Supporting Information

New Multifunctional Chiral Phosphines and BINOL Derivatives Co-catalyzed Enantioselective aza-Morita-Baylis-Hillman Reaction of 5,5-Disubstituted Cyclopent-2-enone and *N*-Sulfonated Imines

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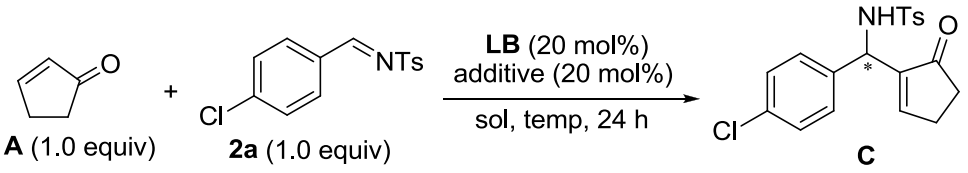
CONTENTS

General Remarks: ^{1}H NMR spectra were recorded on a Bruker AM-300 or AM-400 spectrometer for solution in $CDCl_3$ with tetramethylsilane (TMS) as internal standard; J-values are in Hz. Mass spectra were recorded with a HP-5989 instrument. All of the compounds reported in this paper gave satisfactory HRMS analytic data. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. Optical rotations were determined at 589 nm (sodium D line) by using a Perkin-Elmer-341 MC digital polarimeter; $[\alpha]_D$-values are given in unit of 10 deg^{-1} cm^2 g^{-1}. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm^{-1}. Chiral HPLC was performed on a SHIMADZU SPD-10A vp series with chiral columns (Chiralpak AD-H, IC-H columns 4.6 × 250 mm, (Daicel Chemical Ind., Ltd.)). THF, toluene and Et_2O were distilled from sodium (Na) under argon (Ar) atmosphere. CH_3CN, 1,2-dichloroethane and dichloromethane were distilled from CaH_2 under argon (Ar) atmosphere. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF254 silica gel coated plates. Flash column chromatography was carried out using 300-400 mesh silica gel at increased pressure.

Table S1. Screening for the reaction conditions: effect of choice of chiral phosphine catalysts and additives



A (1.0 equiv) **2a** (1.0 equiv) **C**

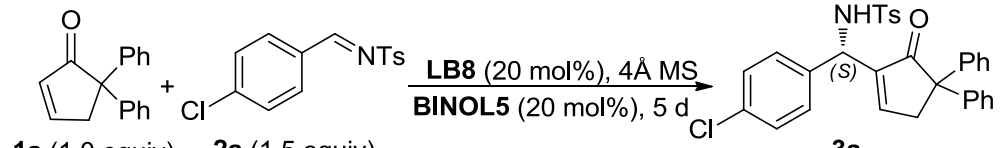
entry	solvent	temperature	catalyst	additive	yield (%)[a]	ee (%)[b]
1	THF	-78 °C ~ rt	**LB1**	-	NR	-
2	THF	-78 °C ~ rt	**LB2**	-	NR	-
3	THF	-78 °C ~ rt	**LB3**	-	NR	-
4	THF	-78 °C ~ rt	**LB4**	-	71	16
5	THF	-78 °C ~ rt	**LB5**	-	NR	-
6	THF	-78 °C ~ rt	**LB6**	-	NR	-
7	THF	-78 °C ~ rt	**LB7**	-	NR	-
8	THF	rt	**LB7**	**BINOL1**	85	15
9	THF	rt	**LB1**	**BINOL1**	72	6
10	THF	rt	**LB8**	**BINOL1**	80	41
11	THF	rt	**LB8**	**BINOL2**	99	15
12	THF	0 °C	**LB8**	**BINOL1**	80	15
13	THF	-20 °C	**LB8**	**BINOL1**	75	17
14	THF	-40 °C	**LB8**	**BINOL1**	76	18
15	THF	35 °C	**LB8**	**BINOL1**	83	21
16	THF	rt	**LB8**	**BINOL4**	Complex	-
17	MTBE	0 °C	**LB8**	**BINOL4**	75	31
18	MTBE	rt	**LB8**	L-Threonine	46	trace

[a]Isolated yields. [b]Determined by chiral HPLC.

Results and Discussion

In order to explore the scope of the reaction, further experiments were conducted using different chiral Lewis bases (**LB1**-**LB9**) and additives (chiral binols) in THF or MTBE (tert-Butyl Methyl ether) (Figure 1). The results were reported in Table S1. The aza-MBH reactions could not proceed smoothly without additive at the temperature range from -78 ^{o}C to room temperature excluding **LB4** (Table S1, entries 1-7). Even so, the corresponding adduct **C** was produced in a moderated yield (71%) with poor enantioselectivity (16% ee) in the presence of **LB4** (Table S1, entry 4). Next, under the above conditions, the additive was added, and the reaction was conducted at room temperature for 24 h. The ee's increased remarkably in the presence of **LB8** (Table S1, entry 10). When using **BINOL4** as an additive, the reaction system was disordered (Table S1, entry 16). In order to obtain excellent enantioselectivities, we decided to take the effect of temperature into consideration. Though the reactions went well at different temperatures, the enantioselectivities of **C** were still poor (Table S1, entries 12-15). Switching THF to MTBE had a negative influence on yields and enantioselectivities (Table S1, entries 17, 18). Finally, when using chiral amino acid (L-Threonine) as an additive, the product was racemic. Comparing entry 10 with entry 11 (Table S1), we found that the different configuration of chiral binols did not have impact on the product configuration. In addition, the acidity of free OH may affect the yield of product (Table S1, entry 11 vs 16).

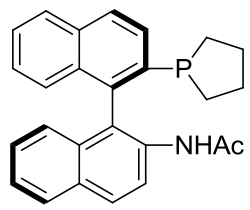
Table S2. Screening of Solvent Effects on the aza-MBH Reaction **1a** with **2a** in the Presence of **LB8**



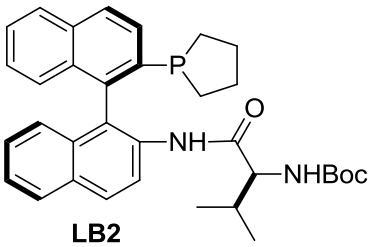
1a (1.0 equiv) **2a** (1.5 equiv) **3a**

entry	temperature	solvent	yield (%)[a]	ee (%)[b]
1	-50 °C	DCM	92	50
2	-50 °C	toluene	85	82
3	-50 °C	$CHCl_3$	81	43
4	-50 °C	Et_2O	-	-
5	-25 °C	Et_2O	-	-
6	-50 °C	DMF	54	51
7	-50 °C	THF	92	81
8	-40 °C	MeCN	-	-
9	-25 °C	MeCN	65	35
10	-25 °C	trifluoromethylbenzene	70	60
11	-50 °C	MTBE	-	-
12	-25 °C	MTBE	58	72
13	-25 °C	CH_3NO_2	-	-
14	-40 °C	fluorobenzene	92	64
15	-50 °C	toluene/THF = 1:1	58	62
16	-50 °C	*fluorobenzene/THF = 1:1*	*90*	*82*
17	-50 °C	$CHCl_3$/THF = 1 :1	81	62
18	-50 °C	fluorobenzene/THF = 1:4	92	78
19	-50 °C	toluene/$CHCl_3$ = 1:1	81	70
20	-50 °C	MTBE/DCM = 1:1	73	79
21	-50 °C	toluene/fluorobenzene = 2:1	88	66
22	-50 °C	trifluoromethylbenzene/THF = 1:2	81	64
23	-50 °C	trifluoromethylbenzene/toluene = 1:2	88	77
24	-50 °C	fluorobenzene/THF =1:2	85	61
25	-50 °C	$CHCl_3$/THF = 1:2	77	51
26[c]	-50 °C	THF	69	70

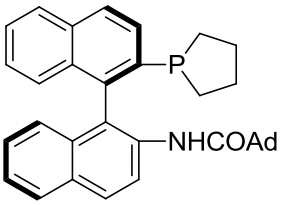
[a]Isolated yield. [b]Determined by chiral HPLC. [c]The catalyst and additive were reduced by half (10 mol%).



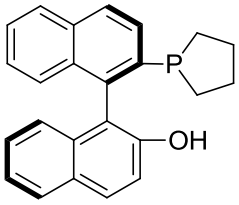
LB1



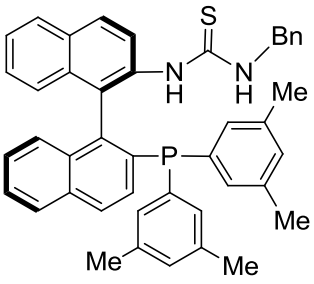
LB2



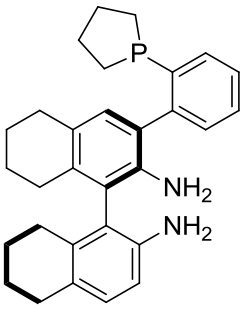
LB3



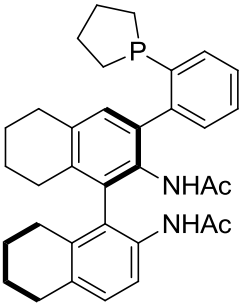
LB4



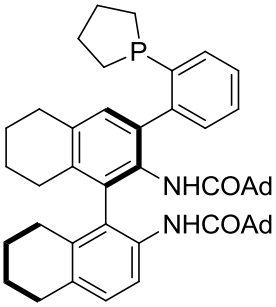
LB5



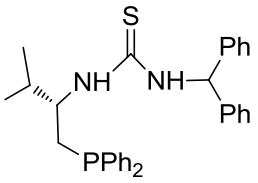
LB6



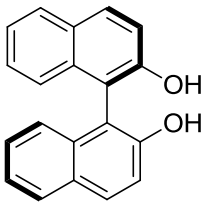
LB7



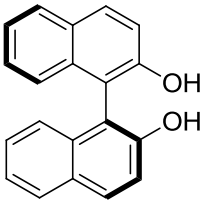
LB8
Ad = 1-adamantane



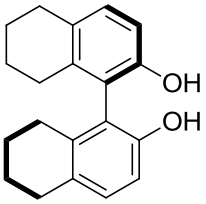
LB9



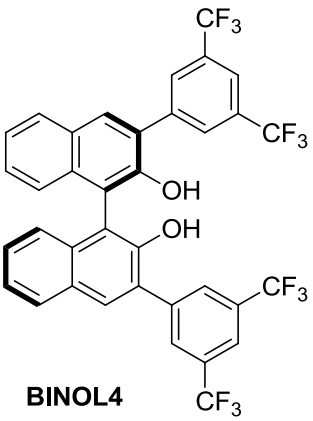
BINOL1



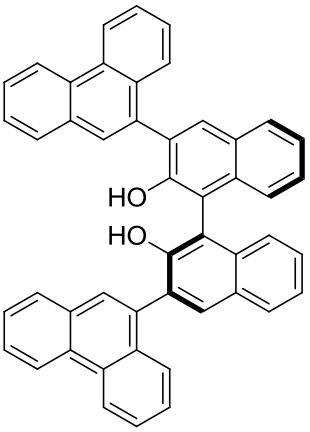
BINOL2



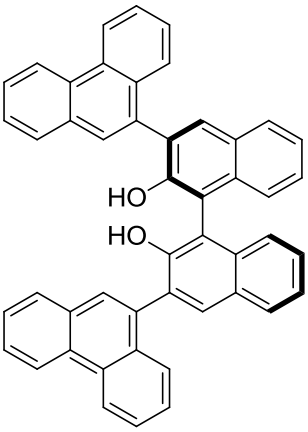
BINOL3



BINOL4



BINOL5



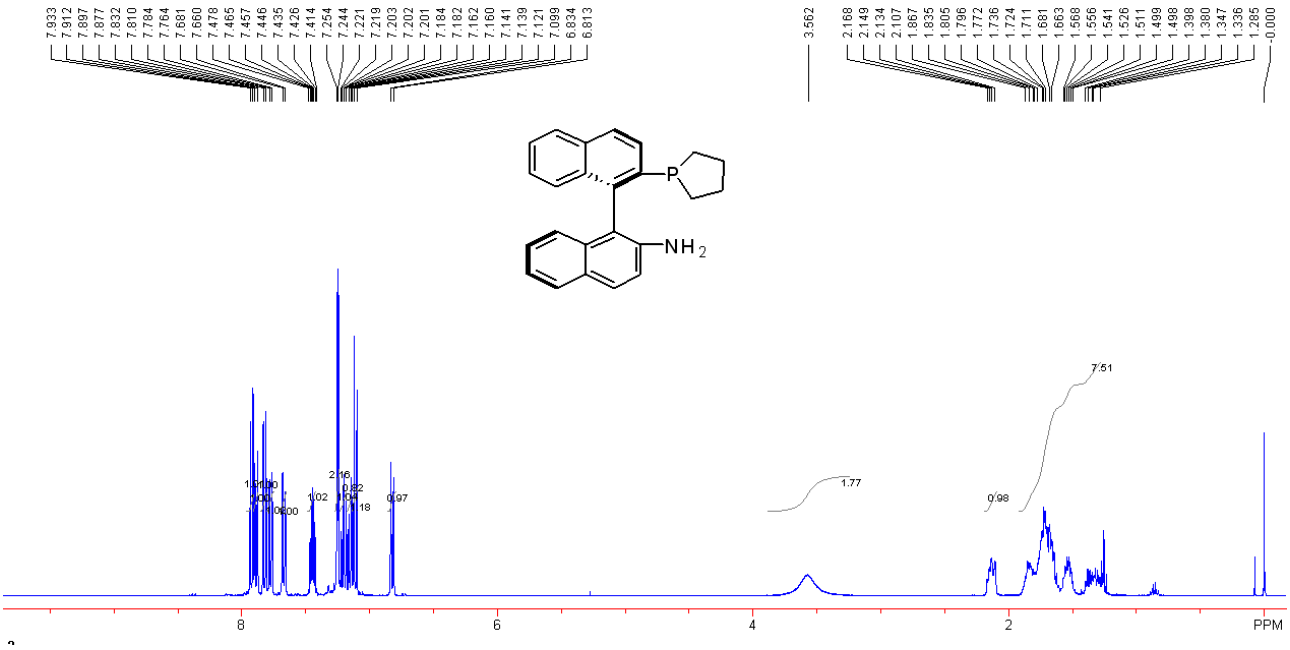
BINOL6

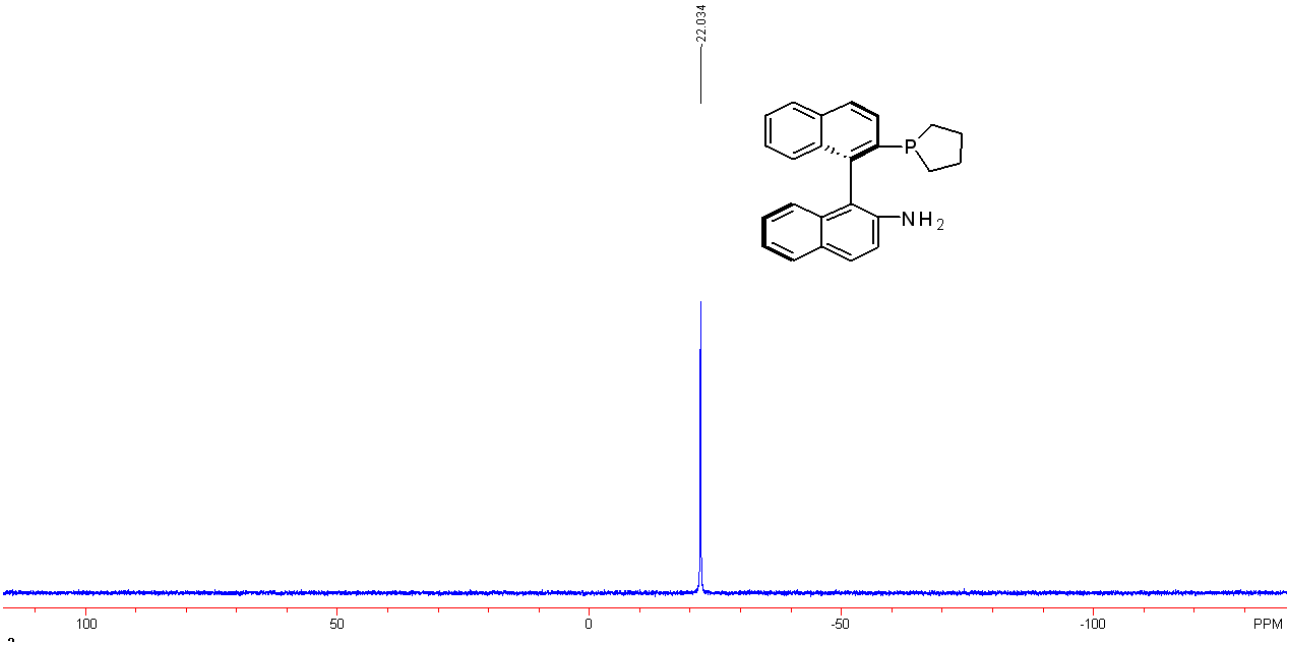
Reaction Procedure for the Preparation of Catalysts:

Amine precursor of LB1: (*R*)-2'-(phospholan-1-yl)-1,1'-binaphthyl-2-amine

Procedure: This compound was prepared according to the previous literature.[1] A white solid. m.p. 178-180 ^{o}C; $[\alpha]^{20}_{D}$ = -92.9 (c 0.6, CH_2Cl_2). IR (CH_2Cl_2) ν 3378, 3050, 2927, 2855, 1618, 1511, 1471, 1431, 1379, 1351, 1262, 1211, 1144, 1094, 1022, 963, 933, 810, 773, 734 cm^{-1}; ^{1}H NMR

(400 MHz, $CDCl_3$, TMS): δ 7.92 (1H, d, *J* = 8.4 Hz), 7.89 (1H, d, *J* = 8.0 Hz), 7.82 (1H, d, *J* = 8.8 Hz), 7.77 (1H, d, *J* = 8.0 Hz), 7.67 (1H, d, *J* = 8.4 Hz), 7.45 (1H, qu, *J* = 8.4 Hz), 7.25 (1H, s), 7.24 (1H, s), 7.22-7.18 (1H, m), 7.16-7.14 (1H, m), 7.11 (1H, d, *J* = 9.2 Hz), 6.82 (1H, d, *J* = 8.4 Hz), 3.56 (2H, brs), 2.17-2.11 (1H, m), 1.87-1.29 (7H, m); ^{31}P NMR (162 MHz, $CDCl_3$, 85% H_3PO_4): δ -22.0; MS (ESI) *m/z* (%) 356.1 [M^++H]; HRMS (ESI) Calcd for $C_{24}H_{23}NP^{+1}$ [M^++H] requires 356.1490, Found 356.1488.

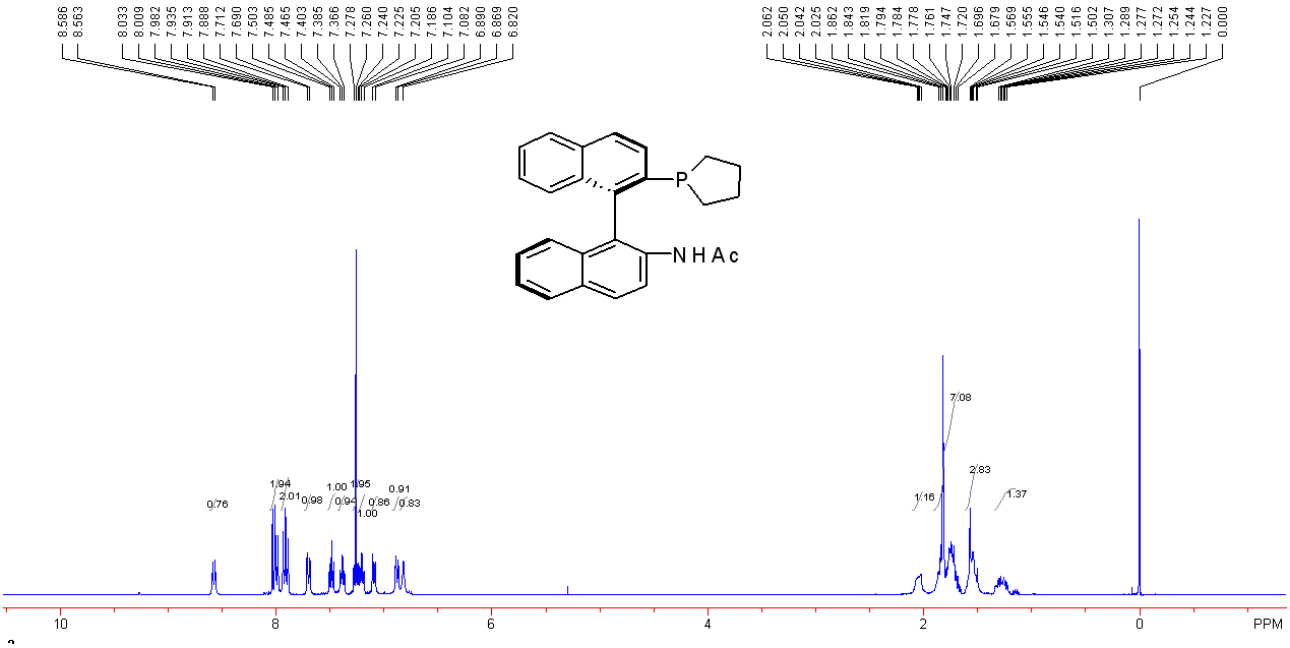


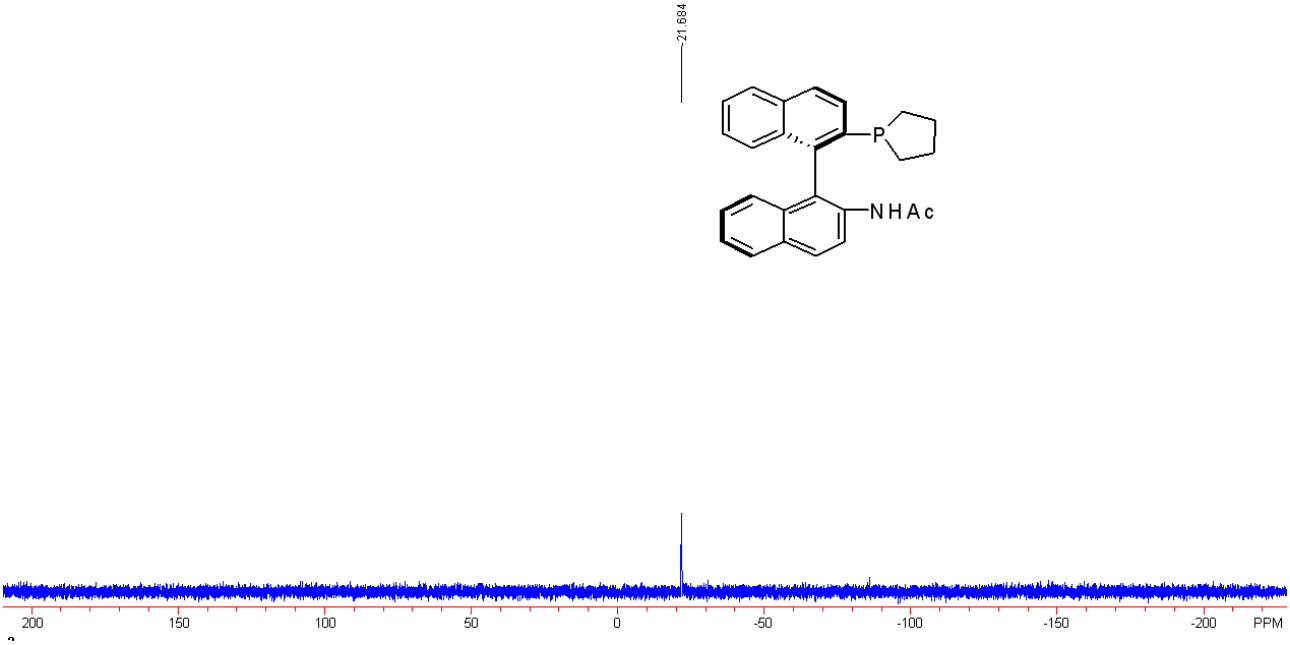


LB1: **(*R*)-N-(2'-(phospholan-1-yl)-1,1'-binaphthyl-2-yl)acetamide**

Procedure: This compound was prepared according to the previous literature.[1] A white solid. m.p.

102-104 °C; $[\alpha]^{20}_{D}$ = -81.0 (c 0.3, CH_2Cl_2). IR (CH_2Cl_2) ν 3411, 3064, 2959, 2925, 2857, 1693, 1596, 1496, 1424, 1263, 1096, 1016, 867, 798, 733 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 8.57 (1H, d, *J* = 9.2 Hz), 8.01 (2H, t, *J* = 9.2 Hz), 7.91 (2H, t, *J* = 8.8 Hz), 7.70 (1H, d, *J* = 8.8 Hz), 7.49 (1H, t, *J* = 8.0 Hz), 7.39 (1H, t, *J* = 7.8 Hz), 7.26 (1H, t, *J* = 7.8 Hz), 7.21 (1H, t, *J* = 7.8 Hz), 7.10 (1H, d, *J* = 7.2 Hz), 6.88 (1H, d, *J* = 8.4 Hz), 6.82 (1H, s), 2.06-2.02 (1H, m), 1.86-1.68 (4H, m), 1.82 (3H, s), 1.57-1.50 (2H, m), 1.30-1.23 (1H, m); ^{31}P NMR (162 MHz, $CDCl_3$, 85% H_3PO_4): δ -21.7; MS (ESI) *m/z* (%) 398.2 [M^++H]; HRMS (ESI) Calcd for $C_{26}H_{25}NOP^{+1}$ [M^++H] requires 398.1596, Found 398.1595.

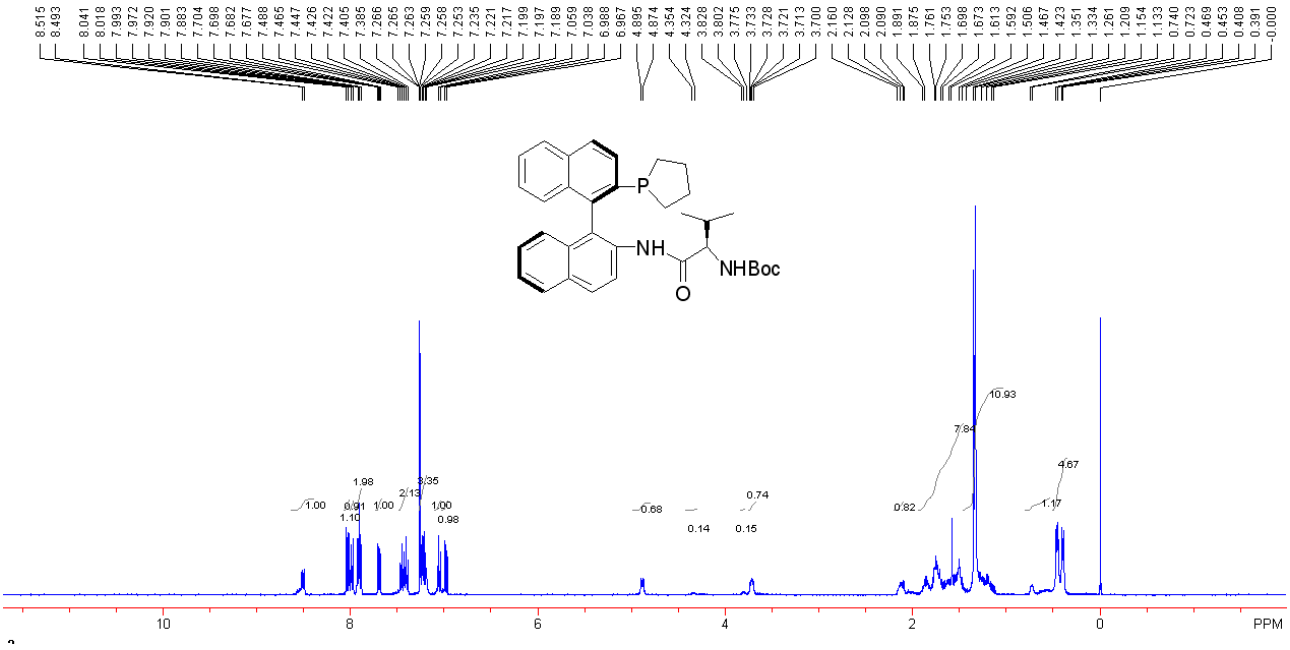


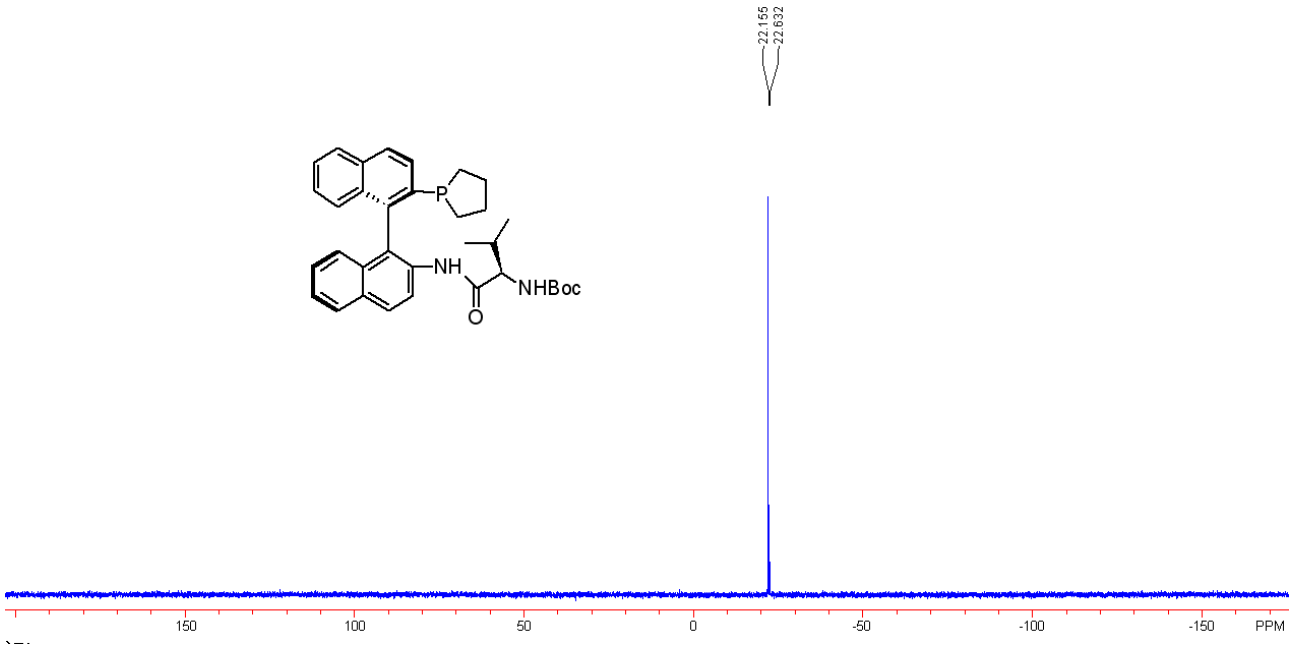


LB2:

tert-butyl (*R*)-3-methyl-1-oxo-1-((*R*)-2'-(phospholan-1-yl)-1,1'-binaphthyl-2-ylamino)butan-2-ylcarbamate

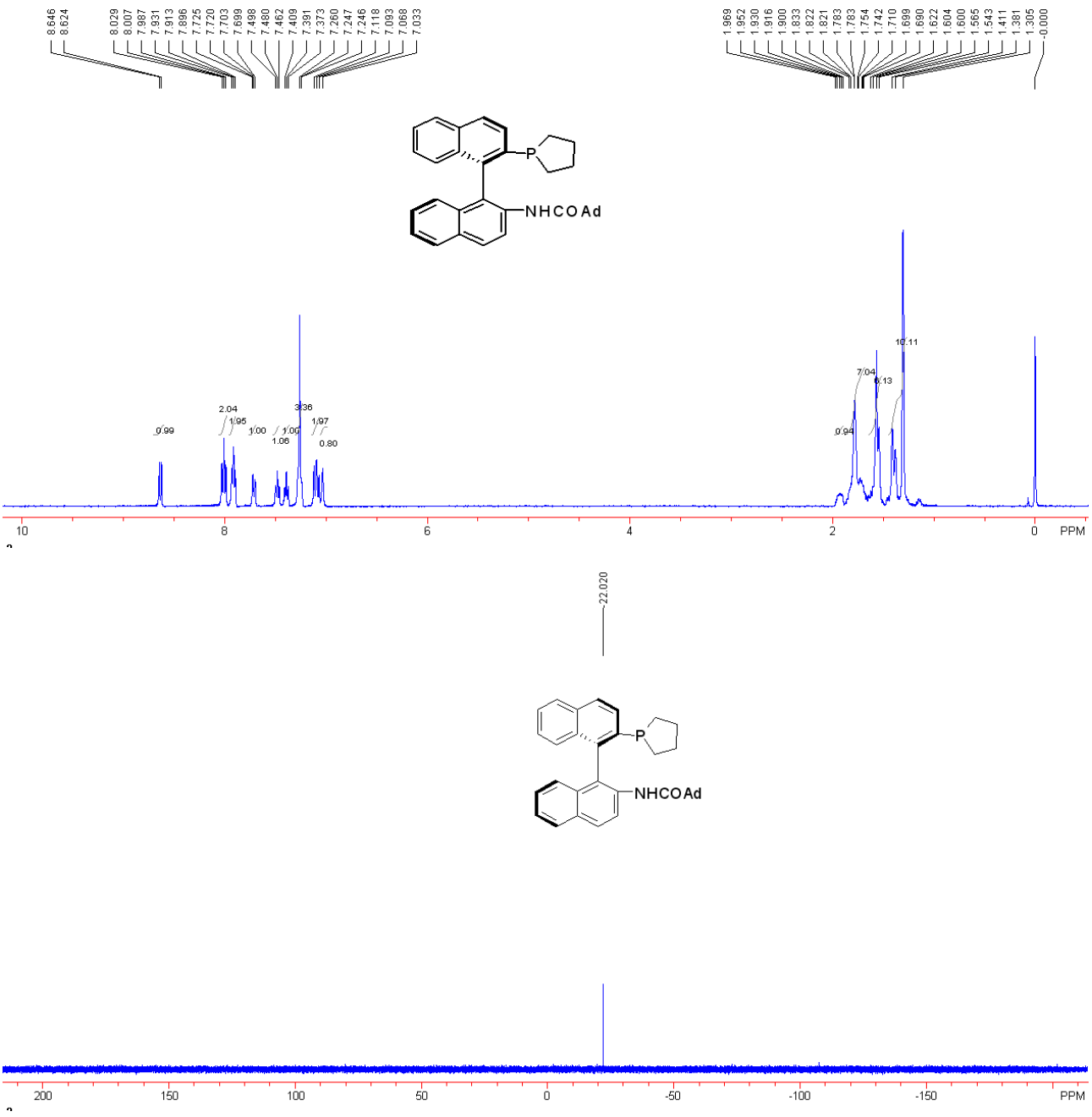
Procedure: This compound was prepared according to the previous literature.[2] A white solid. m.p. 98-100 ^{o}C; $[\alpha]^{20}_{D}$ = + 12 (c 0.3, CH_2Cl_2). IR (CH_2Cl_2) ν 3402, 3369, 3054, 2960, 2931, 2871, 1691, 1500, 1427, 1366, 1331, 1264, 1168, 1019, 895, 736 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (rotamer: major/minor = 5/1) 8.50 (1H, d, *J* = 8.8 Hz), 8.03 (1H, d, *J* = 9.2 Hz), 7.98 (1H, d, *J* = 8.4 Hz), 7.90 (2H, t, *J* = 7.2 Hz), 7.69 (1H, dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz), 7.49-7.39 (2H, m), 7.27-7.19 (3H, m), 7.05 (1H, d, *J* = 8.4 Hz), 6.98 (1H, d, *J* = 8.4 Hz), 4.88 (0.68H, d, *J* = 8.4 Hz), 4.34 (0.14H, d, *J* = 8.4 Hz), 3.83-3.77 (0.15H, m), 3.73-3.70 (0.74H, m), 2.16-2.09 (1H, m), 1.89-1.42 (7H, m), 1.35-1.13 (10H, m), 0.46 (3H, d, *J* = 7.8 Hz), 0.40 (3H, d, *J* = 7.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$, 85% H_3PO_4): δ -22.2, -22.6; MS (ESI) *m/z* (%) 555.3 [M^++H]; HRMS (ESI) Calcd for $C_{34}H_{40}N_2O_3P^{+1}$ [M^++H] requires 555.2689, Found 555.2701.





LB3: (*R*)-N-(2'-(phospholan-1-yl)-1,1'-binaphthyl-2-yl)adamantanecarboxamide

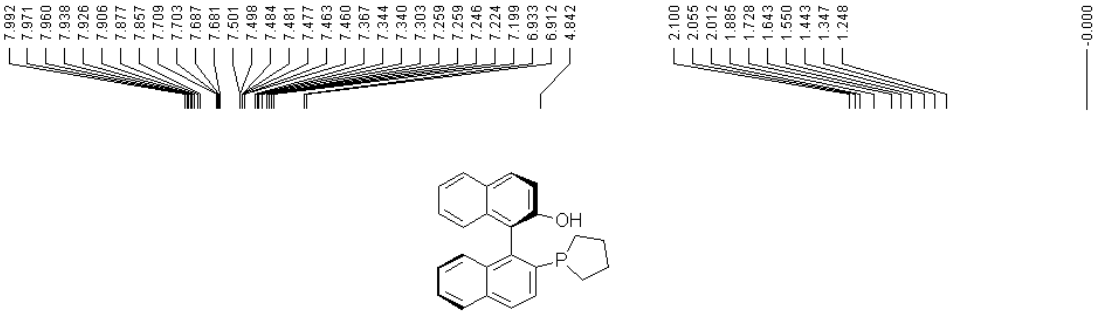
Procedure: This compound was prepared according to the previous literature.[3] A white solid. m.p. 187-190 ^{o}C; $[\alpha]^{20}_{D}$ = -147.9 (c 0.5, CH_2Cl_2). IR (CH_2Cl_2) ν 3417, 3055, 2924, 2851, 1727, 1683, 1620, 1594, 1499, 1453, 1426, 1376, 1332, 1263, 1219, 1103, 937, 814, 736 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.63 (1H, d, *J* = 8.8 Hz), 8.01 (2H, t, *J* = 8.8 Hz), 7.91 (2H, t, *J* = 8.8 Hz), 7.71 (1H, dd, J_1 = 8.8 Hz, J_2 = 2.0 Hz), 7.48 (1H, t, *J* = 7.2 Hz), 7.39 (1H, t, *J* = 7.2 Hz), 7.26-7.25 (1H, m), 7.10 (2H, t, *J* = 10.0 Hz), 7.03 (1H, s), 1.97-1.90 (1H, m), 1.83-1.69 (7H, m), 1.82 (3H, s), 1.62-1.54 (6H, m), 1.41-1.30 (10H, m); ^{31}P NMR (162 MHz, $CDCl_3$, 85% H_3PO_4): δ -22.0; MS (ESI) *m/z* (%) 518.3 [M^{+}+H]; HRMS (ESI) Calcd for $C_{35}H_{37}NOP^{+1}$ [M^{+}+H] requires 518.2535, Found 518.2537.

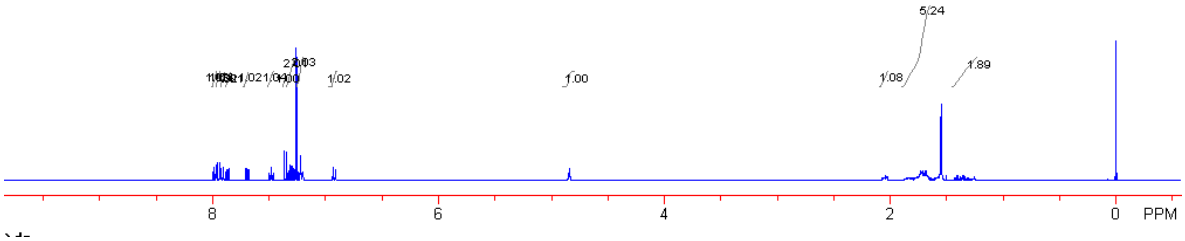


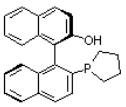
LB4: (R)-2'-(phospholan-1-yl)-1,1'-binaphthyl-2-ol

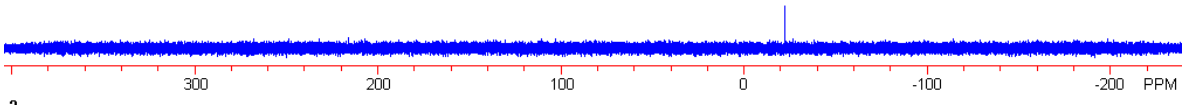
Procedure: This compound was prepared according to the previous literature.[3][4] A white solid. m.p. 188-200 ^{o}C; $[\alpha]^{20}_{D}$ = -120.6 (c 1.0, $CHCl_3$). IR (KBr): ν 3506, 3425, 3054, 2933, 2856, 1619, 1594, 1514, 1501, 1345, 1265, 1203, 1143, 866, 812, 735, 683 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.98 (1H, d, *J* = 8.8 Hz), 7.95 (1H, d, *J* = 8.8 Hz), 7.92 (1H, d, *J* = 8.0 Hz), 7.87 (1H, d, *J* = 8.0 Hz), 7.70 (1H, dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz), 7.48 (1H, dt, J_1 = 8.0 Hz, J_2 = 1.2 Hz), 7.36 (1H, d, *J* = 8.8 Hz), 7.34-7.26 (2H, m), 7.25-7.20 (2H, m), 6.92 (1H, d, *J* = 8.4 Hz), 4.84 (1H, s, OH), 2.10-2.01 (1H, m), 1.89-1.64 (5H, m), 1.44-1.25 (2H, m); ^{31}P NMR ($CDCl_3$, 121.5 MHz, 85%

H_3PO_4): δ -21.69, -21.71; MS (EI) *m/z* (%): 356 (34.94) [M^+], 355 (18.83), 340 (27.25), 399 (100), 281 (14.69), 268 (29.67), 252 (17.67), 239 (20.96); HRMS (EI) Calcd. For $C_{24}H_{21}PO^{+1}$ (M^+) requires 356.1330, Found: 356.1324.

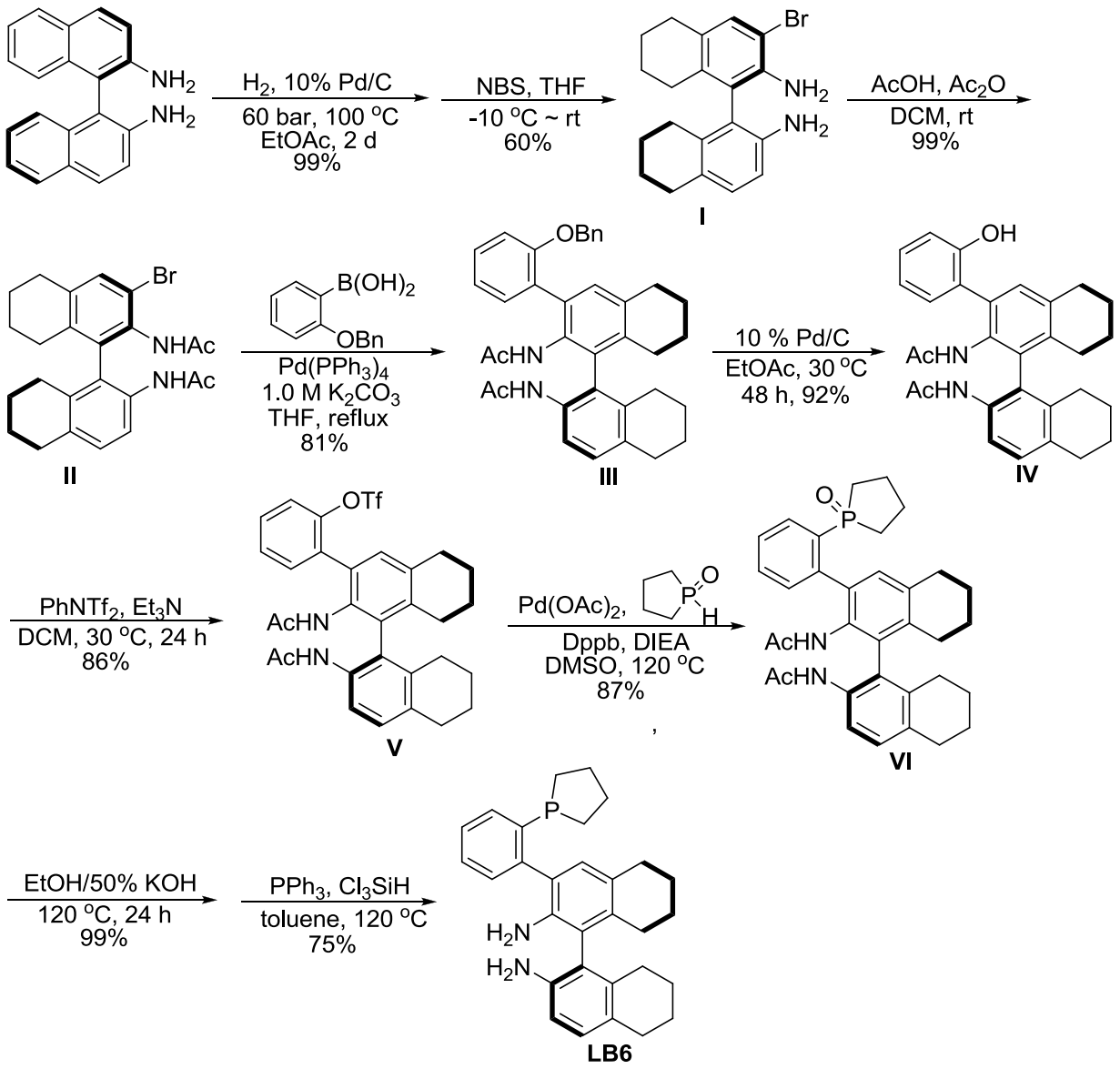








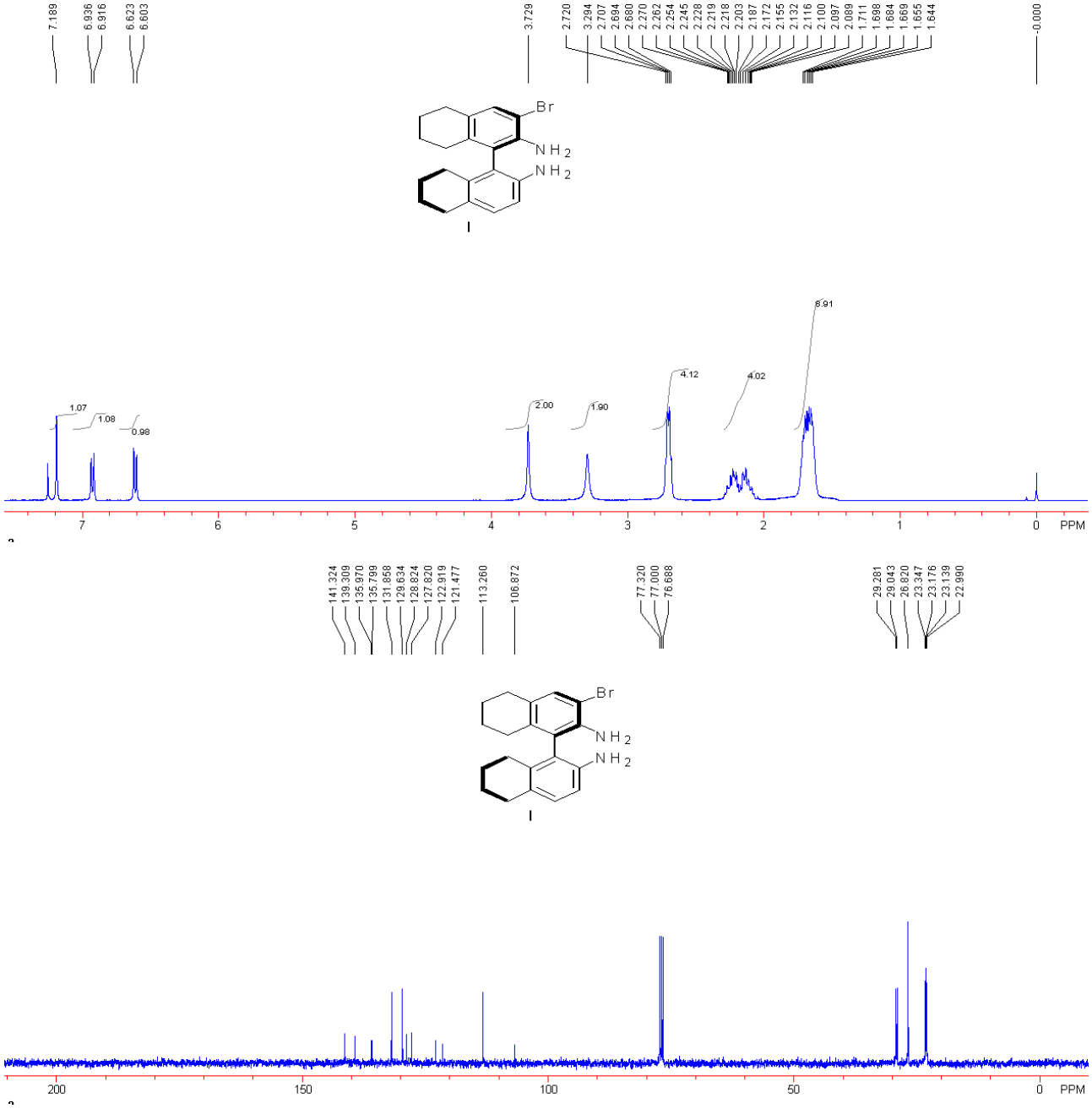
Reaction Procedure for the Preparation of Catalysts: **(*R*)-3-(2-(phospholan-1-yl)phenyl)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl-2,2'-diamine**



Compound I: (*R*)-3-bromo-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl-2,2'-diamine

Procedure: A mixture of (*R*)-1,1'-binaphthyl-2,2'-diamine (2.0 g, 7.0 mmol) and 250 mg 10% Pd/C in 100 mL ethyl acetate was heated to 100 °C under 60 bar H_2 for 2 days. After the catalyst was filtered off, the solvent was removed under reduced pressure and the residue was used for next step without further purification. To a stirred solution of above residue (1.0 g , 3.42 mmol) in dry THF 20 mL at - 10 °C under Ar atmosphere was added dropwise the solution of NBS (670 mg NBS in 10 mL THF, 3.77 mmol). The resultant solution was stirred for 1.5 h before it was quenched with saturated $NaHCO_3$, extracted with CH_2Cl_2 twice, then the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (EtOAc/PE = 1/16

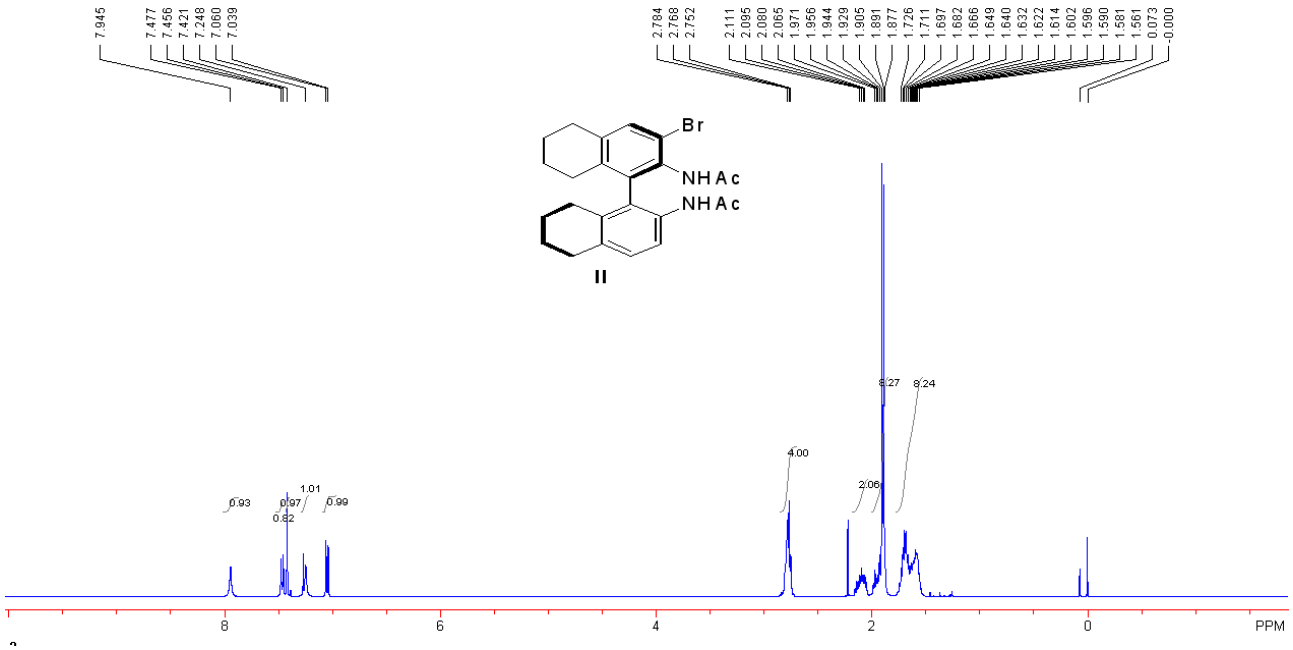
as eluent) to furnish product **I** as yellow solid (750 mg, 2.03 mmol, 60% yield). m.p. 80-82 ^{o}C; $[\alpha]^{20}_{D}$ = +74.3 (c 0.8, CH_2Cl_2). IR (CH_2Cl_2) ν 3466, 3371, 2926, 2854, 2834, 1604, 1482, 1457, 1305, 1286, 1261, 1148, 1099, 945, 909, 864, 810, 736 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.19 (1H, s), 6.93 (1H, d, *J* = 8.0 Hz), 6.61 (1H, d, *J* = 8.0 Hz), 3.73 (2H, s), 3.29 (2H, s), 2.70 (4H, q, J_1 = 5.2 Hz), 2.27-2.09 (4H, m), 1.71-1.64 (8H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.3, 139.3, 136.0, 135.8, 131.9, 129.6, 128.8, 127.8, 122.9, 121.4, 113.3, 106.9, 29.3, 29.0, 26.8, 23.3, 23.2, 23.1, 23.0; MS (EI) *m/z* (%) 375 (0.32) [M^{+}], 372 (100), 371 (34.83), 370 (97.50), 355 (2.23), 342 (2.35), 291 (9.02), 274 (13.96), 262 (4.54), 247 (5.21), 232 (7.49), 217 (5.02) ; HRMS (EI) Calcd for $C_{20}H_{23}N_2Br$ [M^{+}] requires 370.1045, Found 370.1043.

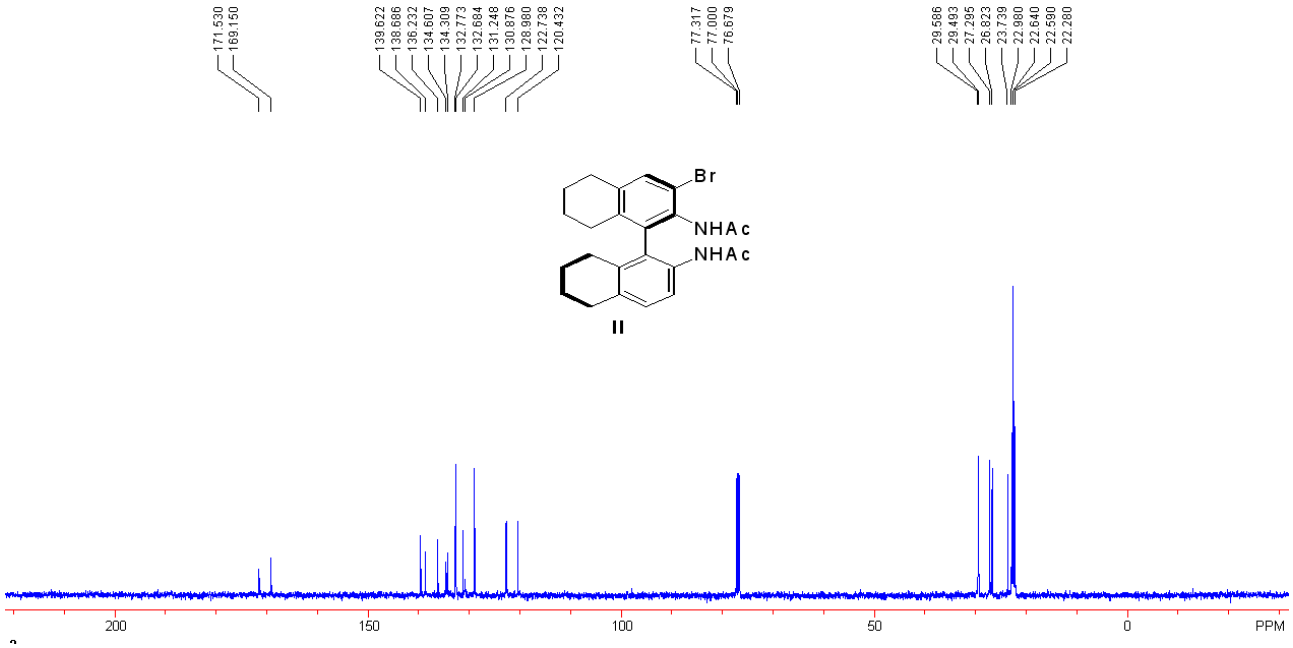


Compound II:

(*R*)-N,N'-(3-bromo-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl-2,2'-diyl)diacetamide

Procedure: Compound **I** (640 mg, 2.0 mmol) was dissolved in 2.0 mL of CH_2Cl_2 mixed with 1.0 mL AcOH and 1.0 mL Ac_2O and the resulting mixture was stirred at room temperature overnight. The reaction was quenched by addition of saturated $NaHCO_3$ solution, and then extracted with CH_2Cl_2, dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel (EtOAc/PE = 1/1 as eluent) to yield product **II** as off-white solid (812 mg, 99% yield). m.p. 170-173 ^oC; $[\alpha]^{20}_D$ = -98.5 (c 0.6, CH_2Cl_2). IR (CH_2Cl_2) ν 3231, 2928, 2856, 1663, 1595, 1519, 1448, 1395, 1368, 1314, 1292, 1262, 1092, 1012, 909, 865, 810, 734 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.95 (1H, brs), 7.47 (1H, d, *J* = 8.4 Hz), 7.42 (1H, s), 7.25 (1H, brs), 7.05 (1H, d, *J* = 8.4 Hz), 2.77 (4H, t, *J* = 6.4 Hz), 2.14-2.05 (2H, m), 1.97-1.88 (2H, m), 1.91 (3H, s), 1.89 (3H, s), 1.73-1.56 (8H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.5, 169.2, 139.6, 138.7, 136.2, 134.6, 134.3, 132.8, 132.7, 131.2, 130.9, 129.0, 122.7, 120.4, 29.6, 29.5, 27.3, 26.8, 23.7, 23.0, 22.7, 22.6, 22.3; MS (ESI) *m/z* (%) 477.3 [M^++Na]; HRMS (ESI) Calcd for $C_{24}H_{27}N_2O_2BrNa^{+1}$ [M^++Na] requires 477.1154, Found 477.1148.

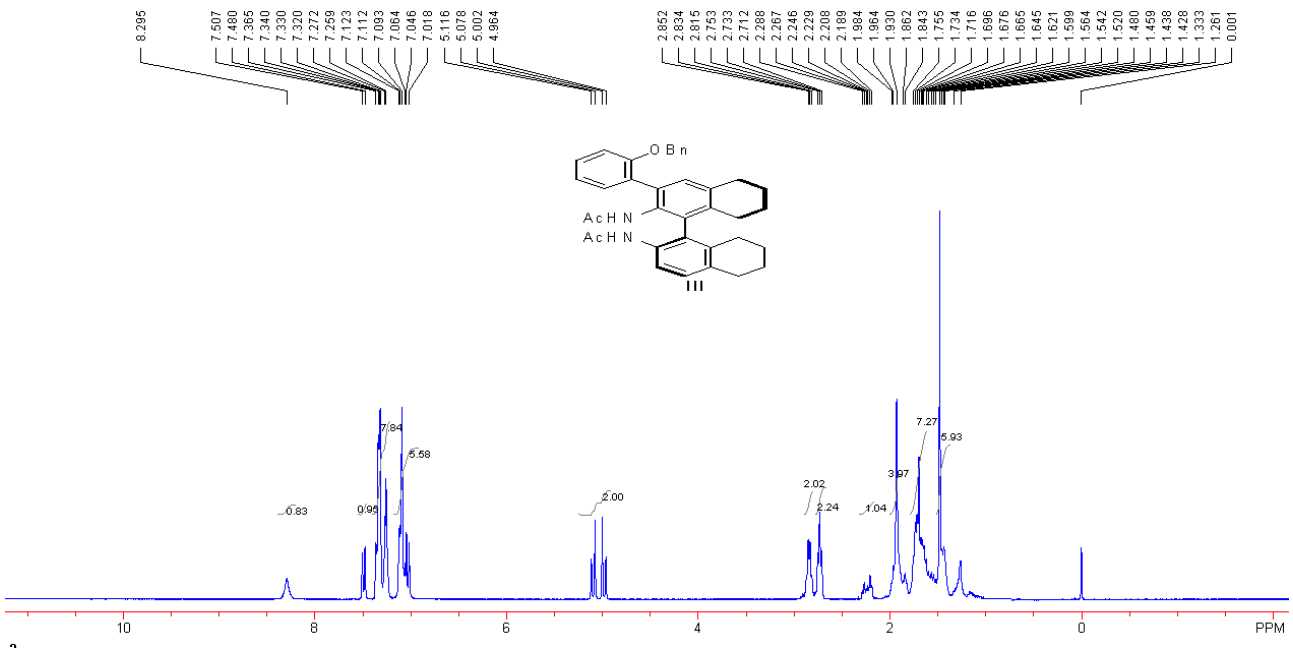


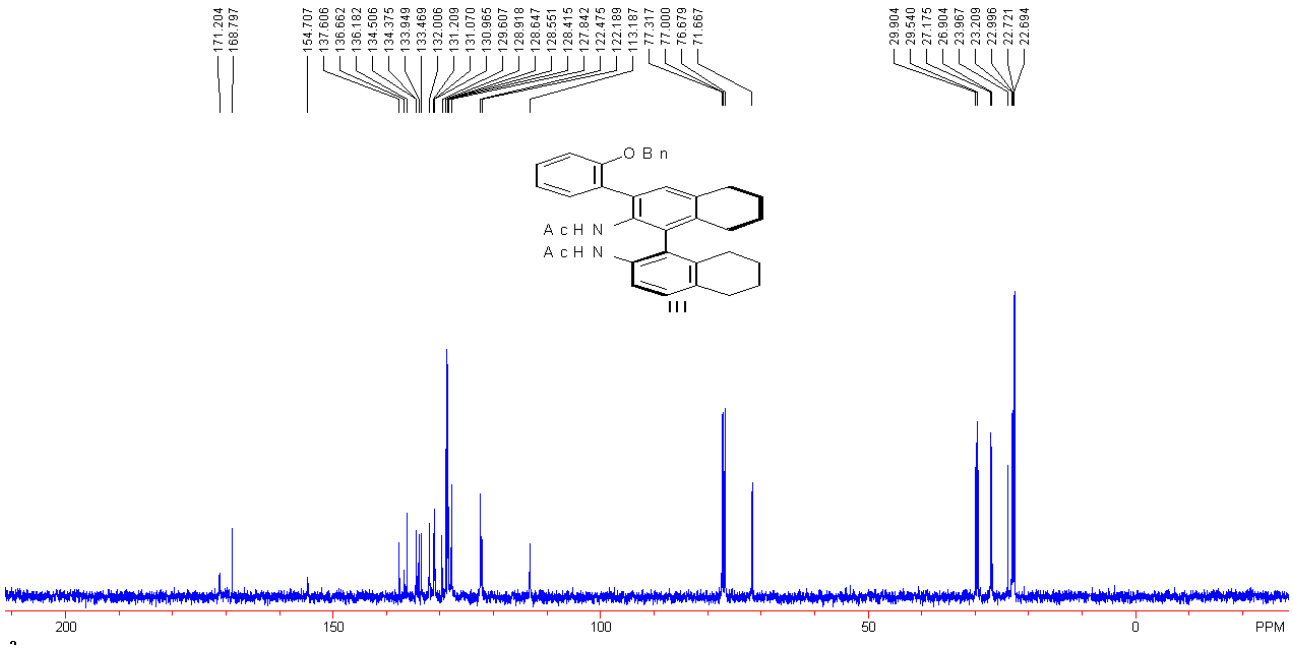


Compound III:

(*R*)-N,N'-(3-(2-(benzyloxy)phenyl)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl-2,2'-diyl)diacetamide

Procedure: To a mixture of Compound **II** (745 mg, 1.64 mmol), 2-(benzyloxy)phenylboronic acid (562 mg, 2.46 mmol) and 1.0 M K_2CO_3 (10 mL) in THF (20 mL) under Ar atmosphere was added $Pd(PPh_3)_4$ (190 mg, 0.16 mol) and the mixture degassed for three times. Then the resulting mixture was heated to reflux for 10 h , cooled to room temperature and quenched by addition of 10% HCl, extracted with CH_2Cl_2 twice, dried by anhydrous Na_2SO_4. The solution was concentrated and the residue was purified by column chromatography on silica gel (EtOAc/PE = 1/2 as eluent), which allowed to isolate Compound **III** as white solid (740 mg, 81% yield). m.p. 127-129 ^oC; $[\alpha]^{20}_D$ = -177.2 (c 0.8, CH_2Cl_2). IR (CH_2Cl_2) ν 3252, 3029, 2928, 2856, 1661, 1595, 1521, 1497, 1435, 1402, 1368, 1314, 1290, 1269, 1222, 1182, 1113, 1009, 981, 752, 735 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 8.30 (1H, brs), 7.49 (1H, d, *J* = 8.1 Hz), 7.37-7.26 (7H, m), 7.12-7.02 (5H, m), 5.10 (1H, d, *J* = 8.4 Hz), 4.98 (1H, d, *J* = 8.4 Hz), 2.85-2.71 (4H, m), 2.27-2.19 (1H, m), 1.98-1.84 (4H, m), 1.76-1.52 (7H, m), 1.48 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.2, 168.8, 154.7, 137.6, 136.7, 136.2, 134.5, 134.4, 133.9, 133.5, 132.0, 131.2, 131.0, 129.6, 128.9, 128.6, 128.5, 128.4, 127.8, 122.5, 122.2, 113.2, 71.7, 29.9, 29.5, 27.2, 26.9, 24.0, 23.2, 23.0, 22.72, 22.70; MS (ESI) *m/z* (%) 581.6 [M^++Na]; HRMS (ESI) Calcd for $C_{37}H_{38}N_2O_3Na^+$ [M^++Na] requires 581.2760, Found 581.2774.



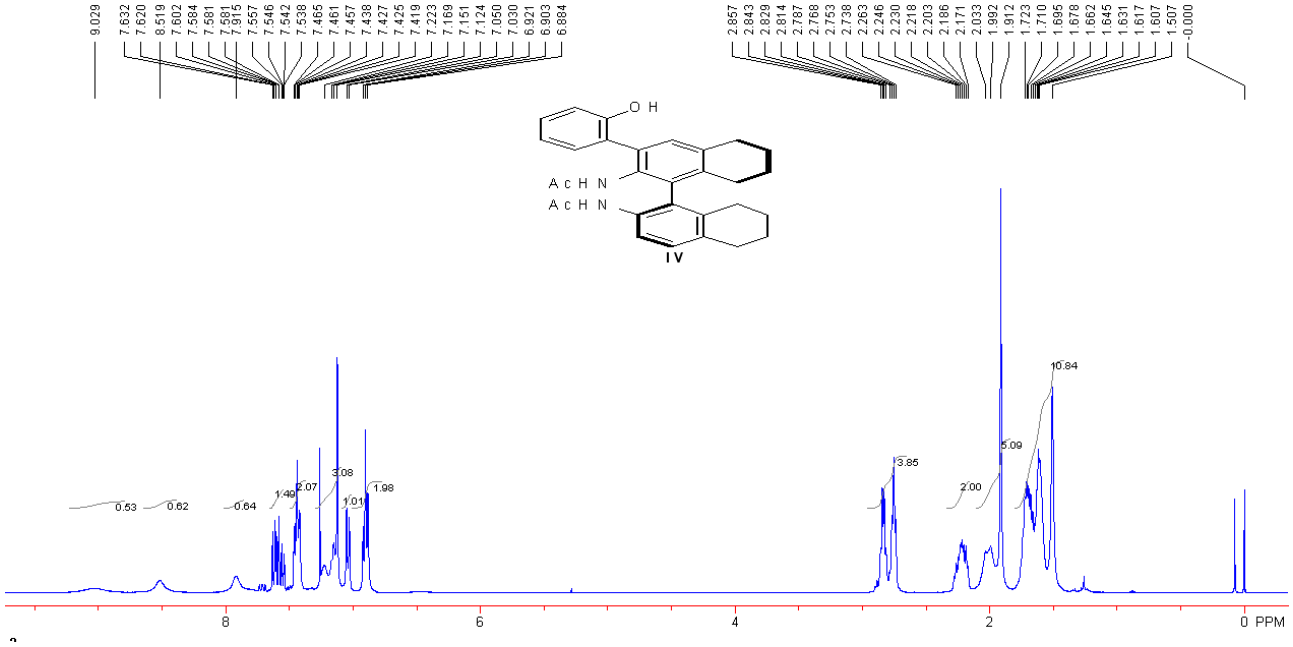


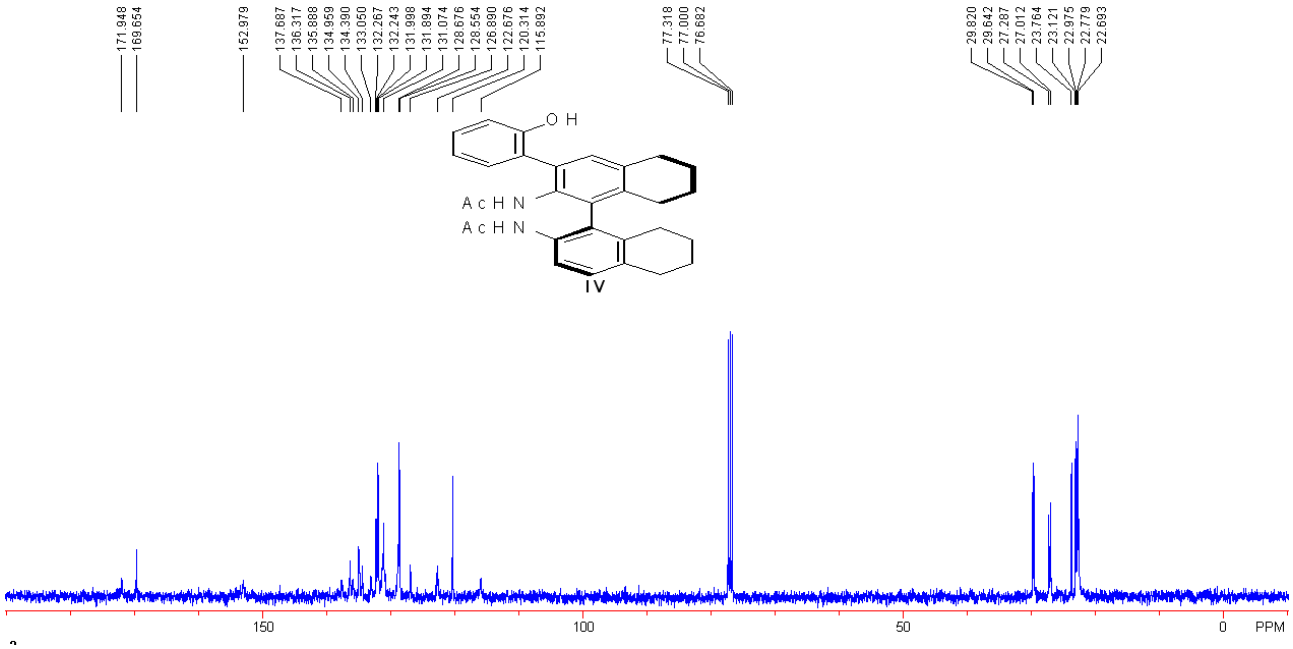
Compound IV:

(*R*)-N,N'-(3-(2-hydroxyphenyl)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl-2,2'-diyl) diacetamide

Procedure: Compound **III** (270 mg, 0.48 mmol) was dissolved in mixed solvent of EtOAc (10 mL), and then 150 mg of 10% Pd/C was added into the solution. The resulting mixture was stirred at 25 ^{o}C for 24 hours. After the catalyst was filtered off, the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (EtOAc/PE = 1/2 as eluent) to give the target product **IV** (222 mg, 99% yield). m.p. 186-189 ^{o}C; $[\alpha]^{20}_{D}$ = -110.3 (c 0.6,

CH_2Cl_2). IR (CH_2Cl_2) ν 3242, 3054, 2927, 2856, 1659, 1593, 1510, 1403, 1369, 1314, 1288, 1263, 1222, 1165, 1119, 1102, 1038, 982, 831, 810, 753, 734 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 9.03 (0.53H, brs), 8.52 (0.62H, brs), 7.92 (0.64H, brs), 7.63-7.54 (1.5H, m), 7.47-7.42 (2H, m), 7.22-7.12 (2H, m), 7.04 (1H, d, *J* = 8.0 Hz), 6.90 (1H, t, *J* = 7.2 Hz), 2.86-2.74 (4H, m), 2.27-2.17 (2H, m), 2.03-1.90 (2H, m), 1.91 (3H, s), 1.72-1.61 (8H, m), 1.51 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.9, 170.0, 153.0, 137.7, 136.3, 135.9, 135.0, 134.4, 133.1, 132.3, 132.2, 132.0, 131.9, 131.1, 128.7, 128.6, 126.9, 122.7, 120.3, 115.9, 29.8, 29.6, 27.3, 27.0, 23.8, 23.1, 23.0, 22.8, 22.7; MS (ESI) *m/z* (%) 491.5 [M^++Na]; HRMS (ESI) Calcd for $C_{30}H_{32}N_2O_3Na^{+1}$ [M^++Na] requires 491.2306, Found 491.2305.

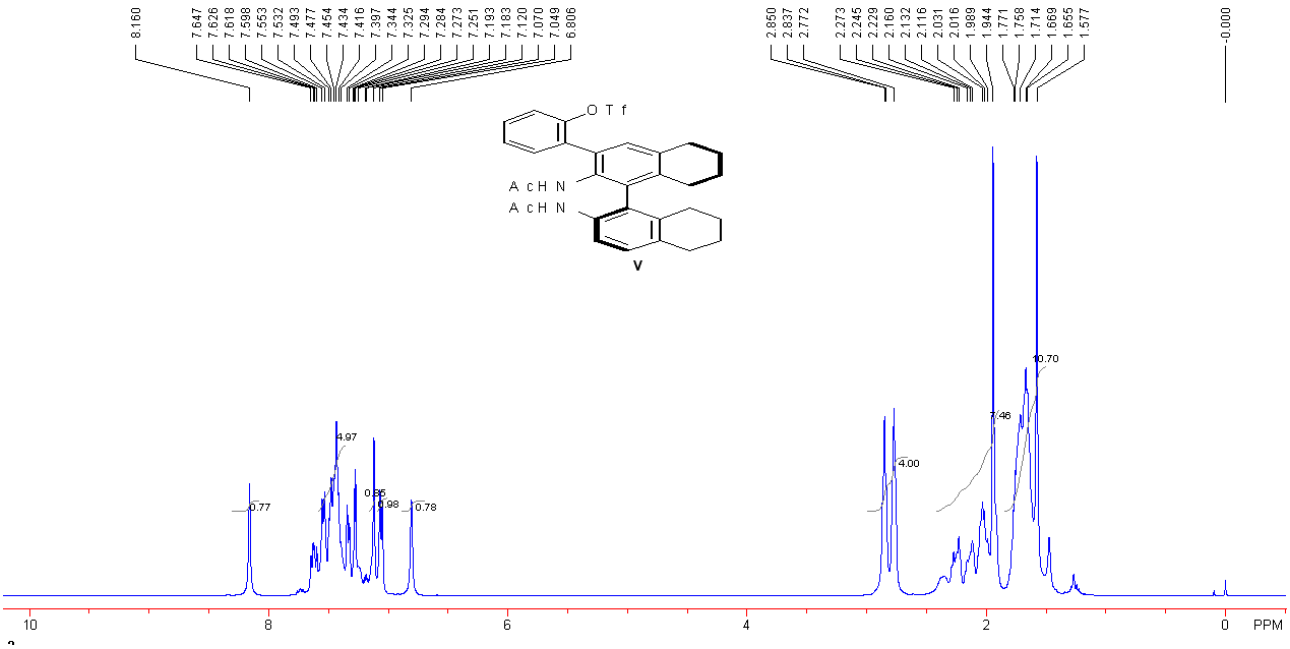


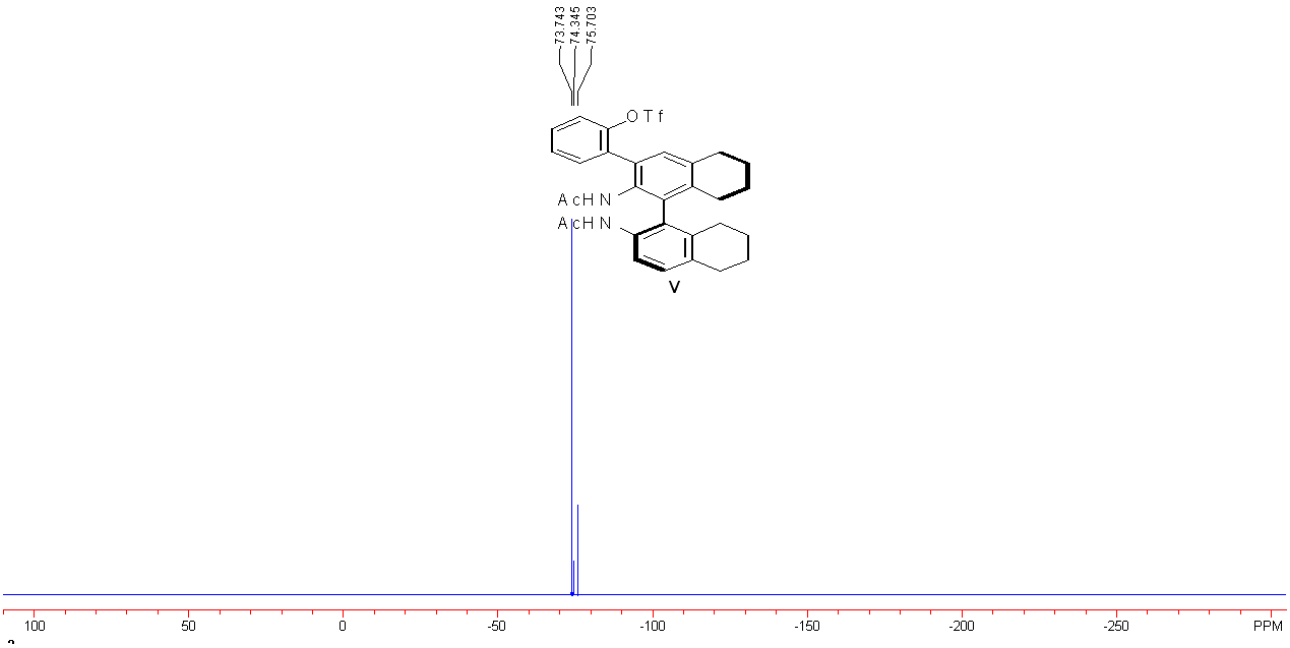


Compound V:

(R)-2-(2,2'-diacetamido-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl-3-yl)phenyl trifluoromethanesulfonate

Procedure: To a solution of **IV** (1.32 g, 2.82 mmol) in CH_2Cl_2 (10 mL) was added $PhNTf_2$ (1.51 g, 4.23 mmol) and Et_3N (0.6 mL, 4.23 mmol). The resultant solution was stirred overnight at 30 ^oC and diluted with dichloromethane and washed with saturated $NaHCO_3$, water and brine sequentially, dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel (EtOAc/PE = 1/1 as eluent) to furnish product **V** as white solid (1.46 g, 86% yield). m.p. 125-127 ^oC; $[\alpha]^{20}_D$ = -125.2 (c 0.7, CH_2Cl_2). IR (CH_2Cl_2) ν 3244, 2930, 2857, 1662, 1596, 1517, 1420, 1370, 1298, 1247, 1209, 1038, 981, 894, 871, 855, 768 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 8.16 (1H, s), 7.65-7.18 (5H, m), 7.12 (1H, s), 7.06 (1H, d, *J* = 8.4 Hz), 6.81 (1H, s), 7.25 (1H, s), 2.85-2.77 (4H, m), 2.27-1.99 (4H, m), 1.94 (3H, s), 1.77-1.66 (8H, m), 1.58 (3H, s); ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -73.7, -74.3, -75.7; MS (ESI) *m/z* (%) 601.5 $[M^+ + H]$; HRMS (ESI) Calcd for $C_{31}H_{32}N_2O_5F_3S^{+1}$ $[M^+ + H]$ requires 601.1968, Found 601.1978.

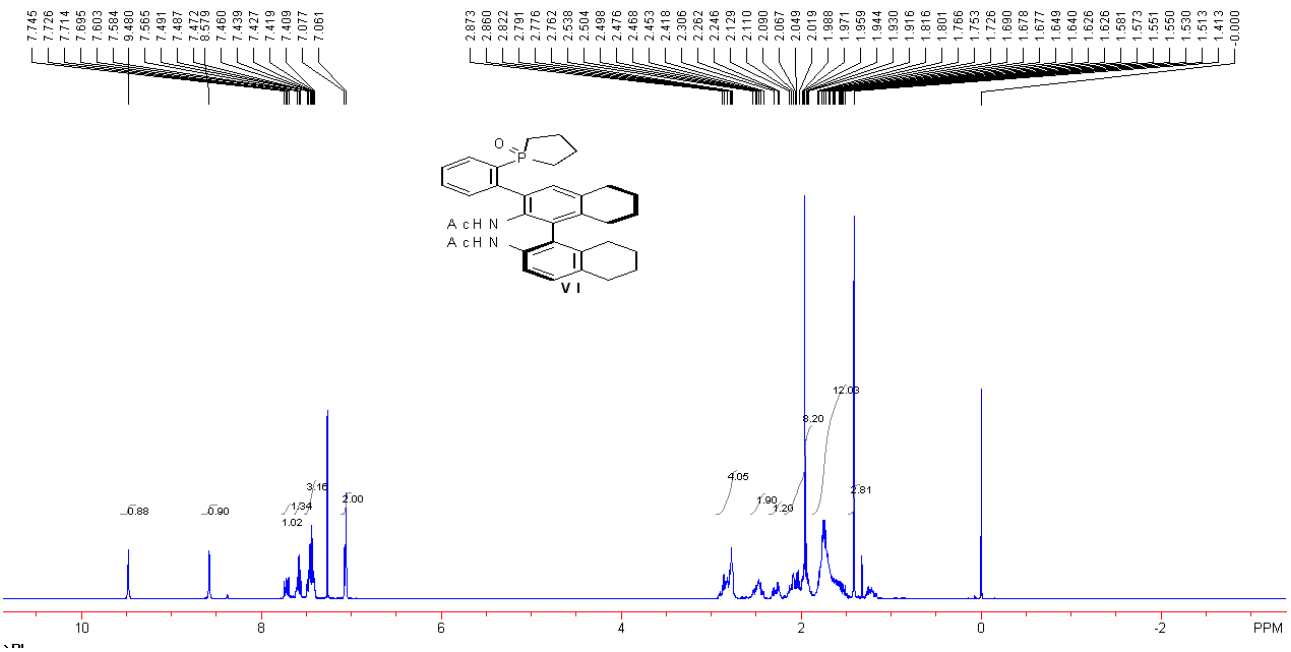


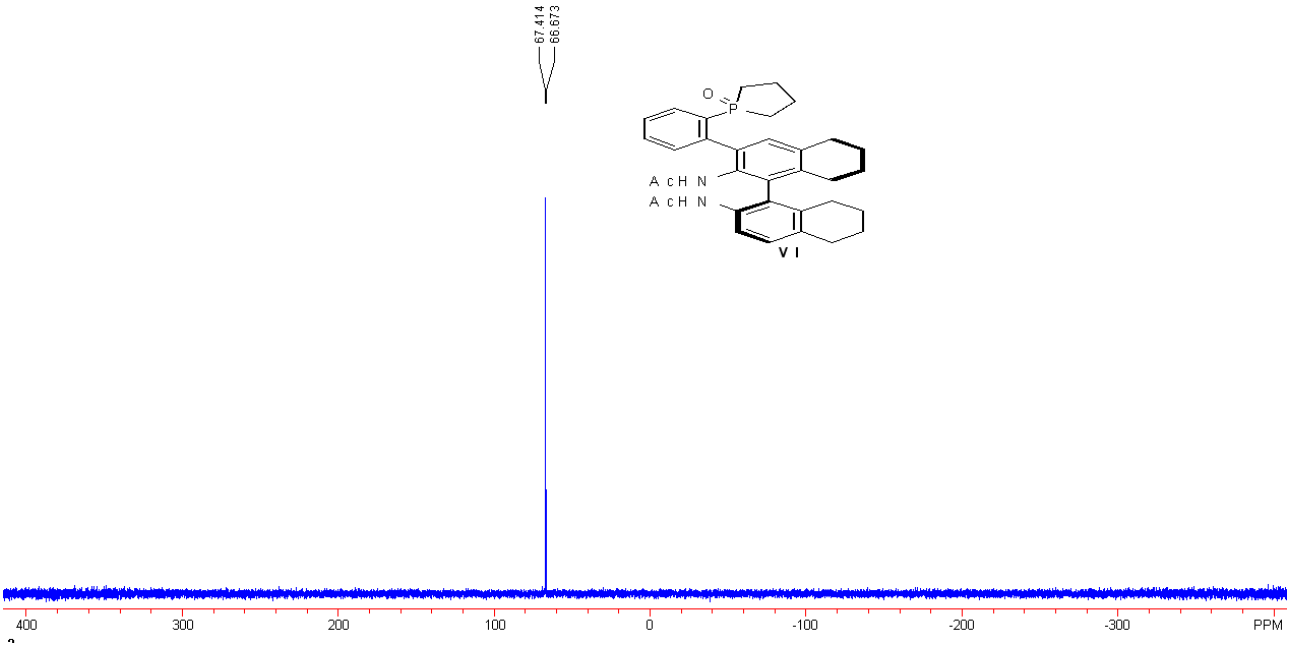


Compound VI:

(*R*)-2-(2,2'-diacetamido-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl-3-yl)phenyl phospholane oxide

Procedure: This compound was prepared according to the previous literature.[1] A white solid. m.p. 138-140 ^{o}C; $[\alpha]^{20}_{D}$ = -137.3 (c 0.6, CH_2Cl_2). IR (CH_2Cl_2) ν 3246, 2929, 2857, 1730, 1682, 1594, 1519, 1435, 1402, 1367, 1315, 1289, 1266, 1155, 1128, 1086, 1014, 979, 874, 853, 733 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 9.48 (1H, s), 8.58 (1H, s), 7.72 (1H, dd, J_1 = 9.3 Hz, J_2 = 5.7 Hz), 7.58 (1H, t, J = 5.7 Hz), 7.49-7.41 (3H, m), 7.07 (2H, d, J = 4.2 Hz), 2.87-2.76 (4H, m), 2.54-2.42 (2H, m), 2.31-2.25 (1H, m), 2.13-1.92 (5H, m), 1.96 (3H, s), 1.82-1.51 (12H, m), 1.41 (3H, s); ^{31}P NMR (121 MHz, $CDCl_3$, 85% H_3PO_4): δ 67.4, 66.6; MS (ESI) *m/z* (%) 555.4 [M^++H]; HRMS (ESI) Calcd for $C_{34}H_{40}N_2O_3P^{+1}$ [M^++H] requires 555.2762, Found 555.2771.



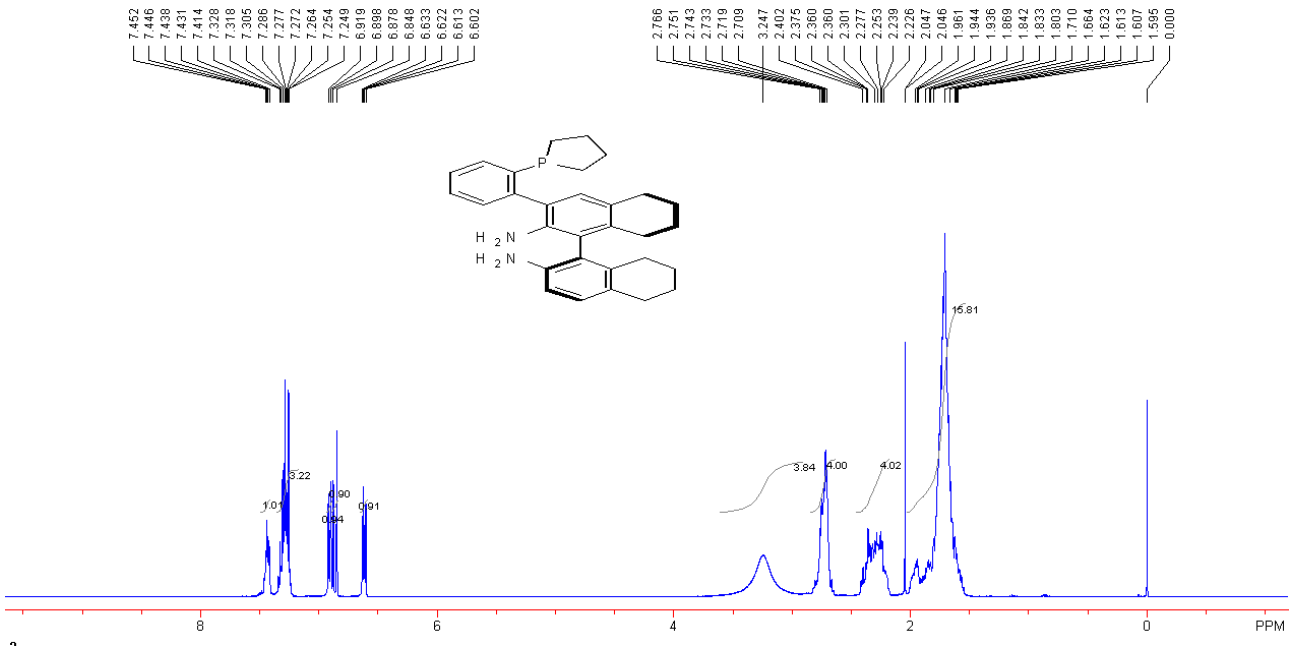


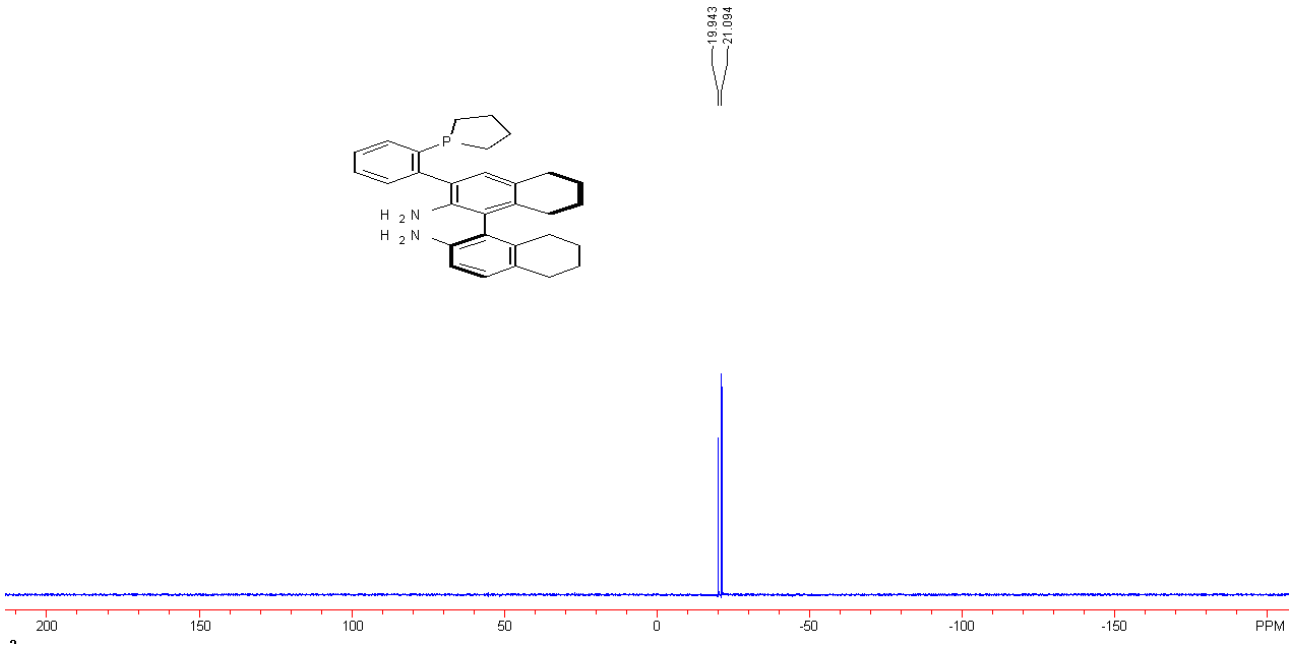
Compound LB6:

(*R*)-3-(2-(phospholan-1-yl)phenyl)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl-2,2'-diamine

Procedure: Compound **VI** (2.52 g, 4.5 mmol) was dissolved in 85 mL of EtOH, and then 85 mL 50% potassium hydroxide aqueous solution was added into the mixture. The resulting solution was heated to 120 ^{o}C overnight and the reaction was quenched by addition of saturated 10% HCl solution, washed with water, extracted by CH_2Cl_2 twice, dried by anhydrous Na_2SO_4. The solution was concentrated for the next step without further purification (quantitative yield). Triphenylphosphine (5.98 g, 22.8 mmol) in toluene (50 mL) was added into this product mixture

(2.12 g, 4.57 mmol) and then trichlorosilane (2.31 mL, 22.8 mmol) was added. The resulting mixture was heated at 110 ^{o}C for three days. After being cooled to room temperature, the product mixture was diluted with dichloromethane, quenched with a small amount of saturated $NaHCO_3$ solution. The resulting suspension was filtered through Celite, and washed with dichloromethane. The combined extracts were dried over anhydrous Na_2SO_4, and the residue was chromatographed on silica gel (PE/EA = 8:1 as eluent) to provide compound **LB6** as white solid (1.56 g, 75% yield). m.p. 171-172 ^{o}C ; $[\alpha]^{20}_{D}$ = +76 (c 0.5, CH_2Cl_2). IR (CH_2Cl_2) ν 3458, 3363, 2926, 2854, 2833, 1606, 1482, 1447, 1422, 1353, 1302, 1286, 1262, 1219, 1106, 1028, 943, 872, 811, 767, 743 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.45-7.41 (1H, m), 7.33-7.25 (3H, m), 6.91 (1H, d, *J* = 8.4 Hz), 6.87 (1H, d, *J* = 12.0 Hz), 6.62 (1H, dd, J_1 = 8.0 Hz, J_2 = 4.4 Hz), 3.25 (4H, brs), 2.77-2.71 (4H, m), 2.40-2.23 (4H, m), 1.96-1.60 (16H, m); ^{31}P NMR (162 MHz, $CDCl_3$, 85% H_3PO_4): δ -19.9, -21.1; MS (ESI) *m/z* (%) 455.3 [M^{+}+H]; HRMS (ESI) Calcd for $C_{30}H_{36}N_2P^{+1}$ [M^{+}+H] requires 455.2604, Found 455.2611.

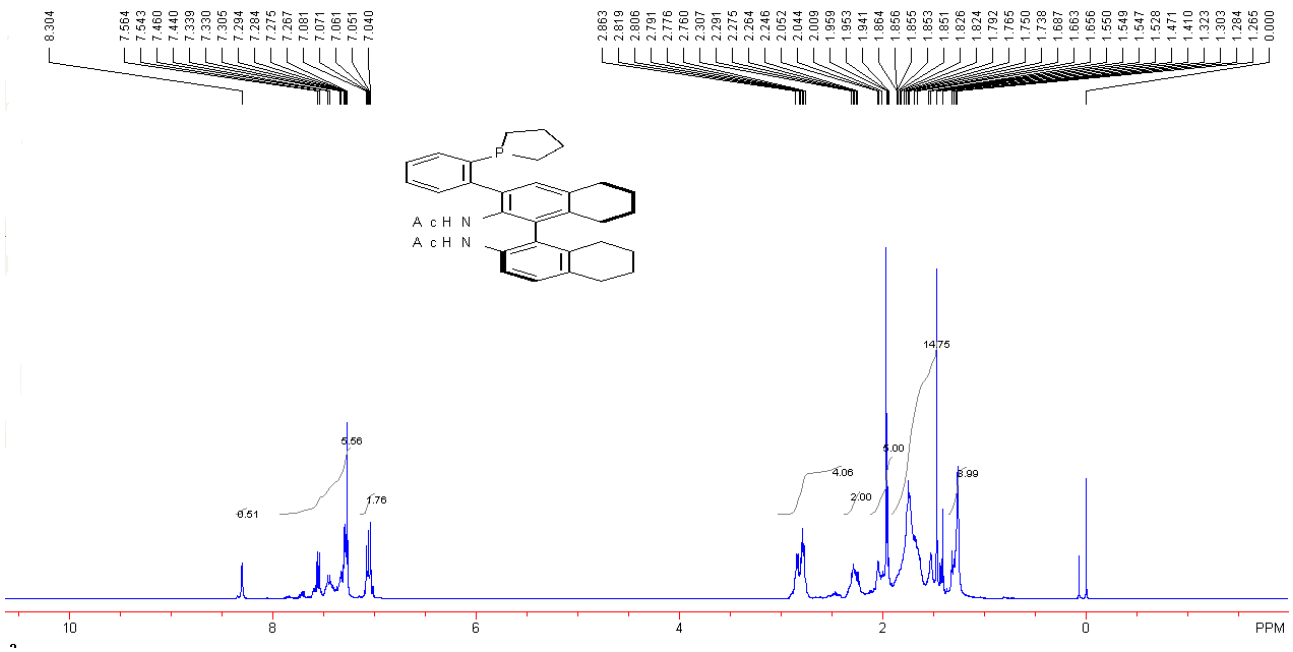


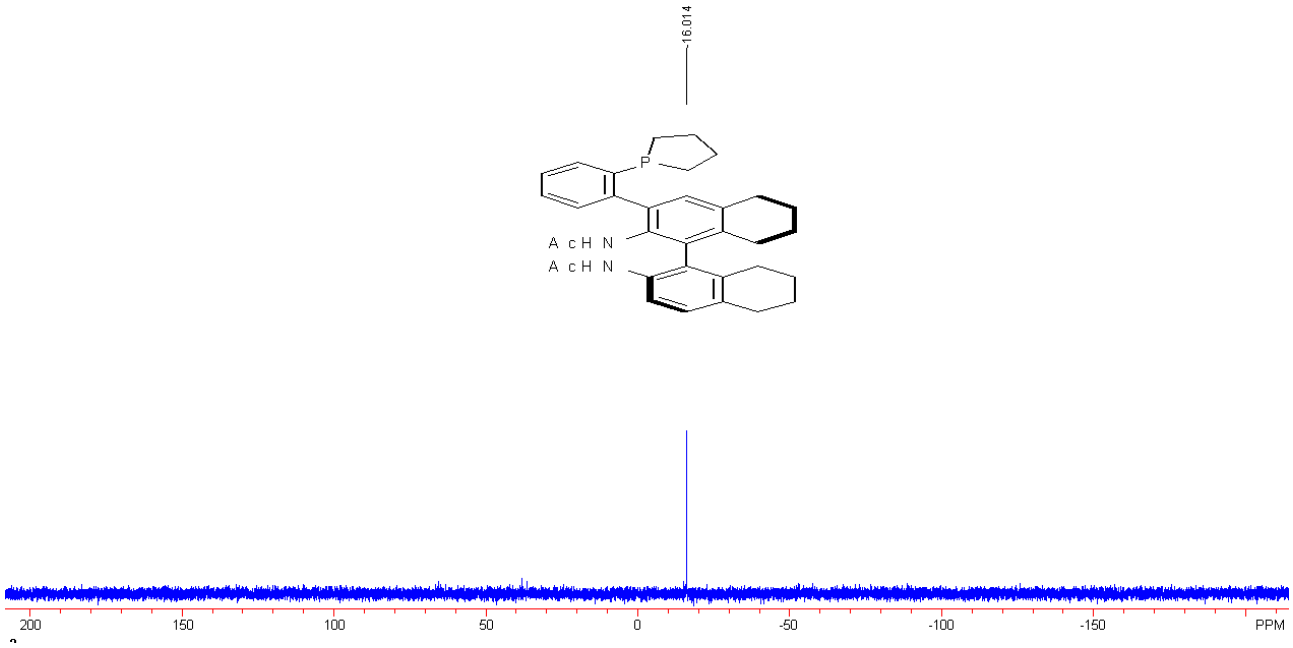


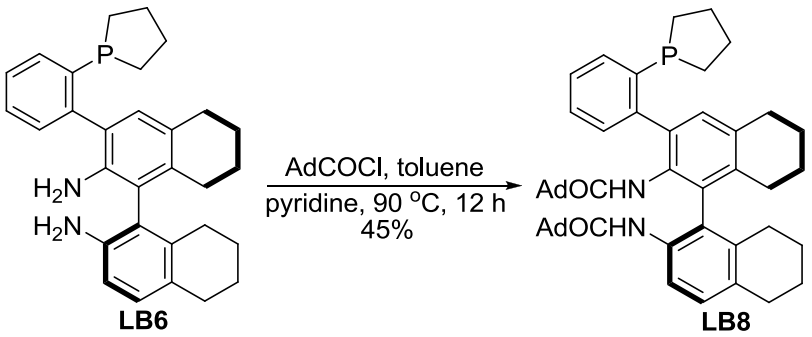
Compound LB7:

(*R*)-N,N'-(3-(2-(phospholan-1-yl)phenyl)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl-2,2'-diyl)diacetamide

Procedure: This compound was prepared according to the previous literature.[5] A white solid (70% yield). m.p. 144-146 ^{o}C; $[\alpha]^{20}_{D}$ = -236.5 (c 1.0, CH_2Cl_2). IR (CH_2Cl_2) ν 3287, 3256, 2929, 2856, 1688, 1665, 1592, 1524, 1434, 1401, 1366, 1292, 1263, 1092, 1060, 1015, 799 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.30 (0.5H, s), 7.56-7.27 (5.5H, m), 7.09-7.04 (2H, m), 2.86-2.76 (4H, m), 2.31-2.25 (2H, m), 2.05-1.94 (5H, m), 1.86-1.41 (15H, m), 1.32-1.27 (4H, m); ^{31}P NMR (162 MHz, $CDCl_3$, 85% H_3PO_4): δ -16.0; MS (ESI) *m/z* (%) 539.3 [M^++H]; HRMS (ESI) Calcd for $C_{34}H_{40}N_2O_2P^{+1}$ [M^++H] requires 539.2812, Found 539.2822.





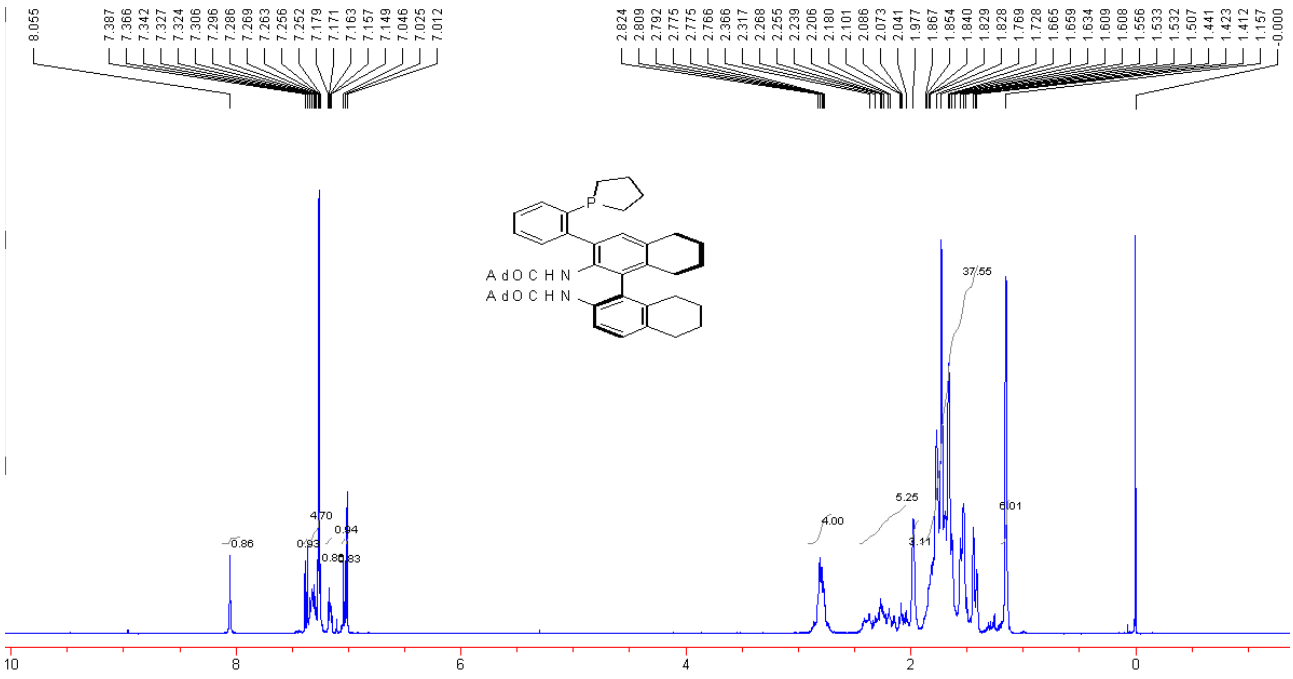


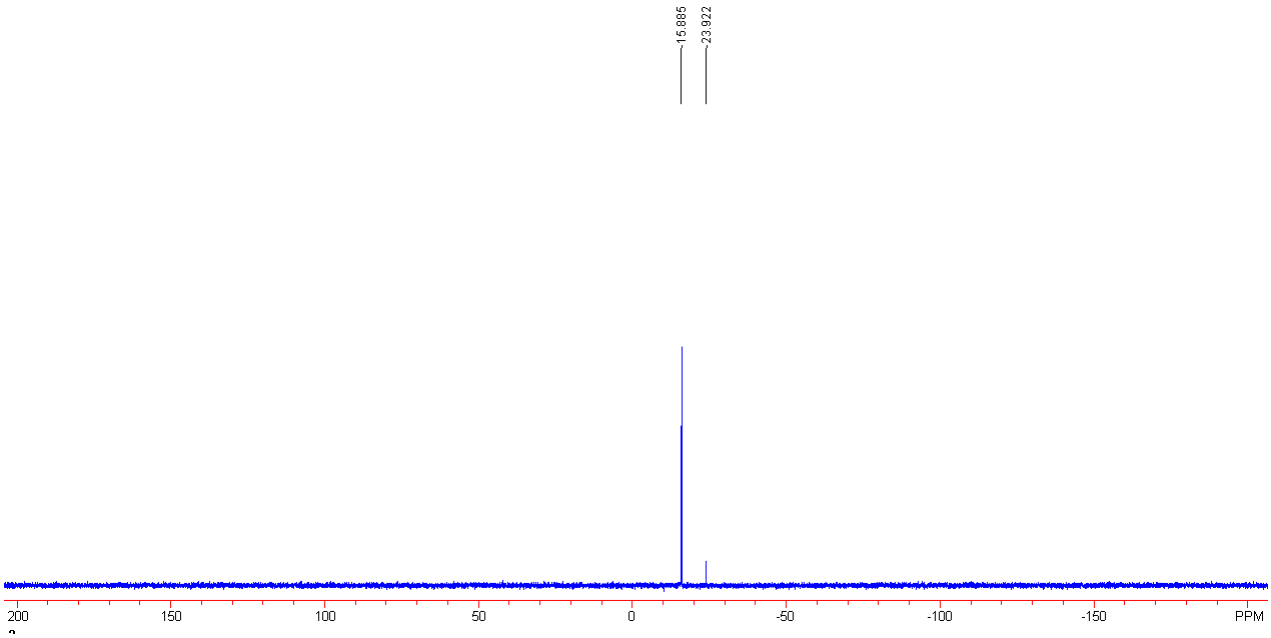
Compound LB8:

(*R*)-N,N'-(3-(2-(phospholan-1-yl)phenyl)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl-2,2'-diyl

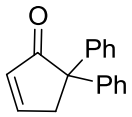
)diadamantanecarboxamide

Procedure: This compound was prepared according to the previous literature.[6] To a solution of resolved **LB6** (454 mg, 1.0 mmol) and pyridine (320 mg, 4.0 mmol) in toluene (10 mL) was added 1-adamantanecarboxylic acid chloride (794 mg, 4.0 mmol) in one portion. The reaction mixture was stirred at 90 °C for 12 h. Then, the reaction mixture was cooled to room temperature and the toluene was removed under high vacuum. The remaining residue was chromatographed on silica gel (PE/EA = 8:1 as eluent) to provide compound **LB8** as a white solid (355 mg, 45% yield). m.p. >320 ^{o}C; $[\alpha]^{20}_{D}$ = -193.6 (c 0.5, CH_2Cl_2). IR (CH_2Cl_2) ν 3312, 2905, 2850, 1725, 1700, 1661, 1590, 1486, 1452, 1344, 1264, 1180, 1102, 1079, 975, 802, 764, 739 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.06 (1H, s), 7.38 (1H, d, *J* = 8.4 Hz), 7.34-7.25 (4H, m), 7.18-7.15 (1H, m), 7.04 (1H, d, *J* = 8.4 Hz), 7.01 (1H, s), 2.82-2.77 (4H, m), 2.37-2.18 (5H, m), 1.98 (3H, s), 1.87-1.41 (36H, m), 1.57 (6H, s); ^{31}P NMR (162 MHz, $CDCl_3$, 85% H_3PO_4): δ -15.9, -23.9; MS (ESI) *m/z* (%) 779.7 [M^{+}+H]; HRMS (ESI) Calcd for $C_{52}H_{64}N_2O_2P^{+1}$ [M^{+}+H] requires 779.4695, Found 779.4699.





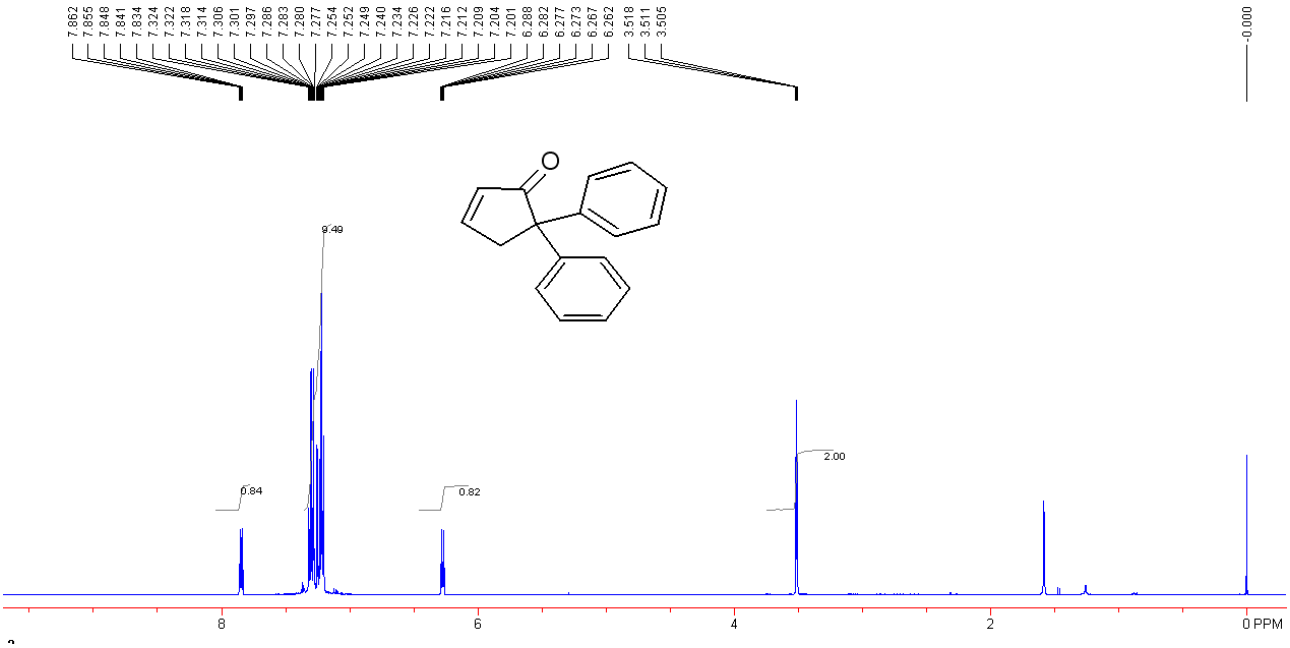
Typical procedure for the preparation of 5,5-disubstituted cyclopent-2-enone.

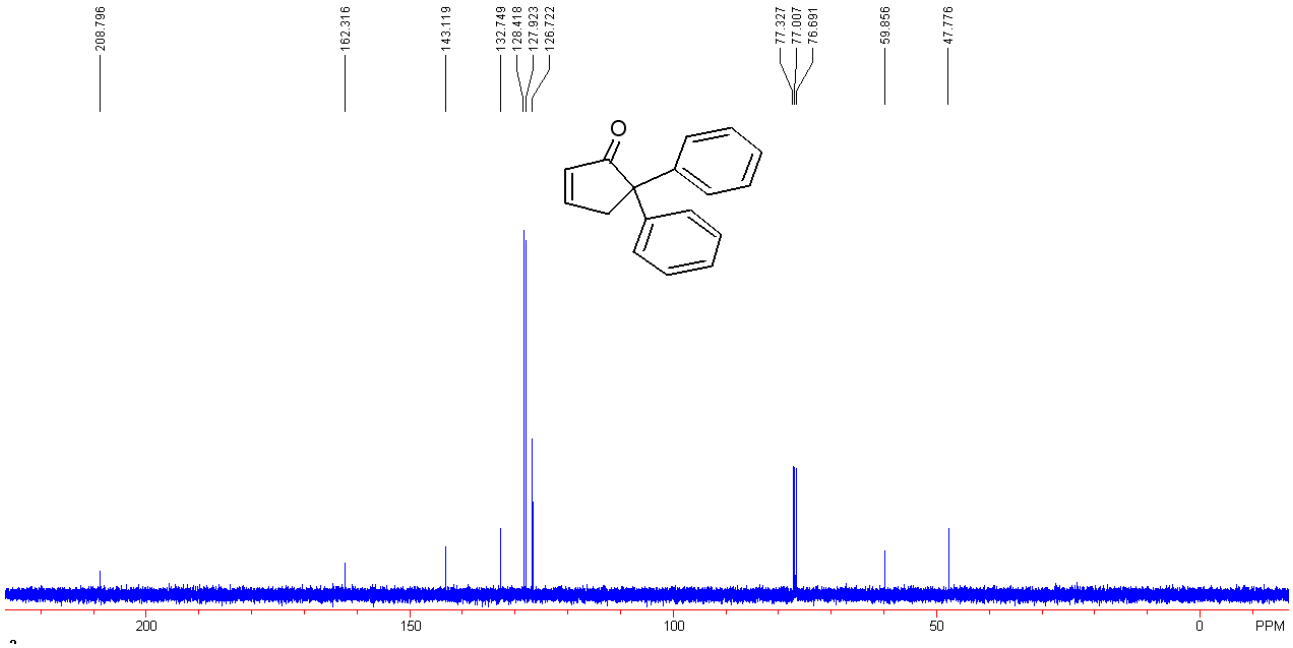


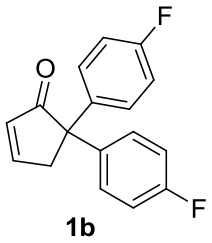
1a

Compound 1a: 5,5-diphenylcyclopent-2-enone

Procedure: This is a known compound. A white solid. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.86-7.83 (1H, m), 7.32-7.20 (10H, m), 6.29-6.26 (1H, m), 3.51 (2H, t, *J* = 2.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 208.8, 162.3, 143.1, 132.7, 128.4, 127.9, 126.7, 59.9, 47.8.

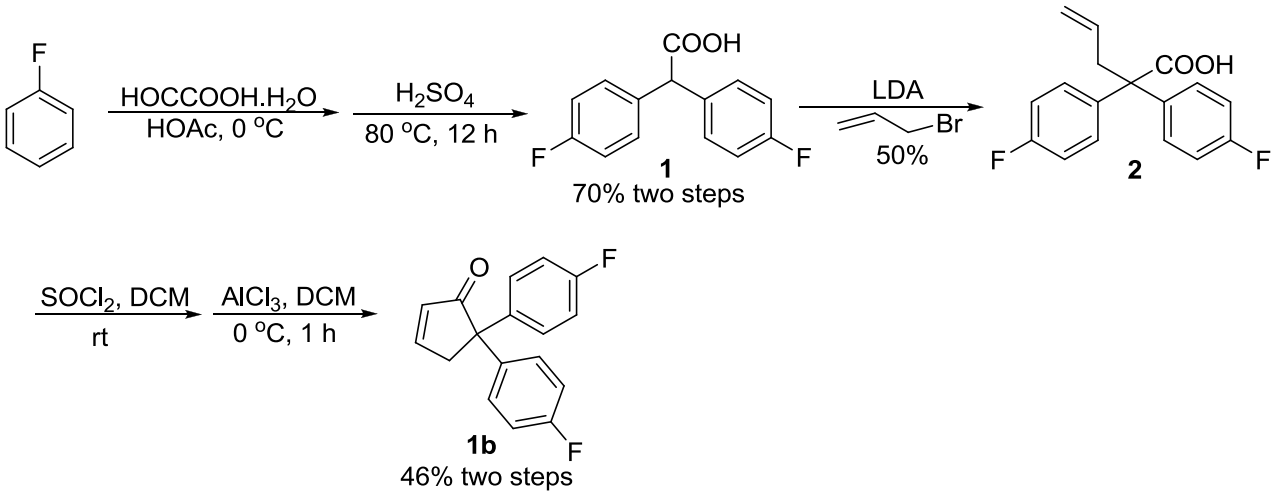






1b

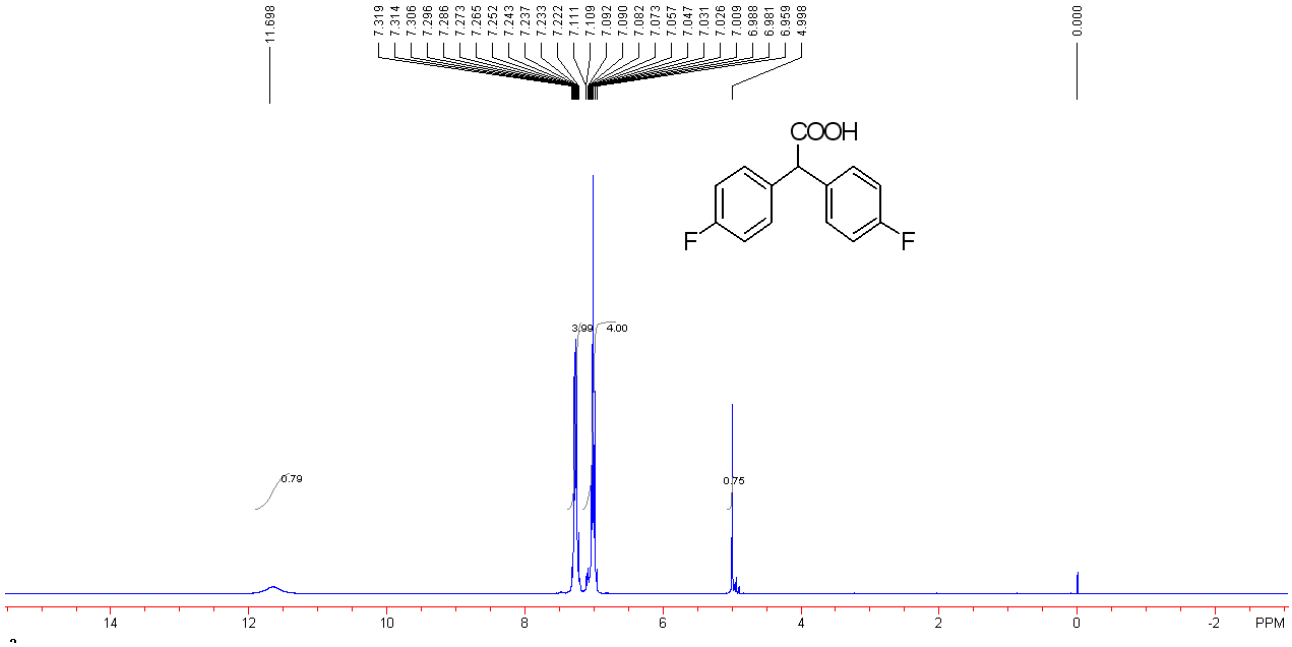
Compound 1b: 5,5-bis(4-fluorophenyl)cyclopent-2-enone

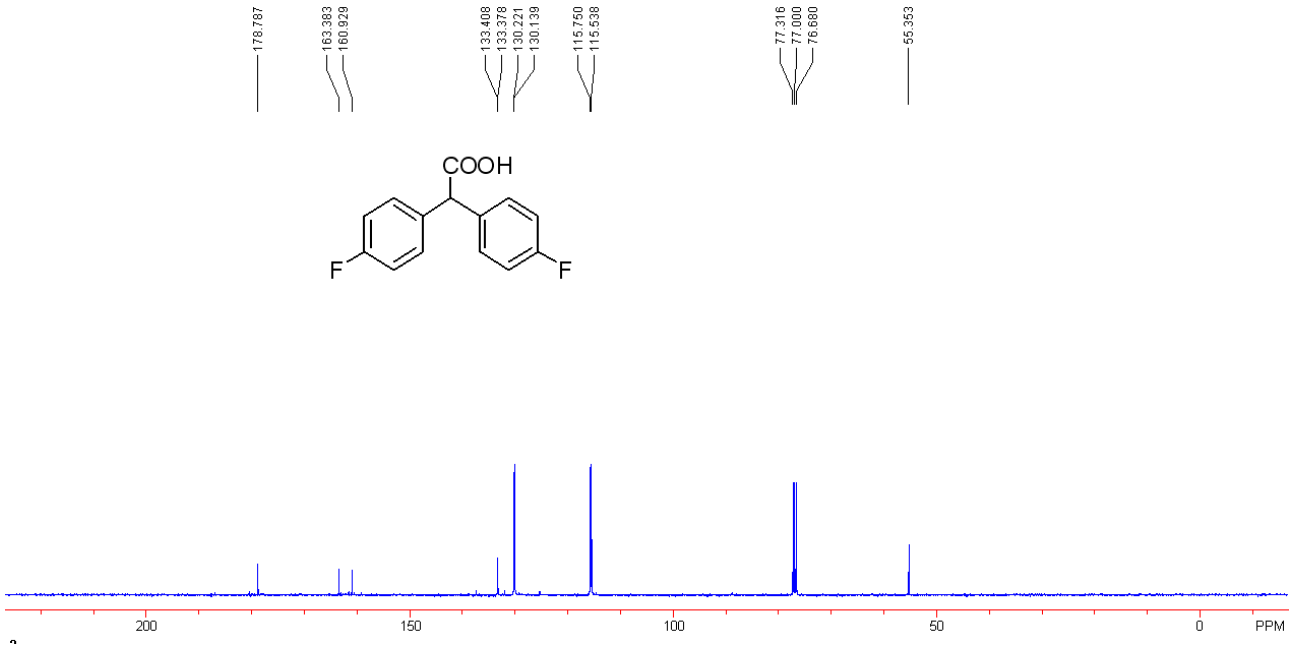


Compound 1: 2,2-bis(4-fluorophenyl)acetic acid

Procedure: This is a known compound. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 11.70 (1H, bs), 7.32-7.22 (4H, m), 7.11-6.96 (4H, m), 5.00 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.8, 162.1 (d, $J_{C\text{-}F}$ = 245.4 Hz), 133.4 (d, $J_{C\text{-}F}$ = 3.0 Hz), 130.2 (d, $J_{C\text{-}F}$ = 8.2 Hz), 115.6 (d, $J_{C\text{-}F}$ = 21.2

Hz), 55.4; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -114.5–-114.6 (m).

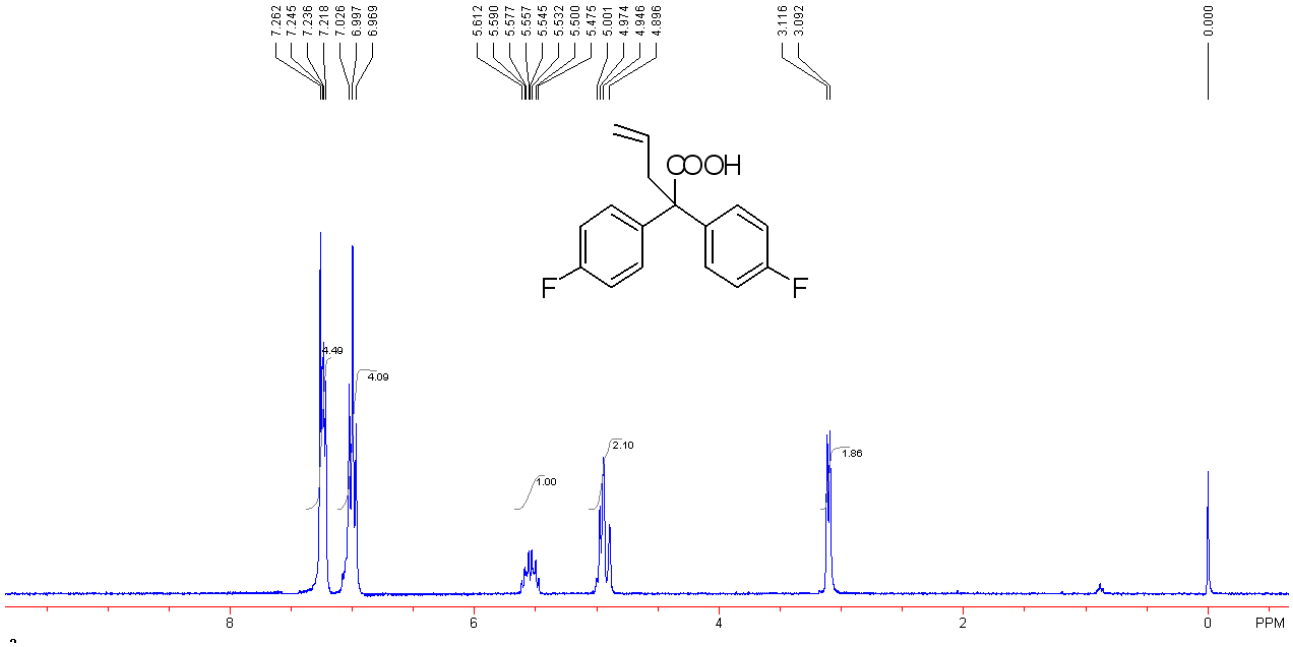


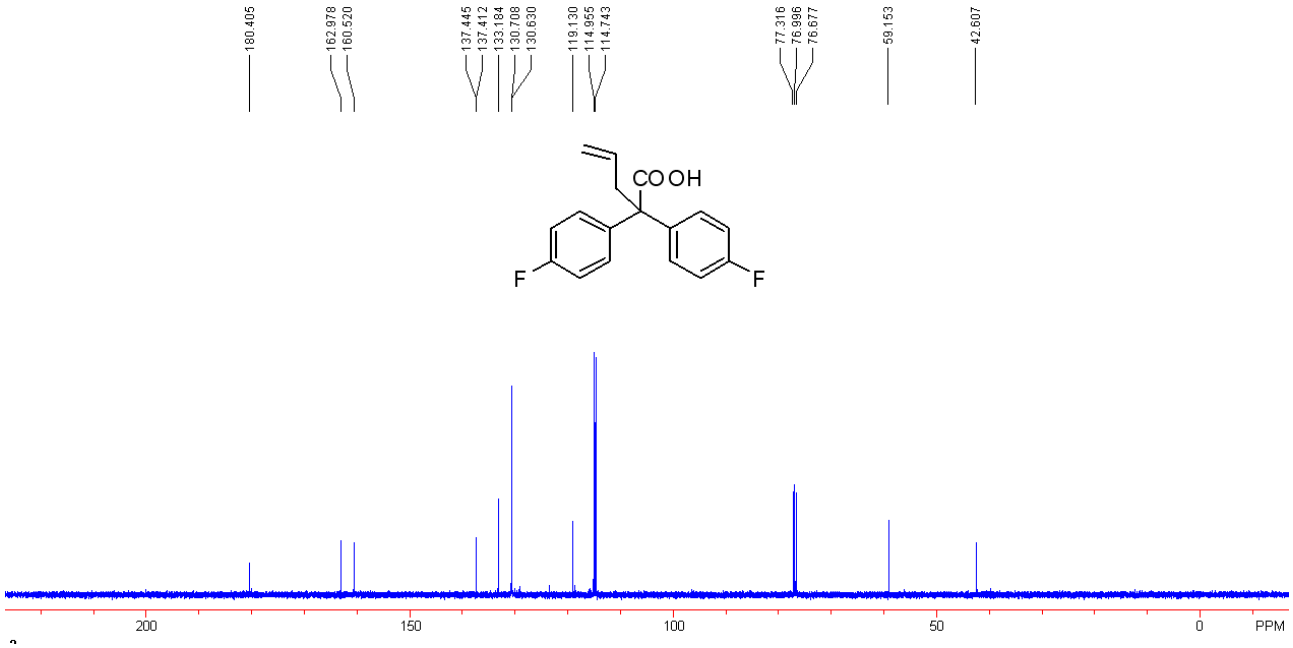


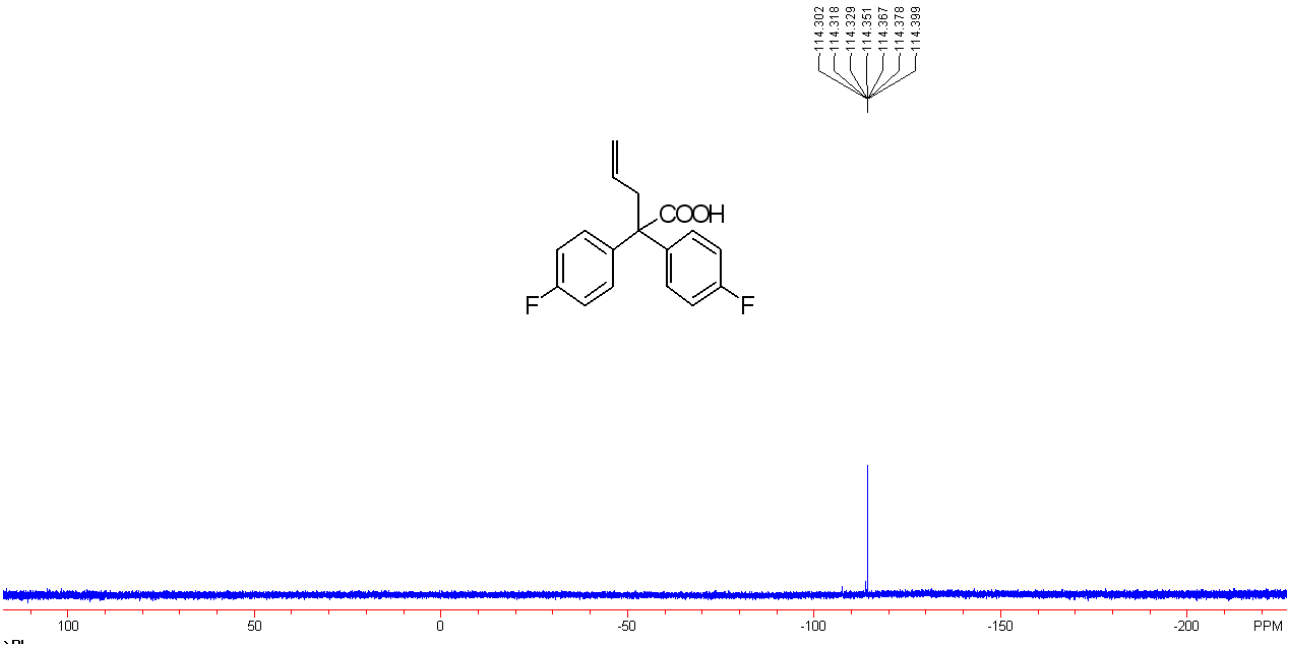
Compound 2: 2,2-bis(4-fluorophenyl)pent-4-enoic acid

Procedure: This compound was prepared according to the previous literature.[7] To a solution of diisopropylamine (1.2 mL, 10 mmol) in THF (15 mL) under Ar at -78 ^{o}C was added n-butyllithium (4.2 mL, 10 mmol). After being stirred at -78 ^{o}C for 30 min, a solution of acid **1** (1.24 g, 5 mmol) in THF (5 mL) was then added. The mixture was warmed to room temperature and stirred for 1 h and then cooled to 0 ^{o}C. Allyl bromide (0.9 mL, 10 mmol) was added and the mixture was warmed to room temperature and stirred for 24 h. The reaction was quenched with saturated ammonium chloride, acidified with 2 N HCl, and extracted with ether. The organic portion was washed with saturated ammonium chloride, dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel (EtOAc/PE = 1/4 as eluent) to furnish product **2** as white solid (720 mg, 50% yield). m.p. 131-133 ^{o}C; IR (CH_2Cl_2) ν 3080, 2964, 2626, 1699, 1602, 1507, 1445, 1398, 1326, 1232, 1163, 1104, 1015, 920, 829, 749 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.24 (4H, dd, J_1 = 7.8 Hz, J_2 = 5.1 Hz), 7.00 (4H, t, J = 8.7 Hz), 5.61-5.48 (1H, m), 5.00-4.90 (2H, m), 3.10 (2H, d, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.4, 161.7 (d, $J_{C\text{-}F}$ = 245.8 Hz), 137.4 (d, $J_{C\text{-}F}$ = 3.3 Hz), 133.2, 130.7 (d, $J_{C\text{-}F}$ = 7.8 Hz), 119.1, 114.8 (d, $J_{C\text{-}F}$ = 21.2 Hz), 59.2, 42.6; ^{19}F NMR (282 MHz, $CDCl_3$, $CFCl_3$): δ -114.3–-114.4 (m); (EI) *m/z* (%) 288 (0.41) [M^+], 247 (100), 219 (12.15), 201 (31.40), 181 (3.34), 151 (15.46), 123 (63.63), 109 (27.86), 95 (20.61); HRMS (EI) Calcd for

$C_{17}H_{14}O_2F_2$ [M^+] requires 288.0962, Found 288.0964.

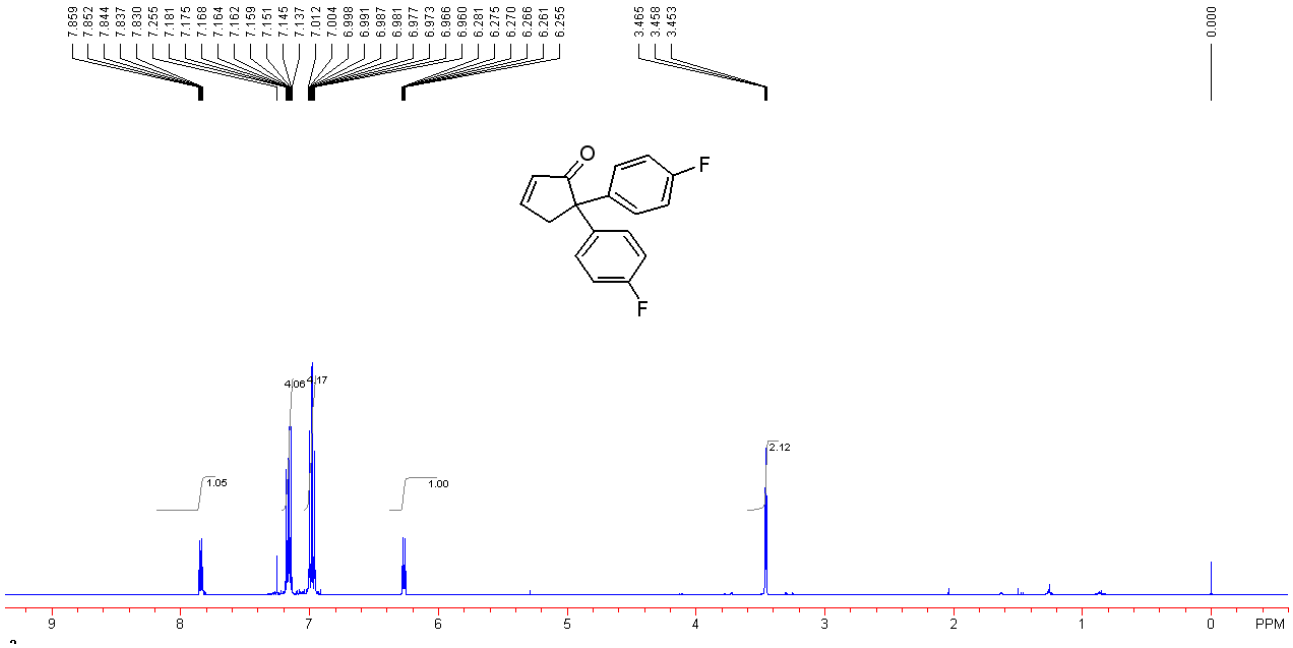


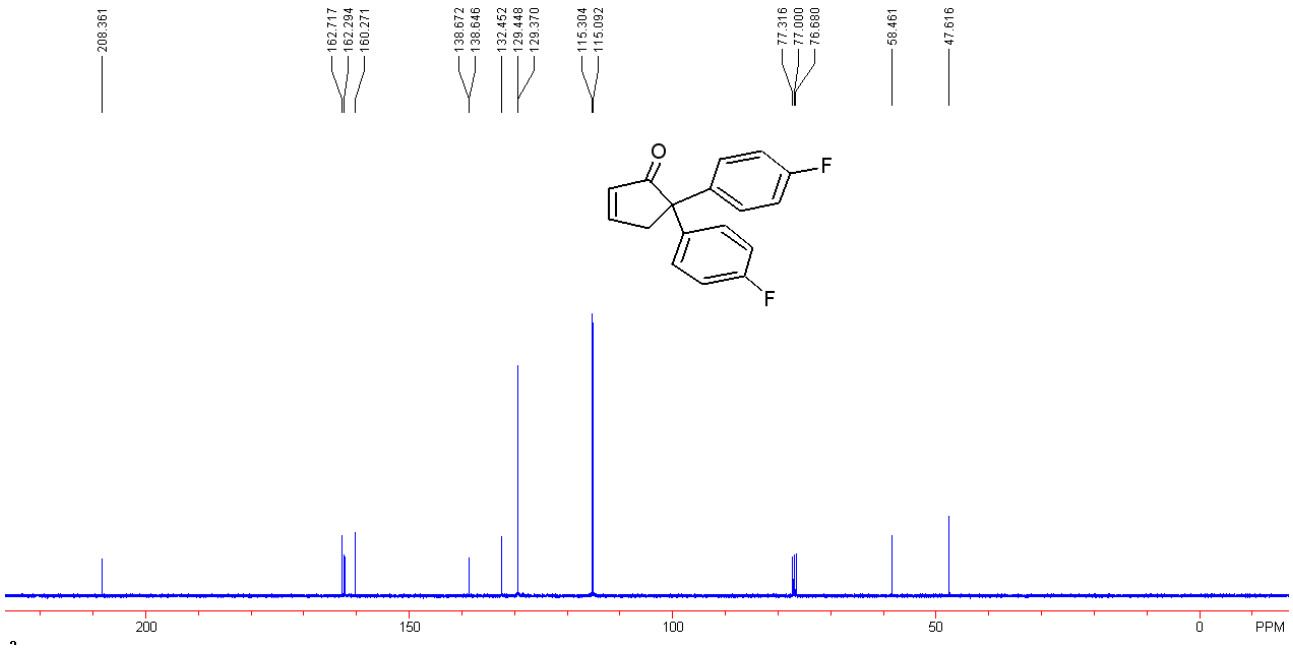


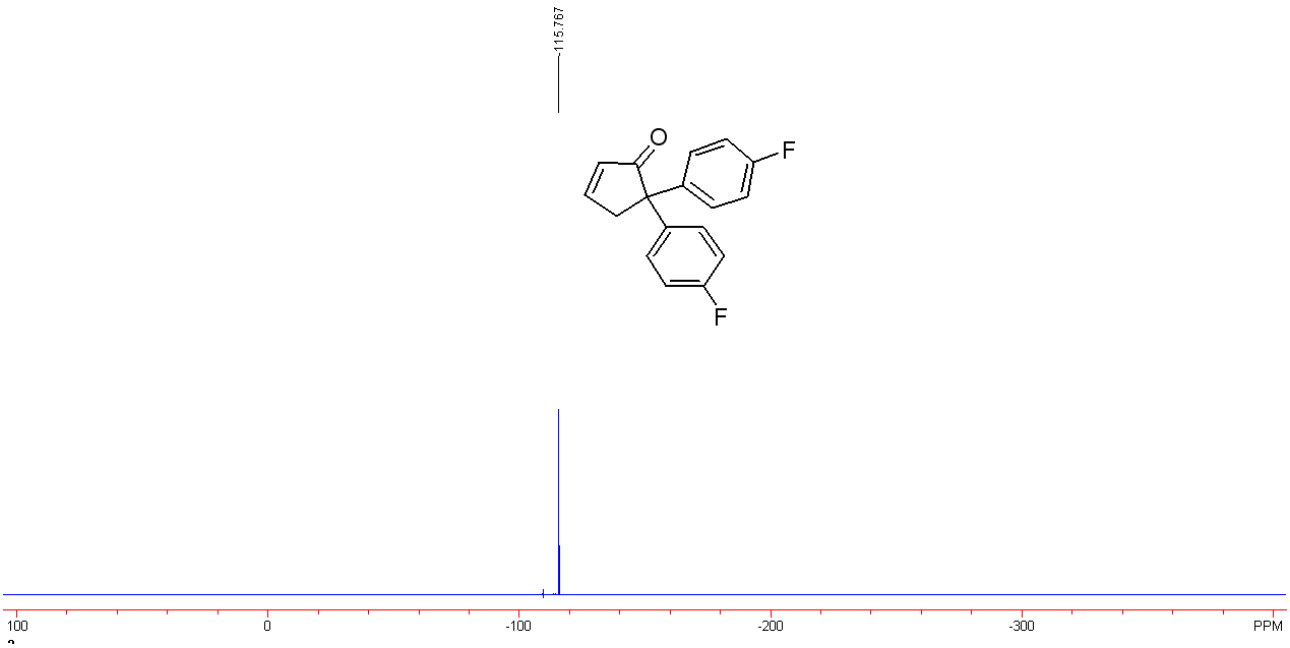


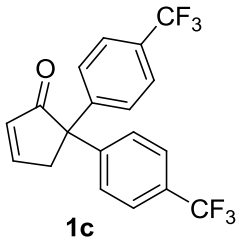
Compound 1b: 5,5-bis(4-fluorophenyl)cyclopent-2-enone

Procedure: This compound was prepared according to the previous literature.[7] A yellow solid. m.p. 64-66 ^{o}C; IR (CH_2Cl_2) ν 3074, 2919, 1702, 1597, 1505, 1436, 1407, 1342, 1229, 1162, 1108, 1015, 951, 830, 738 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.86-7.83 (1H, m), 7.26-7.14 (4H, m), 7.01-6.96 (4H, m), 6.28-6.26 (1H, m), 3.46 (2H, t, J = 2.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 208.4, 162.3, 160.5 (d, J_{C-F} = 244.6 Hz), 138.7 (d, J_{C-F} = 2.6 Hz), 132.5, 129.4 (d, J_{C-F} = 7.8 Hz), 115.2 (d, J_{C-F} = 21.2 Hz), 58.5, 47.6; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -115.8; (EI) *m/z* (%) 270 (100) [M^+], 241 (33.37), 227 (18.15), 201 (43.45), 175 (20.67), 146 (31.31), 133 (13.27), 120 (17.11), 109 (64.97); HRMS (EI) Calcd for $C_{17}H_{12}OF_2$ [M^+] requires 270.0856, Found 270.0860.

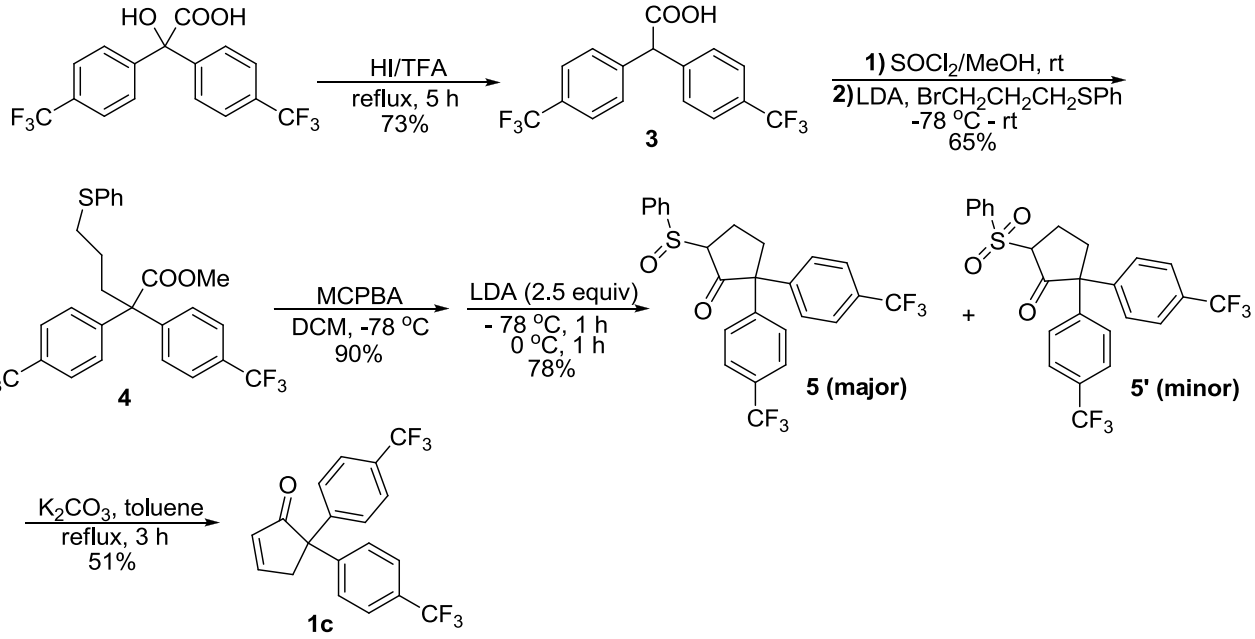








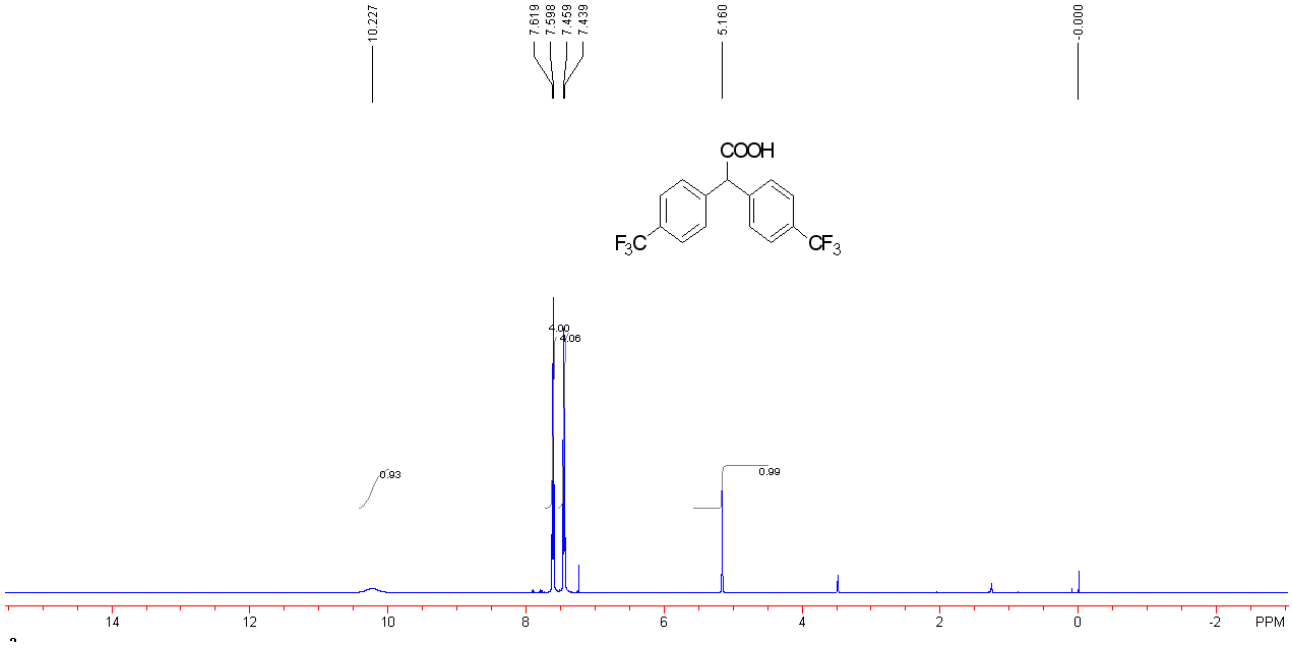
Compound 1c: 5,5-bis(4-(trifluoromethyl)phenyl)cyclopent-2-enone

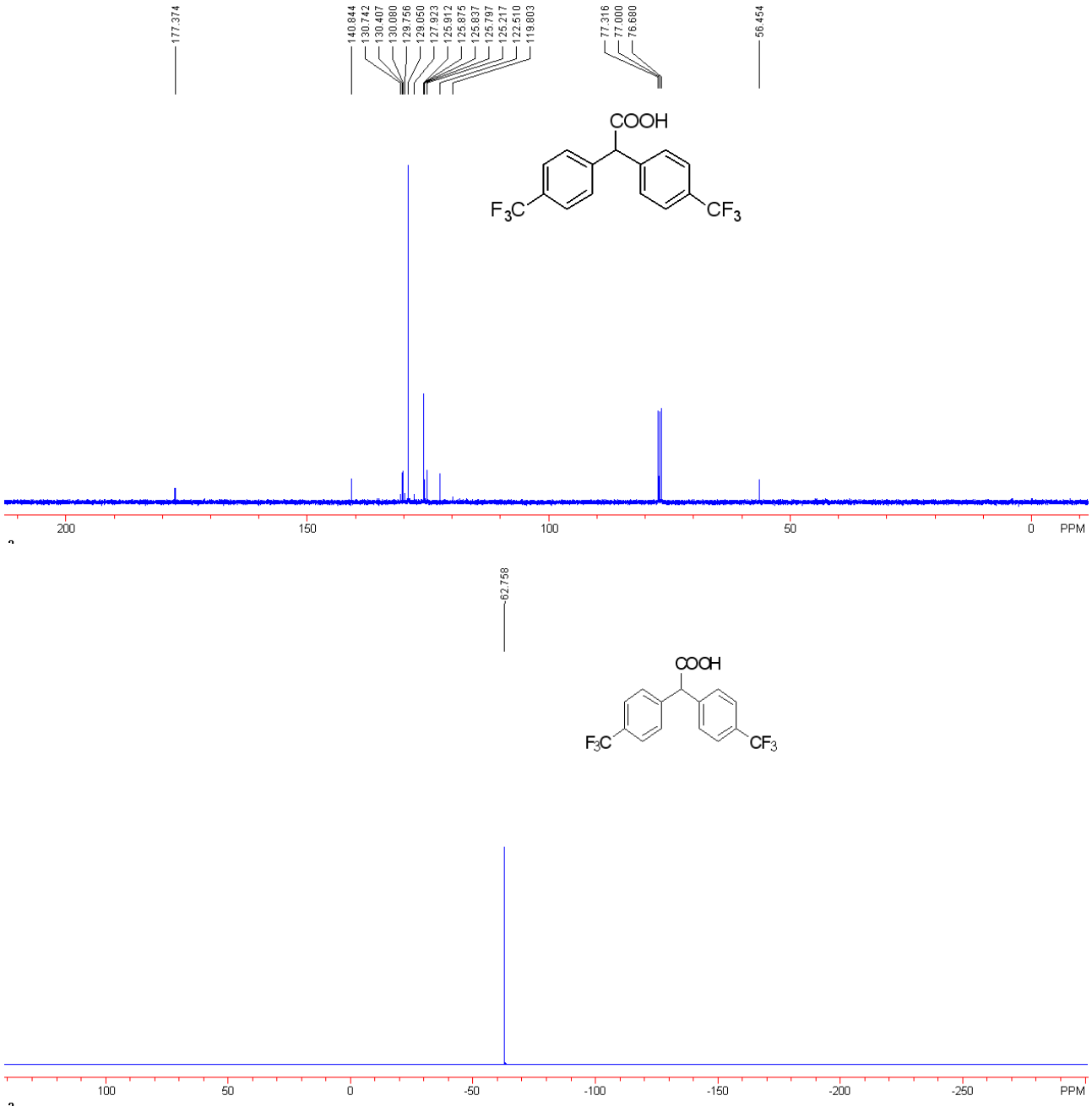


Compound 3: 2,2-bis(4-(trifluoromethyl)phenyl)acetic acid

Procedure: This compound was prepared according to the previous literature.[8] 10 g of constant

boiling hydriodic acid was added to a hot solution of 1.1 g of 2-hydroxy-2,2-bis(4-(trifluoromethyl)phenyl)acetic acid in 15 mL of 2,2,2-trifluoroacetic acid and the resulting solution was refluxed for 5 hours. The solvent was removed under reduced pressure and the residue was adjusted pH to 7 with saturated $NaHCO_3$ and extracted by CH_2Cl_2, dried by anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel (EtOAc/PE = 1/1 as eluent) to furnish product **3** as white solid (800 mg, 73% yield). A white solid. m.p. 146-148 ^oC; IR (CH_2Cl_2) ν 2926, 1713, 1617, 1408, 1322, 1260, 1218, 1163, 1114, 1068, 1018, 911, 864, 720 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 10.22 (1H, bs), 7.61 (4H, t, J = 8.4 Hz), 7.45 (4H, d, J = 8.0 Hz), 5.16 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.4, 140.8, 130.2 (q, $J_{C\text{-}F}$ = 32.4 Hz), 129.1, 125.9 (q, $J_{C\text{-}F}$ = 3.7 Hz), 123.9 (q, $J_{C\text{-}F}$ = 270.6 Hz), 56.5; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -62.8; (EI) *m/z* (%) 348 (17.89) [M^+], 329 (14.07), 303 (100), 283 (35.94), 235 (47.44), 214 (30.08), 183 (12.00), 165 (51.64); HRMS (EI) Calcd for $C_{16}H_{10}O_2F_6$ [M^+] requires 348.0585, Found 348.0586.

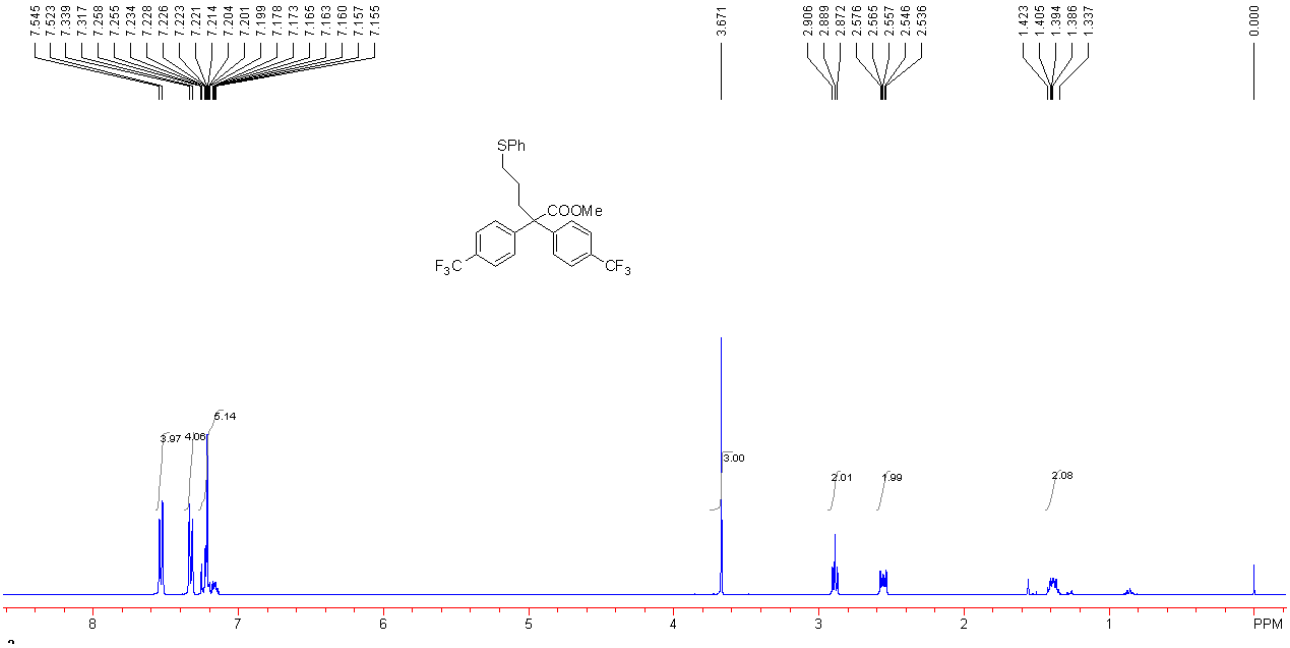


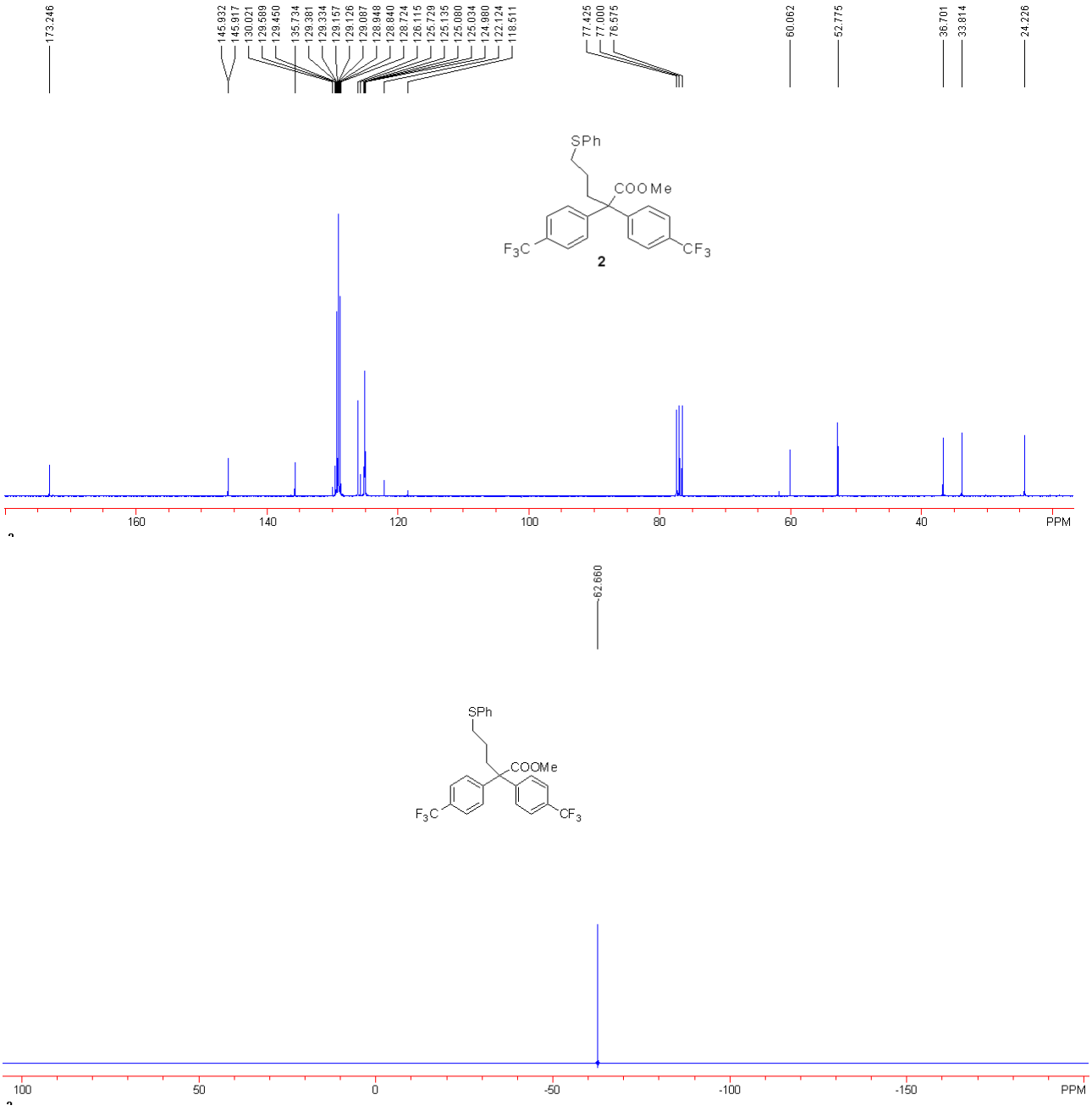


Compound 4: methyl 5-(phenylthio)-2,2-bis(4-(trifluoromethyl)phenyl)pentanoate

Procedure: This compound was prepared according to the previous literature.[9] To a solution of **3** (1.0 g, 2.88 mol) in 15 mL methanol was added 4 mL $SOCl_2$, the resulting mixture was stirred at room temperature overnight. The solvent was reduced by vaccum and the residue was for next step without further purification. The residue was dissolved in 10 mL THF and 1.5 mL LDA (2.0 M in hexane) was added at -78 ^{o}C. The resulting mixture was stirred for 1 hour, then (3-bromopropyl)(phenyl)sulfane (800 mg, 3.3 mmol) was added for 0.5 hour. It was allowed to warm to room temperature. After stirring for 48 h at room temperature, the reaction mixture was

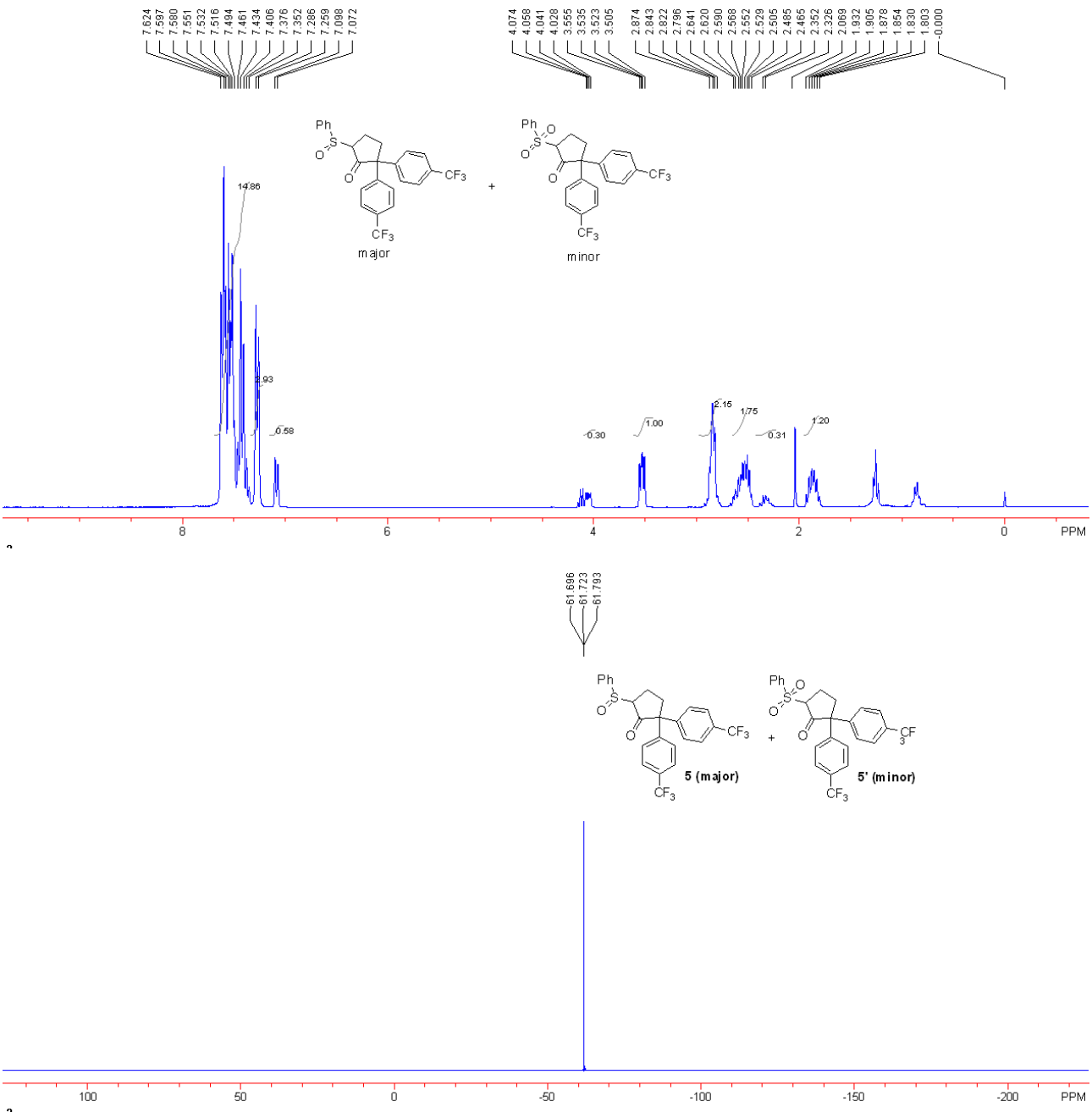
hydrolyzed with a saturated aqueous NH_4Cl solution (50 mL). The aqueous layer was extracted with EtOAc and the combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. Purification of the residue by flash chromatography on silica gel (EtOAc/PE = 1/40 as eluent) allowed to isolate phosphorane **2** (0.95 g, 65%) as colorless oil. IR (CH_2Cl_2) ν 2926, 1713, 1617, 1408, 1322, 1260, 1218, 1163, 1114, 1068, 1018, 911, 864, 720 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.53 (4H, t, J = 8.8 Hz), 7.33 (4H, d, J = 8.8 Hz), 7.26-7.16 (5H, m), 3.67 (3H, s), 2.89 (2H, t, J = 6.8 Hz), 2.58-2.54 (2H, m), 1.42-1.34 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.2, 145.9 (d, $J_{C\text{-}F}$ = 1.1 Hz), 135.7, 129.5, 129.4 (q, $J_{C\text{-}F}$ = 24.3 Hz), 129.1, 126.1, 125.0 (q, $J_{C\text{-}F}$ = 3.0 Hz), 123.9 (q, $J_{C\text{-}F}$ = 202.8 Hz), 52.8, 36.7, 33.8, 24.2; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -62.7; MS (ESI) *m/z* (%) 512.1 [M^++H]; HRMS (ESI) Calcd for $C_{26}H_{22}O_2F_6S^{+1}$ [M^++H] requires 512.1229, Found 512.1239.





Compound 5 (major): 5-(phenylsulfinyl)-2,2-bis(4-(trifluoromethyl)phenyl)cyclopentanone

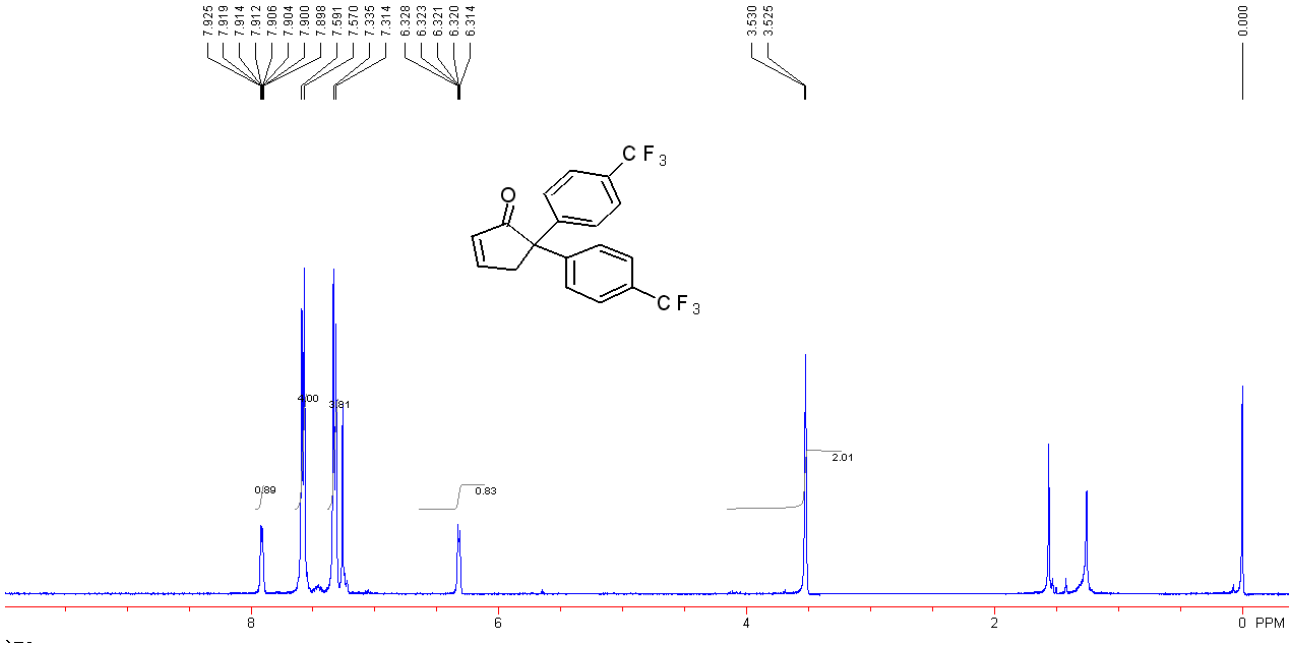
Procedure: This compound was prepared according to the previous literature.[9] As colorless oil. IR (CH_2Cl_2) ν 2961, 1736, 1616, 1444, 1411, 1322, 1260, 1165, 1115, 1084, 1069, 1048, 1016, 837, 747 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 7.62-7.35 (10H, m), 7.27 (3H, d, J = 8.1 Hz), 3.53 (1H, dd, J_1 = 9.6 Hz, J_2 = 6.0 Hz), 2.87-2.80 (2H, m), 2.64-2.47 (1H, m), 1.93-1.80 (1H, m); ^{19}F NMR (282 MHz, $CDCl_3$, $CFCl_3$): δ -61.69, -61.72, -61.80 (major & minor); MS (ESI) for **5** (major) *m/z* (%) 497.0 [M^++H]; HRMS (ESI) Calcd for $C_{25}H_{19}O_2F_6S^{+1}$ [M^++H] requires 497.0998, Found 497.1004.

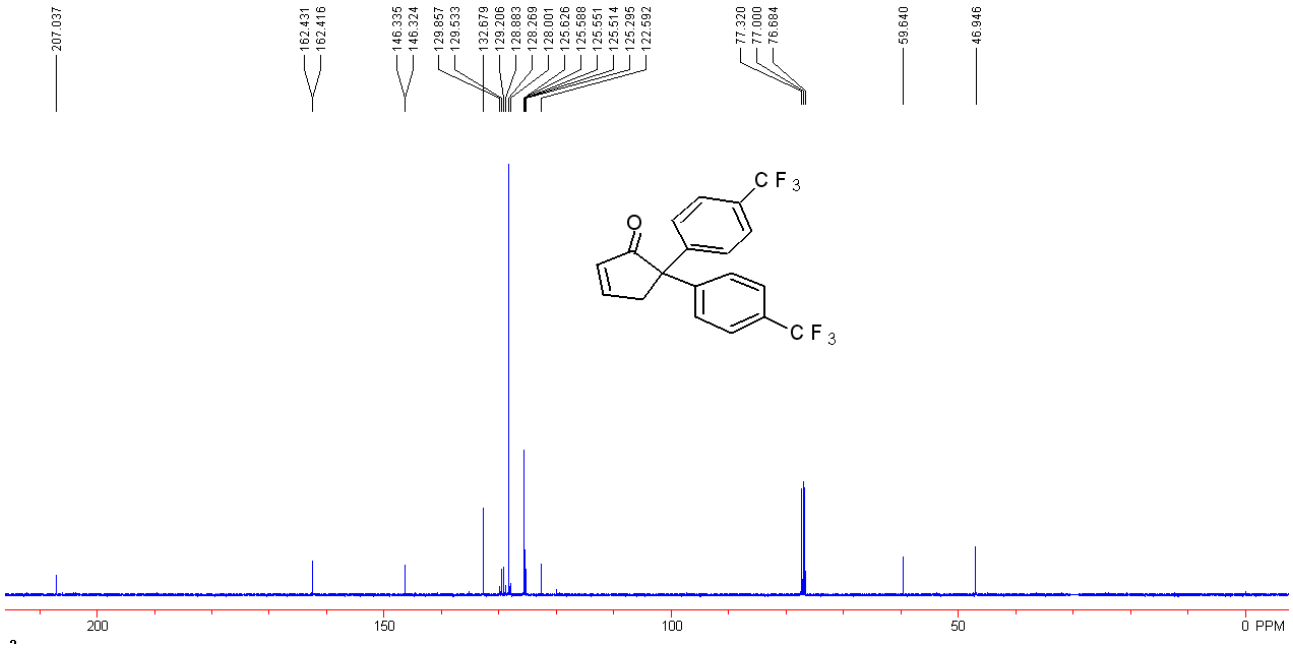


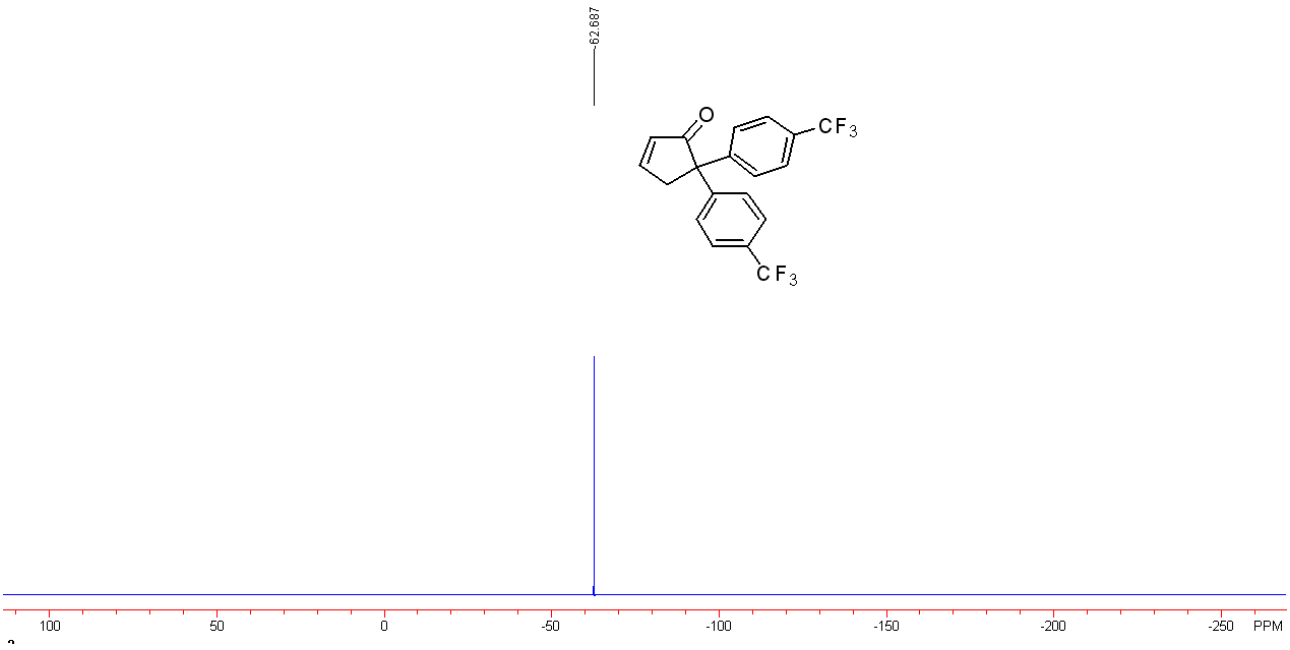
Compound 1c: 5,5-bis(4-(trifluoromethyl)phenyl)cyclopent-2-enone

Procedure: This compound was prepared according to the previous literature.[9] A mixture of **5** and **5'** (400 mg, 0.8 mmol) was dissolved in 15 mL toluene and potassium carbonate (336 mg, 2.4 mmol) was added. The resulting solution was heated to reflux for three hours. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel (EtOAc/PE = 1/4 as eluent) to furnish product **1c** as a white solid (150 mg, 51% yield). m.p. 97-99 ^{o}C; IR (CH_2Cl_2) ν 2926, 1707, 1616, 1595, 1410, 1320, 1261, 1163, 1112, 1017, 958, 936, 831, 802, 766 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.93-7.90 (1H, m), 7.58 (4H, d, *J* =

8.4 Hz), 7.32 (4H, d, J = 8.4 Hz), 6.33-6.31 (1H, m), 3.53 (2H, d, J = 2.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.0, 162.4 (d, $J_{C\text{-}F}$ = 1.5 Hz), 146.3 (d, $J_{C\text{-}F}$ = 1.1 Hz), 132.7, 129.4 (q, $J_{C\text{-}F}$ = 32.4 Hz), 128.3, 125.6 (q, $J_{C\text{-}F}$ = 3.7 Hz), 123.9 (q, $J_{C\text{-}F}$ = 270.3 Hz), 59.6, 46.9; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -62.7; (EI) *m/z* (%) 370 (100.00) [M^+], 351 (17.56), 301 (33.68), 273 (40.35), 225 (40.90), 202 (14.32), 183 (11.08), 177 (16.41), 159 (34.82); HRMS (EI) Calcd for $C_{19}H_{12}OF_6$ [M^+] requires 370.0792, Found 370.0786.







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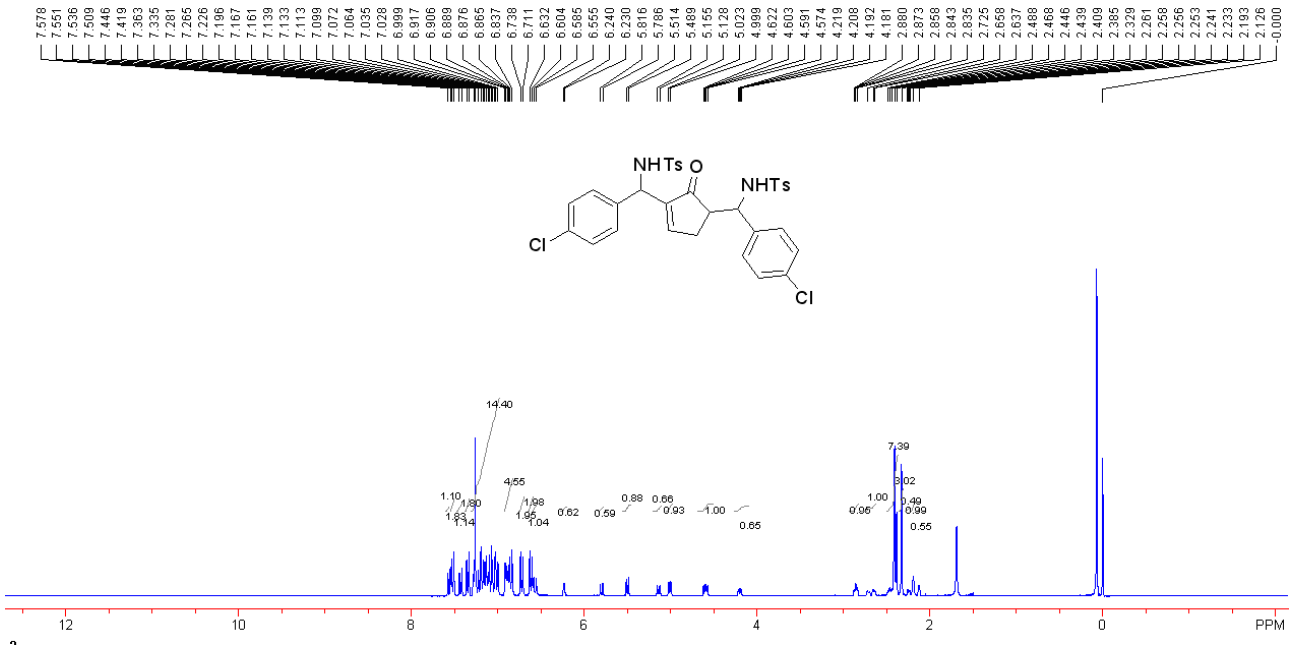
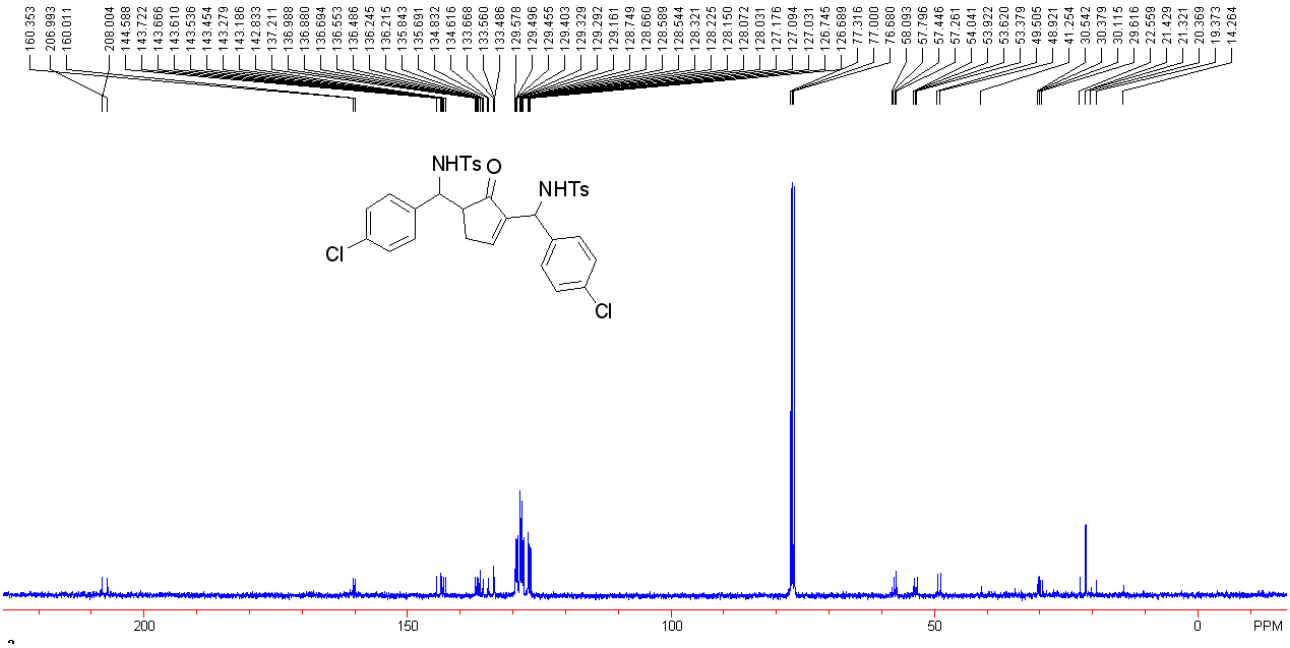
[9] M. Pohmakotr, P. Phinyocheep, *Tetrahedron Lett.*, **1984**, *25*, 2249.

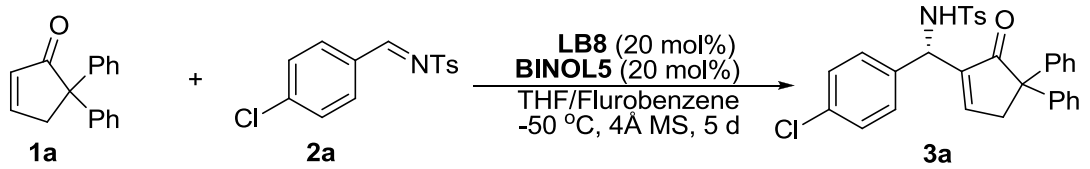
Procedure: **Preparation of syn- and anti-D**

To a mixture of **A** (41 mg, 0.5 mmol) **2a** (147 mg, 0.5 mmol) in 1.0 mL THF was added and the resulting mixture was stirred at room temperature for 16 hours. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel (EtOAc/PE = 1/1 as eluent) to yield product syn- and anti-**D** as a white solid (84 mg, 50% yield). The structure of syn-**D** was confirmed by X-ray diffraction. syn- and anti-mixture **D**: m.p. 133-135 ^{o}C; IR (CH_2Cl_2) ν 3268, 3062, 2923, 1689, 1629, 1596, 1491, 1429, 1412, 1328, 1304, 1262, 1156, 1089, 1013, 969, 915, 812 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.57 (1H, d, *J* = 8.1 Hz), 7.52 (2H, d, *J* = 8.1 Hz), 7.43 (1H, d, *J* = 8.1 Hz), 7.35 (1H, d, *J* = 8.1 Hz), 7.28-7.00 (12H, m), 6.92-6.84 (4H, m), 6.72 (2H, d, *J* = 8.1 Hz), 6.62 (2H, d, *J* = 8.4 Hz), 6.57 (1H, d, *J* = 9.0 Hz), 6.24 (0.62H, d, *J* = 3.0 Hz), 5.80 (0.59H, d, *J* = 9.0 Hz), 5.50 (1H, d, *J* = 7.5 Hz), 5.14 (0.66H, d, *J* = 8.1 Hz), 5.01 (1H, d, *J* = 7.2 Hz), 4.60 (1H, dd, J_1 = 9.3 Hz, J_2 = 5.7 Hz), 4.20 (0.65H, dd, J_1 = 8.1 Hz, J_2 = 3.3 Hz), 2.88-2.84 (1H, m), 2.73-2.64 (1H, m), 2.49-2.39 (7H, m), 2.33 (3H, s), 2.26-2.23 (0.49H, m), 2.19 (1H, bs), 2.13 (1H, bs); ^{13}C NMR (100 MHz, $CDCl_3$): δ 208.0, 207.0, 160.4, 160.0, 144.6, 143.7, 143.66, 143.61, 143.5, 143.3, 143.2, 142.8, 137.2, 137.0, 136.9, 136.7, 136.6, 136.5, 136.24, 136.22, 135.8, 135.7, 134.8, 134.6, 133.7, 133.6, 133.5, 129.6, 129.5, 129.45, 129.40, 129.33, 129.30, 129.2, 128.75, 128.70, 128.6, 128.5, 128.3, 128.22, 128.20, 128.1, 128.0, 127.2, 127.1, 127.0, 126.74, 126.70, 58.1, 58.0, 57.4, 57.3, 54.0, 53.9, 53.6, 53.4, 49.5, 48.9, 41.2, 30.5, 30.4, 30.1, 29.6, 22.6, 21.4, 21.3, 20.4, 19.4, 14.3; MS (ESI) *m/z* (%) 691.1 [M^{+}+Na]; HRMS (ESI) Calcd for $C_{33}H_{30}Cl_2N_2O_5S_2Na^{+}$ [M^{+}+Na] requires 691.0973, Found 691.0980.





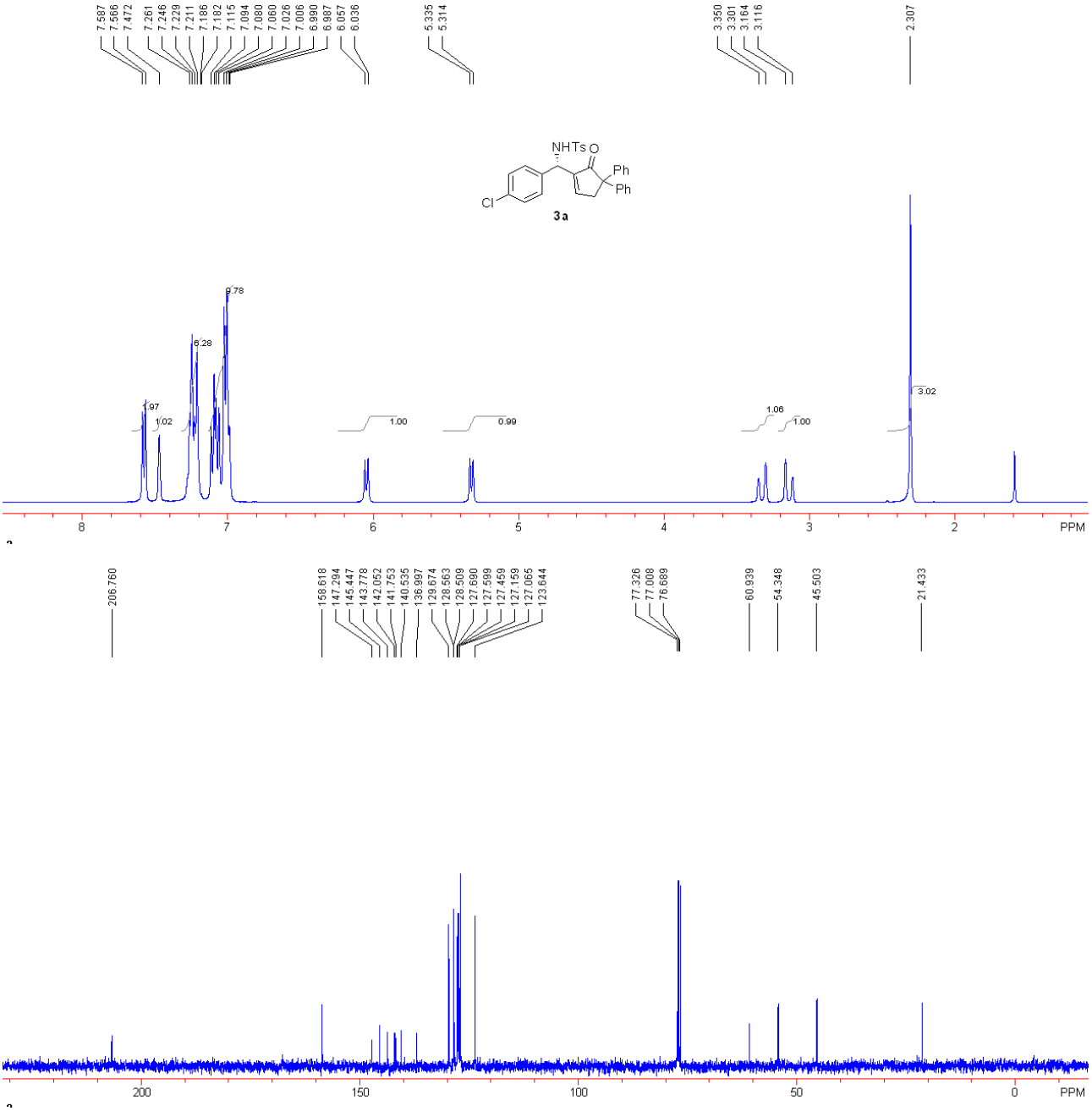
General Procedure for the Preparation of 3a from the Reaction of 1a with 2a. Using 3a as an Example in the Presence of LB8

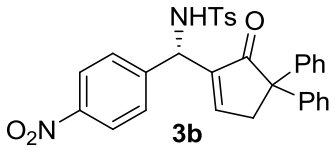


To a mixture of **1a** (0.075 mmol, 18 mg), **2a** (0.1125 mmol, 33 mg), catalyst **LB8** (10 mg, 0.015 mmol), **BINOL5** (12 mg, 0.015 mmol) and 50 mg 4Å MS was added 1.0 mL of THF/Fluorobenzene (1:1) at -50 ^{o}C under argon. The reaction solution was stirred for about 5 days and monitored by TLC. After the reaction completed, the solution was concentrated under reduced pressure and the residue was further purified by silica gel column chromatography (EtOAc/PE = 1/4) to give the target product **3a**.

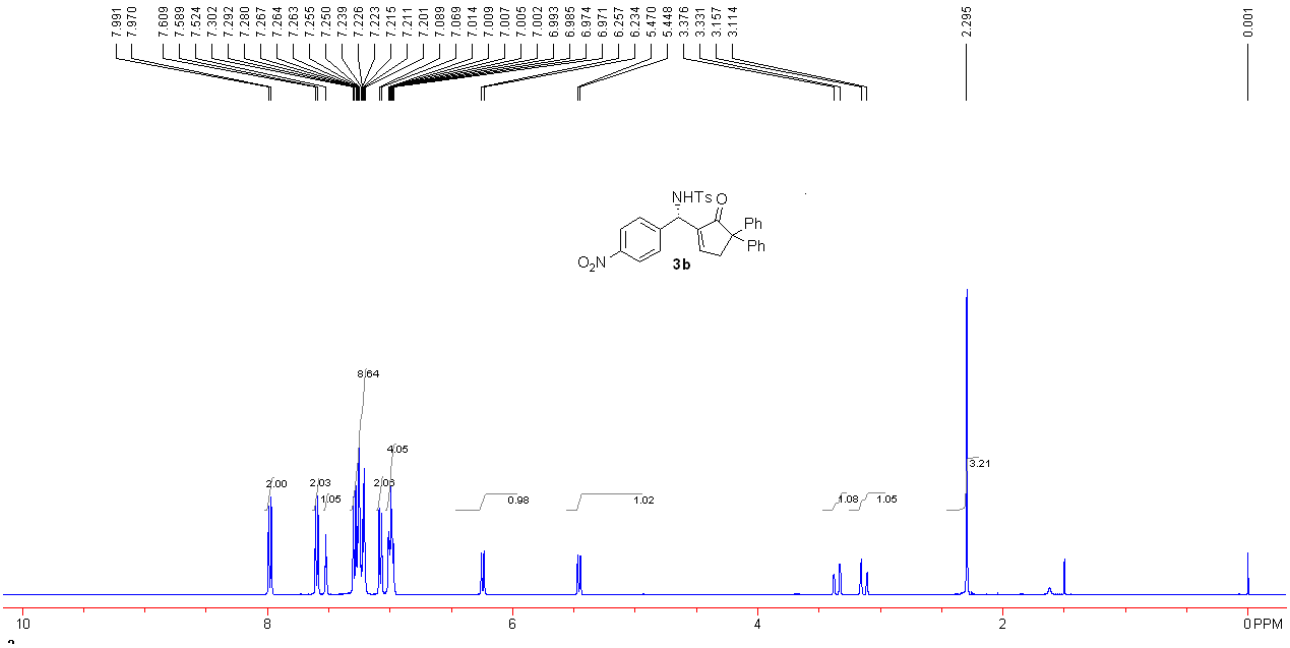
(*S*)-N-((4-chlorophenyl)(5-oxo-4,4-diphenylcyclopent-1-enyl)methyl)-4-methylbenzenesulfonamide 3a: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3a** (36 mg, 90% yield). A white solid. m.p. for racemic **3a** = 206-208 ^{o}C; m.p. for **3a** = 169-170 ^{o}C; $[\alpha]^{20}_{D}$ = +18.0 (c 0.3, CH_2Cl_2). IR (CH_2Cl_2): ν 3277, 3057, 2923, 2585, 1694, 1634, 1596, 1490, 1328, 1157, 1088, 1034, 1013, 919, 883, 812, 756, 734 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.58 (2H, d, *J* = 8.0 Hz), 7.47 (1H, s), 7.26-7.21 (6H,

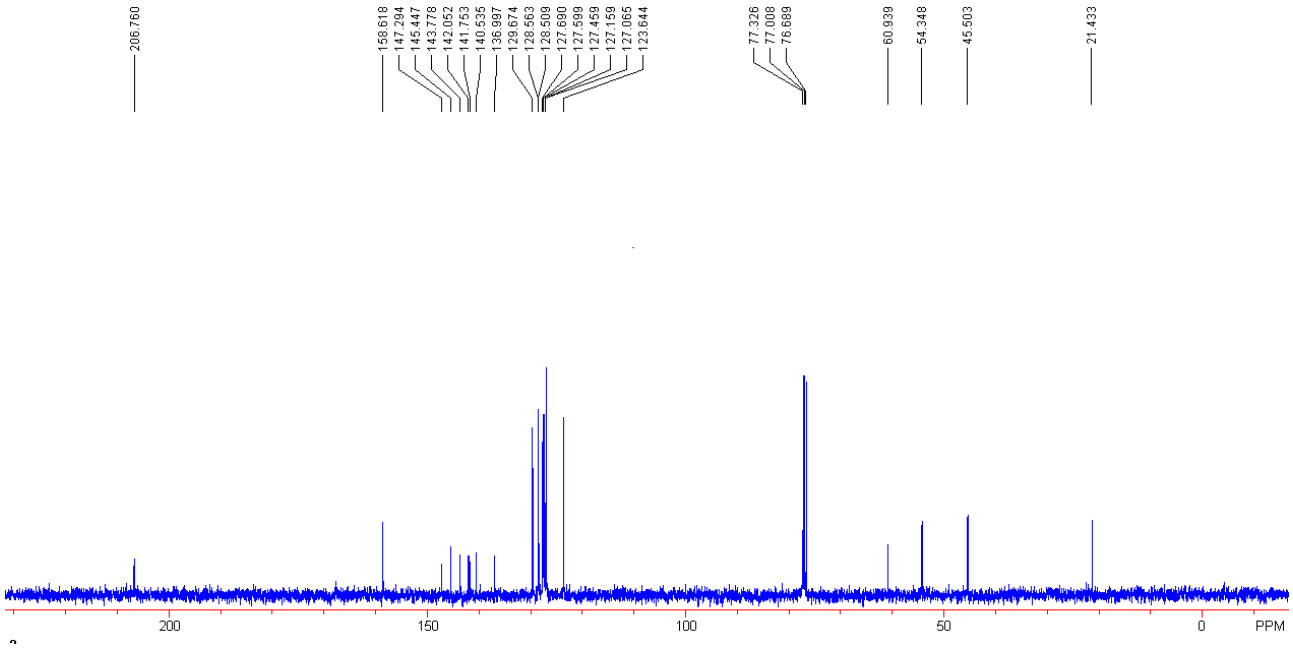
m), 7.11-6.99 (10H, m), 6.05 (1H, d, *J* = 8.4 Hz), 5.32 (1H, d, *J* = 8.4 Hz), 3.32 (1H, d, *J* = 19.2 Hz), 3.14 (1H, d, *J* = 19.2 Hz), 2.31 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 206.9, 158.0, 143.4, 142.3, 142.2, 141.4, 137.2, 136.8, 133.7, 129.6, 128.6, 128.5, 128.4, 128.1, 127.8, 127.6, 127.1, 127.0, 126.9, 61.0, 54.5, 45.4, 21.4; MS (ESI) m/e 550.0 (M^++Na); HRMS (ESI) for $C_{31}H_{26}ClNO_3SNa^{+1}$ (M^++Na): 550.1223, Found: 550.1214. The ee of the **3a** was determined to be 82% [determined by HPLC, Chiralpak AD-H, n-hexane/isopropanol = 70:30, 0.5 mL/min, λ = 214 nm, t (major) = 25.55 min, t (minor) = 34.47 min].

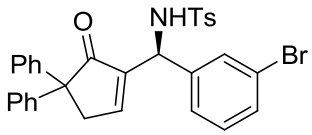




(*S*)-4-methyl-N-((4-nitrophenyl)(5-oxo-4,4-diphenylcyclopent-1-enyl)methyl)benzenesulfonamide 3b: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3b** (40 mg, 99% yield). A white solid. m.p. for racemic **3b** = 160-162 ^{o}C; m.p. for **3b** = 145-148 ^{o}C; $[\alpha]^{20}_{D}$ = +13.6 (c 0.6, CH_2Cl_2). IR (CH_2Cl_2): ν 3279, 3058, 2923, 2583, 1697, 1634, 1597, 1492, 1444, 1345, 1159, 1089, 1034, 1015, 927, 883, 814, 757, 734 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.98 (2H, d, *J* = 8.4 Hz), 7.60 (2H, d, *J* = 8.0 Hz), 7.52 (1H, s), 7.30-7.20 (8H, m), 7.08 (2H, d, *J* = 8.0 Hz), 7.01-6.97 (4H, m), 6.25 (1H, d, *J* = 9.2 Hz), 5.46 (1H, d, *J* = 8.8 Hz), 3.35 (1H, d, *J* = 18.0 Hz), 3.14 (1H, d, *J* = 17.2 Hz), 2.30 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 206.7, 158.6, 147.3, 145.4, 143.8, 142.0, 141.8, 140.5, 137.0, 129.7, 128.6, 128.5, 127.7, 127.6, 127.5, 127.2, 127.1, 123.6, 60.9, 54.3, 45.5, 21.4; MS (ESI) m/e 561.0 (M^{+}+Na); HRMS (ESI) for $C_{31}H_{26}N_2O_5SNa^{+1}$ (M^{+}+Na): 561.1460, Found: 561.1454. The ee of the **3b** was determined to be 85% [determined by HPLC, Chiralpak AD-H, n-hexane/isopropanol = 70:30, 0.5 mL/min, λ = 214 nm, t (major) = 51.21 min, t (minor) = 56.76 min].

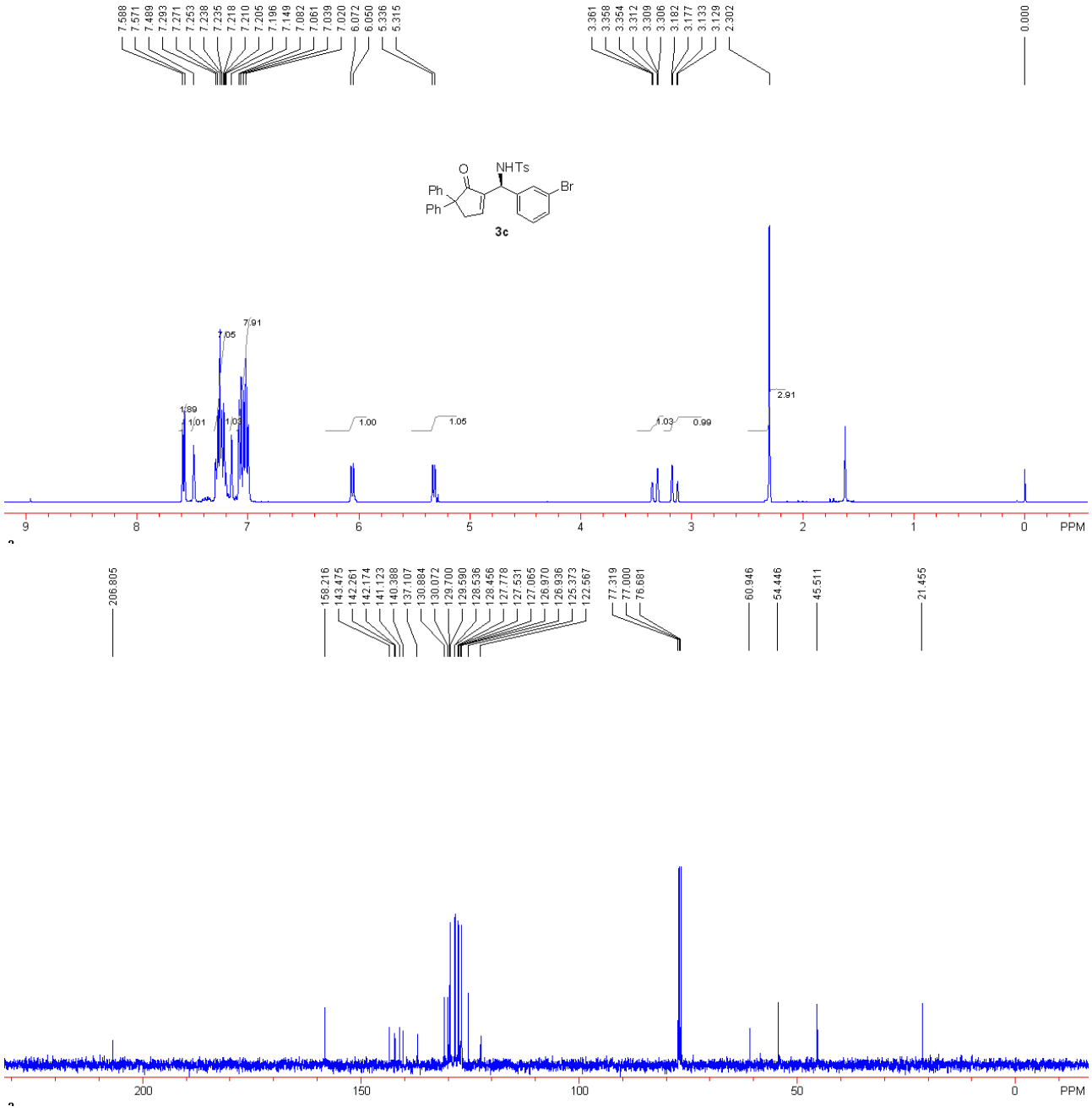


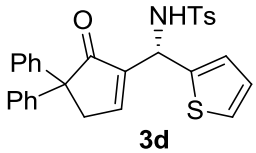




3c

(*S*)-N-((3-bromophenyl)(5-oxo-4,4-diphenylcyclopent-1-enyl)methyl)-4-methylbenzenesulfonamide 3c: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3c** (41 mg, 96% yield). A white solid. m.p. for racemic **3c** = 146-148 ^{o}C; m.p. for **3c** = 150-152 ^{o}C; $[\alpha]^{20}_{D}$ = +22.0 (c 0.3, CH_2Cl_2). IR (CH_2Cl_2): ν 3273, 3058, 2961, 2923, 2846, 1698, 1634, 1595, 1492, 1473, 1443, 1330, 1259, 1158, 1090, 1018, 931, 797, 759 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.58 (2H, d, *J* = 6.8 Hz), 7.49 (1H, s), 7.29-7.20 (7H, m), 7.15 (1H, s), 7.08-7.02 (8H, m), 6.06 (1H, d, *J* = 8.8 Hz), 5.33 (1H, d, *J* = 8.4 Hz), 3.35-3.31 (1H, m), 3.16 (1H, dd, J_1 = 19.6 Hz, J_2 = 2.0 Hz), 2.30 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 206.8, 158.2, 143.5, 142.3, 142.2, 141.1, 140.4, 137.1, 130.9, 130.1, 129.7, 129.6, 128.53, 128.50, 127.8, 127.5, 127.1, 127.0, 126.9, 125.4, 122.6, 60.9, 54.4, 45.5, 21.4; MS (ESI) m/e 594.0 (M^++Na); HRMS (ESI) for $C_{31}H_{26}NO_3SBrNa^{+1}$ (M^++Na): 594.0715, Found: 594.0709. The ee of the **3c** was determined to be 79% [determined by HPLC, Chiralpak AD-H, n-hexane/isopropanol = 70:30, 0.5 mL/min, λ = 214 nm, t (major) = 19.96 min, t (minor) = 12.36 min].

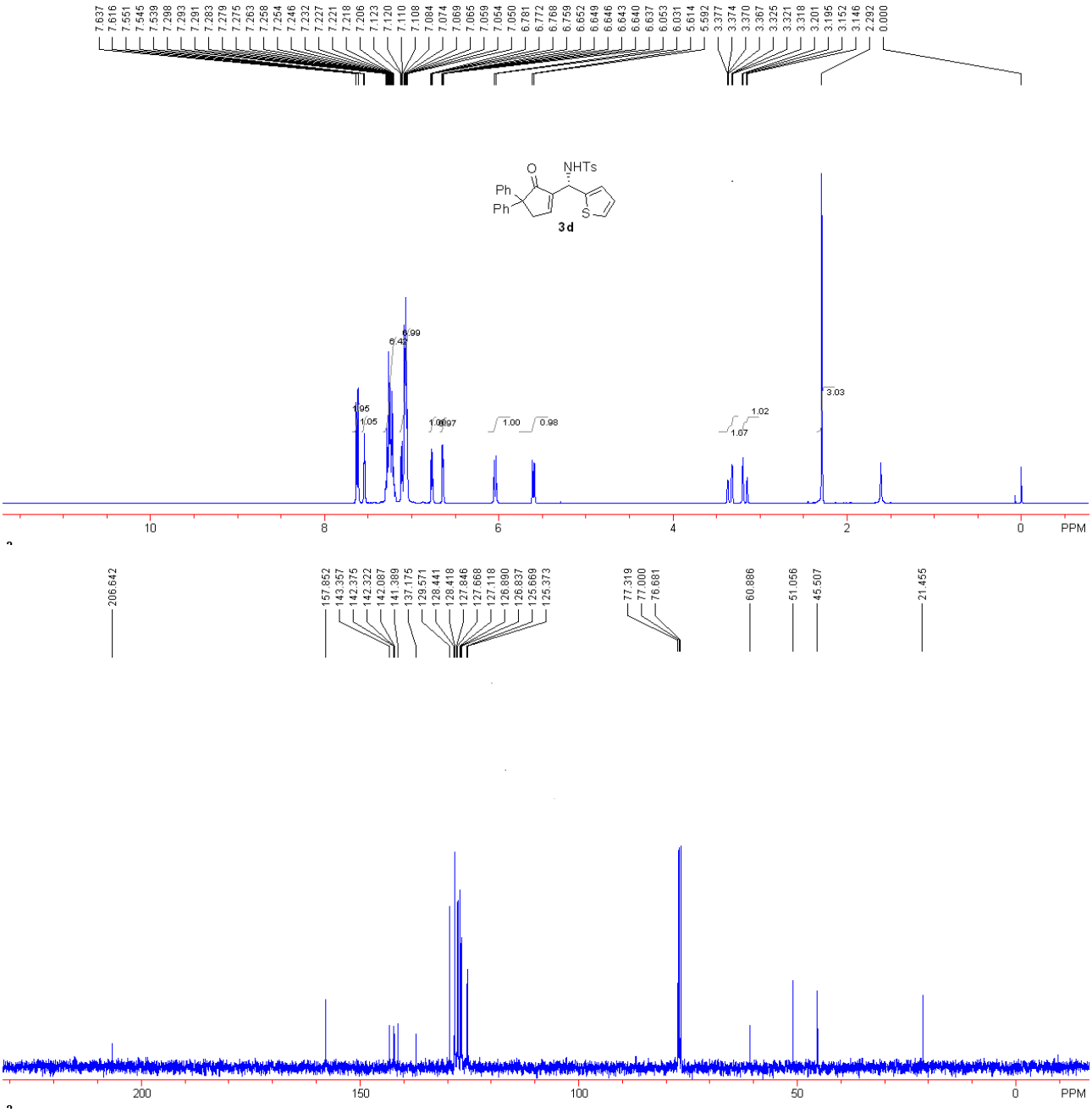


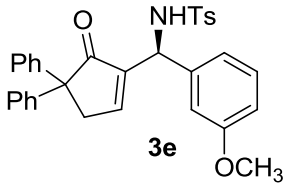


3d

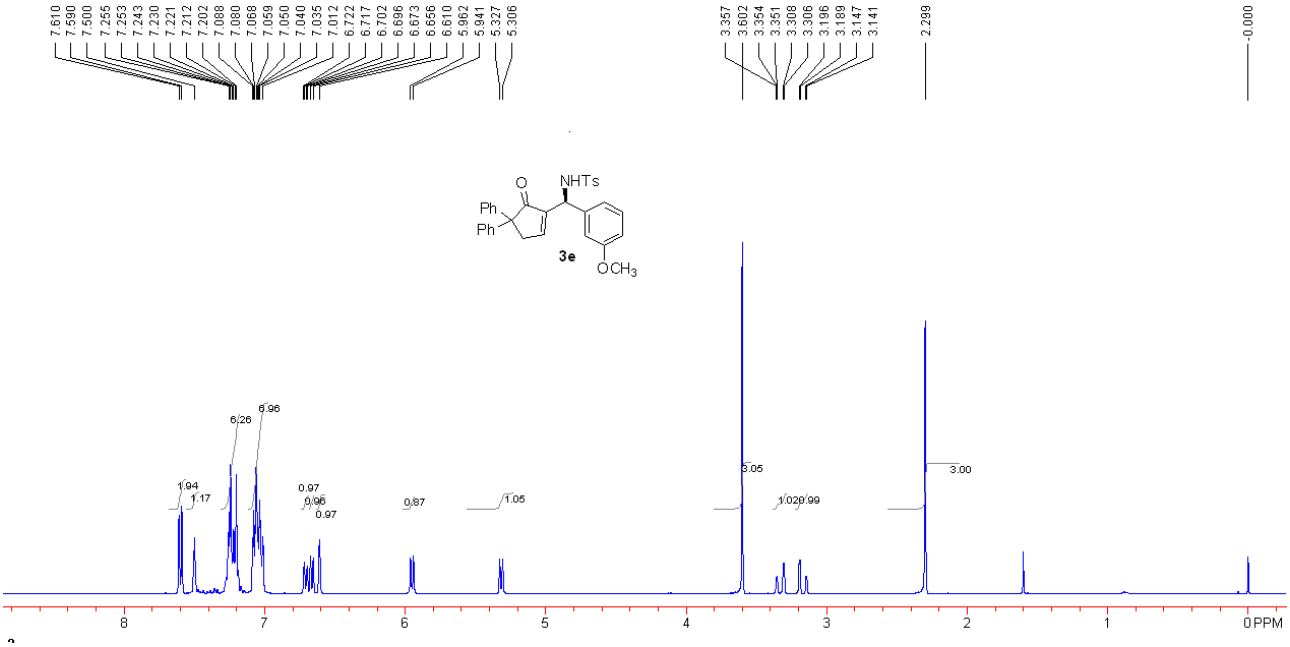
(*S*)-4-methyl-N-((5-oxo-4,4-diphenylcyclopent-1-enyl)(thiophen-2-yl)methyl)benzenesulfonamide 3d: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3d** (35 mg, 94% yield). A white solid. m.p. for racemic **3d** = 185-187 ^{o}C; m.p. for **3d** = 182-184 ^{o}C; $[\alpha]^{20}_{D}$ = +51.6 (c 0.4, CH_2Cl_2). IR (CH_2Cl_2): ν 3275, 3060, 2923, 2852, 1697, 1635, 1597, 1492, 1443, 1331, 1304, 1259, 1106, 1089, 921, 814, 758

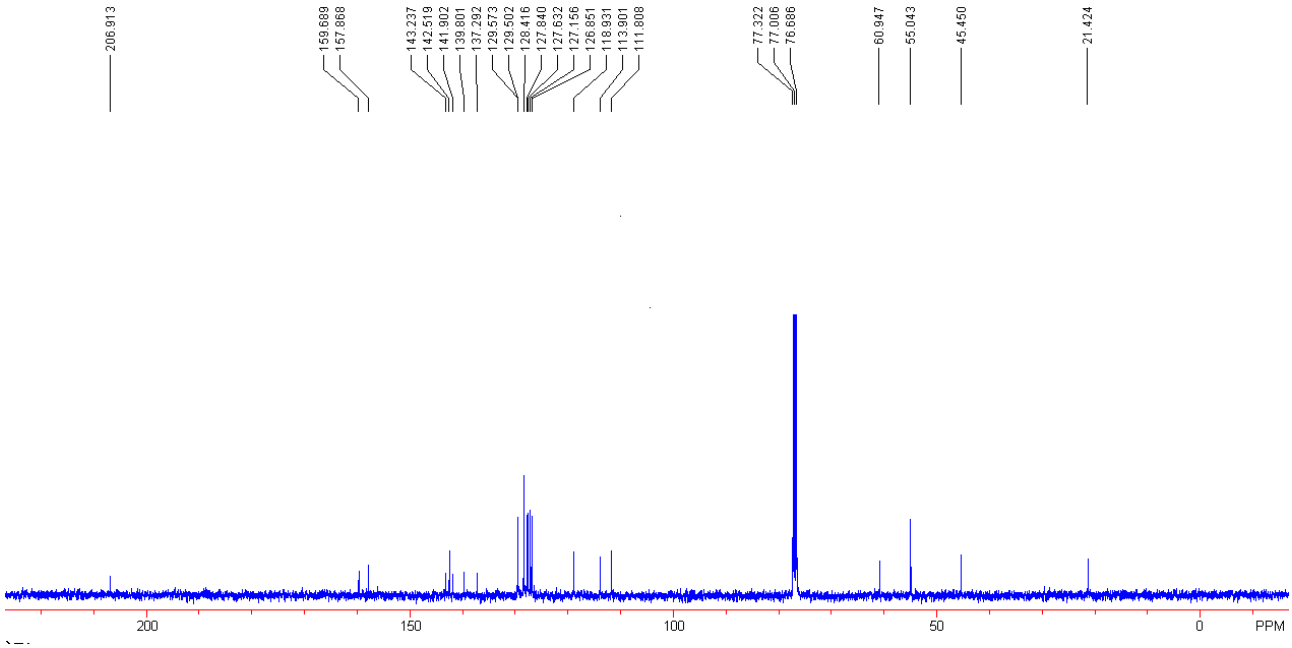
cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.63 (2H, d, J = 8.4 Hz), 7.55 (1H, t, J = 2.4 Hz), 7.30-7.21 (6H, m), 7.12-7.05 (7H, m), 6.77 (1H, dd, J_1 = 5.2 Hz, J_2 = 3.6 Hz), 6.65-6.64 (1H, m), 6.04 (1H, d, J = 8.8 Hz), 5.60 (1H, d, J = 8.8 Hz), 3.38-3.32 (1H, m), 3.17 (1H, dd, J_1 = 19.6 Hz, J_2 = 2.4 Hz), 2.29 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 206.6, 157.9, 143.4, 142.4, 142.3, 142.1, 141.4, 137.2, 129.6, 128.44, 128.42, 127.8, 127.7, 127.1, 126.9, 126.8, 125.7, 125.4, 60.9, 51.1, 45.5, 21.5; MS (ESI) m/e 522.0 (M^++Na); HRMS (ESI) for $C_{29}H_{25}NO_3S_2Na^{+1}$ (M^++Na): 522.1174, Found: 522.1186. The ee of the **3d** was determined to be 76% [determined by HPLC, Chiralpak AD-H, n-hexane/isopropanol = 70:30, 0.5 mL/min, λ = 214 nm, t (major) = 30.22 min, t (minor) = 26.58 min].

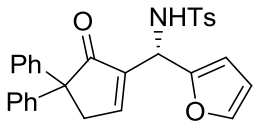




(*S*)-N-((3-methoxyphenyl)(5-oxo-4,4-diphenylcyclopent-1-enyl)methyl)-4-methylbenzenesulfonamide 3e: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3e** (35 mg, 90% yield). A white solid. m.p. for racemic **3e** = 153-154 ^{o}C; m.p. for **3e** = 141-143 ^{o}C; $[\alpha]^{20}_{D}$ = +27.3 (c 0.4, CH_2Cl_2). IR (CH_2Cl_2): ν 3277, 2923, 2853, 1700, 1599, 1492, 1444, 1331, 1262, 1160, 1091, 1036, 917, 814, 698 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.60 (2H, d, *J* = 8.0 Hz), 7.50 (1H, s), 7.26-7.20 (6H, m), 7.09-7.01 (7H, m), 6.71 (1H, dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz), 6.66 (1H, d, *J* = 6.8 Hz), 6.61 (1H, s), 5.95 (1H, d, *J* = 8.4 Hz), 5.32 (1H, d, *J* = 8.4 Hz), 3.60 (3H, s), 3.36-3.31 (1H, m), 3.17 (1H, dd, J_1 = 19.6 Hz, J_2 = 2.8 Hz), 2.30 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 206.9, 159.7, 157.9, 143.2, 142.5, 141.9, 139.8, 137.3, 129.6, 129.5, 128.4, 127.8, 127.6, 127.2, 126.9, 118.9, 113.9, 111.8, 60.9, 55.0, 45.5, 21.4; MS (ESI) m/e 546.0 (M^++Na); HRMS (ESI) for $C_{32}H_{29}NO_4SNa^{+1}$ (M^++Na): 546.1711, Found: 546.1710. The ee of the **3e** was determined to be 75% [determined by HPLC, Chiralpak AD-H, n-hexane/isopropanol = 70:30, 0.5 mL/min, λ = 214 nm, t (major) = 31.59 min, t (minor) = 27.87 min].



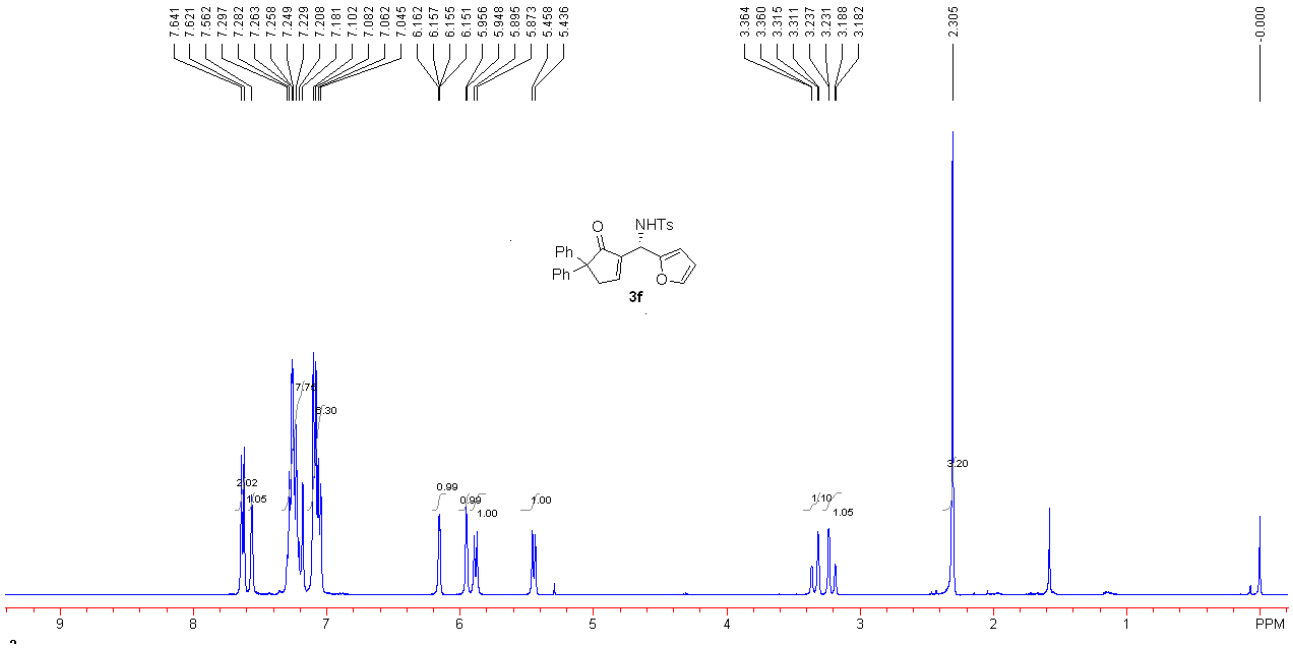


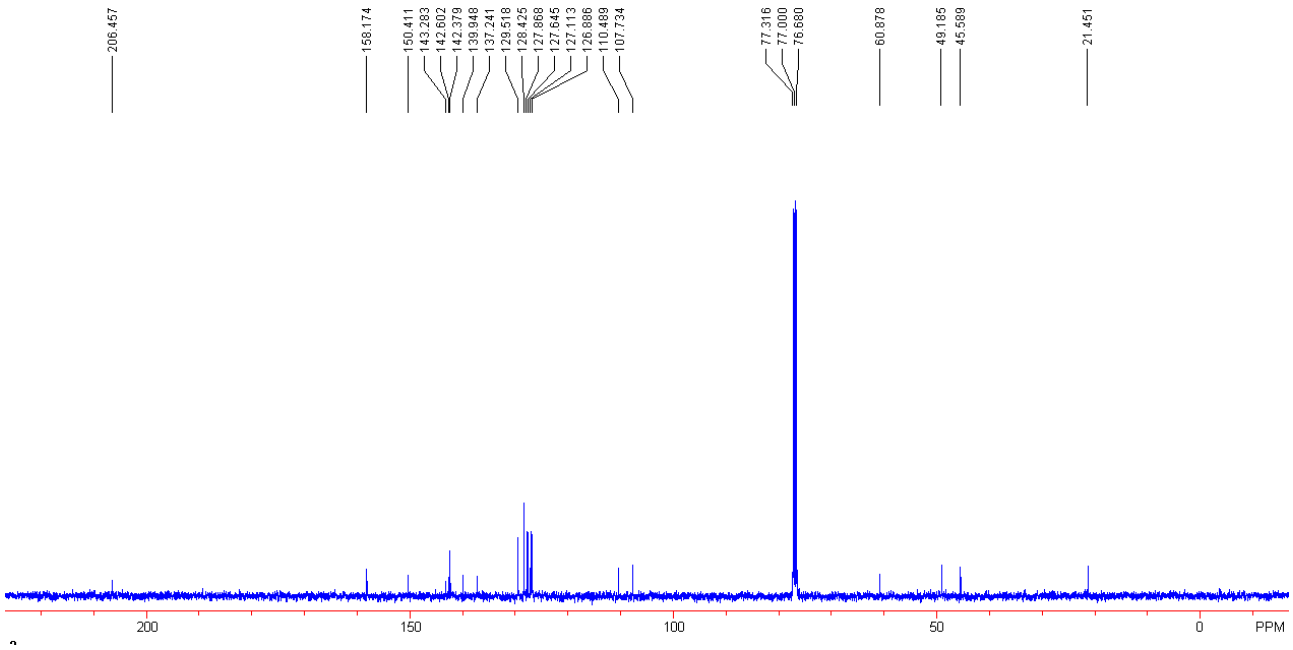


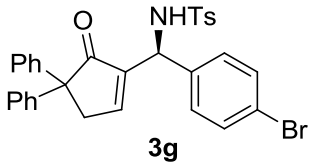
3f

(*S*)-N-(furan-2-yl(5-oxo-4,4-diphenylcyclopent-1-enyl)methyl)-4-methylbenzenesulfonamide

3f: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3f** (23 mg, 61% yield). A white solid. m.p. for racemic **3f** = 160-163 ^{o}C; m.p. for **3f** = 167-168 ^{o}C; $[\alpha]^{20}_{D}$ = +22.0 (c 0.8, CH_2Cl_2). IR (CH_2Cl_2): ν 3278, 3059, 1701, 1638, 1597, 1493, 1444, 1332, 1184, 1106, 1090, 1012, 917, 753 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.63 (2H, d, *J* = 8.0 Hz), 7.56 (1H, s), 7.30-7.18 (7H, m), 7.10-7.04 (6H, m), 6.16-6.15 (1H, m), 5.95 (1H, d, *J* = 3.2 Hz), 5.88 (1H, d, *J* = 8.8 Hz), 5.45 (1H, d, *J* = 8.8 Hz), 3.34 (1H, dd, J_1 = 19.6 Hz, J_2 = 2.0 Hz), 3.19 (1H, dd, J_1 = 19.6 Hz, J_2 = 2.4 Hz), 2.30 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 206.5, 158.2, 150.4, 143.3, 142.6, 142.4, 139.9, 137.2, 129.5, 128.4, 127.9, 127.6, 127.1, 126.9, 110.5, 107.7, 60.9, 49.2, 45.6, 21.5; MS (ESI) m/e 506.0 (M^{+}+Na); HRMS (ESI) for $C_{29}H_{25}NO_4SNa^{+1}$ (M^{+}+Na): 506.1396, Found: 506.1397. The ee of the **3f** was determined to be 68% [determined by HPLC, Chiralpak AD-H, n-hexane/isopropanol = 70:30, 0.5 mL/min, λ = 214 nm, t (major) = 29.53 min, t (minor) = 25.44 min].



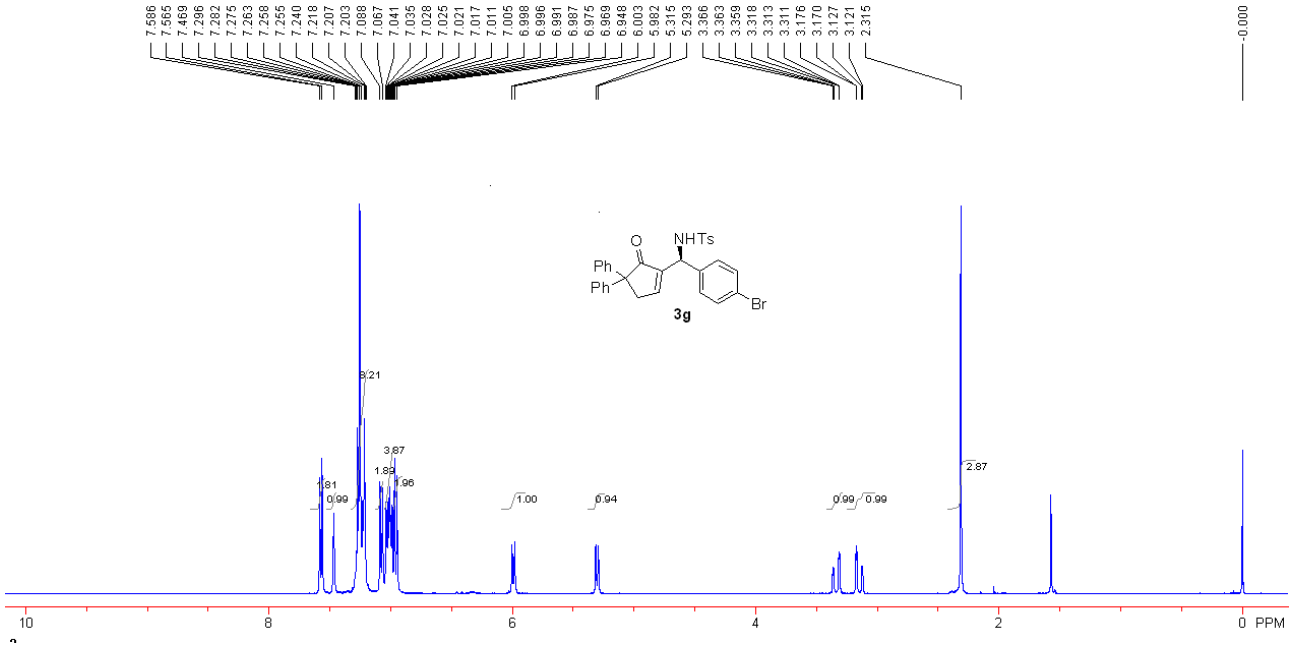


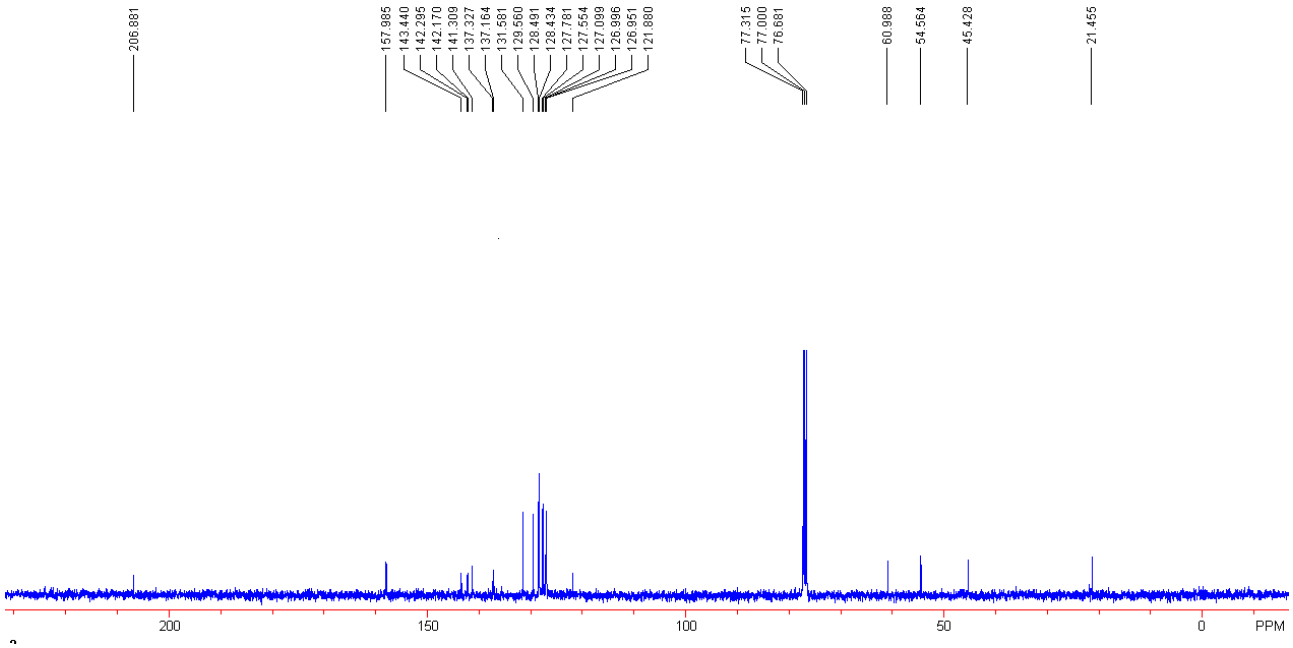


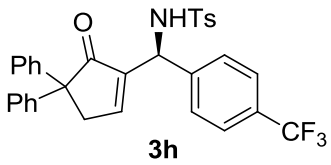
3g

(*S*)-N-((4-bromophenyl)(5-oxo-4,4-diphenylcyclopent-1-enyl)methyl)-4-methylbenzenesulfonamide 3g: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3g** (41 mg, 96% yield). A white solid. m.p. for racemic **3g** = 200-201 ^{o}C; m.p. for **3g** = 183-185 ^{o}C; $[\alpha]^{20}_{D}$ = +30.8 (c 0.8, CH_2Cl_2). IR (CH_2Cl_2): ν 3280,

3059, 2923, 2853, 1701, 1635, 1597, 1491, 1444, 1331, 1262, 1184, 1160, 1090, 1010, 755 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.58 (2H, d, *J* = 8.4 Hz), 7.47 (1H, s), 7.30-7.20 (8H, m), 7.08 (2H, d, *J* = 8.4 Hz), 7.04-7.00 (4H, m), 6.96 (2H, d, *J* = 8.4 Hz), 6.05 (1H, d, *J* = 8.4 Hz), 5.30 (1H, d, *J* = 8.8 Hz), 3.37-3.31 (1H, m), 3.15 (1H, dd, J_1 = 19.6 Hz, J_2 = 2.4 Hz), 2.32 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 206.9, 158.0, 143.4, 142.3, 142.2, 141.3, 137.3, 137.2, 131.6, 130.0, 128.5, 128.4, 127.8, 127.6, 127.1, 127.0, 126.9, 121.9, 61.0, 54.6, 45.4, 21.5; MS (ESI) m/e 594.0 (M^++Na); HRMS (ESI) for $C_{31}H_{26}NO_3SBrNa^{+1}$ (M^++Na): 594.0700, Found: 594.0709. The ee of the **3g** was determined to be 84% [determined by HPLC, Chiralpak AD-H, n-hexane/isopropanol = 70:30, 0.5 mL/min, λ = 214 nm, t (major) = 40.85 min, t (minor) = 28.32 min].

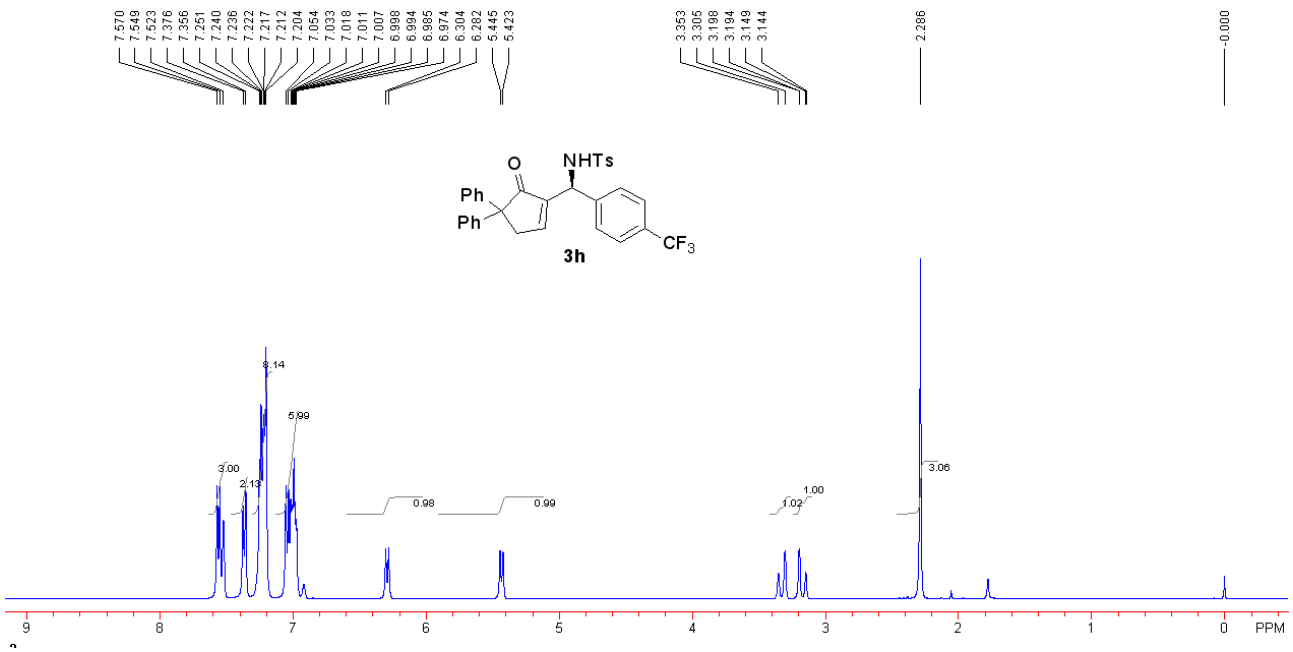


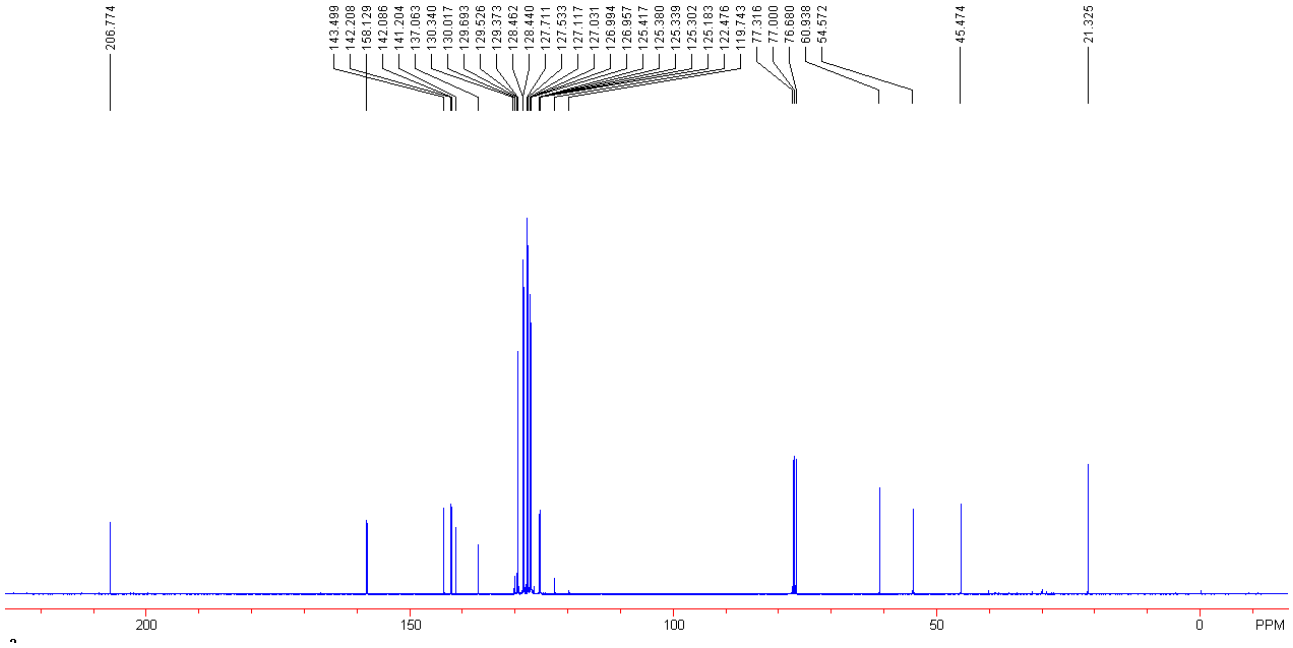


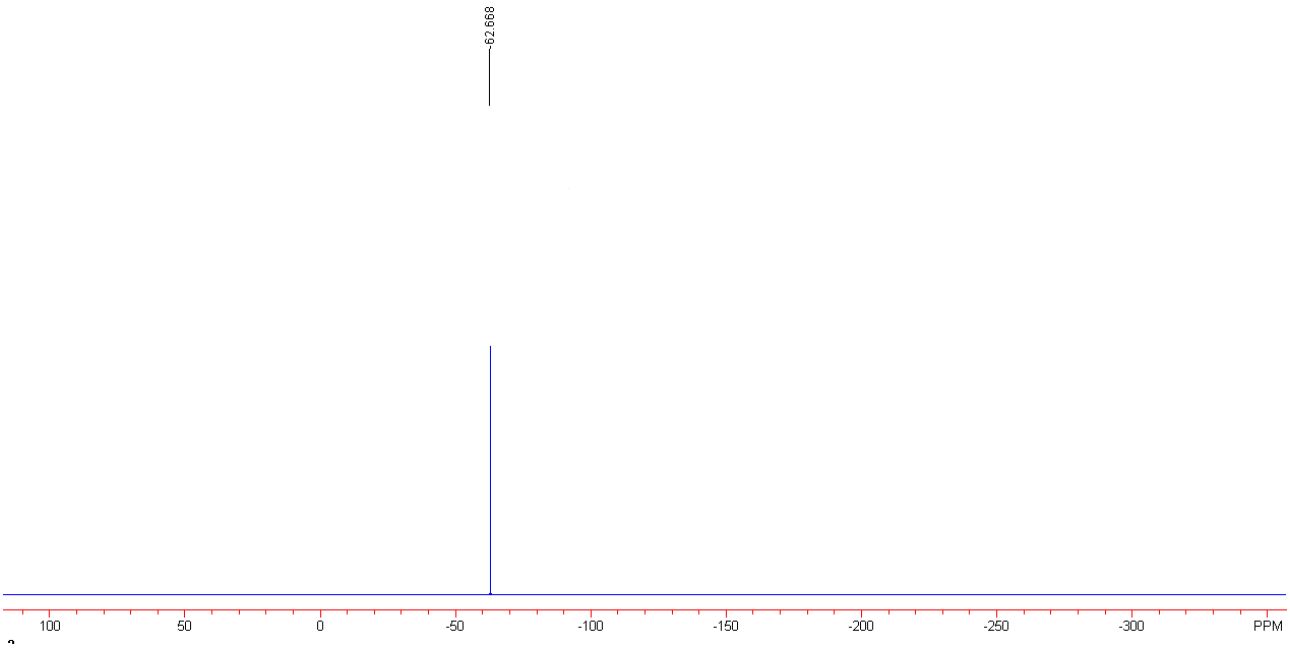


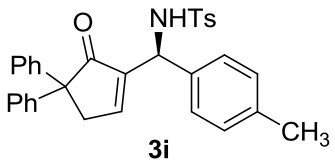
3h

(*S*)-4-methyl-N-((5-oxo-4,4-diphenylcyclopent-1-enyl)(4-(trifluoromethyl)phenyl)methyl)benzenesulfonamide 3h: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3h** (42 mg, 99% yield). A white solid. m.p. for racemic **3h** = 96-98 ^{o}C; m.p. for **3h** = 116-118 ^{o}C; $[\alpha]^{20}_{D}$ = +20.2 (c 0.5, CH_2Cl_2). IR (CH_2Cl_2): ν 3279, 2962, 1695, 1617, 1596, 1493, 1444, 1324, 1260, 1160, 1090, 1017, 798 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.56 (2H, d, *J* = 8.0 Hz), 7.52 (1H, s), 7.37 (2H, d, *J* = 8.0 Hz), 7.25-7.20 (8H, m), 7.05-7.00 (6H, m), 6.29 (1H, d, *J* = 8.8 Hz), 5.43 (1H, d, *J* = 8.8 Hz), 3.32 (1H, d, *J* = 19.2 Hz), 3.17 (1H, dd, J_1 = 19.6 Hz, J_2 = 2.0 Hz), 2.29 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 206.8, 158.1, 143.5, 142.2, 142.1, 141.2, 137.1, 129.9 (q, J_{C-F} = 32.4 Hz), 129.5, 128.5, 128.4, 127.7, 127.5, 127.1, 127.03, 127.00, 126.9, 125.3 (q, J_{C-F} = 3.7 Hz), 123.4 (q, J_{C-F} = 270.7 Hz), 60.9, 54.6, 45.5, 21.3; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -62.7; MS (ESI) m/e 584.0 (M^{+}+Na); HRMS (ESI) for $C_{32}H_{26}NO_3SF_3Na^{+1}$ (M^{+}+Na): 584.1479, Found: 584.1478. The ee of the **3h** was determined to be 80% [determined by HPLC, Chiralpak AD-H, n-hexane/isopropanol = 70:30, 0.5 mL/min, λ = 214 nm, t (major) = 27.69 min, t (minor) = 21.37 min].





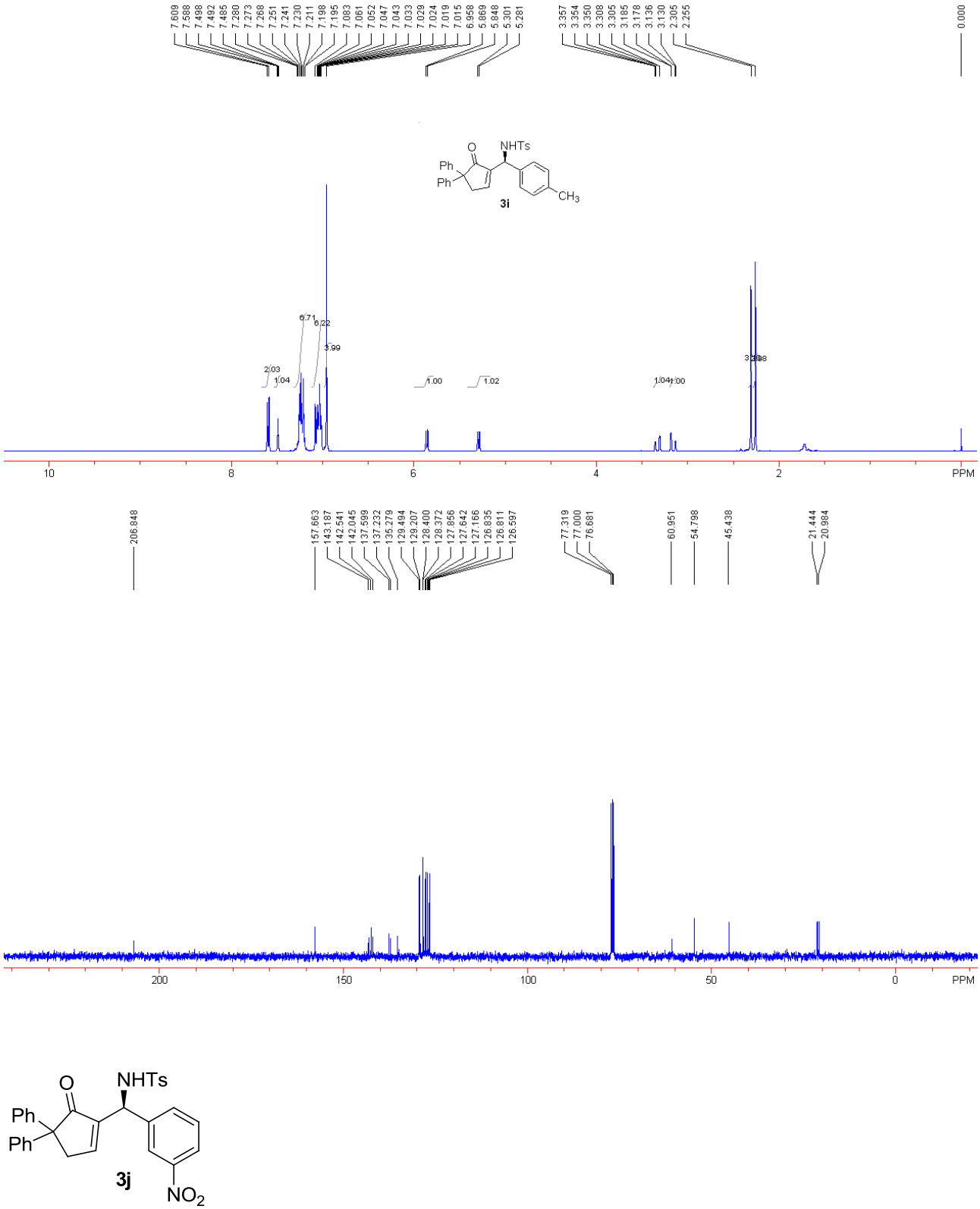




3i

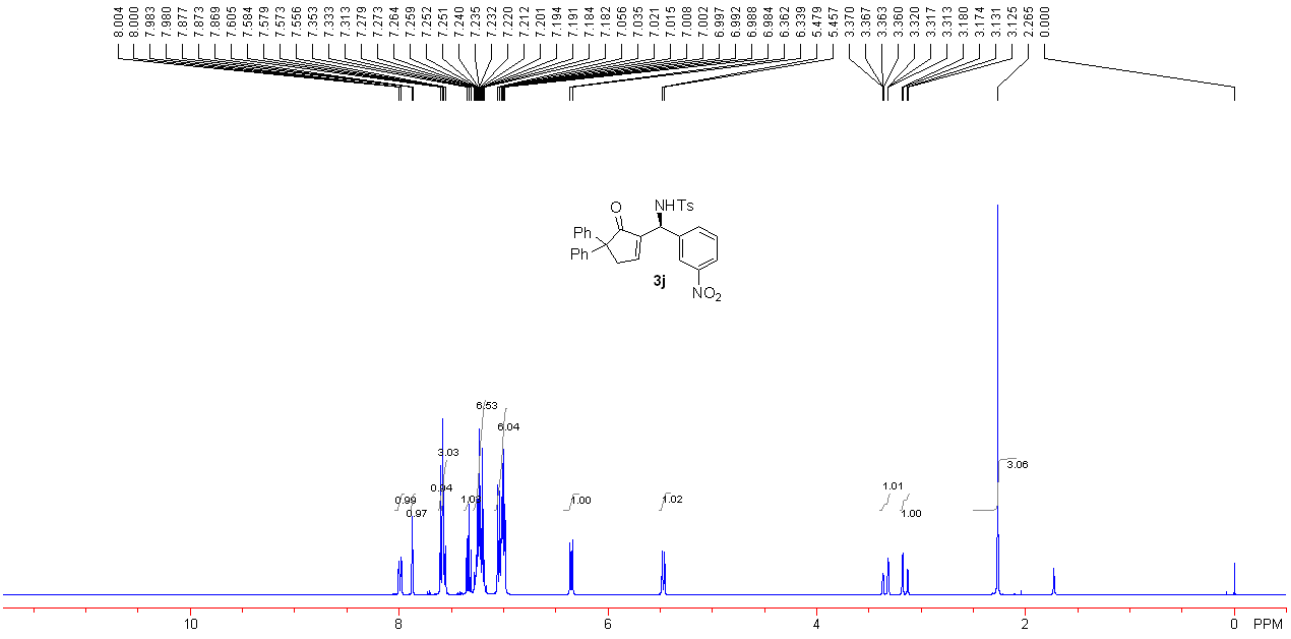
(*S*)-4-methyl-N-((5-oxo-4,4-diphenylcyclopent-1-enyl)(p-tolyl)methyl)benzenesulfonamide

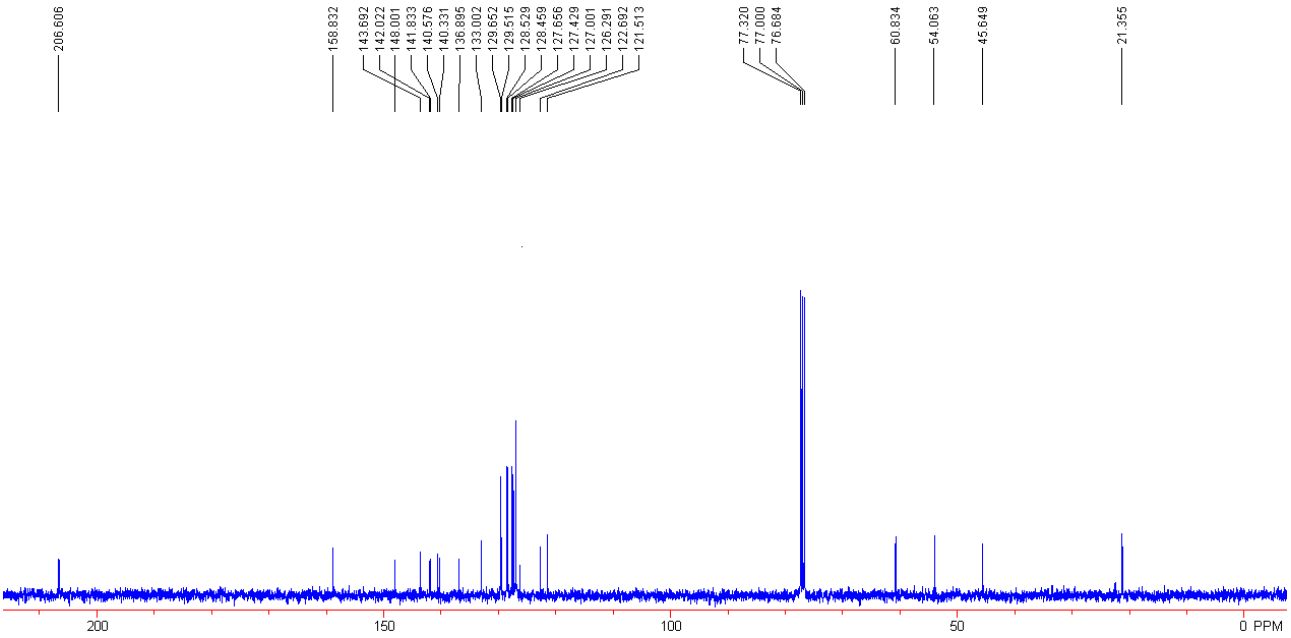
3i: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3i** (32 mg, 84% yield). A white solid. m.p. for racemic **3i** = 223-224 ^{o}C; m.p. for **3i** = 220-222 ^{o}C; $[\alpha]^{20}_{D}$ = +24.5 (c 0.5, CH_2Cl_2). IR (CH_2Cl_2): ν 3289, 2923, 1693, 1615, 1592, 1498, 1444, 1335, 1288, 1157, 1100, 1035, 1018, 931, 863, 813, 754 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.60 (2H, d, *J* = 8.4 Hz), 7.49 (1H, t, *J* = 2.4 Hz), 7.28-7.20 (6H, m), 7.08-7.02 (6H, m), 7.00 (4H, s), 5.86 (1H, d, *J* = 8.4 Hz), 5.29 (1H, d, *J* = 8.4 Hz), 3.36-3.31 (1H, m), 3.16 (1H, dd, J_1 = 19.6 Hz, J_2 = 2.0 Hz), 2.31 (3H, s), 2.26 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 206.8, 157.7, 143.2, 142.5, 142.0, 137.6, 137.2, 135.3, 129.5, 129.2, 128.4, 128.3, 127.9, 127.6, 127.2, 126.83, 126.81, 126.6, 60.9, 54.8, 45.4, 21.4, 20.1; MS (ESI) m/e 530.0 (M^{+}+Na); HRMS (ESI) for $C_{32}H_{29}NO_3SNa^{+1}$ (M^{+}+Na): 530.1761, Found: 530.1760. The ee of the **3i** was determined to be 84% [determined by HPLC, Chiralpak AD-H, n-hexane/isopropanol = 70:30, 0.5 mL/min, λ = 214 nm, t (major) = 24.68 min, t(minor) = 27.06 min].

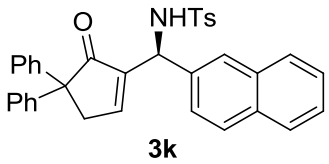


(*S*)-4-methyl-N-((3-nitrophenyl)(5-oxo-4,4-diphenylcyclopent-1-enyl)methyl)benzenesulfonamide 3j: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3j** (40 mg, 99% yield). A white solid. m.p. for racemic **3j** = 153-155 ^{o}C; m.p. for **3j** = 172-174 ^{o}C; $[\alpha]^{20}_{D}$ = +31.3 (c 1.0, CH_2Cl_2). IR (CH_2Cl_2): ν 3273, 3060,

2923, 1700, 1636, 1529, 1493, 1444, 1347, 1265, 1159, 1089, 1018, 912, 781, 732 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.99 (1H, dd, J_1 = 8.4 Hz, J_2 = 1.6 Hz), 7.87 (1H, t, J = 1.6 Hz), 7.60 (1H, s), 7.58-7.56 (3H, m), 7.33 (1H, t, J = 8.0 Hz), 7.28-7.18 (6H, m), 7.06-6.98 (6H, m), 6.35 (1H, d, J = 9.2 Hz), 5.47 (1H, d, J = 8.8 Hz), 3.37-3.31 (1H, m), 3.15 (1H, dd, J_1 = 19.6 Hz, J_2 = 2.4 Hz), 2.27 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 206.6, 158.8, 148.0, 143.7, 142.0, 141.8, 140.6, 140.3, 136.9, 133.0, 129.7, 129.5, 128.5, 128.4, 127.7, 127.4, 127.0, 126.3, 122.7, 121.5, 60.8, 54.1, 45.7, 21.4; MS (ESI) m/e 561.1 (M^++Na); HRMS (ESI) for $C_{31}H_{26}N_2O_5SNa^{+1}$ (M^++Na): 561.1453, Found: 561.1455. The ee of the **3j** was determined to be 82% [determined by HPLC, Chiralpak AD-H, n-hexane/isopropanol = 60:40, 0.5 mL/min, λ = 230 nm, t (major) = 27.18 min, t (minor) = 17.87 min].

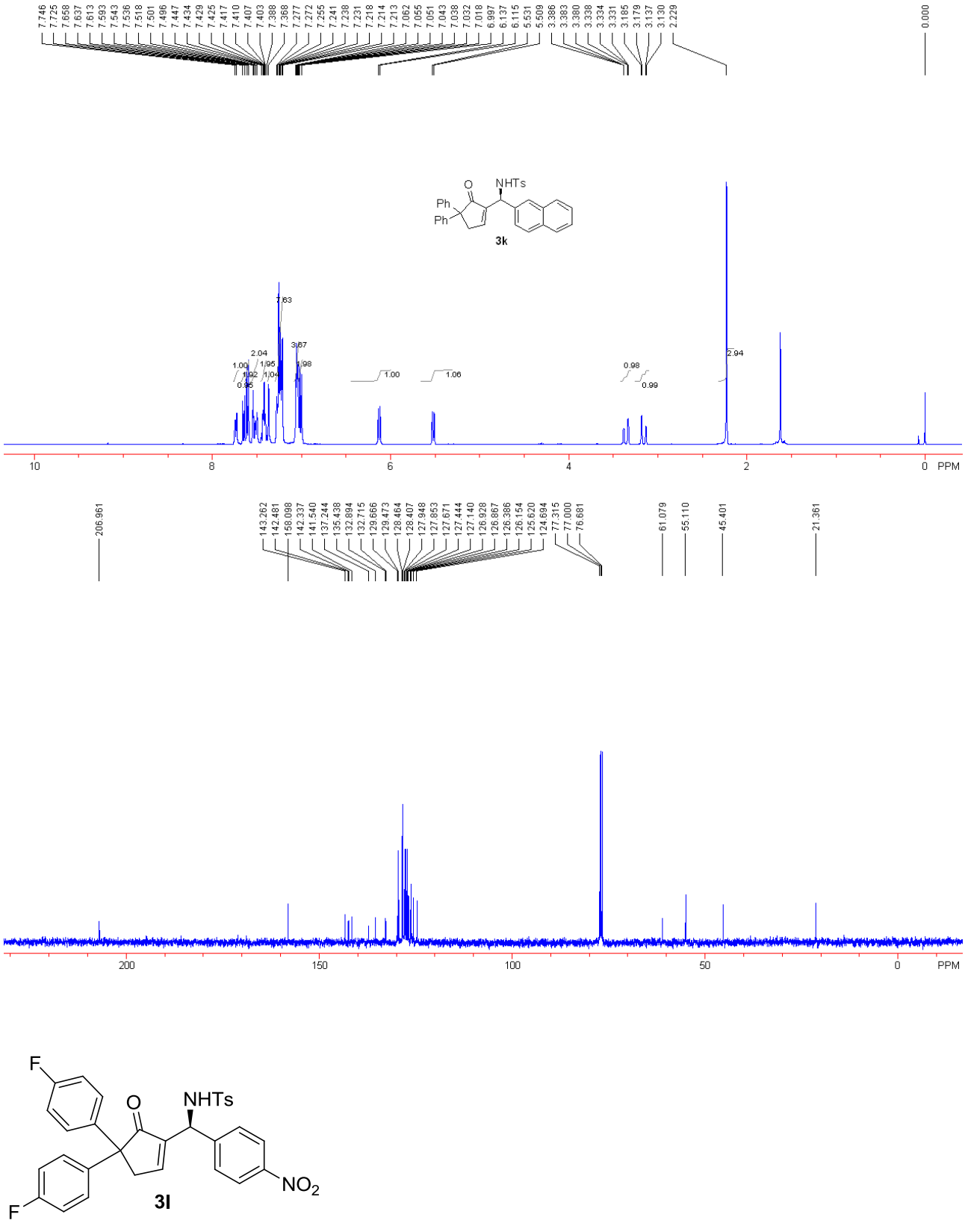






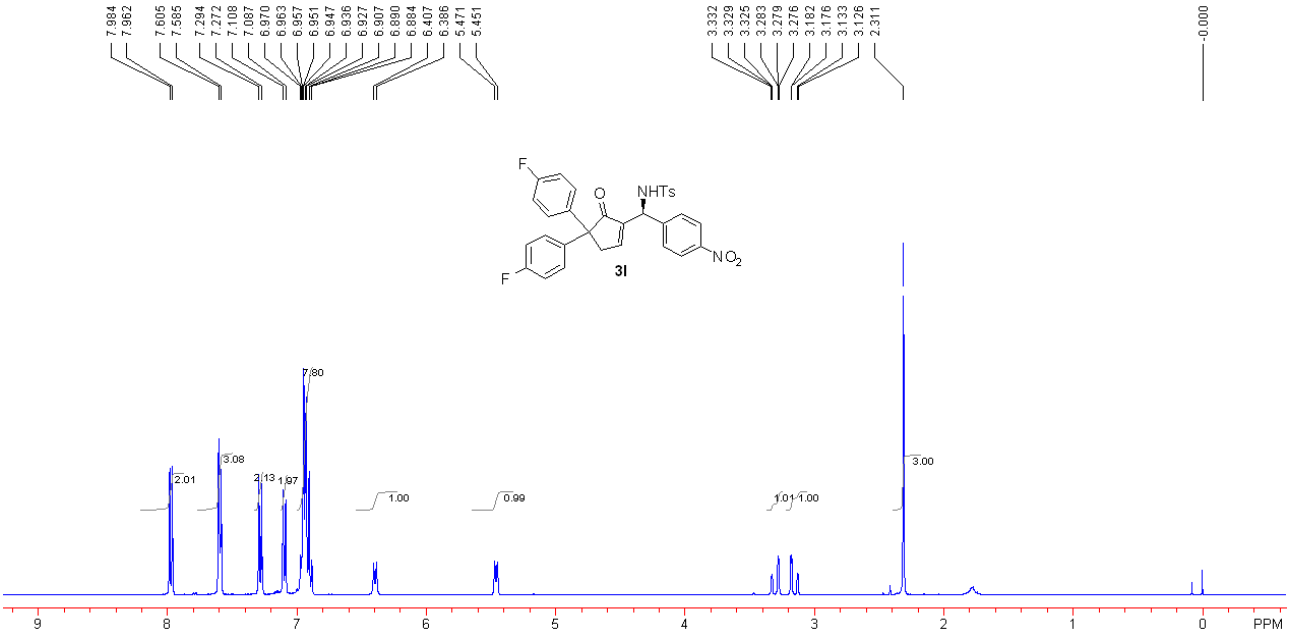
3k

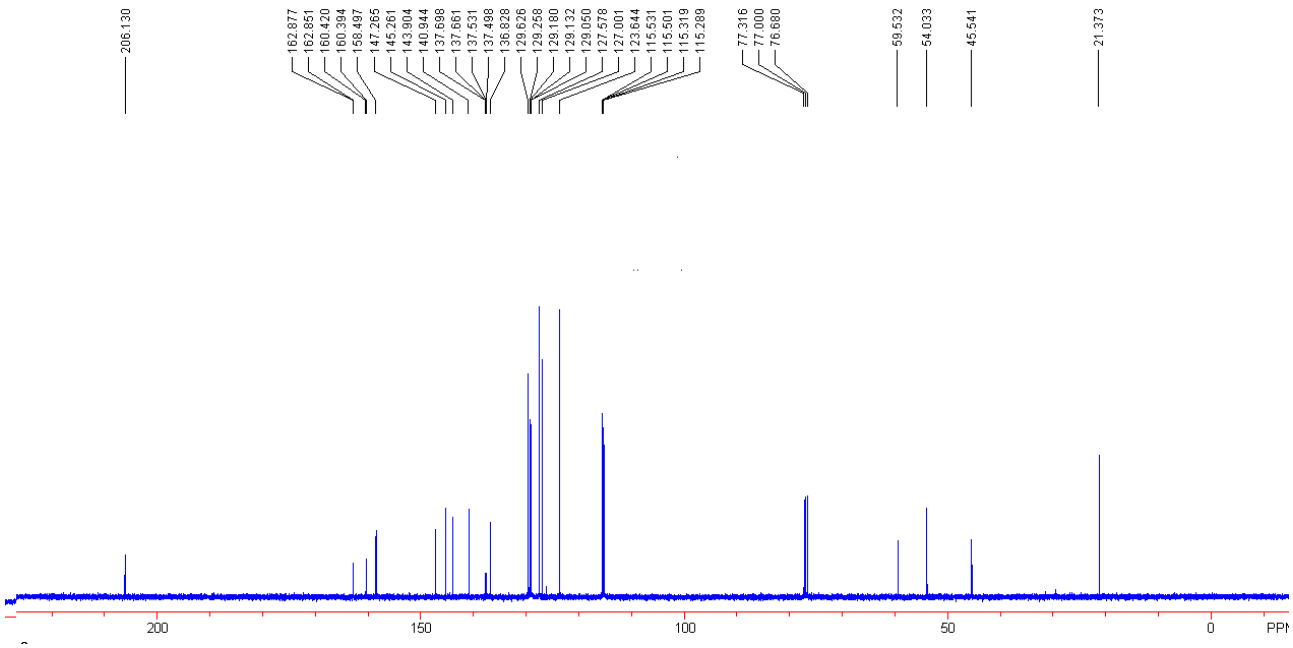
(*S*)-4-methyl-N-(naphthalen-2-yl(5-oxo-4,4-diphenylcyclopent-1-enyl)methyl)benzenesulfonamide 3k: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3k** (18 mg, 44% yield). A white solid. m.p. for racemic **3k** = 214-216 ^{o}C; m.p. for **3k** = 227-229 ^{o}C; $[\alpha]^{20}_{D}$ = +7.0 (c 0.2, CH_2Cl_2). IR (CH_2Cl_2): ν 3278, 2962, 1699, 1635, 1598, 1493, 1444, 1330, 1260, 1160, 1091, 1018, 860, 798, 756 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.74 (1H, d, *J* = 8.4 Hz), 7.65 (1H, d, *J* = 8.4 Hz), 7.60 (1H, d, *J* = 8.0 Hz), 7.54-7.50 (2H, m), 7.45-7.39 (2H, m), 7.37 (1H, s), 7.27-7.21 (7H, m), 7.06-7.03 (4H, m), 7.00 (2H, d, *J* = 8.4 Hz), 6.13 (1H, d, *J* = 8.8 Hz), 5.52 (1H, d, *J* = 8.8 Hz), 3.39-3.33 (1H, m), 3.16 (1H, dd, J_1 = 19.6 Hz, J_2 = 2.4 Hz), 2.30 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 207.0, 158.1, 143.3, 142.5, 142.3, 141.5, 137.2, 135.4, 132.9, 132.7, 129.7, 129.5, 128.5, 128.4, 127.9, 127.8, 127.7, 127.4, 127.1, 127.0, 126.9, 126.4, 126.2, 125.6, 124.7, 61.1, 55.0, 45.4, 21.4; MS (ESI) m/e 566.1 (M^{+}+Na); HRMS (ESI) for $C_{35}H_{29}NO_3SNa^{+1}$ (M^{+}+Na): 566.1868, Found: 566.1853. The ee of the **3k** was determined to be 60% [determined by HPLC, Chiralpak AD-H, n-hexane/isopropanol = 60:40, 0.5 mL/min, λ = 230 nm, t (major) = 48.73 min, t (minor) = 55.92 min].

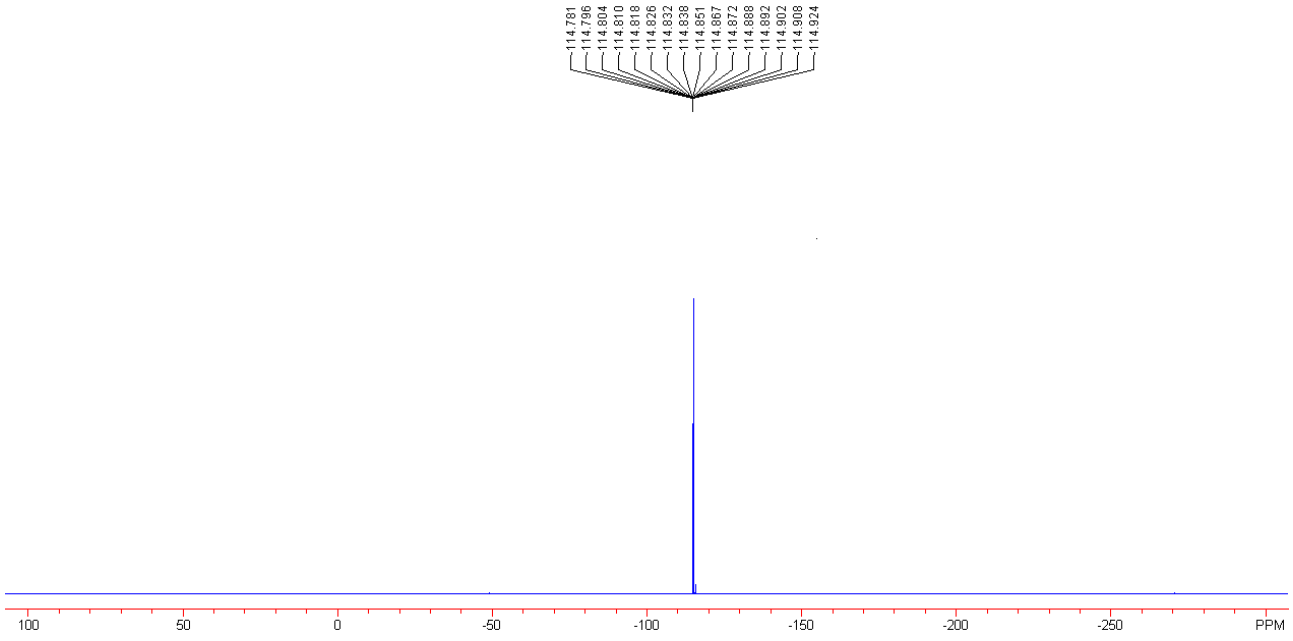


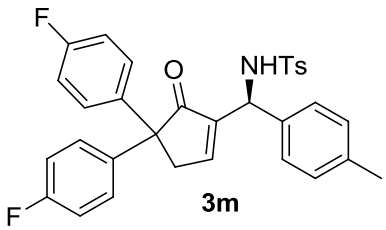
(*S*)-N-((4,4-bis(4-fluorophenyl)-5-oxocyclopent-1-enyl)(4-nitrophenyl)methyl)-4-methylbenzenesulfonamide 3l: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3l** (43 mg, 99% yield). A white solid. m.p. for racemic **3l** = 95-98 ^{o}C; m.p. for **3l** = 77-80 ^{o}C; $[\alpha]^{20}_{D}$ = +15.0 (c 0.3, CH_2Cl_2). IR

(CH_2Cl_2): ν 3281, 2924, 1701, 1635, 1598, 1520, 1507, 1434, 1233, 1184, 1161, 1091, 1015, 817, 735 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.97 (2H, d, J = 8.8 Hz), 7.60 (3H, d, J = 8.0 Hz), 7.28 (2H, d, J = 8.8 Hz), 7.10 (2H, d, J = 8.4 Hz), 6.97-6.88 (8H, m), 6.40 (1H, d, J = 8.4 Hz), 5.46 (1H, d, J = 8.0 Hz), 3.33-3.28 (1H, m), 3.15 (1H, dd, J_1 = 19.6 Hz, J_2 = 2.4 Hz), 2.31 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 206.1, 161.6 (dd, $J_{1C\text{-}F}$ = 245.7 Hz, $J_{2C\text{-}F}$ = 2.6 Hz), 158.5, 147.3, 145.3, 143.9, 140.9, 137.6 (dd, $J_{1C\text{-}F}$ =16.7 Hz, $J_{2C\text{-}F}$ = 3.7 Hz), 136.8, 129.2 (dd, $J_{1C\text{-}F}$ =12.6 Hz, $J_{2C\text{-}F}$ = 7.8 Hz), 127.6, 127.0, 123.6, 115.4 (dd, $J_{1C\text{-}F}$ = 21.2 Hz, $J_{2C\text{-}F}$ = 3.0 Hz), 59.5, 54.0, 45.5, 21.4; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -114.8–-114.9 (m); MS (ESI) m/e 597.0 (M^++Na); HRMS (ESI) for $C_{31}H_{24}N_2O_5SF_2Na^{+1}$ (M^++Na): 597.1251, Found: 597.1266. The ee of the **3l** was determined to be 82% [determined by HPLC, Chiralpak AD-H, n-hexane/isopropanol = 70:30, 0.5 mL/min, λ = 214 nm, t (major) = 45.42 min, t (minor) = 52.19 min].



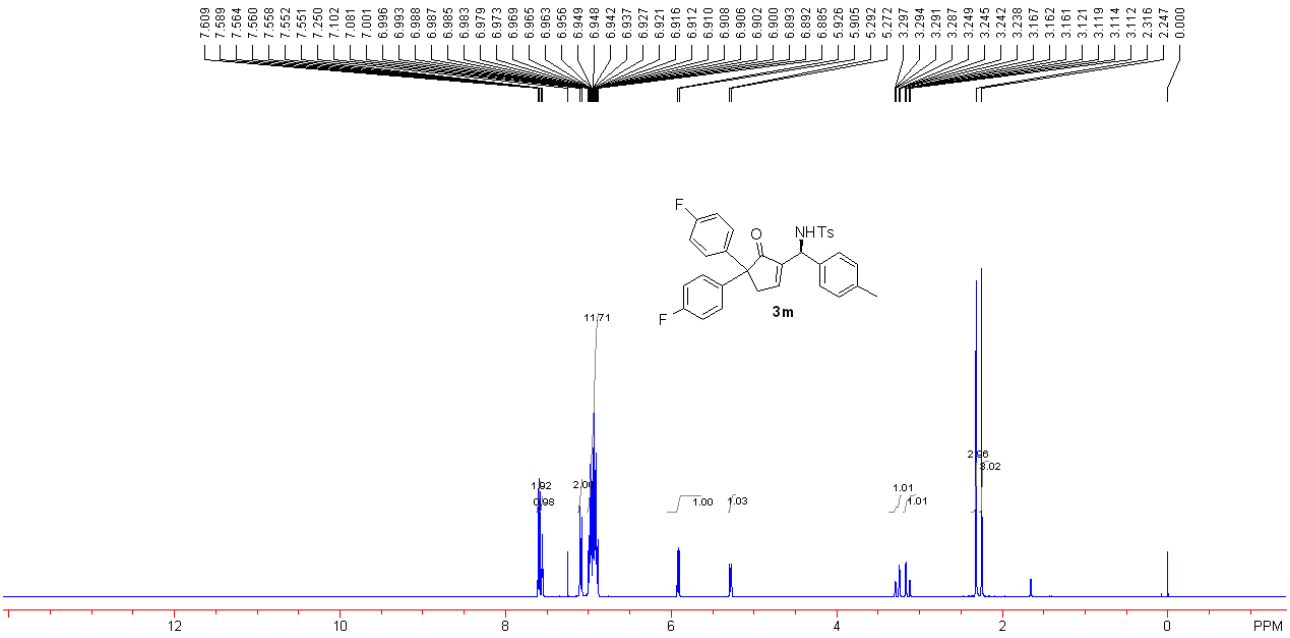


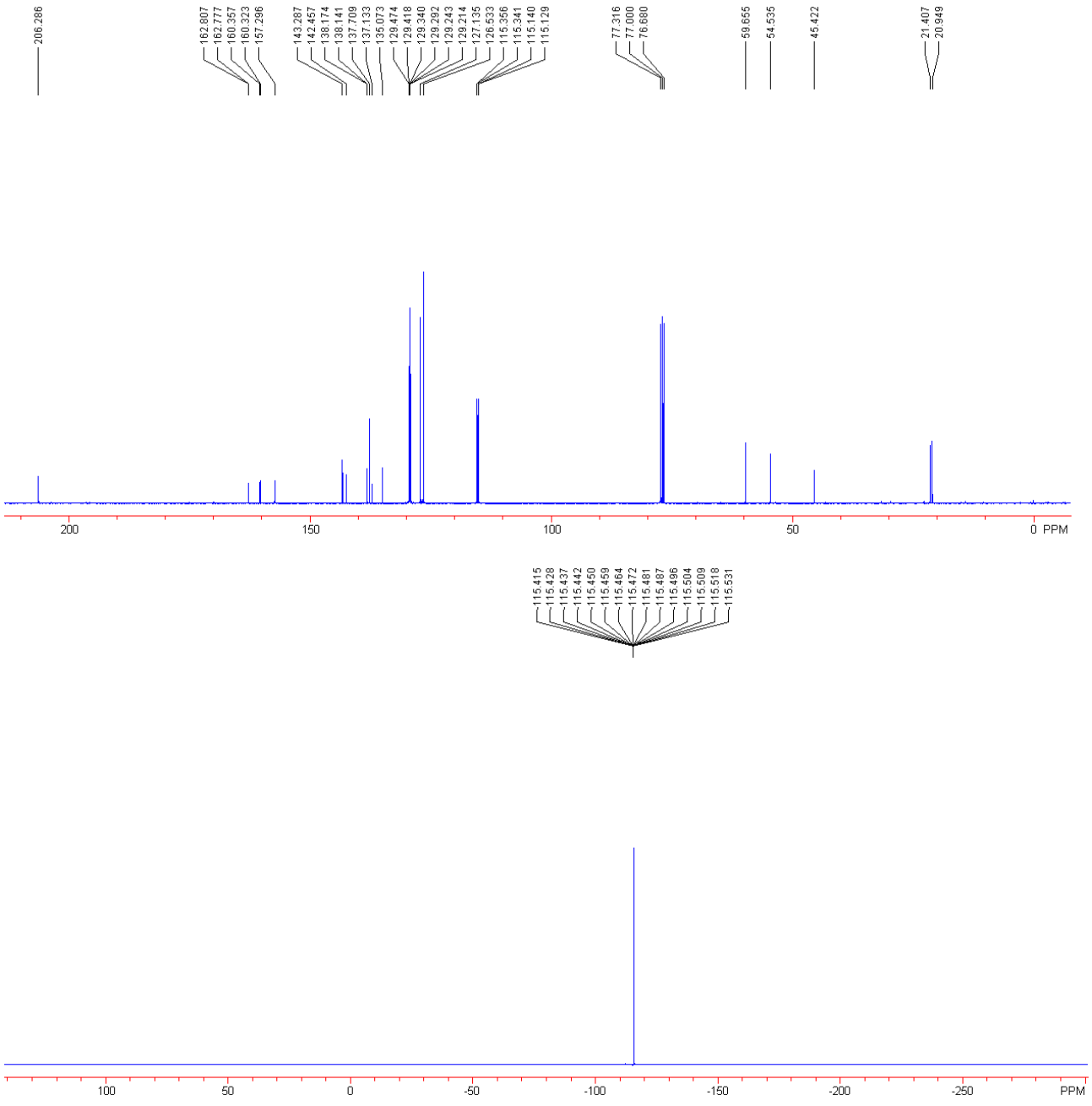


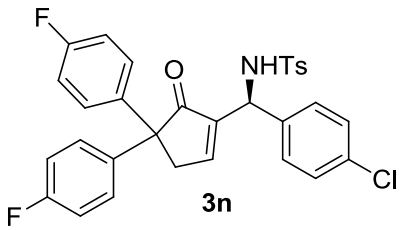


(*S*)-N-((4,4-bis(4-fluorophenyl)-5-oxocyclopent-1-enyl)(p-tolyl)methyl)-4-methylbenzenesulfonamide 3m: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3m** (37 mg, 91% yield). A white solid. m.p. for racemic **3m** = 182-184 ^{o}C; m.p. for **3m** = 181-183 ^{o}C; $[\alpha]^{20}_{D}$ = +19.8 (c 0.4, CH_2Cl_2). IR

(CH_2Cl_2): ν 3248, 2961, 2923, 1702, 1633, 1598, 1506, 1439, 1326, 1259, 1186, 1160, 1092, 1016, 804, 740 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.60 (2H, d, *J* = 8.0 Hz), 7.56-7.55 (1H, m), 7.09 (2H, d, *J* = 8.4 Hz), 7.00-6.89 (12H, m), 5.92 (1H, d, *J* = 8.4 Hz), 5.28 (1H, d, *J* = 8.0 Hz), 3.30-3.24 (1H, s), 3.17-3.11 (1H, m), 2.32 (3H, s), 2.25 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 206.3, 161.6 (dd, $J_{1C\text{-}F}$ = 245.0 Hz, $J_{2C\text{-}F}$ = 3.0 Hz), 157.3, 143.3, 142.5, 138.2 (d, $J_{1C\text{-}F}$ = 3.3 Hz), 137.7, 137.1, 135.1, 129.4 (dd, $J_{1C\text{-}F}$ = 13.4 Hz, $J_{2C\text{-}F}$ = 5.6 Hz), 129.24, 129.21, 127.1, 126.5, 115.2 (dd, $J_{1C\text{-}F}$ = 21.6 Hz, $J_{2C\text{-}F}$ = 1.5 Hz), 60.0, 54.5, 45.4, 21.4, 20.9; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -115.4–-115.5 (m); MS (ESI) m/e 566.1 (M^++Na); HRMS (ESI) for $C_{32}H_{27}NO_3SF_2Na^{+1}$ (M^++Na): 566.1561, Found: 566.1571. The ee of the **3m** was determined to be 84% [determined by HPLC, Chiralpak AD-H, n-hexane/isopropanol = 80:20, 0.5 mL/min, λ = 214 nm, t (major) = 38.68 min, t (minor) = 41.74 min].



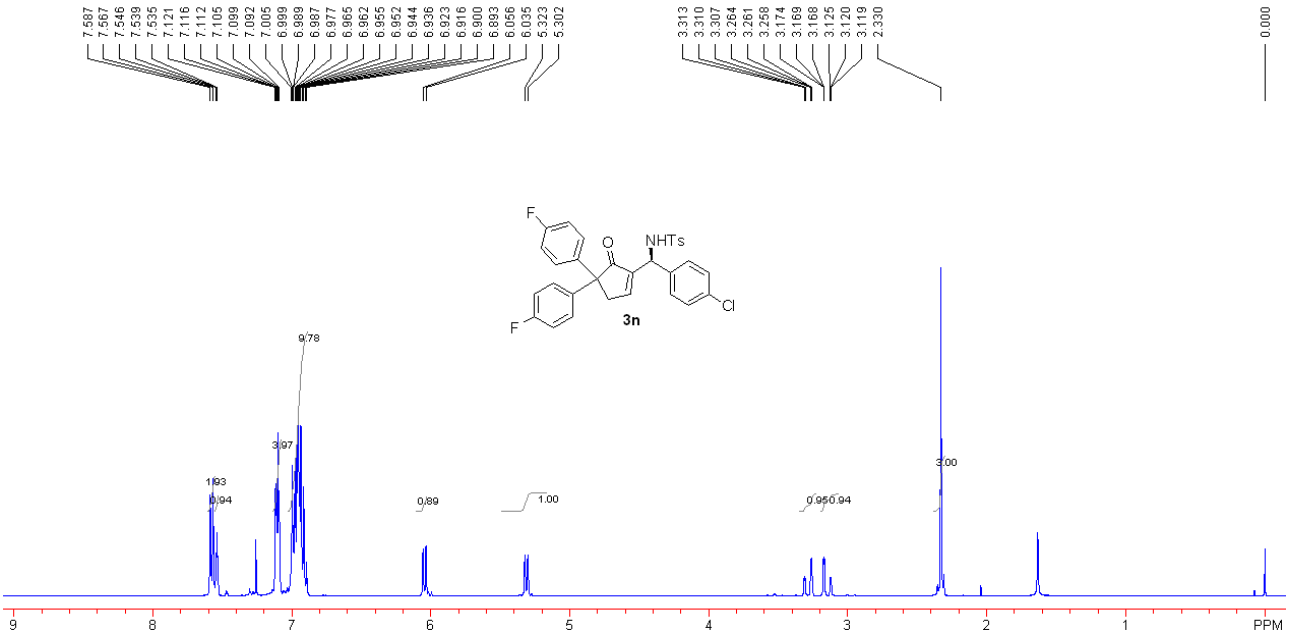


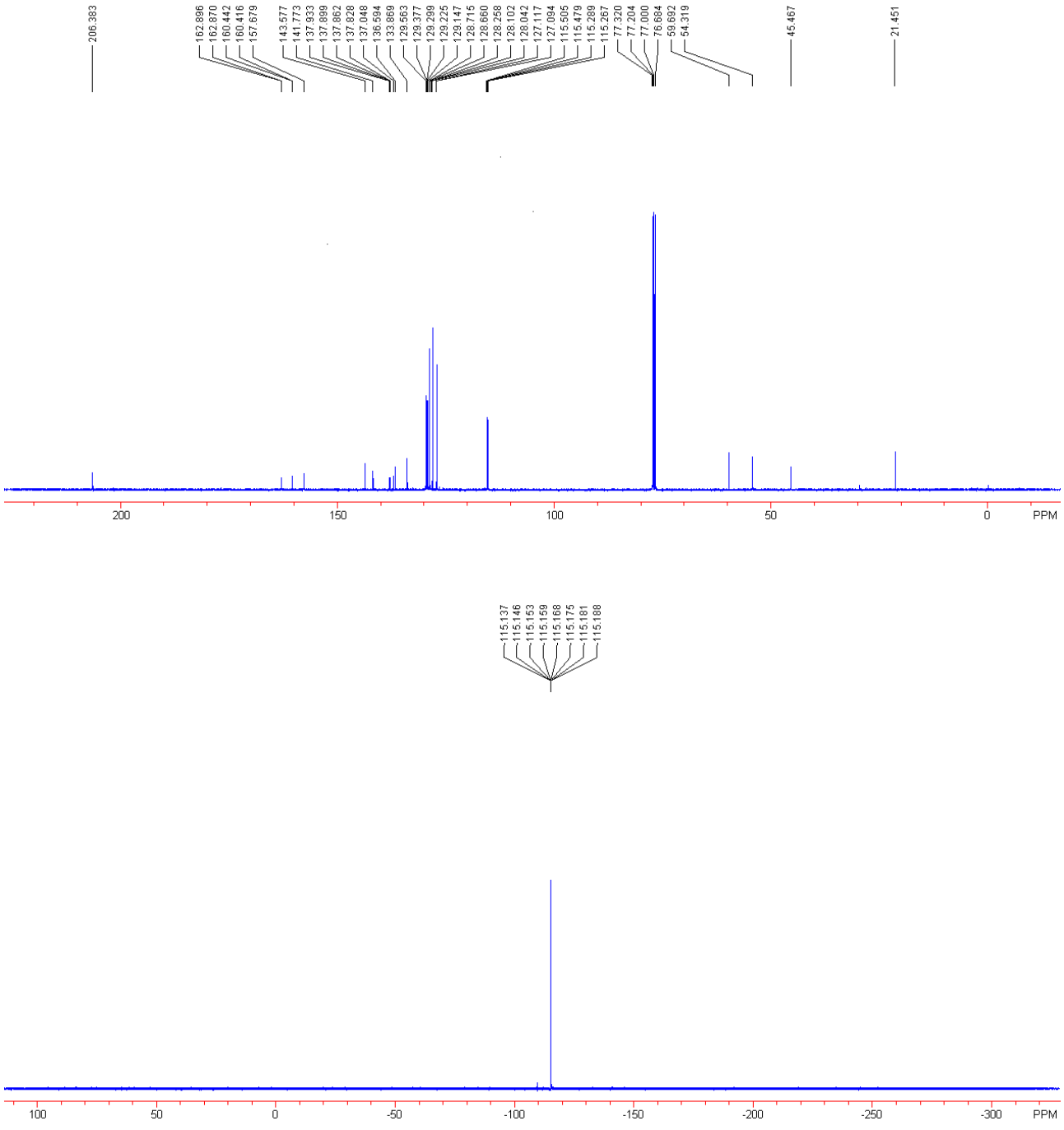


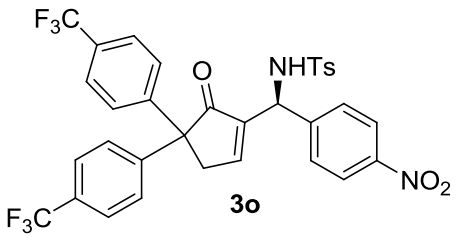
3n

(*S*)-N-((4,4-bis(4-fluorophenyl)-5-oxocyclopent-1-enyl)(4-chlorophenyl)methyl)-4-methylbenzenesulfonamide 3n: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3n** (38 mg, 89% yield). A white solid. m.p. for racemic **3n** = 198-201 ^{o}C; m.p. for **3n** = 179-181 ^{o}C; $[\alpha]^{20}_{D}$ = +10.0 (c 0.3, CH_2Cl_2). IR

(CH_2Cl_2): ν 3278, 2961, 1701, 1634, 1598, 1506, 1434, 1328, 1260, 1233, 1184, 1160, 1089, 1014, 806, 736 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.58 (2H, d, *J* = 8.0 Hz), 7.55-7.54 (1H, m) 7.12-7.09 (4H, m), 7.00-6.89 (10H, m), 6.05 (1H, d, *J* = 8.4 Hz), 5.31 (1H, d, *J* = 8.4 Hz), 3.31-3.26 (1H, m), 3.17-3.12 (1H, m), 2.33 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 206.4, 161.7 (dd, $J_{1C\text{-}F}$ = 245.4 Hz, $J_{2C\text{-}F}$ = 2.6 Hz), 157.8, 143.6, 141.8, 137.9 (dd, $J_{1C\text{-}F}$ = 17.1 Hz, $J_{2C\text{-}F}$ = 3.4 Hz), 137.0, 136.6, 133.9, 129.6, 129.3 (dd, $J_{1C\text{-}F}$ = 15.2 Hz, $J_{2C\text{-}F}$ = 7.8 Hz), 128.7, 128.0, 127.1, 115.4 (dd, $J_{1C\text{-}F}$ = 21.6 Hz, $J_{2C\text{-}F}$ = 2.6 Hz), 60.0, 54.3, 45.5, 21.5; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -115.1–-115.2 (m); MS (ESI) m/e 586.0 (M^++Na); HRMS (ESI) for $C_{31}H_{24}NO_3SF_2ClNa^{+1}$ (M^++Na): 586.1033, Found: 586.1025. The ee of the **3n** was determined to be 75% [determined by HPLC, Chiralpak AD-H, n-hexane/isopropanol = 70:30, 0.5 mL/min, λ = 214 nm, t (major) = 21.53 min, t (minor) = 27.05 min].



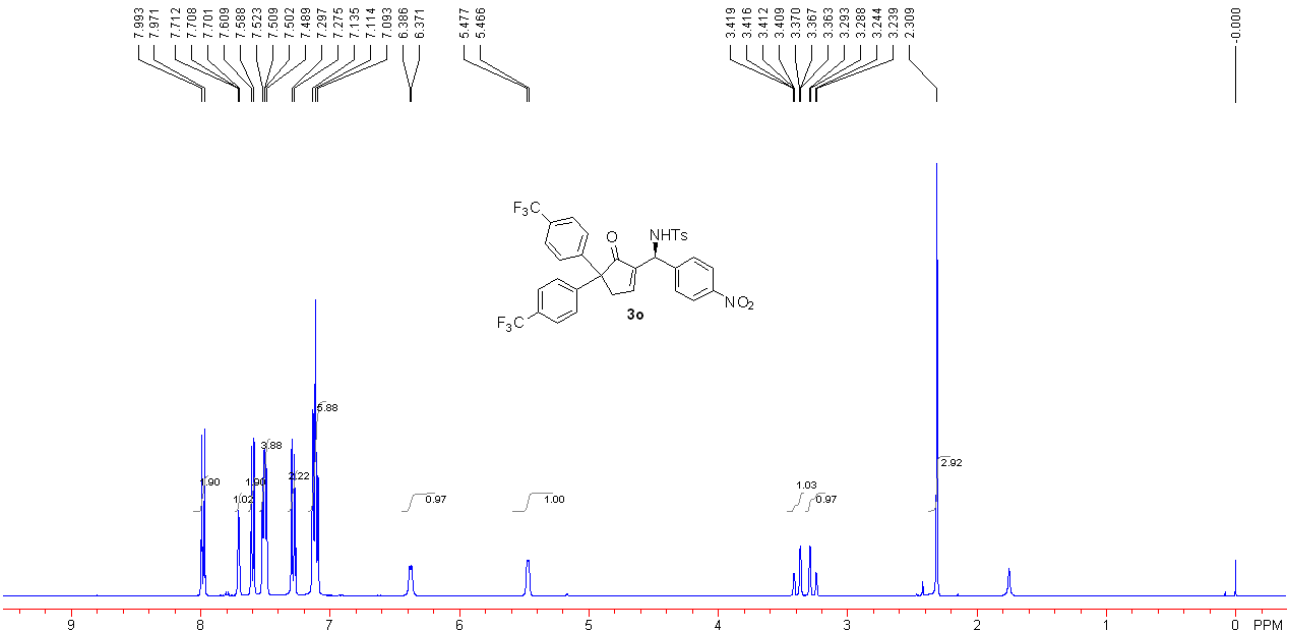


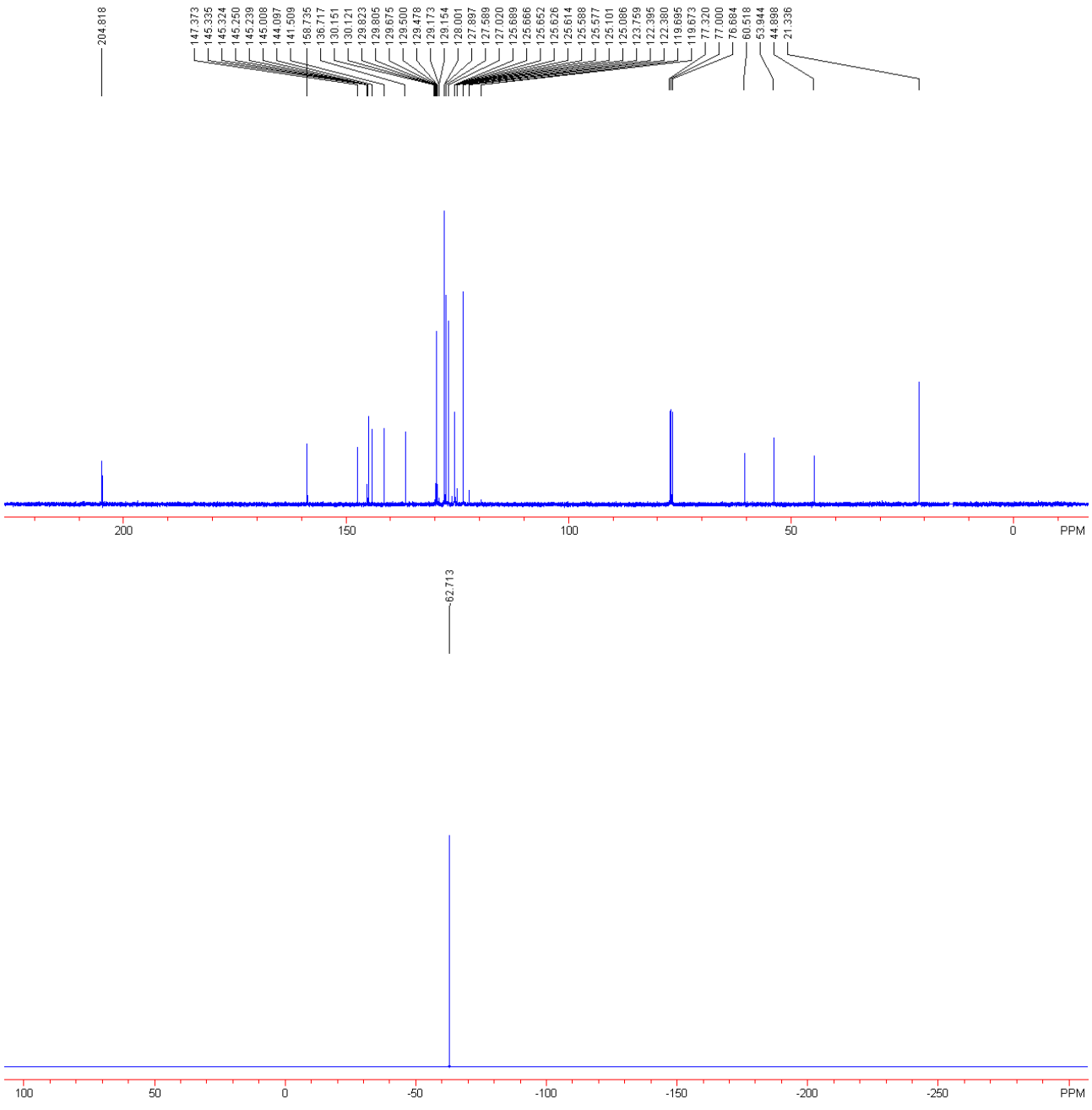


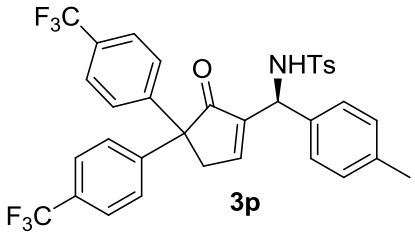
3o

(*S*)-4-methyl-N-((4-nitrophenyl)(5-oxo-4,4-bis(4-(trifluoromethyl)phenyl)cyclopent-1-enyl)methyl)benzenesulfonamide 3o: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3o** (50 mg, 99% yield). A white

solid. m.p. for racemic **3o** = 110-113 ^{o}C; m.p. for **3o** = 70-73 ^{o}C; $[\alpha]^{20}_{D}$ = +6.3 (c 0.9, CH_2Cl_2). IR (CH_2Cl_2): ν 3283, 2926, 1704, 1615, 1522, 1410, 1348, 1324, 1161, 1118, 1092, 1070, 1017, 833 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.98 (2H, d, *J* = 8.8 Hz), 7.71-7.70 (1H, m), 7.60 (2H, d, *J* = 8.4 Hz), 7.51 (4H, dd, J_1 = 8.4 Hz, J_2 = 5.6 Hz), 7.29 (2H, d, *J* = 8.8 Hz), 7.11 (6H, t, *J* = 8.8 Hz), 6.38 (1H, d, *J* = 6.0 Hz), 5.47 (1H, d, *J* = 4.4 Hz), 3.42-3.37 (1H, s), 3.24 (1H, dd, J_1 = 19.6 Hz, J_2 = 2.0 Hz), 2.31 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 204.8, 158.7, 147.4, 145.3 (dd, $J_{1C\text{-}F}$ = 8.5 Hz, $J_{2C\text{-}F}$ = 1.1 Hz), 145.0, 144.1, 141.5, 136.7, 129.67, 129.65 (dq, $J_{1C\text{-}F}$ = 32.7 Hz, $J_{2C\text{-}F}$ = 3.7 Hz), 128.0, 127.9, 127.6, 127.0, 125.6 (dq, $J_{1C\text{-}F}$ = 3.8 Hz, $J_{2C\text{-}F}$ = 2.6 Hz), 123.8, 123.7 (dq, $J_{1C\text{-}F}$ = 270.6 Hz, $J_{2C\text{-}F}$ = 1.5 Hz), 60.5, 53.9, 44.9, 21.3; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -62.7; MS (ESI) m/e 697.0 (M^++Na); HRMS (ESI) for $C_{33}H_{24}N_2O_5SF_6Na^{+1}$ (M^++Na): 697.1202, Found: 697.1202. The ee of the **3o** was determined to be 73% [determined by HPLC, Chiralpak AD-H, n-hexane/isopropanol = 80:20, 0.5 mL/min, λ = 214 nm, t (major) = 40.71 min, t (minor) = 46.40 min].



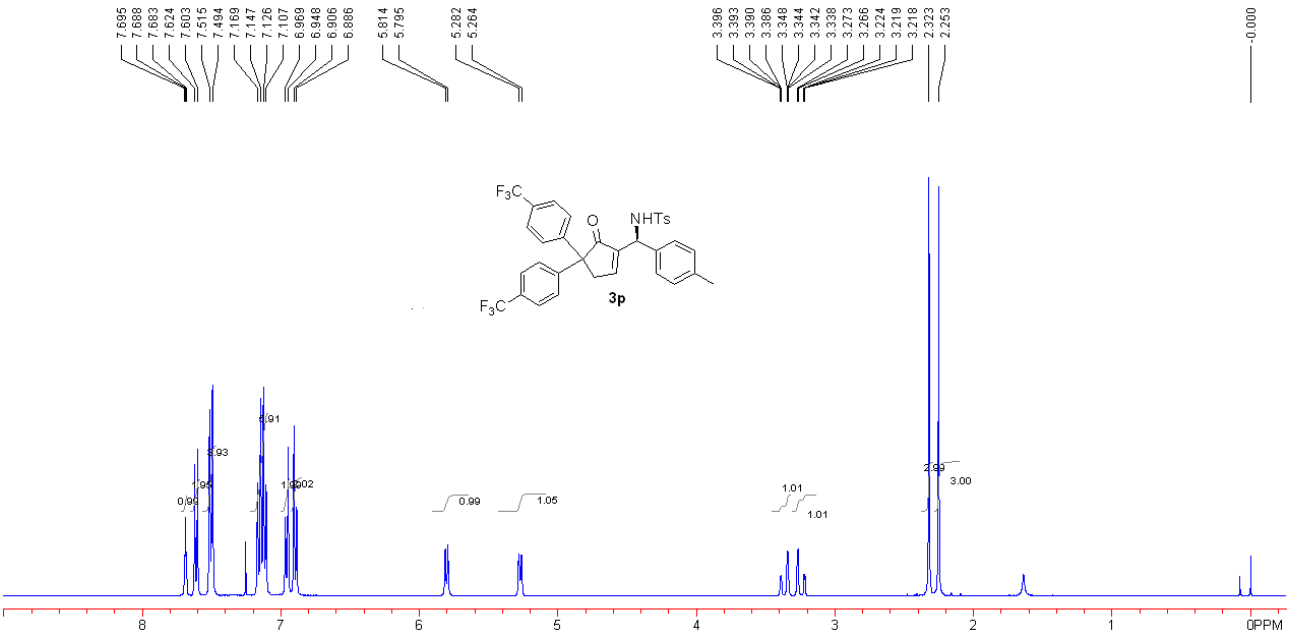


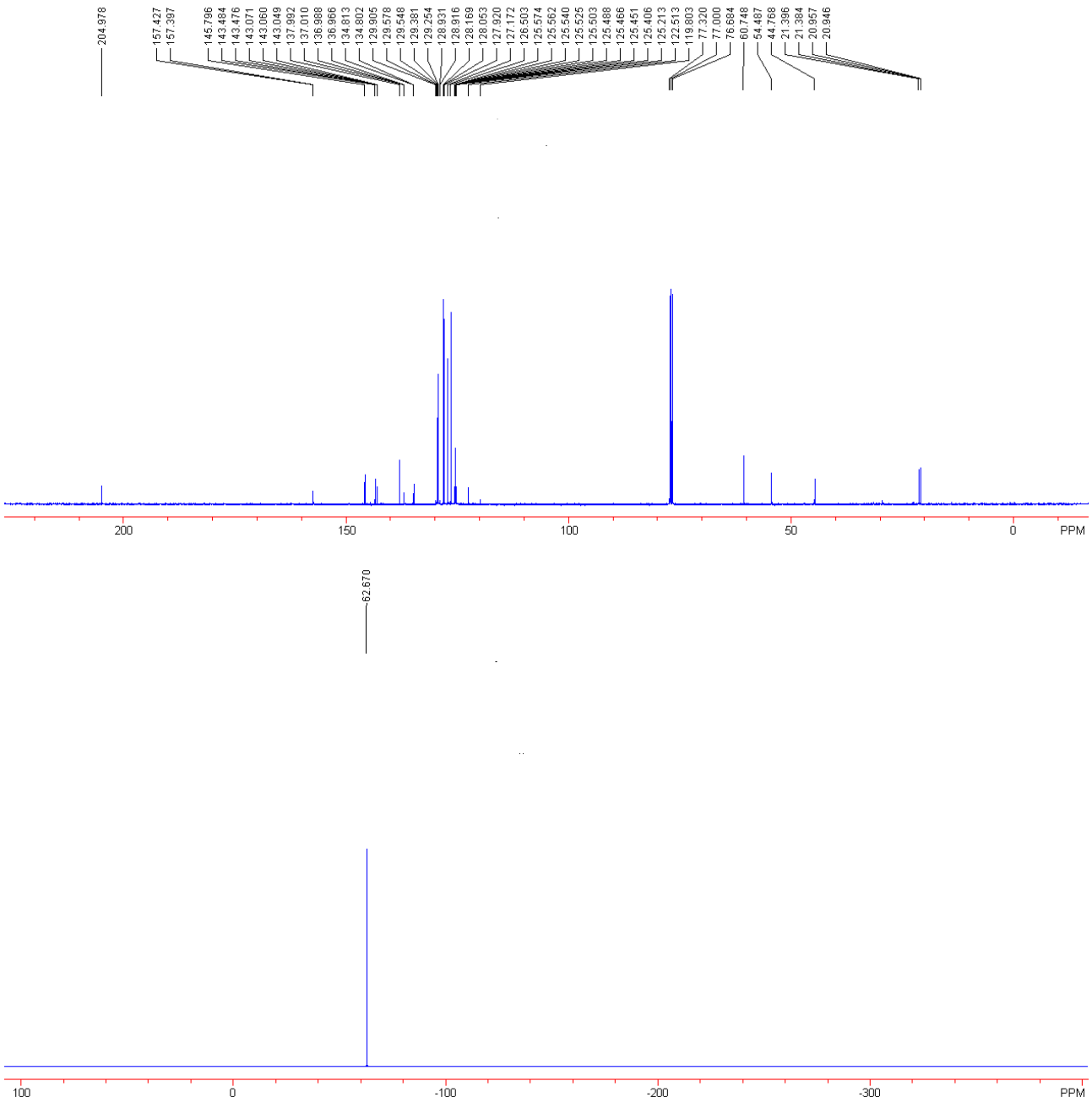


3p

(*S*)-4-methyl-N-((5-oxo-4,4-bis(4-(trifluoromethyl)phenyl)cyclopent-1-enyl)(p-tolyl)methyl)benzenesulfonamide 3p: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3p** (42 mg, 88% yield). A white solid. m.p. for racemic **3p** = 203-204 ^{o}C; m.p. for **3p** = 186-188 ^{o}C; $[\alpha]^{20}_{D}$ = +18.7 (c 0.4, CH_2Cl_2). IR

(CH_2Cl_2): ν 3282, 2960, 2925, 1701, 1615, 1513, 1410, 1323, 1261, 1160, 1117, 1070, 1017, 813, 737 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.69 (1H, t, *J* = 2.8 Hz), 7.61 (2H, d, *J* = 7.6 Hz), 7.50 (4H, d, *J* = 8.4 Hz), 7.14 (6H, q, *J* = 8.4 Hz), 6.96 (2H, d, *J* = 8.4 Hz), 6.90 (2H, d, *J* = 7.2 Hz), 5.80 (1H, d, *J* = 7.8 Hz), 5.27 (1H, d, *J* = 7.2 Hz), 3.40-3.34 (1H, m), 3.27-3.22 (1H, m), 2.32 (3H, s), 2.25 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 205.0, 157.4 (d, J_{C-F} = 3.0 Hz), 145.8, 143.5 (d, J_{C-F} = 0.8 Hz), 143.1 (t, J_{C-F} = 1.1 Hz), 138.0, 137.0 (t, J_{C-F} = 2.2 Hz), 134.8 (d, J_{C-F} = 1.1 Hz), 129.5, 129.4 (q, J_{C-F} = 32.4 Hz), 129.38, 128.2, 128.1, 127.1, 126.5, 125.5 (dq, J_{1C-F} = 3.7 Hz, J_{2C-F} = 1.5 Hz), 123.4 (q, J_{C-F} = 270.0 Hz), 60.7, 54.5, 45.8, 21.4 (d, J_{C-F} = 1.2 Hz), 21.0 (d, J_{C-F} = 1.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -62.7; MS (ESI) m/e 666.0 (M^++Na); HRMS (ESI) for $C_{34}H_{27}NO_3SF_6Na^{+1}$ (M^++Na): 666.1496, Found: 666.1508. The ee of the **3p** was determined to be 85% [determined by HPLC, Chiralpak AD-H, n-hexane/isopropanol = 80:20, 0.5 mL/min, λ = 214 nm, t (major) = 25.86 min, t (minor) = 23.99 min].



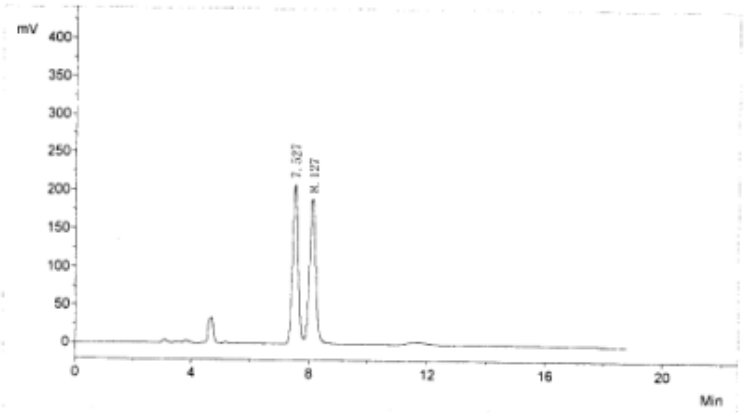

204.978
157.427
157.397
145.796
143.484
143.476
143.071
143.060
143.049
137.992
137.010
136.988
136.966
134.813
134.802
129.905
129.578
129.548
129.381
129.254
128.931
128.916
128.169
128.053
127.920
127.172
126.503
125.574
125.562
125.540
125.525
125.503
125.488
125.466
125.451
125.406
125.213
122.513
119.803
77.320
77.000
76.684
60.748
54.487
44.768
21.396
21.384
20.957
20.946
200
150
100
50
0
PPM
62.670
100
0
-100
-200
-300
PPM

HPLC spectra:

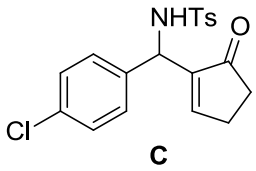
HPLC Report

Sample Name:
Operator:
Time:09:32

Data File:YYL-11-41-1+-IBB730.7214.che
Date:2011-04-20



No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	7.527	209061.9	2737775.5	49.5519
2	2	8.127	189484.0	2787287.2	50.4481
Total			398545.9	5525062.7	100.0000



C

Chiral HPLC report: racemate (**C**)

HPLC Report

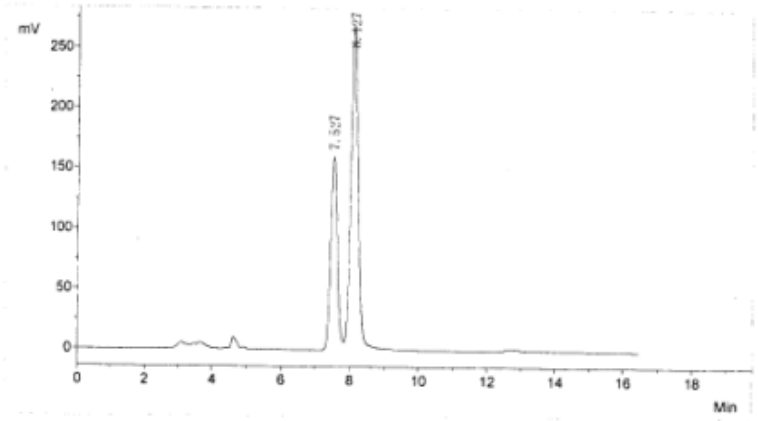
Sample Name:

Operator:

Time:09:57

Data File:YYL-11-40.che

Date:2011-04-20



No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	7.527	160347.4	2145673.5	31.5810
2	2	8.127	267864.7	4059109.9	65.4190
Total			428212.2	6204783.4	100.0000

Take entry 17 as example in Table S1

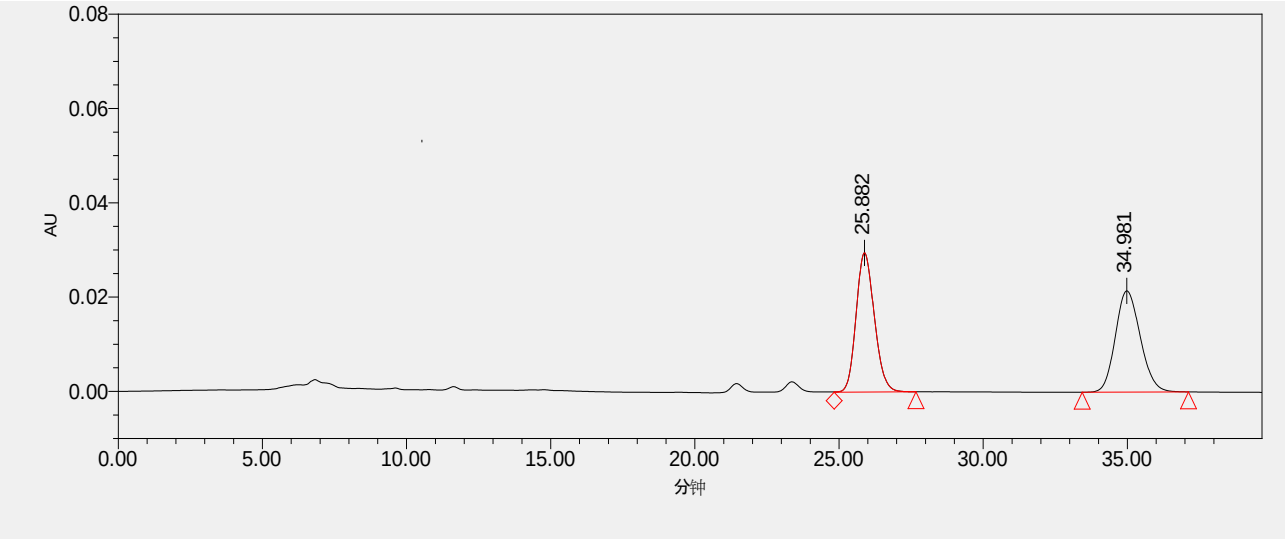
Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak TBB column; λ = 214 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.7 mL/min; t_{minor} = 8.13 min, t_{major} = 7.53 min; ee% = 31.

HPLC REPORT

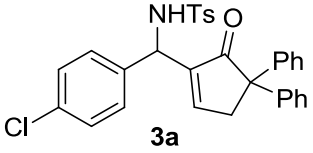
Sample Name: yyl-15-31 Date: ####

Column: AD-H Mobile Phase: hex/ipr = 70/30

Velocity (mL/min): 0.5 Detection Wavelength (nm): 214



NO	R. Time	Peak Area	Percent	Peak Height
1	25.882	1300496	50.22	29537
2	34.981	1466305	49.70	21472



3a

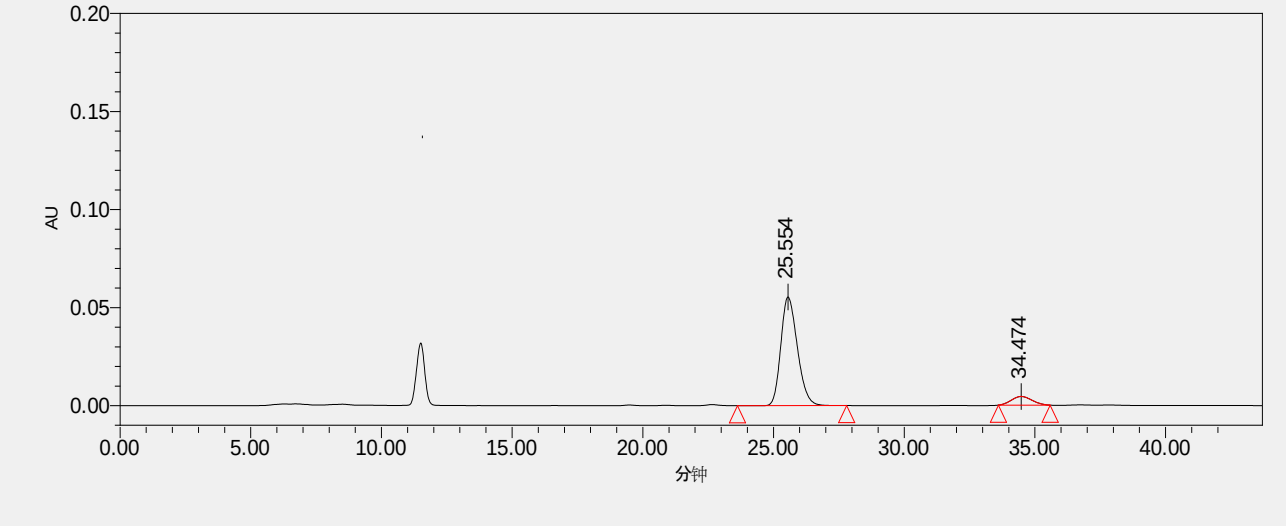
Chiral HPLC report: racemate (**3a**)

HPLC REPORT

Sample Name: yyl-17-43-1 Date: ####

Column: AD-H Mobile Phase: hex/ipr = 70/30

Velocity (mL/min): 0.5 Detection Wavelength (nm): 214



NO	R. Time	Peak Area	Percent	Peak Height
1	25.554	2440246	90.98	55440
2	34.474	241866	9.02	442

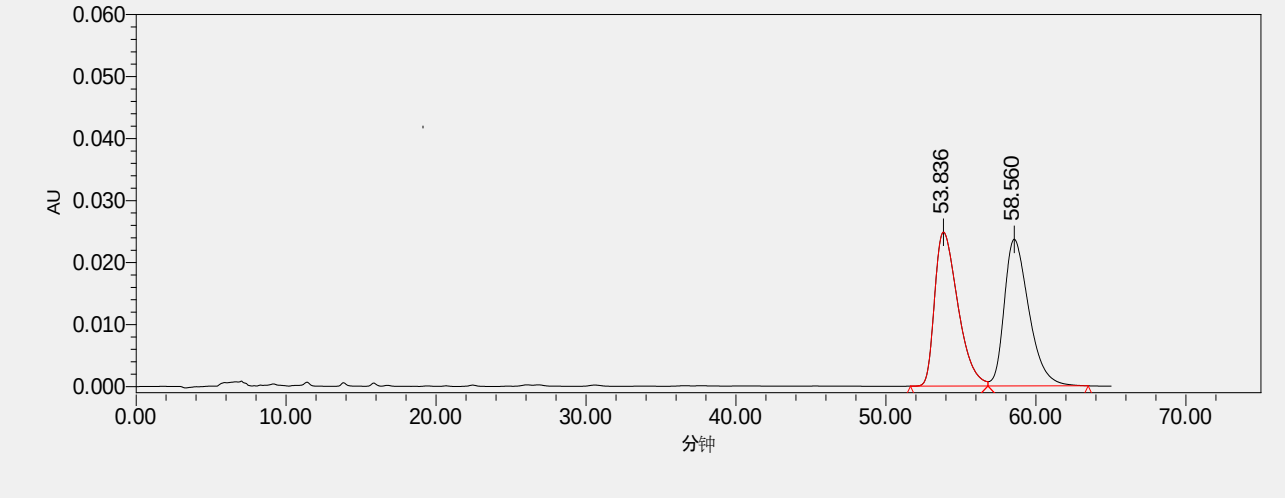
Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak AD column; λ = 214 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.5 mL/min; t_{minor} = 34.47 min, t_{major} = 25.55 min; ee% = 82.

HPLC REPORT

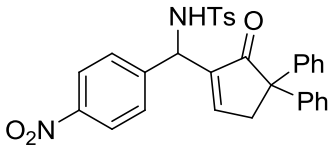
Sample Name: yyl-17-46 Date: ####

Column: AD-H Mobile Phase: hex/ipr = 70/30

Velocity (mL/min): 0.5 Detection Wavelength (nm): 214



NO	R. Time	Peak Area	Percent	Peak Height
1	53.836	2674446	49.74	24840
2	58.560	2702395	50.26	23666



3b

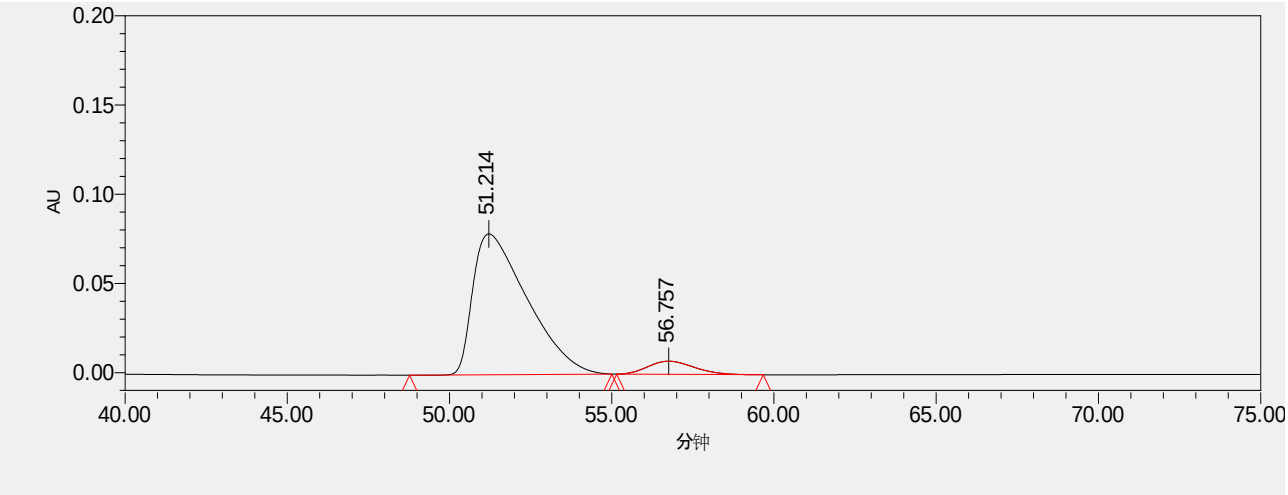
Chiral HPLC report: racemate (**3b**)

HPLC REPORT

Sample Name: yyl-17-59 Date: ####

Column: AD-H Mobile Phase: hex/ipr = 70/30

Velocity (mL/min): 0.5 Detection Wavelength (nm): 214



NO	R. Time	Peak Area	Percent	Peak Height
1	51.214	9191083	92.66	78939
2	56.757	728377	7.34	7374

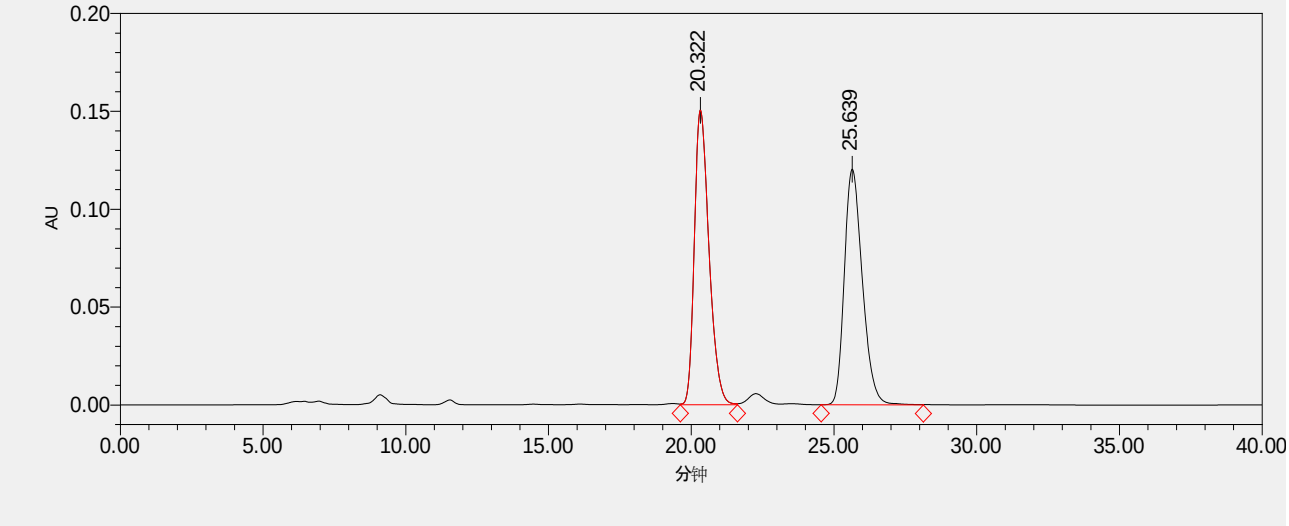
Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak AD column; λ = 214 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.5 mL/min; t_{minor} = 56.76 min, t_{major} = 51.21 min; ee% = 85.

HPLC REPORT

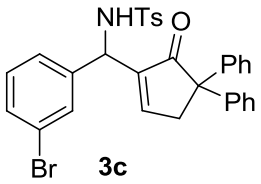
Sample Name: yyl-17-36 Date: ####

Column: AD-H Mobile Phase: hex/ipr = 70/30

Velocity (mL/min): 0.5 Detection Wavelength (nm): 214



NO	R. Time	Peak Area	Percent	Peak Height
1	20.322	5380528	50.42	150563
2	25.639	5291746	49.58	120413



3c

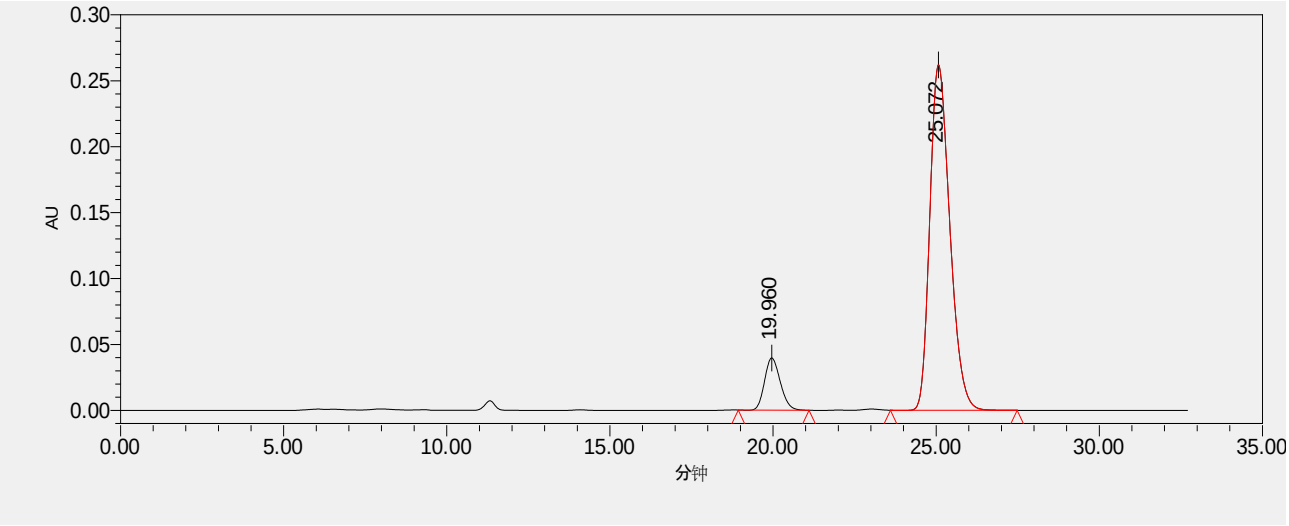
Chiral HPLC report: racemate (**3c**)

HPLC REPORT

Sample Name: yyl-17-68 Date: ####

Column: AD-H Mobile Phase: hex/ipr = 70/30

Velocity (mL/min): 0.5 Detection Wavelength (nm): 214



NO	R. Time	Peak Area	Percent	Peak Height
1	19.960	1322668	10.62	39583
2	25.072	11165287	89.48	26200

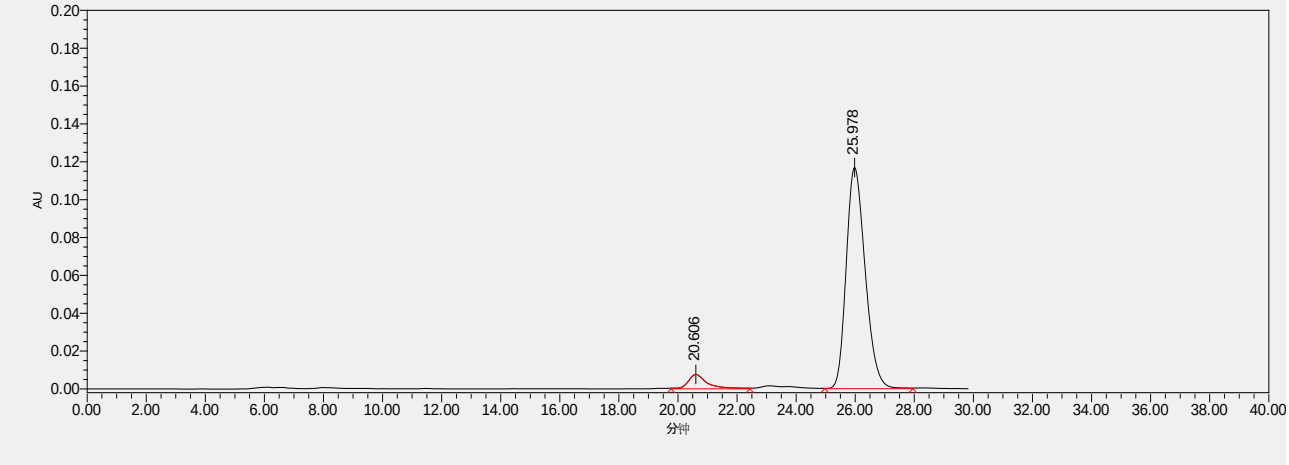
Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak AD column; λ = 214 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.5 mL/min; t_{minor} = 19.96 min, t_{major} = 25.07 min; ee% = 79.

HPLC REPORT

Sample Name: yyl-17-68-re Date: ####

Column: AD-H Mobile Phase: hex/ipr = 70/30

Velocity (mL/min): 0.5 Detection Wavelength (nm): 214



NO	R. Time	Peak Area	Percent	Peak Height
1	20.606	344329	6.19	7626
2	25.978	5218634	93.81	116888

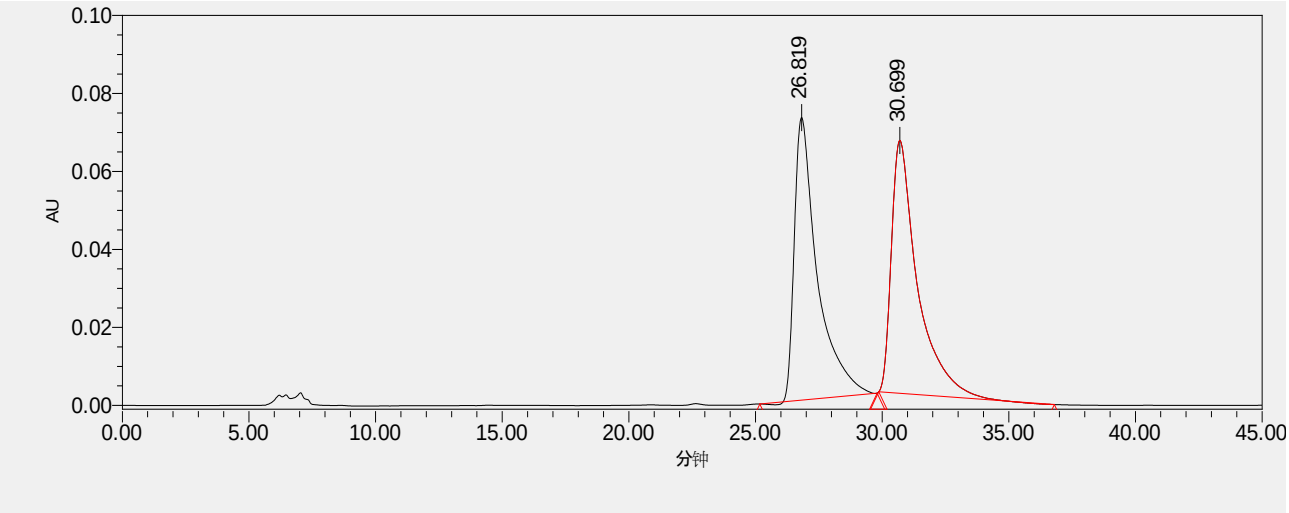
Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak AD column; λ = 214 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.5 mL/min; t_{minor} = 20.60 min, t_{major} = 25.98 min; ee% = 88 (after recrystallization).

HPLC REPORT

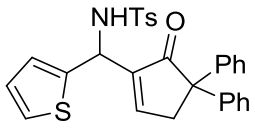
Sample Name: yyl-17-35 Date: ####

Column: AD-H Mobile Phase: hex/ipr = 70/30

Velocity (mL/min): 0.5 Detection Wavelength (nm): 214



NO	R. Time	Peak Area	Percent	Peak Height
1	26.819	4591589	49.69	72492
2	30.699	4649287	50.31	64900



3d

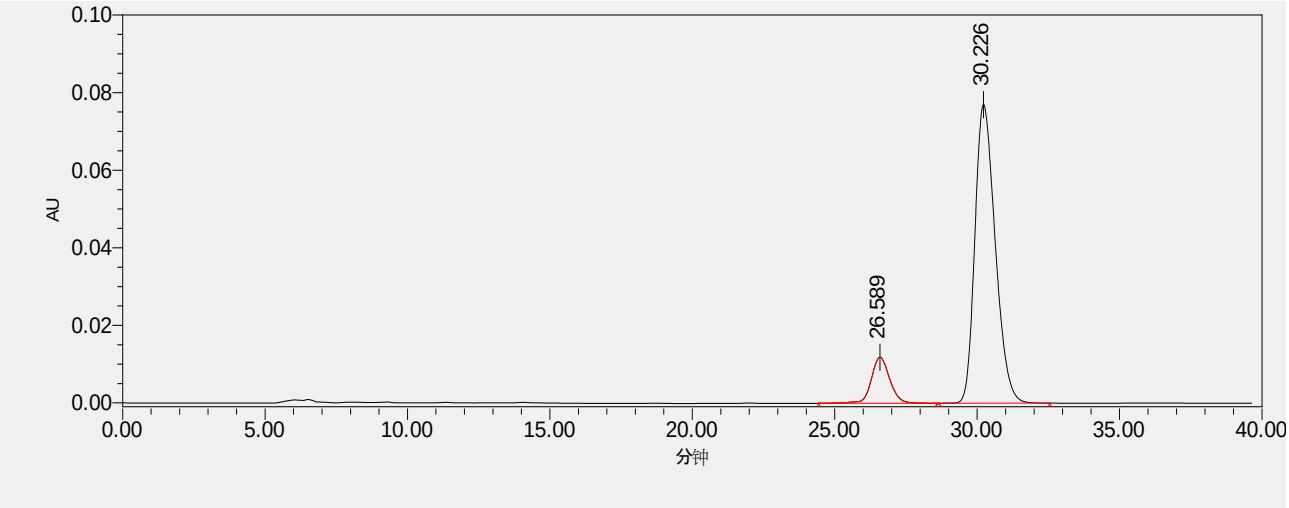
Chiral HPLC report: racemate (**3d**)

HPLC REPORT

Sample Name: yyl-17-67 Date: ####

Column: AD-H Mobile Phase: hex/ipr = 70/30

Velocity (mL/min): 0.5 Detection Wavelength (nm): 214



NO	R. Time	Peak Area	Percent	Peak Height
1	26.589	532160	12.22	11872
2	30.226	3821083	87.78	76995

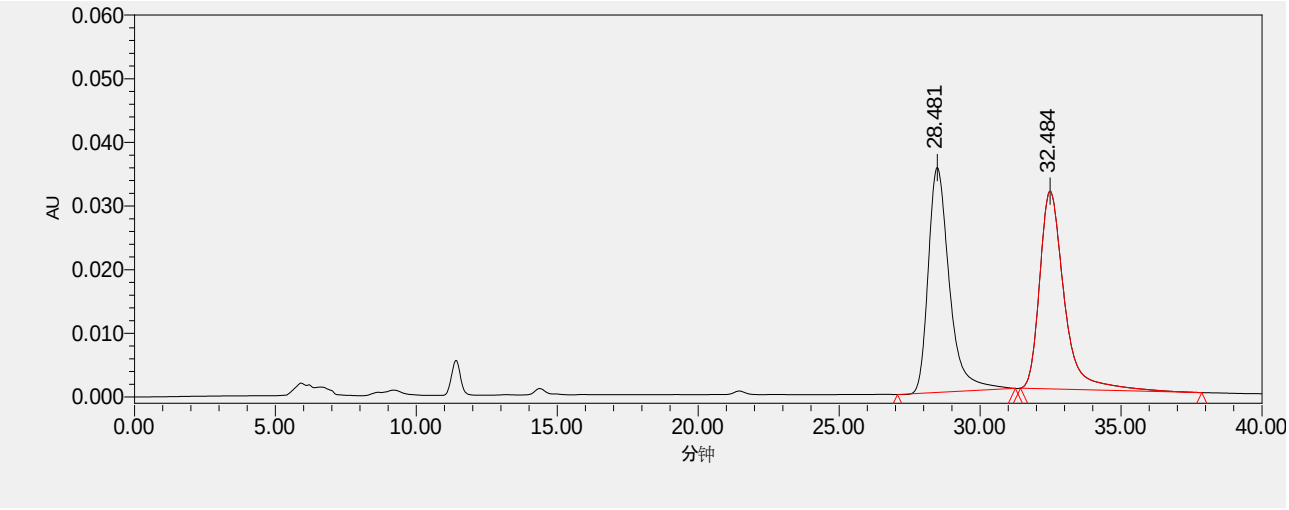
Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak AD column; λ = 214 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.5 mL/min; t_{minor} = 26.58 min, t_{major} = 30.22 min; ee% = 76.

HPLC REPORT

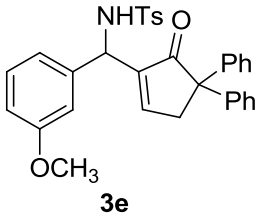
Sample Name: yyl-17-38 Date: ####

Column: AD-H Mobile Phase: hex/ipr = 70/30

Velocity (mL/min): 0.5 Detection Wavelength (nm): 214



NO	R. Time	Peak Area	Percent	Peak Height
1	28.481	1844723	49.42	35341
2	32.484	1887862	50.58	31063



3e

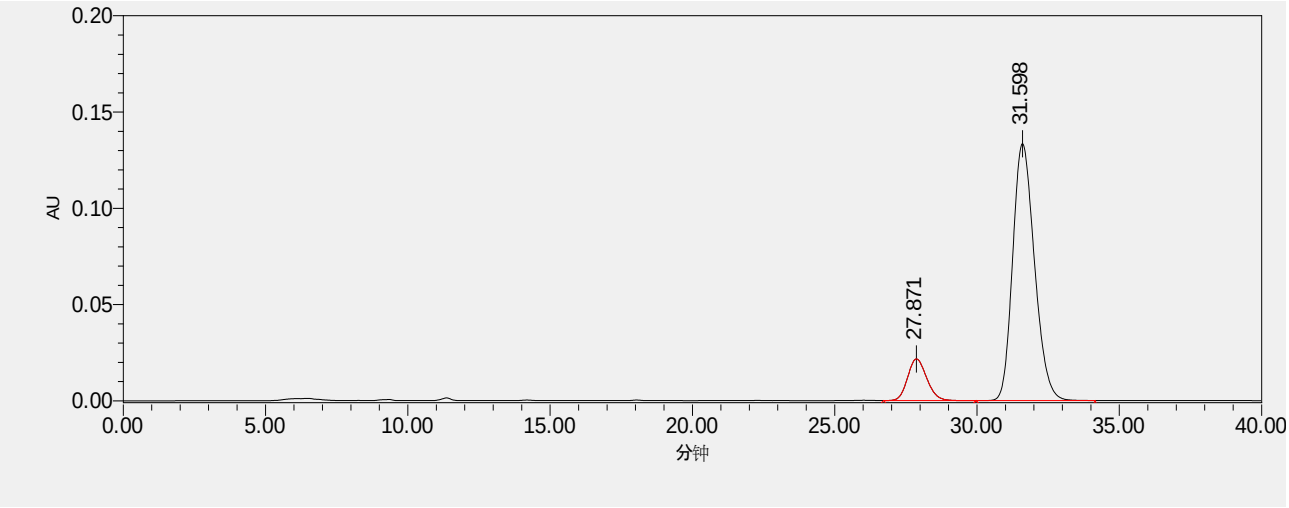
Chiral HPLC report: racemate (**3e**)

HPLC REPORT

Sample Name: yyl-17-69 Date: ####

Column: AD-H Mobile Phase: hex/ipr = 70/30

Velocity (mL/min): 0.5 Detection Wavelength (nm): 214



NO	R. Time	Peak Area	Percent	Peak Height
1	27.871	1011305	12.47	21630
2	31.598	7100048	87.53	13348

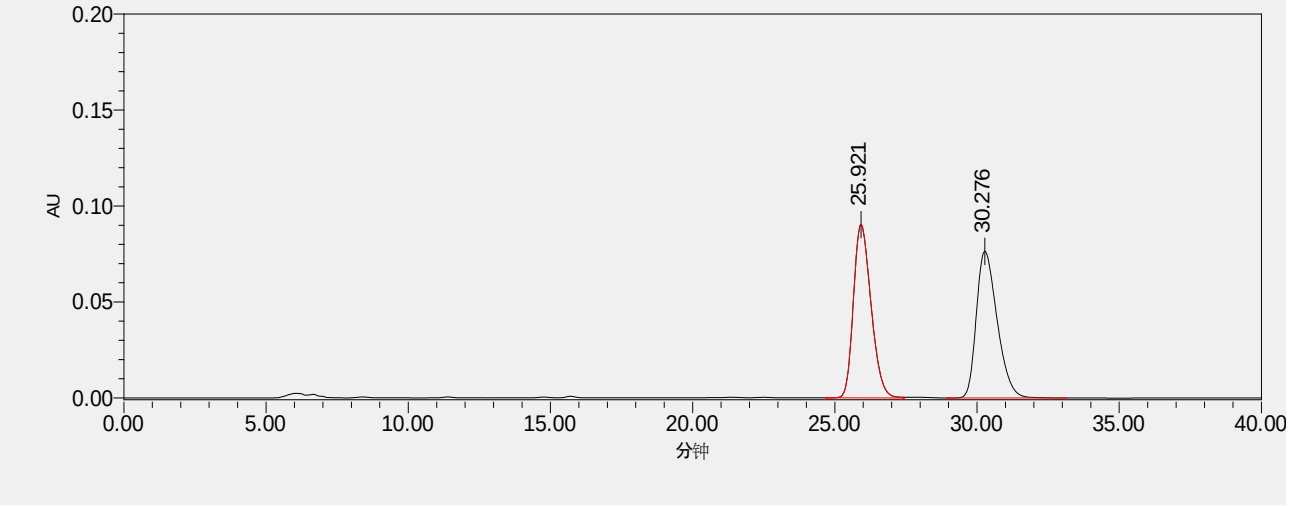
Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak AD column; λ = 214 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.5 mL/min; t_{minor} = 27.87 min, t_{major} = 31.59 min; ee% = 75.

HPLC REPORT

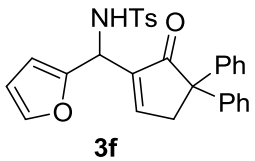
Sample Name: yyl-17-39 Date: ####

Column: AD-H Mobile Phase: hex/ipr = 70/30

Velocity (mL/min): 0.5 Detection Wavelength (nm): 214



NO	R. Time	Peak Area	Percent	Peak Height
1	25.921	3890945	50.03	90343
2	30.276	3886942	49.97	76457



3f

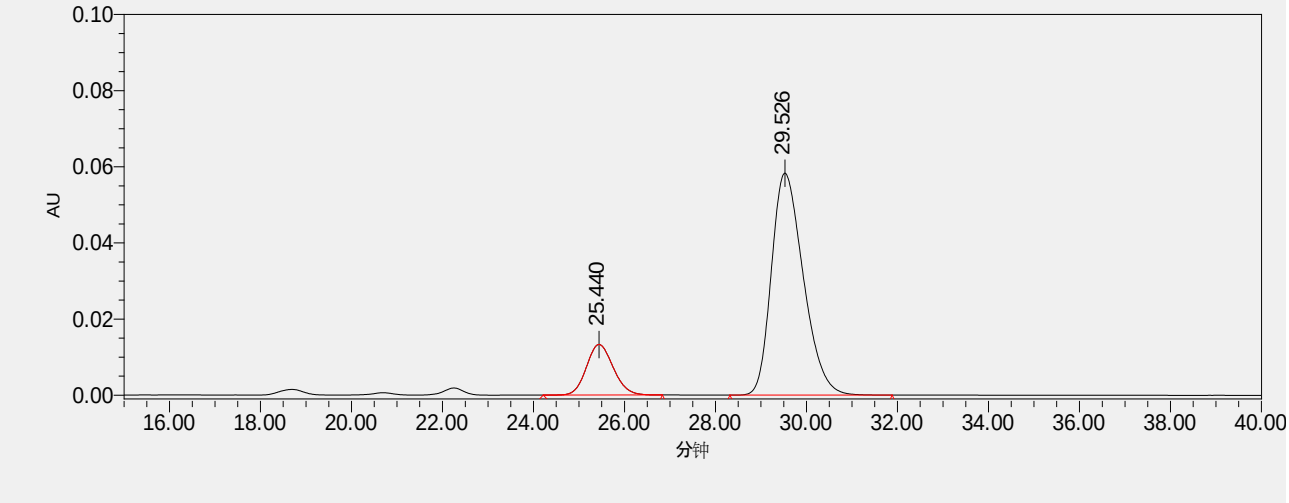
Chiral HPLC report: racemate (**3f**)

HPLC REPORT

Sample Name: yyl-17-70-2 Date: ####

Column: AD-H Mobile Phase: hex/ipr = 70/30

Velocity (mL/min): 0.5 Detection Wavelength (nm): 214



NO	R. Time	Peak Area	Percent	Peak Height
1	25.440	543607	16.06	13282
2	29.526	2840389	83.96	58325

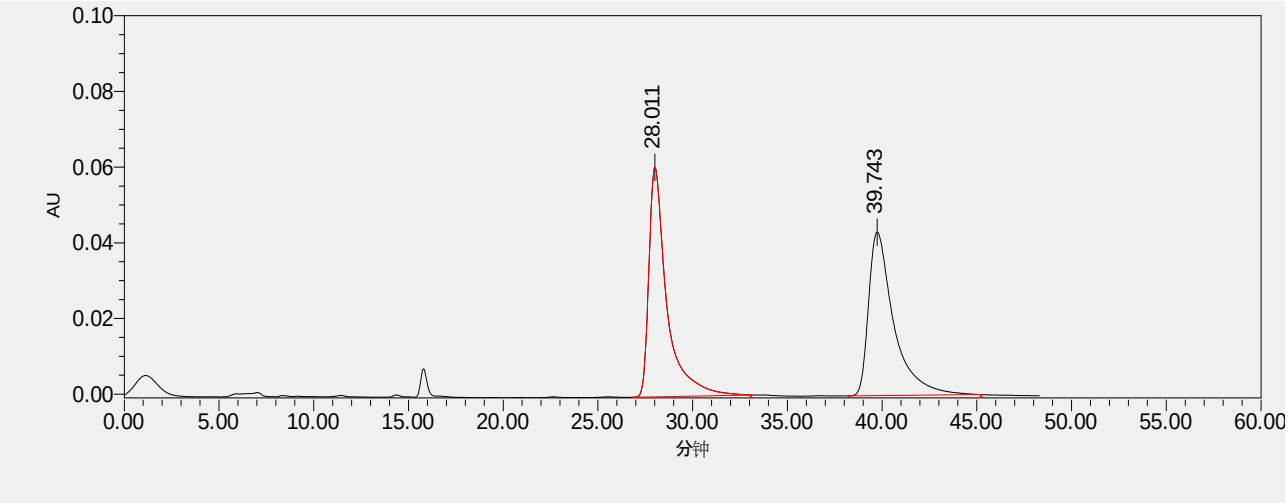
Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak AD column; λ = 214 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.5 mL/min; t_{minor} = 25.44 min, t_{major} = 29.53 min; ee% = 68.

HPLC REPORT

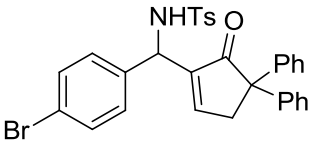
Sample Name: yyl-17-42 Date: ####

Column: AD-H Mobile Phase: hex/ipr = 70/30

Velocity (mL/min): 0.5 Detection Wavelength (nm): 214



NO	R. Time	Peak Area	Percent	Peak Height
1	28.011	4009158	50.04	60679
2	39.743	4002239	49.96	43236



3g

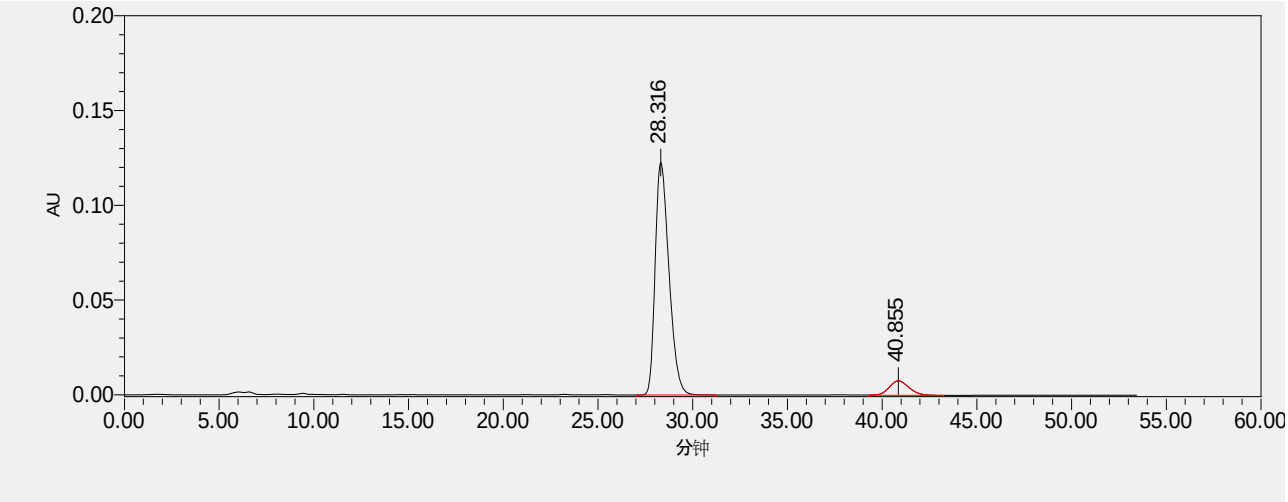
Chiral HPLC report: racemate (**3g**)

HPLC REPORT

Sample Name: yyl-17-81 Date: ####

Column: AD-H Mobile Phase: hex/ipr = 70/30

Velocity (mL/min): 0.5 Detection Wavelength (nm): 214



NO	R. Time	Peak Area	Percent	Peak Height
1	28.316	6222390	91.92	122746
2	40.855	546799	8.08	7564

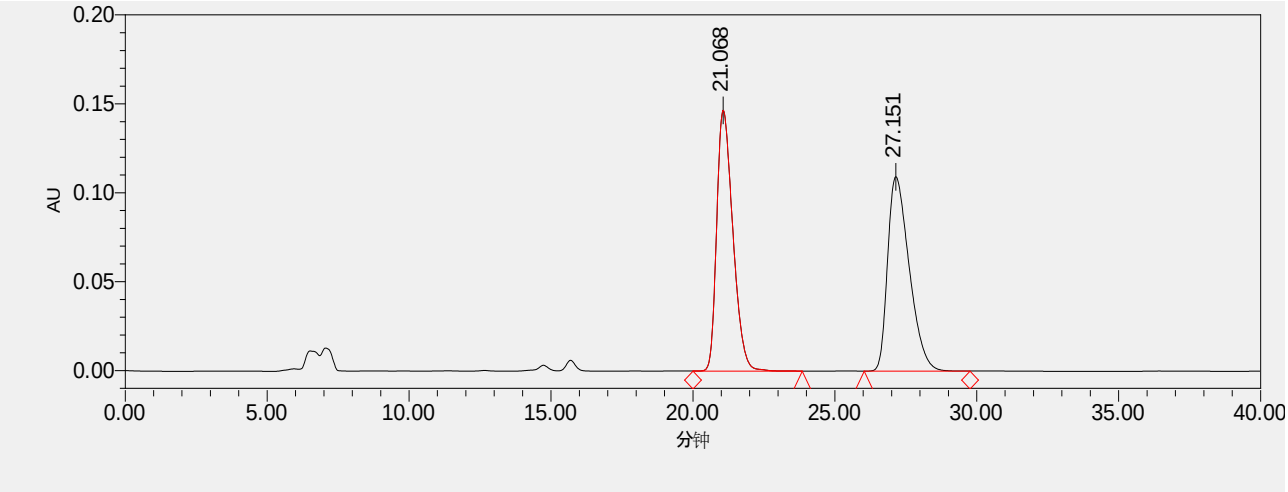
Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak AD column; λ = 214 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.5 mL/min; t_{minor} = 28.32 min, t_{major} = 40.85 min; ee% = 84.

HPLC REPORT

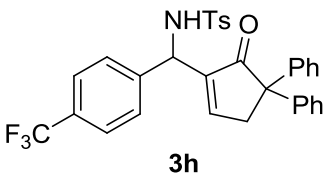
Sample Name: yyl-17-52 Date: ####

Column: AD-H Mobile Phase: hex/ipr = 70/30

Velocity (mL/min): 0.5 Detection Wavelength (nm): 214



NO	R. Time	Peak Area	Percent	Peak Height
1	21.068	5819711	50.13	146689
2	27.151	5790033	49.87	109342



3h

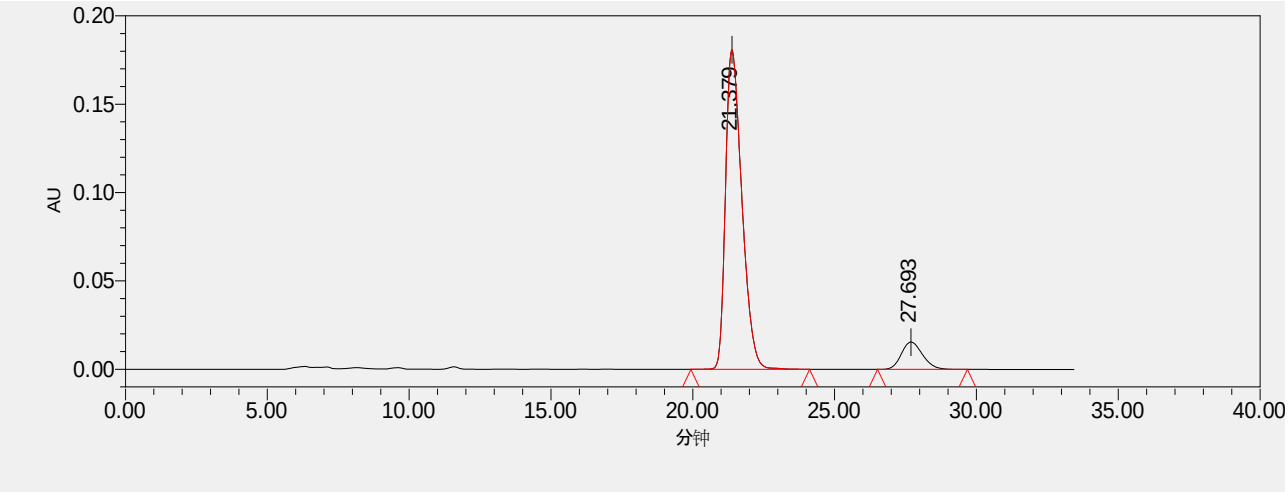
Chiral HPLC report: racemate (**3h**)

HPLC REPORT

Sample Name: yyl-17-60 Date: ####

Column: AD-H Mobile Phase: hex/ipr = 70/30

Velocity (mL/min): 0.5 Detection Wavelength (nm): 214



NO	R. Time	Peak Area	Percent	Peak Height
1	21.379	7258220	90.01	180862
2	27.693	805868	9.99	15470

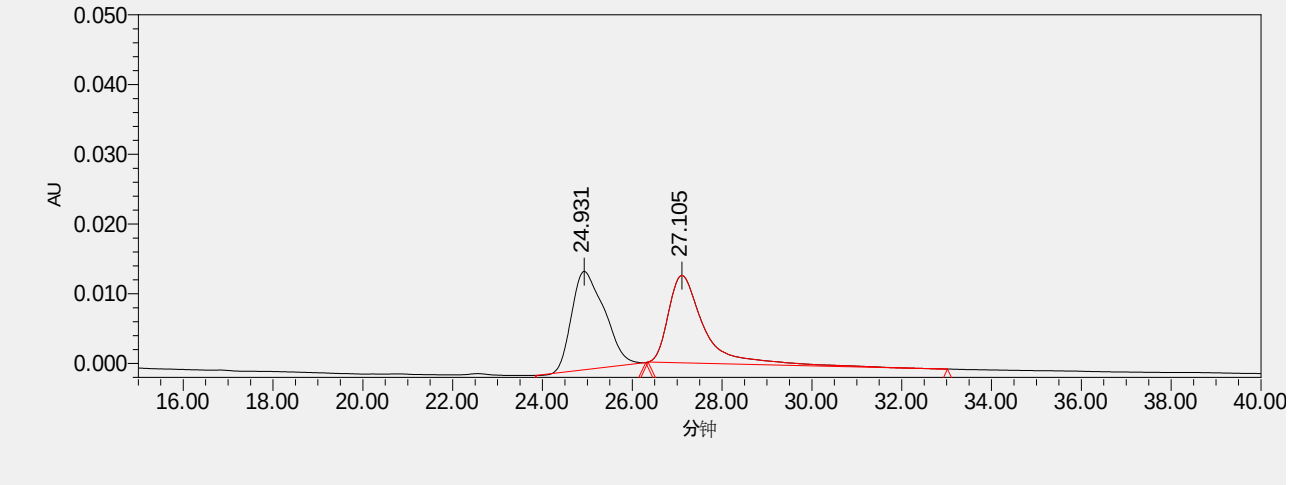
Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak AD column; λ = 214 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.5 mL/min; t_{minor} = 21.37 min, t_{major} = 27.69 min; ee% = 80.

HPLC REPORT

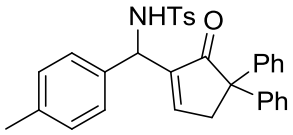
Sample Name: yyl-17-54 Date: ####

Column: AD-H Mobile Phase: hex/ipr = 70/30

Velocity (mL/min): 0.5 Detection Wavelength (nm): 214



NO	R. Time	Peak Area	Percent	Peak Height
1	24.931	713861	50.60	14105
2	27.105	696871	49.40	12542



3i

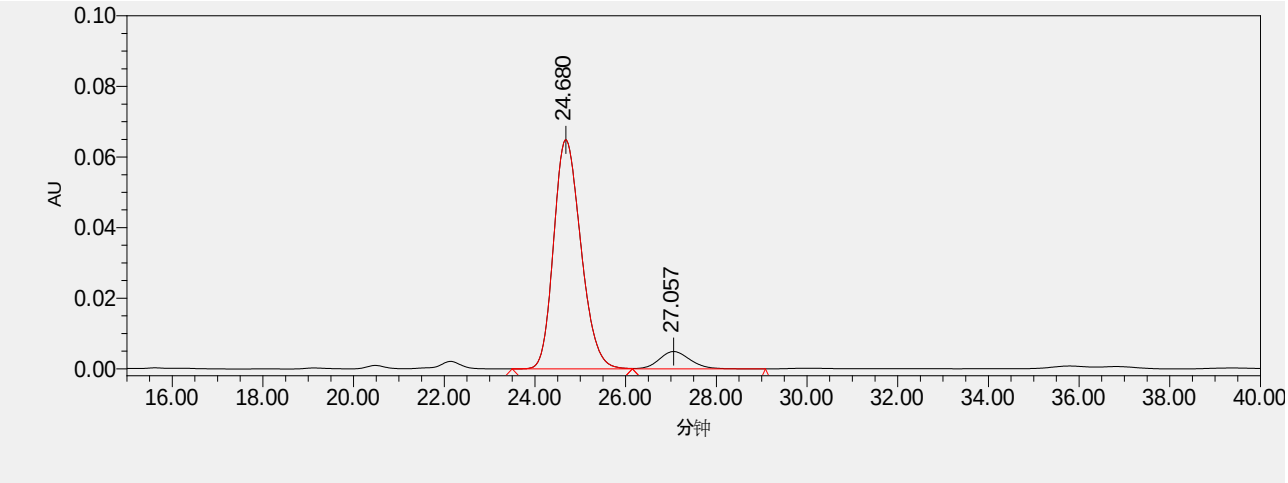
Chiral HPLC report: racemate (**3i**)

HPLC REPORT

Sample Name: yyl-17-57 Date: ####

Column: AD-H Mobile Phase: hex/ipr = 70/30

Velocity (mL/min): 0.5 Detection Wavelength (nm): 214



NO	R. Time	Peak Area	Percent	Peak Height
1	24.680	2709025	92.11	64947
2	27.057	232026	7.89	4909

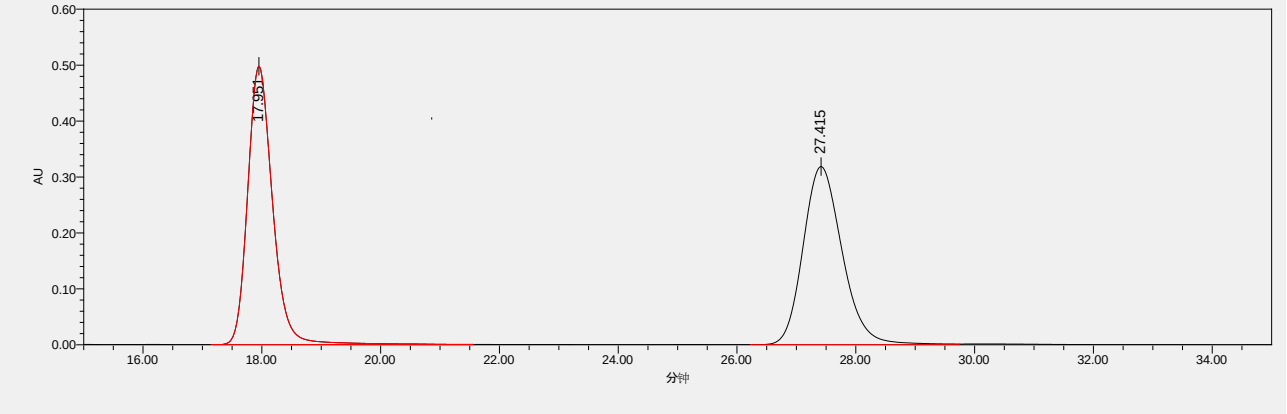
Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak AD column; λ = 214 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.5 mL/min; t_{minor} = 27.06 min, t_{major} = 24.68 min; ee% = 84.

HPLC REPORT

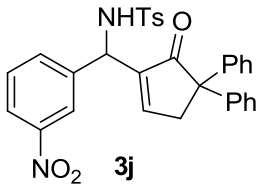
Sample Name: yyl-18-38 Date: ####

Column: AD-H Mobile Phase: hex/ipr = 60/40

Velocity (mL/min): 0.5 Detection Wavelength (nm): 230



NO	R. Time	Peak Area	Percent	Peak Height
1	17.951	14522610	49.96	497662
2	27.415	14548867	50.04	318574



3j

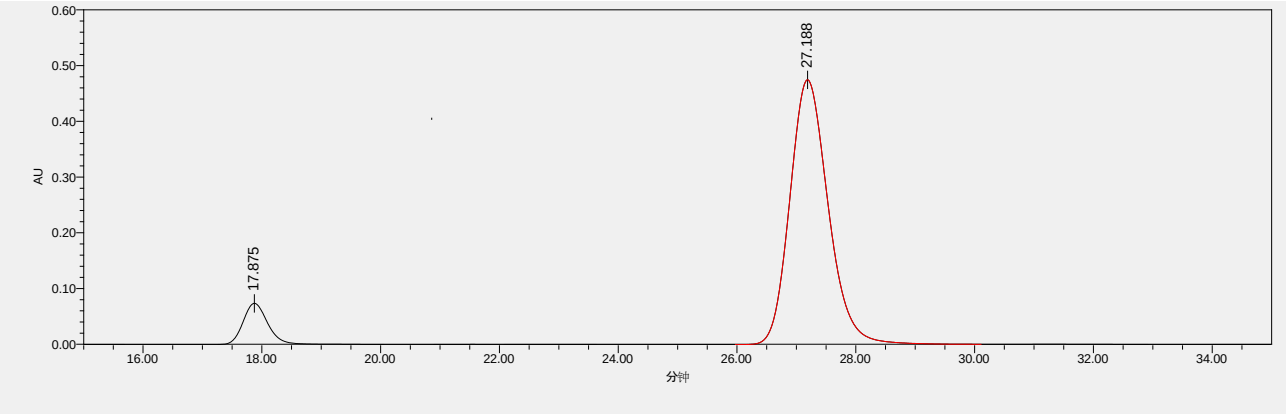
Chiral HPLC report: racemate (**3j**)

HPLC REPORT

Sample Name: yyl-18-39 Date: ####

Column: AD-H Mobile Phase: hex/ipr = 60/40

Velocity (mL/min): 0.5 Detection Wavelength (nm): 230



NO	R. Time	Peak Area	Percent	Peak Height
1	17.875	2153218	9.16	74157
2	27.188	21341454	90.84	475358

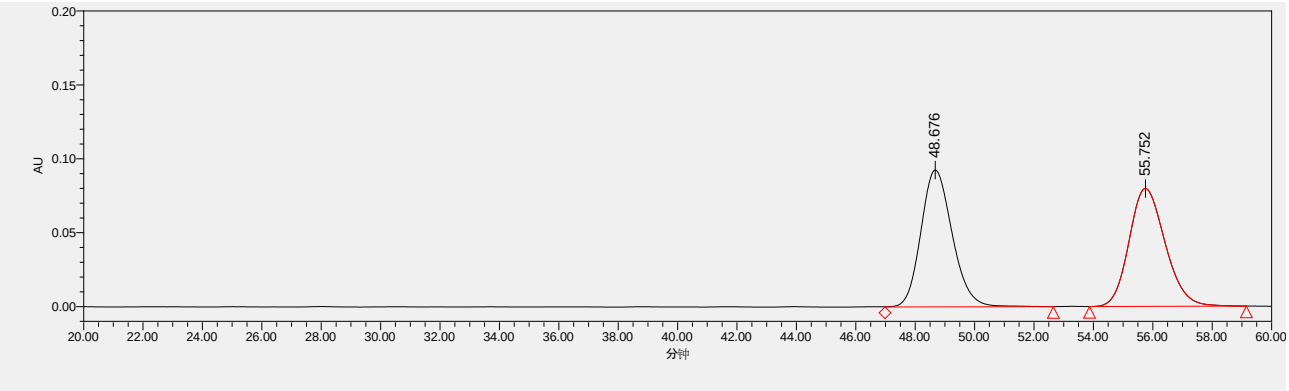
Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak AD column; λ = 230 nm; eluent: Hexane/Isopropanol = 60/40; Flow rate: 0.5 mL/min; t_{minor} = 17.87 min, t_{major} = 27.18 min; ee% = 82.

HPLC REPORT

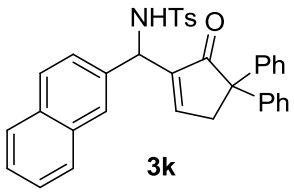
Sample Name: yyl-17-33 Date: ####

Column: AD-H Mobile Phase: hex/ipr = 80/20

Velocity (mL/min): 0.5 Detection Wavelength (nm): 230



NO	R. Time	Peak Area	Percent	Peak Height
1	48.476	6790042	50.20	92639
2	55.752	6734750	49.80	79812



3k

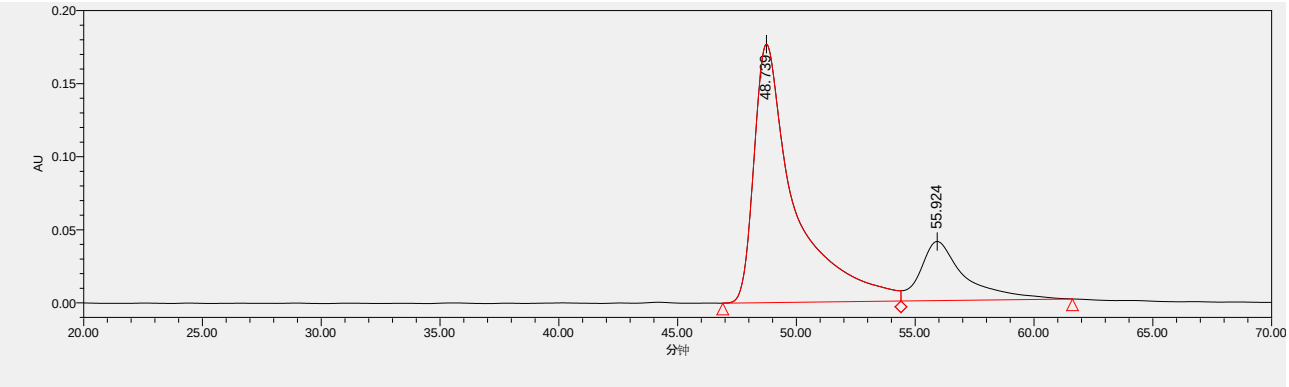
Chiral HPLC report: racemate (**3k**)

HPLC REPORT

Sample Name: yyl-17-65 Date: ####

Column: AD-H Mobile Phase: hex/ipr = 80/20

Velocity (mL/min): 0.5 Detection Wavelength (nm): 230



NO	R. Time	Peak Area	Percent	Peak Height
1	48.739	21098846	79.98	176854
2	55.924	5280086	20.02	40488

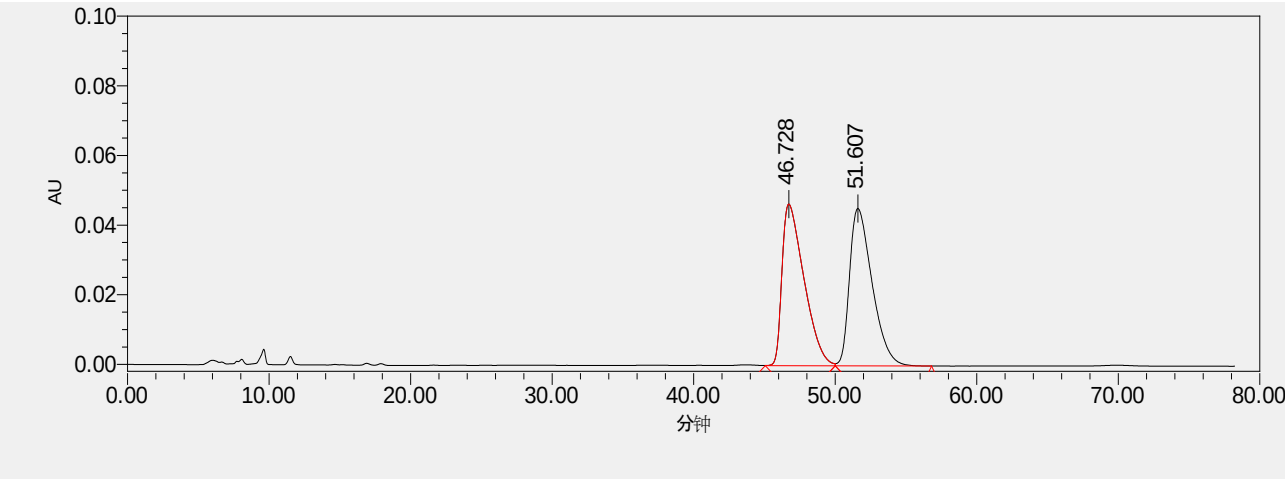
Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak AD column; λ = 230 nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.5 mL/min; t_{minor} = 55.92 min, t_{major} = 48.73 min; ee% = 60.

HPLC REPORT

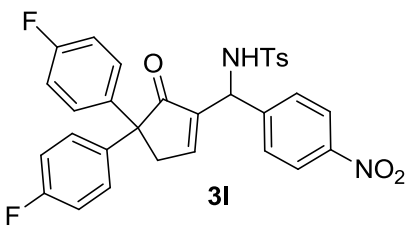
Sample Name: yyl-17-95 Date: ####

Column: AD-H Mobile Phase: hex/ipr = 70/30

Velocity (mL/min): 0.5 Detection Wavelength (nm): 214



NO	R. Time	Peak Area	Percent	Peak Height
1	46.728	5007395	49.94	46413
2	51.607	5019778	50.06	45206



3l

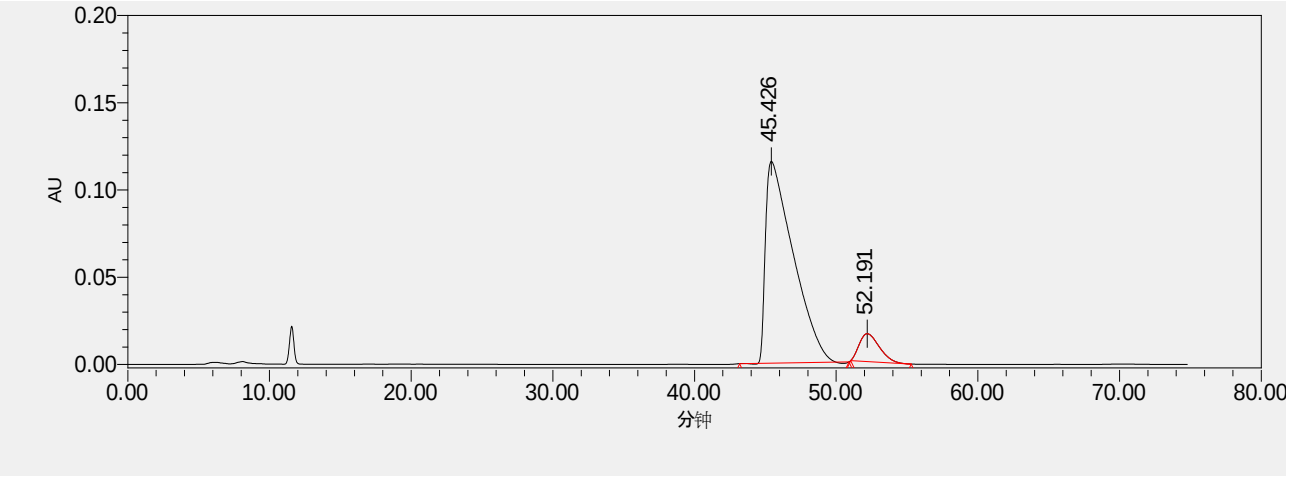
Chiral HPLC report: racemate (**3l**)

HPLC REPORT

Sample Name: yyl-18-3 Date: ####

Column: AD-H Mobile Phase: hex/ipr = 70/30

Velocity (mL/min): 0.5 Detection Wavelength (nm): 214



NO	R. Time	Peak Area	Percent	Peak Height
1	45.426	15772753	90.89	115678
2	52.191	1581475	9.11	16010

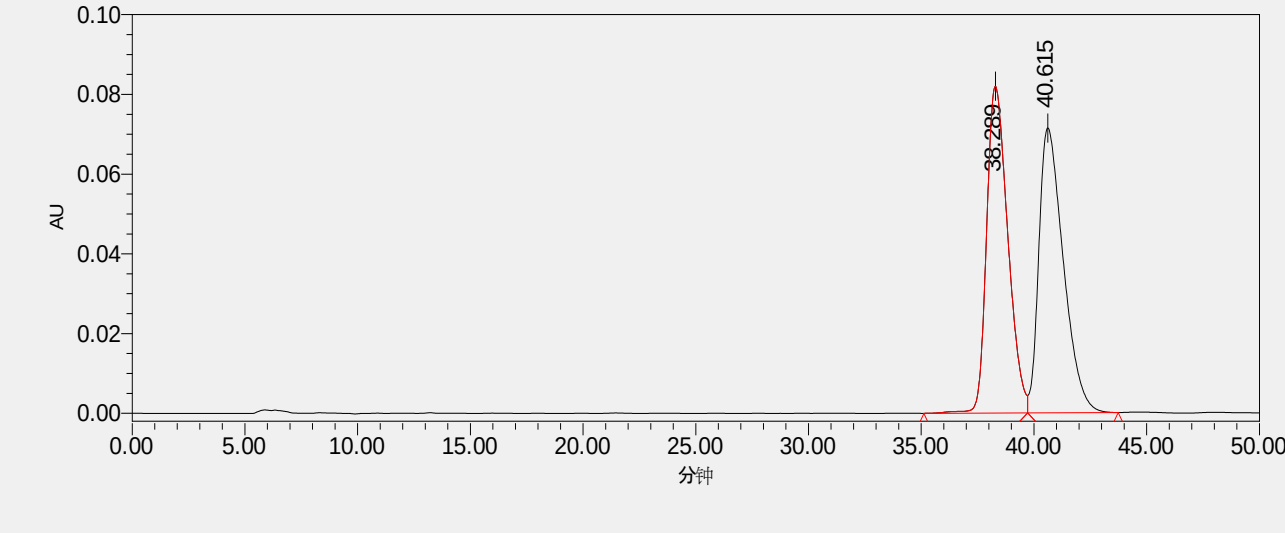
Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak AD column; λ = 214 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.5 mL/min; t_{minor} = 52.19 min, t_{major} = 45.42 min; ee% = 82.

HPLC REPORT

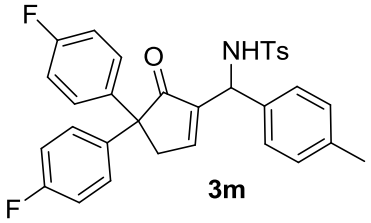
Sample Name: yyl-18-30 Date: ####

Column: AD-H Mobile Phase: hex/ipr = 80/20

Velocity (mL/min): 0.5 Detection Wavelength (nm): 214



NO	R. Time	Peak Area	Percent	Peak Height
1	38.289	5359784	49.82	81992
2	40.615	5397587	50.18	71472



3m

Chiral HPLC report: racemate (**3m**)

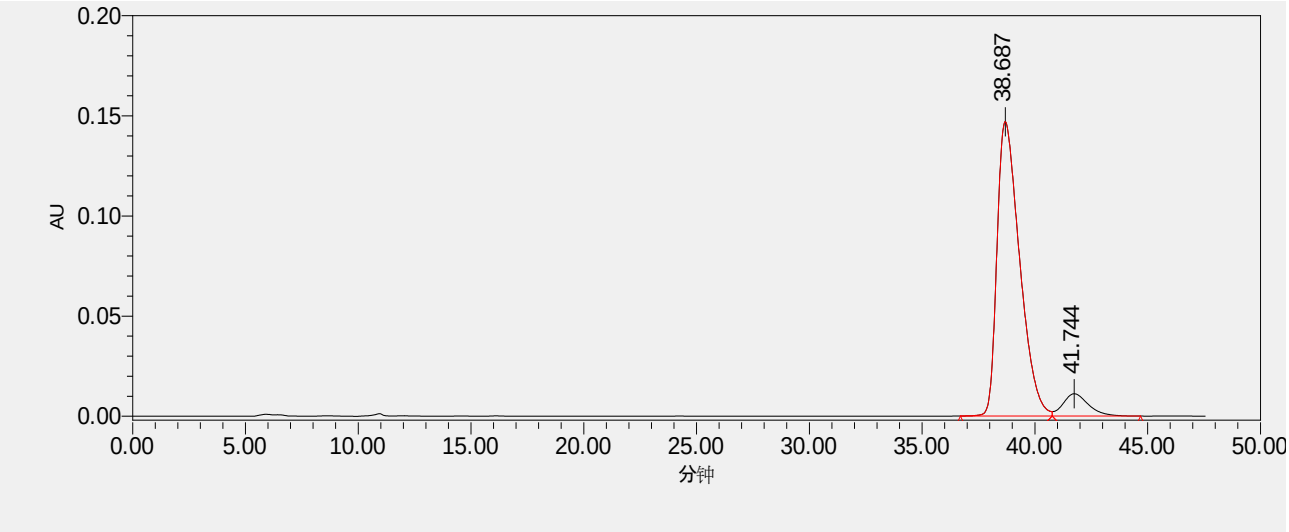
Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

HPLC REPORT

Sample Name: yyl-18-32 Date: ####

Column: AD-H Mobile Phase: hex/ipr = 80/20

Velocity (mL/min): 0.5 Detection Wavelength (nm): 214



NO	R. Time	Peak Area	Percent	Peak Height
1	38.687	10248796	92.11	147013
2	41.744	878426	7.89	11140

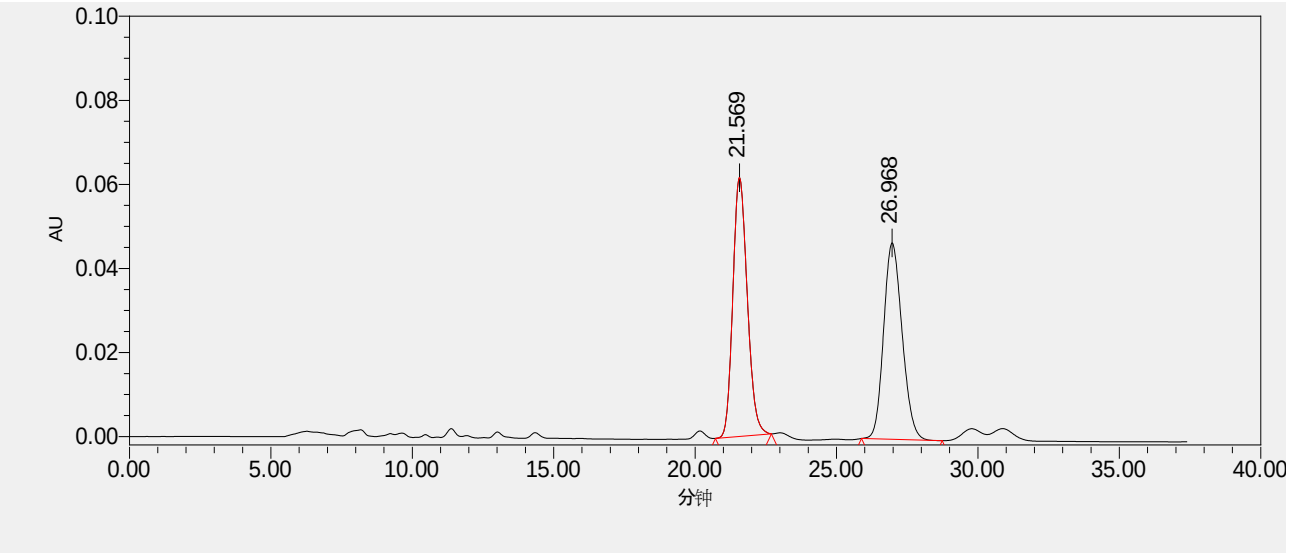
Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak AD column; λ = 214 nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.5 mL/min; t_{minor} = 41.74 min, t_{major} = 38.68 min; ee% = 84.

HPLC REPORT

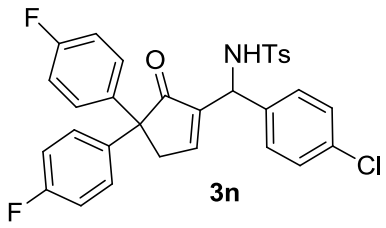
Sample Name: yyl-16-70 Date: ####

Column: AD-H Mobile Phase: hex/ipr = 70/30

Velocity (mL/min): 0.5 Detection Wavelength (nm): 214



NO	R. Time	Peak Area	Percent	Peak Height
1	21.569	2186756	50.73	61615
2	26.968	2123777	49.27	46734



3n

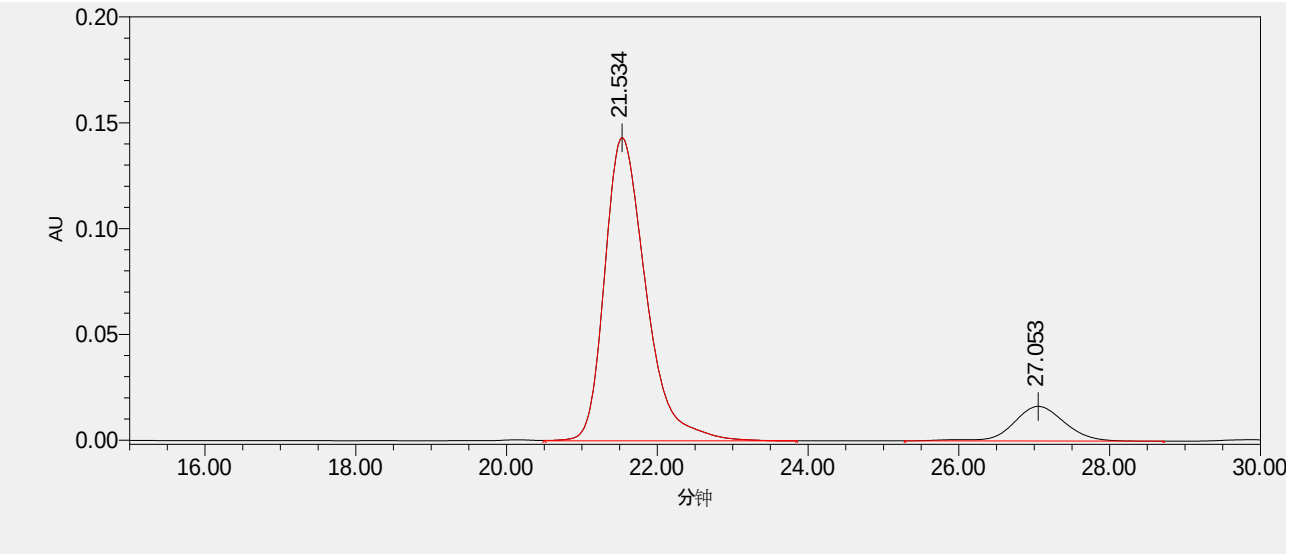
Chiral HPLC report: racemate (**3n**)

HPLC REPORT

Sample Name: yyl-16-71 Date: ####

Column: AD-H Mobile Phase: hex/ipr = 70/30

Velocity (mL/min): 0.5 Detection Wavelength (nm): 214



NO	R. Time	Peak Area	Percent	Peak Height
1	21.534	5433083	87.56	143267
2	27.053	771807	12.44	16385

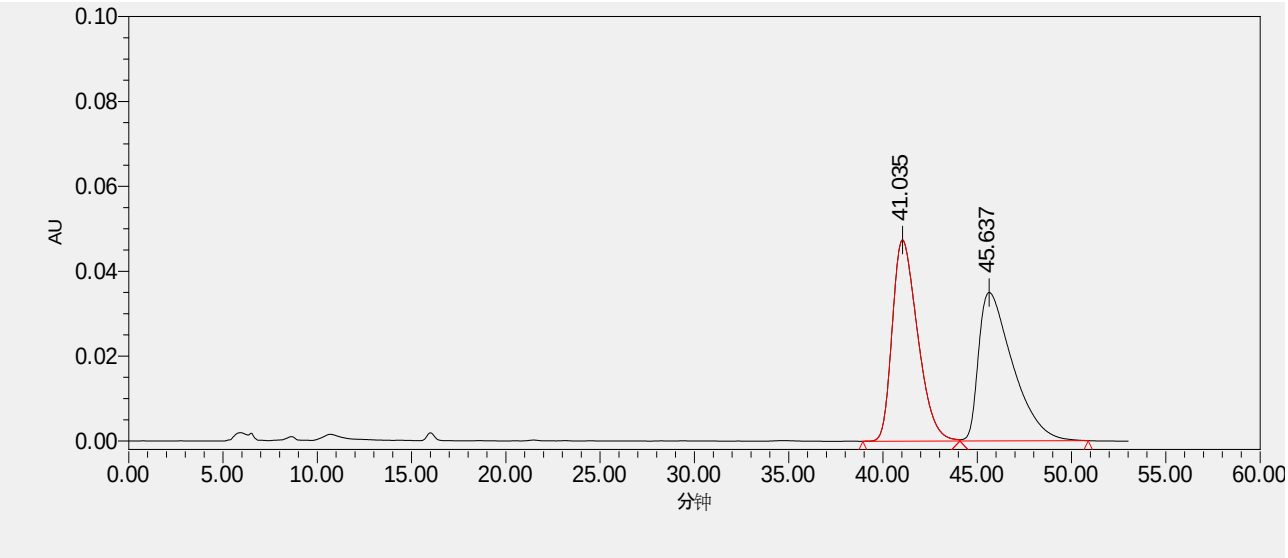
Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak AD column; λ = 214 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.5 mL/min; t_{minor} = 27.05 min, t_{major} = 21.53 min; ee% = 75.

HPLC REPORT

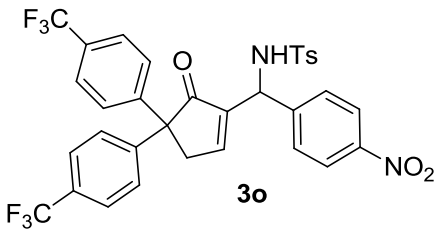
Sample Name: yyl-17-96 Date: ####

Column: IC Mobile Phase: hex/ipr = 80/20

Velocity (mL/min): 0.5 Detection Wavelength (nm): 214



NO	R. Time	Peak Area	Percent	Peak Height
1	41.035	4430578	50.13	47428
2	45.637	4407794	49.87	34985



3o

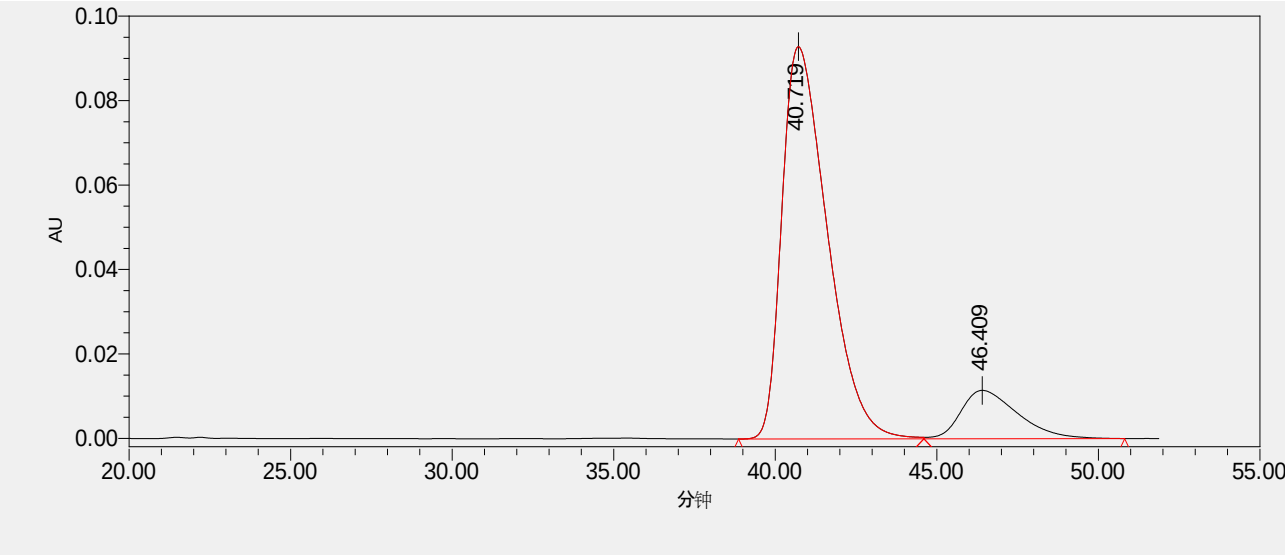
Chiral HPLC report: racemate (**3o**)

HPLC REPORT

Sample Name: yyl-18-4 Date: ####

Column: IC Mobile Phase: hex/ipr = 80/20

Velocity (mL/min): 0.5 Detection Wavelength (nm): 214



NO	R. Time	Peak Area	Percent	Peak Height
1	40.719	9086240	86.69	92904
2	46.409	1394919	13.31	11461

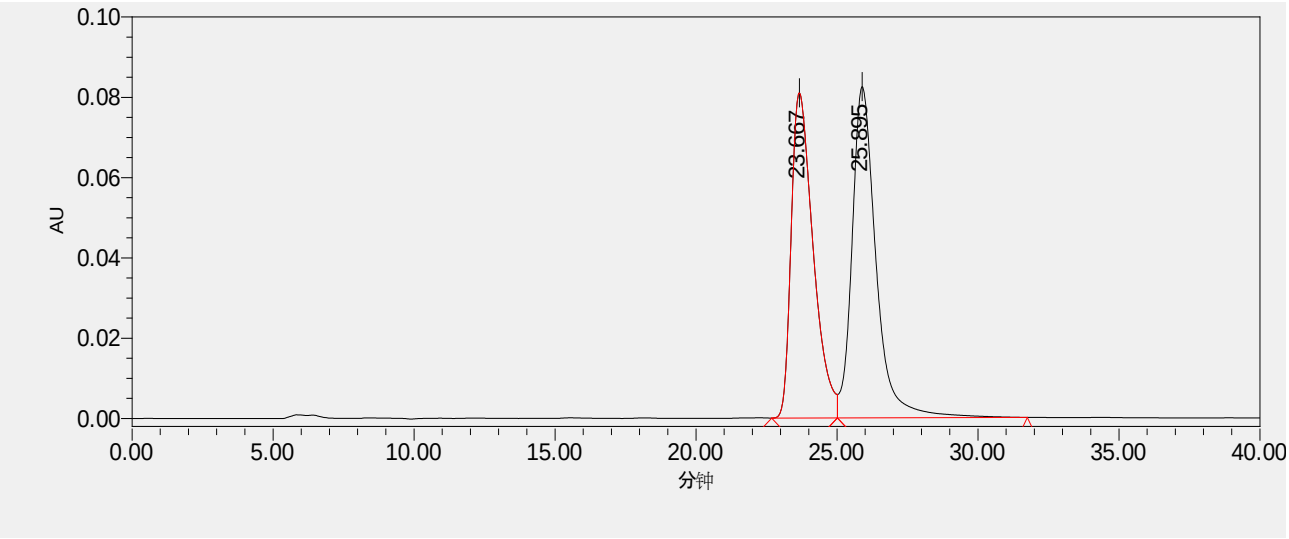
Chiral HPLC report: Enantiomeric excess was determined by HPLC with a IC column; λ = 214 nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.5 mL/min; t_{minor} = 46.40 min, t_{major} = 40.71 min; ee% = 73.

HPLC REPORT

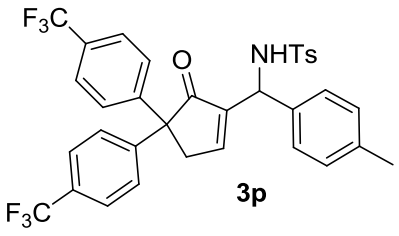
Sample Name: yyl-18-31 Date: ####

Column: AD-H Mobile Phase: hex/ipr = 80/20

Velocity (mL/min): 0.5 Detection Wavelength (nm): 214



NO	R. Time	Peak Area	Percent	Peak Height
1	23.667	3958133	49.50	78197
2	25.895	4038616	50.50	77411

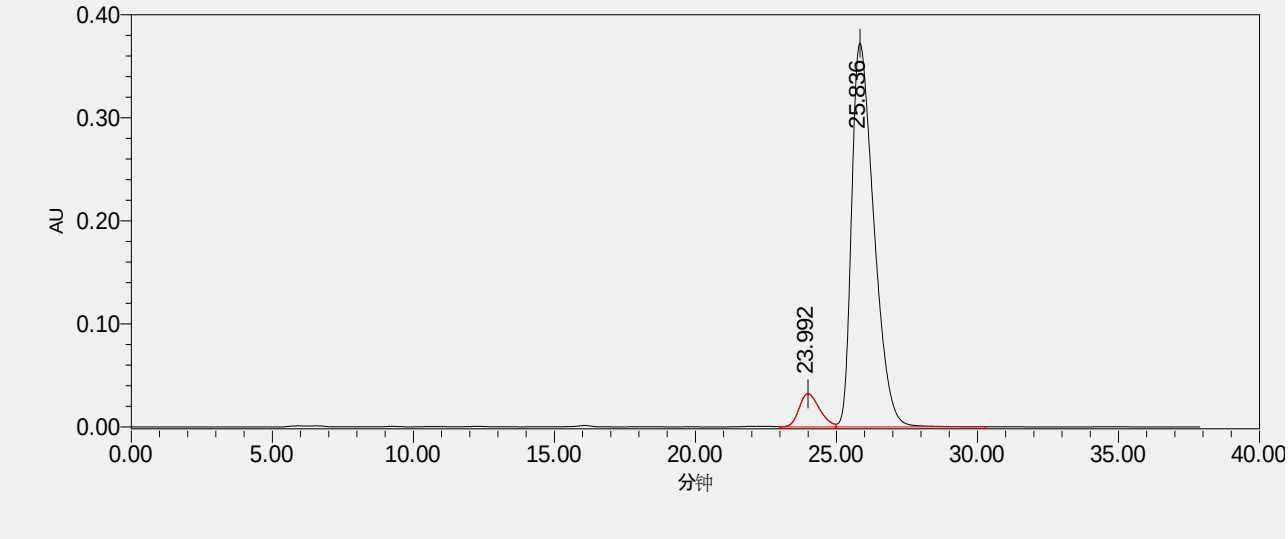


3p

Chiral HPLC report: racemate (**3p**)

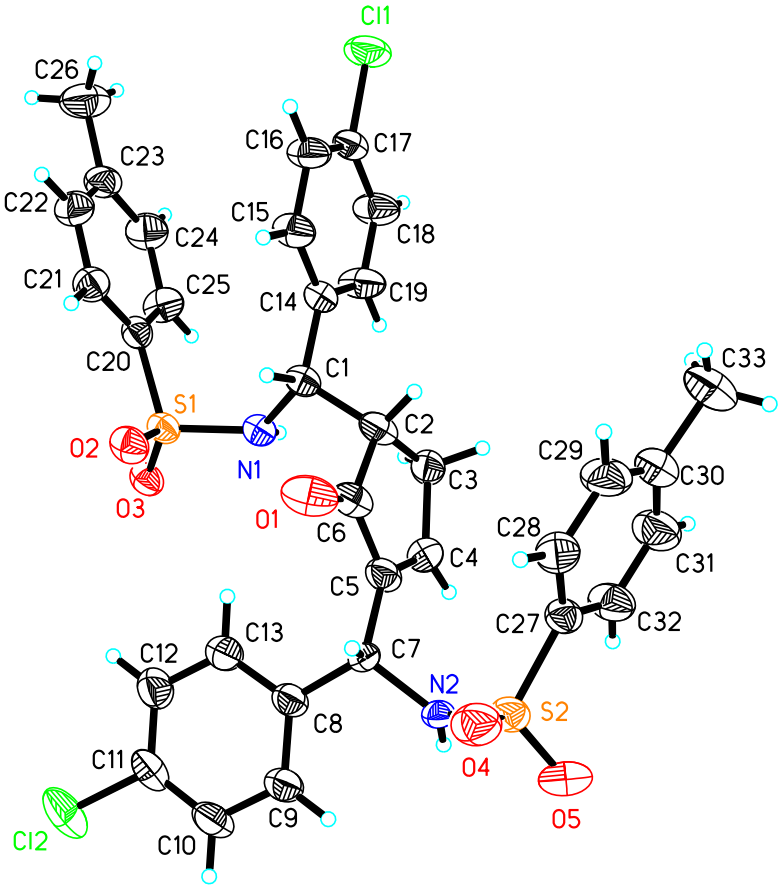
HPLC REPORT

Sample Name: yyl-18-33 Date: ####
Column: AD-H Mobile Phase: hex/ipr = 80/20
Velocity (mL/min): 0.5 Detection Wavelength (nm): 214

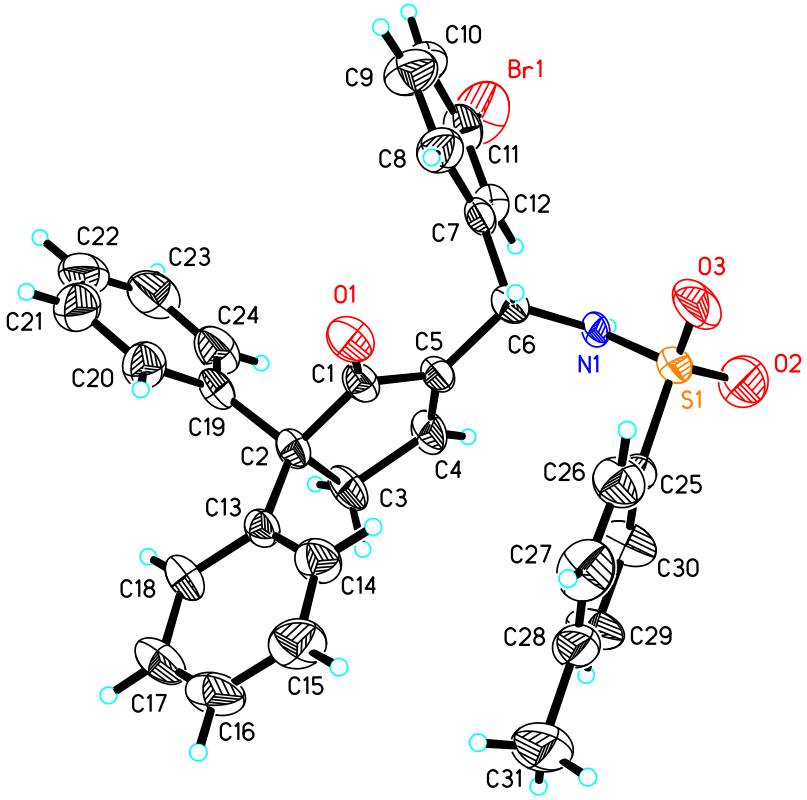


NO	R. Time	Peak Area	Percent	Peak Height
1	23.992	1611949	7.32	32180
2	25.863	20416375	92.68	372586

Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak AD column; λ = 214 nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.5 mL/min; t_{minor} = 23.99 min, t_{major} = 25.86 min; ee% = 85.



The crystal data of compound syn-**D** have been deposited in CCDC with number 823459. Empirical Formula: $C_{33}H_{30}Cl_2N_2O_5S_2$; Formula Weight: 669.61; Crystal Color, Habit: colorless; Crystal Dimensions: 0.319 x 0.311 x 0.257 mm; Crystal System: Triclinic; Lattice Parameters: a = 9.0943(10)Å, b = 11.3949(12)Å, c = 16.0640(18)Å, α = 90.442(2)^o, β = 97.860(2)^o, γ = 94.117(2)^o, V = 1644.5(3)Å^3; Space group: P-1; Z = 2; D_{calc} = 1.352 g/cm^3; F_{000} = 696; Final R indices [I>2sigma(I)] R1 = 0.0560, wR2 = 0.1503.



The crystal data of **3c** have been deposited in CCDC with number 873172. Empirical Formula: $C_{31}H_{26}BrNO_3S$; Formula Weight: 572.50; Crystal Color, Habit: colorless; Crystal Dimensions: 0.241 x 0.223 x 0.145 mm; Crystal System: Monoclinic; Lattice Parameters: a = 13.424(2)Å, b = 9.9313(18)Å, c = 20.607(4)Å, $\alpha = 90^o$, $\beta = 92.308(4)^o$, $\gamma = 90^o$, V = 2744.9(9)Å^3; Space group: P2(1)/n; Z = 4; D_{calc} = 1.385 g/cm^3; F_{000} = 1176; Final R indices [I>2sigma(I)] R1 = 0.0841, wR2 = 0.1619.