Development of spirocyclic phosphoramidite-based hybrid diphosphorus ligands for enantioselective iridium-catalyzed hydrogenation of imines

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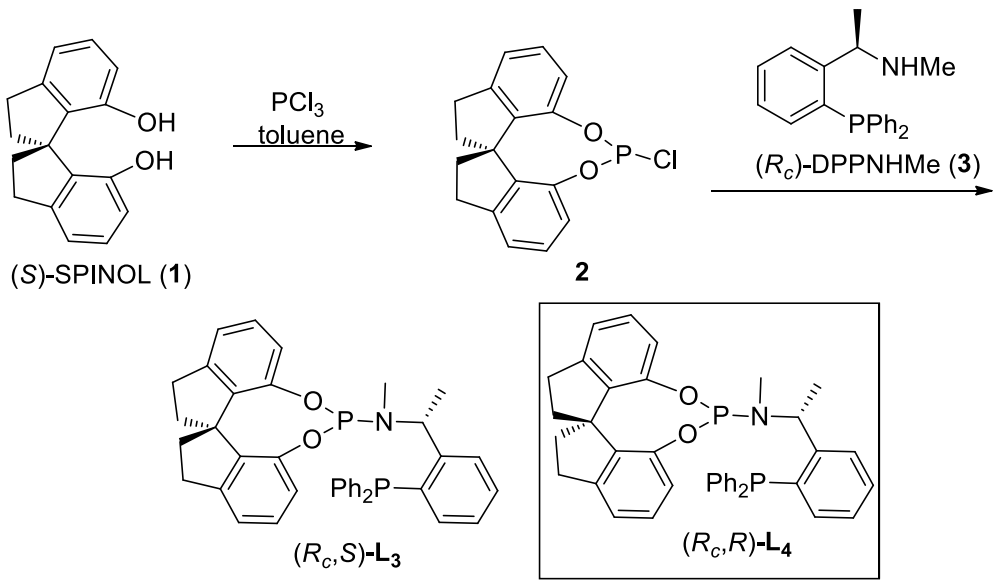
Supporting Information

General information

All reactions were carried out under a nitrogen atmosphere. Solvents were purified by standard procedure before use. Commercial reagents were used without further purification. Flash chromatography was performed on silica gel 60 (40-63μm, 60Å). Thin layer chromatography (TLC) was performed on glass plates coated with silica gel 60 with F254 indicator. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker 400 MHz spectrometer. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CHCl_3$ = δ 7.26). Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker 100 MHz spectrometer. Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent ($CDCl_3$ = δ 77.07). Phosphorus nuclear magnetic resonance (^{31}P NMR) spectra were recorded on a Bruker 162 MHz spectrometer. Chemical shifts for phosphorus are reported in parts per million downfield from the external 85% H_3PO_4 signal at 0.0 ppm as a standard. Data are represented as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz) integration. Enantiomeric ratios were determined by chiral HPLC with *n*-hexane and *i*-PrOH as solvents. Optical rotations were recorded on a JASCO P-1020 polarimeter.

General procedure for synthesis of ligands L_3 and L_4



Step 1: A solution of (*S*) or (*R*)-SPINOL (1.0 mmol), freshly distilled PCl_3 (1.0 mL), and 3 drops

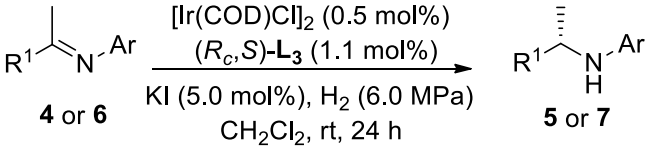
of *N*-Methyl-2-pyrrolidone in dry toluene (10 mL) was stirred for 1 h at refluxing temperature. The reaction mixture was concentrated in vacuo and the residue was distilled twice azeotropically with absolute toluene to give **2**, which could be used directly for the next step with further purification.

Step 2: To a stirred solution of **2** (1.0 mmol) in dried toluene (4.0 mL) at 0 ℃ was added a solution of (*R*)-DPPNHMe (1.0 mmol) and NEt_3 (3.0 mmol) in dried toluene (4.0 mL) within 30 min. The resulting mixture was stirred overnight at room temperature. The precipitate was filtered, and the solid was washed with toluene. The filtrate was collected, and concentrated under reduced pressure to give the crude product which was further purified by column chromatography to afford ligand $\mathbf{L_3}$ or $\mathbf{L_4}$.

(R_c,*S*)-$\mathbf{L_3}$. 390 mg (65% yield) of (R_c,*S*)-$\mathbf{L_3}$ was obtained as a white solid after the purification by silica gel column chromatography using hexanes/triethylamine (20/1). M.p.: 95 – 97 ℃; $[\alpha]_D^{25}$ = −136.9 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (dd, *J* = 7.9, 4.5 Hz, 1H), 7.34 – 7.16 (m, 11H), 7.08 (dt, *J* = 12.0, 7.6 Hz, 2H), 6.98 – 6.84 (m, 4H), 6.77 (d, *J* = 7.9 Hz, 1H), 6.62 (d, *J* = 7.8 Hz, 1H), 5.23 (dt, *J* = 10.8, 6.7 Hz, 1H), 2.96 (ddt, *J* = 18.8, 14.5, 7.1 Hz, 2H), 2.71 (dt, *J* = 15.4, 7.4 Hz, 2H), 2.13 (ddd, *J* = 17.9, 11.8, 6.2 Hz, 2H), 1.93 – 1.83 (m, 2H), 1.59 (d, *J* = 2.4 Hz, 3H), 1.51 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 149.0, 148.9, 147.1, 147.1, 145.6, 145.1, 142.1, 140.6, 137.3, 137.2, 136.1, 134.4, 134.0, 133.8, 128.7, 128.7, 128.6, 128.6, 128.5, 128.5, 128.5, 128.5, 128.4, 128.2, 127.5, 127.4, 121.7, 121.6, 121.5, 121.0, 120.9, 120.3, 58.8, 56.2, 38.3, 38.2, 30.9, 30.6, 29.0, 29.0, 21.2, 21.0; ^{31}P NMR (162 MHz, $CDCl_3$): δ 126.1 (d, *J* = 55.2 Hz), -17.9 (d, *J* = 54.9 Hz). HRMS (ESI): *m/z* calcd for $C_{38}H_{35}NO_2P_2$ $[M+H]^+$: 599.2216, found: 599.2198.

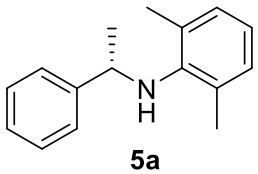
(R_c,*R*)-$\mathbf{L_4}$**.** 354 mg (59% yield) as a white solid after the purification by silica gel column chromatography using hexanes/triethylamine (20/1). M.p.: 99 – 101 ℃; $[\alpha]_D^{25}$ = +74.3 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (dd, *J* = 7.8, 4.5 Hz, 1H), 7.44 – 7.17 (m, 15H), 7.09 – 6.90 (m, 6H), 6.47 (dd, *J* = 5.7, 3.3 Hz, 1H), 5.21 (q, *J* = 7.1 Hz, 1H), 3.16 – 2.94 (m, 1H), 2.84 (dd, *J* = 15.5, 7.8 Hz, 2H), 2.24 (td, *J* = 12.5, 6.3 Hz, 2H), 1.98 (td, *J* = 11.6, 8.0 Hz, 2H), 1.62 (dt, *J* = 10.6, 3.5 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.9, 148.8, 146.5, 146.4, 145.8, 145.8, 145.2, 142.4, 142.3, 140.7, 137.0, 136.9, 136.7, 136.6, 134.1, 134.0, 133.9, 133.9, 133.8, 129.4, 128.8, 128.7, 128.6, 128.6, 128.5, 128.4, 127.3, 126.0, 121.6, 121.4, 121.4, 121.2, 120.3, 58.8, 38.4, 38.2, 31.0, 30.6, 30.4, 30.3; ^{31}P NMR (162 MHz, $CDCl_3$): δ 124.7 (d, *J* = 19.0 Hz), -18.2. HRMS (ESI): *m/z* calcd for $C_{38}H_{35}NO_2P_2$ $[M+H]^+$: 599.2216, found: 599.2215.

General procedure for asymmetric hydrogenation of imines 4 or 6

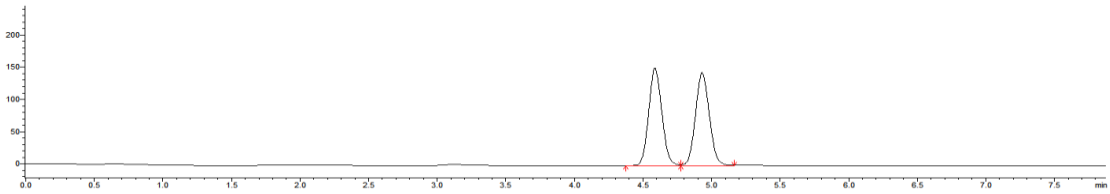


In a nitrogen-filled glovebox, a stainless steel autoclave was charged with $[Ir(COD)Cl]_2$ (0.001 mmol), (R_c,S)-**L3** (0.0022 mmol) and KI (0.01 mmol) in 1.0 mL of degassed CH_2Cl_2. After stirring for 1 h at room temperature, a solution of imines **4** or **6** (0.2 mmol) in 1.0 mL of the same solvent was added to the reaction mixture, and then the hydrogenation was performed at room temperature under a H_2 pressure of 6.0 MPa for 24 or 36 h. The solvent was then evaporated and the residue was purified by flash column chromatography to give the corresponding hydrogenation product **5** or **7** which was analyzed by chiral GC or chiral HPLC to determine enantiomeric excesses.

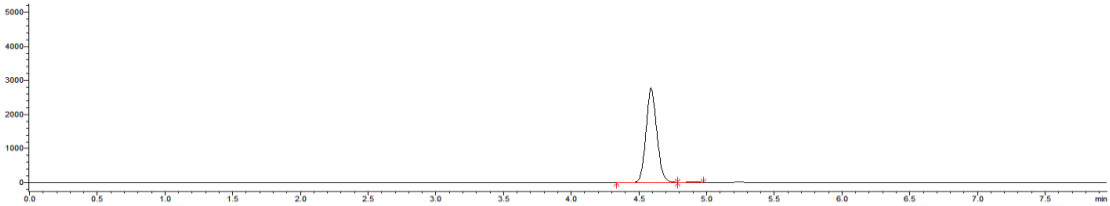
(S)-N-(1-Phenylethyl)-2,6-dimethylbenzenamine 5a.[1] 43.5 mg (97% yield) of **5a** was obtained as a slight yellowish oil after purification with column chromatography on silica gel (hexanes/EtOAc, 20/1). 98% ee was determined by chiral HPLC (chiralcel OJ-H, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, I = 254 nm, T = 40 °C): t_R = 4.6 min (major), 4.9 min (minor). $[\alpha]_D^{25}$ = −131.3 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 – 7.23 (m, 5H), 7.00 (d, *J* = 7.4 Hz, 2H), 6.89 – 6.78 (m, 1H), 4.37 (qd, *J* = 6.7, 2.2 Hz, 1H), 3.00 (s, 1H), 2.22 (d, *J* = 1.8 Hz, 6H), 1.61 – 1.49 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 145.3, 145.0, 129.5 128.9, 128.5, 127.0, 126.2, 121.7, 56.8, 22.7, 19.0.



5a

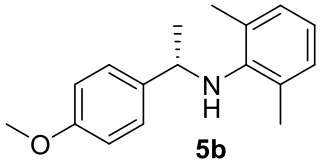


Peak#	Ret. Time	Area	Height	Conc.	Name	Area%
1	4.587	1005224	151119	49.904		49.904
2	4.931	1009075	144521	50.096		50.096
Total		2014299	295641	100.000		100.000



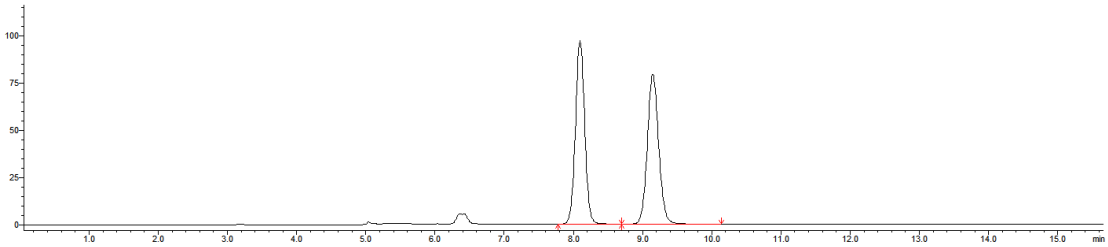
Peak#	Ret. Time	Area	Height	Conc.	Name	Area%
1	4.589	15364898	2781450	99.162		99.162
2	4.903	129813	25893	0.838		0.838
Total		15494712	2807342	100.000		100.000

(S)-N-[1-(4-Methoxyphenyl)ethyl]-2,6-dimethylbenzenamine 5b.[2] 49.8 mg (97% yield) of **5b** was

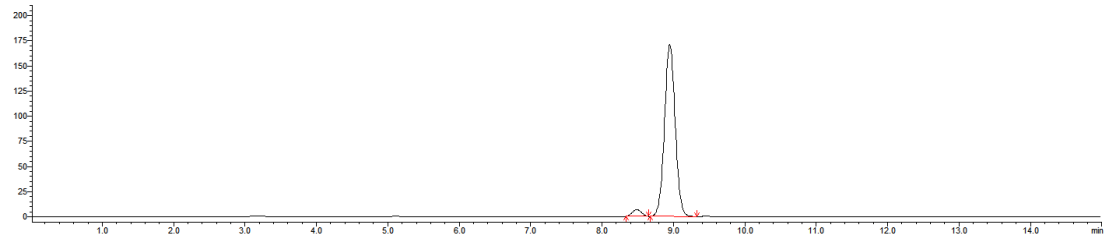


5b

obtained as a slight yellowish oil after purification with column chromatography on silica gel (hexanes/EtOAc, 20/1). 94% ee was determined by chiral HPLC (chiralcel OJ-H, *n*-hexane/*i*-PrOH = 98/2, flow rate = 1.0 mL/min, I = 254 nm, T = 40 ℃): t_R = 8.5 min (minor), 8.9 min (major). $[\alpha]_D^{25}$ = −154.7 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 – 7.19 (m, 2H), 6.98 (d, *J* = 7.5 Hz, 2H), 6.92 – 6.74 (m, 3H), 4.31 (q, *J* = 6.7 Hz, 1H), 3.81 (s, 3H), 3.04 (s, 1H), 2.20 (s, 6H), 1.52 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.6, 145.0, 137.6, 129.5, 128.8, 127.2, 121.6, 113.7, 56.1, 55.3, 22.6, 19.0.

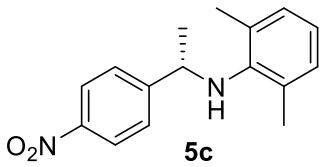


Peak#	Ret. Time	Area	Height	Conc.	Name	Area%
1	8.096	905160	97139	49.991		49.991
2	9.148	905493	79362	50.009		50.009
Total		1810653	176502	100.000		100.000



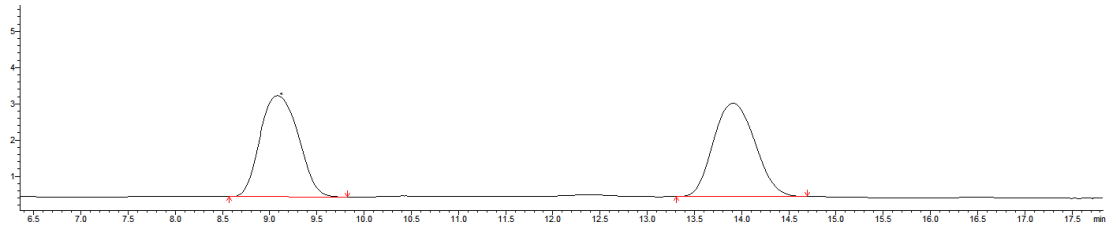
Peak#	Ret. Time	Area	Height	Conc.	Name	Area%
1	8.488	59480	6738	3.238		3.238
2	8.948	1777397	170869	96.762		96.762
Total		1836877	177607	100.000		100.000

(S)-N-[1-(4-nitrophenyl)ethyl]-2,6-dimethylbenzenamine 5c.[1] 54.1 mg (>99% yield) of **5c** was

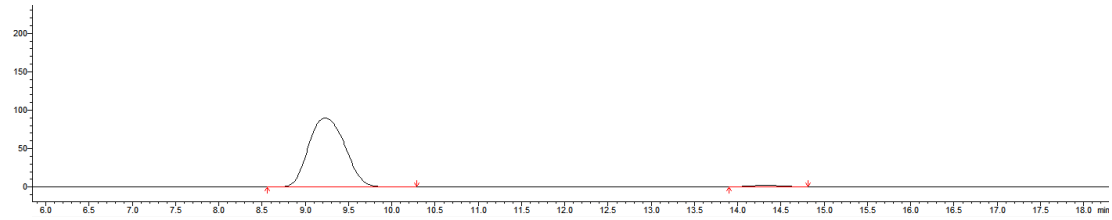


5c

obtained as a yellow oil after purification with column chromatography on silica gel (hexanes/EtOAc, 20/1). 96% ee was determined by chiral HPLC (chiralpak AD-H, *n*-hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, I = 254 nm, T = 40 ℃): t_R = 9.2 min (major), 14.3 min (minor). $[\alpha]_D^{25}$ = −248.1(*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 – 8.08 (m, 2H), 7.44 (d, *J* = 8.7 Hz, 2H), 6.95 (d, *J* = 7.5 Hz, 2H), 6.80 (t, *J* = 7.5 Hz, 1H), 4.39 (q, *J* = 6.8 Hz, 1H), 3.21 (s, 1H), 2.15 (s, 6H), 1.55 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (176 MHz, $CDCl_3$): δ 152.8, 146.9, 144.3, 129.3, 129.1, 127.0, 123.7, 122.1, 56.5, 23.0, 19.0.

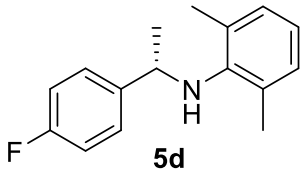


Peak#	Ret. Time	Area	Height	Conc.	Name	Area%
1	9.087	79376	2792	50.121		50.121
2	13.906	78992	2575	49.879		49.879
Total		158368	5367	100.000		100.000



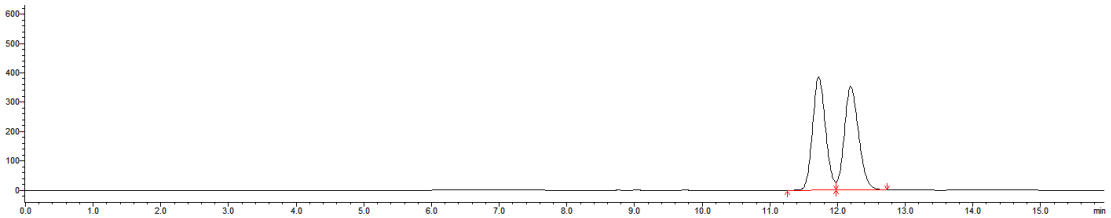
Peak#	Ret. Time	Area	Height	Conc.	Name	Area%
1	9.229	2629337	89858	97.912		97.912
2	14.317	56080	1942	2.088		2.088
Total		2685416	91800	100.000		100.000

(S)-N-(1-(4-fluorophenyl)ethyl)-2,6-dimethylbenzenamine 5d. 47.3 mg (97% yield) of **5d** was

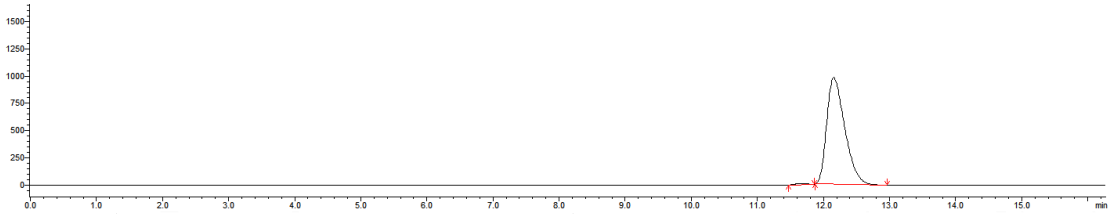


5d

obtained as a colorless oil after purification with column chromatography on silica gel (hexanes/EtOAc, 20/1). 99% ee was determined by chiral HPLC (chiralcel OJ-H, *n*-hexane/*i*-PrOH = 99.9/0.1, flow rate = 0.5 mL/min, I = 254 nm, T = 40 °C): t_R = 12.2 min (major), 11.7 min (minor). $[\alpha]_D^{25} = -135.6$ (*c* 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 7.28 – 7.17 (m, 2H), 7.01 – 6.92 (m, 4H), 6.78 (t, *J* = 7.5 Hz, 1H), 4.28 (q, *J* = 6.7 Hz, 1H), 3.02 (s, 1H), 2.15 (s, 6H), 1.49 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.9 (d, *J* = 244.8 Hz), 144.7, 141.1 (d, *J* = 3.2 Hz), 129.5, 128.9, 127.7 (d, *J* = 7.9 Hz), 121.8, 115.2 (d, *J* = 21.1 Hz), 56.1, 22.7, 18.9; ^{19}F NMR (376 MHz, $CDCl_3$): δ -116.0. HRMS (ESI): m/z calcd for $C_{16}H_{18}FN$ [M+H]+: 244.1496, found: 244.1495.

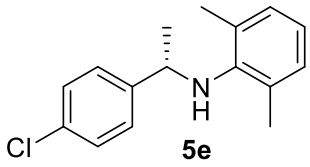


Peak#	Ret. Time	Area	Height	Conc.	Name	Area%
1	11.721	5147288	385003	49.735		49.735
2	12.195	5202052	352512	50.265		50.265
Total		10349341	737515	100.000		100.000



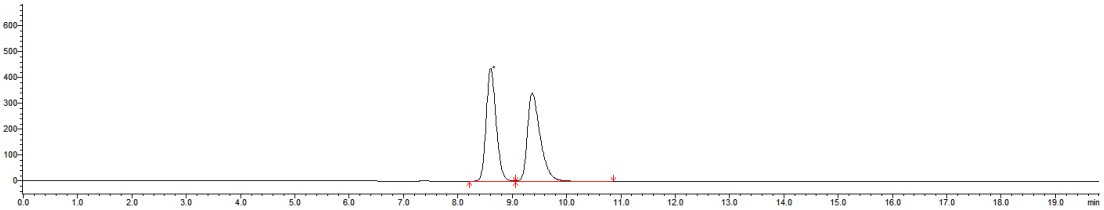
Peak#	Ret. Time	Area	Height	Conc.	Name	Area%
1	11.677	131482	11705	0.703		0.703
2	12.156	18574258	976994	99.297		99.297
Total		18705739	988698	100.000		100.000

(S)-N-[1-(4-chlorophenyl)ethyl]-2,6-dimethylbenzenamine 5e.[1] 51.5 mg (>99% yield) of **5e** was

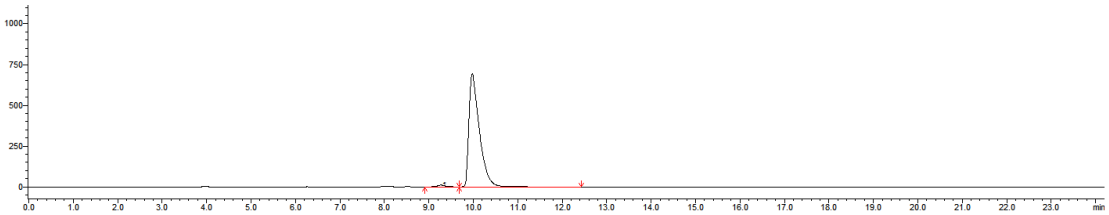


5e

obtained as a colorless oil after purification with column chromatography on silica gel (hexanes/EtOAc, 20/1). 98% ee was determined by chiral HPLC (chiralcel OJ-H, *n*-hexane/*i*-PrOH = 99.8/0.2, flow rate = 0.8 mL/min, I = 254 nm, T = 40 °C): t_R = 10.0 min (major), 9.3 min (minor). $[\alpha]_D^{25}$ = −199.5 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 – 7.13 (m, 4H), 6.94 (d, *J* = 7.5 Hz, 2H), 6.83 – 6.73 (m, 1H), 4.27 (q, *J* = 6.7 Hz, 1H), 3.07 (s, 1H), 2.15 (s, 6H), 1.48 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.7, 143.8, 132.6, 129.4, 129.0, 128.5, 127.6, 121.8, 56.2, 22.8, 19.0.

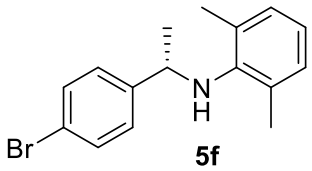


Peak#	Ret. Time	Area	Height	Conc.	Name	Area%
1	8.602	5564403	436047	49.829		49.829
2	9.368	5602627	340464	50.171		50.171
Total		11167030	776512	100.000		100.000



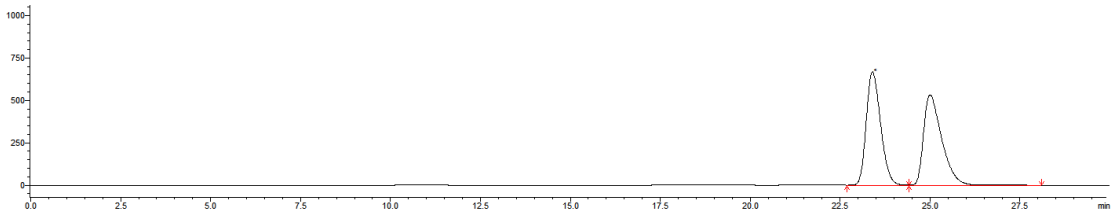
Peak#	Ret. Time	Area	Height	Conc.	Name	Area%
1	9.272	123082	10234	1.082		1.082
2	9.976	11257441	692349	98.918		98.918
Total		11380523	702582	100.000		100.000

(S)-N-[1-(4-bromophenyl)ethyl]-2,6-dimethylbenzenamine 5f.[1] 58.9 mg (97% yield) of **5f** was



5f

obtained as a colorless oil after purification with column chromatography on silica gel (hexanes/EtOAc, 20/1). 96% ee was determined by chiral HPLC (chiralcel OJ-H, *n*-hexane/*i*-PrOH = 99.5/0.5, flow rate = 0.3 mL/min, I = 254 nm, T = 40 °C): t_R = 25.0 min (major), 23.7 min (minor). $[\alpha]_D^{25}$ = −143.8 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 – 7.32 (m, 2H), 7.21 – 7.11 (m, 2H), 6.94 (d, *J* = 7.5 Hz, 2H), 6.78 (dd, *J* = 13.1, 5.6 Hz, 1H), 4.26 (q, *J* = 6.7 Hz, 1H), 3.06 (s, 1H), 2.15 (s, 6H), 1.48 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.7, 144.3, 131.5, 129.4, 128.9, 127.9, 121.8, 120.7, 56.3, 22.8, 18.9.



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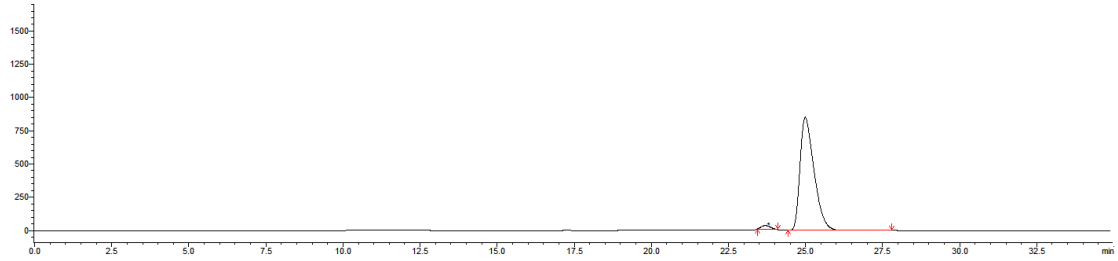
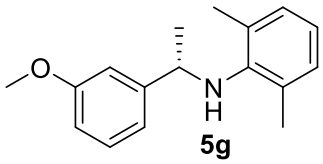
1	23.400	18586379	668296	49.896		49.896
2	25.002	18663662	533104	50.104		50.104
Total		37250040	1201400	100.000		100.000



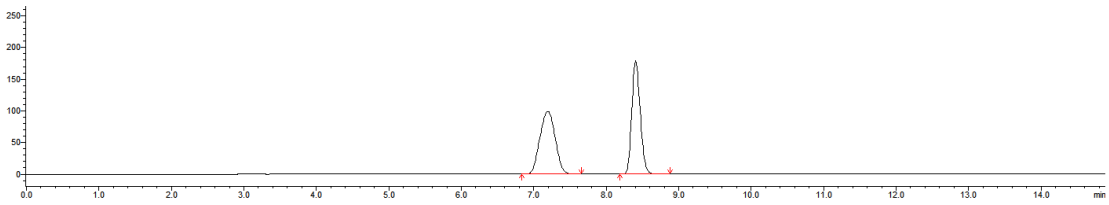
Peak#	Ret. Time	Area	Height	Conc.	Name	Area%
1	23.698	597817	28023	2.163		2.163
2	24.993	27044199	851566	97.837		97.837
Total		27642016	879589	100.000		100.000

(S)-N-[1-(3-methoxyphenyl)ethyl]-2,6-dimethylbenzenamine 5g.[1] 49.9 mg (98% yield) of **5g** was

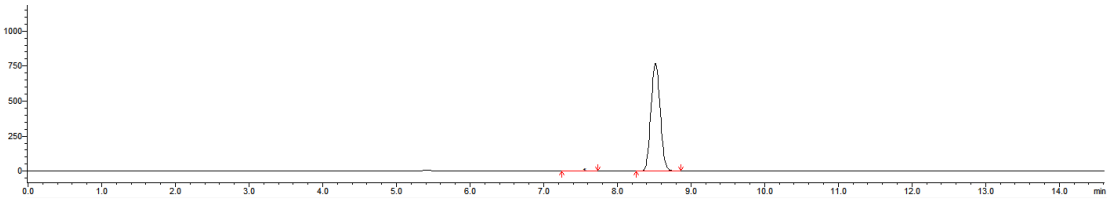


5g

obtained as a colorless oil after purification with column chromatography on silica gel (hexanes/EtOAc, 10/1). 99% ee was determined by chiral HPLC (chiralpak AD-H, *n*-hexane/*i*-PrOH = 99.5/0.5, flow rate = 1.0 mL/min, I = 254 nm, T = 40 °C): t_R = 8.5 min (major), 7.5 min (minor). $[\alpha]_D^{25}$ = −126.7 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 – 7.04 (m, 1H), 6.90 – 6.78 (m, 3H), 6.77 – 6.64 (m, 3H), 4.20 (q, *J* = 6.7 Hz, 1H), 3.65 (d, *J* = 0.5 Hz, 3H), 2.97 (s, *J* = 7.3 Hz, 1H), 2.09 (s, 6H), 1.41 (dd, *J* = 6.7, 1.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.68, 143.83, 132.62, 129.41, 128.95, 128.53, 127.55, 121.83, 56.20, 22.78, 18.95.

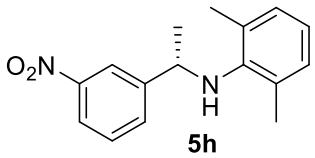


Peak#	Ret. Time	Area	Height	Conc.	Name	Area%
1	7.196	1455522	98983	50.076		50.076
2	8.405	1451095	178485	49.924		49.924
Total		2906617	277468	100.000		100.000



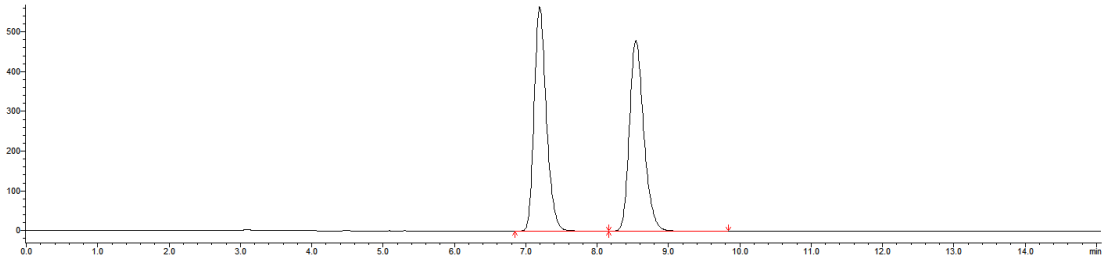
Peak#	Ret. Time	Area	Height	Conc.	Name	Area%
1	7.511	47045	2764	0.696		0.696
2	8.518	6712983	770892	99.304		99.304
Total		6760028	773655	100.000		100.000

(S)-N-[1-(3-nitrophenyl)ethyl]-2,6-dimethylbenzenamine 5h.[1] 53.2 mg (98% yield) of **5h** was

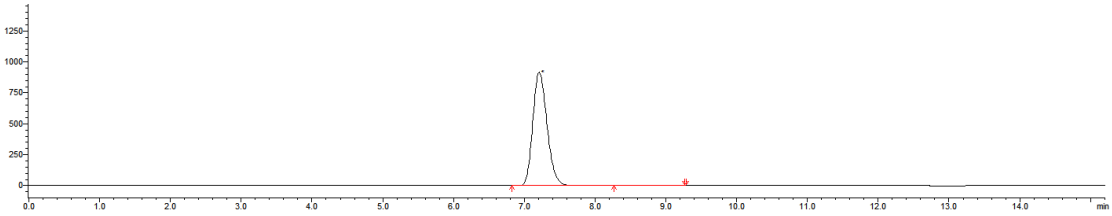


5h

obtained as a yellow oil after purification with column chromatography on silica gel (hexanes/EtOAc, 10/1). >99% ee was determined by chiral HPLC (chiralcel OD-H, *n*-hexane/*i*-PrOH = 95/5, flow rate = 1.0 mL/min, I = 254 nm, T = 40 °C): t_R = 7.2 min (major), 8.6 min (minor). $[\alpha]_D^{25}$ = −187.5 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (t, *J* = 1.9 Hz, 1H), 8.08 (ddd, *J* = 8.2, 2.2, 1.0 Hz, 1H), 7.62 (t, *J* = 9.8 Hz, 1H), 7.44 (t, *J* = 7.9 Hz, 1H), 6.95 (d, *J* = 7.5 Hz, 2H), 6.85 – 6.76 (m, 1H), 4.41 (q, *J* = 6.7 Hz, 1H), 3.22 (s, 1H), 2.17 (s, 6H), 1.56 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.4, 147.5, 144.3, 132.6, 129.4, 129.3, 129.1, 122.2, 122.0, 121.0, 56.3, 23.0, 19.0.

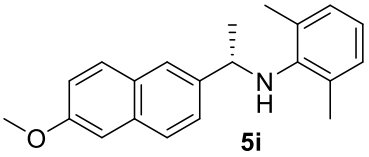


峰号	保留时间	面积	高度	浓度	化合物名	面积%
1	7.194	6689803	563716	50.008		50.008
2	8.544	6687668	479163	49.992		49.992
总计		13377471	1042879	100.000		100.000



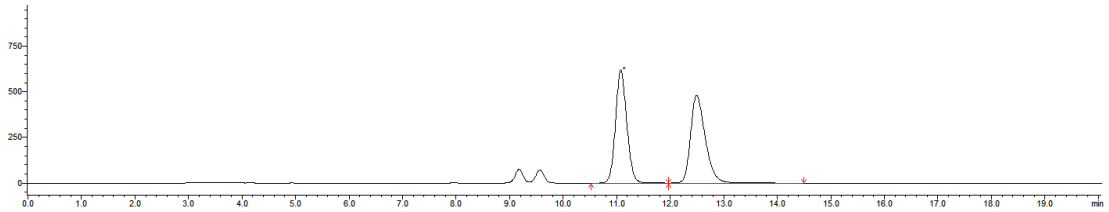
Peak#	Ret. Time	Area	Height	Conc.	Name	Area%
1	7.211	12832892	915664	99.769		99.769
2	8.567	29703	1826	0.231		0.231
Total		12862595	917490	100.000		100.000

(S)-N-[1-(6-Methoxynaphthalen-2-yl)ethyl]-2,6-dimethylbenzenamine 5i.[1] 60.4 mg (98% yield) of

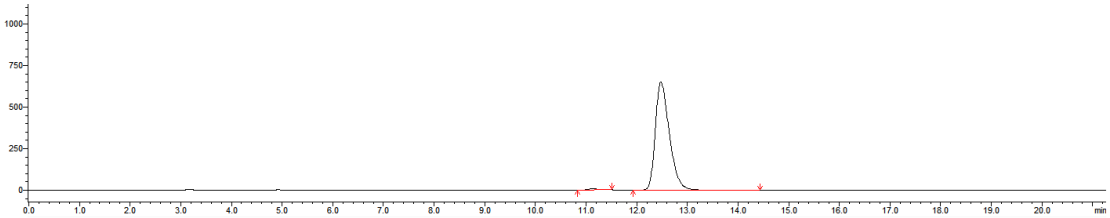


5i

5i was obtained as a slight yellowish oil after purification with column chromatography on silica gel (hexanes/EtOAc, 20/1). 98% ee was determined by chiral HPLC (chiralcel OJ-H, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, I = 254 nm, T = 40 °C): t_R = 12.5 min (major), 11.1 min (minor). $[\alpha]_D^{25}$ = −201.0 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (dd, *J* = 8.7, 2.7 Hz, 3H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.16 – 7.05 (m, 2H), 6.93 (d, *J* = 7.4 Hz, 2H), 6.84 – 6.70 (m, 1H), 4.44 (q, *J* = 6.6 Hz, 1H), 3.86 (s, 3H), 3.29 – 2.92 (s, 1H), 2.18 (d, *J* = 2.9 Hz, 6H), 1.56 (dd, *J* = 6.7, 2.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.6, 145.1, 140.6, 133.8, 129.4, 128.9, 128.9, 127.0, 125.4, 124.4, 121.6, 118.9, 105.7, 56.8, 55.3, 22.9, 19.1.

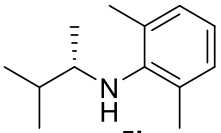


Peak#	Ret. Time	Area	Height	Conc.	Name	Area%
1	11.075	9108376	619278	49.861		49.861
2	12.494	9159028	480996	50.139		50.139
Total		18267404	1100274	100.000		100.000



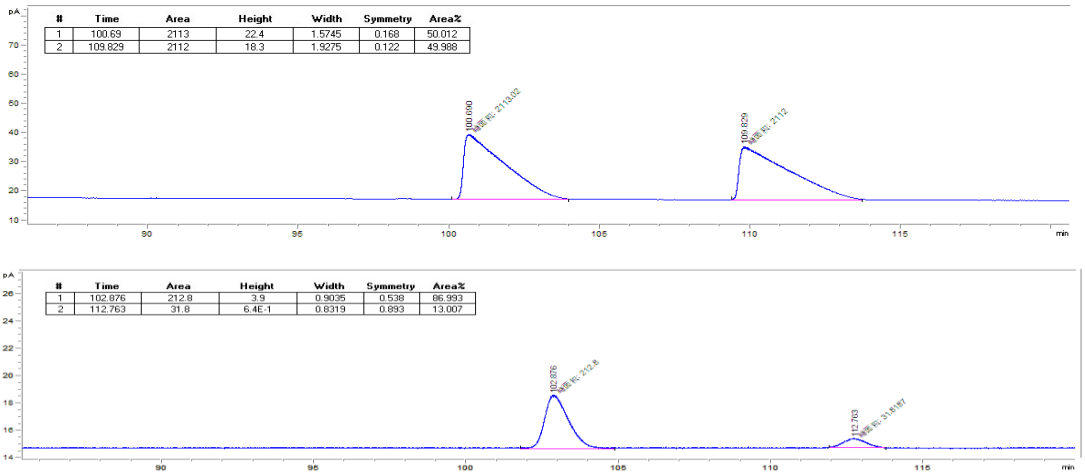
Peak#	Ret. Time	Area	Height	Conc.	Name	Area%
1	11.134	129236	7904	1.015		1.015
2	12.478	12602725	653454	98.985		98.985
Total		12731961	661358	100.000		100.000

(S)-N-(3-methylbutan-2-yl)-2,6-dimethylbenzenamine 5j.[1] 37.2 mg (98% yield) of **5j** was obtained as



5j

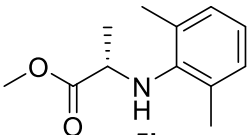
a colorless oil after purification with column chromatography on silica gel (hexanes/EtOAc, 20/1). 74% ee was determined by chiral GC (chiral β-DEX 120 column, column temp.: 100 °C, carrier gas: N_2): t_R = 102.9 min (major), 112.8 min (minor). $[\alpha]_D^{25}$ = −5.7 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.89 (d, *J* = 7.5 Hz, 2H), 6.69 (t, *J* = 7.4 Hz, 1H), 3.10 (m, *J* = 6.5, 4.8 Hz, 1H), 2.42 (s, 1H), 2.18 (s, 6H), 1.81 – 1.59 (m, 1H), 1.01 – 0.81 (m, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 145.3, 128.9, 128.6, 120.8, 57.0, 33.5, 19.5, 19.2, 17.6, 16.9.



#	Time	Area	Height	Width	Symmetry	Area%
1	100.69	2113	22.4	1.5745	0.168	50.012
2	109.829	2112	18.3	1.9275	0.122	49.988

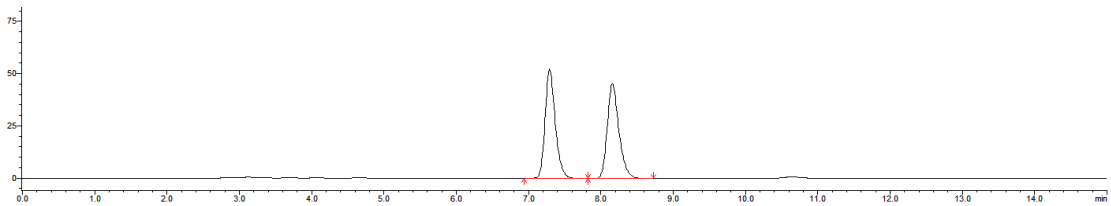
#	Time	Area	Height	Width	Symmetry	Area%
1	102.876	212.8	3.9	0.9035	0.538	86.993
2	112.763	31.8	6.4E-1	0.8319	0.893	13.007

(S)-methyl-2-(2,6-dimethylphenylamino)propanoate 5k.[1] 60.4 mg (98% yield) of **5k** was obtained as

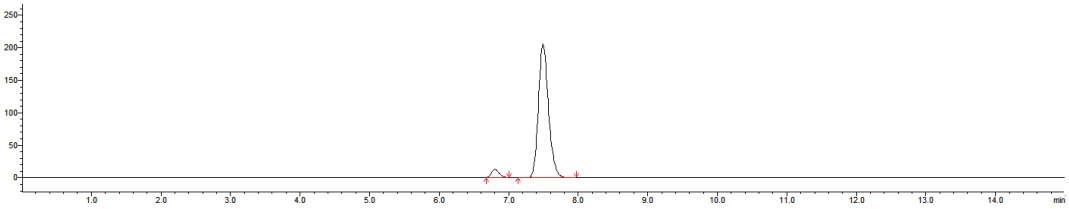


5k

a slight yellowish oil after purification with column chromatography on silica gel (hexanes/EtOAc, 20/1). 91% ee was determined by chiral HPLC (chiralcel OJ-H, *n*-hexane/*i*-PrOH = 97/3, flow rate = 0.8 mL/min, I = 254 nm, T = 40 °C): t_R = 7.5 min (major), 6.8 min (minor). $[\alpha]_D^{25}$ = −21.5 (c 1.0, $CHCl_3$). ^{1}H NMR (700 MHz, $CDCl_3$): δ 6.96 (d, *J* = 7.5 Hz, 2H), 6.80 (t, *J* = 7.5 Hz, 1H), 4.06 – 3.92 (m, 1H), 3.76 (d, *J* = 5.0 Hz, 1H), 3.66 (s, 3H), 2.30 (s, 6H), 1.38 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.7, 143.8, 132.6, 129.4, 129.0, 128.5, 127.6, 121.8, 56.2, 22.8, 19.0.

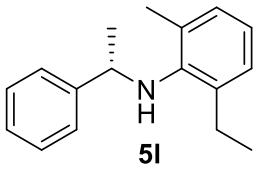


Peak#	Ret. Time	Area	Height	Conc.	Name	Area%
1	7.291	511071	52329	50.104		50.104
2	8.160	508950	45439	49.896		49.896
Total		1020021	97767	100.000		100.000



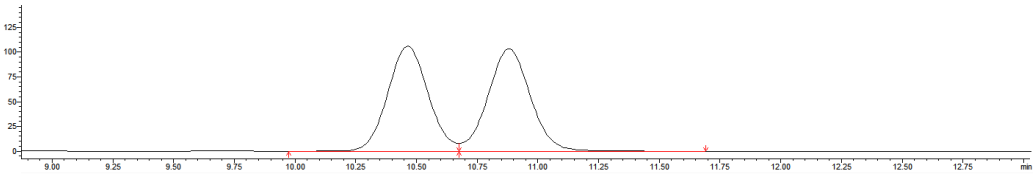
Peak#	Ret. Time	Area	Height	Conc.	Name	Area%
1	6.802	97935	12625	4.513		4.513
2	7.495	2072115	205767	95.487		95.487
Total		2170050	218391	100.000		100.000

(S)-N-(1-phenylethyl)-2-ethyl-6-methylbenzenamine 5l.[1] 46.9 mg (99% yield) of **5l** was obtained as

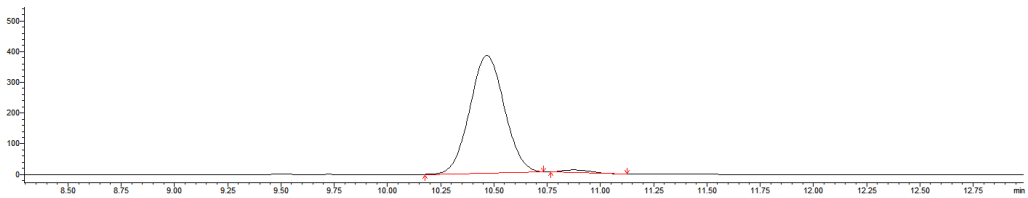


5l

a colorless oil after purification with column chromatography on silica gel (hexanes/EtOAc, 20/1). 97% ee was determined by chiral HPLC (chiralcel OJ-H, *n*-hexane/*i*-PrOH = 96.4/0.6, flow rate = 1.0 mL/min, I = 254 nm, T = 40 °C): t_R = 10.9 min (major), 10.5 min (minor). $[\alpha]_D^{25}$ = −78.4 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 – 7.21 (m, 5H), 7.03 (dd, *J* = 14.1, 7.4 Hz, 2H), 6.90 (t, *J* = 7.5 Hz, 1H), 4.33 (q, *J* = 6.7 Hz, 1H), 3.24 (s, 1H), 2.57 (q, *J* = 7.5 Hz, 2H), 2.24 (s, 3H), 1.55 (d, *J* = 6.8 Hz, 3H), 1.22 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 145.3, 144.4, 135.7, 130.0, 128.8, 128.5, 127.0, 126.6, 126.2, 122.0, 57.4, 24.4, 22.6, 19.2, 14.6.

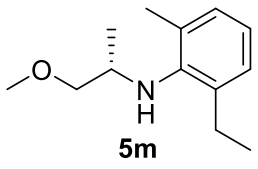


Peak#	Ret. Time	Area	Height	Conc.	Name	Area%
1	10.464	1225318	105966	49.532		49.532
2	10.881	1248467	103429	50.468		50.468
Total		2473785	209394	100.000		100.000



Peak#	Ret. Time	Area	Height	Conc.	Name	Area%
1	10.467	4330395	383805	98.292		98.292
2	10.878	75235	8682	1.708		1.708
Total		4405631	392486	100.000		100.000

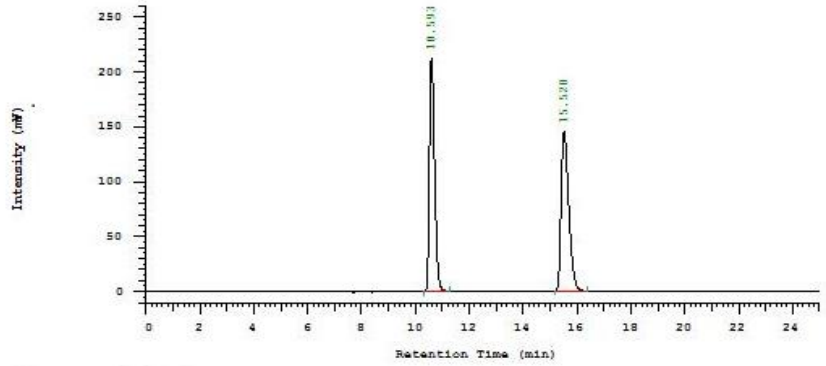
(S)-N-(1-methoxypropan-2-yl)-2-ethyl-6-methylbenzenamine 5m.[1] 40.8 mg (98% yield) of **5m** was



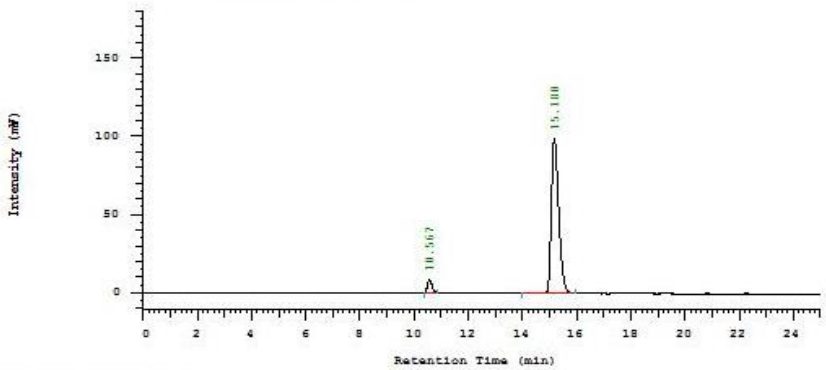
5m

obtained as a colorless oil after purification with column chromatography on silica gel (hexanes/EtOAc, 20/1). 90% ee was determined by chiral HPLC (chiralcel OD-H, *n*-hexane/*i*-PrOH = 100/0, flow rate = 1.0 mL/min, I = 254 nm, T = 40 °C): t_R = 15.2 min (major), 10.6 min (minor). $[\alpha]_D^{25}$ = +10.3 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400

MHz, $CDCl_3$): δ 7.11 – 6.97 (m, 2H), 6.88 (t, *J* = 7.5 Hz, 1H), 3.36 (m, 7H), 2.67 (q, *J* = 7.5 Hz, 2H), 2.30 (s, 3H), 1.33 – 1.10 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.3, 135.5, 129.9, 128.7, 126.5, 121.8, 59.1, 52.9, 24.3, 18.9, 18.5, 14.6.

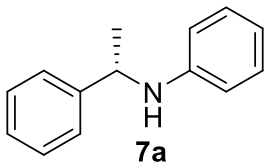


No.	RT	Area	Conc 1	BC
1	10.593	2840614	49.835	BB
2	15.520	2859456	50.165	BB
		5700070	100.000	

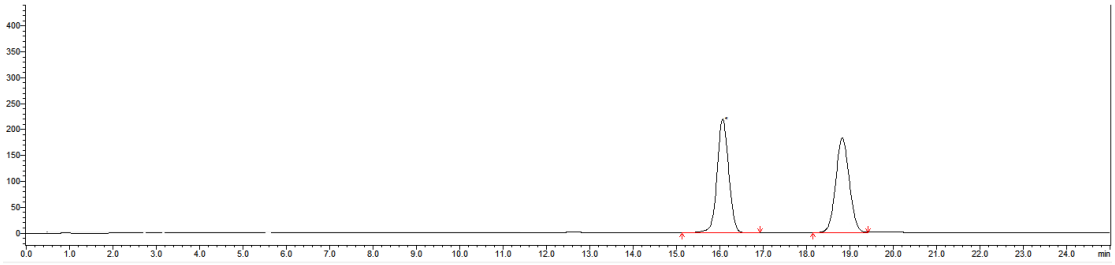


No.	RT	Area	Conc 1	BC
1	10.567	102203	5.225	BB
2	15.180	1853753	94.775	BB
		1955956	100.000	

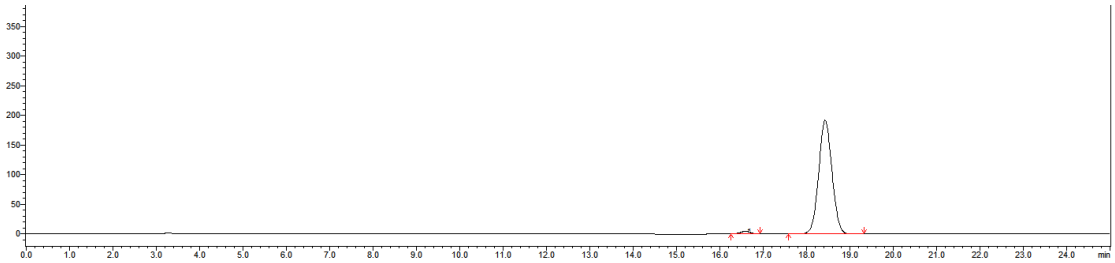
(S)-N-(1-phenylethyl)benzenamine 7a.[3] 39.1 mg (99% yield) of **7a** was obtained as a slight yellowish oil after purification with column chromatography on silica gel (hexanes/EtOAc, 20/1). 96% ee was determined by chiral HPLC (chiralcel OJ-H, *n*-hexane/*i*-PrOH = 97/3, flow rate = 1.0 mL/min, I = 254 nm, T = 40 °C): t_R = 18.4 min (major), 16.6 min (minor). $[\alpha]_D^{25}$ = +13.6 (*c* 1.0, MeOH). ^1H NMR (400 MHz, $CDCl_3$): δ 7.37 – 7.28 (m, 4H), 7.21 – 7.18 (m, 1H), 7.11 – 7.04 (m, 2H), 6.67 – 6.59 (m, 1H), 6.49 (dt, *J* = 8.9, 1.7 Hz, 2H), 4.47 (q, *J* = 6.7 Hz, 1H), 4.00 (s, 1H), 1.49 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (176 MHz, $CDCl_3$): δ 147.4, 145.3, 129.2, 128.7, 126.9, 125.9, 117.3, 113.4, 53.5, 25.1.



7a

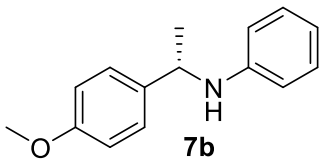


Peak#	Ret. Time	Area	Height	Conc.	Name	Area%
1	16.064	4063280	218960	50.346		50.346
2	18.823	4007360	183000	49.654		49.654
Total		8070641	401960	100.000		100.000



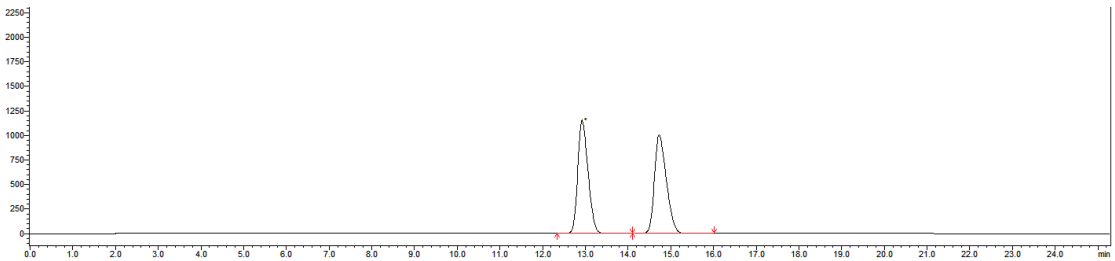
Peak#	Ret. Time	Area	Height	Conc.	Name	Area%
1	16.592	75162	4586	1.801		1.801
2	18.427	4097146	192003	98.199		98.199
Total		4172308	196590	100.000		100.000

(S)-N-(1-(4-methoxyphenyl)ethyl)benzenamine 7b.[3] 44.6 mg (98% yield) of **7b** was obtained as a

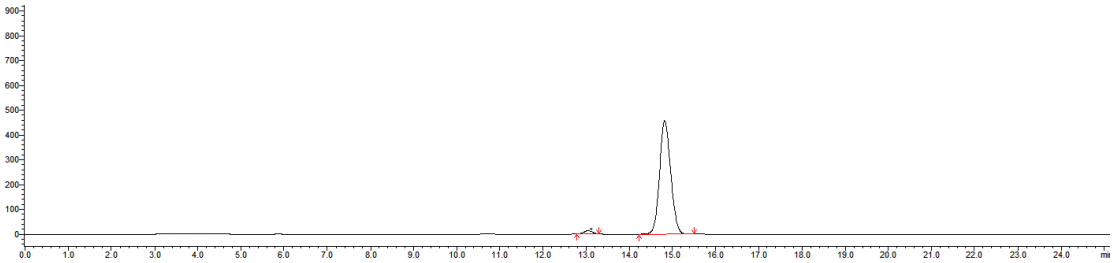


7b

slight yellowish oil after purification with column chromatography on silica gel (hexanes/EtOAc, 20/1). 96% ee was determined by chiral HPLC (chiralcel OJ-H, *n*-hexane/*i*-PrOH = 85/15, flow rate = 1.0 mL/min, I = 254 nm, T = 40 °C): t_R = 14.8 min (major), 13.0 min (minor). $[\alpha]_D^{25}$ = −8.2 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (t, *J* = 5.7 Hz, 2H), 7.10 – 7.03 (m, 2H), 6.89 – 6.80 (m, 2H), 6.63 (td, *J* = 7.3, 1.0 Hz, 1H), 6.53 – 6.48 (m, 2H), 4.43 (q, *J* = 6.7 Hz, 1H), 3.97 (s, 1H), 3.76 (s, 3H), 1.47 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.5, 147.4, 137.3, 129.2, 127.0, 117.2, 114.1, 113.4, 55.3, 52.9, 25.1.

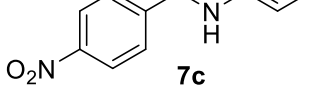


Peak#	Ret. Time	Area	Height	Conc.	Name	Area%
1	12.923	19257694	1153784	49.792		49.792
2	14.728	19418652	1004007	50.208		50.208
Total		38676346	2157791	100.000		100.000

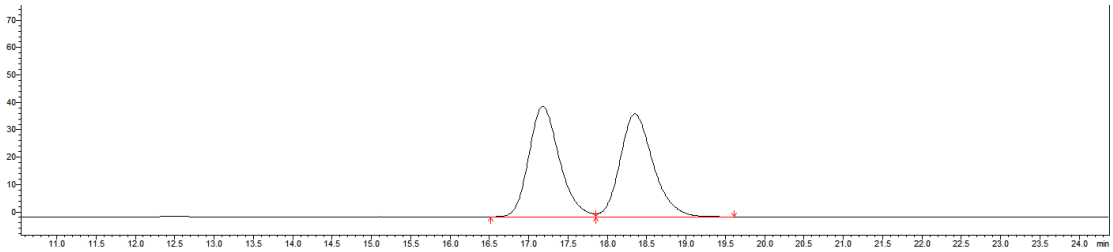


Peak#	Ret. Time	Area	Height	Conc.	Name	Area%
1	13.040	188302	13120	2.235		2.235
2	14.818	8236333	457163	97.765		97.765
Total		8424635	470283	100.000		100.000

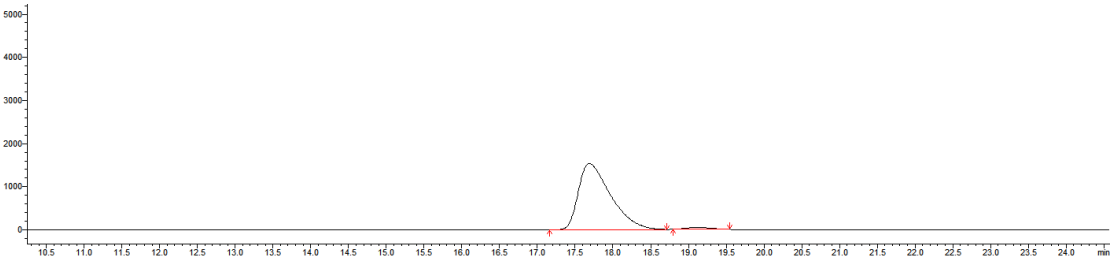
(S)-N-(1-(4-Nitrophenyl)ethyl)benzenamine 7c.[3] 47.6 mg (98% yield) of **7c** was obtained as a yellow oil after purification with column chromatography on silica gel (hexanes/EtOAc, 10/1). 96% ee was determined by chiral HPLC (chiralcel OJ-H, *n*-hexane/*i*-PrOH = 90/10, flow rate = 0.9 mL/min, I = 254 nm, T = 40 °C): t_R = 17.7 min (major), 19.1 min (minor). $[\alpha]_D^{25}$ = −18.9 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 – 7.99 (m, 2H), 7.50 – 7.38 (m, 2H), 7.07 – 6.96 (m, 2H), 6.64 – 6.56 (m, 1H), 6.36 (dt, *J* = 3.2, 1.6 Hz, 2H), 4.47 (q, *J* = 6.8 Hz, 1H), 4.03 (s, 1H), 1.45 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (176 MHz, $CDCl_3$): δ 147.0, 143.9, 132.5, 129.2, 128.9, 127.3, 117.6, 113.4, 53.0, 25.1.



7c

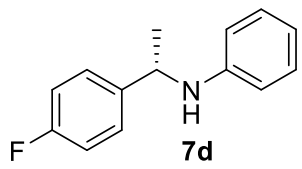


Peak#	Ret. Time	Area	Height	Conc.	Name	Area%
1	17.179	1086815	40274	49.879		49.879
2	18.351	1092106	37544	50.121		50.121
Total		2178921	77818	100.000		100.000

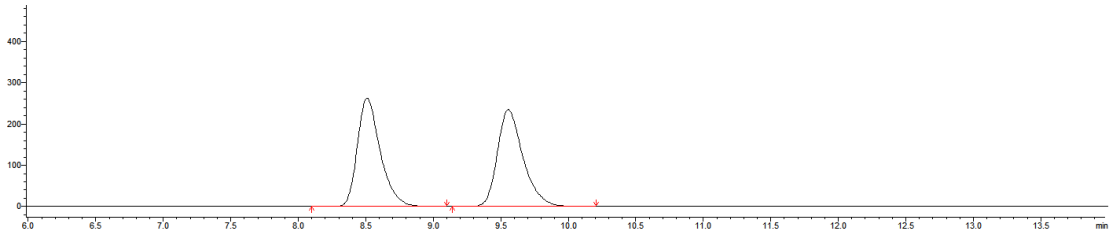


Peak#	Ret. Time	Area	Height	Conc.	Name	Area%
1	17.692	45369848	1535972	97.775		97.775
2	19.120	1032349	43190	2.225		2.225
Total		46402198	1579161	100.000		100.000

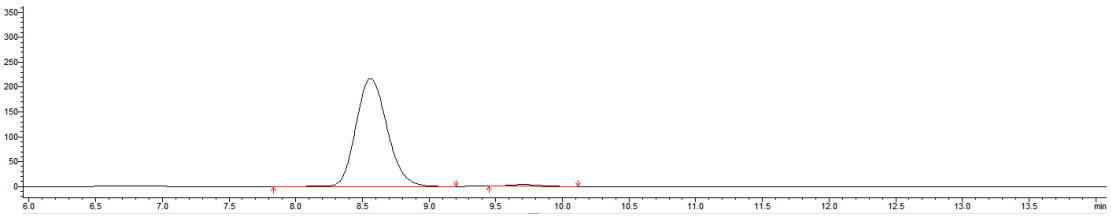
(S)-N-(1-(4-fluorophenyl)ethyl)aniline 7d.[4] 42.2 mg (98% yield) of **7d** was obtained as a colorless oil after purification with column chromatography on silica gel (hexanes/EtOAc, 20/1). 97% ee was determined by chiral HPLC (chiralcel OD-H, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.8 mL/min, I = 254 nm, T = 40 °C): t_R = 8.6 min (major), 9.7 min (minor). $[\alpha]_D^{25}$ = +22.8 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 – 7.27 (m, 2H), 7.16 – 7.05 (m, 2H), 7.03 – 6.94 (m, 2H), 6.64 (td, *J* = 7.4, 0.9 Hz, 1H), 6.53 – 6.44 (m, 2H), 4.45 (q, *J* = 6.7 Hz, 1H), 3.92 (s, 1H), 1.47 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.8 (d, J_{C-F} = 244.3 Hz), 147.1, 140.9 (d, J_{C-F} = 3.0 Hz), 129.2, 127.4 (d, J_{C-F} = 8.0 Hz), 117.5, 115.5(d, J_{C-F} = 21.3 Hz), 113.4, 52.9, 25.2; ^{19}F NMR (376 MHz, $CDCl_3$): δ -116.3.



7d

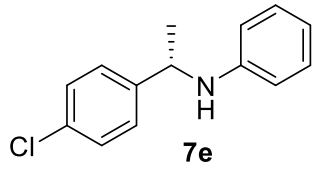


Peak#	Ret. Time	Area	Height	Conc.	Name	Area%
1	8.509	3079154	262548	49.904		49.904
2	9.556	3090952	234111	50.096		50.096
Total		6170106	496659	100.000		100.000

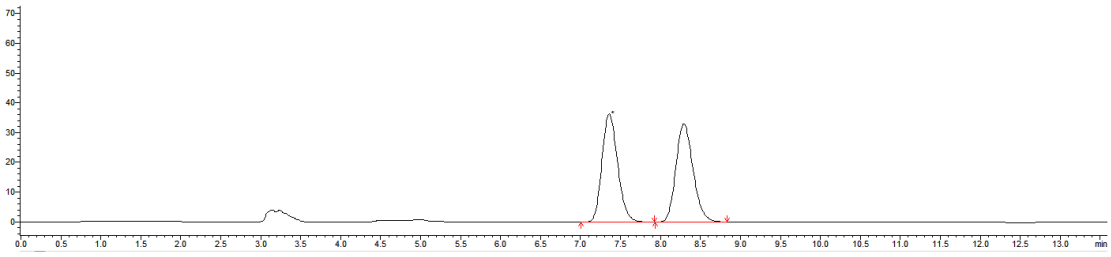


Peak#	Ret. Time	Area	Height	Conc.	Name	Area%
1	8.562	3538133	217181	98.457		98.457
2	9.706	55439	3383	1.543		1.543
Total		3593571	220564	100.000		100.000

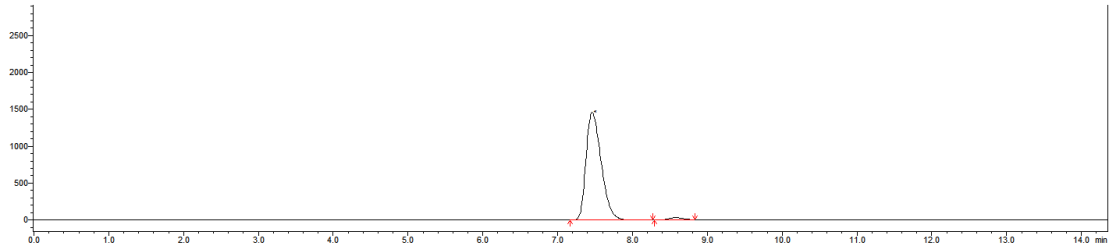
(S)-N-(1-(4-cholrophenyl)ethyl)benzenamine 7e.[3] 45.9 mg (99% yield) of **7e** was obtained as a slight yellowish oil after purification with column chromatography on silica gel (hexanes/EtOAc, 20/1). 96% ee was determined by chiral HPLC (chiralcel OD-H, *n*-hexane/*i*-PrOH = 95/5, flow rate = 1.0 mL/min, I = 254 nm, T = 40 °C): t_R = 7.5 min (major), 8.6 min (minor). $[\alpha]_D^{25}$ = +25.5 (*c* 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 – 7.24 (m, 4H), 7.13 – 7.02 (m, 2H), 6.74 – 6.62 (m, 1H), 6.46 (dd, *J* = 8.6, 0.9 Hz, 2H), 4.43 (q, *J* = 6.7 Hz, 1H), 3.98 (s, 1H), 1.47 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (176 MHz, $CDCl_3$): δ 147.0, 143.9, 132.5, 129.2, 128.9, 127.3, 117.6, 113.4, 53.0, 25.1.



7e

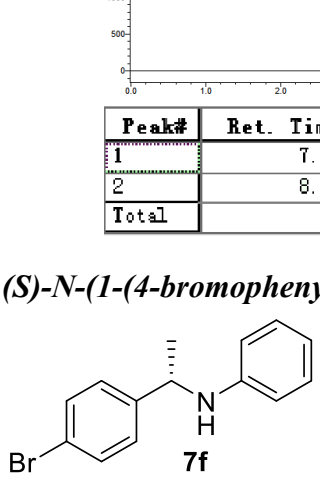


Peak#	Ret. Time	Area	Height	Conc.	Name	Area%
1	7.359	496257	36352	50.116		50.116
2	8.292	493970	32997	49.884		49.884
Total		990227	69349	100.000		100.000

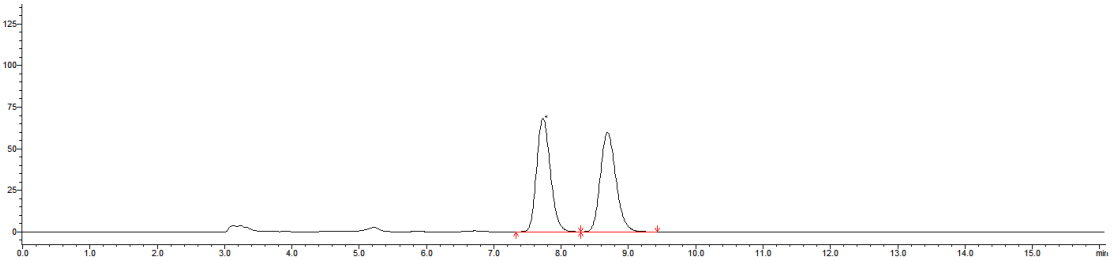


Peak#	Ret. Time	Area	Height	Conc.	Name	Area%
1	7.461	20440949	1456310	98.106		98.106
2	8.579	394663	29412	1.894		1.894
Total		20835612	1485722	100.000		100.000

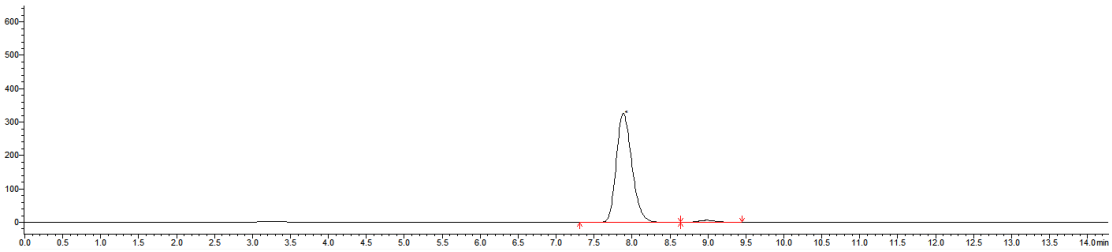
(S)-N-(1-(4-bromophenyl)ethyl)benzenamine 7f.[5] 53.7 mg (97% yield) of **7f** was obtained as a light yellow solid after purification with column chromatography on silica gel (hexanes/EtOAc, 20/1). 96% ee was determined by chiral HPLC (chiralcel OD-H, *n*-hexane/*i*-PrOH = 95/5, flow rate = 1.0 mL/min, I = 254 nm, T = 40 ℃): t_R = 7.9 min (major), 9.0 min (minor). M.p.: 62 – 64 ℃; $[\alpha]_D^{25}$ = −10.7 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (dd, *J* = 8.7, 2.1 Hz, 2H), 7.27 – 7.20 (m, 2H), 7.11 – 7.03 (m, 2H), 6.65 (td, *J* = 7.4, 0.9 Hz, 1H), 6.50 – 6.42 (m, 2H), 4.41 (q, *J* = 6.7 Hz, 1H), 3.98 (s, 1H), 1.46 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (176 MHz, $CDCl_3$): δ 147.0, 143.9, 132.5, 129.2, 128.9, 127.3, 117.6, 113.4, 53.0, 25.1.



7f



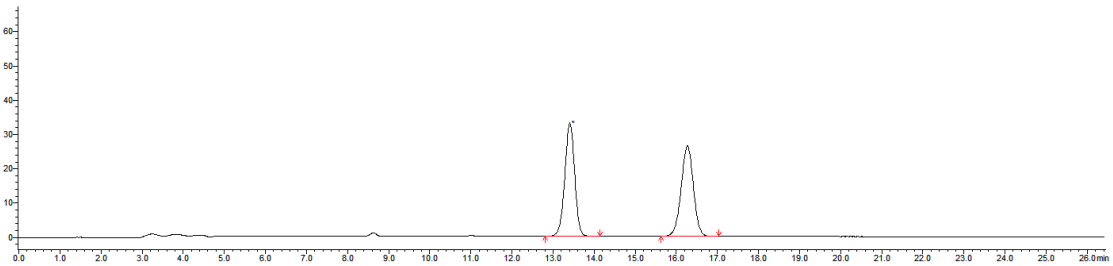
Peak#	Ret. Time	Area	Height	Conc.	Name	Area%
1	7.730	964498	68191	50.123		50.123
2	8.689	959772	59612	49.877		49.877
Total		1924271	127803	100.000		100.000



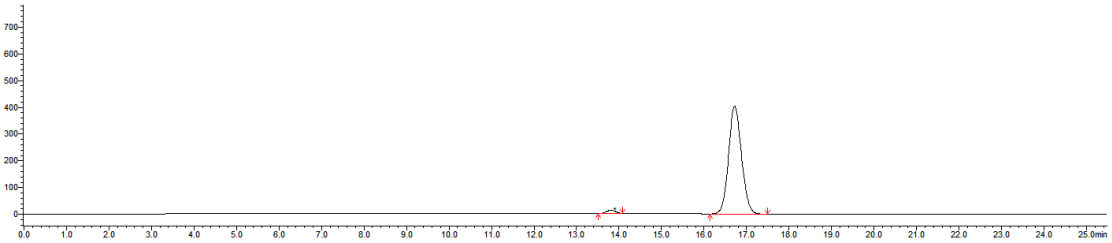
Peak#	Ret. Time	Area	Height	Conc.	Name	Area%
1	7.884	4664724	326182	98.028		98.028
2	8.984	93815	5926	1.972		1.972
Total		4758539	332107	100.000		100.000

(S)-N-(1-(3-nitrophenyl)ethyl)benzenamine 7g.[3] 47.9 mg (99% yield) of **7g** was obtained as a yellow oil after purification with column chromatography on silica gel (hexanes/EtOAc, 10/1). 96% ee was determined by chiral HPLC (chiralcel OJ-H, *n*-hexane/*i*-PrOH = 75/25, flow rate = 1.0 mL/min, I = 254 nm, T = 40 °C): t_R = 16.7 min (major), 13.8 min (minor). $[\alpha]_D^{25}$ = +26.4 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (t, *J* = 1.9 Hz, 1H), 8.07 (ddd, *J* = 8.2, 2.3, 1.0 Hz, 1H), 7.71 (d, *J* = 7.7 Hz, 1H), 7.46 (t, *J* = 7.9 Hz, 1H), 7.12 – 7.04 (m, 2H), 6.73 – 6.63 (m, 1H), 6.46 (dt, *J* = 3.2, 1.6 Hz, 2H), 4.56 (q, *J* = 6.7 Hz, 1H), 4.12 (s, 1H), 1.53 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (176 MHz, $CDCl_3$): δ 147.0, 143.9, 132.5, 129.2, 128.9, 127.3, 117.6, 113.4, 53.0, 25.1.

7g

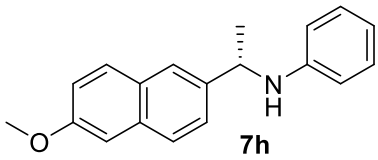


Peak#	Ret. Time	Area	Height	Conc.	Name	Area%
1	13.410	549472	33001	50.087		50.087
2	16.271	547568	26398	49.913		49.913
Total		1097040	59400	100.000		100.000



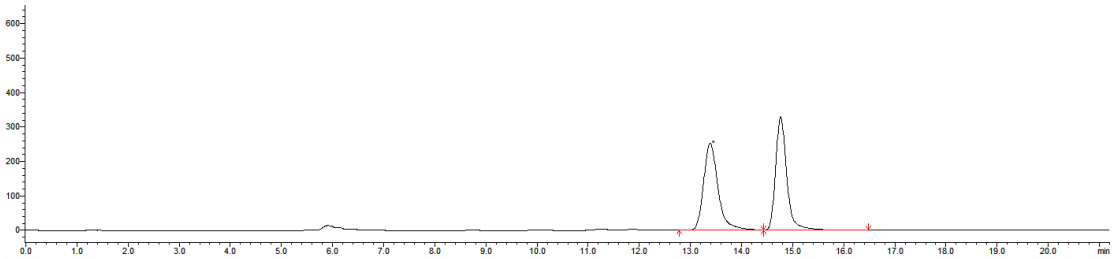
Peak#	Ret. Time	Area	Height	Conc.	Name	Area%
1	13.817	195514	12622	2.233		2.233
2	16.719	8561381	402996	97.767		97.767
Total		8756894	415619	100.000		100.000

(S)-N-(1-(6-methoxynaphthalen-2-yl)ethyl)benzenamine 7h.[3] 54.8 mg (99% yield) of **7h** was

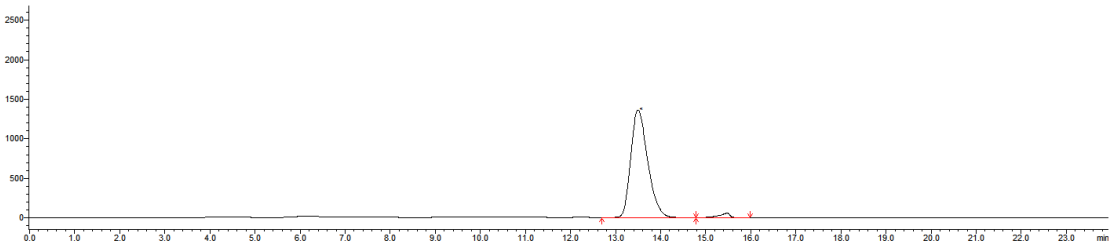


7h

obtained as a white solid after purification with column chromatography on silica gel (hexanes/EtOAc, 20/1). 95% ee was determined by chiral HPLC (chiralcel OD-H, *n*-hexane/*i*-PrOH = 85/15, flow rate = 0.5 mL/min, I = 254 nm, T = 40 ℃): t_R = 13.5 min (major), 15.5 min (minor). M.p.: 131 – 133 ℃; $[\alpha]_D^{25}$ = −20.6 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, DMSO-d^6): δ 7.82 – 7.69 (m, 3H), 7.51 (d, *J* = 8.5 Hz, 1H), 7.24 (d, *J* = 2.1 Hz, 1H), 7.12 (dd, *J* = 8.9, 2.3 Hz, 1H), 6.97 (t, *J* = 7.7 Hz, 2H), 6.58 (d, *J* = 8.1 Hz, 2H), 6.45 (t, *J* = 7.2 Hz, 1H), 6.18 (d, *J* = 6.6 Hz, 1H), 4.57 (q, *J* = 6.5 Hz, 1H), 3.81 (s, 3H), 3.53 (s, 3H), 1.49 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d^6): δ 157.4, 148.5, 141.8, 133.9, 129.5, 129.2, 129.0, 127.5, 125.6, 124.4, 119.0, 116.1, 113.4, 106.3, 55.6, 52.7, 25.1.

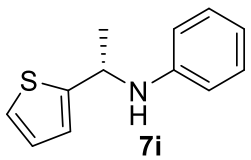


Peak#	Ret. Time	Area	Height	Conc.	Name	Area%
1	13.386	5008008	251911	49.800		49.800
2	14.765	5048214	329370	50.200		50.200
Total		10056221	581282	100.000		100.000



Peak#	Ret. Time	Area	Height	Conc.	Name	Area%
1	13.498	35555841	1361754	97.514		97.514
2	15.472	906606	55171	2.486		2.486
Total		36462446	1416925	100.000		100.000

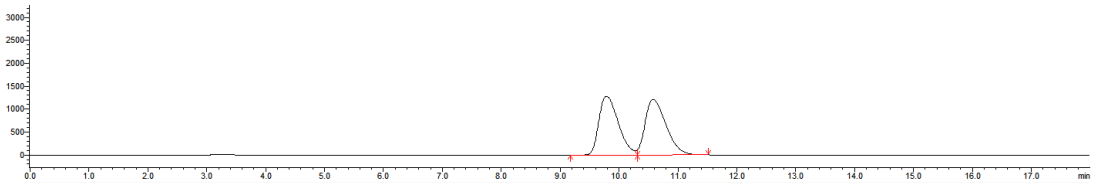
(S)-N-(1-(thiophen-2-yl)ethyl)benzenamine 7i.[3] 40.7 mg (>99% yield) of **7i** was obtained as a



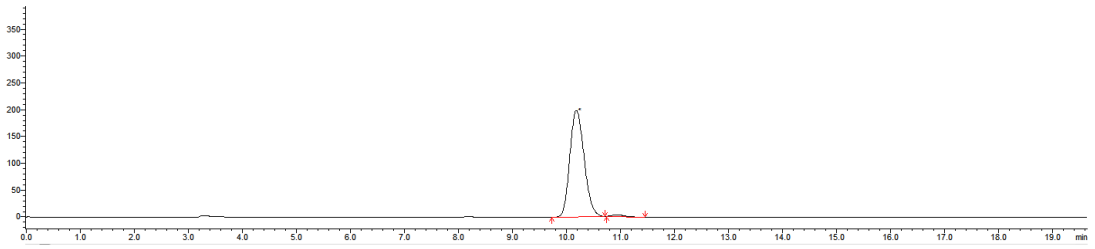
7i

colorless oil after purification with column chromatography on silica gel (hexanes/EtOAc, 20/1). 98% ee was determined by chiral HPLC (chiralcel OD-H, *n*-hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, I = 254 nm, T = 40 ℃): t_R = 10.2 min (major), 10.9 min (minor). $[\alpha]_D^{25}$ = +4.4 (*c* 1.0, CH_3CN). ^{1}H NMR (400 MHz, $CDCl_3$): δ

7.17 – 7.09 (m, 3H), 6.95 (dt, J = 3.3, 0.9 Hz , 1H), 6.92 (dd, J = 5.0, 3.5 Hz, 1H), 6.72 – 6.66 (m, 1H), 6.60 (dd, J = 8.6, 0.9 Hz, 2H), 4.80 (q, J = 6.6 Hz, 1H), 3.94 (s, 1H), 1.60 (d, J = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.3, 147.0, 129.3, 126.8, 123.7, 123.1, 117.9, 113.6, 49.6, 24.7.

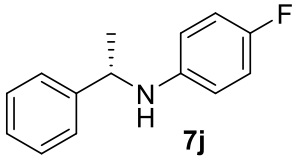


Peak#	Ret. Time	Area	Height	Conc.	Name	Area%
1	9.788	29506821	1281251	49.811		49.811
2	10.579	29730668	1210352	50.189		50.189
Total		59237489	2491603	100.000		100.000

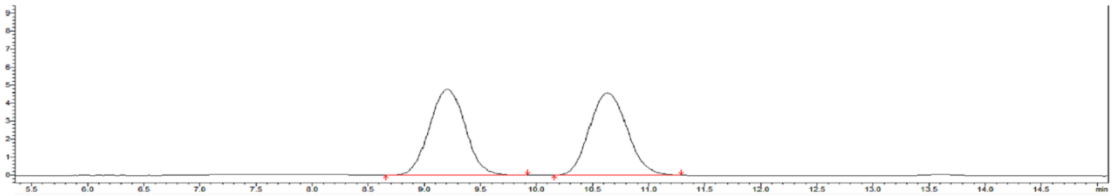


Peak#	Ret. Time	Area	Height	Conc.	Name	Area%
1	10.187	3652705	198272	98.768		98.768
2	10.939	45581	3062	1.232		1.232
Total		3698285	201335	100.000		100.000

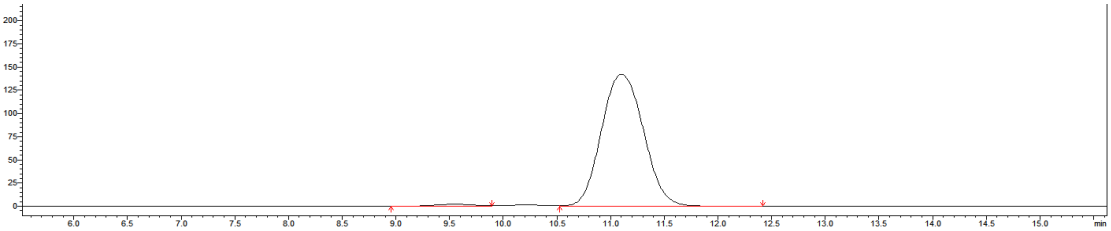
(S)-4-Fluoro-N-(1-phenylethyl)benzenamine 7j.[3] 42.1 mg (98% yield) of **7j** was obtained as a colorless oil after purification with column chromatography on silica gel (hexanes/EtOAc, 20/1). 97% ee was determined by chiral HPLC (chiralcel OD-H, *n*-hexane/*i*-PrOH = 99/1, flow rate = 0.8 mL/min, I = 254 nm, T = 40 °C): t_R = 11.1 min (major), 9.5 min (minor). $[\alpha]_D^{25}$ = +20.1 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 – 7.27 (m, 4H), 7.21 (tt, J = 6.2, 1.8 Hz, 1H), 6.83 – 6.72 (m, 2H), 6.44 – 6.36 (m, 2H), 4.40 (q, = 6.7 Hz, 1H), 3.90 (s, 1H), 1.48 (d, J = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 155.7 (d, $J_{C\text{-}F}$ = 234.7 Hz), 145.1, 143.7 (d, $J_{C\text{-}F}$ = 1.6 Hz), 128.7, 127.0, 125.9, 115.6 (d, $J_{C\text{-}F}$ = 22.2 Hz), 114.2 (d, $J_{C\text{-}F}$ = 7.3 Hz), 54.1, 25.1; ^{19}F NMR (376 MHz, $CDCl_3$): δ -128.2.



7j

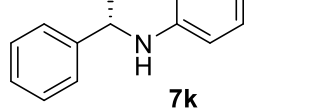


Peak#	Ret. Time	Area	Height	Conc.	Name	Area%
1	9.209	105771	4750	49.828		49.828
2	10.635	106499	4565	50.172		50.172
Total		212270	9315	100.000		100.000

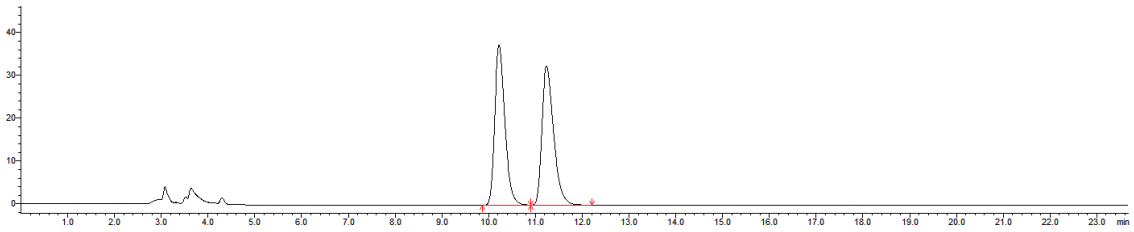


Peak#	Ret. Time	Area	Height	Conc.	Name	Area%
1	9.549	56685	2118	1.444		1.444
2	11.102	3868308	142138	98.556		98.556
Total		3924993	144256	100.000		100.000

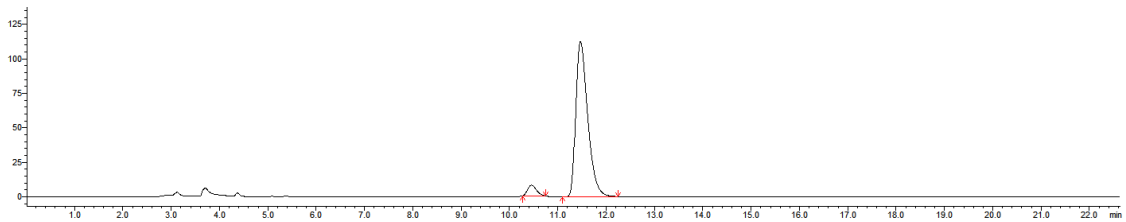
(S)-4-nitrophenyl-N-(1-phenylethyl)aniline 7k.[6] 48 mg (99% yield) of **7k** was obtained as a yellow oil after purification with column chromatography on silica gel (hexanes/EtOAc, 20/1). 90% ee was determined by chiral HPLC (chiralpak AD-H, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, I = 254 nm, T = 40 °C): t_R = 10.5 min (major), 11.5 min (minor). $[\alpha]_D^{25}$ = +5.9 (*c* 1.0, $CHCl_3$). ^{1}H NMR (700 MHz, $CDCl_3$): δ 7.98 (d, *J* = 9.2 Hz, 1H), 7.38 – 7.19 (m, 5H), 6.55 – 6.38 (m, 2H), 5.02 (d, *J* = 5.8 Hz, 1H), 4.58 (q, *J* = 6.6 Hz, 1H), 1.57 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.4, 143.3, 138.1, 129.0, 127.5, 126.3, 125.7, 111.9, 53.3, 24.6.



7k

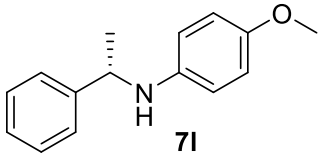


Peak#	Ret. Time	Area	Height	Conc.	Name	Area%
1	10.222	564719	37433	49.958		49.958
2	11.239	565668	32504	50.042		50.042
Total		1130387	69937	100.000		100.000



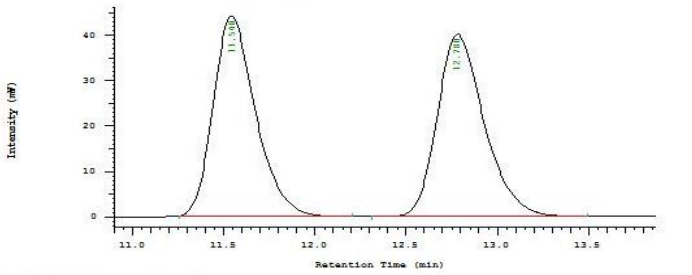
Peak#	Ret. Time	Area	Height	Conc.	Name	Area%
1	10.456	102078	7785	5.033		5.033
2	11.467	1926075	112661	94.967		94.967
Total		2028153	120446	100.000		100.000

(S)-4-Methoxyphenyl-N-(1-phenylethyl)aniline 7l.[7] 41 mg (90% yield) of **7l** was obtained as a slight yellowish oil after purification with column chromatography on silica gel (hexanes/EtOAc, 20/1). 97% ee was determined by chiral HPLC (chiralcel

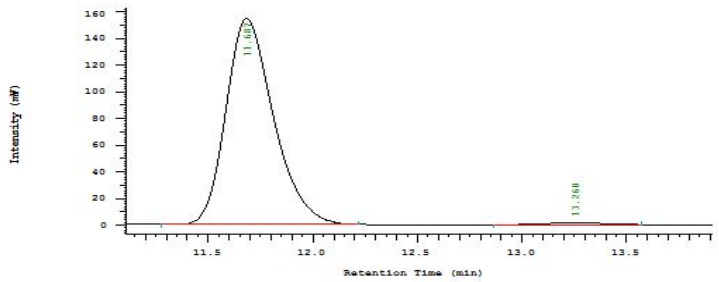


7l

OD-H, *n*-hexane/*i*-PrOH = 98/2, flow rate = 0.8 mL/min, I = 254 nm, T = 40 °C): t_R = 11.7 min (major), 13.3 min (minor). $[\alpha]_D^{25}$ = +8.4 (*c* 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 7.31 (m, 4H), 7.26 – 7.21 (m, 1H), 6.90 – 6.64 (m, 2H), 6.60 – 6.40 (m, 2H), 4.43 (q, *J* = 6.7 Hz, 1H), 3.71 (s, 3H), 1.52 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.93, 145.5, 141.6, 128.6, 126.8, 125.9, 114.8, 114.6, 55.8, 54.3, 25.2.

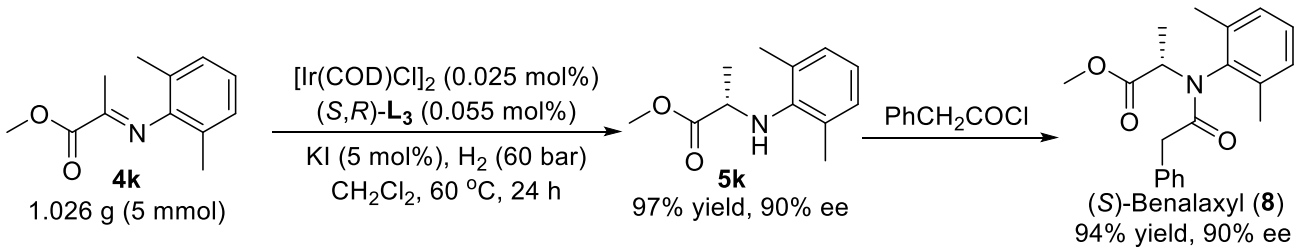


No.	RT	Area	Conc 1	BC
1	11.540	709483	49.756	BB
2	12.780	716428	50.244	BB
		1425911	100.000	



No.	RT	Area	Conc 1	BC
1	11.687	2411954	98.741	BB
2	13.260	30763	1.259	BB
		2442717	100.000	

Gram-scale synthesis and derivatizations of 5k

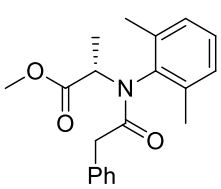


Gram-scale synthesis of 5k. In a nitrogen-filled glovebox, a stainless steel autoclave was charged with $[Ir(COD)Cl]_2$ (0.00125 mmol), (*S*,*R*)-**L$_3$** (0.00275 mmol) and KI (0.25 mmol) in 1.0 mL of degassed CH_2Cl_2. After stirring for 1 h at room temperature, a solution of imines **4k** (5.0 mmol, 1.026 g) in 20 mL of the same solvent was added to the reaction mixture, and then the hydrogenation was performed at 60 °C under a H_2 pressure of 6.0 MPa for 24 h. The solvent was then evaporated and the

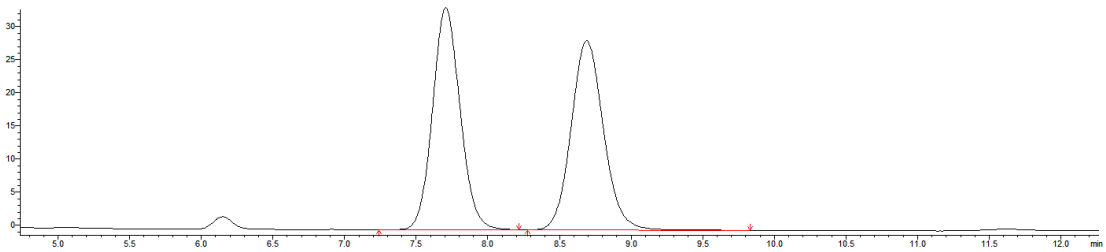
residue was purified by flash column chromatography to give the corresponding hydrogenation product **5k** (97% yield, 1.0003 g, 90% ee).

Synthesis of (*S*)-Benalaxyl 8. To a stirred solution of **5k** (2.0 mmol, 414.5 mg) in toluene was added $NaHCO_3$ (1.2 equiv., 2.4 mmol, 201.6 mg) at 0 ℃. Phenylacetyl chloride (1.2 equiv., 2.4 mmol, 370.0 mg) was then slowly added and the mixture was stirred at room temperature for 3 h. The resulted mixture was washed with 5% Na_2CO_3 and water. The layer was separated and the organic phase was dried over Na_2SO_4. It was filtered and concentrated under reduced pressure to give the crude product which was further purified by column chromatography.

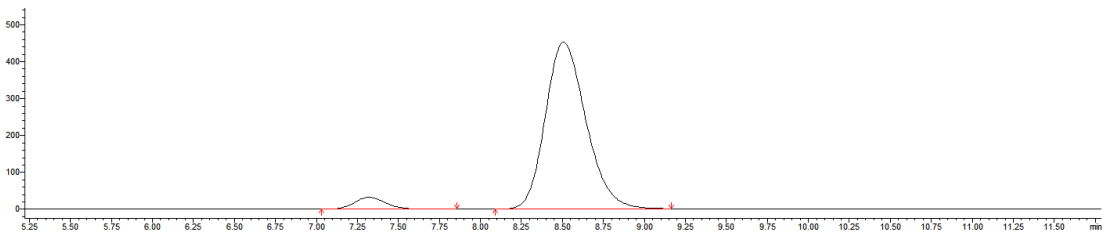
(S)-methyl-N-(2,6-dimethylphenyl)-N-(2-phenylacetyl)alaninate 8.[8] 305.4 mg (94% yield) of **8** was obtained as a white solid after purification with column chromatography on silica gel (hexanes/EtOAc, 20/1). 90% ee was determined by chiral HPLC (chiralcel OJ-H, *n*-hexane/*i*-PrOH = 98/2, flow rate = 1.0 mL/min, I = 254 nm, T = 40 ℃): t_R = 7.3 min (major), 8.5 min (minor). M.p.: 77 – 80 ℃; $[\alpha]_D^{25}$ = +31.9 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 – 7.12 (m, 5H), 7.10 – 6.99 (m, 1H), 6.99 – 6.88 (m, 2H), 4.43 (q, *J* = 7.4 Hz, 1H), 3.76 (s, 3H), 3.33 (d, *J* = 14.5 Hz, 1H), 3.20 (d, *J* = 14.5 Hz, 1H), 2.39 (s, 3H), 1.86 (s, 3H), 0.98 (d, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 173.1, 171.7, 138.8, 138.0, 137.2, 134.2, 129.3, 129.2, 128.8, 128.6, 128.2, 126.7, 55.6, 52.1, 41.2, 18.7, 18.1, 15.1.



8



Peak#	Ret. Time	Area	Height	Conc.	Name	Area%
1	7.707	448493	33502	50.059		50.059
2	8.690	447432	28569	49.941		49.941
Total		895925	62071	100.000		100.000



Peak#	Ret. Time	Area	Height	Conc.	Name	Area%
1	7.321	428193	32190	5.212		5.212
2	8.506	7787660	452248	94.788		94.788
Total		8215853	484438	100.000		100.000

References

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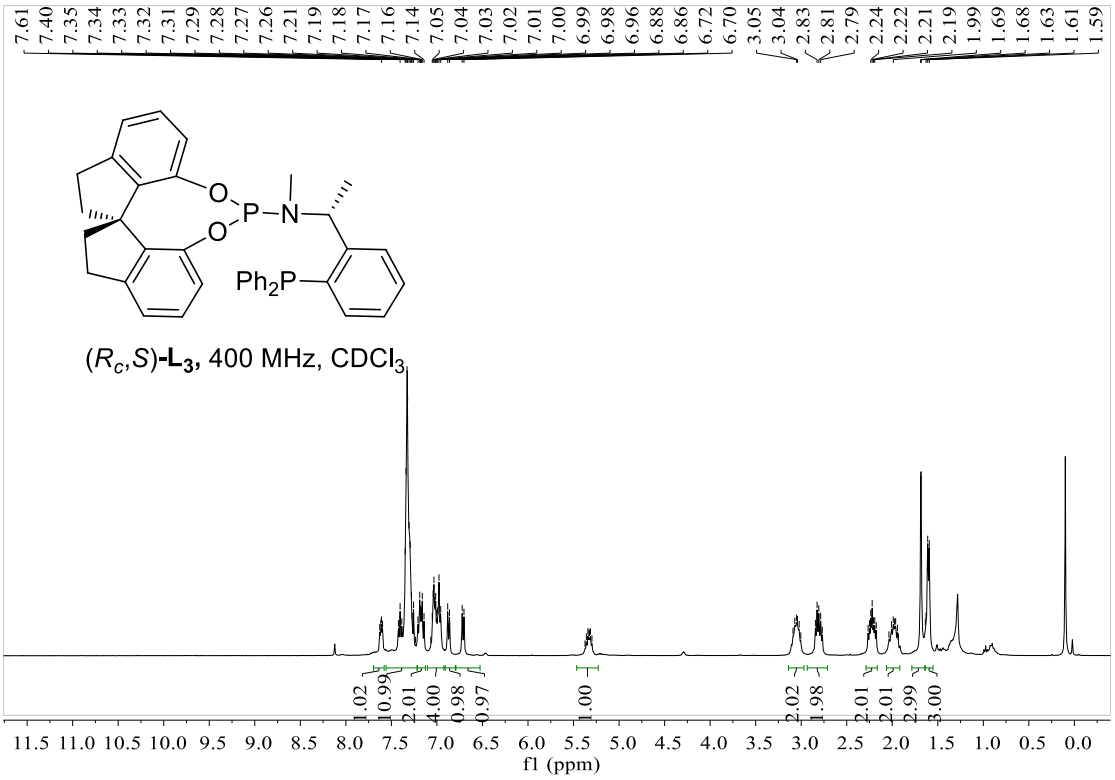
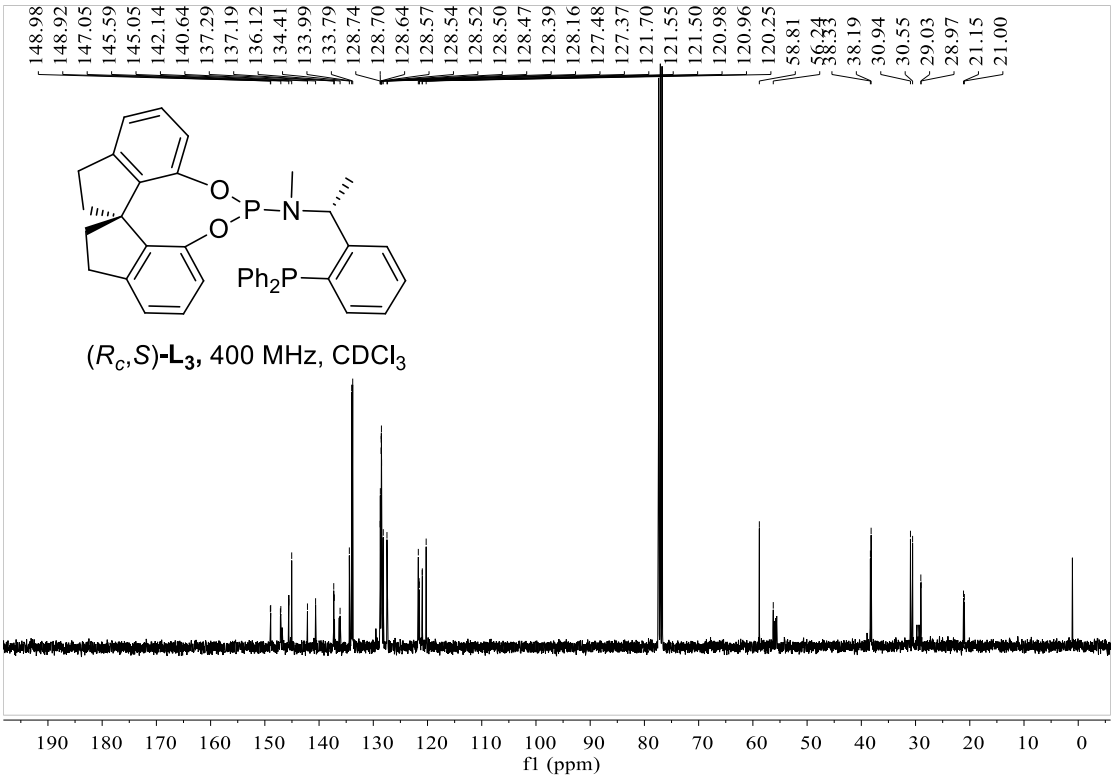
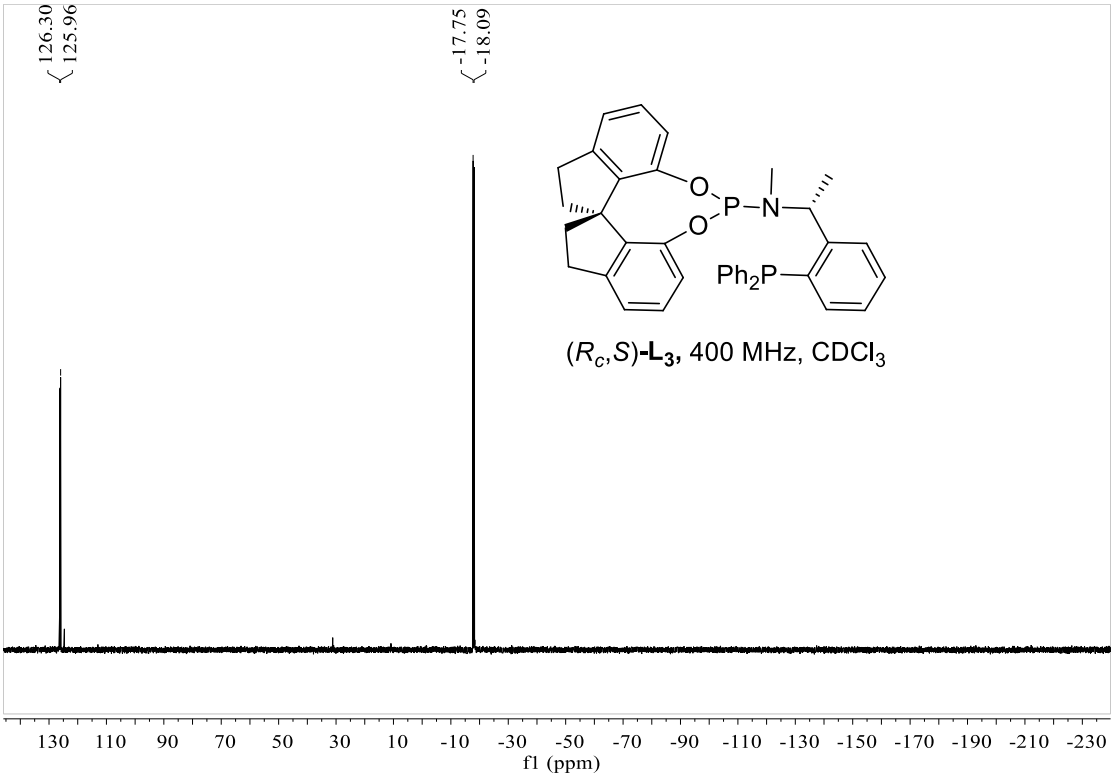
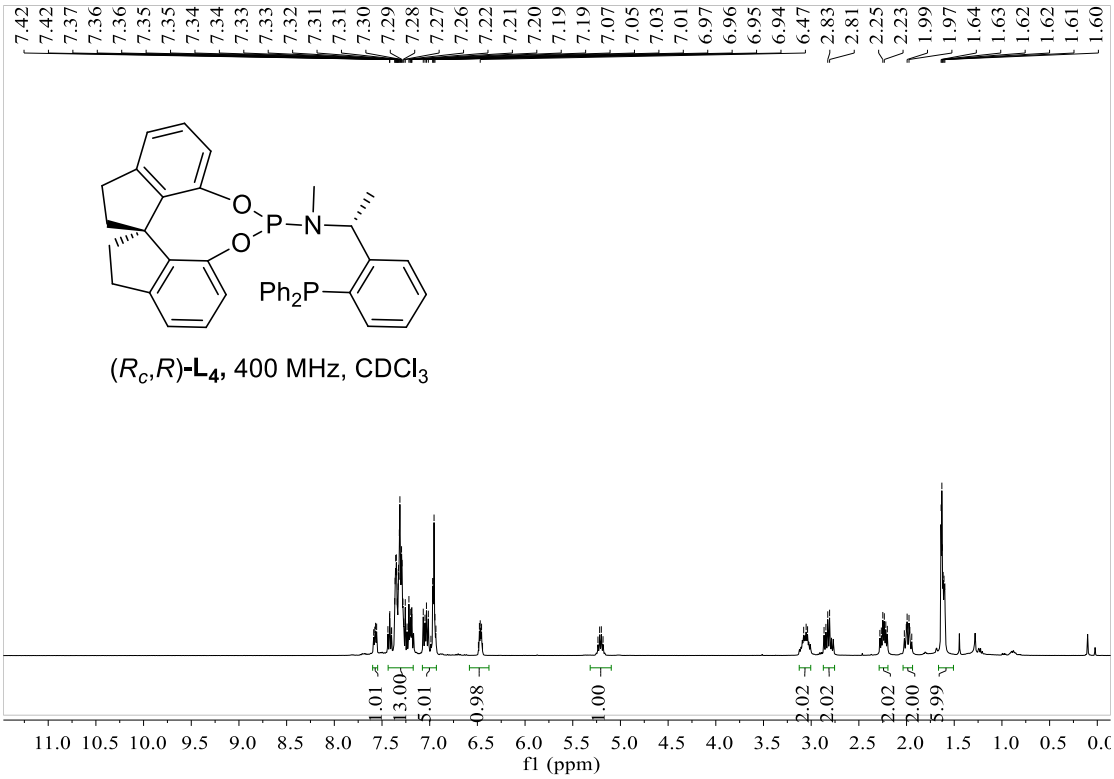
NMR spectra


7.61 7.40 7.35 7.34 7.33 7.32 7.31 7.29 7.28 7.27 7.26 7.21 7.19 7.18 7.17 7.16 7.14 7.05 7.04 7.03 7.02 7.01 7.00 6.99 6.98 6.96 6.88 6.86 6.72 6.70 3.05 3.04 2.83 2.81 2.79 2.24 2.22 2.21 2.19 1.99 1.69 1.68 1.63 1.61 1.59
O
P
N
O
Ph2P
(Rc,S)-L3, 400 MHz, CDCl3
1.02 10.99 2.01 4.00 0.98 0.97 1.00 2.02 1.98 2.01 2.01 2.99 3.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

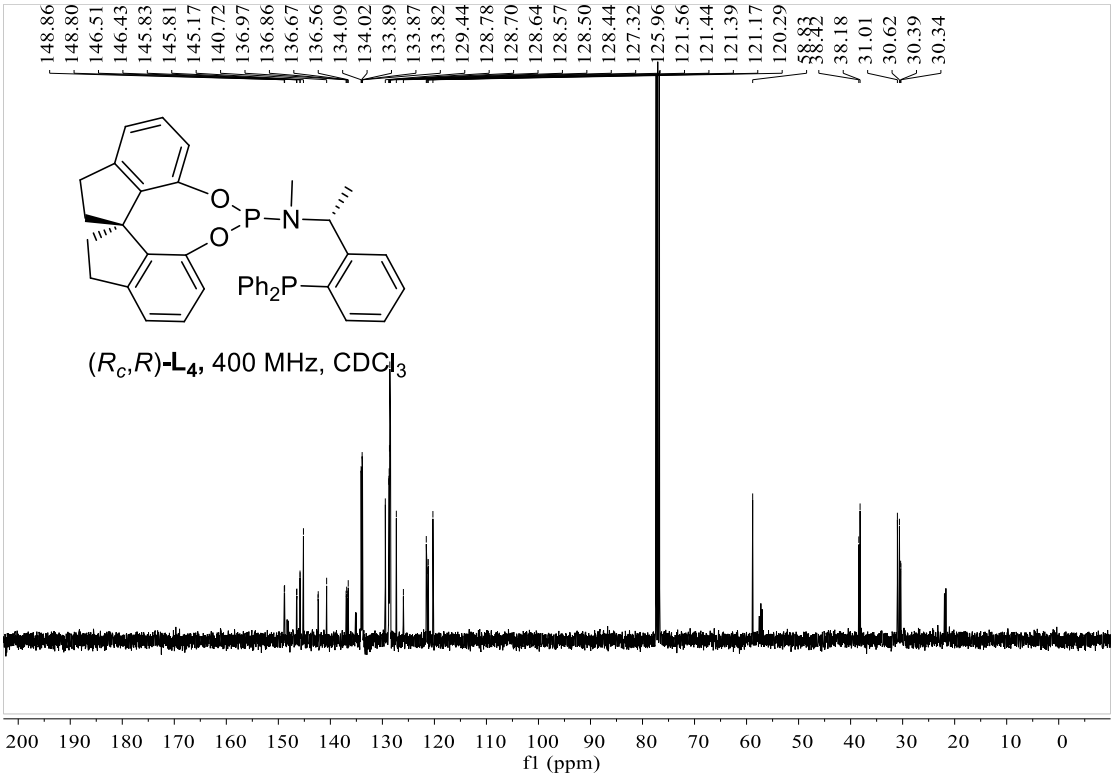

148.98 148.92 147.05 145.59 145.05 142.14 140.64 137.29 137.19 136.12 134.41 133.99 133.79 128.74 128.70 128.64 128.57 128.54 128.52 128.50 128.47 128.39 128.16 127.48 127.37 121.70 121.55 121.50 120.98 120.96 120.25 58.81 56.24 38.33 38.19 30.94 30.55 29.03 28.97 21.15 21.00
O
P
N
O
Ph2P
(Rc,S)-L3, 400 MHz, CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

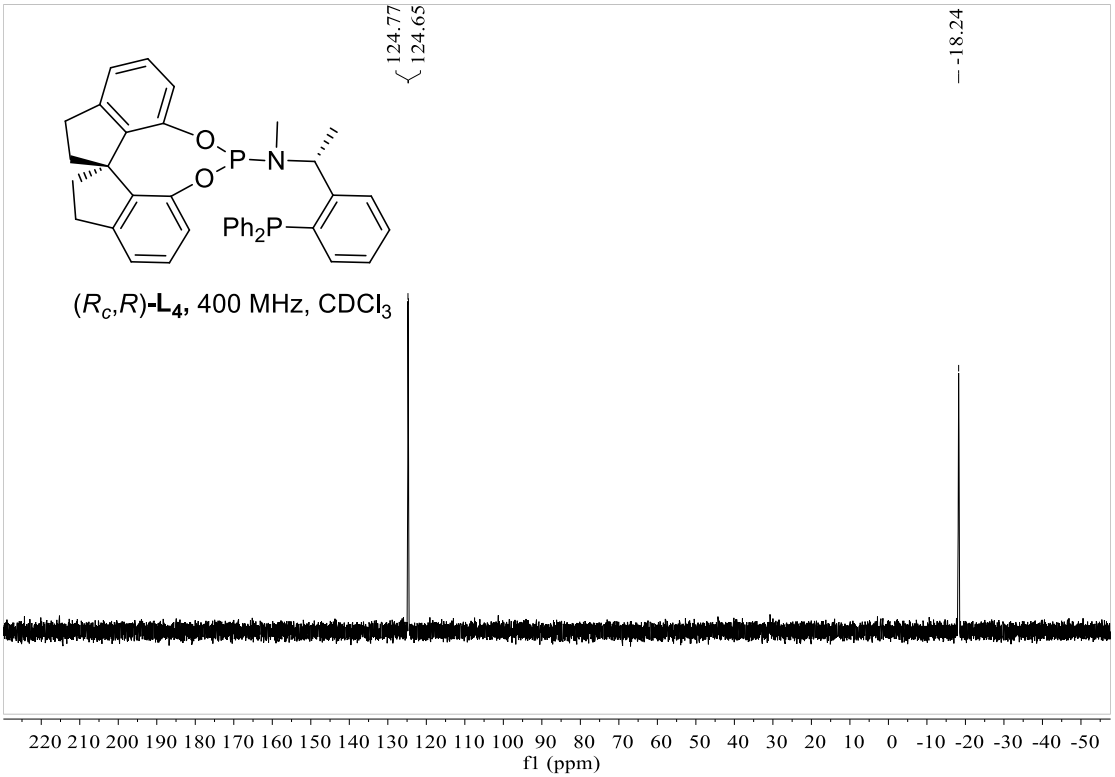


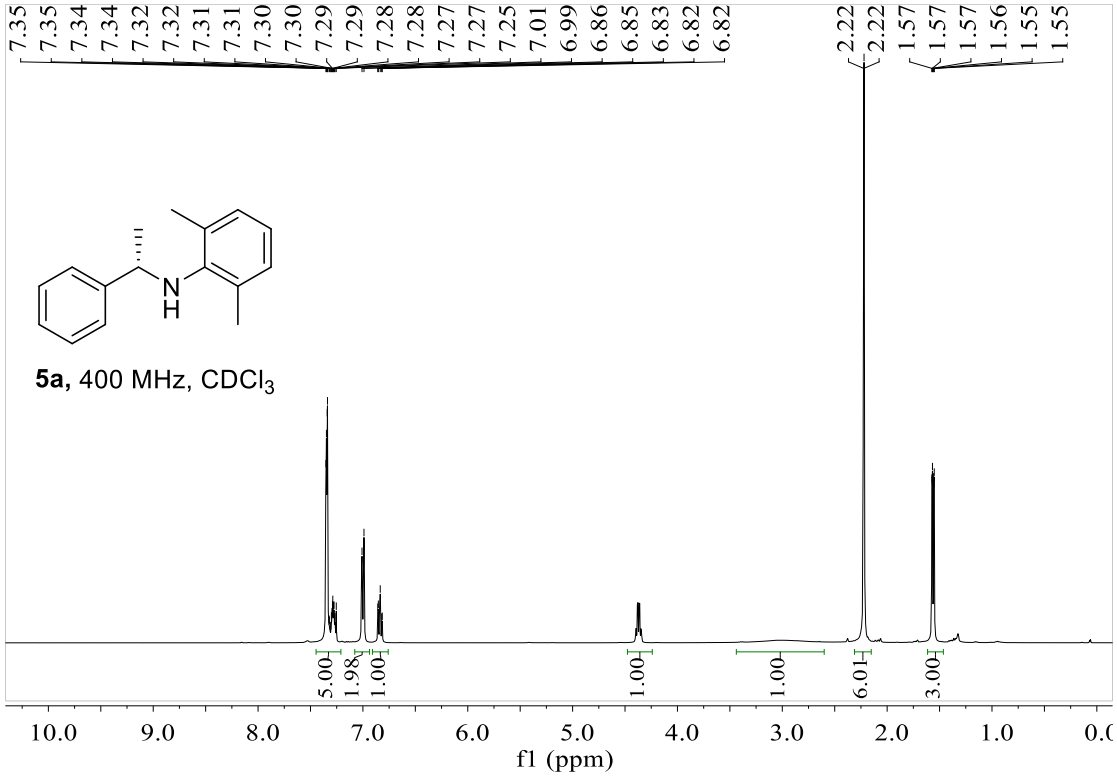
(R_c,S)-**L$_3$**, 400 MHz, $CDCl_3$



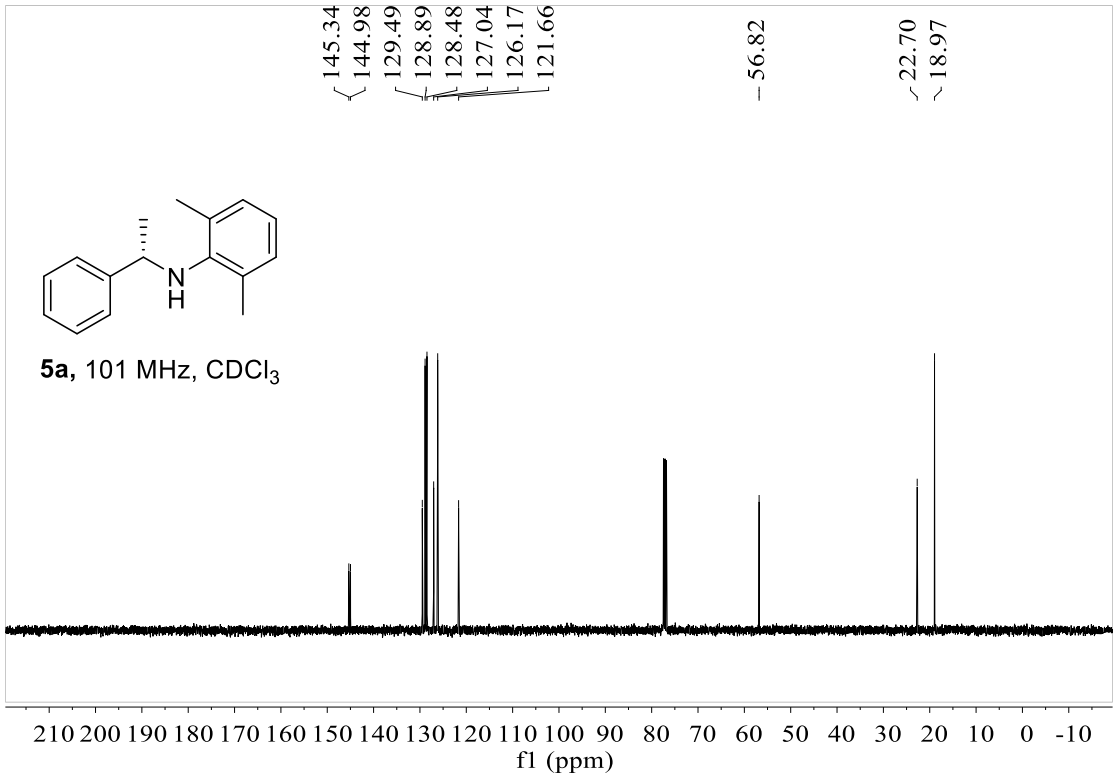
(R_c,R)-**L$_4$**, 400 MHz, $CDCl_3$


148.86
148.80
146.51
146.43
145.83
145.81
145.17
140.72
136.97
136.86
136.67
136.56
134.09
134.02
133.89
133.87
133.82
129.44
128.78
128.70
128.64
128.57
128.50
128.44
127.32
125.96
121.56
121.44
121.39
121.17
120.29
58.83
38.42
38.18
31.01
30.62
30.39
30.34
O
P
N
O
Ph2P
(Rc,R)-L4, 400 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

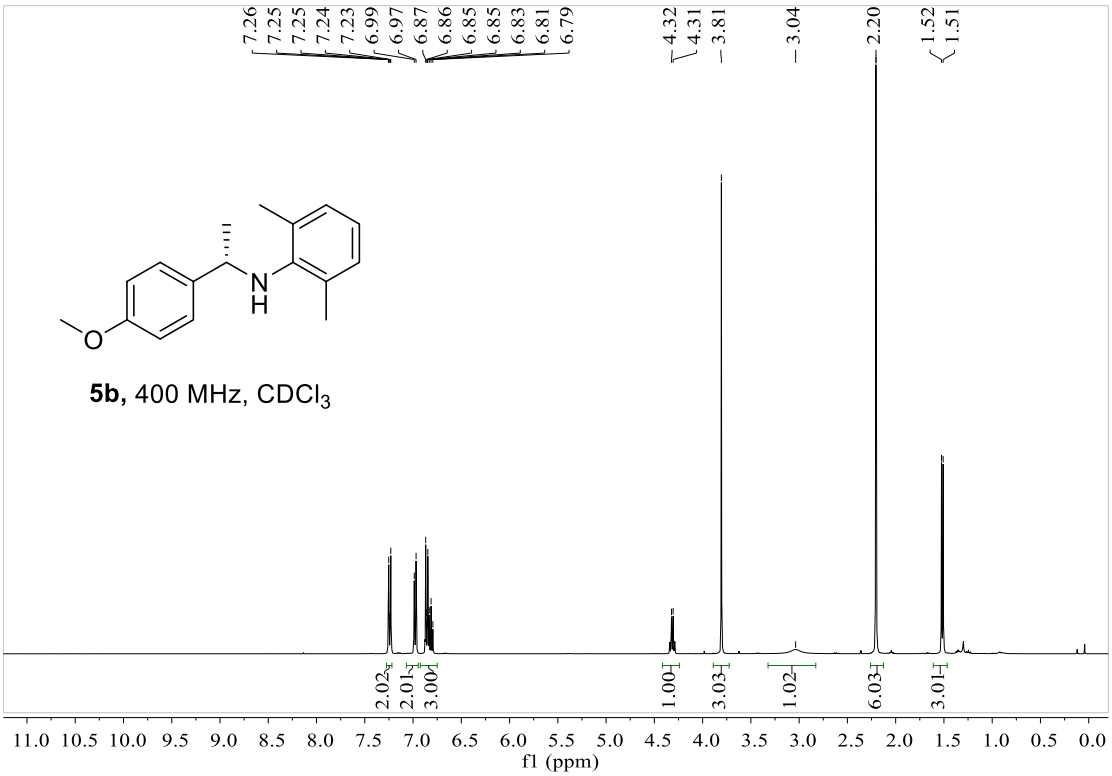

124.77
124.65
-18.24
O
P
N
O
Ph2P
(Rc,R)-L4, 400 MHz, CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50
f1 (ppm)



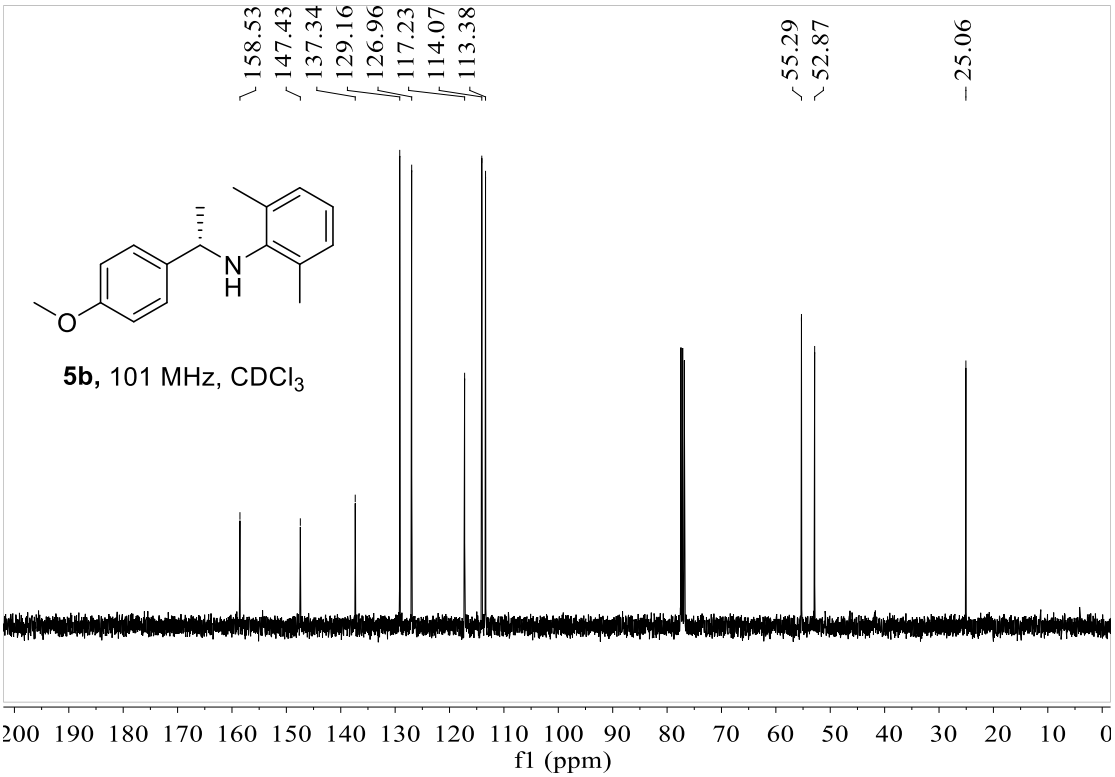
5a, 400 MHz, $CDCl_3$



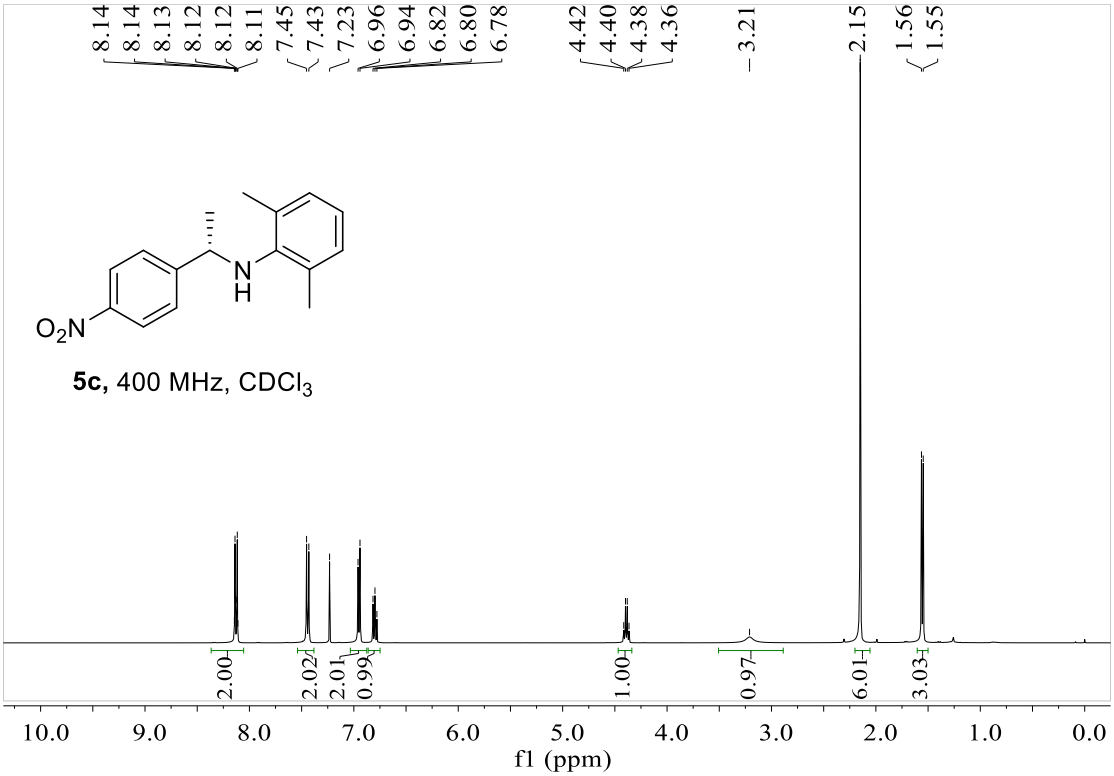
5a, 101 MHz, $CDCl_3$



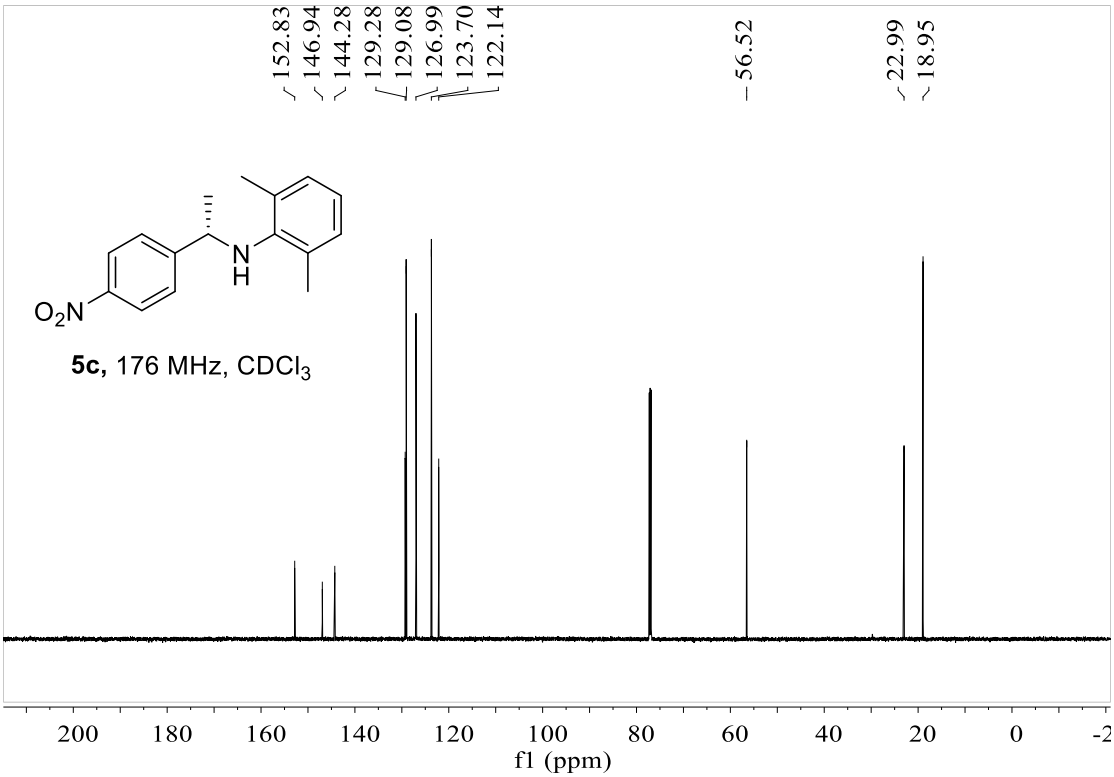
5b, 400 MHz, $CDCl_3$



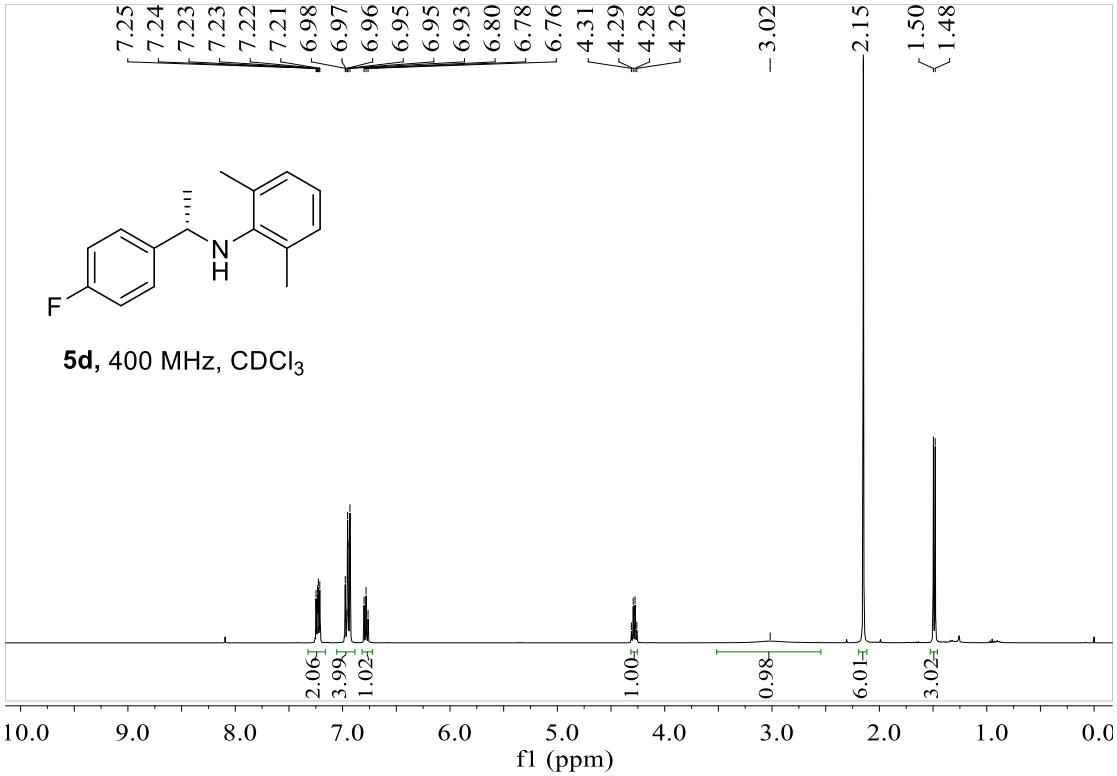
5b, 101 MHz, $CDCl_3$



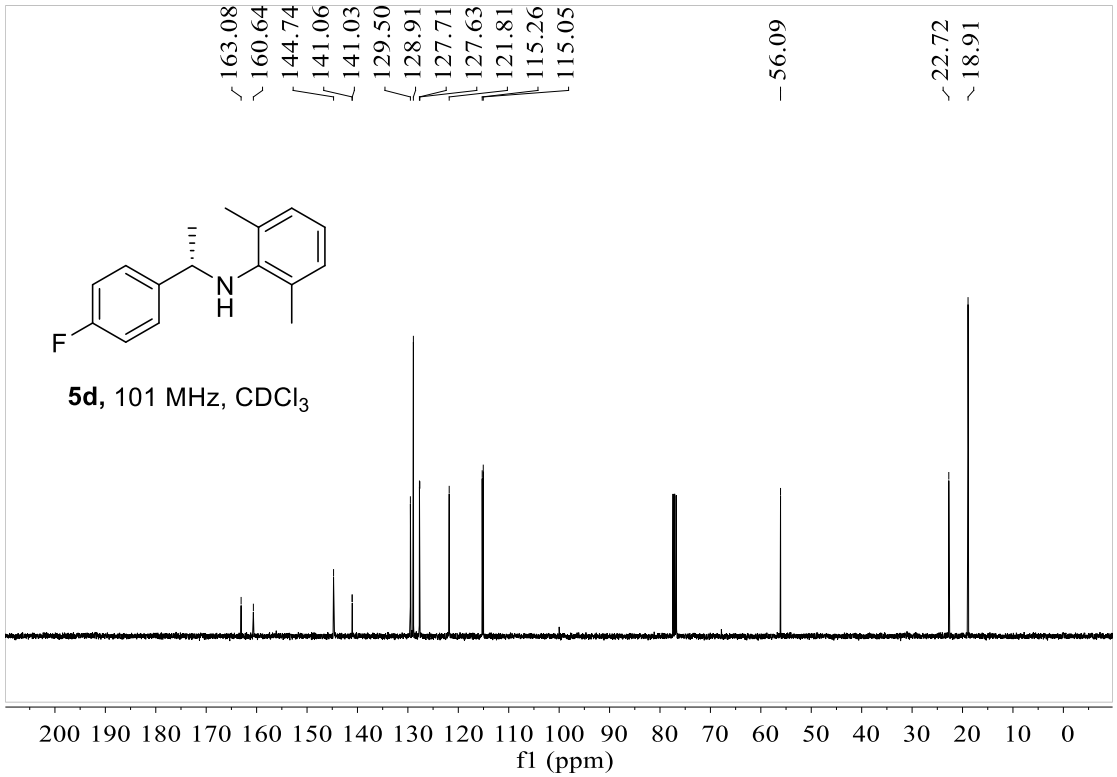
5c, 400 MHz, $CDCl_3$



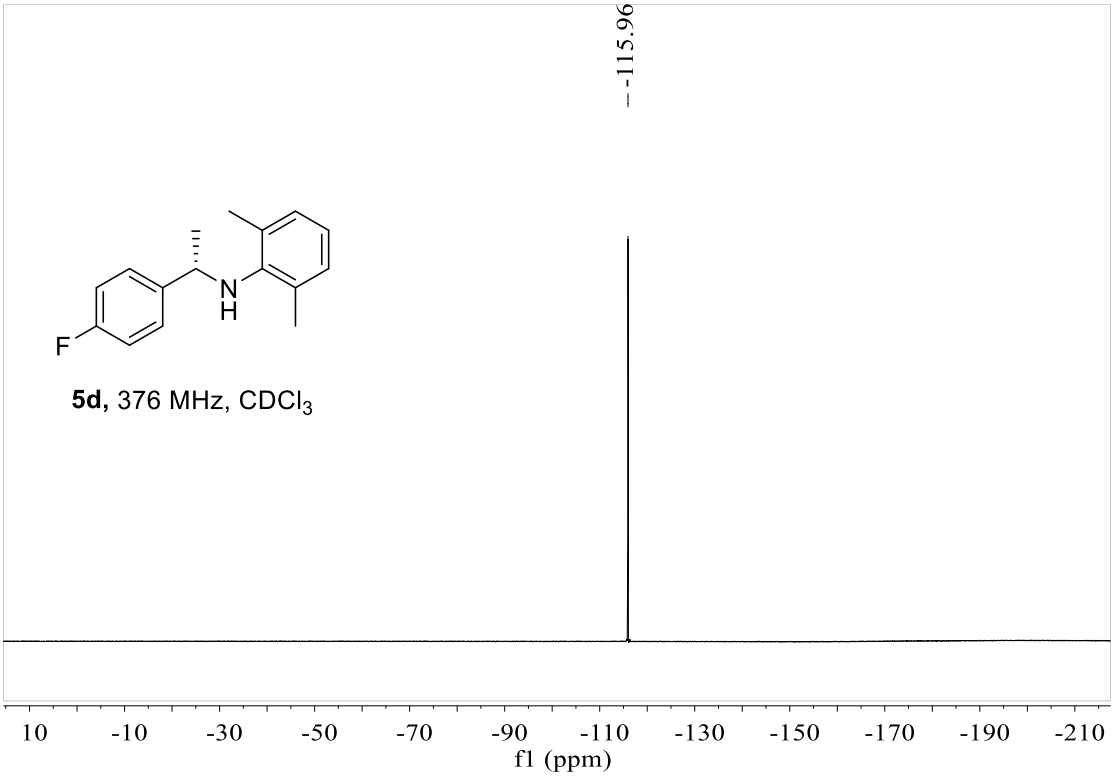
5c, 176 MHz, $CDCl_3$



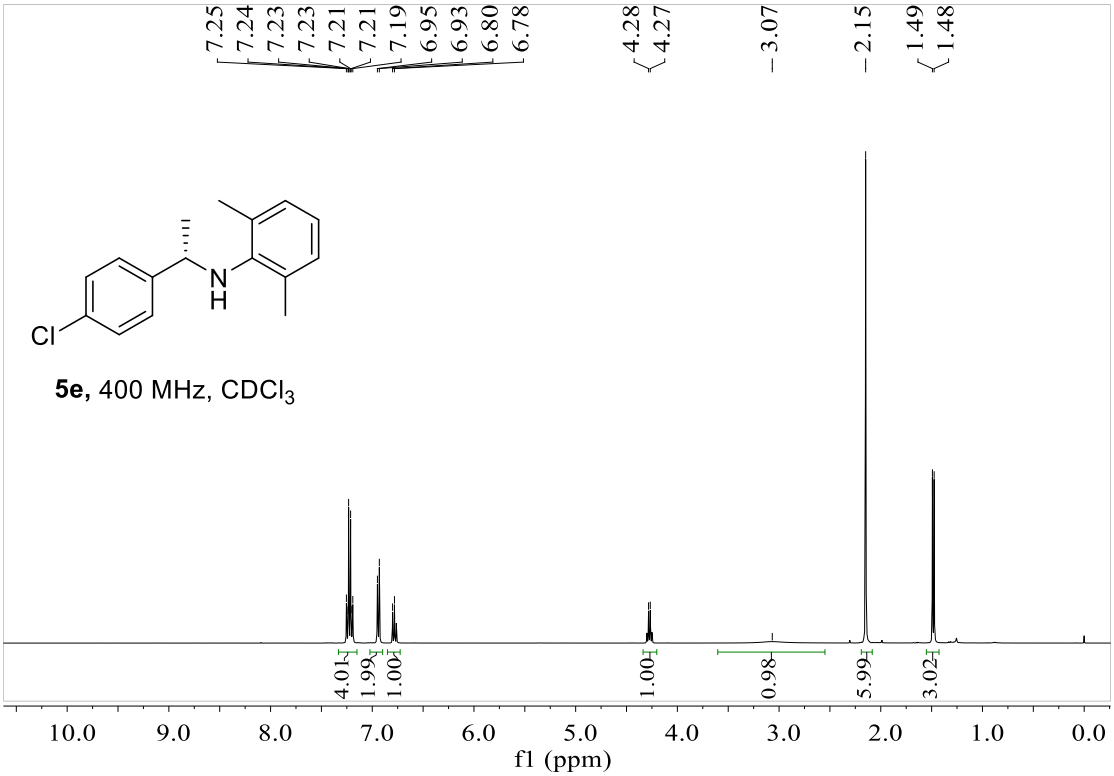
5d, 400 MHz, $CDCl_3$



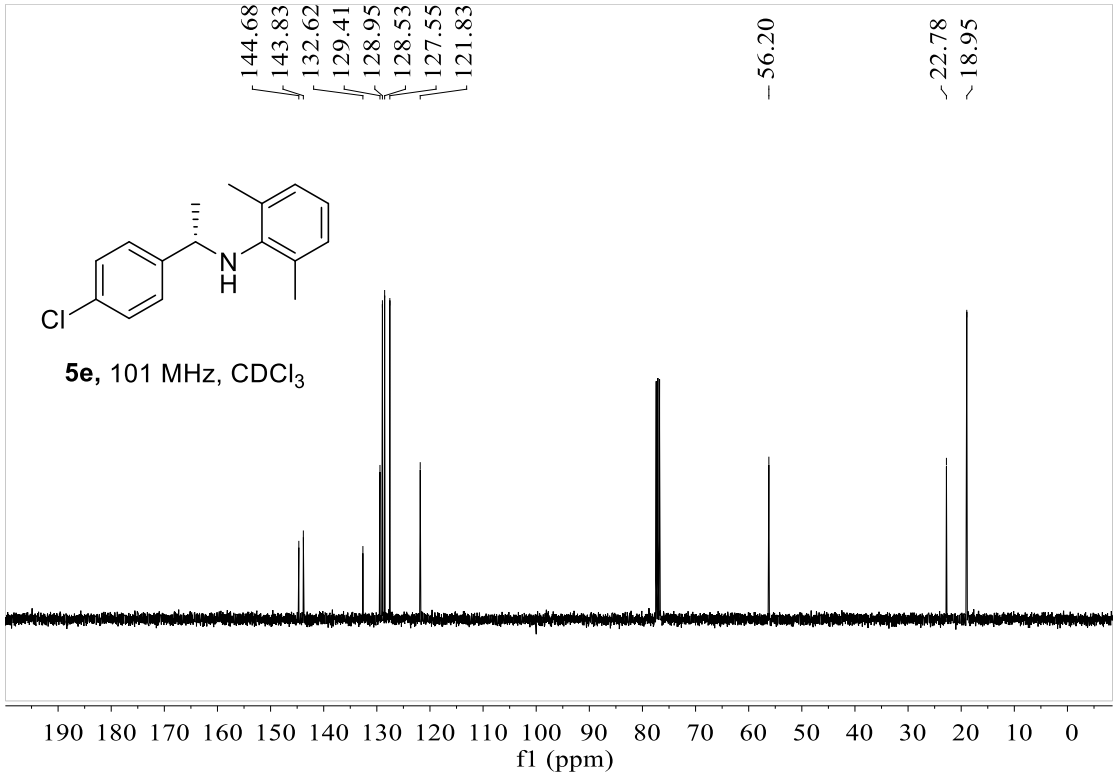
5d, 101 MHz, $CDCl_3$



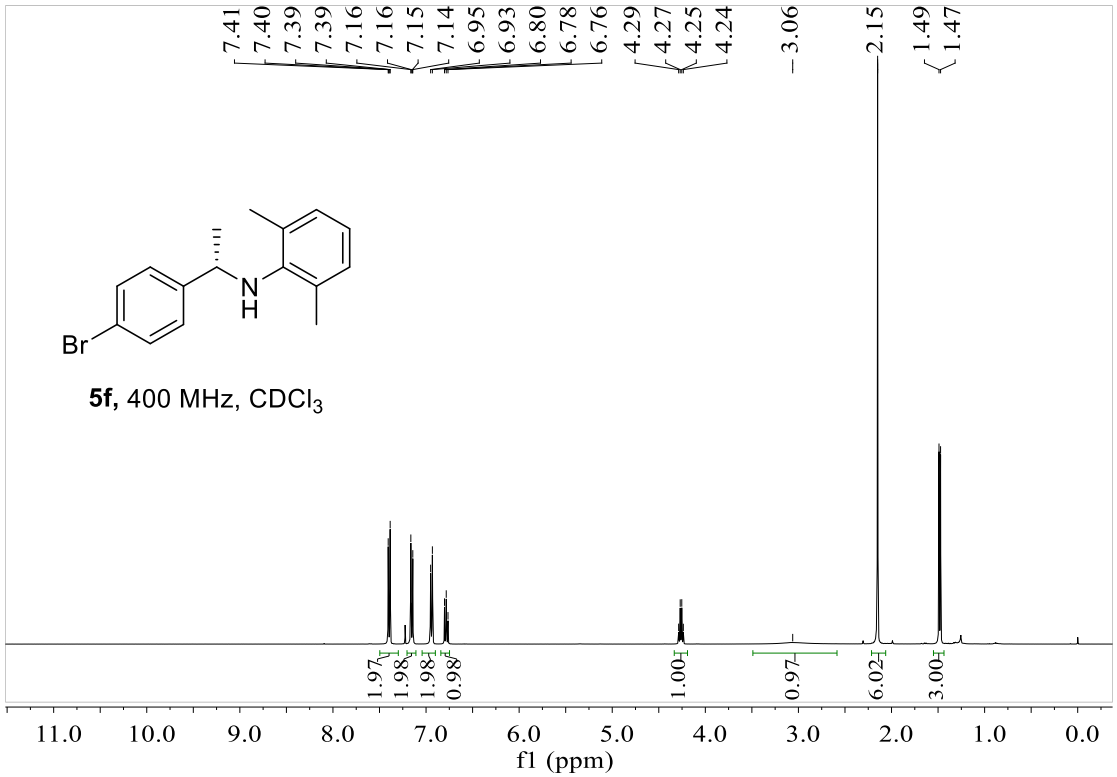
5d, 376 MHz, $CDCl_3$



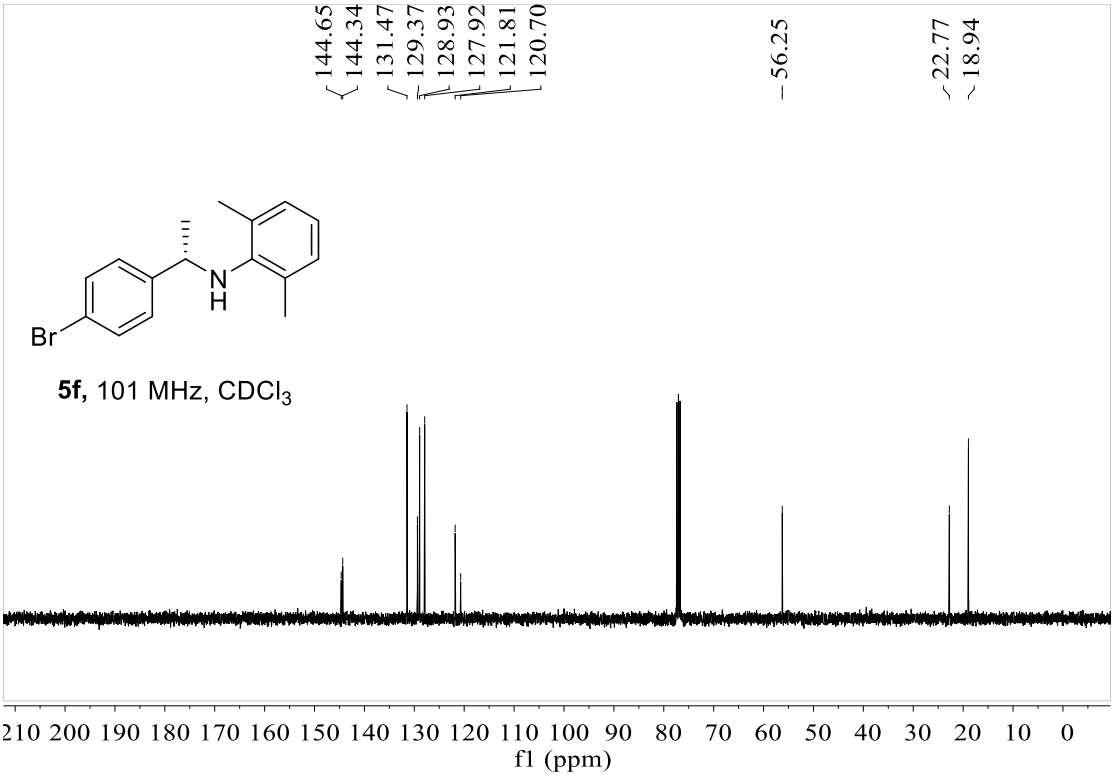
5e, 400 MHz, $CDCl_3$



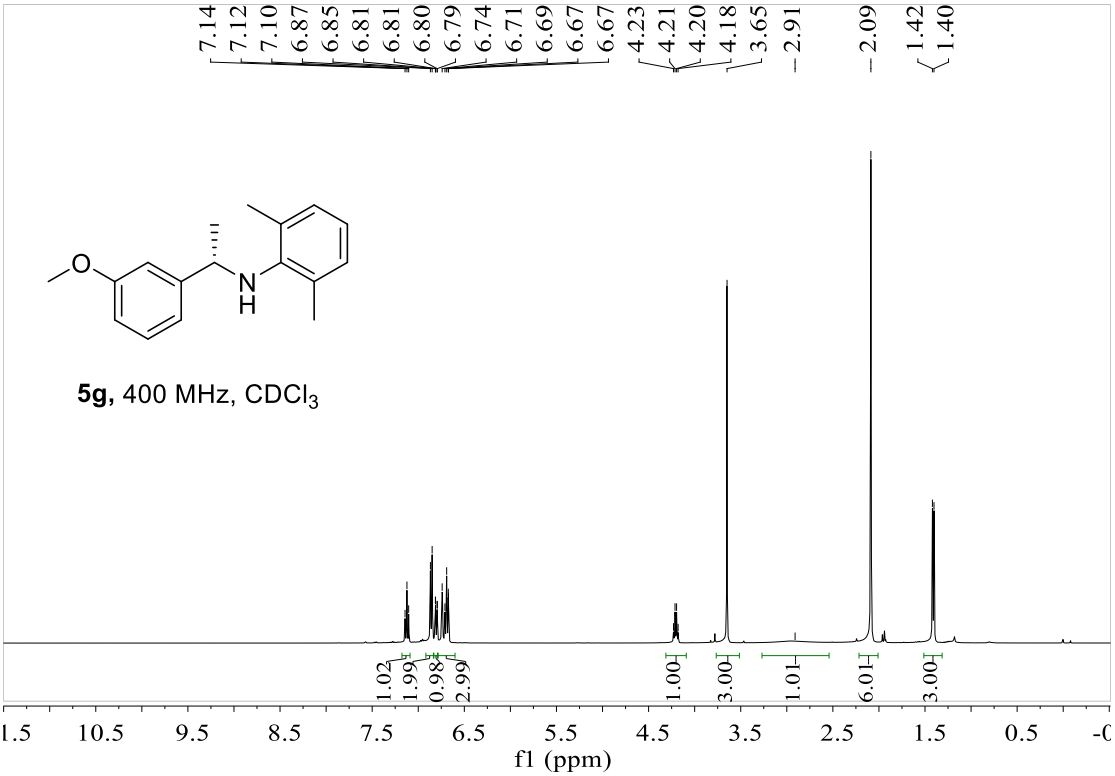
5e, 101 MHz, $CDCl_3$



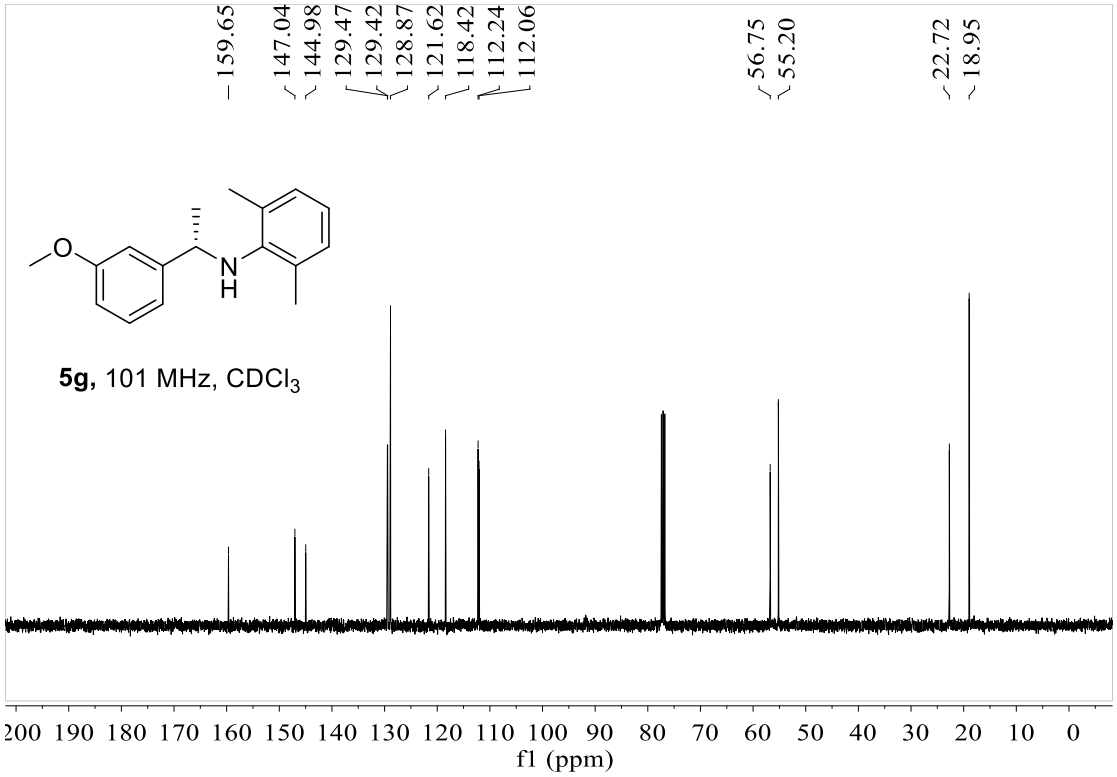
5f, 400 MHz, $CDCl_3$



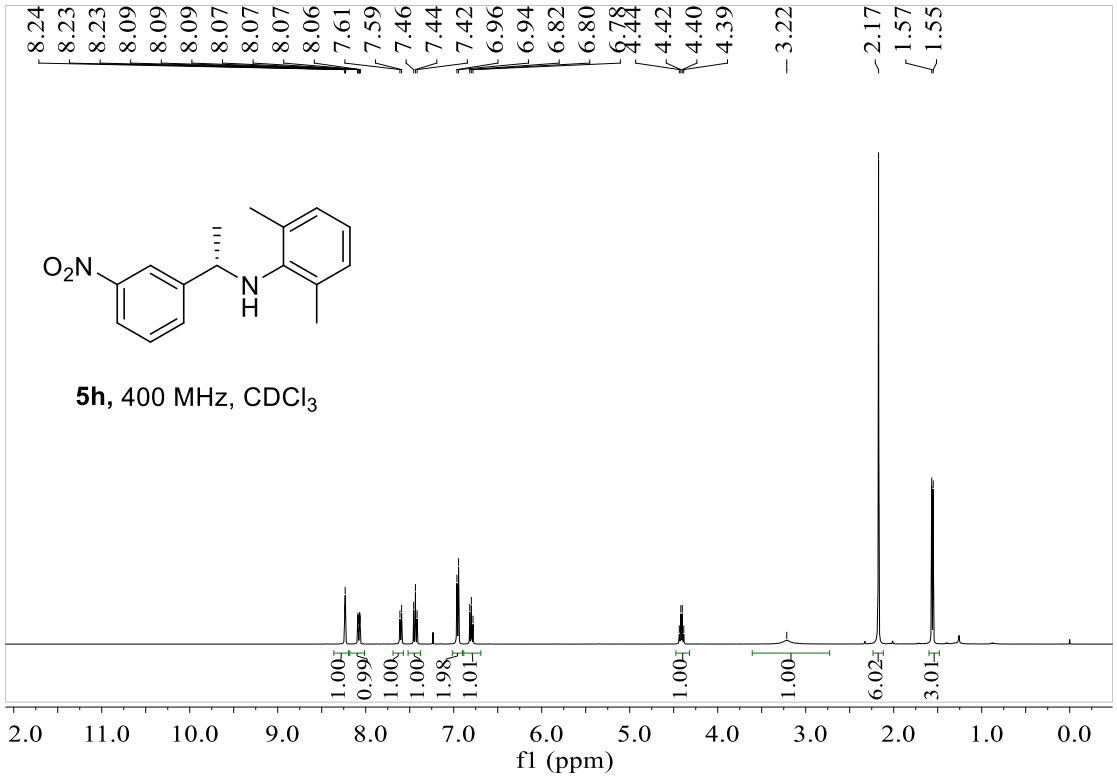
5f, 101 MHz, $CDCl_3$



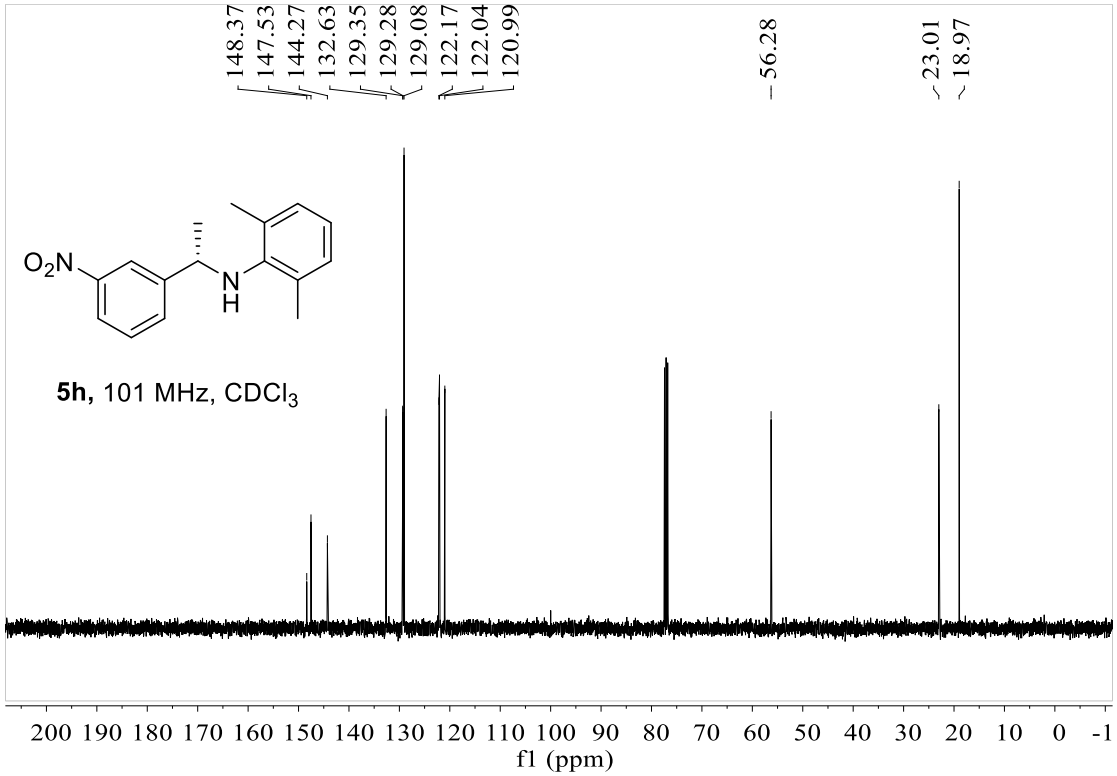
5g, 400 MHz, $CDCl_3$



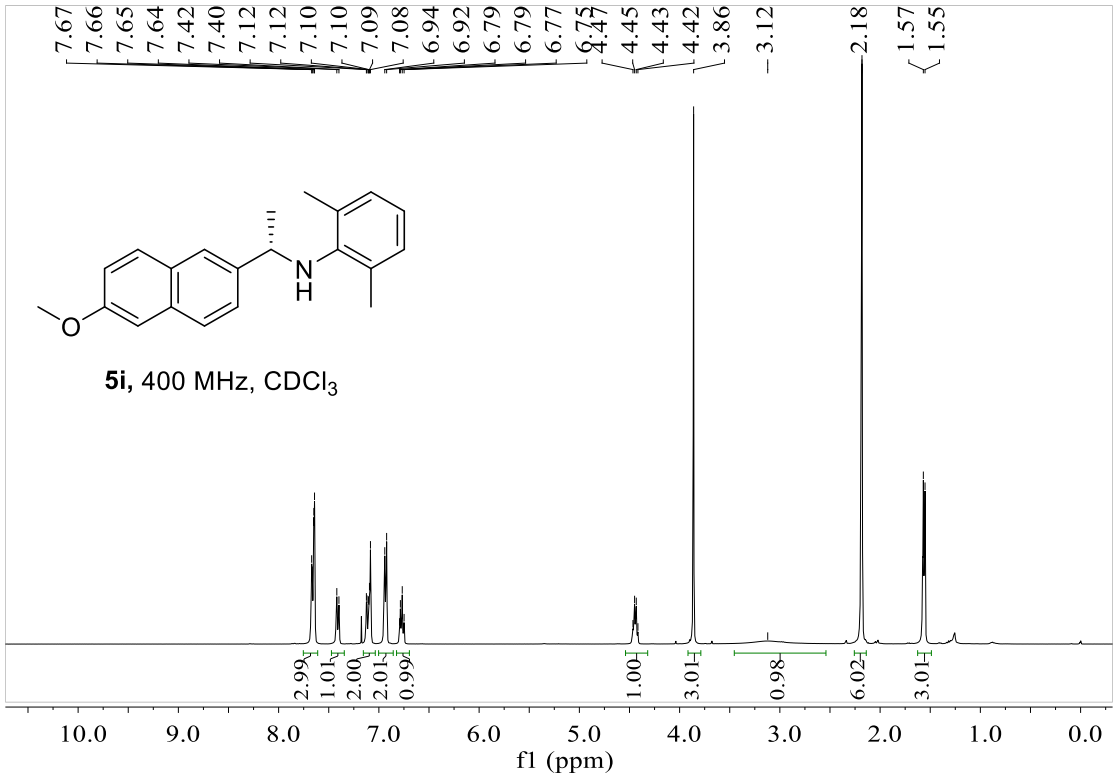
5g, 101 MHz, $CDCl_3$



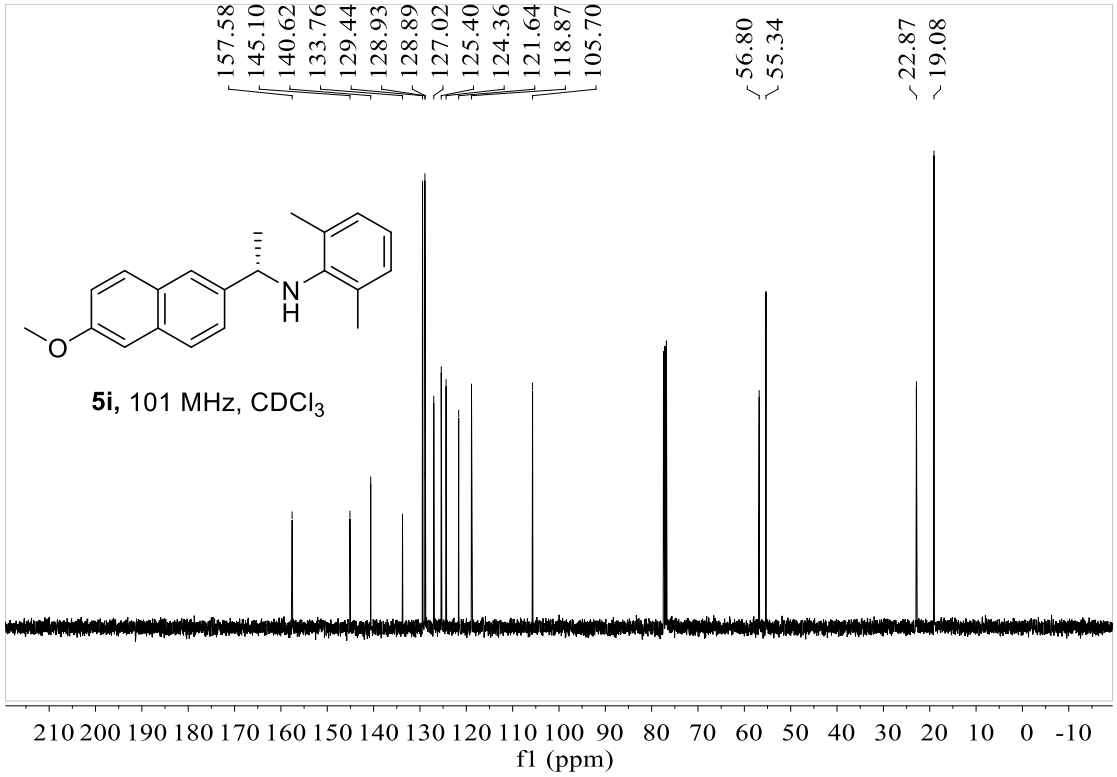
5h, 400 MHz, $CDCl_3$



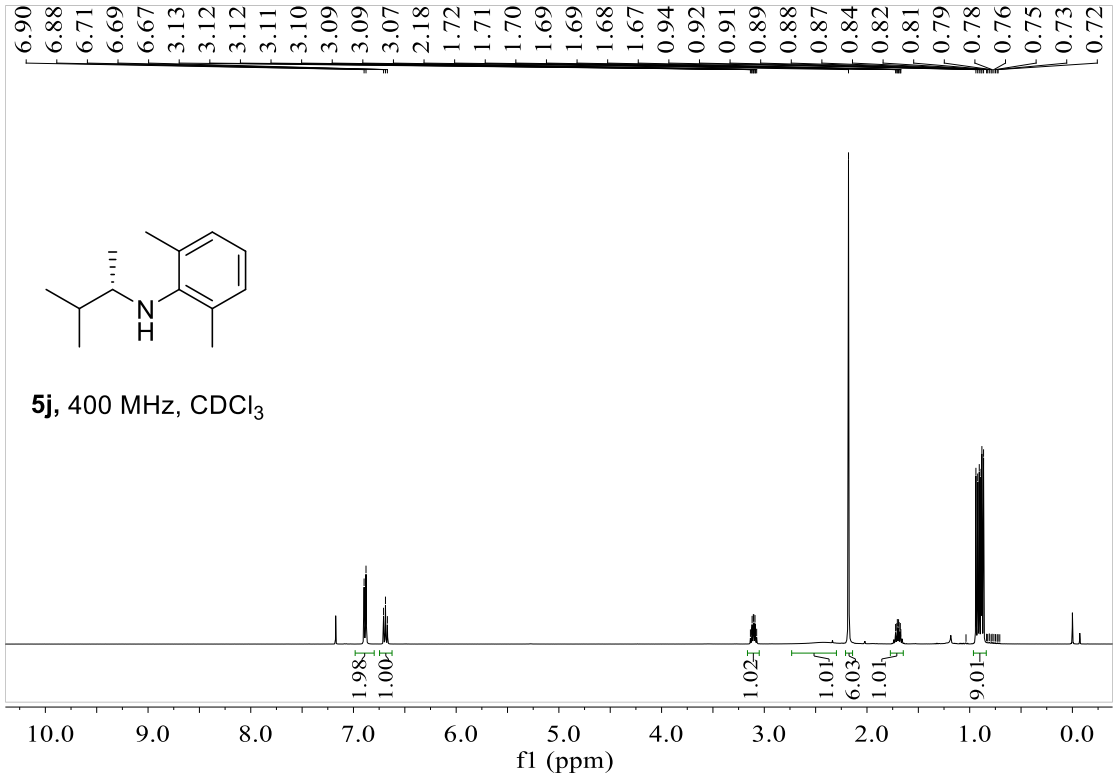
5h, 101 MHz, $CDCl_3$



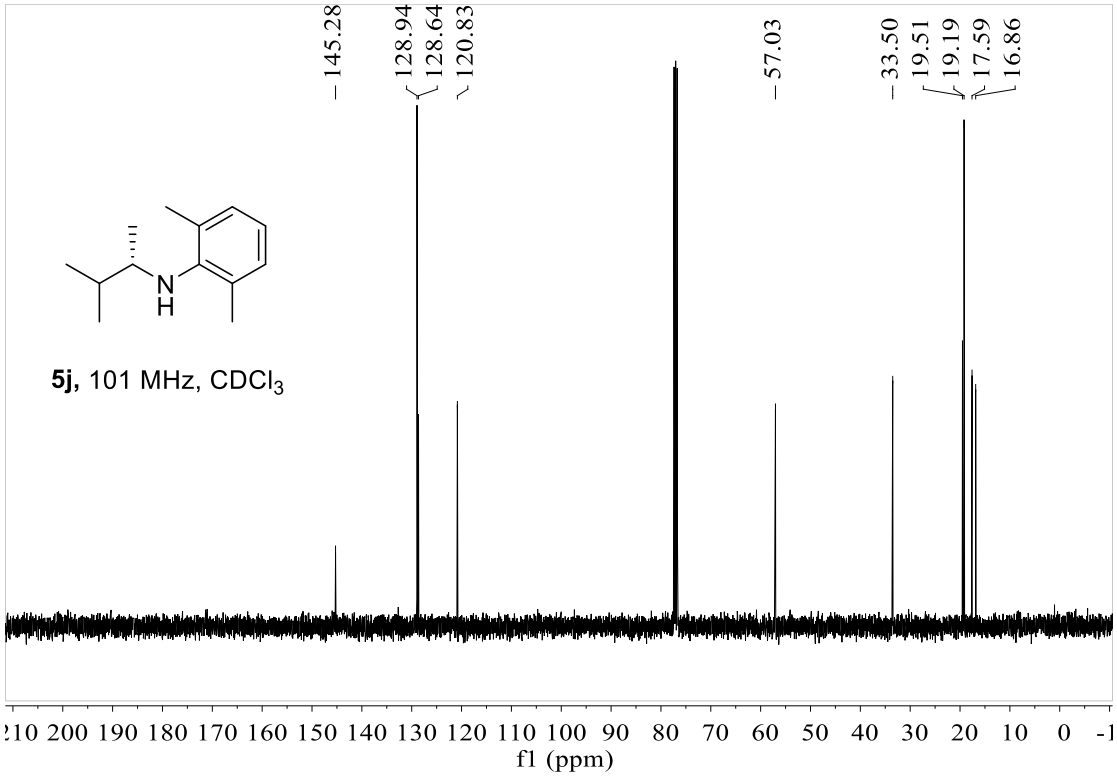
5i, 400 MHz, $CDCl_3$



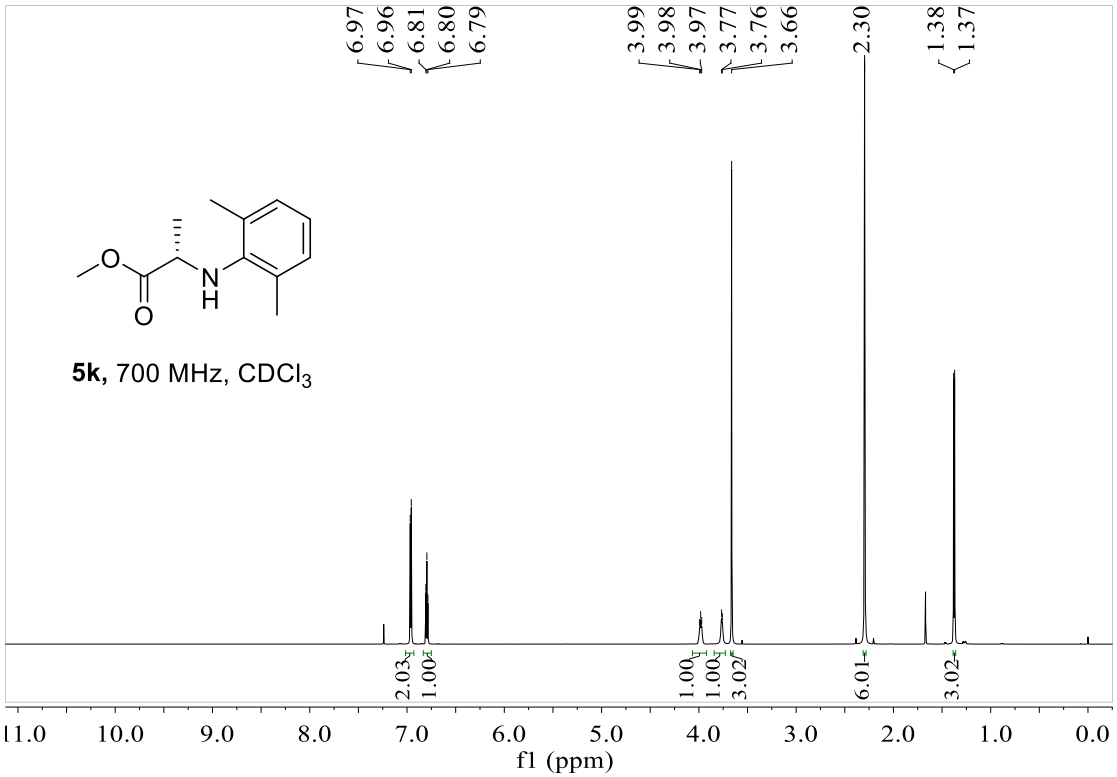
5i, 101 MHz, $CDCl_3$



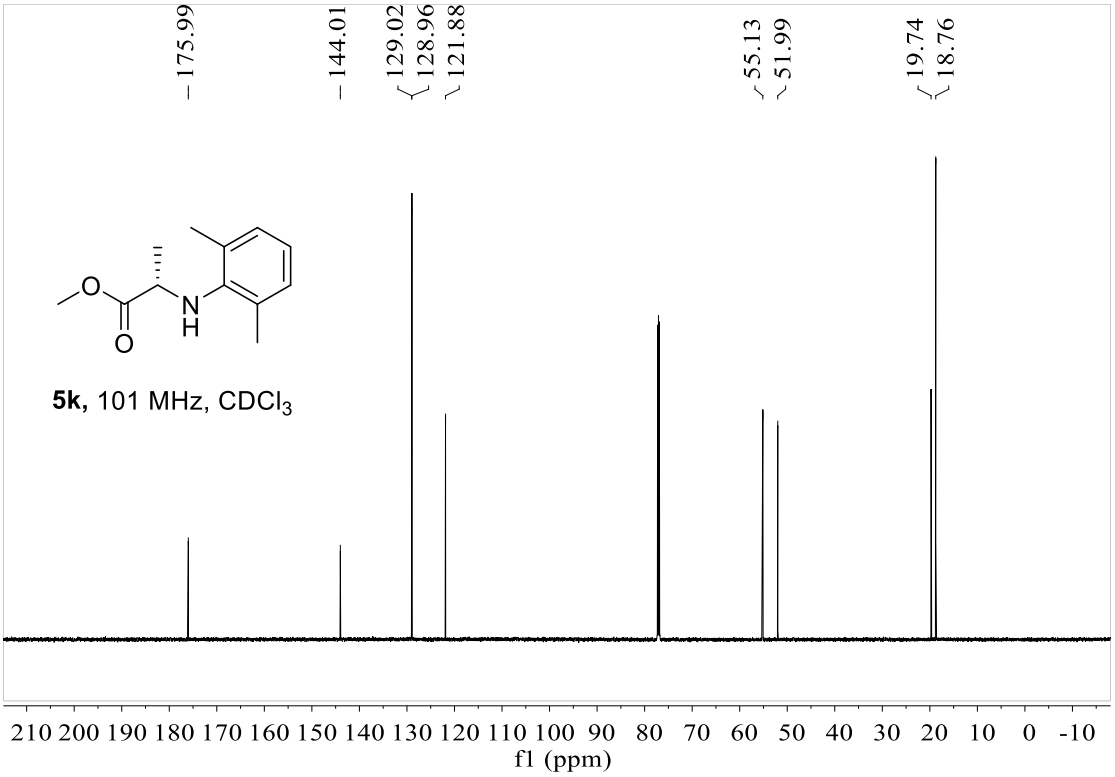
5j, 400 MHz, $CDCl_3$

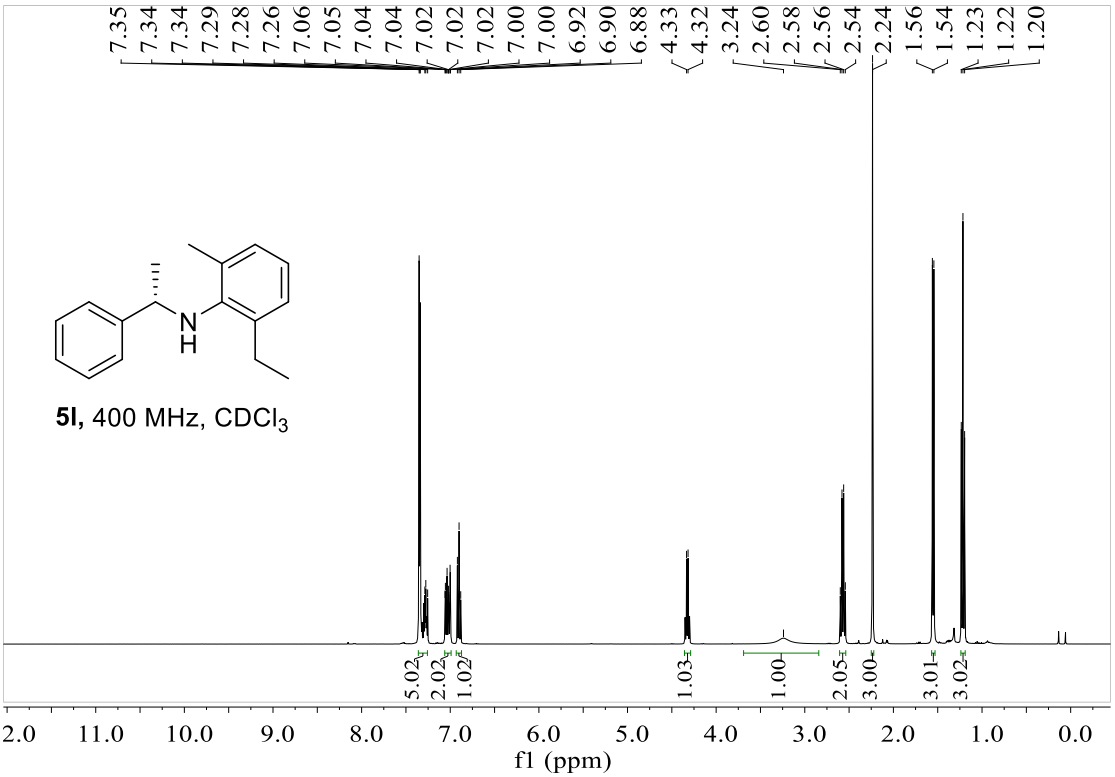


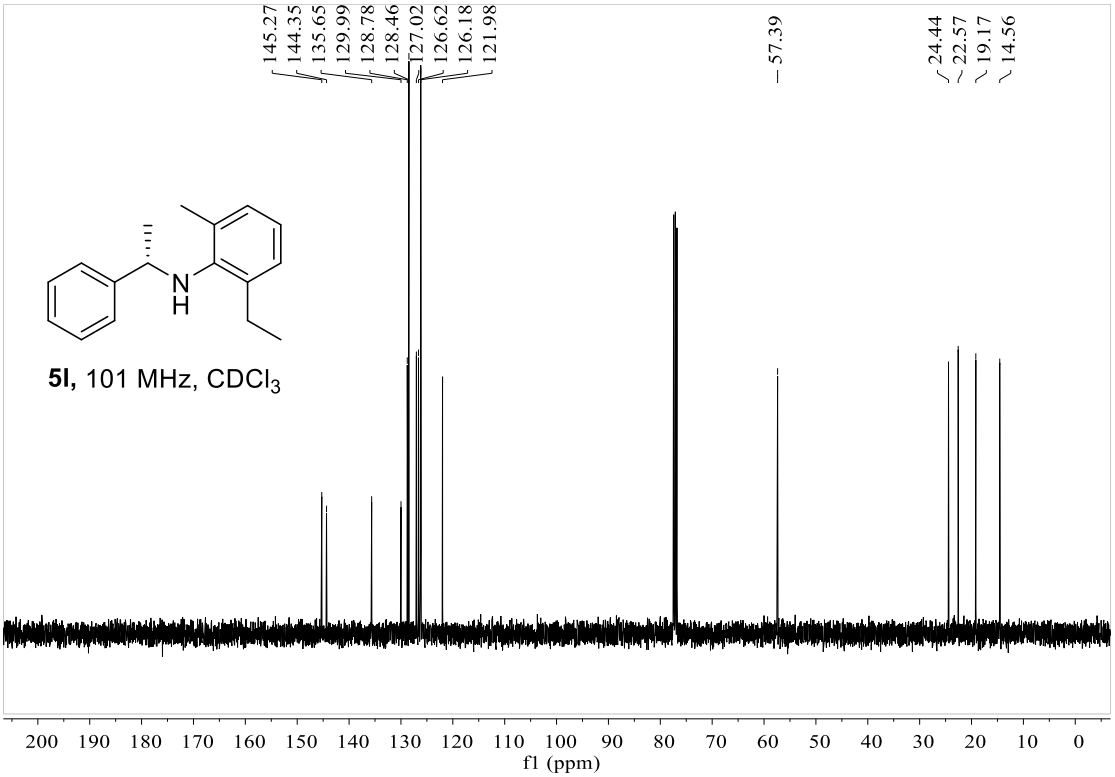
5j, 101 MHz, $CDCl_3$



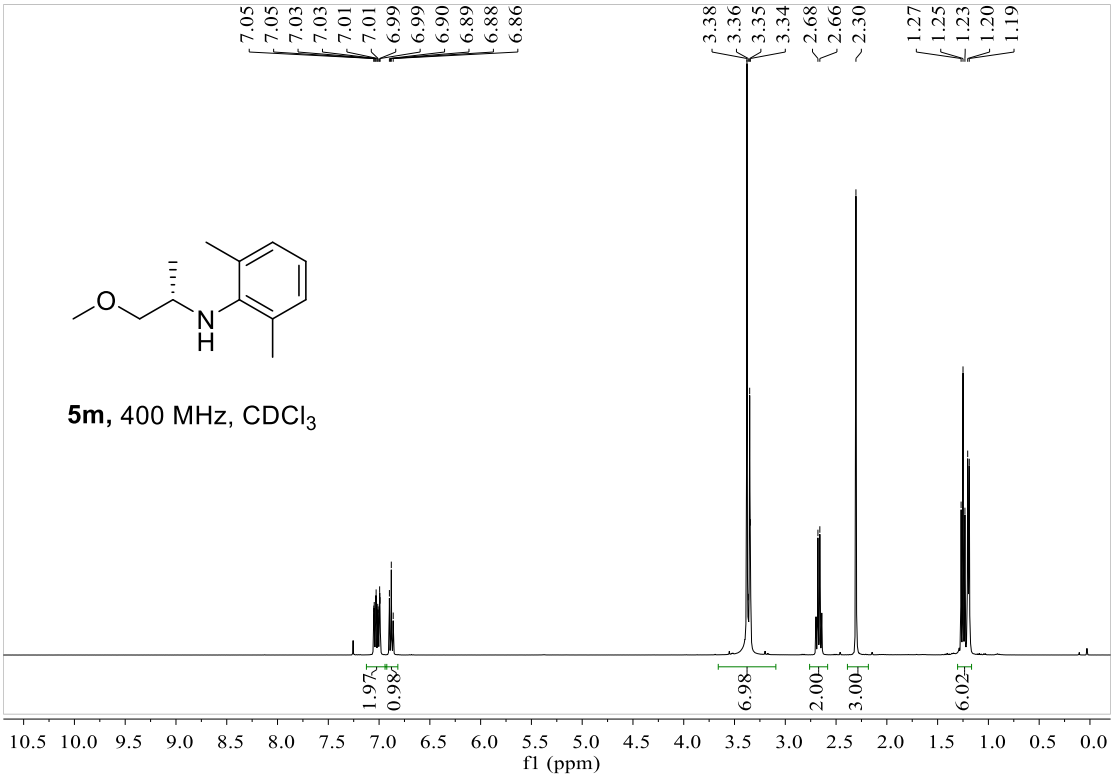
5k, 700 MHz, $CDCl_3$


175.99
144.01
129.02
128.96
121.88
55.13
51.99
19.74
18.76
O
O
N
H
5k, 101 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

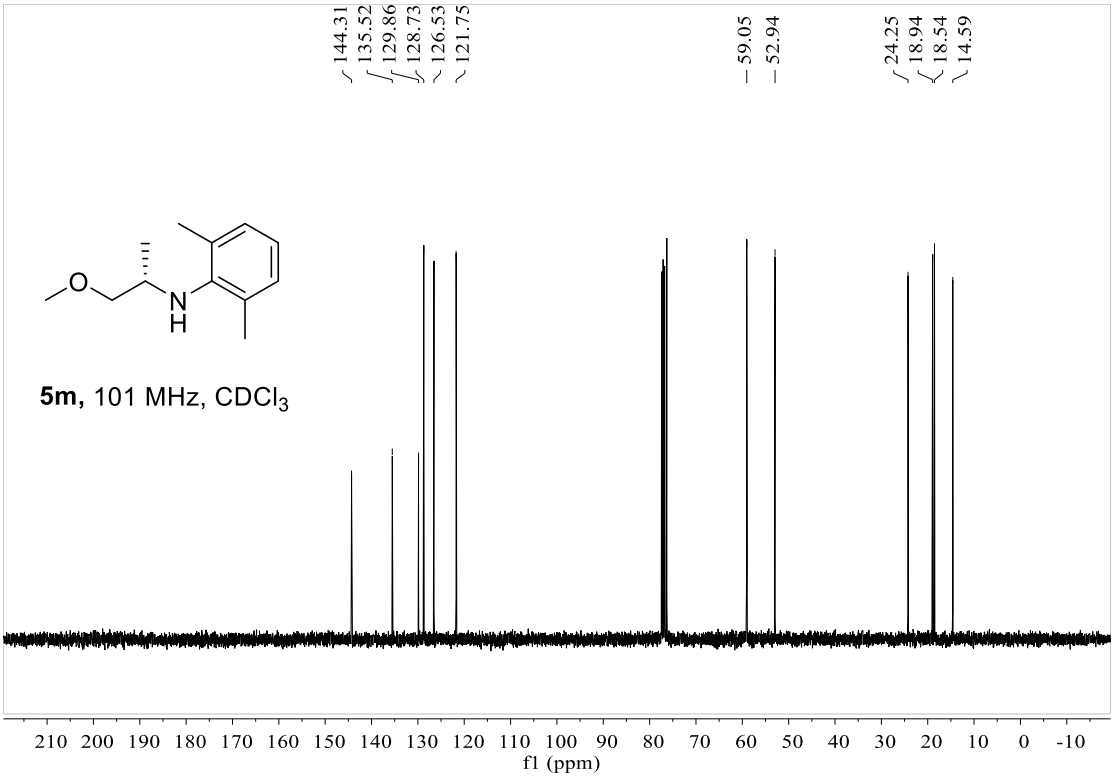

7.35
7.34
7.34
7.29
7.28
7.26
7.06
7.05
7.04
7.04
7.02
7.02
7.02
7.00
7.00
6.92
6.90
6.88
4.33
4.32
3.24
2.60
2.58
2.56
2.54
2.24
1.56
1.54
1.23
1.22
1.20
5.02
2.02
1.02
1.03
1.00
2.05
3.00
3.01
3.02
N
H
5l, 400 MHz, CDCl3
2.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

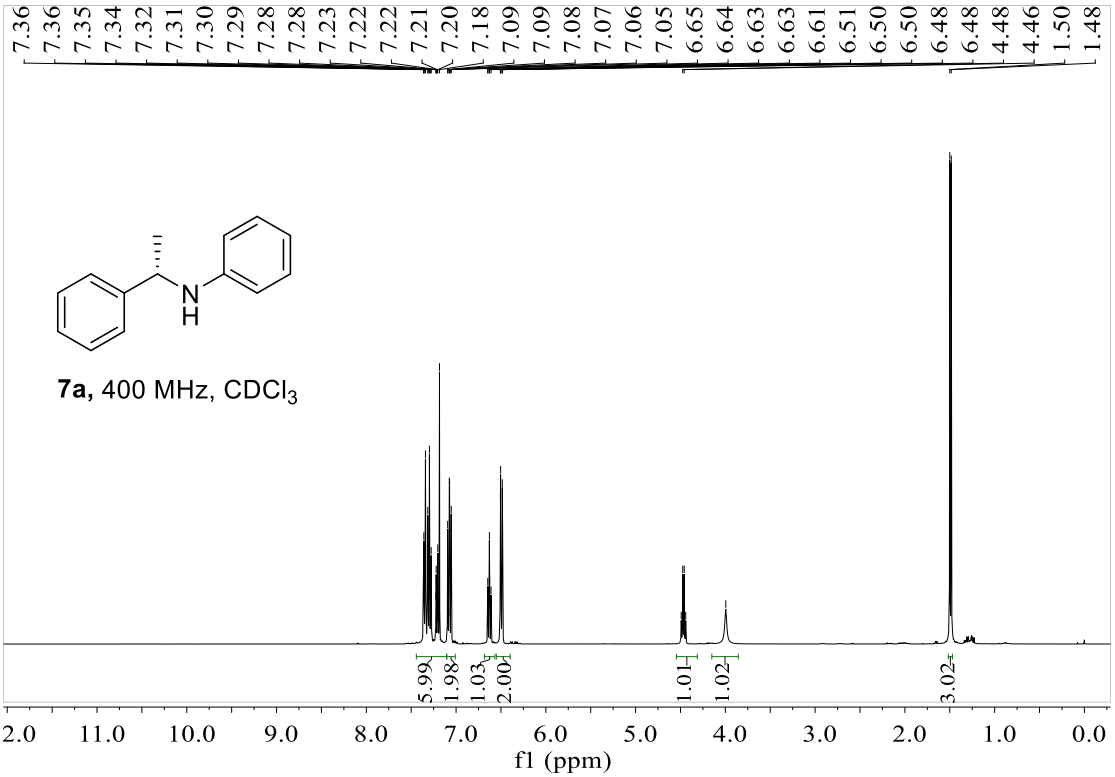


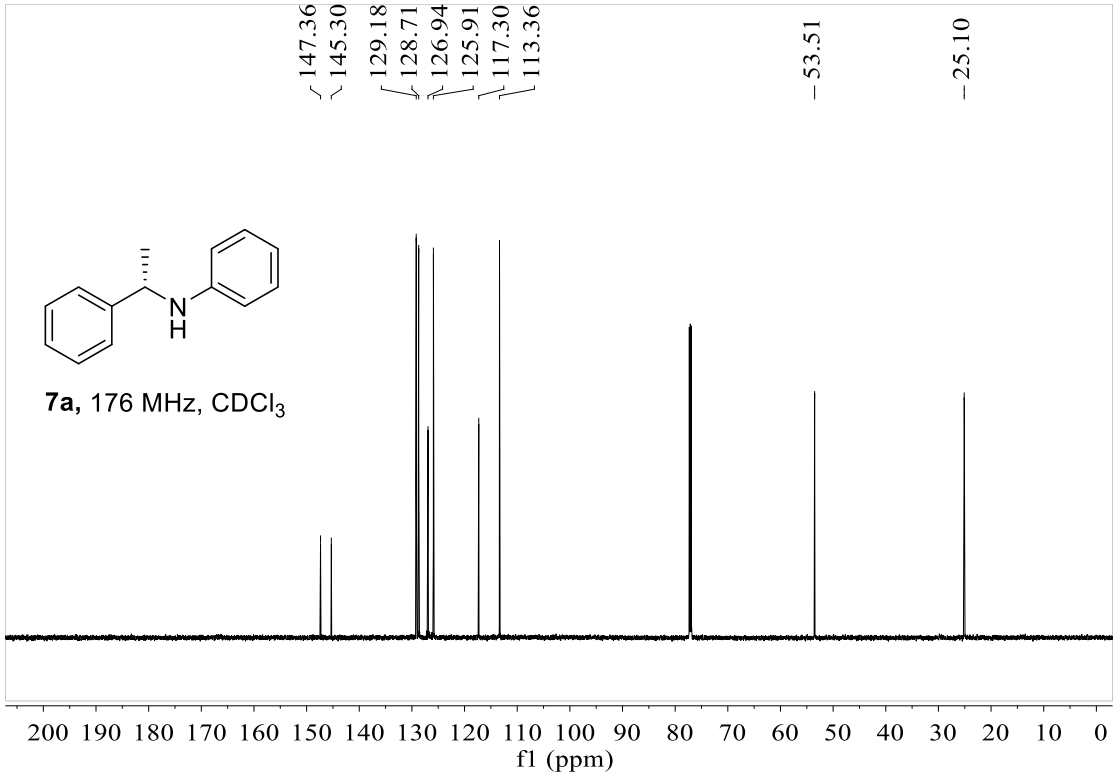
5l, 101 MHz, $CDCl_3$



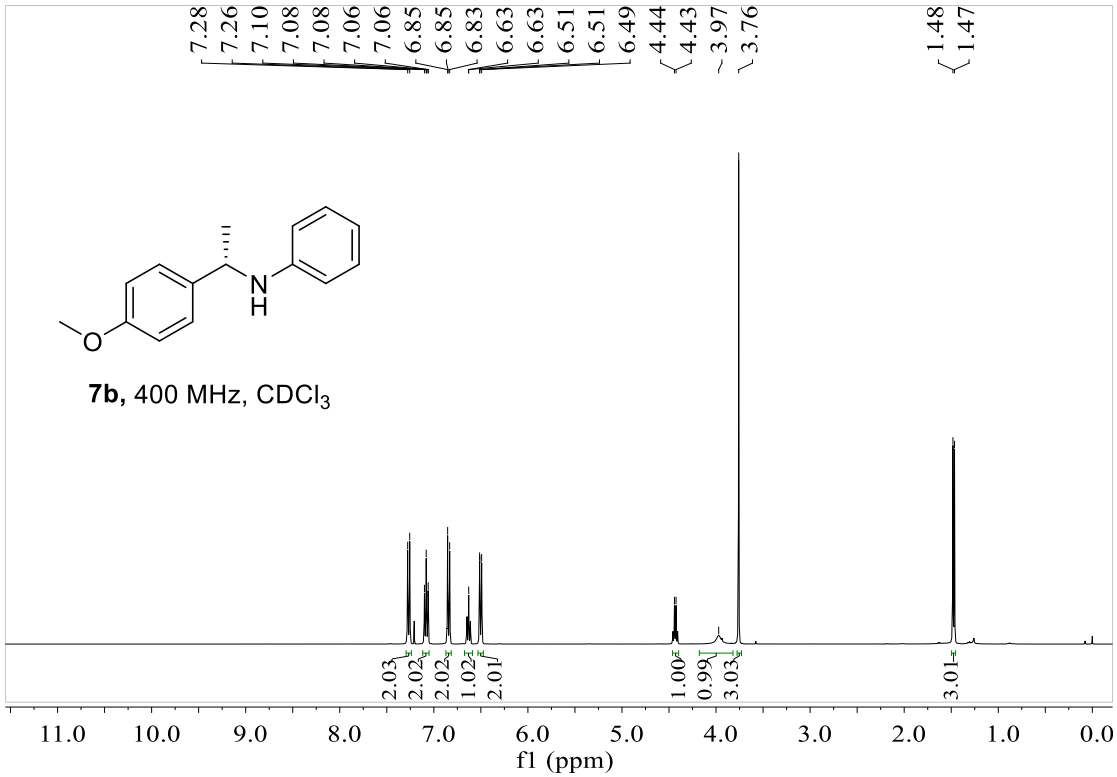
5m, 400 MHz, $CDCl_3$


144.31
135.52
129.86
128.73
126.53
121.75
59.05
52.94
24.25
18.94
18.54
14.59
O
N
H
5m, 101 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

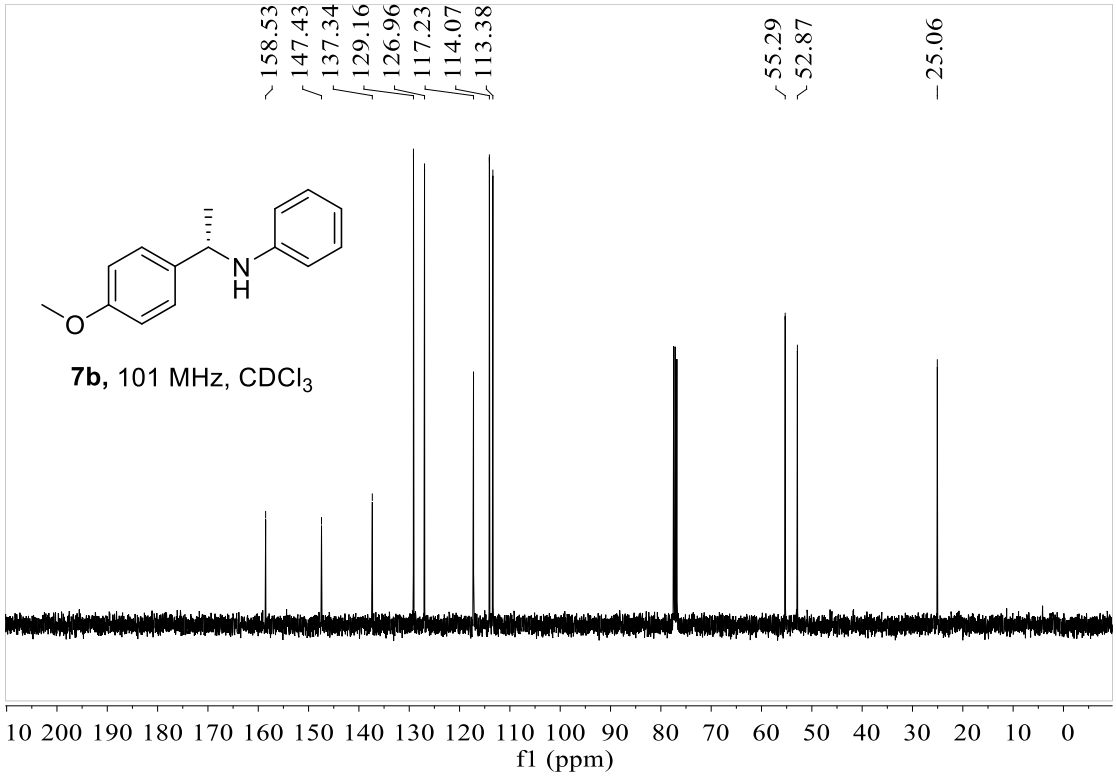

7.36
7.36
7.35
7.34
7.32
7.31
7.30
7.29
7.28
7.28
7.23
7.22
7.22
7.21
7.20
7.18
7.09
7.09
7.08
7.07
7.06
7.05
6.65
6.64
6.63
6.63
6.61
6.51
6.50
6.50
6.48
6.48
4.48
4.46
1.50
1.48
N
H
7a, 400 MHz, CDCl3
5.99
1.98
1.03
2.00
1.01
1.02
3.02
2.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

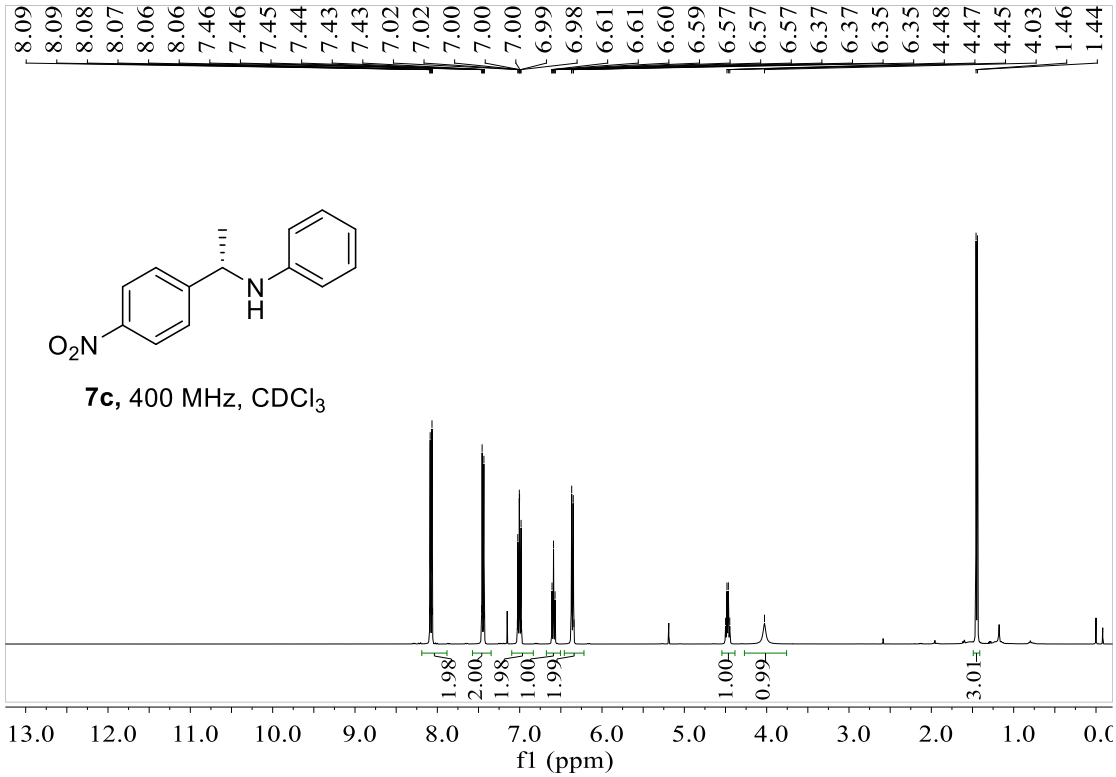


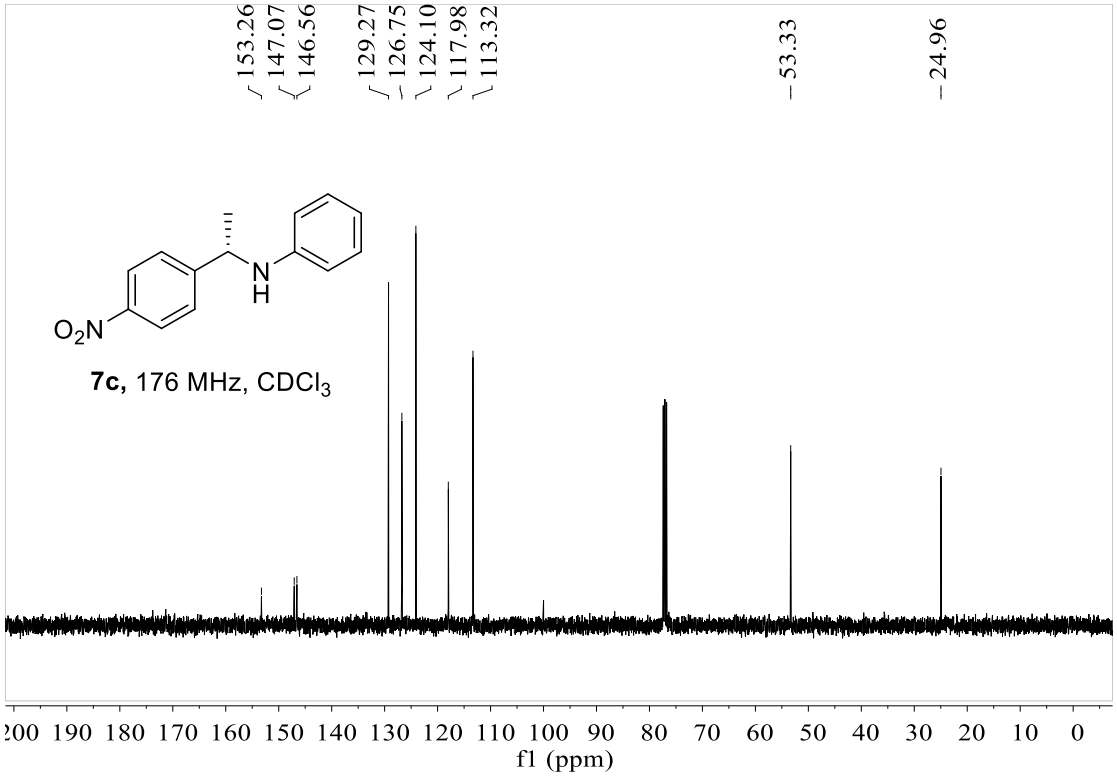
7a, 176 MHz, $CDCl_3$

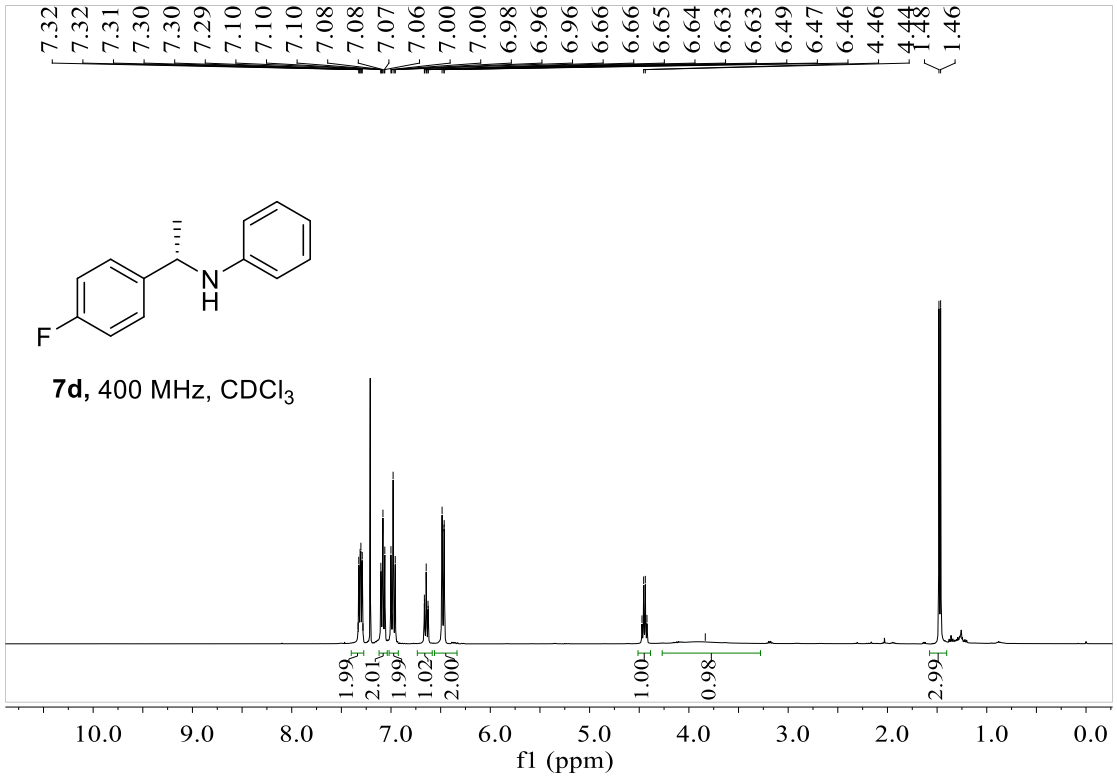


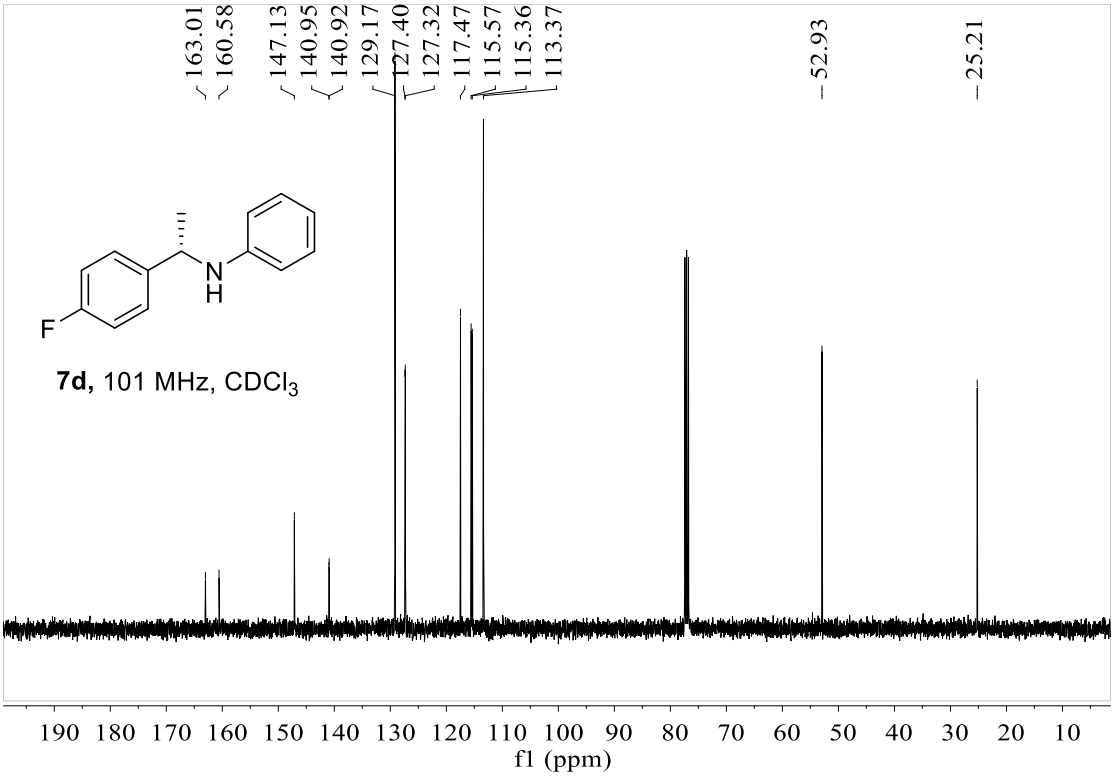
7b, 400 MHz, $CDCl_3$

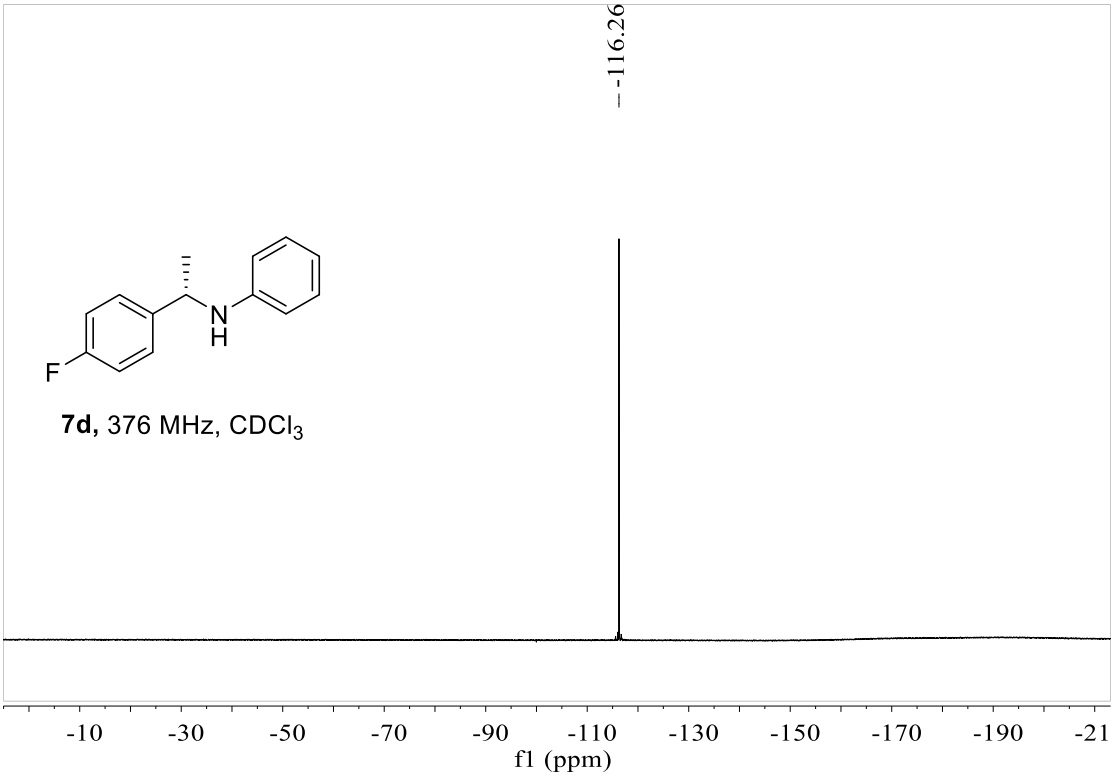

158.53
147.43
137.34
129.16
126.96
117.23
114.07
113.38
55.29
52.87
25.06
N
H
O
7b, 101 MHz, CDCl3
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

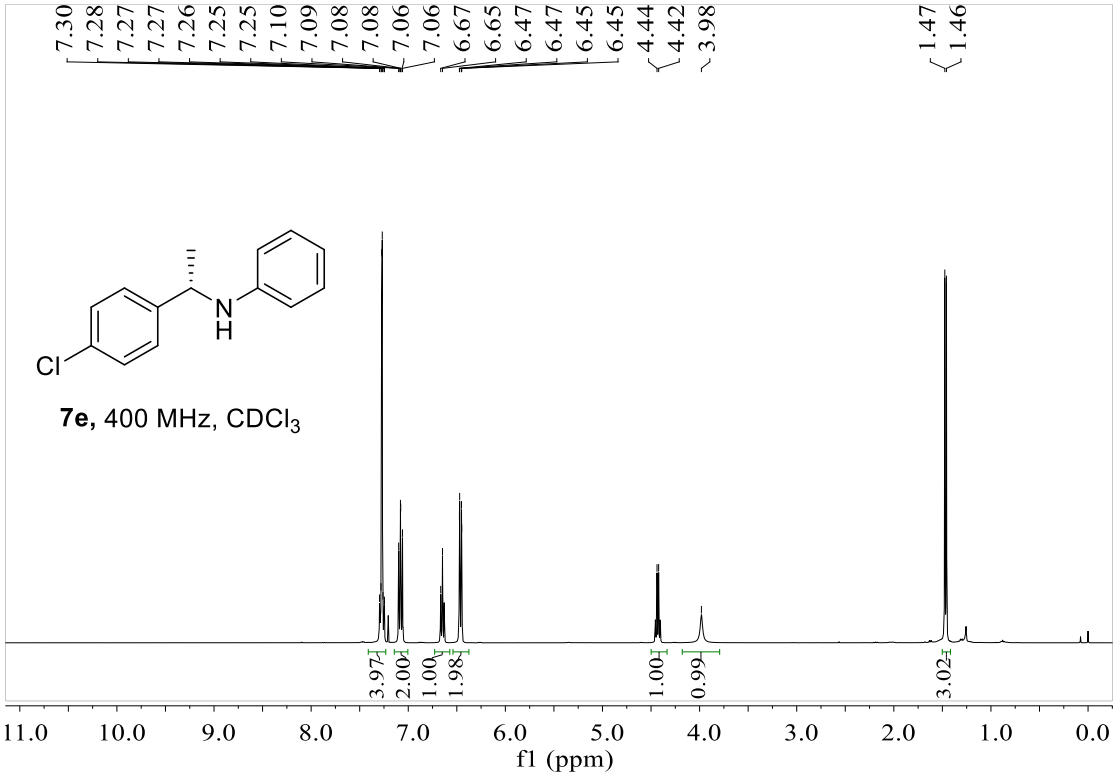

8.09
8.09
8.08
8.07
8.06
8.06
7.46
7.46
7.45
7.44
7.43
7.43
7.02
7.02
7.00
7.00
7.00
6.99
6.98
6.61
6.61
6.60
6.59
6.57
6.57
6.57
6.37
6.37
6.35
6.35
4.48
4.47
4.45
4.03
1.46
1.44
N
H
O2N
7c, 400 MHz, CDCl3
1.98
2.00
1.98
1.00
1.99
1.00
0.99
3.01
13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

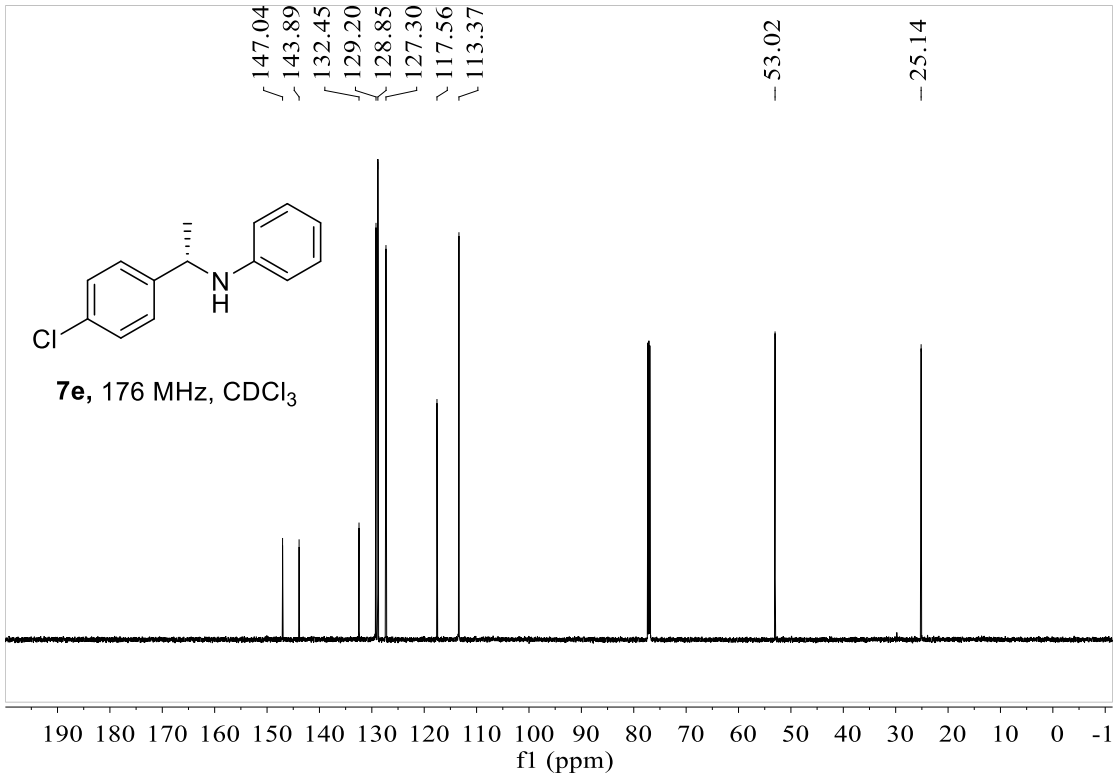

153.26
147.07
146.56
129.27
126.75
124.10
117.98
113.32
53.33
24.96
N
H
O2N
7c, 176 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

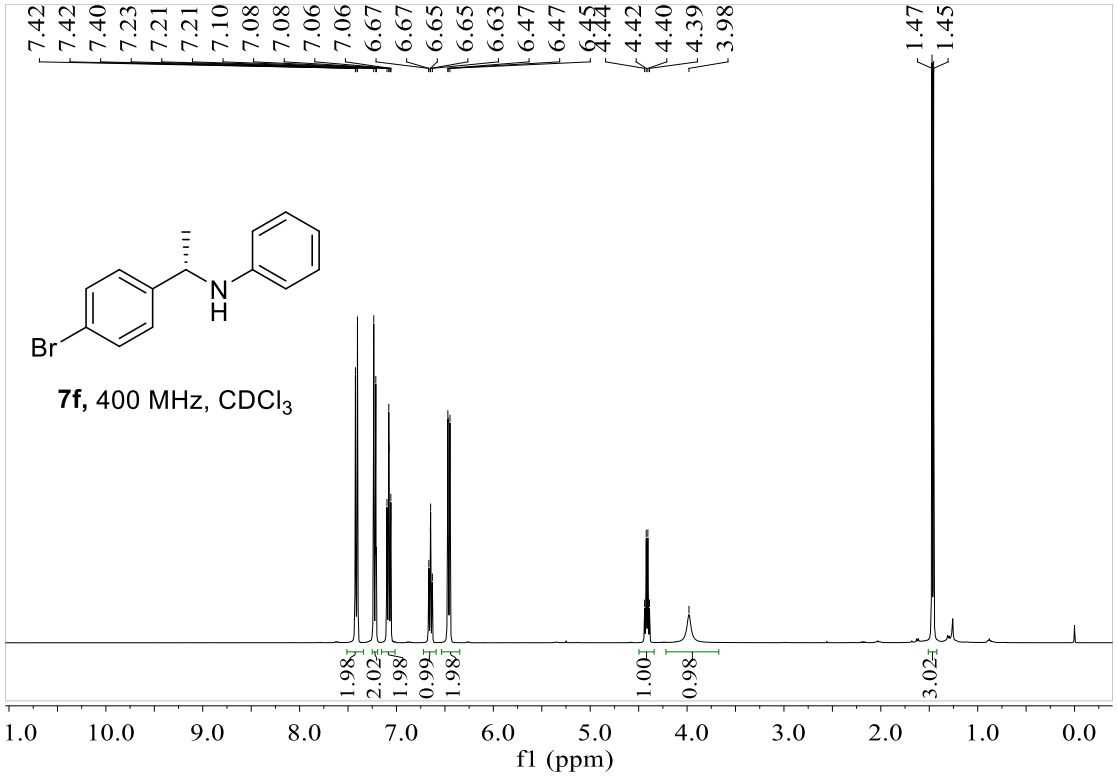

7.32
7.32
7.31
7.30
7.30
7.29
7.10
7.10
7.10
7.08
7.08
7.07
7.06
7.00
7.00
6.98
6.96
6.96
6.66
6.66
6.65
6.64
6.63
6.63
6.49
6.47
6.46
4.46
4.44
4.43
1.48
1.46
N
H
F
7d, 400 MHz, CDCl3
1.99
2.01
1.99
1.02
2.00
1.00
0.98
2.99
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

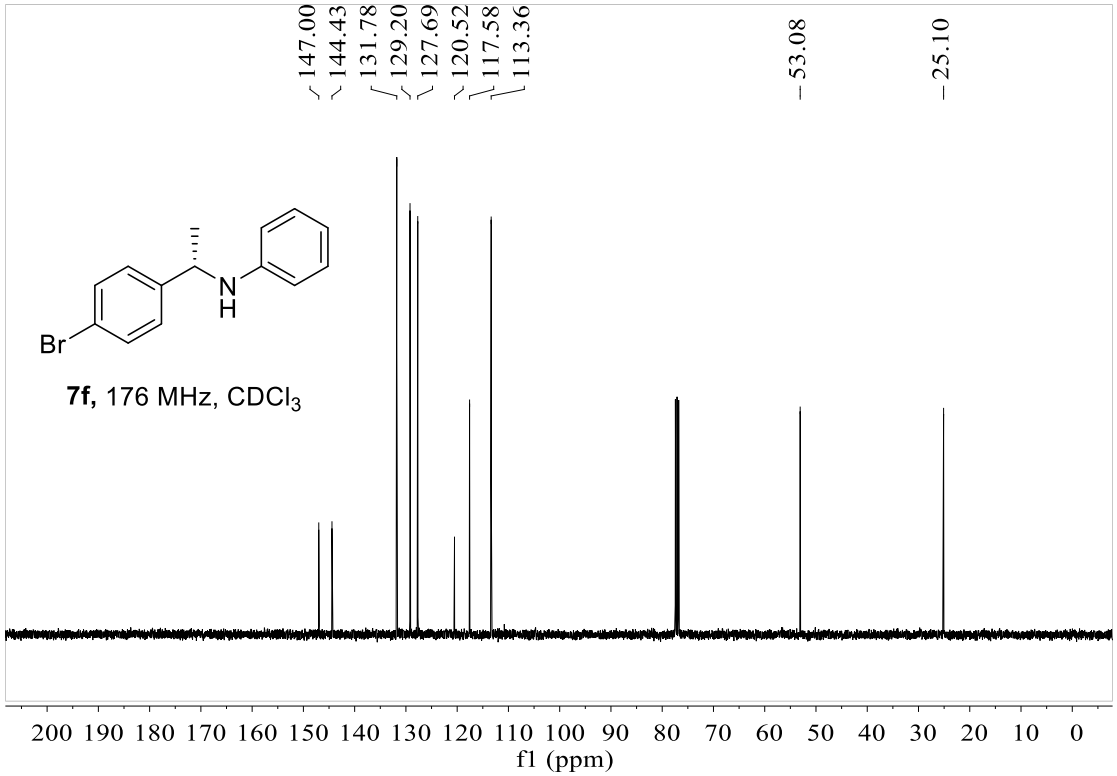

163.01
160.58
147.13
140.95
140.92
129.17
127.40
127.32
117.47
115.57
115.36
113.37
52.93
25.21
N
H
F
7d, 101 MHz, CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

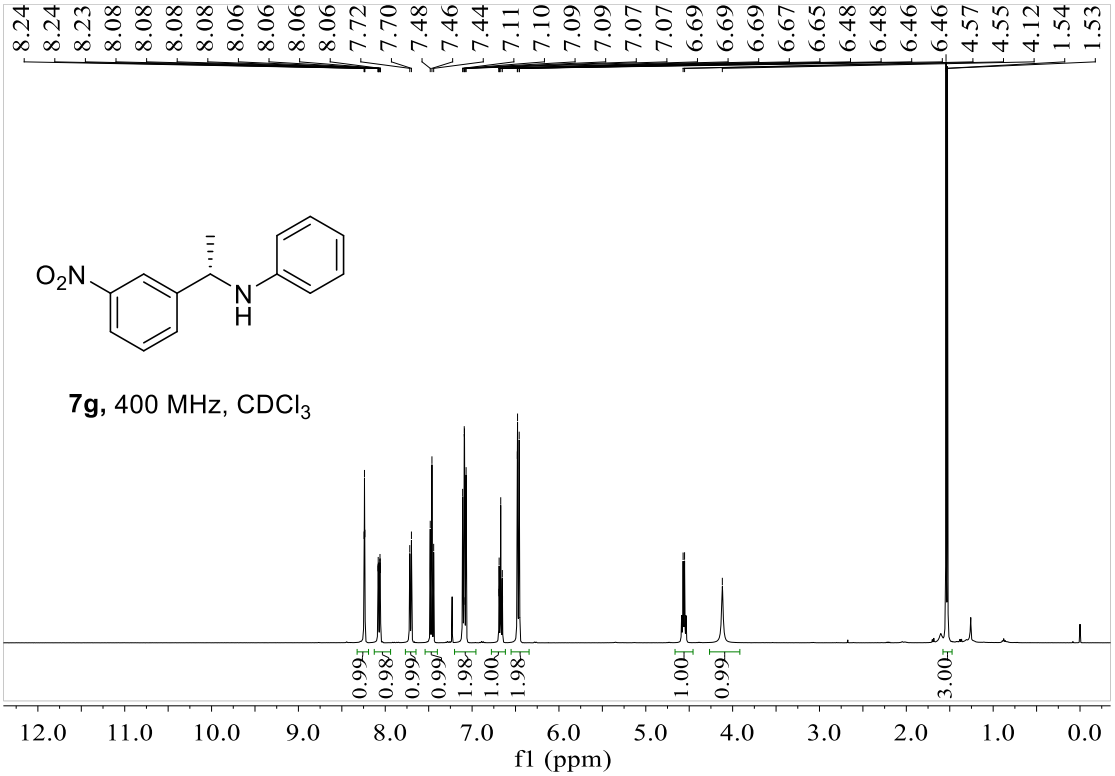

-116.26
N
H
F
7d, 376 MHz, CDCl3
-10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -21
f1 (ppm)

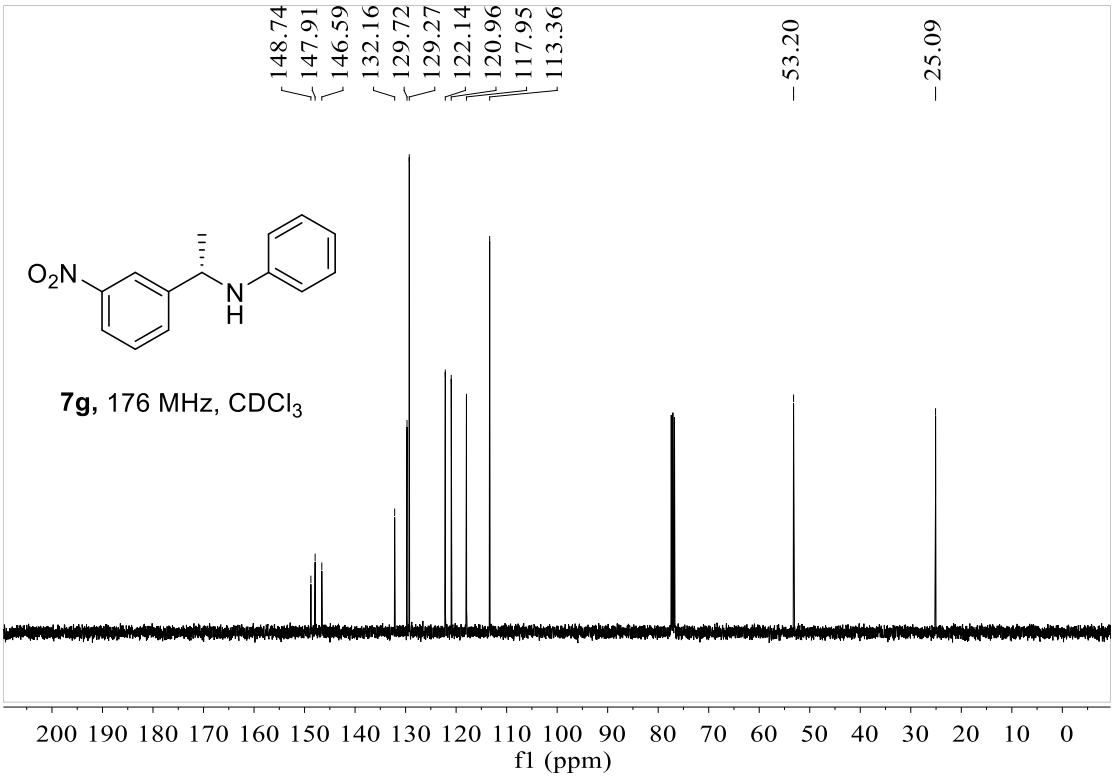

7.30
7.28
7.27
7.27
7.26
7.25
7.25
7.10
7.09
7.08
7.08
7.06
7.06
6.67
6.65
6.47
6.47
6.45
6.45
4.44
4.42
3.98
1.47
1.46
Cl
N
H
7e, 400 MHz, CDCl3
3.97
2.00
1.00
1.98
1.00
0.99
3.02
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

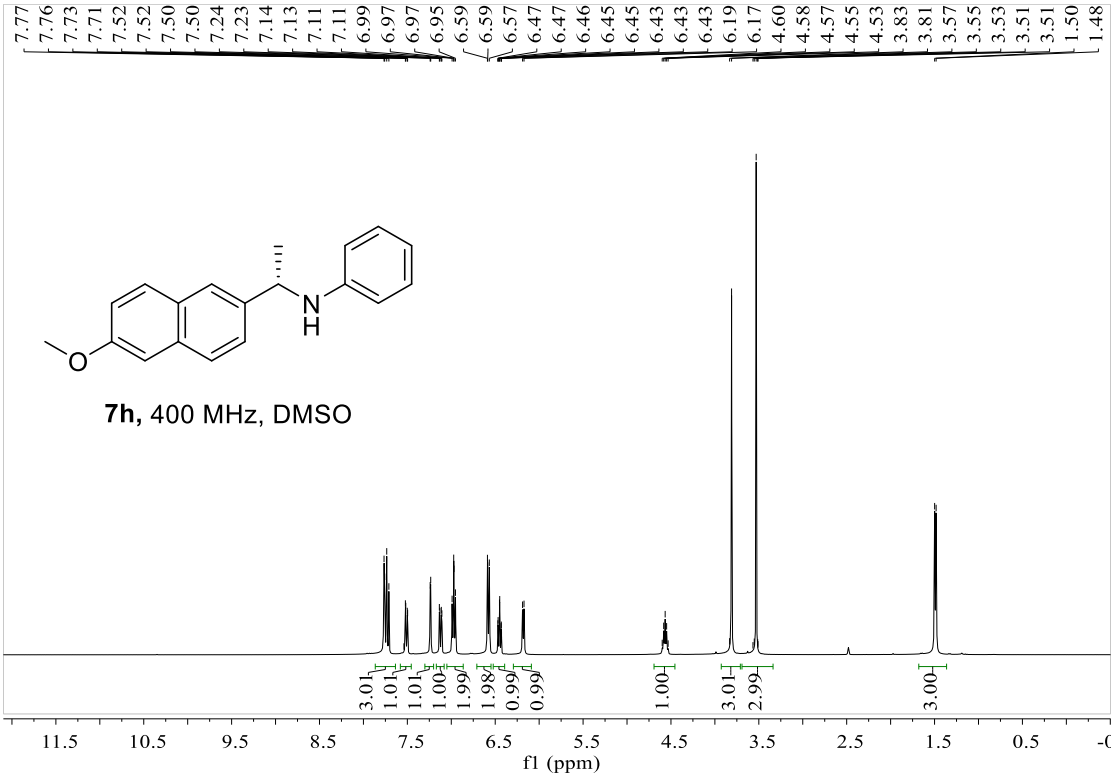

147.04
143.89
132.45
129.20
128.85
127.30
117.56
113.37
53.02
25.14
Cl
N
H
7e, 176 MHz, CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

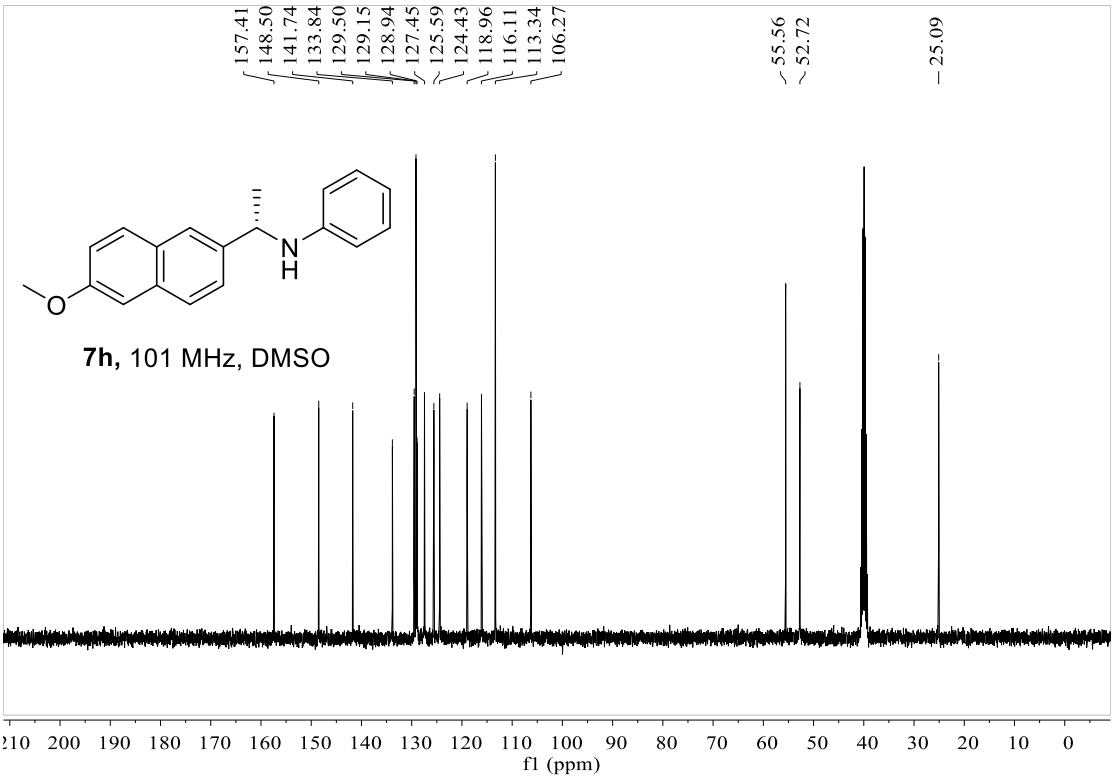

7.42
7.42
7.40
7.23
7.21
7.21
7.10
7.08
7.08
7.06
7.06
6.67
6.67
6.65
6.65
6.63
6.47
6.47
6.45
4.44
4.42
4.40
4.39
3.98
1.47
1.45
Br
N
H
7f, 400 MHz, CDCl3
1.98
2.02
1.98
0.99
1.98
1.00
0.98
3.02
1.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

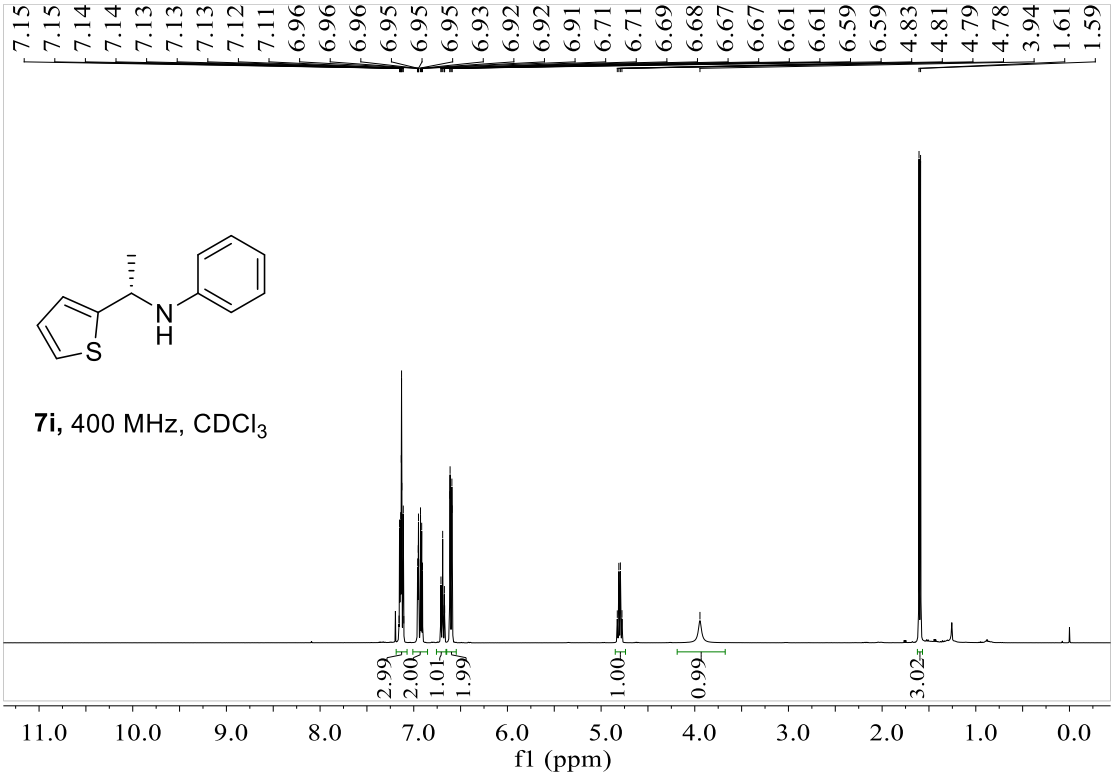

147.00
144.43
131.78
129.20
127.69
120.52
117.58
113.36
53.08
25.10
Br
N
H
7f, 176 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

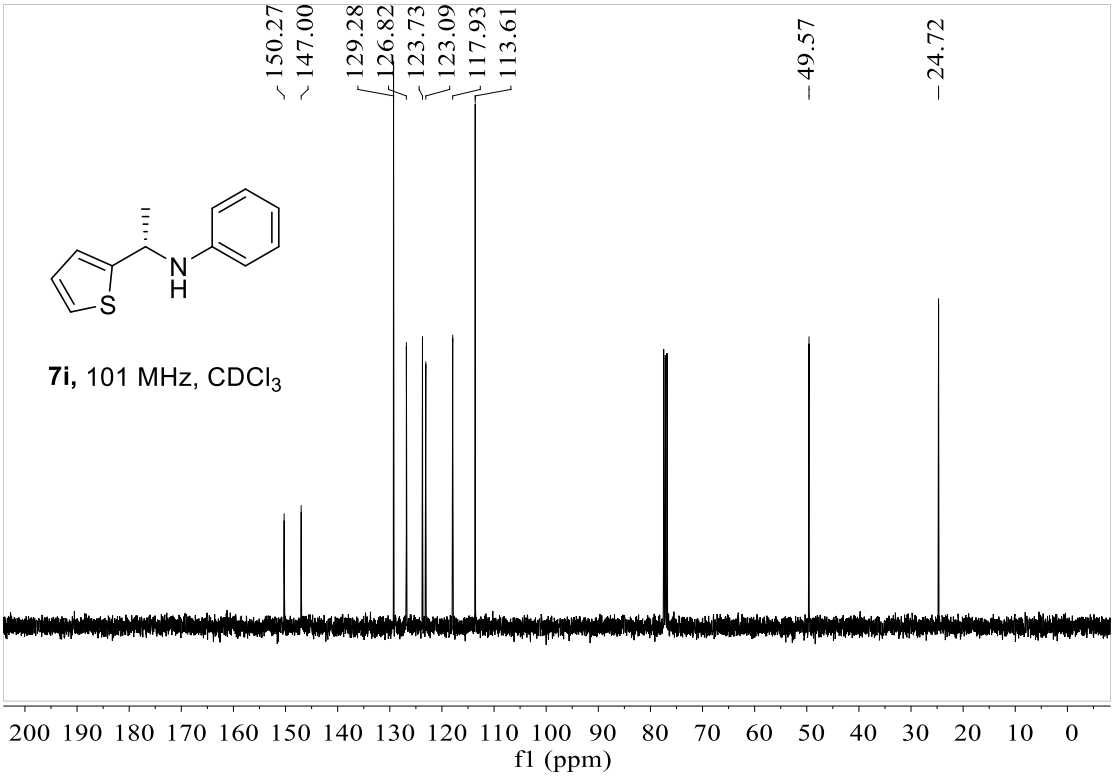

8.24
8.24
8.23
8.08
8.08
8.08
8.08
8.06
8.06
8.06
8.06
7.72
7.70
7.48
7.46
7.44
7.11
7.10
7.09
7.09
7.07
7.07
6.69
6.69
6.69
6.67
6.65
6.48
6.48
6.46
6.46
4.57
4.55
4.12
1.54
1.53
O2N
N
H
7g, 400 MHz, CDCl3
0.99
0.98
0.99
0.99
1.98
1.00
1.98
1.00
0.99
3.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

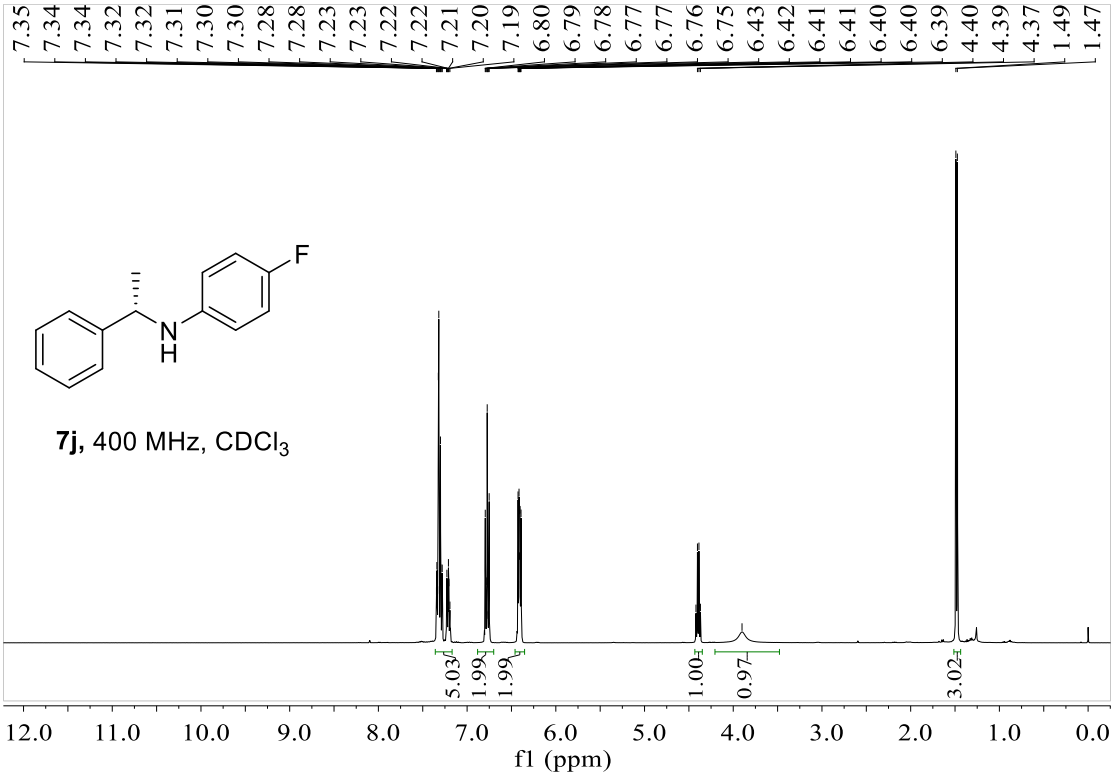

148.74
147.91
146.59
132.16
129.72
129.27
122.14
120.96
117.95
113.36
53.20
25.09
O2N
N
H
7g, 176 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

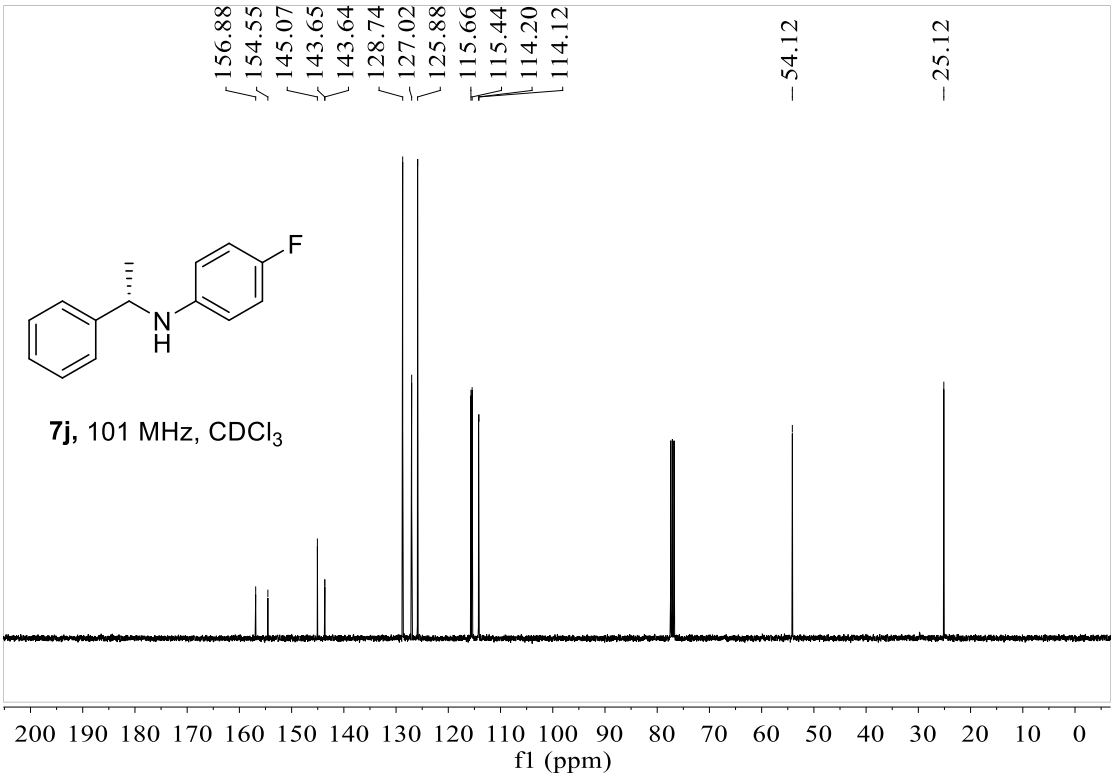

7.77
7.76
7.73
7.71
7.52
7.52
7.50
7.50
7.24
7.23
7.14
7.13
7.11
7.11
6.99
6.97
6.97
6.95
6.59
6.59
6.57
6.47
6.47
6.46
6.45
6.45
6.43
6.43
6.19
6.17
4.60
4.58
4.57
4.55
4.53
3.83
3.81
3.57
3.55
3.53
3.51
3.51
1.50
1.48
N
H
O
7h, 400 MHz, DMSO
3.01
1.01
1.01
1.00
1.99
1.98
0.99
0.99
1.00
3.01
2.99
3.00
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

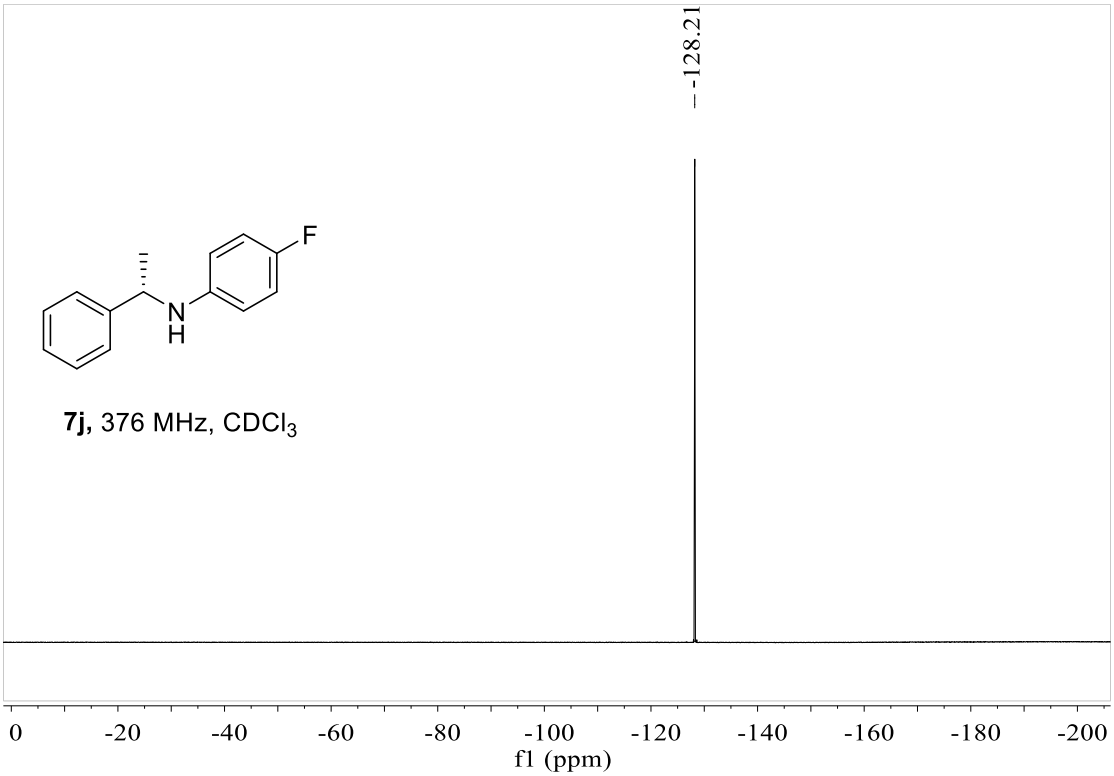

157.41
148.50
141.74
133.84
129.50
129.15
128.94
127.45
125.59
124.43
118.96
116.11
113.34
106.27
55.56
52.72
25.09
N
H
O
7h, 101 MHz, DMSO
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

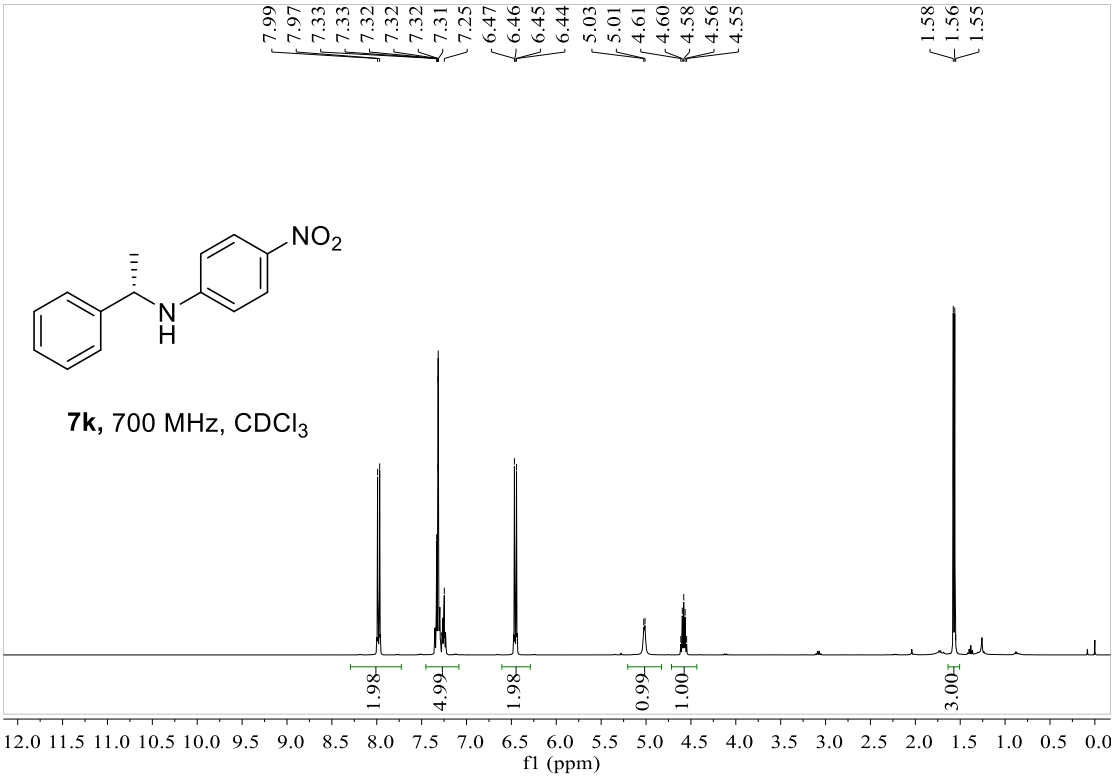

7.15
7.15
7.14
7.14
7.13
7.13
7.13
7.12
7.11
6.96
6.96
6.96
6.95
6.95
6.95
6.93
6.92
6.92
6.91
6.71
6.71
6.69
6.68
6.67
6.67
6.61
6.61
6.59
6.59
4.83
4.81
4.79
4.78
3.94
1.61
1.59
N
H
S
7i, 400 MHz, CDCl3
2.99
2.00
1.01
1.99
1.00
0.99
3.02
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

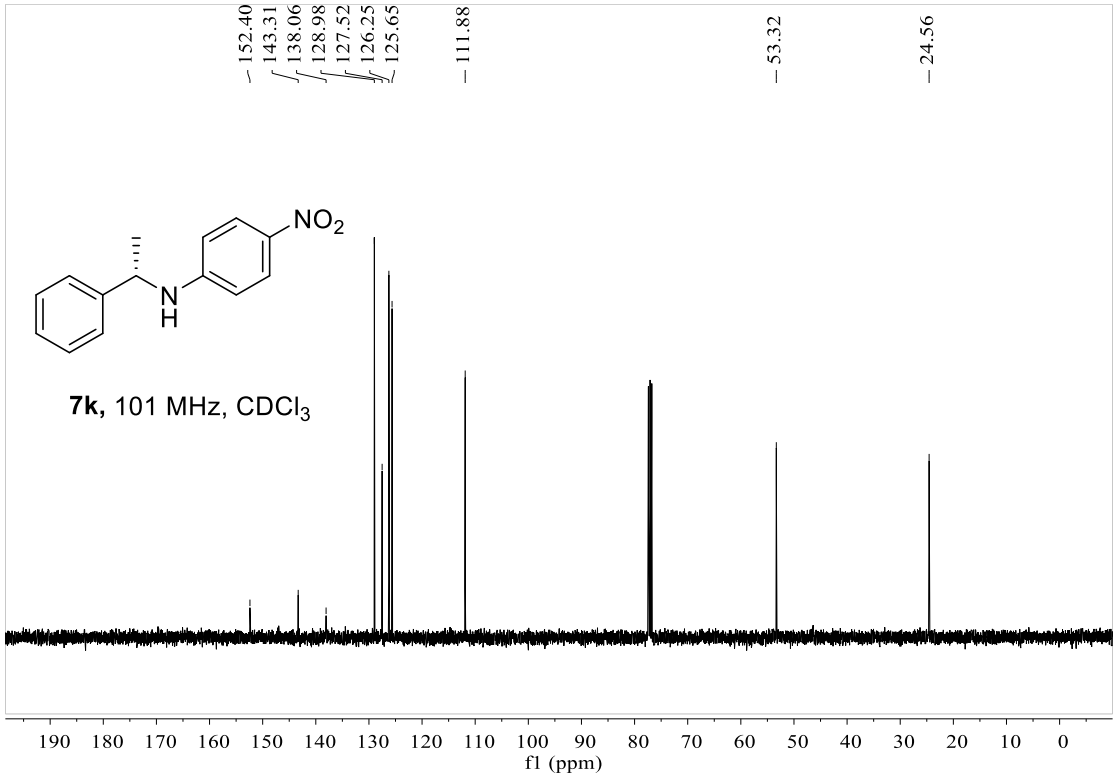

150.27
147.00
129.28
126.82
123.73
123.09
117.93
113.61
49.57
24.72
N
H
S
7i, 101 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

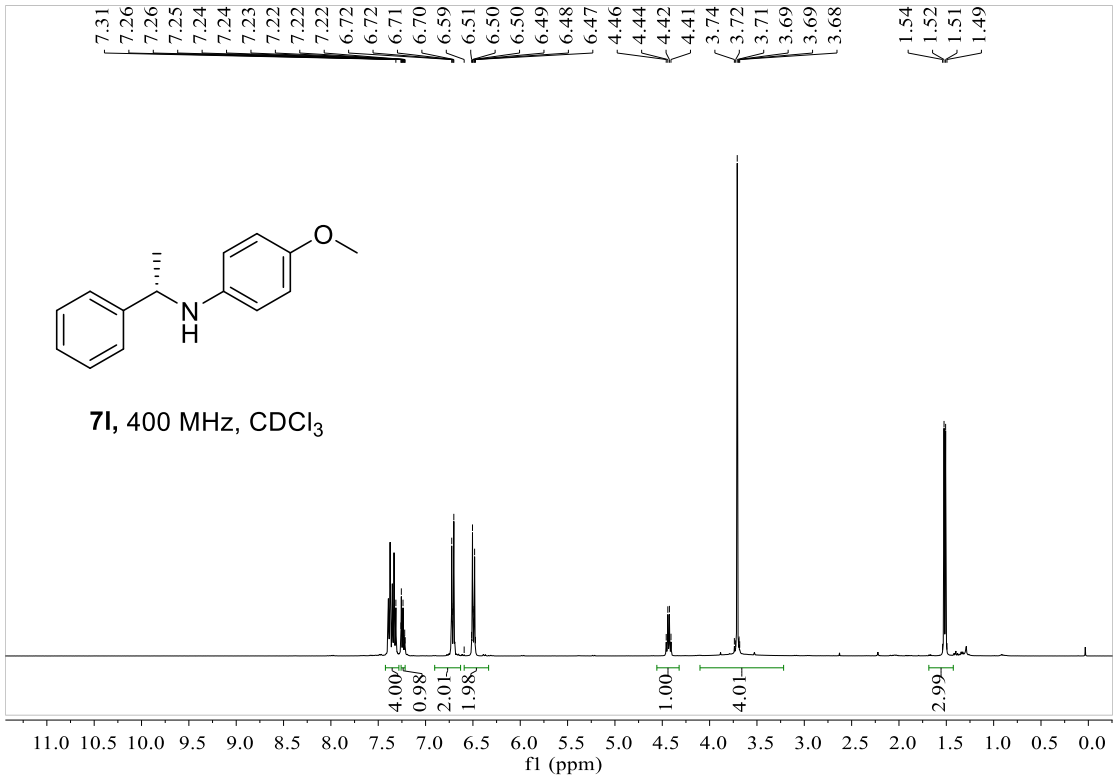

7.35
7.34
7.34
7.32
7.32
7.31
7.30
7.30
7.28
7.28
7.23
7.23
7.22
7.22
7.21
7.20
7.19
6.80
6.79
6.78
6.77
6.77
6.76
6.75
6.43
6.42
6.41
6.41
6.40
6.40
6.39
4.40
4.39
4.37
1.49
1.47
F
N
H
7j, 400 MHz, CDCl3
5.03
1.99
1.99
1.00
0.97
3.02
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

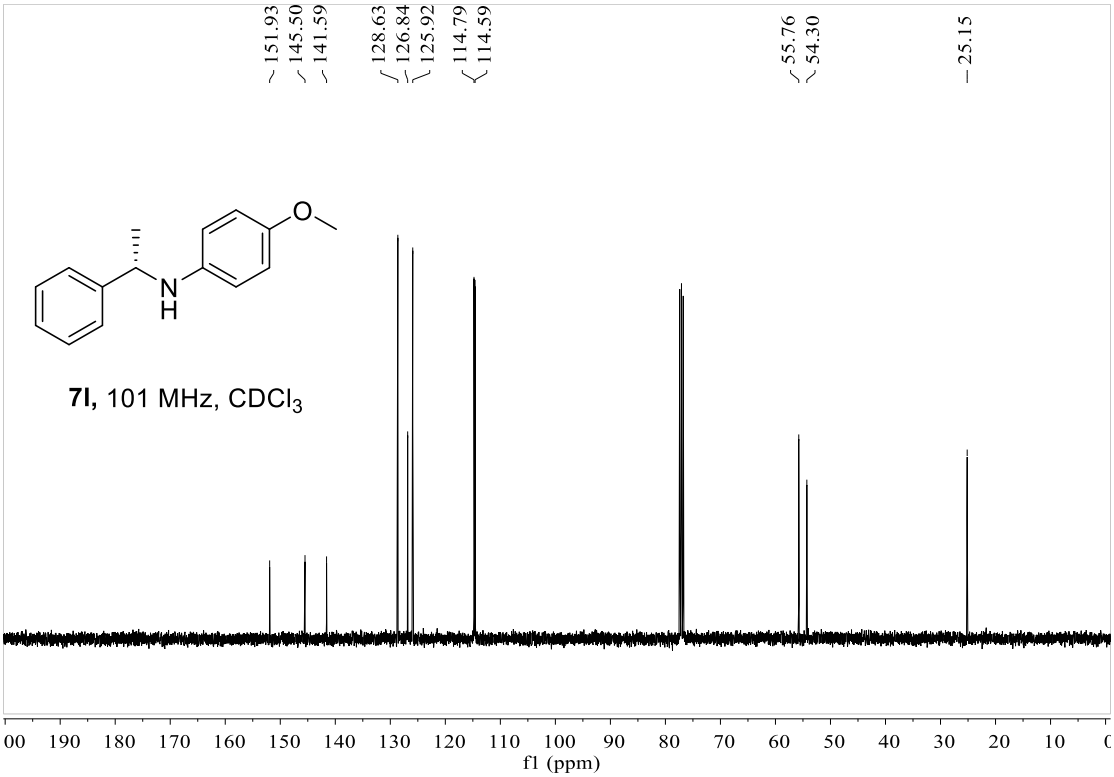

156.88
154.55
145.07
143.65
143.64
128.74
127.02
125.88
115.66
115.44
114.20
114.12
54.12
25.12
F
N
H
7j, 101 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

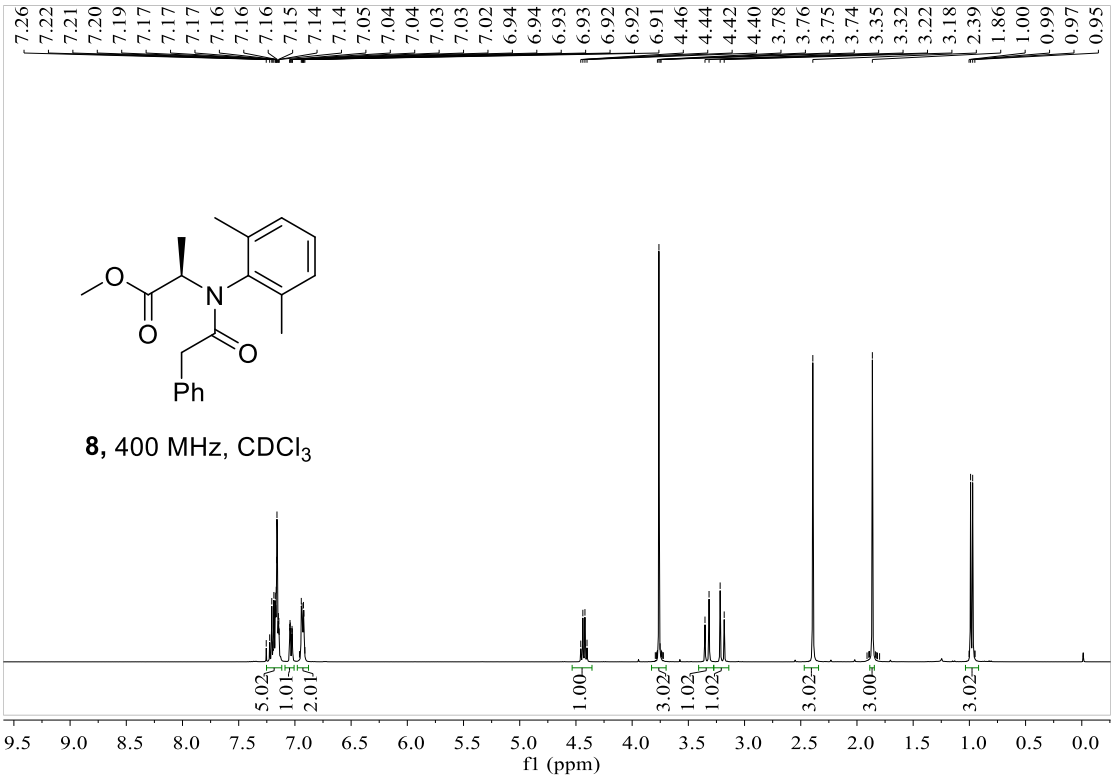

-128.21
F
N
H
7j, 376 MHz, CDCl3
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

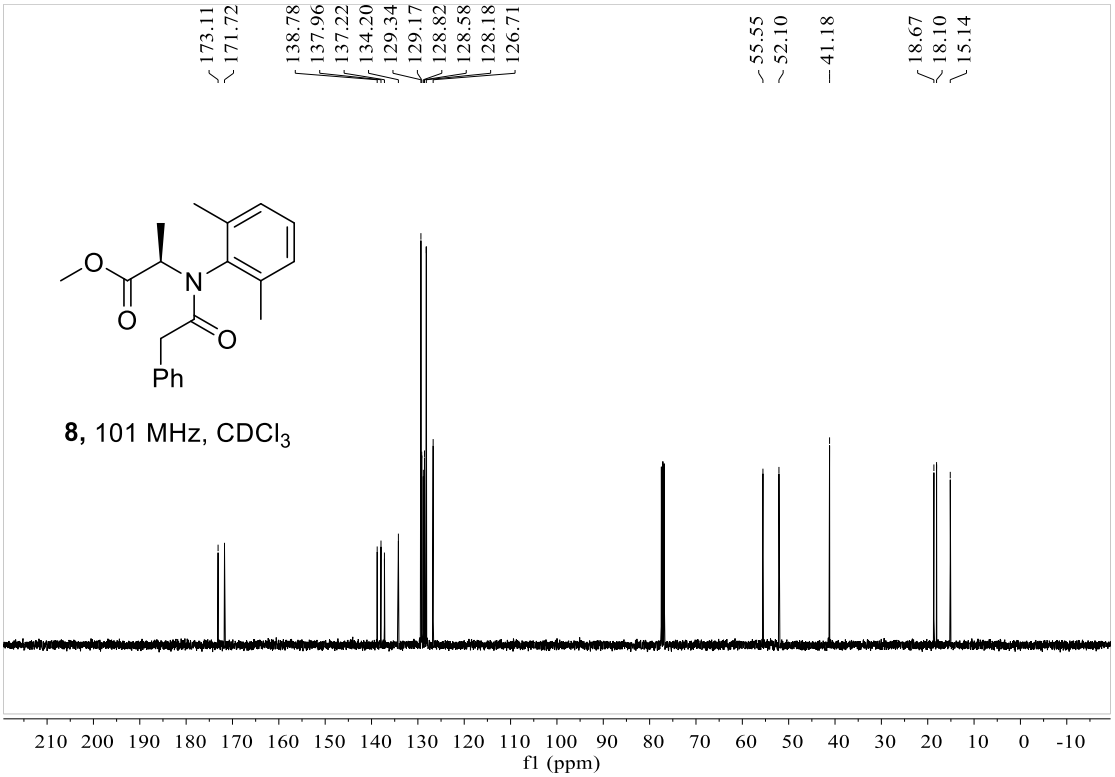

7.99
7.97
7.33
7.33
7.32
7.32
7.32
7.31
7.25
6.47
6.46
6.45
6.44
5.03
5.01
4.61
4.60
4.58
4.56
4.55
1.58
1.56
1.55
NO2
N
H
7k, 700 MHz, CDCl3
1.98
4.99
1.98
0.99
1.00
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


152.40
143.31
138.06
128.98
127.52
126.25
125.65
111.88
53.32
24.56
NO2
N
H
7k, 101 MHz, CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.31
7.26
7.26
7.25
7.24
7.24
7.23
7.22
7.22
7.22
6.72
6.72
6.71
6.70
6.59
6.51
6.50
6.50
6.49
6.48
6.47
4.46
4.44
4.42
4.41
3.74
3.72
3.71
3.69
3.69
3.68
1.54
1.52
1.51
1.49
O
N
H
7l, 400 MHz, CDCl3
4.00
0.98
2.01
1.98
1.00
4.01
2.99
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


151.93
145.50
141.59
128.63
126.84
125.92
114.79
114.59
55.76
54.30
25.15
O
N
H
7l, 101 MHz, CDCl3
f1 (ppm)


7.26
7.22
7.21
7.20
7.19
7.17
7.17
7.17
7.16
7.16
7.16
7.15
7.14
7.14
7.05
7.04
7.04
7.03
7.03
7.02
6.94
6.94
6.93
6.93
6.92
6.92
6.91
4.46
4.44
4.42
4.40
3.78
3.76
3.75
3.74
3.35
3.32
3.22
3.18
2.39
1.86
1.00
0.99
0.97
0.95
O
N
O
O
Ph
8, 400 MHz, CDCl3
5.02
1.01
2.01
1.00
3.02
1.02
1.02
3.02
3.00
3.02
f1 (ppm)


173.11
171.72
138.78
137.96
137.22
134.20
129.34
129.17
128.82
128.58
128.18
126.71
55.55
52.10
41.18
18.67
18.10
15.14
O
N
O
O
Ph
8, 101 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)