Supporting Information

1. General Experiments

NMR spectra were recorded on an Agilent-NMR-VNMRs 400 MHz spectrometer. Chemical shifts are reported in parts per million (ppm) and referenced to residual proton of $CDCl_3$ (7.26 ppm) or DMSO-d_6 (2.50 ppm) for ^1H NMR, and carbon resonance of $CDCl_3$ (77.16 ppm) or DMSO-d_6 (39.52 ppm) for ^{13}C NMR. GC-MS analyses were performed with an Agilent 8890-5977BGCMSD spectrometer. High-resolution mass spectrometry used electro-spraying ionization (ESI) on a Waters G2-Xs QTof. Column chromatography or preparative thin-layer chromatography (TLC) was performed with Qing Dao silica gel. All reagents and solvents were used directly as purchased. DMSO-d_6 (99.8% deuterium, containing 0.03% (v/v) TMS), CD_3CN (99.8% deuterium, containing 0.03% (v/v) TMS), CD_3OD (99.8% deuterium, containing 0.03% (v/v) TMS), CH_3OD (99.0% deuterium), and CD_3OH (99.8% deuterium, containing 0.03% (v/v) TMS) were used directly as purchased in deuteration reactions.

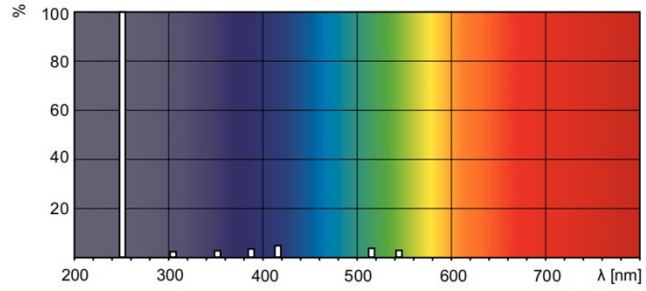
2. Supplement Figures and Tables

Figure S1. Reaction setup.

(a) Photoreactors with household UV lamps (4*8 W). (b) Emission spectrum of the UV-C light (254 nm), Philips TUV G8 T5, 8 W. (c) Emission spectrum of the UV-A light (365 nm), Philips TL 8W, 8 W

(a)

(b)



(c)

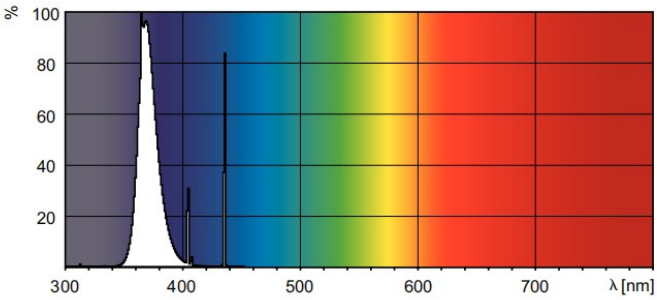
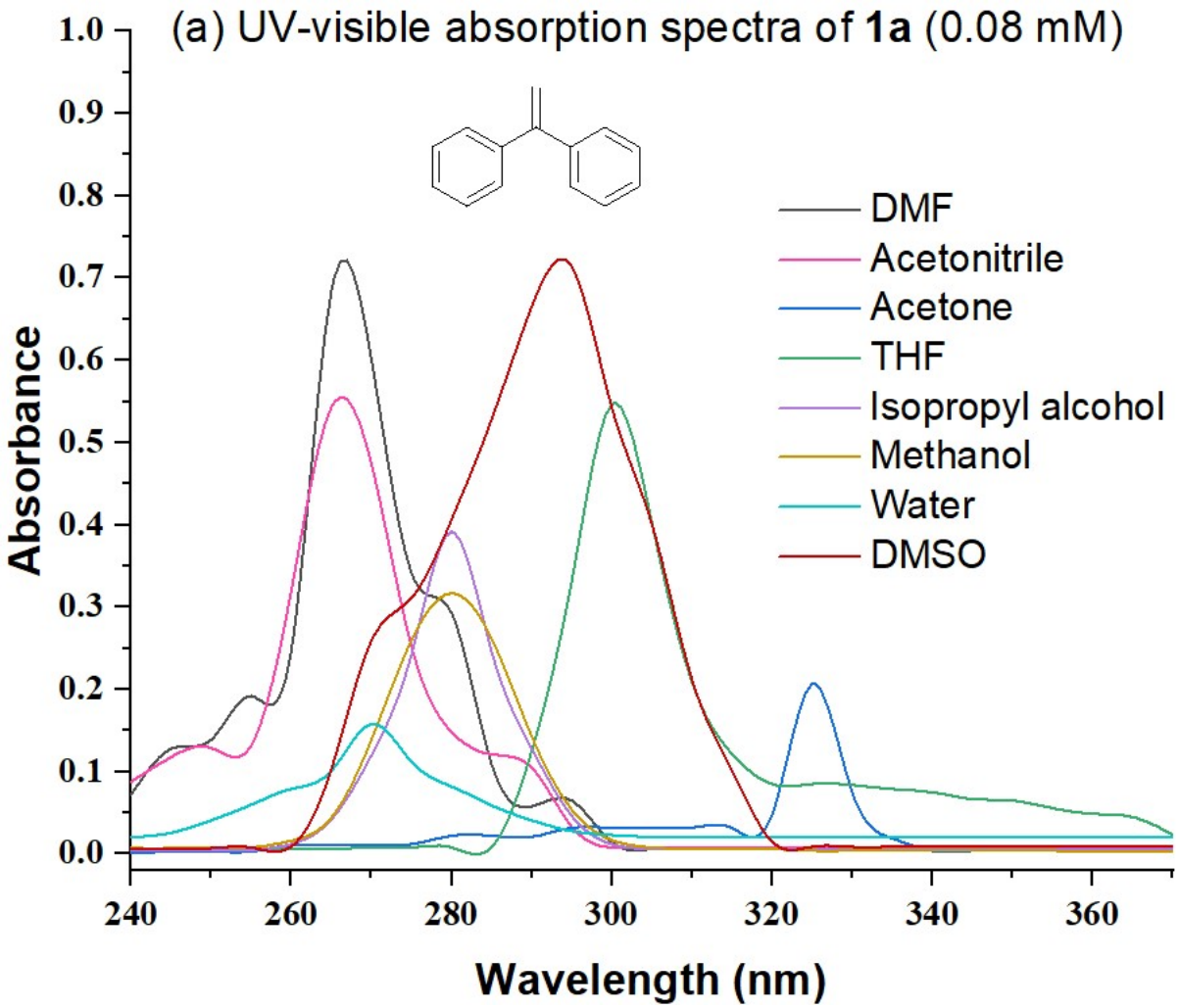
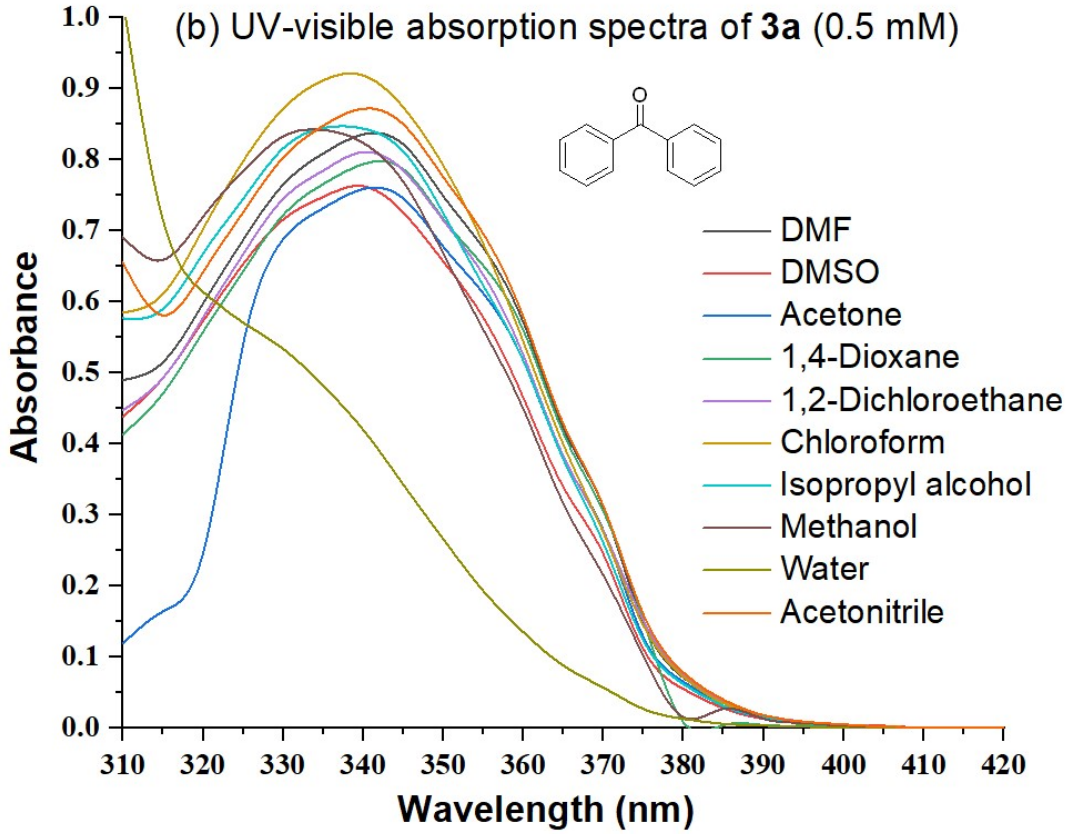
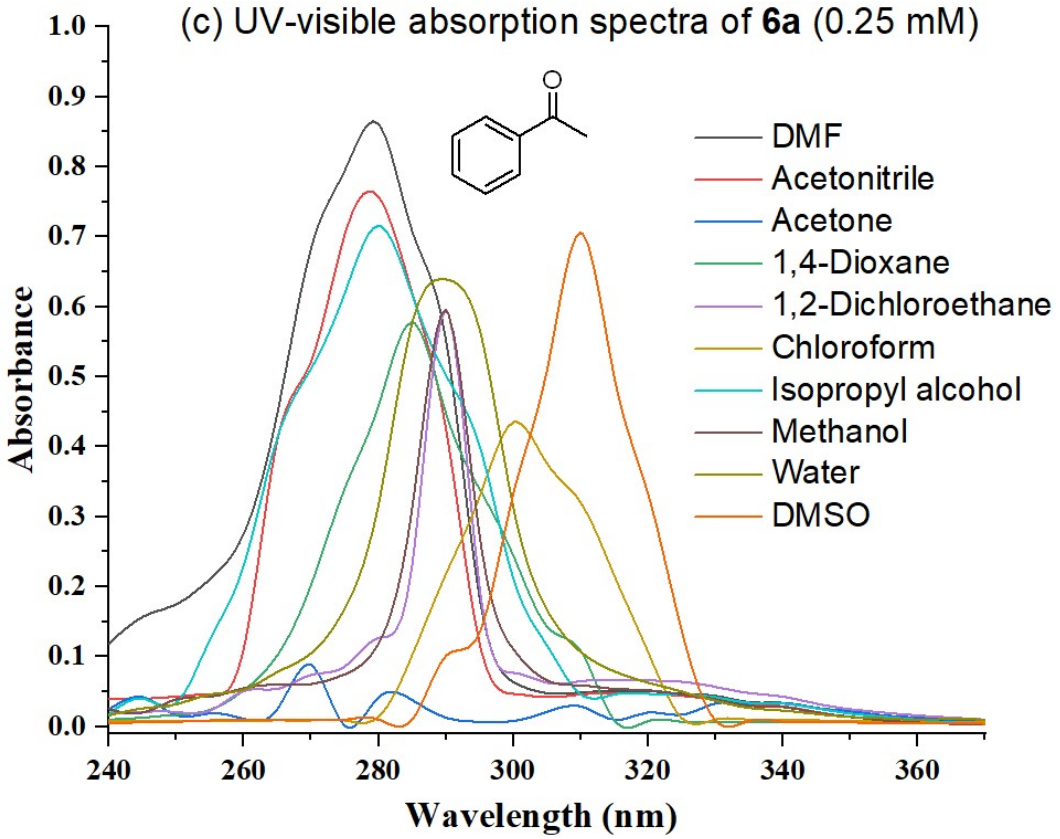
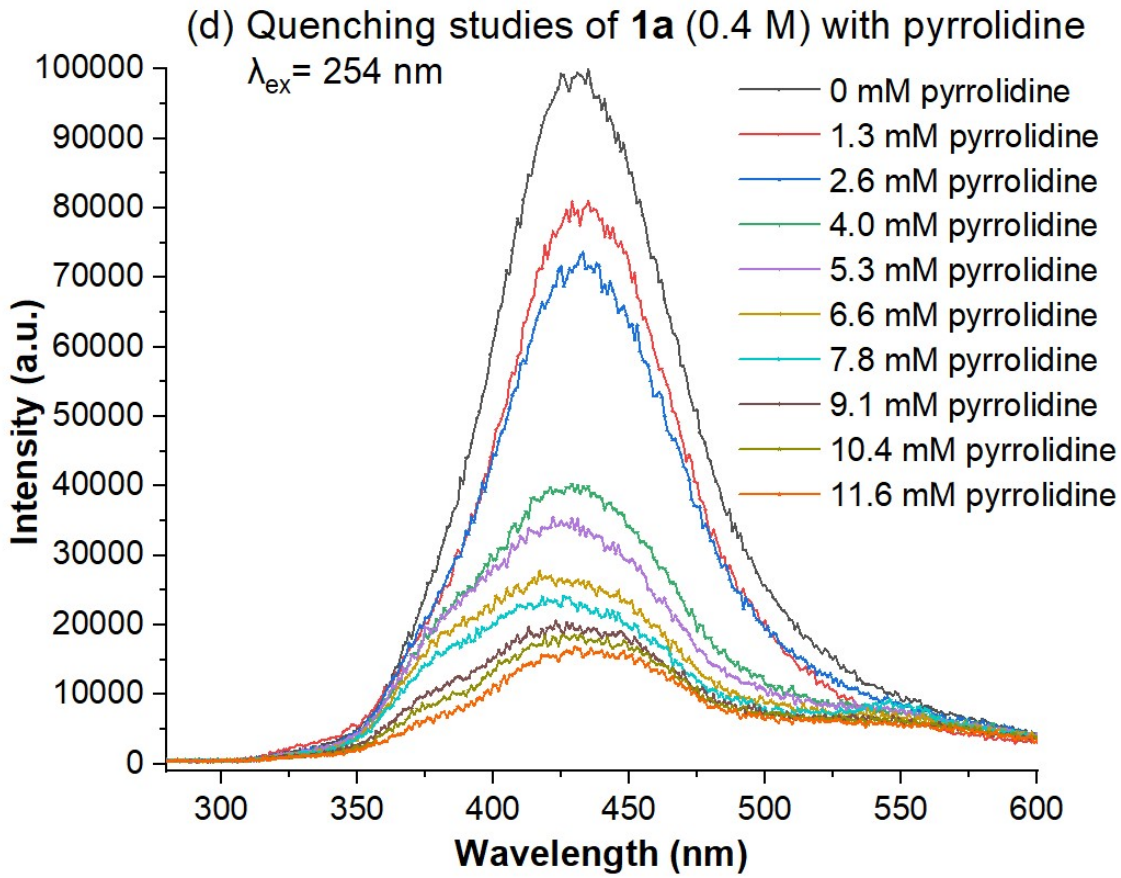


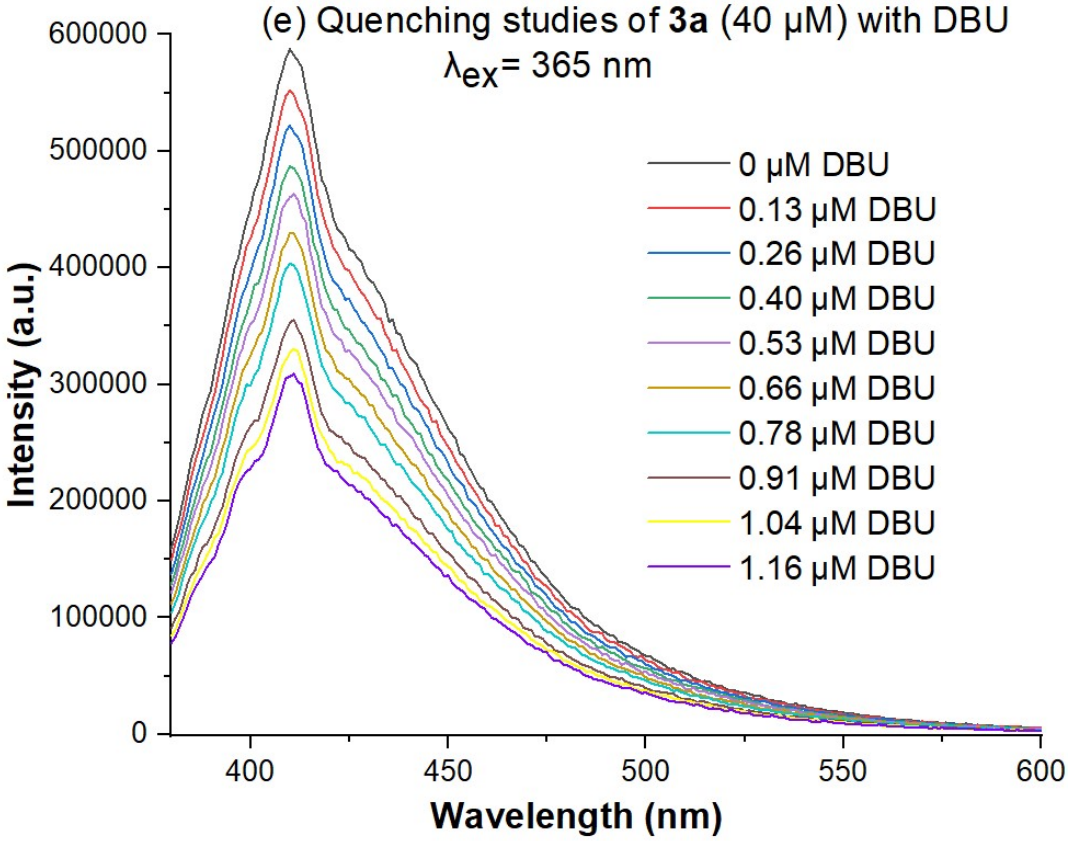
Figure S2. UV-visible absorption spectra and fluorescence quenching studies.
(a) UV-visible absorption spectra of 1a (0.08 mM). (b) UV-visible absorption spectra of 3a (0.5 mM). (c) UV-visible absorption spectra of 6a (0.25 mM). (d) Fluorescence quenching of 1a by pyrrolidine in DMF. (e) Fluorescence quenching of 3a by DBU in MeCN. (f) Fluorescence quenching of 3a by Cs_2CO_3 in MeOH. (g) Fluorescence quenching of 6a by pyrrolidine in DMF. (h) Fluorescence quenching of 1a by KOH in DMF. (i) Fluorescence quenching of 6a by KOH in DMF.

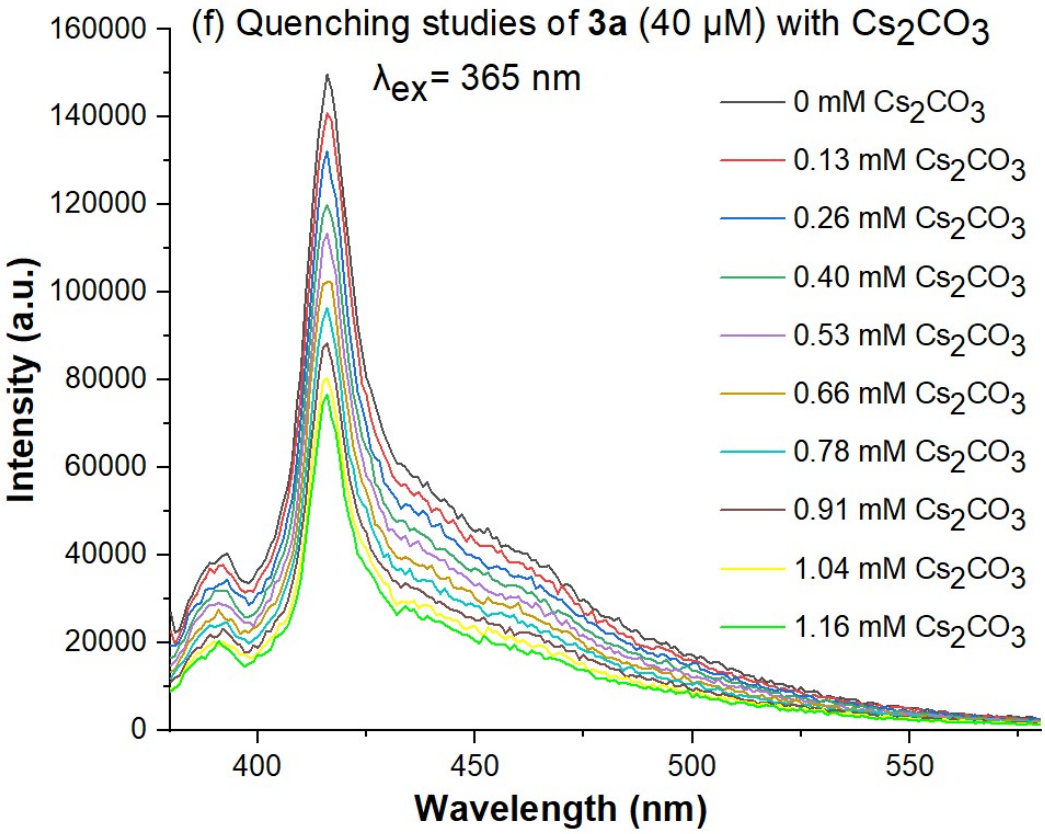


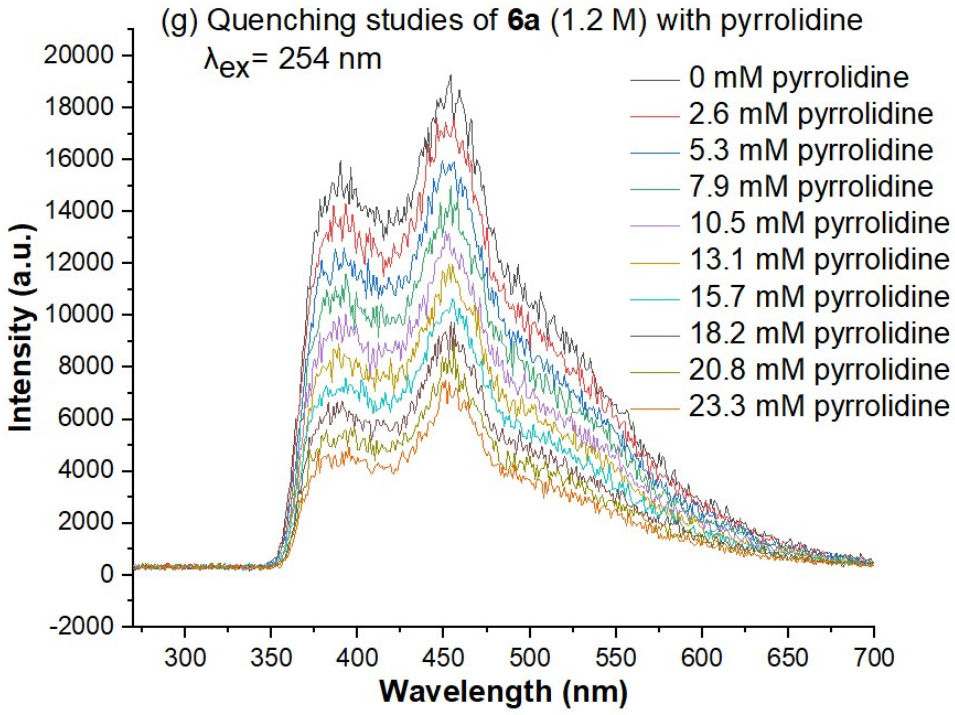

(b) UV-visible absorption spectra of **3a** (0.5 mM)
Absorbance
Wavelength (nm)
DMF
DMSO
Acetone
1,4-Dioxane
1,2-Dichloroethane
Chloroform
Isopropyl alcohol
Methanol
Water
Acetonitrile

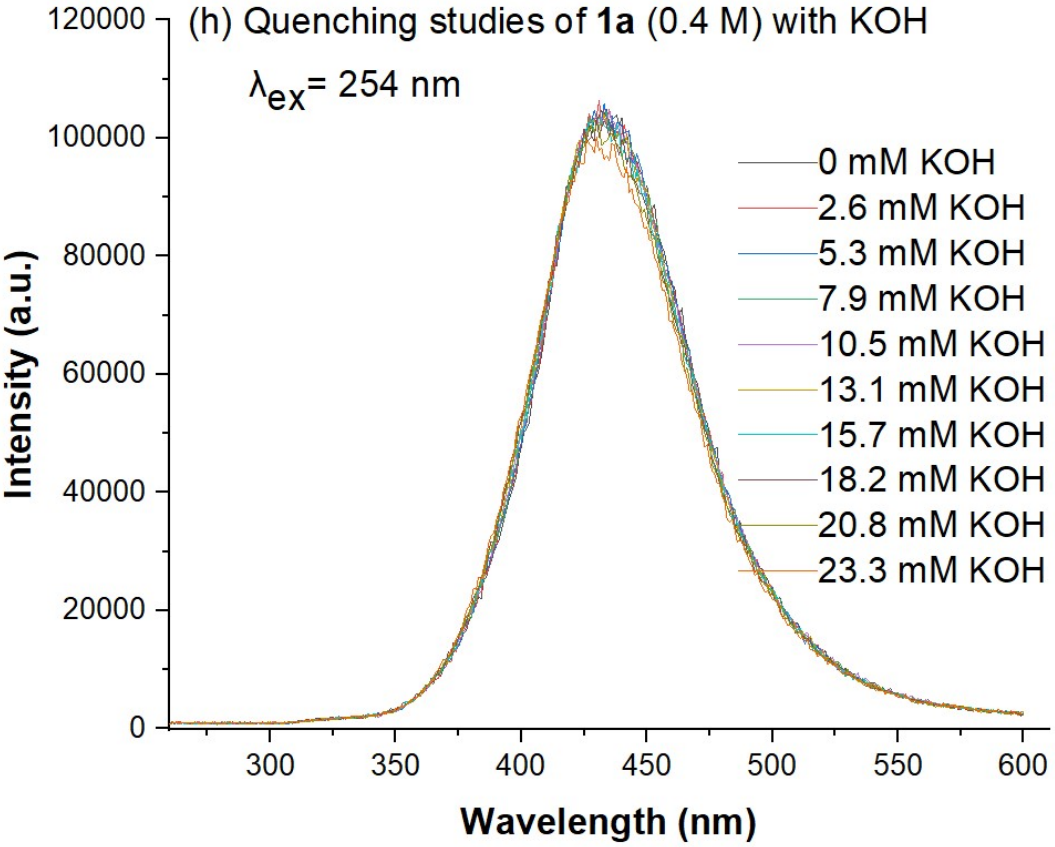

(c) UV-visible absorption spectra of **6a** (0.25 mM)
Absorbance
Wavelength (nm)
DMF
Acetonitrile
Acetone
1,4-Dioxane
1,2-Dichloroethane
Chloroform
Isopropyl alcohol
Methanol
Water
DMSO


(d) Quenching studies of **1a** (0.4 M) with pyrrolidine
λ_{ex}= 254 nm
Intensity (a.u.)
Wavelength (nm)
0 mM pyrrolidine
1.3 mM pyrrolidine
2.6 mM pyrrolidine
4.0 mM pyrrolidine
5.3 mM pyrrolidine
6.6 mM pyrrolidine
7.8 mM pyrrolidine
9.1 mM pyrrolidine
10.4 mM pyrrolidine
11.6 mM pyrrolidine


(e) Quenching studies of **3a** (40 μM) with DBU
λ_{ex}= 365 nm
Intensity (a.u.)
Wavelength (nm)
0 μM DBU
0.13 μM DBU
0.26 μM DBU
0.40 μM DBU
0.53 μM DBU
0.66 μM DBU
0.78 μM DBU
0.91 μM DBU
1.04 μM DBU
1.16 μM DBU


(f) Quenching studies of 3a (40 μM) with Cs2CO3
λex= 365 nm
0 mM Cs2CO3
0.13 mM Cs2CO3
0.26 mM Cs2CO3
0.40 mM Cs2CO3
0.53 mM Cs2CO3
0.66 mM Cs2CO3
0.78 mM Cs2CO3
0.91 mM Cs2CO3
1.04 mM Cs2CO3
1.16 mM Cs2CO3
Intensity (a.u.)
Wavelength (nm)


(g) Quenching studies of 6a (1.2 M) with pyrrolidine
λex= 254 nm
0 mM pyrrolidine
2.6 mM pyrrolidine
5.3 mM pyrrolidine
7.9 mM pyrrolidine
10.5 mM pyrrolidine
13.1 mM pyrrolidine
15.7 mM pyrrolidine
18.2 mM pyrrolidine
20.8 mM pyrrolidine
23.3 mM pyrrolidine
Intensity (a.u.)
Wavelength (nm)


(h) Quenching studies of **1a** (0.4 M) with KOH
λ_{ex}= 254 nm
0 mM KOH
2.6 mM KOH
5.3 mM KOH
7.9 mM KOH
10.5 mM KOH
13.1 mM KOH
15.7 mM KOH
18.2 mM KOH
20.8 mM KOH
23.3 mM KOH
Intensity (a.u.)
Wavelength (nm)
120000
100000
80000
60000
40000
20000
0
300
350
400
450
500
550
600

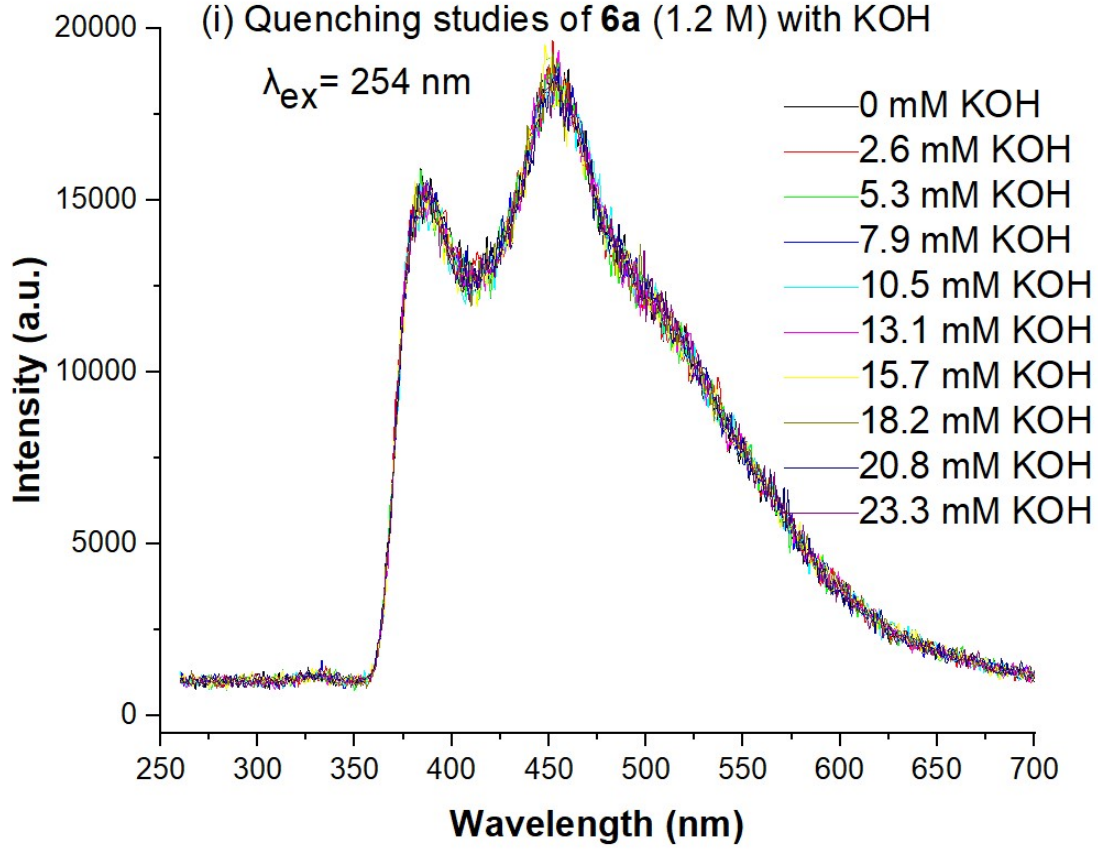
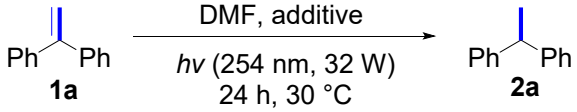

(i) Quenching studies of **6a** (1.2 M) with KOH
λ_{ex}= 254 nm
0 mM KOH
2.6 mM KOH
5.3 mM KOH
7.9 mM KOH
10.5 mM KOH
13.1 mM KOH
15.7 mM KOH
18.2 mM KOH
20.8 mM KOH
23.3 mM KOH
Intensity (a.u.)
Wavelength (nm)
20000
15000
10000
5000
0
250
300
350
400
450
500
550
600
650
700

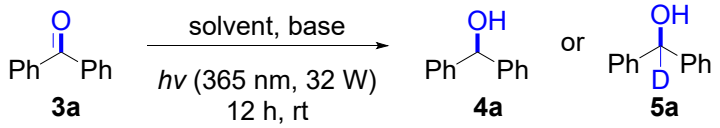
Table S1. Optimization of conditions for the reduction of olefins 1a[a]



Entry	Additive/equiv	Light	Yield [%]
1	pyrrolidine/2+K_2CO_3/2	UV-C light (254 nm, 4*8 W)	49
2	pyrrolidine/2+$NaHCO_3$/2	UV-C light (254 nm, 4*8 W)	21
3	pyrrolidine/2+Cs_2CO_3/2	UV-C light (254 nm, 4*8 W)	51
4	pyrrolidine/2+Na_2SO_4/2	UV-C light (254 nm, 4*8 W)	40
5	pyrrolidine/2+$NaOCH_2CH_3$/2	UV-C light (254 nm, 4*8 W)	36
6	pyrrolidine/2+NaOH/2	UV-C light (254 nm, 4*8 W)	64
7	pyrrolidine/2+**KOH/2**	UV-C light (254 nm, 4*8 W)	**65**
8	pyrrolidine/1+KOH/2	UV-C light (254 nm, 4*8 W)	19
9	pyrrolidine/2+KOH/2	UV-C light (254 nm, 4*8 W)	65
10	pyrrolidine/3+KOH/2	UV-C light (254 nm, 4*8 W)	74
11	**pyrrolidine/4**+KOH/2	UV-C light (254 nm, 4*8 W)	**90**
12	pyrrolidine/4+KOH/2.8	UV-C light (254 nm, 4*8 W)	84
13	pyrrolidine/4+**KOH/0.7**	UV-C light (254 nm, 4*8 W)	**90 (91)**
14	pyrrolidine/4+KOH/0.7	UV-A light (365 nm, 4*8 W)	0
15	pyrrolidine/4+KOH/0.7	Purple LEDs (36 W)	0
16	pyrrolidine/4+KOH/0.7	Blue LEDs (36 W)	0
17[b]	pyrrolidine/4+KOH/0.7	UV-C light (254 nm, 4*8 W)	(89)

[a] Reaction conditions: **1a** (0.2 mmol), DMF (1 mL), *hv* (254 nm, 4*8 W), air, 30 °C, 24 h, GC-MS yield with 1,3,5-trimethylbenzene as internal standard or isolated yield in parentheses after purification. [b] Under argon.

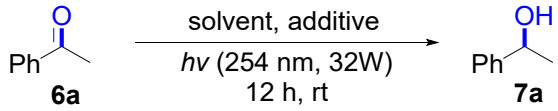
Table S2. Optimization of conditions to reduce benzophenone (**3a**).[a]



Entry	Solvent	Base/equiv	Product	Yield [%]
1	CH_3OH	-	**4a**	7
2	CH_3OH	DMAP/2	**4a**	6
3	CH_3OH	pyridine/2	**4a**	10
4	CH_3OH	DBU/1	**4a**	33
5	acetone	DBU/1	**4a**	0
6	1,4-dioxane	DBU/1	**4a**	60
7	DCE	DBU/1	**4a**	33
8	$CHCl_3$	DBU/1	**4a**	0
9	isopropanol	DBU/1	**4a**	42
10	H_2O	DBU/1	**4a**	0
11	DMSO	DBU/1	**4a**	50
12	**CH_3CN**	**DBU/1**	**4a**	**92 (93)**
13[b]	CH_3CN	DBU/1	**4a**	70
14[c]	CH_3CN	DBU/1	**4a**	5
15[d]	CH_3CN	DBU/1	**4a**	0
16[e]	CH_3CN	DBU/1	**5a**	(93)
17[e]	CD_3CN	DBU/1	**5a**	(91) (D%=82%)
18	CH_3OH	Na_2CO_3/2	**4a**	8
19	CH_3OH	K_2CO_3/2	**4a**	30
20	CH_3OH	Cs_2CO_3/2	**4a**	**88**
21	CH_3OH	NaOH/2	**4a**	11
22	DMSO	Cs_2CO_3/2	**4a**	10
23	Acetone	Cs_2CO_3/2	**4a**	9
24[e]	CH_3OH	Cs_2CO_3/2	**4a**	90
25[e]	**CD_3OD**	**Cs_2CO_3/2**	**5a**	**(95) (D%=96%)**

[a] Reaction conditions: **3a** (0.2 mmol), solvent (0.5 mL), base, *hv* (365 nm, 4*8 W), air, rt, 12 h, GC-MS yield with 1,3,5-trimethylbenzene as internal standard or isolated yield in parentheses after purification. [b] *hv* (254 nm, 4*8 W) was used. [c] Purple LEDs (36 W) was used. [d] Blue LEDs (36 W) was used. [e] Under argon.

Table S3. Optimization of conditions for the reduction of acetophenone (**6a**).[a]

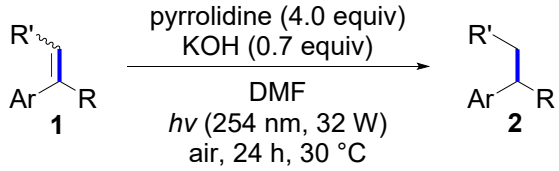


Entry	Solvent	Additive/equiv	Yield [%]
1[b]	CH_3CN (0.5 mL)	DBU/1	2
2[b]	CH_3OH (0.5 mL)	Cs_2CO_3/2	0
3	DMF (0.5 mL)	pyrrolidine/1	0
4	DMF (0.5 mL)	pyrrolidine/1+ Na_2SO_4/2	10
5	DMF (0.5 mL)	pyrrolidine/1+$NH_3{\cdot}H_2O$/2	6
6	DMF (0.5 mL)	pyrrolidine/1+$NaHCO_3$/2	6
7	DMF (0.5 mL)	pyrrolidine/1+Na_2CO_3/2	3
8	DMF (0.5 mL)	pyrrolidine/1+K_2CO_3/2	10
9	DMF (0.5 mL)	pyrrolidine/1+ Cs_2CO_3/2	19
10	DMF (0.5 mL)	pyrrolidine/1+EtONa/2	6
11	DMF (0.5 mL)	pyrrolidine/1+CH_3COONa/2	9
12	DMF (0.5 mL)	pyrrolidine/1+NaOH/2	15
13	**DMF (0.5 mL)**	**pyrrolidine/1+KOH/2**	**40**
14	MeCN (0.5 mL)	pyrrolidine/1+KOH/2	2
15	acetone (0.5 mL)	pyrrolidine/1+KOH/2	0
16	1,4-Dioxane (0.5 mL)	pyrrolidine/1+KOH/2	2
17	DCE (0.5 mL)	pyrrolidine/1+KOH/2	4
18	$CHCl_3$ (0.5 mL)	pyrrolidine/1+KOH/2	0
19	isopropanol (0.5 mL)	pyrrolidine/1+KOH/2	14
20	MeOH (0.5 mL)	pyrrolidine/1+KOH/2	2
21	H_2O (0.5 mL)	pyrrolidine/1+KOH/2	0
22	DMSO (0.5 mL)	pyrrolidine/1+KOH/2	3
23	DMF (0.5 mL)	pyrrolidine/1+KOH/1	8
24	DMF (0.5 mL)	pyrrolidine/1+KOH/3	43
25	DMF (0.5 mL)	**pyrrolidine/1+KOH/4**	**53**
26	DMF (0.5 mL)	pyrrolidine/1+KOH/5	36
27	DMF (0.5 mL)	pyrrolidine/2+KOH/4	54
28	DMF (0.5 mL)	**pyrrolidine/3+KOH/4**	**61**
29	DMF (0.5 mL)	pyrrolidine/4+KOH/4	54
30	DMF (0.5 mL)	pyrrolidine/5+KOH/4	33
31	DMF (1.0 mL)	pyrrolidine/3+KOH/4	56
32	**DMF (1.5 mL)**	pyrrolidine/3+KOH/4	**70 (70)**
33	DMF (2.0 mL)	pyrrolidine/3+KOH/4	65
34	DMF (2.5 mL)	pyrrolidine/3+KOH/4	67

[a] Reaction conditions: **6a** (0.2 mmol), solvent, *hv* (254 nm, 4*8 W), air, r.t., 12 h, GC-MS yield with 1,3,5-trimethylbenzene as internal standard or isolated yield in parentheses after purification. [b] *hv* (365 nm, 4*8 W) was used.

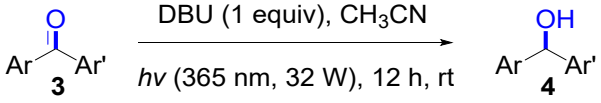
3. Experimental procedure

(1) General procedure for the reduction of aromatic olefins (1)



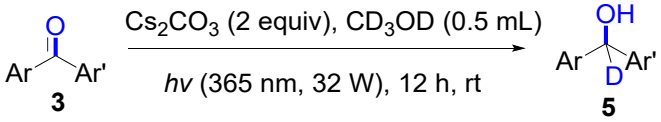
To a 10 mL quartz tube charged with a magnetic stir-bar was added **1** (0.2 mmol), pyrrolidine (0.8 mmol), KOH (0.14 mmol) and DMF (1 mL) under air atmosphere. The mixture was irradiated by UV-C light (254 nm, 4*8 W) for 24 h at 30 °C. Then EtOAc (10 mL) was added, and the mixture was washed with brine (2 mL*3). After dried with anhydrous Na_2SO_4, the filtrate was concentrated, and the residue was purified by preparative TLC with petroleum ether to afford the desired products **2** in yields as indicated in Table 2.

(2) General procedure for the reduction of diaryl ketones (3)



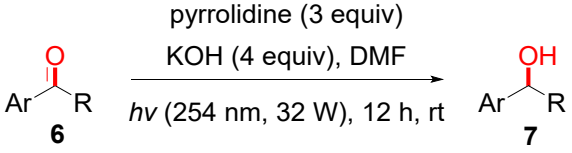
To a 10 mL quartz tube charged with a magnetic stir-bar was added **3** (0.2 mmol), DBU (0.2 mmol) and CH_3CN (0.5 mL) sequentially under air atmosphere. The mixture was irradiated by UV-A light (365 nm, 4*8 W) for 12 h at room temperature. Then it was concentrated and purified by preparative TLC with petroleum ether/EtOAc (10:1) to afford the desired products **4** in yields as indicated in Table 4.

(3) General procedure for the reductive deuteration of diaryl ketones (3)



To a 10 mL quartz tube charged with a magnetic stir-bar under argon atmosphere was added **3** (0.2 mmol), Cs_2CO_3 (0.4 mmol, or 0.6 mmol for **5l**, or 0.8 mmol for **5m**) and CD_3OD (0.5 mL, or 1.0 mL for **5m**, or 0.5 mL of DMSO-d_6 was further added for **5d** and **5j**) sequentially. The reaction mixture was irradiated by UV-A light (365 nm, 4*8 W) for 12 h at room temperature, and then concentrated and purified by preparative TLC with petroleum ether/EtOAc (10:1) to afford the desired products **5** in yields as indicated in Table 4. The deuterium incorporation of **5** was determined by ^{1}H NMR spectroscopy.

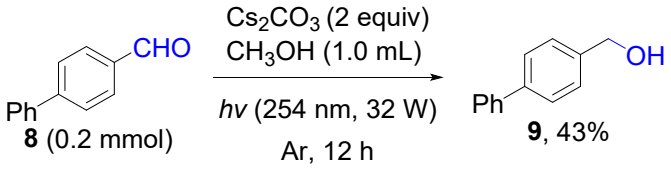
(4) General procedure for the reduction of mono-aryl ketones (6)



To a 10 mL quartz tube charged with a magnetic stir-bar under air atmosphere was added **6** (0.2 mmol), pyrrolidine (0.6 mmol), KOH (0.8 mmol) and DMF (1.5 mL) sequentially. The reaction mixture was irradiated by UV-C light (254 nm, 4*8 W) for 12 h at room temperature. Then EtOAc (10 mL) was added, and the mixture was washed with brine (2 mL*3). After dried with anhydrous Na_2SO_4, the filtrate was

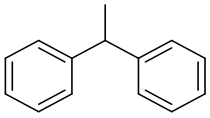
concentrated, and the residue was purified by preparative TLC with petroleum ether/EtOAc (10:1) to afford the products **7** in yields as indicated in Table 4.

(5) General procedure for the reduction of aldehydes (8)

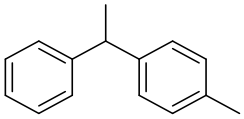


To a 10 mL quartz tube charged with a magnetic stir-bar under argon atmosphere was added **8** (0.2 mmol), Cs_2CO_3 (0.4 mmol) and CH_3OH (1.0 mL) sequentially. The reaction mixture was irradiated by UV-C light (254 nm, 4*8 W) for 12 h at room temperature. Then it was concentrated and purified by preparative TLC with petroleum ether/EtOAc (10:1) to afford the desired products **9** in 43% yield.

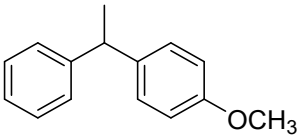
(6) Data of products 2, 4, 5, 7, 9



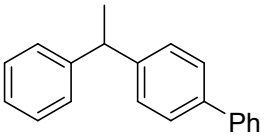
Ethane-1,1-diyldibenzene (2a): Colorless oil, 33 mg, yield 91%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.17 (m, 10H), 4.18 (q, J = 7.2 Hz, 1H), 1.67 (d, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.5, 128.5, 127.8, 126.2, 44.9, 22.0. These data were agreed with literature.[1]



1-Methyl-4-(1-phenylethyl)benzene (2b): Pale yellow oil, 33 mg, yield 85%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.05 (m, 9H), 4.13 (q, J = 7.2 Hz, 1H), 2.32 (s, 3H), 1.63 (d, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.7, 143.5, 135.6, 129.2, 128.5, 127.7, 127.6, 126.1, 44.5, 22.1, 21.1. These data were agreed with literature.[1]

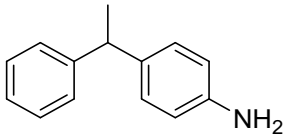


1-Methoxy-4-(1-phenylethyl)benzene (2c): Pale yellow solid, 36 mg, yield 84%, m.p. 75.2-76.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.25 (m, 2H), 7.24-7.17 (m, 3H), 7.15 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 8.6 Hz, 2H), 4.12 (q, J = 7.2 Hz, 1H), 3.79 (s, 3H), 1.62 (d, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 146.9, 138.7, 128.6, 128.5, 127.7, 126.1, 113.8, 55.4, 44.0, 22.2. These data were agreed with literature.[1]

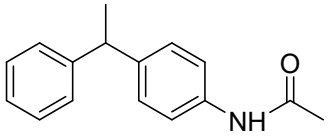


4-(1-phenylethyl)-1,1'-biphenyl (2d): White solid, 42 mg, yield 82%, m.p. 61.2-63.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.56 (d, J = 7.6 Hz, 2H), 7.53 (d, J = 8.2 Hz, 2H), 7.46-7.41 (t, J = 7.4 Hz, 2H), 7.36-7.26 (m, 7H), 7.25-7.19 (m, 1H), 4.22 (q, J = 7.2 Hz, 1H), 1.70 (d, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz,

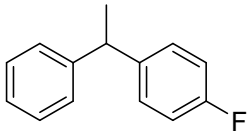
$CDCl_3$) δ 146.4, 145.6, 141.1, 139.1, 128.8, 128.6, 128.2, 127.8, 127.25, 127.19, 127.16, 126.2, 44.6, 22.0. These data were agreed with literature.[2]



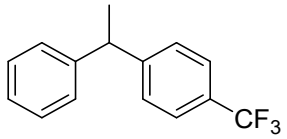
4-(1-Phenylethyl)aniline (2e): Yellow oil, 28 mg, yield 70%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.13 (m, 5H), 7.02 (d, J = 8.2 Hz, 2H), 6.64 (d, J = 8.5 Hz, 2H), 4.06 (q, J = 7.2 Hz, 1H), 3.60 (brs, 2H), 1.60 (d, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.2, 144.4, 136.8, 128.5, 128.4, 127.6, 125.9, 115.4, 44.0, 22.2. These data were agreed with literature.[3]



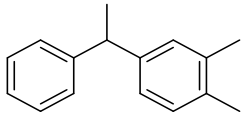
***N*-(4-(1-Phenylethyl)phenyl)acetamide (2f):** Yellow oil, 36 mg, yield 75%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 8.5 Hz, 2H), 7.31-7.24 (m, 2H), 7.23-7.16 (m, 5H), 4.12 (q, J = 7.2 Hz, 1H), 2.15 (s, 3H), 1.61 (d, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 146.4, 142.6, 135.9, 128.5, 128.2, 127.7, 126.2, 120.2, 44.3, 24.7, 22.0. These data were agreed with literature.[1]



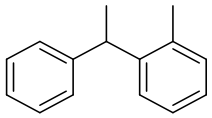
1-Fluoro-4-(1-phenylethyl)benzene (2g): Colorless oil, 35 mg, yield 88%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.24 (m, 2H), 7.23-7.14 (m, 5H), 7.02-6.93 (m, 2H), 4.14 (q, J = 7.3 Hz, 1H), 1.63 (d, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4 (d, J = 243.9 Hz), 146.3, 142.2 (d, J = 3.1 Hz), 129.1 (d, J = 7.8 Hz), 128.6, 127.6, 126.3, 115.2 (d, J = 21.1 Hz), 44.2, 22.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.5. These data were agreed with literature.[1]



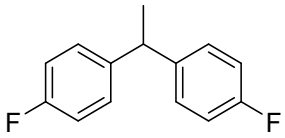
1-(1-Phenylethyl)-4-(trifluoromethyl)benzene (2h): Pale yellow oil, 45 mg, yield 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 8.0 Hz, 2H), 7.37-7.28 (m, 4H), 7.26-7.18 (m, 3H), 4.21 (q, J = 7.2 Hz, 1H), 1.66 (d, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 145.4, 128.7, 128.1, 127.7, 126.6, 125.7, 125.5 (q, J = 3.8 Hz), 124.4 (q, J = 270.3 Hz), 44.8, 21.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.3. These data were agreed with literature.[1]



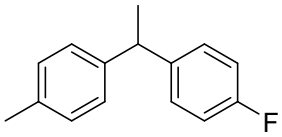
1,2-Dimethyl-4-(1-phenylethyl)benzene (2i): Pale yellow oil, 36 mg, yield 86%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.17 (m, 5H), 7.09-6.97 (m, 3H), 4.11 (q, J = 7.2 Hz, 1H), 2.24 (s, 6H), 1.64 (d, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.8, 144.0, 136.6, 134.3, 129.7, 129.1, 128.4, 127.7, 126.0, 125.0, 44.5, 22.1, 20.0, 19.5. These data were agreed with literature.[4]



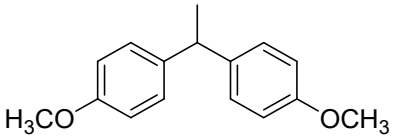
1-Methyl-2-(1-phenylethyl)benzene (2j): Pale yellow oil, 27 mg, yield 70%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.12 (m, 9H), 4.32 (q, J = 7.2 Hz, 1H), 2.24 (s, 3H), 1.61 (d, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.4, 144.0, 136.2, 130.5, 128.4, 127.8, 126.8, 126.2, 126.1, 125.9, 41.1, 22.3, 19.9. These data were agreed with literature.[1]



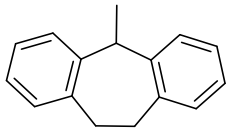
4,4'-(Ethane-1,1-diyl)bis(fluorobenzene) (2k): Colorless oil, 35 mg, yield 81%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20-7.10 (m, 4H), 7.01-6.92 (m, 4H), 4.12 (q, J = 7.3 Hz, 1H), 1.60 (d, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4 (d, J = 244.4 Hz), 142.0 (d, J = 3.6 Hz), 129.0 (d, J = 7.8 Hz), 115.3 (d, J = 21.2 Hz), 43.4, 22.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.3. These data were agreed with literature.[5]



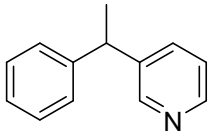
1-Fluoro-4-(1-*p*-tolylethyl)benzene (2l): Colorless oil, 37 mg, yield 86%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (dd, J = 8.4, 5.4 Hz, 2H), 7.14-7.08 (m, 4H), 6.96 (t, J = 8.8 Hz, 2H), 4.11 (q, J = 7.2 Hz, 1H), 2.32 (s, 3H), 1.61 (d, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3 (d, J = 243.7 Hz), 143.3, 142.4, 135.8, 129.2, 129.0 (d, J =7.9 Hz), 127.5, 115.2 (d, J = 21.2 Hz), 43.7, 22.2, 21.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.7. These data were agreed with literature.[6]



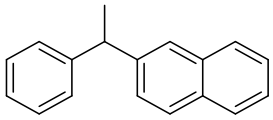
4,4'-(Ethane-1,1-diyl)bis(methoxybenzene) (2m): Pale yellow solid, 36 mg, yield 75%, m.p. 75.2-76.1 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, J = 8.4 Hz, 4H), 6.82 (d, J = 8.7 Hz, 4H), 4.06 (q, J = 7.2 Hz, 1H), 3.78 (s, 6H), 1.58 (d, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 139.1, 128.5, 113.8, 55.4, 43.2, 22.4. These data were agreed with literature.[7]



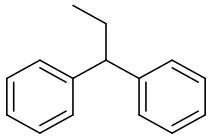
5-Methyl-10,11-dihydro-5*H*-dibenzo[*a*,*d*][7]annulene (2n): Pale yellow oil, 33 mg, yield 80%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.20 (m, 2H), 7.17-7.08 (m, 6H), 4.45 (q, J = 7.4 Hz, 1H), 3.27-3.16 (m, 4H), 1.73 (d, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 139.4, 130.2, 127.5, 126.4, 126.3, 43.7, 33.3, 22.1. These data were agreed with literature.[8]



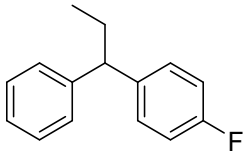
3-(1-phenylethyl)pyridine (2o): Pale yellow oil, 32 mg, yield 87%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, J = 2.0 Hz, 1H), 8.45 (dd, J = 4.8, 1.4 Hz, 1H), 7.53 (d, J = 8.0 Hz, 1H), 7.34-7.28 (m, 2H), 7.25-7.20 (m, 4H), 4.19 (q, J = 7.3 Hz, 1H), 1.67 (d, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 147.2, 144.9, 142.0, 135.6, 128.8, 127.7, 126.7, 123.7, 42.6, 21.7. These data were agreed with literature.[9]



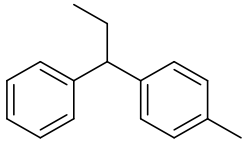
2-(1-Phenylethyl)naphthalene (2p): Pale yellow oil, 38 mg, yield 81%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84-7.70 (m, 4H), 7.49-7.40 (m, 2H), 7.34-7.18 (m, 6H), 4.33 (q, J = 7.1 Hz, 1H), 1.75 (d, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.4, 143.9, 133.6, 132.2, 128.5, 128.1, 127.9, 127.8, 127.7, 127.0, 126.2, 126.1, 125.50, 125.46, 45.0, 21.9. These data were agreed with literature.[10]



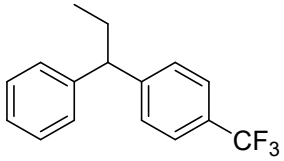
Propane-1,1-diyldibenzene (2q): Colorless oil, 34 mg, yield 88%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.23 (m, 8H), 7.22-7.14 (m, 2H), 3.81 (t, J = 7.8 Hz, 1H), 2.09 (m, 2H), 0.91 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.3, 128.5, 128.0, 126.1, 53.4, 28.7, 12.9. These data were agreed with literature.[3]



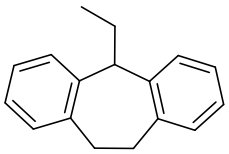
1-Fluoro-4-(1-phenylpropyl)benzene (2r): Pale yellow oil, 40 mg, yield 93%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.15 (m, 7H), 6.97 (t, J = 8.7 Hz, 2H), 3.78 (t, J = 7.8 Hz, 1H), 2.12-1.99 (m, 2H), 0.90 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4 (d, J = 243.9 Hz), 145.1, 141.0 (d, J = 3.1 Hz), 129.4 (d, J = 7.7 Hz), 128.6, 127.9, 126.3, 115.2 (d, J = 21.1 Hz), 52.6, 28.8, 12.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.4. These data were agreed with literature.[3]



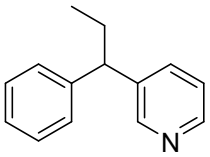
1-Methyl-4-(1-phenylpropyl)benzene (2s): Colorless oil, 36 mg, yield 87%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.06 (m, 9H), 3.77 (t, J = 7.8 Hz, 1H), 2.31 (s, 3H), 2.07 (m, 2H), 0.91 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6, 142.3, 135.6, 129.2, 128.5, 128.0, 127.9, 126.0, 53.0, 28.7, 21.1, 13.0. These data were agreed with literature.[11]



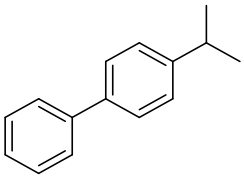
1-(1-Phenylpropyl)-4-(trifluoromethyl)benzene (2t): Pale yellow oil, 46 mg, yield 87%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 8.1 Hz, 2H), 7.37 (d, J = 8.1 Hz, 2H), 7.34-7.28 (m, 2H), 7.27-7.19 (m, 3H), 3.87 (t, J = 7.8 Hz, 1H), 2.18-2.04 (m, 2H), 0.93 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4 (q, J = 1.3 Hz), 144.2, 128.7, 128.4 (q, J = 32.4 Hz), 128.3, 128.0, 126.6, 125.5 (q, J = 3.8 Hz), 124.4 (q, J = 273.1 Hz), 53.2, 28.5, 12.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.2. These data were agreed with literature.[12]



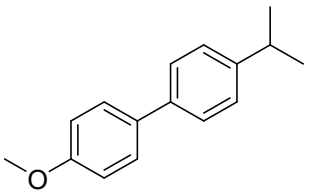
5-Ethyl-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene (2u): Colorless oil, 32 mg, yield 71%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (q, J = 2.6 Hz, 2H), 7.15-7.09 (m, 6H), 3.89 (t, J = 6.9 Hz, 1H), 3.42-3.29 (m, 2H), 3.12-2.97 (m, 2H), 2.17-2.09 (m, 2H), 0.90 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 139.4, 130.4, 129.9, 126.4, 126.0, 55.2, 33.4, 30.6, 13.5. EI-MS 222.1, 193.2, 178.1. These data were agreed with literature.[13]



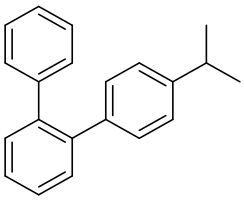
3-(1-Phenylpropyl)pyridine (2v): Colorless oil, 34 mg, yield 86%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, J = 2.0 Hz, 1H), 8.43 (dd, J = 4.7, 1.4 Hz, 1H), 7.51 (dt, J = 7.9 Hz, 2.0 Hz, 1H), 7.30 (t, J = 7.6 Hz, 2H), 7.25-7.16 (m, 4H), 3.81 (t, J = 7.8 Hz, 1H), 2.19-2.00 (m, 2H), 0.91 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 147.6, 143.9, 140.5, 135.2, 128.7, 127.9, 126.6, 123.5, 50.8, 28.4, 12.7. These data were agreed with literature.[1]



4-Isopropyl-1,1'-biphenyl (2w): Colorless oil, 33 mg, yield 84%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69-7.31 (m, 9H), 3.01 (hept, J = 6.8 Hz, 1H), 1.35 (d, J = 6.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 141.3, 138.8, 128.8, 127.21, 127.16, 127.1, 127.0, 33.9, 24.2. These data were agreed with literature.[14]

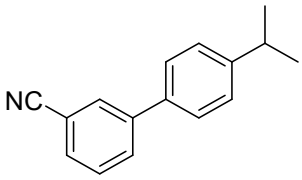


4-Isopropyl-4'-methoxy-1,1'-biphenyl (2x): White solid, 36 mg, yield 80%, m.p. 96.7-97.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 8.9 Hz, 2H), 7.50 (d, J = 8.3 Hz, 2H), 7.29 (d, J = 8.1 Hz, 2H), 6.98 (d, J = 8.8 Hz, 2H), 3.85 (s, 3H), 2.95 (hept, J = 6.9 Hz, 1H), 1.30 (d, J = 6.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 147.5, 138.5, 133.9, 128.1, 126.9, 126.8, 114.2, 55.5, 33.9, 24.2. These data were agreed with literature.[15]

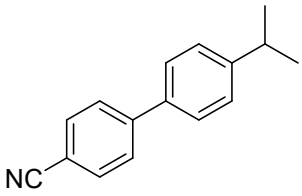


4-Isopropyl-1,1':2',1''-terphenyl (2y): White solid, 41 mg, yield 75%, m.p. 98.8-100.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.38 (m, 4H), 7.27-7.18 (m, 3H), 7.17-7.13 (m, 2H), 7.09-7.05 (m, 4H), 2.86 (hept, J =

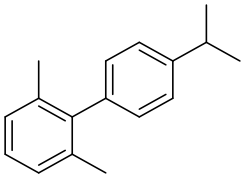
7.0 Hz, 1H), 1.23 (d, J = 6.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.2, 141.8, 140.65, 140.62, 138.9, 130.79, 130.75, 130.0, 129.9, 127.9, 127.6, 127.4, 126.5, 126.0, 33.8, 24.1. These data were agreed with literature.[16]



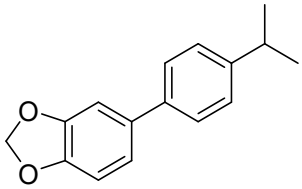
4'-Isopropyl-[1,1'-biphenyl]-3-carbonitrile (2z): Pale yellow oil, 38 mg, yield 87%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88-7.83 (m, 1H), 7.82-7.79 (m, 1H), 7.61 (dt, J = 7.7, 1.4 Hz, 1H), 7.54 (dd, J = 7.8, 0.6 Hz, 1H), 7.52-7.47 (m, 2H), 7.37-7.33 (m, 2H), 2.97 (hept, J = 7.0 Hz, 1H), 1.30 (d, J = 6.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.5, 142.5, 136.5, 131.5, 130.6, 130.5, 129.7, 127.4, 127.1, 119.1, 113.0, 34.0, 24.1. These data were agreed with literature.[17]



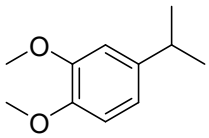
4'-Isopropyl-[1,1'-biphenyl]-4-carbonitrile (2aa): Colorless oil, 36 mg, yield 82%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (q, J = 8.3 Hz, 4H), 7.53 (d, J = 8.2 Hz, 2H), 7.35 (d, J = 8.1 Hz, 2H), 2.98 (hept, J = 6.9 Hz, 1H), 1.30 (d, J = 6.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 145.7, 136.8, 132.7, 127.6, 127.4, 127.3, 119.2, 110.6, 34.0, 24.1. These data were agreed with literature.[17]



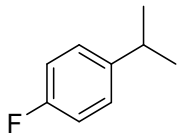
4'-Isopropyl-2,6-dimethyl-1,1'-biphenyl (2ab): Colorless oil, 33 mg, yield 73%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, J = 7.9 Hz, 2H), 7.17 (dd, J = 8.8, 5.9 Hz, 1H), 7.12 (d, J = 6.6 Hz, 2H), 7.07 (d, J = 8.1 Hz, 2H), 2.98 (hept, J = 6.8 Hz, 1H), 2.06 (s, 6H), 1.32 (d, J = 6.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.1, 142.1, 138.4, 136.5, 129.0, 127.3, 127.0, 126.5, 33.9, 24.2, 21.1. HRMS m/z (ESI) calcd. for $C_{17}H_{21}^+$[M+H]$^+$: 225.1638; found: 225.1638.



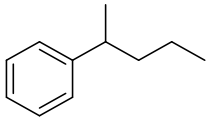
5-(4-Isopropylphenyl)benzo[*d*][1,3]dioxole (2ac): White solid, 41 mg, yield 85%, m.p. 73.1-74.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 8.2 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 7.09-7.04 (m, 2H), 6.88 (d, J = 7.9 Hz, 1H), 6.00 (s, 2H), 2.95 (hept, J = 7.0 Hz, 1H), 1.29 (d, J = 6.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 147.8, 146.9, 138.6, 135.7, 126.93, 126.92, 120.6, 108.7, 107.7, 101.2, 33.9, 24.2. HRMS m/z (ESI) calcd. for $C_{16}H_{17}O_2^+$[M+H]$^+$: 241.1223; found: 241.1224.



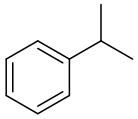
4-Isopropyl-1,2-dimethoxybenzene (2ad): White solid, 32 mg, yield 89%, m.p. 76.1-76.5 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83-6.75 (m, 3H), 3.89 (s, 3H), 3.86 (s, 3H), 2.86 (hept, J = 6.9 Hz, 1H), 1.24 (d, J = 6.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8, 147.1, 141.7, 118.0, 111.1, 110.0, 56.0, 55.9, 33.9, 24.3. These data were agreed with literature.[18]



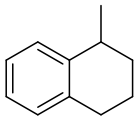
1-Fluoro-4-isopropylbenzene (2ae): The yield (86%) was determined by GC-MS using 1,3,5-trimethylbenzene as an internal standard. EI-Ms 138.1, 123.1. These data were agreed with literature.[19]



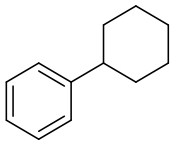
Pentan-2-ylbenzene (2af): The yield (78%) was determined by GC-MS using 1,3,5-trimethylbenzene as an internal standard. EI-Ms 148.0, 131, 115, 105. These data were agreed with literature.[20]



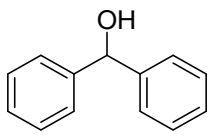
Cumene (2ag): The yield (80%) was determined by GC-MS using 1,3,5-trimethylbenzene as an internal standard. EI-Ms 120.1, 105.1. These data were agreed with literature.[19]



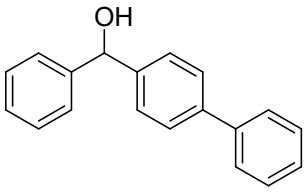
1-Methylene-1,2,3,4-tetrahydronaphthalene (2ah): Colorless oil, 24 mg, yield 82%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, J = 7.4 Hz, 1H), 7.18-7.12 (m, 1H), 7.09 (d, J = 7.6 Hz, 2H), 2.98-2.88 (m, 1H), 2.83-2.71 (m, 2H), 1.99-1.84 (m, 2H), 1.82-1.69 (m, 1H), 1.61-1.51 (m, 1H), 1.31 (d, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 137.0, 129.1, 128.2, 125.7, 125.5, 32.6, 31.6, 30.1, 23.0, 20.5. These data were agreed with literature.[1]



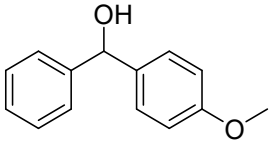
Cyclohexylbenzene (2ai): Colorless oil, 24 mg, yield 75%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.17 (m, 5H), 2.58-2.47 (m, 1H), 1.96-1.73 (m, 5H), 1.52-1.22 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 128.4, 127.0, 125.9, 44.7, 34.6, 27.1, 26.3. These data were agreed with literature.[21]



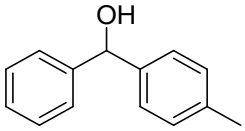
Diphenylmethanol (4a): White solid, 34 mg, yield 93%, m.p. 68.1-68.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.31 (m, 8H), 7.31-7.25 (m, 2H), 5.85 (s, 1H), 2.13 (brs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 128.6, 127.7, 126.7, 76.4. These data were agreed with literature.[22]



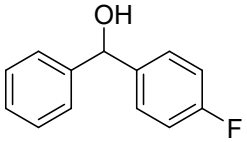
Biphenyl-4-yl(phenyl)methanol (4b): White solid, 42 mg, yield 80%, m.p. 95.5-96.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.27 (m, 14H), 5.90 (s, 1H), 2.10 (brs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 142.9, 140.9, 140.6, 128.9, 128.7, 127.8, 127.44, 127.41, 127.2, 127.1, 126.7, 76.2. These data were agreed with literature.[23]



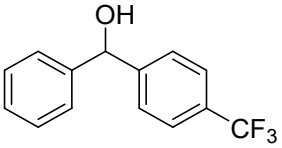
(4-Methoxyphenyl)(phenyl)methanol (4c): White solid, 33 mg, yield 78%, m.p. 58.6-59.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.24 (m, 7H), 6.90-6.84 (m, 2H), 5.80 (s, 1H), 3.79 (s, 3H), 2.26 (brs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 144.1, 136.3, 128.6, 128.0, 127.6, 126.5, 114.0, 75.9, 55.4. These data were agreed with literature.[22]



1-(2-Methylphenyl)-1-phenylmethanol (4d): Pale yellow oil, 32 mg, yield 80%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 7.0 Hz, 2H), 7.34 (t, J = 7.5 Hz, 2H), 7.27 (d, J = 7.9 Hz, 3H), 7.15 (d, J = 7.9 Hz, 2H), 5.82 (s, 1H), 2.34 (s, 3H), 2.18 (brs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 141.1, 137.4, 129.3, 128.6, 127.6, 126.6, 126.6, 76.2, 21.3. These data were agreed with literature.[24]

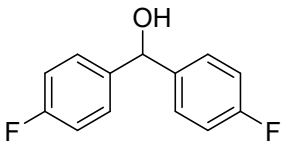


4-Fluorophenyl(phenyl)methanol (4e): Pale yellow oil, 34 mg, yield 85%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.25 (m, 7H), 7.07-6.97 (m, 2H), 5.82 (s, 1H), 2.30 (brs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3 (d, J = 245.7 Hz), 143.7, 139.6 (d, J = 3.2 Hz), 128.7, 128.3 (d, J = 8.2 Hz), 127.9, 126.6, 115.4 (d, J = 21.4 Hz), 75.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -119.8. These data were agreed with literature.[22]

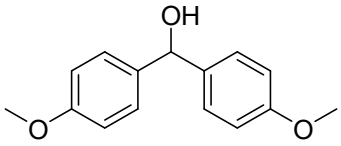


Phenyl(4-(trifluoromethyl)phenyl)methanol (4f): Pale yellow oil, 39 mg, yield 78%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 8.2 Hz, 2H), 7.51 (d, J = 8.1 Hz, 2H), 7.38-7.25 (m, 5H), 5.88 (s, 1H), 2.26 (brs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6 (q, J = 1.2 Hz), 143.2, 129.7 (q, J = 32.2 Hz), 128.9, 128.2, 126.77,

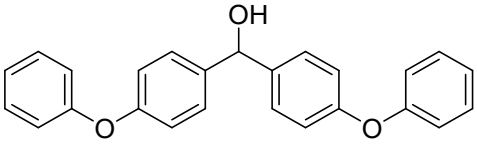
126.75, 125.5 (q, J = 3.8 Hz), 124.2 (q, J = 272.1 Hz), 75.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -67.2. These data were agreed with literature.[23]



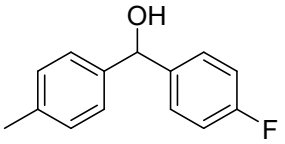
Bis(4-fluorophenyl)methanol (4g): Pale yellow oil, 31 mg, yield 70%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.28 (m, 4H), 7.06-6.99 (m, 4H), 5.80 (s, 1H), 2.32 (brs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3 (d, J = 246.1 Hz), 139.5 (d, J = 2.7 Hz), 128.3 (d, J = 8.2 Hz), 115.5 (d, J = 21.5 Hz), 75.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -119.5. These data were agreed with literature.[22]



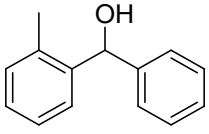
Bis(4-methoxyphenyl)methanol (4h): White solid, 42 mg, yield 87%, m.p. 67.3-68.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.21 (m, 4H), 6.91-6.81 (m, 4H), 5.29 (s, 1H), 3.79 (s, 6H), 1.63(brs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 134.9, 128.6, 113.8, 78.9, 55.3. These data were agreed with literature.[22]



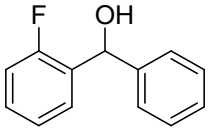
Bis(4-phenoxyphenyl)methanol (4i): White solid, 54 mg, yield 74%, m.p. 90.9-91.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.31 (m, 8H), 7.13 (t, J = 7.4 Hz, 2H), 7.06-6.98 (m, 8H), 5.82 (s, 1H), 2.45 (brs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 156.8, 138.7, 129.9, 128.1, 123.5, 119.1, 118.8, 75.4. These data were agreed with literature.[22]



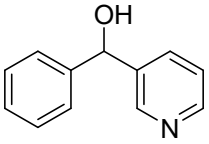
(4-Fluorophenyl)(p-tolyl)methanol (4j): White solid, 35 mg, yield 82%, m.p. 84.1-85.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.26 (m, 2H), 7.22 (d, J = 7.9 Hz, 2H), 7.14 (d, J = 7.8 Hz, 2H), 7.00 (t, J = 8.7 Hz, 2H), 5.75 (s, 1H), 2.37 (brs, 1H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2 (d, J = 245.5 Hz), 140.9, 139.8 (d, J = 3.1 Hz), 137.6, 129.4, 128.2 (d, J = 8.1 Hz), 126.6, 115.3 (d, J = 21.4 Hz), 75.5, 21.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.3. These data were agreed with literature.[25]



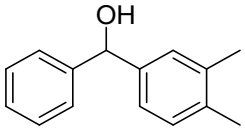
Phenyl(p-tolyl)methanol (4k): White solid, 28 mg, yield 70%, m.p. 50.8-51.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 7.7 Hz, 1H), 7.33 (d, J = 4.3 Hz, 4H), 7.29-7.19 (m, 3H), 7.15 (d, J = 7.3 Hz, 1H), 6.01 (s, 1H), 2.26 (s, 3H), 2.08 (brs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.0, 141.5, 135.5, 130.7, 128.6, 127.7, 127.7, 127.2, 126.4, 126.3, 73.5, 19.6. These data were agreed with literature.[22]



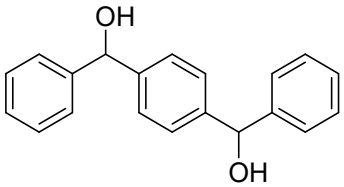
(2-Fluorophenyl)(phenyl)methanol (4l): Pale yellow oil, 35 mg, yield 87%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.49 (m, 1H), 7.44-7.39 (m, 2H), 7.38-7.32 (m, 2H), 7.31-7.23 (m, 2H), 7.19-7.13 (m, 1H), 7.06-6.99 (m, 1H), 6.15 (s, 1H), 2.24 (brs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0 (d, J = 246.3 Hz), 142.8, 131.0 (d, J = 13.0 Hz), 129.3 (d, J = 8.3 Hz), 128.7, 127.9, 127.8 (d, J = 4.1 Hz), 126.5, 124.5 (d, J = 3.6 Hz), 115.5 (d, J = 21.5 Hz), 70.2 (d, J = 3.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -118.5. These data were agreed with literature.[26]



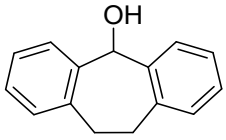
Phenyl(pyridin-3-yl)methanol (4m): Pale yellow oil, 26 mg, yield 70%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49-8.27 (m, 2H), 7.69 (dt, J = 7.9, 1.7 Hz, 1H), 7.37-7.16 (m, 6H), 5.80 (s, 1H), 4.26 (brs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 148.0, 143.4, 140.0, 134.6, 128.8, 127.9, 126.6, 123.6, 73.9. These data were agreed with literature.[25]



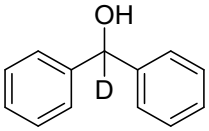
1-(2-Methylphenyl)-1-phenylmethanol (4n): White solid, 39 mg, yield 91%, m.p. 63.1-63.5 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.32 (m, 4H), 7.31-7.25 (m, 1H), 7.19-7.08 (m, 3H), 5.78 (s, 1H), 2.32 (brs, 1H), 2.27 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 141.5, 136.8, 136.1, 129.8, 128.5, 127.9, 127.5, 126.5, 124.1, 76.2, 20.0, 19.6. These data were agreed with literature.[24]



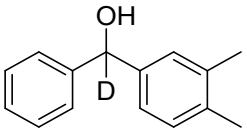
1,4-Bis(phenylhydroxymethyl)benzene (4o): White solid, 41 mg, yield 70%, m.p. 170.9-171.7 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.34 (d, J = 7.1 Hz, 4H), 7.28-7.25 (m, 8H), 7.17 (t, J = 7.2 Hz, 2H), 5.64 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 145.8, 144.2, 128.1, 126.7, 126.2, 126.0, 74.1. These data were agreed with literature.[27]



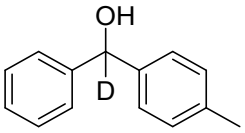
10,11-Dihydro-5*H*-dibenzo[*a*,*d*][7]annulen-5-ol (4p): White solid, 34 mg, yield 81%, m.p. 87.9-88.5 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (dd, J = 8.6 Hz, 2H), 7.22-7.15 (m, 6H), 5.97 (s, 1H), 3.49-3.40 (m, 2H), 3.18-3.06 (m, 2H), 2.28 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.6, 139.0, 130.3, 128.0, 127.1, 126.2, 76.5, 32.4. These data were agreed with literature.[24]



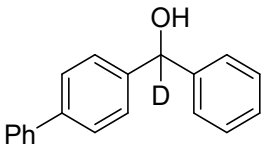
Diphenylmethan-d_1-ol (5a): White solid, 35 mg, yield 95%, deuterium incorporation 96%, m.p. 63.1-64.0 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.33 (m, 8H), 7.30-7.26 (m, 2H), 5.84 (s, 0.04H), 2.25 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 128.6, 127.7, 126.6, 76.3 (CHOH of the undeuterated compound), 75.9 (t, J = 22.2 Hz). These data were agreed with literature.[28]



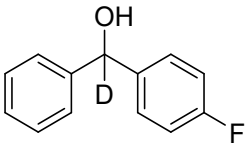
(3,4-Dimethylphenyl)-phenylmethan-d_1-ol (5b): White solid, 38 mg, yield 89%, deuterium incorporation 96%, m.p. 56.8-57.5 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 7.0 Hz, 2H), 7.35 (t, J = 7.4 Hz, 2H), 7.28 (m, 1H), 7.17 (s, 1H), 7.12 (s, 2H), 5.79 (s, 0.04H), 2.26 (s, 6H), 2.19 (brs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 141.5, 136.9, 136.1, 129.8, 128.5, 127.9, 127.5, 126.5, 124.1, 76.2 (CHOH of the undeuterated compound), 75.8 (t, J = 22.2 Hz), 20.0, 19.6. These data were agreed with literature.[28]



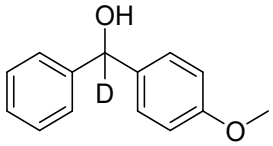
Diphenylmethan-d_1-ol (5c): White solid, 30 mg, yield 75%, deuterium incorporation 97%, m.p. 46.1-46.7 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.33 (m, 4H), 7.29-7.27 (m, 3H), 7.16 (d, J = 7.9 Hz, 2H), 5.81 (s, 0.03H), 2.35 (s, 3H), 2.30 (brs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 141.0, 137.4, 129.3, 128.6, 127.6, 126.6, 126.5, 76.2 (CHOH of the undeuterated compound), 75.7 (t, J = 22.2 Hz), 21.2. These data were agreed with literature.[28]



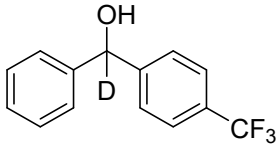
α-Phenyl-4-biphenylmethan-d_1-ol (5d): White solid, 41 mg, yield 79%, deuterium incorporation 94%, m.p. 91.3-92.0 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.58 (m, 4H), 7.48-7.44 (m, 6H), 7.40-7.35 (m, 3H), 7.31 (t, J = 7.2 Hz, 1H), 5.89 (s, 0.06H), 2.41 (brs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 142.8, 140.9, 140.6, 128.9, 128.7, 127.8, 127.41, 127.35, 127.2, 127.1, 126.6, 76.1 (CHOH of the undeuterated compound), 75.7 (t, J = 22.2 Hz). These data were agreed with literature.[28]



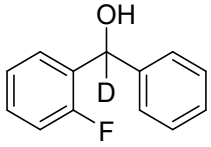
(4-Fluorophenyl)(phenyl)methan-d_1-ol (5e): Yellow oil, 32 mg, yield 79%, deuterium incorporation 96%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.28 (m, 7H), 7.02 (t, J = 8.6 Hz, 2H), 5.81 (s, 0.04H), 2.23 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3 (d, J = 245.7 Hz), 143.7, 139.6 (d, J = 3.1 Hz), 128.7, 128.3 (d, J = 8.1 Hz), 127.9, 126.6, 115.4 (d, J = 21.4 Hz), 75.7 (CHOH of the undeuterated compound), 75.3 (t, J = 22.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.07. These data were agreed with literature.[28]



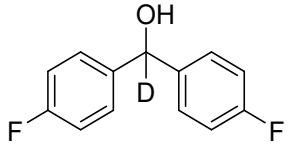
(4-Methoxyphenyl)phenylmethan-d_1-ol (5f): White solid, 31 mg, yield 72%, deuterium incorporation 94%, m.p. 56.7-57.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.25 (m, 7H), 6.89-6.85 (m, 2H), 5.79 (s, 0.06H), 3.79 (s, 3H), 2.37 (brs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 144.0, 136.2, 128.5, 128.0, 127.5, 126.5, 113.9, 75.6 (t, J = 22.2 Hz), 55.4. These data were agreed with literature.[28]



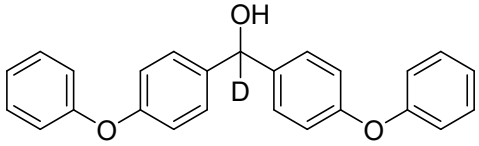
Phenyl(4-(trifluoromethyl)phenyl)methan-d_1-ol (5g): Yellow oil, 39 mg, yield 78%, deuterium incorporation 93%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 7.7 Hz, 2H), 7.48 (d, J = 7.7 Hz, 2H), 7.38-7.26 (m, 5H), 5.87 (s, 0.07H), 2.72 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5, 143.1, 129.7 (q, J = 32.4 Hz), 128.9, 128.2, 126.74, 126.72, 125.5 (q, J = 3.8 Hz), 124.2 (q, J = 273.2 Hz), 75.8 (CHOH of the undeuterated compound), 75.4 (t, J = 22.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.47. These data were agreed with literature.[29]



(2-Fluorophenyl)(phenyl)methan-d_1-ol (5h): Yellow oil, 35 mg, yield 86%, deuterium incorporation 97%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (td, J = 7.5 Hz, 2 Hz, 1H), 7.43 (d, J = 7.6 Hz, 2H), 7.36 (t, J = 7.2 Hz, 2H), 7.31-7.25 (m, 2H), 7.17 (td, J = 7.5 Hz, 0.8 Hz, 1H), 7.06-7.02 (m, 1H), 6.15 (s, 0.03H), 2.33 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0 (d, J = 246.2 Hz), 142.8, 131.0 (d, J = 13.1 Hz), 129.2 (d, J = 8.3 Hz), 128.6, 127.9, 127.8 (d, J = 4.0 Hz), 126.5, 124.4 (d, J = 3.5 Hz), 115.5 (d, J = 21.6 Hz), 69.8 (t, J = 22.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -118.57. These data were agreed with literature.[29]

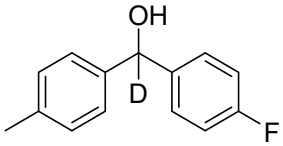


4,4'-Difluorodiphenylmethan-d_1-ol (5i): Yellow oil, 30 mg, yield 68%, deuterium incorporation 95%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.30 (m, 4H), 7.02 (t, J = 8.7 Hz, 4H), 5.80 (s, 0.05H), 2.25 (brs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3 (d, J = 246.1 Hz), 139.4 (d, J = 3.1 Hz), 128.3 (d, J = 8.2 Hz), 115.5 (d, J = 21.4 Hz), 74.6 (t, J = 22.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.74. These data were agreed with literature.[28]

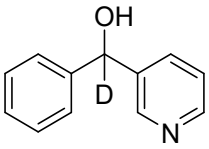


Bis(4-phenoxyphenyl)methan-d_1-ol (5j): White solid, 53 mg, yield 72%, deuterium incorporation 96%, m.p. 84.2-84.9 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.37-7.33 (m, 8H), 7.12 (t, J = 7.4 Hz, 2H), 7.03-6.98 (m, 8H), 5.82 (s, 0.04H), 2.36 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 157.1, 156.8, 138.6, 129.9, 128.1, 123.5,

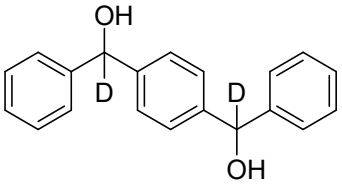
119.1, 118.8, 75.0 (t, J = 22.2 Hz). HRMS m/z (ESI) calcd. for $C_{25}H_{18}DO_2^+$ [M-OH]$^+$: 352.1442; found: 352.1443.



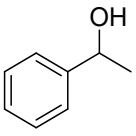
(4-Fluorophenyl)(4-methylphenyl)methan-d$_1$-ol (5k): White solid, 35 mg, yield 81%, deuterium incorporation 97%, m.p. 80.1-80.9 ^{o}C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.39-7.35 (m, 2H), 7.24 (d, J = 8.0 Hz, 2H), 7.13-7.08 (m, 4H), 5.86 (s, 1H), 5.67 (s, 0.03H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2 (d, J = 245.4 Hz), 140.8, 139.7 (d, J = 3.1 Hz), 137.6, 129.4, 128.2 (d, J = 8.1 Hz), 126.5, 115.3 (d, J = 21.4 Hz), 75.5 (CHOH of the undeuterated compound), 75.1 (t, J = 22.2 Hz), 21.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.29. HRMS m/z (ESI) calcd. for $C_{14}H_{11}DF^+$ [M-OH]$^+$: 200.0980; found: 200.0984.



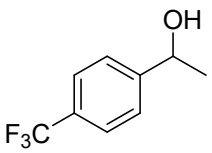
Phenyl(pyridin-3-yl)methan-d$_1$-ol (5l): Yellow oil, 25 mg, yield 67%, deuterium incorporation 93%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 8.32 (d, J = 4.3 Hz, 1H), 7.69 (d, J = 7.7 Hz, 1H), 7.38-7.29 (m, 4H), 7.29-7.26 (m, 1H), 7.22-7.19 (m, 1H), 5.80 (s, 0.07H), 4.16 (brs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 147.9, 143.3, 140.0, 134.7, 128.8, 128.0, 126.6, 123.6, 73.8 (CHOH of the undeuterated compound), 73.4 (t, J = 22.2 Hz). These data were agreed with literature.[29]



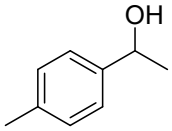
α_1, α_4-Diphenyl-1,4-benzenedimethan-d$_2$-ol (5m): White solid, 41 mg, yield 70%, deuterium incorporation 90%, m.p. 168.9-169.3 ^{o}C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.35 (d, J = 7.6 Hz, 4H), 7.30-7.24 (m, 8H), 7.17 (t, J = 7.2 Hz, 2H), 5.80 (s, 2H), 5.65 (s, 0.19H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 145.8, 144.2, 128.1, 126.7, 126.2, 126.1, 74.2 (CHOH of the undeuterated compound), 73.8 (t, J = 21.5 Hz). HRMS m/z (ESI) calcd. for $C_{20}H_{15}D_2O^+$ [M-OH]$^+$: 275.1400; found: 275.1402.



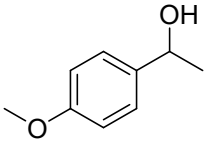
1-Phenylethanol (7a): Pale yellow oil, 17 mg, yield 70%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.31 (m, 4H), 7.31-7.25 (m, 1H), 4.86 (q, J = 6.5 Hz, 1H), 2.41 (brs, 1H), 1.48 (d, J = 6.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.9, 128.5, 127.5, 125.5, 70.4, 25.2. These data were agreed with literature.[22]



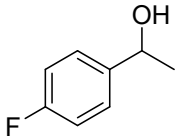
1-(4-Trifluorophenyl)ethanol (7b): Pale yellow oil, 28 mg, yield 73%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.3 Hz, 2H), 7.48 (d, J = 8.1 Hz, 2H), 4.96 (q, J = 6.5 Hz, 1H), 2.03 (brs, 1H), 1.50 (d, J = 6.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 129.7 (q, J = 32.4 Hz), 125.8, 125.5 (q, J = 3.8 Hz), 124.3 (q, J = 271.9 Hz), 69.9, 25.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -67.2. These data were agreed with literature.[30]



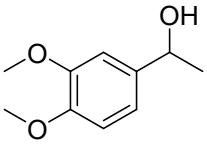
1-(4-Methylphenyl)ethanol (7c): Pale yellow oil, 15 mg, yield 55%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, J = 7.8 Hz, 2H), 7.15 (d, J = 7.8 Hz, 2H), 4.85 (q, J = 6.4 Hz, 1H), 2.34 (s, 3H), 1.84 (s, 1H), 1.47 (d, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.0, 137.3, 129.3, 125.5, 70.4, 25.2, 21.2. These data were agreed with literature.[30]



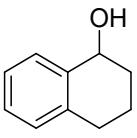
1-(4-Methoxyphenyl)ethanol (7d): Pale yellow oil, 20 mg, yield 65%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, J = 8.4 Hz, 2H), 6.88 (d, J = 8.6 Hz, 2H), 4.85 (q, J = 6.4 Hz, 1H), 3.80 (s, 3H), 1.82 (brs, 1H), 1.48 (d, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 138.1, 126.8, 114.0, 70.1, 55.4, 25.2. These data were agreed with literature.[30]



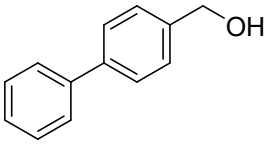
1-(4-Fluorophenyl)ethanol (7e): Pale yellow oil, 21 mg, yield 74%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.30 (m, 2H), 7.07-6.98 (m, 2H), 4.88 (q, J = 6.4 Hz, 1H), 1.92 (brs, 1H), 1.47 (d, J = 6.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2 (d, J = 245.2 Hz), 141.6 (d, J = 3.0 Hz), 127.2 (d, J = 8.1 Hz), 115.4 (d, J = 21.3 Hz), 69.9, 25.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.4. These data were agreed with literature.[30]



1-(3,4-Dimethoxyphenyl) ethanol (7f): Pale yellow oil, 24 mg, yield 67%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96-6.75 (m, 3H), 4.85 (q, J = 6.4 Hz, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 1.82 (brs, 1H), 1.48 (d, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1, 148.4, 138.6, 117.6, 111.0, 108.6, 70.4, 56.0, 55.9, 25.2. These data were agreed with literature.[31]



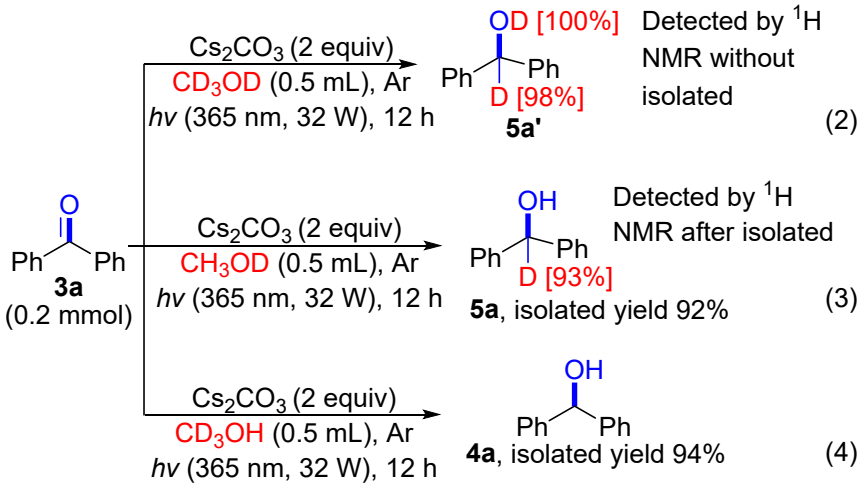
1,2,3,4-Tetrahydro-1-naphthalenol (7g): Pale yellow oil, 21 mg, yield 71%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.40 (m, 1H), 7.24-7.18 (m, 2H), 7.14-7.08 (m, 1H), 4.79 (t, J = 4.7 Hz, 1H), 2.88-2.68 (m, 2H), 2.05-1.78 (m, 4H), 1.78-1.71 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9, 137.2, 129.2, 128.8, 127.7, 126.3, 68.3, 32.4, 29.4, 18.9. These data were agreed with literature.[24]



[1,1'-Biphenyl]-4-ylmethanol (9): White solid, 16 mg, yield 43%, m.p. 98.4-99.3 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.61 (d, J = 8.1 Hz, 4H), 7.48-7.44 (m, 4H), 7.38-7.37 (m, 1H), 4.74 (s, 2H), 1.89-1.85 (brs, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.9, 140.7, 140.0, 128.9, 127.6, 127.4, 127.2, 65.2. These data were agreed with literature.[32]

4. Mechanistic Studies

(1) Deuterated methanol as a solvent in the reduction of 3a



The procedure was the same as the above reductive deuteration of diaryl ketones (**3a**) except with CD_3OD (0.5 mL, Eq. 2), CH_3OD (1.0 mL, Eq. 3), or CD_3OH (1.0 mL, Eq. 4) as a solvent.

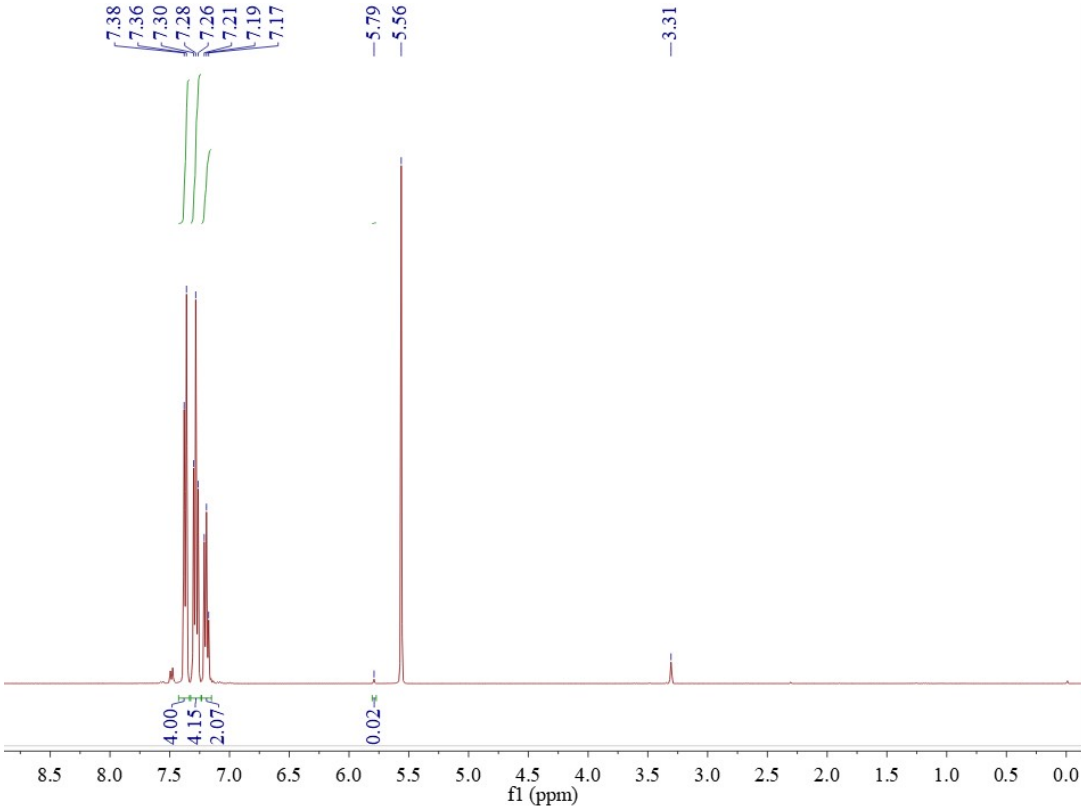
For Eq. 2 with CD_3OD (0.5 mL) as a solvent, the mixture was detected by ^{1}H NMR directly which showed the formation of **5a'** (Figure S3a). ^{1}H NMR (400 MHz, CD_3OD) δ 7.38-7.36 (m, 4H), 7.31-7.27 (m, 4H), 7.22-7.18 (m, 2H), 5.79 (s, 0.04 H).

For Eq. 3 with CH_3OD (0.5 mL) as a solvent, 34 mg of **5a** was afforded in 92% yield and 93% deuterium ratio after purification by TLC with petroleum ether/EtOAc (10:1) as eluants (Figure S3b). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.33 (m, 8H), 7.30-7.26 (m, 2H), 5.84 (s, 0.07 H), 2.26 (s, 1 H).

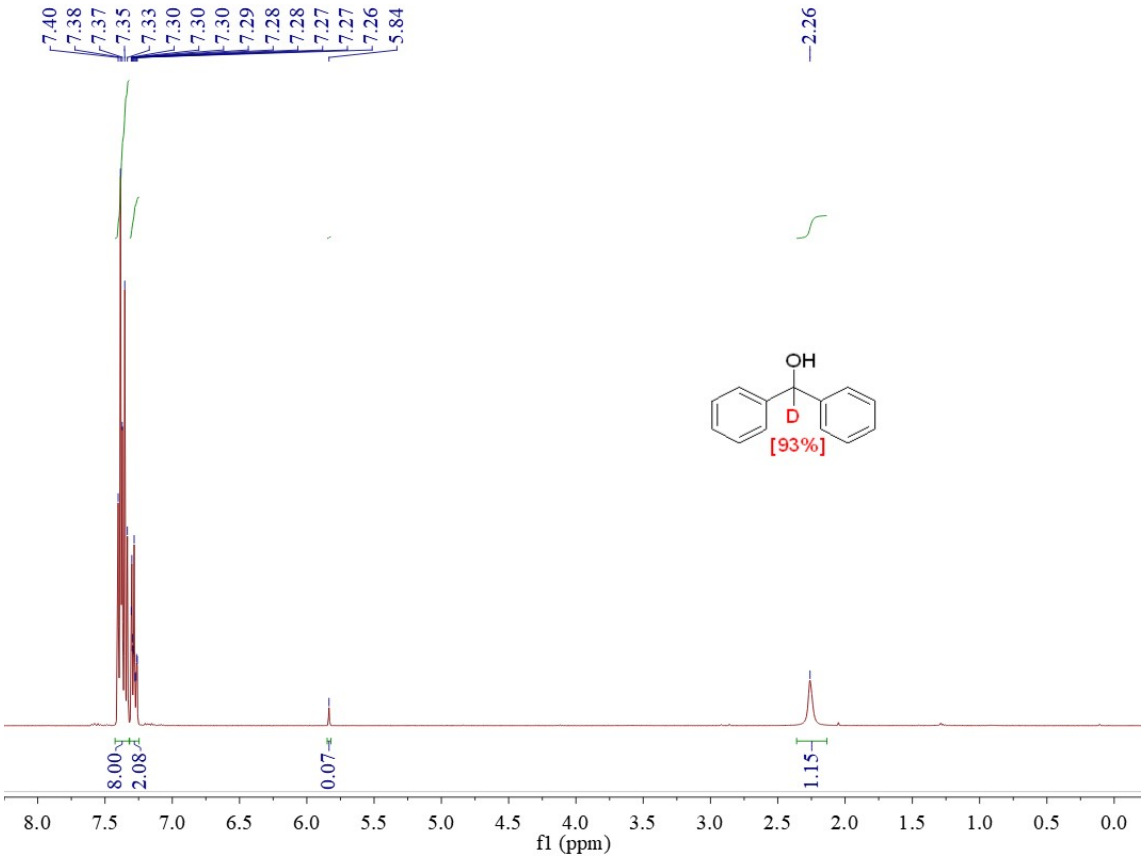
For Eq. 4 with CD_3OH (0.5 mL) as a solvent, 35 mg of **4a** was isolated in 94% yield after purification by TLC with petroleum ether/EtOAc (10:1) as eluants (Figure S3c). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.33 (m, 8H), 7.30-7.26 (m, 2H), 5.85 (s, 1 H), 2.13 (s, 1 H).

Figure S3. ^{1}H NMR spectrum for products in Eqs. 2-4

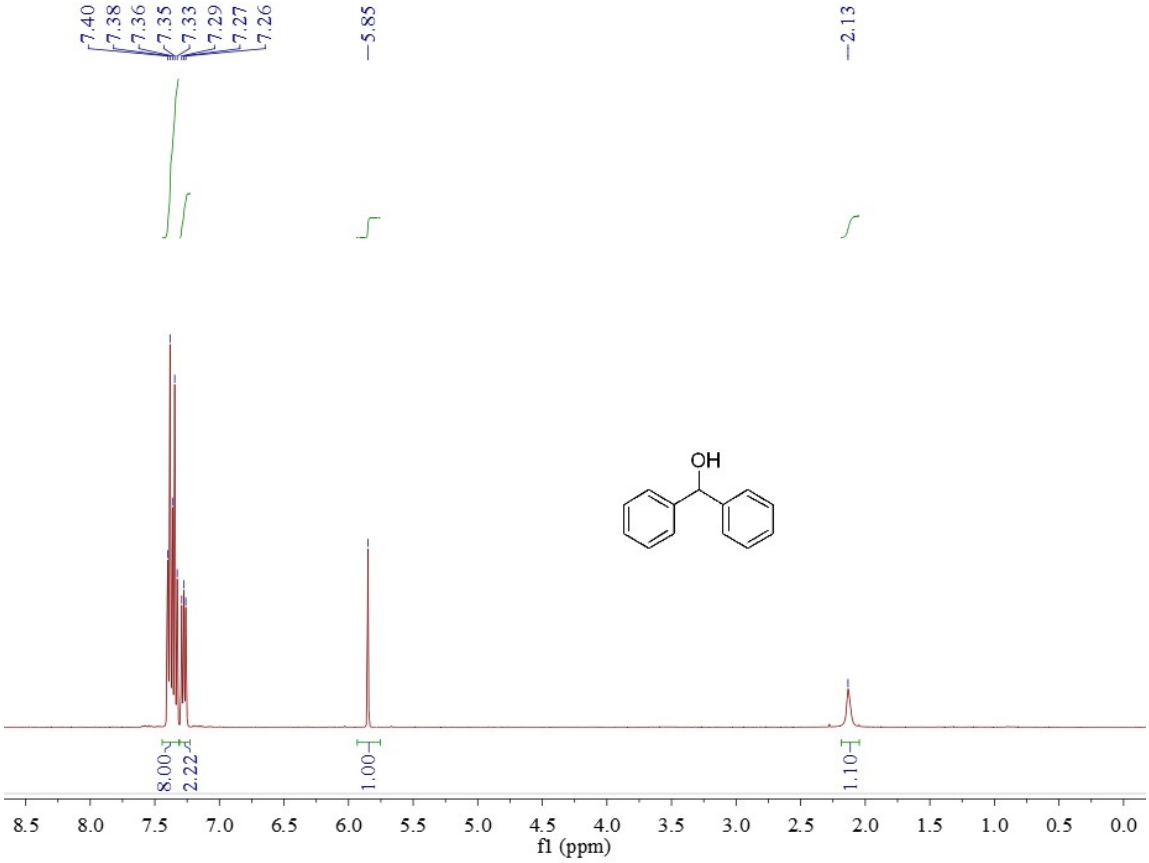
(a) ^{1}H NMR spectrum of **5a'** (400 MHz, CD_3OD) without purification in Eq. 2



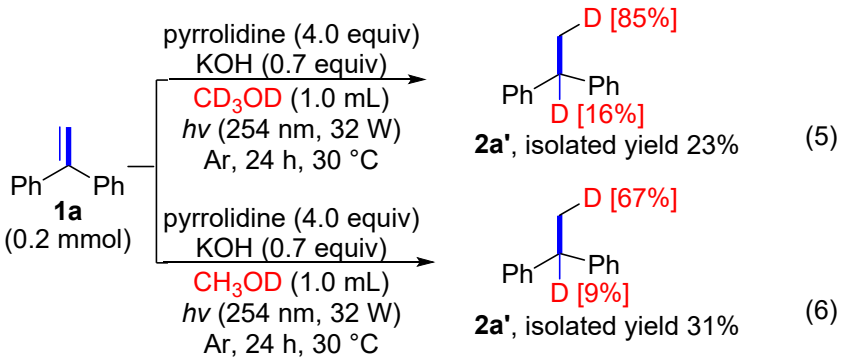
(b) ^{1}H NMR spectrum of **5a** (400 MHz, $CDCl_3$) after purification in Eq. 3



(c) ^{1}H NMR spectrum of **4a** (400 MHz, $CDCl_3$) after purification in Eq. 4



(2) Deuterated methanol as a solvent in the reduction of 1a



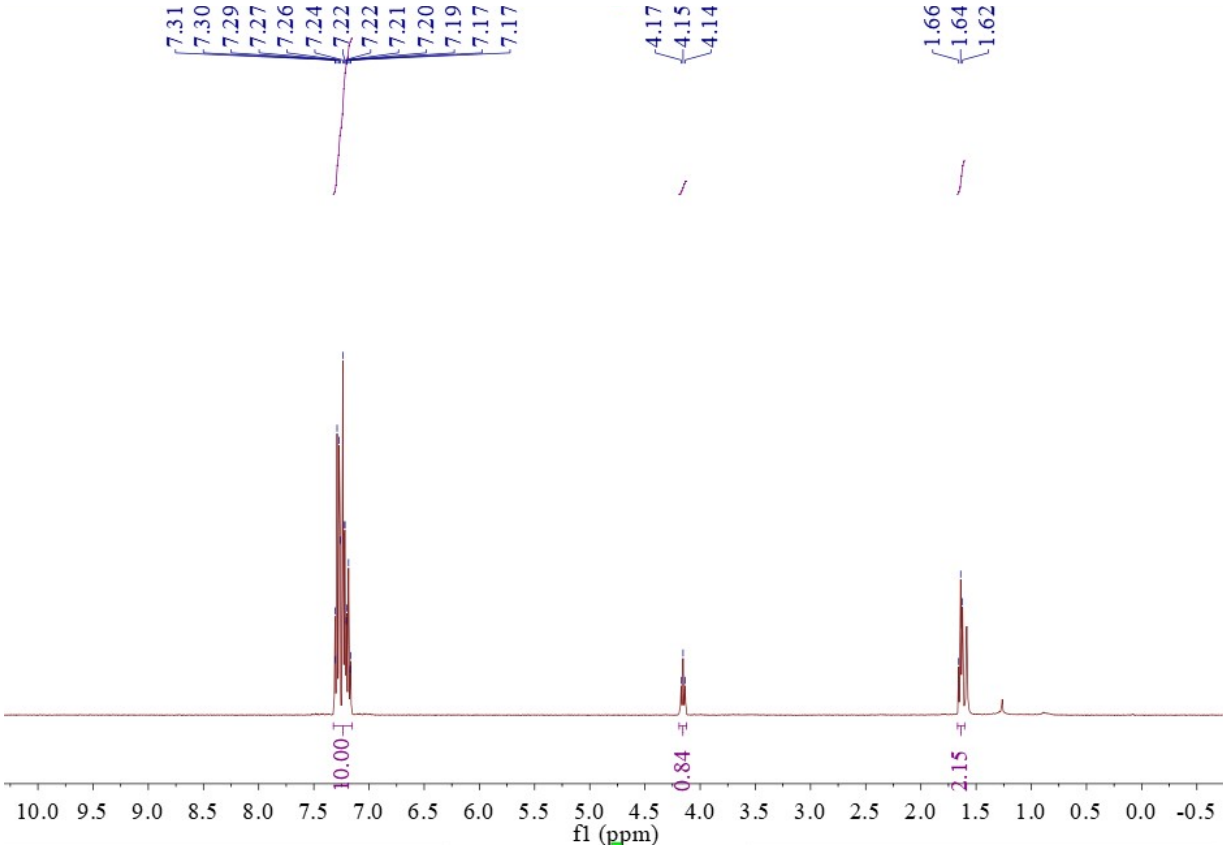
The procedure was the same as the above reduction of aromatic olefin (**1a**) except under argon in solvent of CD_3OD (0.5 mL, Eq. 5) or CH_3OD (0.5 mL, Eq. 6).

2a' in Eq. 5: 8 mg, yield 23%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.17 (m, 10 H), 4.15 (t, J = 7.1 Hz, 0.84 H), 1.64 (t, J = 6.9 Hz, 2.15 H). EI-MS 183.1, 167.1, 152.0.

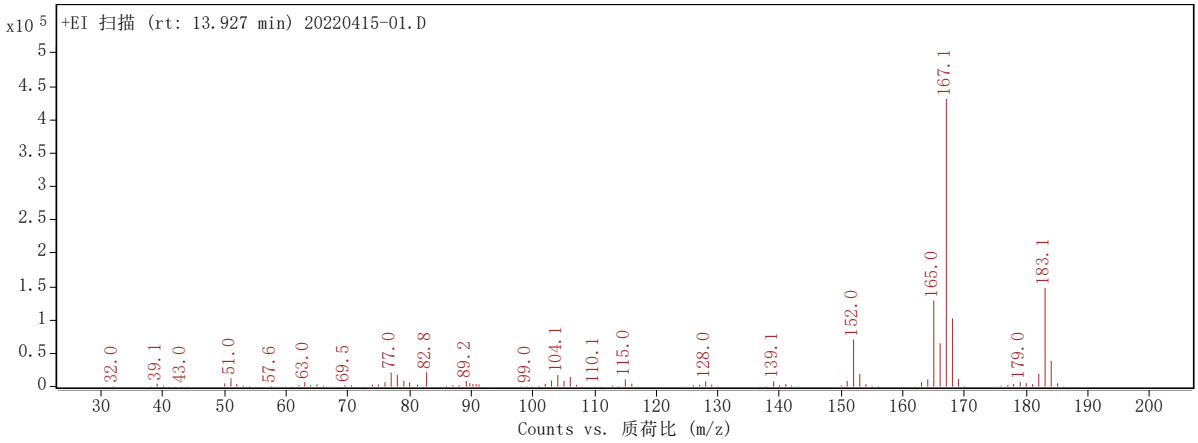
2a' in Eq. 6: 11 mg, yield 31%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.17 (m, 10H), 4.16 (t, J = 7.1 Hz, 0.91H), 1.65 (t, J = 6.9 Hz, 2.33 H). EI-MS 183.1, 167.1, 152.0.

Figure S4. ^{1}H NMR spectrum and EI-MS report of **2a'**

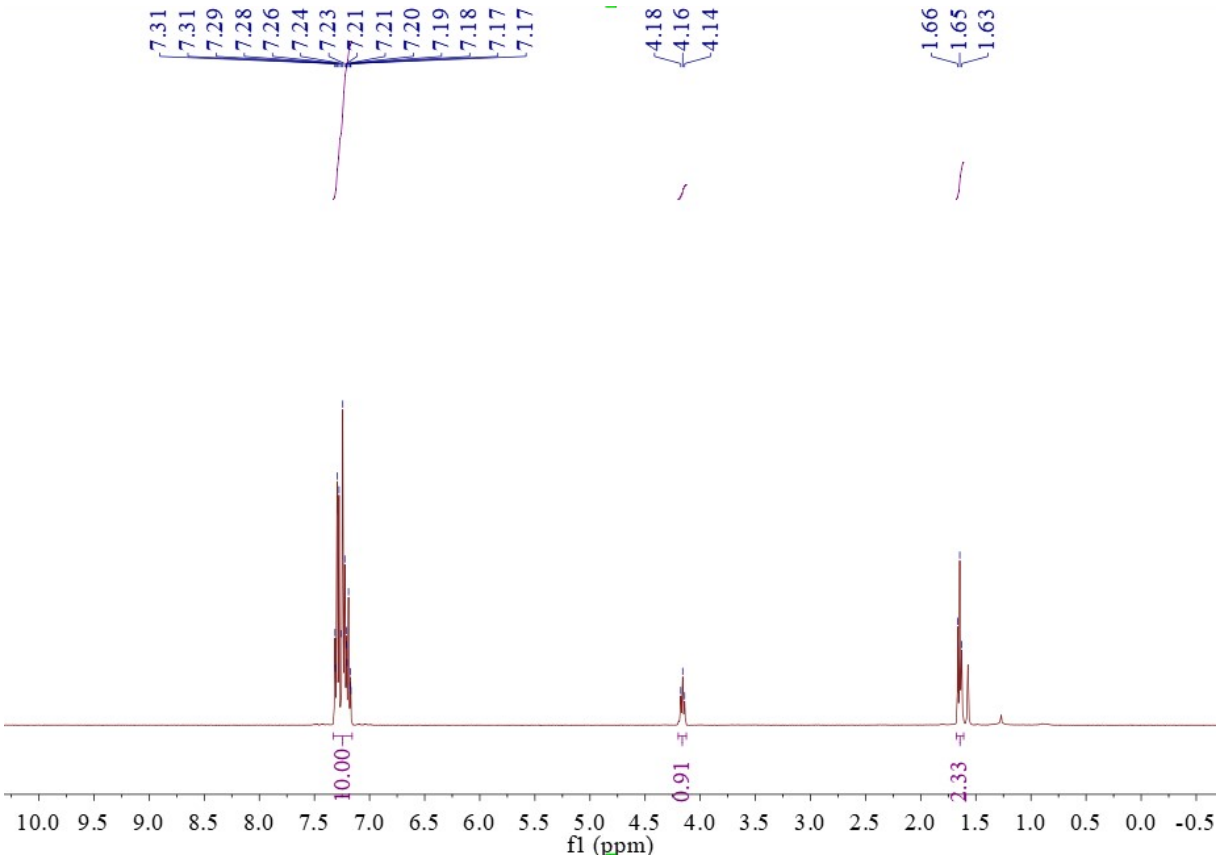
(a) ^{1}H NMR spectrum of **2a'** (400 MHz, $CDCl_3$) In Eq. 5



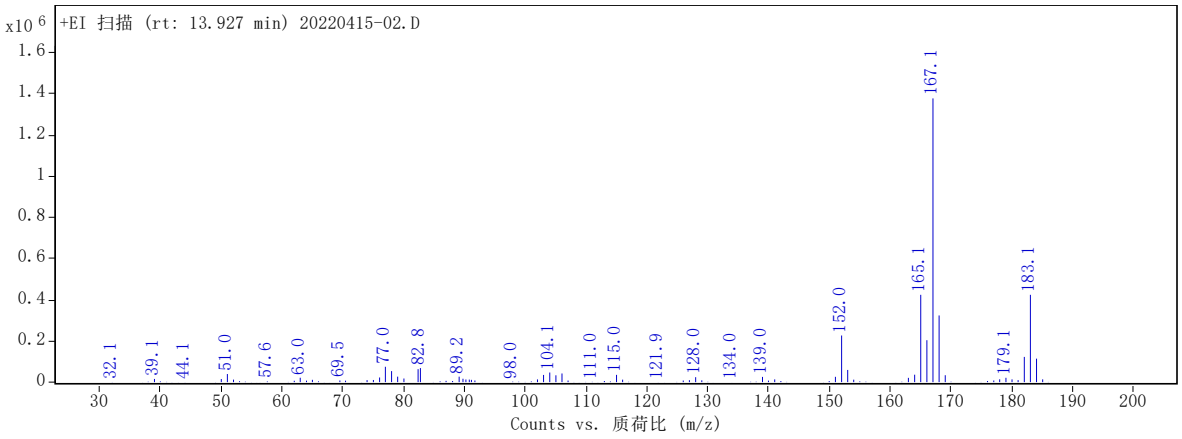
(b) EI-MS report of **2a'** In Eq. 5



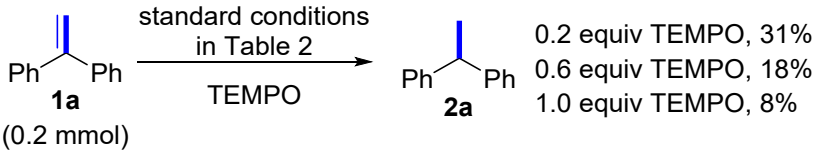
(c) ^{1}H NMR spectrum of **2a'** (400 MHz, $CDCl_3$) In Eq. 6



(d) EI-MS report of **2a'** In Eq. 6

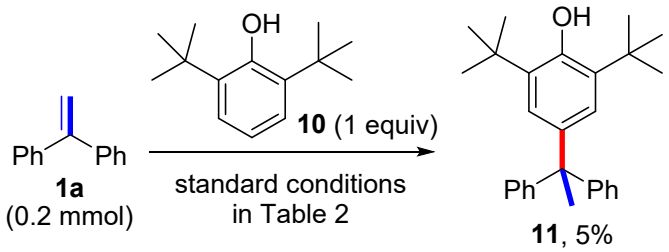


(3) TEMPO as an additive



The procedure with TEMPO as a radical-trapping agent was the same as the standard reduction of aromatic olefin **1a**, except with the addition of TEMPO (0.2/0.6/1.0 equiv), which afforded **2a** in yields of 31%, 18%, or 8%, respectively, as determined by GC-MS with 1,3,5-trimethylbenzene as internal standard.

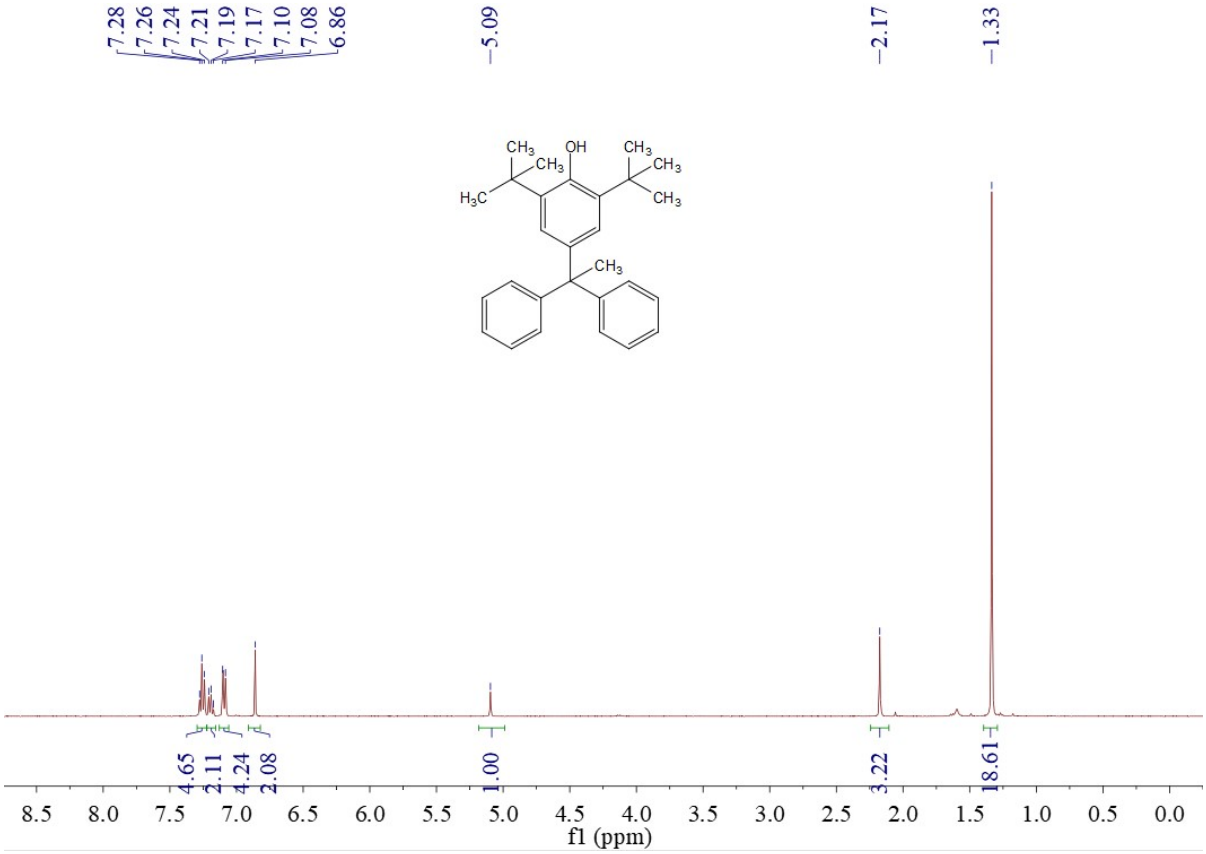
(4) Radical trapping experiment



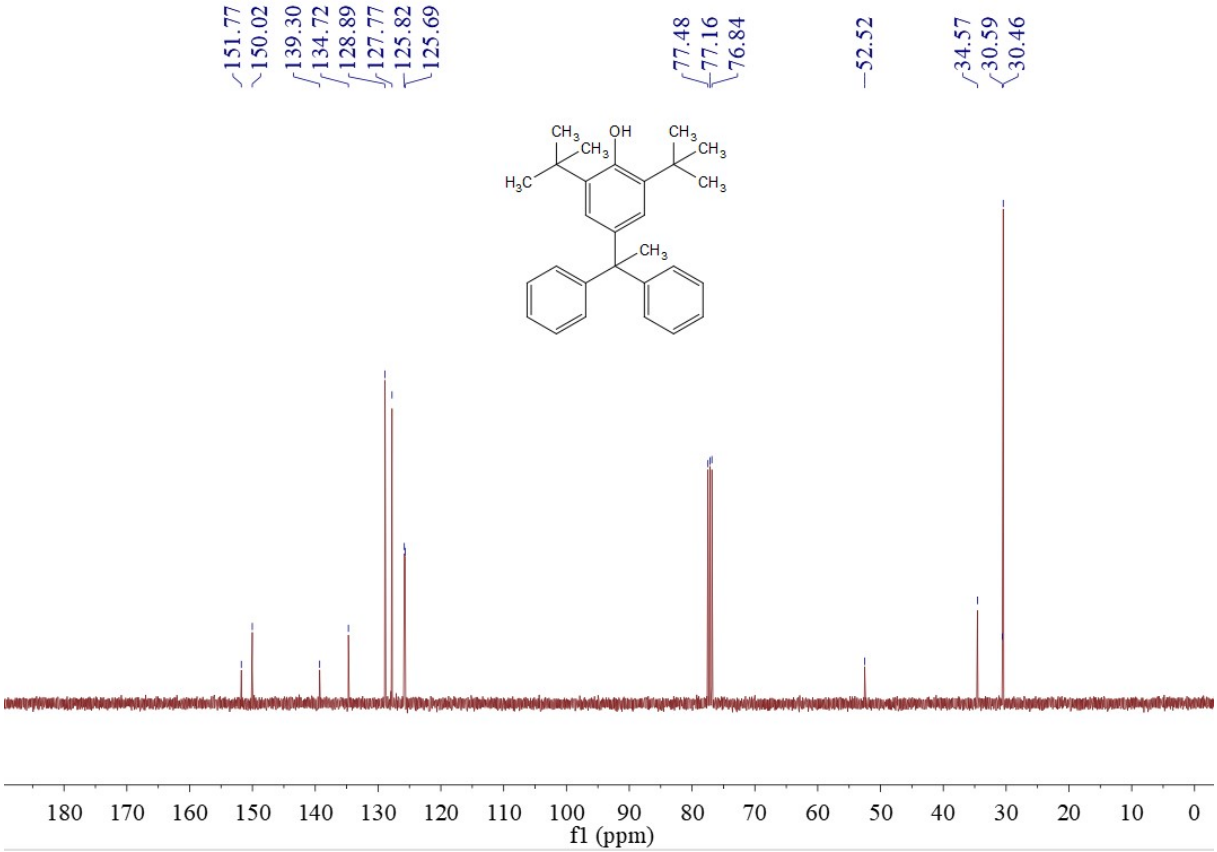
The procedures for the radical trapping experiments were the same as the standard reduction of olefin **1a** (0.2 mmol) , except with the addition of 2,6-di-tert-butylphenol (**10**, 0.2 mmol), which gave 10 mg of **11** (yield 5%) after purification by preparative TLC with hexane as light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (t, J = 7.3 Hz, 4H), 7.19 (t, J = 7.2 Hz, 2H), 7.09 (d, J = 8.4 Hz, 4H), 6.86 (s, 2H), 5.09 (s, 1H), 2.17 (s, 3H), 1.33 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.8, 150.0, 139.3, 134.7, 128.9, 127.8, 125.8, 125.7, 52.5, 34.6, 30.6, 30.5. EI-MS: m/z 386.2, 371.2, 355.1. HRMS m/z (ESI) calcd. for $C_{28}H_{35}O^{+}$ $[M+H]^{+}$: 387.2682; found: 387.2696.

Figure S5. NMR spectrum and GC-MS report of **11**.

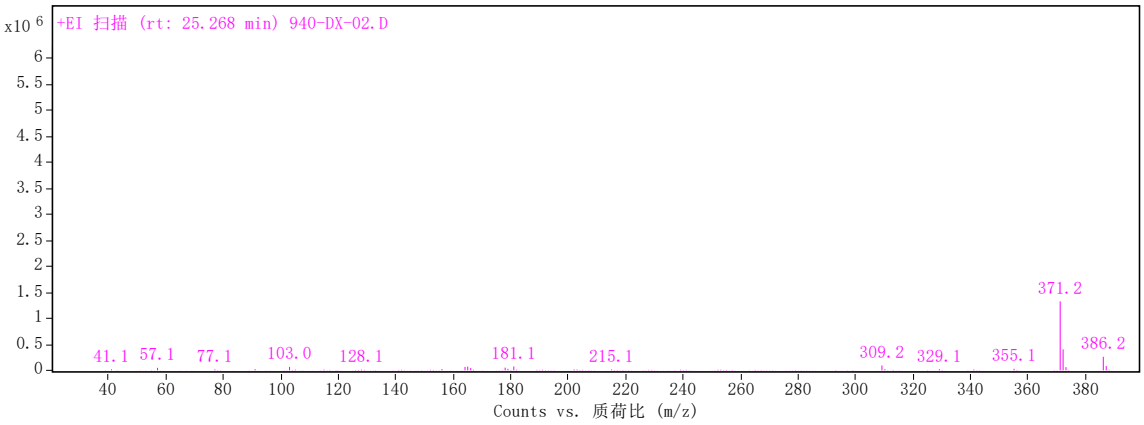
(a) ^{1}H NMR of **11** (400 MHz, $CDCl_3$)



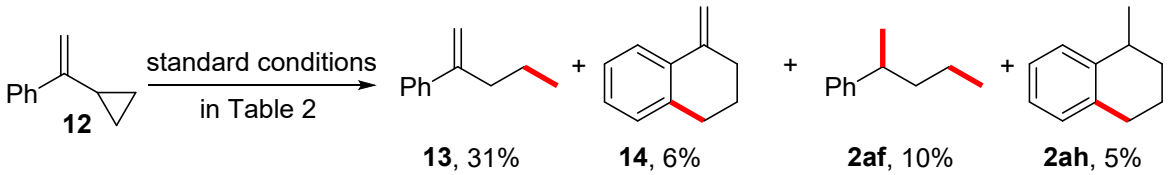
(b) ^{13}C NMR of **11** (100 MHz, $CDCl_3$)



(c) EI-MS report of **11**



(5) Radical clock experiment



The procedure for the radical clock experiment was the same as the standard reduction of aromatic olefin with the addition of (1-cyclopropylvinyl)benzene (**12**, 0.2 mmol). The reaction mixture was analyzed by GC-MS with 1,3,5-trimethylbenzene as internal standard, which indicated the formation of **13** (yield 31%), **2af**

(yield 10%), **14** (yield 6%), and **2ah** (yield 5%), whose retention times were 9.064 min, 8.464 min, 11.123 min, and 10.359 min, respectively. Because of their similar polarity, these products were not separated, and the structures of **13** and **14** were further confirmed by reference with standard substances that were prepared by Wittig reaction which had the same retention time and MS spectrum in GC-MS (Figure S6).[1]

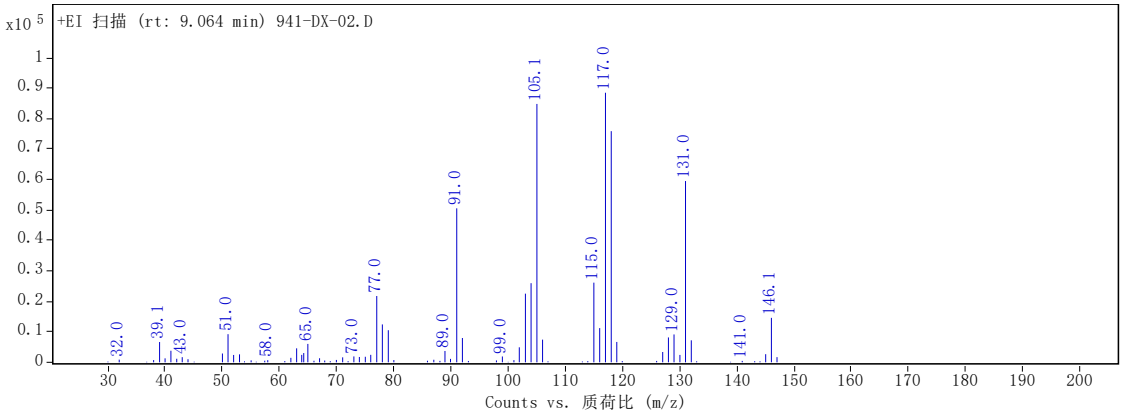
Procedure for the preparation of **13** or **14** by Wittig reaction[1]: To a 25 mL round bottom flask equipped with a stir bar under argon was added methyltriphenylphosphonium bromide (2.143 g, 6 mmol) and THF (10 mL). After the reaction was cooled to 0 ºC, *n*-BuLi (2.5 M in *n*-hexane, 2.4 mL, 6 mmol) was added and the mixture was stirred for 1 h at room temperature. Then 1-phenylbutan-1-one (0.724 mL, 5 mmol) or 3,4-dihydronaphthalen-1(2H)-one (0.664 mL, 5 mmol) was added to the system and the reaction mixture was stirred overnight. Upon completion, the reaction was quenched with water (5 mL), extracted with ether (3×10 mL), and dried with anhydrous Na_2SO_4. The mixture was filtered, and the resulting filtrate was concentrated and purified by flash column chromatography (petroleum ether) to give product **13** or **14**.

Compound **13**: Colorless oil, 633 mg, yield 87%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 8.4 Hz, 2H), 7.38-7.29 (m, 2H), 7.30-7.24 (m, 1H), 5.28 (s, 1H), 5.07 (s, 1H), 2.54-2.45 (t, J = 7.4 Hz, 2H), 1.55-1.42 (m, 2H), 0.93 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6, 141.5, 128.4, 127.4, 126.3, 112.3, 37.6, 21.4, 13.9. These data were agreed with literature.[1]

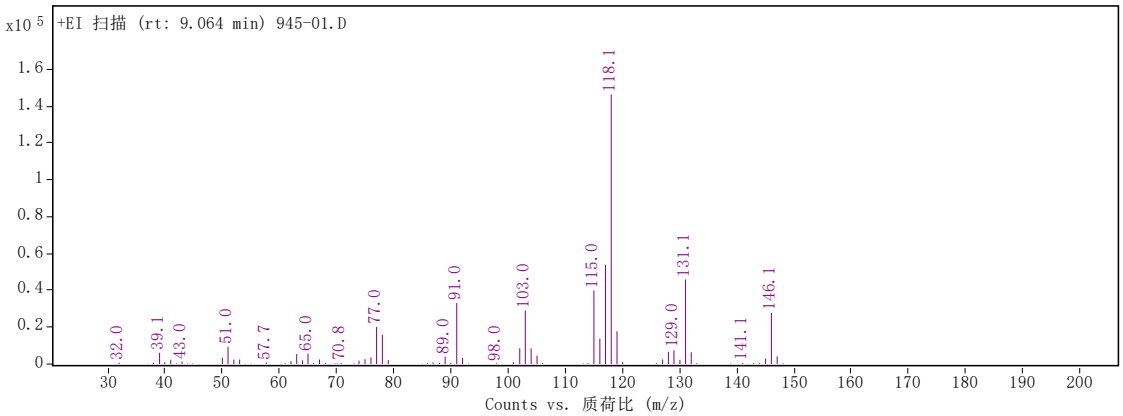
Compound **14**: Colorless oil, 566 mg, yield 79%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71-7.63 (m, 1H), 7.23-7.08 (m, 3H), 5.49 (s, 1H), 4.97 (s, 1H), 2.87 (t, J = 6.3 Hz, 2H), 2.60-2.53 (m, 2H), 1.93-1.87 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 137.4, 134.8, 129.3, 127.7, 126.0, 124.3, 108.0, 33.4, 30.6, 23.9. These data were agreed with literature.[1]

Figure S6. GC-MS report and ^{1}H NMR spectrum of **13** and **14**

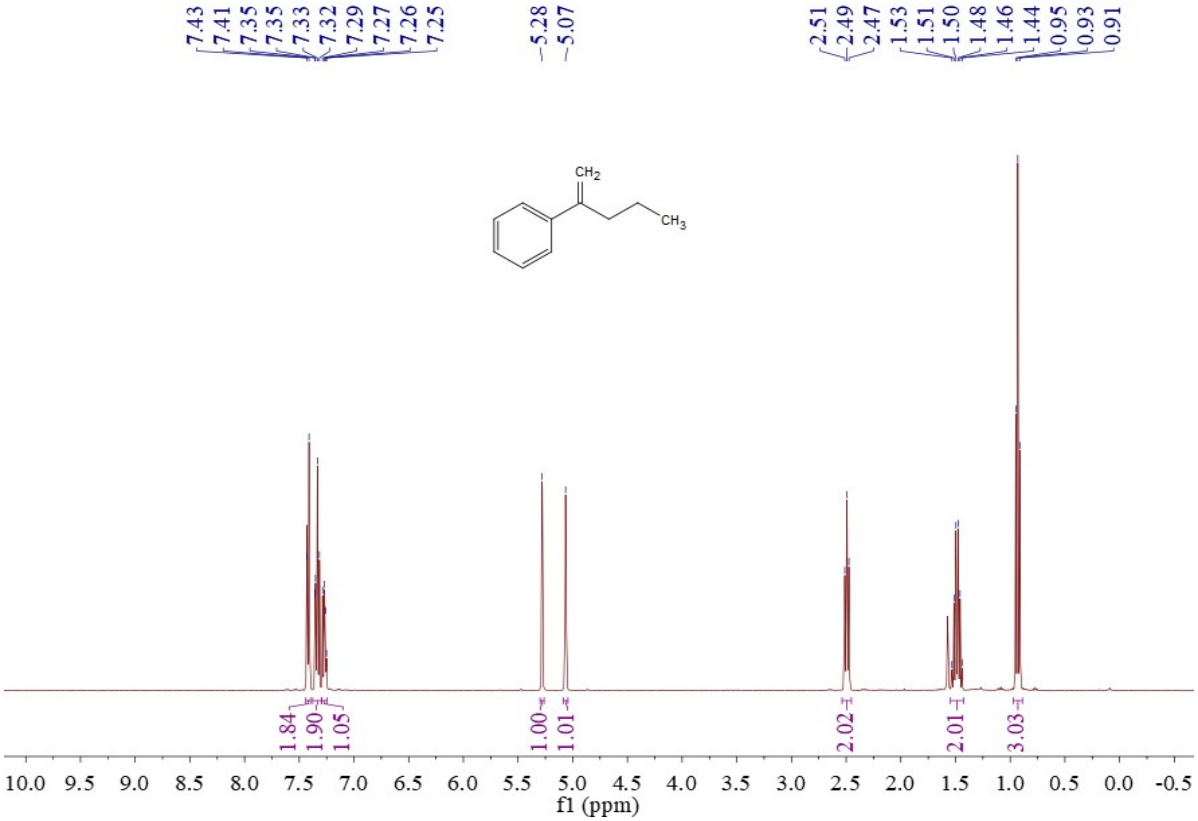
(a) GC-MS report of **13** (t_R=9.064 min) from the reduction of **12**



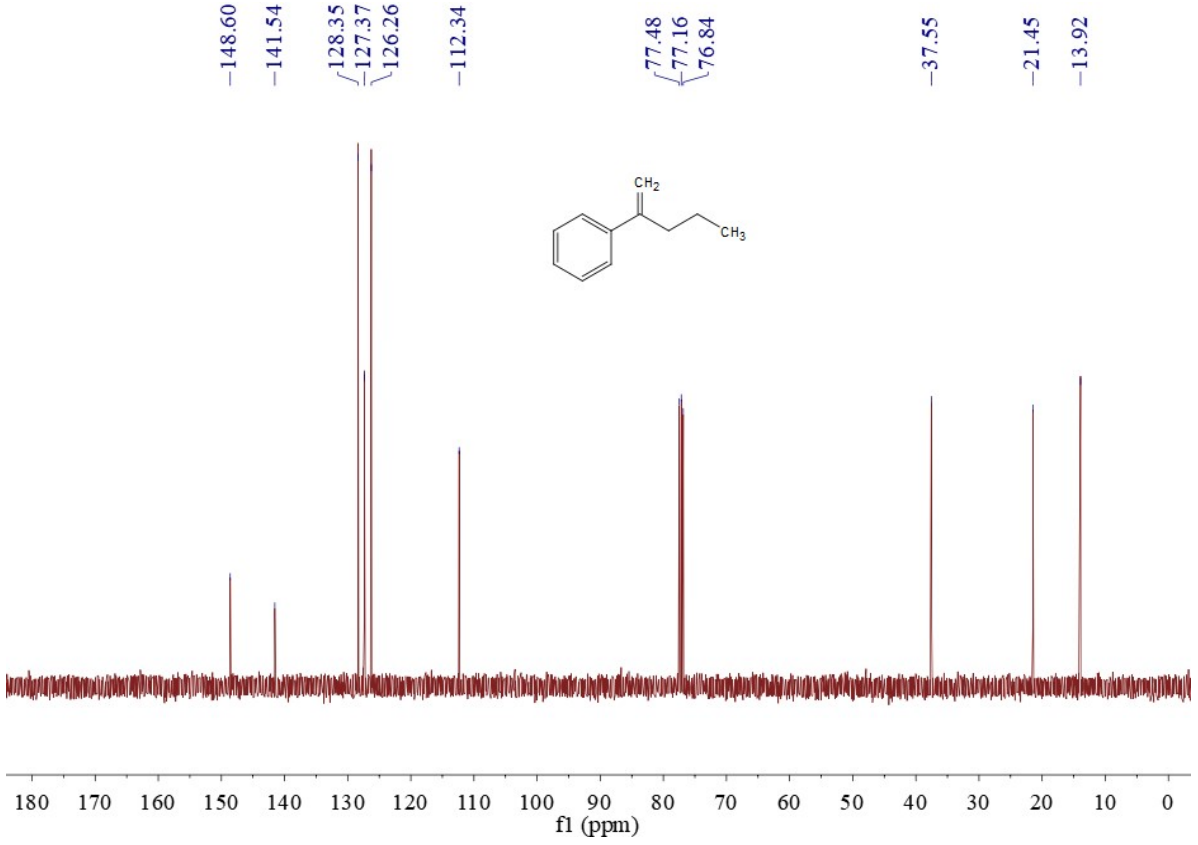
(b) GC-MS report of **13** (t_R=9.064 min) prepared by Wittig reaction[1]



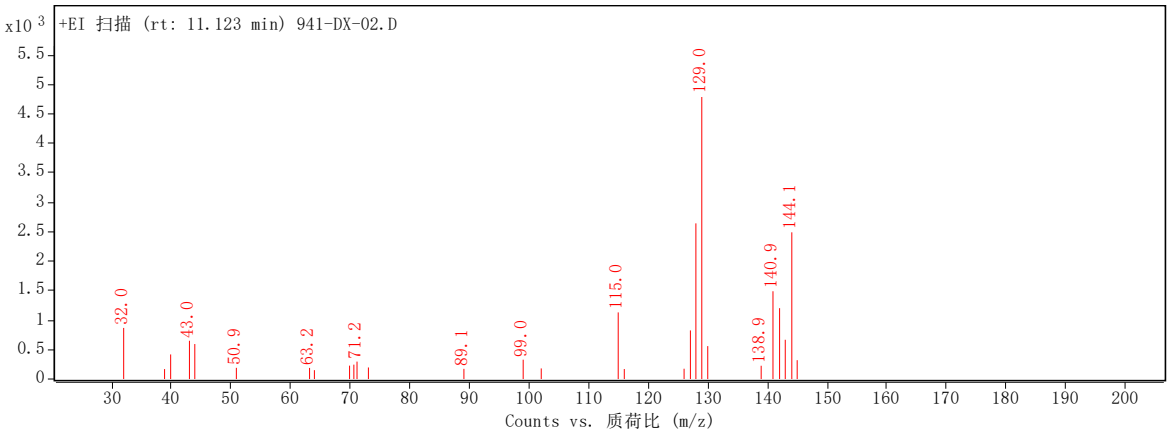
(c) ^{1}H NMR of **13** (400 MHz, $CDCl_3$) prepared by Wittig reaction[1]



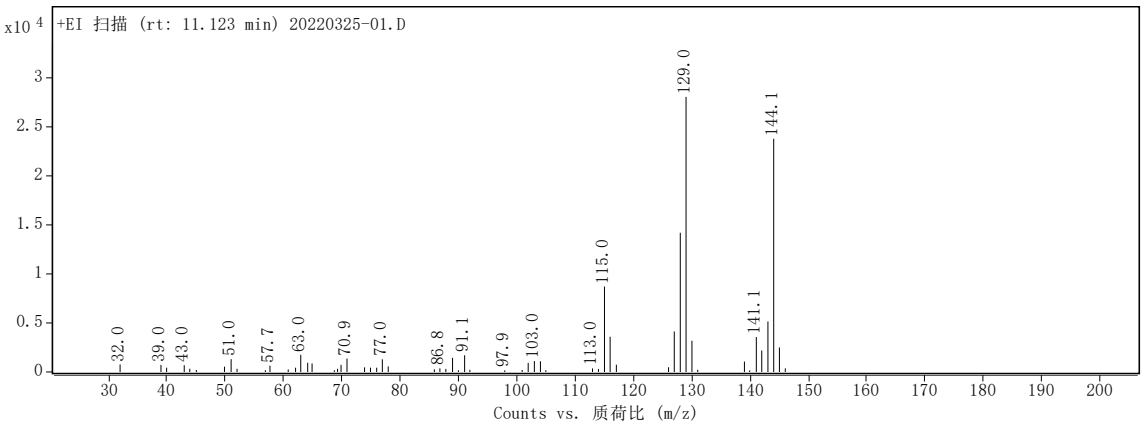
(d) ^{13}C NMR of **13** (100 MHz, $CDCl_3$) prepared by Wittig reaction[1]



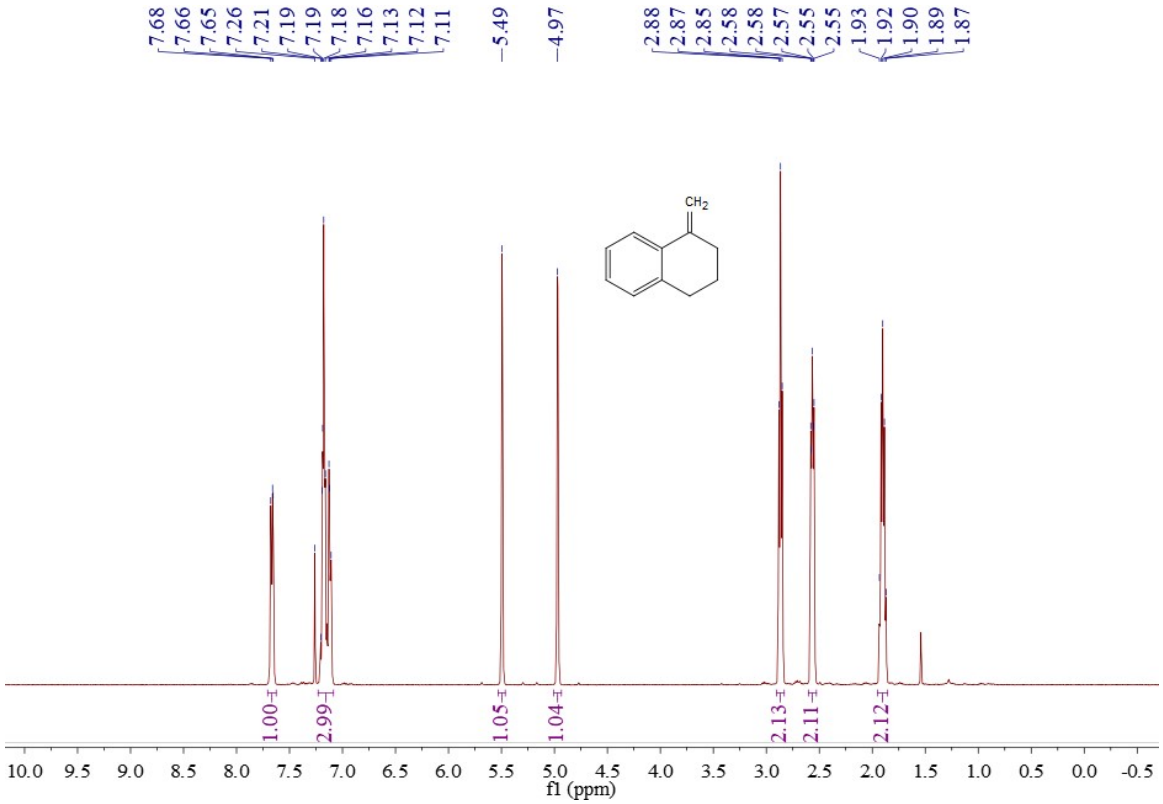
(e) GC-MS report of **14** (t_R=11.123 min) from the reduction of **12**



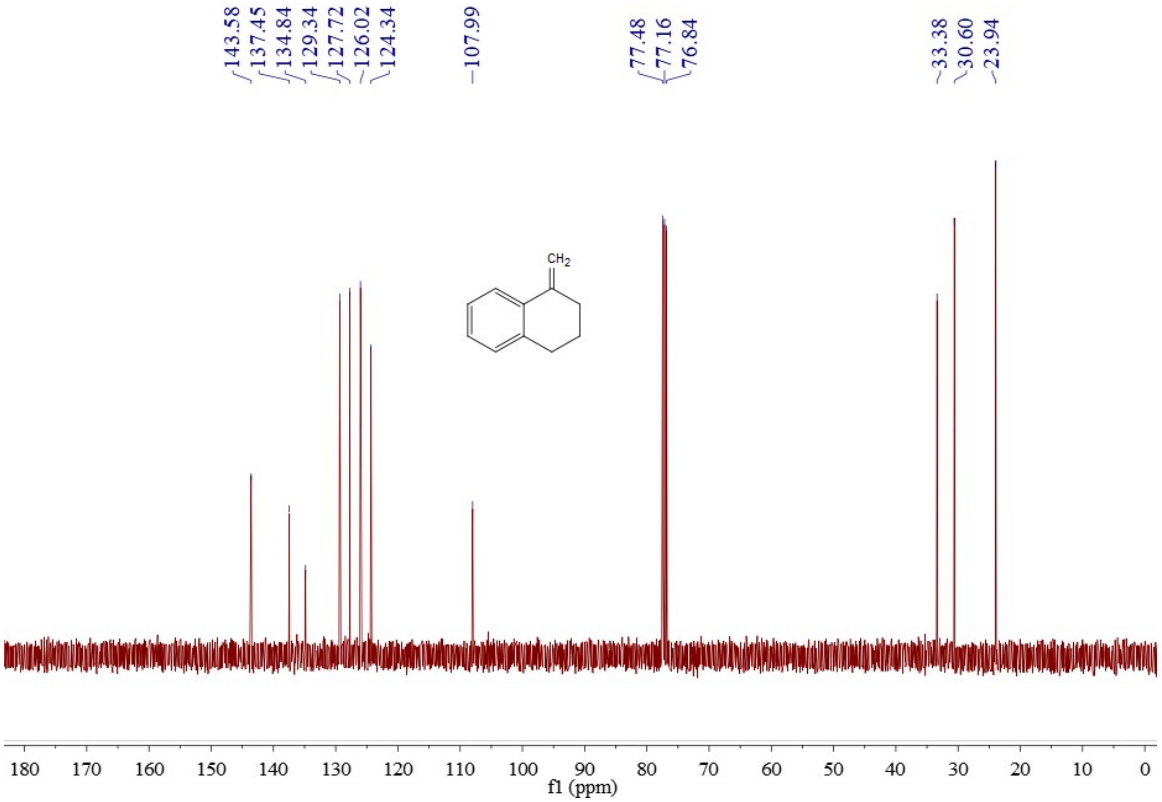
(f) GC-MS report of **14** (t_R=11.123 min) prepared by Wittig reaction[1]



(g) ^{1}H NMR of **14** (400 MHz, $CDCl_3$) prepared by Wittig reaction[1]



(h) ^{13}C NMR of **14** (100 MHz, $CDCl_3$) prepared by Wittig reaction[1]



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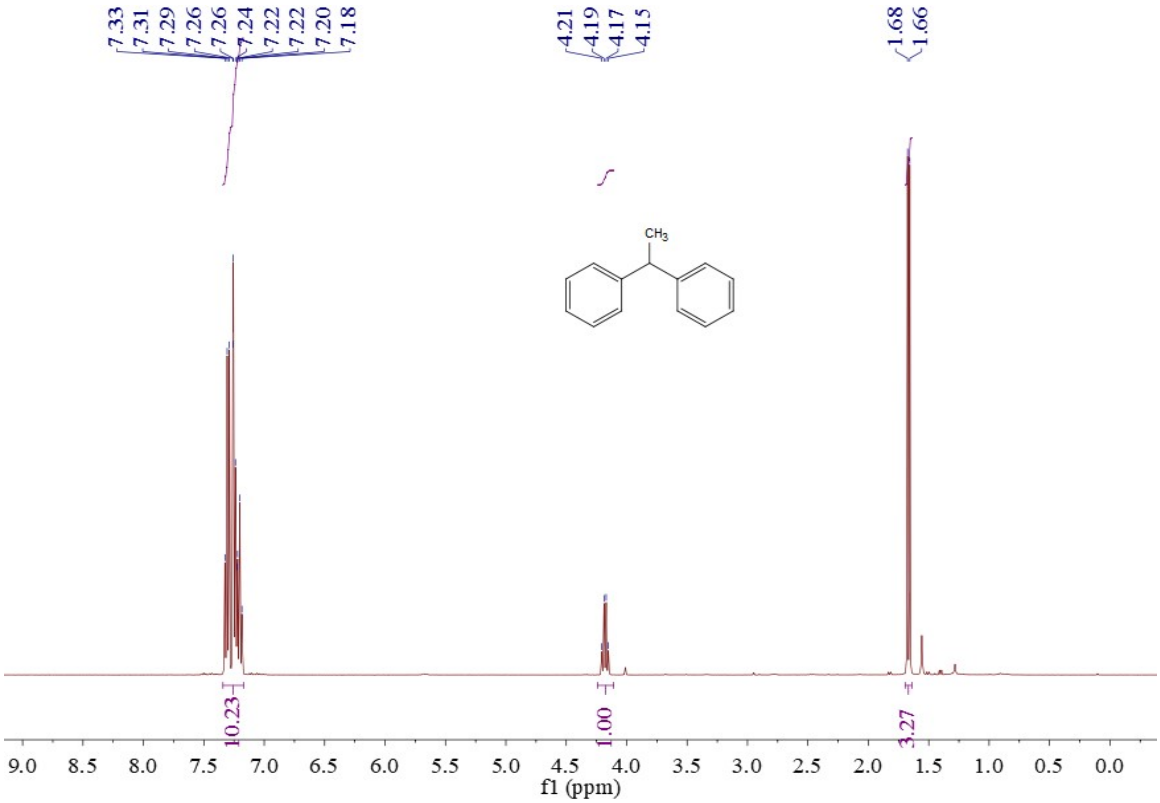
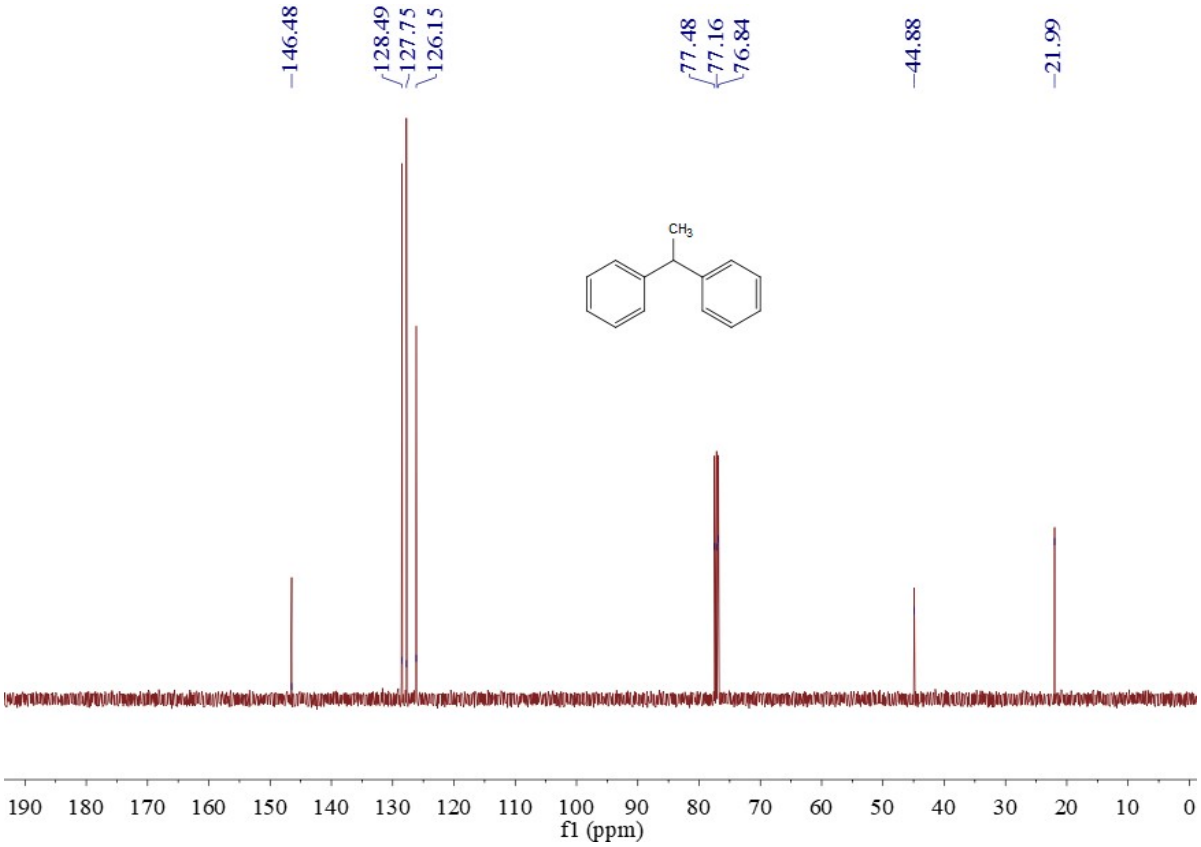
6. NMR Spectra

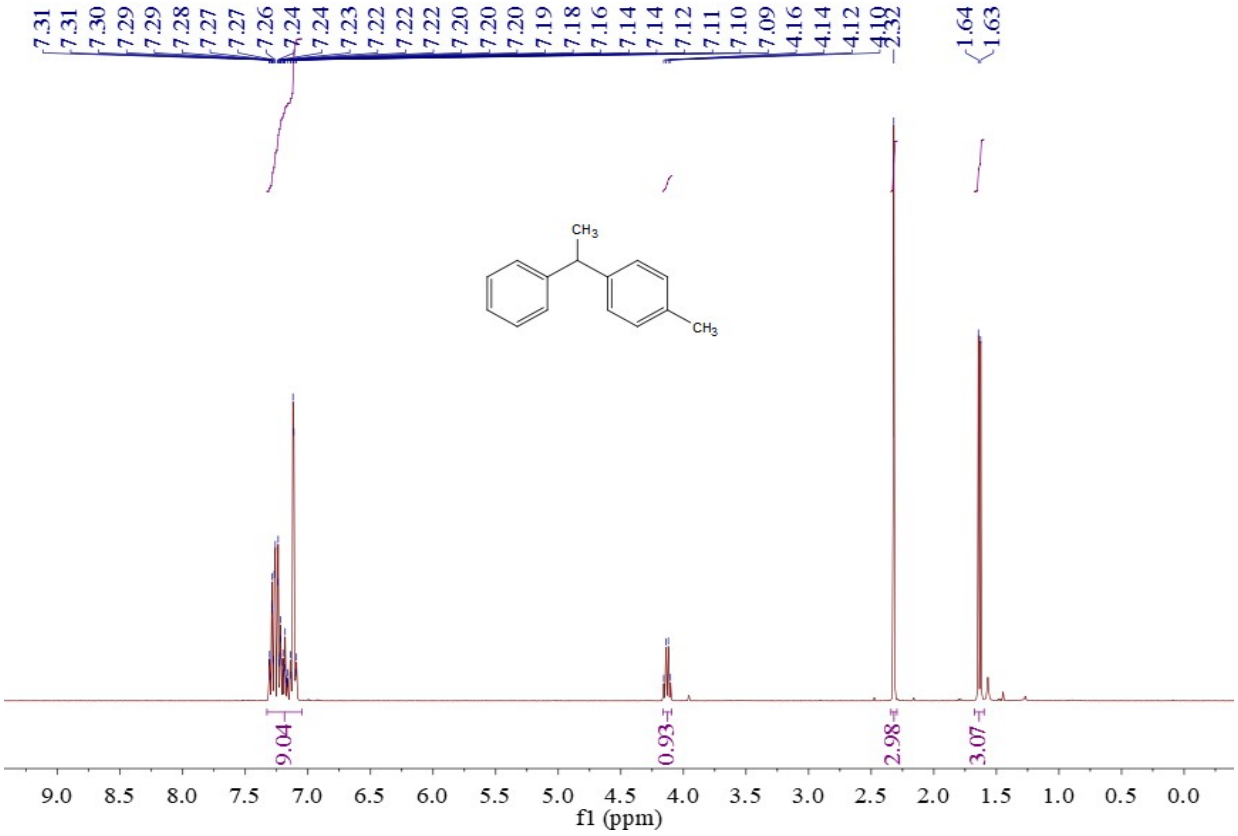
^{1}H NMR of compound 2a (400 MHz, $CDCl_3$):



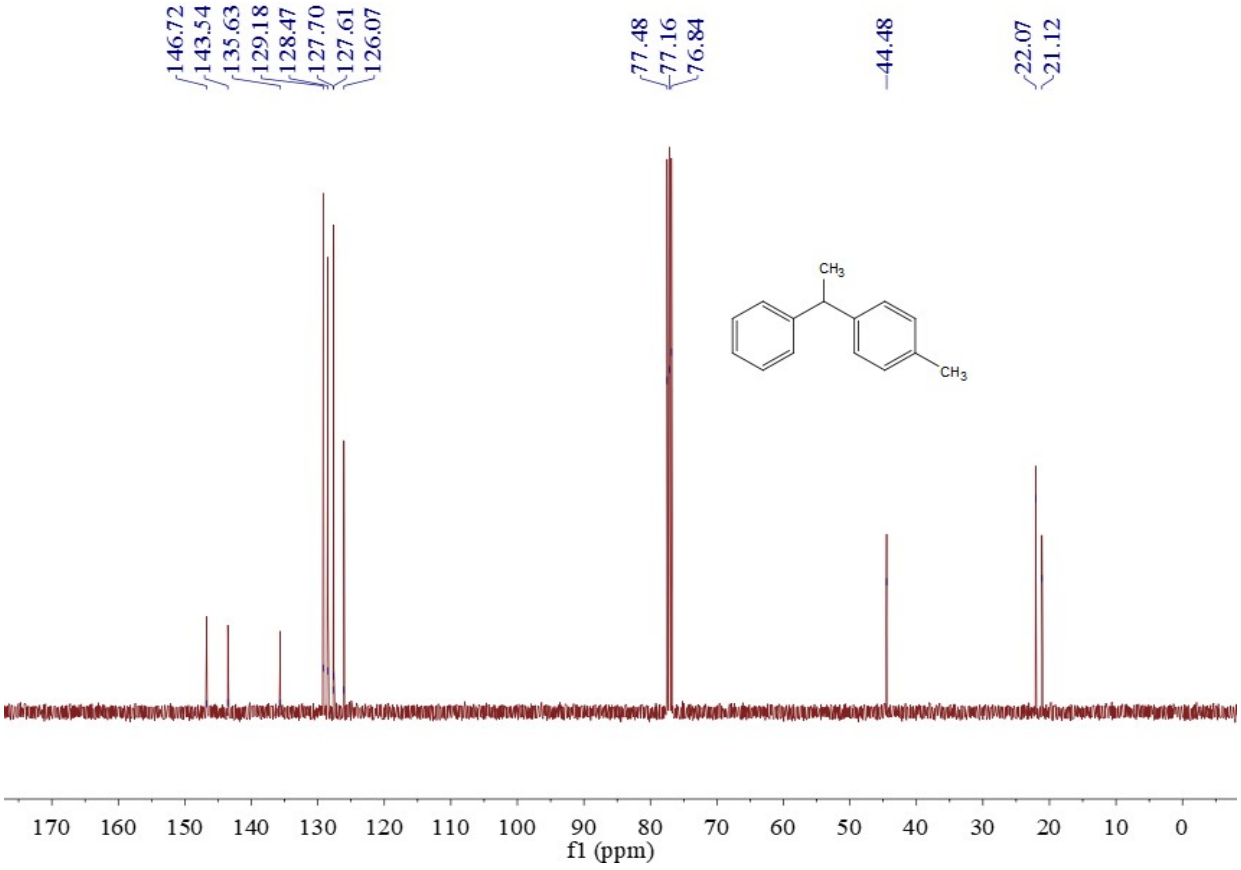
^{13}C NMR of compound 2a (100 MHz, $CDCl_3$):



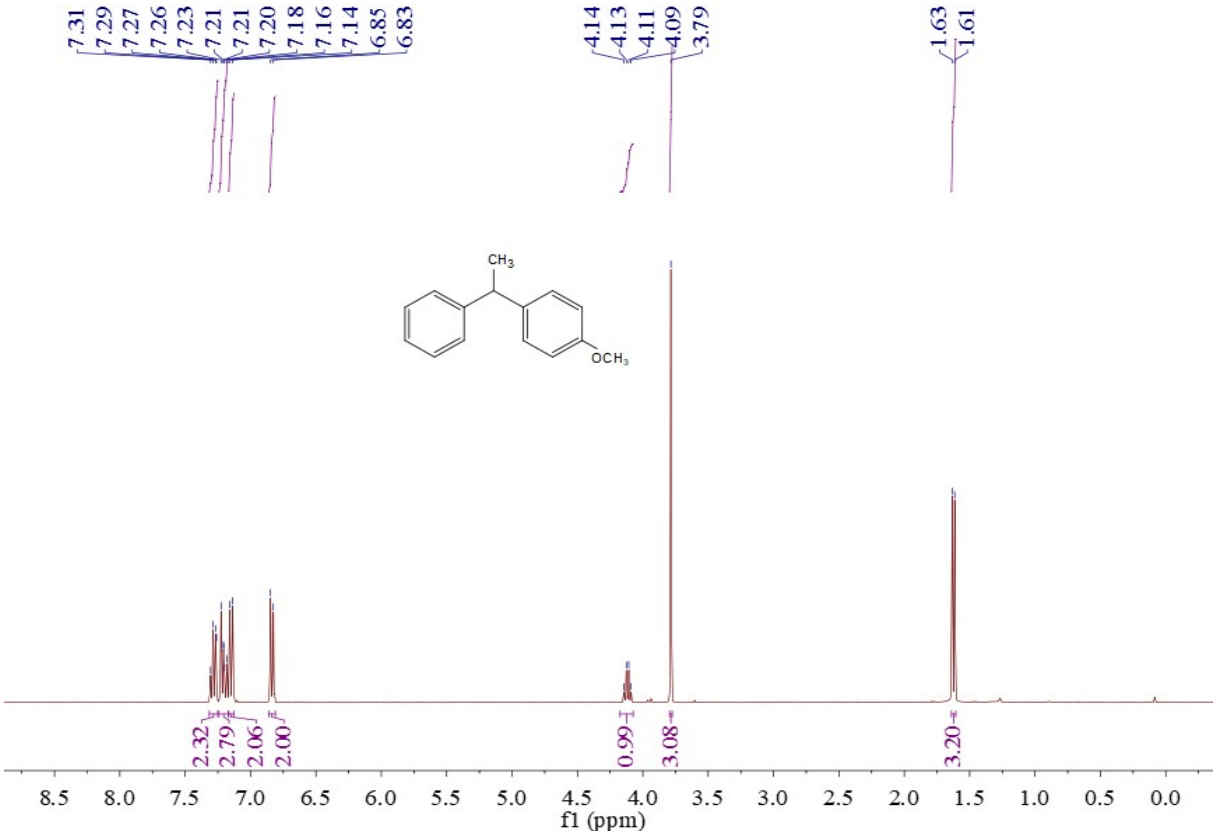
^{1}H NMR of compound 2b (400 MHz, $CDCl_3$):



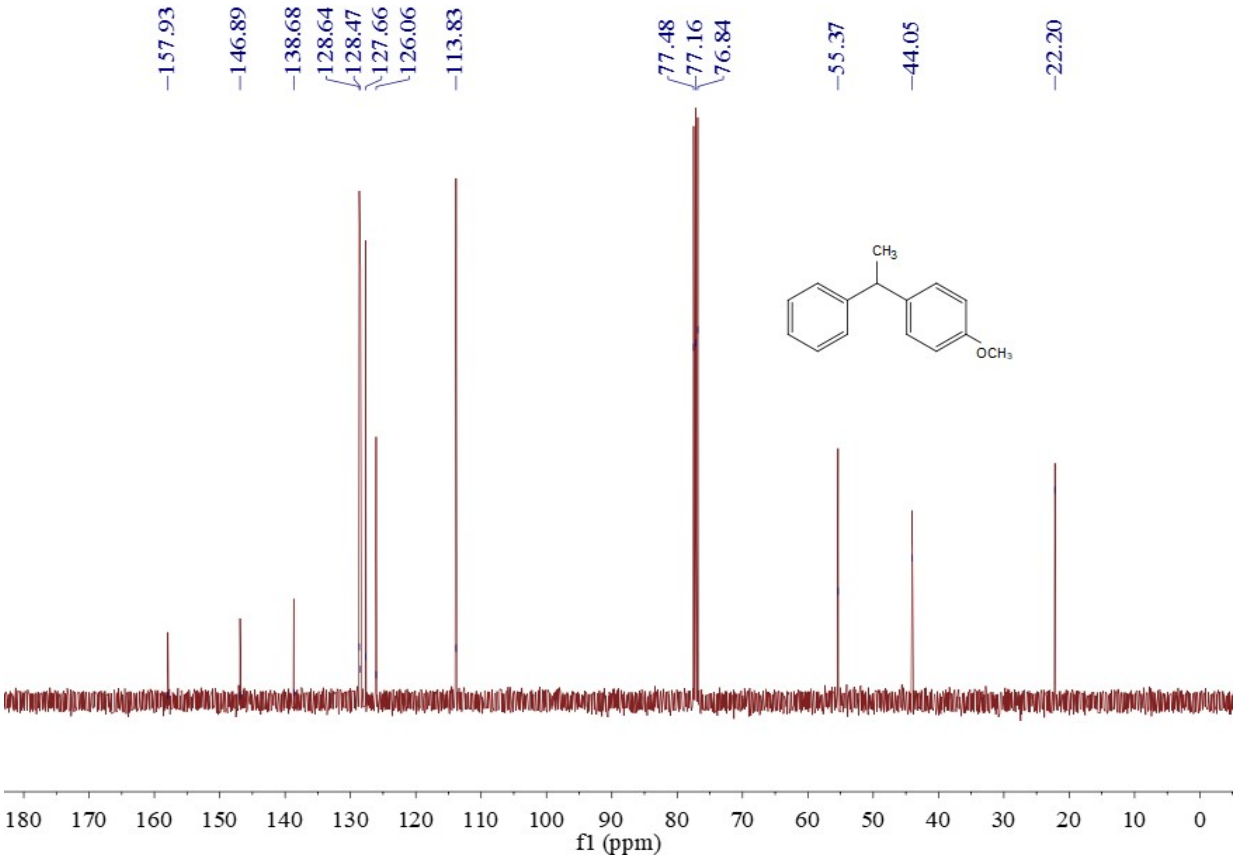
^{13}C NMR of compound 2b (100 MHz, $CDCl_3$):



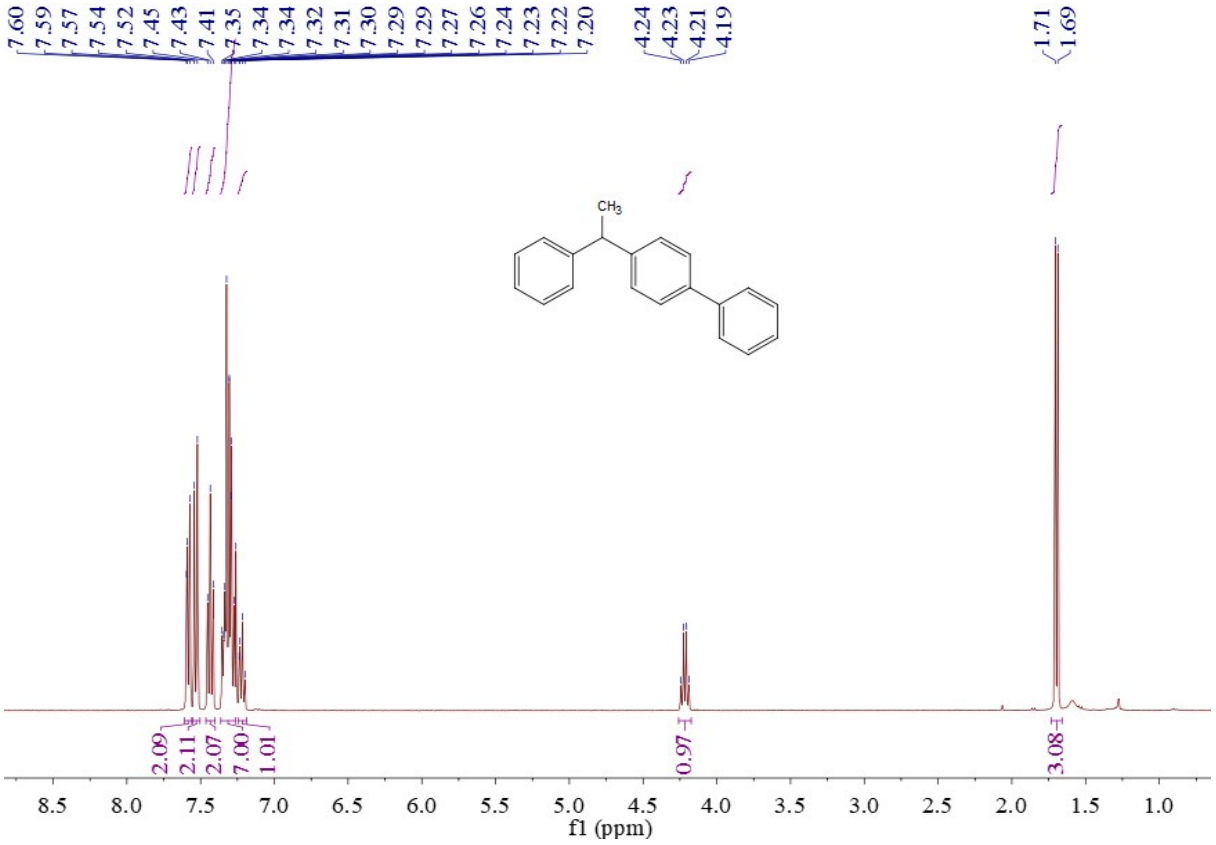
^{1}H NMR of compound 2c (400 MHz, $CDCl_3$):



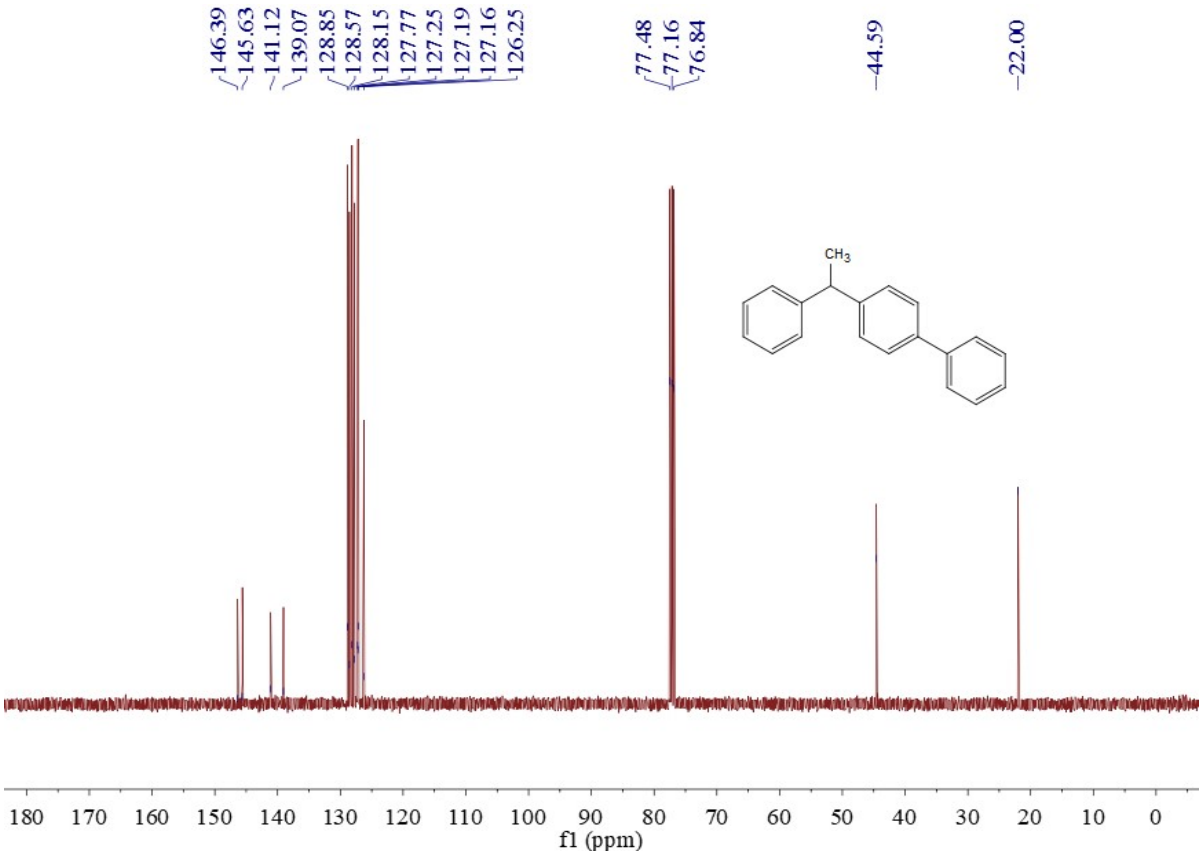
^{13}C NMR of compound 2c (100 MHz, $CDCl_3$):



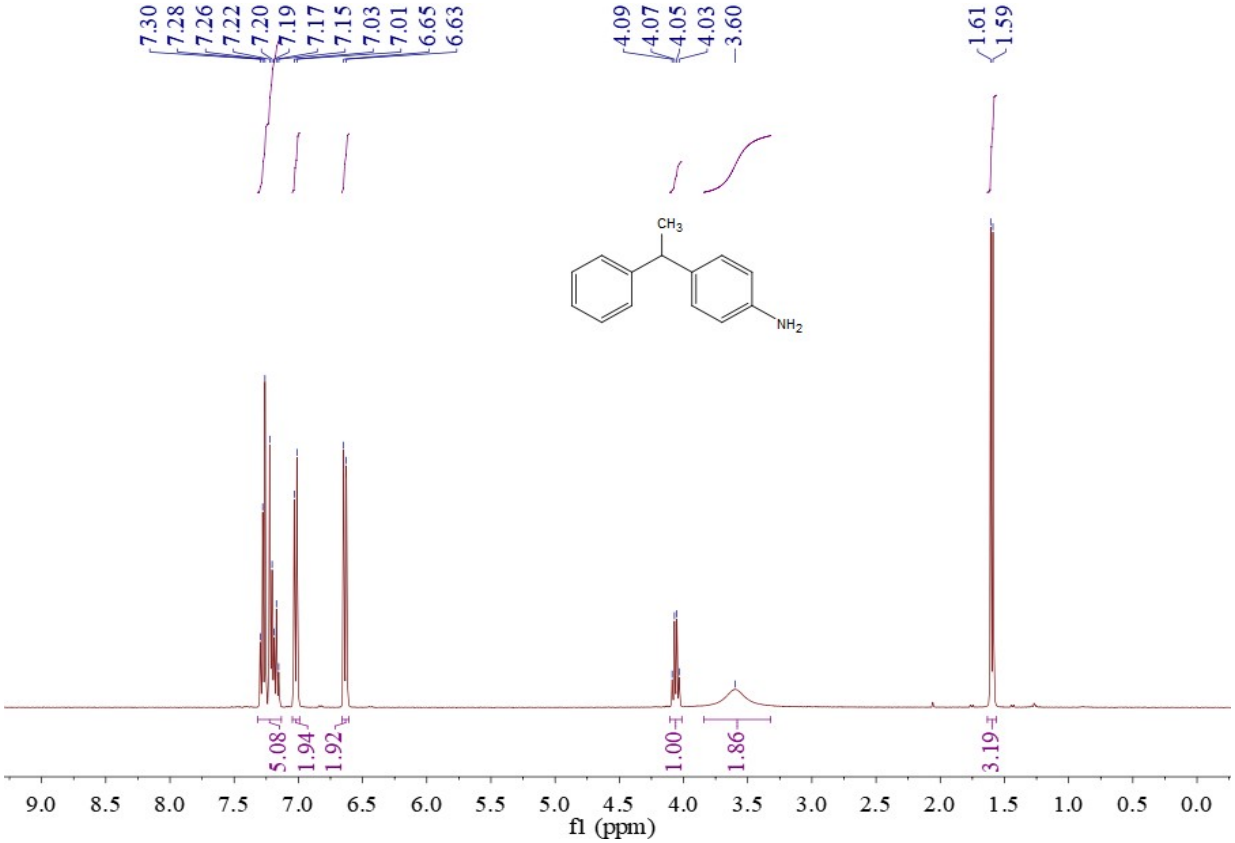
^{1}H NMR of compound 2d (400 MHz, $CDCl_3$):



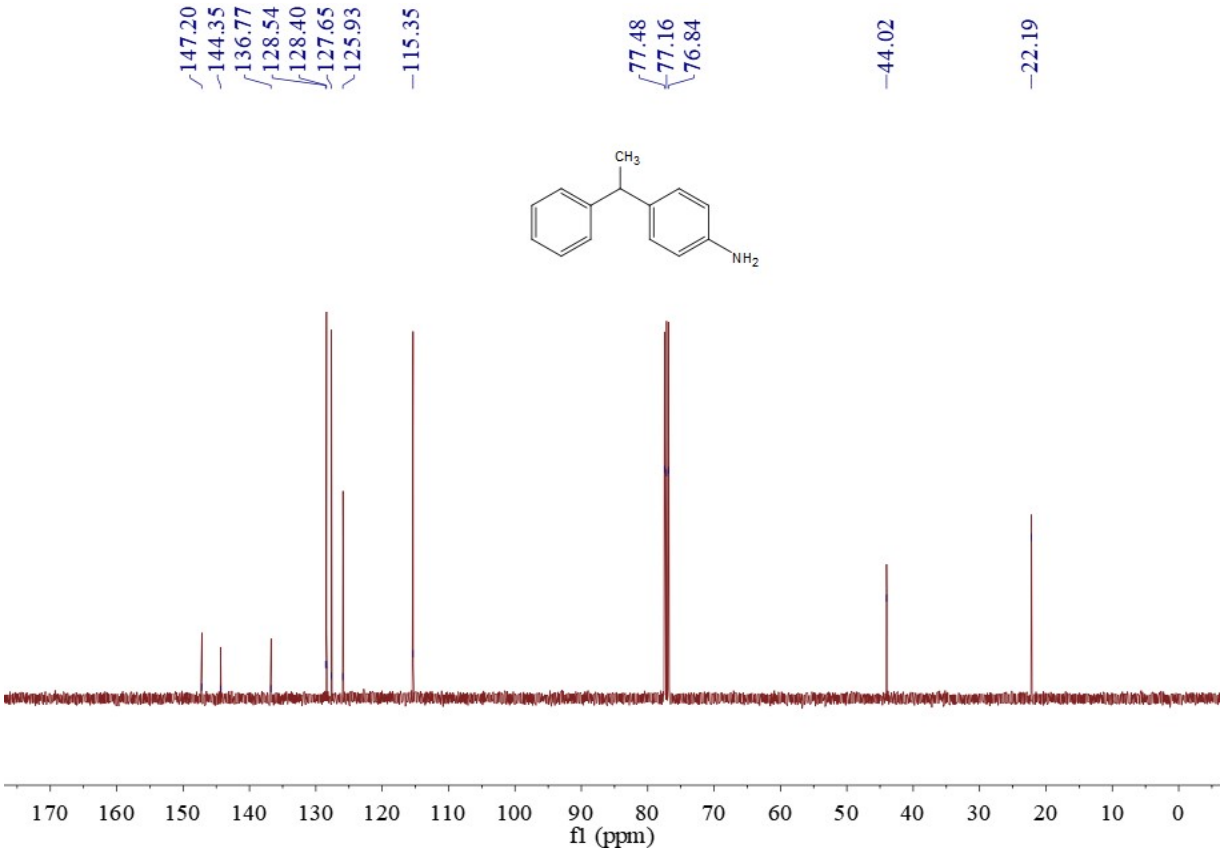
^{13}C NMR of compound 2d (100 MHz, $CDCl_3$):



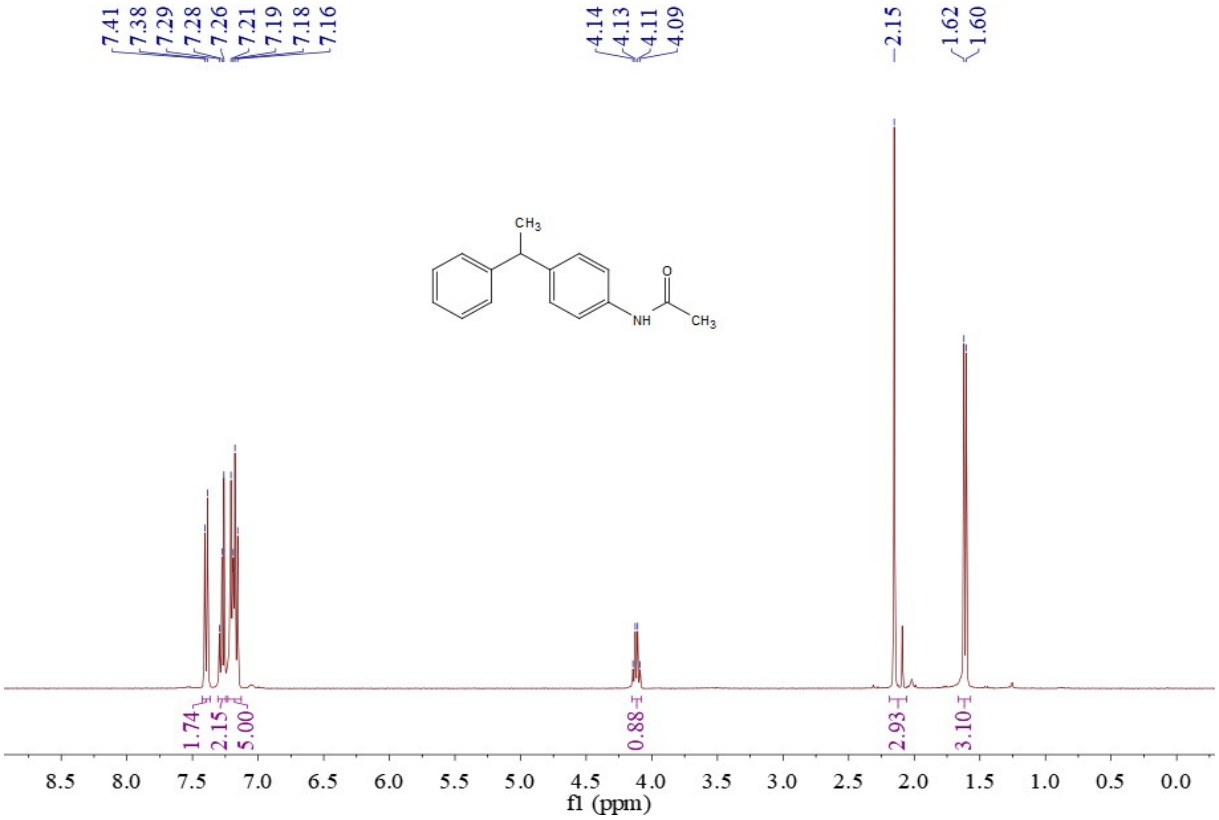
^{1}H NMR of compound 2e (400 MHz, $CDCl_3$):



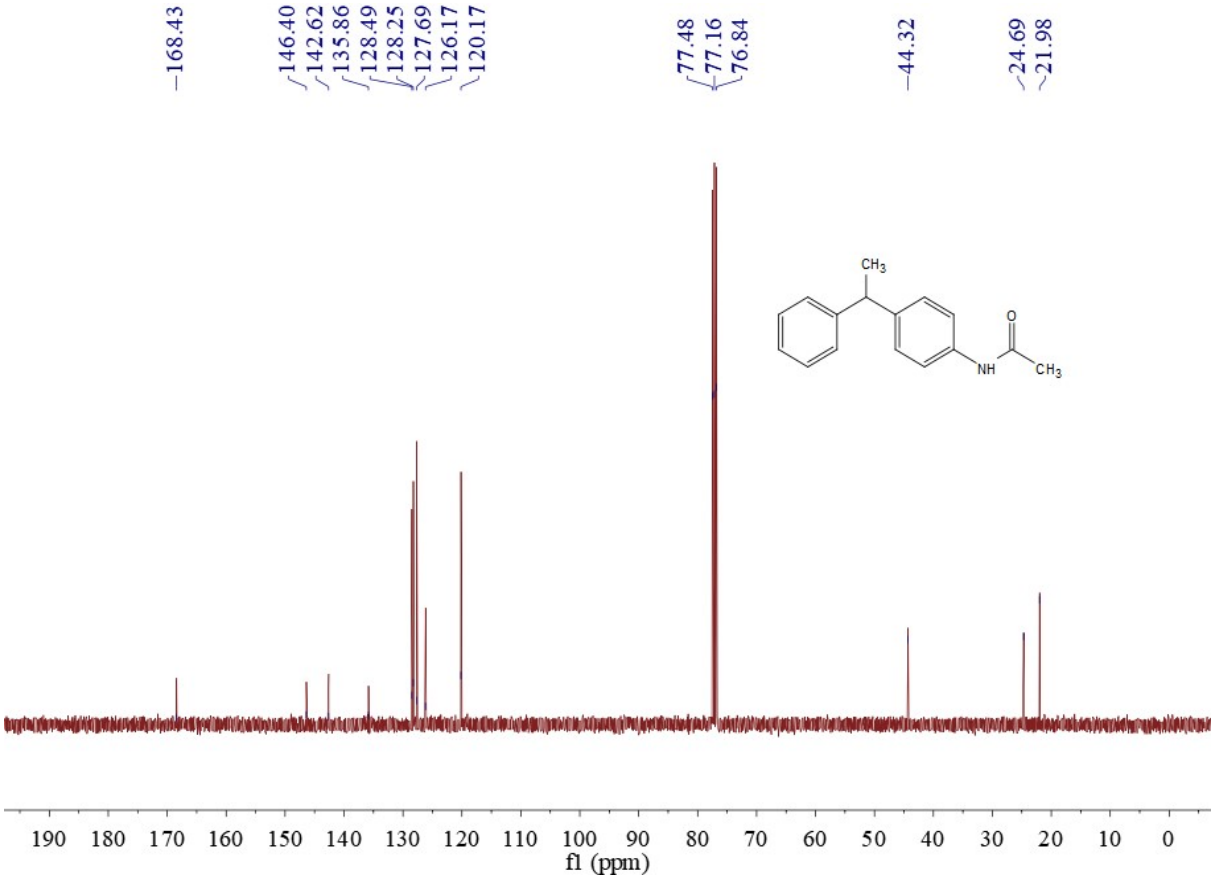
^{13}C NMR of compound 2e (100 MHz, $CDCl_3$):



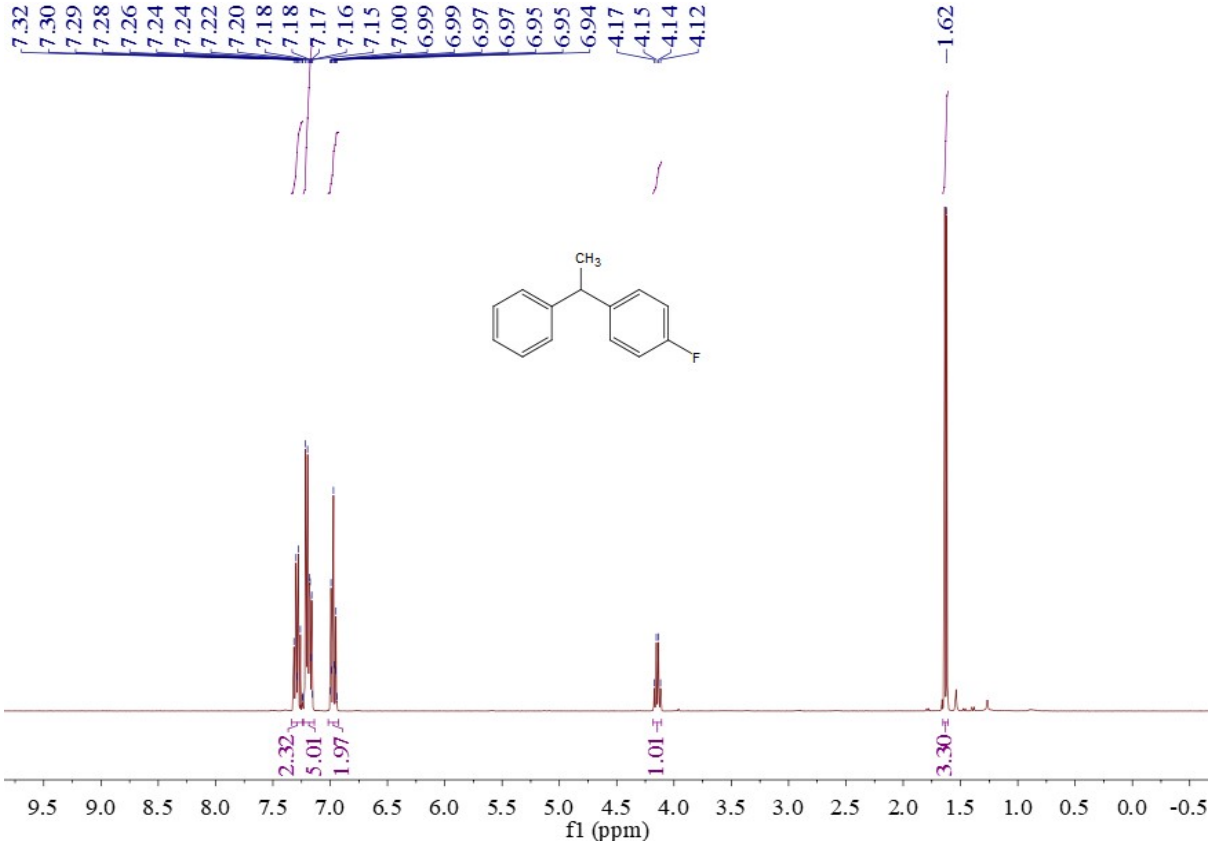
^{1}H NMR of compound 2f (400 MHz, $CDCl_3$):



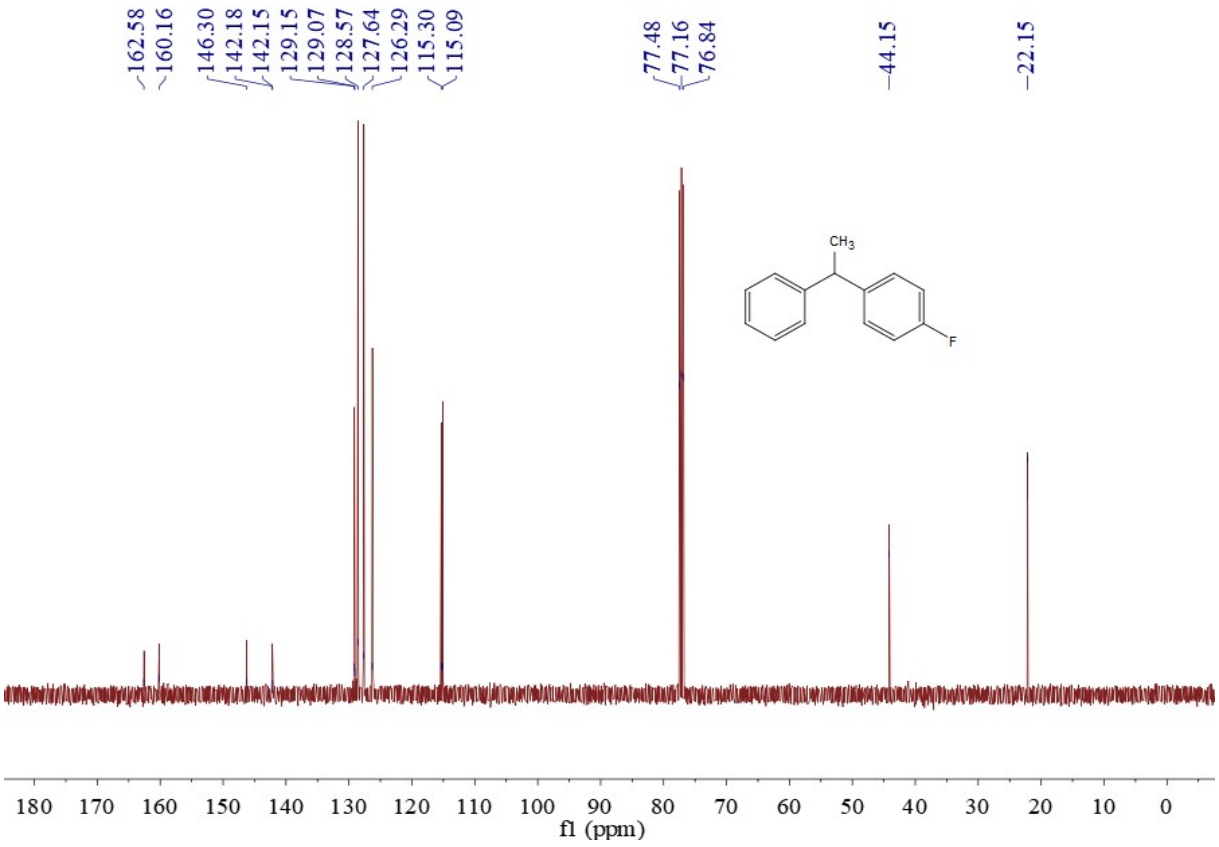
^{13}C NMR of compound 2f (100 MHz, $CDCl_3$):



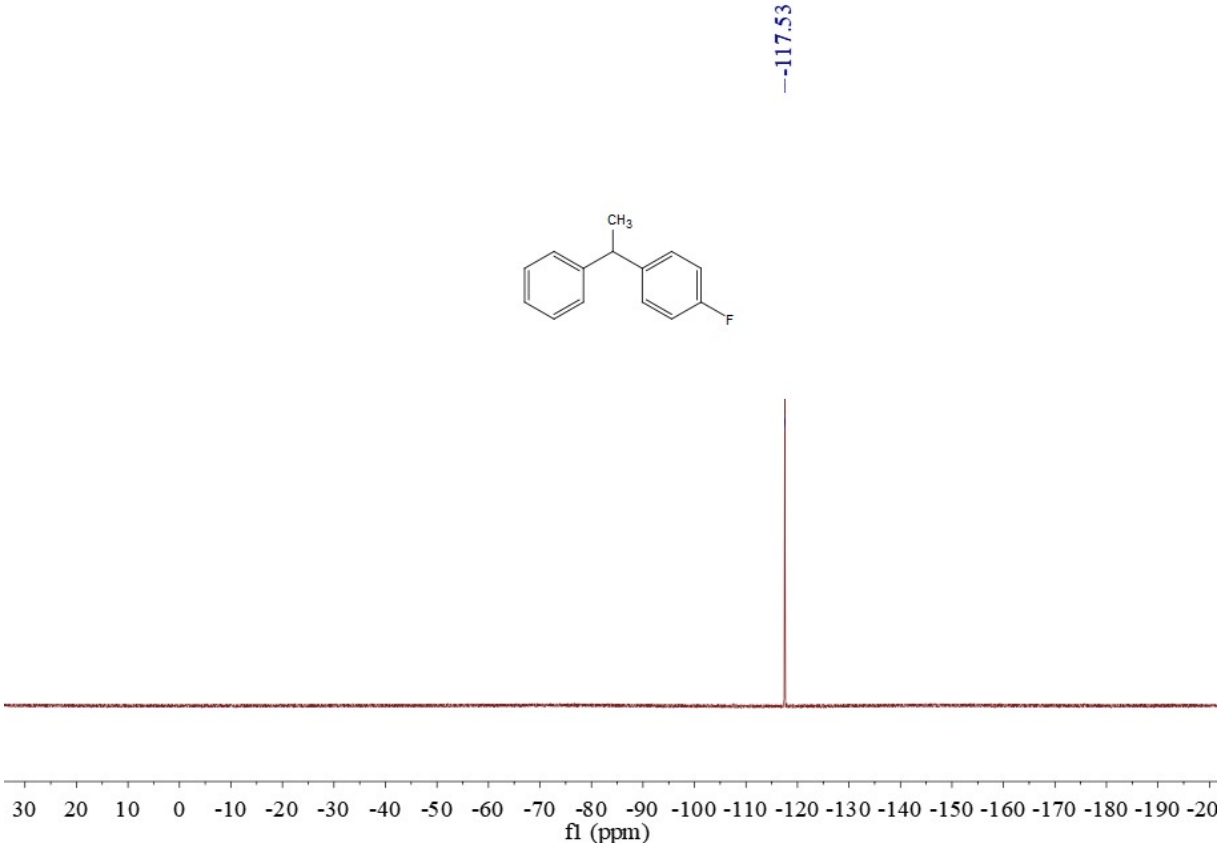
^{1}H NMR of compound 2g (400 MHz, $CDCl_3$):



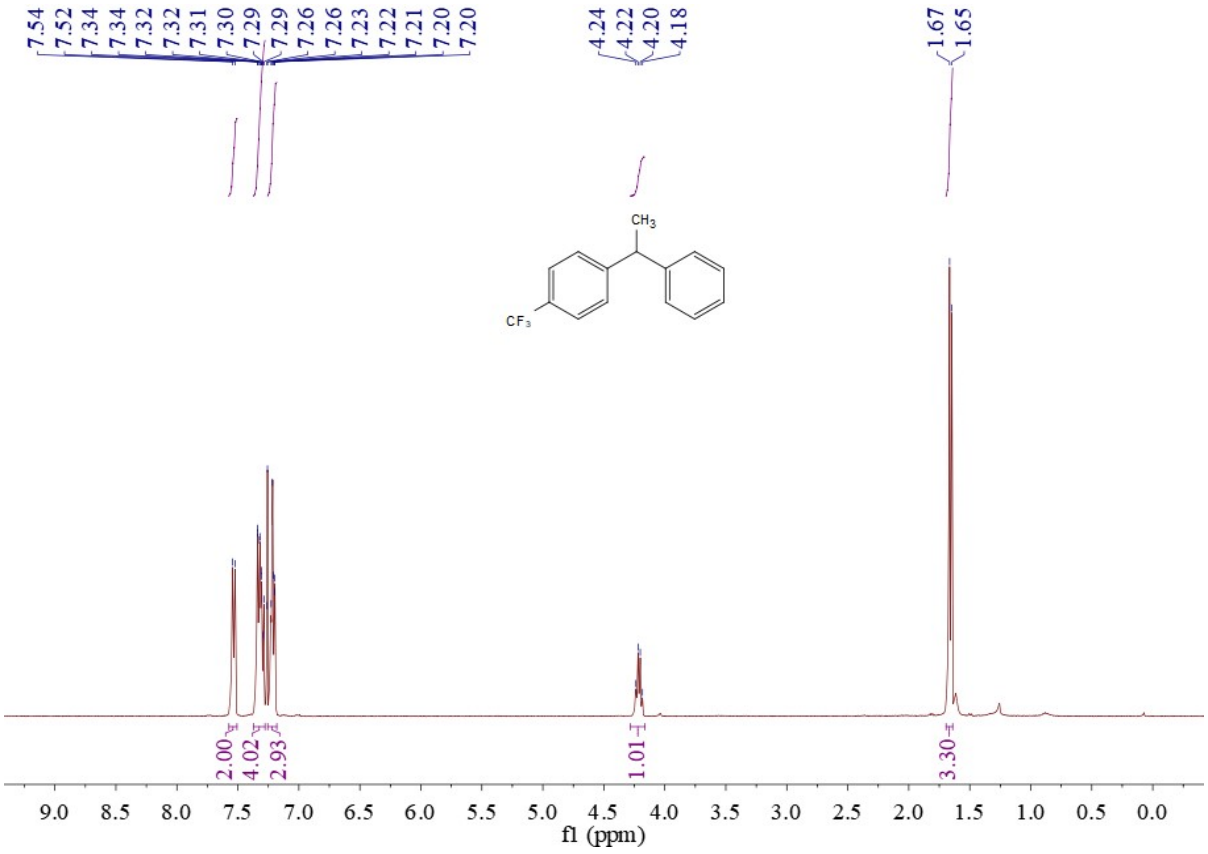
^{13}C NMR of compound 2g (100 MHz, $CDCl_3$):



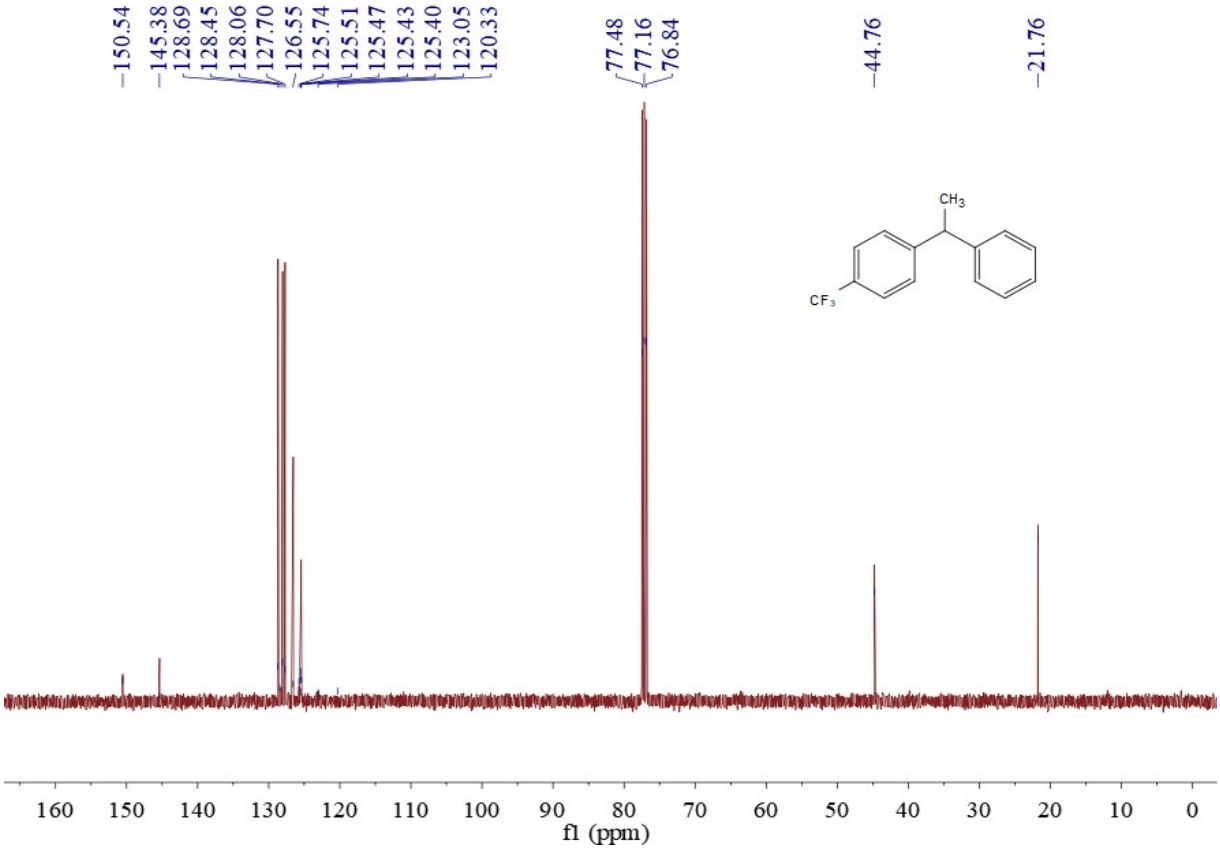
^{19}F NMR of compound 2g (376 MHz, $CDCl_3$):



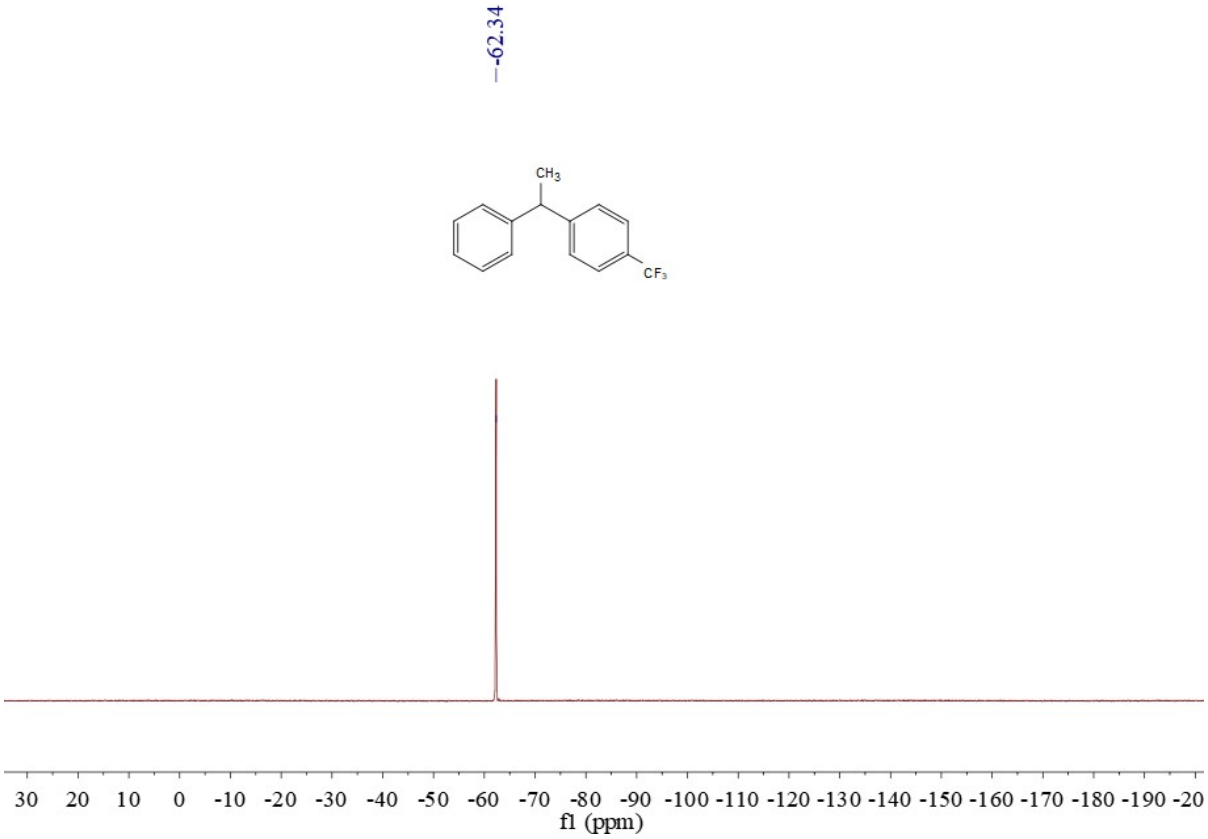
^{1}H NMR of compound 2h (400 MHz, $CDCl_3$):



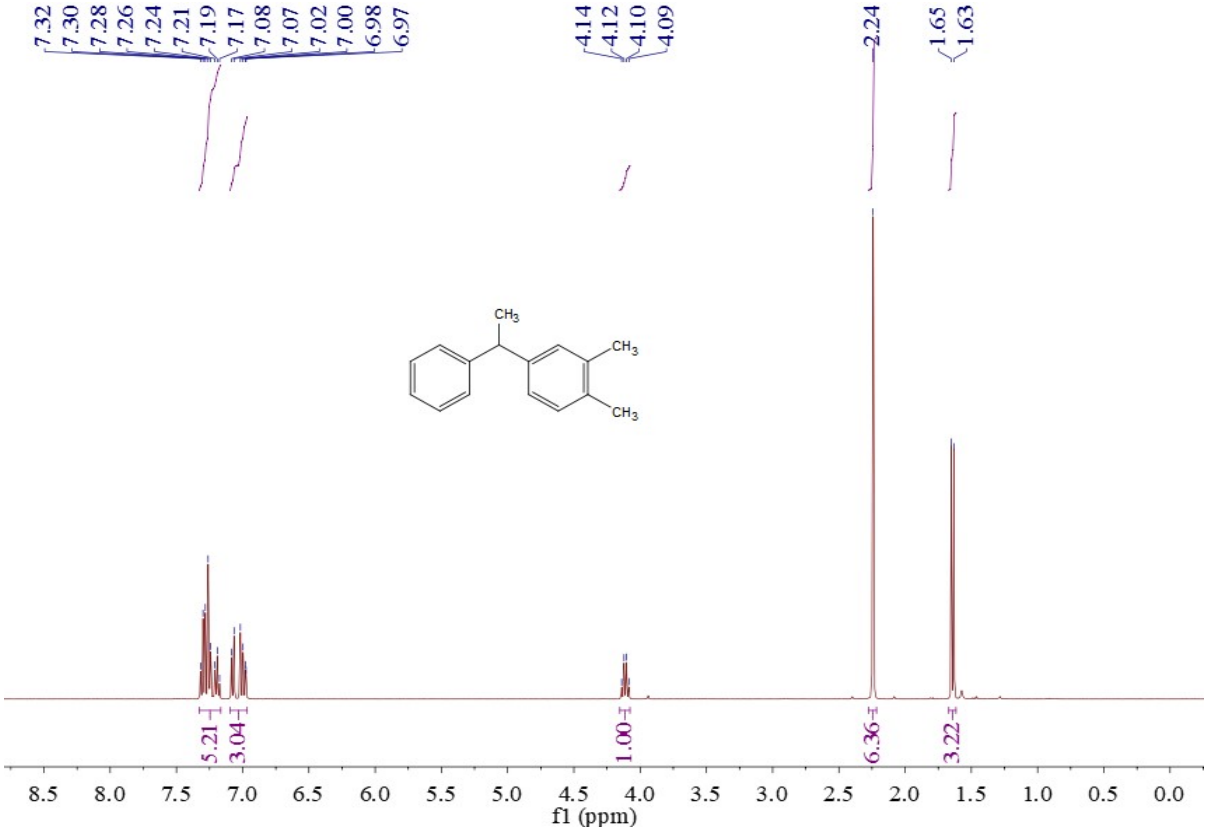
^{13}C NMR of compound 2h (100 MHz, $CDCl_3$):



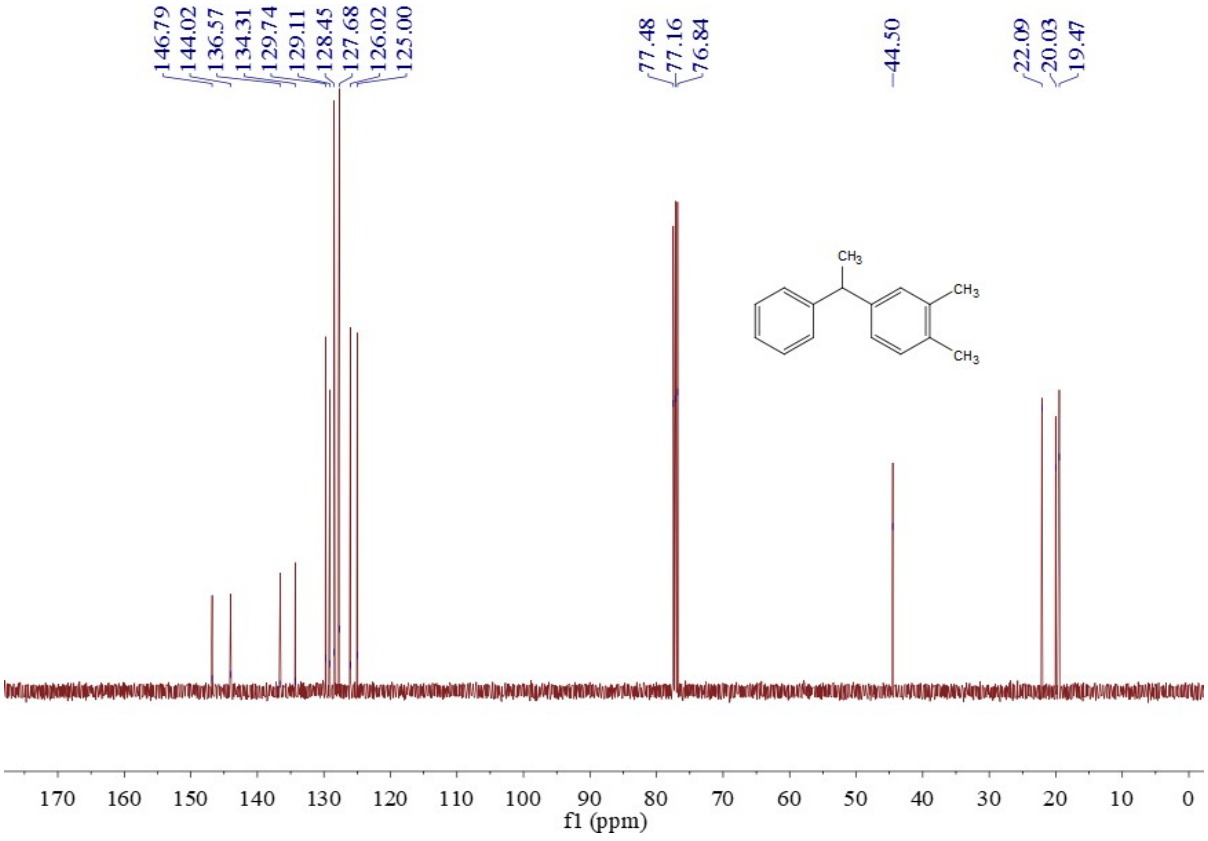
^{19}F NMR of compound 2h (376 MHz, $CDCl_3$):



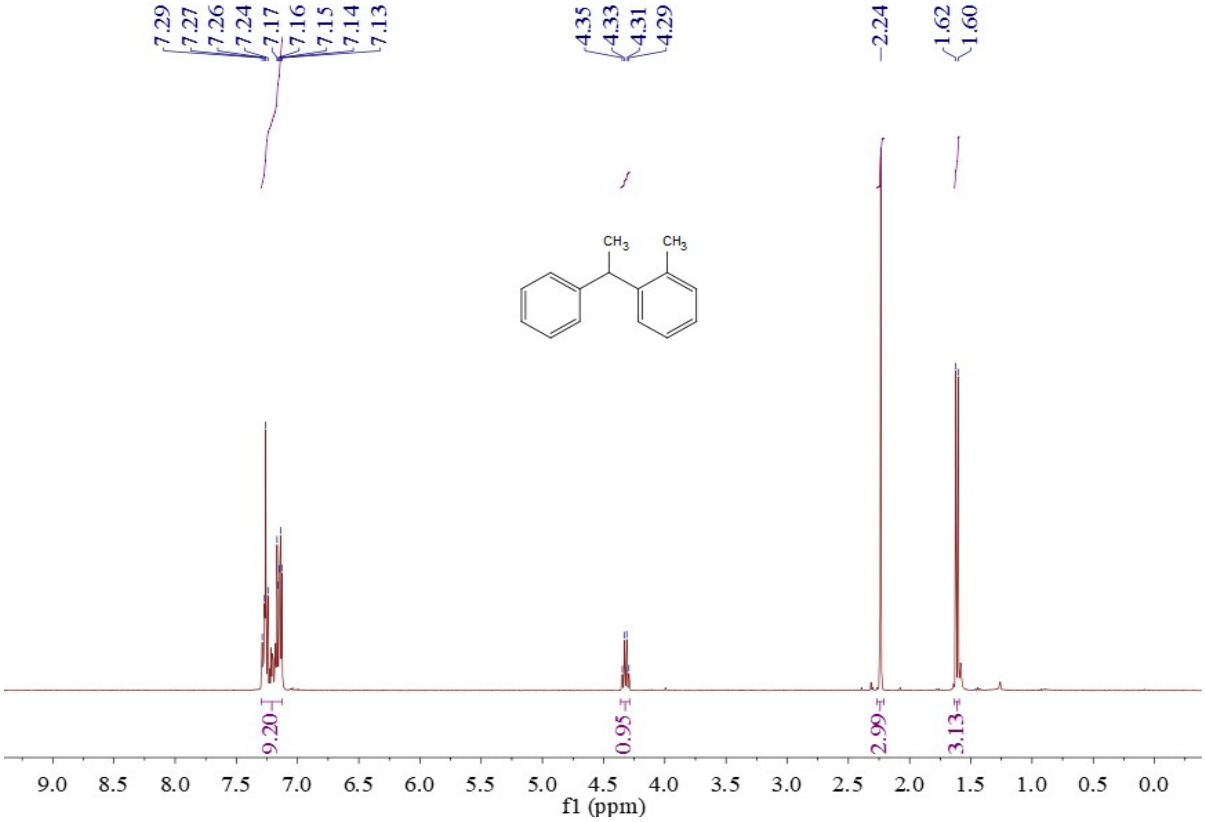
^{1}H NMR of compound 2i (400 MHz, $CDCl_3$):



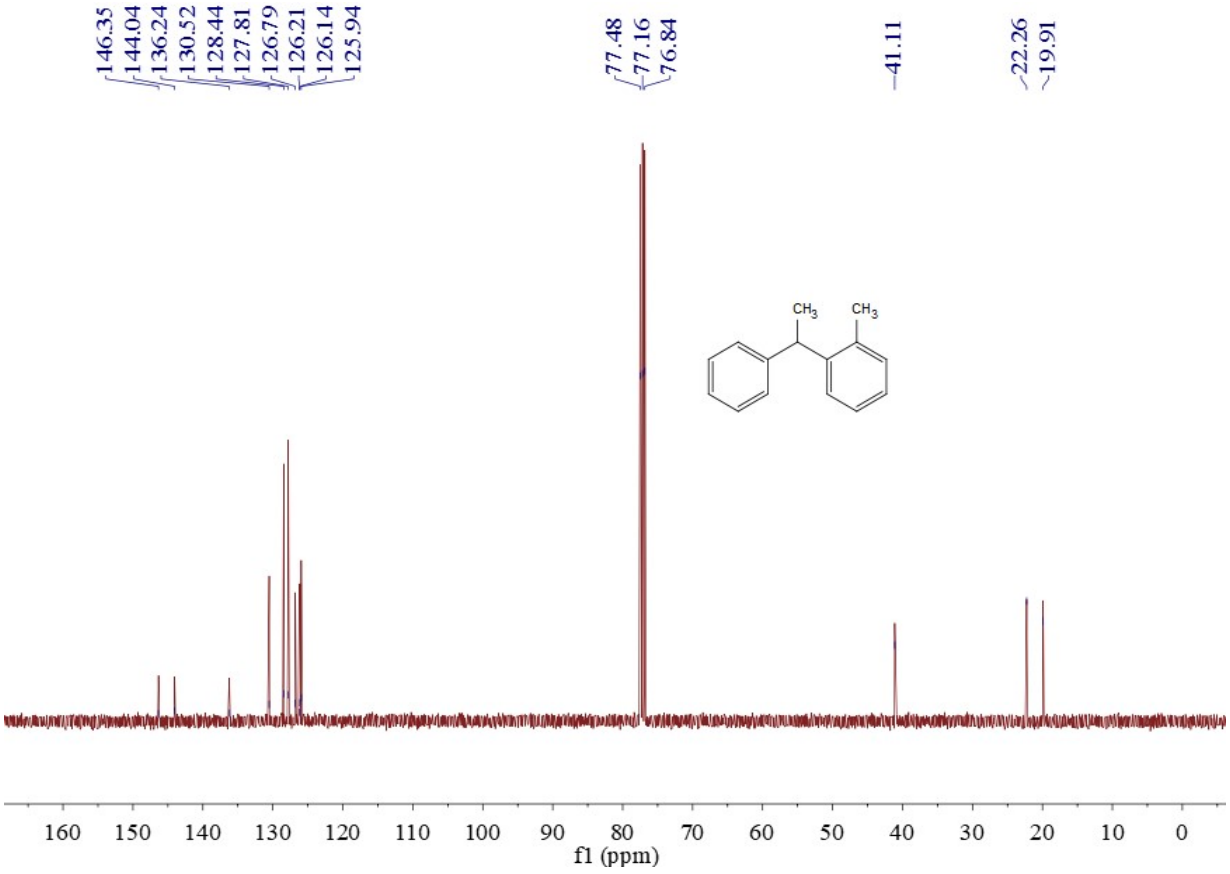
^{13}C NMR of compound 2i (100 MHz, $CDCl_3$):



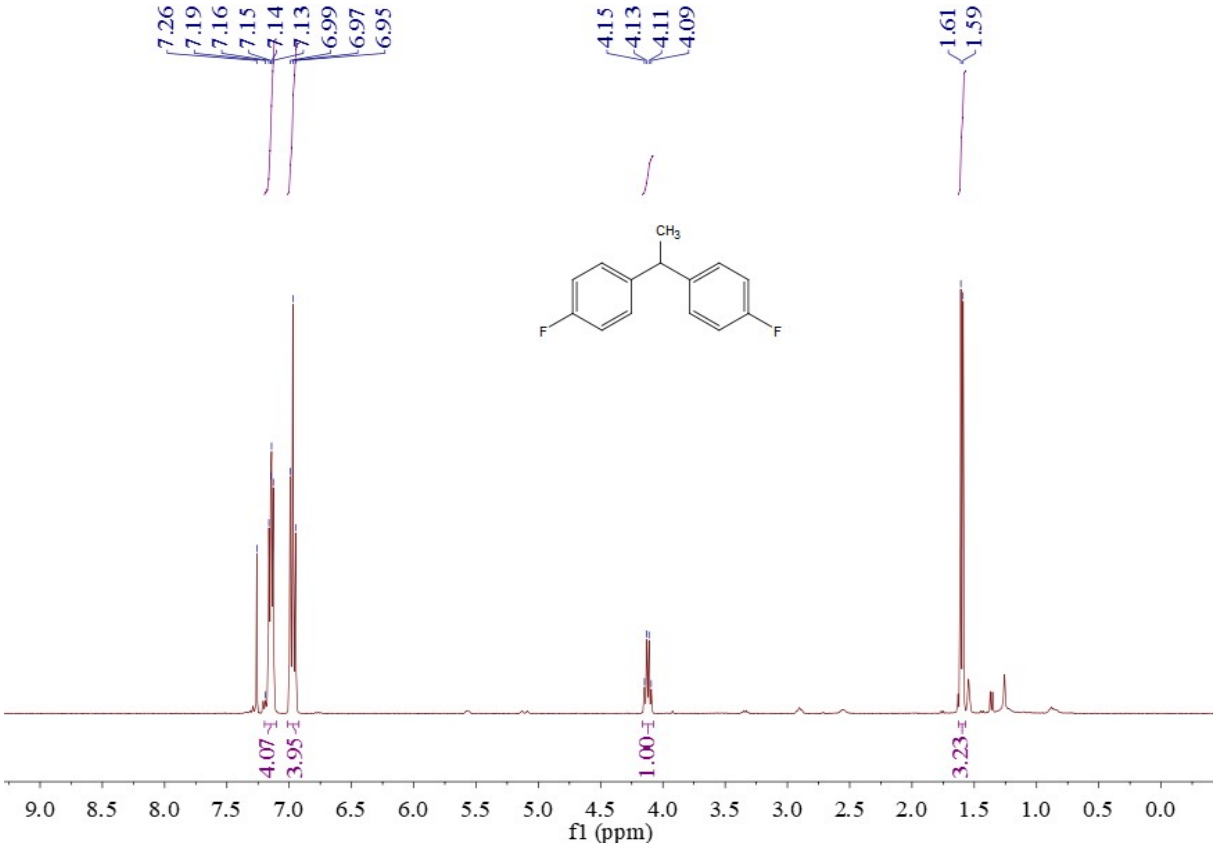
^{1}H NMR of compound 2j (400 MHz, $CDCl_3$):



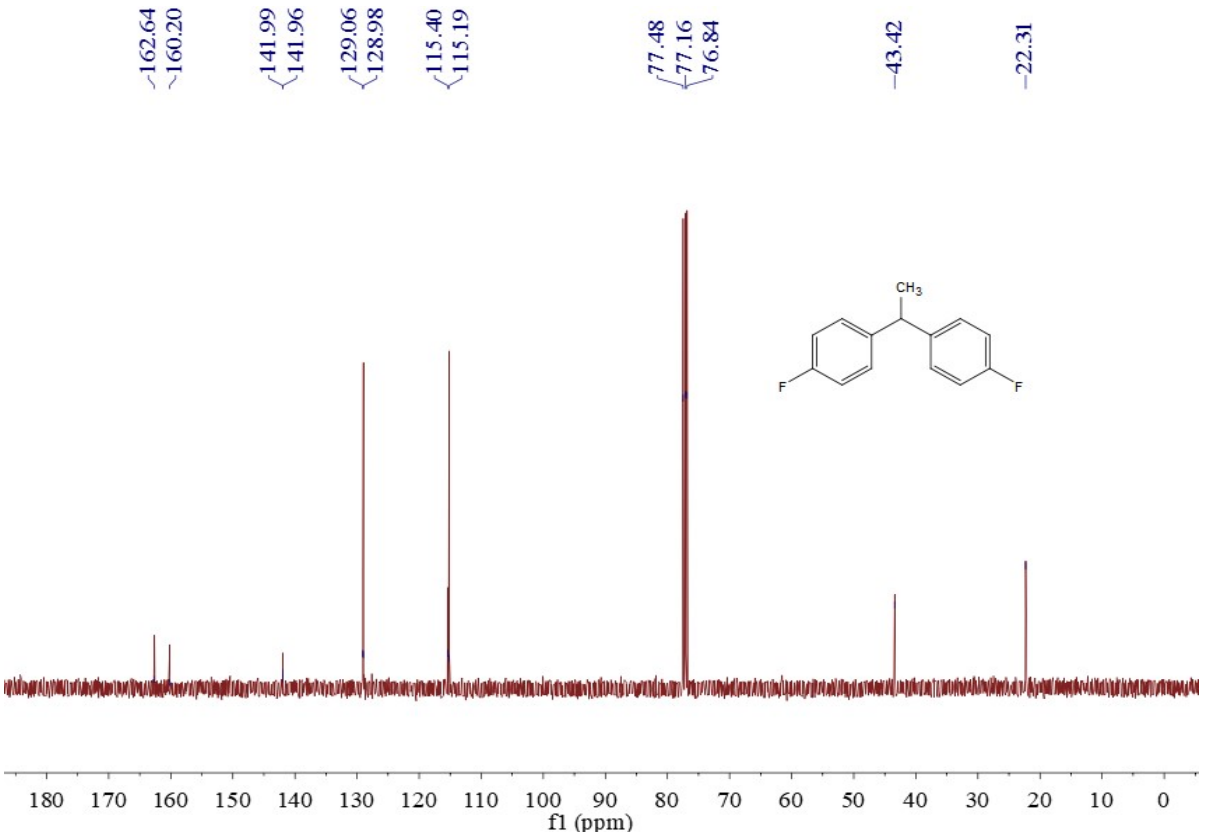
^{13}C NMR of compound 2j (100 MHz, $CDCl_3$):



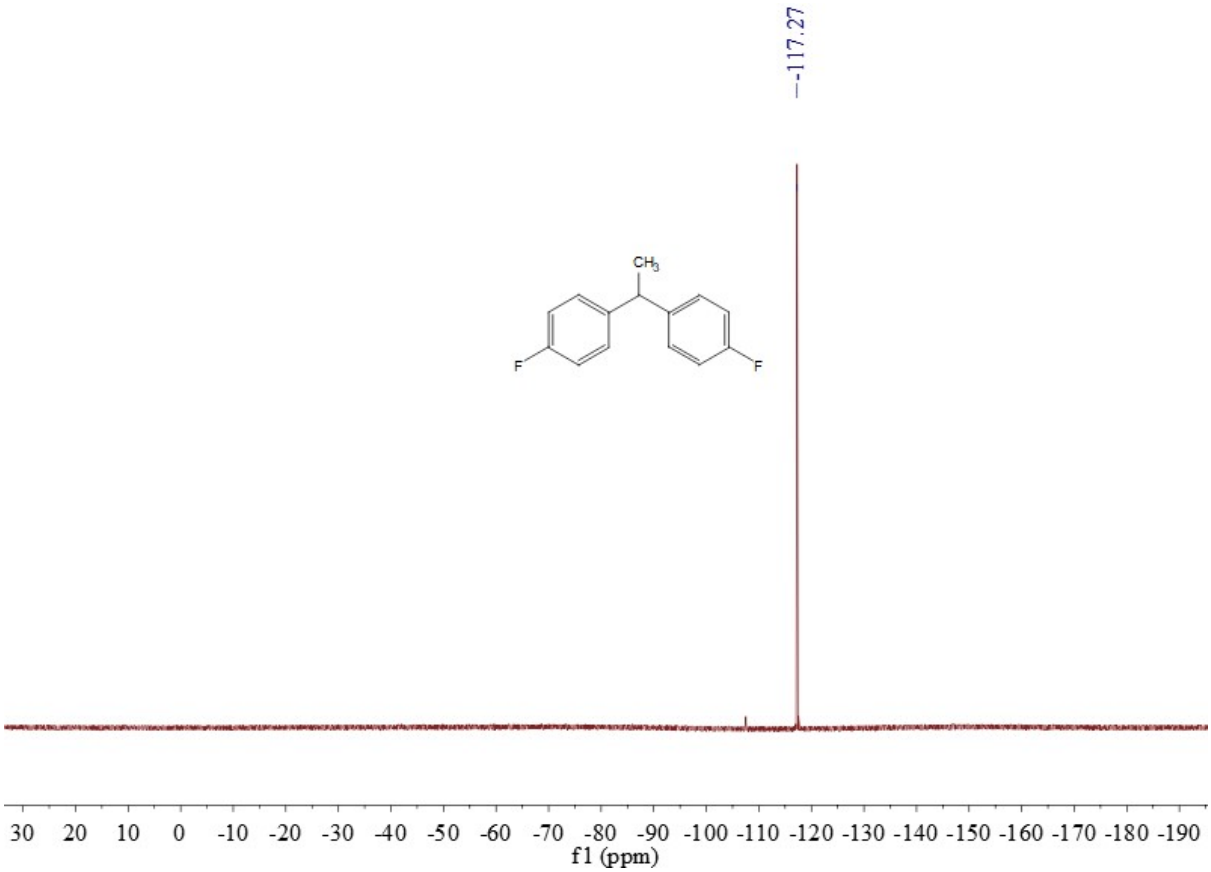
^{1}H NMR of compound 2k (400 MHz, $CDCl_3$):



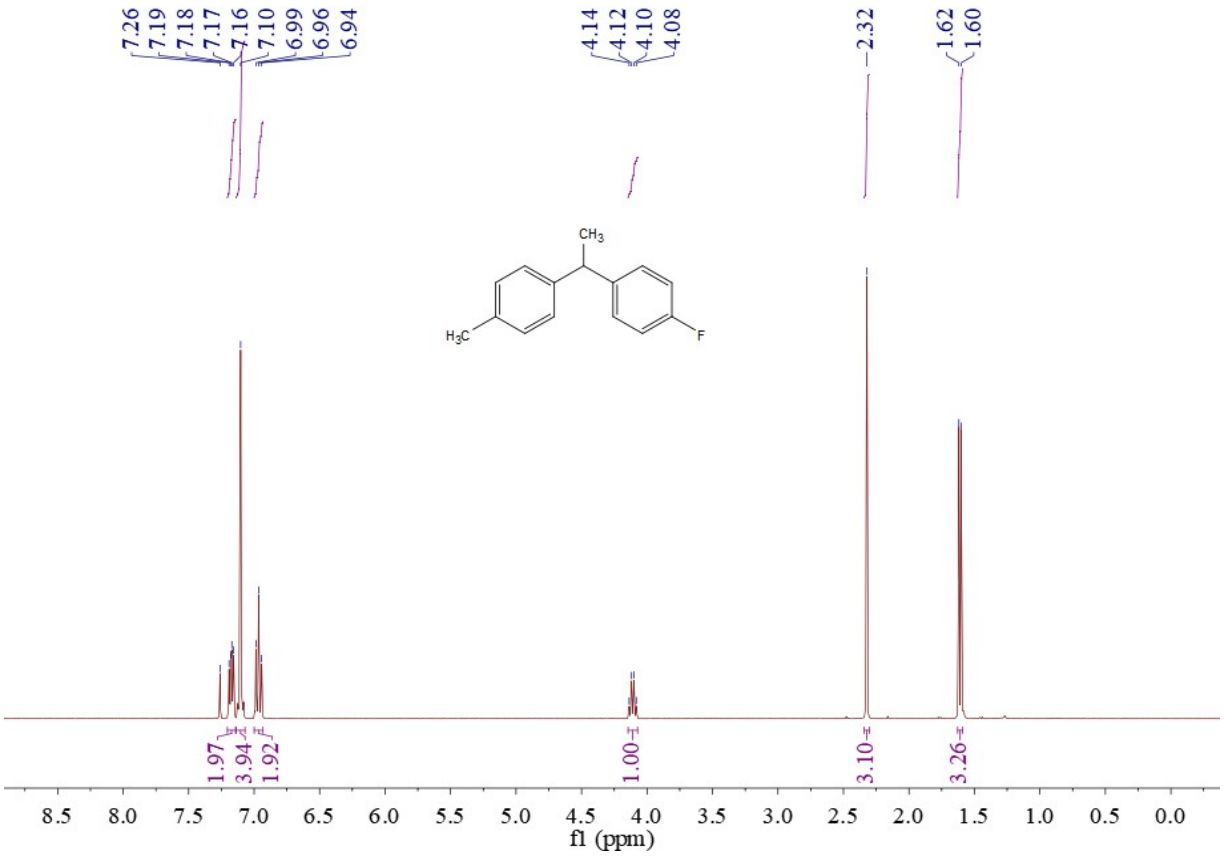
^{13}C NMR of compound 2k (100 MHz, $CDCl_3$):



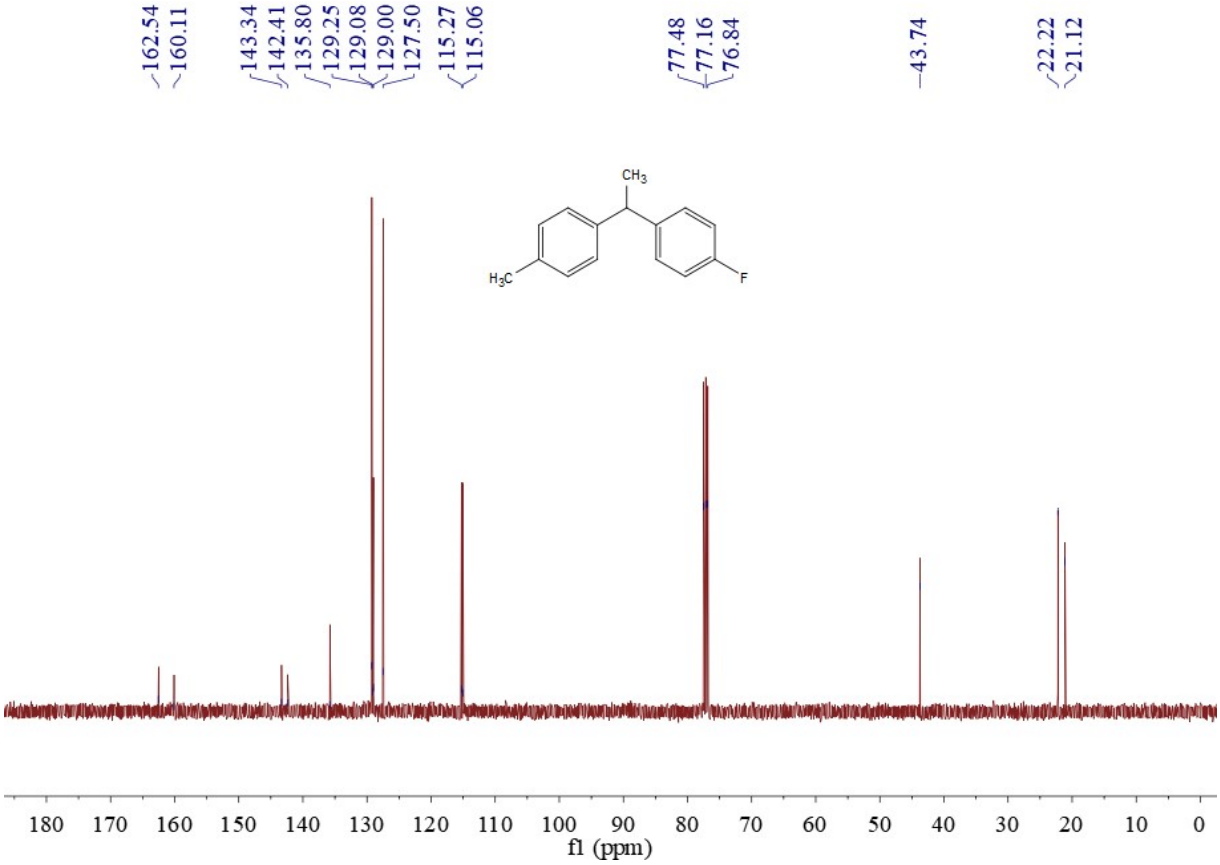
^{19}F NMR of compound 2k (376 MHz, $CDCl_3$):



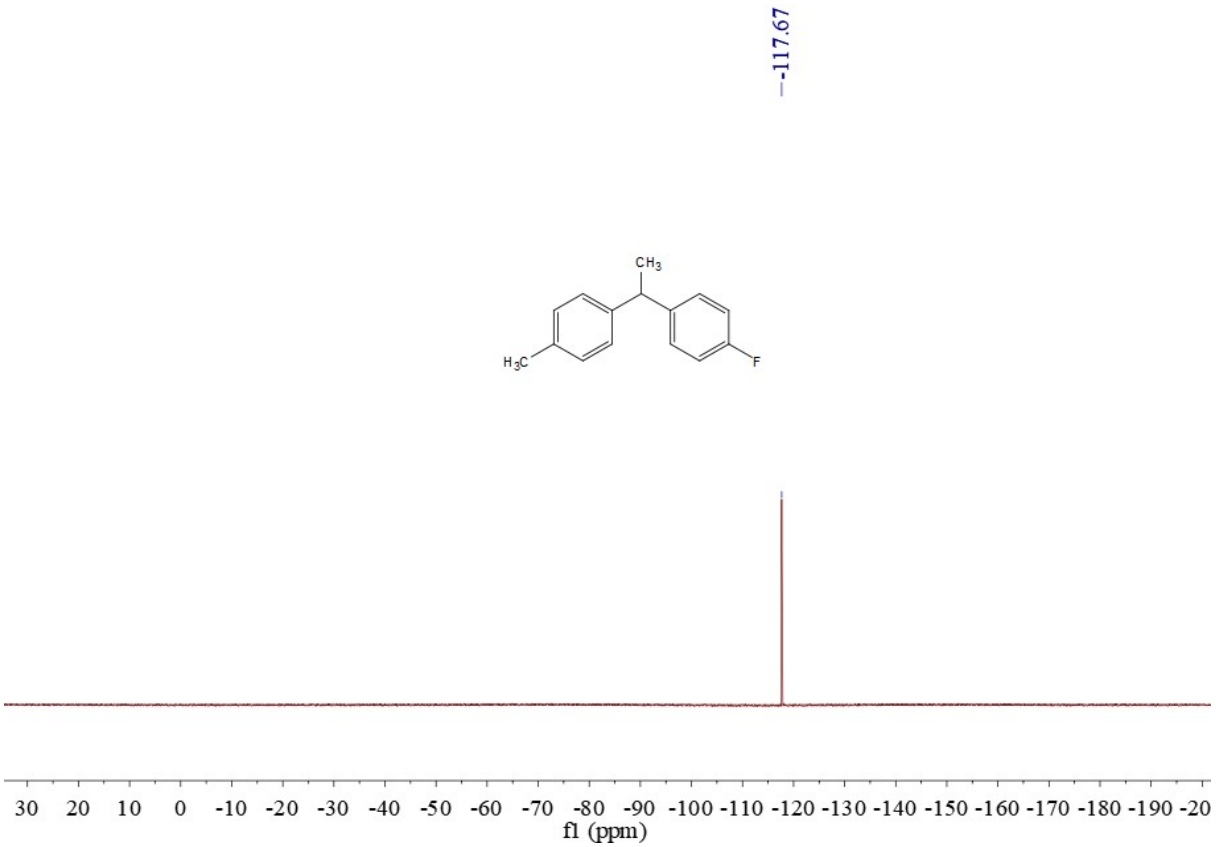
^{1}H NMR of compound 2l (400 MHz, $CDCl_3$):



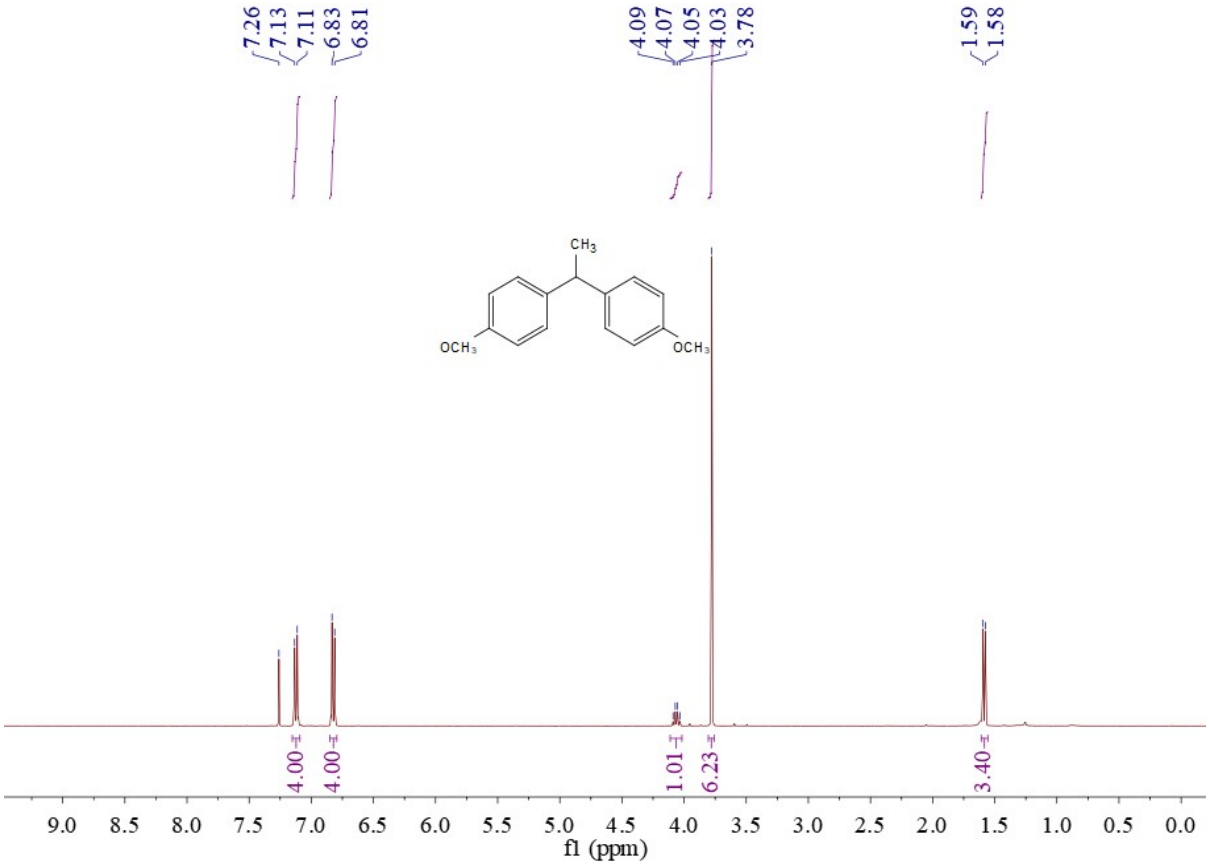
^{13}C NMR of compound 2l (100 MHz, $CDCl_3$):



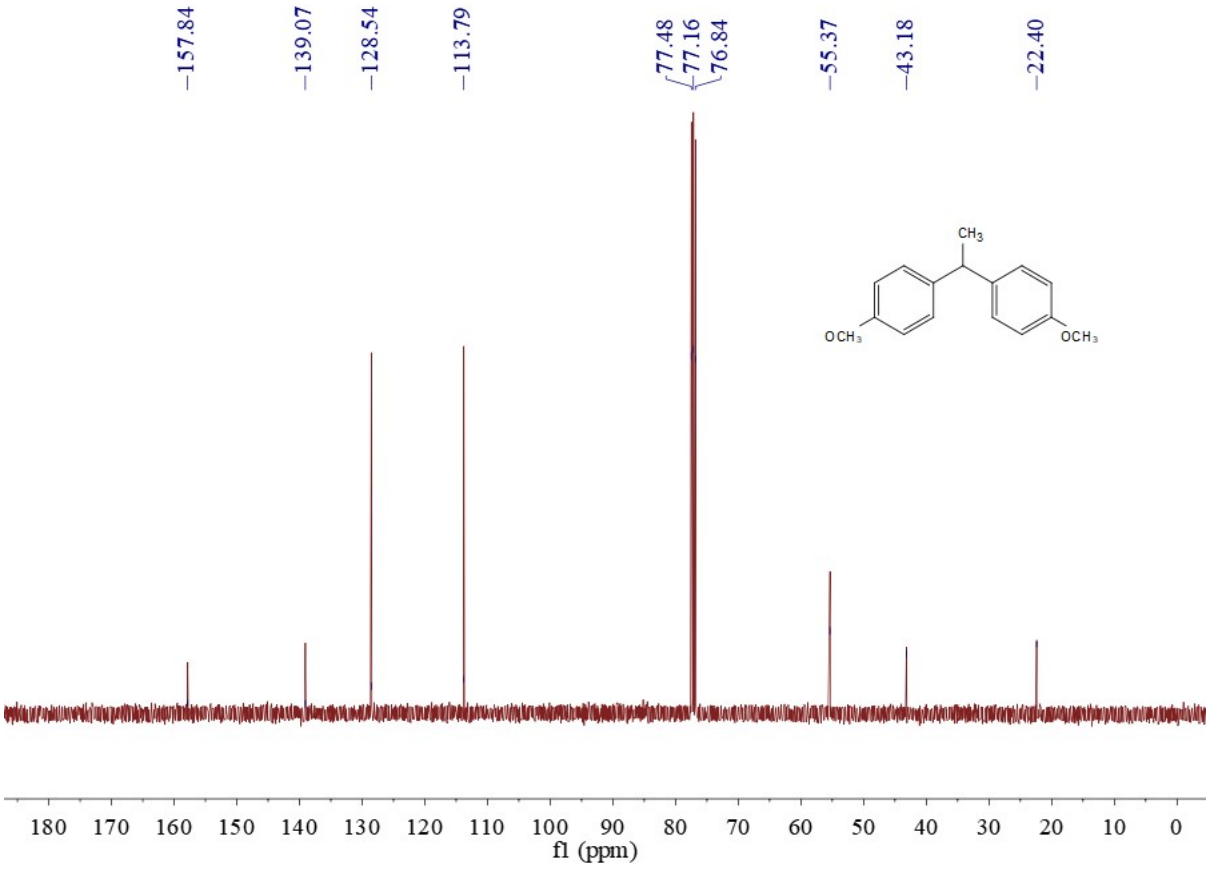
^{19}F NMR of compound 2l (376 MHz, $CDCl_3$):



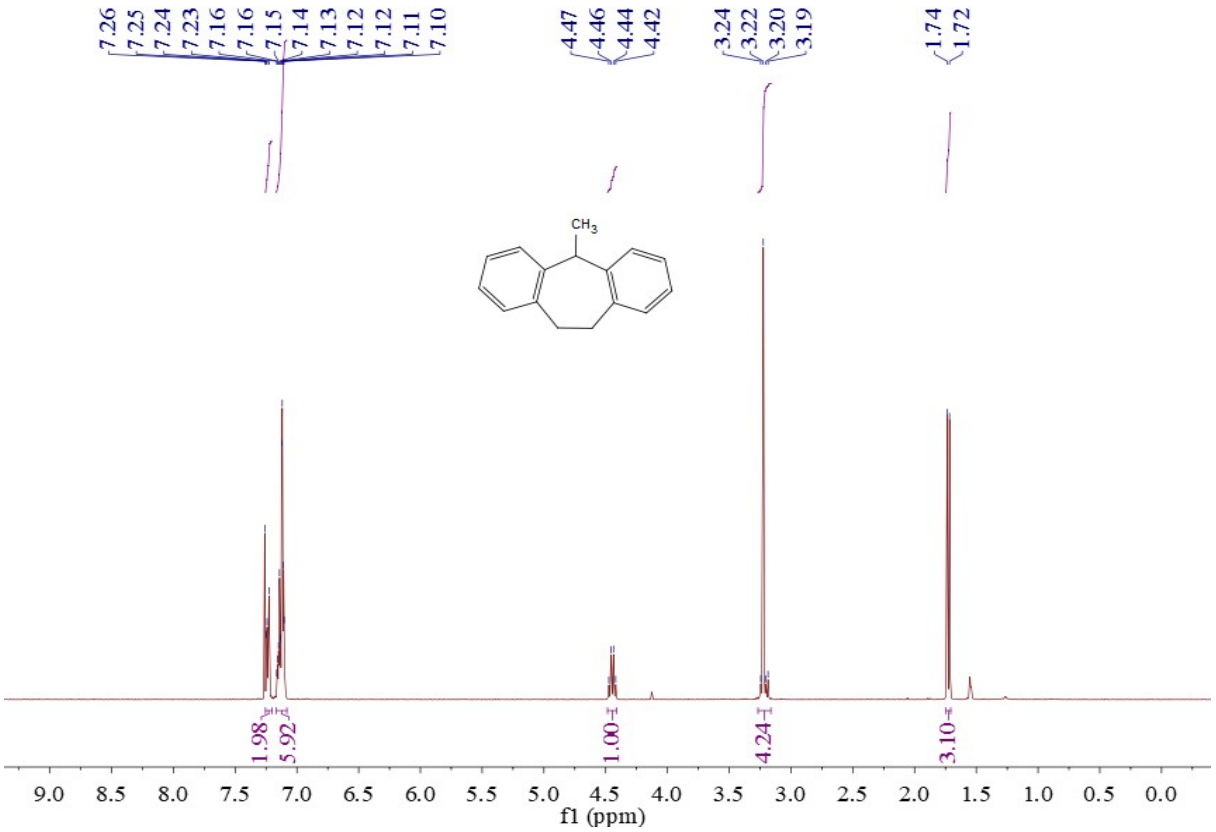
^{1}H NMR of compound 2m (400 MHz, $CDCl_3$):



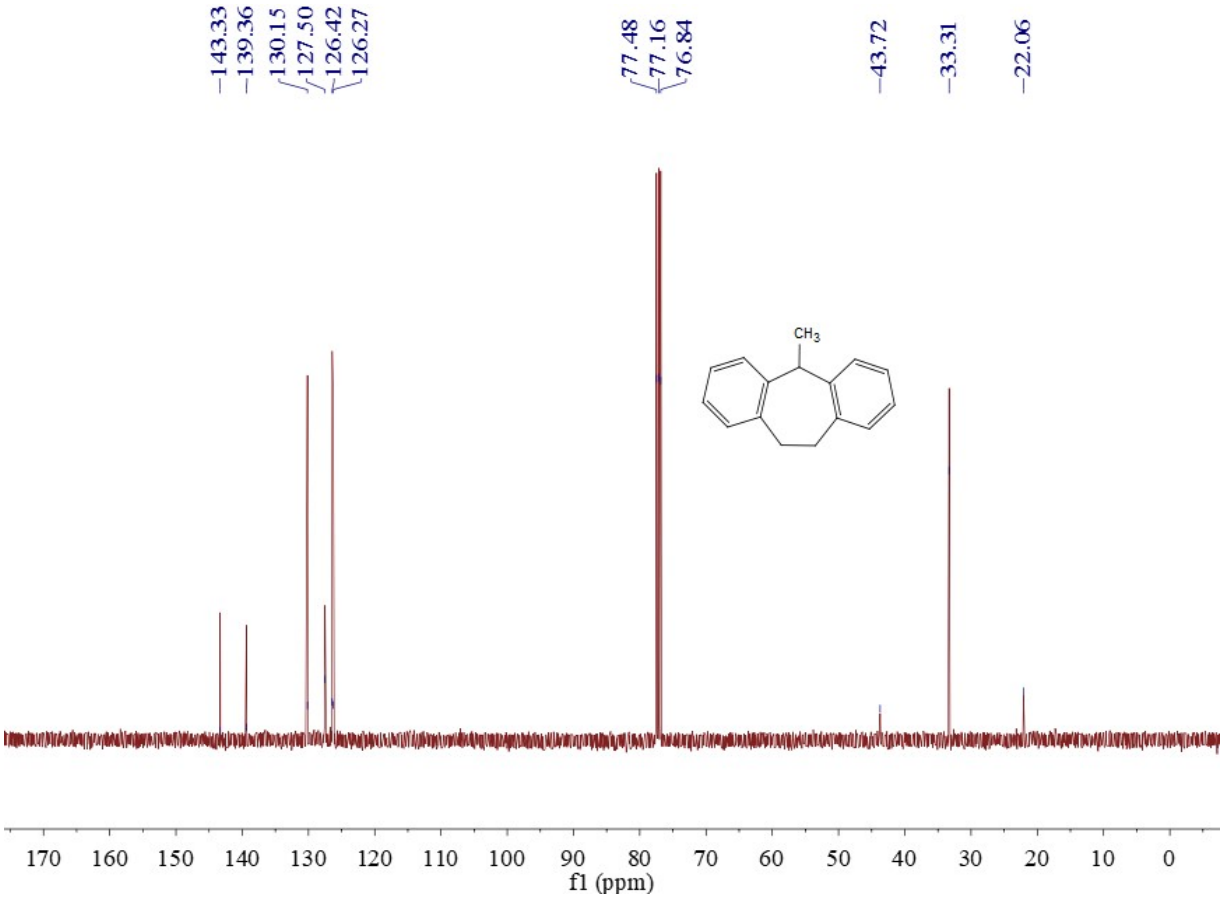
^{13}C NMR of compound 2m (100 MHz, $CDCl_3$):



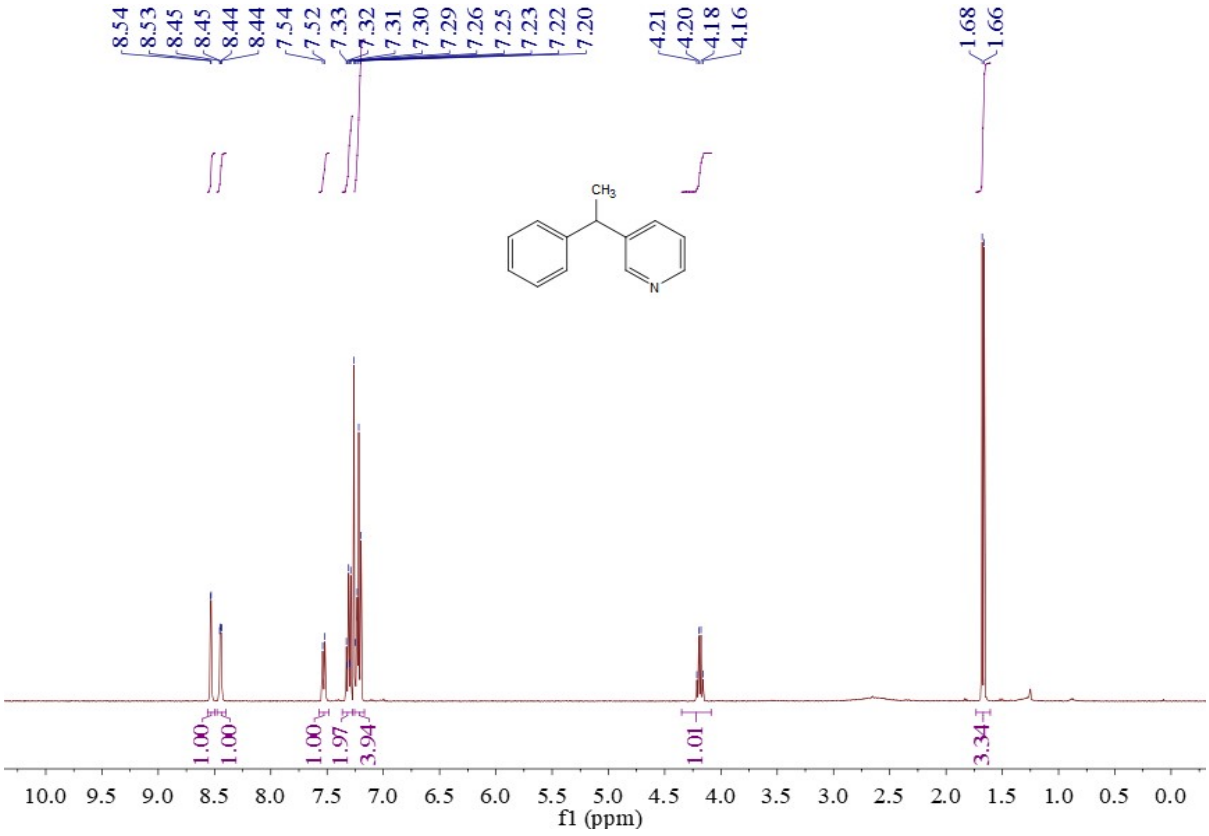
^{1}H NMR of compound 2n (400 MHz, $CDCl_3$):



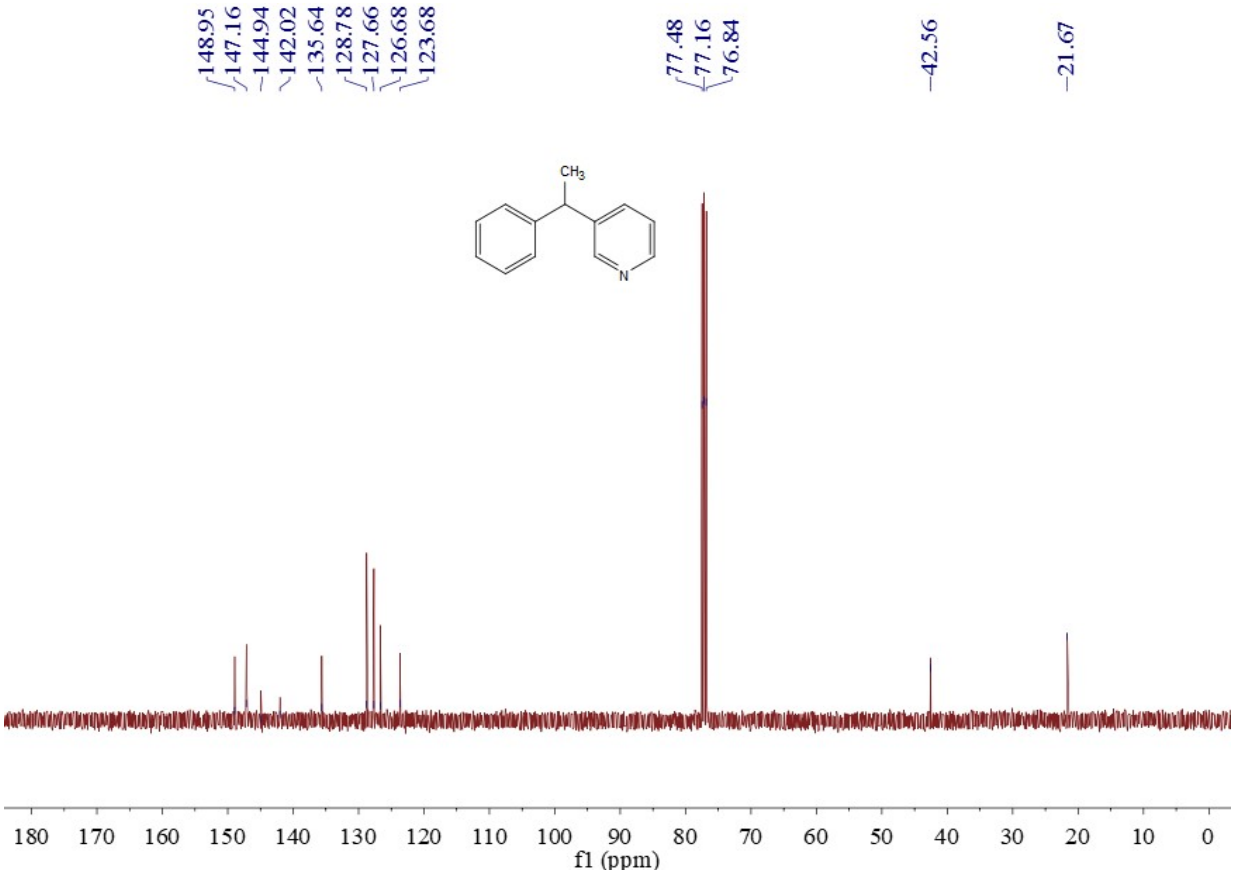
^{13}C NMR of compound 2n (100 MHz, $CDCl_3$):



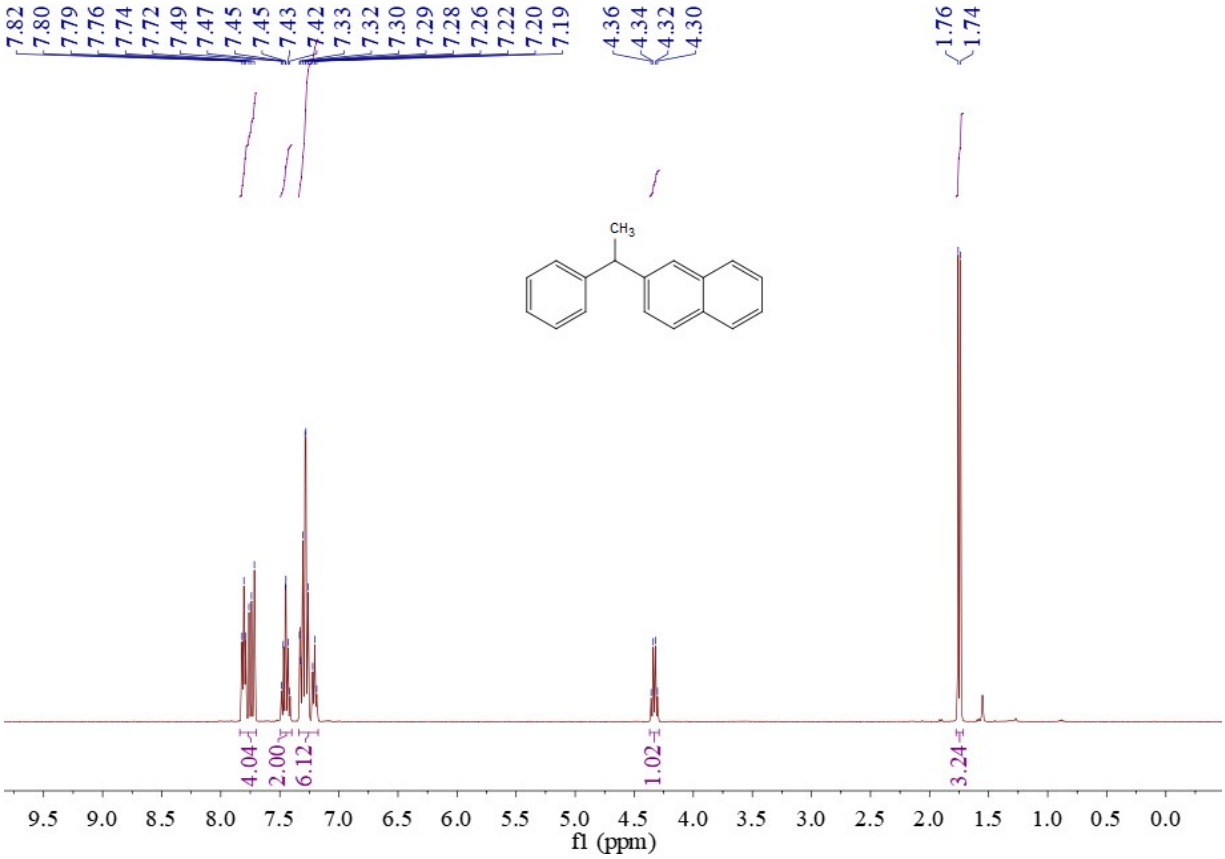
^{1}H NMR of compound 2o (400 MHz, $CDCl_3$):



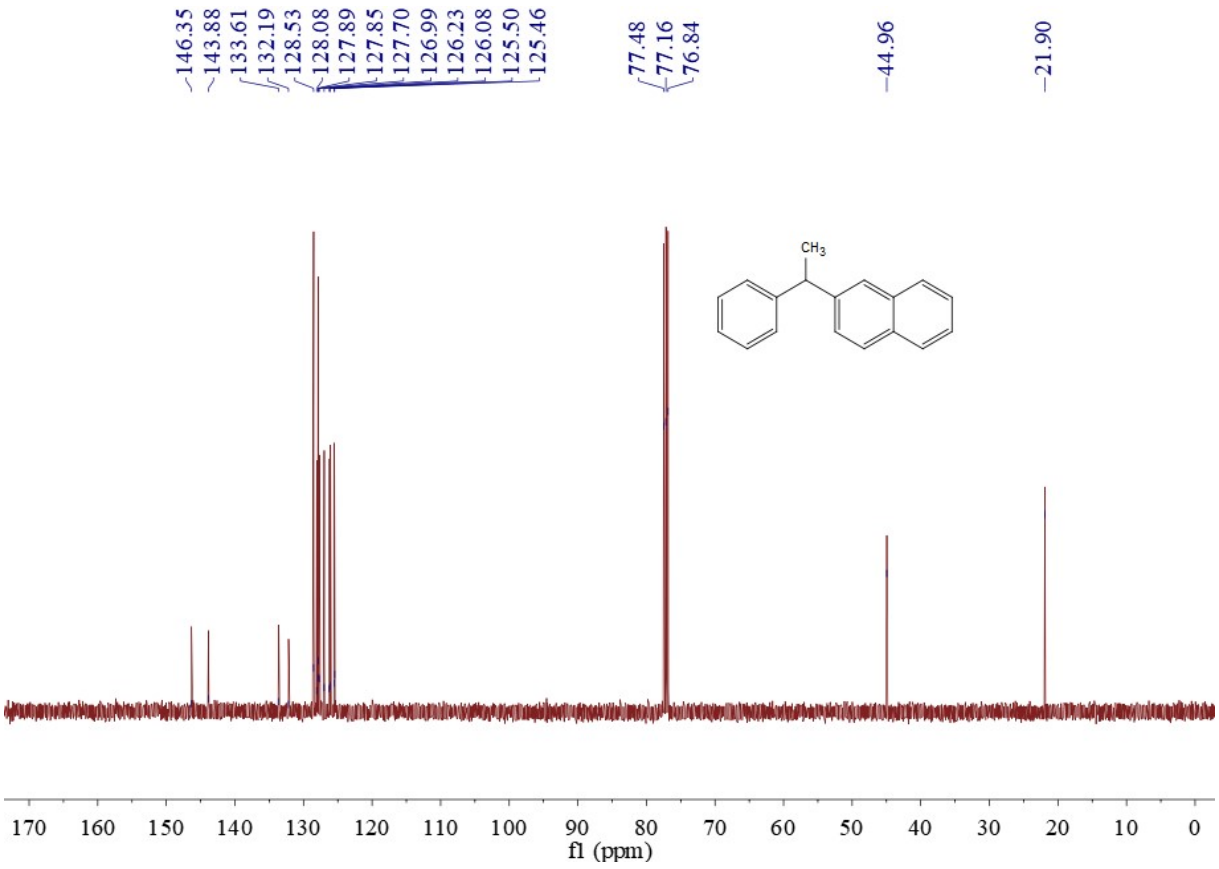
^{13}C NMR of compound 2o (100 MHz, $CDCl_3$):



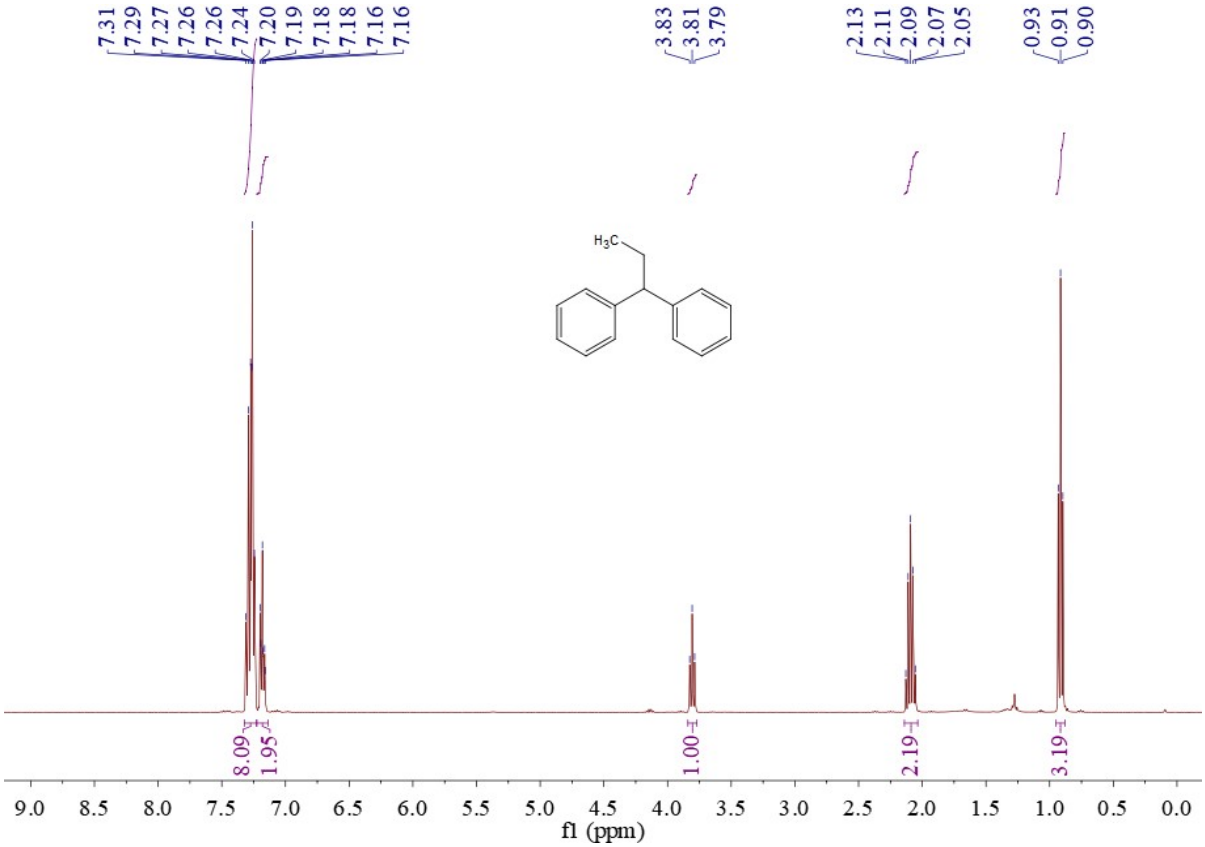
^{1}H NMR of compound 2p (400 MHz, $CDCl_3$):



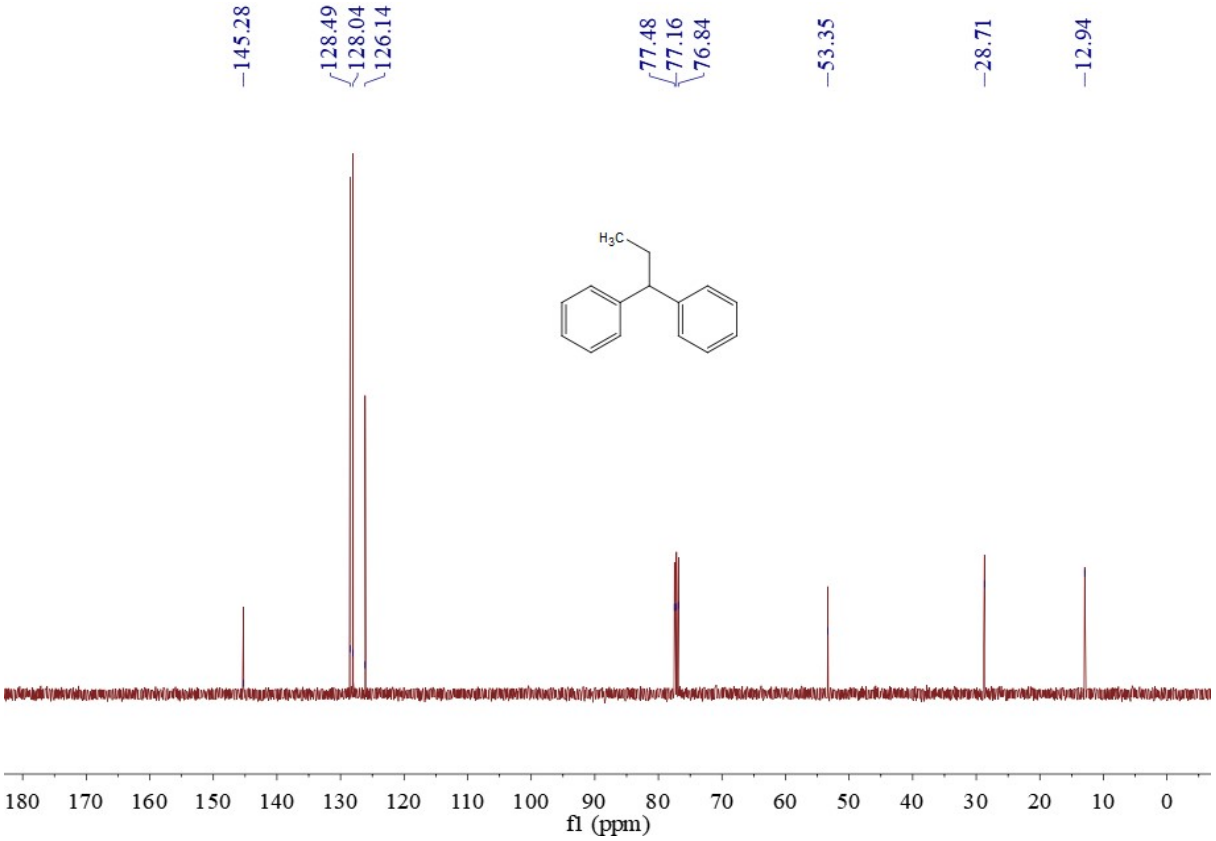
^{13}C NMR of compound 2p (100 MHz, $CDCl_3$):



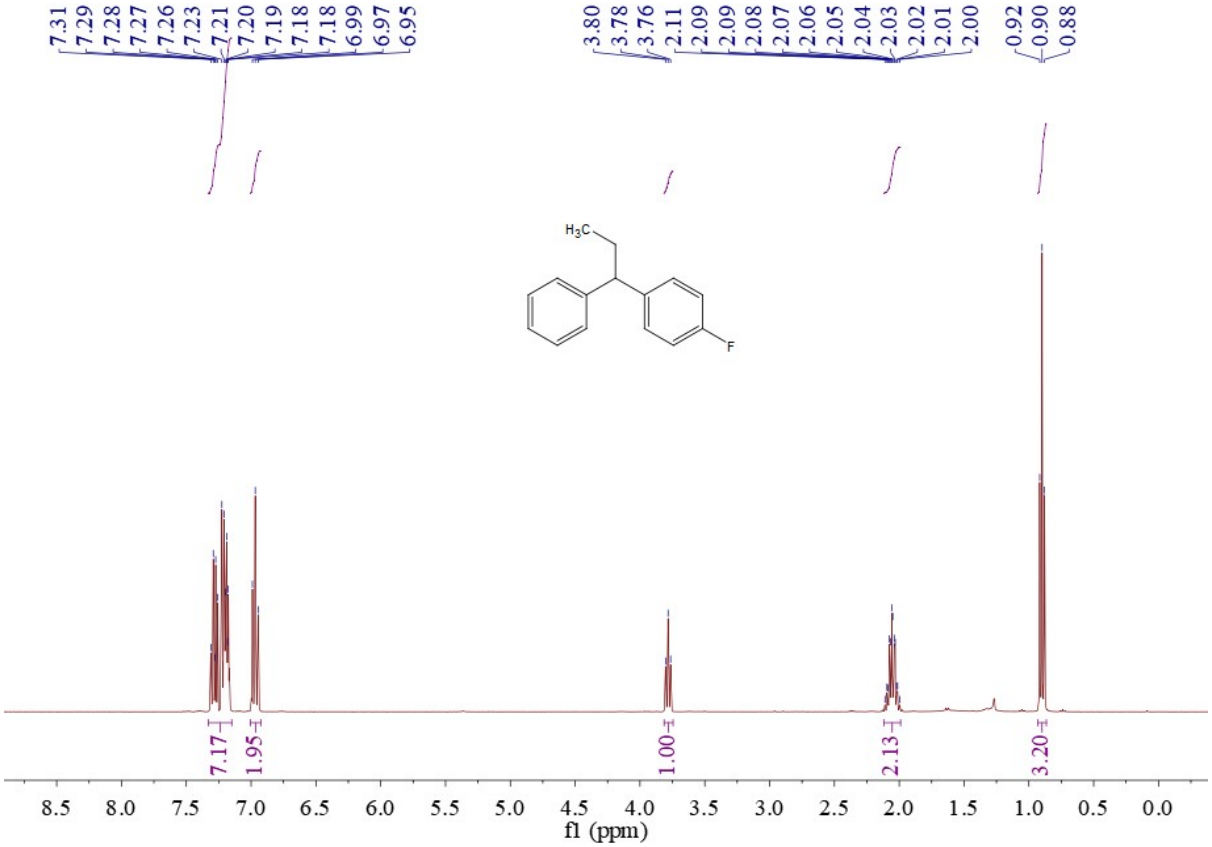
^{1}H NMR of compound 2q (400 MHz, $CDCl_3$):



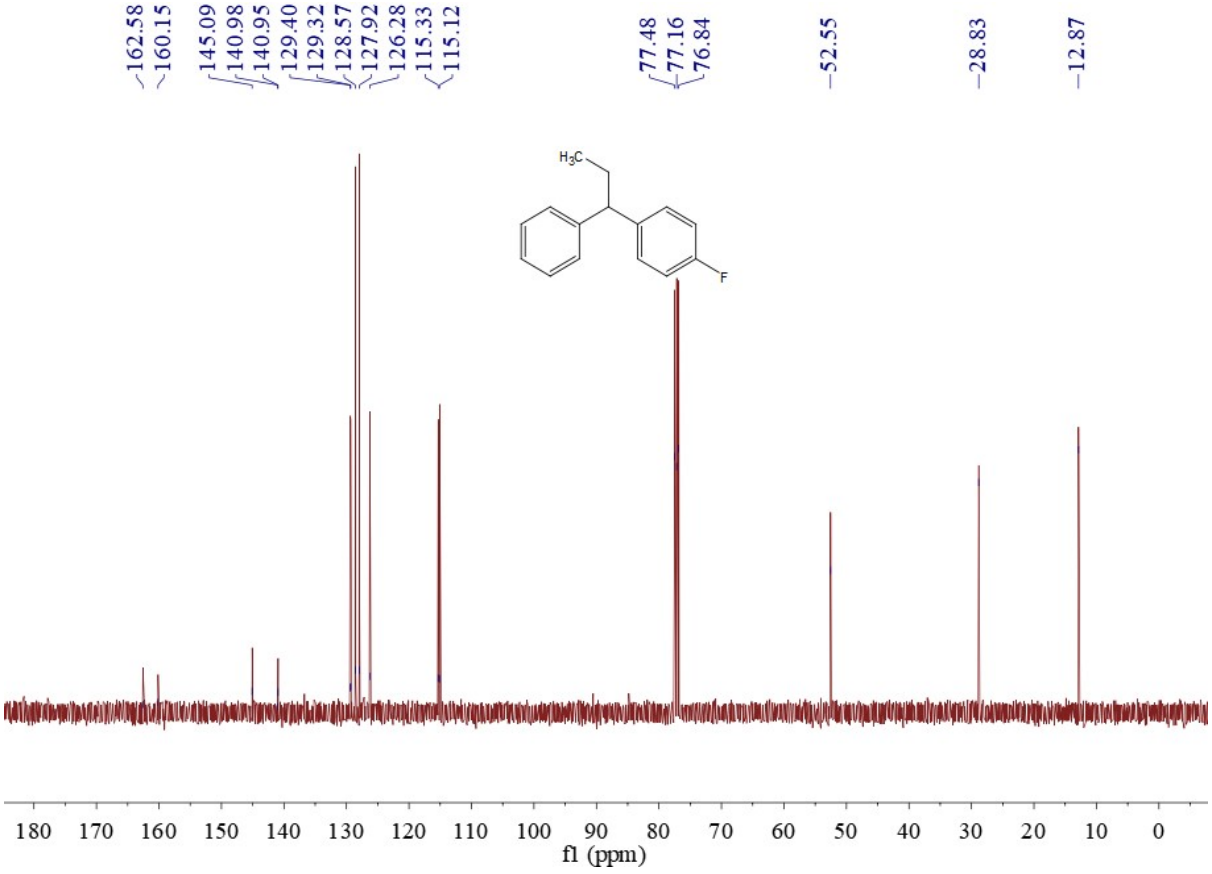
^{13}C NMR of compound 2q (100 MHz, $CDCl_3$):



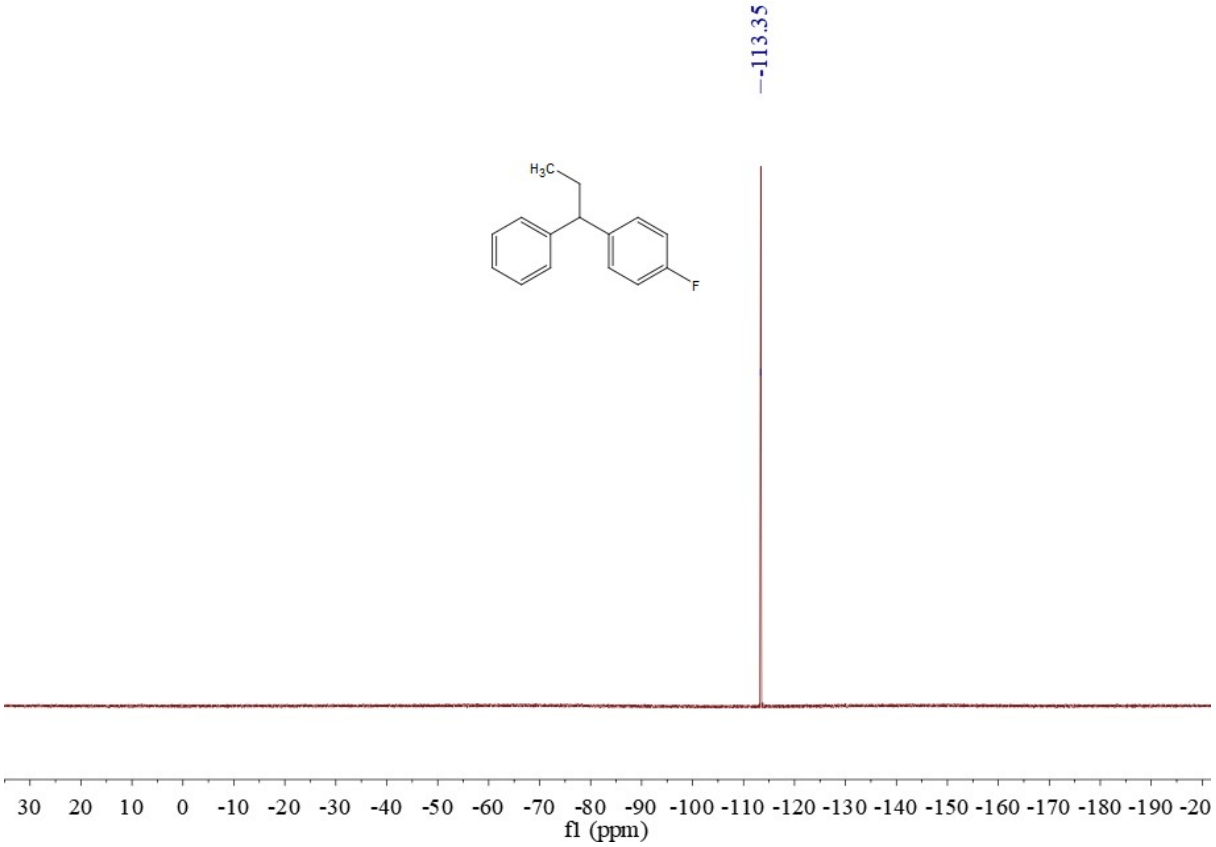
^{1}H NMR of compound 2r (400 MHz, $CDCl_3$):



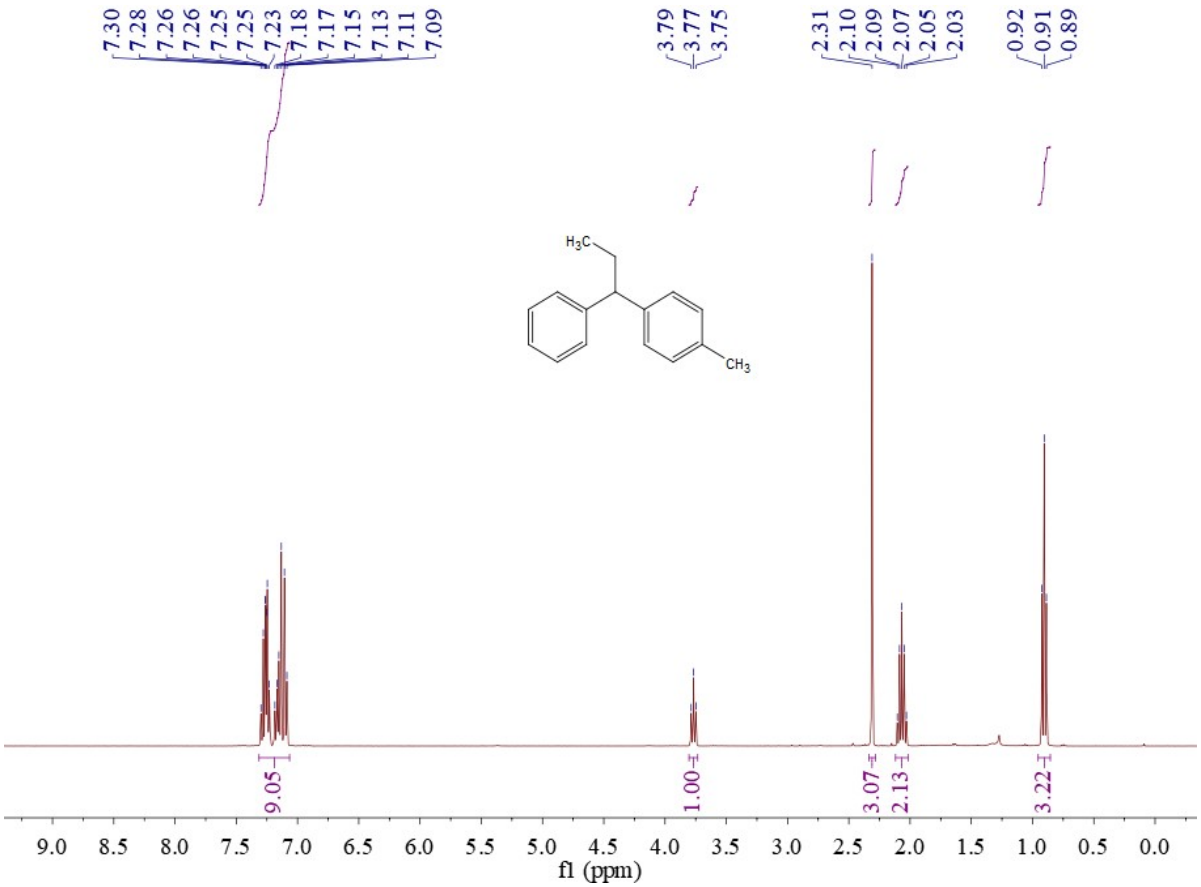
^{13}C NMR of compound 2r (100 MHz, $CDCl_3$):



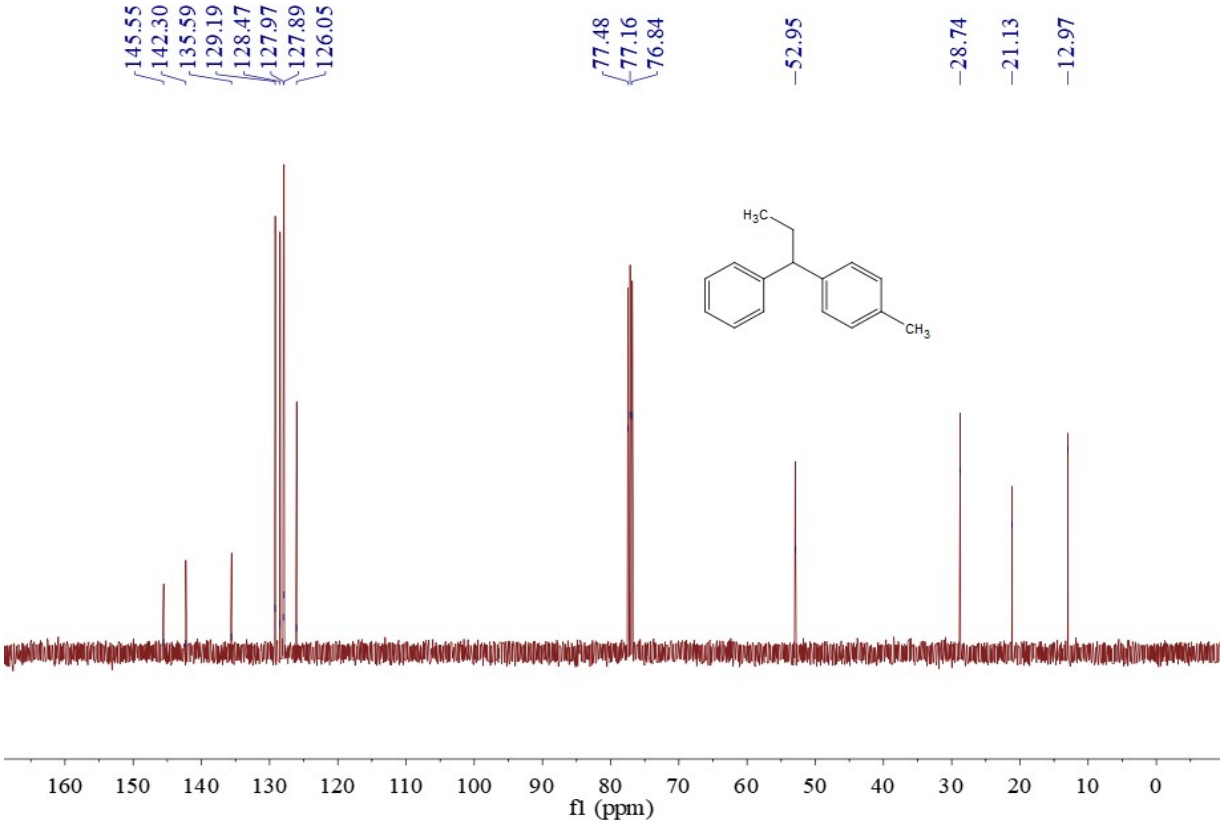
^{19}F NMR of compound 2r (376 MHz, $CDCl_3$):



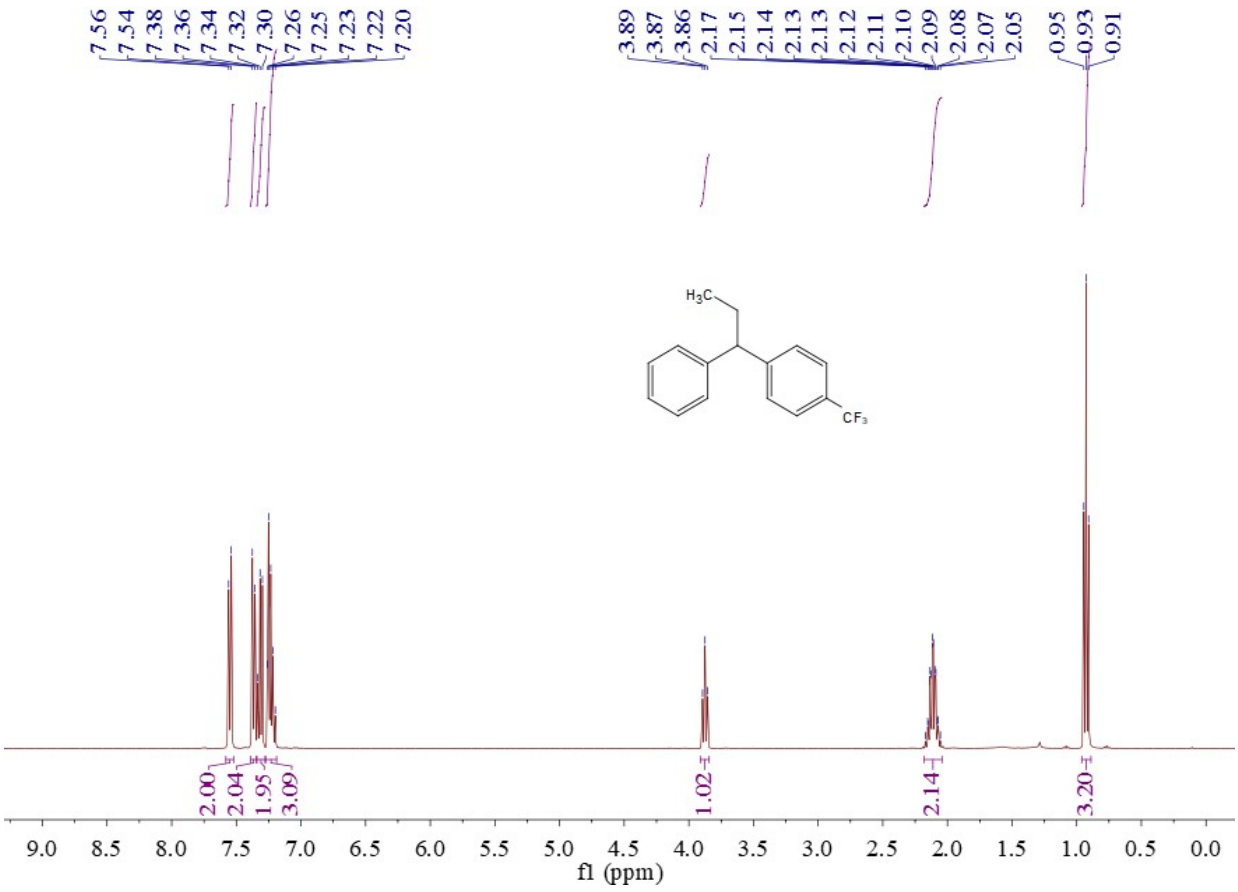
^{1}H NMR of compound 2s (400 MHz, $CDCl_3$):



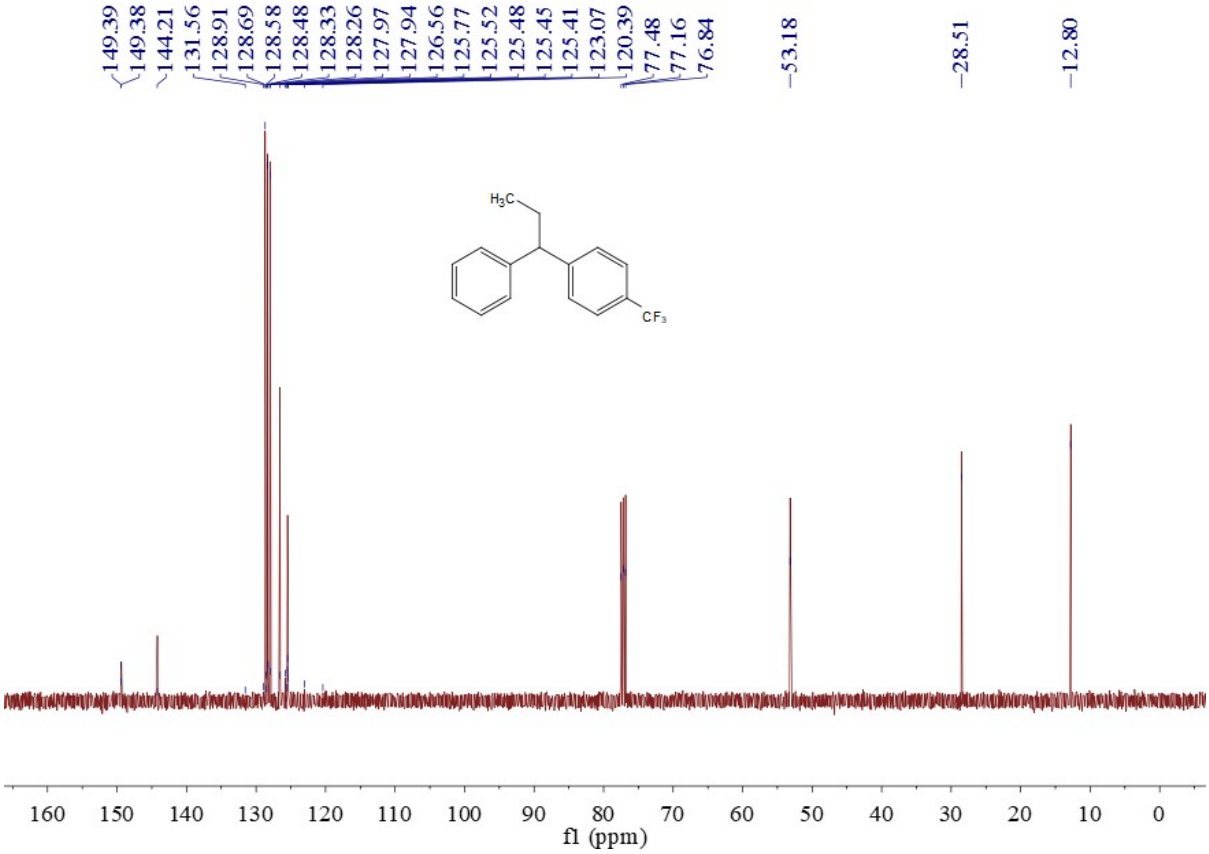
^{13}C NMR of compound 2s (100 MHz, $CDCl_3$):



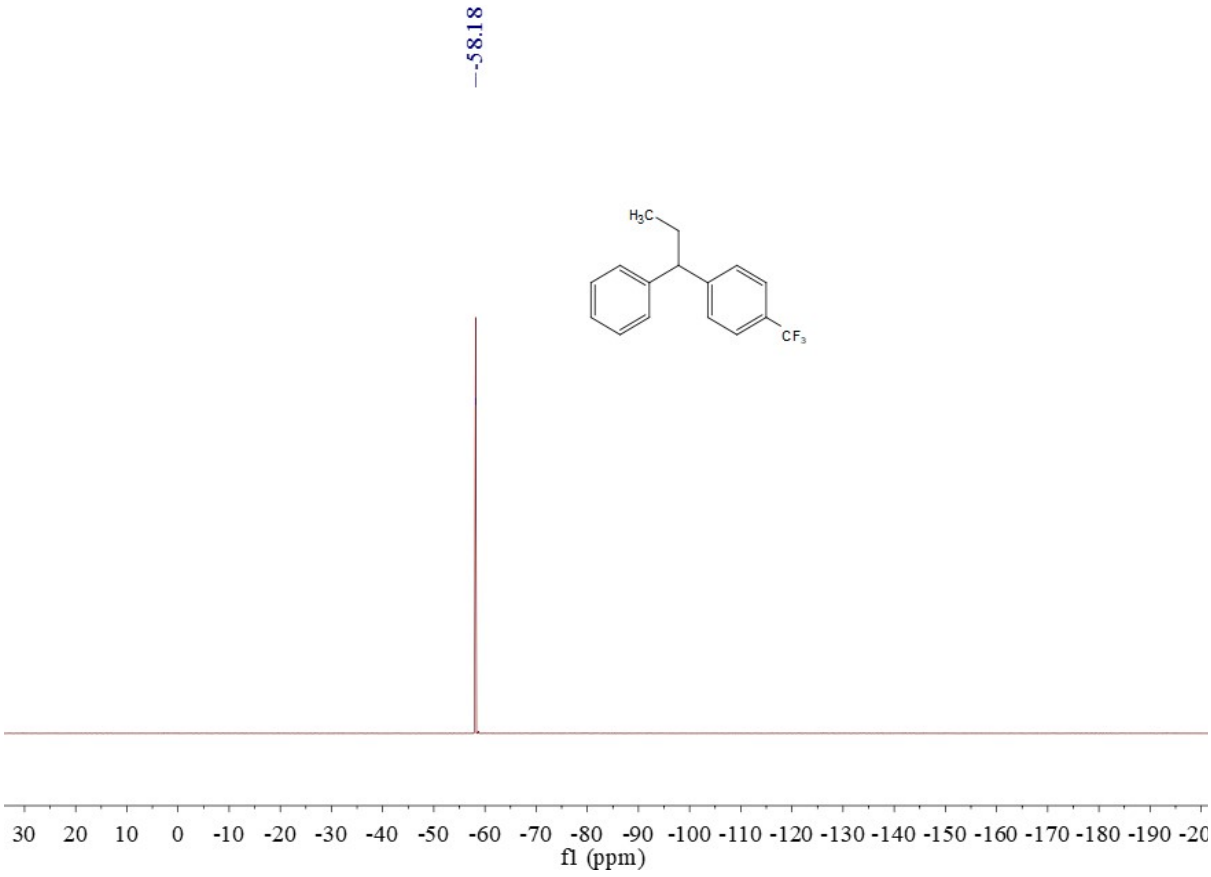
^{1}H NMR of compound 2t (400 MHz, $CDCl_3$):



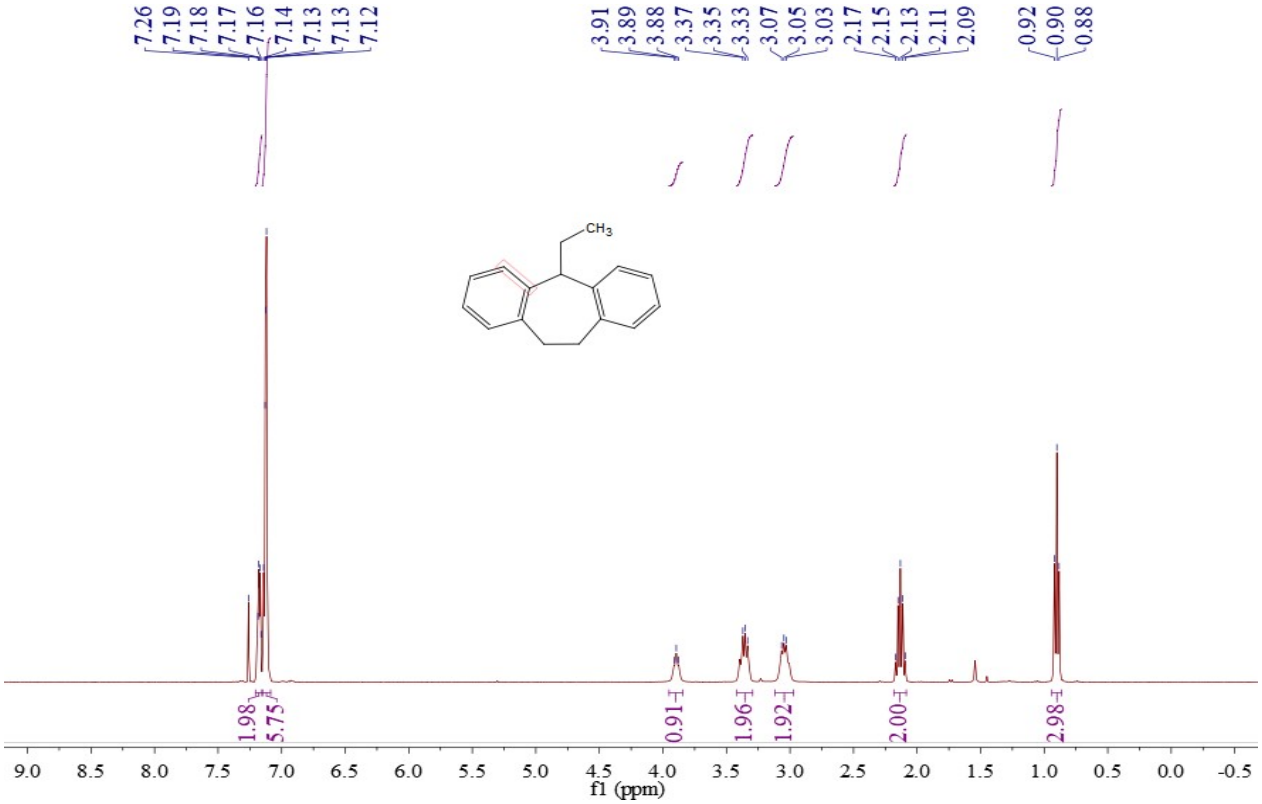
^{13}C NMR of compound 2t (100 MHz, $CDCl_3$):



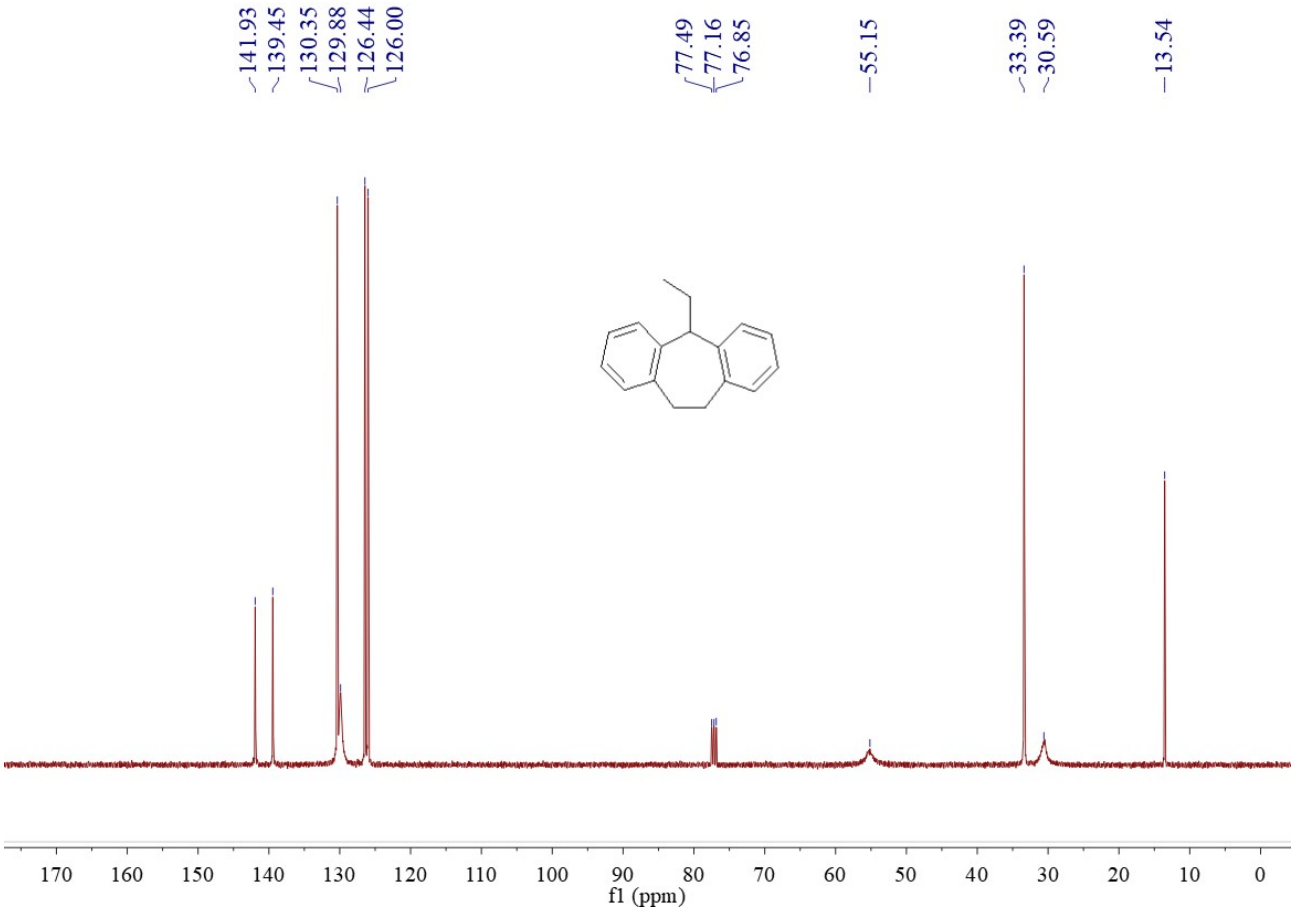
^{19}F NMR of compound 2t (376 MHz, $CDCl_3$):



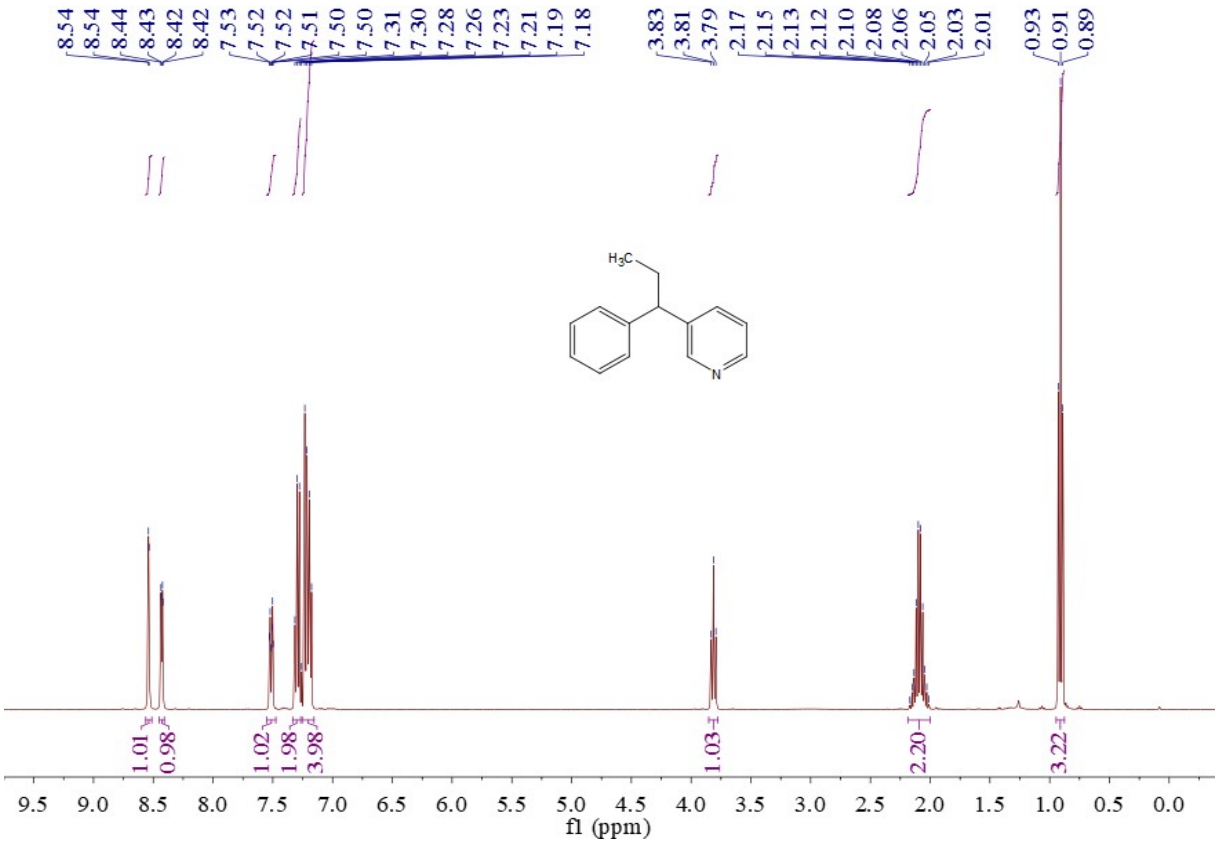
^{1}H NMR of compound 2u (400 MHz, $CDCl_3$):



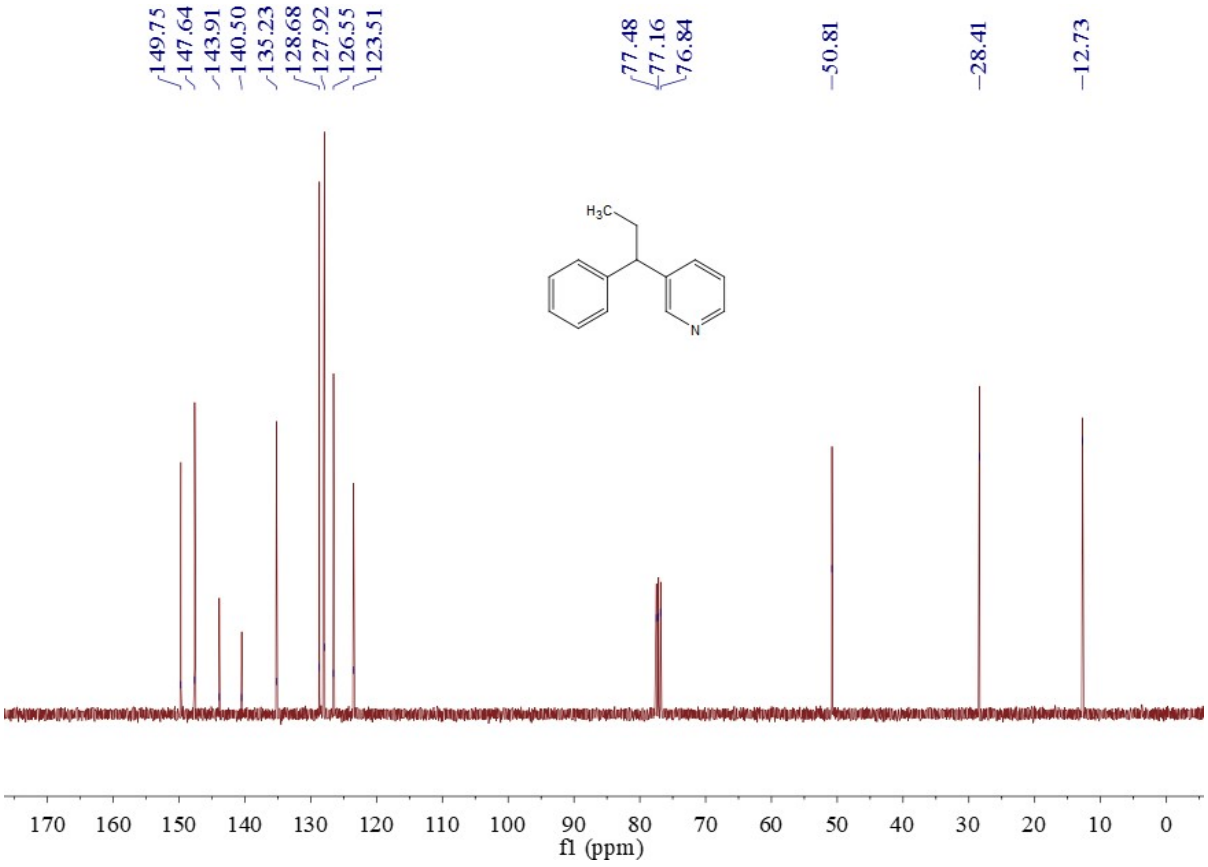
^{13}C NMR of compound 2u (100 MHz, $CDCl_3$):



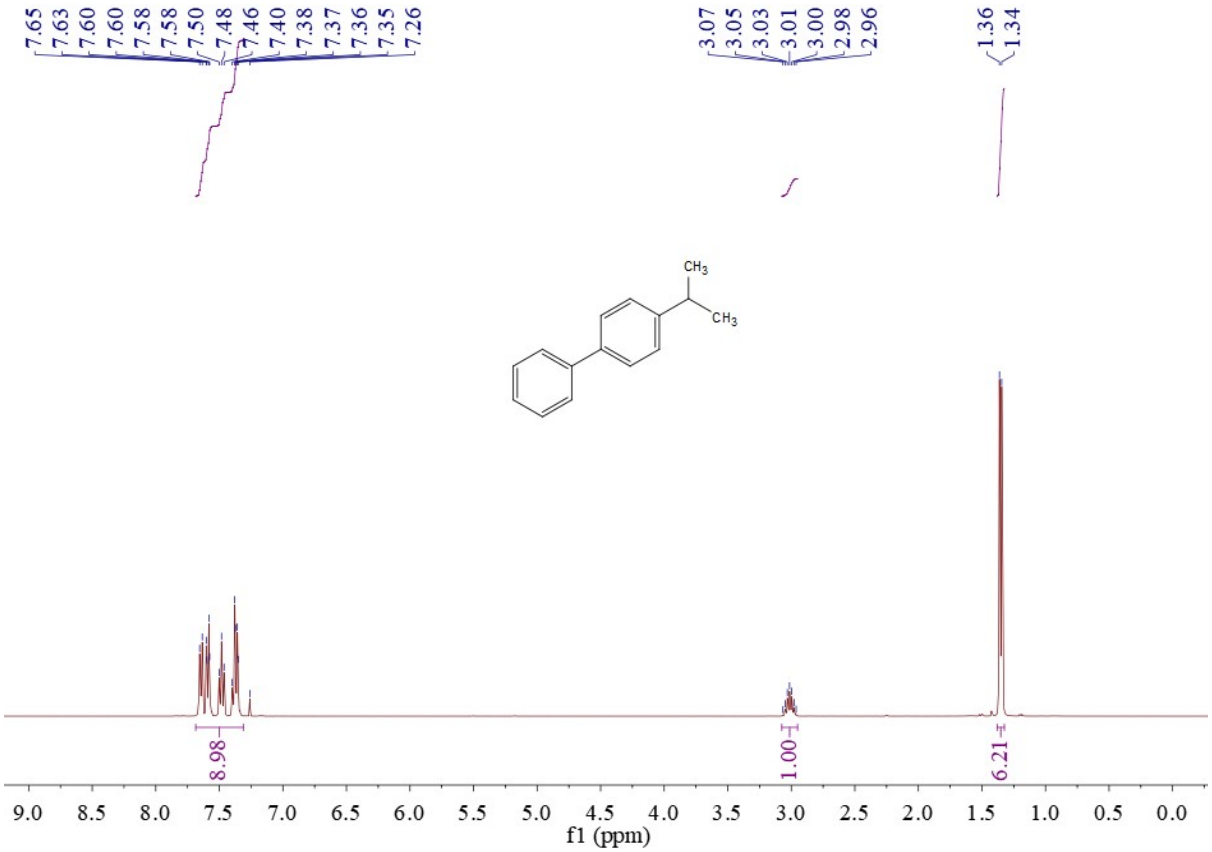
^{1}H NMR of compound 2v (400 MHz, $CDCl_3$):



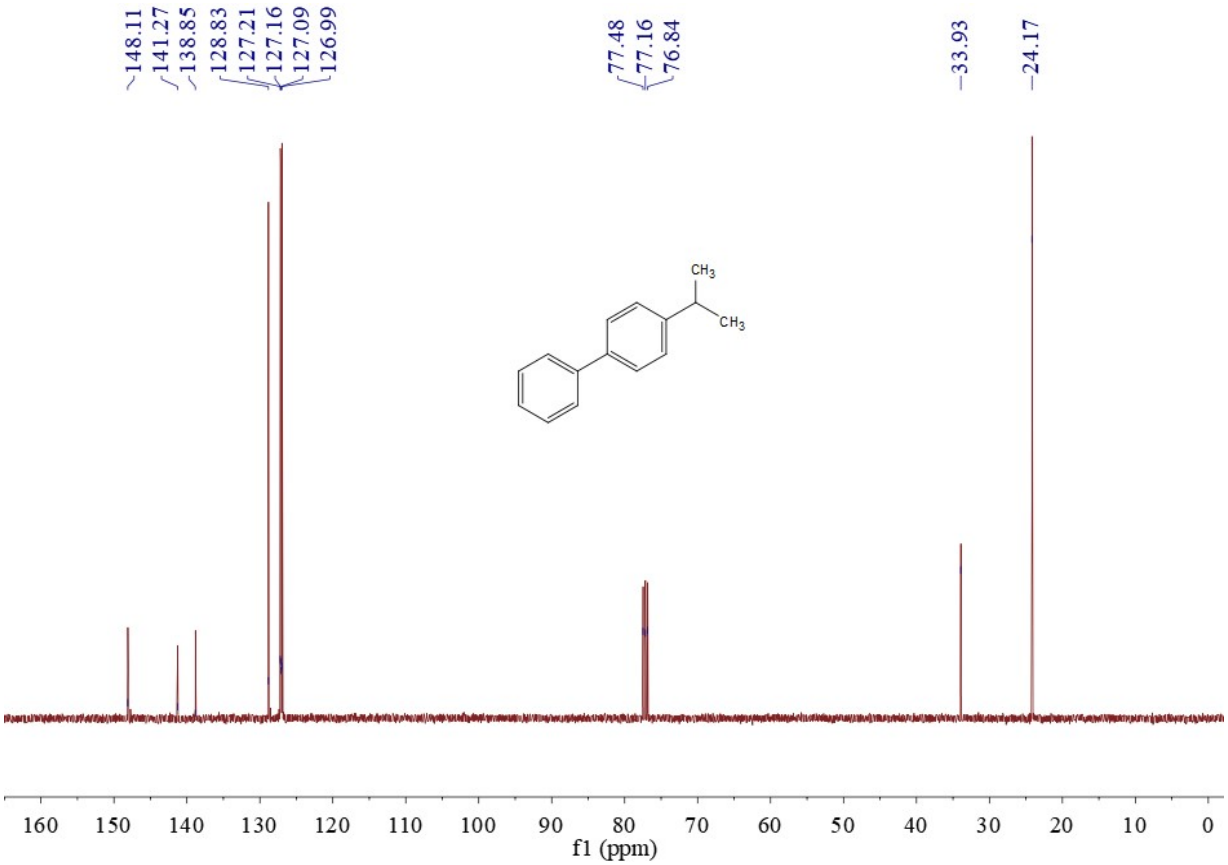
^{13}C NMR of compound 2v (100 MHz, $CDCl_3$):



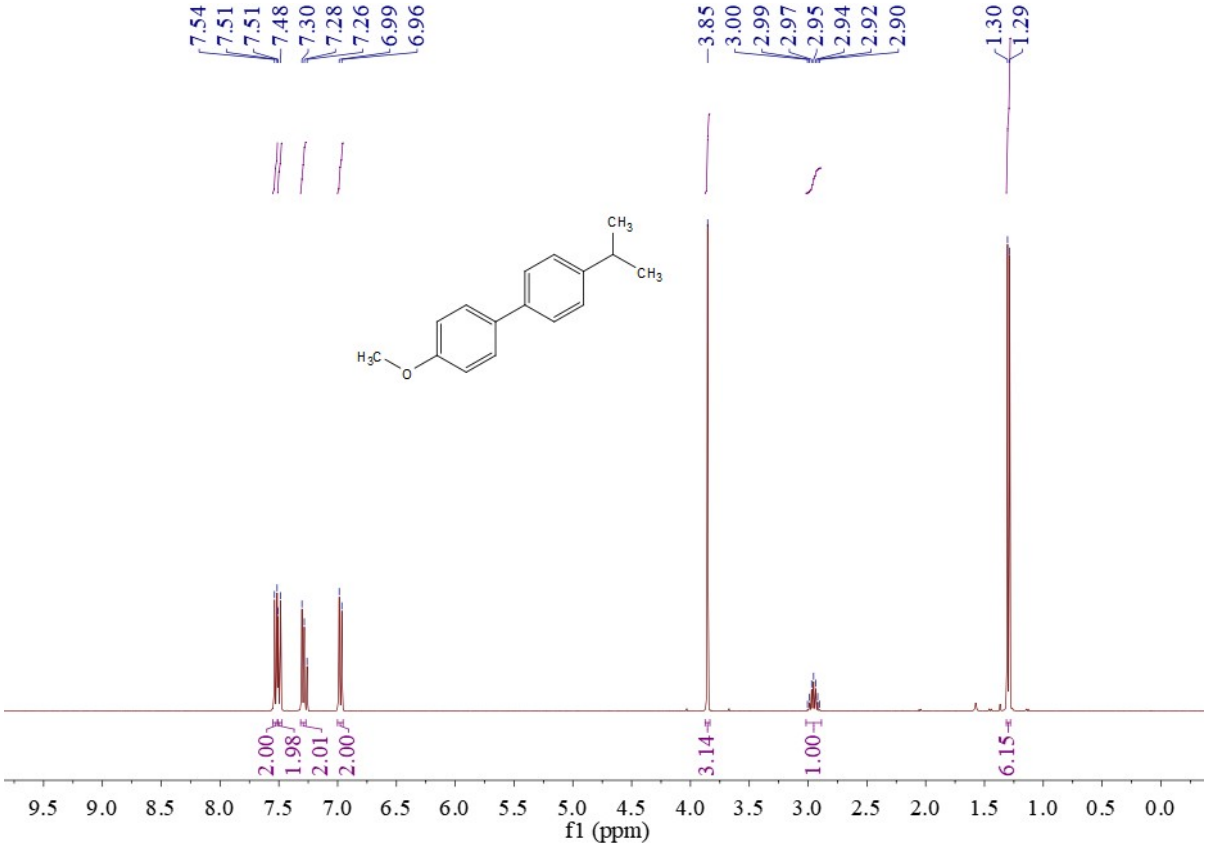
^{1}H NMR of compound 2w (400 MHz, $CDCl_3$):



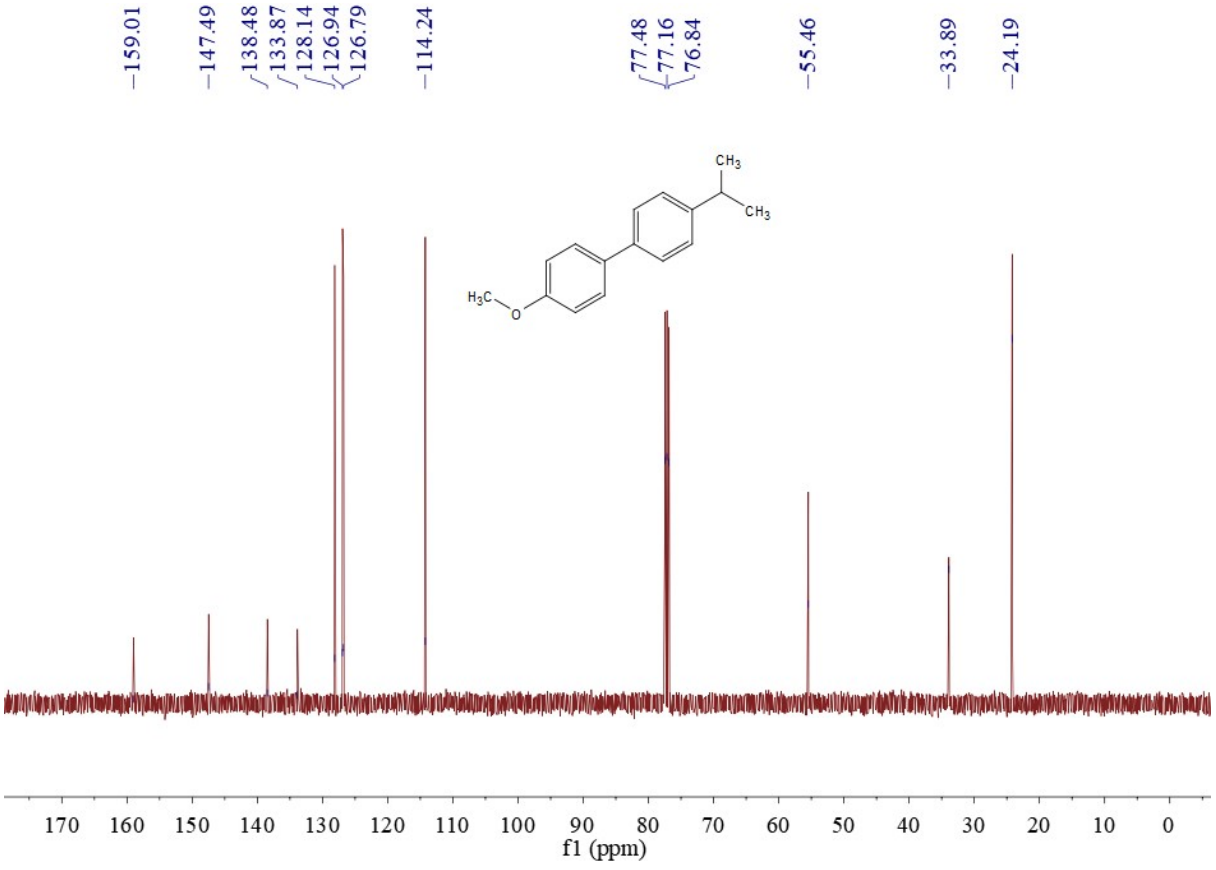
^{13}C NMR of compound 2w (100 MHz, $CDCl_3$):



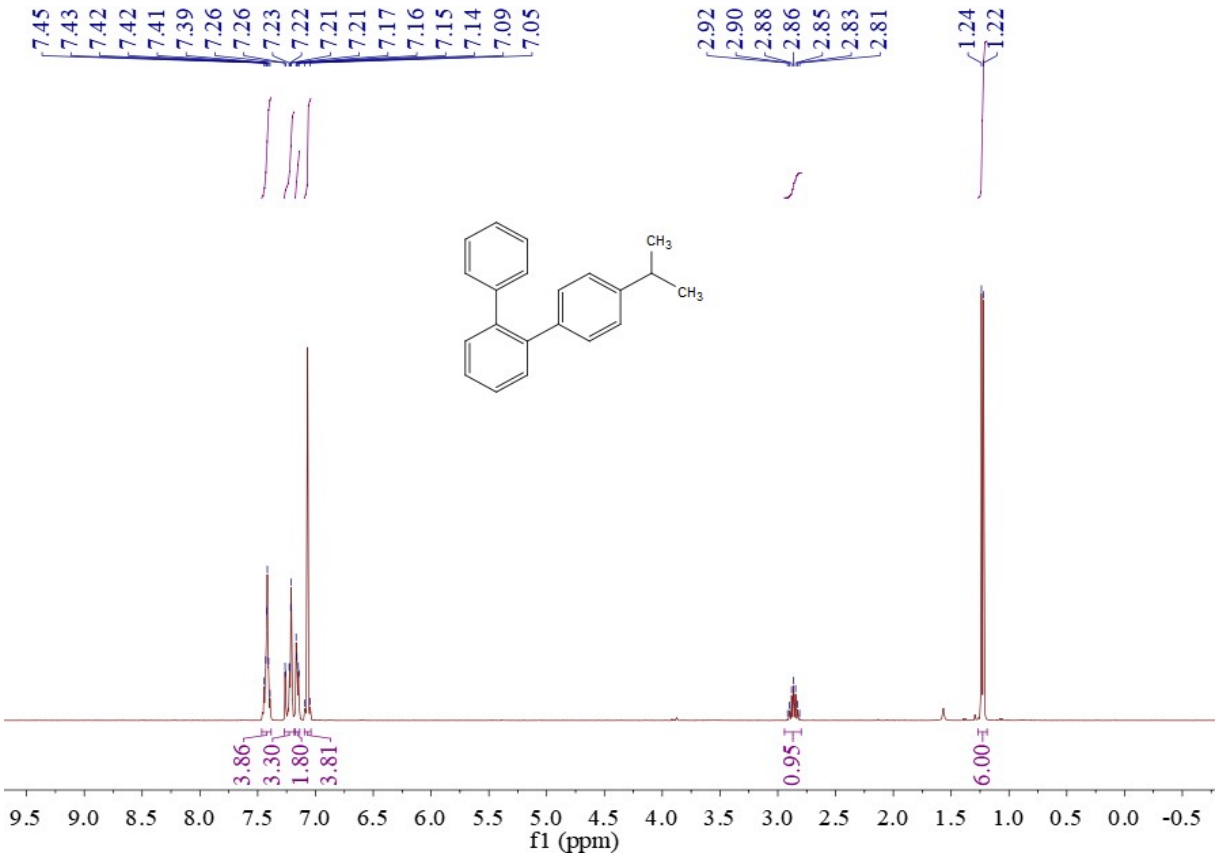
^{1}H NMR of compound 2x (400 MHz, $CDCl_3$):



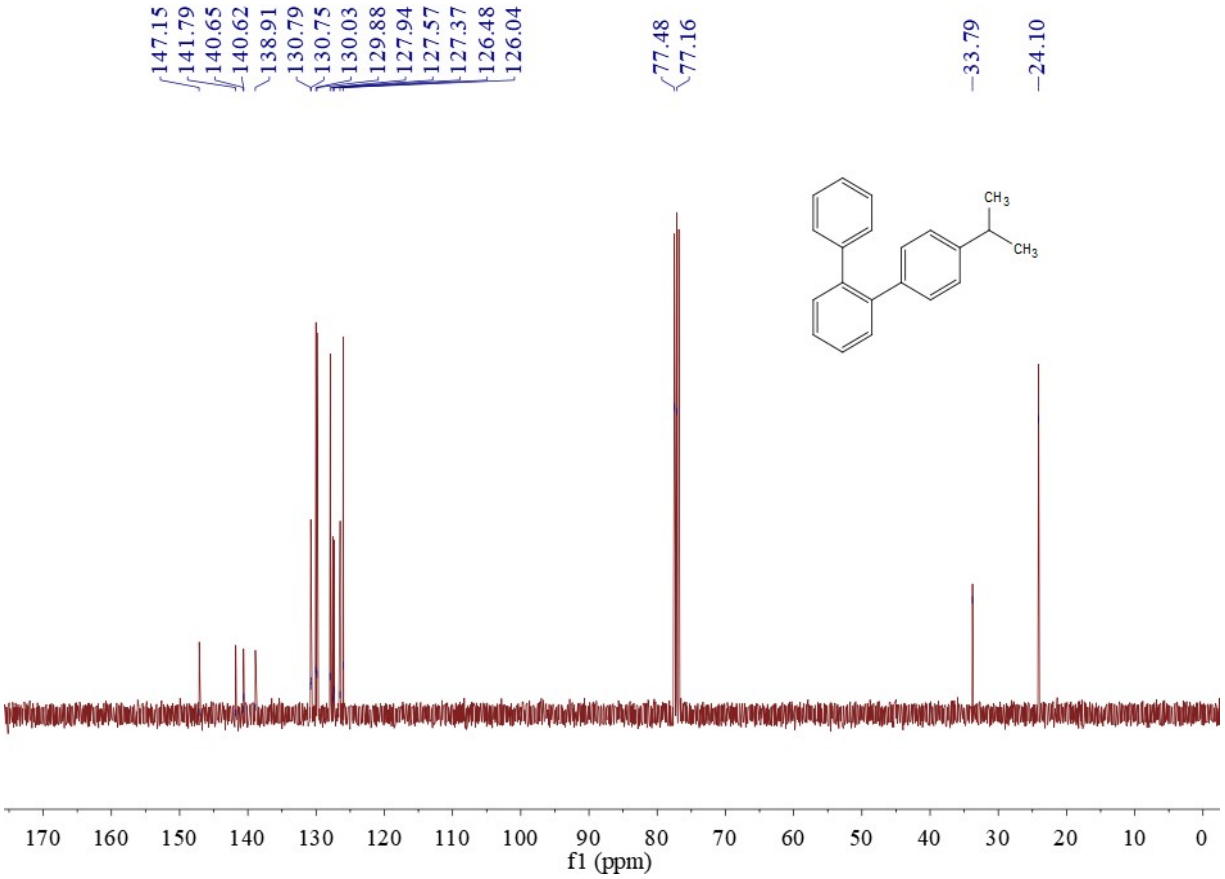
^{13}C NMR of compound 2x (100 MHz, $CDCl_3$):



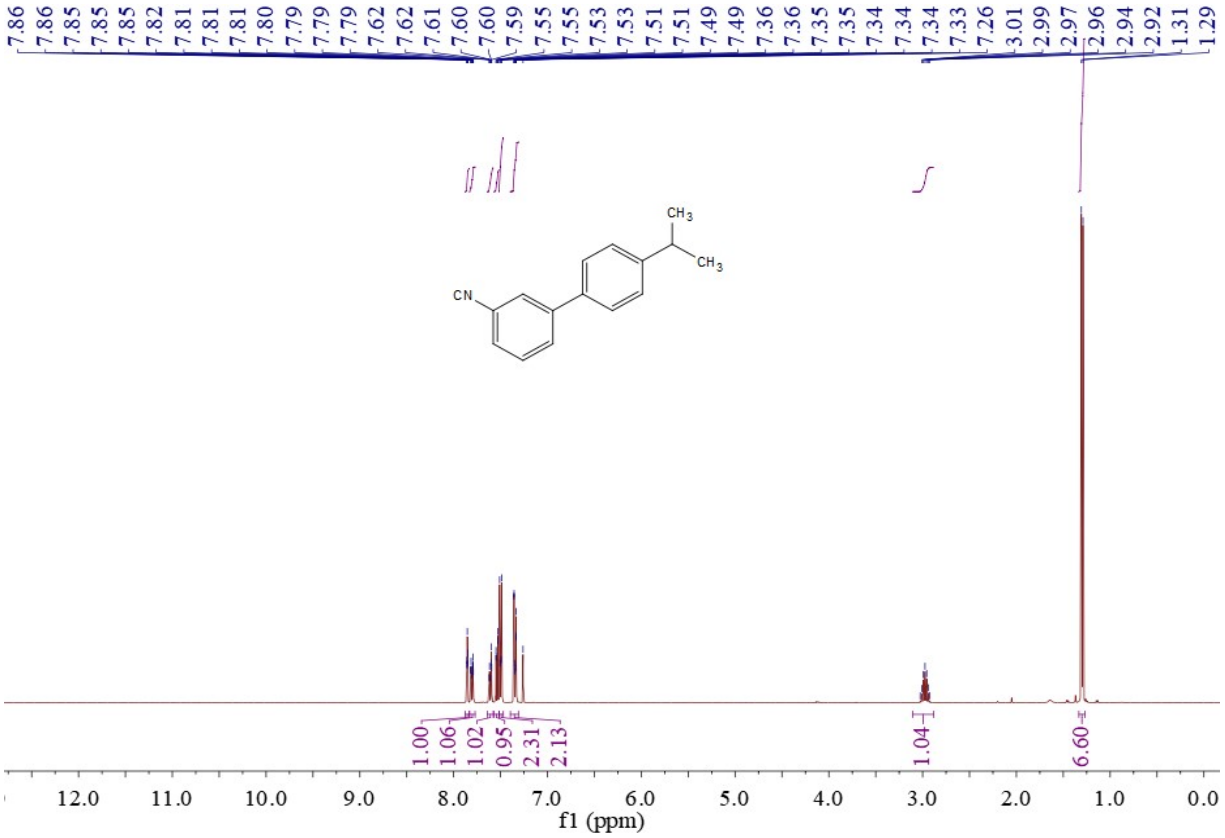
^{1}H NMR of compound 2y (400 MHz, $CDCl_3$):



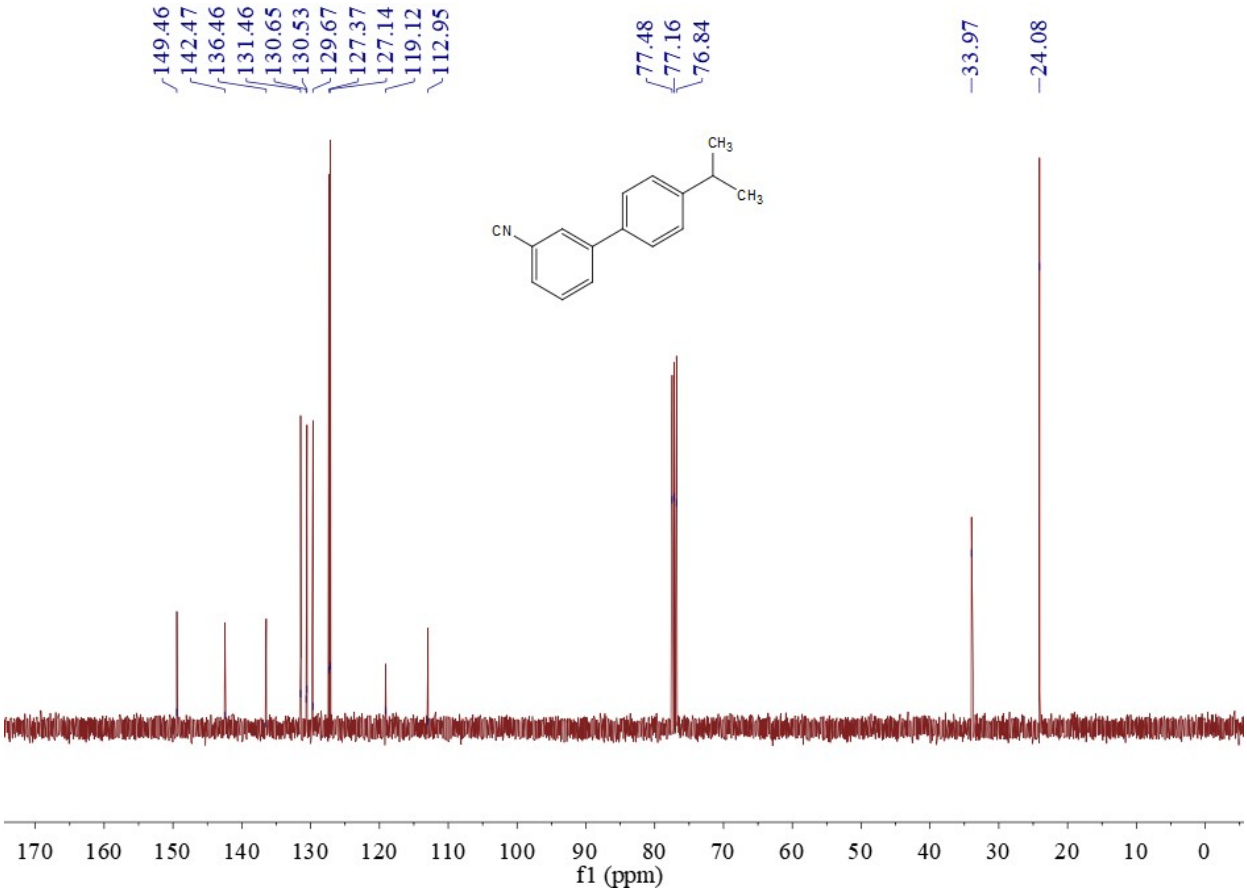
^{13}C NMR of compound 2y (100 MHz, $CDCl_3$):



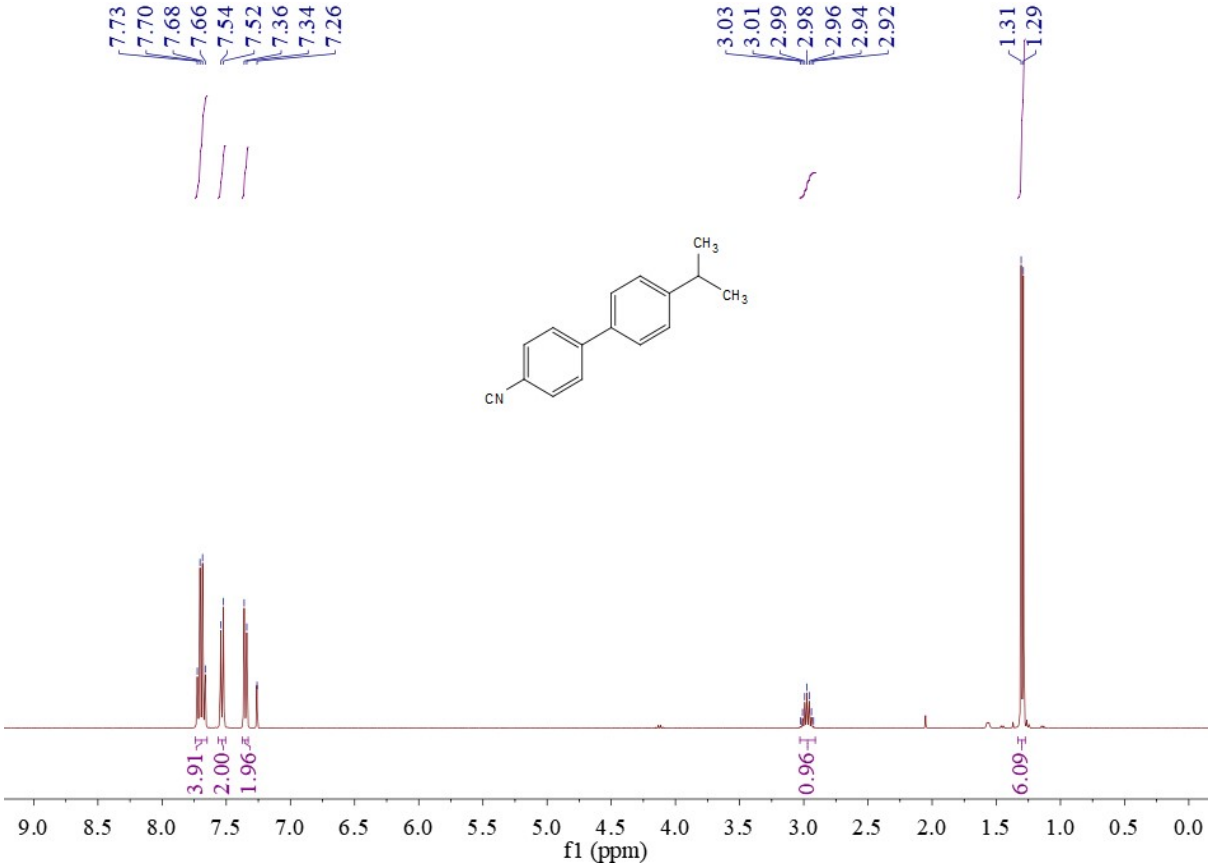
^{1}H NMR of compound 2z (400 MHz, $CDCl_3$):



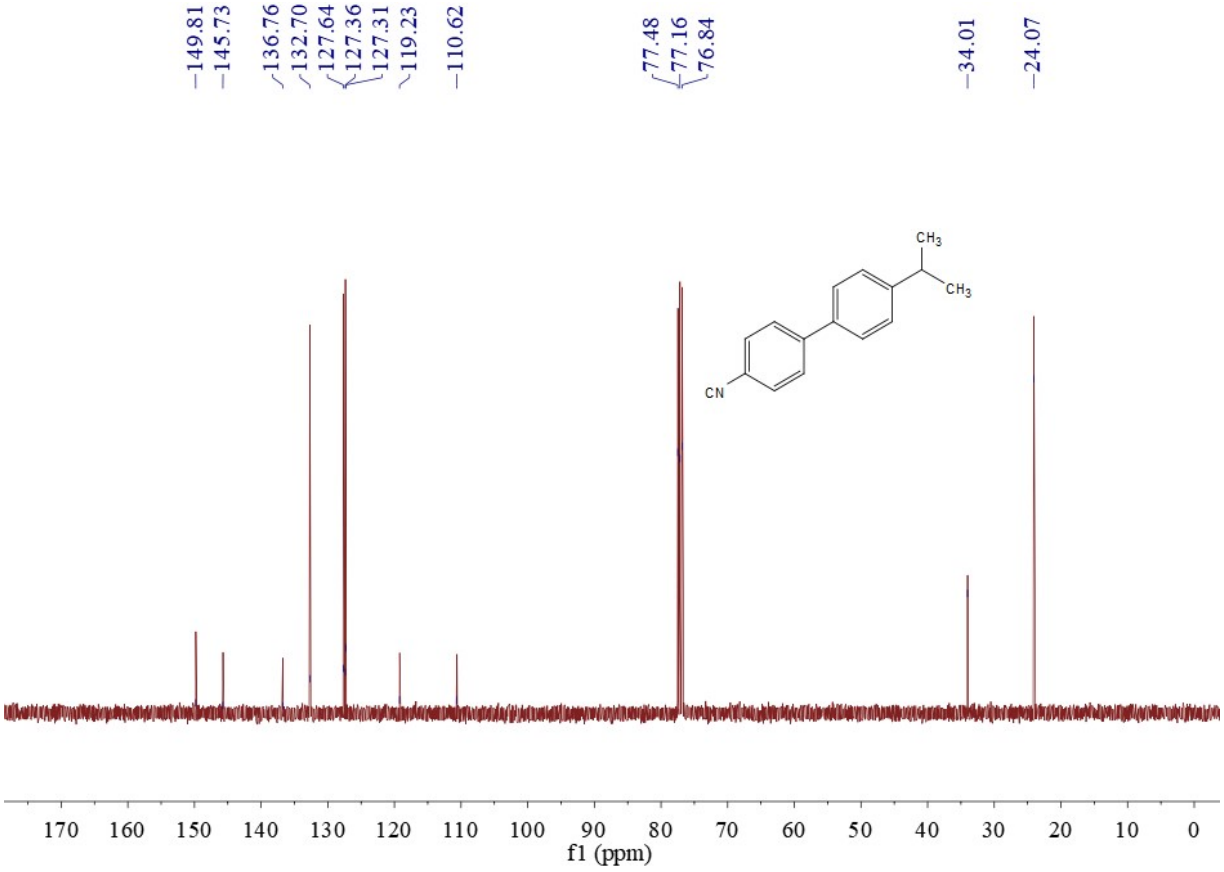
^{13}C NMR of compound 2z (100 MHz, $CDCl_3$):



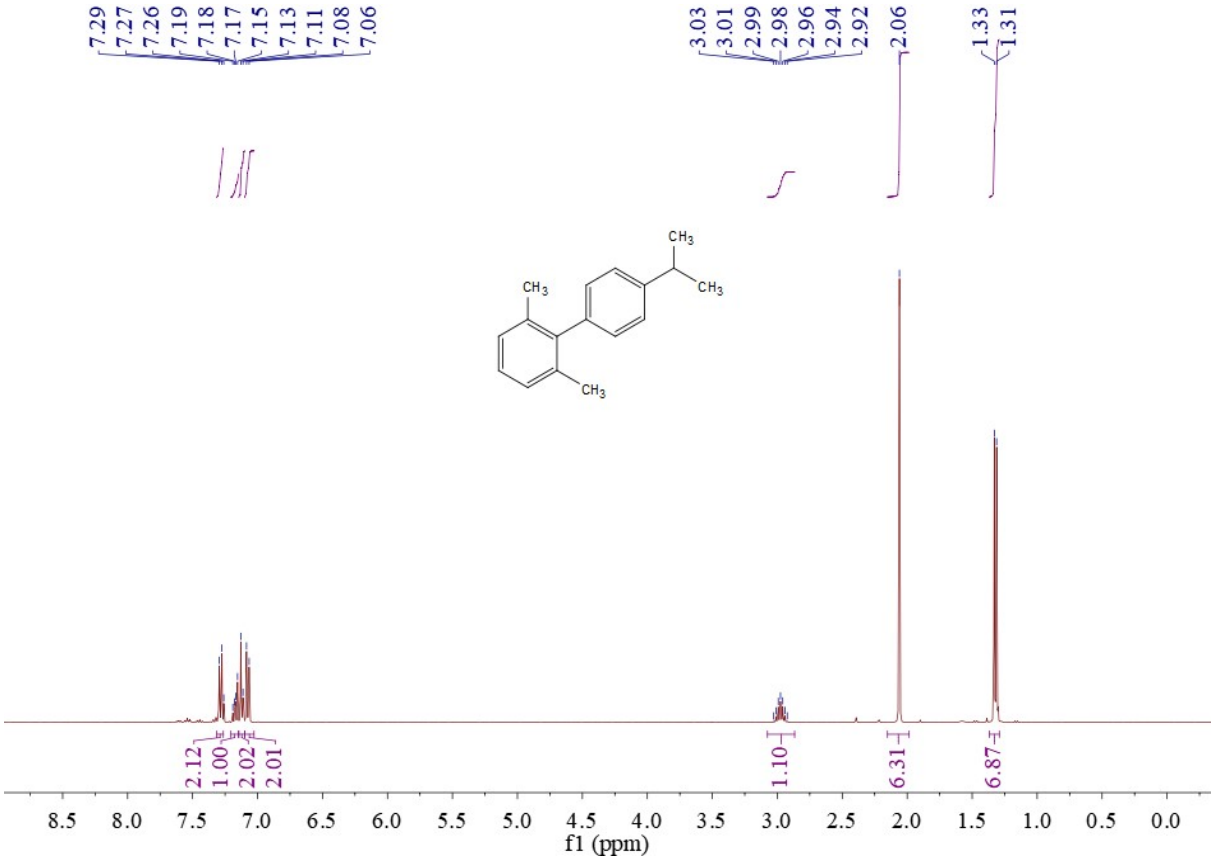
^{1}H NMR of compound 2aa (400 MHz, $CDCl_3$):



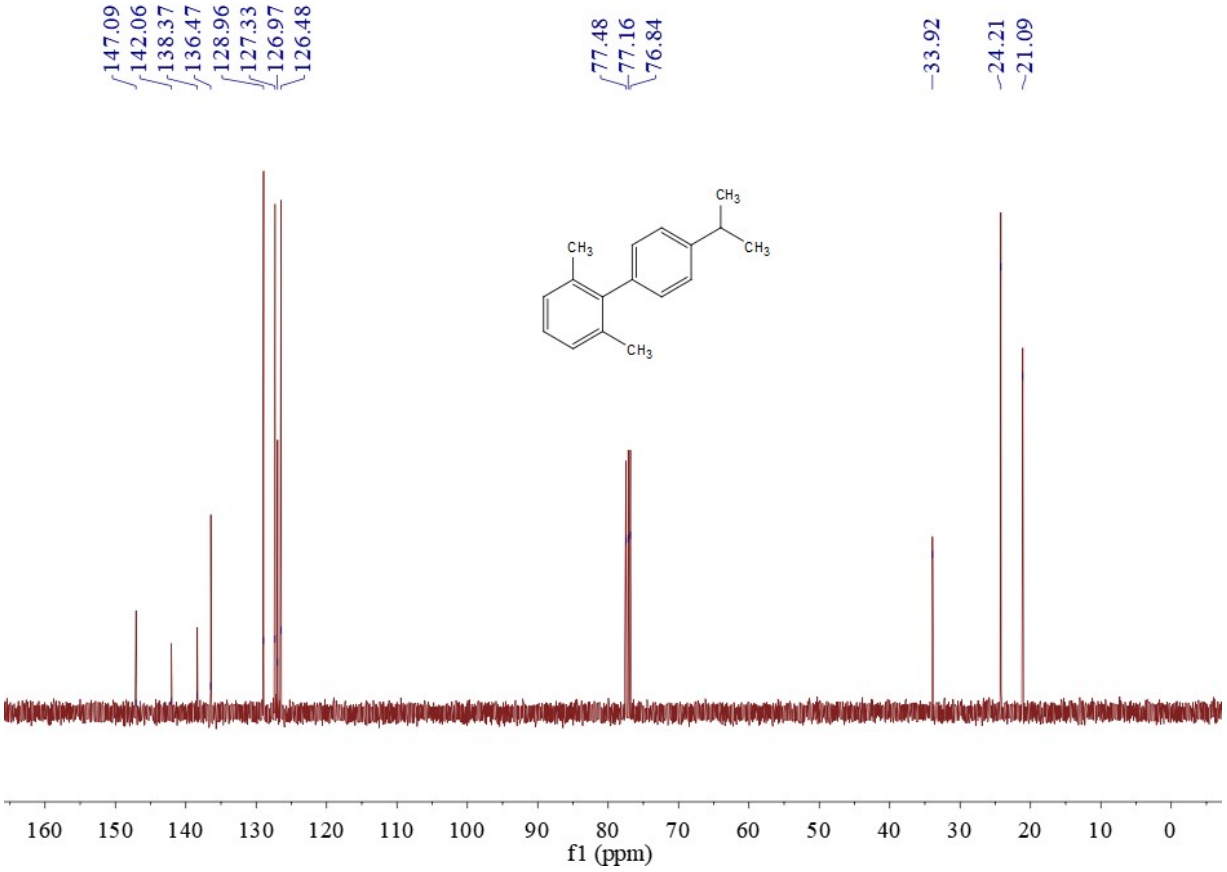
^{13}C NMR of compound 2aa (100 MHz, $CDCl_3$):



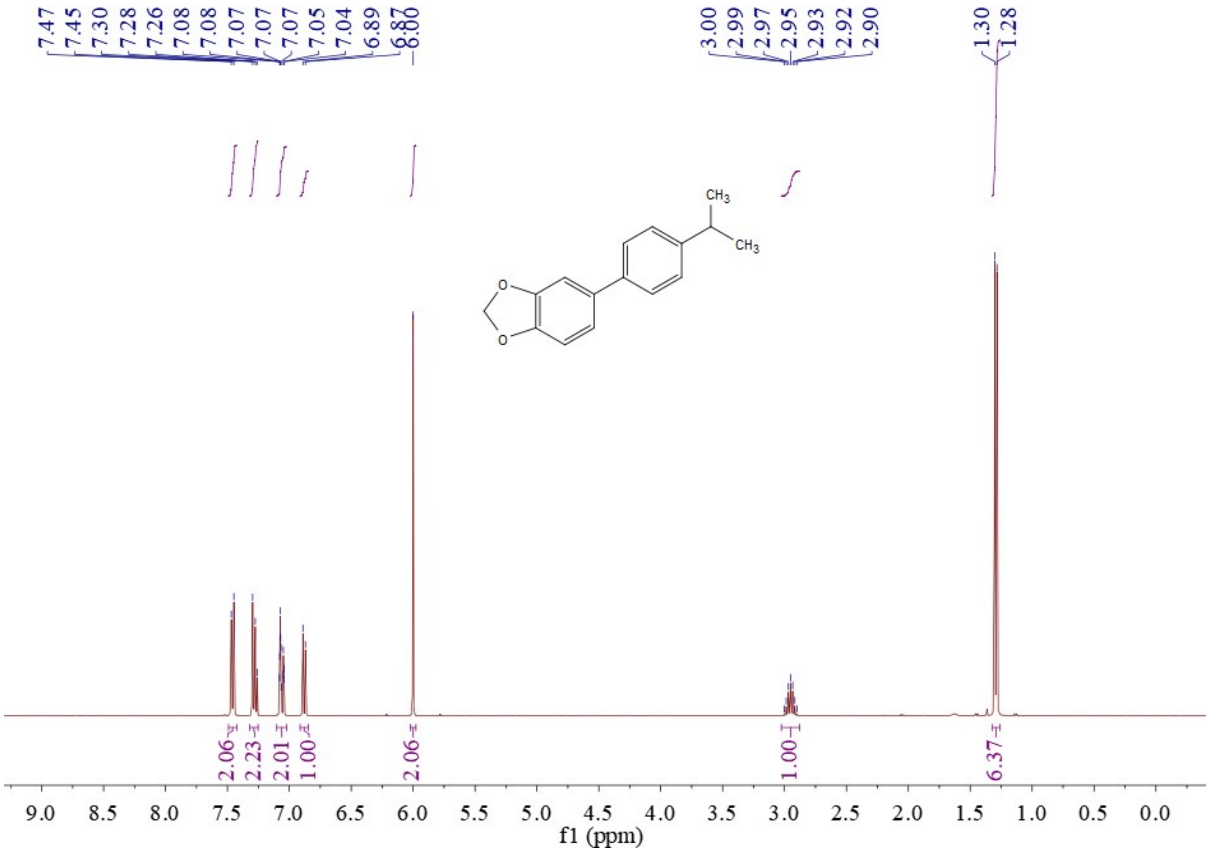
^{1}H NMR of compound 2ab (400 MHz, $CDCl_3$):



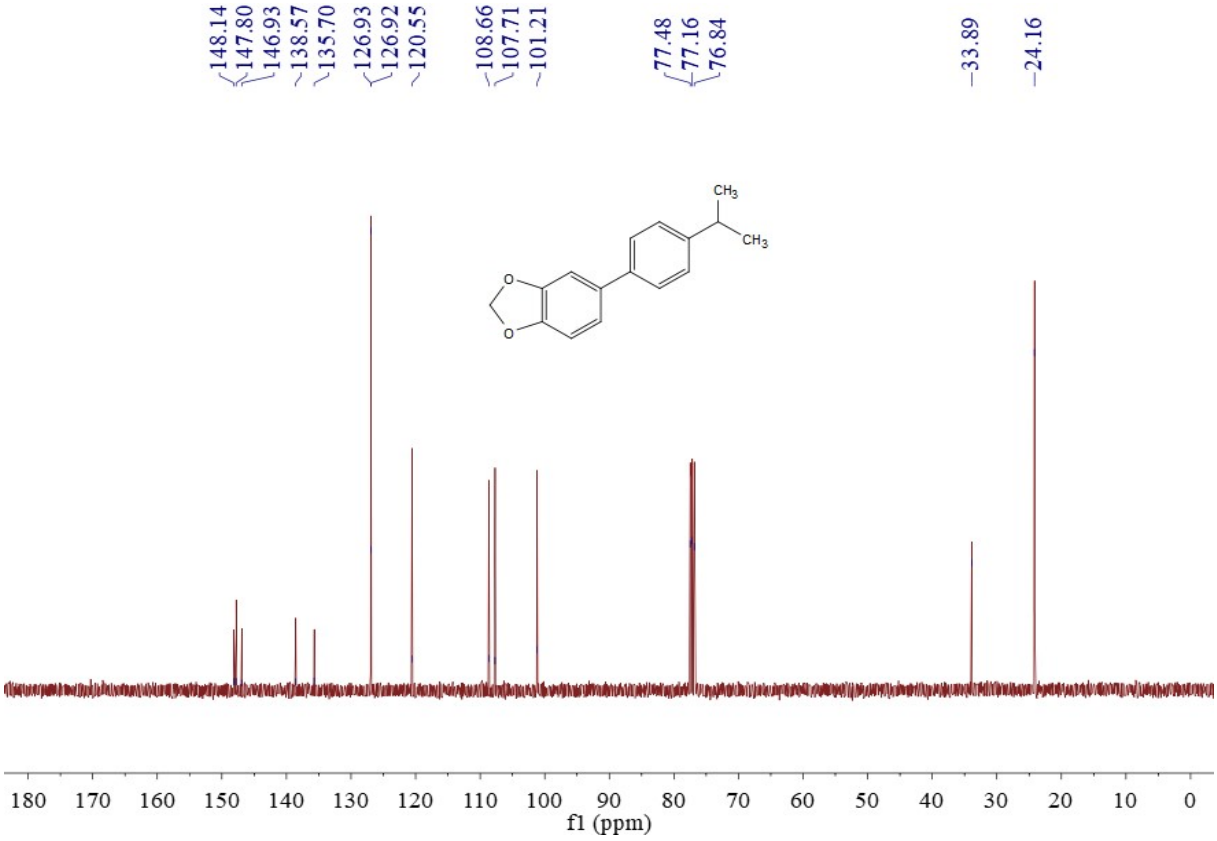
^{13}C NMR of compound 2ab (100 MHz, $CDCl_3$):



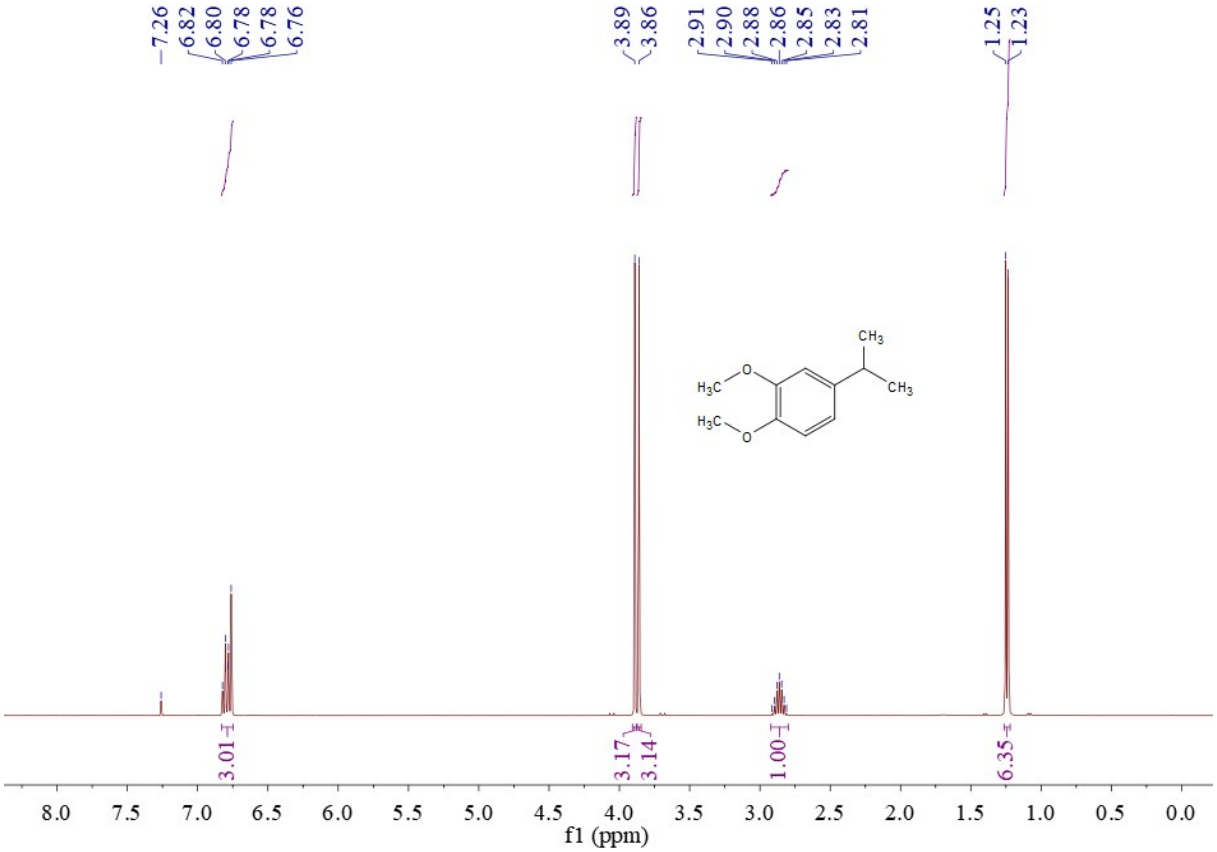
^{1}H NMR of compound 2ac (400 MHz, $CDCl_3$):



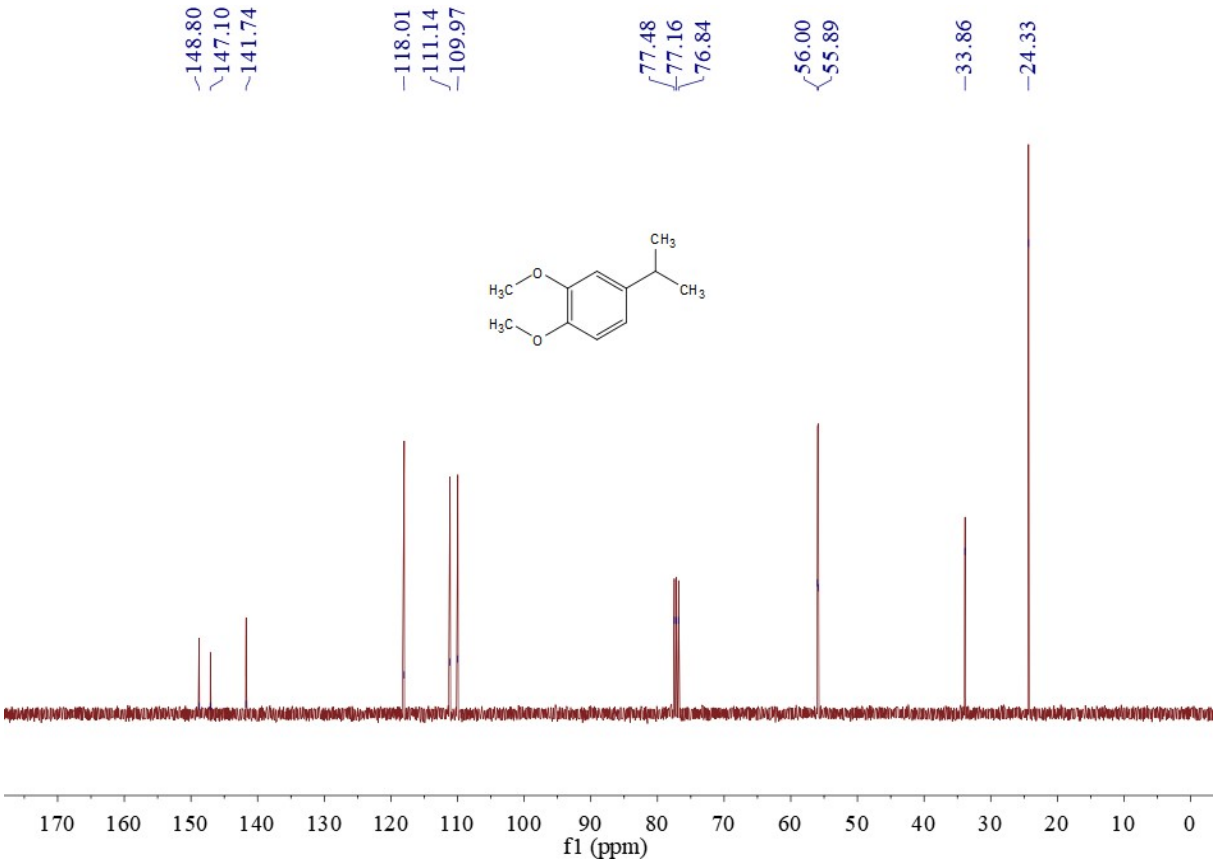
^{13}C NMR of compound 2ac (100 MHz, $CDCl_3$):



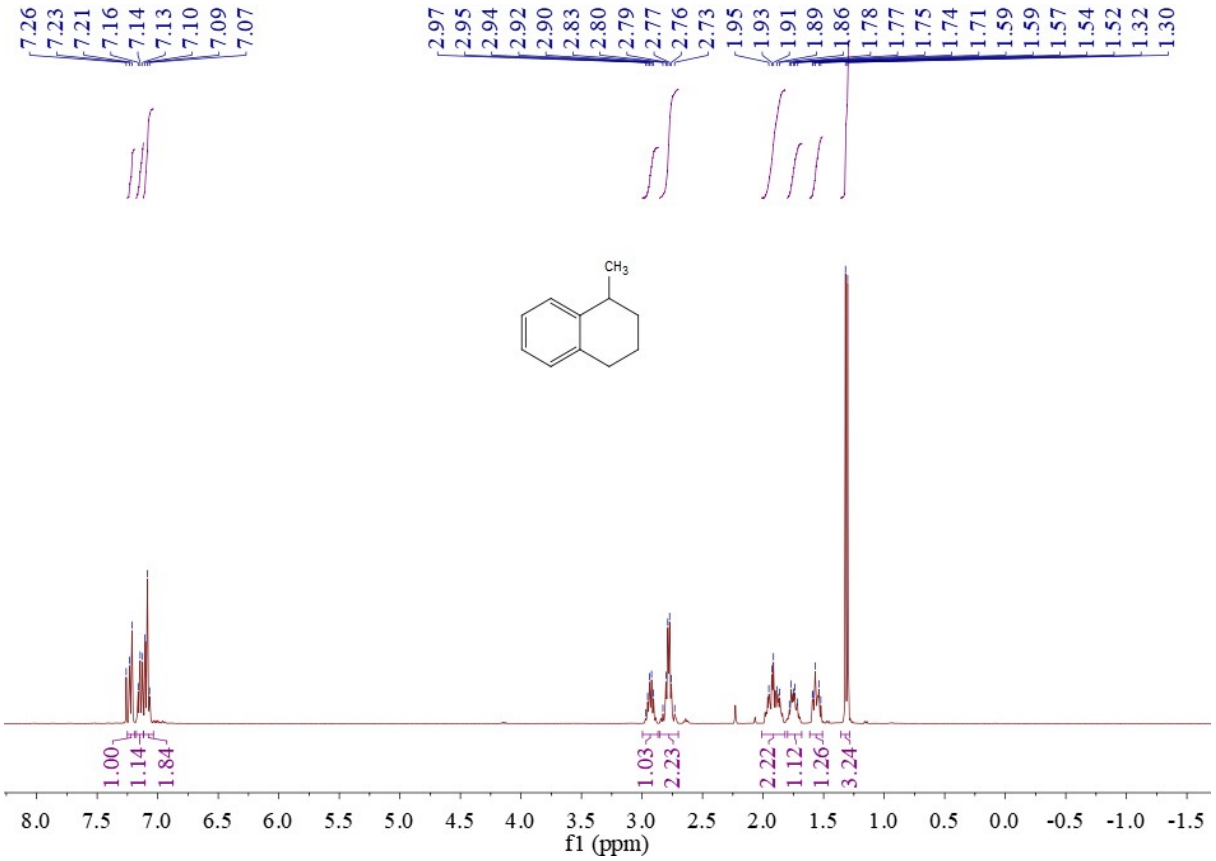
^{1}H NMR of compound 2ad (400 MHz, $CDCl_3$):



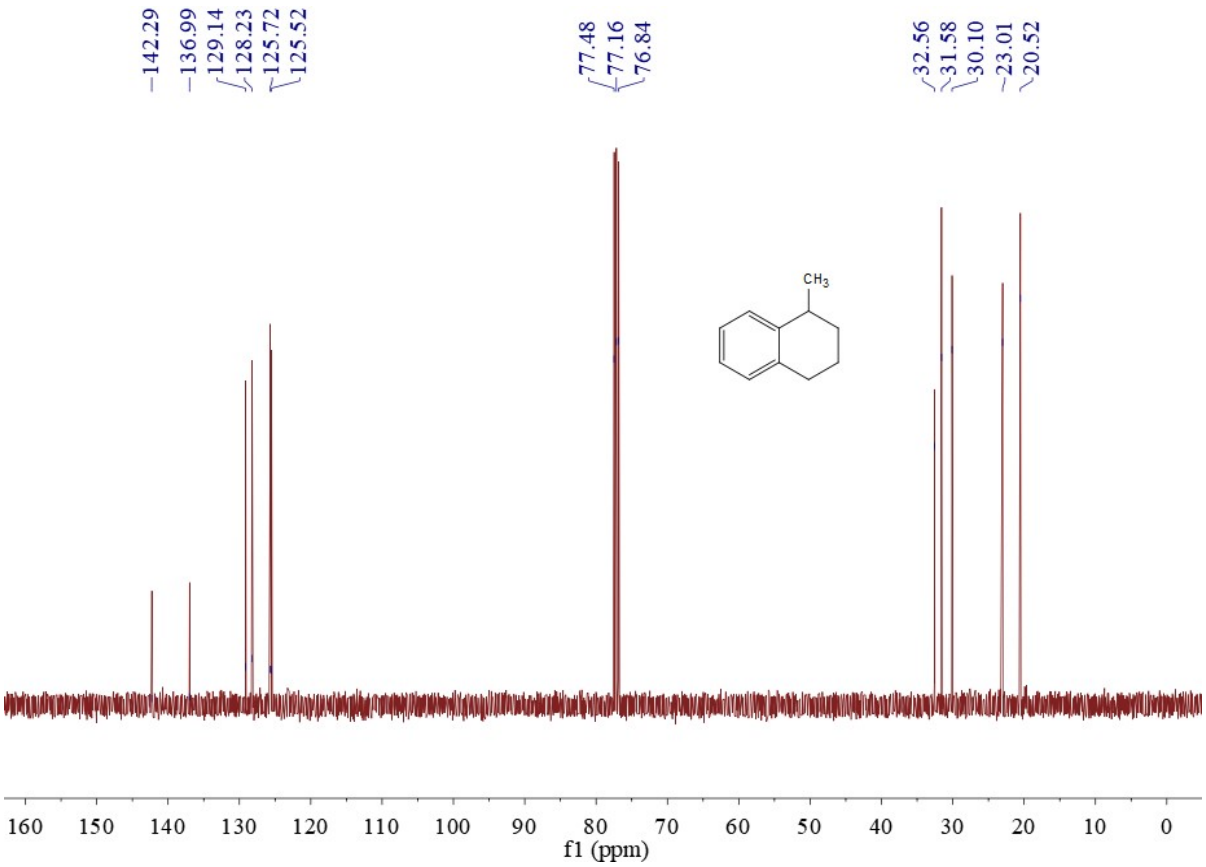
^{13}C NMR of compound 2ad (100 MHz, $CDCl_3$):



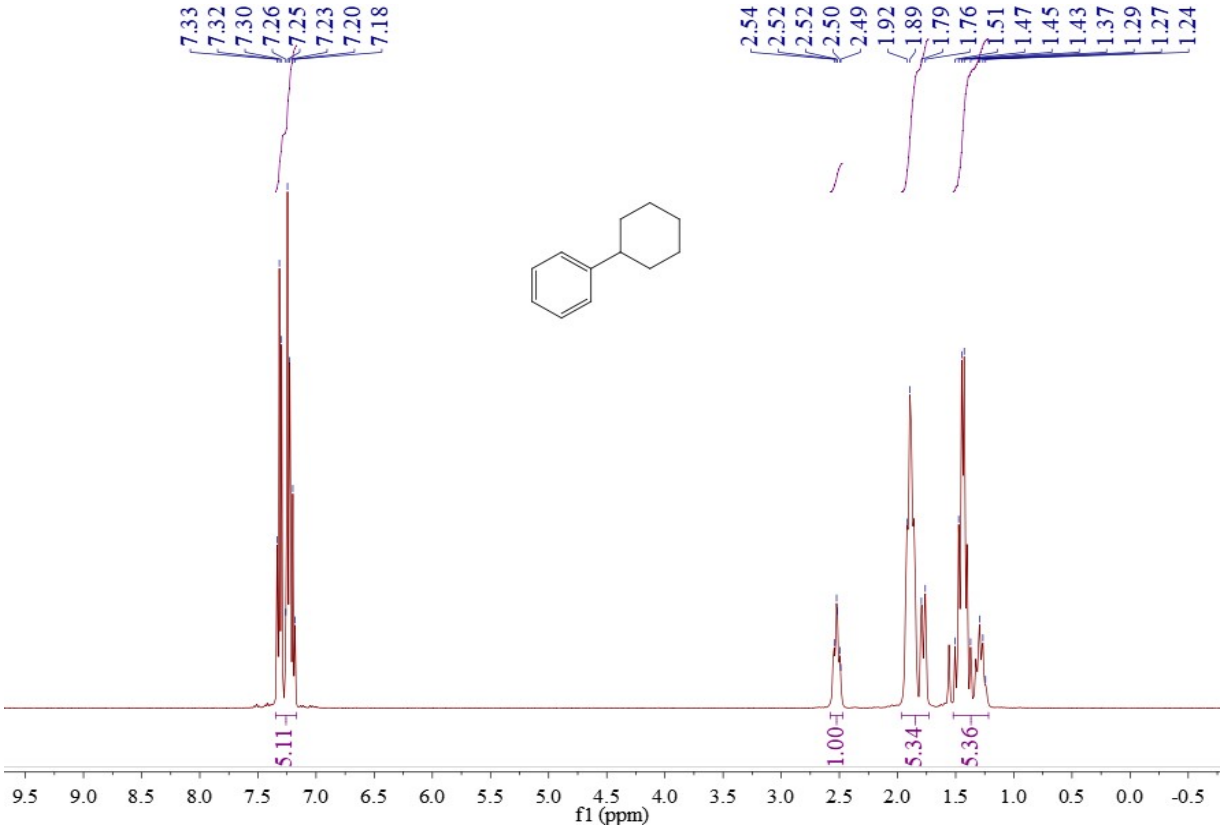
^{1}H NMR of compound 2ah (400 MHz, $CDCl_3$):



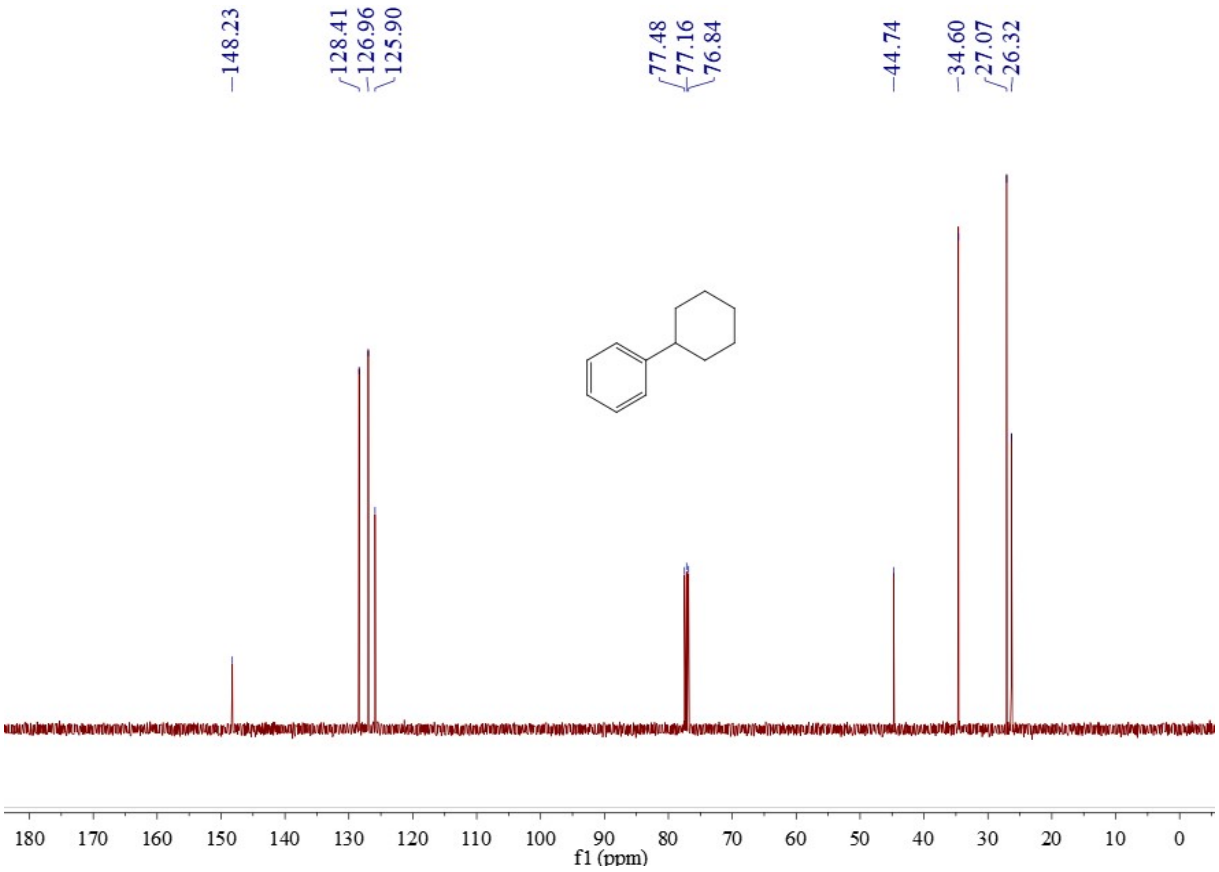
^{13}C NMR of compound 2ah (100 MHz, $CDCl_3$):



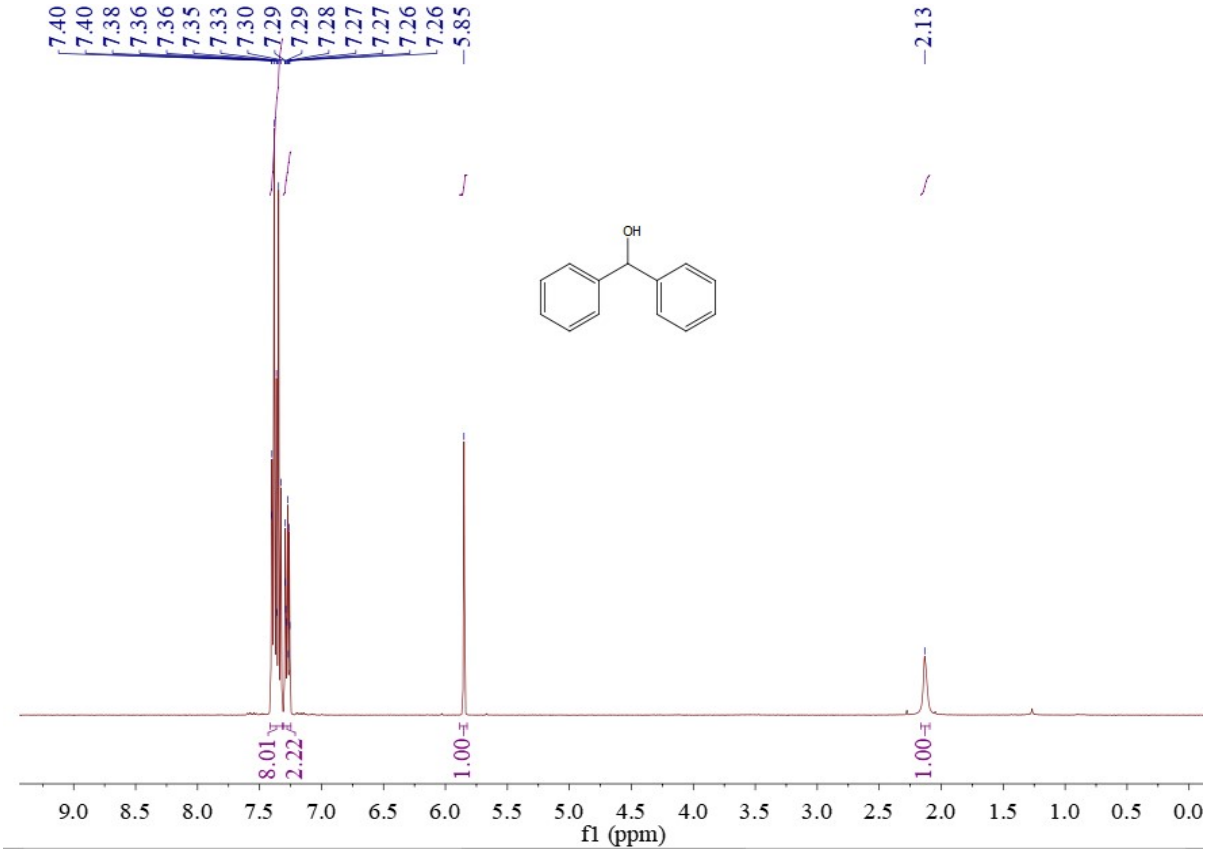
^{1}H NMR of compound 2ai (400 MHz, $CDCl_3$):



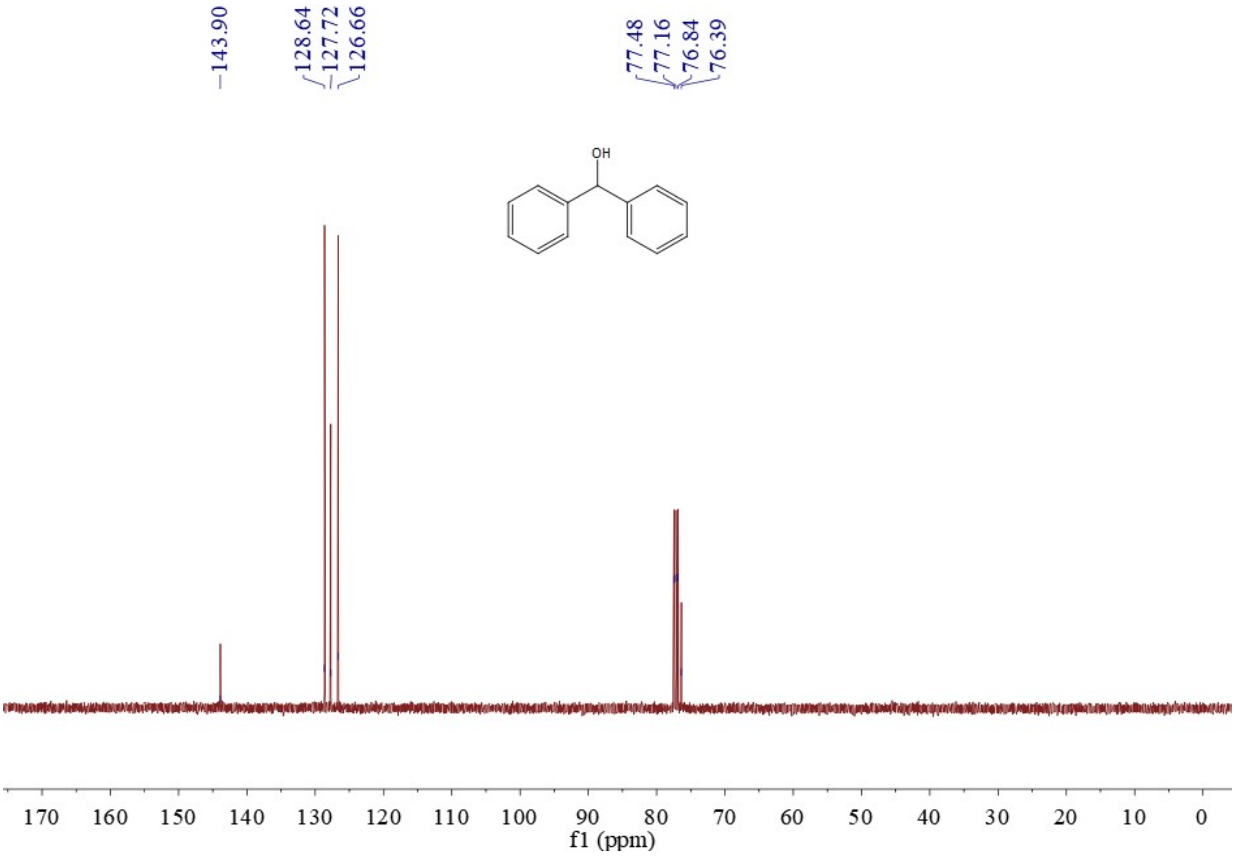
^{13}C NMR of compound 2ai (100 MHz, $CDCl_3$):



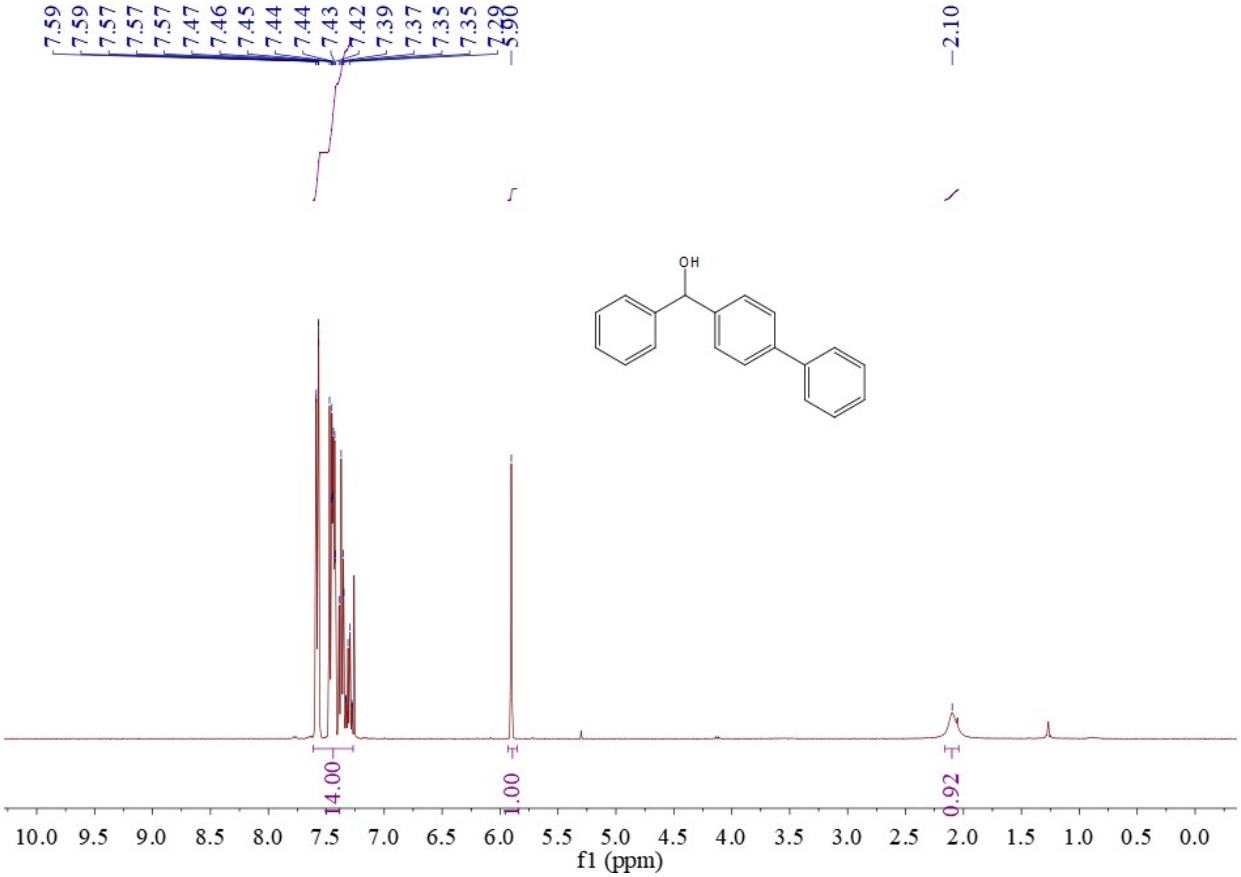
^{1}H NMR of compound 4a (400 MHz, $CDCl_3$):



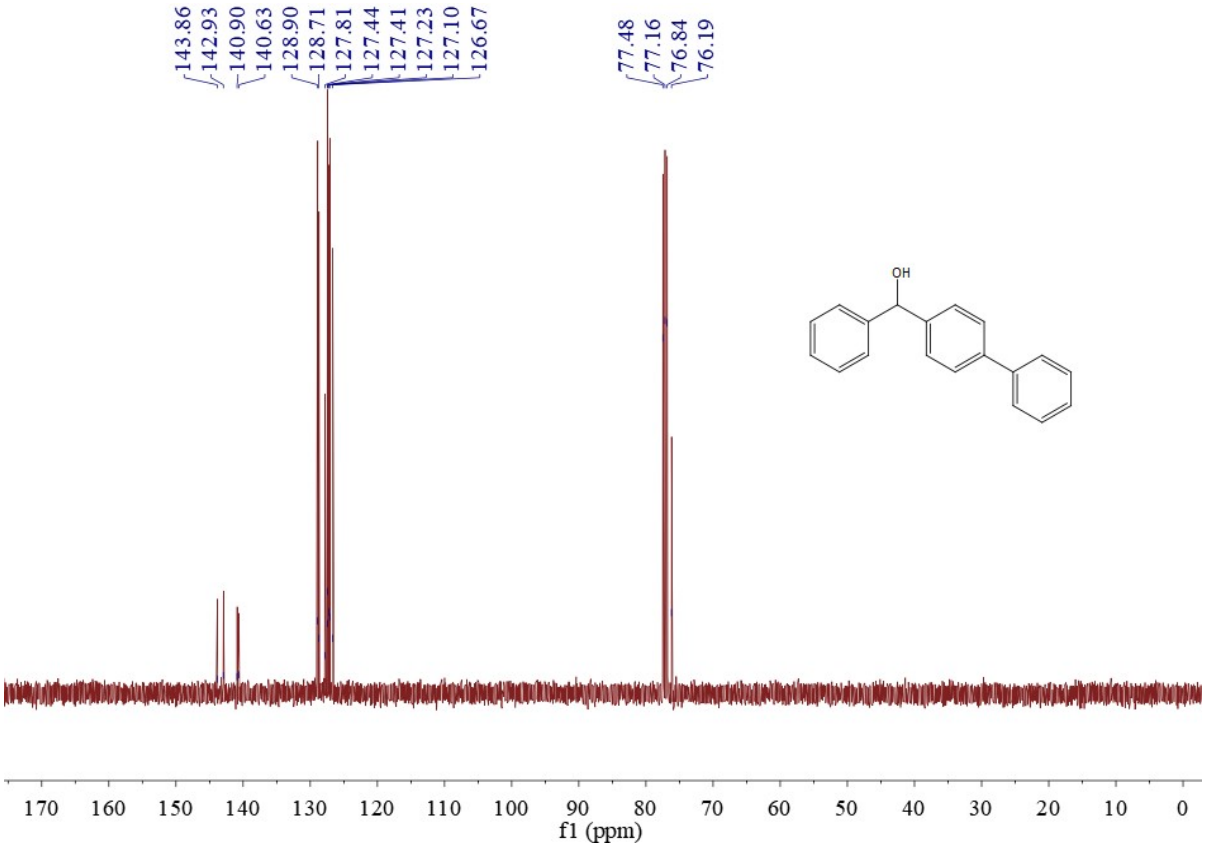
^{13}C NMR of compound 4a (100 MHz, $CDCl_3$):



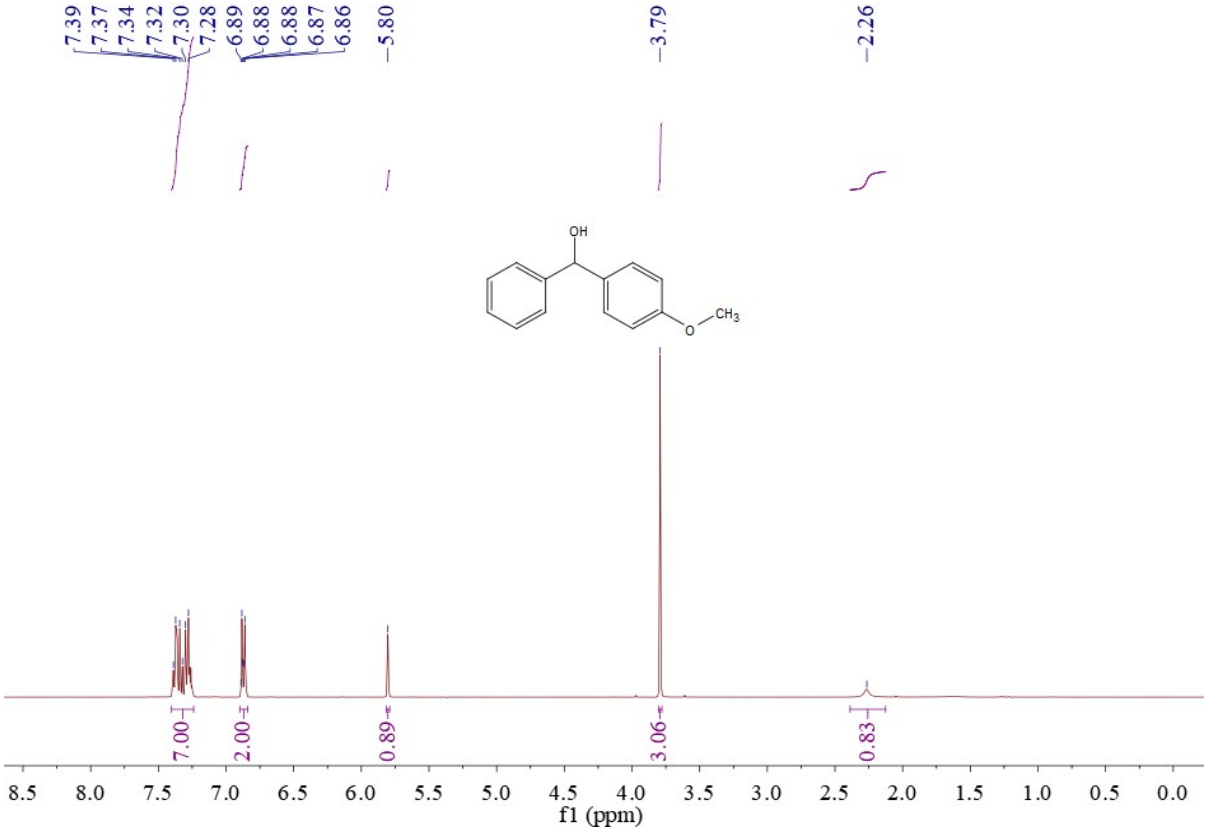
^{1}H NMR of compound 4b (400 MHz, $CDCl_3$):



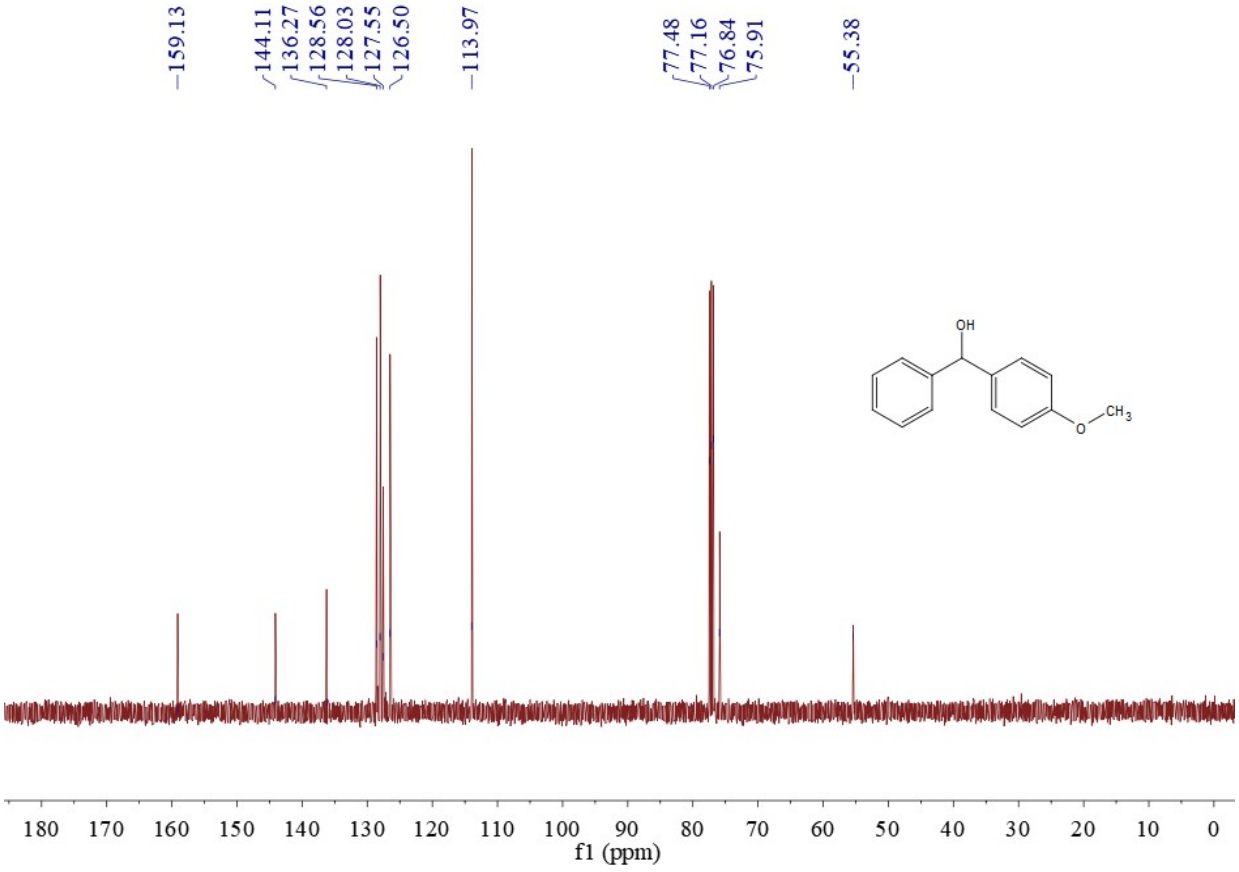
^{13}C NMR of compound 4b (100 MHz, $CDCl_3$):



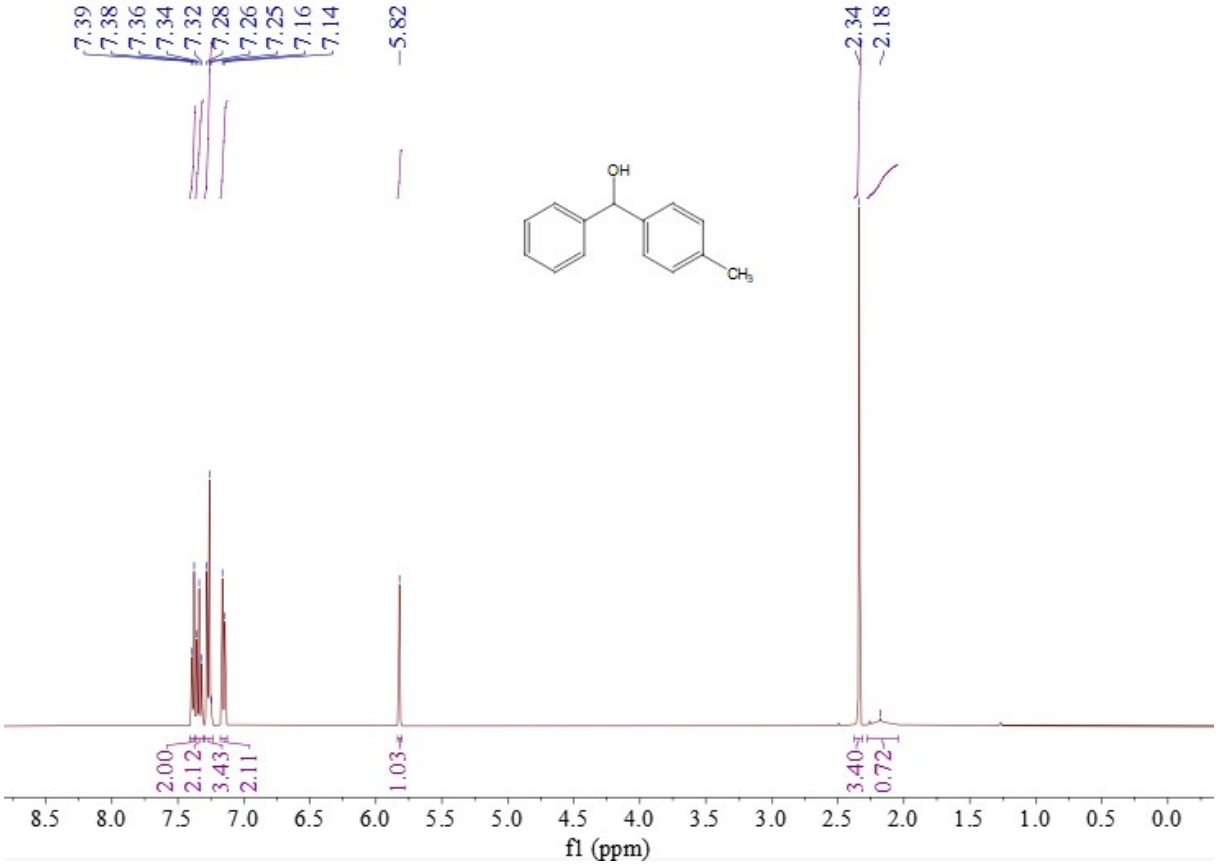
^{1}H NMR of compound 4c (400 MHz, $CDCl_3$):



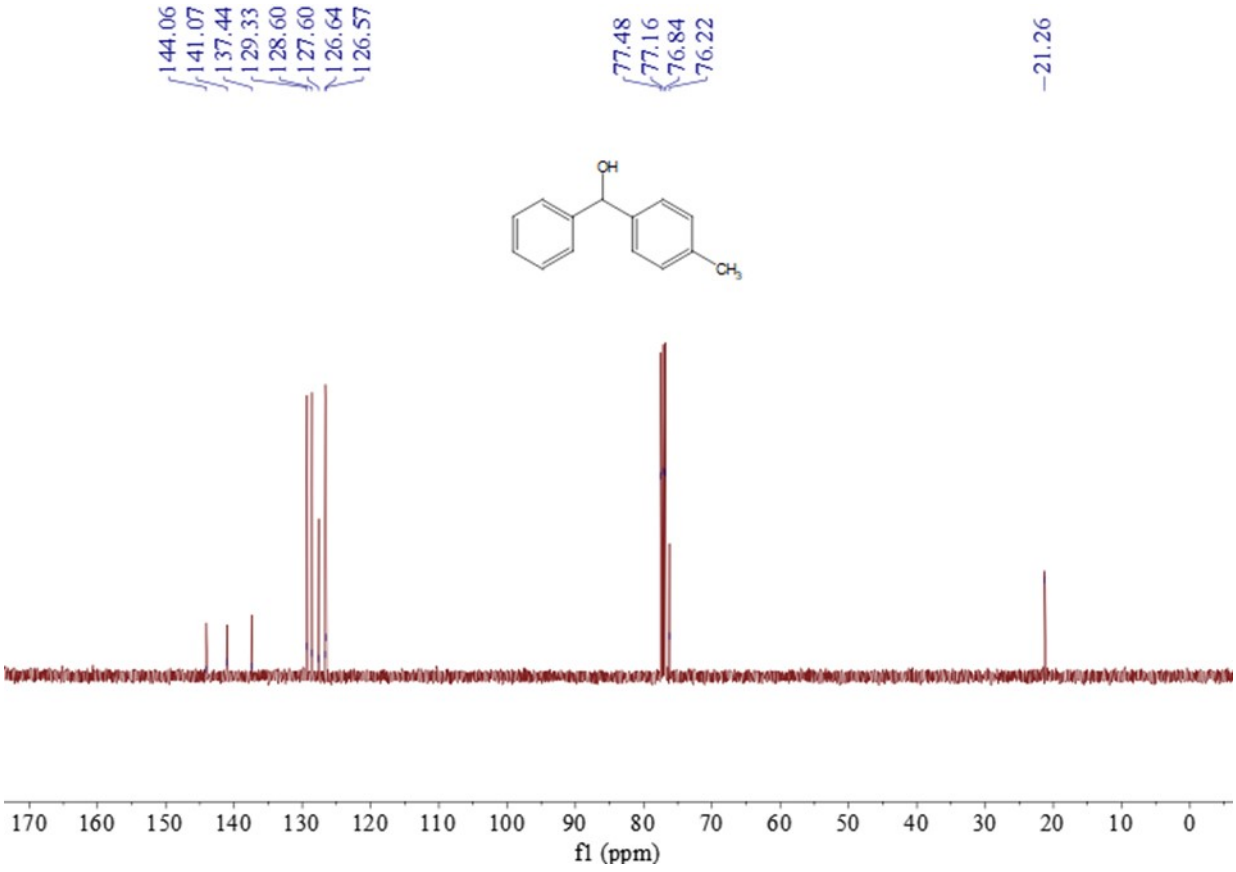
^{13}C NMR of compound 4c (100 MHz, $CDCl_3$):



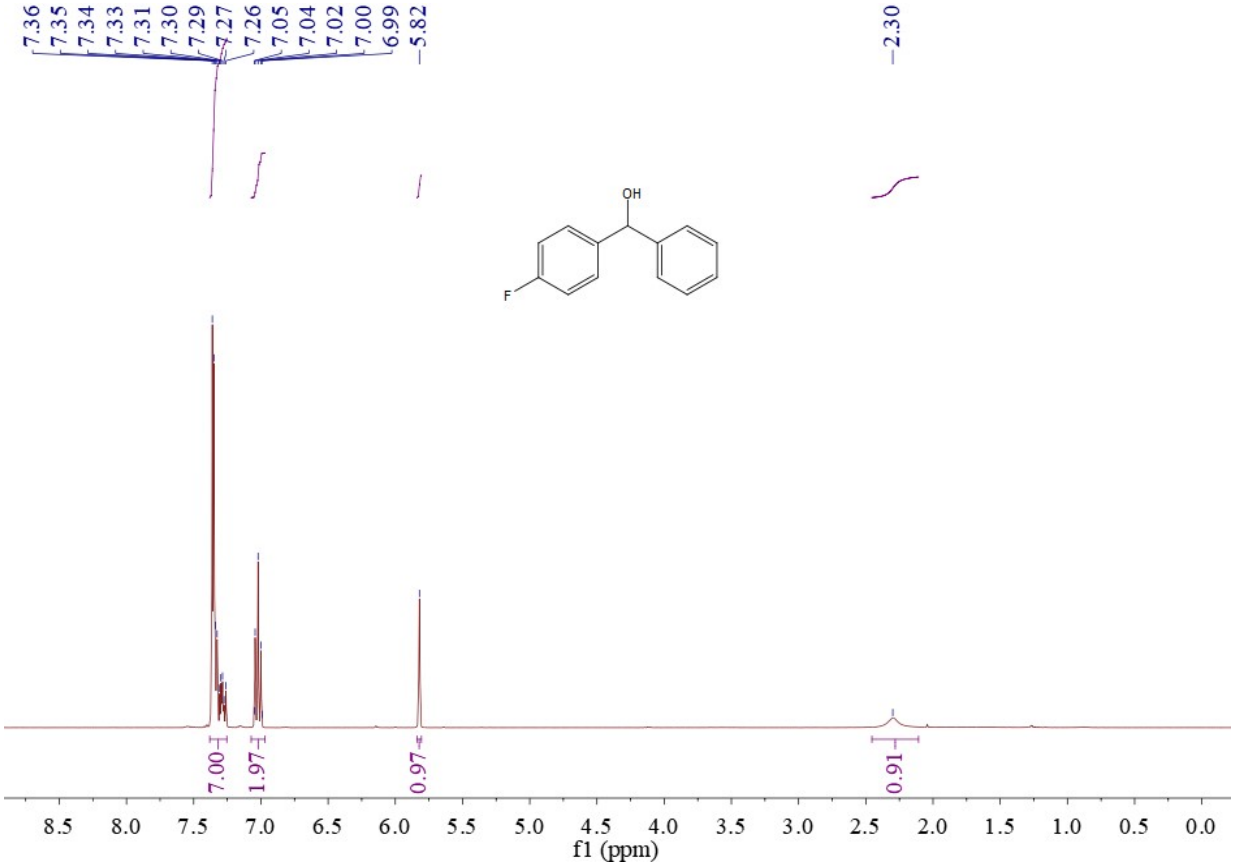
^{1}H NMR of compound 4d (400 MHz, $CDCl_3$):



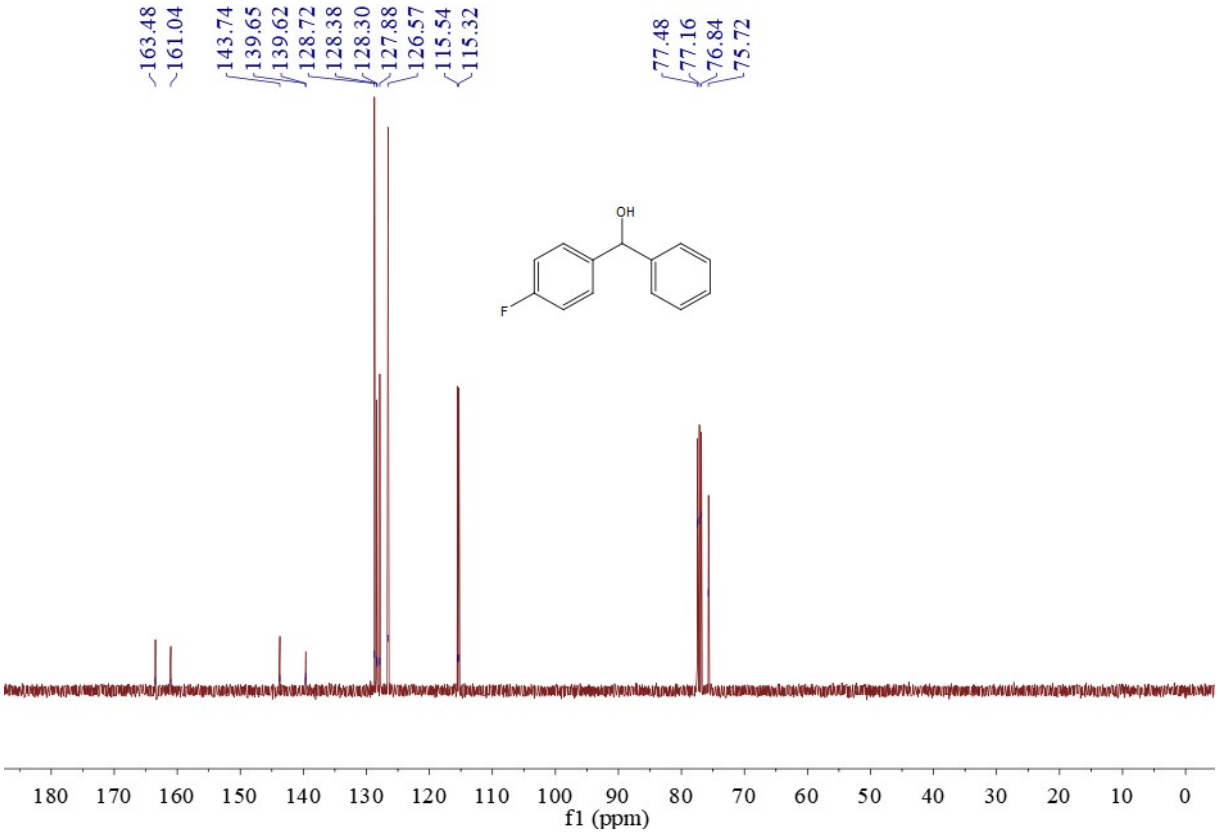
^{13}C NMR of compound 4d (100 MHz, $CDCl_3$):



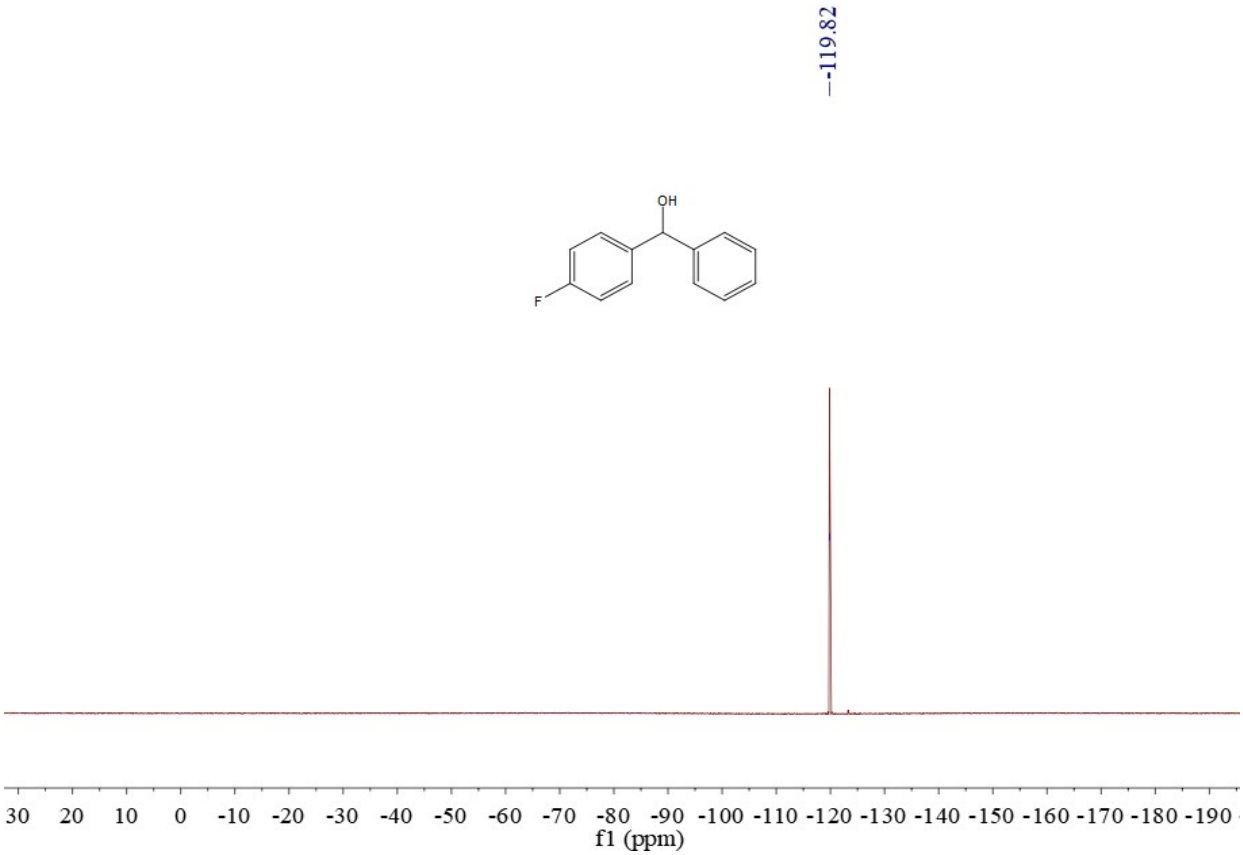
^{1}H NMR of compound 4e (400 MHz, $CDCl_3$):



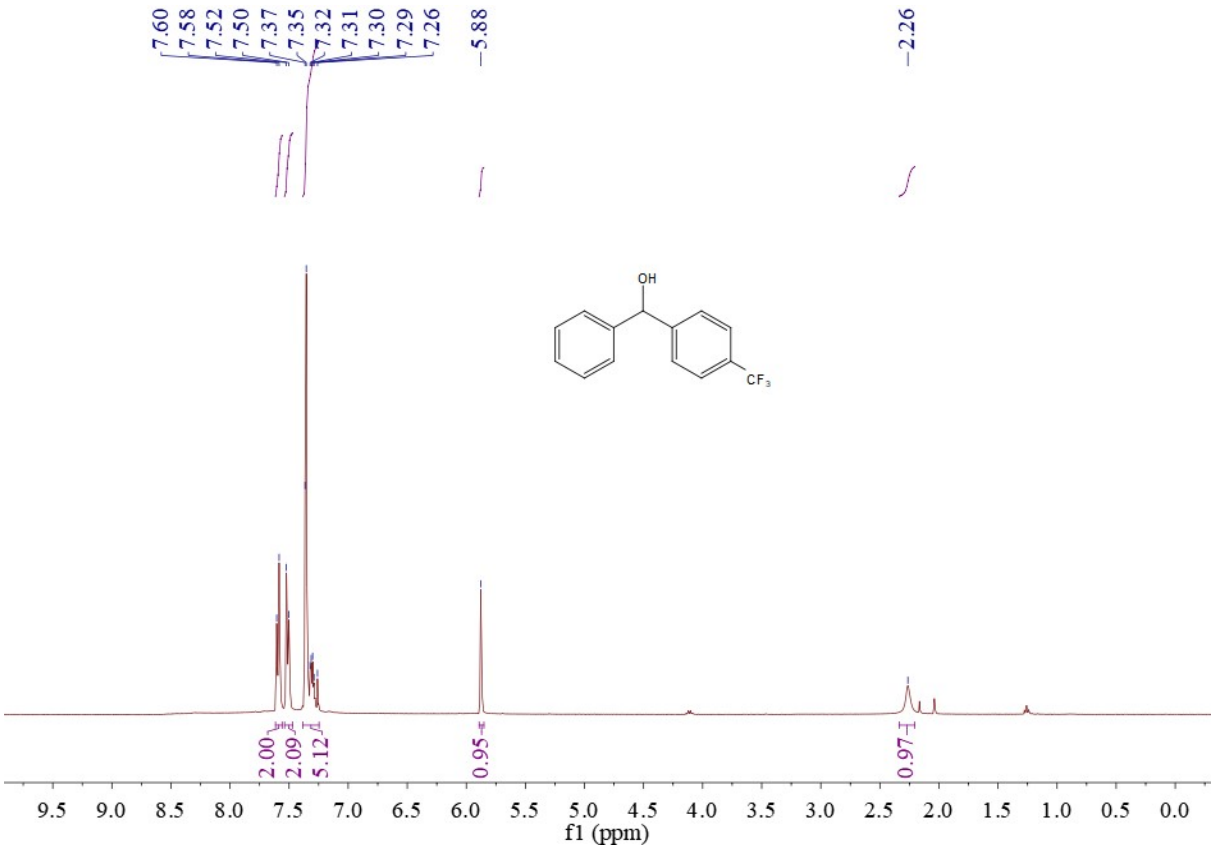
^{13}C NMR of compound 4e (100 MHz, $CDCl_3$):



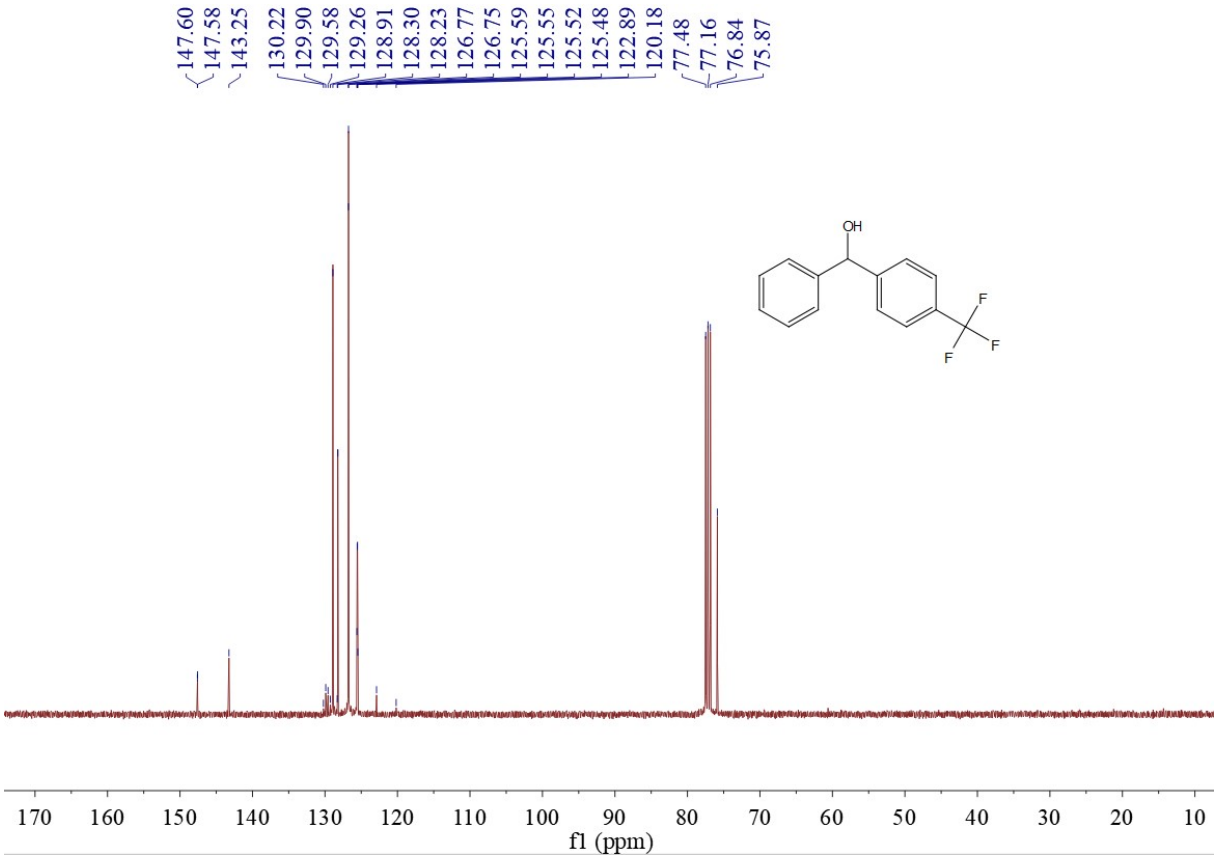
^{19}F NMR of compound 4e (376 MHz, $CDCl_3$):



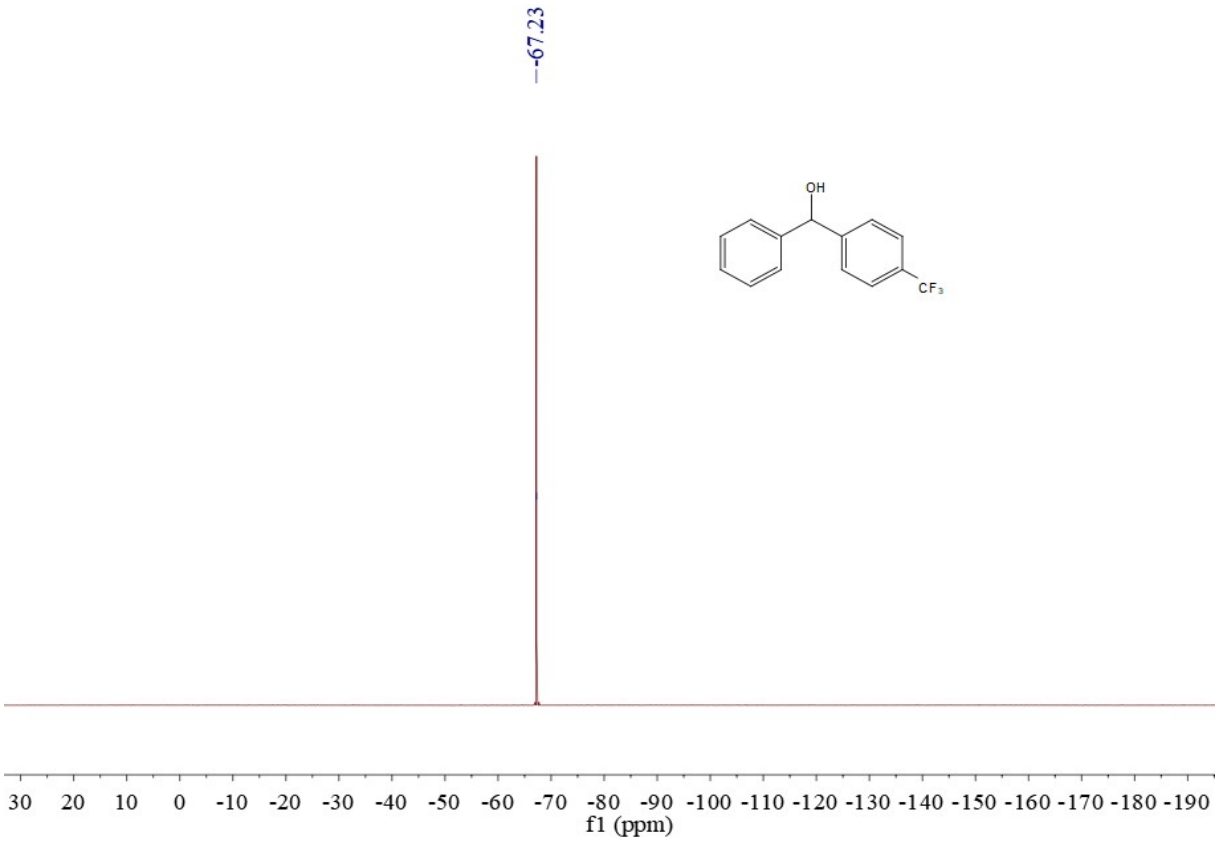
^{1}H NMR of compound 4f (400 MHz, $CDCl_3$):



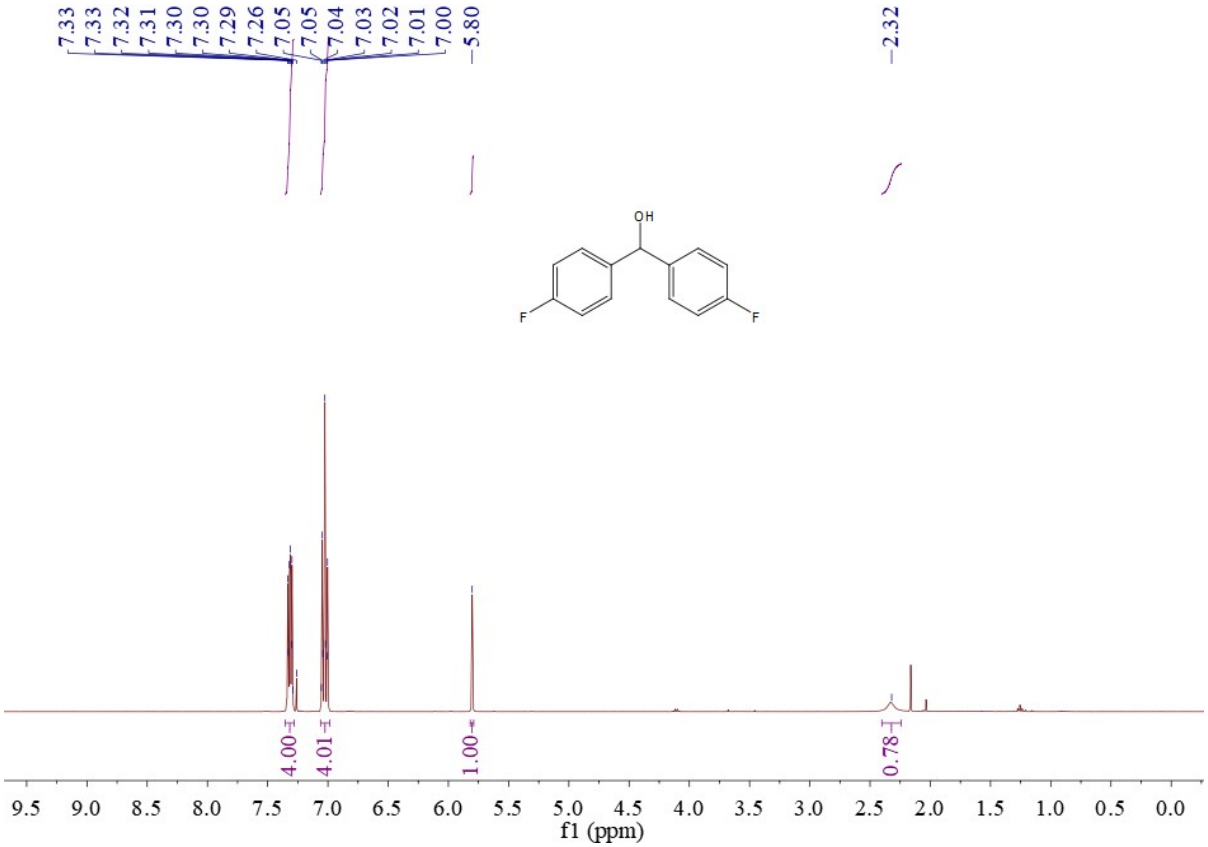
^{13}C NMR of compound 4f (100 MHz, $CDCl_3$):



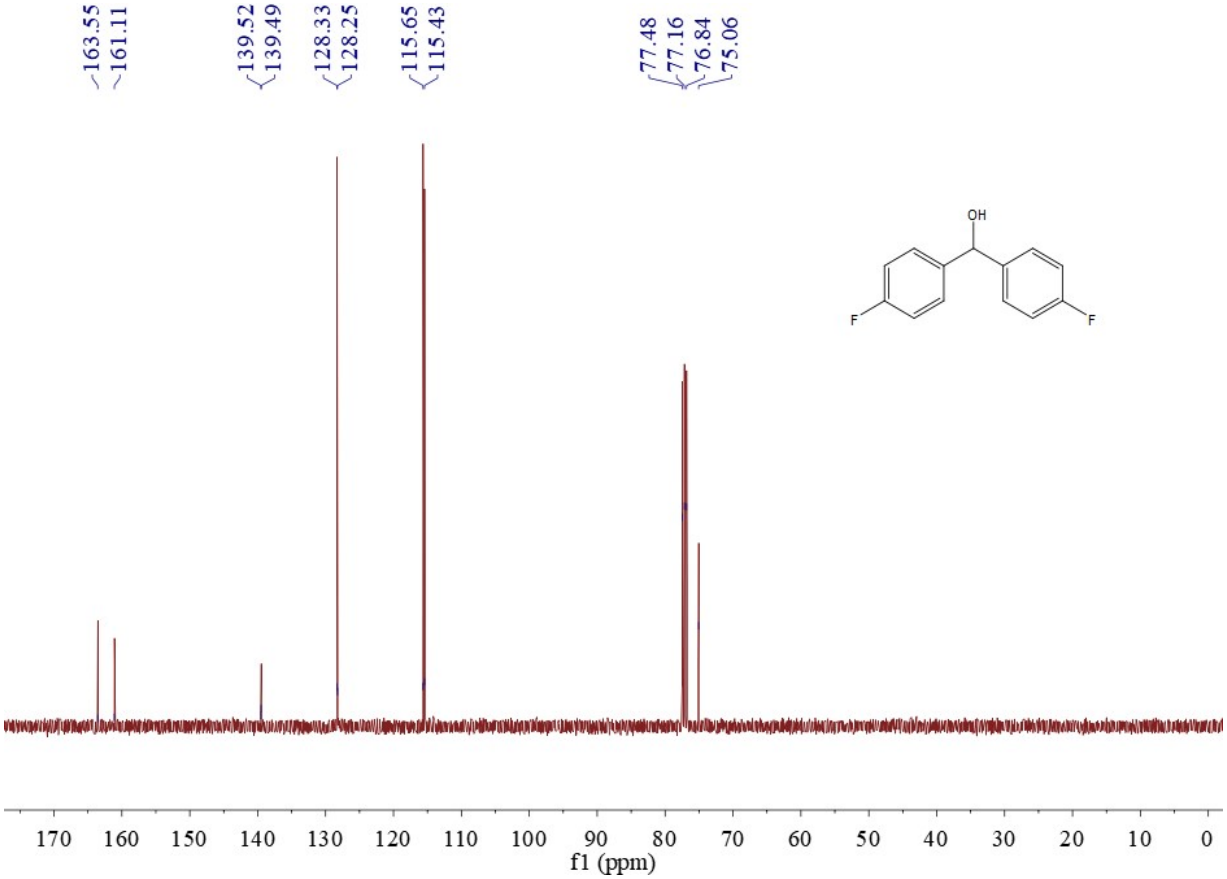
^{19}F NMR of compound 4f (376 MHz, $CDCl_3$):



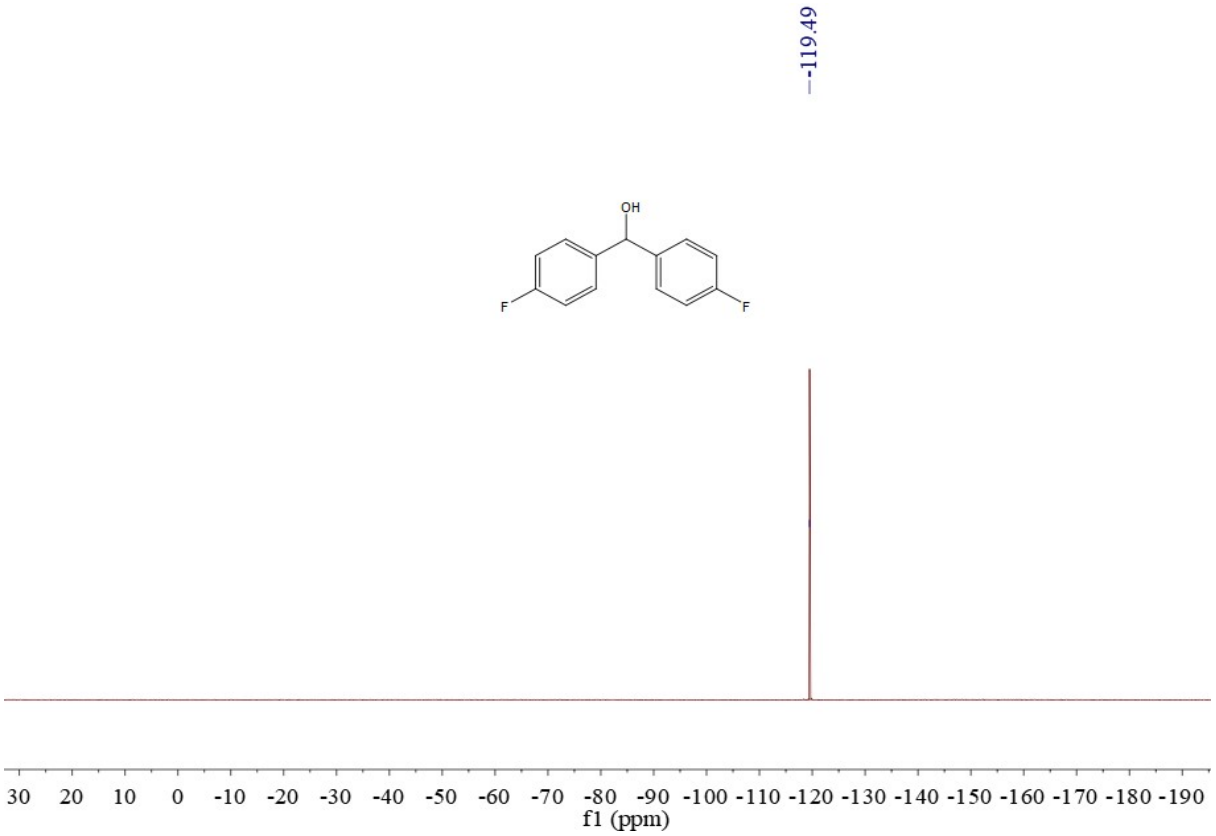
^{1}H NMR of compound 4g (400 MHz, $CDCl_3$):



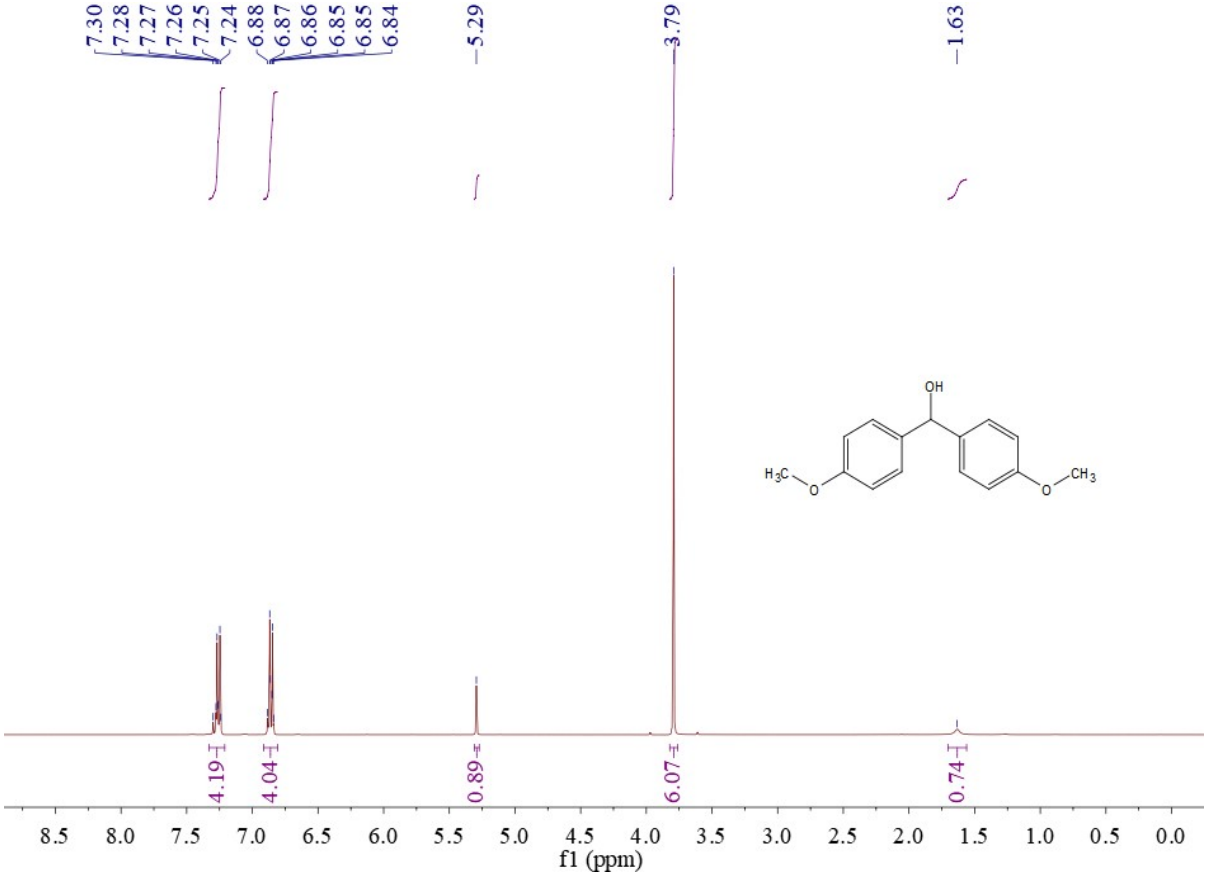
^{13}C NMR of compound 4g (100 MHz, $CDCl_3$):



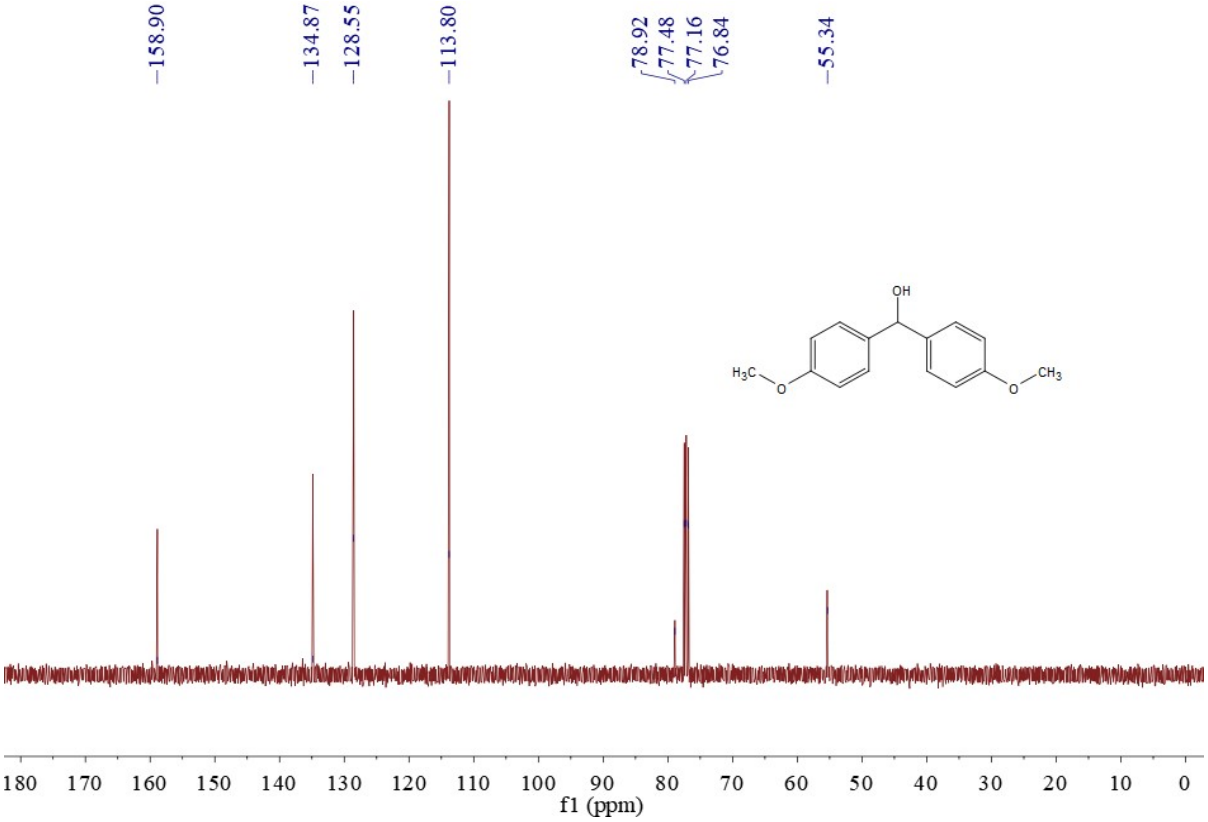
^{19}F NMR of compound 4g (376 MHz, $CDCl_3$):



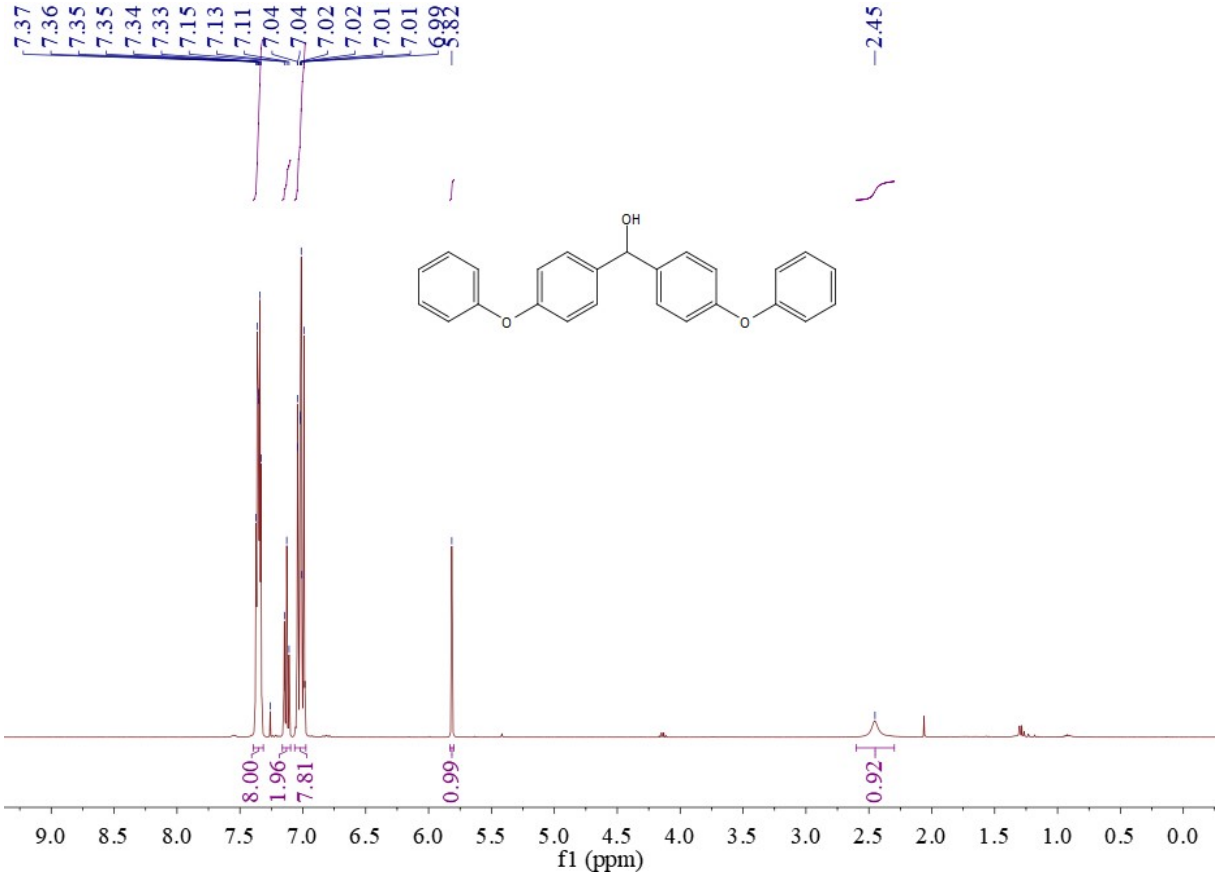
^{1}H NMR of compound 4h (400 MHz, $CDCl_3$):



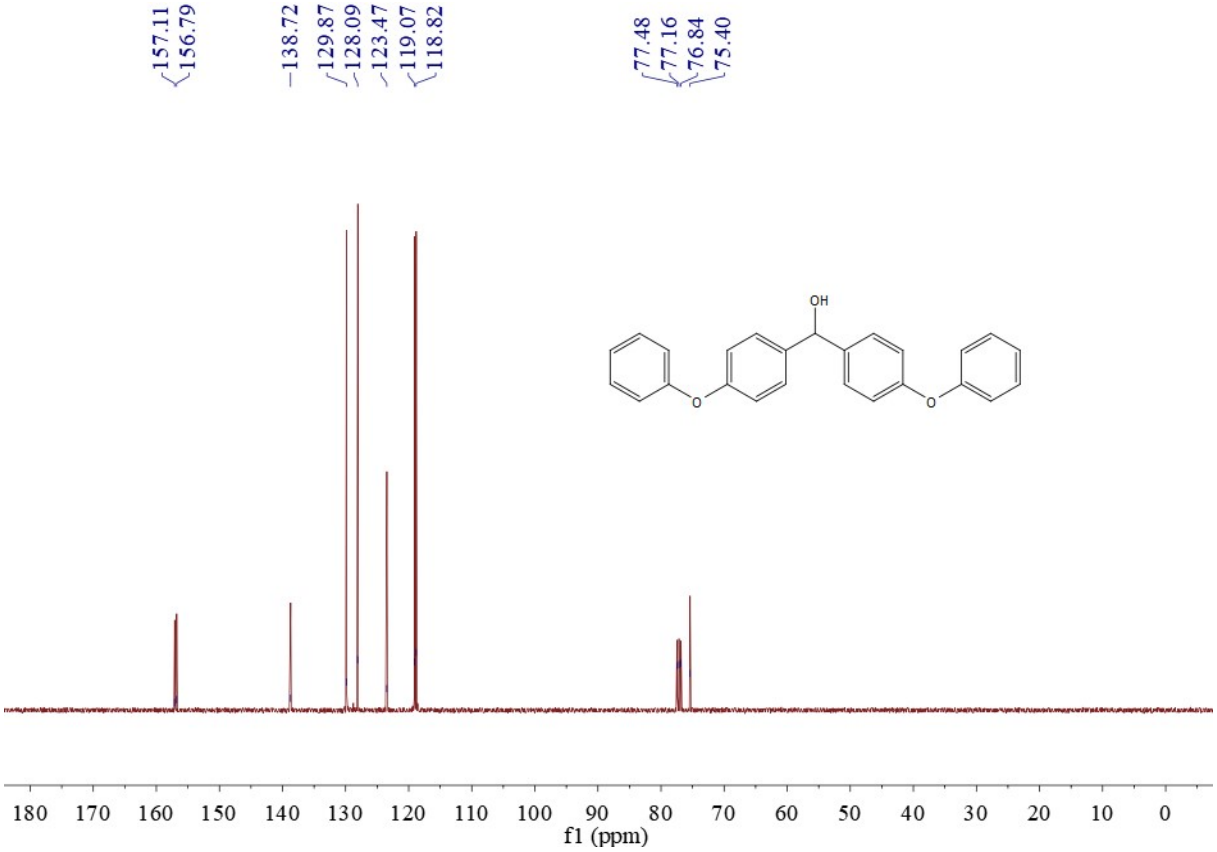
^{13}C NMR of compound 4h (100 MHz, $CDCl_3$):



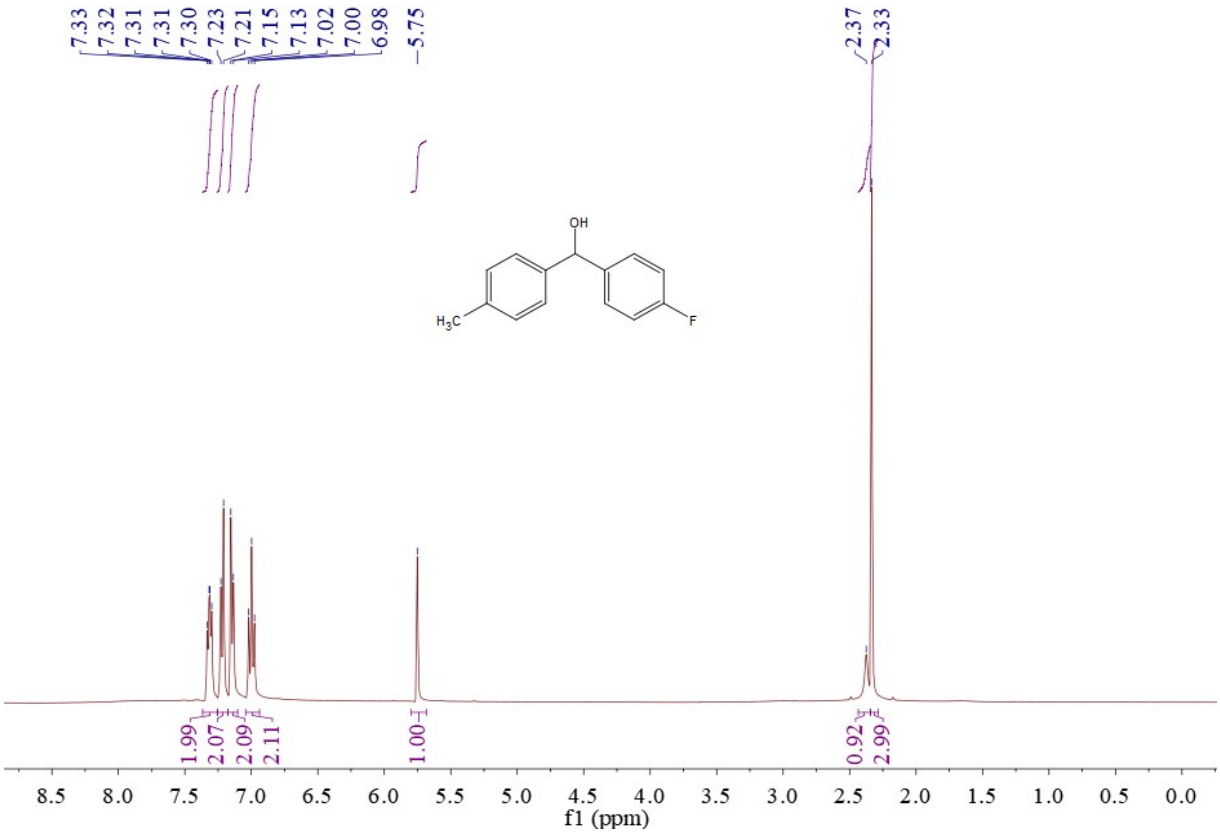
^{1}H NMR of compound 4i (400 MHz, $CDCl_3$):



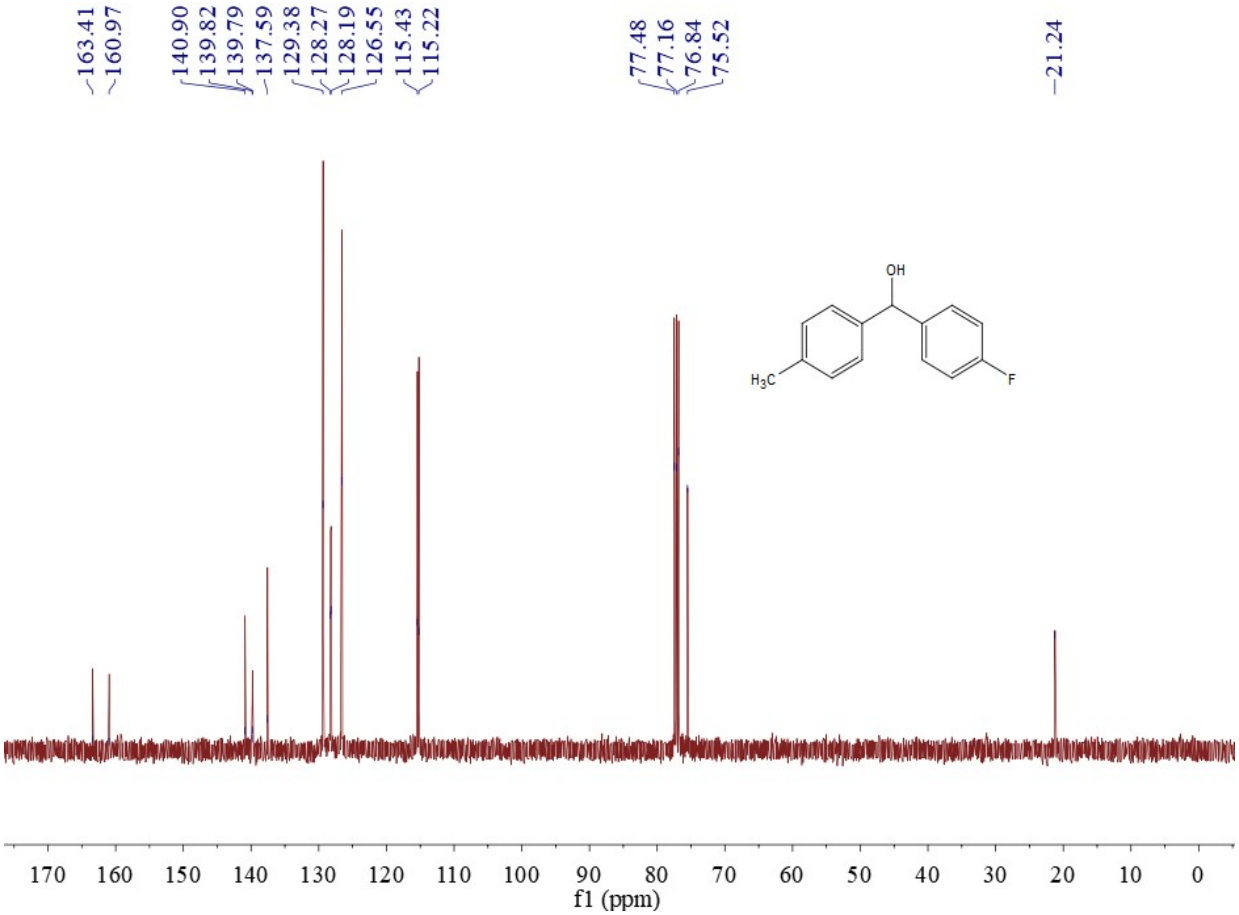
^{13}C NMR of compound 4i (100 MHz, $CDCl_3$):



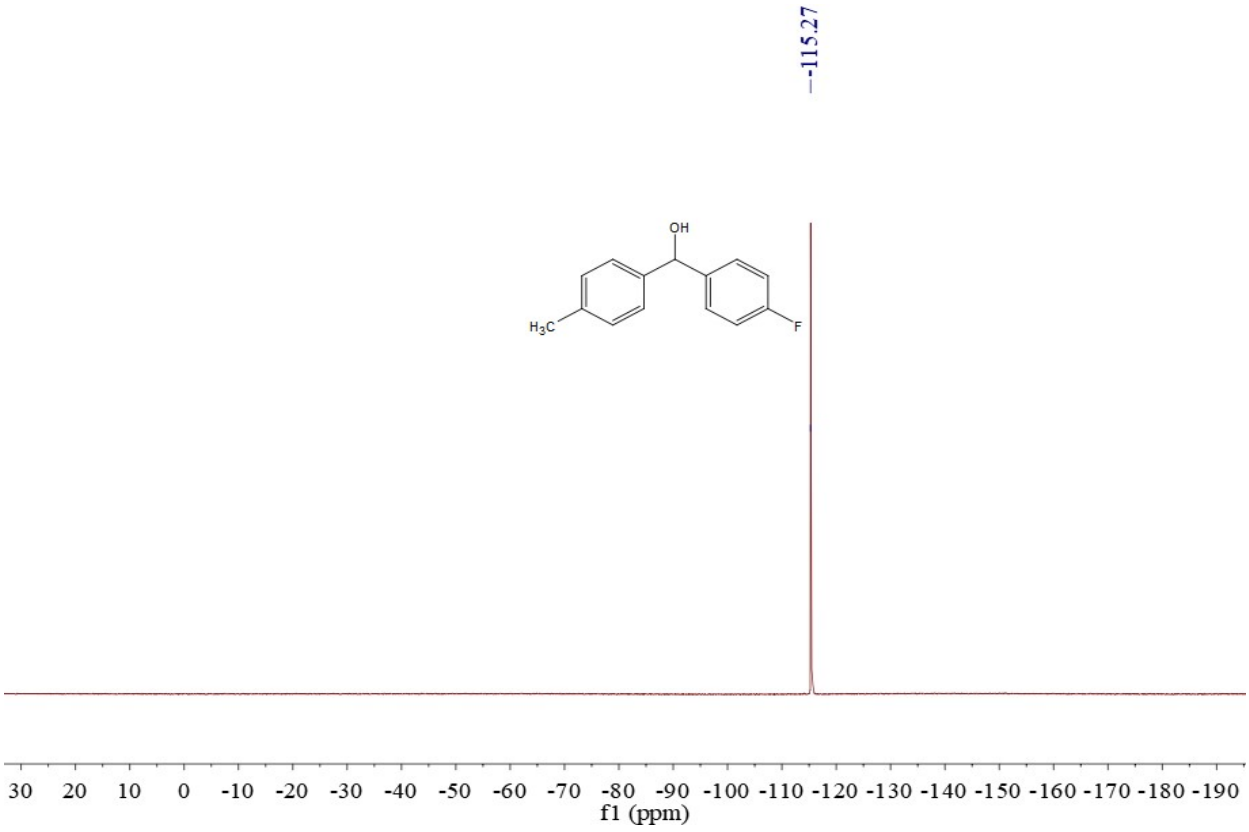
^{1}H NMR of compound 4j (400 MHz, $CDCl_3$):



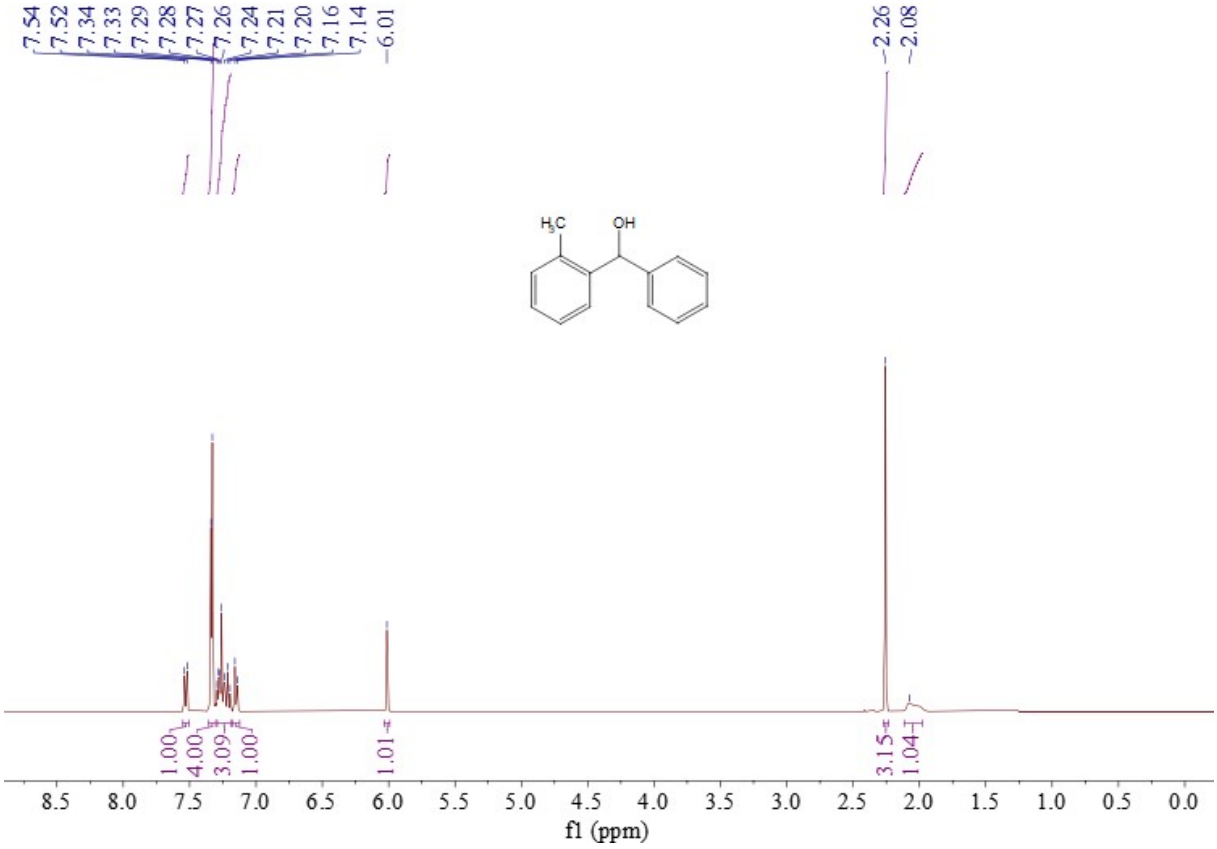
^{13}C NMR of compound 4j (100 MHz, $CDCl_3$):



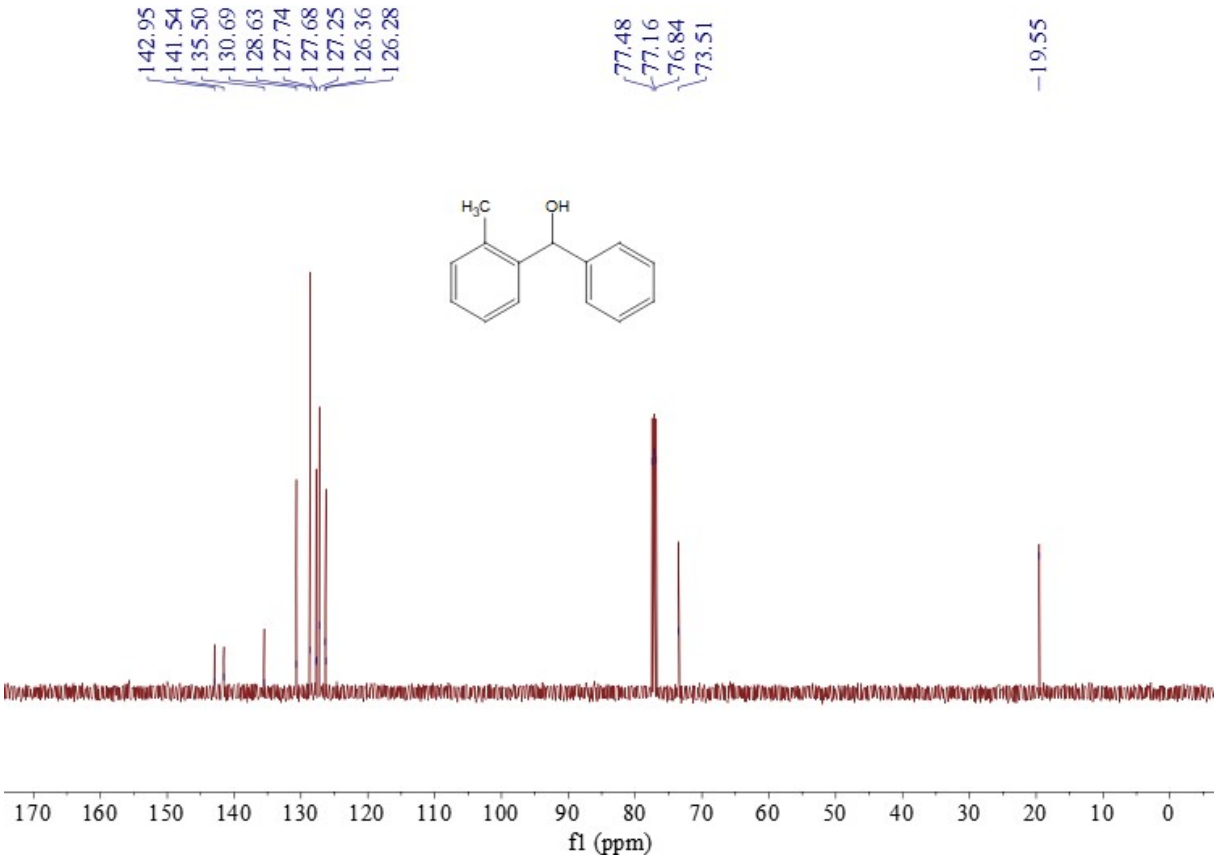
^{19}F NMR of compound 4j (376 MHz, $CDCl_3$):



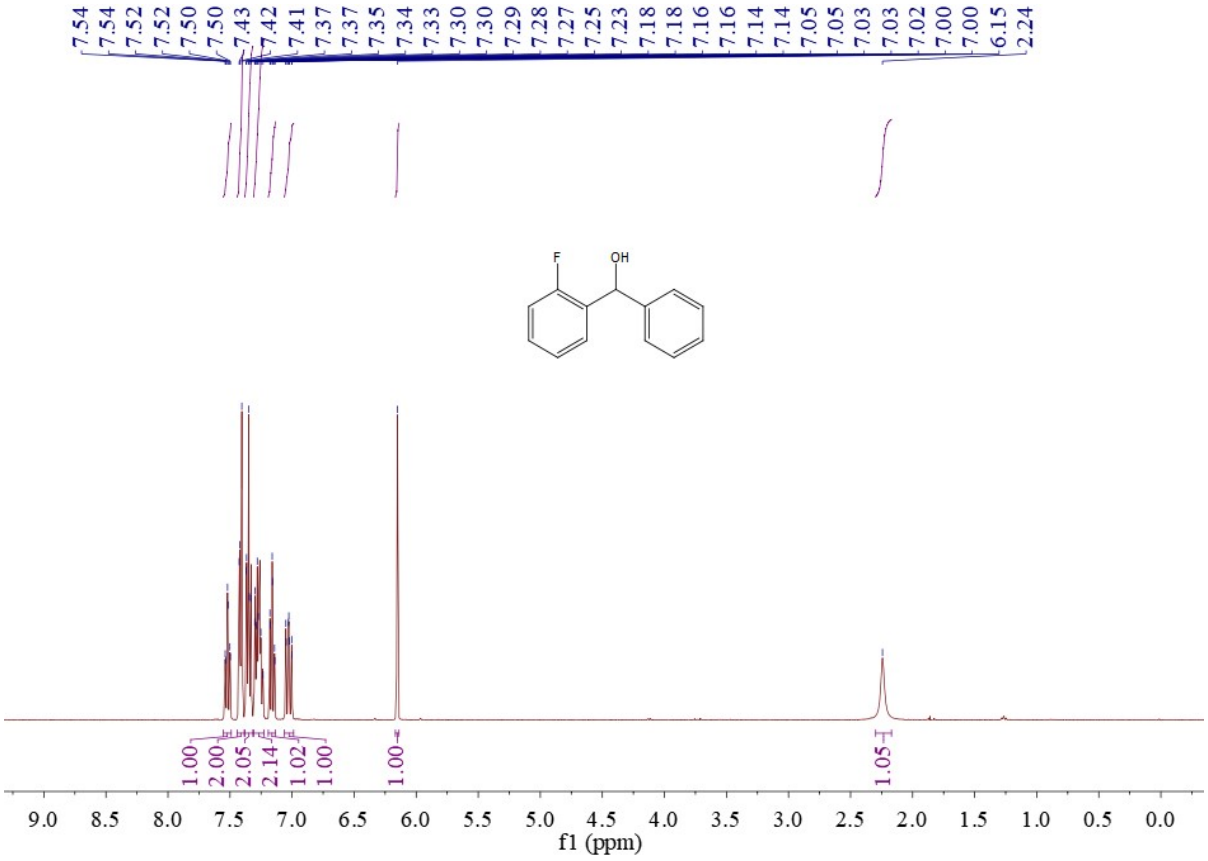
^{1}H NMR of compound 4k (400 MHz, $CDCl_3$):



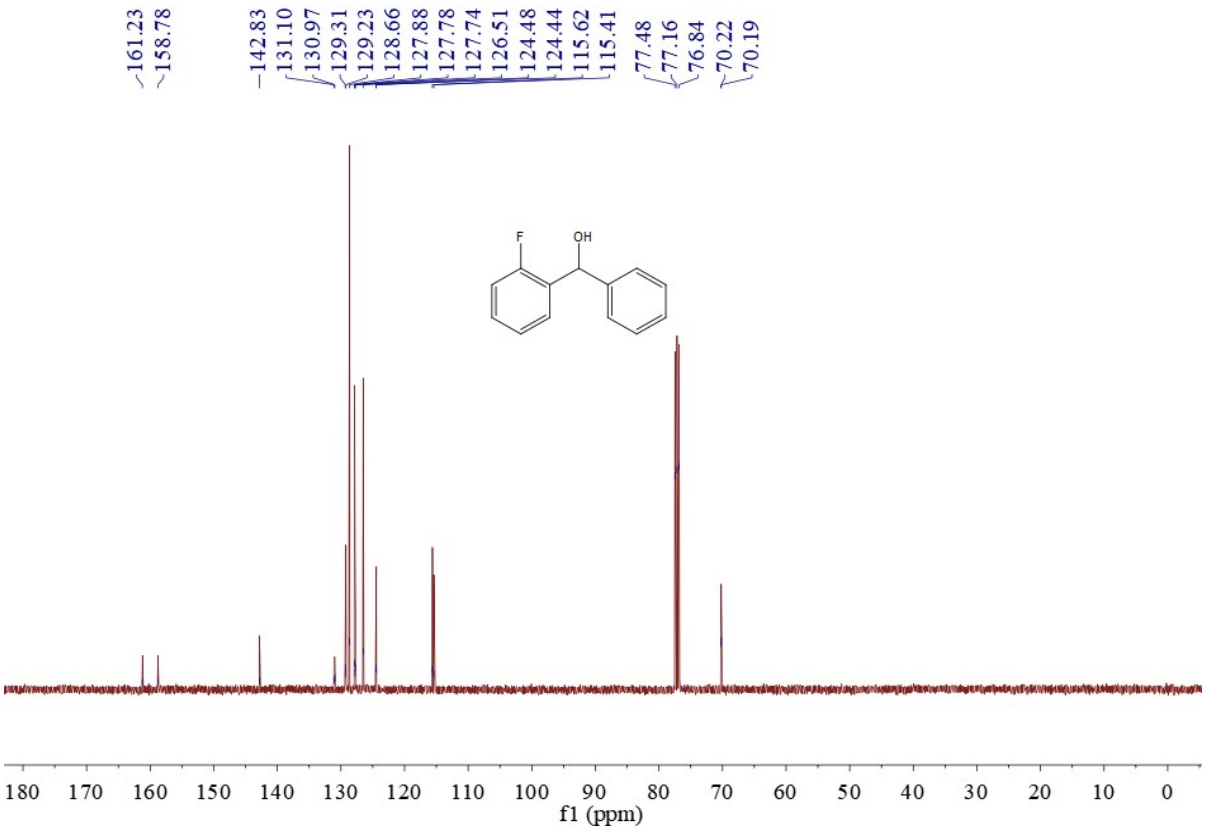
^{13}C NMR of compound 4k (100 MHz, $CDCl_3$):



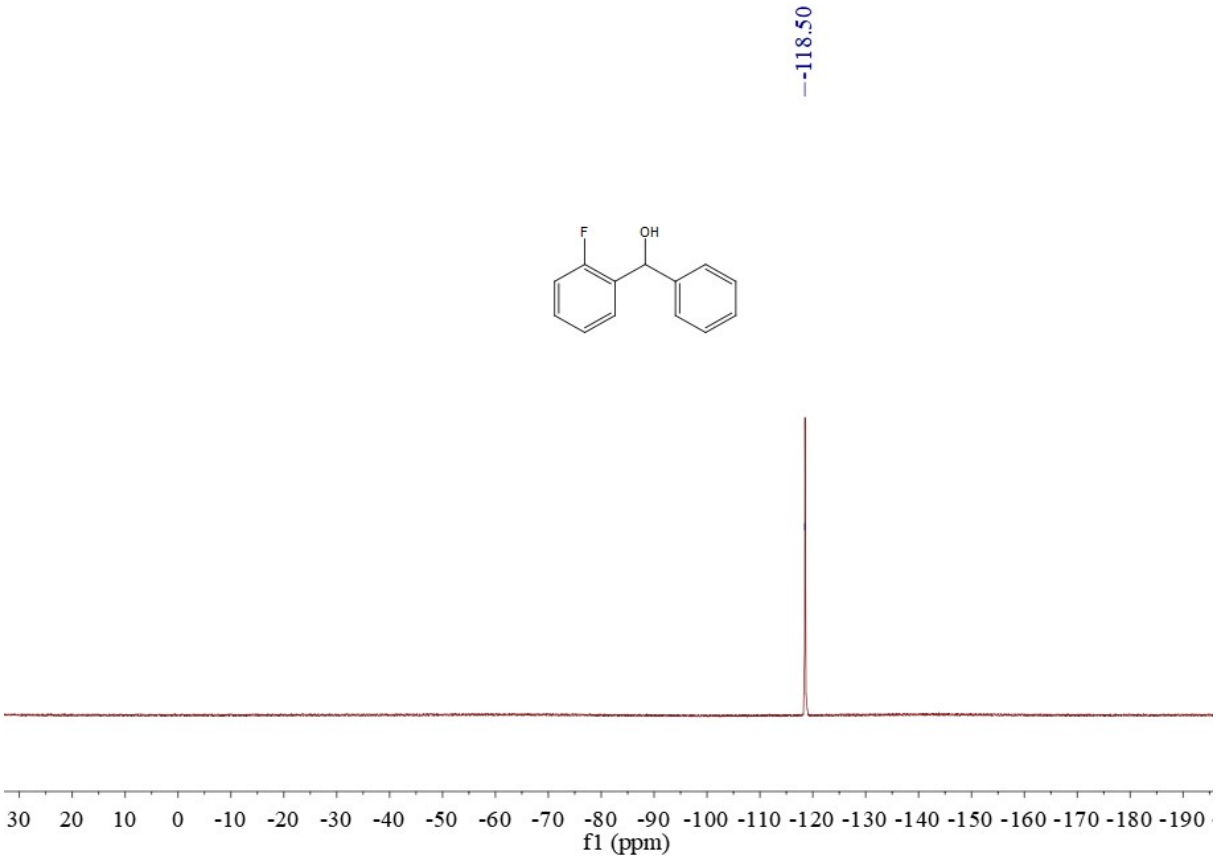
^{1}H NMR of compound 4l (400 MHz, $CDCl_3$):



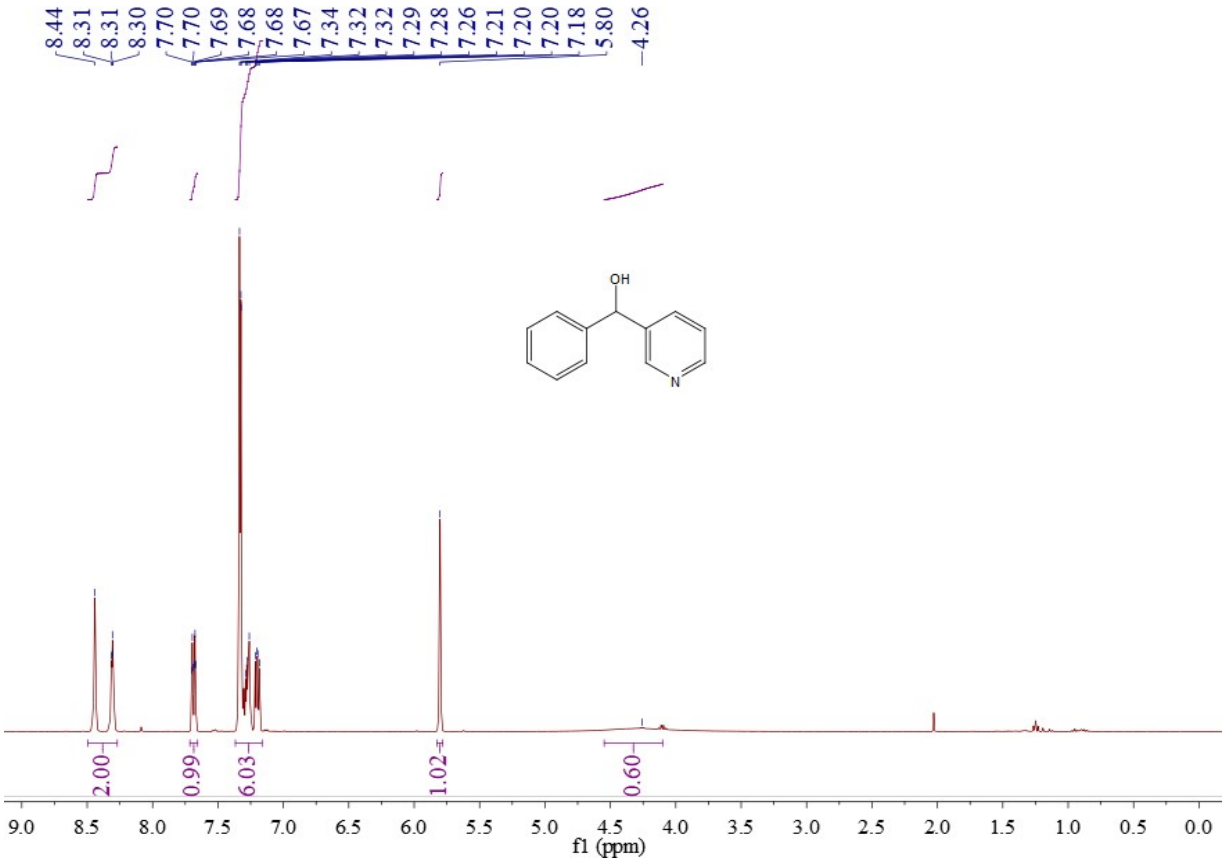
^{13}C NMR of compound 4l (100 MHz, $CDCl_3$):



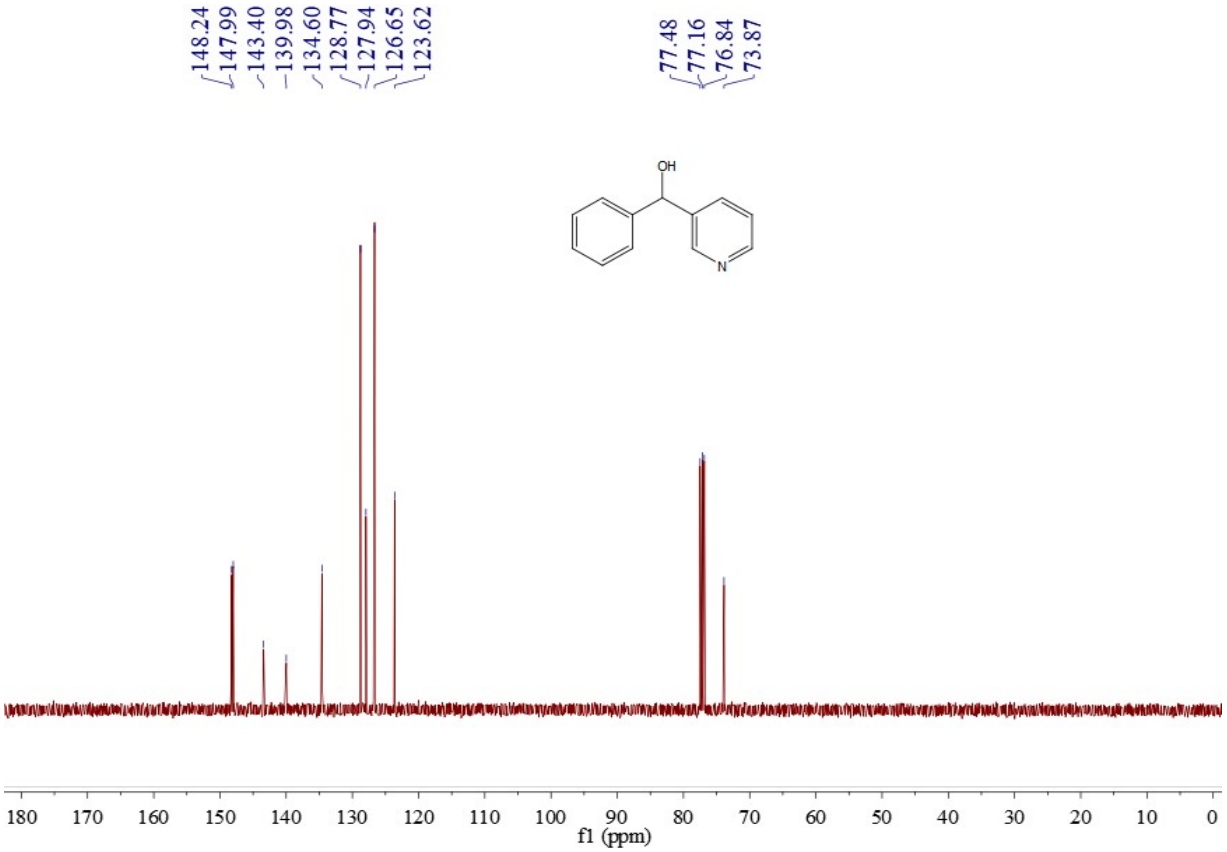
^{19}F NMR of compound 4l (376 MHz, $CDCl_3$):



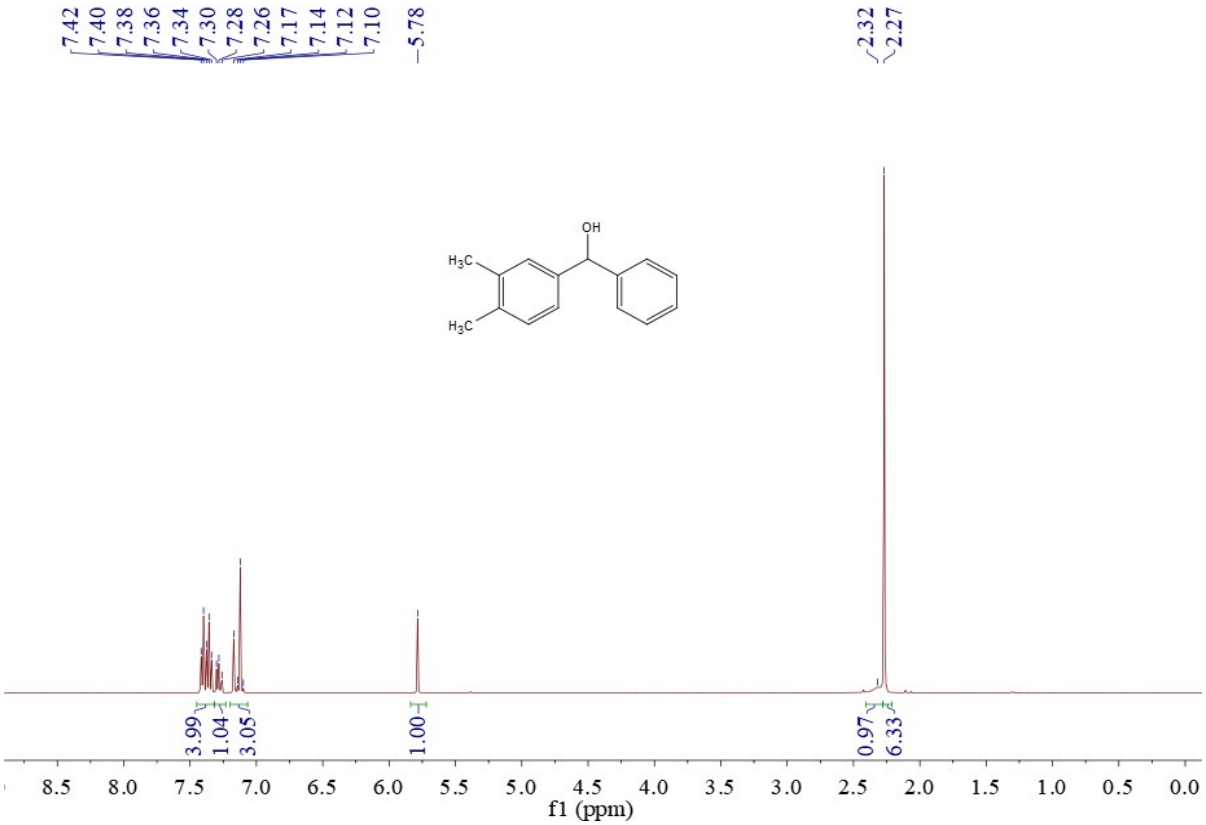
^{1}H NMR of compound 4m (400 MHz, $CDCl_3$):



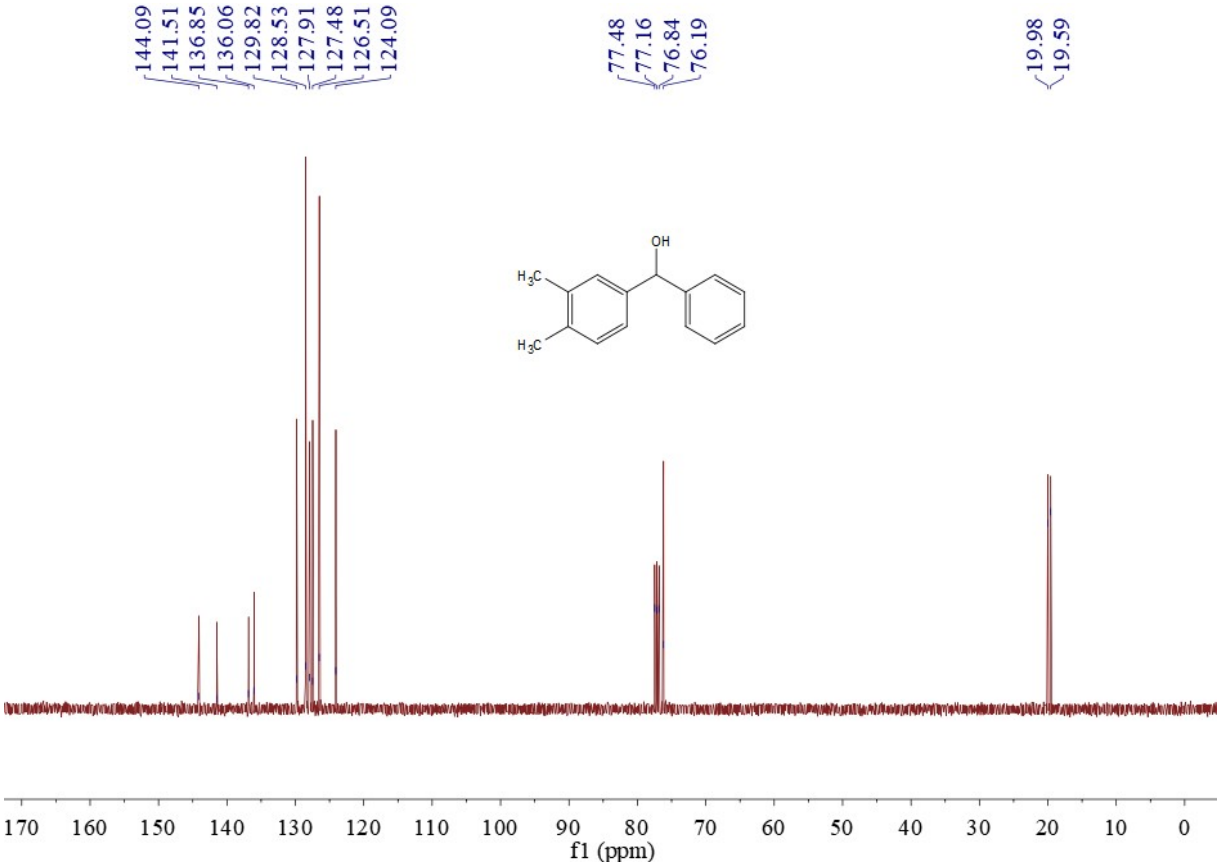
^{13}C NMR of compound 4m (100 MHz, $CDCl_3$):



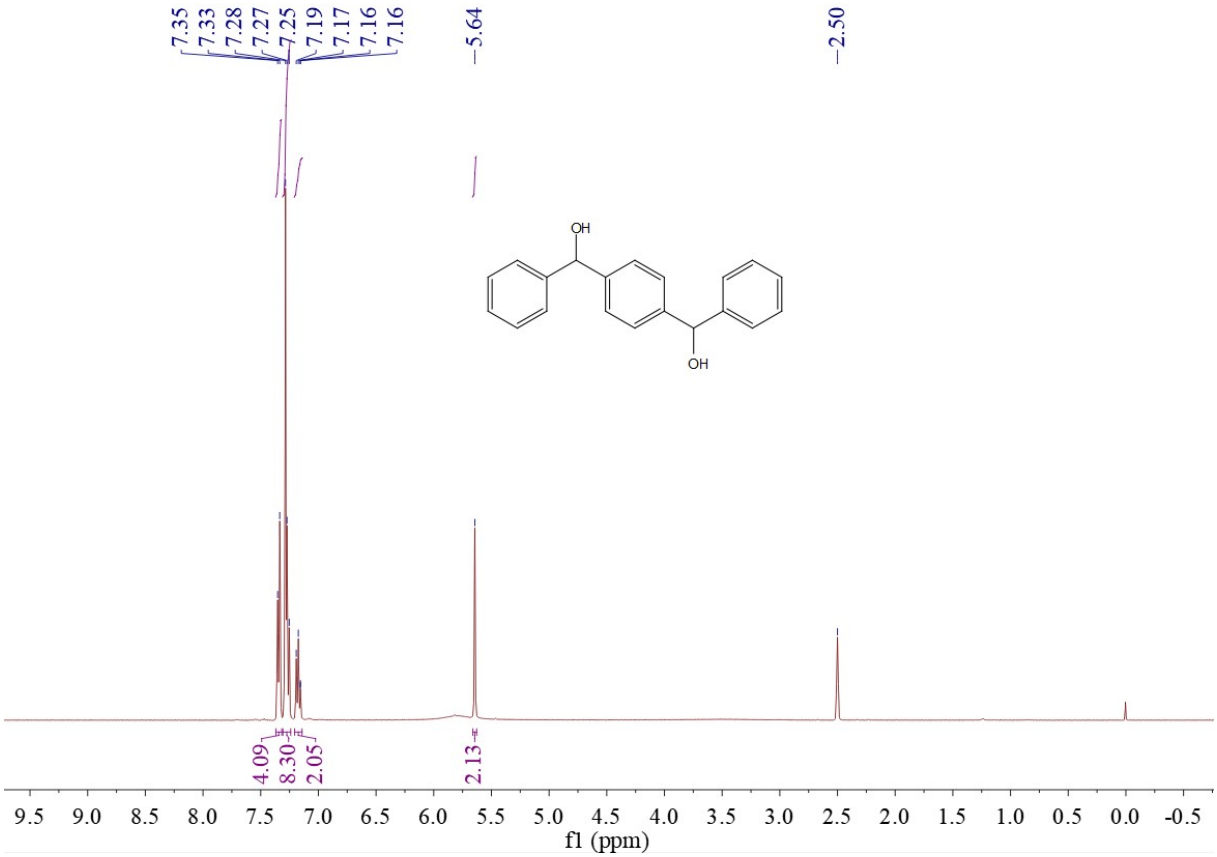
^{1}H NMR of compound 4n (400 MHz, $CDCl_3$):



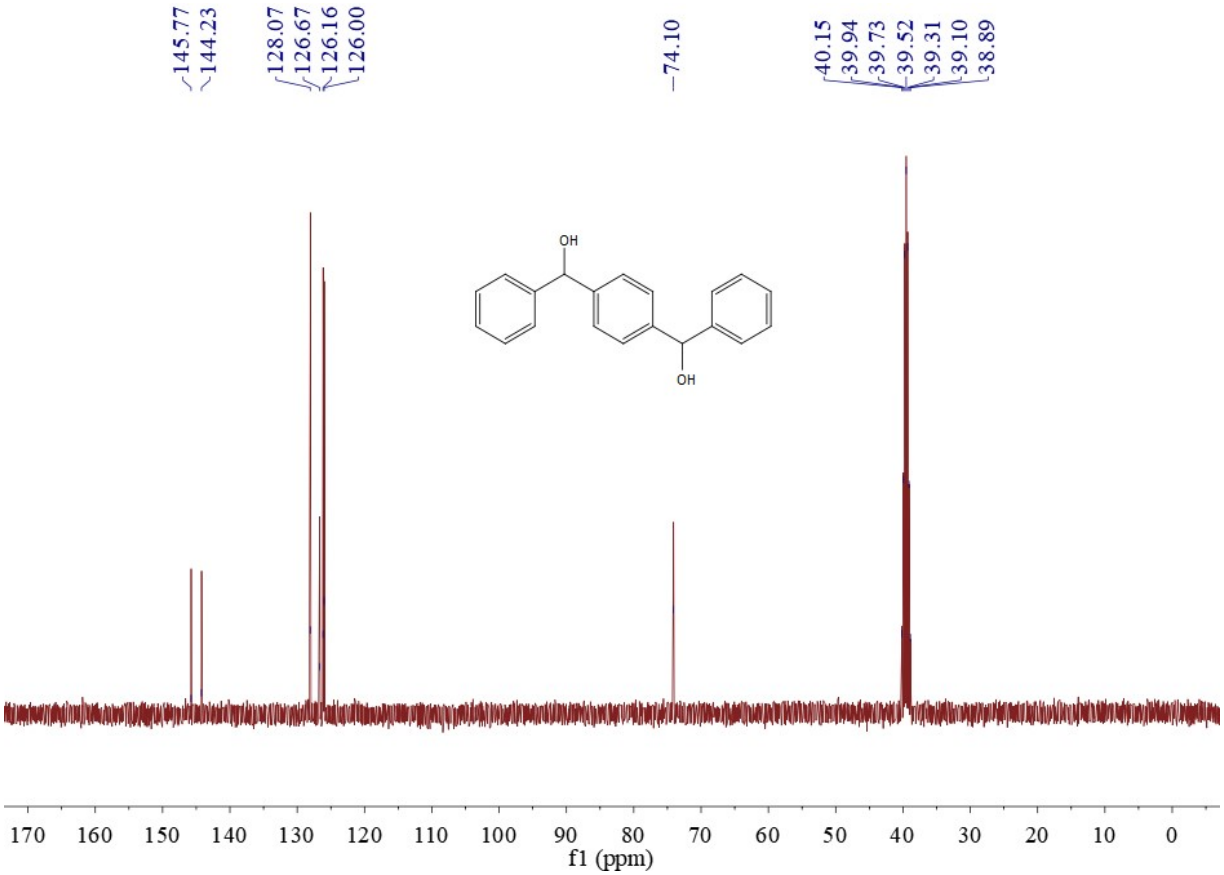
^{13}C NMR of compound 4n (100 MHz, $CDCl_3$):



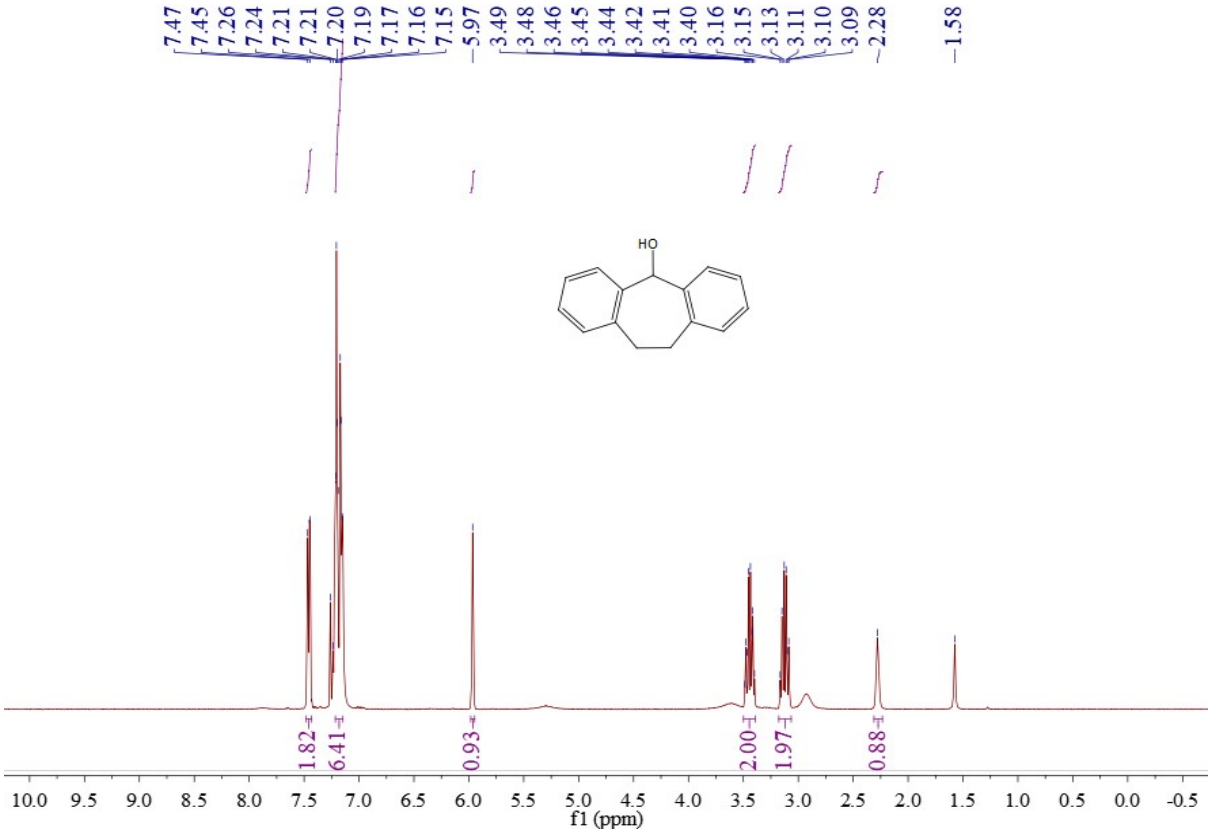
^{1}H NMR of compound 4o (400 MHz, DMSO-d_6):



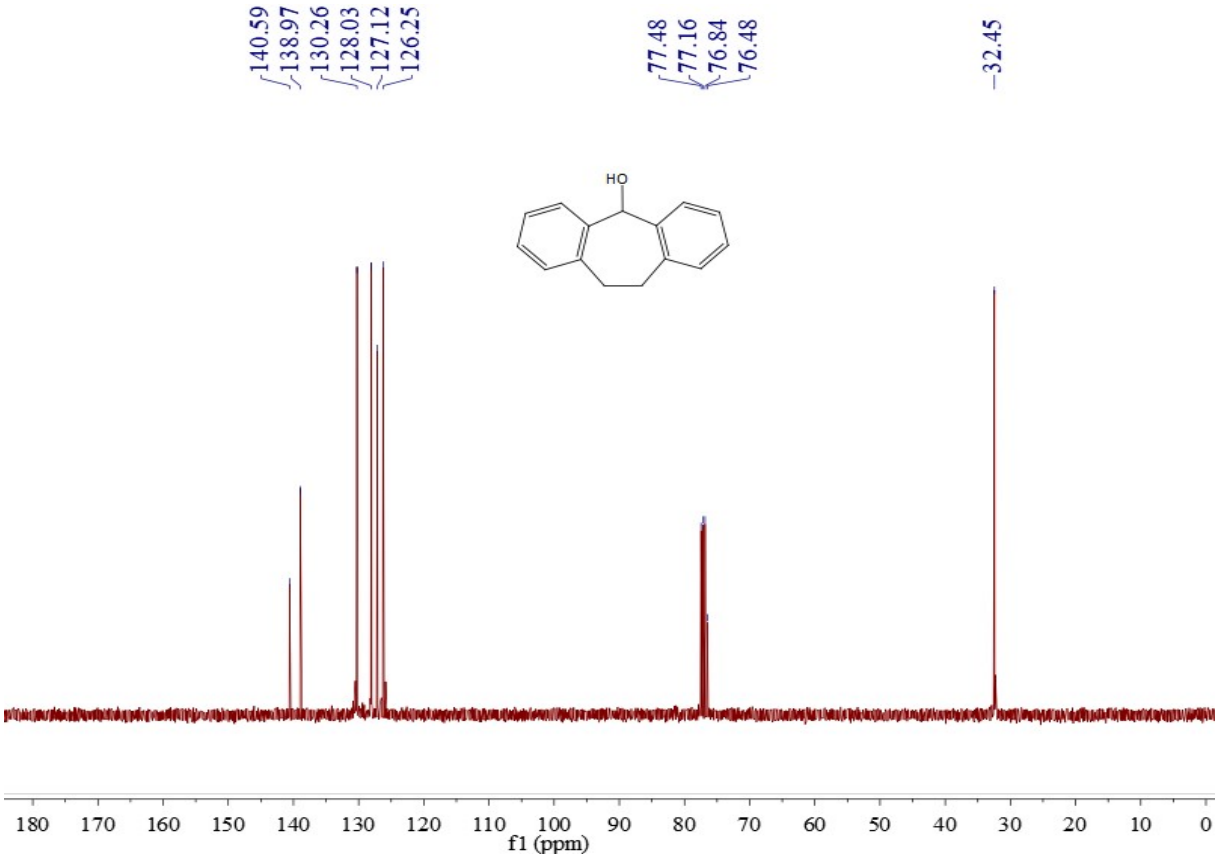
^{13}C NMR of compound 4o (100 MHz, DMSO-d_6):



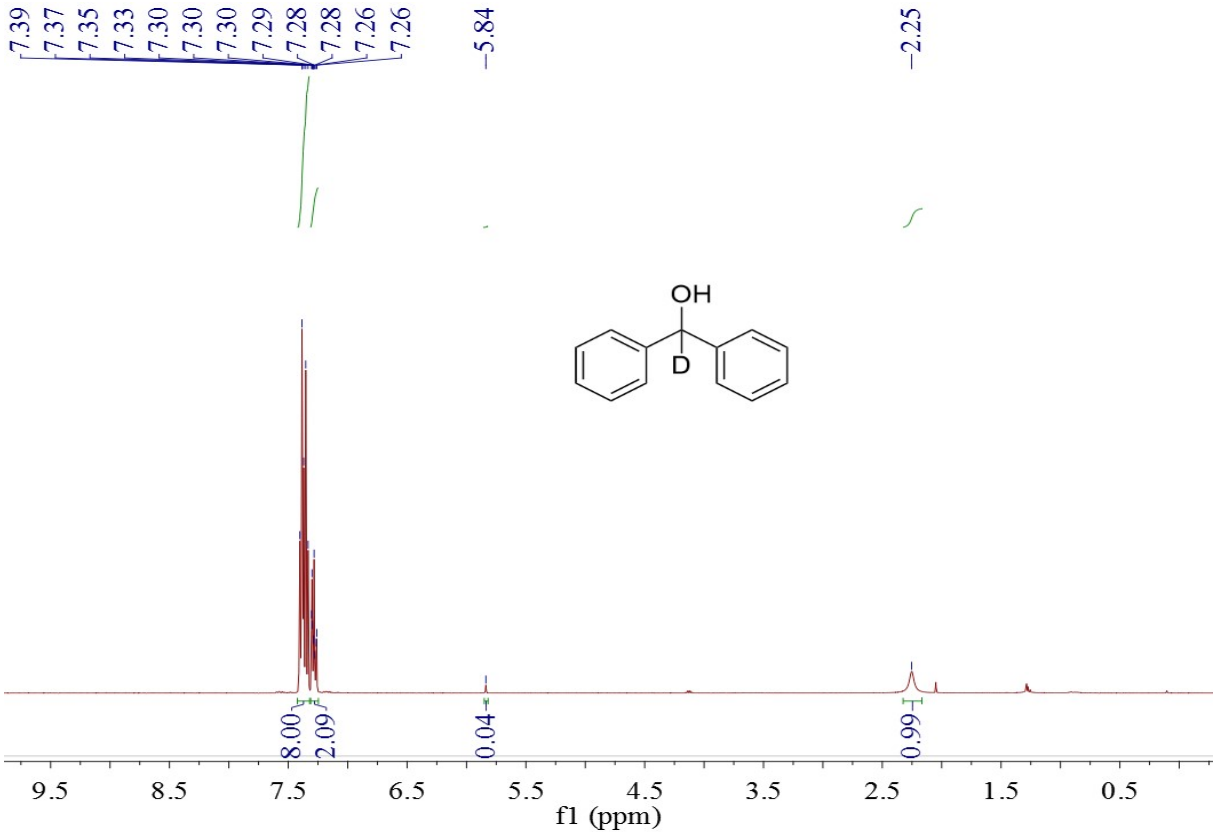
^{1}H NMR of compound 4p (400 MHz, $CDCl_3$):



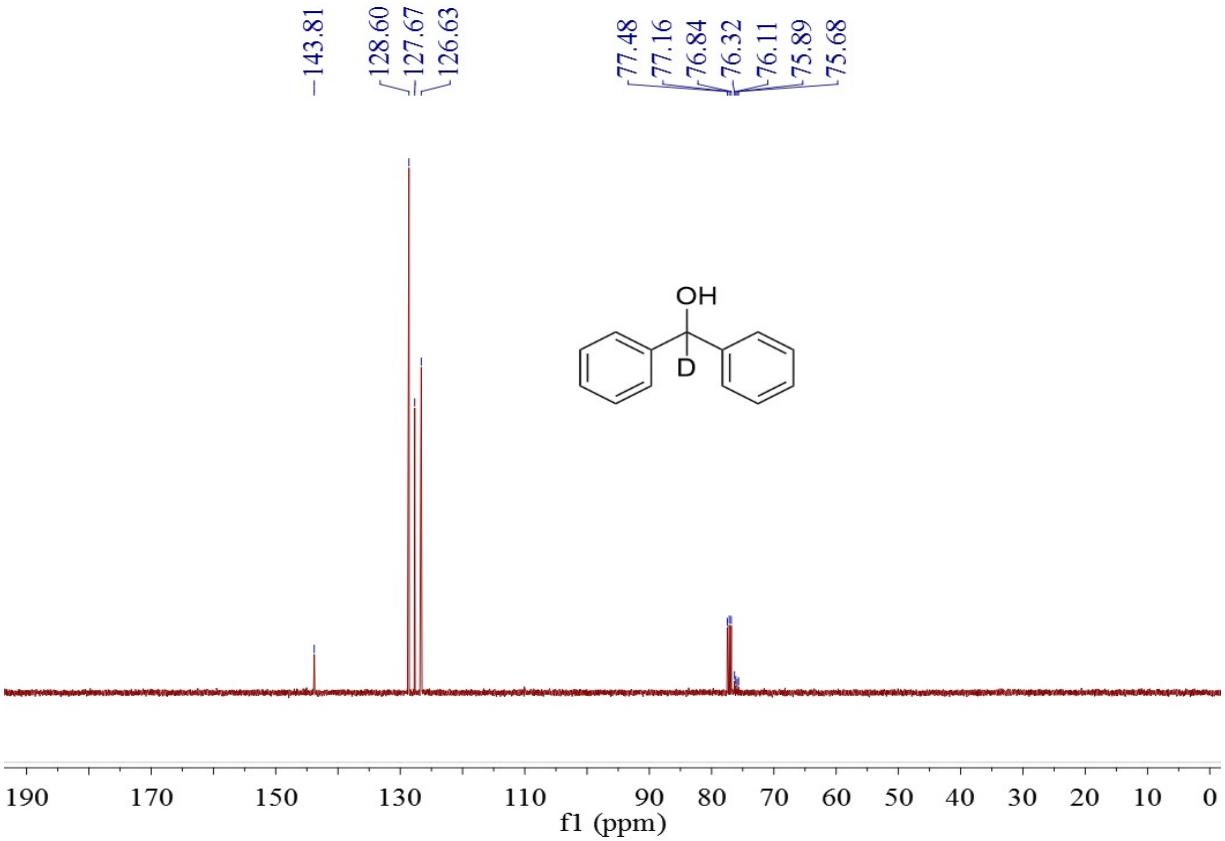
^{13}C NMR of compound 4p (100 MHz, $CDCl_3$):



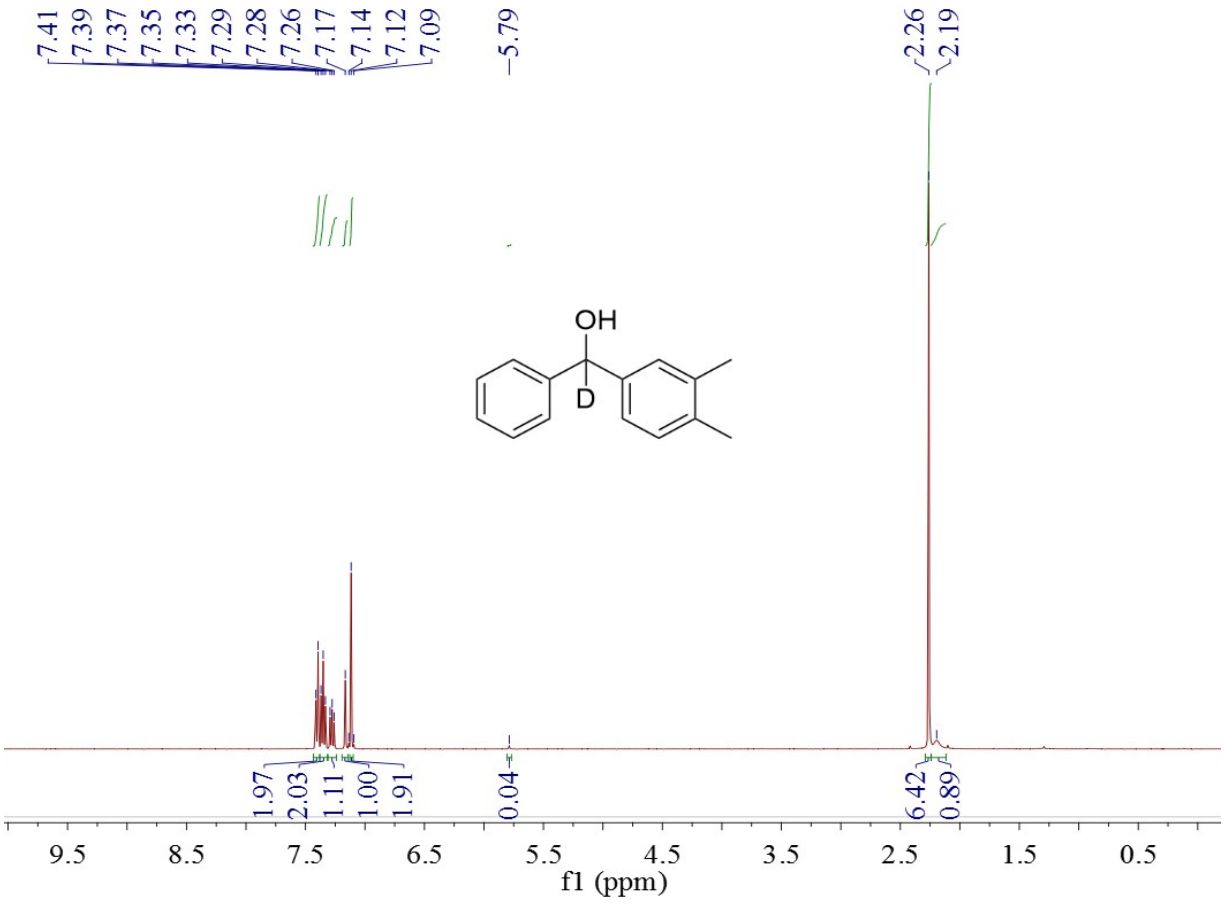
^{1}H NMR of compound 5a (400 MHz, $CDCl_3$):



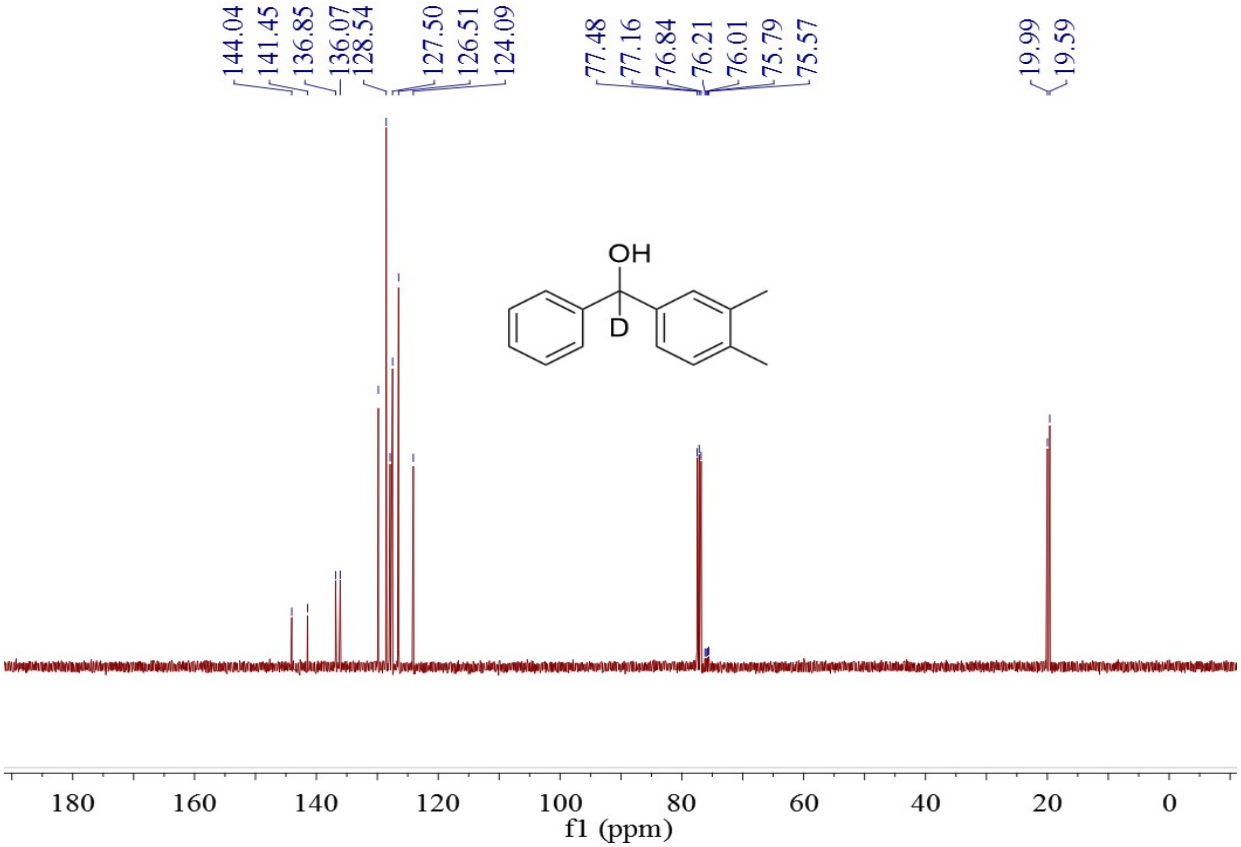
^{13}C NMR of compound 5a (100 MHz, $CDCl_3$):



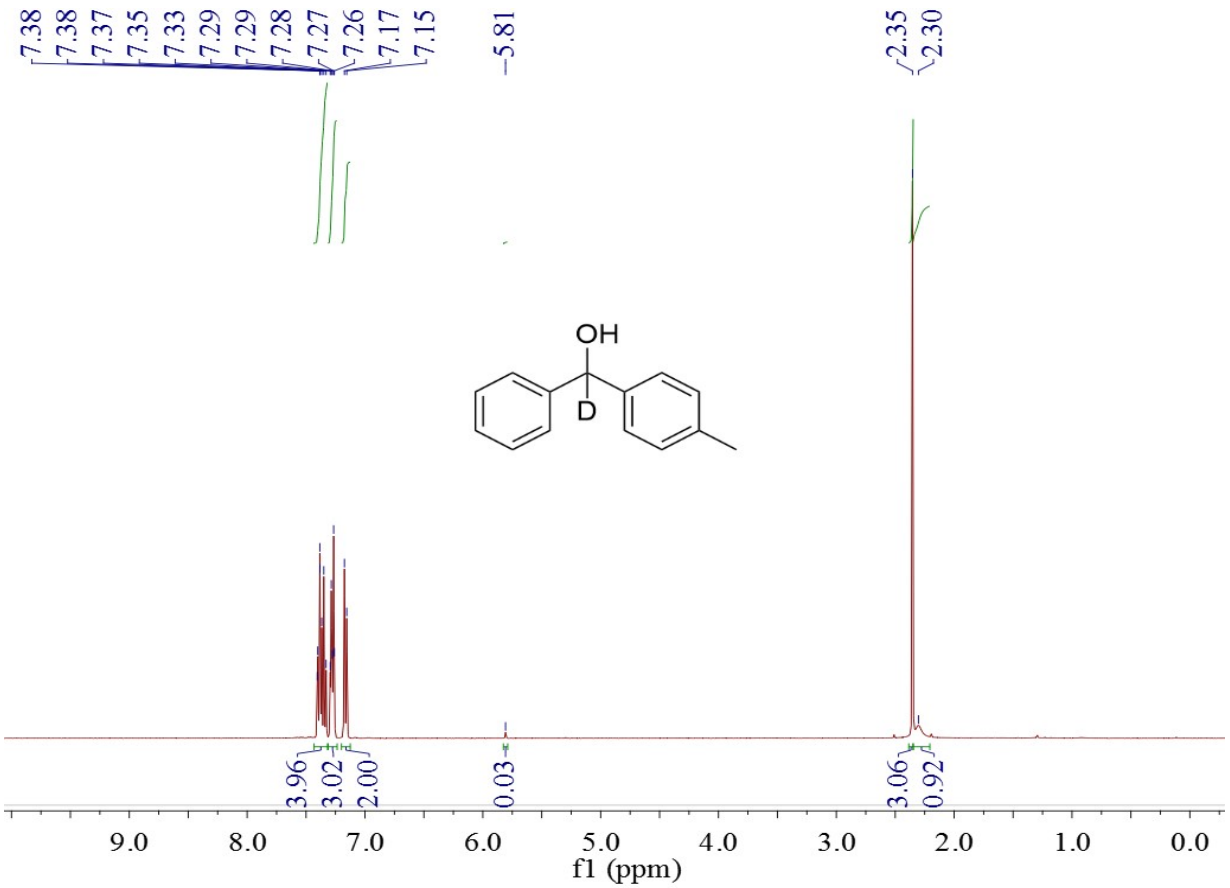
^{1}H NMR of compound 5b (400 MHz, $CDCl_3$):



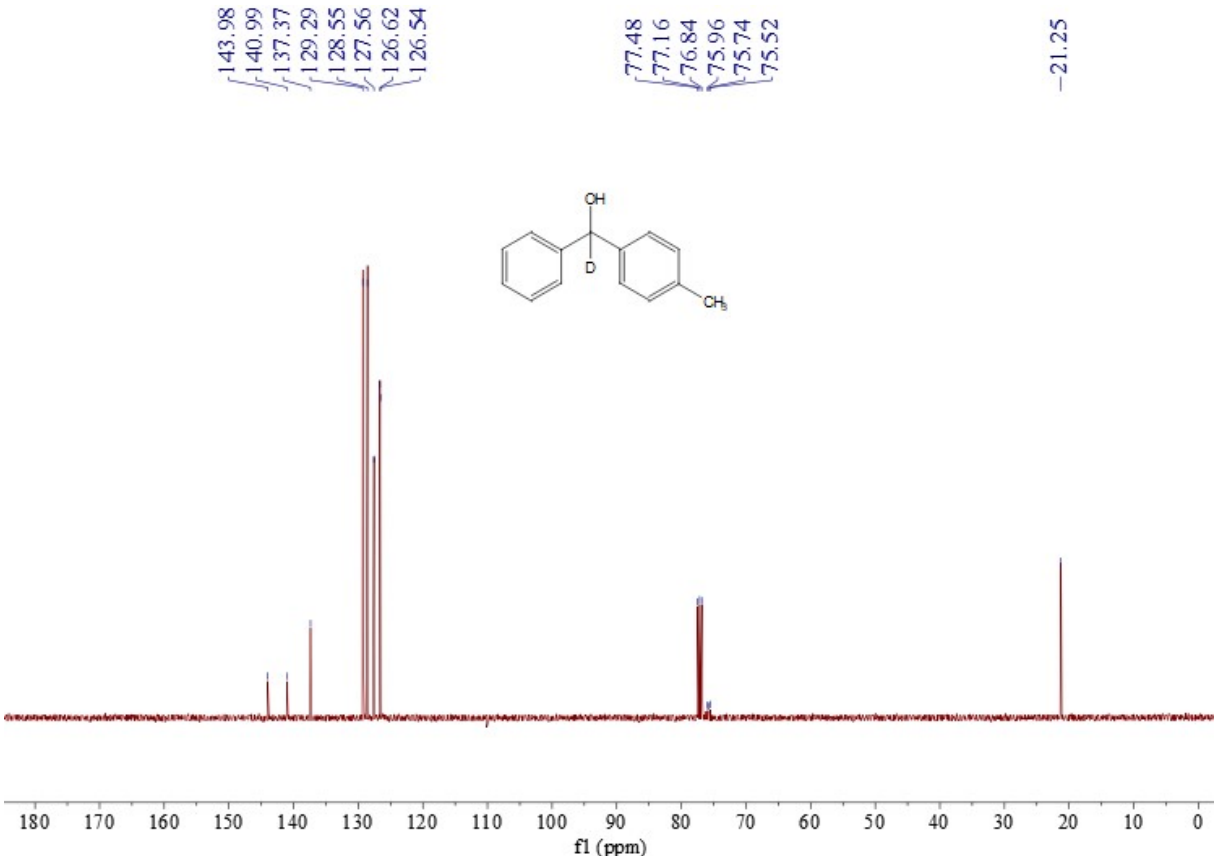
^{13}C NMR of compound 5b (100 MHz, $CDCl_3$):



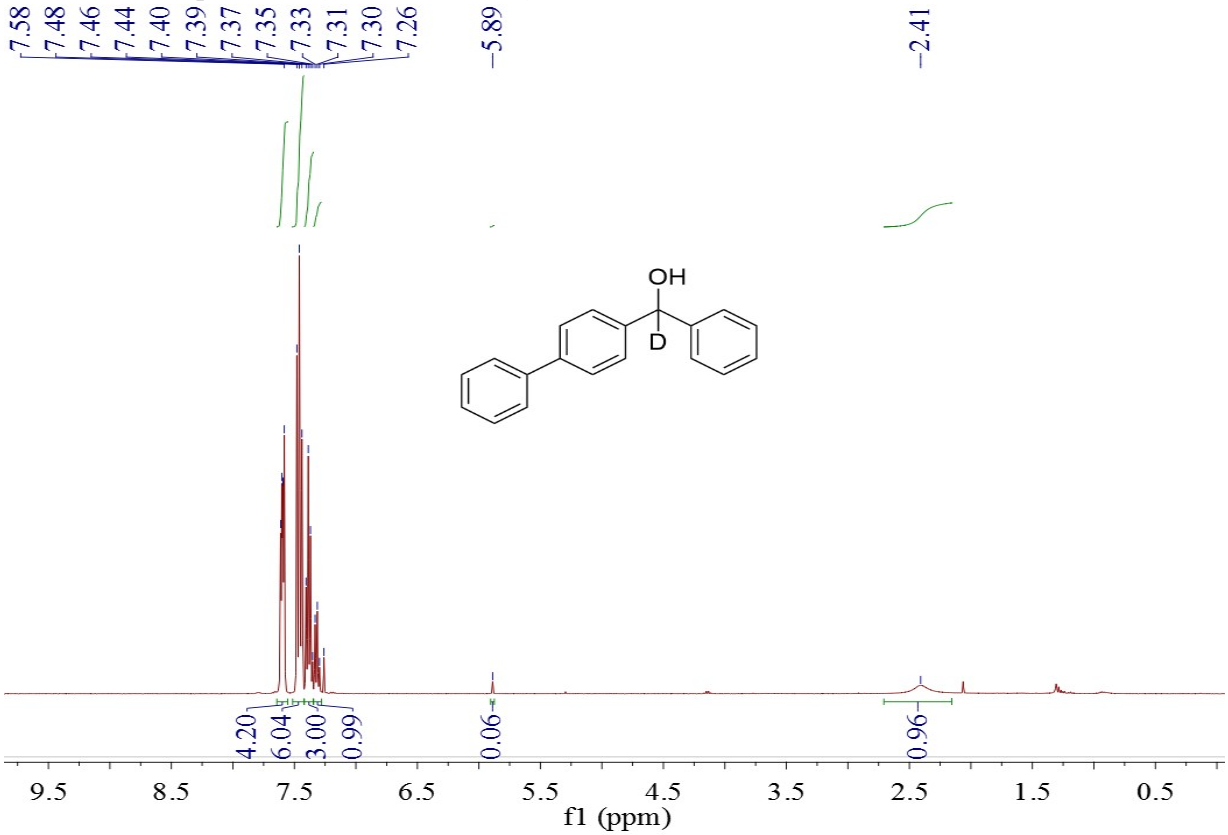
^{1}H NMR of compound 5c (400 MHz, $CDCl_3$):



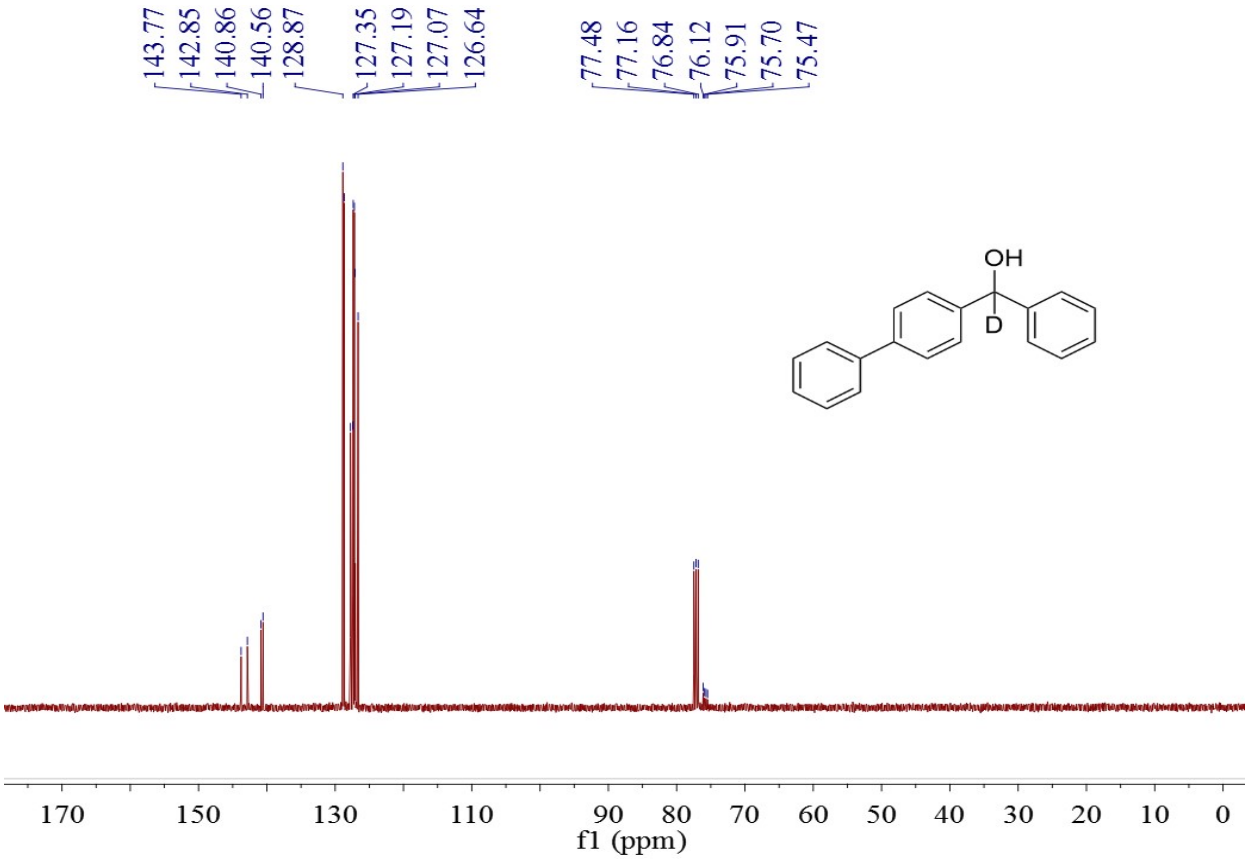
^{13}C NMR of compound 5c (100 MHz, $CDCl_3$):



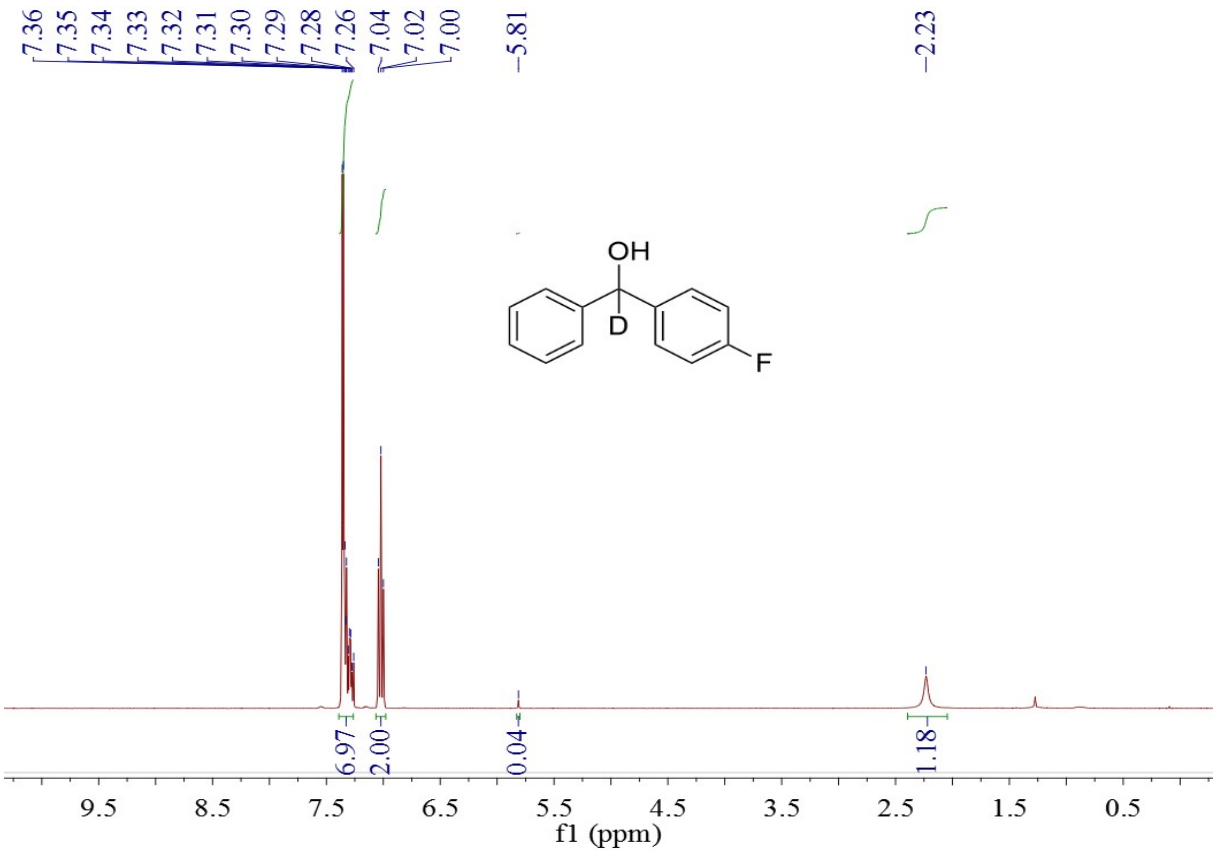
^{1}H NMR of compound 5d (400 MHz, $CDCl_3$):



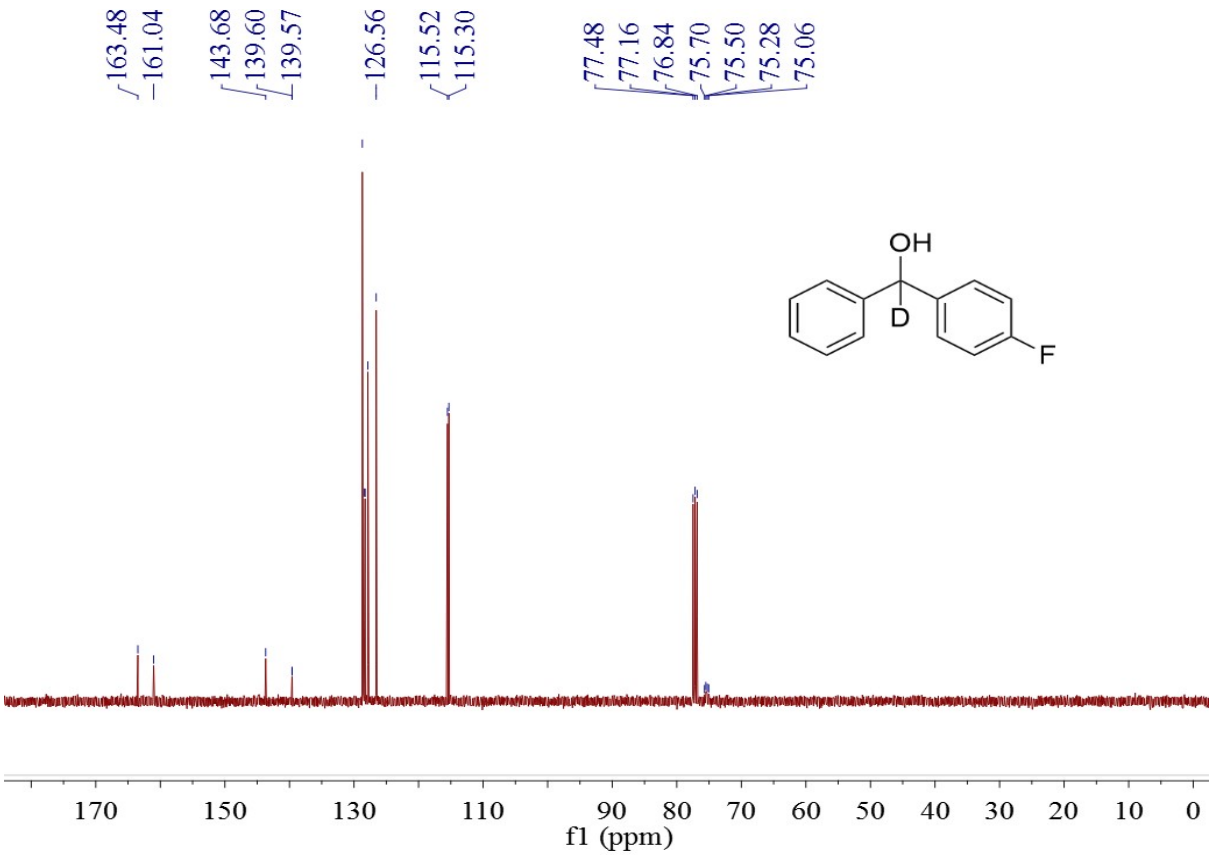
^{13}C NMR of compound 5d (100 MHz, $CDCl_3$):



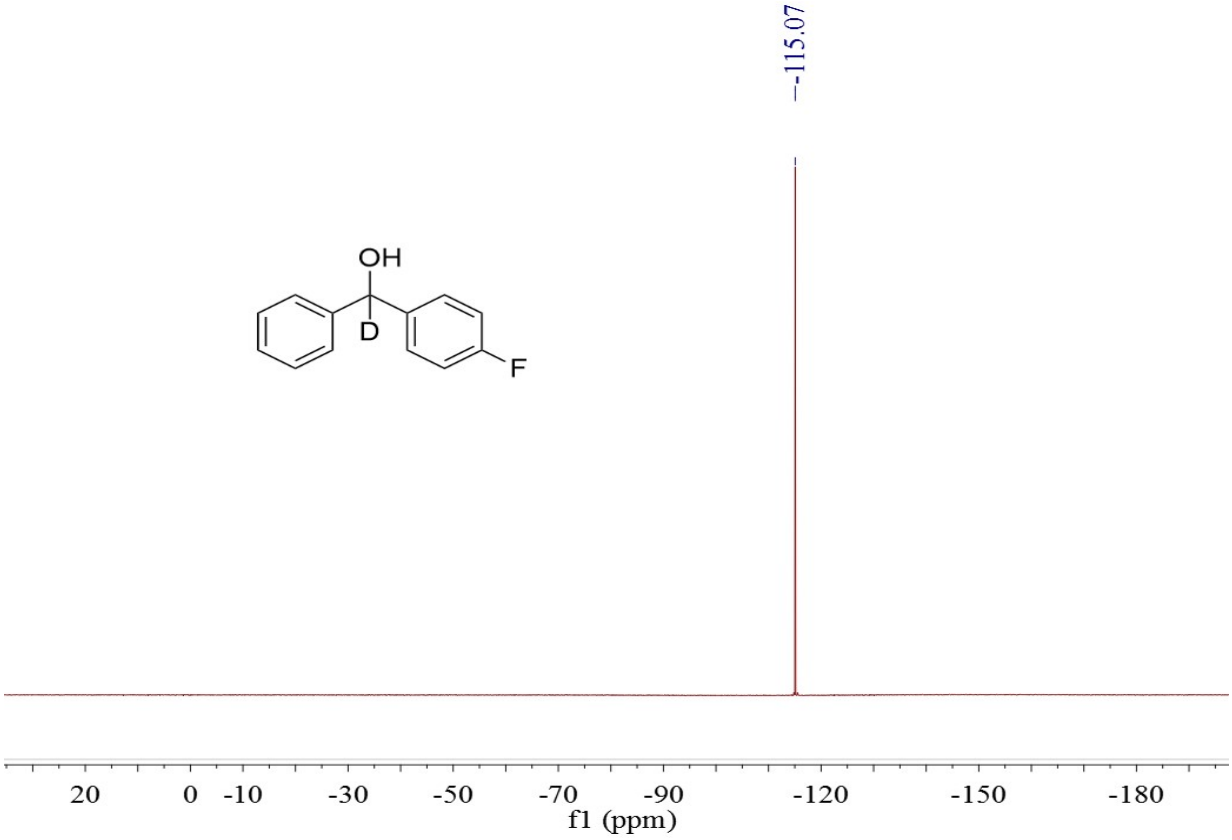
^{1}H NMR of compound 5e (400 MHz, $CDCl_3$):



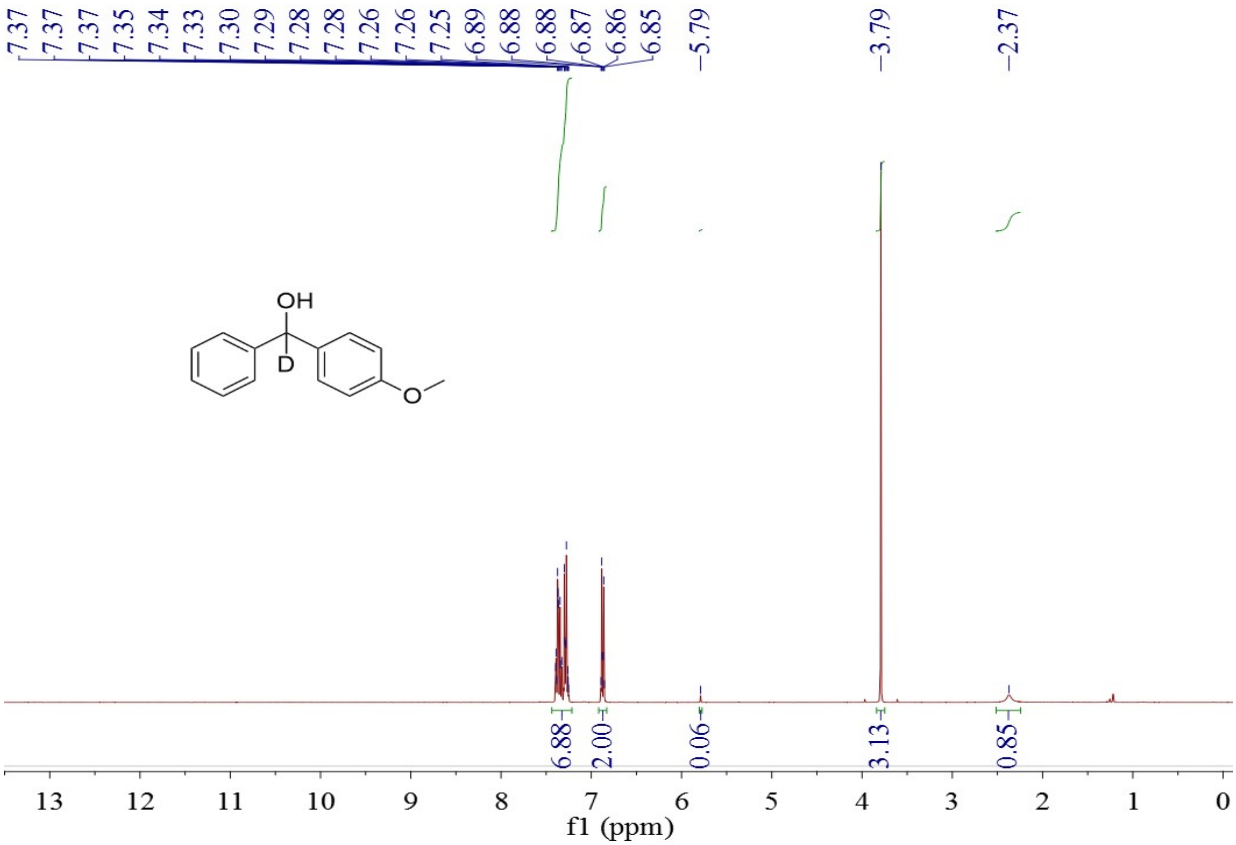
^{13}C NMR of compound 5e (100 MHz, $CDCl_3$):



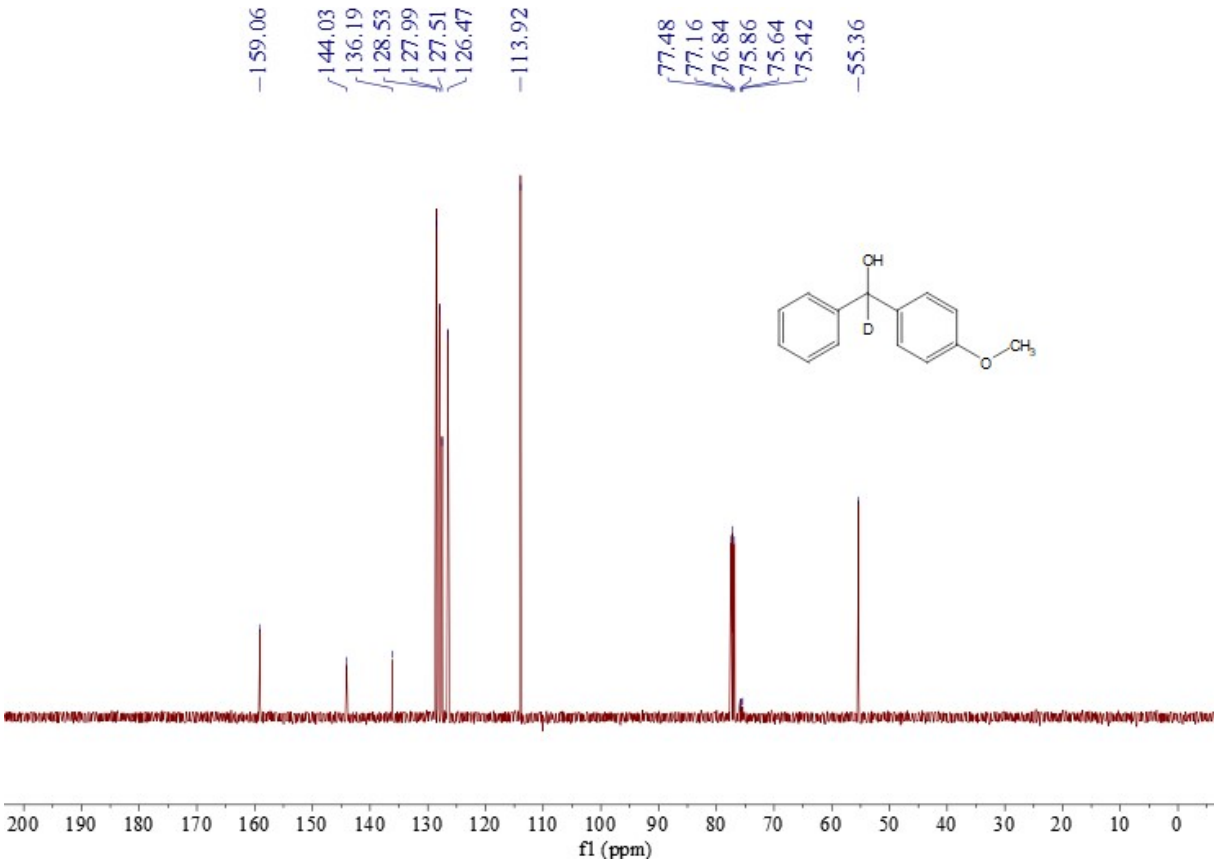
^{19}F NMR of compound 5e (376 MHz, $CDCl_3$):



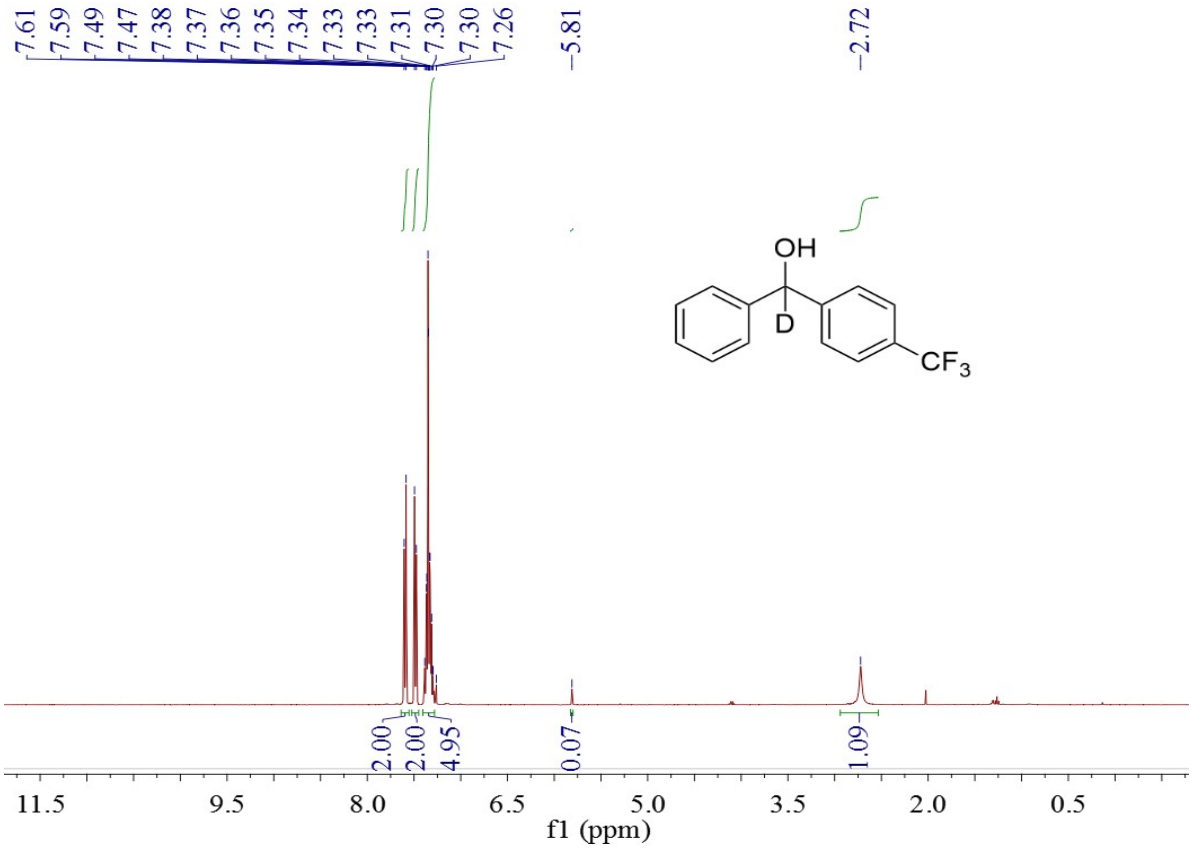
^{1}H NMR of compound 5f (400 MHz, $CDCl_3$):



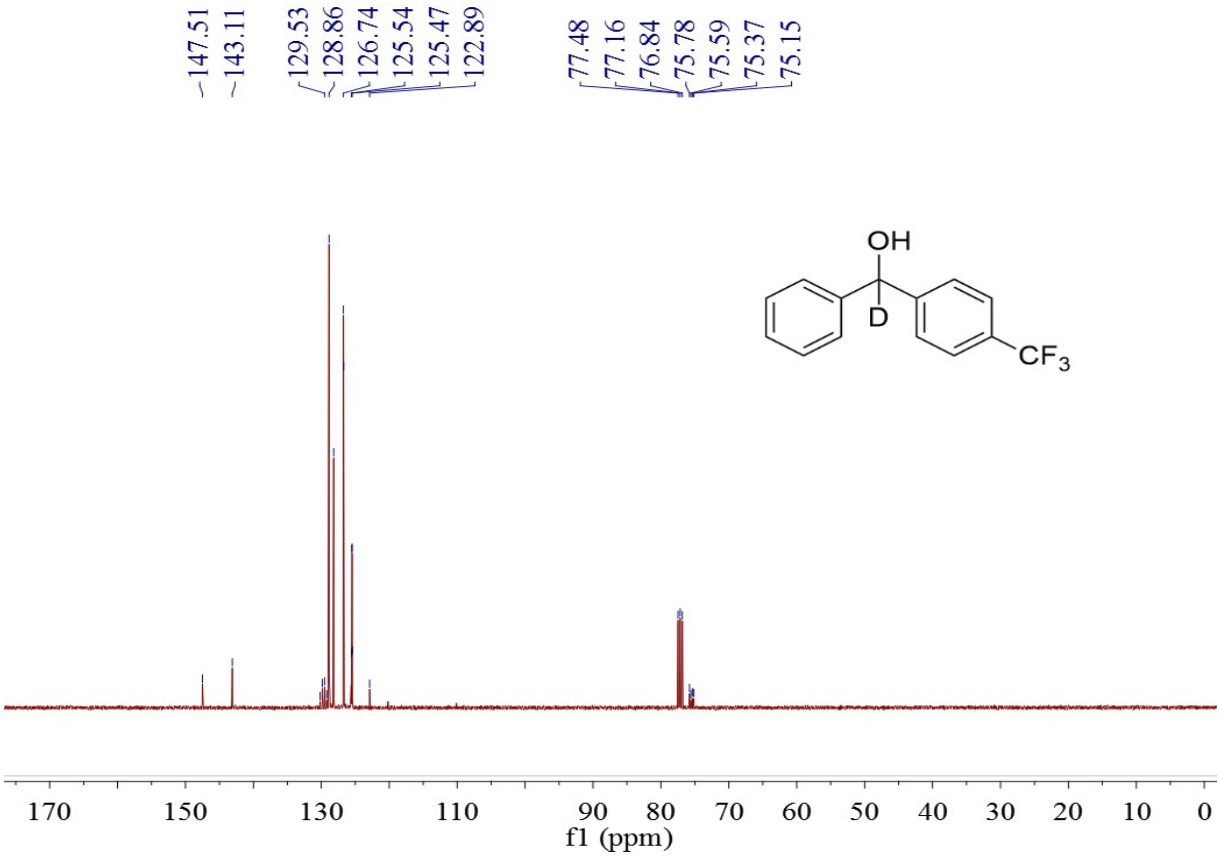
^{13}C NMR of compound 5f (100 MHz, $CDCl_3$):



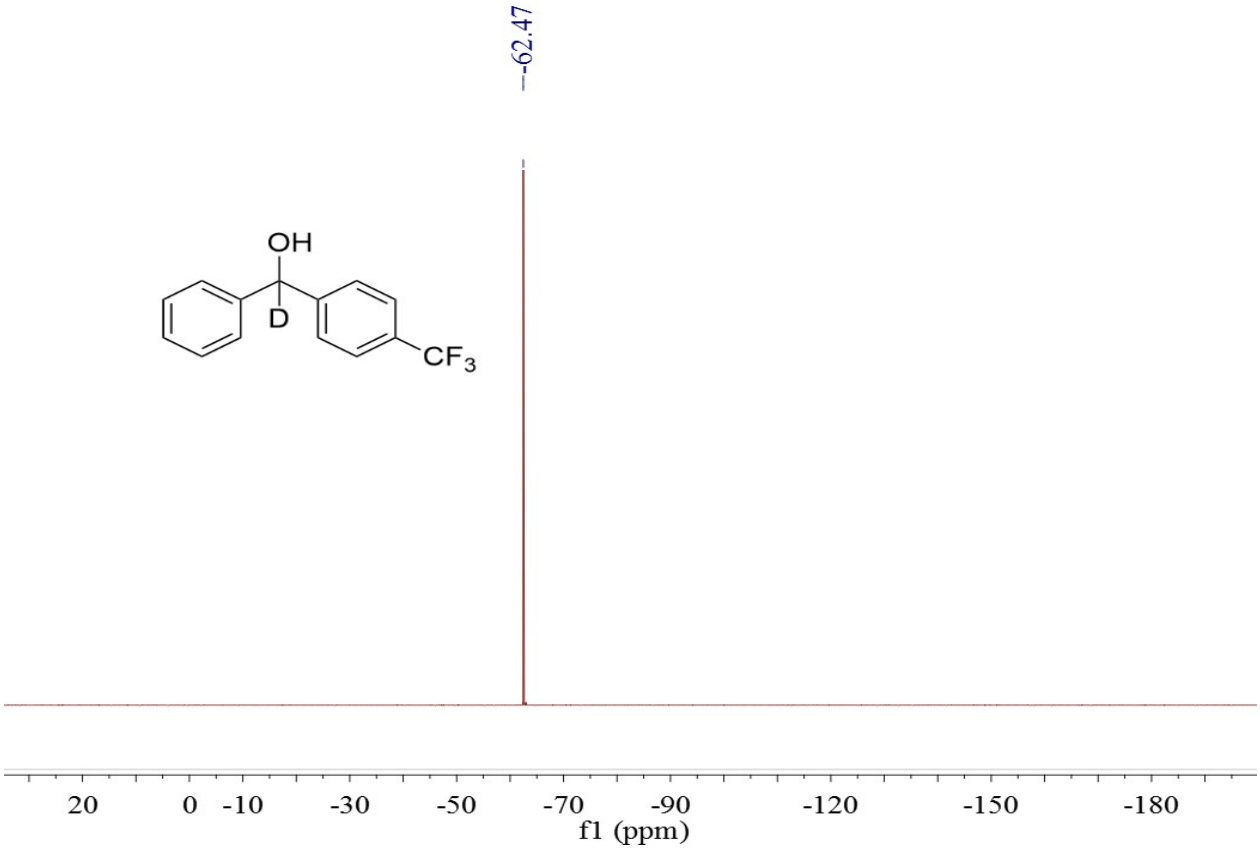
^{1}H NMR of compound 5g (400 MHz, $CDCl_3$):



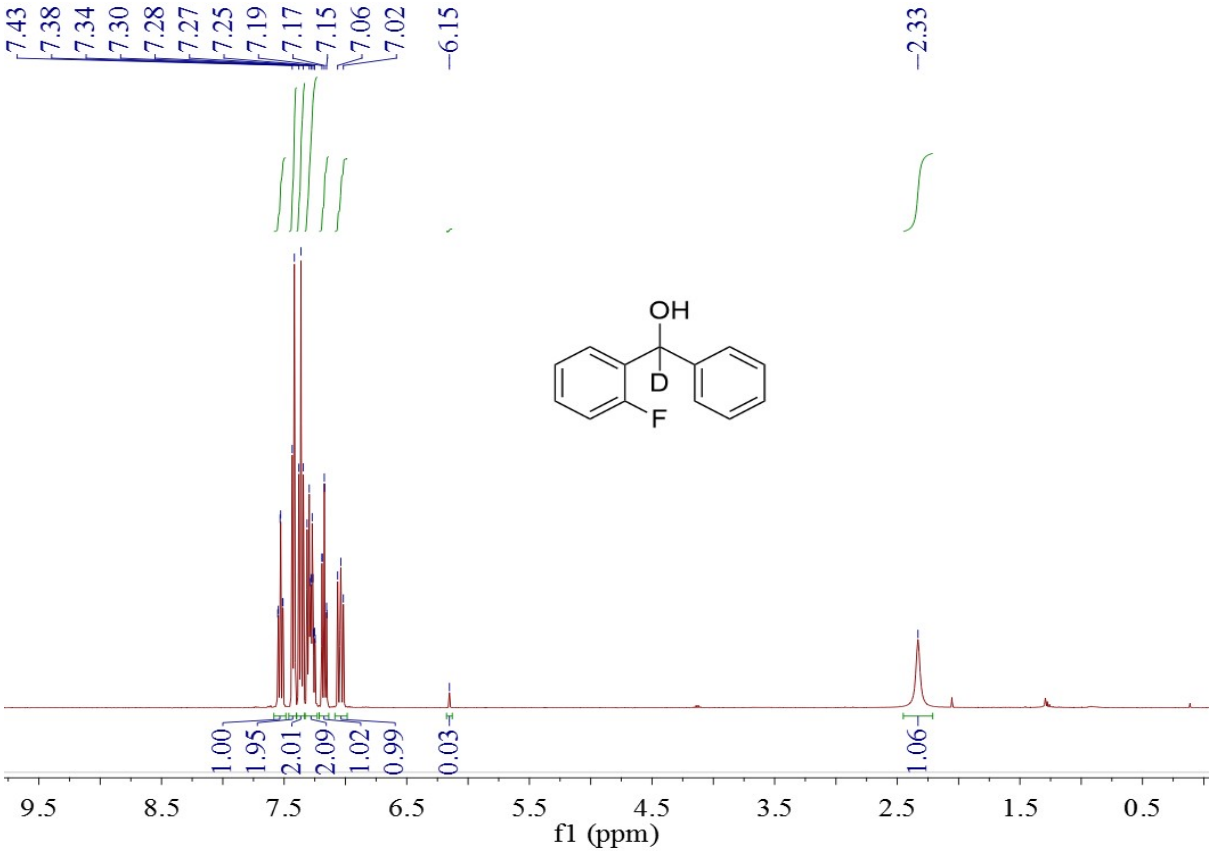
^{13}C NMR of compound 5g (100 MHz, $CDCl_3$):



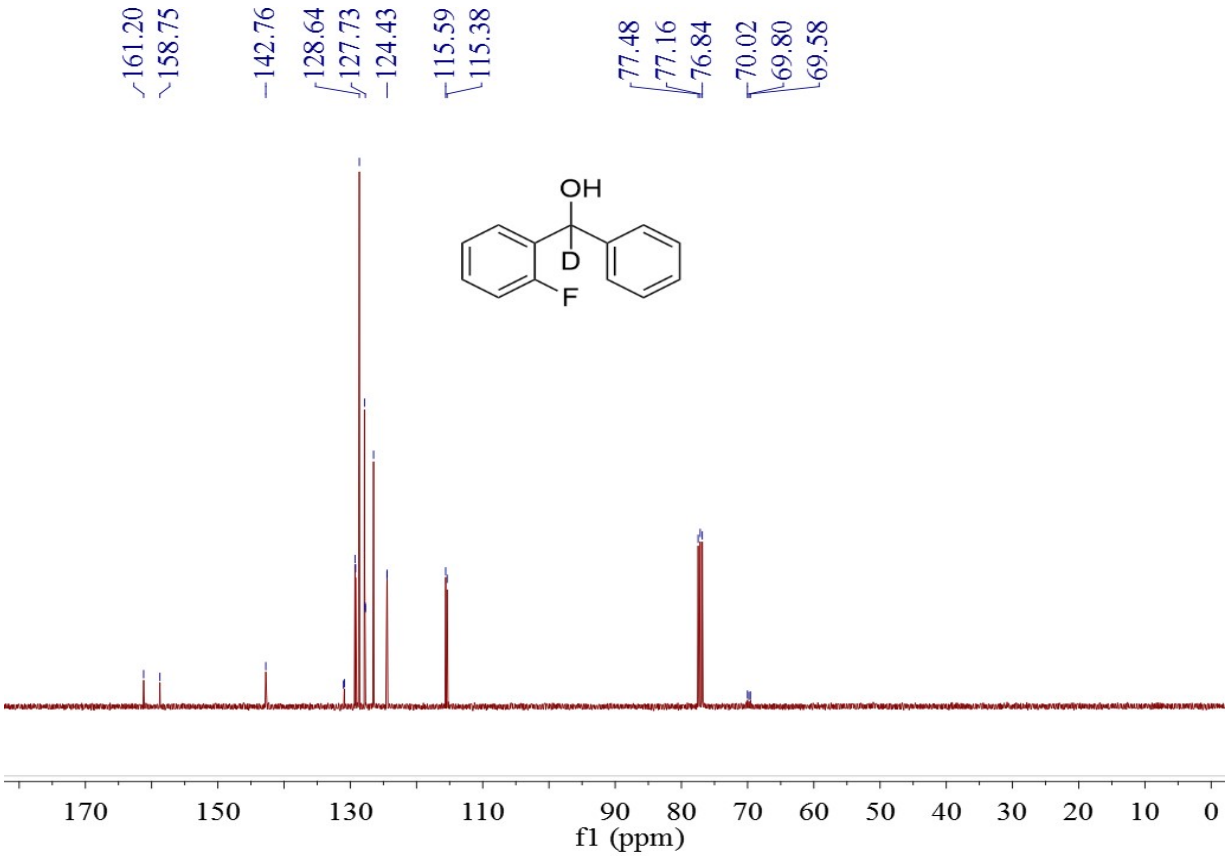
^{19}F NMR of compound 5g (376 MHz, $CDCl_3$):



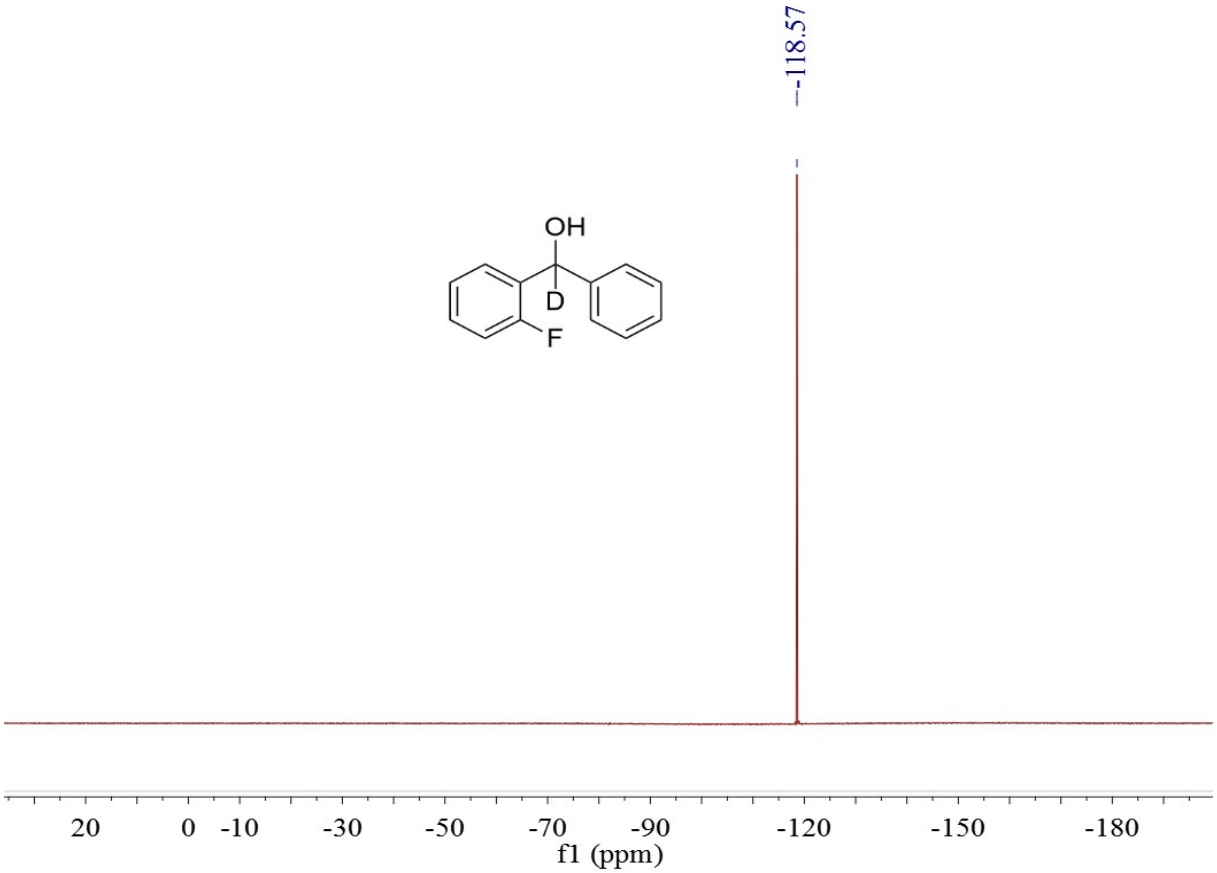
^{1}H NMR of compound 5h (400 MHz, $CDCl_3$):



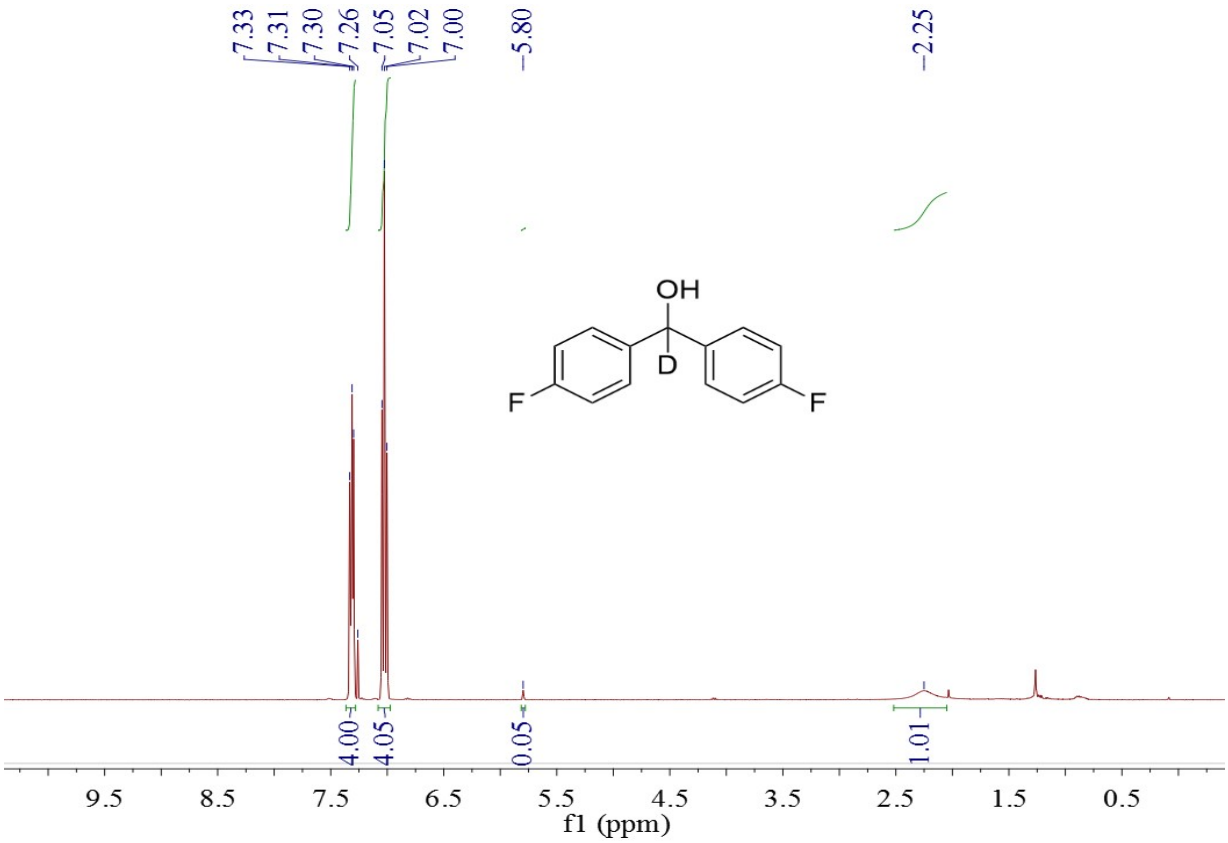
^{13}C NMR of compound 5h (100 MHz, $CDCl_3$):



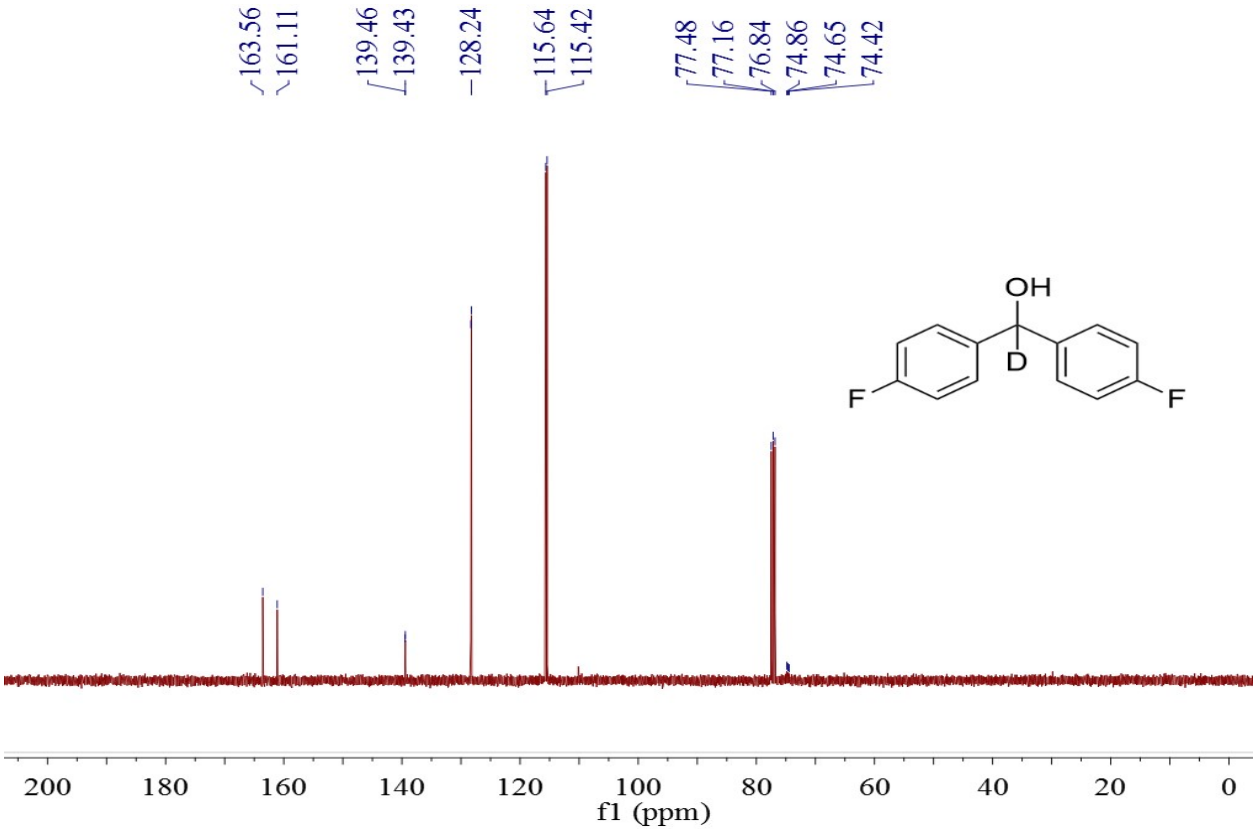
^{19}F NMR of compound 5h (376 MHz, $CDCl_3$):



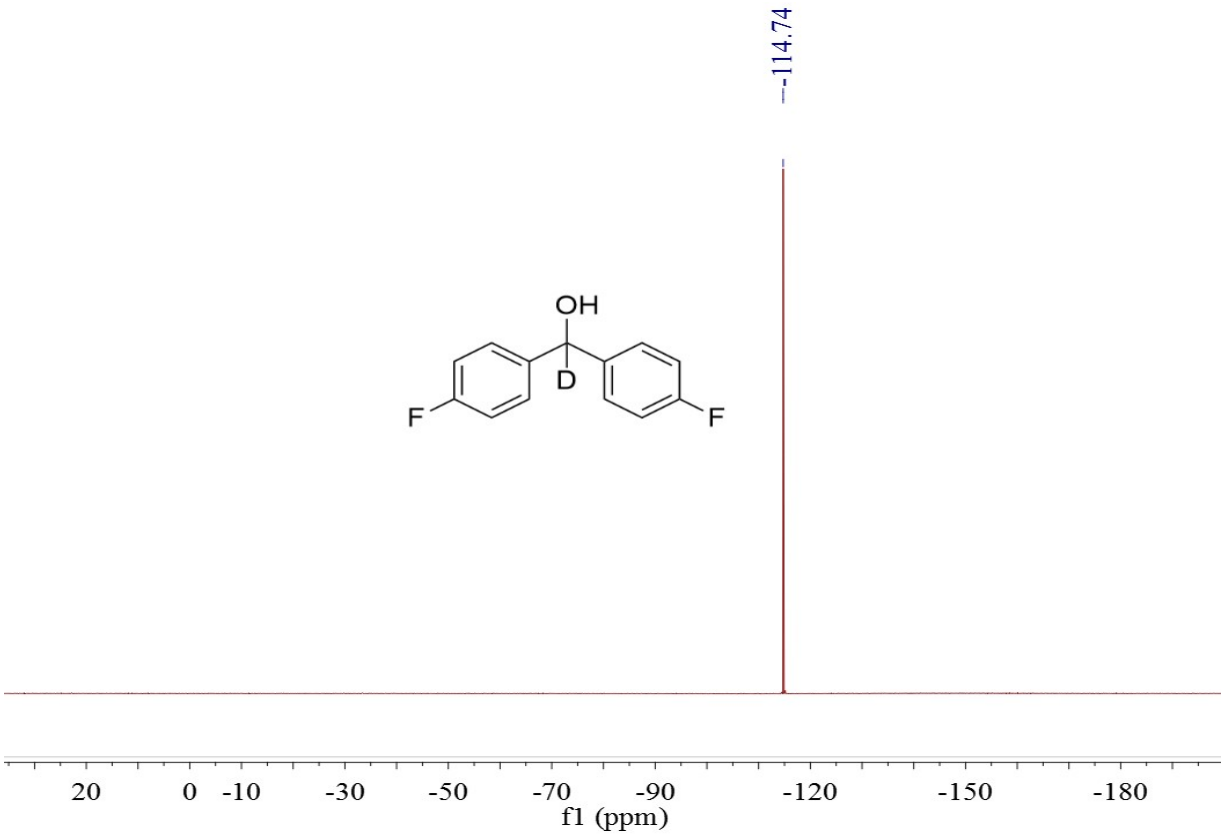
^{1}H NMR of compound 5i (400 MHz, $CDCl_3$):



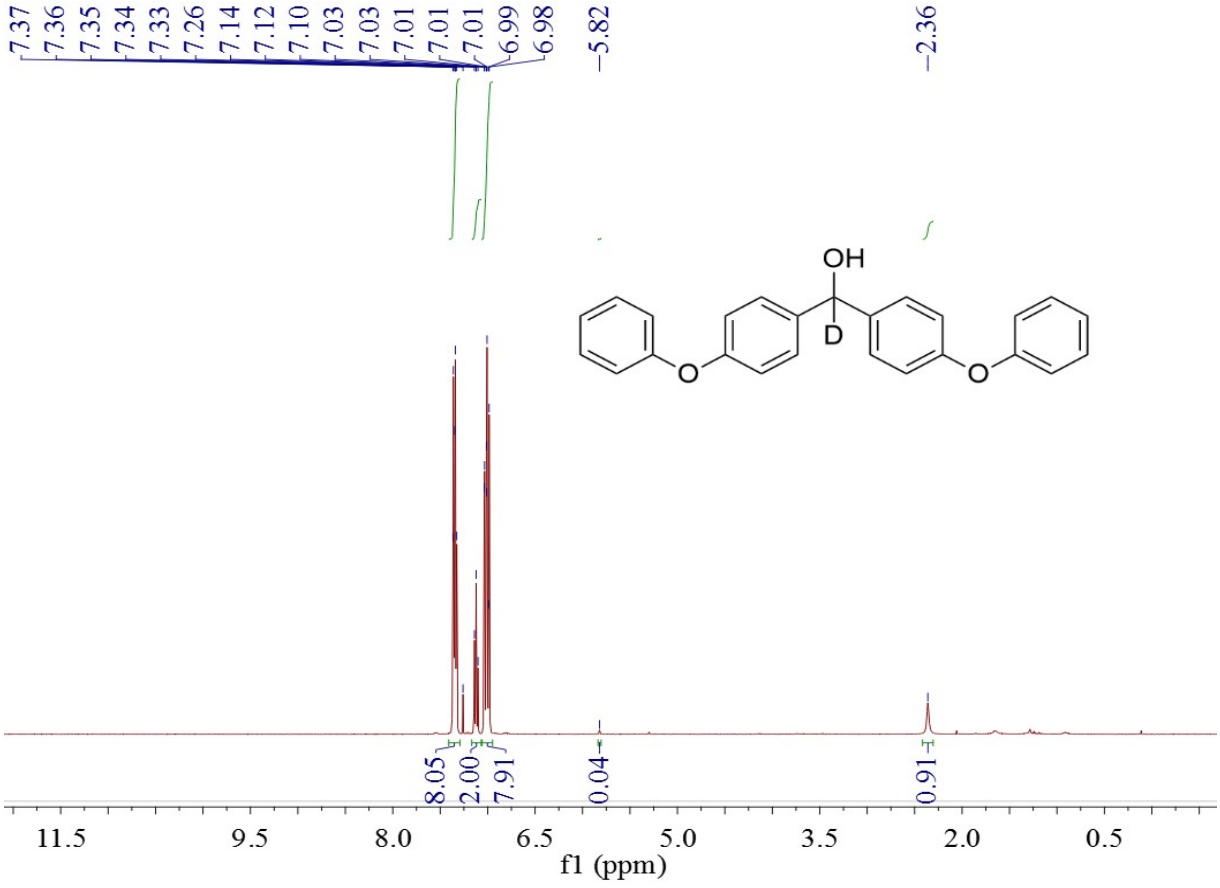
^{13}C NMR of compound 5i (100 MHz, $CDCl_3$):



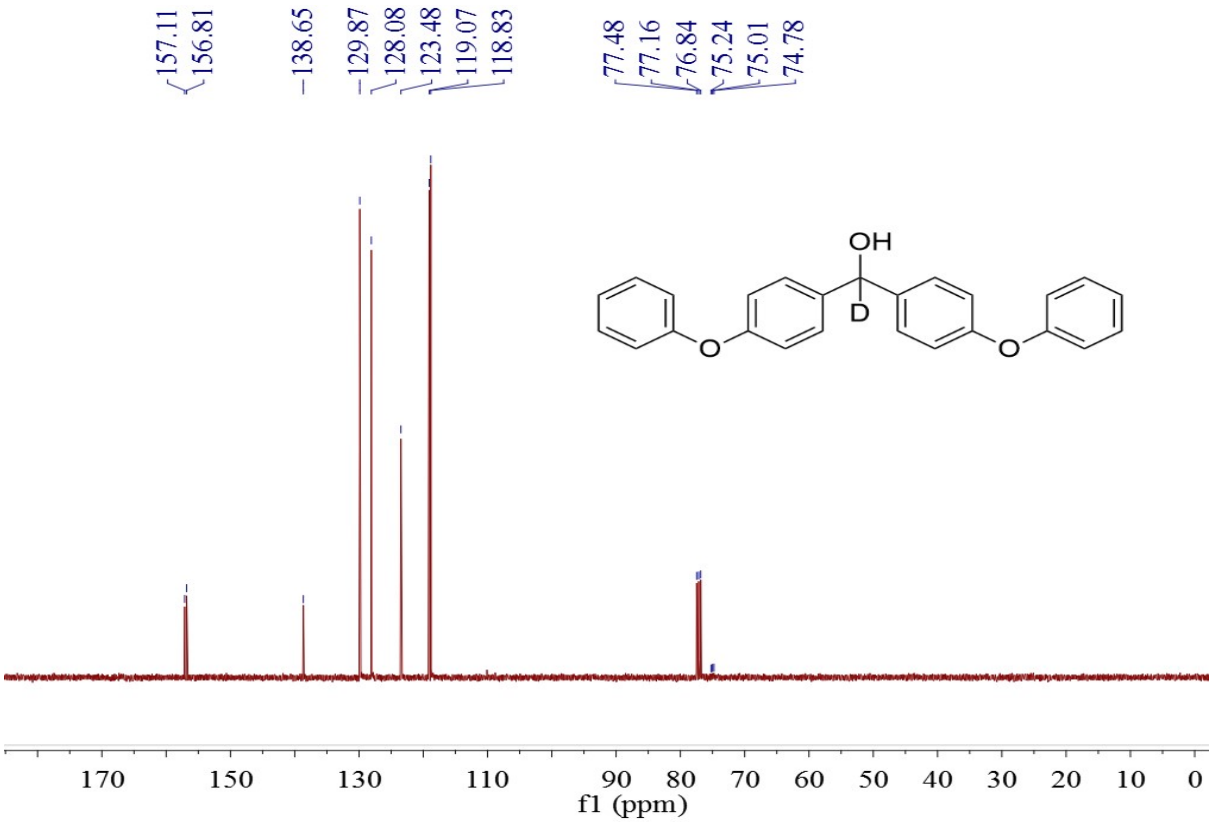
^{19}F NMR of compound 5i (376 MHz, $CDCl_3$):



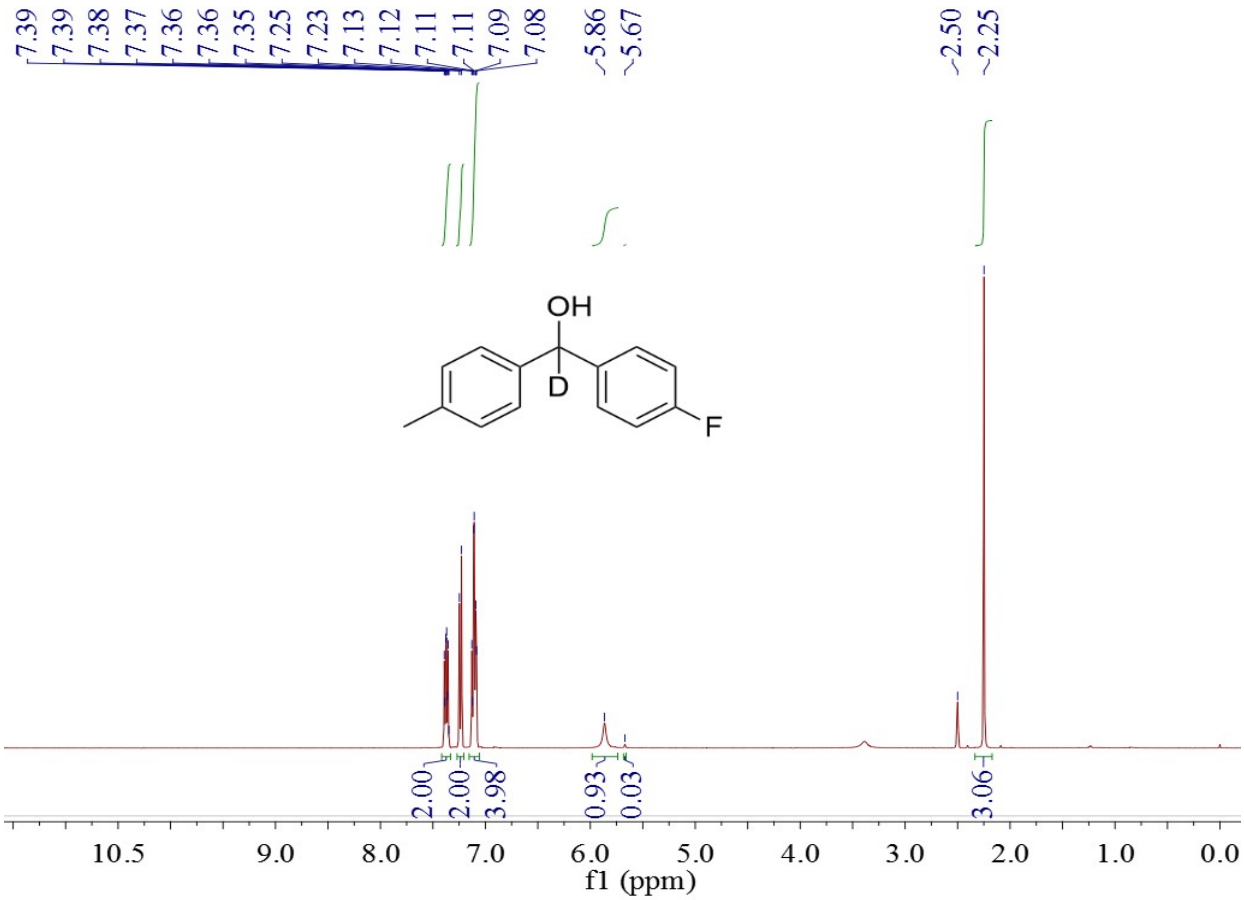
^{1}H NMR of compound 5j (400 MHz, $CDCl_3$):



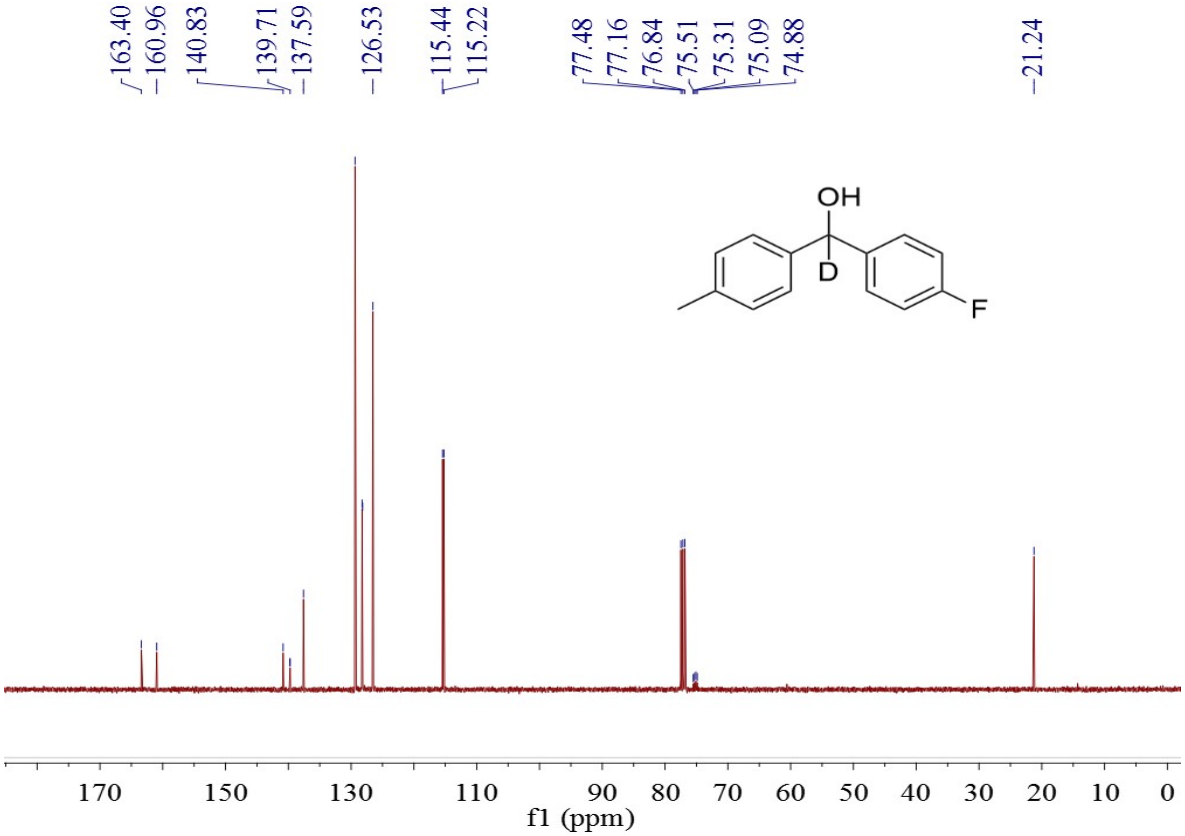
^{13}C NMR of compound 5j (100 MHz, $CDCl_3$):



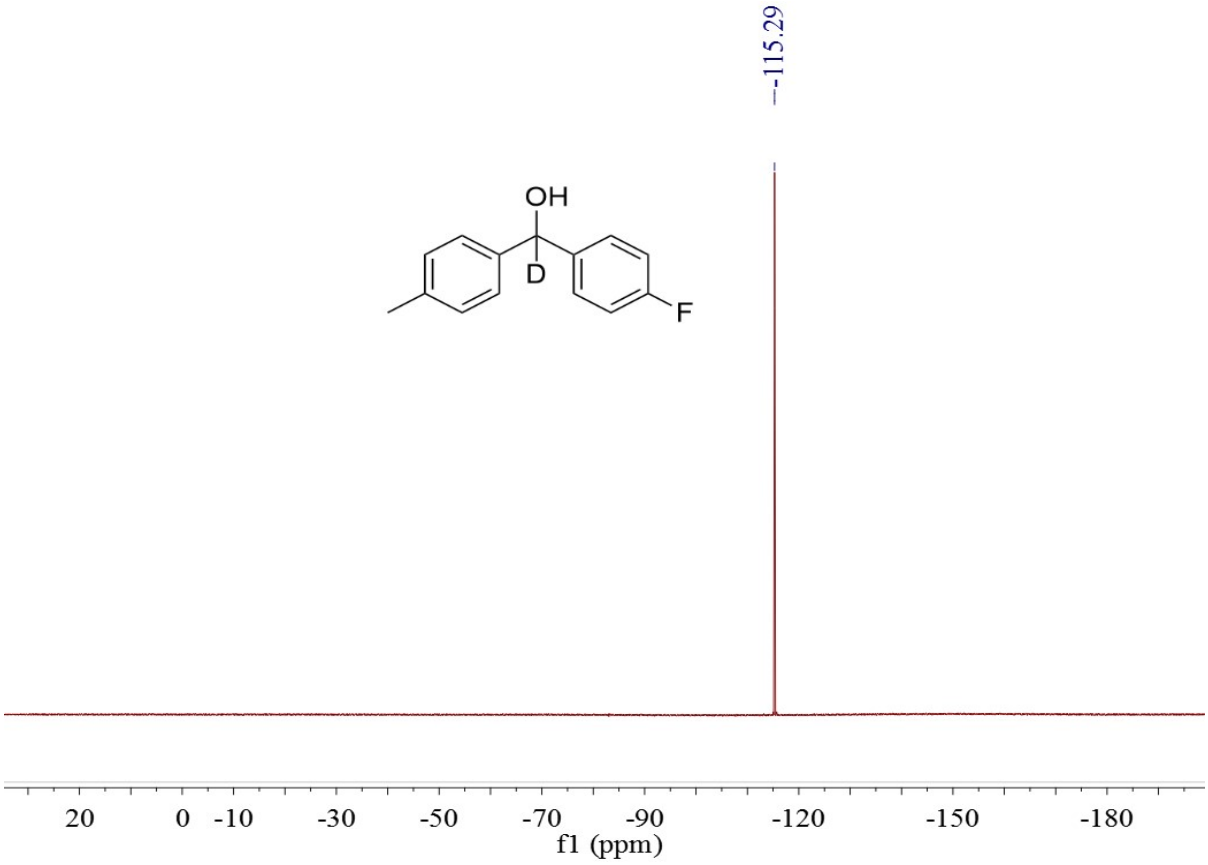
^{1}H NMR of compound 5k (400 MHz, $CDCl_3$):



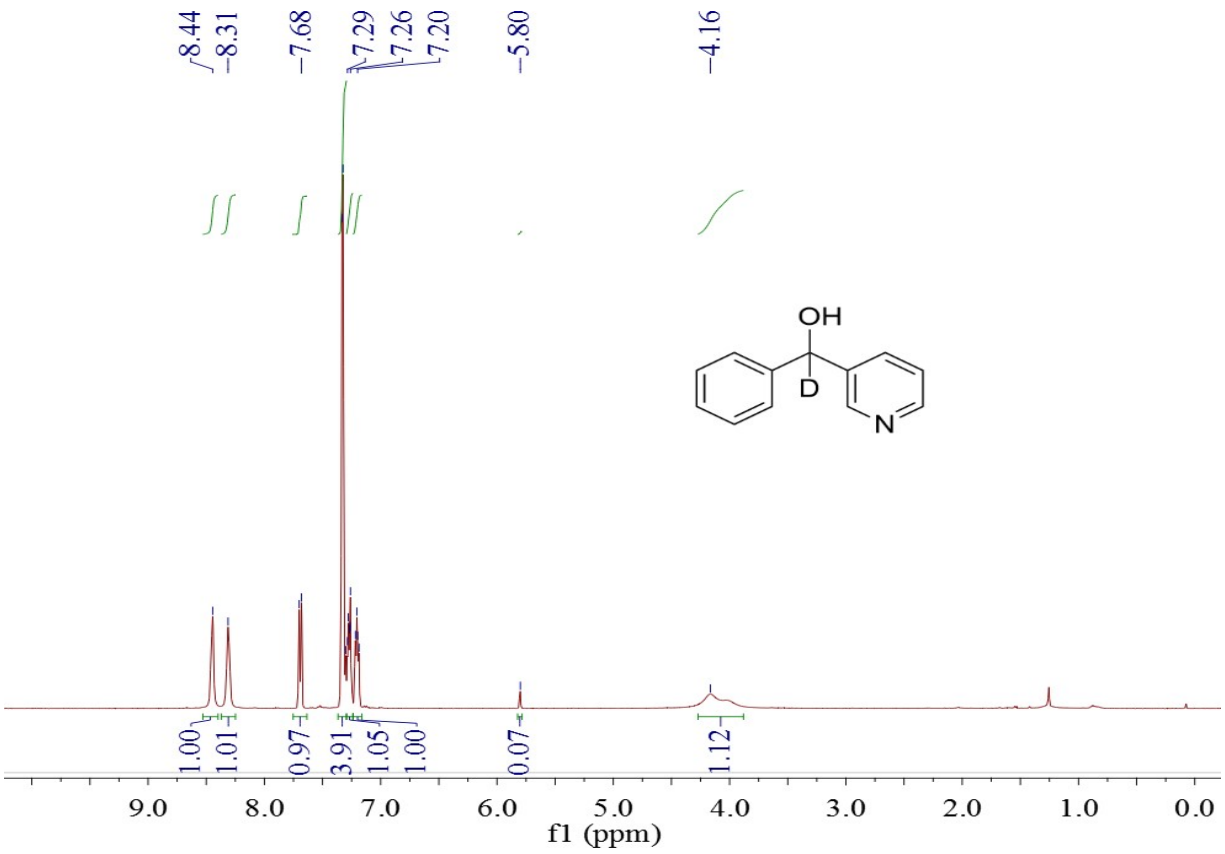
^{13}C NMR of compound 5k (100 MHz, $CDCl_3$):



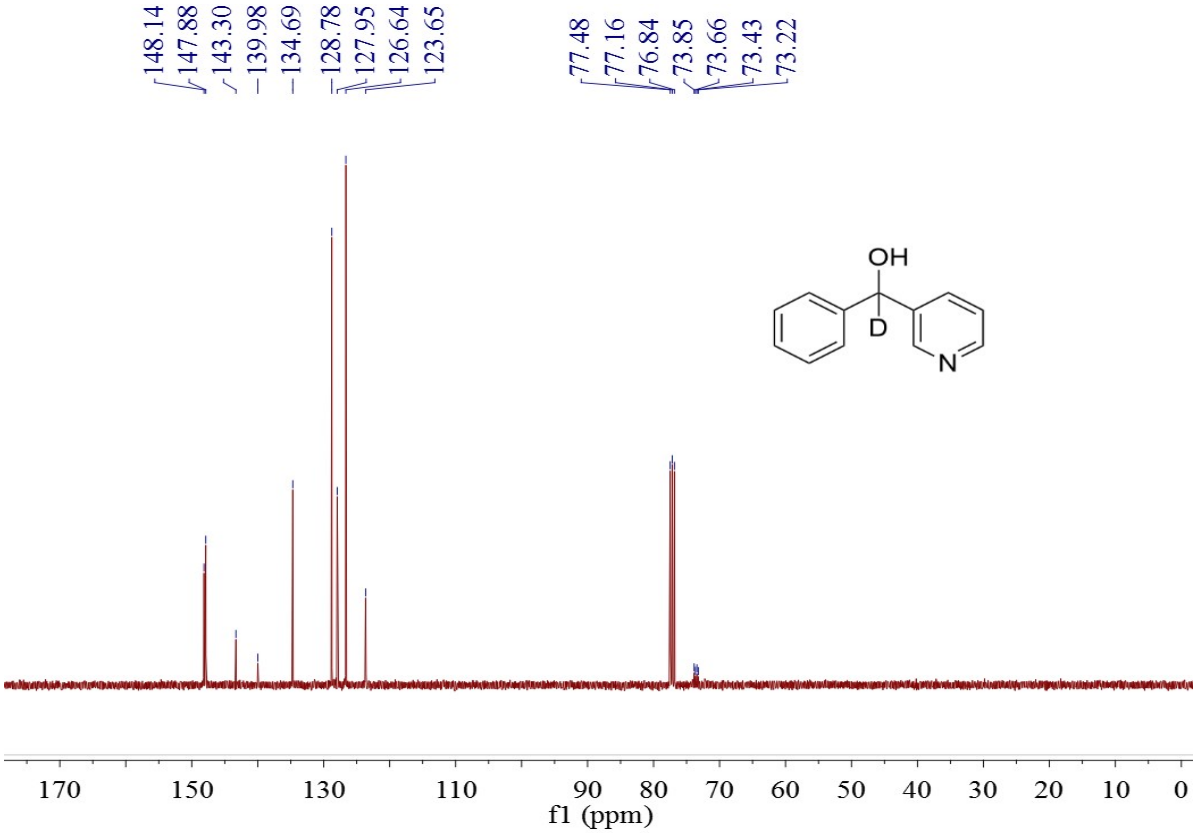
^{19}F NMR of compound 5k (376 MHz, $CDCl_3$):



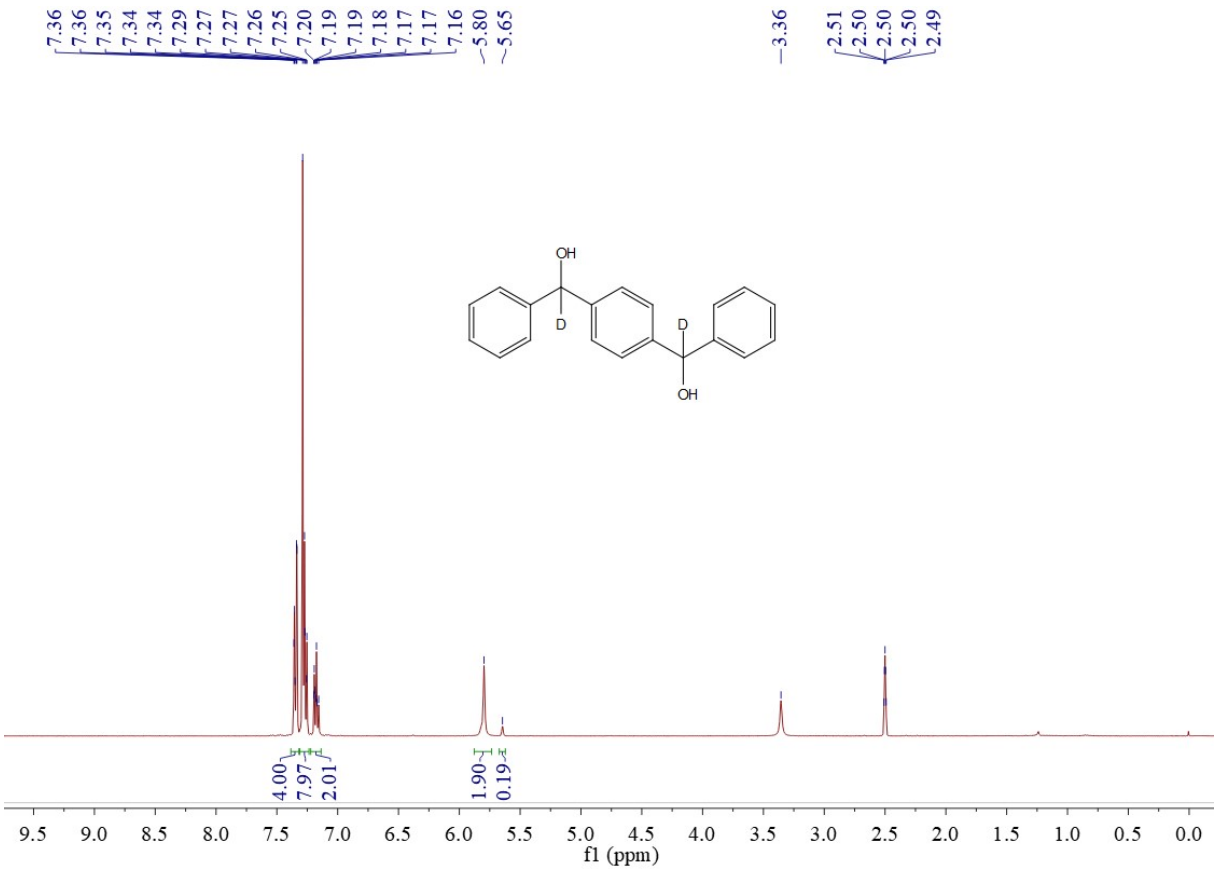
^{1}H NMR of compound 5l (400 MHz, $CDCl_3$):



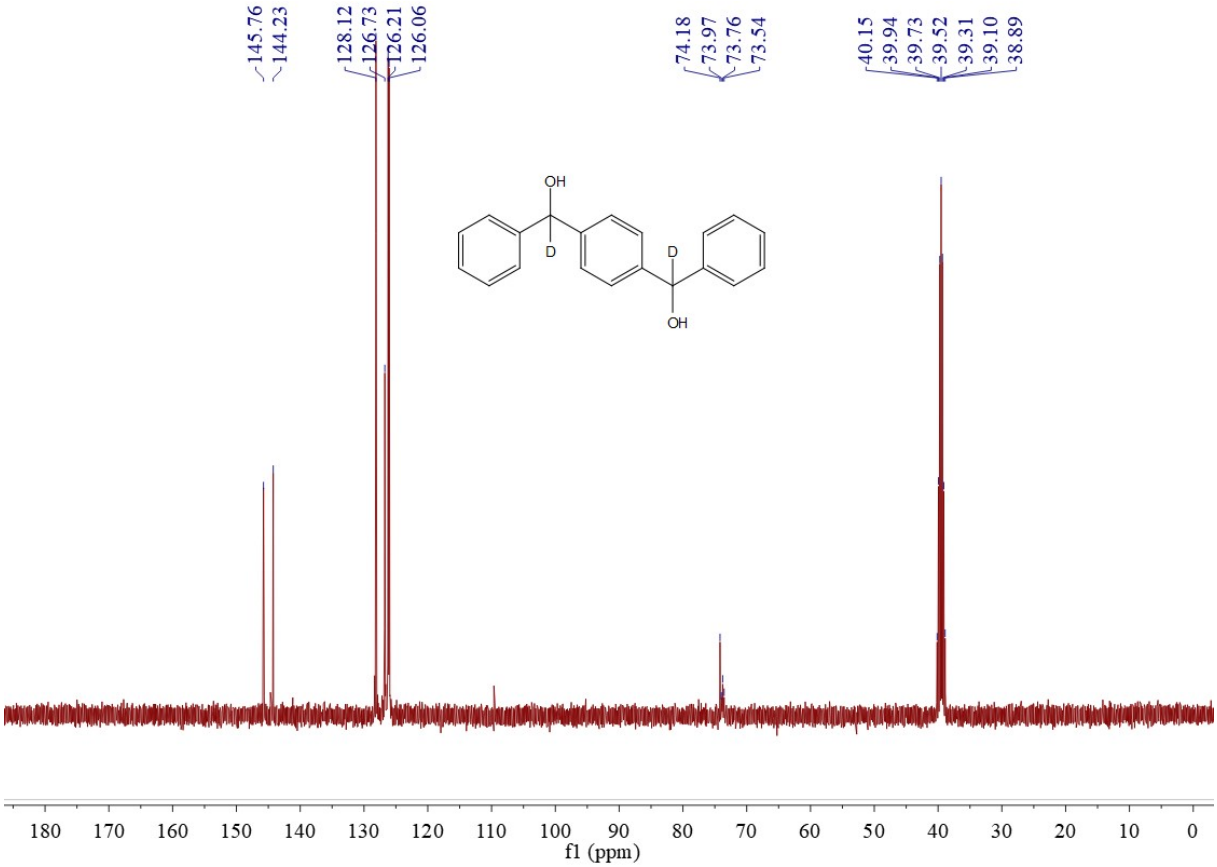
^{13}C NMR of compound 5l (100 MHz, $CDCl_3$):



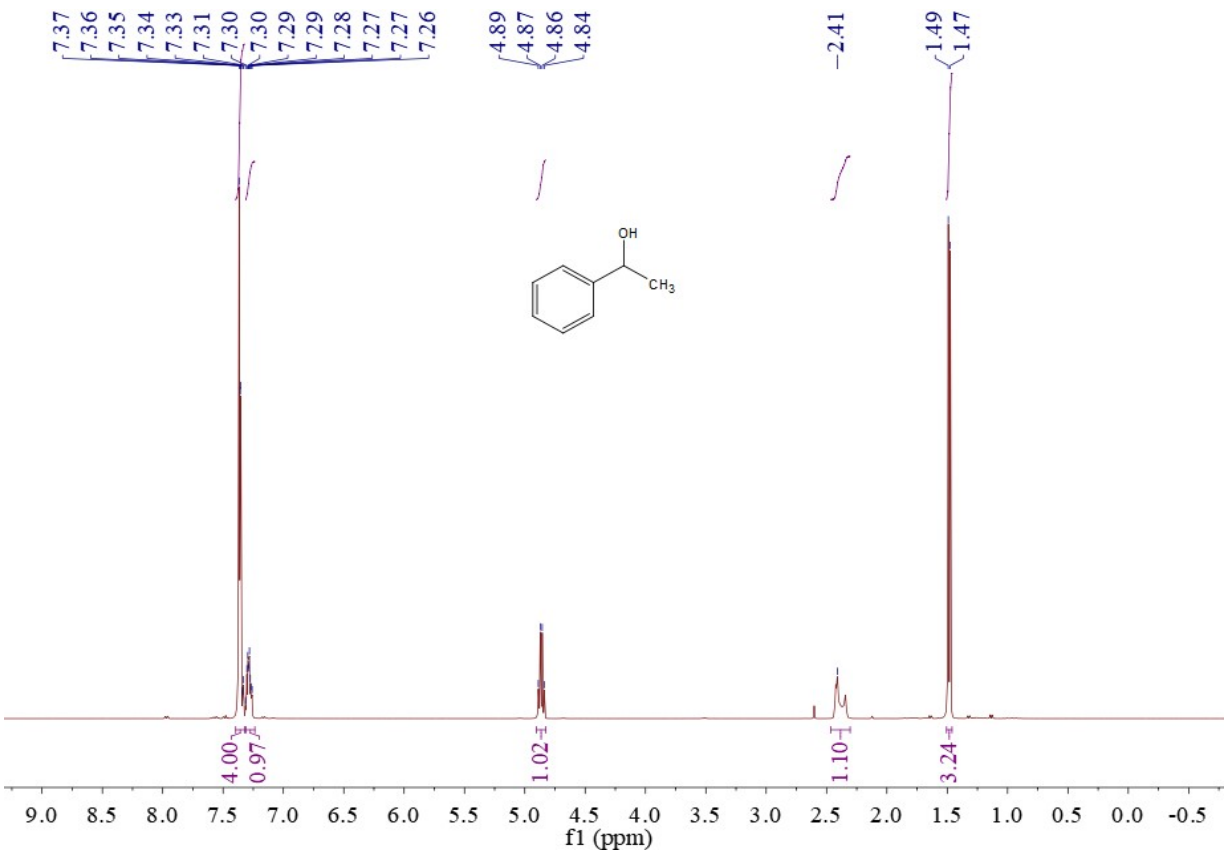
^{1}H NMR of compound 5m (400 MHz, DMSO-d_6):



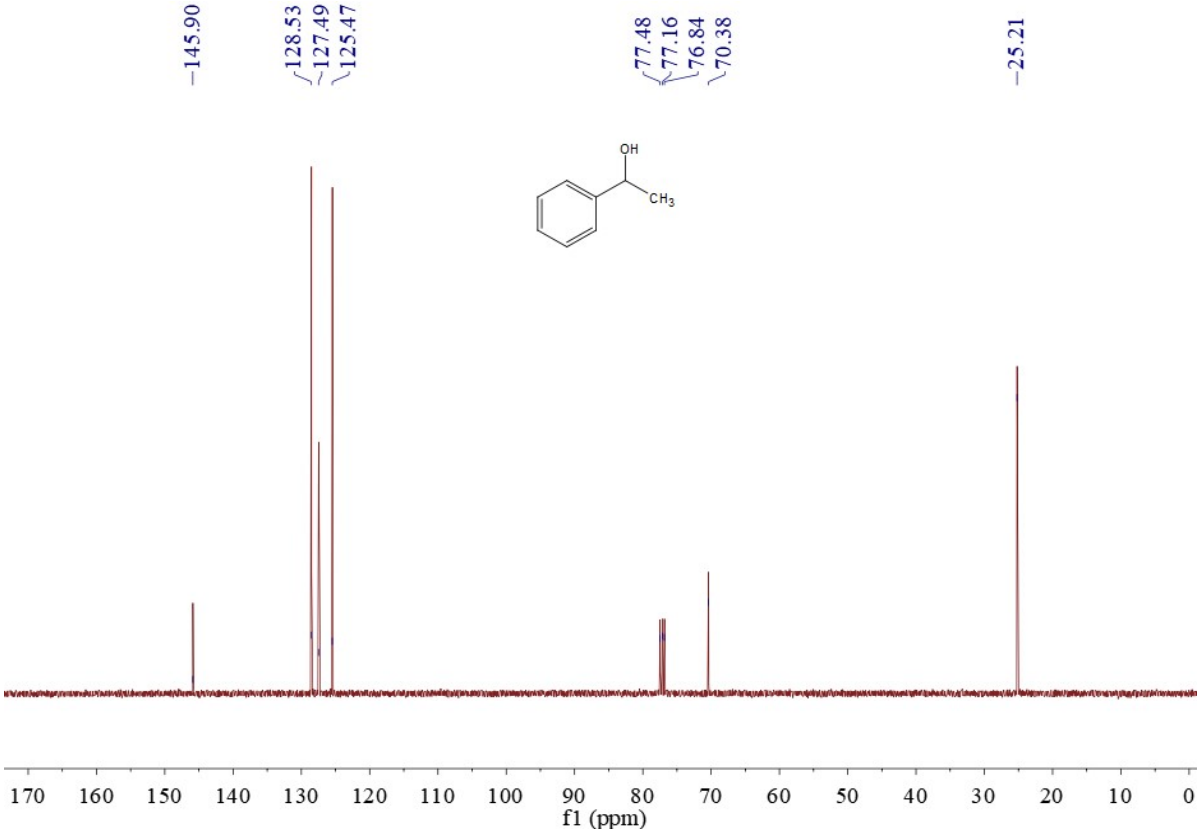
^{13}C NMR of compound 5m (100 MHz, DMSO-d_6):



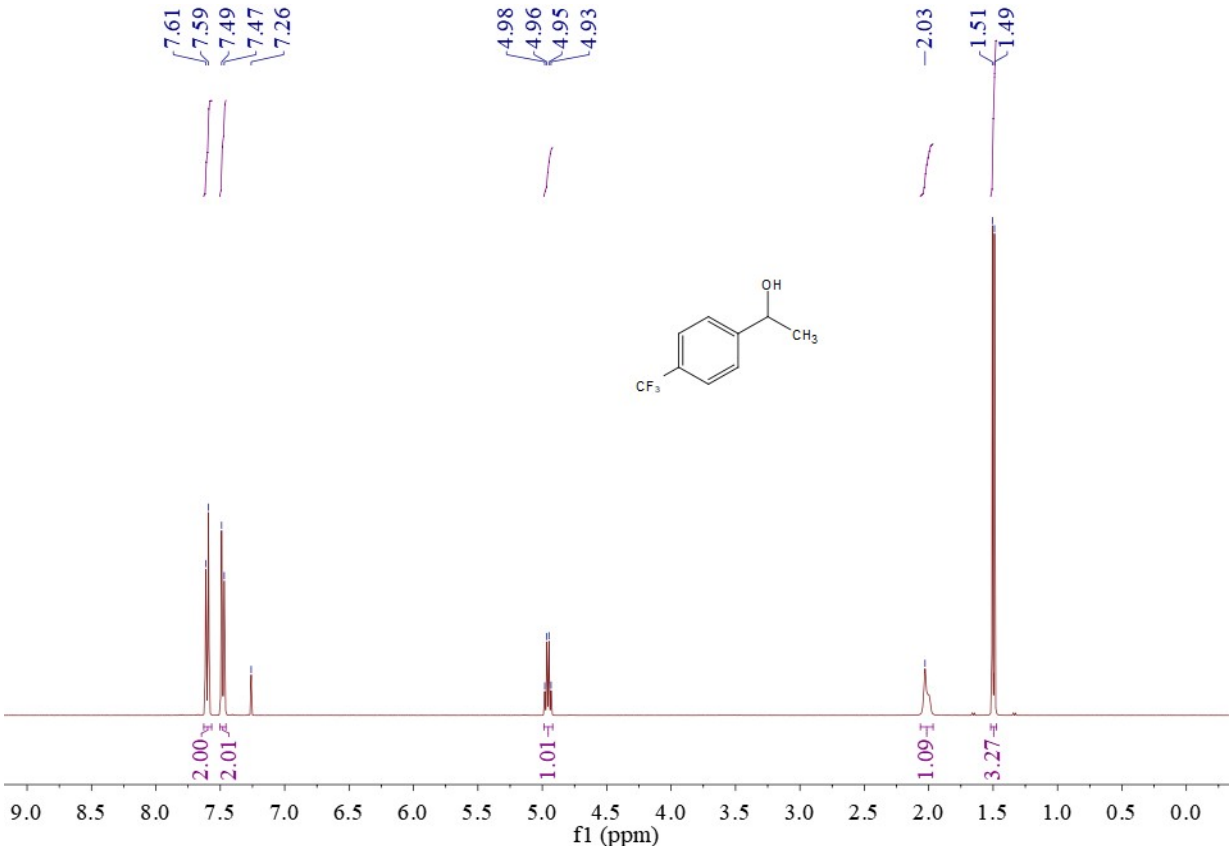
^{1}H NMR of compound 7a (400 MHz, $CDCl_3$):



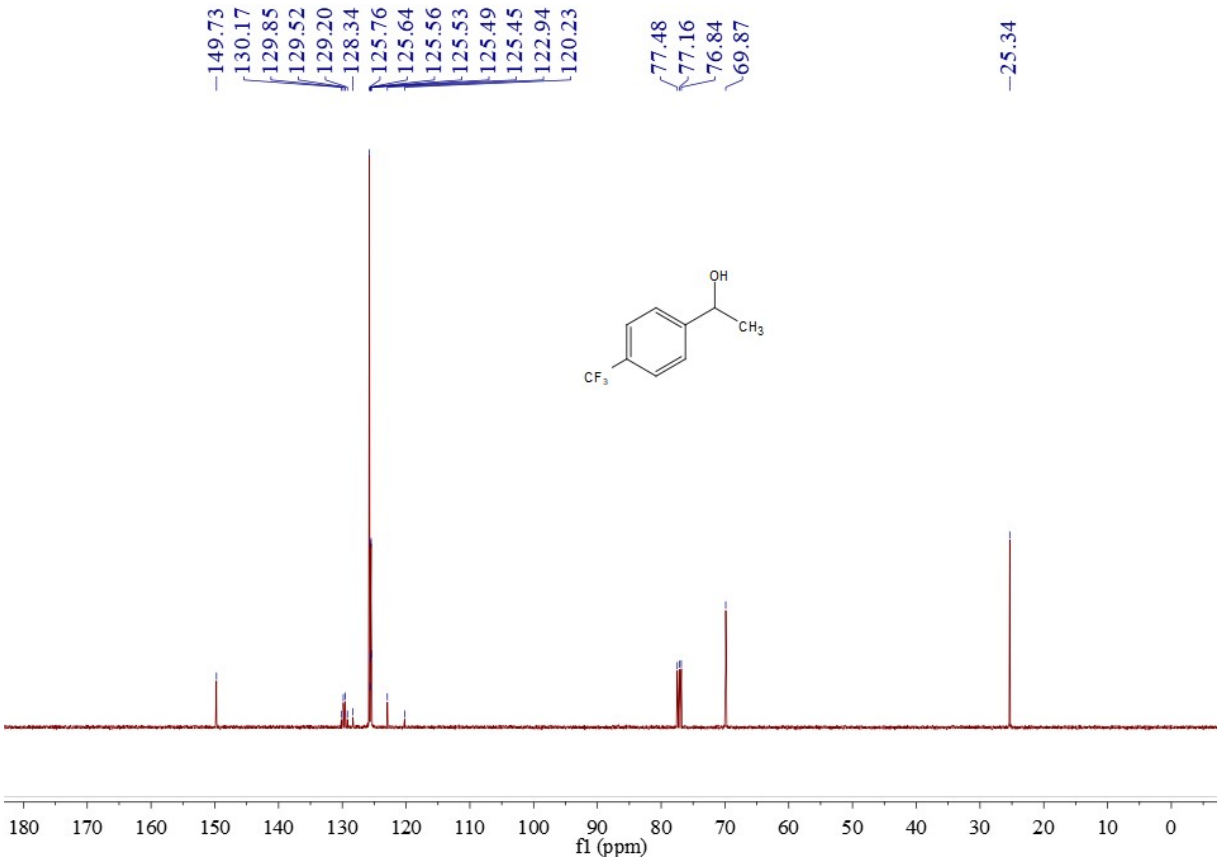
^{13}C NMR of compound 7a (100 MHz, $CDCl_3$):



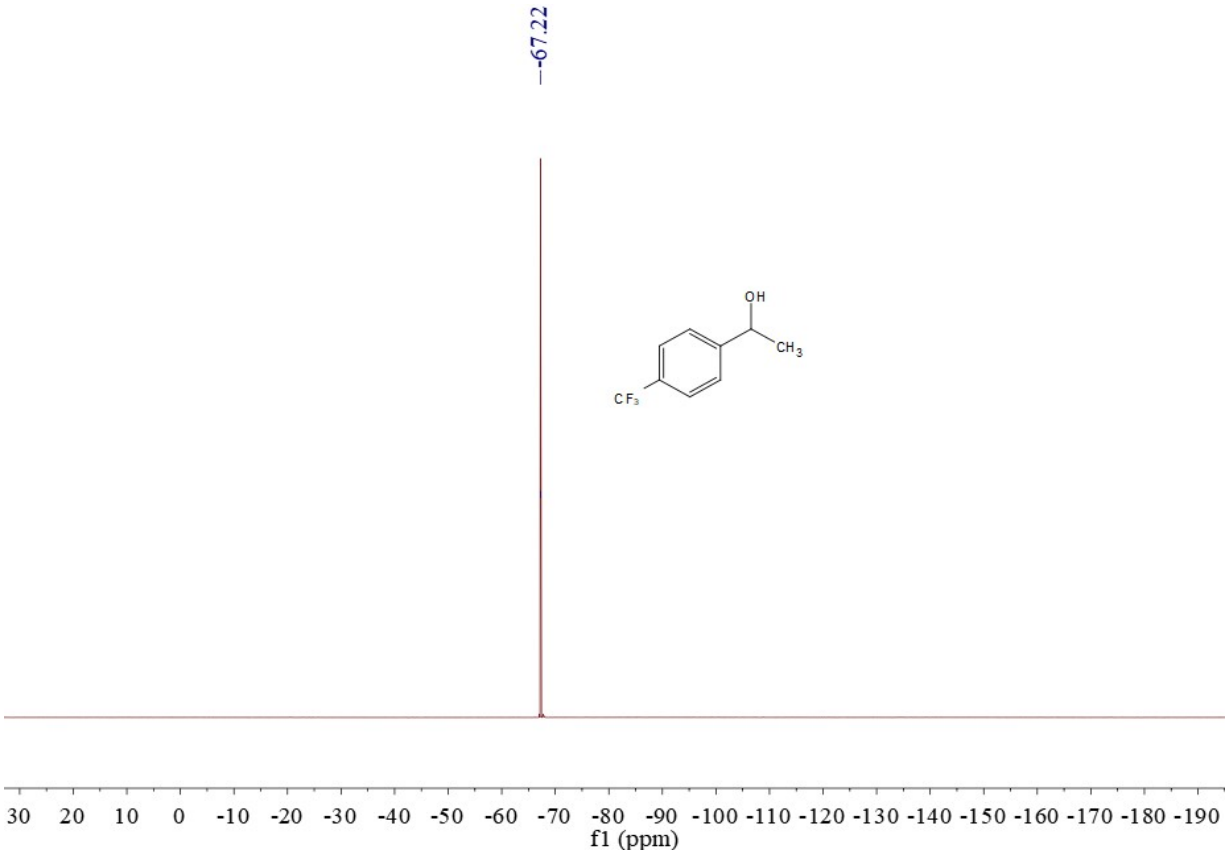
^{1}H NMR of compound 7b (400 MHz, $CDCl_3$):



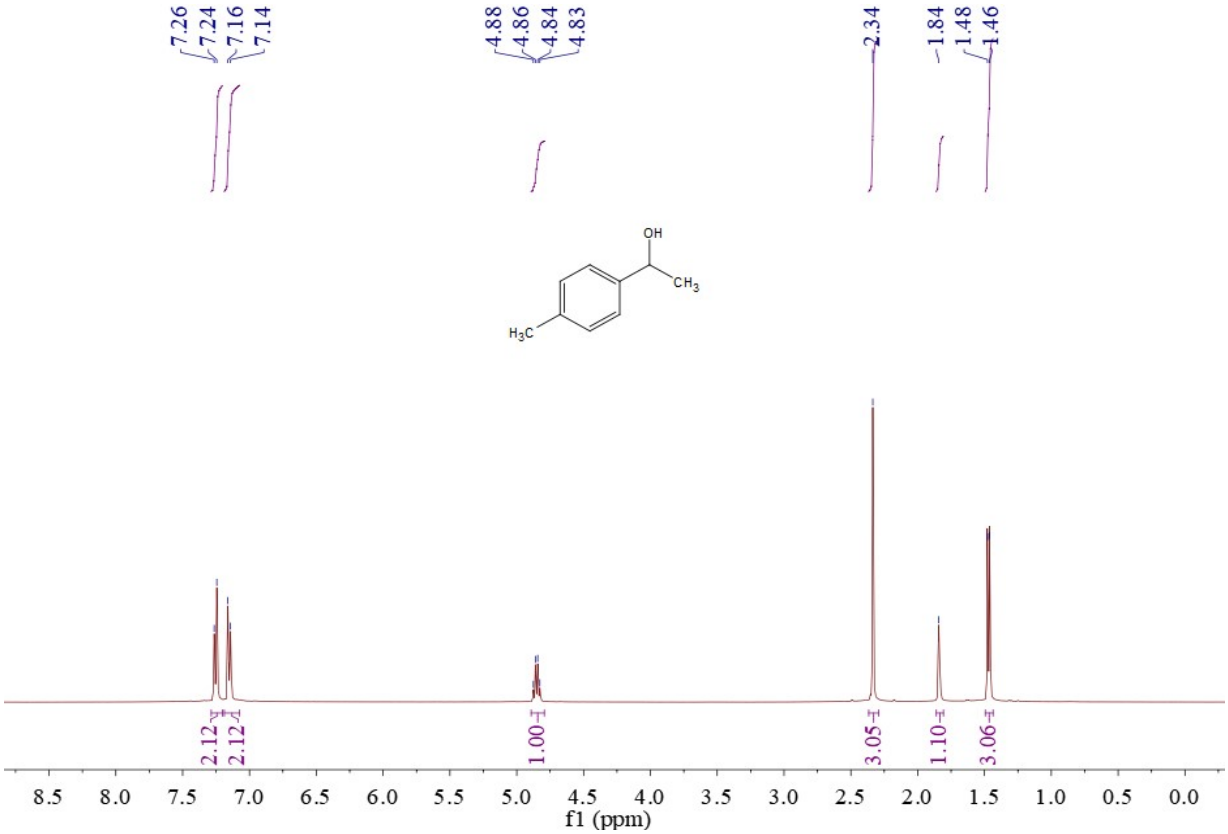
^{13}C NMR of compound 7b (100 MHz, $CDCl_3$):



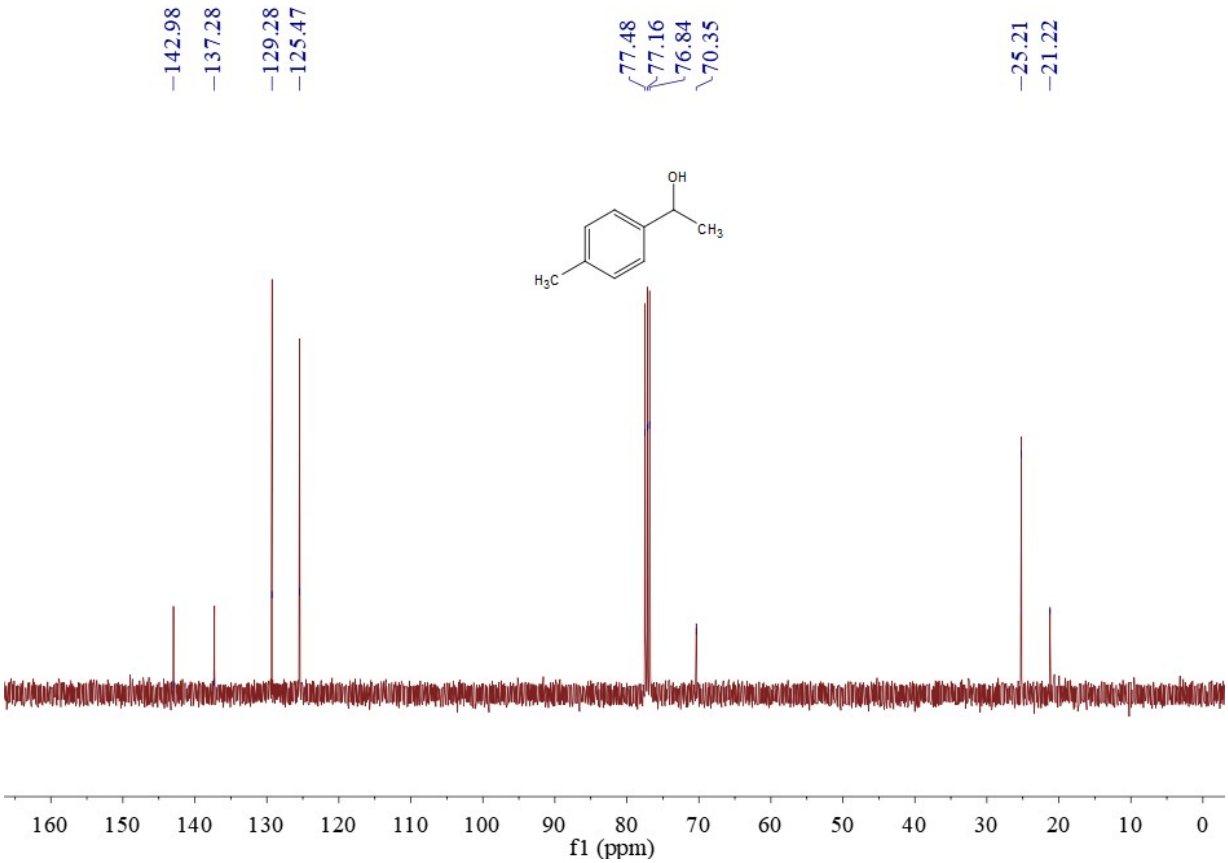
^{19}F NMR of compound 7b (376 MHz, $CDCl_3$):



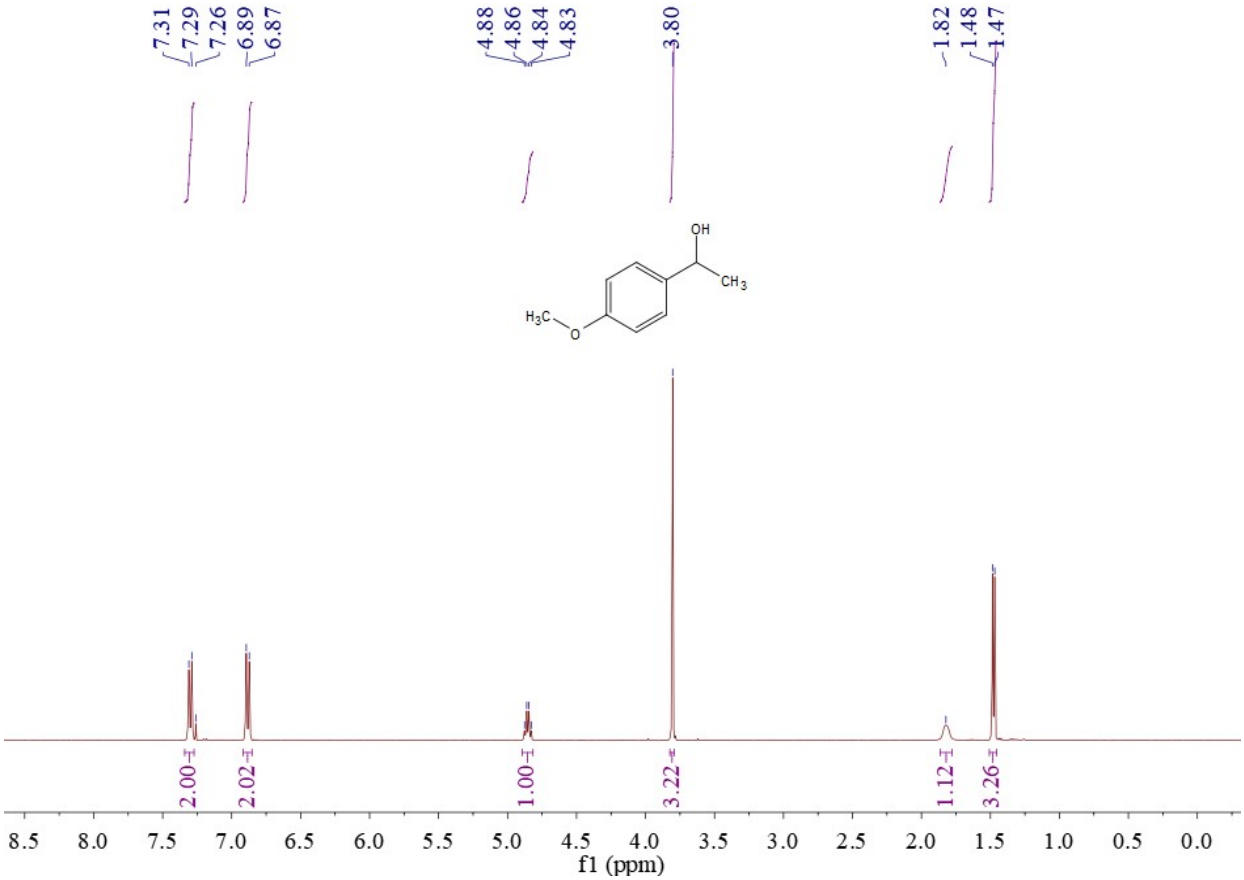
^{1}H NMR of compound 7c (400 MHz, $CDCl_3$):



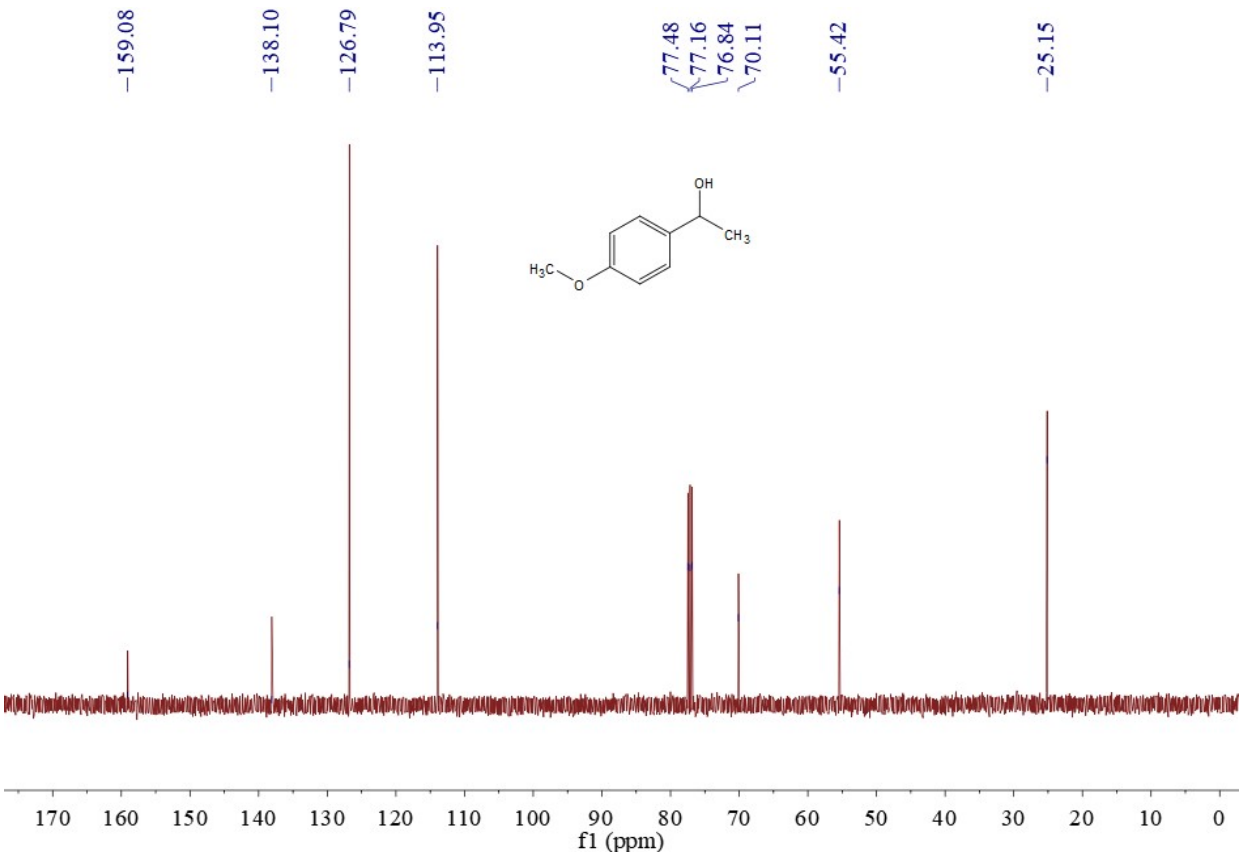
^{13}C NMR of compound 7c (100 MHz, $CDCl_3$):



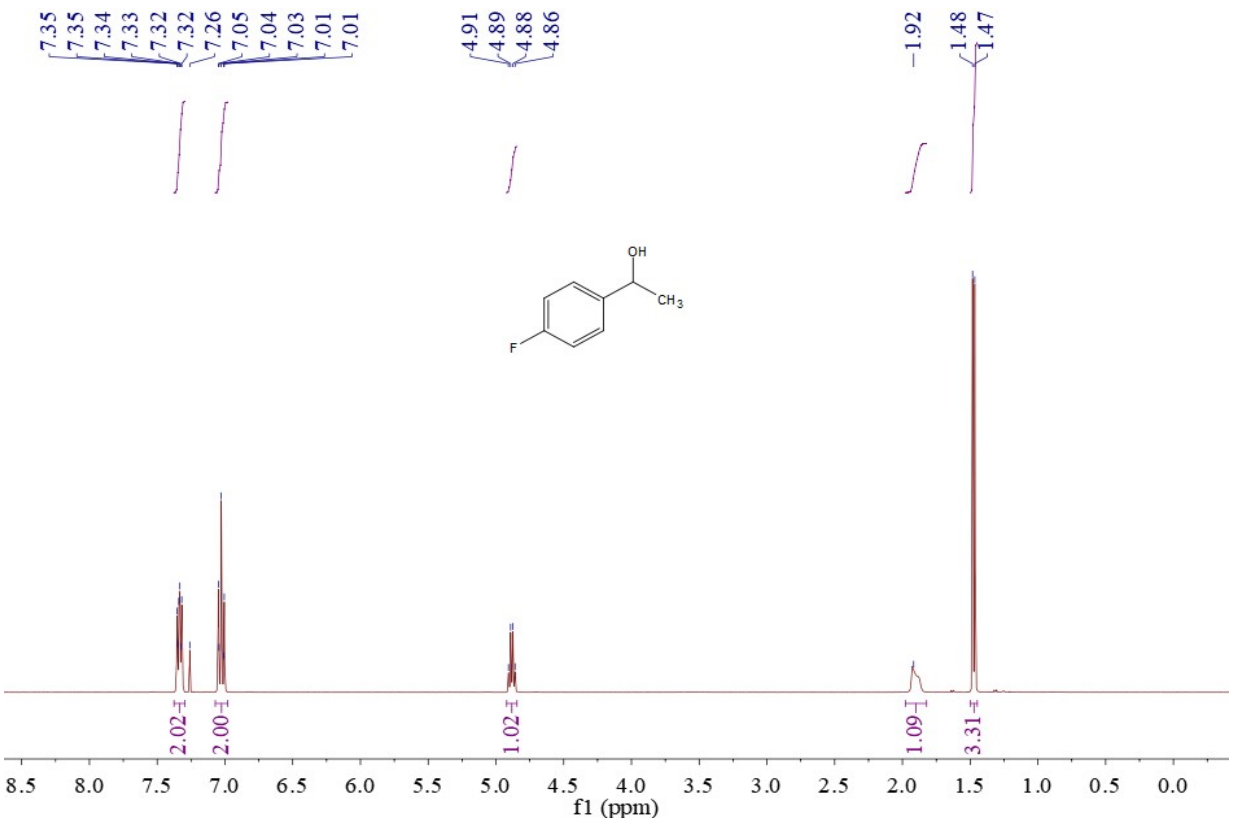
^{1}H NMR of compound 7d (400 MHz, $CDCl_3$):



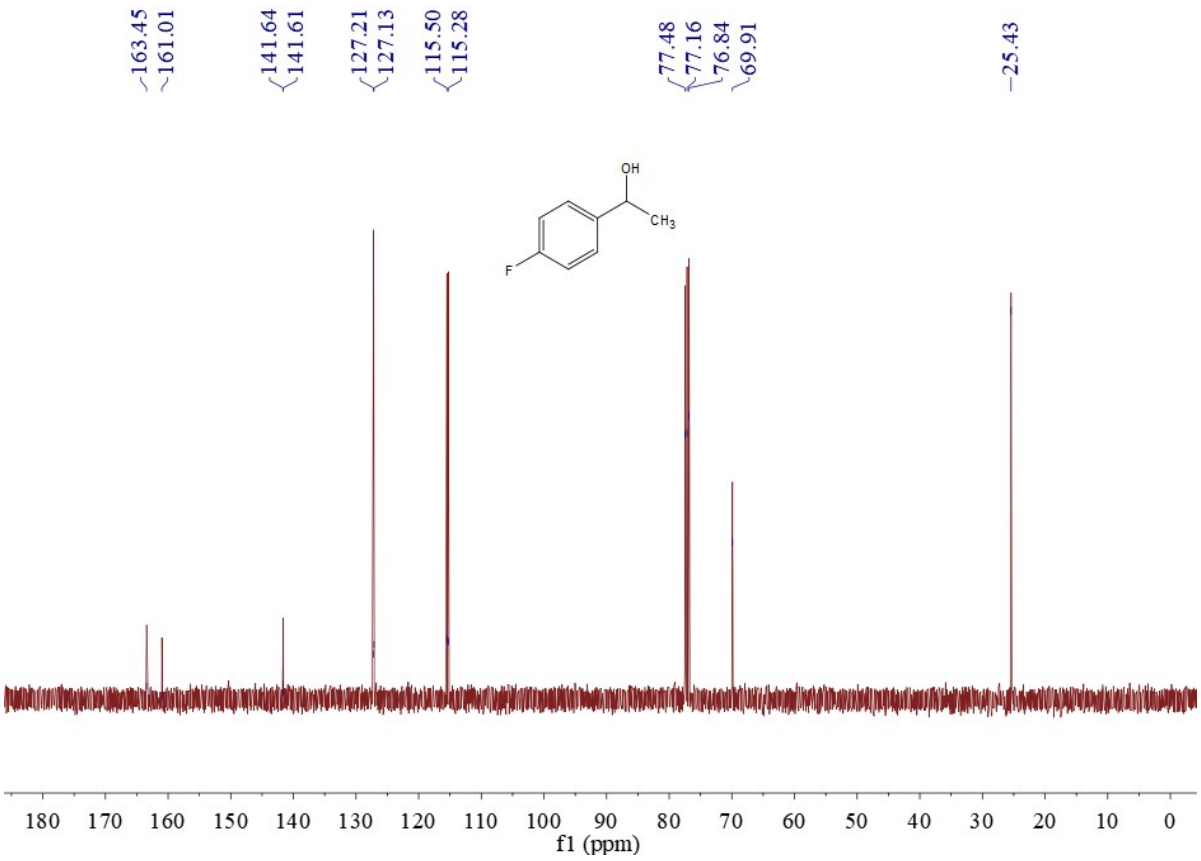
^{13}C NMR of compound 7d (100 MHz, $CDCl_3$):



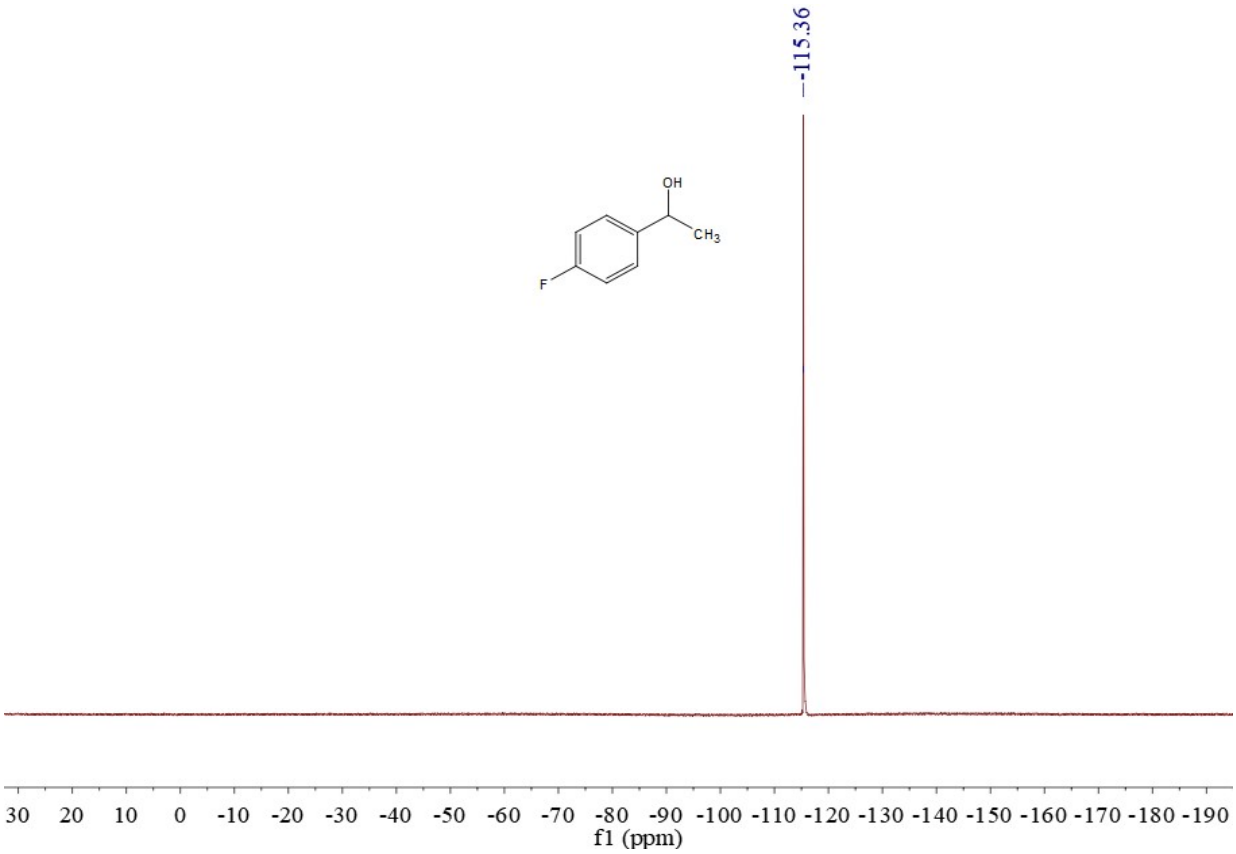
^{1}H NMR of compound 7e (400 MHz, $CDCl_3$):



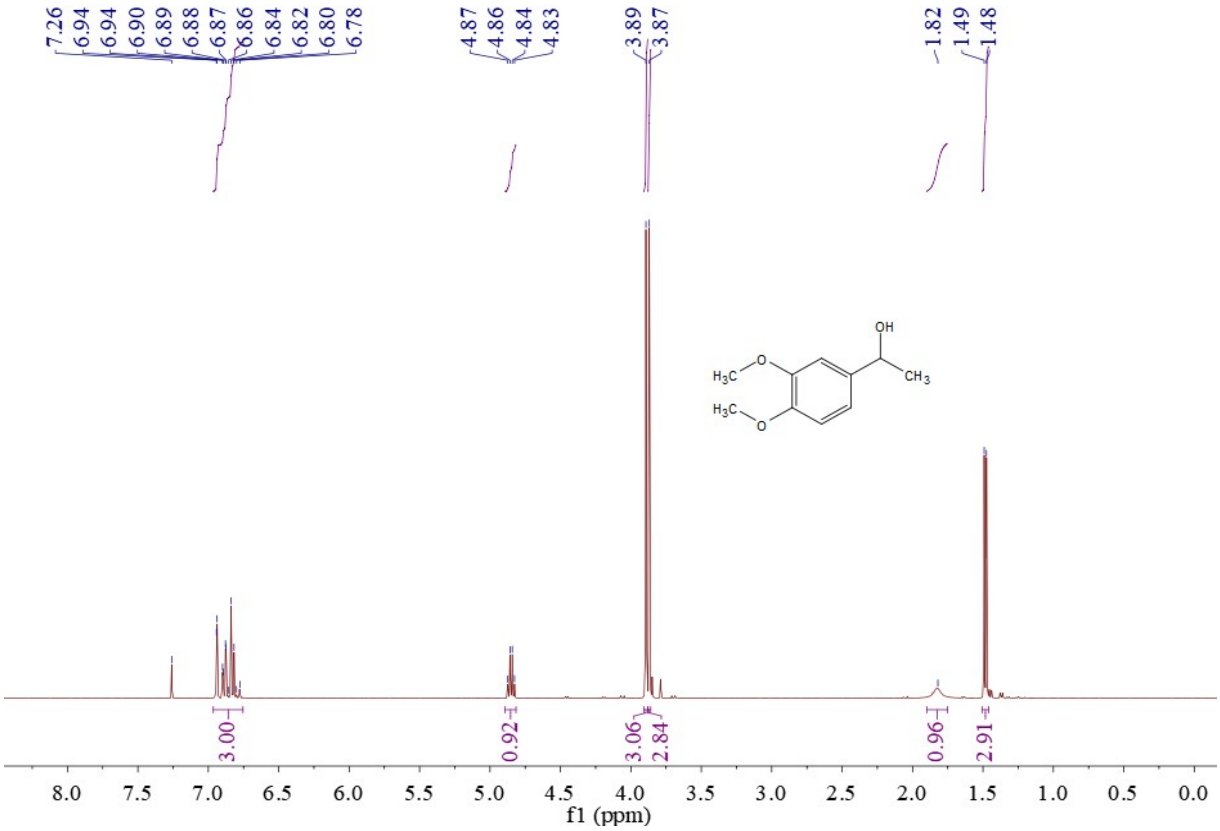
^{13}C NMR of compound 7e (100 MHz, $CDCl_3$):



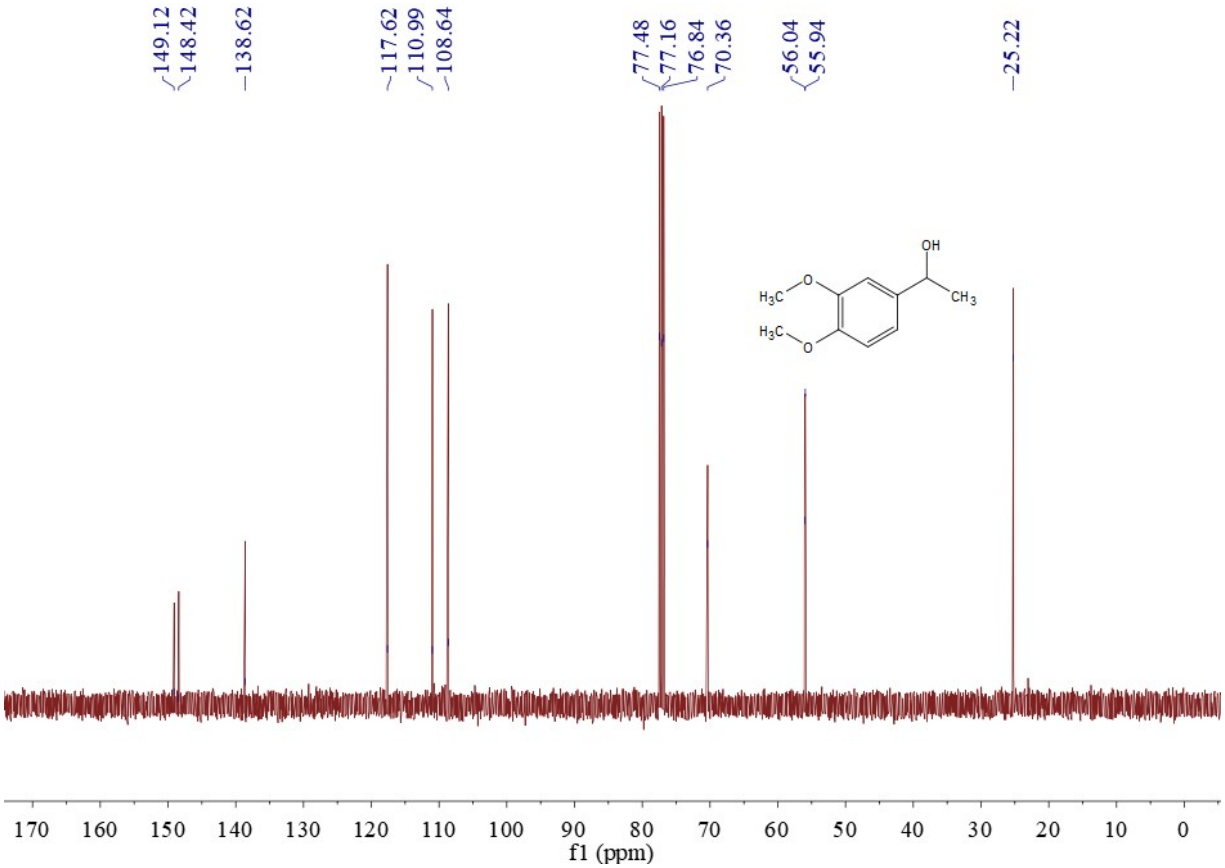
^{19}F NMR of compound 7e (376 MHz, $CDCl_3$):



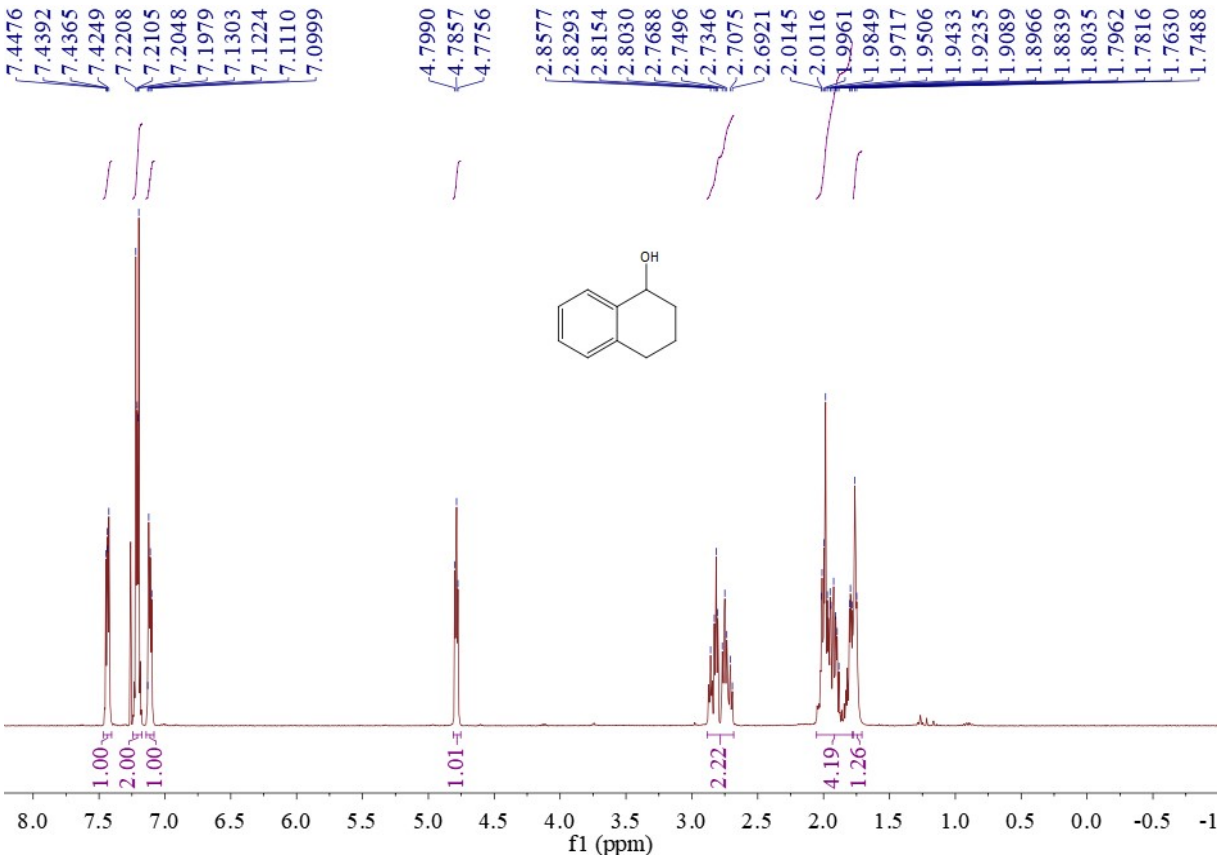
^{1}H NMR of compound 7f (400 MHz, $CDCl_3$):



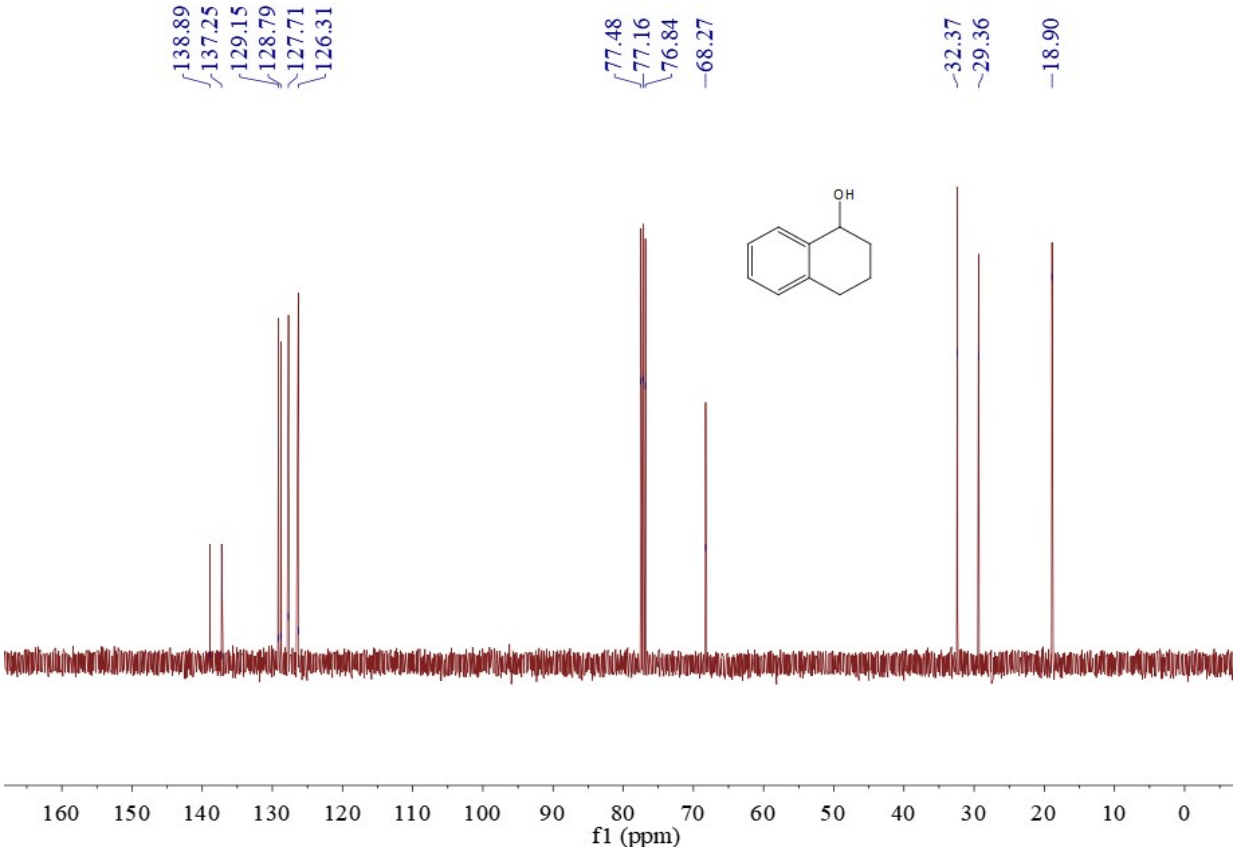
^{13}C NMR of compound 7f (100 MHz, $CDCl_3$):



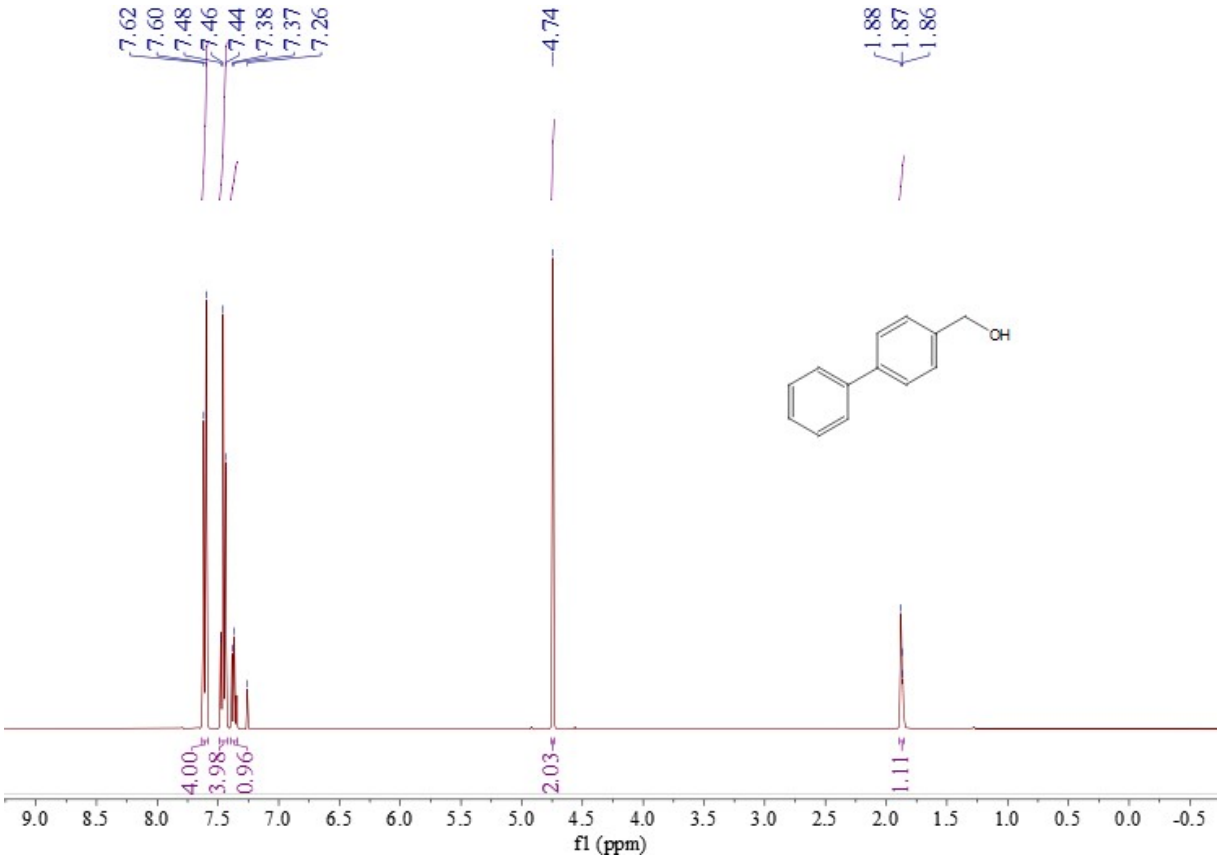
^{1}H NMR of compound 7g (400 MHz, $CDCl_3$):



^{13}C NMR of compound 7g (100 MHz, $CDCl_3$):



^{1}H NMR of compound 9 (400 MHz, $CDCl_3$):



^{13}C NMR of compound 9 (100 MHz, $CDCl_3$):