Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supplementary Information:

Design of a New Series of Chiral Phosphite–Olefin Ligands and Their Application in Asymmetric Catalysis

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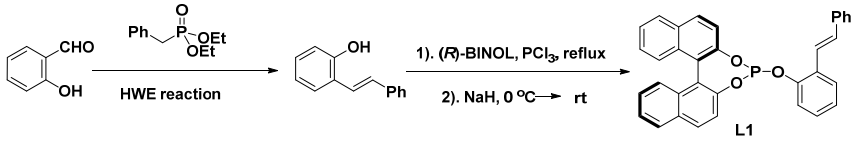
1. General

All reactions, unless otherwise noted, were run under an atmosphere of argon using standard Schlenk techniques. Microwave reactions were performed in a monomode microwave (MW) reactor (CEM Discovery-SP). NMR spectra were recorded at ambient temperature on a standard spectrometer operating at 300 MHz, 400 MHz and 500 MHz. Chemical shifts are reported in δ ppm referenced to an internal $SiMe_4$ standard for ^1H NMR and chloroform-*d* (δ77.16) for ^{13}C NMR. HRMS spectra were measured in EI or ESI mode, and the mass analyzer of the HRMS was Q-TOF for ESI and MAT-95 for EI. Enantiomeric excess values of all compounds were determined by HPLC analysis on chiral columns.

2. General procedure for the synthesis of ligands

Ligand **L1:**



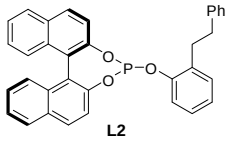
To a 35 mL microwave reaction tube was added salicylaldehyde (0.5 g, 4.5 mmol), benzyl phosphonate (1.1g, 4.5 mmol), 15 mL of dry toluene, and *t*-BuOK (1.38 g, 12 mmol) in turn. The suspension was heated under microwave irridation (maximum power 150 W, ramp time 10 min, hold time 30 min at 120 ^oC). The mixture was allowed to cool to room temperature, quenched with water (5 mL), and then extracted with ethyl acetate. The extract was washed with water, brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to afford (*E*)-2-(2-Phenylethenyl)phenol as a pale yellow solid (0.41g, 51% yield).

A solution of (*R*)-BINOL (1 equiv) and PCl_3 (5 equiv) was stirred at 70 ^oC under argon overnight. The mixture was concentrated on a rotary evaporator and gave corresponding (*R*)-binol-PCl. To a suspension of sodium hydride (1.30 mmol, 1.1 equiv) in THF (*E*)-2-(2-Phenylethenyl)phenol (1.20 mmol, 1 equiv) was added at 0 ^oC under argon. After stirring for 30 mins, the mixture was added of freshly prepared (*R*)-binol-PCl (1.68 mmol, 1.4 equiv) in 2 ml dry THF. Subsequently, it was allowed to come to RT and the mixture was stirred for 3 h. The solvent was removed under vacuum and the residue was purified by silica gel column chromatography to afford the corresponding ligand **L1** as white foam (447 mg, 73% yield).

^1H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.6 Hz, 1H), 7.94 (d, *J* = 8.2 Hz, 1H), 7.88 (d, *J* = 7.9 Hz, 1H), 7.78 (d, *J* = 8.6 Hz, 1H), 7.69 (d, *J* = 6.7 Hz, 1H), 7.56 (d, *J* = 8.7 Hz, 1H), 7.51 – 7.21 (m, 15H), 7.20 – 7.05 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.4 (d, $^2J_{CP}$= 7.5 Hz), 147.7 (d, $^4J_{CP}$ = 2.9 Hz), 147.2, 137.5, 133.0, 132.7, 131.8, 131.4, 130.7, 130.3 (d, $^2J_{CP}$ = 16.0 Hz), 129.6, 128.9, 128.7, 128.6, 127.8, 127.2 (d, $^2J_{CP}$ = 9.8 Hz), 126.9, 126.8, 126.7, 126.5, 125.4, 125.2, 124.6, 124.5 (d, $^4J_{CP}$ = 2 Hz),

123.0, 122.9, 121.9 (d, $^{4}J_{CP}$ = 4.9 Hz), 120.4 (d, $^{2}J_{CP}$ = 13.7 Hz); ^{31}P NMR (200 MHz, $CDCl_3$) δ 145.4; HRMS (EI) for $C_{34}H_{23}O_3P$ $[M]^+$ calcd 510.1385, found 510.1383.

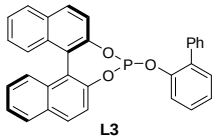
Ligand **L2:**



L2

white foam, 492 mg, 80% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.8 Hz, 1H), 7.96 (d, *J* = 8.2 Hz, 1H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.86 (d, *J* = 8.8 Hz, 1H), 7.57 (d, *J* = 8.8 Hz, 1H), 7.51 – 7.40 (m, 5H), 7.35 – 7.27 (m, 3H), 7.25 – 7.14 (m, 5H), 7.13 - 7.00 (m, 3H), 3.03 – 2.74 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.2 (d, $^{3}J_{CP}$ = 7.7 Hz), 147.9 (d, $^{3}J_{CP}$ = 4.7 Hz), 147.2, 141.9, 133.3, 133.0, 132.7, 131.8, 131.4, 130.9, 130.6, 130.1, 128.6, 128.4, 127.5, 127.2 (d, $^{2}J_{CP}$ = 10.1 Hz), 126.5 (d,$^{2}J_{CP}$ = 16.1 Hz), 125.9, 125.4, 125.2, 124.5, 123.1, 121.9, 119.9 (d, $^{3}J_{CP}$ = 12.8 Hz), 36.7, 32.9; ^{31}P NMR (200 MHz, $CDCl_3$) δ 145.2; HRMS (EI) for $C_{34}H_{25}O_3P$ $[M]^+$ calcd 512.1541, found 512.1538.

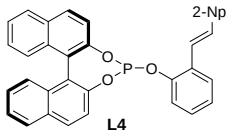
Ligand **L3**



L3

white foam, 348 mg, 60% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 – 7.85 (m, 3H), 7.80 (d, *J* = 8.7 Hz, 1H), 7.52 – 7.30 (m, 12H), 7.29 – 7.15 (m, 4H), 7.06 (d, *J* = 8.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.9 (d, $^{3}J_{CP}$ = 7.6 Hz), 147.9 (d, $^{3}J_{CP}$ = 4.8 Hz), 147.1 (d, $^{4}J_{CP}$ = 2.0 Hz), 137.8, 134.1 (d, $^{4}J_{CP}$ = 2.9 Hz), 132.9, 132.6, 131.7, 131.6, 131.4, 130.5, 130.1, 130.0, 128.8, 128.5 (d, $^{2}J_{CP}$ = 7.5 Hz), 128.3, 127.5, 127.1 (d, $^{2}J_{CP}$ = 11.8 Hz), 126.5, 126.3, 125.3, 125.1, 124.8, 124.5 (d, $^{3}J_{CP}$ = 5.1 Hz), 122.8 (d, $^{4}J_{CP}$ = 1.8 Hz), 121.9, 121.1 (d, $^{2}J_{CP}$ = 11.2 Hz); ^{31}P NMR (200 MHz, $CDCl_3$) δ 145.1; HRMS (EI) for $C_{32}H_{21}O_3P$ $[M]^+$ calcd 484.1228, found 484.1223.

Ligand **L4**

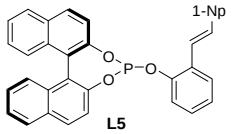


L4

white foam, 470 mg, 70% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.8 Hz, 1H), 7.94 (d, *J* = 8.2 Hz, 1H), 7.86 – 7.70 (m, 7H), 7.58 (t, *J* = 8.3 Hz, 2H), 7.51 – 7.37 (m, 8H), 7.35 (d, *J* = 7.9 Hz, 1H), 7.32 – 7.23 (m, 4H), 7.19 (t, *J* = 7.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.5 (d, $^{2}J_{CP}$ = 8.0 Hz), 147.7 (d, $^{3}J_{CP}$ = 4.7 Hz), 147.2 (d, $^{4}J_{CP}$ = 1.5 Hz), 135.1, 133.8, 133.3, 133.0, 132.7, 131.9, 131.4, 130.7, 130.3 (d, $^{2}J_{CP}$ = 20.3 Hz), 129.6 (d, $^{3}J_{CP}$ = 2.5 Hz), 128.7, 128.6 (d, $^{4}J_{CP}$ = 1.3 Hz), 128.3 (d, ^{2}J

$_{CP}$ = 10.0 Hz), 127.8, 127.2, 127.1, 127.0, 126.7, 126.6, 126.4 (d, $^{3}J_{CP}$ = 2.5 Hz), 126.1, 125.4, 125.2, 124.7, 124.6 (d, J = 5.0 Hz), 124.0, 123.3, 123.0 (d, $^{4}J_{CP}$ = 1.9 Hz), 121.9, 120.5 (d, $^{2}J_{CP}$ = 14.1 Hz); ^{31}P NMR (200 MHz, $CDCl_3$) δ 145.4; HRMS (EI) for $C_{38}H_{25}O_3P$ $[M]^+$ calcd 560.1541, found 560.1529.

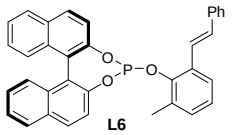
Ligand **L5**



L5

white foam, 437 mg, 65% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 8.2 Hz, 1H), 7.97 (d, J = 8.7 Hz, 1H), 7.94 – 7.84 (m, 3H), 7.84 – 7.72 (m, 3H), 7.62 (d, J = 7.1 Hz, 1H), 7.57 – 7.30 (m, 12H), 7.30 – 7.17 (m, 4H);^{13}C NMR (125 MHz, $CDCl_3$) δ 149.6 (d, $^{3}J_{CP}$ = 7.8 Hz), 147.7 (d, $^{3}J_{CP}$ = 4.6 Hz), 147.1 (d, $^{4}J_{CP}$ = 1.8 Hz), 135.1, 133.9, 133.0, 132.7, 131.8, 131.5, 131.3, 130.7, 130.1, 129.8 (d, $^{4}J_{CP}$ = 1.9 Hz), 128.8 (d, $^{2}J_{CP}$ = 12.9 Hz), 128.5 (d, $^{3}J_{CP}$ = 6.3 Hz), 128.2, 127.5, 127. 2 (d, $^{4}J_{CP}$ = 3.8 Hz), 127.1, 127.5, 126.5, 126.3 (d, $^{2}J_{CP}$ = 10.0 Hz), 126.1, 125.9 (d, $^{2}J_{CP}$ = 11.3 Hz), 125.4, 125.1, 124.7, 124.5 (d, $^{3}J_{CP}$ = 6.0 Hz), 124.1, 123.9, 122.9 (d, $^{4}J_{CP}$ = 1.8 Hz), 121.8, 120.5 (d, $^{2}J_{CP}$ = 13.7 Hz); ^{31}P NMR (200 MHz, $CDCl_3$) δ 145.3; HRMS (EI) for $C_{38}H_{25}O_3P$ $[M]^+$ calcd 560.1541, found 560.1530.

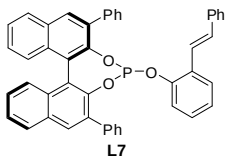
Ligand **L6**



L6

white foam, 440 mg, 70% yield; ; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 – 7.81 (m, 4H), 7.65 (d, J = 16.3 Hz, 1H), 7.59 – 7.48 (m, 4H), 7.46 – 7.33 (m, 5H), 7.32 – 7.20 (m, 5H), 7.12 (d, J = 7.1 Hz, 1H), 7.09 – 7.01 (m, 2H), 2.47 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.3 (d, $^{3}J_{CP}$ = 6.9 Hz), 147.9 (d, $^{3}J_{CP}$ = 5.3 Hz), 147.1 (d, $^{4}J_{CP}$ = 1.3 Hz), 137.6, 132.9, 132.7, 131.8, 131.4, 131.0 (d, $^{3}J_{CP}$ = 3.8 Hz), 130.9, 130.6 (d, $^{2}J_{CP}$ = 12.3 Hz), 130.1, 128.8, 128.5, 127.9, 127.2, 126.9, 126.4 (d, $^{2}J_{CP}$ = 13.6 Hz), 125.3, 125.2, 125.0, 124.5 (d, $^{3}J_{CP}$ = 5.1 Hz), 124.20, 123.9, 123.0 (d, $^{4}J_{CP}$ = 2.0 Hz), 121.9 (d, $^{2}J_{CP}$ = 11.9 Hz), 18.121 (d, $^{4}J_{CP}$ = 3.0 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 148.0; HRMS (EI) for $C_{35}H_{25}O_3P$ $[M]^+$ calcd 524.1541, found 524.1551.

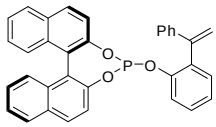
Ligand **L7**



L7

white foam, 516 mg, 65% yield; 1H NMR (300 MHz, CDCl3) δ 8.05 (d, *J* = 12.6 Hz, 4H), 7.69 (s, 4H), 7.51 (s, 5H), 7.33 (dd, *J* = 27.0, 10.3 Hz, 9H), 7.13 (s, 4H), 6.96 (d, *J* = 15.4 Hz, 3H), 6.78 (s, 1H), 5.66 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.1 (d, $^3J_{CP}$ = 10.0 Hz), 145.3 (d, $^3J_{CP}$ = 4.3 Hz), 144.7 (d, $^4J_{CP}$ = 1.9 Hz), 138.4, 137.7, 137.2, 135.0, 134.9, 132.6, 132.4, 131.7, 131.4, 130.8, 130.6, 130.4, 130.0, 129.9, 129.7 (d, $^4J_{CP}$ = 2.5 Hz), 128.7, 128.5, 128.2, 127.7 (d, $^3J_{CP}$ = 4.7 Hz), 127.5, 127.2 (d, $^3J_{CP}$ = 2.8 Hz), 126.8, 126.4 (d, $^2J_{CP}$ = 15.2 Hz), 125.9, 125.7, 125.5, 124.4, 122.6, 120.6 (d, $^2J_{CP}$ = 11.2 Hz); ^{31}P NMR (200 MHz, $CDCl_3$) δ 143.2; HRMS (EI) for $C_{46}H_{31}O_3P$ $[M]^+$ calcd 662.2011, found 662.2012.

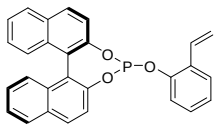
Ligand **L8**



L8

white foam, 453 mg, 74% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 – 7.80 (m, 3H), 7.76 (d, *J* = 8.8 Hz, 1H), 7.44 – 7.27 (m, 11H), 7.26 – 7.10 (m, 5H), 7.03 (d, *J* = 8.8 Hz, 1H), 5.81 (s, 1H), 5.36 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.2 (d, $^3J_{CP}$ = 7.3 Hz), 147.8 (d, $^3J_{CP}$ = 4.7 Hz), 147.1 (d, $^4J_{CP}$ = 2.0 Hz), 146.1, 140.7, 134.6, 132.9, 132.6, 131.9, 131.7, 131.3, 130.4, 129.8, 129.2, 128.5, 128.4 (d, $^2J_{CP}$ = 8.8 Hz), 127.9, 127.1 (d, $^2J_{CP}$ = 15.0 Hz), 127.0, 126.4, 126.2, 125.2, 125.0, 124.8, 124.5 (d, $^3J_{CP}$ = 5.0 Hz), 122.9 (d, $^4J_{CP}$ = 2.2 Hz), 121.9, 121.4 (d, $^2J_{CP}$ = 8.8 Hz), 117.2; ^{31}P NMR (200 MHz, $CDCl_3$) δ 143.6; HRMS (EI) for $C_{34}H_{23}O_3P$ $[M]^+$ calcd 510.1385, found 510.1377.

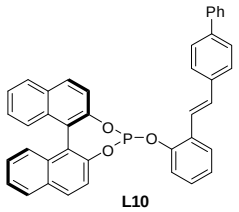
Ligand **L9**



L9

white foam, 427 mg, 82% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.7 Hz, 1H), 7.96 – 7.86 (m, 3H), 7.56 (dd, *J* = 8.7, 1.0 Hz, 2H), 7.49 – 7.36 (m, 5H), 7.34 – 7.17 (m, 4H), 7.16 – 7.07 (m, 1H), 7.00 (dd, *J* = 17.7, 11.1 Hz, 1H), 5.75 (dd, *J* = 17.7, 1.3 Hz, 1H), 5.29 (dd, *J* = 11.1, 1.3 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.2 (d, $^3J_{CP}$ = 7.1 Hz), 147.8 (d, $^3J_{CP}$ = 4.8 Hz), 147.1 (d, $^4J_{CP}$ = 1.5 Hz), 133.0, 132.7, 131.8, 131.4, 131.1, 130.7, 130.1, 130.0, 129.8 (d, $^4J_{CP}$ = 2.5 Hz), 129.0, 128.5 (d, $^3J_{CP}$ = 7.6 Hz), 127.2 (d, $^2J_{CP}$ = 12.5 Hz), 126.7, 126.5 (d, $^2J_{CP}$ = 19.6 Hz), 125.4, 125.2, 124.6, 124.5 (d, $^3J_{CP}$ = 5.0 Hz), 123.0 (d, $^4J_{CP}$ = 1.8 Hz), 121.9 (d, $^4J_{CP}$ = 3.7 Hz), 120.5 (d, $^2J_{CP}$ = 12.2 Hz), 115.8; ^{31}P NMR (200 MHz, $CDCl_3$) δ 144.4; HRMS (EI) for $C_{28}H_{19}O_3P$ $[M]^+$ calcd 434.1072, found 434.1071.

Ligand **L10**



L10

white foam, 785 mg, 67% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.8 Hz, 1H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.83 (d, *J* = 8.5 Hz, 1H), 7.77 (d, *J* = 8.8 Hz, 1H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.56 – 7.47 (m, 3H), 7.46 – 7.30 (m, 11H), 7.29 – 7.03 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4 (d, $^{3}J_{CP}$ = 7.6 Hz), 147.7 (d, $^{3}J_{CP}$ = 4.4 Hz), 147.1 (d, $^{4}J_{CP}$ = 1.7 Hz), 140.8, 140.4, 136.6, 133.0, 132.7, 131.8, 131.4, 130.7, 130.2, 129.8, 129.5 (d, $^{4}J_{CP}$ = 1.9 Hz), 129.0, 128.7, 128.6 (d, $^{3}J_{CP}$ = 3.8 Hz), 127.5, 127.3 (d, $^{3}J_{CP}$ = 3.8 Hz), 127.3 (d, $^{3}J_{CP}$ = 6.3 Hz), 127.0, 126.7, 126.5 (d, $^{2}J_{CP}$ = 13.8 Hz), 125.4, 125.2, 124.6, 124.5 (d, $^{2}J_{CP}$ = 6.3 Hz), 123.0 (d, $^{4}J_{CP}$ = 2.5 Hz), 122.9, 121.9 (d, $^{3}J_{CP}$ = 6.4 Hz), 120.4 (d, $^{2}J_{CP}$ = 13.7 Hz); ^{31}P NMR (200 MHz, $CDCl_3$) δ 145.6; HRMS (EI) for $C_{40}H_{27}O_3P$ $[M]^+$ calcd 586.1698, found 586.1712.

3. General procedures for Rh-catalyzed 1,2-additions of α-diketones

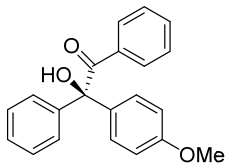
Under an argon atmosphere, a solution of α-diketone (**10**, 0.25 mmol), $[Rh(coe)_2Cl]_2$ (1.5 mol%, 2.7 mg, 0.0075 mmol of Rh), ligand **L1** (3 mol%, 3.8 mg, 0.0075 mmol), and arylboronic acid (0.5 mmol) in 1.0 mL of toluene was stirred at room temperature for 30 min. To this mixture was added aqueous K_3PO_4 (83 ul, 2.5 M). After being stirred at room temperature overnight, the mixture was concentrated under reduced pressure. The residue was purified by silica gel column chromatography to afford the corresponding addition product **11**.

4. General procedures for Rh-catalyzed 1,2-additions of cyclic imines

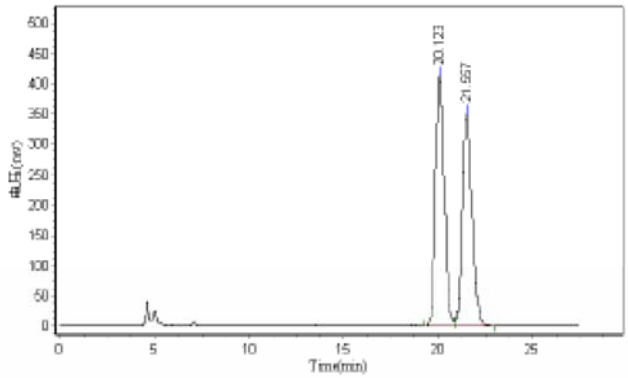
Under an argon atmosphere, a solution of cyclic imine (**12,** 0.25 mmol), $[Rh(coe)_2Cl]_2$ (2.5 mol%, 4.5 mg, 0.0125 mmol of Rh), ligand **L4** or **L10** (5 mol% 0.0125 mmol), and boronic acid in 1.0 mL of dioxane was stirred at room temperature for 30 min. To this mixture were added aqueous K_3PO_4 (83 ul, 2.5 M). After being stirred at room temperature or designated temperature for 3-6 hours, the reaction mixture was passed through a pad of silica gel with EtOAc and the solvent was removed under vacuum. The residue was purified by silica gel column chromatography to afford the corresponding addition product **13**.

5. Characterization data and HPLC of addition products

(*R*)-2-hydroxy-2-(4-methoxyphenyl)-1,2-diphenylethan-1-one (11a)

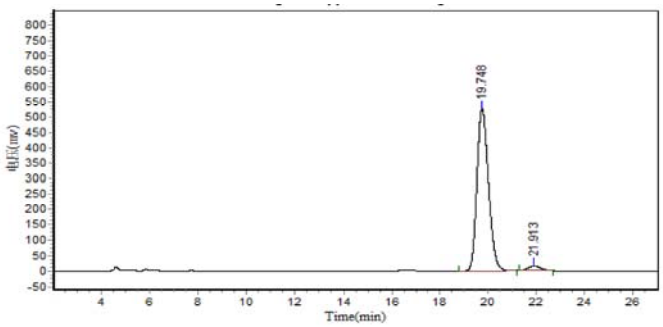


white solid, 93% yield, 94% ee; 7.88 – 7.57 (m, 2H), 7.56 – 7.10 (m, 10H), 6.84 (d, *J* = 6.1 Hz, 2H), 4.99 (s, 1H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.0, 159.3, 142.2, 135.2, 134.1, 133.0, 130.9, 129.7, 128.4, 128.3, 128.2, 128.1, 113.8, 84.8, 55.3; HPLC: Chiral OZ-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 95/5; flow = 0.7 mL/min; Rentention time: 19.7 min (maj), 21.9 min.



Results

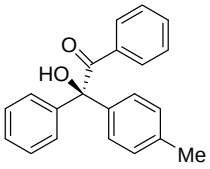
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		20.123	412313.750	13218834.000	50.8972
2		21.557	350684.406	12752770.000	49.1028
Total			762998.156	25971594.000	100.0000



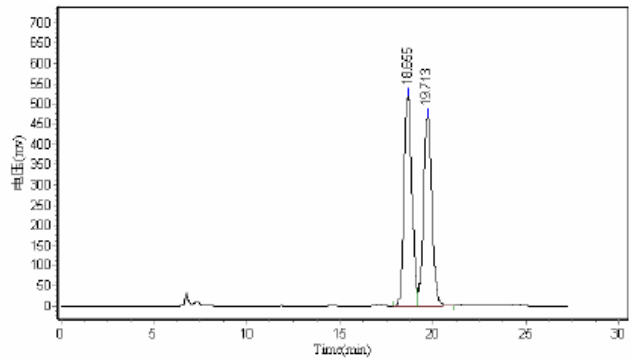
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		19.748	528537.375	17489778.000	96.9634
2		21.913	15090.246	547724.750	3.0366
Total			543627.621	18037502.750	100.0000

(*R*)-2-hydroxy-1,2-diphenyl-2-(p-tolyl)ethan-1-one (11b)

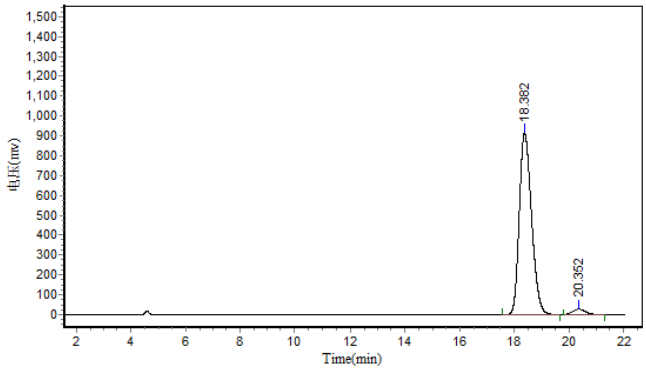


white solid, 80% yield, 94% ee; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.3 Hz, 2H), 7.47 – 7.37 (m, 3H), 7.36 – 7.20 (m, 7H), 7.13 (d, *J* = 8.0 Hz, 2H), 4.97 (s, 1H), 2.32 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 201.04, 142.2, 139.1, 138.0, 135.3, 133.0, 130.9, 129.2, 128.4, 128.4, 128.3, 128.2, 85.1, 21.2; HPLC: Chiral OZ-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 95/5; flow = 0.5 mL/min; Rentention time: 18.4 min (maj), 20.4 min.



Results

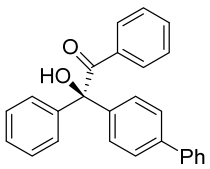
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		18.655	518740.938	14889290.000	50.3899
2		19.713	466022.594	14658891.000	49.6101
Total			984763.531	29548181.000	100.0000



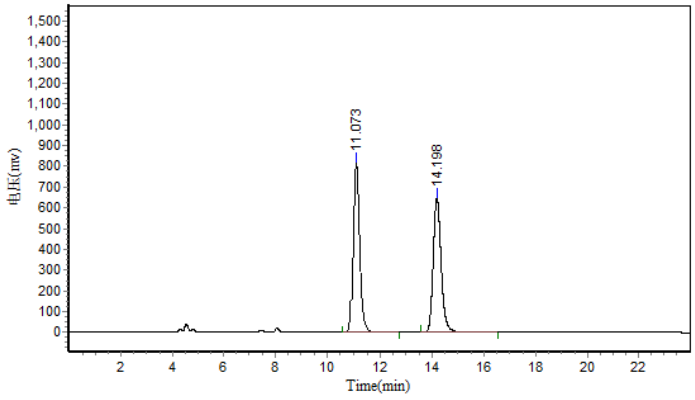
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		18.382	914772.625	28500398.000	96.9030
2		20.352	27209.283	910857.688	3.0970
Total			941981.908	29411255.688	100.0000

(*R*)-2-([1,1'-biphenyl]-4-yl)-2-hydroxy-1,2-diphenylethan-1-one (11c)

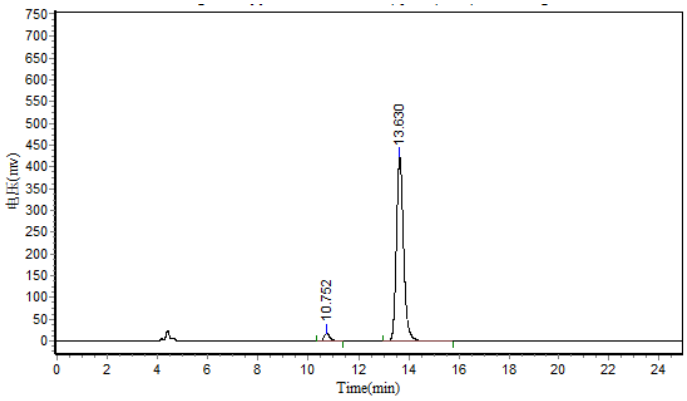


white solid, 83% yield, 93% ee; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 – 7.71 (m, 2H), 7.58 (dd, *J* = 8.2, 2.5 Hz, 4H), 7.53 – 7.39 (m, 7H), 7.39 – 7.22 (m, 6H), 5.03 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.8, 142.0, 141.0, 140.9, 140.4, 135.2, 133.1, 130.9, 128.9, 128.8, 128.5, 128.3, 128.3, 128.2, 127.6, 127.1, 127.1, 85.1; Chiral AD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 70/30; flow =0.7 mL/min; Rentention time: 10.8 min, 13.6 min (maj).



Results

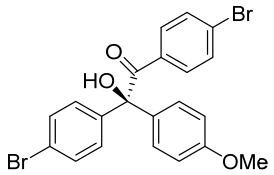
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.073	812971.188	13635799.000	49.6581
2		14.198	649129.375	13823594.000	50.3420
Total			1462100.563	27459393.000	100.0000



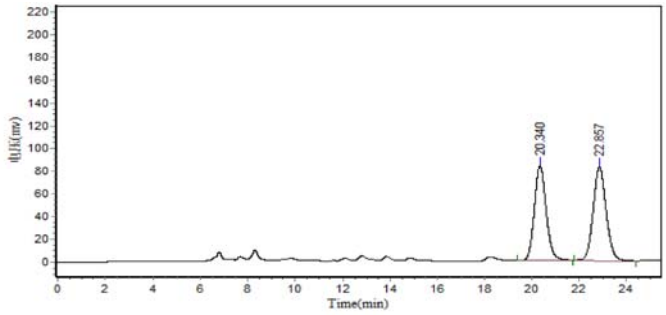
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.752	18417.047	288310.625	3.3144
2		13.630	422684.719	8410498.000	96.6856
Total			441101.766	8698808.625	100.0000

(*S*)-1,2-bis(4-bromophenyl)-2-hydroxy-2-(4-methoxyphenyl)ethan-1-one (11d)

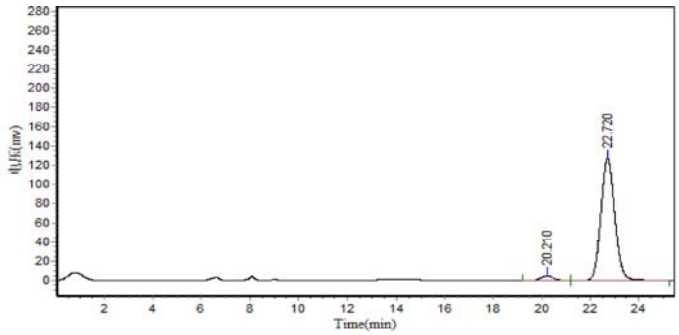


white solid, 87% yield, 94% ee; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.6 Hz, 2H), 7.49 – 7.37(m, 4H), 7.28 – 7.15 (m, 4H), 6.85 (d, *J* = 8.8 Hz, 2H), 4.79 (s, 1H), 3.77 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.5, 159.7, 141.0, 133.6, 133.5, 132.4, 131.7, 130.0, 129.4, 128.6, 122.6, 114.1, 84.6, 55.4; HPLC: Chiral OZ-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 95/5; flow = 0.5 mL/min; Rentention time: 20.2 min, 22.7min(maj); HRMS (ESI) for $C_{21}H_{16}Br_2O_3Na$ $[M+Na]^+$ calcd , 496.9364, found 496.9366.



Results

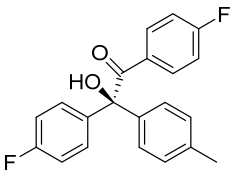
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		20.340	83689.945	2869904.000	47.8269
2		22.857	82794.258	3130698.250	52.1731
Total			166484.203	6000602.250	100.0000



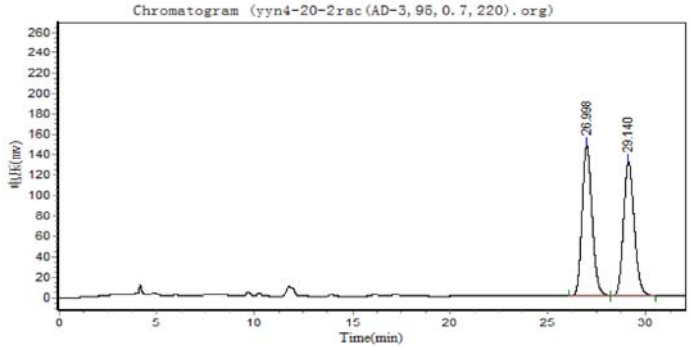
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		20.210	4813.986	162795.813	3.1550
2		22.720	126651.352	4997111.000	96.8450
Total			131465.337	5159906.813	100.0000

(*S*)-1,2-bis(4-fluorophenyl)-2-hydroxy-2-(p-tolyl)ethan-1-one (11e)

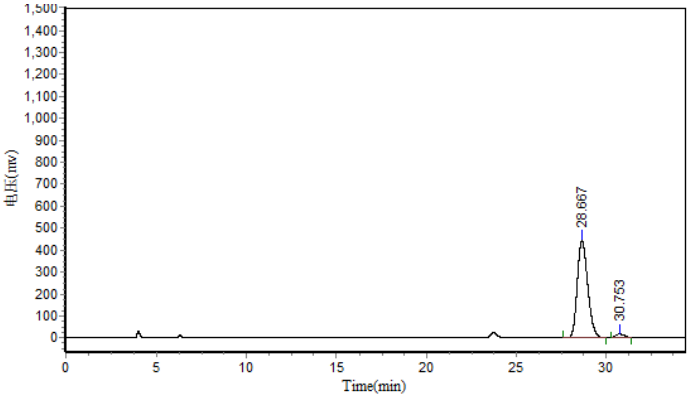


white solid, 90% yield, 94% ee; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 – 7.74 (m, 2H), 7.40 – 7.29 (m, 2H), 7.23 (d, *J* = 8.2 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.04 – 6.88 (m, 4H), 4.83 (s, 1H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.0, 165.5 (d, $^{1}J_{CF}$ = 255.0 Hz), 162.5 (d, $^{1}J_{CF}$ = 246 Hz), 138.9, 138.4, 138.0 (d, $^{3}J_{CF}$ = 3.1 Hz), 133.8, 133.7, 131.2 (d, $^{3}J_{CF}$ =2.5 Hz), 130.2, 130.1, 129.4, 128.0, 115.4 (d, $^{2}J_{CF}$ = 22.0), 115.4 (d, $^{2}J_{CF}$ = 22.0), 84.6, 21.2. HPLC: Chiral AD-3 column (250 mm); detected at 220 nm; hexane/*i*-propanol = 95/5; flow = 0.7 mL/min; Rentention time: 28.7 min (maj), 30.8 min.



Results

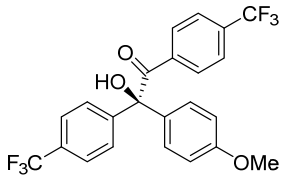
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		26.998	146980.656	5221841.500	51.0796
2		29.140	130319.617	5001109.000	48.9204
Total			277300.273	10222950.500	100.0000



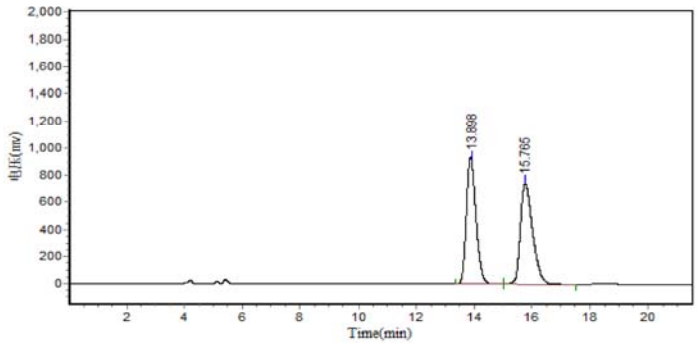
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		28.667	444320.000	17911356.000	97.1555
2		30.753	14746.133	524401.500	2.8445
Total			459066.133	18435757.500	100.0000

(*R*)-2-hydroxy-2-(4-methoxyphenyl)-1,2-bis(4-(trifluoromethyl)phenyl)ethan-1-one (11f)

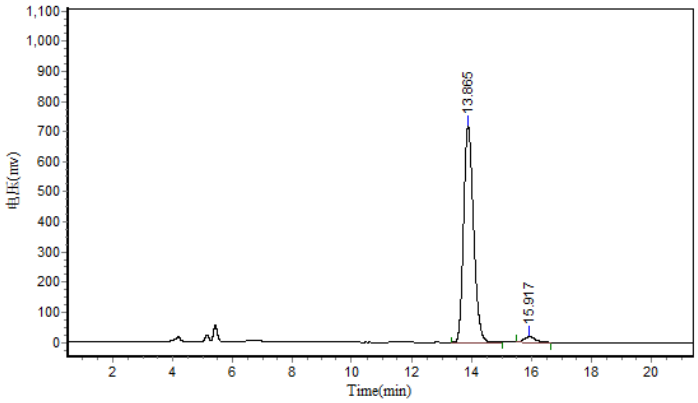


solid, 96% yield, 95% ee; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.1 Hz, 2H), 7.65 – 7.46 (m, 6H), 7.24 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 8.9 Hz, 2H), 4.53 (s, 1H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.6, 159.9, 145.6, 138.1, 134.3(q, $^{2}J_{CF}$ = 32.6 Hz),133.2, 131.1, 130.6 (q, $^{2}J_{CF}$ = 32.4 Hz), 129.2, 128.5, 125.6 (q, $^{3}J_{CF}$ = 3.5 Hz), 125.4 (q, $^{3}J_{CF}$ = 3.4 Hz), 124.0 (q, $^{1}J_{CF}$ =271 Hz), 123.5 (q, $^{1}J_{CF}$ =271 Hz), 114.3, 85.1, 55.4; HPLC: Chiral AD-3 column (250 mm); detected at 220 nm; hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; Rentention time: 13.9 min (maj), 15.9 min; HRMS (ESI) for $C_{23}H_{16}F_6O_3Na$ $[M+Na]^+$ calcd ,477.0901, found 477.0890.



Results

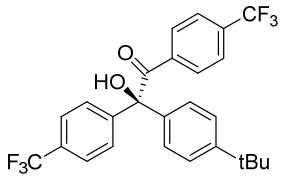
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.898	931283.000	21563952.000	49.7053
2		15.765	737120.938	21819650.000	50.2947
Total			1668403.938	43383602.000	100.0000



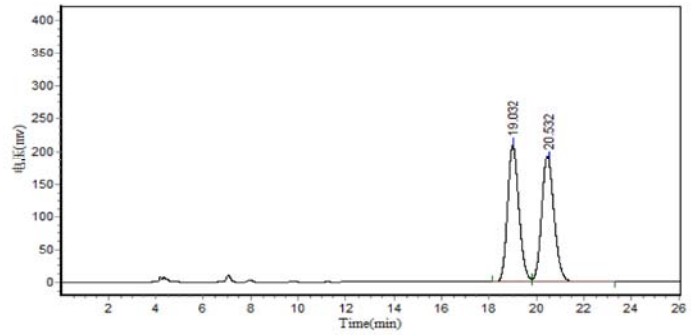
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.865	719138.688	16560955.000	97.4704
2		15.917	17321.205	429802.906	2.5296
Total			736459.893	16990757.906	100.0000

(*S*)-2-(4-(tert-butyl)phenyl)-2-hydroxy-1,2-bis(4-(trifluoromethyl)phenyl)ethan-1-one (11g)

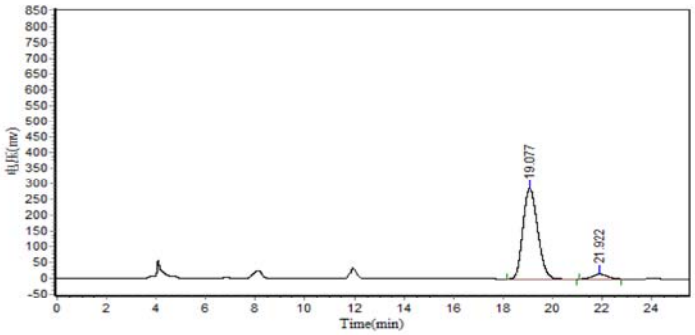


solid, 93% yield, 90% ee; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.2 Hz, 2H), 7.67 – 7.49 (m, 6H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.5 Hz, 2H), 4.49 (s, 1H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.5, 151.9, 145.3, 138.1, 138.0, 134.2 (q, $^{2}J_{CF}$ = 32.0 Hz), 131.0, 130.4(q, $^{2}J_{CF}$ = 32.0 Hz), 128.4, 127.4, 125.8, 125.4 (q, $^{3}J_{CF}$ = 3.0 Hz), 125.2 (q, $^{3}J_{CF}$ = 3.5 Hz), 124.0 (q, $^{1}J_{CF}$ =271 Hz), 123.5 (q, $^{1}J_{CF}$ =271 Hz), 85.1, 34.6, 31.2; HPLC: Chiral AD-3 column (250 mm); detected at 220 nm; hexane/*i*-propanol = 97/3; flow = 0.7 mL/min; Rentention time: 19.1 min (maj), 21.9 min; HRMS (ESI) for $C_{26}H_{21}F_6O_2$ $[M-H]^-$ calcd 479.1446, found 479.1465.



Results

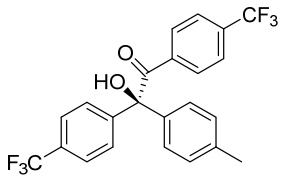
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		19.032	209014.953	7003248.000	49.7356
2		20.532	190805.625	7077719.000	50.2644
Total			399820.578	14080967.000	100.0000



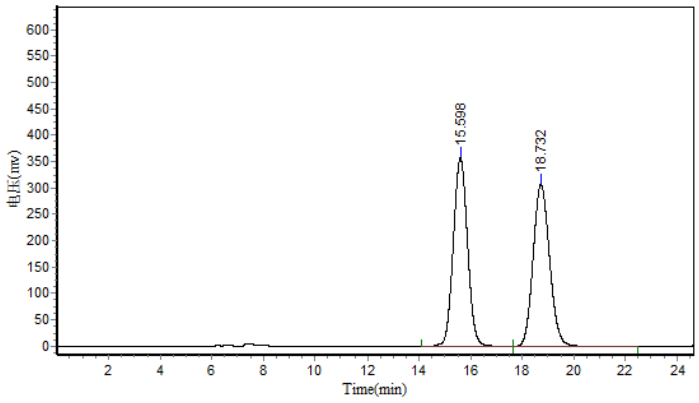
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		19.077	285777.313	11811664.000	95.0101
2		21.922	14466.486	620344.750	4.9899
Total			300243.799	12432008.750	100.0000

(*S*)-2-hydroxy-2-(p-tolyl)-1,2-bis(4-(trifluoromethyl)phenyl)ethan-1-one (11h)

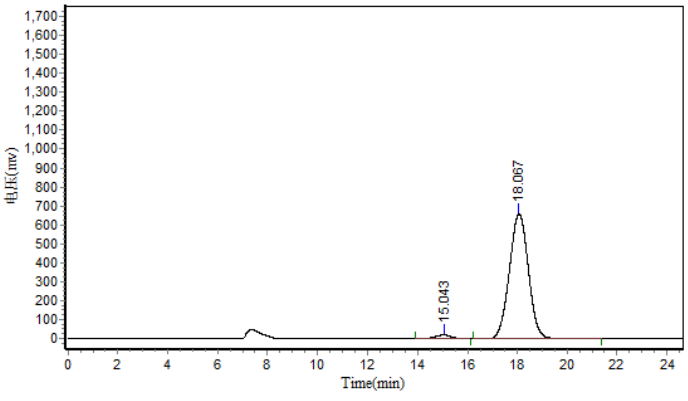


solid, 94% yield, 95% ee; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (d, J = 8.0 Hz, 2H), 7.65 – 7.47 (m, 6H), 7.28 – 7.13 (m, 4H), 4.48 (s, 1H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.5, 145.5, 139.0, 138.2, 138.1, 134.3 (q, $^{2}J_{CF}$ = 32.6 Hz), 131.1, 130.6 (q, $^{2}J_{CF}$ = 32.4Hz), 129.7, 128.6, 127.8, 125.5 (q, $^{3}J_{CF}$ = 3.6 Hz), 125.4 (q, $^{3}J_{CF}$ = 3.6 Hz), 124.0 (q, $^{1}J_{CF}$ =271 Hz), 123.5 (q, $^{1}J_{CF}$ =271 Hz), 85.3, 21.2; HPLC: Chiral OZ-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 99/1; flow = 0.5 mL/min; Rentention time: 15.0 min, 18.1min (maj); HRMS (ESI) for $C_{23}H_{15}F_6O_2$ $[M-H]^-$ calcd 437.0976, found 437.0980.



Results

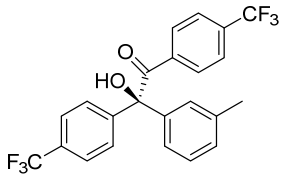
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		15.598	357131.156	13861791.000	50.1440
2		18.732	307522.344	13782153.000	49.8560
Total			664653.500	27643944.000	100.0000



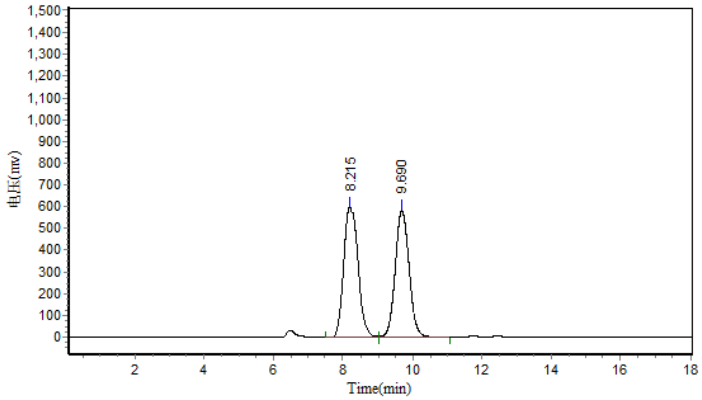
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		15.043	20055.639	971265.188	2.7045
2		18.067	660349.063	34942004.000	97.2955
Total			680404.701	35913269.188	100.0000

(*R*)-2-hydroxy-2-(m-tolyl)-1,2-bis(4-(trifluoromethyl)phenyl)ethan-1-one (11i)

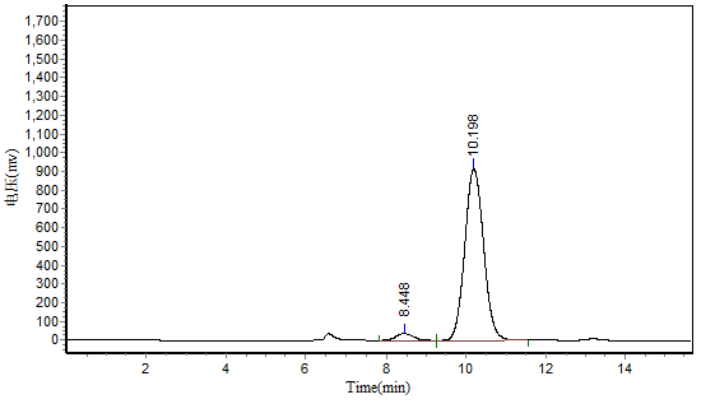


solid, 94% yield, 93% ee; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.1 Hz, 2H), 7.71 – 7.43 (m, 6H), 7.33 – 7.15 (m, 3H), 7.11 (d, *J* = 7.6 Hz, 1H), 4.45 (s, 1H), 2.34 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.6, 145.4, 141.1, 139.0, 138.1, 134.3 (q, $^{2}J_{CF}$ = 32.9 Hz), 131.1，130.6 (q, $^{2}J_{CF}$ = 32.5 Hz), 129.8, 128.9, 128.6, 128.4, 125.5 (q, $^{3}J_{CF}$ = 3.5 Hz), 125.4 (q, $^{3}J_{CF}$ = 3.5 Hz), 124.9, 124.0 (q, $^{1}J_{CF}$ =271.1 Hz), 123.5 (q, $^{1}J_{CF}$ =271.3 Hz), 85.4, 21.7; HPLC: Chiral OZ-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 97/3; flow = 0.5 mL/min; Rentention time: 8.4 min, 10.2 min (maj); HRMS (ESI) for $C_{23}H_{16}F_6O_2Na$ $[M+Na]^+$ calcd 461.0952, found 461.0942.



Results

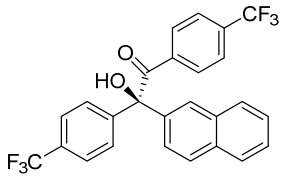
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.215	596628.438	16228680.000	49.8902
2		9.690	583329.438	16300119.000	50.1098
Total			1179957.875	32528799.000	100.0000



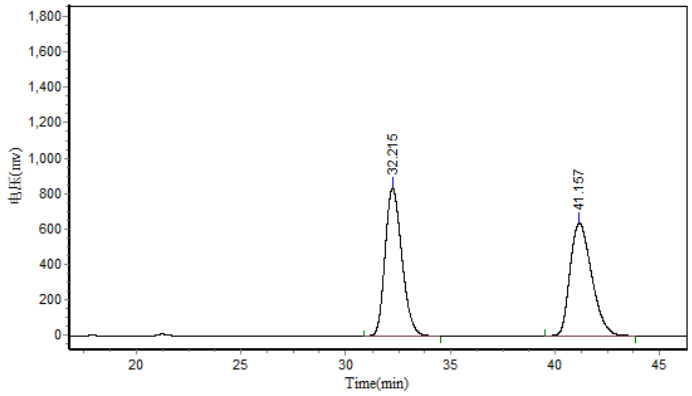
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.448	37046.332	1172550.250	3.7289
2		10.198	912150.750	30272360.000	96.2711
Total			949197.082	31444910.250	100.0000

(*R*)-2-hydroxy-2-(naphthalen-2-yl)-1,2-bis(4-(trifluoromethyl)phenyl)ethan-1-one (11j)

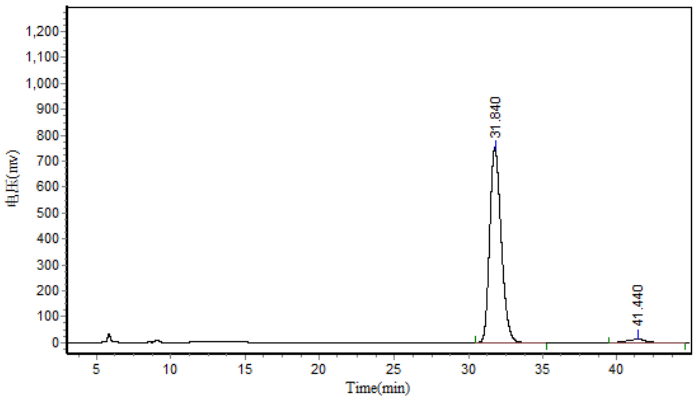


solid, 93% yield, 94% ee; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 – 7.82 (m, 4H), 7.81 – 7.72 (m, 2H), 7.62 (d, *J* = 8.5 Hz, 2H), 7.59 – 7.39 (m, 7H), 4.58 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.5, 145.4, 138.4, 138.0, 134.4 (q, $^{2}J_{CF}$ = 32.5 Hz), 133.2, 133.0, 131.1, 130.7 (q, $^{2}J_{CF}$ = 32.5 Hz), 129.0, 128.7, 128.6, 127.8, 127.3, 127.0, 126.7, 125.6 (q, $^{3}J_{CF}$ = 3.3 Hz), 125.4 (q, $^{3}J_{CF}$ = 3.3 Hz), 125.3, 125.1, 124.0 (q, $^{1}J_{CF}$ =271.4 Hz), 123.5 (q, $^{1}J_{CF}$ =271.4 Hz), 85.6; HPLC: Chiral AD-3 column (250 mm); detected at 220 nm; hexane/*i*-propanol = 95/5; flow = 0.5 mL/min; Rentention time: 31.8 min (maj), 41.4 min; HRMS (ESI) for $C_{26}H_{16}F_6O_2Na$ $[M+Na]^+$ calcd 497.0952, found 497.0943.



Results

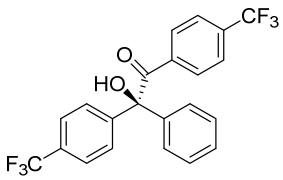
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		32.215	832343.313	46347644.000	50.5064
2		41.157	633303.375	45418284.000	49.4936
Total			1465646.688	91765928.000	100.0000



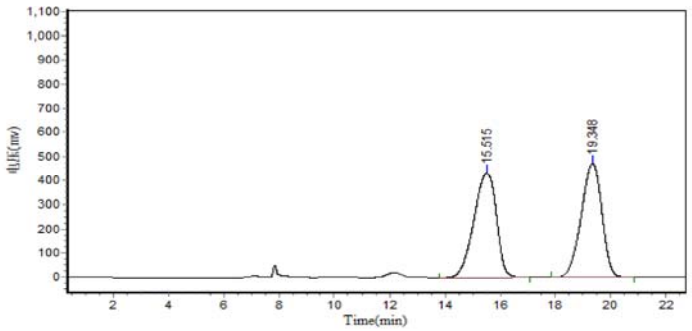
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		31.840	748283.125	40631864.000	96.9748
2		41.440	13861.396	1267531.125	3.0252
Total			762144.521	41899395.125	100.0000

(*S*)-2-hydroxy-2-phenyl-1,2-bis(4-(trifluoromethyl)phenyl)ethan-1-one (11k)

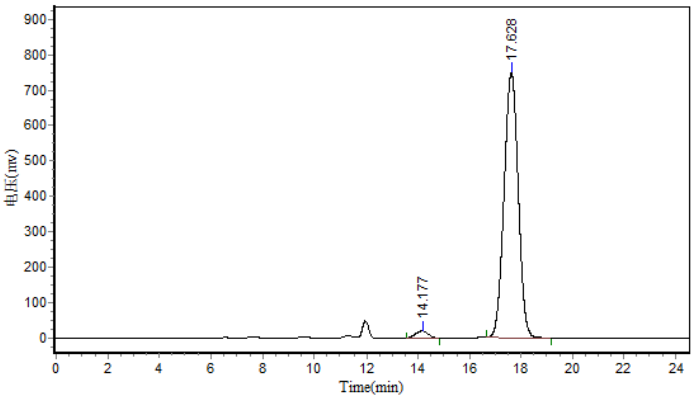


solid, 91% yield, 95% ee; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (d, J = 8.2 Hz, 2H), 7.70 – 7.48 (m, 6H), 7.46 – 7.30 (m, 5H), 4.55 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.5, 145.4, 141.1, 138.0, 134.4 (q, $^{2}J_{CF}$ = 32.5 Hz), 131.1, 130.7 (q, $^{2}J_{CF}$ = 32.5 Hz), 129.0, 129.0, 128.6, 127.8, 125.6 (q, $^{3}J_{CF}$ = 3.3 Hz), 125.4 (q, $^{3}J_{CF}$ = 3.3 Hz), 124.0 (q, $^{1}J_{CF}$ =271.2 Hz), 123.5 (q, $^{1}J_{CF}$ =271.2 Hz), 85.4; HPLC: Chiral OZ-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 99/1; flow = 0.5 mL/min; Rentention time: 14.2 min, 17.6 min (maj); HRMS (ESI) for $C_{22}H_{13}F_6O_2$ $[M-H]^-$ calcd 423.0820, found 423.0838.



Results

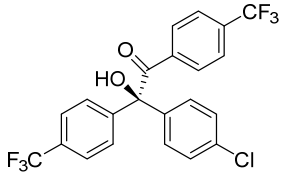
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		15.515	428287.906	24394402.000	49.8482
2		19.348	469025.000	24542998.000	50.1518
Total			897312.906	48937400.000	100.0000



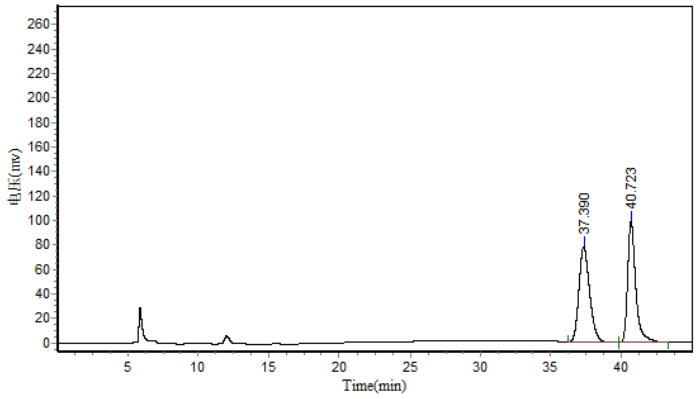
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		14.177	19943.941	710699.250	2.4272
2		17.628	747749.375	28570278.000	97.5728
Total			767693.316	29280977.250	100.0000

(*R*)-2-(4-chlorophenyl)-2-hydroxy-1,2-bis(4-(trifluoromethyl)phenyl)ethan-1-one (11l)

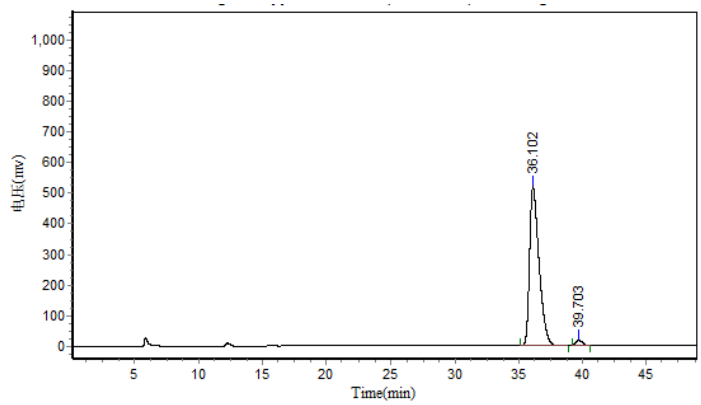


solid, 94% yield, 96% ee; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (d, J = 8.1 Hz, 2H), 7.70 – 7.57 (m, 4H), 7.51 (d, J = 8.2 Hz, 2H), 7.42 – 7.21 (m, 4H), 4.56 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.0, 145.1, 139.6, 137.7, 135.1, 134.6 (q, $^{2}J_{CF}$ = 32.7 Hz), 131.1, 130.7 (q, $^{2}J_{CF}$ = 32.7 Hz), 129.3, 129.2, 128.4, 125.8 (q, $^{3}J_{CF}$ = 3.6 Hz), 125.5 (q, $^{3}J_{CF}$ = 3.3 Hz), 124.0 (q, $^{1}J_{CF}$ =271.0 Hz), 123.5 (q, $^{1}J_{CF}$ =271.0 Hz), 85.0; HPLC: Chiral AD-3 column (250 mm); detected at 220 nm; hexane/*i*-propanol = 97/3; flow = 0.5 mL/min; Rentention time: 36.1 min (maj), 39.7 min; HRMS (ESI) for $C_{22}H_{12}ClF_6O_2$ $[M-H]^-$ calcd 457.0430, found 457.0449.



Results

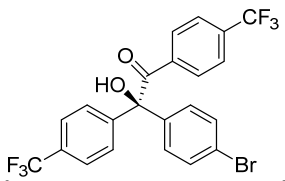
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		37.390	77517.336	4077926.750	50.8762
2		40.723	98320.453	3937471.750	49.1238
Total			175837.789	8015398.500	100.0000



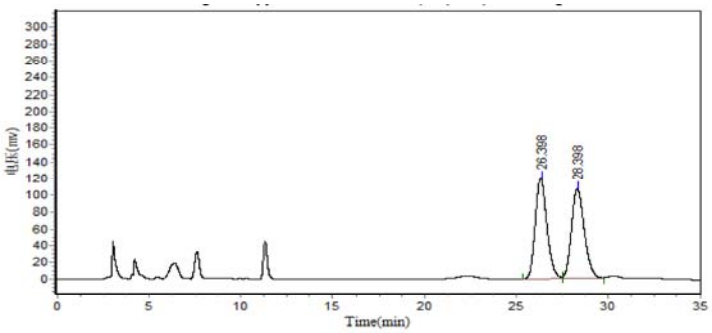
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		36.102	517665.531	26694500.000	97.9505
2		39.703	16262.043	558542.688	2.0495
Total			533927.574	27253042.688	100.0000

(*R*)-2-(4-bromophenyl)-2-hydroxy-1,2-bis(4-(trifluoromethyl)phenyl)ethan-1-one (11m)

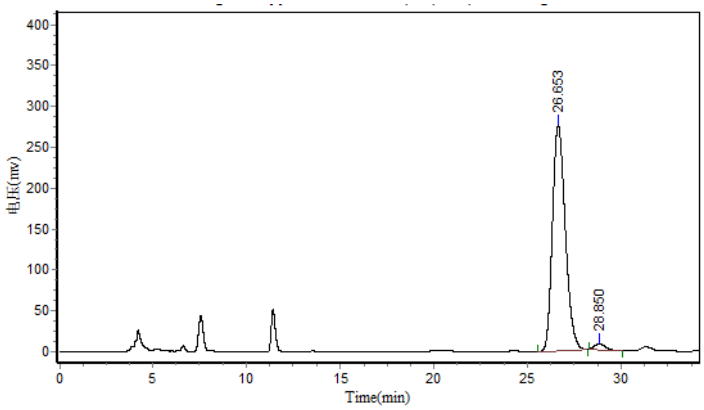


solid, 90% yield, 95% ee; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.1 Hz, 2H), 7.74 – 7.45 (m, 8H), 7.24 (d, *J* = 8.7 Hz, 2H), 4.56 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.0, 145.0, 140.1, 137.6, 134.8, 134.6 (q, $^{2}J_{CF}$ = 33.3 Hz), 132.2, 131.1, 131.0 (q, $^{2}J_{CF}$ = 32.3 Hz), 129.6, 128.4, 125.8 (q, $^{3}J_{CF}$ = 3.4 Hz), 125.4 (q, $^{3}J_{CF}$ = 3.8 Hz), 124.0 (q, $^{1}J_{CF}$ =273 Hz), 123.4 (q, $^{1}J_{CF}$ =273 Hz), 123.3, 85.0; HPLC: Chiral AD-3 column (250 mm); detected at 220 nm; hexane/*i*-propanol = 95/5; flow = 0.7 mL/min; Rentention time: 26.7 min (maj), 28.7 min; HRMS (ESI) for $C_{22}H_{12}BrF_6O_2$ $[M-H]^-$ calcd 500.9925, found 500.9940.



Results

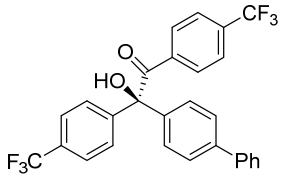
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		26.398	120320.188	5434519.000	49.9963
2		28.398	108240.352	5435314.000	50.0037
Total			228560.539	10869833.000	100.0000



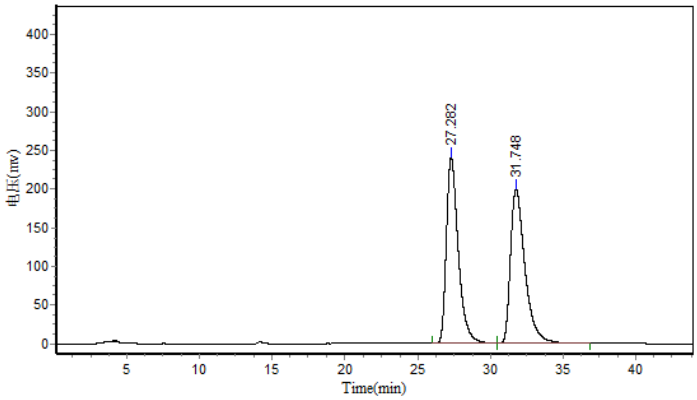
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		26.653	275846.563	13195752.000	97.7454
2		28.850	7040.746	304377.688	2.2546
Total			282887.309	13500129.688	100.0000

(*S*)-2-([1,1'-biphenyl]-4-yl)-2-hydroxy-1,2-bis(4-(trifluoromethyl)phenyl)ethan-1-one (11n)

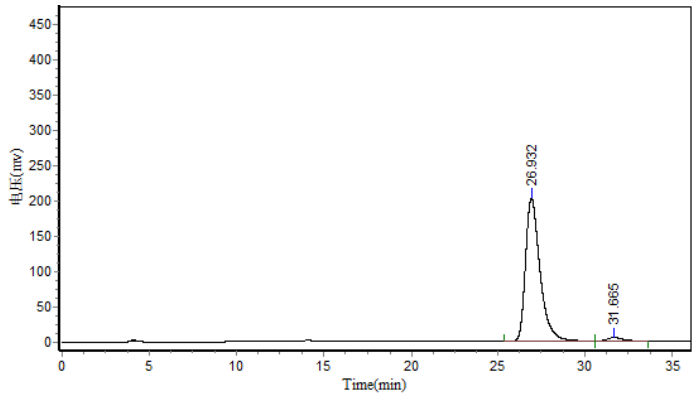


solid, 95% yield, 94% ee; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (d, J = 8.1 Hz, 2H), 7.69 – 7.50 (m, 10H), 7.48 – 7.29 (m, 5H), 4.57 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.4, 145.4, 141.8, 140.1, 140.0, 138.0, 134.4 (q, $^{2}J_{CF}$ = 33.0 Hz), 131.1, 130.7 (q, $^{2}J_{CF}$ = 32.0 Hz), 129.1, 128.6, 128.3, 128.0, 127.6, 127.2, 125.7 (q, $^{3}J_{CF}$ = 3.3 Hz), 125.4 (q, $^{3}J_{CF}$ = 4.0 Hz), 124.0 (q, $^{1}J_{CF}$ =271 Hz), 123.5 (q, $^{1}J_{CF}$ =271 Hz), 85.3; HPLC: Chiral AD-3 column (250 mm); detected at 220 nm; hexane/*i*-propanol = 97/3; flow = 0.7 mL/min; Rentention time: 26.9 min (maj), 31.7 min; HRMS (ESI) for $C_{28}H_{17}F_6O_2$ $[M-H]^-$ calcd 499.1133, found 499.1153.



Results

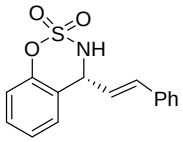
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		27.282	240322.438	13728695.000	49.7720
2		31.748	198895.266	13854449.000	50.2280
Total			439217.703	27583144.000	100.0000



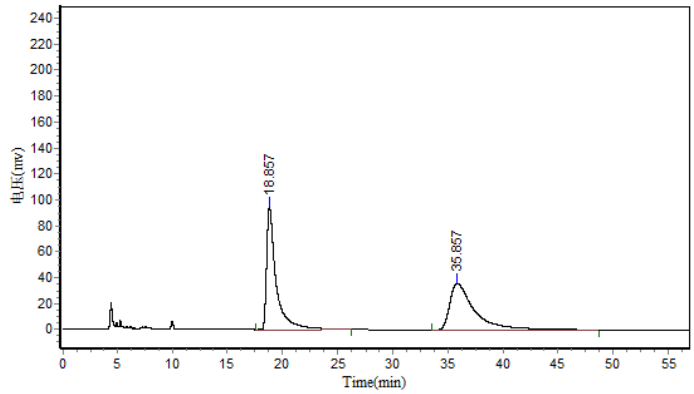
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		26.932	202211.750	11782496.000	96.9314
2		31.665	5138.808	373007.313	3.0686
Total			207350.558	12155503.313	100.0000

(*R*,*E*)-4-styryl-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide (13a)

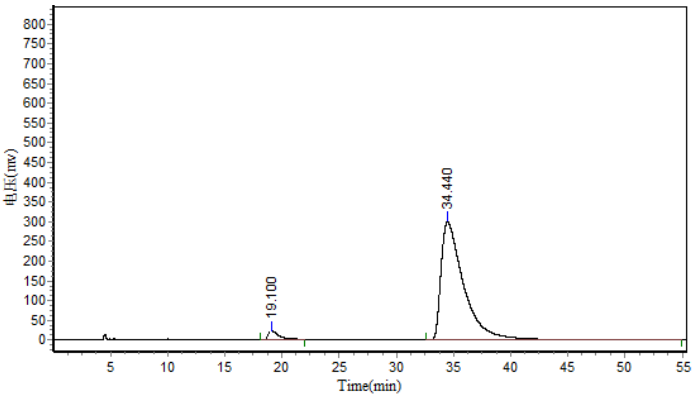


oil, 87% yield, 92% ee; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 – 7.37 (m, 2H), 7.36 – 7.24 (m, 3H), 7.20 – 7.05 (m, 2H), 6.99 – 6.88 (m, 1H), 6.79 (dd, *J* = 15.7, 2.8 Hz, 1H), 6.23 (dd, *J* = 15.7, 8.6 Hz, 1H), 5.38 (td, *J* = 8.4, 3.5 Hz, 1H), 5.04 – 4.82 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1, 136.9, 135.3, 130.0, 129. 1, 129. 0, 128.0, 127.1, 125.5, 124.2, 121.3, 119.0, 60.2; HPLC: Chiral AY-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 80/20; flow = 0.7 mL/min; Rentention time: 19.1 min, 34.4 min (maj); HRMS (ESI) for $C_{15}H_{12}NO_3S$ $[M-H]^-$ calcd 286.0538, found 286.0551.



Results

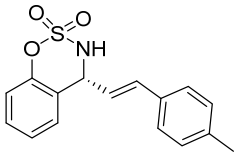
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		18.857	94529.547	5737516.000	50.3701
2		35.857	35950.609	5653203.500	49.6299
Total			130480.156	11390719.500	100.0000



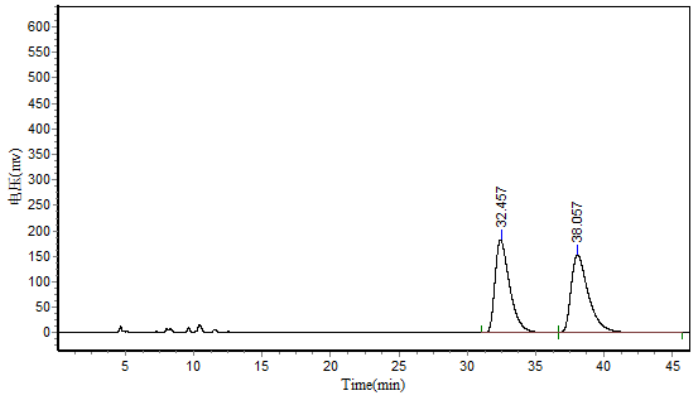
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		19.100	24273.293	1644258.000	3.7622
2		34.440	299166.906	42060640.000	96.2378
Total			323440.199	43704898.000	100.0000

(*R*,*E*)-4-(4-methylstyryl)-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide (13b)

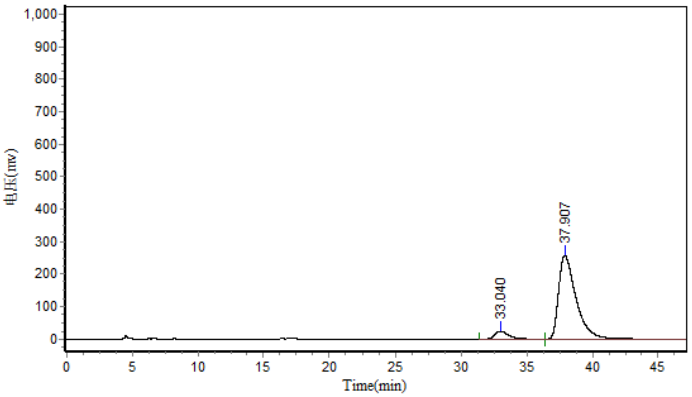


oil, 93% yield, 87% ee; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 – 7.24 (m, 3H), 7.23 – 7.07 (m, 4H), 6.96 (d, *J* = 8.2 Hz, 1H), 6.77 (d, *J* = 15.7 Hz, 1H), 6.18 (dd, *J* = 15.7, 8.6 Hz, 1H), 5.37 (t, *J* = 8.4 Hz, 1H), 4.95 (d, *J* = 8.2 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9, 139.1, 136.8, 132.5, 129.9, 129.6, 128.0, 127.0, 125.4, 123.0, 121.4, 118.8, 60.2, 21.4; HPLC: Chiral IC-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; Rentention time: 33.0 min, 37.9 min (maj); HRMS (ESI) for $C_{16}H_{14}NO_3S$ $[M-H]^-$ calcd 300.0694, found 300.0708.



Results

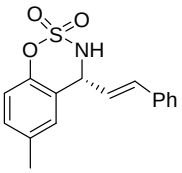
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		32.457	181792.891	13683214.000	49.8676
2		38.057	152566.781	13755865.000	50.1324
Total			334359.672	27439079.000	100.0000



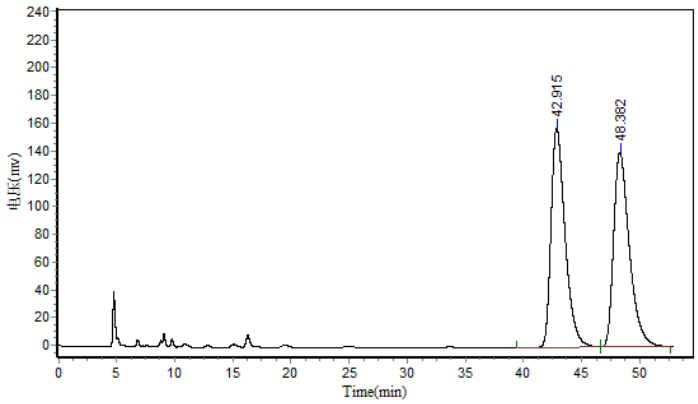
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		33.040	24018.639	1729827.375	6.7784
2		37.907	256896.781	23789740.000	93.2216
Total			280915.420	25519567.375	100.0000

(*R*,*E*)-6-methyl-4-styryl-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide (13c)

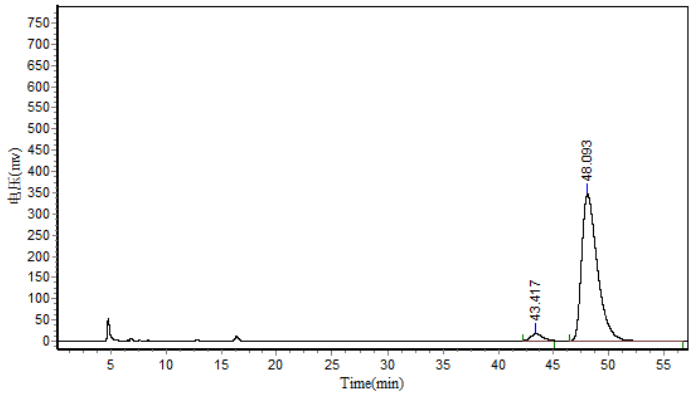


oil, 92% yield, 93% ee; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (d, *J* = 6.6 Hz, 2H), 7.39 – 7.25 (m, 3H), 7.08 (d, *J* = 8.2 Hz, 1H), 6.96 (s, 1H), 6.82 (dd, *J* = 14.2, 12.1 Hz, 2H), 6.25 (dd, *J* = 15.7, 8.6 Hz, 1H), 5.34 (s, 1H), 4.99 (s, 1H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8, 136.6, 135.4, 135.3, 130.5, 128.9, 128.1, 127.1, 124.3, 120.8, 118.6, 60.1, 20.9; HPLC: Chiral IC-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; Rentention time: 43.4 min, 48.1 min (maj); HRMS (ESI) for $C_{16}H_{16}NO_3S$ $[M+H]^+$ calcd 302.0851, found 302.0846.



Results

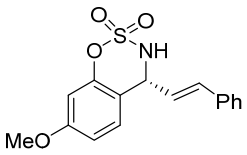
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		42.915	157518.844	13278950.000	50.1106
2		48.382	139738.625	13220325.000	49.8894
Total			297257.469	26499275.000	100.0000



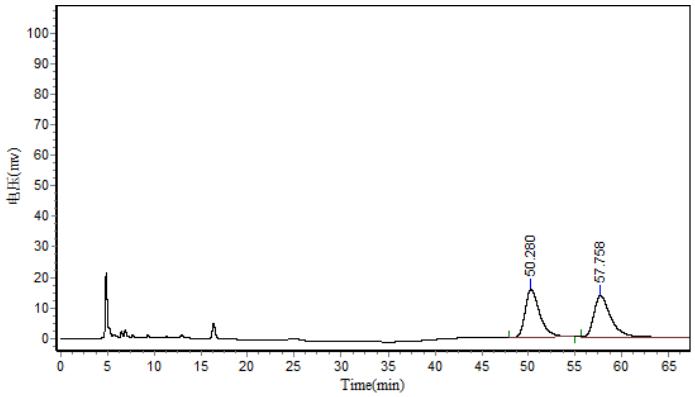
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		43.417	15515.896	1169031.625	3.3143
2		48.093	345340.969	34103084.000	96.6857
Total			360856.864	35272115.625	100.0000

(*R*,*E*)-7-methoxy-4-styryl-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide (13d)

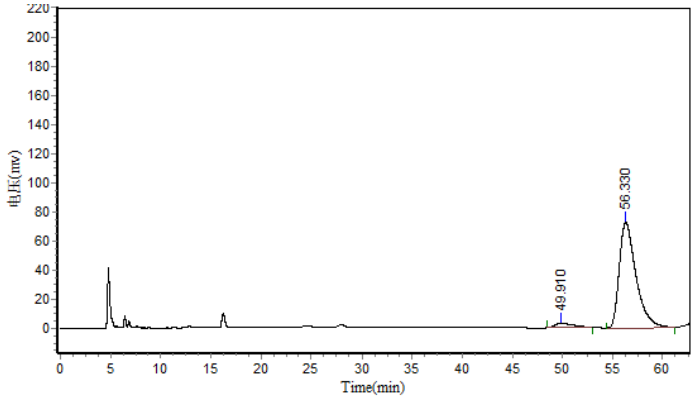


oil, 64% yield, 91% ee; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 - 7.15 (m, 6H), 7.06 (d, *J* = 8.6 Hz, 1H), 6.75 (dd, *J* = 24.9, 12.2 Hz, 2H), 6.50 (s, 1H), 6.23 (dd, *J* = 15.6, 8.6 Hz, 1H), 5.33 (d, *J* = 8.2 Hz, 1H), 3.76 (d, *J* = 2.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6, 151.7, 136.5, 135.4, 128.9, 128.6, 127.0, 124.4, 113.0, 112.3, 103.6, 59.8, 55.7; HPLC: Chiral IC-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; Rentention time: 49.9 min, 56.3 min (maj); HRMS (ESI) for $C_{16}H_{16}NO_4S$ $[M+H]^+$ calcd 318.0800, found 318.0798.



Results

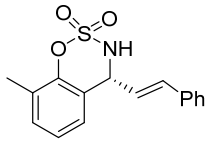
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		50.280	15634.077	1680818.000	48.4337
2		57.758	13717.068	1789531.875	51.5663
Total			29351.146	3470349.875	100.0000



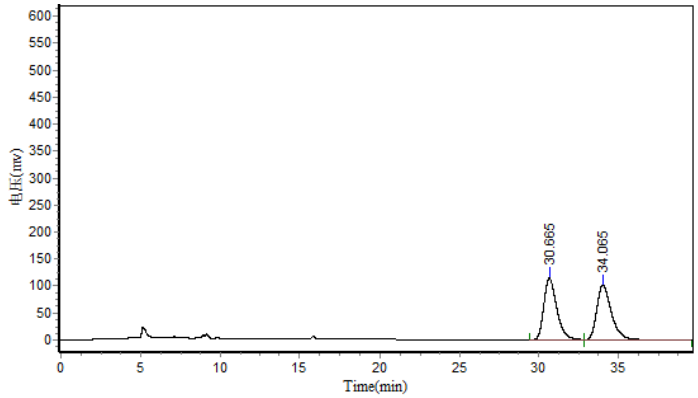
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		49.910	3125.923	407561.469	4.6562
2		56.330	72110.406	8345512.000	95.3438
Total			75236.329	8753073.469	100.0000

(*R*,*E*)-8-methyl-4-styryl-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide (13e)

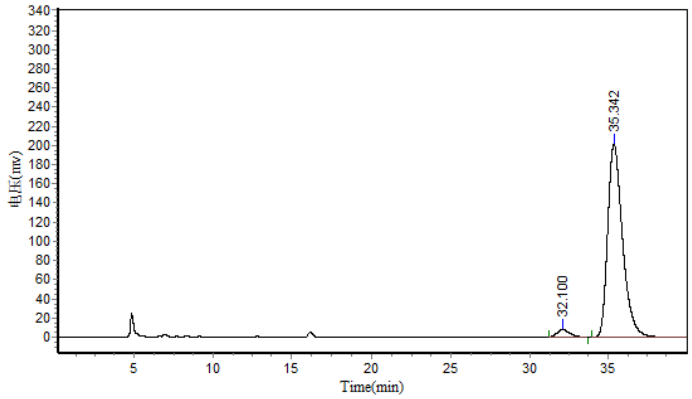


oil, 89% yield, 94% ee; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 – 7.41 (m, 2H), 7.41 – 7.28 (m, 3H), 7.18 (dd, *J* = 6.4, 1.1 Hz, 1H), 7.12 – 7.01 (m, 2H), 6.82 (d, *J* = 15.7 Hz, 1H), 6.28 (dd, *J* = 15.7, 8.5 Hz, 1H), 5.40 (d, *J* = 8.5 Hz, 1H), 5.02 (s, 1H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 136.5, 135.4, 131.3, 128.9, 128.3, 127.0, 125.4, 124.8, 124.4, 121.1, 60.1, 15.5; HPLC: Chiral IC-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; Rentention time: 32.1 min, 35.3 min (maj); HRMS (ESI) for $C_{16}H_{16}NO_3S$ $[M+H]^+$ calcd 302.0851, found 302.0842.



Results

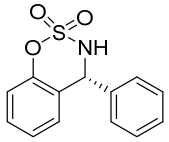
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		30.665	113451.547	6467568.500	49.8814
2		34.065	101639.867	6498318.000	50.1186
Total			215091.414	12965886.500	100.0000



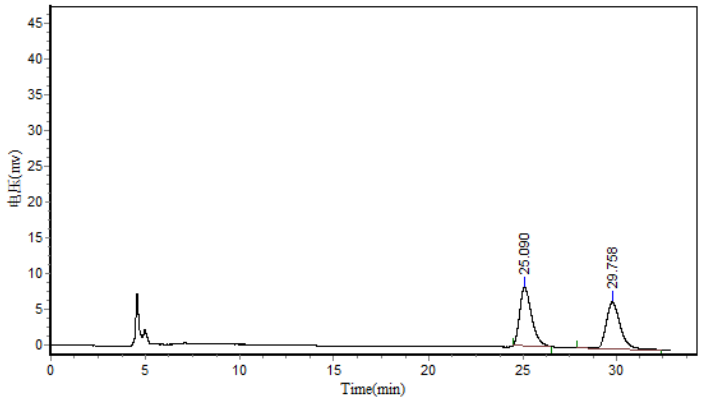
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		32.100	7583.869	423167.813	3.1174
2		35.342	201279.797	13151326.000	96.8826
Total			208863.666	13574493.813	100.0000

(*R*)-4-phenyl-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide (13f)

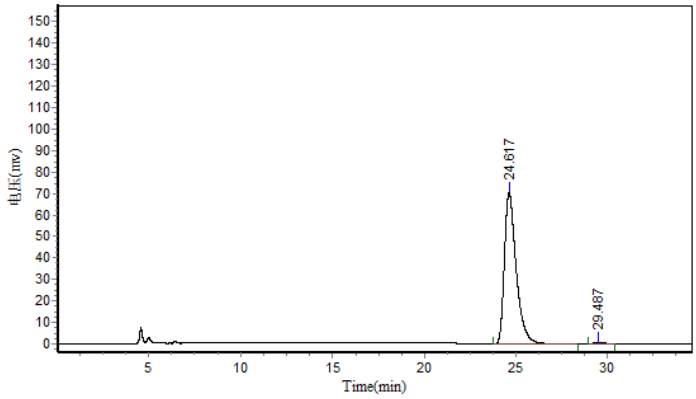


oil, 97% yield, 98% ee; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 – 7.10 (m, 6H), 7.07 - 6.90 (m, 2H), 6.72 (d, *J* = 7.1 Hz, 1H), 5.78 (s, 1H), 4.93 (s, 1H); HPLC: Chiral IC-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; Rentention time: 24.6 min (maj), 29.5 min.



Results

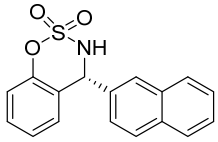
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		25.090	8107.287	353069.719	51.5894
2		29.758	6544.003	331314.781	48.4106
Total			14651.290	684384.500	100.0000



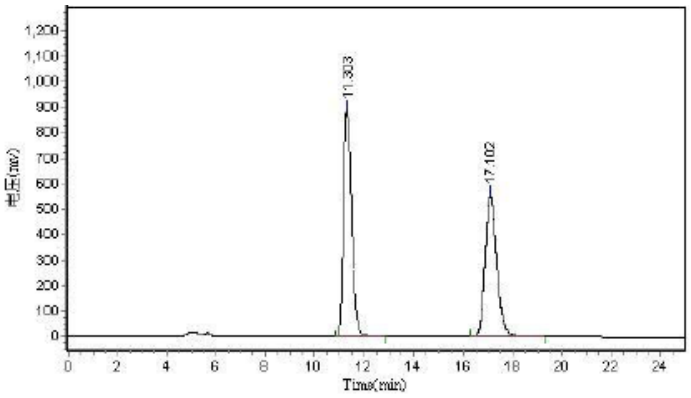
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		24.617	70087.617	3141216.250	99.1499
2		29.487	650.808	26931.898	0.8501
Total			70738.425	3168148.148	100.0000

(*R*)-4-(naphthalen-2-yl)-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide (13g)

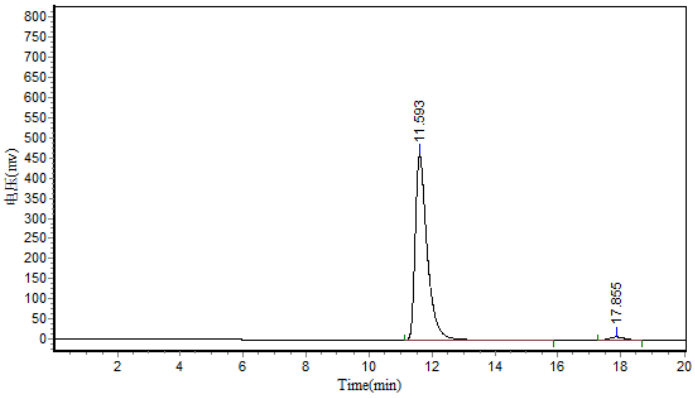


oil, 96% yield, 95% ee; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 – 7.72 (m, 4H), 7.66 – 7.43 (m, 2H), 7.18 – 7.40 (m, 2H), 7.02 (t, *J* = 8.2 Hz, 2H), 6.79 (t, *J* = 8.3 Hz, 1H), 6.00 (s, 1H), 5.18 (s, 1H); HPLC: Chiral IC-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 70/30; flow = 0.7 mL/min; Rentention time: 11.6 min (maj), 17.9 min.



Results

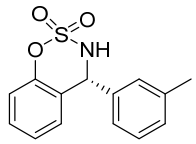
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.303	885204.000	18280686.000	50.3508
2		17.102	550278.000	18025938.000	49.6492
Total			1435482.000	36306624.000	100.0000



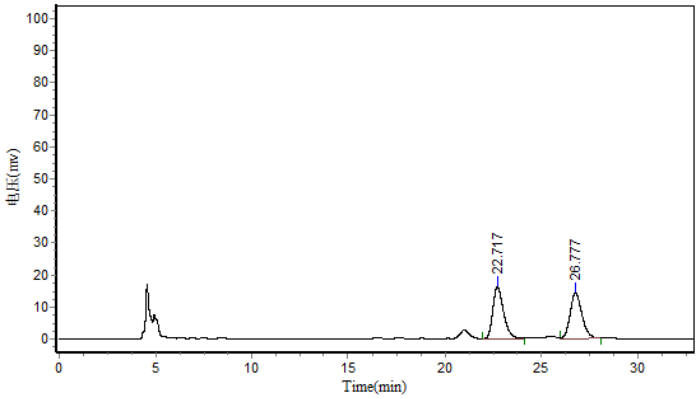
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.593	460070.813	12254902.000	97.5491
2		17.855	8413.923	307900.281	2.4509
Total			468484.735	12562802.281	100.0000

(*R*)-4-(m-tolyl)-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide (13h)

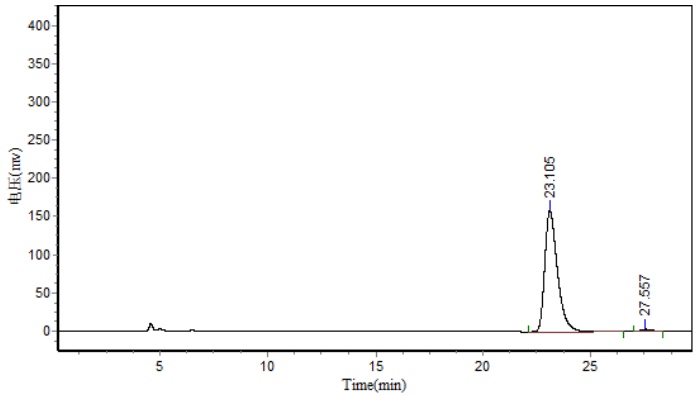


oil, 93% yield, 97% ee; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.5 Hz, 2H), 7.22 (d, *J* = 7.7 Hz, 1H), 7.17 – 6.95 (m, 4H), 6.81 (d, *J* = 7.8 Hz, 1H), 5.83 (d, *J* = 8.7 Hz, 1H), 4.89 (d, *J* = 8.5 Hz, 1H), 2.36 (s, 3H); HPLC: Chiral IC-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; Rentention time: 23.1 min (maj), 27.6 min.



Results

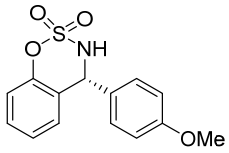
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		22.717	16245.121	630689.250	51.0996
2		26.777	14153.888	603544.938	48.9004
Total			30399.009	1234234.188	100.0000



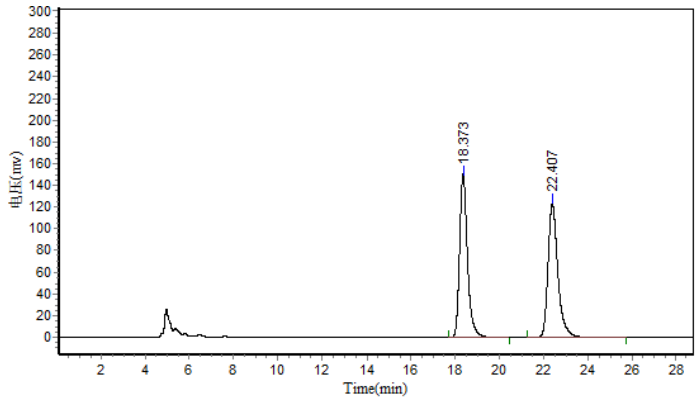
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		23.105	158649.813	6522257.500	98.2652
2		27.557	2916.841	115147.297	1.7348
Total			161566.653	6637404.797	100.0000

(*R*)-4-(4-methoxyphenyl)-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide (13i)

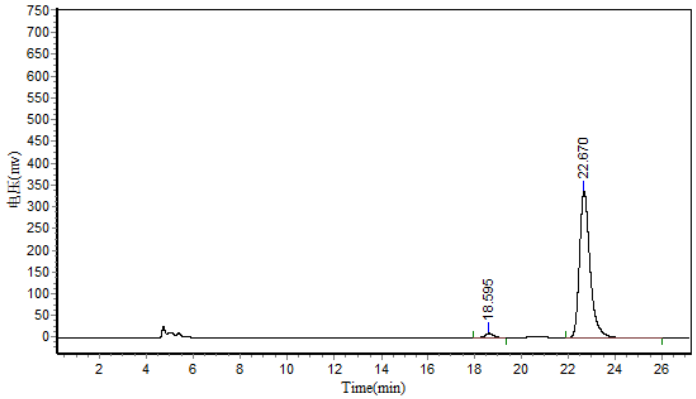


oil, 94% yield, 95% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 1H), 7.27 – 7.19 (m, 2H), 7.14 – 7.02 (m, 2H), 6.98 – 6.87 (m, 2H), 6.83 (dd, *J* = 7.8, 1.1 Hz, 1H), 5.85 (d, *J* = 7.7 Hz, 1H), 4.80 (d, *J* = 7.7 Hz, 1H), 3.83 (s, 3H); HPLC: Chiral AD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 80/20; flow = 0.6 mL/min; Rentention time: 18.6 min, 22.7 min (maj).



Results

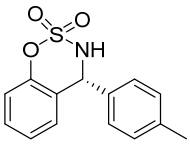
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		18.373	150073.844	3737233.250	49.2843
2		22.407	123245.359	3845772.500	50.7157
Total			273319.203	7583005.750	100.0000



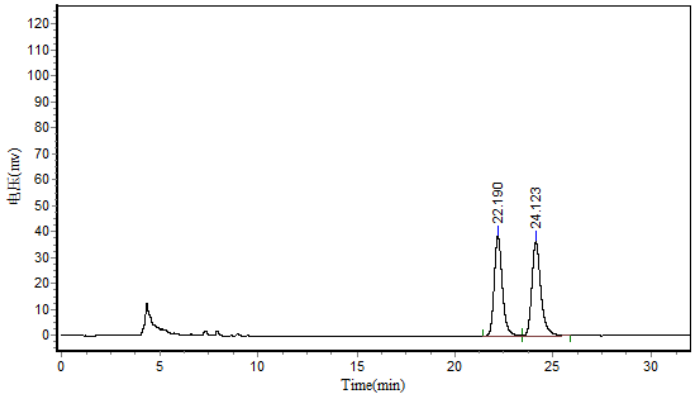
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		18.595	9861.221	256356.391	2.3656
2		22.670	337637.688	10580612.000	97.6344
Total			347498.908	10836968.391	100.0000

(*R*)-4-(p-tolyl)-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide (13j)

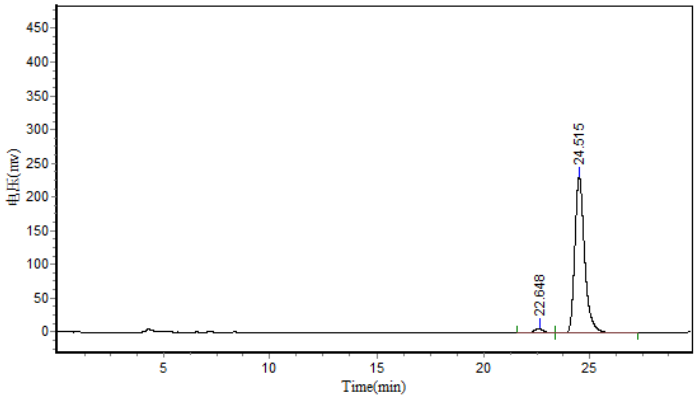


oil, 97% yield, 95% ee; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 – 7.16 (m, 5H), 7.15 – 6.91 (m, 2H), 6.80 (d, *J* = 7.6 Hz, 1H), 5.83 (d, *J* = 7.9 Hz, 1H), 4.90 (d, *J* = 7.7 Hz, 1H), 2.37 (s, 3H); HPLC: Chiral AD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; Rentention time: 22.6 min, 24.5 min (maj)



Results

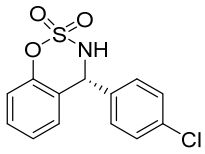
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		22.190	38651.750	1117564.000	49.0271
2		24.123	36416.082	1161916.000	50.9729
Total			75067.832	2279480.000	100.0000



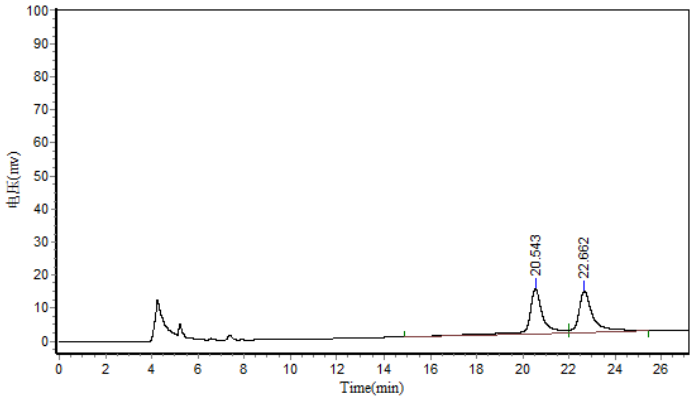
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		22.648	7117.525	211906.469	2.7618
2		24.515	231453.438	7460865.000	97.2382
Total			238570.963	7672771.469	100.0000

(*R*)-4-(4-chlorophenyl)-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide (13k)

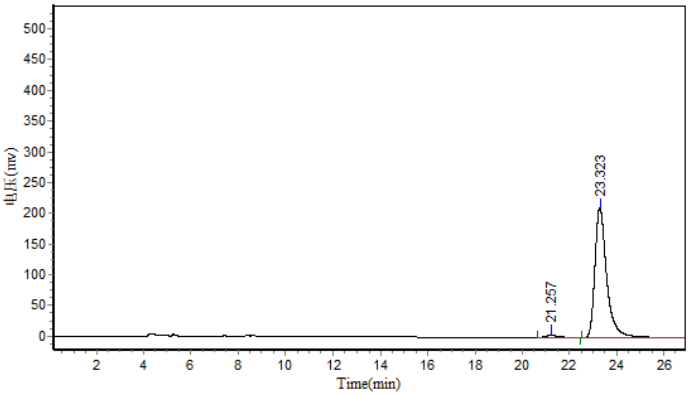


oil, 95% yield, 97% ee; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 – 7.21 (m, 5H), 7.10 (t, *J* = 7.3 Hz, 1H), 7.00 (d, *J* = 8.2 Hz, 1H), 6.79 (d, *J* = 7.8 Hz, 1H), 5.85 (d, *J* = 7.4 Hz, 1H), 5.06 (d, *J* = 7.3 Hz, 1H); HPLC: Chiral AD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; Rentention time: 21.3 min, 23.3 min (maj).



Results

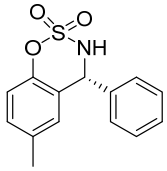
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		20.543	13475.336	509792.125	50.4973
2		22.662	12326.993	499751.531	49.5027
Total			25802.329	1009543.656	100.0000



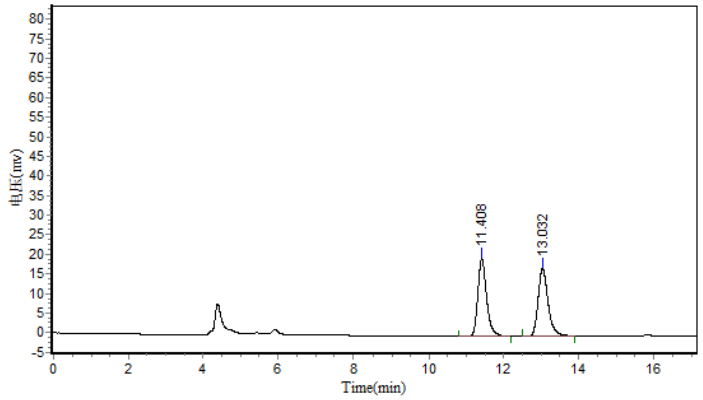
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		21.257	3332.613	112275.992	1.5161
2		23.323	210872.609	7293079.000	98.4839
Total			214205.222	7405354.992	100.0000

(*R*)-6-methyl-4-phenyl-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide (13l)

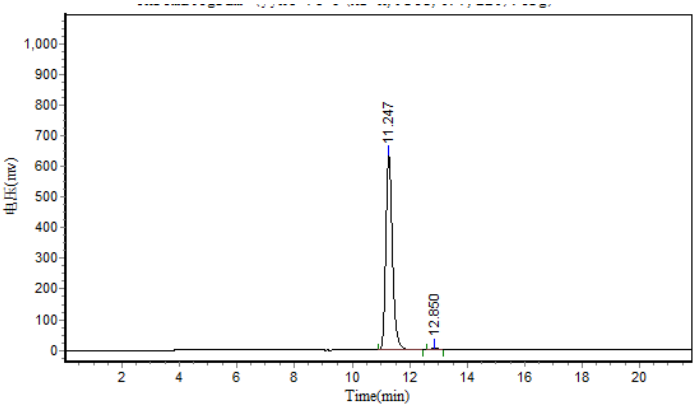


oil, 98% yield, 98% ee; ^{1}H NMR (300 MHz, $CDCl_3$) ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (d, J = 2.0 Hz, 3H), 7.36 – 7.28 (m, 2H), 7.09 (d, J = 8.2 Hz, 1H), 6.89 (d, J = 8.4 Hz, 1H), 6.58 (s, 1H), 5.82 (s, 1H), 4.92 (s, 1H), 2.19 (s, 3H).; HPLC: Chiral AD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 80/20; flow = 0.7 mL/min; Rentention time: 11.2 min (maj), 12.9 min.



Results

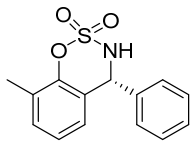
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.408	19830.408	325596.906	50.5950
2		13.032	17302.553	317939.344	49.4050
Total			37132.961	643536.250	100.0000



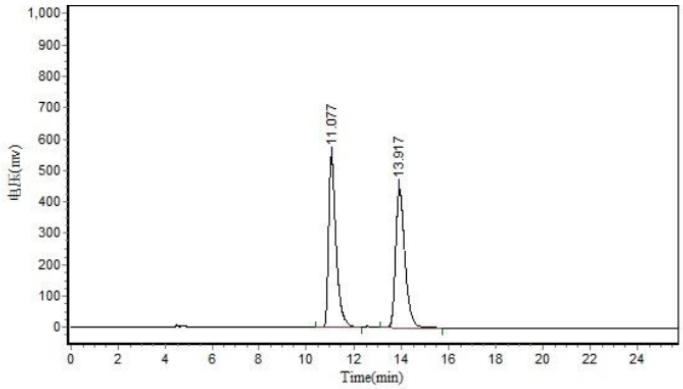
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.247	632492.813	10203340.000	98.8734
2		12.850	7355.982	116261.406	1.1266
Total			639848.794	10319601.406	100.0000

(*R*)-8-methyl-4-phenyl-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide (13m)

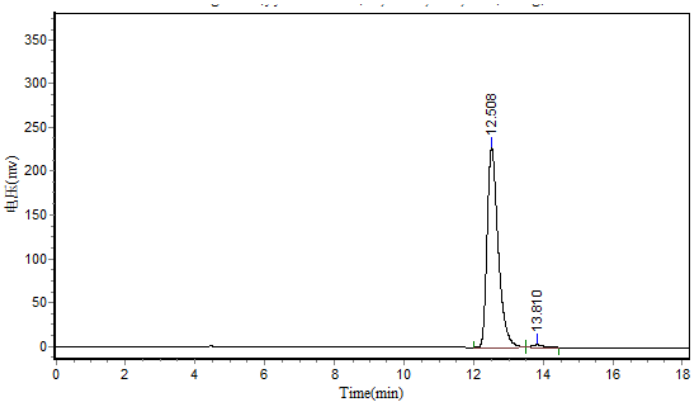


oil, 96% yield, 98% ee; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 – 7.38 (m, 3H), 7.38 – 7.28 (m, 2H), 7.15 (d, *J* = 7.4 Hz, 1H), 6.95 (t, *J* = 7.6 Hz, 1H), 6.62 (d, *J* = 7.7 Hz, 1H), 5.86 (s, 1H), 4.95 (s, 1H), 2.23 (s, 3H); HPLC: Chiral IC-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 80/20; flow = 0.7 mL/min; Rentention time: 12.5 min (maj), 13.8 min.



Results

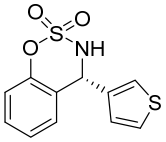
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.077	544713.813	12123511.000	49.8398
2		13.917	441729.750	12201441.000	50.1602
Total			986443.563	24324952.000	100.0000



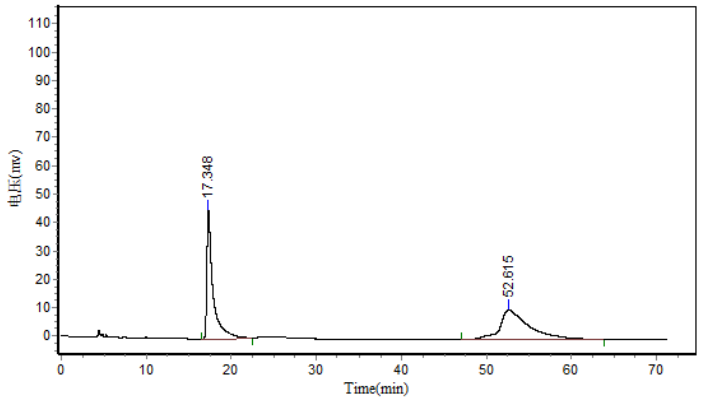
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.508	227557.344	5005347.000	98.9508
2		13.810	2462.699	53074.500	1.0492
Total			230020.042	5058421.500	100.0000

(*S*)-4-(thiophen-3-yl)-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide (13n)

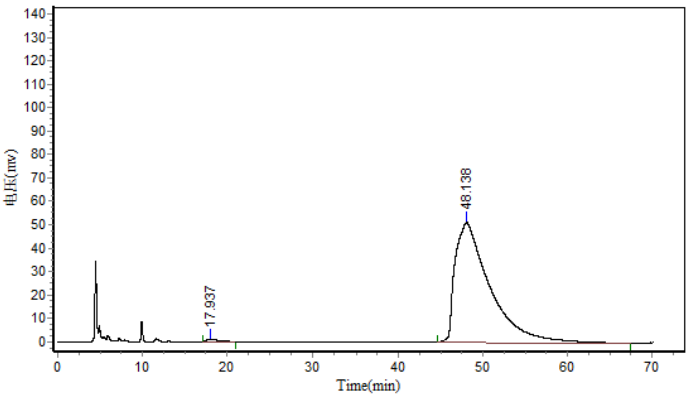


oil, 83% yield, 99% ee; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 – 7.38 (m, 2H), 7.38 – 7.29 (m, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.06 (d, *J* = 8.3 Hz, 1H), 7.02 (dd, *J* = 4.9, 1.4 Hz, 1H), 6.94 (d, *J* = 7.8 Hz, 1H), 6.05 (d, *J* = 8.7 Hz, 1H), 4.79 (d, *J* = 8.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.2, 138.1, 130.0, 128.4, 128.0, 126.7, 126.1, 125.4, 121.8, 119.0, 57.1; HPLC: Chiral AY-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 80/20; flow = 0.7 mL/min; Rentention time: 17.9 min, 48. 1min (maj); HRMS (ESI) for $C_{11}H_8NO_3S_2$ $[M-H]^-$ calcd 265.9946, found 265.9958.



Results

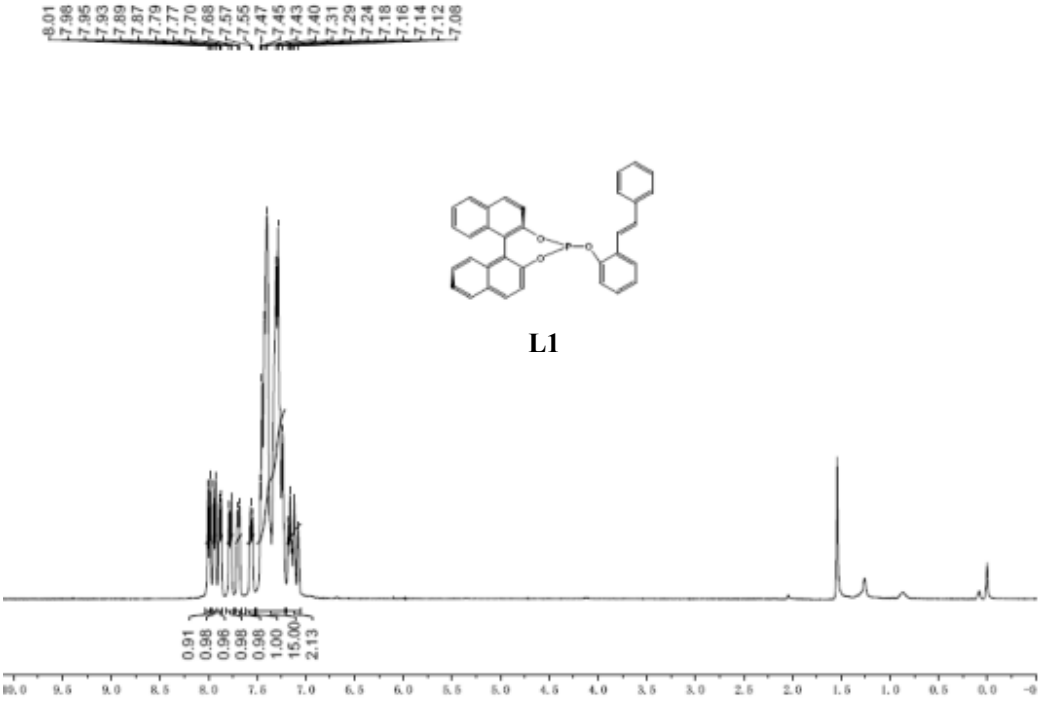
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		17.348	45098.605	2344647.750	48.3263
2		52.615	10396.484	2507055.500	51.6737
Total			55495.090	4851703.250	100.0000



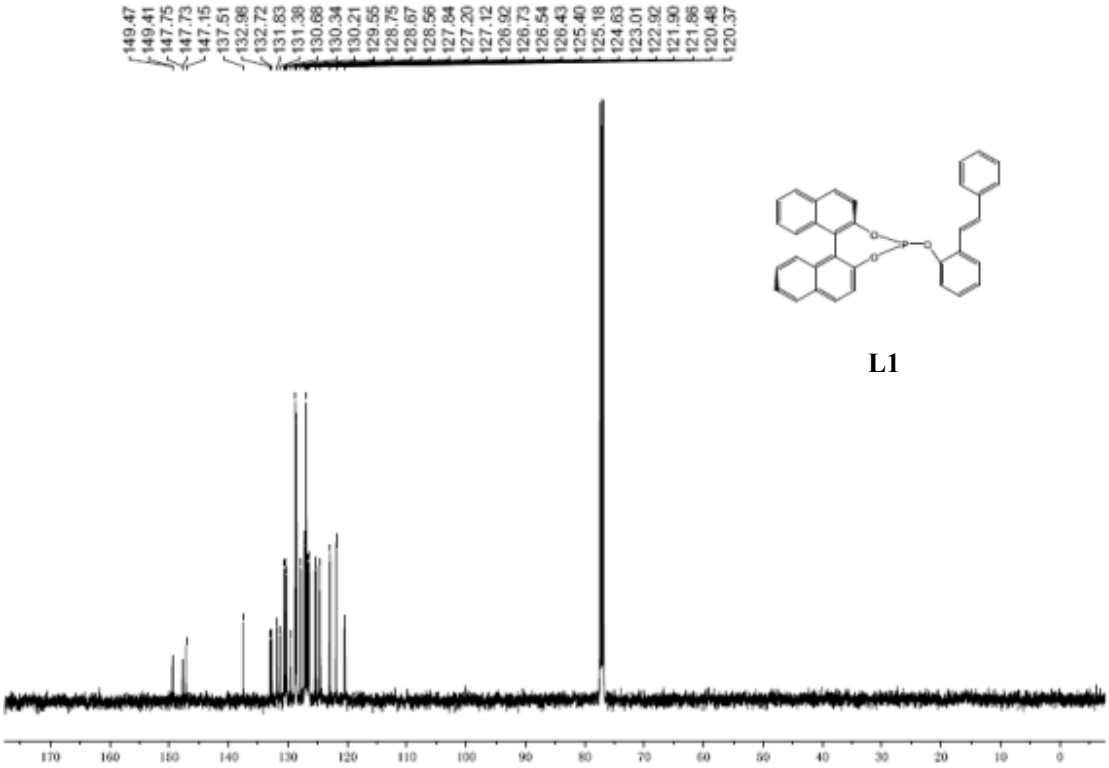
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		17.937	1114.475	111013.695	0.7560
2		48.138	51271.418	14574266.000	99.2440
Total			52385.893	14685279.695	100.0000

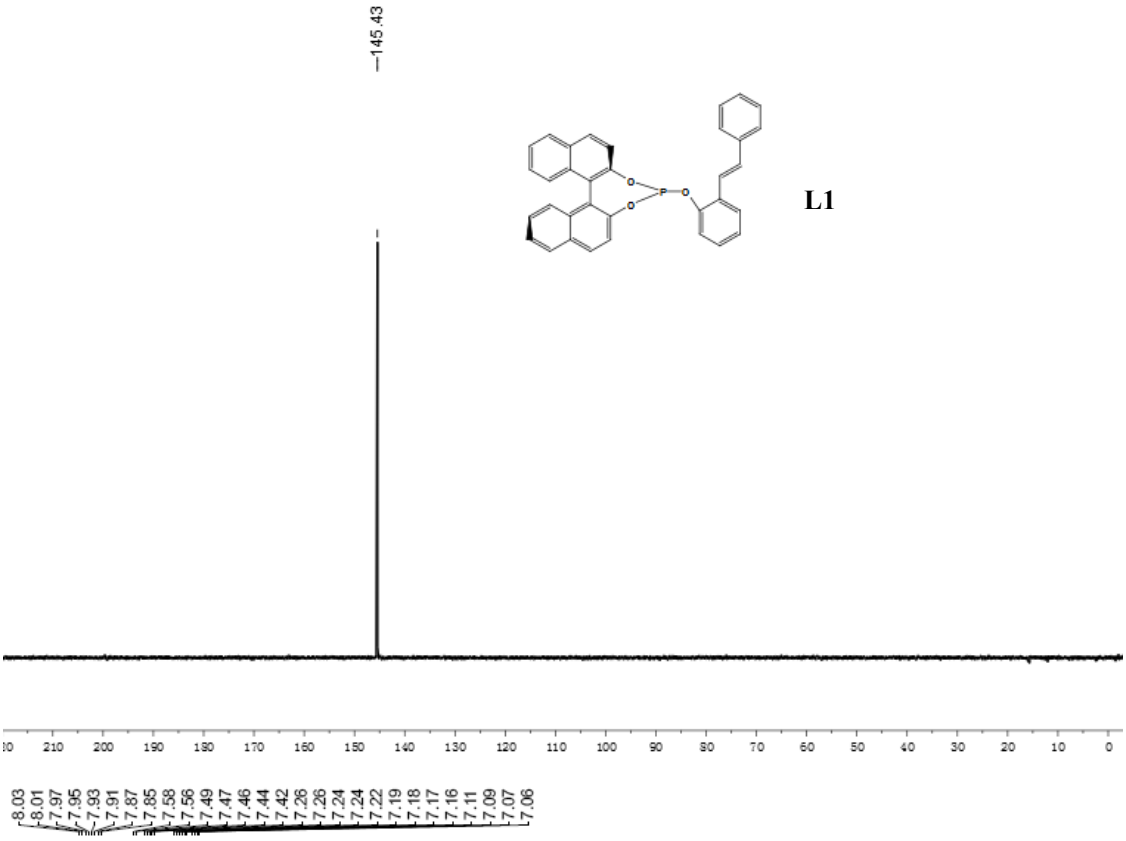
6. Copies of ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra



L1



L1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7.93
7.91
7.87
7.85
7.58
7.56
7.49
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7.46
7.44
7.42
7.26
7.26
7.24
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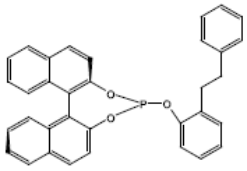
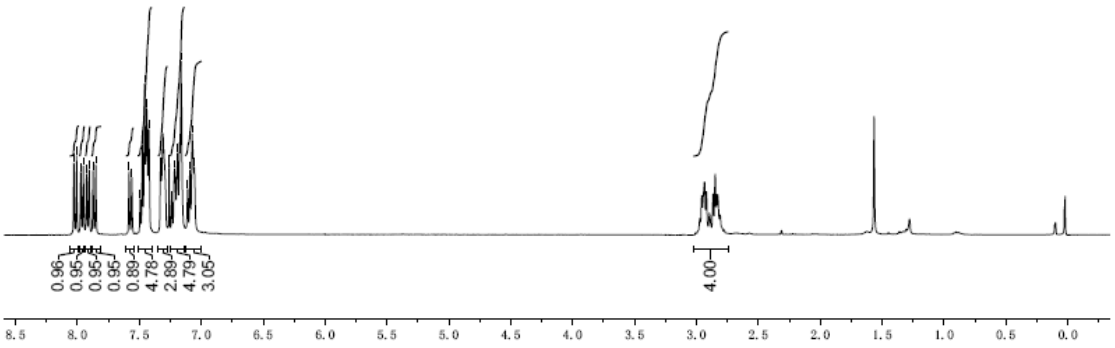
7.22
7.19
7.18
7.17
7.16
7.11
7.09
7.07
7.06

L1



L2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0.95
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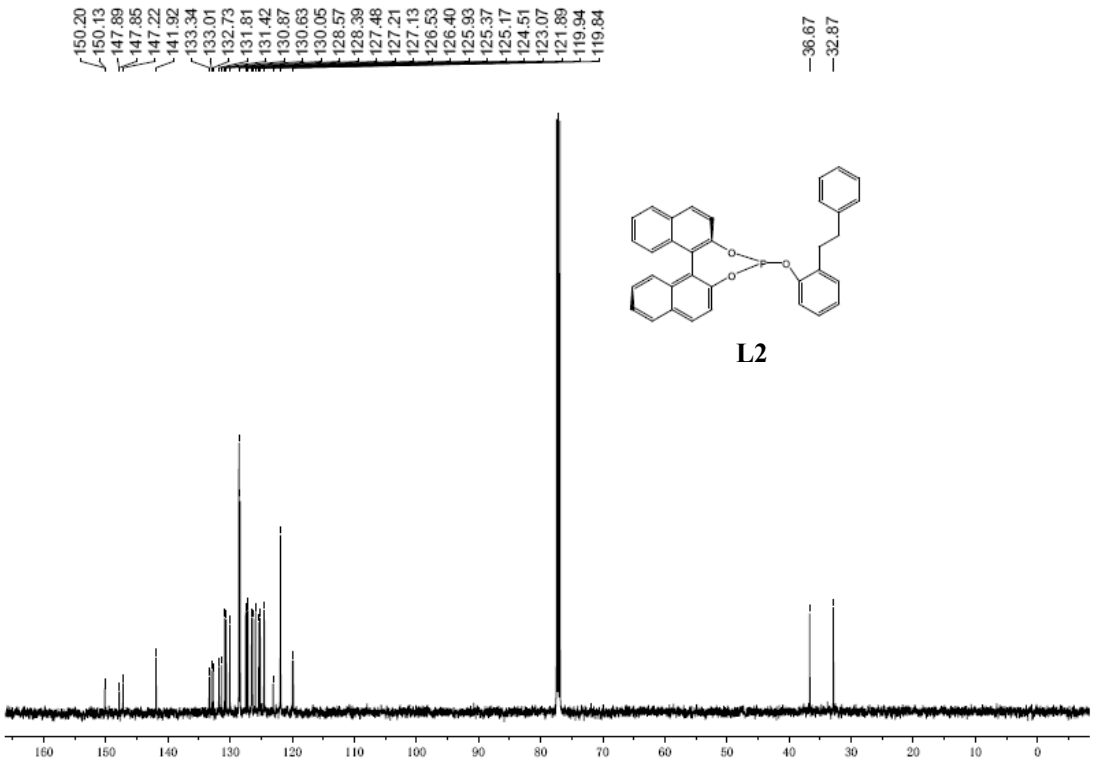
2.89
4.79
3.05
4.00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147.89
147.85
147.22
141.92
133.34
133.01
132.73
131.81
131.42
130.87
130.63
130.05
128.57
128.39
127.48
127.21
127.13
126.53
126.40
125.93
125.37
125.17
124.51
123.07
121.89
119.94
119.84
36.67
32.87
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120
110
100
90
80
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60
50
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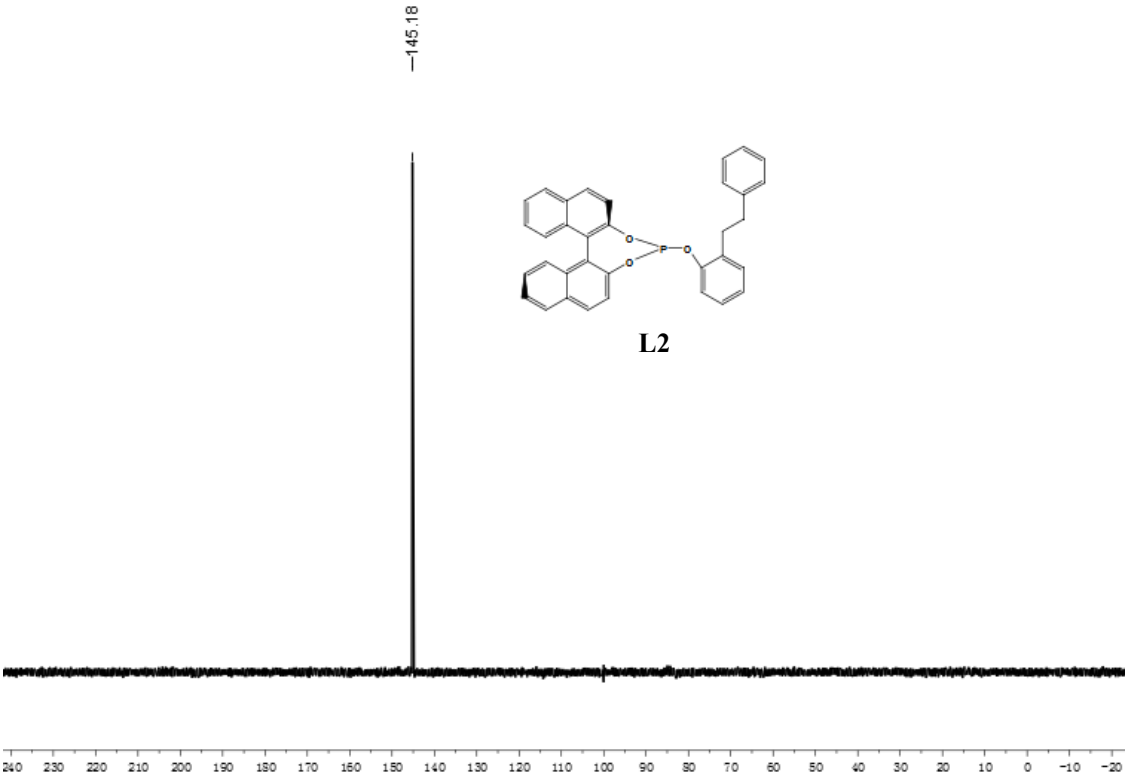
30
20
10
0

L2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200
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180
170
160
150
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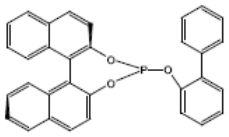
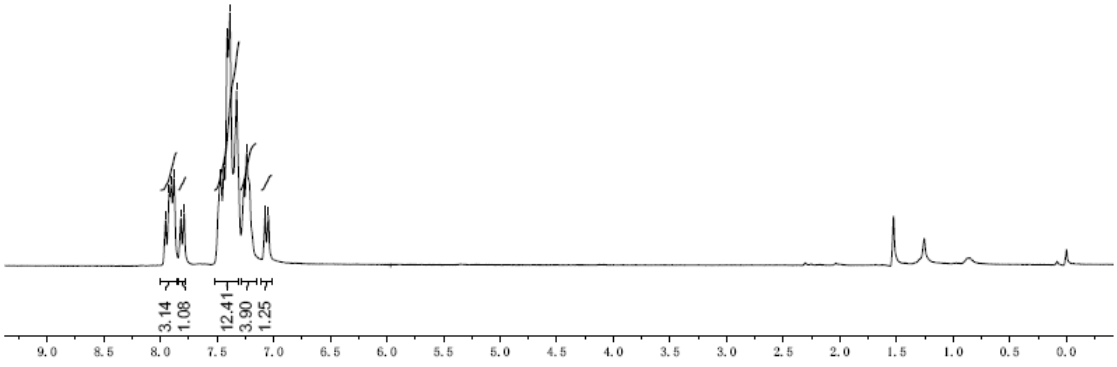
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20

L2


7.95
7.92
7.91
7.88
7.82
7.79
7.47
7.44
7.41
7.39
7.33
7.26
7.24
7.07
7.05



L3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1.25
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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4.0
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3.0
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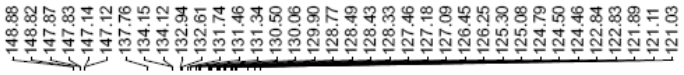
2.0
1.5
1.0
0.5
0.0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147.14
147.12
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134.15
134.12
132.94
132.61
131.74
131.46
131.34
130.50
130.06
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128.49
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128.33
127.46
127.18
127.09
126.45
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125.08
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124.46
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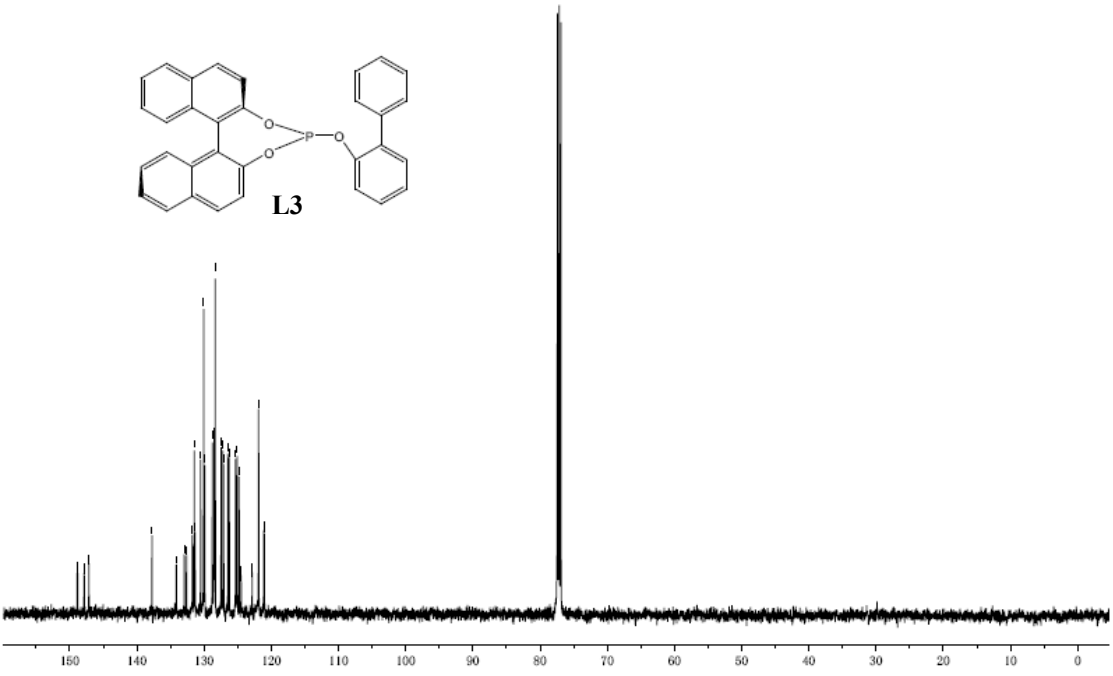
122.83
121.89
121.11
121.03

L3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30
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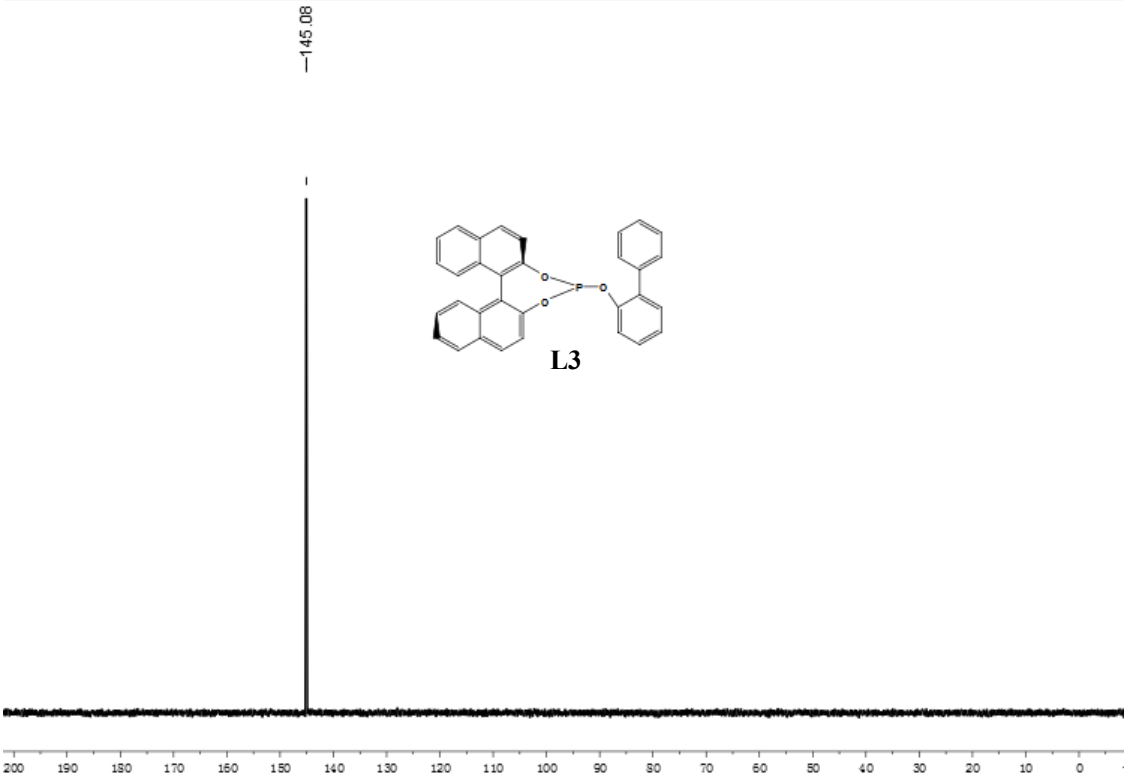
10
0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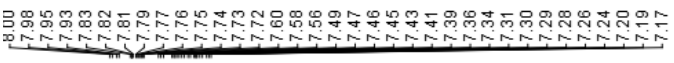
L3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7.73
7.72
7.60
7.58
7.56
7.49
7.47
7.46
7.45
7.43
7.41
7.39
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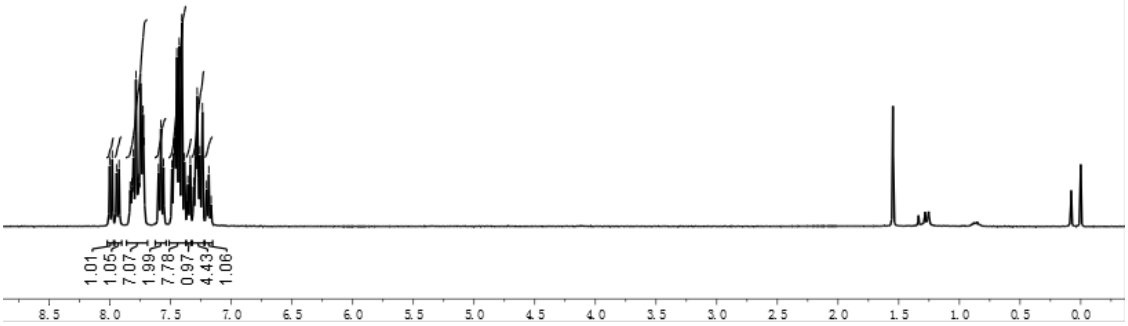
7.17

L4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1.99
7.78
0.97
4.43
1.06
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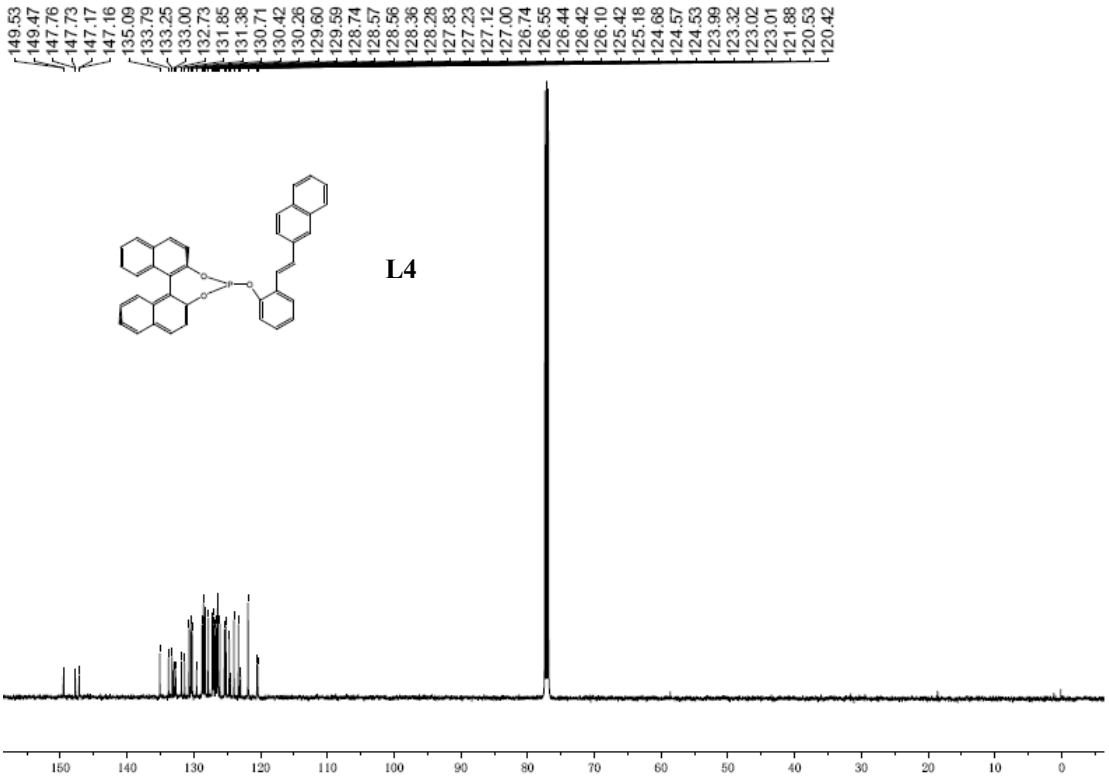
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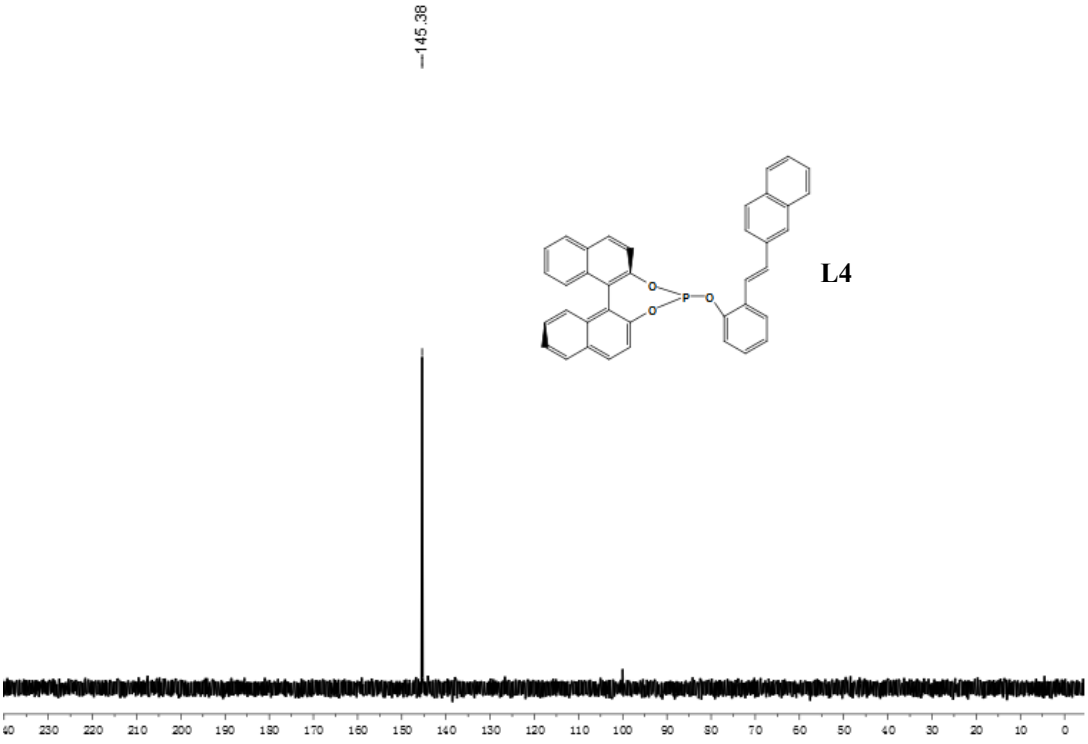
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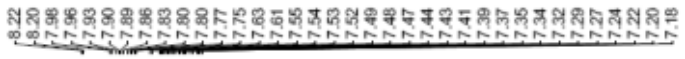
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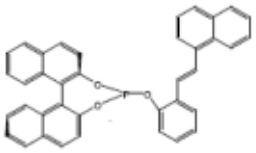
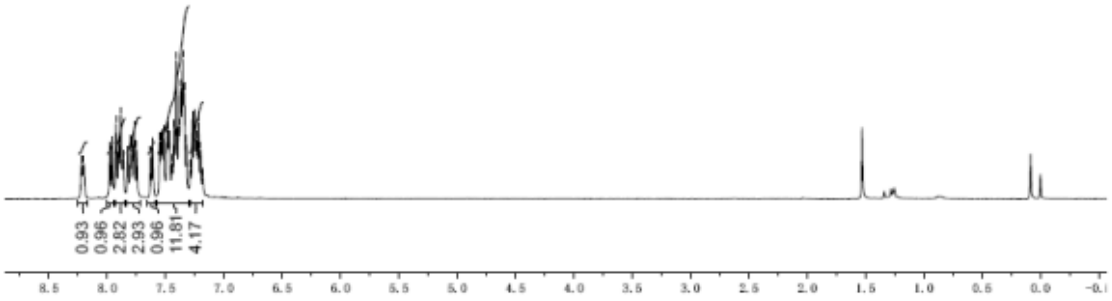


L5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6.0
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2.0
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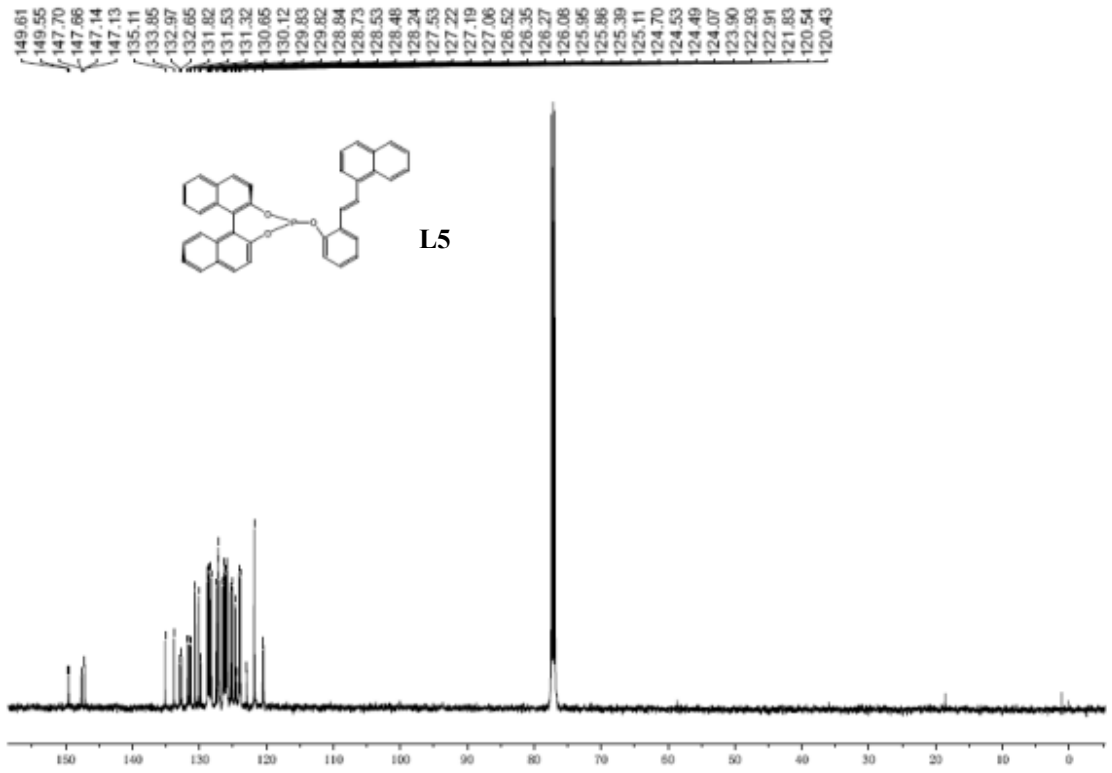
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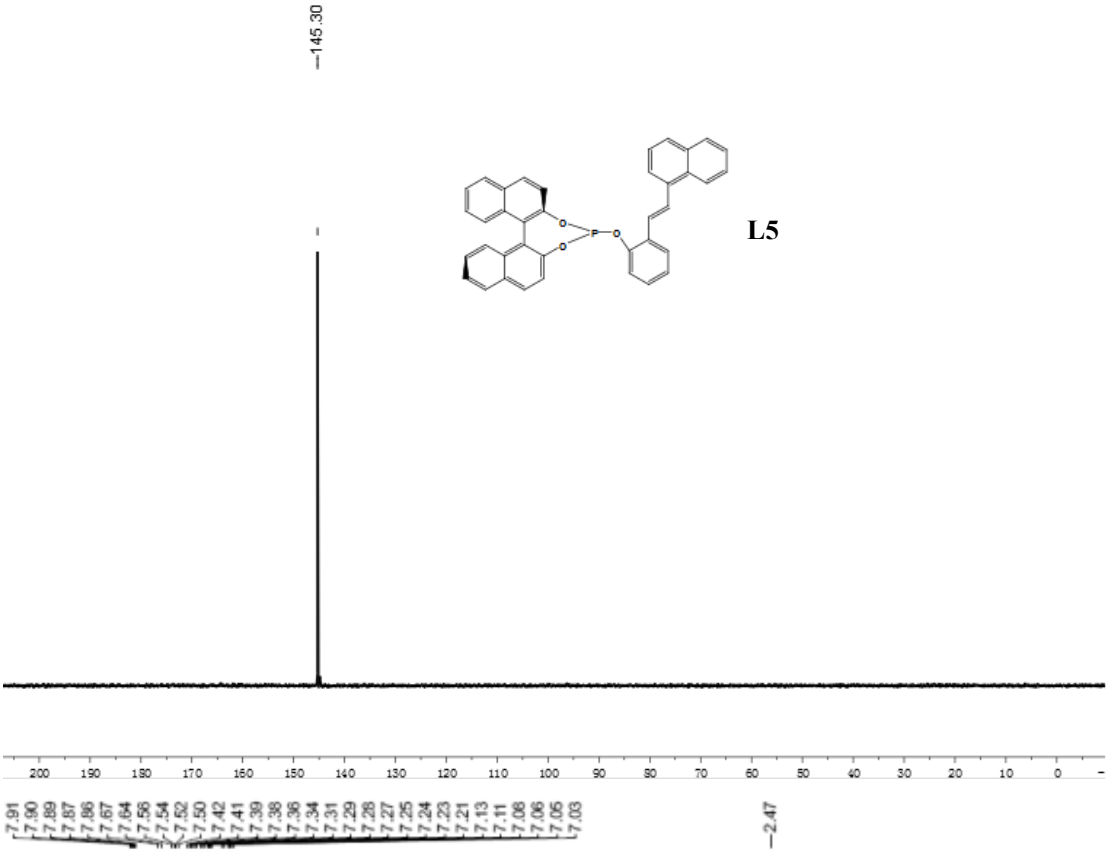
0

L5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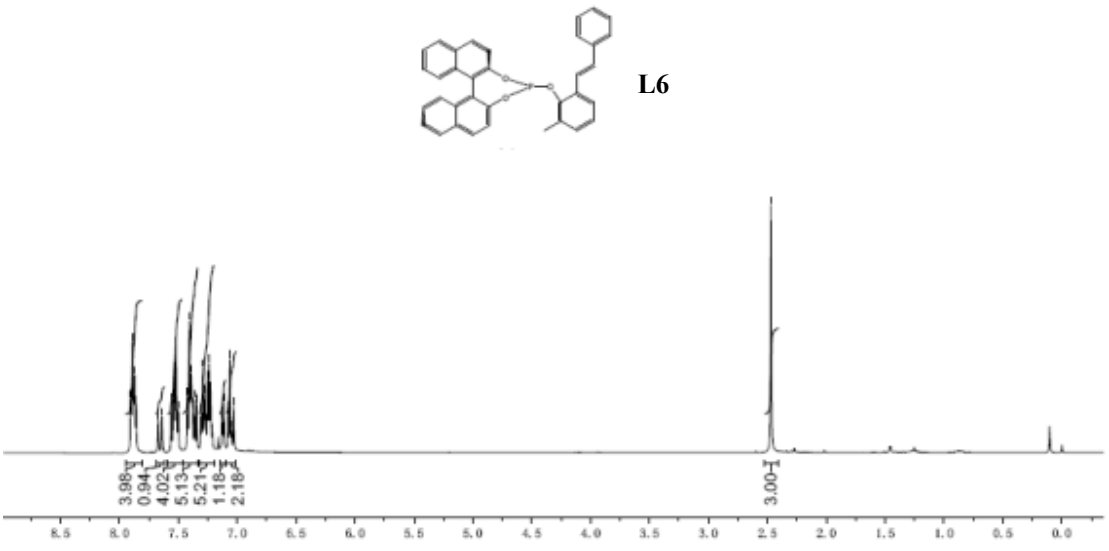
7.05
7.03
2.47

L5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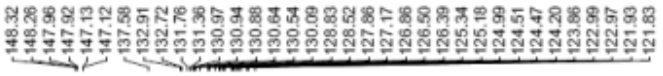
L6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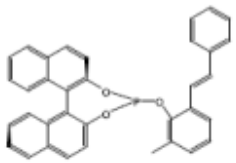
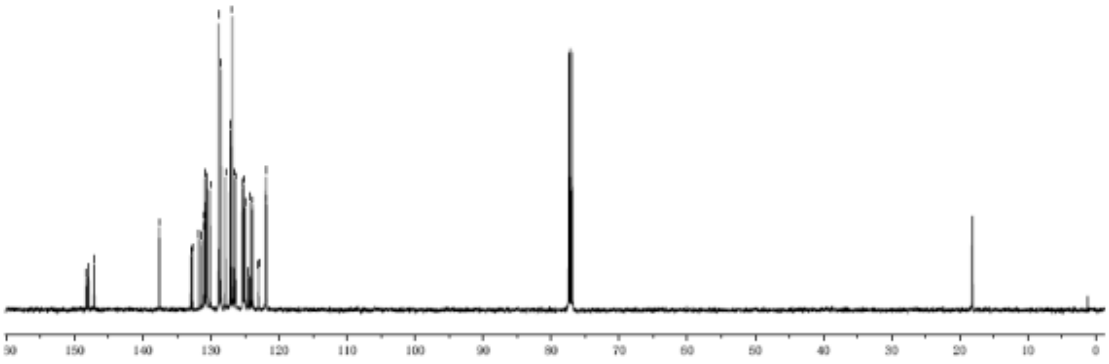
121.83
18.13
18.11



L6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30
20
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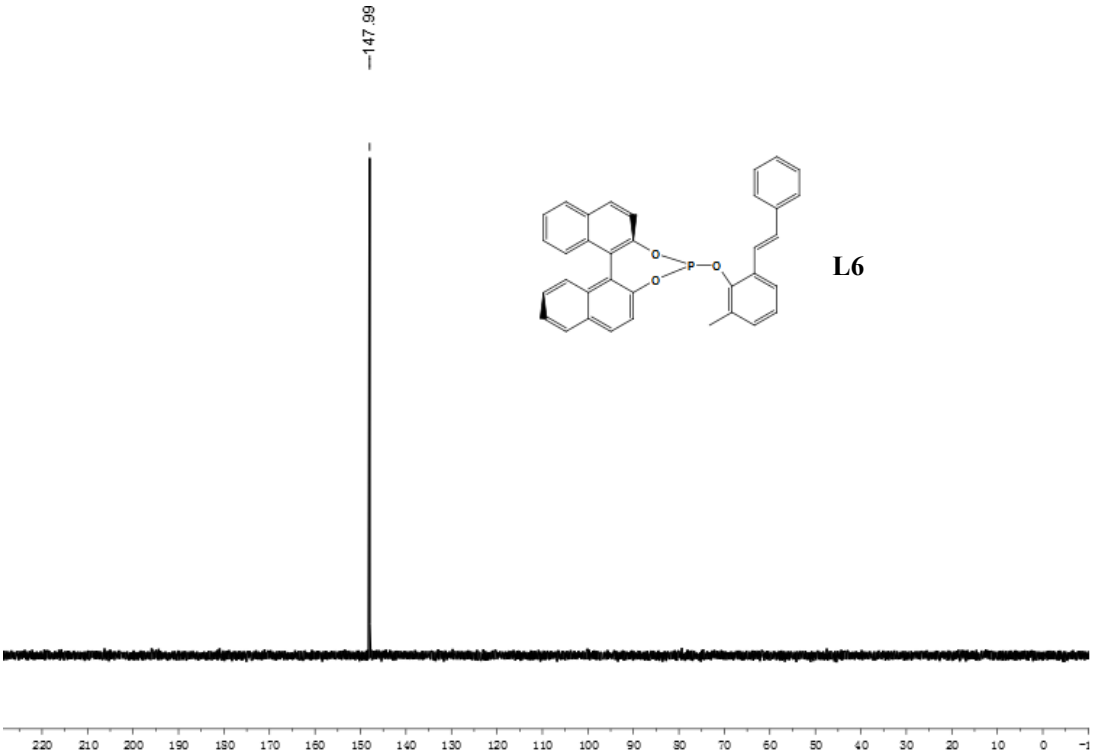
0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80
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40
30
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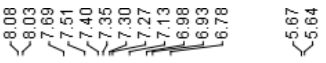
0
-1

L6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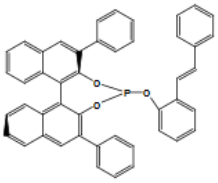
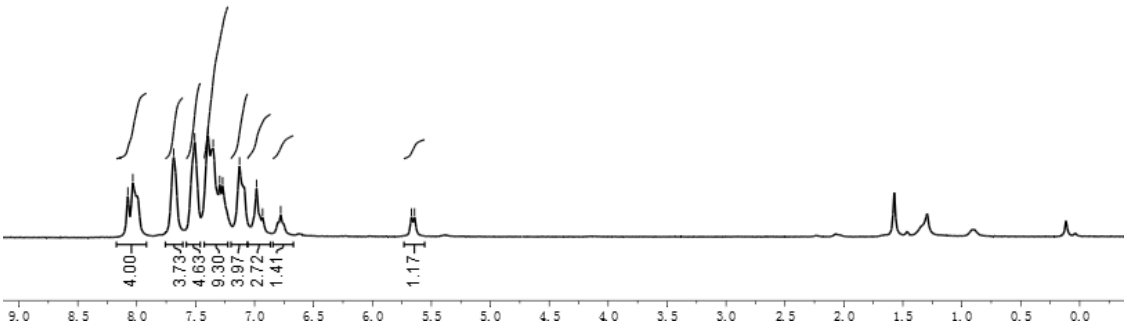
5.67
5.64



L7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6.5
6.0
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3.0
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2.0
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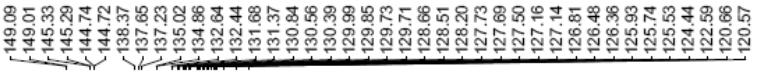
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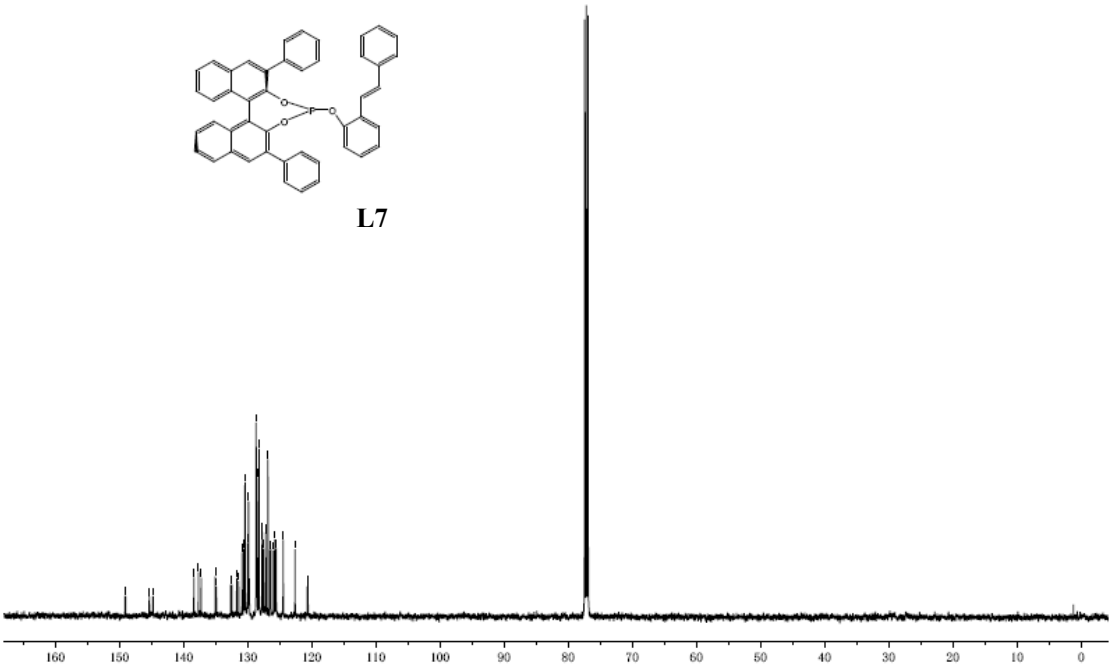
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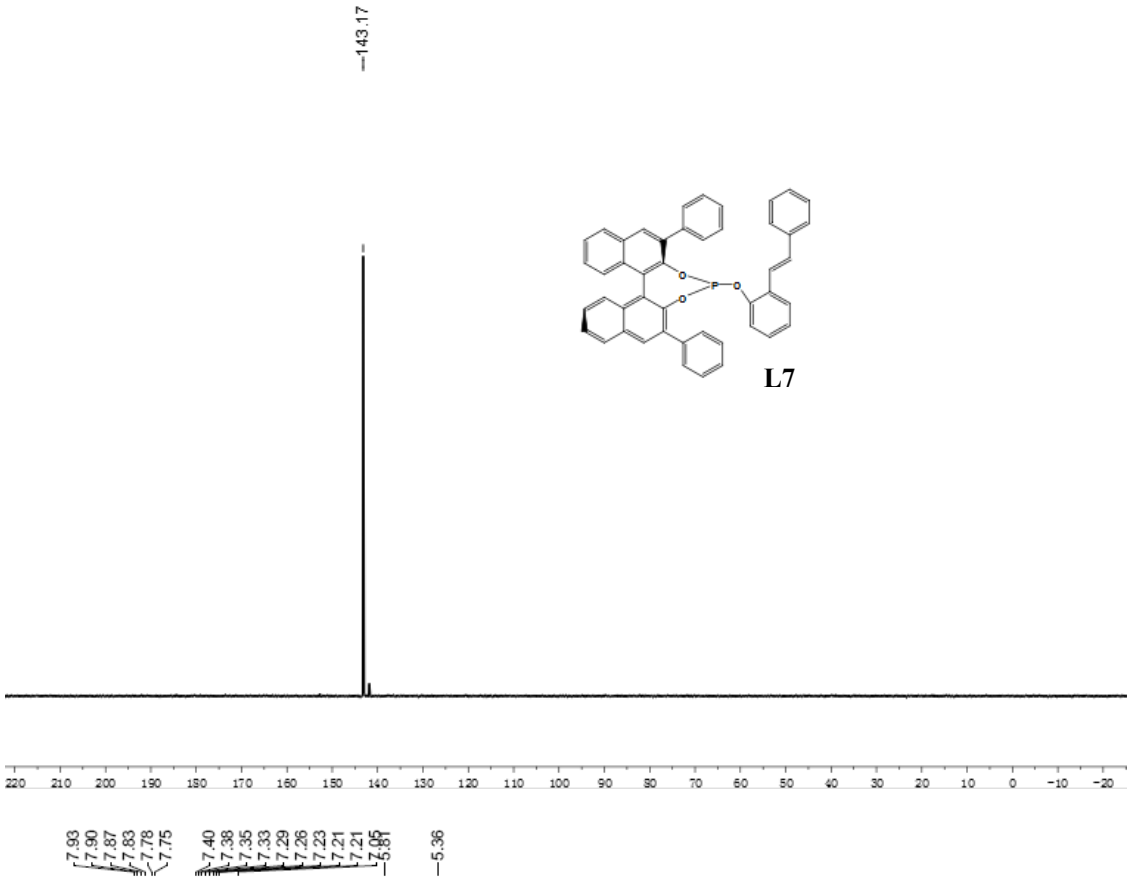
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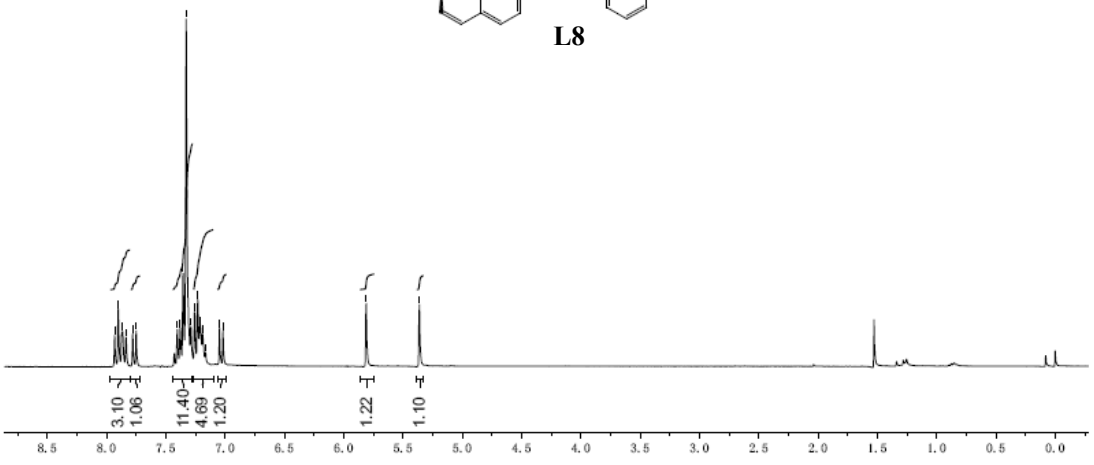
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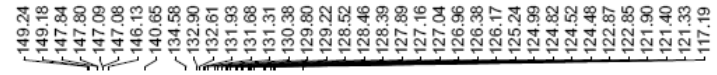
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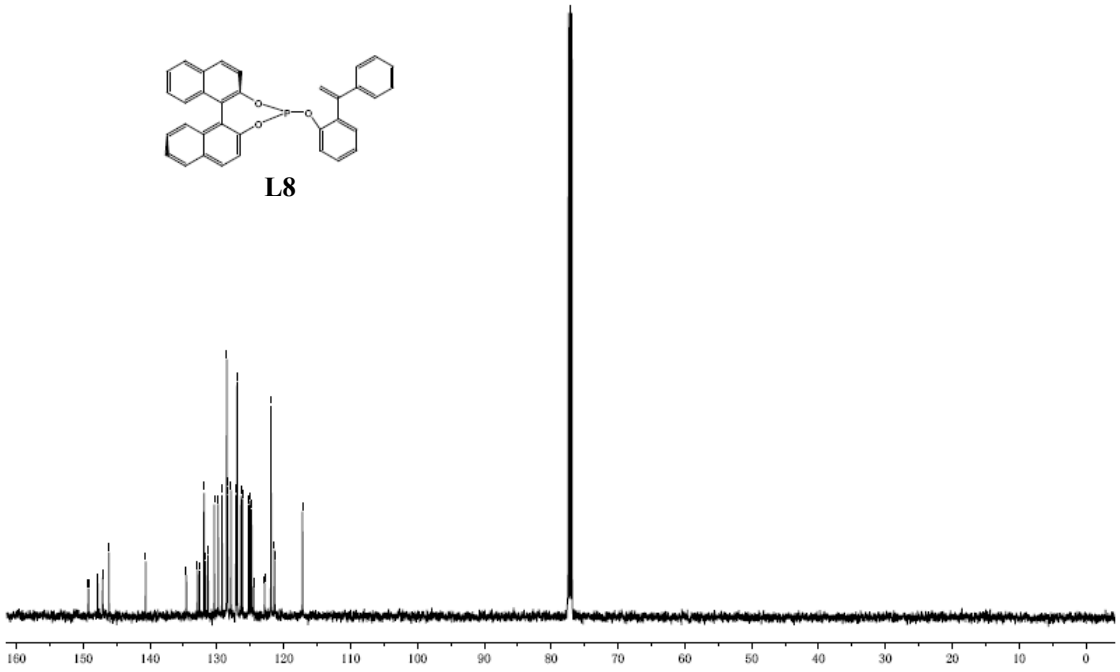
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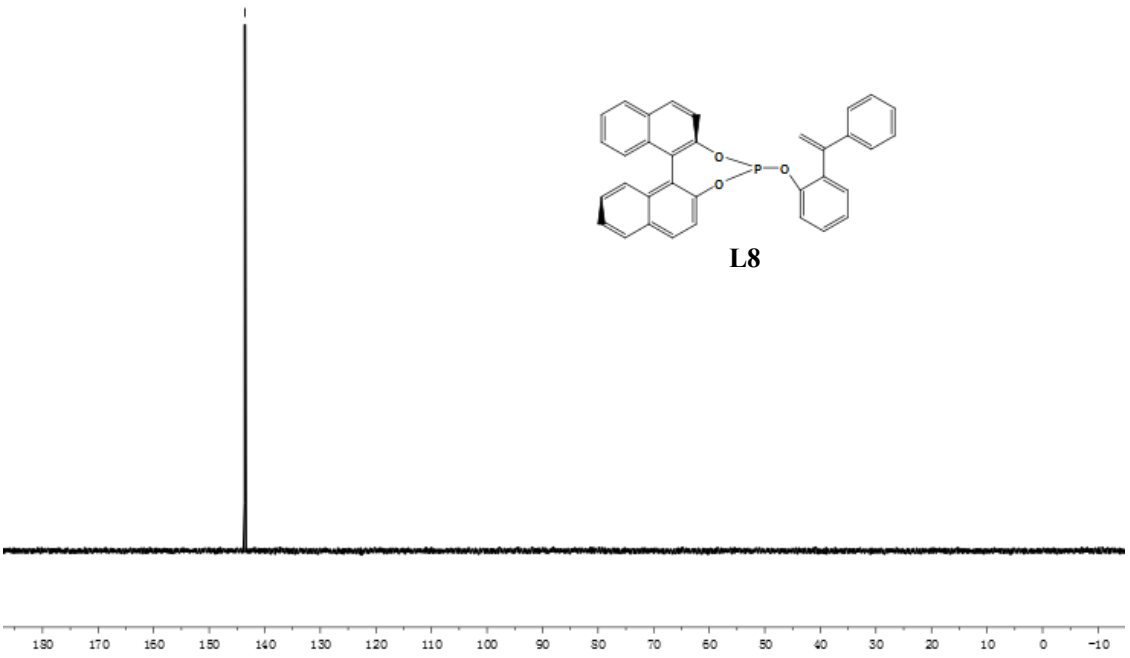
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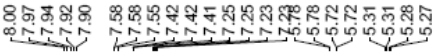
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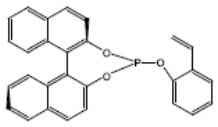

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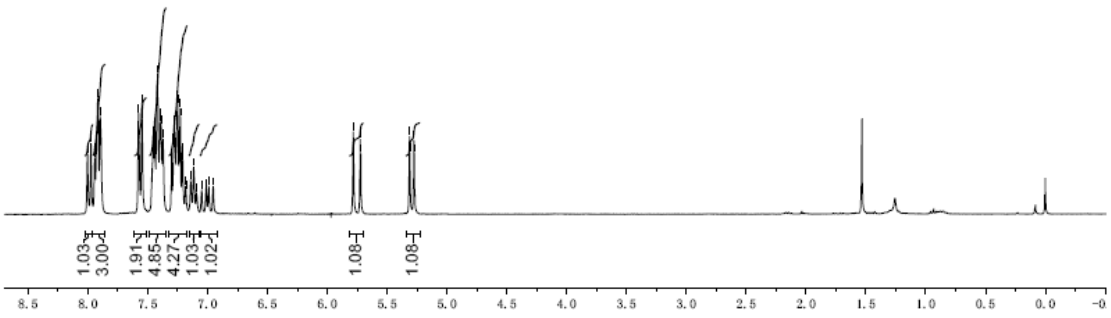
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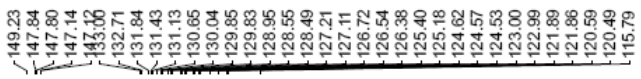
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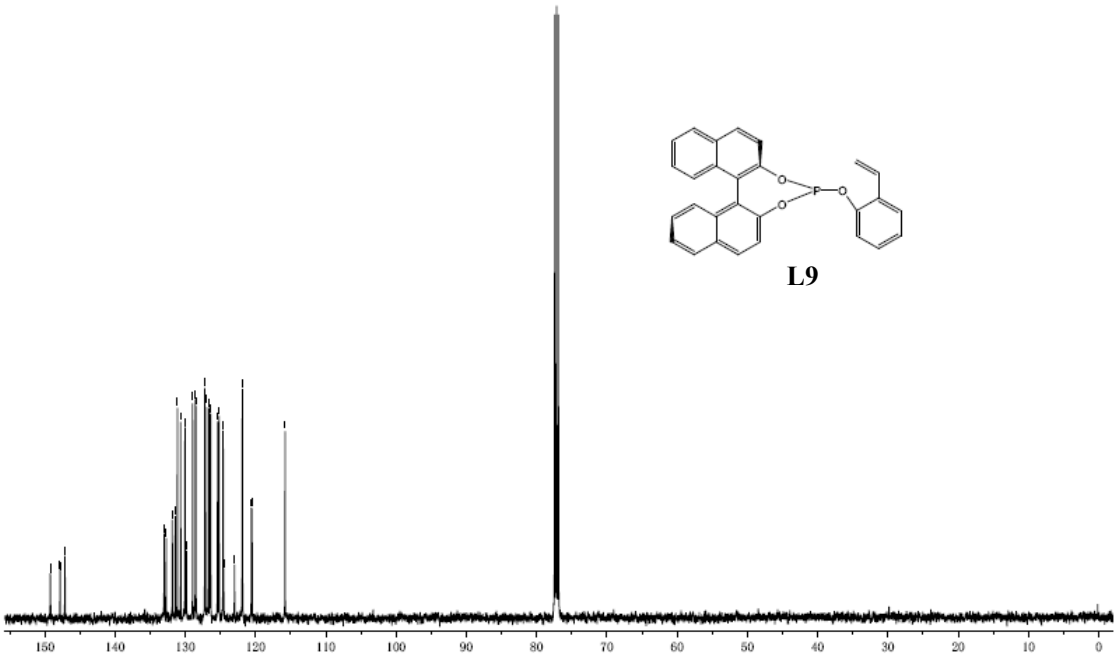
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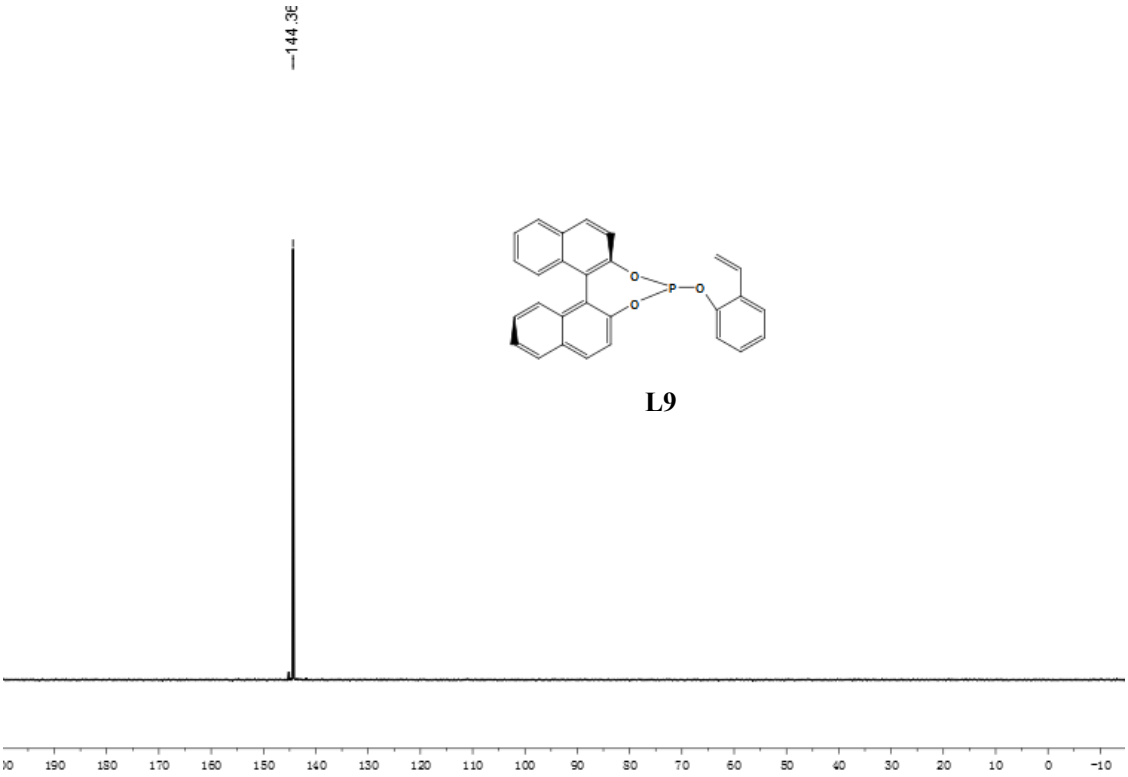
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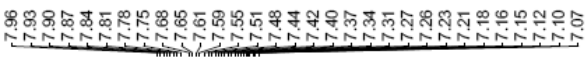
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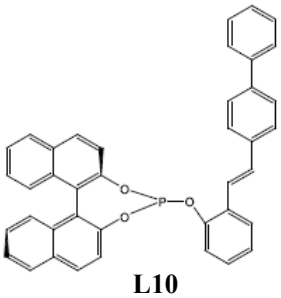

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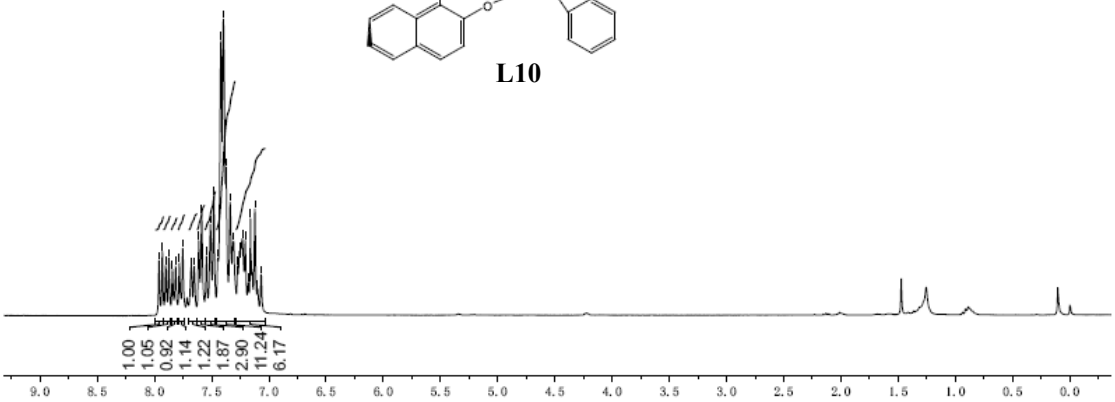
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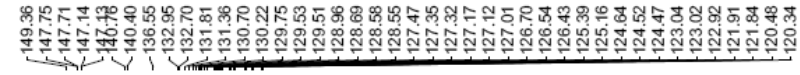
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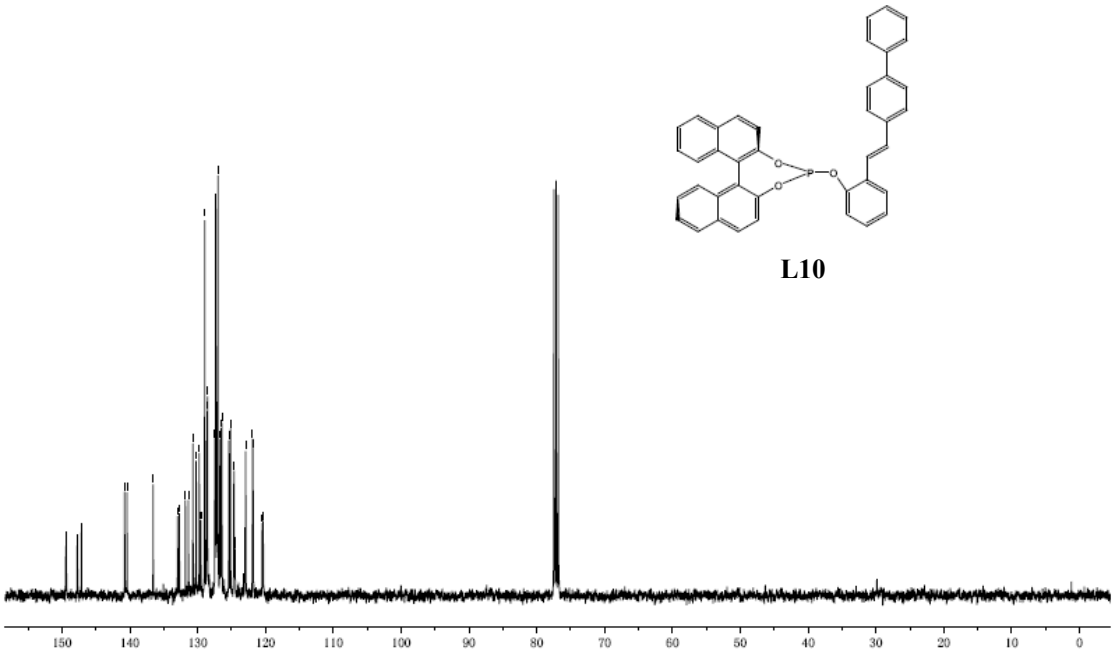
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L10


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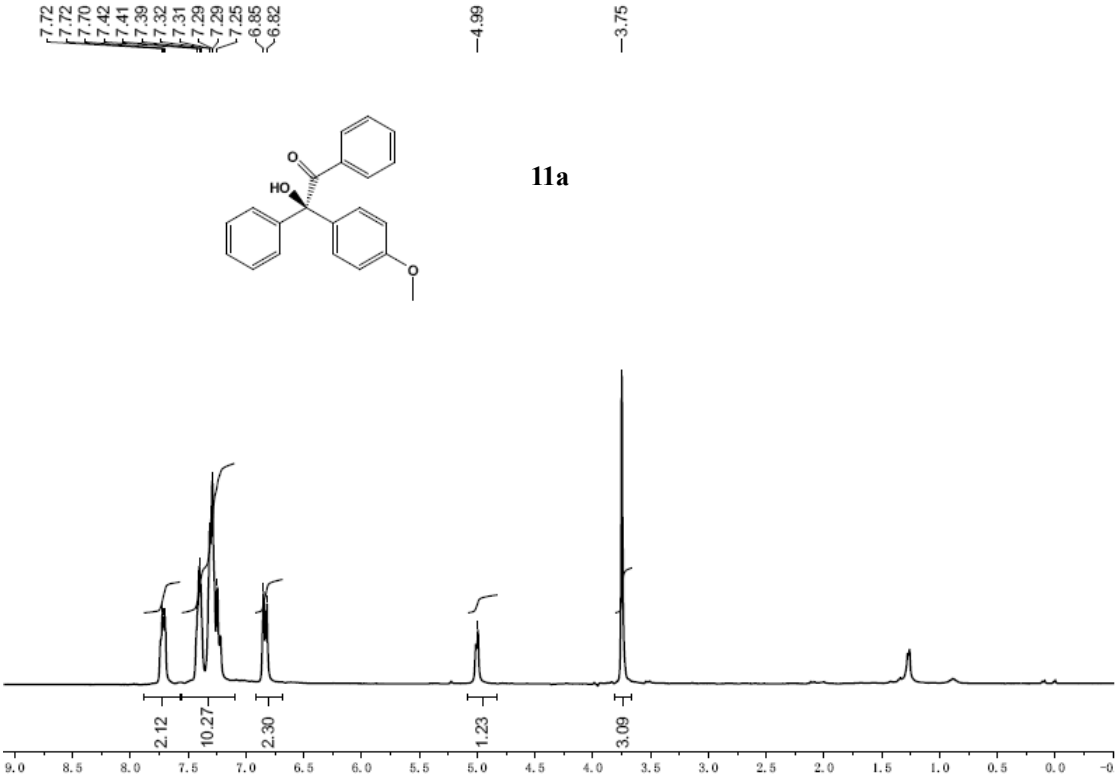
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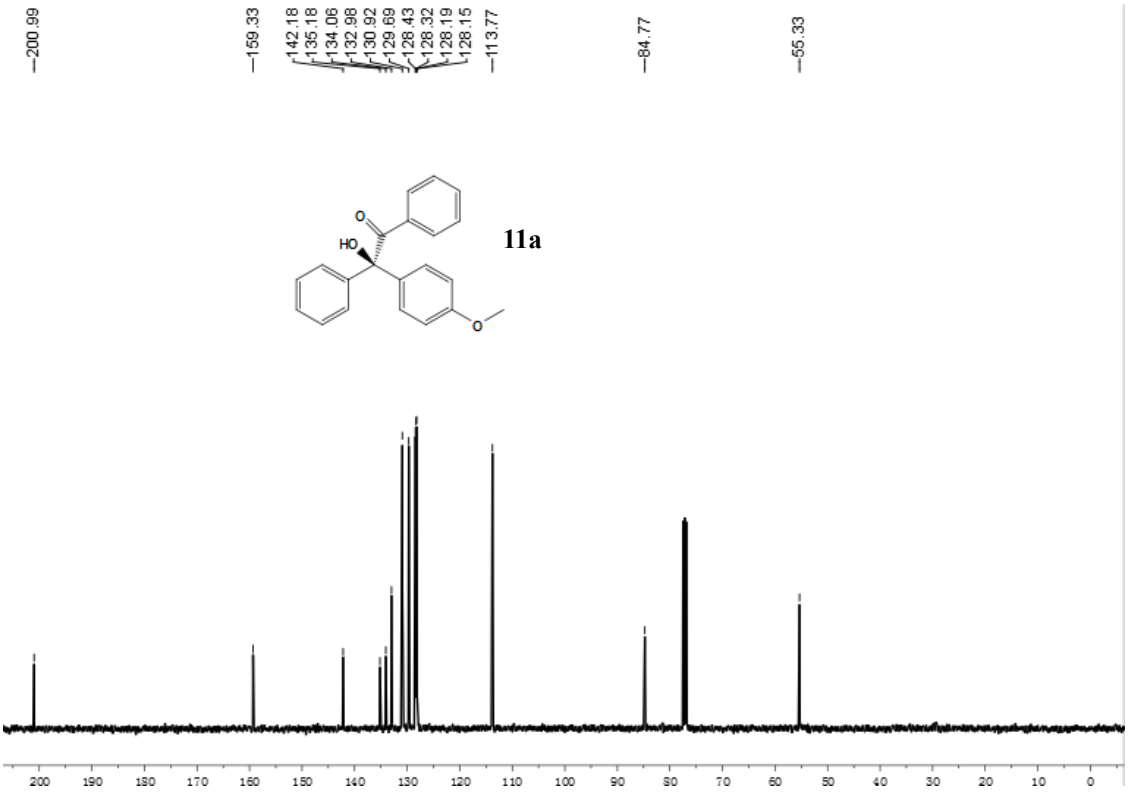
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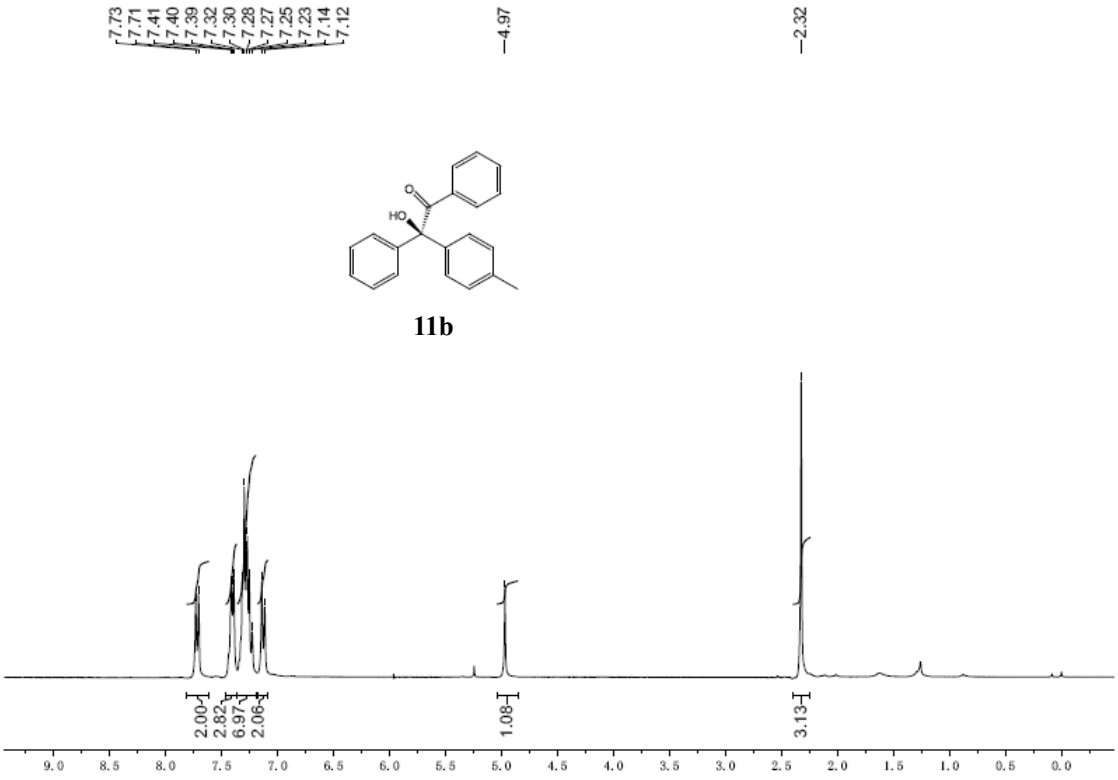
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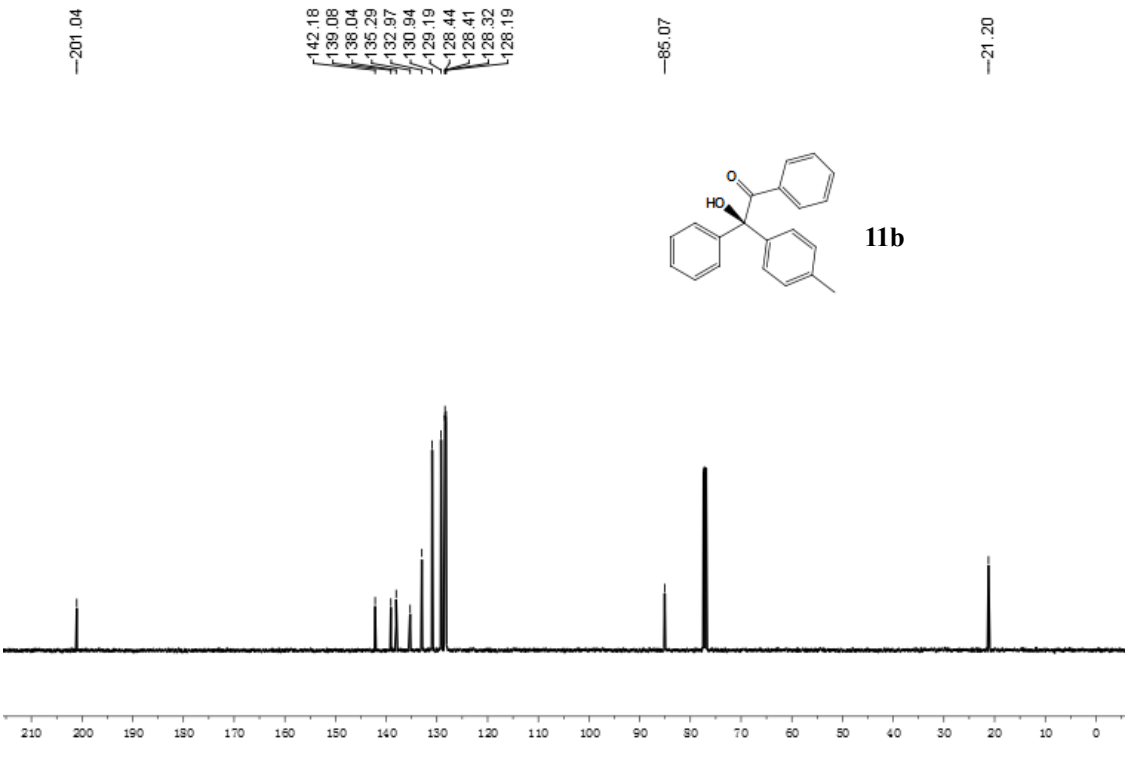
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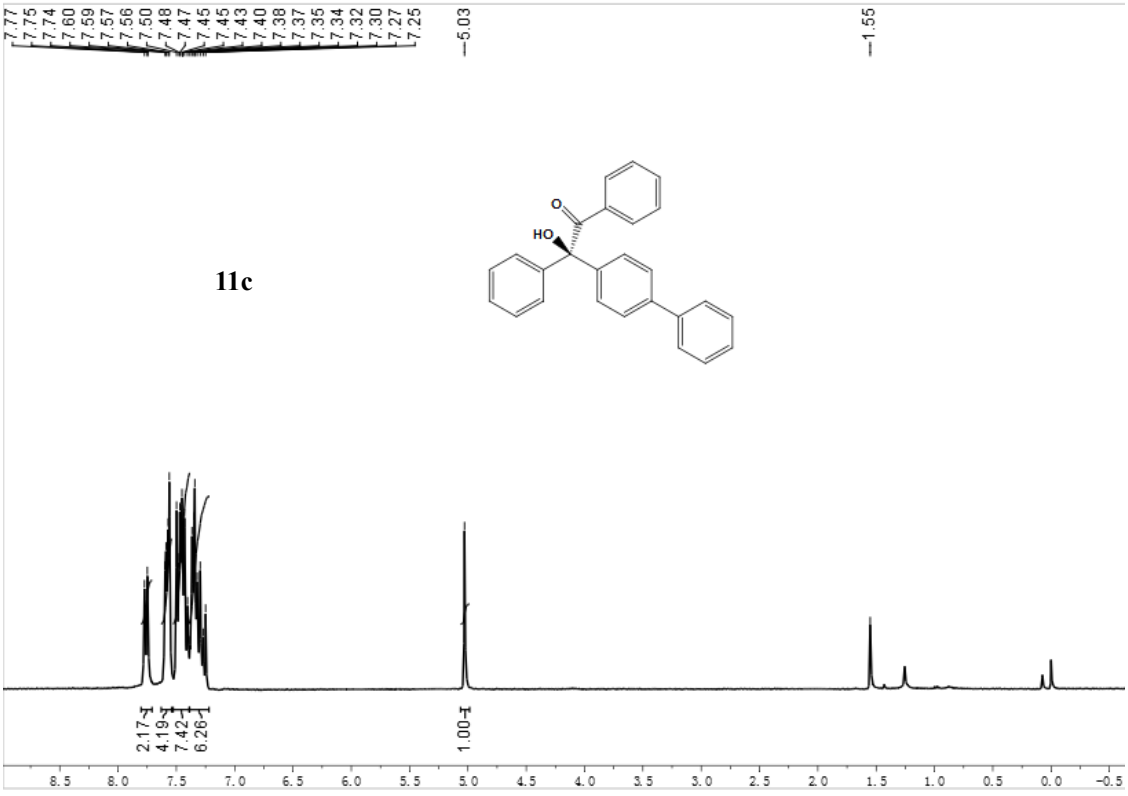
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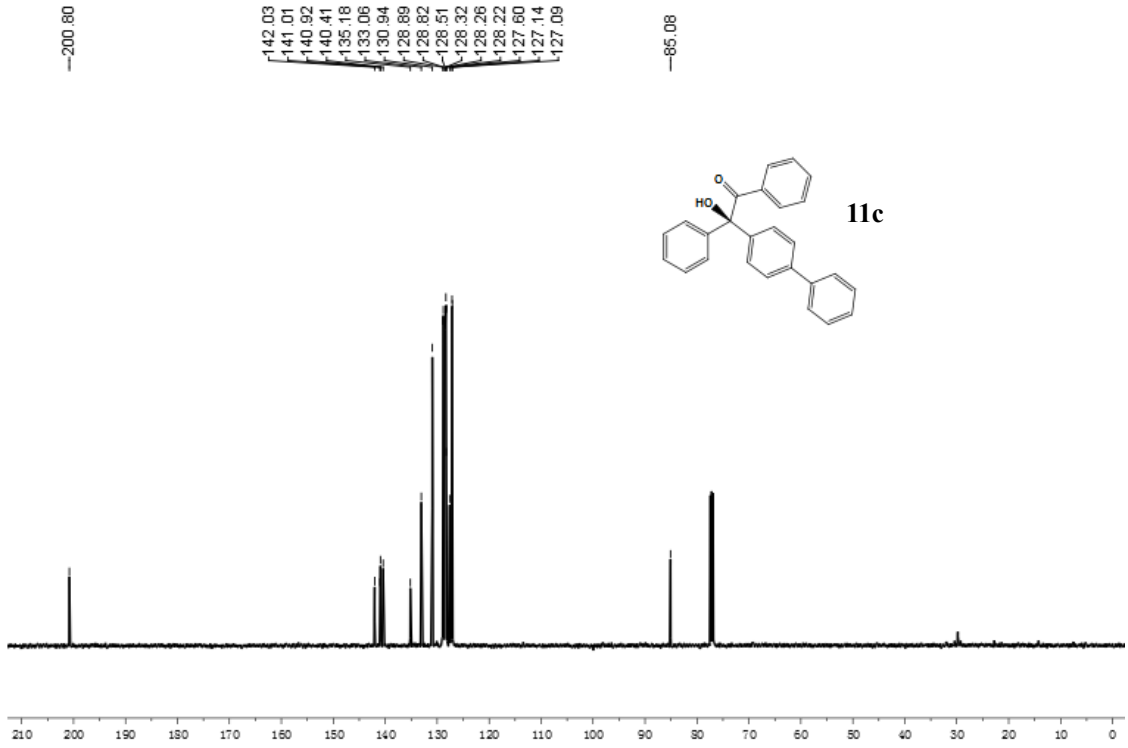
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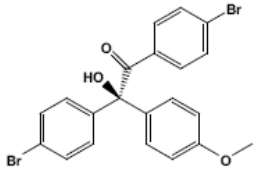
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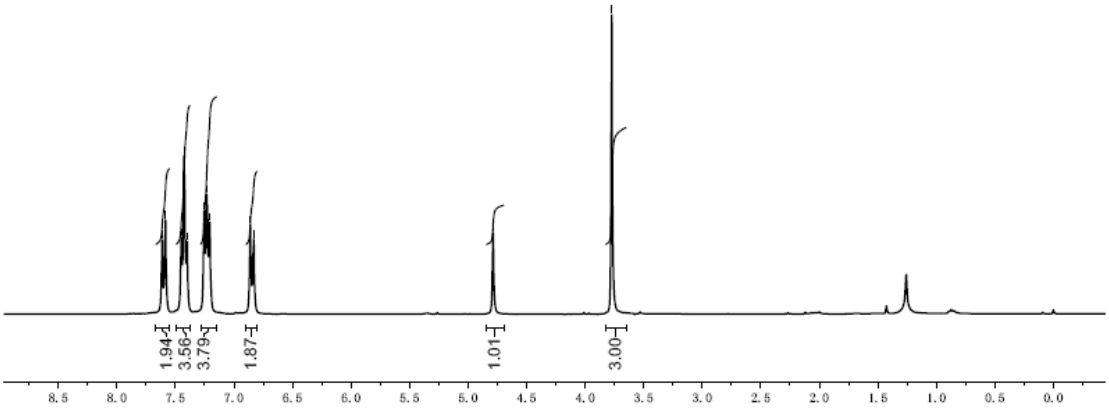
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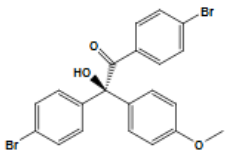
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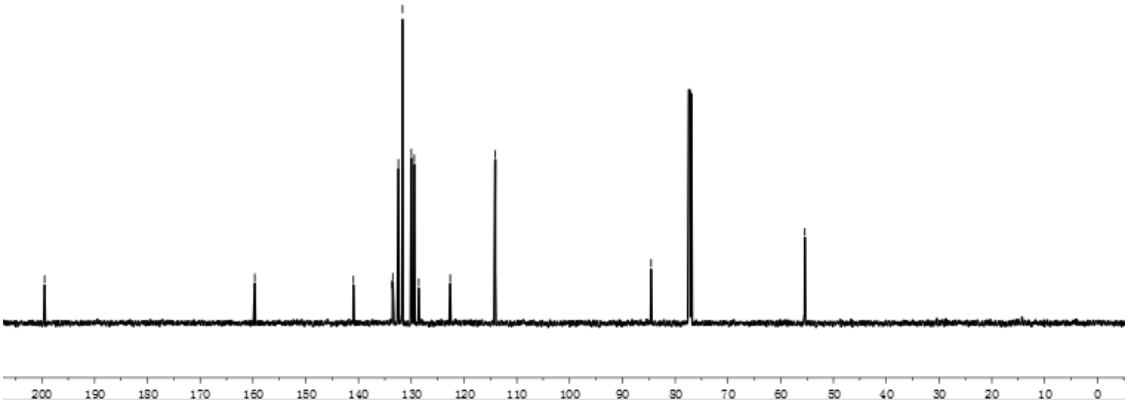
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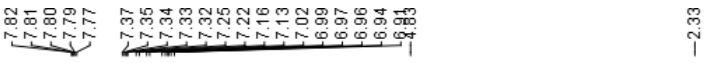
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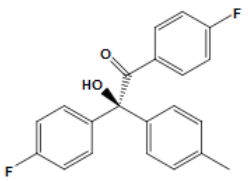
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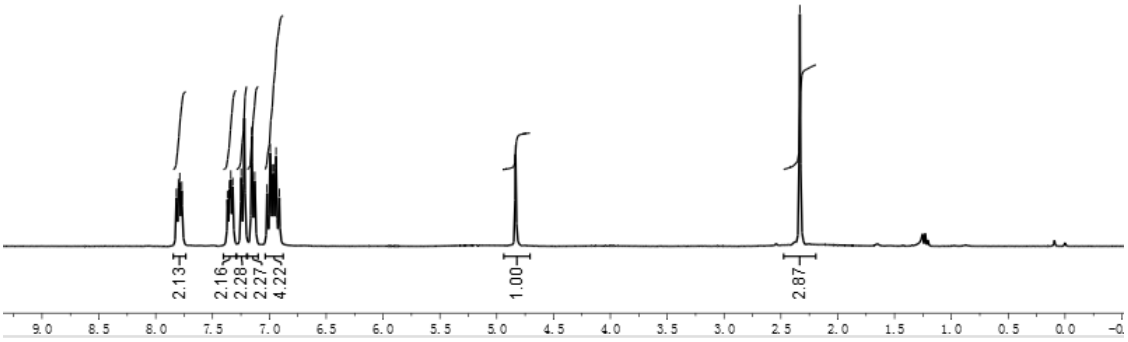
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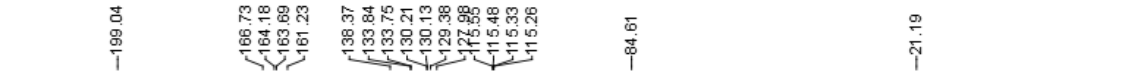
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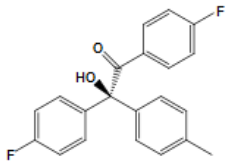
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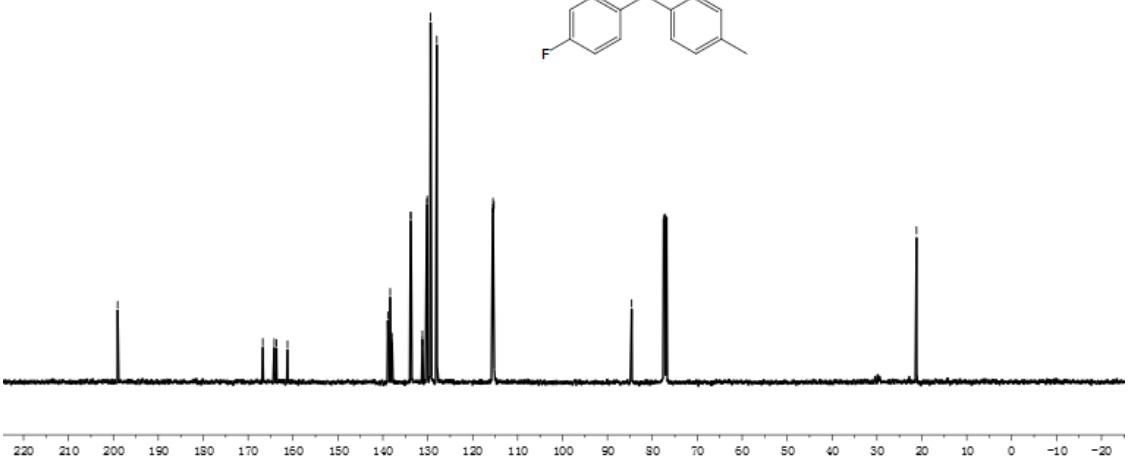
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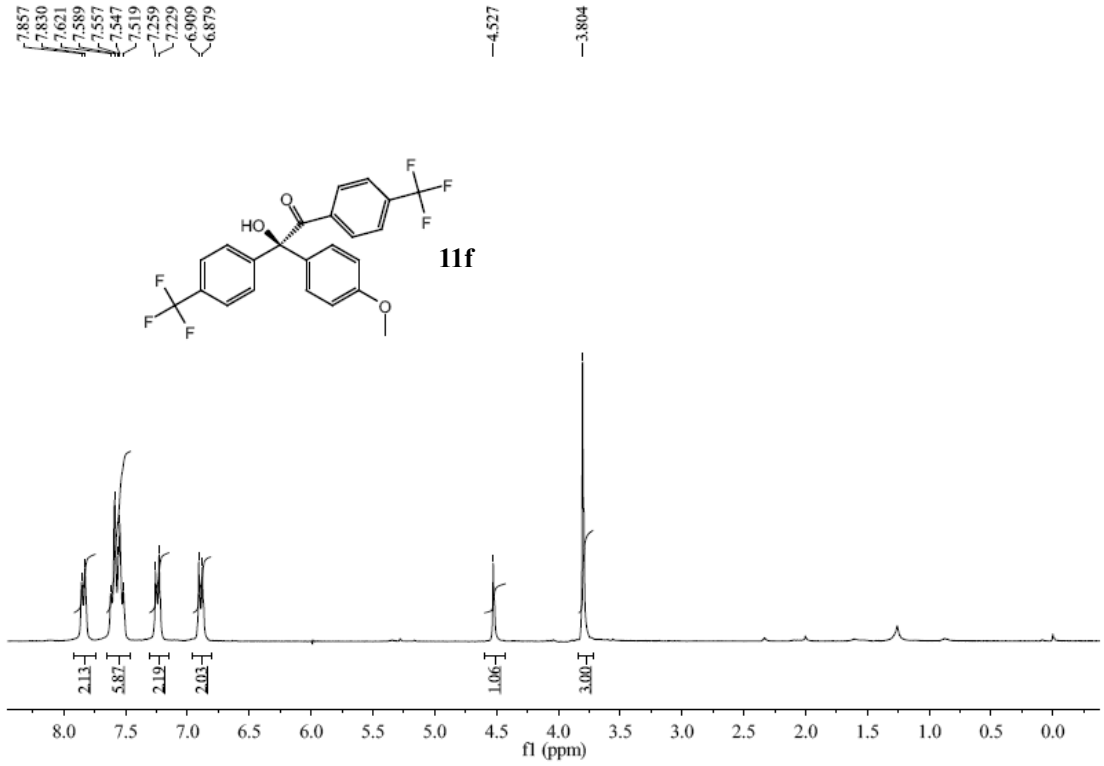
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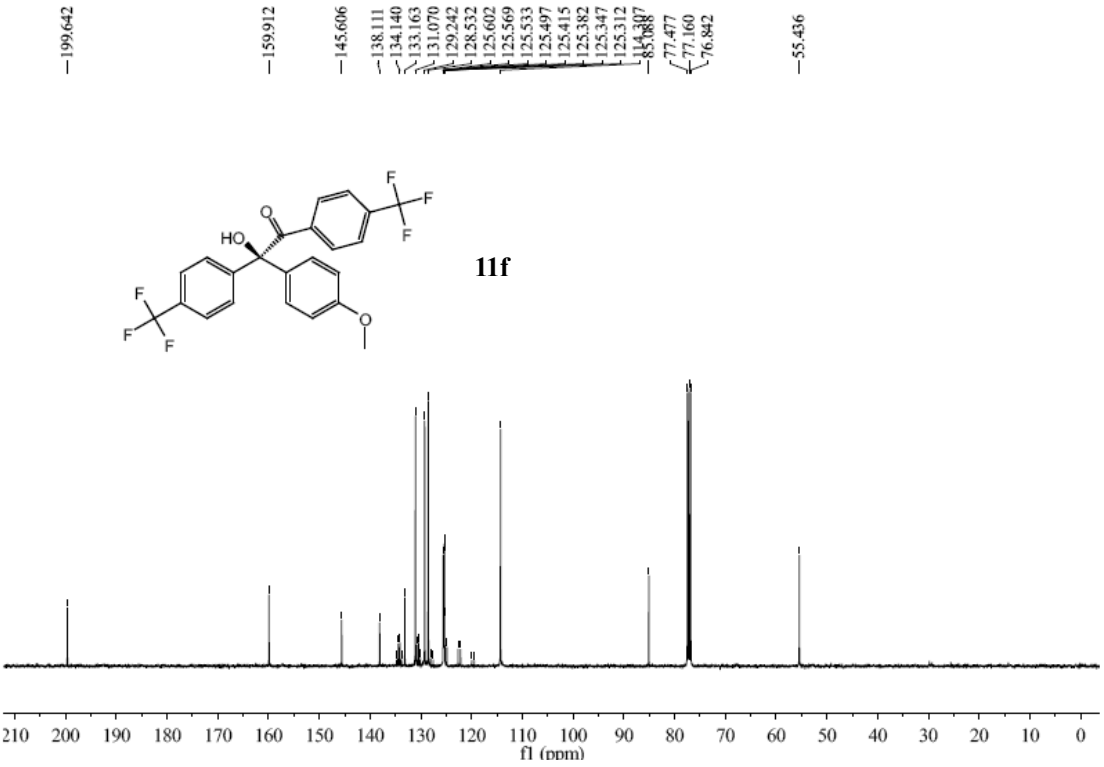
f1 (ppm)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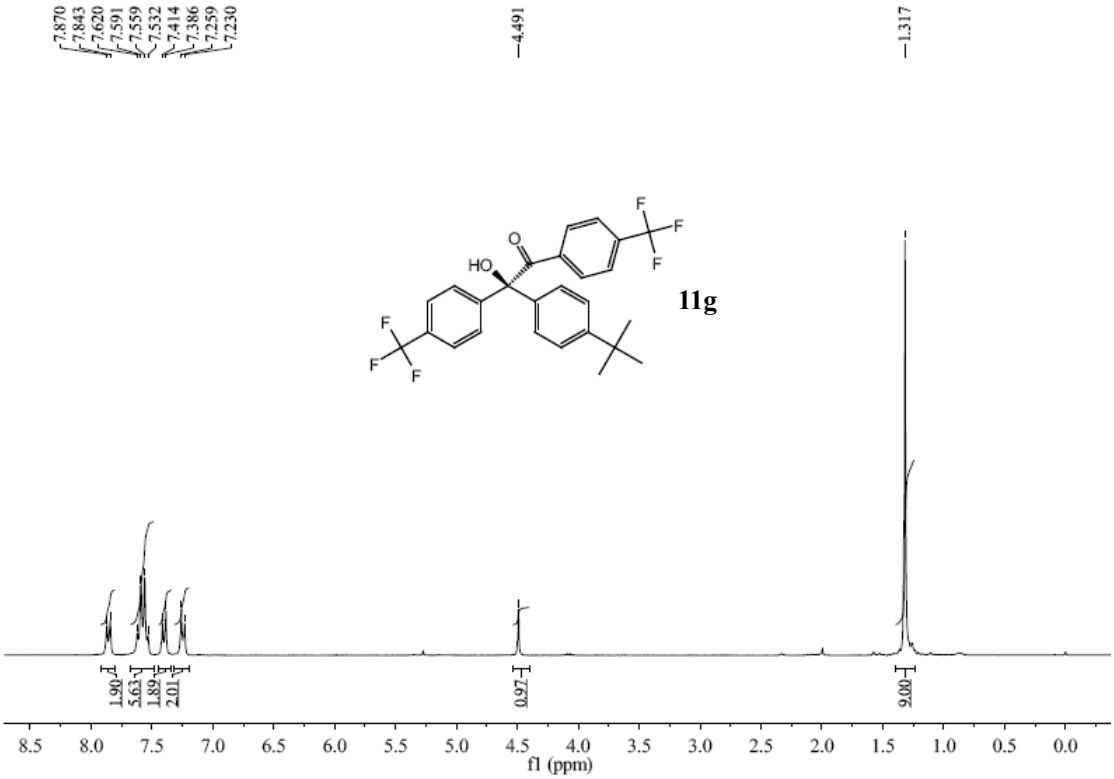
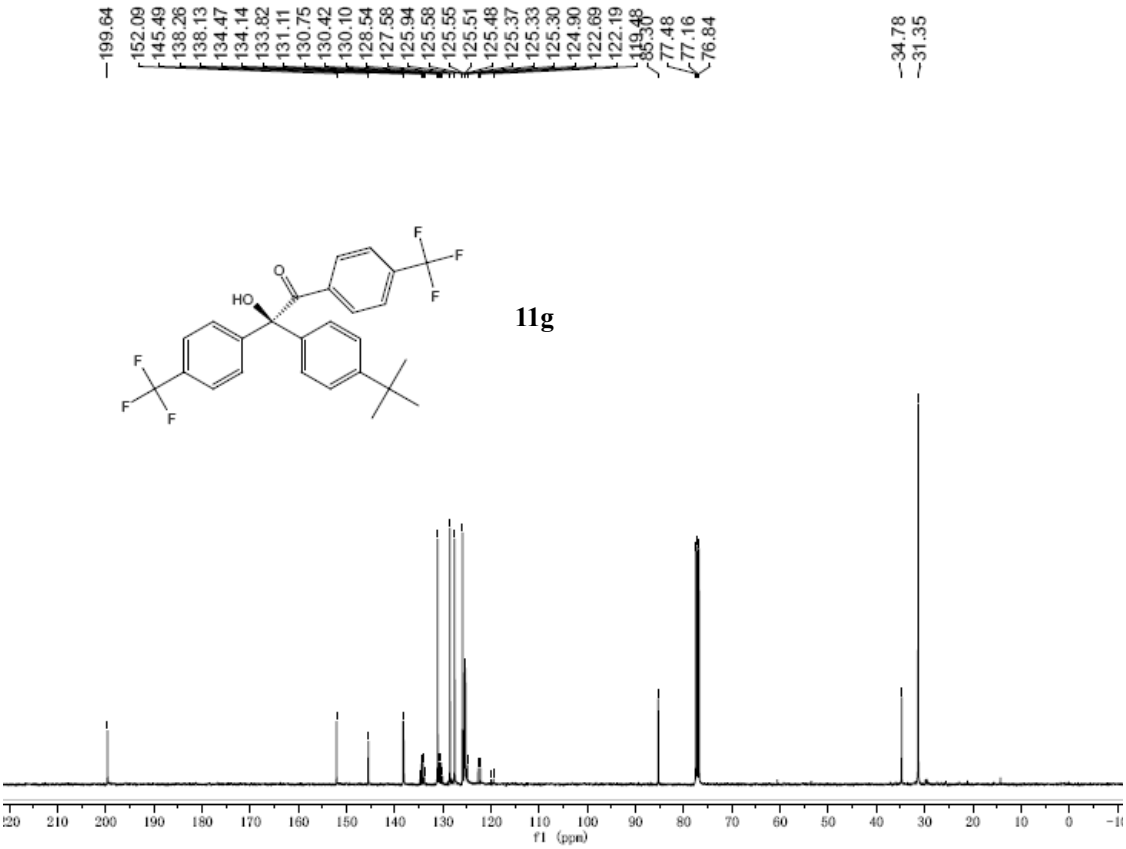
159.912
145.606
138.111
134.140
133.163
131.070
129.242
128.532
125.602
125.569
125.533
125.497
125.415
125.382
125.347
125.312
85.088
77.477
77.160
76.842
55.436
HO
O
F
F
F
F
F
F
O
11f
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.870
7.843
7.620
7.591
7.559
7.532
7.414
7.386
7.259
7.230
4.491
1.317
11g
1.90
5.63
1.89
2.01
0.97
9.00
f1 (ppm)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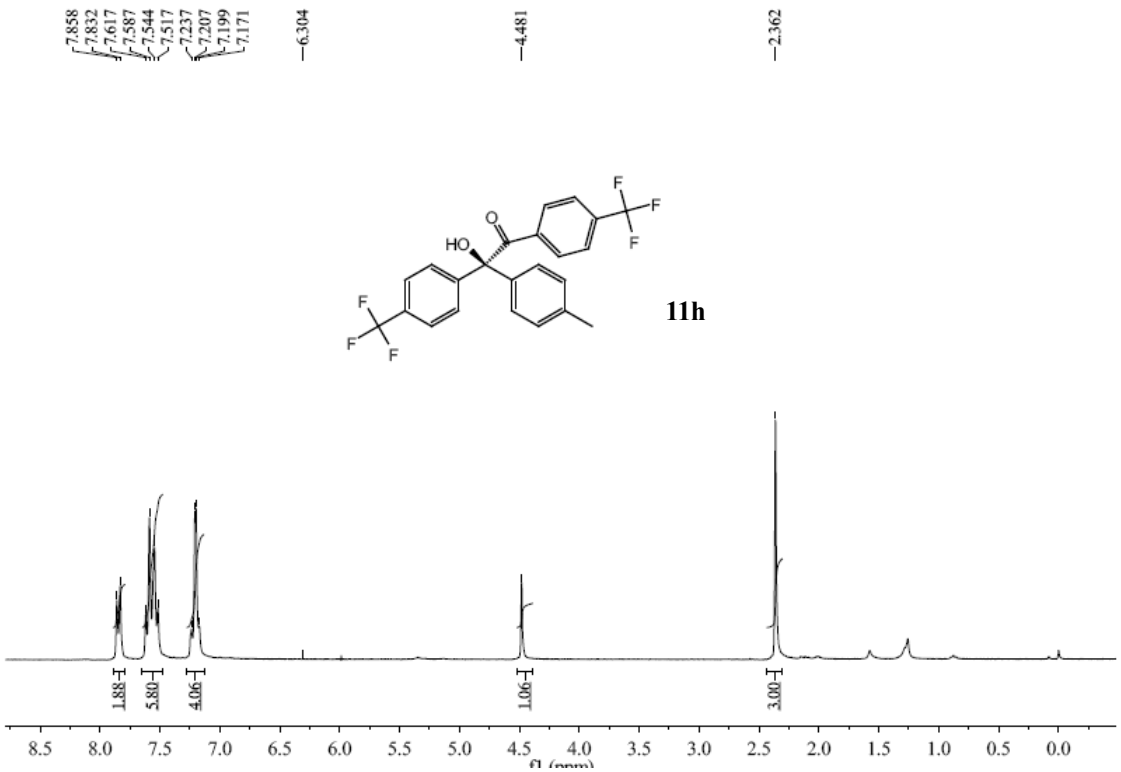
152.09
145.49
138.26
138.13
134.47
134.14
133.82
131.11
130.75
130.42
130.10
128.54
127.58
125.94
125.58
125.55
125.51
125.48
125.37
125.33
125.30
124.90
122.69
122.19
119.48
85.30
77.48
77.16
76.84
34.78
31.35
11g
f1 (ppm)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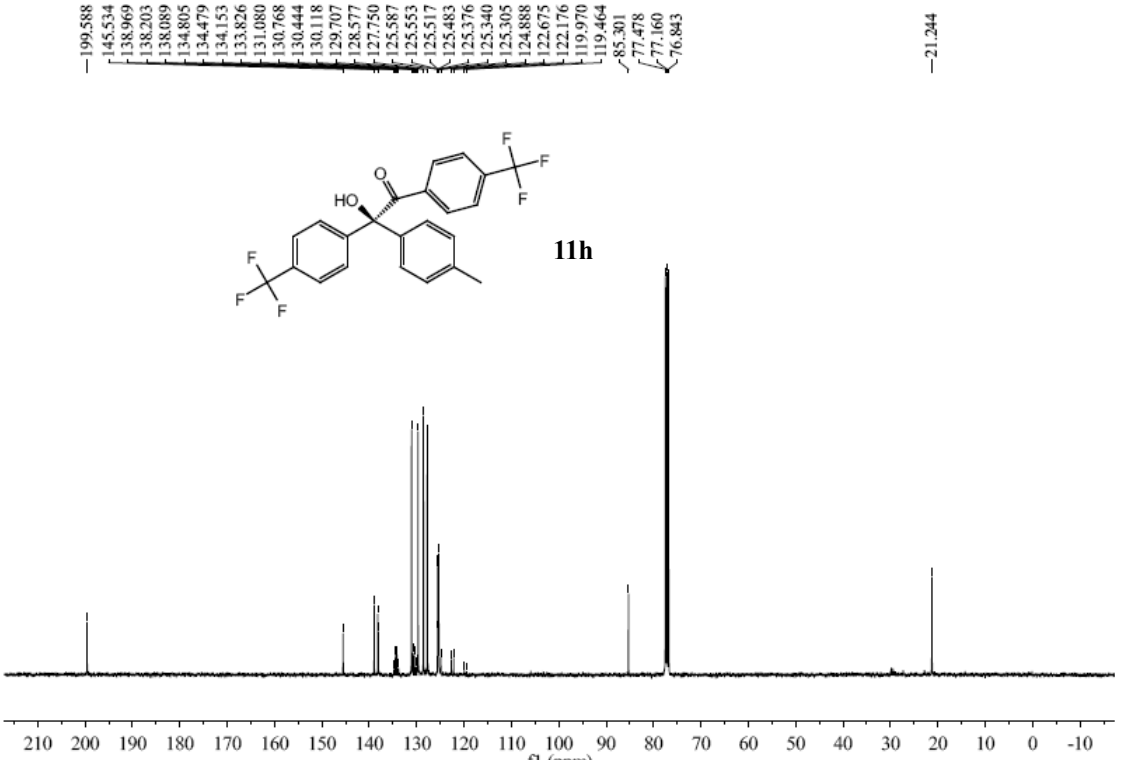
7.832
7.617
7.587
7.544
7.517
7.237
7.207
7.199
7.171
6.304
4.481
2.362
11h
1.88
5.80
4.06
1.06
3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


199.588
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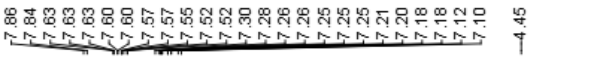
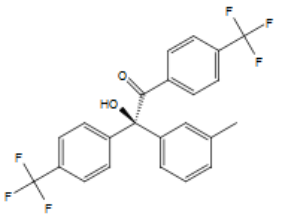
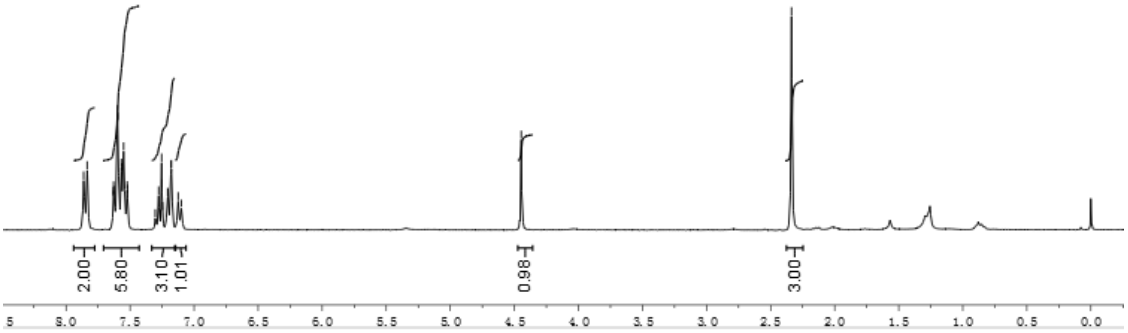
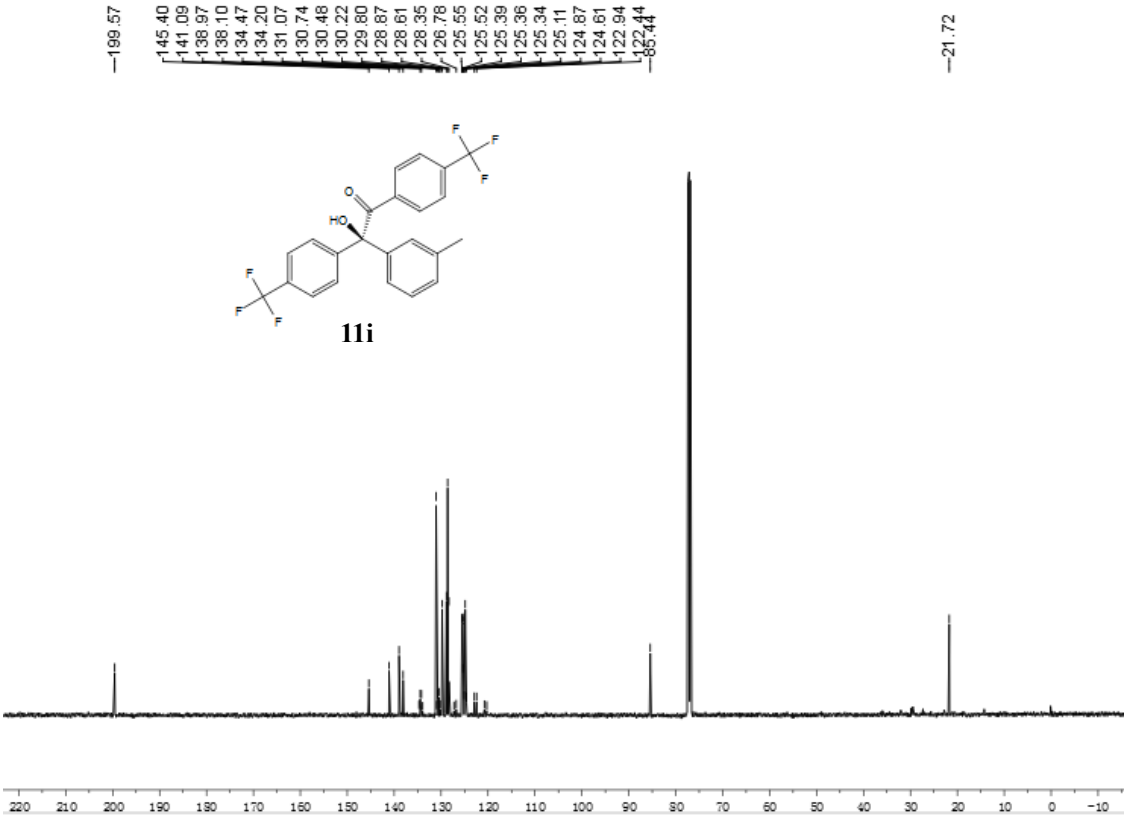
138.969
138.203
138.089
134.805
134.479
134.153
133.826
131.080
130.768
130.444
130.118
129.707
128.577
127.750
125.587
125.553
125.517
125.483
125.376
125.340
125.305
124.888
122.675
122.176
119.970
119.464
85.301
77.478
77.160
76.843
21.244
11h
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.86
7.84
7.63
7.63
7.63
7.60
7.60
7.57
7.57
7.55
7.52
7.52
7.30
7.28
7.26
7.26
7.25
7.25
7.25
7.21
7.20
7.18
7.18
7.12
7.10
4.45
2.34


F
F
F
O
HO
F
F
F

11i


2.00
5.80
3.10
1.01
0.98
3.00
5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0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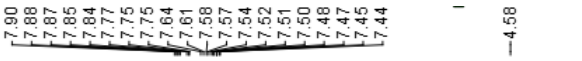
141.09
138.97
138.10
134.47
134.20
131.07
130.74
130.48
130.22
129.80
128.87
128.61
128.35
126.78
125.55
125.52
125.39
125.36
125.34
125.11
124.87
124.61
122.94
122.44
85.44
21.72
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

F
F
F
O
HO
F
F
F

11i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7.88
7.87
7.85
7.84
7.77
7.75
7.75
7.64
7.61
7.58
7.57
7.54
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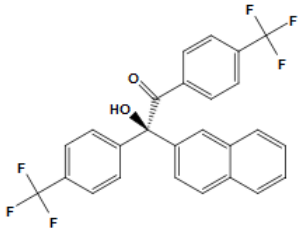
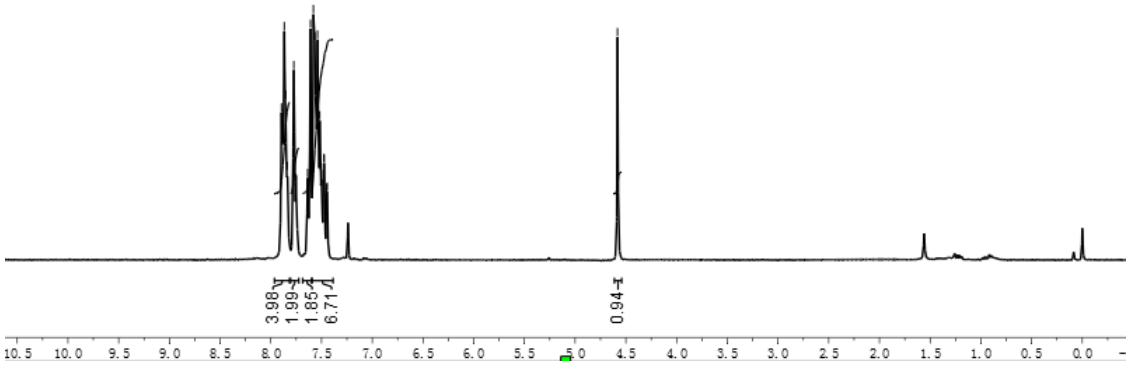
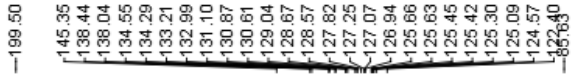
7.50
7.48
7.47
7.45
7.44
4.58


F
F
F
O
HO
F
F
F

11j


3.98
1.99
1.85
6.71
0.94
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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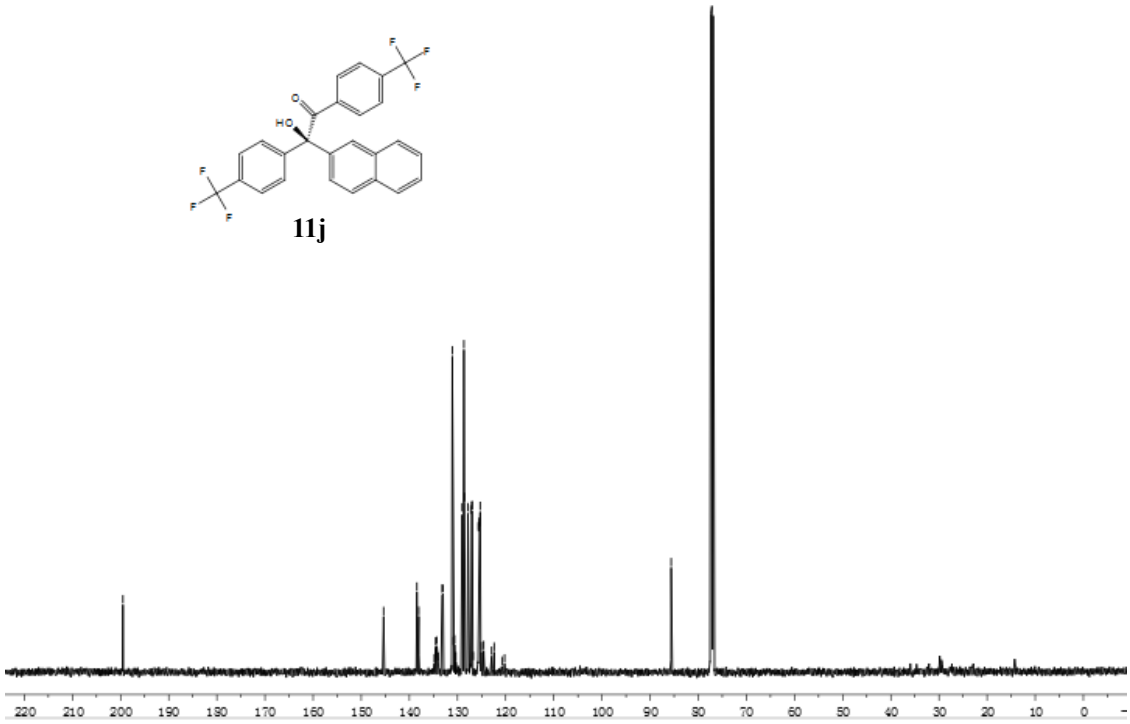
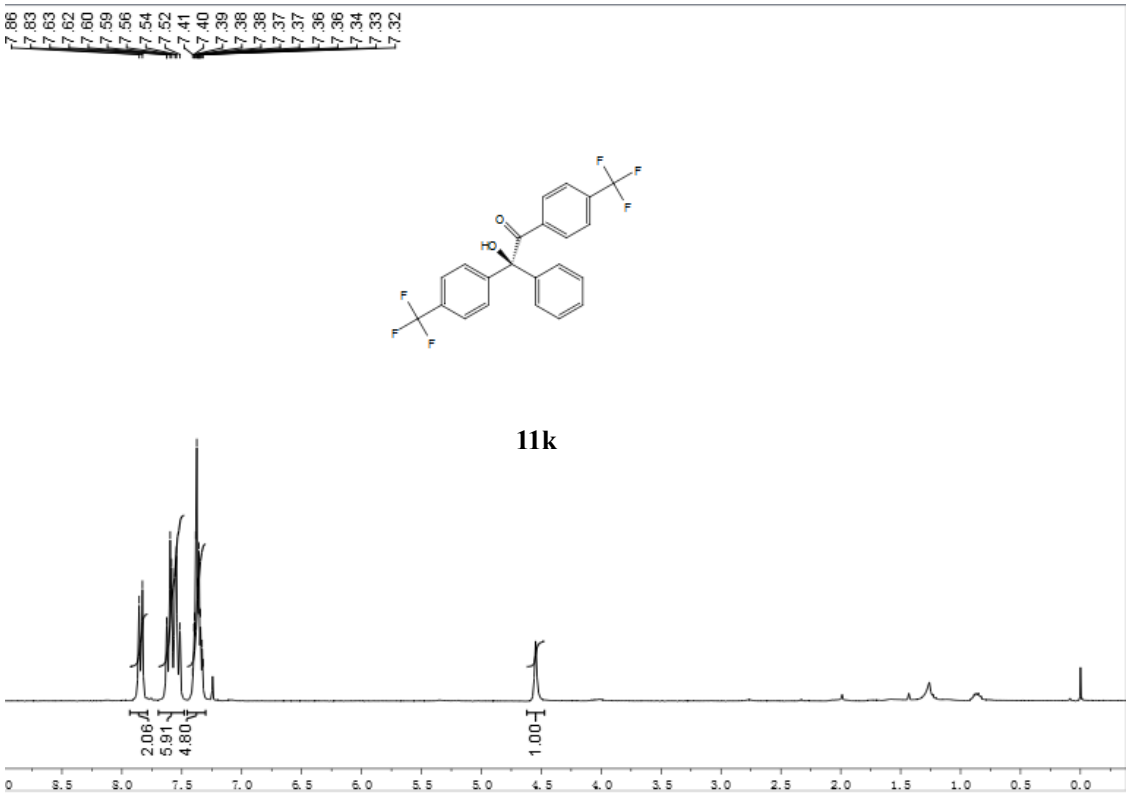
145.35
138.44
138.04
134.55
134.29
133.21
132.99
131.10
130.87
130.61
129.04
128.67
128.57
127.82
127.25
127.07
126.94
125.66
125.63
125.45
125.42
125.30
125.09
124.57
122.40
85.63

F
F
F
O
HO
F
F
F

11j


220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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7.83
7.63
7.62
7.60
7.59
7.56
7.54
7.52
7.41
7.40
7.39
7.38
7.38
7.37
7.37
7.36
7.36
7.34
7.33
7.32
O
HO
F
F
F
F
F
F
2.06
5.91
4.80
1.00
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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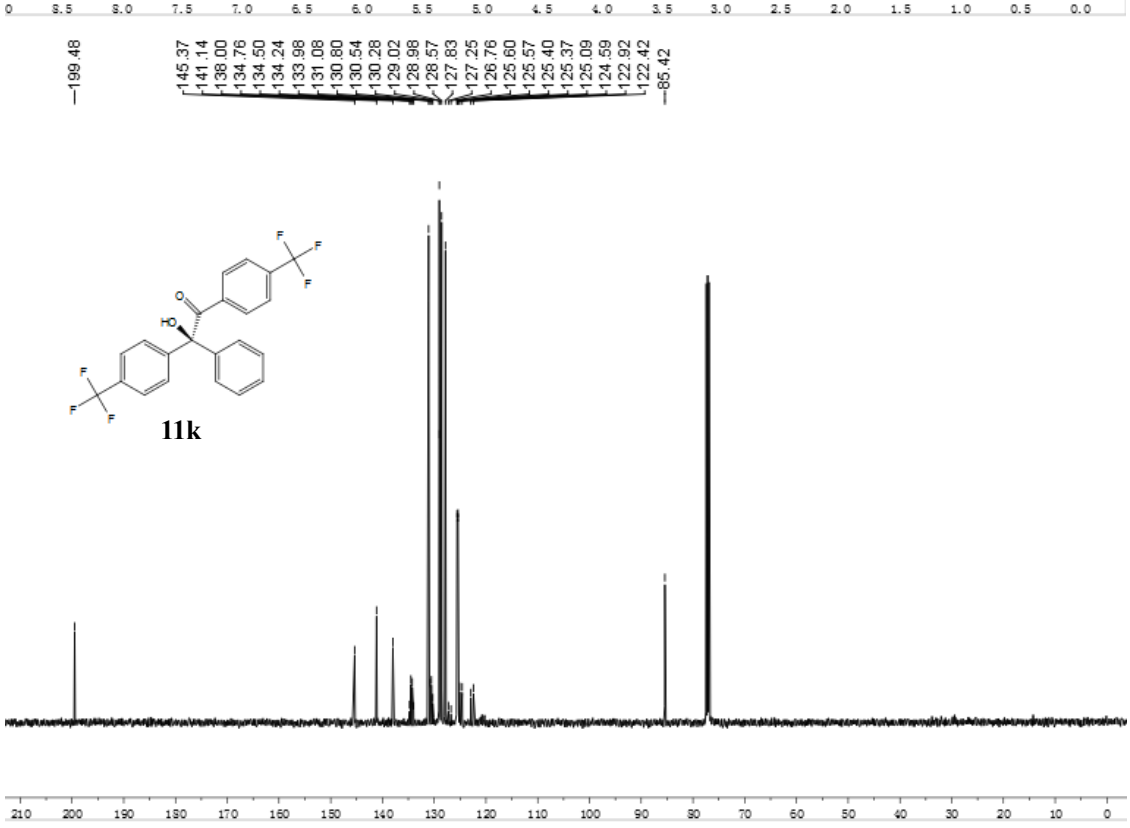
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

11k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141.14
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134.76
134.50
134.24
133.98
131.08
130.80
130.54
130.26
129.02
128.98
128.57
127.83
127.25
126.76
125.60
125.57
125.40
125.37
125.09
124.59
122.92
122.42
85.42
O
HO
F
F
F
F
F
F
210
200
190
180
170
160
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140
130
120
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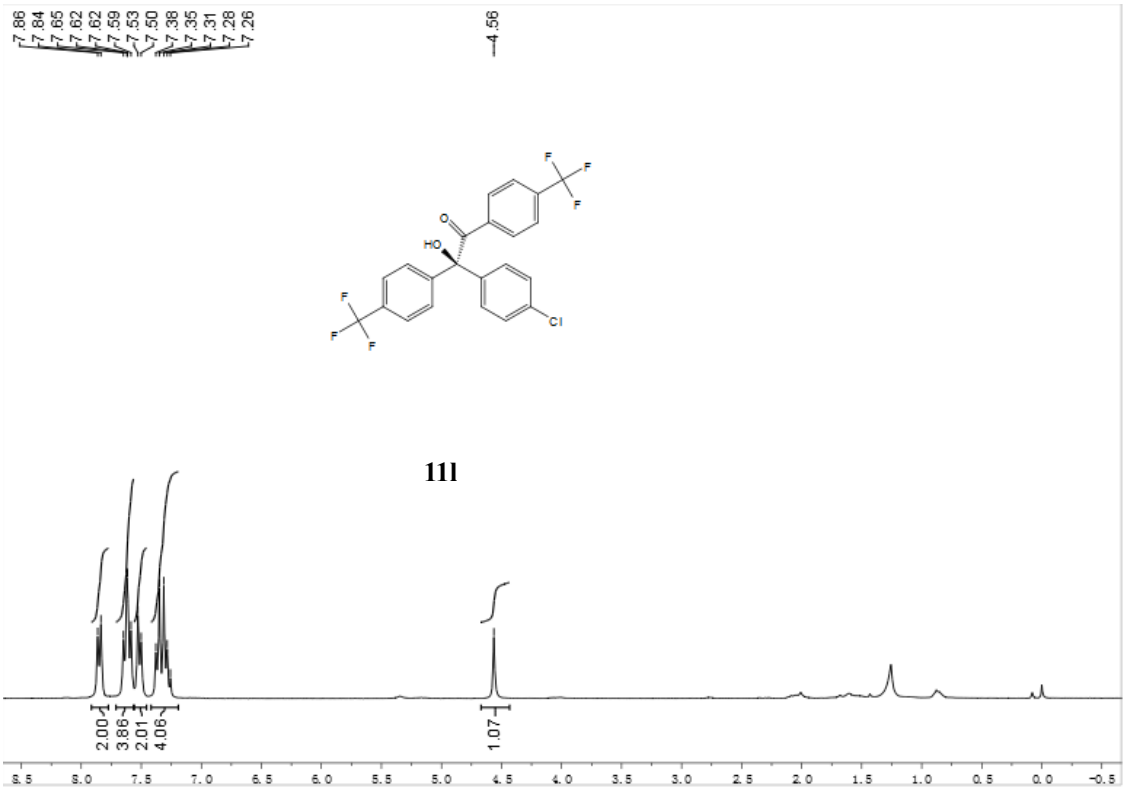
100
90
80
70
60
50
40
30
20
10
0

11k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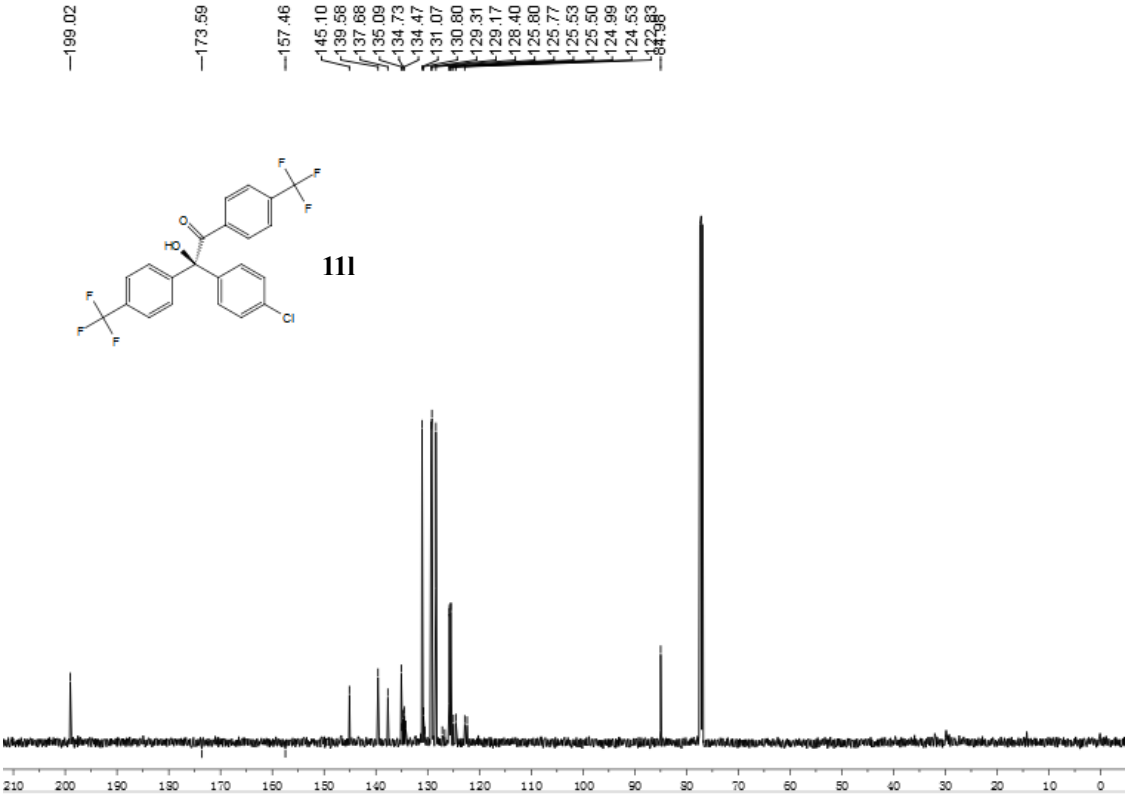
7.84
7.65
7.62
7.62
7.59
7.53
7.50
7.38
7.35
7.31
7.28
7.26
4.56
F
F
F
O
HO
F
F
F
Cl
2.00
3.86
2.01
4.06
1.07

11l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173.59
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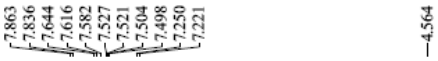
137.68
135.09
134.73
134.47
131.07
130.80
129.31
129.17
128.40
125.80
125.77
125.53
125.50
124.99
124.53
122.83
84.96
F
F
F
O
HO
F
F
F
Cl

11l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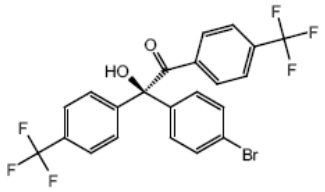
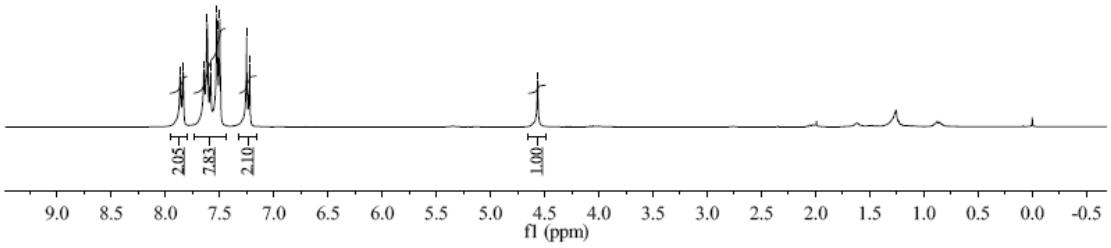
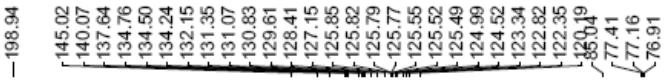
7.616
7.582
7.527
7.521
7.504
7.498
7.250
7.221
4.564


O
HO
F
F
F
F
F
F
Br

11m


2.05
2.83
2.10
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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140.07
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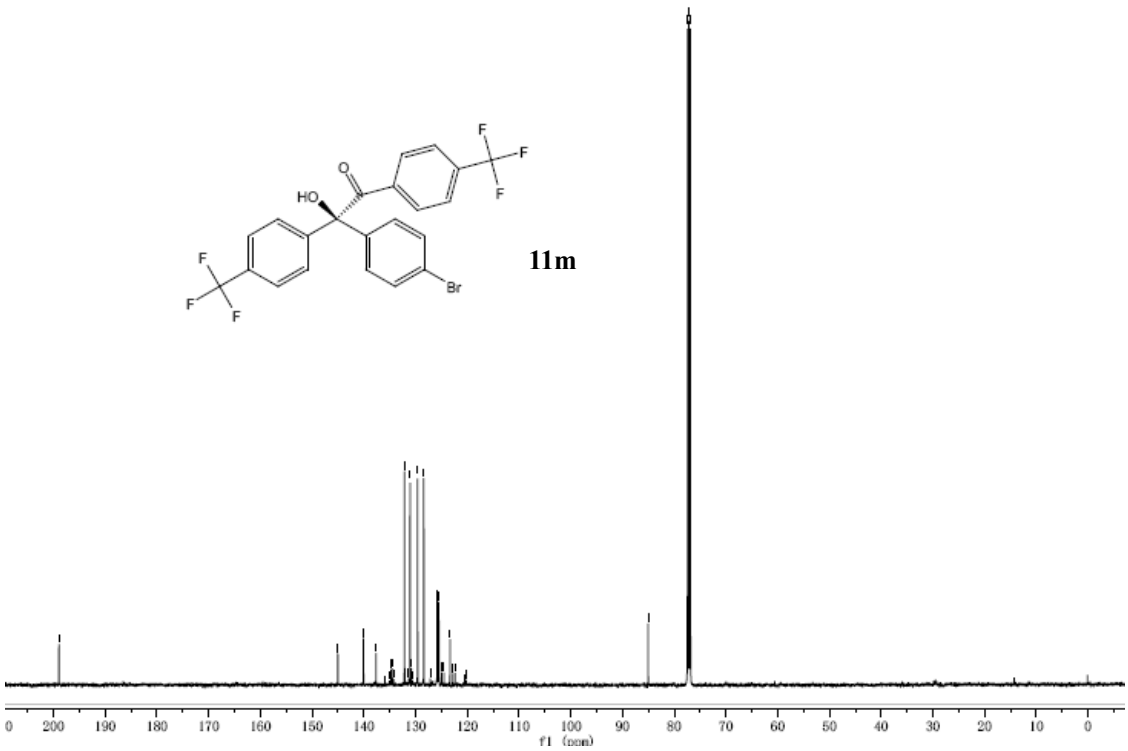
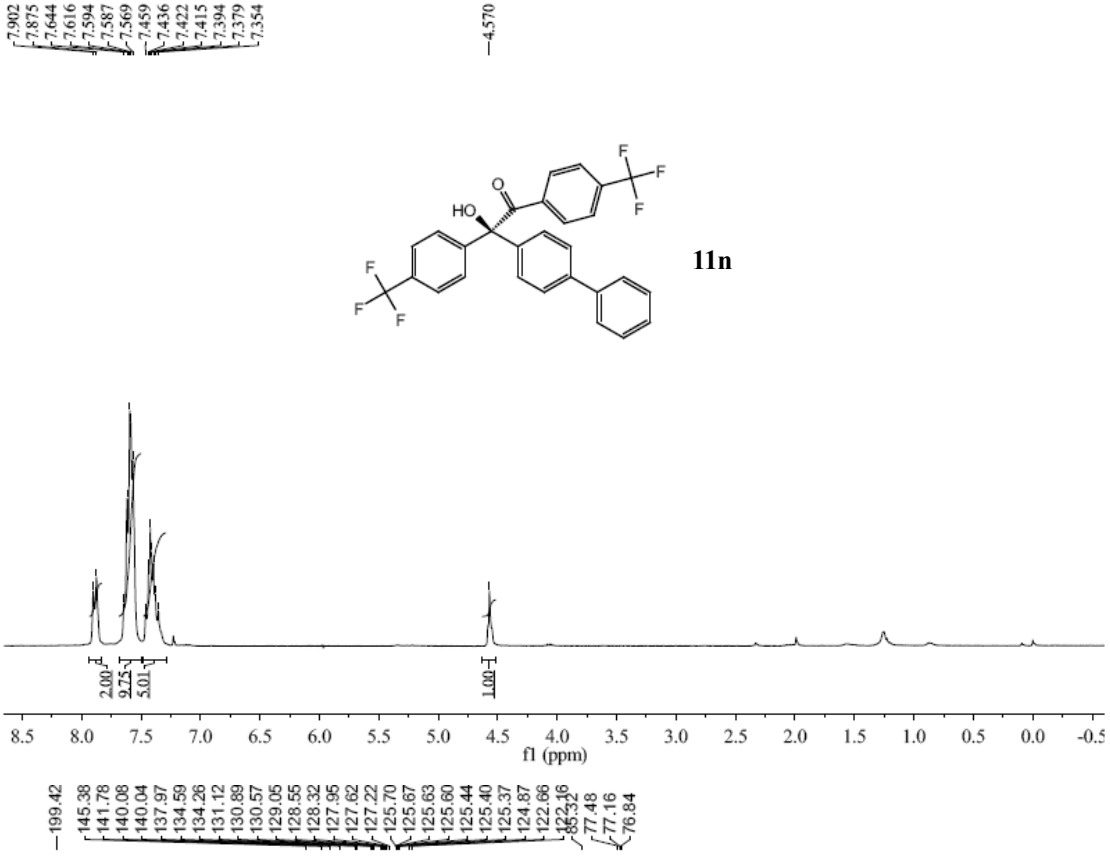
134.50
134.24
132.15
131.35
131.07
130.83
129.61
128.41
127.15
125.85
125.82
125.79
125.77
125.55
125.52
125.49
124.99
124.52
123.34
122.82
122.35
120.19
85.04
77.41
77.16
76.91

O
HO
F
F
F
F
F
F
Br

11m


0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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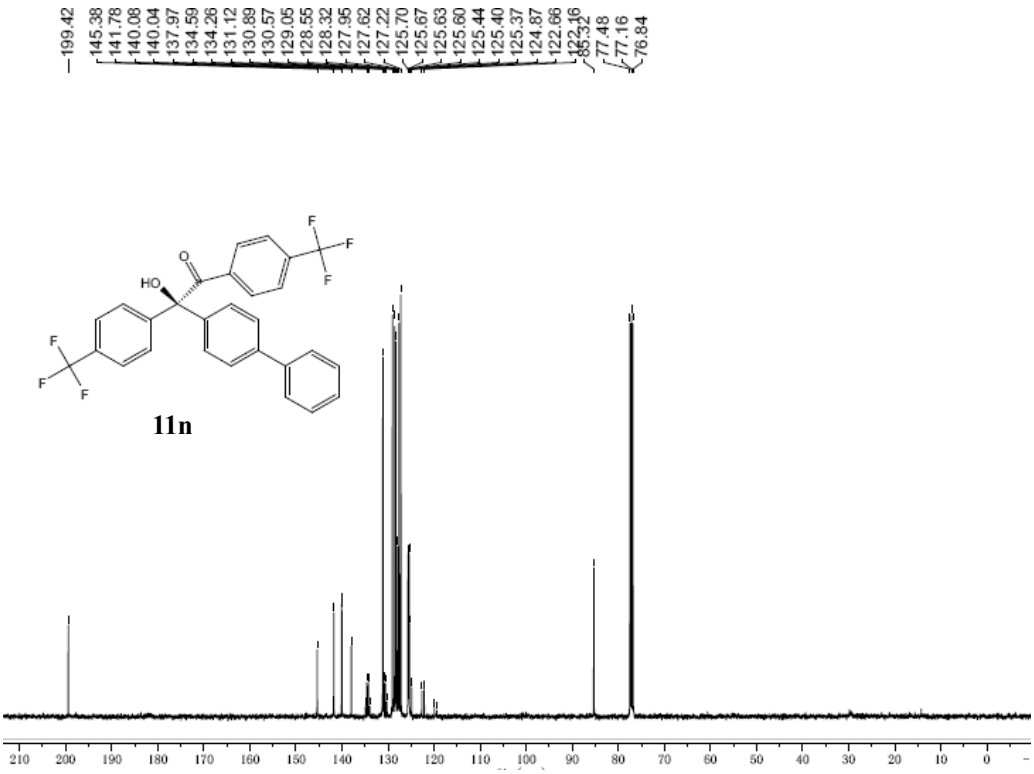
7.587
7.569
7.459
7.436
7.422
7.415
7.394
7.379
7.354
4.570
HO
O
F
F
F
F
F
F
11n
2.00
9.75
5.01
1.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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134.26
131.12
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129.05
128.55
128.32
127.95
127.62
127.22
125.70
125.67
125.63
125.60
125.44
125.40
125.37
124.87
122.66
122.16
77.48
77.16
76.84
HO
O
F
F
F
F
F
F
11n
210
200
190
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150
140
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100
90
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70
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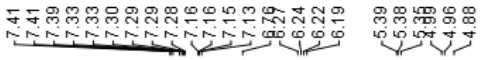
10
0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7.29
7.29
7.28
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7.16
7.15
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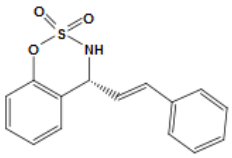
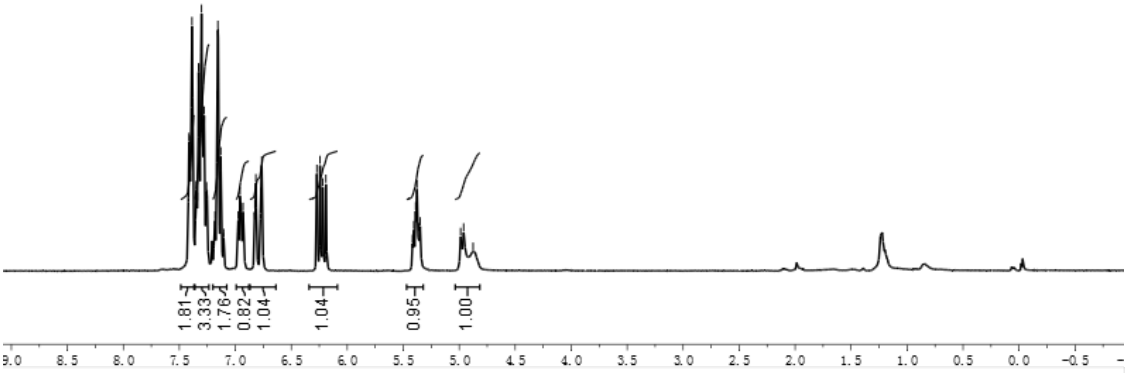
5.38
4.96
4.88



13a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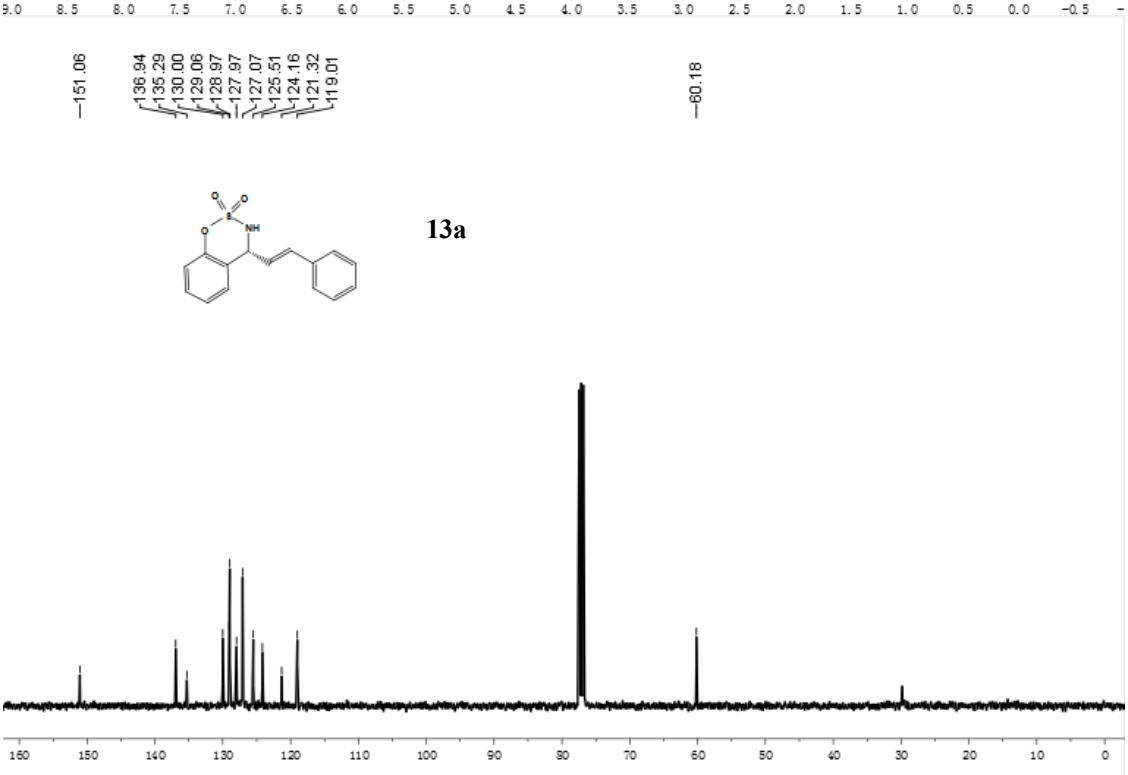
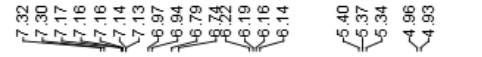
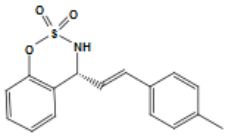
3.33
1.76
0.82
1.04
1.04
0.95
1.00

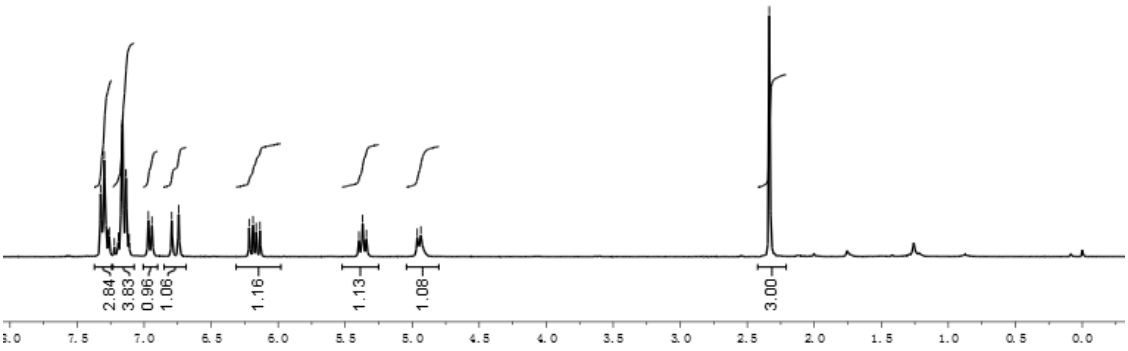

151.06
136.94
135.29
130.00
129.06
128.97
127.97
127.07
125.51
124.16
121.32
119.01
60.18

13a


7.32
7.30
7.17
7.16
7.16
7.14
7.13
6.97
6.94
6.79
6.74
6.22
6.19
6.16
6.14
5.40
5.37
5.34
4.96
4.93
2.34



13b


2.84
3.83
0.96
1.06
1.16
1.13
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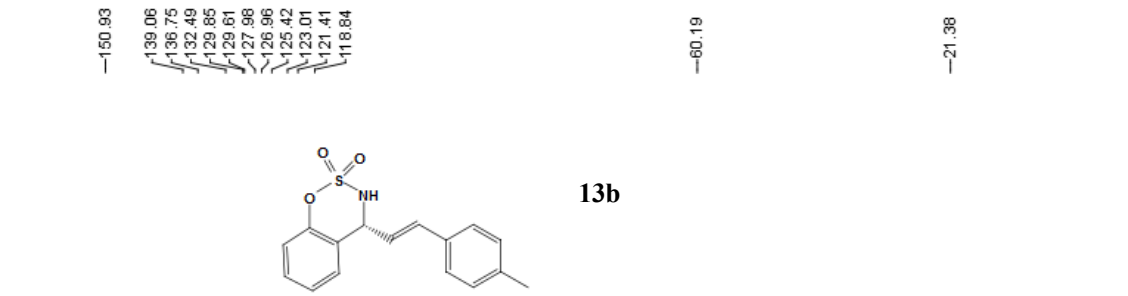
3.00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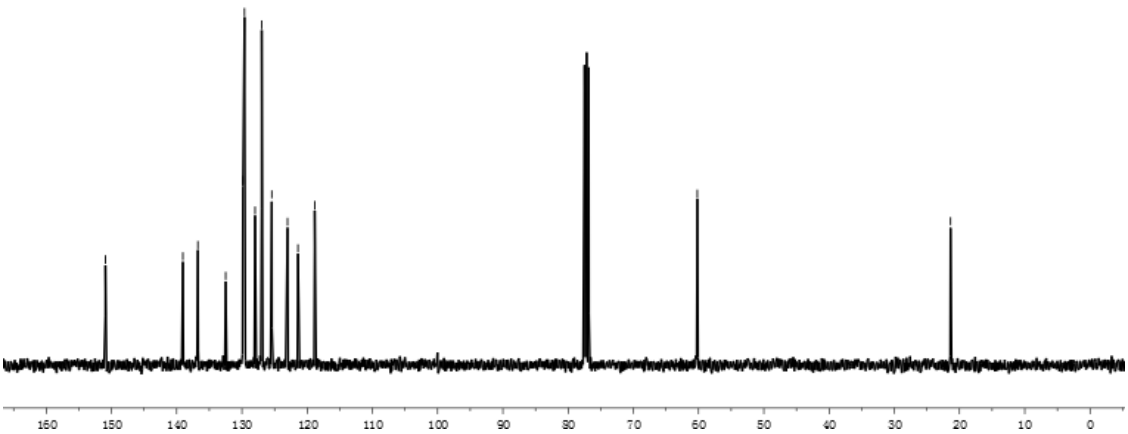
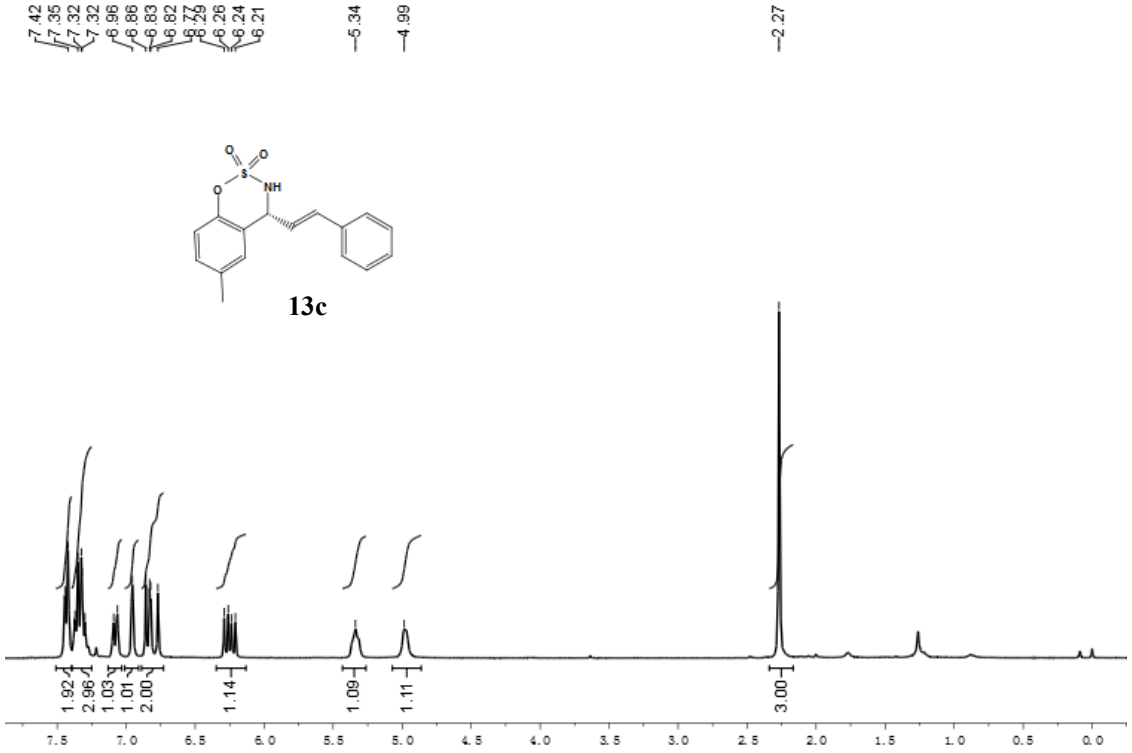
13b

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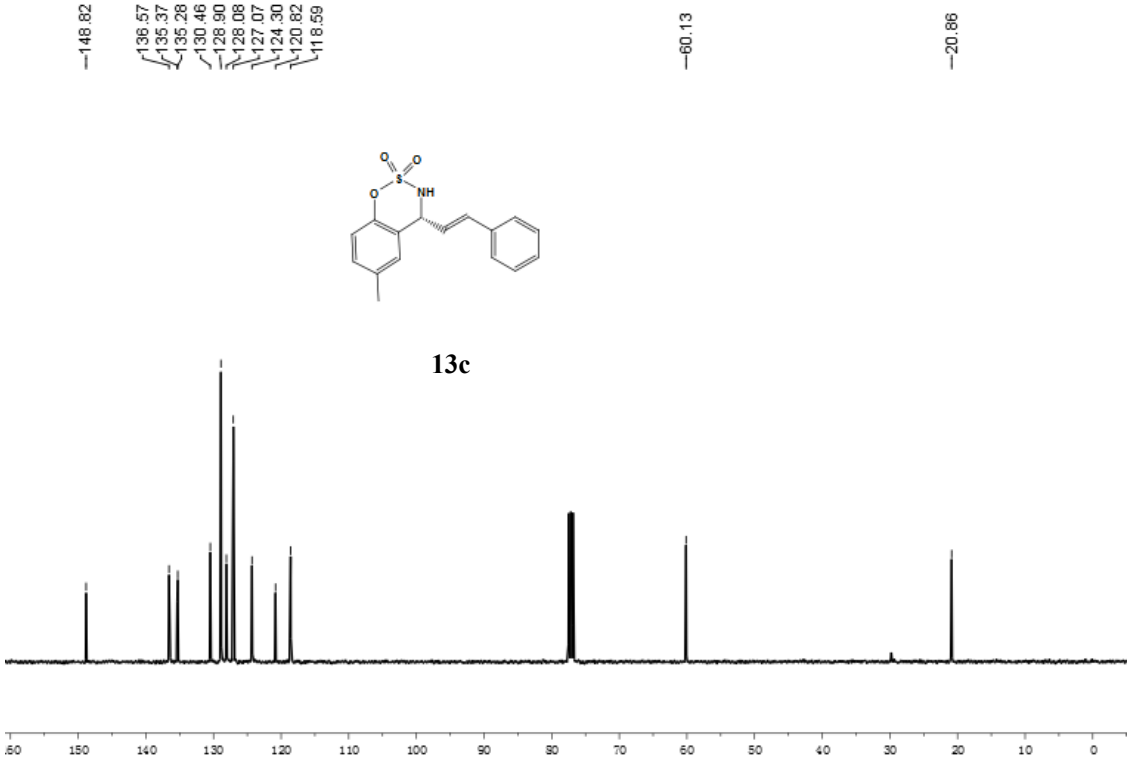
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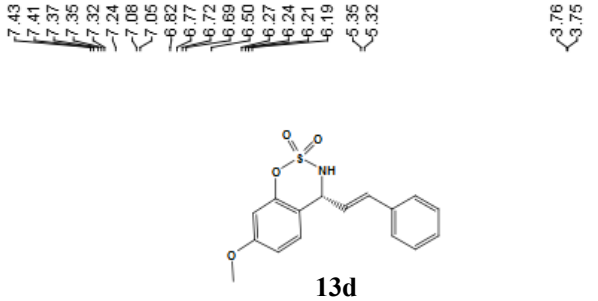
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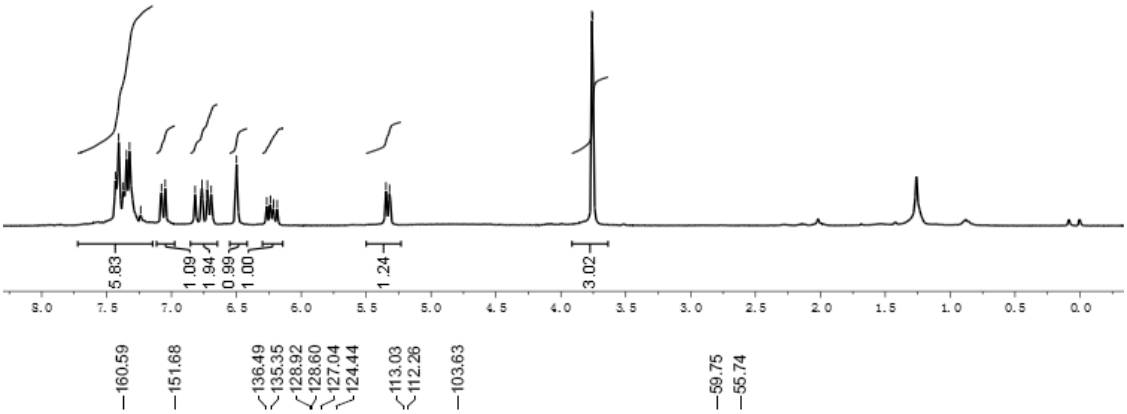
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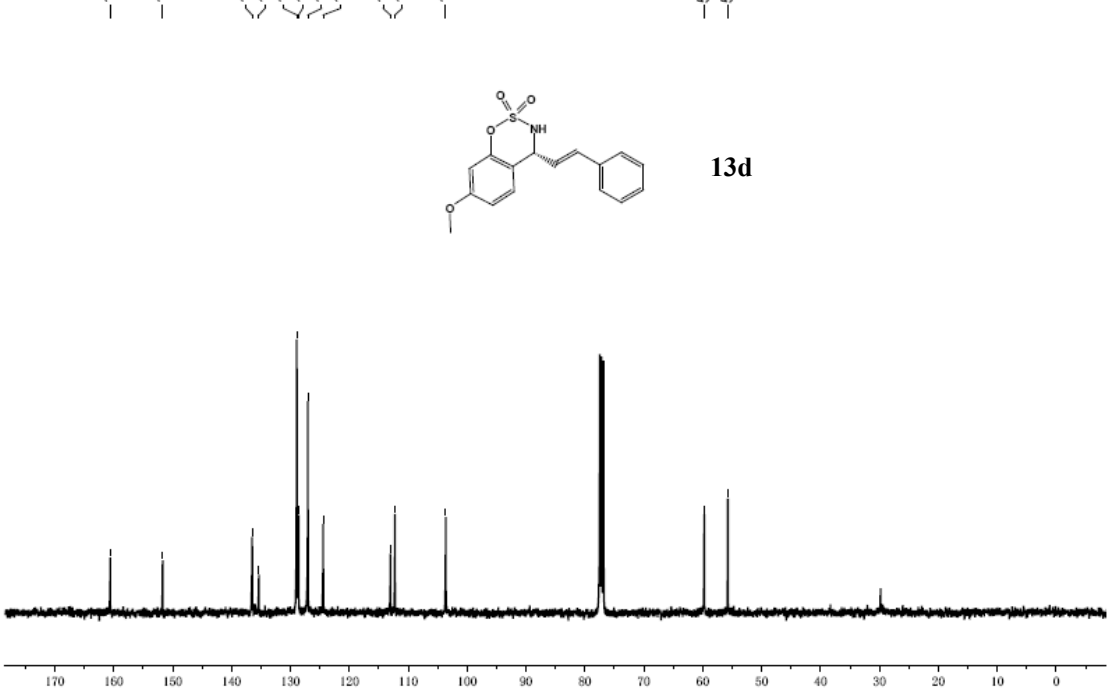
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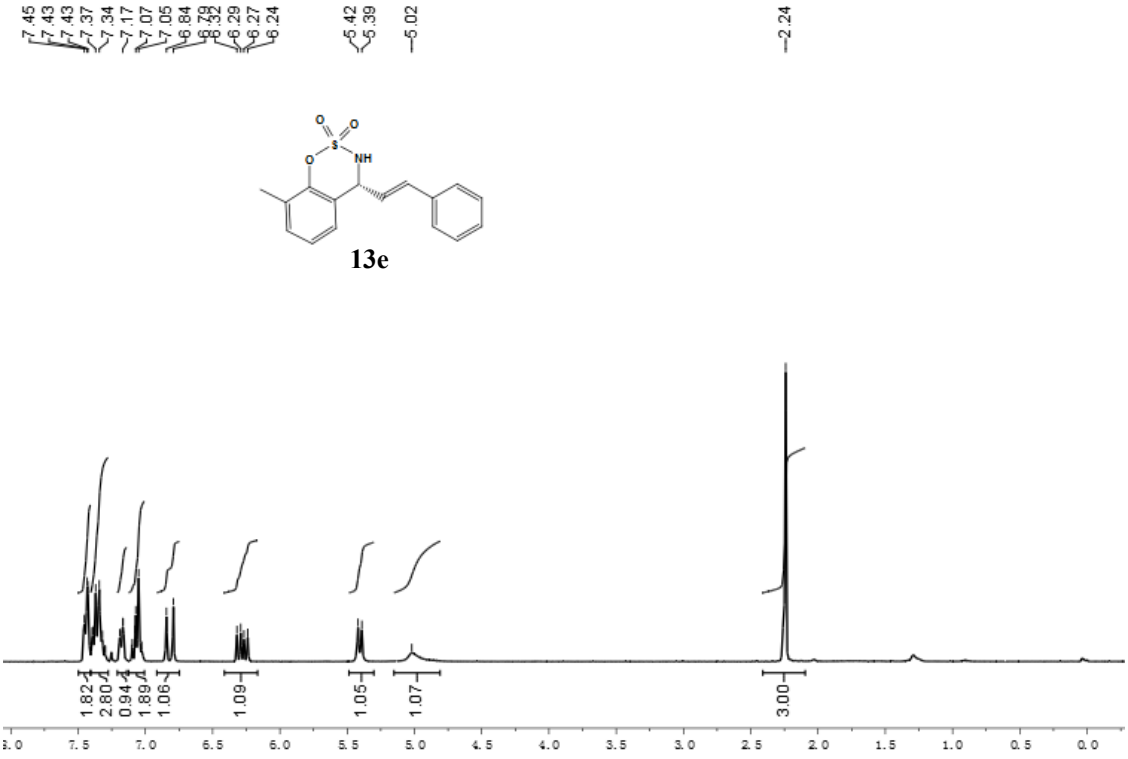
13d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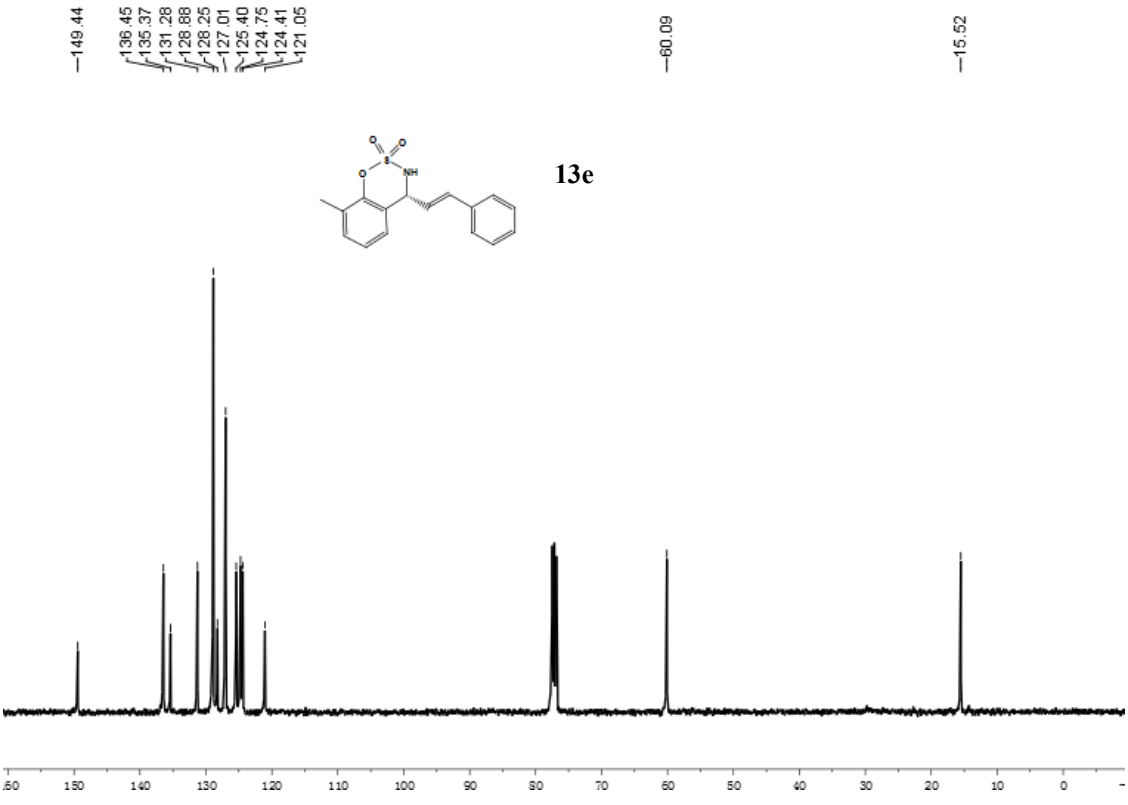
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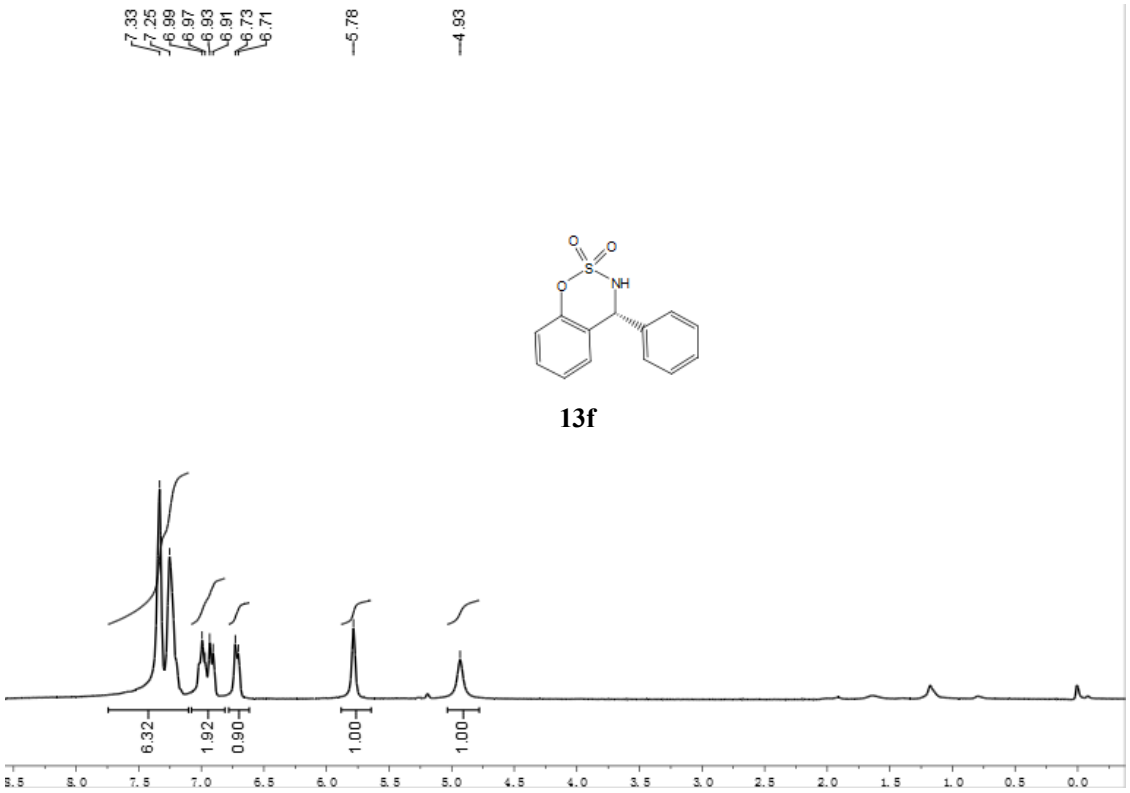
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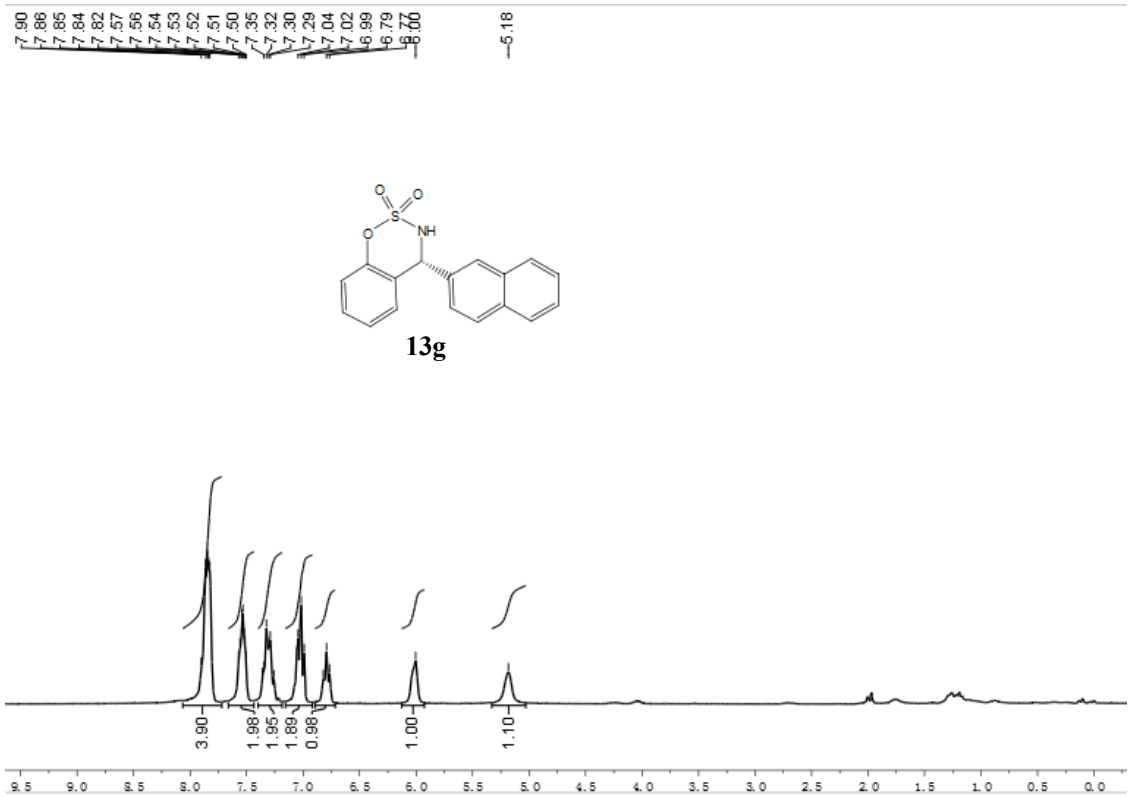
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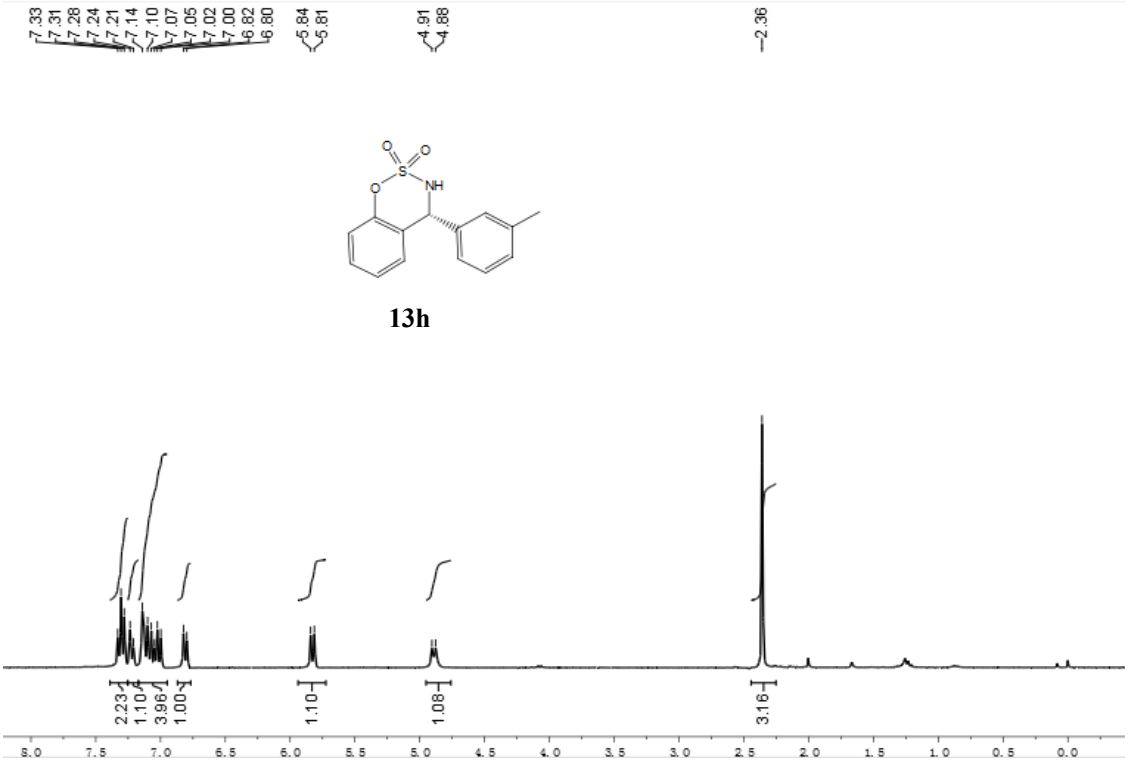
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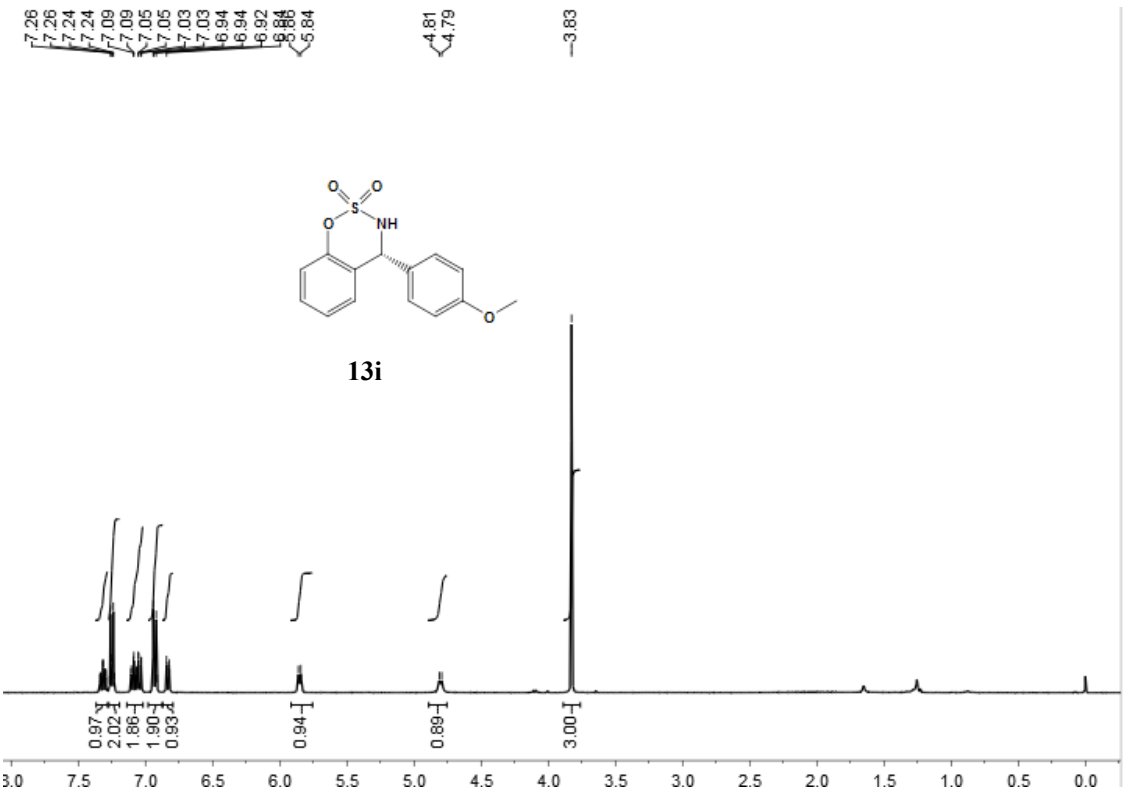
13h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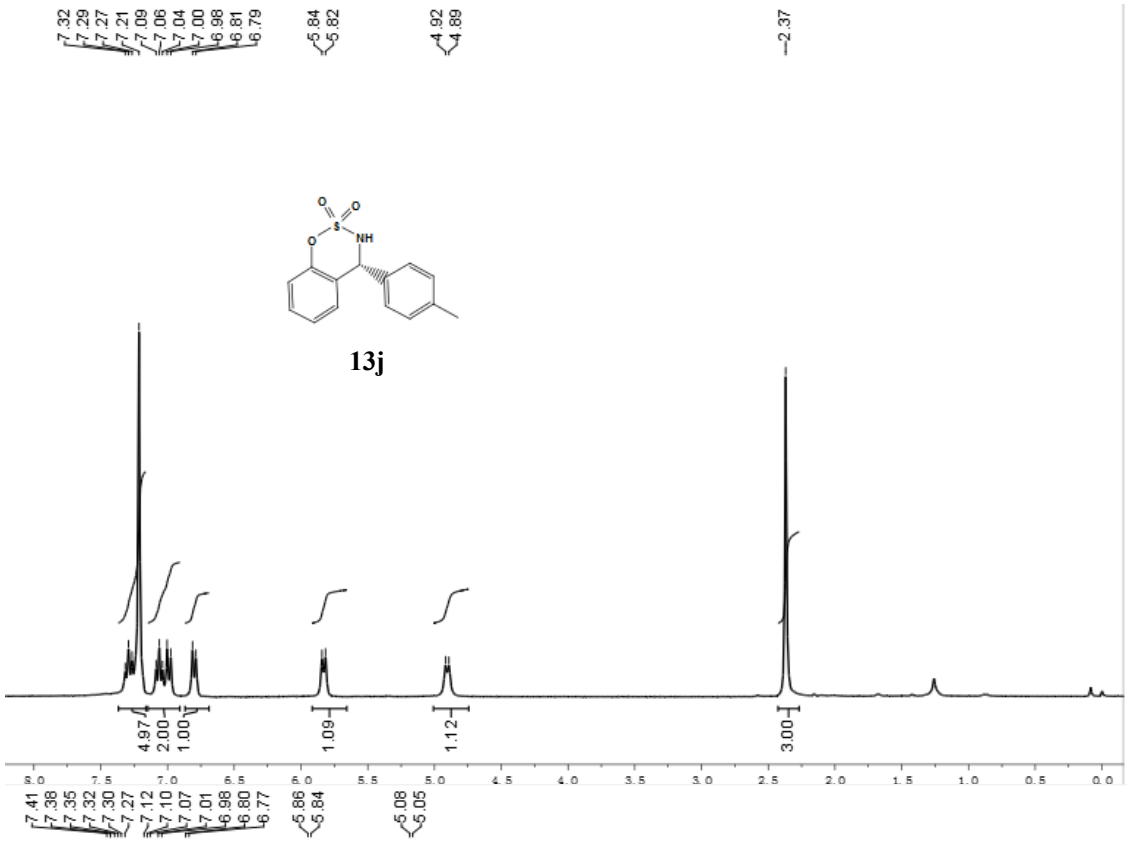
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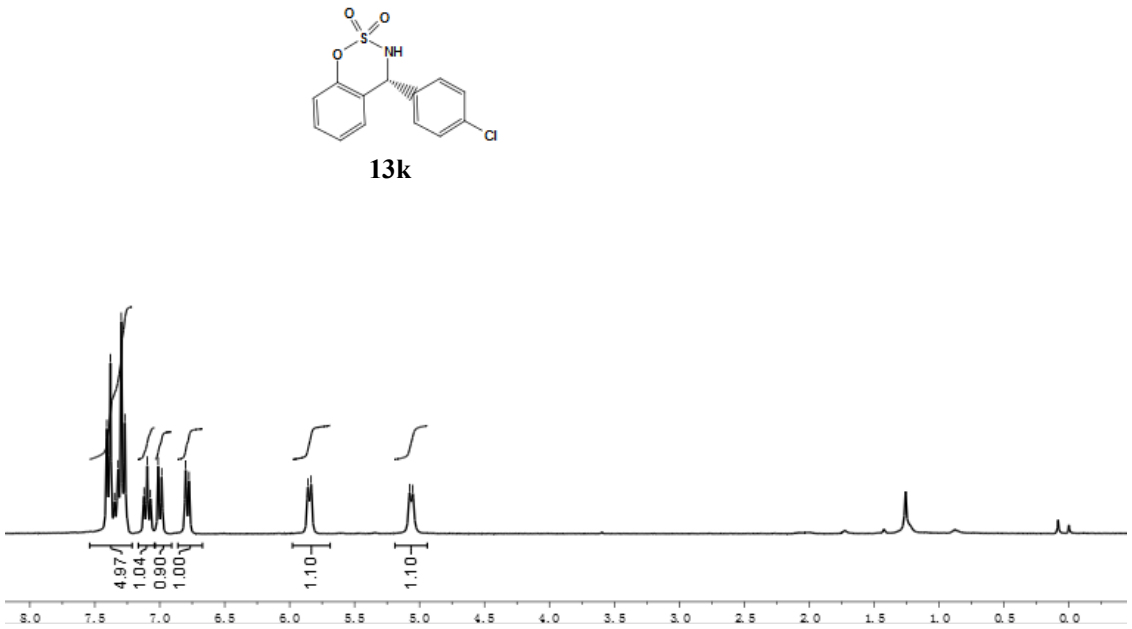
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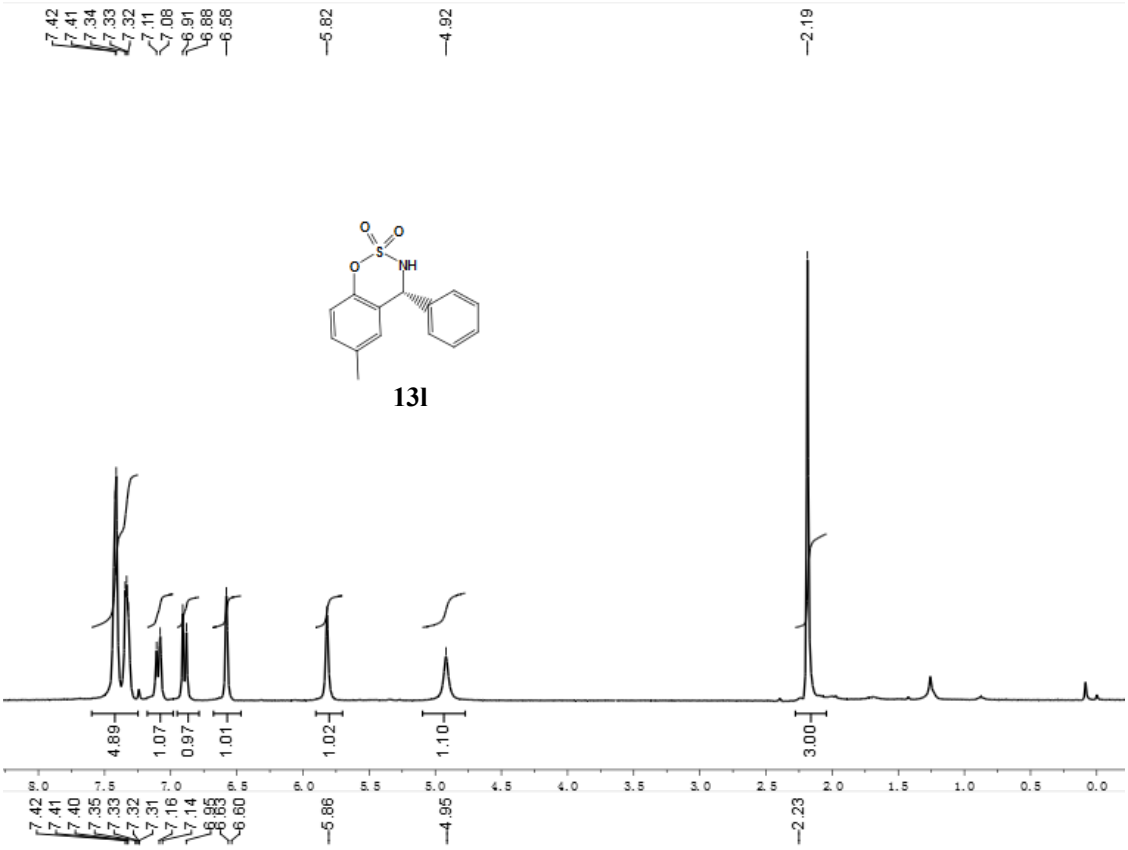
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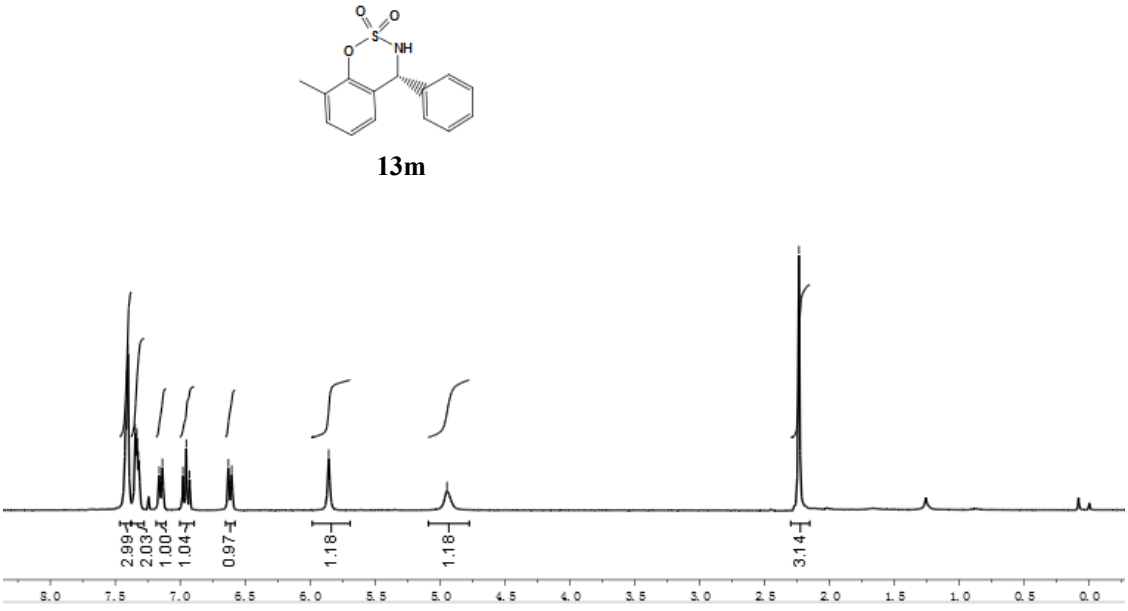
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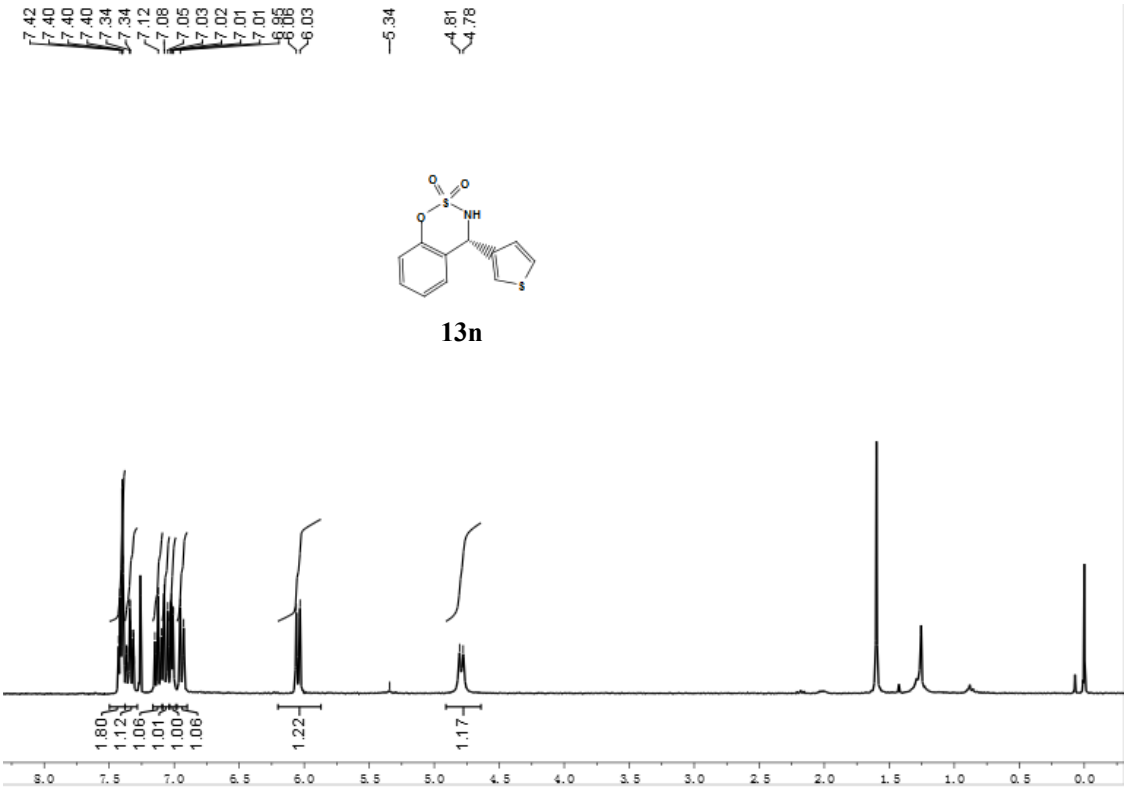
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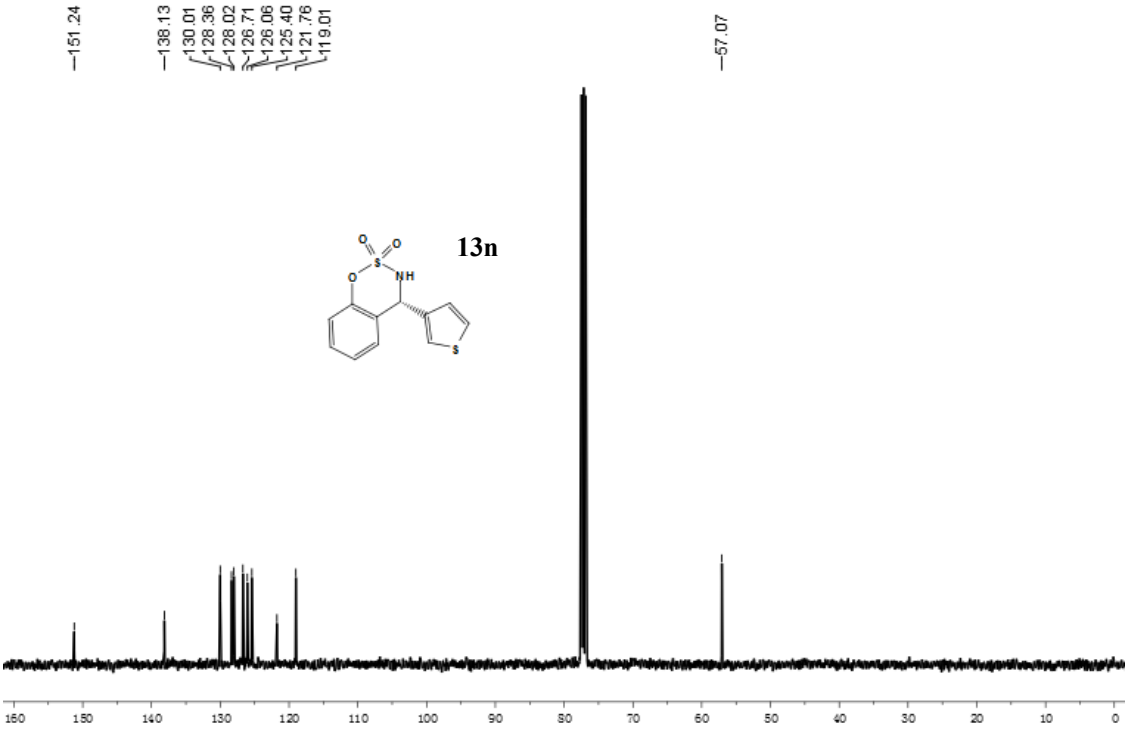
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13n