Supporting Information for

Design of Chiral Sulfoxide–Schiff Base Hybrids and Their Application in Cu-Catalyzed Asymmetric Henry Reactions

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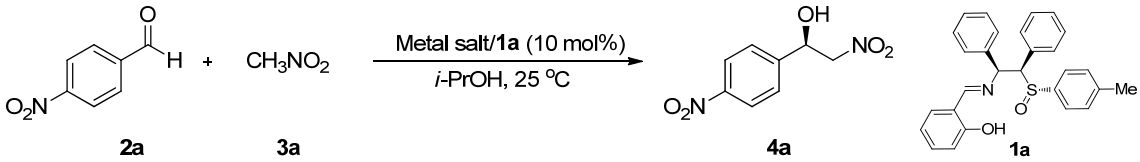
Contents

1. General Information

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. All the solvents were treated according to general methods. Flash column chromatography was performed using 200-300 mesh silica gel. ^{1}H NMR spectra were recorded on 400 MHz spectrophotometers. Chemical shifts (δ) are reported in ppm from the solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR spectra were recorded on 100 MHz with complete proton decoupling spectrophotometers ($CDCl_3$: 77.0 ppm). Mass spectra were measured on a MS spectrometer. Elemental analysis was taken on an elementary analysis instrument. Enantiomeric ratios were determined by chiral HPLC with chiral columns (chiralpak AS-H column, chiralpak AD-H column, chiralpak OJ-H column or chiralcel OD-H column) with hexane and *i*-PrOH as solvents. Optical rotations were measured with a polarimeter.

2. Detailed Optimizations of Reaction Conditions

***Table 1S*. Metal salt screening for the asymmetric Henry reaction[a]**

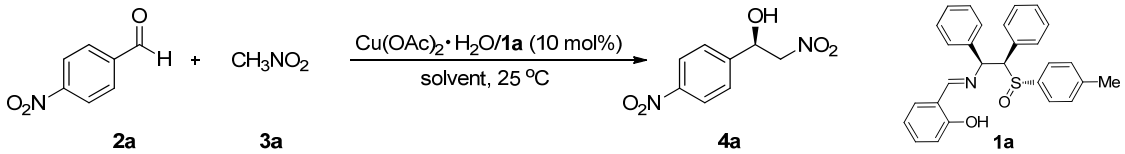


Entry	Metal salt	Ligand	t (h)	Yield (%)[b]	ee (%)[c]
1	$Cu(OAc)_2•H_2O$	**1a**	36	88	80
2	$Cu(OAc)_2$	**1a**	36	85	81
3	$CuBr_2$	**1a**	96	trace	-
4	$CuCl_2•2H_2O$	**1a**	96	trace	-
5	$CuSO_4$	**1a**	96	trace	-
6	CuBr	**1a**	96	trace	-
7	$Cu(OTf)_2$	**1a**	96	trace	-
8	AgOAc	**1a**	36	69	0
9	$Co(OAc)_2$	**1a**	36	90	0
10	$Zn(OAc)_2•H_2O$	**1a**	36	93	0
11	$Cu(OAc)_2•H_2O$		240	94	0
12	-	**1a**	96	trace	-
13	-		96	trace	-

[a] Unless otherwise noted, reactions were carried out with **2a** (0.40 mmol), **3a** (0.6 mL), Metal salt/**1a** (0.04 mmol), in *i*-PrOH (4 mL) at 25 °C. [b] Yield of isolated product. [c] Determined by chiral HPLC, the absolute configuration was established as *R* by comparison with literature data.

As shown in Table 1S, among the metal salts tested, the $Cu(OAc)_2•H_2O$ gave the best result in terms of yield and enantioselectivity (entry 1), and was thus selected for further optimization studies.

***Table 2S*. Solvent screening for the asymmetric Henry reaction[a]**

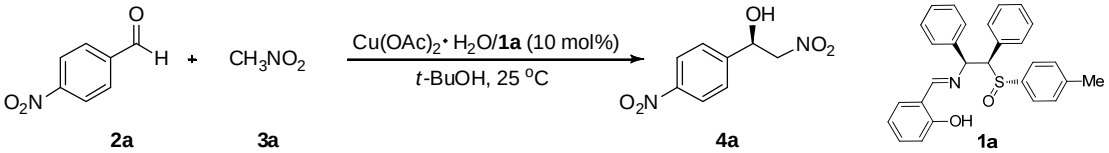


Entry	Solvent	t (h)	Yield (%)[b]	ee (%)[c]
1	*i*-PrOH	36	88	80
2	MeOH	48	90	38
3	EtOH	40	85	70
4	*t*-BuOH	24	94	85
5	DMF	20	94	20
6	MeCN	74	60	70
7	$MeNO_2$	56	66	77
8	CH_2Cl_2	70	42	68
9	toluene	72	21	53
10	THF	68	55	0

[a] Unless otherwise noted, reactions were carried out with **2a** (0.40 mmol), **3a** (0.6 mL), $Cu(OAc)_2•H_2O$/**1a** (0.04 mmol) in solvent (4 mL) at 25 °C. [b] Yield of isolated product. [c] Determined by chiral HPLC.

As shown in Table 2S, among the solvents tested, the *t*-BuOH gave the best result in terms of yield and enantioselectivity (entry 4), and was thus selected for further optimization studies.

***Table 3S*. Nitromethane loading screening for the asymmetric Henry reaction**[a]



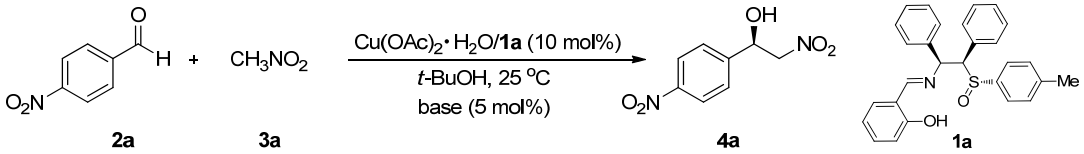
2a **3a** **4a** **1a**

Entry	Nitromethane (mL)	t (h)	Yield (%)[b]	ee (%)[c]
1	2.0	24	89	87
2	1.2	24	92	87
3	1.0	24	94	87
4	0.9	24	94	86
5	0.6	24	94	85
6	0.5	24	95	83
7	0.4	24	91	82
8	0.2	32	91	84
9	0.1	46	76	82

[a] Unless otherwise noted, reactions were carried out with **2a** (0.40 mmol), **3a**, $Cu(OAc)_2$•H_2O/**1a** (0.04 mmol) in *t*-BuOH (4 mL) at 25 °C. [b] Yield of isolated product. [c] Determined by chiral HPLC.

As shown in Table 3S, among the nitromethane loading tested, 1.0 mL of nitromethane gave the best result in terms of yield and enantioselectivity (entry 3), and was thus selected for further optimization studies.

***Table 4S*. Screening the base for the asymmetric Henry reaction**[a]



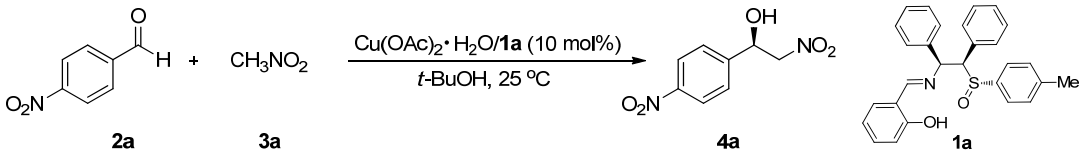
2a **3a** **4a** **1a**

Entry	Base	t (h)	Yield (%)[b]	ee (%)[c]
1	Et_3N	11	92	70
2	Py	11.5	91	82
3	DIPEA	12	93	69
4	DMAP	12.5	91	60
5	DBU	13.5	96	74
6	-	24	94	87

[a] Unless otherwise noted, reactions were carried out with **2a** (0.40 mmol), **3a** (1.0 mL), $Cu(OAc)_2$•H_2O/**1a** (0.04 mmol) in *t*-BuOH (4 mL) at 25 °C. [b] Yield of isolated product. [c] Determined by chiral HPLC.

As shown in Table 4S, the result in entry 6 was the best in terms of enantioselectivity, and was thus selected for further optimization studies.

***Table 5S*. Concentration screening for the asymmetric Henry reaction**[a]



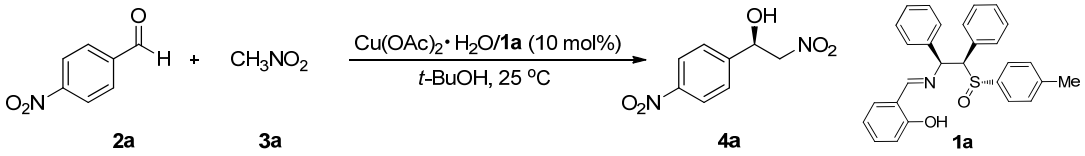
2a **3a** **4a** **1a**

Entry	Concentration (M)	t (h)	Yield (%)[b]	ee (%)[c]
1	0.4	21.5	91	84
2	0.2	22	95	85
3	0.1	24	94	87
4	0.05	42	88	72
5[d]	0.1	19	93	87

[a] Unless otherwise noted, reactions were carried out with **2a** (0.40 mmol), **3a** (1.0 mL), $Cu(OAc)_2$•H_2O/**1a** (0.04 mmol) in *t*-BuOH at 25 °C. [b] Yield of isolated product. [c] Determined by chiral HPLC.
[d] 4Å MS (100 mg) was added.

As shown in Table 5S, the result in entry 3 was the best in terms of yield and enantioselectivity, and was thus selected for further optimization studies.

***Table 6S*. Screening of equiv. of ligand for the the asymmetric Henry reaction**[a]

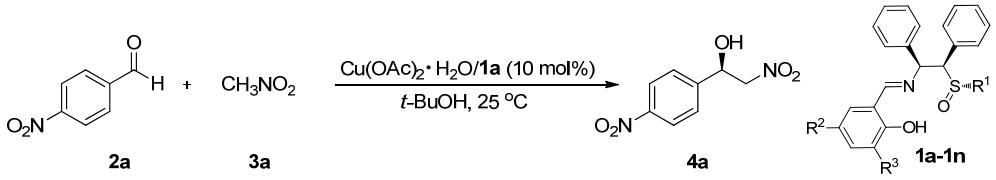


Entry	Equiv. of **1a**	t (h)	Yield (%)[b]	ee (%)[c]
1	0.10	26	94	85
2	0.11	26	88	86
3	0.12	25	96	88
4	0.13	25	94	86
5[d]	0.15	24	96	88
5[d]	0.20	24	95	89

[a] Unless otherwise noted, reactions were carried out with **2a** (0.40 mmol), **3a** (1.0 mL), $Cu(OAc)_2•H_2O$ (0.04 mmol) and **1a** in *t*-BuOH (4.0 mL) at 25 °C. [b] Yield of isolated product. [c] Determined by chiral HPLC.

As shown in Table 6S, among the equiv. of ligand tested, the 0.12 equiv. of ligand gave the best result (entry 3), and was thus selected for further studies.

***Table 7S*. Screening of ligands for the the asymmetric Henry reaction**[a]



Entry	Ligand	R^1	R^2	R^3	Time (h)	yield (%)[b]	ee (%)[c]
1	**1a**	4-MePh	H	H	24	95	88
2	**1b**	Ph	H	H	24	92	88
3	**1c**	4-BrPh	H	H	24	91	87
4	**1d**	3,5-Me_2Ph	H	H	24	94	80
5	**1e**	2-OMePh	Cl	H	108	53	24
6	**1f**	Bn	H	H	20	96	90
7	**1g**	4-MePh	Cl	H	32	92	90
8	**1h**	4-MePh	CH_3	H	24	93	86
9	**1i**	4-MePh	Cl	Cl	48	90	90
10	**1j**	4-MePh	*t*-butyl	*t*-butyl	24	94	80
11	**1k**	2-naphthyl	Cl	H	28	88	88
12	**1l**	4-MePh	Br	H	28	82	87
13	**1m**	4-MePh	F	H	28	91	89
14	**1n**	4-MePh	Br	Br	48	82	92
15[d]	**1f**	Bn	H	H	30	94	93

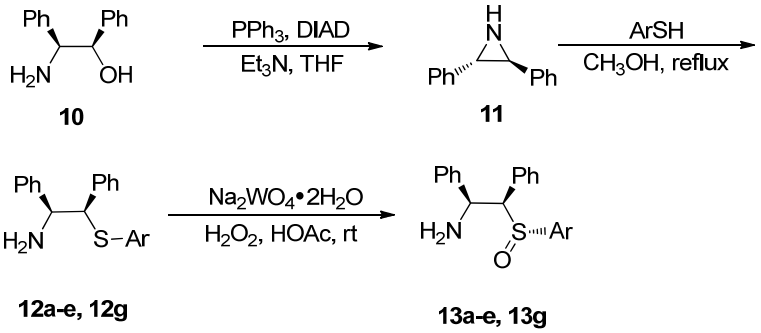
[a] Unless otherwise noted, the reaction was carried out with **2a** (0.4 mmol), **3a** (1.0 mL), $Cu(OAc)_2•H_2O$ (0.04 mmol) and **1** (0.048 mmol) in *t*-BuOH (4.0 mL) at 25 °C. [b] Isolated yield. [c] Determined by chiral HPLC, the absolute configuration was established as *R* by comparison with literature data. [d] 2.5 mol% of $Cu(OAc)_2•H_2O$ and 3 mol% of **1f** were used.

As shown in Table 7S, among the ligands tested, 2.5 mol% of ligand **1f** gave the best result (entry 15), and was thus selected for further studies.

3. General Procedures for the Synthesis of Ligands

3.1 General Procedure for the Preparation of Aminosulfoxides 13

(1) Synthesis of Aminosulfoxides 13a-13e, 13g



a) Mitsunobu reaction

(1*R*,2*S*)-2-amino-1,2-diphenylethanol (4.26 g, 20 mmol) was treated with Ph_3P (6.30 g, 24 mmol), Et_3N (8.40 mL) and diisopropyl azodicarboxylate (DIAD, 4.45 g, 22 mmol) in THF (60 mL) at room temperature for 20 h. After the solids were filtered, the filtrate was concentrated and purified by flash chromatography to give (2*S*,3*S*)-2,3-diphenylaziridine **11** as a white solid, 3.48 g, yield: 89%.

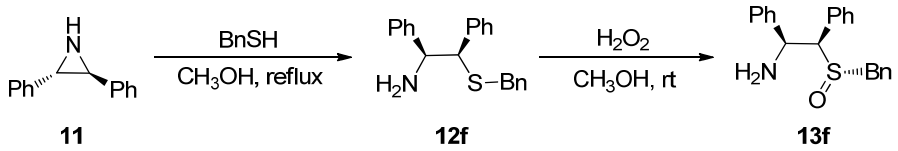
b) Ring opening reaction

Benzenethiol (11 mmol) was added to a solution of aziridine **11** (1.95 g, 10 mmol) in methanol. The solution was heated to reflux for 8 h. After the solvent was evaporated under vacuum, the crude product was purified by flash chromatography to give **12**.

c) Oxidation reaction

To a solution of **12** (8.5 mmol) and $Na_2WO_4{\cdot}2H_2O$ (85 mg) in HOAc (8.5 mL), H_2O_2 (30% in water, 0.85 mL, 8.5 mmol) was added dropwisely. The mixture was stirred for another 2 min. Then the reaction mixture was quenched with water, extracted with CH_2Cl_2 (3*50 mL), and the organic layer was washed with Sat. $NaHCO_3$ (aq.), dried over Na_2SO_4. After the solvent was evaporated under vacuum, the crude product was purified by flash chromatography to give a mixture of two diastereomeric aminosulfoxides. The major diastereoisomer **13** was obtained in pure form after a simple recrystallization with petroleum ether and ethanol as a white solid.

(2) Synthesis of Aminosulfoxide 13f[1]



b) Ring opening reaction

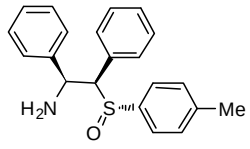
Phenylmethanethiol (1.86g, 15 mmol) was added to a solution of aziridine **11** (1.95 g, 10 mmol) in methanol. The solution was heated to reflux for 5 days. After the solvent was evaporated under vacuum, the crude product was purified by flash chromatography to give **12f** as a white solid, 2.07 g, yield: 65%.

c) Oxidation reaction

To a solution of **12f** (2.07g, 6.5 mmol) in methanol (10 mL) at room temperature, H_2O_2 (30% in water, 0.65 mL, 6.5 mmol) was added dropwisely. The mixture was stirred at room temperature for 3 days. Then the solvent was evaporated under vacuum, the crude product was purified by flash chromatography to give a mixture of two diastereomeric aminosulfoxides. The major diastereoisomer **13f** was obtained in pure form after a simple recrystallization with petroleum ether and ethanol as a white solid, 0.85 g, yield: 39%.

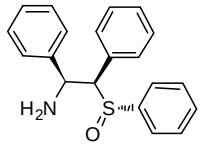
3.2 Characterization Data of Aminosulfoxides 13

(1*S*,2*R*)-1,2-diphenyl-2-((*R*)-*p*-tolylsulfinyl)ethanamine (13a)



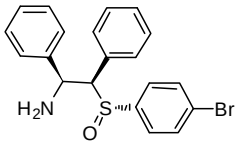
White solid, 47% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27 – 7.23 (m, 1H), 7.20 – 7.14 (m, 7H), 7.06 (d, *J* = 8.2 Hz, 2H), 7.00 – 6.94 (m, 4H), 5.02 (d, *J* = 3.1 Hz, 1H), 3.79 (d, *J* = 3.6 Hz, 1H), 2.29 (s, 3H), 1.82 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.43, 141.13, 139.46, 130.88, 130.47, 129.15, 128.19, 128.14, 128.05, 127.14, 126.71, 124.70, 78.91, 53.93, 21.27. MS: m/z = 335.04 (M^+). Anal. calcd for ($C_{21}H_{21}NOS$): C, 75.19; H, 6.31; N, 4.18; S, 9.56; found: C, 75.41; H, 6.146; N, 4.446; S, 9.801.

(1*S*,2*R*)-1,2-diphenyl-2-((*R*)-phenylsulfinyl)ethanamine (13b)



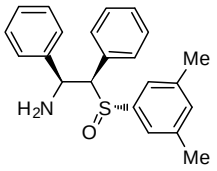
White solid, 49% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.31 (m, 1H), 7.27 – 7.24 (m, 5H), 7.20 – 7.15 (m, 5H), 7.00 – 6.94 (m, 4H), 5.03 (d, *J* = 3.3 Hz, 1H), 3.80 (d, *J* = 3.6 Hz, 1H), 1.83 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.76, 142.30, 130.69, 130.39, 128.34, 128.22, 128.10, 128.04, 127.12, 126.64, 124.61, 78.97, 53.82. MS: m/z = 321.14 (M^+). Anal. calcd for ($C_{20}H_{19}NOS$): C, 74.73; H, 5.96; N, 4.36; S, 9.98; found: C, 74.77; H, 5.818; N, 4.539; S, 9.752.

(1*S*,2*R*)-2-((*R*)-(4-bromophenyl)sulfinyl)-1,2-diphenylethanamine (13c)



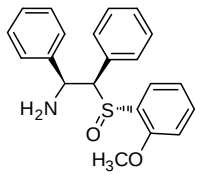
White solid, 52% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.36 (m, 2H), 7.31 – 7.27 (m, 1H), 7.22 – 7.18 (m, 5H), 7.10 – 7.07 (m, 2H), 6.99 – 6.95 (m, 4H), 5.01 (d, *J* = 3.5 Hz, 1H), 3.76 (d, *J* = 3.7 Hz, 1H), 1.82 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.19, 142.15, 131.56, 130.46, 130.42, 128.56, 128.31, 128.24, 127.30, 126.67, 126.23, 125.22, 79.23, 53.90. MS: m/z = 400.06 ($[M+1]^+$). Anal. calcd for ($C_{20}H_{18}BrNOS$): C, 60.00; H, 4.53; N, 3.50; S, 8.01; found: C, 60.11; H, 4.567; N, 3.389; S, 8.263.

(1*S*,2*R*)-2-((*R*)-(3,5-dimethylphenyl)sulfinyl)-1,2-diphenylethanamine (13d)



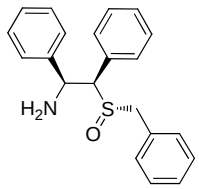
White solid, 41% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 – 7.24 (m, 1H), 7.21 – 7.16 (m, 5H), 7.02 – 6.93 (m, 5H), 6.81 (s, 2H), 5.01 (d, *J* = 2.4 Hz, 1H), 3.78 (d, *J* = 3.7 Hz, 1H), 2.17 (s, 6H), 1.83 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.78, 138.30, 137.47, 133.00, 130.91, 129.98, 128.97, 128.44, 128.34, 128.06, 127.92, 122.46, 75.74, 56.75, 20.89. MS: m/z = 349.26 (M^+). Anal. calcd for ($C_{22}H_{23}NOS$): C, 75.61; H, 6.63; N, 4.01; S, 9.17; found: C, 75.52; H, 6.910; N, 4.131; S, 9.341.

(1*S*,2*R*)-2-((*R*)-(2-methoxyphenyl)sulfinyl)-1,2-diphenylethanamine (13e)



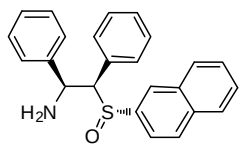
White solid, 45% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.41 – 7.36 (m, 1H), 7.29 – 7.21 (m, 3H), 7.18 – 7.09 (m, 6H), 6.88 – 6.86 (m, 2H), 6.77 (d, *J* = 8.2 Hz, 1H), 4.89 (d, *J* = 3.5 Hz, 1H), 4.04 (d, *J* = 3.6 Hz, 1H), 3.61 (s, 3H), 1.85 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.45, 142.47, 132.58, 132.18, 130.54, 130.24, 128.00, 127.87, 127.76, 126.96, 126.59, 125.94, 121.37, 110.41, 74.41, 55.28, 53.86. MS: m/z = 351.94 ($[M+1]^+$). Anal. calcd for ($C_{21}H_{21}NO_2S$): C, 71.76; H, 6.02; N, 3.99; S, 9.12; found: C, 72.00; H, 5.976; N, 3.791; S, 9.056.

(1*S*,2*R*)-2-((*S*)-benzylsulfinyl)-1,2-diphenylethanamine (13f)



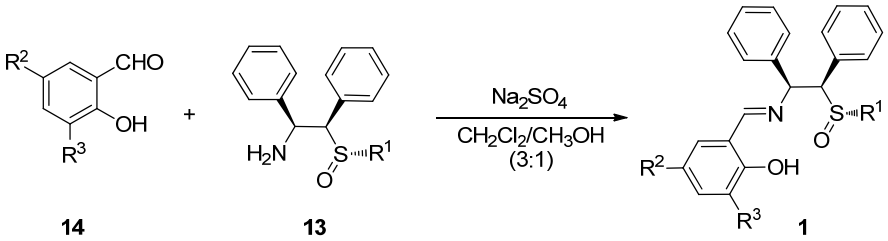
White solid, 39% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.25 (m, 6H), 7.19 – 7.15 (m, 3H), 7.14 – 7.11 (m, 2H), 7.02 (d, *J* = 7.0 Hz, 2H), 6.90 – 6.88 (m, 2H), 4.88 (d, *J* = 3.1 Hz, 1H), 3.84 – 3.77 (m, 2H), 3.49 (d, *J* = 13.4 Hz, 1H), 1.74 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.26, 131.08, 130.28, 130.08, 129.77, 128.58, 128.52, 128.40, 128.00, 127.96, 127.04, 126.57, 72.96, 55.16, 53.52. MS: m/z = 335.8 ($[M]^+$). Anal. calcd for ($C_{21}H_{21}NOS$): C, 75.19; H, 6.31; N, 4.18; S, 9.56; found: C, 75.21; H, 6.254; N, 4.029; S, 9.664.

(1*S*,2*R*)-2-((*R*)-naphthalen-2-ylsulfinyl)-1,2-diphenylethanamine (13g)



White solid, 48% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.79 – 7.73 (m, 2H), 7.69 (d, *J* = 8.6 Hz, 1H), 7.53 – 7.47 (m, 2H), 7.28 – 7.24 (m, 1H), 7.18 – 7.14 (m, 6H), 7.01 – 6.97 (m, 4H), 5.07 (d, *J* = 3.5 Hz, 1H), 3.90 (d, *J* = 3.6 Hz, 1H), 1.86 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.31, 140.02, 134.13, 132.38, 130.79, 130.52, 128.33, 128.17, 128.14, 127.74, 127.43, 127.20, 126.79, 126.71, 125.31, 120.65, 78.79, 54.00. MS: m/z = 373.23 ($[M+2]^+$). Anal. calcd for ($C_{24}H_{21}NOS$): C, 77.59; H, 5.70; N, 3.77; S, 8.63; found: C, 77.60; H, 5.590; N, 3.642; S, 8.892.

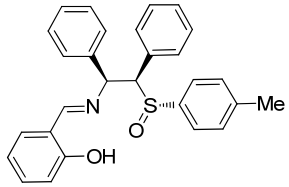
3.3 General Procedure for the Preparation of Ligands



A mixture of dry CH_2Cl_2/methanol (3:1) (16 mL), **13** (2 mmol), **14** (2 mmol) and anhydrous Na_2SO_4 (1.1 g) was refluxed for 4 h. The solution was filtered and the solvent was evaporated under reduced pressure. Then, the residue was recrystallized with ethanol to afford the ligands.

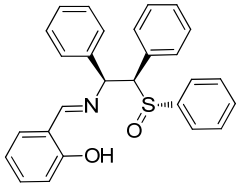
3.4 Spectral Data of Ligands

2-((*E*)-(((1*S*,2*R*)-1,2-diphenyl-2-((*R*)-*p*-tolylsulfinyl)ethyl)imino)methyl)phenol (1a)



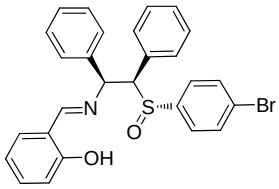
Yellow solid, yield: 93%. 100% ee, determined by chiral HPLC analysis (Chiralcel OD-H, hexane/isopropanol, 85:15 v/v, 0.8 mL/min, 25 °C, UV 215 nm): Retension times: t_r = 8.171 min for (*S, R, R*)-isomer (major), t_r = 9.918 min for (*R, S, S*)-isomer. **^{1}H NMR** (400 MHz, DMSO) δ 13.16 (s, 1H), 8.86 (s, 1H), 7.60 (d, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.23 – 7.12 (m, 12H), 7.01 – 6.91 (m, 4H), 5.52 (d, *J* = 3.4 Hz, 1H), 4.41 (d, *J* = 3.8 Hz, 1H), 2.24 (s, 3H). **^{13}C NMR** (100 MHz, DMSO) δ 167.53, 159.78, 141.26, 139.63, 138.78, 133.09, 132.19, 130.92, 130.28, 129.22, 128.28, 128.15, 127.92, 127.38, 127.20, 125.40, 119.18, 118.71, 116.40, 76.41, 70.32, 20.82. MS: m/z = 440.1 ([M+1]$^+$). Anal. calcd for ($C_{28}H_{25}NO_2S$): C, 76.51; H, 5.73; N, 3.19; S, 7.29; found: C, 76.29; H, 6.025; N, 3.068; S, 7.461. $[\alpha]_D^{25}$ = -177.72 (*c* = 0.5, $CHCl_3$).

2-((*E*)-(((1*S*,2*R*)-1,2-diphenyl-2-((*R*)-phenylsulfinyl)ethyl)imino)methyl)phenol (1b)



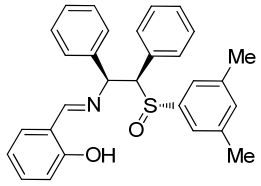
Yellow solid, yield: 94%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 13.28 (s, 1H), 8.80 (s, 1H), 7.42 – 7.36 (m, 2H), 7.33 – 7.29 (m, 1H), 7.25 – 7.22 (m, 5H), 7.20 – 7.16 (m, 5H), 7.07 – 7.04 (m, 3H), 6.96 – 6.88 (m, 3H), 5.63 (d, *J* = 3.0 Hz, 1H), 3.95 (d, *J* = 3.1 Hz, 1H). **^{13}C NMR** (100 MHz, DMSO) δ 167.54, 159.78, 141.98, 139.59, 133.10, 132.19, 131.26, 130.87, 130.27, 128.62, 128.29, 128.20, 127.95, 127.40, 127.22, 125.30, 119.20, 118.73, 116.41, 76.57, 70.27. MS: m/z = 426.0 ([M+1]$^+$). Anal. calcd for ($C_{27}H_{23}NO_2S$): C, 76.21; H, 5.45; N, 3.29; S, 7.54; found: C, 76.29; H, 5.705; N, 3.244; S, 7.656. $[\alpha]_D^{25}$ = -165.04 (*c* = 0.5, $CHCl_3$).

2-((*E*)-(((1*S*,2*R*)-2-((*R*)-(4-bromophenyl)sulfinyl)-1,2-diphenylethyl)imino)methyl)phenol (1c)



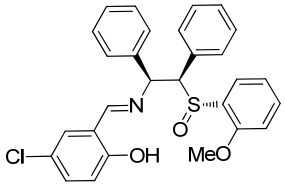
Yellow solid, yield: 93%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 13.22 (s, 1H), 8.77 (s, 1H), 7.41 – 7.38 (m, 4H), 7.30 – 7.17 (m, 6H), 7.07 – 7.04 (m, 5H), 6.96 – 6.90 (m, 3H), 5.60 (d, *J* = 2.0 Hz, 1H), 3.91 (d, *J* = 2.1 Hz, 1H). **^{13}C NMR** (100 MHz, DMSO) δ 167.53, 160.11, 159.73, 141.44, 139.44, 133.11, 132.13, 131.56, 130.72, 130.26, 128.30, 128.06, 127.44, 127.35, 127.27, 124.81, 119.18, 118.71, 116.39, 76.20, 70.18. MS: m/z = 504.8 ([M+1]$^+$). Anal. calcd for ($C_{27}H_{22}BrNO_2S$): C, 64.29; H, 4.40; N, 2.78; S, 6.36; found: C, 63.99; H, 4.689; N, 2.581; S, 6.374. $[\alpha]_D^{25}$ = -162.90 (*c* = 0.5, $CHCl_3$).

2-((*E*)-(((1*S*,2*R*)-2-((*R*)-(3,5-dimethylphenyl)sulfinyl)-1,2-diphenylethyl)imino)methyl)phenol (1d)



Yellow solid, yield: 87%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 13.31 (s, 1H), 8.79 (s, 1H), 7.42 – 7.38 (m, 2H), 7.26 – 7.23 (m, 2H), 7.20 – 7.15 (m, 5H), 7.08 – 7.03 (m, 3H), 6.96 – 6.89 (m, 4H), 6.76 (s, 2H), 5.61 (d, *J* = 3.0 Hz, 1H), 3.92 (d, *J* = 3.0 Hz, 1H), 2.14 (s, 6H). **^{13}C NMR** (100 MHz, DMSO) δ 167.39, 160.15, 159.77, 141.63, 139.65, 137.87, 133.06, 132.53, 132.15, 131.15, 130.42, 128.27, 128.08, 127.86, 127.40, 127.29, 122.63, 119.17, 118.73, 116.39, 76.33, 70.25, 20.59. MS: m/z = 454.1 ([M+1]$^+$). Anal. calcd for ($C_{29}H_{27}NO_2S$): C, 76.79; H, 6.00; N, 3.09; S, 7.07; found: C, 76.63; H, 6.178; N, 3.008; S, 7.170. $[\alpha]_D^{25}$ = -159.42 (*c* = 0.5, $CHCl_3$).

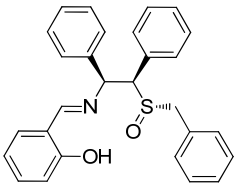
4-chloro-2-((*E*)-(((1*S*,2*R*)-2-((*R*)-(2-methoxyphenyl)sulfinyl)-1,2-diphenylethyl)imino)methyl)phenol (1e)



Yellow solid, yield: 85%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 13.18 (s, 1H), 8.60 (s, 1H), 7.78 – 7.74 (m, 1H), 7.32 – 7.27 (m, 3H), 7.22 – 7.14 (m, 6H), 7.05 – 7.00 (m, 5H), 6.94 (d, *J* = 8.7 Hz, 1H), 6.60 (d, *J* = 8.2 Hz, 1H), 5.55 (d, *J* = 3.9 Hz, 1H), 4.22 (d, *J* = 4.0 Hz, 1H), 3.40 (s, 3H). **^{13}C NMR** (100 MHz, CDCl3) δ 166.20, 159.47, 156.15, 139.25, 132.57, 132.46, 131.29, 131.25, 130.53,

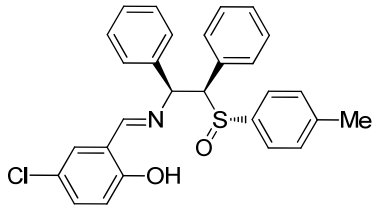
130.49, 128.36, 128.13, 127.74, 127.65, 127.45, 125.73, 123.44, 121.40, 119.54, 118.41, 110.40, 77.51, 70.93, 55.08. MS: m/z = 490.0 ([M+1]$^+$). HRMS (ESI) for $C_{28}H_{24}ClNO_3S$ [M+H]$^+$: calcd 490.1244, found 490.12382. $[\alpha]_D^{25}$ = 13.76 (*c* = 0.5, $CHCl_3$).

2-((*E*)-(((1*S*,2*R*)-2-((*S*)-benzylsulfinyl)-1,2-diphenylethyl)imino)methyl)phenol (1f)



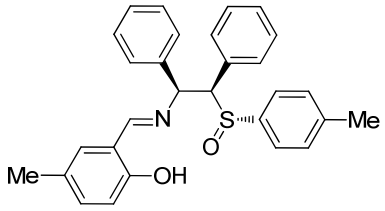
Yellow solid, yield: 93%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 13.19 (s, 1H), 8.66 (s, 1H), 7.39 – 7.31 (m, 8H), 7.19 – 7.16 (m, 3H), 7.13 – 7.11 (m, 2H), 7.03 – 6.95 (m, 5H), 6.90 (t, *J* = 7.5 Hz, 1H), 5.40 (d, *J* = 2.9 Hz, 1H), 3.97 (d, *J* = 3.0 Hz, 1H), 3.81 (d, *J* = 13.3 Hz, 1H), 3.53 (d, *J* = 13.3 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.90, 160.80, 139.14, 132.94, 132.38, 130.57, 130.21, 130.06, 129.85, 129.03, 128.79, 128.71, 128.57, 128.27, 127.53, 127.24, 118.93, 118.56, 116.78, 72.95, 70.71, 55.12. MS: m/z = 439.8 (M$^+$). Anal. calcd for ($C_{28}H_{25}NO_2S$): C, 76.51; H, 5.73; N, 3.19; S, 7.29; found: C, 76.67; H, 5.455; N, 3.448; S, 7.104. $[\alpha]_D^{16}$ = - 155.54 (*c* = 0.5, $CHCl_3$).

4-chloro-2-((*E*)-(((1*S*,2*R*)-1,2-diphenyl-2-((*R*)-*p*-tolylsulfinyl)ethyl)imino)methyl)phenol (1g)



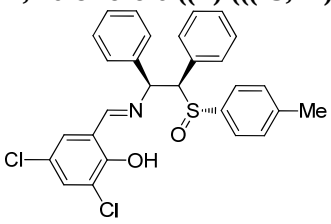
Yellow solid, yield: 91%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 13.25 (s, 1H), 8.70 (s, 1H), 7.36 (d, *J* = 2.5 Hz, 1H), 7.32 – 7.29 (m, 1H), 7.26 – 7.22 (m, 1H), 7.18 – 7.15 (m, 5H), 7.10 (d, *J* = 8.2 Hz, 2H), 7.03 – 7.00 (m, 4H), 6.97 (d, *J* = 8.8 Hz, 1H), 6.86 (d, *J* = 7.3 Hz, 2H), 5.61 (d, *J* = 3.1 Hz, 1H), 3.93 (d, *J* = 3.1 Hz, 1H), 2.26 (s, 3H). **^{13}C NMR** (100 MHz, DMSO) δ 166.09, 158.82, 141.31, 139.40, 138.73, 132.71, 130.87, 130.69, 130.31, 129.25, 128.35, 128.21, 127.97, 127.49, 127.25, 125.44, 122.59, 120.01, 118.57, 76.21, 70.30, 20.85.MS: m/z = 474.9 ([M+2]$^+$). HRMS (ESI) for $C_{28}H_{24}ClNO_2S$ [M+H]$^+$: calcd 474.1295, found 474.12890. $[\alpha]_D^{25}$ = -155.94 (*c* = 0.5, $CHCl_3$).

2-((*E*)-(((1*S*,2*R*)-1,2-diphenyl-2-((*R*)-*p*-tolylsulfinyl)ethyl)imino)methyl)-4-methylphenol (1h)



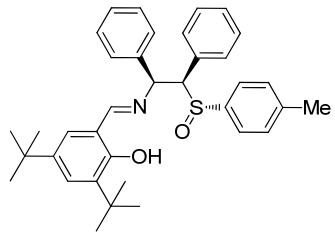
Yellow solid, yield: 92%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 13.03 (s, 1H), 8.74 (s, 1H), 7.23 – 7.15 (m, 8H), 7.11 (d, *J* = 8.2 Hz, 2H), 7.06 – 7.02 (m, 4H), 6.95 (d, *J* = 8.1 Hz, 1H), 6.88 (d, *J* = 7.4 Hz, 2H), 5.61 (d, *J* = 2.9 Hz, 1H), 3.93 (d, *J* = 3.0 Hz, 1H), 2.31 (s, 3H), 2.27 (s, 3H). **^{13}C NMR** (100 MHz, DMSO) δ 167.66, 158.01, 141.26, 139.62, 138.82, 133.82, 132.05, 130.92, 130.30, 129.23, 128.29, 128.16, 127.94, 127.71, 127.38, 127.22, 125.42, 118.32, 116.34, 76.44, 70.29, 20.84, 19.88.MS: m/z = 454.1 ([M+1]$^+$). Anal. calcd for ($C_{29}H_{27}NO_2S$): C, 76.79; H, 6.00; N, 3.09; S, 7.07; found: C, 76.90; H, 5.999; N, 2.859; S, 7.123. $[\alpha]_D^{25}$ = -171.34 (*c* = 0.5, $CHCl_3$).

2,4-dichloro-6-((*E*)-(((1*S*,2*R*)-1,2-diphenyl-2-((*R*)-*p*-tolylsulfinyl)ethyl)imino)methyl)phenol (1i)



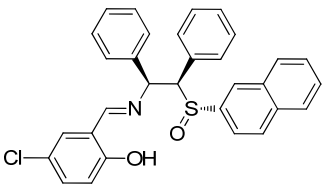
Yellow solid, yield: 88%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 14.07 (s, 1H), 8.72 (s, 1H), 7.47 (d, *J* = 2.1 Hz, 1H), 7.32 (d, *J* = 2.2 Hz, 1H), 7.28 – 7.24 (m, 1H), 7.21 – 7.16 (m, 5H), 7.11 (d, *J* = 8.1 Hz, 2H), 7.05 – 7.03 (m, 4H), 6.86 (d, *J* = 7.2 Hz, 2H), 5.65 (d, *J* = 2.8 Hz, 1H), 3.94 (d, *J* = 3.0 Hz, 1H), 2.28 (s, 3H). **^{13}C NMR** (100 MHz, DMSO) δ 166.85, 155.89, 141.30, 138.70, 138.51, 132.24, 130.68, 130.36, 130.12, 129.21, 128.41, 128.26, 128.04, 127.65, 127.28, 125.35, 122.02, 121.58, 119.73, 75.66, 69.72, 20.81. MS: m/z = 507.9 ([M+1]$^+$). Anal. calcd for ($C_{28}H_{23}Cl_2NO_2S$): C, 66.14; H, 4.56; N, 2.75; S,6.31; found: C, 66.01; H, 4.375; N, 2.696; S, 6.521. $[\alpha]_D^{25}$ = -140.36 (*c* = 0.5, $CHCl_3$).

2,4-di-*tert*-butyl-6-((*E*)-(((1*S*,2*R*)-1,2-diphenyl-2-((*R*)-*p*-tolylsulfinyl)ethyl)imino)methyl)phenol (1j)



Yellow solid, yield: 93%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 13.58 (s, 1H), 8.81 (s, 1H), 7.44 (d, *J* = 1.8 Hz, 1H), 7.24 – 7.21 (m, 2H), 7.17 – 7.08 (m, 9H), 7.01 (d, *J* = 8.1 Hz, 2H), 6.88 (d, *J* = 7.2 Hz, 2H), 5.61 (d, *J* = 2.4 Hz, 1H), 3.91 (d, *J* = 2.6 Hz, 1H), 2.26 (s, 3H), 1.50 (s, 9H), 1.31 (s, 9H). **^{13}C NMR** (100 MHz, DMSO) δ 169.10, 157.43, 141.27, 140.12, 139.59, 138.71, 135.69, 130.74, 130.39, 129.23, 128.34, 128.24, 127.86, 127.42, 127.20, 127.07, 125.98, 125.40, 117.71, 76.37, 70.03, 34.65, 33.87, 31.23, 29.25, 20.83. MS: m/z = 551.63 ([M+1]$^+$). Anal. calcd for ($C_{36}H_{41}NO_2S$): C, 78.36; H, 7.49; N, 2.54; S, 5.81; found: C, 78.55; H, 7.663; N, 2.362; S, 6.096. $[\alpha]_D^{25}$ = - 131.12 (*c* = 0.5, $CHCl_3$).

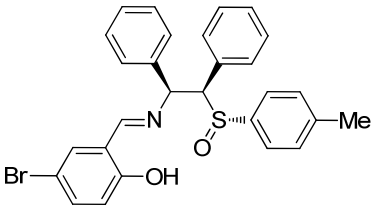
4-chloro-2-((*E*)-(((1*S*,2*R*)-2-((*R*)-naphthalen-2-ylsulfinyl)-1,2-diphenylethyl)imino)methyl)phenol (1k)



Yellow solid, yield: 90%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 13.28 (s, 1H), 8.74 (s, 1H), 7.82 – 7.66 (m, 4H), 7.53 – 7.48 (m, 2H), 7.40 (d, *J* = 2.3 Hz, 1H), 7.35 – 7.32 (m, 1H), 7.27 – 7.23 (m, 1H), 7.18 – 7.12 (m, 6H), 7.06 – 6.99 (m, 3H), 6.89 (d, *J* = 7.2 Hz, 2H), 5.68 (d, *J* = 2.9 Hz, 1H), 4.05 (d, *J* = 3.0 Hz, 1H). **^{13}C NMR** (100 MHz, DMSO) δ 166.04, 158.79, 139.37, 139.13, 133.91, 132.72, 131.86, 130.96, 130.63, 130.29, 128.34, 127.98, 127.50, 127.31, 127.07, 126.35, 122.61, 121.13, 120.06, 118.58, 75.93, 70.29. MS: m/z = 509.4 (M$^+$). Anal. calcd for

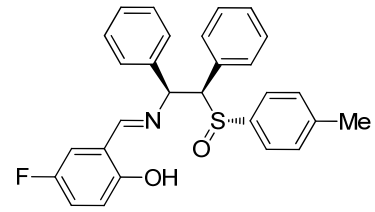
($C_{31}H_{24}ClNO_2S$): C, 73.00; H, 4.74; N, 2.75; S, 6.29; found: C, 72.87; H, 5.025; N, 2.661; S, 6.320. $[\alpha]_D^{25}$ = - 161.70 (*c* = 0.5, $CHCl_3$).

4-bromo-2-((*E*)-(((1*S*,2*R*)-1,2-diphenyl-2-((*R*)-*p*-tolylsulfinyl)ethyl)imino)methyl)phenol (1l)



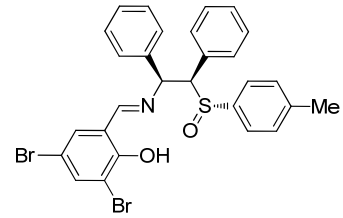
Yellow solid, yield: 89%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 13.29 (s, 1H), 8.70 (s, 1H), 7.51 (d, *J* = 2.4 Hz, 1H), 7.48 – 7.43 (m, 1H), 7.28 – 7.23 (m, 1H), 7.19 – 7.16 (m, 5H), 7.12 (*d*, J = 8.2 Hz, 2H), 7.05 – 7.01 (m, 4H), 6.94 (d, *J* = 8.8 Hz, 1H), 6.87 (d, *J* = 7.4 Hz, 2H), 5.62 (d, *J* = 3.0 Hz, 1H), 3.94 (d, *J* = 3.1 Hz, 1H), 2.27 (s, 3H). **^{13}C NMR** (100 MHz, DMSO) δ 166.06, 159.25, 141.29, 139.38, 138.72, 135.47, 133.66, 130.85, 130.30, 129.24, 128.34, 128.20, 127.96, 127.47, 127.24, 125.41, 120.60, 118.99, 109.93, 76.25, 70.29, 20.85. MS: m/z = 518.0 ($[M+1]^+$). Anal. calcd for ($C_{28}H_{24}BrNO_2S$): C, 64.86; H, 4.67; N, 2.70; S, 6.18; found: C, 64.81; H, 4.942; N, 2.611; S, 6.438. $[\alpha]_D^{25}$ = -147.24 (*c* = 0.5, $CHCl_3$).

2-((*E*)-(((1*S*,2*R*)-1,2-diphenyl-2-((*R*)-*p*-tolylsulfinyl)ethyl)imino)methyl)-4-fluorophenol (1m)



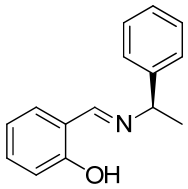
Yellow solid, yield: 90%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 13.03 (s, 1H), 8.72 (s, 1H), 7.27 – 7.23 (m, 1H), 7.20 – 7.16 (m, 5H), 7.13 – 7.08 (m, 4H), 7.05 – 6.97 (m, 5H), 6.88 (d, *J* = 7.2 Hz, 2H), 5.63 (d, *J* = 2.8 Hz, 1H), 3.94 (d, *J* = 3.0 Hz, 1H), 2.27 (s, 3H). **^{13}C NMR** (100 MHz, DMSO) δ 166.13, 156.33, 156.10, 153.76, 141.29, 139.48, 138.76, 130.87, 130.32, 129.23, 128.31, 128.18, 127.95, 127.43, 127.24, 125.43, 119.98, 118.97, 117.87, 116.88, 76.31, 70.32, 20.84. MS: m/z = 457.46 (M^+). Anal. calcd for ($C_{28}H_{24}FNO_2S$): C, 73.50; H, 5.29; N, 3.06; S, 7.01; found: C, 73.42; H, 5.555; N, 2.939; S, 7.206. $[\alpha]_D^{25}$ = - 157.08 (*c* = 0.5, $CHCl_3$).

2,4-dibromo-6-((*E*)-(((1*S*,2*R*)-1,2-diphenyl-2-((*R*)-*p*-tolylsulfinyl)ethyl)imino)methyl)phenol (1n)



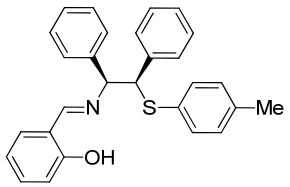
Yellow solid, yield: 89%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 14.16 (s, 1H), 8.69 (s, 1H), 7.76 (d, *J* = 2.2 Hz, 1H), 7.50 (d, *J* = 2.2 Hz, 1H), 7.28 – 7.24 (m, 1H), 7.21 – 7.16 (m, 5H), 7.11 (d, *J* = 8.2 Hz, 2H), 7.05 – 7.02 (m, 4H), 6.85 (d, J = 7.5 Hz, 2H), 5.65 (d, *J* = 3.0 Hz, 1H), 3.94 (d, *J* = 3.2 Hz, 1H), 2.28 (s, 3H). **^{13}C NMR** (100 MHz, DMSO) δ 166.82, 157.29, 141.34, 138.69, 138.47, 137.56, 133.99, 130.68, 130.12, 129.25, 128.46, 128.30, 128.07, 127.70, 127.31, 125.40, 120.14, 111.45, 109.37, 75.54, 69.62, 20.85. MS: m/z = 598.0 ($[M+1]^+$). Anal. calcd for ($C_{28}H_{23}Br_2NO_2S$): C, 56.30; H, 3.88; N, 2.34; S, 5.37; found: C, 56.53; H, 4.124; N, 2.300; S, 5.424. $[\alpha]_D^{25}$ = -126.48 (*c* = 0.5, $CHCl_3$).

(*R*,*E*)-2-(((1-phenylethyl)imino)methyl)phenol (5)[2]



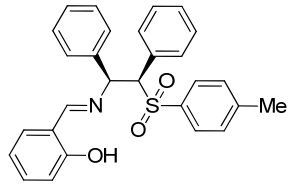
Pale yellow solid, yield: 82%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 13.55 (s, 1H), 8.41 (s, 1H), 7.38 – 7.23 (m, 7H), 6.96 (d, *J* = 8.3 Hz, 1H), 6.87 (t, *J* = 7.4 Hz, 1H), 4.55 (q, *J* = 6.6 Hz, 1H), 1.63 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.39, 161.01, 143.78, 132.24, 131.34, 128.63, 127.22, 126.35, 118.79, 118.58, 116.92, 68.50, 24.93. MS: m/z = 225.1 (M^+).

2-((*E*)-(((1*S*,2*R*)-1,2-diphenyl-2-(*p*-tolylthio)ethyl)imino)methyl)phenol (6)



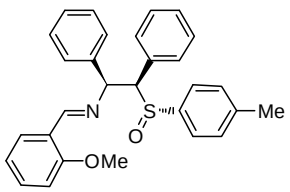
Yellow solid, yield: 93%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 13.09 (s, 1H), 8.19 (s, 1H), 7.31 – 7.23 (m, 4H), 7.19 – 7.11 (m, 10H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.95 (d, *J* = 8.3 Hz, 1H), 6.84 (t, *J* = 7.5 Hz, 1H), 4.73 (d, *J* = 5.8 Hz, 1H), 4.61 (d, *J* = 5.8 Hz, 1H), 2.27 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.56, 160.83, 140.24, 137.61, 137.25, 132.50, 132.32, 131.70, 130.84, 129.65, 129.28, 128.26, 127.87, 127.64, 127.49, 127.45, 118.62, 116.87, 60.72, 21.07. MS: m/z = 423.4 (M^+). Anal. calcd for ($C_{28}H_{25}NOS$): C, 79.40; H, 5.95; N, 3.31; S, 7.57; found: C, 79.61; H, 6.064; N, 3.179; S, 7.802. $[\alpha]_D^{25}$ = -84.58 (*c* = 0.5, $CHCl_3$).

2-((*E*)-(((1*S*,2*R*)-1,2-diphenyl-2-tosylethyl)imino)methyl)phenol (7)



Yellow solid, yield: 88%. **^{1}H NMR** (400 MHz, DMSO) δ 12.83 (s, 1H), 8.62 (s, 1H), 7.47 – 7.39 (m, 6H), 7.22 – 7.19 (m, 10H), 6.88 (t, *J* = 7.3 Hz, 2H), 5.56 (d, *J* = 5.5 Hz, 1H), 5.30 (d, *J* = 5.6 Hz, 1H), 2.29 (s, 3H). **^{13}C NMR** (100 MHz, DMSO) δ 178.09, 166.65, 159.63, 143.86, 139.60, 135.92, 132.76, 132.00, 131.01, 130.79, 129.18, 128.42, 128.18, 127.88, 127.58, 127.52, 118.91, 118.64, 116.25, 73.02, 70.99, 20.96. MS: m/z = 455.2 (M^+). Anal. calcd for ($C_{28}H_{25}NO_3S$): C, 73.82; H, 5.53; N, 3.07; S, 7.04; found: C, 73.83; H, 5.612; N, 2.980; S, 7.245. $[\alpha]_D^{25}$ = -182.38 (*c* = 0.5, $CHCl_3$).

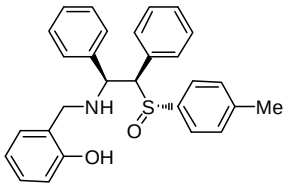
(1*S*,2*R*,*E*)-*N*-(2-methoxybenzylidene)-1,2-diphenyl-2-((*R*)-*p*-tolylsulfinyl)ethanamine (8)



White solid, yield: 81%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.11 (s, 1H), 8.28 (d, *J* = 7.7 Hz, 1H), 7.43 (t, *J* = 7.2 Hz, 1H), 7.20 – 7.04 (m, 13H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.94 (d, *J* = 8.3 Hz, 1H),

5.62 (d, *J* = 2.8 Hz, 1H), 3.92 (d, *J* = 3.0 Hz, 1H), 3.86 (s, 3H), 2.27 (s, 3H). **^{13}C NMR** (100 MHz, DMSO) δ 158.82, 158.75, 141.01, 140.92, 139.16, 132.96, 131.15, 131.03, 129.09, 127.98, 127.90, 127.67, 127.30, 126.92, 126.81, 125.30, 123.51, 120.76, 111.97, 77.99, 71.07, 55.66, 20.84. MS: m/z = 454.1 ($[M+1]^+$). Anal. calcd for ($C_{29}H_{27}NO_2S$): C, 76.79; H, 6.00; N, 3.09; S, 7.07; found: C, 76.88; H, 6.239; N, 2.934; S, 7.349. $[\alpha]_D^{25}$ = -155.74 (*c* = 0.5, $CHCl_3$).

2-((((1*S*,2*R*)-1,2-diphenyl-2-((*R*)-*p*-tolylsulfinyl)ethyl)amino)methyl)phenol (9)



The title compound was prepared by reduction of ligand **5a** with $NaBH_4$ in methanol and purified by column chromatography (petroleum ether/ethyl acetate, 3:1) to give a white solid in 95% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.27 (s, 1H), 7.29 – 7.24 (m, 4H), 7.21 – 7.12 (m, 5H), 7.06 (d, *J* = 8.1 Hz, 2H), 7.02 – 7.00 (m, 2H), 6.93 (d, *J* = 8.1 Hz, 1H), 6.84 – 6.80 (m, 3H), 6.74 (t, *J* = 7.4 Hz, 1H), 4.72 (s, 1H), 3.91 (d, *J* = 3.4 Hz, 1H), 3.81 (d, *J* = 4.2 Hz, 2H), 2.86 (s, 1H), 2.29 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.82, 141.41, 139.09, 137.49, 130.81, 130.14, 129.24, 128.89, 128.57, 128.47, 127.98, 127.93, 127.86, 124.71, 122.43, 119.06, 116.45, 77.88, 61.37, 50.36, 21.25. MS: m/z = 441.31 (M^+). Anal. calcd for ($C_{28}H_{27}NO_2S$): C, 76.16; H, 6.16; N, 3.17; S, 7.26; found: C, 76.28; H, 6.412; N, 3.121; S, 7.271. $[\alpha]_D^{25}$ = -113.38 (*c* = 0.5, $CHCl_3$).

3.5 References

[1] Petra, D. G. I.; Kamer. P. C. J.; Spek, A. L.; Schoemaker, H. E.; Van Leeuwen, P. W. N. M. *J. Org. Chem.* **2000**, *65*, 3010.

[2] Guo, J.; *Mao,* J. *Chirality* **2009**, *21*, 619.

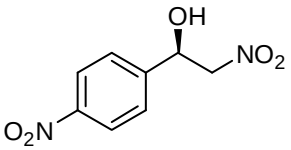
4. General Procedure for the Asymmetric Henry Reactions and Spectral Data

4.1 General Procedure for the Asymmetric Henry Reactions

Ligand **1f** (5.3 mg, 0.012 mmol, 3 mol%) and $Cu(OAc)_2 \cdot H_2O$ (2.0 mg, 0.01 mmol, 2.5 mol%) were dissolved in *t*-BuOH (4.0 mL) in a Schlenk tube. The mixture was stirred at 25 °C for 1 h, then aldehyde **2** (0.4 mmol) and nitromethane **3** (1 mL) were successively added. The resulting solution was stirred at the same temperature until the reaction completed (TLC). The crude reaction mixture was concentrated and directly purified by flash column chromatograpy, eluting with petroleum ether and ethyl acetate to afford the corresponding product **4**.

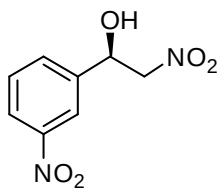
4.2 Spectral Data of Henry Products

(*R*)-2-nitro-1-(4-nitrophenyl)ethanol (4a)



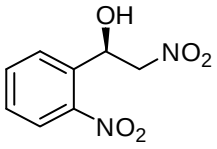
White solid, 30 h, 94% yield and 93% ee, determined by chiral HPLC analysis (Chiralcel OD-H, hexane/isopropanol, 85:15 v/v, 0.8 mL/min, 25 °C, UV 215 nm): Retension times: t_r = 26.419 min for (*R*)-isomer (major), t_r = 33.402 min for (*S*)-isomer. **^{1}H NMR** (400 MHz, DMSO) δ 8.23 (d, *J* = 8.6 Hz, 2H), 7.74 (d, *J* = 8.6 Hz, 2H), 6.43 (d, *J* = 4.9 Hz, 1H), 5.46 – 5.44 (m, 1H), 4.95 (dd, *J* = 12.7, 3.2 Hz, 1H), 4.64 (dd, *J* = 12.7, 9.5 Hz, 1H). **^{13}C NMR** (100 MHz, DMSO) δ 148.00, 147.13, 127.56, 123.43, 81.21, 69.09. $[\alpha]_D^{16}$ = - 35.12 (*c* = 1.00, CH_2Cl_2). [lit.: $[\alpha]_D^{25}$ = -33.1 (*c* = 0.56, CH_2Cl_2) (85% ee)]. Reference: Qin, B.; Xiao, X.; Liu, X.; Huang, J.; Wen, Y.; Feng, X. *J. Org. Chem.* **2007**, *72*, 9323.

(*R*)-2-nitro-1-(3-nitrophenyl)ethanol (4b)



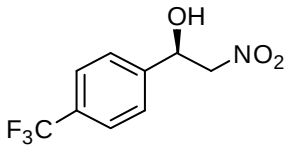
White solid, 48 h, 94% yield and 94% ee, determined by chiral HPLC analysis (Chiralcel OD-H, hexane/isopropanol, 90:10 v/v, 0.8 mL/min, 25 °C, UV 215 nm): Retension times: t_r = 41.363 min for (*R*)-isomer (major), t_r = 48.262 min for (*S*)-isomer. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 8.22 (d, *J* = 8.1 Hz, 1H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.62 (t, *J* = 7.9 Hz, 1H), 5.63 – 5.61 (m, 1H), 4.67 – 4.58 (m, 2H), 3.39 (d, *J* = 4.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.50, 140.25, 131.99, 130.08, 123.75, 121.10, 80.66, 69.80. $[\alpha]_D^{16}$ = -27.47 (*c* = 1.00, CH_2Cl_2). [lit.: $[\alpha]_D^{25}$ = -26.7 (*c* = 0.43, CH_2Cl_2) (85% ee)]. Reference: Qin, B.; Xiao, X.; Liu, X.; Huang, J.; Wen, Y.; Feng, X. *J. Org. Chem.* **2007**, *72*, 9323.

(*R*)-2-nitro-1-(2-nitrophenyl)ethanol (4c)



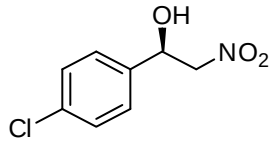
Brown solid, 42 h, 95% yield and 96% ee, determined by chiral HPLC analysis (Chiralcel OD-H, hexane/isopropanol, 95:05 v/v, 0.8 mL/min, 25 °C, UV 215 nm): Retension times: t_r = 45.211 min for (*R*)-isomer (major), t_r = 51.895 min for (*S*)-isomer. **^{1}H NMR** (400 MHz, DMSO) δ 8.05 (d, *J* = 8.2 Hz, 1H), 7.93 (d, *J* = 7.8 Hz, 1H), 7.81 (t, *J* = 7.6 Hz, 1H), 7.61 (t, *J* = 7.7 Hz, 1H), 6.44 (s, 1H), 5.83 (d, *J* = 9.2 Hz, 1H), 4.98 (dd, *J* = 12.8, 2.2 Hz, 1H), 4.61 (dd, *J* = 12.7, 9.6 Hz, 1H). **^{13}C NMR** (100 MHz, DMSO) δ 147.26, 135.64, 134.08, 129.49, 129.20, 124.51, 81.01, 66.29. $[\alpha]_D^{16}$ = 231.82 (*c* = 1.00, CH_2Cl_2). [lit.: $[\alpha]_D^{21}$ = 227.1 (*c* = 1.00, CH_2Cl_2) (89% ee)]. Reference: Evans, D. A.; Seidel, D.; Rueping, M.; Lam, H. W.; Shaw, J. T.; Downey, C. W. *J. Am. Chem. Soc.* **2003**, *125*, 12692.

(*R*)-2-nitro-1-(4-(trifluoromethyl)phenyl)ethanol (4d)



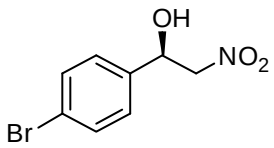
Yellow oil, 48 h, 96% yield and 94% ee, determined by chiral HPLC analysis (Chiralcel OD-H, hexane/isopropanol, 90:10 v/v, 0.8 mL/min, 25 °C, UV 220 nm): Retension times: t_r = 16.856 min for (*R*)-isomer (major), t_r = 21.680 min for (*S*)-isomer. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.1 Hz, 2H), 7.52 (d, *J* = 8.1 Hz, 2H), 5.51 (d, *J* = 8.8 Hz, 1H), 4.81 – 4.50 (m, 2H), 3.53 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.97, 131.14, 130.81, 126.32, 125.89, 122.42, 80.84, 70.27. $[\alpha]_D^{17}$ = - 31.84 (*c* = 1.00, CH_2Cl_2). [lit.: $[\alpha]_D^{23}$ = -49.2 (*c* = 1.25, $CHCl_3$) (86% ee)]. Reference: Bulut, A.; Aslan, A.; Dogan, Ö. *J. Org. Chem.* **2008**, *73*, 7373.

(*R*)-1-(4-chlorophenyl)-2-nitroethanol (4e)



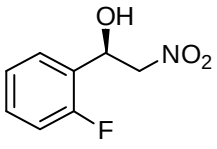
Colorless oil, 96 h, 91% yield and 92% ee, determined by chiral HPLC analysis (Chiralcel OD-H, hexane/isopropanol, 90:10 v/v, 0.8 mL/min, 25 °C, UV 220 nm): Retension times: t_r = 21.448 min for (*R*)-isomer (major), t_r = 27.463 min for (*S*)-isomer. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 4H), 5.40 (d, *J* = 9.2 Hz, 1H), 4.58 – 4.45 (m, 2H), 3.36 (d, *J* = 3.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 136.55, 134.64, 129.08, 127.28, 80.92, 70.20. $[\alpha]_D^{15}$ = -38.01 (*c* = 1.00, CH_2Cl_2). [lit.: $[\alpha]_D^{23}$ = -37.6 (*c* = 2.03, CH_2Cl_2) (90% ee)]. Reference: Evans, D. A.; Seidel, D.; Rueping, M.; Lam, H. W.; Shaw, J. T.; Downey, C. W. *J. Am. Chem. Soc.* **2003**, *125*, 12692.

(*R*)-1-(4-bromophenyl)-2-nitroethanol (4f)



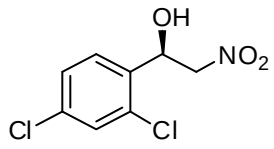
Colorless solid, 96 h, 94% yield and 92% ee, determined by chiral HPLC analysis (Chiralcel OD-H, hexane/isopropanol, 90:10 v/v, 0.8 mL/min, 25 °C, UV 220 nm): Retension times: t_r = 25.761 min for (*R*)-isomer (major), t_r = 33.990 min for (*S*)-isomer. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.8 Hz, 2H), 5.39 (d, *J* = 8.8 Hz, 1H), 4.58 – 4.45 (m, 2H), 3.28 (d, *J* = 2.8 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.05, 132.06, 127.58, 122.82, 80.86, 70.25. $[\alpha]_D^{16}$ = -36.51 (*c* = 1.00, CH_2Cl_2). [lit.: $[\alpha]_D^{25}$ = -34.6 (*c* = 1.00, CH_2Cl_2) (92% ee)]. Reference: Panov, I.; Drabina, P.; Padělková, Z. k.; Šimůnek, P.; Sedlák, M. *J. Org. Chem.* **2011**, *76*, 4787.

(*R*)-1-(2-fluorophenyl)-2-nitroethanol (4g)



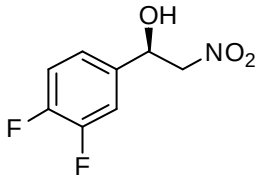
Colorless oil, 96 h, 93% yield and 93% ee, determined by chiral HPLC analysis (Chiralcel AD-H, hexane/isopropanol, 90:10 v/v, 0.8 mL/min, 25 °C, UV 215 nm): Retension times: t_r = 15.054 min for (*R*)-isomer (major), t_r = 13.866 min for (*S*)-isomer. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (t, *J* = 7.6 Hz, 1H), 7.37 – 7.33 (m, 1H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.11 – 7.07 (m, 1H), 5.75 (d, *J* = 4.2 Hz, 1H), 4.65 – 4.56 (m, 2H), 2.98 (d, *J* = 4.8 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 130.42, 130.34, 127.53, 124.79, 115.62, 115.42, 79.63, 65.31. $[\alpha]_D^{16}$ = -49.58 (*c* = 1.00, CH_2Cl_2). [lit.: $[\alpha]_D^{23}$ = 24.6 (*c* = 1.2, CH_2Cl_2) (46% ee) (*S*) isomer]. Reference: Kowalczyk, R.; Sidorowicz, Ł.; Skarżewski, J. *Tetrahedron: Asymmetry* **2007**, *18*, 2581.

(*R*)-1-(2,4-dichlorophenyl)-2-nitroethanol (4h)



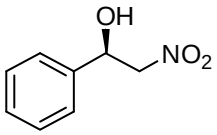
White solid, 36 h, 98% yield and 95% ee, determined by chiral HPLC analysis (Chiralpak AD-H, hexane/isopropanol, 85:15 v/v, 0.8 mL/min, 25 °C, UV 215 nm): Retension times: t_r = 9.510 min for (*R*)-isomer (major), t_r = 11.137 min for (*S*)-isomer. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.4 Hz, 1H), 7.39 (d, *J* = 1.8 Hz, 1H), 7.33 (dd, *J* = 8.4, 1.7 Hz, 1H), 5.78 (dd, *J* = 6.3, 3.2 Hz, 1H), 4.64 (dd, *J* = 13.6, 2.1 Hz, 1H), 4.42 (dd, *J* = 13.6, 9.5 Hz, 1H), 3.36 (d, *J* = 4.3 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 135.12, 134.11, 132.00, 129.40, 128.50, 127.89, 79.03, 67.37. $[\alpha]_D^{15}$ = -50.91 (*c* = 1.00, CH_2Cl_2). [lit.: $[\alpha]_D^{23}$ = -47.6 (*c* = 0.95, CH_2C_2) (86% ee)]. Reference: Kogami, Y.; Nakajima, T.; Ikeno, T.; Yamada, T. *Synthesis* **2004**, 1947.

(*R*)-1-(3,4-difluorophenyl)-2-nitroethanol (4i)



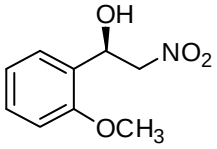
Colorless oil, 72 h, 90% yield and 94% ee, determined by chiral HPLC analysis (Chiralcel OD-H, hexane/isopropanol, 90:10 v/v, 0.8 mL/min, 25 °C, UV 220 nm): Retension times: t_r = 17.619 min for (*R*)-isomer (major), t_r = 21.361 min for (*S*)-isomer. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.13 (m, 3H), 5.43 (d, *J* = 8.7 Hz, 1H), 4.58 – 4.47 (m, 2H), 3.37 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.34, 149.20, 135.14, 122.03, 117.93, 117.75, 115.28, 115.10, 80.88, 69.74. MS: m/z = 203.08 (M^+). Anal. calcd for ($C_8H_7F_2NO_3$): C, 47.30; H, 3.47; N, 6.89; found: C, 47.57; H, 3.676; N, 6.637. $[\alpha]_D^{16}$ = -38.49 (*c* = 0.5, CH_2Cl_2).

(*R*)-2-nitro-1-phenylethanol (4j)



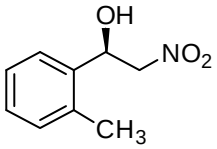
Colorless oil, 120 h, 85% yield and 93% ee, determined by chiral HPLC analysis (Chiralcel OD-H, hexane/isopropanol, 90:10 v/v, 0.8 mL/min, 25 °C, UV 220 nm): Retension times: t_r = 21.602 min for (*R*)-isomer (major), t_r = 27.350 min for (*S*)-isomer. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.34 (m, 5H), 5.41 – 5.37 (m, 1H), 4.59 – 4.44 (m, 2H), 3.17 (d, *J* = 3.8 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.10, 128.90, 128.84, 125.87, 81.11, 70.88. $[\alpha]_D^{16}$ = -40.16 (*c* = 1.00, CH_2Cl_2). [lit.: $[\alpha]_D^{21}$ = -41.6 (*c* = 1.03, CH_2Cl_2) (94% ee)]. Reference: Evans, D. A.; Seidel, D.; Rueping, M.; Lam, H. W.; Shaw, J. T.; Downey, C. W. ***J. Am. Chem. Soc.*** **2003**, *125*, 12692.

(*R*)-1-(2-methoxyphenyl)-2-nitroethanol (4k)



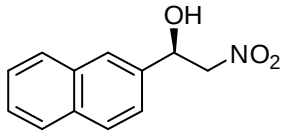
Yellow oil, 132 h, 92% yield and 94% ee, determined by chiral HPLC analysis (Chiralcel OD-H, hexane/isopropanol, 90:10 v/v, 0.8 mL/min, 25 °C, UV 220 nm): Retension times: t_r = 17.698 min for (*R*)-isomer (major), t_r = 21.585 min for (*S*)-isomer. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 7.8 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.91 (d, *J* = 8.2 Hz, 1H), 5.63 – 5.61 (m, 1H), 4.67 – 4.54 (m, 2H), 3.88 (s, 3H), 3.16 (d, *J* = 6.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.91, 129.69, 127.08, 125.93, 121.03, 110.45, 79.78, 67.69, 55.32. $[\alpha]_D^{15}$ = -39.94 (*c* = 1.00, CH_2Cl_2). [lit.: $[\alpha]_D^{21}$ = -44.5 (*c* = 1.00, CH_2Cl_2) (93% ee)]. Reference: Evans, D. A.; Seidel, D.; Rueping, M.; Lam, H. W.; Shaw, J. T.; Downey, C. W. ***J. Am. Chem. Soc.*** **2003**, *125*, 12692.

(*R*)-2-nitro-1-(*o*-tolyl)ethanol (4l)



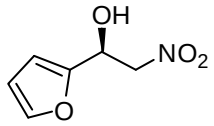
Colorless oil, 132 h, 84% yield and 91% ee, determined by chiral HPLC analysis (Chiralcel OD-H, hexane/isopropanol, 85:15 v/v, 0.8 mL/min, 25 °C, UV 210 nm): Retension times: t_r = 12.673 min for (*R*)-isomer (major), t_r = 19.695 min for (*S*)-isomer. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 – 7.52 (m, 1H), 7.30 – 7.24 (m, 2H), 7.21 – 7.18 (m, 1H), 5.71 – 5.67 (m, 1H), 4.56 (dd, *J* = 13.4, 9.7 Hz, 1H), 4.45 (dd, *J* = 13.4, 2.5 Hz, 1H), 2.74 (d, *J* = 3.6 Hz, 1H), 2.40 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 136.15, 134.40, 130.77, 128.61, 126.70, 125.53, 80.14, 67.83, 18.81. $[\alpha]_D^{15}$ = -45.88 (*c* = 1.00, CH_2Cl_2). [lit.: $[\alpha]_D^{25}$ = -33.4 (*c* = 0.5, CH_2Cl_2) (88% ee)]. Reference: Qin, B.; Xiao, X.; Liu, X.; Huang, J.; Wen, Y.; Feng, X. ***J. Org. Chem.*** **2007**, *72*, 9323.

(*R*)-1-(naphthalen-2-yl)-2-nitroethanol (4m)



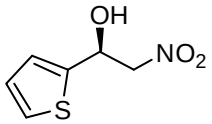
Yellow solid, 108 h, 75% yield and 93% ee, determined by chiral HPLC analysis (Chiralcel OD-H, hexane/isopropanol, 85:15 v/v, 0.8 mL/min, 25 °C, UV 220 nm): Retension times: t_r = 43.653 min for (*R*)-isomer (major), t_r = 60.632 min for (*S*)-isomer. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 – 7.79 (m, 4H), 7.50 – 7.48 (m, 2H), 7.39 (d, *J* = 8.4 Hz, 1H), 5.53 (d, *J* = 9.5 Hz, 1H), 4.64 – 4.49 (m, 2H), 3.20 (d, *J* = 2.7 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 135.38, 133.29, 133.07, 128.87, 127.99, 127.70, 126.60, 125.23, 123.15, 81.07, 71.03. $[\alpha]_D^{16}$ = -35.69 (*c* = 1.00, CH_2Cl_2). [lit.: $[\alpha]_D^{25}$ = -45.0 (*c* = 0.38, CH_2Cl_2) (95% ee)]. Reference: Qin, B.; Xiao, X.; Liu, X.; Huang, J.; Wen, Y.; Feng, X. ***J. Org. Chem.*** **2007**, *72*, 9323.

(*S*)-1-(furan-2-yl)-2-nitroethanol (4n)



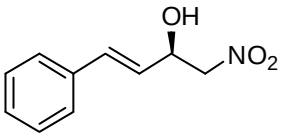
Colorless oil, 96 h, 91% yield and 95% ee, determined by chiral HPLC analysis (Chiralpak AD-H, hexane/isopropanol, 95:5 v/v, 0.5 mL/min, 26 °C, UV 210 nm): Retension times: t_r = 52.803 min for (*S*)-isomer (major), t_r = 55.511 min for (*R*)-isomer. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 (s, 1H), 6.41 – 6.39 (m, 2H), 5.49 – 5.47 (m, 1H), 4.79 (dd, *J* = 13.5, 9.1 Hz, 1H), 4.67 (dd, *J* = 13.5, 3.4 Hz, 1H), 2.96 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.63, 143.03, 110.54, 108.07, 78.27, 64.63. $[\alpha]_D^{16}$ = -33.20 (*c* = 1.00, CH_2Cl_2). [lit.: $[\alpha]_D^{25}$ = -37.1 (*c* = 0.24, CH_2Cl_2) (98% ee)]. Reference: Qin, B.; Xiao, X.; Liu, X.; Huang, J.; Wen, Y.; Feng, X. ***J. Org. Chem.*** **2007**, *72*, 9323.

(*S*)-2-nitro-1-(thiophen-2-yl)ethanol (4o)



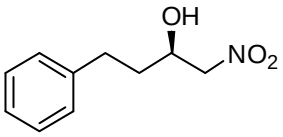
Brown oil, 96 h, 61% yield and 92% ee, determined by chiral HPLC analysis (Chiralcel OD-H, hexane/isopropanol, 90:10 v/v, 0.8 mL/min, 25 °C, UV 220 nm): Retension times: t_r = 23.948 min for (*S*)-isomer (major), t_r = 26.444 min for (*R*)-isomer. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.08 – 7.07 (m, 1H), 7.02 (dd, *J* = 5.0, 3.6 Hz, 1H), 5.75 – 5.71 (m, 1H), 4.72 (dd, *J* = 13.4, 9.3 Hz, 1H), 4.61 (dd, *J* = 13.4, 3.3 Hz, 1H), 3.07 (d, *J* = 3.8 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.15, 127.14, 126.04, 125.01, 80.64, 66.91. $[\alpha]_D^{17}$ = -39.55 (*c* = 0.5, CH_2Cl_2). [lit.: $[\alpha]_D^{25}$ = -27.5 (*c* = 0.28, CH_2Cl_2) (95% ee)]. Reference: Qin, B.; Xiao, X.; Liu, X.; Huang, J.; Wen, Y.; Feng, X. *J. Org. Chem.* **2007**, *72*, 9323.

(*R*,*E*)-1-nitro-4-phenylbut-3-en-2-ol (4p)



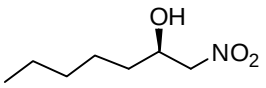
Yellow solid, 108 h, 72% yield and 91% ee, determined by chiral HPLC analysis (Chiralcel OD-H, hexane/isopropanol, 80:20 v/v, 0.8 mL/min, 20 °C, UV 220 nm): Retension times: t_r = 28.155 min for (*R*)-isomer (major), t_r = 24.980 min for (*S*)-isomer. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.26 (m, 5H), 6.79 (d, *J* = 15.9 Hz, 1H), 6.14 (dd, *J* = 15.9, 6.3 Hz, 1H), 5.09 – 5.03 (m, 1H), 4.52 (d, *J* = 5.8 Hz, 2H), 2.72 (t, *J* = 4.1 Hz, 1H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 135.42, 133.49, 128.66, 128.43, 126.65, 124.89, 79.81, 69.53. $[\alpha]_D^{22}$ = -8.86 (*c* = 1.00, CH_2Cl_2). [lit.: $[\alpha]_D^{25}$ = -32.4 (*c* = 0.1, CH_2Cl_2) (92% ee)]. Reference: Xiong, Y.; Wang, F.; Huang, X.; Wen, Y.; Feng, X. *Chem. Eur. J.* **2007**, *13*, 829.

(*R*)-1-nitro-4-phenylbutan-2-ol (4q)



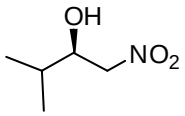
White solid, 96 h, 90% yield and 92% ee, determined by chiral HPLC analysis (Chiralpak AD-H, hexane/isopropanol, 90:10 v/v, 0.8 mL/min, 25 °C, UV 210 nm): Retension times: t_r = 28.317 min for (*R*)-isomer (major), t_r = 35.971 min for (*S*)-isomer. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.0 Hz, 2H), 7.26 – 7.20 (m, 3H), 4.41 – 4.39 (m, 2H), 4.34 – 4.28 (m, 1H), 2.90 – 2.83 (m, 1H), 2.79 – 2.71 (m, 2H), 1.92 – 1.75 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.58, 128.54, 128.32, 126.20, 80.50, 67.77, 35.04, 31.22. $[\alpha]_D^{16}$ = 12.03 (*c* = 1.00, CH_2Cl_2). [lit.: $[\alpha]_D^{25}$ = 13.1 (*c* = 0.51, CH_2Cl_2) (74% ee)]. Reference: Blay. G., Climent. E., Fernández. I., Hernández-Olmos. V., Pedro. J. R. *Tetrahedron: Asymmetry* **2007**, *18*, 1603.

(*R*)-1-nitroheptan-2-ol (4r)



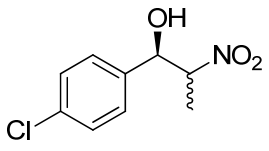
Colorless oil, 96 h, 90% yield and 92% ee, determined by chiral HPLC analysis (Chiralpak AD-H, hexane/isopropanol, 95:5 v/v, 0.8 mL/min, 26 °C, UV 210 nm): Retension times: t_r = 28.794 min for (*R*)-isomer (major), t_r = 40.104 min for (*S*)-isomer.**^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.48 – 4.38 (m, 2H), 4.35 – 4.32 (m, 1H), 2.59 (d, *J* = 4.6 Hz, 1H), 1.57 – 1.32 (m, 8H), 0.90 (t, *J* = 6.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 80.64, 68.66, 33.63, 31.36, 24.75, 22.36, 13.83. $[\alpha]_D^{16}$ = -7.06 (*c* = 1.00, CH_2Cl_2). [lit.: $[\alpha]_D^{25}$ = -2.3 (*c* = 0.13, CH_2Cl_2) (90% ee)]. Reference: Xiong, Y.; Wang, F.; Huang, X.; Wen, Y.; Feng, X. *Chem. Eur. J.* **2007**, *13*, 829.

(*R*)-3-methyl-1-nitrobutan-2-ol (4s)



Colorless oil, 96 h, 66% yield and 92% ee, determined by chiral HPLC analysis (Chiralcel OD-H, hexane/isopropanol, 98:2 v/v, 0.5 mL/min, 25 °C, UV 210 nm): Retension times: t_r = 39.99 min for (*R*)-isomer (major), t_r = 45.238 min for (*S*)-isomer. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.50 – 4.38 (m, 2H), 4.14 – 4.08 (m, 1H), 2.57 (d, *J* = 4.2 Hz, 1H), 1.85 – 1.78 (m, 1H), 1.00 (t, *J* = 6.2 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 79.29, 73.35, 31.68, 18.29, 17.35. $[\alpha]_D^{16}$ = -24.23 (*c* = 1.00, CH_2Cl_2). [lit.: $[\alpha]_D^{23}$ = -29.2 (*c* = 1.84, $CHCl_3$) (94% ee)]. Reference: Evans, D. A.; Seidel, D.; Rueping, M.; Lam, H. W.; Shaw, J. T.; Downey, C. W. *J. Am. Chem. Soc.* **2003**, *125*, 12692.

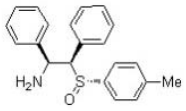
(1*R*)-1-(4-chlorophenyl)-2-nitropropan-1-ol (4t)



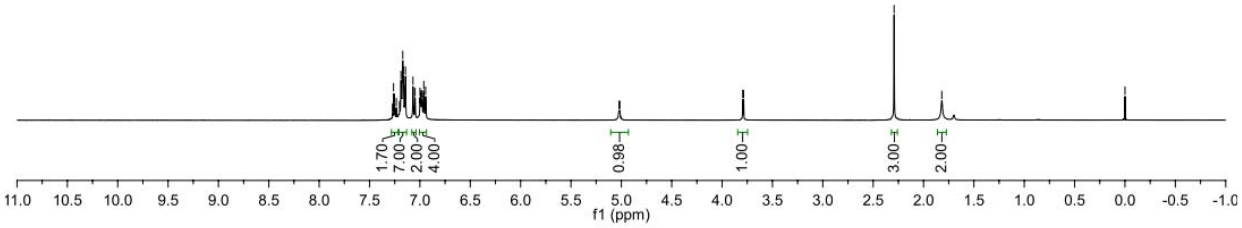
Colorless oil, 96 h, 87% yield, 3:2 *anti*/*syn* and 68/81% ee (*anti*/*syn*), determined by chiral HPLC analysis (Chiralcel AD-H, hexane/isopropanol, 95:5 v/v, 1 mL/min, 25 °C, UV 210 nm): Retension times: t_r = 18.243 min for (1*R*,2*R*)-isomer ($anti_{major}$), t_r = 16.660 min for (1*S*,2*S*)-isomer ($anti_{minor}$), t_r = 24.161 min for (1*R*,2*S*)-isomer (syn_{major}), t_r = 26.950 min for (1*S*,2*R*)-isomer (syn_{minor}). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.35 (m, 2H, *anti*+*syn*), 7.32 – 7.29 (m, 2H, *anti*+*syn*), 5.38 – 5.36 (m, 0.66H, *anti*), 5.02 – 4.98 (m, 0.34H, *syn*), 4.75 – 4.69 (m, 0.34H, *syn*), 4.68 – 4.62 (m, 0.66H, *anti*), 3.01 (d, *J* = 3.7 Hz, 0.66H, *anti*), 2.97 (d, *J* = 4.1 Hz, 0.34H, *syn*), 1.47 (d, *J* = 6.8 Hz, 1.98H, *anti*), 1.31 (d, *J* = 6.8 Hz, 1.02H, *syn*). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 136.81 (*anti*), 136.64 (*syn*), 134.94 (*syn*), 134.23 (*anti*), 129.12 (*syn*), 128.84 (*anti*), 128.22 (*syn*), 127.29 (*anti*), 88.12 (*syn*), 87.12 (*anti*), 75.42 (*syn*), 73.14 (*anti*), 16.29 (*syn*), 11.88 (*anti*). $[\alpha]_D^{16}$ = -12.09 (*c* = 1.00, CH_2Cl_2, mixture of diastereomers). [lit.: $[\alpha]_D^{25}$ = -15.8 (*c* = 1.00, $CHCl_3$, for the 1*R* enantiomer, 71% ee, mixture of diastereomers]. Reference: Borah, J. C.; Boruwa, J.; Kalita, B.; Hazarika, A. K.; Barua, N. C. *Indian J. Chem.* **2005**, *44B*, 1961-1965.

5. Copies of ^{1}H NMR and ^{13}C NMR Spectra

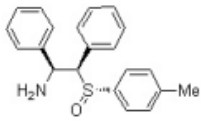
CHG1215 CDCl3



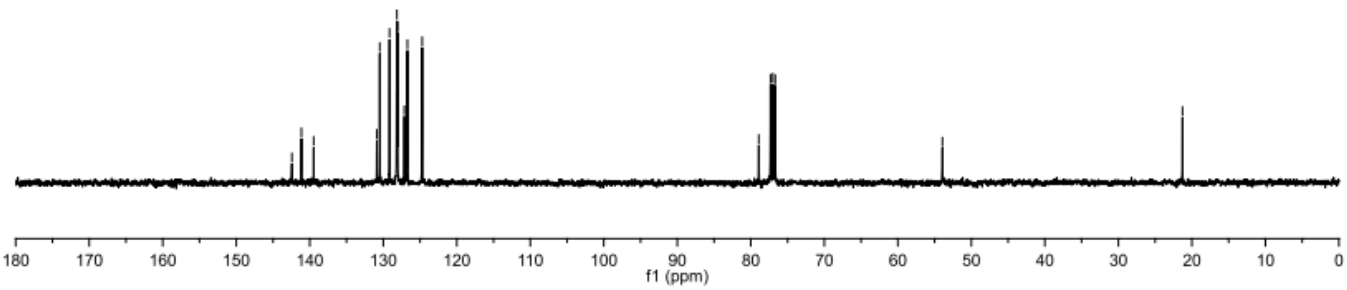
13a



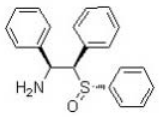
CHG1215



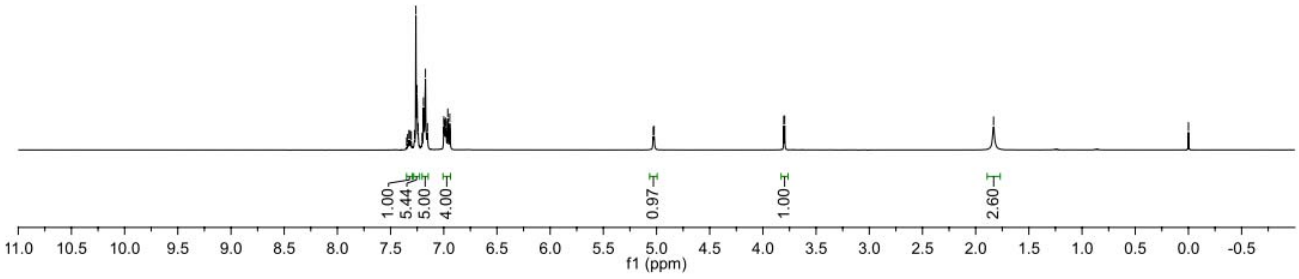
13a



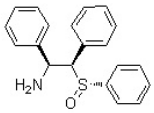
CHG1151 CDCl3



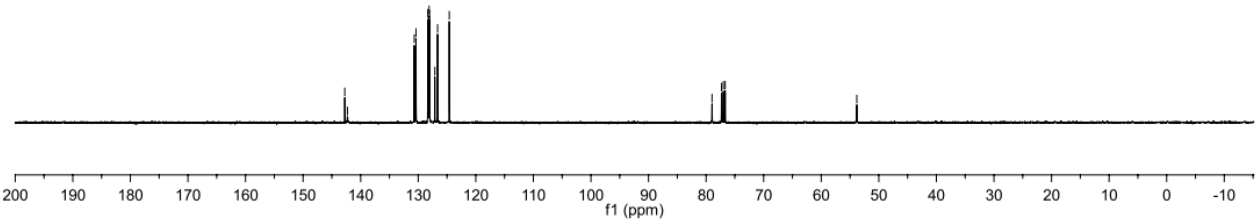
13b



CHG1151 CDCl3



13b



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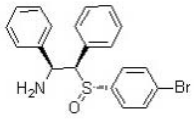

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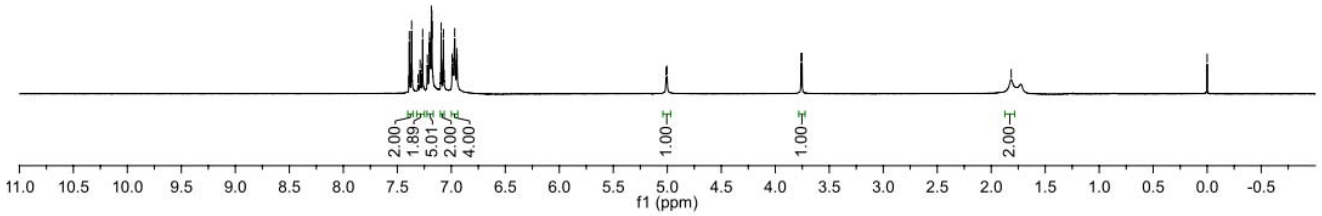

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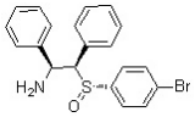

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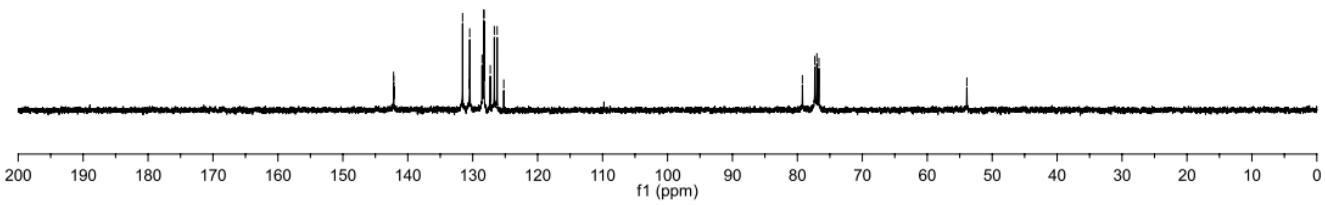

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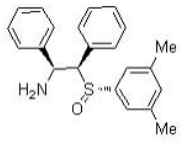

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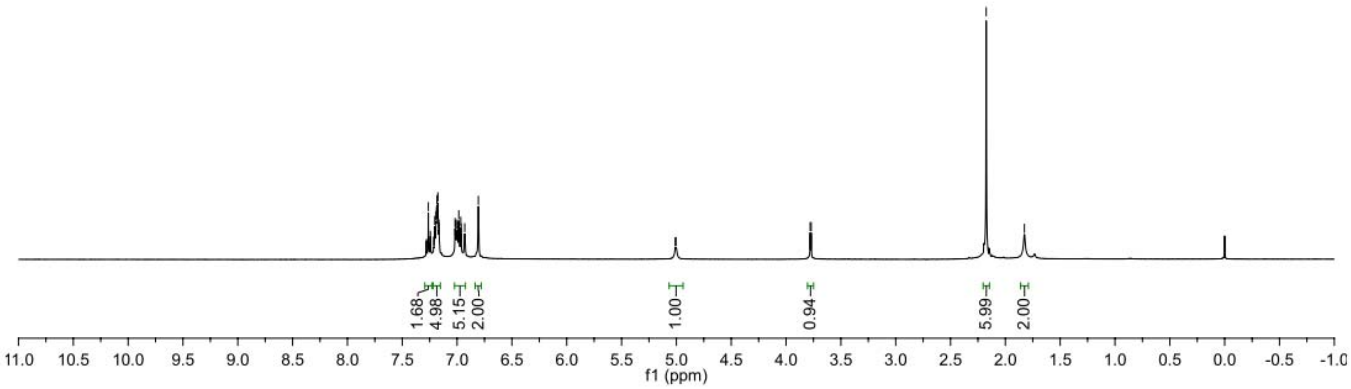

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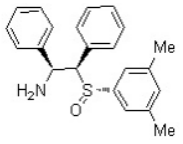

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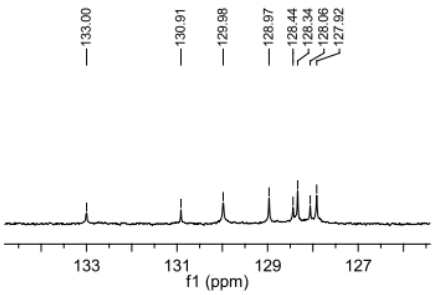

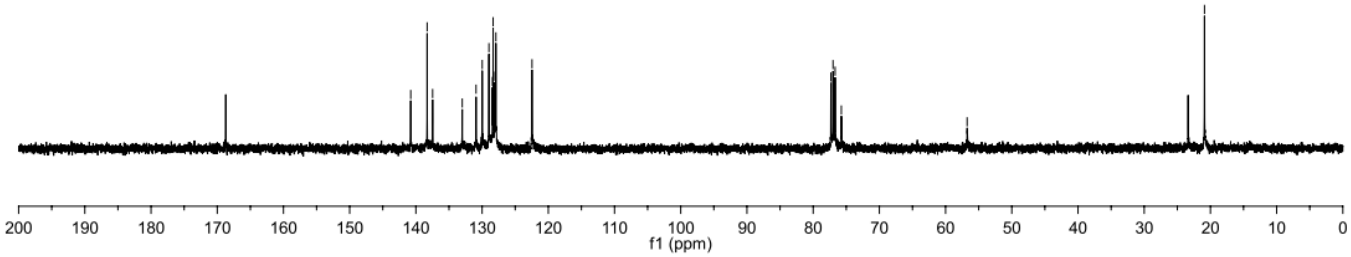

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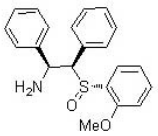

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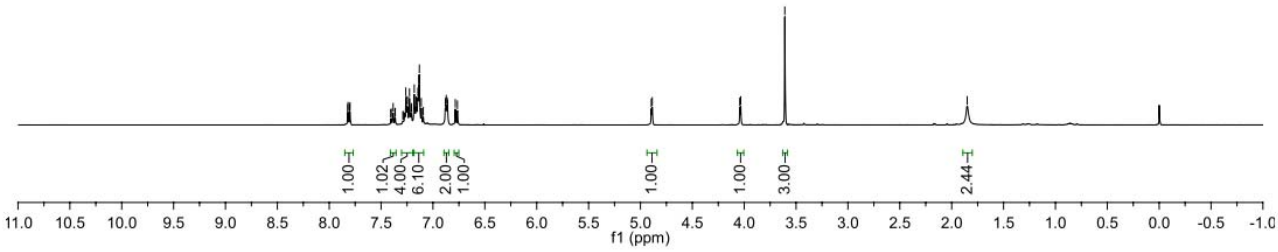

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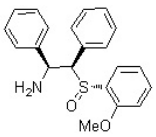

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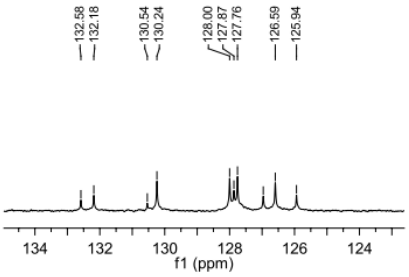
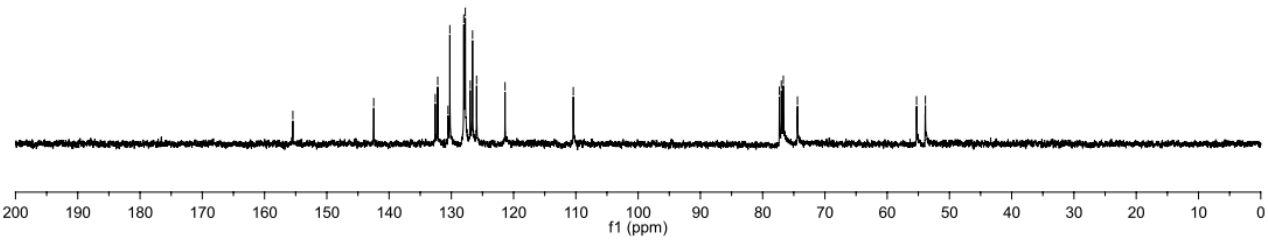
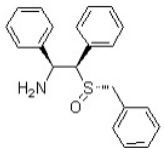




CHG1396 CDC13



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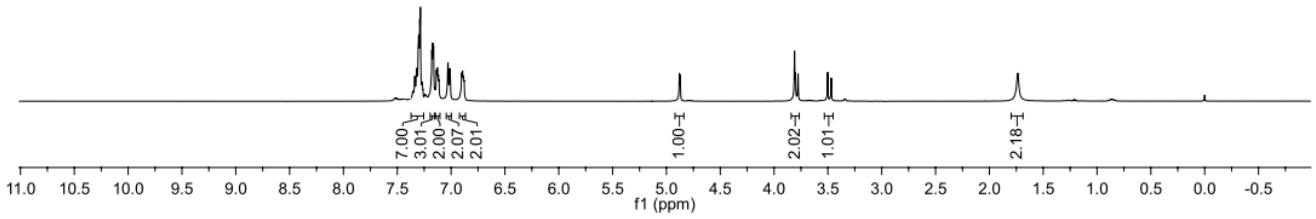
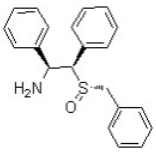


CHG1396 CDCl3



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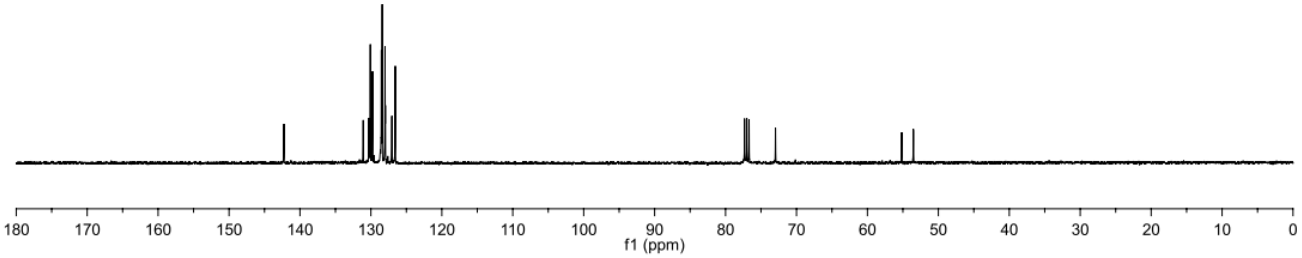
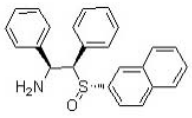
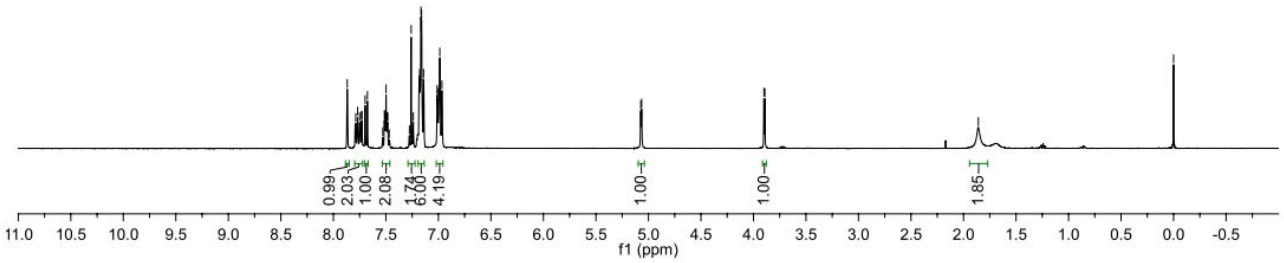


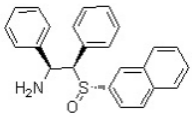
CHG1225 CDCl3



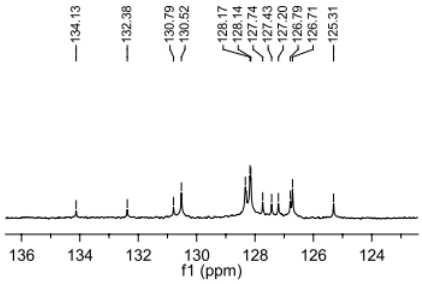
13g

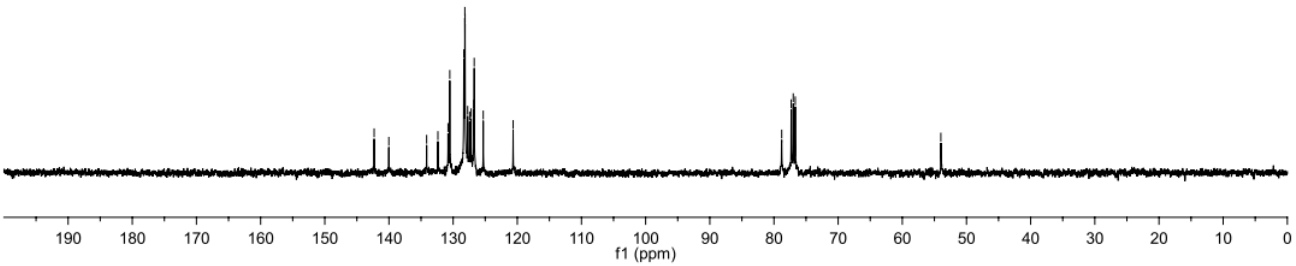


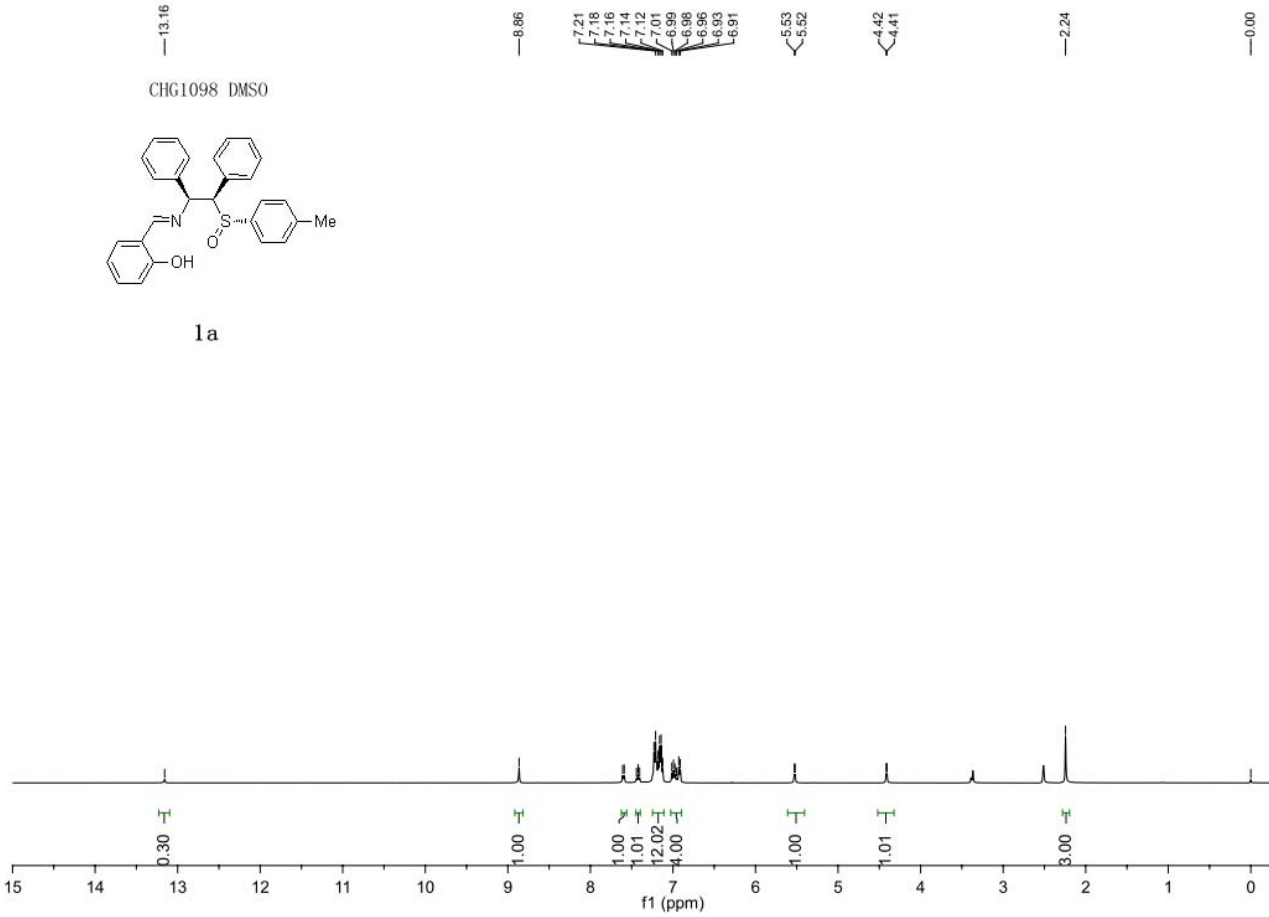
CHG1225 CDCl3



13g



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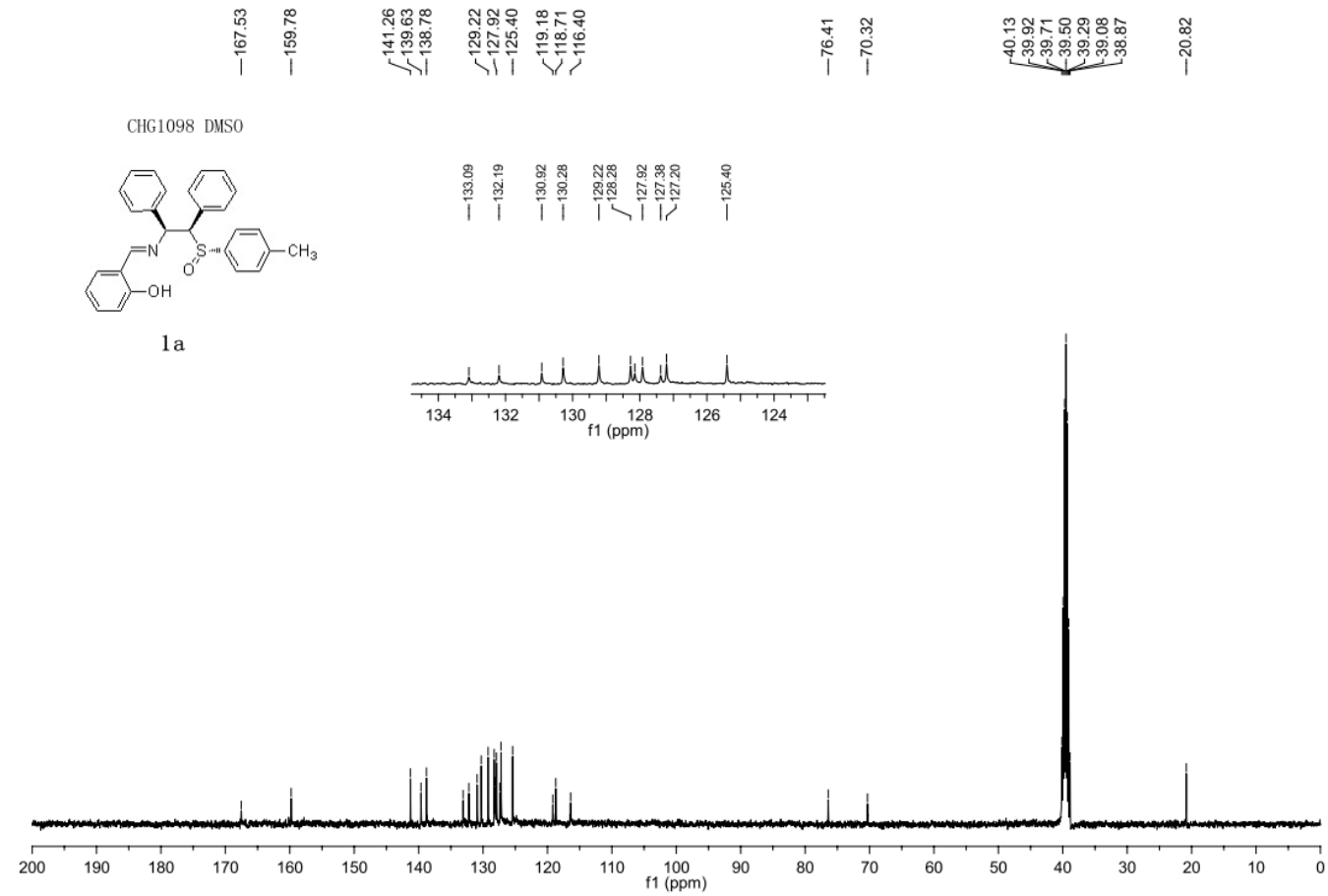
7.18
7.16
7.14
7.12
7.01
6.99
6.98
6.96
6.93
6.91
5.53
5.52
4.42
4.41
2.24
0.00
CHG1098 DMSO
N
S
O
Me
OH
0.30
1.00
1.00
1.01
12.02
4.00
1.00
1.01
3.00
f1 (ppm)

1a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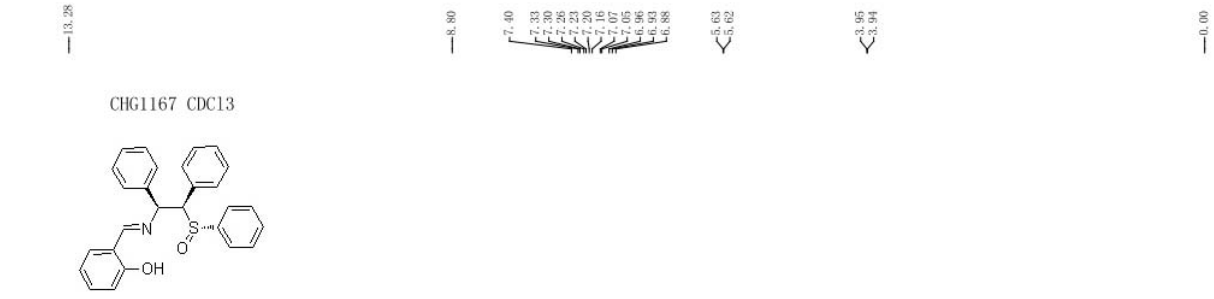
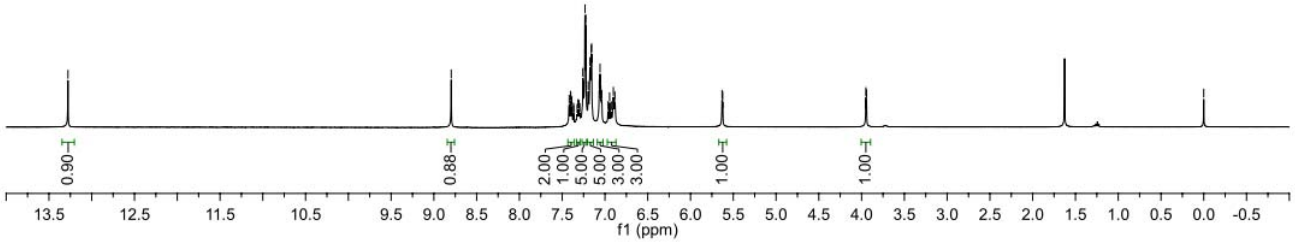
127.92
125.40
119.18
118.71
116.40
76.41
70.32
40.13
39.92
39.71
39.50
39.29
39.08
38.87
20.82
CHG1098 DMSO
N
S
O
CH3
OH
133.09
132.19
130.92
130.28
129.22
128.28
127.92
127.38
127.20
125.40
f1 (ppm)
f1 (ppm)

1a

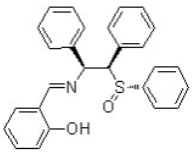


CHG1167 CDCl3

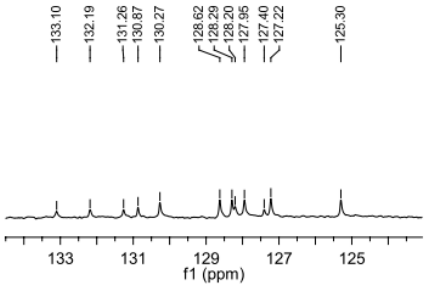
1b

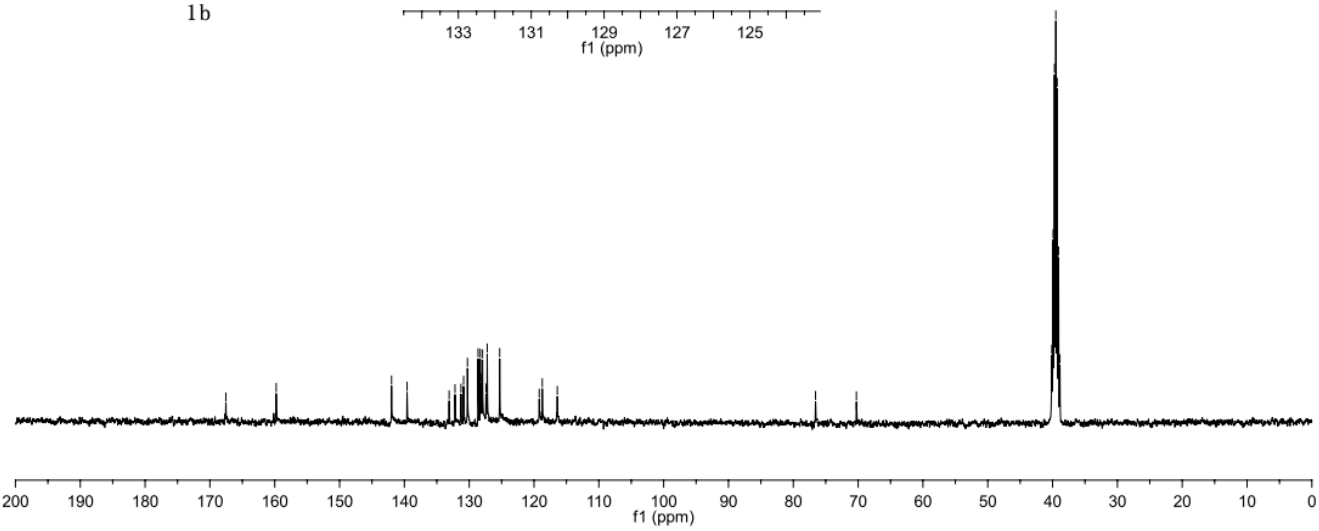


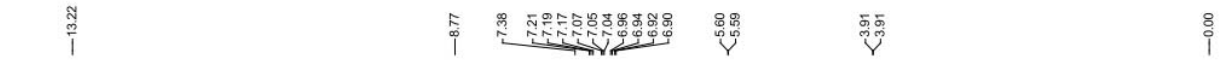
CHG1167 DMSO



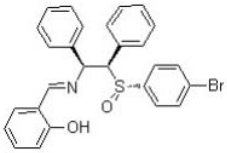
1b



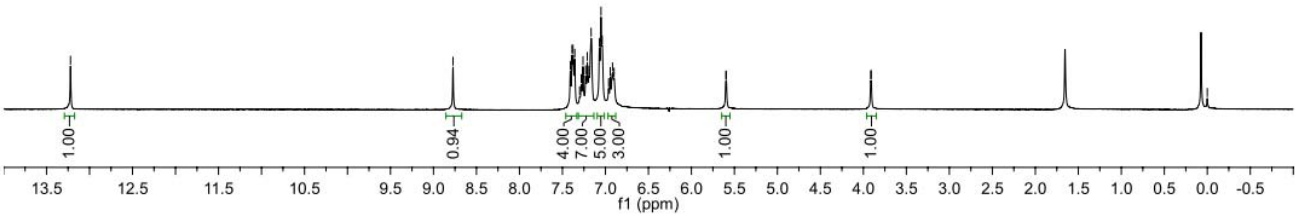




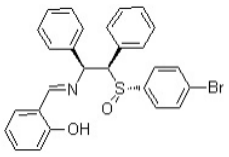
CHG1166 CDC13



1c



CHG1166 DMSO



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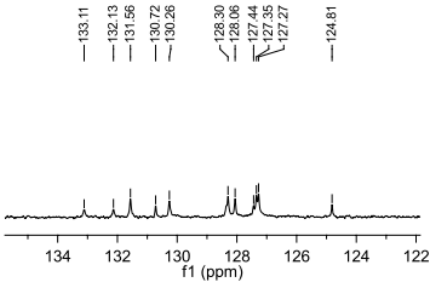

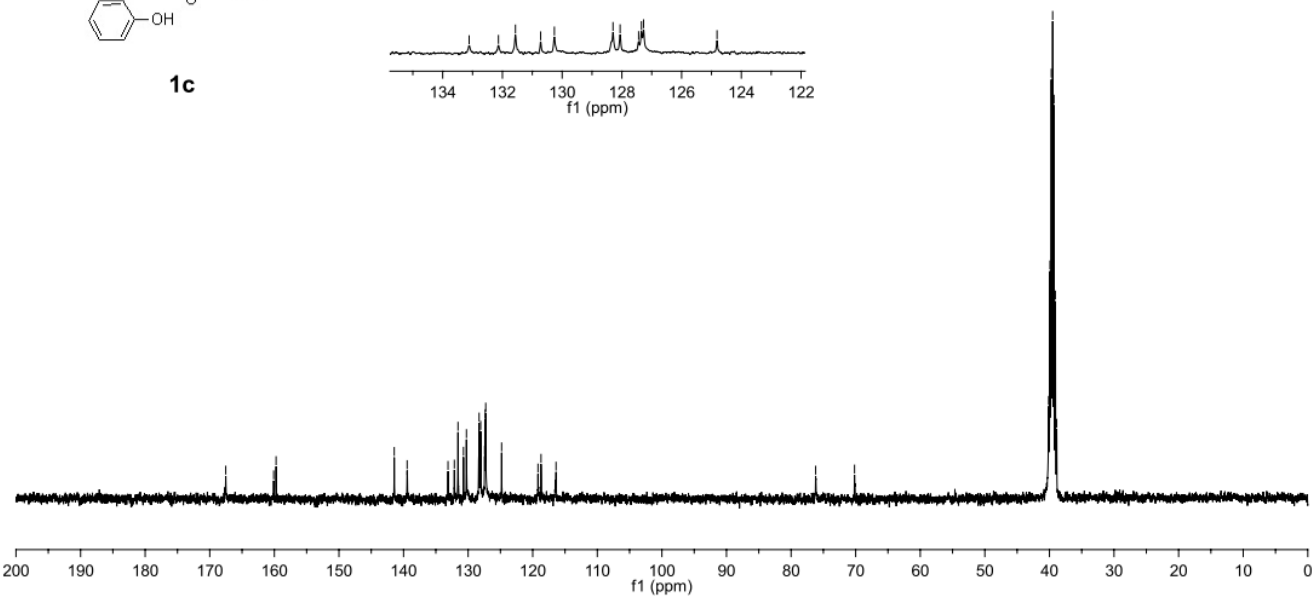

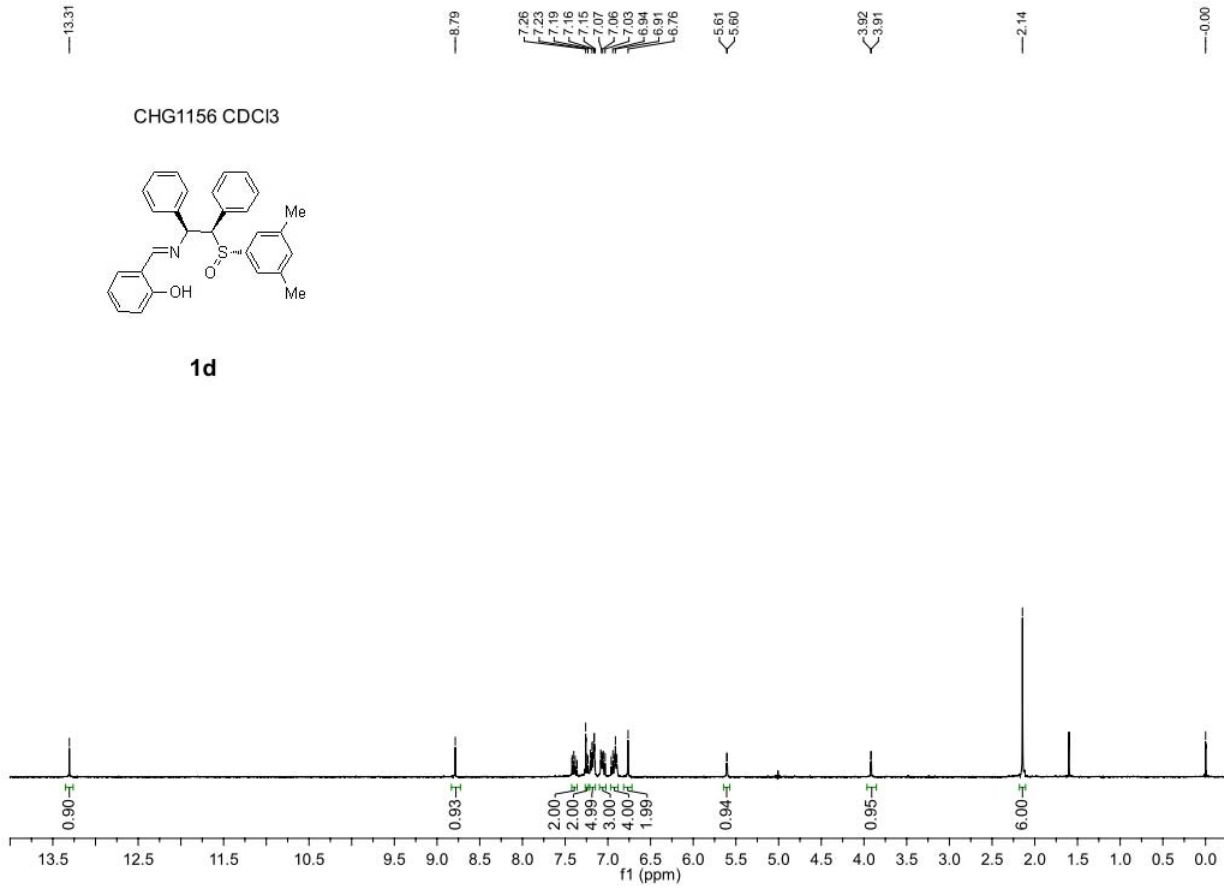
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7.07
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7.03
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6.91
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5.61
5.60
3.92
3.91
2.14
0.00
CHG1156 CDCl3
Me
N
S
O
OH
Me
1d
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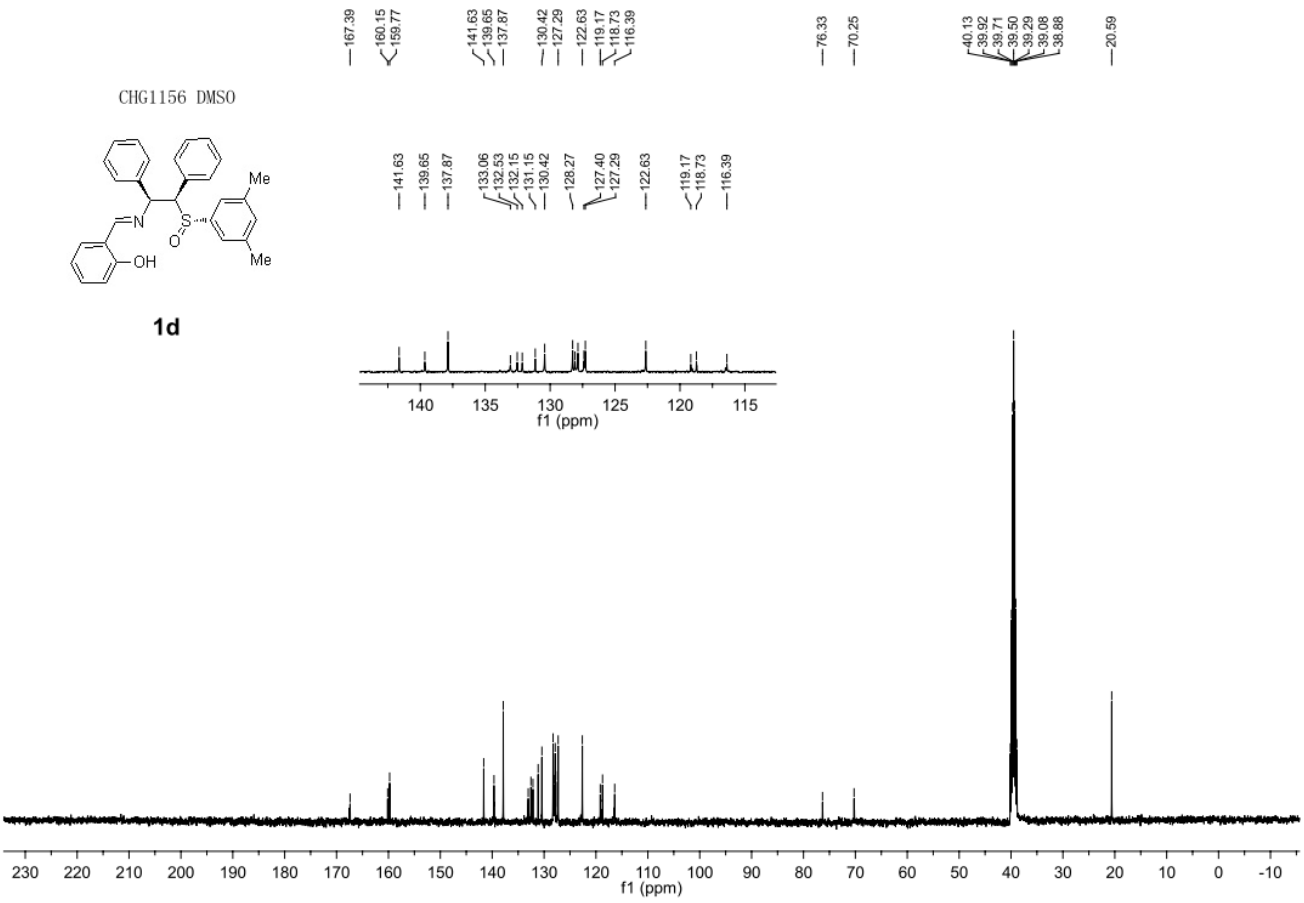
0.93
2.00
2.00
4.99
3.00
4.00
1.99
0.94
0.95
6.00
f1 (ppm)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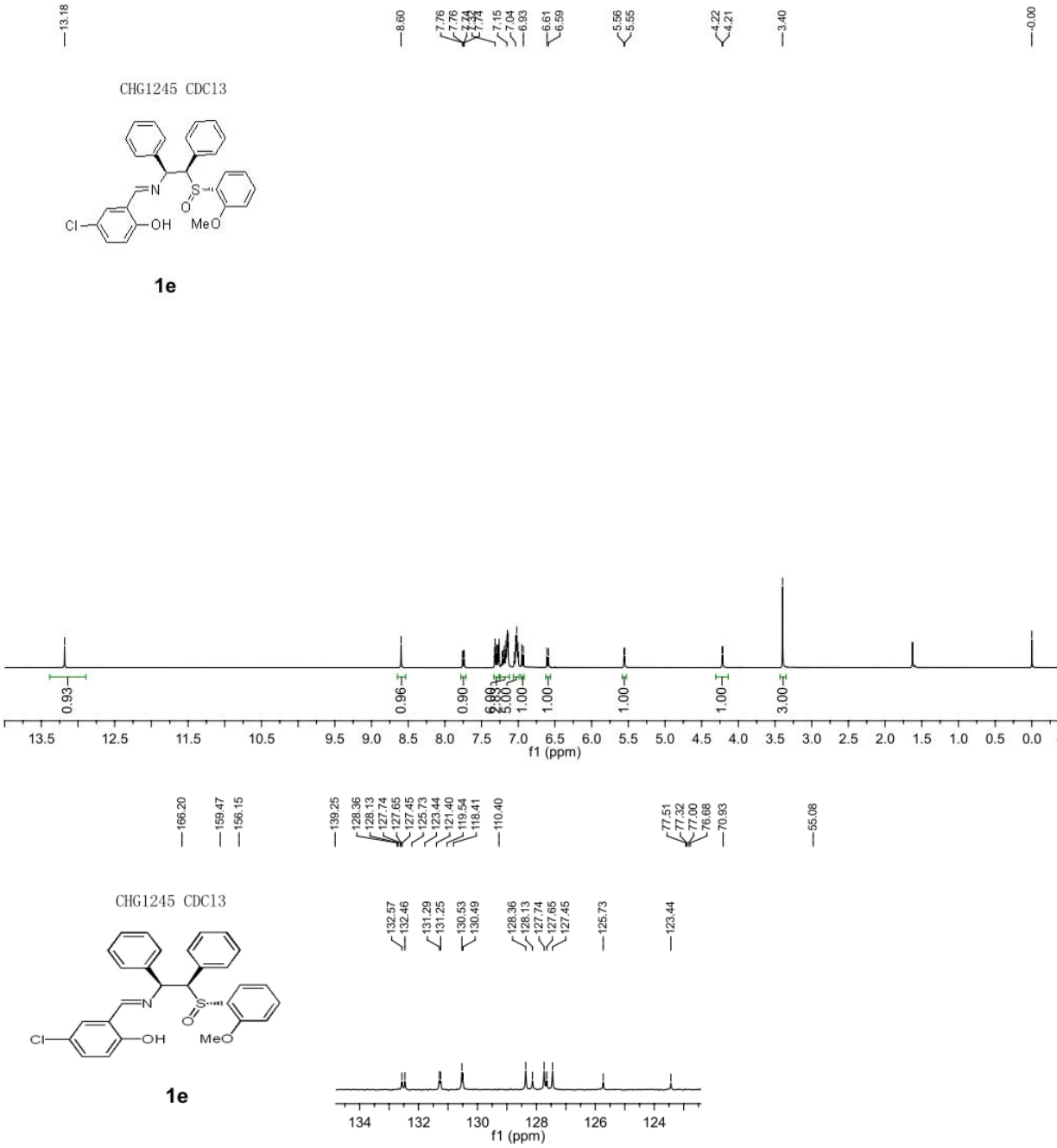
118.73
116.39
76.33
70.25
40.13
39.92
39.71
39.50
39.29
39.08
38.88
20.59
CHG1156 DMSO
Me
N
S
O
OH
Me
1d
141.63
139.65
137.87
133.06
132.53
132.15
131.15
130.42
128.27
127.40
127.29
122.63
119.17
118.73
116.39
f1 (ppm)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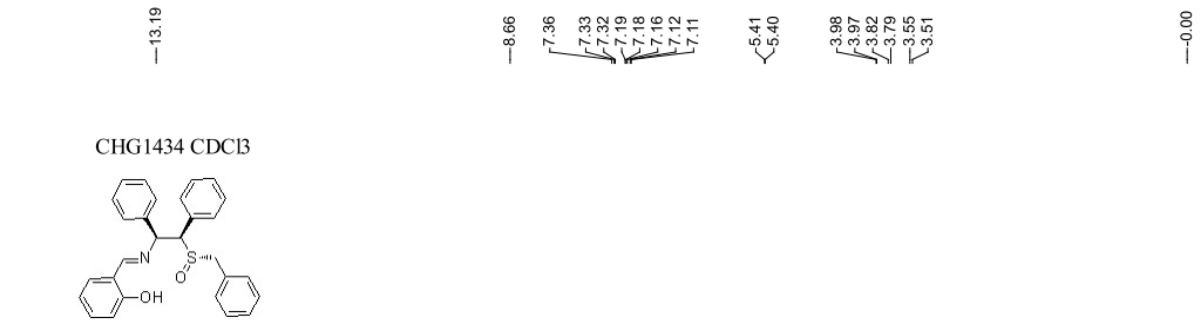
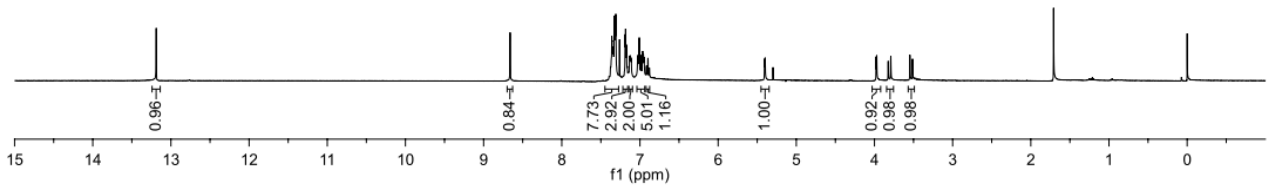
7.76
7.74
7.74
7.15
7.04
6.93
6.61
6.59
5.56
5.55
4.22
4.21
3.40
0.00
CHG1245 CDC13
Cl
OH
MeO
1e
0.93
0.96
0.90
1.00
1.00
1.00
1.00
3.00
f1 (ppm)
166.20
159.47
156.15
139.25
128.36
128.13
127.74
127.65
127.45
125.73
123.44
121.40
119.54
118.41
110.40
77.51
77.32
77.00
76.68
70.93
55.08
CHG1245 CDC13
Cl
OH
MeO
1e
132.57
132.46
131.29
131.25
130.53
130.49
128.36
128.13
127.74
127.65
127.45
125.73
123.44
f1 (ppm)
f1 (ppm)

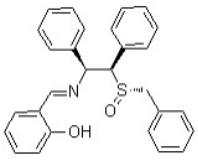


CHG1434 CDCl3

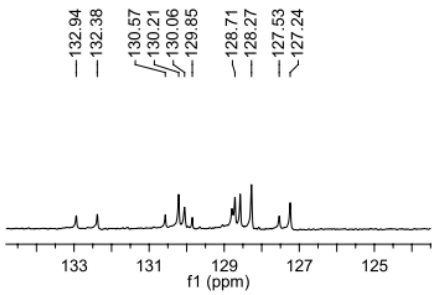
1f

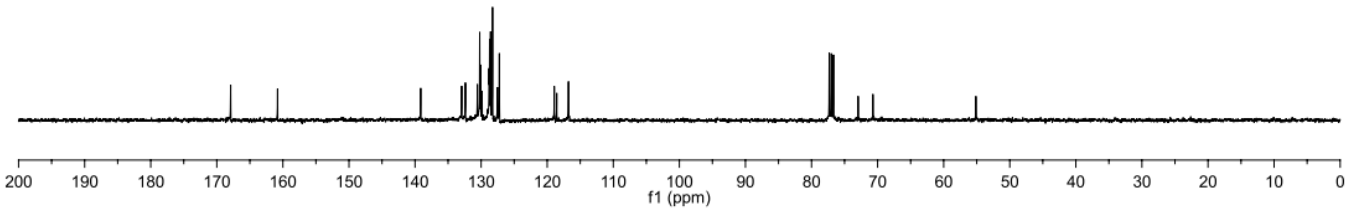


CHG1434 CDCl3

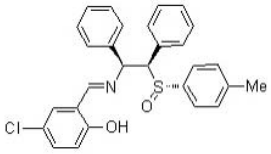


1f

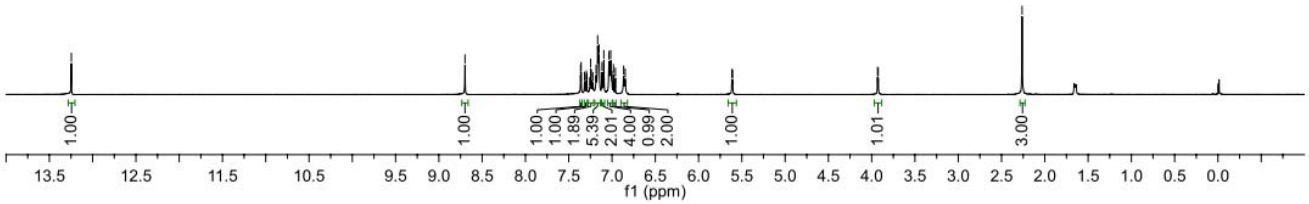




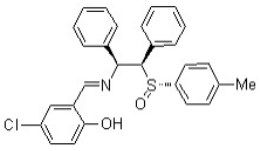
CHG1217 CDCl3



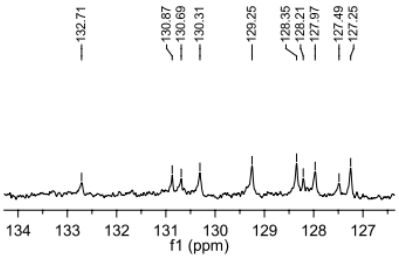
1g

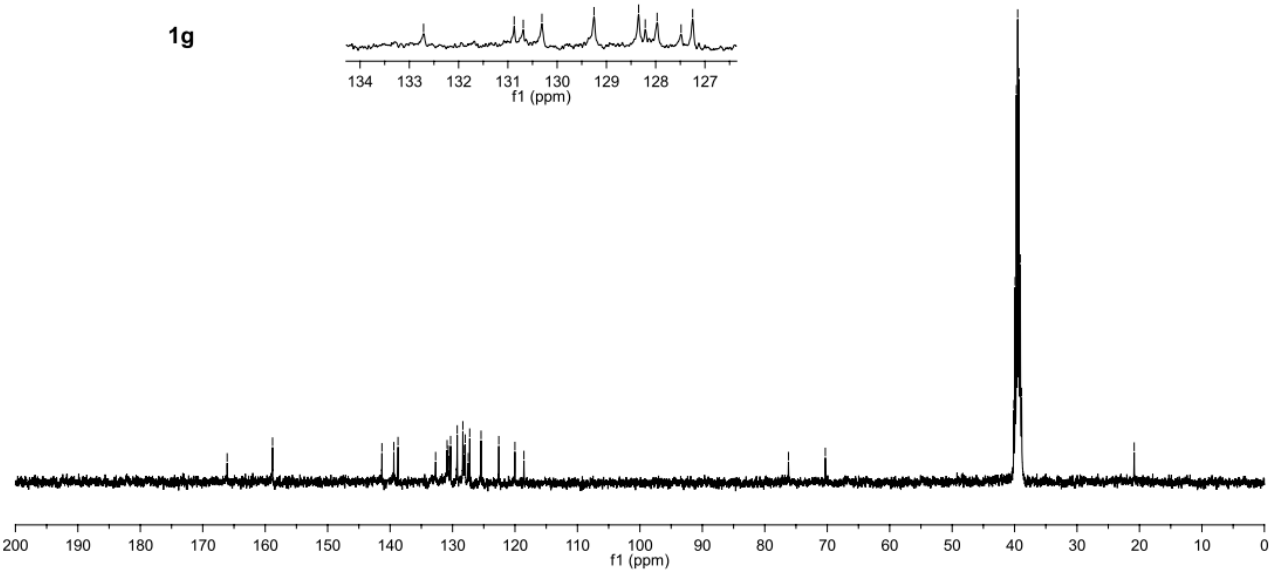


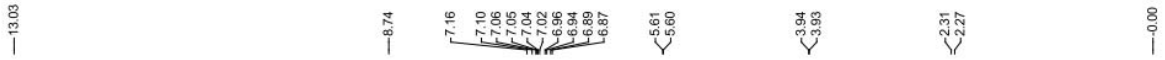
CHG1217 DMSO



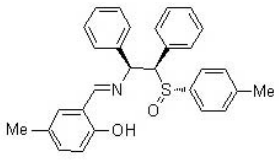
1g



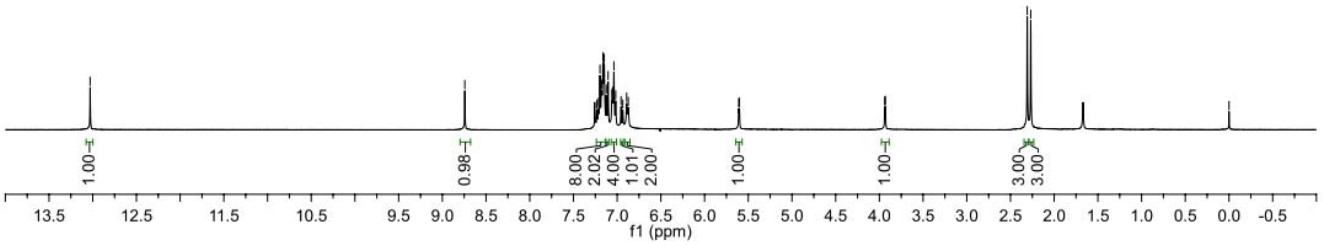




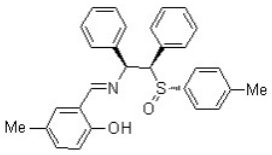
CHG1194 CDC13



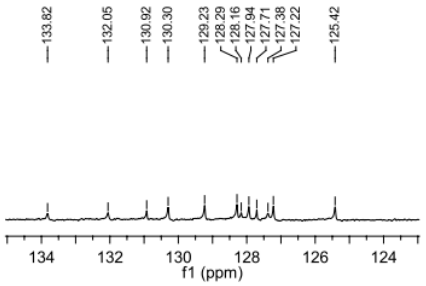
1h

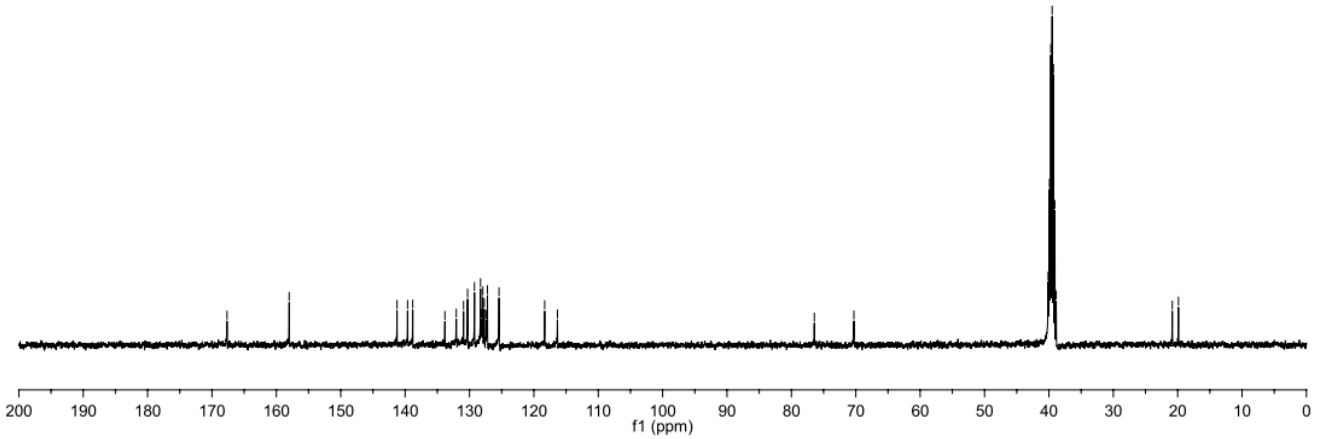


CHG1194 DMSO

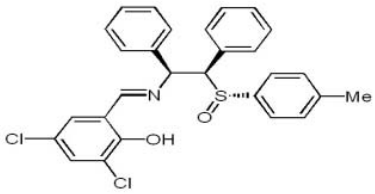


1h

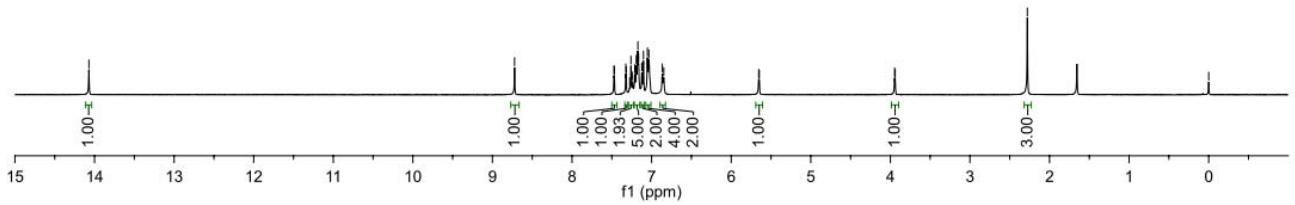




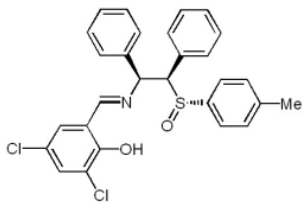
CHG1202 CDC13



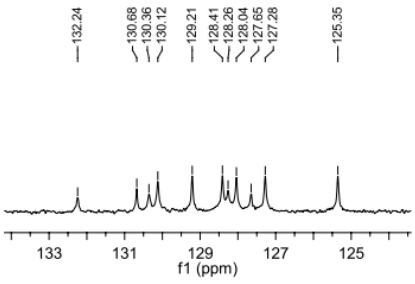
1i

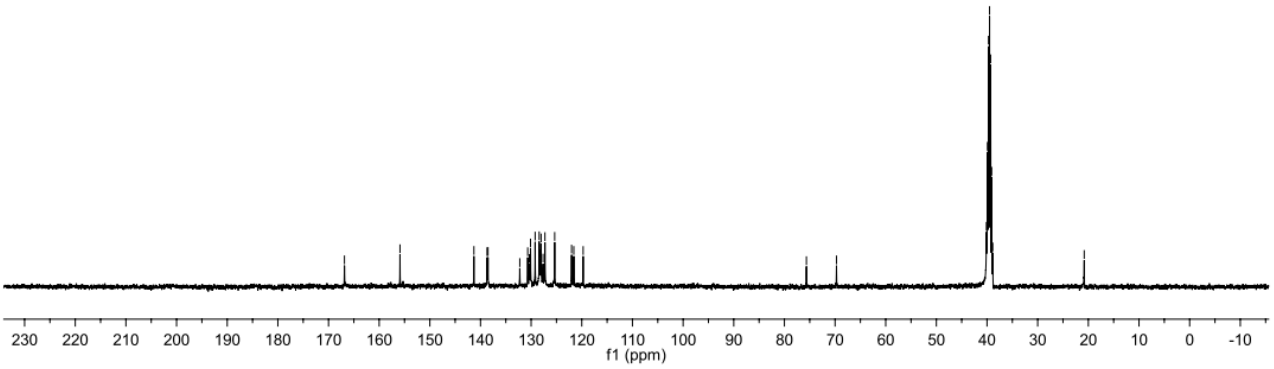


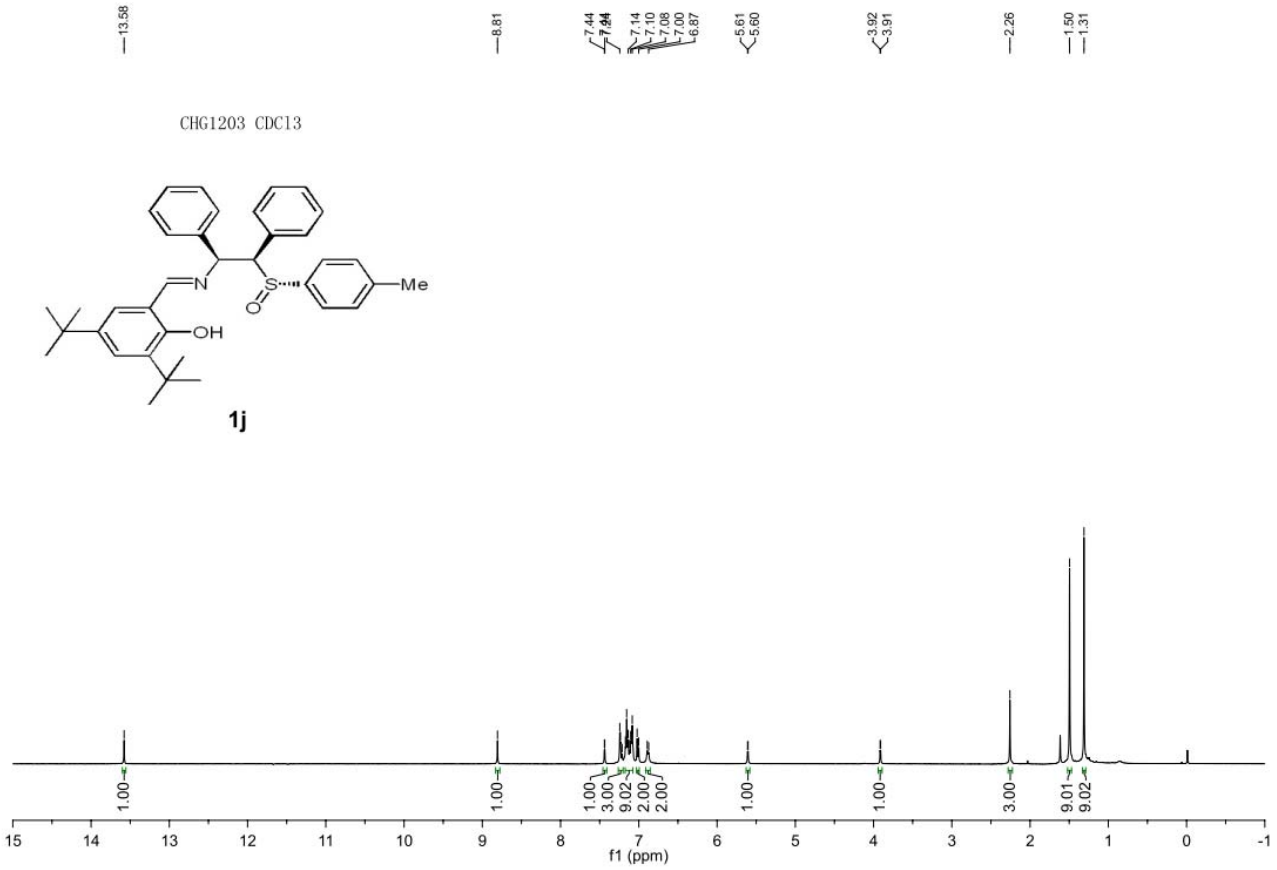
CHG1202 DMSO

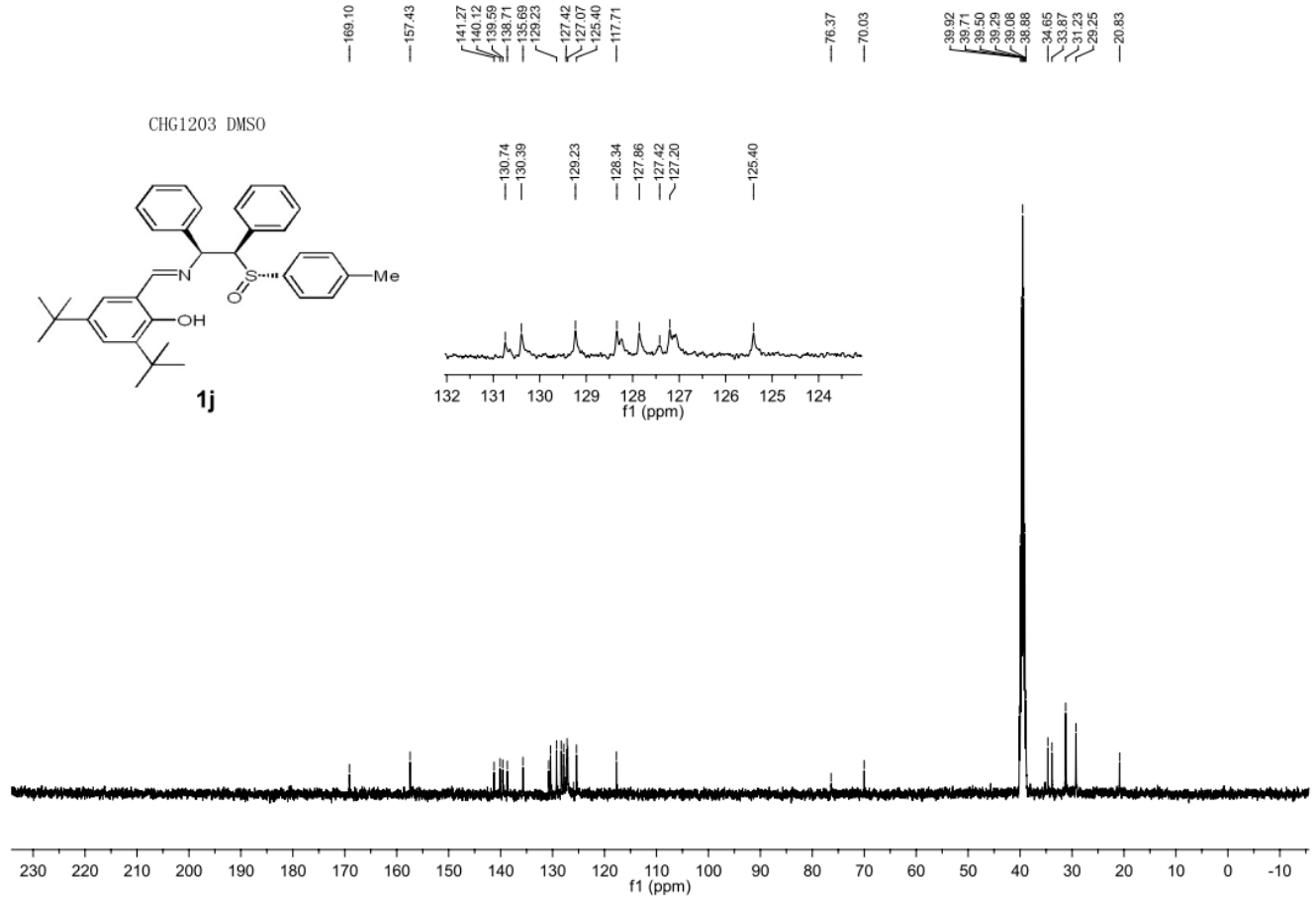


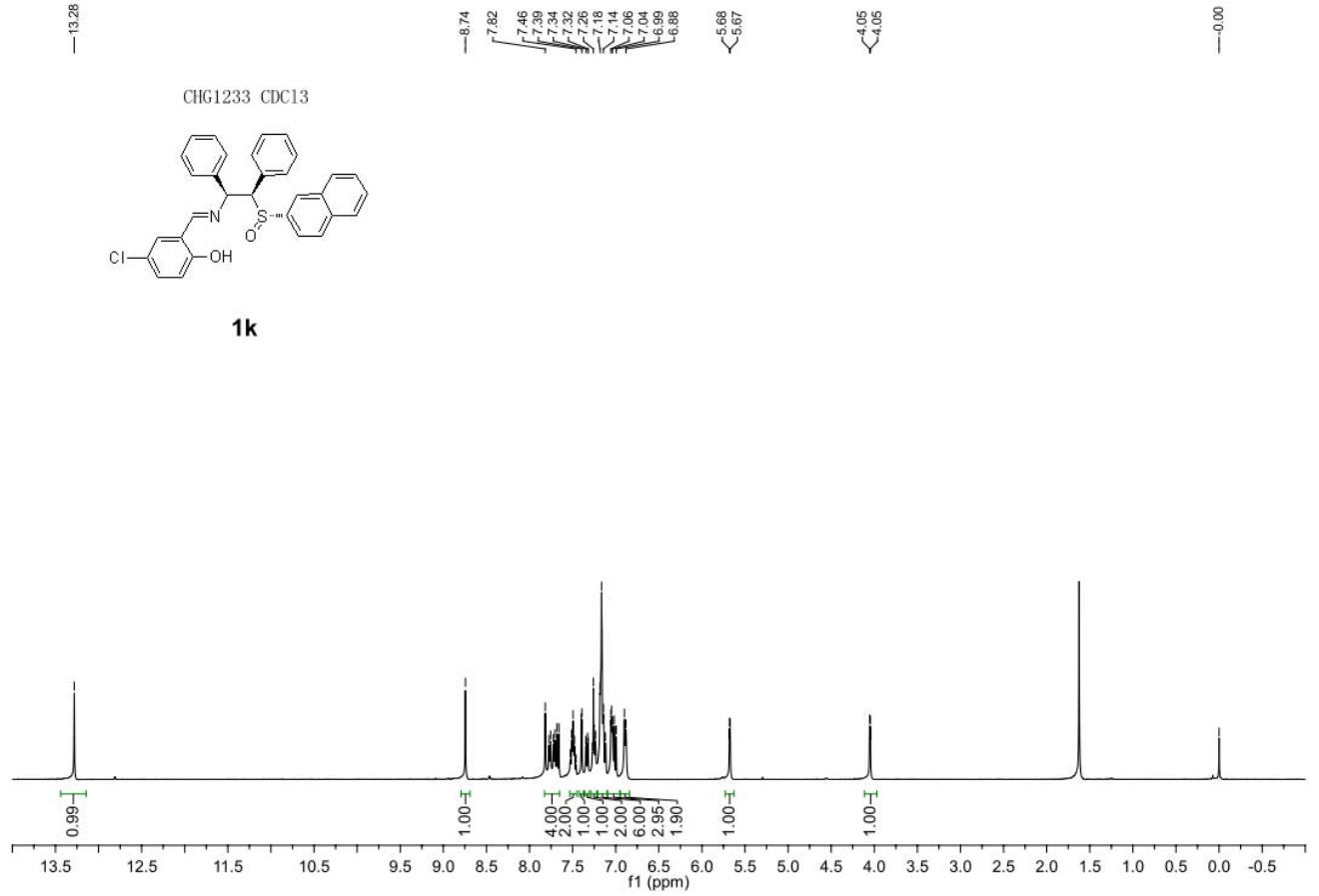
1i

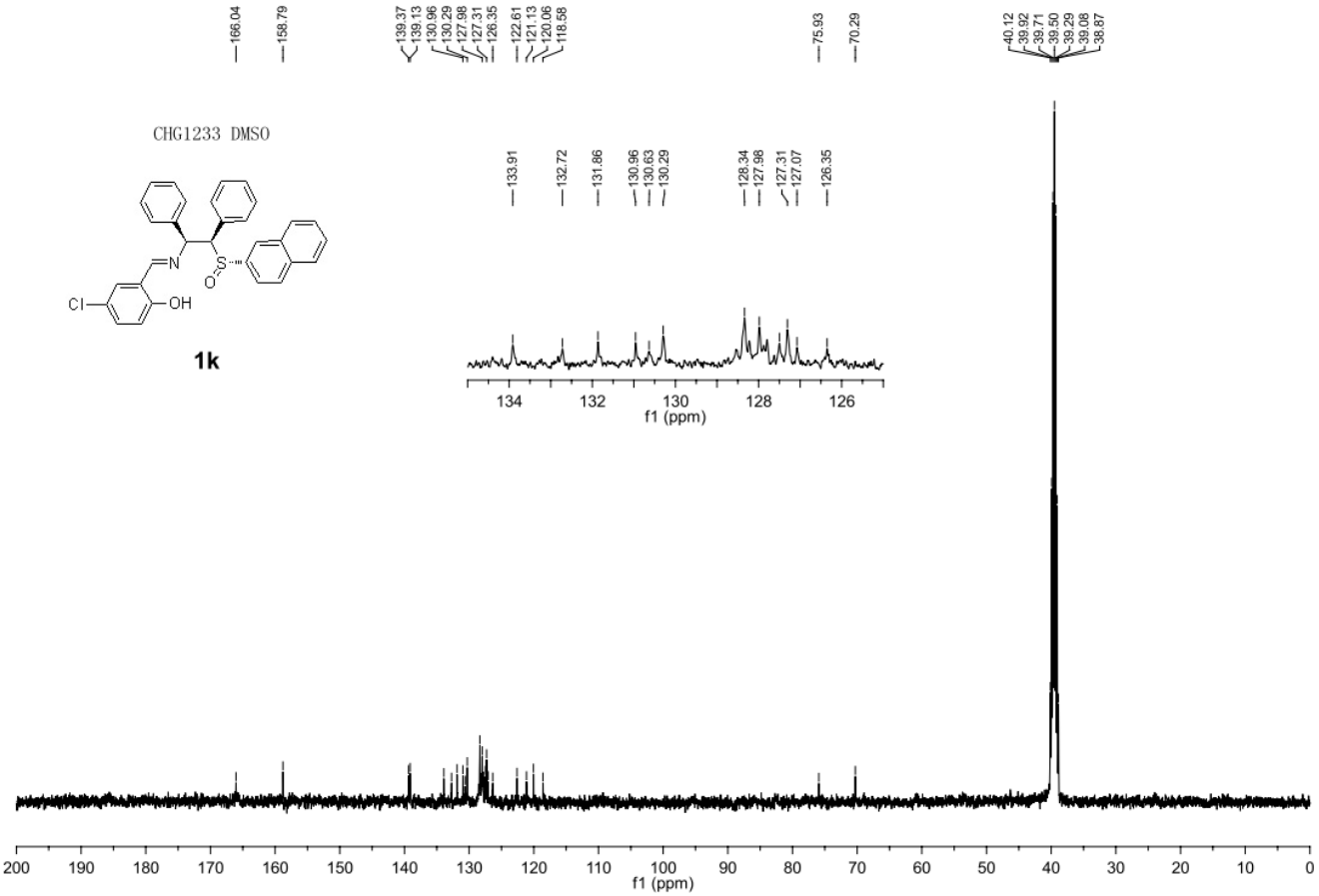


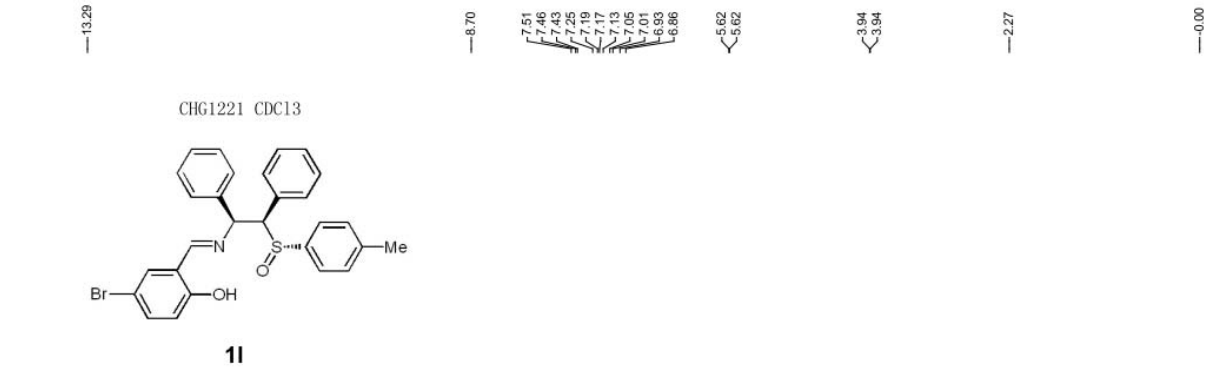



13.58
8.81
7.44
7.14
7.10
7.08
7.00
6.87
5.61
5.60
3.92
3.91
2.26
1.50
1.31
CHG1203 CDCl3
Me
OH
1j
1.00
1.00
1.00
3.00
9.02
2.00
2.00
1.00
1.00
3.00
9.01
9.02
f1 (ppm)


169.10
157.43
141.27
140.12
139.59
138.71
135.69
129.23
127.42
127.07
125.40
117.71
76.37
70.03
39.92
39.71
39.50
39.29
39.08
38.88
34.65
33.87
31.23
29.25
20.83
CHG1203 DMSO
130.74
130.39
129.23
128.34
127.86
127.42
127.20
125.40
Me
OH
1j
f1 (ppm)

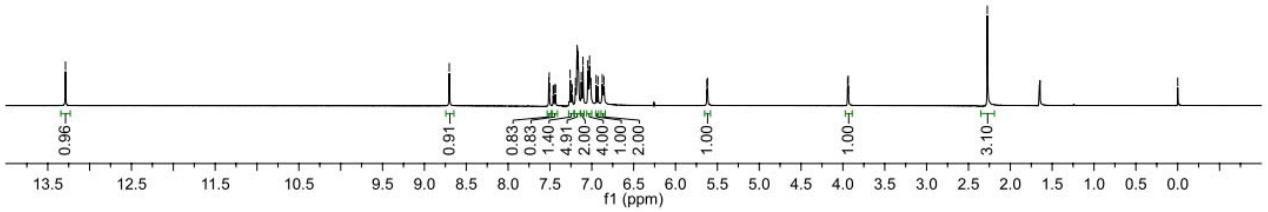

13.28
8.74
7.82
7.46
7.39
7.34
7.32
7.26
7.18
7.14
7.06
7.04
6.99
6.88
5.68
5.67
4.05
4.05
0.00
CHG1233 CDC13
Cl
OH
1k
0.99
1.00
4.00
2.00
1.00
1.00
2.00
6.00
2.95
1.90
1.00
1.00
f1 (ppm)


166.04
158.79
139.37
139.13
130.96
130.29
127.98
127.31
126.35
122.61
121.13
120.06
118.58
75.93
70.29
40.12
39.92
39.71
39.50
39.29
39.08
38.87
CHG1233 DMSO
Cl
OH
1k
133.91
132.72
131.86
130.96
130.63
130.29
128.34
127.98
127.31
127.07
126.35
f1 (ppm)

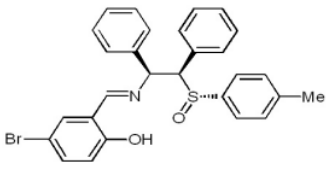


CHG1221 CDCl3

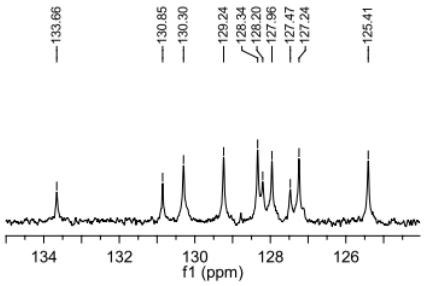
1l

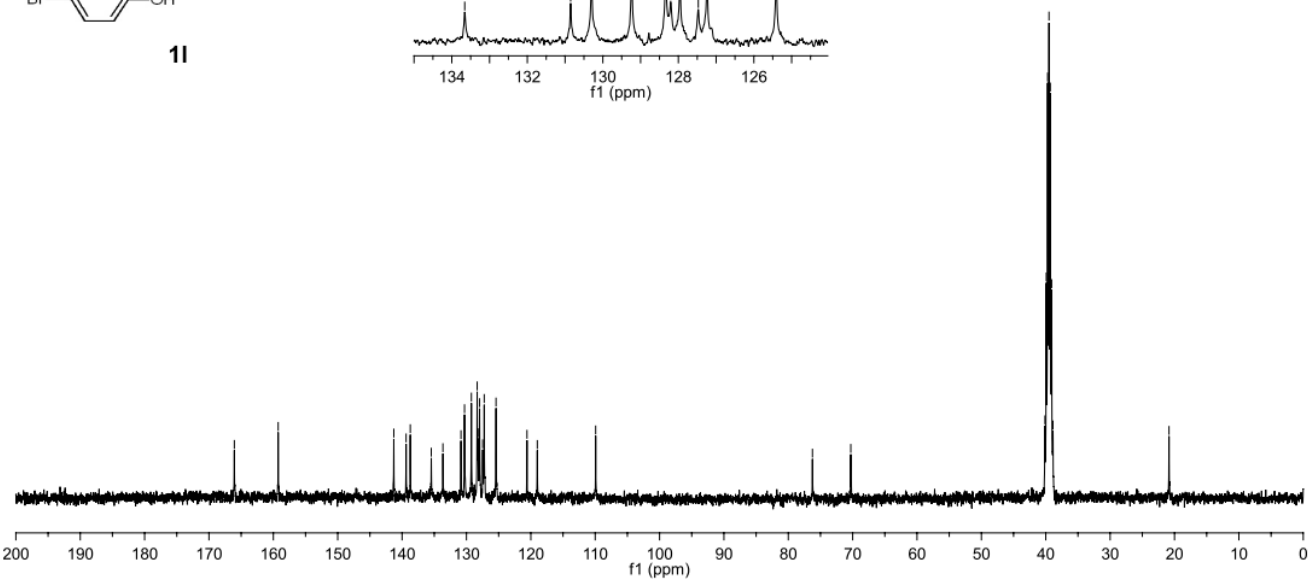


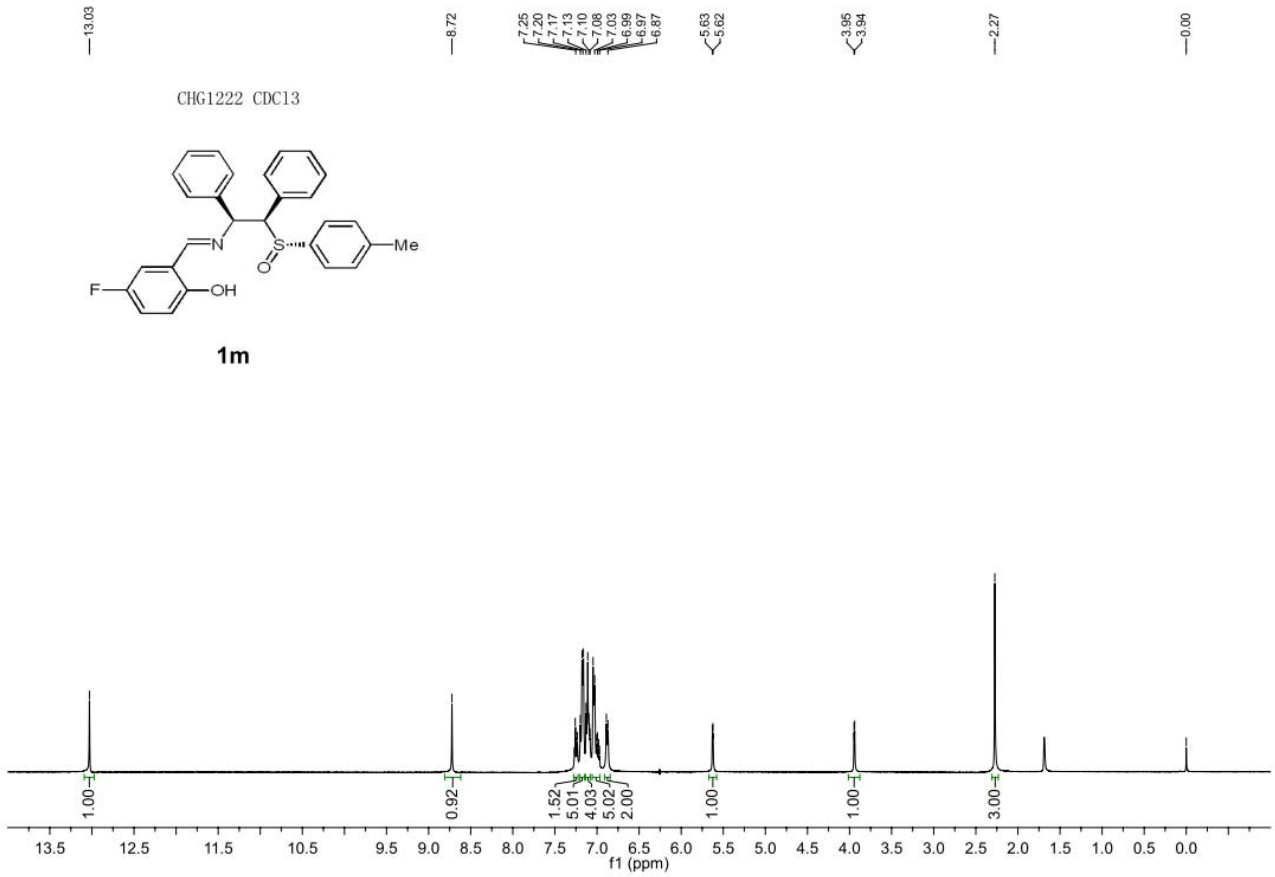
CHG1221 DMSO

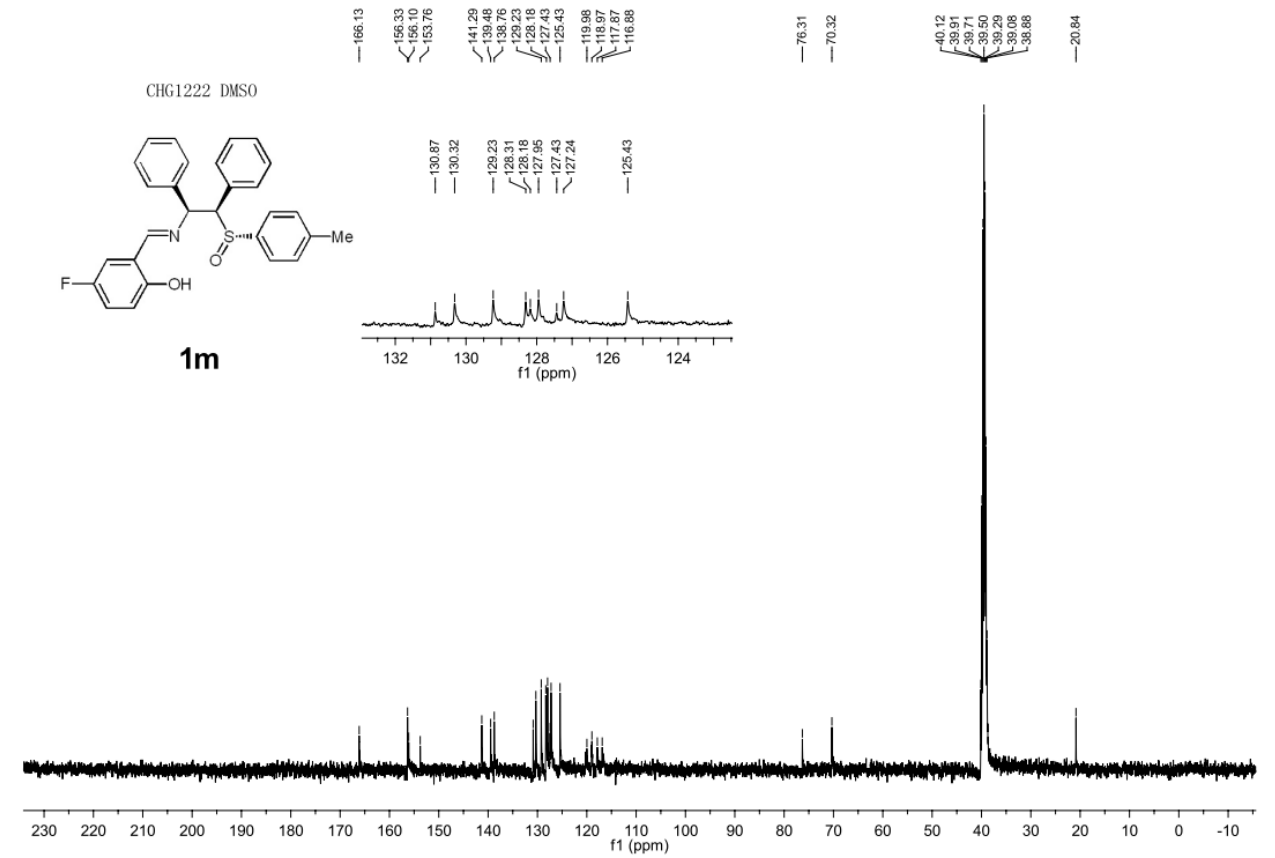


1l

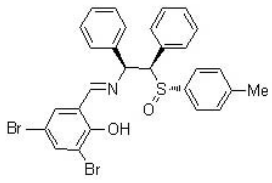




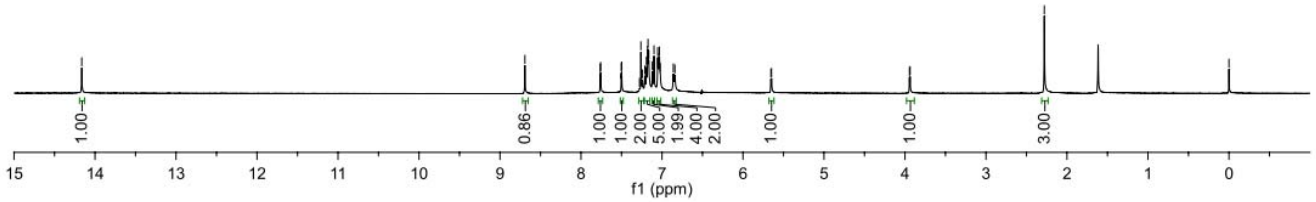

13.03
8.72
7.25
7.20
7.17
7.13
7.10
7.08
7.03
6.99
6.97
6.87
5.63
5.62
3.95
3.94
2.27
0.00
CHG1222 CDCl3
N
S
O
Me
F
OH
1m
1.00
0.92
1.52
5.01
4.03
5.02
2.00
1.00
1.00
3.00
f1 (ppm)


166.13
156.33
156.10
153.76
141.29
139.48
138.76
129.23
128.18
127.43
125.43
119.98
118.97
117.87
116.88
76.31
70.32
40.12
39.91
39.71
39.50
39.29
39.08
38.88
20.84
CHG1222 DMSO
130.87
130.32
129.23
128.31
128.18
127.95
127.43
127.24
125.43
N
S
O
Me
F
OH
1m
f1 (ppm)
f1 (ppm)

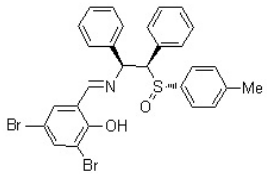
CHG1196 CDC13



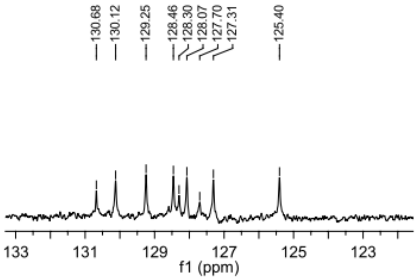
1n

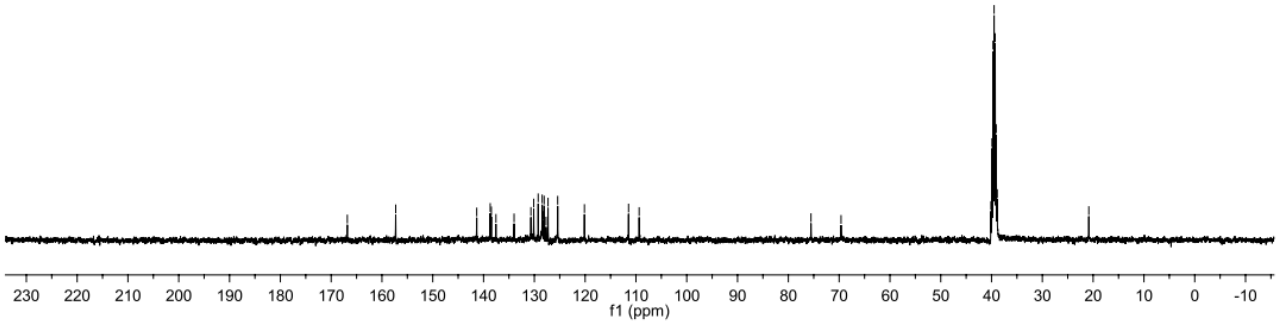


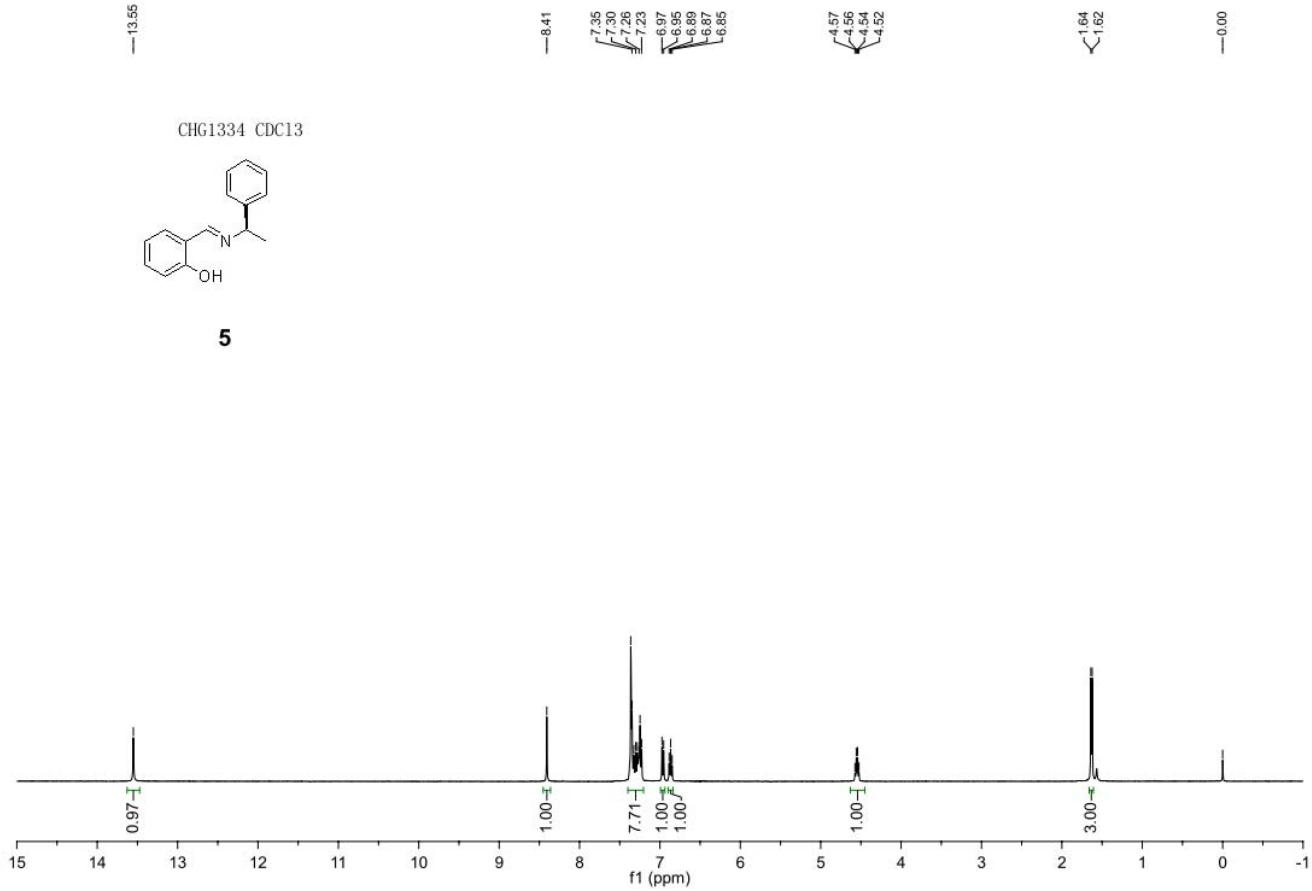
CHG1196 DMSO



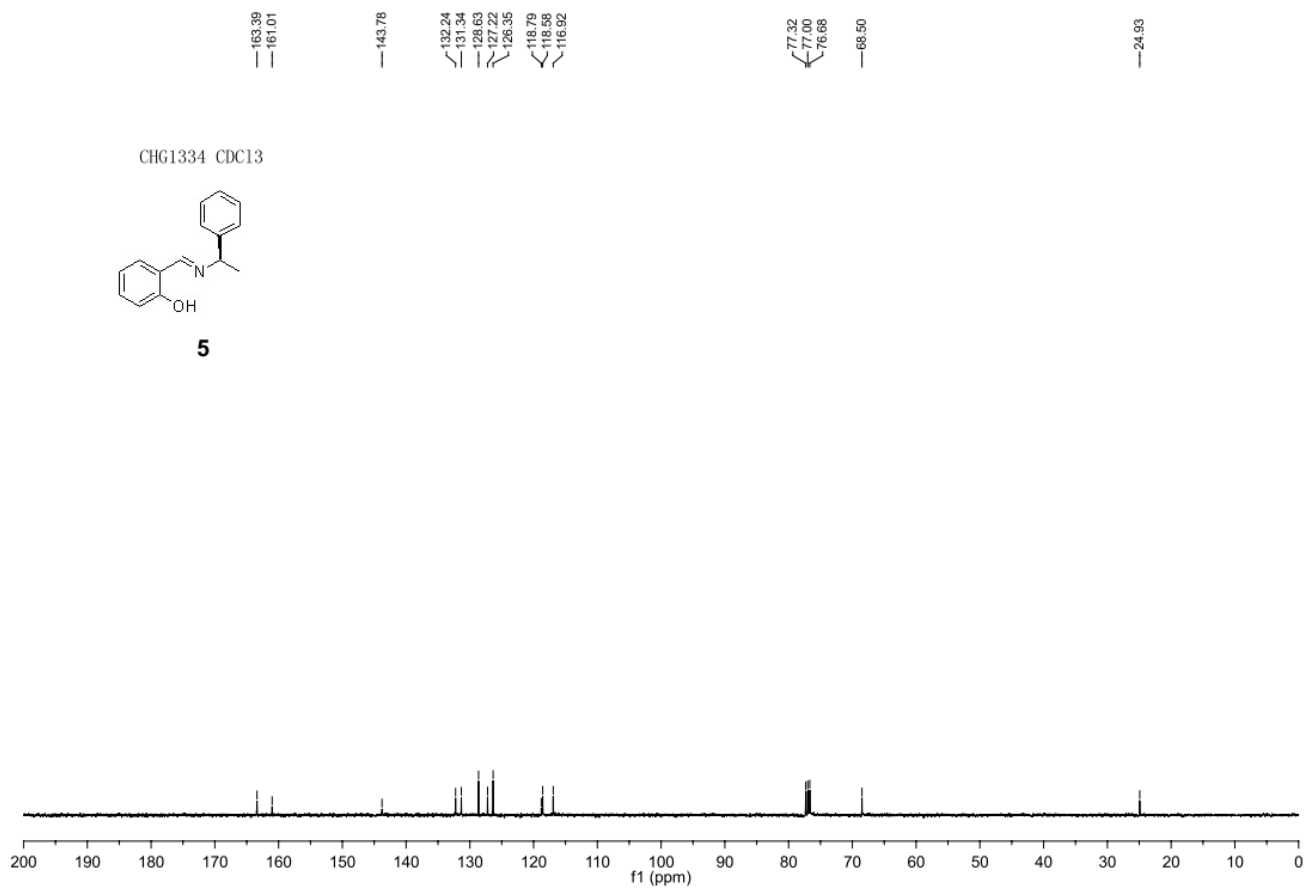
1n



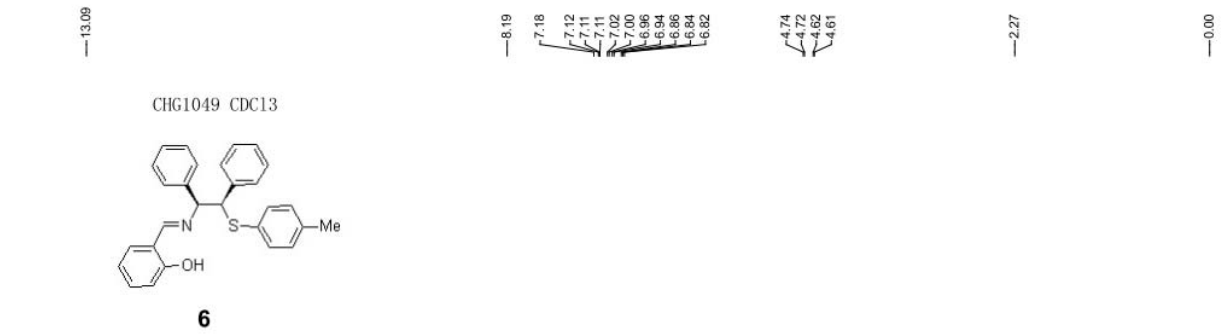



13.55
8.41
7.35
7.30
7.26
7.23
6.97
6.95
6.89
6.87
6.85
4.57
4.56
4.54
4.52
1.64
1.62
0.00
CHG1334 CDC13
N
OH
0.97
1.00
7.71
1.00
1.00
1.00
3.00
f1 (ppm)

5

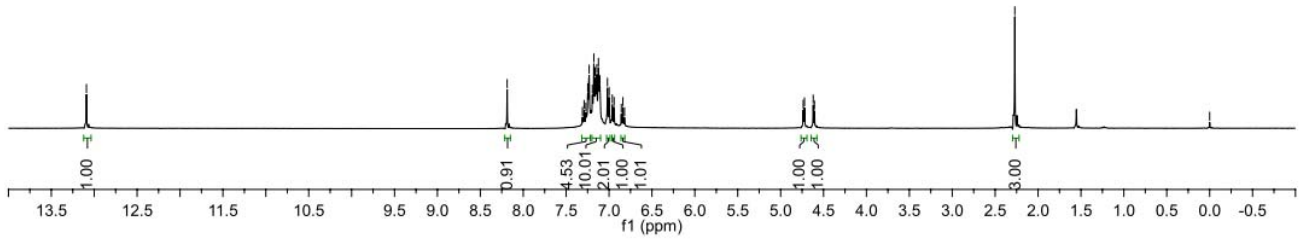

163.39
161.01
143.78
132.24
131.34
128.63
127.22
126.35
118.79
118.58
116.92
77.32
77.00
76.68
68.50
24.93
CHG1334 CDC13
N
OH
f1 (ppm)

5

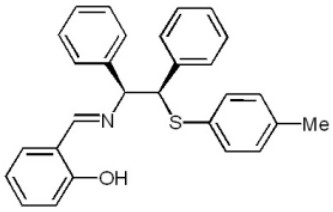


CHG1049 CDCl3

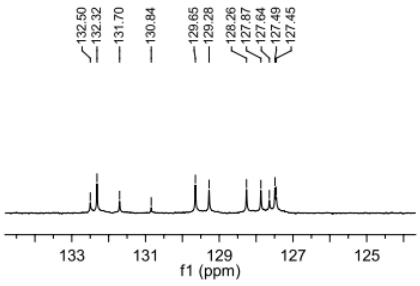
6

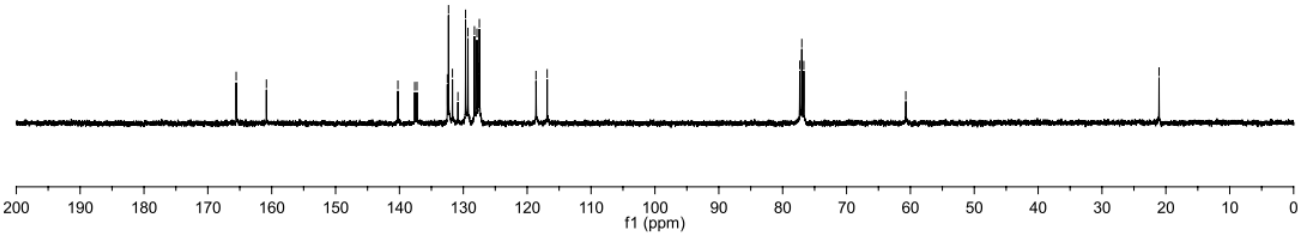


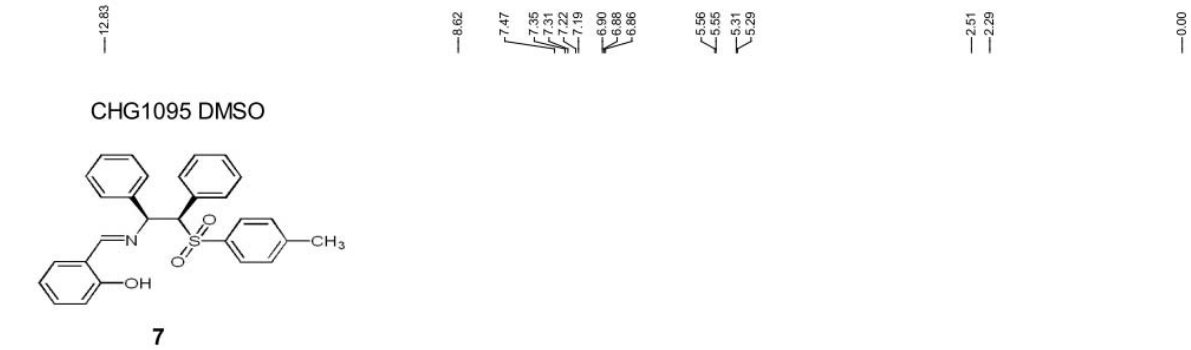
CHG1049 CDCl3



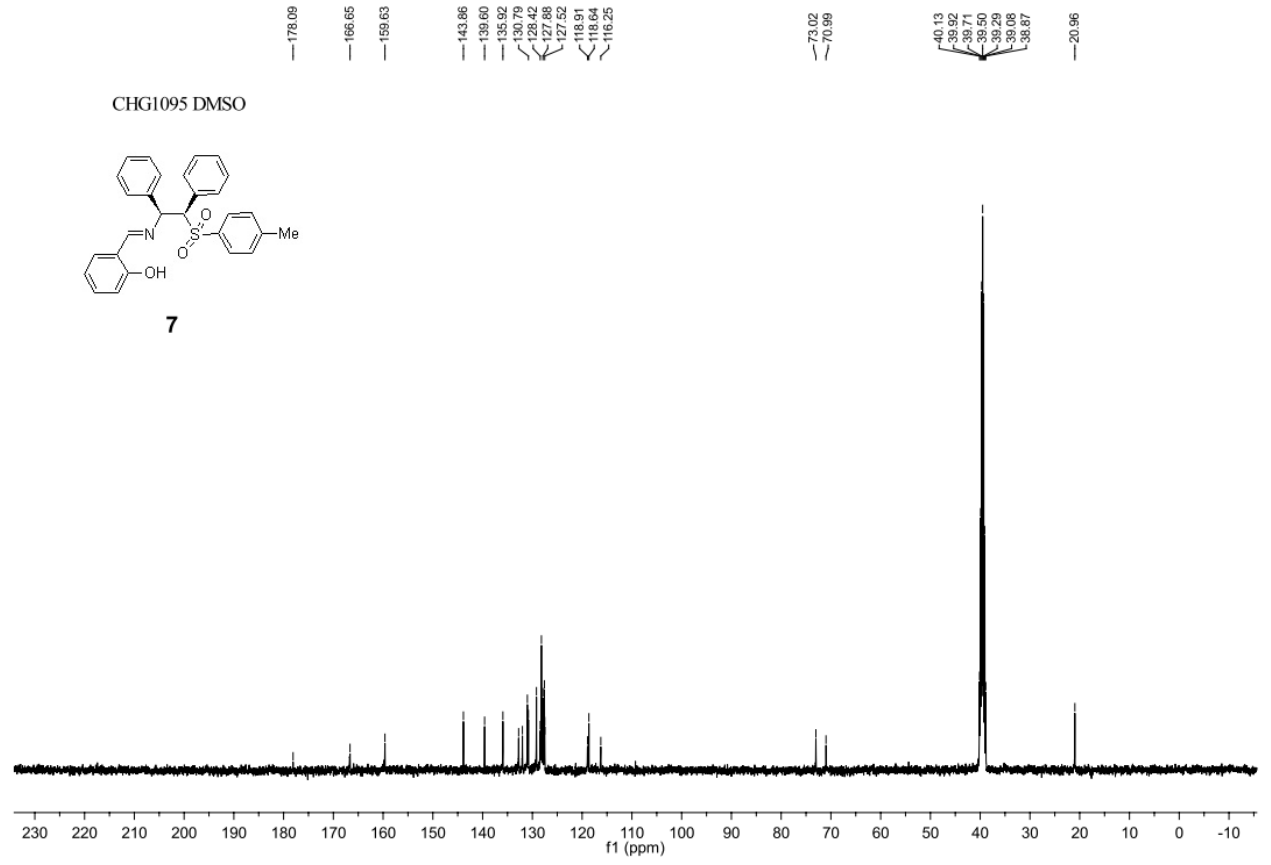
6





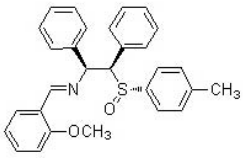

12.83
8.62
7.47
7.35
7.31
7.22
7.19
6.90
6.88
6.86
5.56
5.55
5.31
5.29
2.51
2.29
0.00
CHG1095 DMSO
N
O
S
O
CH3
OH
0.21
0.96
6.00
10.00
2.00
1.00
1.00
3.00
f1 (ppm)

7

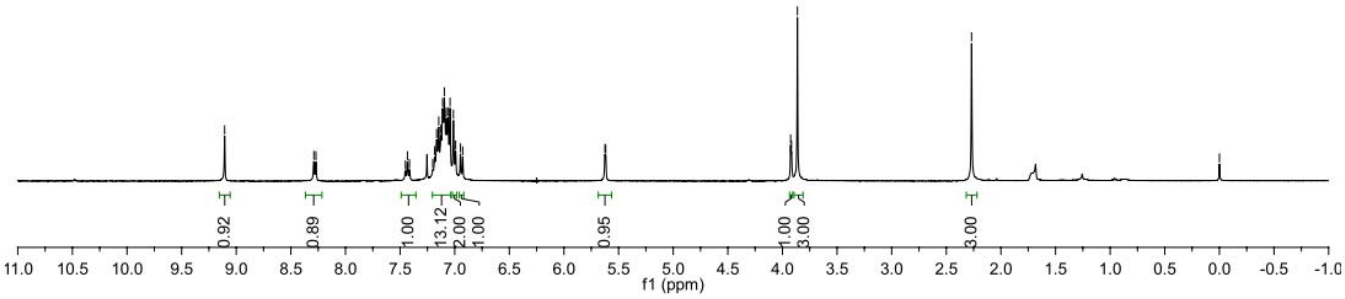

178.09
166.65
159.63
143.86
139.60
135.92
130.79
128.42
127.88
127.52
118.91
118.64
116.25
73.02
70.99
40.13
39.92
39.71
39.50
39.29
39.08
38.87
20.96
CHG1095 DMSO
N
O
S
O
Me
OH
f1 (ppm)

7

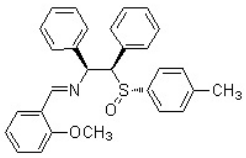
CHG1220 CDC13



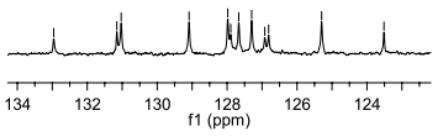
8

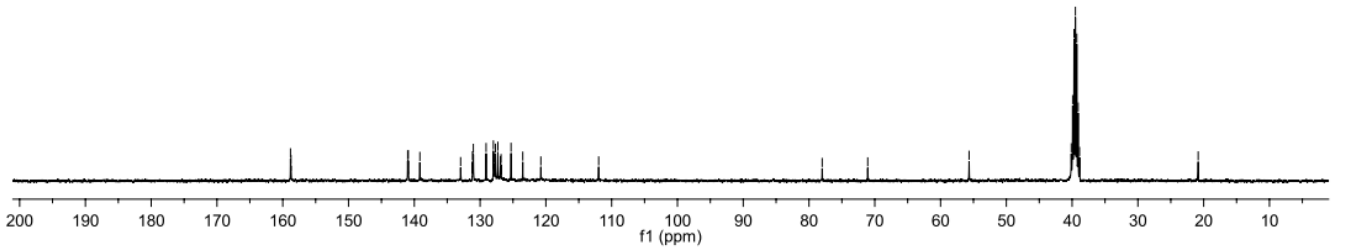


CHG1220 DMSO

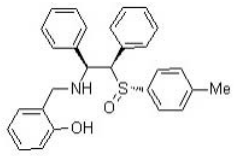


8

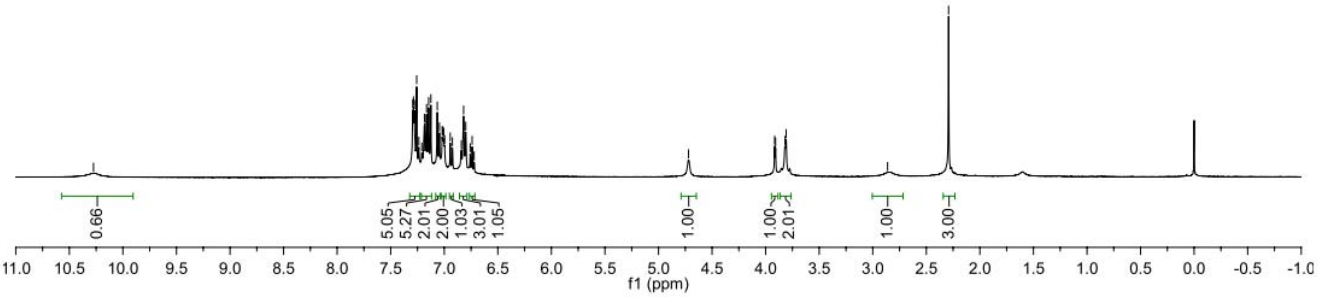




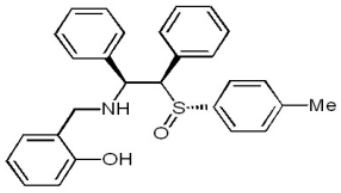
CHG1081 CDCl3



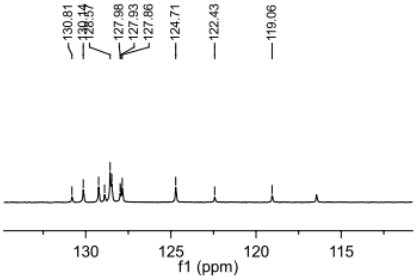
9

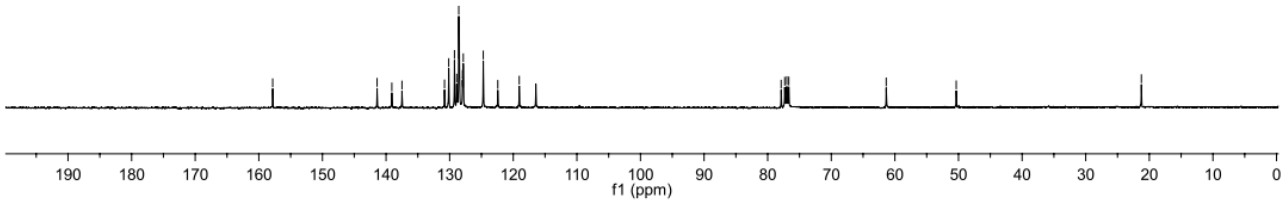


CHG1081 CDCl3

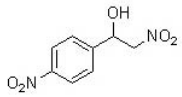


9

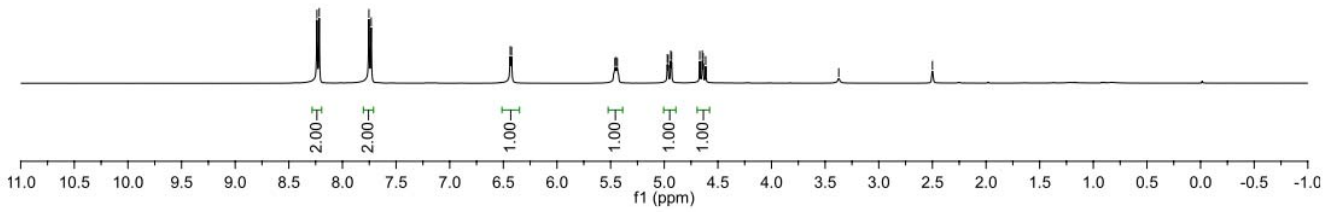




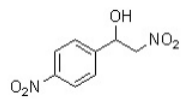
CHG1099 DMSO



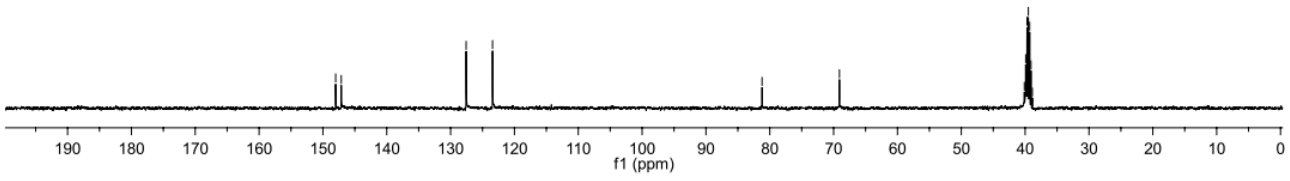
4a

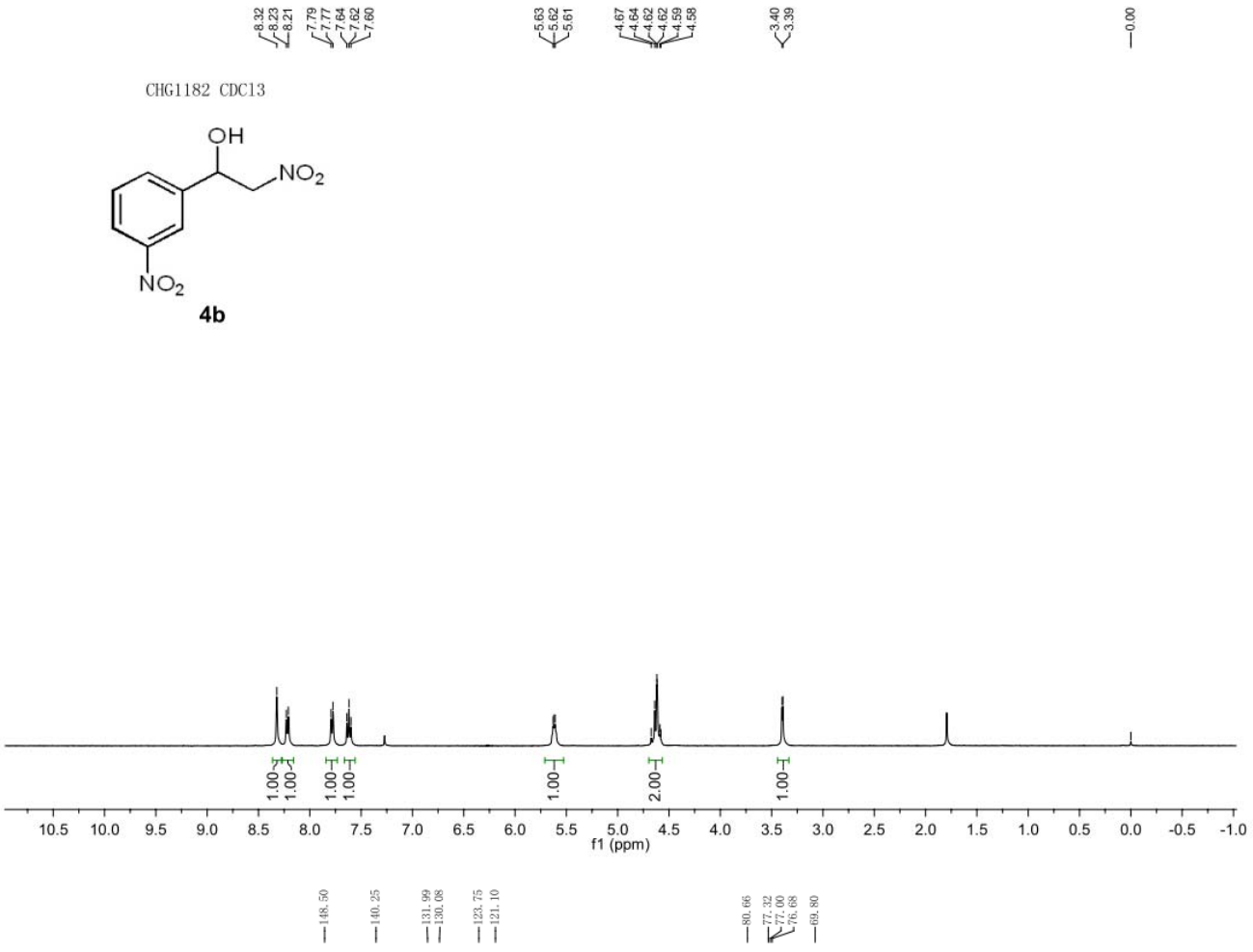


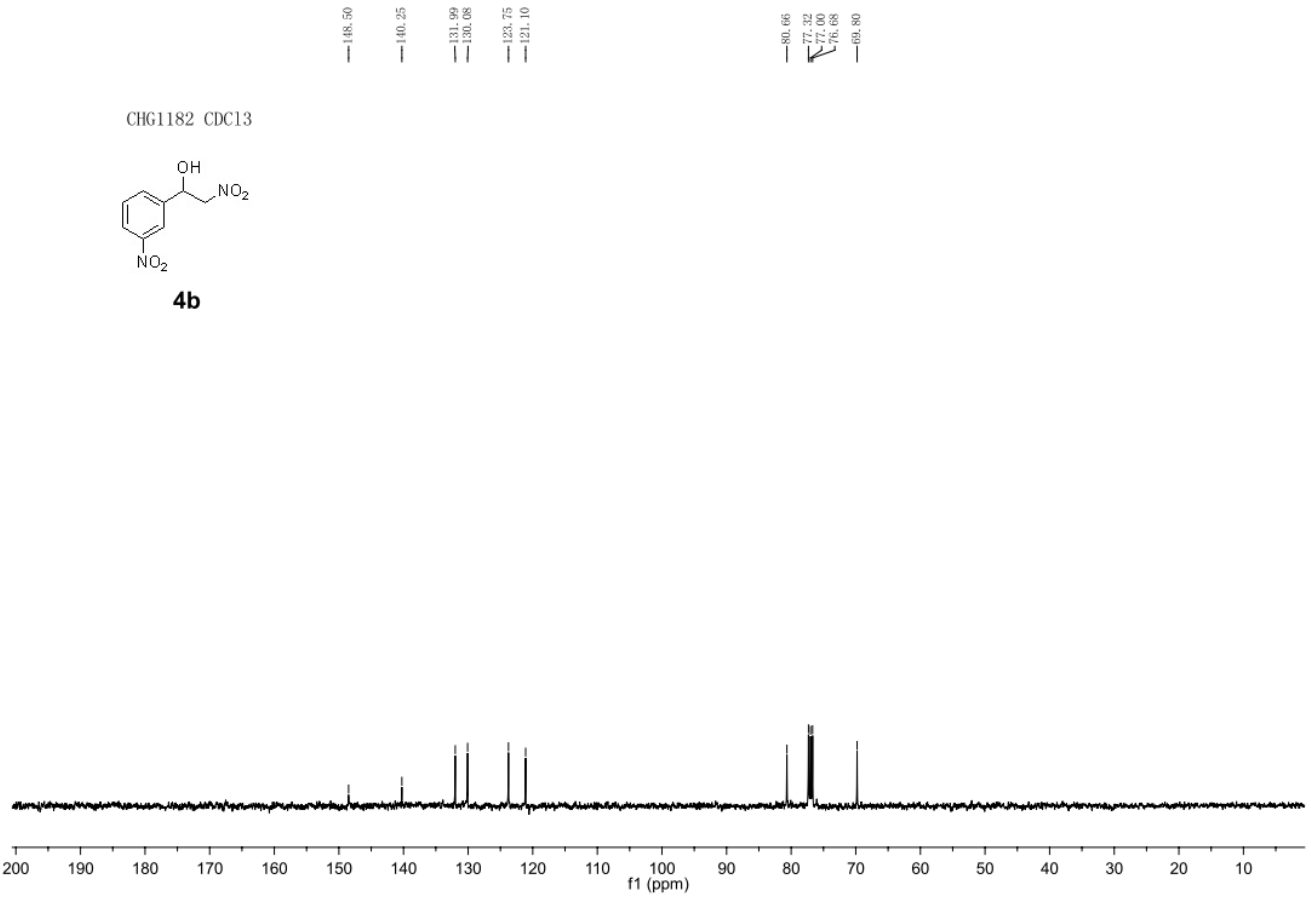
CHG1099 DMSO

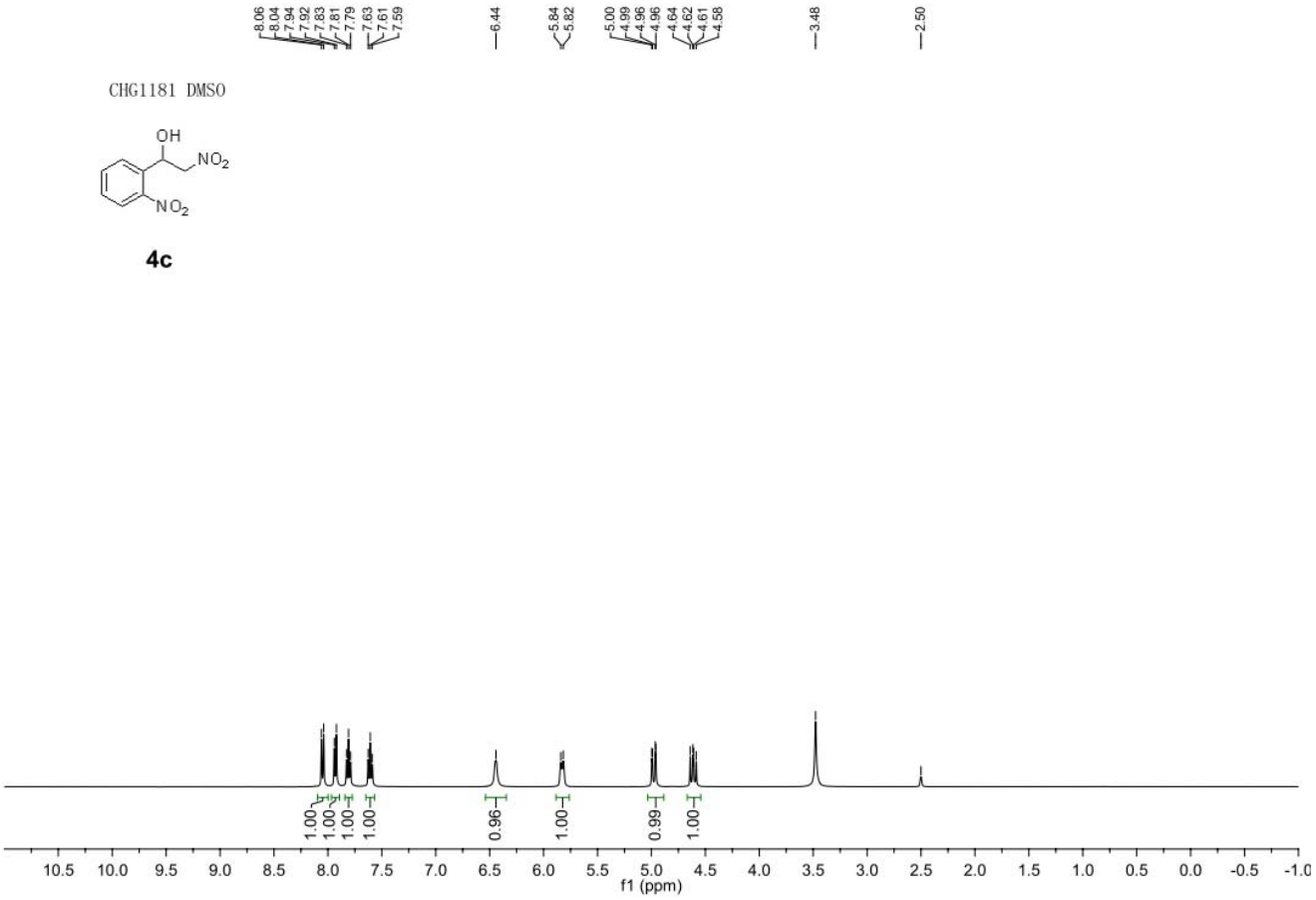


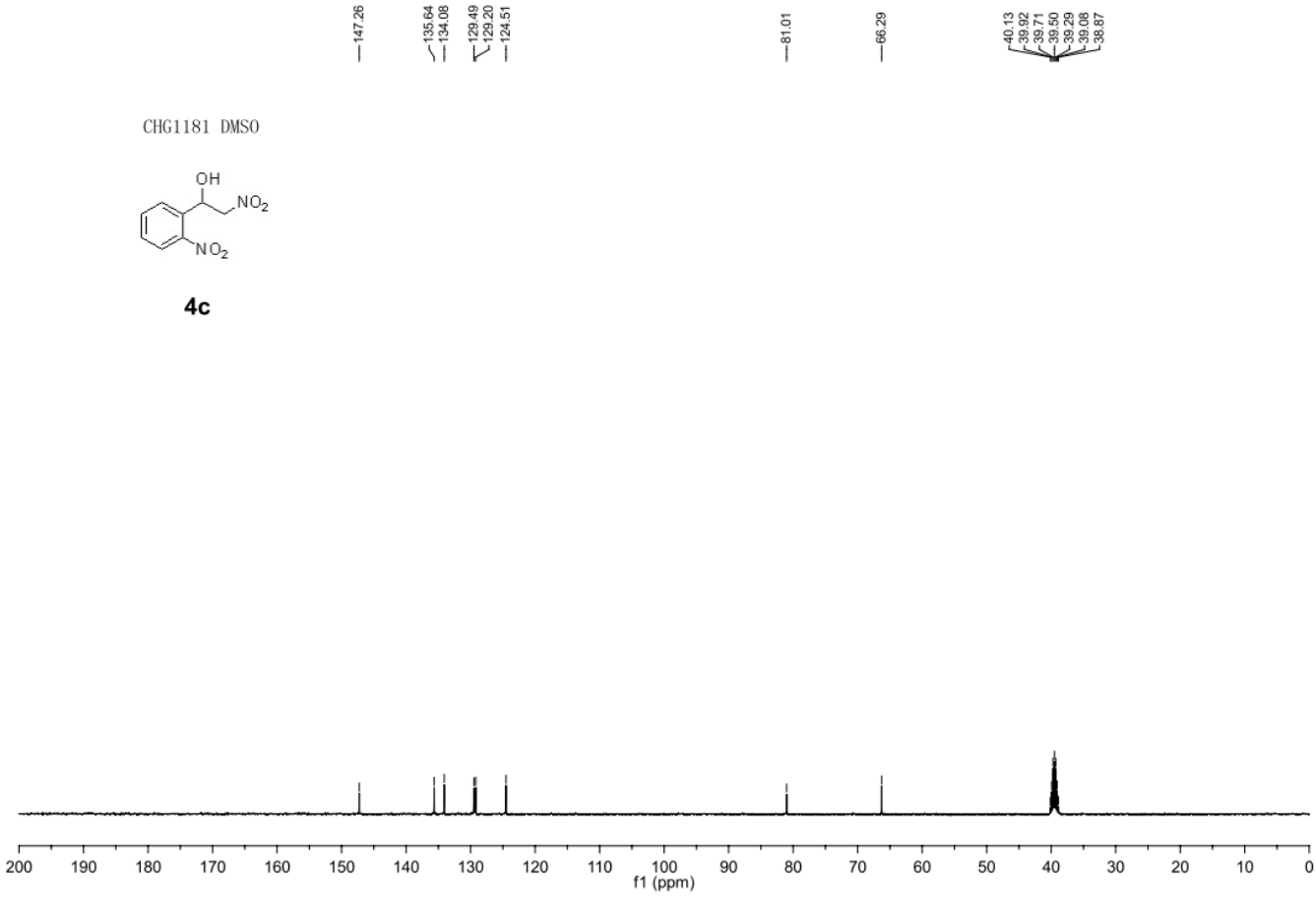
4a

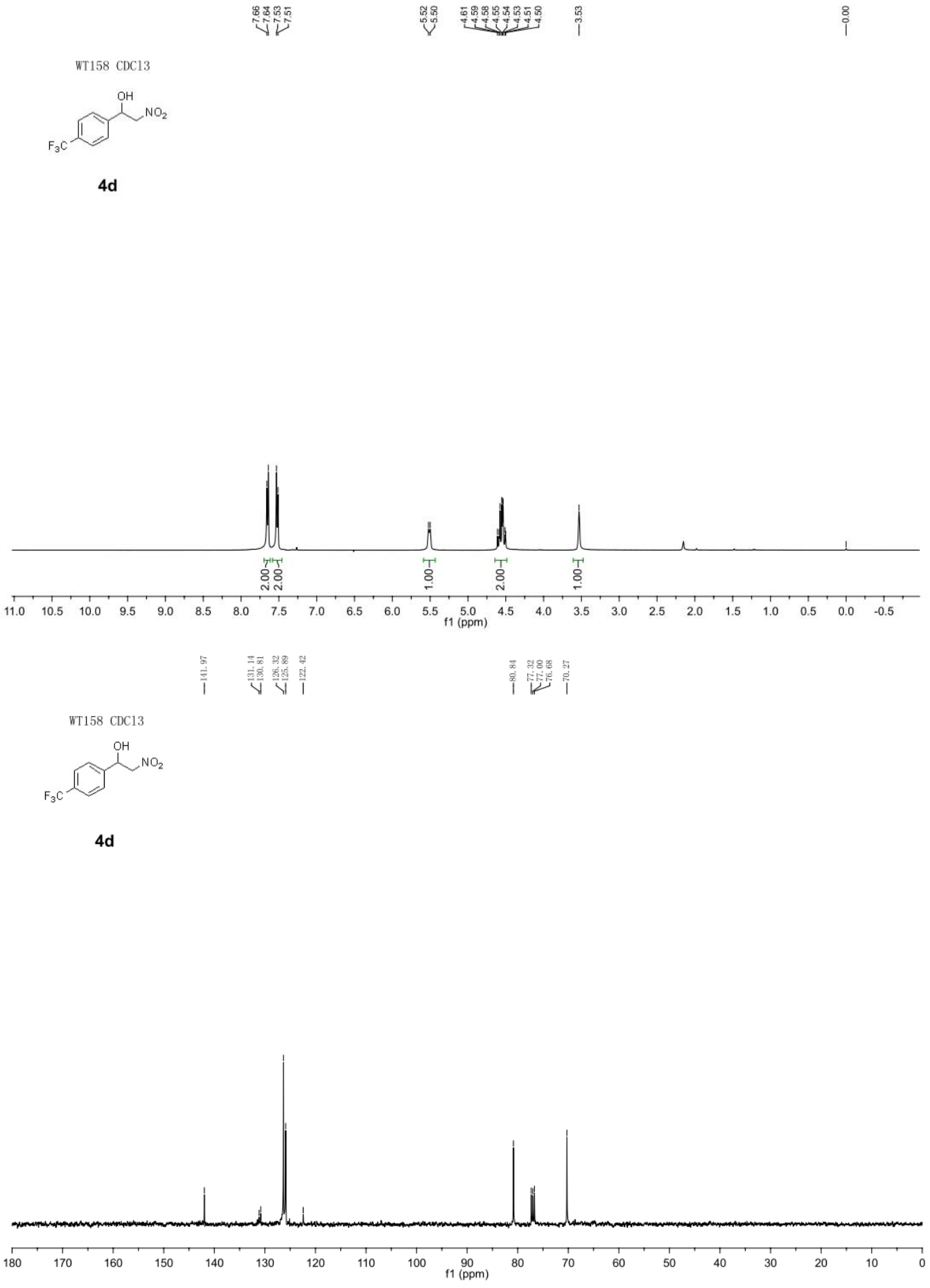


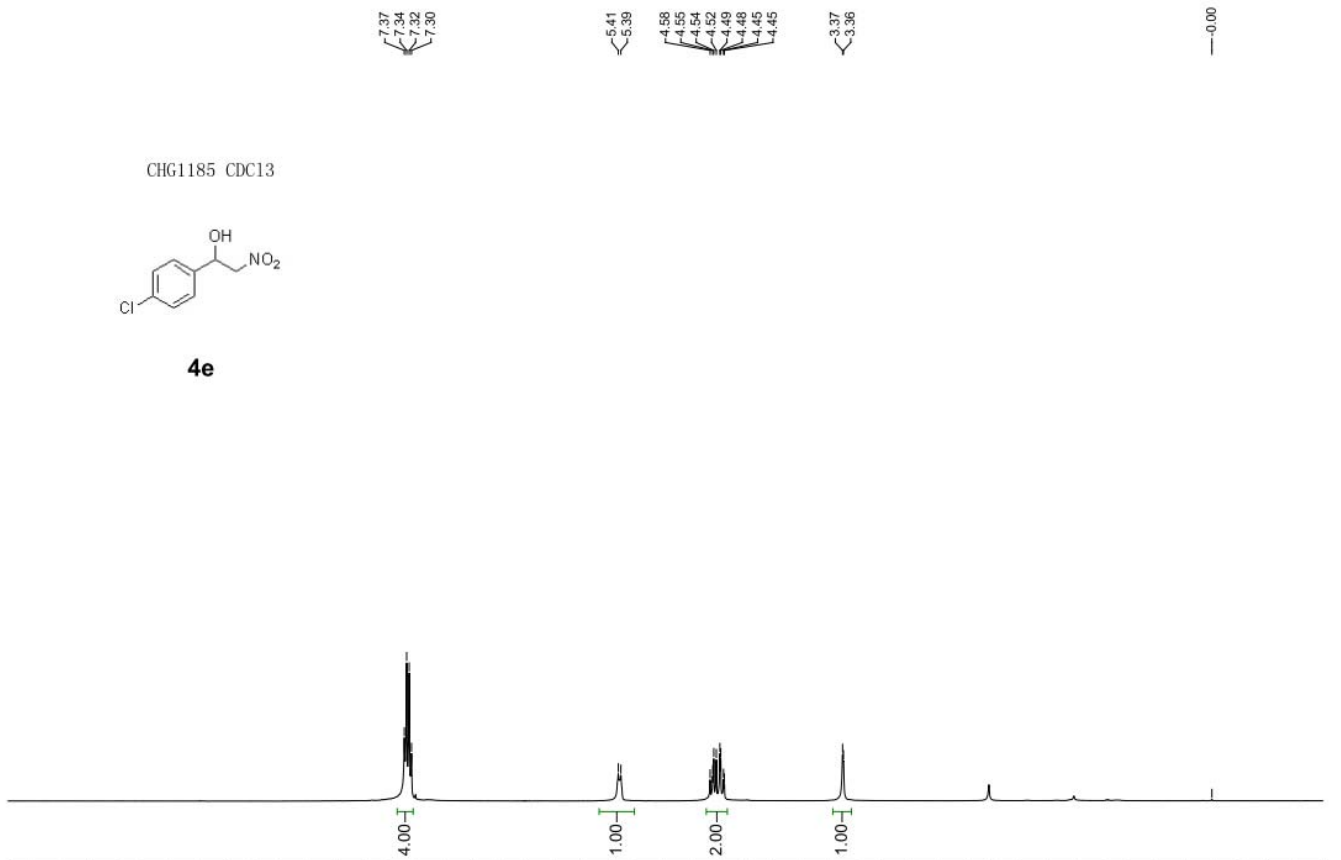

8.32
8.23
8.21
7.79
7.77
7.64
7.62
7.60
5.63
5.62
5.61
4.67
4.64
4.62
4.62
4.62
4.59
4.58
3.40
3.39
0.00
CHG1182 CDC13
OH
NO2
NO2
4b
1.00
1.00
1.00
1.00
1.00
2.00
1.00
f1 (ppm)

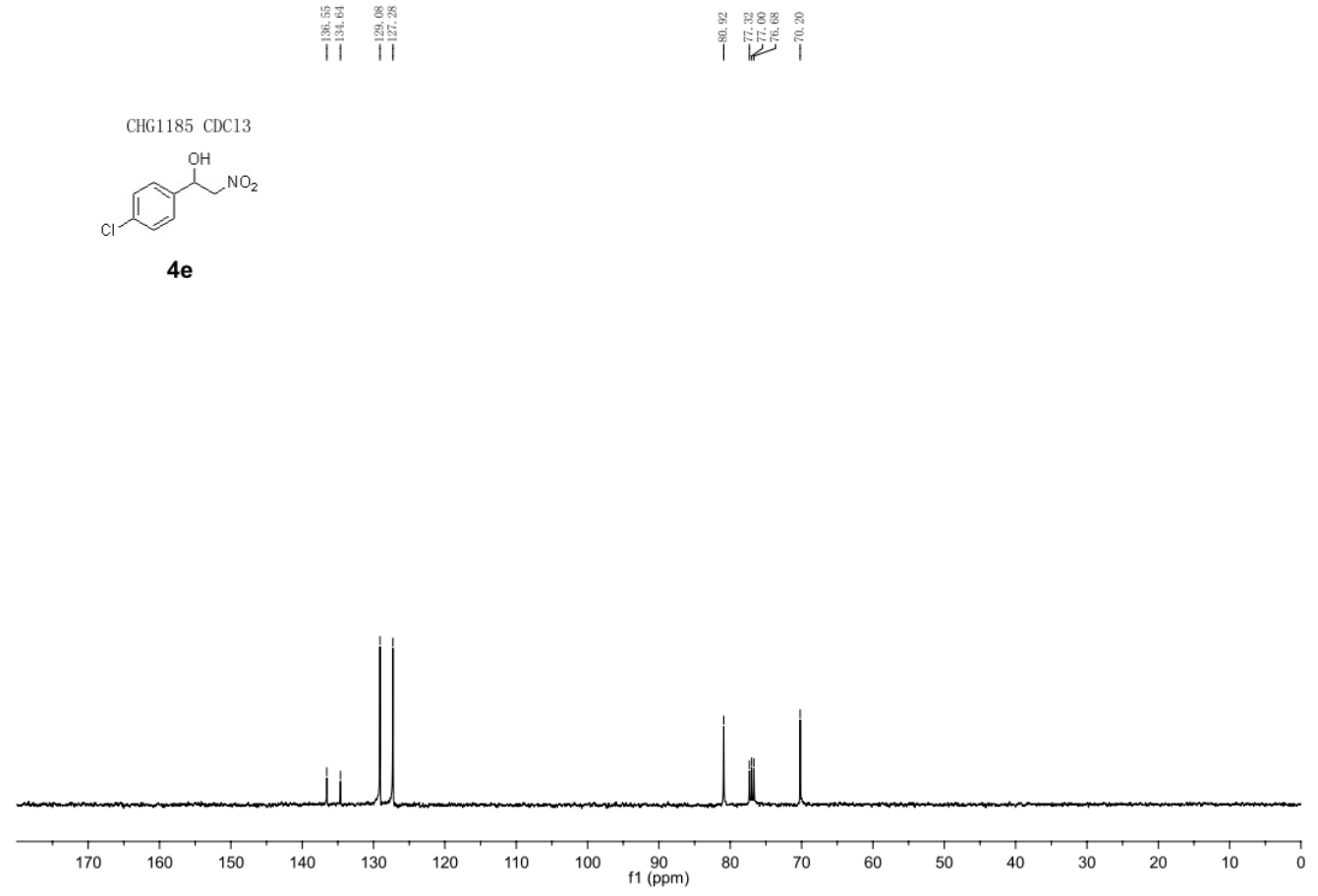

148.50
140.25
131.99
130.08
123.75
121.10
80.66
77.32
77.00
76.68
69.80
CHG1182 CDC13
OH
NO2
NO2
4b
f1 (ppm)

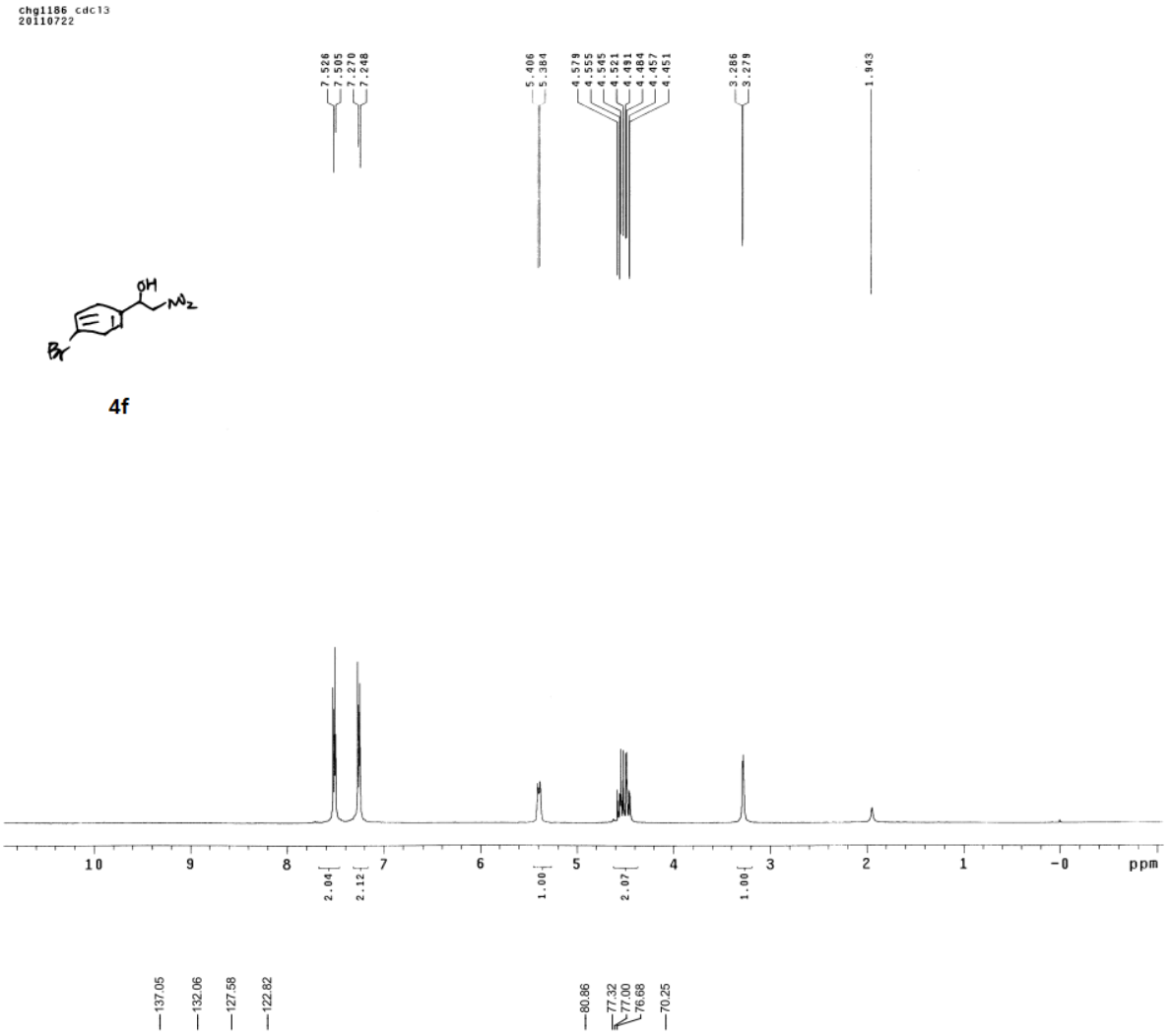

8.06
8.04
7.94
7.92
7.83
7.81
7.79
7.63
7.61
7.59
6.44
5.84
5.82
5.00
4.99
4.96
4.96
4.64
4.62
4.61
4.58
3.48
2.50
CHG1181 DMSO
OH
NO2
NO2
4c
1.00
1.00
1.00
1.00
0.96
1.00
0.99
1.00
f1 (ppm)


147.26
135.64
134.08
129.49
129.20
124.51
81.01
66.29
40.13
39.92
39.71
39.50
39.29
39.08
38.87
CHG1181 DMSO
OH
NO2
NO2
4c
f1 (ppm)


7.66
7.64
7.53
7.51
5.52
5.50
4.61
4.59
4.58
4.55
4.54
4.53
4.51
4.50
3.53
0.00
WT158 CDC13
OH
NO2
F3C
4d
2.00
2.00
1.00
2.00
1.00
f1 (ppm)
141.97
131.14
130.81
126.32
125.89
122.42
80.84
77.32
77.00
76.68
70.27
WT158 CDC13
OH
NO2
F3C
4d
f1 (ppm)

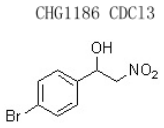

7.37
7.34
7.32
7.30
5.41
5.39
4.58
4.55
4.54
4.52
4.49
4.48
4.45
4.45
3.37
3.36
0.00
CHG1185 CDC13
OH
NO2
Cl
4e
4.00
1.00
2.00
1.00
f1 (ppm)


136.55
134.64
129.08
127.28
80.92
77.32
77.00
76.68
70.20
CHG1185 CDC13
OH
NO2
Cl
4e
f1 (ppm)

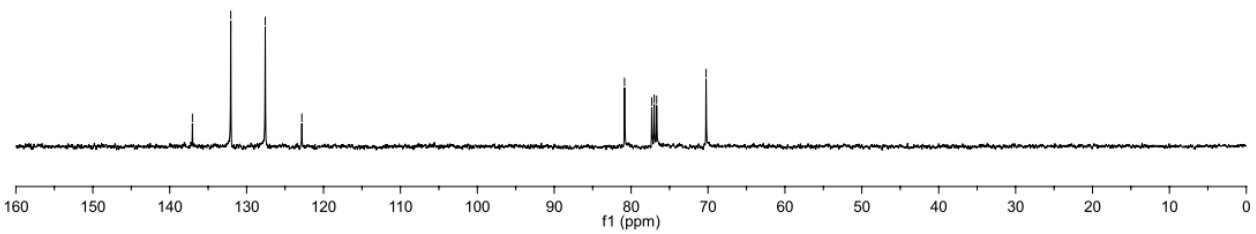

chg1186 cdcl3
20110722
7.526
7.505
7.270
7.248
5.406
5.384
4.579
4.555
4.545
4.521
4.491
4.484
4.457
4.451
3.286
3.279
1.943
OH
NO2
Br
10
9
8
7
6
5
4
3
2
1
-0
ppm
2.04
2.12
1.00
2.07
1.00

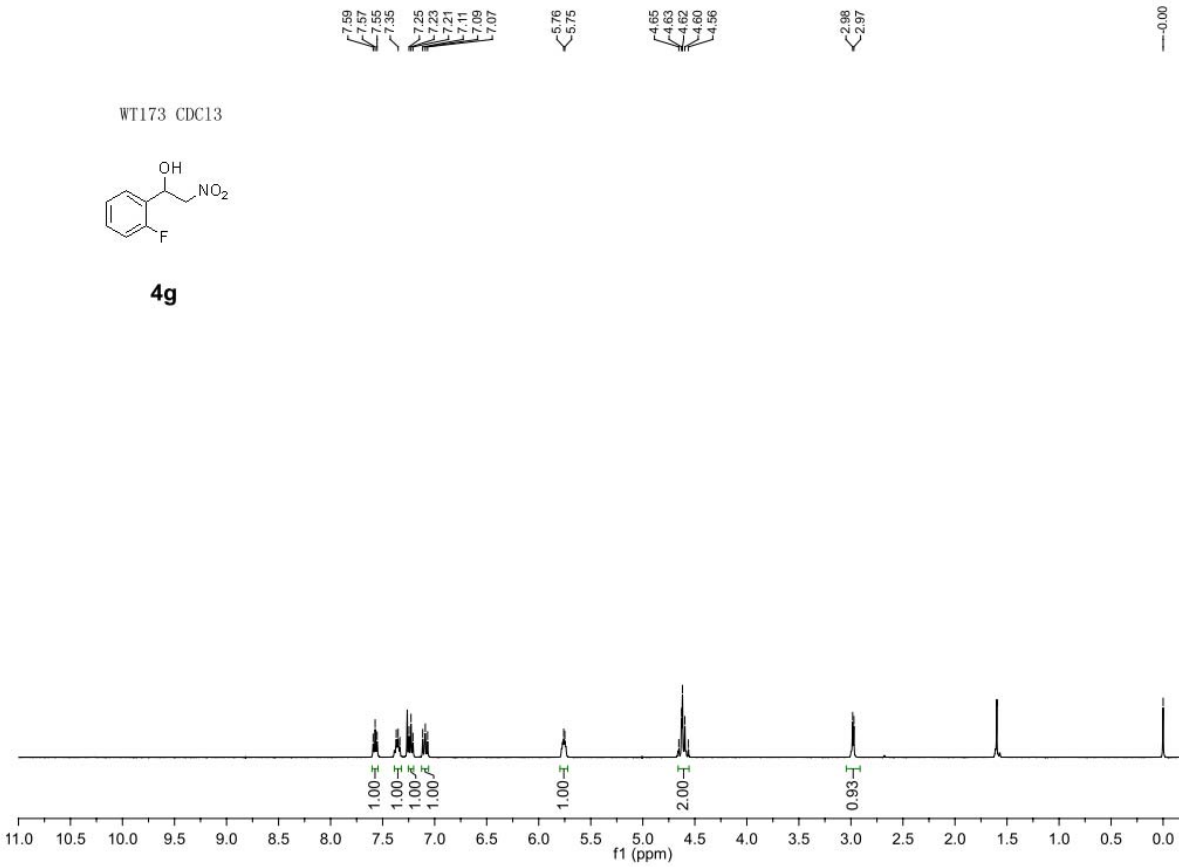
4f

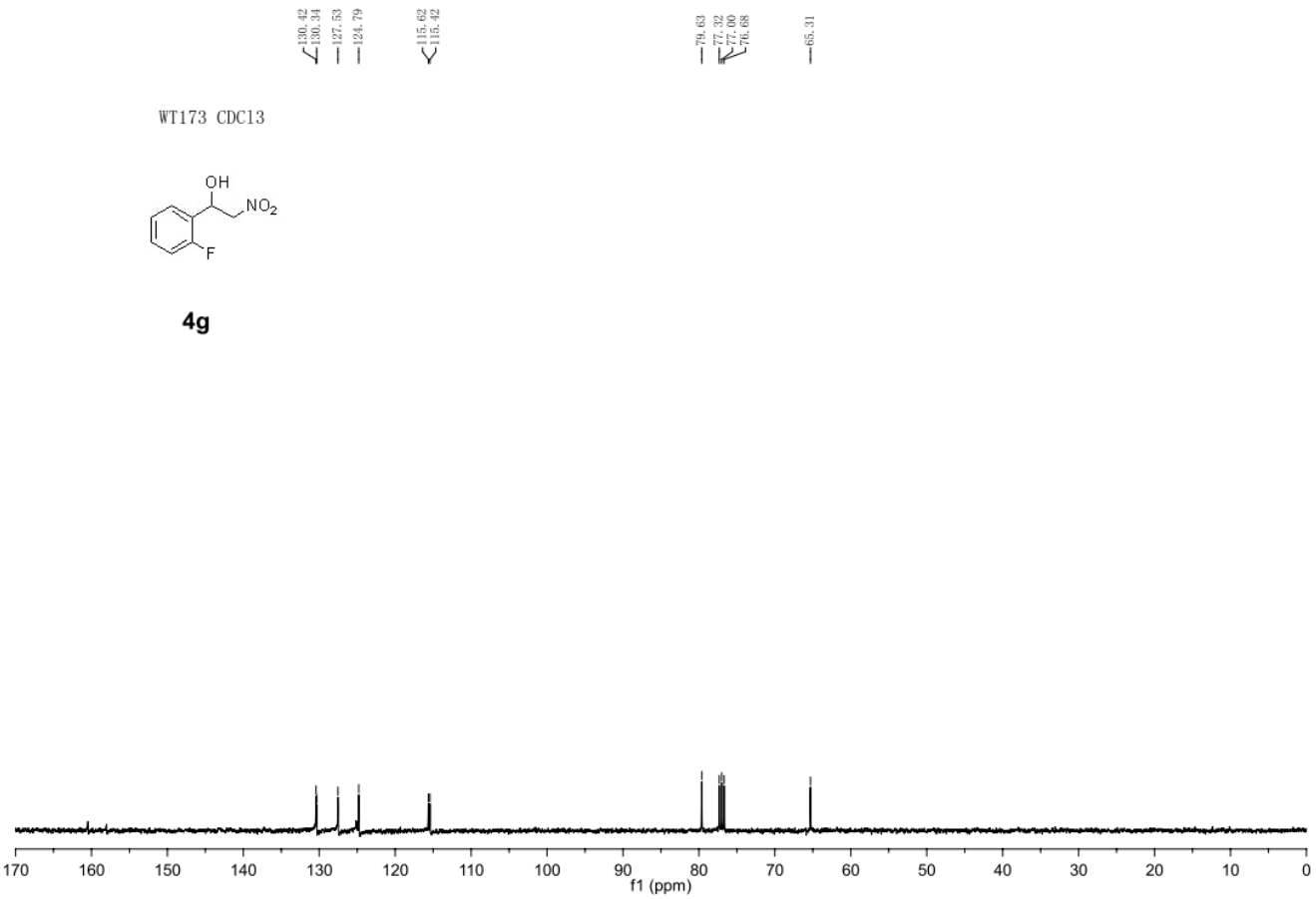
137.05
132.06
127.58
122.82
80.86
77.32
77.00
76.68
70.25

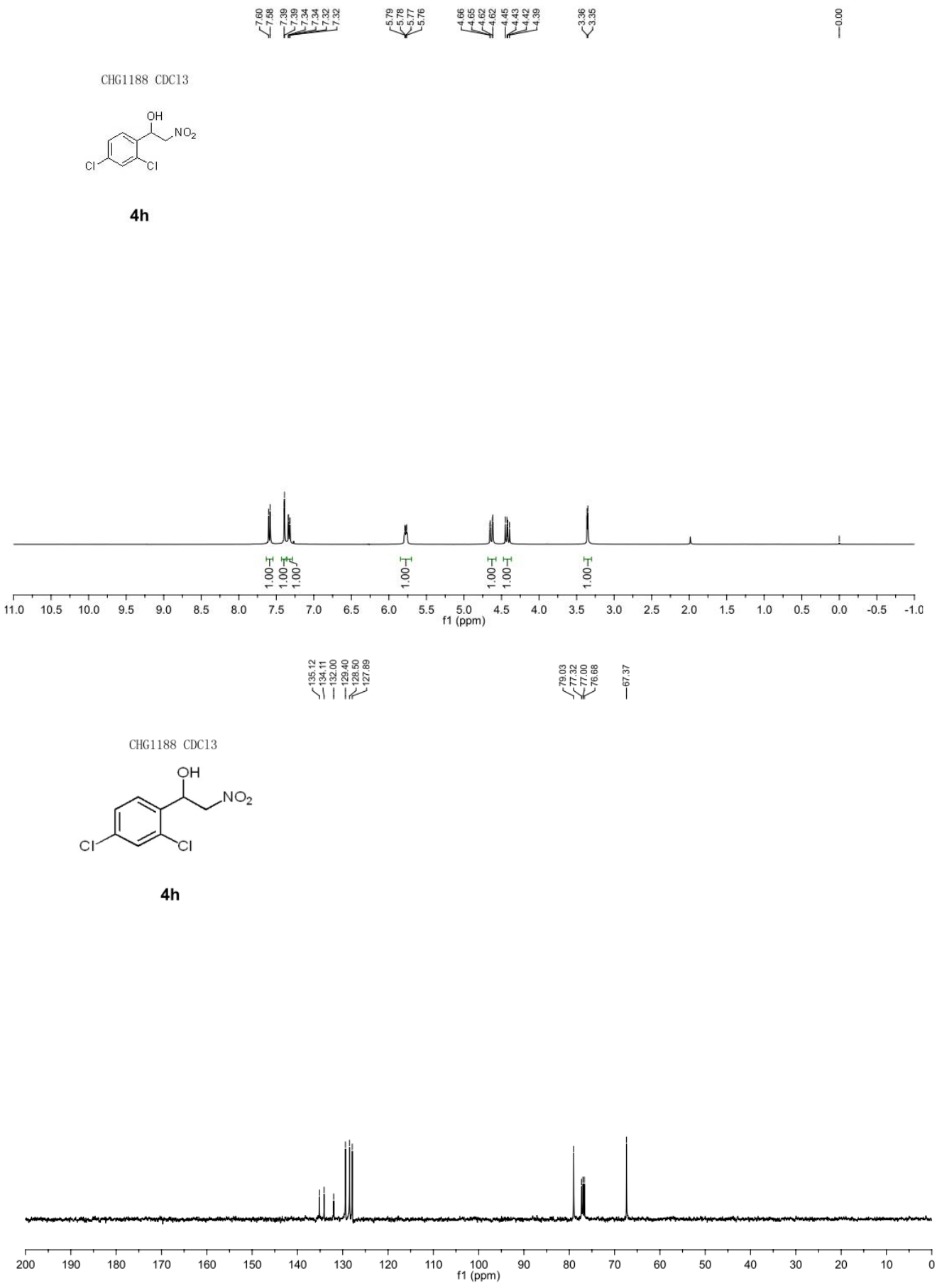

CHG1186 CDCl3
OH
NO2
Br

4f

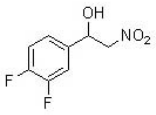

160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.59
7.57
7.55
7.35
7.25
7.23
7.21
7.11
7.09
7.07
5.76
5.75
4.65
4.63
4.62
4.60
4.56
2.98
2.97
0.00
WT173 CDCl3
OH
NO2
F
4g
1.00
1.00
1.00
1.00
1.00
2.00
0.93
f1 (ppm)

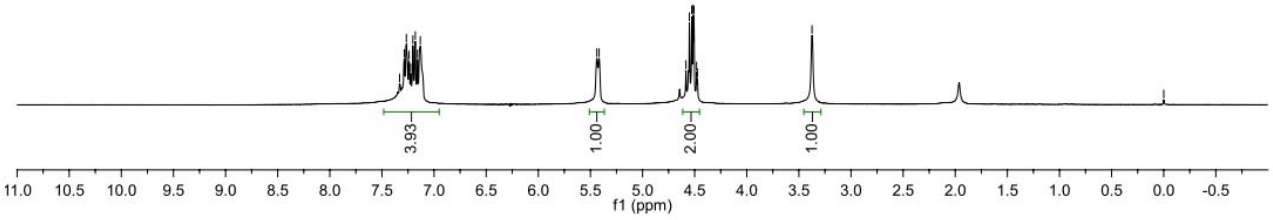

130.42
130.34
127.53
124.79
115.62
115.42
79.63
77.32
77.00
76.68
65.31
WT173 CDCl3
OH
NO2
F
4g
f1 (ppm)


7.60
7.58
7.39
7.39
7.34
7.34
7.32
7.32
5.79
5.78
5.77
5.76
4.66
4.65
4.62
4.62
4.45
4.43
4.42
4.39
3.36
3.35
0.00
CHG1188 CDCl3
OH
NO2
Cl
Cl
4h
1.00
1.00
1.00
1.00
1.00
1.00
1.00
f1 (ppm)
135.12
134.11
132.00
129.40
128.50
127.89
79.03
77.32
77.00
76.68
67.37
CHG1188 CDCl3
OH
NO2
Cl
Cl
4h
f1 (ppm)

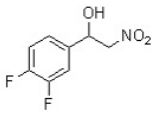
CHG1189 CDC13



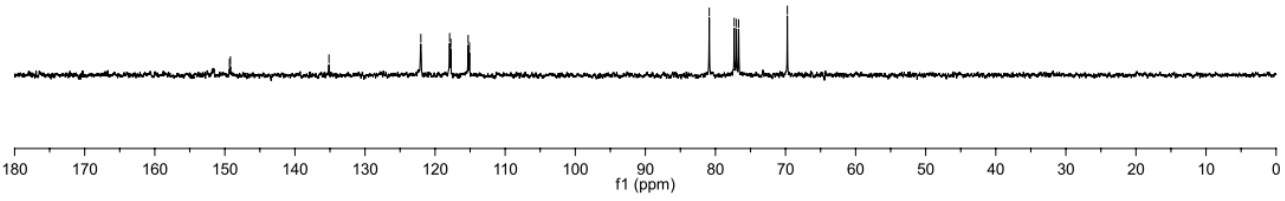
4i

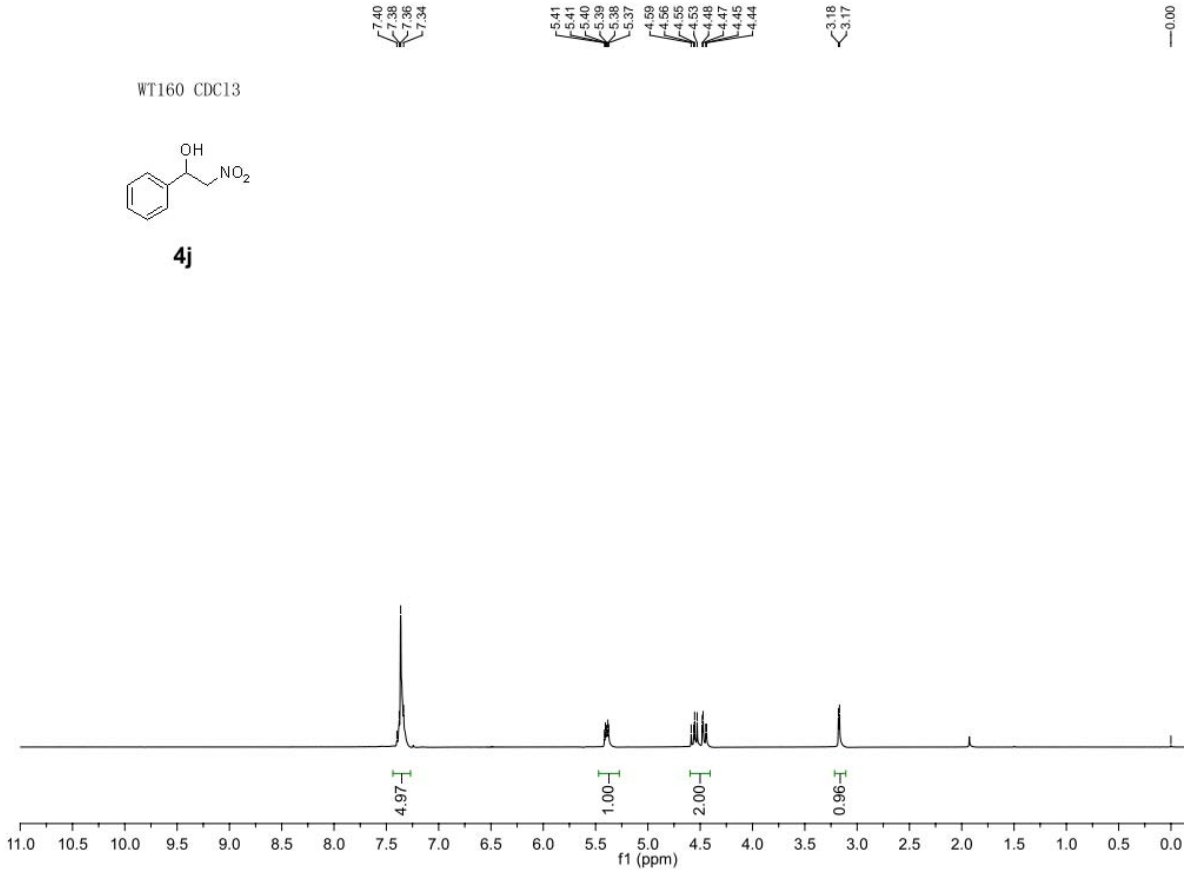


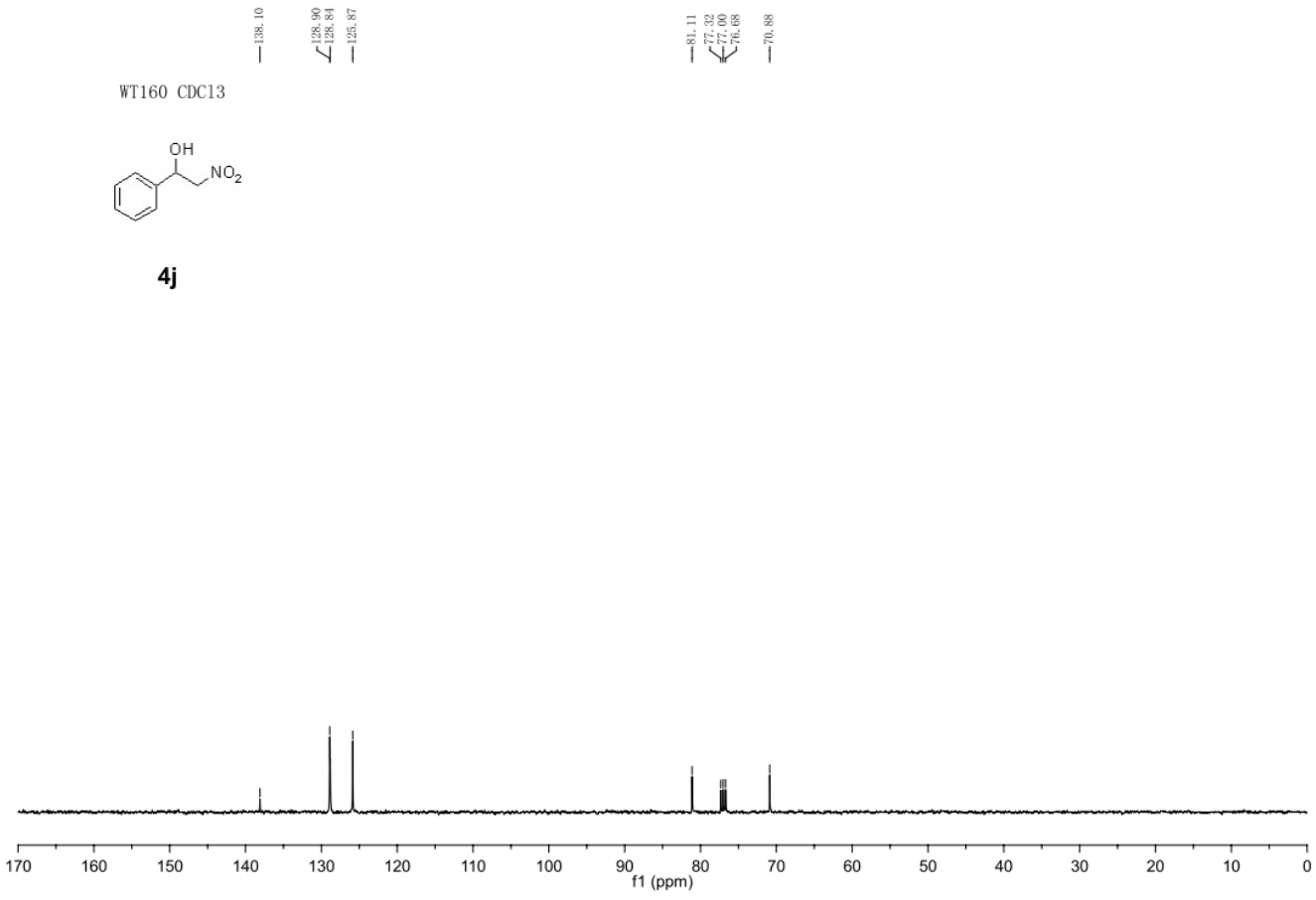
CHG1189 CDC13

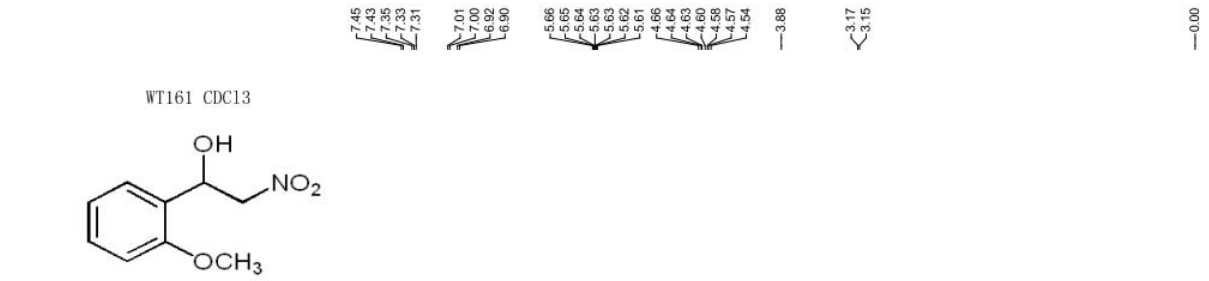


4i



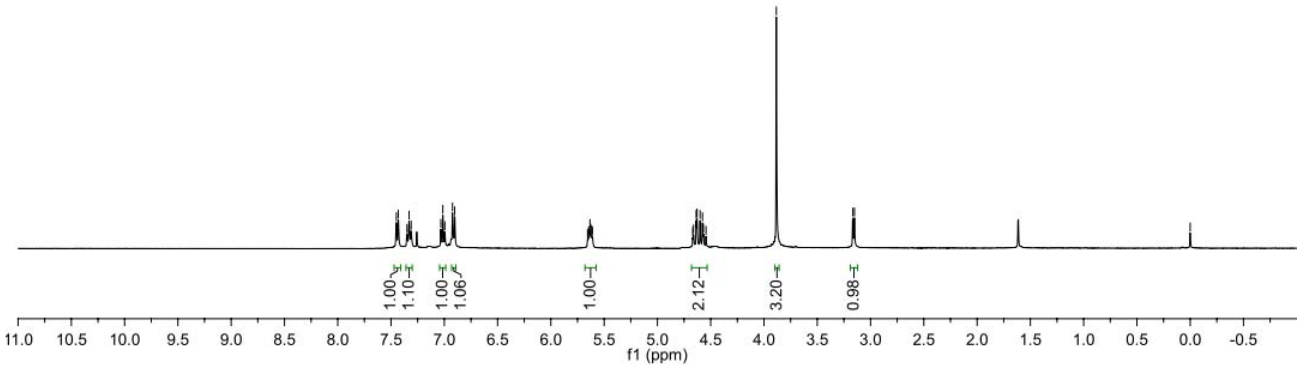

7.40
7.38
7.36
7.34
5.41
5.41
5.40
5.39
5.38
5.37
4.59
4.56
4.55
4.53
4.48
4.47
4.45
4.44
3.18
3.17
0.00
WT160 CDCl3
OH
NO2
4j
4.97
1.00
2.00
0.96
f1 (ppm)


138.10
128.90
128.84
125.87
81.11
77.32
77.00
76.68
70.88
WT160 CDCl3
OH
NO2
4j
f1 (ppm)

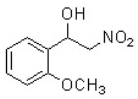


WT161 CDCl3

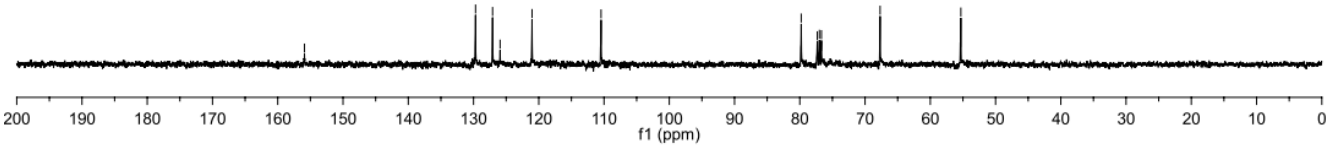
4k

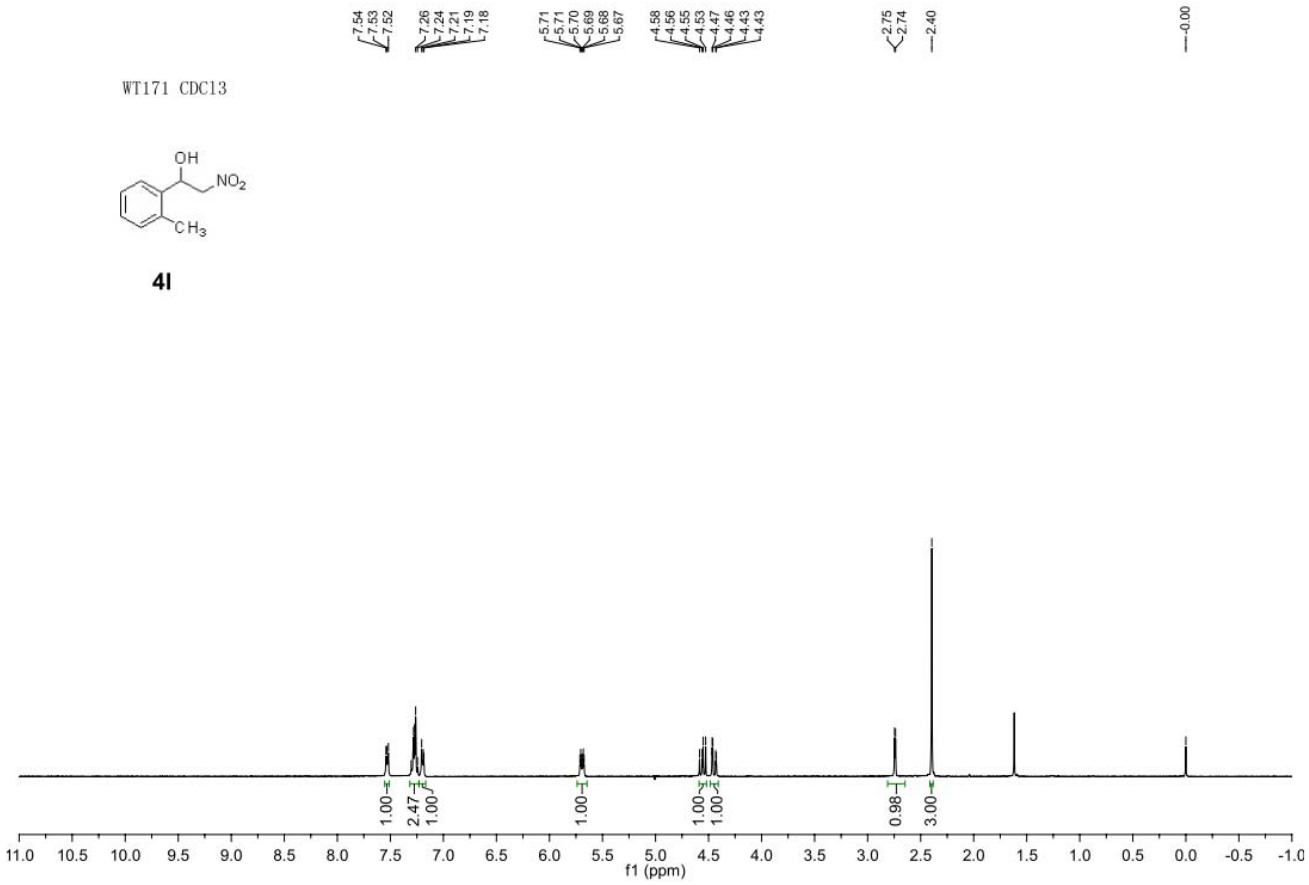


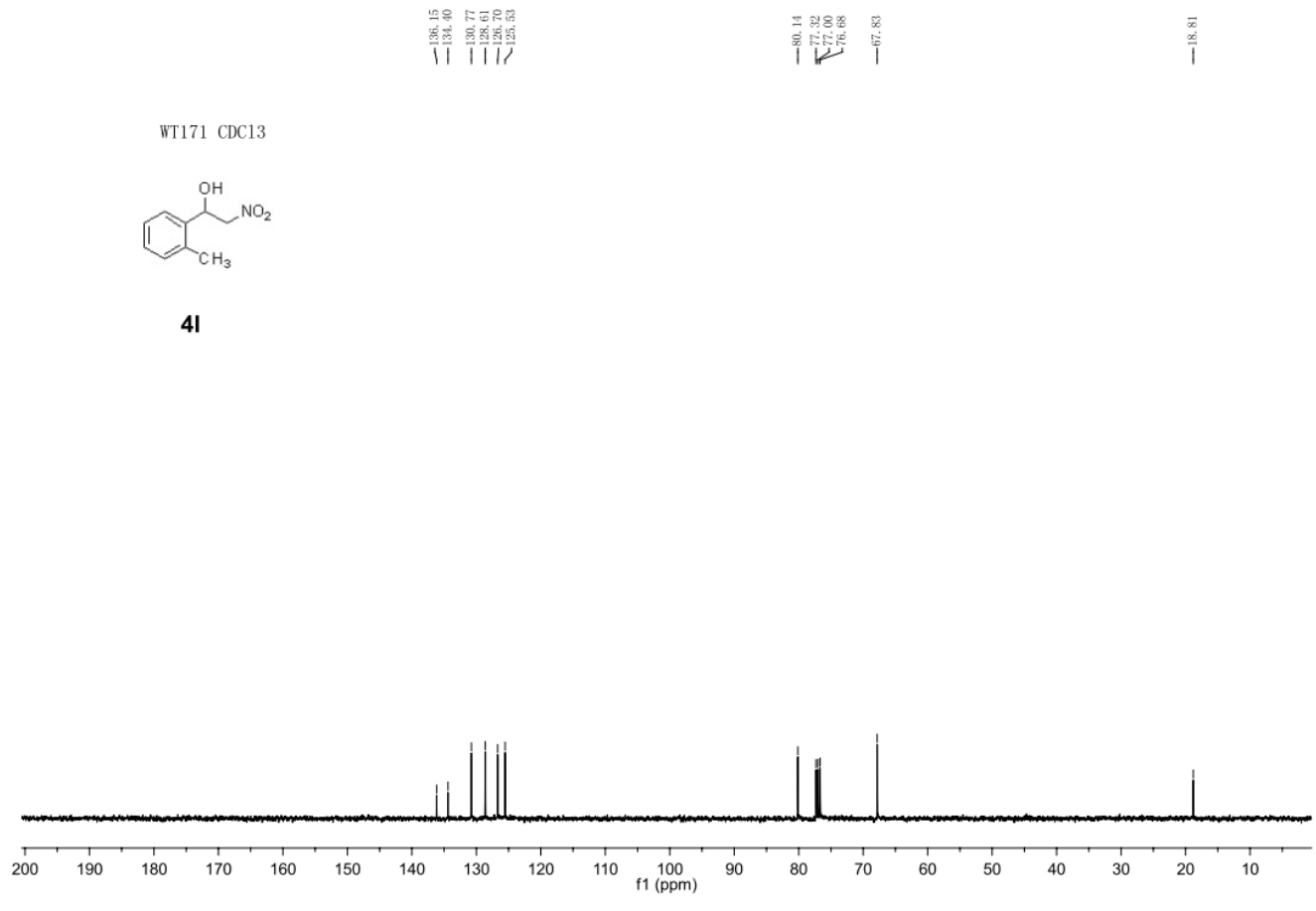
WT161 CDCl3

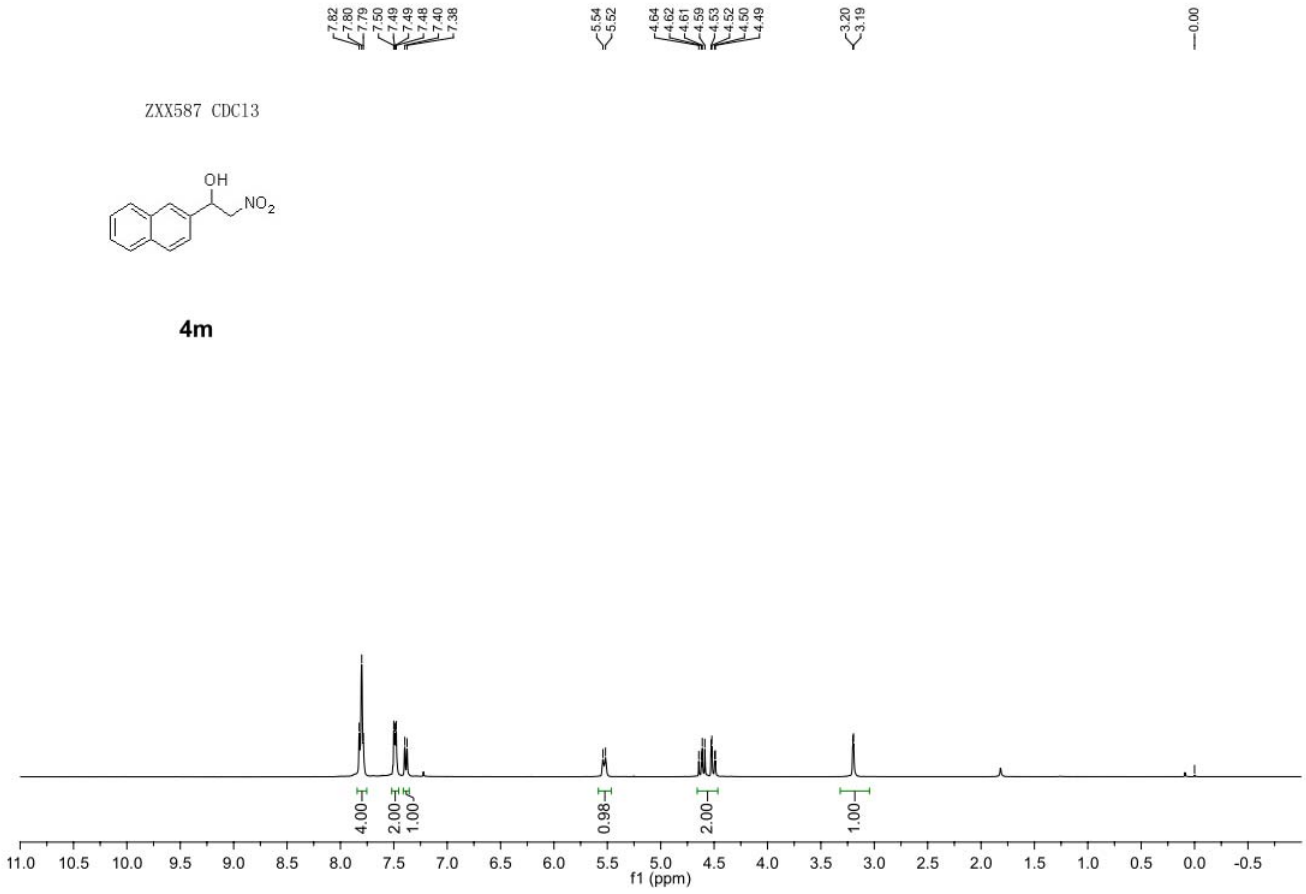


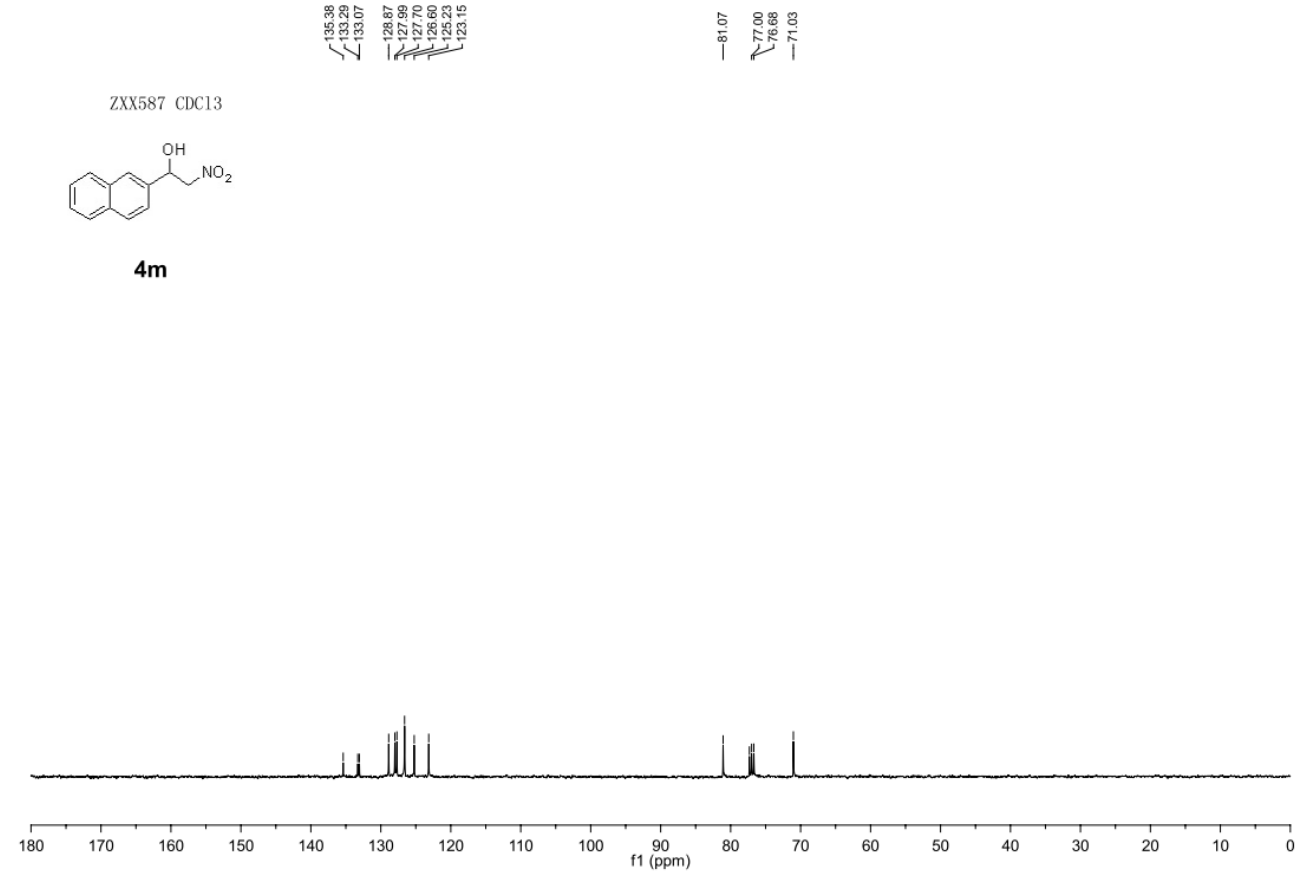
4k

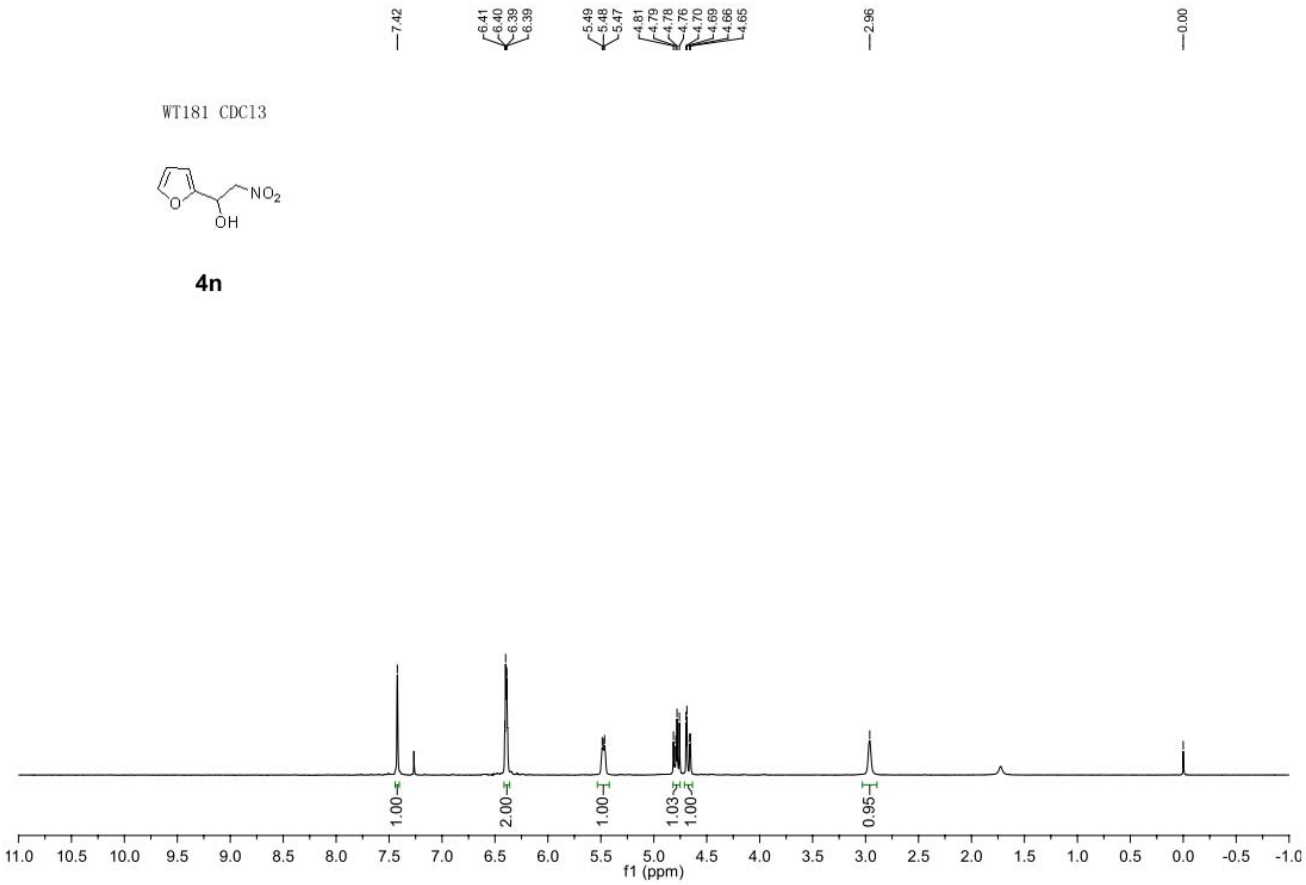


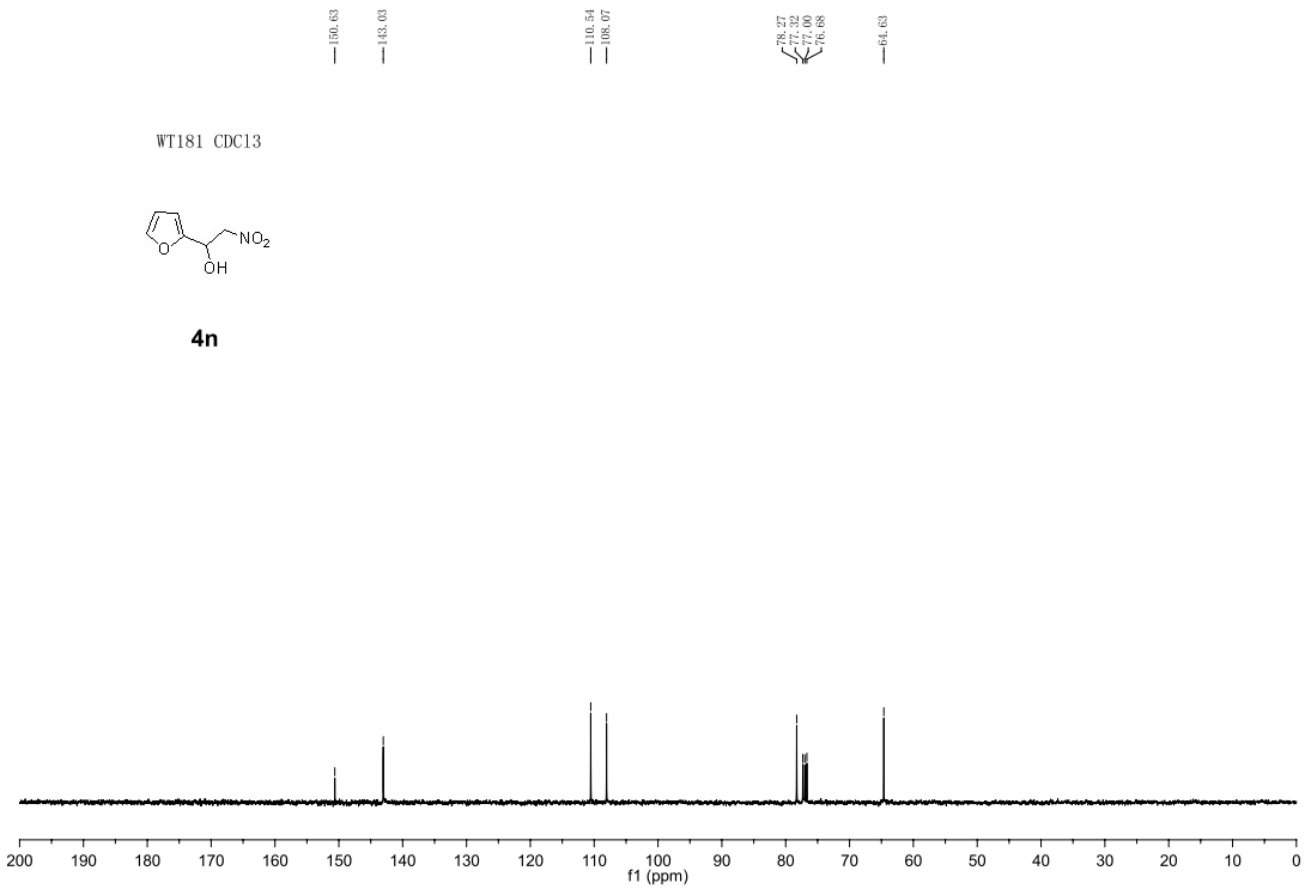

7.54
7.53
7.52
7.26
7.24
7.21
7.19
7.18
5.71
5.71
5.70
5.69
5.68
5.67
4.58
4.56
4.55
4.53
4.47
4.46
4.43
4.43
2.75
2.74
2.40
0.00
WT171 CDC13
OH
NO2
CH3
4l
1.00
2.47
1.00
1.00
1.00
1.00
0.98
3.00
f1 (ppm)

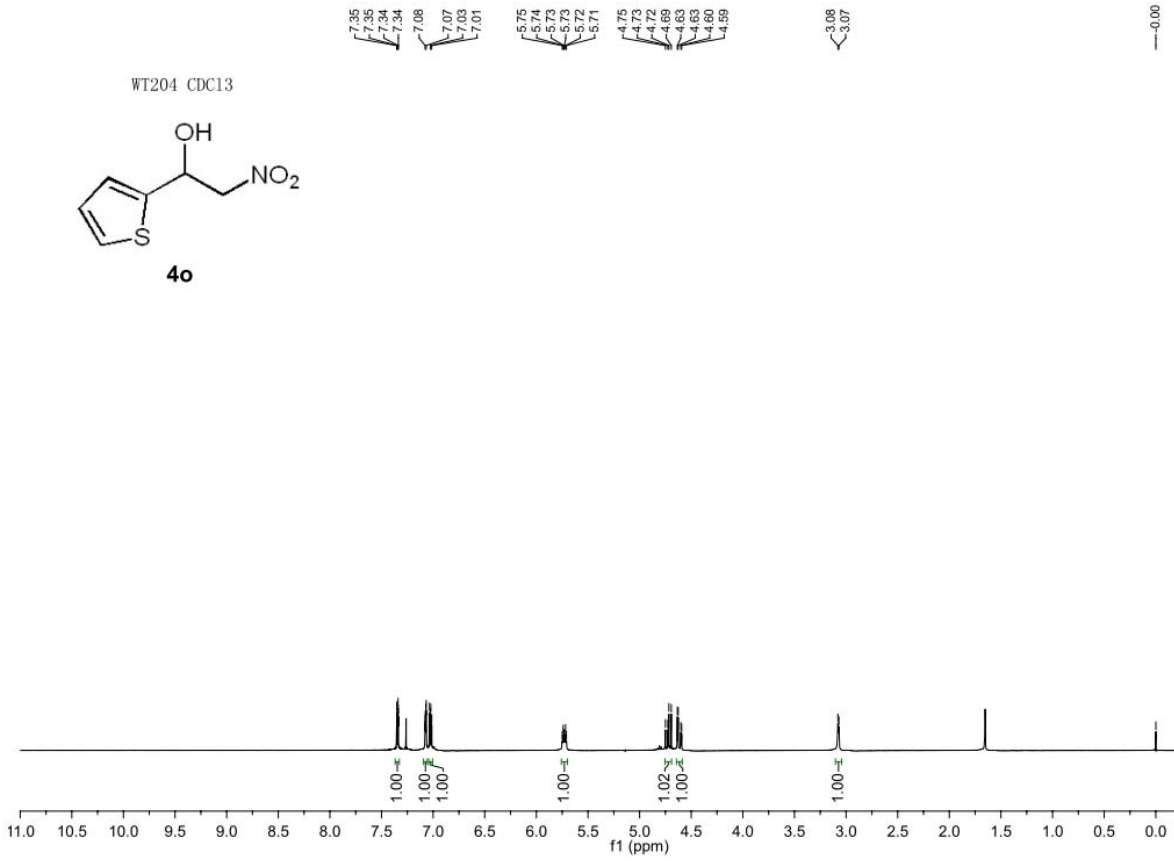

136.15
134.40
130.77
128.61
126.70
125.53
80.14
77.32
77.00
76.68
67.83
18.81
WT171 CDC13
OH
NO2
CH3
4l
f1 (ppm)

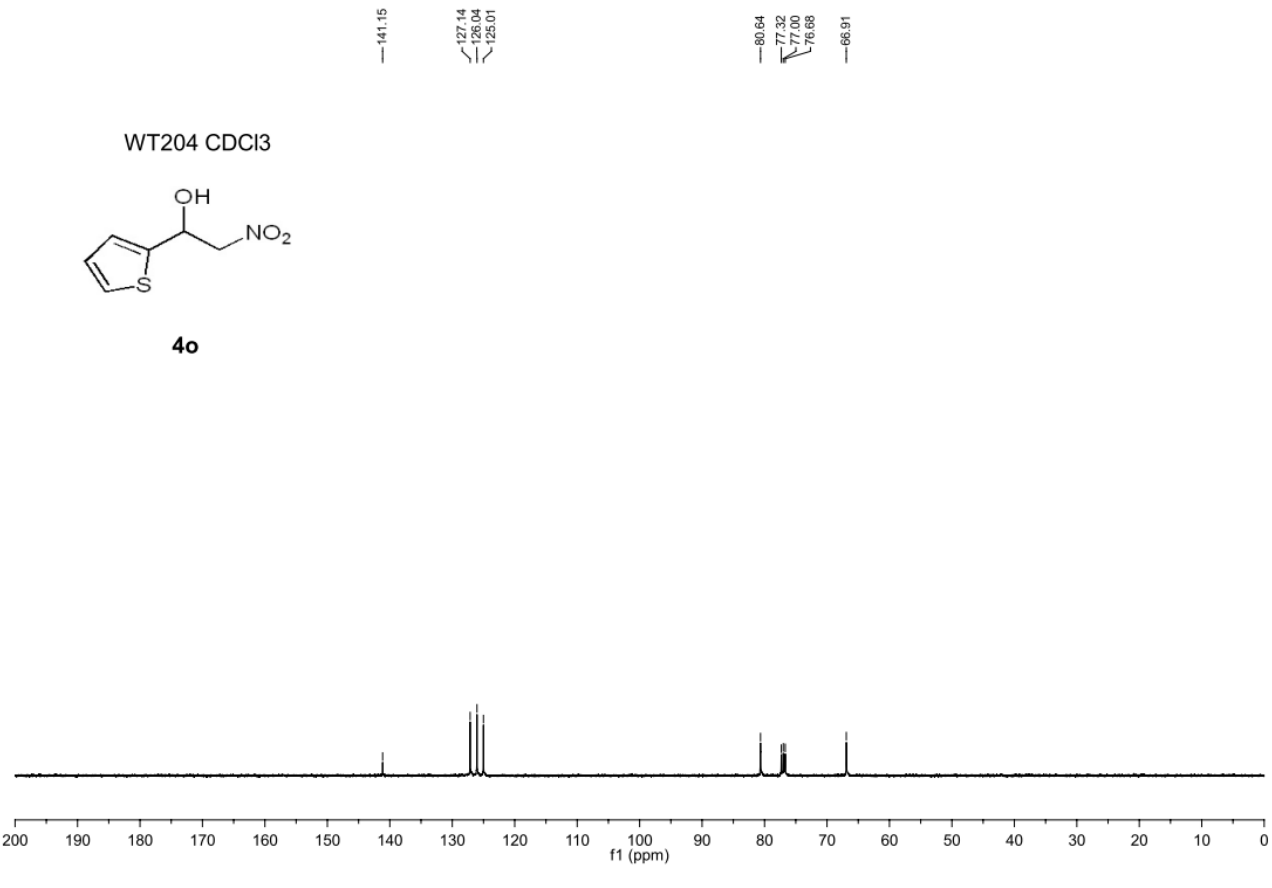

7.82
7.80
7.79
7.50
7.49
7.49
7.48
7.40
7.38
5.54
5.52
4.64
4.62
4.61
4.59
4.53
4.52
4.50
4.49
3.20
3.19
0.00
ZXX587 CDC13
OH
NO2
4m
4.00
2.00
1.00
0.98
2.00
1.00
f1 (ppm)


135.38
133.29
133.07
128.87
127.99
127.70
126.60
125.23
123.15
81.07
77.00
76.68
71.03
ZXX587 CDC13
OH
NO2
4m
f1 (ppm)

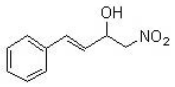

7.42
6.41
6.40
6.39
6.39
5.49
5.48
5.47
4.81
4.79
4.78
4.76
4.70
4.69
4.66
4.65
2.96
0.00
WT181 CDCl3
NO2
OH
4n
1.00
2.00
1.00
1.03
1.00
0.95
f1 (ppm)


150.63
143.03
110.54
108.07
78.27
77.32
77.00
76.68
64.63
WT181 CDCl3
NO2
OH
4n
f1 (ppm)

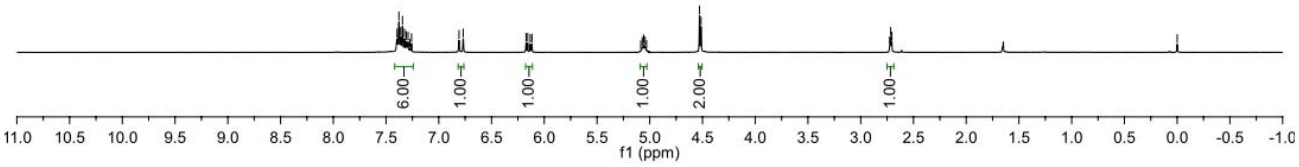

WT204 CDC13
OH
NO2
S
4o
7.35
7.35
7.34
7.34
7.08
7.07
7.03
7.01
5.75
5.74
5.73
5.73
5.72
5.71
4.75
4.73
4.72
4.69
4.63
4.63
4.60
4.59
3.08
3.07
0.00
1.00
1.00
1.00
1.00
1.02
1.00
1.00
f1 (ppm)


WT204 CDCl3
OH
NO2
S
4o
141.15
127.14
126.04
125.01
80.64
77.32
77.00
76.68
66.91
f1 (ppm)

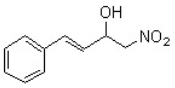
WT174 CDC13



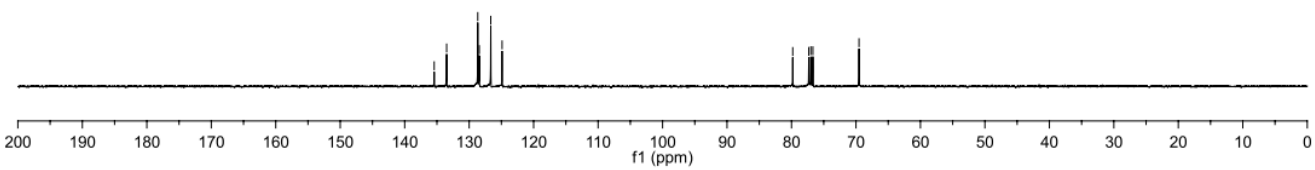
4p



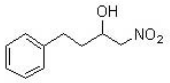
WT174 CDC13



4p



WT165 CDCl3



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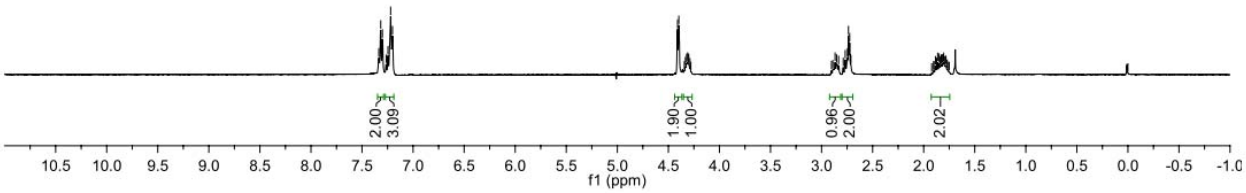
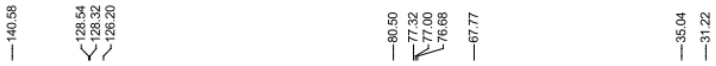
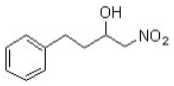




WT165 CDCl3



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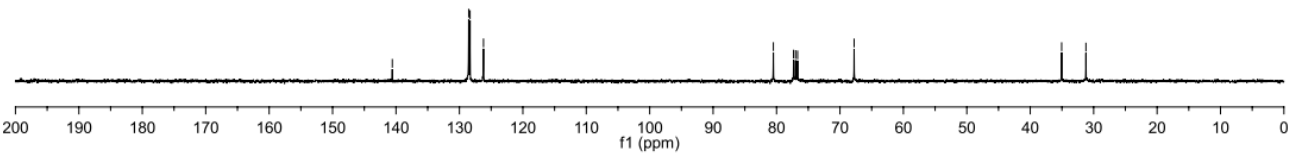

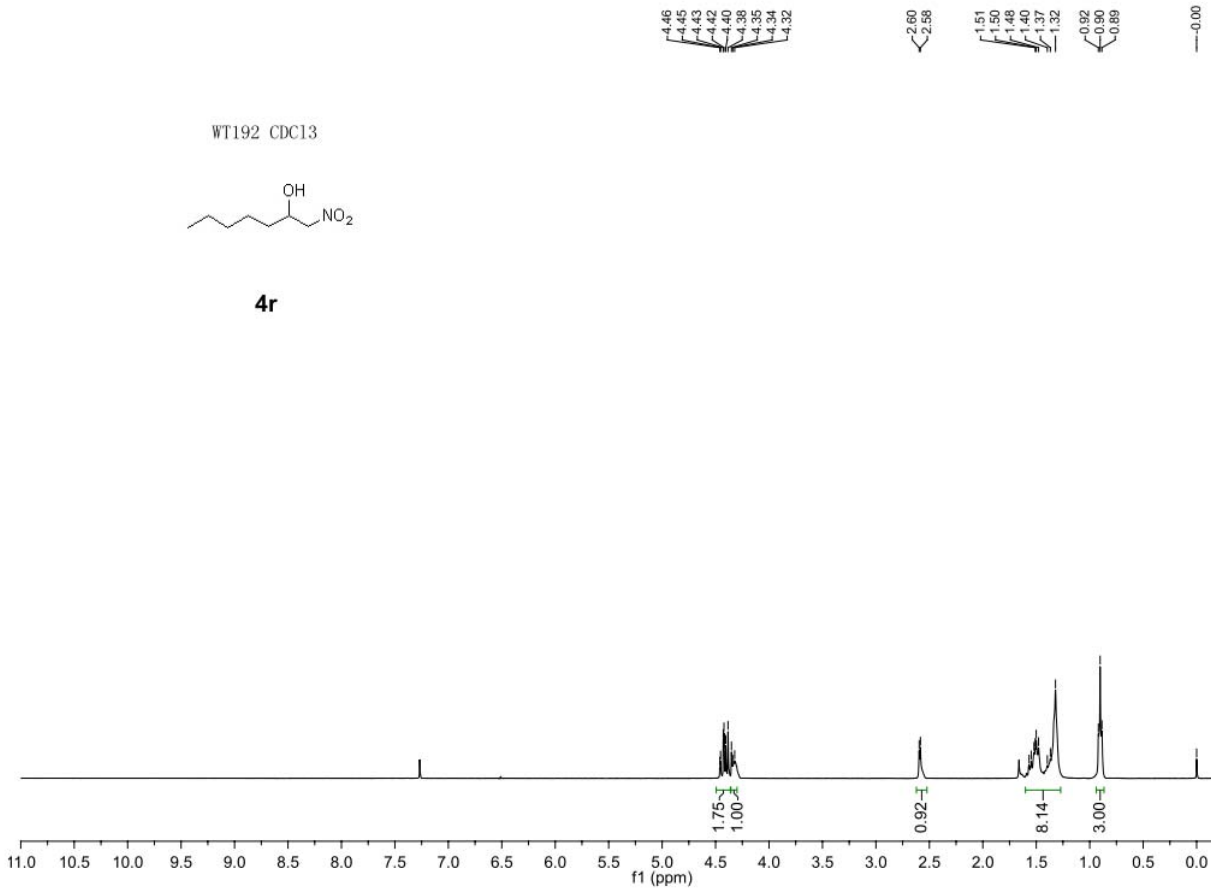
4.46
4.45
4.43
4.42
4.40
4.38
4.35
4.34
4.32
2.60
2.58
1.51
1.50
1.48
1.40
1.37
1.32
0.92
0.90
0.89
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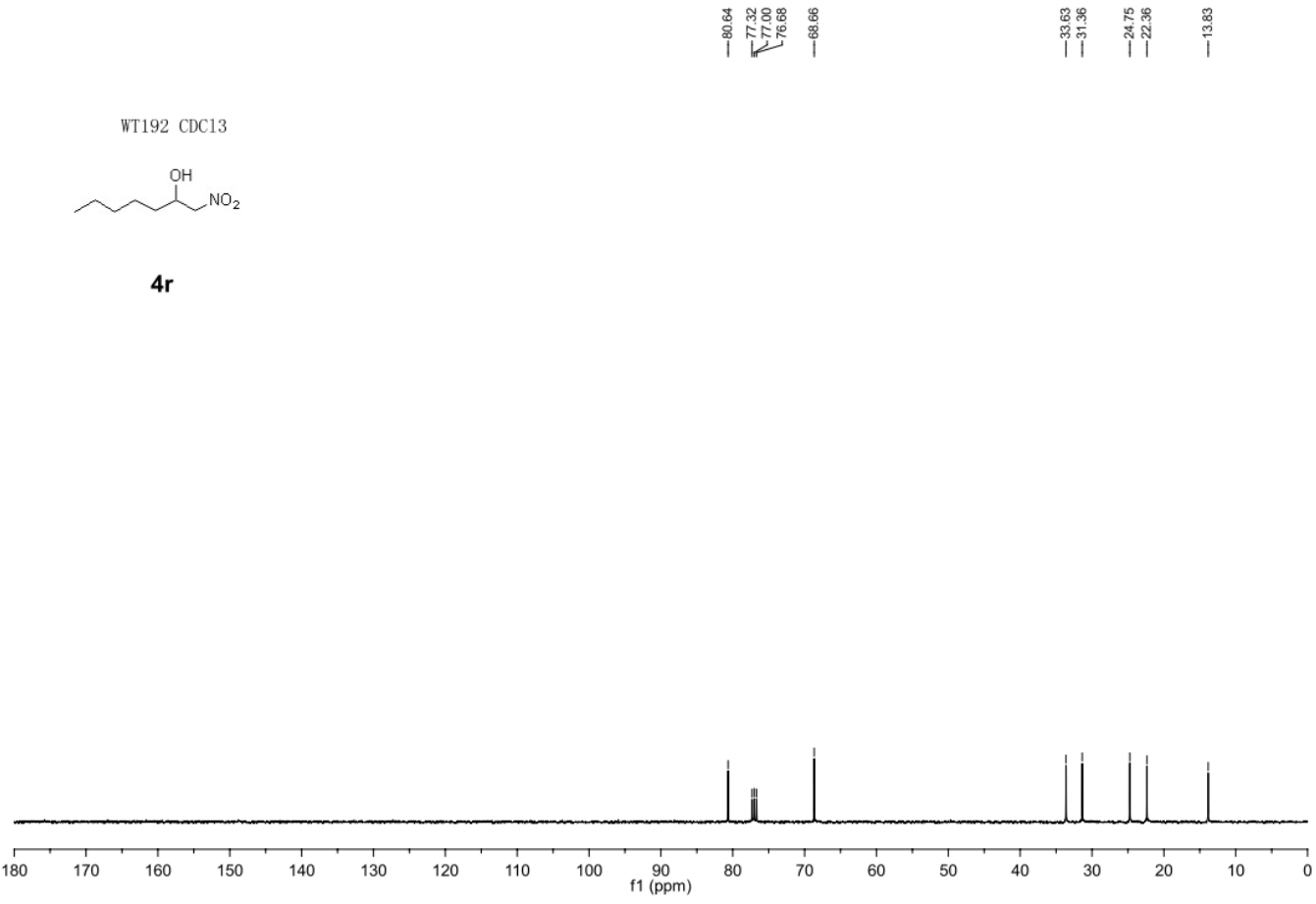
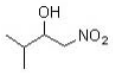
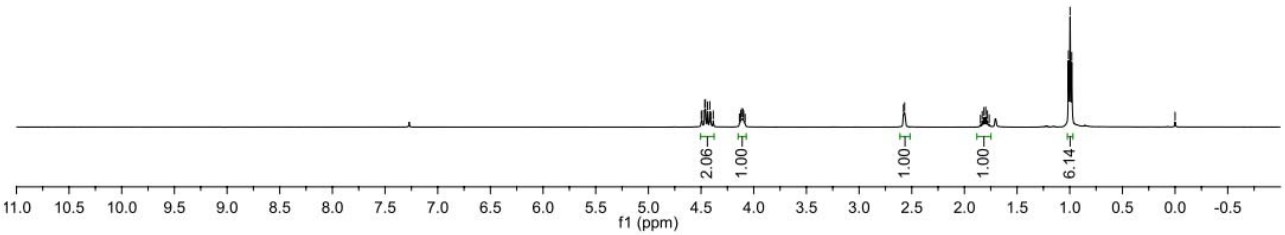
WT192 CDC13
OH
NO2
4r
1.75
1.00
0.92
8.14
3.00
f1 (ppm)


80.64
77.32
77.00
76.68
68.66
33.63
31.36
24.75
22.36
13.83
WT192 CDC13
OH
NO2
4r
f1 (ppm)

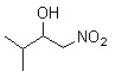
WT163 CDCl3



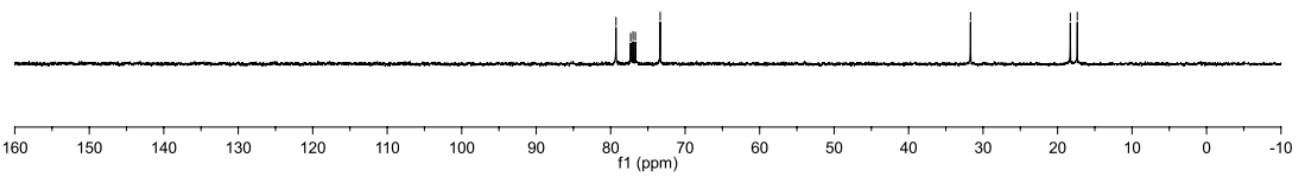
4s



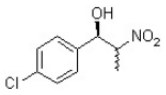
WT163 CDCl3



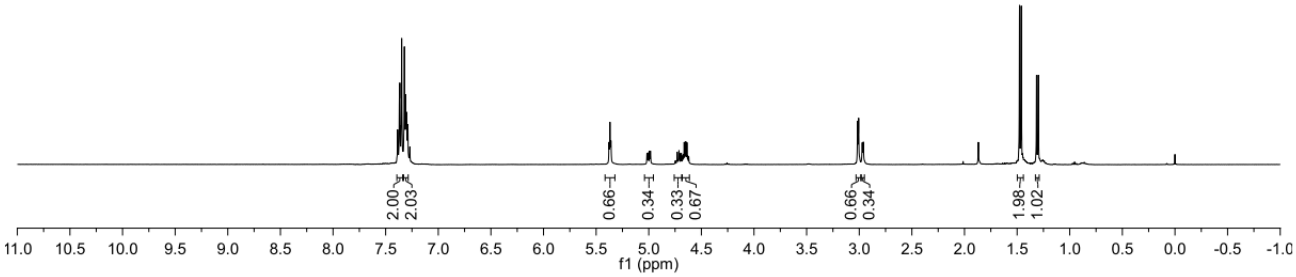
4s

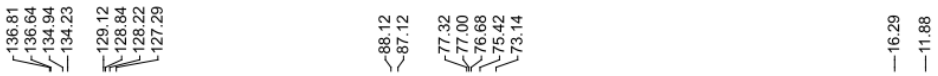


CHG1387 CDCl3

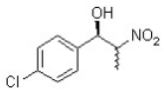


4t





CHG1387 CDCl3



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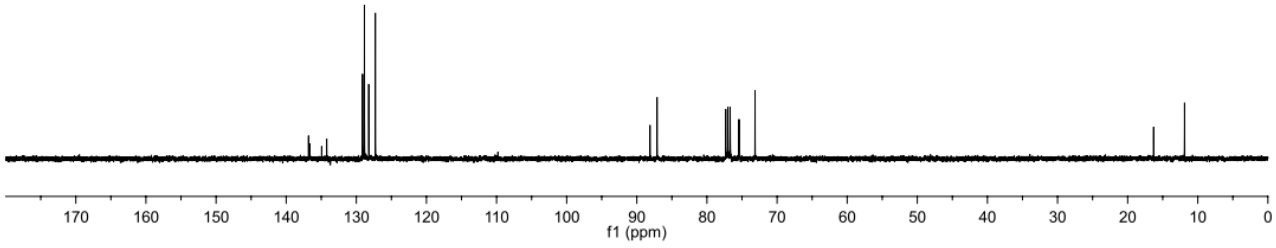
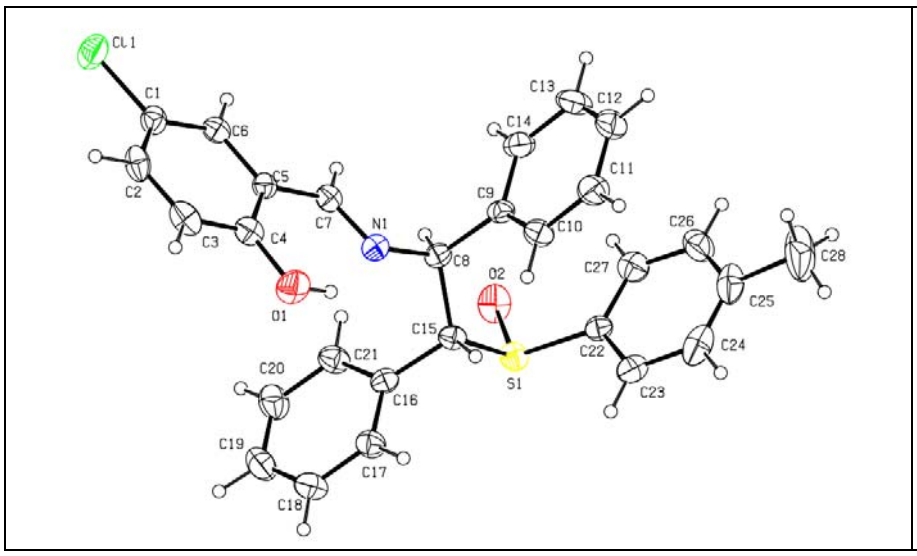
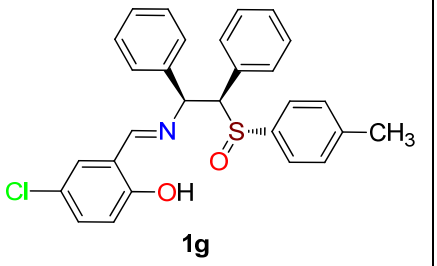


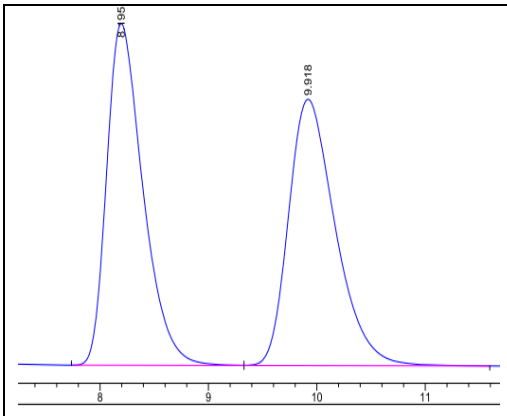
6. X-Ray Structure of Ligand 1g

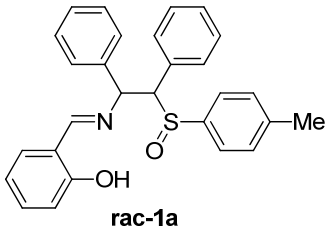




1g

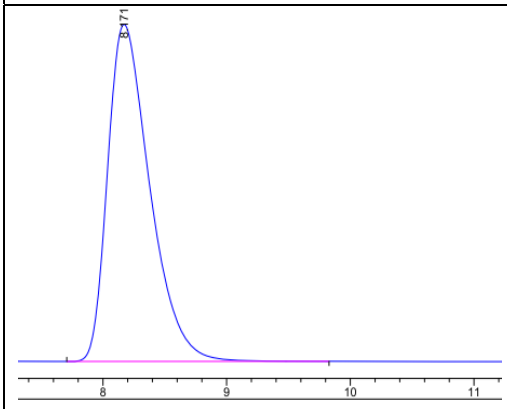
7. Copies of HPLC Chromatograms

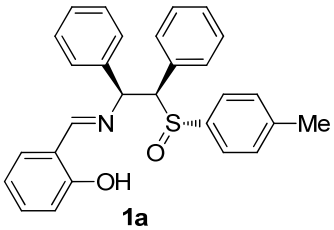




rac-1a

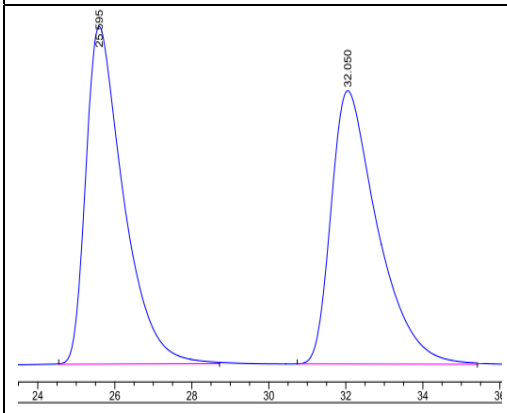
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.195	VV	0.3541	1.12789e4	485.40530	49.8858
2	9.918	VB	0.4586	1.13306e4	378.37656	50.1142

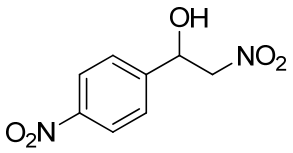




1a

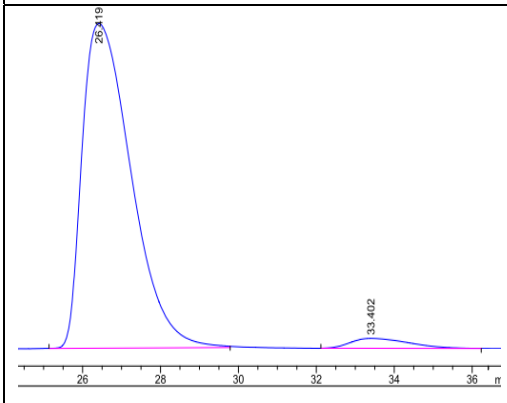
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.171	VB	0.3625	2.92398e4	1233.20239	100.0000

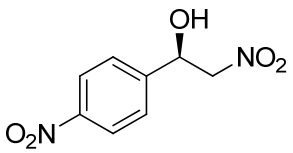




rac-4a

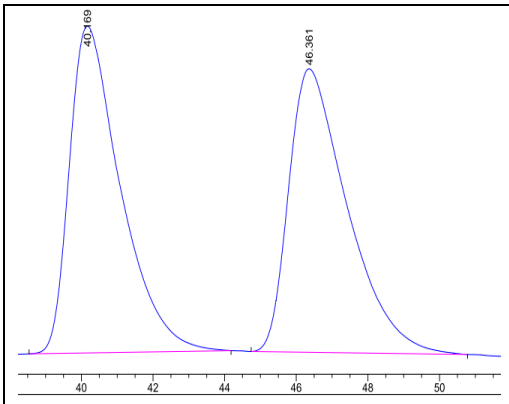
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	25.595	BB	1.0083	1.33865e4	196.99080	50.0796
2	32.050	BB	1.2444	1.33439e4	159.42043	49.9204

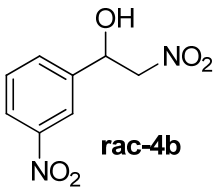




4a

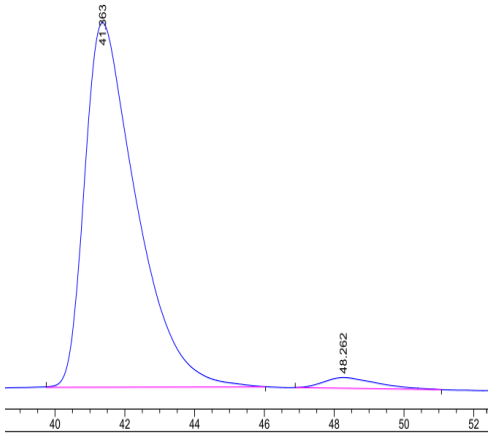
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	26.419	BB	1.3868	1.74625e4	199.74876	96.4519
2	33.402	PB	1.6202	642.38300	6.15151	3.5481

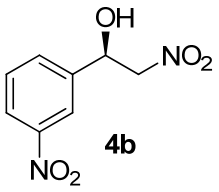




rac-4b

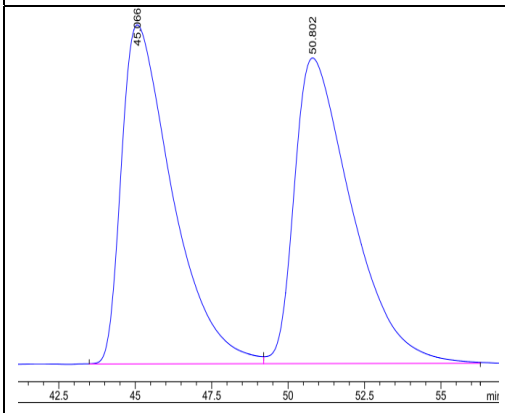
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	40.169	BB	1.4694	1.82319e4	183.94449	50.1071
2	46.361	PB	1.6385	1.81540e4	159.61436	49.8929

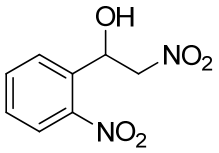




4b

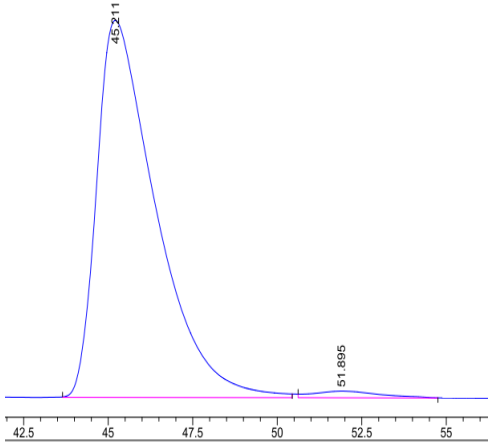
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	41.363	BB	1.4925	2.36665e4	228.72639	97.0561
2	48.262	BB	1.2586	717.83838	6.74766	2.9439

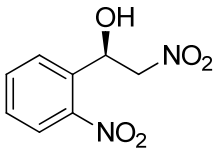




rac-4c

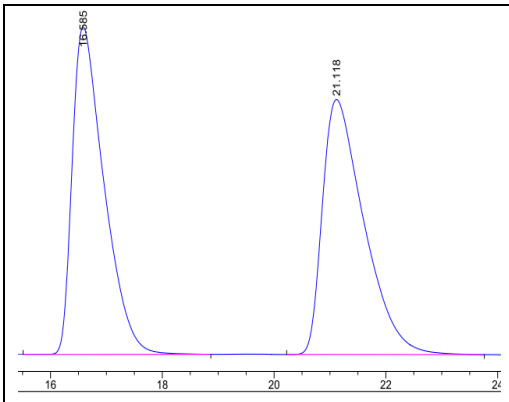
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	45.066	BV	1.7683	2.28133e4	196.45657	49.7050
2	50.802	VB	1.9230	2.30841e4	177.04944	50.2950

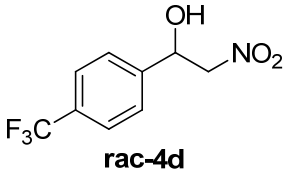




4c

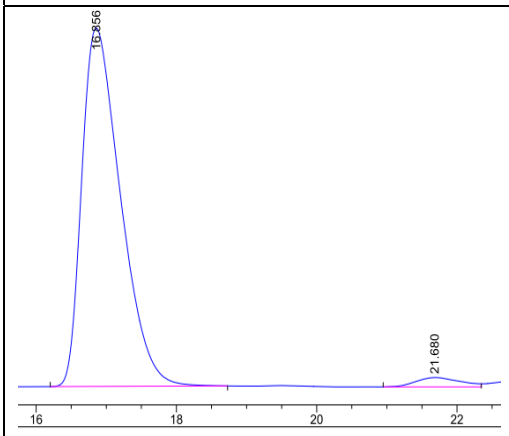
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	45.211	BB	1.7825	2.48953e4	204.33069	98.0298
2	51.895	BB	1.6486	500.33630	3.64377	1.9702

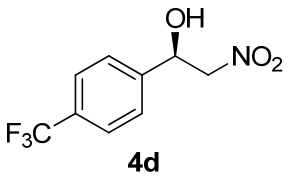




rac-4d

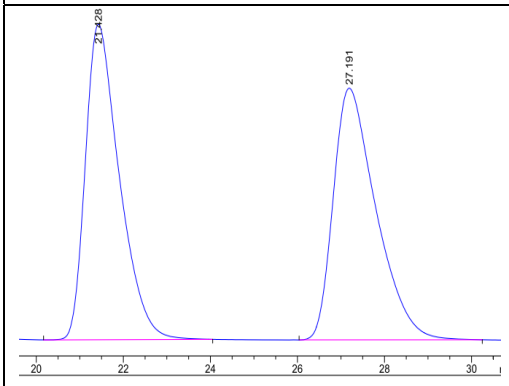
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.585	VB	0.5895	2.00767e4	507.65228	49.6190
2	21.118	VB	0.7706	2.03850e4	395.23459	50.3810

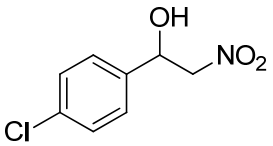




4d

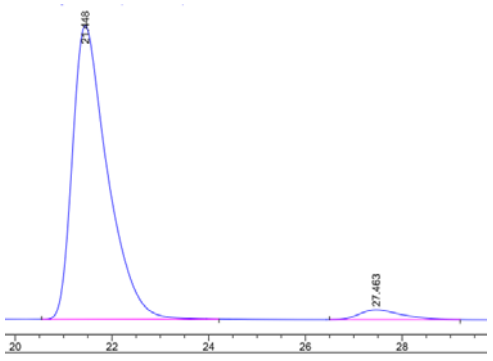
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.856	BB	0.5862	1.43181e4	374.14941	97.0721
2	21.680	BV	0.6474	431.86691	9.72941	2.9279

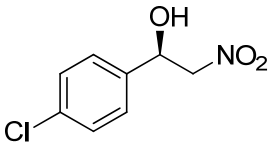




rac-4e

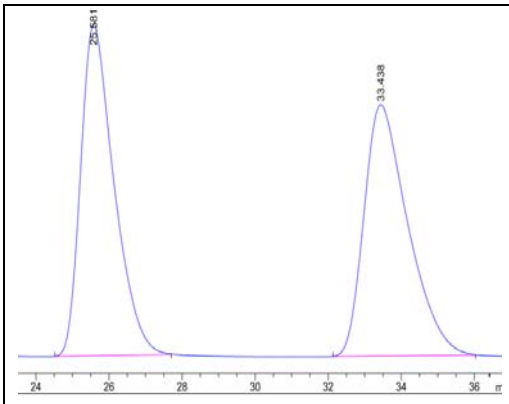
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	21.428	VB	0.8040	2.00628e4	369.40033	49.9541
2	27.191	BB	1.0156	2.00997e4	294.68384	50.0459

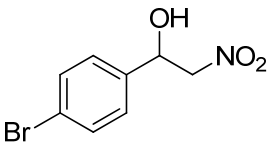




4e

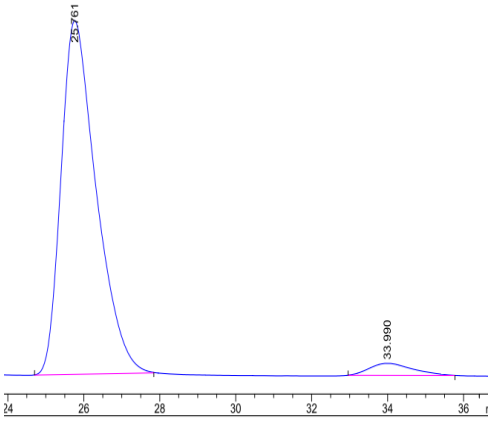
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	21.448	BB	0.7421	2.36890e4	471.35461	95.9245
2	27.463	BB	0.8996	1006.46136	16.36394	4.0755

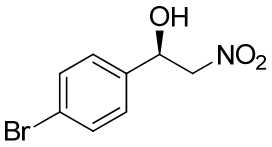




rac-4f

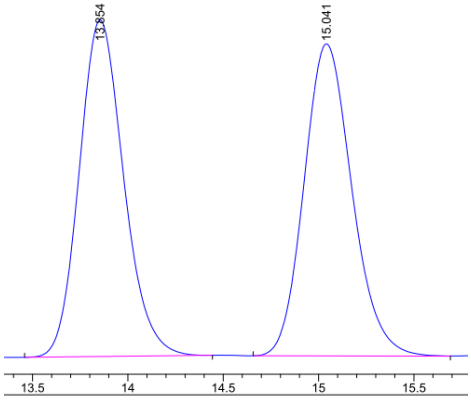
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	25.581	BB	0.9465	2.06353e4	325.42981	50.0247
2	33.438	BB	1.2207	2.06149e4	247.13690	49.9753

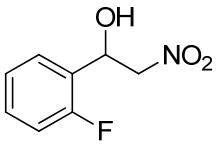




4f

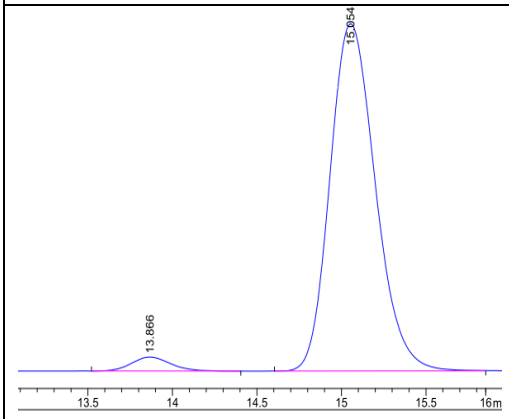
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	25.761	BB	0.9482	1.81548e4	281.78165	95.9406
2	33.990	BB	1.0128	768.14960	9.65387	4.0594

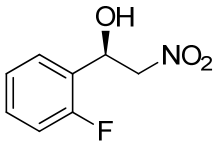




rac-4g

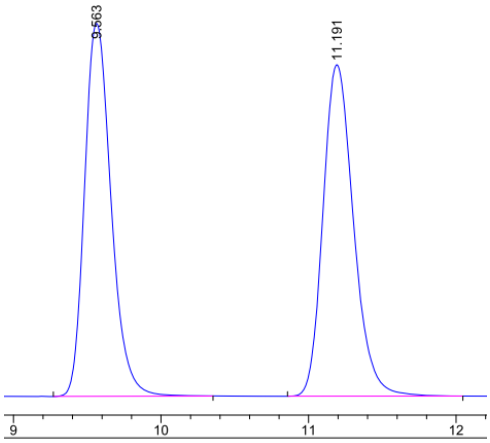
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.854	PB	0.2514	6999.04736	432.54568	49.9320
2	15.041	PV	0.2710	7018.11426	401.22430	50.0680

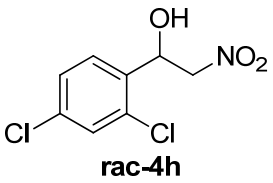




4g

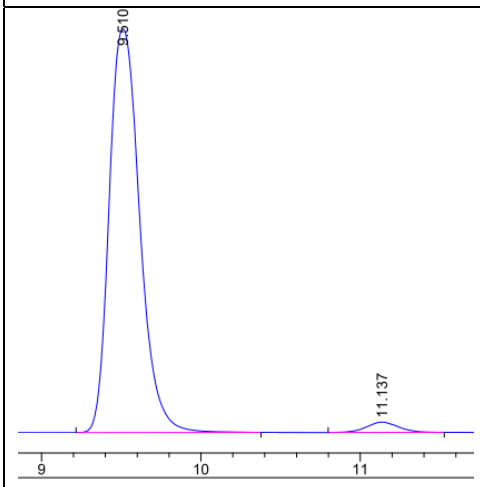
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.866	BP	0.2472	736.27228	45.81345	3.3628
2	15.054	PB	0.2937	2.11583e4	1132.46289	96.6372

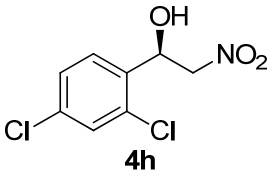




rac-4h

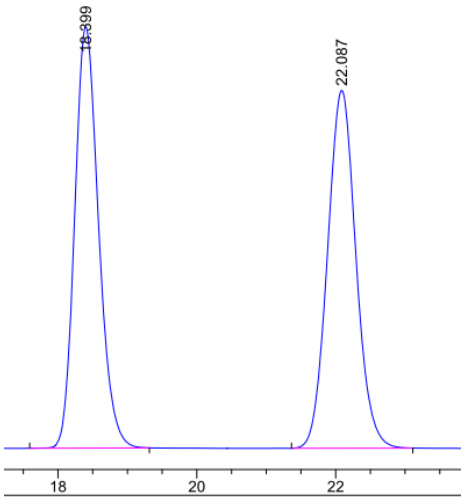
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.563	PB	0.1937	1.95865e4	1568.41870	49.4283
2	11.191	PB	0.2216	2.00396e4	1394.15271	50.5717

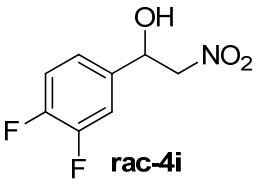




4h

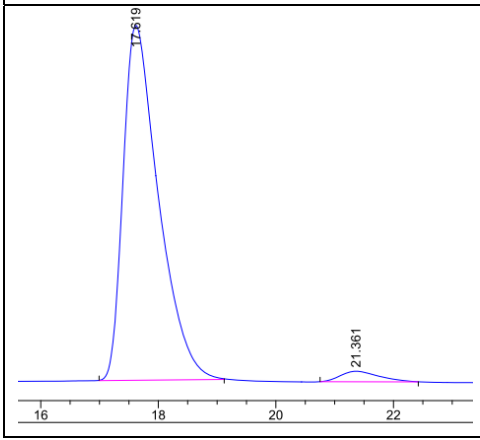
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.510	PB	0.2078	2.44511e4	1835.52979	97.3718
2	11.137	PB	0.2142	659.98022	47.17414	2.6282

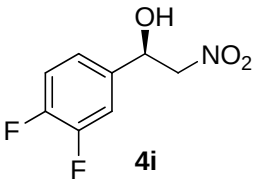




rac-4i

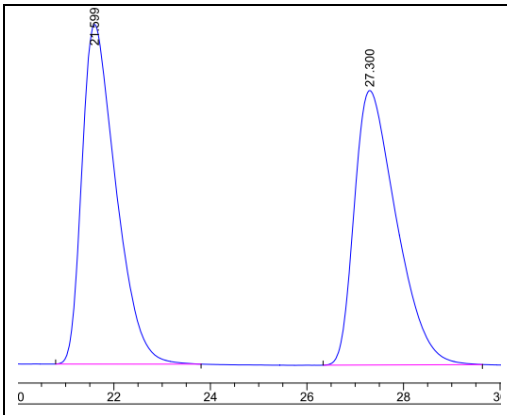
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.399	BB	0.3690	5587.81982	233.91452	49.6991
2	22.087	BB	0.4413	5655.48584	198.67061	50.3009

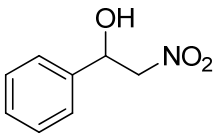




4i

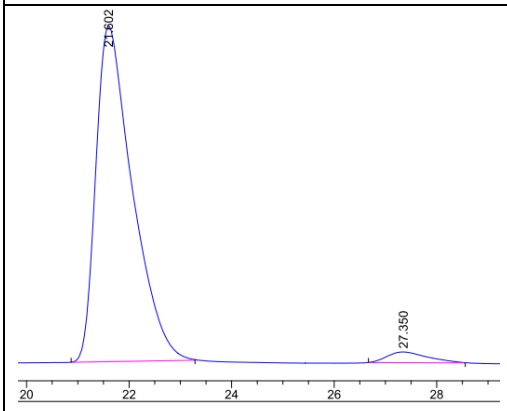
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.619	BB	0.6194	1.36827e4	326.90247	96.8331
2	21.361	BB	0.6694	447.49408	9.74942	3.1669

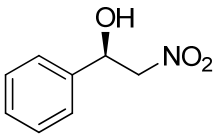




rac-4j

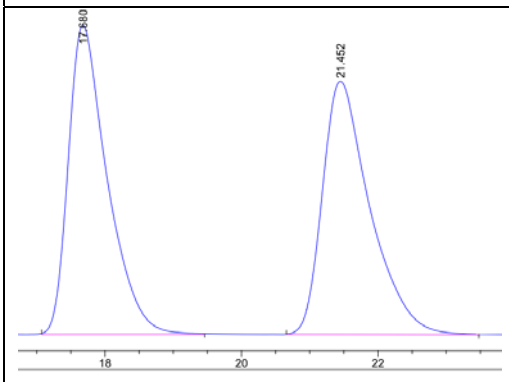
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	21.599	BB	0.7273	7358.49316	150.59378	49.9722
2	27.300	BB	0.9029	7366.68506	121.67929	50.0278

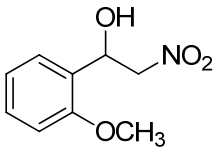




4j

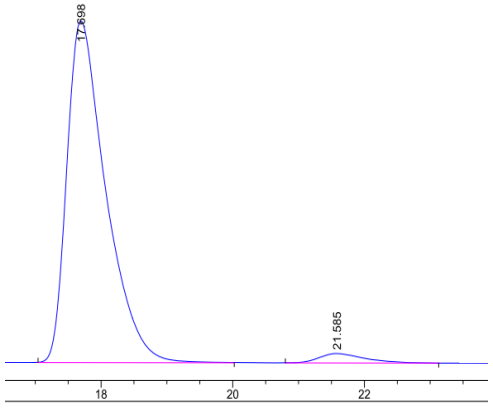
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	21.602	BB	0.7210	9855.74414	199.33162	96.5582
2	27.350	BB	0.7761	351.31009	6.36795	3.4418

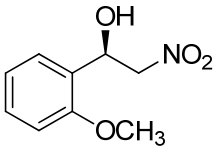




rac-4k

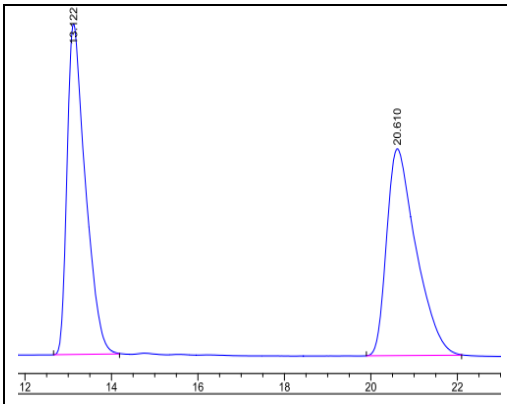
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.680	BB	0.5842	6297.51465	159.06024	50.0203
2	21.452	BB	0.7214	6292.40820	130.13844	49.9797

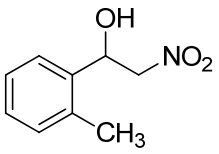




4k

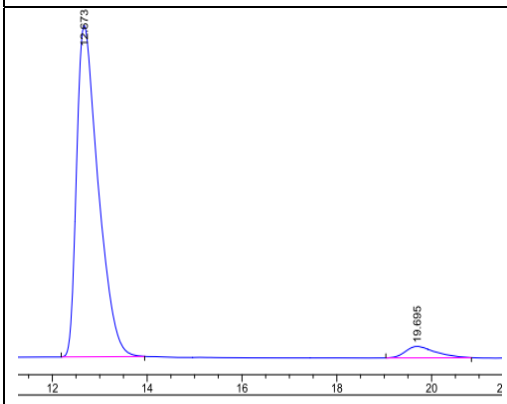
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.698	BB	0.6137	2.37182e4	576.80762	96.8450
2	21.585	BB	0.7181	772.69946	16.07431	3.1550

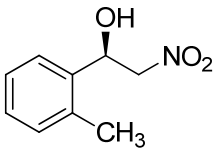




rac-4l

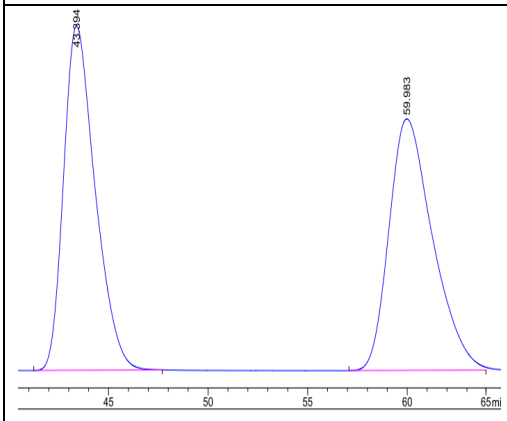
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.122	BB	0.4303	1.21128e4	413.81586	49.7981
2	20.610	BB	0.7004	1.22111e4	258.83865	50.2019

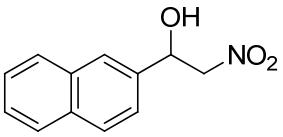




4l

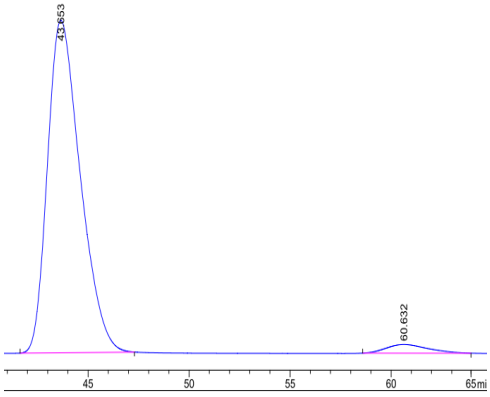
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.673	BB	0.4711	3.75844e4	1192.38342	95.3793
2	19.695	BB	0.6433	1820.79932	41.47054	4.6207

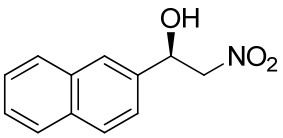




rac-4m

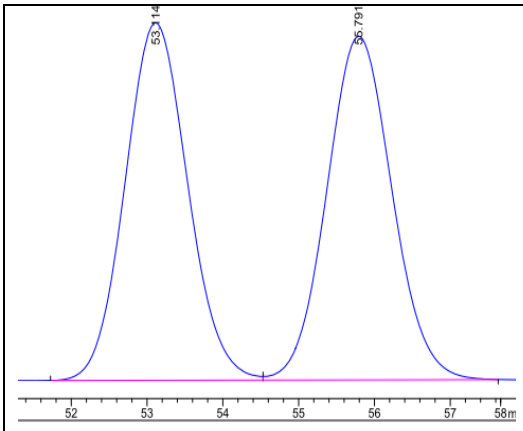
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	43.394	BB	1.6391	7.50271e4	680.25421	49.7550
2	59.983	BB	2.1962	7.57660e4	497.04749	50.2450

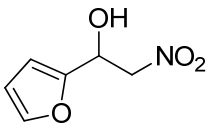




4m

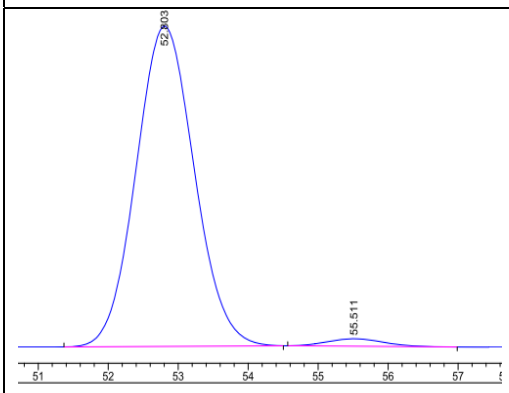
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	43.653	BB	1.6700	1.15024e5	1019.53461	96.7175
2	60.632	BB	1.7160	3903.83398	26.92997	3.2825

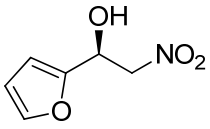




rac-4n

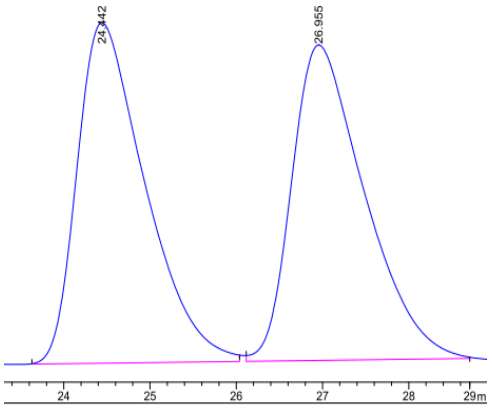
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	53.114	BV	0.8684	2.89341e4	503.50574	49.9220
2	55.791	VB	0.9006	2.90245e4	483.93814	50.0780

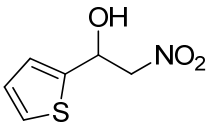




4n

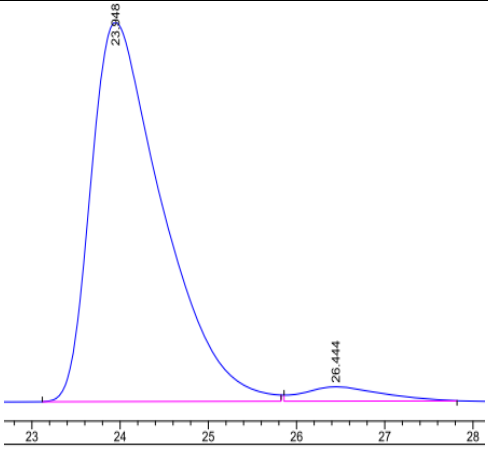
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	52.803	BB	0.8593	3.87481e4	668.87427	97.7894
2	55.511	PP	0.8058	875.93604	15.68605	2.2106

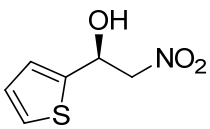




rac-4o

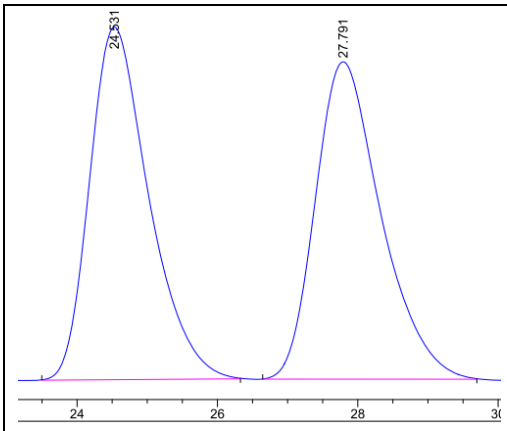
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	24.442	BB	0.8111	6674.56836	121.80189	50.1692
2	26.955	BB	0.8792	6629.54004	112.82285	49.8308

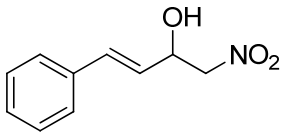




4o

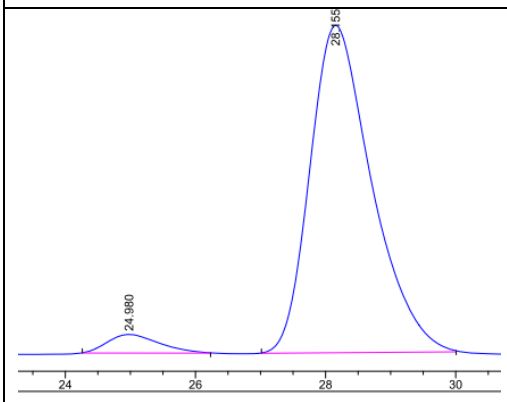
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	23.948	BB	0.8268	2.19519e4	388.38864	96.0158
2	26.444	BB	0.8511	910.90515	14.81973	3.9842

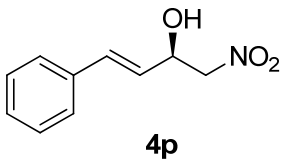




rac-4p

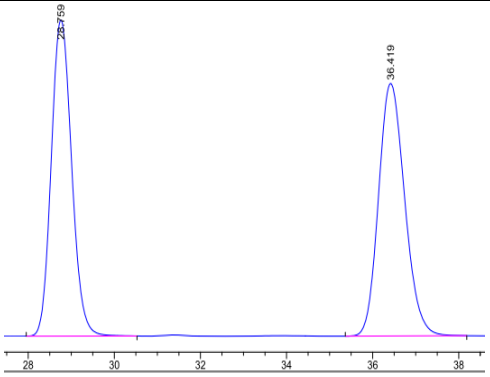
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	24.531	BB	0.8868	1.28007e4	218.21866	50.0477
2	27.791	BB	0.9814	1.27763e4	196.47523	49.9523

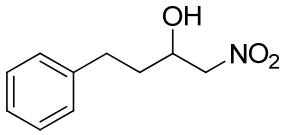




4p

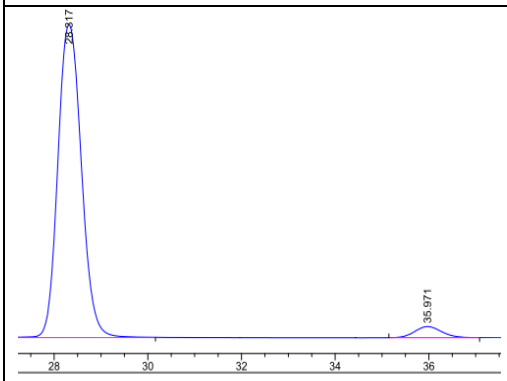
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	24.980	BB	0.7886	407.12381	7.35318	4.5677
2	28.155	BB	0.9930	8506.03711	129.08563	95.4323

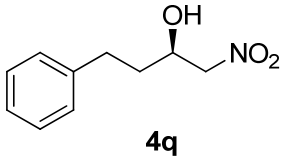




rac-4q

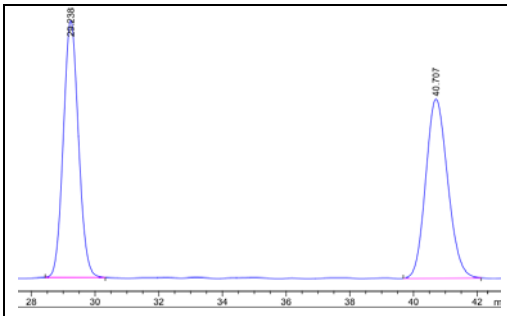
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	28.759	BB	0.5048	3.34879e4	1017.55164	49.4074
2	36.419	BB	0.6348	3.42911e4	812.90198	50.5926

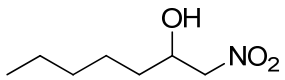




4q

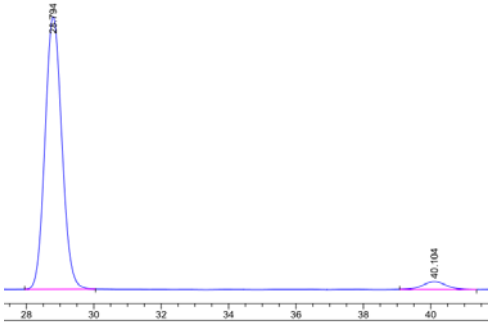
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	28.317	BB	0.5438	4.35737e4	1253.68030	96.0329
2	35.971	BB	0.6084	1800.01160	44.81355	3.9671

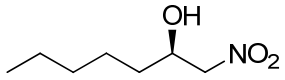




rac-4r

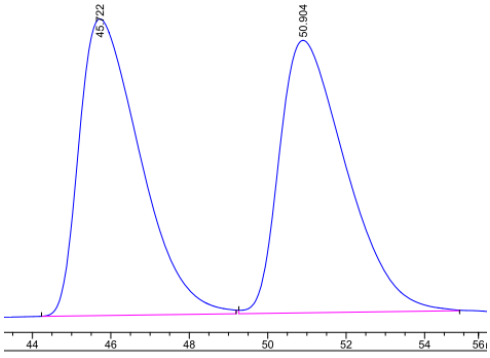
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	29.238	BB	0.5197	1.55708e4	470.87073	49.6969
2	40.707	BB	0.7385	1.57607e4	328.68909	50.3031

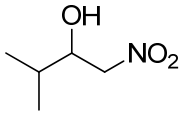




4r

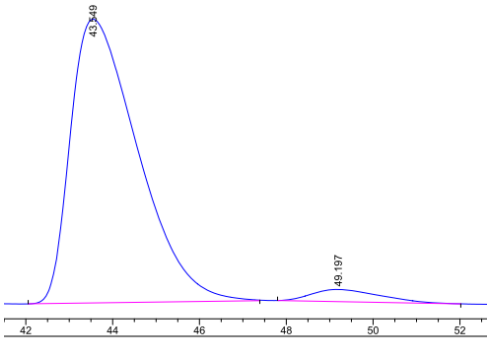
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	28.794	BB	0.5420	3.19972e4	921.49512	95.9316
2	40.104	BB	0.7338	1356.98450	27.59771	4.0684

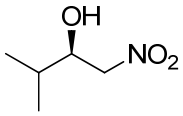




rac-4s

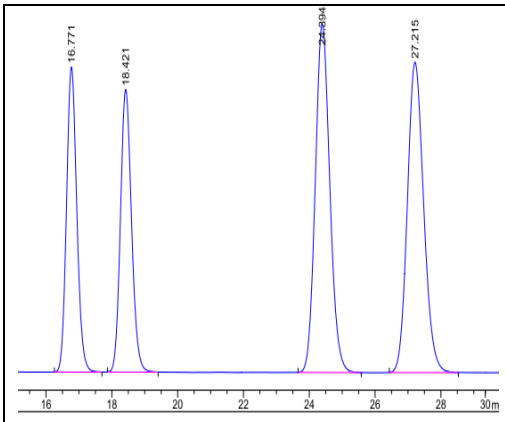
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	45.722	BB	1.5198	2.55413e4	236.38252	49.9692
2	50.904	BB	1.6743	2.55728e4	217.08615	50.0308

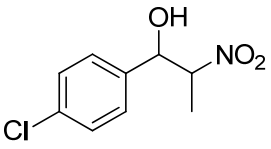




4s

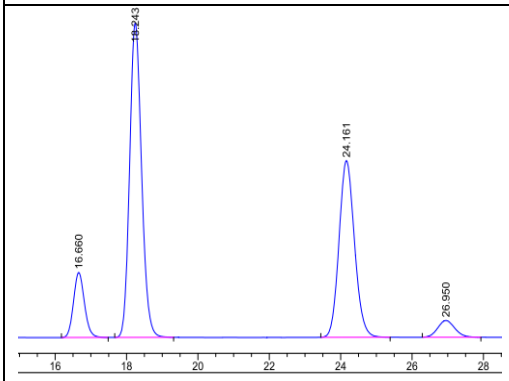
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	43.549	PB	1.5540	3.38660e4	314.33649	95.8117
2	49.197	BB	1.2978	1480.42590	13.49029	4.1883

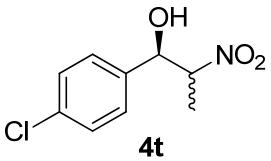




rac-4t

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.771	BB	0.3341	6505.79004	300.48267	19.1030
2	18.421	BB	0.3600	6502.14160	278.27350	19.0923
3	24.394	BB	0.4739	1.05168e4	343.32358	30.8806
4	27.215	BB	0.5330	1.05316e4	305.70712	30.9240





4t

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.660	BB	0.3269	2612.41284	122.73810	9.4990
2	18.243	BB	0.3607	1.37508e4	593.29620	49.9994
3	24.161	BB	0.4690	1.00780e4	333.52454	36.6449
4	26.950	BB	0.5153	1060.65674	31.72115	3.8567

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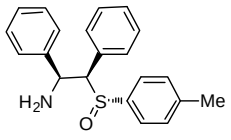
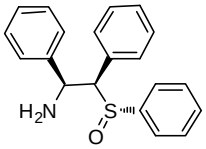
VarioEL III CHNS
serial number 11033032

10.12.11

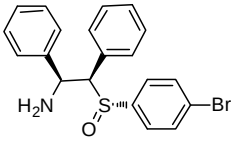
No.	Name	Weight [mg]		Content [%]	Peak Area
87	chg1278	1.2600	N:	5.264	2390
			C:	69.62	22285
			S:	12.65	1789
			H:	6.884	4056
94	chg1215	1.3620	N:	4.446	2179
			C:	75.41	26125
			S:	9.801	1488
			H:	6.146	3885
105	chg1151	1.4670	N:	4.539	2400
			C:	74.77	27912
			S:	9.752	1599
			H:	5.818	3978
106	chg1068	1.3180	N:	3.778	1785
			C:	71.63	24000
			S:	9.291	1360
			H:	6.237	3800
113	chg1157	1.1990	N:	3.389	1450
			C:	60.11	18277
			S:	8.263	1089
			H:	4.567	2252
115	chg1318	1.2940	N:	3.791	1758
			C:	72.00	23682
			S:	9.056	1299
			H:	5.976	3525
117	chg1132	1.2140	N:	4.131	1798
			C:	75.52	23300
			S:	9.341	1255
			H:	6.910	3895
119	chg1225	1.2170	N:	3.642	1585
			C:	77.60	24007
			S:	8.892	1195
			H:	5.590	3000
121	chg1050	1.4220	N:	4.597	2355
			C:	79.05	28611
			S:	10.14	1612
			H:	6.429	4321



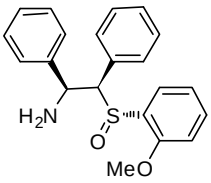
CHG1215, **13a**



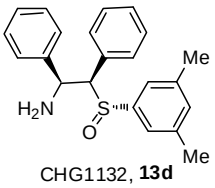
CHG1151, **13b**



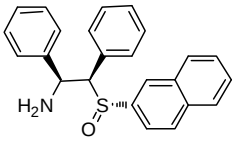
CHG1157, **13c**



CHG1318, **13e**



CHG1132, **13d**



CHG1225, **13g**

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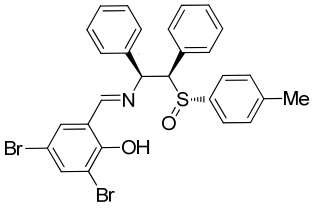
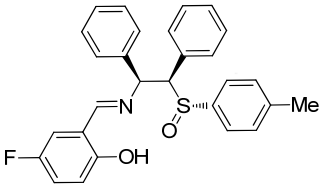
VarioEL III CHNS
serial number 11033032

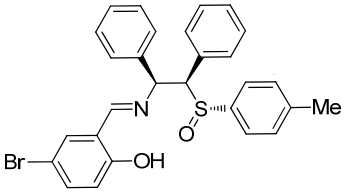
No.	Name	Weight [mg]	Content [%]
85	chg1196	1.3860	N: 2.300 C: 56.53 S: 5.424 H: 4.124
88	chg1222	1.1510	N: 2.939 C: 73.42 S: 7.206 H: 5.555
89	chg1221	1.0470	N: 2.611 C: 64.81 S: 6.438 H: 4.942
90	chg1234	1.3920	N: 2.129 C: 58.56 S: 5.313 H: 3.759
91	chg1220	1.1250	N: 2.934 C: 76.88 S: 7.349 H: 6.239
92	chg1167	1.3200	N: 3.244 C: 76.29 S: 7.656 H: 5.705
95	chg1203	1.1340	N: 2.362 C: 78.55 S: 6.096 H: 7.663
97	chg1218	1.0850	N: 2.694 C: 78.80 S: 6.841 H: 5.832
98	chg1233	1.1540	N: 2.661 C: 72.87 S: 6.320 H: 5.025



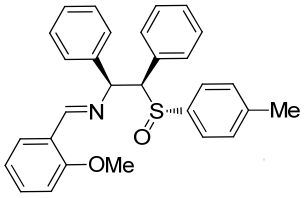
CHG1196, **1n**



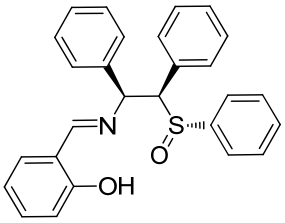
CHG1222, **1m**



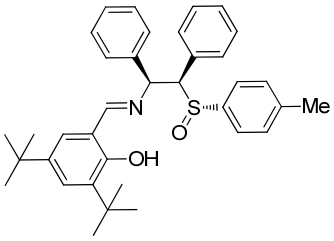
CHG1221, **1l**



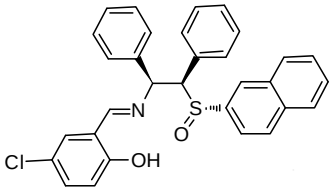
CHG1220, **8**



CHG1167, **1b**



CHG1203, **1j**



CHG1233, **1k**

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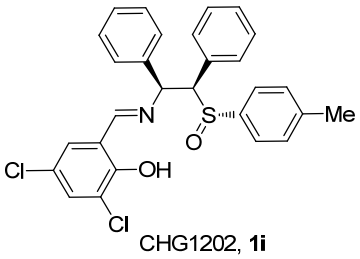
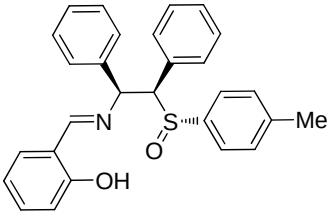
华中师范大学分析测试中心
VarioEL III CHNS
serial number 11033032

22.07.11

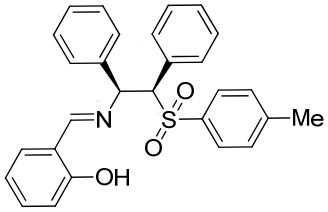
No.	Name	Weight [mg]	Content [%]
86	chg1202	1.2210	N: 2.696 C: 66.01 S: 6.521 H: 4.375
93	chg1155	1.2350	N: 3.068 C: 76.29 S: 7.461 H: 6.025
96	chg1095	1.1130	N: 2.980 C: 73.83 S: 7.245 H: 5.612
101	chg1194	1.3120	N: 2.963 C: 76.90 S: 6.880 H: 5.999
103	chg1219	1.2650	N: 2.859 C: 73.56 S: 7.123 H: 5.507



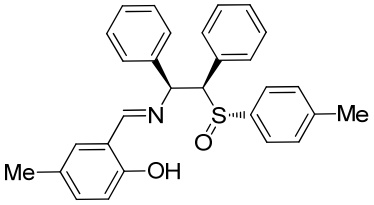
CHG1202, **1i**



CHG1155, **1a**



CHG1095, **7**



CHG1194, **1h**

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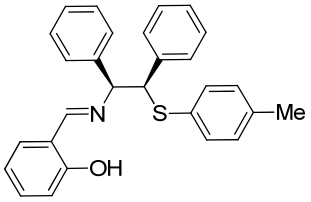
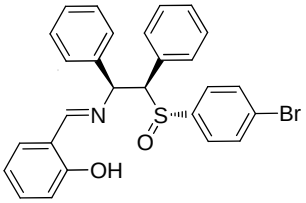
华中师范大学分析测试中心 22.07.11
VarioEL III CHNS
serial number 11033032

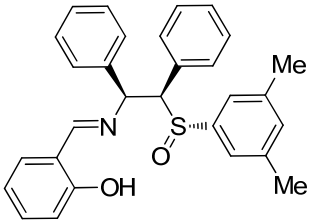
No.	Name	Weight [mg]	Content [%]
99	chg1049	1.3650	N: 3.179 C: 79.61 S: 7.802 H: 6.064
102	chg1166	1.1780	N: 2.581 C: 63.99 S: 6.374 H: 4.689
104	chg1239	1.3120	N: 2.745 C: 78.27 S: 6.716 H: 5.862
106	chg1156	1.3180	N: 3.008 C: 76.63 S: 7.170 H: 6.178



CHG1049, **6**



CHG1166, **1c**



CHG1156, **1d**

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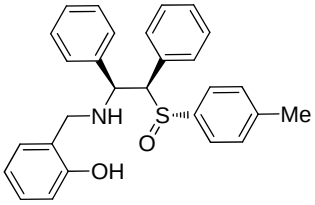
华中师范大学分析测试中心

22.07.11

VarioEL III CHNS
serial number 11033032

No.	Name	Weight [mg]	Content [%]
41	chg1081	1.2820	N: 3.121
			C: 76.28
			S: 7.271
			H: 6.412



CHG1081, **9**

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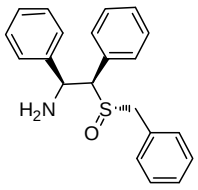
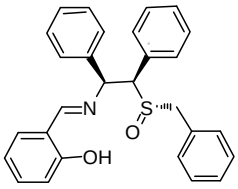
analytic functional testing
VarioEL III CHNS
serial number 11033032

24.07.11

No.	Name	Weight [mg]		Content [%]	Peak Area
45	chg1396	1.4640	N:	4.029	2112
			C:	75.21	28714
			S:	9.664	1630
			H:	6.254	3896
46	chg1385	1.7150	N:	2.471	1507
			C:	82.33	36875
			S:	6.233	1217
			H:	5.687	4205
47	chg1434	1.2620	N:	3.448	1548
			C:	76.67	25212
			S:	7.104	1011
			H:	5.455	2721



CHG1396, **13f**



CHG1434, **1f**

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Shanghai Mass Spectrometry Center
Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences
High Resolution MS DATA REPORT

Instrument: IonSpec 4.7 Tesla FTMS

Card Serial Number : I11 3028

Sample Serial Number: CHG1217

Operator : HuaQin Date: 2011/10/31

Operation Mode: MALDI/DHB

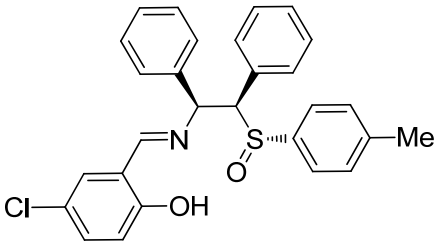
Elemental Composition Search Report:

Target Mass:

Target m/z = 474.1283 ± 0.002
Charge = +1

Possible Elements:

Element:	Exact Mass:	Min:	Max:
C	12.000000	0	100
H	1.007825	0	100
N	14.003074	0	3
O	15.994915	0	3
S	31.972071	0	1
Cl	34.968853	0	1



$C_{28}H_{24}ClNO_2S$, CHG1217, **1g**

Additional Search Restrictions:

DBE Limit Mode = Both Integer and Half-Integer
Minimum DBE = 0

Search Results:

Number of Hits = 4

m/z	Delta m/z	DBE	Formula
474.12842	-0.00012	21.0	$C_{31}H_{22}O_3S^{+1}$
474.12773	0.00057	30.5	$C_{37}H_{16}N^{+1}$
474.12890	-0.00060	17.0	$C_{28}H_{25}NO_2SCl^{+1}$
474.12707	0.00123	21.5	$C_{29}H_{20}N_3O_2S^{+1}$

Shanghai Mass Spectrometry Center
Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences
High Resolution MS DATA REPORT

Instrument: IonSpec 4.7 Tesla FTMS

Card Serial Number : I11 3030

Sample Serial Number: CHG1245

Operator : HuaQin Date: 2011/10/31

Operation Mode: MALDI/DHB

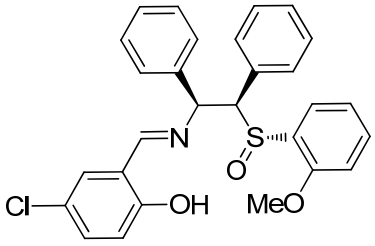
Elemental Composition Search Report:

Target Mass:

Target m/z = 490.1235 ± 0.002
Charge = +1

Possible Elements:

Element:	Exact Mass:	Min:	Max:
C	12.000000	0	100
H	1.007825	0	100
N	14.003074	0	3
O	15.994915	0	3
S	31.972071	0	1
Cl	34.968853	0	1



$C_{28}H_{24}ClNO_3S$, CHG1245, **1e**

Additional Search Restrictions:

DBE Limit Mode = Both Integer and Half-Integer
Minimum DBE = 0

Search Results:

Number of Hits = 4

m/z	Delta m/z	DBE	Formula
490.12382	-0.00032	17.0	$C_{28}H_{25}NO_3SCl^{+1}$
490.12313	0.00037	26.5	$C_{34}H_{19}N_2Cl^{+1}$
490.12264	0.00086	30.5	$C_{37}H_{16}NO^{+1}$
490.12199	0.00151	21.5	$C_{29}H_{20}N_3O_3S^{+1}$