Supporting Information for

Access to Chiral Tetrahydrofluorenes through Palladium-Catalyzed Enantioselective Tandem Intramolecular Heck/Tsuji–Trost Reaction

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1. General Data

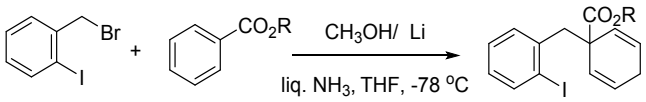
NMR spectra were recorded on a Bruker-400 MHz spectrometer.Chemical shifts (δ) are given in ppm relative to TMS. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δH = 7.26 ppm, δC = 77.16 ppm). Optical rotations were determined at 589 nm (sodium D line) by using a Perkin-Elmer-343 polarimeter. The high resolution mass spectra were recorded on a Thermo LTQ Orbitrap XL (ESI+) or a P-SIMS-Gly of Bruker DaltonicsInc (EI+). HPLC analysis was performed on Waters-Breeze (2487 Dual λ Absorbance Detector and 1525 Binary HPLC Pump). Chiralpak IC, ID, IE columns were purchased from Daicel Chemical Industries, LTD. Infrared spectra were recorded on a Nicolet MX-1E FT-IR spectrometer. The absolute configuration of **4ah** was assigned by X-ray analysis of the single crystal. The absolute configuration of **3hb** was assigned by X-ray analysis of the single crystal of its derivative **12**.

Materials:

Analytical grade solvents for the column chromatography were used as received. Starting materials were purchased from commercial suppliers (Aldrich, Alfa, TCI, Adamas-beta, Energychemical, and Accela) and used as supplied unless otherwise stated. All solvents were purified and dried according to standard methods prior to use, unless stated otherwise. $Pd(dba)_2$ was purchased from Aldrich. Ligands **L1-5** were prepared by following the literature report.[1]

2. Preparation of Starting Materials

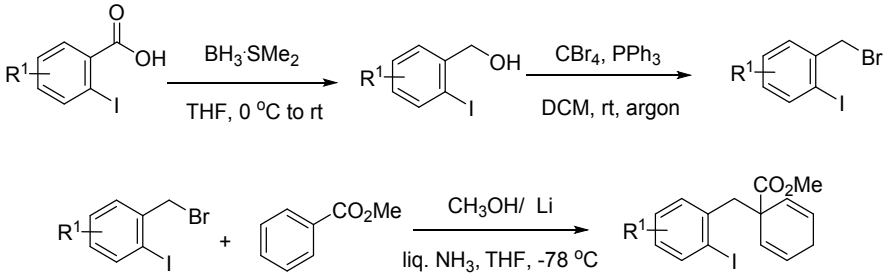
Preparation of **6a**, **6l**, **6m**.



Birch reduction-alkylation procedure:

To a solution of benzoate (1.0 equiv), MeOH (1.1 equiv) and THF (0.5 mL/mmol) in liq. NH_3 (7ml/mol) was added lithium wire (3.3 equiv) at -78 °C under a nitrogen atmosphere. After being stirred for 10 min, 1-(bromomethyl)-2-iodobenzene (1.1 equiv) in THF (0.43 mL/mmol) was added slowly dropwise at the same temperature. After additional 20 min, the reaction mixture was quenched with saturated aqueous NH_4Cl. After removal of NH_3 at rt, the solution was extracted with AcOEt. The organic phase was washed with brine, dried over $MgSO_4$, and concentrated in vacuo and purified with flash chromatography on silica gel (petroleum ether/ethyl acetate =150:1).

Preparation of **6b-d**,**6f-k.**



General carboxylic acid reduction procedure:

A flame-dried flask with a stir bar, under argon was charged with commercially available *o*-

iodobenzoic acid (1.0 equiv) which was dissolved in THF(1 mL/mmol). Boran–dimethylsulfide complex was added slowly at 0 °C. After stirring for 15 h at room temperature, phosphate buffer (pH 7) was added. Organic materials were extracted with ethyl acetate three times. The combined extracts were washed with brine and dried over anhydrous sodium sulfate. After removal of the solvent under reduced pressure, *o*-iodobenzylalcohol was obtained and used for the next step without further purifcation.

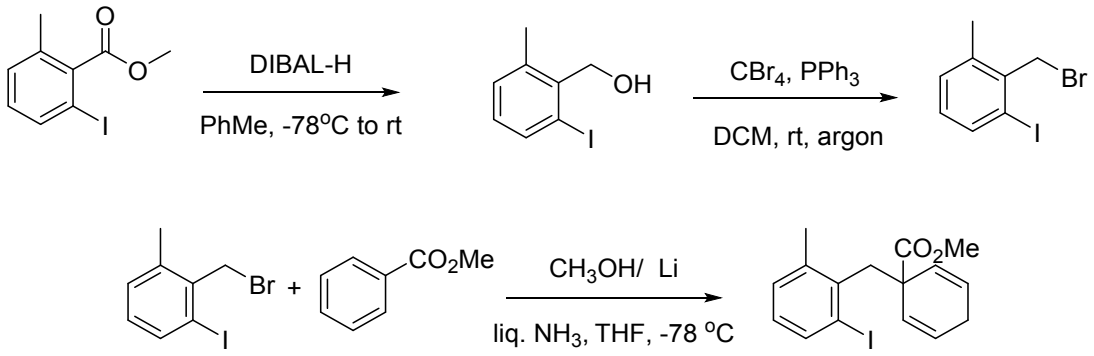
General bromination procedure:

A flame-dried flask with a stir bar, under argon was charged with alcohol (1.0 equiv) and PPh_3 (1.2 equiv) which was then dissolved in DCM (1mL/mmol). A separate flame-dried flask under argon was charged with CBr_4 (1.2 equiv) which was dissolved in DCM (0.5 mL/mmol). The alcohol flask was cooled to 0 °C and the CBr_4 solution was added dropwise with stirring. The solution was warmed to room temperature and monitored by TLC. Once complete the reaction was concentrated in vacuo and purified with flash chromatography on silica gel (petroleum ether).

Birch reduction-alkylation procedure:

To a solution of methyl benzoate (1.0 equiv), MeOH (1.1 equiv) and THF (0.5 mL/mmol) in liq. NH_3 (7ml/mmol) was added lithium wire (3.3 equiv) at -78 °C under a nitrogen atmosphere. After being stirred for 10 min, Alkylating agent (1.1 equiv) in THF (0.43 mL/mmol) was added slowly dropwise at the same temperature. After additional 20 min, the reaction mixture was quenched with saturated aqueous NH_4Cl. After removal of NH_3 at rt, the solution was extracted with AcOEt. The organic phase was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The crude product was purified with flash chromatography on silica gel(petroleum ether/ethyl acetate =150:1).

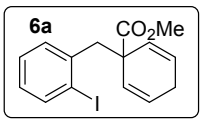
Preparation of **6e.**



DIBAL-H (3.0 equiv, 1.5 M in PhMe) was added dropwise to a stirred and cooled (−78 °C) solution of methyl 2-iodo-6-methylbenzoate (1.0 equiv) in PhMe (4 mL/mmol). The reaction was stirred for 2.25 h. Then the cooling bath was removed, and stirring was continued for 15 min. The mixture was quenched with saturated aqueous NH_4Cl and extracted with Et_2O. The combined organic extracts were dried ($MgSO_4$) and evaporated to give (2-iodo-6-methylphenyl)methanol. The following steps are the same as above.

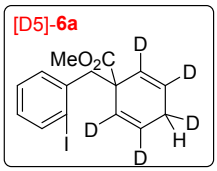
3. Analytical data for the Substrates

methyl 1-(2-iodobenzyl)cyclohexa-2,5-diene-1-carboxylate (6a)



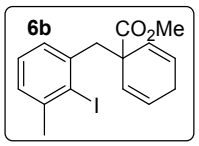
(Flash column chromatography eluent, petroleum ether/ethyl acetate = 150 : 1) **Yield**: 86%, 1.52 g; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.23 – 7.12 (m, 2H), 6.86 (ddd, *J* = 7.9, 6.8, 2.3 Hz, 1H), 5.97 – 5.89 (m, 2H), 5.85 – 5.77 (m, 2H), 3.74 (s, 3H), 3.26 (s, 2H), 2.51 (m, 1H), 2.33 – 2.21 (m, 1H);**^{13}C NMR** (101 MHz, CDCl3) δ 174.76, 139.96, 139.65, 131.01, 128.26, 127.60, 126.59, 126.51, 103.63, 52.54, 49.67, 48.80, 25.97; **IR** (KBr, cm^{-1}) *γ* 3033, 2942, 2893, 1724, 1583, 1460, 1310, 1265, 1208, 1173, 1121, 1035, 745, 695 cm^{-1}; **HRMS** (ESI) m/z $(M+H)^+$: calculated for $C_{15}H_{16}IO_2$: 355.0195, found: 355.0194.

((λ^1-methyl)peroxy)methane compound with 1-iodo-2-((1-methylcyclohexa-2,5-dien-1-yl-2,3,4,5,6-d$_5$)methyl)benzene (1:1) ([D5]**-6a)**



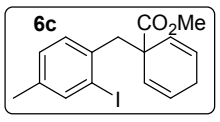
(Flash column chromatography eluent, petroleum ether/ethyl acetate = 150 : 1) **Yield**: 78%, 1.40 g; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.23 – 7.13 (m, 2H), 6.86 (ddd, *J* = 7.9, 6.9, 2.2 Hz, 1H), 3.74 (s, 3H), 3.26 (s, 2H), 2.51 – 2.44 (m, 0.5H), 2.27 – 2.19 (m, 0.5H); **HRMS** (ESI) m/z $(M+Na)^+$: calculated for $C_{15}H_{10}D_5INaO_2$: 382.0328, found:382.0336.

methyl 1-(2-iodo-3-methylbenzyl)cyclohexa-2,5-diene-1-carboxylate (6b)



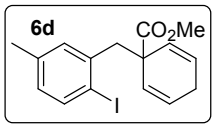
(Flash column chromatography eluent, petroleum ether/ethyl acetate = 150 : 1) Yield: 60%, 1.10g; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.06 (t, *J* = 4.0 Hz, 2H), 7.00 – 6.94 (m, 1H), 5.93 (dt, *J* = 10.5, 2.0 Hz, 2H), 5.85 – 5.76 (m, 2H), 3.73 (s, 3H), 3.38 (s, 2H), 2.57 – 2.48 (m, 1H), 2.48 (d, *J* = 2.6 Hz, 3H), 2.33 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.73, 142.21, 140.59, 127.95, 127.83, 126.93, 126.75, 126.14, 111.00, 52.41, 49.85, 49.51, 30.87, 25.95; **IR** (KBr, cm^{-1}) γ 3035, 2949, 2813, 1728, 1574, 1435, 1406, 1380, 1232, 1204, 1173, 1118, 1049, 1008, 782, 734, 715, 696 cm^{-1}; **HRMS** (ESI) m/z $(M+H)^+$: calculated for $C_{16}H_{18}IO_2$: 369.0351, found: 369.0348.

methyl 1-(2-iodo-4-methylbenzyl)cyclohexa-2,5-diene-1-carboxylate (6c)



(Flash column chromatography eluent, petroleum ether/ethyl acetate = 150 : 1) **Yield**: 30%, 0.55g; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.0 Hz, 1H), 6.98 (d, *J* = 2.0 Hz, 1H), 6.69 (dd, *J* = 8.0, 2.2 Hz, 1H), 5.91 (dt, *J* = 10.5, 1.9 Hz, 2H), 5.85 – 5.78 (m, 2H), 3.74 (s, 3H), 3.21 (s, 2H), 2.52 (ddd, *J* = 7.0, 3.6, 1.8 Hz, 1H), 2.31 (dtd, *J* = 5.2, 3.0, 1.5 Hz, 1H), 2.23 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.74, 139.57, 139.27, 137.38, 131.81, 129.29, 126.70, 126.25, 99.47, 52.43, 49.56, 48.70, 26.00, 20.97; **IR** (KBr, cm^{-1}) *γ* 3033, 2949, 1728, 1433, 1402, 1231, 1203, 1176, 1116, 1051, 1011, 807, 743, 713, 692 cm^{-1}; **HRMS** (ESI) m/z $(M+H)^+$: calculated for $C_{16}H_{18}IO_2$: 369.0351, found: 369.0352.

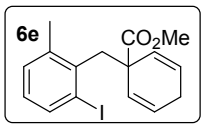
methyl 1-(2-iodo-5-methylbenzyl)cyclohexa-2,5-diene-1-carboxylate (6d)



(Flash column chromatography eluent, petroleum ether/ethyl acetate = 150 : 1) **Yield**: 68%, 1.25 g; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.0 Hz, 1H), 6.98 (d, *J* = 2.0 Hz, 1H), 6.70 (dd, *J* = 8.0, 2.0 Hz, 1H), 5.96 – 5.87 (m, 2H), 5.85 – 5.79 (m, 2H), 3.74 (s, 3H), 3.21 (s, 2H), 2.52 (m, 1H), 2.37 – 2.26 (m, 1H), 2.23 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl^3$) δ 174.81, 139.62, 139.32, 137.43, 131.86,

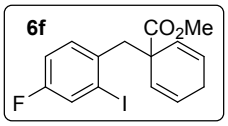
129.33, 126.74, 126.30, 99.50, 52.47, 49.60, 48.74, 26.03, 21.00; **IR** (KBr, cm^{-1}) γ 3033, 2949, 2923, 1724, 1601, 1468, 1435, 1279, 1238, 1204, 1177, 1012, 809, 714cm^{-1}; **HRMS** (ESI) m/z $(M+H)^+$: calculated for $C_{16}H_{18}IO_2$: 369.0351, found: 369.0359.

methyl 1-(2-iodo-6-methylbenzyl)cyclohexa-2,5-diene-1-carboxylate (6e)



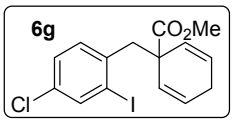
(Flash column chromatography eluent, petroleum ether/ethyl acetate = 150 : 1) **Yield**: 70%, 1.29g; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (dt, *J* = 7.9, 4.1 Hz, 1H), 7.07 (d, *J* = 7.5 Hz, 1H), 6.76 (dd, *J* = 9.7, 5.7 Hz, 1H), 5.94 (dt, *J* = 10.4, 1.9 Hz, 2H), 5.85 – 5.70 (m, 2H), 3.74 (s, 3H), 3.45 (s, 2H), 2.51 (dtt, *J* = 23.0, 3.7, 1.8 Hz, 1H), 2.39 – 2.28 (m, 4H); **^{13}C NMR** (101 MHz, CDCl3) δ 175.14, 139.34, 138.56, 137.84, 130.60, 128.20, 127.42, 125.65, 105.18, 52.63, 48.36, 47.05, 25.78, 22.76; **IR** (KBr, cm^{-1}) γ 2948, 1729, 1557, 1446, 1234, 1202, 1112, 1042, 769, 692 cm^{-1}; **HRMS** (ESI) m/z $(M+H)^+$: calculated for $C_{16}H_{18}IO_2$: 369.0351, found: 369.0350.

methyl 1-(4-fluoro-2-iodobenzyl)cyclohexa-2,5-diene-1-carboxylate (6f)



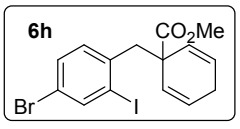
(Flash column chromatography eluent, petroleum ether/ethyl acetate = 150 : 1) Yield: 35%,0.65 g; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 (dd, J = 8.2, 2.7 Hz, 1H), 7.12 (dd, J = 8.6, 6.0 Hz, 1H), 6.93 (td, J = 8.3, 2.7 Hz, 1H), 5.90 (dt, J = 10.5, 2.0 Hz, 2H), 5.81 (ddd, J = 6.5, 5.0, 2.6 Hz, 2H), 3.74 (s, 3H), 3.22 (s, 2H), 2.51 (m, 1H), 2.32 – 2.17 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.64, 160.66 (d, J = 250.4 Hz), 135.91 (d, J = 3.5 Hz), 131.31 (d, J = 7.8 Hz), 126.73, 126.37, 126.13, 114.62 (d, J = 20.6 Hz), 102.43 (d, J = 7.9 Hz), 52.59, 49.72, 49.71, 47.64, 25.95; **IR** (KBr, cm^{-1}) γ 3033, 2950, 2864, 1731, 1592, 1580, 1482, 1434, 1224, 1046, 1029, 944, 867, 822, 805, 740, 713, 685 cm^{-1}; **HRMS** (ESI) m/z $(M+H)^+$: calculated for $C_{15}H_{15}FIO_2$: 373.0101, found: 373.0095.

methyl 1-(4-chloro-2-iodobenzyl)cyclohexa-2,5-diene-1-carboxylate (6g)



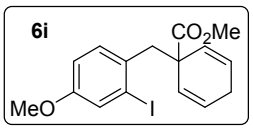
(Flash column chromatography eluent, petroleum ether/ethyl acetate = 150 : 1) **Yield**: 39%, 0.76 g; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 2.2 Hz, 1H), 7.17 (dd, *J* = 8.3, 2.2 Hz, 1H), 7.08 (d, *J* = 8.3 Hz, 1H), 5.92 – 5.86 (m, 2H), 5.85 – 5.78 (m, 2H), 3.73 (s, 3H), 3.21 (s, 2H), 2.50 (m, 1H), 2.31 – 2.20 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.50, 138.69, 138.59, 132.77, 131.34, 127.66, 126.79, 126.25, 103.28, 52.58, 49.64, 47.87, 25.92; **IR** (KBr, cm^{-1}) γ 3033, 2949, 2813, 1731, 1578, 1550, 1465, 1433, 1233, 1203, 1173, 1103, 1046, 1028, 795,708 cm^{-1}; **HRMS** (ESI) m/z $(M+H)^+$: calculated for $C_{15}H_{15}ClIO_2$: 388.9805, found: 388.9796.

methyl 1-(4-bromo-2-iodobenzyl)cyclohexa-2,5-diene-1-carboxylate (6h)



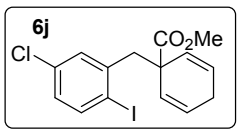
(Flash column chromatography eluent, petroleum ether/ethyl acetate = 150 : 1) **Yield**: 57%,1.23 g; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 2.1 Hz, 1H), 7.32 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.03 (d, *J* = 8.3 Hz, 1H), 5.89 (dt, *J* = 10.5, 1.9 Hz, 2H), 5.82 (ddd, *J* = 8.5, 5.6, 3.3 Hz, 2H), 3.74 (s, 3H), 3.21 (s, 2H), 2.51 (m, 1H), 2.33 – 2.21 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.58, 141.40, 139.13, 131.86, 130.64, 126.88, 126.27, 120.83, 103.86, 52.66, 49.66, 48.01, 25.97; **IR** (KBr, cm^{-1}) γ 3033, 2949, 2813, 1730, 1573, 1481, 1463, 1433, 1233, 1203, 1024, 794, 739, 697 cm^{-1}; **HRMS** (ESI) m/z $(M+H)^+$: calculated for $C_{15}H_{15}BrIO_2$: 432.9300, found: 432.9316.

methyl 1-(2-iodo-4-methoxybenzyl)cyclohexa-2,5-diene-1-carboxylate (6i)



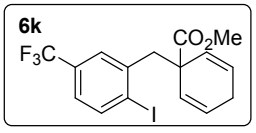
(Flash column chromatography eluent, petroleum ether/ethyl acetate = 150 : 1) **Yield**: 30%,0.58 g; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 2.7 Hz, 1H), 7.05 (d, *J* = 8.6 Hz, 1H), 6.76 (dd, *J* = 8.6, 2.7 Hz, 1H), 5.91 (dt, *J* = 10.5, 1.9 Hz, 2H), 5.84 – 5.77 (m, 2H), 3.75 (s, 3H), 3.73 (s, 3H), 3.19 (s, 2H), 2.51 (m, 1H), 2.35 – 2.24 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.81, 158.29, 131.99, 130.93, 126.69, 126.37, 124.34, 113.91, 103.30, 55.48, 52.47, 49.70, 47.88, 25.99; **IR** (KBr, cm^{-1}) *γ* 3031, 2949, 1729, 1597, 1561, 1490, 1438, 1285, 1236, 1202, 1037, 1020, 858, 801, 713, 687 cm^{-1}; **HRMS** (ESI) m/z $(M+H)^+$: calculated for $C_{16}H_{18}IO_3$: 385.0301, found: 385.0294.

methyl 1-(5-chloro-2-iodobenzyl)cyclohexa-2,5-diene-1-carboxylate (6j)



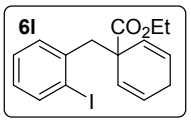
(Flash column chromatography eluent, petroleum ether/ethyl acetate = 150 : 1) **Yield**: 68%, 1.32g; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.4 Hz, 1H), 7.16 (d, *J* = 2.6 Hz, 1H), 6.87 (dd, *J* = 8.4, 2.6 Hz, 1H), 5.92 – 5.81 (m, 4H), 3.75 (s, 3H), 3.21 (s, 2H), 2.52 (m, 1H), 2.34 – 2.22 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.44, 141.85, 140.40, 133.74, 130.84, 128.40, 126.88, 126.18, 100.57, 52.62, 49.62, 48.38, 25.95; **IR** (KBr, cm^{-1}) *γ* 2949, 1728, 1637, 1456, 1405, 1297, 1234, 1172, 1106, 1047, 1011, 945, 885, 798, 739,700 cm^{-1}; **HRMS** (ESI) m/z $(M+H)^+$: calculated for $C_{15}H_{15}ClIO_2$: 388.9805, found: 388.9799.

methyl 1-(2-iodo-5-(trifluoromethyl)benzyl)cyclohexa-2,5-diene-1-carboxylate (6k)



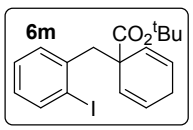
(Flash column chromatography eluent, petroleum ether/ethyl acetate = 150 : 1) **Yield**: 40%, 0.84g; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.2 Hz, 1H), 7.42 (d, *J* = 2.0 Hz, 1H), 7.11 (dd, *J* = 8.3, 2.0 Hz, 1H), 5.91 (dt, *J* = 10.5, 1.9 Hz, 2H), 5.82 (ddd, *J* = 6.5, 5.0, 2.6 Hz, 2H), 3.76 (s, 3H), 3.30 (s, 2H), 2.49 (m, 1H), 2.22 – 2.12 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.41, 141.19, 140.09, 129.98 (q, *J* = 32.7 Hz), 127.34 (q, *J* = 3.7 Hz), 127.13, 126.04, 124.54 (q, *J* = 3.7 Hz), 124.02 (q, *J* = 272.2 Hz),107.80, 52.66, 49.77, 48.37, 25.90; **IR** (KBr, cm^{-1}) *γ* 3035, 2952, 2865, 1731, 1602, 1435, 1403, 1333, 1275, 1237, 1168, 1129, 1083, 1013, 897, 824, 798, 744, 701,655 cm^{-1}; **HRMS** (ESI) m/z $(M+H)^+$: calculated for $C_{16}H_{15}F_3IO_2$: 423.0069, found: 423.0066.

ethyl 1-(2-iodobenzyl)cyclohexa-2,5-diene-1-carboxylate (6l)



(Flash column chromatography eluent, petroleum ether/ethyl acetate = 150 : 1) **Yield**: 80%, 1.47 g; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.7 Hz, 1H), 7.22 – 7.15 (m, 2H), 6.86 (ddd, *J* = 8.0, 5.3, 3.7 Hz, 1H), 5.93 (dq, *J* = 10.5, 1.9 Hz, 2H), 5.85 – 5.76 (m, 2H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.25 (s, 2H), 2.49 (m, 1H), 2.33 – 2.20 (m, 1H), 1.28 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.28, 140.06, 139.61, 131.00, 128.21, 127.56, 126.71, 126.41, 103.67, 61.30, 49.61, 48.82, 26.00, 14.27; **IR** (KBr, cm^{-1}) *γ* 3033, 2979, 2929, 1719, 1561, 1465, 1231, 1201, 1178, 1110, 1042, 1011, 750, 732, 694 cm^{-1}; **HRMS** (ESI) m/z $(M+H)^+$: calculated for $C_{16}H_{18}IO_2$: 369.0351, found: 369.0358.

tert-butyl 1-(2-iodobenzyl)cyclohexa-2,5-diene-1-carboxylate (6m)

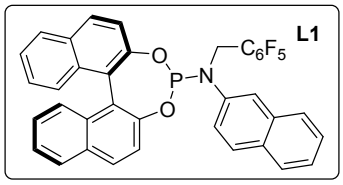


(Flash column chromatography eluent, petroleum ether/ethyl acetate = 150 : 1)

Yield: 70%, 1.39 g; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.24 – 7.15 (m, 2H), 6.85 (ddd, *J* = 7.9, 7.2, 2.0 Hz, 1H), 5.91 (dt, *J* = 10.5, 2.0 Hz, 2H), 5.82 – 5.72 (m, 2H), 3.22 (s, 2H), 2.47 (dtt, *J* = 22.9, 3.6, 1.8 Hz, 1H), 2.26 – 2.15 (m, 1H), 1.54 – 1.43 (m, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.52, 140.35, 139.53, 130.94, 128.10, 127.51, 127.00, 126.23, 103.86, 81.26, 50.46, 48.68, 28.14, 26.02; **IR** (KBr, cm^{-1}) *γ* 3034, 2977, 2930, 2813, 1724, 1585, 1561, 1470, 1368, 1248, 1157, 1116, 1011, 846, 748, 731, 694 cm^{-1}; **HRMS** (ESI) m/z $(M+Na)^+$: calculated for $C_{18}H_{21}INaO_2$: 419.0484, found: 419.0481.

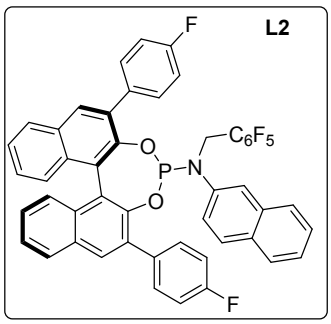
Analytical data for the Ligands

N-(naphthalen-2-yl)-N-(7,7,7,7,7-pentafluoro-7l8-hepta-2,4,6-triyn-1-yl)dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-amine (L1)



(Flash column chromatography eluent, petroleum ether/ethyl acetate = 100 : 1) **Yield**: 60%,0.38g; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.8 Hz, 1H), 7.97 (d, *J* = 8.1 Hz, 1H), 7.94 – 7.88 (m, 2H), 7.83 – 7.76 (m, 2H), 7.72 – 7.63 (m, 3H), 7.52 – 7.41 (m, 7H), 7.37 (d, *J* = 8.3 Hz, 1H), 7.35 – 7.27 (m, 2H), 4.77 (d, *J* = 14.5 Hz, 1H), 4.41 (dd, *J* = 14.8, 1.5 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.55, 149.50, 149.04, 146.64, 144.16, 141.83, 139.49, 139.31, 138.46, 135.95, 133.90, 133.89, 132.95, 132.93, 132.73, 131.75, 131.53, 131.52, 131.00, 130.76, 130.42, 129.31, 128.56, 128.43, 127.66, 127.58, 127.09, 127.05, 126.58, 126.48, 126.43, 125.78, 125.20, 125.08, 124.92, 124.84, 124.44, 124.35, 124.08, 124.03, 123.00, 122.98, 121.98, 121.96, 121.40, 111.52, 38.63; **IR** (KBr, cm^{-1}) *γ* 3351, 3057, 1630, 1592, 1521, 1505, 1464, 1265, 1228, 1125, 1071, 1034, 947, 823, 749cm^{-1}; **HRMS** (ESI) m/z $(M+H)^+$: calculated for $C_{37}H_{22}F_5NO_2P$: 638.1309, found: 638.1302; **$[\alpha]^{20}_D$** = +10.6 (c = 0.32, acetone).

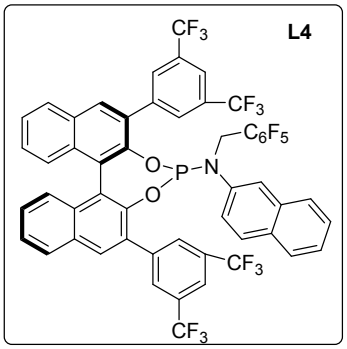
2,6-bis(4-fluorophenyl)-N-(naphthalen-2-yl)-N-(7,7,7,7,7-pentafluoro-7l8-hepta-2,4,6-triyn-1-yl)dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-amine (L2)



(Flash column chromatography eluent, petroleum ether/ethyl acetate = 30 : 1) **Yield**: 71%, 0.59g; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 14.0 Hz, 2H), 8.02 (d, *J* = 8.3 Hz, 2H), 7.99 – 7.91 (m, 2H), 7.88 – 7.79 (m, 2H), 7.66 (t, *J* = 7.7 Hz, 1H), 7.52 (dt, *J* = 7.2, 4.7 Hz, 4H), 7.48 – 7.40 (m, 3H), 7.40 – 7.32 (m, 3H), 7.32 – 7.24 (m, 4H), 6.51 (s, 1H), 6.28 (dd, *J* = 8.7, 2.0 Hz, 1H), 4.58 (d, *J* = 13.1 Hz, 1H), 4.14 (d, *J* = 14.3 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.09, 163.92, 161.63, 161.47, 146.91, 146.86, 146.41, 138.31, 138.07, 134.16, 134.13, 133.91, 133.89, 133.45, 133.34, 133.30, 132.74, 132.48, 132.38, 132.11, 132.03, 131.99, 131.91, 131.54, 131.42, 131.40, 130.92, 130.65, 130.52, 129.32, 128.70, 128.55, 128.45, 127.63, 127.50, 127.43, 127.07, 126.91, 126.52, 126.41, 126.32, 125.69, 125.64, 125.45, 125.36, 124.98, 124.90, 124.38, 124.14, 124.04, 115.92, 115.71, 115.18, 114.97, 37.29; **IR** (KBr, cm^{-1}) *γ* 3056, 2926, 1597, 1506, 1423, 1394, 1226, 1180, 1161, 1126, 1035, 954, 851, 836, 752, 740cm^{-1}; **HRMS** (ESI) m/z $(M+H)^+$: calculated for $C_{49}H_{28}F_7NO_2P$: 826.1746, found: 826.1754; **$[\alpha]^{20}_D$** = -169.3 (c = 0.82, acetone).

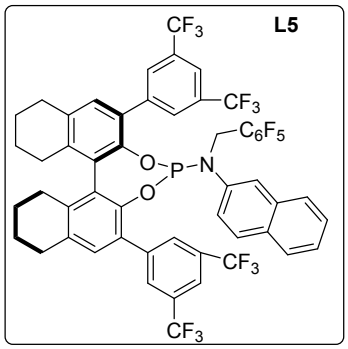
2,6-bis(3,5-bis(trifluoromethyl)phenyl)-N-(naphthalen-2-yl)-N-(7,7,7,7,7-pentafluoro-7l8-

hepta-2,4,6-triyn-1-yl)dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-amine (L4)



(Flash column chromatography eluent, petroleum ether/ dichloromethane = 50 : 1) **Yield**: 73%, 0.78g; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.45 (s, 2H), 8.36 (s, 2H), 8.22 (d, *J* = 8.2 Hz, 2H), 8.12 – 8.01 (m, 4H), 7.69 – 7.63 (m, 1H), 7.62 – 7.51 (m, 3H), 7.48 – 7.35 (m, 7H), 6.52 (s, 1H), 6.11 (dd, *J* = 8.7, 1.7 Hz, 1H), 4.51 (d, *J* = 14.1 Hz, 1H), 3.99 (d, *J* = 14.2 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.24, 146.19, 145.97, 140.16, 139.72, 137.70, 137.47, 133.50, 133.13, 132.97, 132.64, 132.31, 132.13, 131.92, 131.80, 131.68, 131.58, 131.51, 131.33, 130.99, 130.89, 130.34, 129.05, 129.01, 128.93, 127.72, 127.60, 127.54, 127.39, 127.18, 126.97, 126.65, 126.37, 126.26, 126.07, 125.49, 125.43, 124.97, 124.78, 124.69, 124.31, 124.21, 124.03, 123.96, 122.26, 122.07, 121.72, 37.73.; **IR** (KBr, cm^{-1}) *γ* 3061, 1521, 1506, 1377, 1326, 1279, 1246, 1177, 1137, 1083, 1036, 985, 957, 895, 787, 751, 683 cm^{-1}; **HRMS** (ESI) m/z $(M+H)^+$: calculated for $C_{53}H_{26}F_{17}NO_2P$: 1062.1429, found: 1062.1455; **$[\alpha]^{20}_D$** = -143.1 (c = 0.22, acetone).

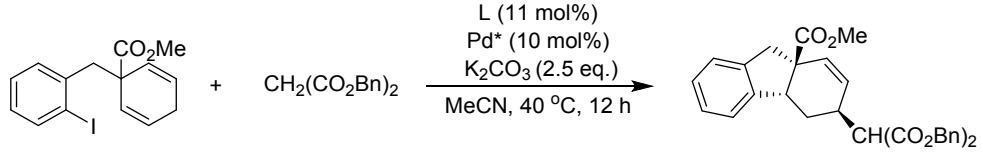
2,6-bis(3,5-bis(trifluoromethyl)phenyl)-N-(naphthalen-2-yl)-N-(7,7,7,7,7-pentafluoro-7l8-hepta-2,4,6-triyn-1-yl)-8,9,10,11,12,13,14,15-octahydrodinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-amine (L5)



(Flash column chromatography eluent, petroleum ether/ dichloromethane = 50 : 1) **Yield**: 65%,0.70g; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.31 (s, 2H), 8.22 (s, 2H), 7.95 (s, 2H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.46 – 7.29 (m, 6H), 6.50 (s, 1H), 6.13 (dd, *J* = 8.7, 1.5 Hz, 1H), 4.41 (d, *J* = 14.4 Hz, 1H), 3.97 (d, *J* = 14.3 Hz, 1H), 3.10 – 2.90 (m, 4H), 2.88 – 2.69 (m, 2H), 2.58 – 2.40 (m, 2H), 2.04 – 1.83 (m, 6H), 1.81 – 1.66 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.52, 144.92, 144.75, 144.71, 144.07, 140.29, 139.84, 139.82, 139.70, 139.68, 138.49, 138.21, 137.99, 135.98, 135.81, 135.80, 135.00, 133.53, 133.51, 132.68, 132.35, 132.20, 132.02, 131.87, 131.69, 131.54, 131.52, 131.50, 131.21, 130.60, 130.34, 130.29, 129.94, 129.79, 129.77, 129.22, 129.20, 128.82, 127.88, 127.73, 127.56, 127.41, 126.47, 125.86, 125.02, 124.85, 124.18, 124.10, 123.98, 123.88, 122.31, 122.13, 121.18, 121.14, 121.10, 121.04, 121.00, 119.60, 119.42, 110.72, 37.74, 29.43, 29.31, 28.30, 27.96, 22.75, 22.69, 22.58; **IR** (KBr, cm^{-1}) *γ* 3060, 2939, 2863, 1521, 1505, 1388, 1373, 1279, 1183, 1136, 955, 900, 846, 743, 683cm^{-1}; **HRMS** (ESI) m/z $(M+H)^+$: calculated for $C_{53}H_{34}F_{17}NO_2P$: 1070.2056, found: 1070.2054; **$[\alpha]^{20}_D$** = -140.6 (c = 0.65, acetone).

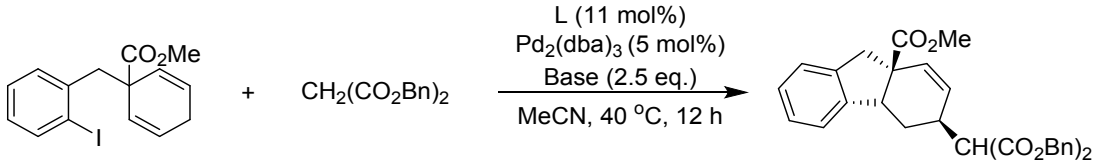
4. Detailed optimal conditions

Screening of the sources of the Pd catalysts



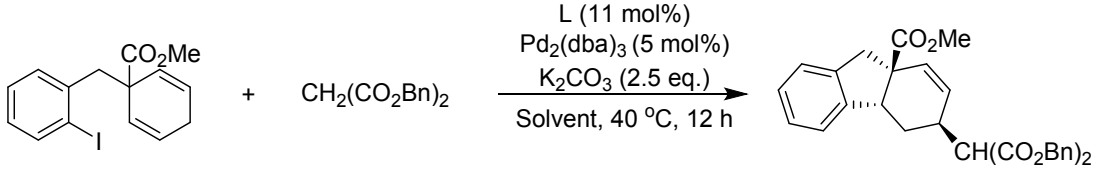
entry	Pd*	Yield(%)	Ee(%)
1	$Pd(PPh_3)_4$	trace	--
2	$Pd(dba)_2$	95	91
3	$Pd_2(dba)_3$	85	92
4	$Pd(OAc)_2$	24	74
5	$Pd(TFA)_2$	trace	--
6	$Pd(CH_3CN)_2Cl_2$	trace	--
7	$Pd(acac)_2$	n.r.	--
8	$PdCl_2$	n.r.	--

Screening of bases



entry	base	Yield(%)	Ee(%)
1	K_2CO_3	85	92
2	NaOAc	--	--
3	NaF	--	--
4	Na_2CO_3	--	--
5	$NaHCO_3$	--	--
6	$KHCO_3$	--	--
7	Cs_2CO_3	92	91
8	Ag_2CO_3	23	65
9	KOH	72	89
10	Et_3N	--	--
11	Cy_2NMe	--	--
12	Pyridine	--	--
13	^iPrNEt	--	--
14	DBU	15	48

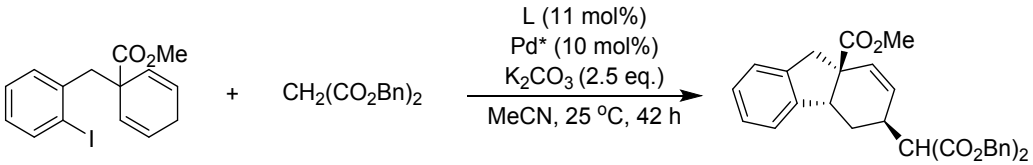
Screening of solvents



entry	solvent	Yield(%)	Ee(%)
1	MeCN	85	92
2	DMSO	42	38
3	DMF	98	80
4	1,4-dioxane	--	--

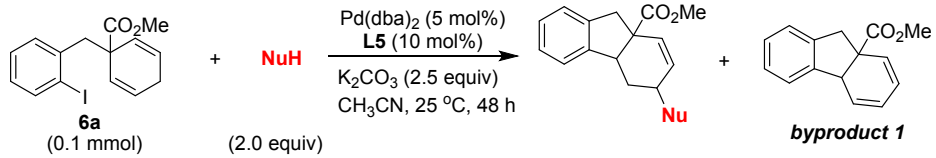
5	DCE	--	--
6	Toluene	--	--
7	EtOH	--	--

Screening of the proportion of Pd catalysts and ligands



$Pd_2(dba)_3$/L	Yield(%)	Ee(%)
5%/11%	92	90
2.5%/10%	87	93
1.5%/9%	82	92
$Pd(dba)_2$/L	Yield(%)	Ee(%)
10%/11%	92	93
10%/20%	84	94
5%/10%	90	93
5%/15%	93	93

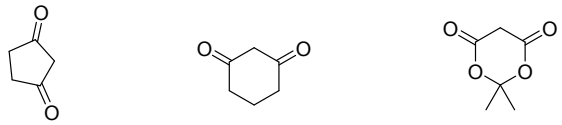
Screening of nucleophiles



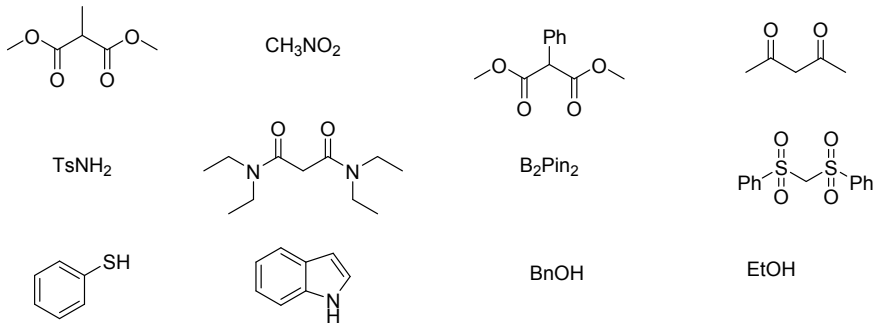
poor results:

NaN_3	$CH_2(CN)_2$
90% yield 48% ee >20/1 dr	54% yield 8% ee >20/1 dr

only **byproduct 1**:



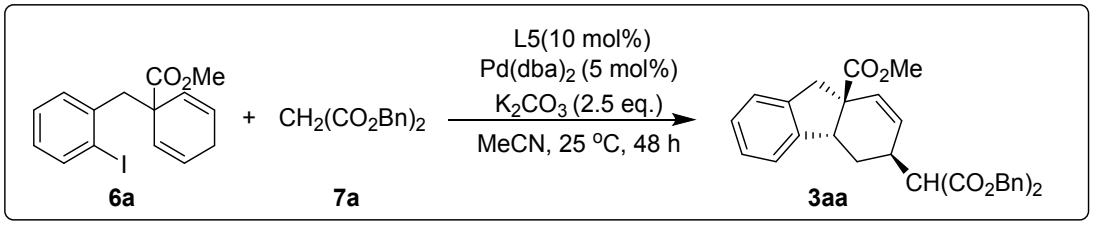
no reaction:



5. General Experimental Procedure

Synthesis of **3**, **4**, **5**

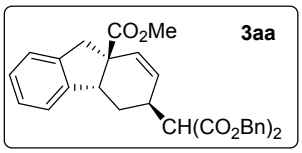
Synthesis of **3aa** is described as a typical procedure.



To a flame-dried and Ar-purged Schlenk tube (10 mL) were added $Pd(dba)_2$(0.005 mmol, 2.9mg), **6a** (0.1 mmol, 35.4 mg), **L5** (0.01 mmol, 10.7 mg), K_2CO_3 (0.25 mmol, 34.6 mg) and a stirring bar. The Schlenk tube was then evacuated and filled with argon. This cycle was repeated three times and followed by addition of **7a** (0.2 mmol, 56.9mg), MeCN (1.0 mL) via syringe. The mixture was stirred at 25 °C for 48 h. Afterwards the mixture was filtrated through silica gel and washed with EtOAc (3 × 10 mL). The combined organic solution was concentrated under vacuum. Finally, the residue was purified by flash column chromatography (petroleum ether/EtOAc = 10 : 1) on silica gel to afford the **3aa**.

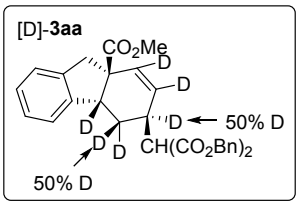
6. Analytical Data for the Products

dibenzyl 2-((3*S*,4a*R*,9a*S*)-9a-(methoxycarbonyl)-4,4a,9,9a-tetrahydro-3H-fluoren-3-yl)malonate (3aa)



(Flash column chromatography eluent, petroleum ether/ethyl acetate = 10 : 1) **Yield**: 89%, 45.5 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.29 (m, 8H), 7.29 – 7.24 (m, 2H), 7.18 – 7.06 (m, 3H), 7.01 – 6.91 (m, 1H), 5.66 (dd, *J* = 10.2, 1.6 Hz, 1H), 5.58 (d, *J* = 10.2 Hz, 1H), 5.23 (d, *J* = 12.2 Hz, 1H), 5.15 (d, *J* = 12.3 Hz, 1H), 5.10 (d, *J* = 11.8 Hz, 2H), 3.83 (d, *J* = 3.4 Hz, 1H), 3.71 (s, 3H), 3.41 (dd, *J* = 12.4, 5.6 Hz, 2H), 2.96 (d, *J* = 15.8 Hz, 1H), 2.79 – 2.67 (m, 1H), 2.26 (dt, *J* = 13.5, 4.0 Hz, 1H), 1.88 (ddd, *J* = 13.6, 11.2, 3.9 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.18, 167.97, 167.94, 142.75, 140.44, 135.38, 130.53, 130.15, 128.70, 128.65, 128.56, 128.51, 128.46, 128.32, 127.03, 126.85, 125.00, 123.15, 67.26, 67.22, 56.44, 53.74, 52.41, 44.79, 43.25, 31.31, 26.11; **IR** (KBr, cm^{-1}) γ 3066, 3033, 2951, 1732, 1498, 1482, 1456, 1434, 1377, 1333, 1224, 1151, 1048, 744, 698 cm^{-1}; **HRMS** (ESI) m/z $(M+H)^+$: calculated for $C_{32}H_{31}O_6$: 511.2121, found: 511.2117; **$[\alpha]^{20}_D$** = +14.0 (c = 0.63, acetone); **The product was analyzed by HPLC to determine the enantiomeric excess:** 93% *ee*; (CHIRALPAK IE, hexane/*i*-PrOH = 85/15, flow rate: 1.0 mL/min, T = 30 °C, 254 nm), t_R (major) = 12.364 min, t_R = 13.182 min. The absolute configuration was assigned tentatively by analogy.

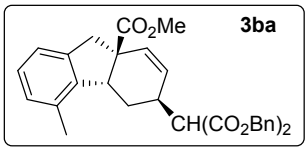
[D]-**3aa**



(Flash column chromatography eluent, petroleum ether/ethyl acetate = 10 : 1) **Yield**: 90%, 46.4 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.31 (m, 8H), 7.31 – 7.27 (m, 2H), 7.18 – 7.11 (m, 3H), 7.02 – 6.95 (m, 1H), 5.25 (d, *J* = 12.2 Hz, 1H), 5.17 (d, *J* = 12.3 Hz, 1H), 5.12 (d, *J* = 11.8 Hz, 2H), 3.73 (s, 3H), 3.43 (dd, *J* = 12.0, 6.6 Hz,

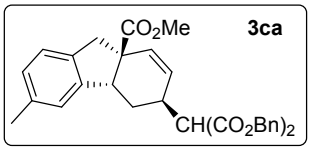
2H), 2.97 (d, *J* = 15.8 Hz, 1H), 2.75 (t, *J* = 7.0 Hz, 0.5H), 2.24 (s, 0.5H); **HRMS** (ESI) m/z $(M+Na)^+$: calculated for $C_{32}H_{25}D_5NaO_6$: 538.2254, found: 538.2254.

dibenzyl 2-((3*S*,4a*R*,9a*S*)-9a-(methoxycarbonyl)-5-methyl-4,4a,9,9a-tetrahydro-3H-fluoren-3-yl)malonate (3ba)



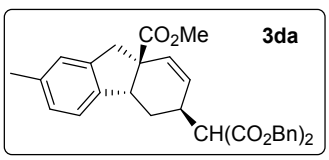
(Flash column chromatography eluent, petroleum ether/ethyl acetate = 10 : 1) **Yield**: 71%, 37.0 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 8H), 7.28 (dd, *J* = 6.9, 3.0 Hz, 2H), 7.05 (t, *J* = 7.4 Hz, 1H), 6.98 (d, *J* = 7.2 Hz, 1H), 6.93 (d, *J* = 7.4 Hz, 1H), 5.87 (dd, *J* = 10.1, 3.7 Hz, 1H), 5.82 (dd, *J* = 10.1, 1.0 Hz, 1H), 5.23 (d, *J* = 12.2 Hz, 1H), 5.20 – 5.11 (m, 3H), 3.91 (dd, *J* = 8.7, 5.0 Hz, 1H), 3.66 (s, 3H), 3.62 (t, *J* = 6.5 Hz, 1H), 3.51 (d, *J* = 15.9 Hz, 1H), 2.97 (d, *J* = 15.9 Hz, 1H), 2.90 (dt, *J* = 9.5, 4.7 Hz, 1H), 2.22 (s, 3H), 1.96 – 1.86 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.70, 168.13, 167.98, 142.41, 140.51, 135.45, 135.36, 134.16, 131.04, 129.59, 128.71, 128.66, 128.56, 128.44, 128.24, 127.12, 122.13, 67.40, 67.26, 56.30, 54.71, 52.62, 43.00, 42.65, 33.07, 27.91, 18.86; **IR** (KBr, cm^{-1}) *γ* 3033, 2952, 1732, 1498, 1455, 1379, 1259, 1213, 1155, 1042, 746, 697 cm^{-1}; **HRMS** (ESI) m/z $(M+H)^+$: calculated for $C_{33}H_{33}O_6$: 525.2277, found: 525.2286; **$[\alpha]^{20}_D$** = +26.0 (c = 0.07, acetone); **The product was analyzed by HPLC to determine the enantiomeric excess:** 83% *ee*; (CHIRALPAK IE, hexane/*i*-PrOH = 85/15, flow rate: 0.5 mL/min, T = 30 °C, 210 nm), t_R (major) = 21.613 min, t_R = 20.547 min. The absolute configuration was assigned tentatively by analogy.

dibenzyl 2-((3*S*,4a*R*,9a*S*)-9a-(methoxycarbonyl)-6-methyl-4,4a,9,9a-tetrahydro-3H-fluoren-3-yl)malonate (3ca)



(Flash column chromatography eluent, petroleum ether/ethyl acetate = 10 : 1) **Yield**: 86%, 45.0 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.31 (m, 8H), 7.31 – 7.27 (m, 2H), 7.02 – 6.92 (m, 2H), 6.87 (d, *J* = 7.7 Hz, 1H), 5.70 – 5.64 (m, 1H), 5.60 (d, *J* = 10.2 Hz, 1H), 5.24 (d, *J* = 12.2 Hz, 1H), 5.16 (d, *J* = 12.3 Hz, 1H), 5.11 (dd, *J* = 12.2, 1.4 Hz, 2H), 3.81 (s, 1H), 3.72 (s, 3H), 3.41 (dd, *J* = 12.4, 5.5 Hz, 2H), 2.92 (d, *J* = 15.8 Hz, 1H), 2.84 – 2.71 (m, 1H), 2.31 (s, 3H), 2.25 (dt, *J* = 8.1, 4.3 Hz, 1H), 1.88 (ddd, *J* = 13.6, 11.1, 3.9 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.26, 167.99, 167.97, 140.55, 139.78, 136.71, 135.43, 130.61, 130.14, 128.71, 128.66, 128.56, 128.51, 128.46, 128.33, 127.66, 125.72, 122.89, 67.25, 67.22, 56.47, 53.90, 52.38, 44.47, 43.18, 31.33, 26.23, 21.41; **IR** (KBr, cm^{-1}) *γ* 3032, 2951, 1731, 1496, 1455, 1378, 1223, 1151, 1047, 804, 749, 698 cm^{-1}; **HRMS** (ESI) m/z $(M+H)^+$: calculated for $C_{33}H_{33}O_6$: 525.2277, found: 525.2274; **$[\alpha]^{20}_D$** = +6.8 (c = 0.53, acetone); **The product was analyzed by HPLC to determine the enantiomeric excess:** 95% *ee*; (CHIRALPAK IC, hexane/*i*-PrOH = 70/30, flow rate: 1.0 mL/min, T = 30 °C, 254 nm), t_R (major) = 13.548 min, t_R = 7.686 min. The absolute configuration was assigned tentatively by analogy.

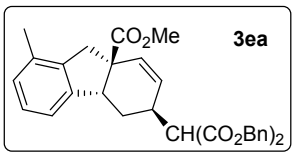
dibenzyl 2-((3*S*,4a*R*,9a*S*)-9a-(methoxycarbonyl)-7-methyl-4,4a,9,9a-tetrahydro-3H-fluoren-3-yl)malonate (3da)



(Flash column chromatography eluent, petroleum ether/ethyl acetate = 10 : 1) **Yield**: 56%, 29.2 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.32 (m, 8H), 7.32 – 7.27 (m, 2H), 7.02 – 6.94 (m,

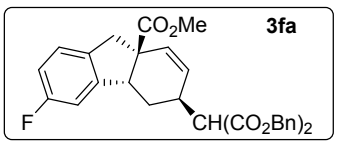
2H), 6.89 (d, *J* = 7.6 Hz, 1H), 5.69 (dd, *J* = 10.2, 2.1 Hz, 1H), 5.62 (d, *J* = 10.3 Hz, 1H), 5.26 (d, *J* = 12.2 Hz, 1H), 5.18 (d, *J* = 12.3 Hz, 1H), 5.13 (d, *J* = 11.0 Hz, 2H), 3.83 (s, 1H), 3.74 (s, 3H), 3.43 (dd, *J* = 12.3, 6.7 Hz, 2H), 2.94 (d, *J* = 15.8 Hz, 1H), 2.86 – 2.71 (m, 1H), 2.32 (s, 3H), 2.27 (dt, *J* = 13.4, 4.4 Hz, 1H), 1.95 – 1.85 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.21, 167.95, 167.93, 140.52, 139.77, 136.67, 135.41, 130.59, 130.12, 128.68, 128.62, 128.52, 128.48, 128.43, 128.30, 127.63, 125.69, 122.86, 67.21, 67.17, 56.45, 53.88, 52.33, 44.46, 43.16, 31.31, 26.22, 21.38; **IR** (KBr, cm^{-1}) *γ* 3033, 2951, 1731, 1496, 1455, 1378, 1223, 1151, 1048, 749, 698 cm^{-1}; **HRMS** (ESI) m/z $(M+H)^+$: calculated for $C_{33}H_{33}O_6$: 525.2277, found: 525.2283; **$[\alpha]^{20}_D$** = +7.2 (c = 1.23, acetone); **The product was analyzed by HPLC to determine the enantiomeric excess:** 94% *ee*; (CHIRALPAK IC, hexane/*i*-PrOH = 70/30, flow rate: 1.0 mL/min, T = 30 °C, 254 nm), t_R (major) = 13.353 min, t_R = 7.643 min. The absolute configuration was assigned tentatively by analogy.

dibenzyl 2-((3*S*,4a*R*,9a*S*)-9a-(methoxycarbonyl)-8-methyl-4,4a,9,9a-tetrahydro-3H-fluoren-3-yl)malonate (3ea)



(Flash column chromatography eluent, petroleum ether/ethyl acetate = 10 : 1) **Yield**: 75%, 39.2 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 8H), 7.29 – 7.26 (m, 2H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 7.4 Hz, 1H), 6.81 (d, *J* = 7.4 Hz, 1H), 5.67 (dd, *J* = 10.2, 1.6 Hz, 1H), 5.60 (d, *J* = 10.2 Hz, 1H), 5.23 (d, *J* = 12.2 Hz, 1H), 5.16 (d, *J* = 12.3 Hz, 1H), 5.11 (dd, *J* = 12.3, 2.2 Hz, 2H), 3.84 (s, 1H), 3.73 (s, 3H), 3.41 (d, *J* = 8.9 Hz, 1H), 3.30 (d, *J* = 15.8 Hz, 1H), 2.94 (d, *J* = 15.9 Hz, 1H), 2.82 – 2.70 (m, 1H), 2.25 (dt, *J* = 13.4, 4.0 Hz, 1H), 2.21 (s, 3H), 1.88 (ddd, *J* = 13.6, 11.2, 4.0 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.38, 168.01, 167.99, 142.55, 139.21, 135.44, 134.40, 130.77, 130.12, 128.73, 128.68, 128.58, 128.53, 128.48, 128.35, 128.01, 127.16, 120.49, 67.28, 67.25, 56.50, 53.35, 52.43, 45.02, 42.07, 31.37, 26.33, 18.97; **IR** (KBr, cm^{-1}) *γ* 3065, 3033, 2950, 1732, 1498, 1456, 1378, 1334, 1222, 1151, 1049, 1002, 749, 698 cm^{-1}; **HRMS** (ESI) m/z $(M+H)^+$: calculated for $C_{33}H_{33}O_6$: 525.2277, found: 525.2286; **$[\alpha]^{20}_D$** = +1.9 (c = 0.20, acetone); **The product was analyzed by HPLC to determine the enantiomeric excess:** 92% *ee*; (CHIRALPAK ID, hexane/*i*-PrOH = 90/10, flow rate: 1.0 mL/min, T = 30 °C, 254 nm), t_R (major) = 21.021 min, t_R = 18.229 min. The absolute configuration was assigned tentatively by analogy.

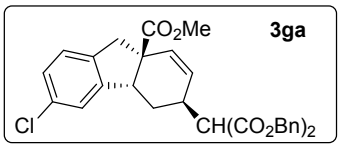
dibenzyl 2-((3*S*,4a*R*,9a*S*)-6-fluoro-9a-(methoxycarbonyl)-4,4a,9,9a-tetrahydro-3H-fluoren-3-yl)malonate (3fa)



(Flash column chromatography eluent, petroleum ether/ethyl acetate = 10 : 1) **Yield**: 96%, 50.6 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.31 (m, 8H), 7.29 (dd, *J* = 7.0, 2.8 Hz, 2H), 7.08 (dd, *J* = 8.2, 5.1 Hz, 1H), 6.89 – 6.81 (m, 1H), 6.67 (dd, *J* = 8.8, 1.3 Hz, 1H), 5.70 – 5.65 (m, 1H), 5.62 (d, *J* = 10.3 Hz, 1H), 5.25 (d, *J* = 12.2 Hz, 1H), 5.21 – 5.07 (m, 3H), 3.82 (s, 1H), 3.72 (s, 3H), 3.38 (dd, *J* = 19.2, 12.2 Hz, 2H), 2.92 (d, *J* = 15.7 Hz, 1H), 2.81 – 2.69 (m, 1H), 2.17 (dt, *J* = 13.7, 4.2 Hz, 1H), 1.88 (ddd, *J* = 13.8, 11.1, 4.0 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.84, 167.90, 167.82, 162.52 (d, *J* = 243.9 Hz), 145.19 (d, *J* = 7.6 Hz), 135.73, 135.70, 135.38, 135.37, 130.29 (d, *J* = 9.6 Hz), 128.79, 128.69, 128.65, 128.58, 128.50, 128.35, 125.99 (d, *J* = 8.7 Hz), 114.05 (d, *J* = 22.5 Hz), 110.39 (d, *J* = 22.3 Hz), 67.33,

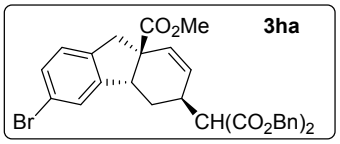
67.29, 56.39, 54.25, 52.46, 44.82, 44.80, 42.51, 31.26, 26.01; **IR** (KBr, cm^{-1}) γ 3033, 2951, 1732, 1614, 1599, 1488, 1455, 1378, 1327, 1227, 1153, 1083, 1048, 867, 812, 740, 698 cm^{-1}; **HRMS** (ESI) m/z $(M+H)^+$: calculated for $C_{32}H_{30}FO_6$: 529.2026, found: 529.2030; $[\alpha]^{20}_D$ = +10.1 (c = 0.76, acetone); **The product was analyzed by HPLC to determine the enantiomeric excess:** 94% *ee*; (CHIRALPAK ID, hexane/*i*-PrOH = 70/30, flow rate: 1.0 mL/min, T = 30 °C, 254 nm), t_R (major) = 9.921 min, t_R = 9.311 min. The absolute configuration was assigned tentatively by analogy.

Dibenzyl 2-((3*S*,4a*R*,9a*S*)-6-chloro-9a-(methoxycarbonyl)-4,4a,9,9a-tetrahydro-3H-fluoren-3-yl)malonate (3ga)



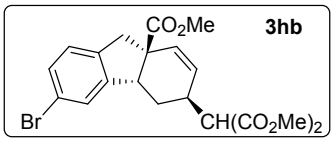
(Flash column chromatography eluent, petroleum ether/ethyl acetate = 10 : 1) **Yield**: 94%, 50.9 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.31 (m, 8H), 7.31 – 7.27 (m, 2H), 7.13 (ddd, *J* = 8.0, 1.9, 0.8 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 6.98 (s, 1H), 5.71 – 5.61 (m, 2H), 5.25 (d, *J* = 12.2 Hz, 1H), 5.19 – 5.09 (m, 3H), 3.81 (t, *J* = 3.8 Hz, 1H), 3.72 (s, 3H), 3.41 (d, *J* = 8.8 Hz, 1H), 3.36 (d, *J* = 15.9 Hz, 1H), 2.93 (d, *J* = 16.0 Hz, 1H), 2.76 (td, *J* = 10.6, 5.0 Hz, 1H), 2.15 (dt, *J* = 13.7, 4.5 Hz, 1H), 1.89 (ddd, *J* = 13.8, 10.9, 4.1 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.77, 167.89, 167.81, 145.04, 138.94, 135.38, 135.35, 132.73, 130.30, 130.20, 128.81, 128.69, 128.65, 128.60, 128.50, 128.35, 127.36, 126.15, 123.41, 67.36, 67.29, 56.36, 54.02, 52.50, 44.74, 42.68, 31.24, 25.93; **IR** (KBr, cm^{-1}) γ 3033, 2952, 1732, 1476, 1455, 1223, 1151, 1081, 1048, 869, 809, 737, 698 cm^{-1}; **HRMS** (ESI) m/z $(M+H)^+$: calculated for $C_{32}H_{30}ClO_6$: 545.1731, found: 545.1740; $[\alpha]^{20}_D$ = +28.8 (c = 0.82, acetone); **The product was analyzed by HPLC to determine the enantiomeric excess:** 96% *ee*; (CHIRALPAK ID, hexane/*i*-PrOH = 85/15, flow rate: 1.0 mL/min, T = 30 °C, 254 nm), t_R (major) = 14.398 min, t_R = 13.558 min. The absolute configuration was assigned tentatively by analogy.

dibenzyl 2-((3*S*,4a*R*,9a*S*)-6-bromo-9a-(methoxycarbonyl)-4,4a,9,9a-tetrahydro-3H-fluoren-3-yl)malonate (3ha)



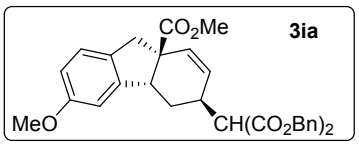
(Flash column chromatography eluent, petroleum ether/ethyl acetate = 10 : 1) **Yield**: 72%, 42.7 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.31 (m, 8H), 7.30 – 7.26 (m, 3H), 7.14 (s, 1H), 7.02 (d, *J* = 8.0 Hz, 1H), 5.69 – 5.60 (m, 2H), 5.24 (d, *J* = 12.2 Hz, 1H), 5.19 – 5.09 (m, 3H), 3.81 (t, *J* = 3.8 Hz, 1H), 3.71 (s, 3H), 3.41 (d, *J* = 8.8 Hz, 1H), 3.34 (d, *J* = 16.0 Hz, 1H), 2.91 (d, *J* = 16.0 Hz, 1H), 2.80 – 2.67 (m, 1H), 2.20 – 2.08 (m, 1H), 1.88 (ddd, *J* = 13.9, 10.9, 4.1 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.76, 167.91, 167.83, 145.48, 139.52, 135.40, 135.37, 130.33, 130.27, 130.17, 128.83, 128.71, 128.67, 128.62, 128.51, 128.37, 126.62, 126.34, 120.72, 67.39, 67.32, 56.37, 53.96, 52.53, 44.75, 42.75, 31.26, 25.95; **IR** (KBr, cm^{-1}) γ 3033, 2927, 1732, 1498, 1455, 1404, 1223, 1151, 1048, 899, 808, 737, 698 cm^{-1}; **HRMS** (ESI) m/z $(M+H)^+$: calculated for $C_{32}H_{30}BrO_6$: 589.1226, found: 589.1229; $[\alpha]^{20}_D$ = +36.0 (c = 0.41, acetone); **The product was analyzed by HPLC to determine the enantiomeric excess:** 97% *ee*; (CHIRALPAK ID, hexane/*i*-PrOH = 85/15, flow rate: 1.0 mL/min, T = 30 °C, 254 nm), t_R (major) = 14.998 min, t_R = 14.129 min. The absolute configuration was assigned tentatively by analogy.

dimethyl 2-((3*S*,4a*R*,9a*S*)-6-bromo-9a-(methoxycarbonyl)-4,4a,9,9a-tetrahydro-3H-fluoren-3-yl)malonate (3hb)



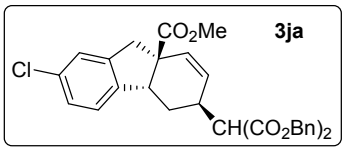
(Flash column chromatography eluent, petroleum ether/ethyl acetate = 10 : 1) **Yield**: 95%, 41.6 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 (dd, *J* = 5.7, 4.8 Hz, 2H), 7.03 (d, *J* = 7.8 Hz, 1H), 5.68 (ddd, *J* = 10.3, 2.1, 0.8 Hz, 1H), 5.65 – 5.60 (m, 1H), 3.86 (t, *J* = 3.8 Hz, 1H), 3.77 (s, 3H), 3.74 (s, 3H), 3.72 (s, 3H), 3.34 (dd, *J* = 12.3, 6.7 Hz, 2H), 2.92 (d, *J* = 16.0 Hz, 1H), 2.80 – 2.66 (m, 1H), 2.26 (dt, *J* = 9.2, 4.2 Hz, 1H), 1.89 (ddd, *J* = 13.8, 11.0, 4.1 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.76, 168.61, 168.56, 145.47, 139.56, 130.28, 130.20, 126.66, 126.40, 120.74, 56.06, 53.98, 52.67, 52.61, 52.53, 44.83, 42.75, 31.20, 26.12; **IR** (KBr, cm^{-1}) *γ* 2921, 2852, 1729, 1659, 1633, 1470, 1409, 1264, 1110, 806, 736, 698 cm^{-1}; **HRMS** (ESI) m/z $(M+H)^+$: calculated for $C_{20}H_{22}BrO_6$: 437.0600, found: 437.0605; **$[\alpha]^{20}_D$** = +71.8 (c = 0.54, acetone); **The product was analyzed by HPLC to determine the enantiomeric excess:** 97% *ee*; (CHIRALPAK ID, hexane/*i*-PrOH = 85/15, flow rate: 1.0 mL/min, T = 30 °C, 210 nm), t_R (major) = 11.629 min, t_R = 9.529 min.

dibenzyl 2-((3S,4aR,9aS)-6-methoxy-9a-(methoxycarbonyl)-4,4a,9,9a-tetrahydro-3H-fluoren-3-yl)malonate (3ia)



(Flash column chromatography eluent, petroleum ether/ethyl acetate = 10 : 1) **Yield**: 51%, 27.4 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 8H), 7.28 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.05 (d, *J* = 8.2 Hz, 1H), 6.71 (dd, *J* = 8.2, 1.7 Hz, 1H), 6.65 (d, *J* = 1.4 Hz, 1H), 5.70 – 5.65 (m, 1H), 5.61 (d, *J* = 10.3 Hz, 1H), 5.21 (d, *J* = 12.3 Hz, 1H), 5.17 – 5.09 (m, 3H), 3.83 (t, *J* = 3.5 Hz, 1H), 3.75 (s, 3H), 3.72 (s, 3H), 3.42 (d, *J* = 8.7 Hz, 1H), 3.35 (d, *J* = 15.4 Hz, 1H), 2.90 (d, *J* = 15.5 Hz, 1H), 2.85 – 2.74 (m, 1H), 2.25 (dt, *J* = 13.4, 4.0 Hz, 1H), 1.88 (ddd, *J* = 13.6, 11.1, 4.0 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.18, 168.01, 167.98, 159.27, 144.45, 135.44, 135.43, 132.31, 130.61, 130.15, 128.73, 128.67, 128.53, 128.46, 128.41, 128.31, 125.57, 112.82, 108.99, 67.29, 67.24, 56.44, 55.53, 54.24, 52.39, 44.88, 42.55, 31.37, 26.23; **IR** (KBr, cm^{-1}) *γ* 3032, 2950, 1732, 1610, 1492, 1455, 1433, 1331, 1228, 1146, 1046, 811, 738, 698 cm^{-1}; **HRMS** (ESI) m/z $(M+H)^+$: calculated for $C_{33}H_{33}O_7$: 541.2226, found: 541.2219; **$[\alpha]^{20}_D$** = +16.6 (c = 0.36, acetone); **The product was analyzed by HPLC to determine the enantiomeric excess:** 97% *ee*; (CHIRALPAK ID, hexane/*i*-PrOH = 70/30, flow rate: 1.0 mL/min, T = 30 °C, 254 nm), t_R (major) = 15.233 min, t_R = 12.609 min. The absolute configuration was assigned tentatively by analogy.

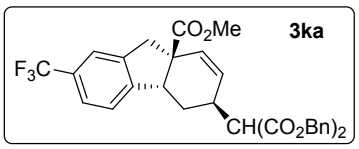
dibenzyl 2-((3*S*,4a*R*,9a*S*)-7-chloro-9a-(methoxycarbonyl)-4,4a,9,9a-tetrahydro-3H-fluoren-3-yl)malonate (3ja)



(Flash column chromatography eluent, petroleum ether/ethyl acetate = 10 : 1) **Yield**: 99%, 54.5 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.31 (m, 8H), 7.28 (dd, *J* = 6.8, 3.0 Hz, 2H), 7.13 (s, 1H), 7.09 (d, *J* = 8.0 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 5.65 (dd, *J* = 10.2, 1.4 Hz, 1H), 5.60 (d, *J* = 10.3 Hz, 1H), 5.24 (d, *J* = 12.2 Hz, 1H), 5.16 (d, *J* = 12.3 Hz, 1H), 5.11 (dd, *J* = 12.2, 6.5 Hz, 2H), 3.78 (s, 1H), 3.72 (s, 3H), 3.45 – 3.35 (m, 2H), 2.93 (d, *J* = 16.0 Hz, 1H), 2.70 (tdd, *J* = 9.1, 4.9, 2.5 Hz, 1H), 2.21 (dt, *J* = 13.5, 4.2 Hz, 1H), 1.87 (ddd, *J* = 13.7, 11.2, 3.9 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.76, 167.88, 167.84, 142.45, 141.30, 135.33, 132.62, 130.32, 130.23, 128.73, 128.67, 128.63, 128.57,

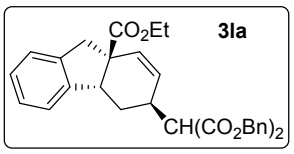
128.52, 128.36, 127.08, 125.29, 124.25, 67.30, 56.31, 53.93, 52.52, 44.31, 42.93, 31.20, 25.99; **IR** (KBr, cm^{-1}) γ 3033, 2951, 1732, 1477, 1455, 1435, 1378, 1288, 1224, 1152, 1048, 738, 698 cm^{-1}; **HRMS** (ESI) m/z $(M+H)^+$: calculated for $C_{32}H_{30}ClO_6$: 545.1731, found: 545.1739; $[\alpha]^{20}_D$ = +1.0 (c = 0.66, acetone); **The product was analyzed by HPLC to determine the enantiomeric excess:** 95% *ee*; (CHIRALPAK IC, hexane/*i*-PrOH = 85/15, flow rate: 1.0 mL/min, T = 30 °C, 254 nm), t_R (major) = 9.612 min, t_R = 11.884 min. The absolute configuration was assigned tentatively by analogy.

dibenzyl 2-((3*S*,4a*R*,9a*S*)-9a-(methoxycarbonyl)-7-(trifluoromethyl)-4,4a,9,9a-tetrahydro-3H-fluoren-3-yl)malonate (3ka)



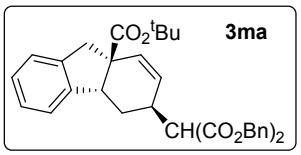
(Flash column chromatography eluent, petroleum ether/ethyl acetate = 10 : 1) **Yield**: 49%, 28.2 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.31 (m, 10H), 7.28 (dd, *J* = 7.8, 4.1 Hz, 2H), 7.02 (d, *J* = 7.9 Hz, 1H), 5.66 (dd, *J* = 10.2, 1.6 Hz, 1H), 5.60 (d, *J* = 10.3 Hz, 1H), 5.24 (d, *J* = 12.2 Hz, 1H), 5.16 (d, *J* = 12.3 Hz, 1H), 5.11 (dd, *J* = 12.2, 4.9 Hz, 2H), 3.86 (s, 1H), 3.73 (s, 3H), 3.42 (t, *J* = 13.4 Hz, 2H), 3.01 (d, *J* = 16.1 Hz, 1H), 2.74 – 2.61 (m, 1H), 2.26 (dt, *J* = 13.6, 4.1 Hz, 1H), 1.91 (ddd, *J* = 13.7, 11.2, 4.0 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.68, 167.87, 167.83, 147.07, 141.39, 135.38, 135.37, 130.45, 130.17, 129.61 (q, *J* = 31.9 Hz), 128.77, 128.71, 128.68, 128.61, 128.57, 128.40, 124.22 (q, *J* = 3.8 Hz), 123.48, 122.00 (q, *J* = 3.7 Hz), 67.37, 67.36, 56.34, 53.97, 52.59, 44.84, 42.98, 31.29, 25.94; **IR** (KBr, cm^{-1}) γ 3034, 2953, 1732, 1456, 1434, 1324, 1287, 1225, 1156, 1122, 1059, 750, 698 cm^{-1}; **HRMS** (ESI) m/z $(M+H)^+$: calculated for $C_{33}H_{30}F_3O_6$: 579.1994, found: 579.2002; $[\alpha]^{20}_D$ = +3.8 (c = 0.26, acetone); **The product was analyzed by HPLC to determine the enantiomeric excess:** 94% *ee*; (CHIRALPAK ID, hexane/*i*-PrOH = 90/10, flow rate: 1.0 mL/min, T = 30 °C, 254 nm), t_R (major) = 13.132 min, t_R = 14.704 min. The absolute configuration was assigned tentatively by analogy.

dibenzyl 2-((3*S*,4a*R*,9a*S*)-9a-(ethoxycarbonyl)-4,4a,9,9a-tetrahydro-3H-fluoren-3-yl)malonate (3la)



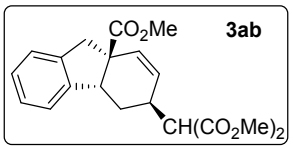
(Flash column chromatography eluent, petroleum ether /ethyl acetate = 10 : 1) **Yield**: 80%, 41.9 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.29 (m, 8H), 7.29 – 7.25 (m, 2H), 7.16 – 7.09 (m, 3H), 7.01 – 6.93 (m, 1H), 5.67 (dd, *J* = 10.2, 1.6 Hz, 1H), 5.58 (d, *J* = 10.2 Hz, 1H), 5.23 (d, *J* = 12.2 Hz, 1H), 5.18 – 5.06 (m, 3H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.84 (t, *J* = 3.6 Hz, 1H), 3.41 (dd, *J* = 12.4, 6.1 Hz, 2H), 2.96 (d, *J* = 15.8 Hz, 1H), 2.81 – 2.68 (m, 1H), 2.26 (dt, *J* = 13.5, 4.1 Hz, 1H), 1.89 (ddd, *J* = 13.6, 11.2, 4.0 Hz, 1H), 1.32 – 1.20 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.72, 168.00, 167.97, 142.88, 140.54, 135.41, 130.73, 130.04, 128.72, 128.67, 128.58, 128.53, 128.48, 128.35, 127.02, 126.85, 125.02, 123.18, 67.27, 67.24, 61.13, 56.50, 53.78, 44.75, 43.25, 31.35, 26.18, 14.34; **IR** (KBr, cm^{-1}) γ 3033, 2939, 1731, 1456, 1378, 1333, 1221, 1151, 1047, 748, 697 cm^{-1}; **HRMS** (ESI) m/z $(M+H)^+$: calculated for $C_{33}H_{33}O_6$: 525.2277, found: 525.2277; $[\alpha]^{20}_D$ = +19.3 (c = 0.71, acetone); **The product was analyzed by HPLC to determine the enantiomeric excess:** 92% *ee*; (CHIRALPAK IE, hexane/*i*-PrOH = 85/15, flow rate: 1.0 mL/min, T = 30 °C, 254 nm), t_R (major) = 10.729 min, t_R = 11.812 min. The absolute configuration was assigned tentatively by analogy.

dibenzyl 2-((3*S*,4a*R*,9a*S*)-9a-(tert-butoxycarbonyl)-4,4a,9,9a-tetrahydro-3H-fluoren-3-yl)malonate (3ma)



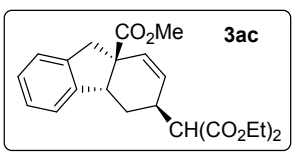
(Flash column chromatography eluent, petroleum ether/ethyl acetate = 10 : 1) **Yield**: 84%, 46.3 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.29 (m, 8H), 7.26 (dd, *J* = 6.7, 2.8 Hz, 2H), 7.16 – 7.08 (m, 3H), 6.96 (d, *J* = 5.7 Hz, 1H), 5.65 (dd, *J* = 10.3, 1.9 Hz, 1H), 5.57 (d, *J* = 10.3 Hz, 1H), 5.22 (d, *J* = 12.2 Hz, 1H), 5.15 – 5.06 (m, 3H), 3.79 (s, 1H), 3.44 – 3.33 (m, 2H), 2.91 (d, *J* = 15.9 Hz, 1H), 2.74 (td, *J* = 11.3, 2.4 Hz, 1H), 2.23 (dt, *J* = 13.3, 4.3 Hz, 1H), 1.95 – 1.83 (m, 1H), 1.45 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.91, 168.00, 167.97, 143.10, 140.68, 135.42, 131.21, 129.63, 128.71, 128.66, 128.56, 128.51, 128.46, 128.32, 126.93, 126.75, 124.97, 123.15, 81.00, 67.22, 67.19, 56.59, 54.58, 44.60, 43.16, 31.38, 28.14, 26.23; **IR** (KBr, cm^{-1}) *γ* 3033, 2976, 1731, 1456, 1393, 1369, 1331, 1293, 1252, 1155, 1029, 748, 697 cm^{-1}; **HRMS** (ESI) m/z $(M+H)^+$: calculated for $C_{35}H_{37}O_6$: 553.2590, found: 553.2607; **$[\alpha]^{20}_D$** = +31.8 (c = 0.84, acetone); **The product was analyzed by HPLC to determine the enantiomeric excess:** 90% *ee*; (CHIRALPAK IE, hexane/*i*-PrOH = 85/15, flow rate: 1.0 mL/min, T = 30 °C, 254 nm), t_R (major) = 7.258 min, t_R = 7.711 min. The absolute configuration was assigned tentatively by analogy.

dimethyl 2-((3*S*,4a*R*,9a*S*)-9a-(methoxycarbonyl)-4,4a,9,9a-tetrahydro-3H-fluoren-3-yl)malonate (3ab)



(Flash column chromatography eluent, petroleum ether/ethyl acetate = 10 : 1) **Yield**: 84%, 30.0 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 – 7.14 (m, 4H), 5.69 (dd, *J* = 10.2, 1.6 Hz, 1H), 5.58 (d, *J* = 10.2 Hz, 1H), 3.89 (t, *J* = 3.8 Hz, 1H), 3.77 (s, 3H), 3.75 (s, 3H), 3.71 (s, 3H), 3.44 (d, *J* = 15.8 Hz, 1H), 3.32 (d, *J* = 9.0 Hz, 1H), 2.98 (d, *J* = 15.8 Hz, 1H), 2.73 (dqd, *J* = 7.1, 4.6, 2.1 Hz, 1H), 2.39 – 2.28 (m, 1H), 1.87 (ddd, *J* = 13.6, 11.1, 4.0 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.21, 168.77, 168.66, 142.82, 140.50, 130.57, 130.13, 127.12, 126.94, 125.08, 123.18, 56.22, 53.81, 52.62, 52.58, 52.43, 44.85, 43.27, 31.32, 26.25; **IR** (KBr, cm^{-1}) *γ* 3024, 2953, 1732, 1482, 1435, 1401, 1335, 1291, 1225, 1154, 1048, 893, 782, 745, 699 cm^{-1}; **HRMS** (ESI) m/z $(M+H)^+$: calculated for $C_{20}H_{23}O_6$: 359.1495, found: 359.1497; **$[\alpha]^{20}_D$** = +45.4 (c = 0.33, acetone); **The product was analyzed by HPLC to determine the enantiomeric excess:** 93% *ee*; (CHIRALPAK ID, hexane/*i*-PrOH = 70/30, flow rate: 1.0 mL/min, T = 30 °C, 210 nm), t_R (major) = 8.333 min, t_R = 7.437 min. The absolute configuration was assigned tentatively by analogy.

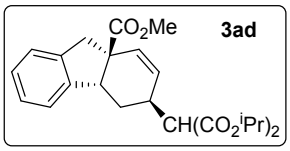
diethyl 2-((3*S*,4a*R*,9a*S*)-9a-(methoxycarbonyl)-4,4a,9,9a-tetrahydro-3H-fluoren-3-yl)malonate (3ac)



(Flash column chromatography eluent, petroleum ether/ethyl acetate = 10 : 1) **Yield**: 88%, 34.2 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18 (dt, *J* = 18.5, 6.5 Hz, 4H), 5.69 (dd, *J* = 10.3, 1.9 Hz, 1H), 5.62 (d, *J* = 10.3 Hz, 1H), 4.28 – 4.12 (m, 4H), 3.89 (t, *J* = 3.6 Hz, 1H), 3.75 (s, 3H), 3.44 (d, *J* = 15.8 Hz, 1H), 3.28 (d, *J* = 8.8 Hz, 1H), 2.99 (d, *J* = 15.8 Hz, 1H), 2.72 (ddd, *J* = 13.5, 8.9, 2.5 Hz, 1H), 2.36 (dt, *J* = 13.5, 4.3 Hz, 1H), 1.97 – 1.82 (m, 1H), 1.27 (dt, *J* = 22.6, 7.1 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.26, 168.36, 168.30,

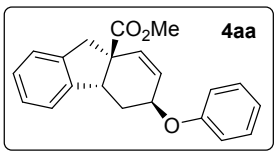
142.92, 140.52, 130.41, 130.36, 127.08, 126.91, 125.07, 123.19, 61.54, 61.51, 56.49, 53.81, 52.39, 44.89, 43.33, 31.20, 26.21, 14.29, 14.21; **IR** (KBr, cm^{-1}) γ 3031, 2982, 1732, 1459, 1394, 1369, 1292, 1225, 1178, 1153, 1096, 1047, 743 cm^{-1}; **HRMS** (ESI) m/z $(M+H)^+$: calculated for $C_{22}H_{27}O_6$: 387.1808, found: 387.1804; $[\alpha]^{20}_D$ = +34.9 (c = 0.41, acetone); **The product was analyzed by HPLC to determine the enantiomeric excess:** 94% *ee*; (CHIRALPAK ID, hexane/*i*-PrOH = 85/15, flow rate: 1.0 mL/min, T = 30 °C, 210 nm), t_R (major) = 11.022 min, t_R = 9.165 min. The absolute configuration was assigned tentatively by analogy.

diisopropyl 2-((3*S*,4a*R*,9a*S*)-9a-(methoxycarbonyl)-4,4a,9,9a-tetrahydro-3H-fluoren-3-yl)malonate (3ad)



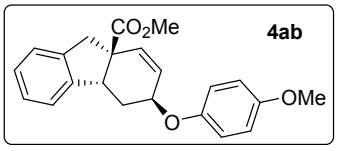
(Flash column chromatography eluent, petroleum ether/ethyl acetate = 10 : 1) **Yield**: 87%, 36.0 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24 – 7.13 (m, 4H), 5.71 – 5.66 (m, 1H), 5.64 (d, *J* = 10.3 Hz, 1H), 5.06 (ddt, *J* = 23.2, 12.5, 6.3 Hz, 2H), 3.89 (t, *J* = 3.7 Hz, 1H), 3.74 (s, 3H), 3.43 (d, *J* = 15.8 Hz, 1H), 3.22 (d, *J* = 8.5 Hz, 1H), 2.98 (d, *J* = 15.8 Hz, 1H), 2.70 (ddd, *J* = 11.1, 7.9, 5.9 Hz, 1H), 2.36 (dt, *J* = 13.5, 4.3 Hz, 1H), 1.91 (ddd, *J* = 13.7, 11.2, 4.0 Hz, 1H), 1.27 (dd, *J* = 6.3, 2.3 Hz, 6H), 1.22 (t, *J* = 6.4 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.31, 167.91, 167.86, 143.00, 140.55, 130.66, 130.16, 127.05, 126.88, 125.07, 123.18, 69.04, 56.78, 53.79, 52.37, 44.92, 43.39, 31.01, 26.12, 21.85, 21.82, 21.79, 21.70; **IR** (KBr, cm^{-1}) γ 2981, 2936, 1731, 1457, 1375, 1291, 1225, 1179, 1103, 1049, 980, 743, 699 cm^{-1}; **HRMS** (ESI) m/z $(M+H)^+$: calculated for $C_{24}H_{31}O_6$: 415.2121, found: 415.2117; $[\alpha]^{20}_D$ = +24.7 (c = 0.37, acetone); **The product was analyzed by HPLC to determine the enantiomeric excess:** 93% *ee*; (CHIRALPAK ID, hexane/*i*-PrOH = 85/15, flow rate: 1.0 mL/min, T = 30 °C, 210 nm), t_R (major) = 8.771 min, t_R = 6.963 min. The absolute configuration was assigned tentatively by analogy.

methyl (4b*R*,6*S*,8a*S*)-6-phenoxy-4b,5,6,9-tetrahydro-8aH-fluorene-8a-carboxylate (4aa)



(Flash column chromatography eluent, petroleum ether/ethyl acetate = 10 : 1) **Yield**: 80%, 26.4 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 – 7.19 (m, 6H), 6.98 – 6.90 (m, 1H), 6.85 (dd, *J* = 8.7, 0.9 Hz, 2H), 5.90 (dt, *J* = 10.3, 1.5 Hz, 1H), 5.84 – 5.78 (m, 1H), 4.71 – 4.57 (m, 1H), 4.04 (t, *J* = 3.8 Hz, 1H), 3.78 (s, 3H), 3.49 (d, *J* = 16.0 Hz, 1H), 3.05 (d, *J* = 16.0 Hz, 1H), 2.83 – 2.67 (m, 1H), 2.35 – 2.17 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.95, 157.64, 142.81, 140.39, 131.29, 129.92, 129.68, 127.35, 127.10, 125.30, 122.96, 121.07, 115.87, 69.07, 54.05, 52.61, 44.69, 43.37, 28.72; **IR** (KBr, cm^{-1}) γ 3025, 2950, 1732, 1596, 1586, 1494, 1291, 1238, 1173, 1052, 813, 753, 692 cm^{-1}; **HRMS** (ESI) m/z $(M+H)^+$: calculated for $C_{21}H_{21}O_3$: 321.1491, found: 321.1487; $[\alpha]^{20}_D$ = -6.4 (c = 0.07, acetone); **The product was analyzed by HPLC to determine the enantiomeric excess:** 91% *ee*; (CHIRALPAK ID, hexane/*i*-PrOH = 90/10, flow rate: 1.0 mL/min, T = 30 °C, 254 nm), t_R (major) = 6.057 min, t_R = 5.222 min. The absolute configuration was assigned tentatively by analogy.

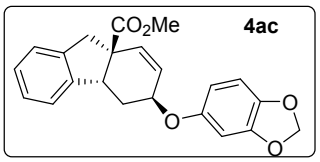
methyl (4b*R*,6*S*,8a*S*)-6-(4-methoxyphenoxy)-4b,5,6,9-tetrahydro-8aH-fluorene-8a-carboxylate (4ab)



(Flash column chromatography eluent, petroleum ether/ethyl acetate = 10 : 1) **Yield**: 80%, 27.9 mg; **^{1}H NMR** (400 MHz,

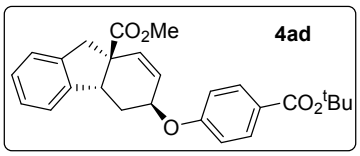
$CDCl_3$) δ 7.25 – 7.17 (m, 4H), 6.81 (s, 4H), 5.89 (dt, *J* = 10.2, 1.5 Hz, 1H), 5.82 – 5.75 (m, 1H), 4.55 – 4.46 (m, 1H), 4.03 (t, *J* = 3.9 Hz, 1H), 3.78 (s, 3H), 3.76 (s, 3H), 3.48 (d, *J* = 15.9 Hz, 1H), 3.03 (d, *J* = 16.0 Hz, 1H), 2.75 – 2.63 (m, 1H), 2.29 – 2.14 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.97, 154.24, 151.59, 142.86, 140.37, 131.10, 130.13, 127.29, 127.05, 125.26, 122.95, 117.34, 114.83, 70.11, 55.84, 54.06, 52.59, 44.67, 43.35, 28.79; **IR** (KBr, cm^{-1}) *γ* 2950, 1731, 1654, 1506, 1458, 1395, 1290, 1232, 1214, 1052, 826, 762, 741 cm^{-1}; **HRMS** (ESI) m/z $(M+H)^+$: calculated for $C_{22}H_{23}O_4$: 351.1596, found: 351.1598; **$[\alpha]^{20}_D$** = -2.1 (c = 0.51, acetone); **The product was analyzed by HPLC to determine the enantiomeric excess:** 90% *ee*; (CHIRALPAK ID, hexane/*i*-PrOH = 85/15, flow rate: 1.0 mL/min, T = 30 °C, 254 nm), t_R (major) = 9.892 min, t_R = 7.093 min. The absolute configuration was assigned tentatively by analogy.

methyl (4b*R*,6*S*,8a*S*)-6-(benzo[d][1,3]dioxol-5-yloxy)-4b,5,6,9-tetrahydro-8aH-fluorene-8a-carboxylate (4ac)



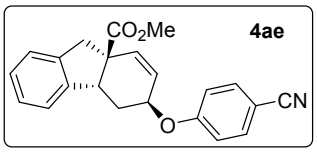
(Flash column chromatography eluent, petroleum ether/ethyl acetate = 10 : 1) **Yield**: 78%, 28.3 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22 (ddd, *J* = 12.5, 6.5, 3.1 Hz, 4H), 6.67 (d, *J* = 8.5 Hz, 1H), 6.46 (d, *J* = 2.5 Hz, 1H), 6.29 (dd, *J* = 8.5, 2.5 Hz, 1H), 5.92 – 5.84 (m, 3H), 5.79 (ddd, *J* = 10.3, 1.6, 1.1 Hz, 1H), 4.52 – 4.39 (m, 1H), 4.02 (t, *J* = 4.0 Hz, 1H), 3.78 (s, 3H), 3.48 (d, *J* = 15.9 Hz, 1H), 3.03 (d, *J* = 16.0 Hz, 1H), 2.77 – 2.61 (m, 1H), 2.30 – 2.09 (m, 1H); **^{13}C NMR** (101 MHz, CDCl3) δ 174.92, 152.91, 148.40, 142.78, 142.06, 140.35, 131.21, 129.91, 127.32, 127.08, 125.27, 122.92, 108.14, 107.91, 101.28, 99.67, 70.51, 54.05, 52.59, 44.64, 43.32, 28.74; **IR** (KBr, cm^{-1}) *γ* 3023, 2950, 1731, 1630, 1502, 1485, 1459, 1393, 1290, 1238, 1183, 1131, 1097, 1039, 932, 813, 780, 754, 743 cm^{-1}; **HRMS** (ESI) m/z $(M+H)^+$: calculated for $C_{22}H_{21}O_5$: 365.1389, found: 365.1390; **$[\alpha]^{20}_D$** = -7.1 (c = 0.40, acetone); **The product was analyzed by HPLC to determine the enantiomeric excess:** 90% *ee*; (CHIRALPAK ID, hexane/*i*-PrOH = 85/15, flow rate: 1.0 mL/min, T = 30 °C, 254 nm), t_R (major) = 10.851 min, t_R = 8.479 min. The absolute configuration was assigned tentatively by analogy.

methyl (4b*R*,6*S*,8a*S*)-6-(4-(tert-butoxycarbonyl)phenoxy)-4b,5,6,9-tetrahydro-8aH-fluorene-8a-carboxylate (4ad)



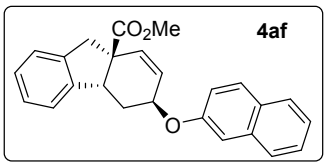
(Flash column chromatography eluent, petroleum ether/ethyl acetate = 10 : 1) **Yield**: 82%, 34.5 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 – 7.88 (m, 2H), 7.29 – 7.21 (m, 4H), 6.86 – 6.81 (m, 2H), 5.87 (d, *J* = 10.3 Hz, 1H), 5.83 (d, *J* = 10.3 Hz, 1H), 4.70 (dd, *J* = 10.0, 5.5 Hz, 1H), 4.05 (t, *J* = 3.9 Hz, 1H), 3.78 (s, 3H), 3.50 (d, *J* = 16.0 Hz, 1H), 3.05 (d, *J* = 16.0 Hz, 1H), 2.74 (dt, *J* = 9.6, 4.3 Hz, 1H), 2.25 (ddd, *J* = 13.9, 10.0, 4.1 Hz, 1H), 1.58 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.78, 165.63, 161.04, 142.51, 140.29, 131.78, 131.55, 129.12, 127.43, 127.16, 125.34, 124.64, 122.85, 114.91, 80.65, 69.18, 53.95, 52.67, 44.54, 43.24, 28.46, 28.35; **IR** (KBr, cm^{-1}) *γ* 2953, 1732, 1708, 1604, 1506, 1458, 1393, 1368, 1291, 1247, 1161, 1116, 1052, 851, 812, 772 cm^{-1}; **HRMS** (ESI) m/z $(M+H)^+$: calculated for $C_{26}H_{29}O_5$: 421.2015, found: 421.2044; **$[\alpha]^{20}_D$** = -34.5 (c = 0.63, acetone); **The product was analyzed by HPLC to determine the enantiomeric excess:** 92% *ee*; (CHIRALPAK ID, hexane/*i*-PrOH = 85/15, flow rate: 1.0 mL/min, T = 30 °C, 254 nm), t_R (major) = 9.645 min, t_R = 6.087 min. The absolute configuration was assigned tentatively by analogy.

methyl (4b*R*,6*S*,8a*S*)-6-(4-cyanophenoxy)-4b,5,6,9-tetrahydro-8aH-fluorene-8a-carboxylate (4ae)



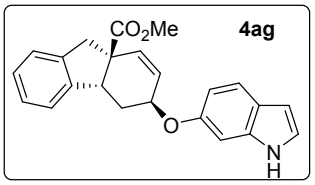
(Flash column chromatography eluent, petroleum ether/ethyl acetate = 10 : 1) **Yield**: 87%, 30.0 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 – 7.51 (m, 2H), 7.29 – 7.20 (m, 4H), 6.91 – 6.85 (m, 2H), 5.86 (d, *J* = 10.3 Hz, 1H), 5.82 (d, *J* = 10.3 Hz, 1H), 4.69 (dd, *J* = 10.0, 5.5 Hz, 1H), 4.05 (t, *J* = 3.8 Hz, 1H), 3.79 (s, 3H), 3.50 (d, *J* = 16.0 Hz, 1H), 3.05 (d, *J* = 16.0 Hz, 1H), 2.72 (dt, *J* = 9.6, 4.4 Hz, 1H), 2.31 – 2.22 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.64, 161.01, 142.30, 140.27, 134.18, 132.28, 128.42, 127.53, 127.20, 125.40, 122.76, 119.30, 116.10, 104.01, 69.58, 53.92, 52.72, 44.44, 43.18, 28.41; **IR** (KBr, cm^{-1}) *γ* 3024, 2952, 1731, 1604, 1505, 1292, 1252, 1172, 1052, 1016, 836, 814, 755 cm^{-1}; **HRMS** (ESI) m/z $(M+H)^+$: calculated for $C_{22}H_{20}NO_3$: 346.1443, found: 346.1437; **$[\alpha]^{20}_D$** = -42.8 (c = 0.45, acetone); **The product was analyzed by HPLC to determine the enantiomeric excess:** 91% *ee*; (CHIRALPAK ID, hexane/*i*-PrOH = 70/30, flow rate: 1.0 mL/min, T = 30 °C, 254 nm), t_R (major) = 8.152 min, t_R = 7.259 min. The absolute configuration was assigned tentatively by analogy.

methyl (4b*R*,6*S*,8a*S*)-6-(naphthalen-2-yloxy)-4b,5,6,9-tetrahydro-8aH-fluorene-8a-carboxylate (4af)



(Flash column chromatography eluent, petroleum ether/ethyl acetate = 10 : 1) **Yield**: 92%, 34.1 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 8.5, 5.4 Hz, 2H), 7.65 (d, *J* = 8.2 Hz, 1H), 7.43 – 7.37 (m, 1H), 7.34 – 7.23 (m, 5H), 7.12 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.04 (d, *J* = 2.4 Hz, 1H), 5.99 (d, *J* = 10.2 Hz, 1H), 5.84 (d, *J* = 10.3 Hz, 1H), 4.83 – 4.73 (m, 1H), 4.07 (t, *J* = 3.8 Hz, 1H), 3.78 (s, 3H), 3.51 (d, *J* = 16.0 Hz, 1H), 3.07 (d, *J* = 16.0 Hz, 1H), 2.80 (ddd, *J* = 9.6, 8.4, 4.2 Hz, 1H), 2.39 – 2.24 (m, 1H); **^{13}C NMR** (101 MHz, CDCl3) δ 174.92, 155.43, 142.82, 140.41, 134.57, 131.47, 129.74, 129.61, 129.15, 127.74, 127.39, 127.16, 126.82, 126.48, 125.32, 123.83, 123.02, 119.66, 108.37, 69.11, 54.06, 52.62, 44.71, 43.37, 28.70; **IR** (KBr, cm^{-1}) *γ* 3024, 2950, 1731, 1629, 1599, 1509, 1467, 1392, 1290, 1256, 1237, 1214, 1179, 1120, 1052, 1027, 839, 814,749 cm^{-1}; **HRMS** (ESI) m/z $(M+H)^+$: calculated for $C_{25}H_{23}O_3$: 371.1647, found: 371.1642; **$[\alpha]^{20}_D$** = -20.0 (c = 0.56, acetone); **The product was analyzed by HPLC to determine the enantiomeric excess:** 90% *ee*; (CHIRALPAK ID, hexane/*i*-PrOH = 85/15, flow rate: 1.0 mL/min, T = 30 °C, 254 nm), t_R (major) = 8.539 min, t_R = 5.784 min. The absolute configuration was assigned tentatively by analogy.

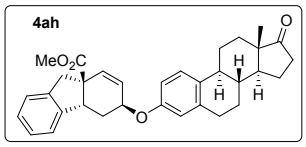
methyl (4b*R*,6*S*,8a*S*)-6-((1H-indol-6-yl)oxy)-4b,5,6,9-tetrahydro-8aH-fluorene-8a-carboxylate (4ag)



(Flash column chromatography eluent, petroleum ether/ethyl acetate = 10 : 1) **Yield**: 74%, 26.6 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.28 – 7.18 (m, 5H), 7.14 (t, *J* = 2.7 Hz, 1H), 7.06 (d, *J* = 2.1 Hz, 1H), 6.83 (dd, *J* = 8.8, 2.3 Hz, 1H), 6.42 (s, 1H), 5.98 (d, *J* = 10.2 Hz, 1H), 5.78 (d, *J* = 10.2 Hz, 1H), 4.71 – 4.52 (m, 1H), 4.03 (t, *J* = 3.7 Hz, 1H), 3.77 (s, 3H), 3.48 (d, *J* = 15.9 Hz, 1H), 3.04 (d, *J* = 16.0 Hz, 1H), 2.74 (dt, *J* = 12.9, 4.5 Hz, 1H), 2.36 – 2.19 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.11, 151.83,

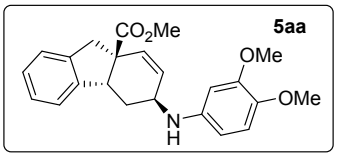
143.00, 140.38, 131.49, 130.83, 130.52, 128.43, 127.22, 127.03, 125.21, 125.10, 123.06, 114.22, 111.86, 106.12, 102.48, 70.36, 54.10, 52.57, 44.75, 43.39, 28.92; **IR** (KBr, cm^{-1}) γ 3026, 2950, 1728, 1623, 1581, 1475, 1456, 1290, 1239, 1216, 1149, 1052, 1021, 809, 755, 727 cm^{-1}; **HRMS** (ESI) m/z $(M+H)^+$: calculated for $C_{23}H_{22}NO_3$: 360.1600, found: 360.1591; $[\alpha]^{20}_D$ = -7.1 (c = 0.42, acetone); **The product was analyzed by HPLC to determine the enantiomeric excess:** 87% *ee*; (CHIRALPAK ID, hexane/*i*-PrOH = 70/30, flow rate: 1.0 mL/min, T = 30 °C, 254 nm), t_R (major) = 8.230 min, t_R = 5.691 min. The absolute configuration was assigned tentatively by analogy.

methyl (4b*R*,6*S*,8a*S*)-6-(((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)oxy)-4b,5,6,9-tetrahydro-8aH-fluorene-8a-carboxylate (4ah)



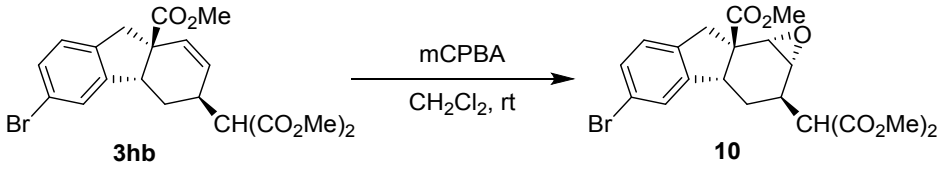
(Flash column chromatography eluent, petroleum ether/ethyl acetate = 10 : 1) **Yield**: 70%, 34.7 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27 – 7.19 (m, 4H), 7.16 (d, *J* = 8.5 Hz, 1H), 6.66 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.59 (d, *J* = 2.6 Hz, 1H), 5.94 – 5.86 (m, 1H), 5.79 (dd, *J* = 11.8, 1.1 Hz, 1H), 4.65 – 4.50 (m, 1H), 4.03 (t, *J* = 3.9 Hz, 1H), 3.78 (s, 3H), 3.49 (d, *J* = 15.9 Hz, 1H), 3.04 (d, *J* = 16.0 Hz, 1H), 2.93 – 2.81 (m, 2H), 2.76 – 2.64 (m, 1H), 2.50 (dd, *J* = 18.8, 8.5 Hz, 1H), 2.41 – 2.31 (m, 1H), 2.26 – 1.91 (m, 6H), 1.64 – 1.40 (m, 6H), 0.90 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 221.10, 174.93, 155.60, 142.84, 140.37, 137.99, 132.45, 131.15, 130.02, 127.30, 127.05, 126.52, 125.27, 122.95, 115.92, 113.25, 69.01, 53.98, 52.61, 50.52, 48.13, 44.64, 44.10, 43.34, 38.45, 36.00, 31.69, 29.76, 28.73, 26.65, 26.00, 21.71, 13.98; **IR** (KBr, cm^{-1}) γ 2929, 1736, 1608, 1497, 1456, 1434, 1281, 1236, 1215, 1054, 1029, 815, 740 cm^{-1}; **HRMS** (ESI) m/z $(M+H)^+$: calculated for $C_{33}H_{37}O_4$: 497.2692, found: 497.2688; $[\alpha]^{20}_D$ = +67.0 (c = 0.14, acetone); **The product was analyzed by HPLC to determine the enantiomeric excess:** 92% *ee*; (CHIRALPAK ID, hexane/*i*-PrOH = 70/30, flow rate: 1.0 mL/min, T = 30 °C, 254 nm), t_R (major) = 13.004 min, t_R = 11.629 min. The absolute configuration was assigned tentatively by analogy.

methyl (4b*R*,6*S*,8a*S*)-6-((3,4-dimethoxyphenyl)amino)-4b,5,6,9-tetrahydro-8aH-fluorene-8a-carboxylate (5aa)

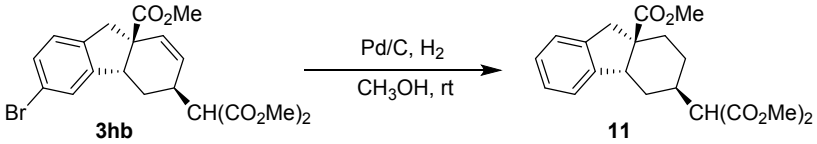


(Flash column chromatography eluent, petroleum ether/ethyl acetate = 10 : 1) **Yield**: 81%, 30.9 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 – 7.18 (m, 4H), 6.71 (d, *J* = 8.6 Hz, 1H), 6.22 (d, *J* = 2.6 Hz, 1H), 6.11 (dd, *J* = 8.6, 2.6 Hz, 1H), 5.82 (d, *J* = 10.2 Hz, 1H), 5.71 (dd, *J* = 10.1, 1.0 Hz, 1H), 3.96 (t, *J* = 3.6 Hz, 1H), 3.82 (s, 3H), 3.80 (s, 3H), 3.77 (s, 3H), 3.76 – 3.73 (m, 1H), 3.49 (d, *J* = 15.9 Hz, 1H), 3.02 (d, *J* = 15.9 Hz, 1H), 2.65 (dt, *J* = 13.4, 4.2 Hz, 1H), 1.99 – 1.85 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.31, 150.22, 143.06, 141.98, 141.66, 140.58, 132.07, 130.18, 127.21, 126.92, 125.24, 122.93, 113.37, 104.82, 99.99, 56.78, 55.88, 54.03, 52.51, 46.24, 45.07, 43.23, 29.91; **IR** (KBr, cm^{-1}) γ 3370, 2932, 1729, 1614, 1515, 1460, 1404, 1291, 1234, 1168, 1138, 1047, 1026, 752 cm^{-1}; **HRMS** (ESI) m/z $(M+H)^+$: calculated for $C_{23}H_{26}NO_4$: 380.1862, found: 380.1858; $[\alpha]^{20}_D$ = -1.4 (c = 0.51, acetone); **The product was analyzed by HPLC to determine the enantiomeric excess:** 89% *ee*; (CHIRALPAK ID, hexane/*i*-PrOH = 70/30, flow rate: 1.0 mL/min, T = 30 °C, 254 nm), t_R (major) = 18.605 min, t_R = 14.612 min. The absolute configuration was assigned tentatively by analogy.

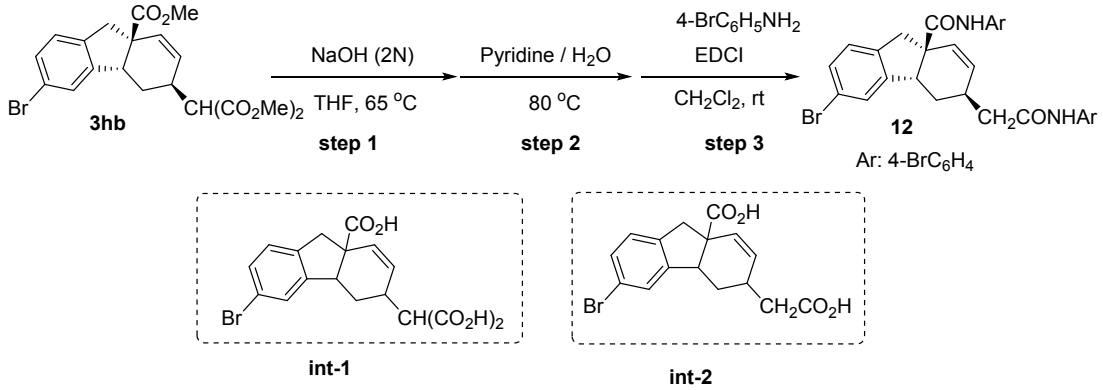
Synthesis of 10, 11, 12, 13



3hb (0.1 mmol, 43.7 mg, 97% ee) was dissolved in CH_2Cl_2 (2 mL) in a flame-dried and Ar-purged Schlenk tube (20 mL) at 0 °C. To this solution was added mCPBA (0.2 mmol, 40.6 mg), and then the reaction mixture was stirred with a magnetic stir bar and allowed to gradually warm to room temperature. After 16 h, the solution was diluted with CH_2Cl_2 and washed with aqueous $NaHCO_3$ solution. The organic phase was dried with $MgSO_4$ and concentrated under vacuum. The product was purified by flash silica gel chromatography (petroleum ether/dichloromethane/ethyl acetate = 4 : 1 : 1).



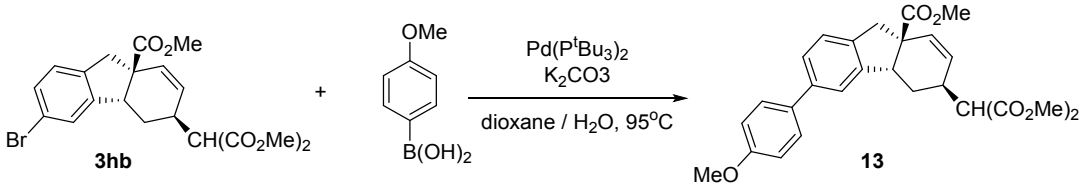
To the Schlenk tube charged with a solution of **3hb** (0.1 mmol, 43.7mg, 97% ee) in anhydrous CH_3OH (2 mL) were added 10% Pd/C (0.1 equiv, 0.01 mmol, 10 mg) and a stir ball. After being stirred at 25 °C under a H_2 atmosphere overnight, the mixture was filtrated with silica gel and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10 : 1) to give **11** in 93% yield.



Step 1: To a solution of **3hb** (0.5 mmol, 0.2186 g) in 5 mL THF was added 2N NaOH (5 mL). The solution was stirred overnight at 65 °C, then cooled down and acidified with 10% citric acid to pH 2-3. The solution was extracted with DCM and the organic layer dried over anhydrous $MgSO_4$ then concentrated under vacuum. The residue was used for the next step without further purification.

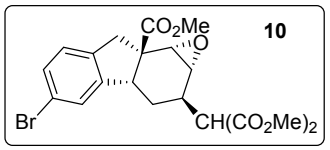
Step 2: A stirred solution of **int-1** in pyridine (2 mL) and H_2O (0.09 mL) was heated to 80 °C for 8 h. The reaction mixture then was allowed to cool to rt, diluted with H_2O, acidified with 2 N HCl to pH 2, and extracted with CH_2Cl_2. The organic layer was dried over anhydrous $MgSO_4$ then concentrated under vacuum. The residue was used for the next step without further purification.

Step 3: To a solution of **int-2** and EDCI (1.5 mmol, 0.2876 g) in 3mL anhydrous DCM was added 4-bromoaniline (1.5 mmol, 0.1847 g) dropwisely. The solution was stirred overnight at rt. Then it was washed with water. The organic phase was combined and dried with $MgSO_4$ and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel (petroleum ether/acetone = 5 : 1) to give **12** in 57% yield.



To a flame-dried Ar-purged schlenk tube were added $Pd(P^tBu_3)_2$ (0.005 mmol, 2.3 mg), **3hb** (0.1 mmol, 43.7 mg, 97% ee), (4-methoxyphenyl)boronic acid(0.3 mmol, 45.6 mg), K_2CO_3 (0.3 mmol, 41.5 mg), Then 0.9 mL 1,4-dioxane and 0.3 mL H_2O was added to the mixture under Ar atmosphere. The resulting solution was subjected to three freeze-pump-thaw cycles using liquid nitrogen to degas the solution, then the mixture was stirred at 95 °C for 24 hours. Afterwards the mixture was diluted with ethyl acetate and washed with 1N HCl. The organic phase was dried with $MgSO_4$ and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5 : 1) to give **13** in 70% yield.

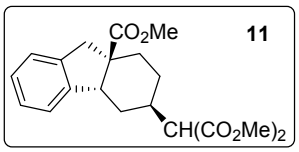
dimethyl 2-((1a*R*,2*R*,3a*R*,8a*R*,8b*S*)-5-bromo-8a-(methoxycarbonyl)-1a,3,3a,8,8a,8b-hexahydro-2H-fluoreno[1,2-b]oxiren-2-yl)malonate (10)



(Flash column chromatography eluent, petroleum ether/dichloromethane /ethyl acetate = 4 : 1: 1) **Yield**: 72%, 32.6 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 1H), 7.25 (s, 1H), 7.04 (d, *J* = 8.0 Hz, 1H), 3.82 (d, *J* = 3.6 Hz, 1H), 3.80 (s, 3H), 3.78 (s, 3H), 3.72 (s, 3H), 3.45 (d, *J* = 9.1 Hz, 1H), 3.28 (d, *J* = 16.7 Hz, 1H), 3.24 (dd, *J* = 3.9, 1.0 Hz, 1H), 3.15 (d, *J* = 3.9 Hz, 1H), 3.08 (d, *J* = 16.7 Hz, 1H), 2.56 – 2.43 (m, 1H), 1.91 – 1.76 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.90, 168.45, 144.86, 138.41, 130.53, 126.81, 125.98, 121.32, 58.03, 54.44, 54.23, 52.77, 52.76, 52.60, 51.71, 43.26, 41.50, 30.80, 21.90; **IR** (KBr, cm^{-1}) *γ* 2959, 2924, 2853, 1735, 1435, 1404, 1261, 1099, 1054, 801 cm^{-1}; **HRMS** (ESI) m/z $(M+H)^+$: calculated for $C_{20}H_{22}BrO_7$: 453.0549, found: 453.0546; **$[\alpha]^{20}_D$** = +6.3 (c = 0.28, acetone); **The product was analyzed by HPLC to determine the enantiomeric excess:** 97% *ee*; (CHIRALPAK ID, hexane/*i*-PrOH = 70/30, flow rate: 1.0 mL/min, T = 30 °C, 210 nm), t_R (major) = 18.836 min, t_R = 11.899 min.

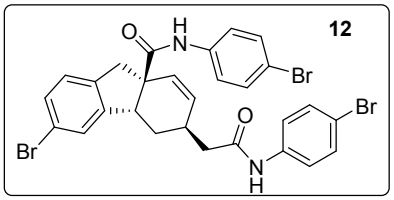
dimethyl 2-((3*R*,4a*R*,9a*R*)-9a-(methoxycarbonyl)-2,3,4,4a,9,9a-hexahydro-1H-fluoren-3-yl)malonate (11)

(Flash column chromatography eluent, petroleum ether/ethyl acetate = 10 : 1) **Yield**: 93%, 33.5 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 – 7.12 (m, 4H), 3.78 (s, 3H), 3.76 (s, 4H), 3.69 (s, 3H), 3.23 – 3.14 (m, 2H), 2.74 (d, *J* = 15.3 Hz, 1H), 2.40 – 2.25 (m, 1H), 2.12 – 1.98 (m, 2H), 1.80 – 1.65 (m, 1H), 1.48 – 1.32 (m, 2H), 1.27 – 1.10 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.72, 169.06, 169.02, 143.55, 140.79, 127.02, 126.77, 125.23, 123.15, 57.70, 52.98, 52.50, 52.44, 52.12, 46.21, 43.55, 32.82, 30.48, 28.40, 27.34; **IR** (KBr, cm^{-1}) *γ* 3022, 2952, 2856, 1732, 1479, 1435,



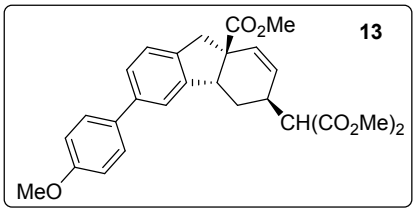
1402, 1332, 1233, 1197, 1154, 1111, 1066, 1036, 767, 741 cm^{-1}; **HRMS** (ESI) m/z $(M+H)^+$: calculated for $C_{20}H_{25}O_6$: 361.1651, found: 361.1646; **$[\alpha]^{20}_D$** = -44.5 (c = 0.59, acetone); **The product was analyzed by HPLC to determine the enantiomeric excess:** 97% *ee*; (CHIRALPAK IC, hexane/*i*-PrOH = 70/30, flow rate: 1.0 mL/min, T = 30 °C, 210 nm), t_R (major) = 10.853 min, t_R = 8.215 min.

(4b*S*,6*S*,8a*R*)-3-bromo-N-(4-bromophenyl)-6-(2-((4-bromophenyl)amino)-2-oxoethyl)-4b,5,6,9-tetrahydro-8aH-fluorene-8a-carboxamide (12)



(Flash column chromatography eluent, petroleum ether/acetone = 5 : 1) **Yield**: 57%, 187.8 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.87 (s, 1H), 7.76 – 7.62 (m, 2H), 7.46 – 7.28 (m, 8H), 7.24 (s, 1H), 7.10 (d, *J* = 7.9 Hz, 1H), 5.90 (d, *J* = 10.1 Hz, 1H), 5.65 (dd, *J* = 10.1, 1.5 Hz, 1H), 4.01 (d, *J* = 15.8 Hz, 1H), 3.63 (s, 1H), 2.83 – 2.65 (m, 2H), 2.53 (dd, *J* = 16.1, 4.1 Hz, 1H), 2.46 (s, 1H), 2.35 – 2.18 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.27, 169.77, 144.79, 141.17, 137.63, 136.26, 135.68, 132.00, 131.61, 130.14, 128.04, 126.80, 125.63, 121.80, 120.00, 117.50, 116.76, 56.60, 47.54, 41.02, 39.80, 27.82, 25.52; **IR** (KBr, cm^{-1}) *γ* 3310, 2925, 2854, 1662, 1590, 1521, 1489, 1394, 1305, 1243, 1178, 1071, 1010, 822, 738 cm^{-1}; **HRMS** (ESI) m/z $(M+H)^+$: calculated for $C_{28}H_{24}Br_3N_2O_4$: 656.9388, found: 656.9407; **$[\alpha]^{20}_D$** = +41.5 (c = 0.44, acetone); **The product was analyzed by HPLC to determine the enantiomeric excess:** 97% *ee*; (CHIRALPAK IE, hexane/*i*-PrOH = 85/15, flow rate: 1.0 mL/min, T = 30 °C, 254 nm), t_R (major) = 10.944 min, t_R = 9.045 min.

dimethyl 2-((3*S*,4a*R*,9a*S*)-9a-(methoxycarbonyl)-6-(4-methoxyphenyl)-4,4a,9,9a-tetrahydro-3H-fluoren-3-yl)malonate (13)



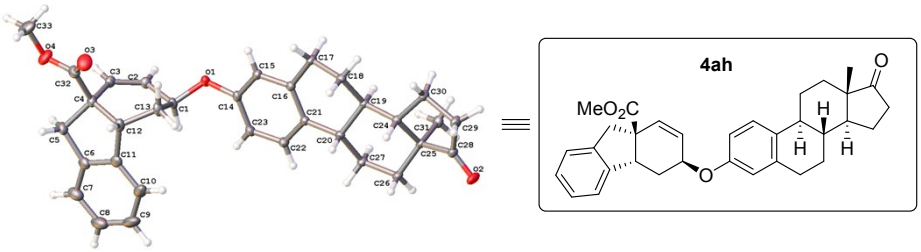
(Flash column chromatography eluent, petroleum ether/ethyl acetate = 5 : 1) **Yield**: 70%, 28.3 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 – 7.48 (m, 2H), 7.40 – 7.33 (m, 2H), 7.24 – 7.19 (m, 1H), 7.02 – 6.94 (m, 2H), 5.77 – 5.69 (m, 1H), 5.63 (d, *J* = 10.3 Hz, 1H), 3.93 (s, 1H), 3.85 (s, 3H), 3.77 (s, 3H), 3.76 (s, 3H), 3.71 (s, 3H), 3.46 (d, *J* = 15.9 Hz, 1H), 3.35 (d, *J* = 8.8 Hz, 1H), 3.01 (d, *J* = 15.9 Hz, 1H), 2.89 – 2.73 (m, 1H), 2.39 (dt, *J* = 13.6, 4.1 Hz, 1H), 1.92 (ddd, *J* = 13.7, 11.1, 4.0 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.19, 168.71, 168.64, 159.15, 143.55, 139.94, 139.08, 134.18, 130.58, 130.20, 128.34, 125.98, 125.31, 121.53, 114.31, 56.19, 55.48, 54.08, 52.61, 52.56, 52.45, 44.87, 42.97, 31.33, 26.34; **IR** (KBr, cm^{-1}) *γ* 3003, 2952, 2841, 1732, 1609, 1520, 1488, 1435, 1247, 1180, 1111, 1042, 840, 821, 732 cm^{-1}; **HRMS** (ESI) m/z $(M+H)^+$: calculated for $C_{27}H_{29}O_7$: 465.1913, found: 465.1903; **$[\alpha]^{20}_D$** = +94.0 (c = 0.50, acetone); **The product was analyzed by HPLC to determine the enantiomeric excess:** 97% *ee*; (CHIRALPAK IC, hexane/*i*-PrOH = 70/30, flow rate: 1.0 mL/min, T = 30 °C, 254 nm), t_R (major) = 22.322 min, t_R = 12.367 min.

References

(1) Lin, H. C.; Wang, P. S.; Tao, Z. L.; Chen, Y. G.; Han Z. Y.; Gong, L. Z. *J. Am. Chem. Soc.* **2016**, *138*, 14354.

7. X-ray Single Crystal Data for 4ah

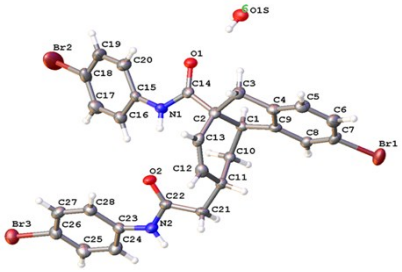
CCDC 1879991

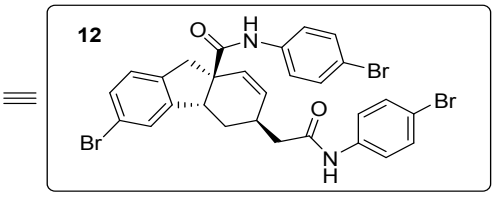


Empirical formula	C33 H36 O4
Formula weight	496.62
Temperature	170.0 K
Wavelength	1.34139 Å
Crystal system	Monoclinic
Space group	P 1 21 1
Unit cell dimensions	a = 6.83500(10) Å α= 90°
	b = 7.9694(2) Å β= 96.5050(10)°
	c = 24.6235(5) Å γ= 90°
Volume	1332.63(5) $Å^3$
Z	2
Density (calculated)	1.238 Mg/m^3
Absorption coefficient	0.406 mm^{-1}
F(000)	532
Crystal size	0.15 x 0.1 x 0.03 mm^3
Theta range for data collection	4.718 to 54.936°.
Index ranges	-8<=h<=8, -9<=k<=9, -29<=l<=30
Reflections collected	16789
Independent reflections	4937 [R(int) = 0.0473]
Completeness to theta = 53.594°	99.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7508 and 0.5224
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4937/1/336
Goodness-of-fit on F^2	1.058
Final R indices [I>2sigma(I)]	R1 = 0.0416, wR2 = 0.1107
R indices (all data)	R1 = 0.0428, wR2 = 0.1121
Absolute structure parameter	0.06(12)
Extinction coefficient	n/a
Largest diff. peak and hole	0.225 and -0.252 $e.Å^{-3}$

8. X-ray Single Crystal Data for 10

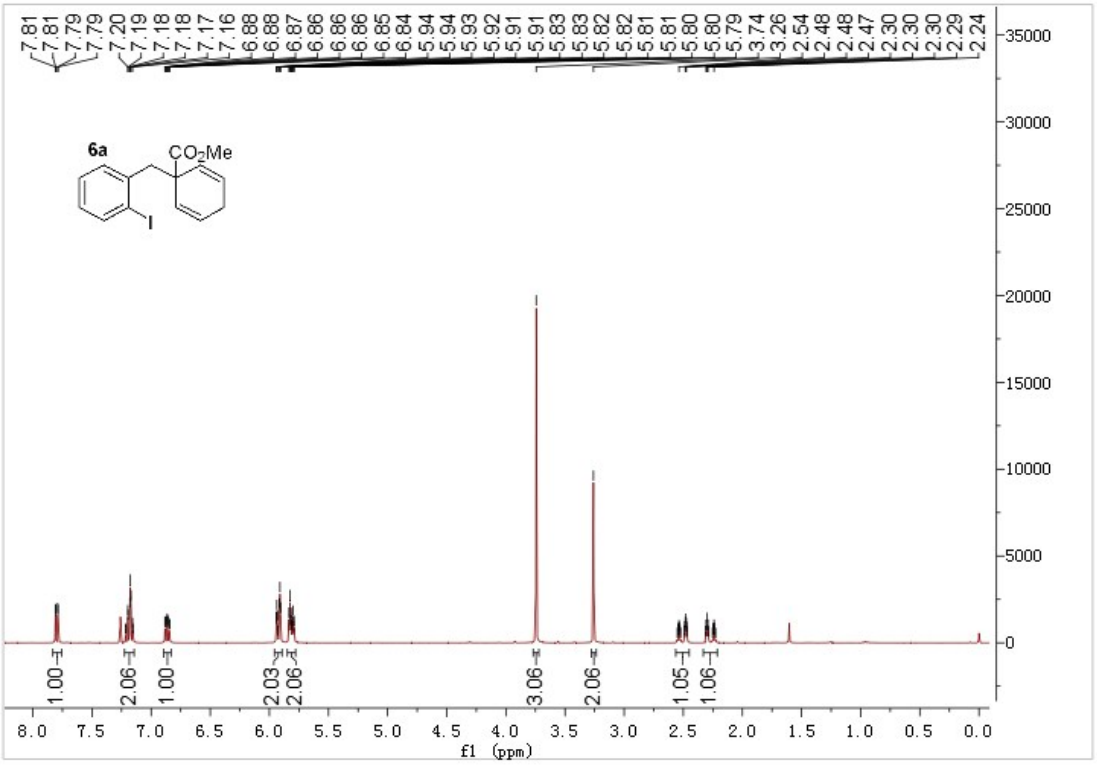
CCDC 1879992

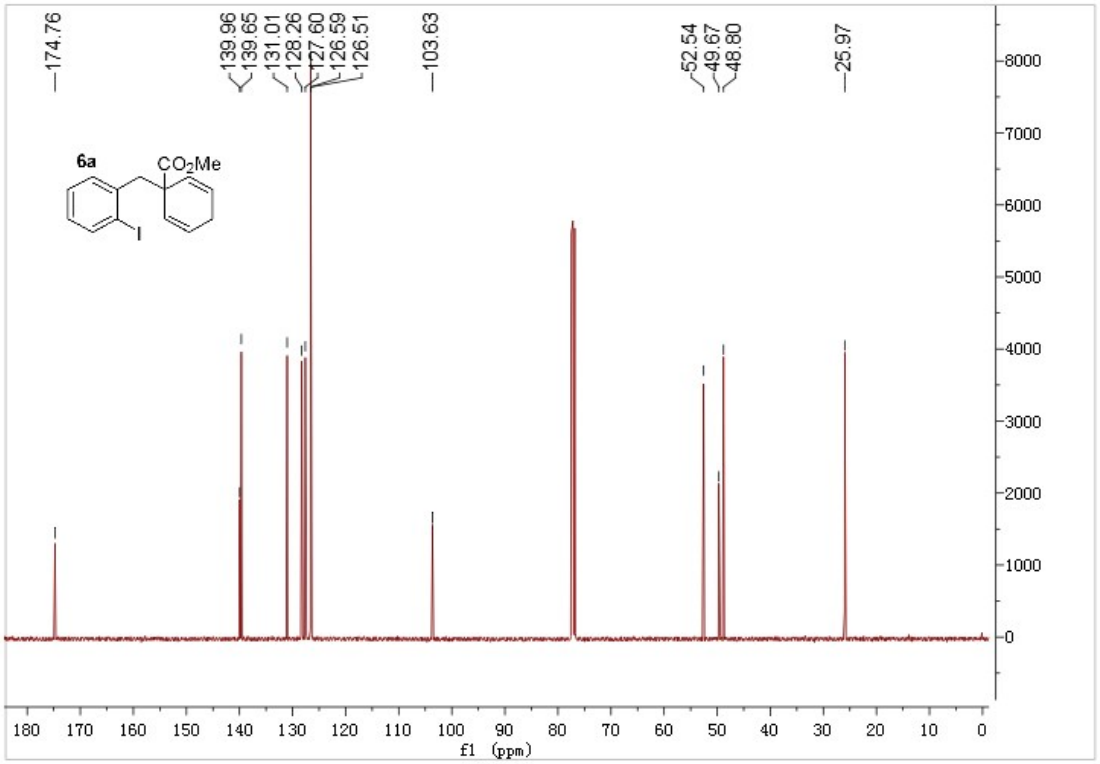


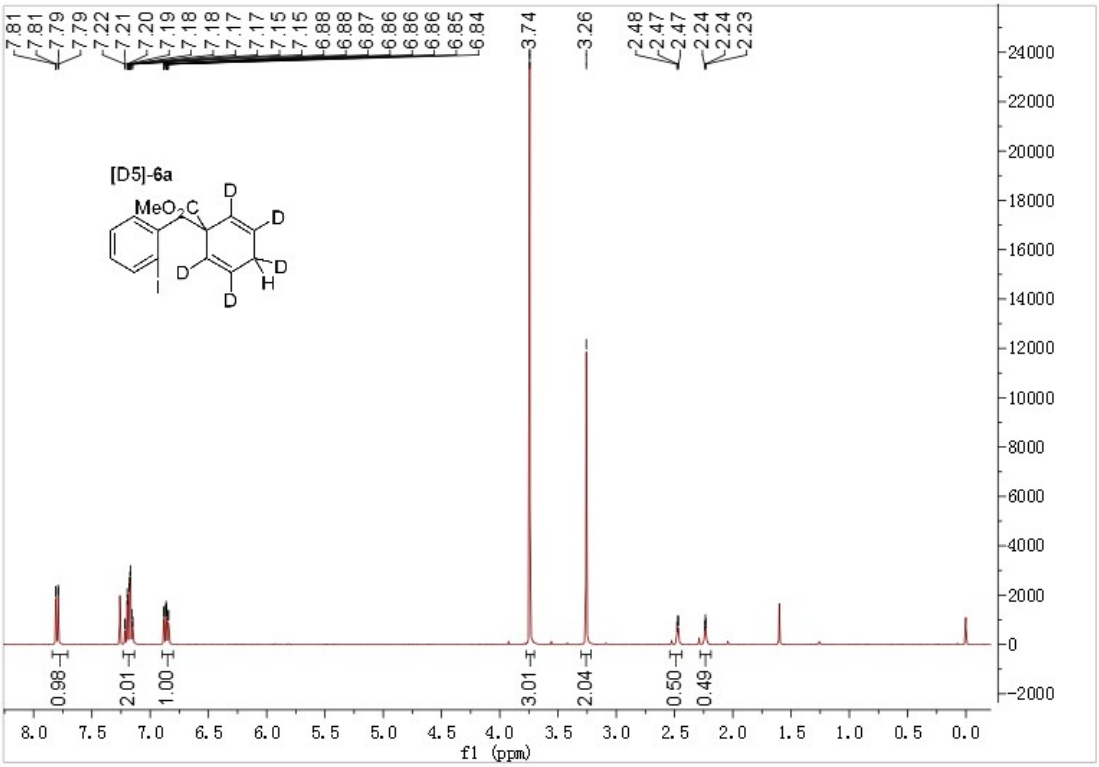


Empirical formula	C28 H25 Br3 N2 O3
Formula weight	677.23
Temperature	296.15 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 1 21 1
Unit cell dimensions	a = 7.4998(9) Å α= 90°
	b = 23.790(3) Å β= 100.688(2)°
	c = 7.8325(9) Å γ= 90°
Volume	1373.2(3) $Å^3$
Z	2
Density (calculated)	1.638 Mg/m^3
Absorption coefficient	4.438 mm^{-1}
F(000)	672
Crystal size	0.12 x 0.05 x 0.02 mm^3
Theta range for data collection	1.712 to 27.461°.
Index ranges	-9<=h<=9, -29<=k<=30, -10<=l<=8
Reflections collected	11233
Independent reflections	5403 [R(int) = 0.0527]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.4261
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5403/1/328
Goodness-of-fit on F^2	0.992
Final R indices [I>2sigma(I)]	R1 = 0.0443, wR2 = 0.0872
R indices (all data)	R1 = 0.0963, wR2 = 0.1035
Absolute structure parameter	0.028(11)
Extinction coefficient	n/a
Largest diff. peak and hole	0.381 and -0.431 $e.Å^{-3}$

9. NMR Spectra for Substrates



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D
D
D
H
D
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7.19
7.18
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7.17
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6.86
6.86
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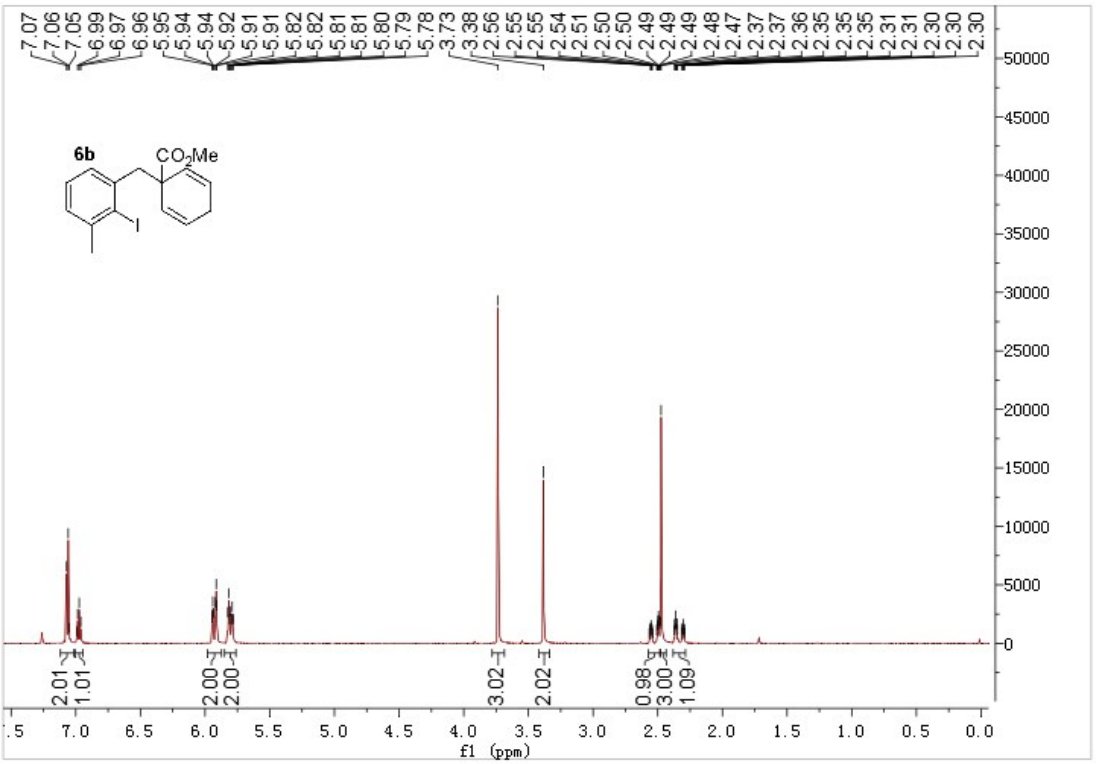
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2.31
2.30
2.30
2.30
6b
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2.02
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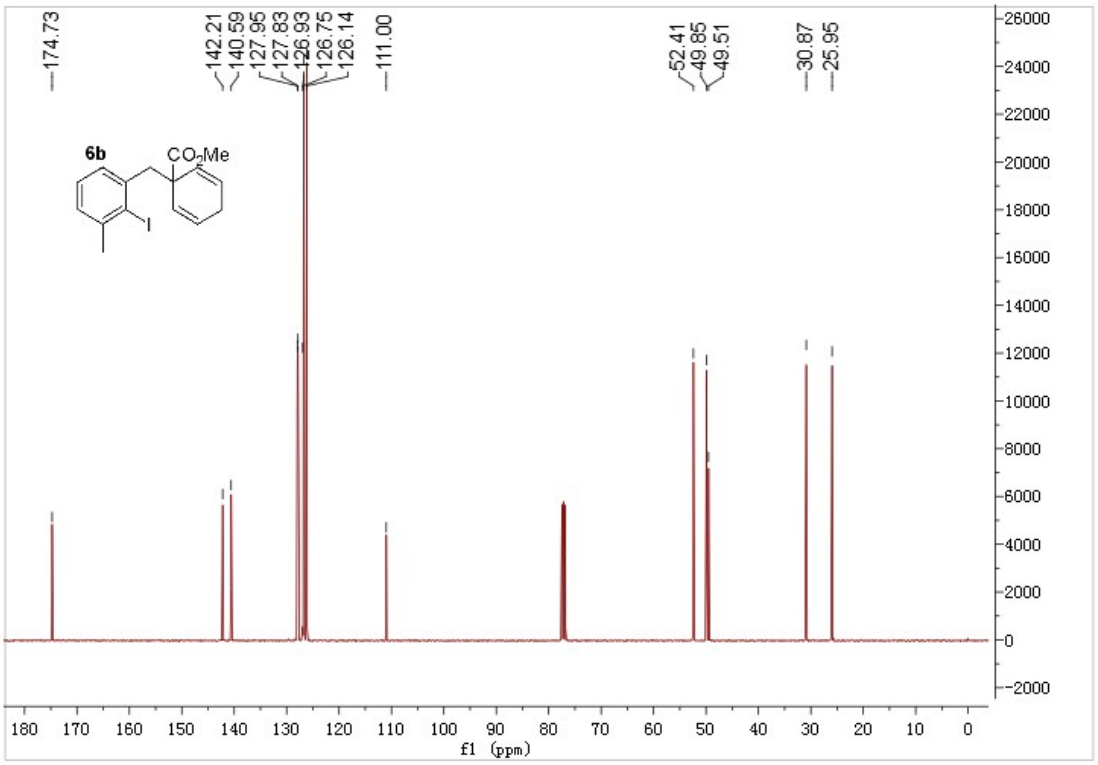
1.09
f1 (ppm)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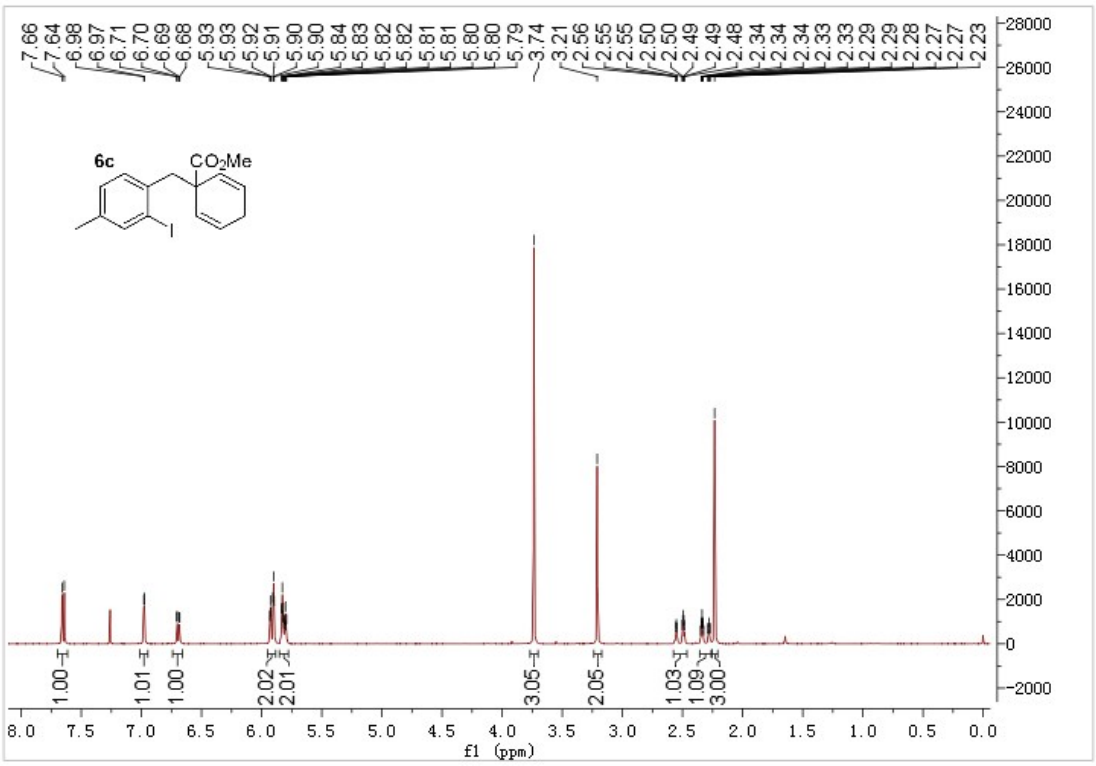
f1 (ppm)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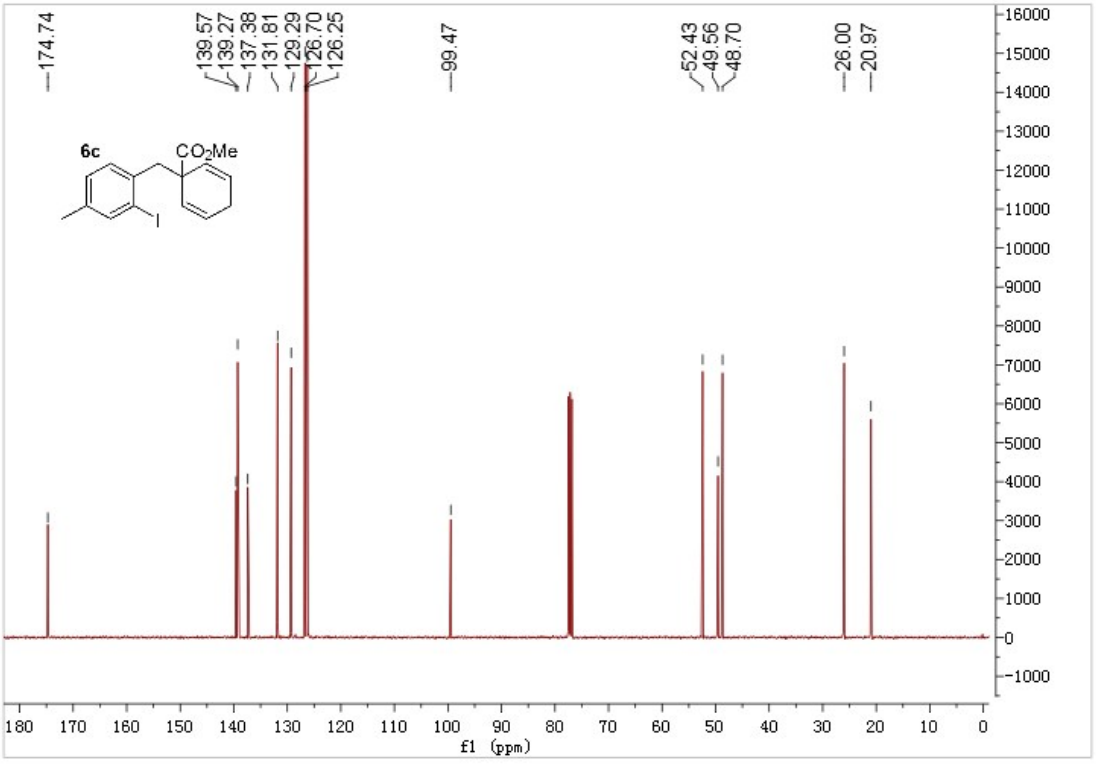
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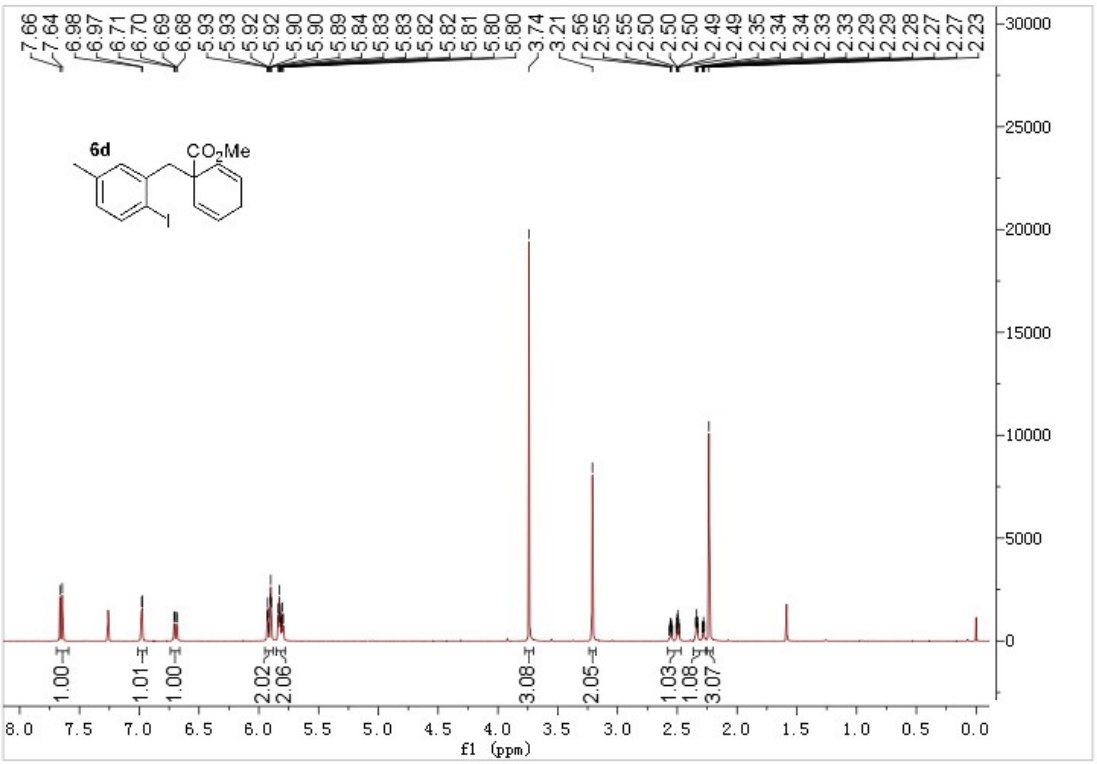
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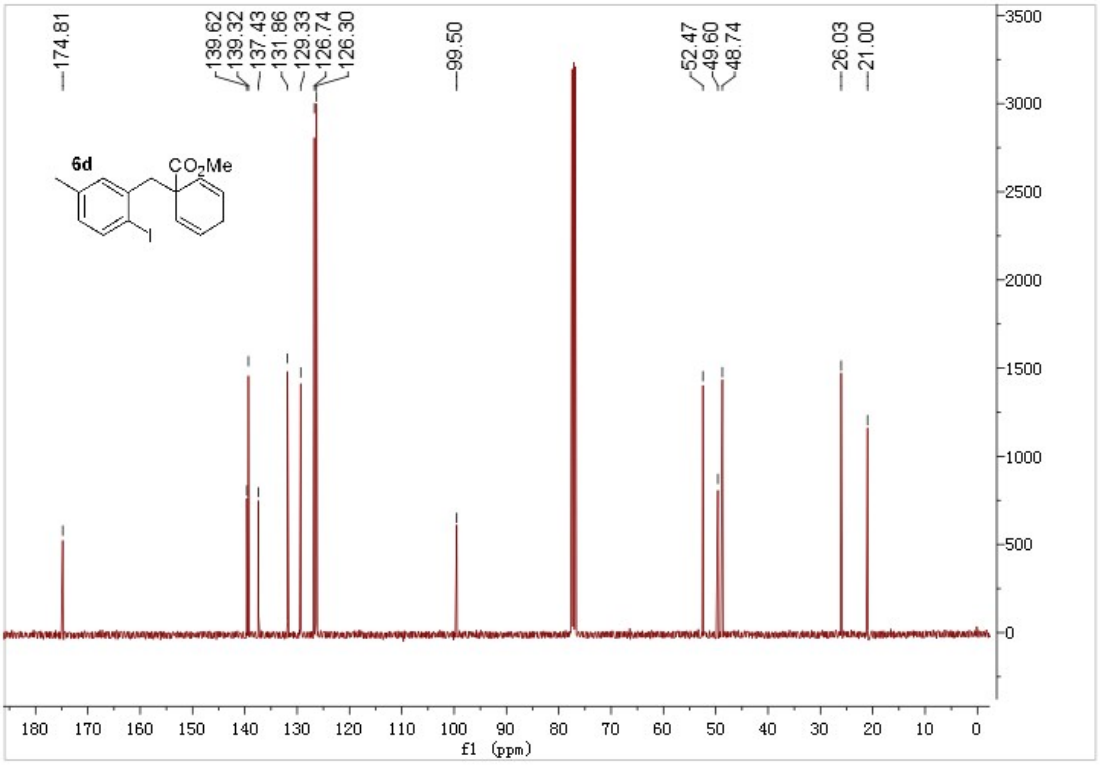
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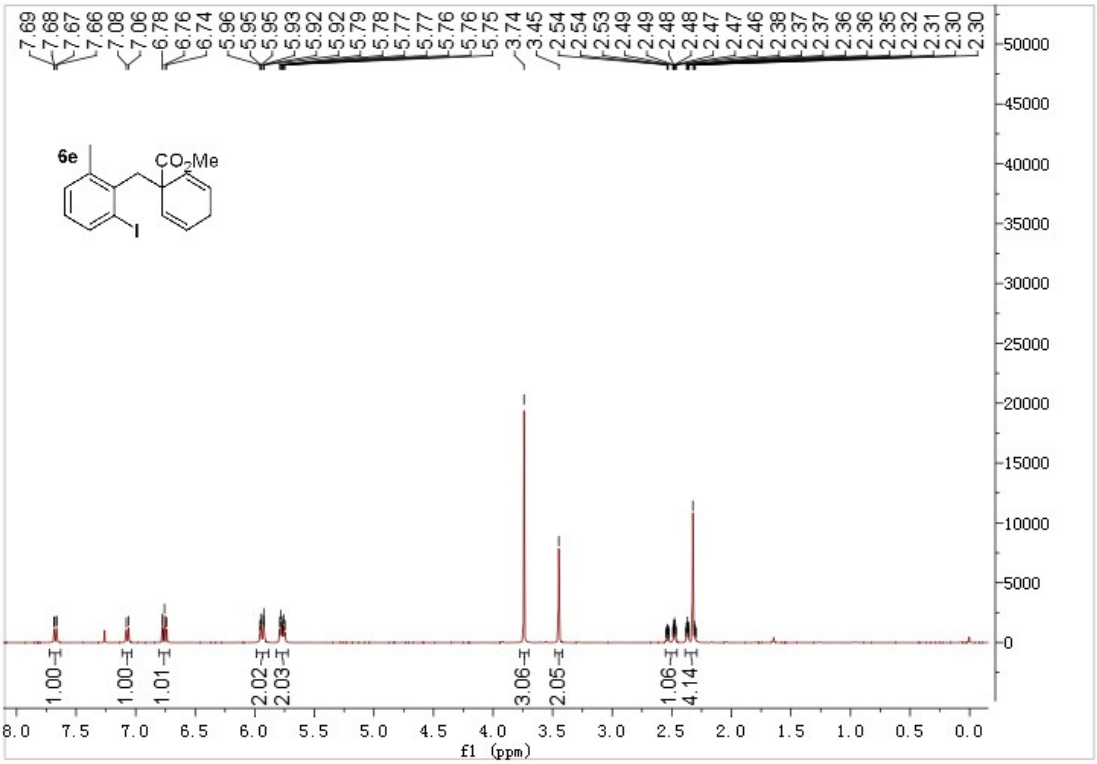
I
f1 (ppm)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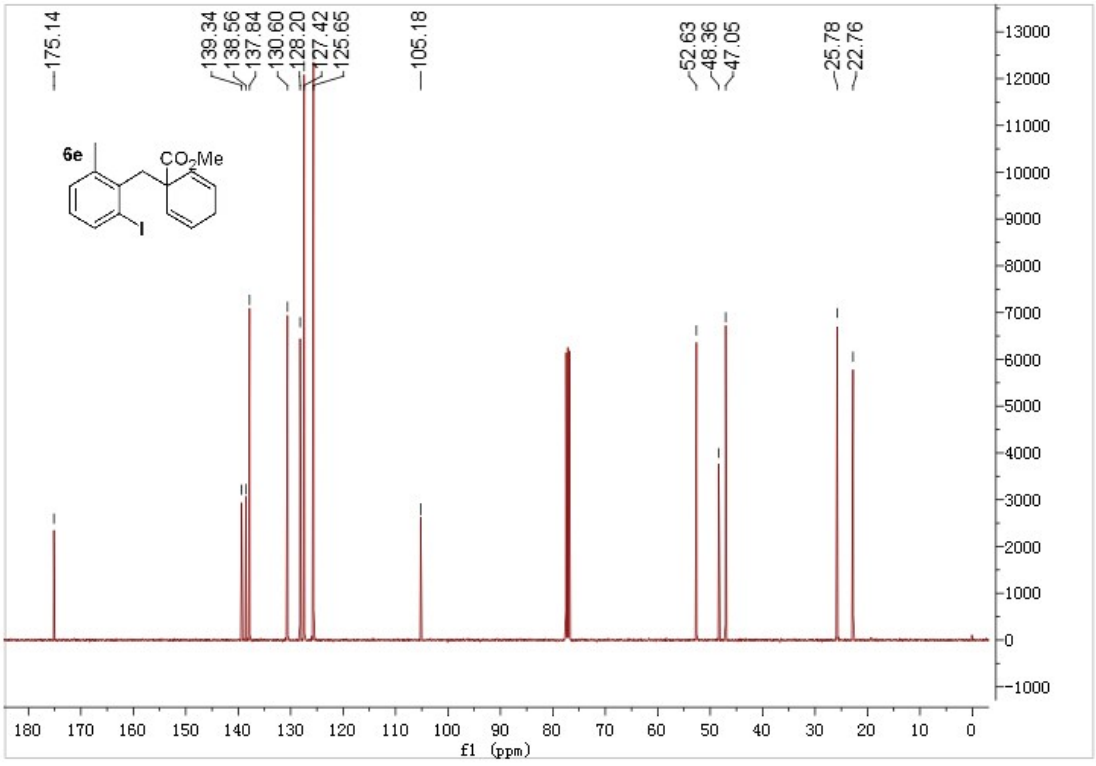
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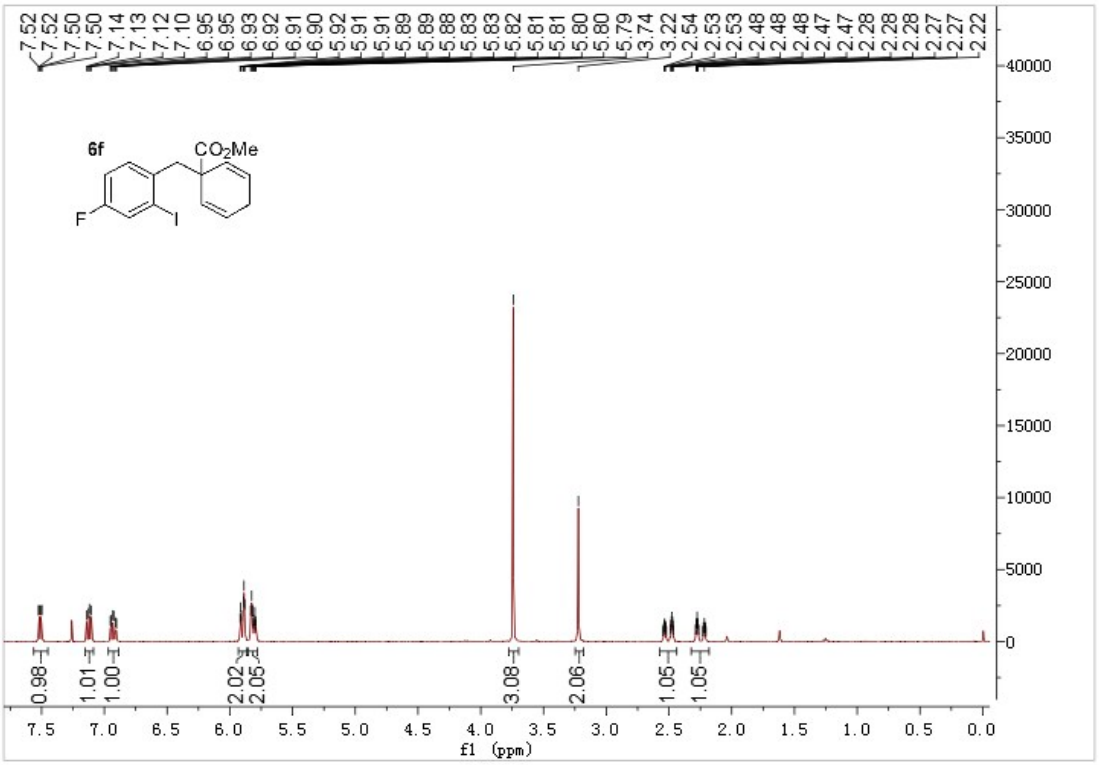
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2.27
2.27
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CO2Me
F
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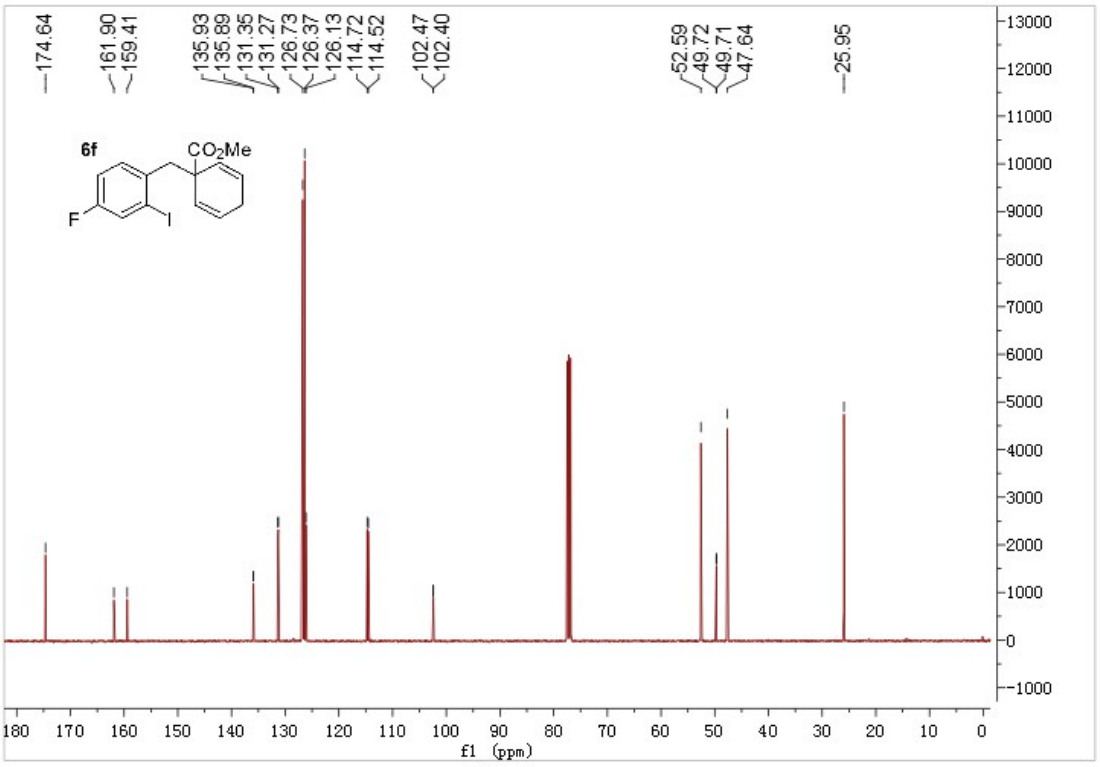
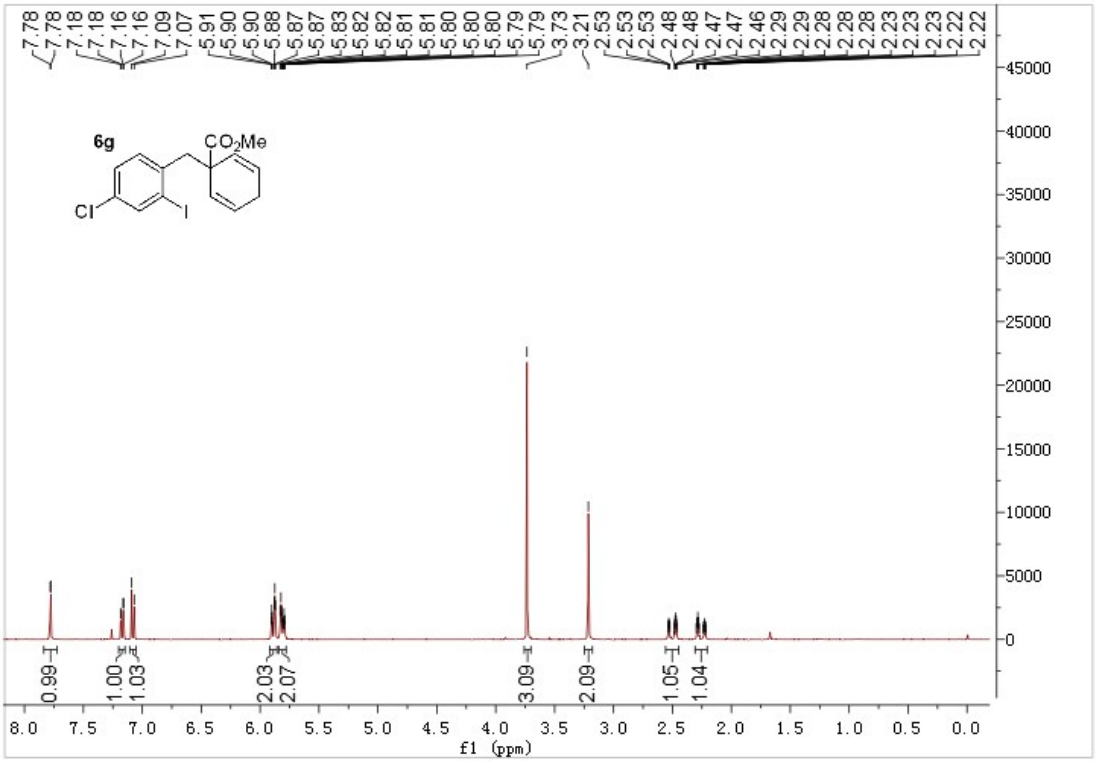
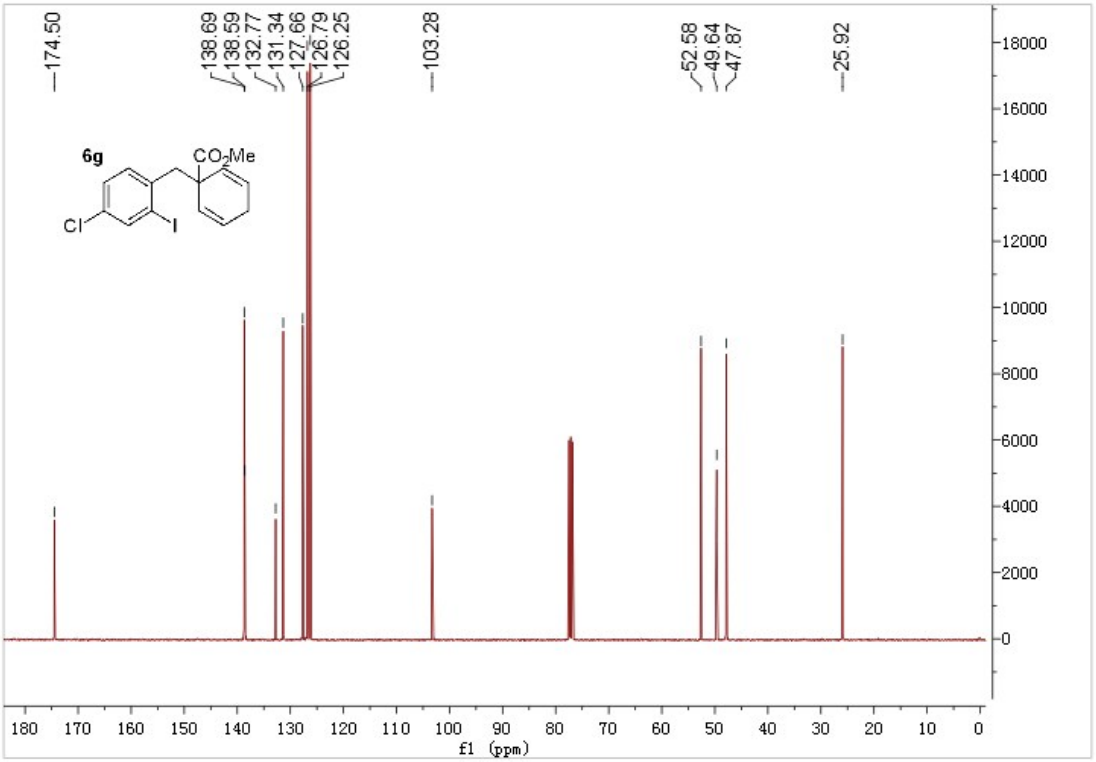
1.00
2.02
2.05
3.08
2.06
1.05
1.05
f1 (ppm)


174.64
161.90
159.41
135.93
135.89
131.35
131.27
126.73
126.37
126.13
114.72
114.52
102.47
102.40
52.59
49.72
49.71
47.64
25.95
6f
CO2Me
F
I
f1 (ppm)


7.78
7.78
7.18
7.16
7.16
7.09
7.07
5.91
5.90
5.90
5.88
5.87
5.87
5.83
5.82
5.82
5.81
5.81
5.80
5.80
5.80
5.79
5.79
3.73
3.21
2.53
2.53
2.48
2.48
2.47
2.47
2.46
2.29
2.29
2.28
2.28
2.28
2.23
2.23
2.22
2.22
6g
CO2Me
Cl
I
0.99
1.00
1.03
2.03
2.07
3.09
2.09
1.05
1.04
f1 (ppm)


174.50
138.69
138.59
132.77
131.34
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126.79
126.25
103.28
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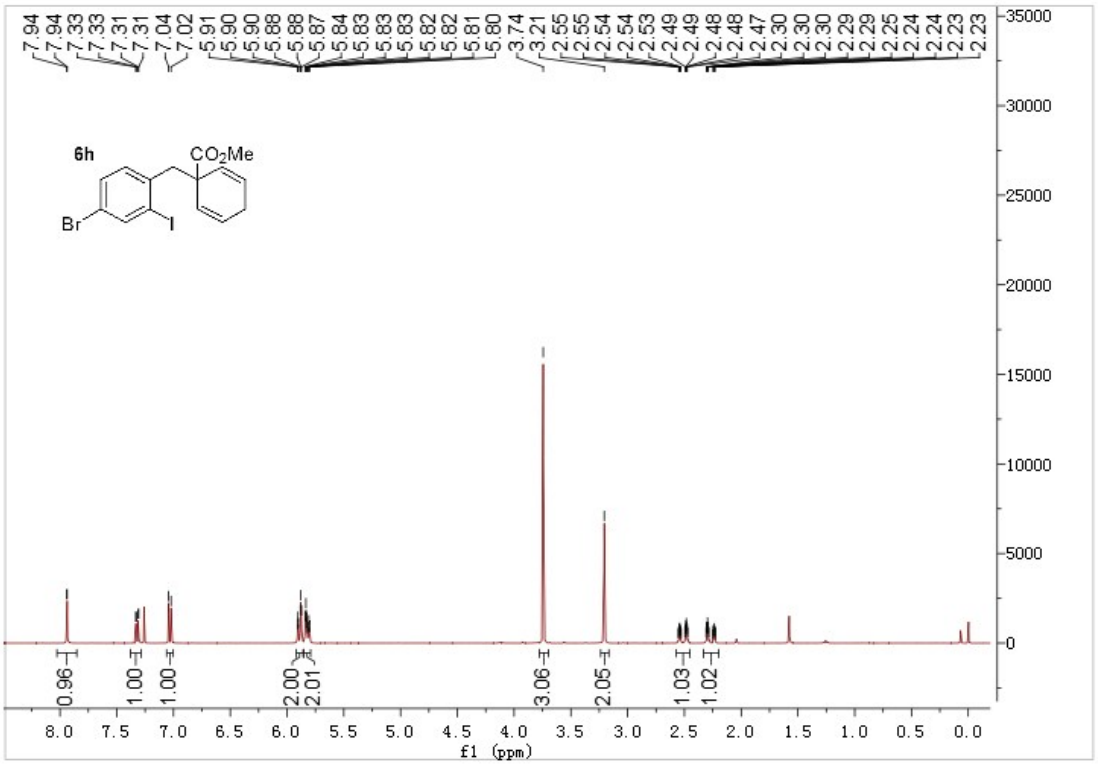
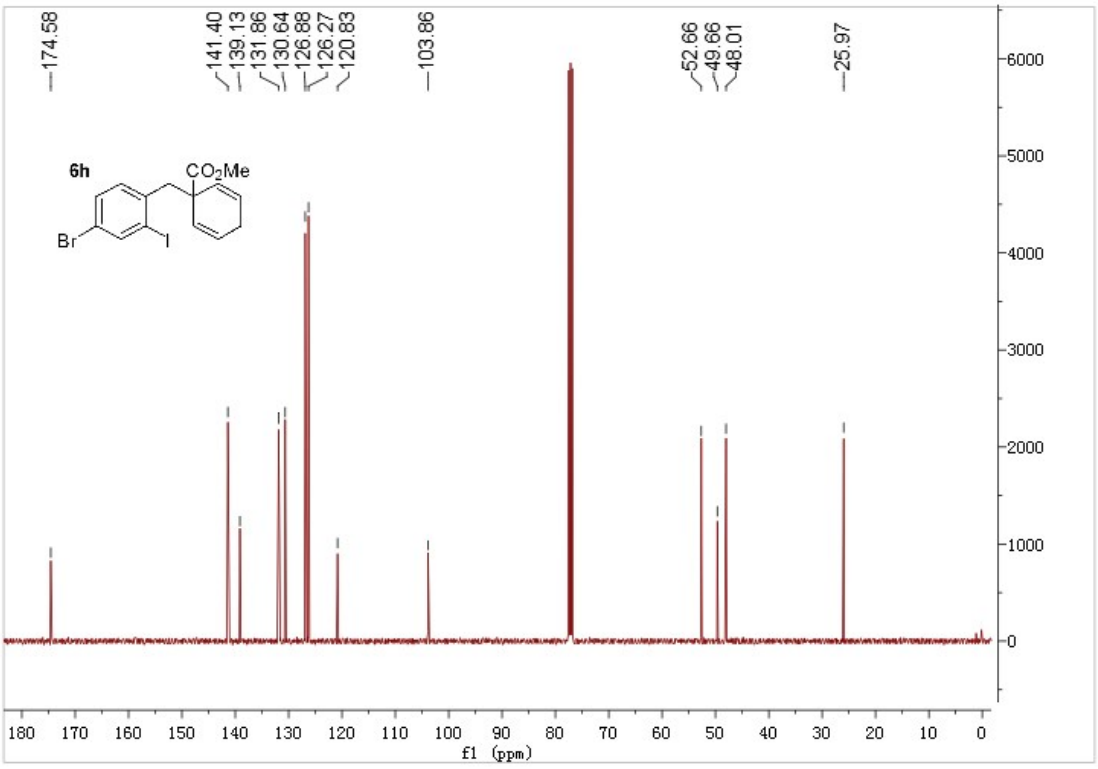
49.64
47.87
25.92
6g
CO2Me
Cl
I
f1 (ppm)


7.94
7.94
7.33
7.31
7.31
7.04
7.02
5.91
5.90
5.90
5.88
5.87
5.84
5.83
5.83
5.82
5.82
5.81
5.80
3.74
3.21
2.55
2.55
2.54
2.54
2.53
2.49
2.49
2.48
2.48
2.47
2.30
2.30
2.29
2.29
2.25
2.24
2.24
2.23
2.23
6h
CO2Me
Br
I
0.96
1.00
1.00
2.00
2.01
3.06
2.05
1.03
1.02
f1 (ppm)


174.58
141.40
139.13
131.86
130.64
126.88
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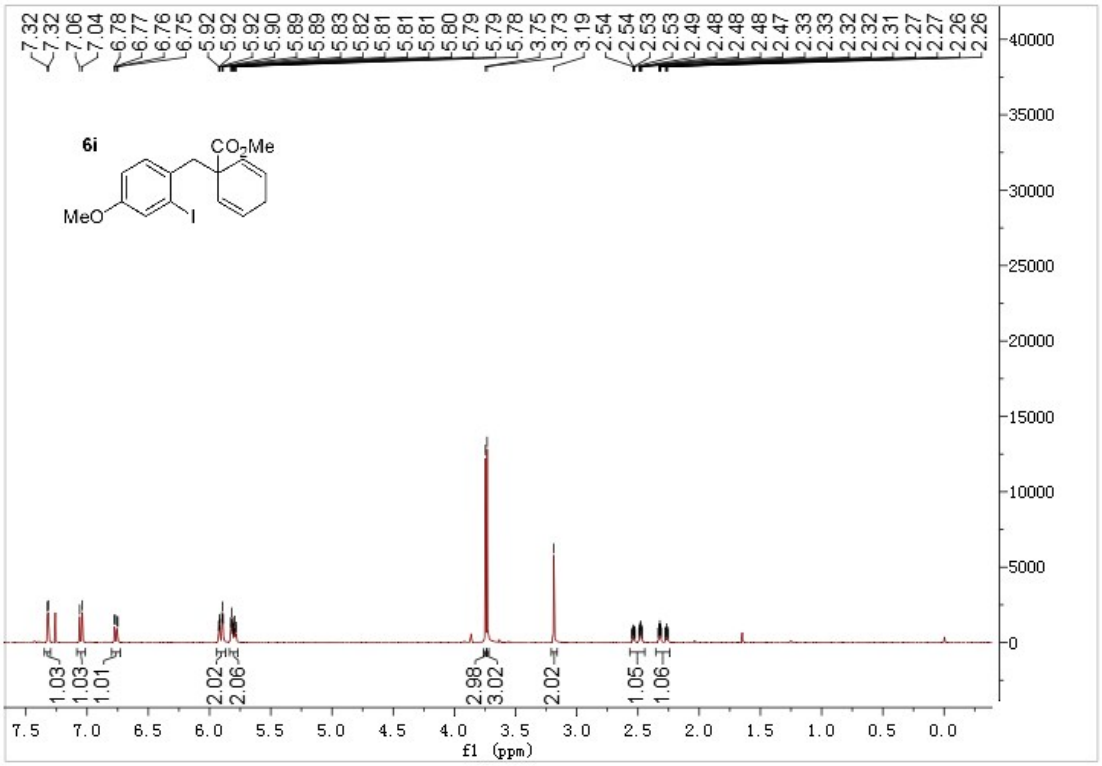
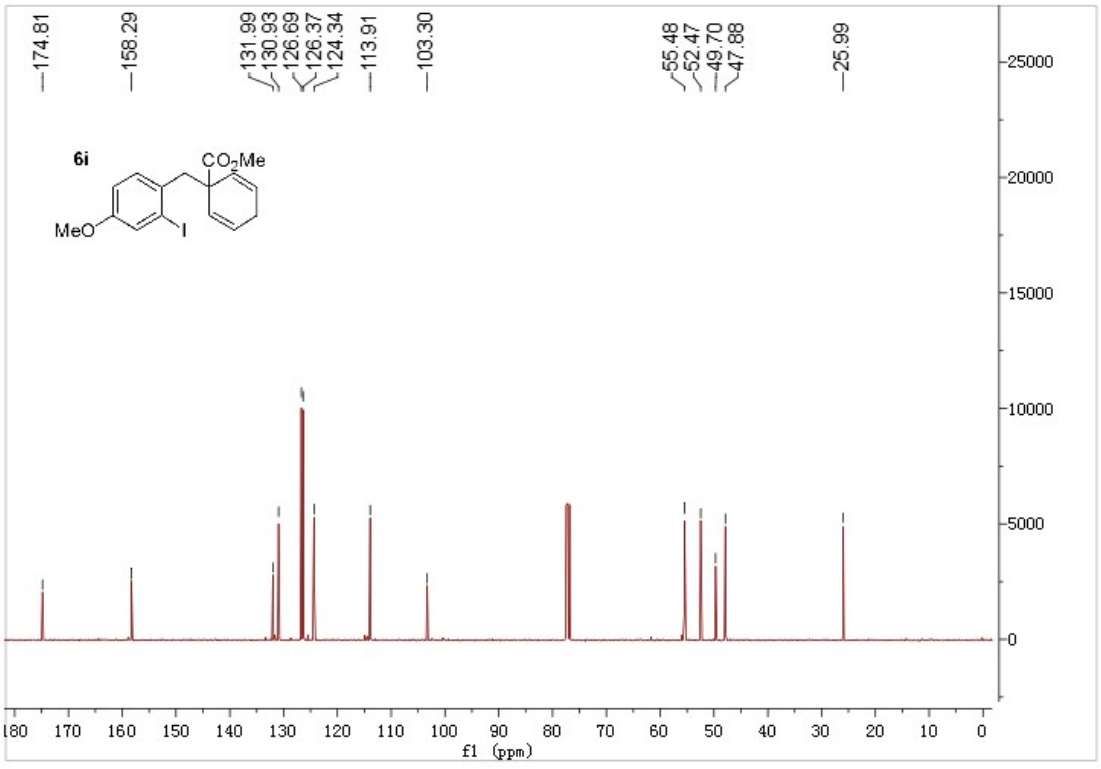
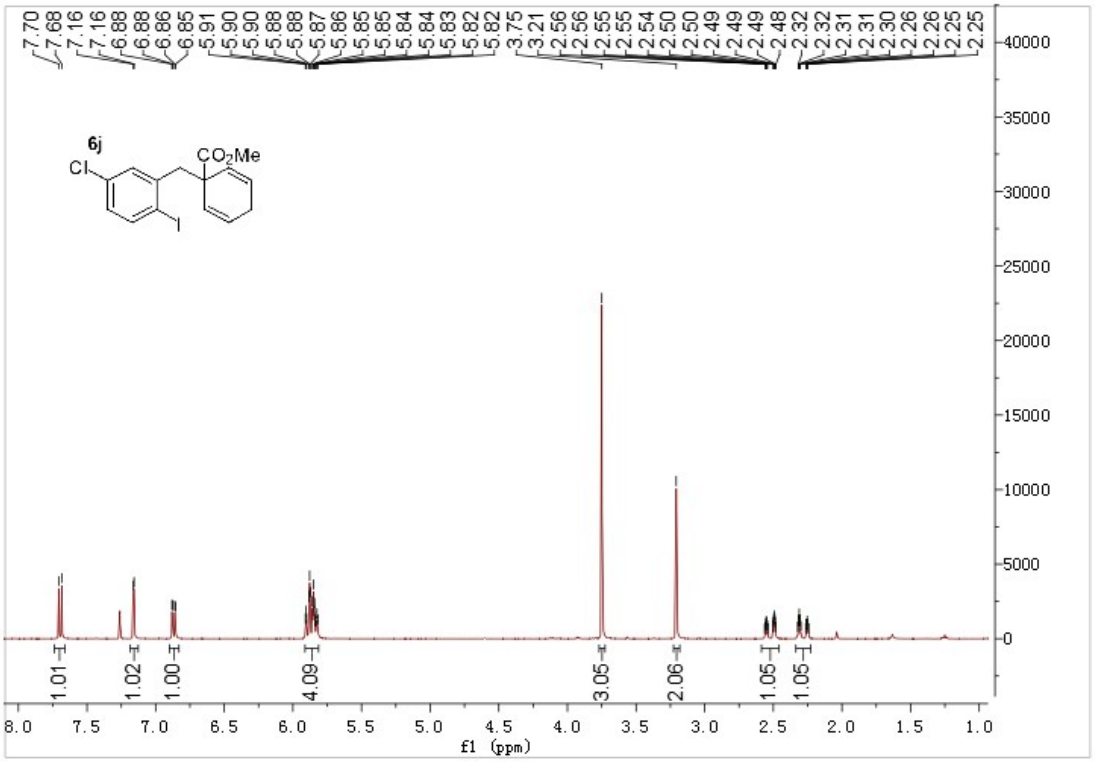
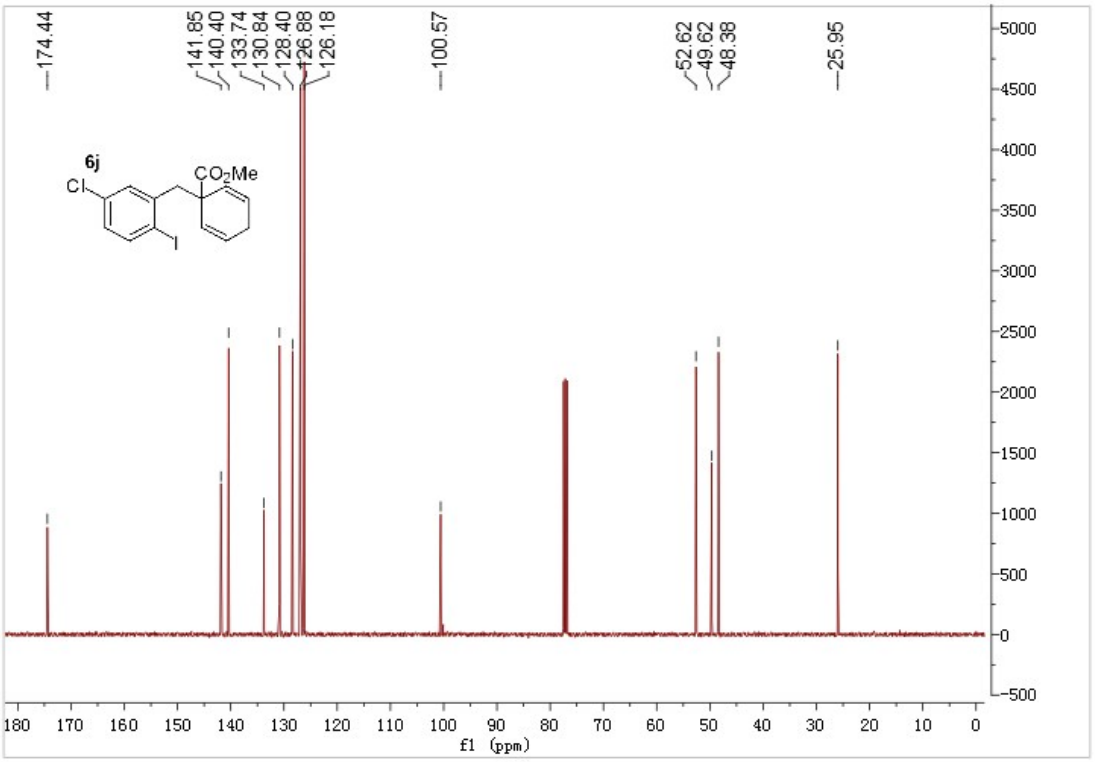
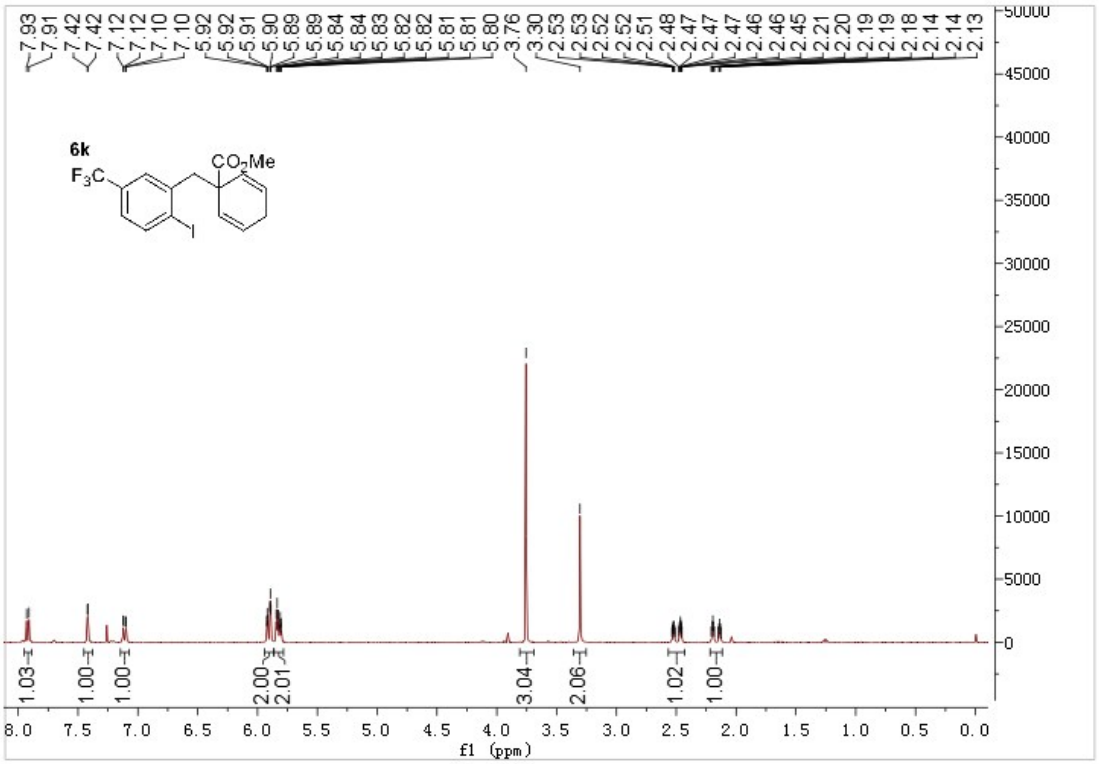
120.83
103.86
52.66
49.66
48.01
25.97
6h
CO2Me
Br
I
f1 (ppm)

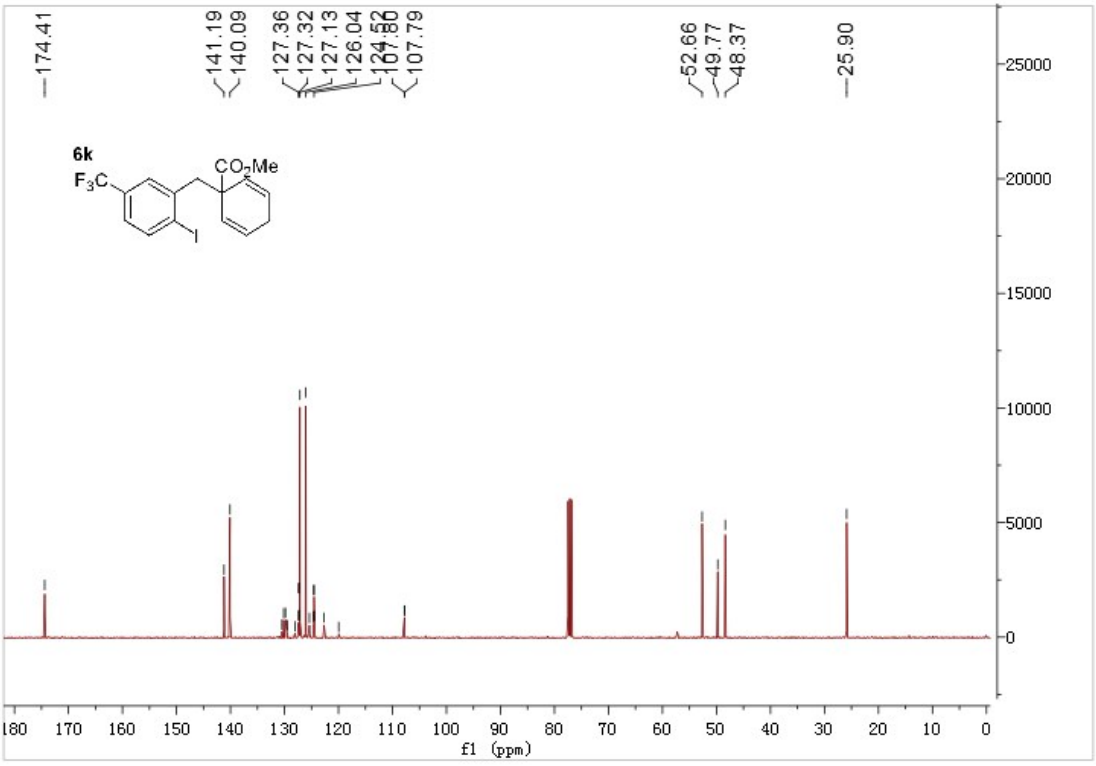

7.32
7.32
7.06
7.04
6.78
6.77
6.76
6.75
5.92
5.92
5.92
5.90
5.89
5.89
5.83
5.82
5.81
5.81
5.81
5.80
5.79
5.79
5.78
3.75
3.73
3.19
2.54
2.54
2.53
2.53
2.49
2.48
2.48
2.48
2.47
2.33
2.32
2.32
2.31
2.27
2.27
2.26
2.26
6i
CO2Me
MeO
I
1.03
1.03
1.01
2.02
2.06
2.98
3.02
2.02
1.05
1.06
f1 (ppm)

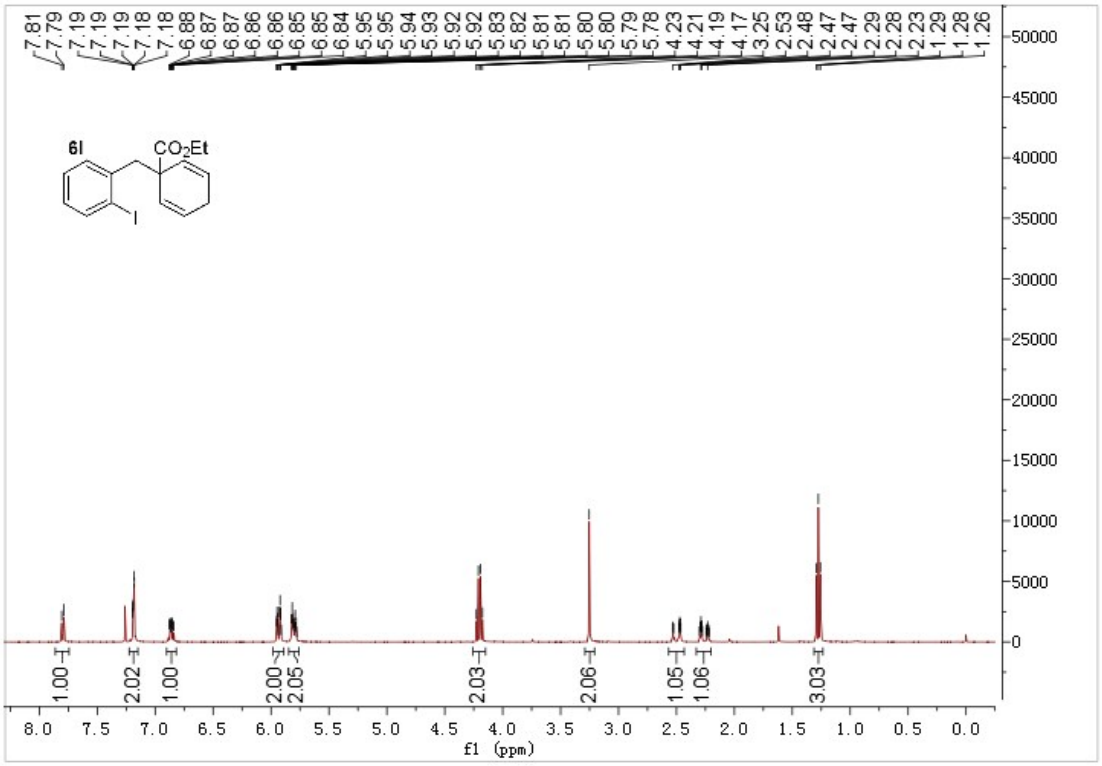

174.81
158.29
131.99
130.93
126.69
126.37
124.34
113.91
103.30
55.48
52.47
49.70
47.88
25.99
6i
CO2Me
MeO
I
f1 (ppm)

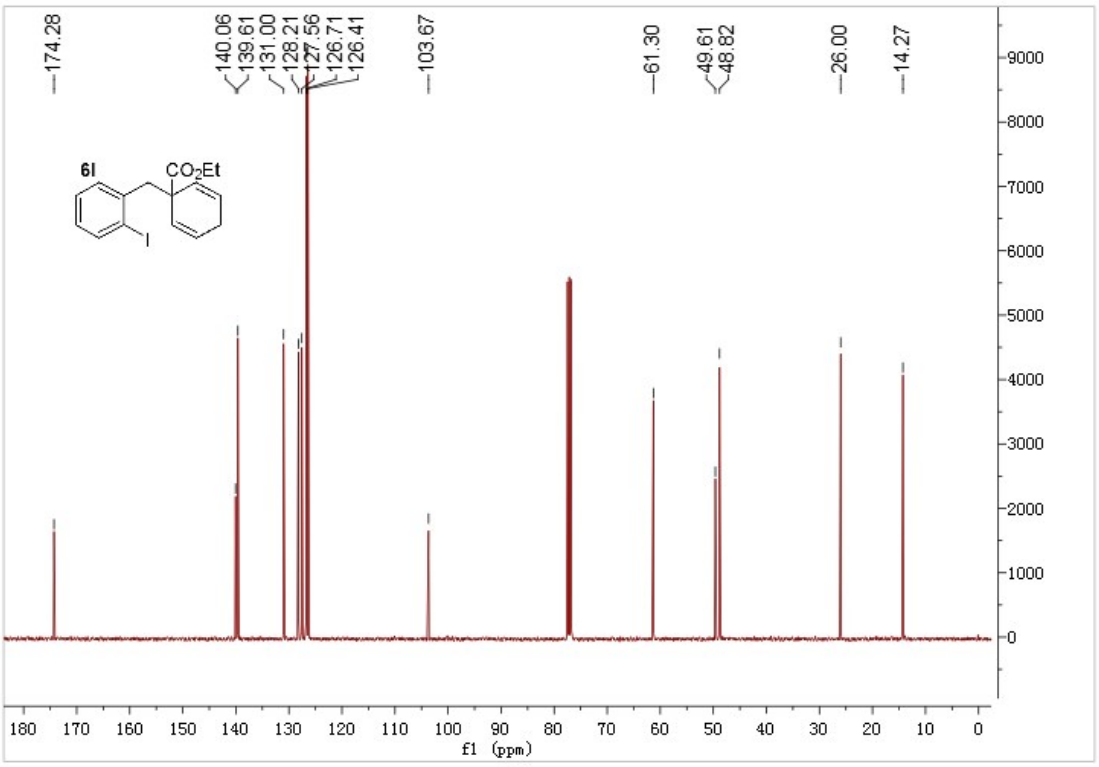

7.70
7.68
7.16
6.88
6.88
6.86
6.85
5.91
5.90
5.90
5.88
5.88
5.87
5.86
5.85
5.85
5.84
5.84
5.83
5.82
5.82
3.75
3.21
2.56
2.56
2.55
2.55
2.54
2.50
2.50
2.49
2.49
2.49
2.48
2.32
2.32
2.31
2.31
2.30
2.26
2.26
2.25
2.25
6j
Cl
CO2Me
I
1.01
1.02
1.00
4.09
3.05
2.06
1.05
1.05
f1 (ppm)

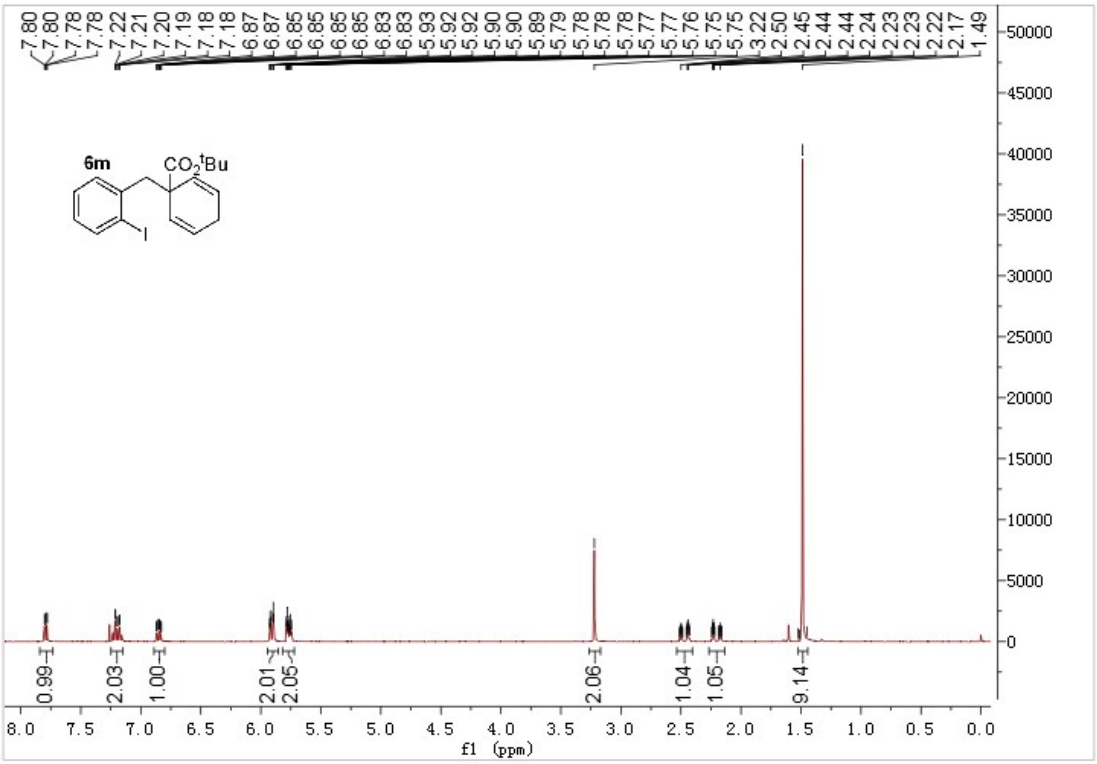

174.44
141.85
140.40
133.74
130.84
128.40
126.88
126.18
100.57
52.62
49.62
48.38
25.95
6j
Cl
CO2Me
I
f1 (ppm)

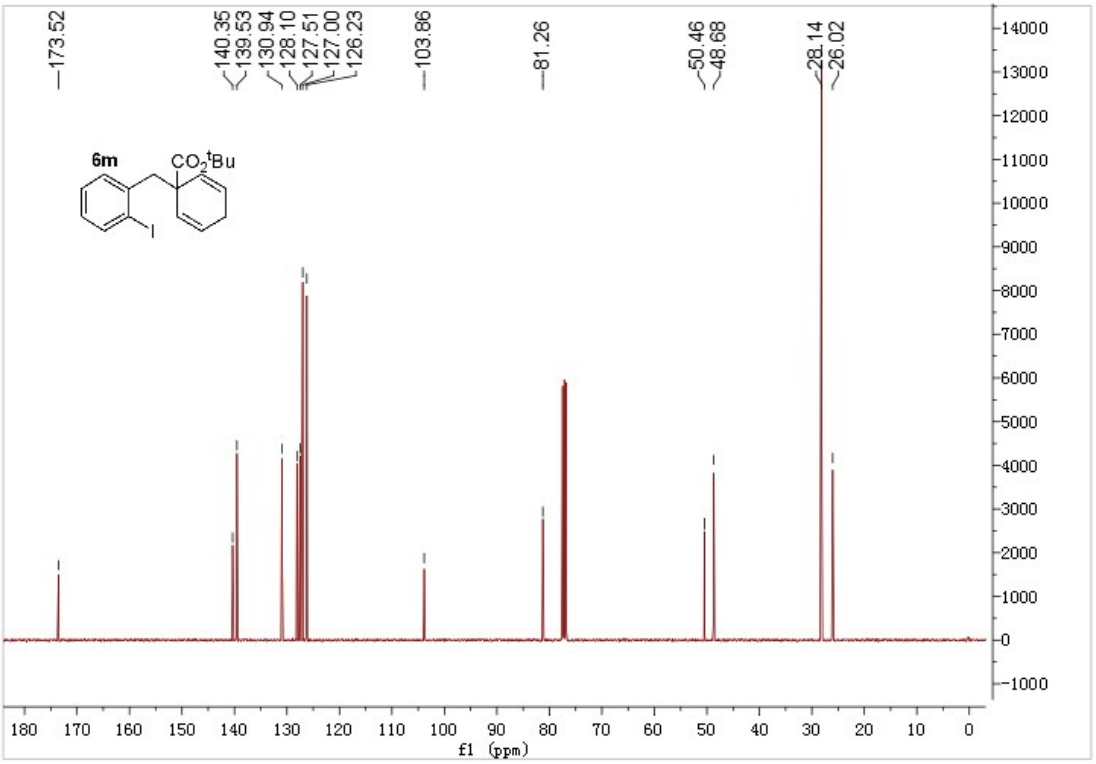

7.93
7.91
7.42
7.42
7.12
7.12
7.10
7.10
5.92
5.92
5.91
5.90
5.89
5.89
5.84
5.84
5.83
5.82
5.82
5.81
5.81
5.80
3.76
3.30
2.53
2.53
2.52
2.52
2.51
2.48
2.47
2.47
2.47
2.46
2.46
2.45
2.21
2.20
2.19
2.19
2.18
2.14
2.14
2.13
6k
F3C
CO2Me
I
1.03
1.00
1.00
2.00
2.01
3.04
2.06
1.02
1.00
f1 (ppm)


174.41
141.19
140.09
127.36
127.32
127.13
126.04
107.79
52.66
49.77
48.37
25.90
6k
F3C
CO2Me
I
f1 (ppm)

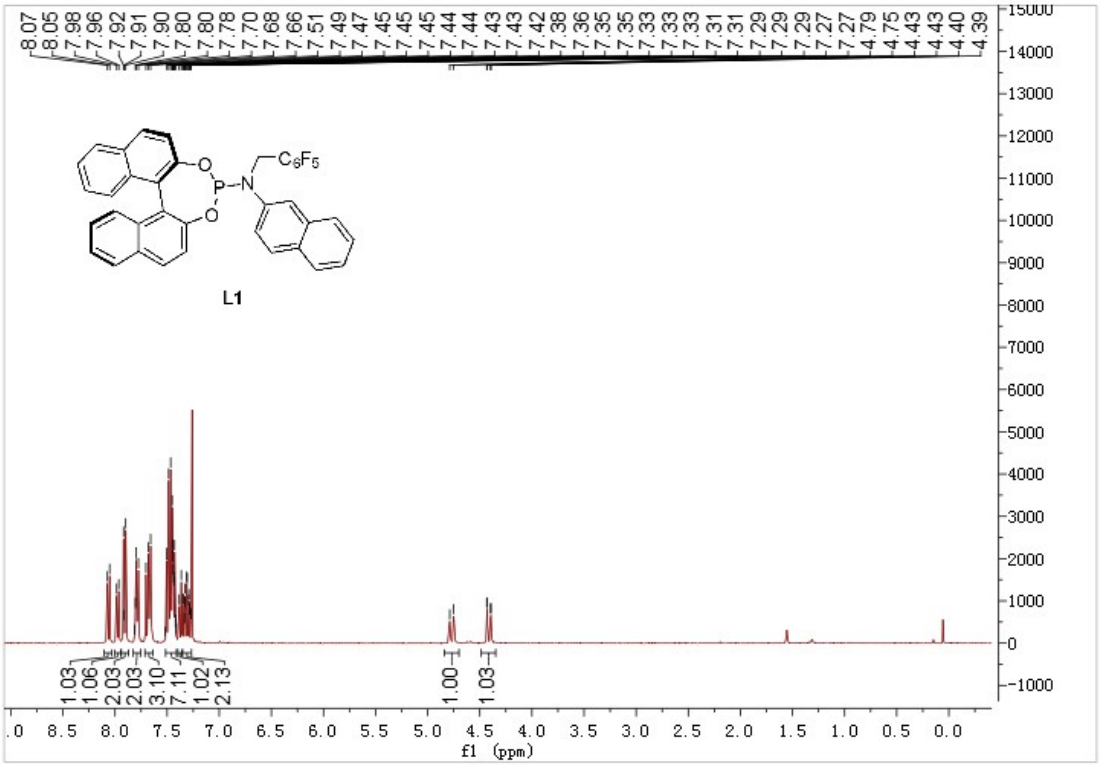

7.81
7.79
7.19
7.19
7.19
7.18
7.18
6.88
6.87
6.87
6.86
6.86
6.85
6.85
6.84
5.95
5.95
5.94
5.93
5.92
5.92
5.83
5.82
5.81
5.81
5.80
5.80
5.79
5.78
4.23
4.21
4.19
4.17
3.25
2.53
2.48
2.47
2.47
2.29
2.28
2.23
1.29
1.28
1.26
6l
CO2Et
I
1.00
2.02
1.00
2.00
2.05
2.03
2.06
1.05
1.06
3.03
f1 (ppm)

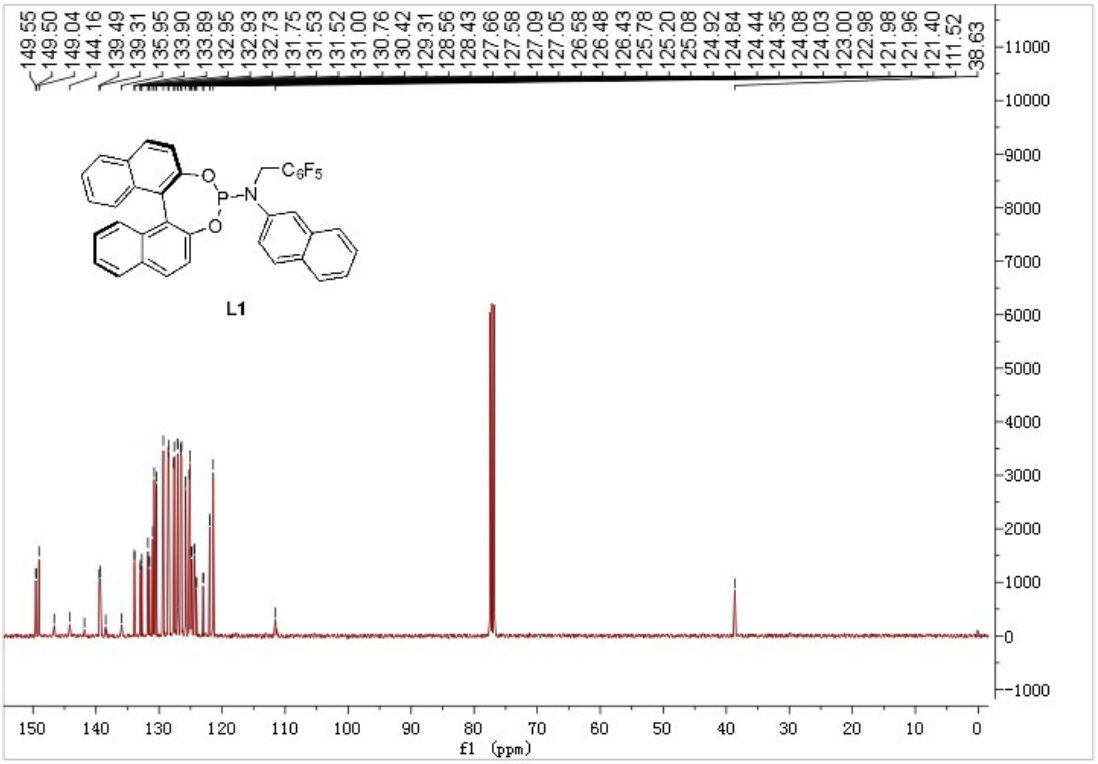

174.28
140.06
139.61
131.00
128.21
127.56
126.71
126.41
103.67
61.30
49.61
48.82
26.00
14.27
6l
CO2Et
I
f1 (ppm)

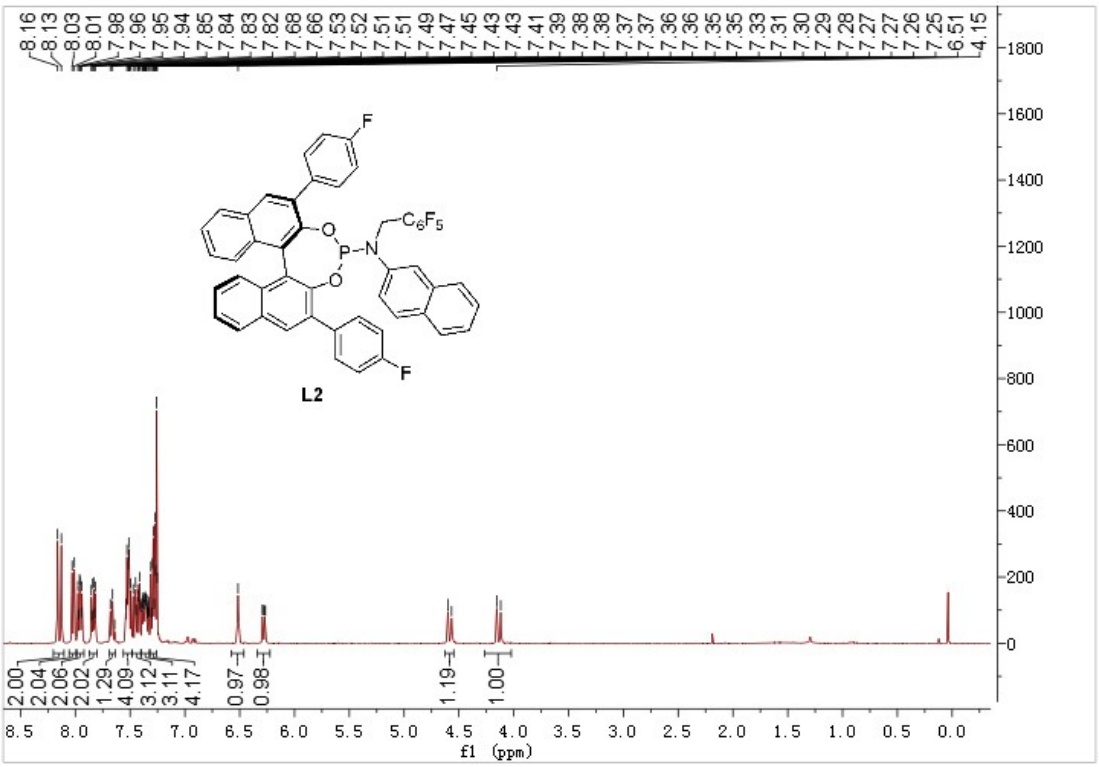

7.80
7.80
7.78
7.78
7.22
7.21
7.20
7.19
7.18
7.18
6.87
6.87
6.85
6.85
6.85
6.85
6.83
6.83
5.93
5.92
5.92
5.90
5.90
5.89
5.79
5.78
5.78
5.78
5.77
5.77
5.76
5.75
5.75
3.22
2.50
2.45
2.44
2.44
2.24
2.23
2.23
2.22
2.17
1.49
6m
CO2tBu
I
0.99
2.03
1.00
2.01
2.05
2.06
1.04
1.05
9.14
f1 (ppm)

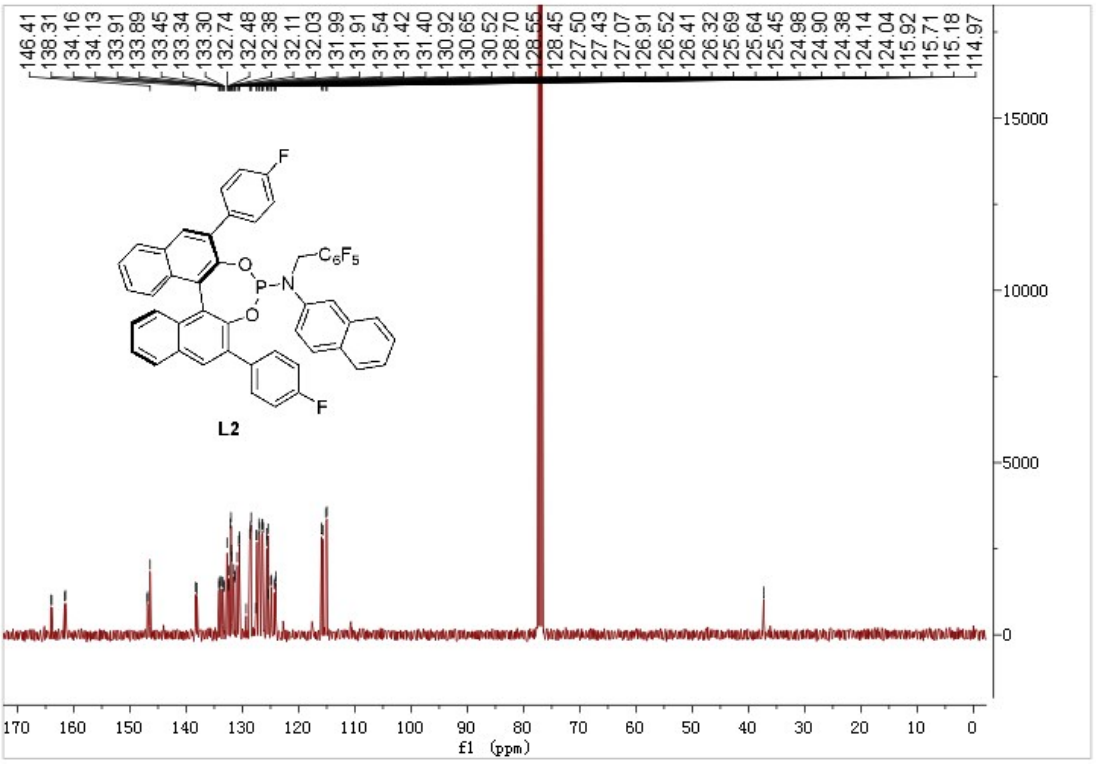

173.52
140.35
139.53
130.94
128.10
127.51
127.00
126.23
103.86
81.26
50.46
48.68
28.14
26.02
6m
CO2tBu
I
f1 (ppm)

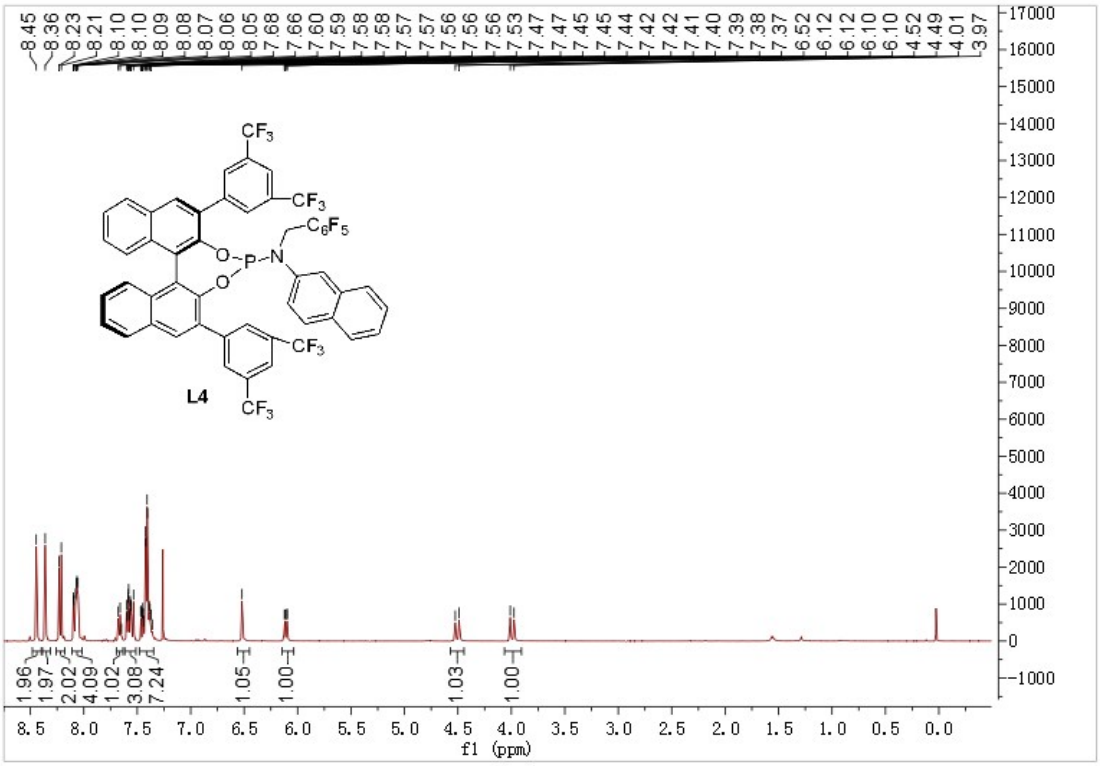
10. NMR Spectra for Ligands

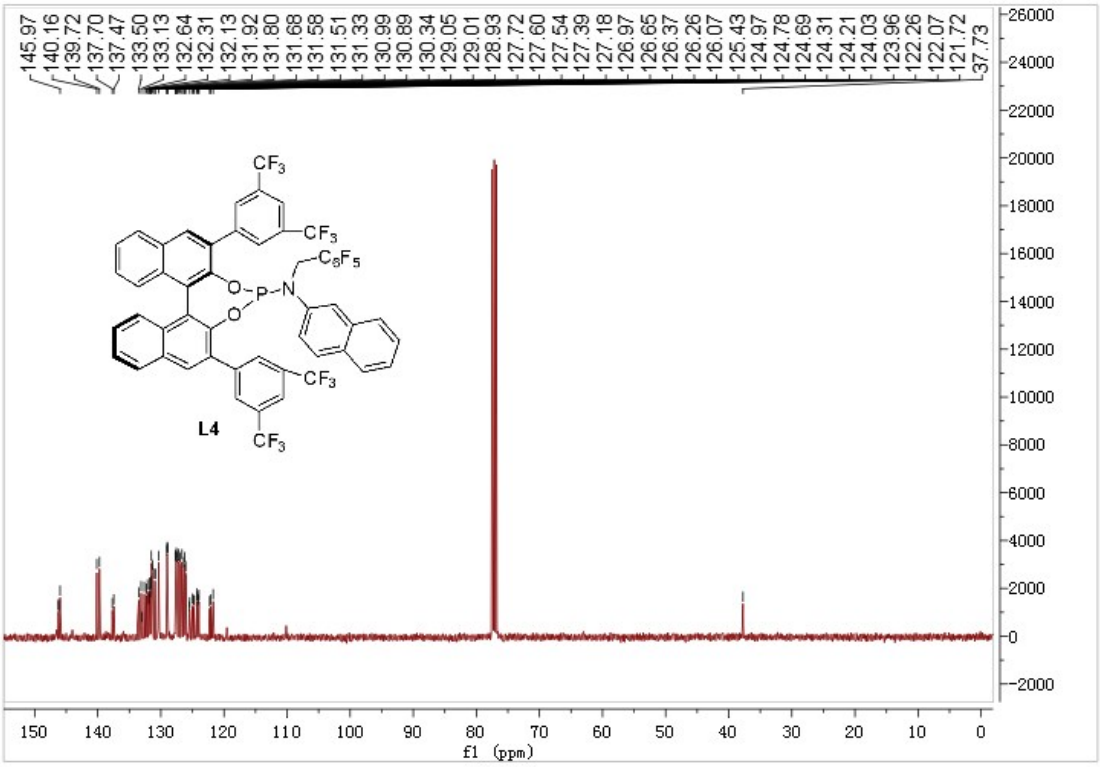


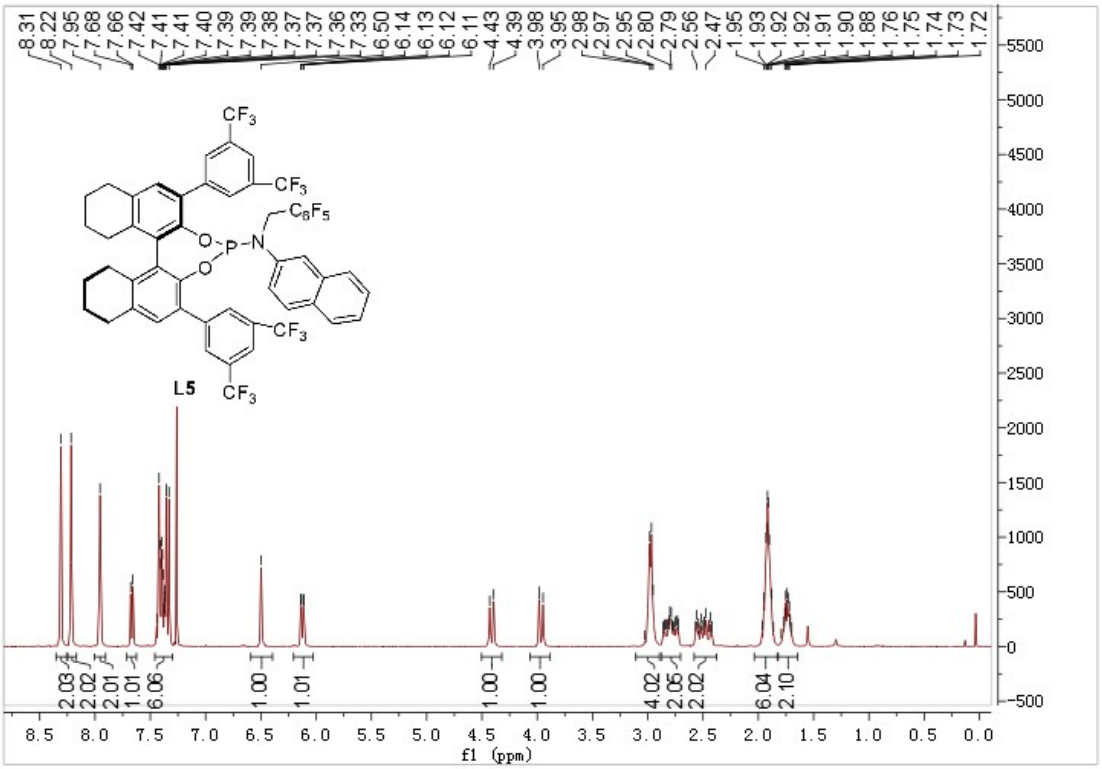


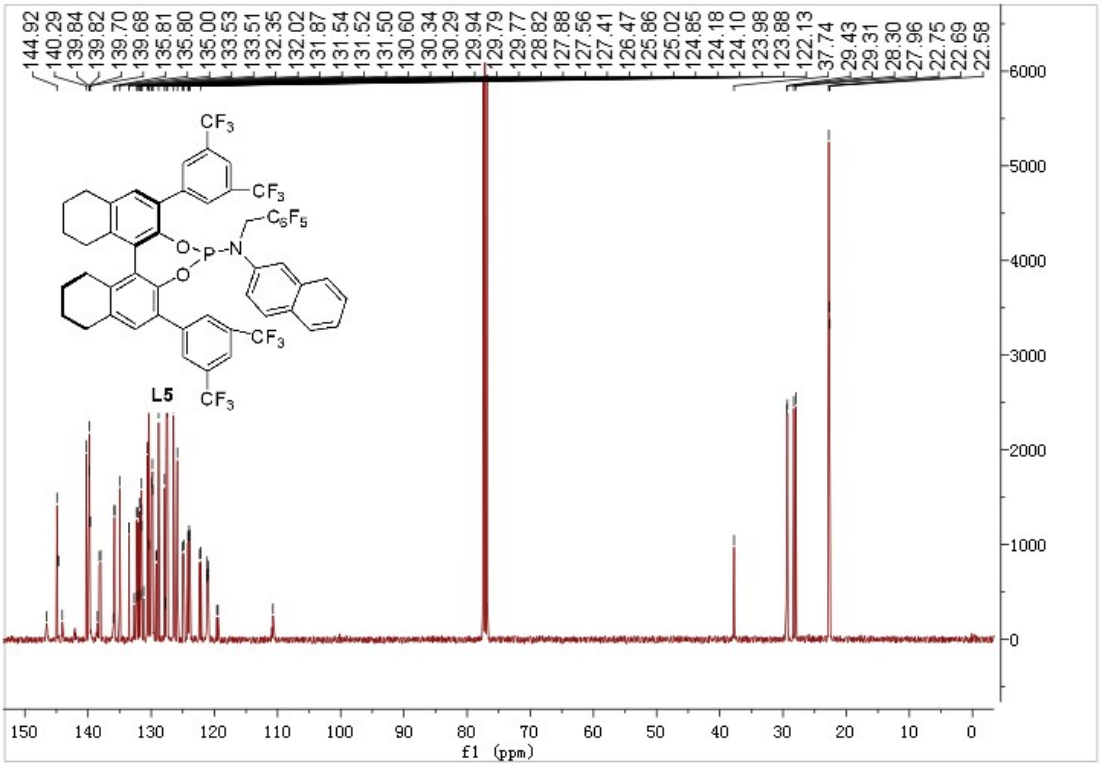

L2
f1 (ppm)


L2
f1 (ppm)

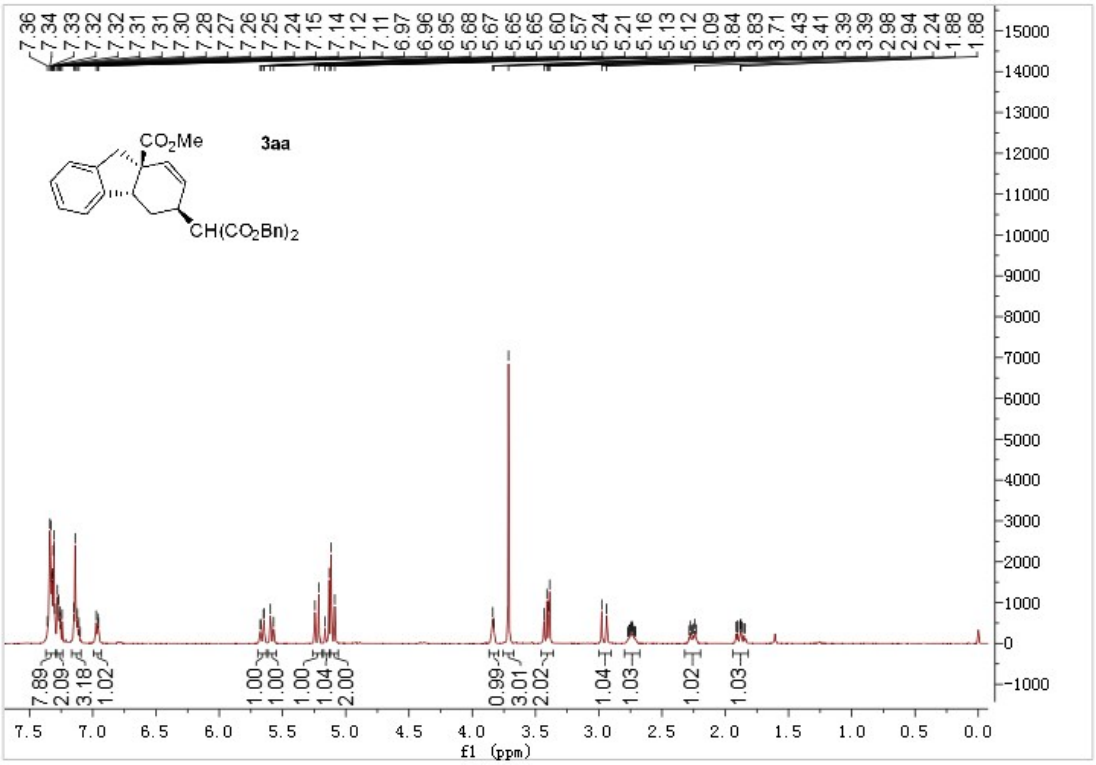

L4
f1 (ppm)

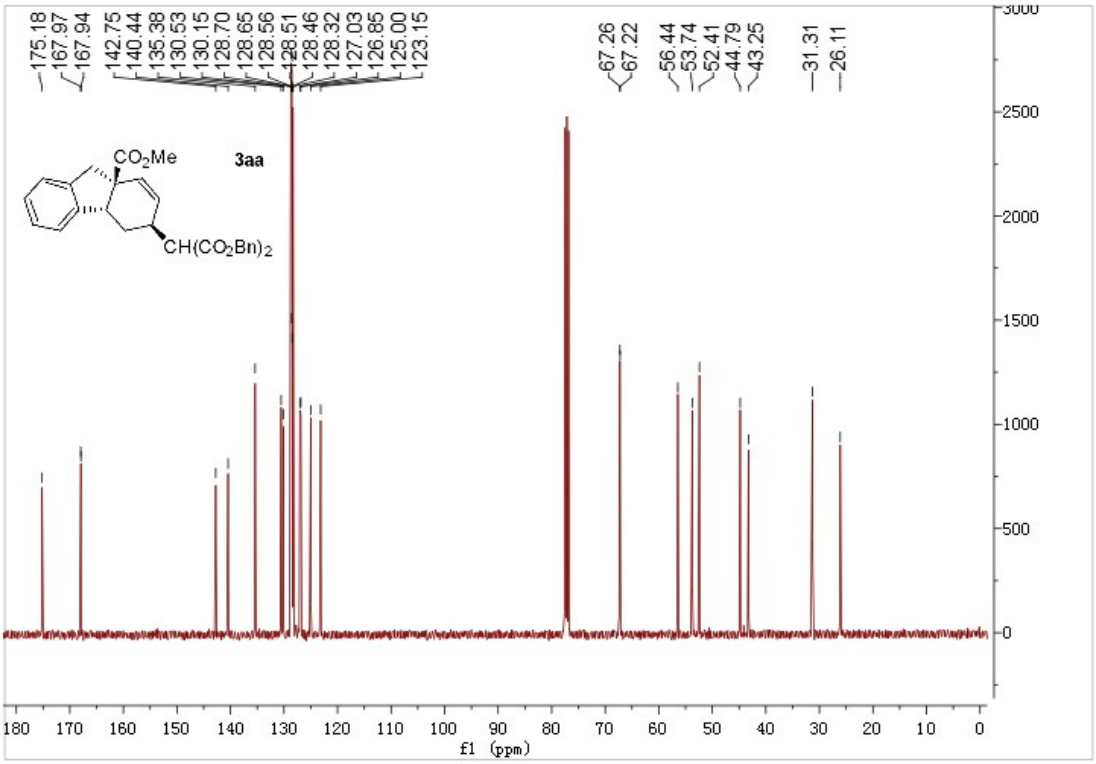

L4
f1 (ppm)

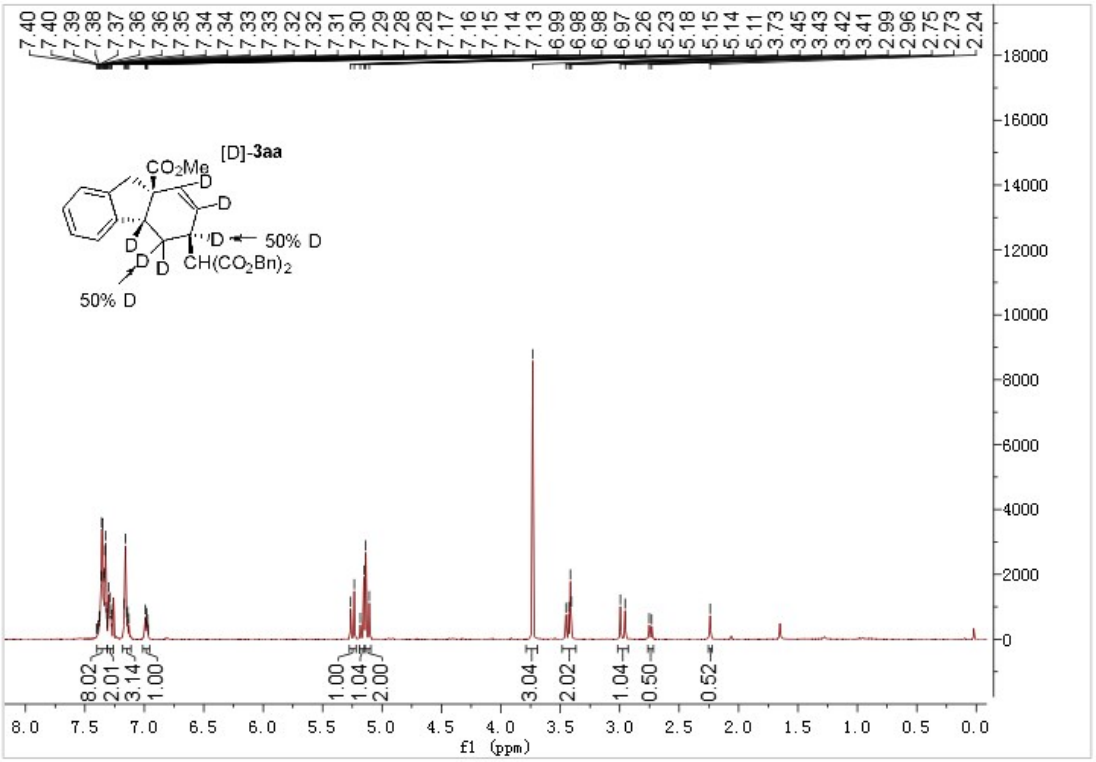

L5
f1 (ppm)

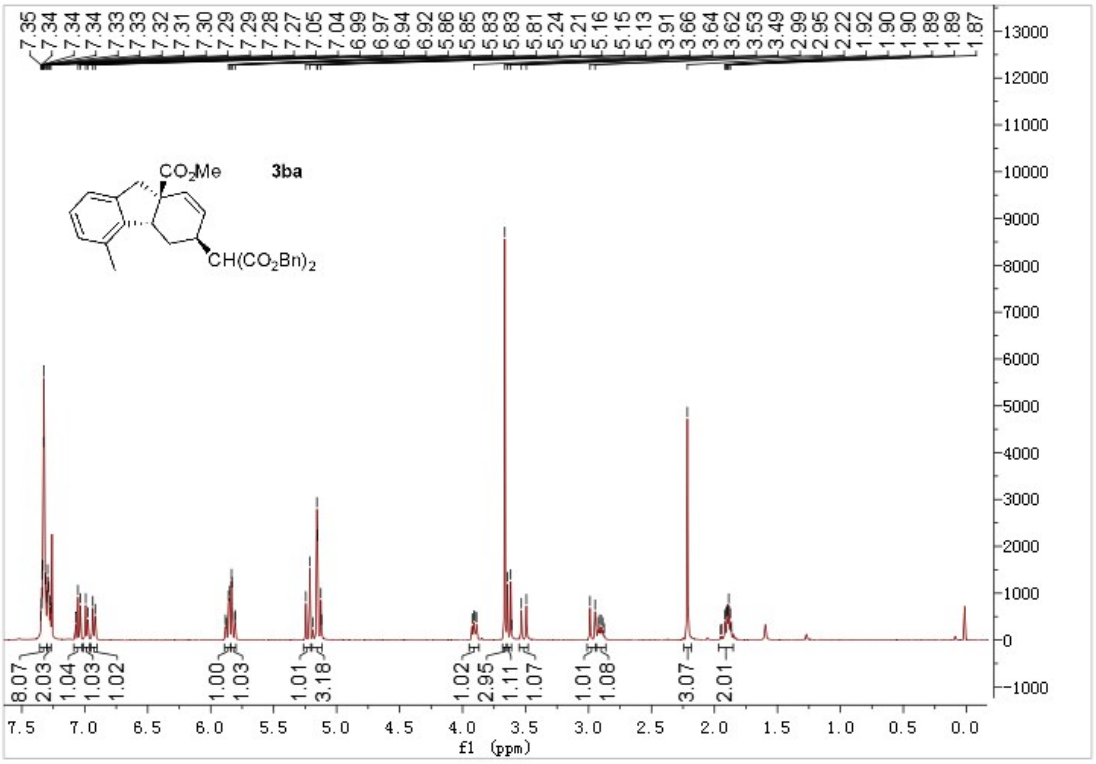

L5
f1 (ppm)

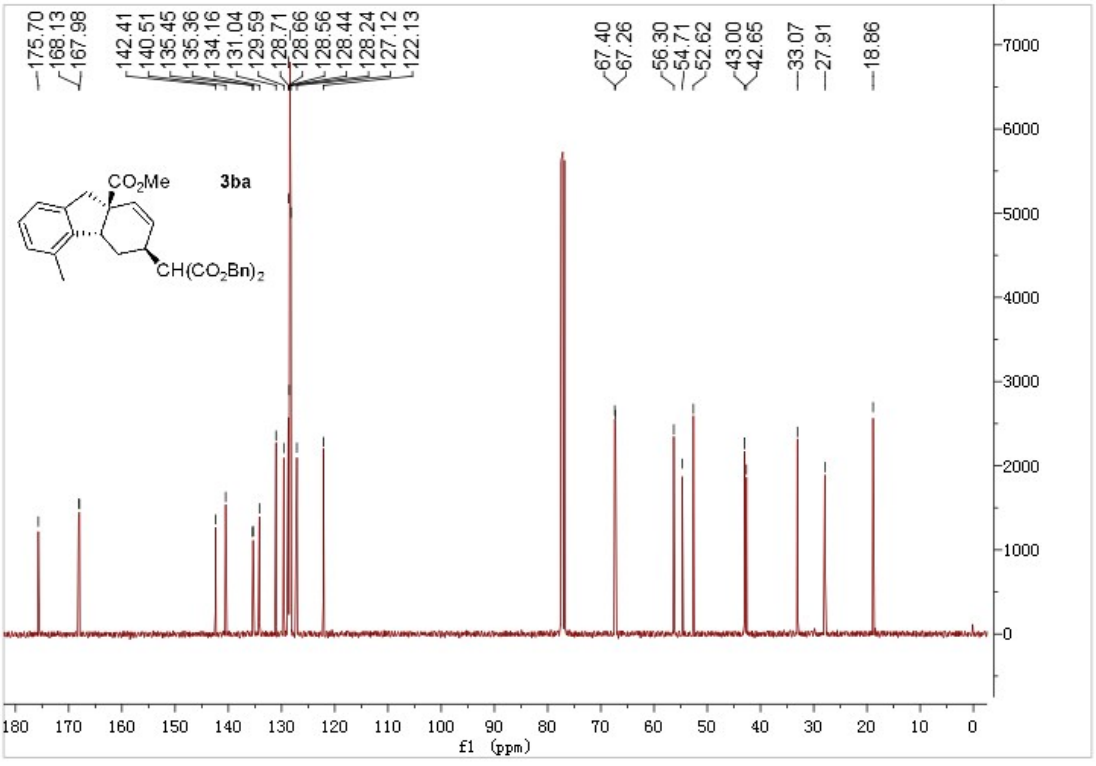
11. NMR Spectra for Products

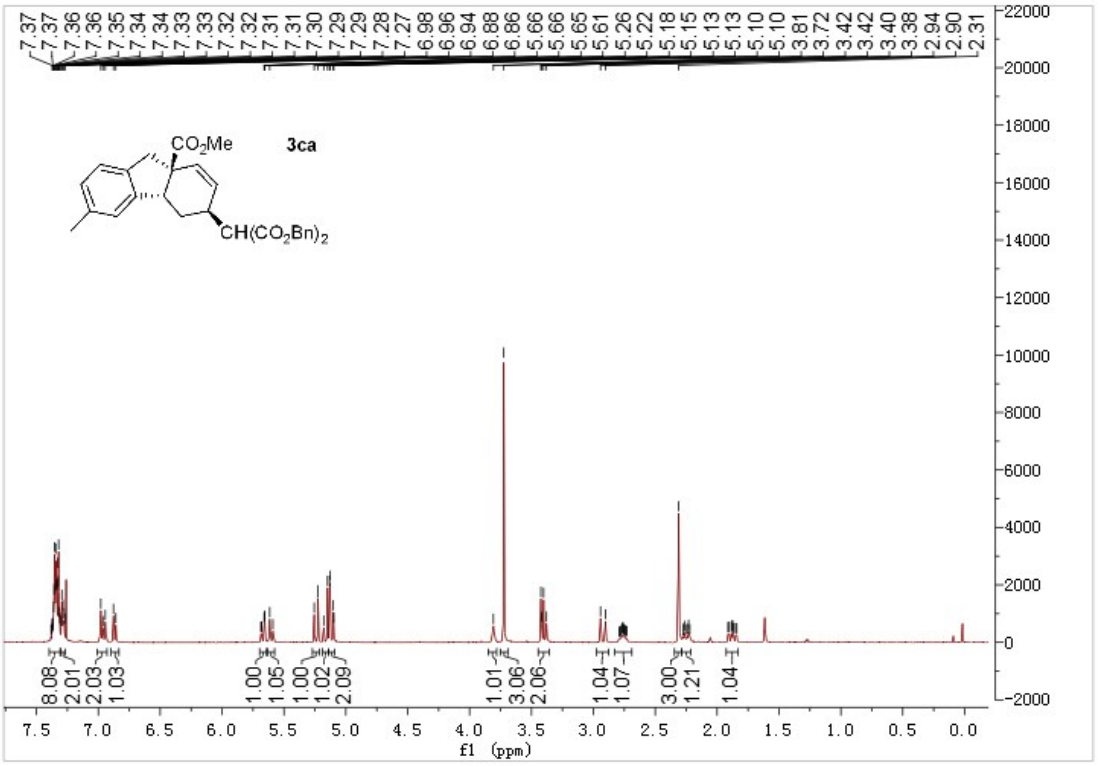


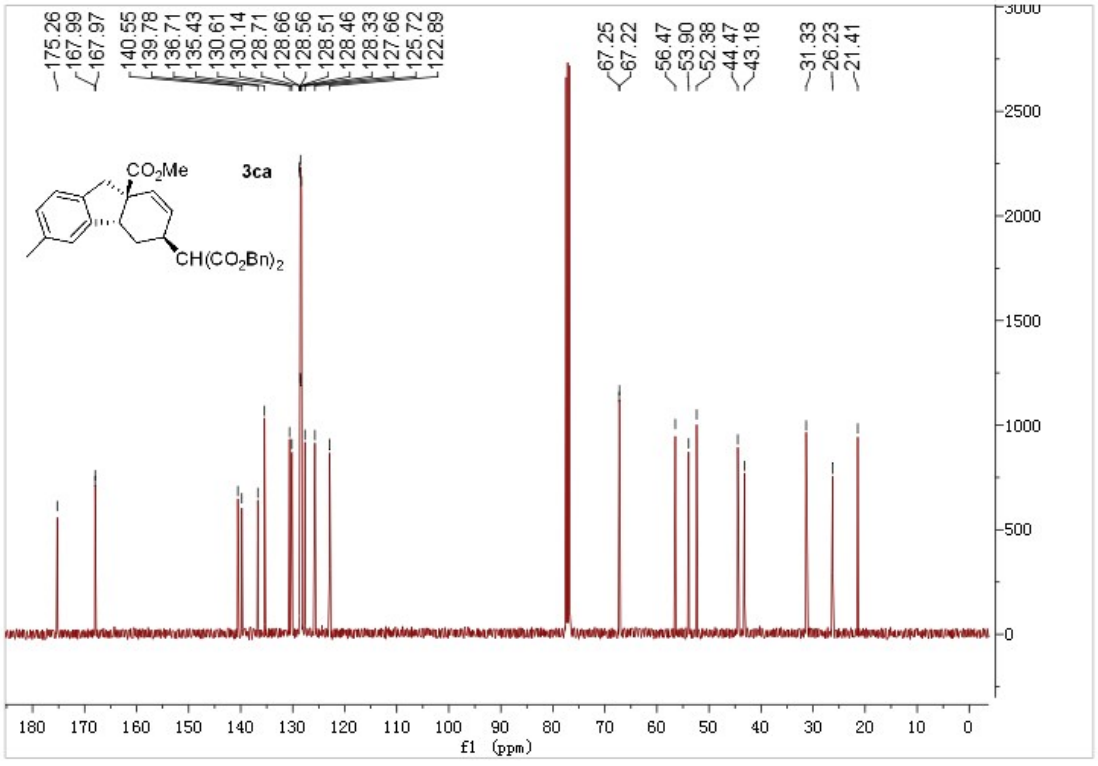


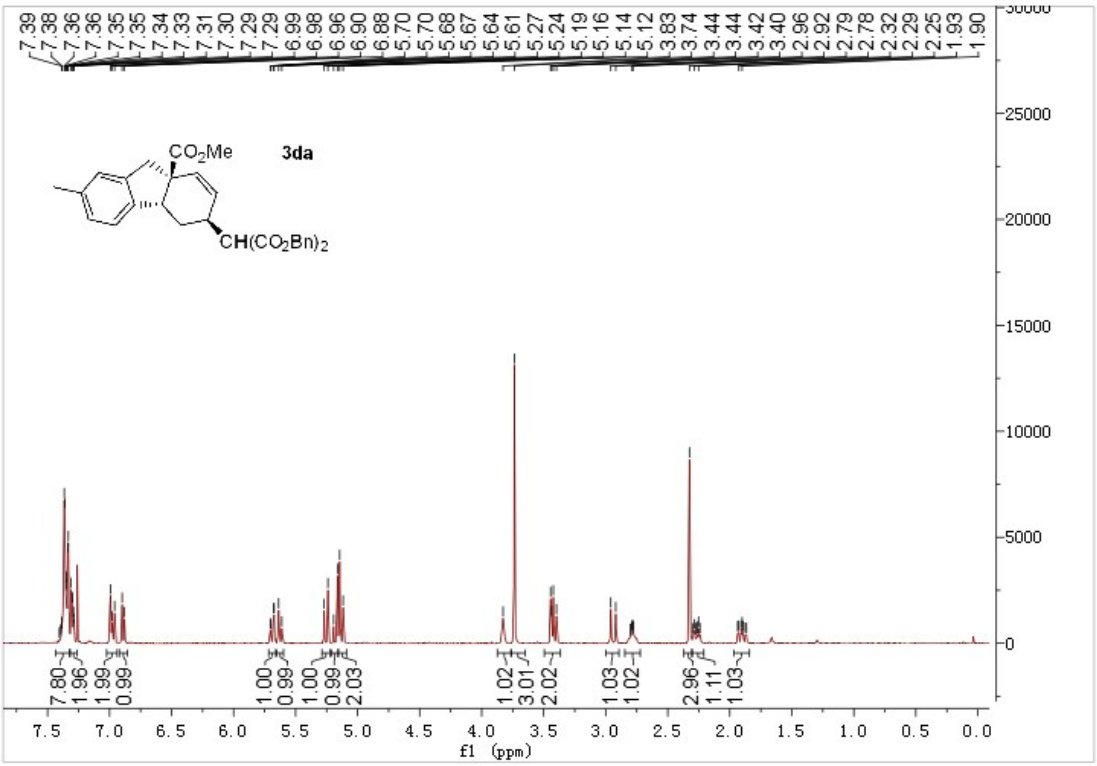

[D]-3aa
CO2Me
D
D
D
D
D
D
50% D
CH(CO2Bn)2
50% D
f1 (ppm)

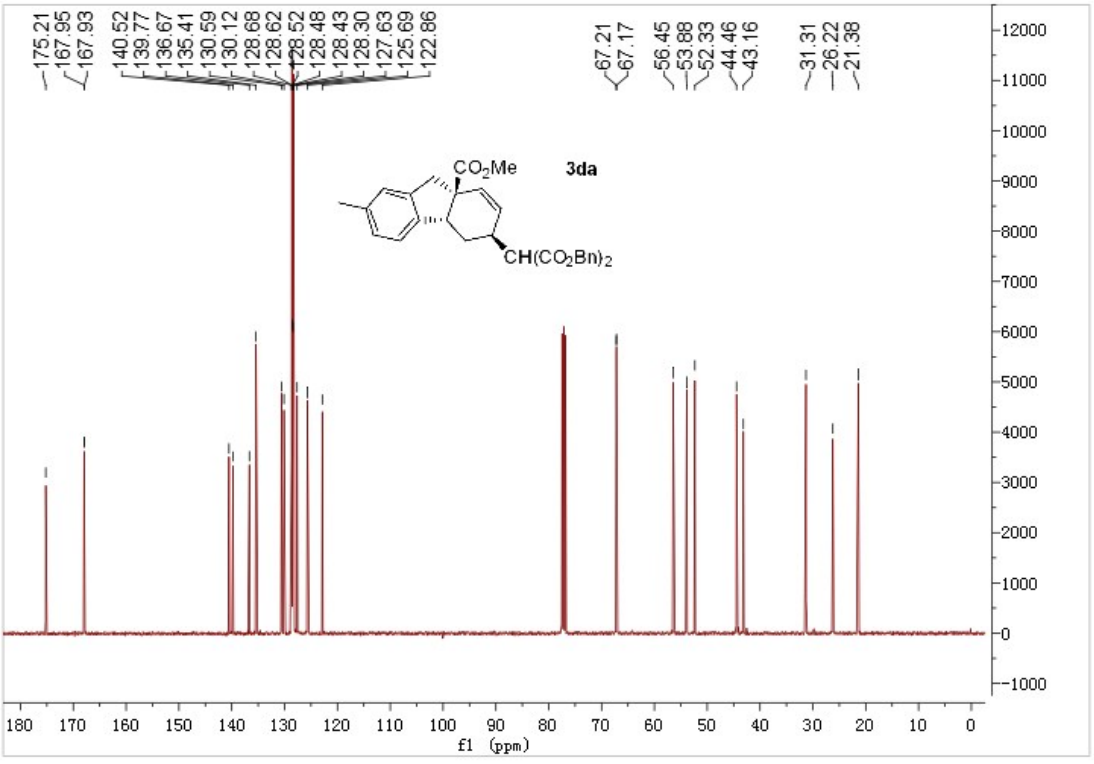

CO2Me
3ba
CH(CO2Bn)2
f1 (ppm)

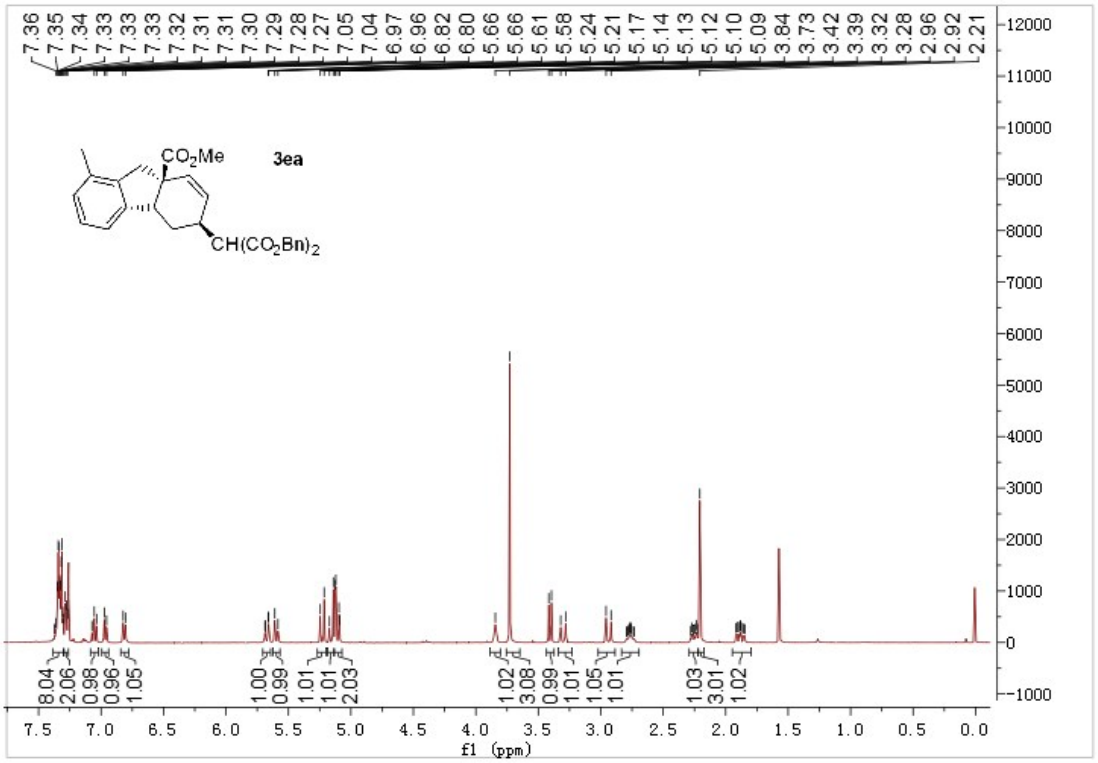

CO2Me
3ba
CH(CO2Bn)2
f1 (ppm)


7.37 7.37 7.36 7.36 7.35 7.34 7.34 7.33 7.33 7.32 7.32 7.31 7.31 7.30 7.29 7.29 7.28 7.27 6.98 6.96 6.94 6.88 6.86 5.66 5.66 5.65 5.61 5.26 5.22 5.18 5.15 5.13 5.13 5.10 5.10 3.81 3.72 3.42 3.42 3.40 3.38 2.94 2.90 2.31
CO2Me
3ca
CH(CO2Bn)2
8.08 2.01 2.03 1.03 1.00 1.05 1.00 1.02 2.09 1.01 3.06 2.06 1.04 1.07 3.00 1.21 1.04
f1 (ppm)


175.26 167.99 167.97 140.55 139.78 136.71 135.43 130.61 130.14 128.71 128.66 128.56 128.51 128.46 128.33 127.66 125.72 122.89 67.25 67.22 56.47 53.90 52.38 44.47 43.18 31.33 26.23 21.41
CO2Me
3ca
CH(CO2Bn)2
f1 (ppm)


7.39 7.38 7.36 7.36 7.35 7.35 7.34 7.33 7.31 7.30 7.29 7.29 6.99 6.98 6.96 6.90 6.88 5.70 5.70 5.68 5.67 5.64 5.61 5.27 5.24 5.19 5.16 5.14 5.12 3.83 3.74 3.44 3.44 3.42 3.40 2.96 2.92 2.79 2.78 2.32 2.29 2.25 1.93 1.90
CO2Me
3da
CH(CO2Bn)2
7.80 1.96 1.99 0.99 1.00 0.99 1.00 0.99 2.03 1.02 3.01 2.02 1.03 1.02 2.96 1.11 1.03
f1 (ppm)


175.21 167.95 167.93 140.52 139.77 136.67 135.41 130.59 130.12 128.68 128.62 128.52 128.48 128.43 128.30 127.63 125.69 122.86 67.21 67.17 56.45 53.88 52.33 44.46 43.16 31.31 26.22 21.38
CO2Me
3da
CH(CO2Bn)2
f1 (ppm)


7.36
7.35
7.34
7.33
7.33
7.33
7.32
7.31
7.31
7.30
7.29
7.28
7.27
7.05
7.04
6.97
6.96
6.82
6.80
5.66
5.66
5.61
5.58
5.24
5.21
5.17
5.14
5.13
5.12
5.10
5.09
3.84
3.73
3.42
3.39
3.32
3.28
2.96
2.92
2.21
CO2Me
3ea
CH(CO2Bn)2
8.04
2.06
0.98
0.96
1.05
1.00
0.99
1.01
1.01
2.03
1.02
3.08
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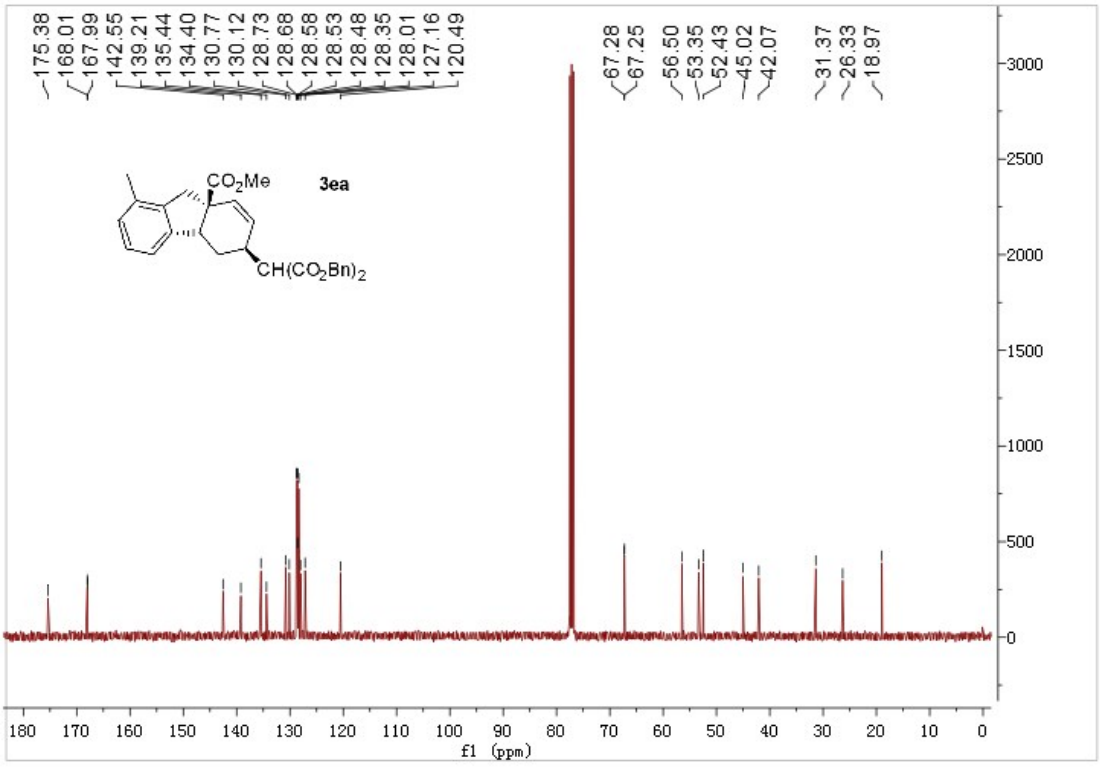
1.05
1.01
1.03
3.01
1.02
f1 (ppm)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128.35
128.01
127.16
120.49
67.28
67.25
56.50
53.35
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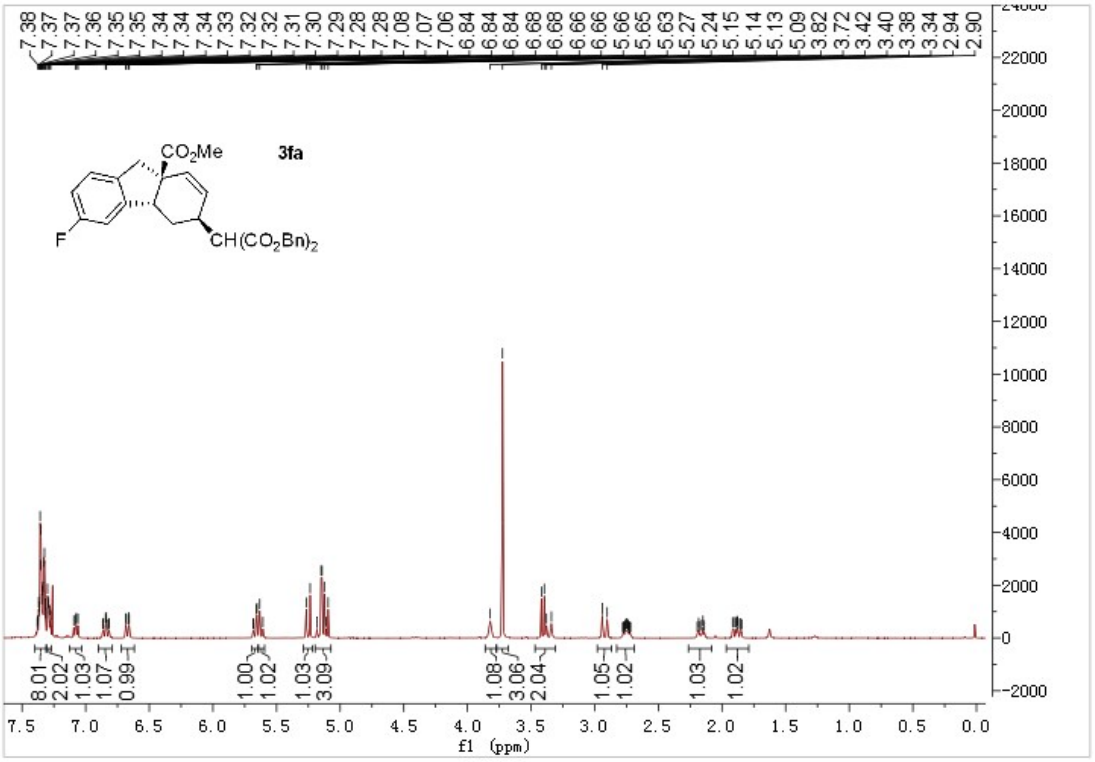
42.07
31.37
26.33
18.97
CO2Me
3ea
CH(CO2Bn)2
f1 (ppm)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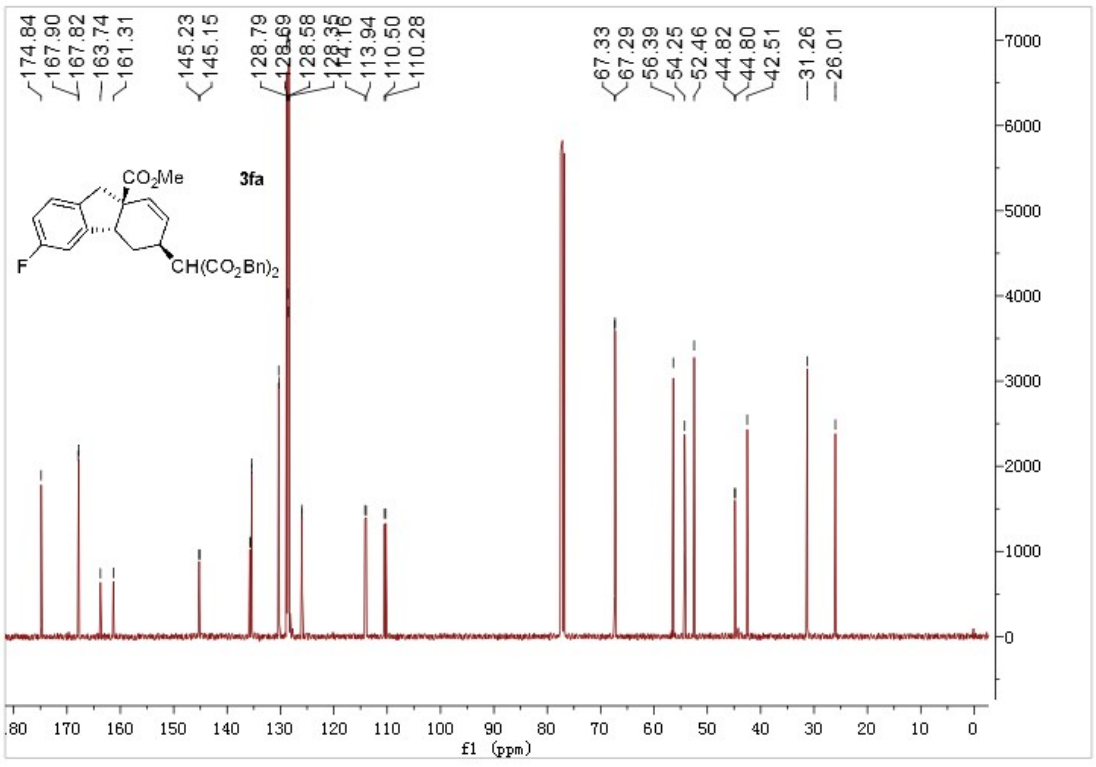
7.28
7.08
7.07
7.06
6.84
6.84
6.68
6.68
6.66
6.66
5.66
5.65
5.63
5.27
5.24
5.15
5.14
5.13
5.09
3.82
3.72
3.42
3.40
3.38
3.34
2.94
2.90
CO2Me
3fa
F
CH(CO2Bn)2
8.01
2.02
1.03
1.07
0.99
1.00
1.02
1.03
3.09
1.08
3.06
2.04
1.05
1.02
1.03
1.02
f1 (ppm)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113.94
110.50
110.28
67.33
67.29
56.39
54.25
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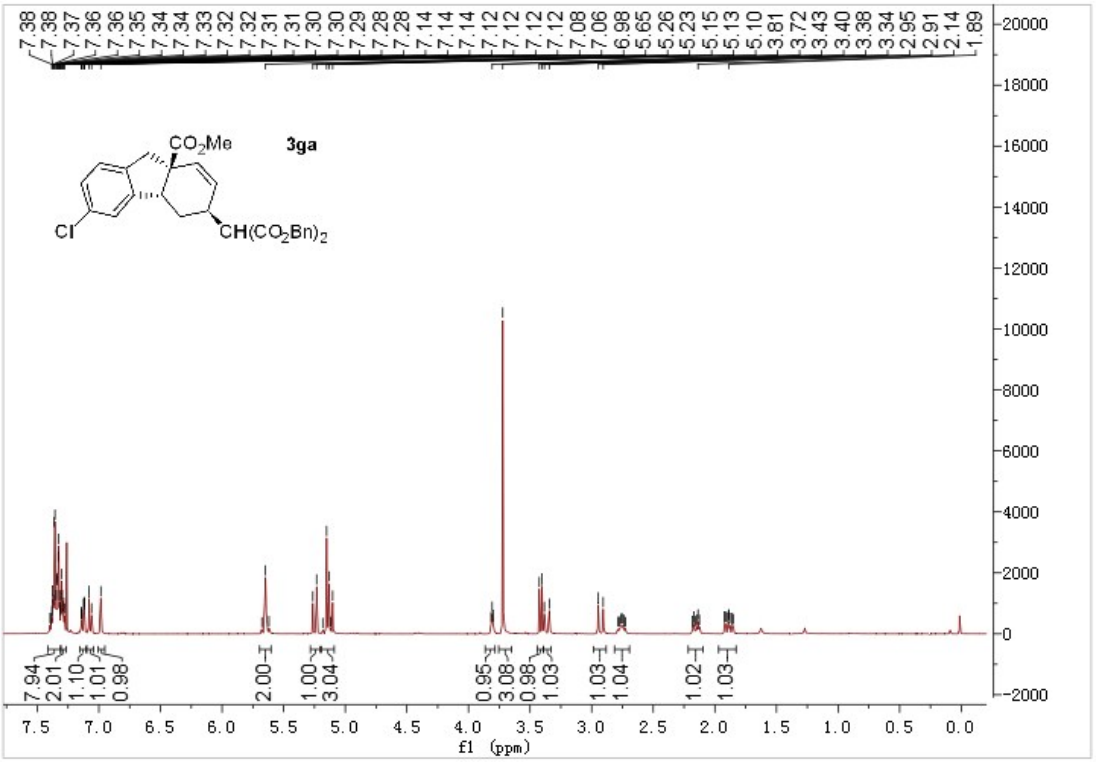
44.80
42.51
31.26
26.01
CO2Me
3fa
F
CH(CO2Bn)2
f1 (ppm)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Cl
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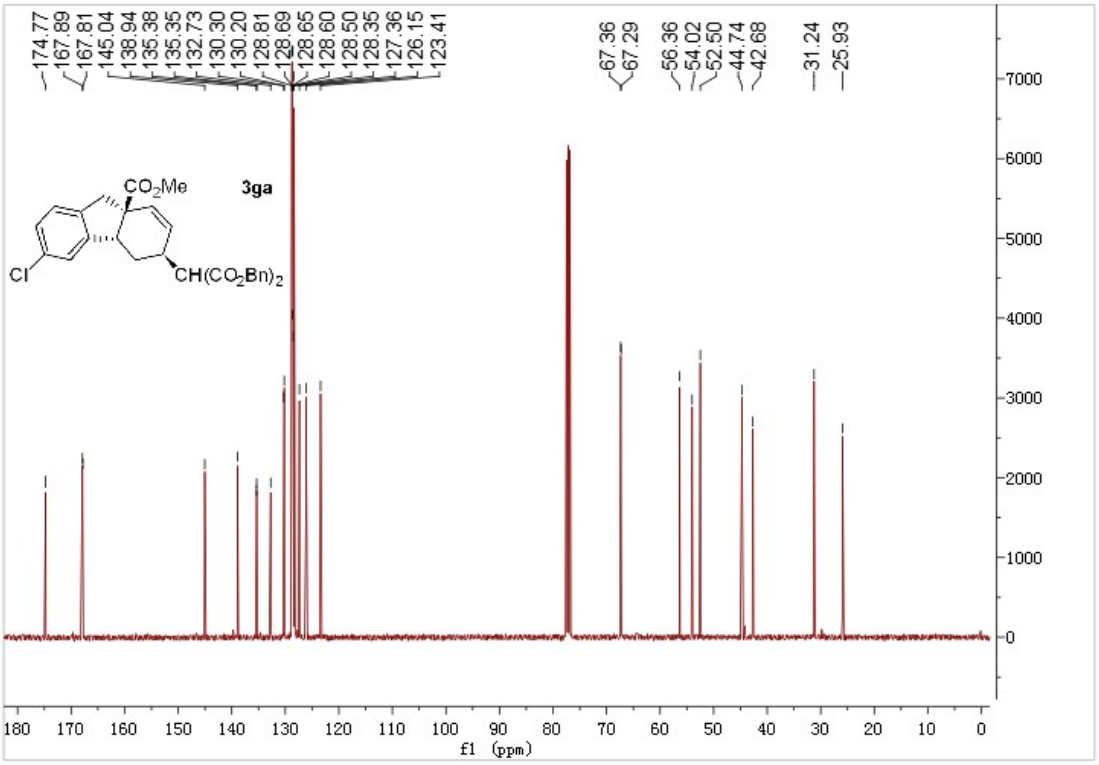
f1 (ppm)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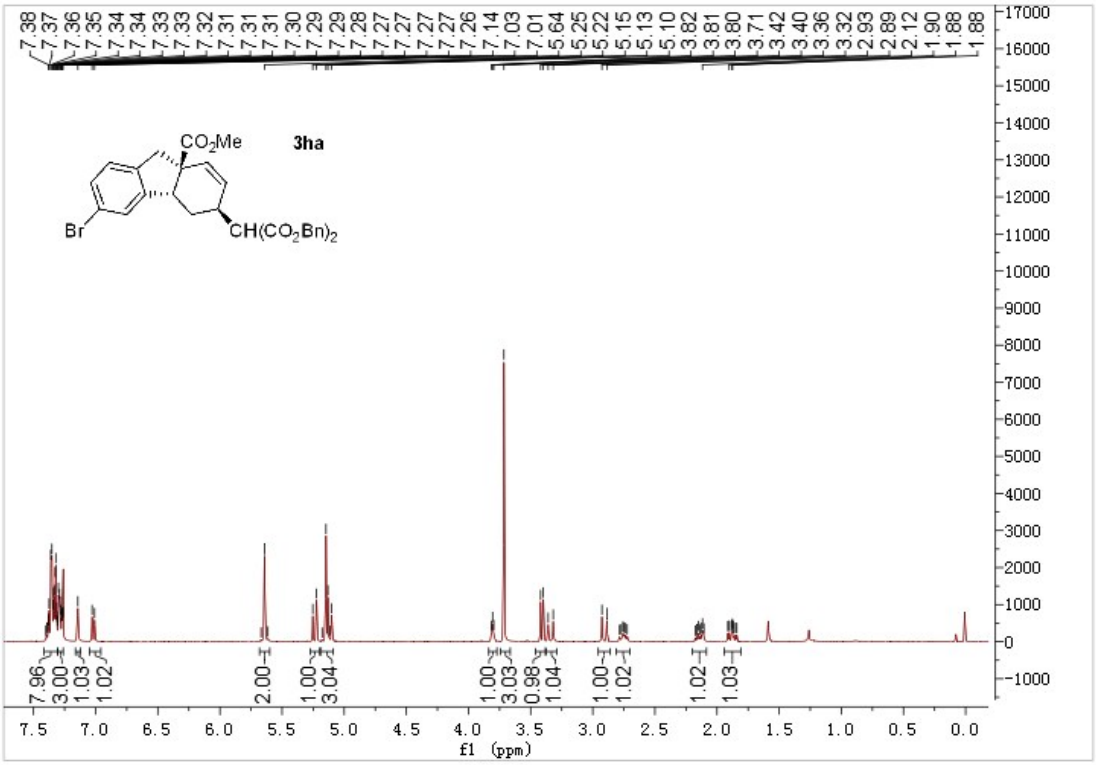
Cl
CH(CO2Bn)2
f1 (ppm)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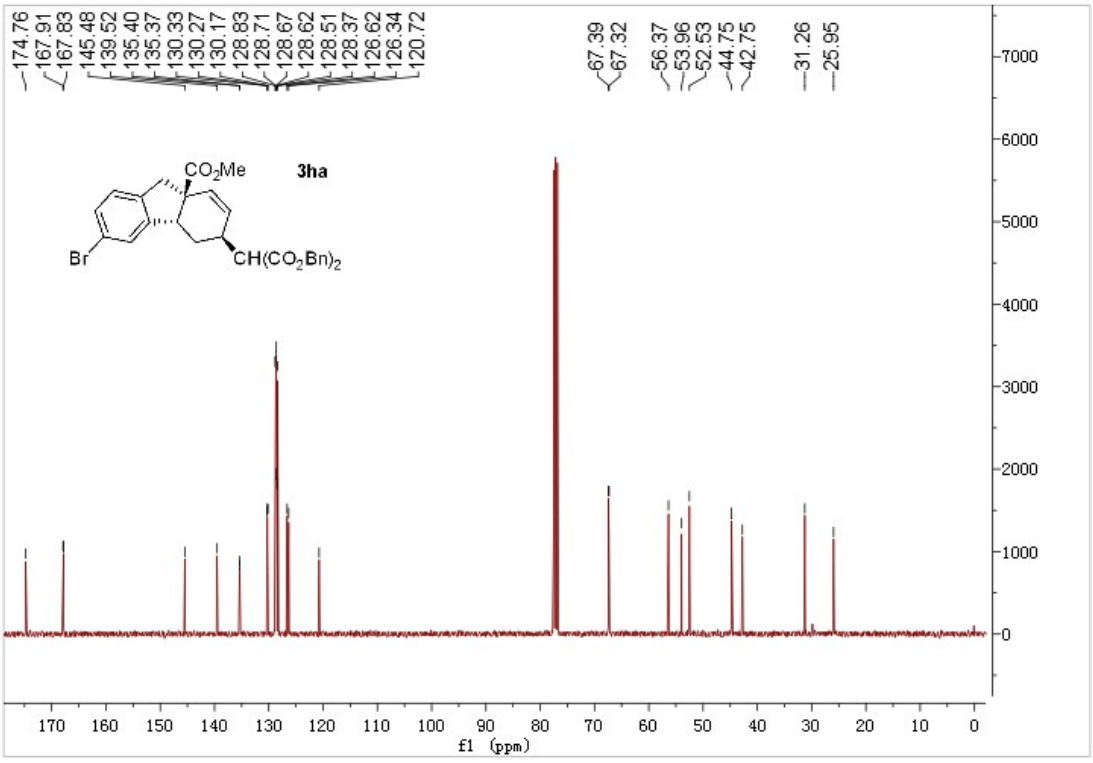
CO2Me
Br
CH(CO2Bn)2
f1 (ppm)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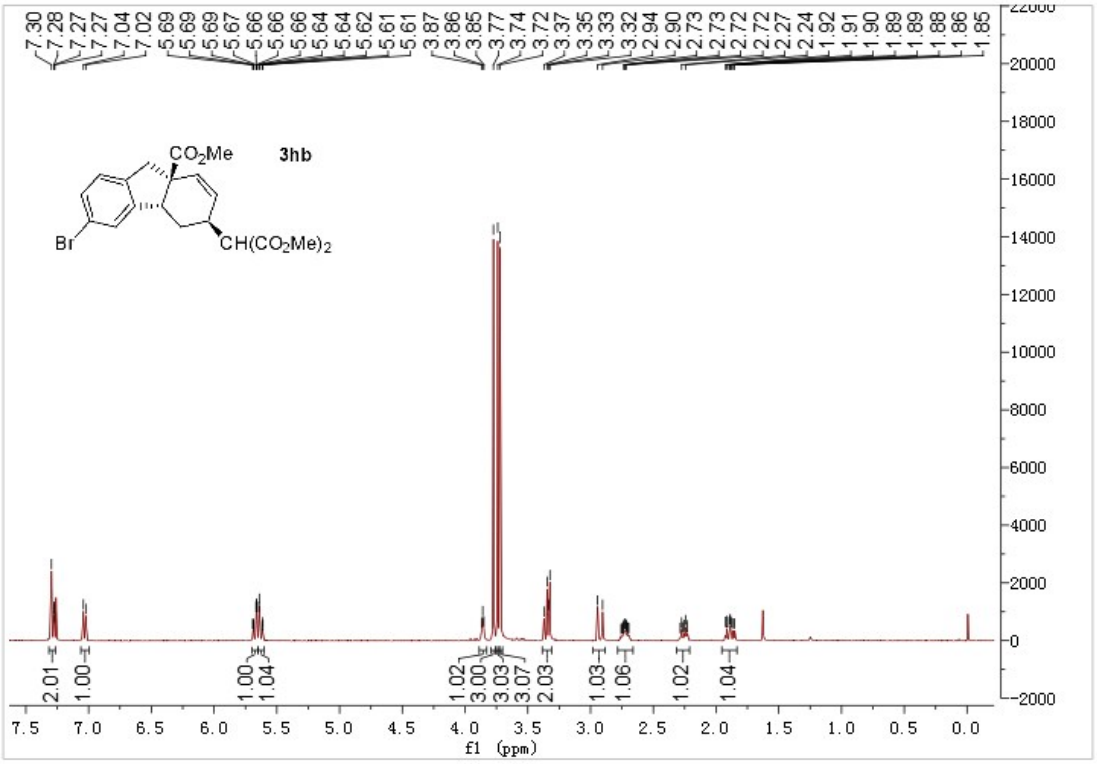
CO2Me
Br
CH(CO2Bn)2
f1 (ppm)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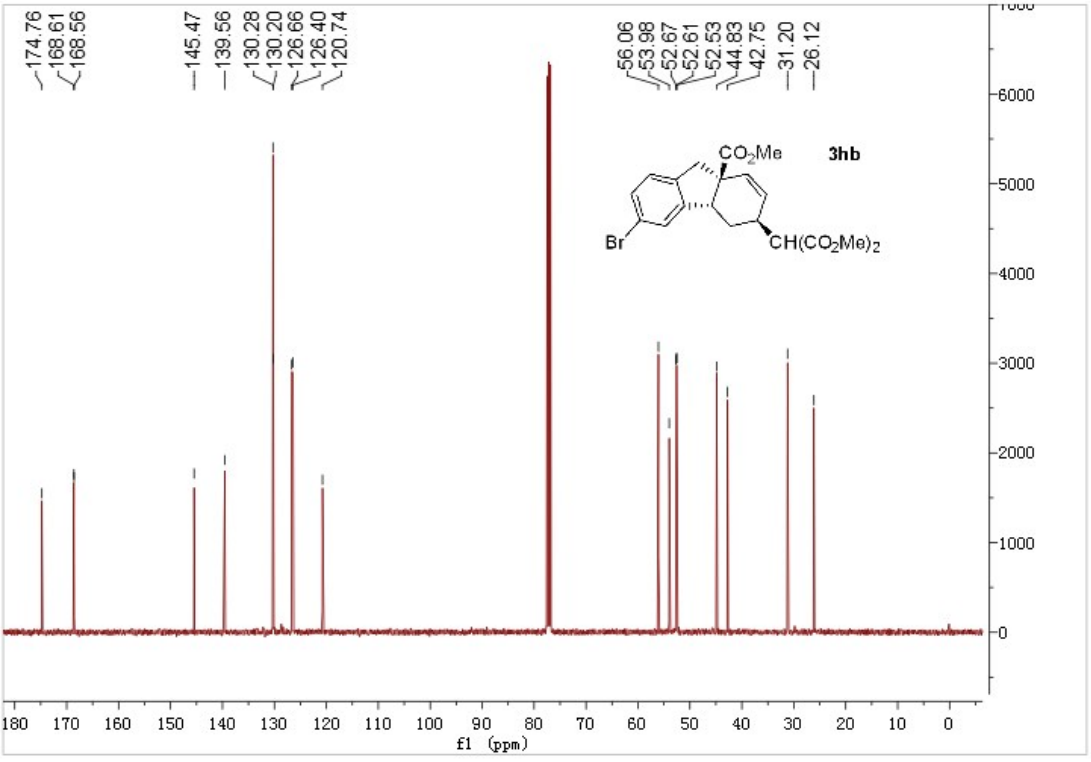
5.64
5.64
5.62
5.61
5.61
3.87
3.86
3.85
3.77
3.74
3.72
3.37
3.35
3.33
3.32
2.94
2.90
2.73
2.73
2.72
2.72
2.27
2.24
1.92
1.91
1.90
1.89
1.89
1.88
1.86
1.85
CO2Me
3hb
Br
CH(CO2Me)2
2.01
1.00
1.00
1.04
1.02
3.00
3.03
3.07
2.03
1.03
1.06
1.02
1.04
f1 (ppm)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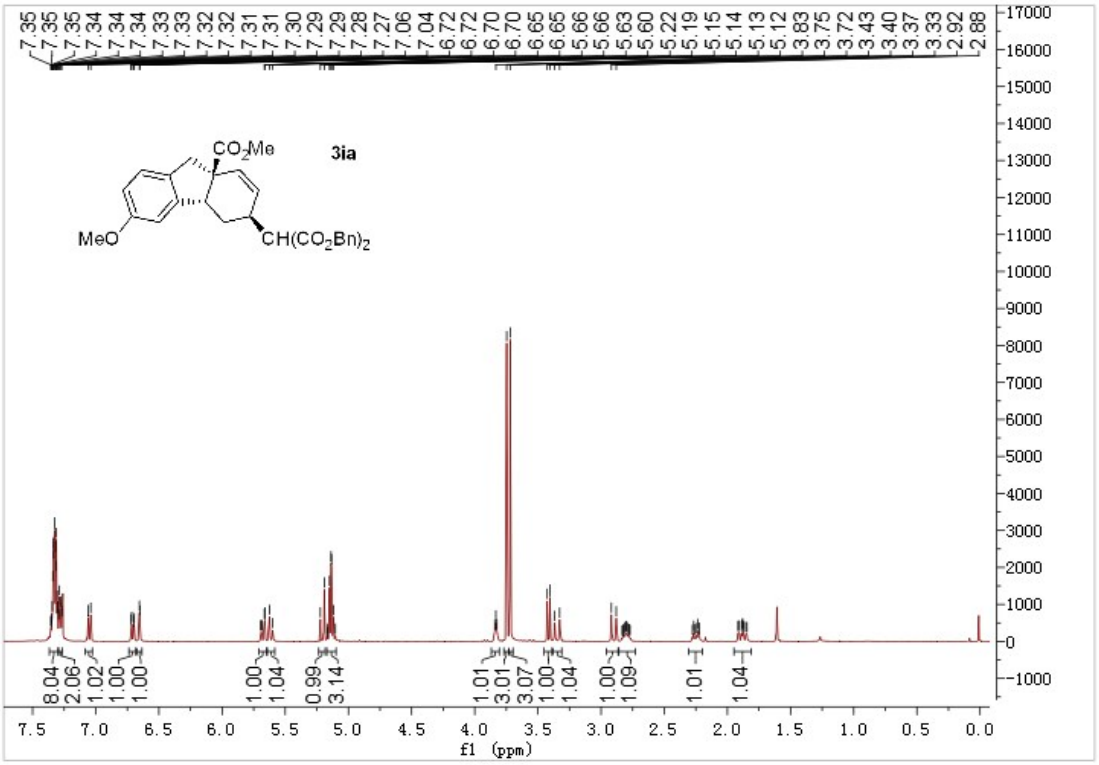
126.66
126.40
120.74
56.06
53.98
52.67
52.61
52.53
44.83
42.75
31.20
26.12
CO2Me
3hb
Br
CH(CO2Me)2
f1 (ppm)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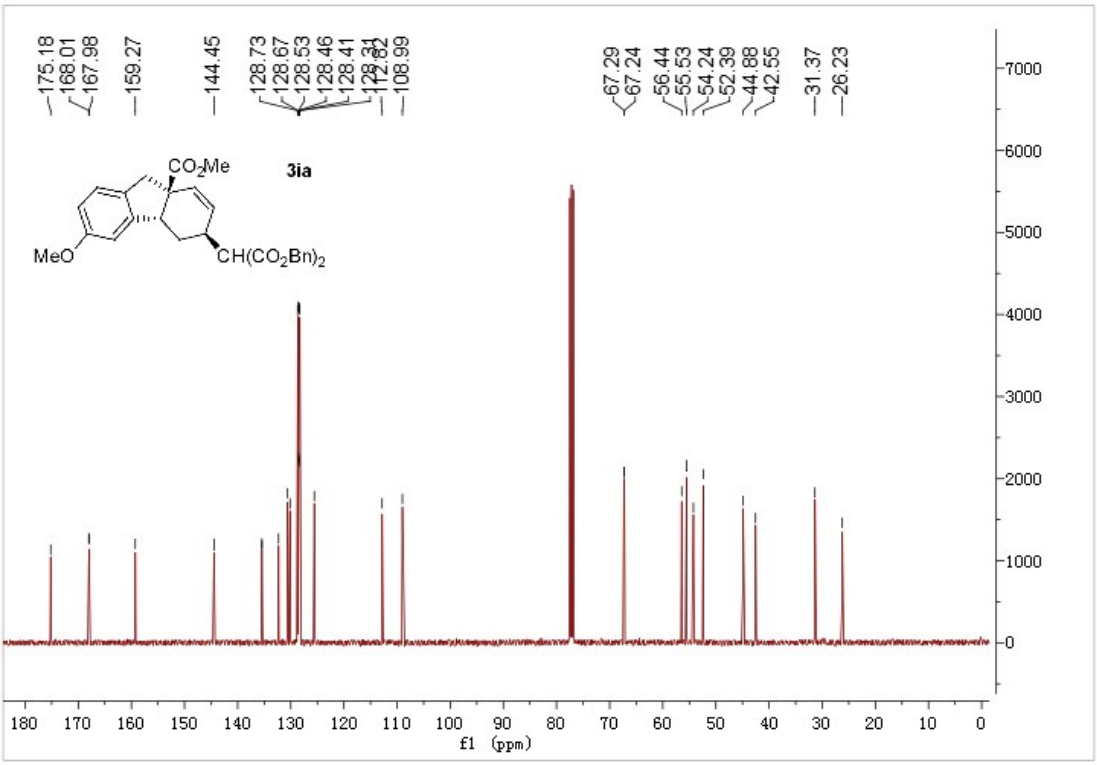
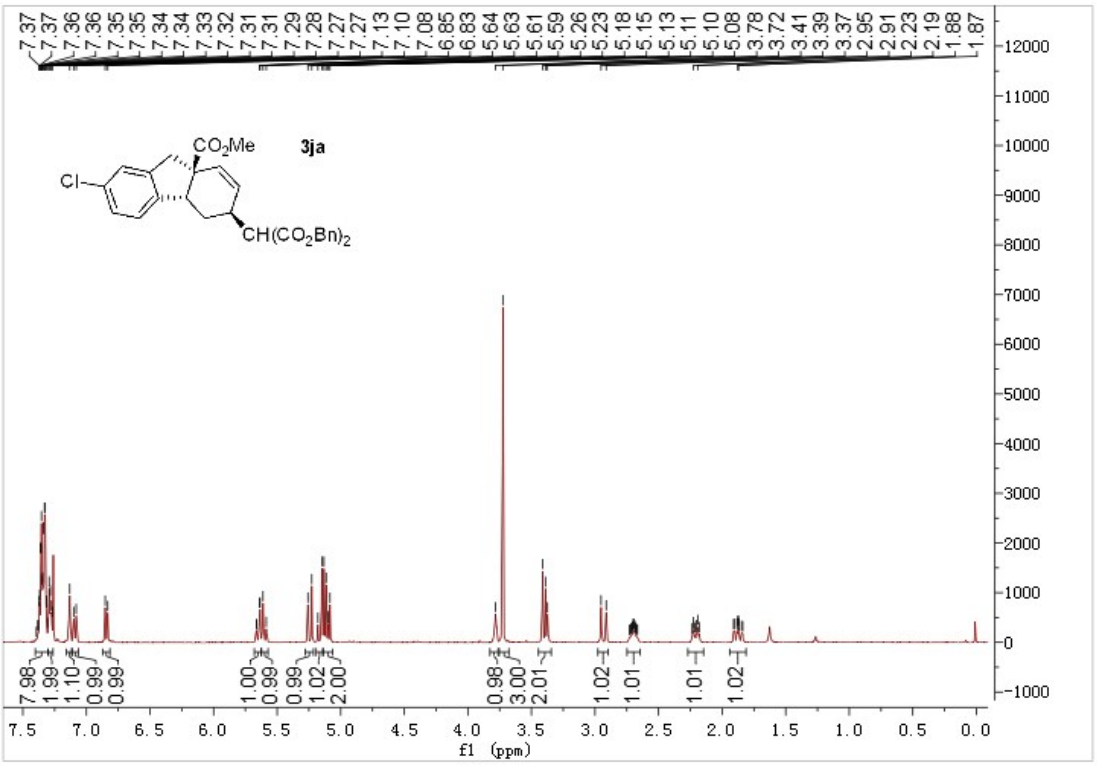
CO2Me
MeO
CH(CO2Bn)2
f1 (ppm)


3ia
CO2Me
MeO
CH(CO2Bn)2
f1 (ppm)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7.27
7.13
7.10
7.08
6.85
6.83
5.64
5.63
5.61
5.59
5.26
5.23
5.18
5.15
5.13
5.11
5.10
5.08
3.78
3.72
3.41
3.39
3.37
2.95
2.91
2.23
2.19
1.88
1.87
CO2Me
3ja
Cl
CH(CO2Bn)2
7.98
1.99
1.10
0.99
0.99
1.00
0.99
0.99
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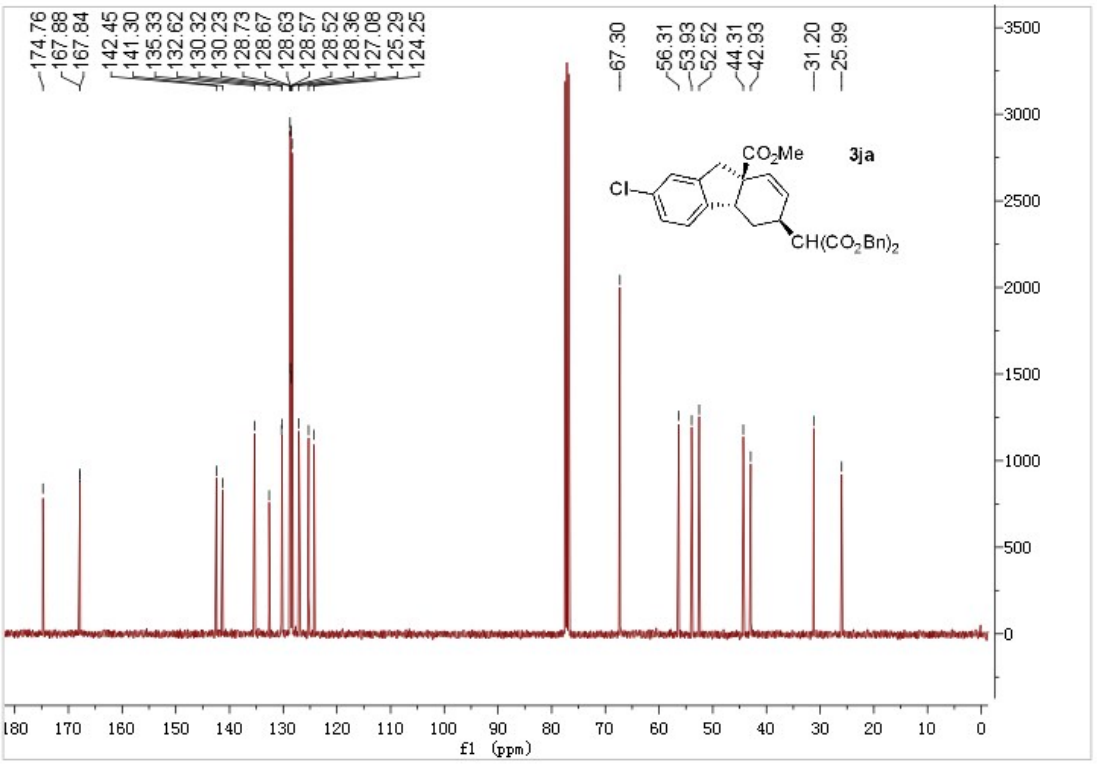
2.00
0.98
3.00
2.01
1.02
1.01
1.01
1.02
f1 (ppm)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128.36
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125.29
124.25
67.30
56.31
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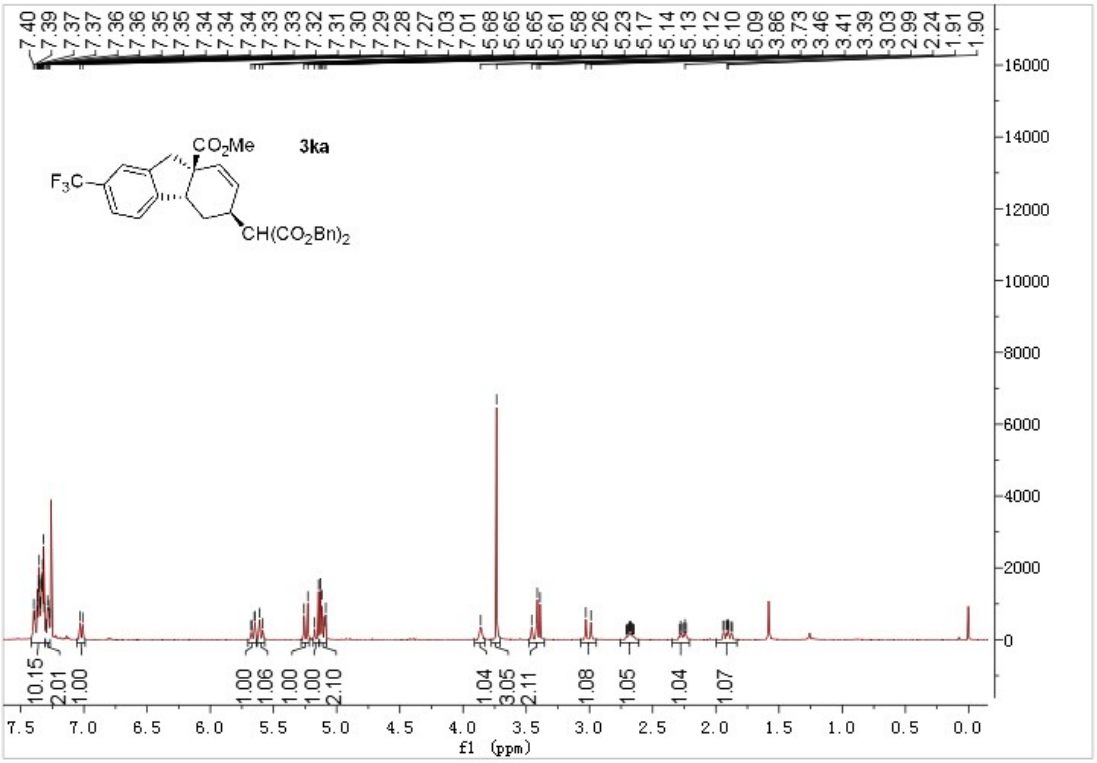
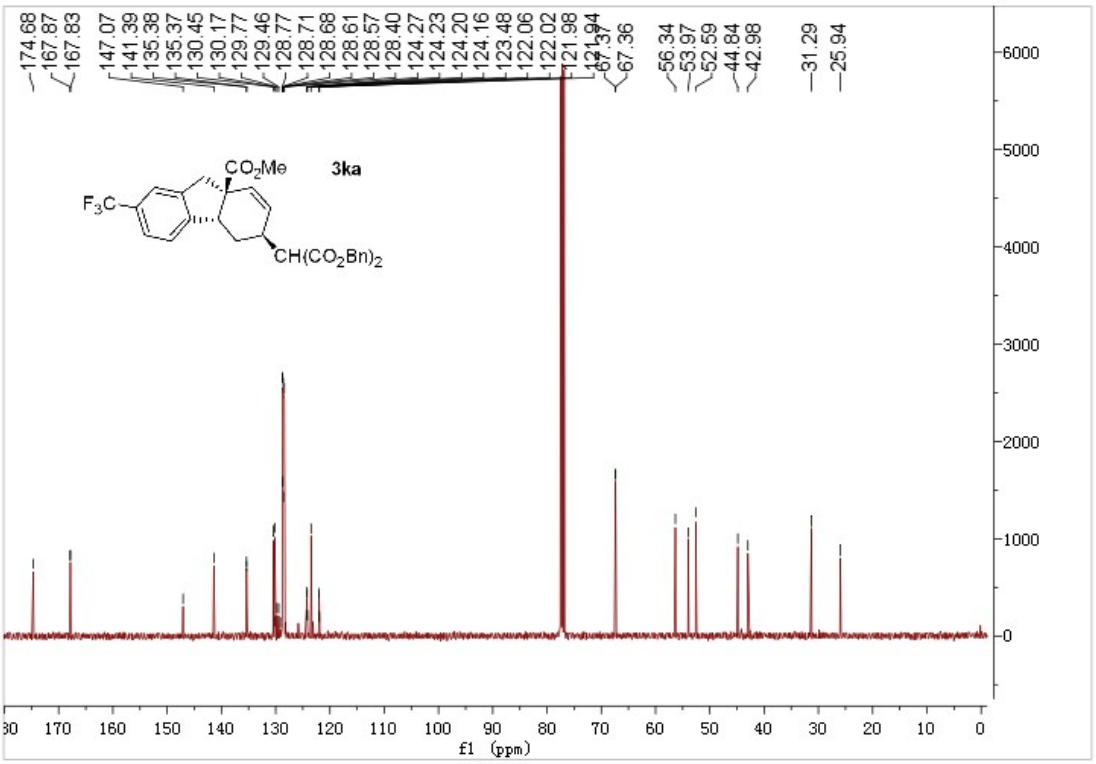
42.93
31.20
25.99
CO2Me
3ja
Cl
CH(CO2Bn)2
f1 (ppm)


3ka
CO2Me
F3C
CH(CO2Bn)2
f1 (ppm)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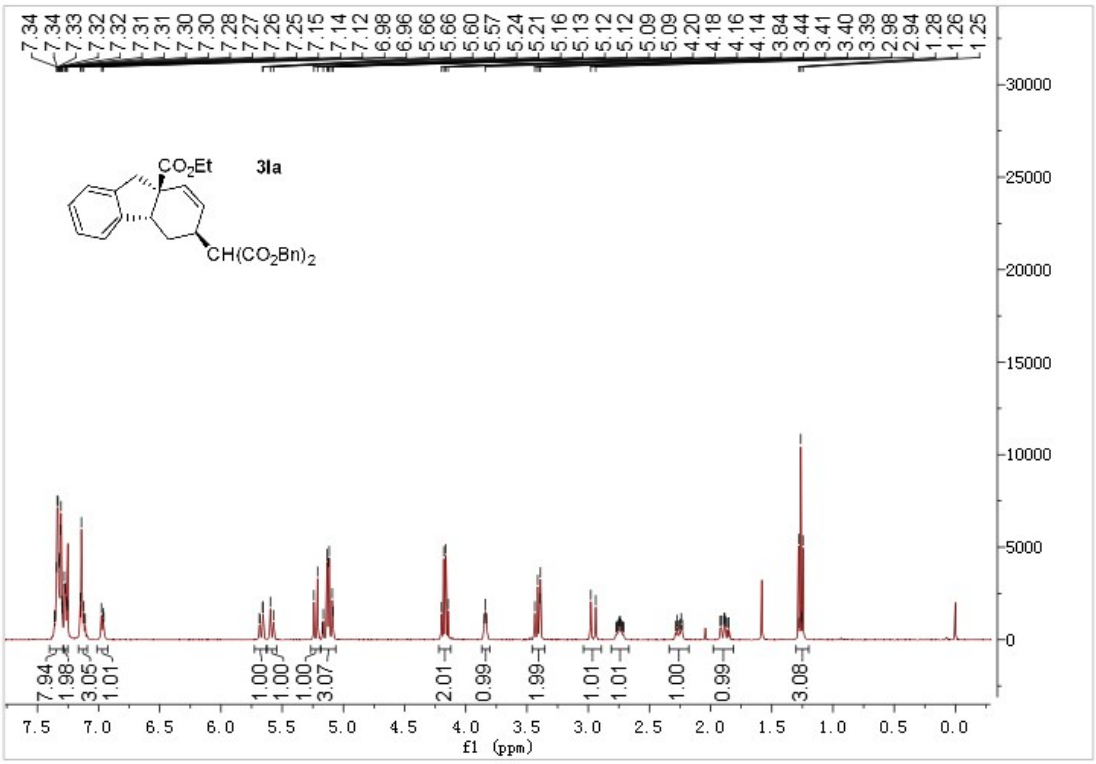
F3C
CH(CO2Bn)2
f1 (ppm)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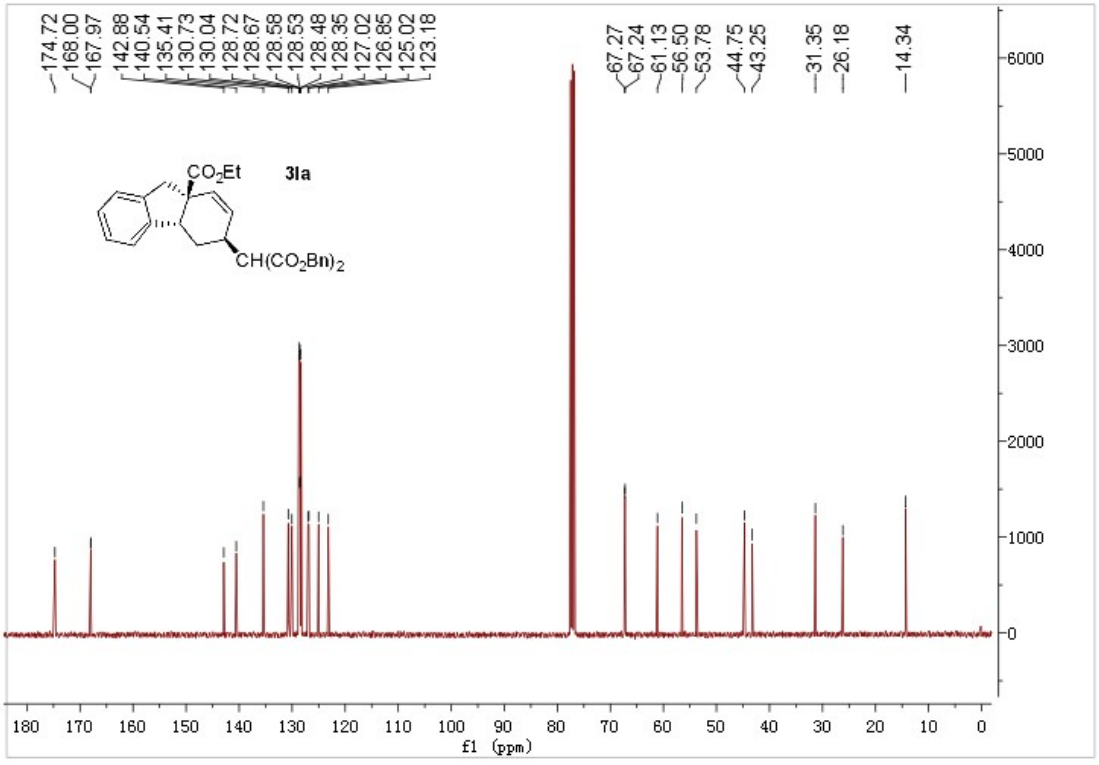
CO2Et
3la
CH(CO2Bn)2
7.94 1.98 3.05 1.01 1.00 1.00 1.00 3.07 2.01 0.99 1.99 1.01 1.01 1.00 0.99 3.08
f1 (ppm)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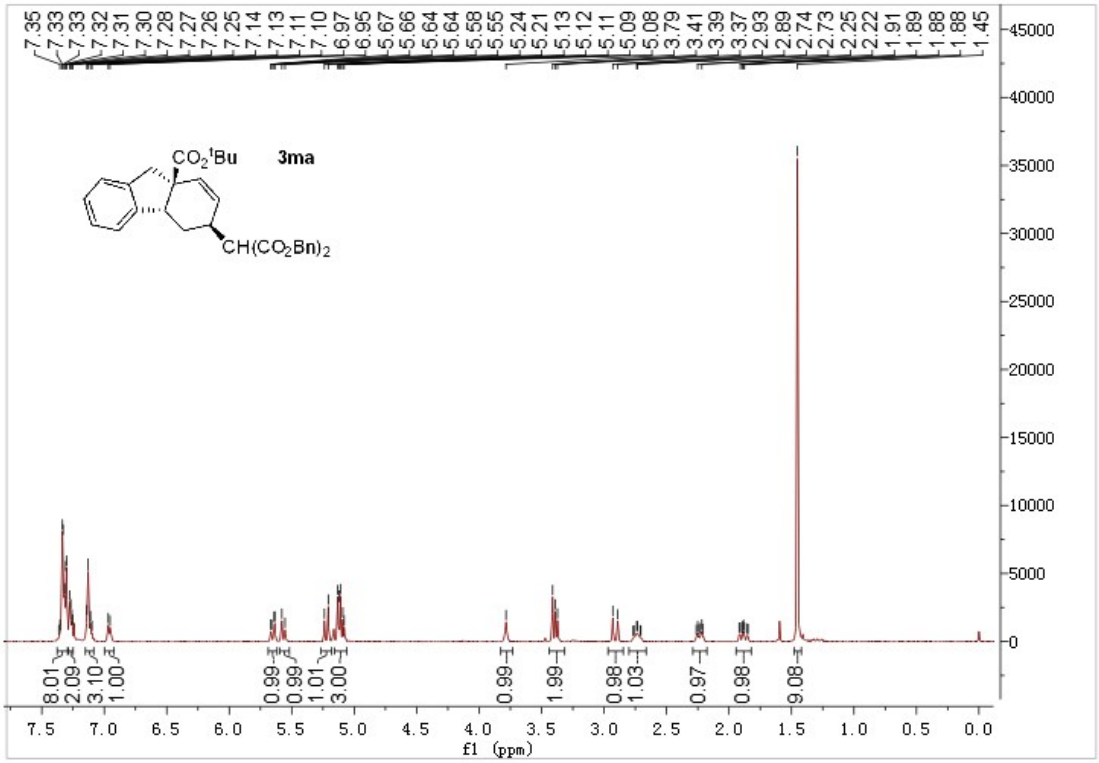
67.27 67.24 61.13 56.50 53.78 44.75 43.25 31.35 26.18 14.34
CO2Et
3la
CH(CO2Bn)2
f1 (ppm)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5.12
5.11
5.09
5.08
3.79
3.41
3.39
3.37
2.93
2.89
2.74
2.73
2.25
2.22
1.91
1.89
1.88
1.88
1.45
CO2tBu
3ma
CH(CO2Bn)2
8.01
2.09
3.10
1.00
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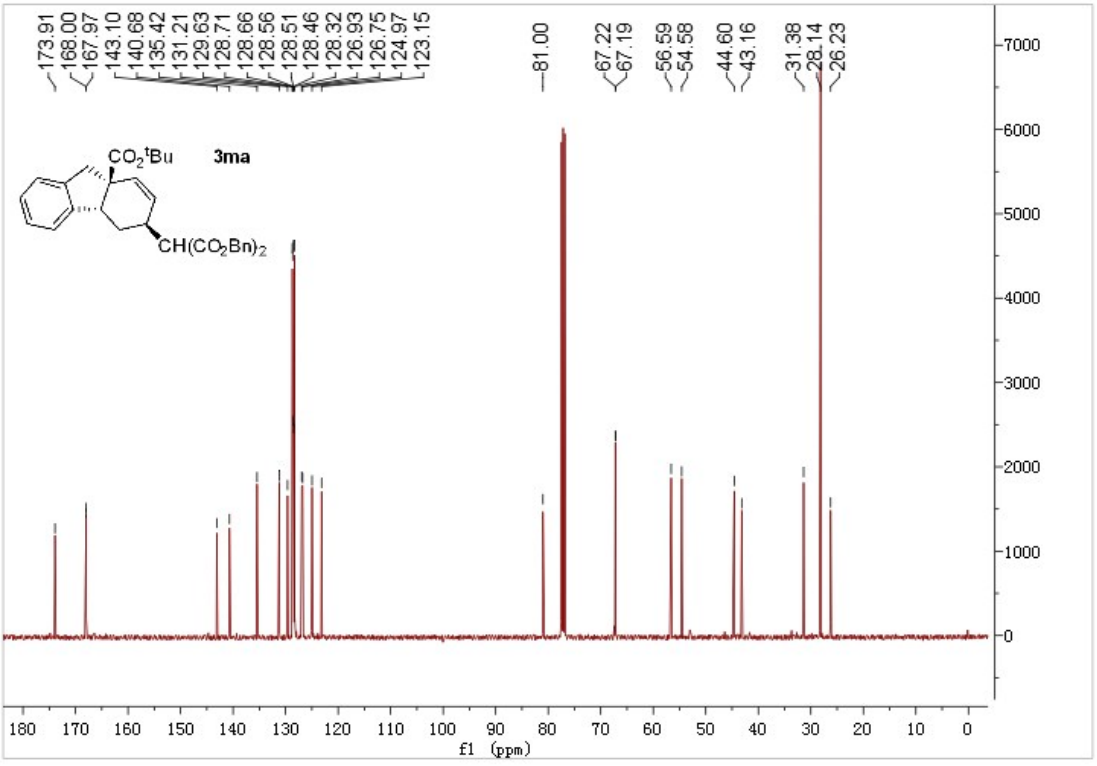
0.99
1.01
3.00
0.99
1.99
0.98
1.03
0.97
0.98
9.08
f1 (ppm)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126.75
124.97
123.15
81.00
67.22
67.19
56.59
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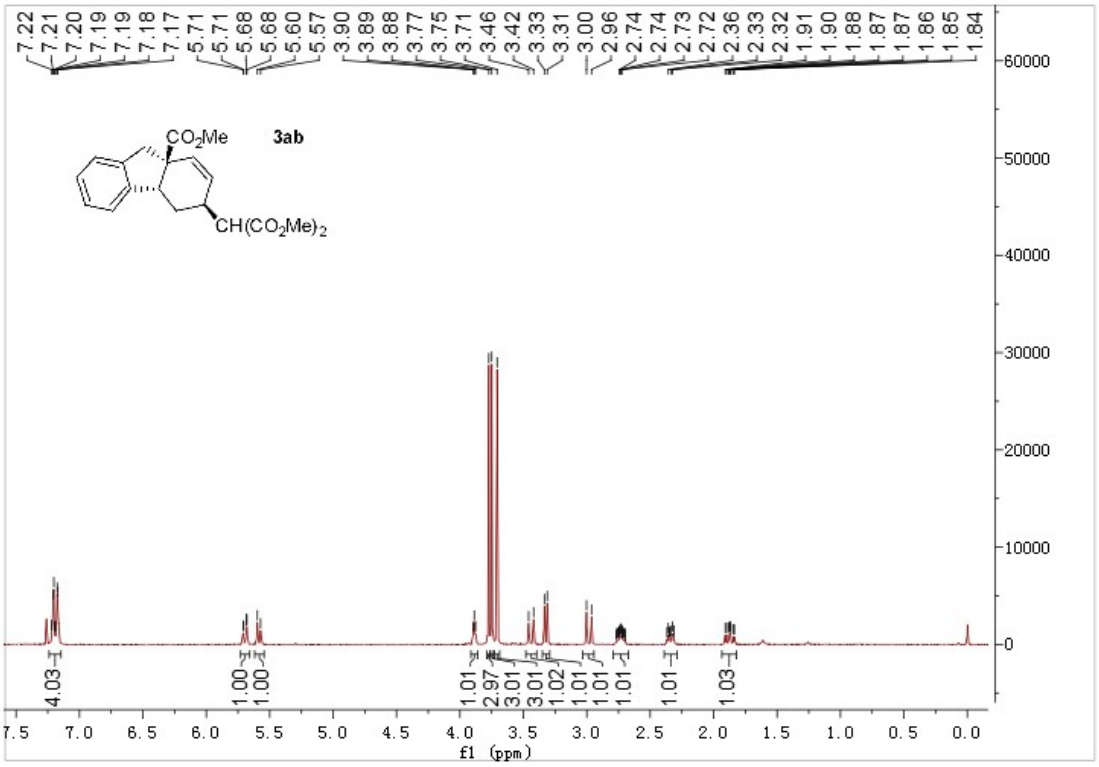
43.16
31.38
28.14
26.23
CO2tBu
3ma
CH(CO2Bn)2
f1 (ppm)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5.60
5.57
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3.89
3.88
3.77
3.75
3.71
3.46
3.42
3.33
3.31
3.00
2.96
2.74
2.73
2.72
2.36
2.33
2.32
1.91
1.90
1.88
1.87
1.87
1.86
1.85
1.84
CO2Me
3ab
CH(CO2Me)2
4.03
1.00
1.00
1.01
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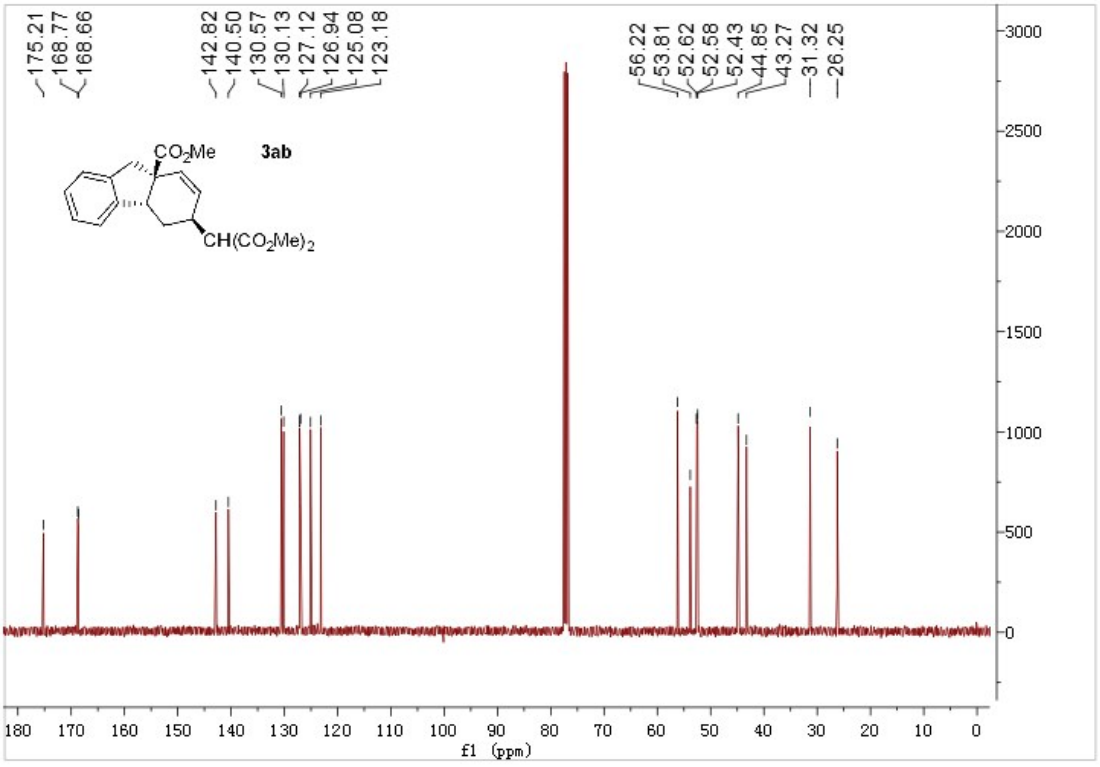
3.01
3.01
1.02
1.01
1.01
1.01
1.01
1.03
f1 (ppm)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125.08
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56.22
53.81
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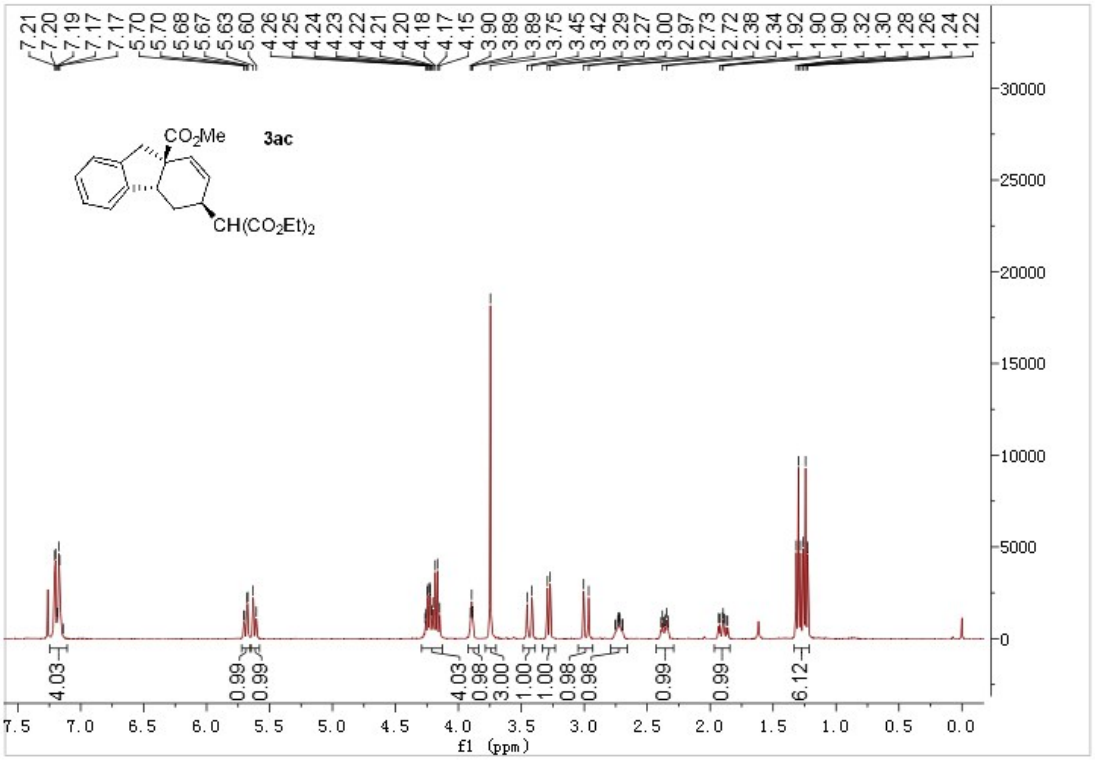
44.85
43.27
31.32
26.25
CO2Me
3ab
CH(CO2Me)2
f1 (ppm)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4.25
4.24
4.23
4.22
4.21
4.20
4.18
4.17
4.15
3.90
3.89
3.89
3.75
3.45
3.42
3.29
3.27
3.00
2.97
2.73
2.72
2.38
2.34
1.92
1.90
1.90
1.32
1.30
1.28
1.26
1.24
1.22
CO2Me
3ac
CH(CO2Et)2
4.03
0.99
0.99
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3.00
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0.98
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0.99
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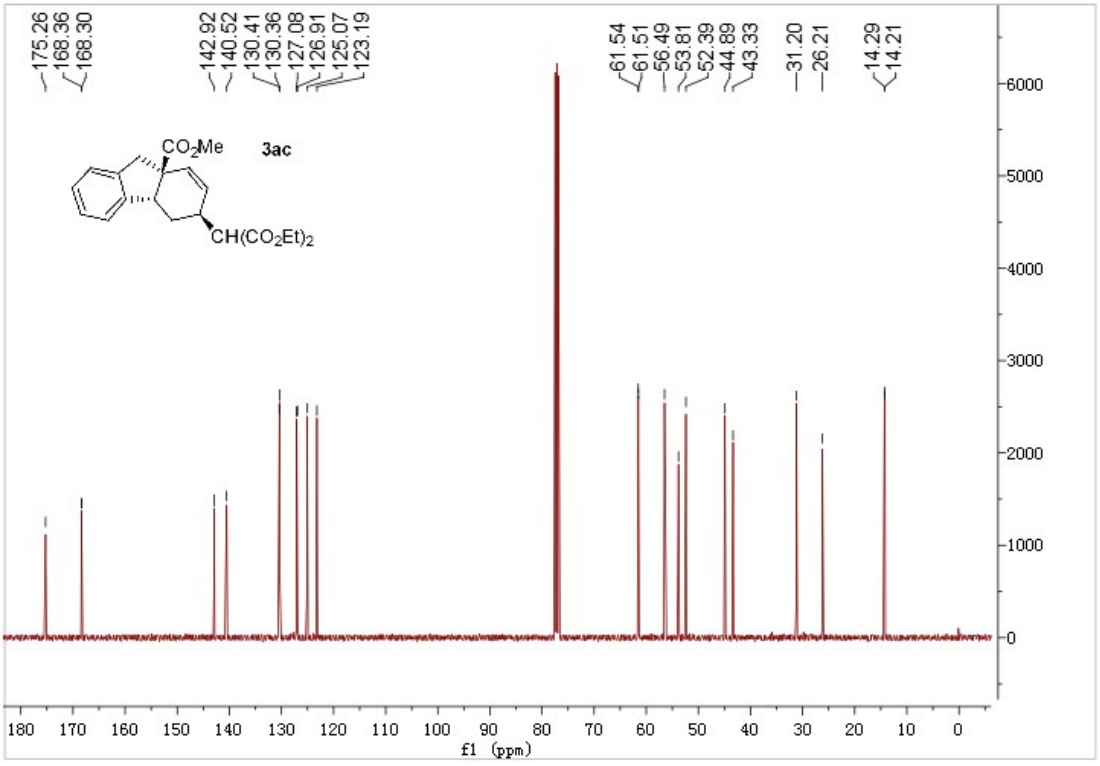
6.12
f1 (ppm)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125.07
123.19
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61.51
56.49
53.81
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44.89
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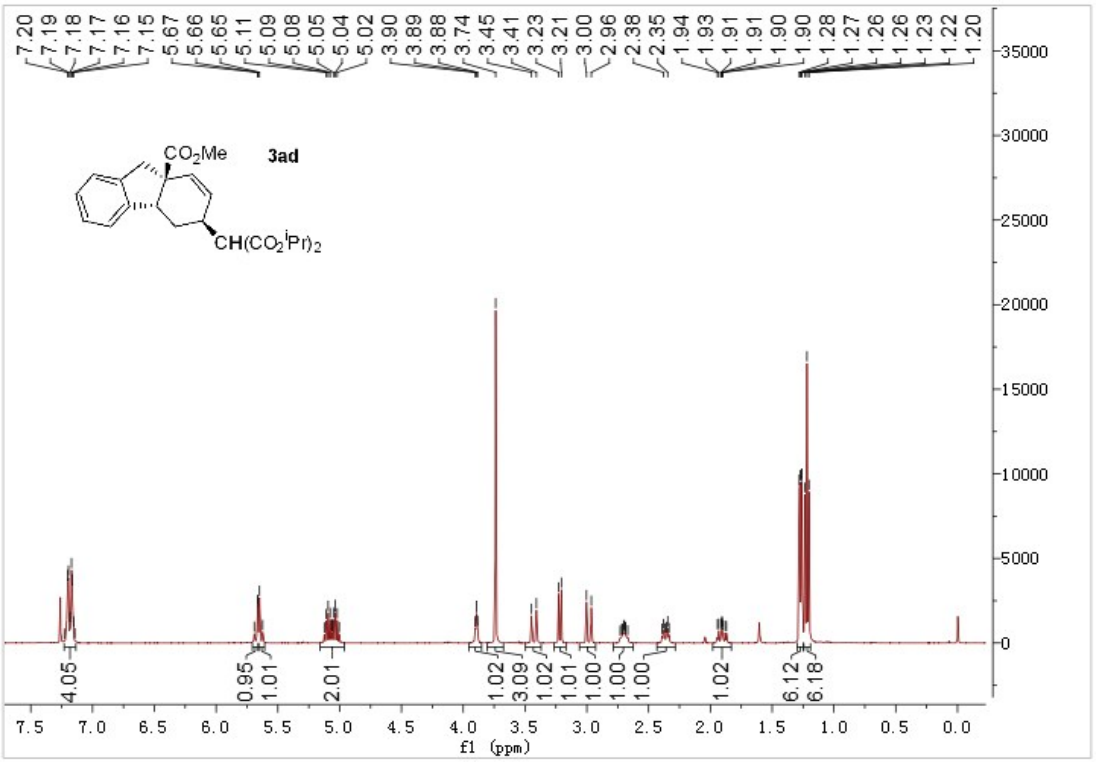
31.20
26.21
14.29
14.21
CO2Me
3ac
CH(CO2Et)2
f1 (ppm)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5.05
5.04
5.02
3.90
3.89
3.88
3.74
3.45
3.41
3.23
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3.00
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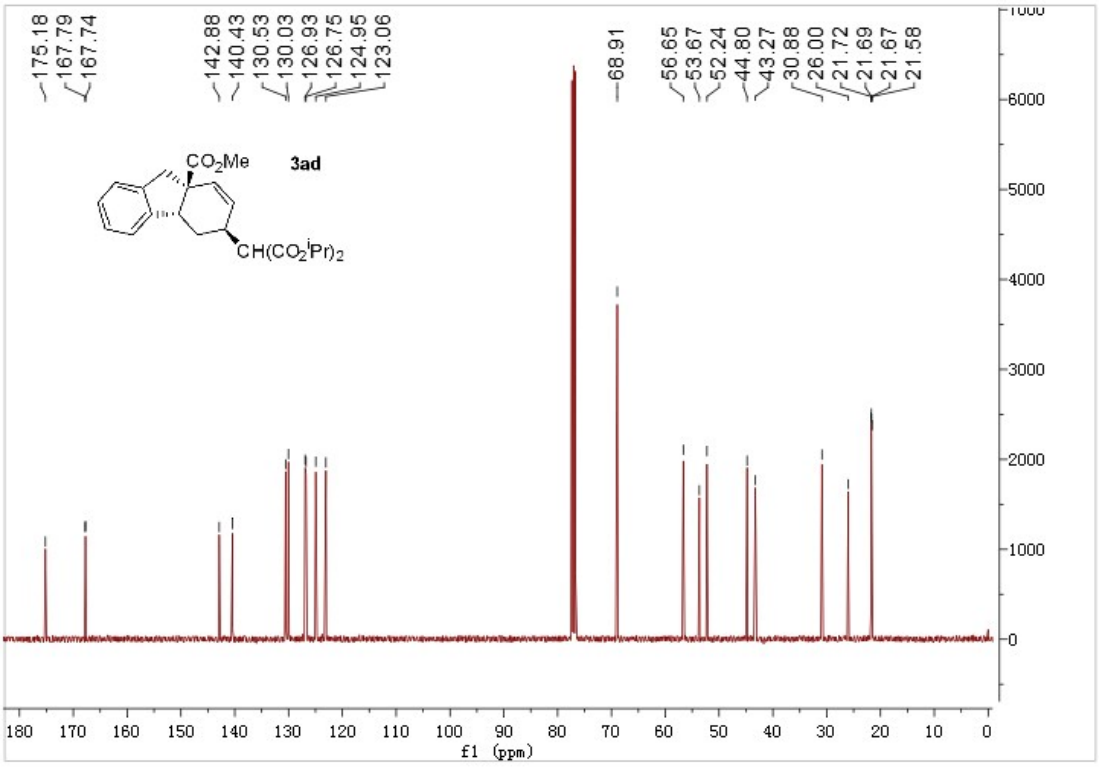
1.93
1.91
1.91
1.90
1.90
1.28
1.27
1.26
1.26
1.23
1.22
1.20
CO2Me
3ad
CH(CO2iPr)2
4.05
0.95
1.01
2.01
1.02
3.09
1.02
1.01
1.00
1.00
1.00
1.02
6.12
6.18
f1 (ppm)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53.67
52.24
44.80
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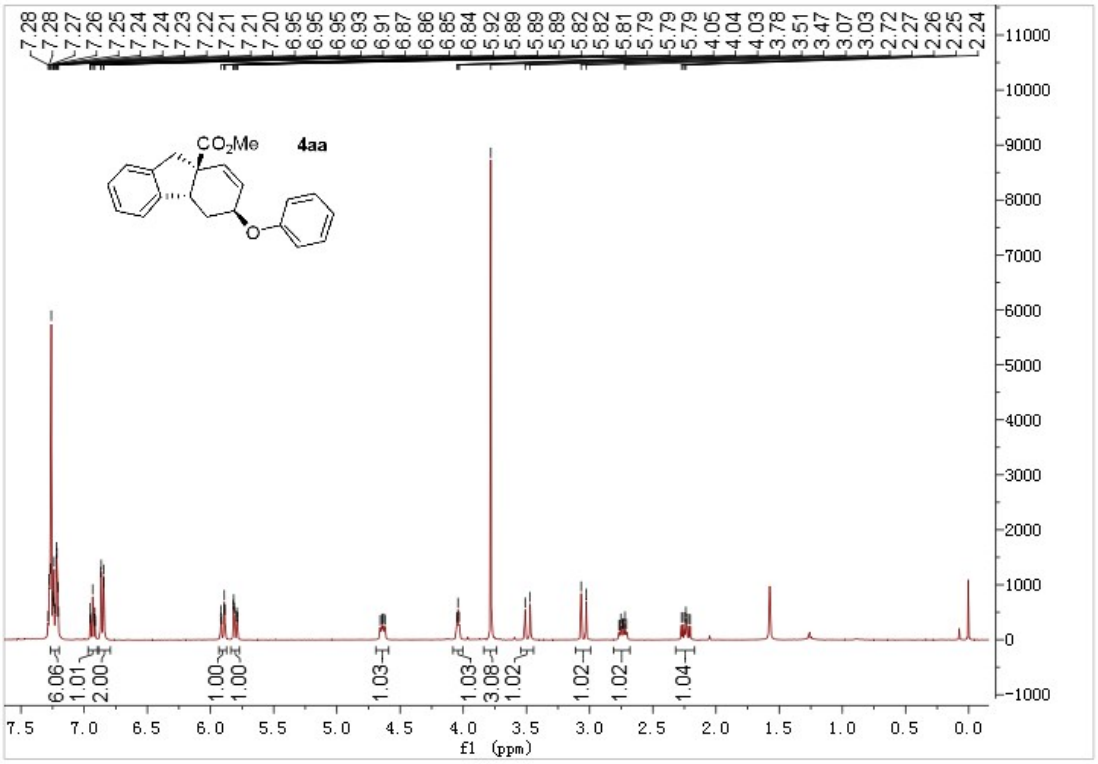
21.67
21.58
CO2Me
3ad
CH(CO2iPr)2
f1 (ppm)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5.89
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5.79
4.05
4.04
4.03
3.78
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3.07
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2.72
2.27
2.26
2.25
2.24
CO2Me
4aa
O
6.06
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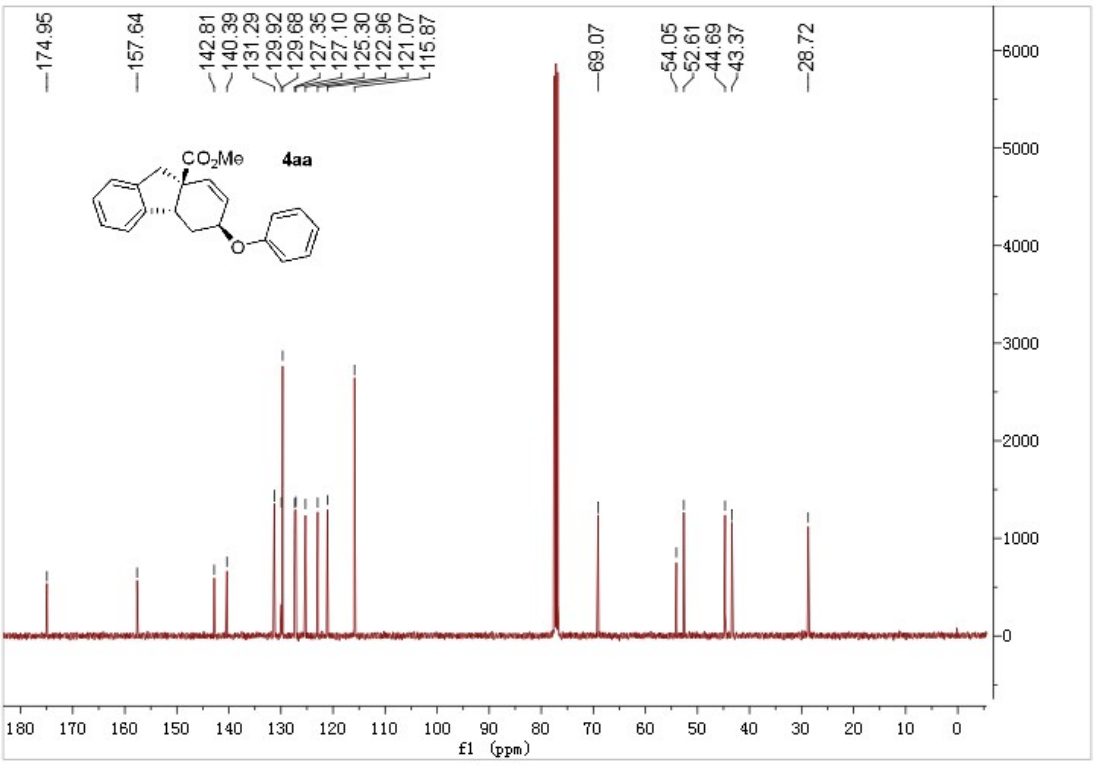
1.00
1.03
1.03
3.08
1.02
1.02
1.02
1.04
f1 (ppm)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122.96
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54.05
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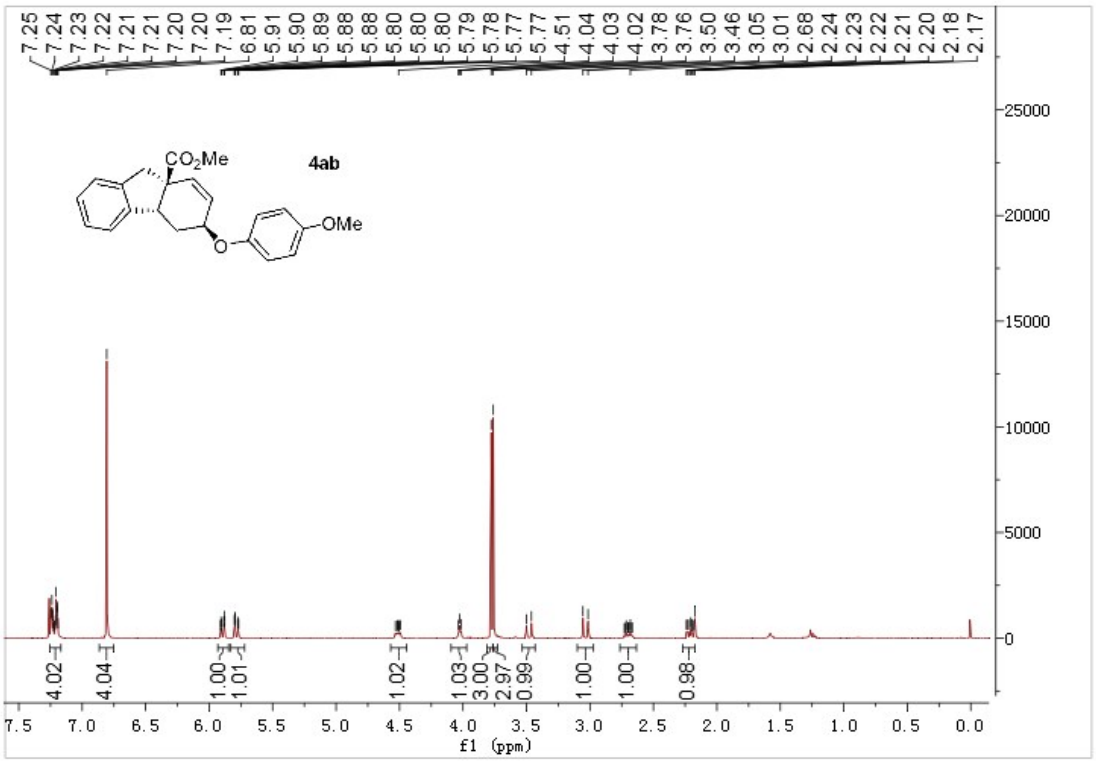
28.72
CO2Me
4aa
O
f1 (ppm)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4.02
3.78
3.76
3.50
3.46
3.05
3.01
2.68
2.24
2.23
2.22
2.21
2.20
2.18
2.17
CO2Me
4ab
OMe
O
25000
20000
15000
10000
5000
0
4.02
4.04
1.00
1.01
1.02
1.03
3.00
2.97
0.99
1.00
1.00
0.98
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.5
3.0
2.5
2.0
1.5
1.0
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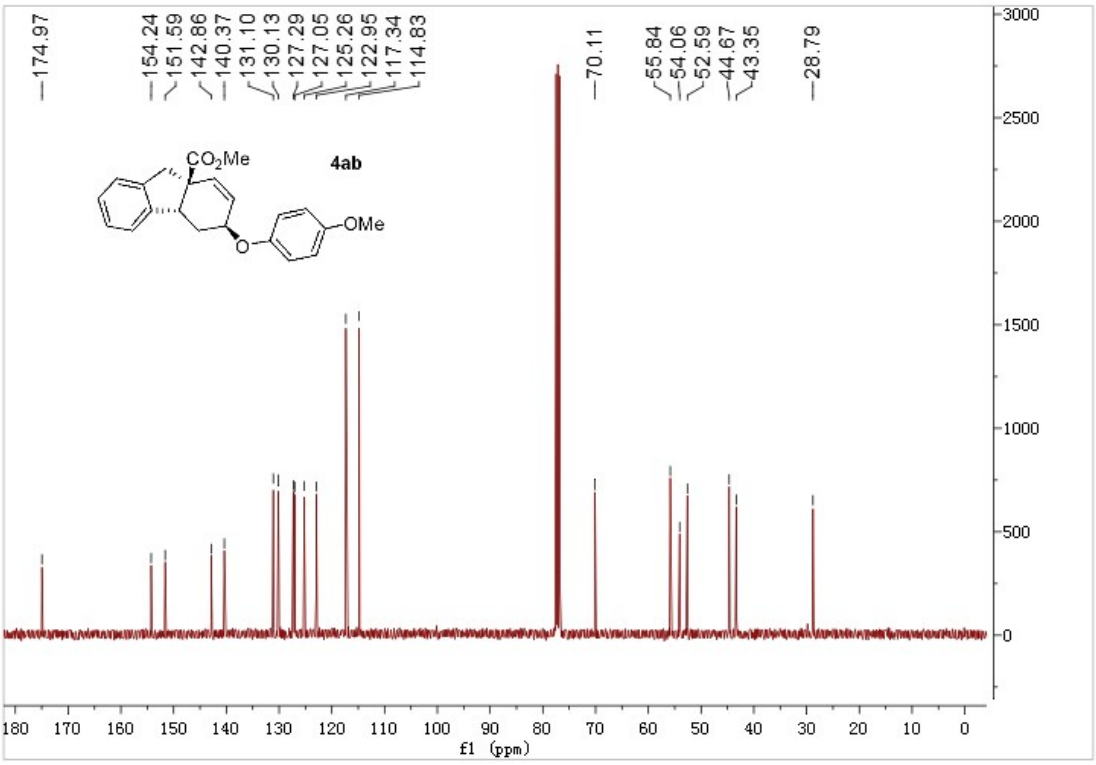
0.0
f1 (ppm)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154.24
151.59
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127.29
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125.26
122.95
117.34
114.83
70.11
55.84
54.06
52.59
44.67
43.35
28.79
CO2Me
4ab
OMe
O
3000
2500
2000
1500
1000
500
0
180
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130
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110
100
90
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70
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50
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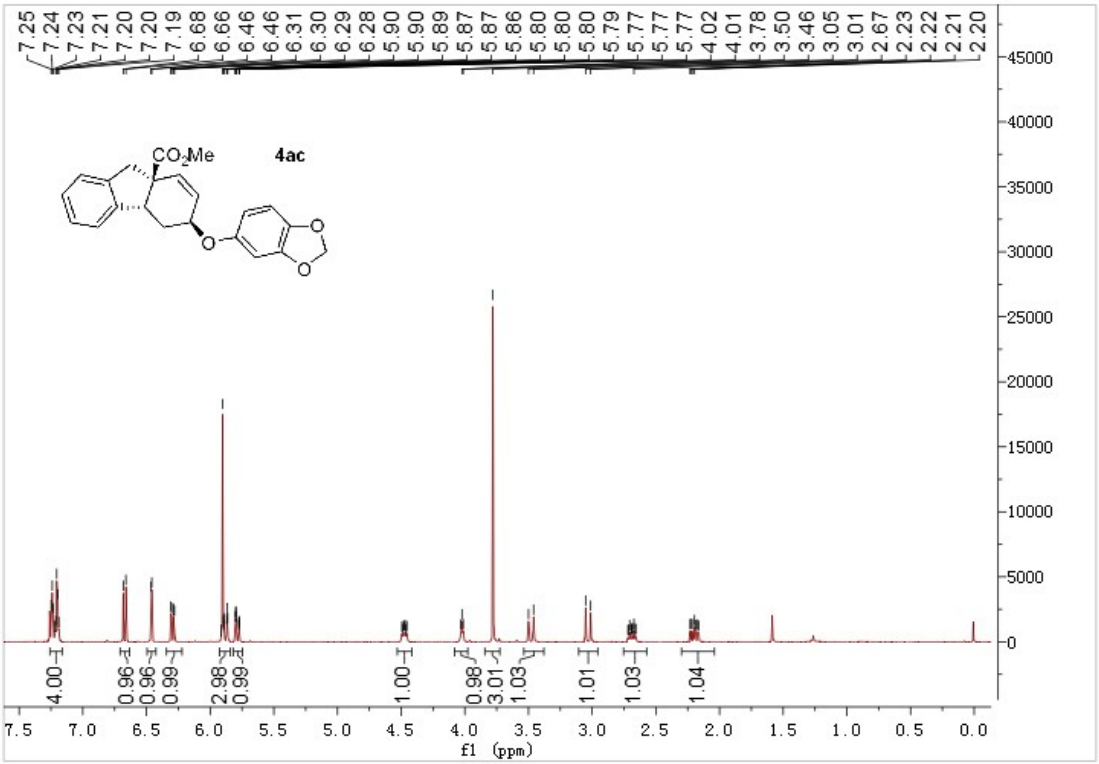
30
20
10
0
f1 (ppm)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6.29
6.28
5.90
5.90
5.89
5.87
5.87
5.86
5.80
5.80
5.80
5.79
5.77
5.77
5.77
4.02
4.01
3.78
3.50
3.46
3.05
3.01
2.67
2.23
2.22
2.21
2.20
CO2Me
4ac
O
O
O
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
4.00
0.96
0.96
0.99
2.98
0.99
1.00
0.98
3.01
1.03
1.01
1.03
1.04
7.5
7.0
6.5
6.0
5.5
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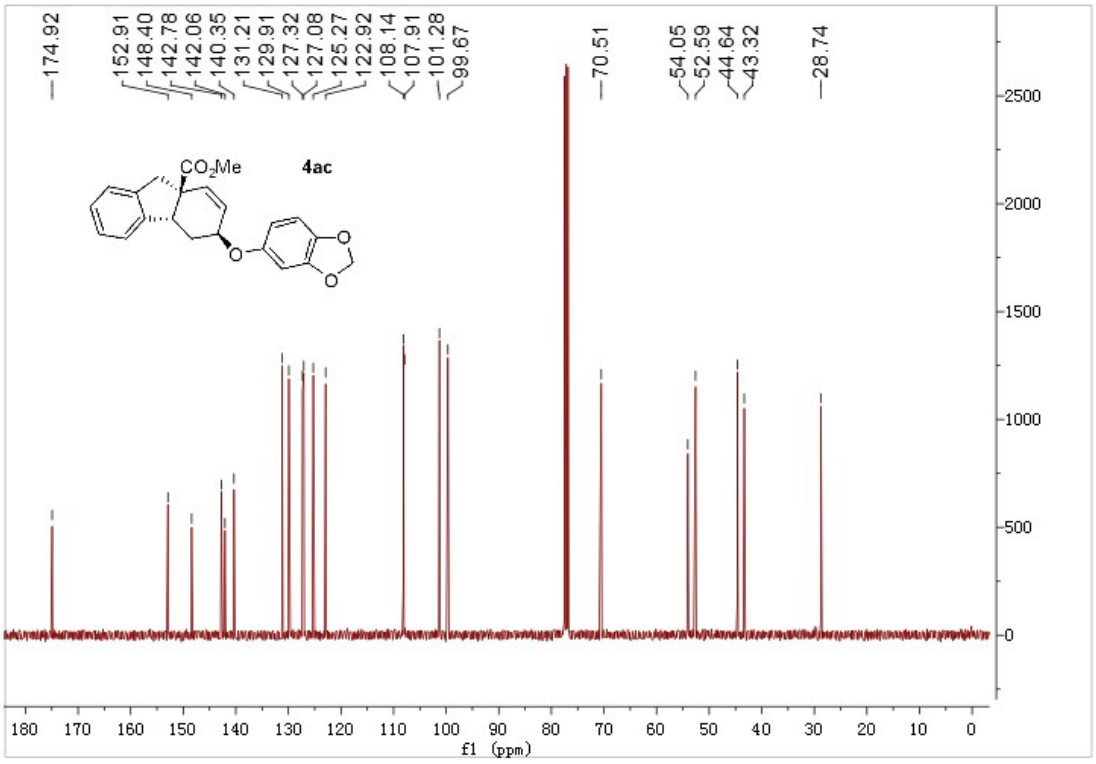
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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152.91
148.40
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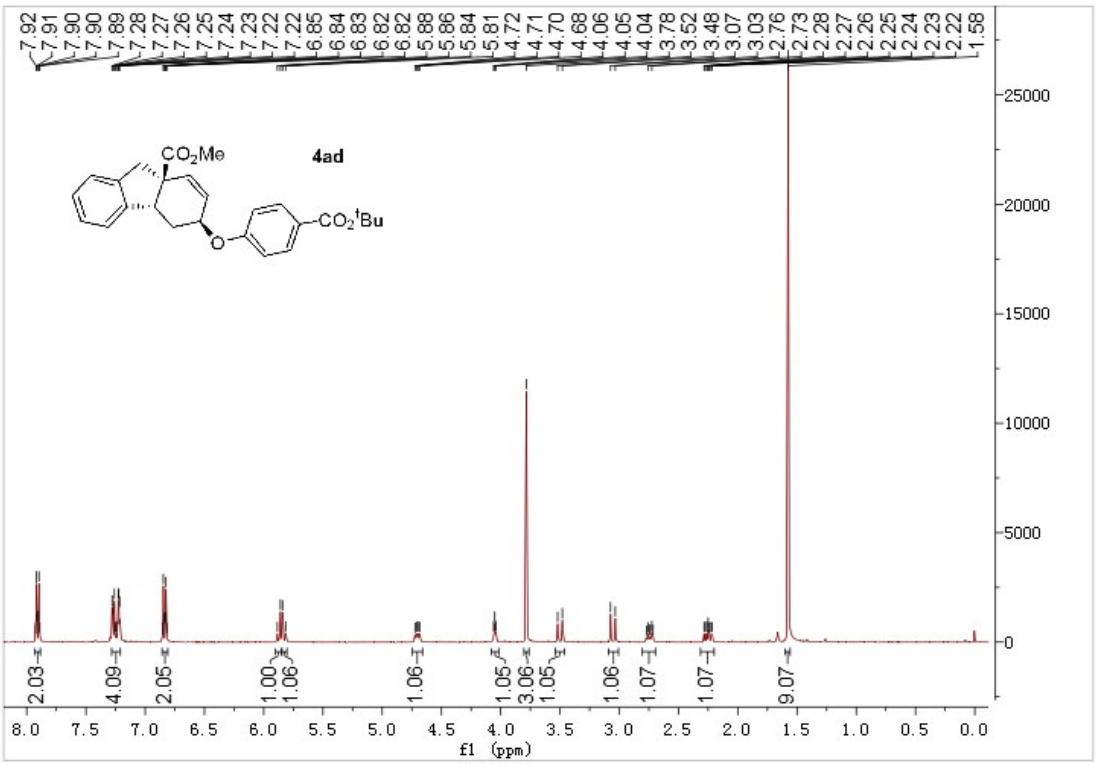
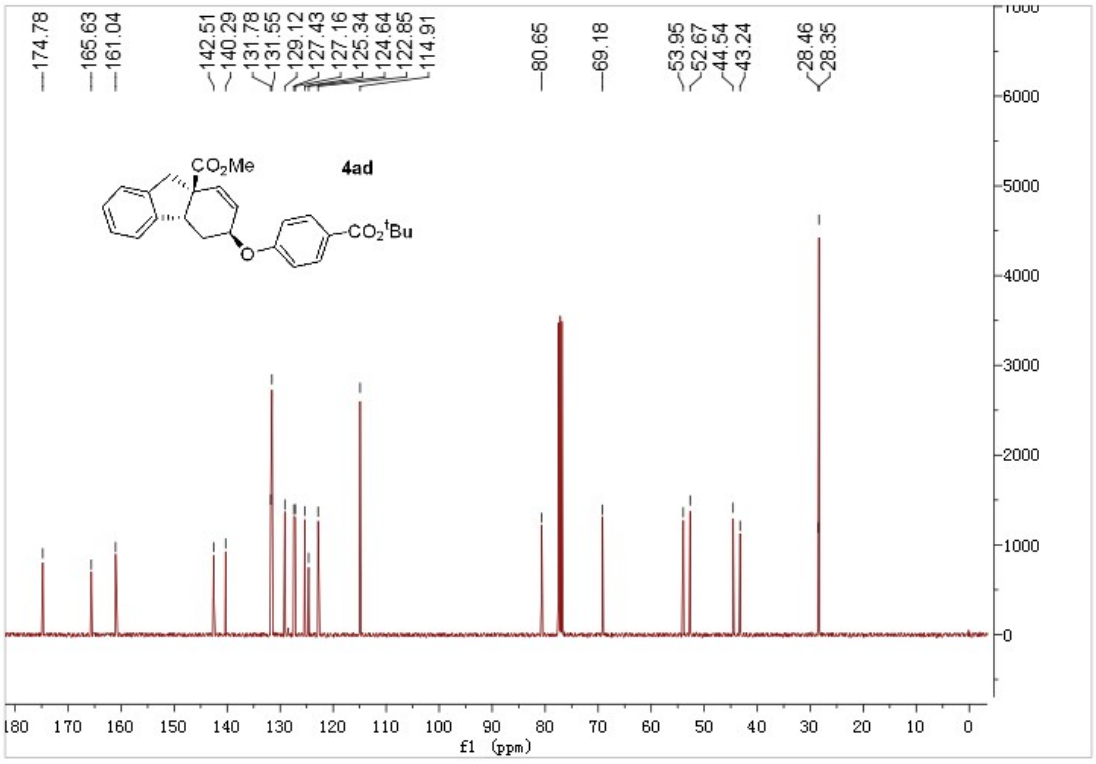
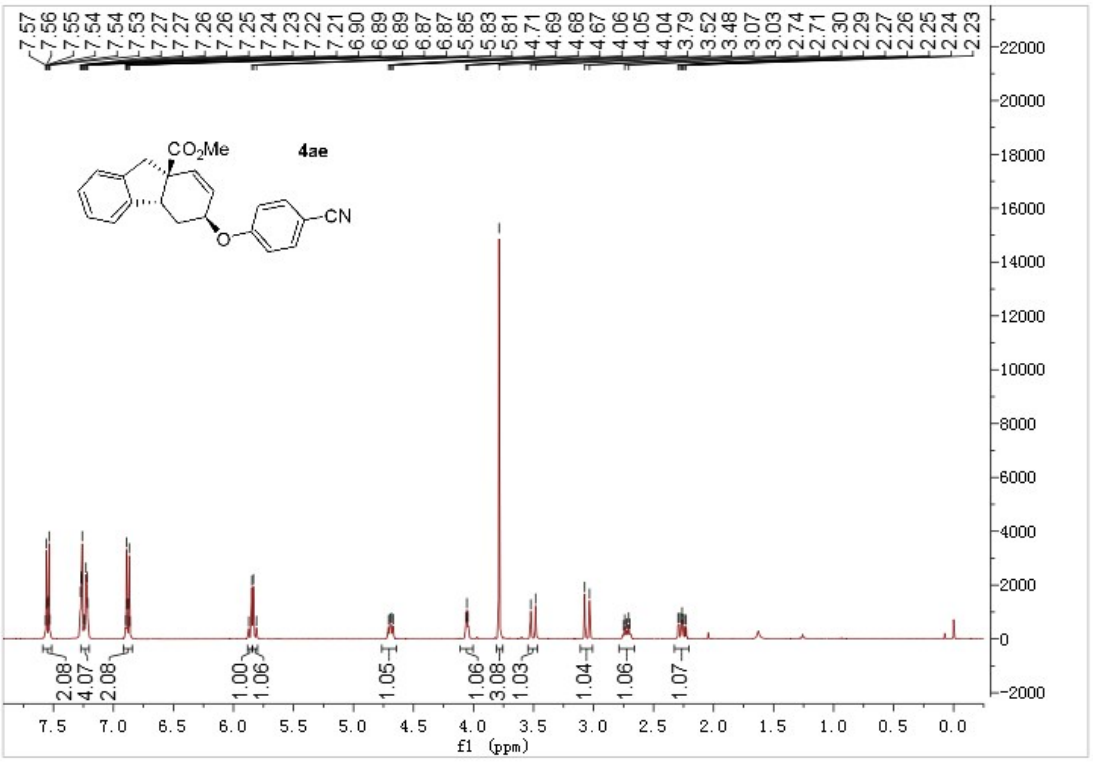
140.35
131.21
129.91
127.32
127.08
125.27
122.92
108.14
107.91
101.28
99.67
70.51
54.05
52.59
44.64
43.32
28.74
CO2Me
4ac
O
O
O
2500
2000
1500
1000
500
0
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


4ad
CO2Me
CO2tBu
f1 (ppm)


4ad
CO2Me
CO2tBu
f1 (ppm)


7.57
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7.54
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7.27
7.27
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7.26
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7.24
7.23
7.22
7.21
6.90
6.89
6.89
6.87
6.87
5.85
5.83
5.81
4.71
4.69
4.68
4.67
4.06
4.05
4.04
3.79
3.52
3.48
3.07
3.03
2.74
2.71
2.30
2.29
2.27
2.26
2.25
2.24
2.23
CO2Me
4ae
CN
O
2.08
4.07
2.08
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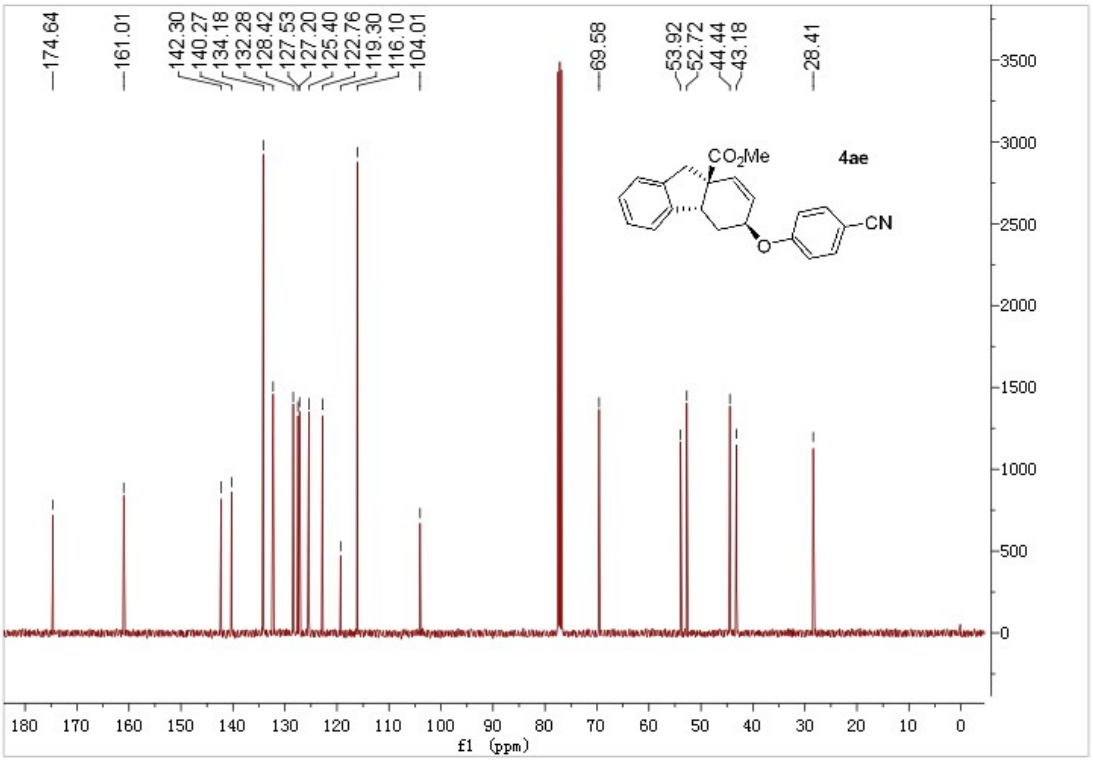
1.06
1.05
1.06
3.08
1.03
1.04
1.06
1.07
f1 (ppm)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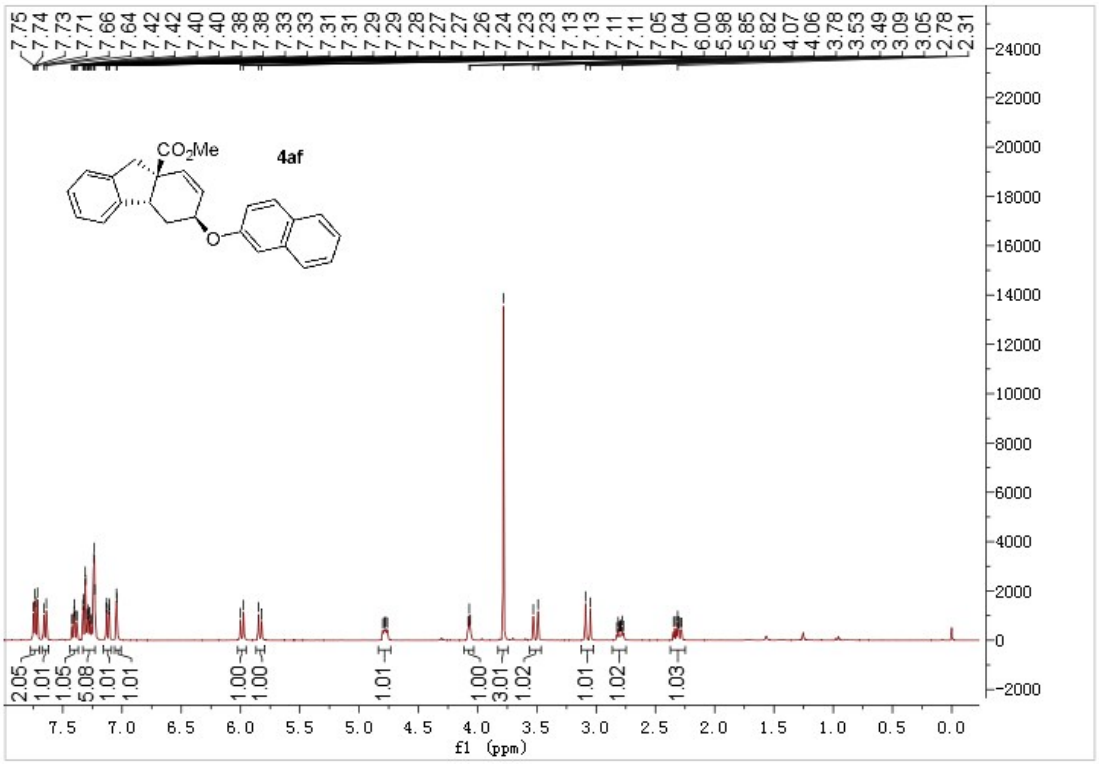
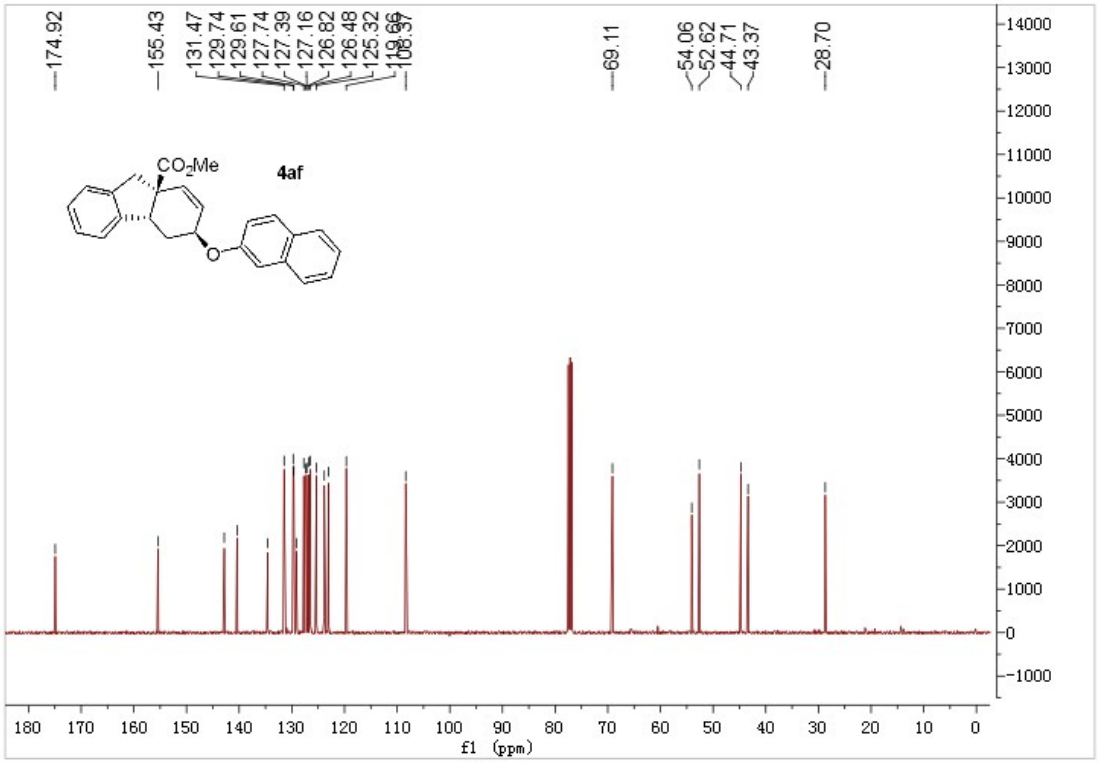
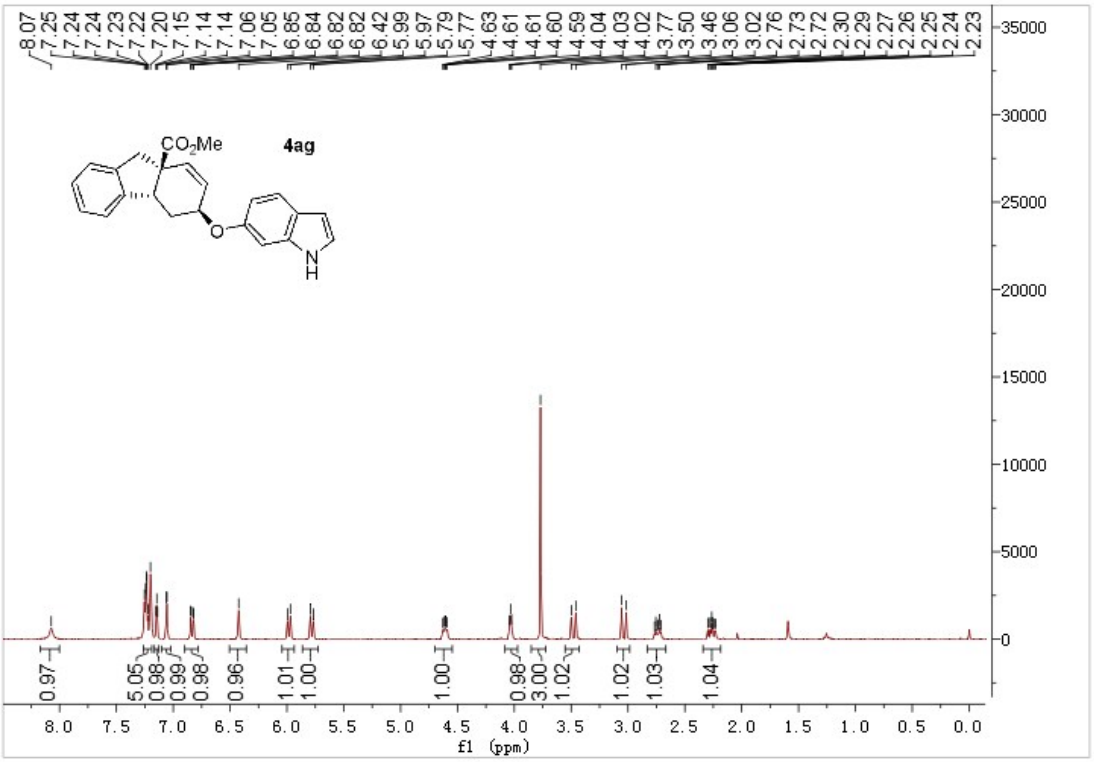
161.01
142.30
140.27
134.18
132.28
128.42
127.53
127.20
125.40
122.76
119.30
116.10
104.01
69.58
53.92
52.72
44.44
43.18
28.41
CO2Me
4ae
CN
O
f1 (ppm)


7.75 7.74 7.73 7.71 7.66 7.64 7.42 7.42 7.40 7.40 7.38 7.38 7.33 7.33 7.31 7.31 7.29 7.29 7.28 7.27 7.27 7.26 7.24 7.23 7.23 7.13 7.13 7.11 7.11 7.05 7.04 6.00 5.98 5.85 5.82 4.07 4.06 3.78 3.53 3.49 3.09 3.05 2.78 2.31
CO2Me
4af
O
2.05 1.01 1.05 5.08 1.01 1.01 1.00 1.00 1.01 1.00 3.01 1.02 1.01 1.02 1.03
f1 (ppm)


174.92 155.43 131.47 129.74 129.61 127.74 127.39 127.16 126.82 126.48 125.32 119.66 108.37 69.11 54.06 52.62 44.71 43.37 28.70
CO2Me
4af
O
f1 (ppm)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7.25
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7.24
7.23
7.22
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7.15
7.14
7.14
7.06
7.05
6.85
6.84
6.82
6.82
6.42
5.99
5.97
5.79
5.77
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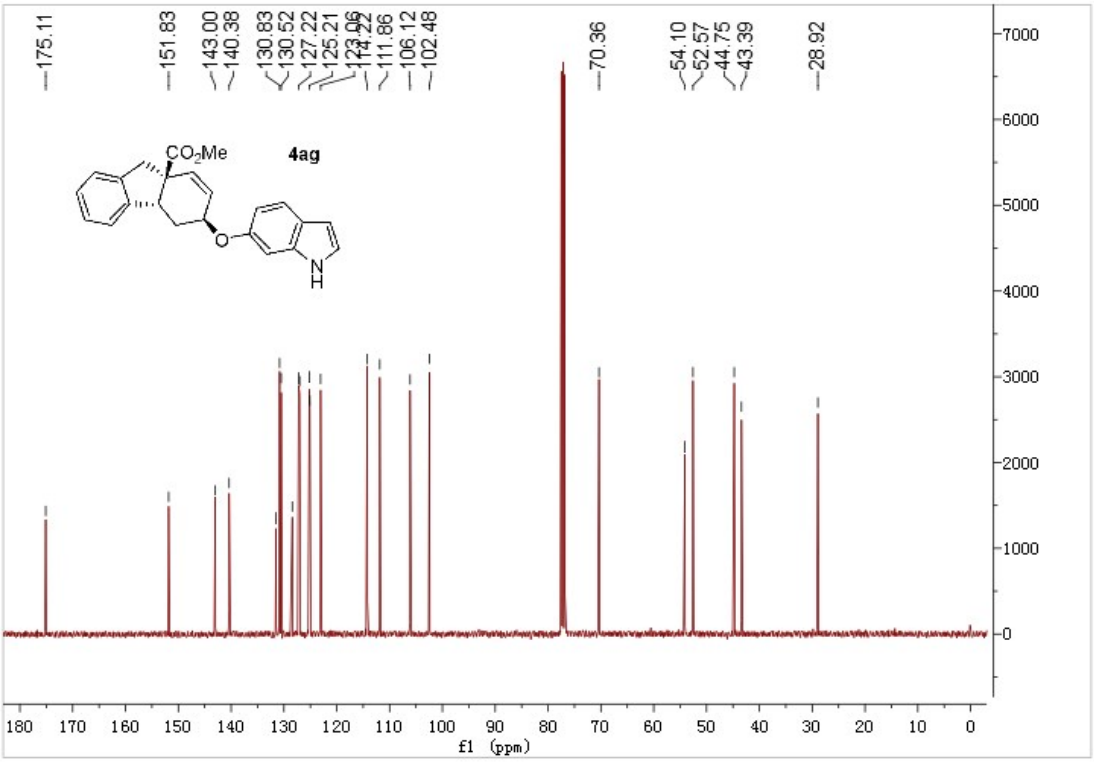
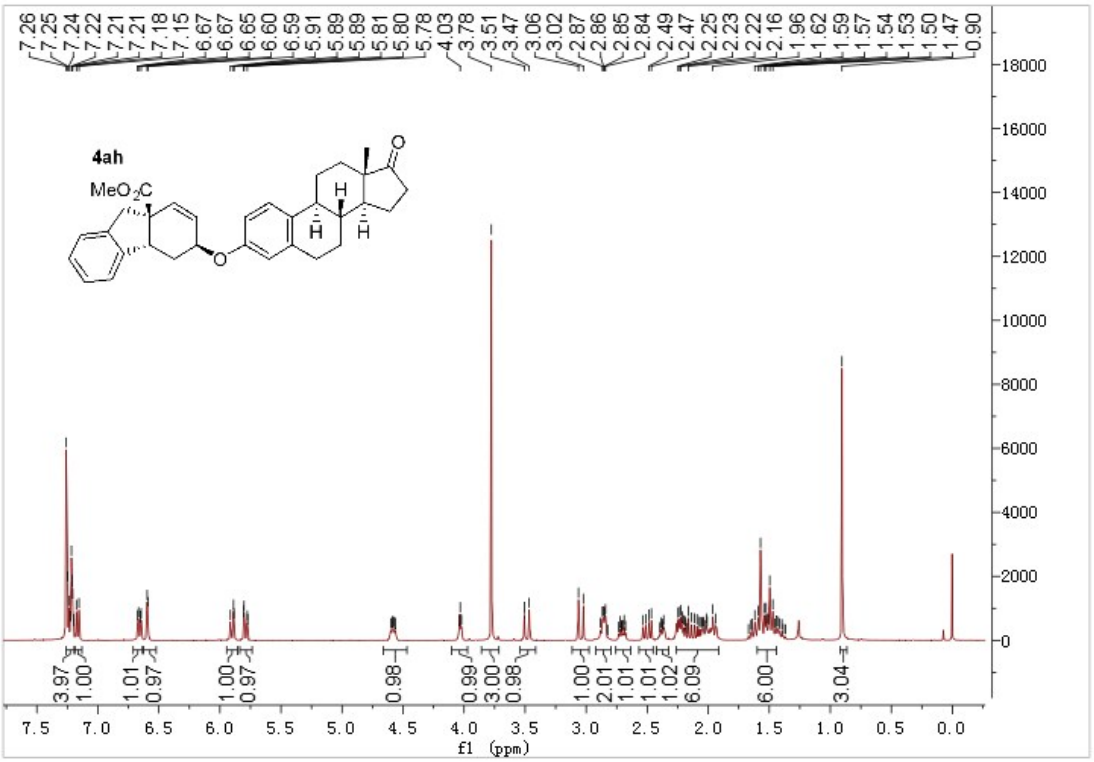
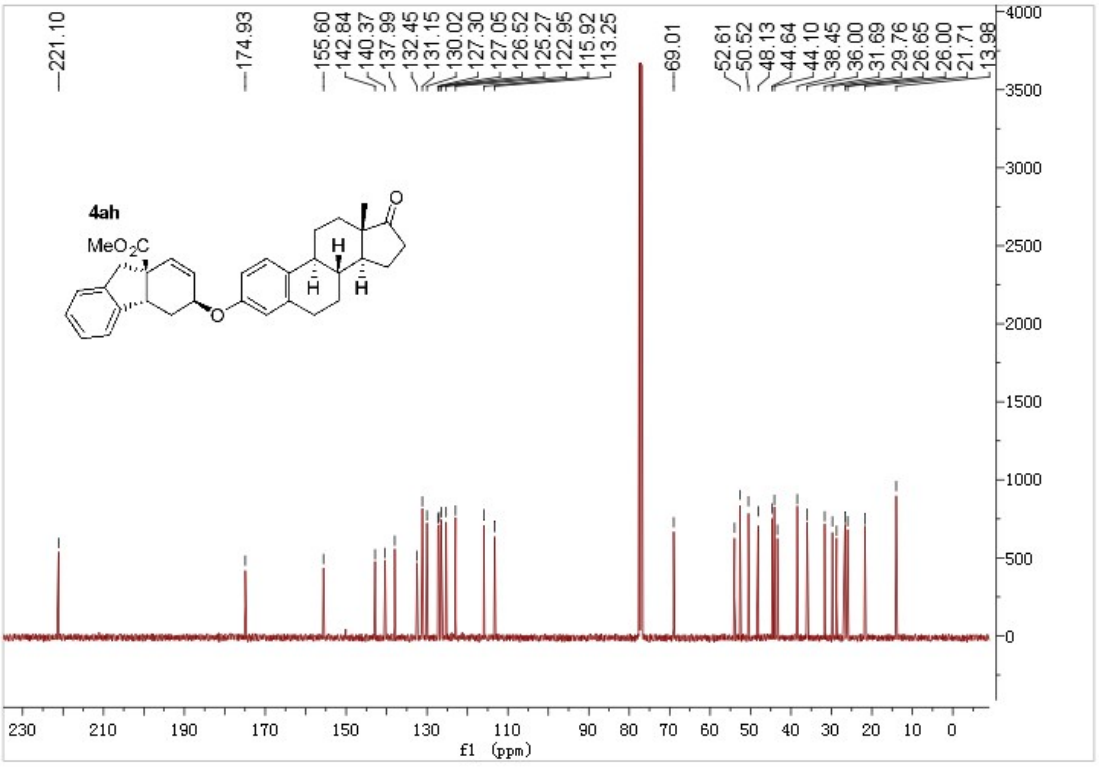
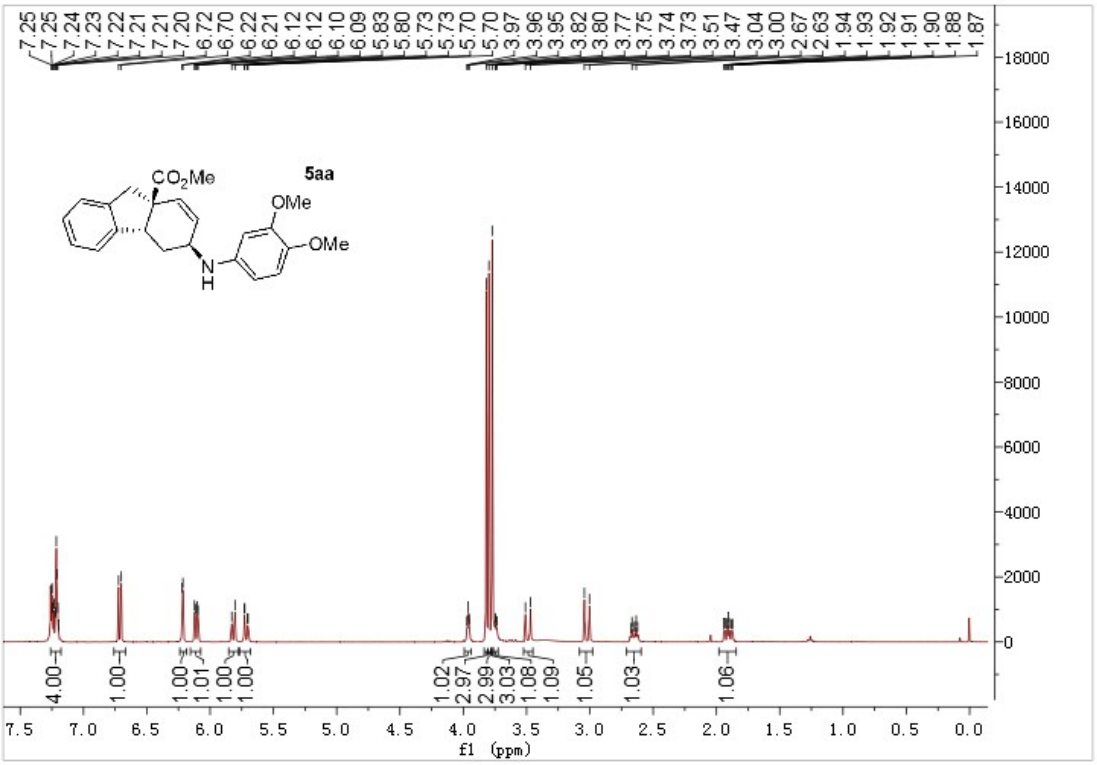
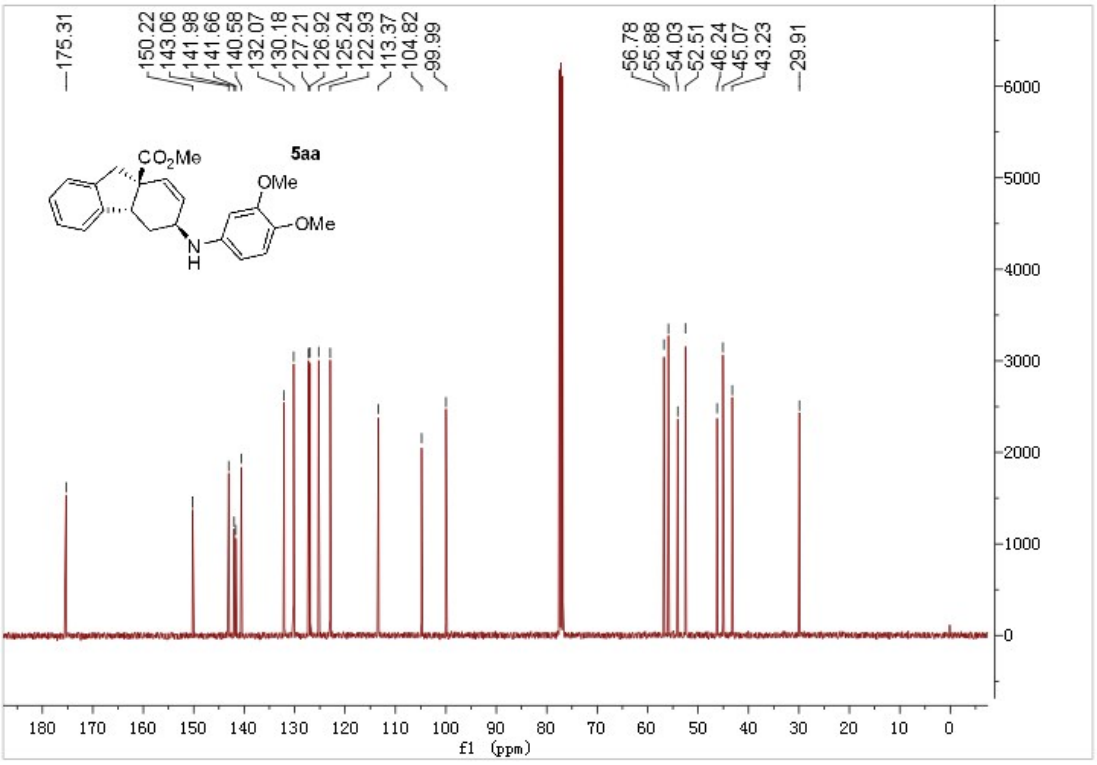
4.61
4.61
4.60
4.59
4.04
4.03
4.02
3.77
3.50
3.46
3.06
3.02
2.76
2.73
2.72
2.30
2.29
2.27
2.26
2.25
2.24
2.23
CO2Me
4ag
O
N
H
0.97
5.05
0.98
0.99
0.98
0.96
1.01
1.00
1.00
0.98
3.00
1.02
1.02
1.03
1.04
f1 (ppm)

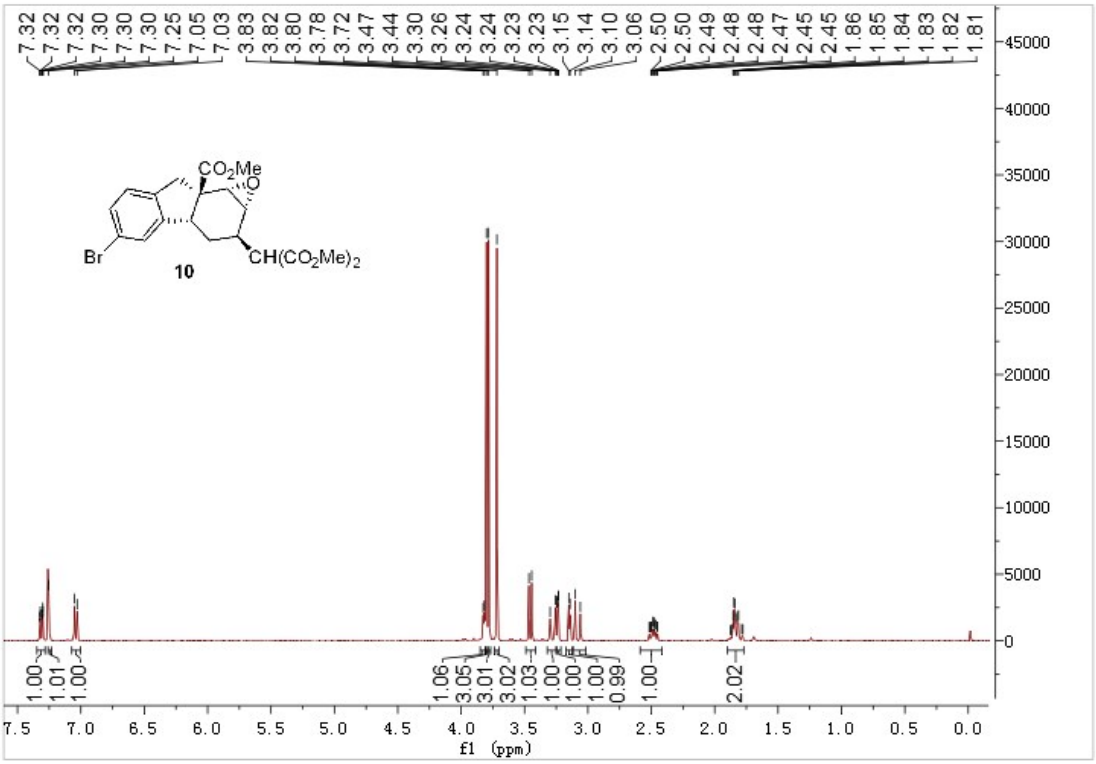

175.11
151.83
143.00
140.38
130.83
130.52
127.22
125.21
123.06
114.22
111.86
106.12
102.48
70.36
54.10
52.57
44.75
43.39
28.92
CO2Me
4ag
O
N
H
f1 (ppm)

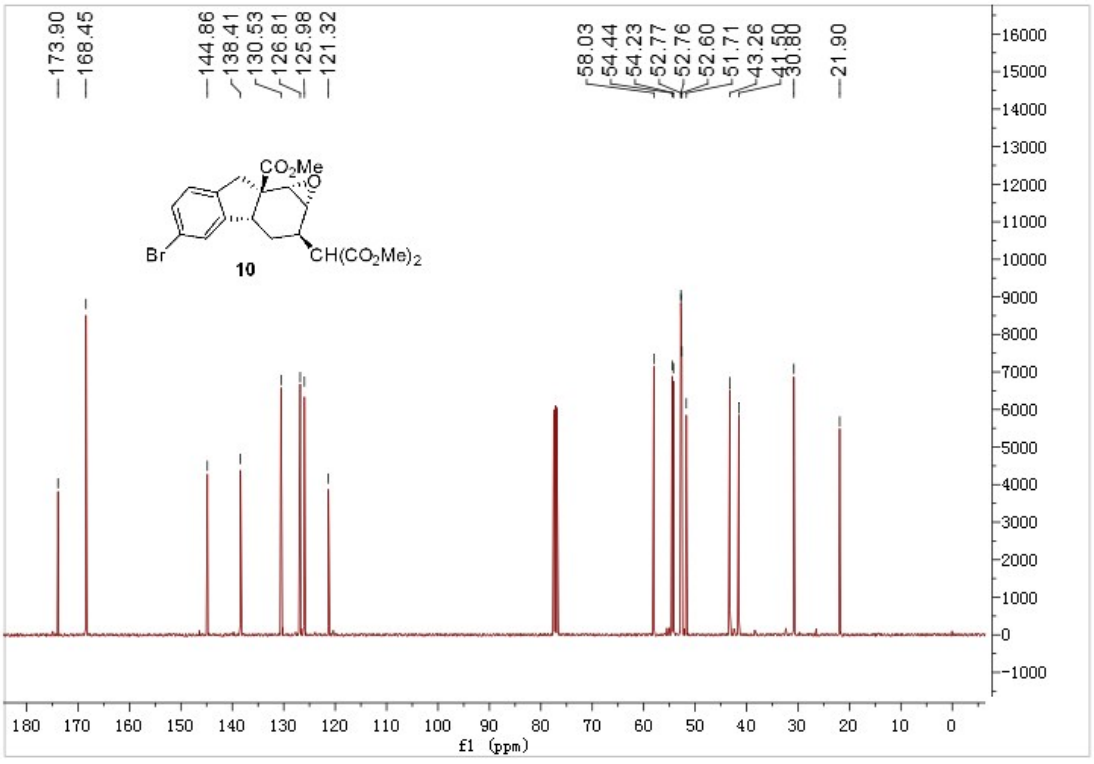

4ah
MeO2C
f1 (ppm)


4ah
MeO2C
f1 (ppm)

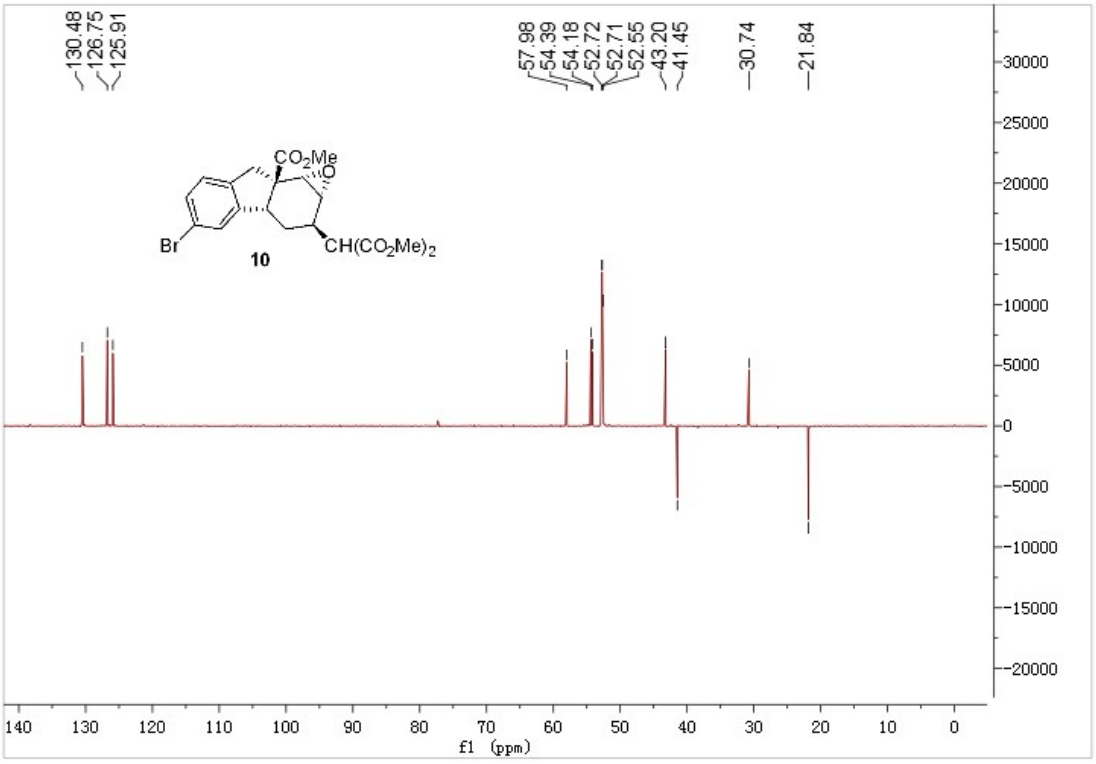

7.25 7.25 7.24 7.23 7.22 7.21 7.21 7.20 6.72 6.70 6.22 6.21 6.12 6.12 6.10 6.09 5.83 5.80 5.73 5.73 5.70 5.70 3.97 3.96 3.95 3.82 3.80 3.77 3.75 3.74 3.73 3.51 3.47 3.04 3.00 2.67 2.63 1.94 1.93 1.92 1.91 1.90 1.88 1.87
5aa
CO2Me
OMe
OMe
N
H
4.00 1.00 1.00 1.01 1.00 1.00 1.02 2.97 2.99 3.03 1.08 1.09 1.05 1.03 1.06
f1 (ppm)


175.31 150.22 143.06 141.98 141.66 140.58 132.07 130.18 127.21 126.92 125.24 122.93 113.37 104.82 99.99 56.78 55.88 54.03 52.51 46.24 45.07 43.23 29.91
5aa
CO2Me
OMe
OMe
N
H
f1 (ppm)

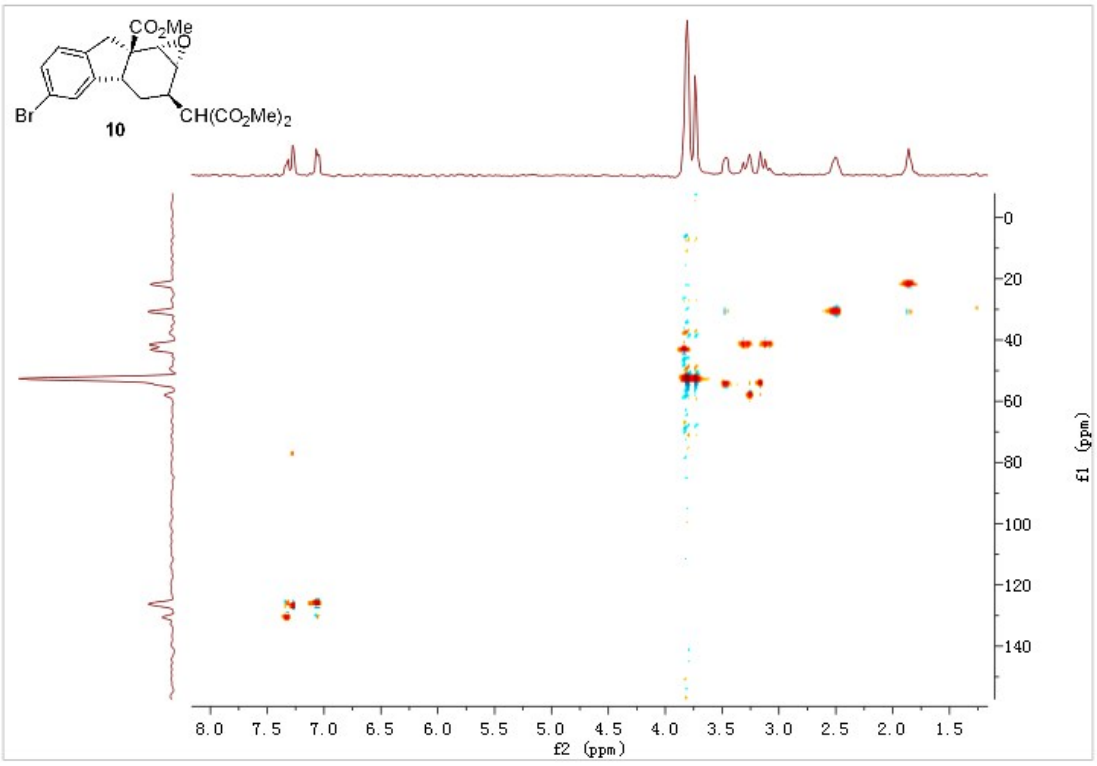

7.32 7.32 7.32 7.30 7.30 7.30 7.25 7.05 7.03 3.83 3.82 3.80 3.78 3.72 3.47 3.44 3.30 3.26 3.24 3.24 3.23 3.23 3.15 3.14 3.10 3.06 2.50 2.50 2.49 2.48 2.48 2.47 2.45 2.45 1.86 1.85 1.84 1.83 1.82 1.81
CO2Me
O
Br
CH(CO2Me)2
10
1.00 1.01 1.00 1.06 3.05 3.01 3.02 1.03 1.00 1.00 1.00 0.99 1.00 2.02
f1 (ppm)


173.90 168.45 144.86 138.41 130.53 126.81 125.98 121.32 58.03 54.44 54.23 52.77 52.76 52.60 51.71 43.26 41.50 30.80 21.90
CO2Me
O
Br
CH(CO2Me)2
10
f1 (ppm)

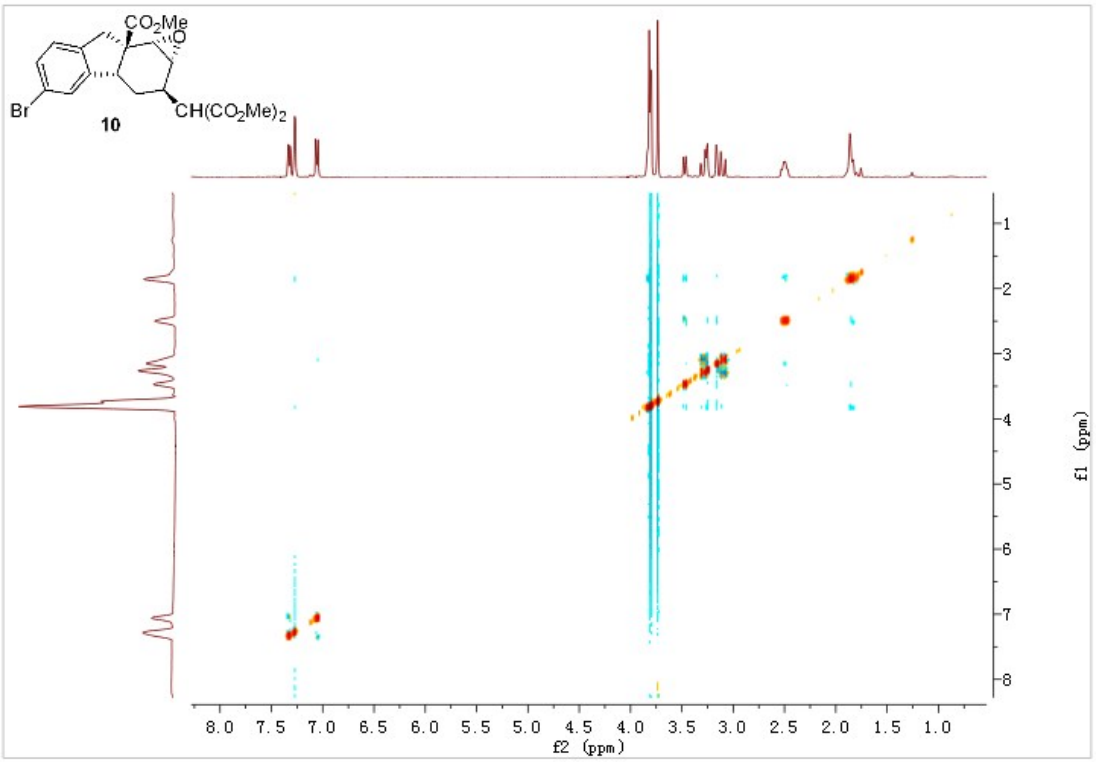
^{13}C DEPT135 NMR spectrum of compound **10**

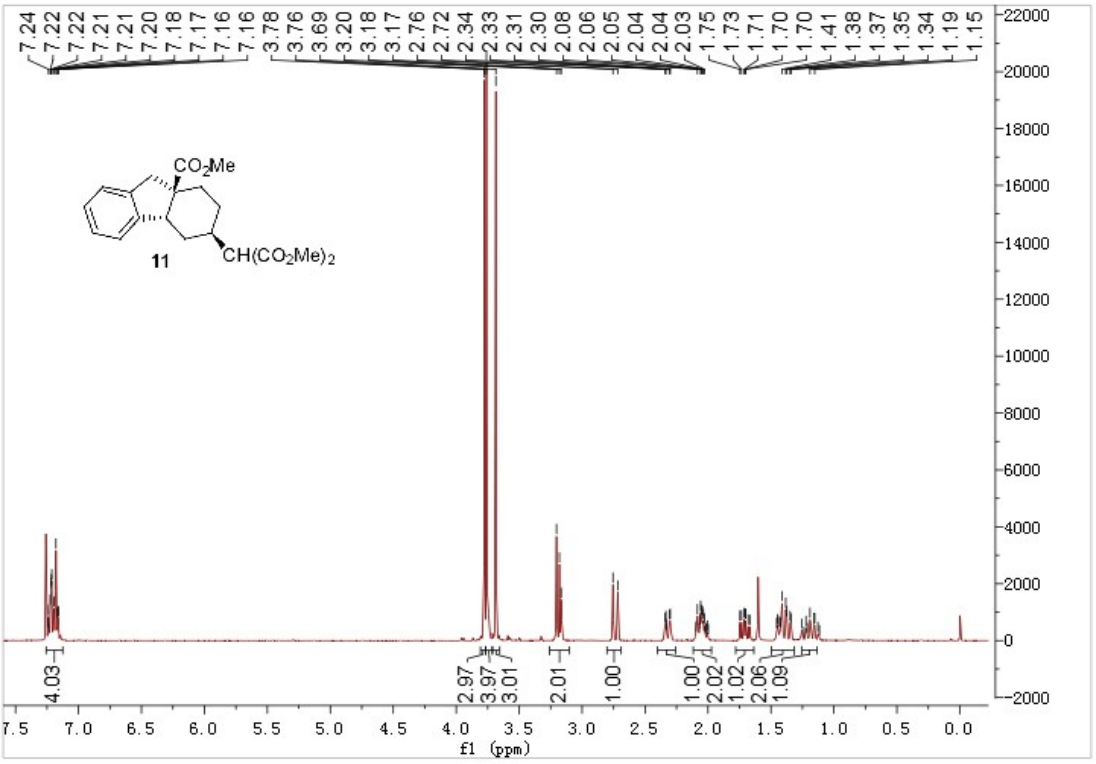


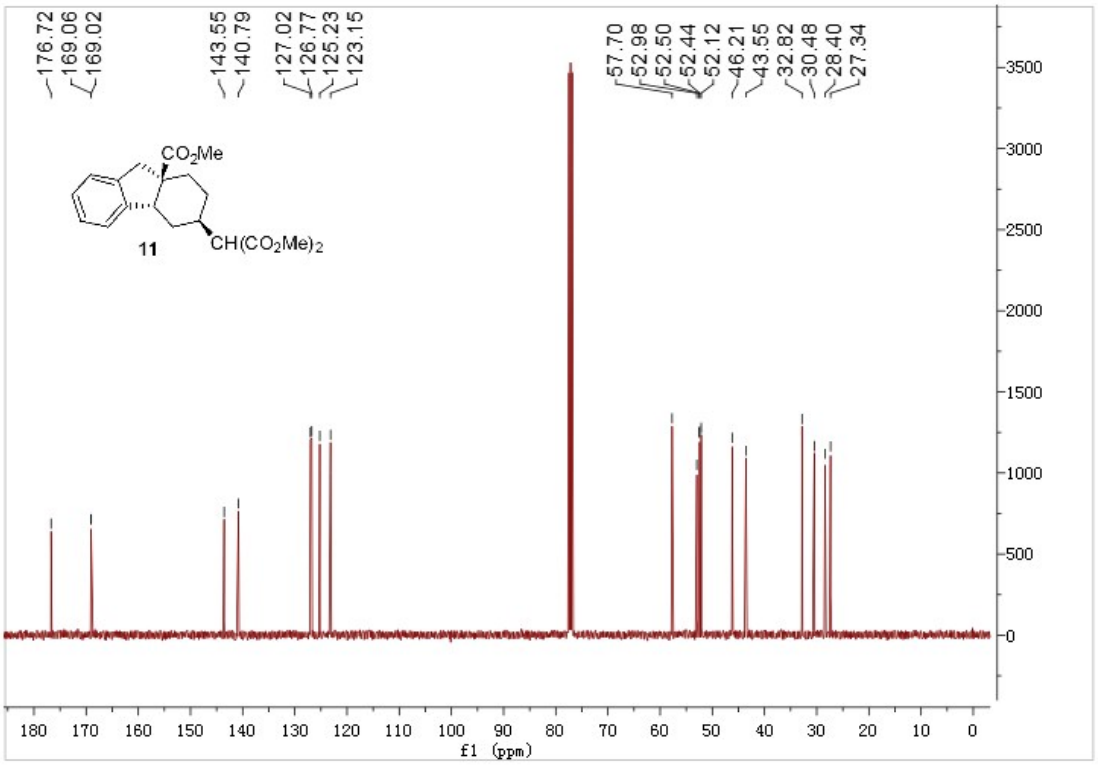
SHQC NMR spectrum of compound **10**

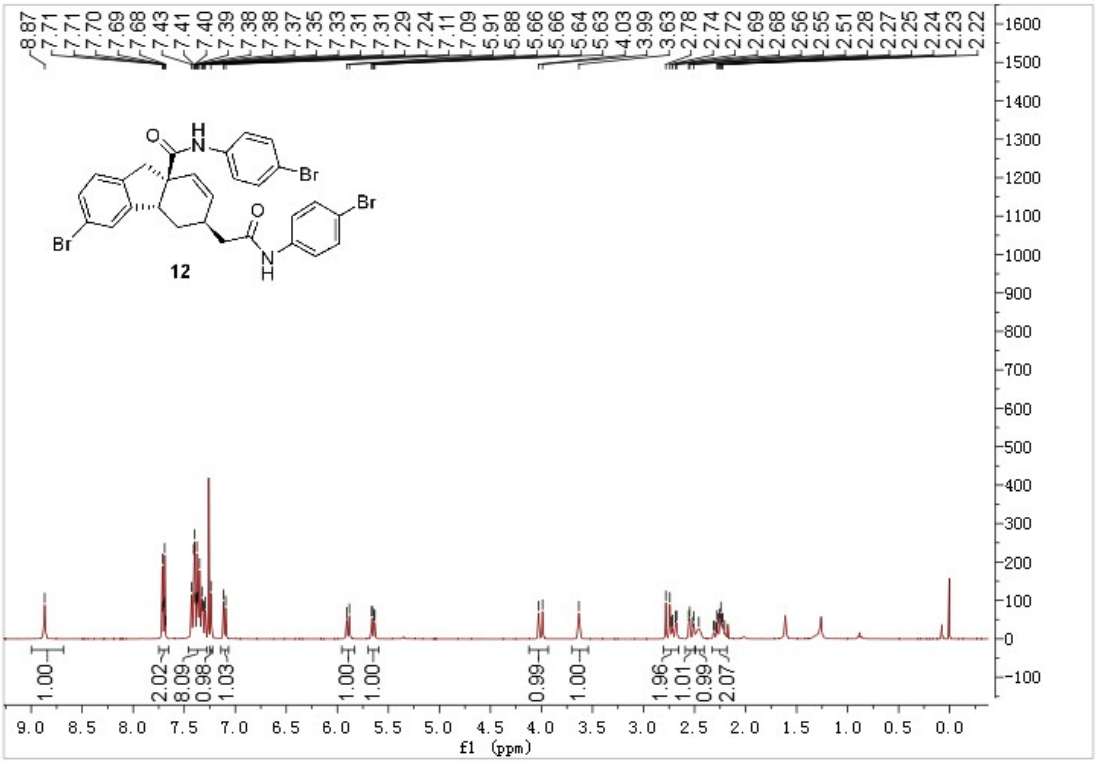


COSY NMR spectrum of compound **10**


CO2Me
O
Br
CH(CO2Me)2
10
f2 (ppm)
f1 (ppm)


7.24 7.22 7.22 7.21 7.21 7.20 7.18 7.17 7.16 7.16 3.78 3.76 3.69 3.20 3.18 3.17 2.76 2.72 2.34 2.33 2.31 2.30 2.08 2.06 2.05 2.04 2.04 2.03 1.75 1.73 1.71 1.70 1.70 1.41 1.38 1.37 1.35 1.34 1.19 1.15
CO2Me
CH(CO2Me)2
11
4.03 2.97 3.97 3.01 2.01 1.00 1.00 2.02 1.02 2.06 1.09
f1 (ppm)


176.72 169.06 169.02 143.55 140.79 127.02 126.77 125.23 123.15 57.70 52.98 52.50 52.44 52.12 46.21 43.55 32.82 30.48 28.40 27.34
CO2Me
CH(CO2Me)2
11
f1 (ppm)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7.38
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7.37
7.35
7.33
7.31
7.31
7.29
7.24
7.11
7.09
5.91
5.88
5.66
5.66
5.64
5.63
4.03
3.99
3.63
2.78
2.74
2.72
2.69
2.68
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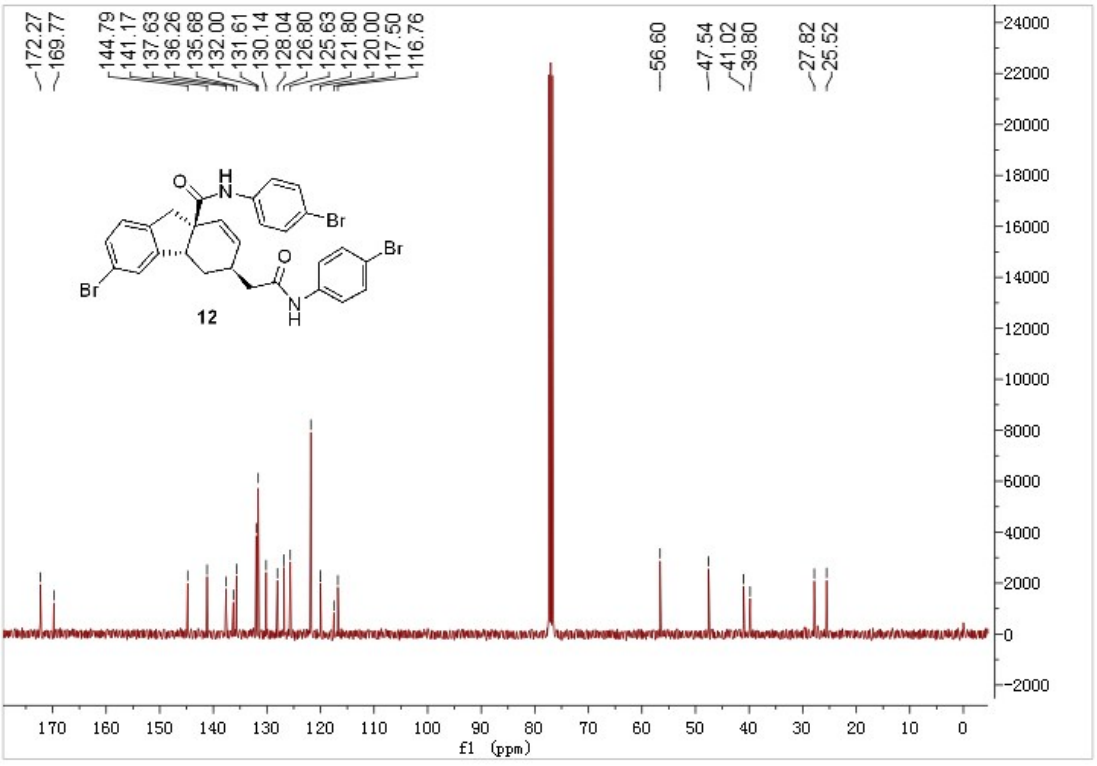
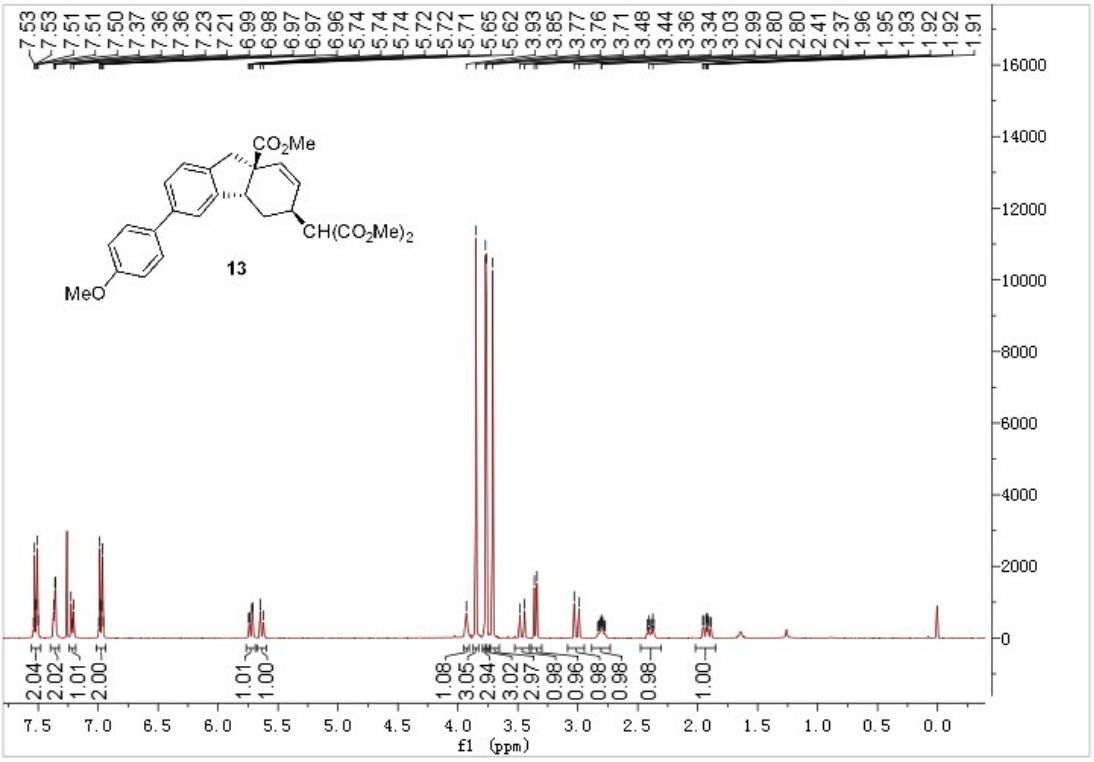
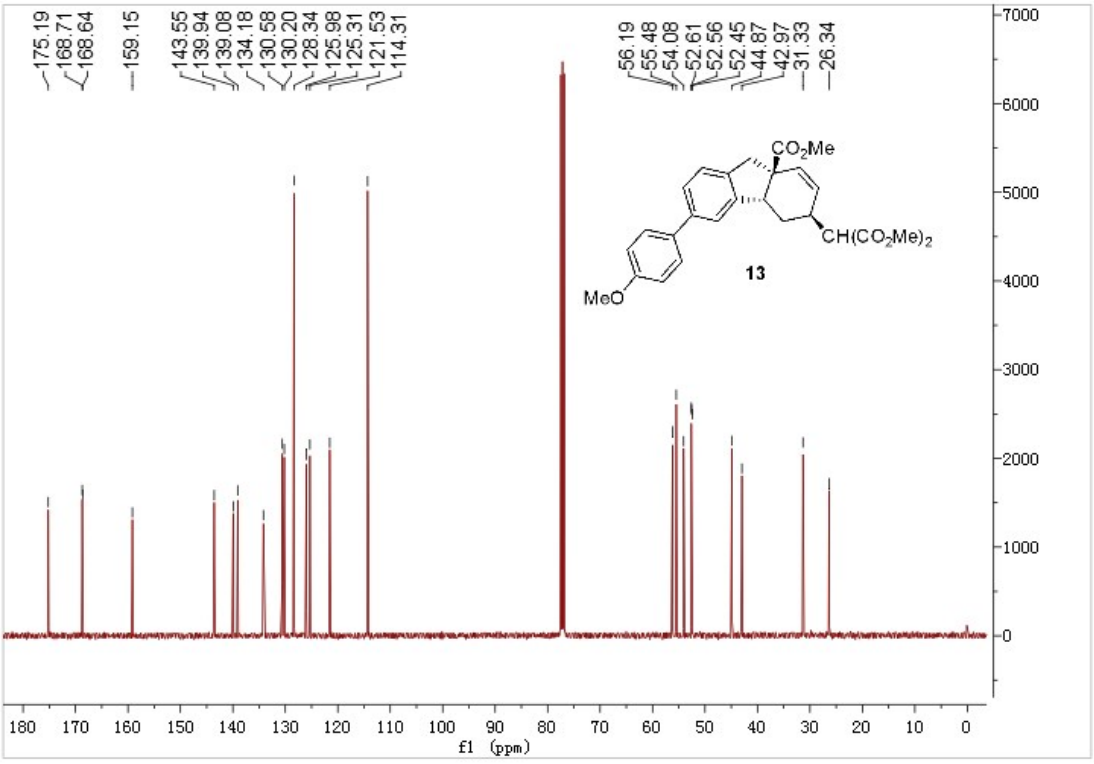
2.23
2.22
O
H
N
Br
Br
O
Br
N
H
12
1.00
2.02
8.09
0.98
1.03
1.00
1.00
0.99
1.00
1.96
1.01
0.99
2.07
f1 (ppm)

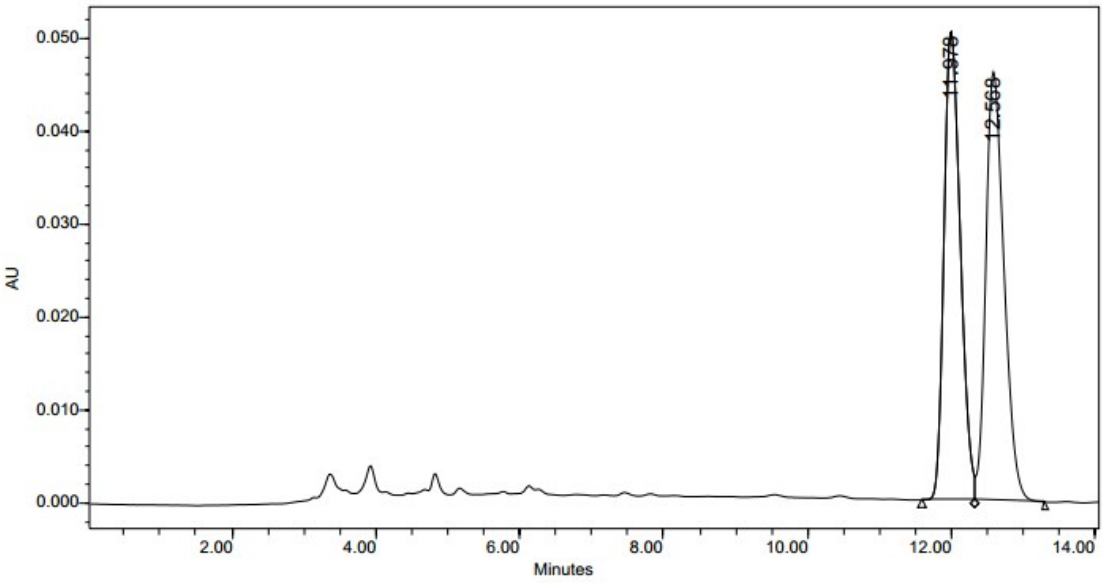

172.27
169.77
144.79
141.17
137.63
136.26
135.68
132.00
131.61
130.14
128.04
126.80
125.63
121.80
120.00
117.50
116.76
56.60
47.54
41.02
39.80
27.82
25.52
O
H
N
Br
Br
O
Br
N
H
12
f1 (ppm)


7.53 7.53 7.51 7.51 7.50 7.37 7.36 7.36 7.23 7.21 6.99 6.98 6.97 6.97 6.96 5.74 5.74 5.72 5.72 5.71 5.65 5.62 3.93 3.85 3.77 3.76 3.71 3.48 3.44 3.36 3.34 3.03 2.99 2.80 2.41 2.37 1.96 1.95 1.93 1.92 1.92 1.91
CO2Me
CH(CO2Me)2
MeO
13
2.04 2.02 1.01 2.00 1.01 1.00 1.08 3.05 2.94 3.02 2.97 0.98 0.96 0.98 0.98 0.98 1.00
f1 (ppm)

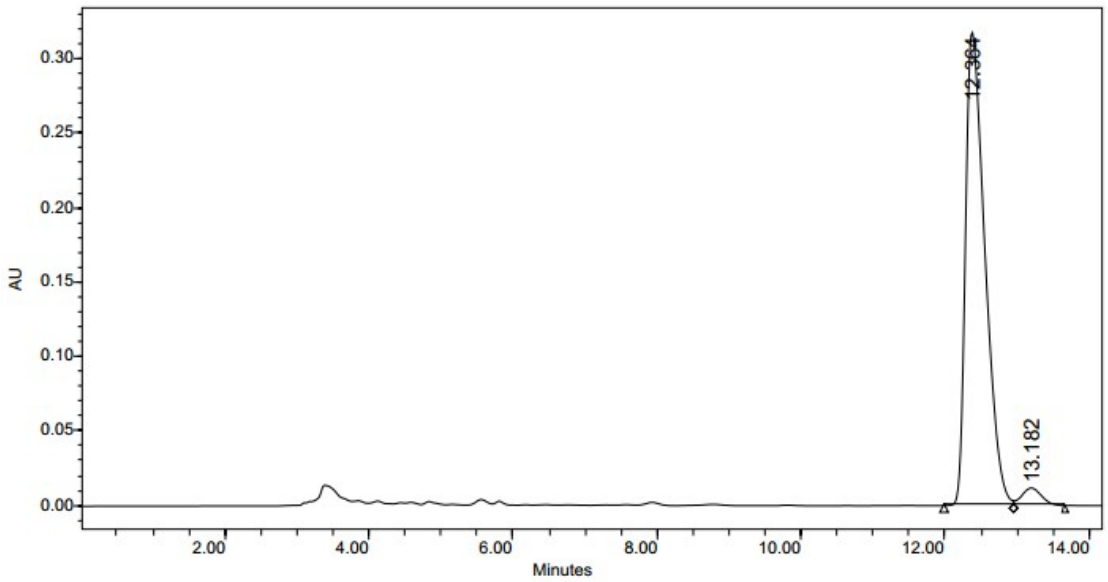

175.19 168.71 168.64 159.15 143.55 139.94 139.08 134.18 130.58 130.20 128.34 125.98 125.31 121.53 114.31
56.19 55.48 54.08 52.61 52.56 52.45 44.87 42.97 31.33 26.34
CO2Me
CH(CO2Me)2
MeO
13
f1 (ppm)

12. HPLC Spectra for Products

3aa

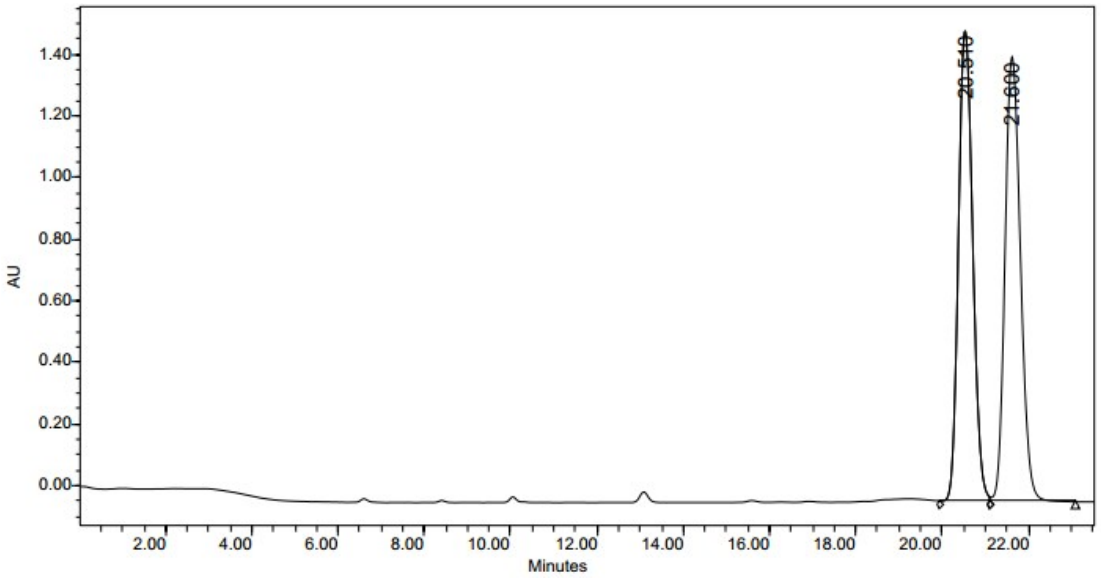


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	11.978	799492	49.57	50485	52.25
2	12.568	813337	50.43	46139	47.75

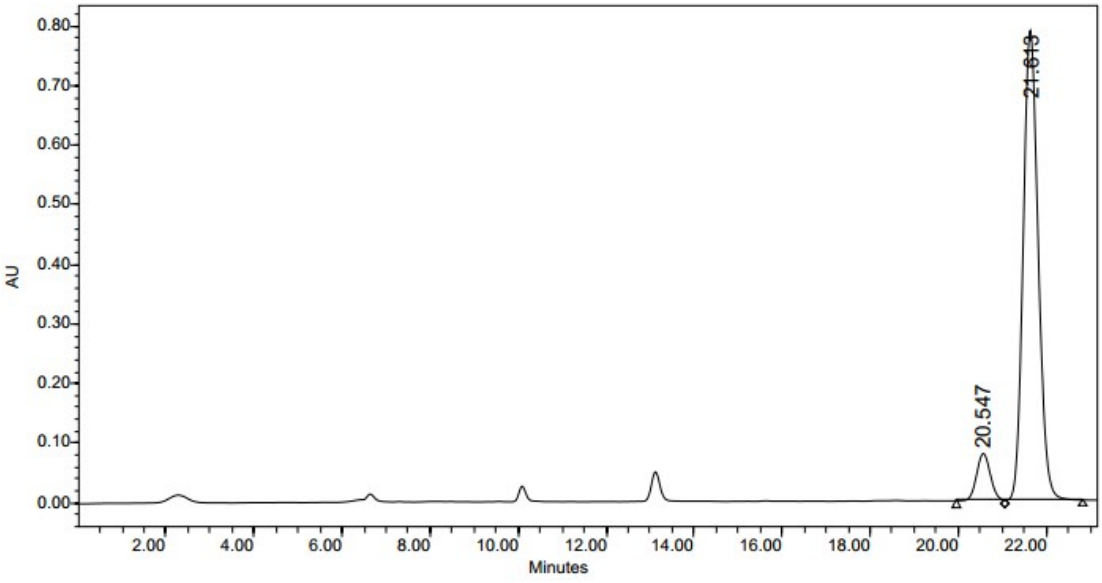


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	12.364	5953961	96.38	317784	96.43
2	13.182	223495	3.62	11771	3.57

3ba

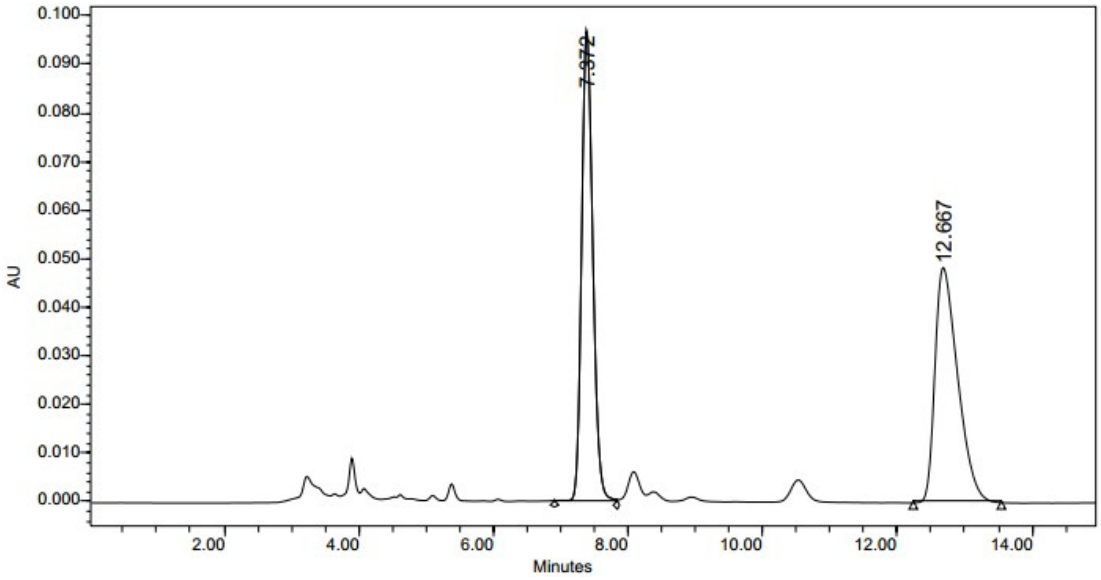


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	20.510	35319152	49.45	1528070	51.43
2	21.600	36099617	50.55	1443112	48.57

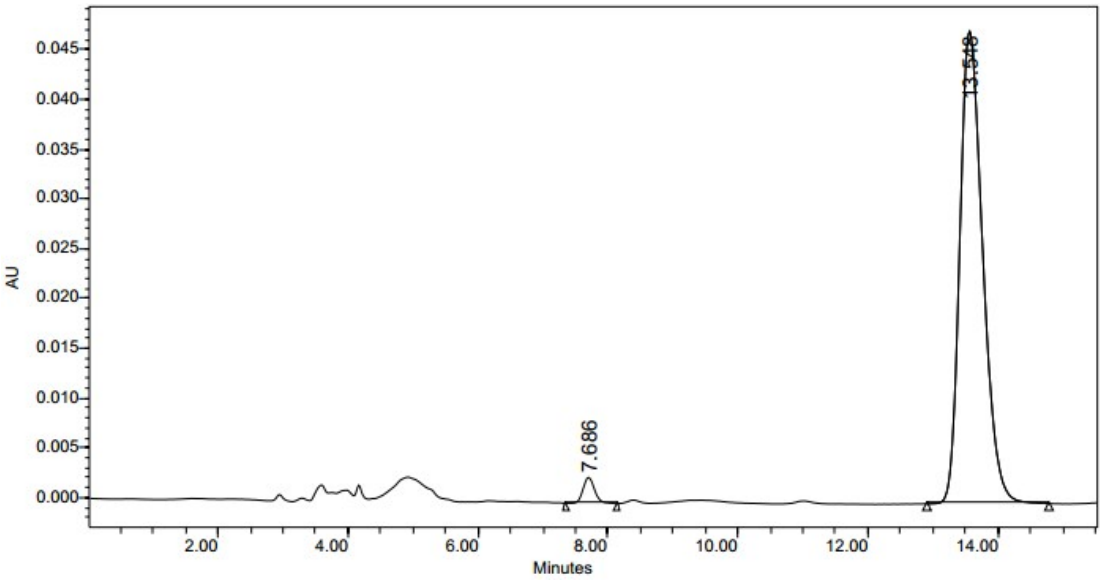


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	20.547	1713035	8.41	78940	9.10
2	21.613	18664365	91.59	788915	90.90

3ca

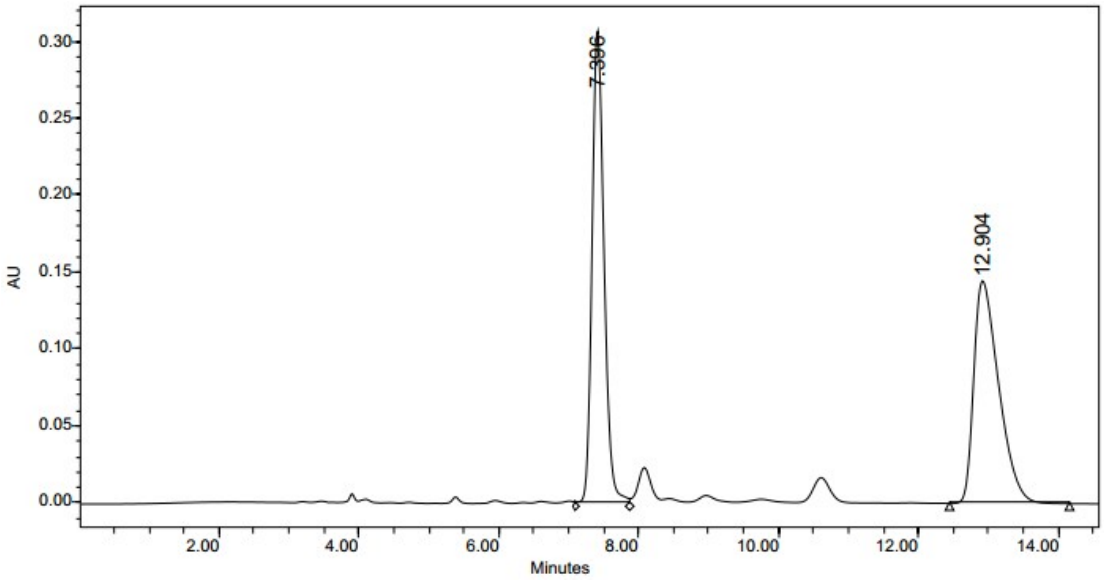


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	7.372	1118821	49.51	96881	66.69
2	12.667	1140788	50.49	48382	33.31

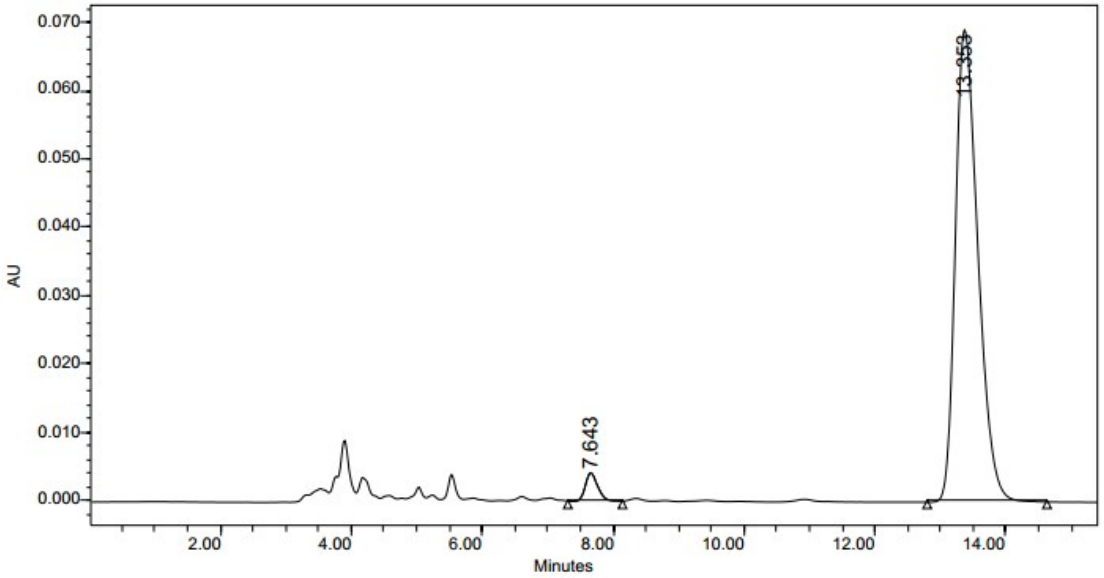


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	7.686	31858	2.67	2600	5.20
2	13.548	1162244	97.33	47442	94.80

3da

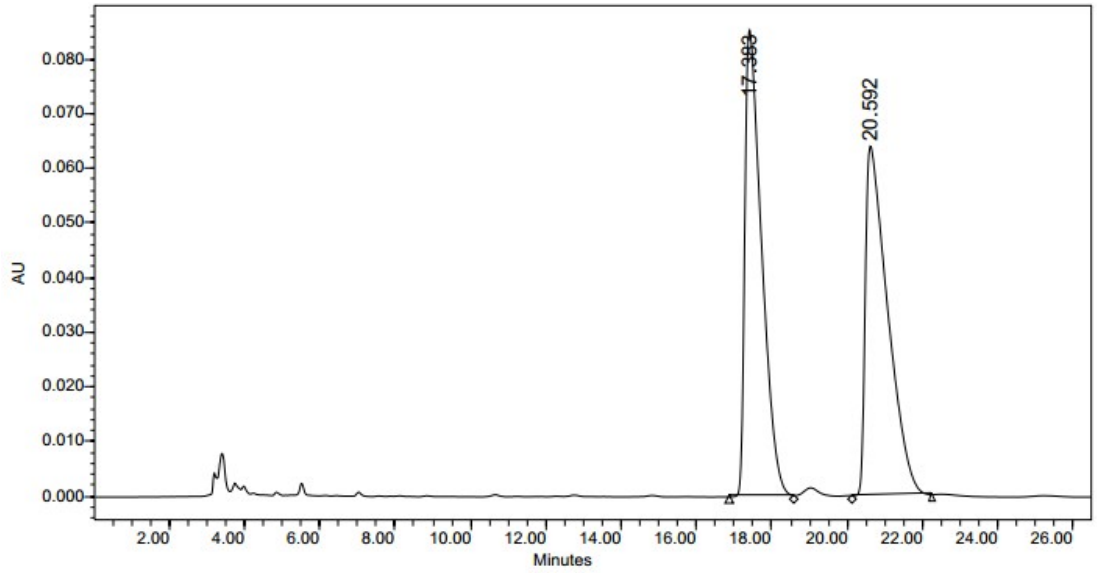


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	7.396	3661774	50.51	306856	67.98
2	12.904	3588454	49.49	144521	32.02

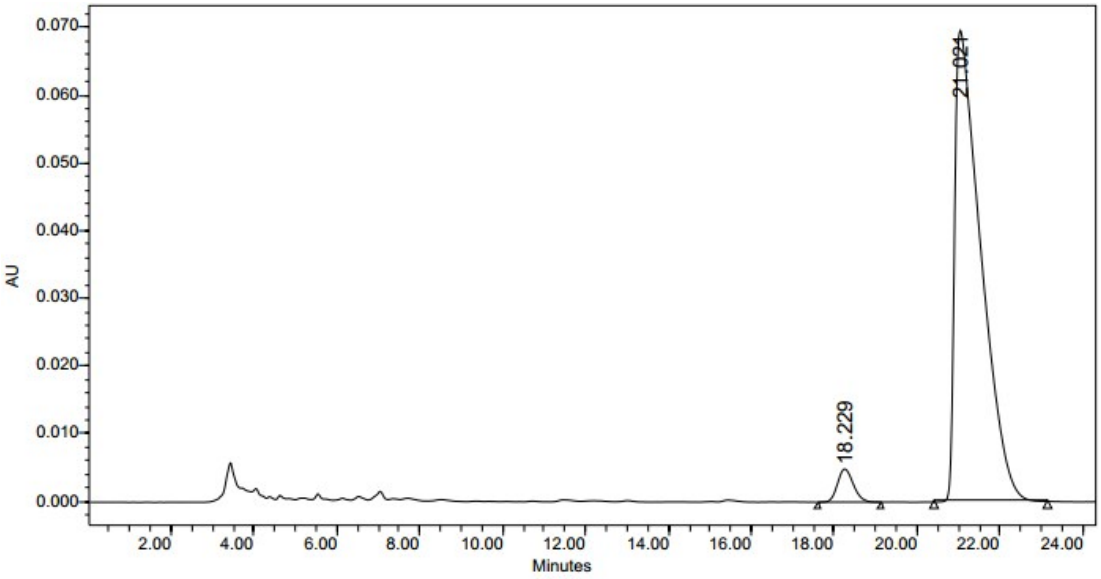


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	7.643	53134	3.11	4118	5.63
2	13.353	1656274	96.89	69035	94.37

3ea

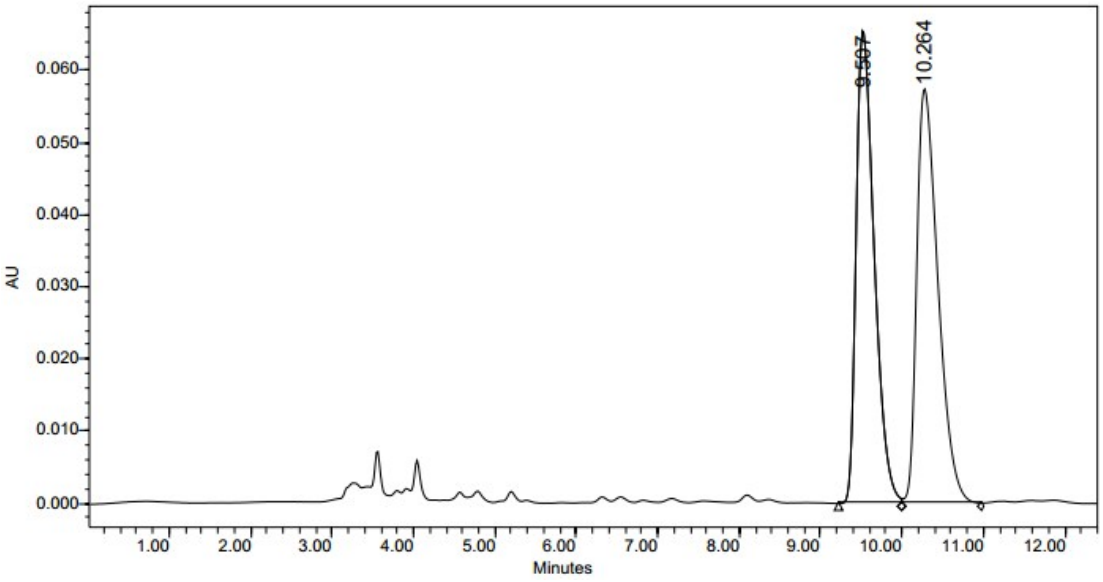


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	17.383	2650394	50.21	85434	57.16
2	20.592	2628347	49.79	64033	42.84

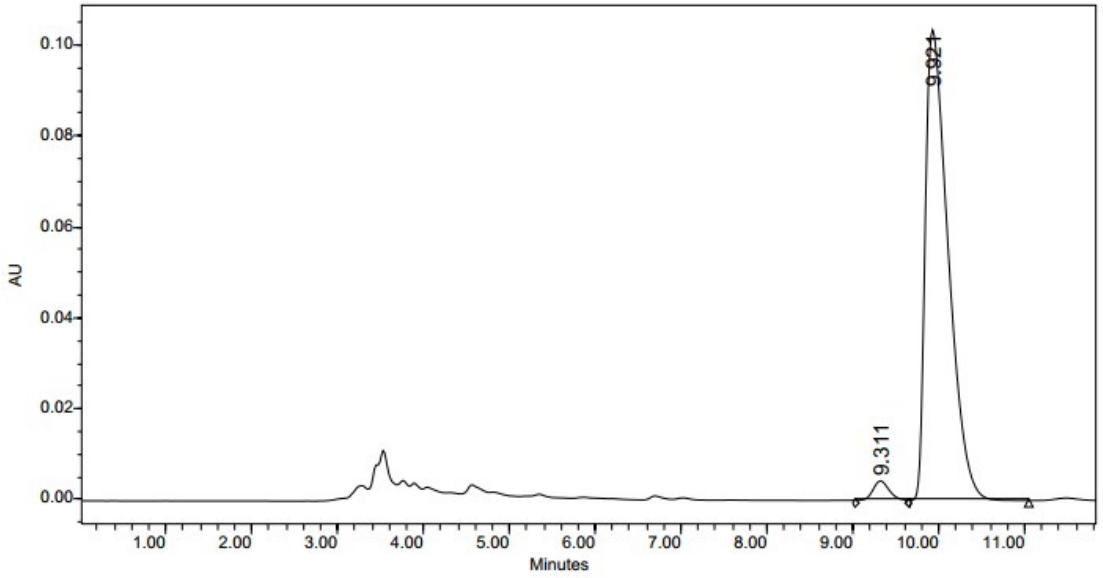


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	18.229	130228	4.08	4896	6.56
2	21.021	3059523	95.92	69715	93.44

3fa

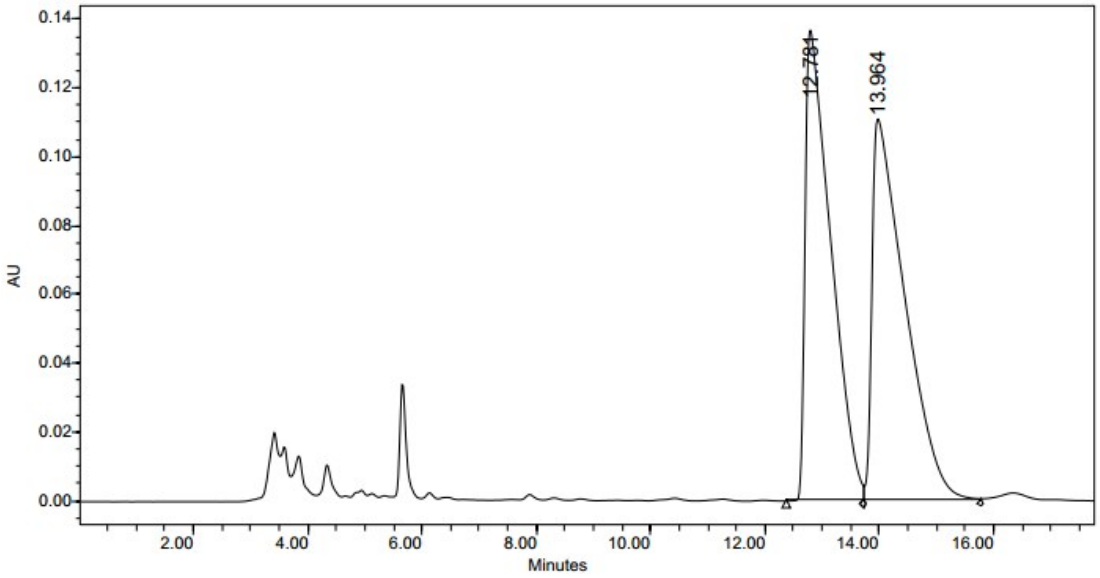


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	9.507	1012653	49.28	65648	53.32
2	10.264	1042098	50.72	57468	46.68

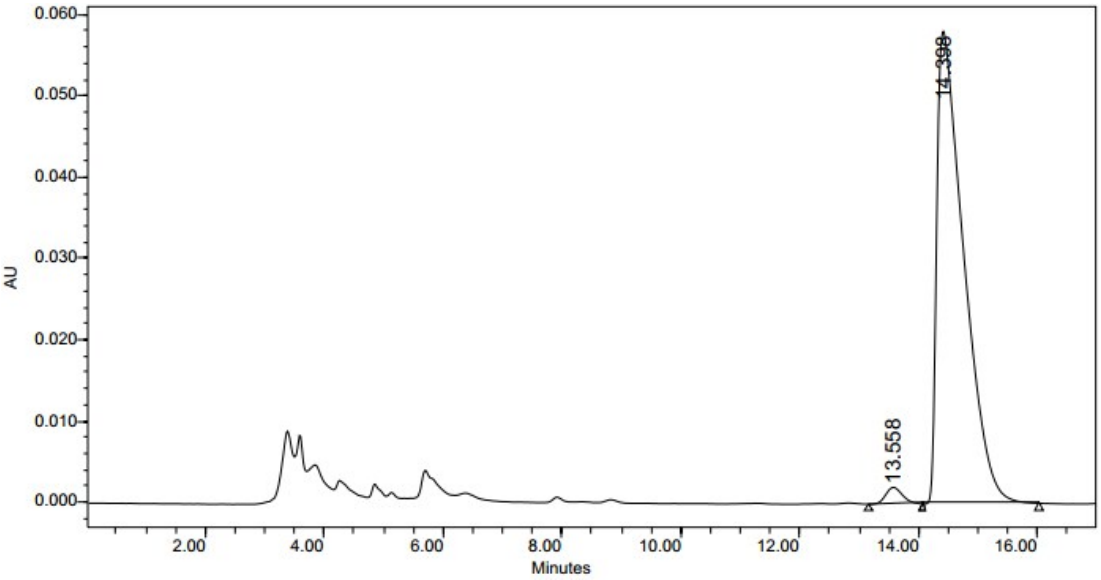


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	9.311	57820	2.93	4319	4.00
2	9.921	1916904	97.07	103547	96.00

3ga

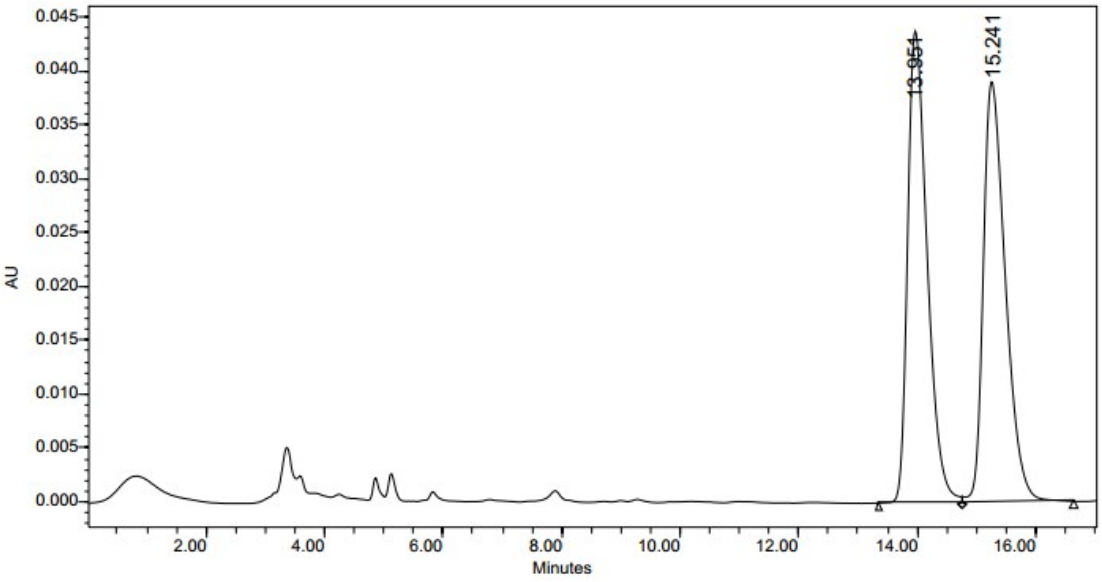


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	12.781	4271863	49.07	136821	55.23
2	13.964	4434672	50.93	110919	44.77

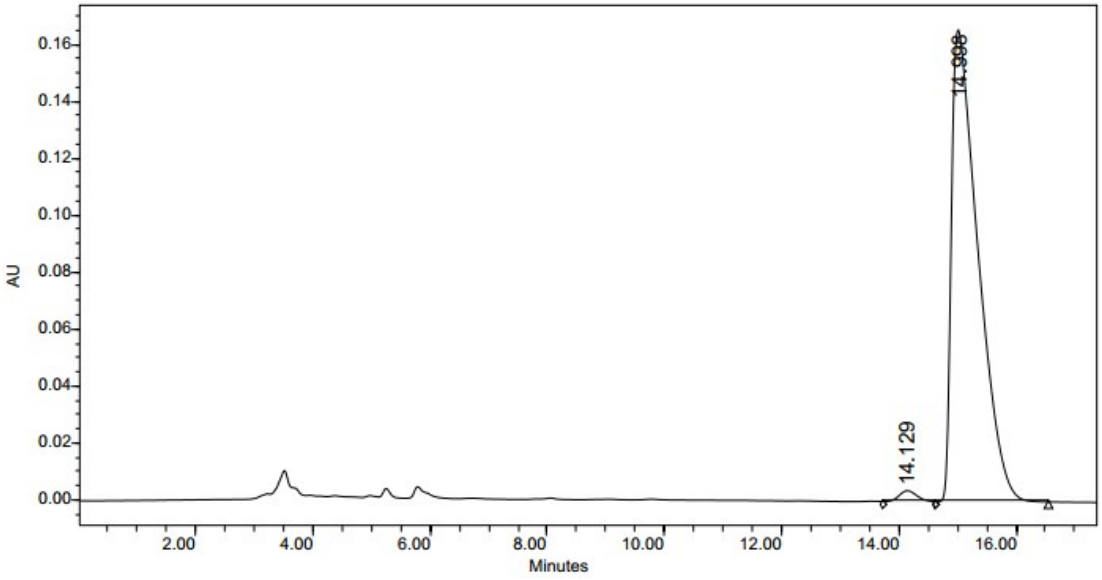


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	13.558	40382	2.16	2049	3.41
2	14.398	1827984	97.84	58127	96.59

3ha

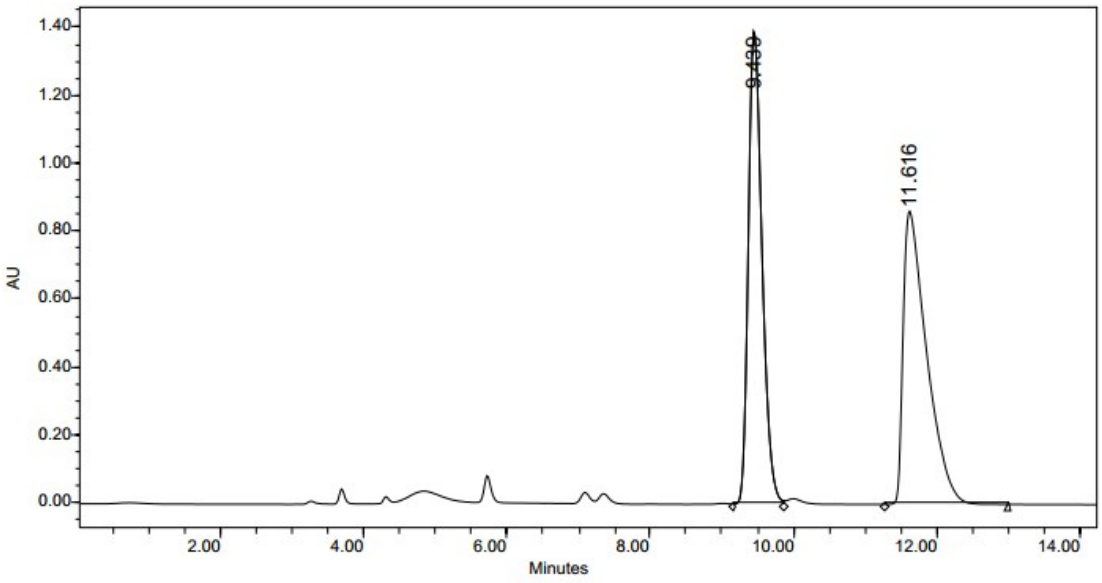


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	13.951	999198	49.77	43733	52.86
2	15.241	1008503	50.23	39006	47.14

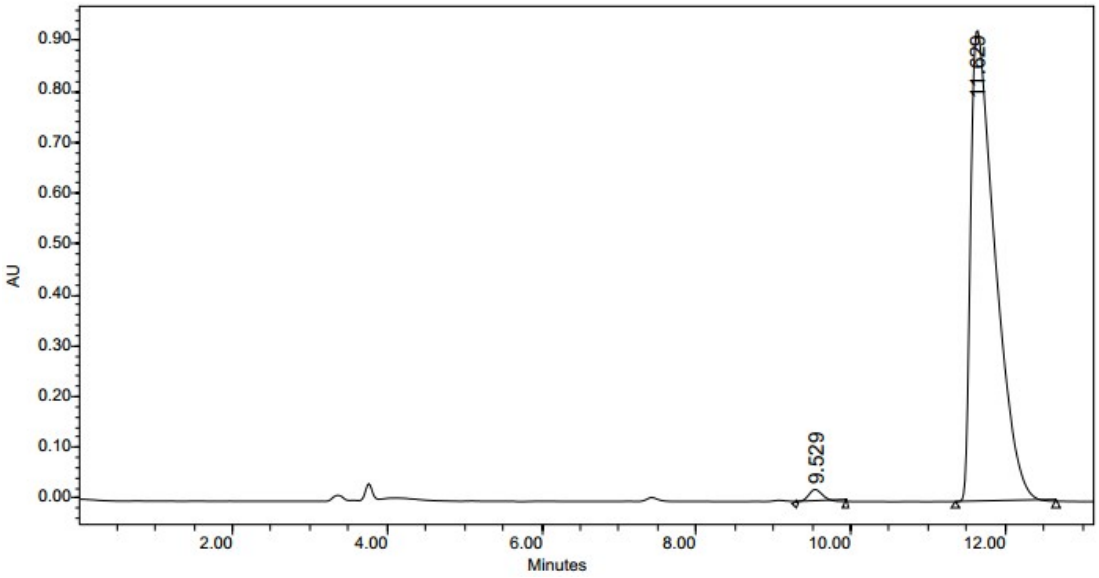


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	14.129	81905	1.54	3841	2.26
2	14.998	5224572	98.46	165790	97.74

3hb

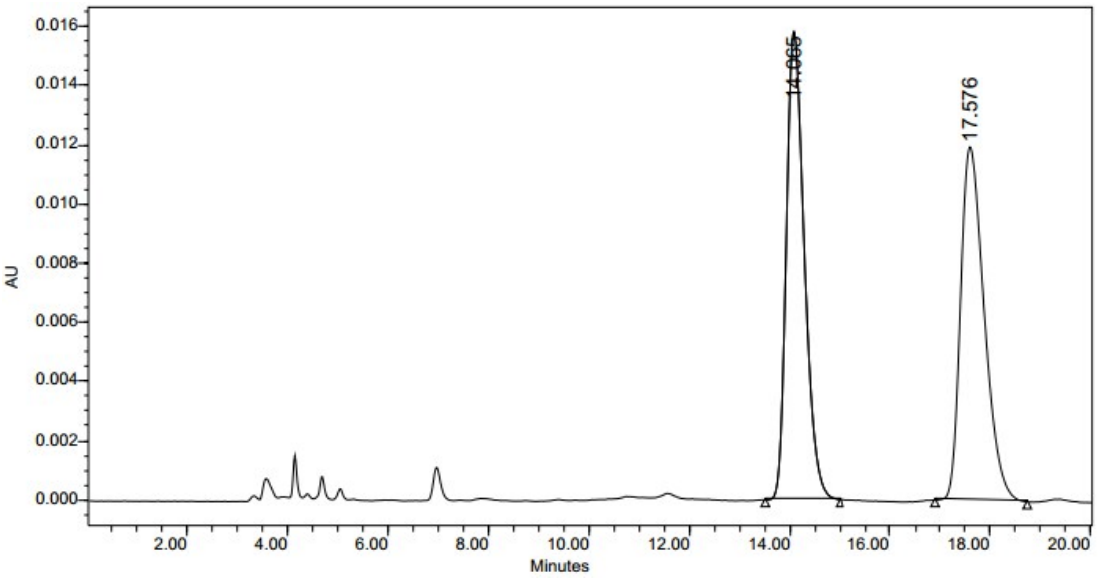


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	9.439	18636297	48.62	1393520	61.76
2	11.616	19691763	51.38	862946	38.24

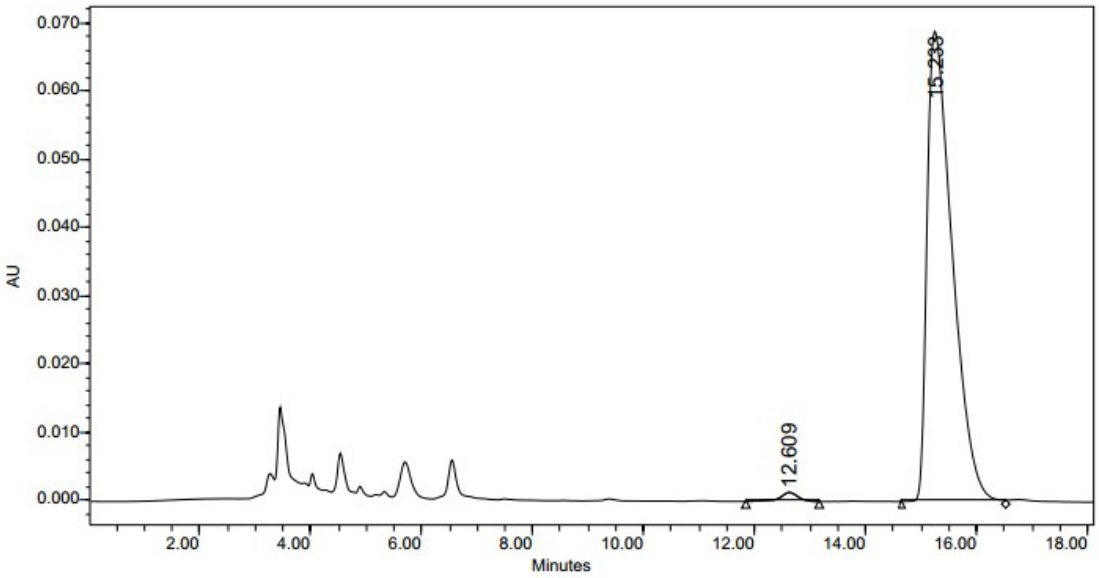


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	9.529	297767	1.44	23445	2.47
2	11.629	20405557	98.56	925493	97.53

3ia

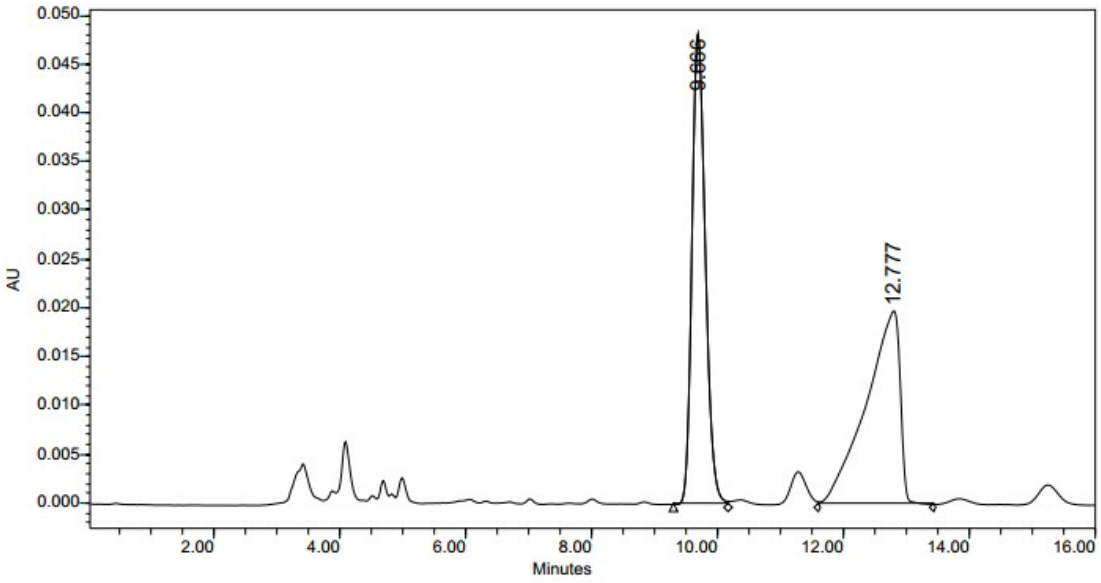


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	14.065	393572	50.12	15806	56.94
2	17.576	391620	49.88	11953	43.06

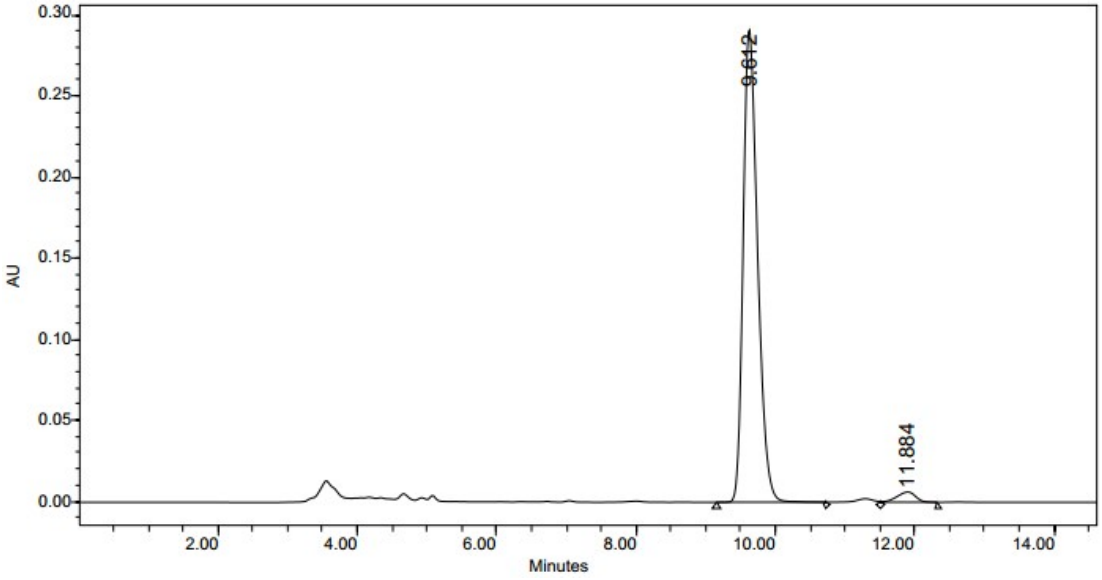


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	12.609	29472	1.34	1314	1.87
2	15.233	2170712	98.66	68871	98.13

3ja

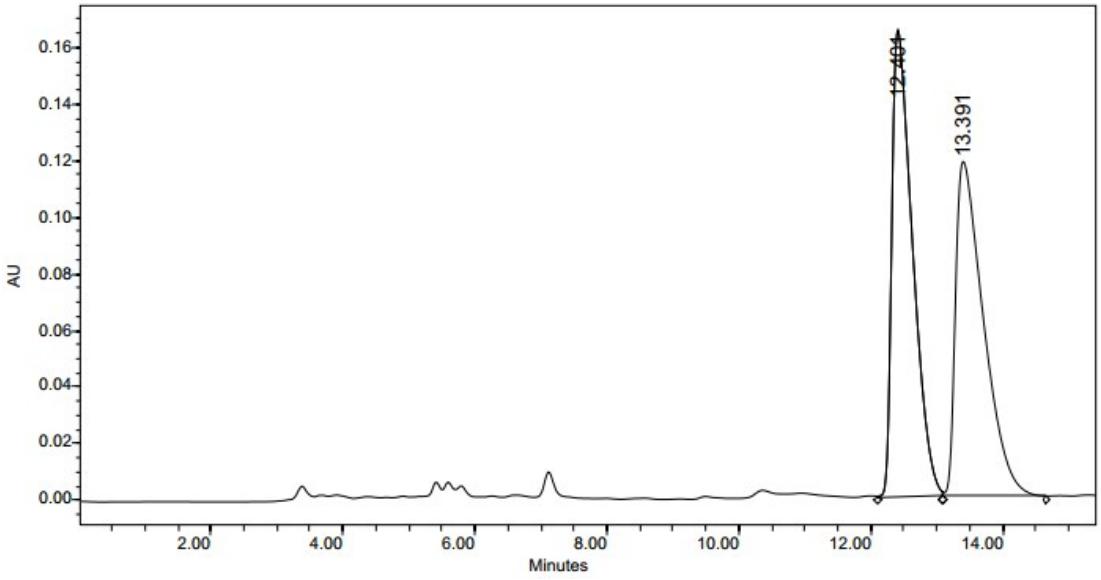


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	9.666	711663	48.71	48138	70.79
2	12.777	749329	51.29	19865	29.21

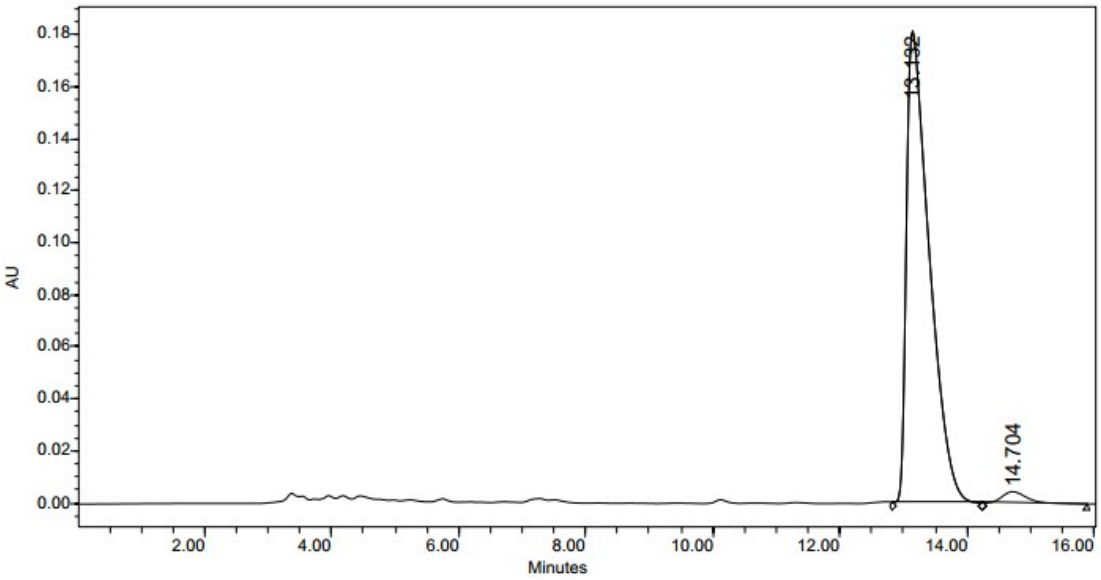


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	9.612	4197717	97.25	291553	97.87
2	11.884	118583	2.75	6340	2.13

3ka

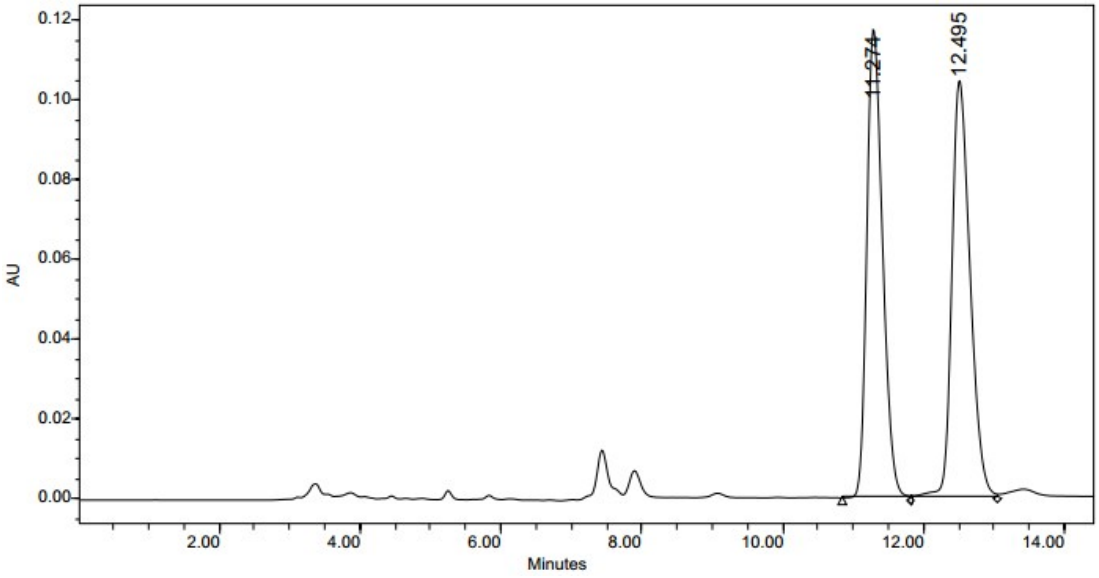


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	12.401	3610009	50.80	164996	58.18
2	13.391	3496395	49.20	118584	41.82

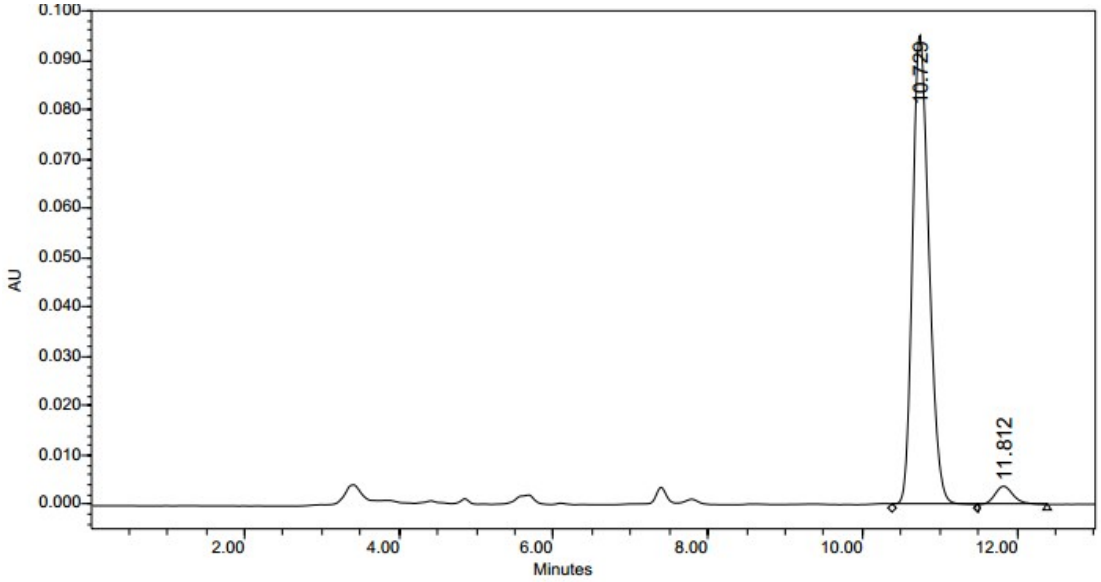


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	13.132	4548983	97.15	181452	97.51
2	14.704	133490	2.85	4639	2.49

3la

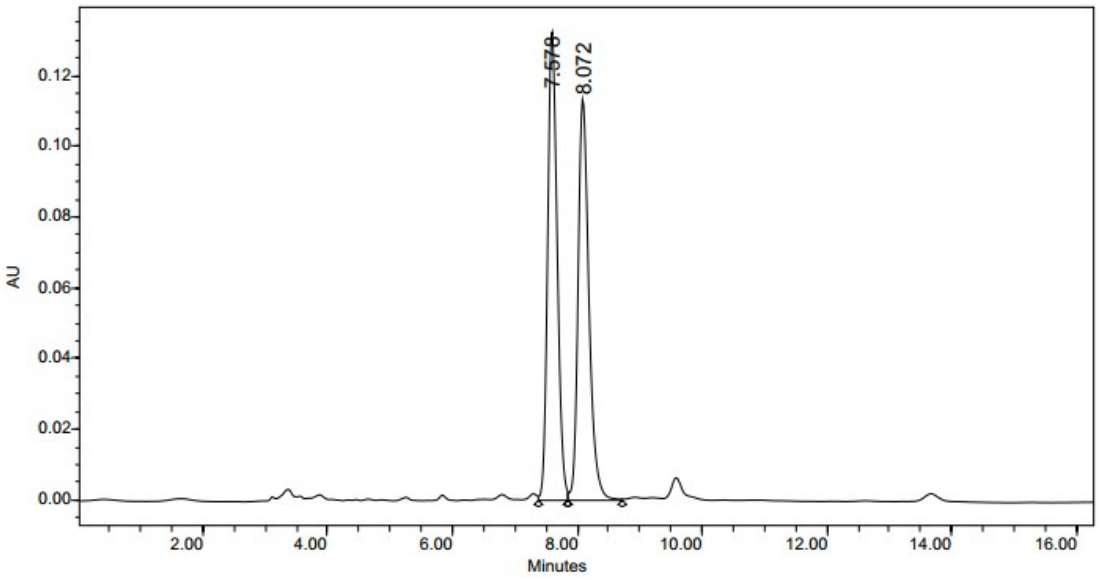


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	11.274	1819337	49.25	117494	52.98
2	12.495	1874521	50.75	104288	47.02

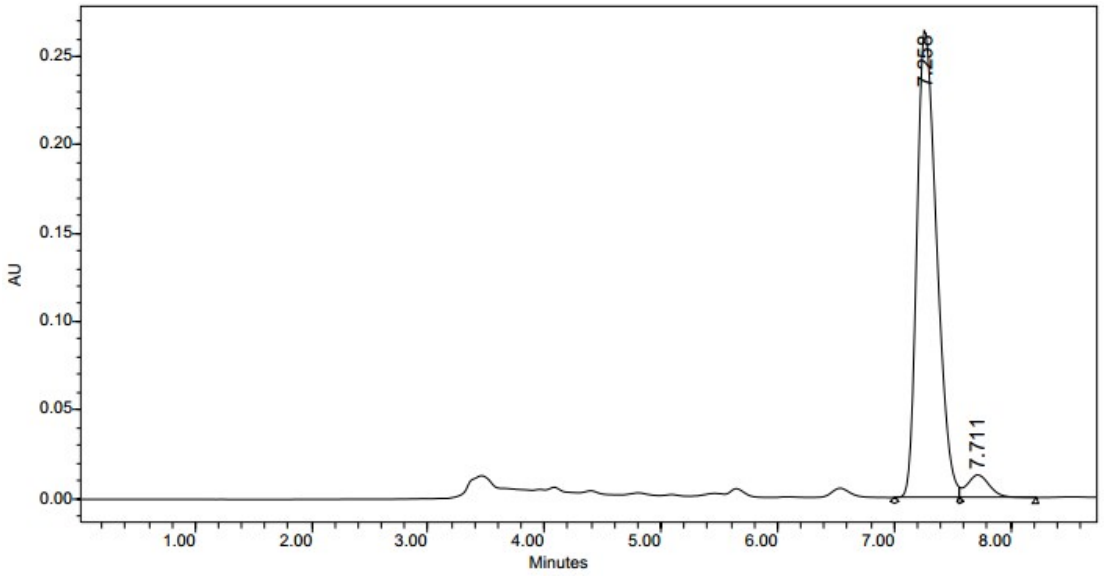


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	10.729	1405340	95.77	95044	96.26
2	11.812	62096	4.23	3695	3.74

3ma

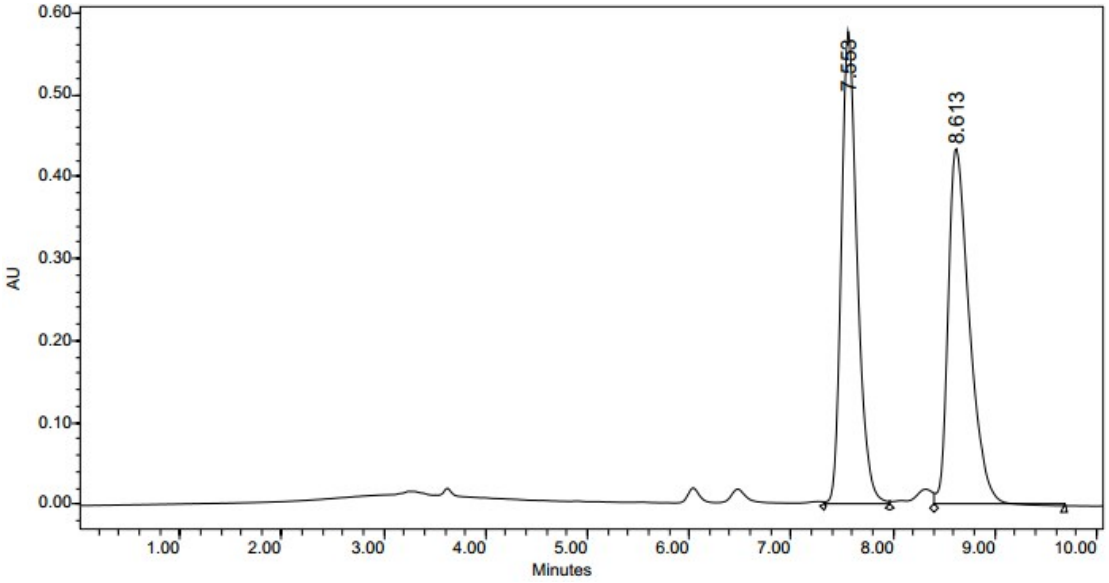


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	7.578	1415872	50.73	132910	53.89
2	8.072	1375351	49.27	113710	46.11

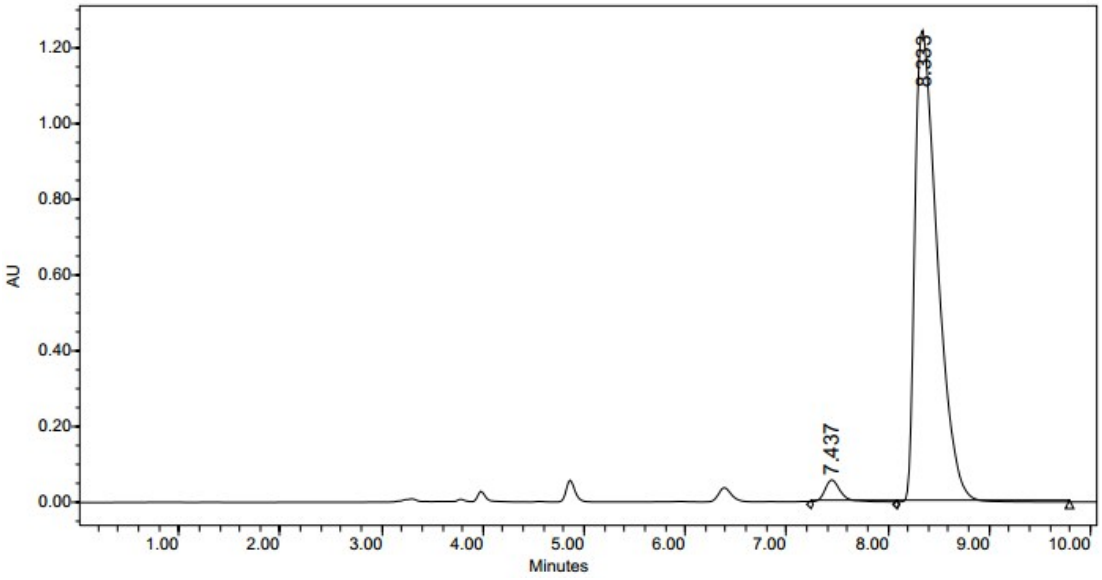


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	7.258	3125856	94.84	265400	95.38
2	7.711	170112	5.16	12854	4.62

3ab

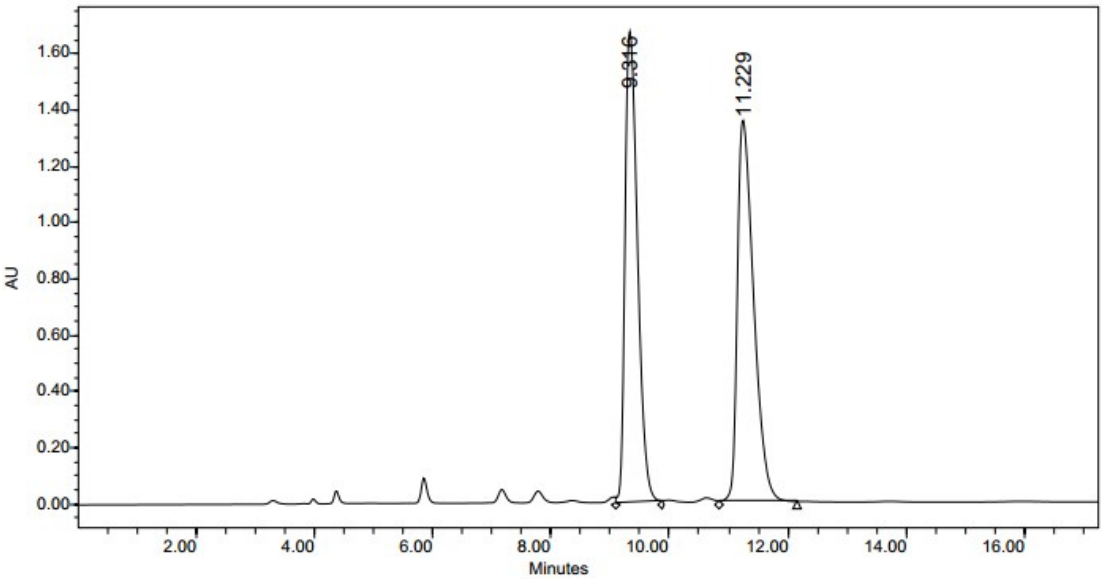


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	7.553	6290426	49.80	576234	57.01
2	8.613	6339938	50.20	434538	42.99

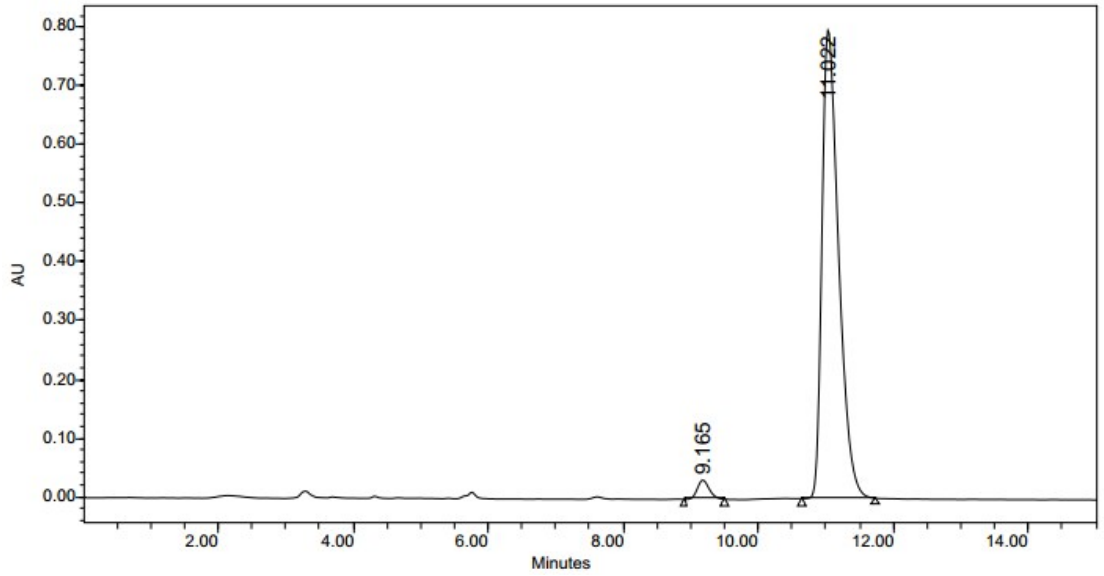


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	7.437	663213	3.33	58428	4.47
2	8.333	19279884	96.67	1248123	95.53

3ac

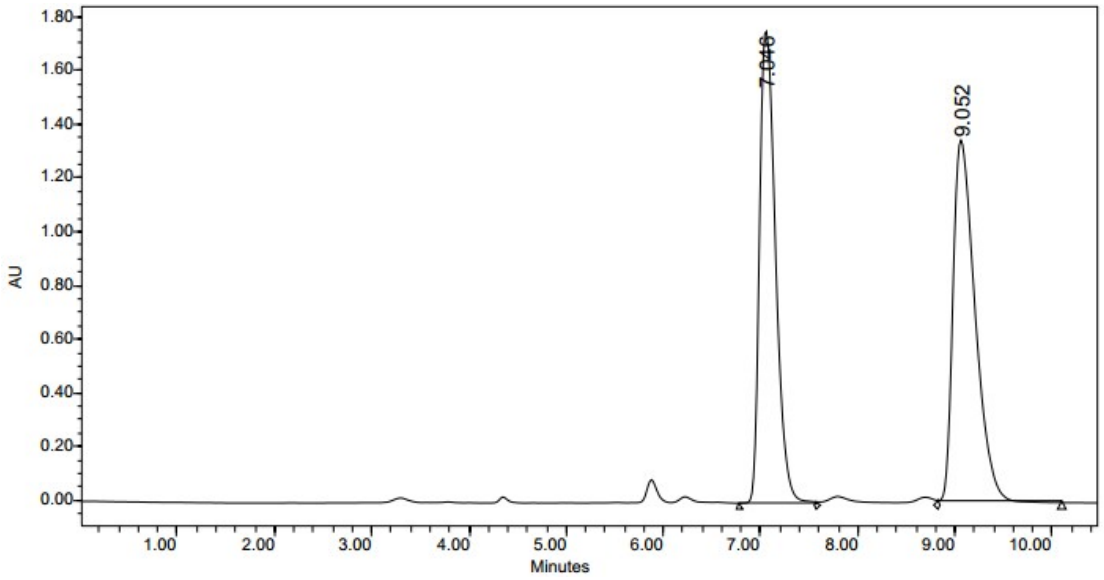


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	9.316	24545908	48.59	1673937	55.24
2	11.229	25968776	51.41	1356569	44.76

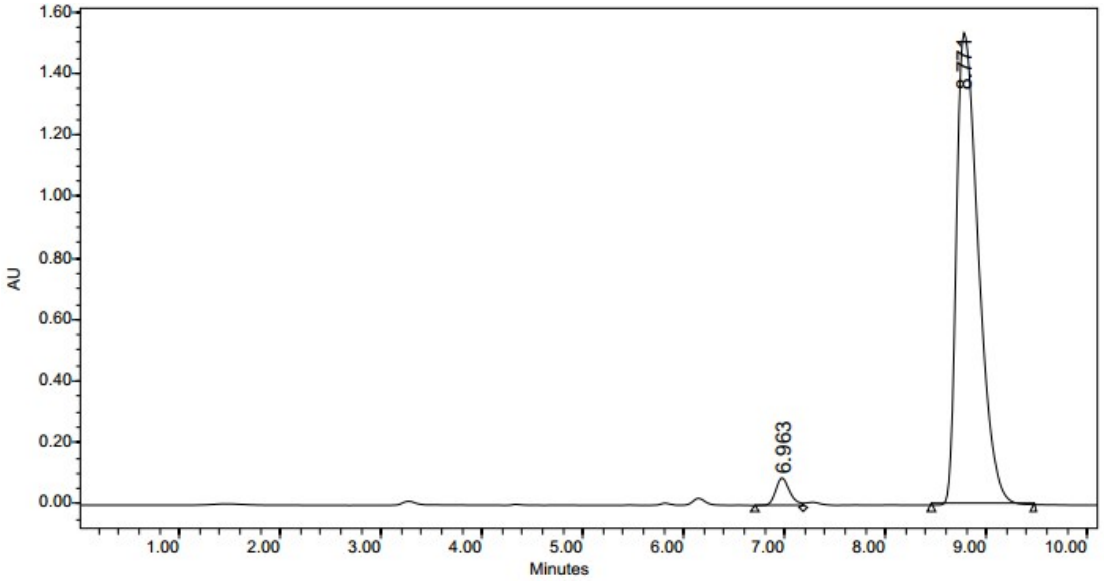


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	9.165	401505	2.86	32537	3.92
2	11.022	13655908	97.14	798138	96.08

3ad

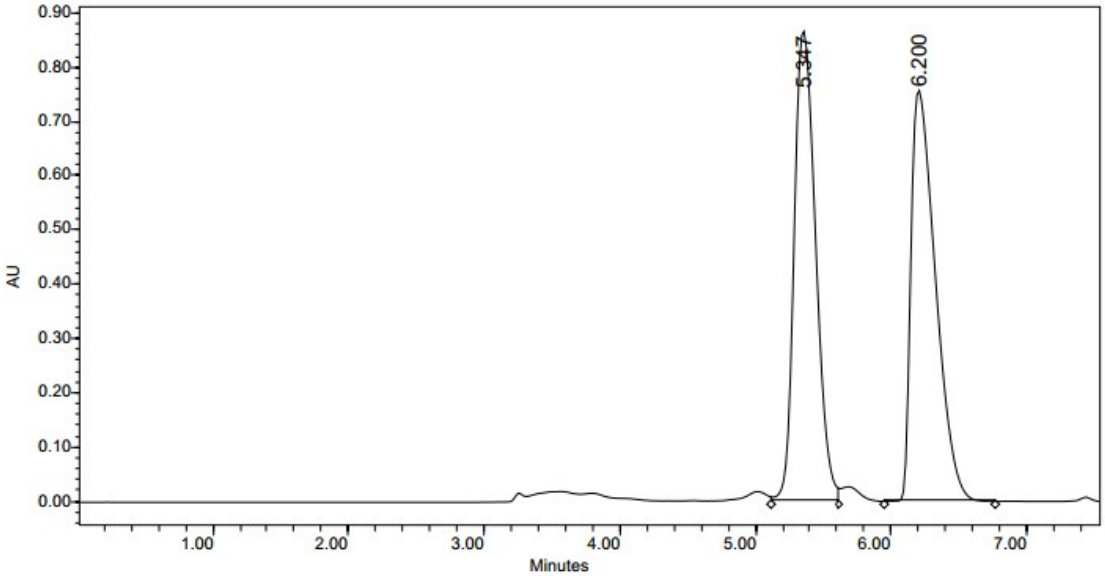


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	7.046	20077624	48.37	1758055	56.57
2	9.052	21429147	51.63	1349580	43.43

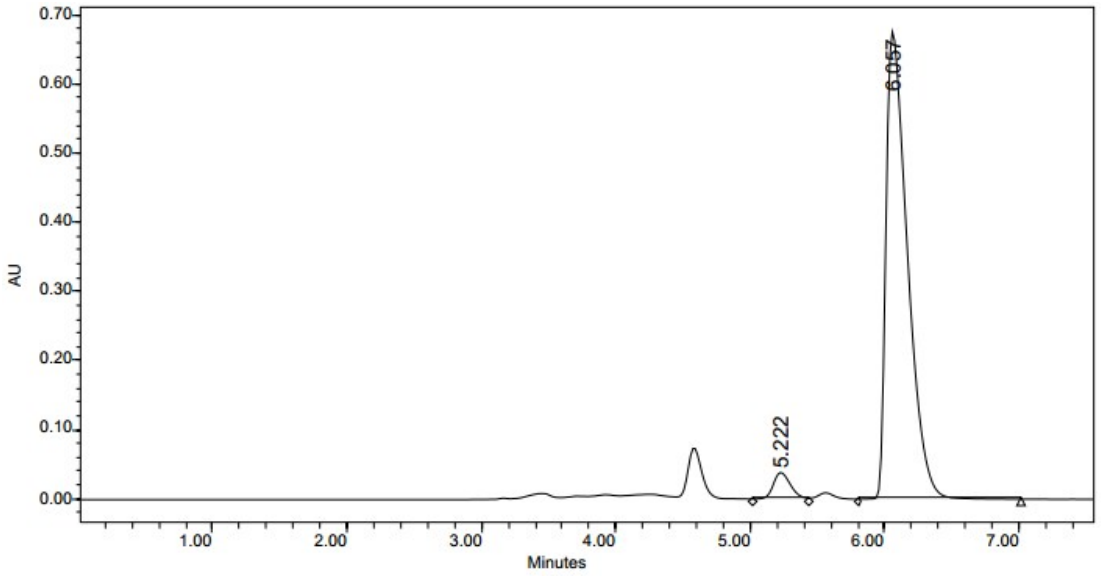


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	6.963	857142	3.56	89017	5.48
2	8.771	23248483	96.44	1536025	94.52

4aa

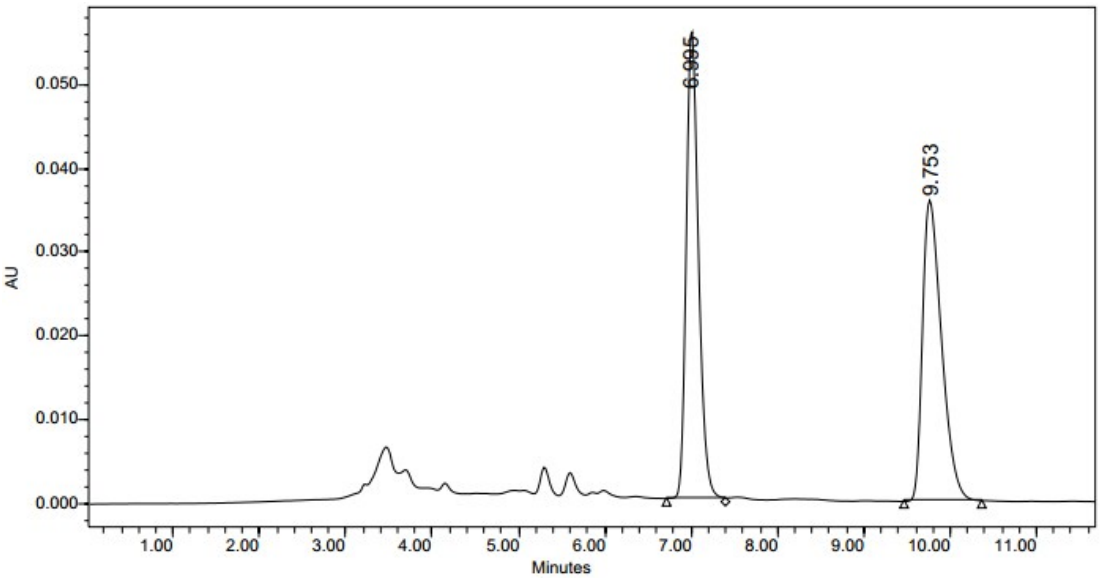


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	5.347	9600997	50.18	867483	53.36
2	6.200	9530761	49.82	758234	46.64

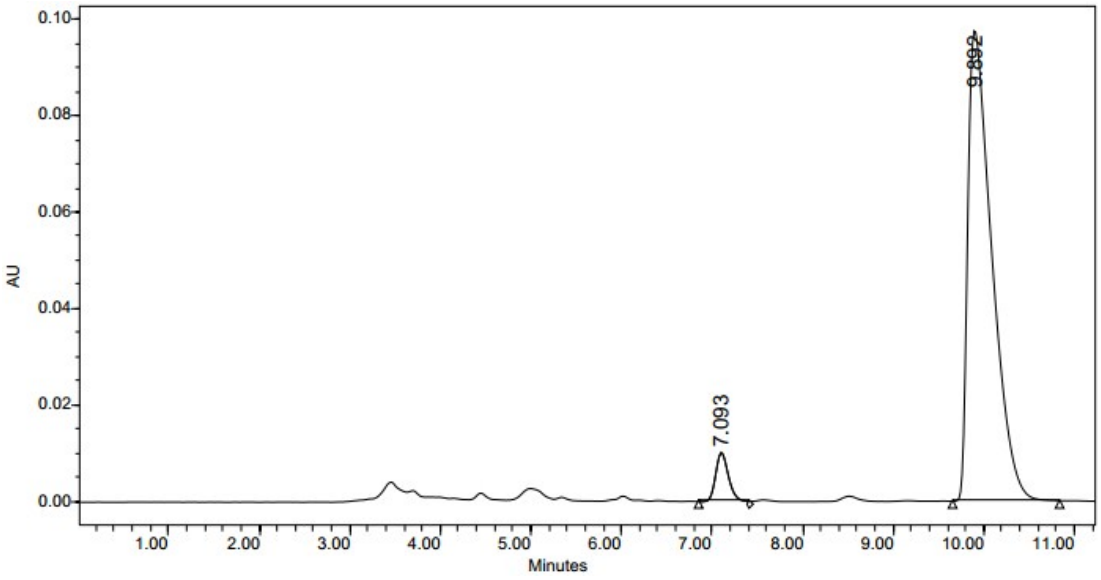


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	5.222	352756	4.49	38877	5.40
2	6.057	7504721	95.51	681132	94.60

4ab

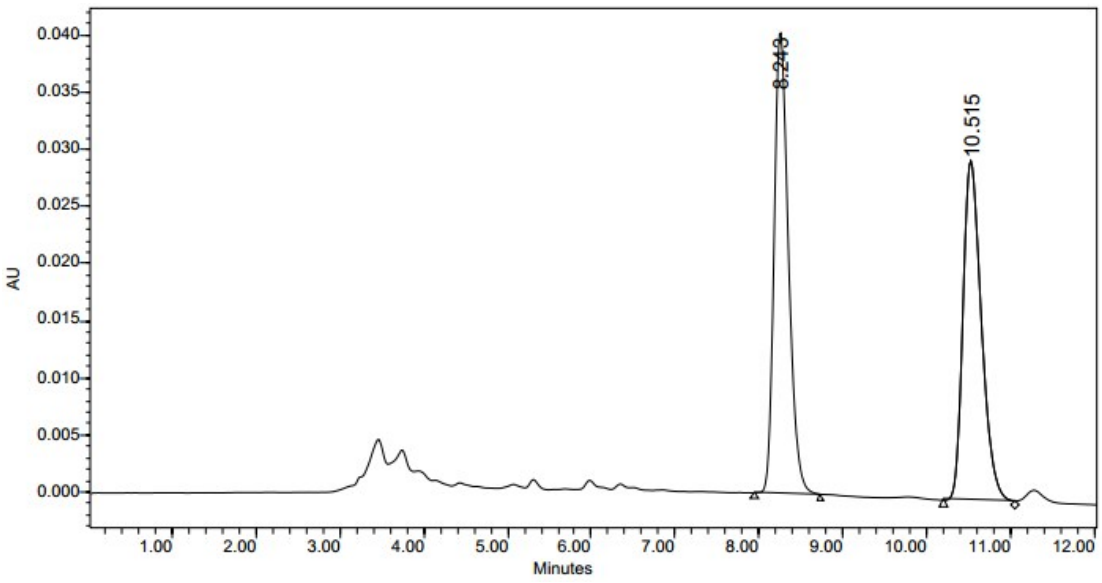


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	6.995	552810	50.06	55930	60.86
2	9.753	551514	49.94	35972	39.14

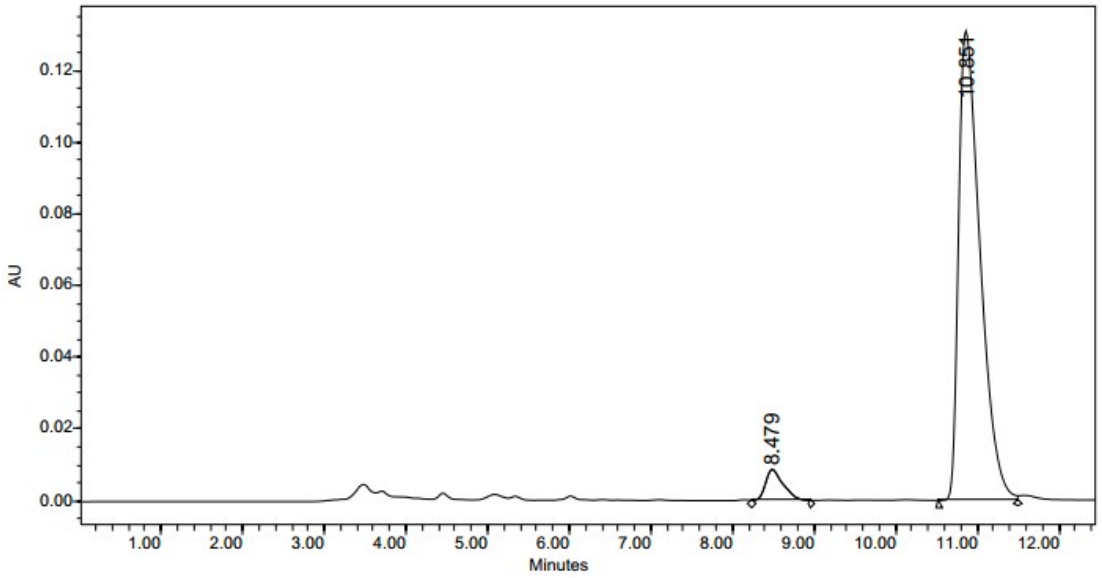


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	7.093	99269	5.24	10110	9.36
2	9.892	1795126	94.76	97934	90.64

4ac

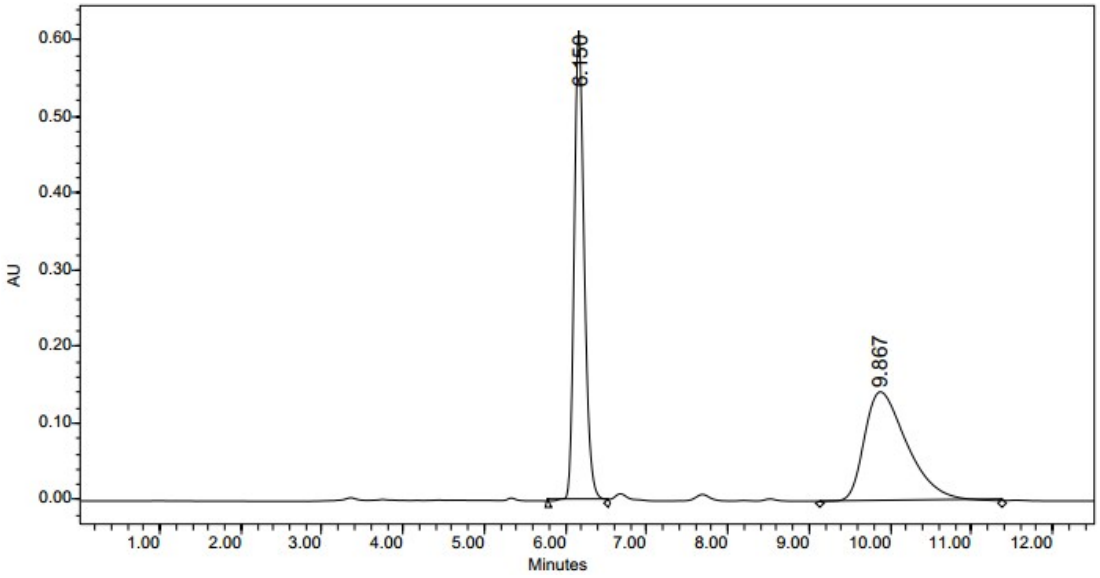


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	8.243	479595	51.25	40428	57.61
2	10.515	456193	48.75	29747	42.39

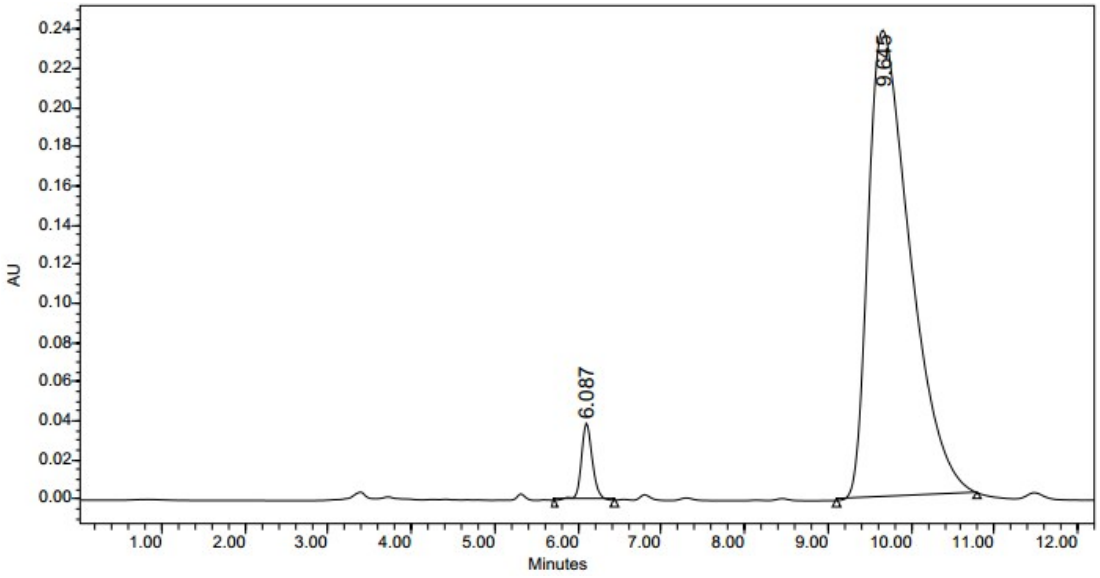


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	8.479	131358	5.19	8694	6.23
2	10.851	2399953	94.81	130876	93.77

4ad

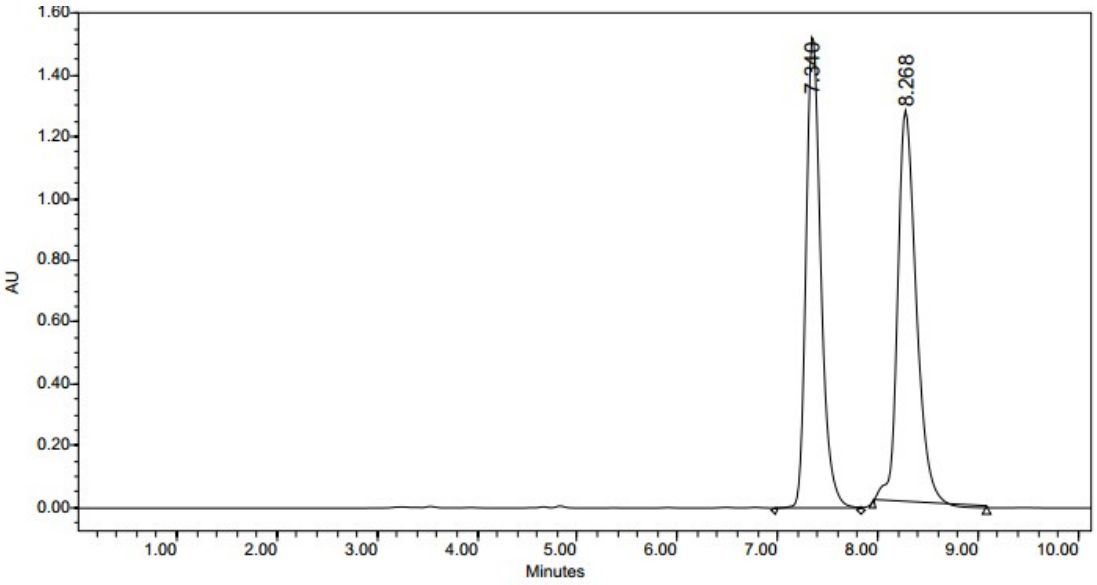


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	6.150	5290071	50.13	612164	81.13
2	9.867	5262528	49.87	142374	18.87

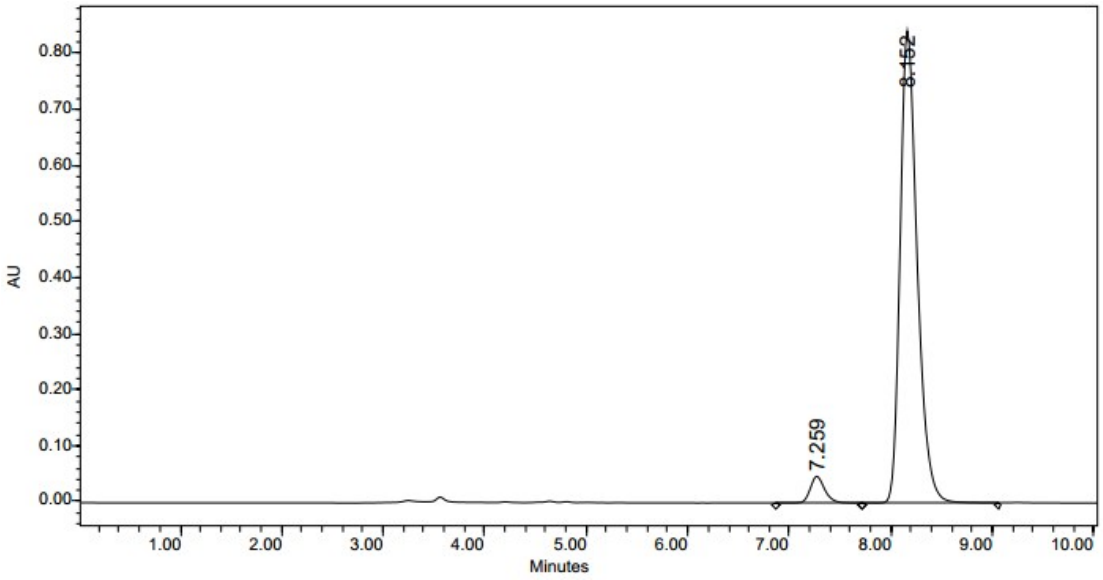


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	6.087	369128	4.23	39235	14.10
2	9.645	8359728	95.77	239038	85.90

4ae

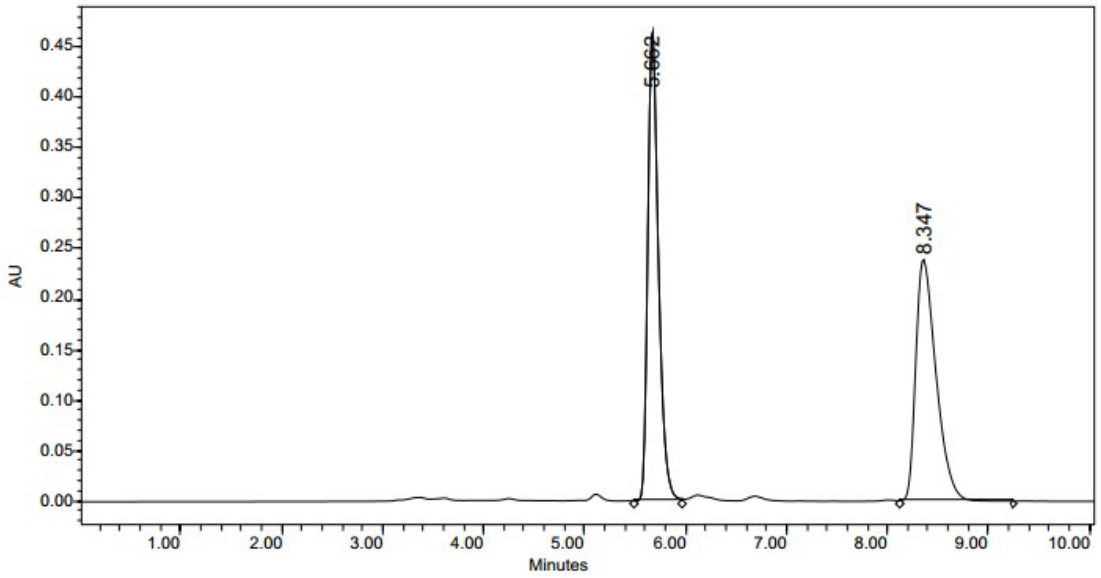


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	7.340	15684153	48.71	1531763	54.67
2	8.268	16514236	51.29	1269952	45.33

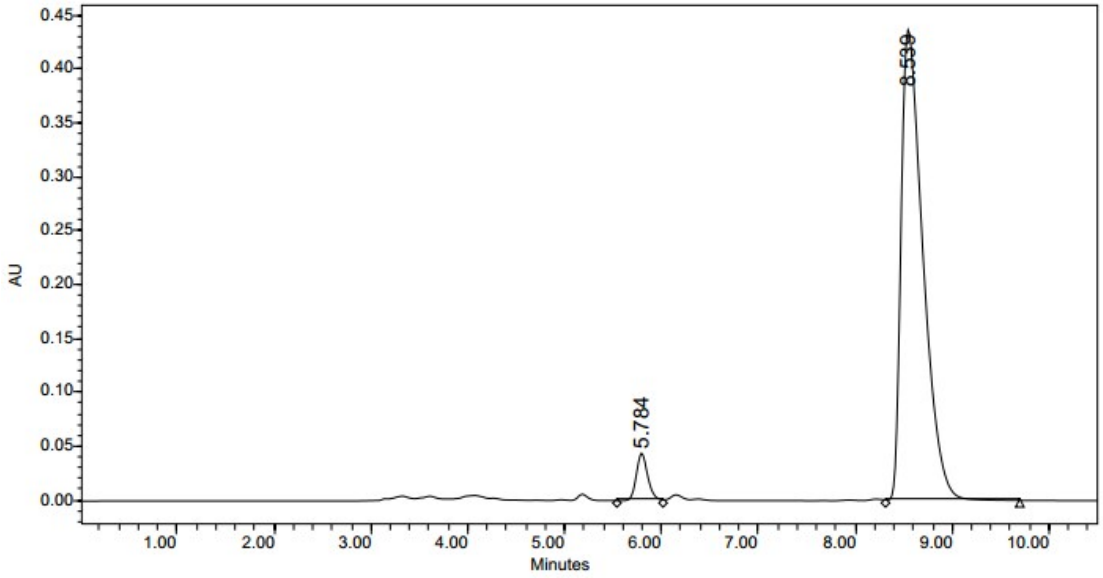


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	7.259	464335	4.50	47190	5.31
2	8.152	9845849	95.50	841855	94.69

4af

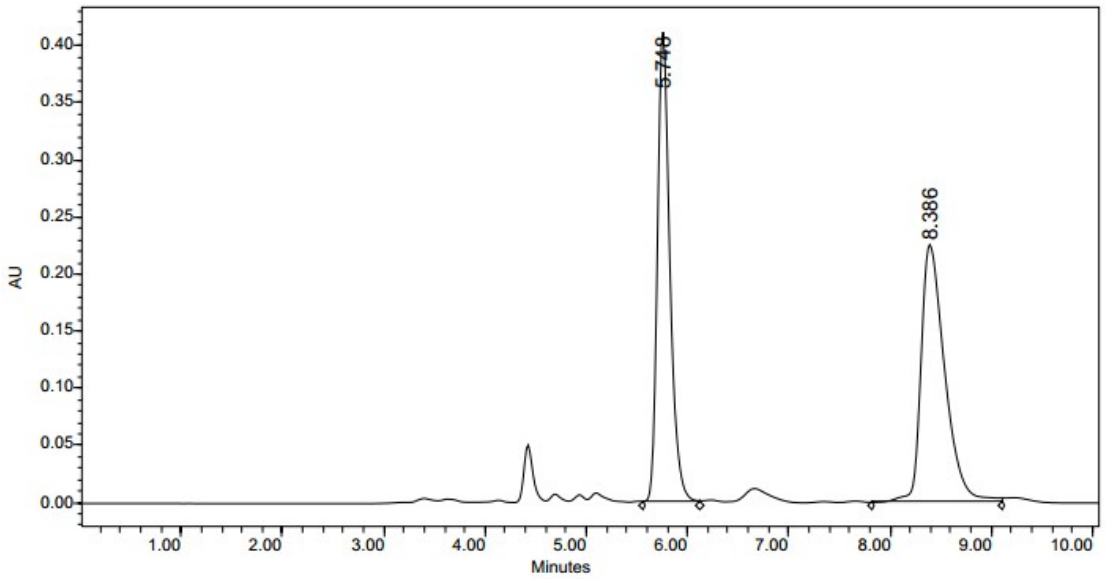


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	5.662	3448115	50.58	466824	66.05
2	8.347	3368531	49.42	239922	33.95

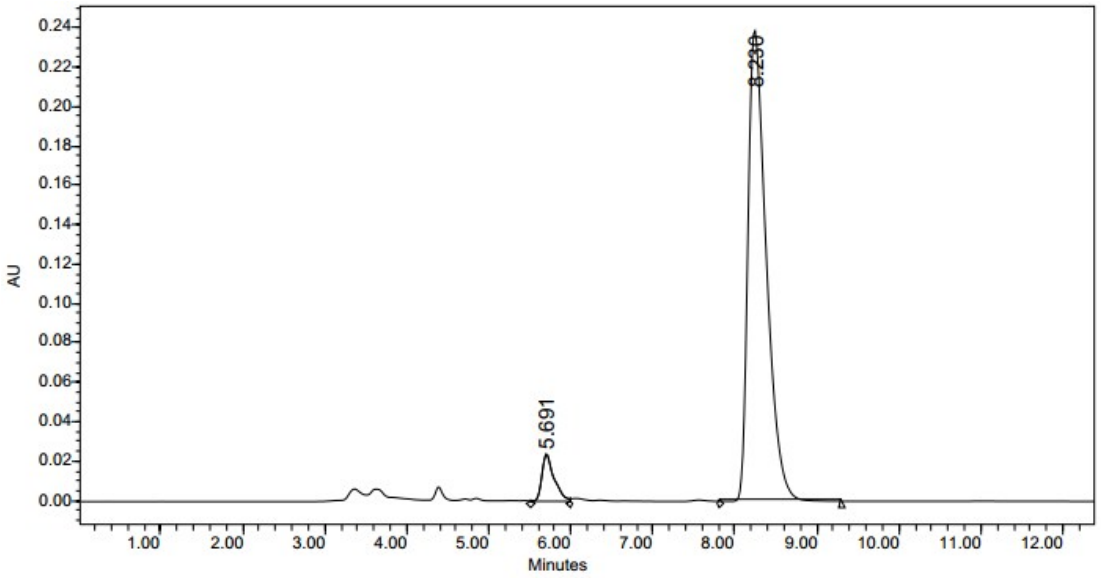


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	5.784	361299	5.00	43830	9.11
2	8.539	6858871	95.00	437450	90.89

4ag

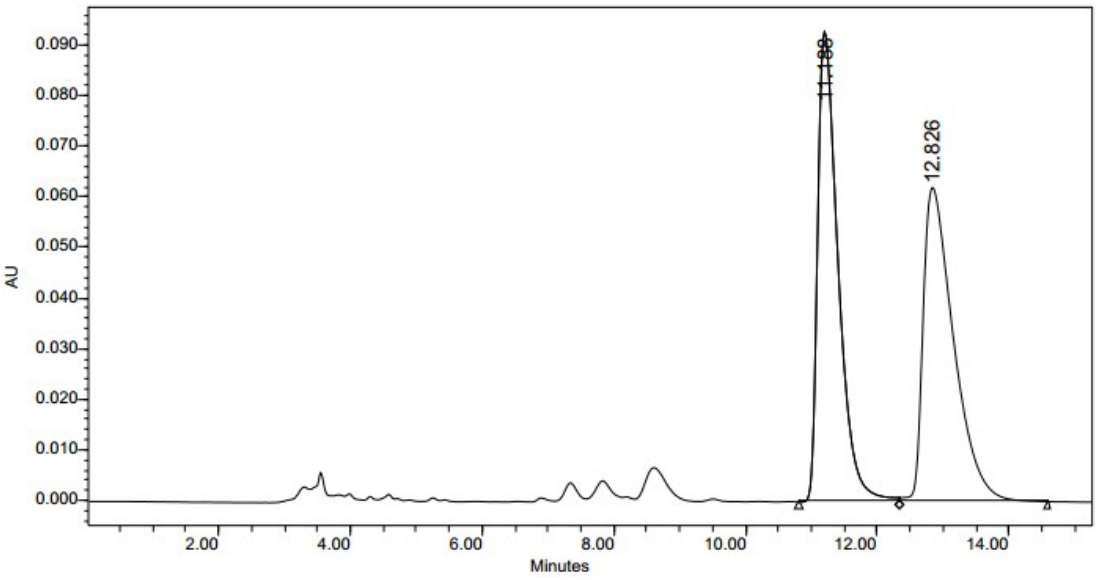


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	5.748	3559690	48.67	412288	64.55
2	8.386	3754740	51.33	226460	35.45

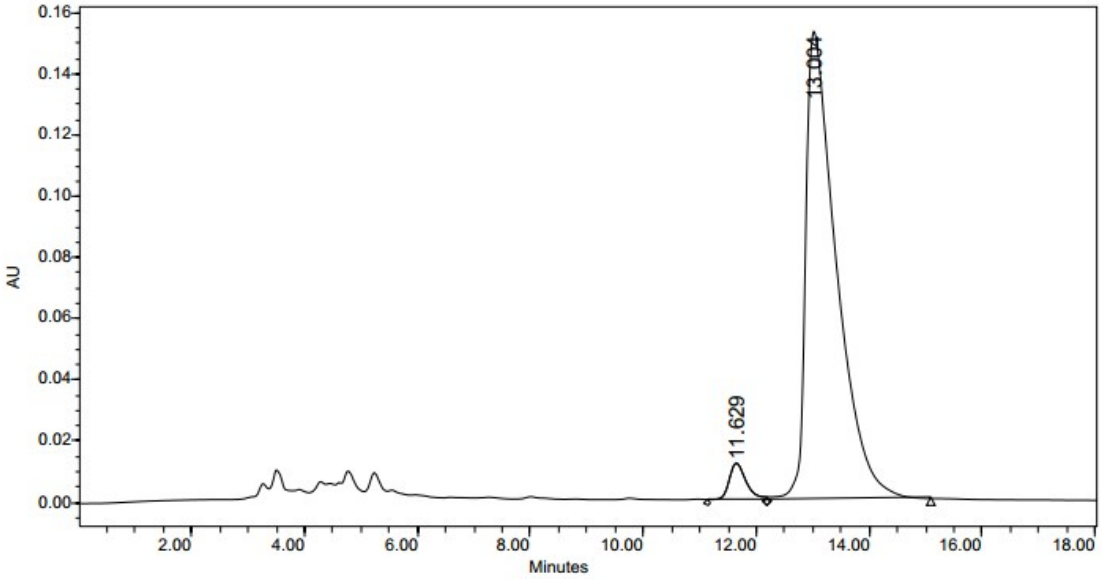


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	5.691	248559	6.28	24048	9.15
2	8.230	3710561	93.72	238843	90.85

4ah

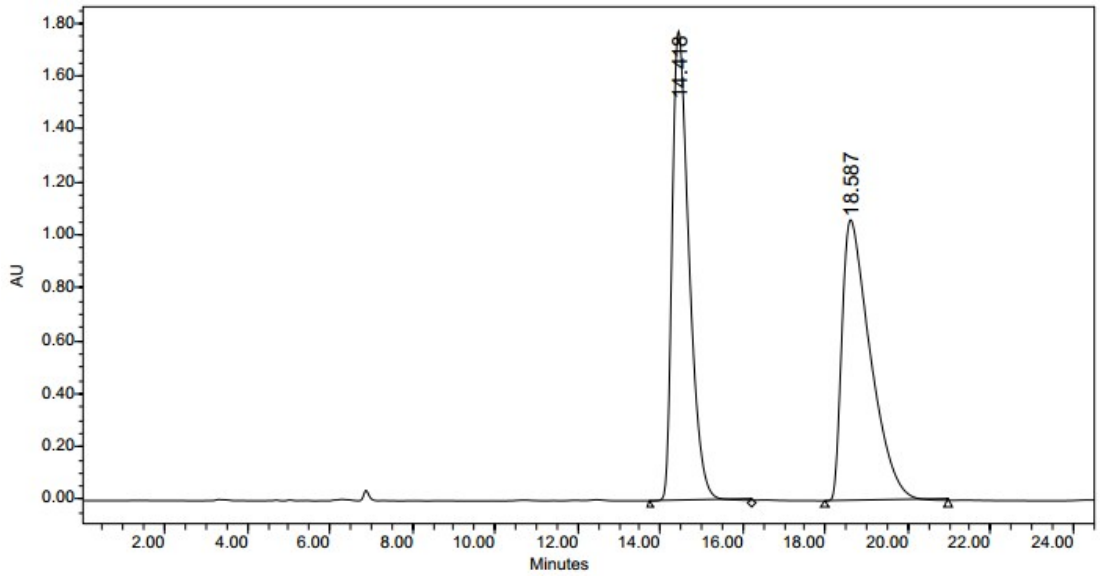


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	11.188	2008942	50.09	92887	59.95
2	12.826	2001830	49.91	62065	40.05

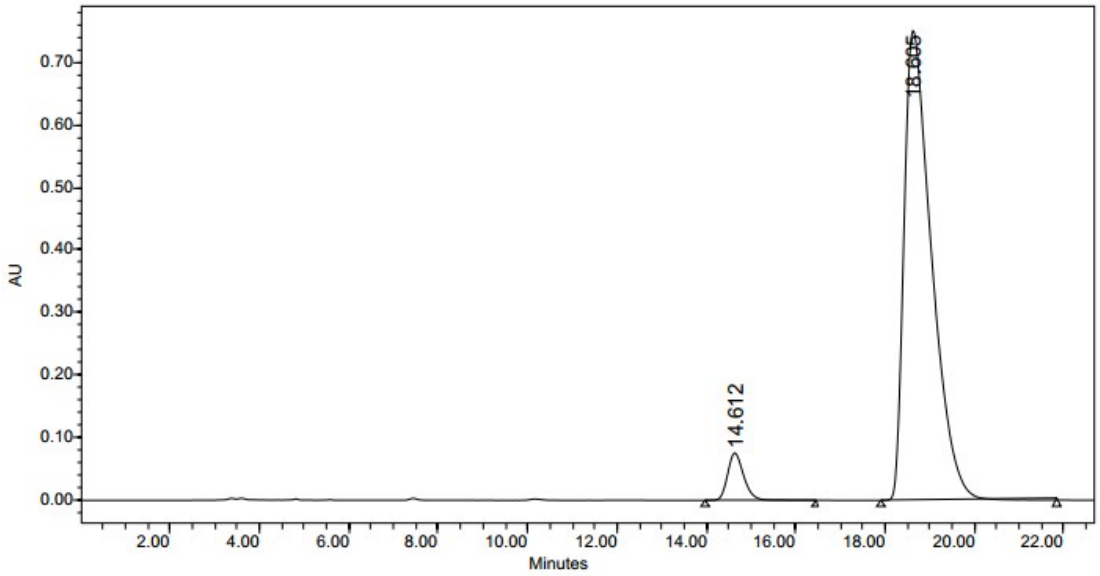


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	11.629	246136	4.09	11843	7.20
2	13.004	5767424	95.91	152708	92.80

5aa

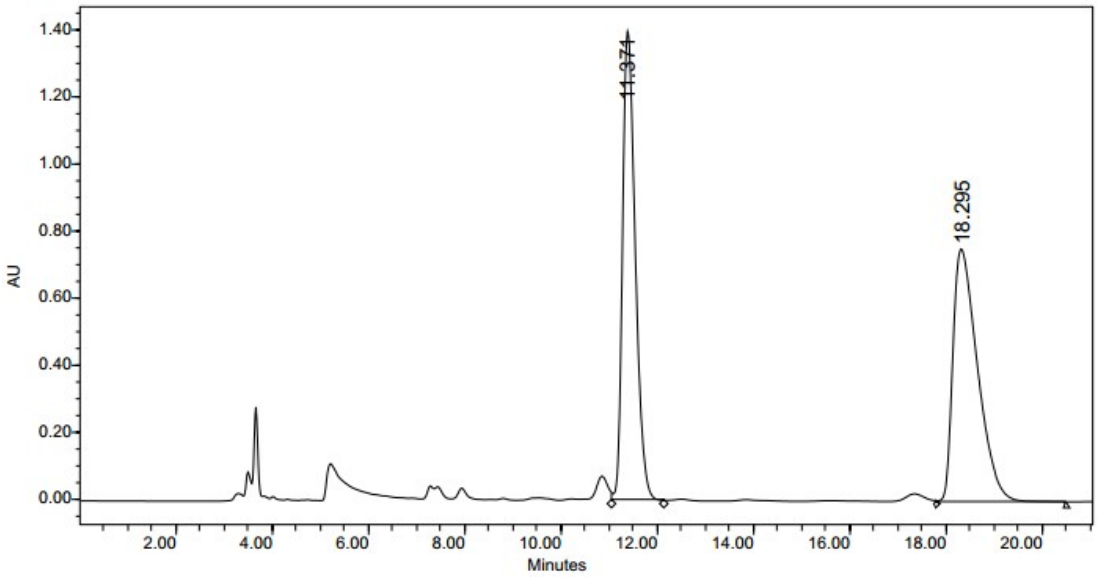


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	14.418	50457365	49.84	1773262	62.56
2	18.587	50781757	50.16	1061096	37.44

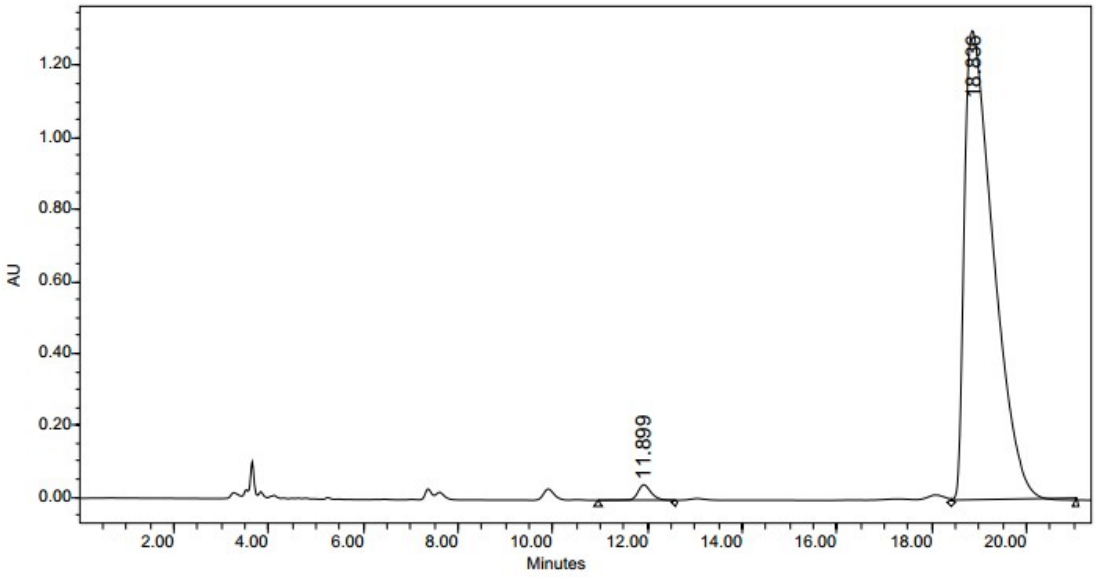


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	14.612	1888885	5.54	75710	9.14
2	18.605	32189412	94.46	753000	90.86

10

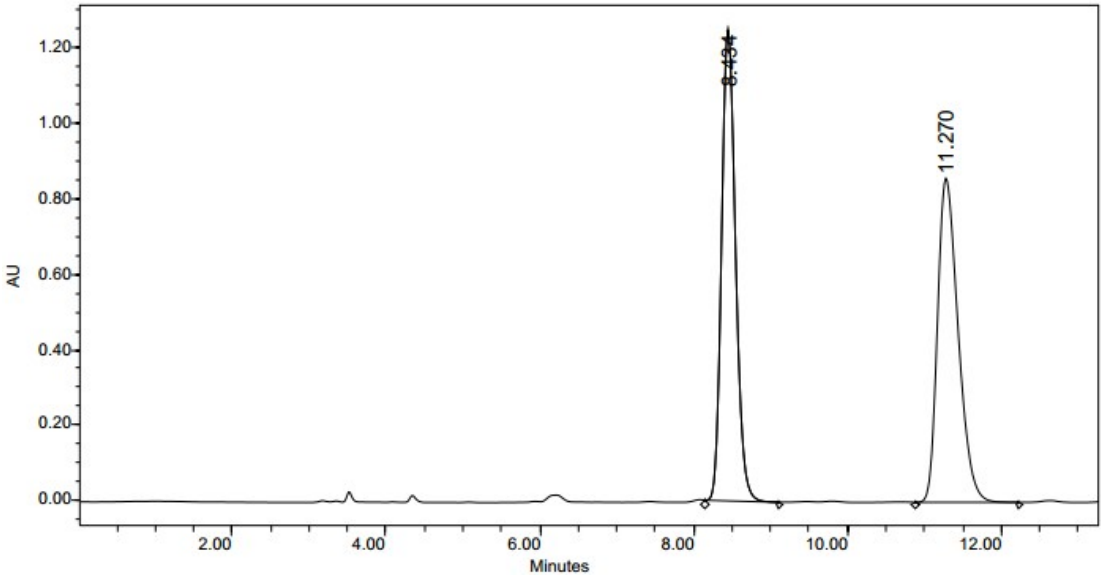


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	11.371	25873628	49.14	1402523	65.05
2	18.295	26774092	50.86	753383	34.95

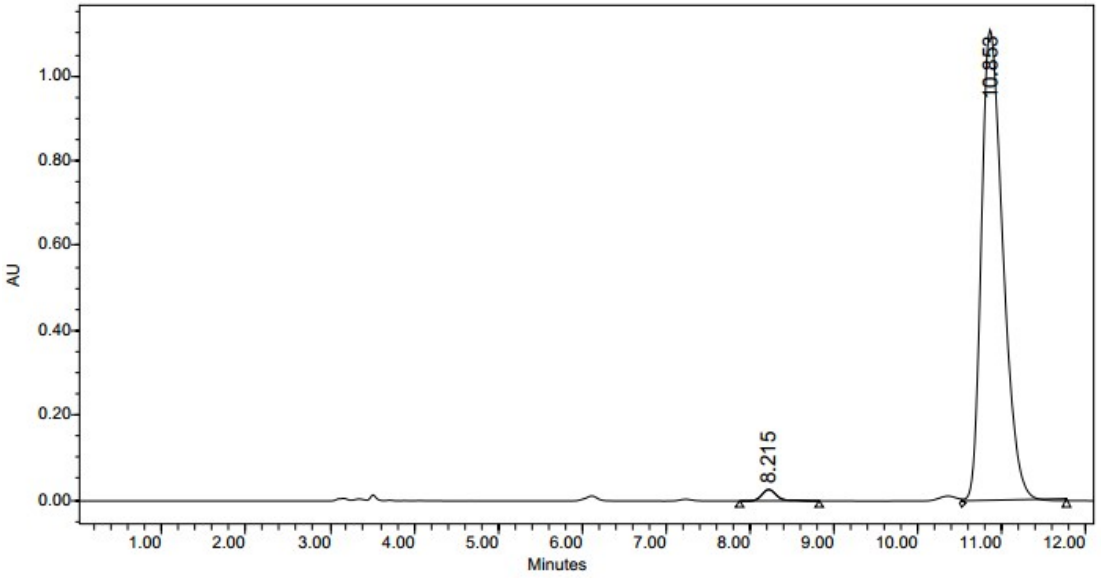


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	11.899	843608	1.49	42989	3.19
2	18.836	55603652	98.51	1305580	96.81

11

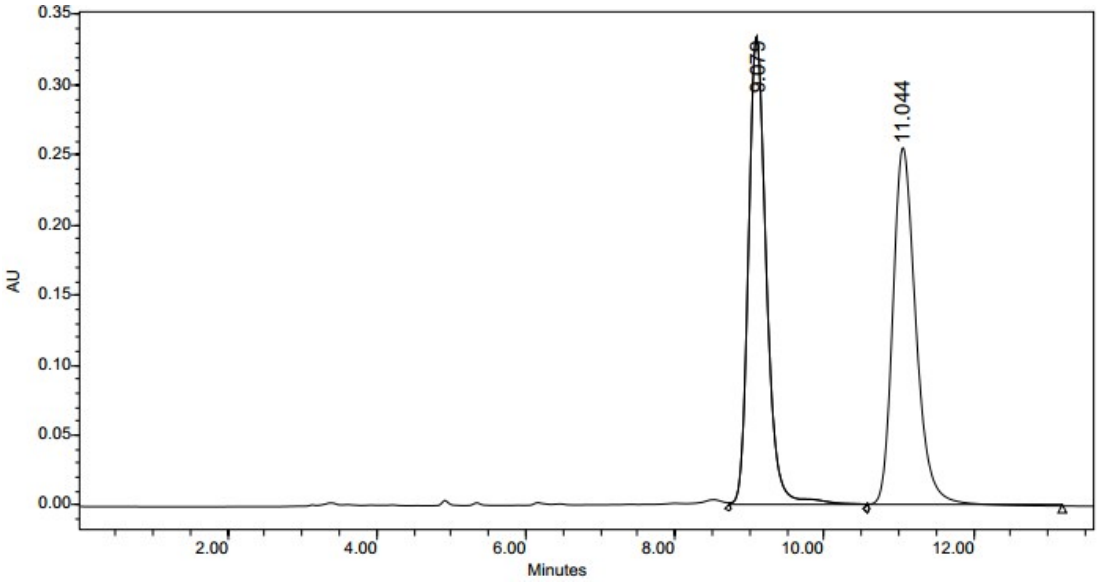


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	8.434	15875087	49.83	1249654	59.29
2	11.270	15985831	50.17	858001	40.71

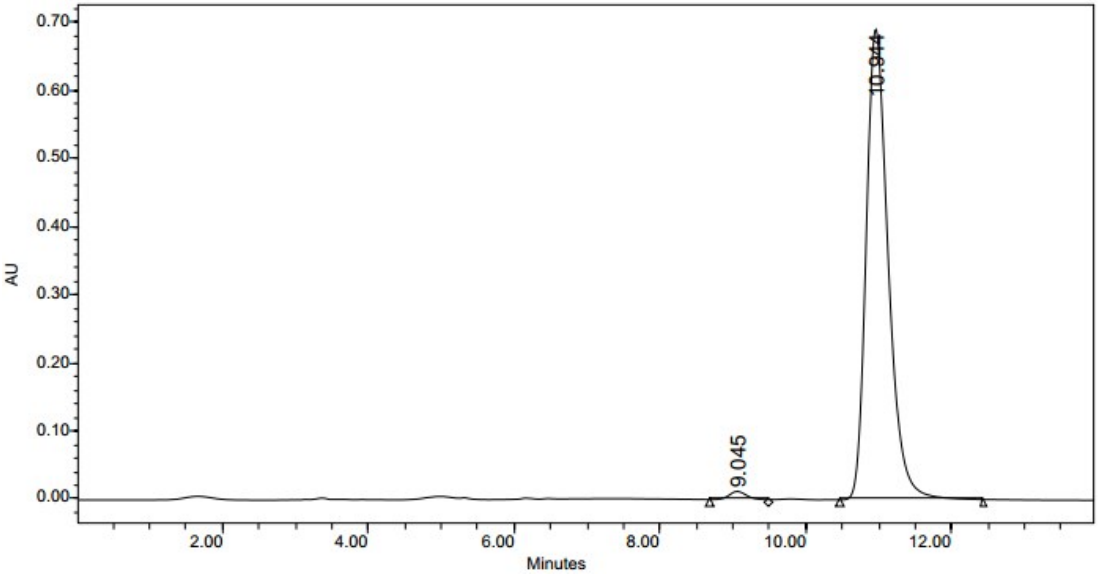


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	8.215	338483	1.68	27040	2.38
2	10.853	19869176	98.32	1110799	97.62

12

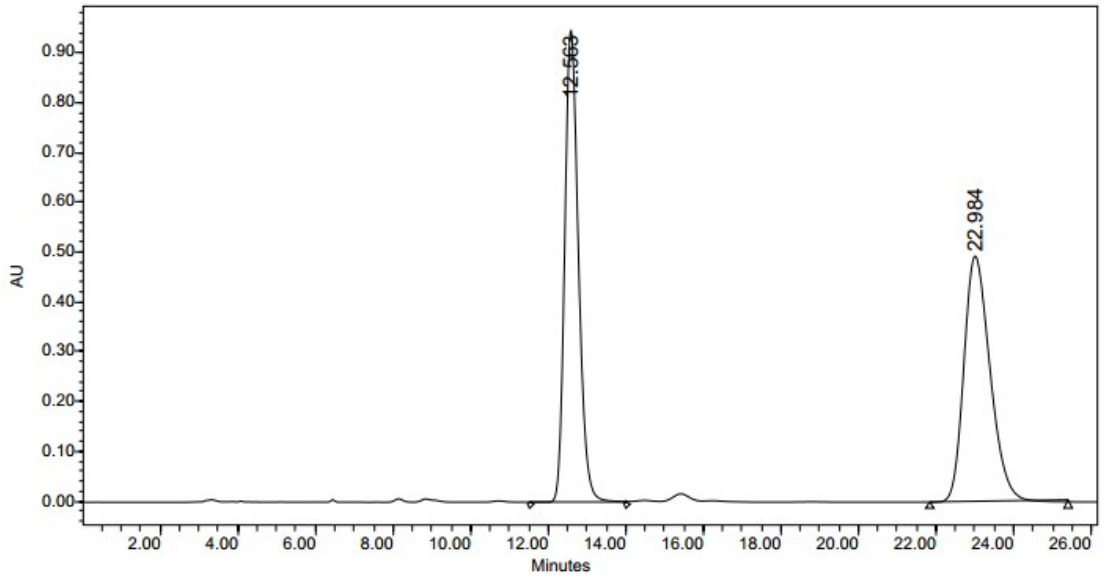


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	9.079	5640820	50.50	334561	56.71
2	11.044	5528523	49.50	255414	43.29

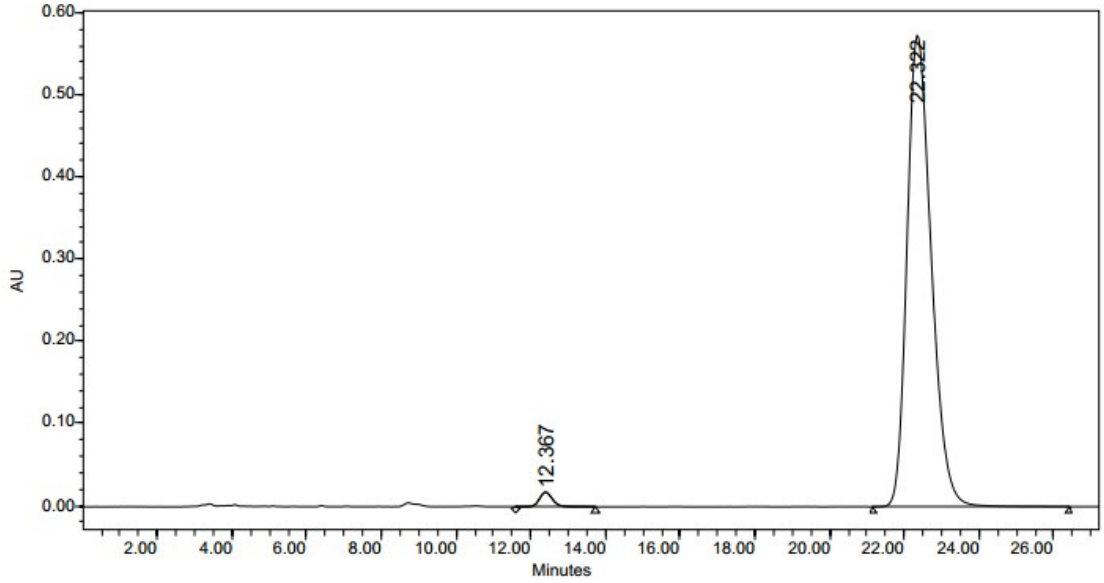


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	9.045	195398	1.33	11908	1.70
2	10.944	14485034	98.67	690278	98.30

13



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	12.563	23240631	50.01	945556	65.71
2	22.984	23233819	49.99	493353	34.29



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	12.367	426231	1.62	17685	2.99
2	22.322	25828706	98.38	573422	97.01