Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Copper catalyzed diastereoselective and enantioselective hydroborylation of cyclopentenylcarboxyesters

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1. General information

Unless otherwise stated, all reactions were magnetically stirred and conducted in anhydrous solvents under N_2, applying standard Schlenk techniques. Solvents were removed under reduced pressure at 40°C using a rotary evaporator, and unless otherwise stated, the remaining compound was dried in high *vacuum* at ambient temperature.

Chemicals

Chemicals were purchased from commercial suppliers (including Energy Chemical, Bidepharm, Aladdin, Meryer, SCR) and used without further purification unless otherwise stated.

Solvents

Solvents (CH_2Cl_2, THF) were dried by distillation from an appropriate drying agent. In addition, dioxane and more solvents were purchased from commercial suppliers.

Gas

Dry N_2 were purchased from Hangzhou Jingong Materials with > 99.9% purity.

Column Chromatography

Column chromatography (CC) was carried out using Nuotai silica gel (90 Å, 100-200 mesh) using technical grade solvents. Elution was accelerated using compressed air. All reported yields, unless otherwise specified, refer to spectroscopically and chromatographically pure compounds.

Nuclear Magnetic Resonance Spectroscopy

^1H, ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AV-500, AV-400 spectrometer in a suitable deuterated solvent. The solvent employed and respective measuring frequency are indicated for each experiment. Chemical shifts are reported with tetramethylsilane (TMS) serving as a universal reference of all nuclides and with two or one digits after the comma. The resonance multiplicity is described as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and bs (broad singlet). All spectra were recorded at 298 K unless otherwise noted, processed with program MestReNova 14.0, and coupling constants are reported as observed. The residual deuterated solvent signal relative to tetramethylsilane (TMS) was used as the internal reference in ^1H NMR spectra ($CDCl_3$ δ 7.26, THF δ 1.72, 3.58, C_6D_6 δ 7.16, CD_3OD δ 3.31), and are reported as follows: chemical shift δ in ppm (multiplicity, coupling constant *J* in Hz, number of protons). ^{13}C NMR spectra reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard ($CDCl_3$ δ 77.2, THF δ 67.21, 25.31, C_6D_6 δ 128.1, CD_3OD δ 49.0). All spectra are broadband decoupled unless

otherwise noted.

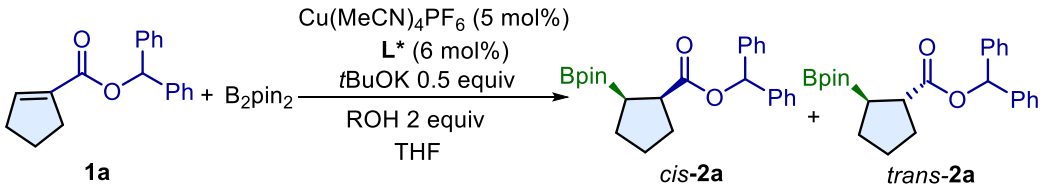
High Resolution Mass Spectrometry

Electrospray ionization (ESI) mass spectrometry was conducted on a Bruker micro QII-ESI-TOF. The ionization method and mode of detection employed is indicated for the respective experiment and all masses are reported in atomic units per elementary charge (m/z) with an intensity normalized to the most intense peak.

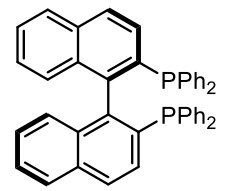
High Performance Liquid Chromatography

High performance liquid chromatography (HPLC) was performed on Shimadzu LC-2030C liquid chromatograph using Daicel columns with a chiral stationary phase. All solvents used were HPLC-grade solvents purchased from MERYER. The column employed and respective solvent mixture are indicated for each experiment.

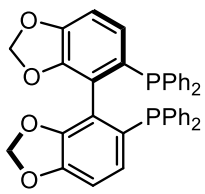
2. Reaction Screen



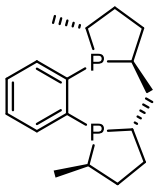
entry	L*	T (℃)	alchohol	Yield (%)	dr	er (%)	
						cis-**2a**	*trans*-**2a**
1	**L1**	rt	MeOH	74	1:2	60:40	58:42
2	**L2**	rt	MeOH	75	1:2	18:82	30:70
3	**L3**	rt	MeOH	85	1:1	60:40	59:41
4	**L4**	rt	MeOH	74	1:2	62:38	86:14
5	**L5**	rt	MeOH	91	1:2	40:60	24:76
6	**L6**	rt	MeOH	45	1:4	52:48	88:12
7	**L7**	rt	MeOH	83	1:3	76:24	89:11
8	**L7**	-50	MeOH	94	8:1	95:5	93:7
9	**L7**	-50	*i*PrOH	97[b]	3:1	83:17	84:16
10	**L7**	-50	*t*BuOH	71[b]	2:1	80:20	84:16
11	**L7**	-50	*t*AmOH	77[b]	2:1	91:9	94:6



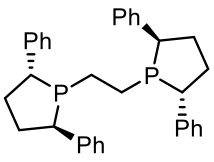
L1 (*R*)-*p*-TolBinap



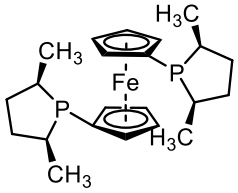
L2 (*R*)-Segphos



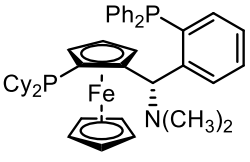
L3 (*R*,*R*)-Me-Duphos



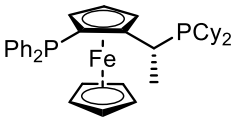
L4 (*R*,*R*)-Ph-BPE



L5 (*S*,*S*)-Me-Ferrocelane



L6 (*R*,*S*)-Taniaphos



L7 (*R*,*S*)-JosiPhos

Table S1. Reaction optimization

[a]Reactions were performed with substrate **1a** (0.11 mmol, 30 mg, 1equiv.), B_2Pin_2 (0.117 mmol, 30.09 mg, 1.1 equiv.), $Cu(MeCN)_4PF_6$ (5 mol %, 2.01 mg), **L7** (6 mol %, 3.53 mg), *t*BuOK (0.054 mmol, 6.05 mg, 0.5 equiv.), MeOH (0.216 mmol, 9 μL, 2 equiv.) in tetrahydrofuran; yields are for the isolated compounds; diastereo ratio (dr) and enan-tiomeric ratio (er) were determined by HPLC analysis.

The following borylated products could be obtained while the corresponding

substrates were applied under the standard conditions. However, due to their low polarity, these racemates separation were not successful.

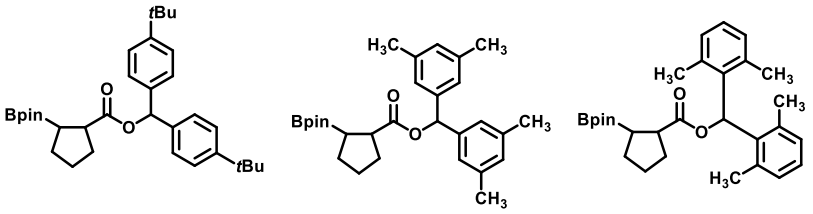
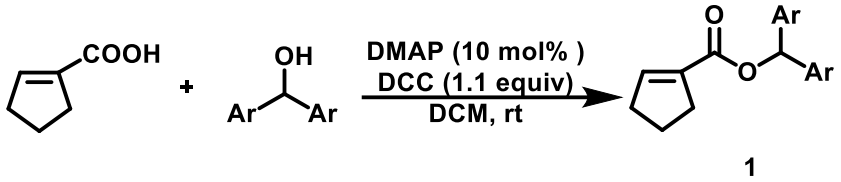


Figure S1. The unsuccessful racemate separation

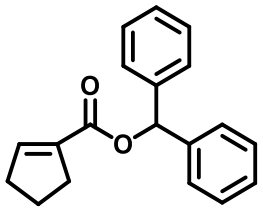
3. General procedure of substrates synthesis



Scheme S1 General procedure of substrate synthesis

A reaction flask was charged with cyclopentenoic acid (1 equiv.), alcohols (1.1 equiv.), 4-dimethylaminopyridine (0.1 equiv.) and dicyclohexylcarbodiimide (1.1 equiv.), capped, and purged with nitrogen, dichloromethane was added. Then, the reaction mixture allowed to stir for 3-5 h at room temperature. After full consumption of the starting material, add ammonium chloride saturated solution, organic phase extraction with methylene chloride, concentrated under reduced pressure, and purified the crude mixture by silica gel column chromatography (petroleum ether: ethyl acetate = 20 : 1—10 : 1) to afford the desired product **1**.

Benzhydryl cyclopent-1-ene-1-carboxylate (**1a**)



Acid (4 g, 1 equiv.), alcohols (7.2 g, 1.1 equiv.) obtain product 5.9 g, 60% yield, white solid.

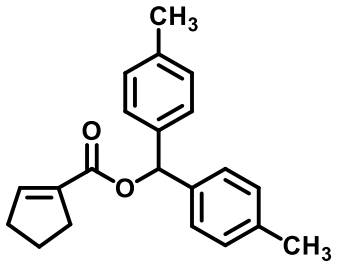
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.23 (m, 10H), 6.96–6.90 (m, 2H), 2.64 (tq, *J*=7.5, 2.4 Hz, 2H), 2.52 (tq, *J*=7.8, 2.6 Hz, 2H), 1.97 (P, *J*=7.7 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.2, 144.6, 140.6, 136.5, 128.5, 127.8, 127.1, 76.4, 33.5, 31.4, 23.1.

HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{19}H_{18}O_2Na$:301.1199, found: 301.1198.

The structure was confirmed by comparison of the NMR spectra with the literature[1].

Di-*p*-tolylmethyl cyclopent-1-ene-1-carboxylate (**1b**)



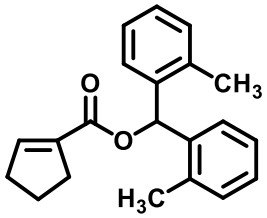
Acid (1 g, 1 equiv.), alcohols (2.16 g, 1.1 equiv.), obtain product 2.11 g, 77% yield, white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (d, *J* = 7.9 Hz, 4H), 7.04 (d, *J* = 7.9 Hz, 4H), 6.80 (d, *J* = 2.5 Hz, 2H), 2.53 (tq, *J* = 7.6, 2.4 Hz, 2H), 2.40 (tq, *J* = 7.8, 2.6 Hz, 2H), 2.22 (s, 6H), 1.91 –1.83 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.3, 144.3, 137.8, 137.4, 136.7, 129.1, 127.0, 76.2, 33.4, 31.4, 23.1, 21.2.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{21}H_{23}O_2$: 314.1621, found: 314.1603.

Di-*o*-tolylmethyl cyclopent-1-ene-1-carboxylate (**1c**)



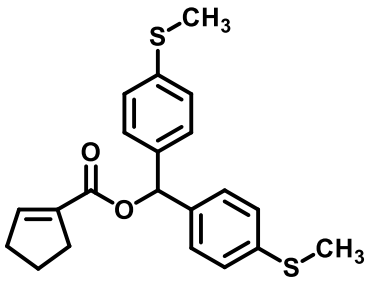
Acid (200 mg, 1 equiv.), alcohols (417 mg, 1.1 equiv.), obtain product 291 mg, 53% yield, white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18–7.06 (m, 9H), 6.90–6.84 (m, 1H), 2.61–2.49 (m, 2H), 2.55–2.39 (m, 2H), 2.29 (s, 6H), 1.99–1.82 (m, 2H).

^{13}C NMR (101 MHz, CDCl3) δ164.3, 144.6, 137.5, 136.4, 130.5, 127.9, 127.4, 126.0, 71.4, 33.5, 31.4, 23.0, 19.3.

HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{21}H_{22}O_2Na$: 329.1512, found: 329.1516.

Bis(4-(methylthio)phenyl)methyl cyclopent-1-ene-1-carboxylate (**1d**)



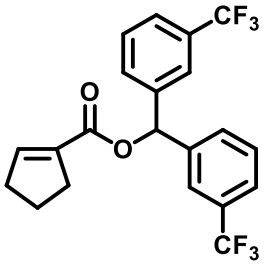
Acid (200 mg, 1 equiv.), alcohols (540 mg, 1.1 equiv.), obtain product 400 mg, 60% yield, yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.18 (m, 8H), 6.90 (t, *J* = 2.3 Hz, 1H), 6.85 (s, 1H), 2.67–2.58 (m, 2H), 2.57–2.48 (m, 2H), 2.46 (s, 6H), 1.97 (p, *J* = 7.6 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.2, 144.7, 138.3, 137.3, 136.5, 127.6, 126.5, 75.8, 33.5, 31.4, 23.1, 15.7.

HRMS (ESI) m/z: $[M+K]^+$ calculated for $C_{21}H_{22}O_2S_2K$: 409.0693, found: 409.0701.

Bis(3-(trifluoromethyl)phenyl)methyl cyclopent-1-ene-1-carboxylate (**1e**)



Acid (100 mg, 1 equiv.), alcohols (315 mg, 1.1 equiv.), obtain product 347 mg, 94% yield, white solid.

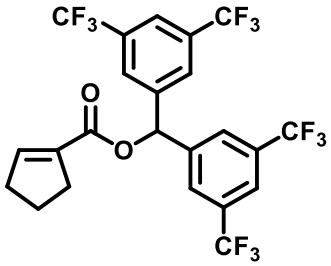
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64–7.45 (m, 8H), 6.99 (s, 1H), 6.96 (q, *J* = 2.2 Hz, 1H), 2.64 (tq, *J* = 7.3, 2.4 Hz, 2H), 2.56 (tq, *J* = 7.7, 2.6 Hz, 2H), 2.00 (p, *J* = 7.7 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.8, 145.7, 140.7, 135.9, 130.5, 129.3, 125.1, 123.8, 123.7, 75.1, 33.6, 31.3, 23.0.

^{19}F NMR (471 MHz, $CDCl_3$) δ -62.6.

HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{21}H_{16}F_6O_2Na$: 437.0947, found: 437.0947.

Bis(3,5-bis(trifluoromethyl)phenyl)methyl cyclopent-1-ene-1-carboxylate (**1f**)



Acid (100 mg, 1 equiv.), alcohols (448 mg, 1.1 equiv.), obtain product 479 mg, 97% yield, white solid.

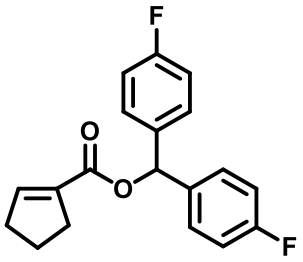
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 2H), 7.79 (s, 4H), 7.07 (s, 1H), 7.01 (t, *J* = 2.3 Hz, 1H), 2.75–2.52 (m, 4H), 2.02 (p, *J* = 7.6 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.3, 146.8, 141.4, 132.7, 132.4, 127.2, 124.3, 122.8, 121.6, 73.9, 33.7, 31.3, 23.0.

^{19}F NMR (471 MHz, $CDCl_3$) δ -62.9.

HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{23}H_{14}F_{12}O_2Na$: 573.0694, found: 573.0677.

Bis(4-fluorophenyl)methyl cyclopent-1-ene-1-carboxylate (**1g**)



Acid (1 g, 1 equiv.), alcohols (2.16 g, 1.1 equiv.), obtain product 2.44g, 87% yield, white solid.

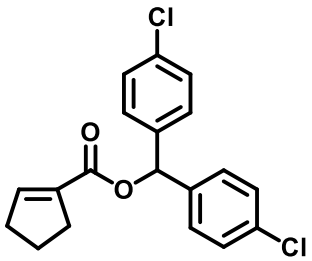
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.28 (m, 4H), 7.07–6.98 (m, 4H), 6.94–6.88 (m, 2H), 2.63 (tq, *J* = 7.4, 2.5 Hz, 2H), 2.53 (tq, *J* = 7.7, 2.7 Hz, 2H), 1.98 (p, *J* = 7.7 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1, 163.6, 161.1, 145.0, 136.3, 136.2(×2), 128.8(×2), 115.6, 115.4, 75.1, 33.5, 31.4, 23.1.

^{19}F NMR (471 MHz, $CDCl_3$) δ -114.2.

HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{19}H_{16}F_2O_2Na$: 337.1011, found: 337.1015.

Bis(4-chlorophenyl)methyl cyclopent-1-ene-1-carboxylate (**1h**)



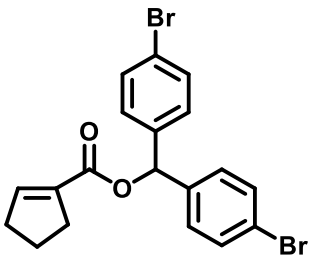
Acid (224 mg, 1 equiv.), alcohols (557 mg, 1.1 equiv.), obtain product 431 mg, 62% yield, white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.23 (m, 8H), 6.94–6.89 (m, 1H), 6.85 (s, 1H), 2.62 (tq, *J* = 7.6, 2.5 Hz, 2H), 2.53 (tq, *J* = 7.8, 2.7 Hz, 2H), 1.98 (p, *J* = 7.7 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.0, 145.2, 138.6, 136.2, 133.9, 128.8, 128.5, 75.1, 33.5, 31.34, 23.1.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{19}H_{17}Cl_2O_2$: 347.0600, found: 347.1264.

Bis(4-bromophenyl)methyl cyclopent-1-ene-1-carboxylate (**1i**)



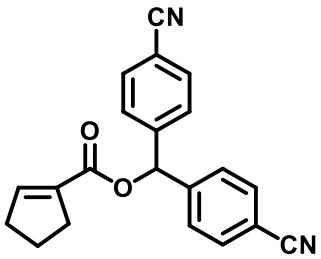
Acid (224 mg, 1 equiv.), alcohols (752 mg, 1.1 equiv.), obtain product 422 mg, 48% yield, white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50–7.43 (m, 4H), 7.24–7.17 (m, 4H), 6.95–6.88 (m, 1H), 6.81 (s, 1H), 2.67–2.58 (m, 2H), 2.57–2.48 (m, 2H), 1.98 (p, *J* = 7.7 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.0, 145.3, 139.0, 136.1, 131.8, 128.8, 122.1, 75.1, 33.5, 31.3, 23.0.

HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{19}H_{16}Br_2O_2Na$: 456.9409, found: 456.9583.

Bis(4-cyanophenyl)methyl cyclopent-1-ene-1-carboxylate (**1j**)



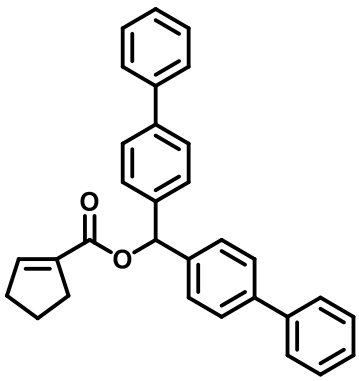
Acid (224 mg, 1 equiv.), alcohols (515 mg, 1.1 equiv.), obtain product 489 mg, 75% yield, white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73–7.59 (m, 4H), 7.47 (d, *J* = 8.1 Hz, 4H), 7.00–6.95 (m, 1H), 6.93 (s, 1H), 2.63 (td, *J* = 7.6, 7.1, 3.7 Hz, 2H), 2.56 (td, *J* =8.2, 5.7, 2.6 Hz, 2H), 2.07–1.96 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6, 146.2, 144.3, 135.6, 132.7, 127.8, 127.7, 118.3, 112.4, 74.9, 33.6, 31.3, 23.0.

HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{21}H_{16}N_2O_2Na$: 351.1104, found: 351.1090.

Di([1,1'-biphenyl]-4-yl)methyl cyclopent-1-ene-1-carboxylate (**1k**)



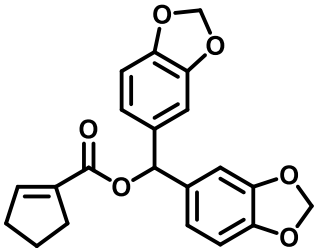
Acid (113 mg, 1 equiv.), alcohols (374 mg, 1.1 equiv.), obtain product 326 mg, 75% yield, white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60–7.54 (m, 8H), 7.52–7.40 (m, 8H), 7.38–7.31(m,2H), 7.02 (s, 1H), 7.00–6.94 (m, 1H), 2.66 (d, *J* = 7.9 Hz, 2H), 2.60–2.50 (m, 2H), 2.00 (p, *J* = 7.6 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.3, 144.8, 140.8, 140.7, 140.5, 139.5, 138.4, 136.5,

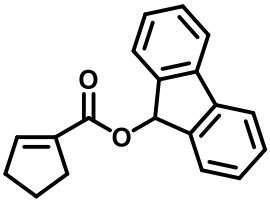
128.8, 128.8, 127.6, 127.5, 127.4, 127.4, 127.3, 127.1, 76.1, 33.5, 31.4, 23.1.
HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{31}H_{26}O_2Na$: 453.1825, found: 453.2727.

Bis(benzo[d][1,3]dioxol-5-yl)methyl cyclopent-1-ene-1-carboxylate (**1l**)



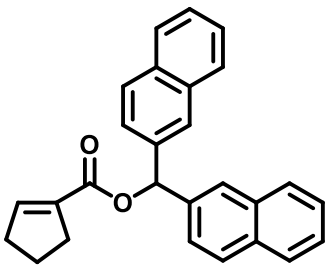
Acid (200 mg, 1 equiv.), alcohols (535 mg, 1.1 equiv.), obtain product 475 mg, 73% yield, white solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (t, J = 2.3 Hz, 1H), 6.83 (d, *J* = 9.7 Hz, 4H), 6.79–6.73 (m, 3H), 5.94 (s, 4H), 2.69–2.57 (m, 2H), 2.56–2.45 (m, 2H), 1.97 (p, *J* = 7.5 Hz, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1, 147.8, 147.2, 144.7, 136.5, 134.6, 120.6, 108.1, 107.5, 101.1, 76.0, 33.5, 31.4, 23.01.
HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{21}H_{18}O_6Na$: 389.0996, found: 389.1006.

9H-fluoren-9-yl cyclopent-1-ene-1-carboxylate (**1m**)



Acid (279 mg, 1 equiv.), alcohols (500 mg, 1.1 equiv.), obtain product 590 mg, 86% yield, oily liquid.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.6 Hz, 2H), 7.63 (d, *J* = 7.5 Hz, 2H), 7.44 (t, *J* = 10 Hz, 2H), 7.37–7.39 (m, 2H), 6.92 (s, 1H), 6.87 (p, *J* = 2.3 Hz, 1H), 2.73–2.64 (m, 2H), 2.58–2.48 (m, 2H), 2.01 (p, *J* = 7.7 Hz, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 145.2, 142.4, 141.0, 136.2, 129.4, 127.8, 126.0, 120.0, 74.9, 33.5, 31.5, 23.1.
HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{19}H_{16}O_2Na$: 299.1043, found: 299.1048.

Di(naphthalen-2-yl)methyl cyclopent-1-ene-1-carboxylate (**1n**)



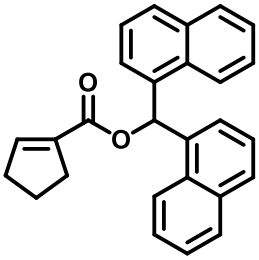
Acid (224 mg, 1 equiv.), alcohols (626 mg, 1.1 equiv.), obtain product 417 mg, 55% yield, white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 2H), 7.86–7.78 (m, 6H), 7.52–7.44 (m, 6H), 7.28 (s, 1H), 6.99 (p, *J* = 2.3 Hz, 1H), 2.74–2.63 (m, 2H), 2.60–2.48 (m, 2H), 1.99 (p, *J* = 7.6 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.3, 144.8, 137.7, 136.5, 133.1, 133.0, 128.4, 128.2, 127.7, 126.3, 126.2, 125.2, 76.6, 33.5, 31.4, 23.1.

HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{27}H_{22}O_2Na$: 401.1512, found: 401.1529.

Di(naphthalen-1-yl)methyl cyclopent-1-ene-1-carboxylate (**1o**)



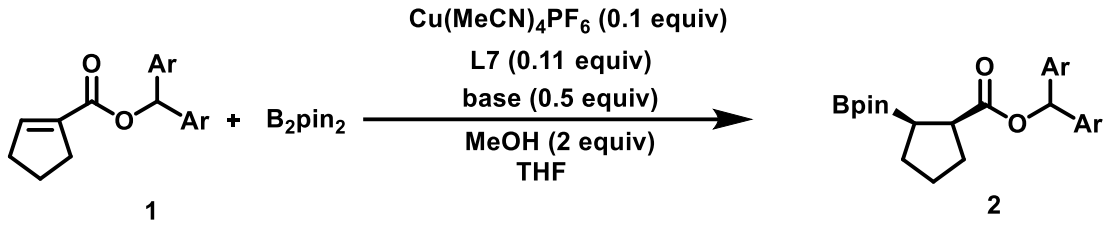
Acid (224mg, 1 equiv.), alcohols (626 mg, 1.1 equiv.), obtain product 430 mg, 57% yield, white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 8.06–7.98 (m, 2H), 7.93–7.81 (m, 4H), 7.53 – 7.43 (m, 4H), 7.43–7.36 (m, 4H), 6.93–6.86 (m, 1H), 2.68–2.57 (m, 2H), 2.55–2.44 (m, 2H), 1.95 (p, *J* = 7.7 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.4, 145.1, 136.2, 135.3, 133.8, 131.2, 123.0, 128.8, 126.7, 125.8, 125.3, 123.7, 70.5, 33.5, 31. 5, 23.0.

HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{27}H_{22}O_2Na$: 401.1512, found: 401.1521.

4. General procedure of the hydroboration of cyclopentenylcarboxyesters



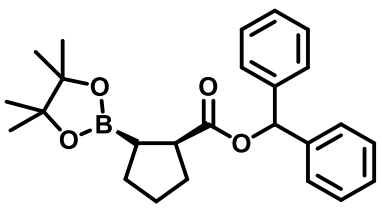
Scheme S2 General procedure for the synthesis of **2**

Condition a: A Schlenk tube was charged with substrate **1** (0.1 mmol, 1 equiv.), $Cu(MeCN)_4PF_6$ (3.73 mg, 0.01 mmol, 10 mol%), B_2pin_2 (27.93 mg, 0.11 mmol, 1.1 equiv.), *t*BuOK (5.61 mg, 0.05 mmol, 0.5 equiv.) and **L7** (6.54mg, 0.011mmol, 11mol%), capped, and purged with nitrogen, cooled at -78°C before Tetrahydrofuran (0.4 mL) and methanol (8μL, 2 equiv.) was added. Then, the reaction mixture allowed to stir for 43 h at -50°C. After full consumption of the starting material, the reaction mixture was diluted with dichloromethane, filtered by diatomaceous earth, concentrated under reduced pressure, and purified the crude mixture by silica gel column chromatography (petroleum ether: ethyl ether = 20 : 1) to afford the desired product **2**.

Condition b: A Schlenk tube was charged with substrate **1** (0.1 mmol, 1 equiv.), $Cu(MeCN)_4PF_6$ (3.73 mg, 0.01 mmol, 10 mol%), B_2pin_2 (27.93 mg, 0.11 mmol, 1.1 equiv.), *t*BuOK (5.61 mg, 0.05 mmol, 0.5 equiv.) and **L7** (6.54mg, 0.011mmol, 11mol%), capped, and purged with nitrogen, cooled at -78°C before Tetrahydrofuran (0.4 mL) and methanol (8μL, 2 equiv.) was added. Then, the reaction mixture allowed to stir for 43 h at -60°C.

Condition c: A Schlenk tube was charged with substrate **1** (0.1 mmol, 1 equiv.), $Cu(MeCN)_4PF_6$ (3.73 mg, 0.01 mmol, 10 mol%), B_2pin_2 (27.93 mg, 0.11 mmol, 1.1 equiv.), *t*AmONa (5.51 mg, 0.05 mmol, 0.5 equiv.) and **L7** (6.54mg, 0.011mmol, 11mol%), capped, and purged with nitrogen, cooled at -78°C before Tetrahydrofuran (0.4 mL) and methanol (8μL, 2 equiv.) was added. Then, the reaction mixture allowed to stir for 43 h at -60°C.

Benzhydryl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentane-1-carboxylate (**2a**)[a]



Under the **condition a**, 0.1 mmol scale, starting material (**1a**) 30 mg, obtain product 28 mg, 64% yield, white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.19 (m, 65H), 7.26 (m, 3H), 6.86 (s, 1H, minor diastereomer), 6.82 (s, 5H, major diastereomer), 3.16 (m, 5H, major diastereomer), 2.96 (q, *J* = 8.2 Hz, 1H, minor diastereomer), 2.06–1.48 (m, 36H), 1.18 (s, 12H), 1.14 (s, 30H), 1.07 (s, 30H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.9, 140.6 (×2), 128.4 (×2), 128.3 (×2), 127.7 (×2), 127.3, 127.1 (×3), 83.2, 83.0, 76.6, 46.6, 31.2, 27.4, 25.7, 24.8, 24.7, 24.6 (×2).

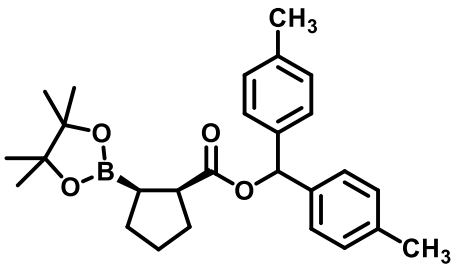
HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{25}H_{31}BO_4Na$: 428.2244, found: 428.2234.

The enantiomeric ratio was measured by HPLC analysis using following parameters: Daicel Chiralcel OD column: *n*Hexane:*i*PrOH = 99.7:0.3, flow rate 0.4 mL/ min, t_{major} = 23.7 min, t_{minor} = 21.1, 26.6, 29.5 min.

$[\alpha]_D^{25}$ = 5.75 (c 0.8, THF)

The structure was confirmed by comparison of the NMR spectra with the literature[1].

Di-*p*-tolylmethyl (1S,2R)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentane-1-carboxylate (**2b**)[b]



Under the **condition b**, 0.1 mmol scale, starting material (**1b**) 30.641 mg, obtain product 32.3mg, 74% yield, white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15–7.12 (m, 25H), 7.05–7.02 (m, 25H), 6.72 (s, 1H, minor diastereomer), 6.69 (s, 5H, major diastereomer), 3.10–3.00 (m, 5H, major diastereomer), 2.92–2.78 (m, 1H, minor diastereomer), 2.23 (s, 36H), 1.95–1.40 (m, 36H), 1.11 (s, 12H), 1.08 (s, 30H), 1.01 (s, 30H).

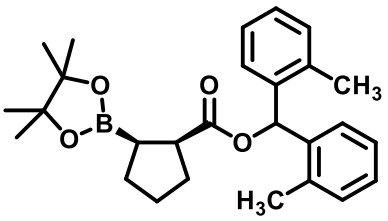
^{13}C NMR (101 MHz, $CDCl_3$) δ 175.9, 175.5,137.9,137.8, 137.3 (×2), 129.1,129.0, 127.2, 127.0(×2), 126.9, 83.2, 83.0, 76.4, 46.7, 31.2, 30.7, 29.7, 28.9, 27.4, 26.7, 25.7, 24.8, 24.7, 24.6 (×2), 21.1.

HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{27}H_{35}BO_4Na$: 456.2557, found: 456.2514.

The enantiomeric ratio was measured by HPLC analysis using following parameters: Daicel Chiralcel OD column: *n*Hexane:*i*PrOH = 99.7:0.3, flow rate 0.4 mL/ min, t_{major} = 34.3 min, t_{minor} = 37.6, 41.0, 43.1 min.

$[\alpha]_D^{25}$ = 9.18 (c 1.7, THF)

Di-*o*-tolylmethyl (1S,2R)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentane-1-carboxylate (**2c**)[b]



Under the **condition b**, 0.1 mmol scale, starting material (**1c**) 30.641 mg, obtain product 38.8 mg, 89% yield, white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15–7.00 (m, 63H), 3.14–3.02 (m, 6H, major diastereomer), 2.92–2.80(m, 1H, minor diastereomer), 2.22 (s,21H), 2.18 (s,21H), 1.98–1.39 (m, 36H), 1.08 (s, 36H), 1.04 (s, 12H), 0.98 (s, 36H).

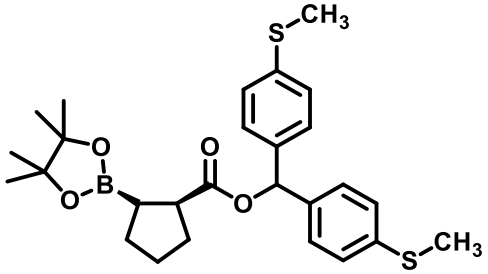
^{13}C NMR (101 MHz, $CDCl_3$) δ 175.9, 175.3,137.5,137.4, 136.4, 136.3, 130.5,130.4, 127.9, 127.7, 127.2, 125.9, 83.2, 83.0, 71.6, 71.5, 46.7, 46.5, 31.7,31.5, 30.7, 29.7, 28.9, 27.3, 26.6, 25.6, 24.7, 24.6, 19.4, 19.2.

HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{27}H_{35}BO_4Na$:456.2557, found: 456.2576.

The enantiomeric ratio was measured by HPLC analysis using following parameters: Daicel Chiralcel AD column: *n*Hexane:*i*PrOH = 99:1, flow rate 0.3 mL/ min, t_{major} = 19.0 min, t_{minor} = 28.0 min. Daicel Chiralcel IC column: *n*Hexane:*i*PrOH = 99.7:0.3, flow rate 0.5 mL/ min, t_{major} = 11.2 min, t_{minor} = 12.8 min.

$[\alpha]_D^{25}$ = 9.82 (c 1.65, THF)

Bis(4-(methylthio)phenyl)methyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentane-1-carboxylate (**2d**)[b]



Under the **condition b**, 0.1 mmol scale, starting material (**1n**) 37.05 mg, obtain product 40 mg, 80% yield, white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ7.32–7.15 (m, 36H), 6.77 (s, 1H, minor diastereomer), 6.73 (s, 3H, major diastereomer), 3.12 (td, *J* = 8.3, 4.9 Hz, 3H, major diastereomer), 2.92 (q, *J* = 8.3 Hz, 1H, minor diastereomer), 2.46 (q, *J* = 1.5 Hz, 24H), 2.03–1.44 (m, 24H), 1.21 –1.02 (m, 48H).

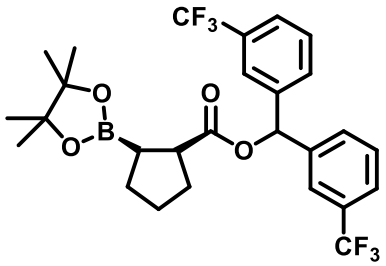
^{13}C NMR (101 MHz, $CDCl_3$) δ175.9, 140.6, 138.0 (×2), 137.4, 137.3, 127.8, 127.7, 127.6 (×2), 127.0, 126.7, 126.5 (×2), 83.2, 83.1, 75.9, 75.5, 46.6, 31.2, 27.4, 25.7, 24.8, 24.7, 24.6 (×2), 15.9, 15.8.

HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{27}H_{35}BO_4S_2Na$: 520.1998, found: 520.1990.

The enantiomeric ratio was measured by HPLC analysis using following parameters: Daicel Chiralcel IC column: *n*Hexane:*i*PrOH = 99:1, flow rate 0.5 mL/ min, t_{major} = 15.6

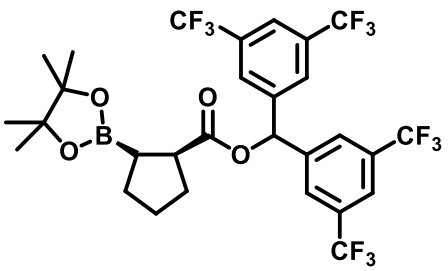
min, t_{minor} = 16.0, 25.4, 26.9 min.
$[\alpha]_D^{25}$ = 6.18 (c 0.5, THF)

Bis(3-(trifluoromethyl)phenyl)methyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentane-1-carboxylate (**2e**)[b]



Under the **condition b**, 0.1 mmol scale, starting material (**1d**) 55.034 mg, obtain product 50.9mg, 94% yield, white solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66–7.44 (m, 40H), 6.92 (s, 1H, minor diastereomer), 6.87 (s, 4H, major diastereomer), 3.22–3.10 (m, 4H, major diastereomer), 3.02–2.90 (m, 1H, minor diastereomer), 2.08–1.50 (m, 30H), 1.17 (s, 12H), 1.12(s, 24H), 1.01 (s, 24H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 175.6, 140.8,130.6, 130.4, 129.2(×2), 125.2(×3), 124.1(×2), 123.6(×2), 83.3, 83.1, 75.2, 46.4, 31.5, 31.1, 29.7, 28.9, 27.4, 26.7, 25.6, 24.8, 24.7, 24.6 (×2), 24.5.
^{19}F NMR (471 MHz, $CDCl_3$) δ -62.6.
HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{27}H_{29}BF_6O_4Na$: 564.1992, found: 564.1984.
The enantiomeric ratio was measured by HPLC analysis using following parameters: Daicel Chiralcel AD column: *n*Hexane:*i*PrOH = 98:2, flow rate 0.4 mL/ min, t_{major} = 10.3 min, t_{minor} = 10.8, 13.4, 17.6 min.
$[\alpha]_D^{25}$ = 8.0 (c 1.3, THF)

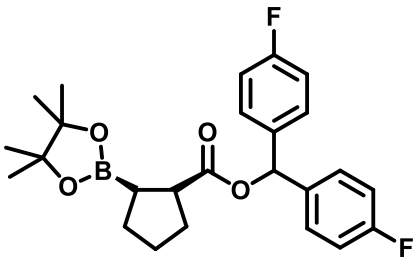
Bis(3,5-bis(trifluoromethyl)phenyl)methyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentane-1-carboxylate (**2f**)[c]



Under the **condition c**, 0.1 mmol scale, starting material (**1e**) 30.641 mg, obtain product 60.1mg, 88% yield, white solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, 14H), 7.71(d, 22H), 6.92 (s, 1H, minor diastereomer), 6.87 (s, 5H, major diastereomer), 3.16–3.06 (m, 5H, major

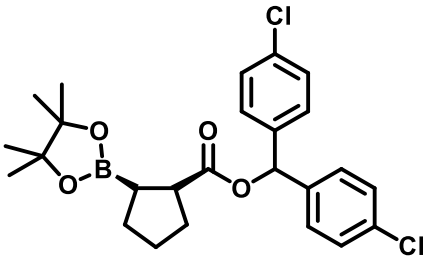
diastereomer), 2.95–2.86 (m, J = 8.5 Hz, 1H, minor diastereomer), 2.04–1.37(m, 36H), 1.09 (s, 12H), 1.03 (s, 30H), 0.97 (s, 30H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 175.4, 174.9, 141.5(×3), 141.4, 132.9, 132.8,132.6, 132.5, 132.3 (×2), 132.1,132.0, 127.5(×2), 127.0(×2), 126.2, 124.0, 122.7(×3), 122.6, 121.9, 119.7, 83.4, 83.2, 74.1, 74.0, 46.2, 30.9, 30.6, 29.7, 28.9, 27.5, 26.8, 25.6, 24.6, 24.5(×2), 24.4.
^{19}F NMR (471 MHz, $CDCl_3$) δ -62.9 (ddd, *J* = 29.3, 18.9, 8.3 Hz).
HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{29}H_{27}BF_{12}O_4Na$: 700.1739, found: 700.1731.
The enantiomeric ratio was measured by HPLC analysis using following parameters: Daicel Chiralcel OD column: *n*Hexane:*i*PrOH = 99.88:0.12, flow rate 0.4 mL/ min, t_{major} = 17.3 min, t_{minor} = 13.5, 13.9, 14.4 min.
$[\alpha]_D^{25}$ = 4.25 (c 0.8, THF)

Bis(4-fluorophenyl)methyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentane-1-carboxylate (**2g**)[b]



Under the **condition b**, 0.1 mmol scale, starting material (**1f**) 31.433 mg, obtain product 43.7 mg, 90% yield, white solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27–7.16 (m, 20H), 7.00–6.87 (m, 20H), 6.74 (s, 1H, minor diastereomer), 6.70 (s, 4H, major diastereomer), 3.12–3.00 (m, 4H, major diastereomer), 2.92–2.78 (m, 1H, minor diastereomer), 1.97–1.41 (m, 30H), 1.10 (s, 12H), 1.08 (s, 24H), 1.01 (s, 24H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 175.8,175.3, 163.5, 161.1, 136.3(×2), 136.2(×2), 129.0(×2), 128.9(×2), 128.8 (×2), 115.5 (×2), 115.4, 115.3(×3), 115.2, 83.3, 83.1, 75.2, 46.6, 46.5, 31.1, 27.4, 26.7, 25.7, 24.8, 24.7, 24.6 (×2).
^{19}F NMR (471 MHz, $CDCl_3$) δ -114.4 (d, *J* = 87.6 Hz).
HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{25}H_{29}BF_2O_4Na$: 464.2055, found: 464.2056.
The enantiomeric ratio was measured by HPLC analysis using following parameters: Daicel Chiralcel OD column: *n*Hexane:*i*PrOH = 99.85:0.15, flow rate 0.4 mL/ min, t_{major} = 49.2 min, t_{minor} = 38.9, 45.6, 57.1 min.
$[\alpha]_D^{25}$ = 6.05 (c 1.69, THF)

Bis(4-chlorophenyl)methyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentane-1-carboxylate (**2h**)[b]



Under the **condition b**, 0.1 mmol scale, starting material (**1g**) 34.724 mg, obtain product 34 mg, 71% yield, white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.22 (m, 54H), 6.78 (s, 1H, minor diastereomer), 6.73 (s, 5H, major diastereomer), 3.22–3.04 (m, 5H, major diastereomer), 2.98–2.82 (m, 1H, minor diastereomer), 2.08–1.48 (m, 36H), 1.18 (s, 12H), 1.15 (s, 30H), 1.08 (s, 30H).

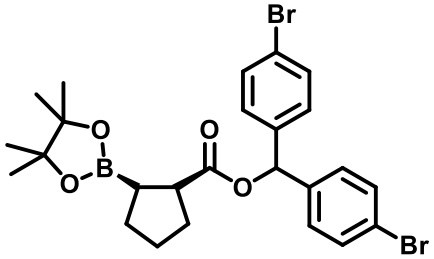
^{13}C NMR (101 MHz, $CDCl_3$) δ 175.7, 175.2, 138.7, 138.6, 133.8 (×2), 128.7 (×2), 128.6 (×2), 128.5(×2), 83.3, 83.1, 75.2, 46.5(×2), 31.1, 27.5, 25.6, 24.8, 24.6.

HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{25}H_{29}BCl_2O_4Na$: 496.1464, found: 496.1477.

The enantiomeric ratio was measured by HPLC analysis using following parameters: Daicel Chiralcel OD column: *n*Hexane:*i*PrOH = 99.85:0.15, flow rate 0.4 mL/ min, t_{major} = 60.8 min, t_{minor} = 48.7, 51.3, 68.7 min.

$[\alpha]_D^{25}$ = 14.6 (c 1, THF)

Bis(4-bromophenyl)methyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentane-1-carboxylate (**2i**)[b]



Under the **condition b**, 0.1 mmol scale, starting material (**1h**) 43.614 mg, obtain product 36 mg, 64% yield, white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50–7.40 (m, 44H), 7.22-7.13 (m, 44H), 6.74 (s, 1H, minor diastereomer), 6.69 (s, 10H, major diastereomer), 3.19–3.04 (m, 10H, major diastereomer), 3.00–2.85 (m, 1H, minor diastereomer), 2.06–1.45 (m, 66H), 1.18 (s, 12H), 1.14 (s, 60H), 1.07 (s, 60H).

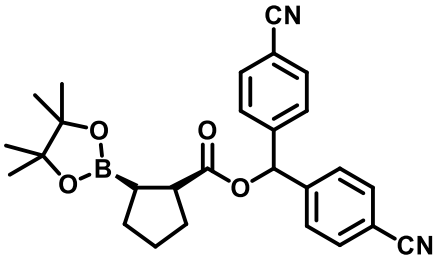
^{13}C NMR (101 MHz, $CDCl_3$) δ 175.7, 139.1 (×2), 131.7, 131.6, 128.9, 128.8, 122.0 (×2), 83.3, 83.1, 75.3, 46.5, 46.4, 31.1, 27.5, 25.6, 24.7, 24.6.

HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{25}H_{29}BBr_2O_4Na$: 584.0454, found: 584.0458.

The enantiomeric ratio was measured by HPLC analysis using following parameters: Daicel Chiralcel OD column: *n*Hexane:*i*PrOH = 99.85:0.15, flow rate 0.4 mL/ min, t_{major} = 76.5 min, t_{minor} = 48.3, 66.9, 90.8 min.

$[\alpha]_D^{25}$ = 14.5 (c 1.7, THF)

Bis(4-cyanophenyl)methyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentane-1-carboxylate (**2j**)[b]



Under the **condition b**, 0.1 mmol scale, starting material (**1i**) 32.837 mg, obtain product 35 mg, 77% yield, white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70–7.61 (m, 39.5H), 7.48–7.39 (m, 37H), 6.85 (s, 1H, minor diastereomer), 6.81 (s, 7.5H, major diastereomer), 3.22–3.06 (m, 7.5H, major diastereomer), 3.01–2.88 (m, 1H, minor diastereomer), 2.07–1.48 (m, 51H), 1.19 (s, 12H), 1.12 (s, 45H), 1.06 (s, 45H).

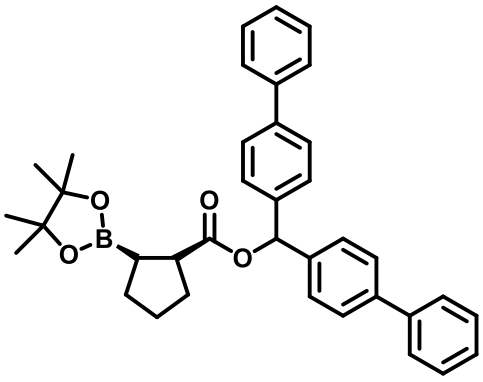
^{13}C NMR (101 MHz, $CDCl_3$) δ 175.5, 144.4, 144.3, 132.6, 132.5, 127.8, 127.7, 118.3, 112.4, 112.3, 83.1, 83.0, 75.0, 46.3, 31.0, 27.5, 25.6, 24.7, 24.6.

HRMS (ESI) m/z: $[M+K]^+$ calculated for $C_{27}H_{29}BN_2O_4K$: 494.1888, found: 494.1879.

The enantiomeric ratio was measured by HPLC analysis using following parameters: Daicel Chiralcel AD column: *n*Hexane:*i*PrOH = 90:10, flow rate 1 mL/ min, t_{major} = 14.2 min, t_{minor} = 21.8, 28.3, 30.0 min.

$[\alpha]_D^{25}$ = 16.35 (c 0.37, THF)

Di([1,1'-biphenyl]-4-yl)methyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentane-1-carboxylate (**2k**)[b]

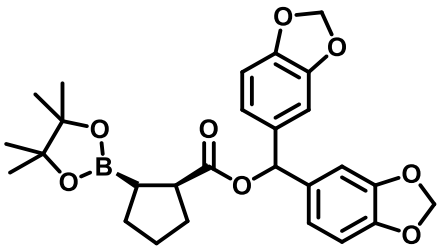


Under the **condition b**, 0.1 mmol scale, starting material (**1m**) 43.06 mg, obtain product 30 mg, 54% yield, white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (dd, 188H), 7.44 (q, 164H),7.38–7.30 (m, 47H), 6.94 (s, 1H, minor diastereomer), 6.90 (s, 20H, major diastereomer), 3.28–3.10 (m, 20H, major diastereomer), 3.06–2.92 (m, 1H, minor diastereomer), 2.11–1.51 (m, 126H),

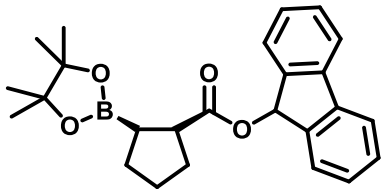
1.11 (t, 252H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 176.0, 140.8,140.7, 139.6, 139.5, 128.8, 127.8, 127.5, 127.4, 127.3, 127.2, 127.1, 83.1, 76.3, 46.6, 31.2, 29.7, 27.5, 25.7, 24.8, 24.6.
HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{37}H_{39}BO_4Na$: 580.2870, found: 580.2863.
The enantiomeric ratio was measured by HPLC analysis using following parameters: Daicel Chiralcel IB column: *n*Hexane:*i*PrOH = 99.7:0.3, flow rate 0.5 mL/ min, t_{major} = 95.4 min, t_{minor} = 82.0, 91.1 min.
$[\alpha]_D^{25}$ = 5.9 (c 1.4, THF)

Bis(benzo[d][1,3]dioxol-5-yl)methyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentane-1-carboxylate (**2l**)[b]



Under the **condition b**, 0.1 mmol scale, starting material (**1o**) 36.637 mg, yield was not measured due to the hydroborylation product is easy to decompose at room temperature.
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86–6.71 (m, 36H), 6.67 (s, 1H, minor diastereomer), 6.64 (s, 4H, major diastereomer), 5.93 (d, *J* = 2.6 Hz, 20H), 3.11 (td, *J* = 8.4, 5.1 Hz, 4H, major diastereomer), 2.91 (q, *J* = 8.3 Hz, 1H, minor diastereomer), 2.06–1.46 (m, 30H), 1.22 –1.09 (m, 60H).
^{13}C NMR (101 MHz, $CDCl_3$) δ175.8, 147.7, 147.7, 147.1, 134.6, 134.5, 120.8, 120.6, 119.8, 108.1, 107.9, 107.8, 107.5, 107.0, 101.1, 101.1, 83.3, 83.1, 76.1, 46.6, 31.1, 27.4, 25.7, 24.8, 24.7, 24.6.
HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{27}H_{32}BO_8$: 495.3177, found: 495.3167.
The enantiomeric ratio was measured by HPLC analysis using following parameters: Daicel Chiralcel IC column: *n*Hexane:*i*PrOH = 95:5, flow rate 0.6 mL/ min, t_{major} = 9.8 min, t_{minor} = 10.2, 13.7, 15.0 min.
$[\alpha]_D^{25}$ = 7.24 (c 0.39, THF)

9H-fluoren-9-yl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentane-1-carboxylate (**2m**)[b]



Under the **condition b**, 0.1 mmol scale, starting material (**1l**) 27.634 mg, obtain product 22.8 mg, 56% yield, white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (dd, 6H), 7.52 (d, 2H),7.49–7.43 (m, 4H), 7.36–7.28 (m, 6H), 7.25–7.15 (m, 6H), 6.74 (s, 1H, minor diastereomer), 6.70 (s, 2H, major diastereomer), 3.12–3.02 (m, 2H, major diastereomer), 2.90–2.77 (m, 1H, minor diastereomer), 1.95–1.42 (m, 18H), 1.20 (s, 23H), 1.01 (s, 13H).

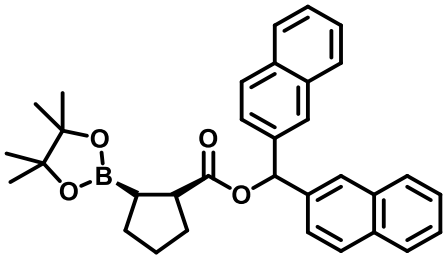
^{13}C NMR (101 MHz, $CDCl_3$) δ 177.7, 177.2, 142.4, 141.0, 129.3 (×2), 127.8, 127.7, 126.0, 125.9, 125.8 (×2), 120.0, 119.9 (×3), 83.2, 75.0, 74.8, 47.0, 46.6, 31.4, 30.5, 28.8, 27.6, 26.5, 25.7, 24.9, 24.9, 24.6, 24.4.

HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{25}H_{29}BO_4Na$: 426.2087, found: 426.2084.

The enantiomeric ratio was measured by HPLC analysis using following parameters: Daicel Chiralcel OD column: *n*Hexane:*i*PrOH = 99:1, flow rate 0.7 mL/ min, t_{major} = 18.4 min, t_{minor} = 20.7, 27.9, 35.5 min.

$[\alpha]_D^{25}$ = 7.68 (c 0.8, THF)

Di(naphthalen-2-yl)methyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentane-1-carboxylate (**2n**)[b]



Under the **condition b**, 0.1 mmol scale, starting material (**1j**) 37.847 mg, obtain product 27.2 mg, 54% yield, white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 30H), 7.72 (m, 90H), 7.75–7.67f (m, 90H), 7.12(s, 1H, minor diastereomer), 7.08 (s, 14H, major diastereomer), 3.23–3.08 (m, 14H, major diastereomer), 3.02–2.91 (m, 1H, minor diastereomer), 2.02–1.89 (m, 90H), 1.01 (s, 90H), 0.92 (s, 90H).

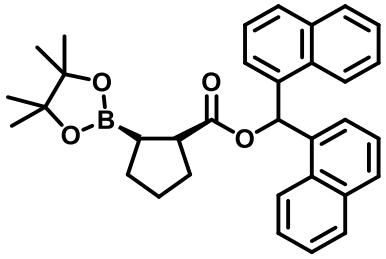
^{13}C NMR (101 MHz, $CDCl_3$) δ 176.0, 137.8, 137.7, 133.1, 133.0, 128.3, 128.2 (×3), 127.7, 127.6, 126.4, 126.2(×2), 126.1, 125.4, 125.2, 83.3, 83.0, 76.8, 46.7, 31.3, 29.7, 27.5, 25.7, 24.7, 24.5.

HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{33}H_{35}BO_4Na$: 528.2557, found:528.2572.

The enantiomeric ratio was measured by HPLC analysis using following parameters: Daicel Chiralcel AD column: *n*Hexane:*i*PrOH = 98:2, flow rate 0.4 mL/ min, t_{major} = 37.4 min, t_{minor} = 33.3 min. Daicel Chiralcel IC column: *n*Hexane:*i*PrOH = 99:1, flow rate 0.5

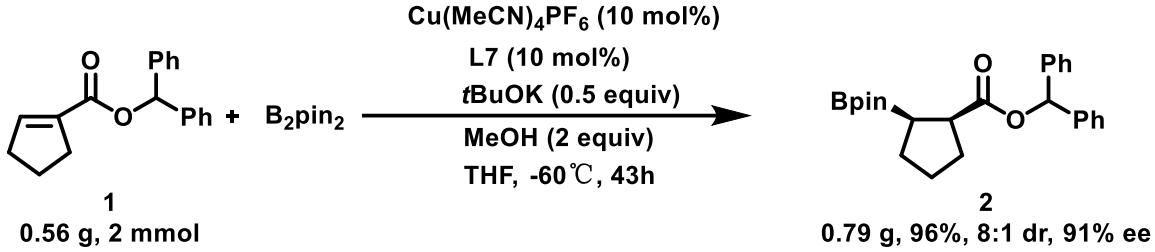
mL/ min, t_{major} = 20.2 min, t_{minor} = 17.5 min.
$[\alpha]_D^{25}$ = 27.86 (c 1.5, THF)

Di(naphthalen-1-yl)methyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentane-1-carboxylate (**2o**)[c]



Under the **condition c**, 0.1 mmol scale, starting material (**1k**) 37.847 mg, obtain product 40.4 mg, 80% yield, white solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H, minor diastereomer), 8.34 (s, 7.5H, major diastereomer), 7.96 (t, 16H), 7.92–7.86 (m, 17H), 7.86–7.79 (m, 19H), 7.54–7.40 (m, 55H), 7.40–7.28 (m, 20H), 3.27–3.15 (m, 7.5H, major diastereomer), 2.98 (q, J = 8.6 Hz, 1H, minor diastereomer), 2.00–1.49 (m, 51H), 1.18–0.99 (m, 102H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 176.2, 135.3, 135.1, 133.9, 133.8, 131.2, 131.1, 128.9, 128.8(×2), 128.7, 126.5, 126.0, 125.9, 125.8, 125.7, 125.3, 125.2, 123.8, 123.5, 83.0, 77.2, 70.8, 46.7, 31.7, 27.2, 25.5, 24.8, 24.6.
HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{33}H_{35}BO_4Na$: 528.2557, found: 528.2521.
The enantiomeric ratio was measured by HPLC analysis using following parameters: Daicel Chiralcel IC column: *n*Hexane:*i*PrOH = 99.4:0.6, flow rate 0.4 mL/ min, t_{major} = 15.8 min, t_{minor} = 17.6, 48.3, 52.0 min.
$[\alpha]_D^{25}$ = 26.84 (c 0.38, THF)

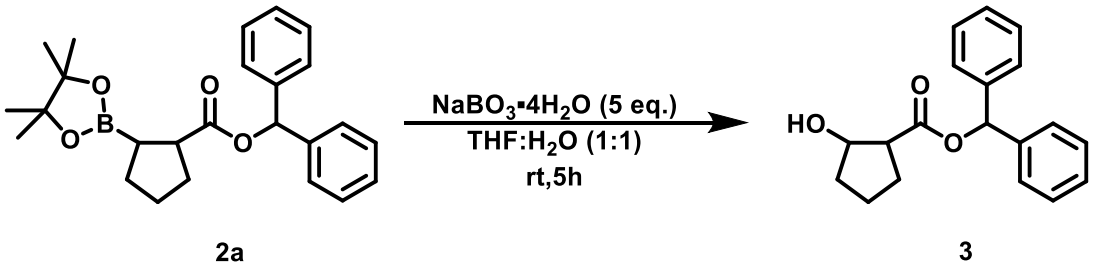
5. Gram scale reaction



Scheme S3 Scale-up reaction

A flask was charged with substrate **1** (2 mmol, 1 equiv.), $Cu(MeCN)_4PF_6$ (74.5 mg, 0.2 mmol, 10 mol%), B_2pin_2 (558.7 mg, 2.2 mmol, 1.1 equiv.), *t*BuOK (112.2 mg, 1 mmol, 0.5 equiv.) and L7 (130.8 mg, 10mol%), capped, and purged with nitrogen, cooled at -78°C before Tetrahydrofuran (6 mL) and methanol (167μL, 2 equiv.) was added. Then, the reaction mixture allowed to stir for 43 h at -60°C. After full consumption of the starting material, the reaction mixture was diluted with dichloromethane, filtered by diatomaceous earth, concentrated under reduced pressure, and purified the crude mixture by silica gel column chromatography (petroleum ether: ethyl ether = 20 : 1) to afford the desired product **2**, white solid.

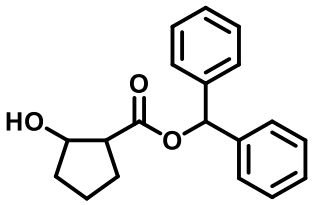
6. Synthetic transformations



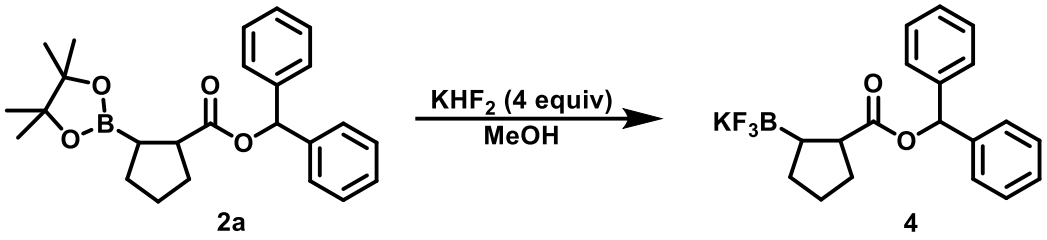
Scheme S4 Synthetic transformations

This reaction was adapted from the literature procedures[1]. A Schlenk tube was charged with **2a** (40.6 mg, 0.1 mmol, 1 equiv.), THF (1 mL), H_2O (1 mL) and $NaBO_3 \bullet 4H_2O$ (76.9 mg, 0.5 mmol, 5 equiv.). The mixture was allowed to stir at room temperature for 5 h. Then the reaction was quenched by saturated aqueous $NaHCO_3$. The mixture was extracted by CH_2Cl_2 three times. The combined organic extracts were then dried over Na_2SO_4. After removal of the solvent, the residue was purified column chromatography on silica gel using PEE/EtOAc (4:1) as eluent to afford the product **3** as colorless oil (27 mg, 90% yield).

benzhydryl 2-hydroxycyclopentane-1-carboxylate (**3**)



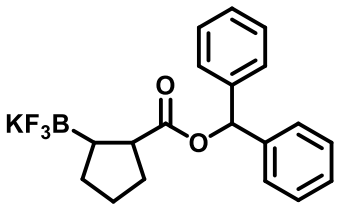
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.27 (m, 11H), 6.89 (s, 1H), 4.40 (q, *J* = 6.4 Hz, 1H), 2.80 (m, 1H), 2.21–1.59 (m, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.9, 140.1, 140.1, 128.6, 128.57, 128.0, 128.0, 127.0, 126.9, 76.3, 52.8, 34.1, 29.7, 27.1, 22.0.
HRMS (ESI) m/z: $[M+K]^+$ calculated for $C_{19}H_{20}O_3K$: 335.1044, found: 335.1059.
The enantiomeric ratio was measured by HPLC analysis using following parameters: Daicel Chiralcel AD column: *n*Hexane:*i*PrOH = 90:10, flow rate 1.0 mL/ min, t_{major} = 12.9 min, t_{minor} = 14.9 min.
$[\alpha]_D^{25}$ = -22.58 (c 0.31, THF)



2a 4

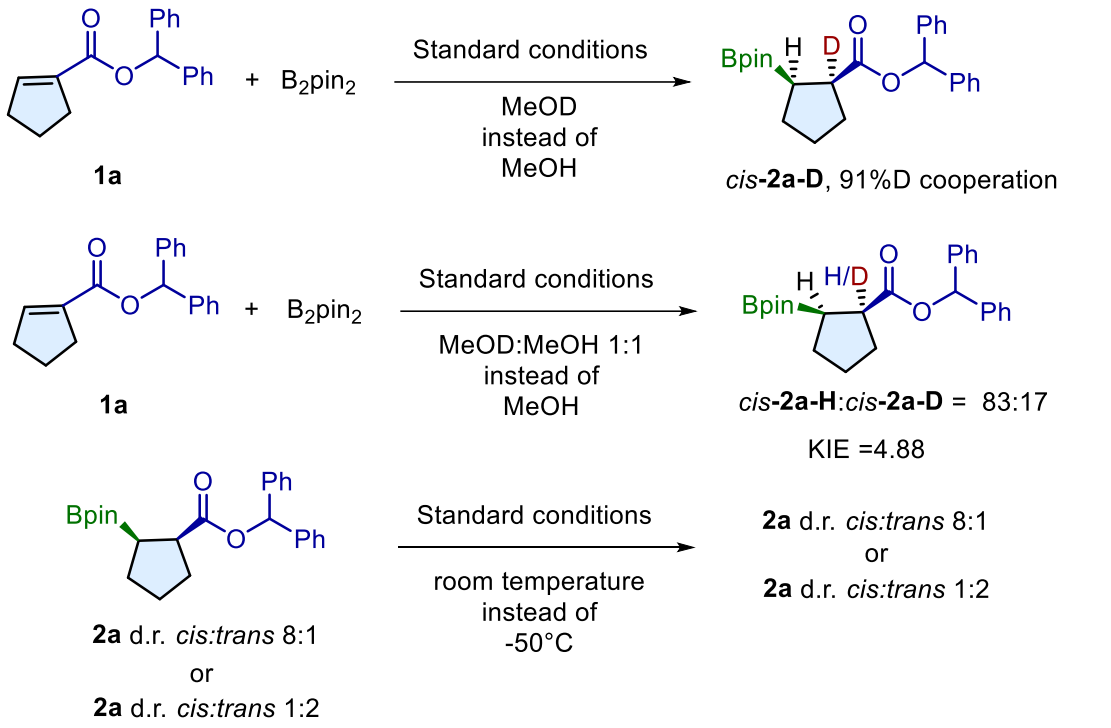
A Schlenk tube was charged with 2a (40.6 mg, 0.1 mmol, 1 equiv.), KHF_2 (31.2 mg, 0.4 mmol, 4 equiv.) and methanol (0.4 mL). The mixture was allowed to stir at room temperature for 48 h. The mixture is diluted with acetone, filtered with diatomaceous earth, and the filtrate evaporates under reduced pressure to produce a white solid (32 mg, 82% yield).

benzhydryl 2-(trifluoro-l4-boraneyl)cyclopentane-1-carboxylate, potassium salt (**4**)



^{1}H NMR (500 MHz, Methanol-d_4) δ 7.46–7.18 (m, 11H), 6.77 (d, *J* = 10.7 Hz, 1H), 2.94 –2.70 (m, 1H), 1.99–1.46 (m, 6H).
^{13}C NMR (101 MHz, Methanol-d_4) δ 180.1, 180.0, 142.5, 142.4, 142.3, 142.3, 129.5, 129.5, 129.4, 129.4, 129.3, 128.8, 128.8, 128.7, 128.7, 128.3, 128.2, 128.1, 128.0, 127.8, 78.1, 77.9, 48.4, 32.9, 32.0, 31.2, 30.9, 30.1, 29.0, 28.2, 26.7, 25.2.
HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{19}H_{19}BF_3KO_2Na$: 409.0963, found: 409.0983.

7.Control experiments



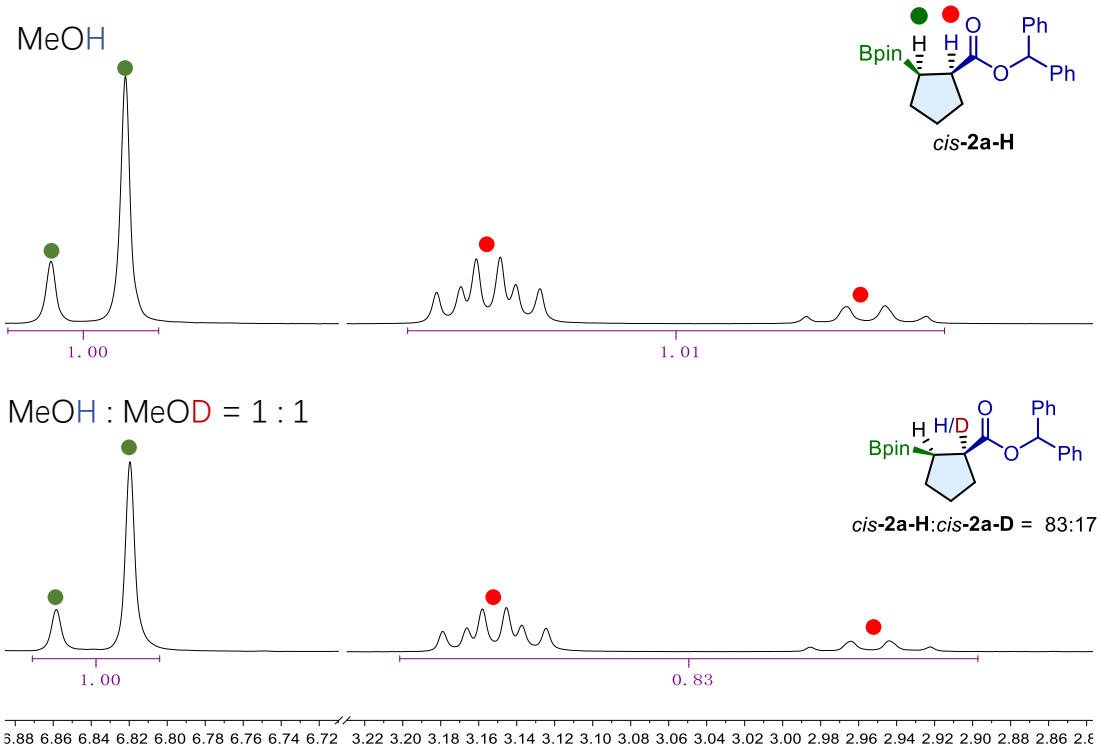


Figure S2 control experiments

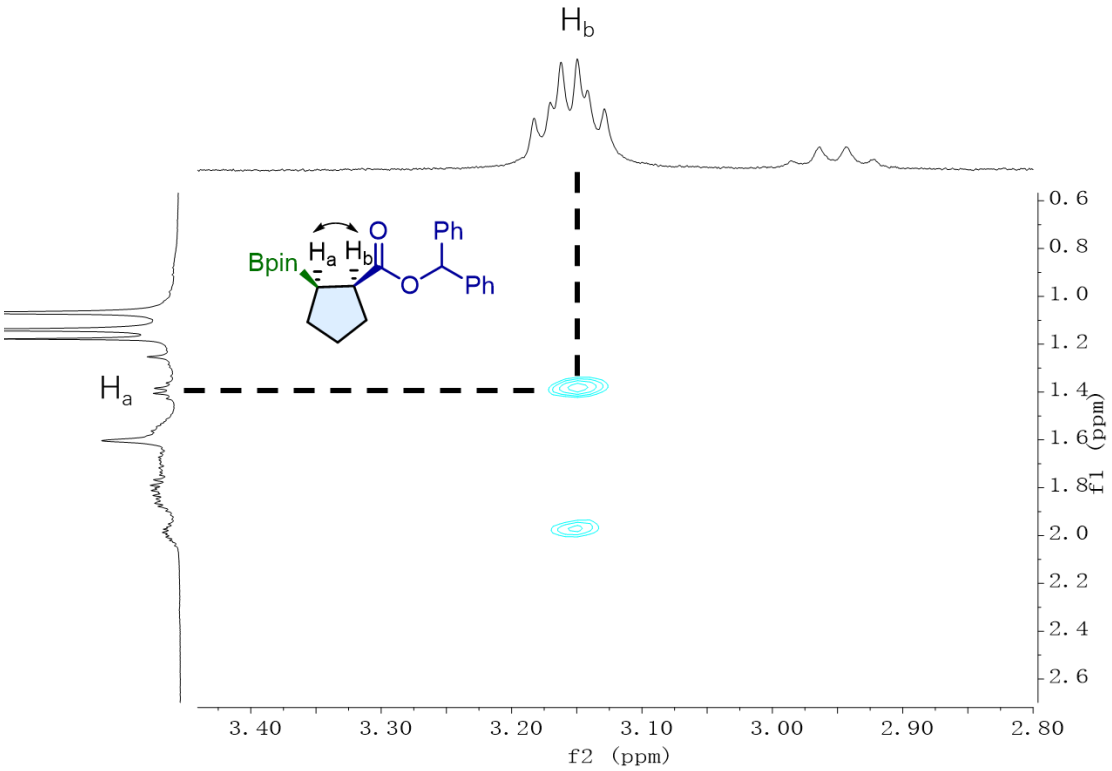


Figure S3. NOE interactions of *cis*-**2a**

8.X-Ray analysis

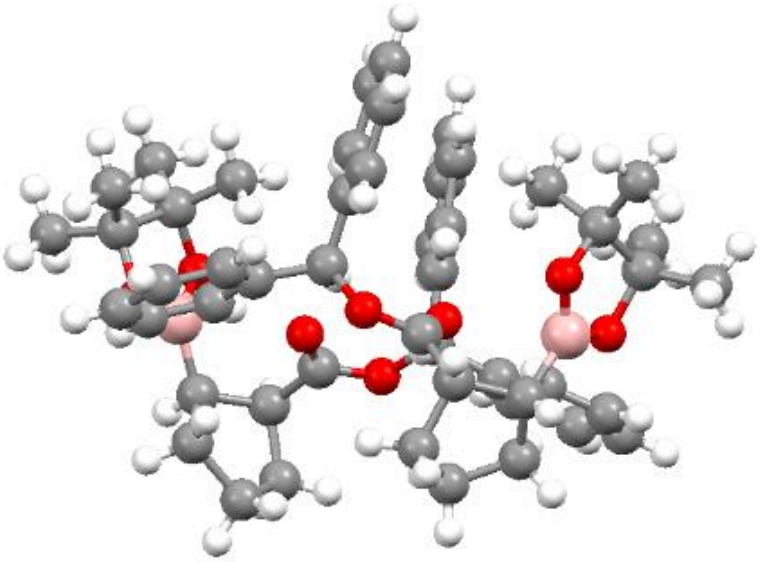


Figure S4. Single-crystal X-Ray diffraction of **2a** (dimer)

Table S2 Crystal data and structure refinement

Identification code	cu_230831LU_LGPZ257259_0m
Empirical formula	$C_{25}H_{31}BO_4$
Formula weight	406.31
Temperature/K	193.00
Crystal system	tetragonal
Space group	$P4_3$
a/Å	10.51710(10)
b/Å	10.51710(10)
c/Å	41.3028(9)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	4568.48(13)
Z	8
ρ_{calc}g/cm^3	1.181
μ/mm^{-1}	0.617
F(000)	1744.0
Crystal size/mm^3	0.13 × 0.12 × 0.1
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	8.406 to 159.616
Index ranges	-12 ≤ h ≤ 13, -13 ≤ k ≤ 13, -51 ≤ l ≤ 45
Reflections collected	106323

Independent reflections	9443 [R_{int} = 0.0466, R_{sigma} = 0.0194]
Data/restraints/parameters	9443/1/549
Goodness-of-fit on F^2	1.035
Final R indexes [I>=2σ (I)]	R_1 = 0.0349, wR_2 = 0.0901
Final R indexes [all data]	R_1 = 0.0365, wR_2 = 0.0915
Largest diff. peak/hole / e $Å^{-3}$	0.18/-0.22
Flack parameter	0.02(3)

Table S3 Fractional Atomic Coordinates (×10^4) and Equiv.alent Isotropic Displacement Parameters ($Å^2$×10^3) for cu_230831LU_LGPZ257259_0m. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O4	10232.0(12)	5784.5(13)	4905.2(3)	32.1(3)
O3	9020.4(14)	7270.4(15)	4665.1(4)	40.1(3)
O8	4464.4(13)	6854.5(13)	4737.1(4)	36.4(3)
O2	10964.0(14)	9518.9(13)	4524.2(4)	37.2(3)
O1	9453.7(14)	9755.8(13)	4131.7(4)	38.4(3)
O6	3600.8(14)	5073.8(15)	5586.3(3)	40.1(3)
O7	5728.2(15)	5816.8(15)	5086.0(4)	45.1(4)
O5	5262.1(18)	3736.9(18)	5670.4(4)	51.6(4)
C14	9969.8(17)	6628.3(17)	4668.9(4)	28.2(3)
C7	9268.7(17)	5662.6(18)	5156.5(5)	29.8(4)
C39	4804.3(17)	5838.5(18)	4912.8(4)	29.6(4)
C19	10684.9(17)	7608.9(17)	4145.8(4)	27.8(3)
C6	9476.7(18)	4397.3(18)	5322.6(5)	31.1(4)
C33	4801(2)	8799.7(19)	5042.5(5)	35.6(4)
C44	4167(2)	3663.0(18)	5103.1(5)	33.5(4)
C32	5271.1(19)	7984.9(19)	4764.7(5)	35.2(4)
C40	3919.5(18)	4734.1(18)	4856.3(4)	30.5(4)
C15	10997.1(18)	6639.2(17)	4413.5(4)	28.7(4)
C31	5241.3(19)	8616.1(18)	4436.5(5)	33.7(4)
C9	10503(2)	7159(2)	5522.2(6)	40.1(5)
C48	4119(2)	5448(2)	5899.4(5)	40.0(5)
C11	9416(2)	8630(2)	5870.3(5)	39.9(4)
C5	10683(2)	3939(2)	5389.6(5)	37.9(4)
C8	9351.9(18)	6744.5(18)	5395.3(4)	30.2(4)
C10	10533(2)	8091(2)	5758.7(6)	42.1(5)
C34	5686(2)	9434(2)	5234.4(6)	45.4(5)
C18	9710(2)	6904.2(18)	3931.8(5)	33.5(4)
C12	8267(2)	8234(2)	5743.9(6)	47.7(5)
C30	6361(2)	8733(2)	4263.8(5)	40.7(5)
C13	8240(2)	7300(2)	5504.2(6)	40.8(5)
C45	4980(3)	4307(2)	5985.9(5)	48.4(6)

Atom	*x*	*y*	*z*	U(eq)
C28	5248(3)	9670(2)	3818.0(6)	45.6(5)
C29	6360(2)	9263(2)	3957.2(6)	47.2(5)
C16	11030(2)	5364.9(19)	4231.8(5)	39.2(4)
C23	10319(2)	10716(2)	4598.3(6)	43.4(5)
C38	3516(2)	8955(3)	5112.0(6)	48.6(5)
C20	9648(2)	11022(2)	4272.4(6)	43.2(5)
C35	5282(3)	10203(3)	5490.0(7)	56.1(7)
C3	9783(3)	2146(2)	5664.5(6)	57.8(7)
C1	8422(2)	3722(2)	5431.0(6)	46.2(5)
B1	10325(2)	8969(2)	4273.9(5)	29.3(4)
C4	10838(3)	2813(2)	5560.0(6)	48.6(5)
C43	5212(3)	2827(2)	4947.2(6)	49.2(6)
C41	4219(2)	4113(2)	4527.4(5)	41.0(5)
C26	4114(2)	9053(3)	4299.1(6)	49.9(6)
B2	4383(2)	4168(2)	5457.2(5)	32.2(4)
C37	3130(3)	9728(3)	5364.3(7)	56.6(6)
C2	8579(3)	2607(3)	5602.0(8)	61.7(7)
C27	4124(2)	9559(3)	3988.6(7)	54.2(6)
C17	10027(3)	5485(2)	3973.1(8)	62.5(8)
C24	11312(3)	11672(3)	4703.1(8)	65.3(8)
C21	10498(3)	11736(2)	4035.1(7)	62.2(7)
C49	3025(3)	5667(4)	6131.3(7)	79.7(11)
C36	4008(3)	10344(3)	5553.9(7)	58.0(7)
C42	5329(3)	3254(3)	4598.2(7)	66.4(8)
C22	8376(3)	11686(3)	4304.1(10)	73.8(9)
C25	9405(4)	10431(3)	4872.7(8)	68.4(8)
C50	4798(5)	6681(3)	5844.7(9)	89.9(13)
C46	4329(6)	3278(3)	6178.6(8)	101.3(16)
C47	6229(4)	4666(6)	6144.4(10)	109.4(19)

Table S4 Anisotropic Displacement Parameters ($Å^2×10^3$) for cu_230831LU_LGPZ257259_0m. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O4	31.9(7)	38.1(7)	26.1(7)	5.0(5)	2.7(5)	4.8(5)
O3	36.9(7)	46.7(8)	36.8(8)	7.7(6)	3.1(6)	13.6(6)
O8	37.2(7)	31.0(7)	41.1(8)	8.1(6)	-10.2(6)	-4.8(5)
O2	41.4(8)	32.9(7)	37.2(8)	-6.3(6)	-6.4(6)	1.8(6)
O1	42.3(8)	29.0(7)	44.1(8)	-5.5(6)	-10.4(6)	6.5(6)
O6	40.5(8)	52.7(9)	27.0(7)	-3.4(6)	-5.8(6)	8.8(7)
O7	44.0(8)	45.7(8)	45.5(9)	16.2(7)	-16.9(7)	-9.7(7)
O5	63.3(11)	62.6(10)	28.8(8)	-4.7(7)	-6.9(7)	27.7(9)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C14	31.6(9)	29.9(8)	23.1(8)	-1.3(6)	-3.1(7)	0.8(7)
C7	26.4(8)	36.4(9)	26.7(9)	1.0(7)	2.3(7)	0.4(7)
C39	32.0(9)	31.2(9)	25.6(9)	4.2(7)	-1.5(7)	-1.9(7)
C19	30.7(9)	27.5(8)	25.2(8)	0.8(6)	1.3(7)	0.4(7)
C6	36.1(9)	32.5(9)	24.6(9)	-3.5(7)	3.1(7)	-3.8(7)
C33	43.0(11)	29.8(9)	34.1(10)	8.8(7)	-6.8(8)	-4.7(8)
C44	43.0(10)	30.2(9)	27.3(9)	4.8(7)	-0.1(7)	-1.4(8)
C32	33.0(9)	33.0(9)	39.7(11)	8.4(8)	-7.4(8)	-6.2(8)
C40	33.5(9)	33.0(9)	25.1(9)	2.4(7)	-2.4(7)	-2.7(7)
C15	30.8(9)	29.3(8)	26.0(9)	1.3(7)	-0.1(7)	3.0(7)
C31	35.6(10)	30.9(9)	34.6(10)	3.4(7)	-4.2(8)	-2.8(7)
C9	30.7(10)	45.9(11)	43.7(12)	-7.7(9)	2.6(8)	-0.3(8)
C48	42.8(11)	51.0(12)	26.2(10)	-2.9(8)	-5.3(8)	5.5(9)
C11	53.2(12)	33.3(10)	33.1(10)	-1.3(8)	0.1(9)	-0.2(9)
C5	41.1(11)	35.8(10)	36.7(11)	5.3(8)	2.4(8)	1.3(8)
C8	31.5(9)	32.2(9)	26.9(9)	4.1(7)	0.8(7)	2.1(7)
C10	41.2(11)	44.2(12)	41.0(12)	-3.9(9)	-2.7(9)	-9.2(9)
C34	50.9(13)	41.0(12)	44.4(12)	8.3(9)	-14.2(10)	-8.1(10)
C18	39.4(10)	33.0(9)	28.2(9)	-0.5(7)	-4.2(7)	-0.7(8)
C12	42.9(12)	53.3(13)	46.7(14)	-13.5(10)	1.5(9)	11.5(10)
C30	37.1(10)	46.8(12)	38.1(11)	1.4(9)	-2.5(8)	3.3(9)
C13	32.6(10)	48.3(12)	41.5(12)	-8.4(9)	-2.0(8)	5.0(9)
C45	60.7(14)	58.8(14)	25.7(10)	-1.8(9)	-6.8(9)	20.1(12)
C28	61.0(14)	40.5(11)	35.3(11)	7.8(9)	0.2(10)	-0.7(10)
C29	45.2(12)	58.8(14)	37.6(12)	1.9(10)	6.7(9)	-1.7(10)
C16	55.8(12)	28.9(9)	32.8(10)	-1.0(7)	3.9(9)	9.7(9)
C23	55.4(13)	33.5(10)	41.2(12)	-10.8(8)	0.4(9)	1.8(9)
C38	46.3(12)	54.2(13)	45.3(13)	0.0(10)	-3.6(10)	-6.3(10)
C20	54.9(13)	29.0(10)	45.8(12)	-8.5(8)	-3.2(10)	8.3(9)
C35	77.2(19)	47.0(13)	44.0(14)	0.5(10)	-18.2(12)	-12.1(12)
C3	104(2)	28.9(10)	40.2(13)	3.1(9)	11.1(13)	-5.9(12)
C1	43.6(12)	47.6(12)	47.5(13)	-4.7(10)	8.5(10)	-12.8(10)
B1	30.7(10)	27.3(9)	29.9(10)	0.0(8)	1.1(8)	-0.6(8)
C4	68.1(16)	36.9(11)	40.9(12)	3.5(9)	1.0(11)	9.3(10)
C43	66.5(15)	45.6(12)	35.6(12)	-2.1(9)	-3.9(10)	21.7(11)
C41	56.6(13)	40.1(11)	26.5(10)	-0.5(8)	-4.1(9)	-1.9(9)
C26	33.3(11)	67.3(16)	49.1(14)	20.0(11)	0.0(9)	2.1(10)
B2	35.0(11)	33.6(10)	27.9(10)	4.4(8)	1.4(8)	-3.2(8)
C37	61.1(15)	61.3(15)	47.2(14)	2.9(11)	3.2(11)	4.0(12)
C2	81(2)	45.2(13)	58.7(16)	0.7(12)	21.9(14)	-25.7(14)
C27	46.2(13)	67.0(16)	49.4(14)	20.3(12)	-8.5(11)	10.0(11)
C17	80.2(19)	35.3(12)	72.1(19)	-13.5(12)	-35.4(15)	4.5(12)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C24	86(2)	41.9(13)	68.5(19)	-17.7(12)	-20.2(16)	-9.4(13)
C21	103(2)	31.6(11)	52.6(15)	-0.2(10)	8.2(15)	-0.3(12)
C49	64.2(18)	137(3)	38.2(14)	-16.0(17)	-3.4(12)	43.2(19)
C36	86(2)	47.1(13)	40.4(13)	1.3(10)	-1.5(12)	6.0(13)
C42	78.3(19)	82(2)	38.5(14)	-1.4(12)	10.3(12)	34.3(16)
C22	68.3(18)	51.2(16)	102(3)	-19.4(16)	-13.8(17)	27.9(14)
C25	95(2)	59.4(17)	50.9(16)	-14.9(12)	23.7(15)	6.5(15)
C50	160(4)	63.3(19)	46.7(17)	-5.7(14)	-10(2)	-41(2)
C46	205(5)	59.6(18)	39.7(16)	17.0(14)	19(2)	2(2)
C47	64(2)	200(5)	64(2)	-51(3)	-34.7(17)	57(3)

Table S5 Bond Lengths for cu_230831LU_LGPZ257259_0m.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O4	C14	1.347(2)	C31	C26	1.392(3)
O4	C7	1.456(2)	C9	C8	1.389(3)
O3	C14	1.206(2)	C9	C10	1.384(3)
O8	C39	1.340(2)	C48	C45	1.545(3)
O8	C32	1.465(2)	C48	C49	1.514(4)
O2	C23	1.463(3)	C48	C50	1.499(4)
O2	B1	1.362(3)	C11	C10	1.384(3)
O1	C20	1.467(3)	C11	C12	1.381(3)
O1	B1	1.367(3)	C5	C4	1.387(3)
O6	C48	1.457(2)	C8	C13	1.383(3)
O6	B2	1.367(3)	C34	C35	1.397(4)
O7	C39	1.207(2)	C18	C17	1.539(3)
O5	C45	1.465(3)	C12	C13	1.395(3)
O5	B2	1.355(3)	C30	C29	1.384(3)
C14	C15	1.510(3)	C45	C46	1.507(5)
C7	C6	1.513(3)	C45	C47	1.516(4)
C7	C8	1.508(3)	C28	C29	1.372(4)
C39	C40	1.506(3)	C28	C27	1.381(4)
C19	C15	1.540(2)	C16	C17	1.507(3)
C19	C18	1.543(3)	C23	C20	1.553(3)
C19	B1	1.571(3)	C23	C24	1.512(3)
C6	C5	1.386(3)	C23	C25	1.516(4)
C6	C1	1.391(3)	C38	C37	1.383(4)
C33	C32	1.515(3)	C20	C21	1.524(4)
C33	C34	1.393(3)	C20	C22	1.515(4)
C33	C38	1.392(3)	C35	C36	1.374(5)
C44	C40	1.541(2)	C3	C4	1.382(4)
C44	C43	1.548(3)	C3	C2	1.380(5)
C44	B2	1.572(3)	C1	C2	1.379(4)

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C32	C31	1.510(3)	C43	C42	1.515(4)
C40	C41	1.540(3)	C41	C42	1.505(4)
C15	C16	1.536(3)	C26	C27	1.389(3)
C31	C30	1.382(3)	C37	C36	1.373(4)

Table S6 Bond Angles for cu_230831LU_LGPZ257259_0m.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C14	O4	C7	115.58(14)	C13	C8	C7	118.82(18)
C39	O8	C32	116.77(15)	C13	C8	C9	118.82(19)
B1	O2	C23	107.20(16)	C11	C10	C9	120.4(2)
B1	O1	C20	106.59(16)	C33	C34	C35	120.3(2)
B2	O6	C48	108.02(16)	C17	C18	C19	104.98(16)
B2	O5	C45	107.62(17)	C11	C12	C13	120.0(2)
O4	C14	C15	111.38(15)	C31	C30	C29	120.5(2)
O3	C14	O4	123.23(17)	C8	C13	C12	120.7(2)
O3	C14	C15	125.38(17)	O5	C45	C48	103.36(16)
O4	C7	C6	107.46(15)	O5	C45	C46	105.5(2)
O4	C7	C8	111.06(15)	O5	C45	C47	108.1(2)
C8	C7	C6	111.01(15)	C46	C45	C48	114.4(3)
O8	C39	C40	111.48(15)	C46	C45	C47	110.1(3)
O7	C39	O8	123.42(17)	C47	C45	C48	114.5(3)
O7	C39	C40	125.06(18)	C29	C28	C27	119.3(2)
C15	C19	C18	103.58(15)	C28	C29	C30	120.7(2)
C15	C19	B1	114.36(15)	C17	C16	C15	104.90(17)
C18	C19	B1	118.04(16)	O2	C23	C20	101.96(16)
C5	C6	C7	121.93(17)	O2	C23	C24	108.2(2)
C5	C6	C1	119.2(2)	O2	C23	C25	106.3(2)
C1	C6	C7	118.68(19)	C24	C23	C20	115.1(2)
C34	C33	C32	119.0(2)	C24	C23	C25	110.8(2)
C38	C33	C32	122.66(19)	C25	C23	C20	113.6(2)
C38	C33	C34	118.4(2)	C37	C38	C33	120.7(2)
C40	C44	C43	105.07(16)	O1	C20	C23	102.66(16)
C40	C44	B2	113.12(16)	O1	C20	C21	105.91(19)
C43	C44	B2	118.44(18)	O1	C20	C22	109.2(2)
O8	C32	C33	109.22(16)	C21	C20	C23	113.1(2)
O8	C32	C31	105.96(15)	C22	C20	C23	114.9(2)
C31	C32	C33	115.12(17)	C22	C20	C21	110.3(2)
C39	C40	C44	110.90(16)	C36	C35	C34	120.3(2)
C39	C40	C41	109.71(16)	C2	C3	C4	120.0(2)
C41	C40	C44	103.81(16)	C2	C1	C6	120.3(2)
C14	C15	C19	110.75(15)	O2	B1	O1	113.57(17)
C14	C15	C16	110.54(16)	O2	B1	C19	121.55(17)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C16	C15	C19	103.42(15)	O1	B1	C19	124.59(18)
C30	C31	C32	119.00(18)	C3	C4	C5	119.8(2)
C30	C31	C26	119.0(2)	C42	C43	C44	106.56(18)
C26	C31	C32	121.93(19)	C42	C41	C40	104.01(18)
C10	C9	C8	120.6(2)	C27	C26	C31	119.8(2)
O6	C48	C45	102.40(17)	O6	B2	C44	120.77(18)
O6	C48	C49	108.6(2)	O5	B2	O6	112.97(19)
O6	C48	C50	106.1(2)	O5	B2	C44	126.14(19)
C49	C48	C45	114.7(2)	C36	C37	C38	120.6(3)
C50	C48	C45	115.3(3)	C1	C2	C3	120.3(2)
C50	C48	C49	109.0(3)	C28	C27	C26	120.6(2)
C12	C11	C10	119.5(2)	C16	C17	C18	108.15(18)
C6	C5	C4	120.4(2)	C35	C36	C37	119.7(3)
C9	C8	C7	122.27(17)	C41	C42	C43	107.5(2)

Table S7 Torsion Angles for cu_230831LU_LGPZ257259_0m.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O4	C14	C15	C19	-179.90(15)	C8	C7	C6	C1	93.4(2)
O4	C14	C15	C16	66.1(2)	C8	C9	C10	C11	-0.5(4)
O4	C7	C6	C5	39.7(2)	C10	C9	C8	C7	-175.2(2)
O4	C7	C6	C1	-144.97(18)	C10	C9	C8	C13	1.4(3)
O4	C7	C8	C9	-45.1(2)	C10	C11	C12	C13	-0.3(4)
O4	C7	C8	C13	138.27(19)	C34	C33	C32	O8	143.10(18)
O3	C14	C15	C19	1.0(3)	C34	C33	C32	C31	-97.9(2)
O3	C14	C15	C16	-113.0(2)	C34	C33	C38	C37	0.4(3)
O8	C39	C40	C44	-169.66(16)	C34	C35	C36	C37	-0.2(4)
O8	C39	C40	C41	76.2(2)	C18	C19	C15	C14	-79.74(18)
O8	C32	C31	C30	-117.8(2)	C18	C19	C15	C16	38.69(19)
O8	C32	C31	C26	60.4(3)	C18	C19	B1	O2	163.32(18)
O2	C23	C20	O1	27.7(2)	C18	C19	B1	O1	-23.3(3)
O2	C23	C20	C21	-85.9(2)	C12	C11	C10	C9	-0.1(4)
O2	C23	C20	C22	146.2(2)	C30	C31	C26	C27	2.0(4)
O6	C48	C45	O5	23.2(2)	C45	O5	B2	O6	6.1(3)
O6	C48	C45	C46	-91.1(3)	C45	O5	B2	C44	-170.0(2)
O6	C48	C45	C47	140.5(3)	C29	C28	C27	C26	0.6(4)
O7	C39	C40	C44	12.4(3)	C23	O2	B1	O1	10.8(2)
O7	C39	C40	C41	-101.7(2)	C23	O2	B1	C19	-175.14(18)
C14	O4	C7	C6	159.82(15)	C38	C33	C32	O8	-37.7(3)
C14	O4	C7	C8	-78.59(19)	C38	C33	C32	C31	81.3(2)
C14	C15	C16	C17	84.0(2)	C38	C33	C34	C35	0.1(3)
C7	O4	C14	O3	1.6(3)	C38	C37	C36	C35	0.8(4)
C7	O4	C14	C15	-177.43(15)	C20	O1	B1	O2	8.4(2)

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C7	C6	C5	C4	176.0(2)	C20	O1	B1	C19	-165.49(19)
C7	C6	C1	C2	-175.8(2)	C1	C6	C5	C4	0.7(3)
C7	C8	C13	C12	174.9(2)	B1	O2	C23	C20	-23.7(2)
C39	O8	C32	C33	-88.6(2)	B1	O2	C23	C24	-145.5(2)
C39	O8	C32	C31	146.83(17)	B1	O2	C23	C25	95.5(2)
C39	C40	C41	C42	82.0(2)	B1	O1	C20	C23	-22.4(2)
C19	C15	C16	C17	-34.6(2)	B1	O1	C20	C21	96.4(2)
C19	C18	C17	C16	6.8(3)	B1	O1	C20	C22	-144.8(2)
C6	C7	C8	C9	74.4(2)	B1	C19	C15	C14	50.1(2)
C6	C7	C8	C13	-102.2(2)	B1	C19	C15	C16	168.50(17)
C6	C5	C4	C3	-0.3(4)	B1	C19	C18	C17	-155.6(2)
C6	C1	C2	C3	-0.5(4)	C4	C3	C2	C1	1.0(4)
C33	C32	C31	C30	121.4(2)	C43	C44	C40	C39	-88.2(2)
C33	C32	C31	C26	-60.4(3)	C43	C44	C40	C41	29.6(2)
C33	C34	C35	C36	-0.2(4)	C43	C44	B2	O6	169.1(2)
C33	C38	C37	C36	-0.9(4)	C43	C44	B2	O5	-15.1(3)
C44	C40	C41	C42	-36.6(2)	C26	C31	C30	C29	-0.7(4)
C44	C43	C42	C41	-11.3(3)	B2	O6	C48	C45	-20.5(2)
C32	O8	C39	O7	-0.6(3)	B2	O6	C48	C49	-142.1(2)
C32	O8	C39	C40	-178.55(16)	B2	O6	C48	C50	100.8(3)
C32	C33	C34	C35	179.3(2)	B2	O5	C45	C48	-18.4(3)
C32	C33	C38	C37	-178.7(2)	B2	O5	C45	C46	102.1(3)
C32	C31	C30	C29	177.6(2)	B2	O5	C45	C47	-140.1(3)
C32	C31	C26	C27	-176.2(2)	B2	C44	C40	C39	42.5(2)
C40	C44	C43	C42	-11.7(3)	B2	C44	C40	C41	160.23(17)
C40	C44	B2	O6	45.5(3)	B2	C44	C43	C42	-139.2(2)
C40	C44	B2	O5	-138.7(2)	C2	C3	C4	C5	-0.6(4)
C40	C41	C42	C43	29.8(3)	C27	C28	C29	C30	0.7(4)
C15	C19	C18	C17	-28.0(2)	C24	C23	C20	O1	144.6(2)
C15	C19	B1	O2	41.1(3)	C24	C23	C20	C21	30.9(3)
C15	C19	B1	O1	-145.52(19)	C24	C23	C20	C22	-97.0(3)
C15	C16	C17	C18	17.2(3)	C49	C48	C45	O5	140.5(2)
C31	C30	C29	C28	-0.7(4)	C49	C48	C45	C46	26.3(3)
C31	C26	C27	C28	-1.9(4)	C49	C48	C45	C47	-102.2(3)
C9	C8	C13	C12	-1.8(3)	C25	C23	C20	O1	-86.2(2)
C48	O6	B2	O5	10.0(3)	C25	C23	C20	C21	160.1(2)
C48	O6	B2	C44	-173.70(18)	C25	C23	C20	C22	32.3(3)
C11	C12	C13	C8	1.3(4)	C50	C48	C45	O5	-91.6(3)
C5	C6	C1	C2	-0.3(3)	C50	C48	C45	C46	154.2(3)
C8	C7	C6	C5	-81.9(2)	C50	C48	C45	C47	25.7(3)

Table S8 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement

Parameters ($Å^2 \times 10^3$) for cu_230831LU_LGPZ257259_0m.

Atom	*x*	*y*	*z*	U(eq)
H7	8407.77	5666.51	5053.72	36
H19	11473.32	7709.99	4012.92	33
H44	3377.68	3133.5	5109.34	40
H32	6161.9	7708.87	4811.88	42
H40	3012.45	5016.94	4865.25	37
H15	11843.85	6827.7	4512.57	34
H9	11275.83	6799.82	5446	48
H11	9439.93	9269.2	6032.84	48
H5	11409.22	4399	5318.61	45
H10	11325.72	8361.56	5844.87	51
H34	6568.67	9342.99	5191.17	55
H18A	8831.5	7084.39	4004.56	40
H18B	9796.22	7164.47	3702.5	40
H12	7496.42	8597.19	5820.06	57
H30	7136.69	8447.01	4356.29	49
H13	7447.94	7042	5414.9	49
H28	5250.54	10024.7	3606.43	55
H29	7137.31	9346.37	3842	57
H16A	11877.68	5218.86	4134.3	47
H16B	10832.53	4651.65	4379.92	47
H38	2897.43	8525.86	4984.92	58
H35	5890.94	10631.4	5620.33	67
H3	9885.77	1370.89	5779.5	69
H1	7591.04	4030.46	5387.17	55
H4	11667.01	2500.22	5604.61	58
H43A	6030.75	2941.95	5061.94	59
H43B	4971.7	1917.71	4957.74	59
H41A	3482.46	3619.34	4447.07	49
H41B	4449.34	4762.74	4364.2	49
H26	3341.01	9003.75	4417.29	60
H37	2248.3	9834.35	5406.92	68
H2	7855.31	2154.36	5677.04	74
H27	3349.75	9832.6	3892.64	65
H17A	9255.06	5008.18	4036.76	75
H17B	10345.53	5130.53	3766.35	75
H24A	11707.37	11386.8	4905.21	98
H24B	10907.59	12500.91	4737.35	98
H24C	11962.94	11747.97	4534.49	98
H21A	11328.47	11315.46	4022.95	93
H21B	10610.68	12613.38	4109.52	93
H21C	10101.85	11737.45	3820.4	93

Atom	*x*	*y*	*z*	U(eq)
H49A	2524.47	4885.18	6151.34	120
H49B	2482.44	6351.51	6048.38	120
H49C	3359.8	5907.36	6344.06	120
H36	3735.72	10865.77	5728.41	70
H42A	6138.76	3716.08	4565.42	80
H42B	5315.75	2508.57	4451.8	80
H22A	7994.29	11785.72	4089.23	111
H22B	8500.39	12524.35	4402.51	111
H22C	7811.4	11176.15	4441.18	111
H25A	8767.13	9816.51	4799.26	103
H25B	8981.61	11217.96	4939.97	103
H25C	9876.36	10074.95	5056.21	103
H50A	5048.46	7045.21	6053.66	135
H50B	4232.86	7274.5	5731.81	135
H50C	5558.5	6531.14	5712.89	135
H46A	4283.2	3532.52	6406.49	152
H46B	4814.33	2485.4	6160.03	152
H46C	3468.16	3146.36	6094.42	152
H47A	6733.51	5180.39	5994.09	164
H47B	6700.11	3892.1	6200.11	164
H47C	6060.45	5156.13	6341.54	164

9.DFT calculation

All calculations were carried out with the Gaussian 16 software.

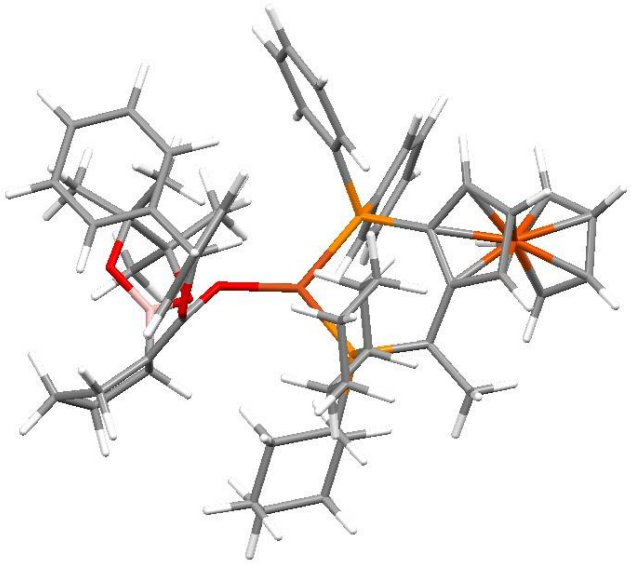
The PBE0 functional was adopted for all calculations. For geometry optimization and frequency calculations, the mixed basis set (SDD ECP basis set[2] for Fe/Cu atoms and the 6-31G(d) basis set[3] for other atoms) was used, and the optimal geometry for each compound was determined.

The singlet point energy calculations were performed with a larger basis set (SDD ECP basis set[2] for Fe/Cu atoms and the def2-TZVP basis set[3] for other atoms).

The DFT-D3 with BJ-damping was applied to correct the weak interaction to improve the calculation accuracy.

The SMD implicit solvation model[4] was used to account for the solvation effect of tetrahydrofuran.

Finally, the single point energy of each compound was added to the free energy correction terms calculated before to obtain the Gibbs free energy.



A

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C	-5.04209100	-0.93697700	-1.40693600
C	-3.11846500	0.16410800	-0.74303500
C	-4.73083400	-1.35330600	-0.08203000
H	-4.01706100	0.51331700	-2.76567100
Fe	-5.00789800	0.66619900	-0.13946000
C	-4.05976500	0.00218900	-1.81280200
C	-3.55281500	-0.67547700	0.35290700
H	-5.90785000	-1.24147400	-1.98105500
H	-5.32885500	-2.02485900	0.51944400

C	-5.54394700	1.62969900	1.58520000
C	-6.84823500	1.52576800	-0.31268200
C	-5.02738100	2.56430600	0.64544200
C	-6.67110300	0.98678000	0.99454900
C	-5.82962400	2.49918800	-0.52987200
H	-5.12817600	1.41961100	2.56272200
H	-7.59472500	1.21326000	-1.03200800
H	-4.15458600	3.18639500	0.78555500
H	-7.25797100	0.19314700	1.43966900
H	-5.66893800	3.06367800	-1.43889700
P	-1.52770700	1.03758100	-0.83530600
C	-2.92275000	-0.80919400	1.71448000
H	-2.71267500	0.20431200	2.07871500
C	-3.84145600	-1.50585400	2.71447900
H	-4.81269500	-1.00046900	2.75292700
H	-4.02302500	-2.55152400	2.44590900
H	-3.41467500	-1.49275300	3.72073700
P	-1.21471200	-1.57937700	1.57412100
Cu	-0.03596200	-0.07274700	0.42070600
C	-0.64980800	-1.74265000	3.33829700
C	0.82108400	-2.18405900	3.38545100
C	-0.78215200	-0.37989400	4.03687100
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C	1.34368000	-2.24774500	4.81905400
H	1.42949300	-1.46842400	2.81450000
H	0.95711100	-3.15434200	2.90221500
C	-0.25104600	-0.42552000	5.46924100
H	-0.21052900	0.36444300	3.45998700
H	-1.82237700	-0.03702900	4.05037000
C	1.19635700	-0.90262600	5.52077900
H	2.39540600	-2.55982000	4.80724300
H	0.79067200	-3.01598400	5.38020800
H	-0.34657600	0.56742400	5.92571500
H	-0.88011800	-1.10698500	6.06077700
H	1.53934100	-0.96813800	6.56075500
H	1.83883100	-0.16476400	5.01881700
C	-1.59931100	-3.26263500	0.87418900
C	-1.56751100	-3.18202500	-0.65830100
C	-0.68689100	-4.39010600	1.36126600
H	-2.62579100	-3.50701800	1.18541100
C	-1.95120800	-4.51327900	-1.29868800
H	-0.55165700	-2.90741200	-0.97325500
H	-2.23842400	-2.39158300	-1.00899800
C	-1.09471800	-5.72225700	0.73361900

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H	-0.72233100	-4.46906200	2.45371600
C	-1.06951900	-5.64888200	-0.78947300
H	-1.87236900	-4.42994200	-2.39002500
H	-3.00542400	-4.73200200	-1.07188700
H	-0.42507600	-6.51520000	1.08897800
H	-2.10700800	-5.98565500	1.07479600
H	-1.38910500	-6.60474300	-1.22337700
H	-0.03835500	-5.47743000	-1.12355300
C	-1.87982900	2.80746900	-0.58999800
C	-1.43754400	3.39930300	0.59588300
C	-2.62606400	3.56206400	-1.50343700
C	-1.75877100	4.72647200	0.87992000
H	-0.83667200	2.82071900	1.29402700
C	-2.93271700	4.88901000	-1.22529000
H	-2.96947300	3.10820700	-2.42910100
C	-2.50573000	5.47014600	-0.02939400
H	-1.41520600	5.17872300	1.80567800
H	-3.51177500	5.47112800	-1.93668600
H	-2.75319800	6.50516700	0.18845700
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C	-1.26245300	-0.29060300	-3.30238800
C	0.08317200	1.81307100	-4.53284300
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C	-0.14181400	0.63090800	-5.23497900
H	0.61408300	2.63548100	-5.00398500
H	-0.98139100	-1.35301300	-5.14724200
H	0.20918000	0.52691700	-6.25755100
O	1.83752500	0.33561500	0.38882200
C	4.70722700	-1.26566200	2.21170400
C	3.58720100	0.92179300	2.55204100
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C	5.75326100	-0.23007000	2.64478400
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H	5.06024900	-1.92875600	1.41280000
H	2.74381600	0.99924900	3.25921400
H	5.45287400	1.81268500	3.39764100
H	4.72108700	0.54482600	4.37922000
H	6.22944300	0.19157900	1.75023900
H	6.54328800	-0.63984200	3.28612800
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O	4.35730400	2.34163300	0.51738900
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B	3.48992400	2.14122400	1.56622900
C	2.99498900	2.93566700	-1.35439300
H	2.63092200	3.74378000	-1.99875900
H	3.58739500	2.24662800	-1.96187900
H	2.14741600	2.37184500	-0.95547300
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H	5.56515300	3.59455700	-1.53758600
H	4.72767800	5.14071900	-1.30983600
H	5.77796400	4.49742100	-0.02687700
C	3.92191300	5.19377700	1.68656100
H	4.25051100	6.06278500	1.10731000
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H	4.80695300	4.67476000	2.06972200
C	1.84480400	4.99177600	0.31626600
H	1.32044700	5.49386400	1.13624400
H	2.14764300	5.75429100	-0.41024100
H	1.14388000	4.30684500	-0.16487700
C	3.56276900	-0.39175700	1.79548800
C	2.68551300	-0.56814300	0.78999300
O	2.65978400	-1.80708100	0.15046100
C	2.26640400	-1.78401800	-1.20481000
H	1.26045500	-1.34626400	-1.29738400
C	2.20965200	-3.21339000	-1.69942000
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C	2.16541100	-5.82095000	-2.72464500
H	0.93566000	-5.00703300	-4.29781200
H	3.38058600	-6.33355400	-1.02305700
H	2.14810200	-6.83238300	-3.12118200
C	3.20704900	-0.96141500	-2.06434600
C	2.71853100	-0.28802100	-3.18323300
C	4.56771100	-0.89353200	-1.76536600
C	3.57989500	0.42705400	-4.00991300
H	1.65452200	-0.30812100	-3.40168300
C	5.42800100	-0.16159000	-2.58011800
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H	3.18213900	0.94857100	-4.87672200
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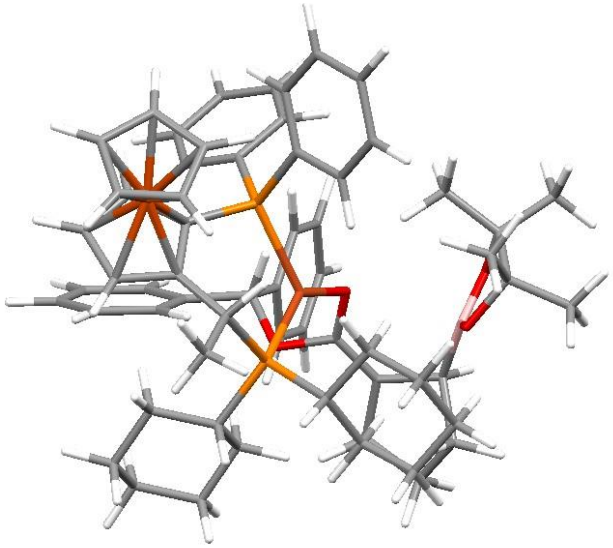

B

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C	3.91047500	-1.64173900	-1.63588000
H	3.43240800	-2.79160800	1.46900000
Fe	4.75209900	-0.80777800	0.02343400
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C	3.03539200	-0.64917100	-1.10355600
H	4.80088700	-3.49026000	-0.74110900
H	4.36322400	-1.61804100	-2.61879800
C	5.88073500	0.89090200	-0.24017700
C	6.68294400	-1.09323400	0.61568400
C	5.45755900	0.79305700	1.11332700
C	6.63843300	-0.27570300	-0.55104400
C	5.94837500	-0.43438100	1.64442300
H	5.64268200	1.69929300	-0.92016400
H	7.15204500	-2.06680600	0.69147200
H	4.84814000	1.51523900	1.63716000
H	7.06930500	-0.51918100	-1.51470400
H	5.76886100	-0.81275300	2.64313800
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C	2.60687900	0.61727100	-1.80365800
H	2.71770700	1.42012000	-1.06286400
C	3.47810200	0.97784100	-3.00514000
H	4.53879700	0.88326600	-2.75023700

H	3.28579000	0.34060400	-3.87331000
H	3.30359400	2.01368300	-3.31005300
P	0.75550500	0.70206200	-2.13173700
Cu	-0.22818200	0.37654100	-0.13887000
C	0.58113000	2.42567500	-2.81651400
C	-0.85276100	2.68134200	-3.29304200
C	0.98500700	3.46007900	-1.76200800
H	1.25155700	2.50938700	-3.68398100
C	-1.04304400	4.11720300	-3.77845200
H	-1.54423700	2.48313500	-2.46291700
H	-1.11149400	1.99225700	-4.10356800
C	0.78635400	4.89151400	-2.25583100
H	0.36291100	3.30147000	-0.87060800
H	2.02994300	3.32119500	-1.45924700
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H	-2.08854900	4.26185400	-4.07898300
H	-0.42916300	4.28211400	-4.67669900
H	1.06320600	5.59412200	-1.45922400
H	1.46874800	5.08418400	-3.09715100
H	-0.77804700	6.15052000	-3.07323400
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C	0.34620000	-0.37656800	-3.59979100
C	1.19383100	-1.64772000	-3.69561700
C	-1.14454300	-0.74705500	-3.54339400
H	0.53354200	0.23269200	-4.49785100
C	0.77074000	-2.51438100	-4.88147000
H	1.08906500	-2.22467600	-2.77015100
H	2.25447800	-1.40213500	-3.78907700
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H	-1.33954300	-1.30424600	-2.61994000
H	-1.76946100	0.14924900	-3.48260600
C	-0.71351100	-2.86101900	-4.83408900
H	1.37875300	-3.42822800	-4.89934000
H	0.98696200	-1.97320800	-5.81488800
H	-2.62304200	-1.85009200	-4.65878900
H	-1.44451700	-1.00995200	-5.66773500
H	-0.99495500	-3.45173000	-5.71518400
H	-0.91049000	-3.48793100	-3.95258600
C	2.29816000	1.02453800	2.27735200
C	2.26536200	2.33924100	1.80374000
C	2.99538600	0.73542200	3.45564300
C	2.92479500	3.35555100	2.49248500
H	1.72300800	2.56503300	0.88925100
C	3.64482700	1.75257000	4.14888600

H	3.03018600	-0.28363000	3.83086700
C	3.61225500	3.06276700	3.66848300
H	2.89137200	4.37432100	2.11542000
H	4.18337300	1.52217200	5.06430200
H	4.12151300	3.85346600	4.21266600
C	0.88267600	-1.47353000	2.50609500
C	0.29475600	-0.99638200	3.68866200
C	0.82254000	-2.84485000	2.23361600
C	-0.30441300	-1.87389000	4.58572400
H	0.30038300	0.06767700	3.90886600
C	0.21765000	-3.72068900	3.13281100
H	1.22351900	-3.23904000	1.30789400
C	-0.34251400	-3.24153600	4.31339300
H	-0.74942500	-1.48494100	5.49775400
H	0.17760900	-4.78048000	2.89634000
H	-0.81529500	-3.92567100	5.01282000
O	-2.03567100	0.29262500	0.60994400
C	-4.89321500	-0.10307100	-1.82281300
C	-4.34586000	1.80915200	-0.38845100
C	-4.66656900	2.35648800	-1.78781000
C	-5.45135700	1.20668700	-2.44497000
H	-4.33911300	-0.70280500	-2.55539100
H	-5.72251200	-0.73588100	-1.47092600
H	-5.30189000	1.80319200	0.17228200
H	-5.23257500	3.29714200	-1.77690800
H	-3.73093000	2.53927300	-2.33085800
H	-6.51626300	1.31054500	-2.20132400
H	-5.37343200	1.21748900	-3.53860200
C	-2.55640400	3.47104000	2.48656300
C	-2.11656800	4.35226000	1.27847100
O	-3.60276500	2.67565900	1.90538800
O	-2.36943800	3.48050300	0.15360500
B	-3.36085900	2.60026700	0.55052400
C	-1.45796700	2.52407300	2.96023400
H	-0.64750200	3.06339100	3.46275400
H	-1.89131300	1.81096300	3.66964100
H	-1.05154800	1.94982400	2.12320700
C	-3.12291200	4.24578200	3.66229700
H	-3.41312900	3.54918100	4.45653700
H	-2.37410900	4.93291000	4.07289300
H	-4.00766100	4.82179300	3.37777600
C	-3.00106600	5.57994000	1.08571100
H	-2.82803400	6.33119800	1.86354100
H	-2.77334900	6.03286800	0.11469000

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C	-0.65952300	4.76627900	1.30524200
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H	-0.45257700	5.36645700	2.19900200
H	0.00271000	3.89938100	1.31454300
C	-3.99616200	0.37777800	-0.70832400
C	-2.89431500	-0.22611300	-0.22380100
O	-2.62332600	-1.53414500	-0.64732200
C	-2.41577500	-2.42345000	0.44829700
H	-1.77997900	-1.91132000	1.18335000
C	-1.64194600	-3.61756700	-0.06554100
C	-2.01017500	-4.93512700	0.20535800
C	-0.46040500	-3.38398900	-0.77735600
C	-1.21610900	-5.99802400	-0.22772300
H	-2.91906900	-5.13709400	0.76435300
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C	-3.81802200	-2.77573700	2.51168200
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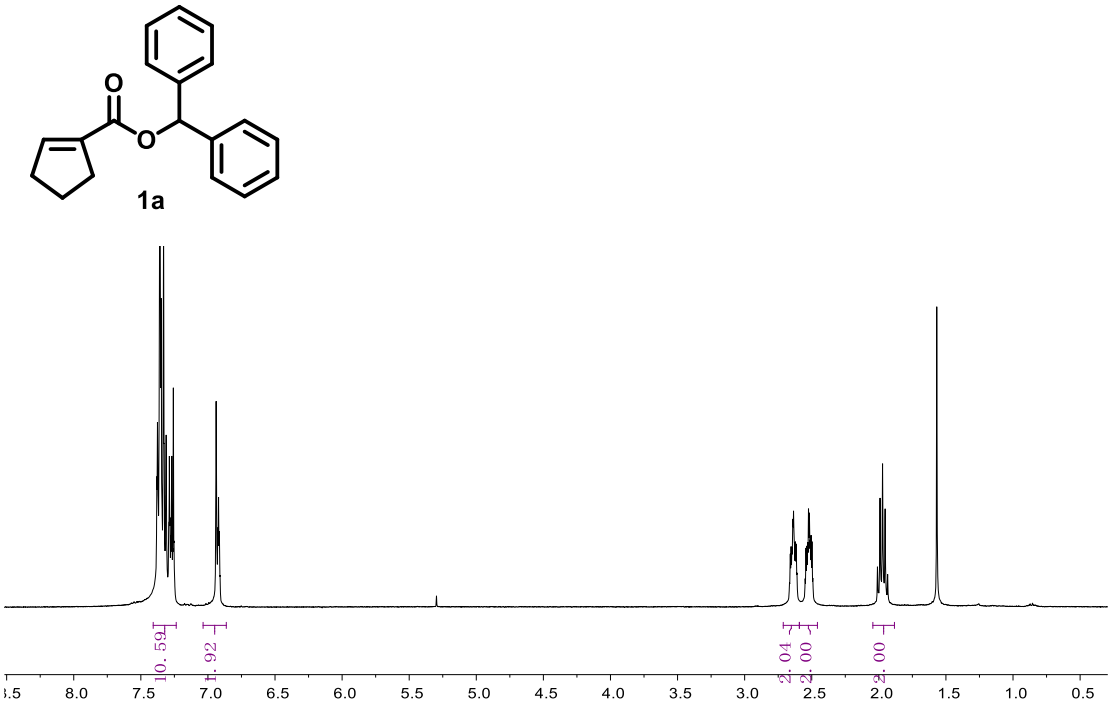
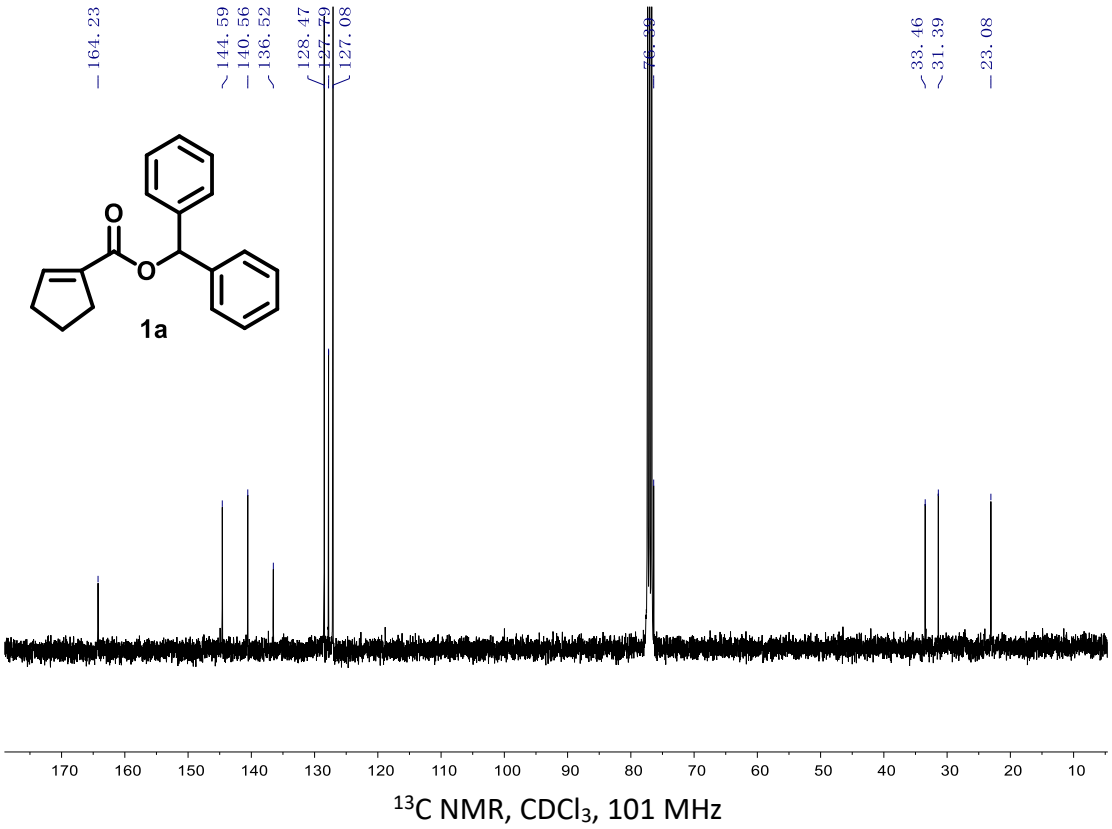
C	-5.01958000	-3.10470000	3.13760200
H	-2.94297600	-2.52096500	3.10585100
C	-6.05424500	-3.40447400	0.98021600
H	-4.78090300	-3.05992900	-0.72516800
C	-6.14047500	-3.41900300	2.37284700
H	-5.08144100	-3.10656200	4.22305500
H	-6.92734300	-3.64462500	0.37842100
H	-7.08019700	-3.66955200	2.85856200

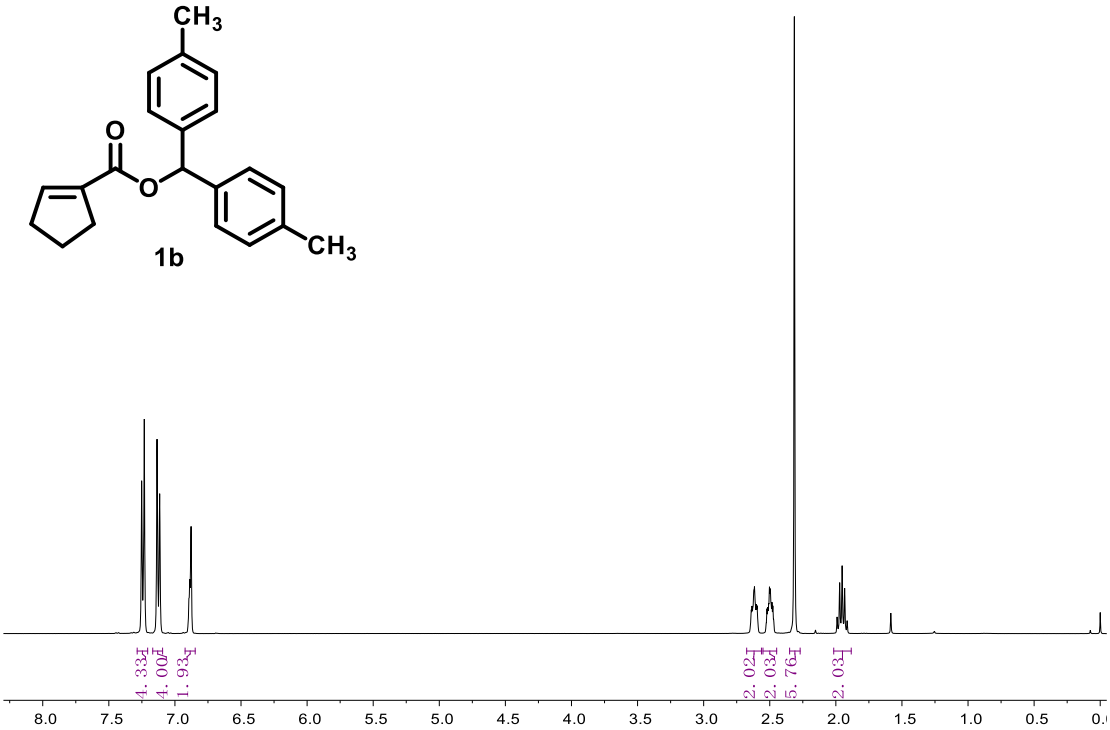
10.NMR spectra and HPLC traces



^{1}H NMR, $CDCl_3$, 400 MHz

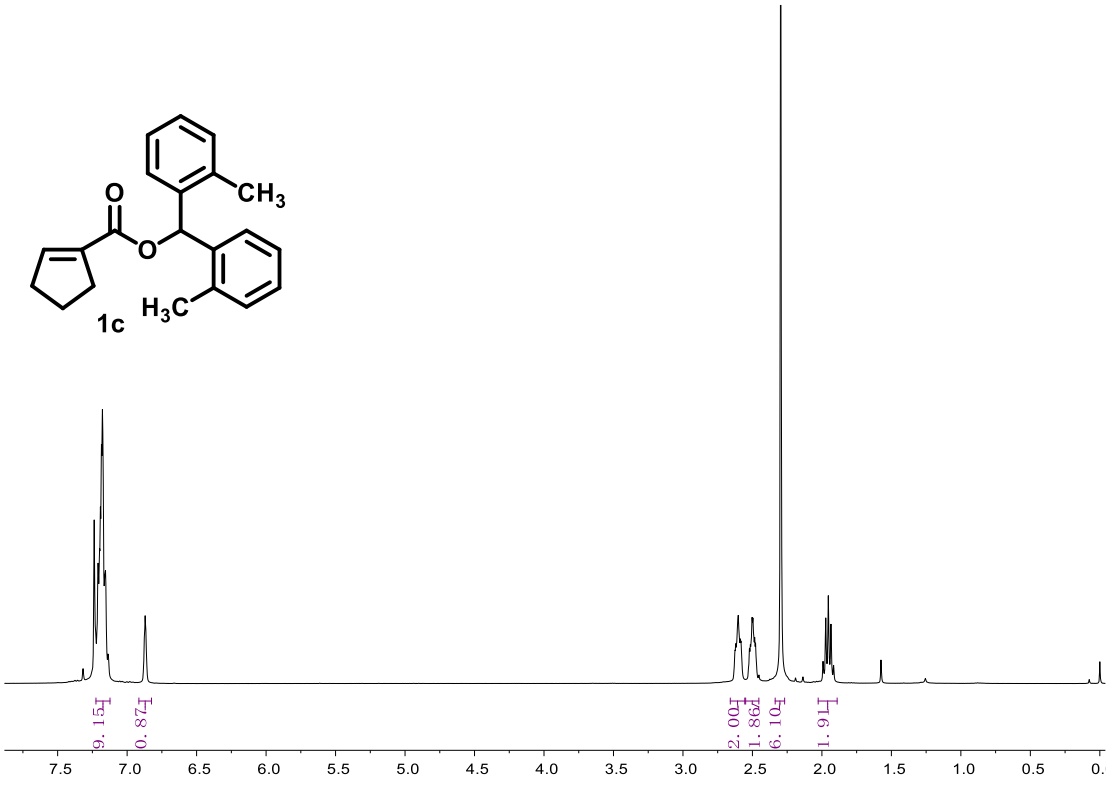


^{13}C NMR, $CDCl_3$, 101 MHz

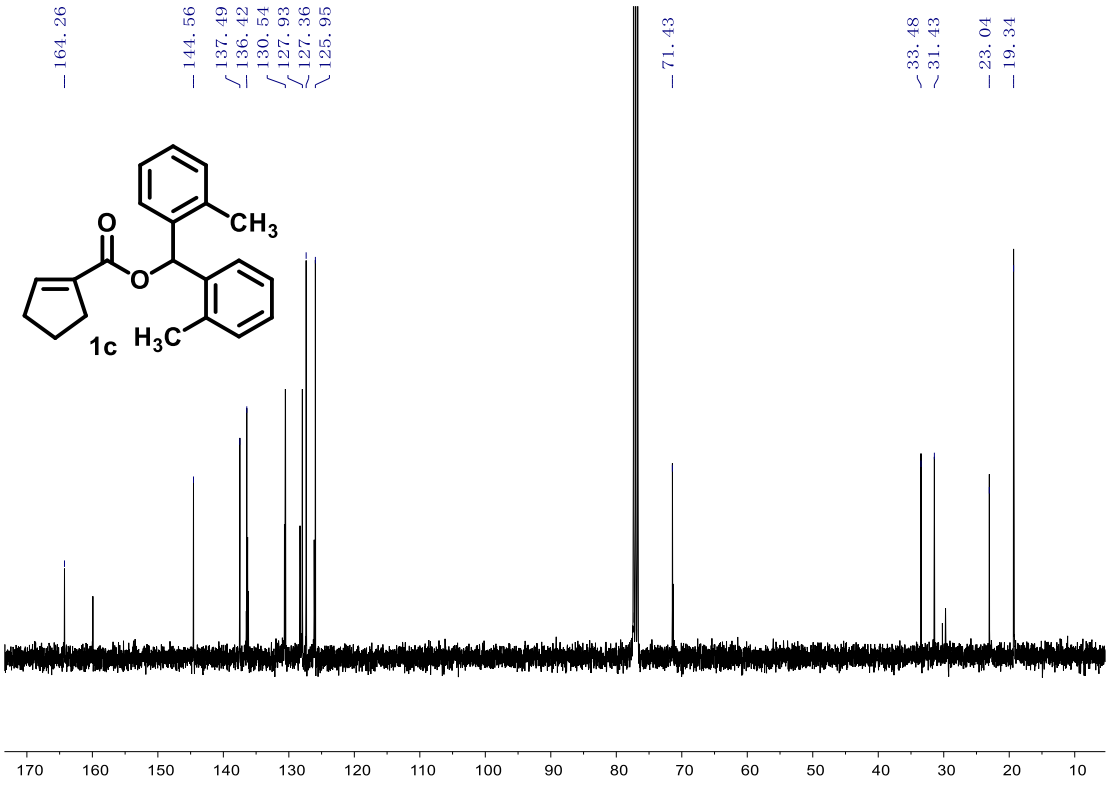


^{1}H NMR, $CDCl_3$, 400 MHz

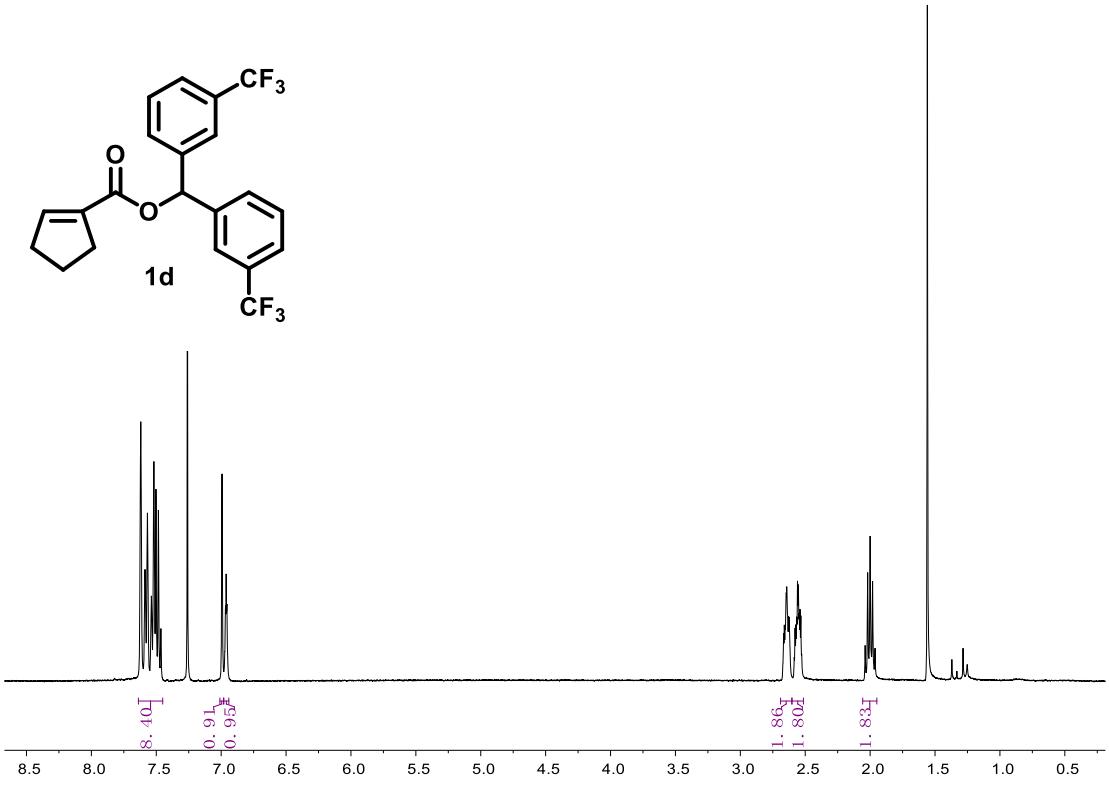
^{13}C NMR, $CDCl_3$, 101 MHz



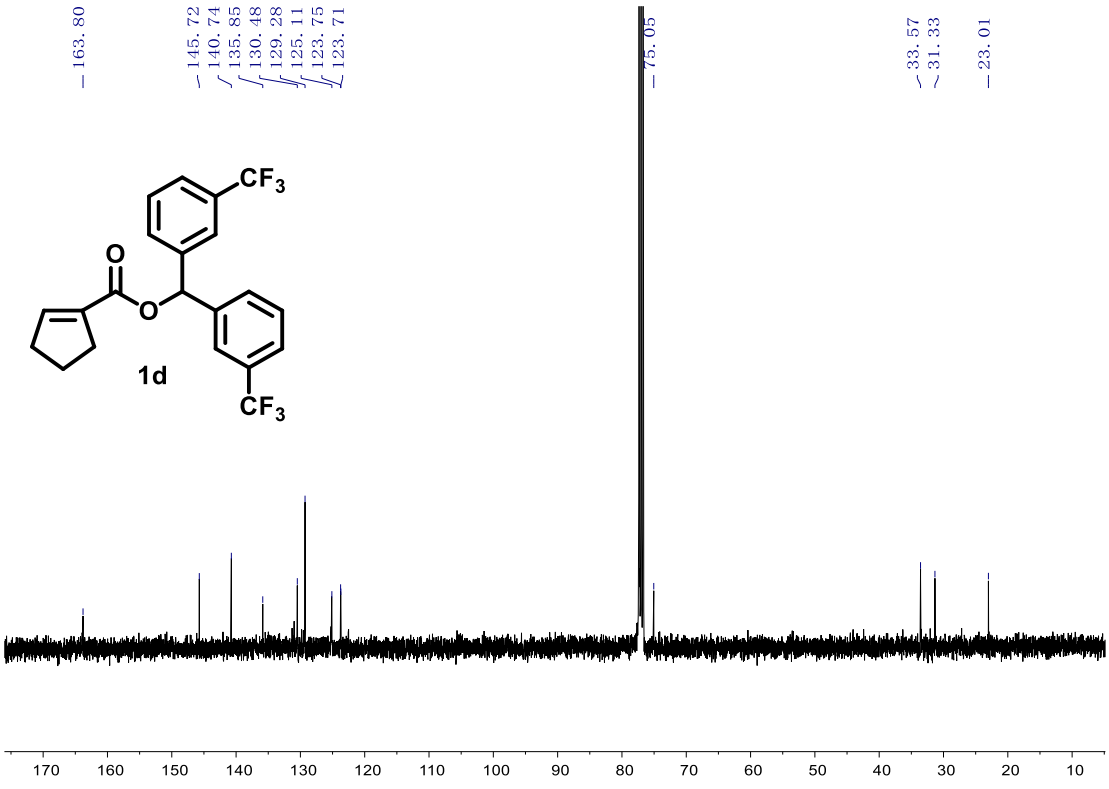
^{1}H NMR, $CDCl_3$, 400 MHz



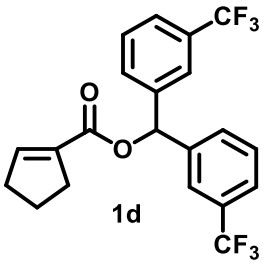
^{13}C NMR, $CDCl_3$, 101 MHz



^{1}H NMR, $CDCl_3$, 400 MHz



^{13}C NMR, $CDCl_3$, 101 MHz



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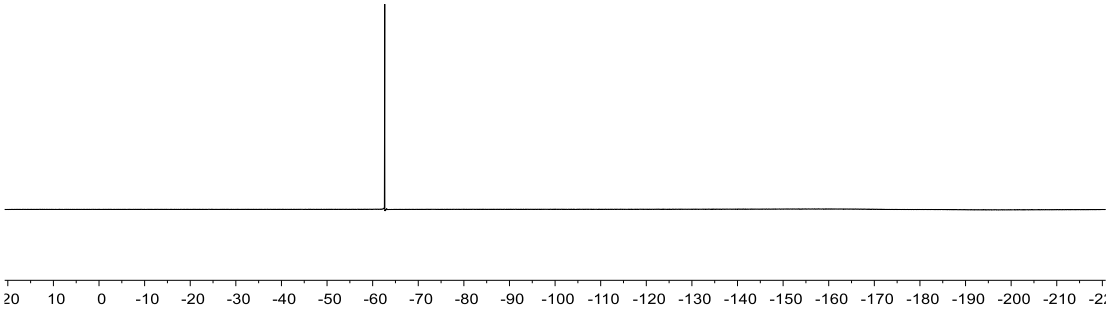
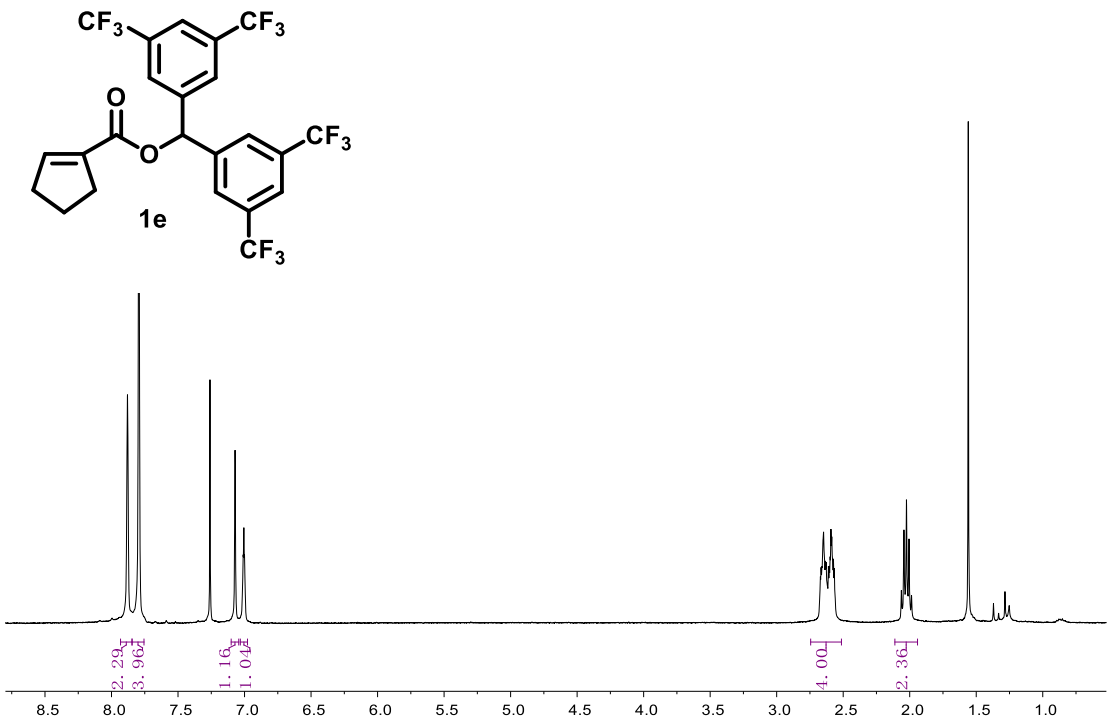
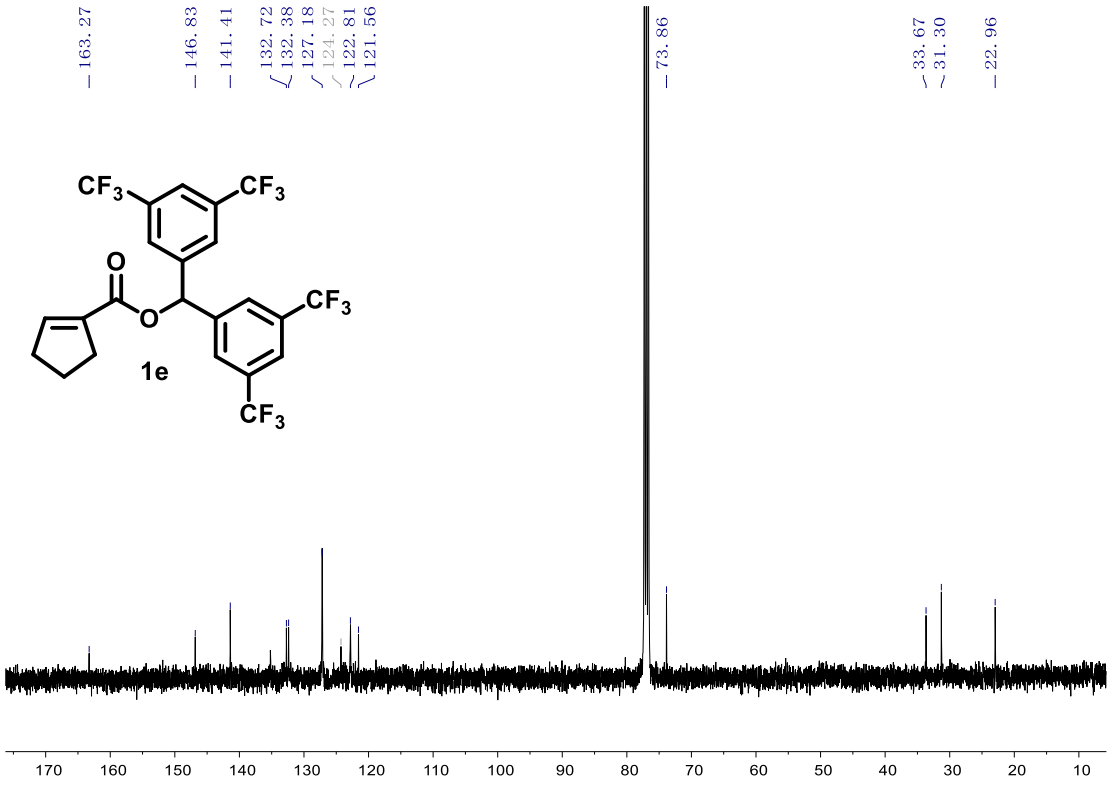


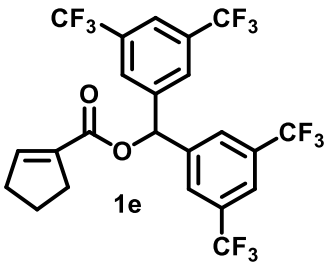
^{19}F NMR, $CDCl_3$, 471 MHz



^{1}H NMR, $CDCl_3$, 400 MHz



^{13}C NMR, $CDCl_3$, 101 MHz



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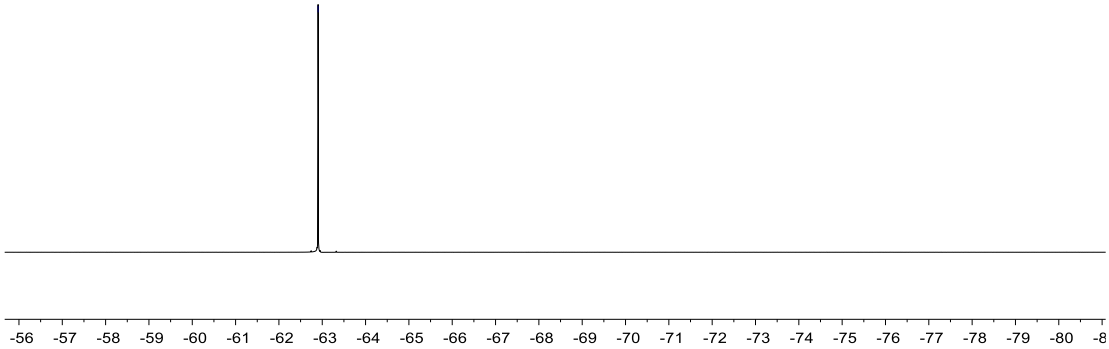
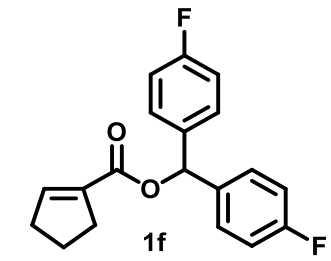
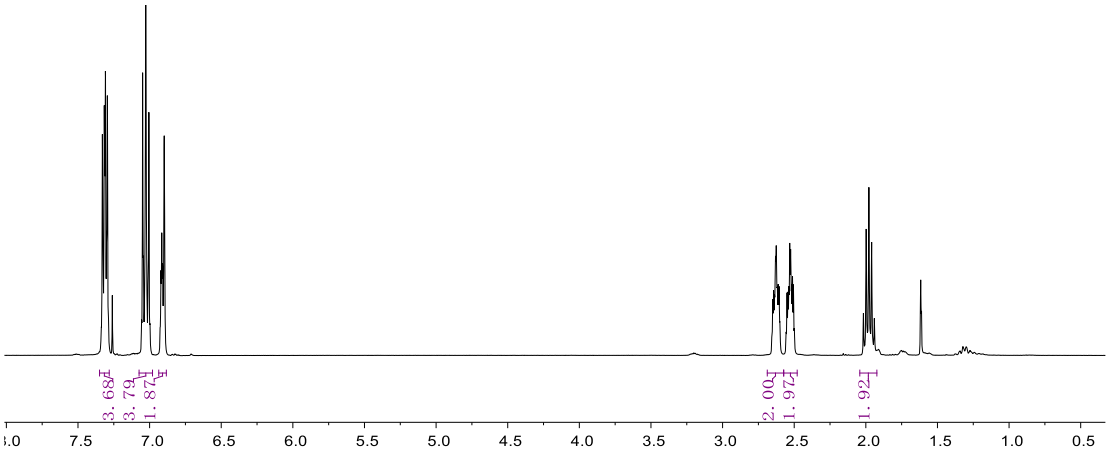
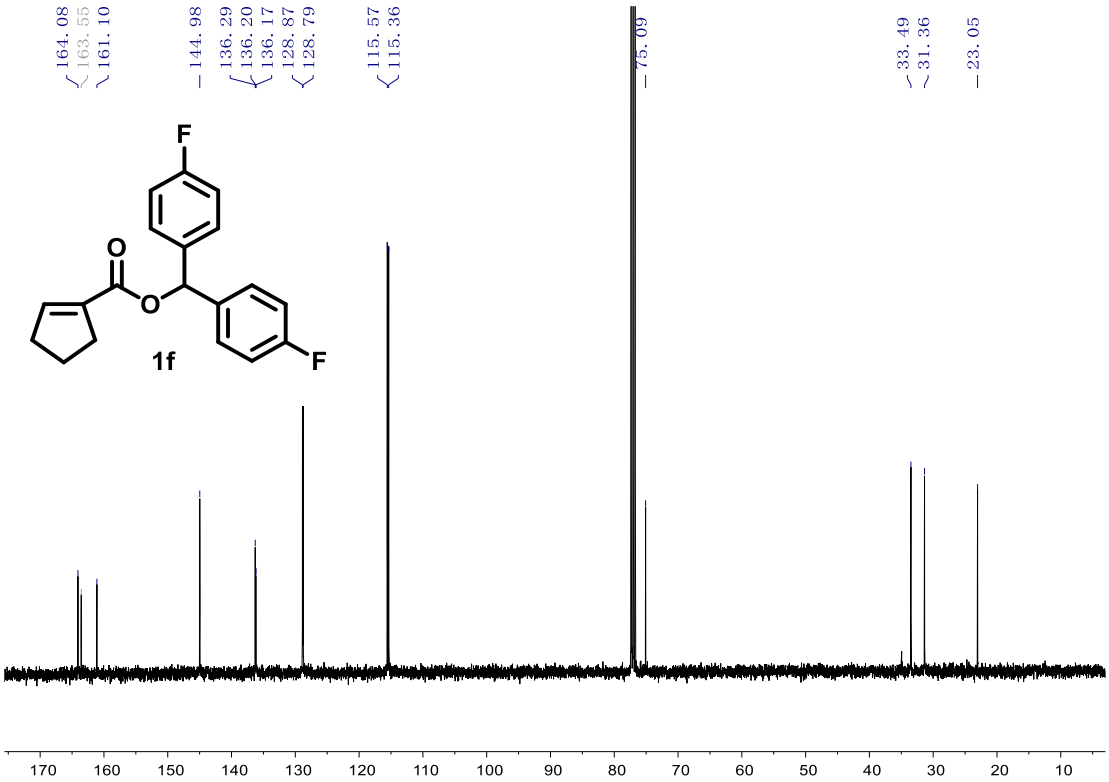


^{19}F NMR, $CDCl_3$, 471 MHz

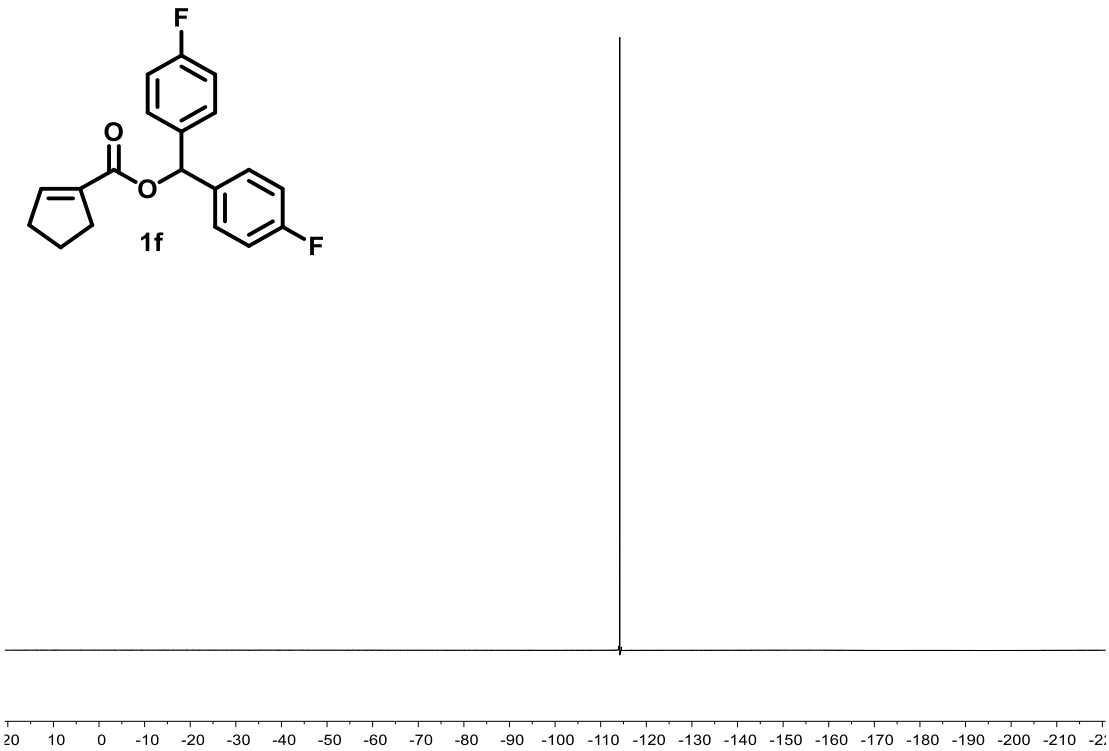




^{1}H NMR, $CDCl_3$, 400 MHz

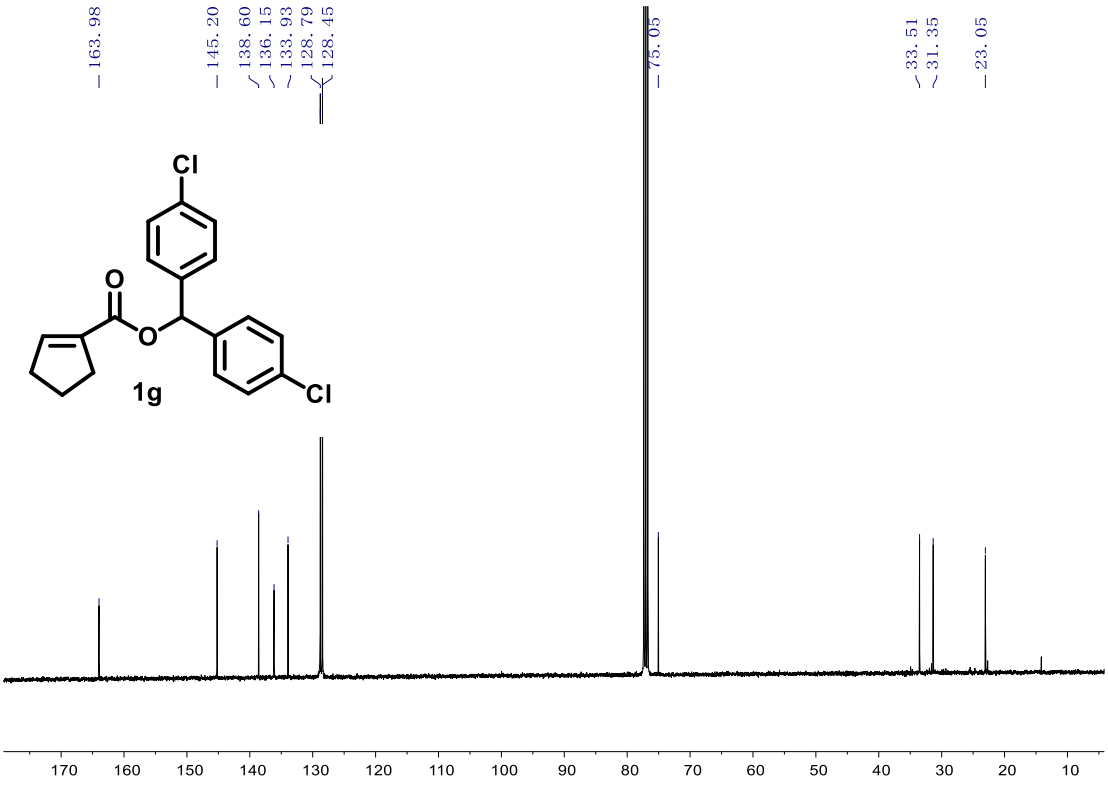


^{13}C NMR, $CDCl_3$, 101 MHz

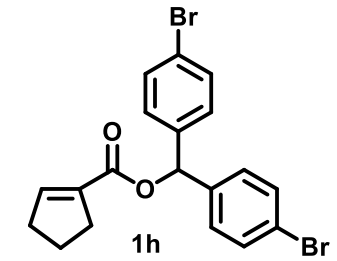


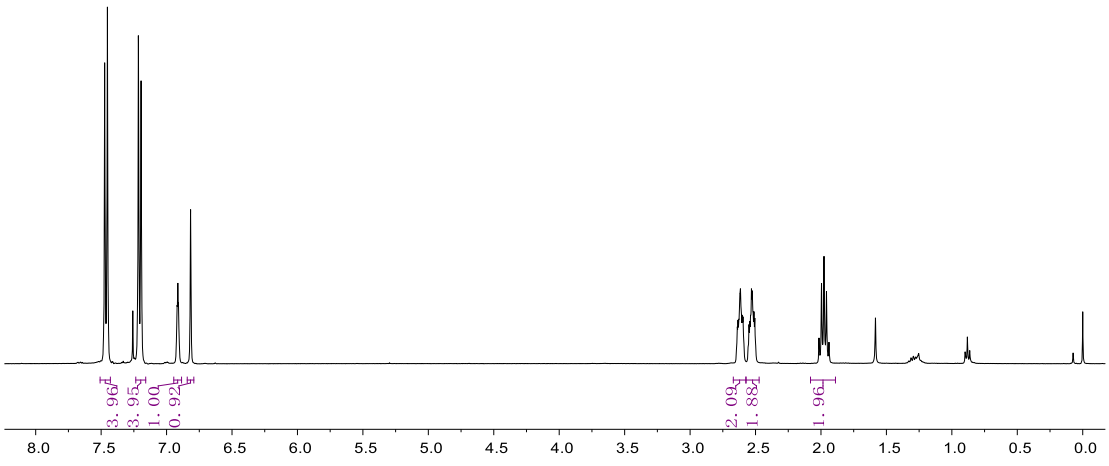
^{19}F NMR, $CDCl_3$, 471 MHz

^{1}H NMR, $CDCl_3$, 400 MHz

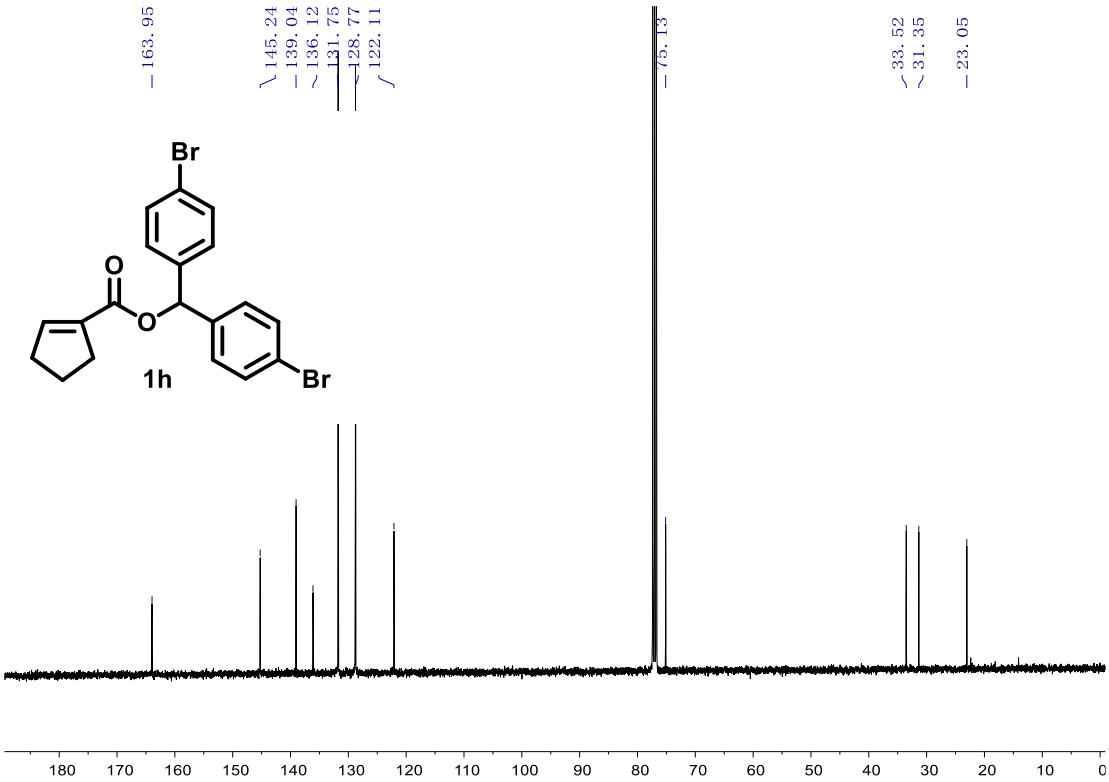


^{13}C NMR, $CDCl_3$, 101 MHz

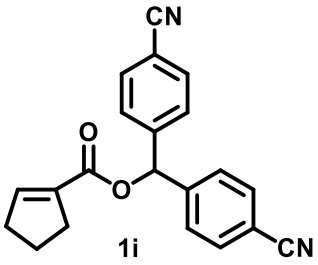




^{1}H NMR, $CDCl_3$, 400 MHz



^{13}C NMR, $CDCl_3$, 101 MHz



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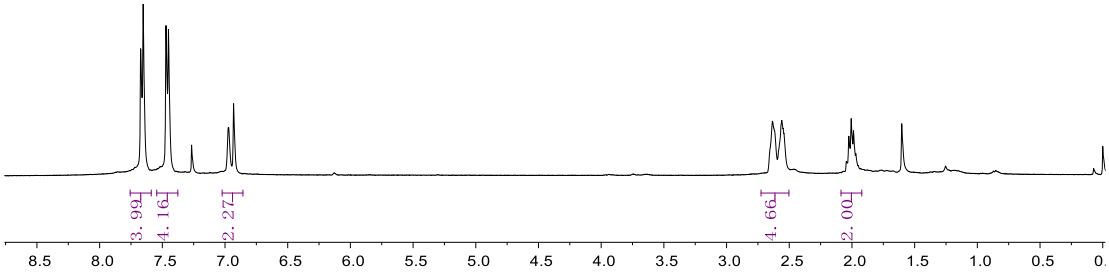
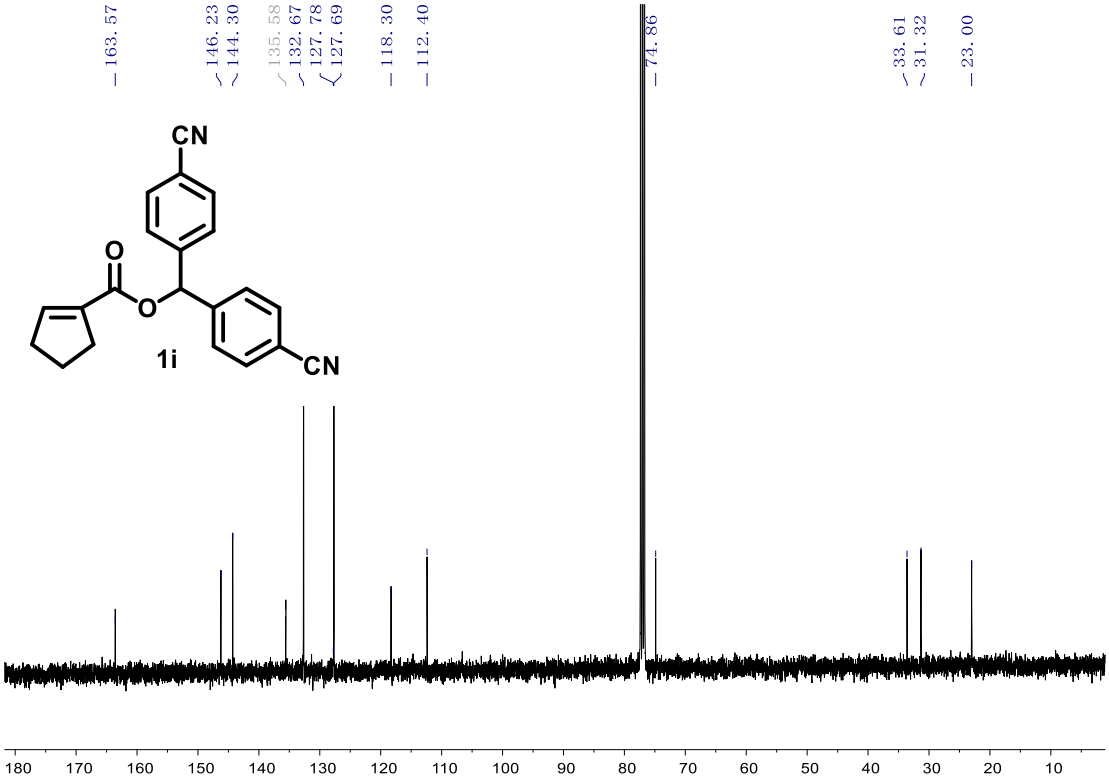


^{1}H NMR, $CDCl_3$, 400 MHz



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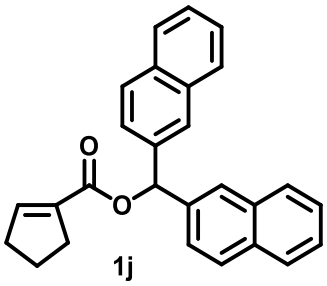
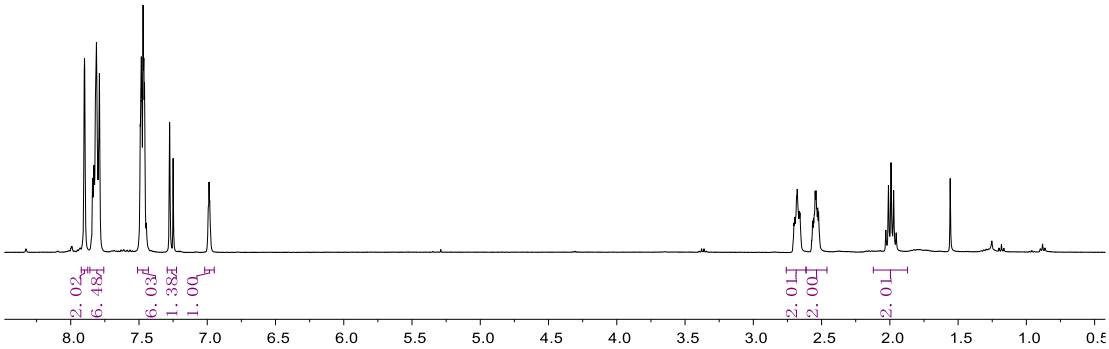
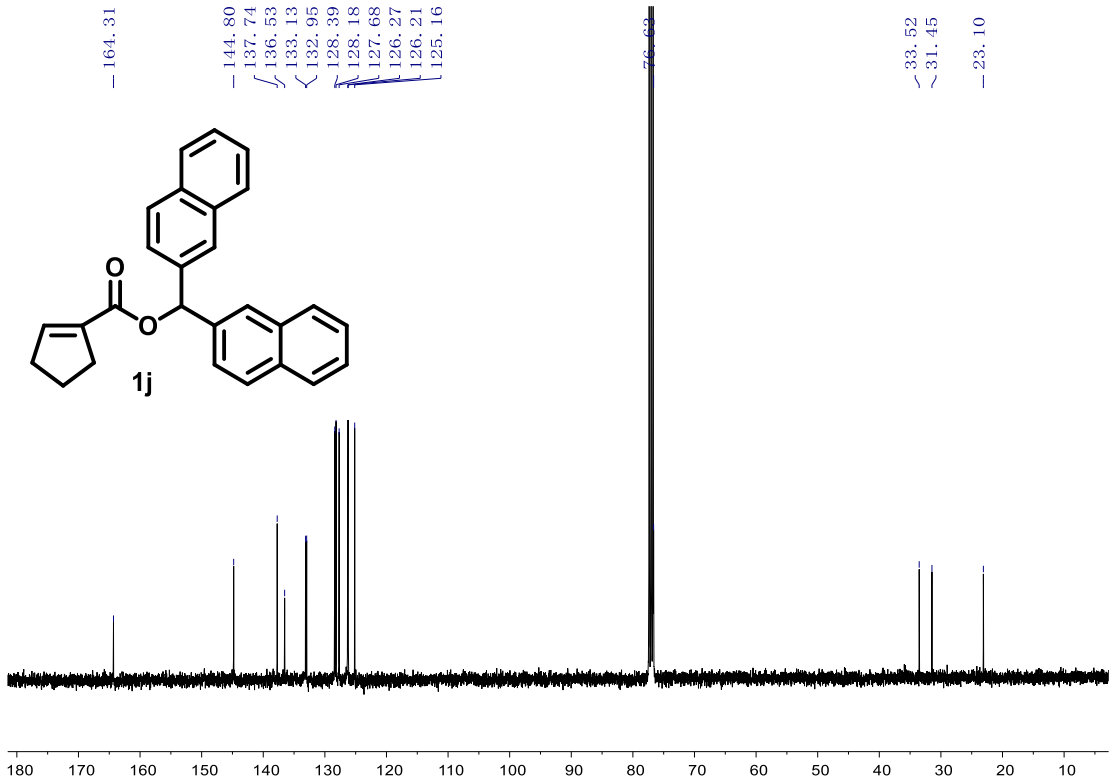
^{13}C NMR, $CDCl_3$, 101 MHz

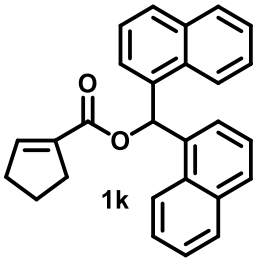


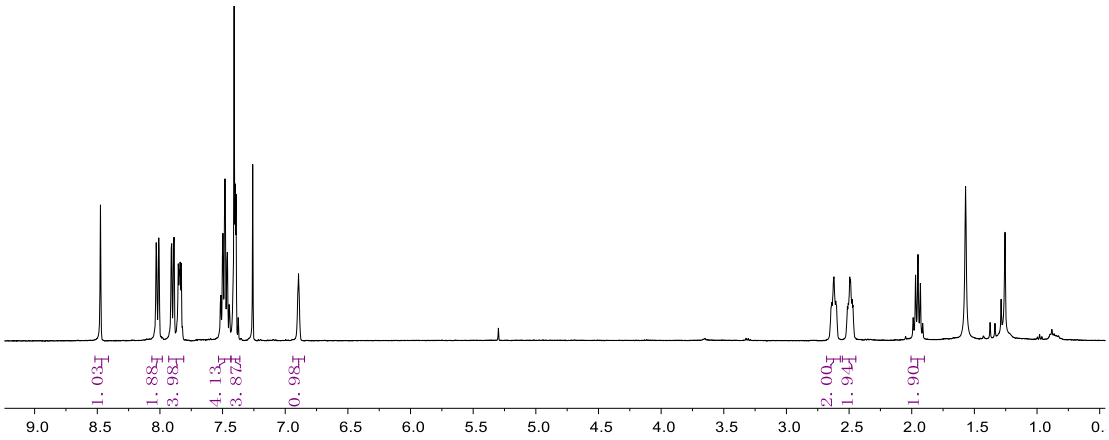


^{1}H NMR, $CDCl_3$, 400 MHz

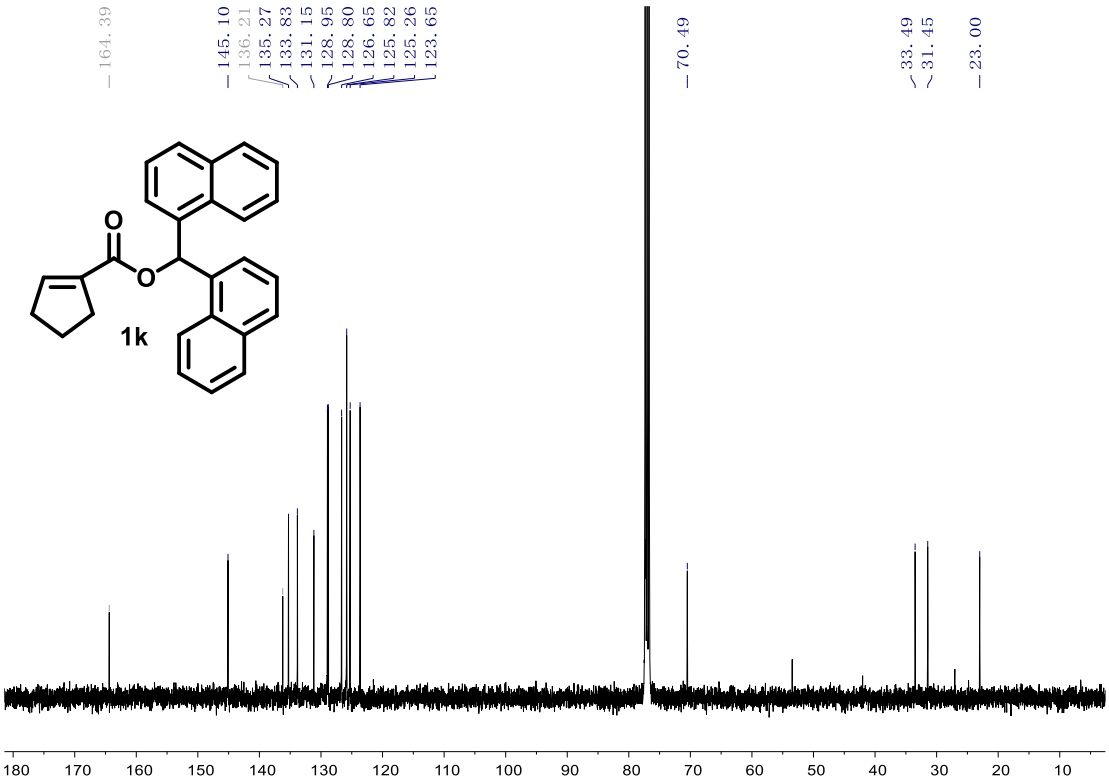


^{13}C NMR, $CDCl_3$, 101 MHz

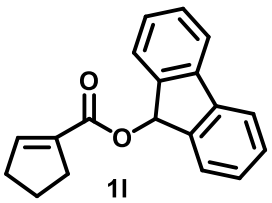




^{1}H NMR, $CDCl_3$, 400 MHz



^{13}C NMR, $CDCl_3$, 101 MHz



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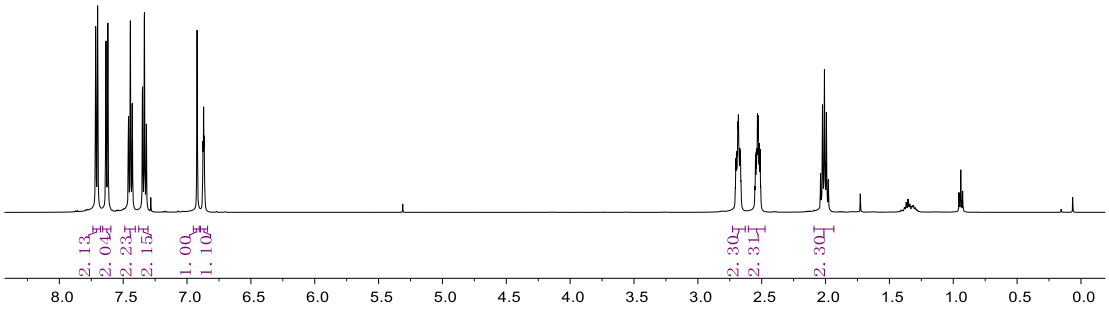
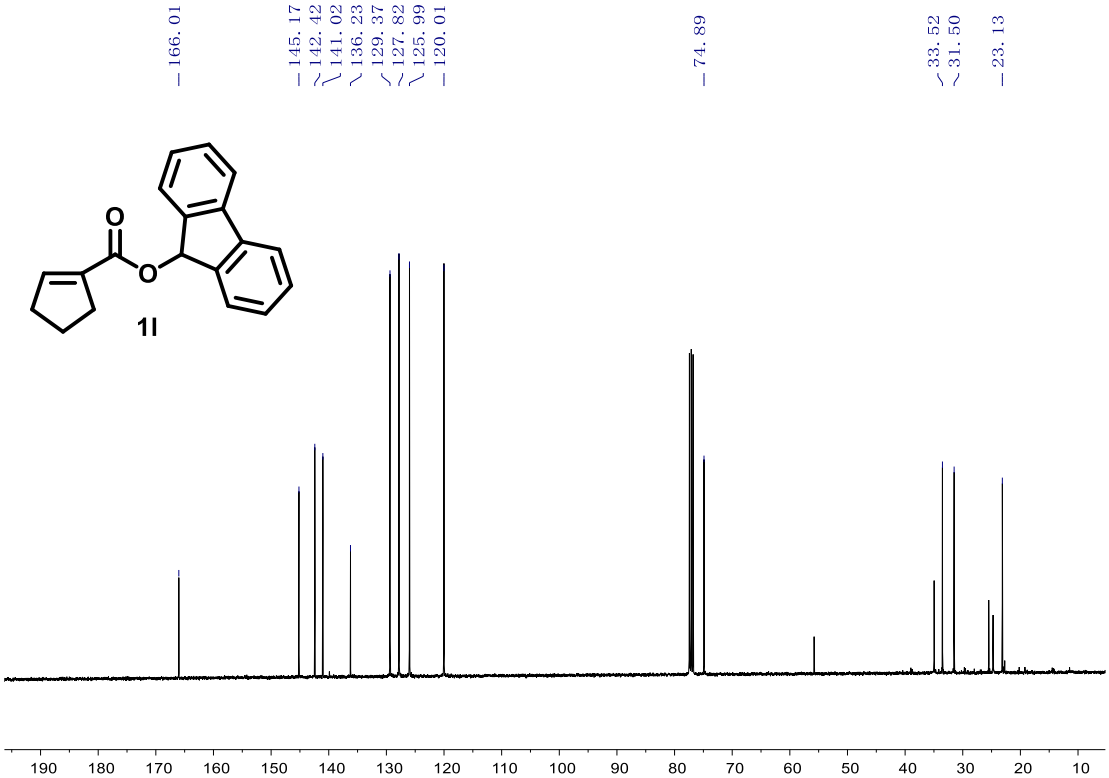


^{1}H NMR, $CDCl_3$, 500 MHz



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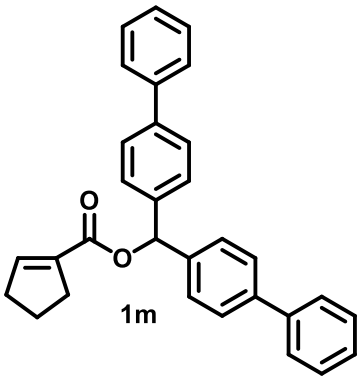
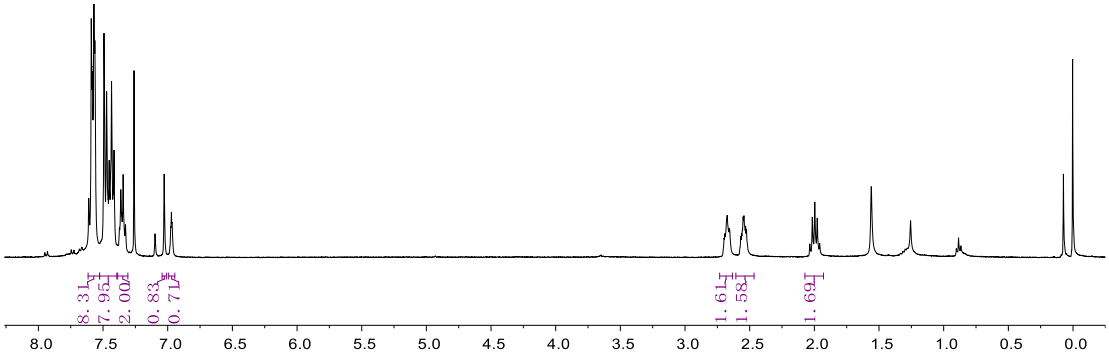
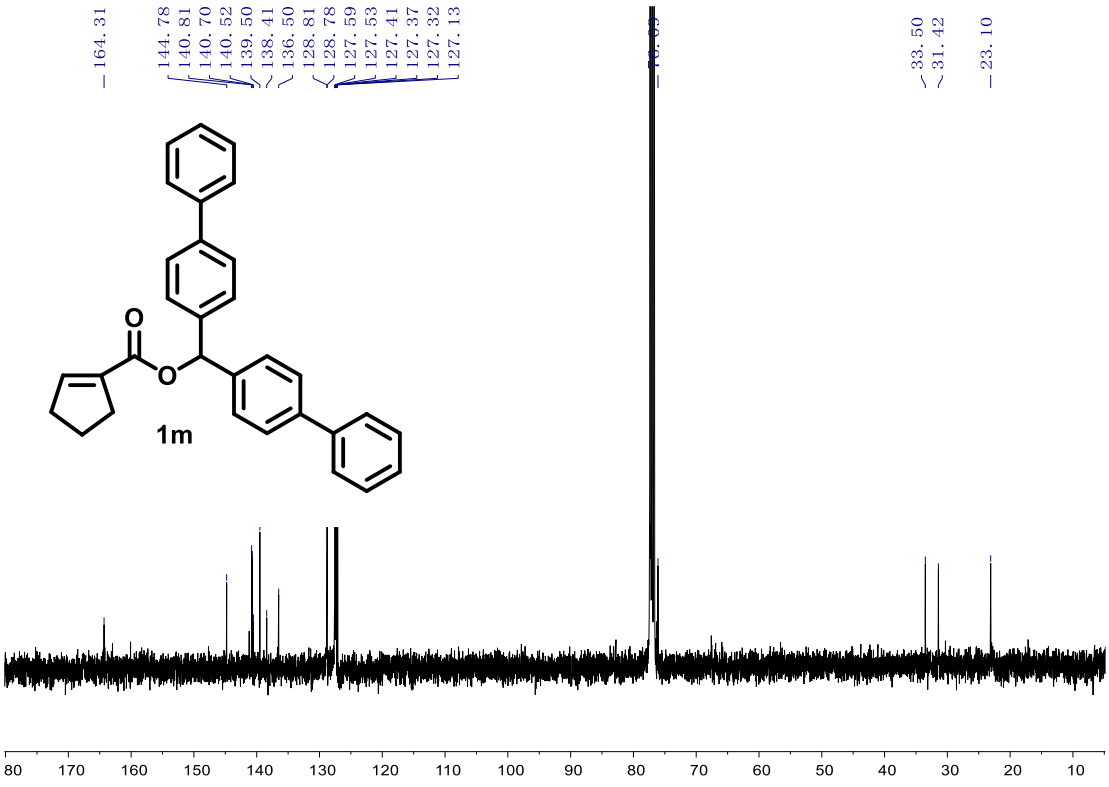
^{13}C NMR, $CDCl_3$, 101 MHz

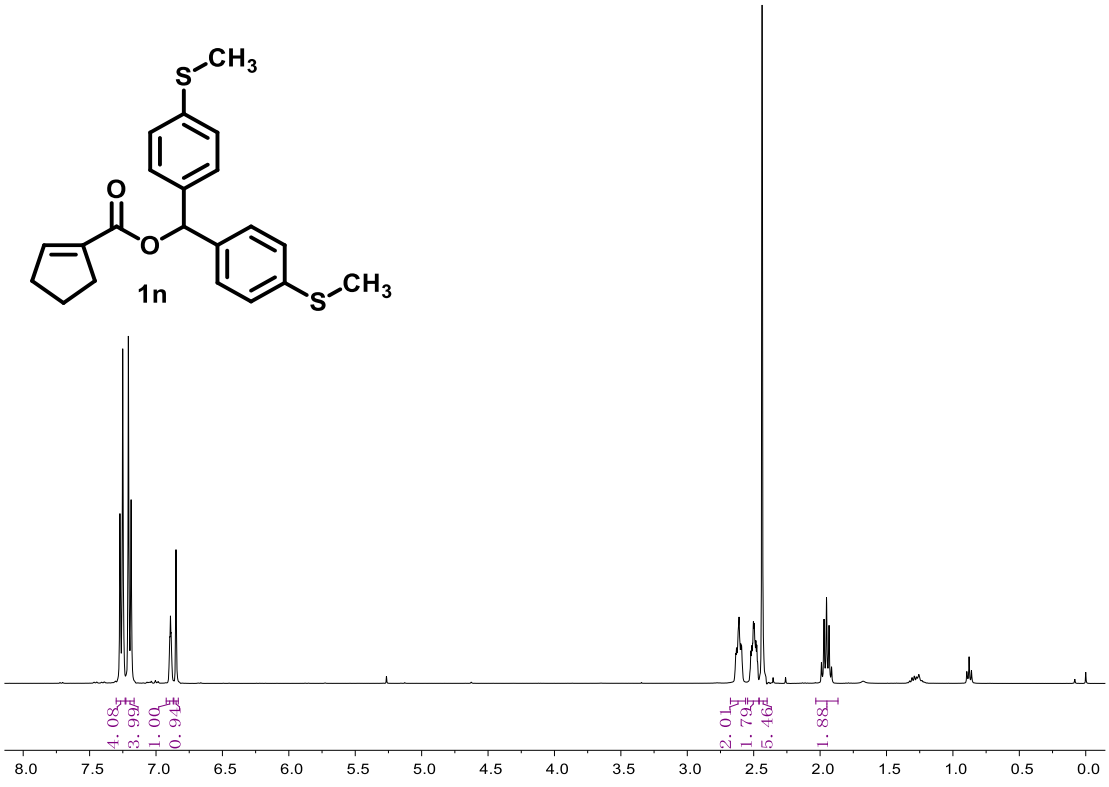




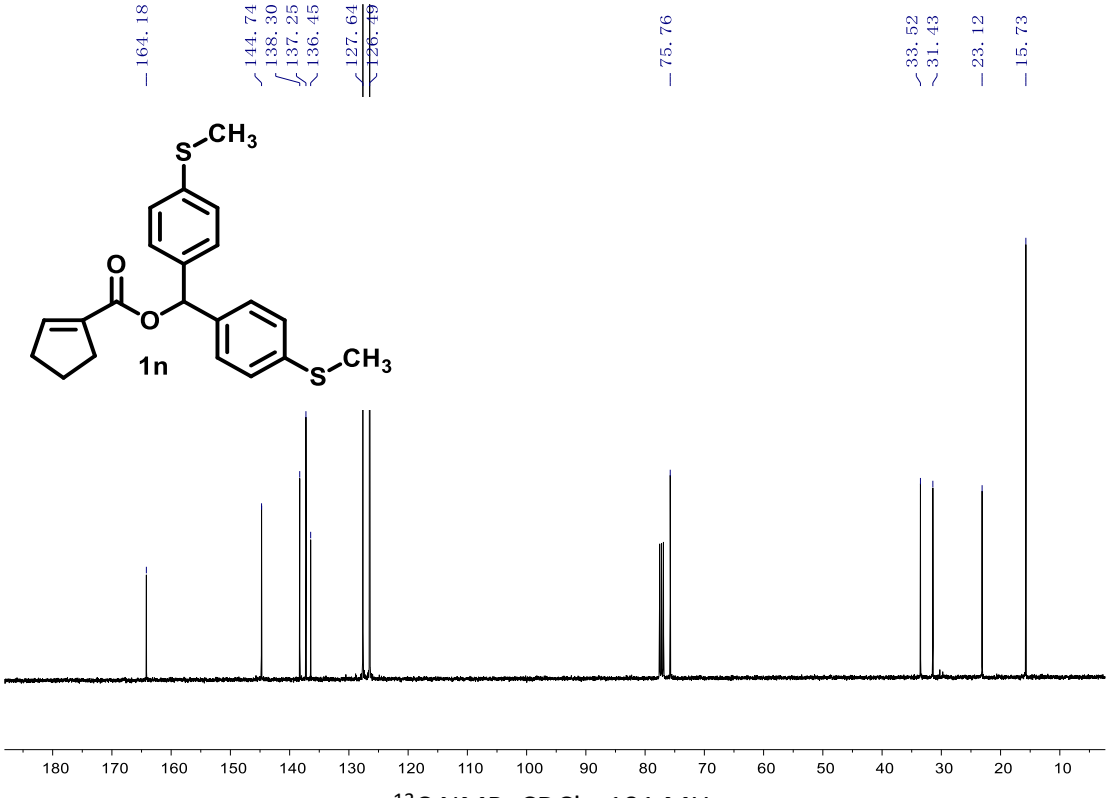
^{1}H NMR, $CDCl_3$, 400 MHz



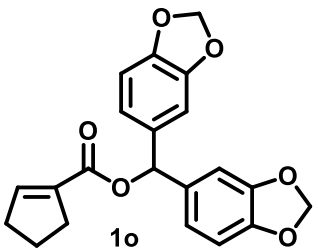
^{13}C NMR, $CDCl_3$, 101 MHz

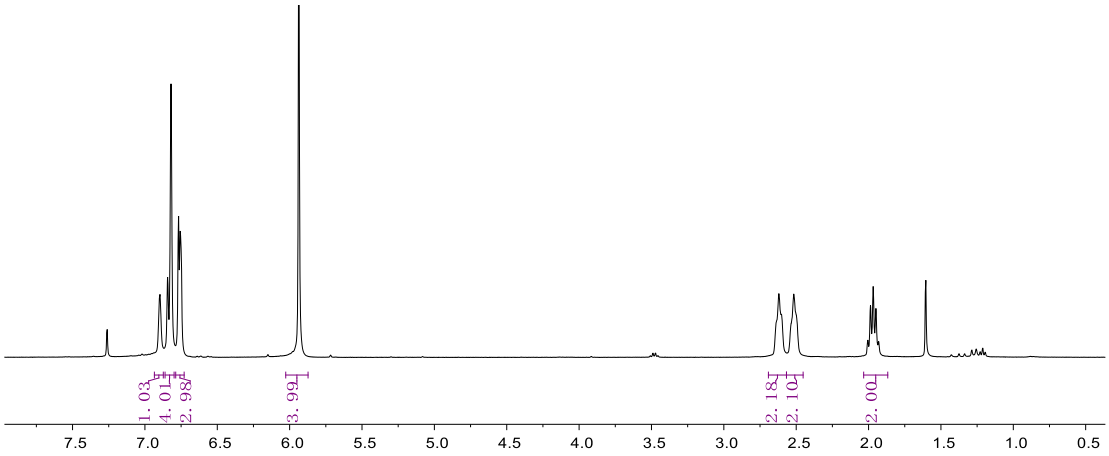


^{1}H NMR, $CDCl_3$, 400 MHz

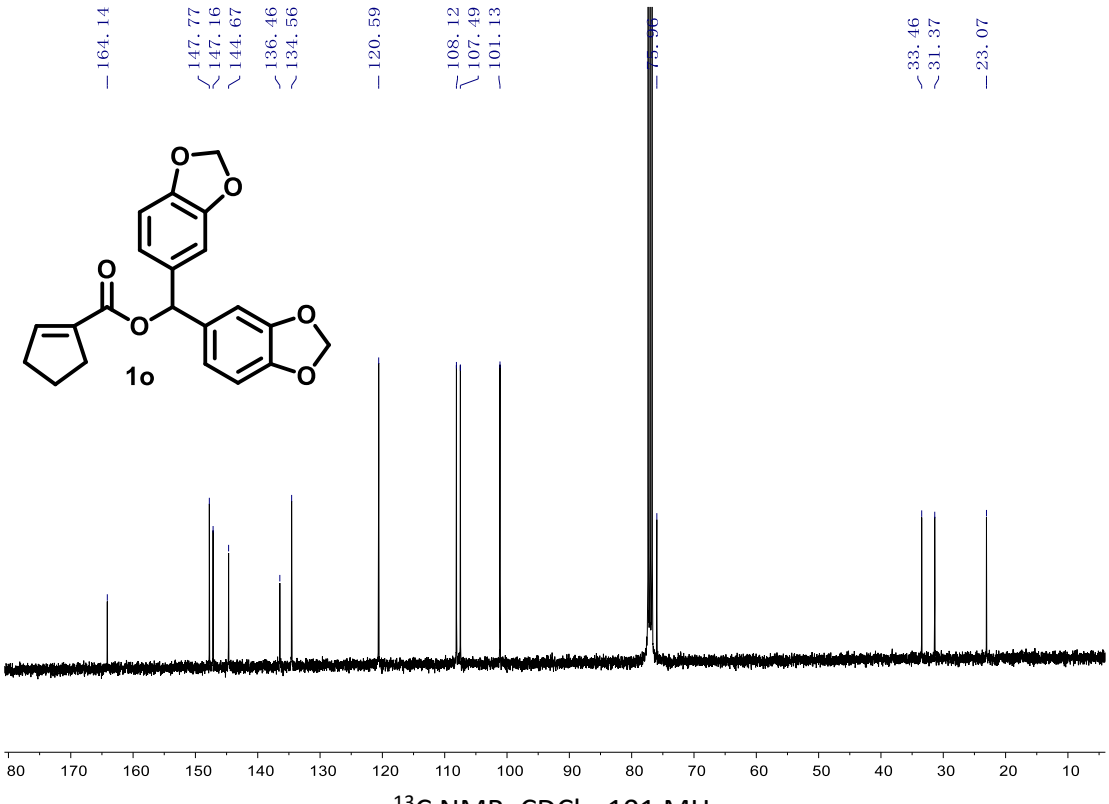


^{13}C NMR, $CDCl_3$, 101 MHz

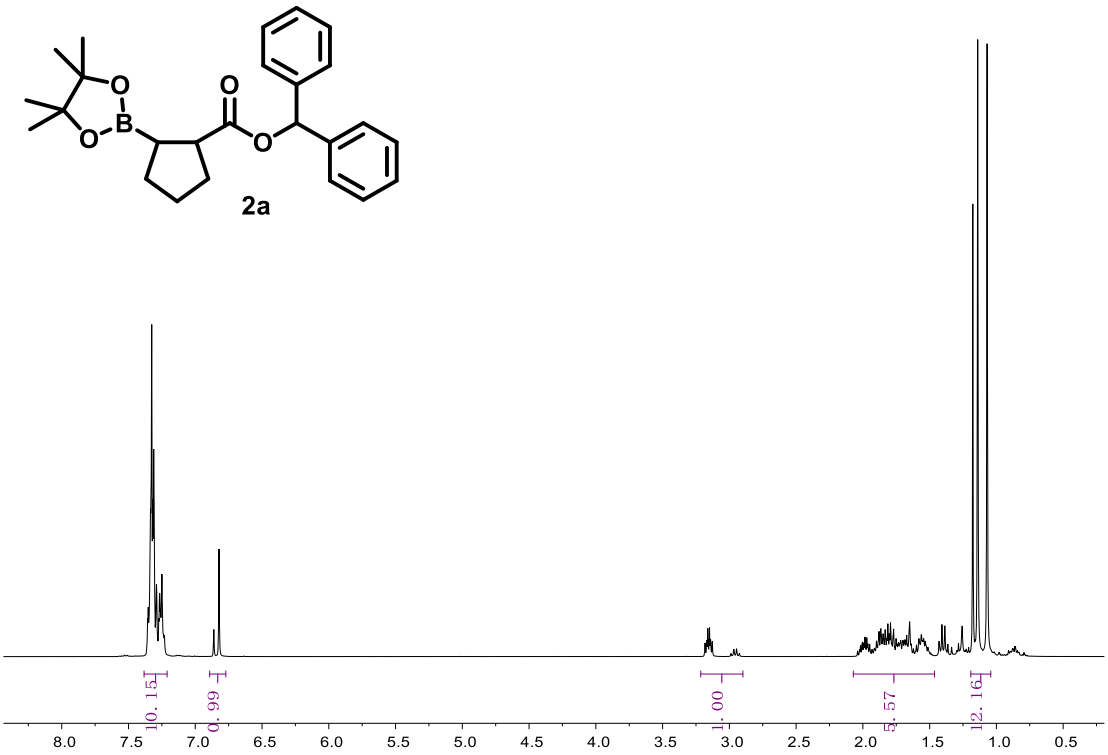




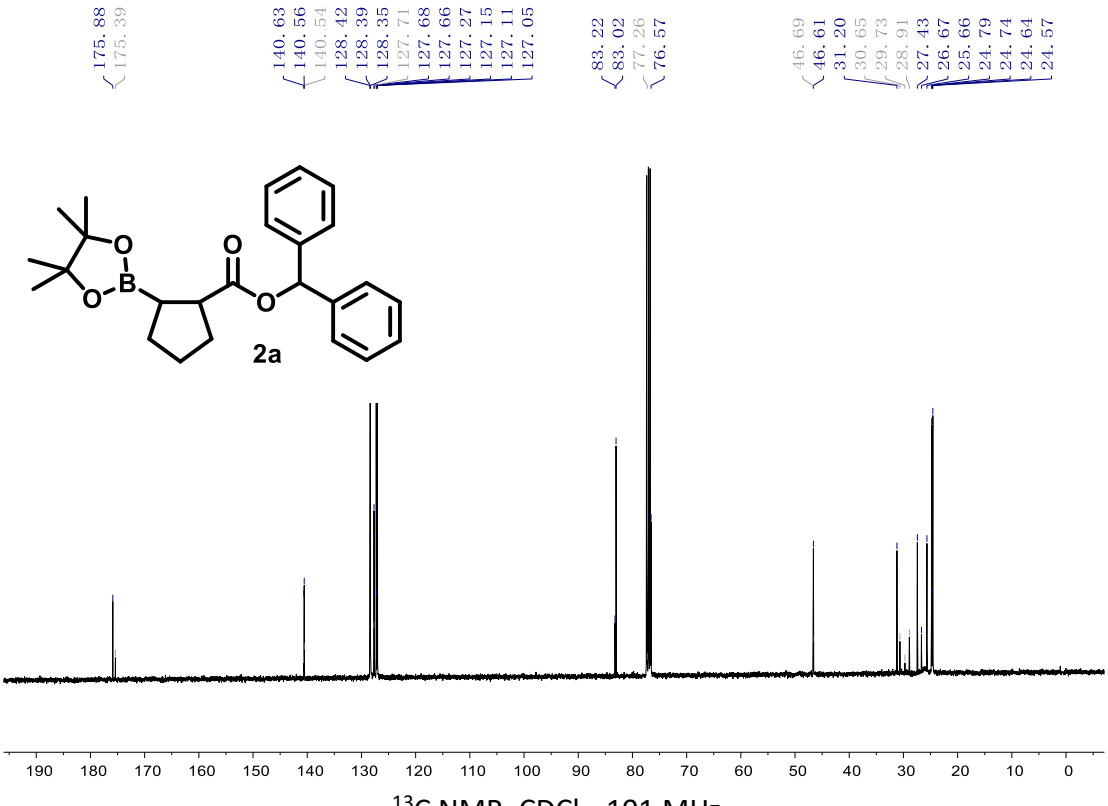
^{1}H NMR, $CDCl_3$, 400 MHz



^{13}C NMR, $CDCl_3$, 101 MHz

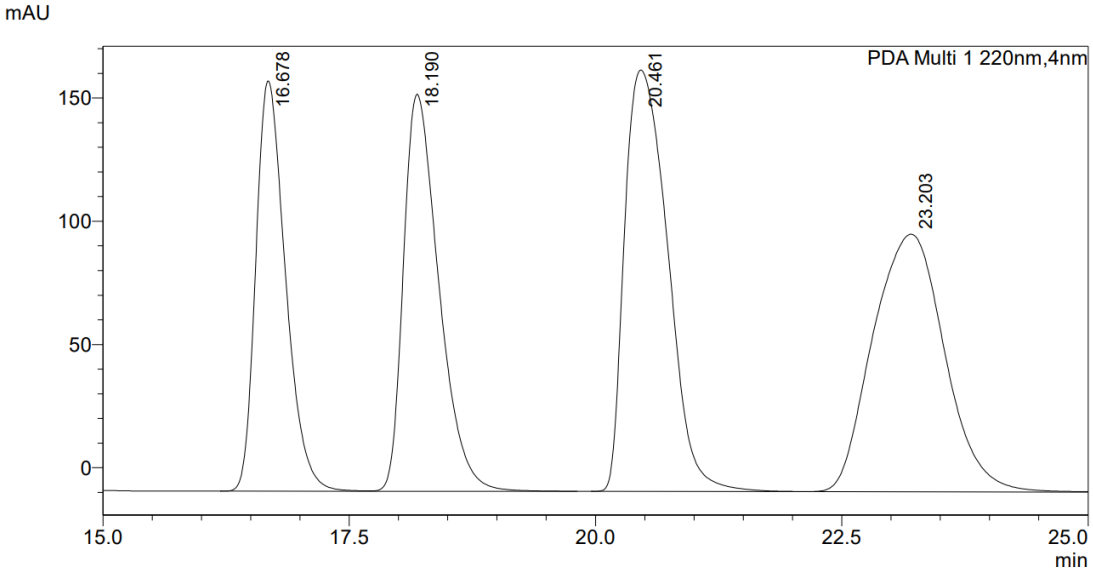


^{1}H NMR, $CDCl_3$, 400 MHz



^{13}C NMR, $CDCl_3$, 101 MHz

<Chromatogram>



<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%	Height	Name
1	16.678	3493729	19.402	166377	
2	18.190	4023907	22.346	161065	
3	20.461	5201273	28.884	171042	
4	23.203	5288342	29.368	104495	
总计		18007251	100.000	602979	

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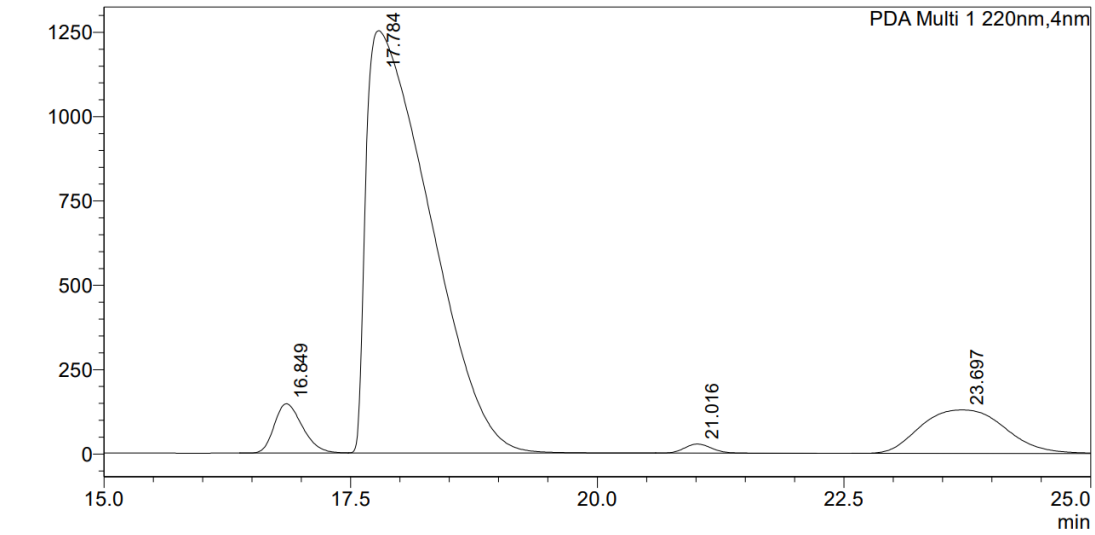
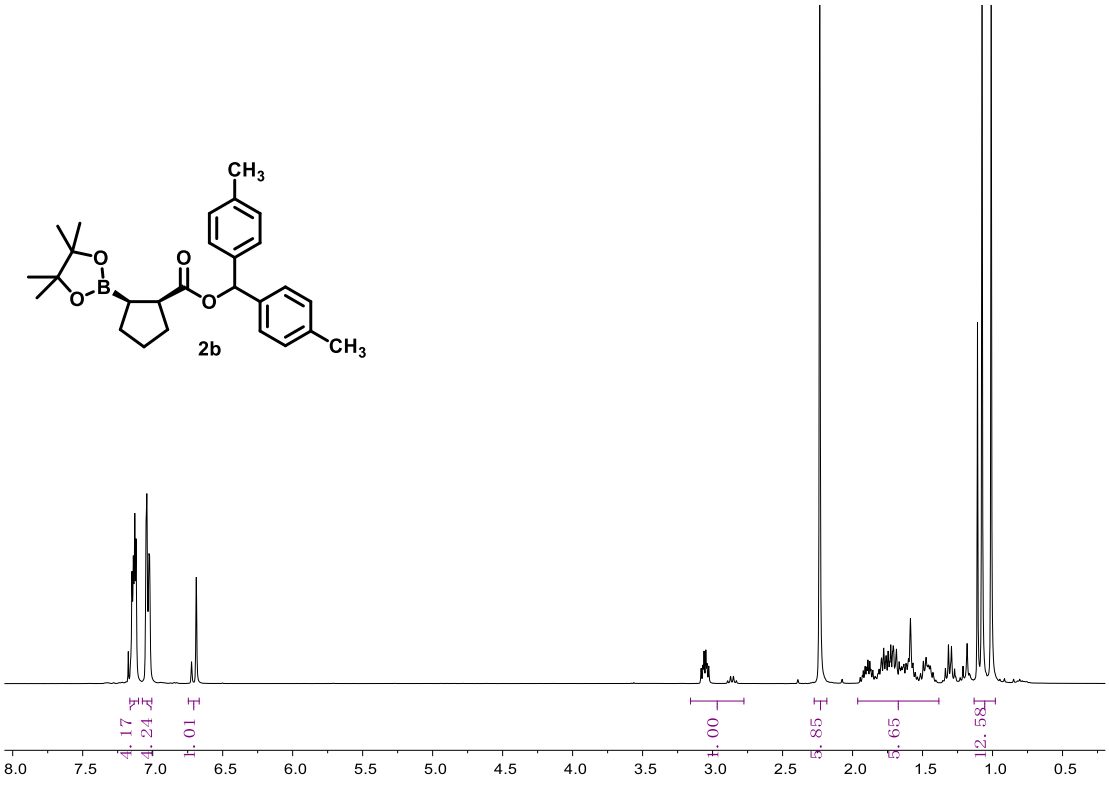


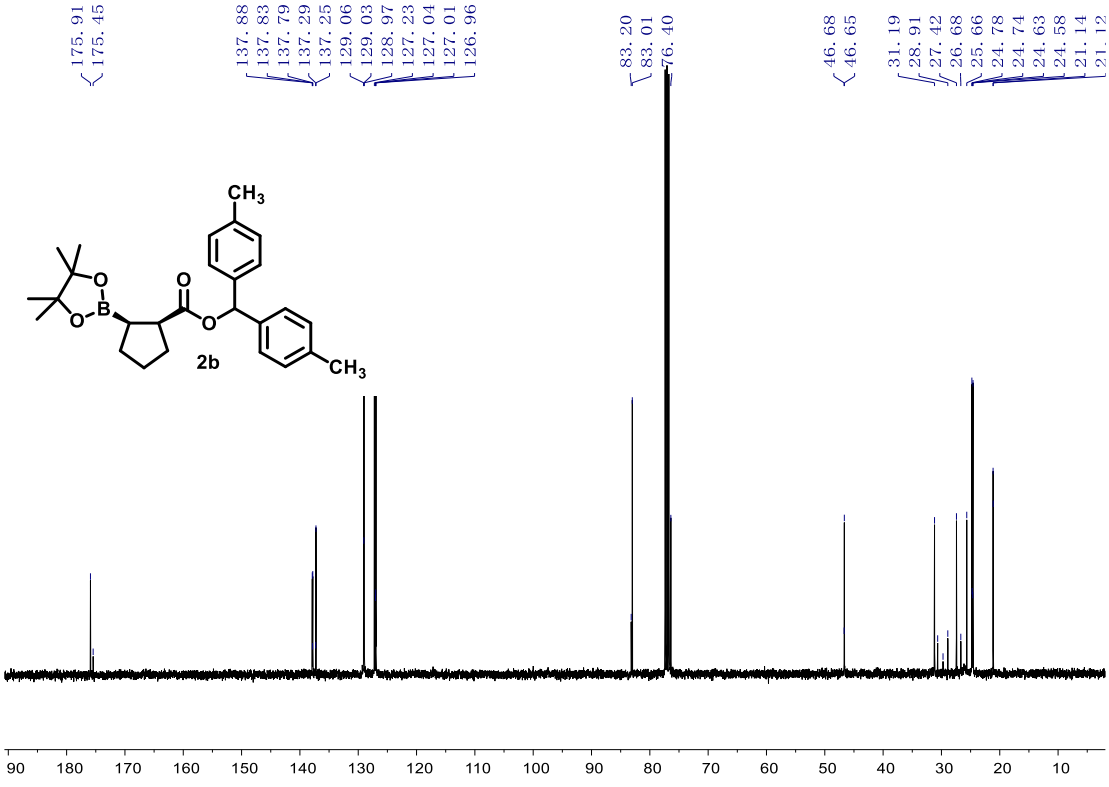
<Peak Table>

PDA Ch1 220nm

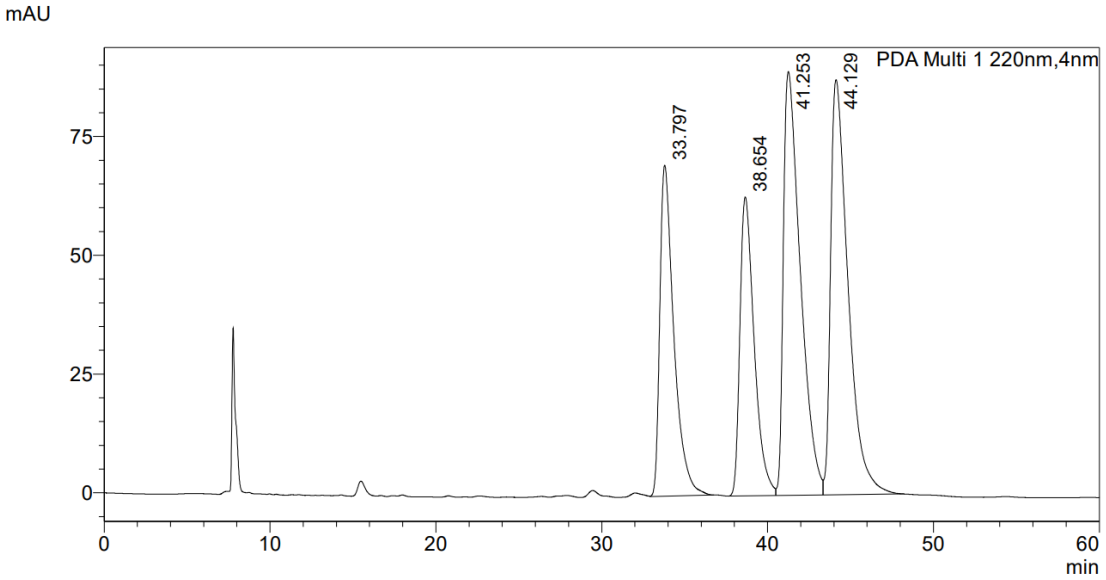
Peak#	Ret. Time	Area	Area%	Height	Name
1	16.849	2918619	4.322	146340	
2	17.784	56380994	83.497	1252422	
3	21.016	525018	0.778	27074	
4	23.697	7700335	11.404	128796	
总计		67524965	100.000	1554632	



^{1}H NMR, $CDCl_3$, 400 MHz



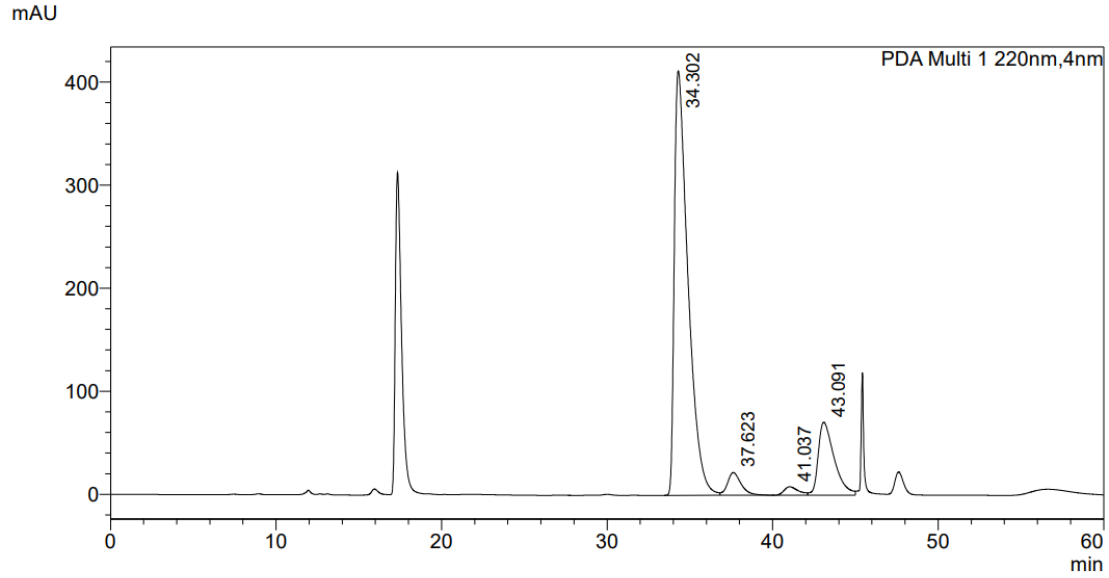
^{13}C NMR, $CDCl_3$, 101 MHz



<Peak Table>

PDA Ch1 220nm

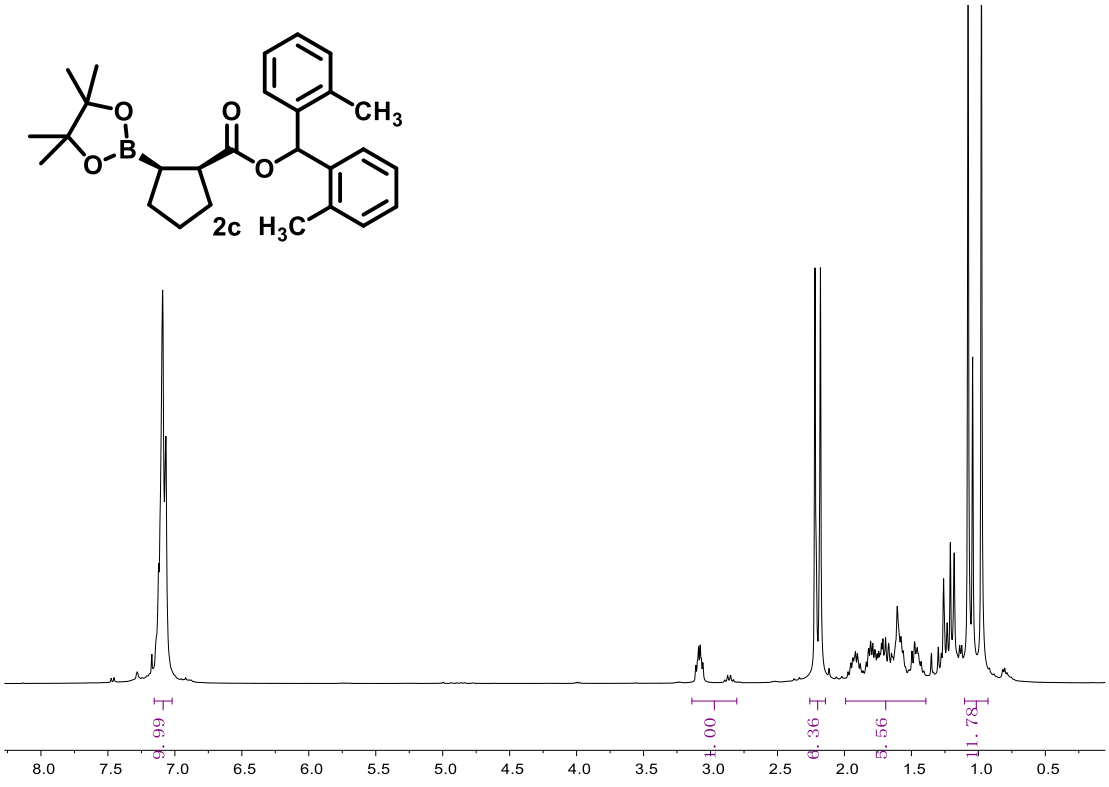
Peak#	Ret. Time	Area	Area%	Height	Name
1	33.797	4094584	19.851	69652	
2	38.654	3767451	18.265	62924	
3	41.253	6362051	30.844	89244	
4	44.129	6402241	31.039	87384	
总计		20626327	100.000	309204	



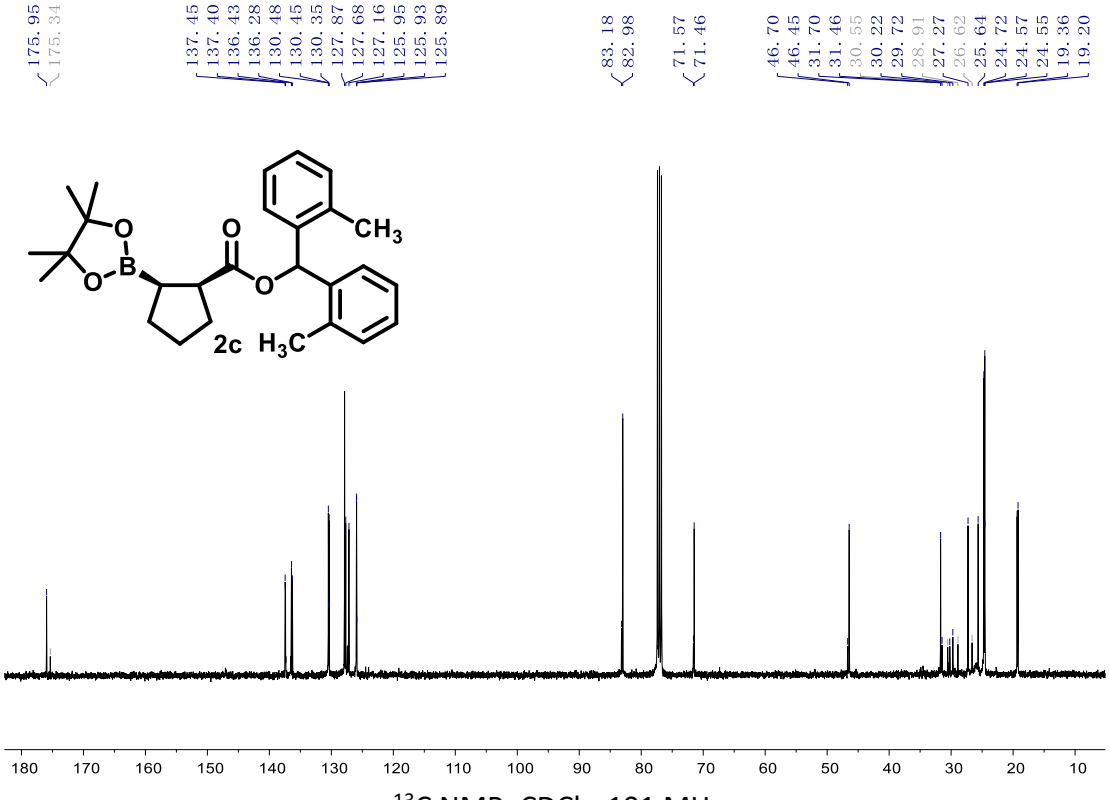
<Peak Table>

PDA Ch1 220nm

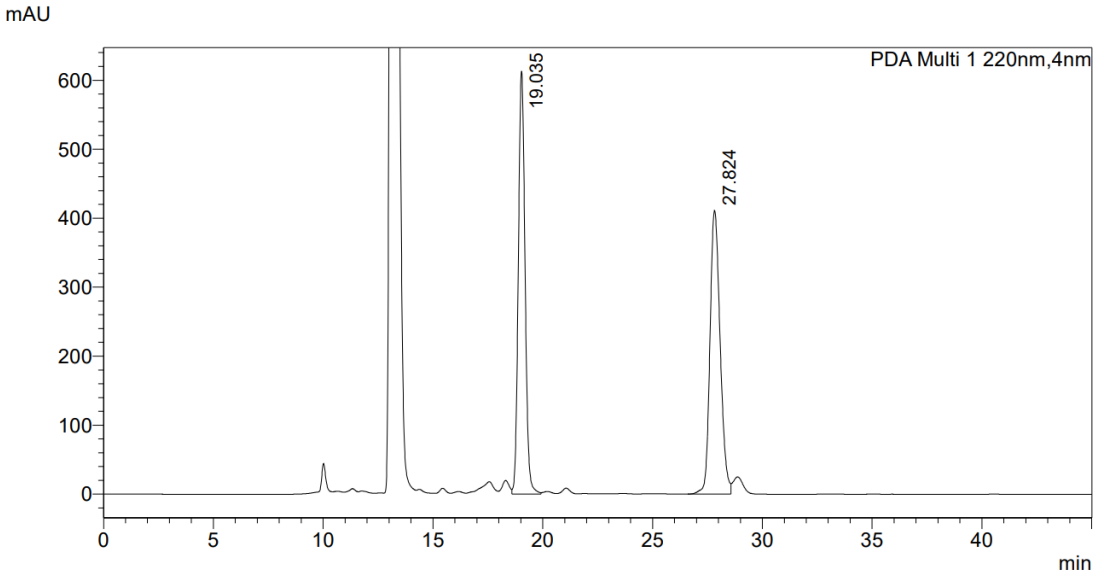
Peak#	Ret. Time	Area	Area%	Height	Name
1	34.302	23690121	78.389	412116	
2	37.623	1275290	4.220	22097	
3	41.037	496675	1.643	8212	
4	43.091	4758976	15.747	70747	
总计		30221062	100.000	513172	



^{1}H NMR, $CDCl_3$, 400 MHz



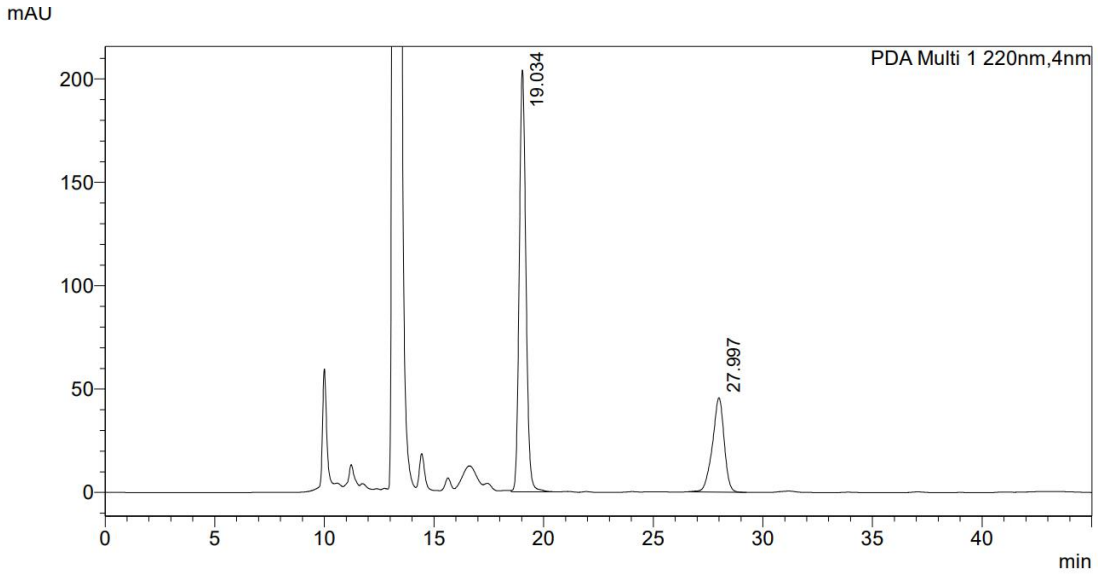
^{13}C NMR, $CDCl_3$, 101 MHz



<Peak Table>

PDA Ch1 220nm

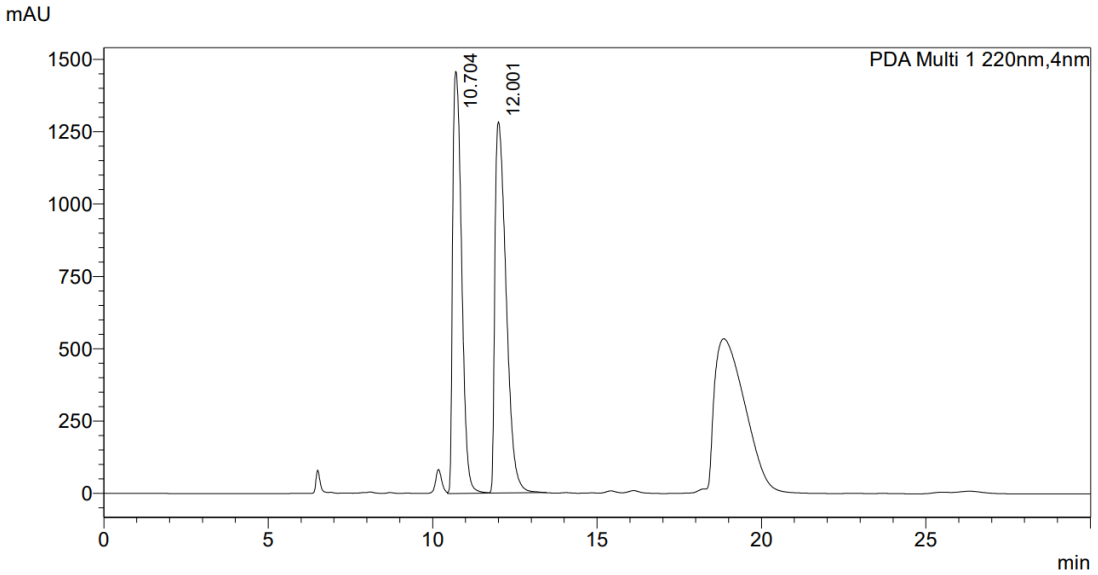
Peak#	Ret. Time	Area	Area%	Height	Name
1	19.035	12972047	49.452	612779	
2	27.824	13259502	50.548	411328	
总计		26231549	100.000	1024106	



<Peak Table>

PDA Ch1 220nm

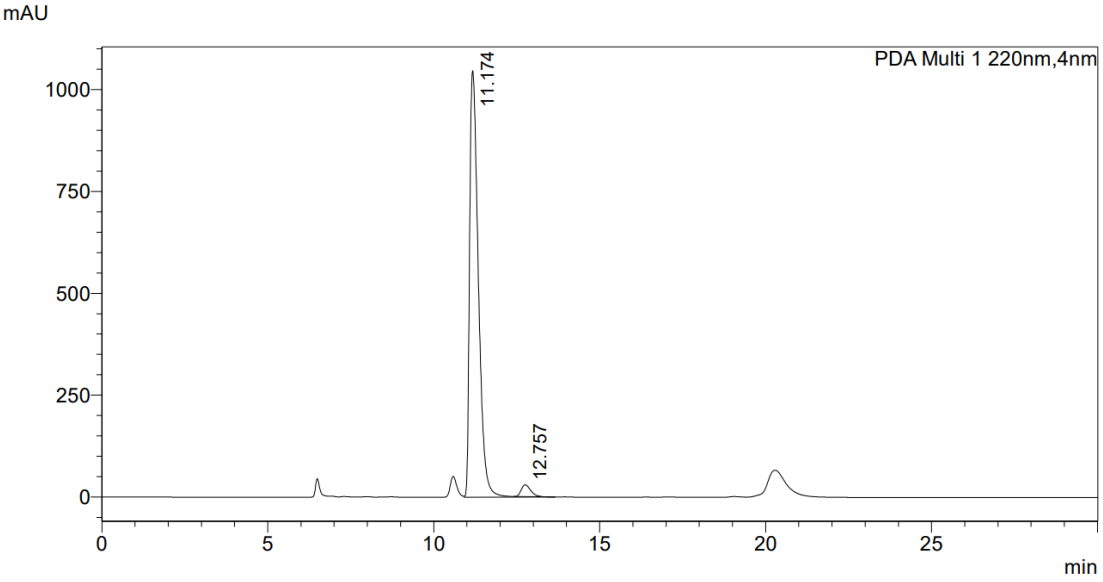
Peak#	Ret. Time	Area	Area%	Height	Name
1	19.034	4290549	71.649	204015	
2	27.997	1697729	28.351	45670	
总计		5988278	100.000	249686	



<Peak Table>

PDA Ch1 220nm

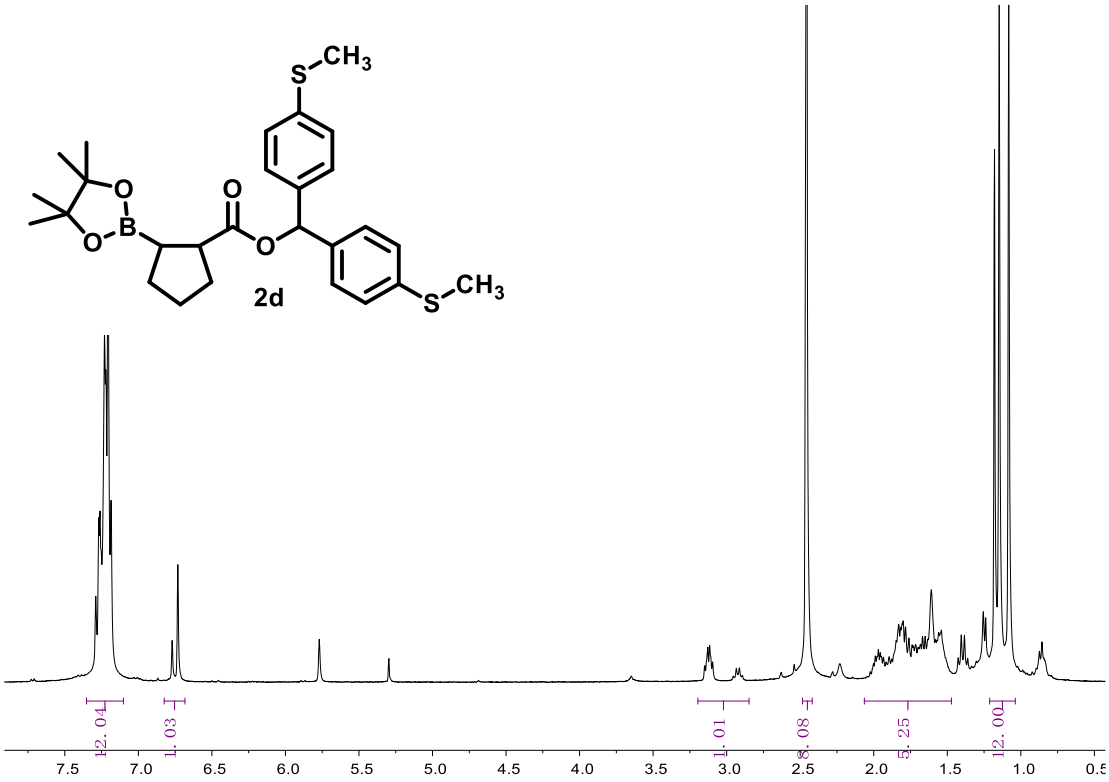
Peak#	Ret. Time	Area	Area%	Height	Name
1	10.704	27716495	47.565	1459447	
2	12.001	30554768	52.435	1283259	
总计		58271263	100.000	2742706	



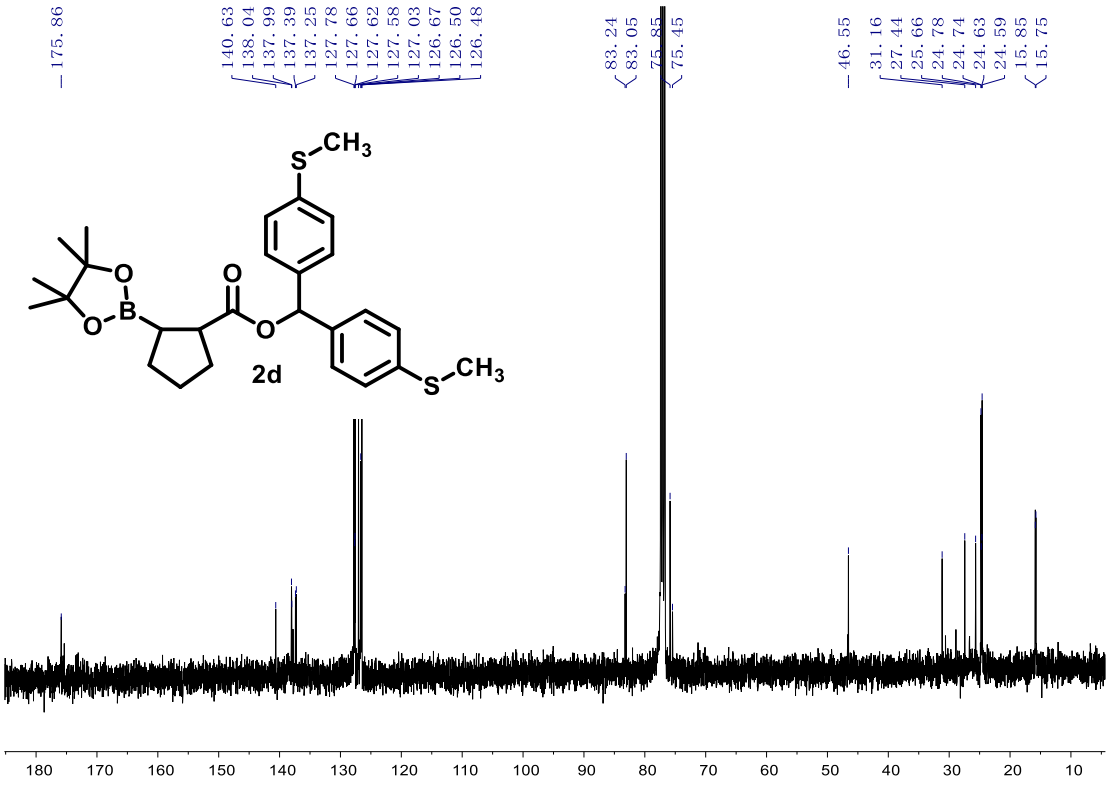
<Peak Table>

PDA Ch1 220nm

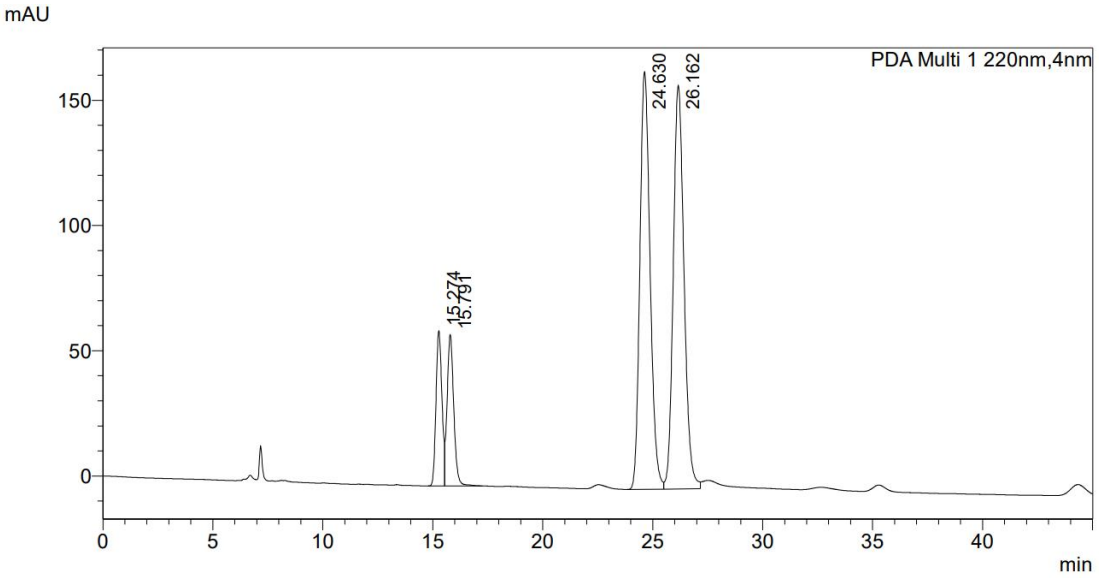
Peak#	Ret. Time	Area	Area%	Height	Name
1	11.174	19253187	97.025	1047057	
2	12.757	590410	2.975	29079	
总计		19843597	100.000	1076136	



^{1}H NMR, $CDCl_3$, 400 MHz



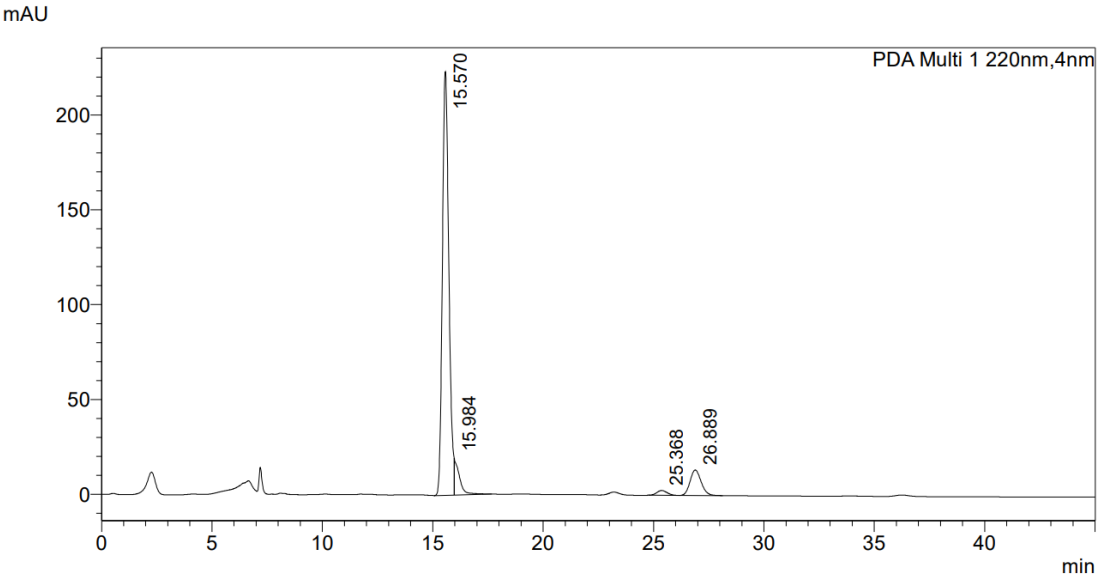
^{13}C NMR, $CDCl_3$, 101 MHz



<Peak Table>

PDA Ch1 220nm

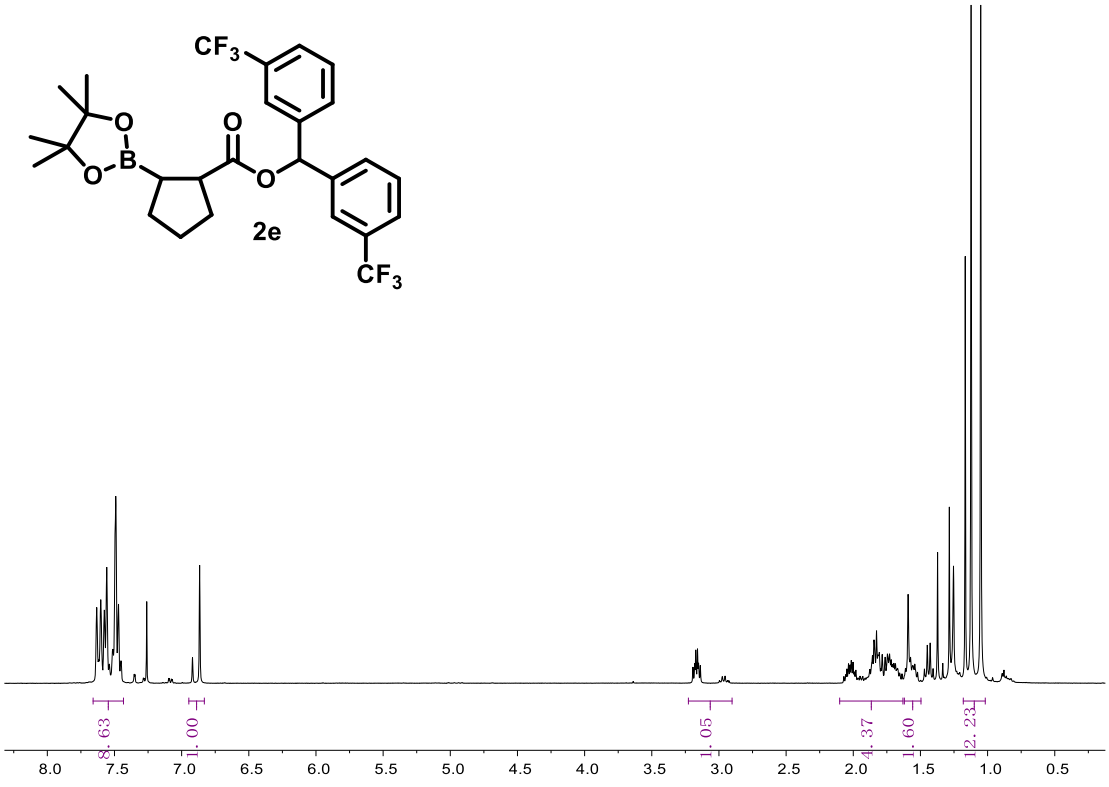
Peak#	Ret. Time	Area	Area%	Height	Name
1	15.274	1166839	8.788	61929	
2	15.791	1262790	9.510	60354	
3	24.630	5365362	40.408	166786	
4	26.162	5482974	41.294	161189	
总计		13277964	100.000	450258	



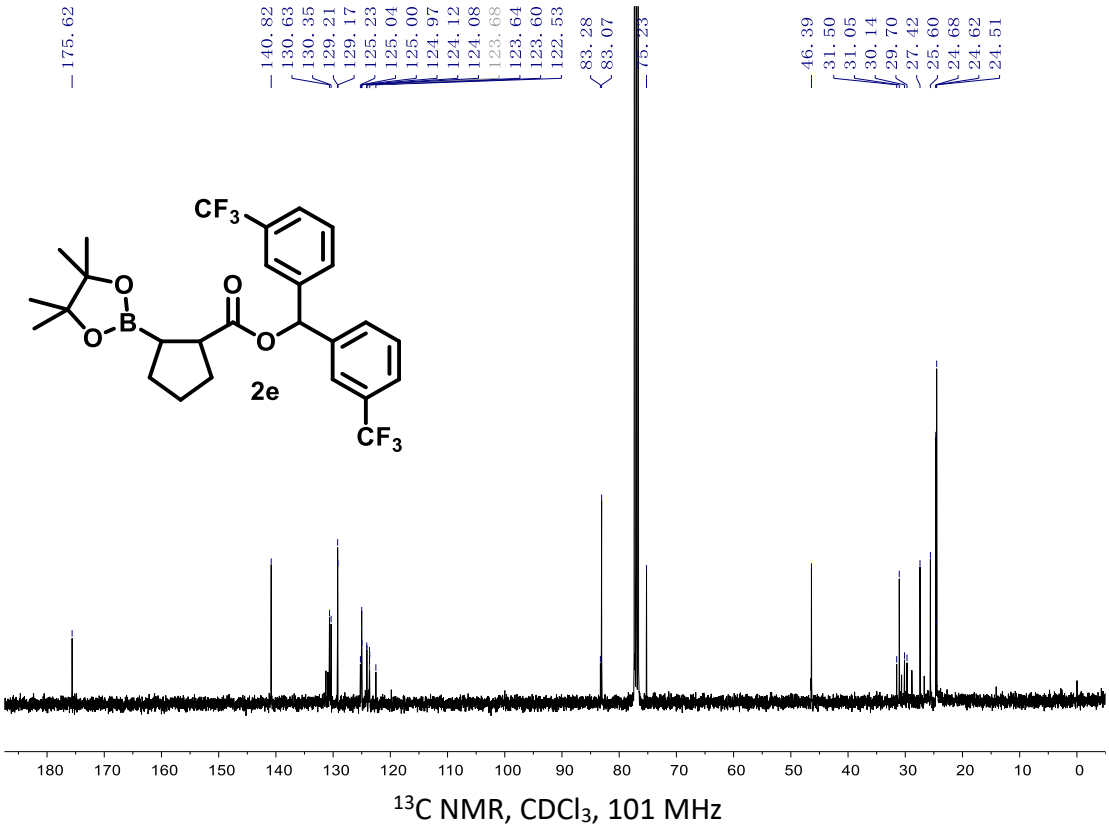
<Peak Table>

PDA Ch1 220nm

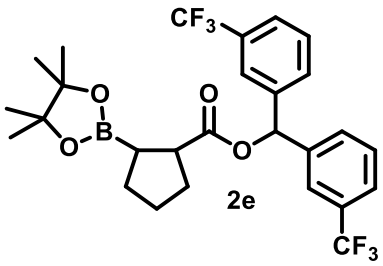
Peak#	Ret. Time	Area	Area%	Height	Name
1	15.570	4535164	83.978	223437	
2	15.984	314838	5.830	18843	
3	25.368	82330	1.525	2545	
4	26.889	468074	8.667	13434	
总计		5400405	100.000	258259	

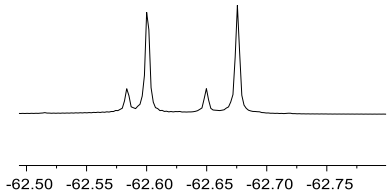


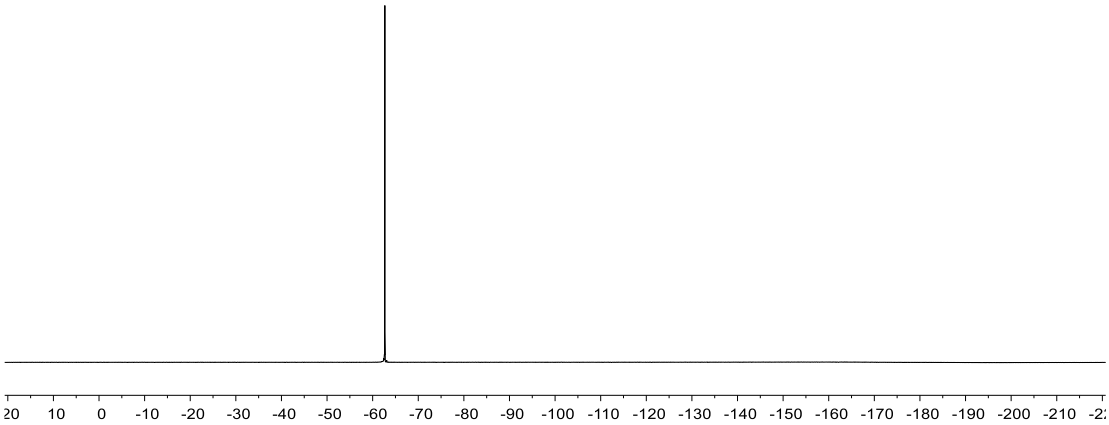
^{1}H NMR, $CDCl_3$, 400 MHz



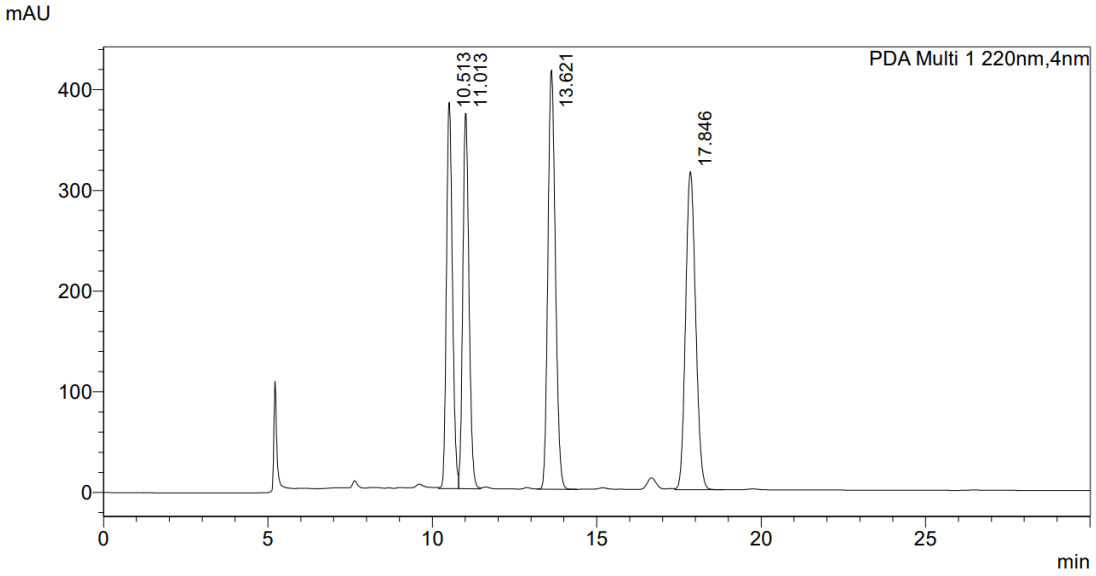
^{13}C NMR, $CDCl_3$, 101 MHz







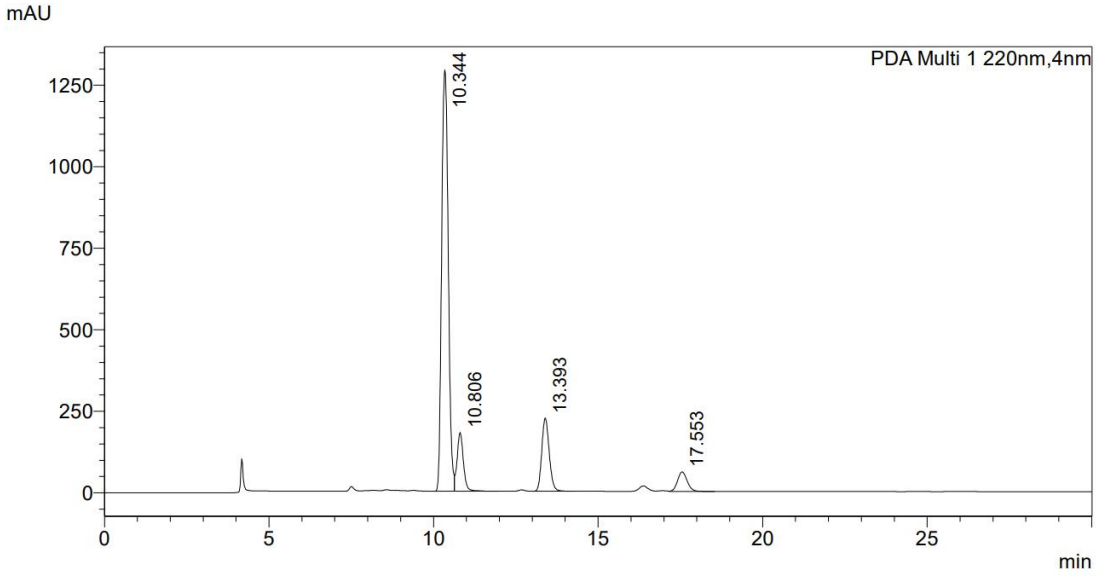
^{19}F NMR, $CDCl_3$, 471 MHz



<Peak Table>

PDA Ch1 220nm

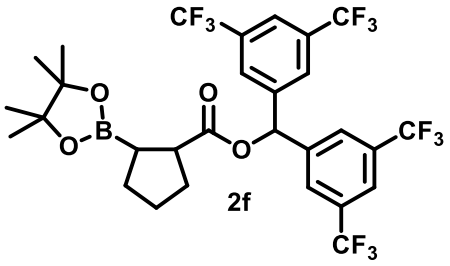
Peak#	Ret. Time	Area	Area%	Height	Name
1	10.513	4839324	21.011	383592	
2	11.013	4877111	21.175	372593	
3	13.621	6609770	28.697	415851	
4	17.846	6706581	29.118	315743	
总计		23032786	100.000	1487779	



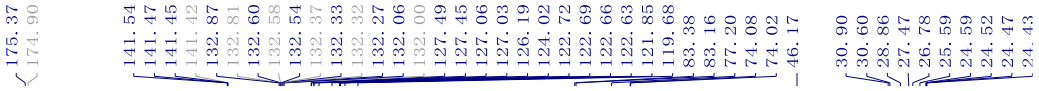
<Peak Table>

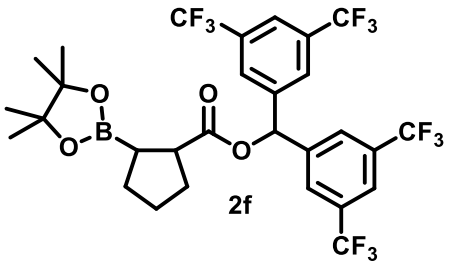
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%	Height	Name
1	10.344	18047415	71.525	1290966	
2	10.806	2408853	9.547	179997	
3	13.393	3550760	14.072	224241	
4	17.553	1225406	4.856	59876	
总计		25232434	100.000	1755080	

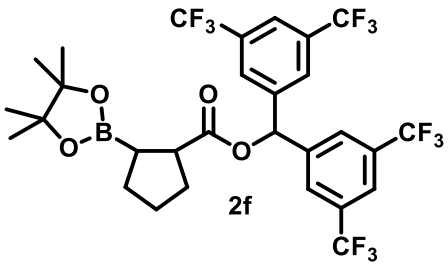


^{1}H NMR, $CDCl_3$, 400 MHz





^{13}C NMR, $CDCl_3$, 101 MHz



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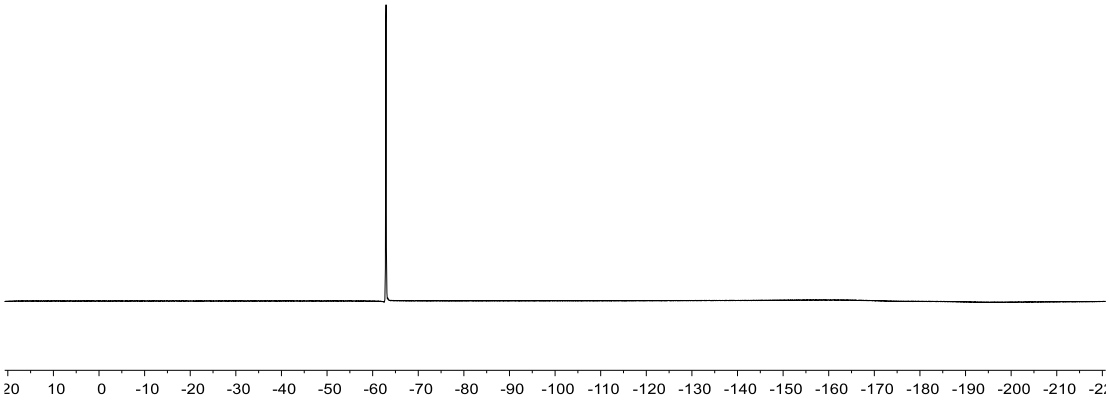
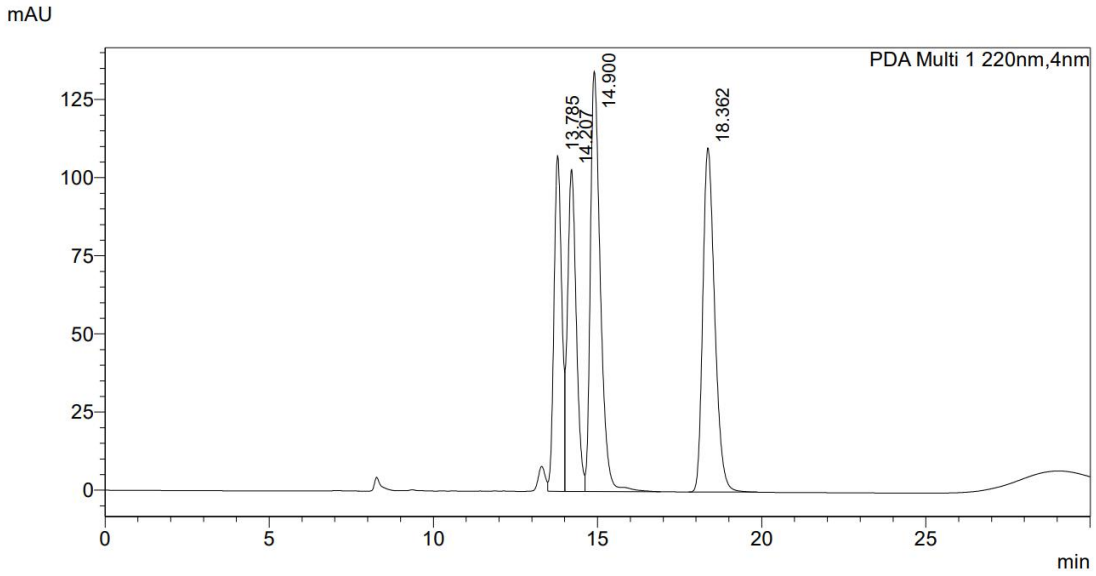


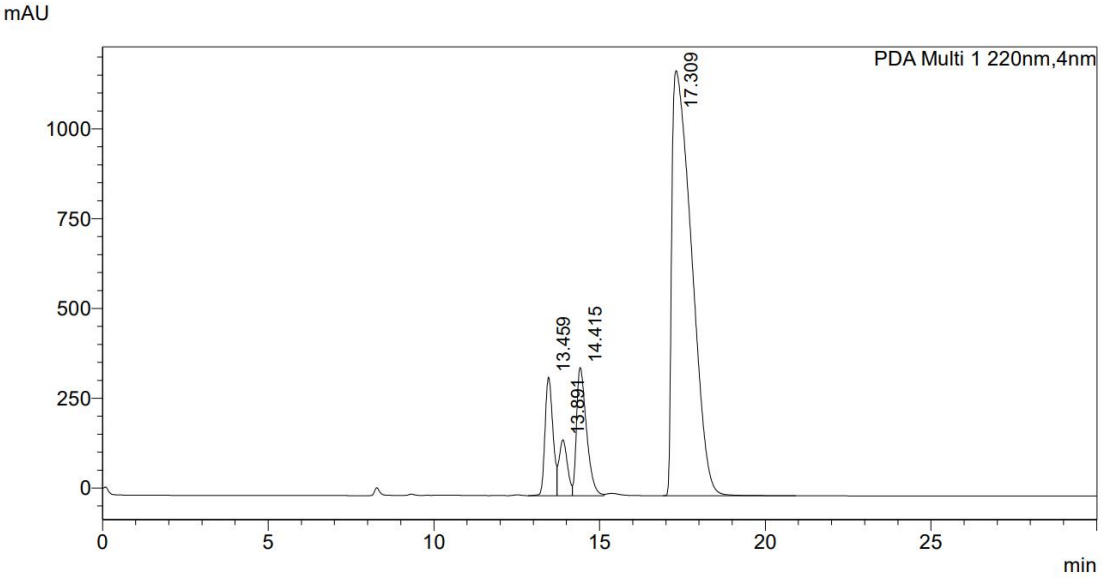
^{19}F NMR, $CDCl_3$, 471 MHz



<Peak Table>

PDA Ch1 220nm

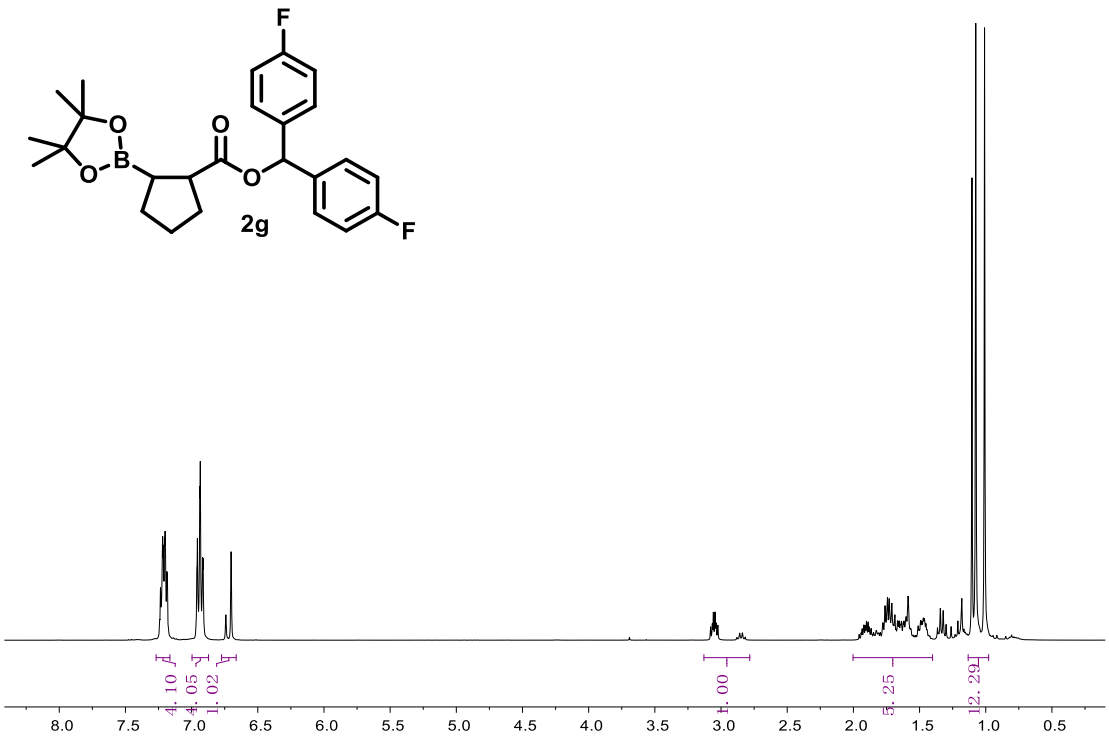
Peak#	Ret. Time	Area	Area%	Height	Name
1	13.785	1773974	19.089	107349	
2	14.207	1903339	20.482	102948	
3	14.900	2838890	30.549	134451	
4	18.362	2776747	29.880	110102	
总计		9292950	100.000	454850	



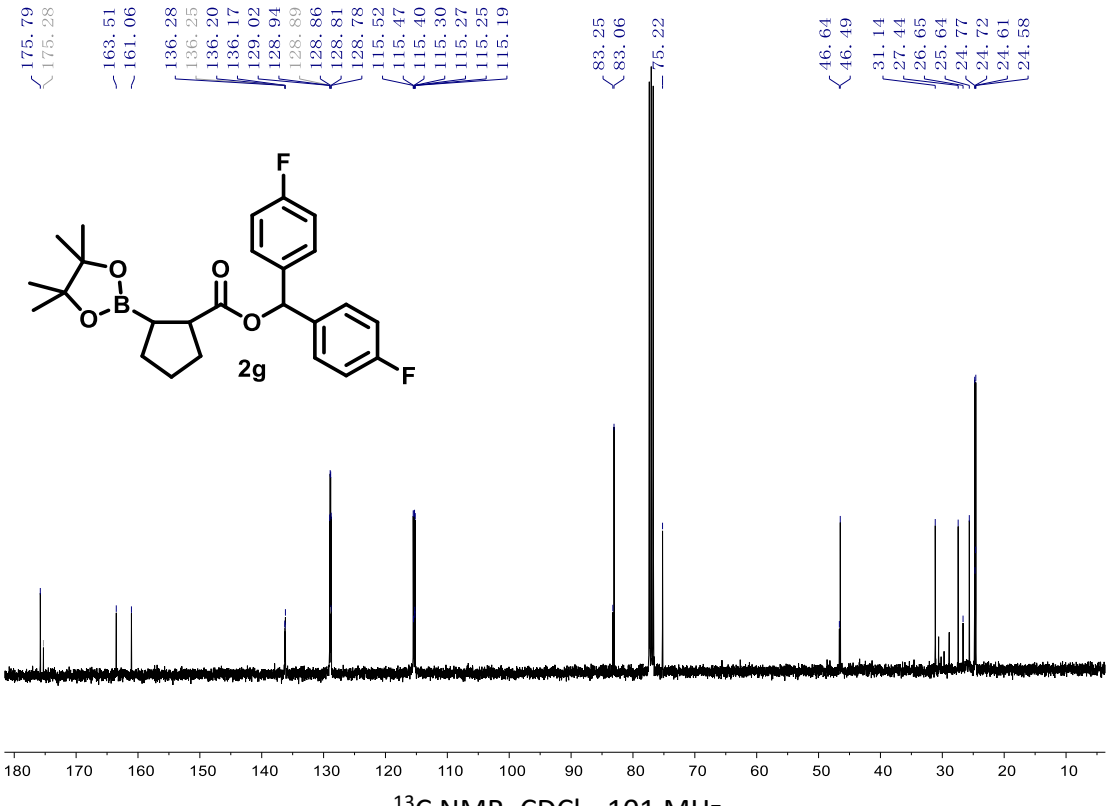
<Peak Table>

PDA Ch1 220nm

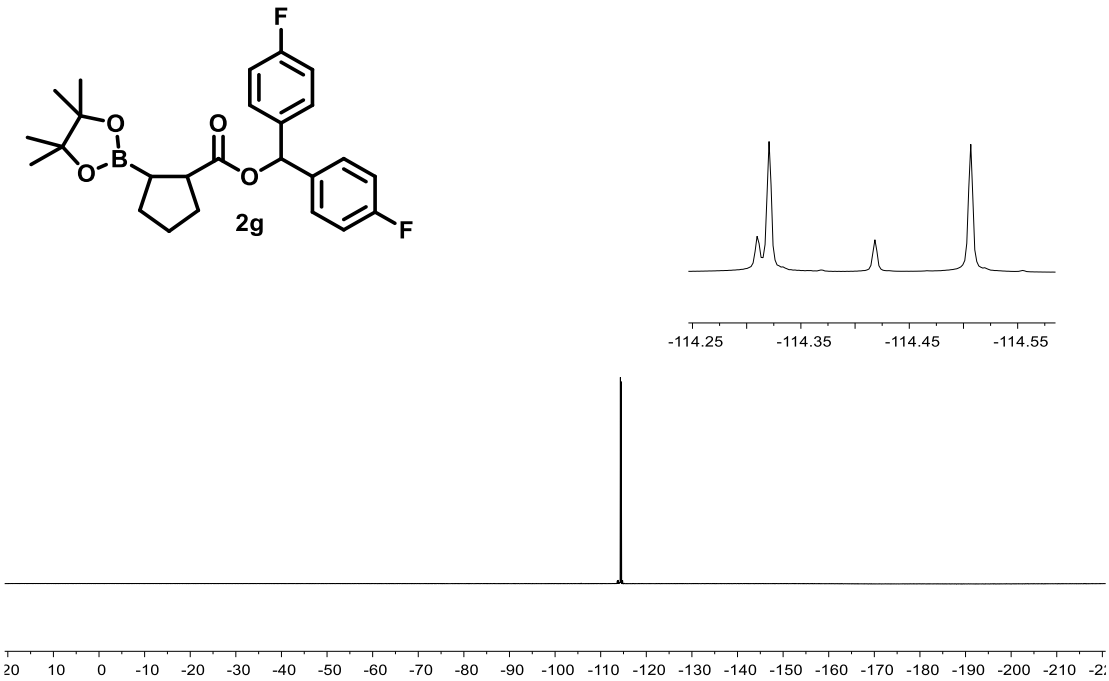
Peak#	Ret. Time	Area	Area%	Height	Name
1	13.459	5475477	8.466	329836	
2	13.891	2724505	4.212	155554	
3	14.415	7450247	11.519	356727	
4	17.309	49028118	75.803	1183892	
总计		64678346	100.000	2026009	



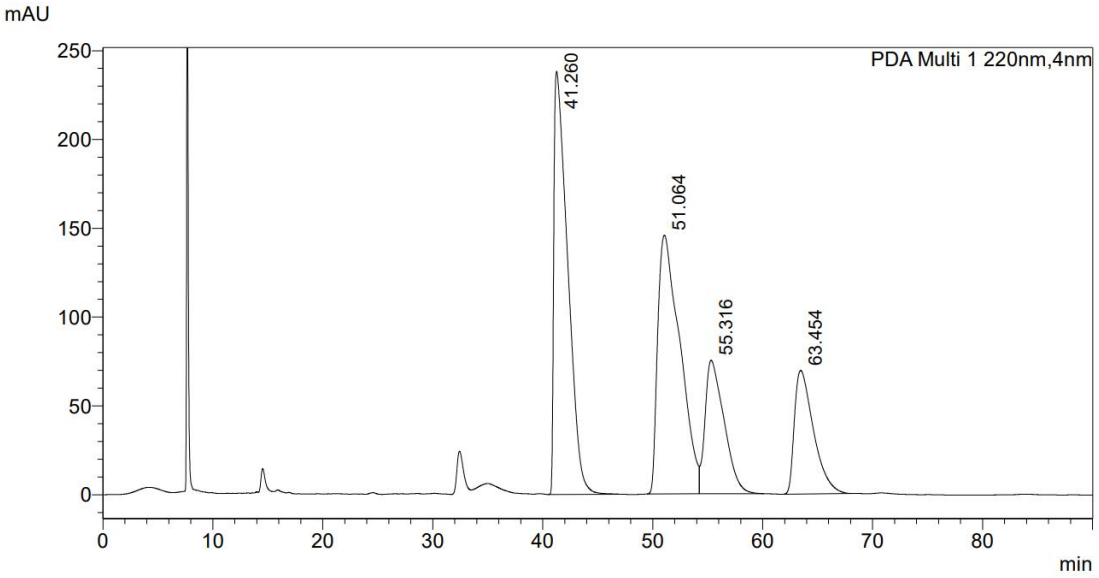
^{1}H NMR, $CDCl_3$, 400 MHz



^{13}C NMR, $CDCl_3$, 101 MHz



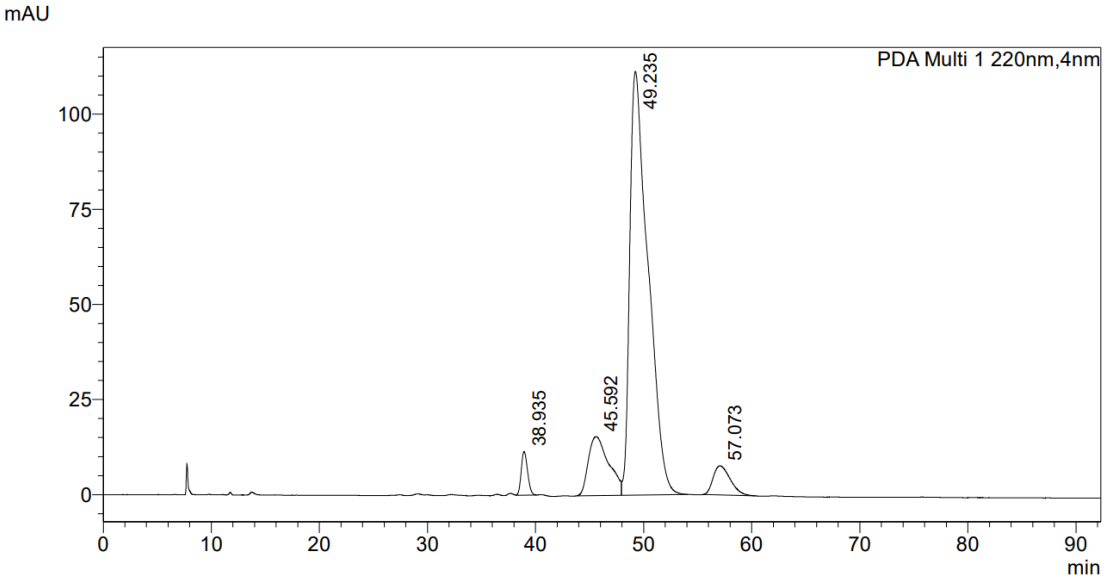
^{19}F NMR, $CDCl_3$, 471 MHz



<Peak Table>

PDA Ch1 220nm

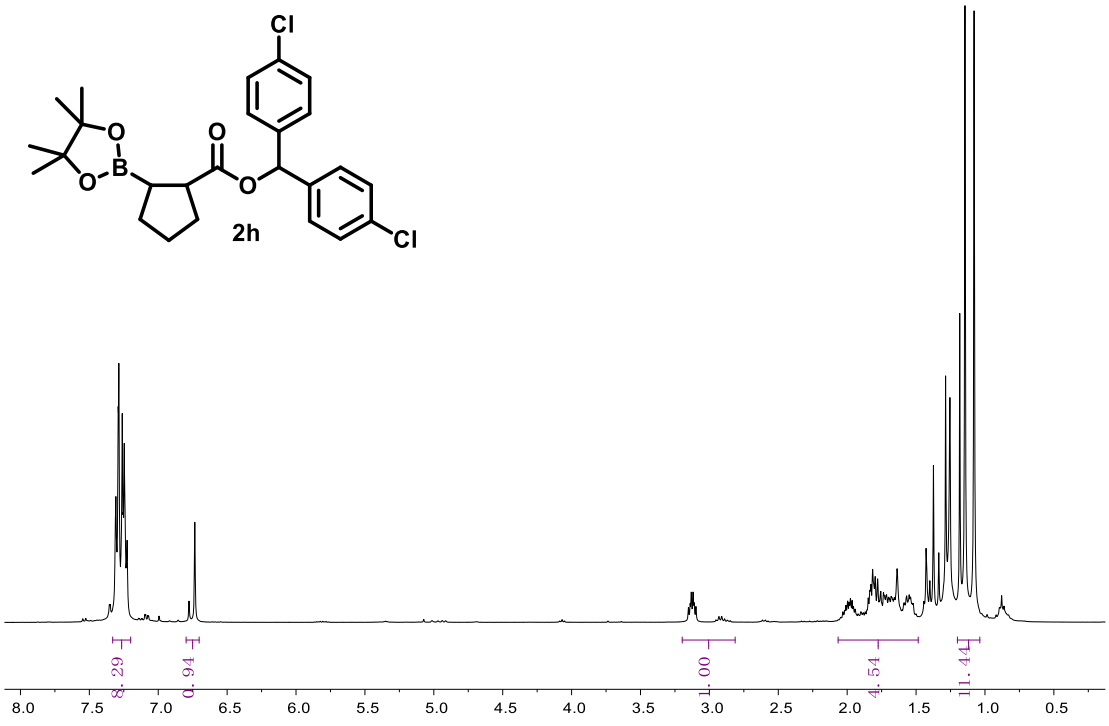
Peak#	Ret. Time	Area	Area%	Height	Name
1	41.260	20873386	35.446	238259	
2	51.064	20553654	34.903	145734	
3	55.316	9059204	15.384	75158	
4	63.454	8401728	14.267	69580	
总计		58887972	100.000	528731	



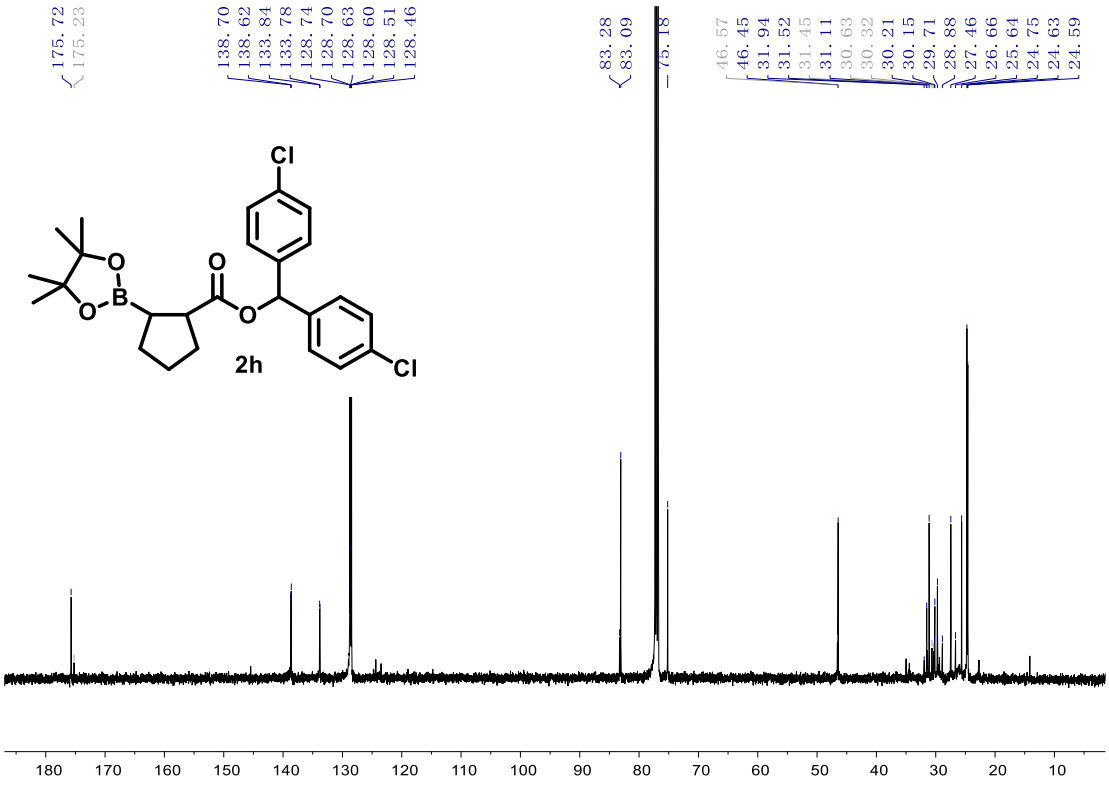
<Peak Table>

PDA Ch1 220nm

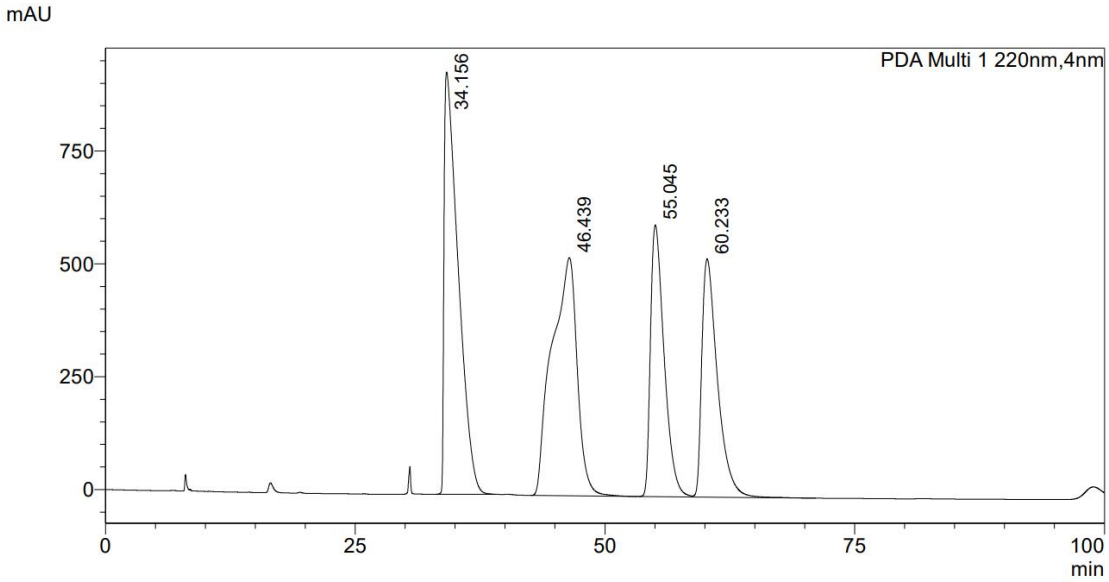
Peak#	Ret. Time	Area	Area%	Height	Name
1	38.935	467690	2.844	11479	
2	45.592	2038132	12.393	15500	
3	49.235	13095255	79.629	111351	
4	57.073	844202	5.133	7649	
总计		16445279	100.000	145978	



^{1}H NMR, $CDCl_3$, 400 MHz



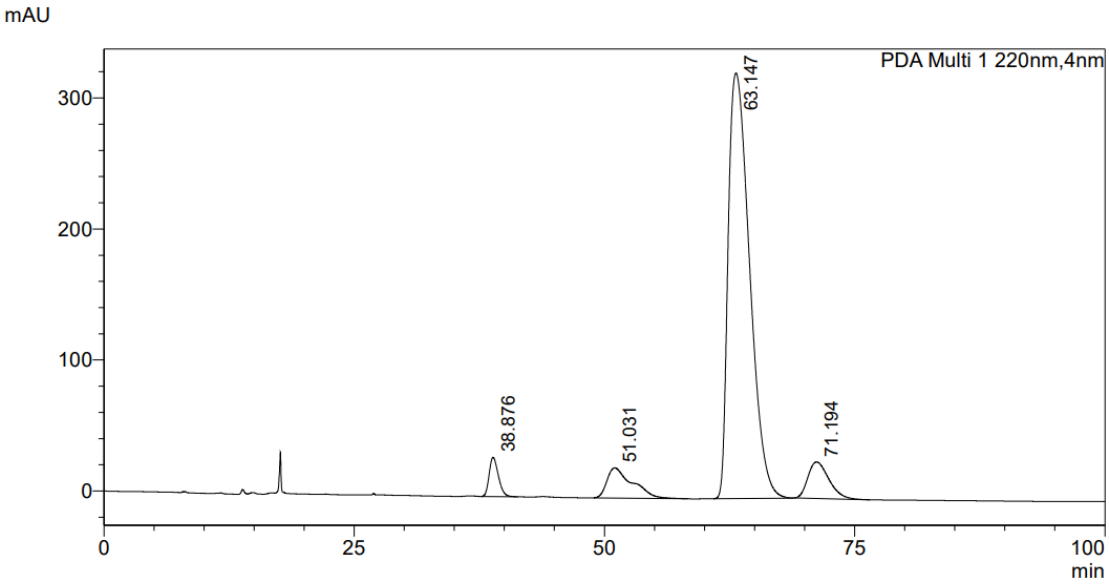
^{13}C NMR, $CDCl_3$, 101 MHz



<Peak Table>

PDA Ch1 220nm

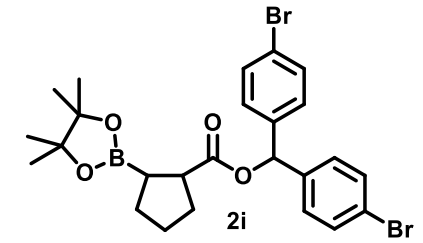
Peak#	Ret. Time	Area	Area%	Height	Name
1	34.156	91978825	30.712	935637	
2	46.439	92581957	30.914	527496	
3	55.045	57192794	19.097	601601	
4	60.233	57733354	19.277	527543	
总计		299486930	100.000	2592276	



<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%	Height	Name
1	38.876	1915207	3.285	29931	
2	51.031	4067600	6.977	23039	
3	63.147	48229398	82.728	324832	
4	71.194	4086852	7.010	27944	
总计		58299056	100.000	405747	



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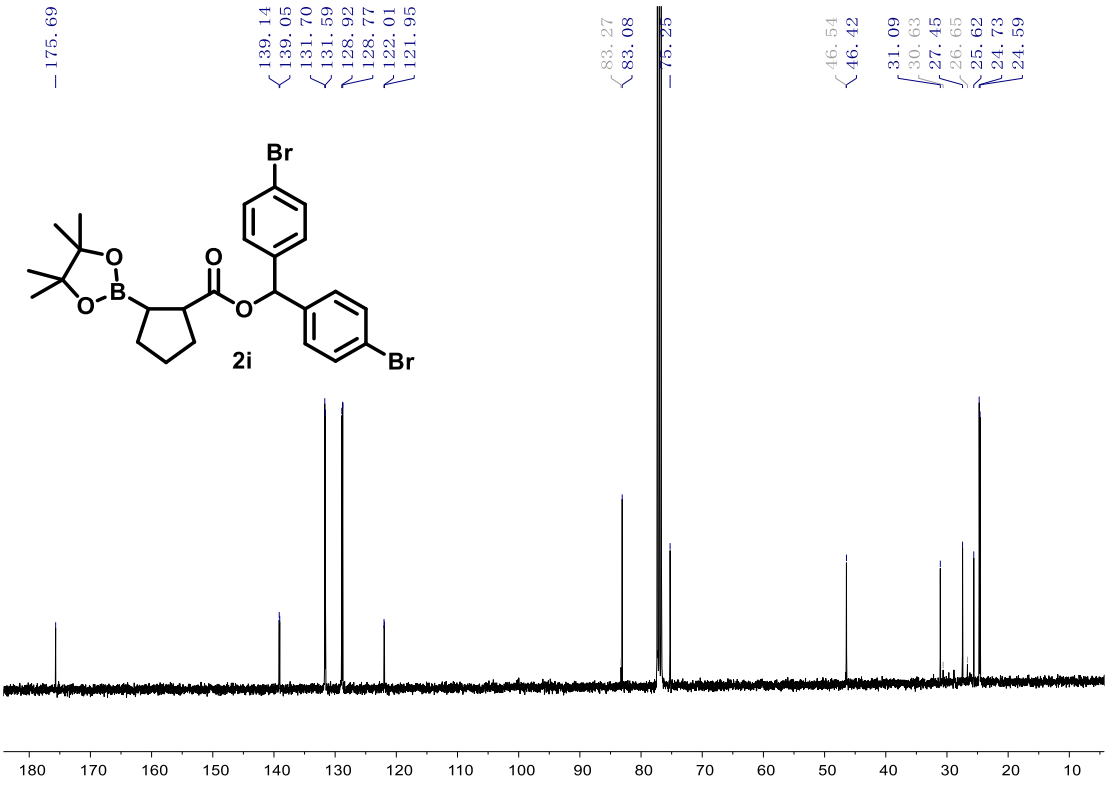
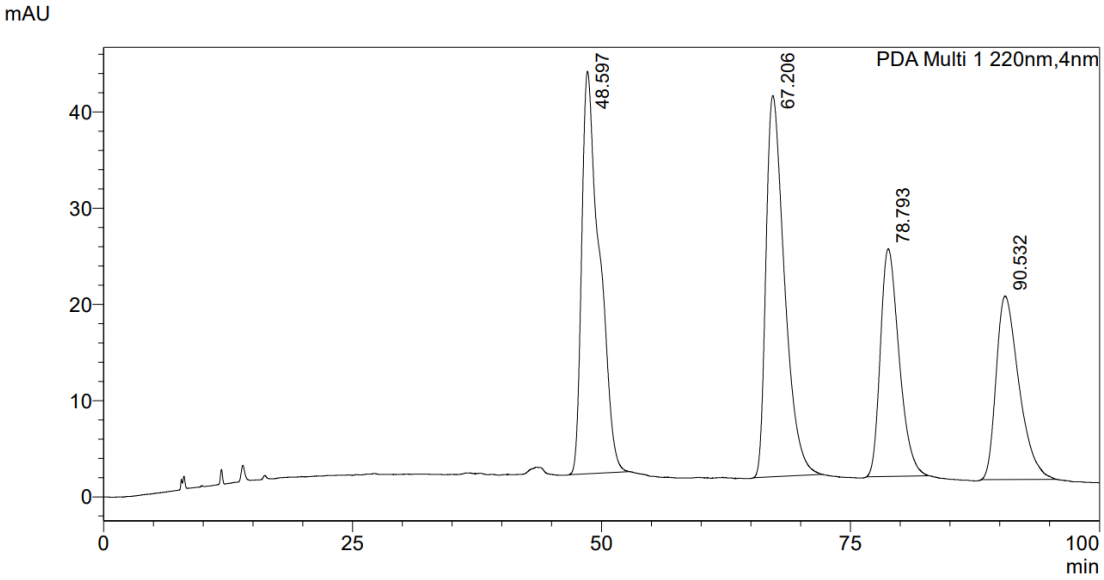
^{1}H NMR, $CDCl_3$, 400 MHz



2i

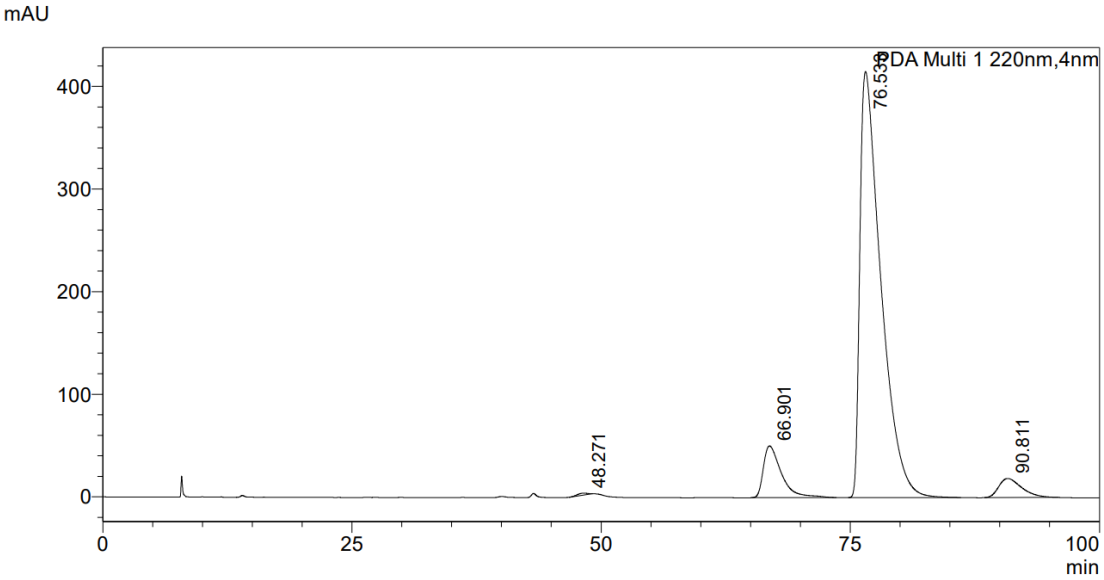
^{13}C NMR, $CDCl_3$, 101 MHz



<Peak Table>

PDA Ch1 220nm

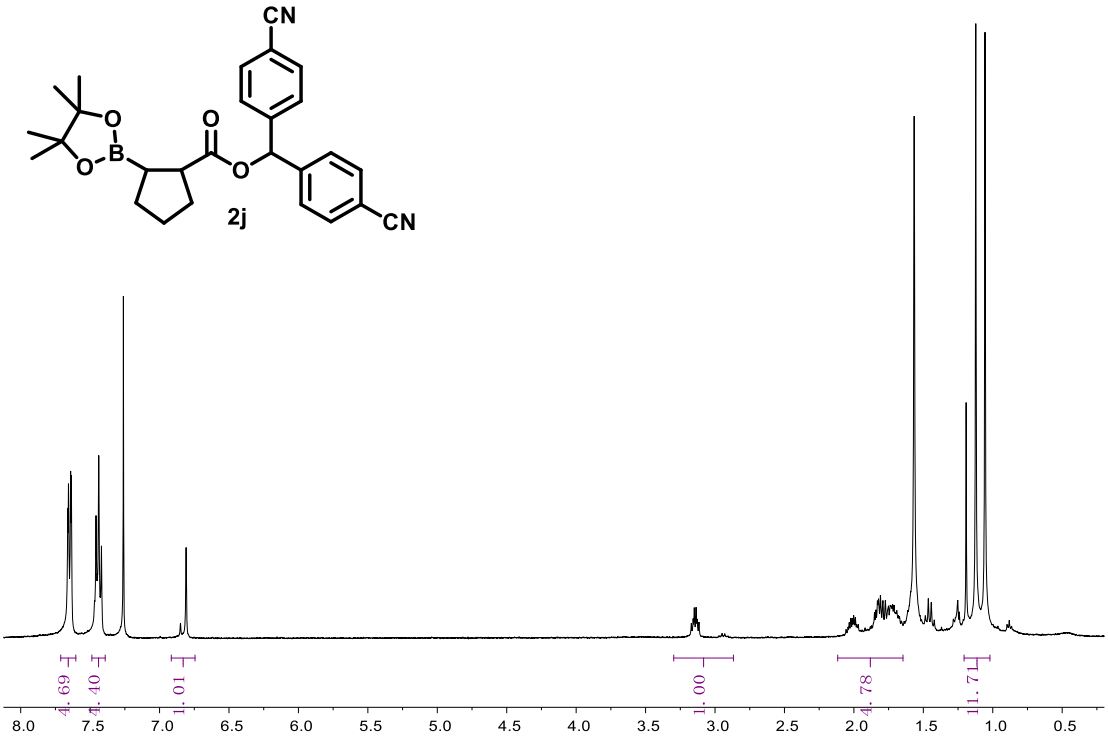
Peak#	Ret. Time	Area	Area%	Height	Name
1	48.597	5170315	31.437	41839	
2	67.206	5124638	31.159	39618	
3	78.793	3103786	18.872	23683	
4	90.532	3048079	18.533	19083	
总计		16446817	100.000	124223	



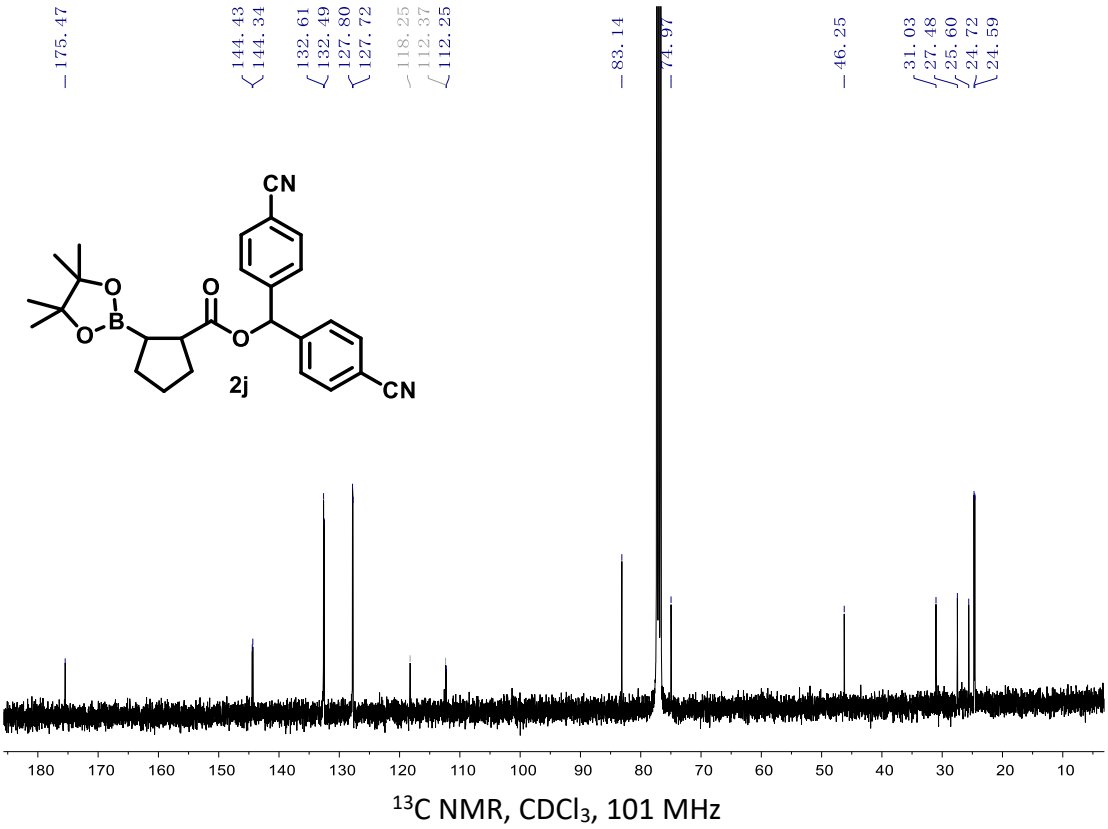
<Peak Table>

PDA Ch1 220nm

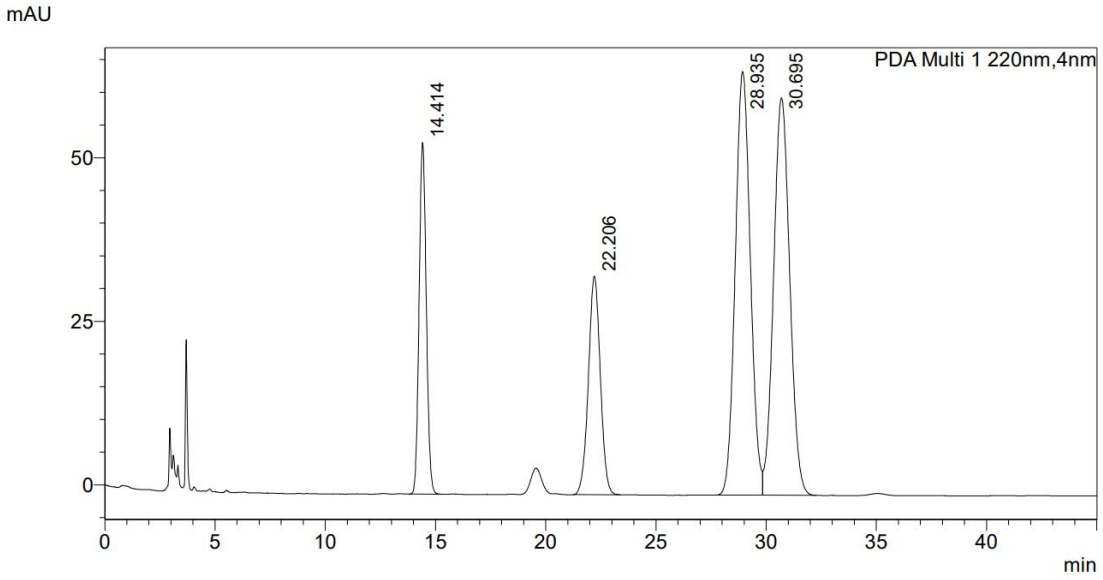
Peak#	Ret. Time	Area	Area%	Height	Name
1	48.271	139981	0.199	1886	
2	66.901	6335865	9.015	50423	
3	76.533	60818671	86.538	415402	
4	90.811	2985015	4.247	18608	
总计		70279532	100.000	486319	



^{1}H NMR, $CDCl_3$, 400 MHz



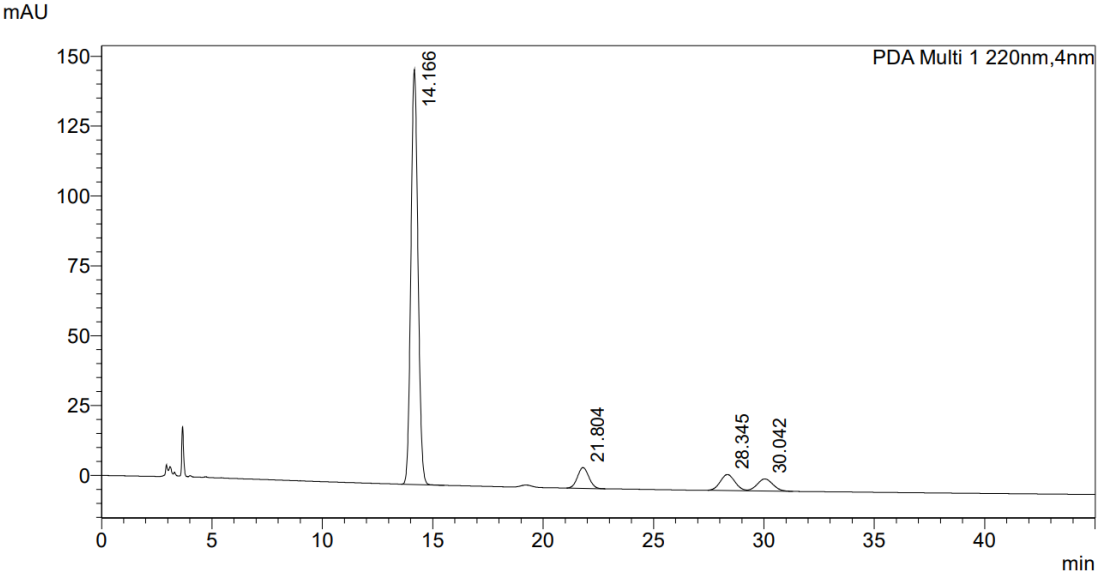
^{13}C NMR, $CDCl_3$, 101 MHz



<Peak Table>

PDA Ch1 220nm

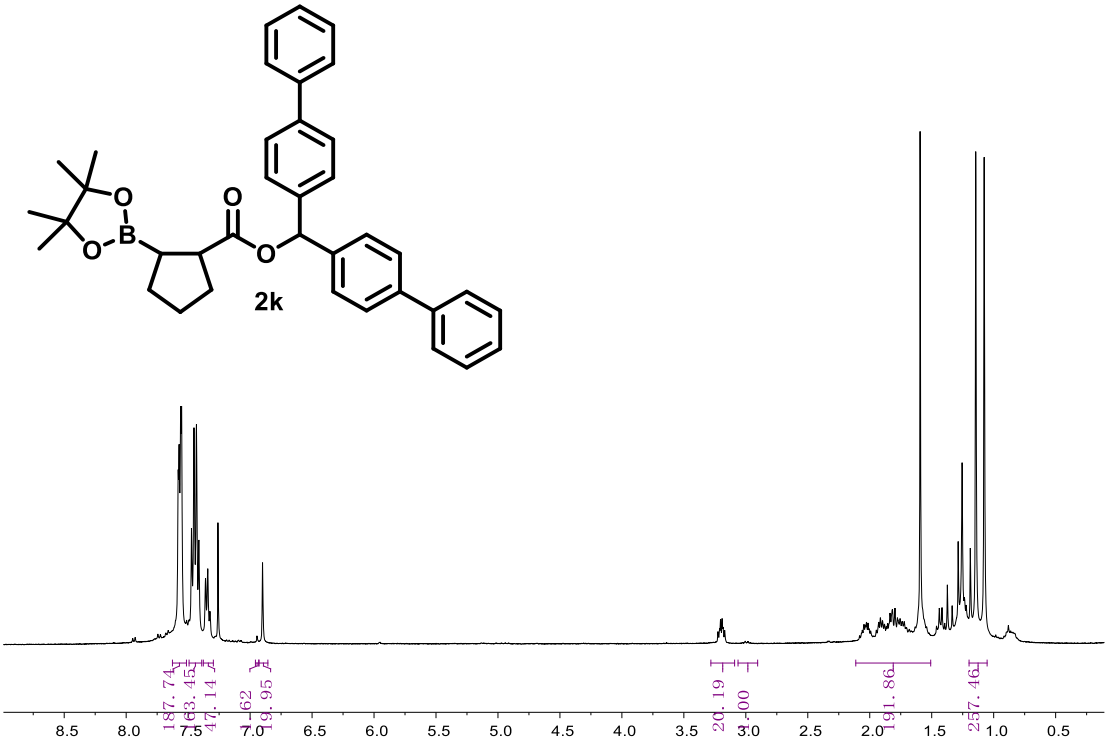
Peak#	Ret. Time	Area	Area%	Height	Name
1	14.414	1217870	14.063	53686	
2	22.206	1257900	14.526	33400	
3	28.935	3081667	35.585	64751	
4	30.695	3102468	35.826	60726	
总计		8659905	100.000	212564	



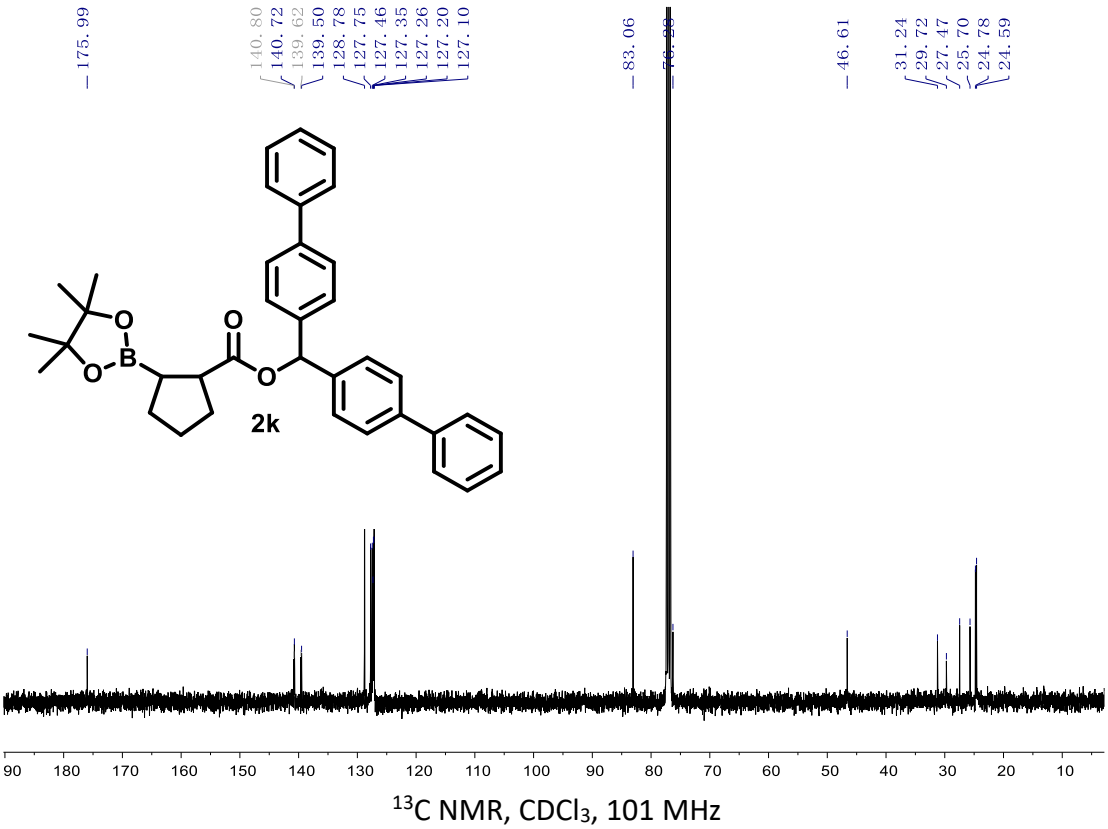
<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%	Height	Name
1	14.166	3312255	81.765	148537	
2	21.804	264943	6.540	7434	
3	28.345	261620	6.458	5710	
4	30.042	212138	5.237	4306	
总计		4050956	100.000	165987	



^{1}H NMR, $CDCl_3$, 400 MHz



^{13}C NMR, $CDCl_3$, 101 MHz

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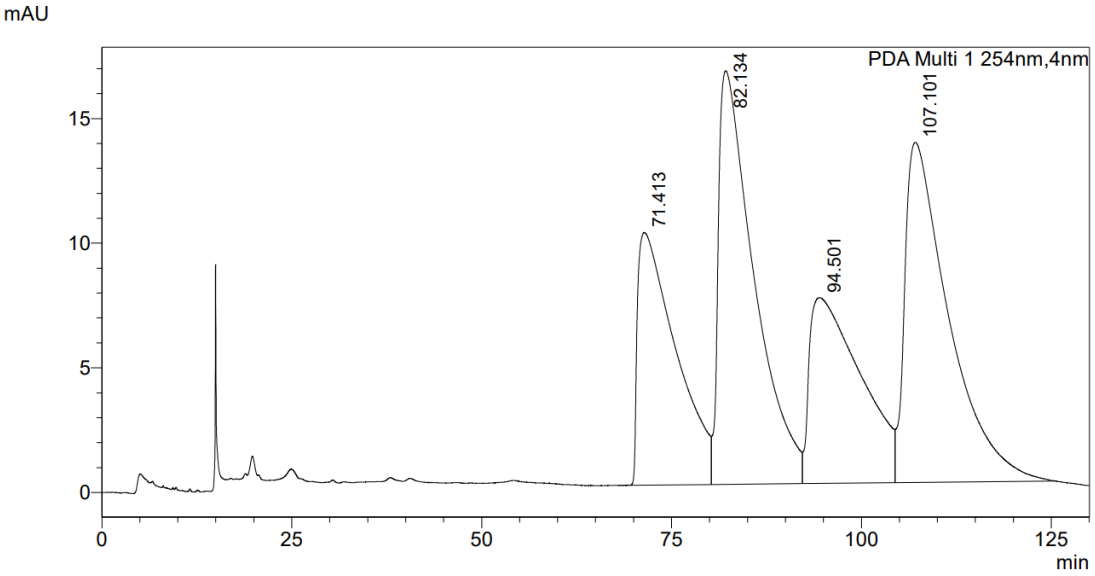

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PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height	Name
1	71.413	3547569	19.759	10133	
2	82.134	5403225	30.095	16586	
3	94.501	3517056	19.589	7453	
4	107.101	5486318	30.557	13643	
总计		17954168	100.000	47815	

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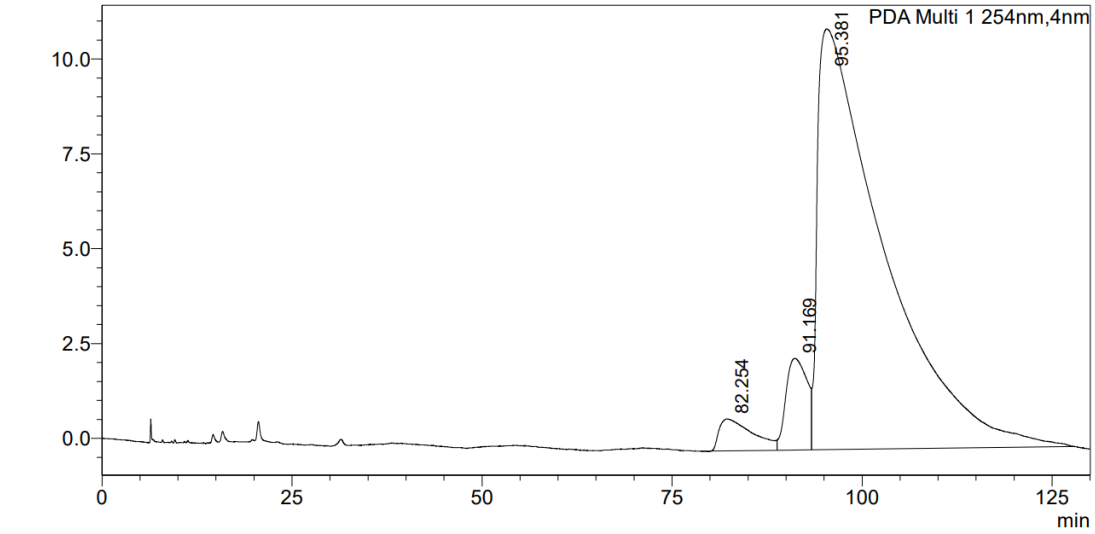

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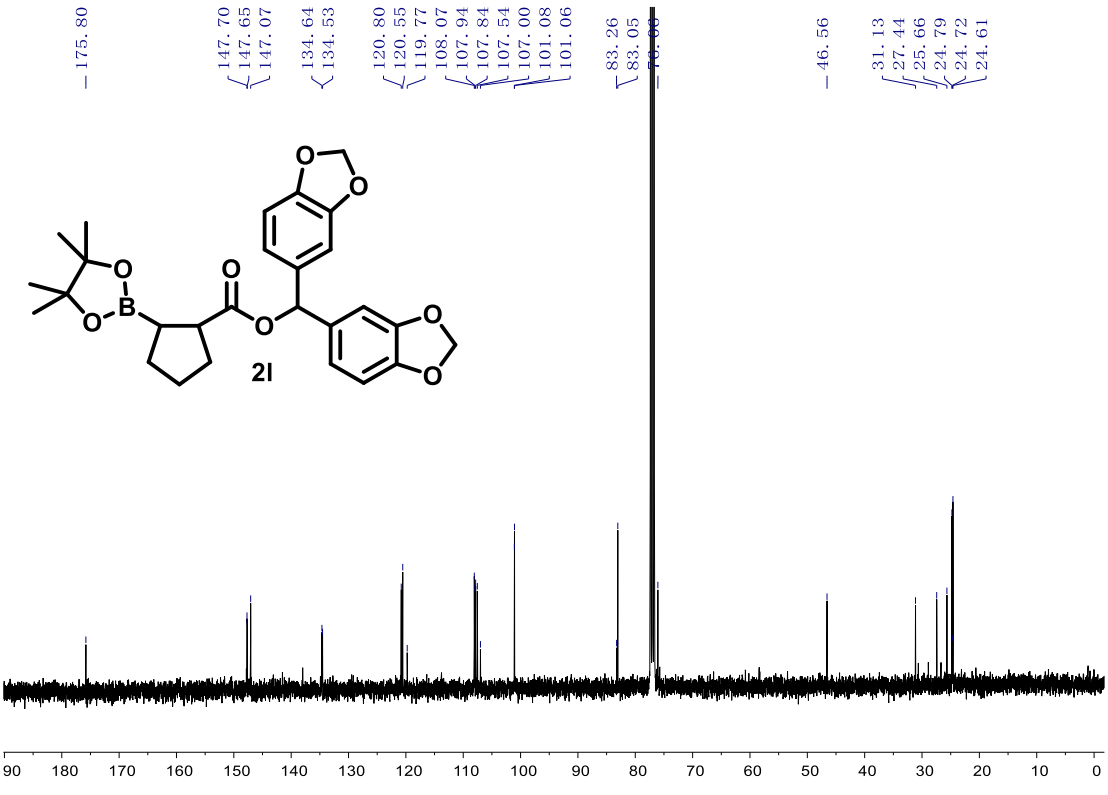
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height	Name
1	82.254	258152	3.468	842	
2	91.169	467542	6.281	2418	
3	95.381	6717832	90.251	11093	
总计		7443526	100.000	14352	

^{1}H NMR, $CDCl_3$, 400 MHz



^{13}C NMR, $CDCl_3$, 101 MHz

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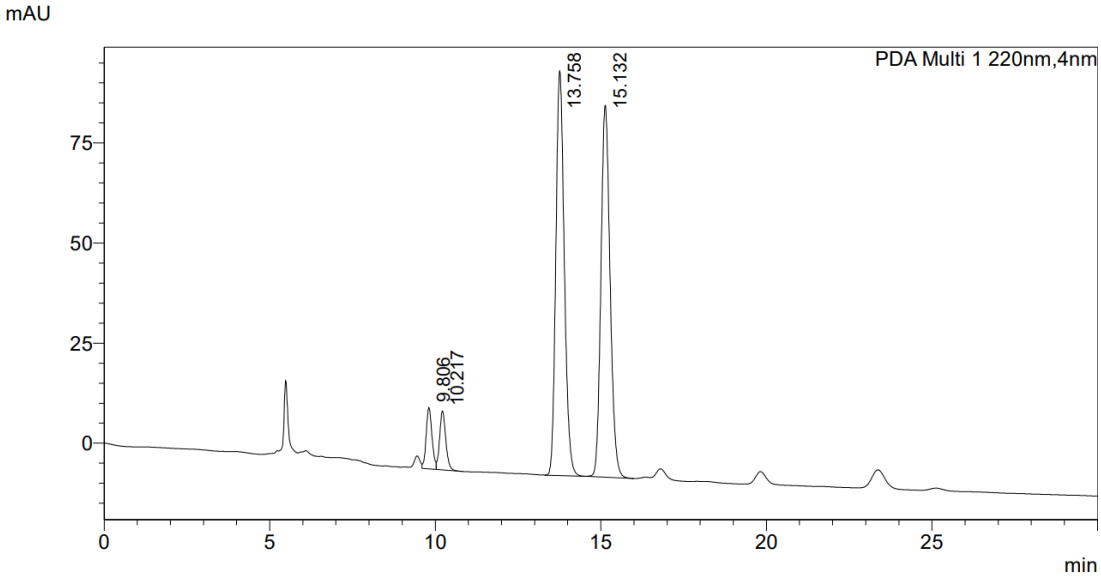

<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%	Height	Name
1	9.806	186988	4.727	15313	
2	10.217	190135	4.807	14700	
3	13.758	1791542	45.289	101080	
4	15.132	1787100	45.177	92904	
总计		3955765	100.000	223998	

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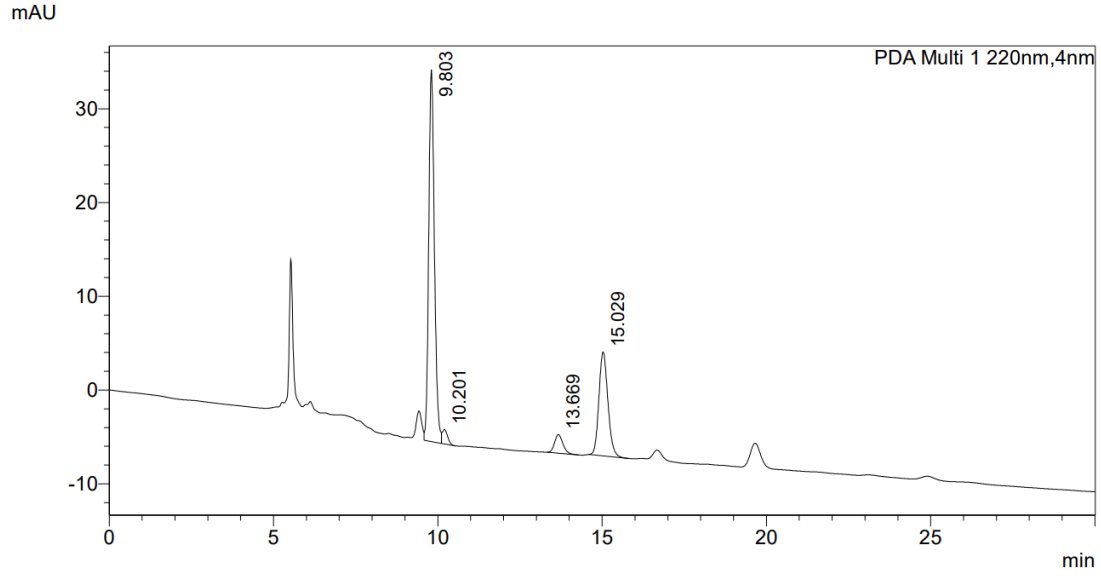
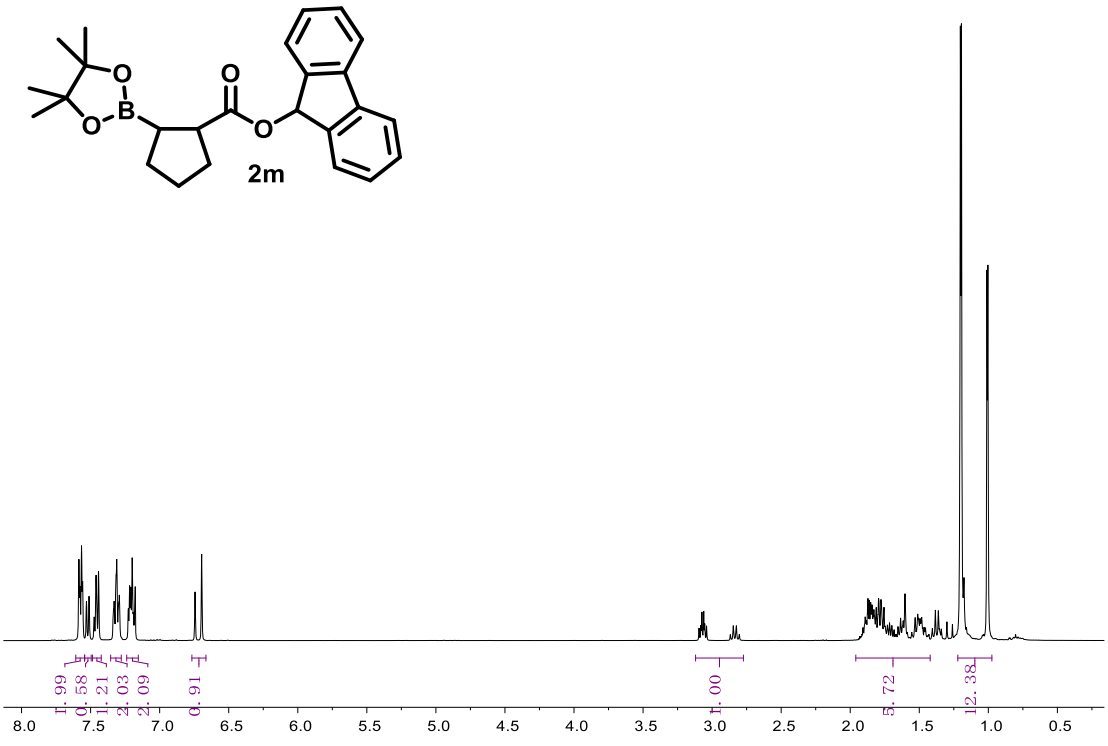


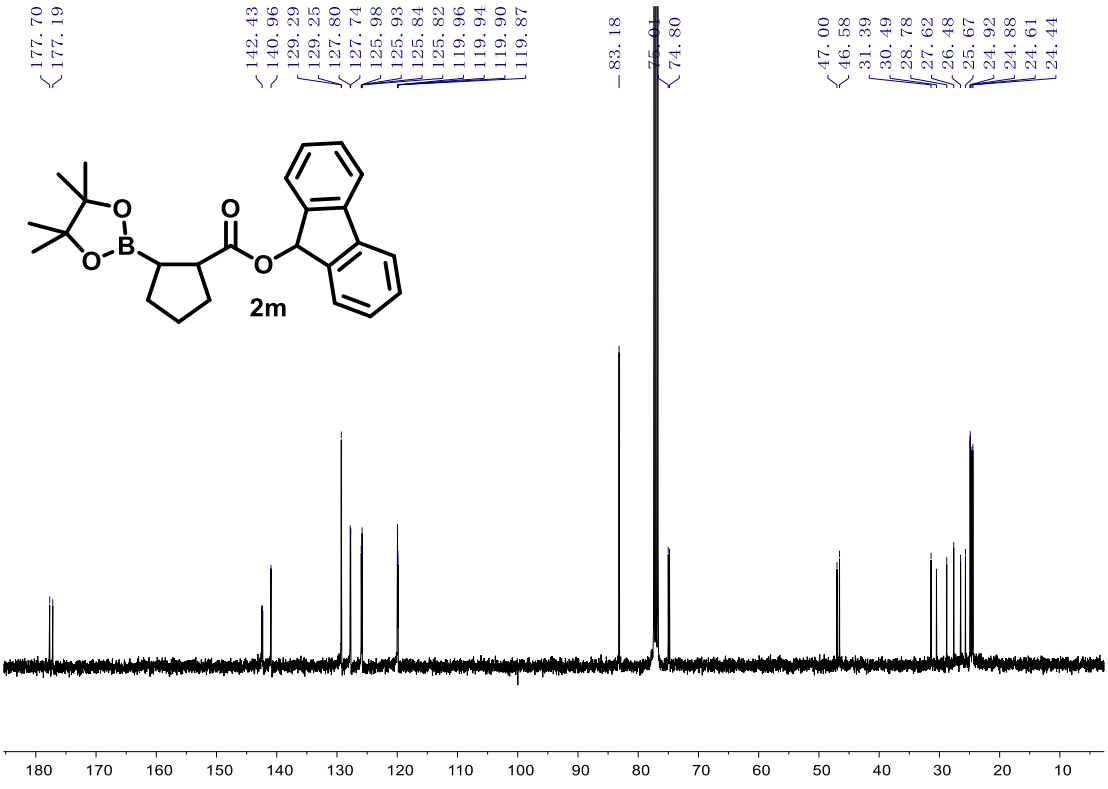
<Peak Table>

PDA Ch1 220nm

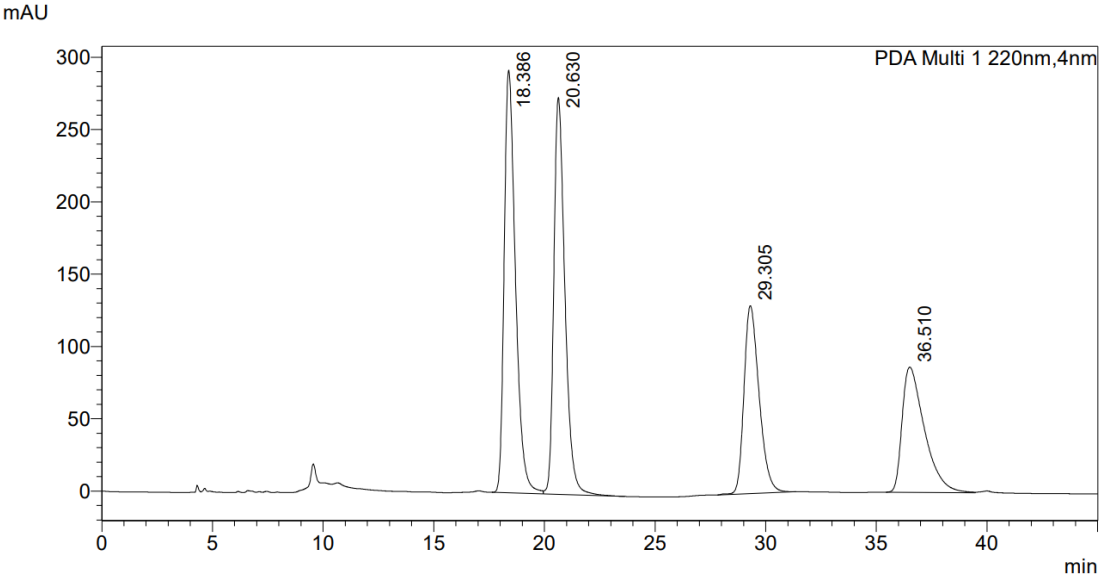
Peak#	Ret. Time	Area	Area%	Height	Name
1	9.803	476076	64.342	39672	
2	10.201	17260	2.333	1536	
3	13.669	34826	4.707	1984	
4	15.029	211748	28.618	11092	
总计		739910	100.000	54283	



^{1}H NMR, $CDCl_3$, 400 MHz



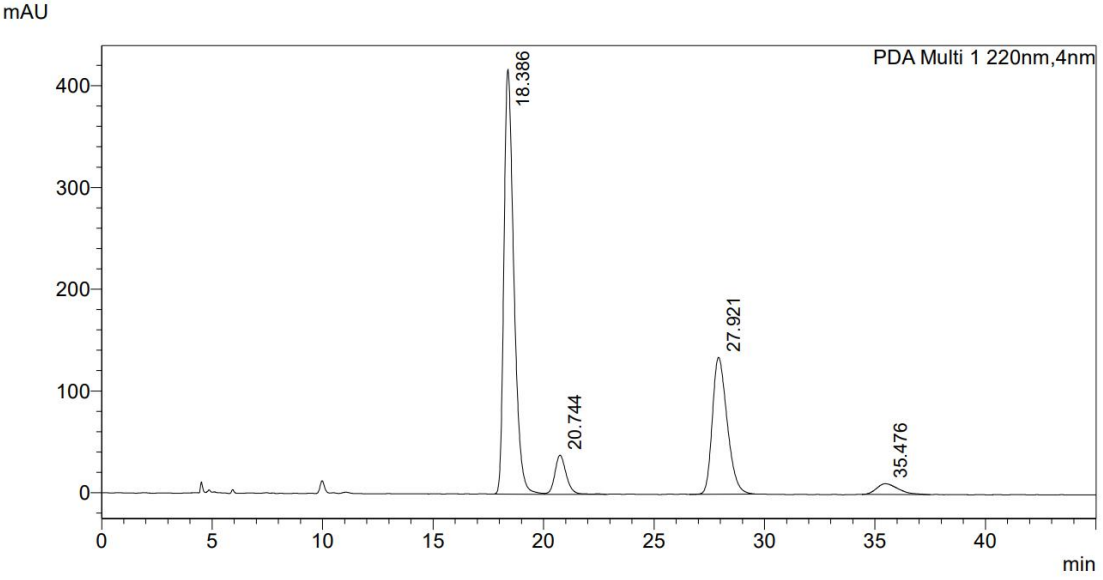
^{13}C NMR, $CDCl_3$, 101 MHz



<Peak Table>

PDA Ch1 220nm

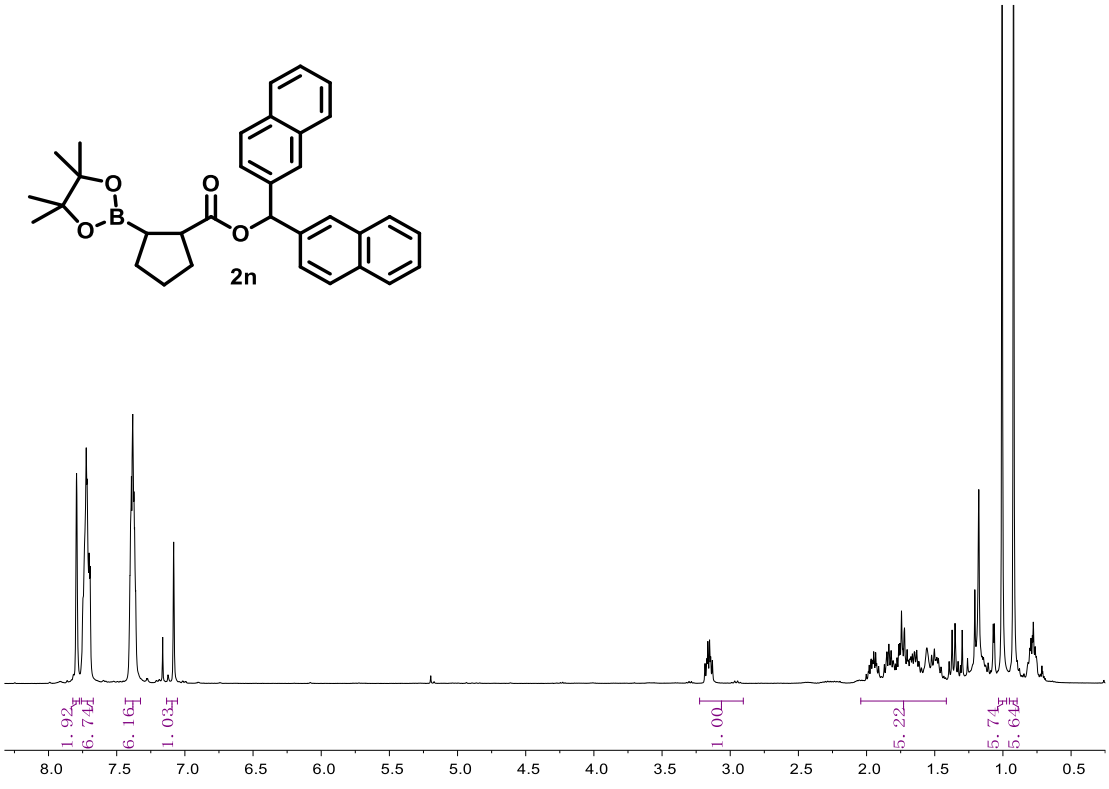
Peak#	Ret. Time	Area	Area%	Height	Name
1	18.386	10382281	32.221	292352	
2	20.630	9586865	29.753	274477	
3	29.305	6176165	19.168	129987	
4	36.510	6076404	18.858	86630	
总计		32221715	100.000	783446	



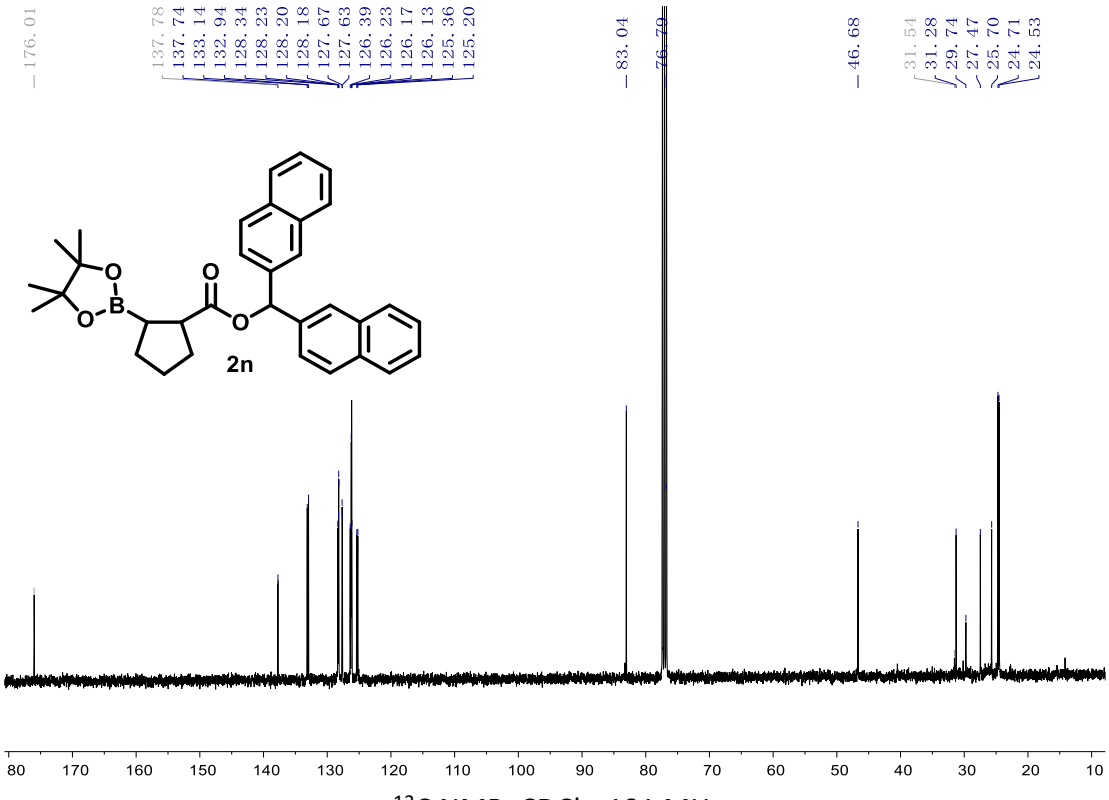
<Peak Table>

PDA Ch1 220nm

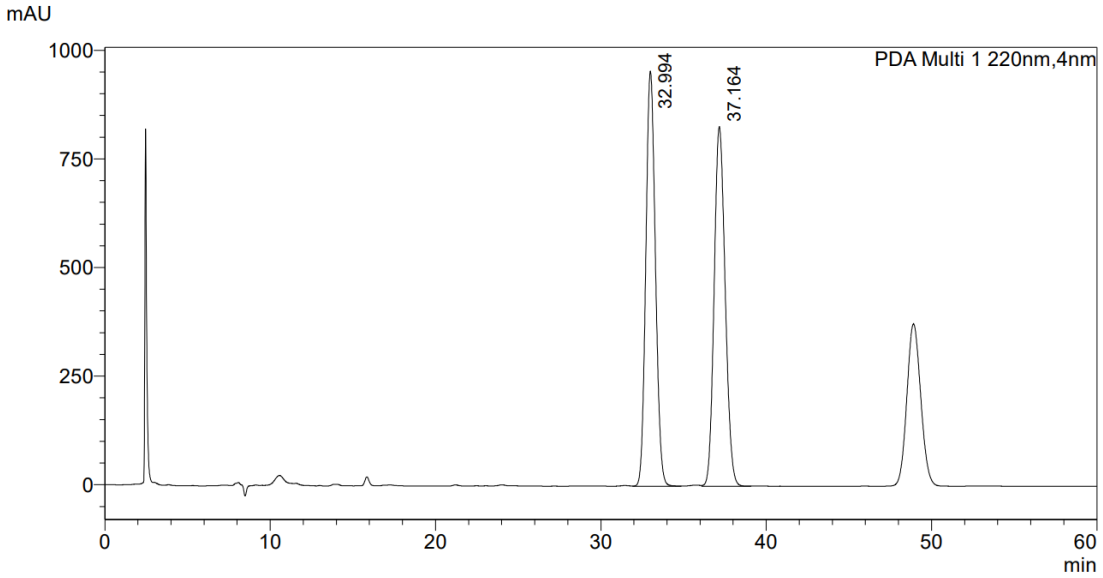
Peak#	Ret. Time	Area	Area%	Height	Name
1	18.386	13082413	60.914	417596	
2	20.744	1375114	6.403	38363	
3	27.921	6292257	29.298	134626	
4	35.476	726908	3.385	10572	
总计		21476692	100.000	601157	



^{1}H NMR, $CDCl_3$, 400 MHz



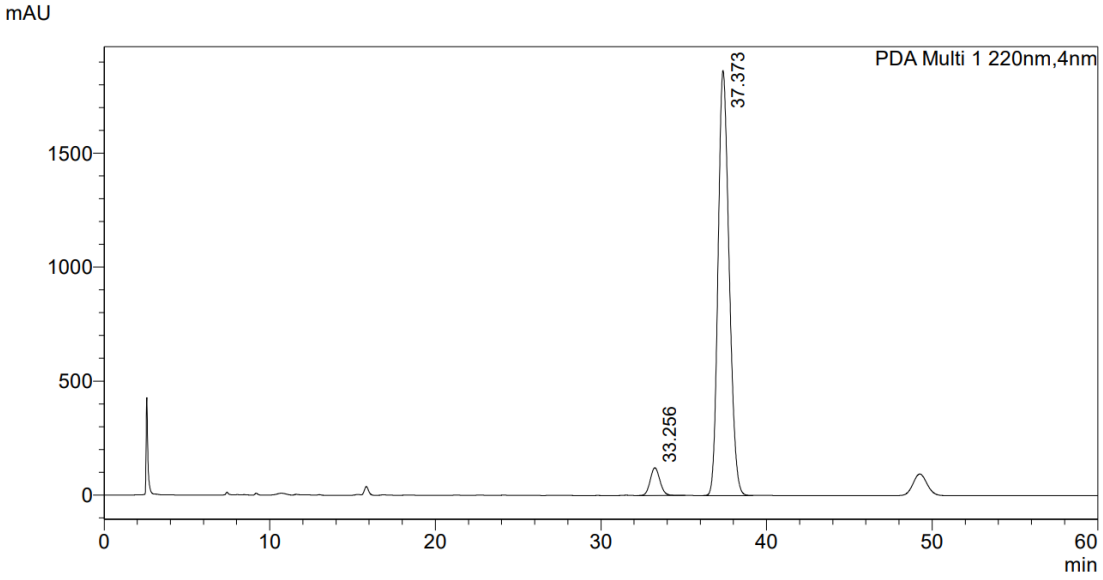
^{13}C NMR, $CDCl_3$, 101 MHz



<Peak Table>

PDA Ch1 220nm

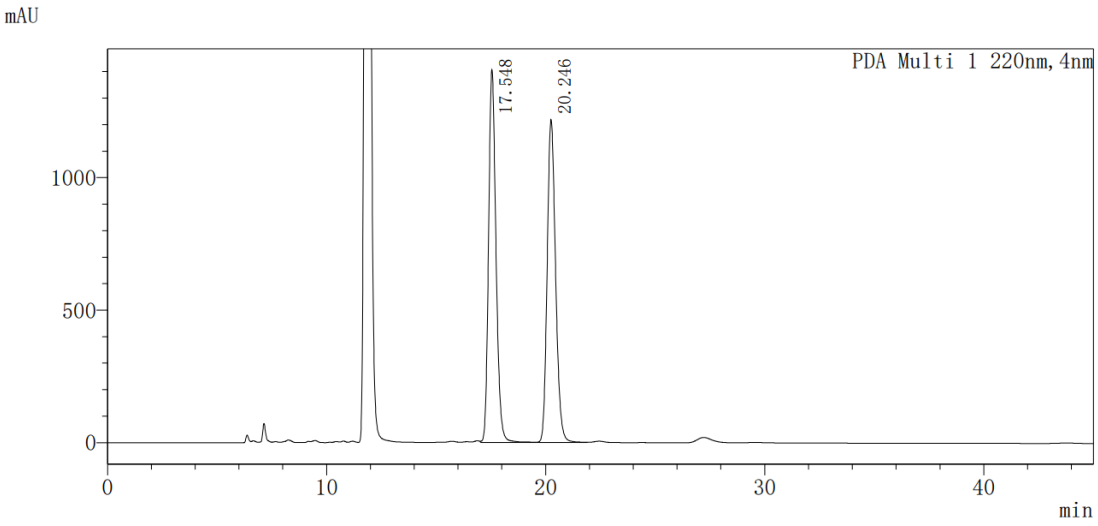
Peak#	Ret. Time	Area	Area%	Height	Name
1	32.994	38545210	50.048	955434	
2	37.164	38471520	49.952	827984	
总计		77016729	100.000	1783418	



<Peak Table>

PDA Ch1 220nm

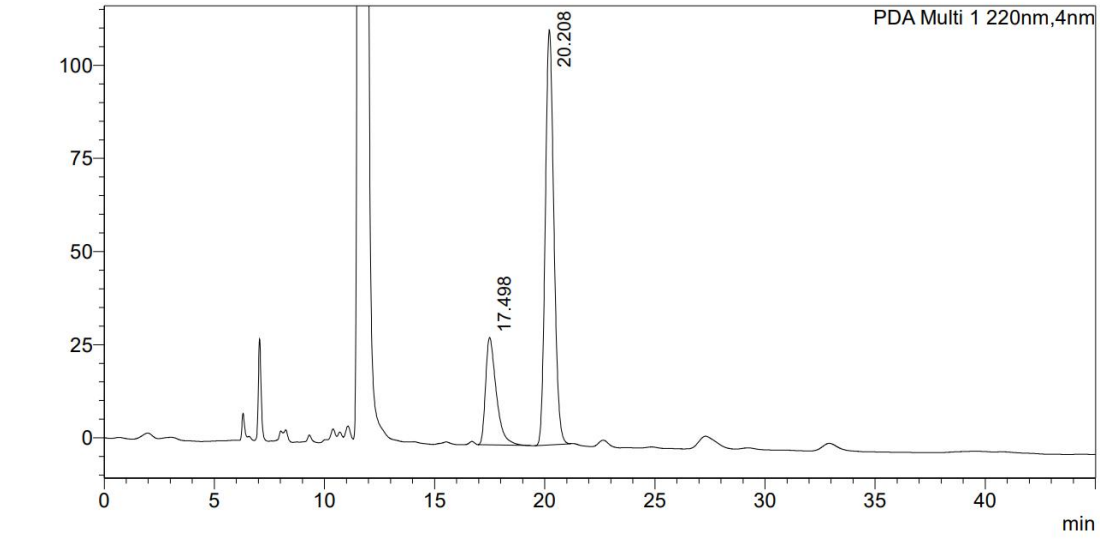
Peak#	Ret. Time	Area	Area%	Height	Name
1	33.256	4992838	5.450	121932	
2	37.373	86623730	94.550	1865598	
总计		91616568	100.000	1987530	



〈峰表〉

PDA Ch1 220nm

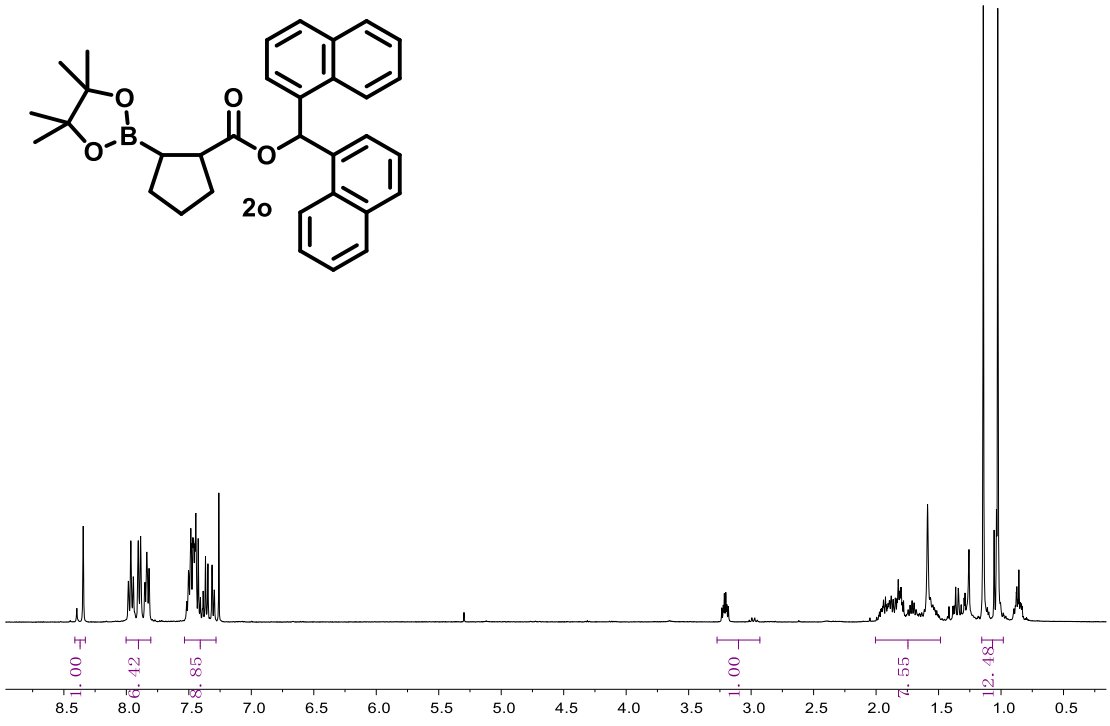
峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	17.548	33176025	1406694	0.000			
2	20.246	32567651	1218701	0.000		V	
总计		65743676	2625396				



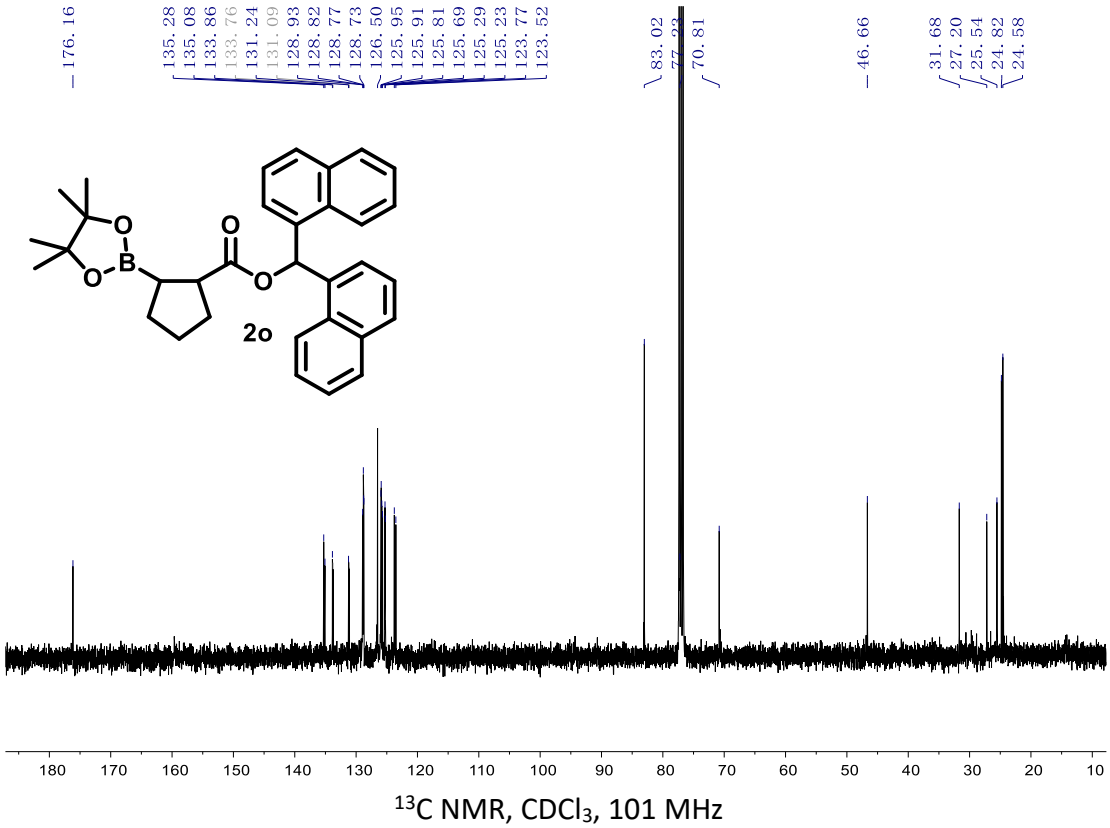
<Peak Table>

PDA Ch1 220nm

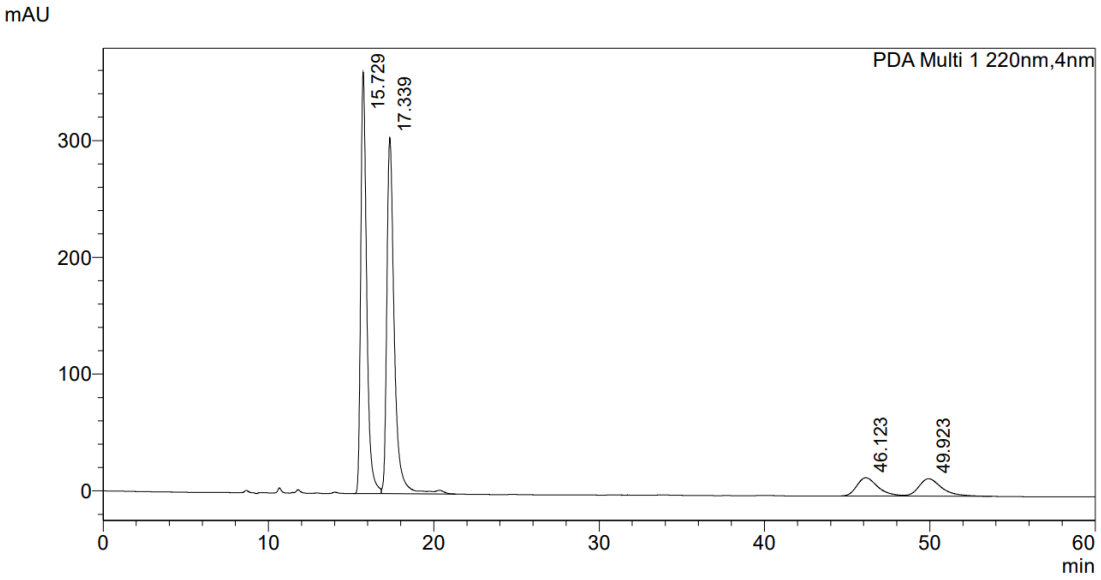
Peak#	Ret. Time	Area	Area%	Height	Name
1	17.498	973186	24.423	28838	
2	20.208	3011555	75.577	111484	
总计		3984741	100.000	140322	



^{1}H NMR, $CDCl_3$, 400 MHz



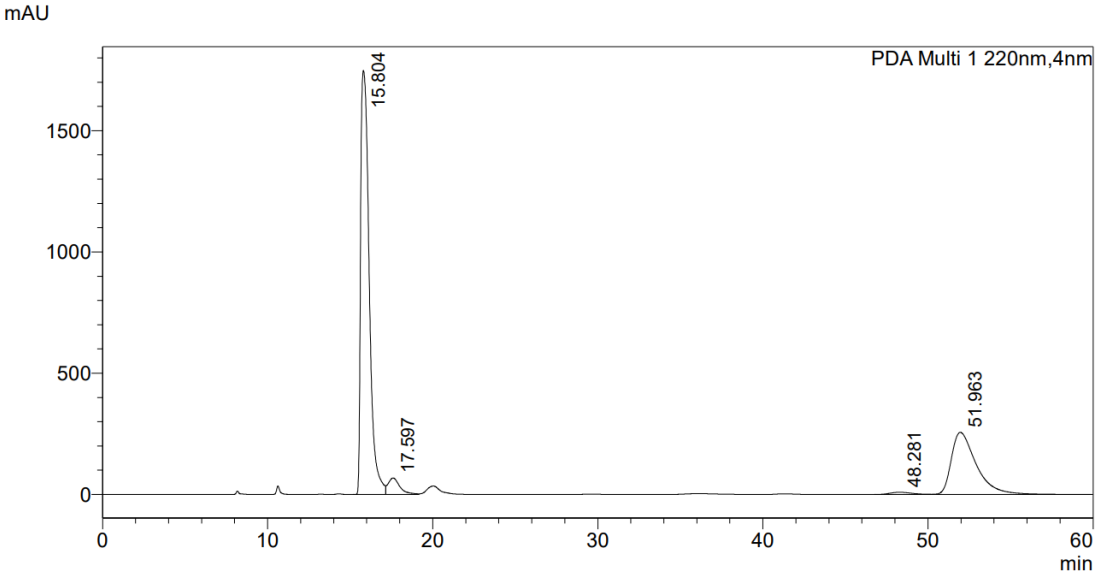
^{13}C NMR, $CDCl_3$, 101 MHz



<Peak Table>

PDA Ch1 220nm

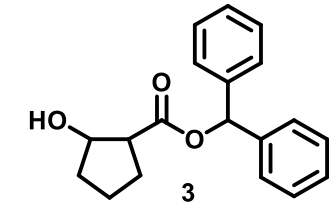
Peak#	Ret. Time	Area	Area%	Height	Name
1	15.729	9022980	41.944	360964	
2	17.339	9652361	44.869	304895	
3	46.123	1385054	6.438	15654	
4	49.923	1451809	6.749	14912	
总计		21512204	100.000	696425	

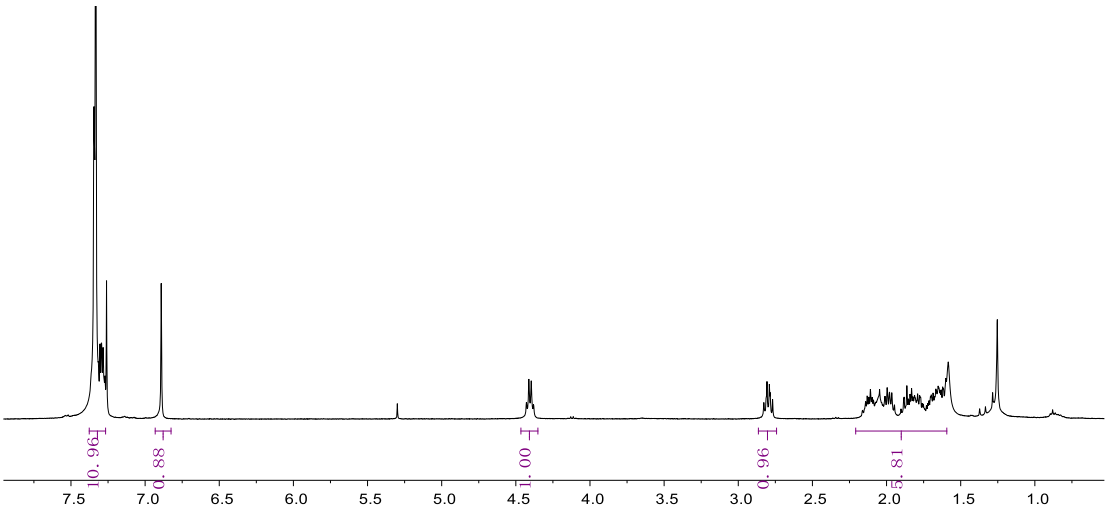


<Peak Table>

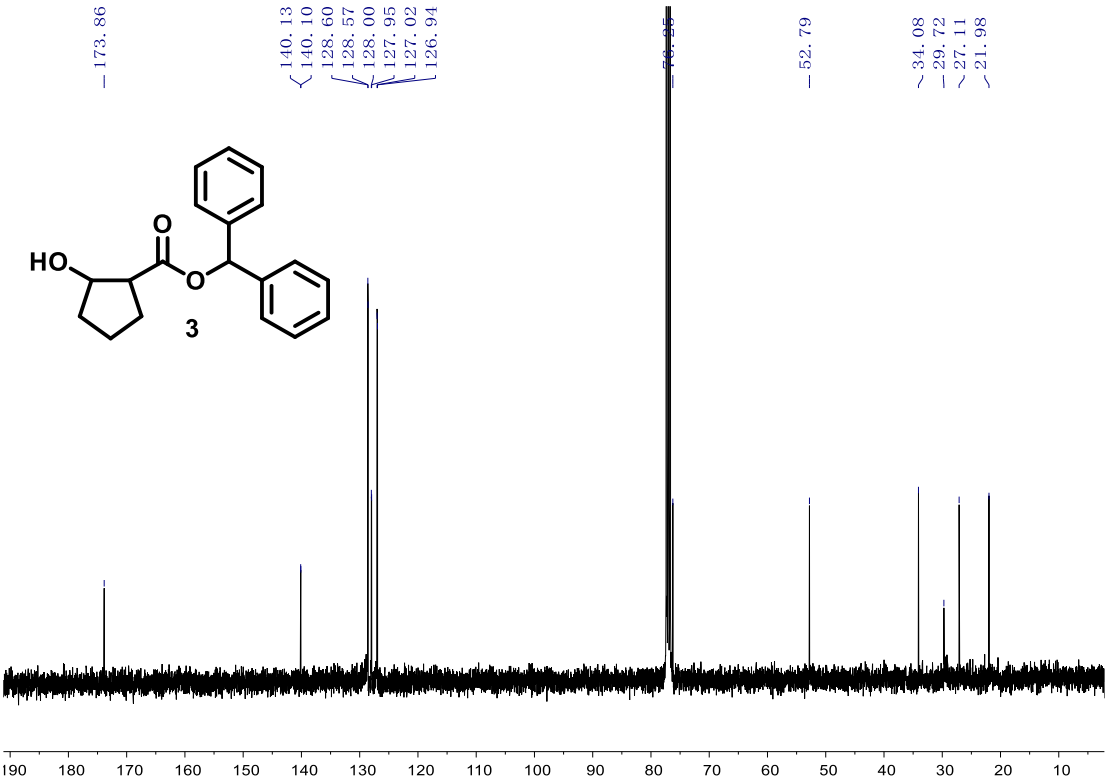
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%	Height	Name
1	15.804	62891057	66.705	1748670	
2	17.597	3418532	3.626	68263	
3	48.281	898167	0.953	9511	
4	51.963	27075173	28.717	256625	
总计		94282929	100.000	2083069	

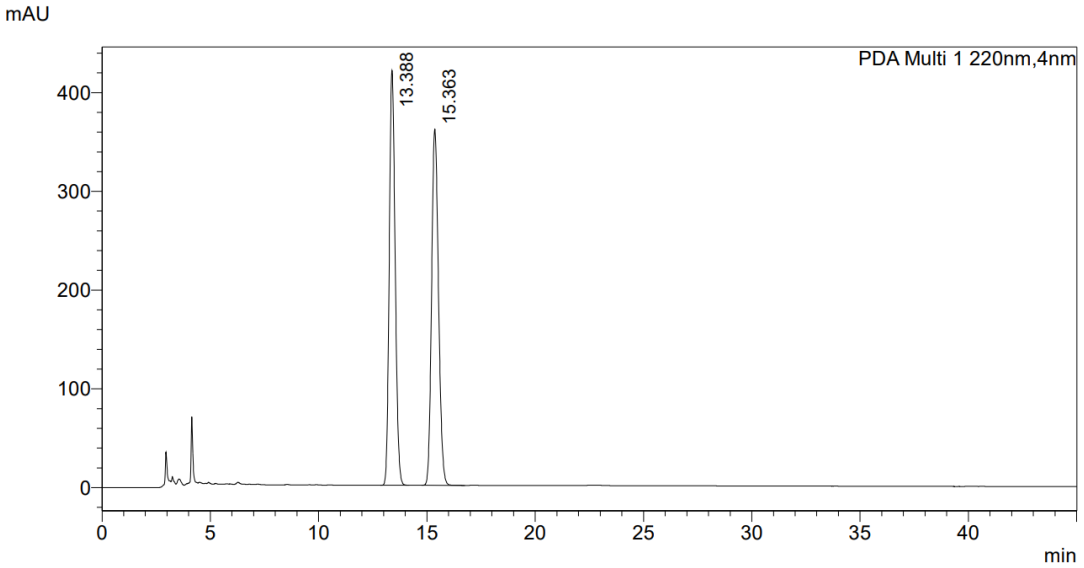




^{1}H NMR, $CDCl_3$, 400 MHz



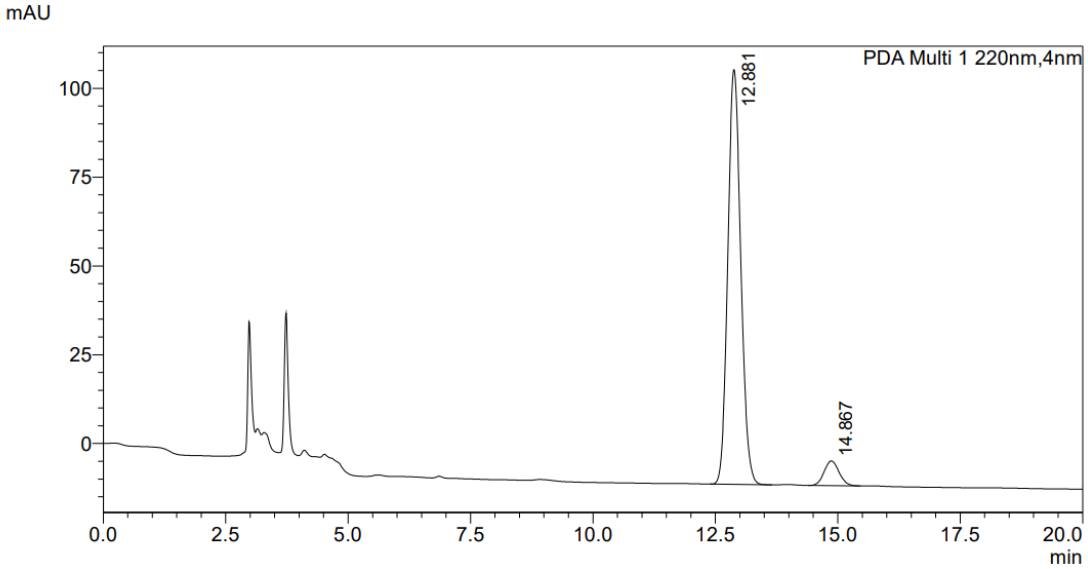
^{13}C NMR, $CDCl_3$, 101 MHz



<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%	Height	Name
1	13.388	7956766	49.853	420266	
2	15.363	8003723	50.147	360753	
总计		15960489	100.000	781019	

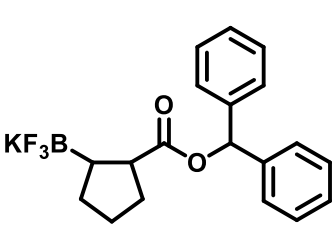


<Peak Table>

PDA Ch1 220nm

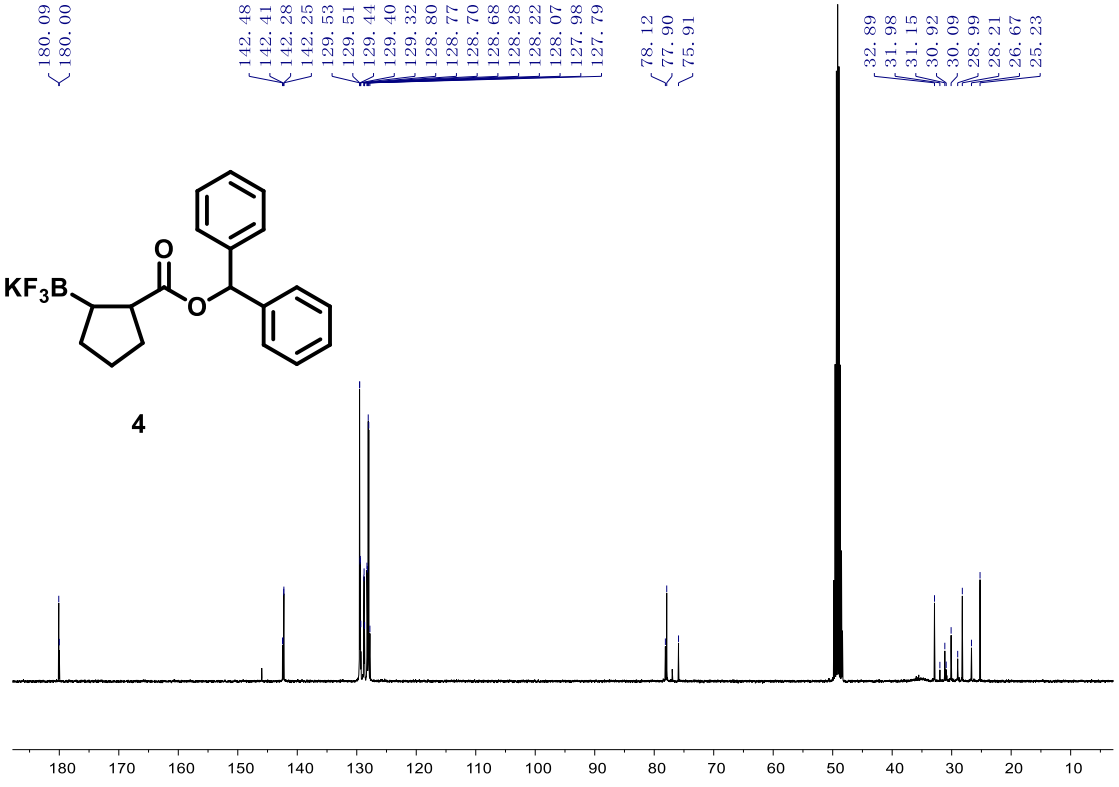
Peak#	Ret. Time	Area	Area%	Height	Name
1	12.881	2152832	93.601	116761	
2	14.867	147170	6.399	6953	
总计		2300002	100.000	123715	

^{1}H NMR, $CDCl_3$, 400 MHz



4

^{1}H NMR, Methanol-d_4, 500 MHz



^{13}C NMR, Methanol-d_4, 101 MHz

11. Reference and notes

(1) Nguyen, K.; Clement, H. A.; Bernier, L.; Coe, J. W.; Farrell, W.; Helal, C. J.; Reese, M. R.; Sach, N. W.; Lee, J. C.; Hall, D. G. *ACS Catal.* **2020**, *11*, 404-413.
(2) Andrae, D.; Häußermann, U.; Dolg, M.; Stoll, H.; Preuß, H. *Thero. Chim. Acta.* **1990**, 77, 123-141.
(3) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, 72, 650-654.
(4) Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. *J. Chem. Phys.* B. **2009**, *113*, 6378-6396.