	16.480	MM	0.2555	654.88867	42.71281	49.7940
2	18.022	MM	0.4130	660.30835	26.64484	50.2060



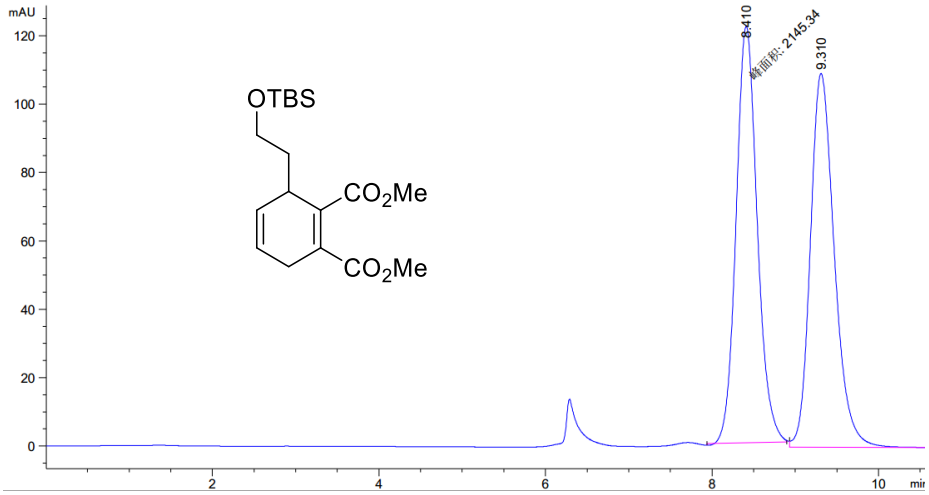
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	16.950	BB	0.2917	3343.82373	180.87341	99.5334
2	18.778	MM	0.2718	15.67494	9.61061e-1	0.4666



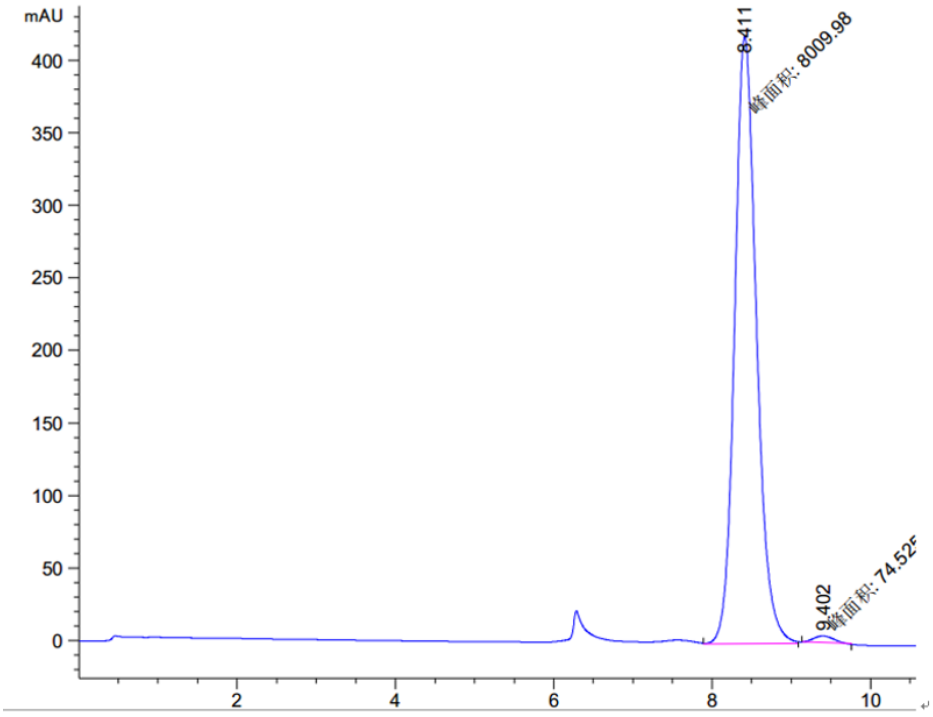
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.649	BB	0.1950	2740.18433	218.98581	49.4997
2	12.337	MM	0.2793	2795.56958	166.79424	50.5003



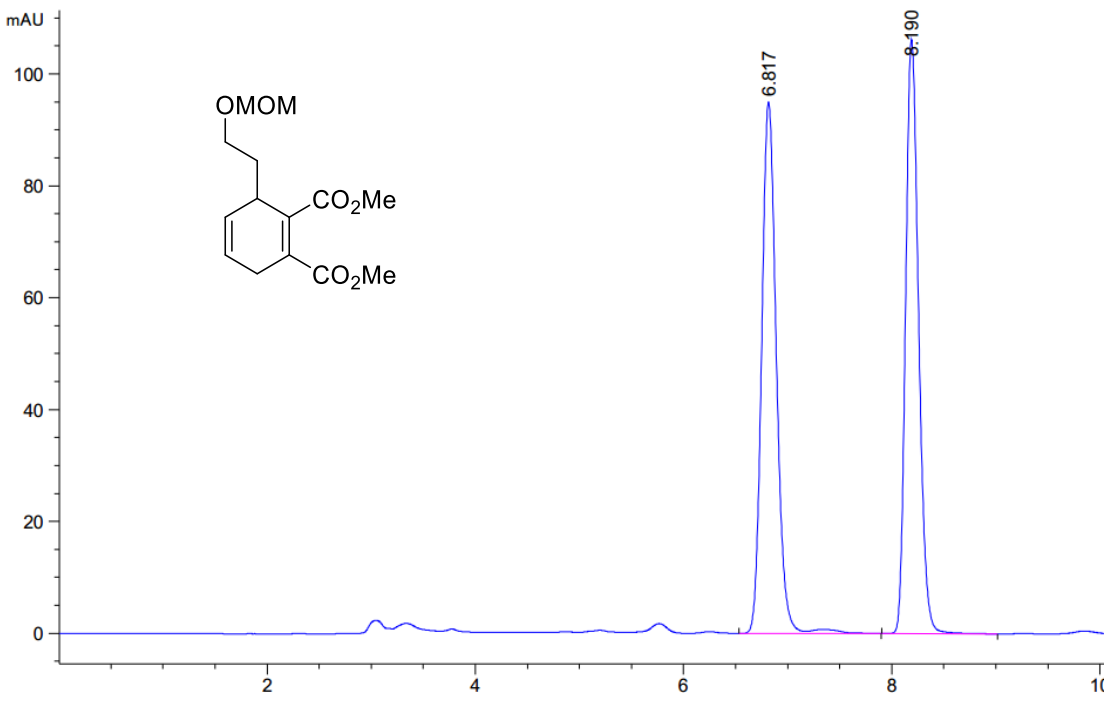
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.712	BV	0.1957	17.15788	1.39271	1.3675
2	12.489	VB	0.2678	1237.50354	72.24730	98.6325



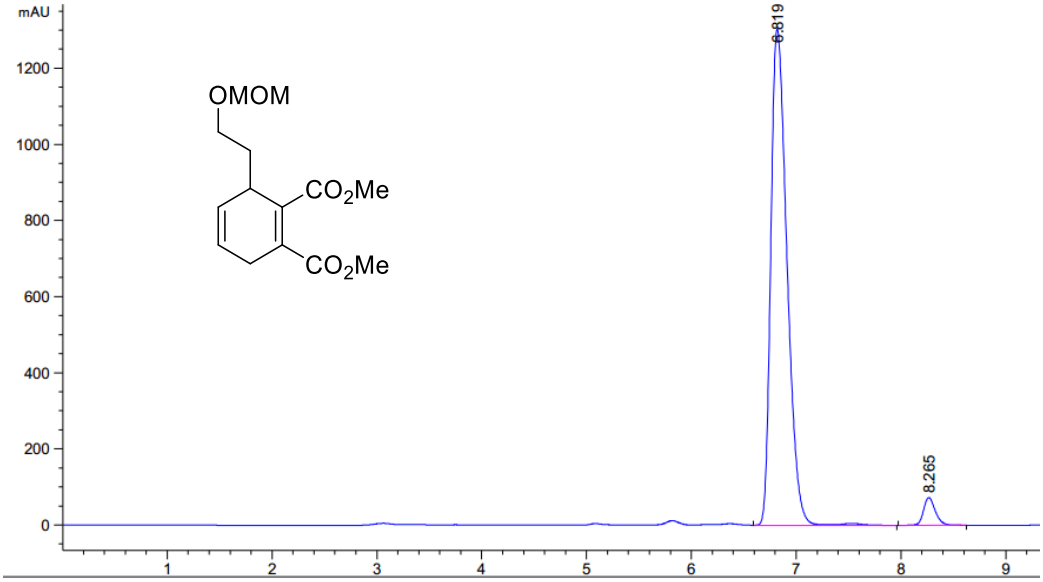
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.410	MM	0.2935	2145.33569	121.84508	49.5240
2	9.310	VBA	0.3074	2186.57471	109.29155	50.4760



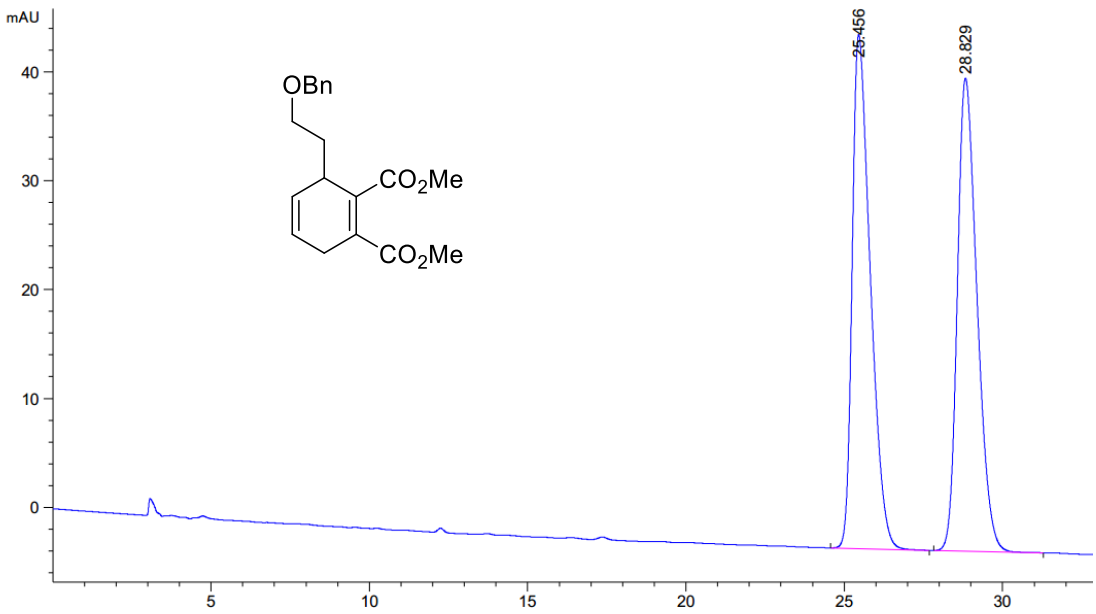
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.411	MM	0.3185	8009.98389	419.09500	99.0782
2	9.402	MM	0.2786	74.52525	4.45830	0.9218



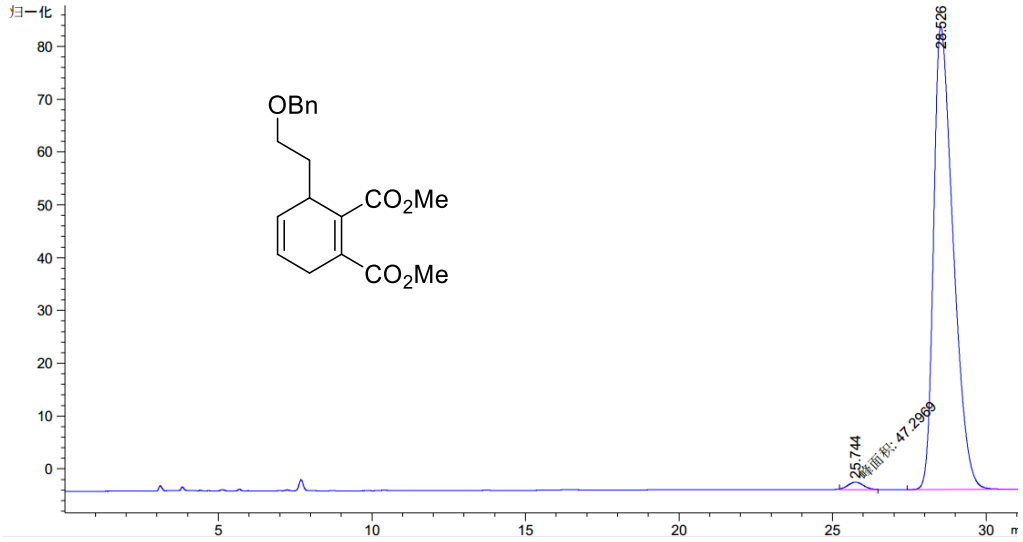
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.817	BV R	0.1509	936.70996	95.08456	50.4537
2	8.190	BB	0.1351	919.86505	106.20216	49.5463



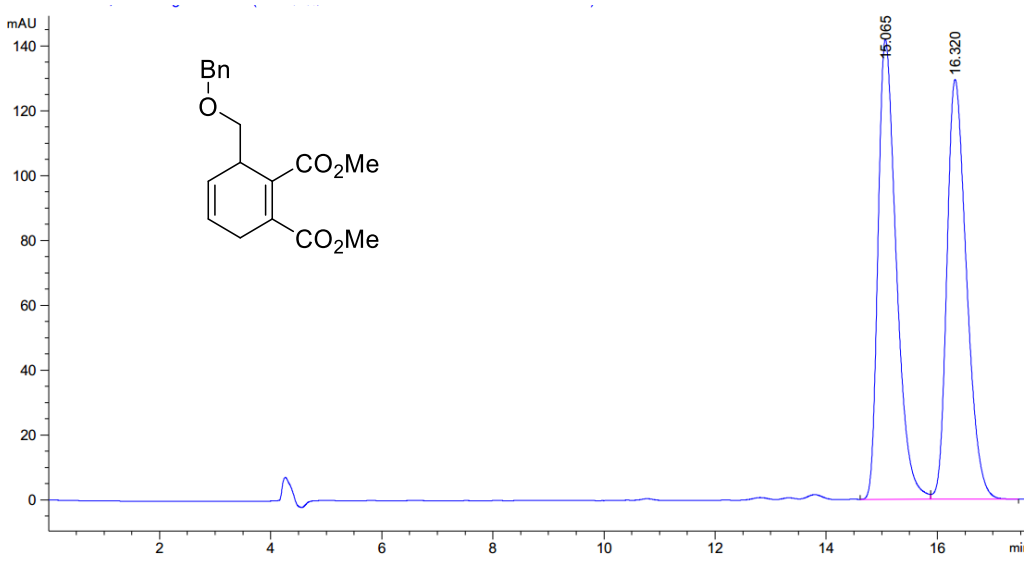
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.819	BV R	0.1652	1.39656e4	1304.11670	96.1135
2	8.265	BB	0.1195	564.72839	72.76264	3.8865



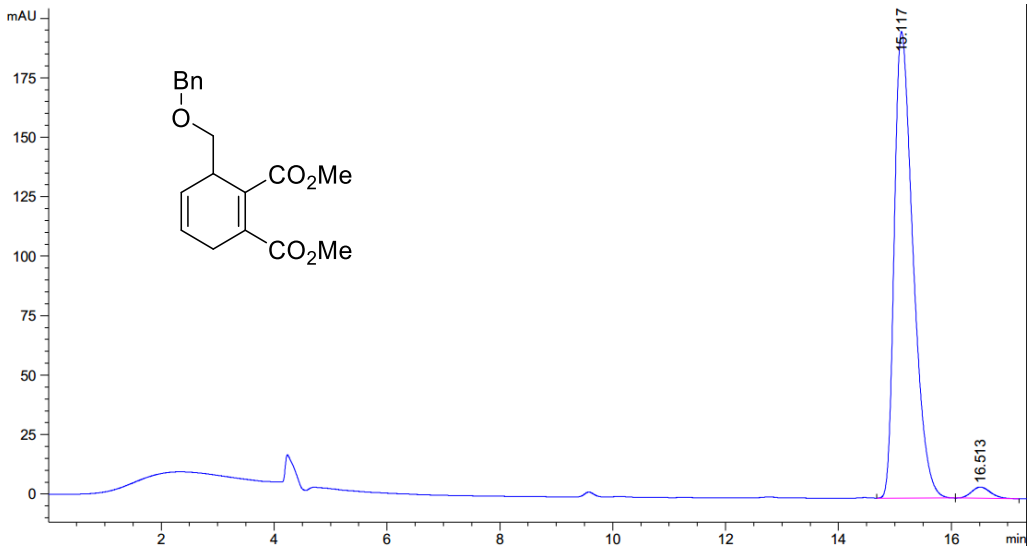
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	25.456	BB	0.6014	1875.69092	47.22232	50.0229
2	28.829	BB	0.6613	1873.97388	43.43925	49.9771



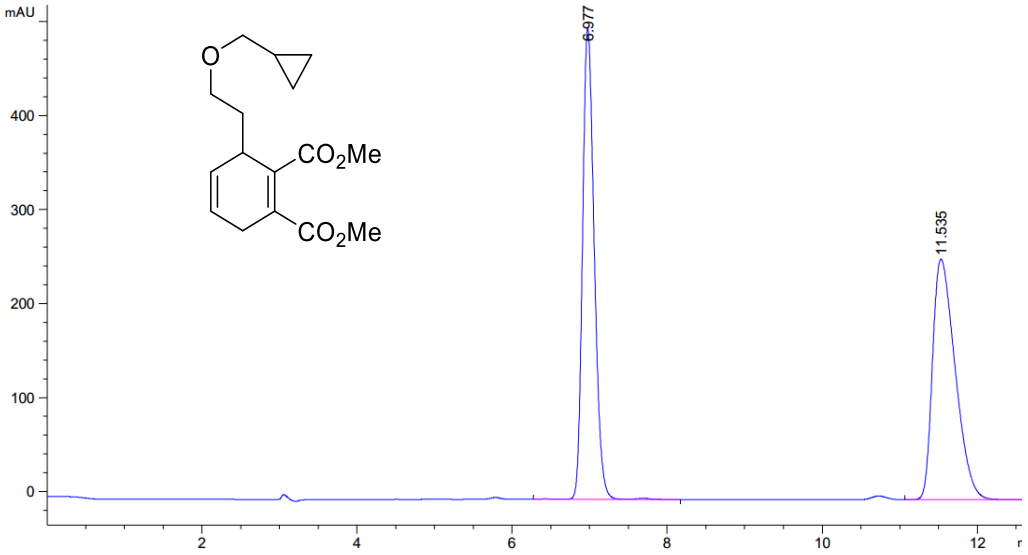
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	25.744	MM	0.6014	47.29687	1.31073	1.3291
2	28.526	BB	0.6749	3511.21582	79.10409	98.6709



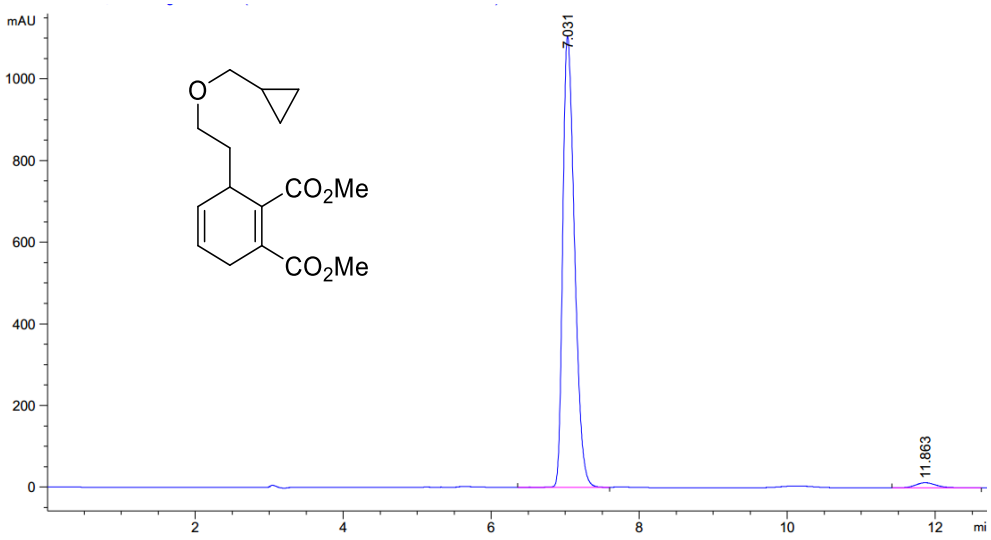
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	15.065	BV	0.3497	3234.30273	141.99049	50.4018
2	16.320	VB	0.3797	3182.73999	129.53677	49.5982



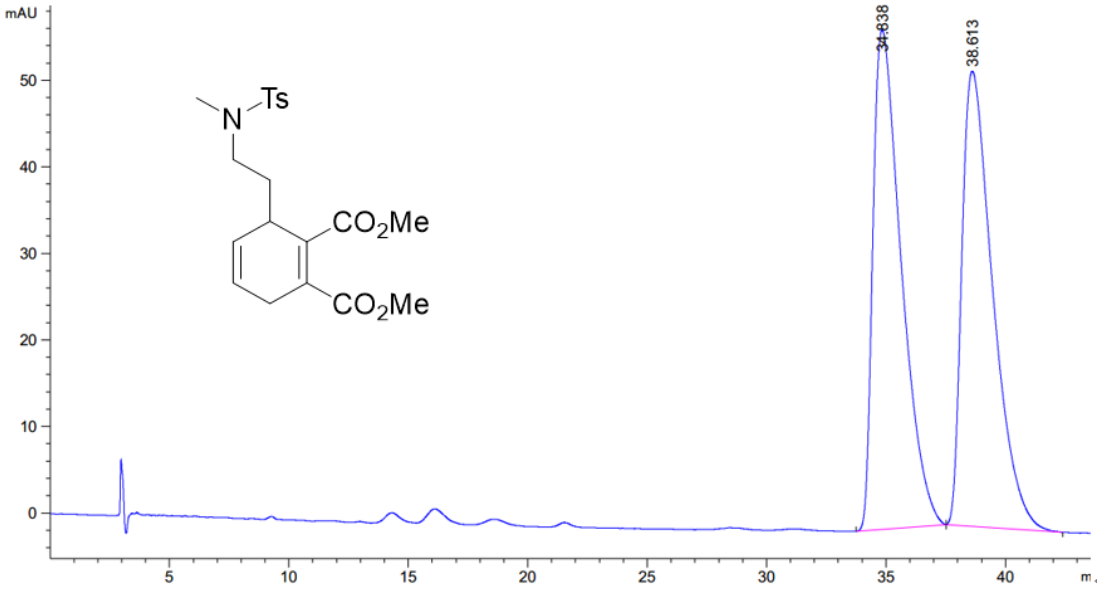
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	15.117	BB	0.3533	4511.49902	196.16005	97.6163
2	16.513	BB	0.3616	110.16707	4.71459	2.3837



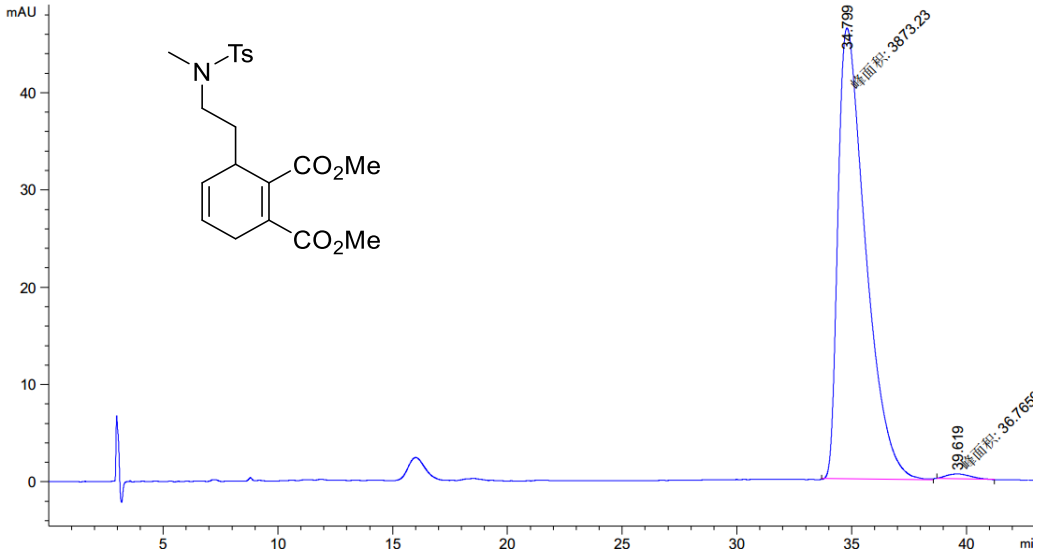
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.977	VV R	0.1664	5270.26709	499.56931	50.3335
2	11.535	VBA	0.3173	5200.42676	255.66975	49.6665



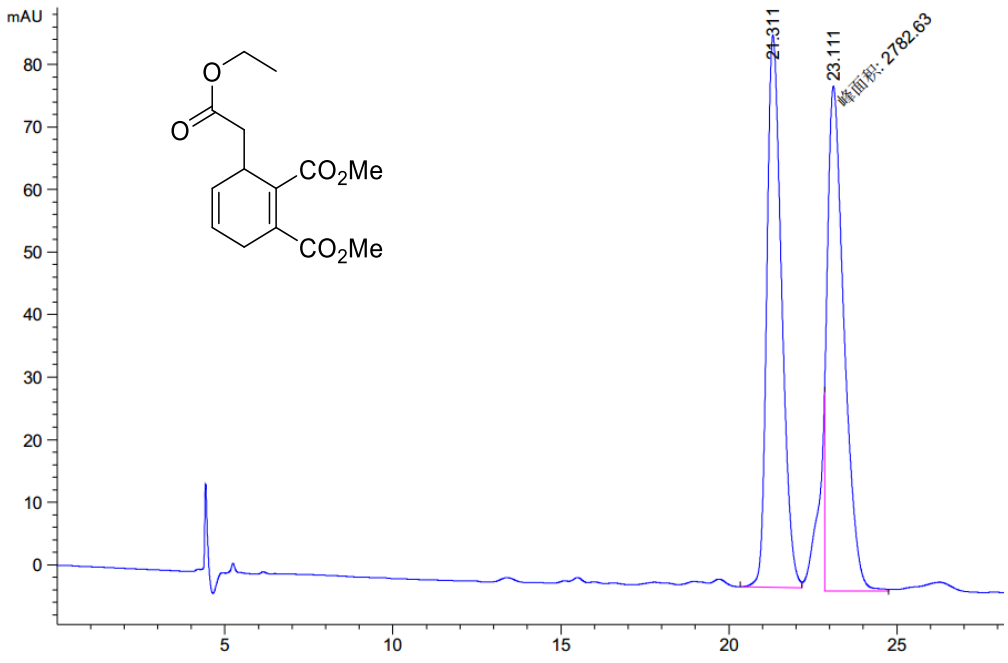
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.031	VB R	0.1718	1.22137e4	1106.03662	98.0047
2	11.863	BB	0.3033	248.66223	12.65432	1.9953



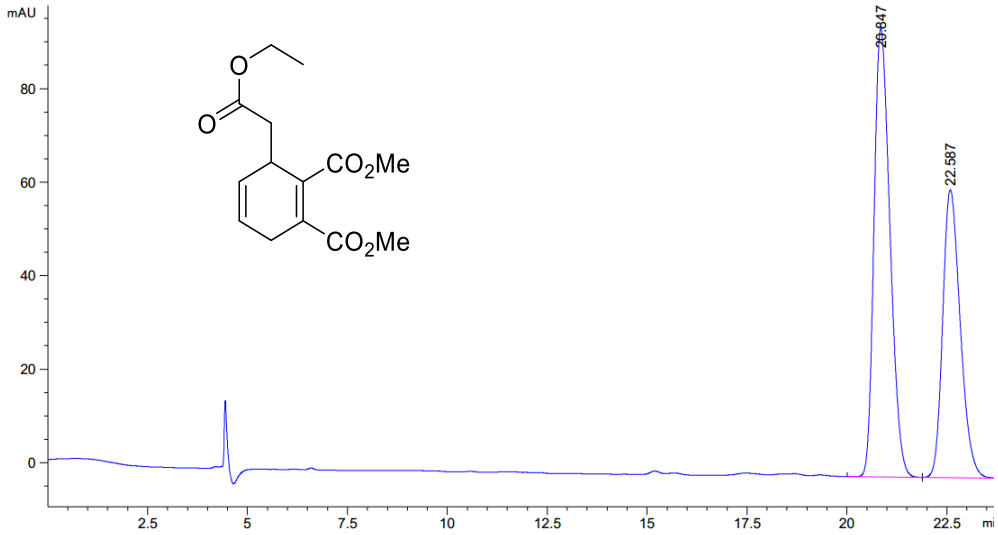
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	34.838	BB	1.2604	4755.47998	57.71040	50.1512
2	38.613	BB	1.3427	4726.80029	52.58365	49.8488



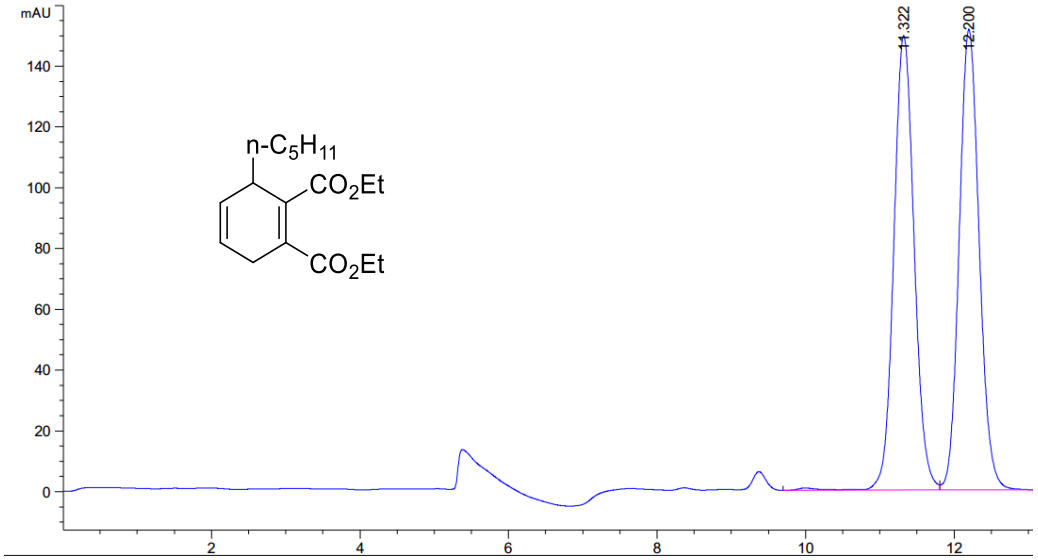
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	34.799	MM	1.3933	3873.23071	46.33017	99.0597
2	39.619	MM	1.2066	36.76590	5.07860e-1	0.9403



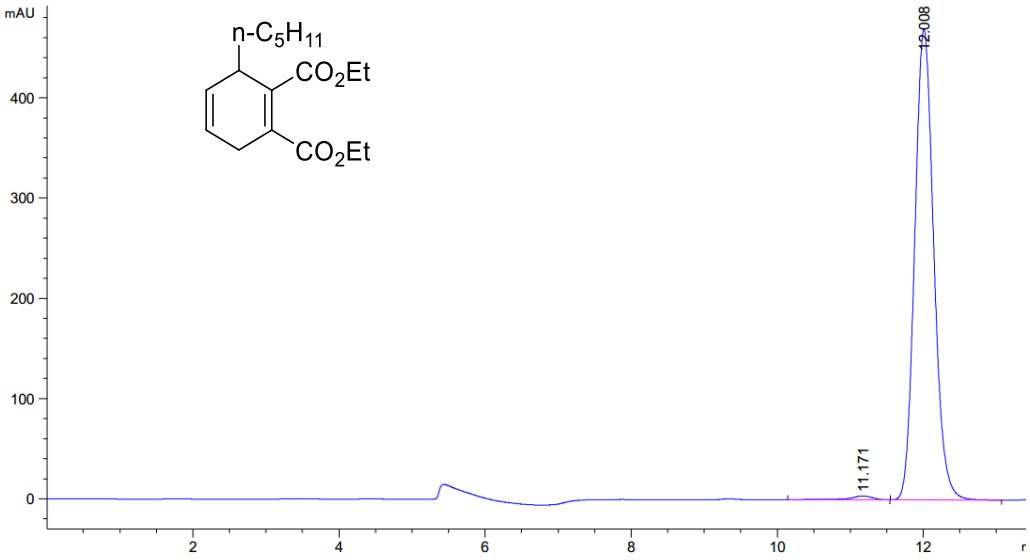
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	21.311	BV	0.4754	2713.55957	88.32459	49.3717
2	23.111	MM	0.5746	2782.62842	80.71676	50.6283



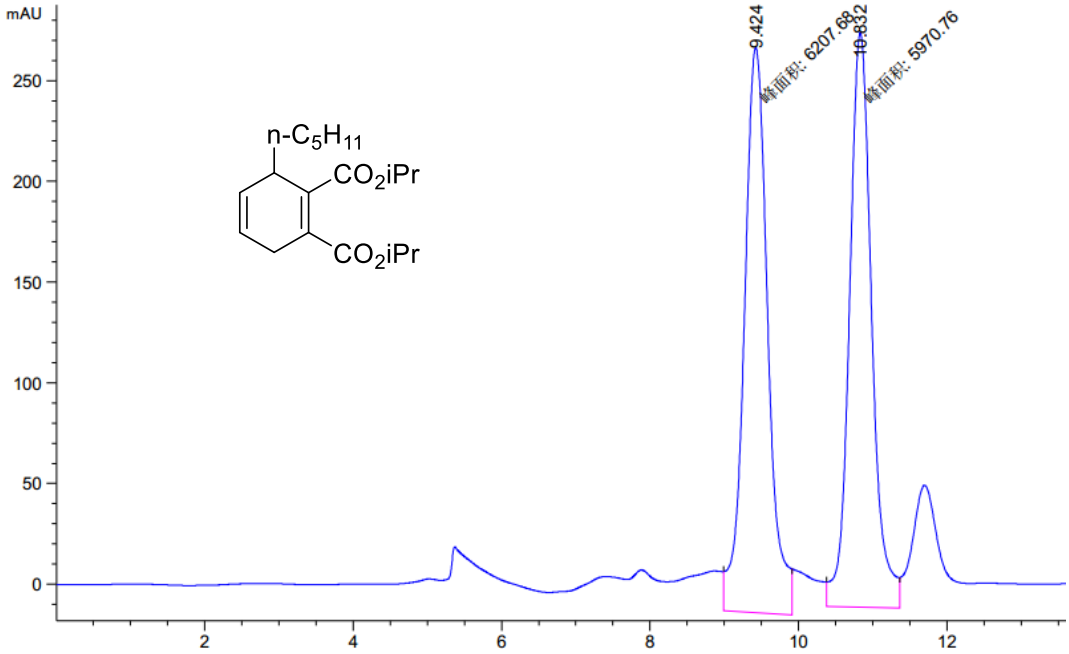
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	20.847	BB	0.4338	2665.74512	96.03628	58.6624
2	22.587	BBA	0.4707	1878.47021	61.61722	41.3376



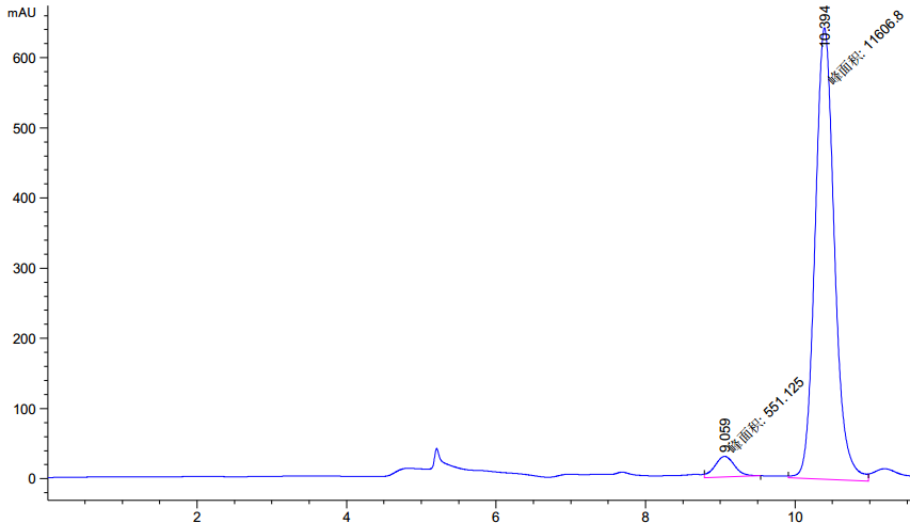
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	11.322	VV R	0.2957	2863.45874	149.34985	50.2399
2	12.200	VB	0.2907	2836.11743	151.31604	49.7601



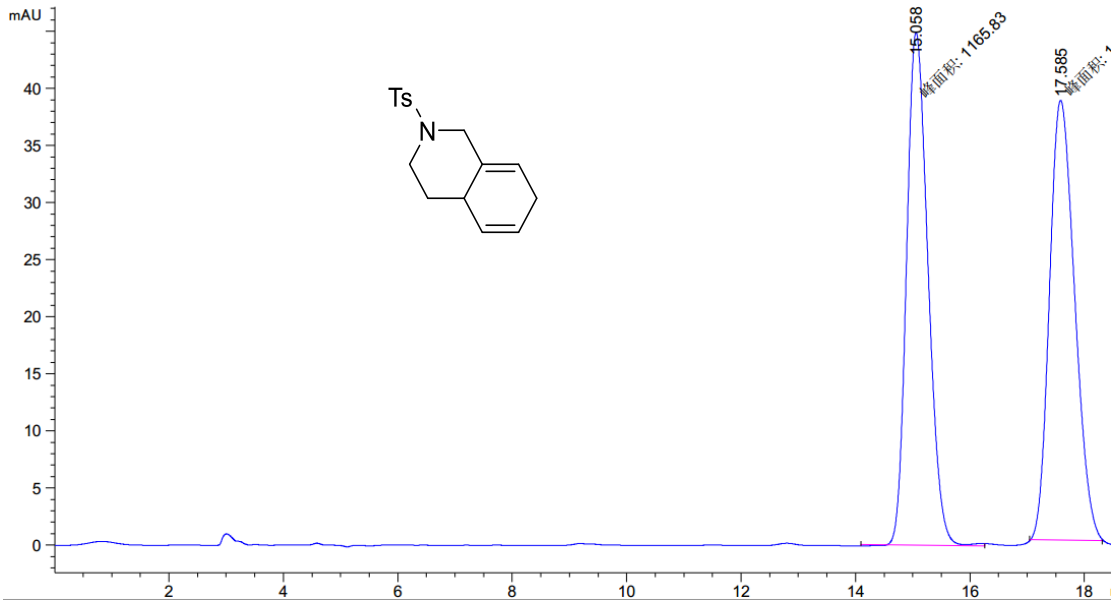
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	11.171	VB R	0.3280	83.96856	3.82595	0.9787
2	12.008	BB	0.2836	8495.95313	468.48328	99.0213



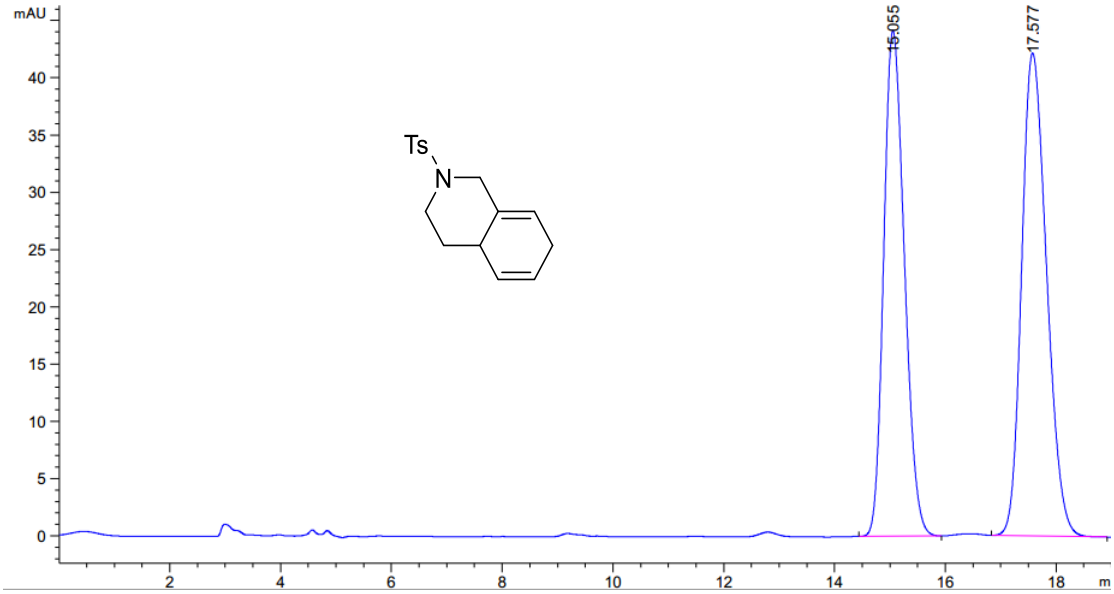
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.424	MM	0.3689	6207.67627	280.45441	50.9727
2	10.832	MM	0.3488	5970.76318	285.32471	49.0273



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.059	MM	0.3106	551.12457	29.57544	4.5330
2	10.394	MM	0.3006	1.16068e4	643.57928	95.4670

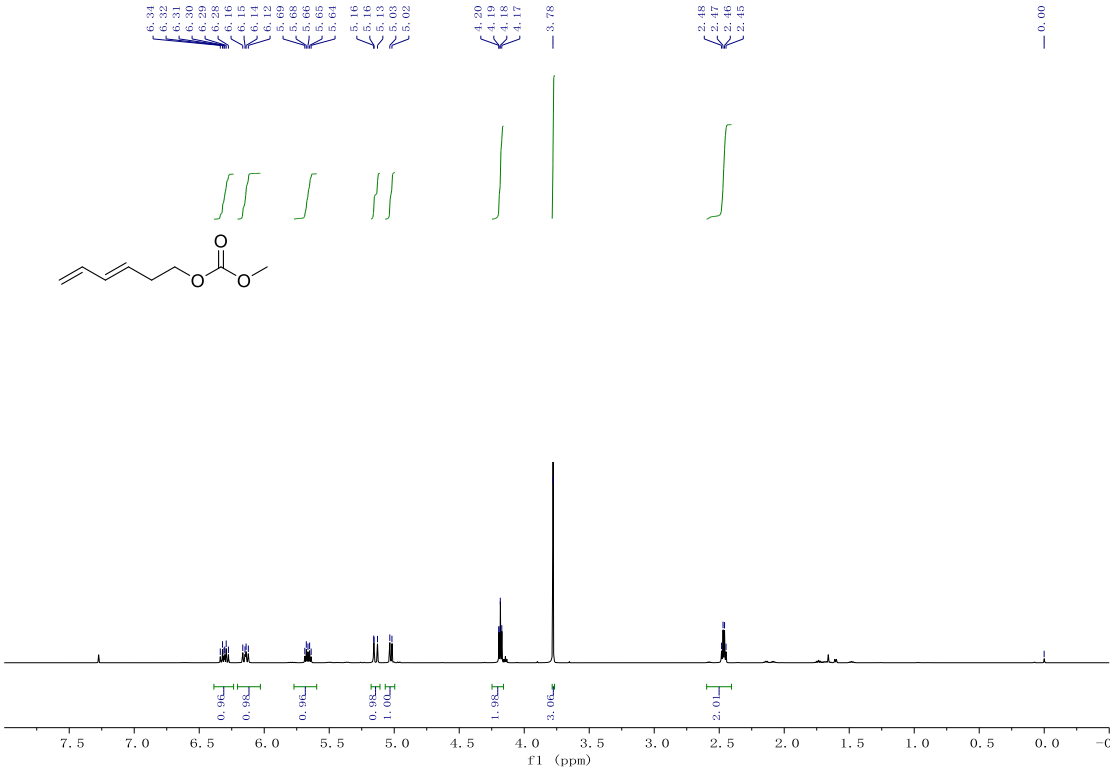


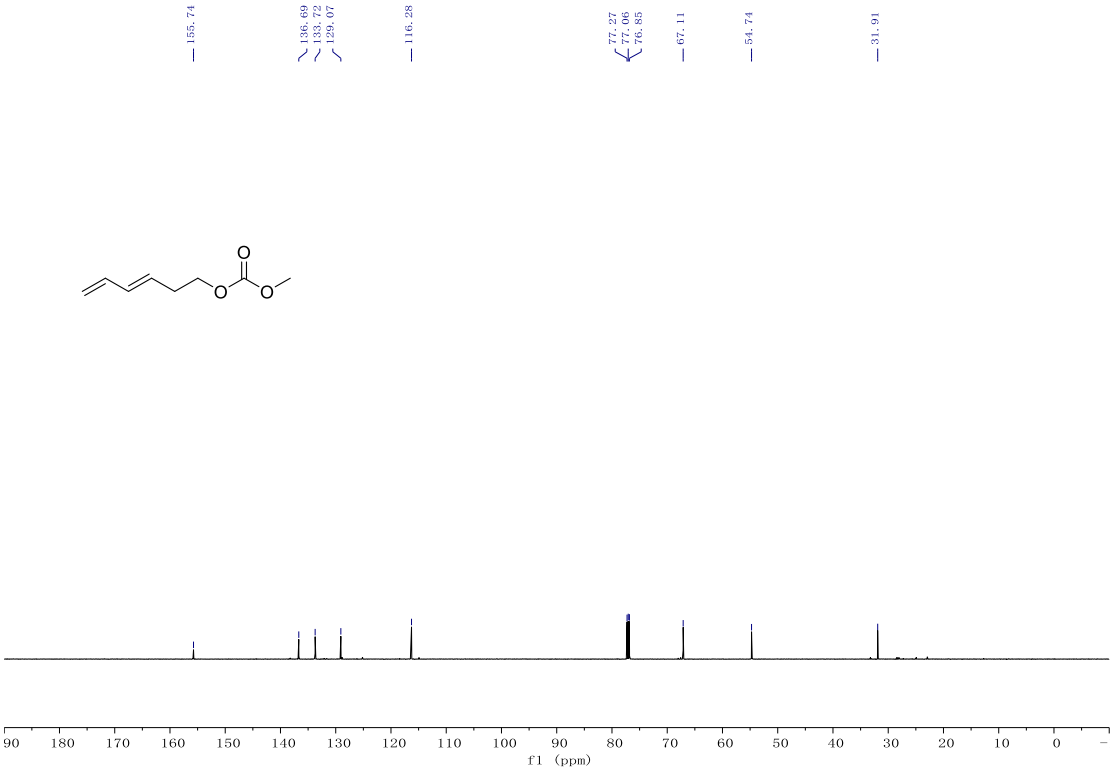
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	15.058	MM	0.4326	1165.82813	44.91981	49.7489
2	17.585	MM	0.5095	1177.59656	38.51940	50.2511

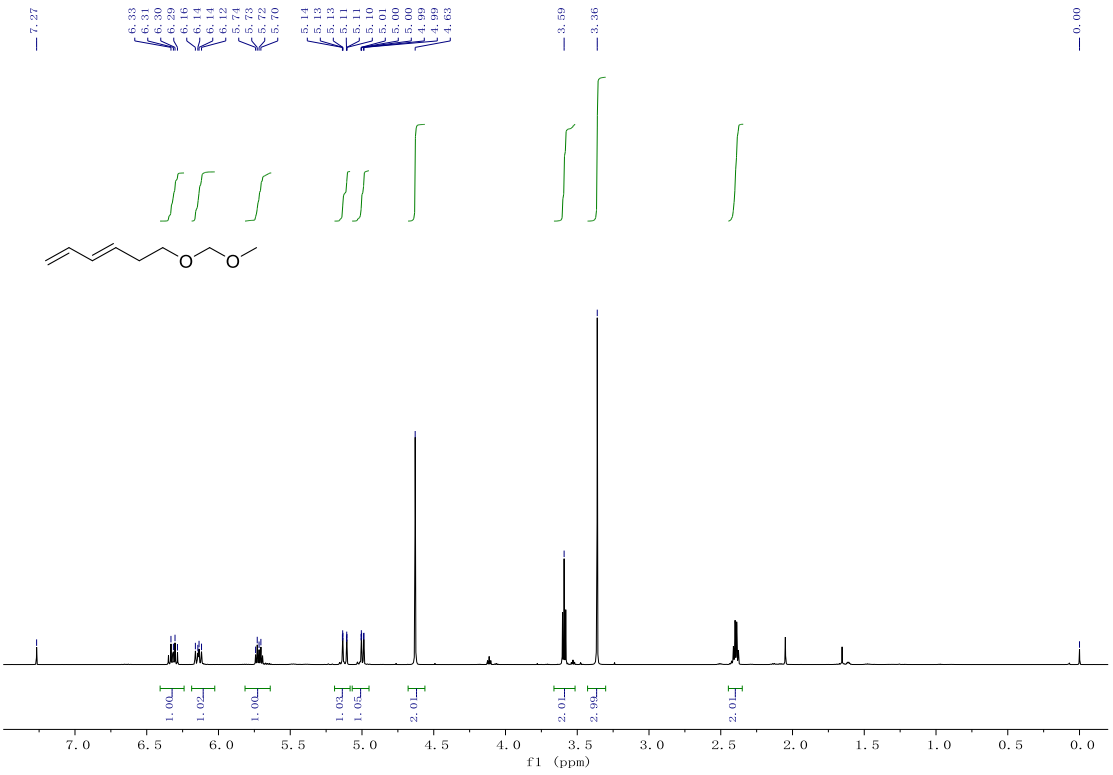


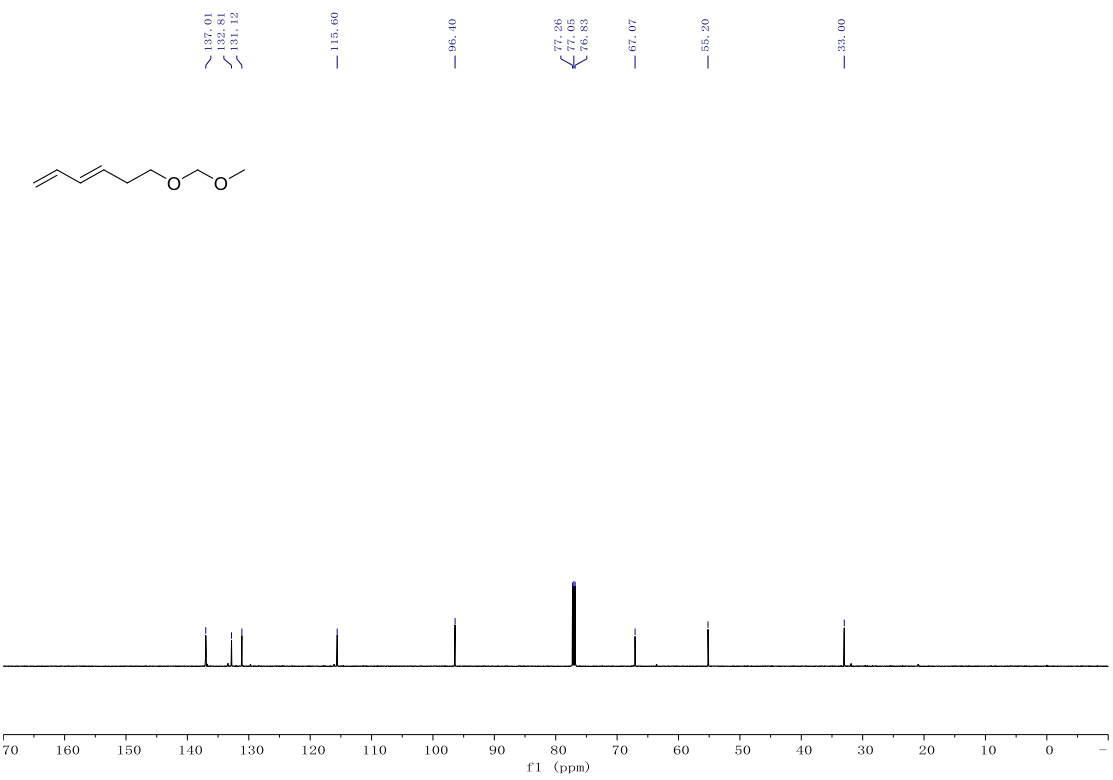
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	15.055	BB	0.4049	1142.67859	44.16047	46.3888
2	17.577	BBA	0.4894	1320.58435	42.16912	53.6112

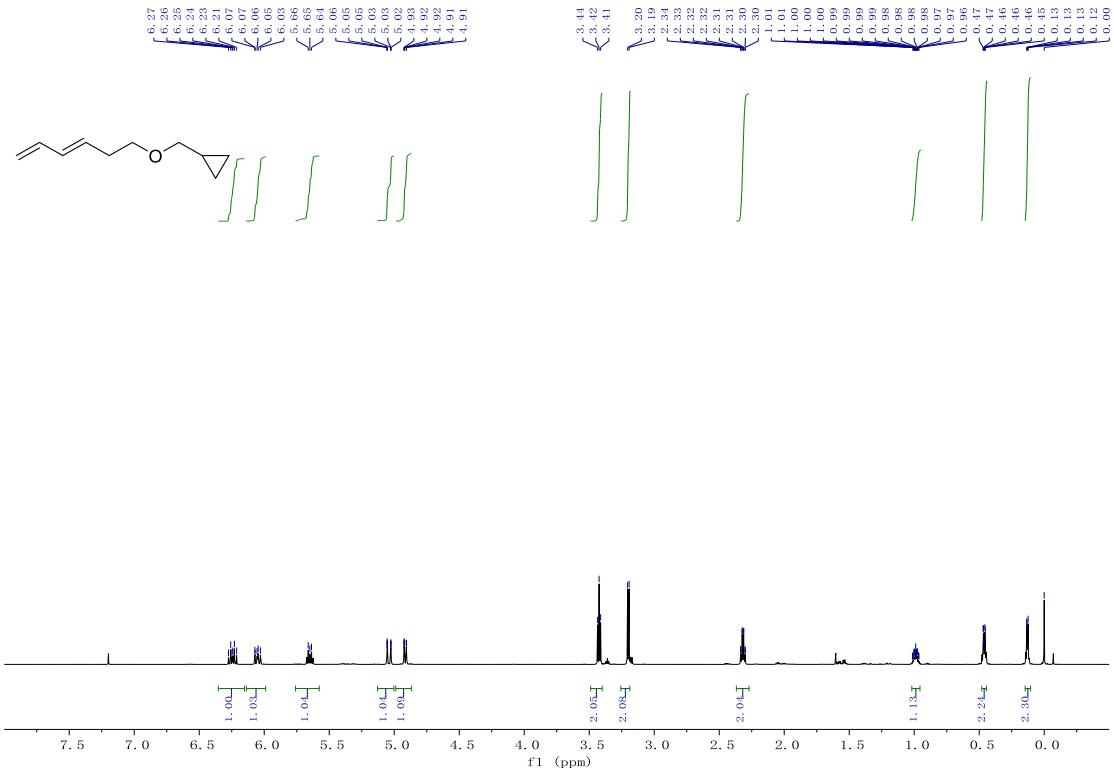
10. Copies of ^{1}H NMR and ^{13}C NMR spectra



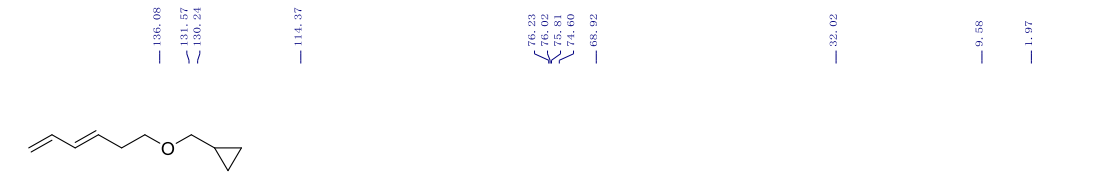


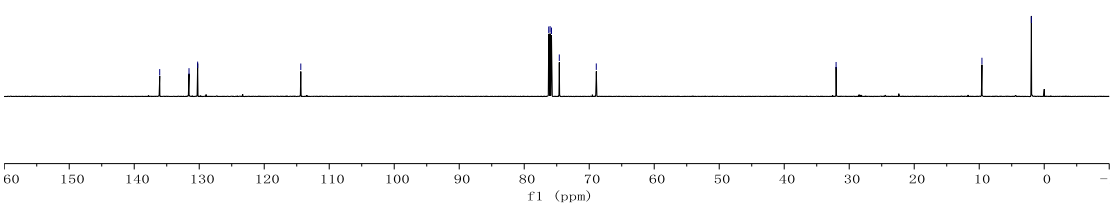

7.27
6.33
6.31
6.30
6.29
6.16
6.14
6.14
6.12
5.74
5.73
5.72
5.70
5.14
5.13
5.13
5.11
5.11
5.10
5.01
5.00
5.00
4.99
4.99
4.63
3.59
3.36
0.00
1.00
1.02
1.00
1.03
1.05
2.01
2.01
2.99
2.01
f1 (ppm)

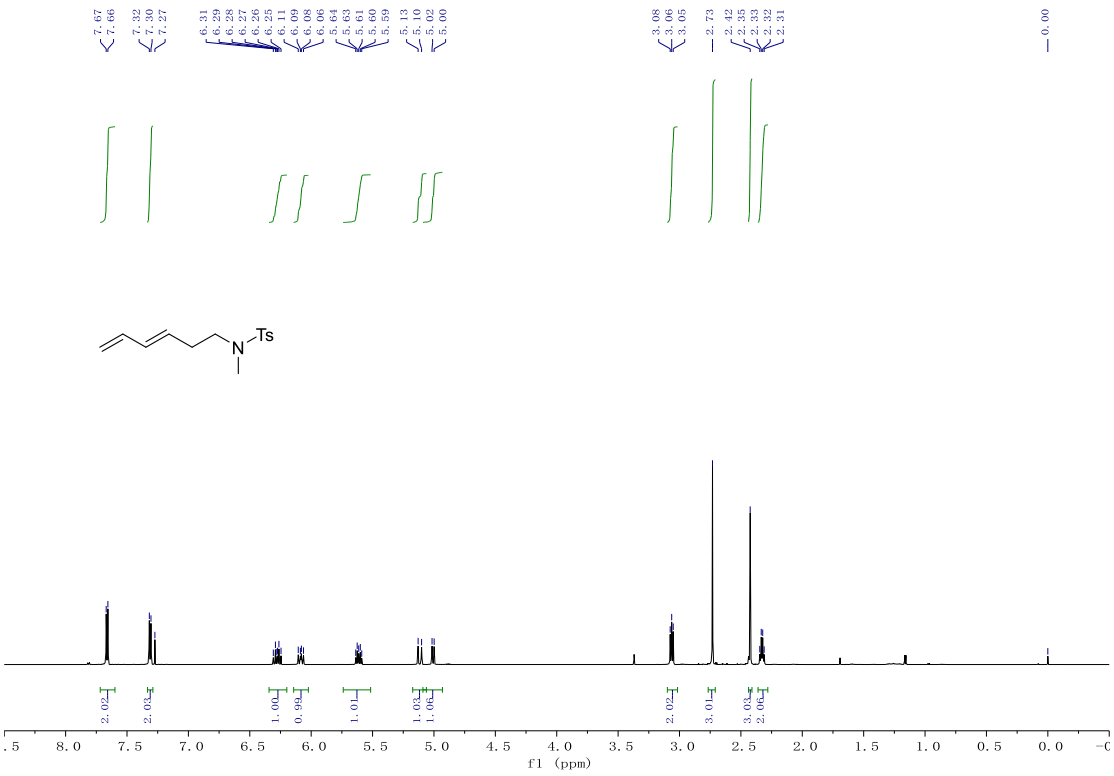

137.01
132.81
131.12
115.60
96.40
77.26
77.05
76.83
67.07
55.20
33.00
f1 (ppm)

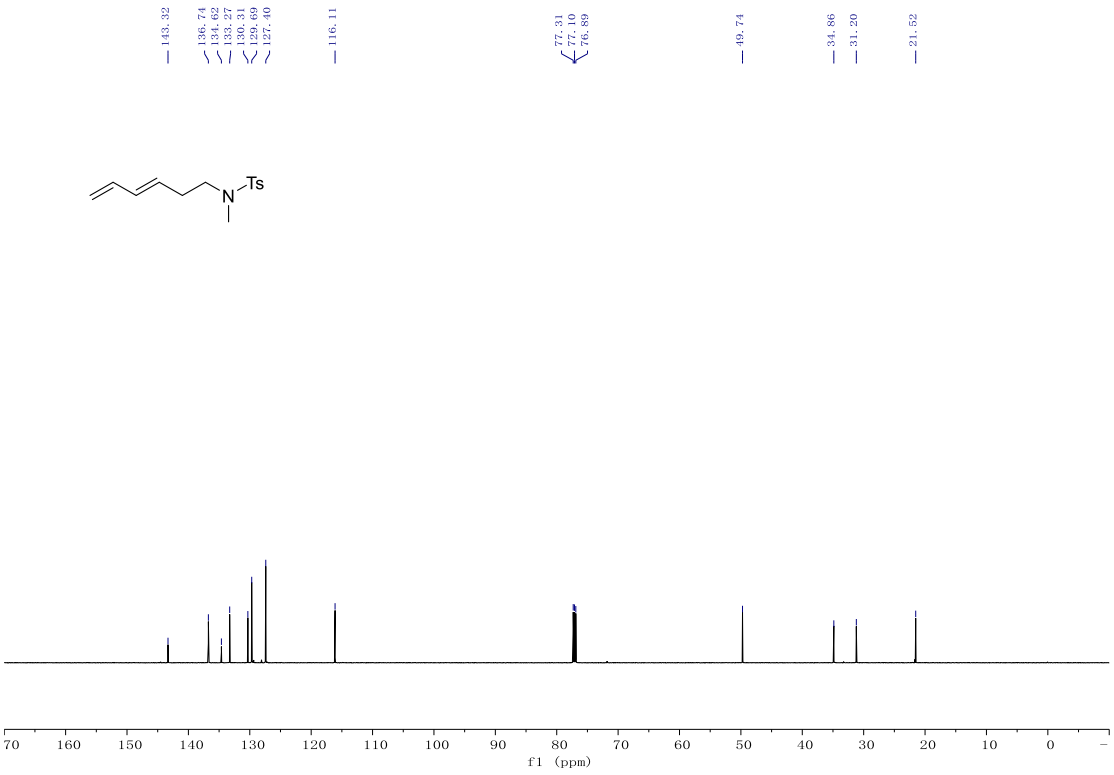

6.27
6.26
6.25
6.24
6.23
6.21
6.07
6.07
6.06
6.05
5.68
5.65
5.64
5.06
5.05
5.05
5.03
5.02
4.93
4.92
4.92
4.91
4.91
3.44
3.42
3.41
3.20
3.19
2.34
2.33
2.32
2.32
2.31
2.31
2.30
2.30
1.01
1.01
1.00
1.00
1.00
0.99
0.99
0.99
0.99
0.98
0.98
0.98
0.97
0.97
0.96
0.47
0.47
0.46
0.46
0.46
0.45
0.13
0.13
0.12
0.00
O

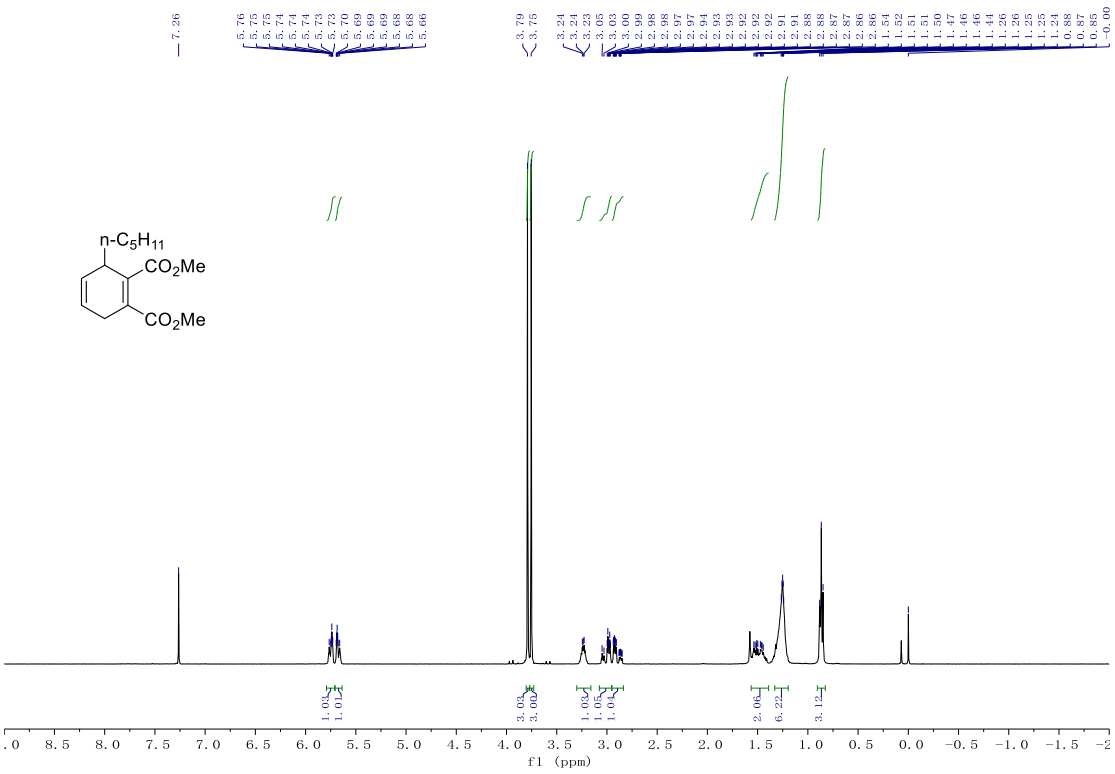
1.00
1.03
1.04
1.04
1.05
2.05
2.08
2.04
1.13
2.24
2.30
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

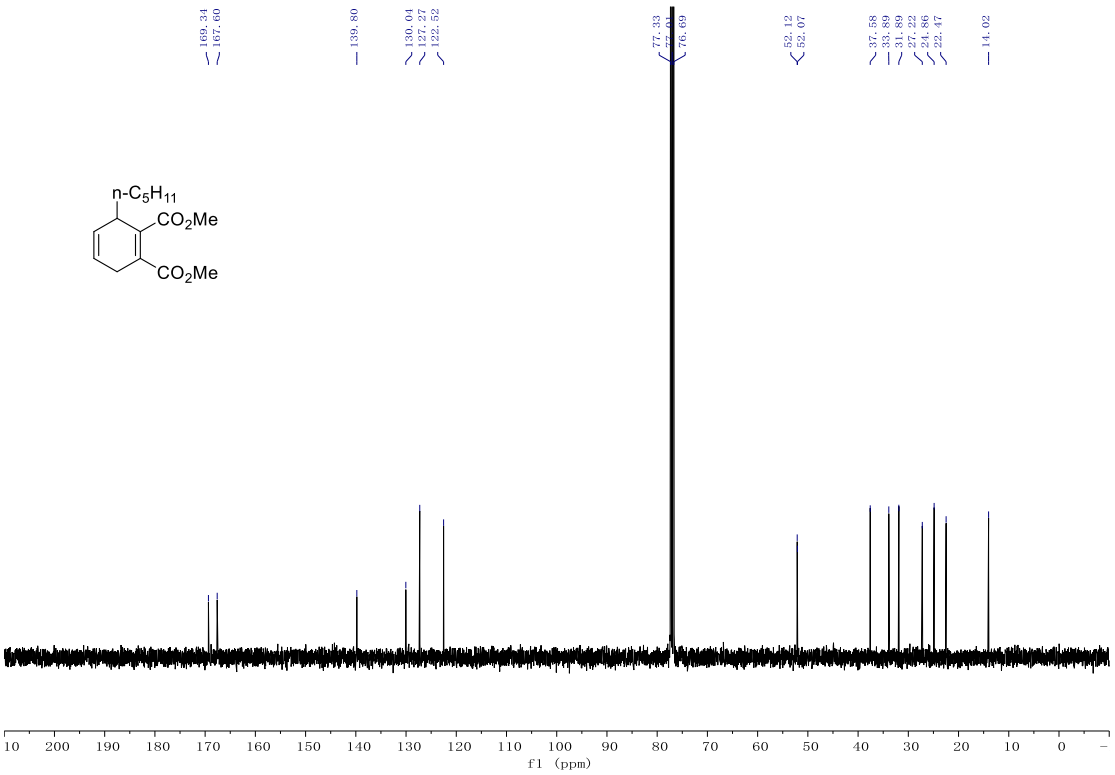

136.08
131.57
130.24
114.37
76.23
76.02
75.81
74.60
68.92
32.02
9.58
1.97
O

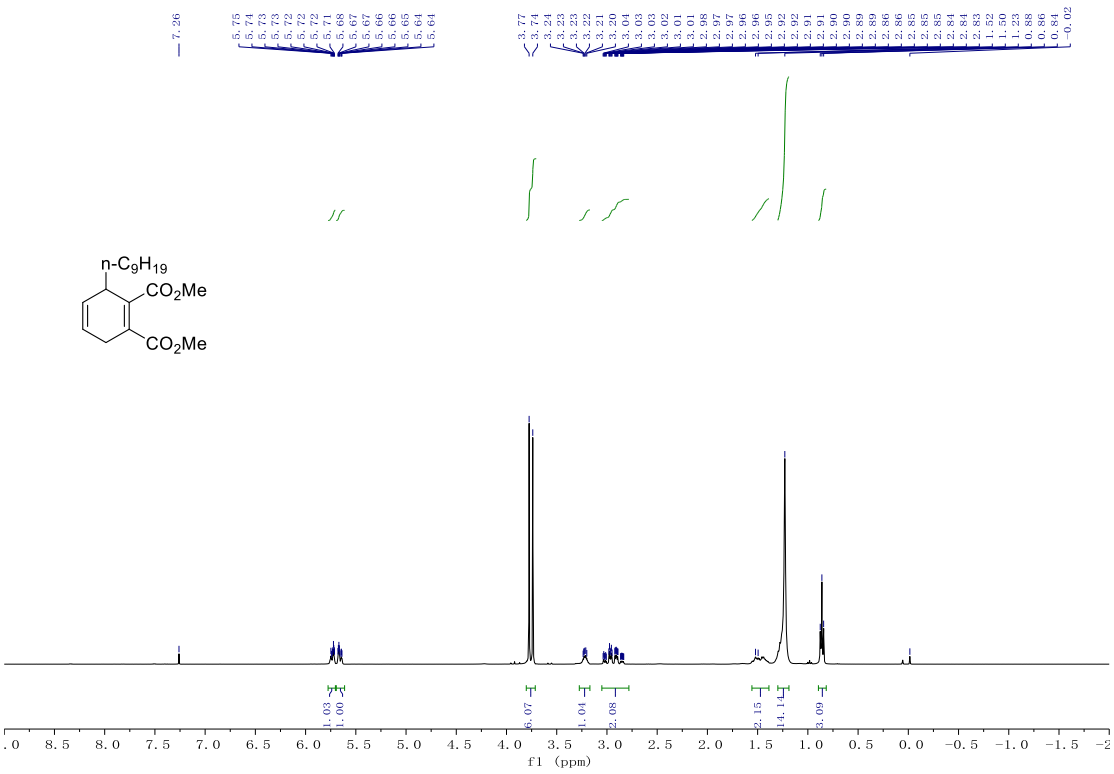

60
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

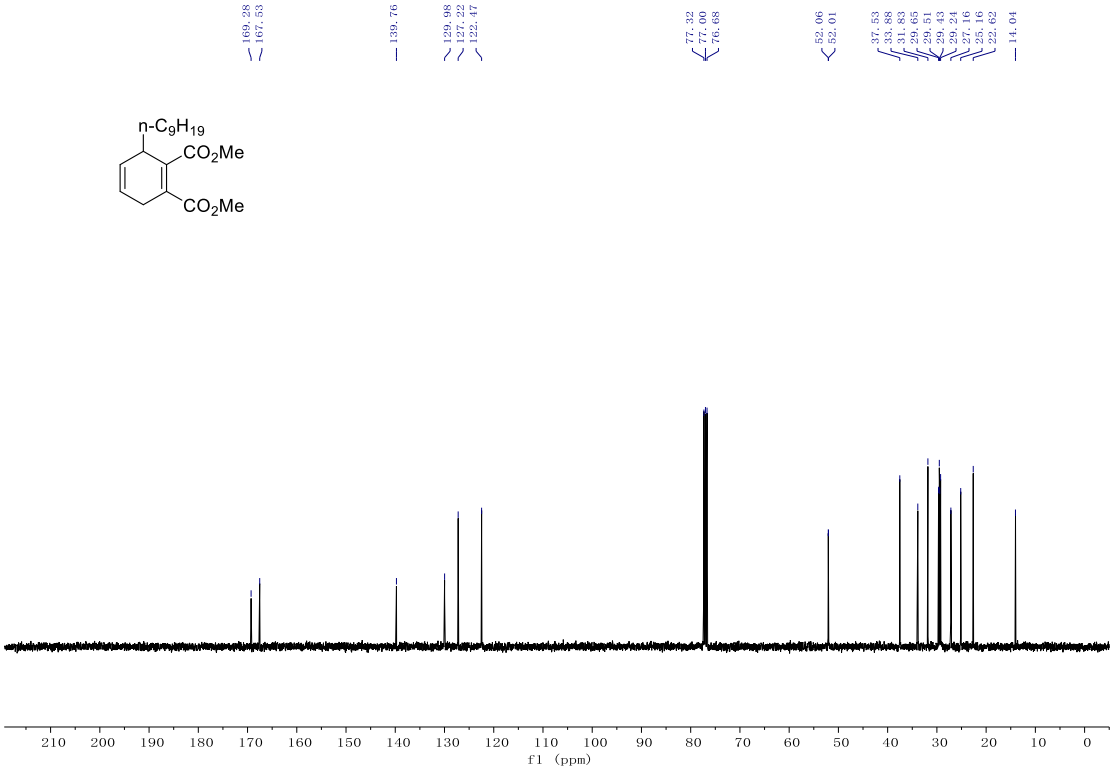

7.67
7.66
7.32
7.30
7.27
6.31
6.29
6.28
6.27
6.26
6.25
6.11
6.09
6.08
6.06
5.64
5.63
5.61
5.60
5.59
5.13
5.10
5.02
5.00
3.08
3.06
3.05
2.73
2.42
2.35
2.33
2.32
2.31
0.00
Ts
N
2.02
2.03
1.00
0.99
1.01
1.03
1.06
2.02
3.01
3.03
2.06
f1 (ppm)

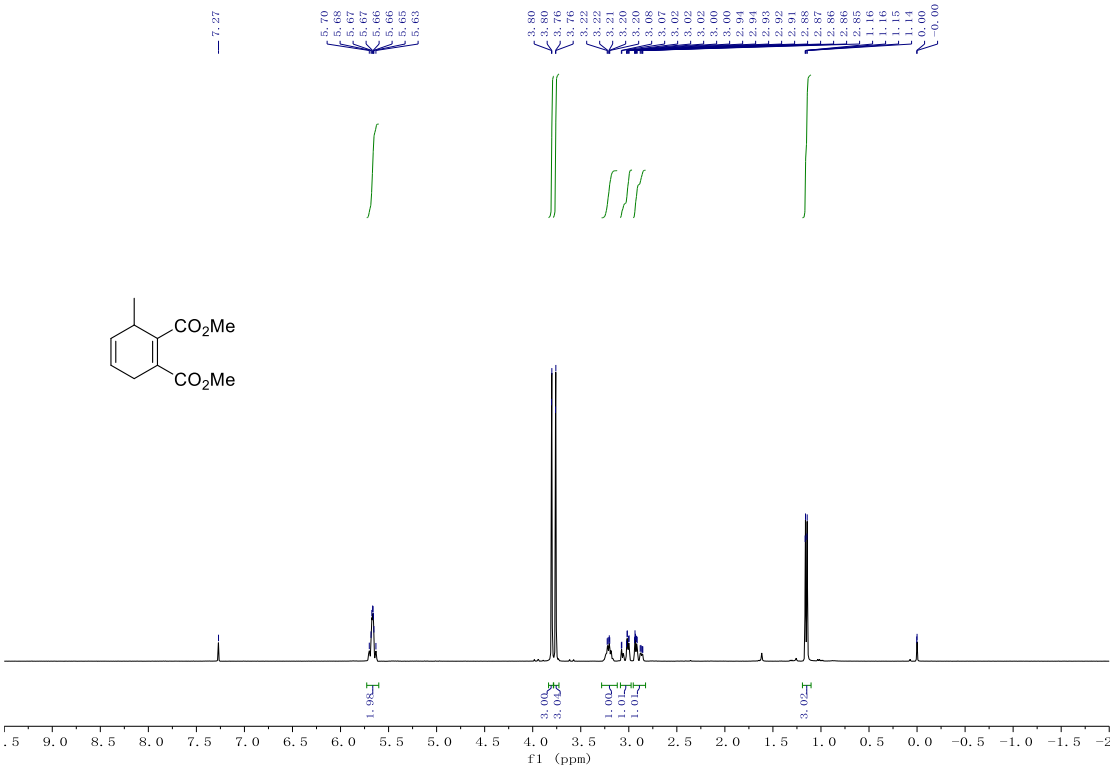

143.32
136.74
134.62
133.27
130.31
129.89
127.40
116.11
77.31
77.10
76.89
49.74
34.86
31.20
21.52
Ts
N
f1 (ppm)

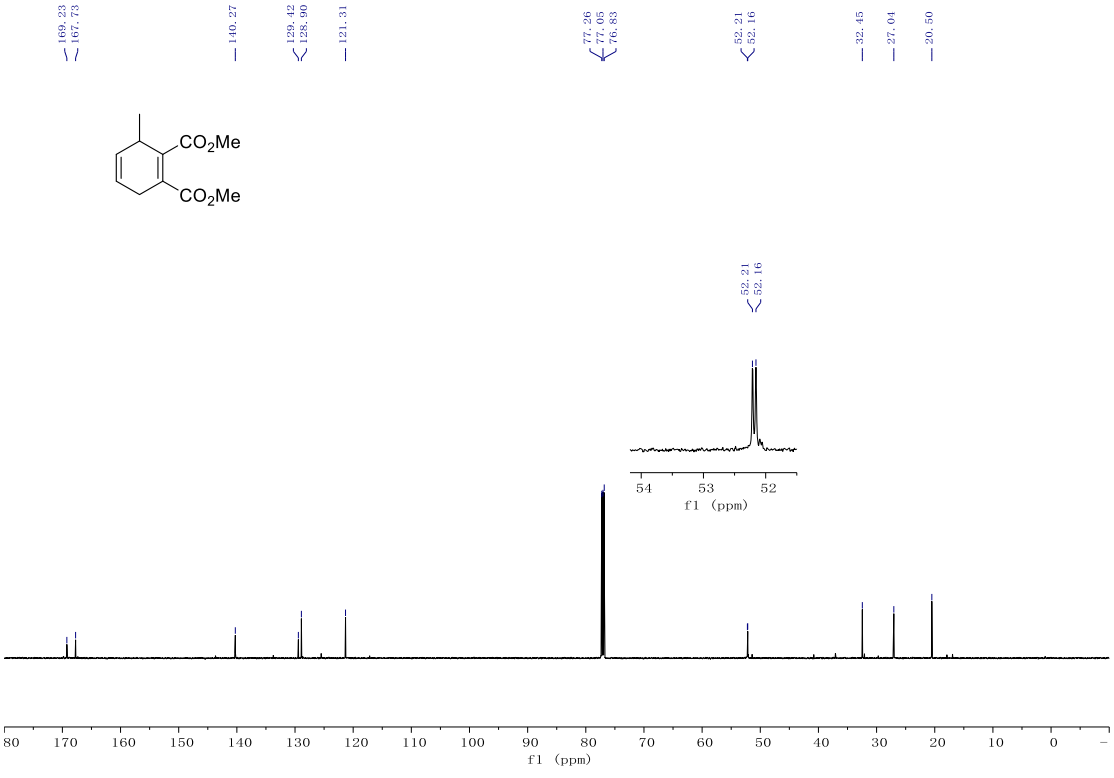

n-C5H11
CO2Me
CO2Me
f1 (ppm)

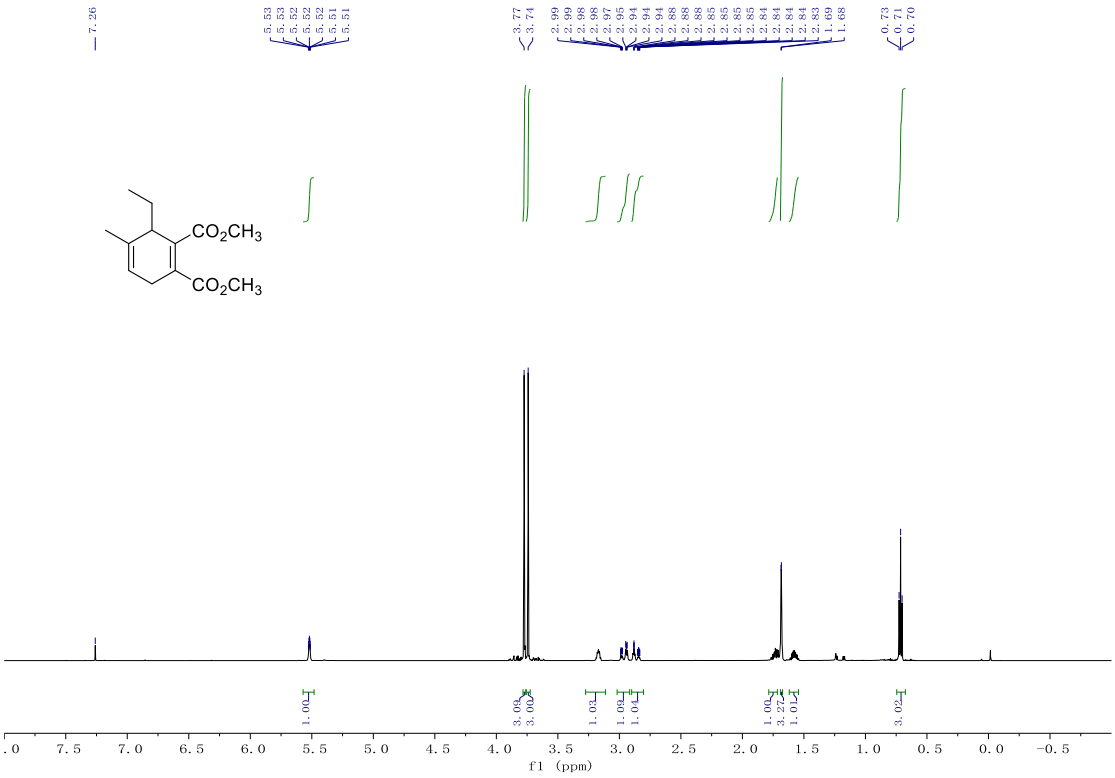

n-C5H11
CO2Me
CO2Me
f1 (ppm)

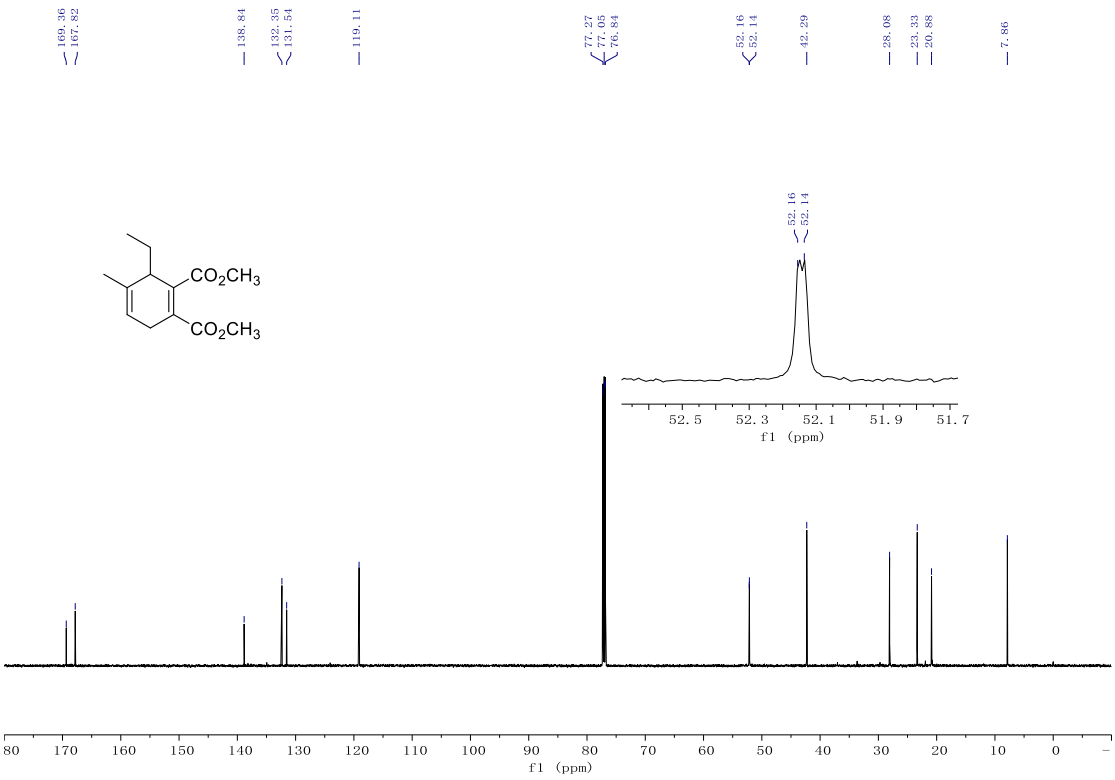

7.26
5.75 5.74 5.73 5.73 5.72 5.72 5.72 5.71 5.68 5.67 5.67 5.66 5.65 5.64 5.64
3.77 3.74 3.74 3.23 3.23 3.22 3.21 3.20 3.04 3.03 3.03 3.02 3.01 3.01 2.98 2.97 2.97 2.96 2.95 2.92 2.92 2.91 2.91 2.90 2.90 2.89 2.86 2.86 2.85 2.85 2.84 2.84 2.83 1.52 1.50 1.23 0.88 0.86 0.84 -0.02
n-C9H19
CO2Me
CO2Me
1.03 1.00 6.07 1.04 2.08 2.15 14.14 3.09
f1 (ppm)

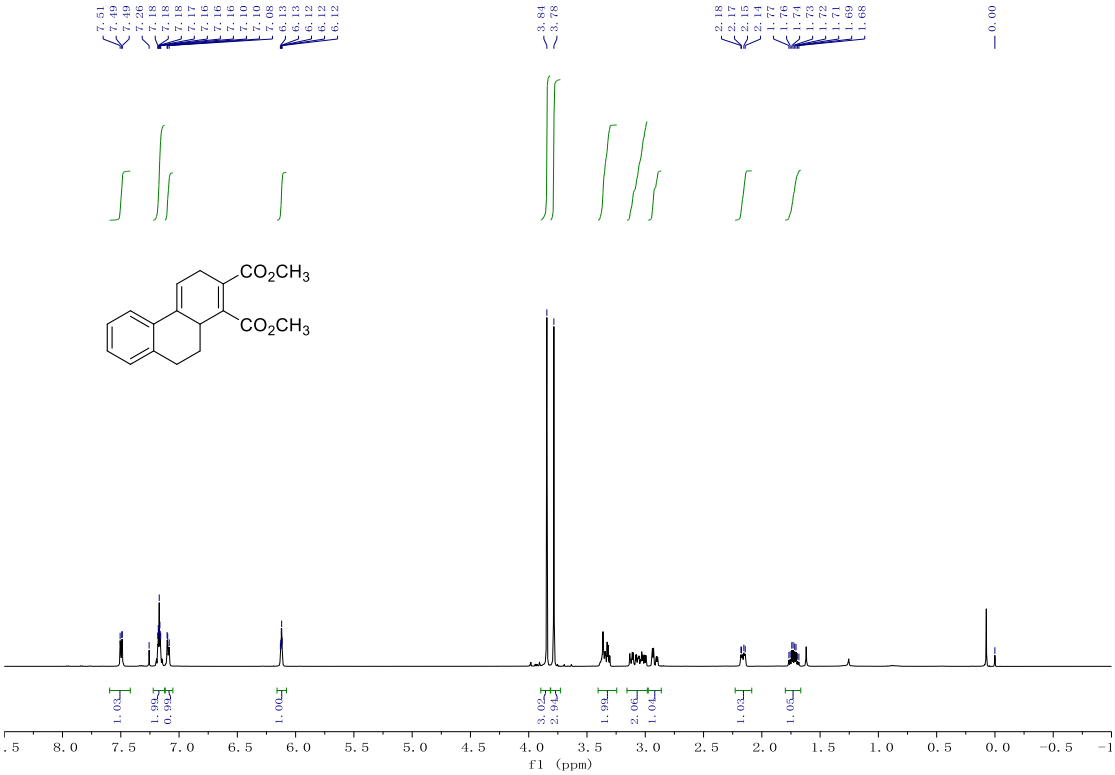

169.28 167.53 139.76 129.98 127.22 122.47 77.32 77.00 76.68 52.06 52.01 37.53 33.88 31.83 29.65 29.51 29.43 29.24 27.16 25.16 22.62 14.04
n-C9H19
CO2Me
CO2Me
f1 (ppm)

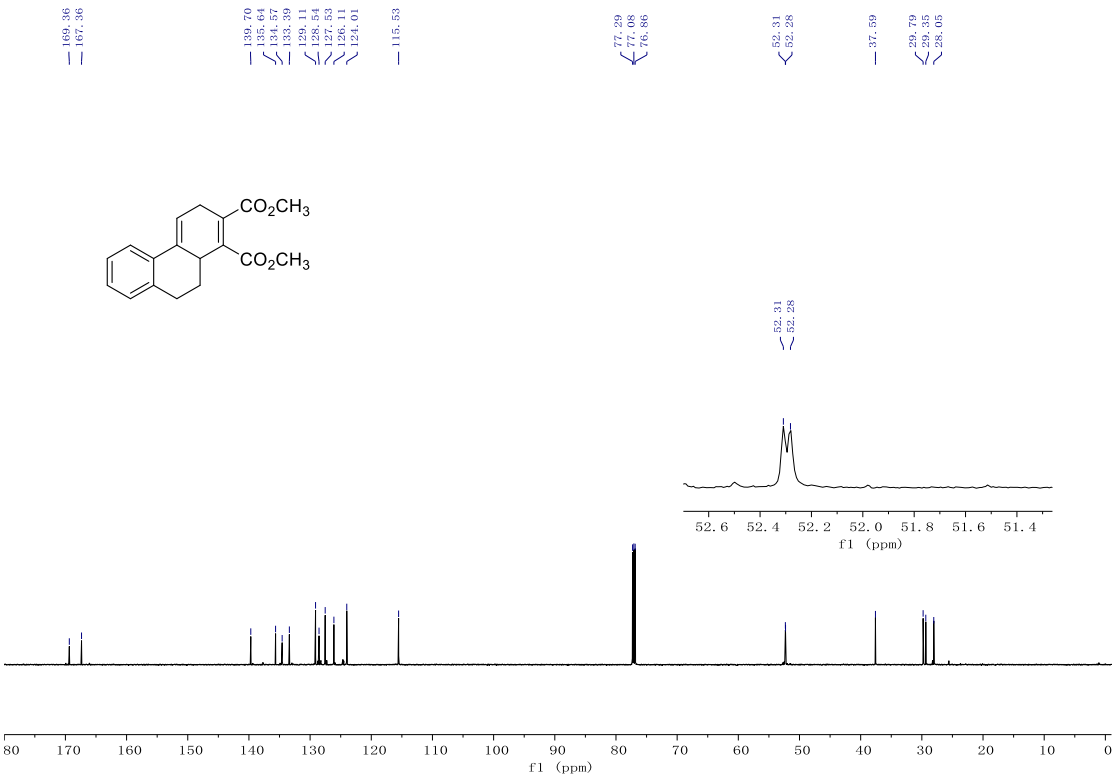

7.27
5.70
5.68
5.67
5.67
5.66
5.66
5.65
5.63
3.80
3.80
3.76
3.76
3.22
3.22
3.21
3.20
3.20
3.08
3.07
3.02
3.02
3.02
3.00
3.00
2.94
2.94
2.93
2.92
2.91
2.88
2.87
2.86
2.86
2.85
1.16
1.16
1.15
1.14
0.00
-0.00
CO2Me
CO2Me
1.98
3.00
3.04
1.00
1.01
1.01
1.01
3.02
f1 (ppm)

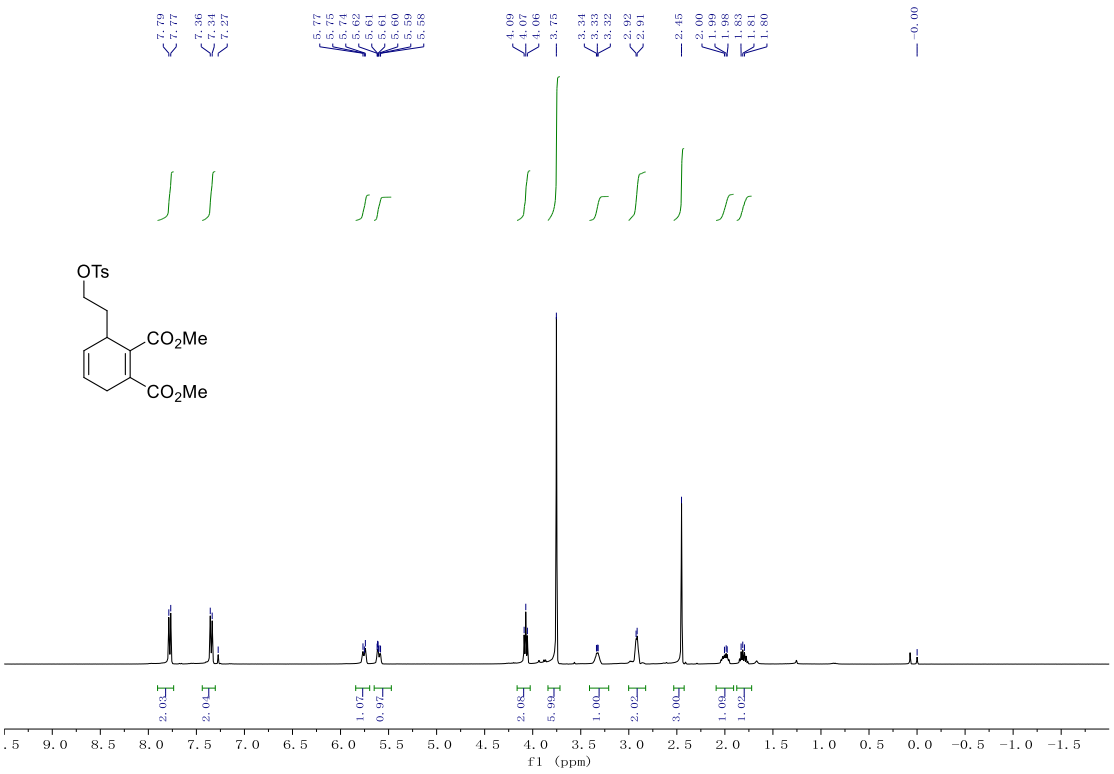

169.23
167.73
140.27
129.42
128.90
121.31
77.26
77.05
76.83
52.21
52.16
32.45
27.04
20.50
CO2Me
CO2Me
52.21
52.16
54
53
52
f1 (ppm)
f1 (ppm)

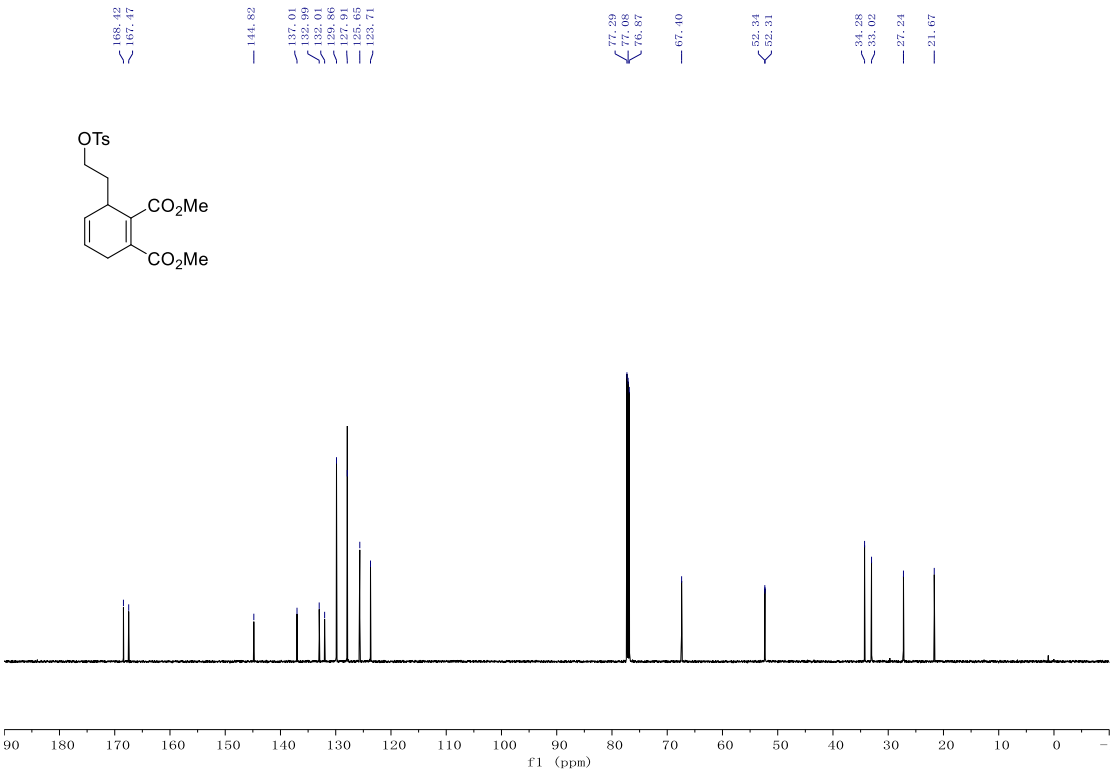

7.26
5.53
5.53
5.52
5.52
5.52
5.51
5.51
3.77
3.74
2.99
2.99
2.98
2.98
2.97
2.95
2.94
2.94
2.94
2.88
2.88
2.85
2.85
2.85
2.85
2.84
2.84
2.84
2.84
2.83
1.69
1.68
0.73
0.71
0.70
CO2CH3
CO2CH3
1.00
3.09
3.00
1.03
1.09
1.04
1.00
3.27
1.01
3.02
f1 (ppm)

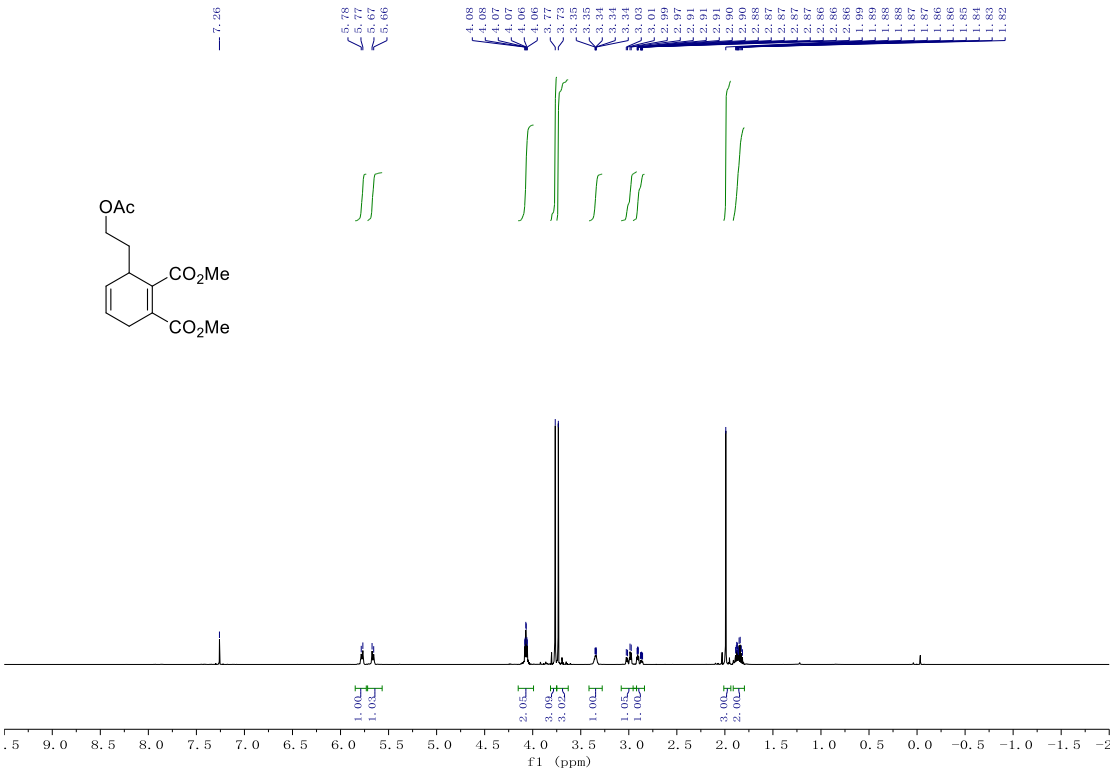

169.36
167.82
138.84
132.35
131.54
119.11
77.27
77.05
76.84
52.16
52.14
42.29
28.08
23.33
20.88
7.86
CO2CH3
CO2CH3
52.16
52.14
f1 (ppm)
f1 (ppm)

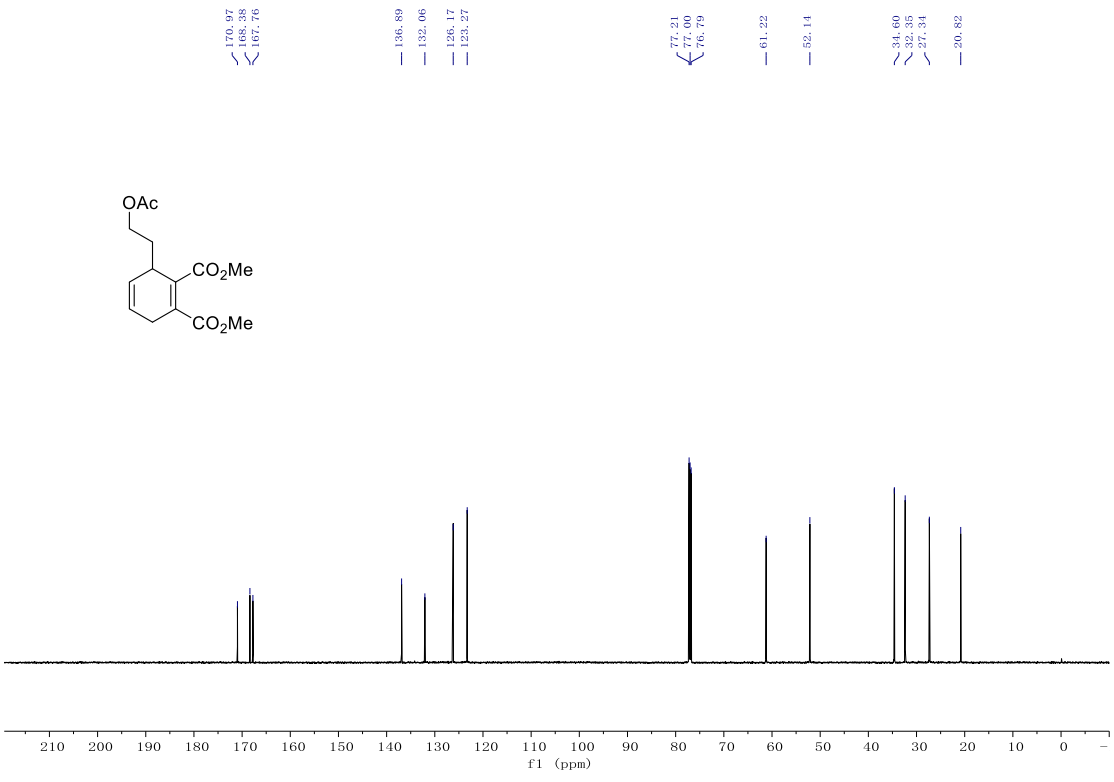

7.51
7.49
7.49
7.26
7.18
7.18
7.18
7.17
7.16
7.16
7.16
7.10
7.10
7.08
6.13
6.13
6.12
6.12
6.12
3.84
3.78
2.18
2.17
2.15
2.14
1.77
1.76
1.74
1.73
1.72
1.71
1.69
1.68
0.00
CO2CH3
CO2CH3
1.03
1.99
0.99
1.00
3.02
2.94
1.99
2.06
1.04
1.03
1.05
f1 (ppm)

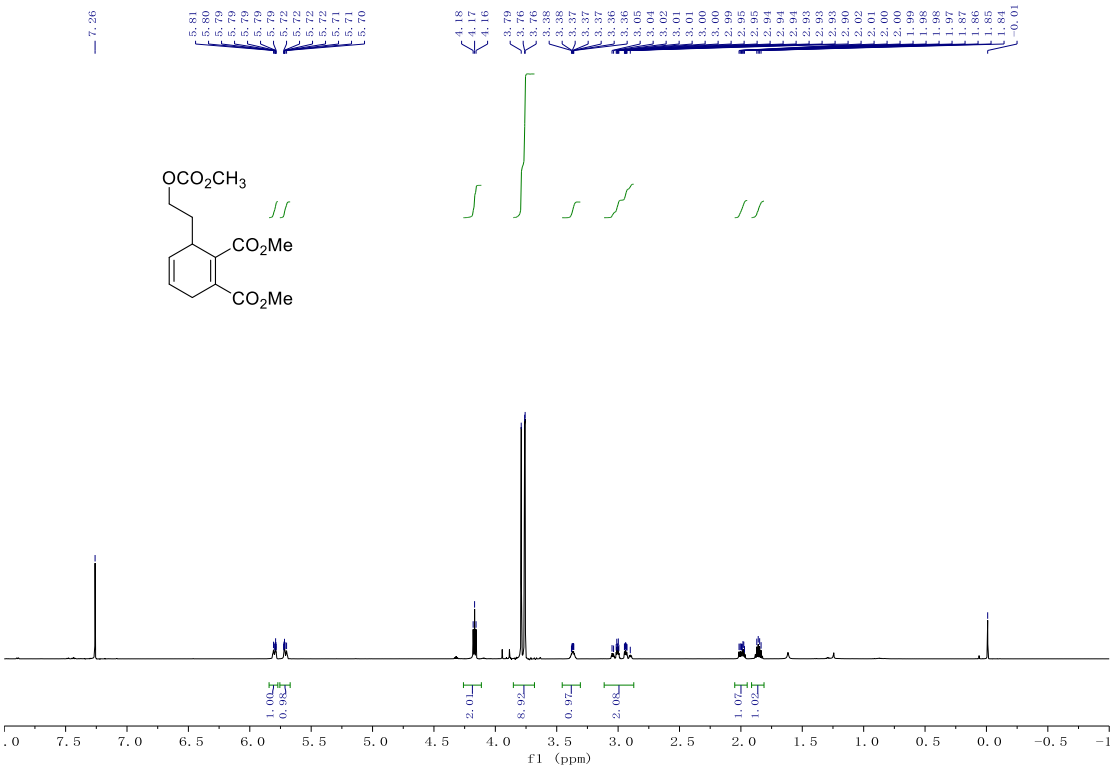

169.36
167.36
139.70
135.64
134.57
133.39
129.11
128.54
127.53
126.11
124.01
115.53
77.29
77.08
76.86
52.31
52.28
37.59
29.79
29.35
28.05
CO2CH3
CO2CH3
52.31
52.28
52.6
52.4
52.2
52.0
51.8
51.6
51.4
f1 (ppm)
f1 (ppm)

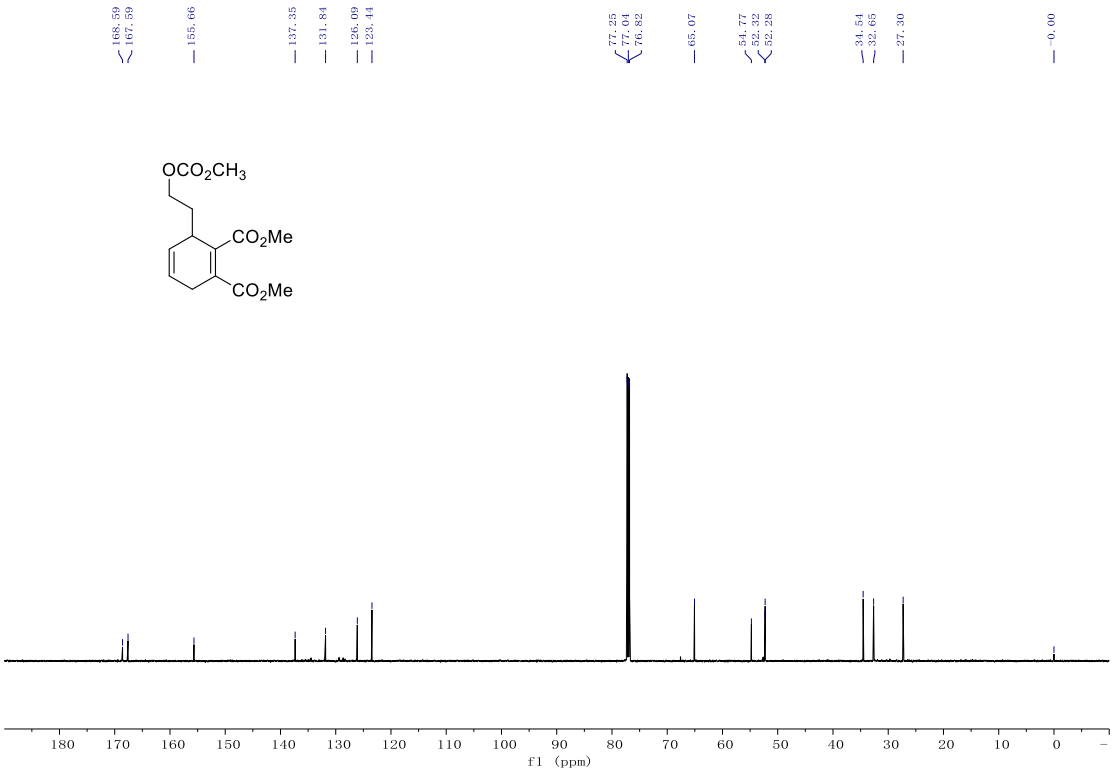

7.79
7.77
7.36
7.34
7.27
5.77
5.75
5.74
5.62
5.61
5.60
5.59
5.58
4.09
4.07
4.06
3.75
3.34
3.33
3.32
2.92
2.91
2.45
2.00
1.99
1.98
1.83
1.81
1.80
0.00
OTs
CO2Me
CO2Me
2.03
2.04
1.07
0.97
2.08
5.99
1.00
2.02
3.00
1.09
1.02
f1 (ppm)

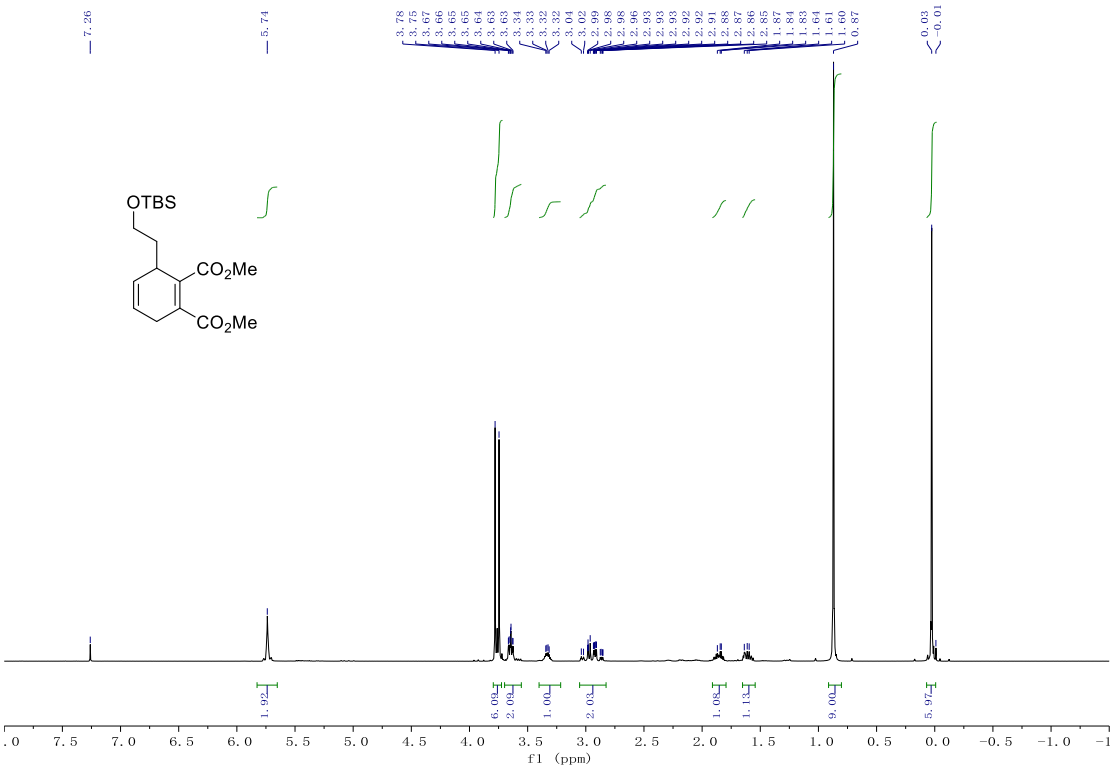

168.42
167.47
144.82
137.01
132.99
132.01
129.86
127.91
125.65
123.71
77.29
77.08
76.87
67.40
52.34
52.31
34.28
33.02
27.24
21.67
OTs
CO2Me
CO2Me
f1 (ppm)

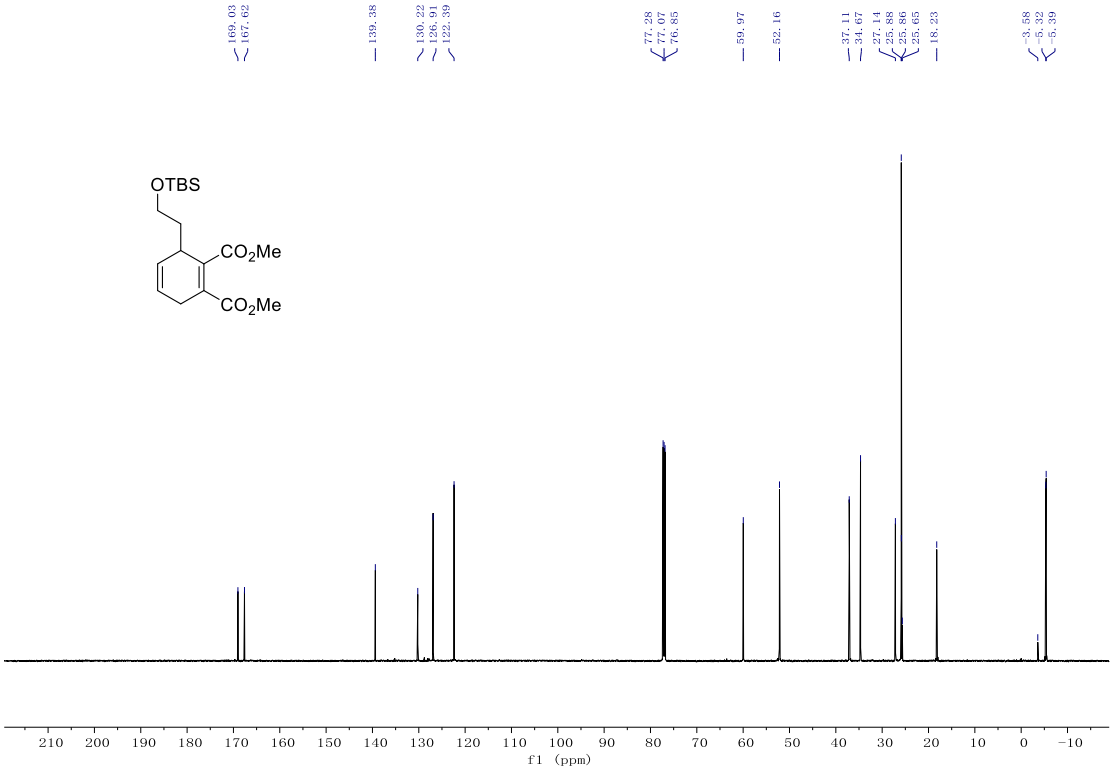

7.26
5.78
5.77
5.67
5.66
4.08
4.08
4.07
4.07
4.06
4.06
3.77
3.73
3.35
3.35
3.34
3.34
3.03
3.01
2.99
2.97
2.91
2.91
2.91
2.90
2.90
2.88
2.87
2.87
2.87
2.87
2.86
2.86
2.86
1.99
1.89
1.88
1.88
1.87
1.87
1.86
1.86
1.85
1.84
1.83
1.82
OAc
CO2Me
CO2Me
1.00
1.03
2.05
3.09
3.02
1.00
1.05
1.00
3.00
2.00
f1 (ppm)

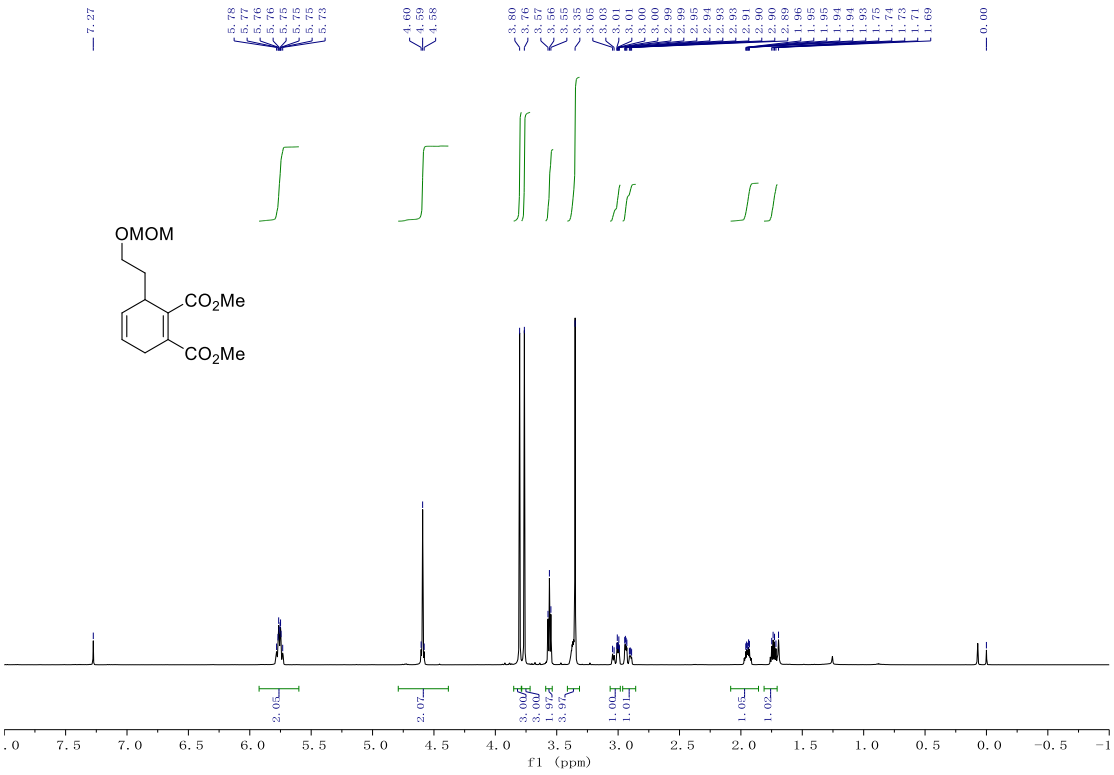

170.97
168.38
167.76
136.89
132.06
126.17
123.27
77.21
77.00
76.79
61.22
52.14
34.60
32.35
27.34
20.82
OAc
CO2Me
CO2Me
f1 (ppm)

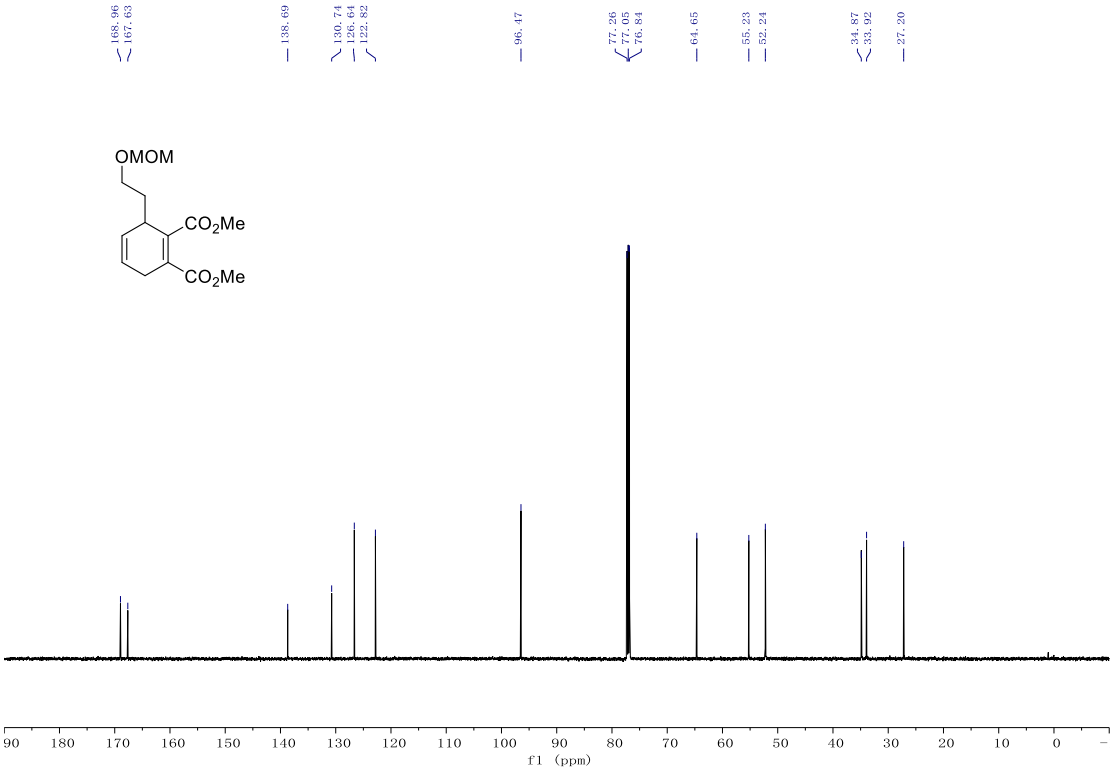

OCO2CH3
CO2Me
CO2Me
f1 (ppm)

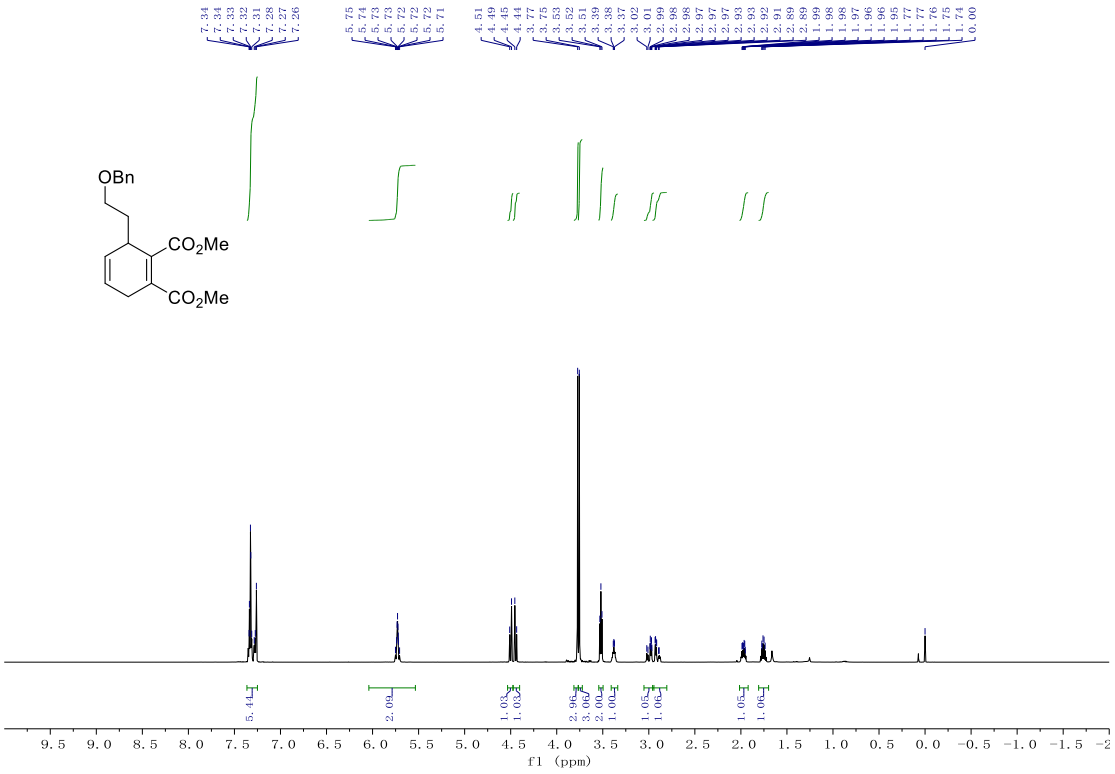

OCO2CH3
CO2Me
CO2Me
f1 (ppm)

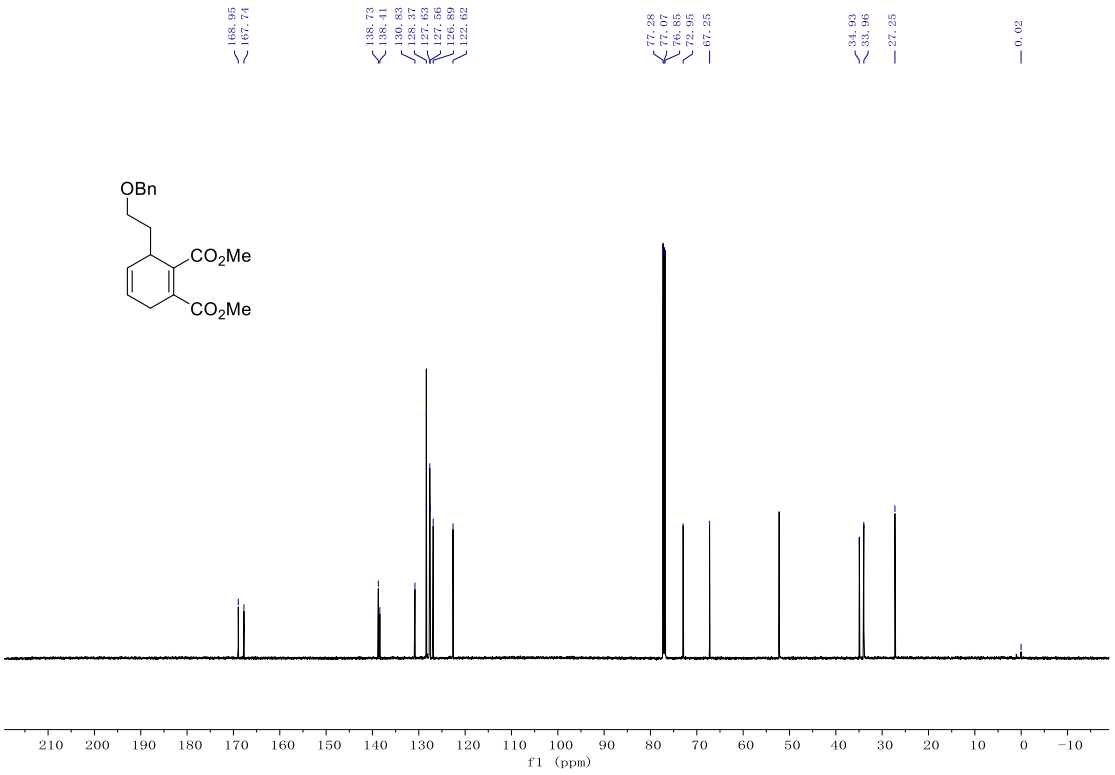

OTBS
CO2Me
CO2Me
f1 (ppm)

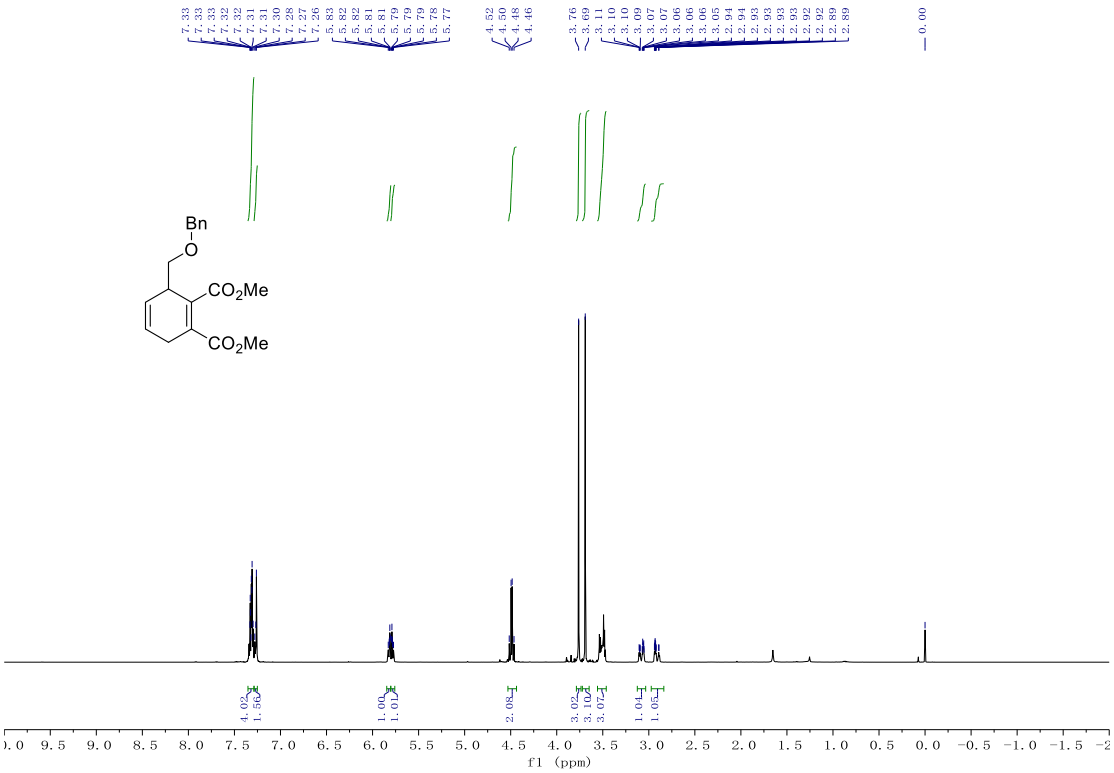

OTBS
CO2Me
CO2Me
f1 (ppm)

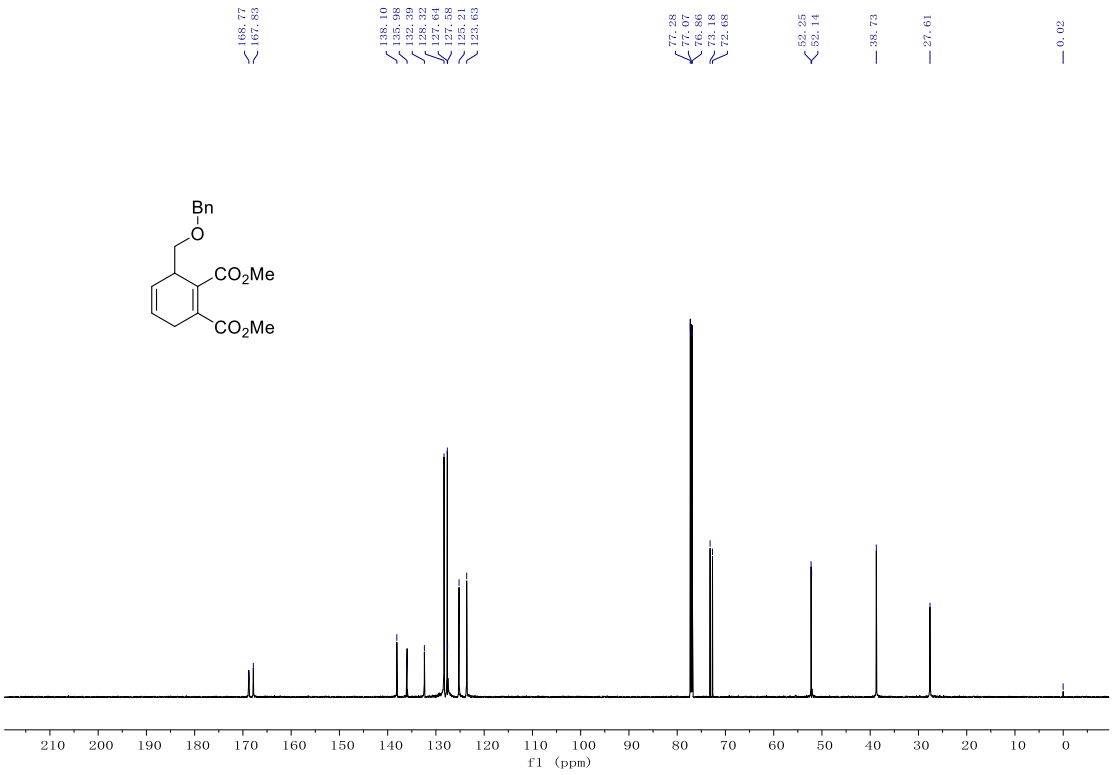

OMOM
CO2Me
CO2Me
f1 (ppm)

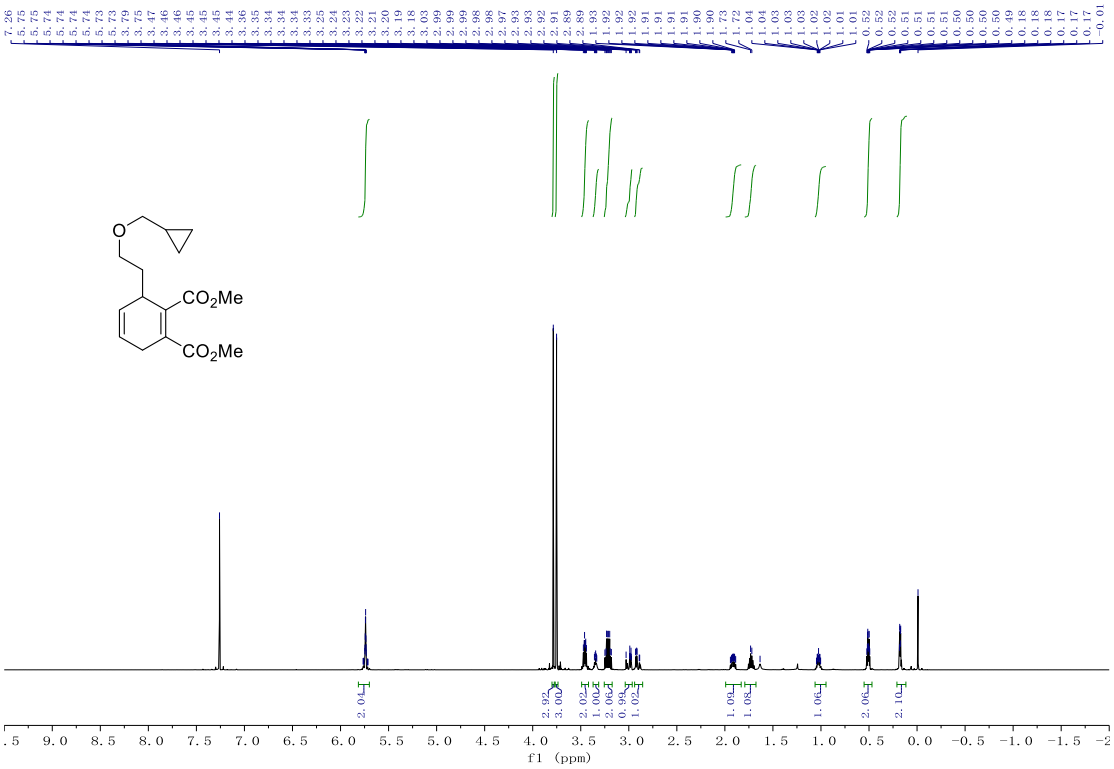

OMOM
CO2Me
CO2Me
f1 (ppm)

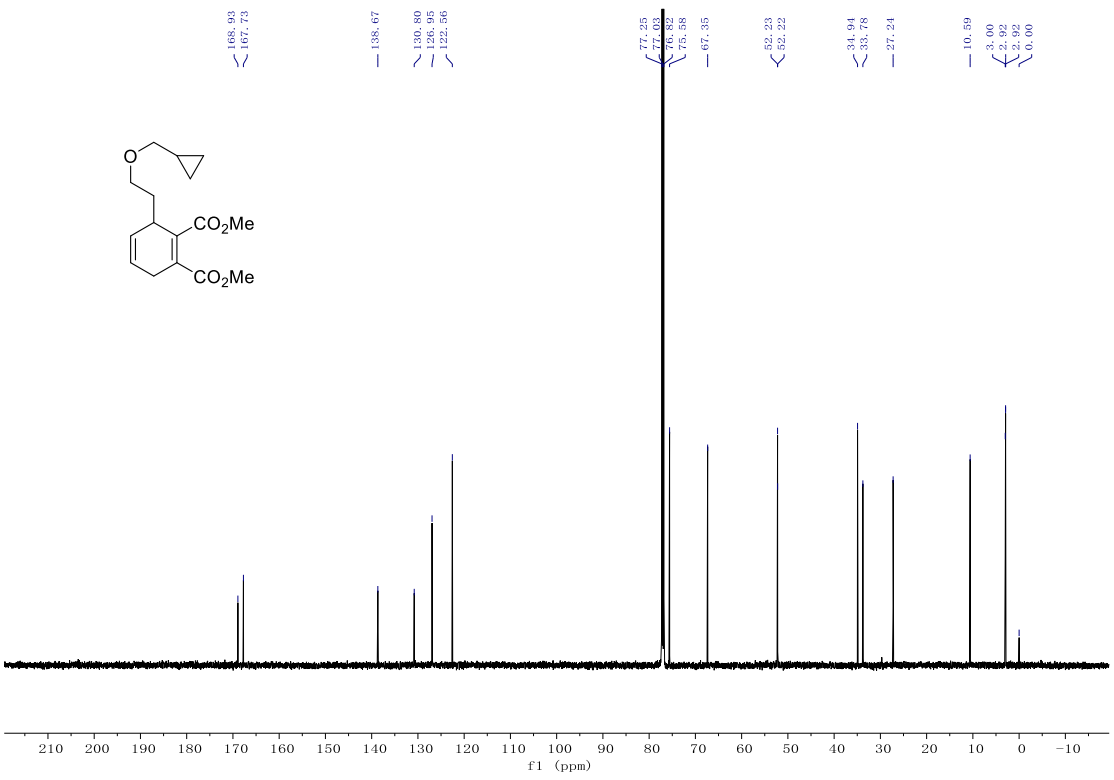

OBn
CO2Me
CO2Me
f1 (ppm)

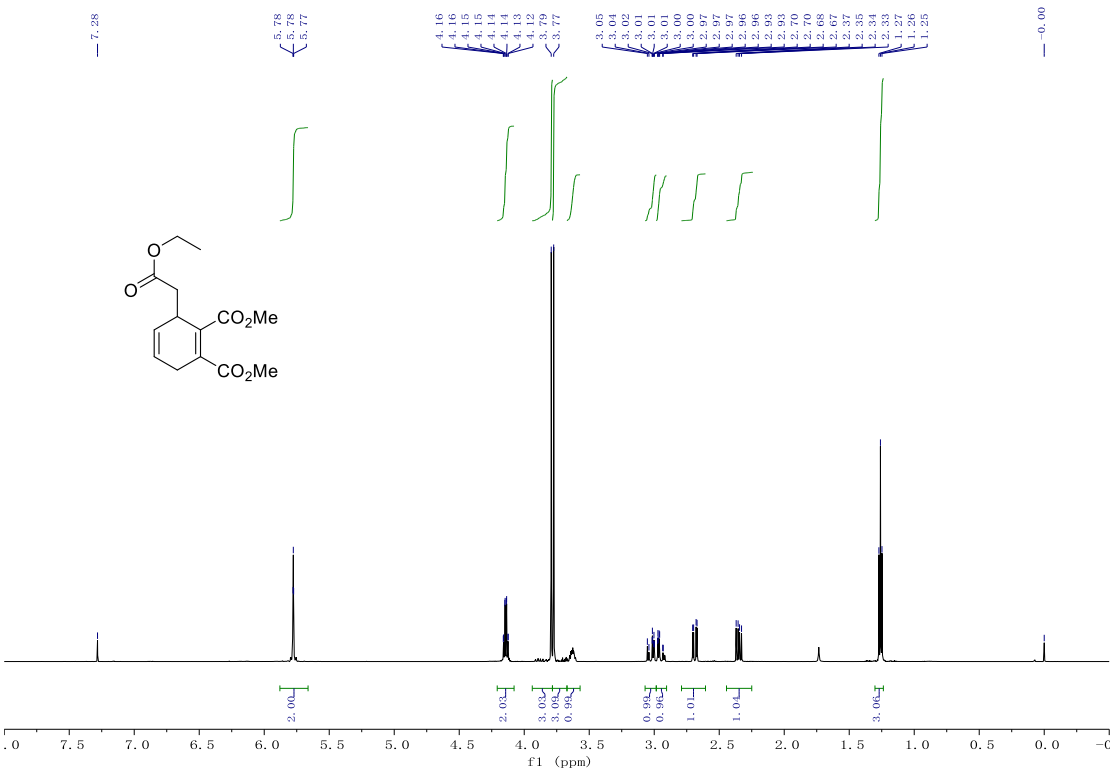

OBn
CO2Me
CO2Me
f1 (ppm)

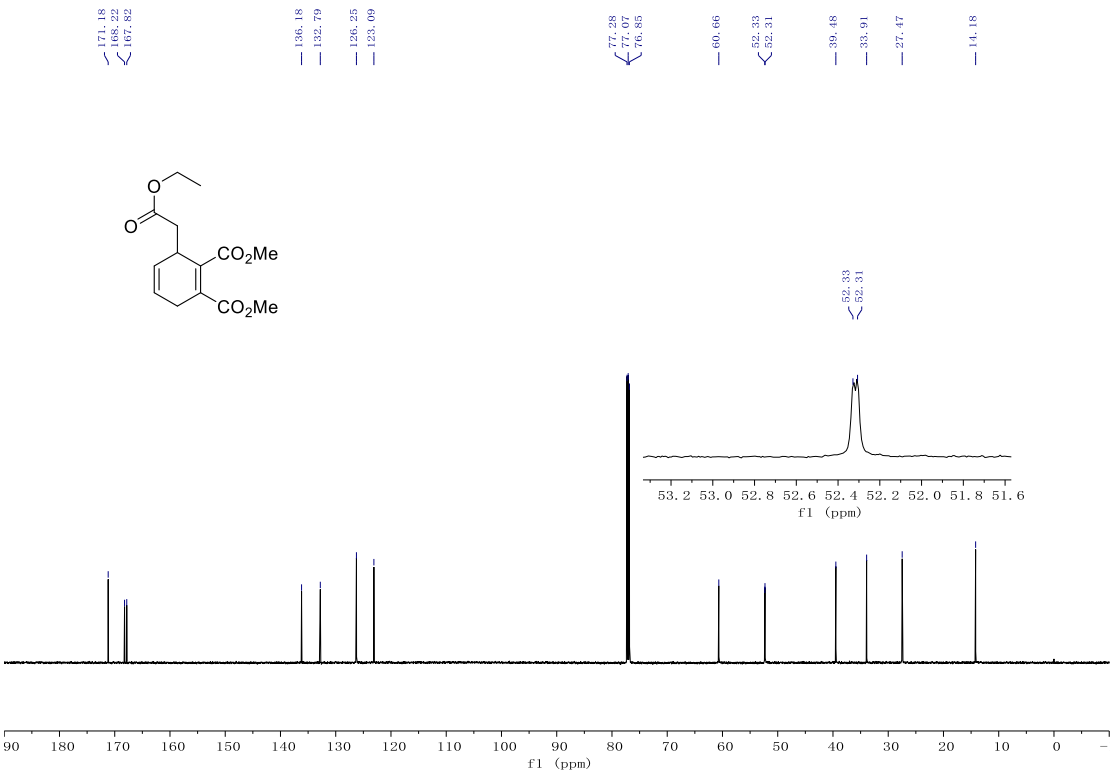

7.33
7.33
7.33
7.32
7.31
7.31
7.30
7.28
7.27
7.26
5.83
5.82
5.82
5.81
5.81
5.79
5.79
5.78
5.77
4.52
4.50
4.48
4.46
3.76
3.69
3.11
3.10
3.10
3.09
3.07
3.06
3.06
3.06
3.05
2.94
2.93
2.93
2.93
2.92
2.92
2.89
2.89
0.00
Bn
O
CO2Me
CO2Me
4.02
1.56
1.00
1.01
2.08
3.02
3.10
3.07
1.04
1.05
f1 (ppm)

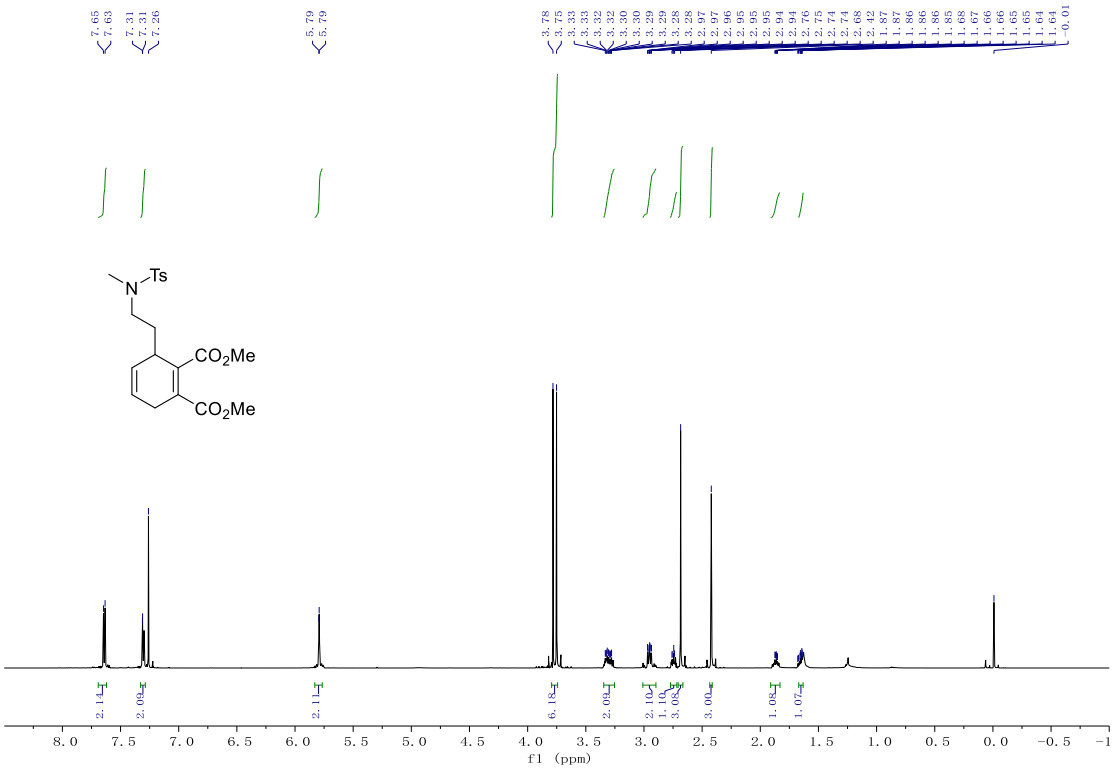

168.77
167.83
138.10
135.98
132.39
128.32
127.64
127.58
125.21
123.63
77.28
77.07
76.86
73.18
72.68
52.25
52.14
38.73
27.61
0.02
Bn
O
CO2Me
CO2Me
f1 (ppm)

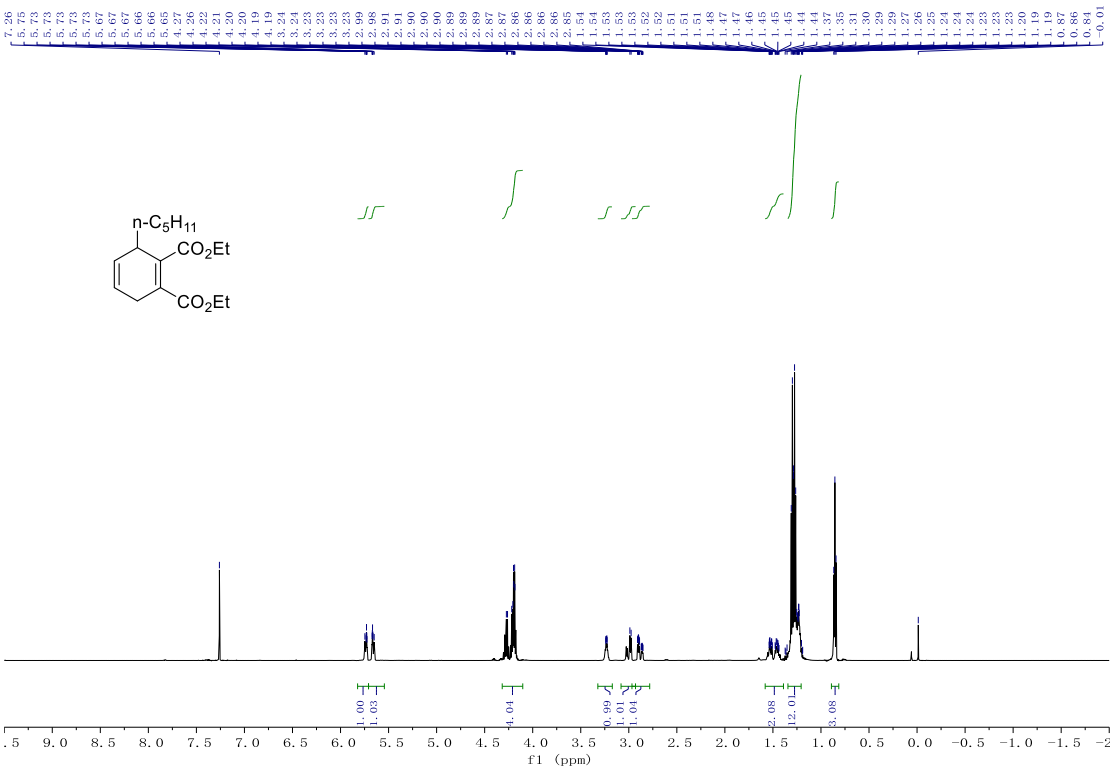

O
CO2Me
CO2Me
f1 (ppm)

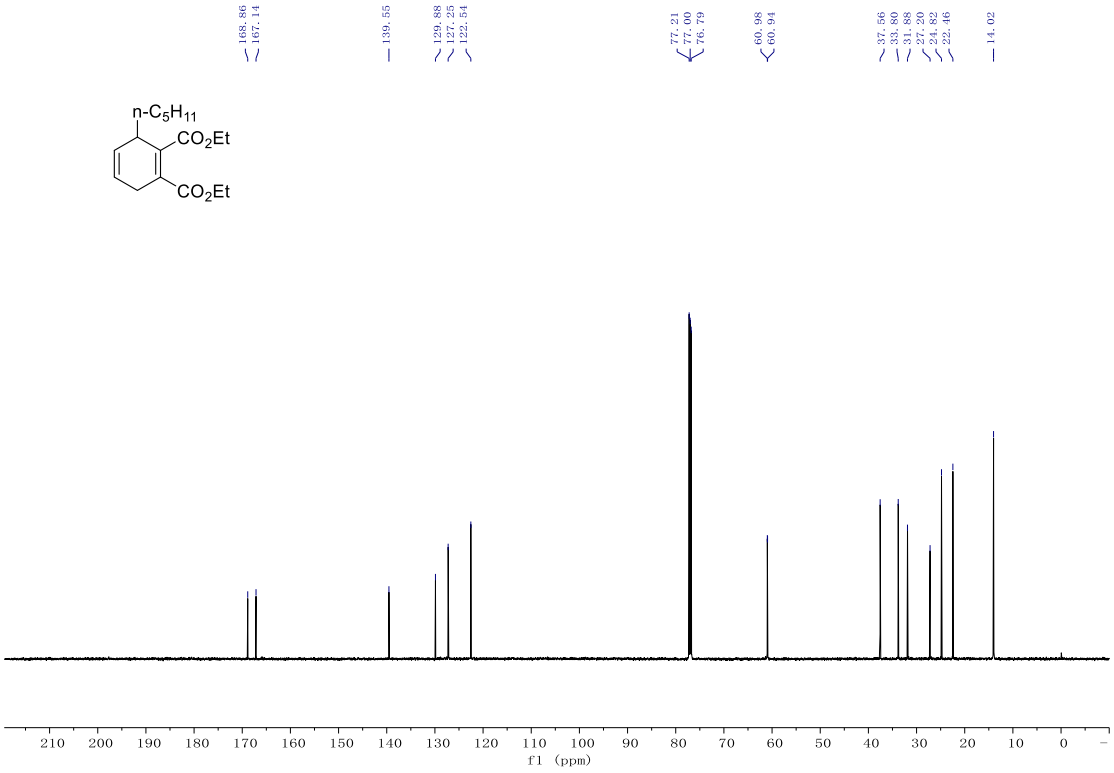

O
CO2Me
CO2Me
f1 (ppm)

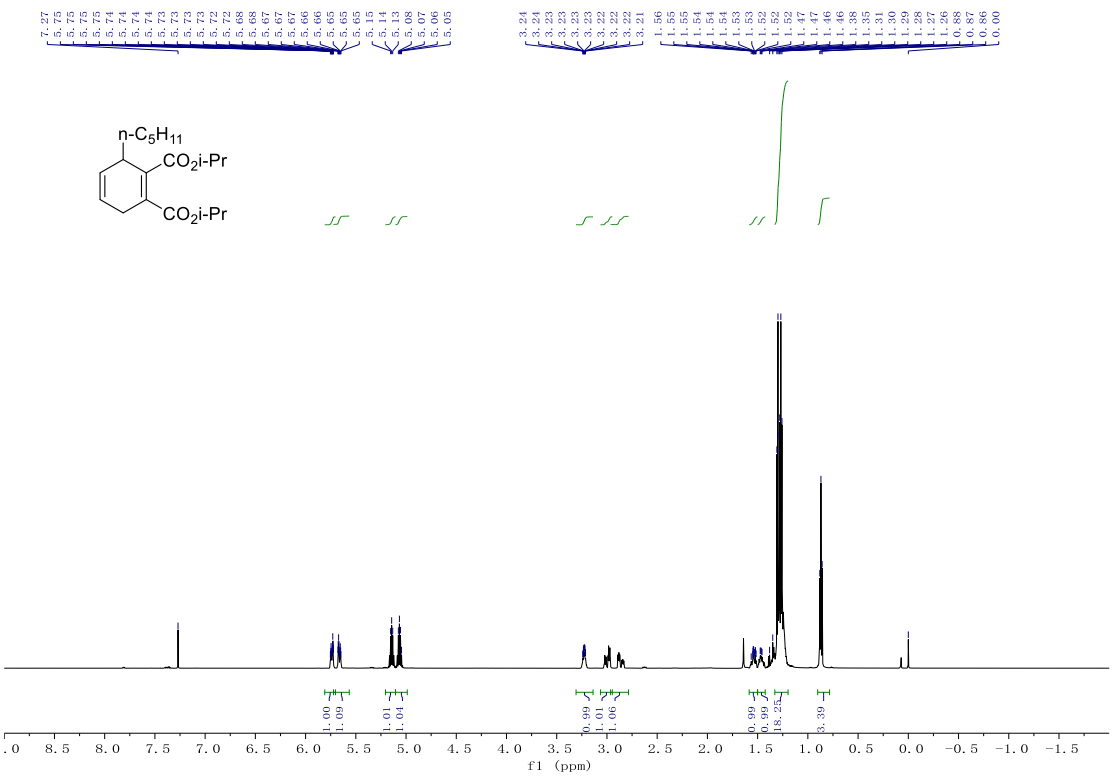

7.28
5.78
5.78
5.77
4.16
4.16
4.15
4.15
4.14
4.14
4.13
4.12
3.79
3.77
3.05
3.04
3.02
3.01
3.01
3.01
3.00
3.00
2.97
2.97
2.97
2.96
2.93
2.93
2.70
2.70
2.68
2.67
2.37
2.35
2.34
2.33
1.27
1.26
1.25
0.00
O
O
CO2Me
CO2Me
2.00
2.03
3.03
3.05
0.99
0.99
1.01
1.04
3.06
f1 (ppm)

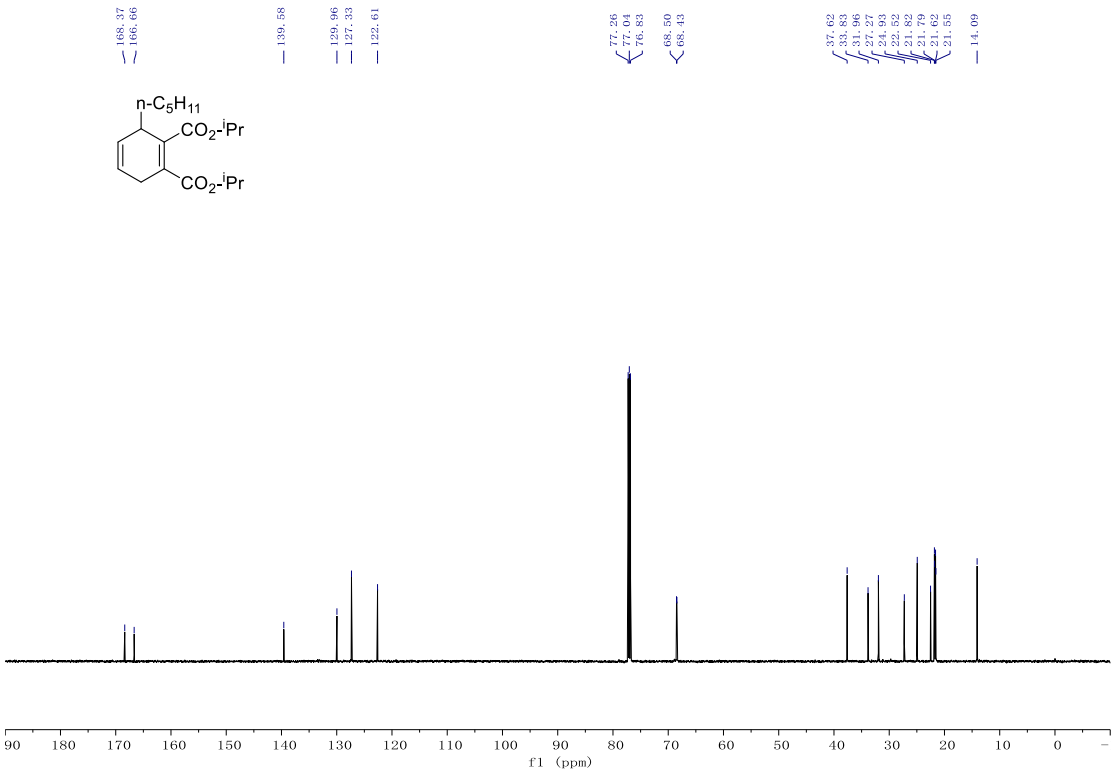

171.18
168.22
167.82
136.18
132.79
126.25
123.09
77.28
77.07
76.85
60.66
52.33
52.31
39.48
33.91
27.47
14.18
O
O
CO2Me
CO2Me
52.33
52.31
53.2 53.0 52.8 52.6 52.4 52.2 52.0 51.8 51.6
f1 (ppm)
f1 (ppm)

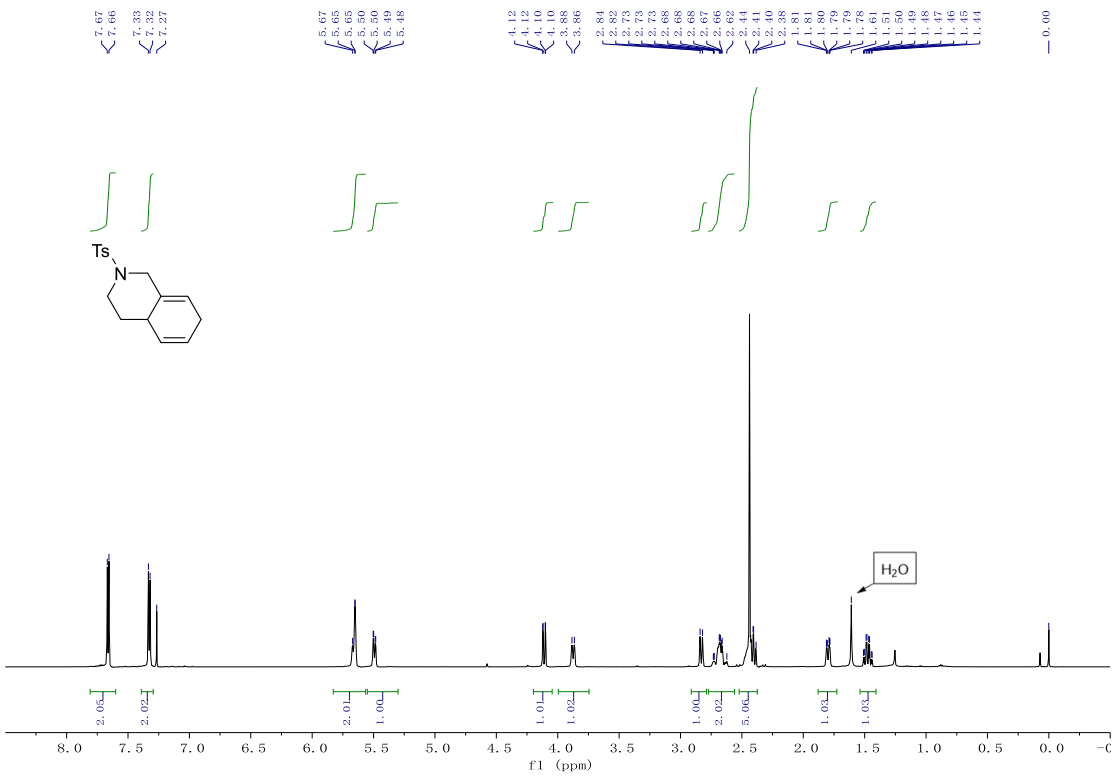

Ts
N
CO2Me
CO2Me
f1 (ppm)

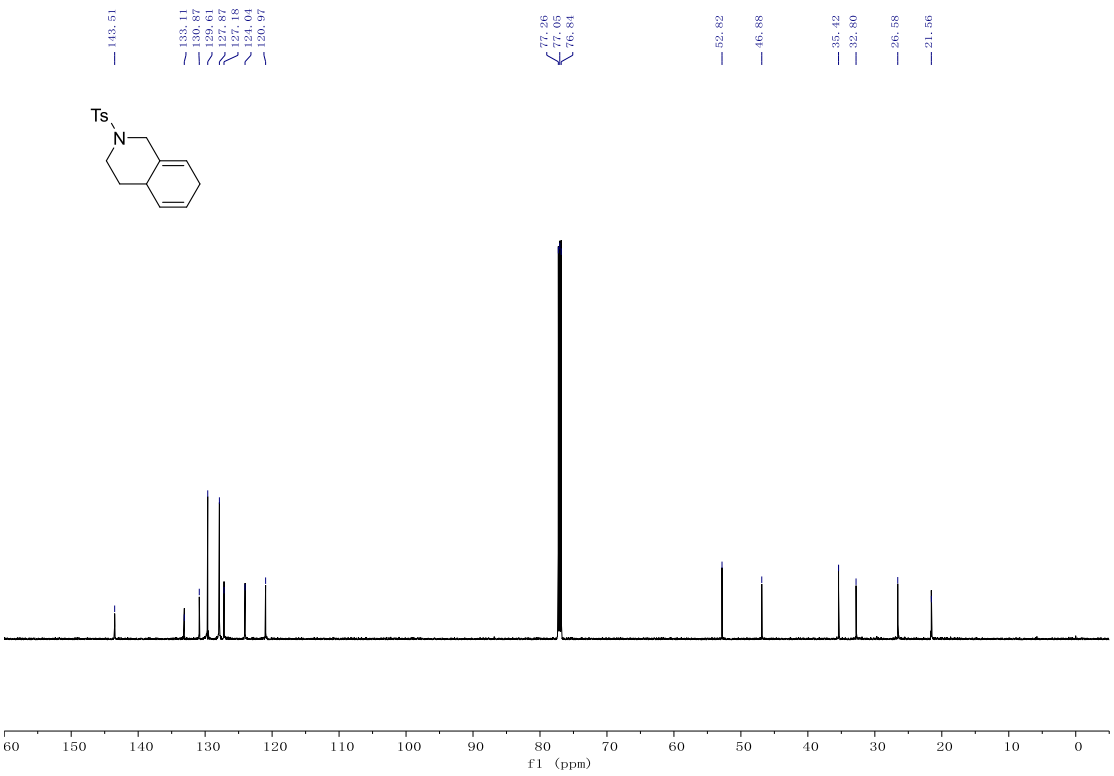

n-C5H11
CO2Et
CO2Et
f1 (ppm)

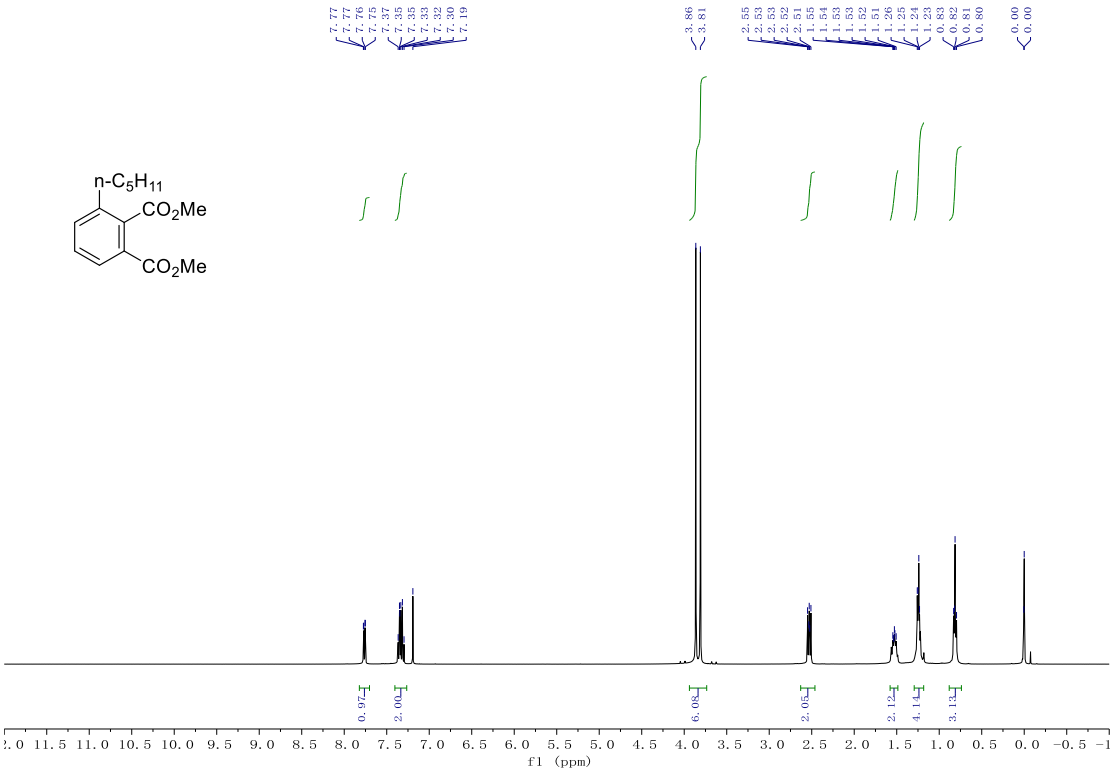

168.86
167.14
139.55
129.88
127.25
122.54
77.21
77.00
76.79
60.98
60.94
37.56
33.80
31.88
27.20
24.82
22.46
14.02
n-C5H11
CO2Et
CO2Et
f1 (ppm)

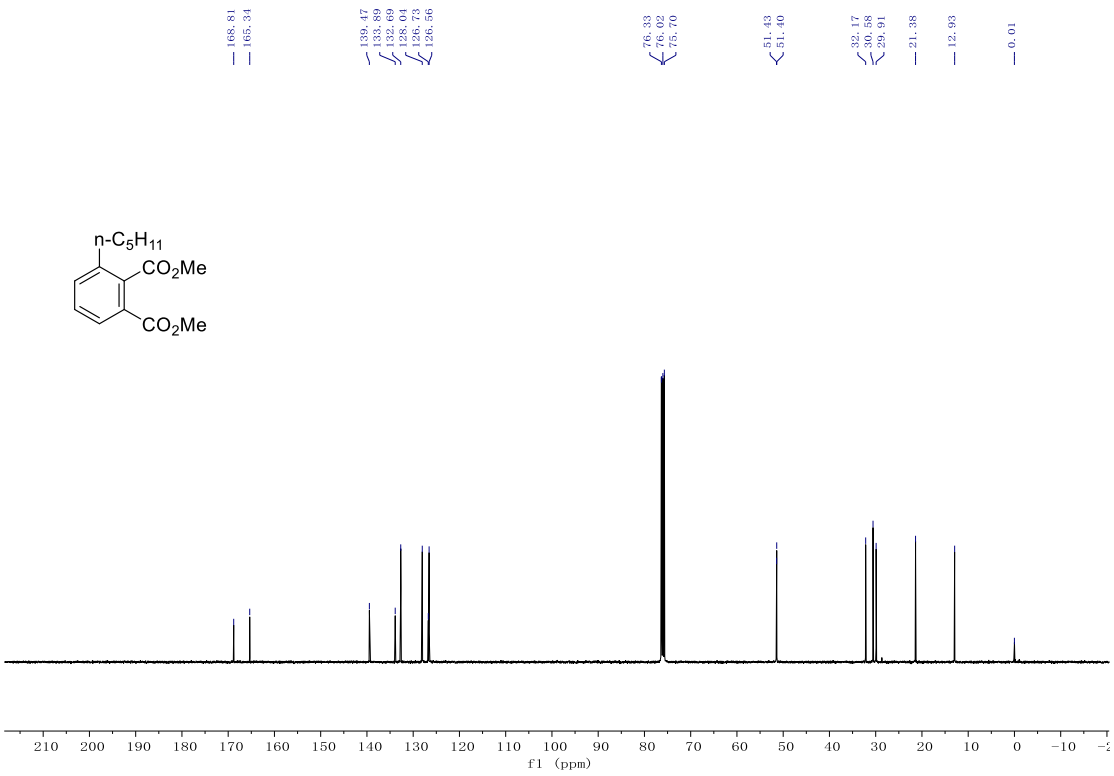

n-C5H11
CO2i-Pr
CO2i-Pr
f1 (ppm)

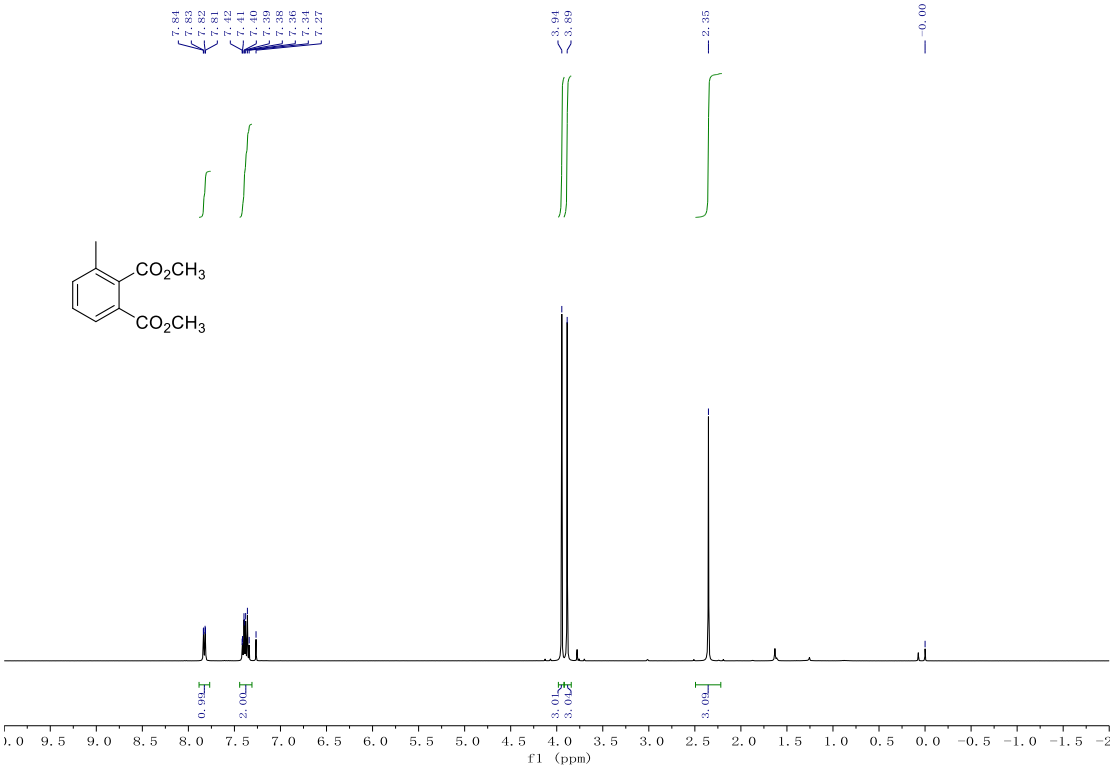

168.37
166.66
139.58
129.96
127.33
122.61
77.26
77.04
76.83
68.50
68.43
37.62
33.83
31.96
27.27
24.93
22.52
21.82
21.79
21.62
21.55
14.09
n-C5H11
CO2-iPr
CO2-iPr
f1 (ppm)

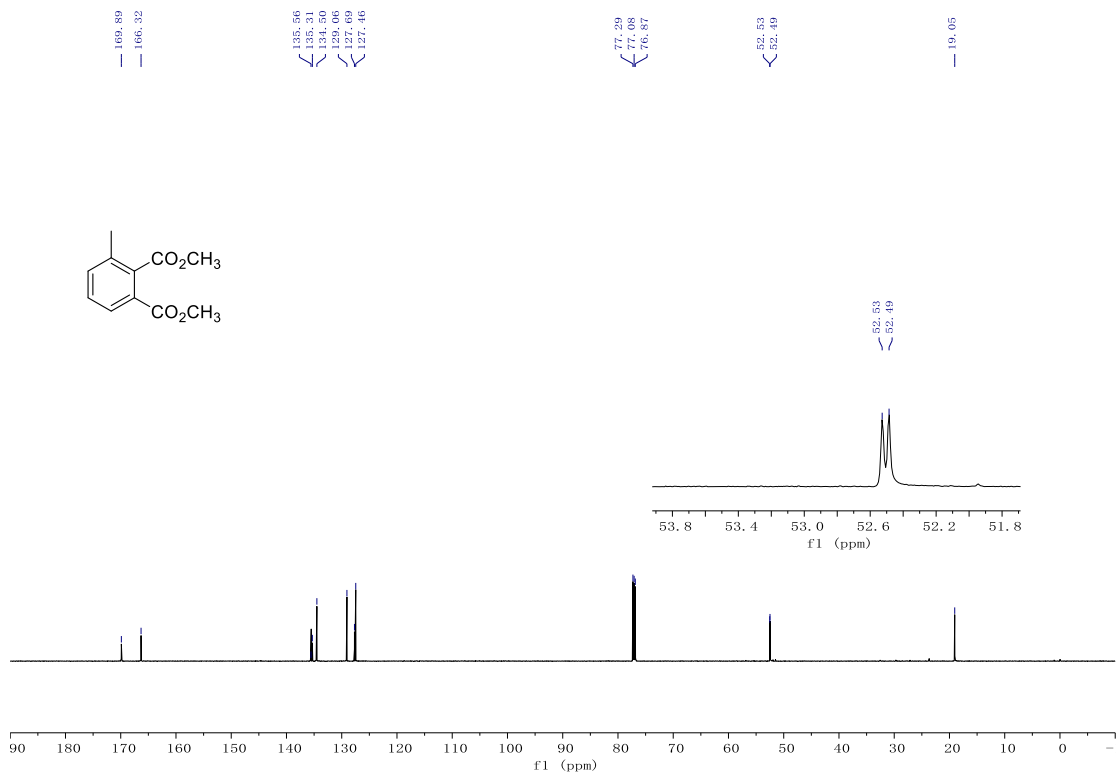

7.67
7.66
7.33
7.32
7.27
5.67
5.65
5.65
5.50
5.50
5.49
5.48
4.12
4.12
4.10
4.10
3.88
3.86
2.84
2.82
2.73
2.73
2.73
2.68
2.68
2.68
2.67
2.66
2.62
2.44
2.41
2.40
2.38
1.81
1.81
1.80
1.79
1.79
1.78
1.61
1.51
1.50
1.49
1.48
1.47
1.46
1.45
1.44
0.00
Ts
N
H2O
2.05
2.02
2.01
1.00
1.01
1.02
1.00
2.02
5.06
1.03
1.03
f1 (ppm)

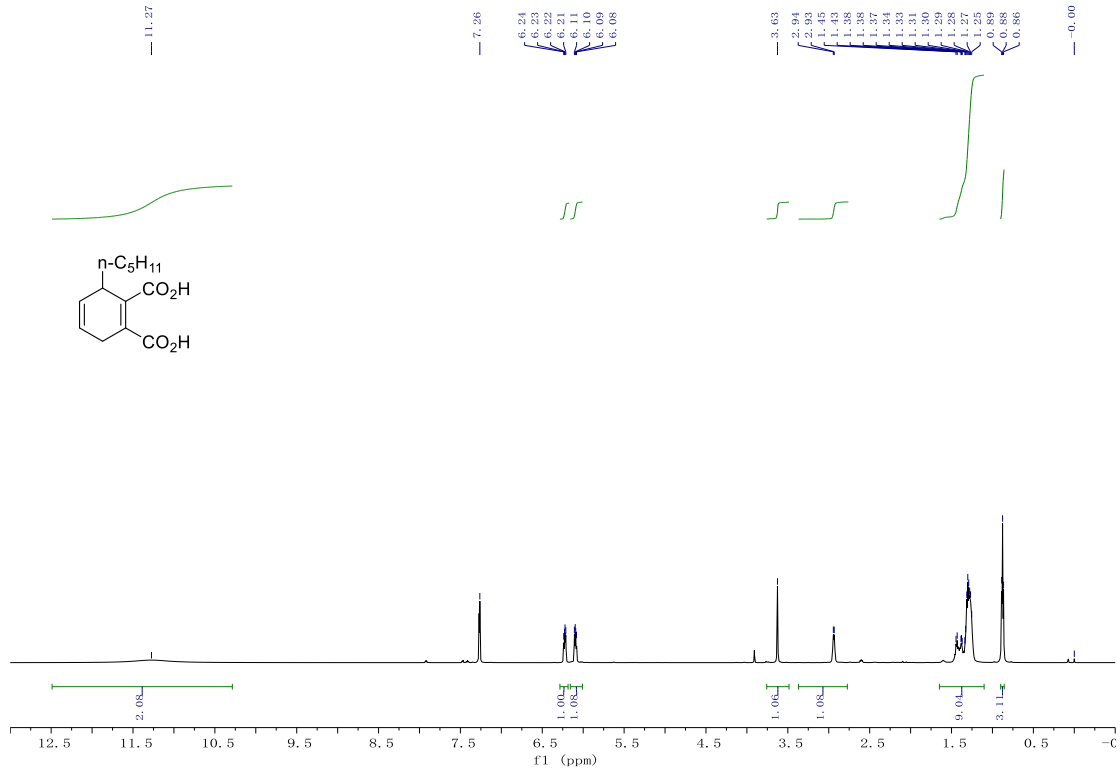

143.51
133.11
130.87
129.61
127.87
127.18
124.04
120.97
77.26
77.05
76.84
52.82
46.88
35.42
32.80
26.58
21.56
Ts
N
f1 (ppm)

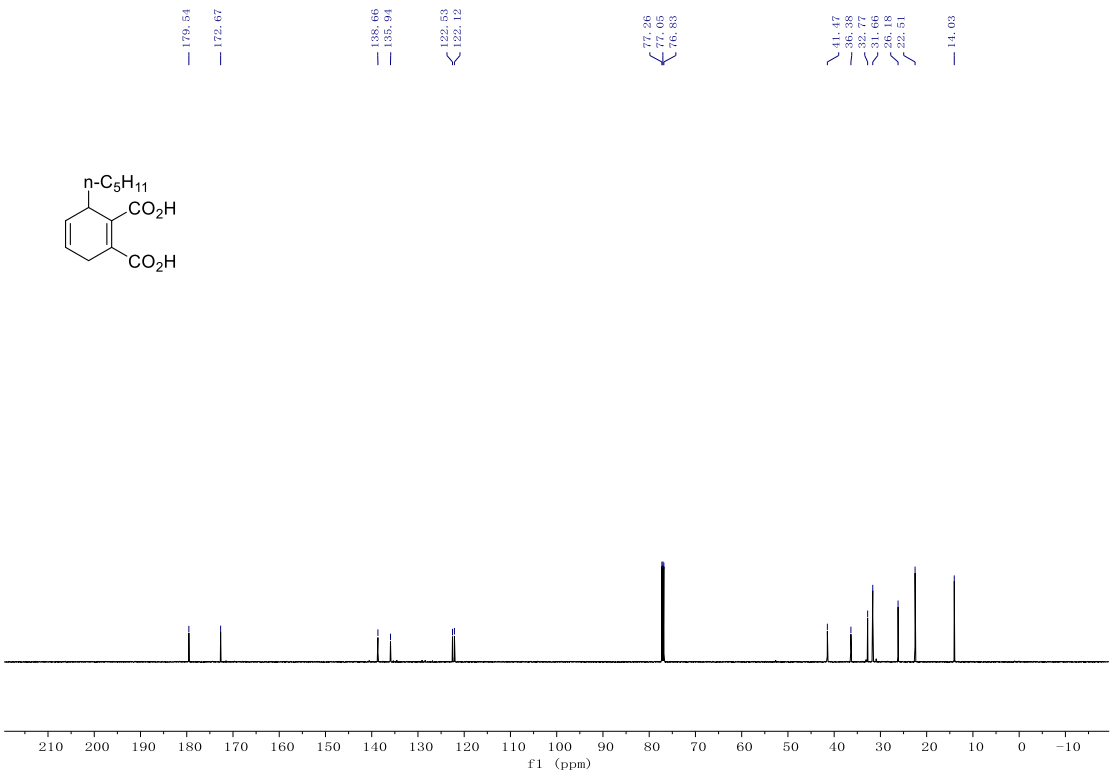

7.77
7.77
7.76
7.75
7.37
7.35
7.35
7.33
7.32
7.30
7.19
3.86
3.81
2.55
2.53
2.53
2.52
2.51
1.55
1.54
1.53
1.53
1.52
1.51
1.26
1.25
1.24
1.23
0.83
0.82
0.81
0.80
0.00
0.00
n-C5H11
CO2Me
CO2Me
0.97
2.00
6.08
2.05
2.12
4.14
3.13
f1 (ppm)


168.81
165.34
139.47
133.89
132.69
128.04
126.73
126.56
76.83
76.62
75.70
51.43
51.40
32.17
30.58
29.91
21.38
12.93
0.01
n-C5H11
CO2Me
CO2Me
f1 (ppm)


7.84
7.83
7.82
7.81
7.42
7.41
7.40
7.39
7.38
7.36
7.34
7.27
3.94
3.89
2.35
0.00
CO2CH3
CO2CH3
0.99
2.00
3.01
3.02
3.09
f1 (ppm)


169.89
166.32
135.56
135.31
134.50
129.06
127.69
127.46
77.29
77.08
76.87
52.53
52.49
19.05
CO2CH3
CO2CH3
52.53
52.49
53.8
53.4
53.0
52.6
52.2
51.8
f1 (ppm)
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


11.27
7.26
6.24
6.23
6.22
6.21
6.11
6.10
6.09
6.08
3.63
2.94
2.93
1.45
1.43
1.38
1.37
1.34
1.33
1.31
1.30
1.29
1.28
1.27
1.25
0.89
0.88
0.86
-0.00
n-C5H11
CO2H
CO2H
2.08
1.00
1.08
1.06
1.08
9.04
3.11
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)


179.54
172.67
138.66
135.94
122.53
122.12
77.26
77.05
76.83
41.47
36.38
32.77
31.66
26.18
22.51
14.03
n-C5H11
CO2H
CO2H
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)