Supporting Information

Light-Driven Asymmetric Coupling of Aromatic Aldehydes and Aryl Iodides Using Simple Amine Reductant

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1. General Information

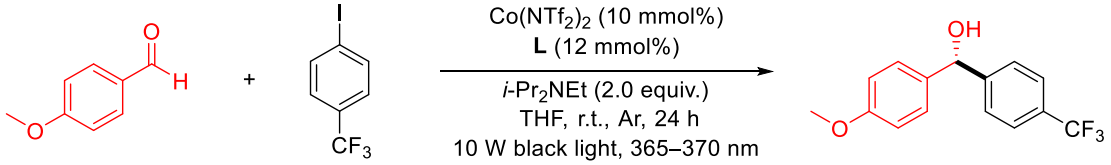
All reactions were carried out under an argon atmosphere in a flame-dried quartz tube with magnetic stirring. Petroleum ether, ethyl acetate and other solvents were dried and purified according to the procedure from ‘‘Purification of Laboratory Chemicals’’.[1] The reactions were monitored by TLC analysis using silica gel GF-254 thin layer plates and compounds were visualized with a UV light at 254 nm. All products were purified by flash chromatography on silica gel. The chemical yields referred are isolated products. ^{1}H and ^{13}C NMR spectra were collected on a Bruker AVANCE III 400MHz and JEOL JNM-ECS 400M at room temperature. Chemical shifts (δ) are expressed in ppm downfield from TMS as internal standard. The letters s, d, t, q, and m are used to indicate singlet, doublet, triplet, quadruplet, and multiplet, respectively. ^{19}F NMR spectra were collected on Bruker AVANCE III 400 MHz spectrometers at room temperature. HRMS was performed on Bruker Apex II FT-ICR mass instrument (ESI) and Waters GCT Premier TOFMS (EI). Enantiomeric excesses (ee) values were determined by chiral HPLC with chiral AD-H, OB, OD-H, OJ, IC columns with hexane and *i*-PrOH as solvents.

The absolute configuration of the product was determined by comparing the specific optical rotation of **3h** ($[\alpha]_D^{24}$ = -39.00, c = 1, CH_2Cl_2) with the literature (*R*-**3h**, $[\alpha]_D^{20}$ = 28.50, c = 0.1, CH_2Cl_2).[2] Therefore, the product **3h** obtained via our protocol with (*S,S*)-BDPP as the chiral ligand is *S* configuration. The absolute configuration of other products were assigned accordingly.

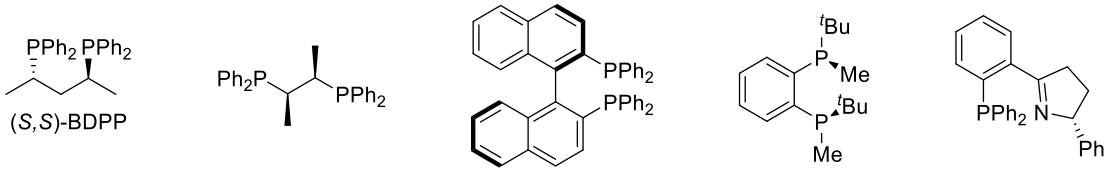
The equipment of light-reaction is a multi-channel photoreactor with 10 W black LED (365−370 nm, composed of 2 LED units in series, manufacturer: Shanghai Yukang Science and Education Instrument and Equipment company, wavelength of peak intensity: 367.2 nm).

2. Optimization of Reaction Conditions[a]

Table S1. The Effect of Chiral Ligand[a]



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

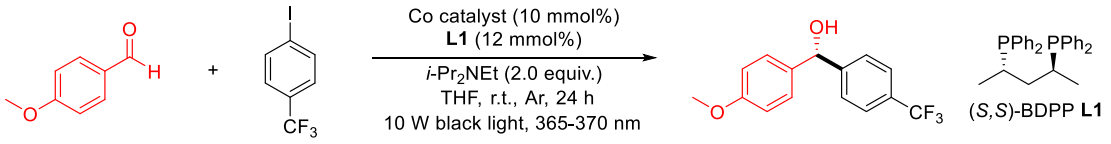


(*S*,*S*)-BDPP **L1** **L2** **L3** **L4** **L5**

Entry	Chiral Ligand	Yield (%)[b]	ee (%)[c]
1	**L1**	39	95
2	**L2**	trace	-
3	**L3**	trace	-
4	**L4**	9	94
5	**L5**	23	–93

[a]Reaction condition: **1a** (0.2 mmol), **2a** (0.3 mmol) $Co(NTf_2)_2$ (10 mmol%), ligand (12 mmol%), *i*-Pr_2NEt (2.0 equiv.), THF (1 mL), 10 W black light, room temperature. [b]Isolated yield. [c]Determined by chiral HPLC.

Table S2. The Effect of Co Catalyst[a]

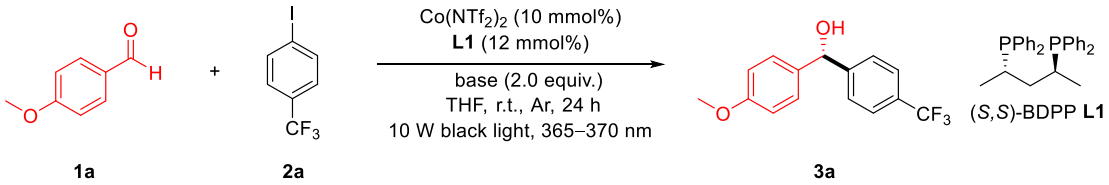


1a **2a** **3a**

Entry	Co catalyst	Yield (%)[b]	ee (%)[c]
1	$Co(NTf_2)_2$	39	95
2	$Co(OTf)_2$	23	95
3	CoI_2	27	95
4	$CoBr_2$	trace	-
5	$Co(acac)_2$	trace	-

[a]Reaction condition: **1a** (0.2 mmol), **2a** (0.3 mmol) Co catalyst (10 mmol%), **L1** (12 mmol%), *i*-Pr_2NEt (2.0 equiv.), THF (1 mL), 10 W black light, room temperature. [b]Isolated yield. [c]Determined by chiral HPLC.

Table S3. The Effect of Base[a]

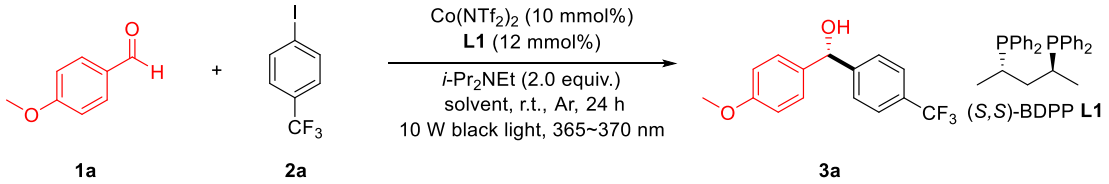


1a 2a 3a

Entry	Base	Yield (%)[b]	ee (%)[c]
1	*i*-Pr_2NEt	39	95
2	Et_3N	trace	-
3	DBACO	trace	-
4	Na_2CO_3	0	-

[a]Reaction condition: **1a** (0.2 mmol), **2a** (0.3 mmol) $Co(NTf_2)_2$ (10 mmol%), **L1** (12 mmol%), base (2.0 equiv.), THF (1 mL), 10 W black light, room temperature. [b]Isolated yield. [c]Determined by chiral HPLC.

Table S4. The Effect of Solvent[a]

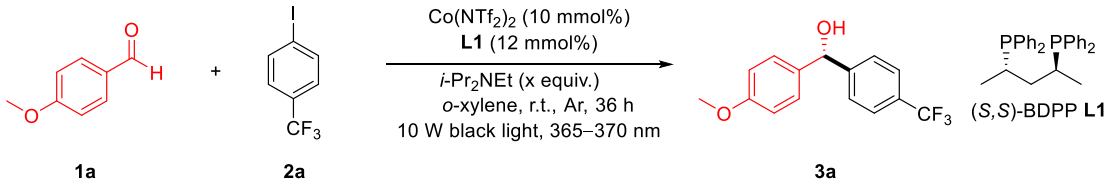


1a 2a 3a

Entry	Solvent	Yield (%)[b]	ee (%)[c]
1	THF	39	95
2	DCM	25	93
3	Toluene	74	95
4	*o*-Xylene	83	95
5	Benzotrifluoride	trace	-
6	1,4-Dioxane	48	95
7[d]	*o*-Xylene	96	95

[a]Reaction condition: **1a** (0.2 mmol), **2a** (0.3 mmol) $Co(NTf_2)_2$ (10 mmol%), **L1** (12 mmol%), *i*-Pr_2NEt (2.0 equiv.), solvent (1 mL), 10 W black light, room temperature. [b]Isolated yield. [c]Determined by chiral HPLC. [d]the reaction time reached 36 hours.

Table S5. The Effect of *i*-Pr_2NEt Equivalent[a]

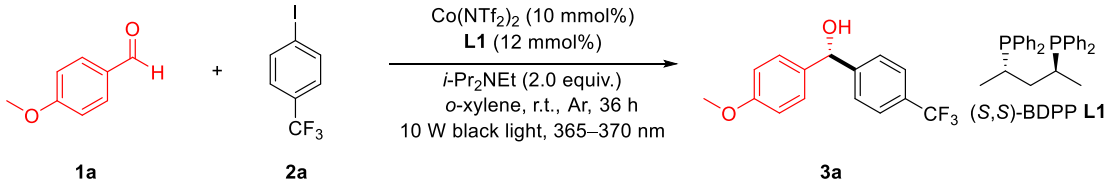


1a 2a 3a

Entry	Equivalent of *i*-Pr_2NEt	Yield (%)[b]	ee (%)[c]
1	1.5	51	95
2	2.0	83	95
3	2.5	82	94

[a]Reaction condition: **1a** (0.2 mmol), **2a** (0.3 mmol) $Co(NTf_2)_2$ (10 mmol%), **L1** (12 mmol%), *i*-Pr_2NEt (x equiv.), *o*-xylene (1 mL), 10 W black light, room temperature. [b]Isolated yield. [c]Determined by chiral HPLC.

Table S6. Control Experiment[a]

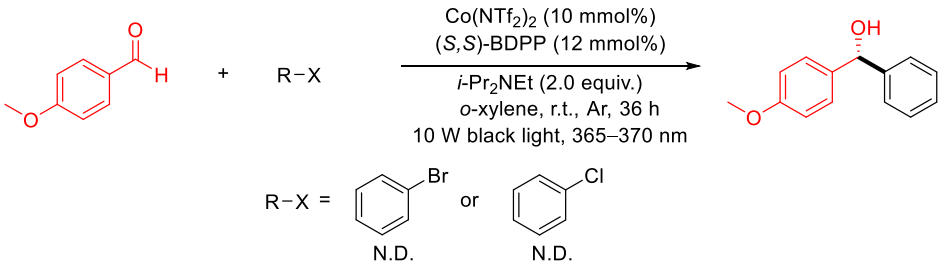


1a 2a 3a

Entry	Variation	Yield (%)[b]	ee (%)[c]
1	No $Co(NTf_2)_2$	0	-
2	No **L1**	0	-
3	No light source	0	-

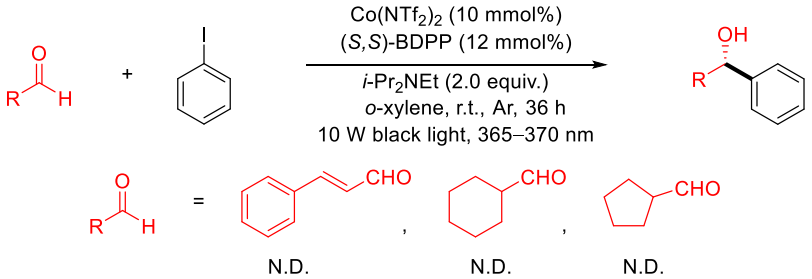
[a]Reaction condition: **1a** (0.2 mmol), **2a** (0.3 mmol) $Co(NTf_2)_2$ (10 mmol%), **L1** (12 mmol%), *i*-Pr_2NEt (2.0 equiv.), *o*-xylene (1 mL), 10 W black light, room temperature. [b]Isolated yield. [c]Determined by chiral HPLC.

Table S7. Other organic halogens[a]



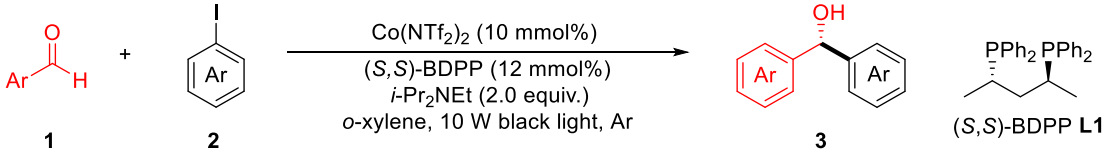
[a]Reaction condition: *p*-anisaldehyde (0.2 mmol), aryl halogens (0.3 mmol) $Co(NTf_2)_2$ (10 mmol%), (*S,S*)-BDPP (12 mmol%), *i*-Pr_2NEt (2.0 equiv.), *o*-xylene (1 mL), 10 W black light, room temperature. [b]N.D.: No detected.

Table S8. Unsaturated or aliphatic aldehydes[a]



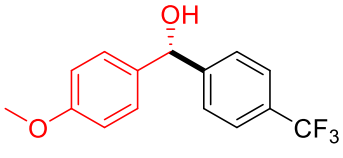
[a]Reaction condition: unsaturated or aliphatic aldehydes (0.2 mmol), iodobenzene (0.3 mmol) $Co(NTf_2)_2$ (10 mmol%), (*S,S*)-BDPP (12 mmol%), *i*-Pr_2NEt (2.0 equiv.), *o*-xylene (1 mL), 10 W black light, room temperature. [b]N.D.: No detected.

3. General Procedures and Characterization Data of Products



In an argon-filled glovebox, a 10 mL flame-dried quartz tube with magnetic stirring was charged sequentially with $Co(NTf_2)_2$ (0.02 mmol, 10 mol%), **L1** (0.024 mmol, 12 mol%) and *o*-xylene (1 mL). After stirring at room temperature for 2 h, substrates **1** (0.2 mmol) and **2** (0.3 mmol), *i*-Pr_2NEt (0.4 mmol, 2.0 eq.) were sequentially added into the quartz tube. Then, the quartz tube was removed from glovebox. The mixture was stirred at room temperature under 10 W black LEDs until the reaction was completed, as monitored by TLC analysis. The reaction mixture was then concentrated in vacuo. The crude product was purified by flash column chromatography (silica gel, PE/EA) to afford the desired product. Note: The racemic products were prepared according to the known procedure by replacing the chiral ligand **L1** with DPPP.[3]

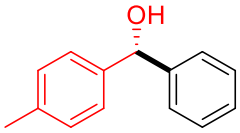
(*R*)-(4-Methoxyphenyl)(4-(trifluoromethyl)phenyl)methanol (3a)



96% (54 mg) isolated yield, white solid, $[\alpha]_D^{25}$ = 53.00 (c = 1.00 in CH_2Cl_2); 95% ee, determined by HPLC analysis (Chiralpak AD-H column, hexane/*i*-PrOH, 95:5 v/v, flow rate 1 mL/min, λ = 254 nm, 25 °C), tR (major) = 21.54 min, tR (minor) = 17.75 min; **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.58 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 5.82 (s, 1H), 3.78 (s, 3H), 2.36 (br, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 159.38, 147.76 (d, J_{C-F} = 1.1 Hz), 135.47,

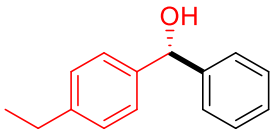
129.48 (q, $J_{C\text{-}F}$ = 32.1 Hz), 128.02, 126.52, 125.31 (q, $J_{C\text{-}F}$ = 3.8 Hz), 124.15 (q, $J_{C\text{-}F}$ = 270.4 Hz), 114.10, 75.27, 55.27. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.45.

(*R*)-Phenyl(*p*-tolyl)methanol (3b)



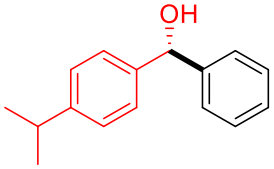
88% (35 mg) isolated yield, white solid, $[\alpha]_D^{25}$ = 7.50 (c = 0.40 in CH_2Cl_2); 94% ee, determined by HPLC analysis (Chiralpak AD-H column, hexane/*i*-PrOH, 95:5 v/v, flow rate 1 mL/min, λ = 254 nm, 25 °C), tR (major) = 14.12 min, tR (minor) = 15.29 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 4H), 7.25 (d, *J* = 8.0 Hz, 3H), 7.13 (d, *J* = 8.0 Hz, 2H), 5.79 (s, 1H), 2.32 (s, 3H), 2.23 (br, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.94, 140.95, 137.25, 129.16, 128.42, 127.42, 126.50, 126.43, 76.07, 21.08.

(*R*)-(4-Ethylphenyl)(phenyl)methanol (3c)



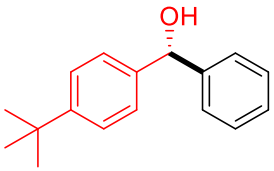
94% (40 mg) isolated yield, white solid, $[\alpha]_D^{25}$ = 10.00 (c = 0.30 in CH_2Cl_2); 95% ee, determined by HPLC analysis (Chiralpak AD-H column, hexane/*i*-PrOH, 95:5 v/v, flow rate 1 mL/min, λ = 254 nm, 25 °C), tR (major) = 14.11 min, tR (minor) = 15.67 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.24 (m, 7H), 7.16 (d, *J* = 8.0 Hz, 2H), 5.80 (s, 1H), 2.62 (q, *J* = 7.6 Hz, 2H), 2.23 (br, 1H), 1.21 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.92, 143.63, 141.17, 128.41, 127.98, 127.42, 126.58, 126.44, 76.11, 28.50, 15.51.

(*R*)-(4-Isopropylphenyl)(phenyl)methanol (3d)



91% (41 mg) isolated yield, yellow oil, $[\alpha]_D^{22}$ = 7.00 (c = 1.00 in CH_2Cl_2); 95% ee, determined by HPLC analysis (Chiralpak AD-H column, hexane/*i*-PrOH, 95:5 v/v, flow rate 1 mL/min, λ = 254 nm, 25 °C), tR (major) = 12.55 min, tR (minor) = 14.52 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.24 (m, 7H), 7.18 (d, *J* = 8.4 Hz, 2H), 5.80 (s, 1H), 2.93 – 2.83 (m, 1H), 2.26 (br, 1H), 1.22 (d, *J* = 6.8 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.24, 143.87, 141.26, 128.40, 127.41, 126.55, 126.43, 76.10, 33.77, 23.95.

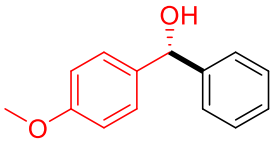
(*R*)-(4-(Tert-butyl)phenyl)(phenyl)methanol (3e)



92% (44 mg) isolated yield, white solid, $[\alpha]_D^{21}$ = 7.00 (c = 1.00 in CH_2Cl_2); 96% ee, determined by HPLC analysis (Chiralpak AD-H column, hexane/*i*-PrOH, 95:5 v/v, flow rate 1 mL/min, λ = 254 nm, 25 °C), tR

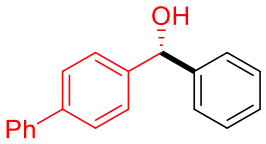
(major) = 11.16 min, tR (minor) = 12.98 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.24 (m, 9H), 5.81 (s, 1H), 2.22 (br, 1H), 1.30 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.51, 143.87, 140.88, 128.41, 127.43, 126.46, 126.29, 125.42, 76.07, 34.49, 31.32.

(*R*)-(4-Methoxyphenyl)(phenyl)methanol (3f)



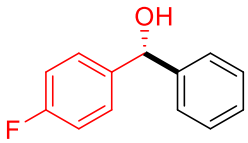
89% (38 mg) isolated yield, white solid, $[\alpha]_D^{25}$ = 32.00 (c = 1.00 in CH_2Cl_2); 94% ee, determined by HPLC analysis (Chiralpak AD-H column, hexane/*i*-PrOH, 90:10 v/v, flow rate 1 mL/min, λ = 254 nm, 25 °C), tR (major) = 12.57 min, tR (minor) = 13.66 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.24 (m, 7H), 6.86 (d, *J* = 8.8 Hz, 2H), 5.80 (s, 1H), 3.78 (s, 3H), 2.22 (br, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.05, 144.04, 136.20, 128.46, 127.94, 127.45, 126.42, 113.89, 75.81, 55.30.

(*S*)-[1,1'-Biphenyl]-4-yl(phenyl)methanol (3g)



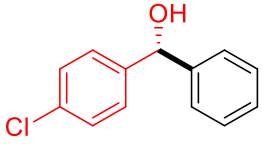
80% (45 mg) isolated yield, white solid, $[\alpha]_D^{25}$ = -1.00 (c = 1.00 in CH_2Cl_2); 96% ee, determined by HPLC analysis (Chiralpak AD-H column, hexane/*i*-PrOH, 95:5 v/v, flow rate 1 mL/min, λ = 254 nm, 25 °C), tR (major) = 27.20 min, tR (minor) = 24.97 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 – 7.54 (m, 4H), 7.41 (t, *J* = 8.0 Hz, 6H), 7.36 – 7.25 (m, 4H), 5.85 (s, 1H), 2.39 (br, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.70, 142.78, 140.73, 140.44, 128.73, 128.52, 127.61, 127.26, 127.21, 127.05, 126.94, 126.51, 75.99.

(*R*)-(4-Fluorophenyl)(phenyl)methanol (3h)



72% (29 mg) isolated yield, yellow oil, $[\alpha]_D^{23}$ = 5.00 (c = 1.00 in CH_2Cl_2); 95% ee, determined by HPLC analysis (Chiralpak OB column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1 mL/min, λ = 209.8 nm, 25 °C), tR (major) = 14.72 min, tR (minor) = 19.01 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 7H), 7.01 (t, *J* = 8.4 Hz, 2H), 5.82 (s, 1H), 2.24 (br, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.13 (d, $J_{C\text{-}F}$ = 244.3 Hz), 143.61, 139.51 (d, $J_{C\text{-}F}$ = 3.0 Hz), 128.57, 128.20 (d, $J_{C\text{-}F}$ = 8.0 Hz), 127.72, 126.43, 115.27 (d, $J_{C\text{-}F}$ = 21.2 Hz), 75.57. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -115.06.

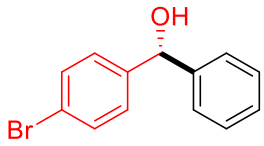
(*S*)-(4-Chlorophenyl)(phenyl)methanol (3i)



75% (33 mg) isolated yield, yellow oil, $[\alpha]_D^{23}$ = -10.00 (c = 1.00 in CH_2Cl_2); 95% ee, determined by HPLC analysis (Chiralpak AD-H column,

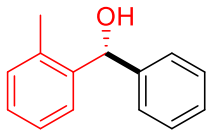
hexane/*i*-PrOH, 95:5 v/v, flow rate 1 mL/min, λ = 254 nm, 25 °C), tR (major) = 14.12 min, tR (minor) = 15.90 min; **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.33 (d, *J* = 4.4 Hz, 4H), 7.30 – 7.27 (m, 4H), 5.79 (s, 1H), 2.30 (br, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 143.45, 142.23, 133.30, 128.66, 128.61, 127.89, 127.88, 126.54, 75.63.

(*S*)-(4-Bromophenyl)(phenyl)methanol (3j)



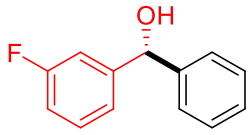
72% (38 mg) isolated yield, yellow oil, $[\alpha]_D^{23}$ = -15.00 (c = 1.00 in CH_2Cl_2); 96% ee, determined by HPLC analysis (Chiralpak OB column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1 mL/min, λ = 209.8 nm, 25 °C), tR (major) = 8.53 min, tR (minor) = 11.28 min; **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.44 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 4.0 Hz, 4H), 7.24 (d, *J* = 8.4 Hz, 3H), 5.77 (s, 1H), 2.32 (br, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 143.34, 142.70, 131.52, 128.63, 128.19, 127.85, 126.50, 121.39, 75.62.

(*S*)-Phenyl(*o*-tolyl)methanol (3k)



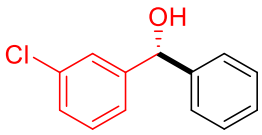
71% (28 mg) isolated yield, yellow oil, $[\alpha]_D^{23}$ = -15.00 (c = 1.00 in CH_2Cl_2); 94% ee, determined by HPLC analysis (Chiralpak OB column, hexane/*i*-PrOH, 94:6 v/v, flow rate 1 mL/min, λ = 209.8 nm, 25 °C), tR (major) = 14.91 min, tR (minor) = 18.16 min; **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.51 (d, *J* = 7.2 Hz, 1H), 7.32 (d, *J* = 4.4 Hz, 4H), 7.28 – 7.18 (m, 3H), 7.14 (d, *J* = 7.6 Hz, 1H), 6.00 (s, 1H), 2.24 (s, 3H), 2.15 (br, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 142.82, 141.40, 135.34, 130.51, 128.45, 127.54, 127.50, 127.08, 126.23, 126.10, 73.34, 19.36.

(*S*)-(3-Fluorophenyl)(phenyl)methanol (3l)



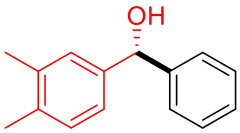
77% (31 mg) isolated yield, yellow oil, $[\alpha]_D^{24}$ = -39.00 (c = 1.00 in CH_2Cl_2); 95% ee, determined by HPLC analysis (Chiralpak OB column, hexane/*i*-PrOH, 80:20 v/v, flow rate 0.75 mL/min, λ = 209.8 nm, 25 °C), tR (major) = 11.01 min, tR (minor) = 12.00 min; **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.34 (d, *J* = 4.4 Hz, 4H), 7.30 – 7.24 (m, 2H), 7.12 (t, *J* = 7.6 Hz, 2H), 6.94 (t, *J* = 8.8 Hz, 1H), 5.79 (s, 1H), 2.38 (br, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 163.00 (d, $J_{C\text{-}F}$ = 244.6 Hz), 146.29 (d, $J_{C\text{-}F}$ = 6.7 Hz), 143.26, 129.92 (d, $J_{C\text{-}F}$ = 8.1 Hz), 128.63, 127.88, 126.54, 122.01 (d, $J_{C\text{-}F}$ = 2.9 Hz), 114.32 (d, $J_{C\text{-}F}$ = 21.1 Hz), 113.35 (d, $J_{C\text{-}F}$ = 22.0 Hz), 75.64 (d, $J_{C\text{-}F}$ = 1.7 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) *δ* -112.75.

(*S*)-(3-Chlorophenyl)(phenyl)methanol (3m)



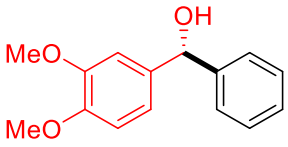
75% (33 mg) isolated yield, yellow oil, $[\alpha]_D^{24}$ = -39.00 (c = 1.00 in CH_2Cl_2); 96% ee, determined by HPLC analysis (Chiralpak OB column, hexane/*i*-PrOH, 90:10 v/v, flow rate 1 mL/min, λ = 209.8 nm, 25 °C), tR (major) = 16.21 min, tR (minor) = 25.75 min; **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.40 (s, 1H), 7.35 (d, *J* = 4.4 Hz, 4H), 7.31 – 7.25 (m, 4H), 5.80 (s, 1H), 2.26 (br, 1H). **^{13}C NMR** (100 MHz, DMSO-d_6) *δ* 148.30, 145.04, 132.80, 130.03, 128.20, 126.96, 126.60, 126.21, 125.86, 124.87, 73.47.

(*R*)-(3,4-Dimethylphenyl)(phenyl)methanol (3n)



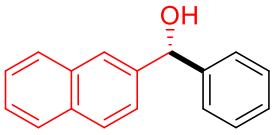
87% (37 mg) isolated yield, white solid, $[\alpha]_D^{22}$ = 28.00 (c = 1.00 in CH_2Cl_2); 96% ee, determined by HPLC analysis (Chiralpak OB column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1 mL/min, λ = 209.8 nm, 25 °C), tR (major) = 7.52 min, tR (minor) = 11.14 min; **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.37 (d, *J* = 7.2 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 2H), 7.26 – 7.23 (m, 1H), 7.13 (s, 1H), 7.08 (s, 2H), 5.76 (s, 1H), 2.23 (s, 7H). **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 143.97, 141.38, 136.70, 135.92, 129.69, 128.39, 127.78, 127.35, 126.38, 123.96, 76.08, 19.82, 19.42.

(*R*)-(3,4-Dimethoxyphenyl)(phenyl)methanol (3o)



84% (41 mg) isolated yield, white solid, $[\alpha]_D^{23}$ = 6.00 (c = 1.00 in CH_2Cl_2); 95% ee, determined by HPLC analysis (Chiralpak OB column, hexane/*i*-PrOH, 60:40 v/v, flow rate 1 mL/min, λ = 215.0 nm, 25 °C), tR (major) = 11.24 min, tR (minor) = 19.37 min; **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.37 – 7.31 (m, 3H), 7.25 (t, *J* = 8.0 Hz, 1H), 6.91 – 6.80 (m, 3H), 5.77 (s, 1H), 3.85 (s, 3H), 3.83 (s, 3H), 2.35 (br, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 149.00, 148.42, 143.84, 136.51, 128.39, 127.44, 126.37, 118.91, 110.90, 109.75, 75.92, 55.86, 55.79.

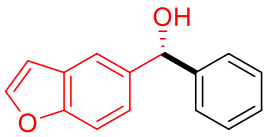
(*R*)-Naphthalen-2-yl(phenyl)methanol (3p)



79% (37 mg) isolated yield, white solid, $[\alpha]_D^{25}$ = -2.50 (c = 0.80 in CH_2Cl_2); 94% ee, determined by HPLC analysis (Chiralpak OB column, hexane/*i*-PrOH, 85:15 v/v, flow rate 1 mL/min, λ = 234.6 nm, 25 °C), tR (major) = 15.62 min, tR (minor) = 15.04 min; **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.88 (s, 1H), 7.84 – 7.77 (m, 3H), 7.48 – 7.45 (m, 2H), 7.43 – 7.40 (m, 3H), 7.33 (t, *J* = 7.2 Hz, 2H), 7.28 – 7.24 (m, 1H), 5.98 (s, 1H), 2.36 (br, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 143.62, 141.10, 133.23, 132.86, 128.53, 128.31, 128.05, 127.66, 126.69,

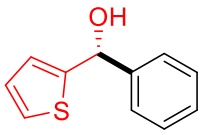
126.17, 125.95, 125.00, 124.75, 76.36.

(*R*)-Benzofuran-5-yl(phenyl)methanol (3q)



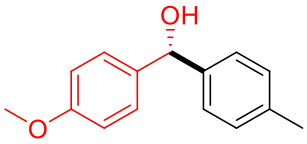
87% (39 mg) isolated yield, white solid, $[\alpha]_D^{24}$ = 13.00 (c = 1.00 in CH_2Cl_2); 95% ee, determined by HPLC analysis (Chiralpak OD-H column, hexane/*i*-PrOH, 95:5 v/v, flow rate 1 mL/min, λ = 254 nm, 25 °C), tR (major) = 22.47 min, tR (minor) = 20.60 min; **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.60 (d, *J* = 2.0 Hz, 2H), 7.45 – 7.23 (m, 7H), 6.72 (d, *J* = 1.6 Hz, 1H), 5.92 (s, 1H), 2.39 (br, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 154.36, 145.46, 144.07, 138.63, 128.43, 127.45, 126.43, 123.23, 119.22, 111.34, 106.68, 76.28.

(*S*)-Phenyl(thiophen-2-yl)methanol (3r)



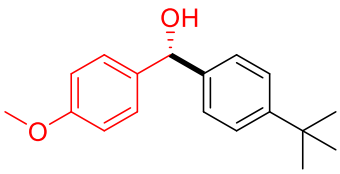
81% (31 mg) isolated yield, yellow oil, $[\alpha]_D^{24}$ = -7.00 (c = 1.00 in CH_2Cl_2); 98% ee, determined by HPLC analysis (Chiralpak OB column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1 mL/min, λ = 209.8 nm, 25 °C), tR (major) = 9.51 min, tR (minor) = 8.74 min; **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.45 (d, *J* = 7.2 Hz, 2H), 7.37 (t, *J* = 7.2 Hz, 2H), 7.32 – 7.29 (m, 1H), 7.26 – 7.25 (m, 1H), 6.95 – 6.93 (m, 1H), 6.88 (d, *J* = 3.6 Hz, 1H), 6.05 (s, 1H), 2.43 (br, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 148.09, 143.08, 128.51, 127.98, 126.63, 126.27, 125.39, 124.87, 72.40. HRMS (ESI) m/z calcd for $C_{11}H_{10}NaOS$ $[M + Na]^+$ 213.0345, found 213.0338.

(*R*)-(4-Methoxyphenyl)(*p*-tolyl)methanol (3s)



90% (41 mg) isolated yield, white solid, $[\alpha]_D^{25}$ = 11.00 (c = 1.00 in CH_2Cl_2); 92% ee, determined by HPLC analysis (Chiralpak OJ column, hexane/*i*-PrOH, 95:5 v/v, flow rate 1 mL/min, λ = 238.6 nm, 25 °C), tR (major) = 45.11 min, tR (minor) = 53.00 min; **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.25 (t, *J* = 8.8 Hz, 4H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 5.75 (s, 1H), 3.77 (s, 3H), 2.32 (s, 3H), 2.23 (br, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 158.92, 141.14, 137.05, 136.31, 129.08, 127.77, 126.34, 113.79, 75.60, 55.23, 21.06.

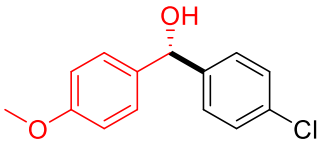
(*R*)-(4-(Tert-butyl)phenyl)(4-methoxyphenyl)methanol (3t)



94% (51 mg) isolated yield, white solid, $[\alpha]_D^{25}$ = 9.00 (c = 1.00 in CH_2Cl_2); 92% ee, determined by HPLC analysis (Chiralpak IC column, hexane/*i*-PrOH, 95:5 v/v, flow rate 1 mL/min, λ = 231.0 nm, 25 °C), tR (major) = 14.00 min, tR (minor) = 19.00 min; **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.34 (d, *J* = 8.4 Hz, 2H), 7.29 – 7.26 (m, 4H), 6.85 (d, *J* = 8.8 Hz, 2H), 5.75

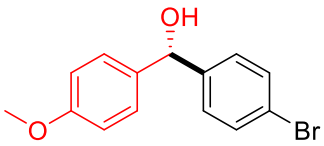
(s, 1H), 3.77 (s, 3H), 2.26 (br, 1H), 1.30 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.90, 150.30, 141.08, 136.22, 127.77, 126.11, 125.32, 113.76, 75.58, 55.22, 34.45, 31.31.

(*R*)-(4-chlorophenyl)(4-methoxyphenyl)methanol (3u)



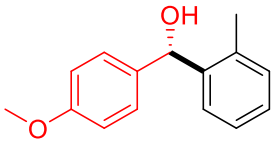
96% (48 mg) isolated yield, white solid, $[\alpha]_D^{25}$ = 42.00 (c = 1.00 in CH_2Cl_2); 94% ee, determined by HPLC analysis (Chiralpak OB column, hexane/*i*-PrOH, 90:10 v/v, flow rate 1 mL/min, λ = 209.8 nm, 25 °C), tR (major) = 28.76 min, tR (minor) = 26.33 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 (s, 4H), 7.23 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 5.74 (s, 1H), 3.78 (s, 3H), 2.30 (br, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.20, 142.42, 135.75, 133.06, 128.49, 127.88, 127.72, 113.97, 75.13, 55.26.

(*R*)-(4-Bromophenyl)(4-methoxyphenyl)methanol (3v)



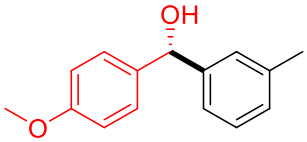
96% (56 mg) isolated yield, white solid, $[\alpha]_D^{25}$ = 30.00 (c = 1.00 in CH_2Cl_2); 94% ee, determined by HPLC analysis (Chiralpak OB column, hexane/*i*-PrOH, 90:10 v/v, flow rate 1 mL/min, λ = 209.8 nm, 25 °C), tR (major) = 28.76 min, tR (minor) = 26.33 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 4H), 6.85 (d, *J* = 8.8 Hz, 2H), 5.72 (s, 1H), 3.78 (s, 3H), 2.31 (br, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.19, 142.92, 135.66, 131.42, 128.06, 127.89, 121.19, 113.97, 75.15, 55.26.

(*R*)-(4-Methoxyphenyl)(*o*-tolyl)methanol (3w)



61% (28 mg) isolated yield, yellow oil, $[\alpha]_D^{25}$ = 15.00 (c = 1.00 in CH_2Cl_2); 84% ee, determined by HPLC analysis (Chiralpak IC column, hexane/*i*-PrOH, 95:5 v/v, flow rate 1 mL/min, λ = 237.1 nm, 25 °C), tR (major) = 13.13 min, tR (minor) = 16.26 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.2 Hz, 1H), 7.27 – 7.11 (m, 5H), 6.84 (d, *J* = 8.8 Hz, 2H), 5.93 (s, 1H), 3.77 (s, 3H), 2.20 (s, 3H), 2.15 (br, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.00, 141.58, 135.14, 135.04, 130.44, 128.47, 127.34, 126.04, 125.85, 113.81, 72.91, 55.23, 19.31.

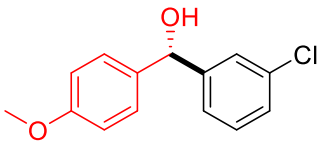
(*R*)-(4-Methoxyphenyl)(m-tolyl)methanol (3x)



88% (40 mg) isolated yield, yellow oil, $[\alpha]_D^{25}$ = 16.00 (c = 1.00 in CH_2Cl_2); 94% ee, determined by HPLC analysis (Chiralpak IC column,

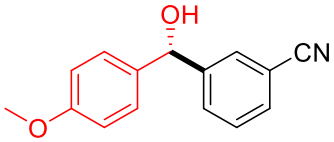
hexane/*i*-PrOH, 95:5 v/v, flow rate 1 mL/min, λ = 209.8 nm, 25 °C), tR (major) = 17.91 min, tR (minor) = 20.05 min; **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.27 (d, *J* = 8.4 Hz, 2H), 7.21 – 7.13 (m, 3H), 7.06 (d, *J* = 7.2 Hz, 1H), 6.85 (d, *J* = 8.8 Hz, 2H), 5.74 (s, 1H), 3.77 (s, 3H), 2.32 (s, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 158.92, 143.95, 138.05, 136.20, 128.29, 128.15, 127.82, 127.00, 123.43, 113.79, 75.76, 55.22, 21.44.

(*R*)-(3-Chlorophenyl)(4-methoxyphenyl)methanol (3y)



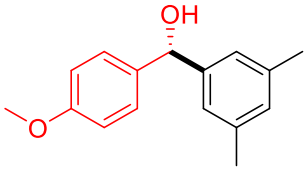
94% (47 mg) isolated yield, colorless oil, $[\alpha]_D^{25}$ = 53.00 (c = 1.00 in CH_2Cl_2); 97% ee, determined by HPLC analysis (Chiralpak OB column, hexane/*i*-PrOH, 85:15 v/v, flow rate 1 mL/min, λ = 248.6 nm, 25 °C), tR (major) = 19.55 min, tR (minor) = 17.36 min; **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.37 (s, 1H), 7.25 – 7.21 (m, 5H), 6.87 – 6.84 (m, 2H), 5.72 (s, 1H), 3.78 (s, 3H), 2.39 (br, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 159.21, 145.96, 135.51, 134.27, 129.63, 127.93, 127.43, 126.41, 124.46, 113.98, 75.15, 55.24.

(*R*)-3-(Hydroxy(4-methoxyphenyl)methyl)benzonitrile (3z)



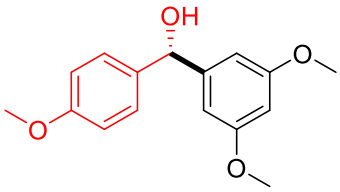
81% (39 mg) isolated yield, colorless oil, $[\alpha]_D^{25}$ = 78.00 (c = 1.00 in CH_2Cl_2); 93% ee, determined by HPLC analysis (Chiralpak IC column, hexane/*i*-PrOH, 90:10 v/v, flow rate 1 mL/min, λ = 254 nm, 25 °C), tR (major) = 25.26 min, tR (minor) = 23.13 min; **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.69 (s, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 8.8 Hz, 2H), 6.90 – 6.86 (m, 2H), 5.79 (s, 1H), 3.79 (s, 3H), 2.51 (br, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 159.45, 145.37, 135.09, 130.88, 130.76, 129.85, 129.07, 128.00, 118.85, 114.18, 112.28, 74.80, 55.28.

(*R*)-(3,5-Dimethylphenyl)(4-methoxyphenyl)methanol (3aa)



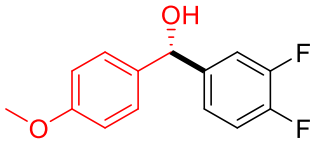
87% (42 mg) isolated yield, white solid, $[\alpha]_D^{25}$ = 14.00 (c = 1.00 in CH_2Cl_2); 94% ee, determined by HPLC analysis (Chiralpak OB column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1 mL/min, λ = 237.0 nm, 25 °C), tR (major) = 12.33 min, tR (minor) = 8.30 min; **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.26 (d, *J* = 8.8 Hz, 2H), 6.96 (s, 2H), 6.88 – 6.83 (m, 3H), 5.69 (s, 1H), 3.76 (s, 3H), 2.28 (s, 7H). **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 158.86, 143.96, 137.92, 136.26, 129.03, 127.77, 124.12, 113.74, 75.76, 55.19, 21.30. HRMS (ESI): m/z calcd for $C_{16}H_{18}NaO_2$ **[**M + Na]$^+$ 265.1199, found 265.1194.

(*R*)-(3,5-Dimethoxyphenyl)(4-methoxyphenyl)methanol (3ab)



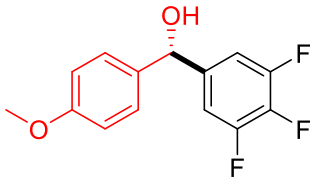
91% (50 mg) isolated yield, yellow oil, $[\alpha]_D^{25}$ = 29.00 (c = 1.00 in CH_2Cl_2); 94% ee, determined by HPLC analysis (Chiralpak IC column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1 mL/min, λ = 254 nm, 25 °C), tR (major) = 13.30 min, tR (minor) = 22.22 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 6.53 (d, J = 2.0 Hz, 2H), 6.36 – 6.34 (m, 1H), 5.69 (s, 1H), 3.77 (s, 3H), 3.75 (s, 6H), 2.31 (br, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.77, 159.01, 146.51, 135.85, 127.84, 113.81, 104.32, 99.24, 75.71, 55.27, 55.22.

(*R*)-(3,4-Difluorophenyl)(4-methoxyphenyl)methanol (3ac)



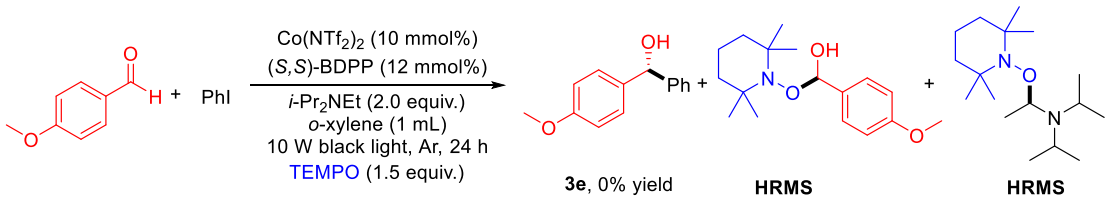
90% (45 mg) isolated yield, colorless oil, $[\alpha]_D^{25}$ = 51.00 (c = 1.00 in CH_2Cl_2); 96% ee, determined by HPLC analysis (Chiralpak OJ column, hexane/*i*-PrOH, 95:5 v/v, flow rate 1 mL/min, λ = 235.0 nm, 25 °C), tR (major) = 53.38 min, tR (minor) = 50.69 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 – 7.16 (m, 3H), 7.12 – 7.03 (m, 2H), 6.86 (d, J = 8.4 Hz, 2H), 5.71 (s, 1H), 3.78 (s, 3H), 2.41 (br, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.31, 151.06 (dd, $J_{C\text{-}F}$ = 74.7, 12.8 Hz), 148.60 (dd, $J_{C\text{-}F}$ = 74.1, 12.7 Hz), 140.98 (t, $J_{C\text{-}F}$ = 4.7 Hz), 135.42, 127.87, 122.20 (dd, $J_{C\text{-}F}$ = 6.3, 3.5 Hz), 116.99 (d, $J_{C\text{-}F}$ = 17.1 Hz), 115.32 (d, $J_{C\text{-}F}$ = 17.8 Hz), 114.04, 74.68 (d, $J_{C\text{-}F}$ = 1.2 Hz), 55.25. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -137.51 (d, J = 21.1 Hz), -140.01 (d, J = 21.4 Hz).

(*R*)-(4-Methoxyphenyl)(3,4,5-trifluorophenyl)methanol (3ac)

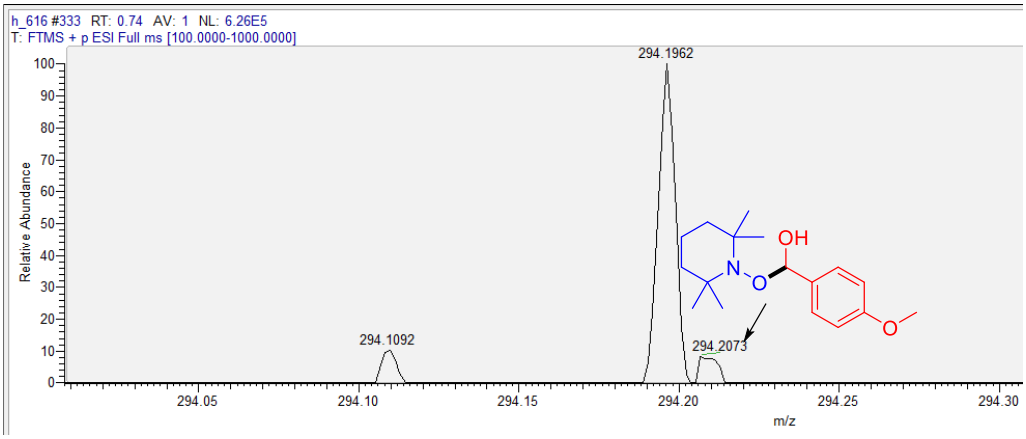


86% (46 mg) isolated yield, colorless oil, $[\alpha]_D^{25}$ = 66.00 (c = 1.00 in CH_2Cl_2); 96% ee, determined by HPLC analysis (Chiralpak OJ column, hexane/*i*-PrOH, 90:10 v/v, flow rate 1 mL/min, λ = 209.8 nm, 25 °C), tR (major) = 13.20 min, tR (minor) = 11.34 min; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 – 7.19 (m, 2H), 7.00 – 6.97 (m, 2H), 6.89 – 6.86 (m, 2H), 5.68 (s, 1H), 3.79 (s, 3H), 2.37 (br, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.57, 151.11 (ddd, $J_{C\text{-}F}$ = 248.4, 10.0, 3.9 Hz), 140.27 – 139.80 (m), 137.46 (t, $J_{C\text{-}F}$ = 15.2 Hz), 134.84, 127.96, 114.21, 110.24 (dd, $J_{C\text{-}F}$ = 16.0, 5.9 Hz), 74.44, 55.29. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -134.06 (d, J = 20.3 Hz), -162.41 (t, J = 20.7 Hz).

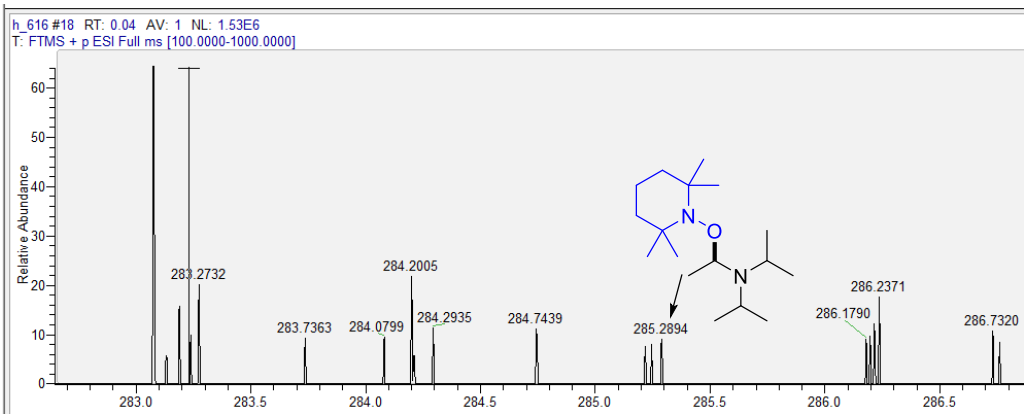
4. Radical Trapping Experiments



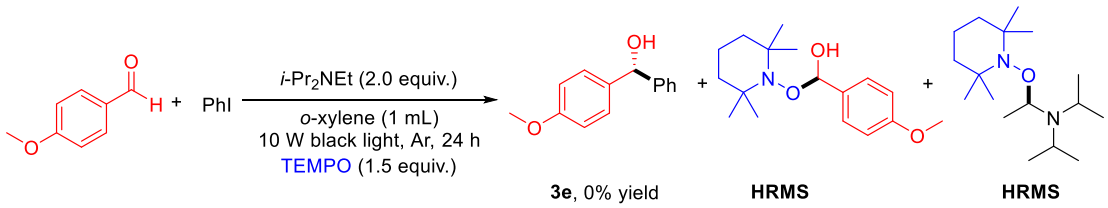
In an argon-filled glovebox, a 10 mL flame-dried quartz tube with magnetic stirring was charged sequentially with $Co(NTf_2)_2$ (0.02 mmol, 10 mol%), **L1** (0.024 mmol, 12 mol%) and *o*-xylene (1 mL). After stirring at room temperature for 2 h, *p*-anisaldehyde (0.2 mmol) and iodobenzene (0.3 mmol), *i*-Pr_2NEt (0.4 mmol, 2.0 eq.) and TEMPO (1.5eq, 0.3 mmol) were sequentially added into the quartz tube. Then, the quartz tube was removed from glovebox. The mixture was stirred at room temperature under 10 W black LEDs for 24 h. The reductive coupling of *p*-anisaldehyde and iodobenzene was inhibited completely by the addition of 1.5 equiv. of 2,2,6,6-tetramethylpiperidinooxy (TEMPO) as a radical scavenger. Moreover, the ketyl radical addition product and *α*-amino radical addition product were detected by HRMS. HRMS (ESI) of ketyl radical addition product: m/z calcd for $C_{17}H_{28}NO_3$ $[M + H]^+$ 294.2064, found 294.2073. HRMS (ESI) of *α*-amino radical addition: m/z calcd for $C_{17}H_{37}N_2O$ $[M + H]^+$ 285.2900, found 285.2894.



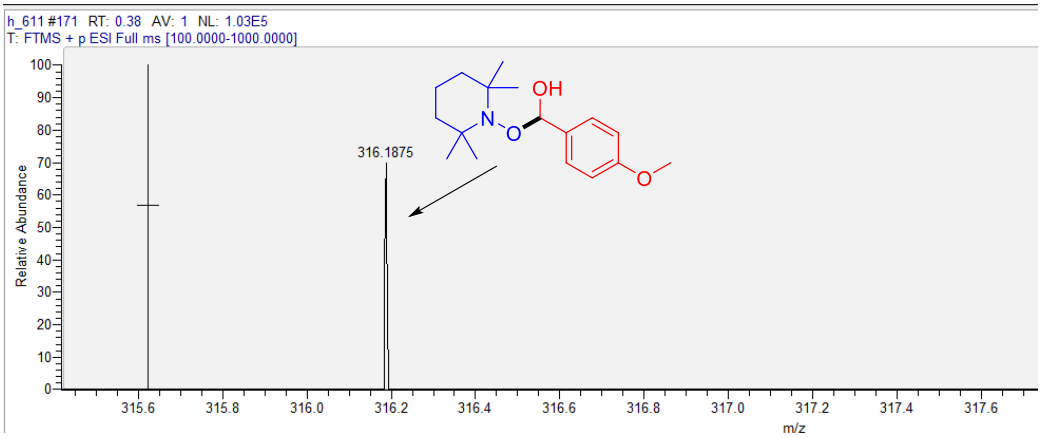
HRMS (ESI) of ketyl radical addition product



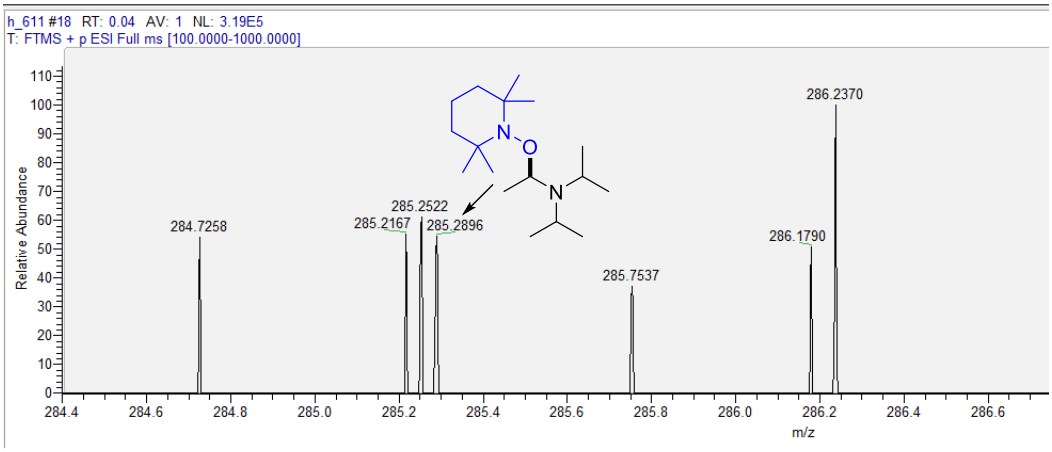
HRMS (ESI) of *α*-amino radical addition



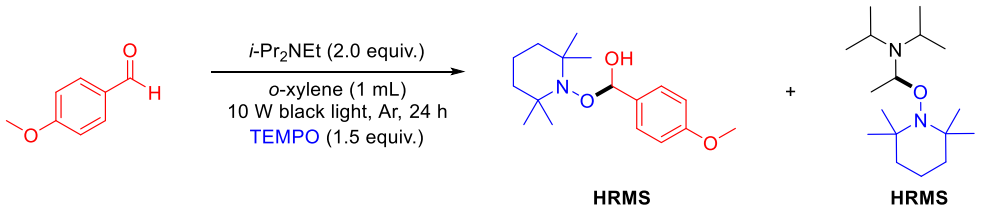
In an argon-filled glovebox, a 10 mL flame-dried quartz tube with magnetic stirring was charged sequentially with *p*-anisaldehyde (0.2 mmol), iodobenzene (0.3 mmol), *i*-Pr_2NEt (0.4 mmol, 2.0 eq.), TEMPO (1.5eq, 0.3 mmol) and *o*-xylene (1 mL). Then, the quartz tube was removed from glovebox. The mixture was stirred at room temperature under 10 W black LEDs for 24 h. This indicated that the generation of ketyl radical and *α*-amino radical was not affected by the cobalt catalyst and ligand. The ketyl radical addition product and *α*-amino radical addition product was detected by HRMS. HRMS (ESI) of ketyl radical addition product: m/z calcd for $C_{17}H_{27}NO_3Na$ **[**M + Na]$^+$ 316.1883, found 316.1875. HRMS (ESI) of *α*-amino radical addition product: m/z calcd for $C_{17}H_{37}N_2O$ **[**M + H]$^+$ 285.2900, found 285.2896.



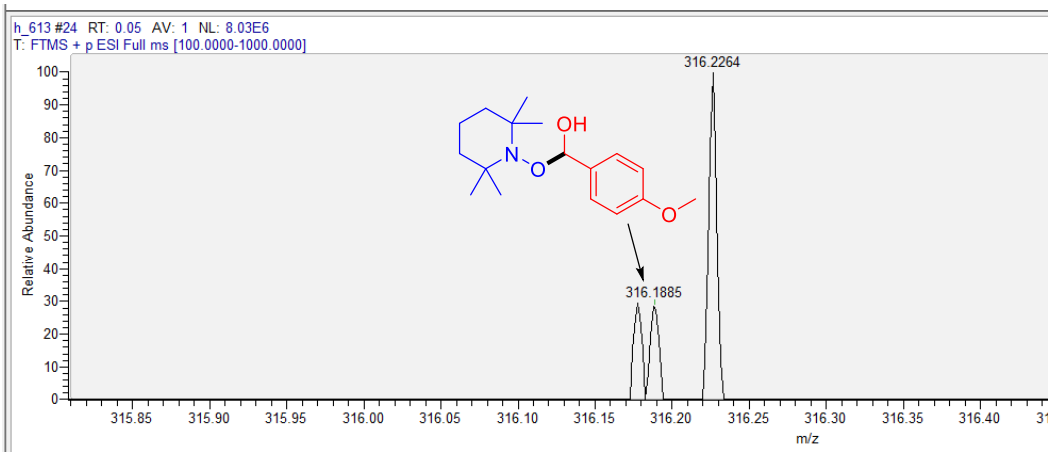
HRMS (ESI) of ketyl radical addition product



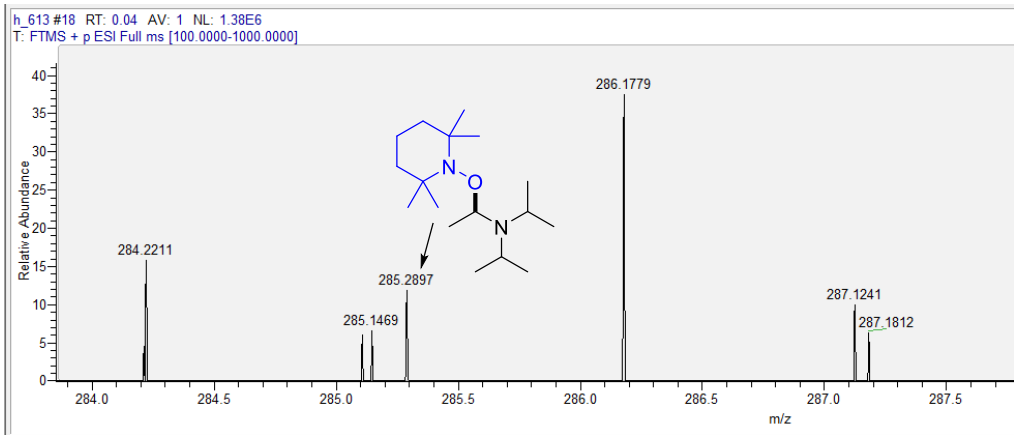
HRMS (ESI) of α-amino radical addition



In an argon-filled glovebox, a 10 mL flame-dried quartz tube with magnetic stirring was charged sequentially with *p*-anisaldehyde (0.2 mmol), *i*-Pr_2NEt (0.4 mmol, 2.0 eq.), TEMPO (1.5eq, 0.3 mmol) and *o*-xylene (1 mL). Then, the quartz tube was removed from glovebox. The mixture was stirred at room temperature under 10 W black LEDs for 24 h. This result suggest that irradiation of a mixture of *p*-anisaldehyde and *i*-Pr_2NEt leads to ketyl radical through a process of the traditional photoinduced sequential electron transfer and proton transfer. The ketyl radical addition product and α-amino radical addition product was detected by HRMS. HRMS (ESI) of ketyl radical addition product: m/z calcd for $C_{17}H_{27}NO_3Na$ **[**M + Na]$^+$ 316.1883, found 316.1885. HRMS (ESI) of α-amino radical addition product: m/z calcd for $C_{17}H_{37}N_2O$ **[**M + H]$^+$ 285.2900, found 285.2897.

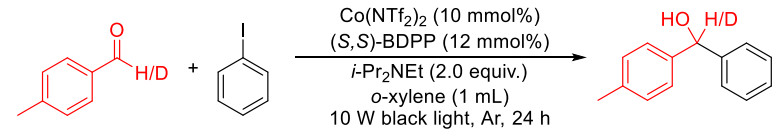


HRMS (ESI) of ketyl radical addition product



HRMS (ESI) of α-amino radical addition

5. Secondary isotope effect



1b/**1b-D** 0.2 mmol, H/D = 1:1 | **2b** 0.3 mmol | 71% yield, **3b**/**3b-D** = 49:51 | **3b**/**3b-D** KIE = 0.96

In an argon-filled glovebox, a 10 mL flame-dried quartz tube with magnetic stirring was charged sequentially with $Co(NTf_2)_2$ (0.02 mmol, 10 mol%), **L1** (0.024 mmol, 12 mol%) and *o*-xylene (1 mL). After stirring at room temperature for 2 h, substrates **1b** (0.1 mmol), **1b-D** (0.1 mmol), **2** (0.3 mmol) and *i*-Pr_2NEt (0.4 mmol, 2.0 eq.) were sequentially added into the quartz tube. Then, the quartz tube was removed from glovebox. The mixture was stirred at room temperature under 10 W black LEDs until the reaction was completed, as monitored by TLC analysis. The reaction mixture was then concentrated in vacuo. The crude product was purified by flash column

chromatography (silica gel, PE/EA) to afford the desired product.

6. UV-vis studies

6.1 UV-vis Absorption Spectrum of cobalt catalytic system

Curve a: in an argon-filled glovebox, a flame-dried glass tube with magnetic stirring was charged sequentially with $Co(NTf_2)_2$ (0.1 mmol, 62 mg) , (*S,S*)-BDPP (0.12 mmol, 53 mg) and MeCN (10 mL). After stirring at room temperature for 2 h, the glass tube was placed in the UV-Vis and a wavelength scan from 800 nm to 300 nm.

Curve b: in an argon-filled glovebox, a flame-dried glass tube with magnetic stirring was charged sequentially with $Co(NTf_2)_2$ (0.1 mmol, 62 mg) , (*S,S*)-BDPP (0.12 mmol, 53 mg) and MeCN (10 mL). After stirring at room temperature for 2 h, *i*-Pr_2NEt (2.0 mmol, 348 µL) was added into the glass tube. Then, this solution was allowed to stir for 8 h inside the glovebox. Finally, the glass tube was placed in the UV-Vis and a wavelength scan from 800 nm to 300 nm.

Curve c: in an argon-filled glovebox, a flame-dried glass tube with magnetic stirring was charged sequentially with $Co(NTf_2)_2$ (0.1 mmol, 62 mg) , (*S,S*)-BDPP (0.12 mmol, 53 mg) and MeCN (10 mL). After stirring at room temperature for 2 h, *i*-Pr_2NEt (2.0 mmol, 348 µL) was added into the glass tube. Then, this solution was allowed to stir for 8 h inside the glovebox. Afterward, *p*-anisaldehyde (0.1 mmol, 12 µL) was added into this solution. Finally, the glass tube was placed in the UV-Vis and a wavelength scan from 800 nm to 300 nm.

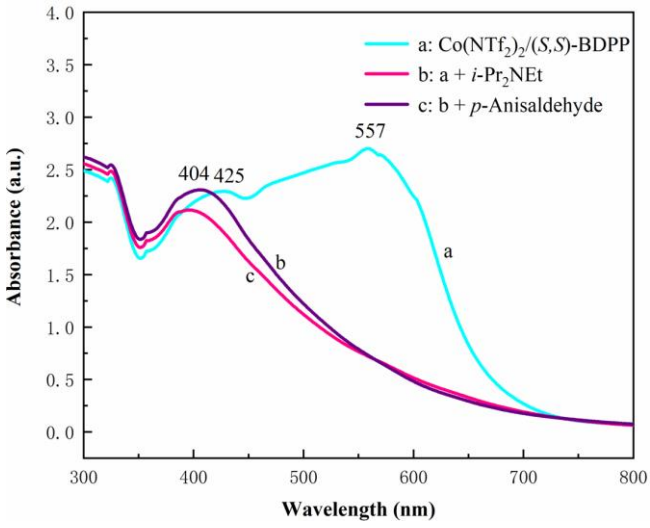


Figure S1. UV-vis absorption spectrum of a, b and c in MeCN (10^{-2} mmol/mL)

6.2 UV-vis Absorption Spectrum of *p*-Anisaldehyde and *i*-Pr_2NEt

In a glass tube, *p*-anisaldehyde (0.1 mmol, 12 μL), *i*-Pr_2NEt (0.1 mmol, 18 μL) and its mixture into EtOH (10 mL). The glass tube was placed in the UV-Vis and a wavelength scan from 380 nm to 340 nm.

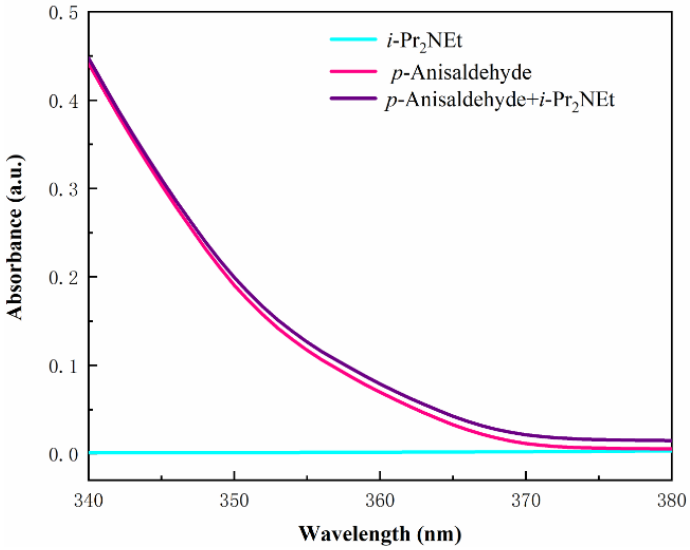
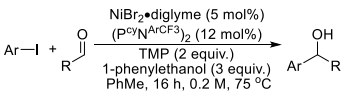
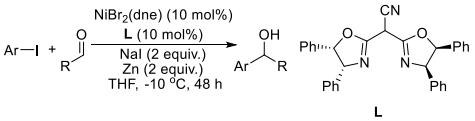
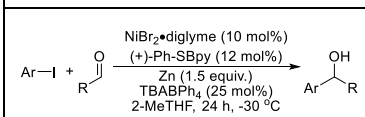
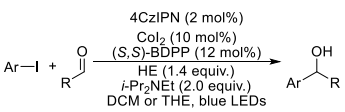
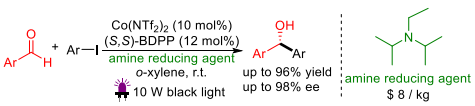


Figure S2. UV-vis absorption spectrum of *p*-Anisaldehyde, *i*-Pr_2NEt in EtOH (10^{-2} mmol/mL)

7. Comparison with previous work

Table S9. Comparison of this work with previous work

	Reaction	enantioselectivity	reductant	additives	reference
Previous work		No	1-phenylethanol	TMP	*J. Am. Chem. Soc.*, 2021, **143**, 14646−14656.
		Yes	Zn	NaI	*Angew. Chem. Int. Ed.*, 2022, **61**, e202201370.
		Yes	Zn	$TBABPh_4$	*Angew. Chem. Int. Ed.*, 2022, **61**, e202117843.
		Yes	HE	*i*-Pr_2NEt	*J. Am. Chem. Soc.*, 2022, **144**, 8347−8354.
This Work		Yes	*i*-Pr_2NEt	No	

8. References

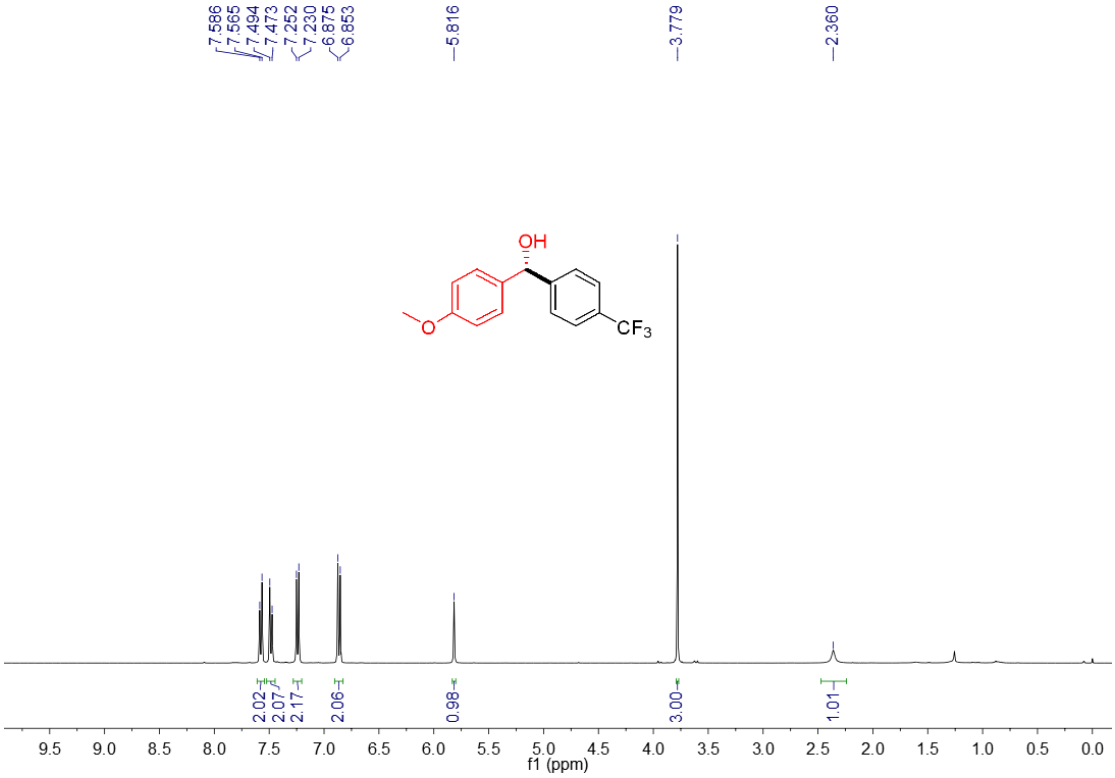
(1) W. L. F. Armarego and C. C. L. Chai, Purification of Laboratory Chemicals, 5th ed., Butterworth-Heinemann, **2003**.

(2) J. Chen, S. Yang, Z. Chen, C. Song and Y. Ma, *Tetrahedron: Asymmetry,* 2015, **26**, 288−385.

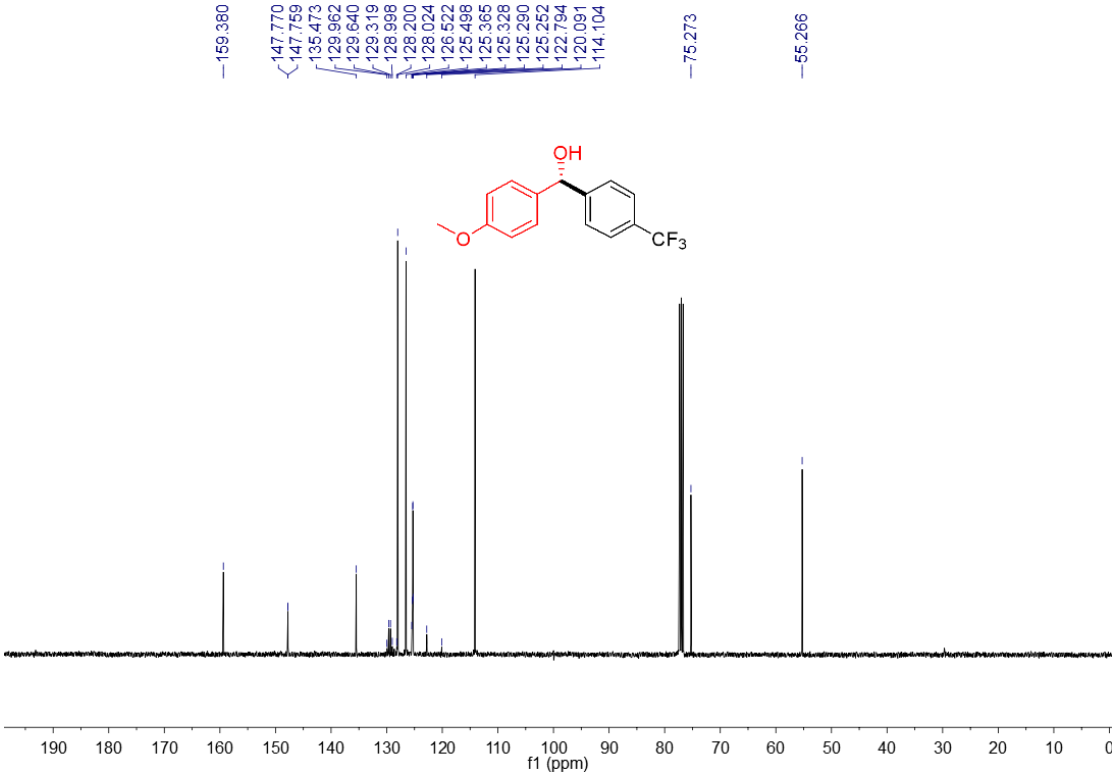
(3) X. Jiang, H. Jiang, Q. Yang, Y. Cheng, L.-Q. Lu, J. Tunge and W.-J. Xiao, *J. Am. Chem. Soc*., 2022, **144**, 8347−8354.

9. Copies of NMR Spectra for the Products

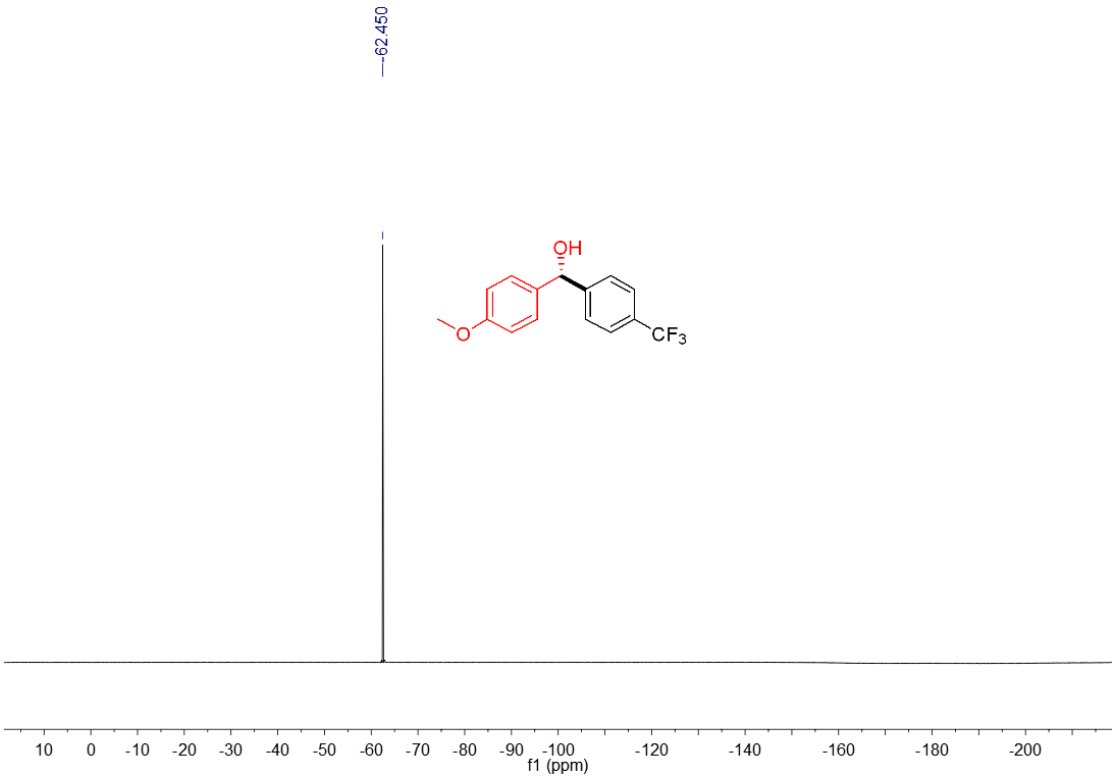
^{1}H NMR spectrum of compound **3a** (400 MHz) in $CDCl_3$



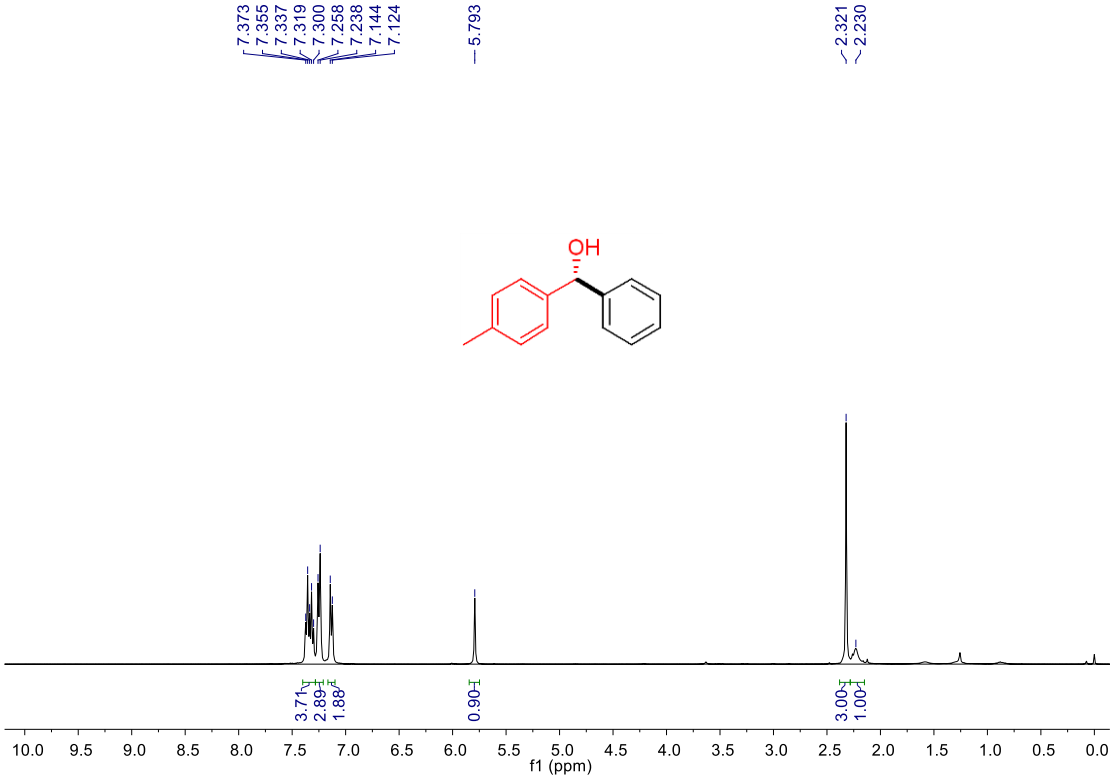
^{13}C NMR spectrum of compound **3a** (100 MHz) in $CDCl_3$



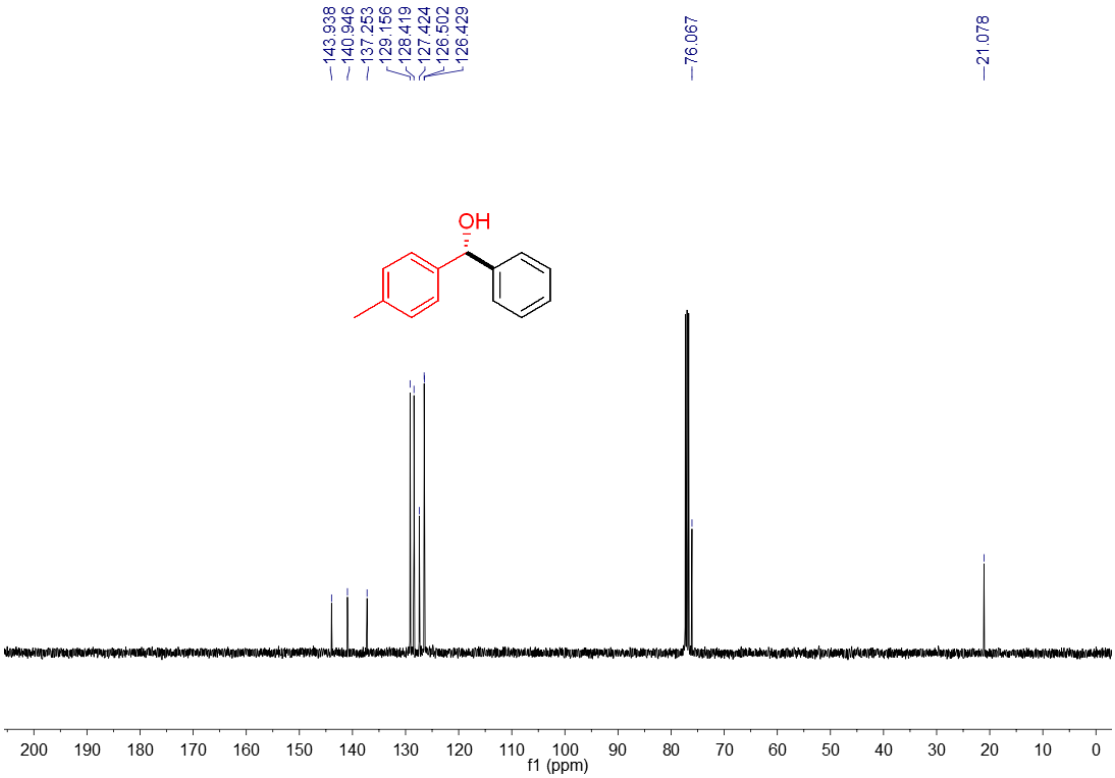
^{19}F NMR spectrum of compound **3a** (376 MHz) in $CDCl_3$



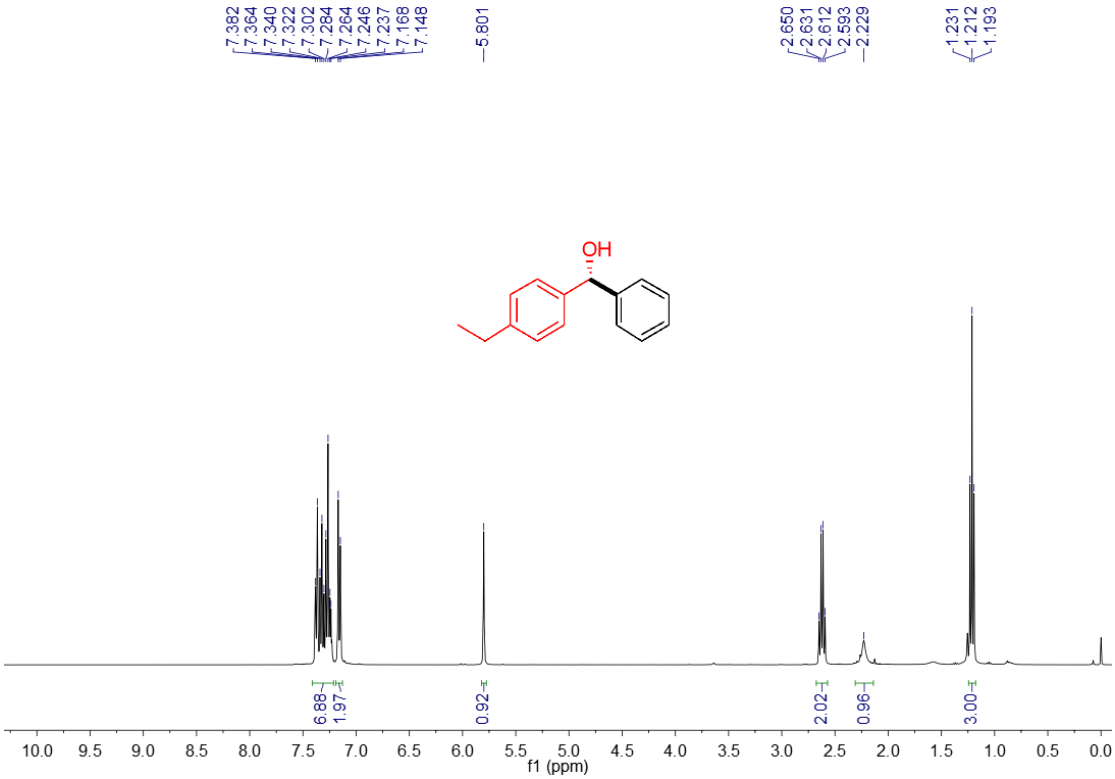
^{1}H NMR spectrum of compound **3b** (400 MHz) in $CDCl_3$



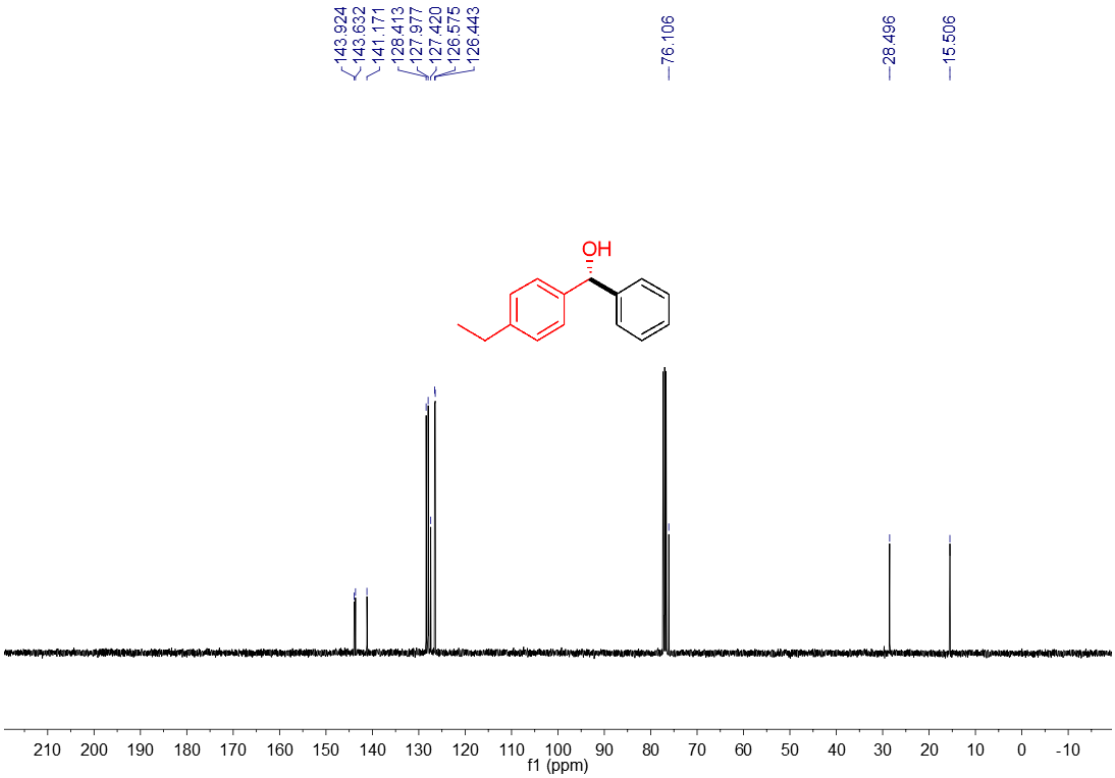
^{13}C NMR spectrum of compound **3b** (100 MHz) in $CDCl_3$



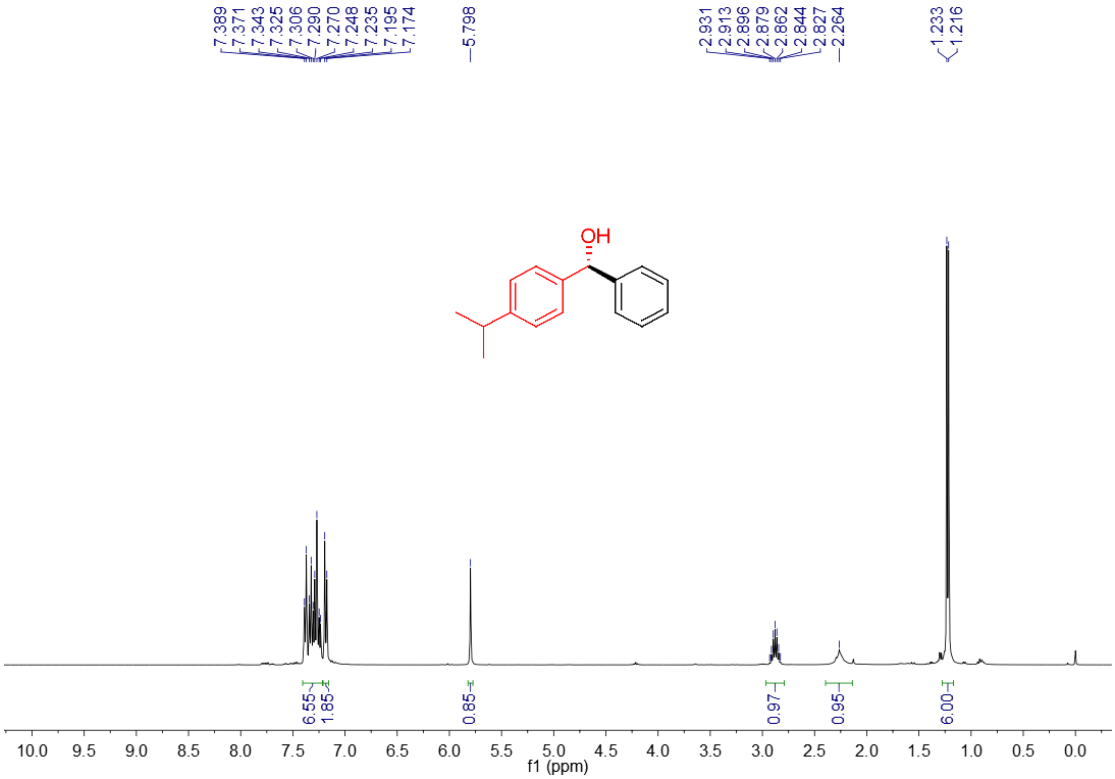
^{1}H NMR spectrum of compound **3c** (400 MHz) in $CDCl_3$



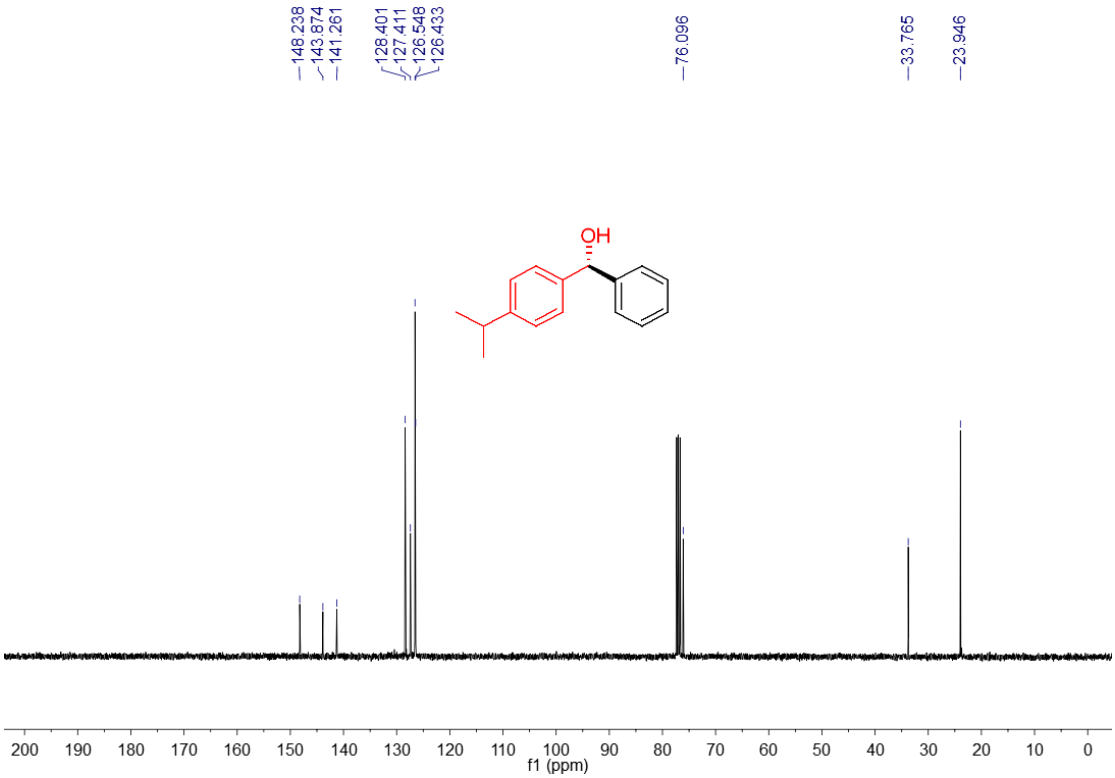
^{13}C NMR spectrum of compound **3c** (100 MHz) in $CDCl_3$



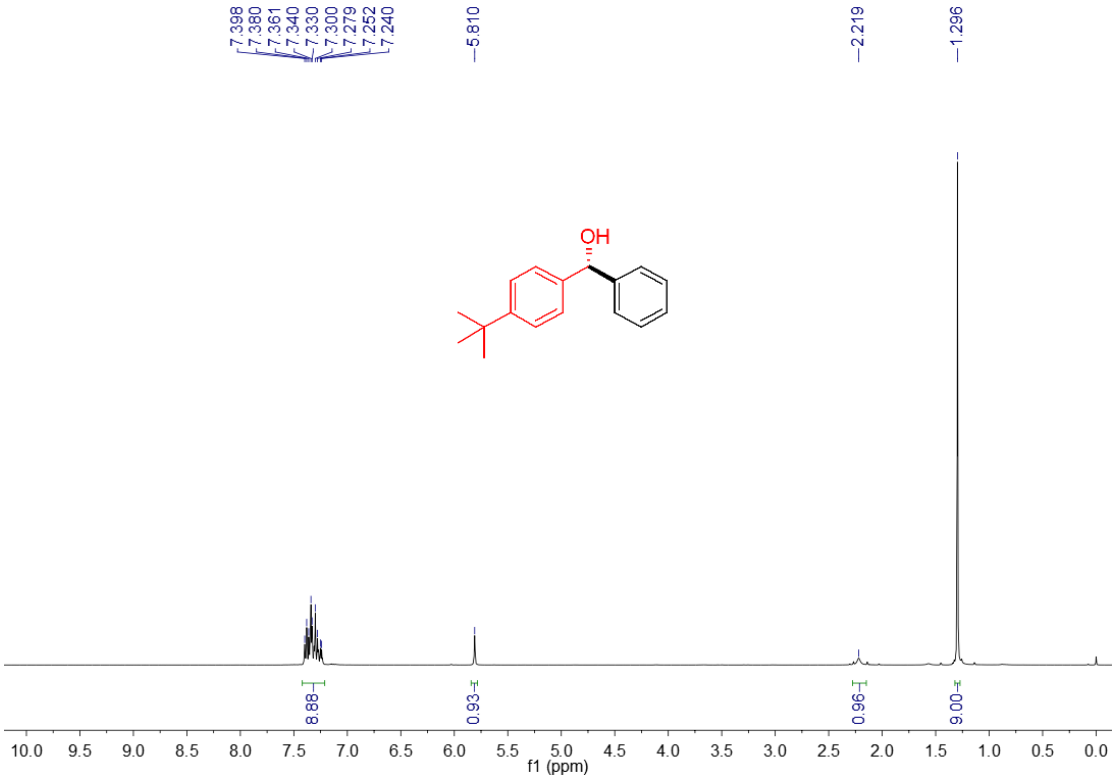
^{1}H NMR spectrum of compound **3d** (400 MHz) in $CDCl_3$



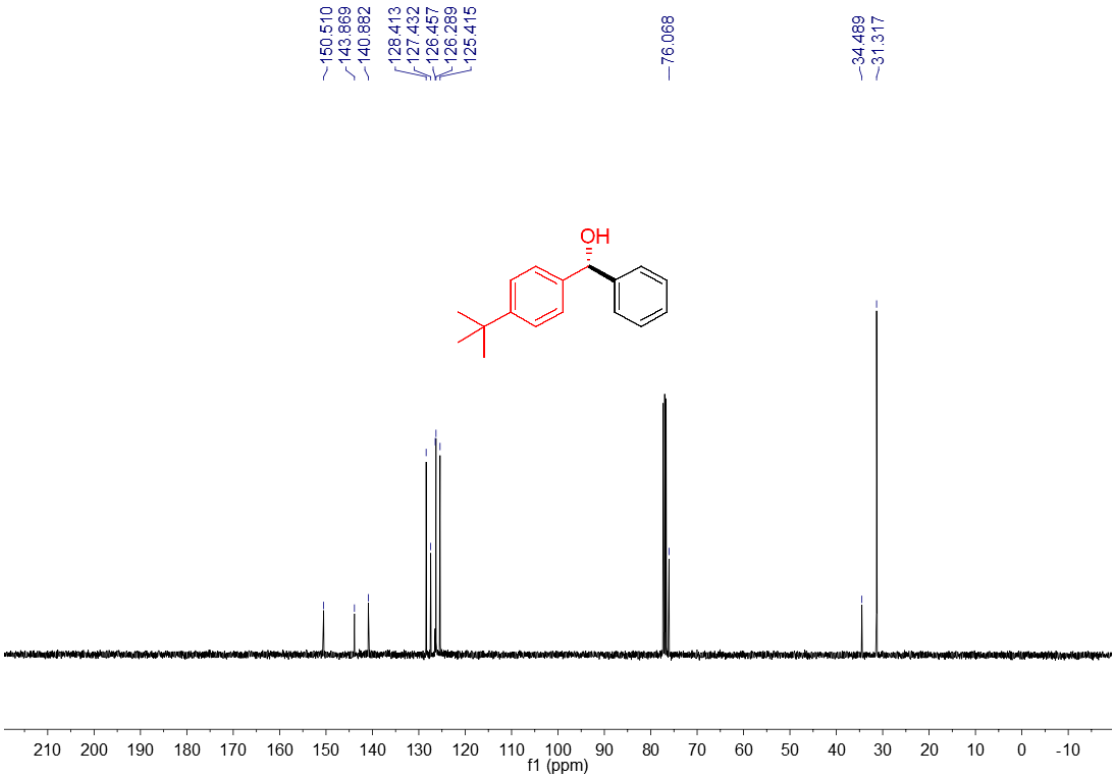
^{13}C NMR spectrum of compound **3d** (100 MHz) in $CDCl_3$



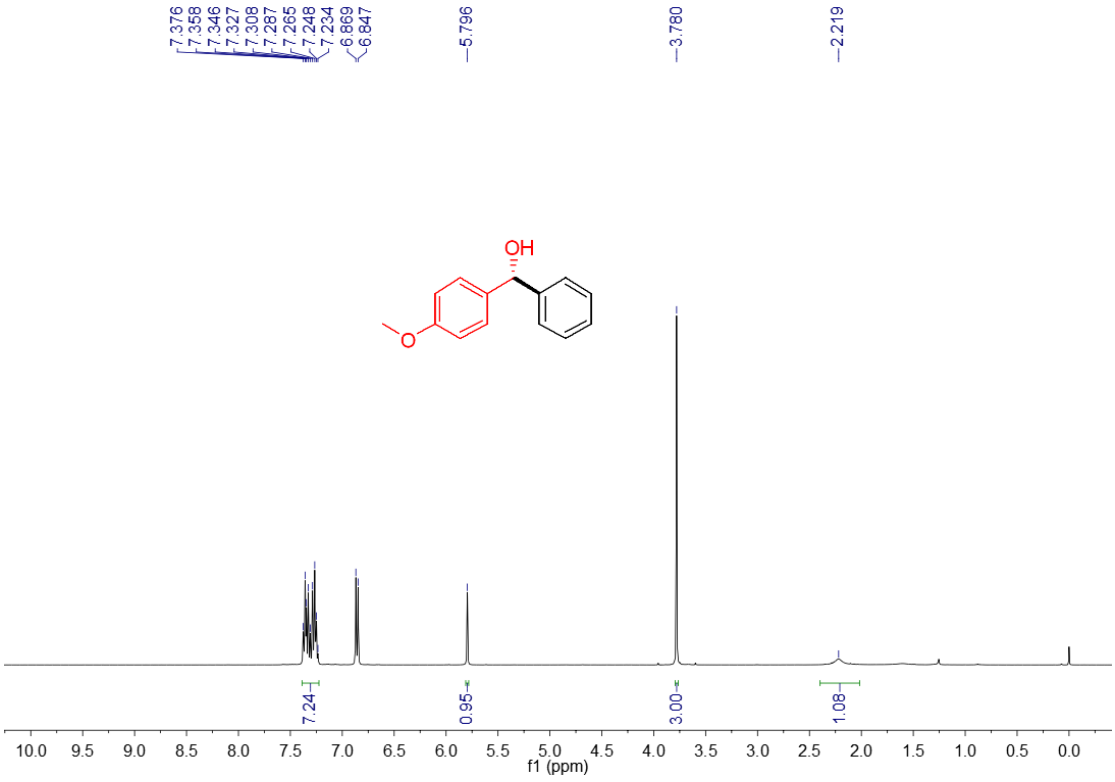
^{1}H NMR spectrum of compound **3e** (400 MHz) in $CDCl_3$



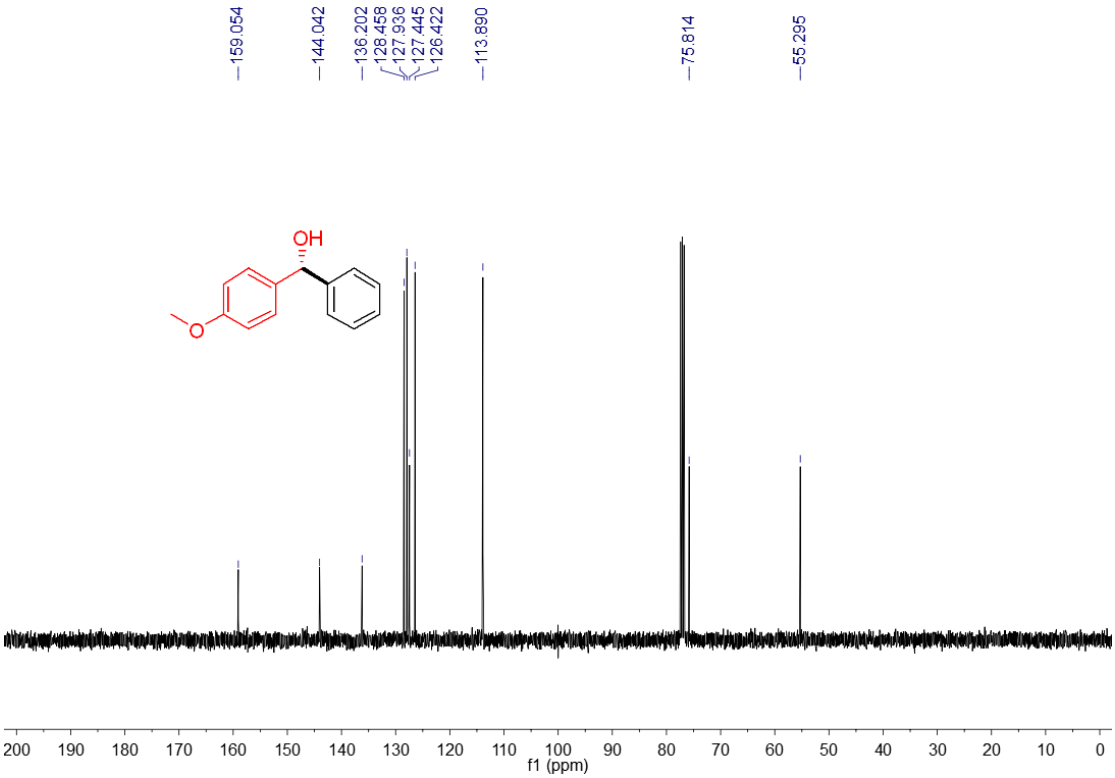
^{13}C NMR spectrum of compound **3e** (100 MHz) in $CDCl_3$



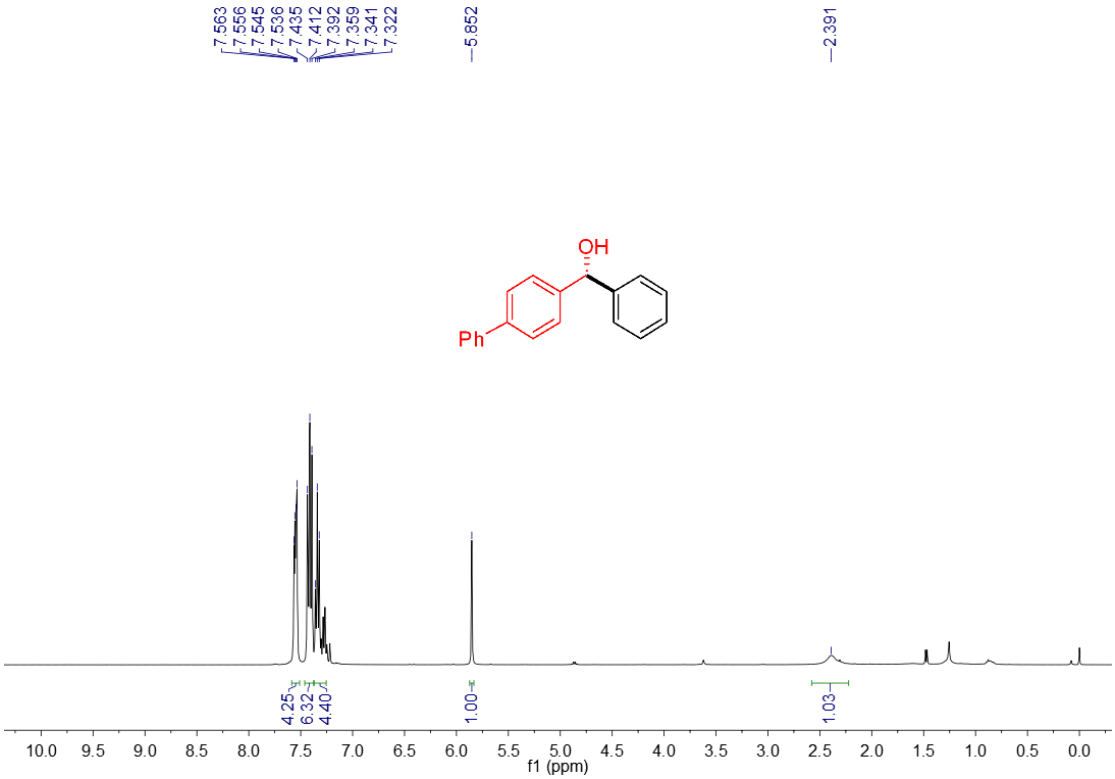
^{1}H NMR spectrum of compound **3f** (400 MHz) in $CDCl_3$



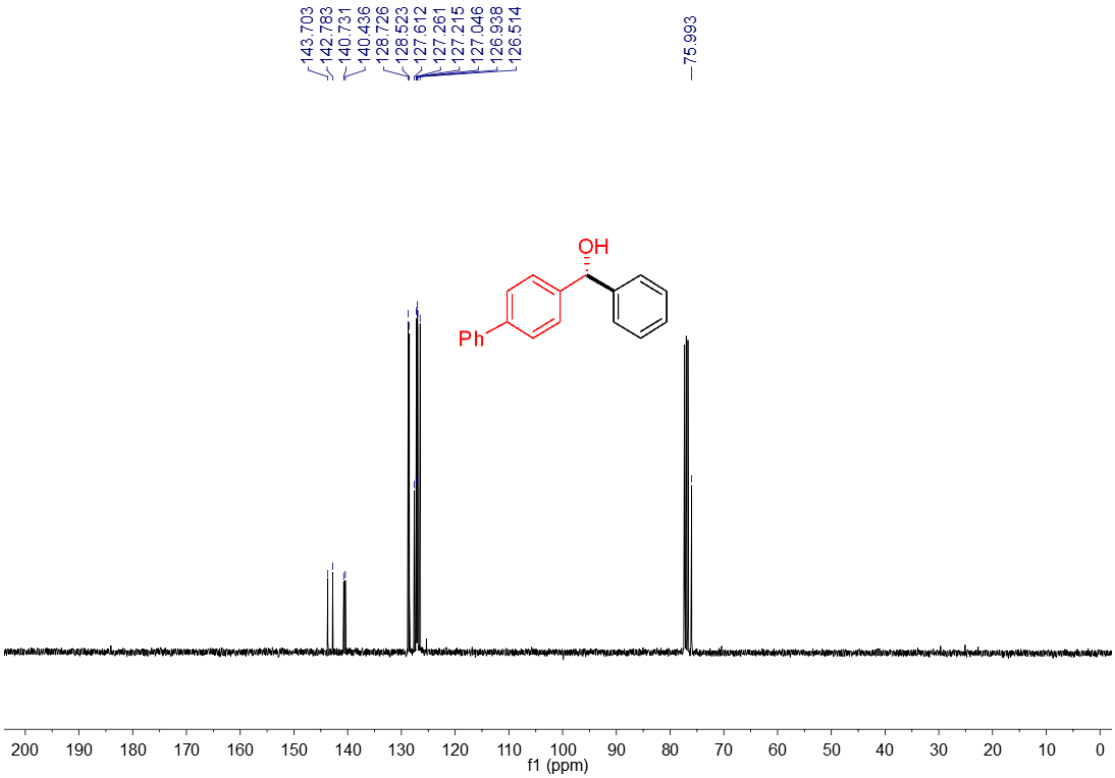
^{13}C NMR spectrum of compound **3f** (100 MHz) in $CDCl_3$



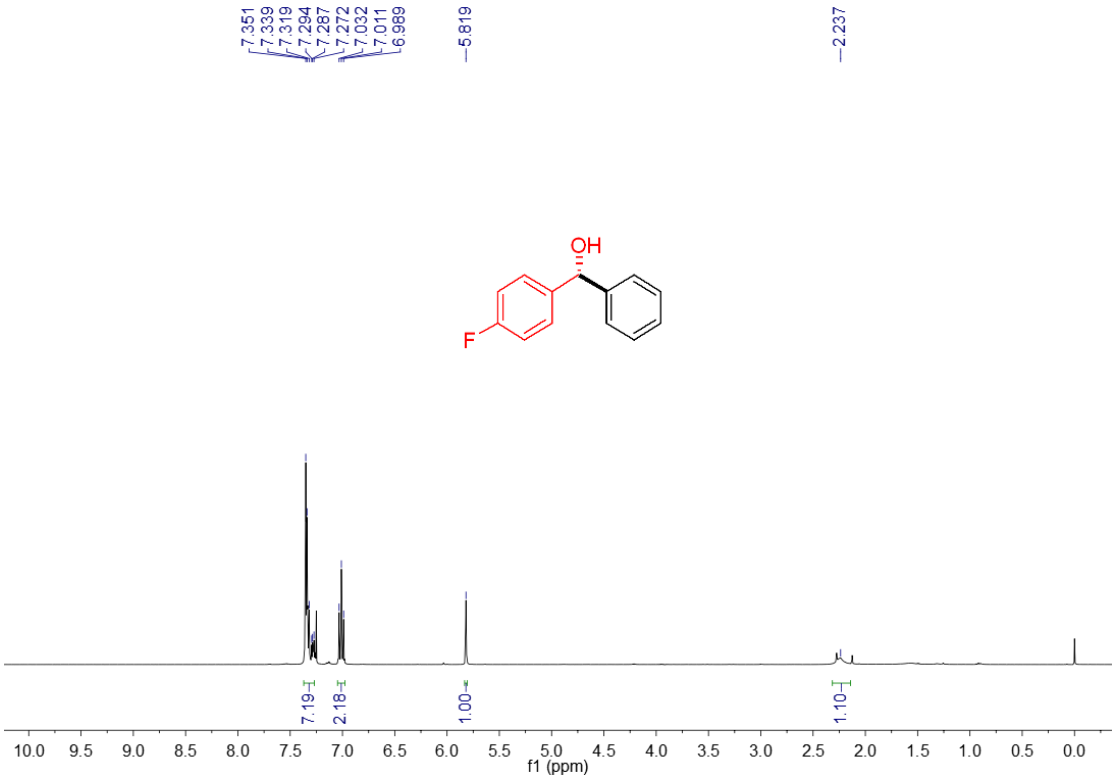
^{1}H NMR spectrum of compound **3g** (400 MHz) in $CDCl_3$



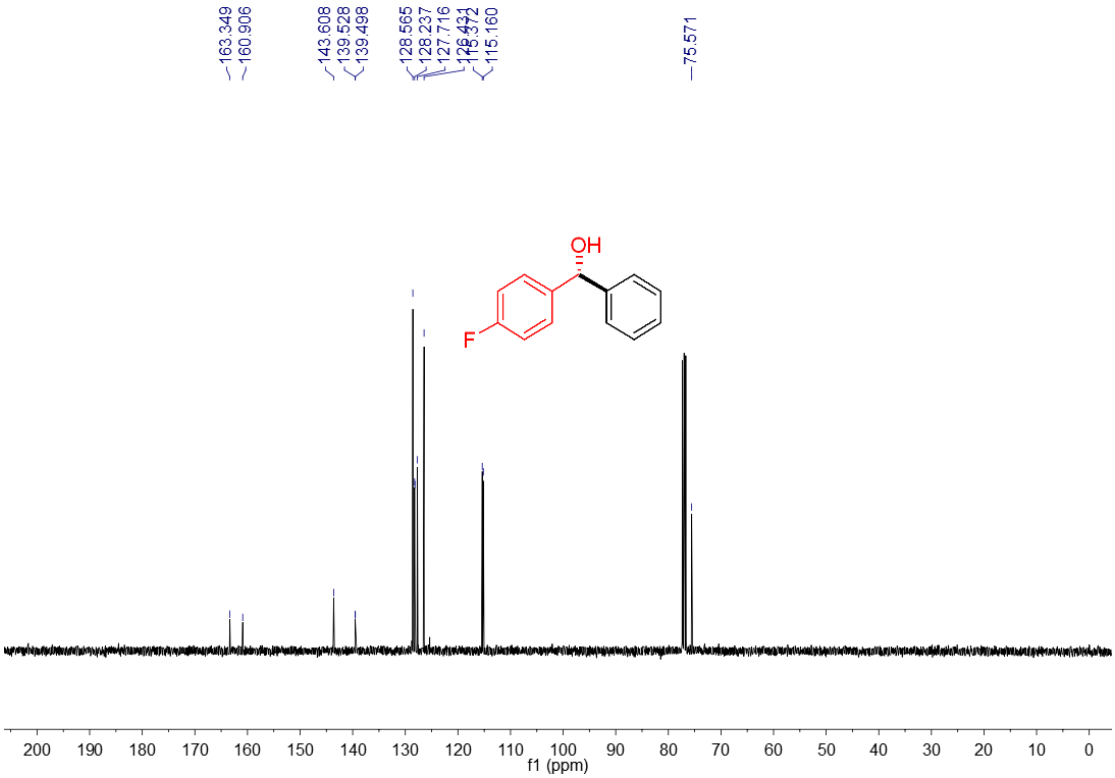
^{13}C NMR spectrum of compound **3g** (100 MHz) in $CDCl_3$



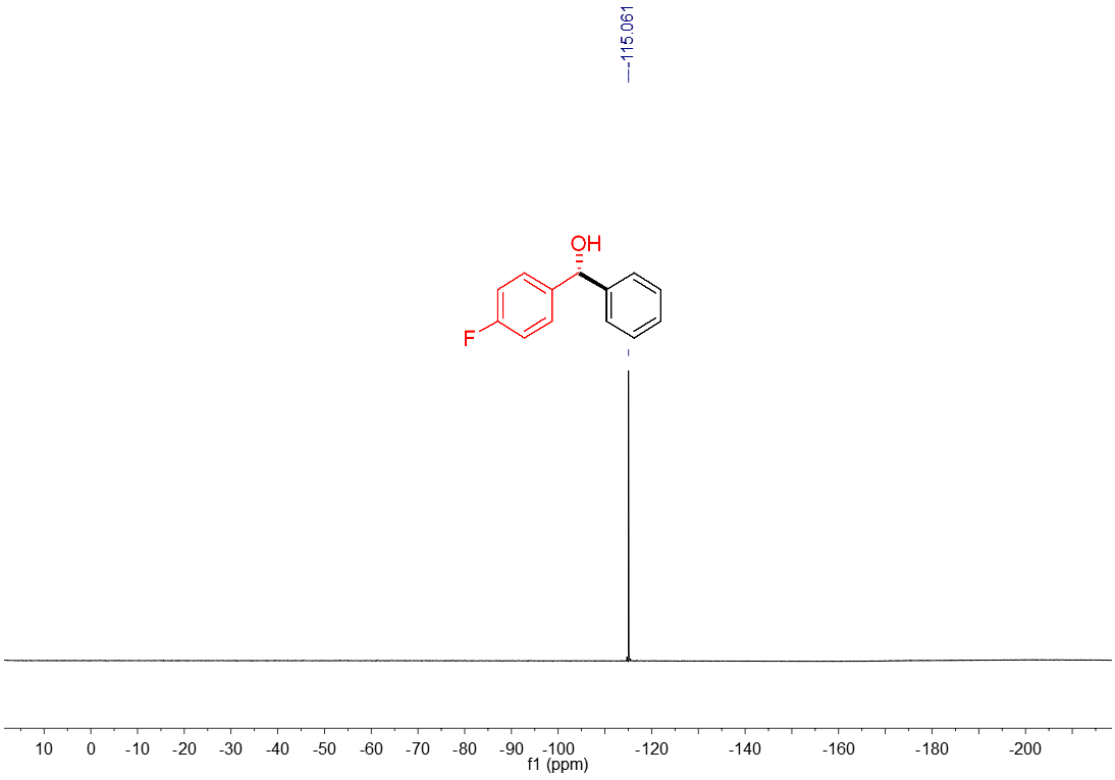
^{1}H NMR spectrum of compound **3h** (400 MHz) in $CDCl_3$



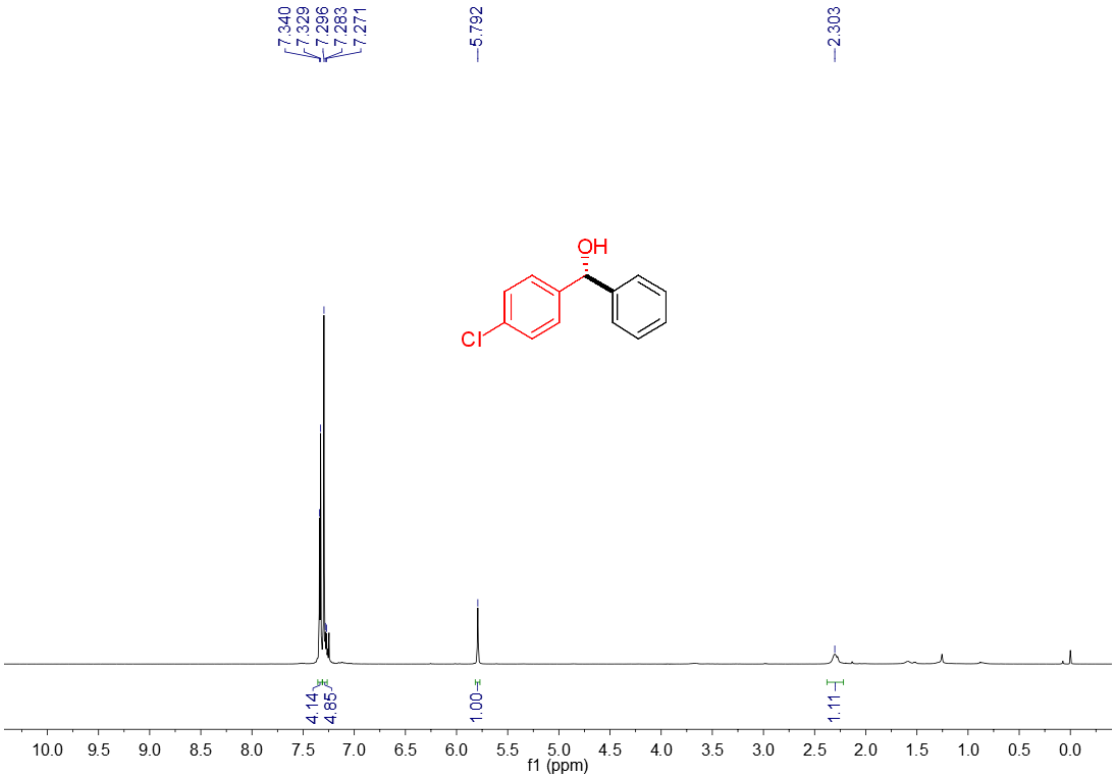
^{13}C NMR spectrum of compound **3h** (100 MHz) in $CDCl_3$



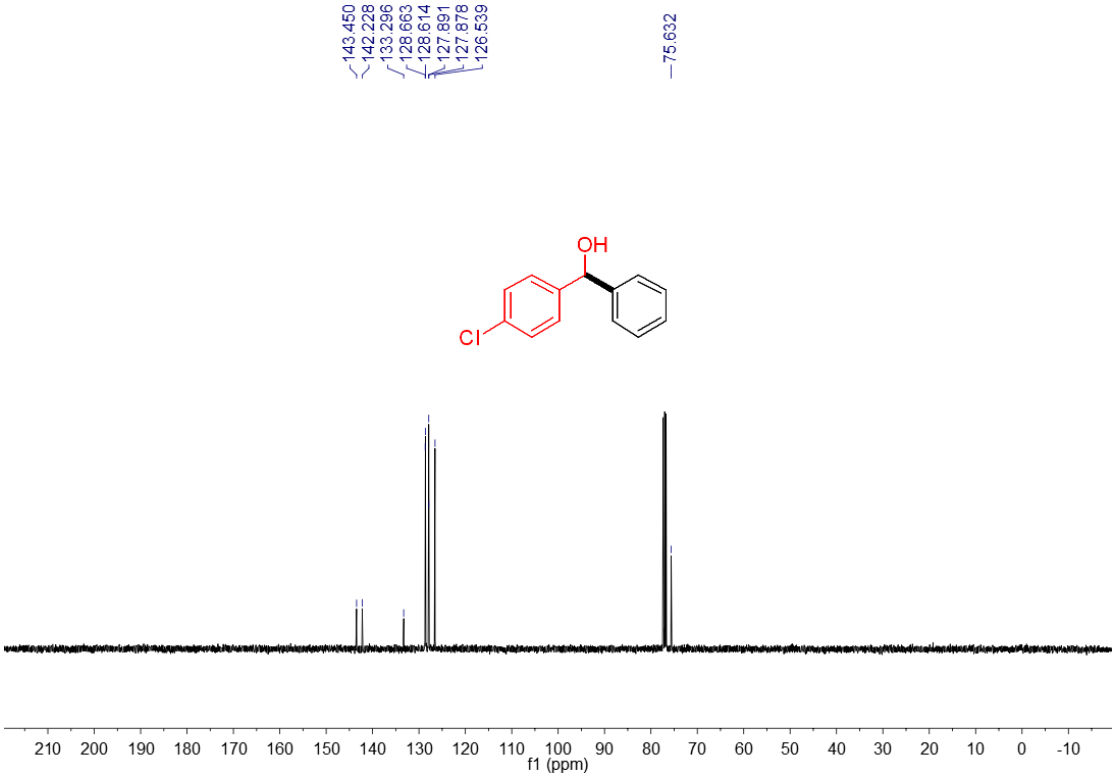
^{19}F NMR spectrum of compound **3h** (376 MHz) in $CDCl_3$



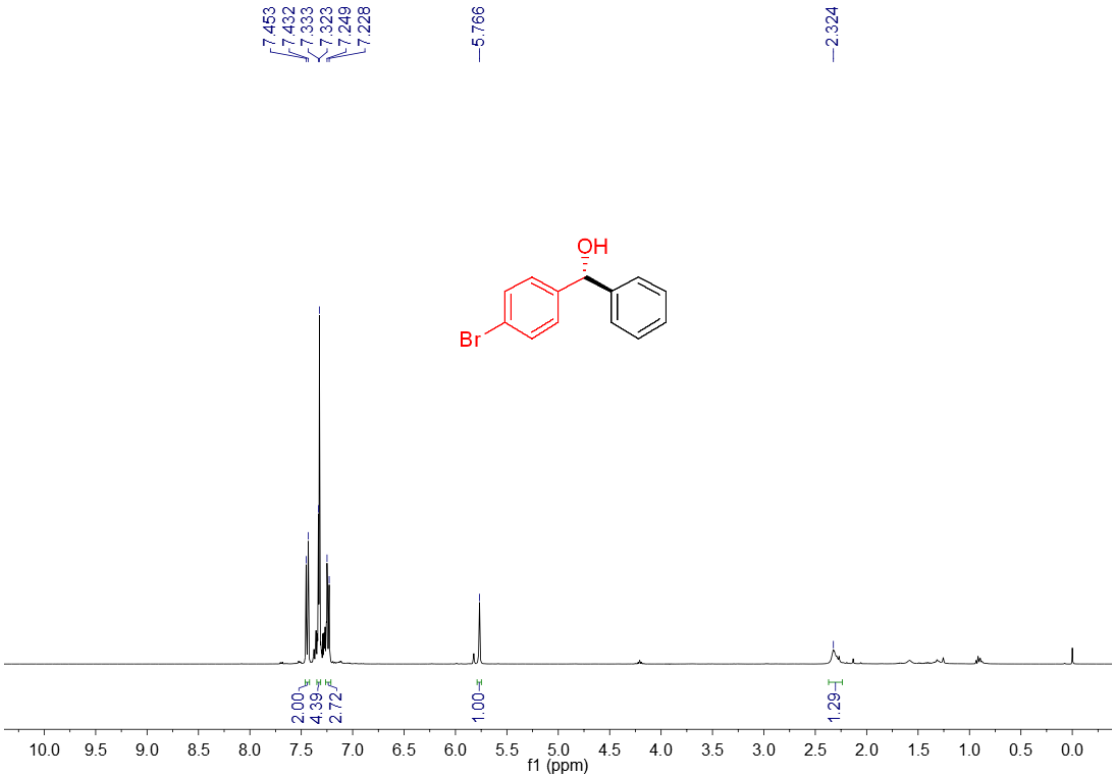
^{1}H NMR spectrum of compound **3i** (400 MHz) in $CDCl_3$



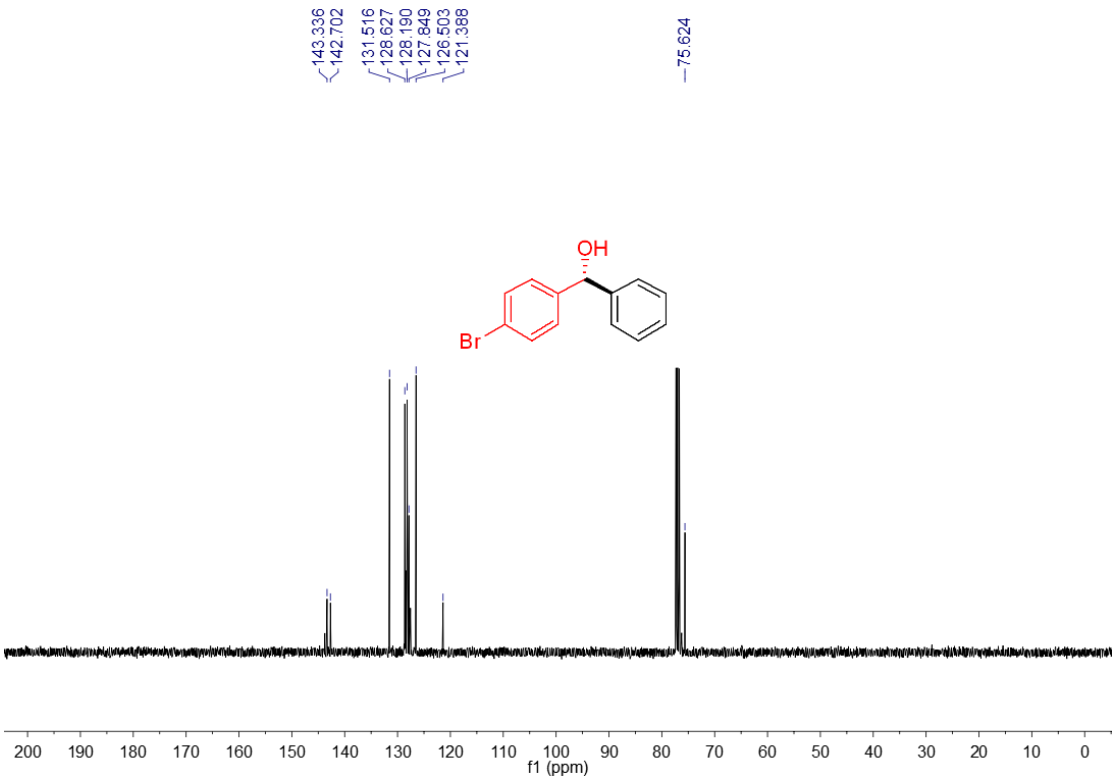
^{13}C NMR spectrum of compound **3i** (100 MHz) in $CDCl_3$



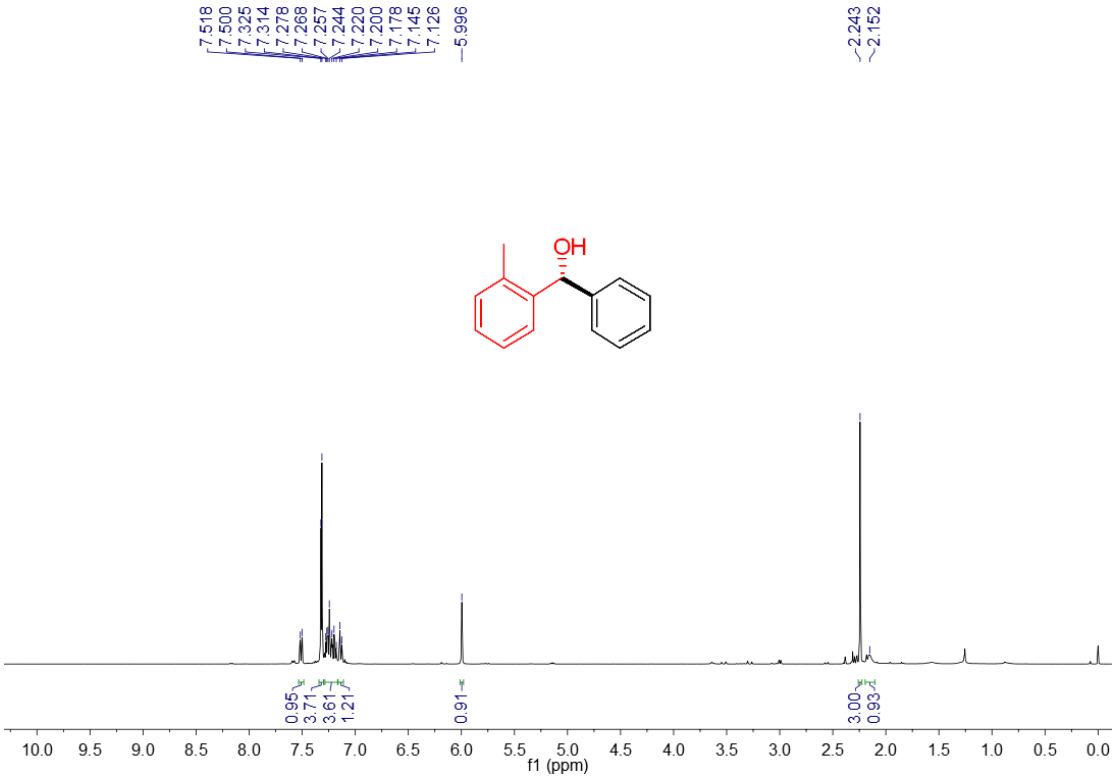
^{1}H NMR spectrum of compound **3j** (400 MHz) in $CDCl_3$



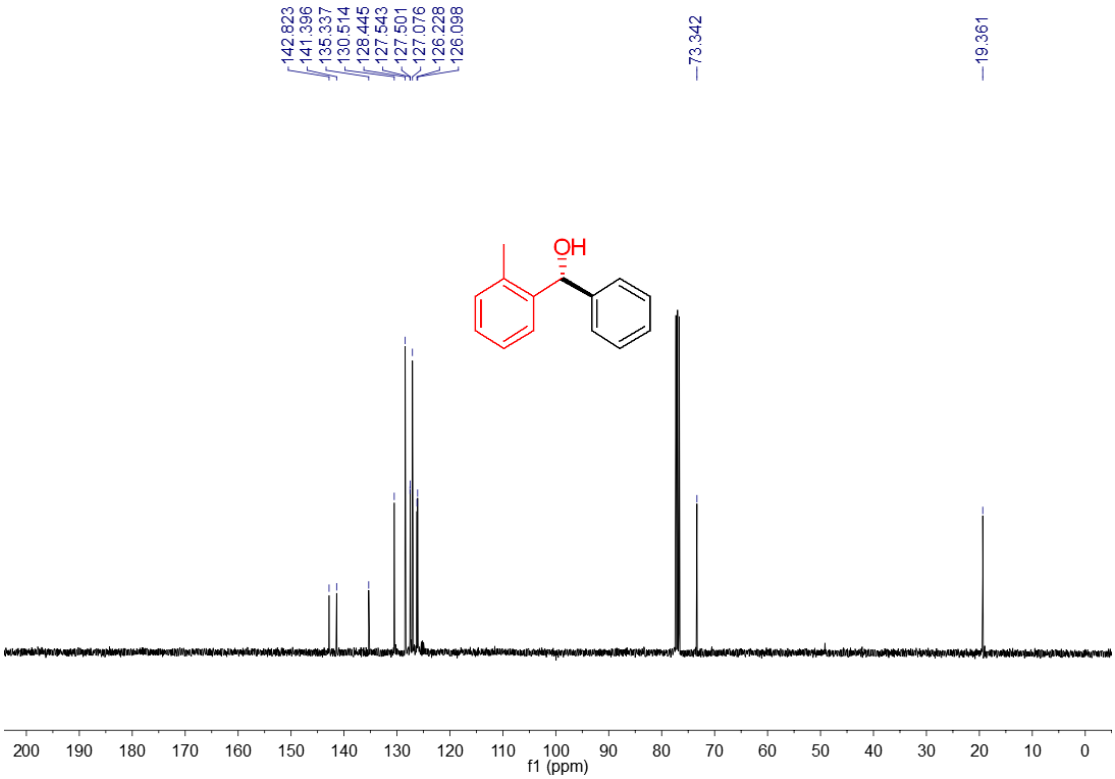
^{13}C NMR spectrum of compound **3j** (100 MHz) in $CDCl_3$



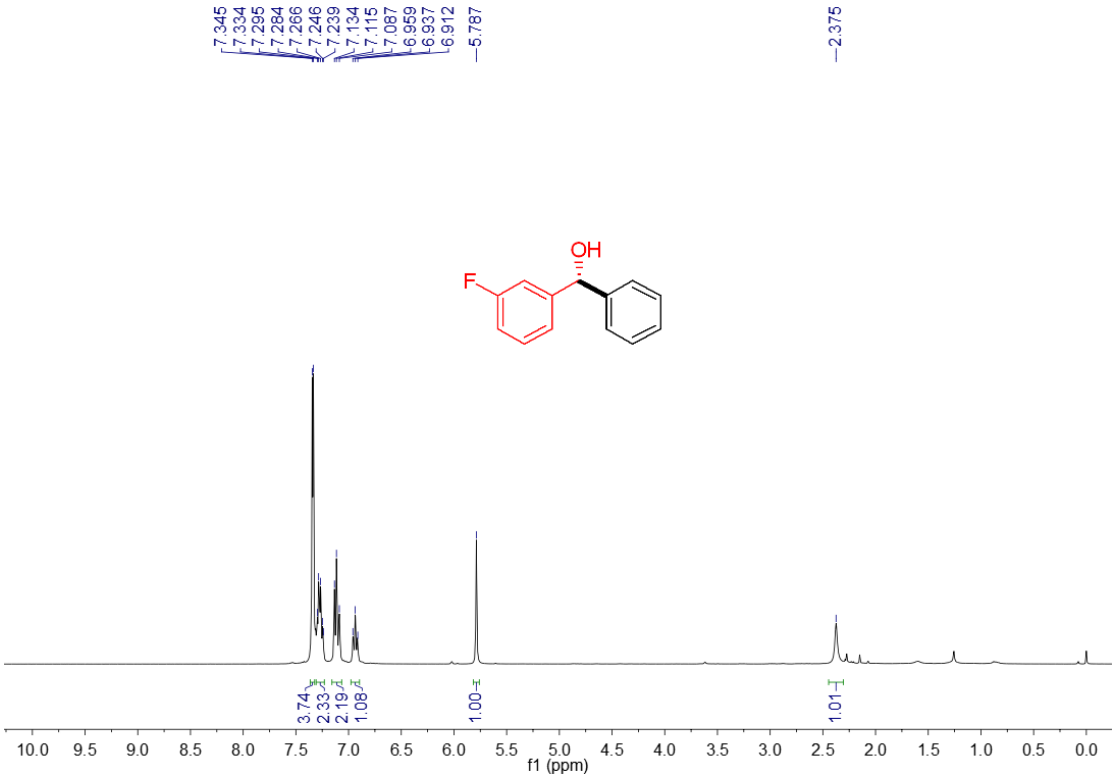
^{1}H NMR spectrum of compound **3k** (400 MHz) in $CDCl_3$



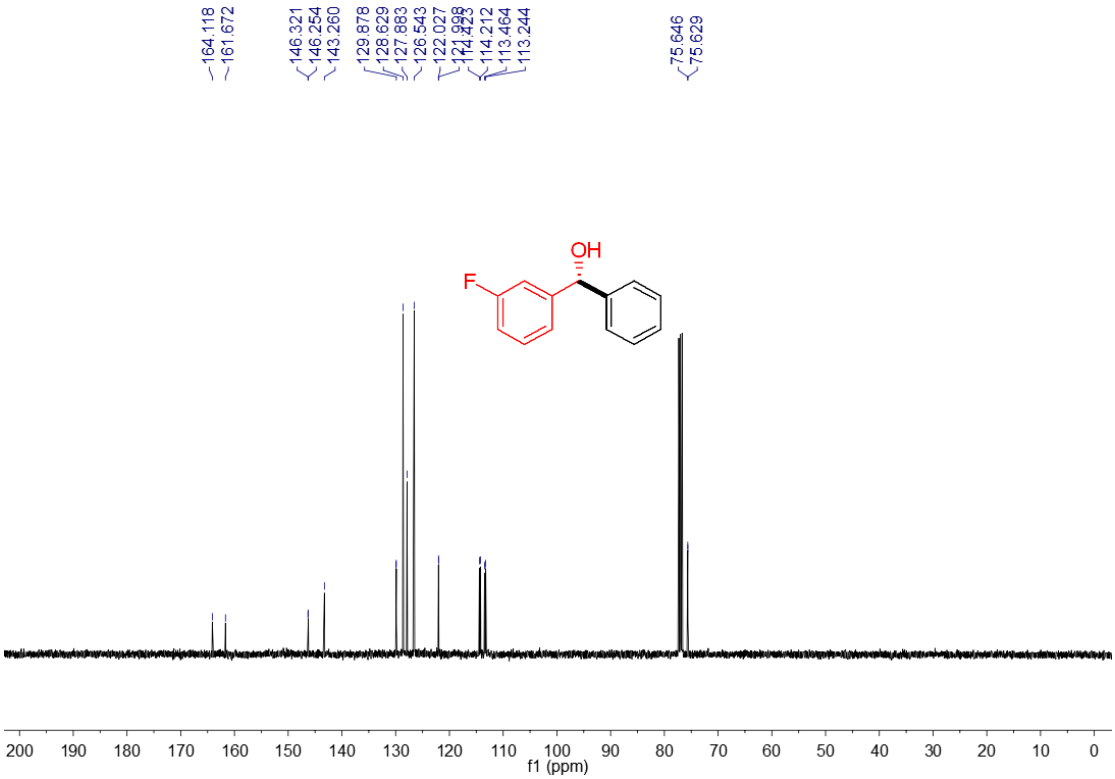
^{13}C NMR spectrum of compound **3k** (100 MHz) in $CDCl_3$



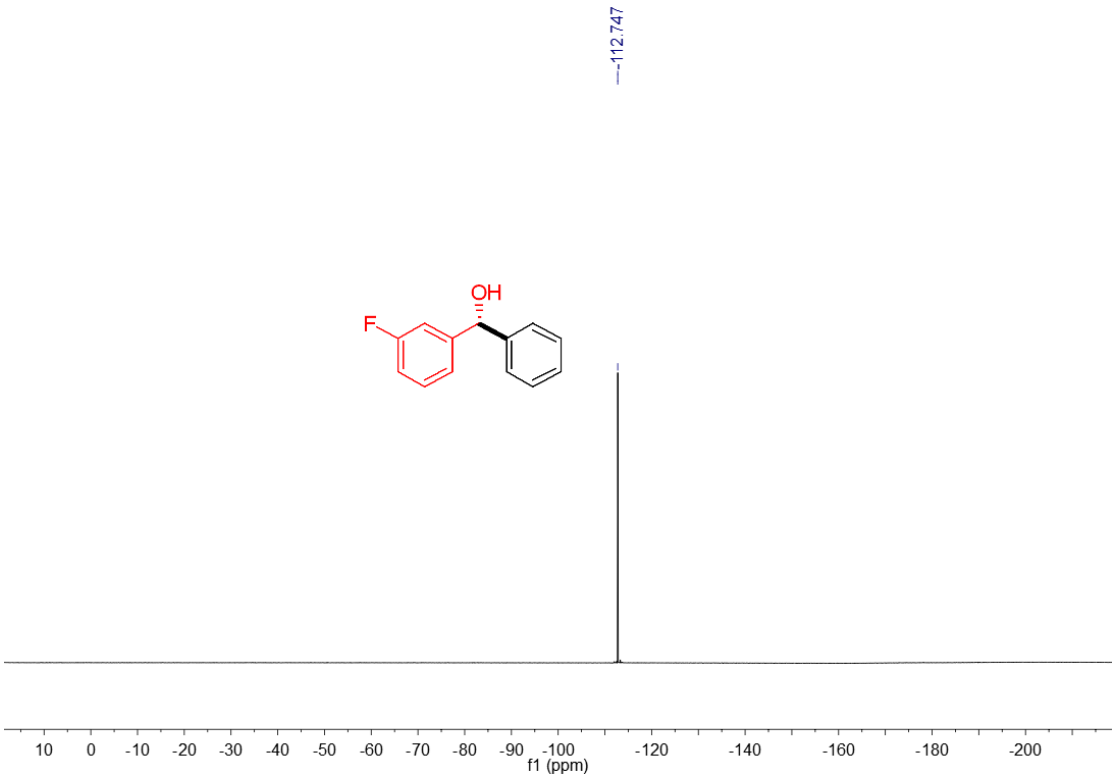
^{1}H NMR spectrum of compound **3l** (400 MHz) in $CDCl_3$



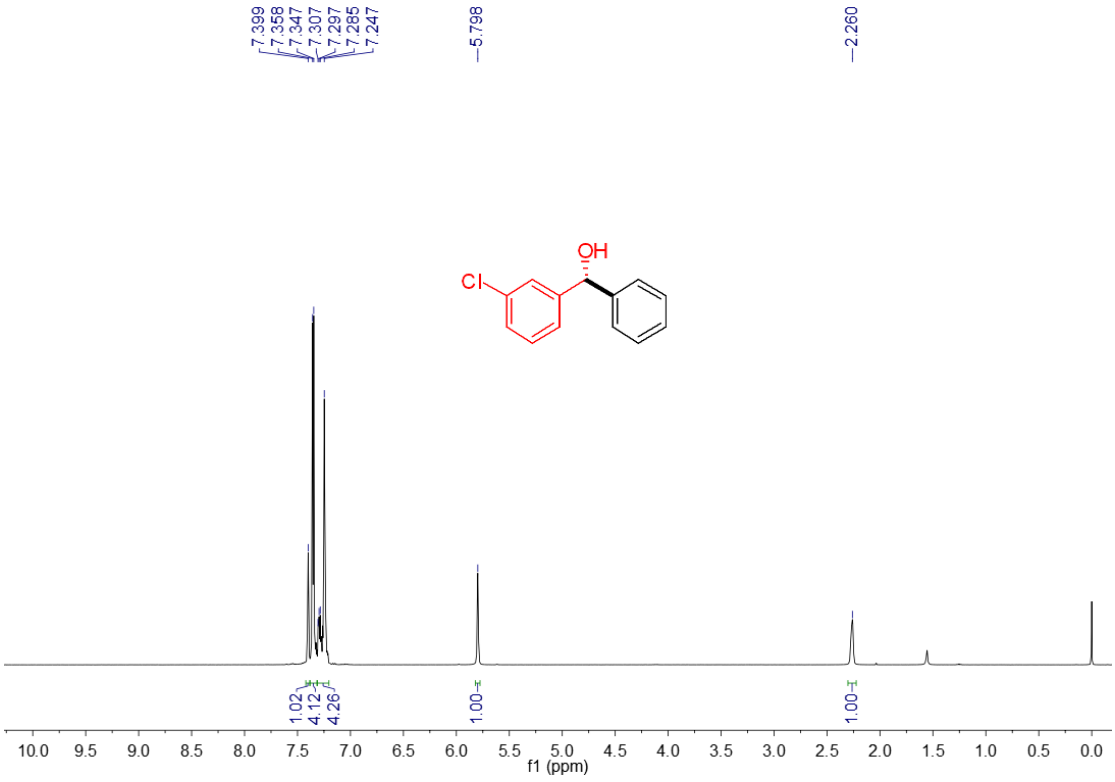
^{13}C NMR spectrum of compound **3l** (100 MHz) in $CDCl_3$



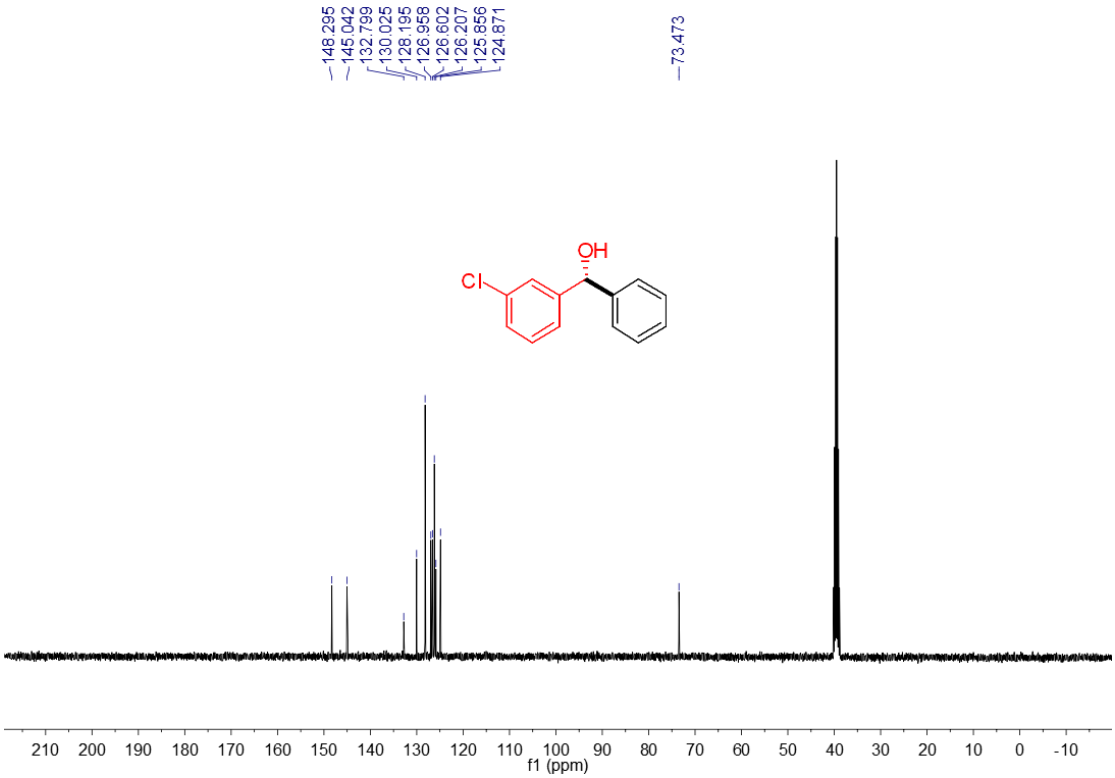
^{19}F NMR spectrum of compound **3l** (376 MHz) in $CDCl_3$



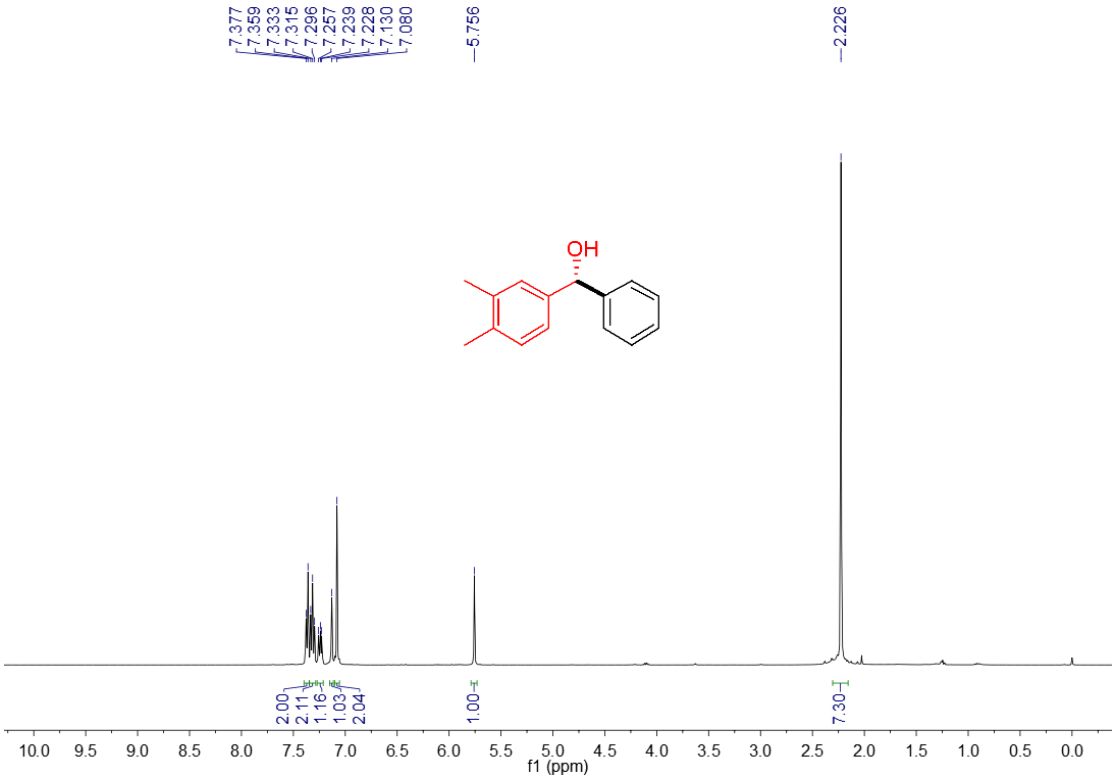
^{1}H NMR spectrum of compound **3m** (400 MHz) in $CDCl_3$



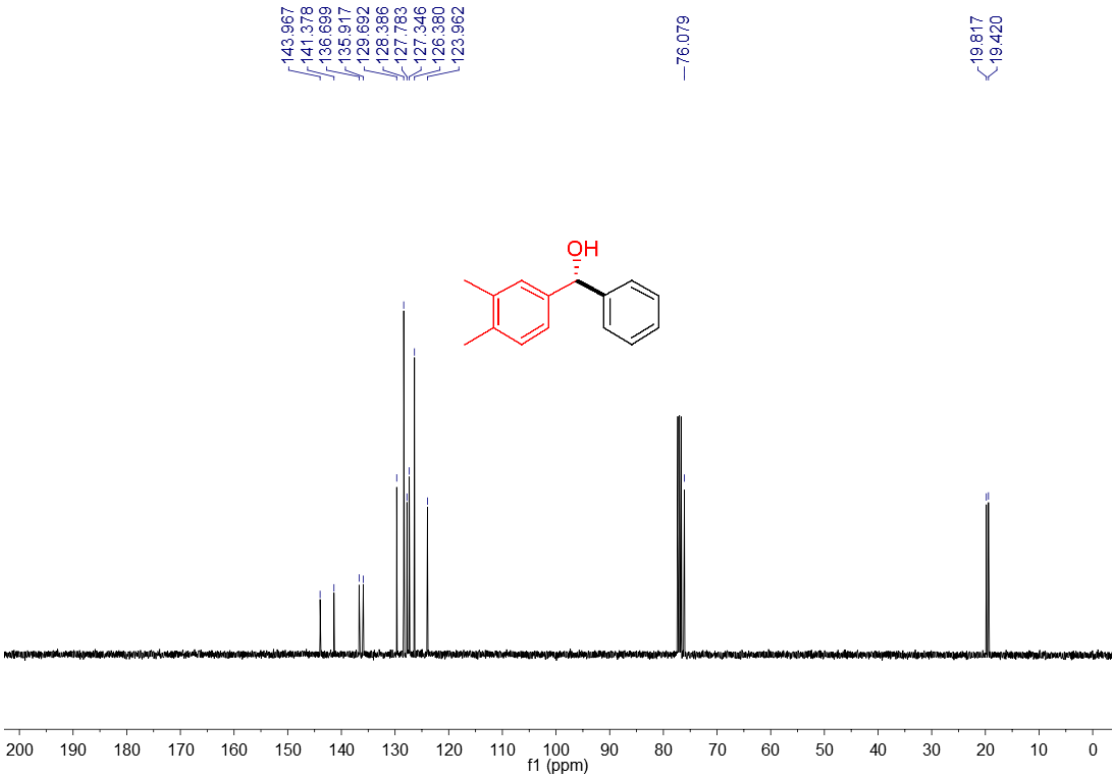
^{13}C NMR spectrum of compound **3m** (100 MHz) in DMSO-d_6



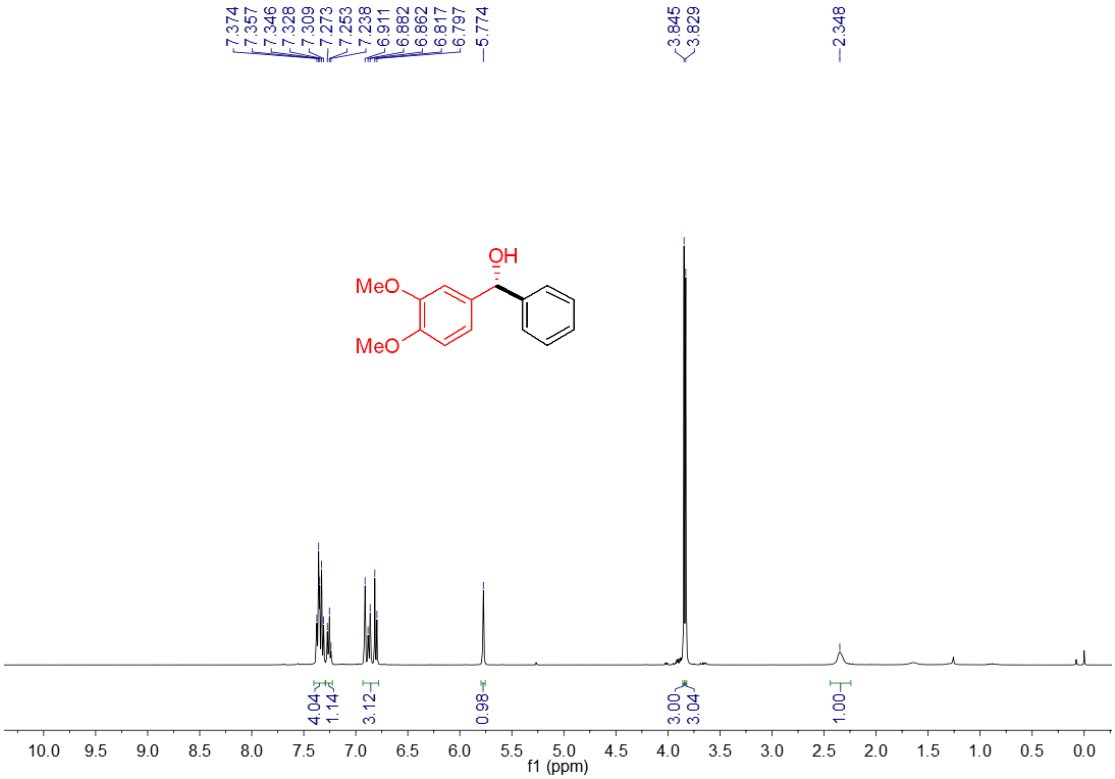
^{1}H NMR spectrum of compound **3n** (400 MHz) in $CDCl_3$



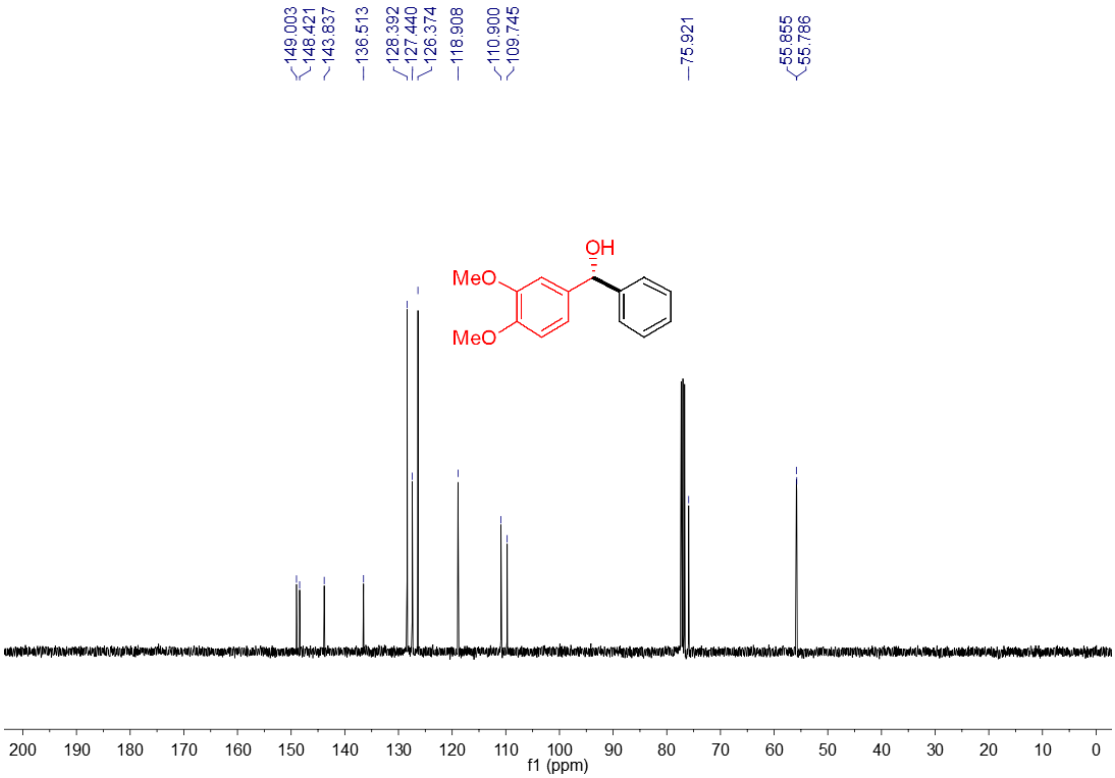
^{13}C NMR spectrum of compound **3n** (100 MHz) in $CDCl_3$



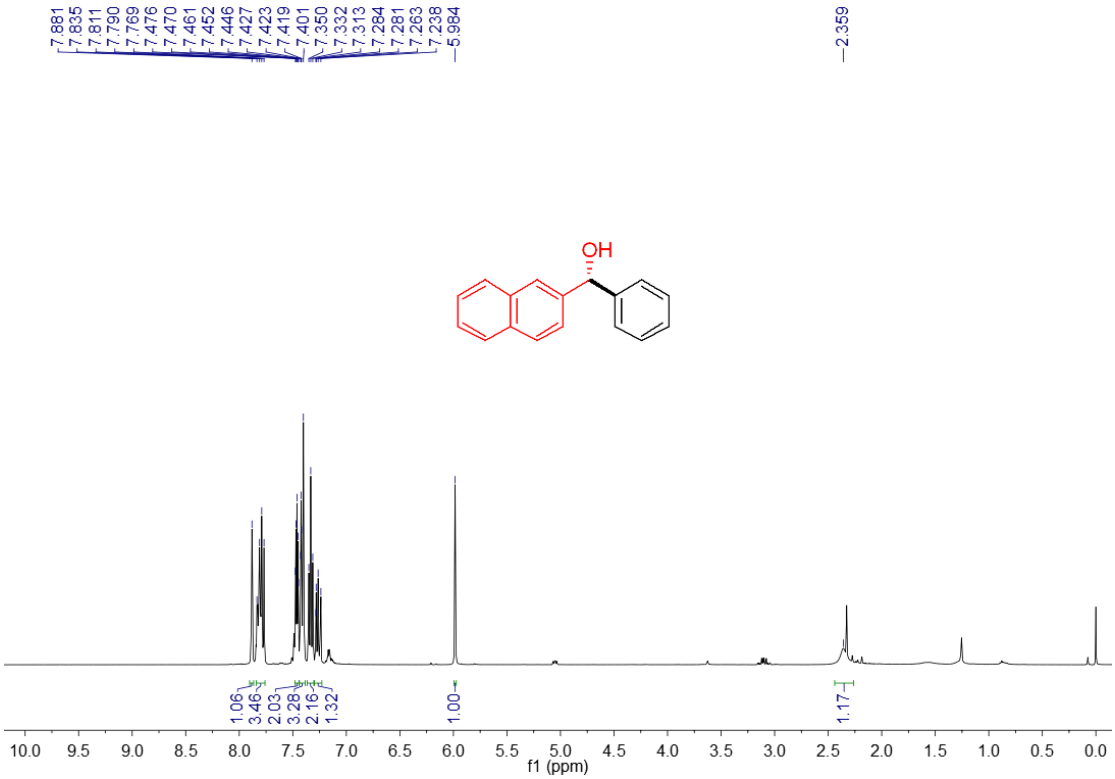
^{1}H NMR spectrum of compound **3o** (400 MHz) in $CDCl_3$



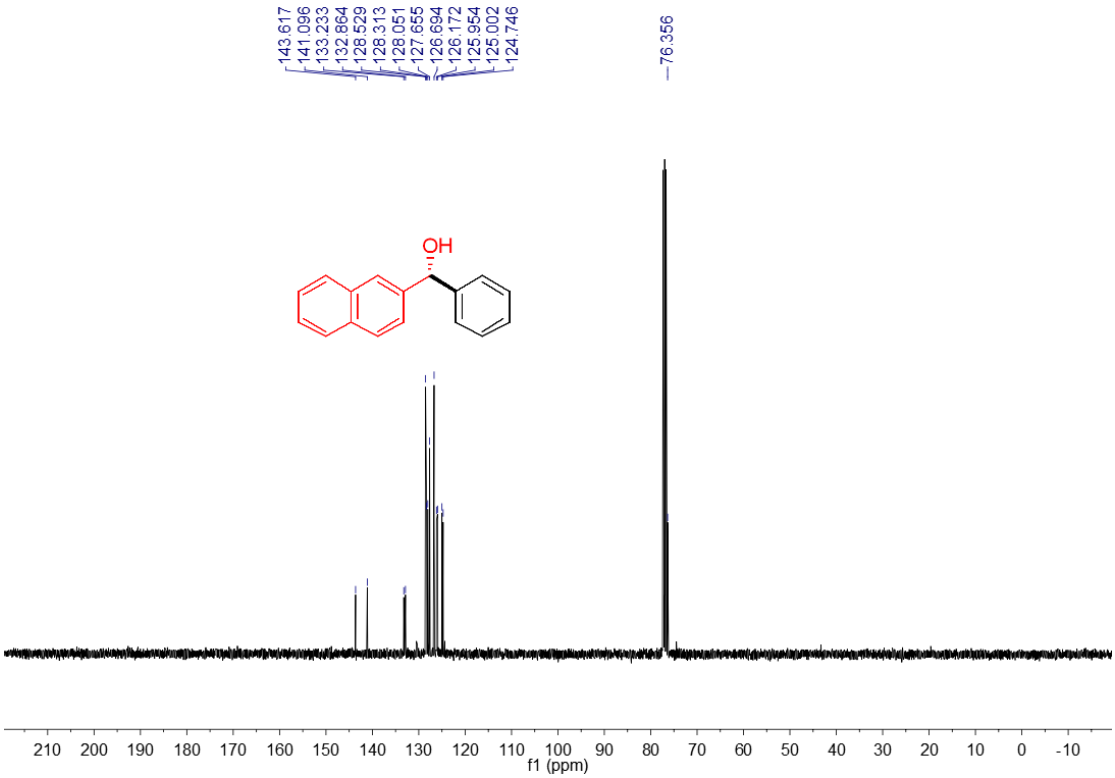
^{13}C NMR spectrum of compound **3o** (100 MHz) in $CDCl_3$



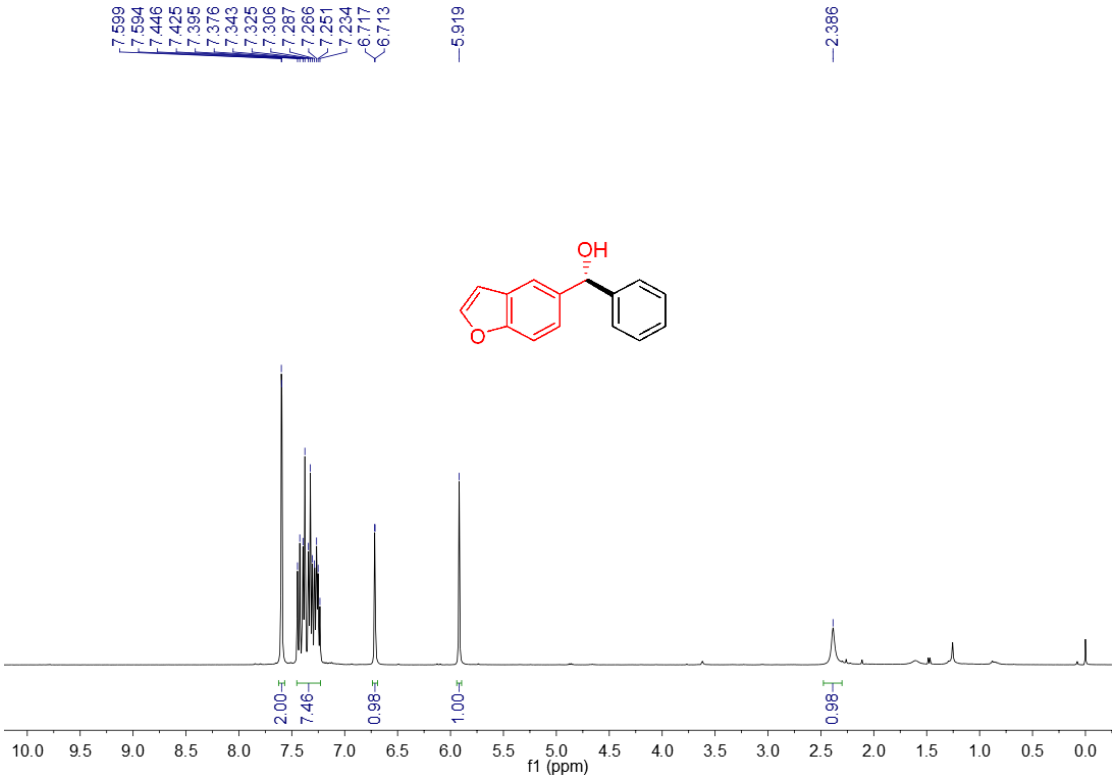
^{1}H NMR spectrum of compound **3p** (400 MHz) in $CDCl_3$



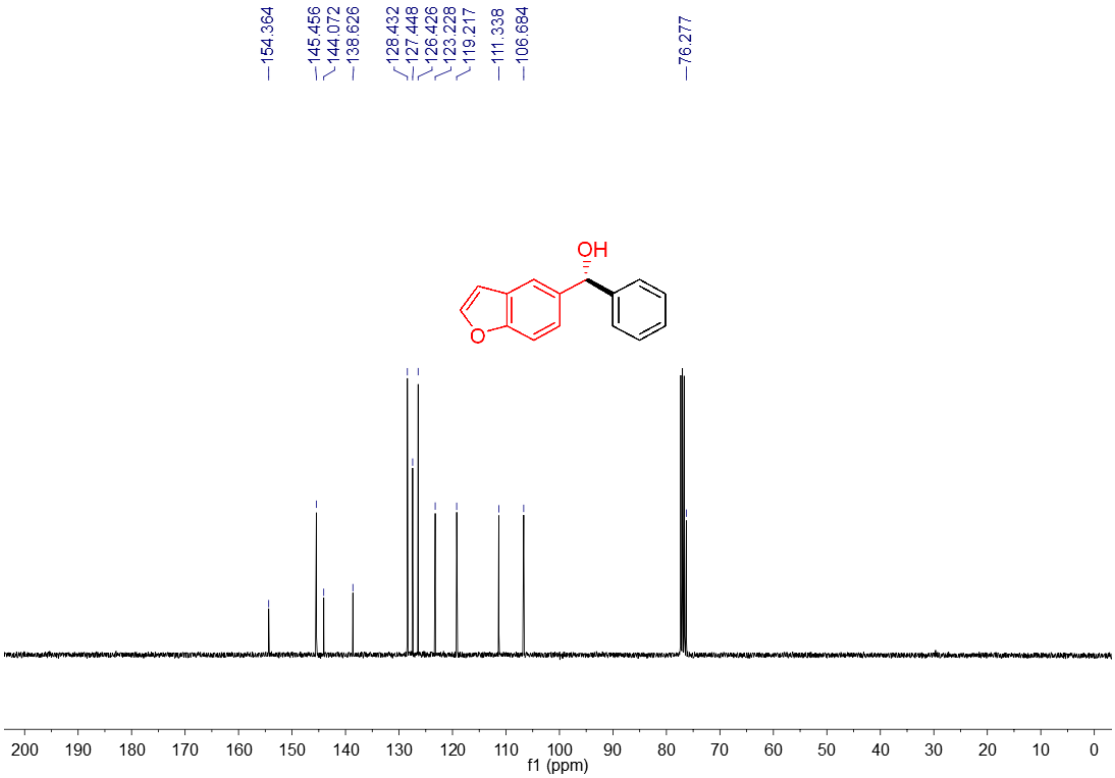
^{13}C NMR spectrum of compound **3p** (100 MHz) in $CDCl_3$



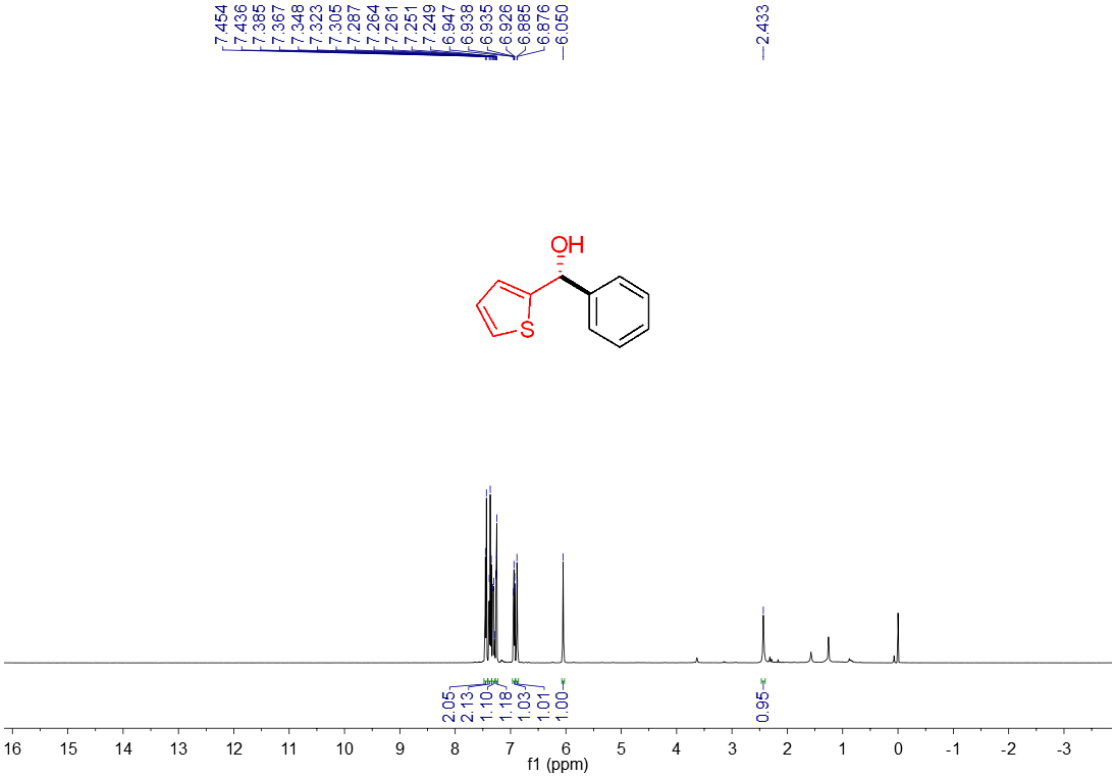
^{1}H NMR spectrum of compound **3q** (400 MHz) in $CDCl_3$



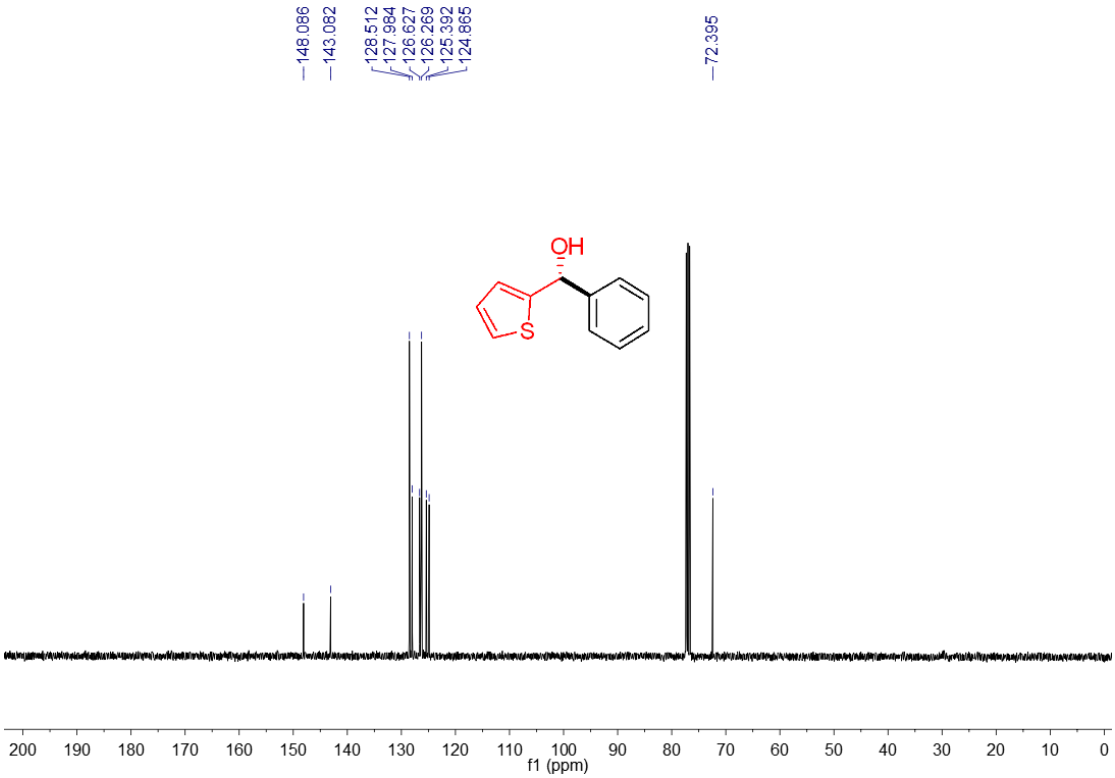
^{13}C NMR spectrum of compound **3q** (100 MHz) in $CDCl_3$



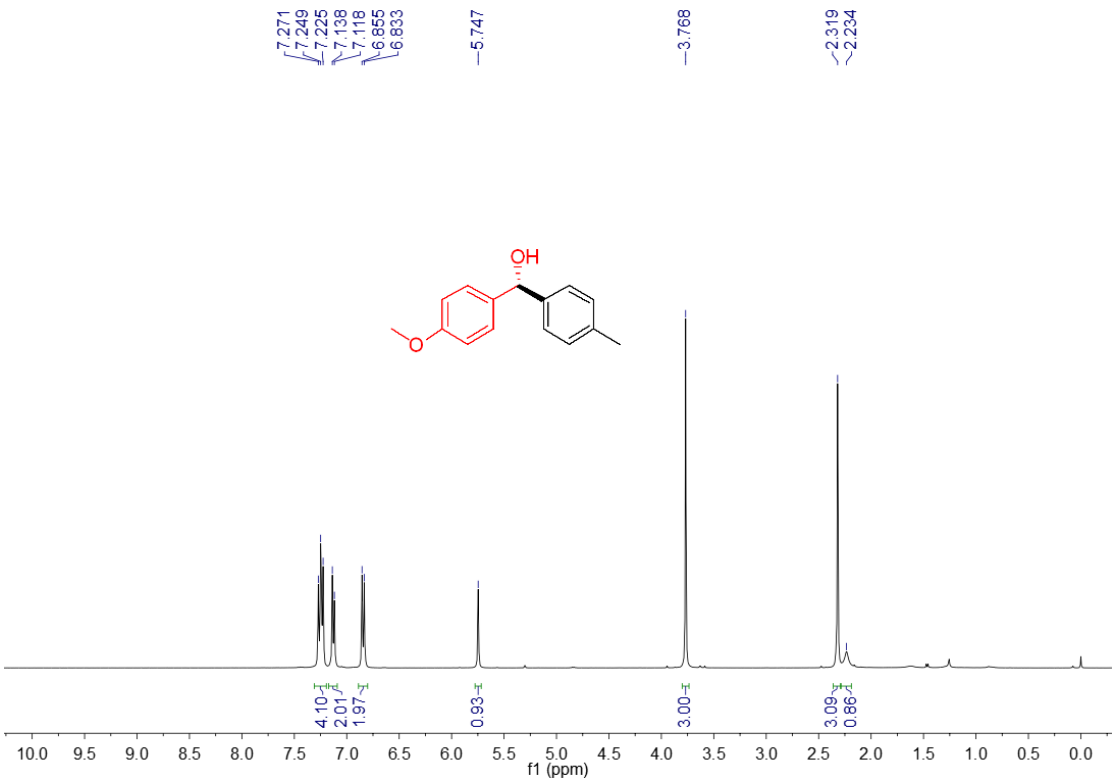
^{1}H NMR spectrum of compound **3r** (400 MHz) in $CDCl_3$



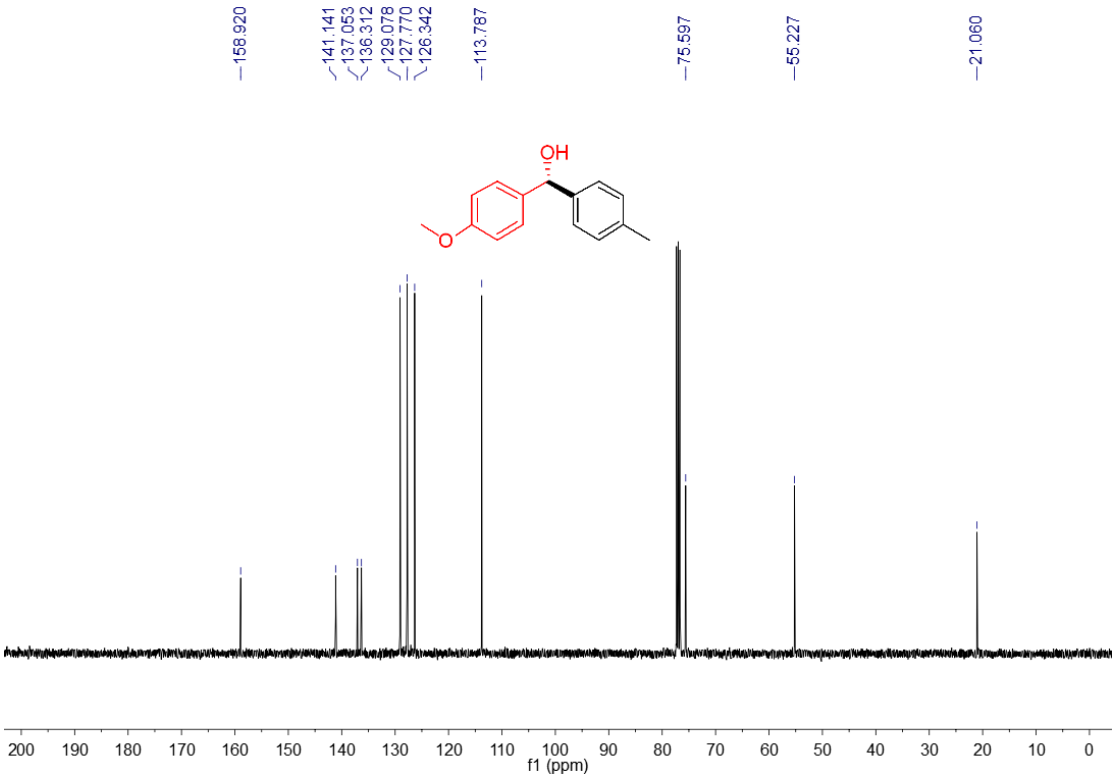
^{13}C NMR spectrum of compound **3r** (100 MHz) in $CDCl_3$



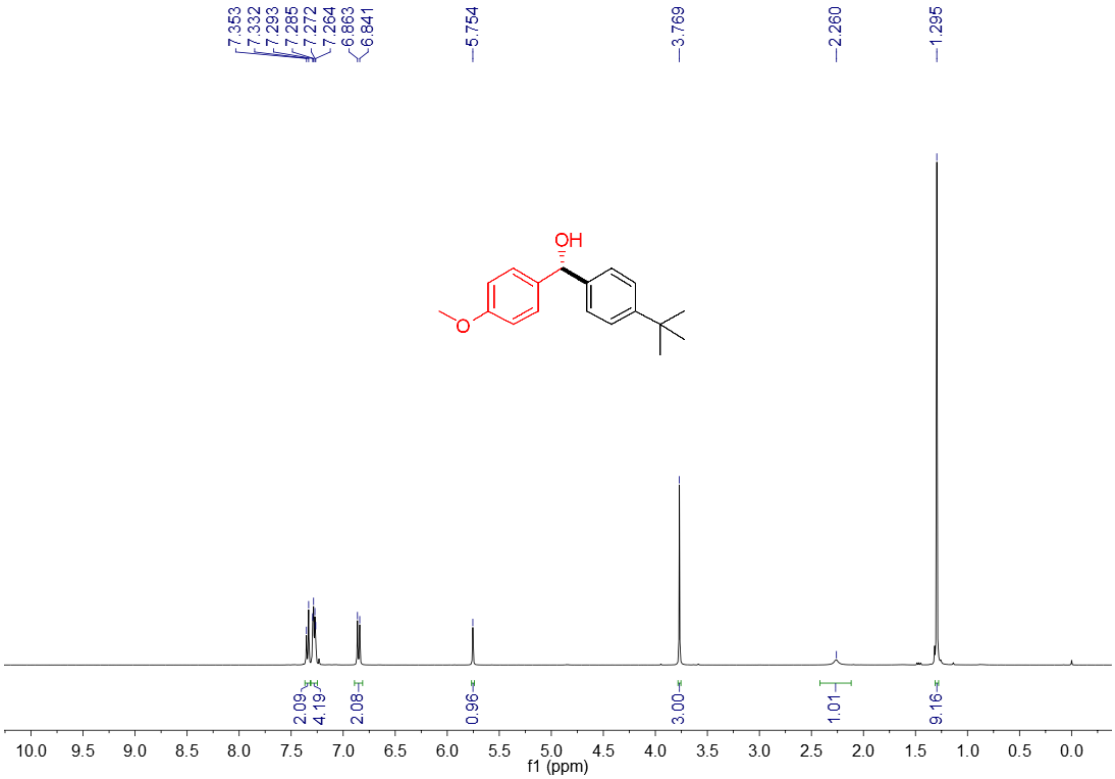
^{1}H NMR spectrum of compound **3s** (400 MHz) in $CDCl_3$



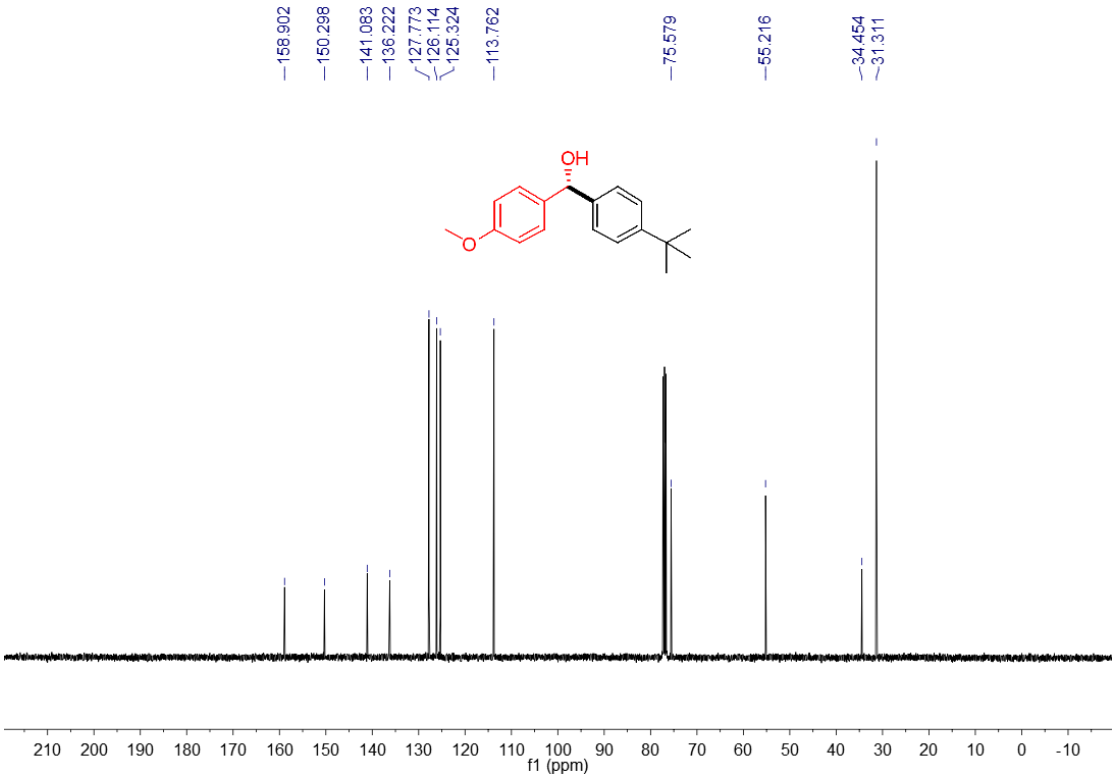
^{13}C NMR spectrum of compound **3s** (100 MHz) in $CDCl_3$



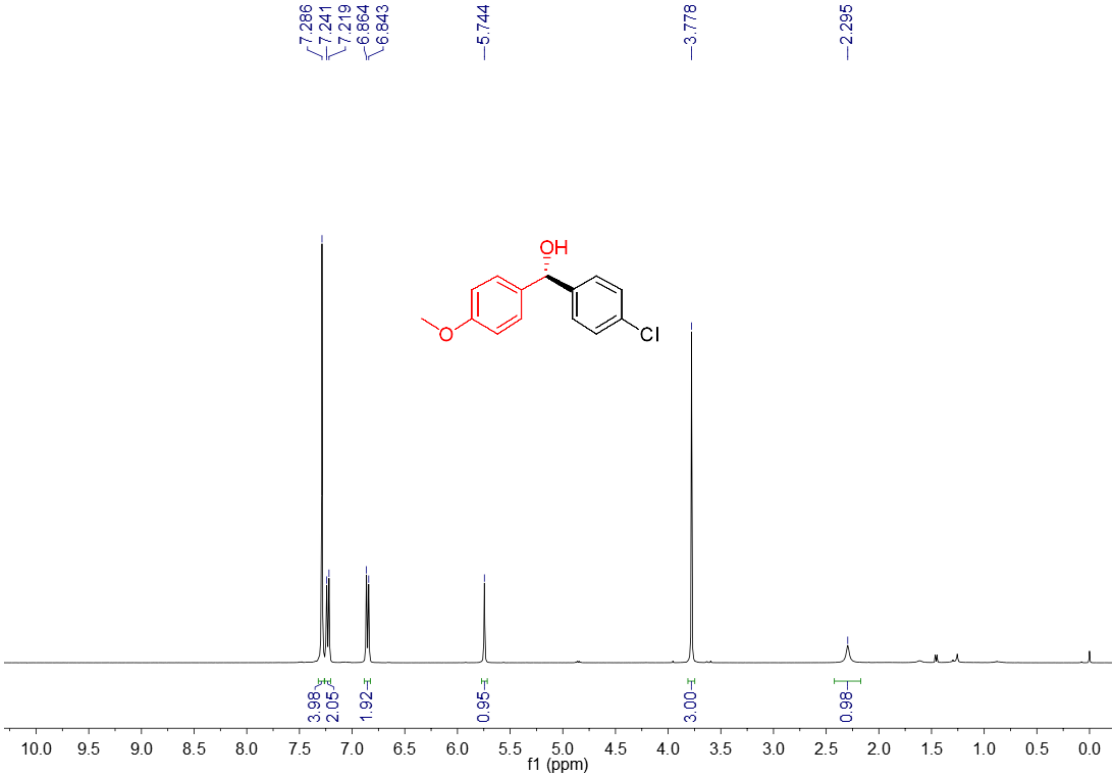
^{1}H NMR spectrum of compound **3t** (400 MHz) in $CDCl_3$



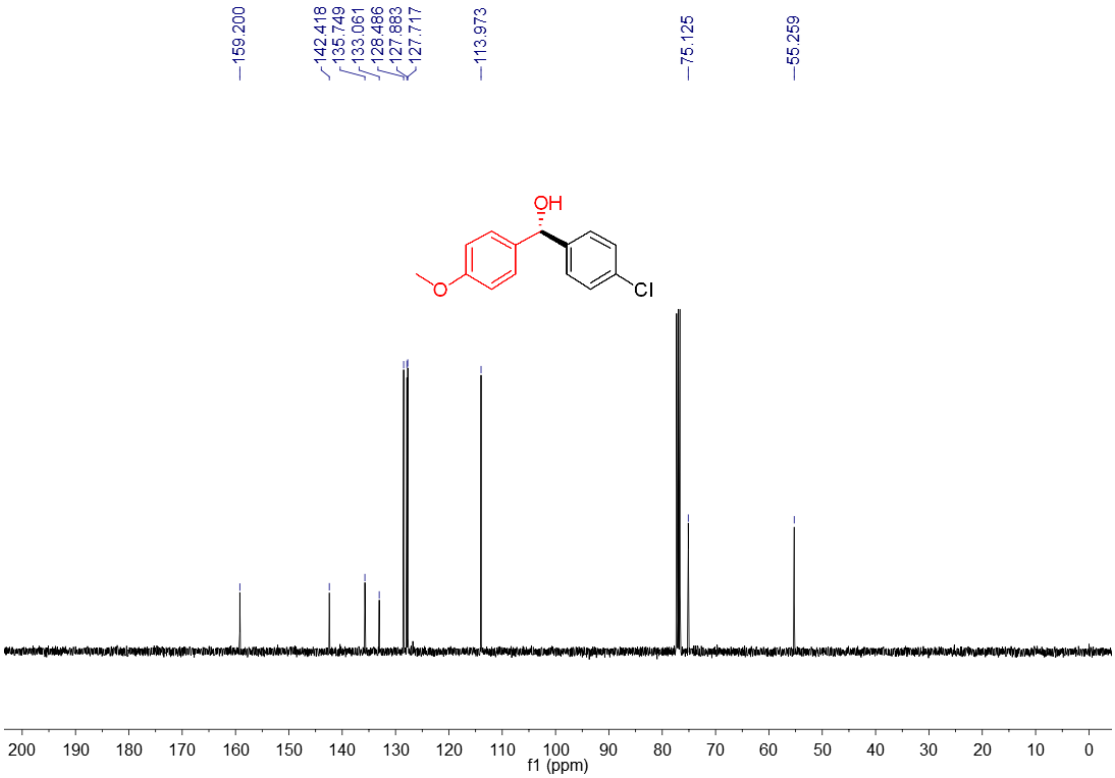
^{13}C NMR spectrum of compound **3t** (100 MHz) in $CDCl_3$



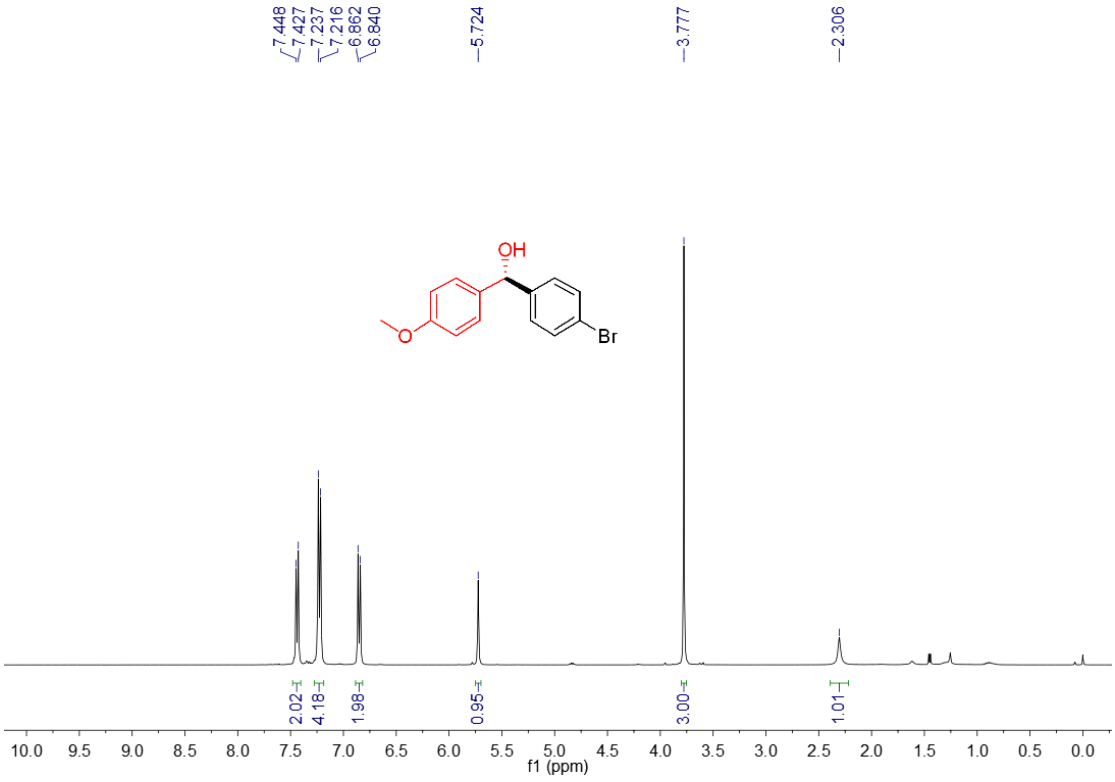
^{1}H NMR spectrum of compound **3u** (400 MHz) in $CDCl_3$



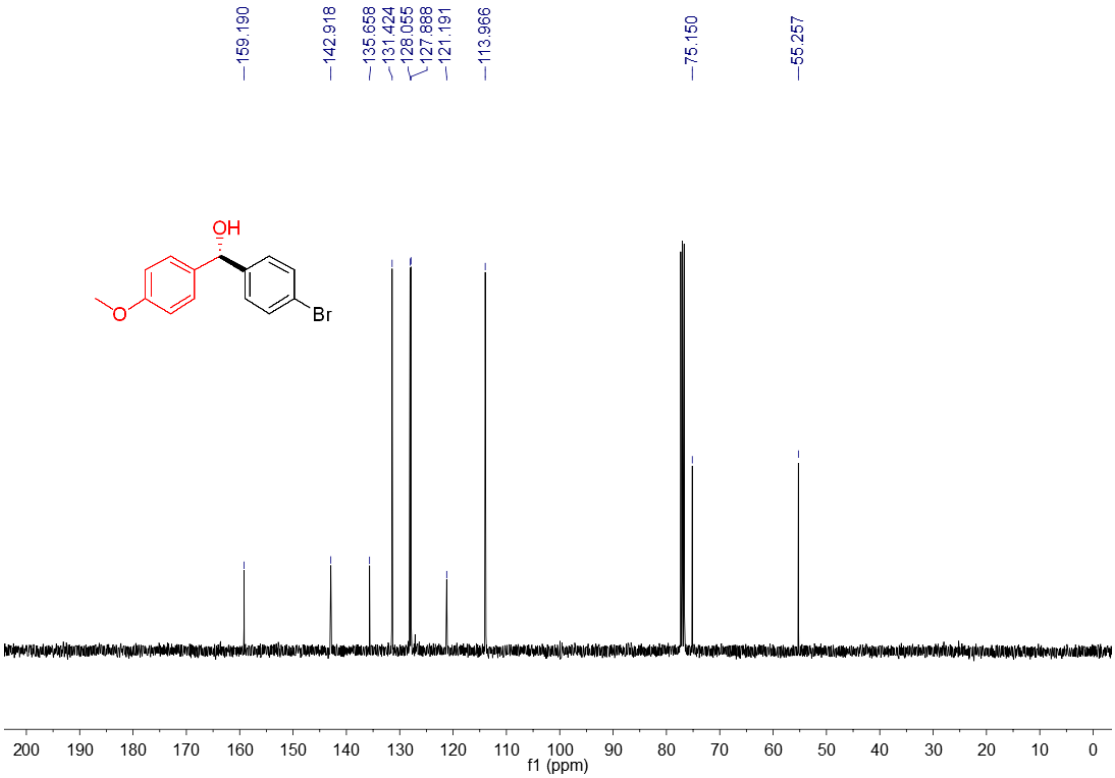
^{13}C NMR spectrum of compound **3u** (100 MHz) in $CDCl_3$



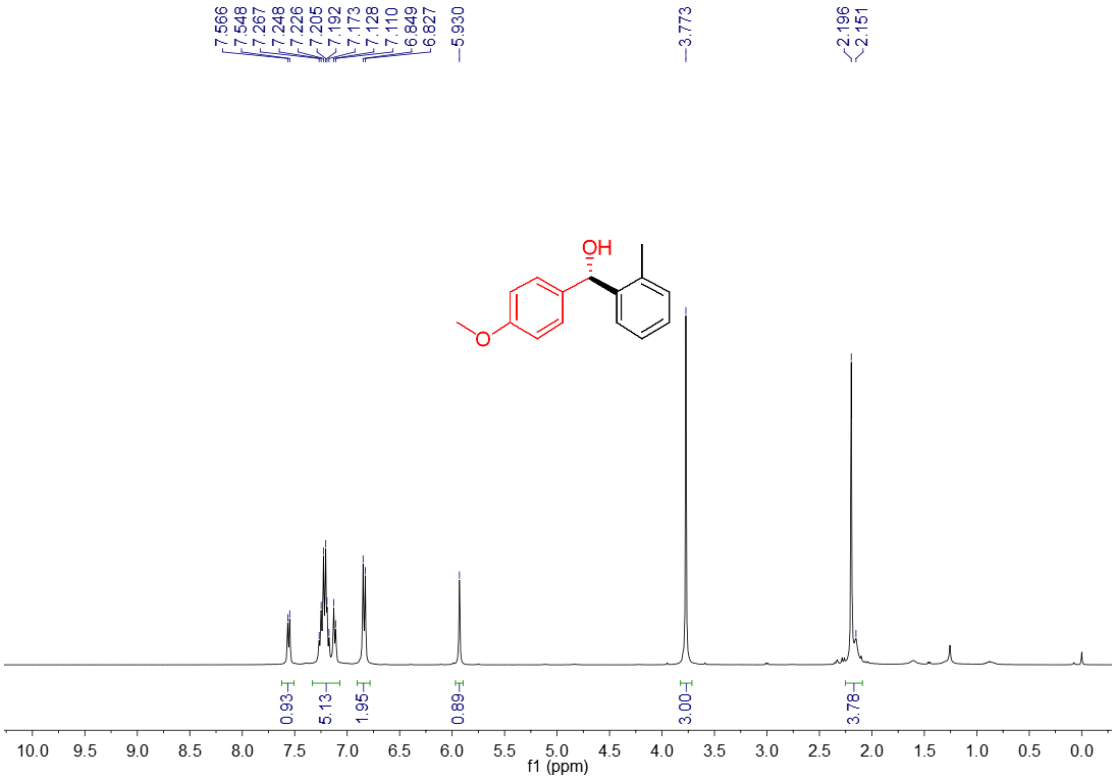
^{1}H NMR spectrum of compound **3v** (400 MHz) in $CDCl_3$



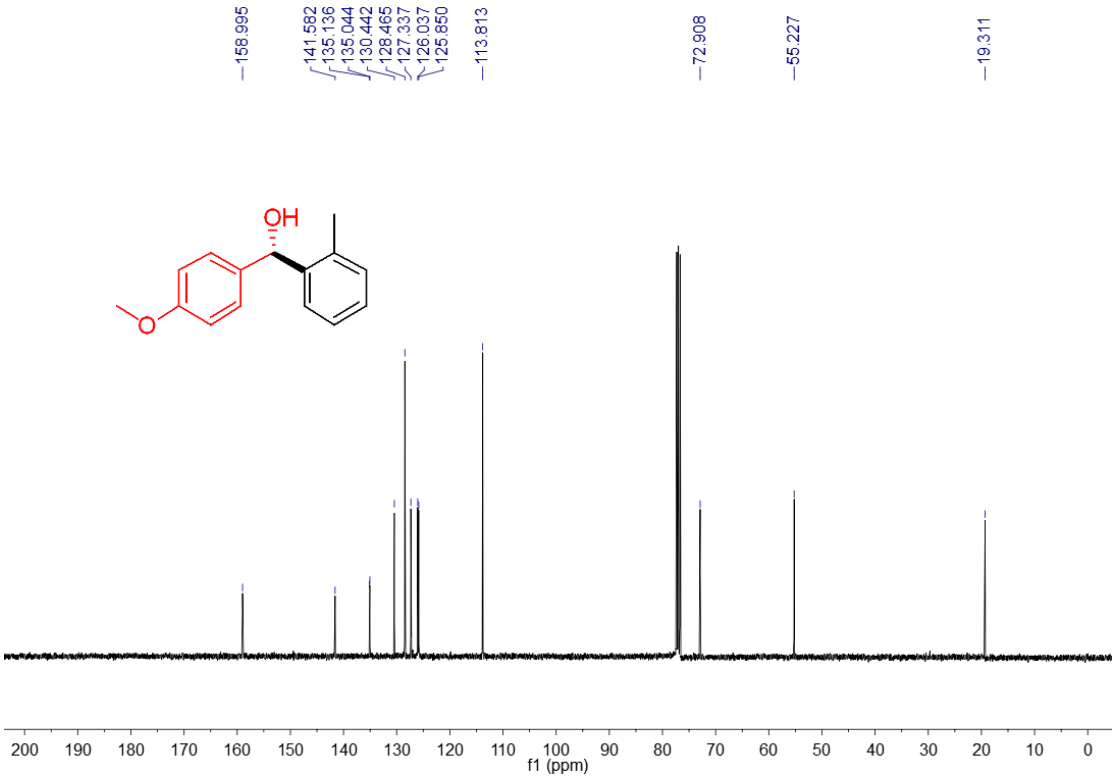
^{13}C NMR spectrum of compound **3v** (100 MHz) in $CDCl_3$



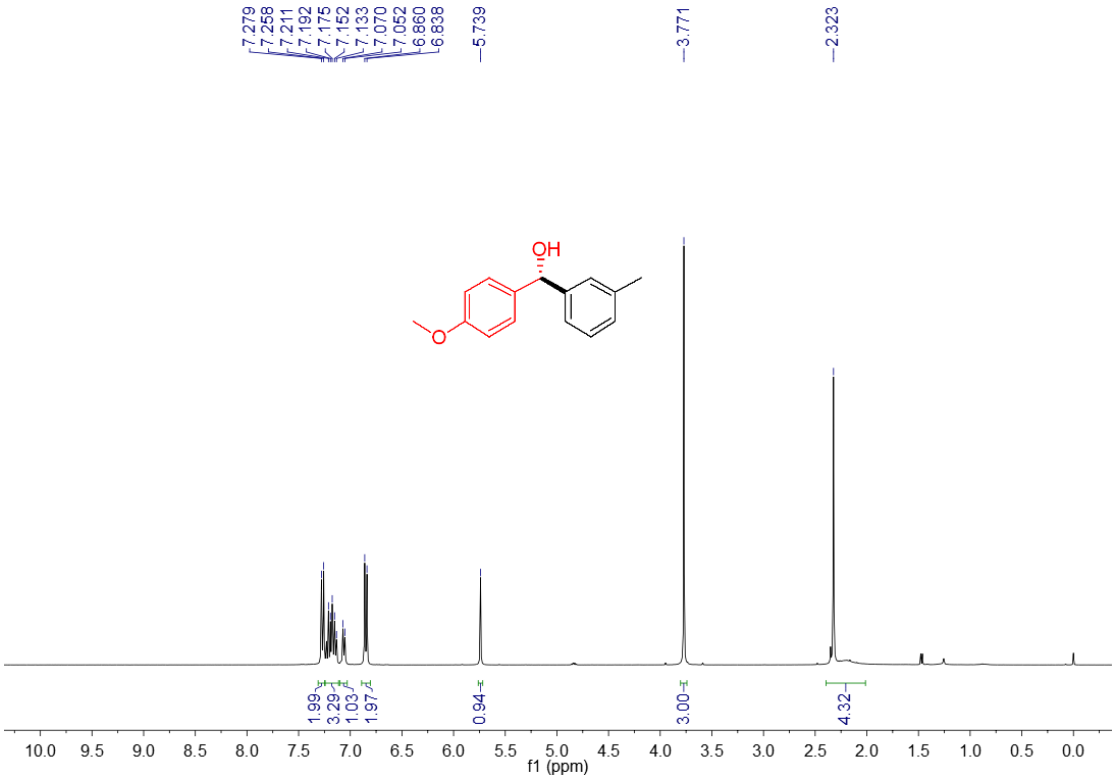
^{1}H NMR spectrum of compound **3w** (400 MHz) in $CDCl_3$



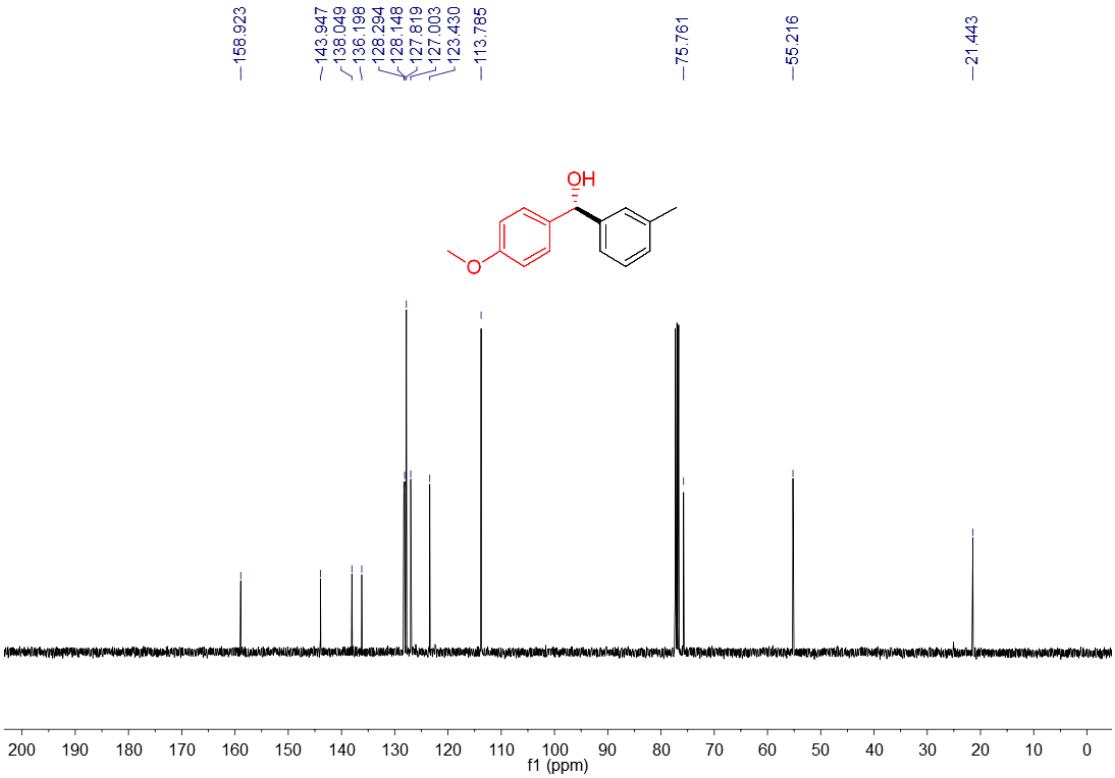
^{13}C NMR spectrum of compound **3w** (100 MHz) in $CDCl_3$



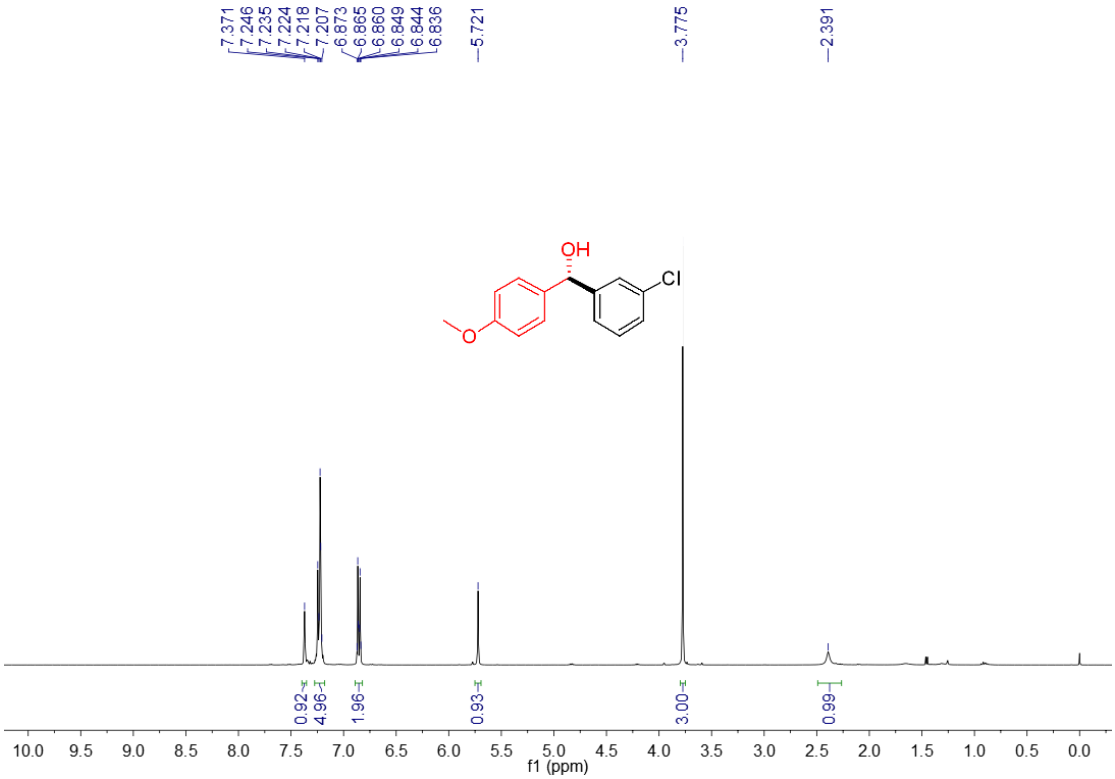
^{1}H NMR spectrum of compound **3x** (400 MHz) in $CDCl_3$



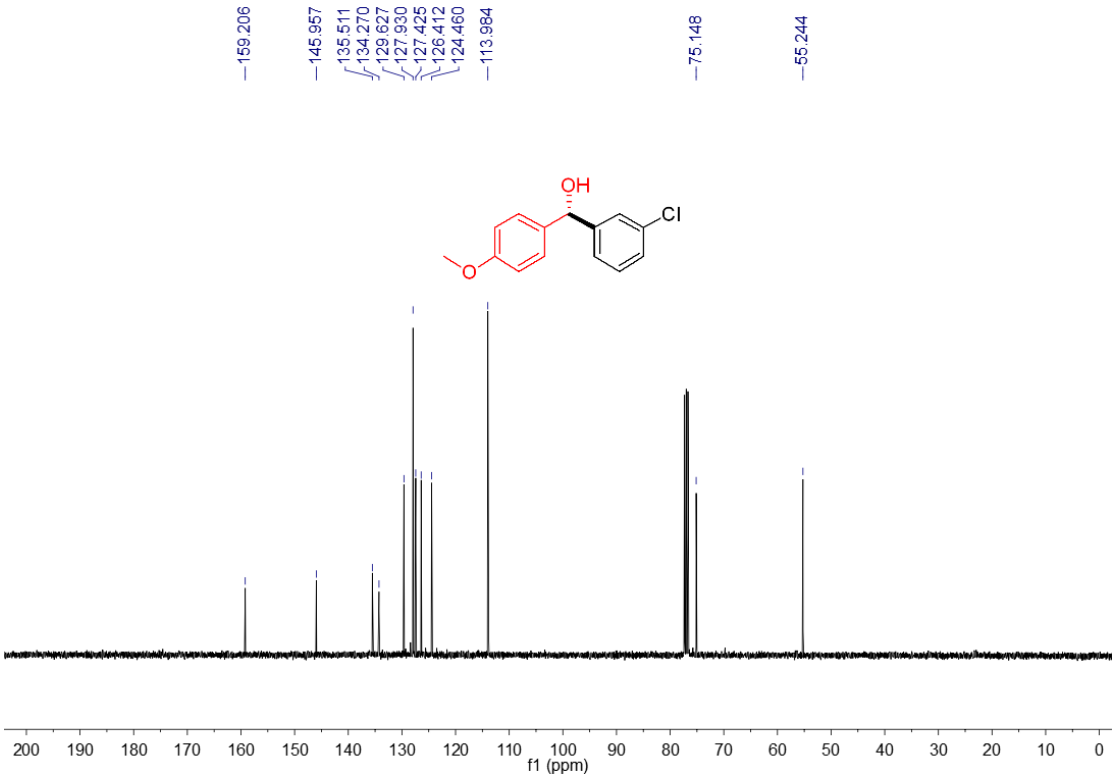
^{13}C NMR spectrum of compound **3x** (100 MHz) in $CDCl_3$



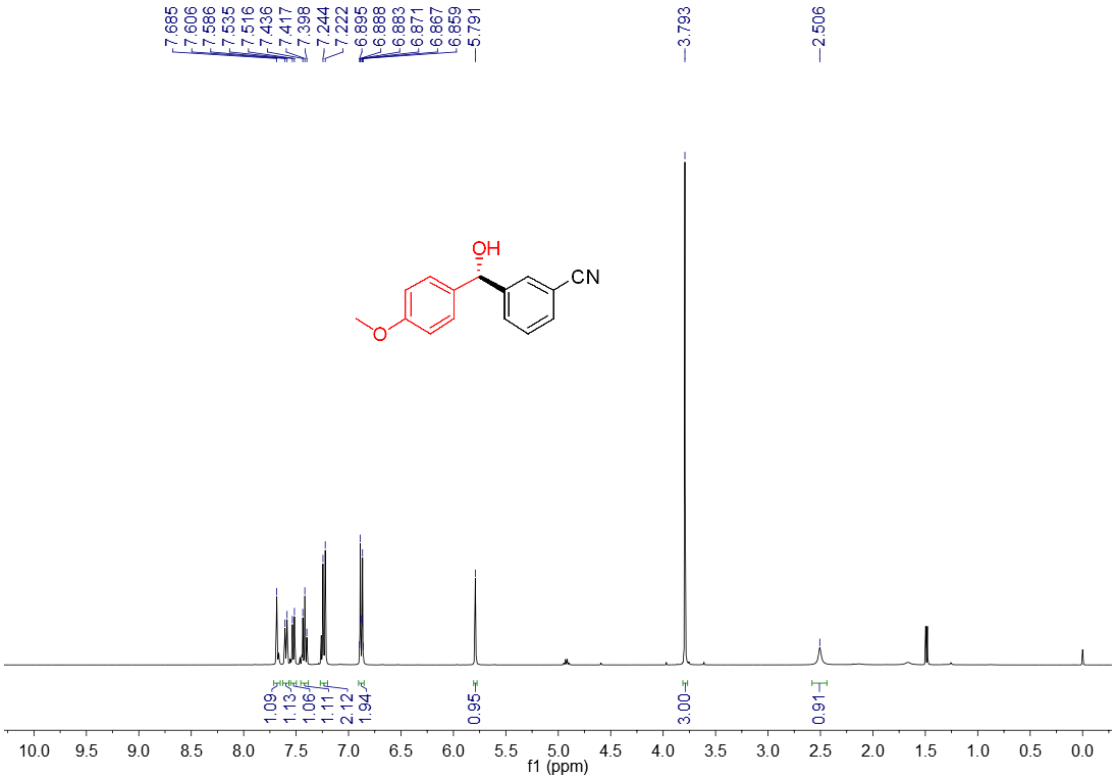
^{1}H NMR spectrum of compound **3y** (400 MHz) in $CDCl_3$



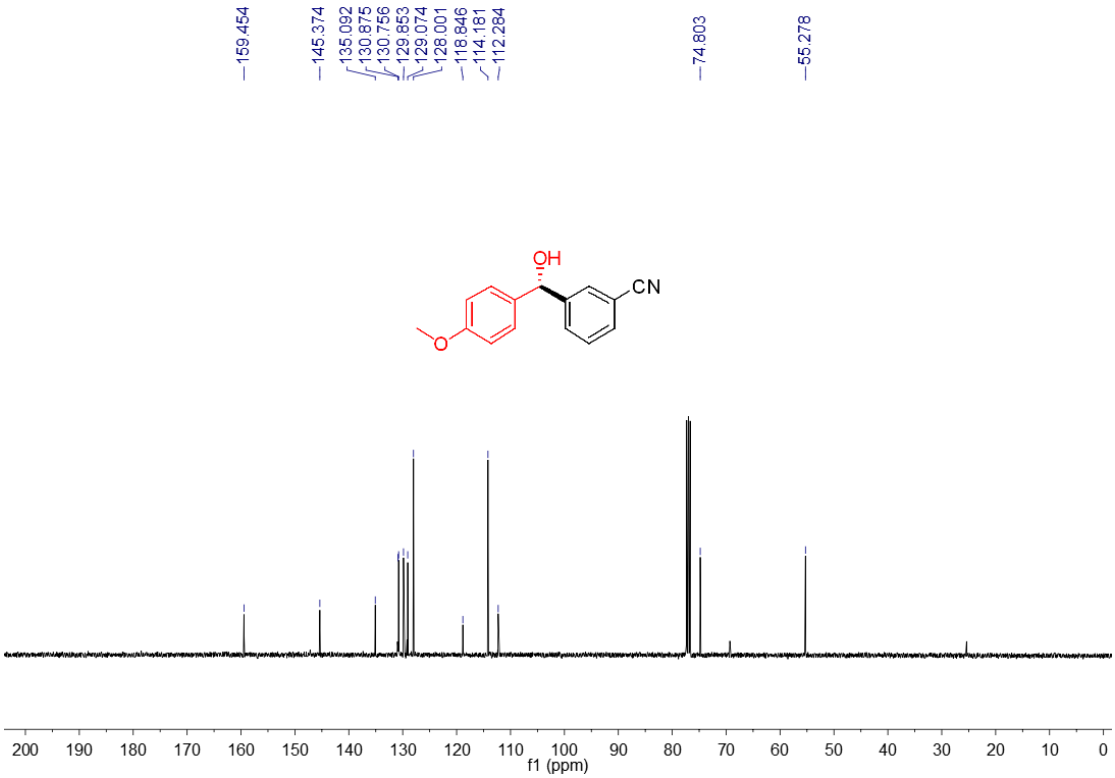
^{13}C NMR spectrum of compound **3y** (100 MHz) in $CDCl_3$



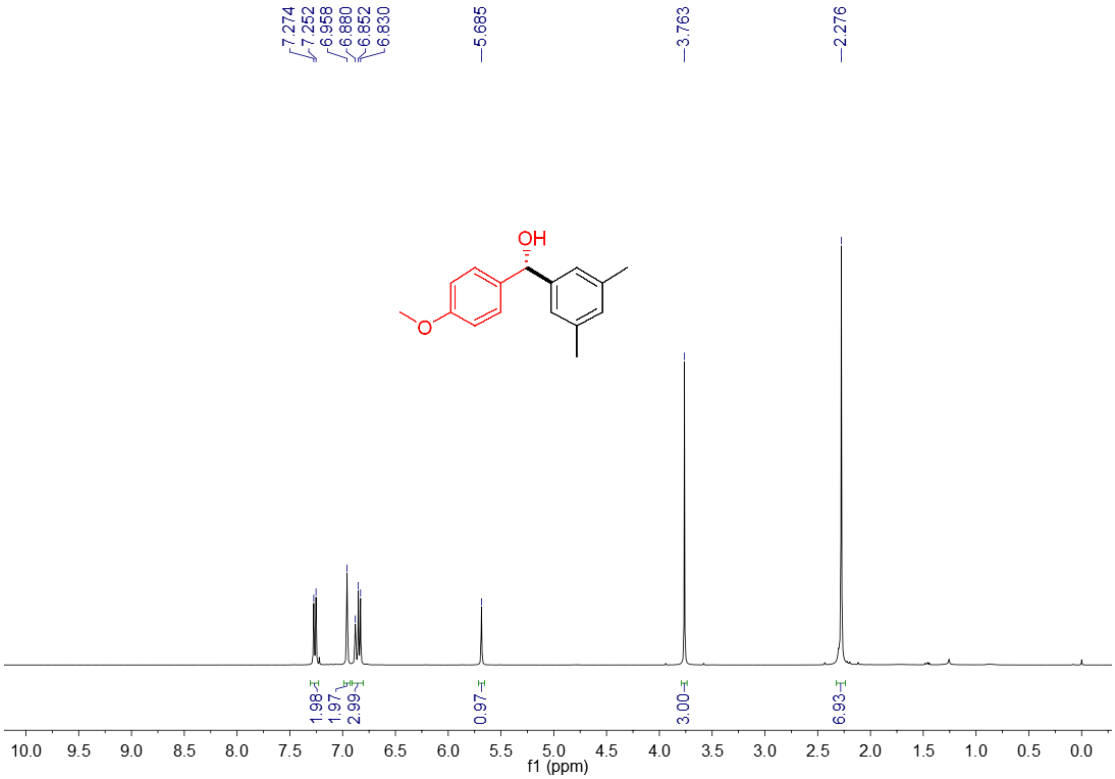
^{1}H NMR spectrum of compound **3z** (400 MHz) in $CDCl_3$



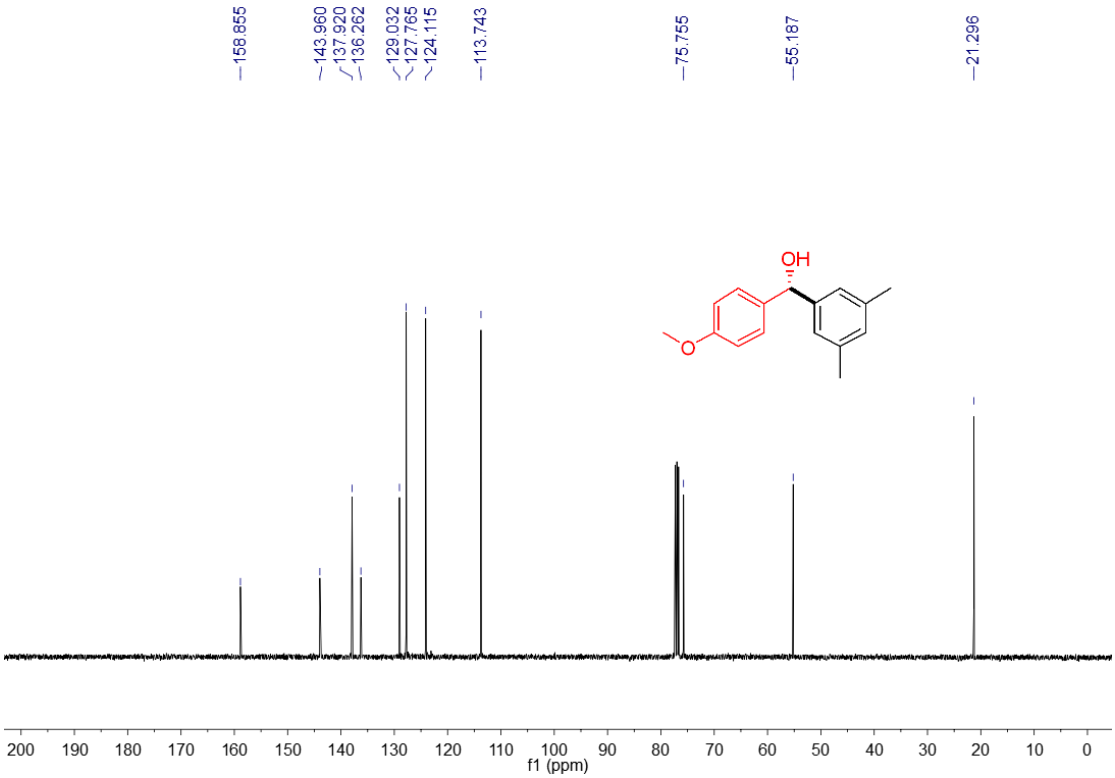
^{13}C NMR spectrum of compound **3z** (100 MHz) in $CDCl_3$



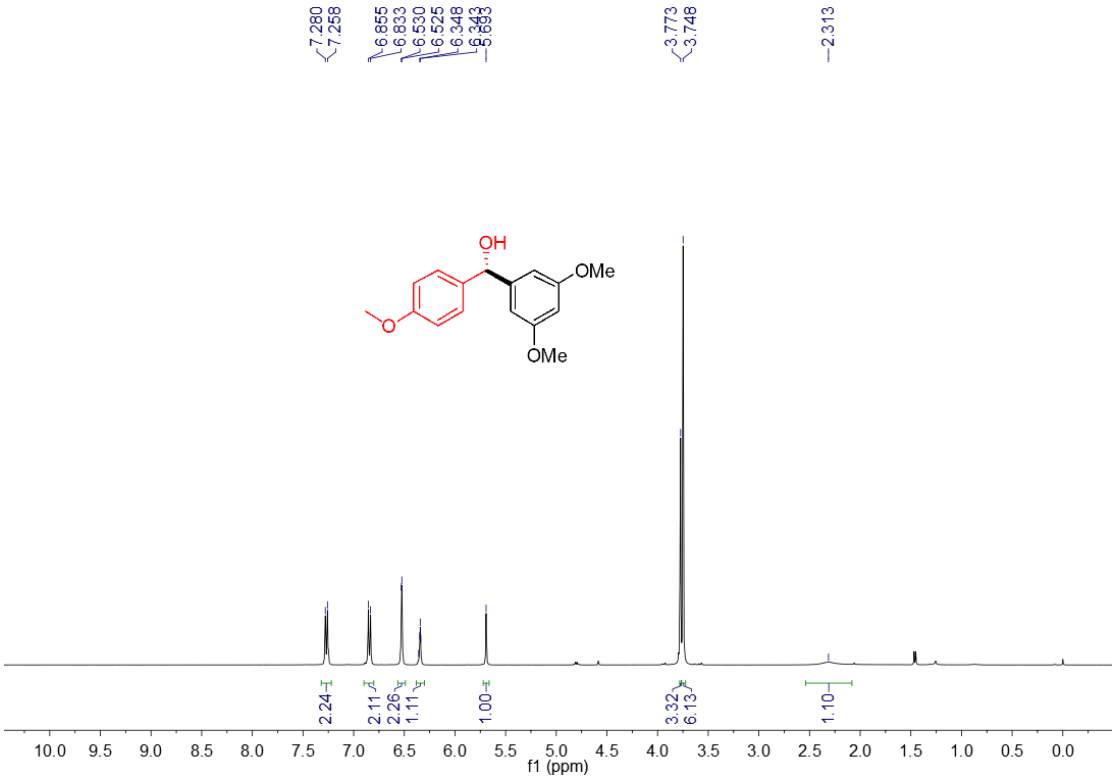
^{1}H NMR spectrum of compound **3aa** (400 MHz) in $CDCl_3$



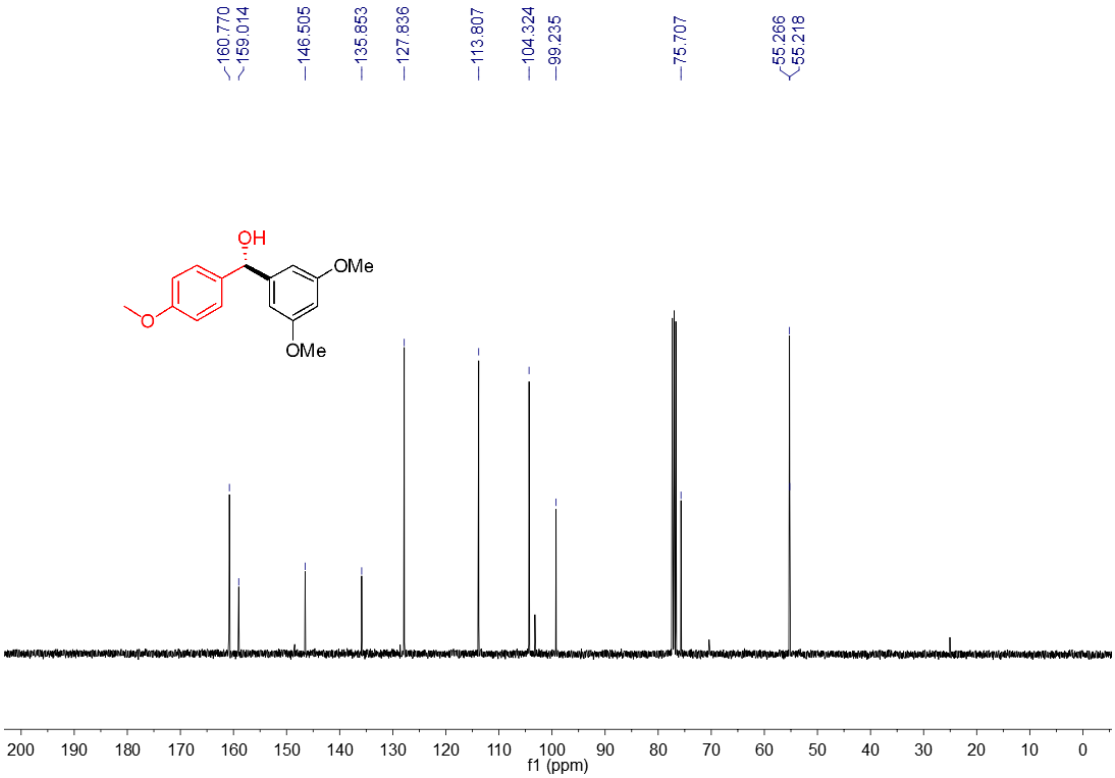
^{13}C NMR spectrum of compound **3aa** (100 MHz) in $CDCl_3$



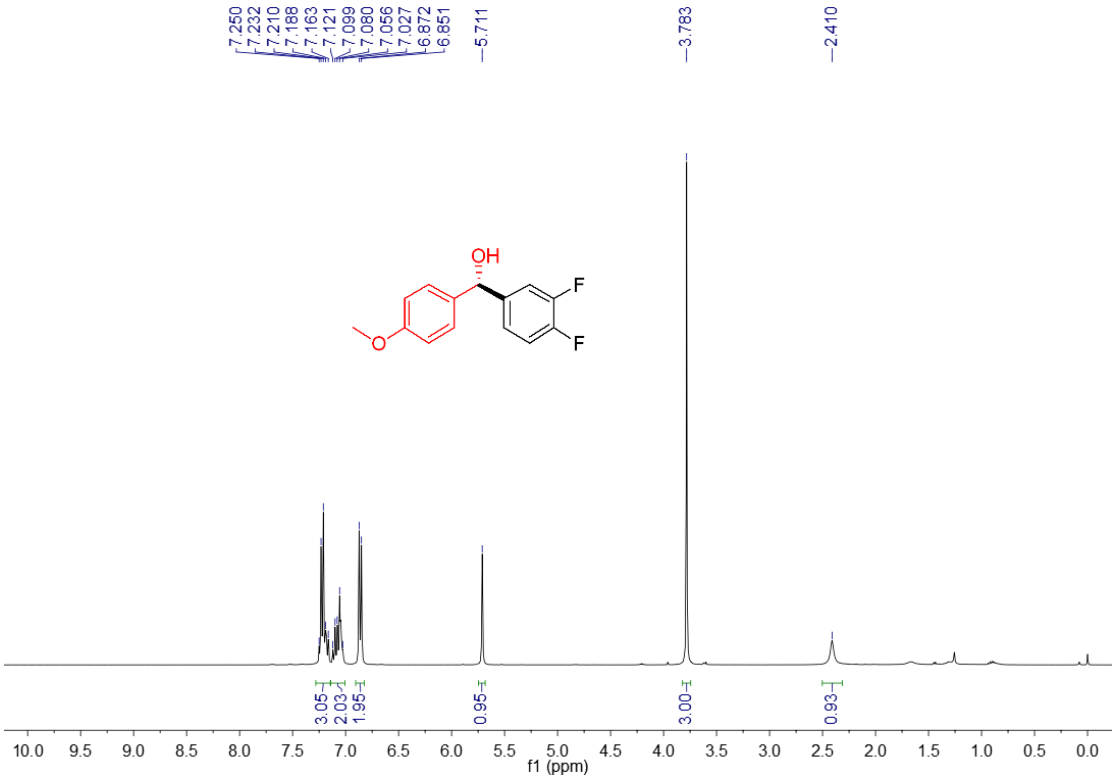
^{1}H NMR spectrum of compound **3ab** (400 MHz) in $CDCl_3$



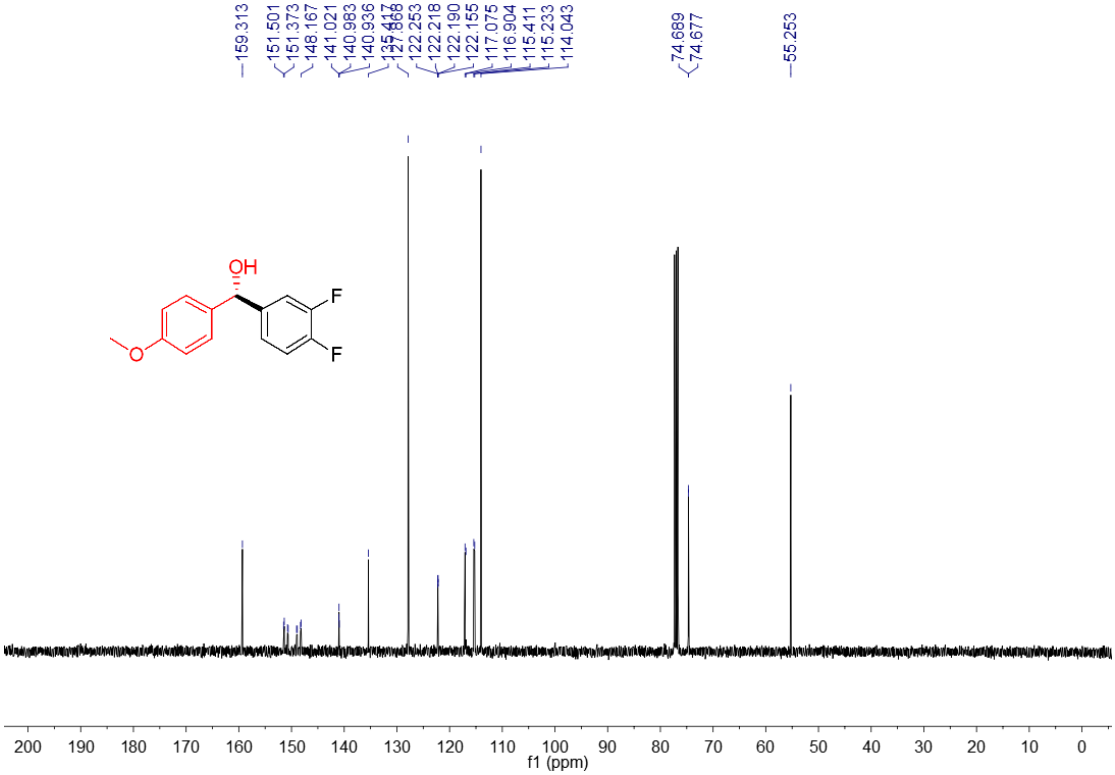
^{13}C NMR spectrum of compound **3ab** (100 MHz) in $CDCl_3$



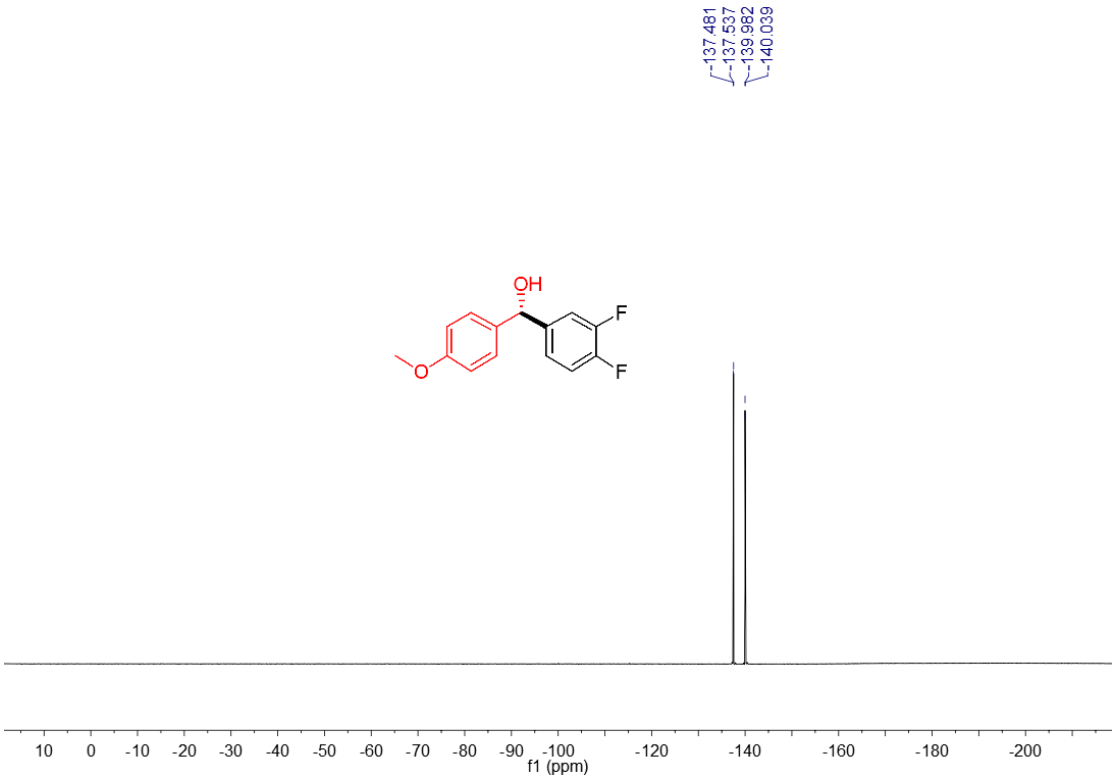
^{1}H NMR spectrum of compound **3ac** (400 MHz) in $CDCl_3$



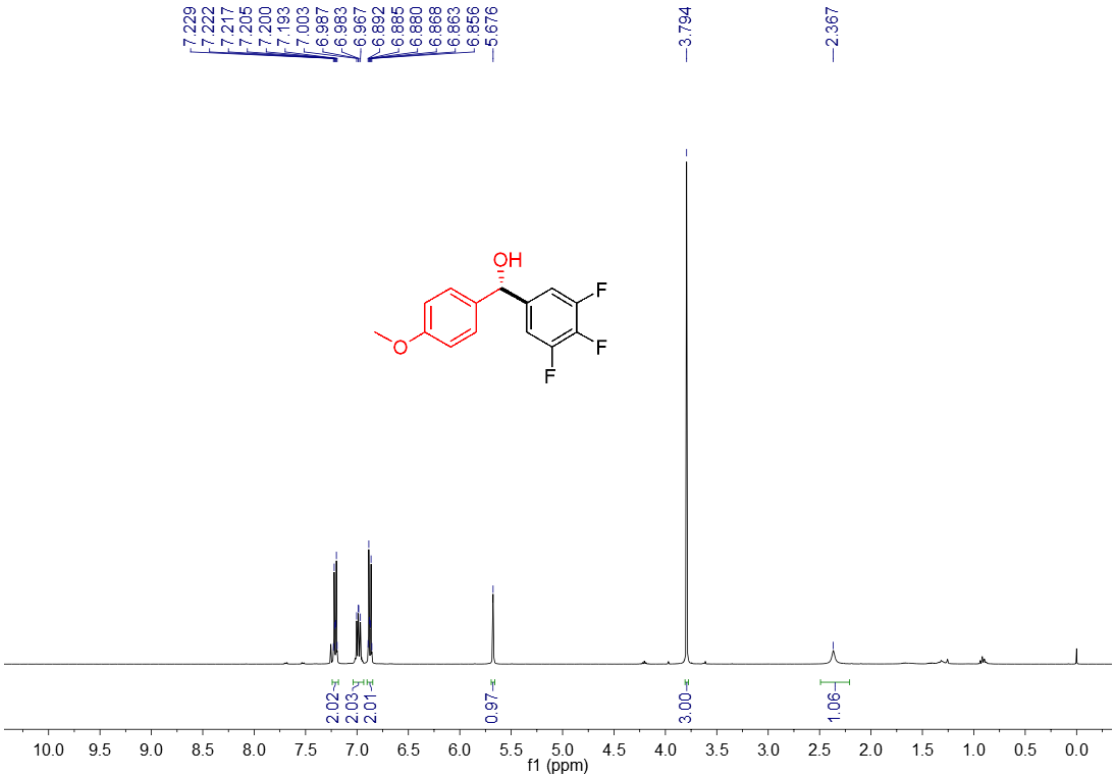
^{13}C NMR spectrum of compound **3ac** (100 MHz) in $CDCl_3$



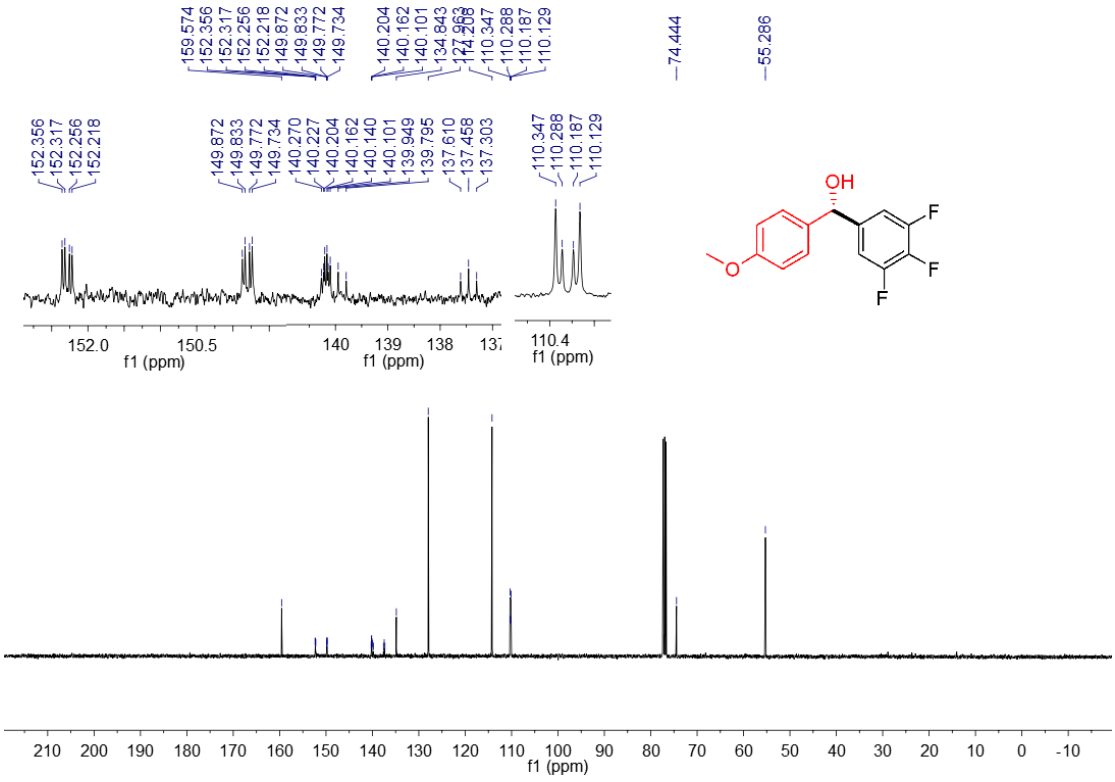
^{19}F NMR spectrum of compound **3ac** (376 MHz) in $CDCl_3$



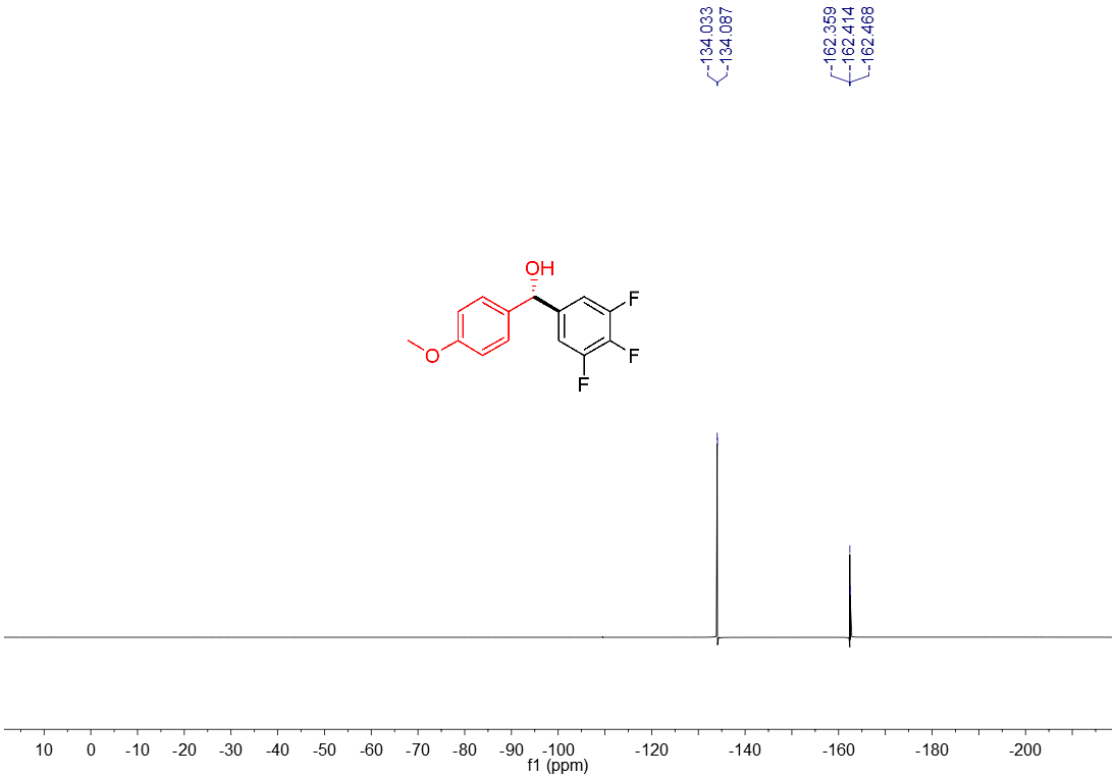
^{1}H NMR spectrum of compound **3ad** (400 MHz) in $CDCl_3$



^{13}C NMR spectrum of compound **3ad** (100 MHz) in $CDCl_3$

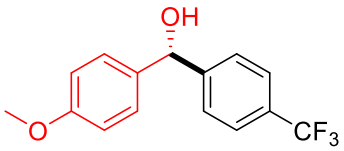


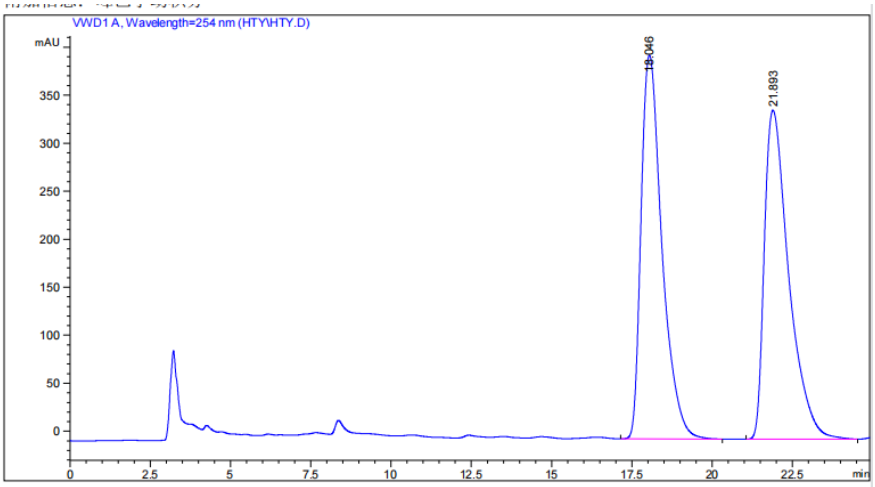
^{19}F NMR spectrum of compound **3ad** (376 MHz) in $CDCl_3$



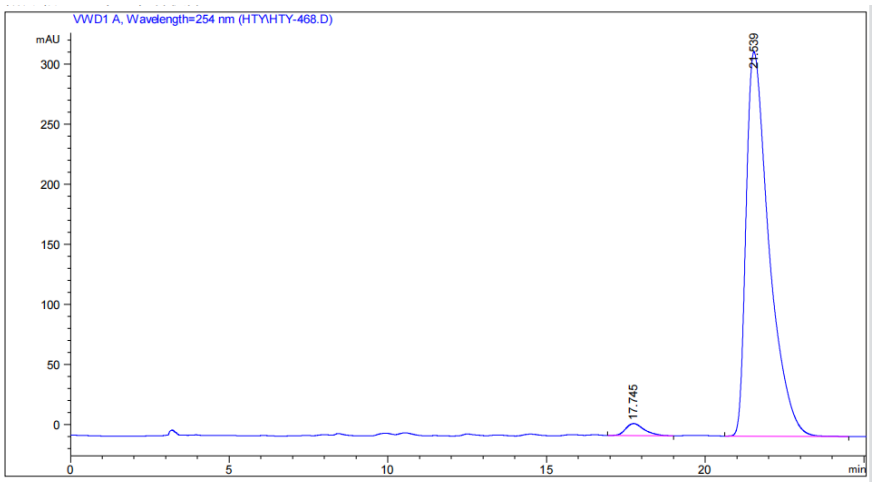
10. Copies of HPLC Spectra for the Products

Chiral HPLC spectrum of compound **3a**



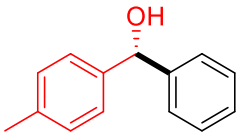


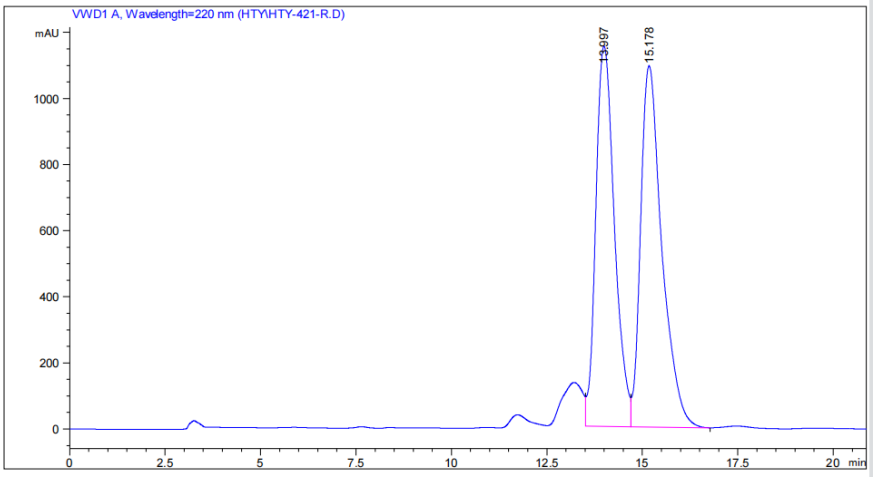
	RT (min)	Height [mAU]	Area [Mau*S]	Area%
1	18.046	399.69394	1.80911e4	49.9732
2	21.893	342.61975	1.81105e4	50.0268



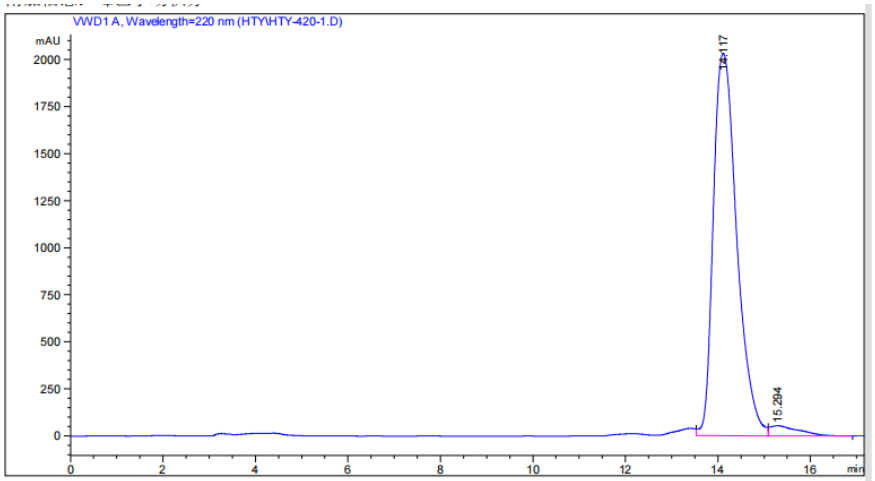
	RT (min)	Height [mAU]	Area [Mau*S]	Area%
1	17.745	10.02051	406.99588	2.4716
2	21.539	320.08087	1.60599e4	97.5284

Chiral HPLC spectrum of compound **3b**



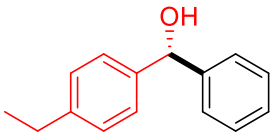


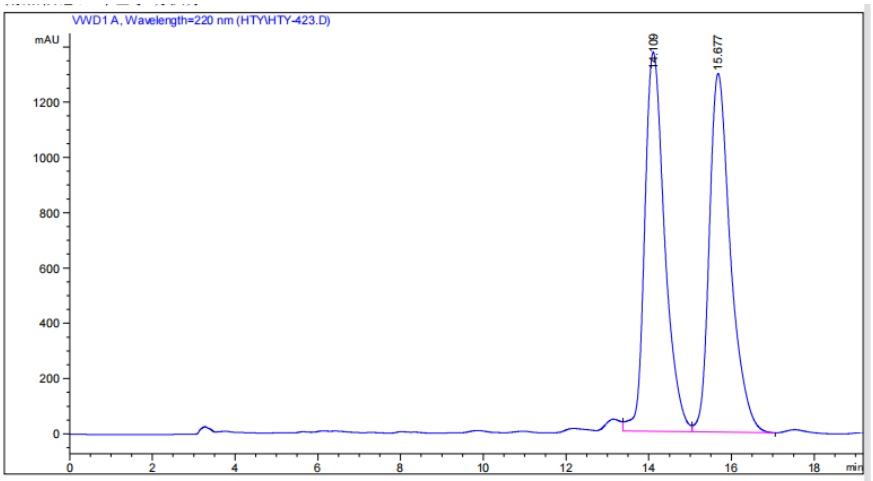
	RT (min)	Height [mAU]	Area [Mau*S]	Area%
1	13.997	1149.92651	3.91717e4	48.0597
2	15.178	1092.19092	4.23347e4	51.9403



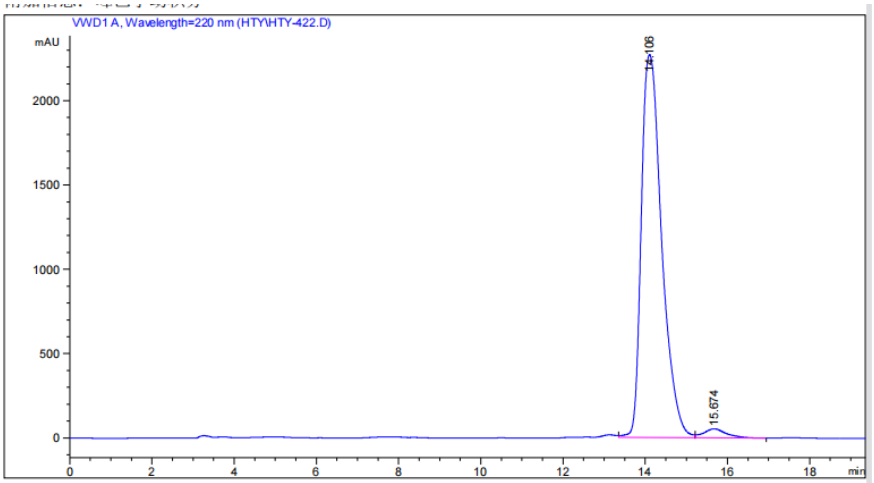
	RT (min)	Height [mAU]	Area [Mau*S]	Area%
1	14.117	2029.96167	7.18252e4	96.8639
2	15.294	52.91184	2325.42188	3.1361

Chiral HPLC spectrum of compound **3c**



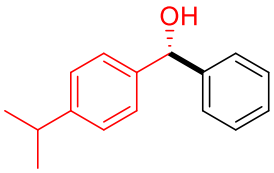


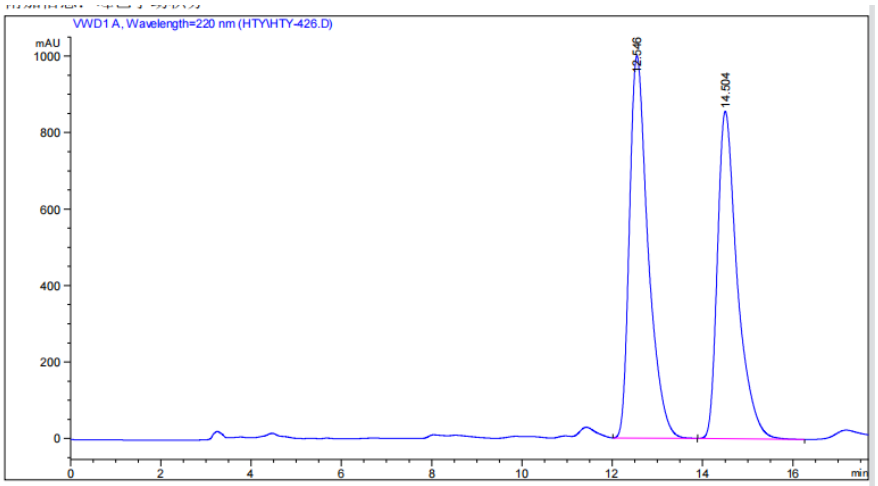
	RT (min)	Height [mAU]	Area [Mau*S]	Area%
1	14.109	1371.14526	4.60885e4	49.9372
2	15.677	1297.07898	4.62045e4	50.0628



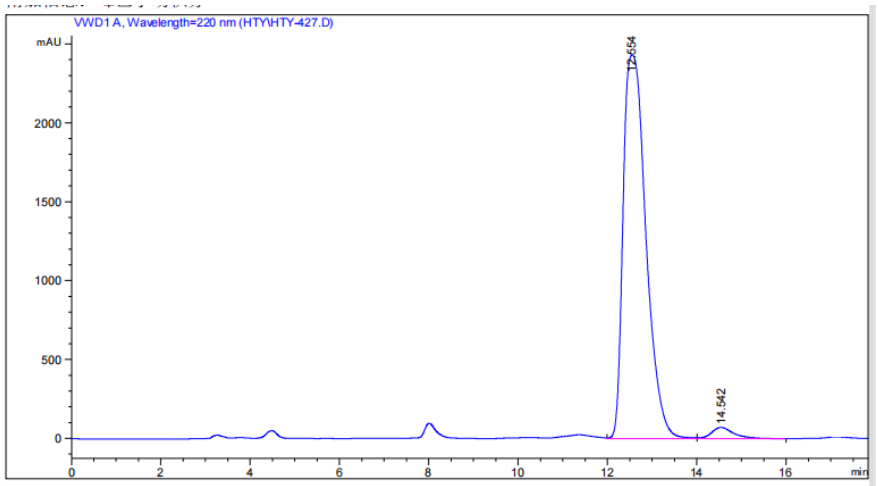
	RT (min)	Height [mAU]	Area [Mau*S]	Area%
1	14.106	2269.35767	7.82337e4	97.4250
2	15.674	53.67068	2067.75659	2.5750

Chiral HPLC spectrum of compound **3d**



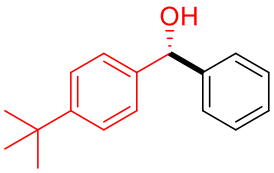


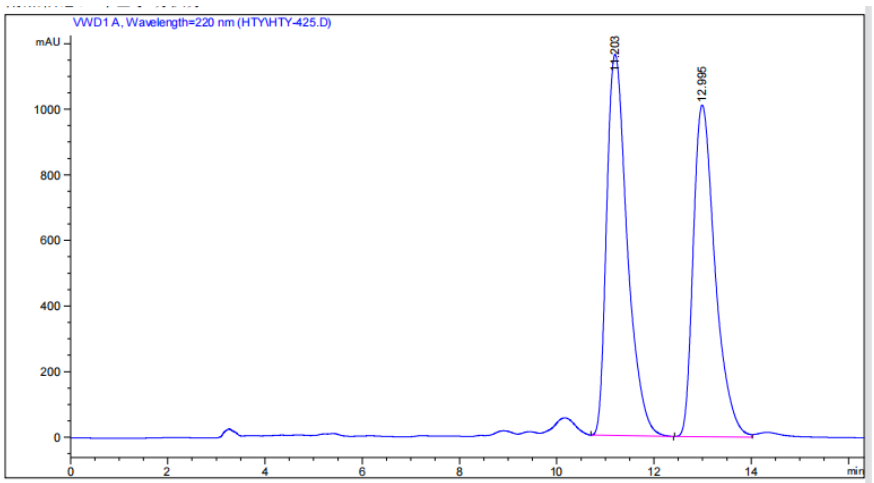
	RT (min)	Height [mAU]	Area [Mau*S]	Area%
1	12.546	999.17963	2.87273e4	52.2778
2	14.504	856.20819	2.62240e4	47.7222



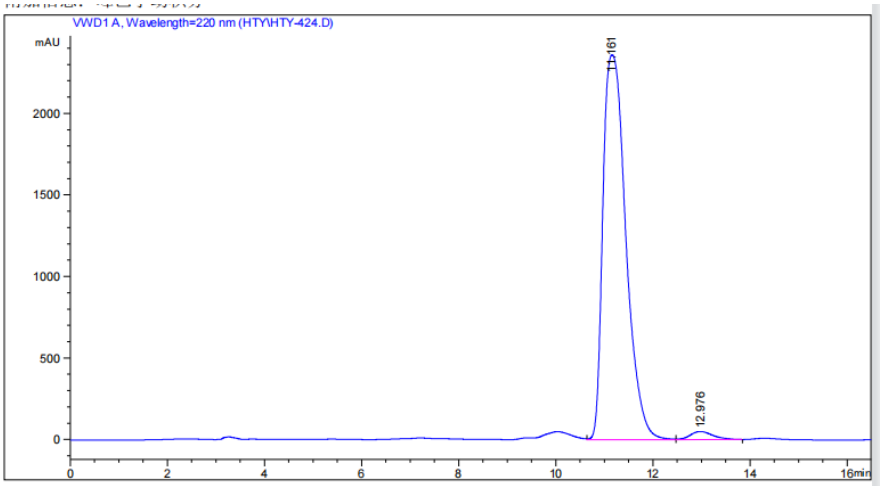
	RT (min)	Height [mAU]	Area [Mau*S]	Area%
1	12.554	2433.56543	8.60845e4	97.2246
2	14.542	70.85519	2457.39478	2.7754

Chiral HPLC spectrum of compound **3e**



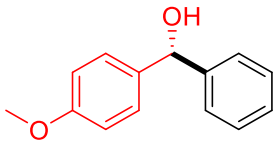


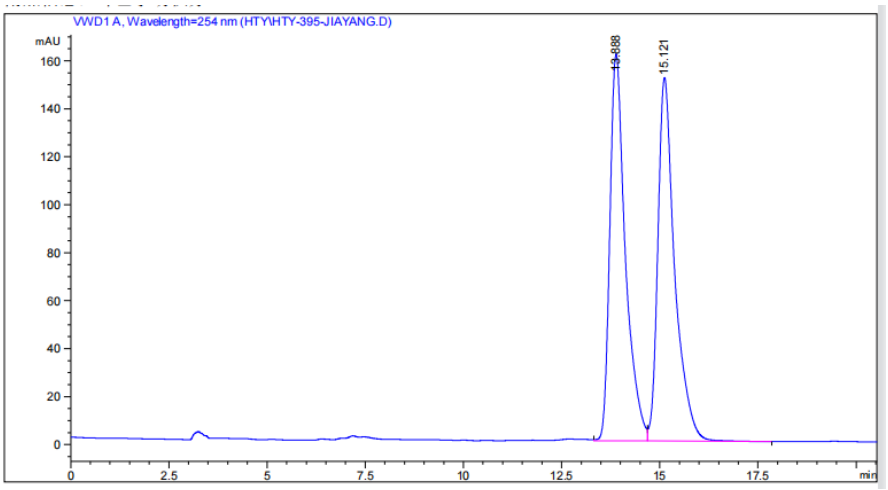
	RT (min)	Height [mAU]	Area [Mau*S]	Area%
1	11.203	1160.31628	3.42560e4	52.0714
2	12.995	1010.29730	3.15305e4	47.9286



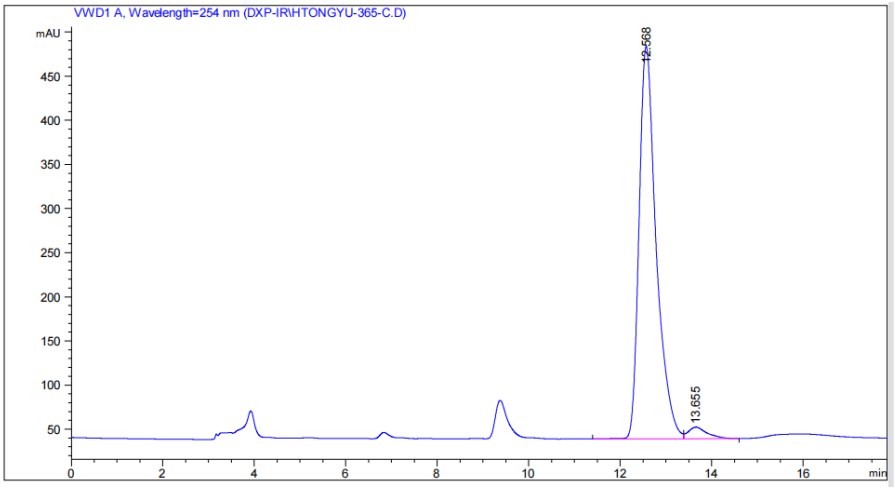
	RT (min)	Height [mAU]	Area [Mau*S]	Area%
1	11.161	2359.32397	7.73329e4	97.9705
2	12.976	49.26589	1602.01257	2.0295

Chiral HPLC spectrum of compound **3f**



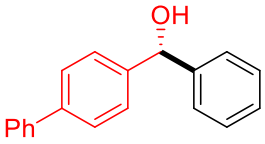


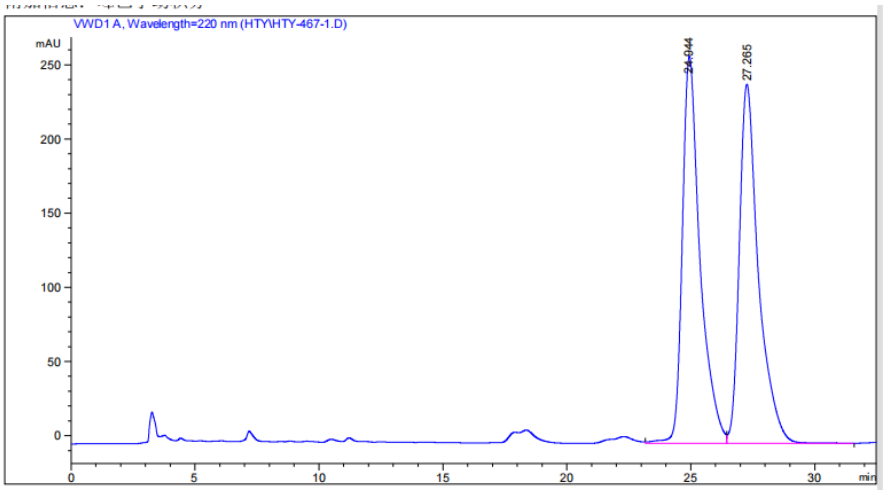
	RT (min)	Height [mAU]	Area [Mau*S]	Area%
1	13.888	161.20901	4445.65771	49.5749
2	15.121	151.46844	4521.89404	50.5251



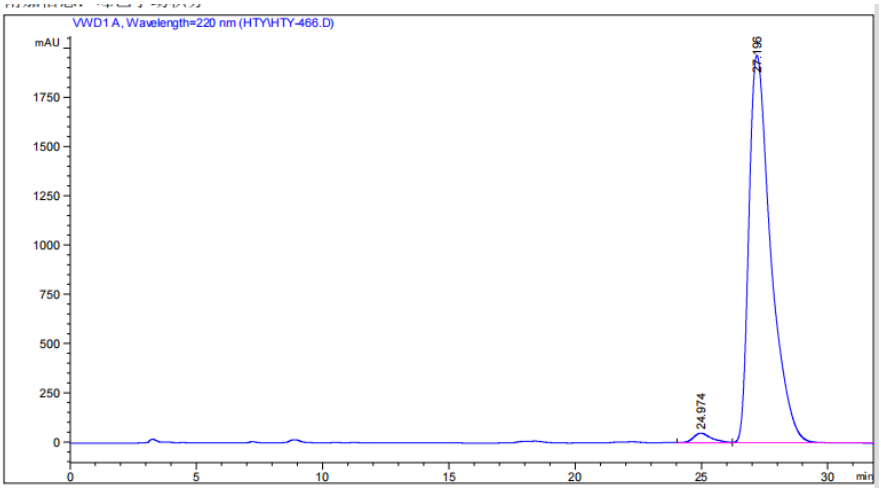
	RT (min)	Height [mAU]	Area [Mau*S]	Area%
1	12.568	444.88535	1.15681e4	96.8596
2	13.655	13.08232	375.06302	3.1404

Chiral HPLC spectrum of compound **3g**



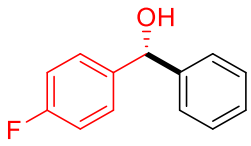


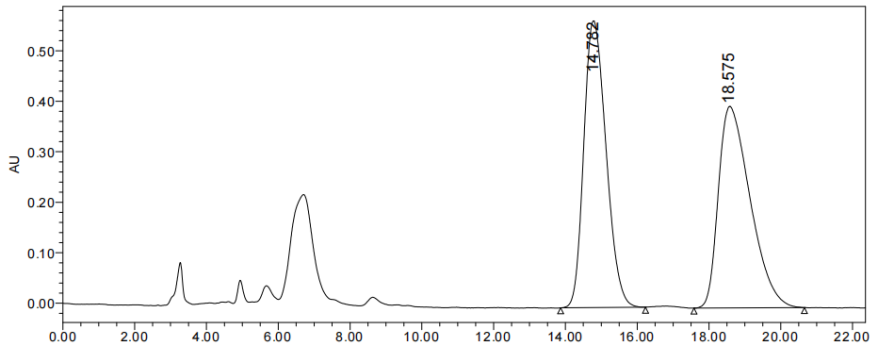
	RT (min)	Height [mAU]	Area [Mau*S]	Area%
1	24.944	260.86072	1.29937e4	49.9882
2	27.265	241.93271	2.29999e4	50.0118



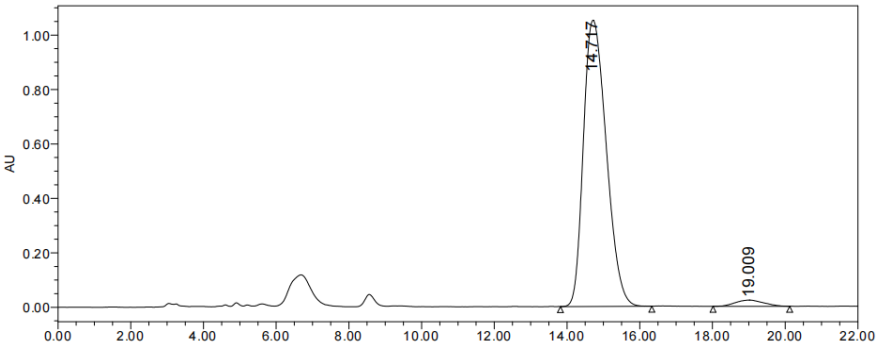
	RT (min)	Height [mAU]	Area [Mau*S]	Area%
1	24.974	49.51934	2508.04785	2.0760
2	27.196	1967.58301	1.18301e5	97.9240

Chiral HPLC spectrum of compound **3h**



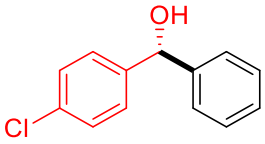


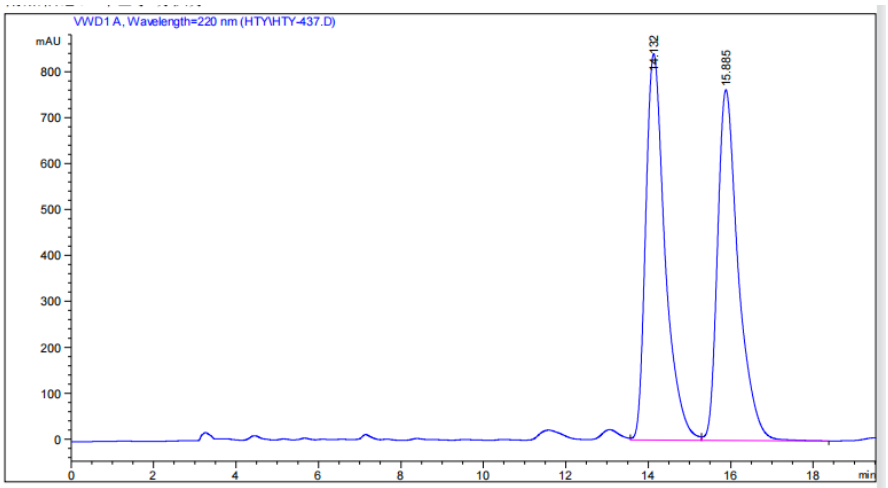
	RT (min)	Height [μV]	Area [μV*S]	Area%
1	14.782	567763	24489828	49.96
2	18.575	399125	24531034	50.04



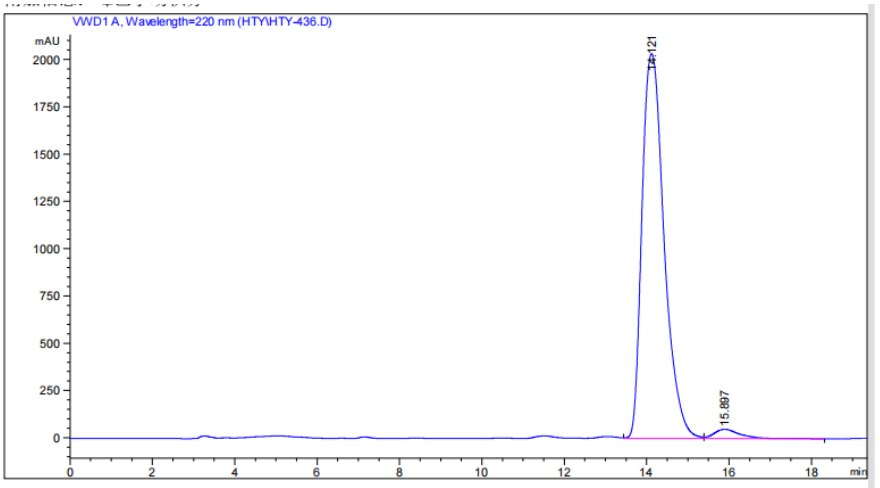
	RT (min)	Height [μV]	Area [μV*S]	Area%
1	14.717	1051605	46023421	97.34
2	19.009	23210	1256477	2.66

Chiral HPLC spectrum of compound **3i**



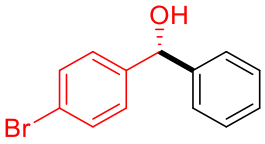


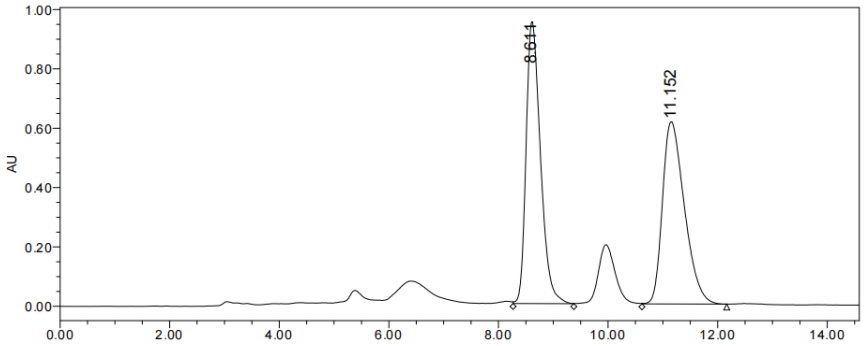
	RT (min)	Height [mAU]	Area [Mau*S]	Area%
1	14.132	839.48822	2.74261e4	50.7364
2	15.885	762.46222	2.66299e4	49.2636



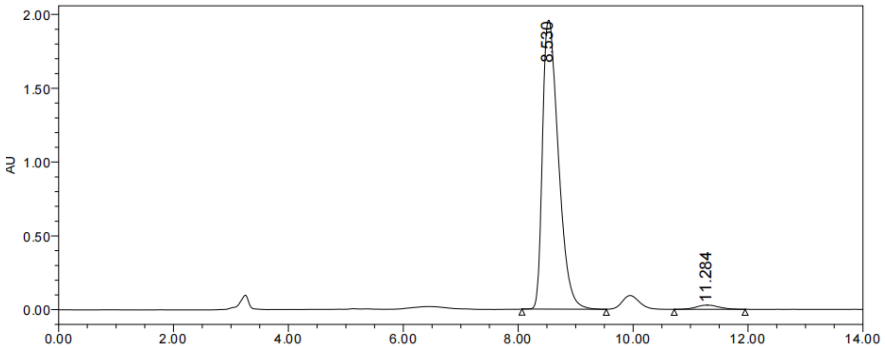
	RT (min)	Height [mAU]	Area [Mau*S]	Area%
1	14.121	2033.58569	7.58115e4	97.2621
2	15.897	48.85918	2134.05493	2.7379

Chiral HPLC spectrum of compound **3j**



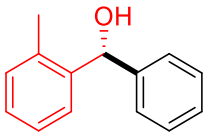


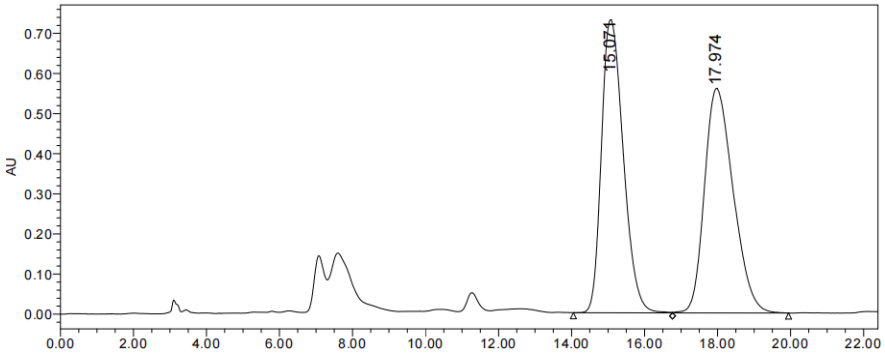
	RT (min)	Height [µV]	Area [µV*S]	Area%
1	8.611	949768	17319933	50.33
2	11.152	614121	17095827	49.67



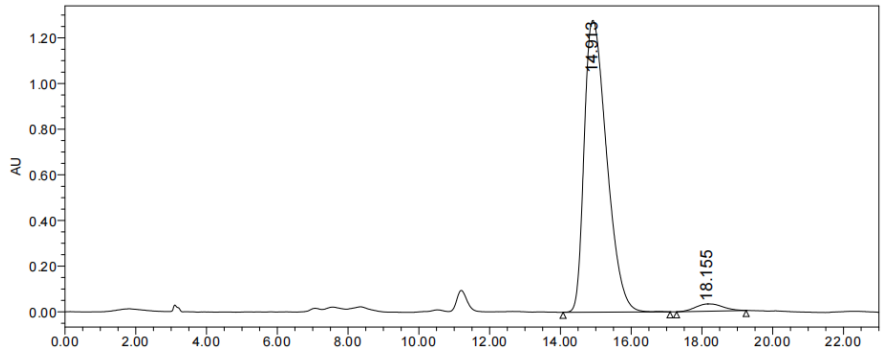
	RT (min)	Height [µV]	Area [µV*S]	Area%
1	8.530	1956879	37656271	97.95
2	11.284	28767	786599	2.05

Chiral HPLC spectrum of compound **3k**



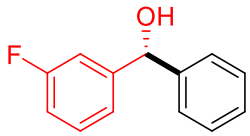


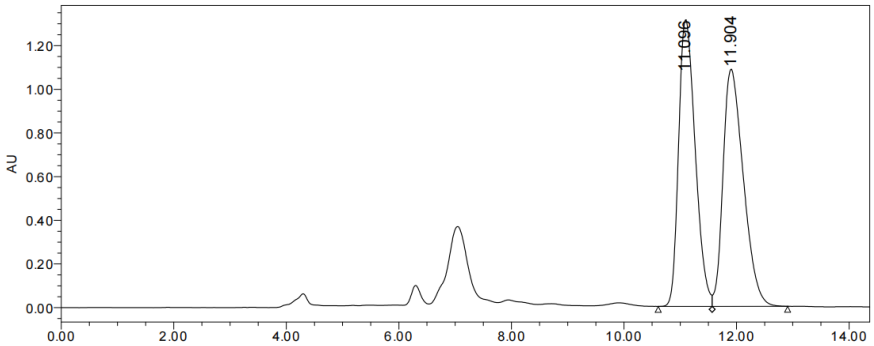
	RT (min)	Height [µV]	Area [µV*S]	Area%
1	15.071	730500	30407921	49.81
2	17.974	559868	30637423	50.19



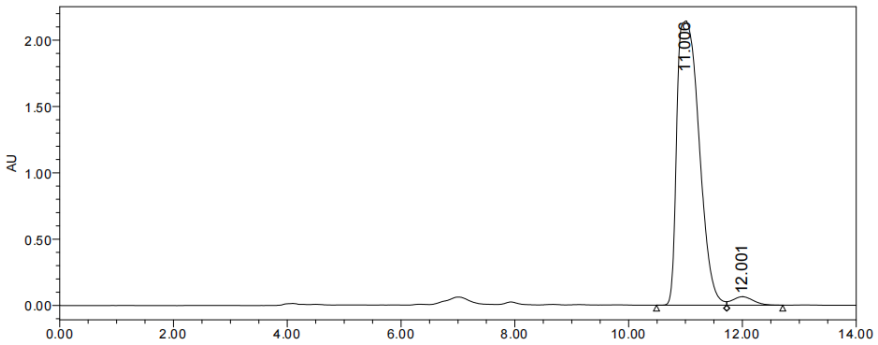
	RT (min)	Height [µV]	Area [µV*S]	Area%
1	14.913	1277539	56297506	97.08
2	18.155	31568	1693906	2.92

Chiral HPLC spectrum of compound **3l**



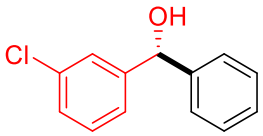


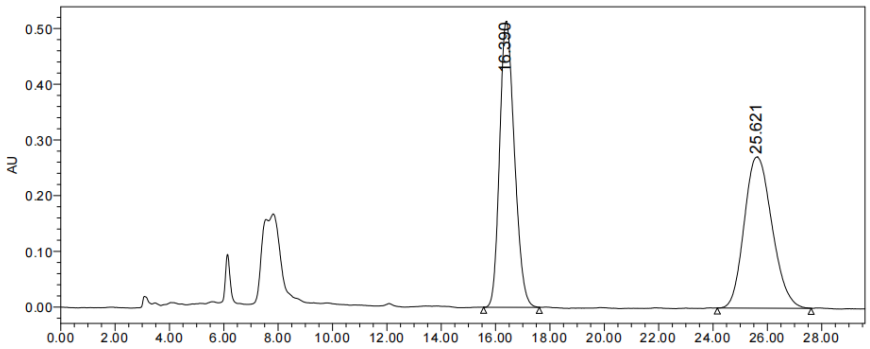
	RT (min)	Height [µV]	Area [µV*S]	Area%
1	11.096	1312421	26939398	49.65
2	11.904	1085945	27315170	50.35



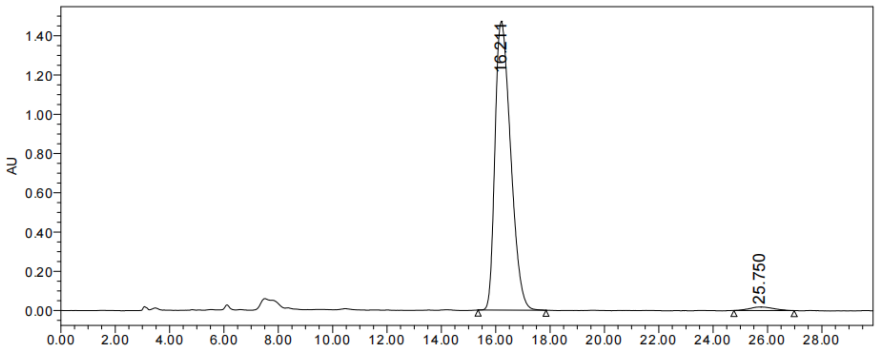
	RT (min)	Height [µV]	Area [µV*S]	Area%
1	11.006	2142464	58141248	97.27
2	12.001	64130	1631618	2.73

Chiral HPLC spectrum of compound **3m**



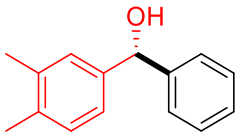


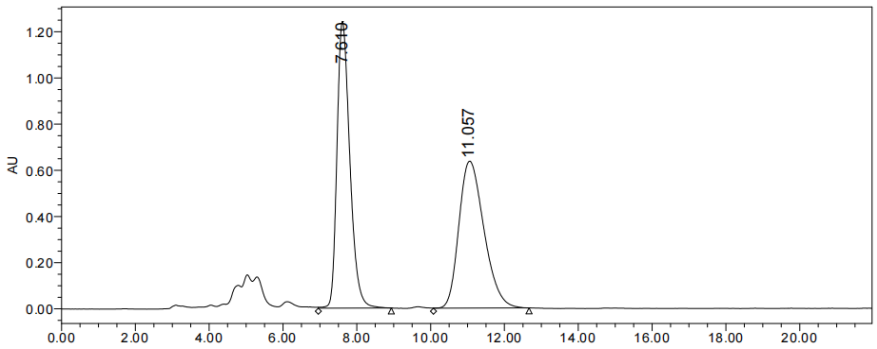
	RT (min)	Height [µV]	Area [µV*S]	Area%
1	16.390	513687	19440732	50.19
2	25.621	271615	19294786	49.81



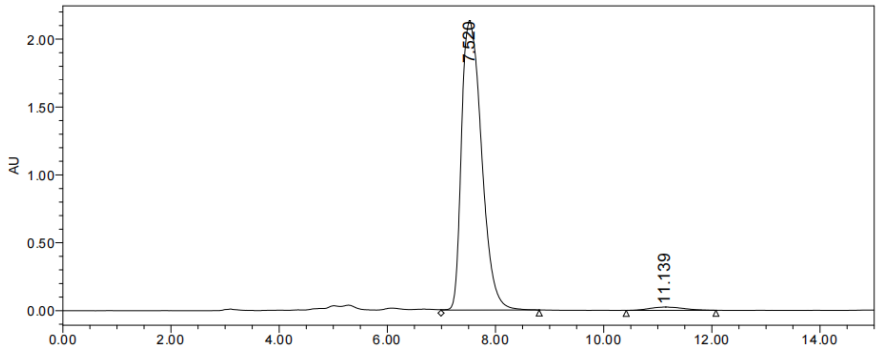
	RT (min)	Height [µV]	Area [µV*S]	Area%
1	16.211	1472582	58850536	98.13
2	25.750	18078	1118508	1.87

Chiral HPLC spectrum of compound **3n**



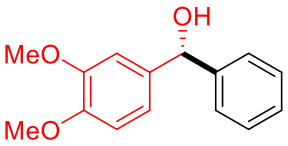


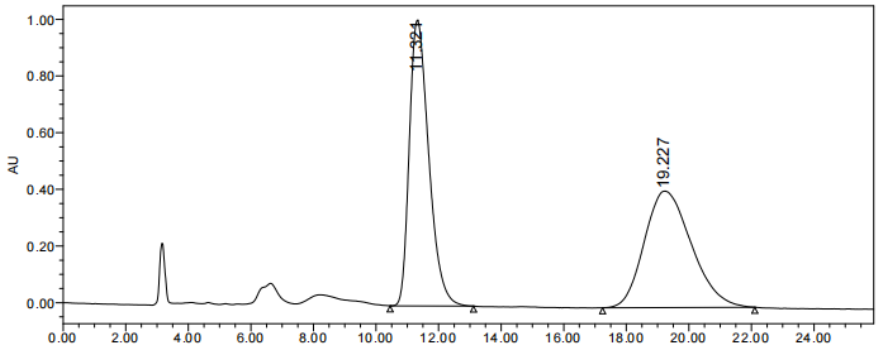
	RT (min)	Height [μV]	Area [μV*S]	Area%
1	7.610	1241933	30084525	50.08
2	11.057	636202	29994167	49.92



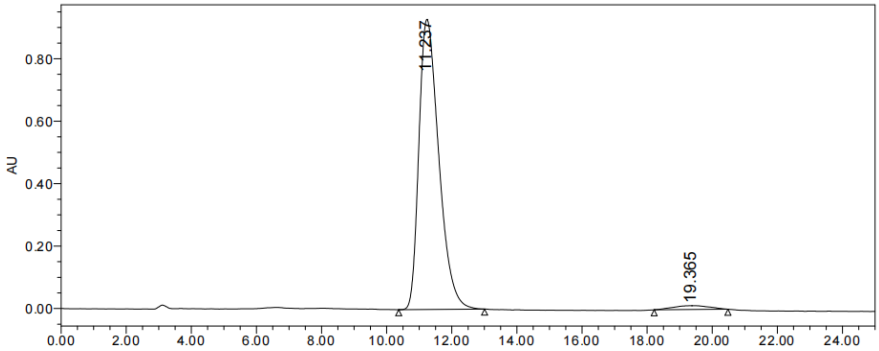
	RT (min)	Height [μV]	Area [μV*S]	Area%
1	7.520	2133862	54861667	98.12
2	11.139	24104	1051727	1.88

Chiral HPLC spectrum of compound **3o**



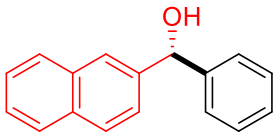


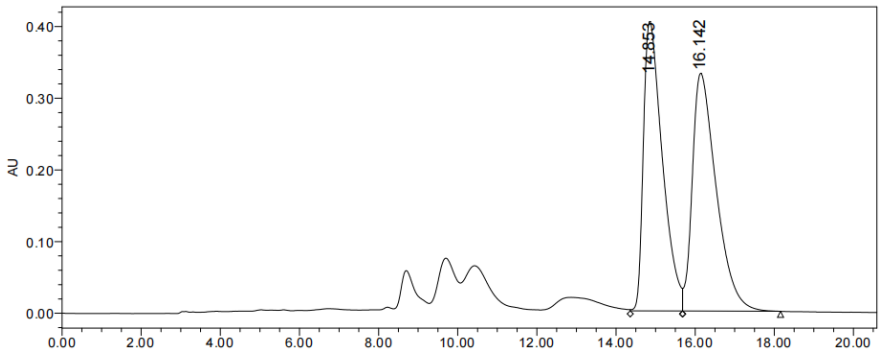
	RT (min)	Height [μV]	Area [μV*S]	Area%
1	11.321	1007859	43556269	50.38
2	19.227	410787	42903925	49.62



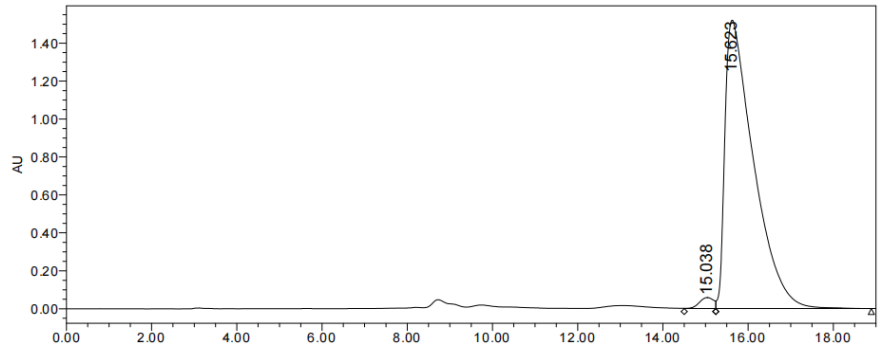
	RT (min)	Height [μV]	Area [μV*S]	Area%
1	11.237	928873	39431874	97.64
2	19.365	12163	952638	2.36

Chiral HPLC spectrum of compound **3p**



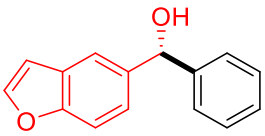


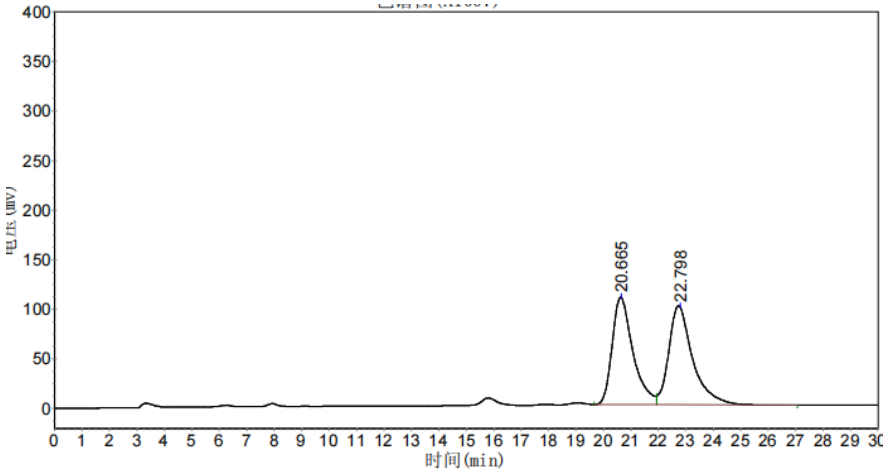
	RT (min)	Height [μV]	Area [μV*S]	Area%
1	14.853	403749	13462495	49.12
2	16.142	331753	13942183	50.88



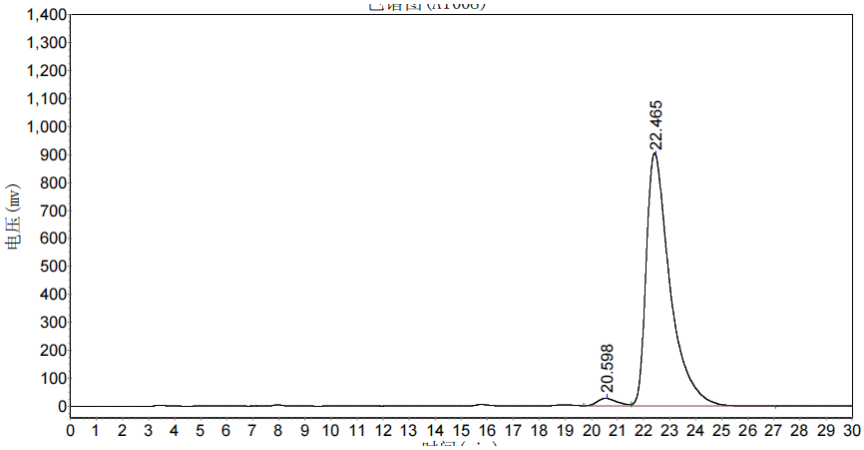
	RT (min)	Height [μV]	Area [μV*S]	Area%
1	15.038	58245	1340171	1.85
2	15.623	1519411	71139782	98.15

Chiral HPLC spectrum of compound **3q**



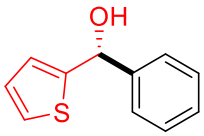


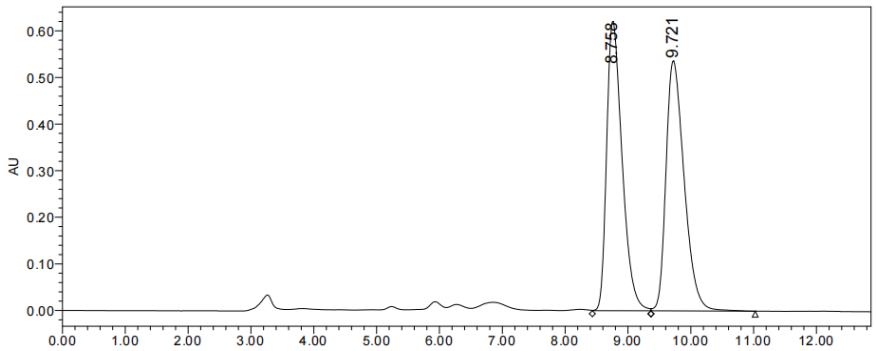
	RT (min)	Height [μV]	Area [μV*S]	Area%
1	20.665	109355	5864324	48.5255
2	22.798	100160	6220722	51.4745



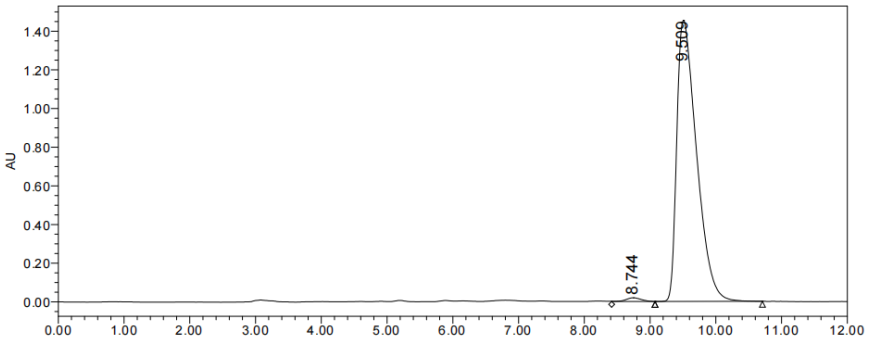
	RT (min)	Height [μV]	Area [μV*S]	Area%
1	20.598	27869	1512734	2.5716
2	22.465	901913	57312856	97.4284

Chiral HPLC spectrum of compound **3r**



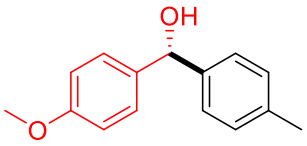


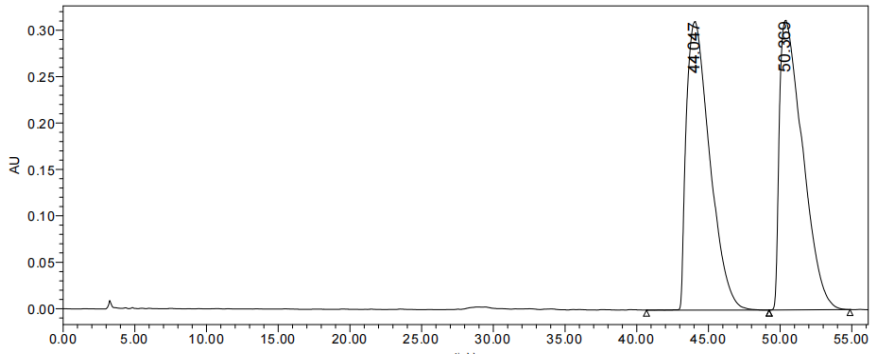
	RT (min)	Height [μV]	Area [μV*S]	Area%
1	8.758	620896	10627071	49.59
2	9.721	536648	10804198	50.41



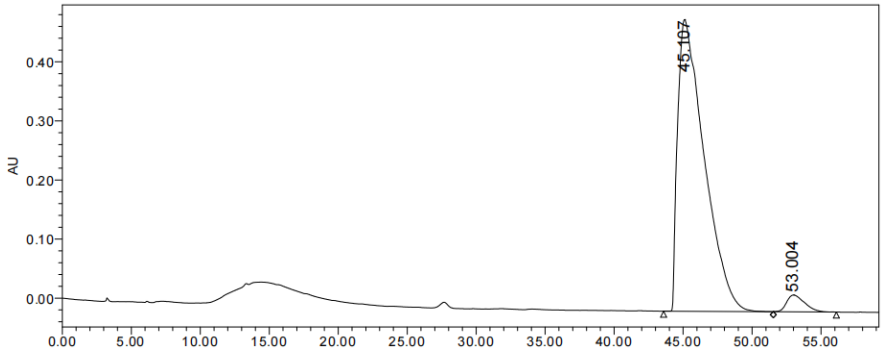
	RT (min)	Height [μV]	Area [μV*S]	Area%
1	8.744	18981	300225	0.98
2	9.509	1454124	30370532	99.02

Chiral HPLC spectrum of compound **3s**



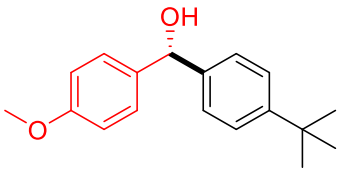


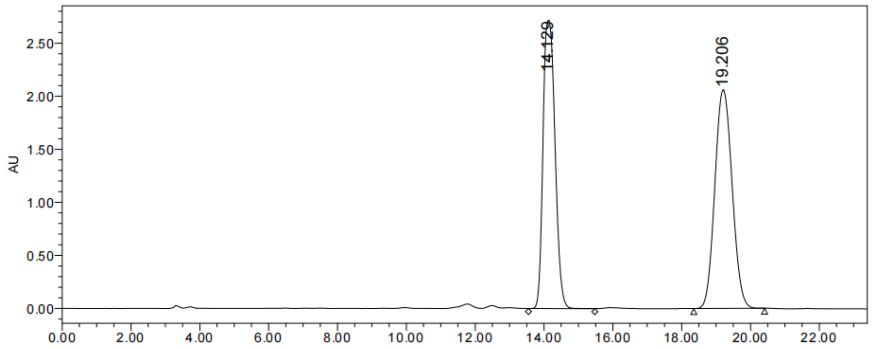
	RT (min)	Height [μV]	Area [μV*S]	Area%
1	44.047	310755	35258815	50.19
2	50.369	311933	34986504	49.81



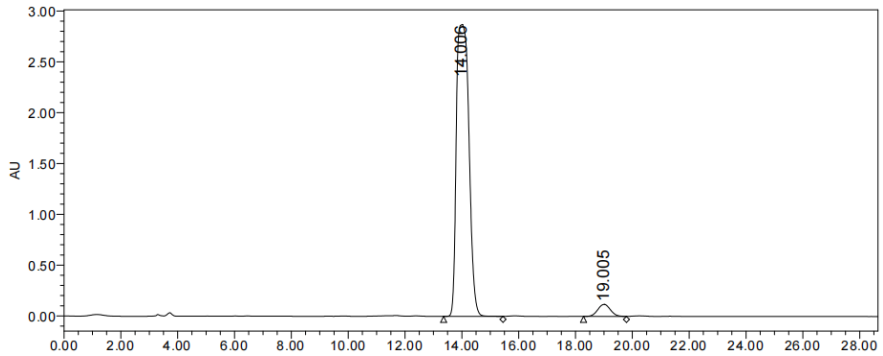
	RT (min)	Height [μV]	Area [μV*S]	Area%
1	45.107	493803	66047726	96.24
2	53.004	28476	2577047	3.76

Chiral HPLC spectrum of compound **3t**



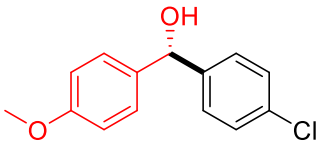


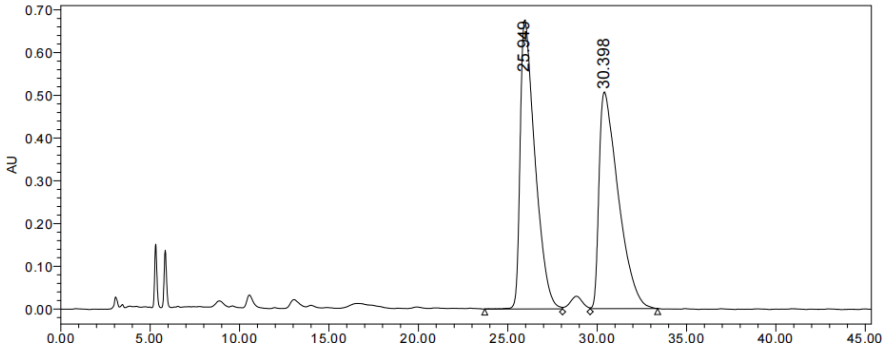
	RT (min)	Height [μV]	Area [μV*S]	Area%
1	14.129	2716649	65709515	47.74
2	19.206	2057882	71921122	52.26



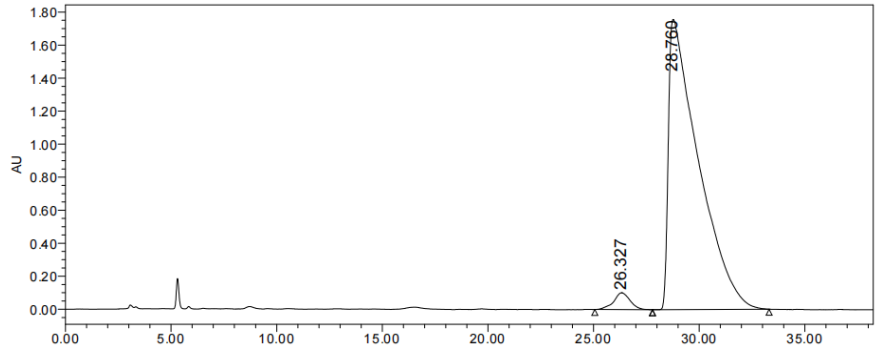
	RT (min)	Height [μV]	Area [μV*S]	Area%
1	14.006	2871335	88234927	96.04
2	19.005	117978	3636467	3.96

Chiral HPLC spectrum of compound **3u**



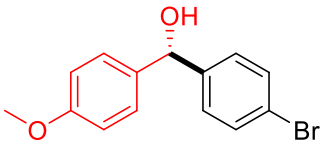


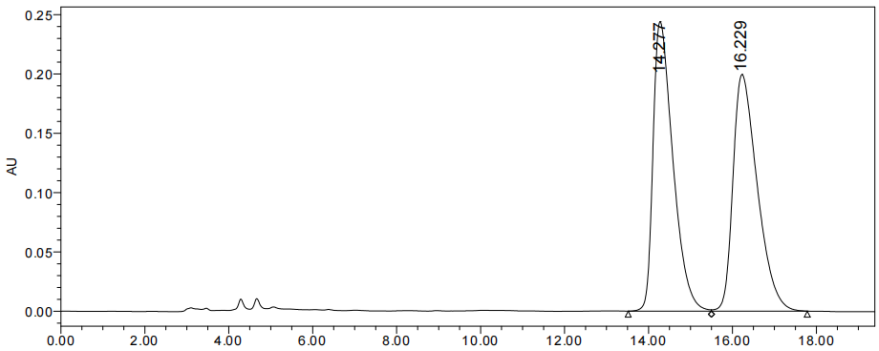
	RT (min)	Height [μV]	Area [μV*S]	Area%
1	25.949	685586	39009308	50.70
2	30.398	506692	37931603	49.30



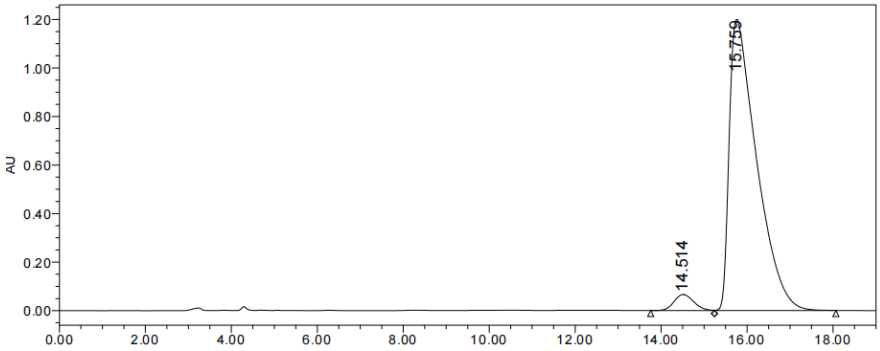
	RT (min)	Height [μV]	Area [μV*S]	Area%
1	26.327	101460	5481368	3.06
2	28.760	1757087	173603625	96.94

Chiral HPLC spectrum of compound **3v**



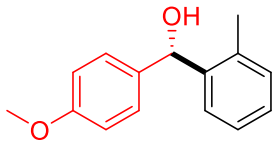


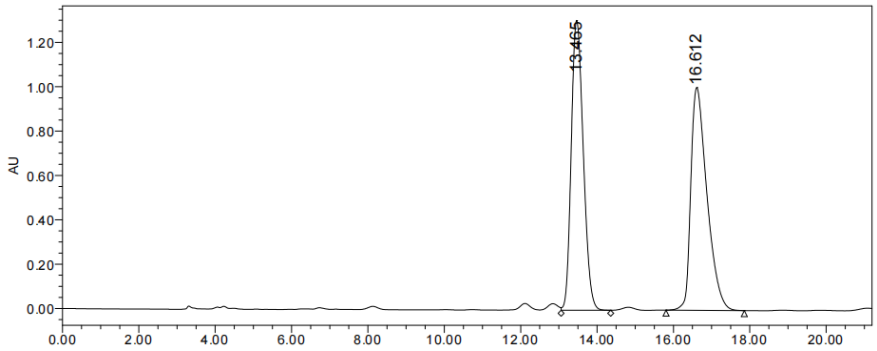
	RT (min)	Height [μV]	Area [μV*S]	Area%
1	14.277	244091	8029403	49.98
2	16.229	199422	8036236	50.02



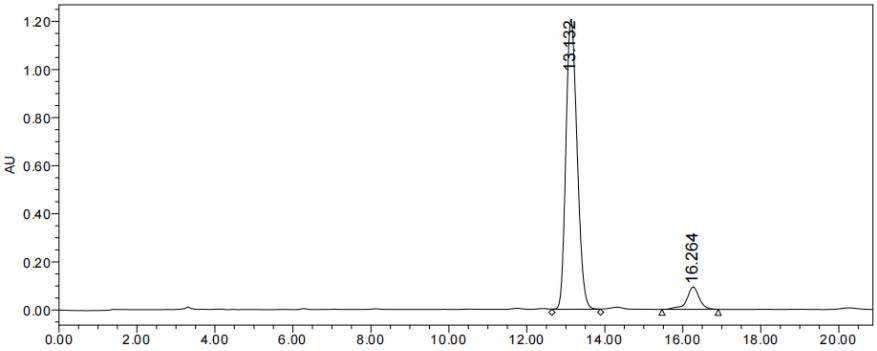
	RT (min)	Height [μV]	Area [μV*S]	Area%
1	14.514	65950	2090241	3.79
2	15.759	1199045	53019632	96.21

Chiral HPLC spectrum of compound **3w**



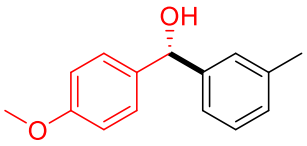


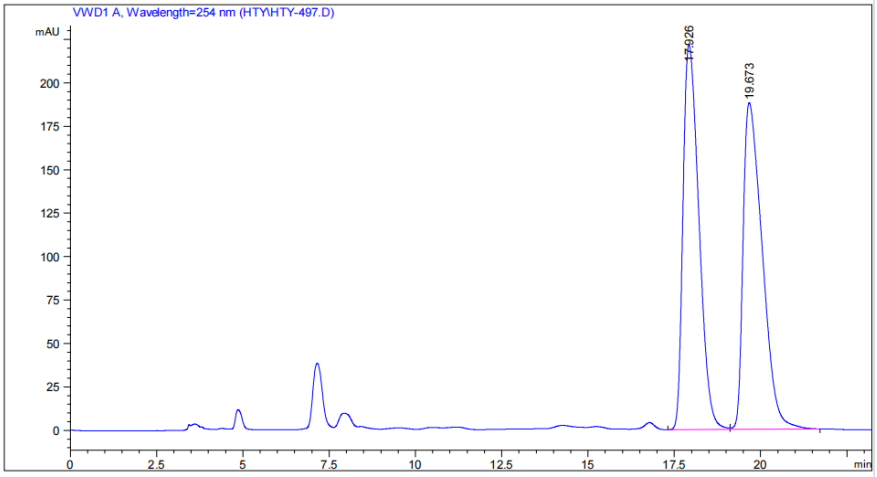
	RT (min)	Height [μV]	Area [μV*S]	Area%
1	13.465	1306383	28621012	49.25
2	16.612	1004778	29497997	50.75



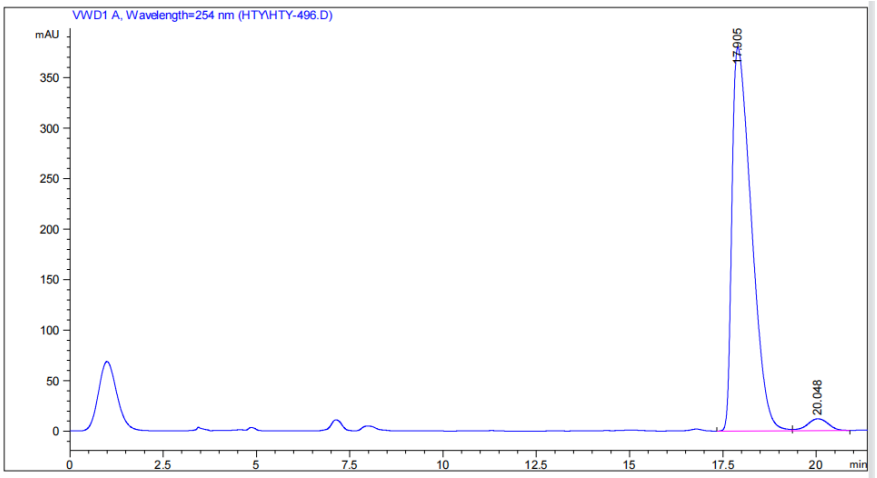
	RT (min)	Height [μV]	Area [μV*S]	Area%
1	13.132	1205285	24048058	92.08
2	16.264	92737	2067017	7.92

Chiral HPLC spectrum of compound **3x**



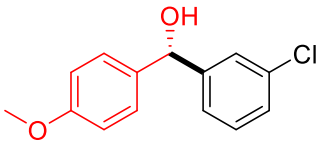


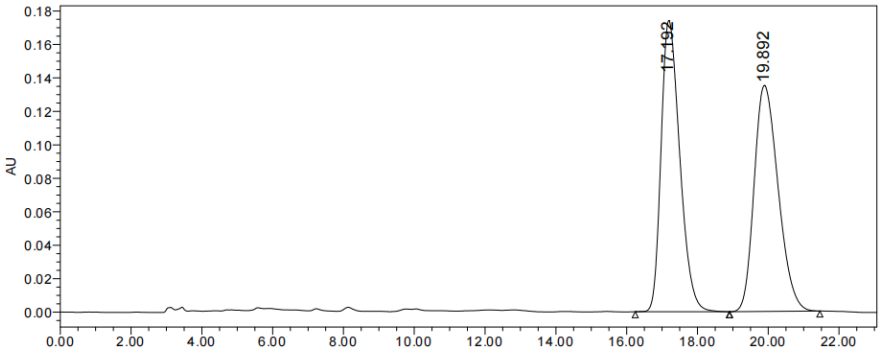
	RT (min)	Height [mAU]	Area [Mau*S]	Area%
1	17.926	221.53233	7092.17432	49.5021
2	19.673	187.93378	7234.84033	50.4979



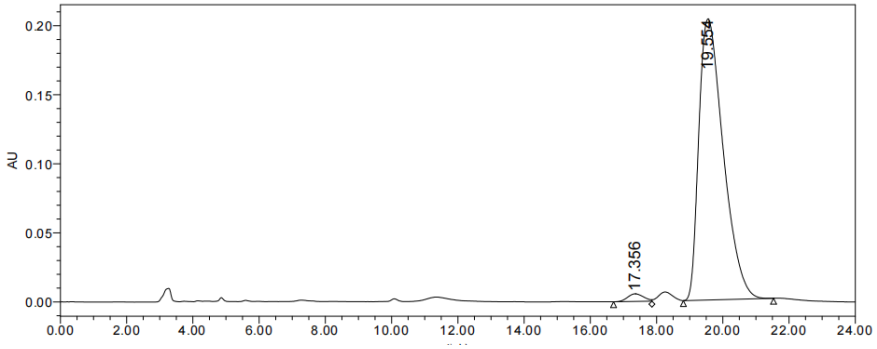
	RT (min)	Height [mAU]	Area [Mau*S]	Area%
1	17.905	379.44431	1.37276e4	96.8522
2	20.048	11.57677	446.15497	3.1478

Chiral HPLC spectrum of compound **3y**



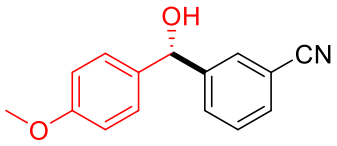


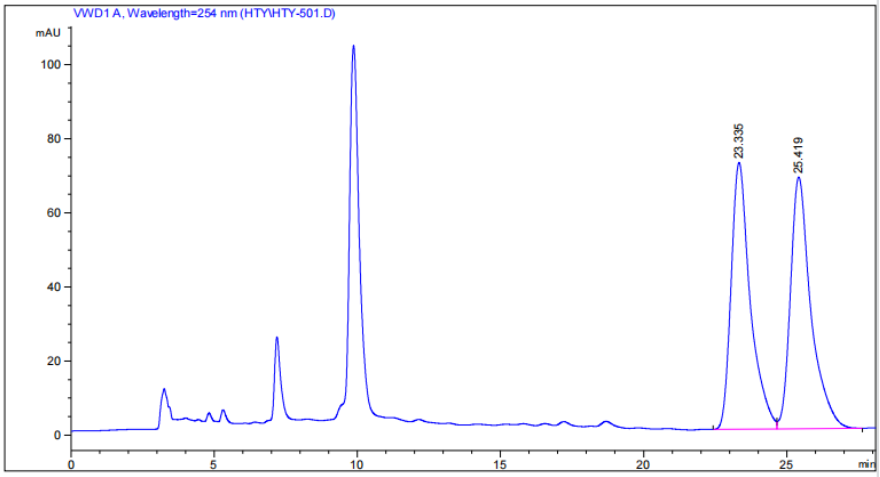
	RT (min)	Height [µV]	Area [µV*S]	Area%
1	17.192	174045	6386665	50.05
2	19.892	135054	6373334	49.95



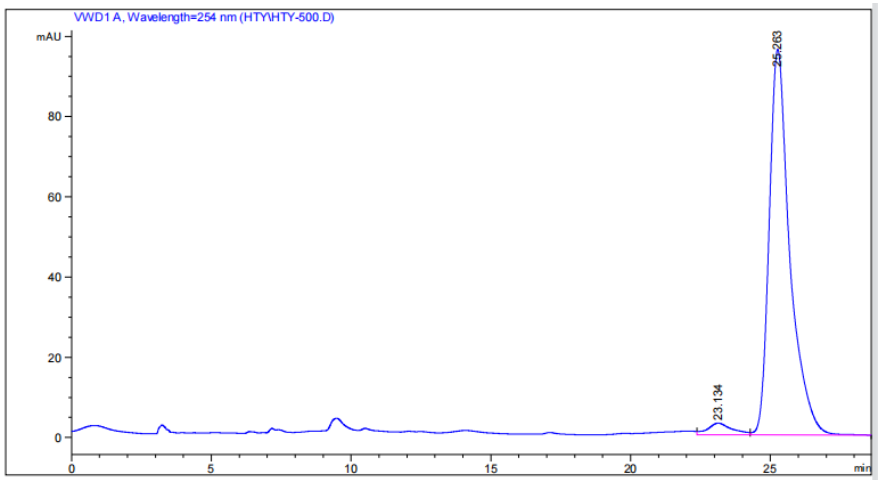
	RT (min)	Height [µV]	Area [µV*S]	Area%
1	17.356	5532	185483	1.75
2	19.554	203545	10425632	98.25

Chiral HPLC spectrum of compound **3z**



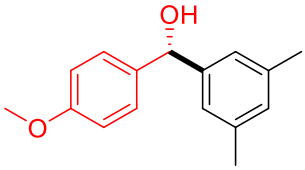


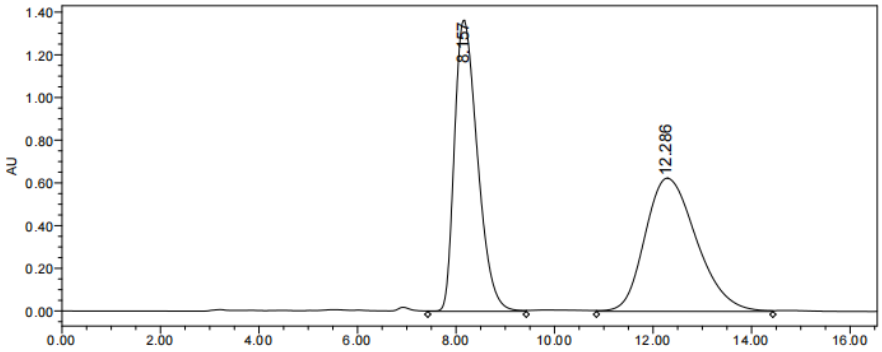
	RT (min)	Height [mAU]	Area [Mau*S]	Area%
1	23.335	71.97838	3349.51807	49.7591
2	25.419	67.91109	3381.94531	50.2409



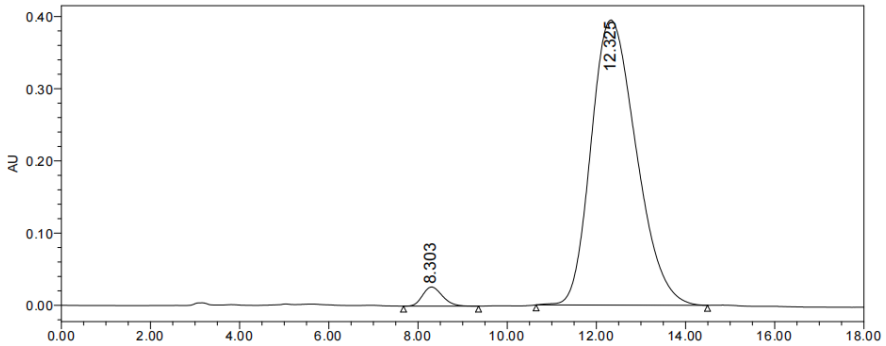
	RT (min)	Height [mAU]	Area [Mau*S]	Area%
1	23.134	2.93562	179.79250	3.5153
2	25.263	96.07359	4934.76514	96.4847

Chiral HPLC spectrum of compound **3aa**



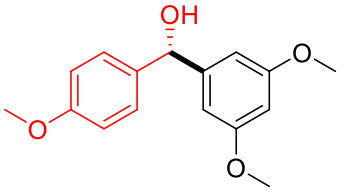


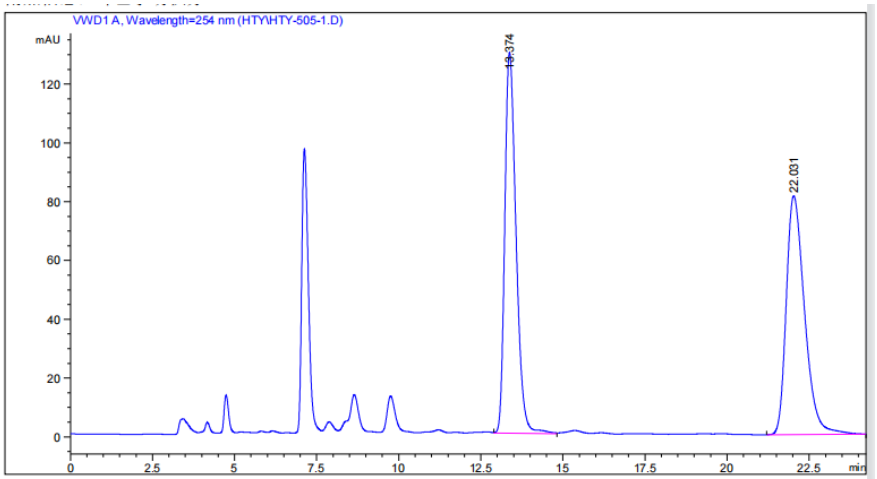
	RT (min)	Height [µV]	Area [µV*S]	Area%
1	8.157	1362824	44284832	49.41
2	12.286	623726	45350352	50.59



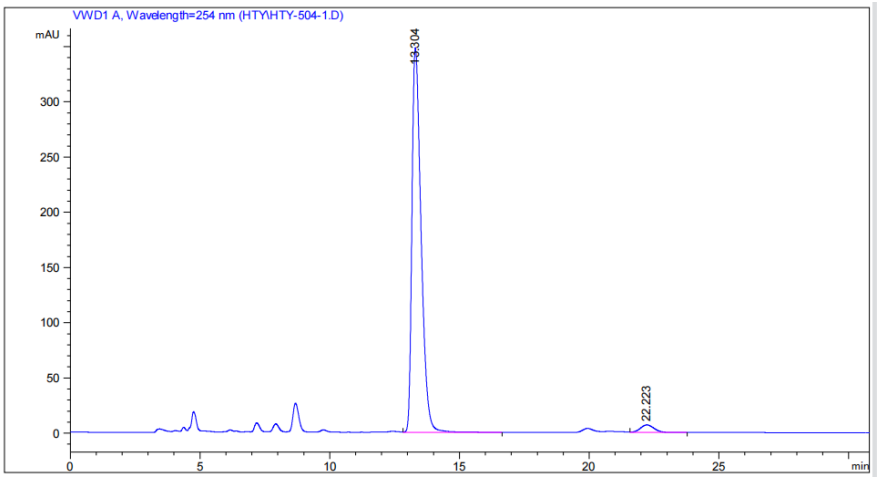
	RT (min)	Height [µV]	Area [µV*S]	Area%
1	8.303	26472	816488	2.86
2	12.325	394622	27761259	97.14

Chiral HPLC spectrum of compound **3ab**



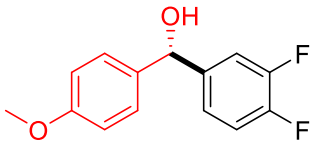


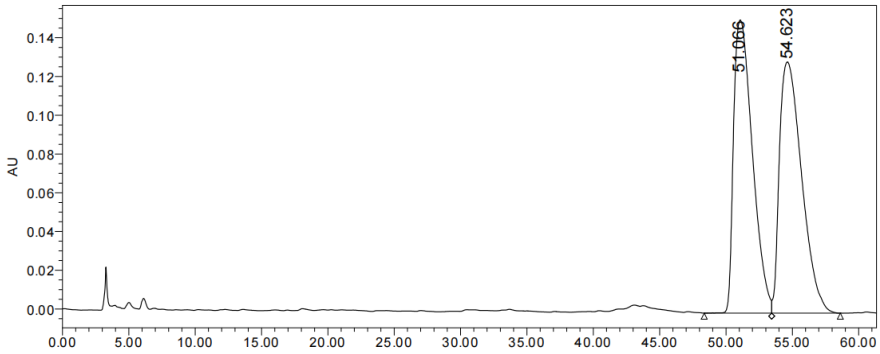
	RT (min)	Height [mAU]	Area [Mau*S]	Area%
1	13.374	129.55150	3083.76953	49.5145
2	22.031	81.23961	3144.24463	50.4855



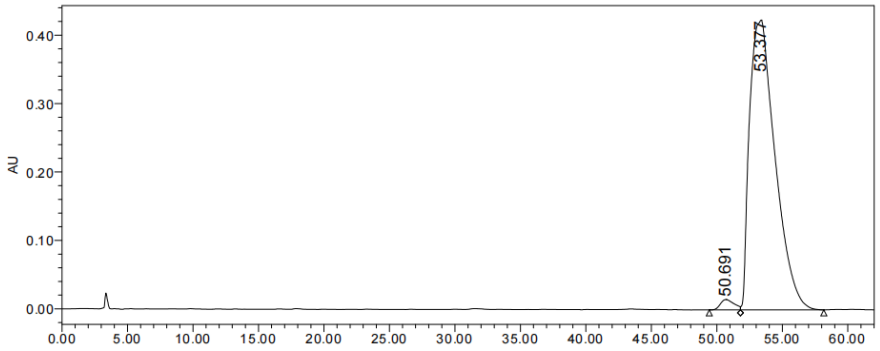
	RT (min)	Height [mAU]	Area [Mau*S]	Area%
1	13.304	348.47696	8509.54492	97.0544
2	22.223	6.90137	258.26291	2.9456

Chiral HPLC spectrum of compound **3ac**



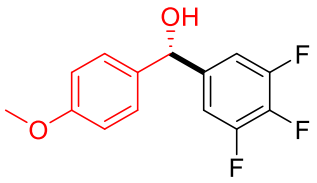


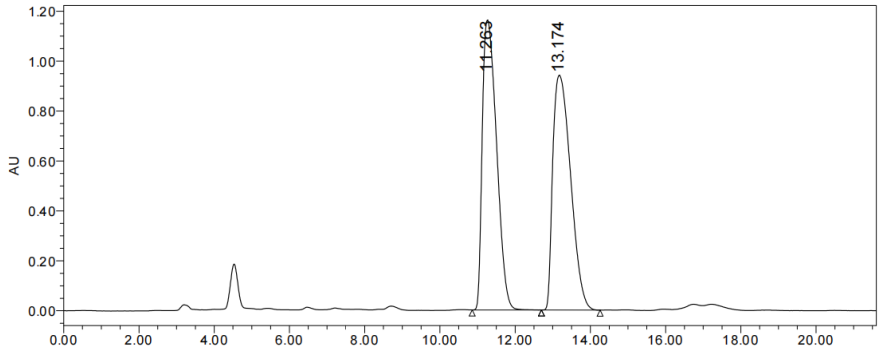
	RT (min)	Height [μV]	Area [μV*S]	Area%
1	51.066	151245	14928268	49.68
2	54.623	129602	15119883	50.32



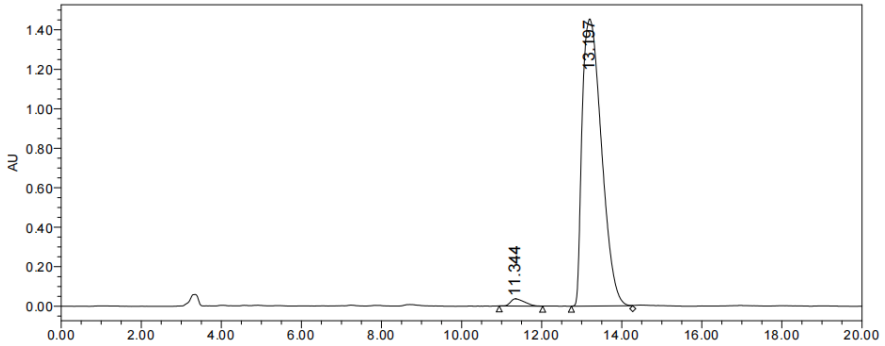
	RT (min)	Height [μV]	Area [μV*S]	Area%
1	50.691	15084	1093454	1.87
2	53.377	423412	57383946	98.13

Chiral HPLC spectrum of compound **3ad**





	RT (min)	Height [μV]	Area [μV*S]	Area%
1	11.263	1160838	30642351	49.72
2	13.174	940134	30989703	50.28



	RT (min)	Height [μV]	Area [μV*S]	Area%
1	11.344	36547	877895	1.77
2	13.197	1453411	48618733	98.23