

Supporting Information

Photocatalytic Synthesis of 2,3-Diamines from Anilines and DIPEA via C-N Bond Cleavage and C-C Bond Formation

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1. General information

The reactions via general procedure was carried out under an atmosphere of argon unless otherwise noted. Column chromatography was performed with silica gel (200-300 mesh) with petroleum ether/ethyl acetate and ethyl acetate as eluents. Unless otherwise noted, all other reagents were obtained from commercial suppliers and used without further purification, all solvents was dried. ^1H NMR spectra were recorded using a Bruker 400 MHz instrument with tetramethylsilane (TMS) as an internal standard. ^{13}C NMR spectra were obtained at 100 MHz and referenced to the internal solvent signals. Mass spectra were measured on Agilent 5977 GC-MS instrument (EI). The structures of known compounds were further corroborated by comparing their ^1H NMR, ^{13}C NMR data and MS data with those in literature. Some new compounds for HRMS were tested on a Q-TOF time-of-flight with Dual ESI mass spectrometer. Some high-resolution mass spectra (HRMS) were obtained by fast atom bombardment (FAB) using a double focusing magnetic sector mass spectrometer and electron impact (EI) ionization technique. Steady-state emission spectra were recorded using a Cary Eclipse Fluorescence spectrophotometer (Agilent Technologies). The light source was 20 W blue LED (454 nm, 1 W*20, 30-50 cd/m², made in Everlight Electronics., Ltd.); borosilicate glass Schlenk tube was used as the irradiation vessel; the distance from the light source to the irradiation vessel; 2-3 cm and no filter was used. The organic photocatalyst 4CzIPN was synthesized using reported procedures.¹

2. General procedure for the diamine reaction

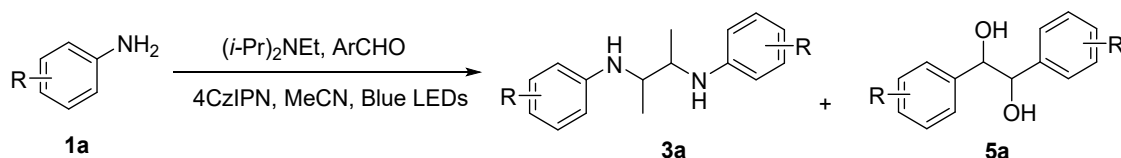


Figure S1

Under the protection of argon, a 25 mL Schlenk tube equipped with a magnetic stir bar was charged with 4CzIPN (23.7 mg, 0.03 mmol, 10 mol%), aniline (27.9 mg, 0.3 mmol, 1.0 equiv), $(i\text{-Pr})_2\text{NEt}$ (77.6 mg, 0.6 mmol, 2.0 equiv), and aromatic aldehydes (31.8 mg, 0.3 mmol, 1.0 equiv), in 2.0 mL acetonitrile. The resulting mixture was stirred for 20 h under irradiation with a 20 W blue LEDs at room temperature, and cooled by a fan to keep the temperature relatively constant. The reaction was monitored by TLC. The resulting solution was concentrated in vacuum and the residue was purified by chromatography on silica gel, eluting with the mixture of ethyl acetate/petroleum ether/ethyl acetate to give the product **3a** and **5a**.

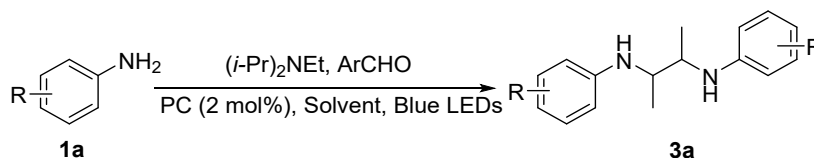
Scale-up experiment

12 mmol scale reaction: Under the protection of argon, a 100 mL oven-dried reaction vessel equipped with a magnetic stir bar was charged with 4CzIPN (189.4 mg, 0.3 mmol, 2 mol%), aniline (1.1 g, 12 mmol, 1.0 equiv), $(i\text{-Pr})_2\text{NEt}$ (3.1 g, 24 mmol, 2.0 equiv), and aromatic aldehydes (1.3 g, 12 mmol, 1.0 equiv), in 50.0 mL acetonitrile. The resulting mixture was stirred

for 20 h under irradiation with a 20 W blue LEDs at room temperature, and cooled by a fan to keep the temperature relatively constant. The reaction was monitored by TLC. The resulting solution was concentrated in vacuum and the residue was purified by chromatography on silica gel, eluting with the mixture of ethyl acetate/petroleum ether/ethyl acetate to give the product **3a** (748.8mg, 52% yield) and **5a** (590.6 mg, 46% yield)

3. Optimization of reaction conditions

Table S1. Conditions for the optimization of solvent and PC ^a

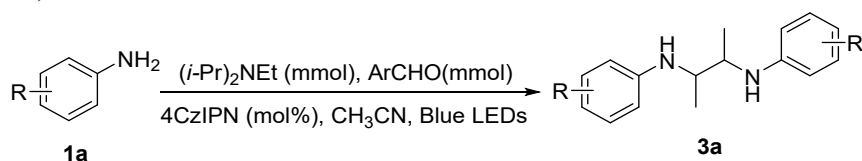


entry	solvent	PC (2 mol%)	Time (h)	Yield (%) ^b
1	THF	4CzIPN	24	34
2	CH ₃ CN	4CzIPN	24	69
3	acetone	4CzIPN	24	58
4	DMF	4CzIPN	24	52
5	toluene	4CzIPN	24	trace
6	DMSO	4CzIPN	24	trace
7	1,4-dioxane	4CzIPN	24	50
8	DCE	4CzIPN	24	65
9	DCM	4CzIPN	24	64
10	EA	4CzIPN	24	28
11	EtOH	4CzIPN	24	trace
12	HFIP	4CzIPN	24	n.d.
13	CH ₃ CN	4CzPN	24	42
14	CH ₃ CN	4CzTPN	24	55
15	CH ₃ CN	4 <i>t</i> -BuCzIPN	24	61
16	CH ₃ CN	4DP-IPN	24	56
17	CH ₃ CN	<i>fac</i> -Ir(ppy) ₃	24	53
18	CH ₃ CN	BP	24	trace
19	CH ₃ CN	Eosin Y	24	trace
20	CH ₃ CN	DDQ	24	trace

21	CH ₃ CN	Ru(bpy) ₃ Cl ₂	24	n.d.
22	CH ₃ CN	Riboflavine	24	n.d.
23	CH ₃ CN	Rhodamine B	24	trace
24	CH ₃ CN	Xanthone	24	n.d.
25	CH ₃ CN	1,4-Dicyanbenzene	24	n.d.
26 ^c	CH ₃ CN	4CzIPN	48	n.d.
27 ^d	CH ₃ CN	4CzIPN	48	n.d.
28 ^e	CH ₃ CN	4CzIPN	48	trace

^a Reaction conditions: **1a** (0.3 mmol), (*i*-Pr)₂NEt (0.6 mmol), ArCHO (0.3 mmol) and photocatalyst (2 mol%) in solvent (2 mL) at room temperature in argon under a 20 W blue LEDs (460-470 nm) irradiation, unless otherwise noted. ^b Isolated yields, *dr* = diastereomeric ratio. ^c The reaction was carried out in dark. ^d The reaction was carried out at 70 °C. ^e The reaction was carried out under air atmosphere.

Table S2. Conditions for the optimization of 4CzIPN (mmol), (*i*-Pr)₂Net (mmol) and ArCHO (mmol).^a



entry	4CzIPN (mol%)	(<i>i</i> -Pr) ₂ Net (mmol)	Time (h)	Yield (%) ^b
1	—	0.6 mmol	48	n.d.
2	2 mol%	0.6 mmol	24	69
3	4 mol%	0.6 mmol	20	72
4	6 mol%	0.6 mmol	20	78
5	8 mol%	0.6 mmol	20	78
6	10 mol%	0.6 mmol	15	82
7	12 mol%	0.6 mmol	20	62
8	10 mol%	—	48	n.d.
9	10 mol%	0.3 mmol	20	42
10	10 mol%	0.45 mmol	20	66
11	10 mol%	0.9 mmol	20	62
12 ^c	10 mol%	0.6 mmol	48	52

13 ^d	10 mol%	0.6 mmol	20	67
14 ^e	10 mol%	0.6 mmol	20	59
15 ^f	10 mol%	0.6 mmol	20	19

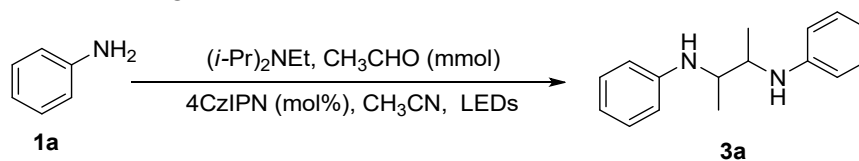
^a Reaction conditions: **1a** (0.3 mmol), (*i*-Pr)₂NEt, ArCHO (0.3 mmol), and 4CzIPN in CH₃CN (2 mL) at room temperature in argon under a 20 W blue LEDs (460-470 nm) irradiation, unless otherwise noted. ^b Isolated yields, dr = diastereomeric ratio. ^c no ArCHO was added. ^d 0.15 mmol ArCHO was added. ^e 0.45 mmol ArCHO was added. ^f 0.60 mmol ArCHO was added.

Table S3. Screening of LEDs, photocatalyst (PC), and the amount of photocatalyst ^a.

Reaction scheme: **1a** (aniline derivative) reacts with (*i*-Pr)₂NEt, ArCHO, PC (mol%), MeCN, and LEDs to produce **3a** (diamine) and **5a** (diol).

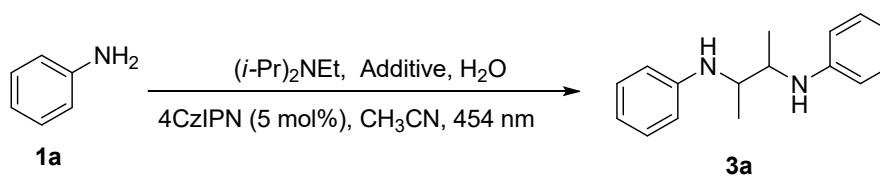
entry	LEDs ^b	PC	PC (mol%)	Diamine yield (%) ^c	Diol yield (%) ^c
1	Blue LEDs	4CzIPN	10 mol%	82	78
2	Purple LEDs	4CzIPN	10 mol%	53	74
3	Purple LEDs	4CzIPN	5 mol%	61	69
4	Purple LEDs	4CzIPN	2 mol%	53	66
5	Purple LEDs	4CzIPN	1 mol%	47	63
6	Purple LEDs	4DPAIPN	1 mol%	50	60
7	Purple LEDs	4DPAIPN	2 mol%	54	58
8	Purple LEDs	4DPAIPN	5 mol%	56	55
9	Purple LEDs	Ir(ppy) ₃	2 mol%	61	69
10	Purple LEDs	PTH	2 mol%	50	66
11	Purple LEDs	BP	2 mol%	47	63

^a Reaction conditions: **1a** (0.3 mmol), (*i*-Pr)₂NEt (0.6 mmol), and ArCHO (0.3 mmol) and PC in CH₃CN (2 mL) at room temperature in argon under a LEDs irradiation, unless otherwise noted. ^b 20 W blue LED (460-470 nm), 20 W Purple LEDs (365 nm) ^c Isolated yields.

Table S4. Screening of LEDs, the amount of CH₃CHO and 4CzIPN. ^a

entry	LEDs ^b	4CzIPN (mol%)	CH ₃ CHO (mmol)	Yield (%) ^c
1	Blue LEDs	2 mol%	0.3 mmol	54
2	Blue LEDs	5 mol%	0.3 mmol	72
3	Blue LEDs	10 mol%	0.3 mmol	85
4	Blue LEDs	10 mol%	0.15 mmol	55
5	Blue LEDs	10 mol%	0.6 mmol	48
6 ^d	Blue LEDs	10 mol%	0.6 mmol	NR
7	Purple LEDs	2 mol%	0.3 mmol	41
8	Purple LEDs	5 mol%	0.3 mmol	46
9	Purple LEDs	10 mol%	0.3 mmol	55

^a Reaction conditions: **1a** (0.3 mmol), (*i*-Pr)₂NEt (0.6 mmol) CH₃CHO and 4CzIPN in CH₃CN (2 mL) at room temperature in argon under a irradiation, unless otherwise noted. ^b 20 W blue LED (460-470 nm), 20 W Purple LEDs (365 nm) ^c Isolated yields. ^d no (*i*-Pr)₂NEt was added.

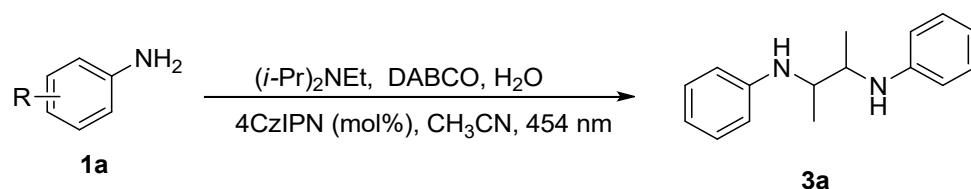
Table S5. Optimization conditions for additive and H₂O^a.

entry	Additive	H ₂ O	Time (h)	Yield (%) ^b
1	KPF ₆	/	48	30.
2	CuI	/	48	42
3	Cu(OTf) ₂	/	48	NR
4	Bu ₄ NBr	/	48	45
5	Cs ₂ CO ₃	0.6 mmol	48	NR

6	^t BuOK	0.6 mmol	48	NR
7	DABCO	0.6 mmol	40	70
8	quinuclidine	/	60	36.
9	LiBr	/	60	18
10	N-Methylpiperidine	/	60	26
11	DBU	/	60	NR

^a Reaction conditions: **1a** (0.3 mmol), (*i*-Pr)₂NEt (0.6 mmol), **additive** (0.6 mmol), **H₂O** (0.6 mmol) and **4CzIPN** (5 mol%) in CH₃CN (2 mL) at room temperature in argon under a 20 W blue LEDs (460-470 nm) irradiation, unless otherwise noted. ^b Isolated yields.

Table S6. Screening of the amount of DABCO, H₂O and 4CzIPN ^a



Entry	4CzIPN (mol%)	DABCO (mmol)	H ₂ O (mmol)	Diamine (yield %) ^b
1	2	0.6	/	44
2	5	0.6	/	25
3	10	0.6	/	trace
4	10	0.3	/	28
5	10	0.15	/	50
6	2	0.6	0.3	35
7	2	0.6	0.6	28
8	5	0.6	0.3	45
9	5	0.6	0.6	70
10	10	0.6	0.3	15
11	10	0.6	0.6	20

^a Reaction conditions: **1a** (0.3 mmol), (*i*-Pr)₂NEt (0.6 mmol), **DABCO**, **H₂O** and **4CzIPN** (5 mol%) in CH₃CN (2 mL) at room temperature in argon under a 20 W blue LEDs (460-470 nm) irradiation, unless otherwise noted. ^b Isolated yields.

Table S7. Screening of the amount of DACBO, ArCHO and 4CzIPN ^a

Entry	4CzIPN (mol%)	DABCO (mmol)	ArCHO (mmol)	Diamine (yield %) ^b
1	2	0.3	0.15	44
2	2	0.6	0.3	64
3	2	0.6	0.06	31
4	4	0.6	0.06	70
5	6	0.6	0.06	56
6	2	0.6	0.15	70
7	5	0.3	0.15	75
8	5	0.6	0.15	67
9	5	0.6	0.06	75

^a Reaction conditions: **1a** (0.3 mmol), (*i*-Pr)₂NEt (0.6 mmol), **DABCO**, **H₂O** and **4CzIPN** in CH₃CN (2 mL) at room temperature in argon under a 20 W blue LEDs (460-470 nm) irradiation, unless otherwise noted. ^b Isolated yields.

Table S8. Effect of photocatalyst, solvent and temperature on d.r. value. ^a

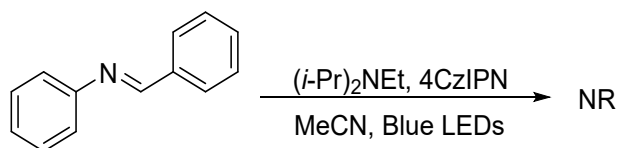
entry	Solvent	PC	Time (h)	Yield (%) ^b	d.r. ^c
1	THF	4CzIPN	24	55	2:1
2	CH ₃ CN	4CzIPN	30	70	2:3
3	CH ₃ COCH ₃	4CzIPN	24	58	1:1
4	DMF	4CzIPN	24	52	2:3
5	DMA	4CzIPN	24	41	2:3
6	DCE	4CzIPN	24	65	1:2
7	DMF:MeCN=1:1	4CzIPN	24	55	2:3
8	DMA:MeCN=1:1	4CzIPN	24	50	2:3

9	CH ₃ CN	4CzPN	48	42	1:1
10	CH ₃ CN	4CzTPN	37	55	1:1
11	CH ₃ CN	4 <i>t</i> BuCzIPN	48	42	1:1
12	CH ₃ CN	<i>fac</i> -Ir(ppy) ₃	48	53	1:1
13	CH ₃ CN	[Ir(dF(CF ₃ ppy) ₂)(5, ,5'-CF ₃ -bpy)]PF ₆	48	50	1:1
14 ^d	CH ₃ CN	4CzIPN	48	NR	
15 ^e	CH ₃ CN	4CzIPN	48	20%	1:1

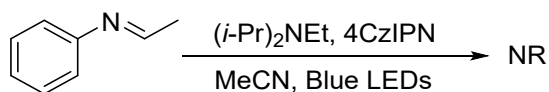
^a Reaction conditions: **1a** (0.3 mmol), (*i*-Pr)₂NEt (0.6 mmol), **ArCHO** (0.3 mmol) and **PC** (2 mol%) in solvent (2 mL) at room temperature in argon under a 20 W blue LEDs (460-470 nm) irradiation, unless otherwise noted. ^b Isolated yields, ^c *dr* = diastereomeric ratio. ^d T = -20 – 0°C. ^e T = 40 – 60°C.

Mechanistic studies

4.1. Control experiment



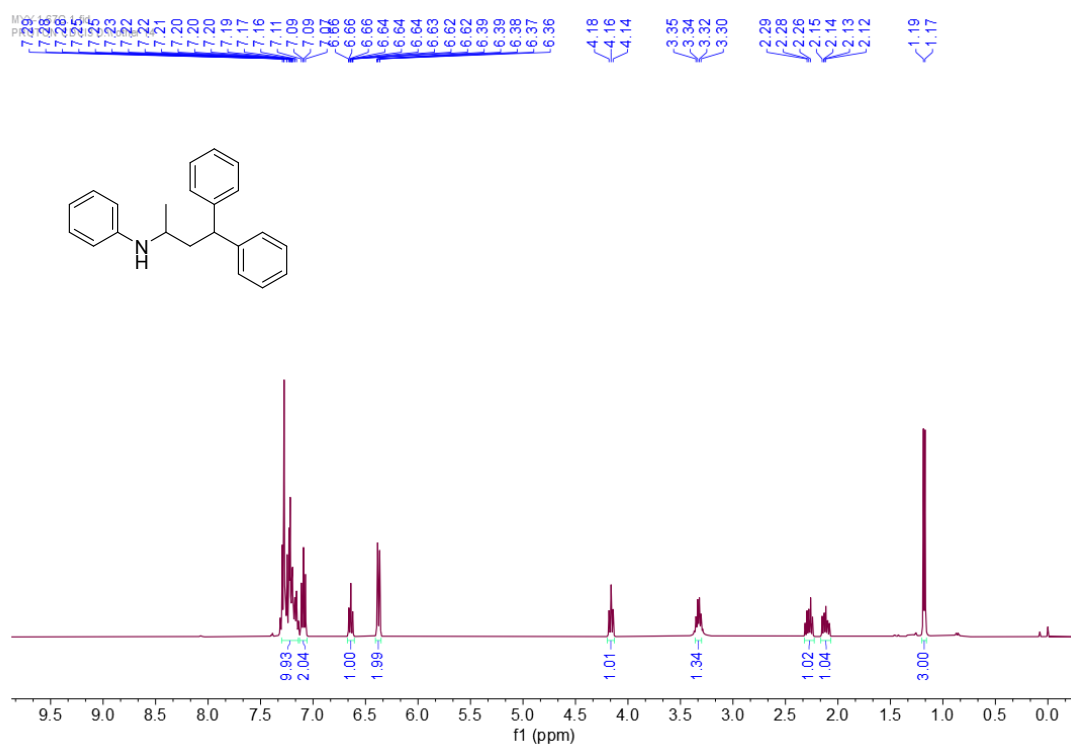
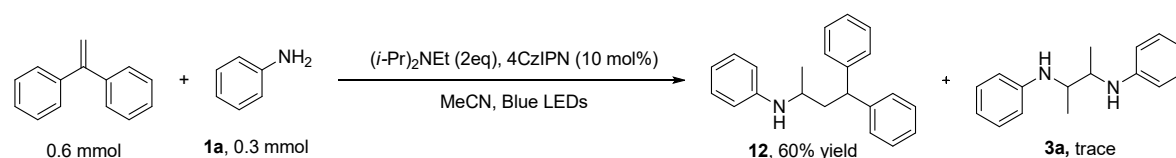
Under the protection of argon, N-benzylideneaniline (54.4 mg, 0.3 mmol, 1.0 equiv), 4CzIPN (23.7 mg, 0.03 mmol, 10 mol%), and (*i*-Pr)₂NEt (77.6 mg, 0.6 mmol, 2.0 equiv), in 2.0 mL acetonitrile, were added sequentially to a 25 mL Schlenk tube equipped with a magnetic stir bar. When reaction mixture was stirred under 20 W blue LEDs irradiation at room temperature, and cooled by a fan to keep the temperature relatively constant. The reaction was monitored by TLC. The product was not detected.



Under the protection of argon, N-phenylethanamine (35.7 mg, 0.3 mmol, 1.0 equiv), 4CzIPN (23.7 mg, 0.03 mmol, 10 mol%), and (*i*-Pr)₂NEt (77.6 mg, 0.6 mmol, 2.0 equiv), in 2.0 mL acetonitrile, were added sequentially to a 25 mL Schlenk tube equipped with a magnetic stir bar. When reaction mixture was stirred under 20 W blue LEDs irradiation at room temperature, and cooled by a fan to keep the temperature relatively constant. The reaction was monitored by TLC. The products was not detected.

4.2. Radical-trapping experiment with 1,1-Diphenylethylene

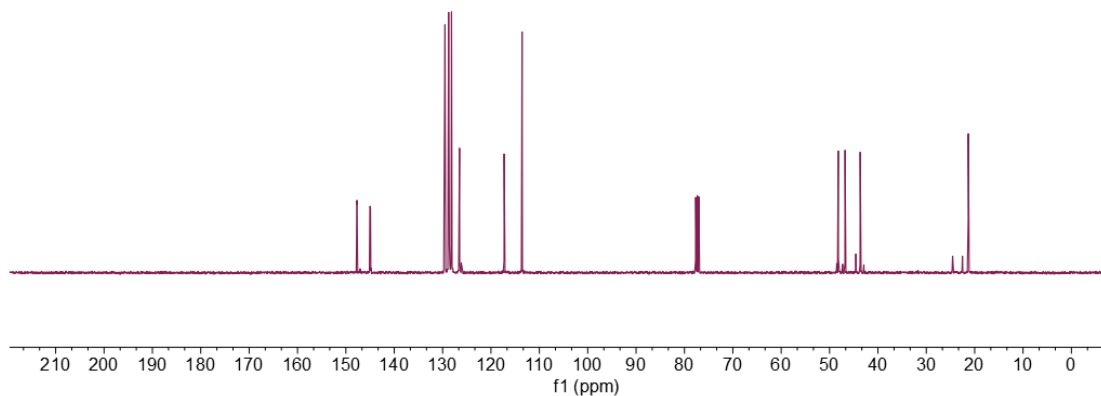
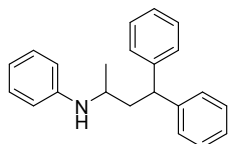
According to general procedure 2, When 1,1-Diphenylethylene was added, the product **3a** was only a trace amount of the product **3a** was detected by GC-MS analysis, the trapped product was obtained as main product, and purified by silica gel chromatography (PE/EA = 50:1) as White solid (MW = 301.4, 58.8 mg, 0.20 mmol, 65% yield, mp:52-53 °C). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.14 (m, 10H), 7.09 (dd, *J* = 8.6, 7.2 Hz, 2H), 6.64 (tt, *J* = 7.3, 1.2 Hz, 1H), 6.41 – 6.35 (m, 2H), 4.16 (t, *J* = 7.8 Hz, 1H), 3.33 (q, *J* = 6.4 Hz, 1H), 2.32 – 2.23 (m, 1H), 2.13 (dd, *J* = 8.1, 6.0 Hz, 1H), 1.18 (d, *J* = 6.2 Hz, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 147.7, 145.0, 144.9, 129.5, 128.8, 128.8, 128.2, 128.2, 126.6, 126.5, 117.3, 113.6, 48.2, 46.8, 43.7, 21.3. HRMS (ESI) calcd for C₁₂H₂₃N, [M+H]⁺ *m/z* 302.1903; Found: 302.1906.



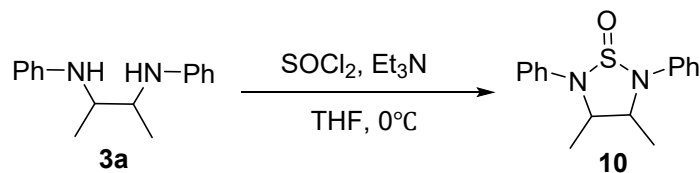
147.7
145.0
144.9
129.5
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128.2
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126.6
126.5
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-113.6

48.2
46.8
43.7

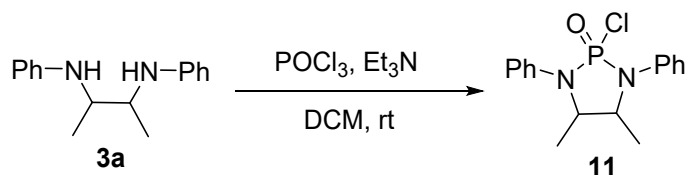
-21.3



4. Product derivatizations



Under the protection of argon, 1,2-diamines (72.0 mg, 0.3 mmol, 1.0 equiv), SOCl_2 (48 mg, 0.4 mmol, 1.5 equiv), and Et_3N (60.6 mg, 0.6 mmol, 2.0 equiv), in 2.0 mL THF. were added sequentially to a 25 mL Schlenk tube equipped with a magnetic stir bar. The resulting solution was stirred at 0 °C under argon atmosphere with TLC monitoring. The resulting solution was concentrated in vacuum and the residue was purified by chromatography on silica gel, eluting with the mixture of ethyl acetate/petroleum ether/ethyl acetate to give the product **10** (35 mg, 40% yield)²



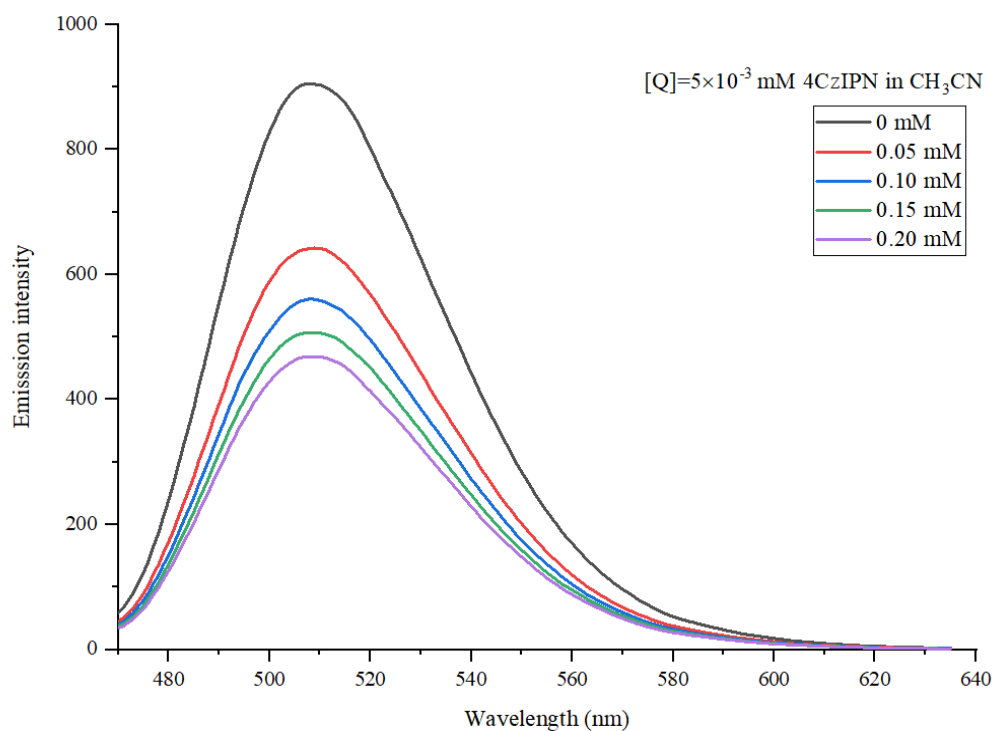
Under the protection of argon, 1,2-diamines (72.0 mg, 0.3 mmol, 1.0 equiv), POCl_2 (61.2 mg, 0.4 mmol, 1.5 equiv), and Et_3N (60.6 mg, 0.6 mmol, 2.0 equiv), in 2.0 mL DCM. were added sequentially to a 25 mL Schlenk tube equipped with a magnetic stir bar. The resulting solution was stirred at room temperature under argon atmosphere with TLC monitoring. The resulting

solution was concentrated in vacuum and the residue was purified by chromatography on silica gel, eluting with the mixture of ethyl acetate/petroleum ether/ethyl acetate to give the product **11** (20 mg, 21% yield)³

5. Stern-Volmer experiment

Formulation solution: N,N-Diisopropylethylamine was dissolved in CH₃CN in a 5 mL volumetric flask to set the concentration to be 0.05 mM, 0.10 mM, 0.15 mM, 0.20 mM. Photocatalyst 4CzIPN was dissolved in CH₃CN (50 mL) to set the concentration to be 0.1 mM.

Experimental procedure: Steady-state emission spectra were recorded using a Cary Eclipse Fluorescence Spectrophotometer (Agilent Technologies) (**Figure S2**). N,N-Diisopropylethylamine was added to an CH₃CN solution of 4CzIPN (0.1 mM) and made to a fixed concentration in a volumetric flask. The solutions were then transferred to a septum topped quartz cuvette. Samples were irradiated at 440 nm and area under the graph was calculated and used for determining the Stern-Volmer quenching values. A pre-weighed amount of N,N-Diisopropylethylamine was dissolved in CH₃CN solution of 4CzIPN (0.1 mM) and made to fixed concentration in a volumetric flask. The solution were then transferred to a septum topped quartz cuvette. Due to competing absorption of the imine substrate, samples were irradiated at 440 nm and the emission intensity at 510 nm was used to determine the Stern-Volmer quenching values.



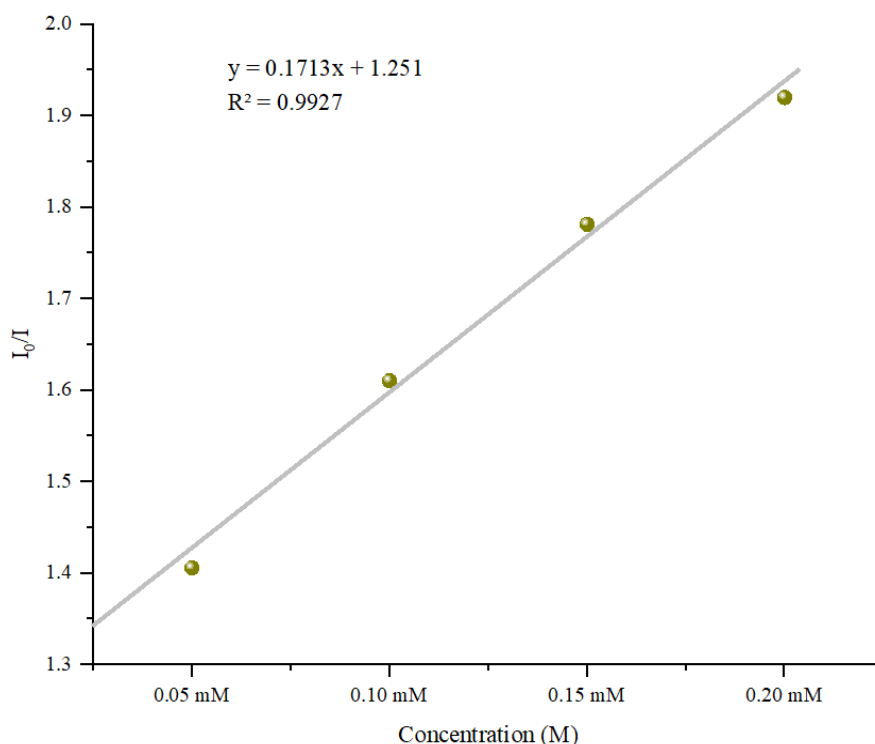
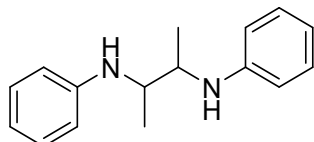


Figure 2. Emission quenching of 4CzIPN with (*i*-Pr)₂NEt in CH₃CN

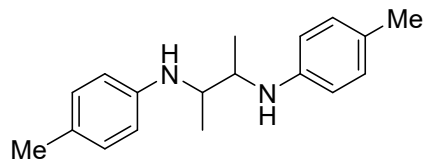
6. Characterization data of products

N², N³-diphenylbutane-2,3-diamine (**3a**)



Purified by silica gel chromatography (petroleum ether/ethyl acetate = 20:1, v/v), the desired product **3a** was obtained as a colourless oil. (30 mg, 82% yield). *meso/dl* 1:1; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.18 (dtd, *J* = 14.3, 7.2, 1.9 Hz, 4H), 6.76 – 6.59 (m, 6H), 3.78 – 3.71 (m, 1H), 3.60 (dt, *J* = 6.1, 4.3 Hz, 1H), 1.26 – 1.18 (m, 6H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 147.6, 147.6, 129.5, 129.4, 117.7, 117.6, 113.8, 113.6, 52.6, 52.3, 17.0, 16.3. HRMS (ESI) calcd for C₁₆H₂₀N₂, [M+H]⁺ *m/z* 241.1699; Found: 241.1692.

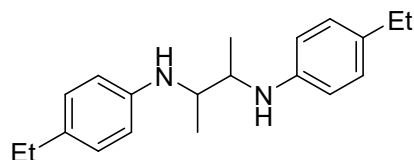
N², N³-di-*p*-tolylbutane-2,3-diamine (**3b**)



Purified by silica gel chromatography (petroleum ether/ethyl acetate = 30:1, v/v), the desired product **3b** was obtained as a colourless oil. (31 mg, 77% yield). *meso/dl* 1:1.5; ¹H NMR (400

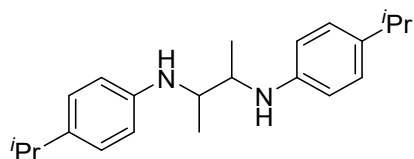
MHz, Chloroform-*d*) δ 7.03 – 6.93 (m, 4H), 6.59 – 6.49 (m, 4H), 3.72 – 3.62 (m, 1H), 3.51 (ddd, $J = 9.8, 7.1, 4.9$ Hz, 2H), 2.24 (d, $J = 4.4$ Hz, 6H), 1.21 – 1.14 (m, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 145.3, 145.2, 129.9, 129.8, 126.9, 126.8, 114.1, 113.9, 52.9, 52.7, 29.7, 20.4, 16.9, 16.2. HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{24}\text{N}_2$, $[\text{M}+\text{H}]^+$ m/z 269.2012; Found: 269.2011.

N^2, N^3 -bis(4-ethylphenyl)butane-2,3-diamine (3c)



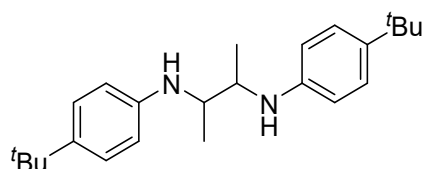
Purified by silica gel chromatography (petroleum ether/ethyl acetate = 30:1, v/v), the desired product **3c** was obtained as a yellow oil. (34 mg, 80% yield). *meso/dl* 1:1.5; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.05 – 6.96 (m, 4H), 6.61 – 6.52 (m, 4H), 3.72 – 3.63 (m, 1H), 3.52 (dt, $J = 5.9, 4.2$ Hz, 1H), 2.54 (qd, $J = 7.6, 4.2$ Hz, 4H), 1.23 – 1.13 (m, 12H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 145.6, 145.5, 133.5, 133.4, 128.8, 128.7, 114.1, 113.8, 52.9, 52.7, 28.0, 17.1, 16.3, 16.0. HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{28}\text{N}_2$, $[\text{M}+\text{H}]^+$ m/z 297.2325; Found: 297.2327.

N^2, N^3 -bis(4-isopropylphenyl)butane-2,3-diamine (3d)



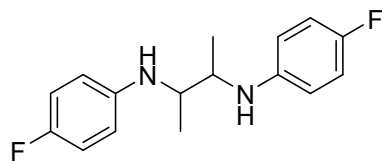
Purified by silica gel chromatography (petroleum ether/ethyl acetate = 30:1, v/v), the desired product **3d** was obtained as a colourless oil. (37 mg, 76% yield). *meso/dl* 1:2; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.09 – 6.96 (m, 4H), 6.62 – 6.51 (m, 4H), 3.70 – 3.61 (m, 1H), 3.50 (dt, $J = 5.9, 4.2$ Hz, 2H), 2.85 – 2.73 (m, 2H), 1.21 – 1.12 (m, 18H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 145.6, 145.5, 138.1, 138.0, 127.2, 127.2, 113.8, 113.6, 52.9, 52.7, 33.1, 33.1, 24.2, 17.1, 16.3. HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{32}\text{N}_2$, $[\text{M}+\text{Na}]^+$ m/z 347.2458; Found: 347.2453.

N^2, N^3 -bis(4-(tert-butyl)phenyl)butane-2,3-diamine (3e)



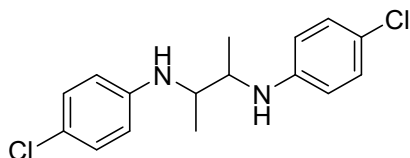
Purified by silica gel chromatography (petroleum ether/ethyl acetate = 30:1, v/v), the desired product **3e** was obtained as a colourless oil. (35 mg, 66% yield). *meso/dl* 1:1.7; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.25 – 7.16 (m, 4H), 6.65 – 6.53 (m, 4H), 3.73 – 3.66 (m, 1H), 3.53 (dt, $J = 5.9, 4.2$ Hz, 2H), 1.29 (d, $J = 3.5$ Hz, 18H), 1.24 – 1.15 (m, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 145.3, 145.2, 140.4, 140.3, 126.2, 126.1, 113.5, 113.3, 52.9, 52.6, 33.9, 33.9, 31.6, 17.2, 16.4. HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{36}\text{N}_2$, $[\text{M}+\text{H}]^+$ m/z 353.2951; Found: 353.2950.

N², N³-bis(4-fluorophenyl)butane-2,3-diamine (**3f**)



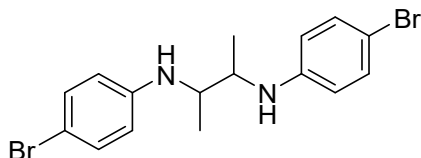
Purified by silica gel chromatography (petroleum ether/ethyl acetate = 15:1, v/v), the desired product **3f** was obtained as a yellow oil. (30 mg, 72% yield). *meso/dl* 1:1.5; ¹H NMR (400 MHz, Chloroform-*d*) δ 6.94 – 6.78 (m, 4H), 6.60 – 6.46 (m, 4H), 3.66 – 3.56 (m, 1H), 3.44 (dd, *J* = 4.6, 1.8 Hz, 2H), 1.23 – 1.11 (m, 6H). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -119.14 – -135.60 (m). ¹³C NMR (101 MHz, Chloroform-*d*) δ 155.9 (dd, *J* = 235.4, 6.3 Hz), 143.9 (dd, *J* = 4.2, 2.0 Hz), 121.1 – 102.1 (m), 53.6, 53.0, 17.0, 16.1. HRMS (ESI) calcd for C₁₆H₁₈F₂N₂, [M+H]⁺ *m/z* 277.1511; Found: 277.1510.

N², N³-bis(4-chlorophenyl)butane-2,3-diamine (**3g**)



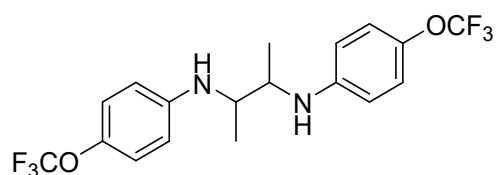
Purified by silica gel chromatography (petroleum ether/ethyl acetate = 15:1, v/v), the desired product **3g** was obtained as a yellow oil. (32 mg, 70% yield). *meso/dl* 1:1.2; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.16 – 7.06 (m, 4H), 6.59 – 6.46 (m, 4H), 3.67 (q, *J* = 6.0 Hz, 1H), 3.61 (s, 2H), 3.51 (dt, *J* = 5.9, 4.2 Hz, 1H), 1.19 (dd, *J* = 11.0, 6.0 Hz, 6H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 146.1, 146.0, 129.3, 129.2, 129.1, 122.2, 122.1, 114.8, 114.6, 52.8, 52.3, 17.0, 16.2. HRMS (ESI) calcd for C₁₆H₁₈Cl₂N₂, [M+H]⁺ *m/z* 309.0920; Found: 309.0924.

N², N³-bis(4-bromophenyl)butane-2,3-diamine (**3h**)



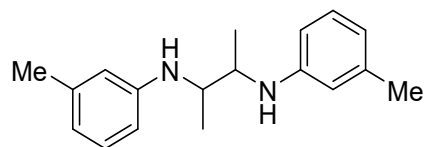
Purified by silica gel chromatography (petroleum ether/ethyl acetate = 15:1, v/v), the desired product **3h** was obtained as a yellow oil. (36 mg, 60% yield). *meso/dl* 1.4:1; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.09 (dtd, *J* = 13.5, 8.1, 6.7 Hz, 2H), 6.45 – 6.24 (m, 6H), 3.69 (q, *J* = 5.9 Hz, 1H), 3.59 – 3.50 (m, 1H), 1.21 (dd, *J* = 11.0, 6.0 Hz, 6H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 146.5, 146.5, 132.1, 132.1, 115.3, 115.1, 109.2, 109.1, 52.7, 52.2, 16.9, 16.2. HRMS (ESI) calcd for C₁₆H₁₈Br₂N₂, [M+H]⁺ *m/z* 398.9890; Found: 398.9886.

N², N³-bis(4-(trifluoromethoxy)phenyl)butane-2,3-diamine (**3i**)



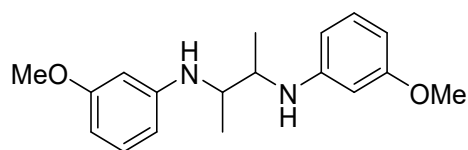
Purified by silica gel chromatography (petroleum ether/ethyl acetate = 7:1, v/v), the desired product **3i** was obtained as a colourless oil. (34 mg, 56% yield). *meso/dl* 2.5:1; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.07 – 6.97 (m, 4H), 6.61 – 6.50 (m, 4H), 3.73 – 3.63 (m, 3H), 3.52 (dd, *J* = 4.5, 1.8 Hz, 1H), 1.21 (dd, *J* = 13.1, 5.9 Hz, 6H). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -58.5. ¹³C NMR (100 MHz, Chloroform-*d*) δ 146.3, 146.3, 122.6, 122.6, 114.0, 113.7, 53.0, 52.4, 17.1, 16.1. HRMS (ESI) calcd for C₁₈H₁₈F₆N₂O₂, [M+H]⁺ *m/z* 409.1345; Found: 409.1342.

N², N³-di-*m*-tolylbutane-2,3-diamine (**3j**)



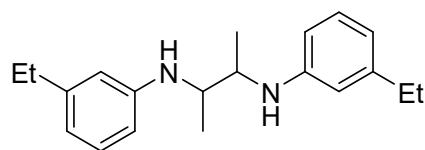
Purified by silica gel chromatography (petroleum ether/ethyl acetate = 30:1, v/v), the desired product **3j** was obtained as a colourless oil. (35 mg, 88% yield). *meso/dl* 1:1.4; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.10 – 7.01 (m, 2H), 6.57 – 6.39 (m, 6H), 3.71 (dt, *J* = 7.1, 1.7 Hz, 1H), 3.58 (dt, *J* = 5.8, 4.3 Hz, 2H), 2.26 (d, *J* = 17.7 Hz, 6H), 1.22 – 1.15 (m, 6H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 147.7, 147.6, 139.2, 139.2, 129.3, 129.3, 118.6, 118.5, 114.6, 114.4, 111.0, 110.8, 52.4, 52.2, 21.7, 21.7, 16.9, 16.4. HRMS (ESI) calcd for C₁₈H₂₄N₂, [M+H]⁺ *m/z* 269.2012; Found: 269.2018.

N², N³-bis(3-methoxyphenyl)butane-2,3-diamine (**3k**)



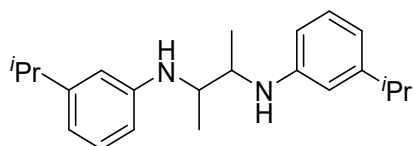
Purified by silica gel chromatography (petroleum ether/ethyl acetate = 10:1, v/v), the desired product **3k** was obtained as a yellow oil. (29 mg, 65% yield). *meso/dl* 1:1; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.09 (dt, *J* = 14.0, 8.1 Hz, 2H), 6.36 – 6.13 (m, 6H), 3.79 (s, 3H), 3.73 (s, 3H), 3.68 (s, 1H), 3.63 – 3.56 (m, 1H), 1.22 (dd, *J* = 11.3, 5.9 Hz, 6H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 160.9, 160.9, 149.0, 148.9, 130.1, 130.1, 106.7, 106.6, 103.0, 102.9, 99.4, 55.1, 55.0, 52.5, 52.2, 29.7, 17.0, 16.3. HRMS (ESI) calcd for C₁₈H₂₄O₂N₂, [M+H]⁺ *m/z* 301.1910; Found: 301.1909.

N², N³-bis(3-ethylphenyl)butane-2,3-diamine (3l)



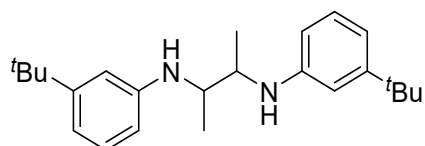
Purified by silica gel chromatography (petroleum ether/ethyl acetate = 30:1, v/v), the desired product **3l** was obtained as a yellow oil. (36 mg, 85% yield). *meso/dl* 1:2.5; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.15 – 7.03 (m, 2H), 6.61 – 6.39 (m, 6H), 3.72 (d, *J* = 6.0 Hz, 1H), 3.62 – 3.56 (m, 1H), 2.55 (dq, *J* = 17.9, 7.6 Hz, 4H), 1.20 (dt, *J* = 15.4, 7.4 Hz, 12H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 147.8, 147.7, 145.7, 145.6, 129.4, 129.3, 117.4, 117.3, 113.6, 113.3, 111.1, 110.9, 52.4, 52.3, 29.2, 29.1, 16.9, 16.4, 15.7, 15.6. HRMS (ESI) calcd for C₂₀H₂₈N₂, [M+H]⁺ *m/z* 297.2325; Found: 297.2324.

N², N³-bis(3-isopropylphenyl)butane-2,3-diamine (3m)



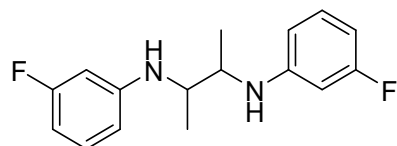
Purified by silica gel chromatography (petroleum ether/ethyl acetate = 30:1, v/v), the desired product **3m** was obtained as a colourless oil. (43 mg, 88% yield). *meso/dl* 1:1.4; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.18 – 7.03 (m, 2H), 6.65 – 6.36 (m, 6H), 3.77 – 3.52 (m, 3H), 2.85 – 2.71 (m, 2H), 1.22 (ddd, *J* = 15.0, 7.0, 2.0 Hz, 18H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 150.3, 150.2, 147.6, 147.5, 129.3, 129.2, 115.9, 115.8, 112.2, 112.0, 111.0, 110.8, 52.3, 52.3, 34.3, 34.2, 24.0, 24.0, 16.8, 16.3. HRMS (ESI) calcd for C₁₈H₂₄N₂, [M+H]⁺ *m/z* 325.2638; Found: 325.2636.

N², N³-bis(3-(tert-butyl)phenyl)butane-2,3-diamine (3n)



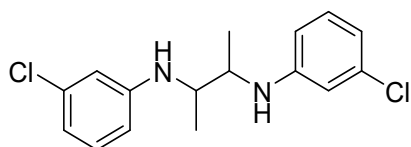
Purified by silica gel chromatography (petroleum ether/ethyl acetate = 30:1, v/v), the desired product **3n** was obtained as a colourless oil. (41 mg, 78% yield). *meso/dl* 1:1.7; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.16 – 7.06 (m, 2H), 6.83 – 6.61 (m, 4H), 6.47 (dddd, *J* = 20.7, 8.0, 2.4, 1.2 Hz, 2H), 3.76 – 3.69 (m, 1H), 3.68 – 3.54 (m, 2H), 1.31 – 1.17 (m, 24H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 152.5, 152.5, 147.4, 147.3, 129.1, 129.0, 115.0, 114.9, 111.5, 111.4, 110.5, 110.2, 52.6, 52.4, 34.7, 34.6, 31.4, 31.4, 17.0, 16.3. HRMS (ESI) calcd for C₂₄H₃₆N₂, [M+H]⁺ *m/z* 353.2951; Found: 353.2950.

N², N³-bis(3-fluorophenyl)butane-2,3-diamine (3o)



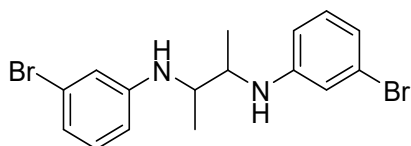
Purified by silica gel chromatography (petroleum ether/ethyl acetate = 15:1, v/v), the desired product **3o** was obtained as a yellow oil. (32 mg, 76% yield). *meso/dl* 2:1; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.09 (dtd, $J = 13.4, 8.2, 6.7$ Hz, 2H), 6.43 – 6.24 (m, 6H), 3.71 – 3.65 (m, 1H), 3.56 – 3.50 (m, 1H), 1.24 – 1.17 (m, 6H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -112.62 (d, $J = 43.2$ Hz). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.1 (dd, $J = 243.0, 2.4$ Hz), 149.2 (d, $J = 10.8$ Hz), 130.5 (dd, $J = 10.3, 4.0$ Hz), 116.1 – 95.7 (m), 52.6, 52.1, 17.1, 16.2. HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{18}\text{F}_2\text{N}_2$, $[\text{M}+\text{H}]^+$ m/z 277.1511; Found: 277.1508.

N^2, N^3 -bis(3-chlorophenyl)butane-2,3-diamine (3p)



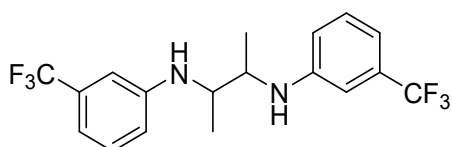
Purified by silica gel chromatography (petroleum ether/ethyl acetate = 15:1, v/v), the desired product **3p** was obtained as a yellow oil. (38 mg, 81% yield). *meso/dl* 1:1.2; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.07 (dt, $J = 13.8, 8.0$ Hz, 2H), 6.68 (td, $J = 7.7, 1.9$ Hz, 2H), 6.59 (dt, $J = 22.2, 2.2$ Hz, 2H), 6.47 (ddd, $J = 23.0, 8.2, 2.4$ Hz, 2H), 3.73 – 3.67 (m, 2H), 3.54 (dd, $J = 4.7, 1.7$ Hz, 1H), 1.20 (dd, $J = 10.0, 6.1$ Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 148.5, 135.2, 135.1, 130.4, 130.3, 117.5, 117.5, 113.2, 113.1, 112.0, 111.8, 52.5, 52.0, 17.0, 16.2. HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{18}\text{Cl}_2\text{N}_2$, $[\text{M}+\text{H}]^+$ m/z 309.0920; Found: 309.0920.

N^2, N^3 -bis(3-bromophenyl)butane-2,3-diamine (3q)



Purified by silica gel chromatography (petroleum ether/ethyl acetate = 15:1, v/v), the desired product **3q** was obtained as a yellow oil. (50 mg, 84% yield). *meso/dl* 1.4:1; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.01 (dt, $J = 14.3, 8.0$ Hz, 2H), 6.85 – 6.76 (m, 3H), 6.72 (t, $J = 2.1$ Hz, 2H), 6.56 – 6.46 (m, 2H), 3.72 – 3.65 (m, 2H), 3.53 (dt, $J = 5.9, 4.3$ Hz, 1H), 1.21 – 1.16 (m, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 148.7, 130.7, 130.7, 123.4, 123.4, 120.5, 120.4, 116.1, 116.0, 112.3, 112.2, 52.4, 52.0, 17.0, 16.2. HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{18}\text{Br}_2\text{N}_2$, $[\text{M}+\text{H}]^+$ m/z 398.9890; Found: 398.9886.

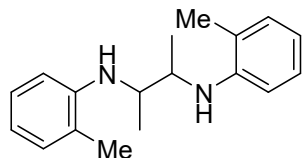
N^2, N^3 -bis(3-(trifluoromethyl)phenyl)butane-2,3-diamine (3r)



Purified by silica gel chromatography (petroleum ether/ethyl acetate = 8:1, v/v), the desired product **3r** was obtained as a colourless oil. (34 mg, 60% yield). *meso/dl* 1:1; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.24 (m, 2H), 6.96 (t, $J = 8.0$ Hz, 2H), 6.88 – 6.70 (m, 4H), 3.84 (s, 1H), 3.80 (d,

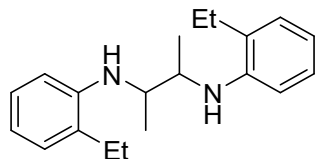
$J = 6.3$ Hz, 1H), 3.65 (dt, $J = 6.1, 4.4$ Hz, 1H), 1.26 (dd, $J = 8.4, 6.0$ Hz, 6H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.88 (d, $J = 5.5$ Hz). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.5, 129.9 (d, $J = 4.3$ Hz), 116.4 (d, $J = 13.6$ Hz), 114.1, 109.7 (d, $J = 10.2$ Hz), 52.4, 52.0, 17.0, 16.2. HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{18}\text{F}_6\text{N}_2$, $[\text{M}+\text{H}]^+$ m/z 377.1447; Found: 377.1444.

N^2, N^3 -di-*o*-tolylbutane-2,3-diamine (3s)



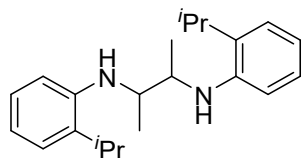
Purified by silica gel chromatography (petroleum ether/ethyl acetate = 50:1, v/v), the desired product **3s** was obtained as a colourless oil. (21 mg, 51% yield). *meso/dl* 1:3.5; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.18 – 6.99 (m, 4H), 6.76 – 6.59 (m, 4H), 3.84 (tdd, $J = 8.3, 6.6, 2.9$ Hz, 1H), 3.68 (dt, $J = 6.0, 4.3$ Hz, 1H), 3.57 (s, 1H), 2.07 (d, $J = 14.4$ Hz, 6H), 1.29 – 1.23 (m, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 145.4, 130.4, 130.4, 127.2, 127.2, 122.5, 117.1, 110.9, 110.6, 52.6, 17.6, 17.6, 17.3, 16.6. HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{24}\text{N}_2$, $[\text{M}+\text{H}]^+$ m/z 269.2012; Found: 269.2018.

N^2, N^3 -bis(2-ethylphenyl)butane-2,3-diamine (3t)



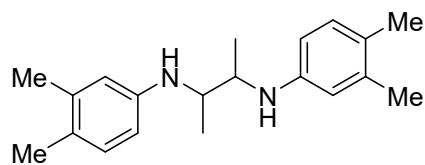
Purified by silica gel chromatography (petroleum ether/ethyl acetate = 30:1, v/v), the desired product **3t** was obtained as a yellow oil. (25 mg, 60% yield). *meso/dl* 1:3; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.04 (dt, $J = 29.1, 7.8$ Hz, 4H), 6.63 (dt, $J = 22.3, 7.9$ Hz, 4H), 3.77 (d, $J = 6.1$ Hz, 1H), 3.61 (q, $J = 5.1$ Hz, 3H), 2.34 (dq, $J = 14.7, 7.5$ Hz, 4H), 1.22 – 1.10 (m, 12H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 143.8, 143.8, 127.2, 127.0, 126.0, 126.0, 116.2, 116.1, 110.1, 109.8, 51.5, 51.0, 22.9, 22.9, 22.7, 16.4, 15.4, 11.9. HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{28}\text{N}_2$, $[\text{M}+\text{H}]^+$ m/z 297.2325; Found: 297.2325.

N^2, N^3 -bis(2-isopropylphenyl)butane-2,3-diamine (3u)



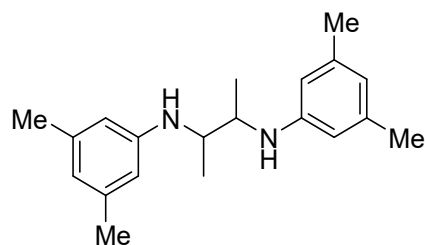
Purified by silica gel chromatography (petroleum ether/ethyl acetate = 30:1, v/v), the desired product **3u** was obtained as a colourless oil. (25 mg, 52% yield). *meso/dl* 1:1.4; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.03 (td, $J = 7.4, 1.7$ Hz, 4H), 6.67 – 6.55 (m, 4H), 3.73 (q, $J = 5.8$ Hz, 1H), 3.68 (s, 1H), 3.60 – 3.52 (m, 1H), 2.68 (dq, $J = 14.2, 6.9$ Hz, 2H), 1.18 – 1.06 (m, 19H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 143.1, 143.1, 131.7, 131.7, 125.7, 125.7, 124.2, 124.2, 116.4, 116.3, 110.7, 110.3, 51.8, 51.3, 26.2, 26.2, 21.4, 21.4, 21.3, 21.1, 16.5, 15.3. HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{24}\text{N}_2$, $[\text{M}+\text{Na}]^+$ m/z 347.2458; Found: 347.2453

N²,N³-bis(3,4-dimethylphenyl)butane-2,3-diamine (3v)



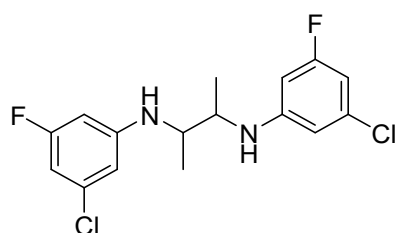
Purified by silica gel chromatography (petroleum ether/ethyl acetate = 20:1, v/v), the desired product **3v** was obtained as a colourless oil. (25 mg, 57% yield). *meso/dl* 1:1.5; ¹H NMR (400 MHz, Chloroform-*d*) δ 6.93 (dd, *J* = 12.7, 8.0 Hz, 2H), 6.51 – 6.34 (m, 4H), 3.66 (td, *J* = 6.2, 4.4 Hz, 1H), 3.53 (dt, *J* = 5.9, 4.3 Hz, 1H), 2.22 – 2.12 (m, 12H), 1.17 (dd, *J* = 11.5, 6.0 Hz, 6H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 148.7, 130.7, 130.7, 123.5, 123.4, 120.5, 120.4, 116.1, 116.0, 112.4, 112.2, 52.4, 52.2, 52.0, 17.0, 16.2. HRMS (ESI) calcd for C₂₀H₂₈N₂, [M+H]⁺ *m/z* 297.2325; Found: 297.2328.

N²,N³-bis(3,5-dimethylphenyl)butane-2,3-diamine (3w)



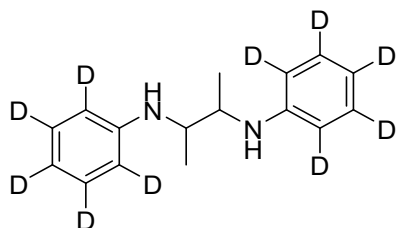
Purified by silica gel chromatography (petroleum ether/ethyl acetate = 20:1, v/v), the desired product **3w** was obtained as a colourless oil. (30 mg, 67% yield). *meso/dl* 1:1.5; ¹H NMR (400 MHz, Chloroform-*d*) δ 6.36 (d, *J* = 10.3 Hz, 2H), 6.25 (d, *J* = 26.5 Hz, 4H), 3.68 (d, *J* = 5.9 Hz, 1H), 3.57 (dt, *J* = 5.9, 3.0 Hz, 2H), 2.21 (d, *J* = 15.9 Hz, 12H), 1.16 (t, *J* = 6.6 Hz, 6H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 147.7, 147.5, 139.1, 139.0, 119.6, 119.4, 111.7, 111.4, 52.1, 52.0, 21.5, 21.5, 16.5, 16.4. HRMS (ESI) calcd for C₂₀H₂₈N₂, [M+H]⁺ *m/z* 297.2325; Found: 297.2323.

N²,N³-bis(3-chloro-5-fluorophenyl)butane-2,3-diamine (3x)



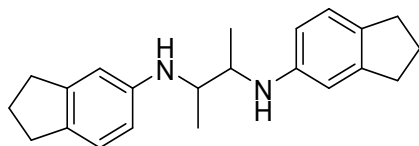
Purified by silica gel chromatography (petroleum ether/ethyl acetate = 8:1, v/v), the desired product **3x** was obtained as a colourless oil. (26 mg, 51% yield). *meso/dl* 1.4:1; ¹H NMR (400 MHz, Chloroform-*d*) δ 6.96 (dt, *J* = 12.2, 8.8 Hz, 2H), 6.62 (ddd, *J* = 22.2, 6.1, 2.9 Hz, 2H), 6.44 (ddt, *J* = 21.5, 8.9, 3.3 Hz, 2H), 3.62 (q, *J* = 5.8 Hz, 2H), 3.49 (s, 1H), 3.44 (dt, *J* = 5.9, 4.2 Hz, 1H), 1.20 (dd, *J* = 13.1, 6.0 Hz, 6H). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -130.60 (d, *J* = 31.8 Hz). ¹³C NMR (101 MHz, Chloroform-*d*) δ 151.1 (dd, *J* = 238.2, 7.5 Hz), 144.3 (d, *J* = 2.2 Hz), 121.2 (dd, *J* = 18.4, 4.5 Hz), 117.2 – 110.3 (m), 53.3, 52.7, 31.5, 31.5, 30.2, 30.6, 17.0, 16.1. HRMS (ESI) calcd for C₁₆H₁₆Cl₂F₂N₂, [M+H]⁺ *m/z* 345.0731; Found: 345.0729.

N²,N³-bis(phenyl-d₅)butane-2,3-diamine (3y)



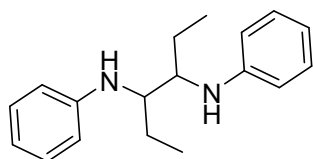
Purified by silica gel chromatography (petroleum ether/ethyl acetate = 20:1, v/v), the desired product **3y** was obtained as a colourless oil. (30 mg, 83% yield). *meso/dl* 1:2.5; ¹H NMR (400 MHz, Chloroform-*d*) δ 3.76 – 3.69 (m, 1H), 3.62 – 3.54 (m, 2H), 1.28 – 1.16 (m, 6H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 52.6, 52.2, 17.0, 16.3. HRMS (ESI) calcd for C₁₆H₁₀D₁₀N₂, [M+H]⁺ *m/z* 251.2325; Found: 251.2327.

N²,N³-bis(2,3-dihydro-1H-inden-5-yl)butane-2,3-diamine (3z)



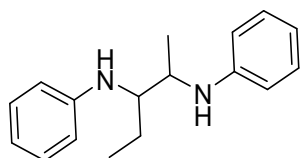
Purified by silica gel chromatography (petroleum ether/ethyl acetate = 20:1, v/v), the desired product **3z** was obtained as a colourless oil. (34 mg, 70% yield). *meso/dl* 1:1; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.02 (dd, *J* = 12.0, 8.0 Hz, 2H), 6.56 (dd, *J* = 20.8, 2.3 Hz, 2H), 6.44 (ddd, *J* = 12.7, 8.0, 2.3 Hz, 2H), 3.68 (dt, *J* = 7.1, 1.8 Hz, 1H), 3.54 (dd, *J* = 4.6, 1.7 Hz, 1H), 2.87 – 2.76 (m, 8H), 2.04 (pd, *J* = 7.4, 4.9 Hz, 4H), 1.22 – 1.15 (m, 6H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 146.4, 146.3, 145.6, 145.6, 133.4, 133.3, 125.0, 124.9, 112.4, 112.2, 110.2, 109.9, 53.0, 52.9, 33.2, 33.2, 32.0, 25.8, 17.0, 16.3. HRMS (ESI) calcd for C₂₂H₂₈N₂, [M+H]⁺ *m/z* 321.2325; Found: 321.2328.

N³,N⁴-diphenylhexane-3,4-diamine (6)



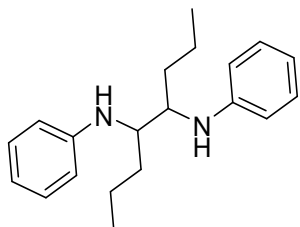
Purified by silica gel chromatography (petroleum ether/ethyl acetate = 50:1, v/v), the desired product **6** was obtained as a colourless oil. (9 mg, 22% yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.14 (dtd, *J* = 18.7, 7.3, 1.9 Hz, 4H), 6.72 – 6.60 (m, 4H), 6.57 – 6.51 (m, 2H), 3.47 (d, *J* = 26.0 Hz, 4H), 1.77 – 1.60 (m, 2H), 1.47 (dt, *J* = 14.7, 7.3 Hz, 2H), 0.97 (dt, *J* = 15.2, 7.4 Hz, 6H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 148.6, 129.4, 129.3, 117.1, 117.1, 113.4, 113.1, 58.0, 57.7, 25.6, 24.6, 11.4, 11.1. HRMS (ESI) calcd for C₁₈H₂₄N₂, [M+H]⁺ *m/z* 269.2012; Found: 269.2015.

N²,N³-diphenylpentane-2,3-diamine (7)



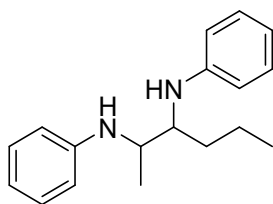
Purified by silica gel chromatography (petroleum ether/ethyl acetate = 20:1, v/v), the desired product **7** was obtained as a colourless oil. (15 mg, 38% yield). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.23 – 7.14 (m, 4H), 6.73 – 6.59 (m, 6H), 3.66 (qd, $J = 6.4, 4.1$ Hz, 1H), 3.39 (dt, $J = 8.4, 4.3$ Hz, 1H), 1.76 (ddp, $J = 14.9, 7.5, 4.3, 3.8$ Hz, 1H), 1.47 (dt, $J = 15.1, 7.6$ Hz, 1H), 1.21 (d, $J = 6.4$ Hz, 3H), 0.96 (t, $J = 7.4$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, Chloroform-*d*) δ 148.9, 148.5, 147.8, 147.5, 129.5, 129.4, 117.5, 117.5, 117.4, 117.3, 113.7, 113.6, 113.3, 59.0, 58.8, 51.2, 50.9, 25.9, 24.6, 17.8, 15.2, 11.5, 10.8. HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{22}\text{N}_2$, $[\text{M}+\text{H}]^+$ m/z 255.1856; Found: 255.1862.

N^4, N^5 -diphenyloctane-4,5-diamine (8)



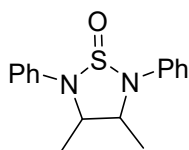
Purified by silica gel chromatography (petroleum ether/ethyl acetate = 50:1, v/v), the desired product **8** was obtained as a colourless oil. (19 mg, 42% yield). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.14 (dtd, $J = 21.5, 7.3, 1.9$ Hz, 4H), 6.71 – 6.59 (m, 4H), 6.55 – 6.46 (m, 2H), 3.58 (dd, $J = 8.0, 3.2$ Hz, 1H), 3.50 (d, $J = 8.3$ Hz, 3H), 1.59 – 1.29 (m, 8H), 0.90 (dt, $J = 15.9, 7.0$ Hz, 6H). $^{13}\text{C NMR}$ (100 MHz, Chloroform-*d*) δ 148.8, 148.5, 147.8, 147.5, 129.5, 129.4, 129.4, 129.2, 117.5, 117.4, 117.3, 117.0, 113.7, 113.6, 113.2, 57.1, 56.9, 51.6, 51.4, 51.2, 35.3, 34.2, 20.0, 19.6, 17.7, 15.2, 14.3, 14.2. HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{28}\text{N}_2$, $[\text{M}+\text{H}]^+$ m/z 297.2325; Found: 297.2330.

N^2, N^3 -diphenylhexane-2,3-diamine (9)



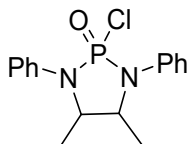
Purified by silica gel chromatography (petroleum ether/ethyl acetate = 20:1, v/v), the desired product **9** was obtained as a colourless oil. (10 mg, 25% yield). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.18 (ddd, $J = 9.1, 7.2, 2.2$ Hz, 4H), 6.68 (dd, $J = 22.0, 7.7$ Hz, 6H), 3.66 (qd, $J = 6.4, 3.9$ Hz, 1H), 3.49 (dt, $J = 8.2, 4.1$ Hz, 1H), 1.68 – 1.62 (m, 1H), 1.50 – 1.40 (m, 2H), 1.35 (td, $J = 7.7, 4.2$ Hz, 1H), 1.20 (d, $J = 6.4$ Hz, 3H), 0.89 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 148.3, 129.4, 129.4, 117.7, 117.3, 113.8, 113.2, 57.0, 51.6, 34.1, 19.5, 17.5, 14.2. HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{24}\text{N}_2$, $[\text{M}+\text{K}]^+$ m/z 307.1571; Found: 307.1575.

3,4-dimethyl-2,5-diphenyl-1,2,5-thiadiazolidine 1-oxide (10)



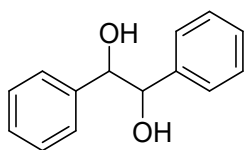
Purified by silica gel chromatography (petroleum ether/ethyl acetate = 5:1, v/v), the desired product **10** was obtained as a white solid (35 mg, 40% yield). mp 126 - 128°C, ¹H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.32 (m, 4H), 7.28 – 7.19 (m, 5H), 7.14 – 7.06 (m, 1H), 4.44 – 4.33 (m, 1H), 3.99 – 3.86 (m, 1H), 1.48 (d, *J* = 6.1 Hz, 3H), 1.28 (d, *J* = 6.0 Hz, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 141.1, 138.5, 129.6, 129.5, 126.4, 126.1, 123.4, 118.8, 63.6, 61.1, 17.6, 16.5. HRMS (ESI) calcd for C₁₆H₁₈N₂OS, [M+H]⁺ *m/z* 287.1213; Found: 287.1211.

2-chloro-4,5-dimethyl-1,3-diphenyl-1,3,2-diazaphospholidine 2-oxide (11)



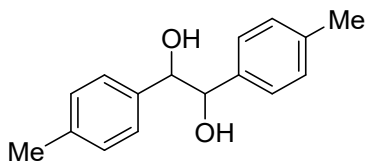
Purified by silica gel chromatography (petroleum ether/ethyl acetate = 7:1, v/v), the desired product **11** was obtained as a white solid. (20 mg, 21% yield). mp 130 - 132°C ¹H NMR (400 MHz, Chloroform-*d*) δ 7.47 – 7.32 (m, 8H), 7.25 – 7.13 (m, 2H), 4.00 (dq, *J* = 12.6, 6.3, 4.6 Hz, 1H), 3.93 – 3.82 (m, 1H), 1.40 (dd, *J* = 6.2, 2.8 Hz, 6H). ³¹P NMR (162 MHz, Chloroform-*d*) δ 13.31. ¹³C NMR (101 MHz, Chloroform-*d*) δ 138.0, 137.9, 137.3, 137.2, 129.6, 129.6, 125.2, 125.2, 124.4, 122.6, 122.5, 121.2, 121.1, 58.4, 58.2, 57.8, 57.6, 18.7, 18.7, 17.8, 17.8. HRMS (ESI) calcd for C₁₆H₁₈ClN₂OP, [M+H]⁺ *m/z* 321.0918; Found: 321.0915.

1,2-diphenylethane-1,2-diol (5a)



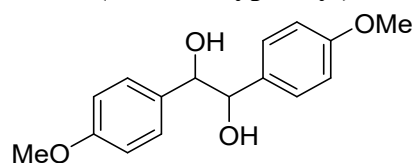
Purified by silica gel chromatography (petroleum ether/ethyl acetate = 7:1, v/v), the desired product **5a** was obtained as a white solid. (25 mg, 78% yield). *meso/dl* 1:1.7; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.20 – 6.97 (m, 8H), 6.94 – 6.90 (m, 2H), 4.63 (s, 1H), 4.47 (s, 1H), 3.40 (s, 1H), 2.71 (s, 1H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 140.0, 140.0, 128.1, 128.1, 128.0, 127.9, 127.2, 127.1, 79.1.

1,2-di-p-tolylolethane-1,2-diol (5b)



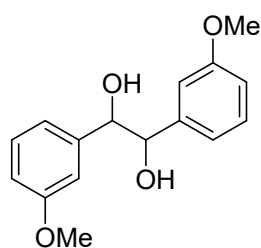
Purified by silica gel chromatography (petroleum ether/ethyl acetate = 7:1, v/v), the desired product **5b** was obtained as a white solid. (29 mg, 80% yield). *meso/dl* 1:1.1; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.13 (q, *J* = 8.2 Hz, 4H), 7.05 – 6.97 (m, 4H), 4.71 (s, 1H), 4.62 (s, 1H), 2.90 (s, 1H), 2.31 (d, *J* = 17.3 Hz, 6H), 2.18 (s, 1H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 137.8, 137.5, 137.0, 137.0, 129, 128.8, 127.1, 126.9, 78.8, 78.0, 21.2, 21.2.

1,2-bis(4-methoxyphenyl)ethane-1,2-diol (**5c**)



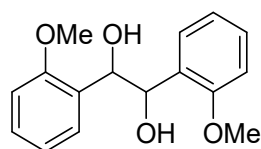
Purified by silica gel chromatography (petroleum ether/ethyl acetate = 3:1, v/v), the desired product **5c** was obtained as a white solid. (26 mg, 63% yield). *meso/dl* 1:1.7; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.21 – 7.16 (m, 2H), 7.05 – 6.99 (m, 2H), 6.88 – 6.82 (m, 2H), 6.77 – 6.72 (m, 2H), 4.72 (s, 1H), 4.61 (s, 1H), 3.77 (d, *J* = 15.3 Hz, 6H), 2.89 (s, 1H), 2.18 (s, 1H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 159.4, 159.2, 132.1, 132.1, 128.3, 128.2, 113.7, 113.5, 78.8, 55.3, 55.2.

1,2-bis(3-methoxyphenyl)ethane-1,2-diol (**5d**)



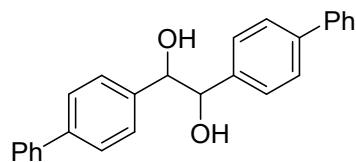
Purified by silica gel chromatography (petroleum ether/ethyl acetate = 3:1, v/v), the desired product **5d** was obtained as a white solid. (32 mg, 73% yield). *meso/dl* 1.1:10; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.63 – 8.48 (m, 2H), 8.21 – 8.03 (m, 6H), 6.13 (s, 1H), 6.00 (s, 1H), 5.08 (d, *J* = 11.5 Hz, 6H), 4.43 (s, 1H), 3.79 (s, 1H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 159.5, 159.4, 141.5, 141.4, 129.3, 129.2, 119.5, 119.3, 114.0, 113.7, 112.3, 112.2, 78.9, 78.0, 55.2, 55.2.

1,2-bis(2-methoxyphenyl)ethane-1,2-diol (**5e**)



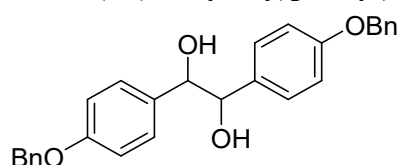
Purified by silica gel chromatography (petroleum ether/ethyl acetate = 5:1, v/v), the desired product **5e** was obtained as a white solid. (36 mg, 82% yield). *meso/dl* 1:1.1; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.26 – 7.13 (m, 4H), 6.86 (dtd, *J* = 15.9, 7.5, 1.1 Hz, 2H), 6.79 (dd, *J* = 8.2, 1.1 Hz, 1H), 6.76 – 6.72 (m, 1H), 5.24 (d, *J* = 4.6 Hz, 1H), 5.03 (d, *J* = 3.5 Hz, 1H), 3.70 – 3.61 (m, 6H), 3.47 (d, *J* = 3.9 Hz, 1H), 3.13 (s, 1H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 156.97, 157.0, 128.6, 128.5, 128.5, 128.3, 120.5, 120.5, 110.3, 110.2, 74.5, 73.7, 73.7, 55.3, 55.2.

1,2-di([1,1'-biphenyl]-4-yl)ethane-1,2-diol (**5f**)



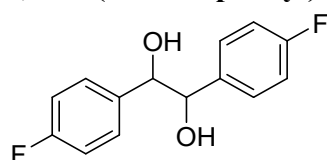
Purified by silica gel chromatography (petroleum ether/ethyl acetate = 5:1, v/v), the desired product **5f** was obtained as a white solid. (24 mg, 43% yield). *meso/dl* 1:1.2 ¹H NMR (400 MHz, Chloroform-*d*) δ 7.62 – 7.04 (m, 18H), 4.82 (s, 1H), 2.90 (s, 1H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 140.8, 140.6, 139.0, 128.8, 127.4, 127.4, 127.0, 126.9, 78.8. HRMS (ESI) calcd for C₂₆H₂₂O₂, [M+Na]⁺ *m/z* 389.1512; Found: 389.1516.

1,2-bis(4-(benzyloxy)phenyl)ethane-1,2-diol (**5g**)



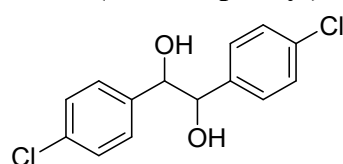
Purified by silica gel chromatography (petroleum ether/ethyl acetate = 3:1, v/v), the desired product **5g** was obtained as a white solid. (30 mg, 47% yield). *meso/dl* 1:1.5; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.30 (m, 10H), 7.21 – 7.15 (m, 2H), 7.04 – 6.99 (m, 2H), 6.92 (d, *J* = 8.7 Hz, 2H), 6.85 – 6.79 (m, 2H), 5.02 (d, *J* = 16.7 Hz, 4H), 4.71 (s, 1H), 4.60 (s, 1H), 2.86 (s, 1H), 2.16 (s, 1H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 158.7, 158.4, 136.9, 132.4, 128.6, 128.6, 128.4, 128.2, 128.0, 128.0, 127.5, 114.7, 114.5, 70.0, 70.0.

1,2-bis(4-fluorophenyl)ethane-1,2-diol (**5h**)



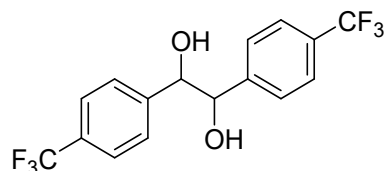
Purified by silica gel chromatography (petroleum ether/ethyl acetate = 5:1, v/v), the desired product **5h** was obtained as a white solid. (27 mg, 71% yield). *meso/dl* 1:1.5; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.17 – 7.09 (m, 2H), 7.07 – 6.86 (m, 6H), 4.80 (s, 1H), 4.60 (s, 1H), 3.02 (s, 1H), 2.42 (s, 1H). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -114.05 (d, *J* = 30.5 Hz). ¹³C NMR (101 MHz, Chloroform-*d*) δ 162.4 (d, *J* = 246.4 Hz), 135.4 (d, *J* = 3.2 Hz), 128.7 (dd, *J* = 8.1, 6.6 Hz), 115.1 (dd, *J* = 21.4, 2.4 Hz), 78.7.

1,2-bis(4-chlorophenyl)ethane-1,2-diol (**5i**)



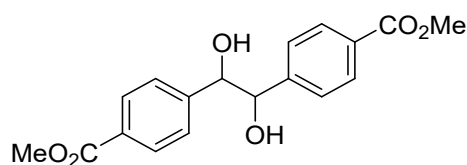
Purified by silica gel chromatography (petroleum ether/ethyl acetate = 3:1, v/v), the desired product **5i** was obtained as a white solid. (25 mg, 59% yield). *meso/dl* 1.2:1; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.27 – 7.15 (m, 4H), 7.10 – 6.94 (m, 4H), 4.78 (s, 1H), 4.56 (s, 1H), 3.12 (s, 1H), 2.58 (s, 1H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 138.0, 137.8, 133.8, 133.8, 128.4, 128.3, 128.3.

1,2-bis(4-(trifluoromethyl)phenyl)ethane-1,2-diol (**5j**)



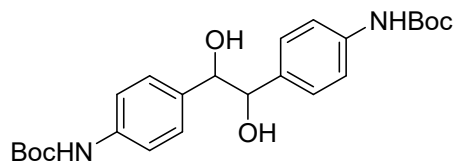
Purified by silica gel chromatography (petroleum ether/ethyl acetate = 3:1, v/v), the desired product **5j** was obtained as a white solid. (35 mg, 67% yield). *meso/dl* 1:1.2; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.52 (t, *J* = 9.0 Hz, 4H), 7.24 (dd, *J* = 23.4, 8.0 Hz, 4H), 4.94 (s, 1H), 4.72 (s, 1H), 3.12 (s, 1H), 2.62 (s, 1H). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -62.54 (d, *J* = 13.1 Hz). ¹³C NMR (101 MHz, Chloroform-*d*) δ 143.3 (d, *J* = 16.1 Hz), 130.4 (dd, *J* = 32.5, 11.1 Hz), 134.2 – 120.8 (m), 122.6 (d, *J* = 6.1 Hz), 78.4.

dimethyl 4,4'-(1,2-dihydroxyethane-1,2-diyl)dibenzoate (**5k**)



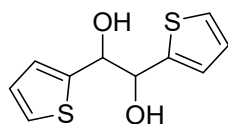
Purified by silica gel chromatography (petroleum ether/ethyl acetate = 3:1, v/v), the desired product **5k** was obtained as a white solid. (25 mg, 51% yield). *meso/dl* 1:1.3; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.27 – 7.19 (m, 2H), 7.15 – 7.08 (m, 2H), 7.04 – 6.91 (m, 4H), 4.76 (s, 1H), 4.63 (s, 1H), 3.11 (s, 1H), 2.54 (s, 1H), 2.27 (d, *J* = 6.4 Hz, 6H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 169.6, 169.4, 150.3, 150.2, 137.4, 137.4, 128.2, 128.0, 121.3, 121.3, 21.1.

di-tert-butyl ((1,2-dihydroxyethane-1,2-diyl)bis(4,1-phenylene))dicarbamate (**5l**)



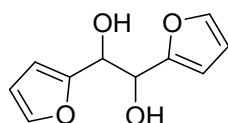
Purified by silica gel chromatography (petroleum ether/ethyl acetate = 2:1, v/v), the desired product **5l** was obtained as a white solid. (55 mg, 82% yield). mp 183 - 185°C *meso/dl* 1:1.3; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.28 – 7.10 (m, 6H), 6.99 (d, *J* = 8.3 Hz, 2H), 6.54 (d, *J* = 16.8 Hz, 2H), 4.72 (s, 1H), 4.57 (s, 1H), 1.50 (d, *J* = 5.2 Hz, 18H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 152.8, 138.1, 137.9, 134.5, 134.4, 127.8, 127.7, 118.2, 118.1, 78.7, 77.6, 60.4, 28.4, 14.2. HRMS (ESI) calcd for C₂₄H₃₂N₂O₆, [M+H]⁺ *m/z* 445.2333; Found: 445.2335.

1,2-di(thiophen-2-yl)ethane-1,2-diol (**5m**)



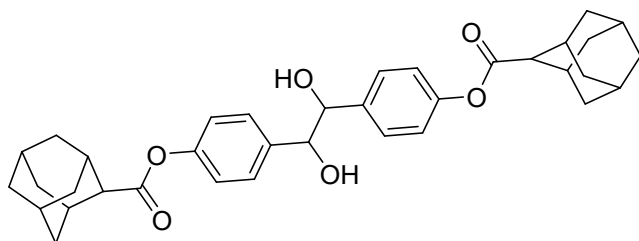
Purified by silica gel chromatography (petroleum ether/ethyl acetate = 7:1, v/v), the desired product **5m** was obtained as a white solid. (11 mg, 32% yield). *meso/dl* 1:1.4; $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.31 (ddd, $J = 11.7, 5.0, 1.2$ Hz, 1H), 7.26 – 7.23 (m, 1H), 7.04 – 6.96 (m, 2H), 6.91 (dd, $J = 5.1, 3.5$ Hz, 1H), 6.83 (dd, $J = 3.5, 1.2$ Hz, 1H), 5.12 (s, 1H), 5.05 (s, 1H), 3.04 (s, 1H), 2.53 (s, 1H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 152.6, 142.5, 142.4, 110.4, 110.3, 108.2, 108.0, 70.1, 69.9.

1,2-di(furan-2-yl)ethane-1,2-diol (**5n**)



Purified by silica gel chromatography (petroleum ether/ethyl acetate = 7:1, v/v), the desired product **5n** was obtained as a white solid. (11 mg, 36% yield). *meso/dl* 1:1.3; $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.38 (ddd, $J = 12.9, 1.9, 0.9$ Hz, 2H), 6.37 – 6.21 (m, 4H), 5.03 (s, 1H), 5.01 (s, 1H), 2.85 (s, 1H), 2.51 (s, 1H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 152.8, 152.6, 142.5, 142.4, 110.4, 110.3, 108.2, 108.0, 70.1, 70.0.

4-(2-(4-(((1S,2R,5R)-adamantane-2-carbonyloxy)phenyl)-1,2-dihydroxyethyl)phenyl)-1,2-dihydroxyethyl)phenyl (1r,3r,5r,7r)-adamantane-2-carboxylate (**5o**)



Purified by silica gel chromatography (petroleum ether/ethyl acetate = 3:1, v/v), the desired product **5o** was obtained as a white solid. (48 mg, 56% yield). mp 195 - 197°C *meso/dl* 1:1.7; $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 6.02 – 5.89 (m, 2H), 5.82 (d, $J = 8.0$ Hz, 2H), 5.67 (dd, $J = 21.3, 8.1$ Hz, 4H), 3.49 (d, $J = 2.7$ Hz, 1H), 3.33 (d, $J = 3.2$ Hz, 1H), 1.94 (s, 1H), 1.38 (d, $J = 16.4$ Hz, 1H), 0.79 (dt, $J = 18.0, 3.2$ Hz, 17H), 0.50 (t, $J = 3.4$ Hz, 11H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 176.2, 137.1, 128.1, 128.0, 121.3, 41.0, 41.0, 38.8, 36.5, 27.9. HRMS (ESI) calcd for $\text{C}_{36}\text{H}_{42}\text{O}_6$, $[\text{M}+\text{H}]^+$ m/z 571.3054; Found: 571.3055.

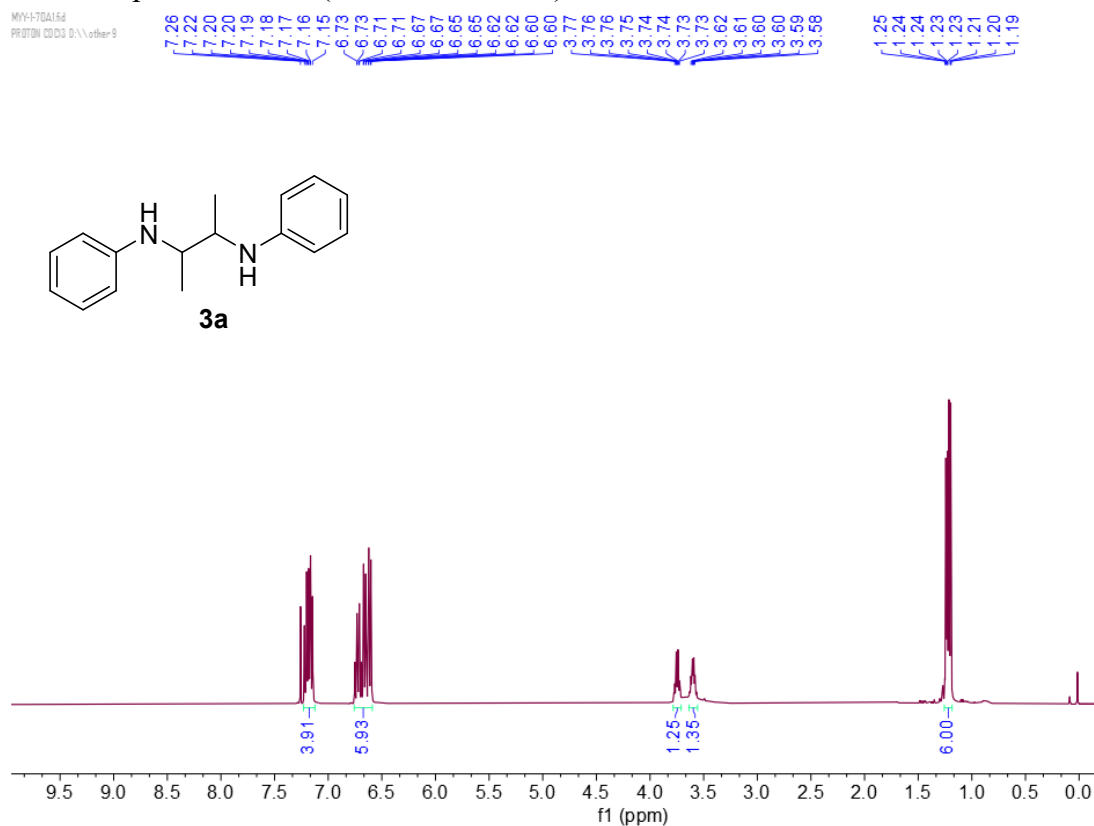
7. Reference

- (1) (a) J. Luo and J. Zhang, *ACS Catal.*, 2020, **10**, 14302-14303; (b) E. Speckmeier, T. G. Fischer and K. Zeitler, *J. Am. Chem. Soc.*, 2018, **140**, 15353-15365.

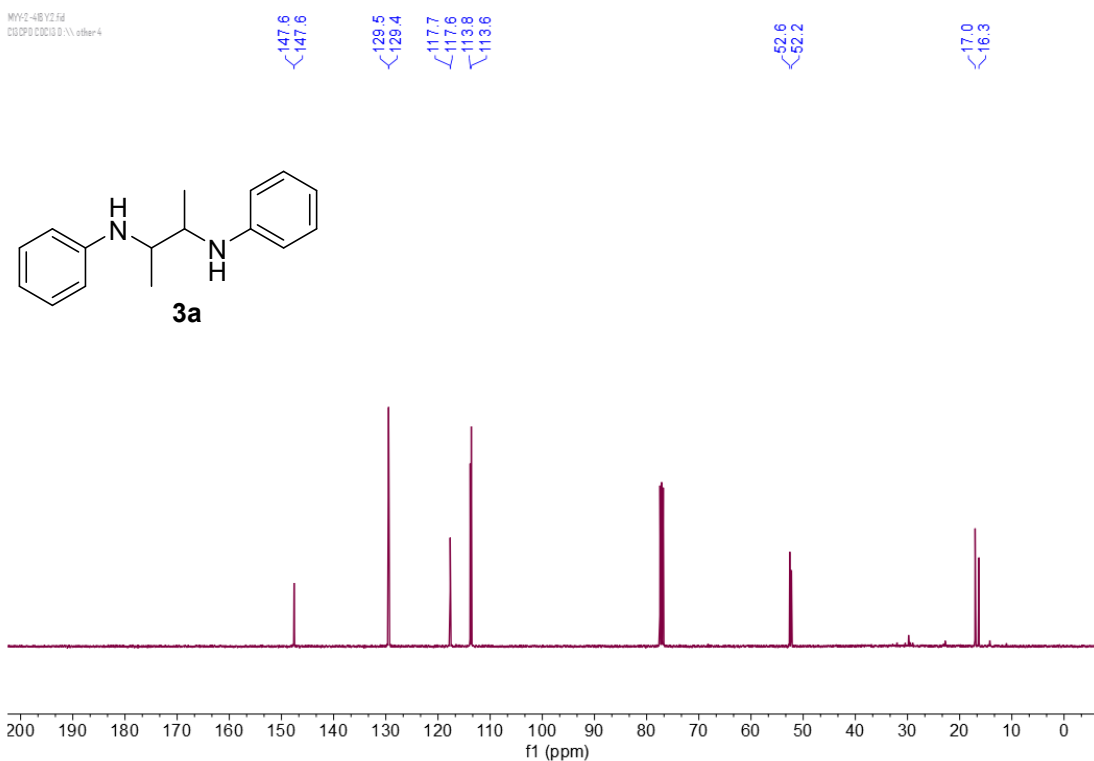
- (2) J. L. Li, D. Zhang, J. H. Chen, C. Q. Ma, and W. H. Hu, *ACS Catal.*, 2020, **10**, 4559–4565.
- (3) D. V. Hrishikesh, R. A. Annadate and S. V. Pansare, *ACS Omega.*, 2023, **8**, 3190-3197.

8. NMR spectra

^1H -NMR spectrum of **3a** (CDCl_3 , 400 MHz)



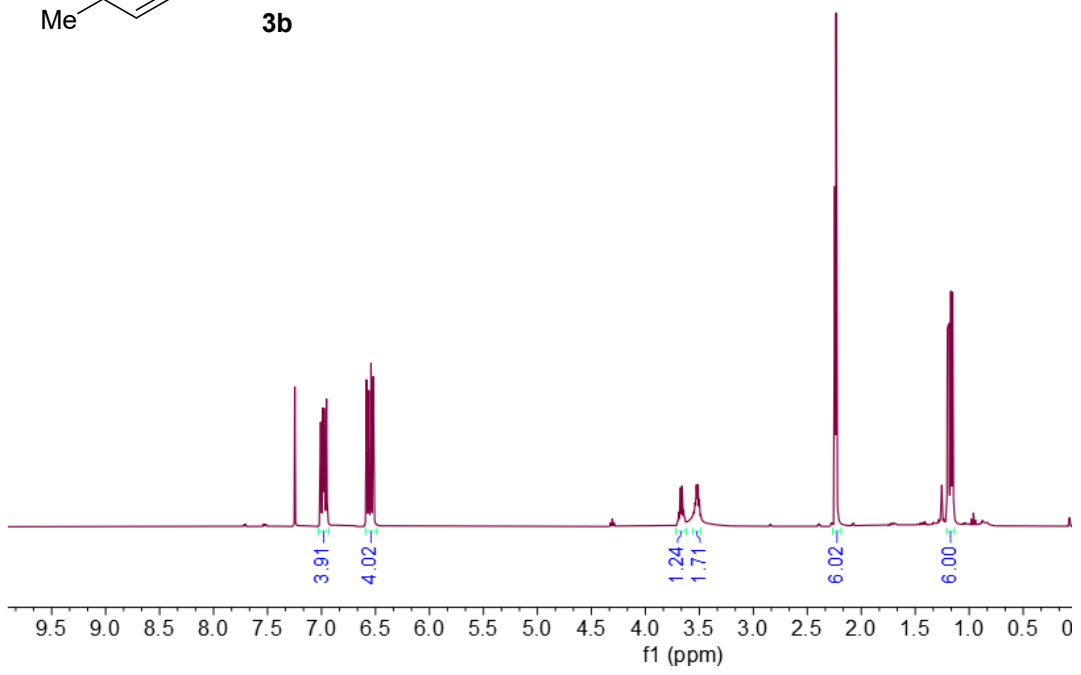
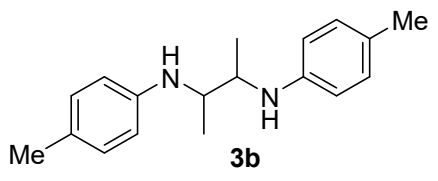
^{13}C -NMR spectrum of **3a** (CDCl_3 , 100 MHz)



^1H -NMR spectrum of **3b** (CDCl_3 , 400 MHz)

MYY-1-98B.4.fid
 PROTON CDCl3 D:\other 13

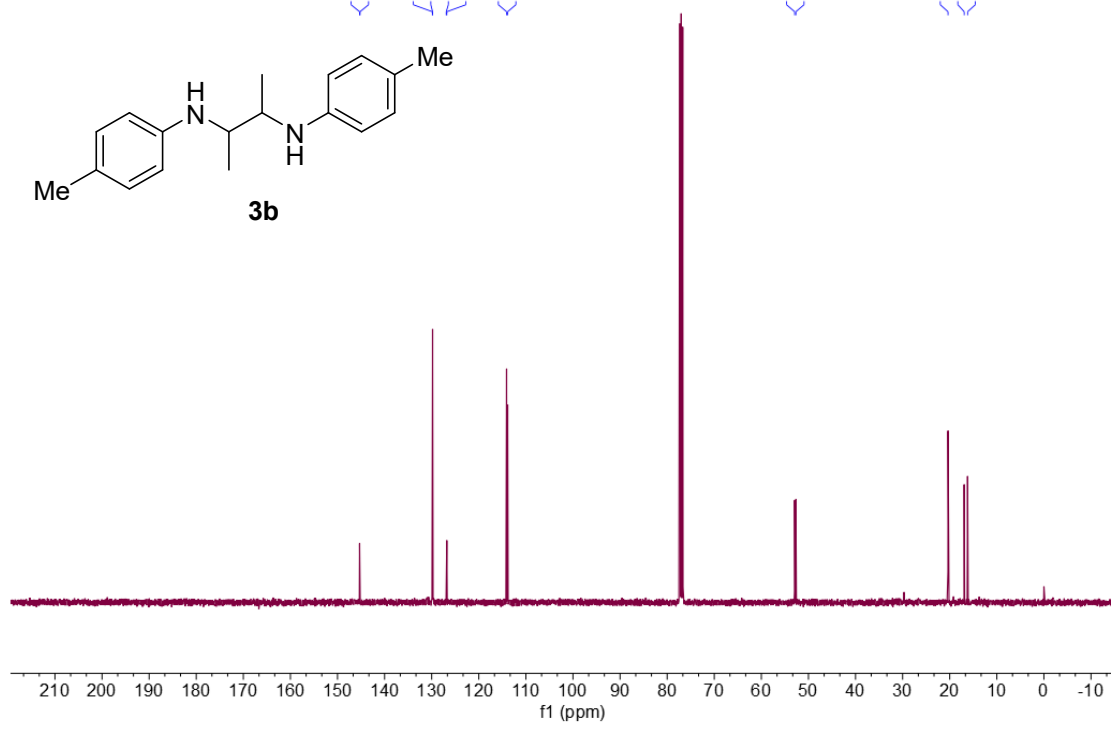
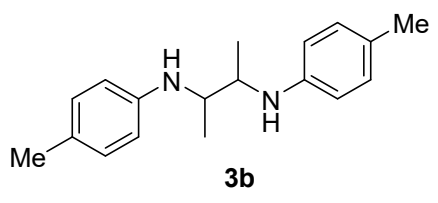
7.00 7.00 7.00 7.00 7.00 6.66 6.66 6.65 6.65 6.65 3.71 3.71 3.71 3.55 3.55 3.55 2.22 1.12 1.12 1.12 1.12



¹³C-NMR spectrum of **3b** (CDCl₃, 100 MHz)

MYY-1-98B.2.fid
 C13CPD CDCl3 D:\other 13

145.3 145.2 129.9 129.8 126.9 126.8 114.1 113.9 52.9 52.7 20.4 16.9 16.2

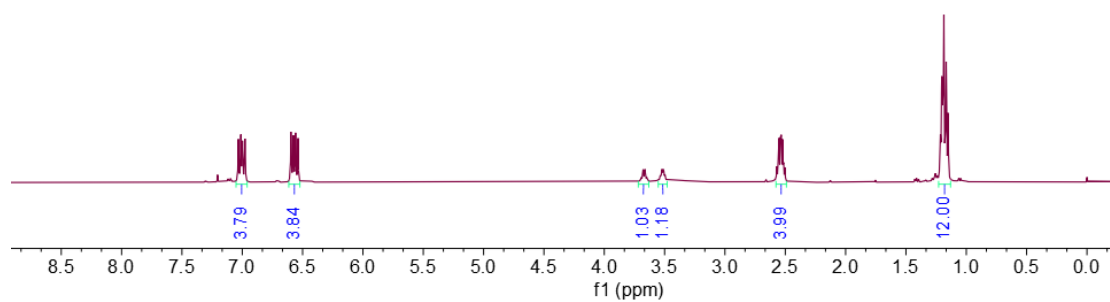
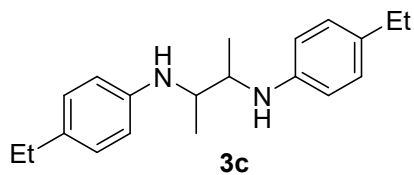


¹H-NMR spectrum of **3c** (CDCl₃, 400 MHz)

MYV-2-47B.1.fid
PROTON CDCl3 D:\other

7.03
7.02
7.01
7.00
6.98
6.60
6.59
6.58
6.56
6.55
6.54

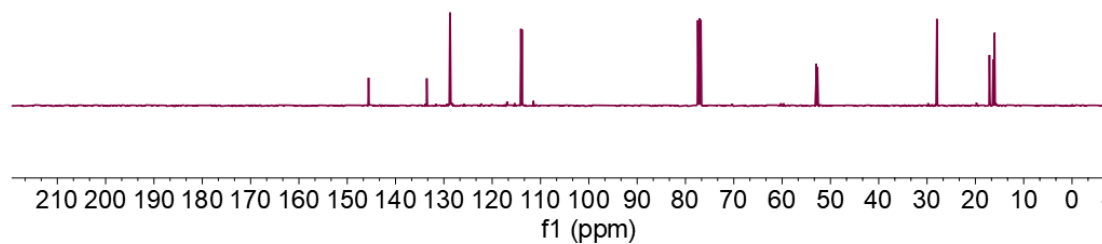
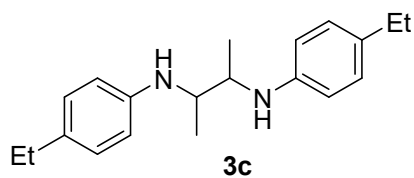
3.69
3.68
3.68
3.67
3.66
3.65
2.57
2.56
2.55
2.54
2.53
2.51
2.50
1.21
1.20
1.19
1.17
1.17
1.15



¹³C-NMR spectrum of **3c** (CDCl₃, 100 MHz)

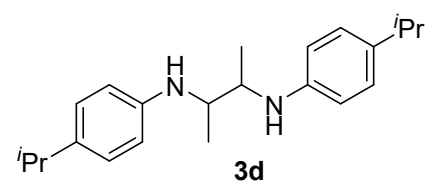
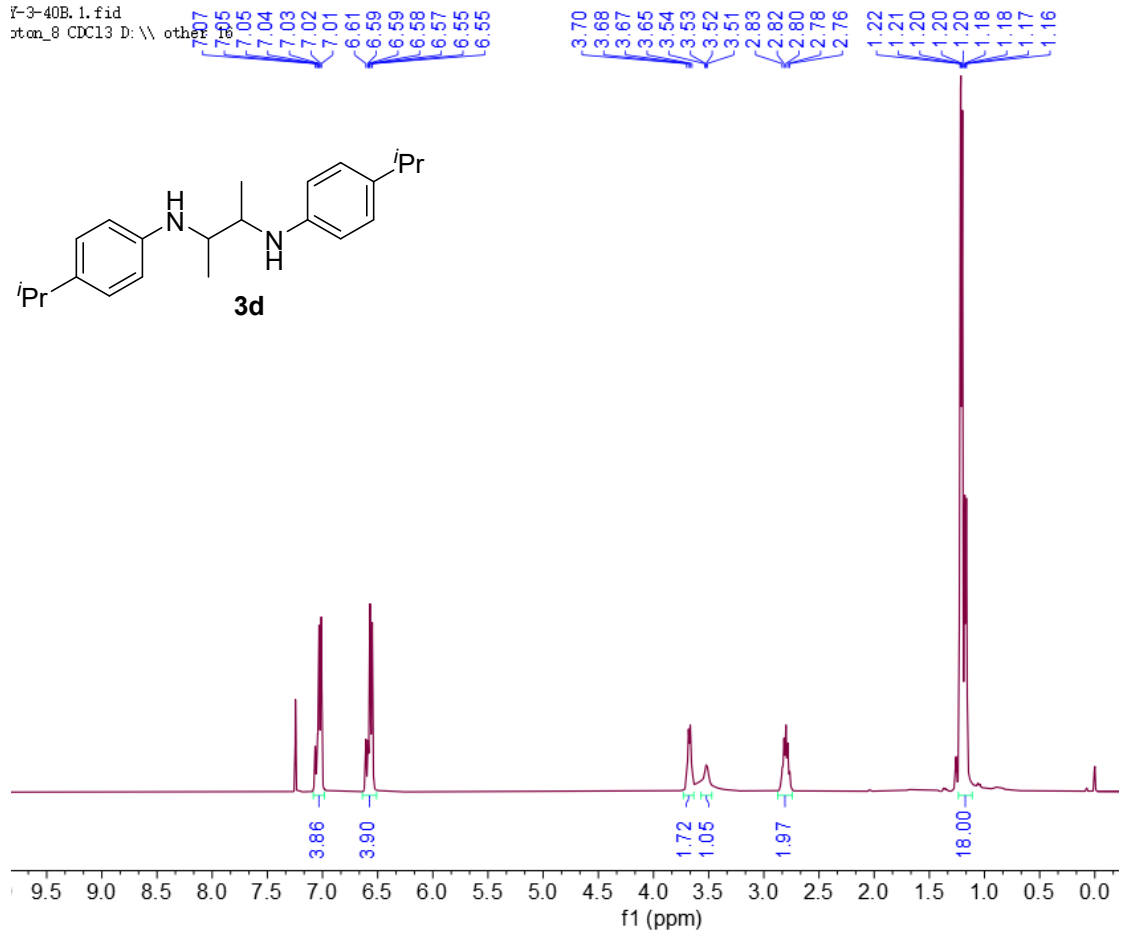
MYV-2-47B.2.fid
C13CPD CDCl3 D:\other 10

145.59
145.53
133.53
133.44
128.75
128.69
114.05
113.80
52.94
52.68
27.97
17.09
16.31
16.02

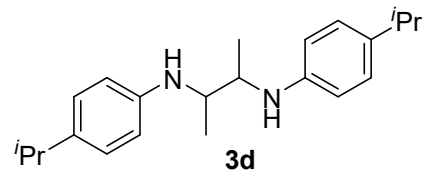
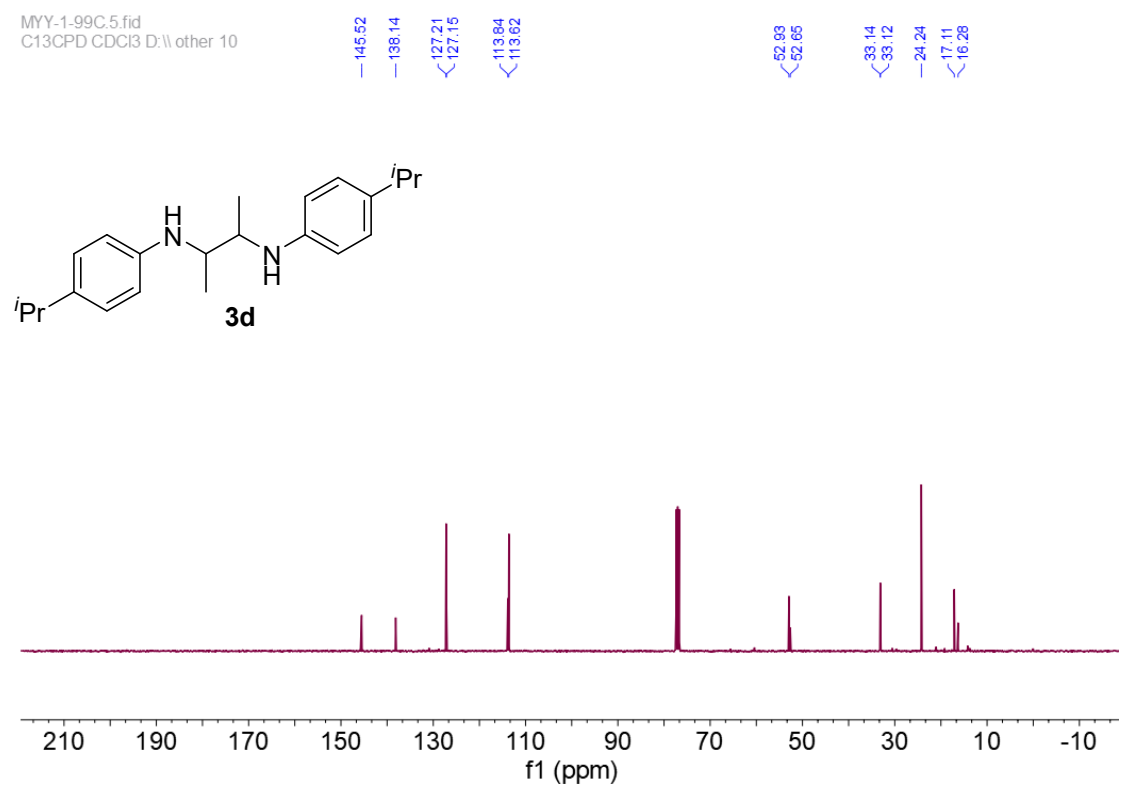


¹H-NMR spectrum of **3d** (CDCl₃, 400 MHz)

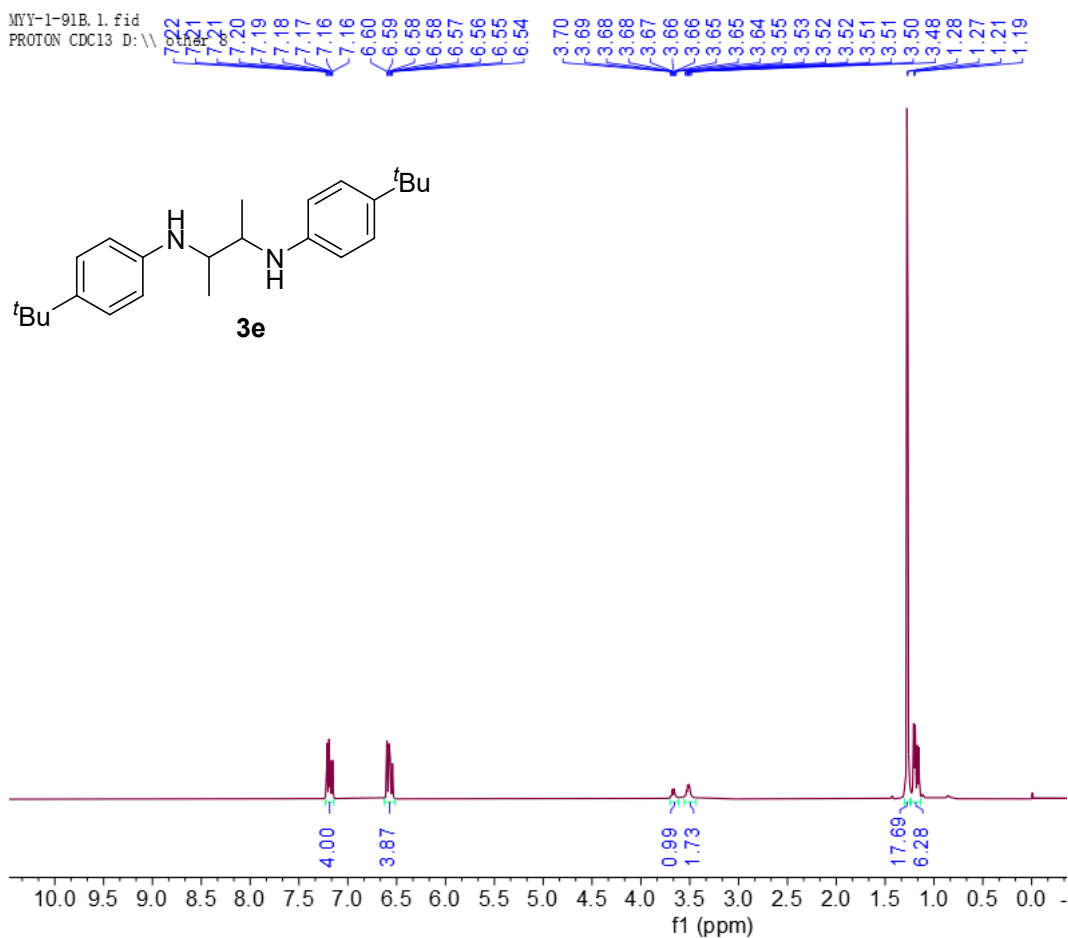
F-3-40B.1.fid
 ston_8 CDCl3 D:\other



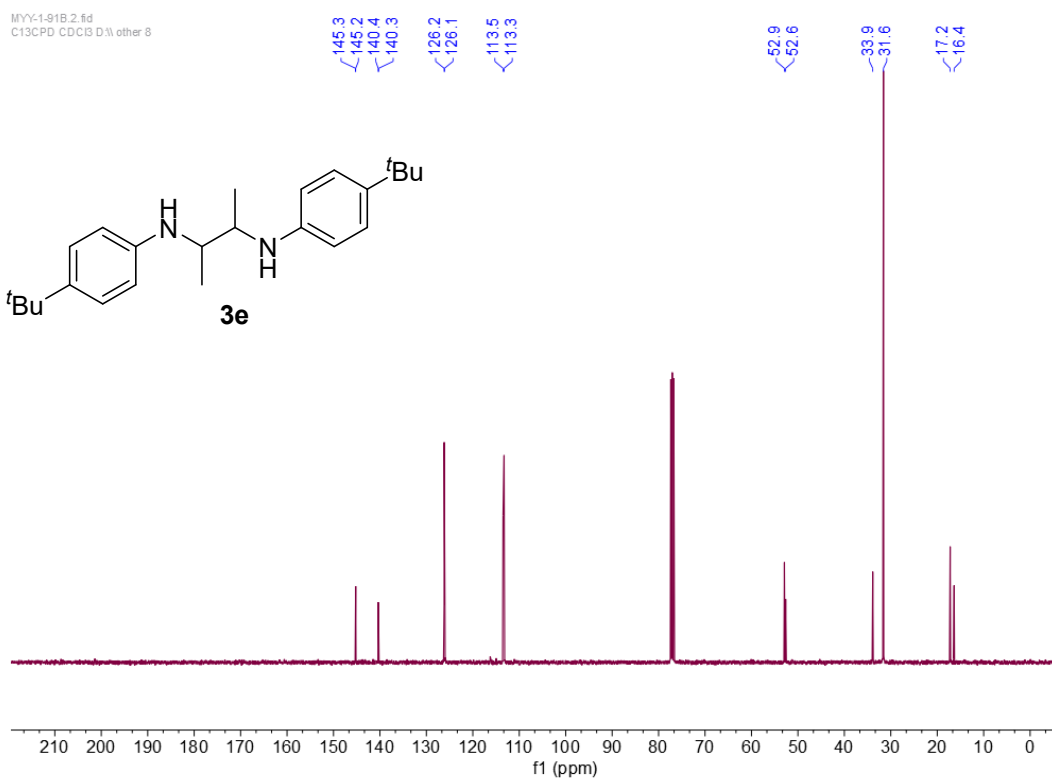
¹³C-NMR spectrum of **3d** (CDCl₃, 100 MHz)



¹H-NMR spectrum of **3e** (CDCl₃, 400 MHz)



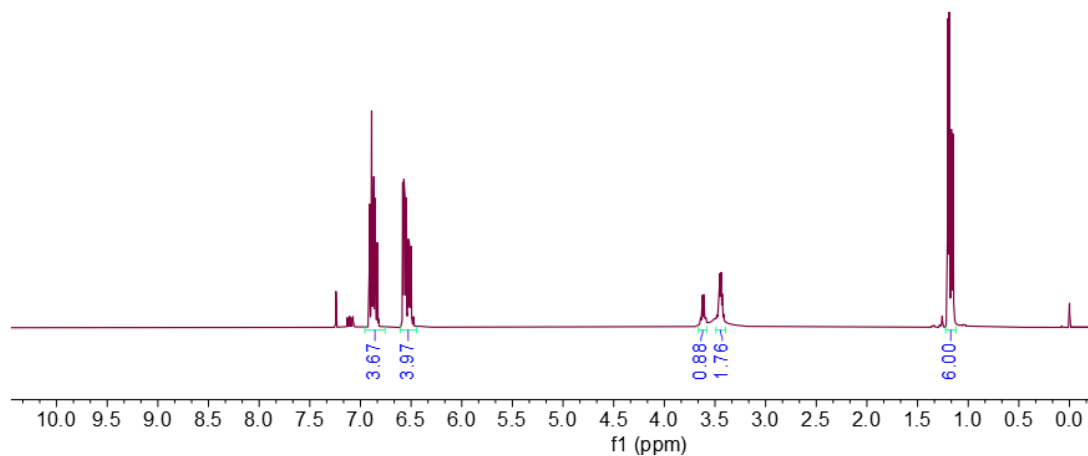
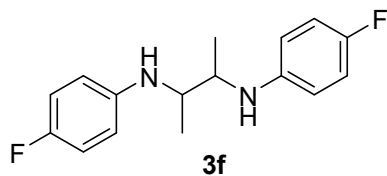
^{13}C -NMR spectrum of **3e** (CDCl_3 , 100 MHz)



^1H -NMR spectrum of **3f** (CDCl_3 , 400 MHz)

MYY-3-37D. 3. fid
proton_8 CDC13 D:\ other

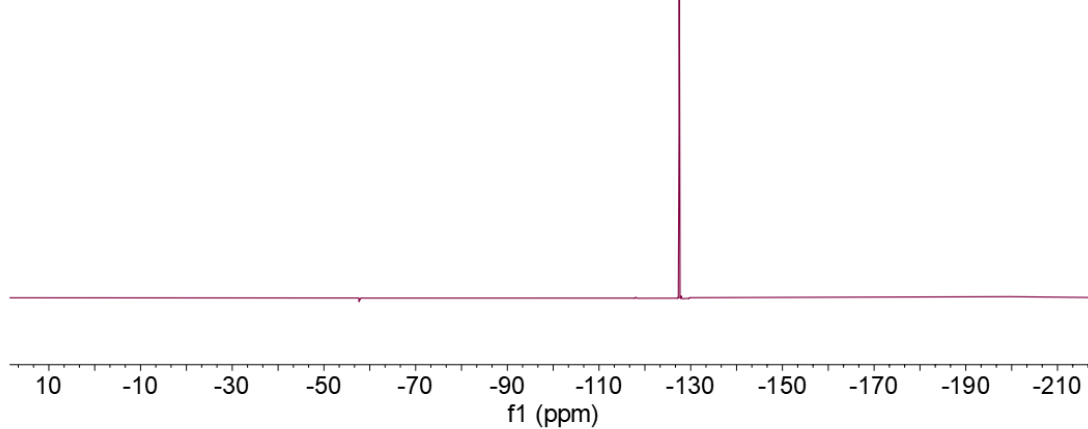
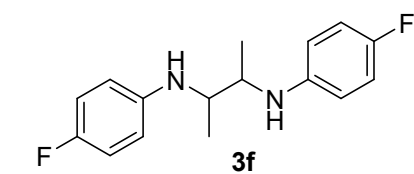
6.91 6.89 6.88 6.87 6.85 6.83 6.57 6.56 6.55 6.53 6.52 6.51 6.50 3.63 3.62 3.61 3.47 3.46 3.45 3.44 3.43 3.43 1.20 1.19 1.19 1.17 1.15



¹H-NMR spectrum of **3f** (CDCl₃, 376 MHz)

MYY-3-37D.12.fid
MYY-3-37D

-127.5
-127.5
-127.5



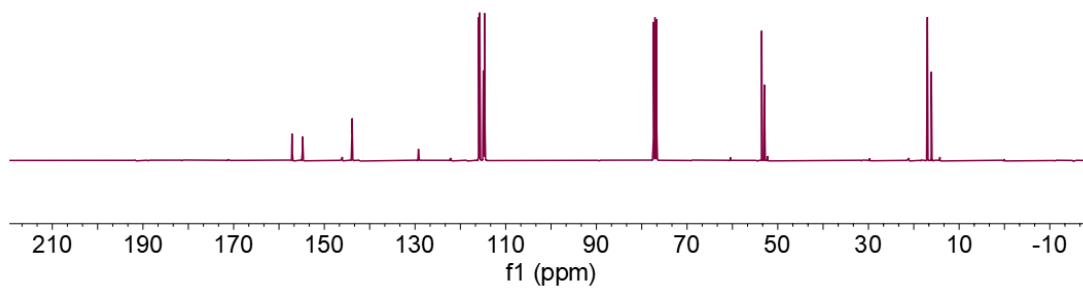
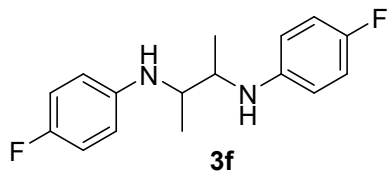
¹³C-NMR spectrum of **3f** (CDCl₃, 100 MHz)

MYY-3-37D.11.fid
MYY-3-37D

157.1
154.8
143.9
143.9
143.9
159.9
159.9
157.7
144.9
144.7
144.6

53.5
53.0

17.0
16.1



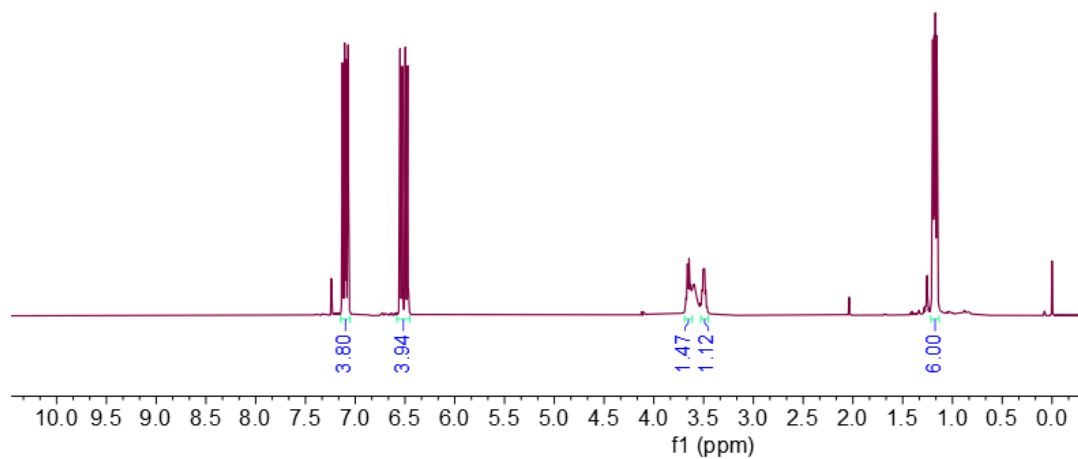
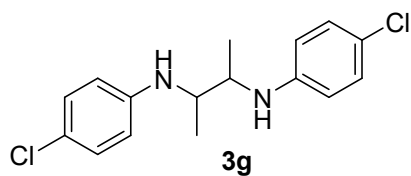
¹H-NMR spectrum of **3g** (CDCl₃, 400 MHz)

MYY-3-31C.1.fid
proton_8 CDCl3 D:\other 10

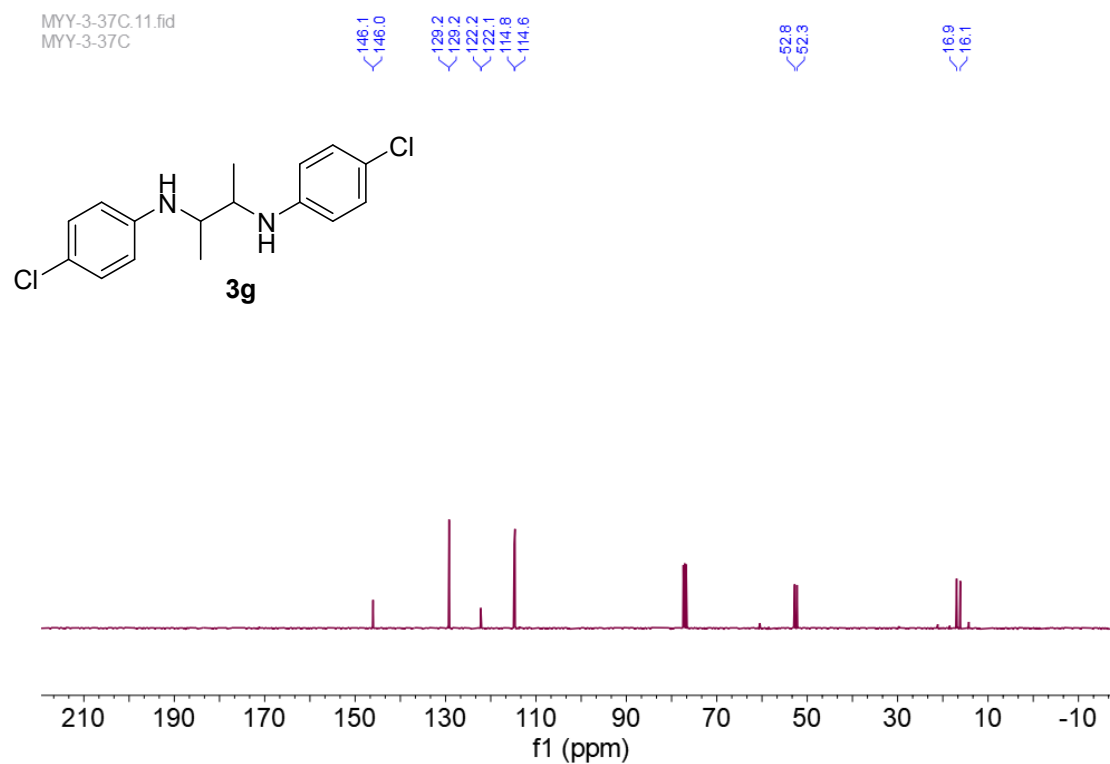
7.73
7.72
7.71
7.11
7.09
7.09
7.08
7.07
6.55
6.54
6.53
6.53
6.50
6.49
6.48
6.47

3.66
3.65
3.63
3.60
3.51
3.50
3.49
3.49

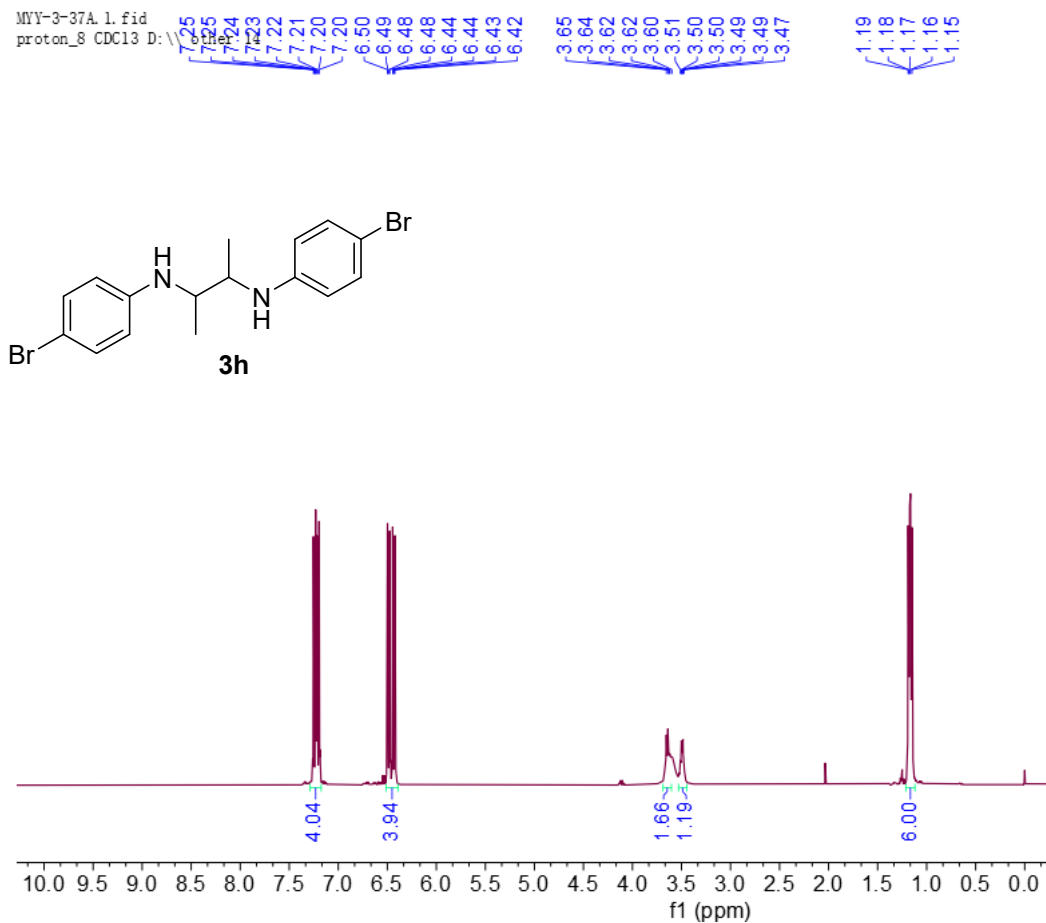
1.20
1.19
1.18
1.17
1.16



^{13}C -NMR spectrum of **3g** (CDCl_3 , 100 MHz)

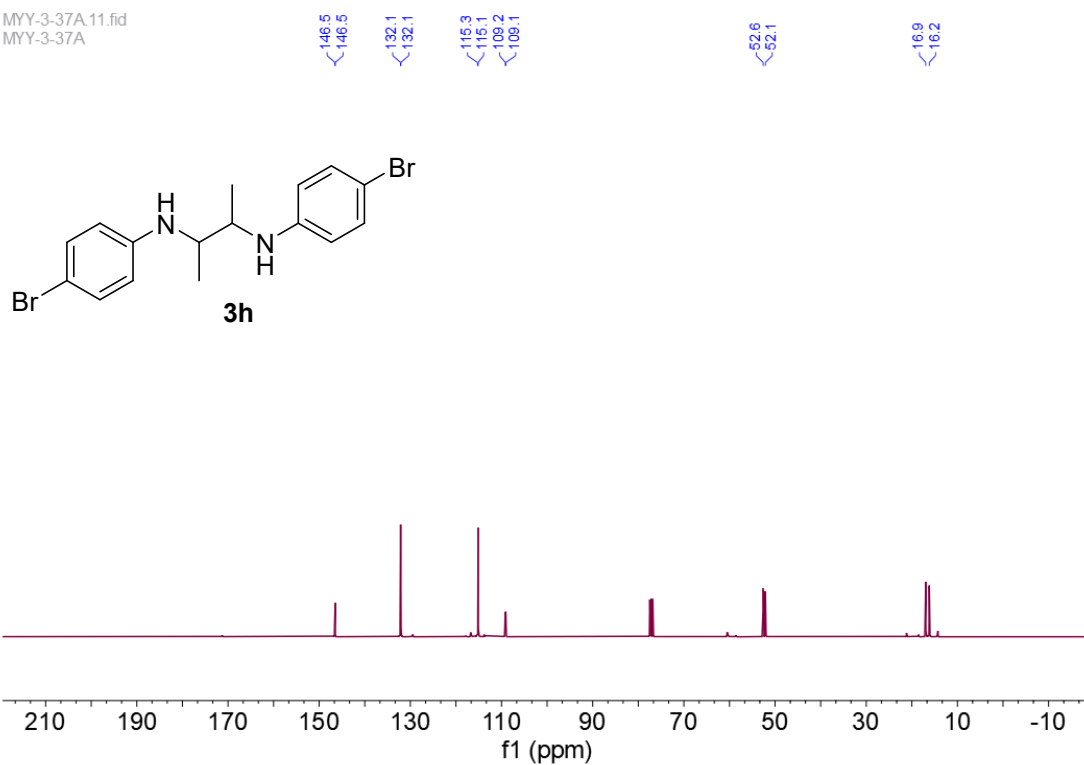


^1H -NMR spectrum of **3h** (CDCl_3 , 400 MHz)



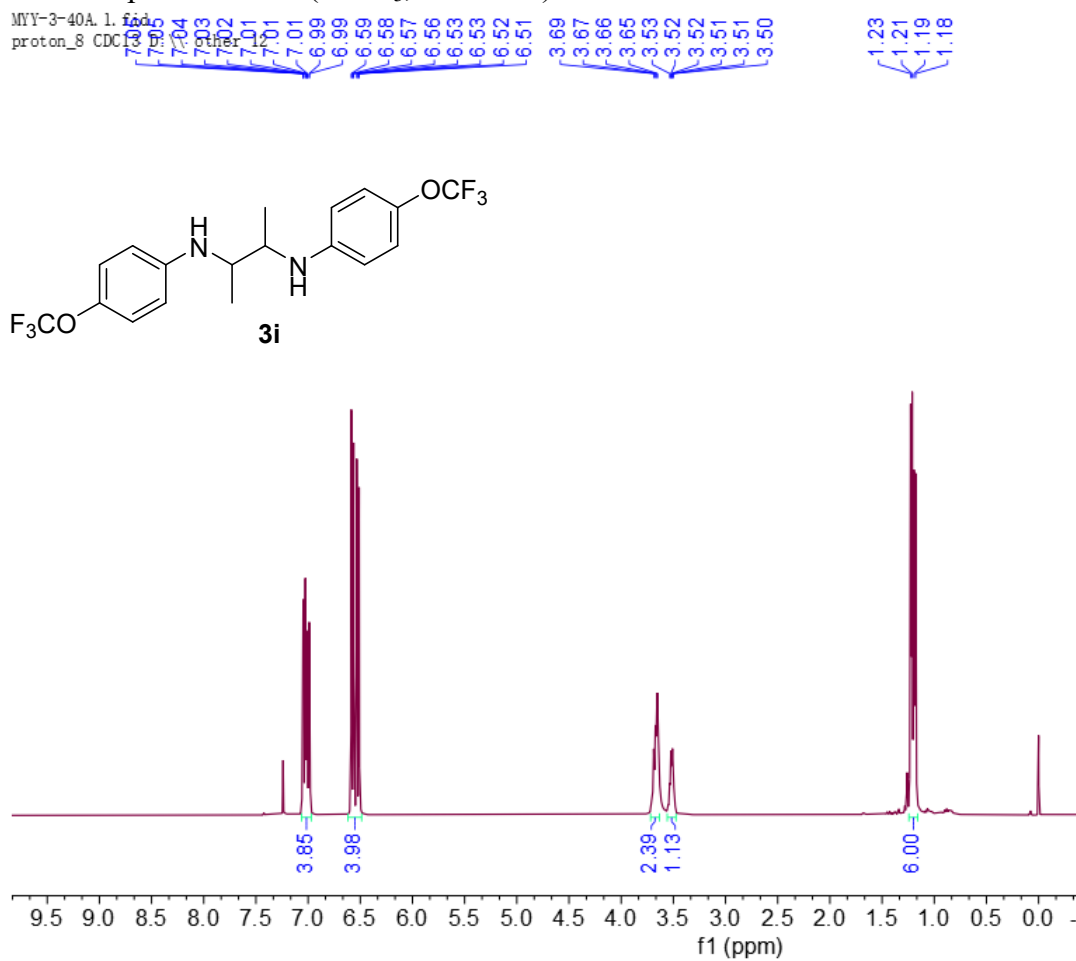
¹³C-NMR spectrum of **3h** (CDCl₃, 100 MHz)

MYY-3-37A.11.fid
MYY-3-37A

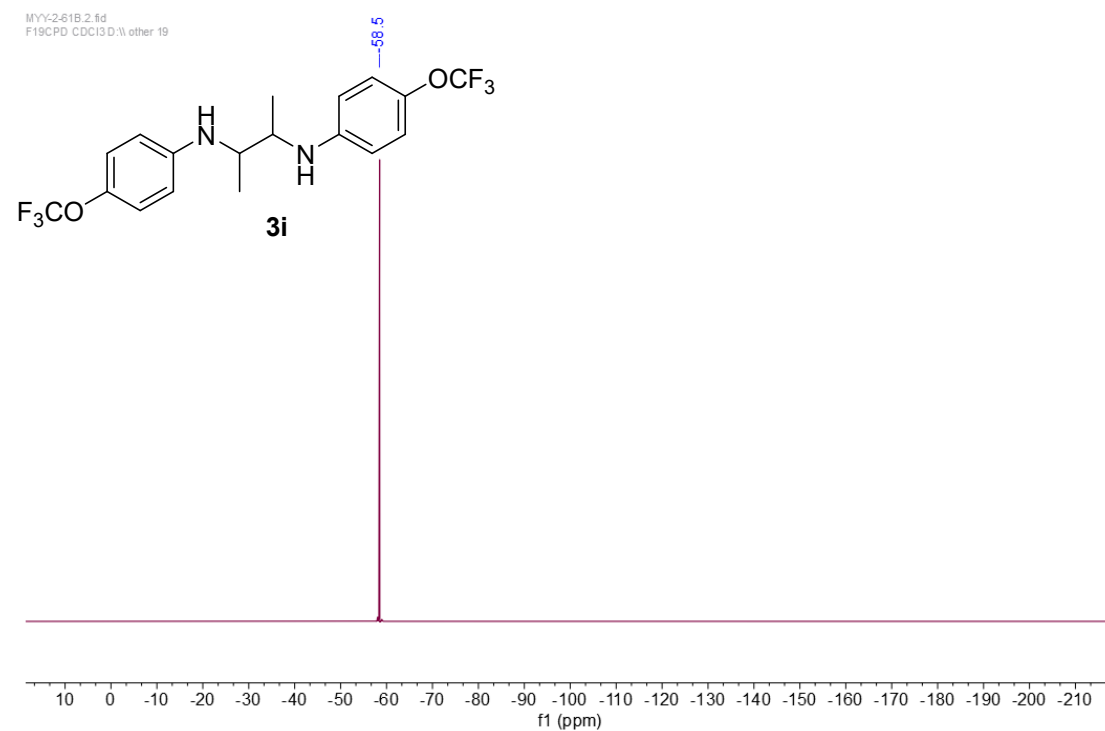


¹H-NMR spectrum of **3i** (CDCl₃, 400 MHz)

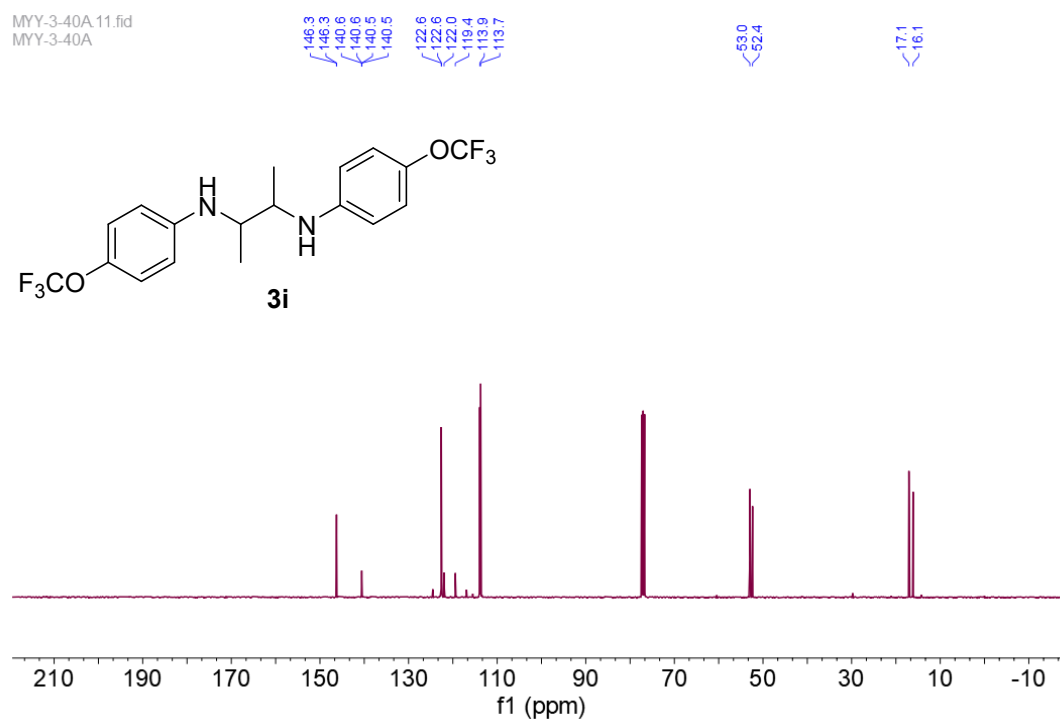
MYY-3-40A.1.164
proton_8 CDCl₃ D₂O



¹⁹F-NMR spectrum of **3i** (CDCl₃, 376 MHz)



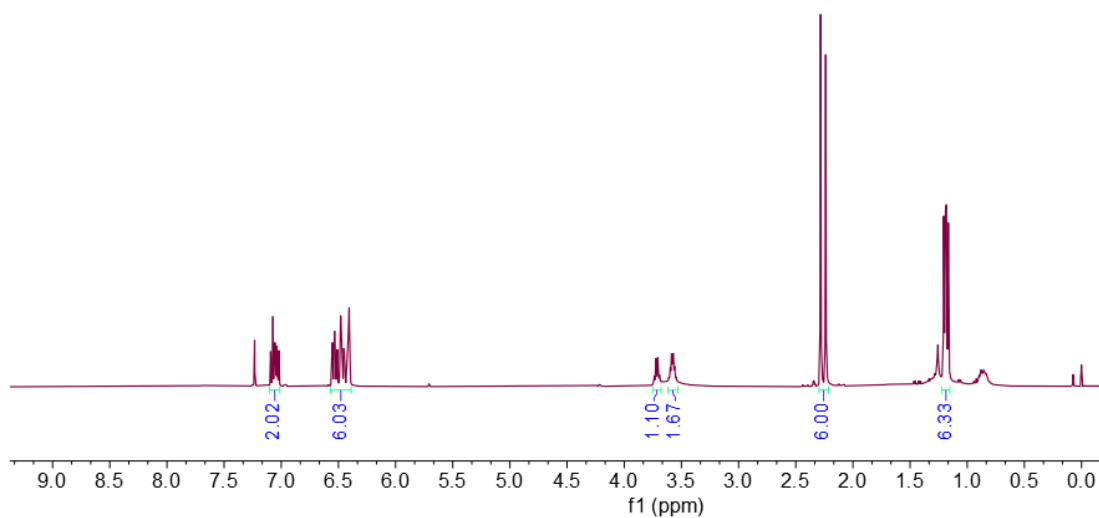
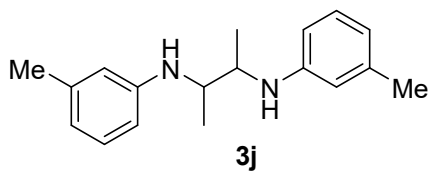
¹³C-NMR spectrum of **3i** (CDCl₃, 100 MHz)



¹H-NMR spectrum of **3j** (CDCl₃, 400 MHz)

MYY-2-26D.1.fid
PROTON CDCl₃

7.99, 7.97, 7.96, 7.95, 7.05, 7.04, 7.03, 7.02, 6.55, 6.54, 6.53, 6.53, 6.53, 6.51, 6.49, 6.48, 6.47, 6.47, 6.45, 6.45, 6.43, 6.42, 6.41, 6.41, 3.73, 3.72, 3.71, 3.70, 3.60, 3.59, 3.57, 3.57, 3.56, 2.28, 2.24, 1.21, 1.20, 1.19, 1.19, 1.18, 1.17



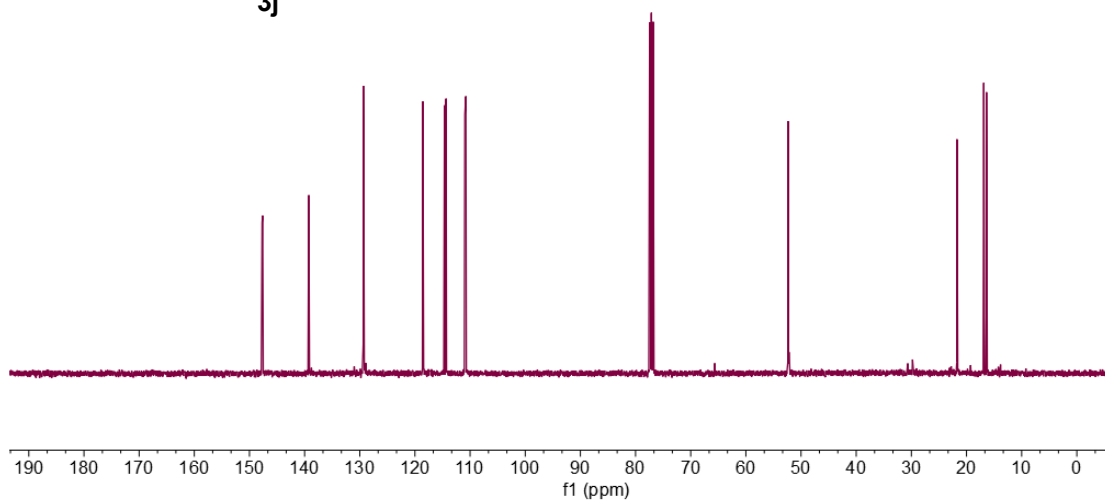
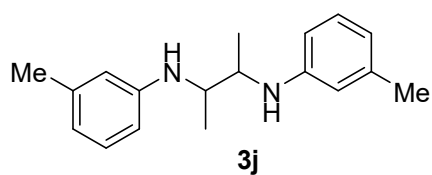
¹³C-NMR spectrum of **3j** (CDCl₃, 100 MHz)

MYY-2-26DY2.fid
C13CPD CDCl₃ D:\other 3

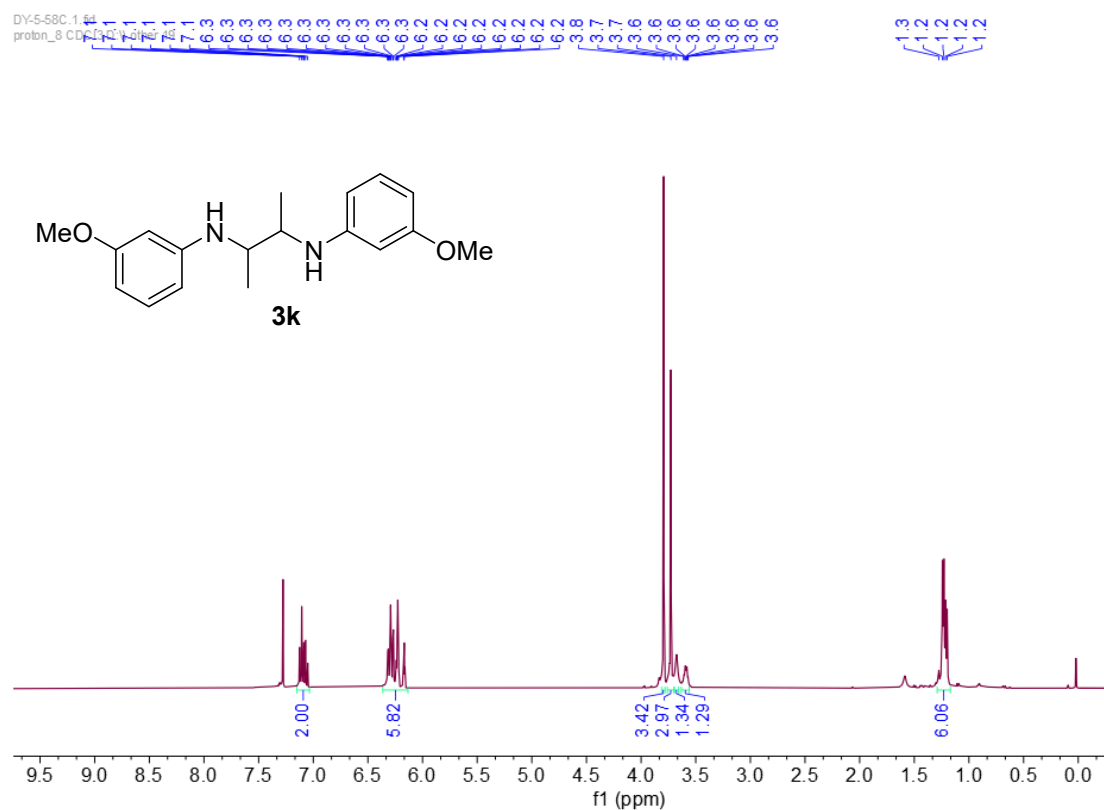
147.6, 147.6, 139.2, 139.2, 129.3, 129.3, 128.9, 118.6, 118.5, 114.6, 114.4, 110.9, 110.8

52.4, 52.2

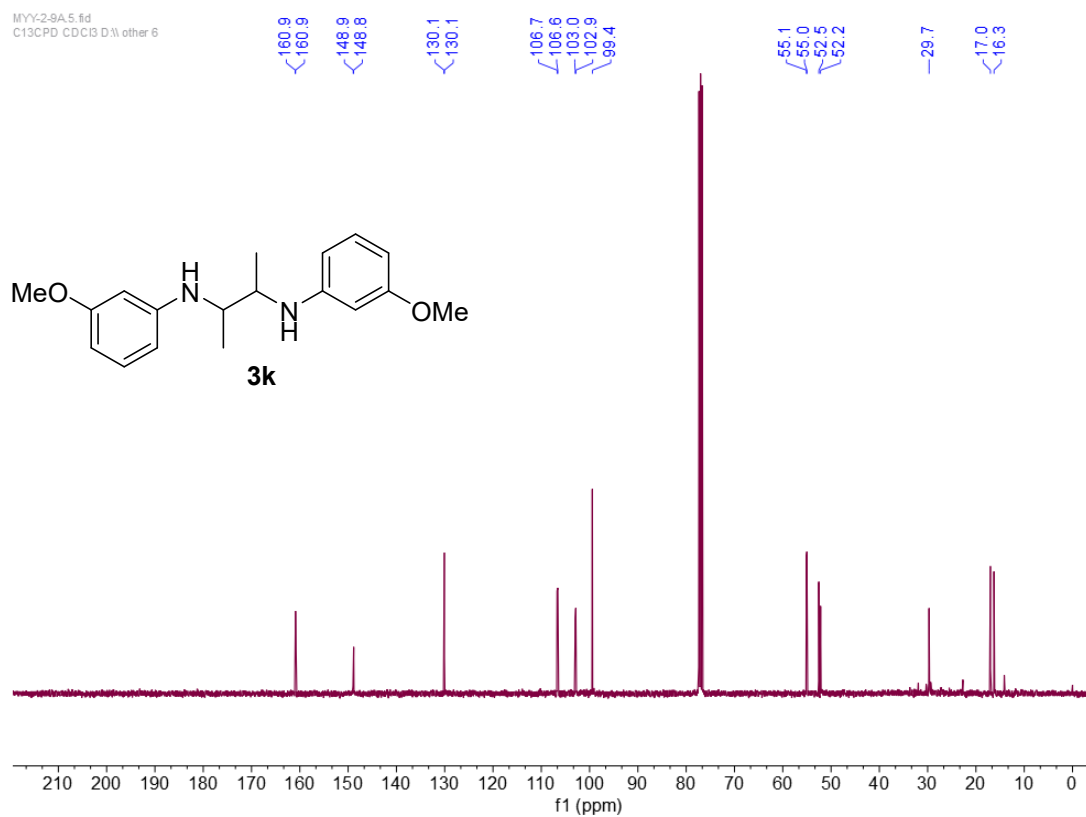
21.7, 21.7, 16.9, 16.4



¹H-NMR spectrum of **3k** (CDCl₃, 400 MHz)



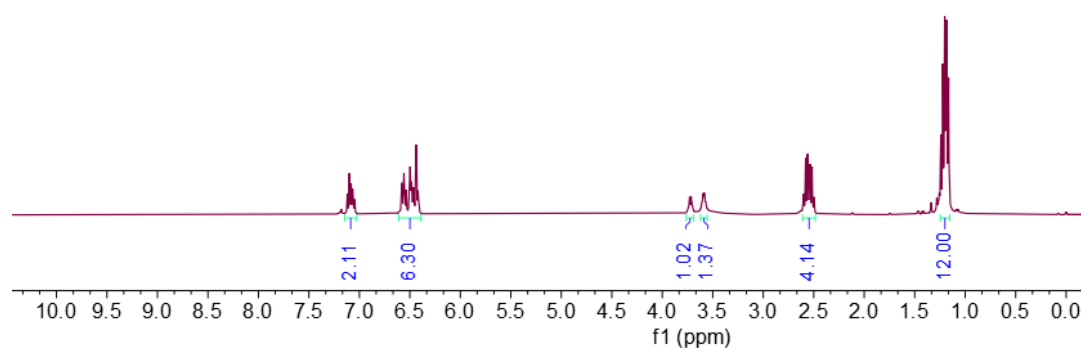
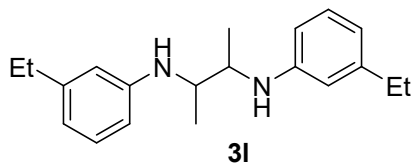
¹³C-NMR spectrum of **3k** (CDCl₃, 100 MHz)



¹H-NMR spectrum of **31** (CDCl₃, 400 MHz)

MYY-2-47A3.fid
PROTON CDCl3 D:\other19

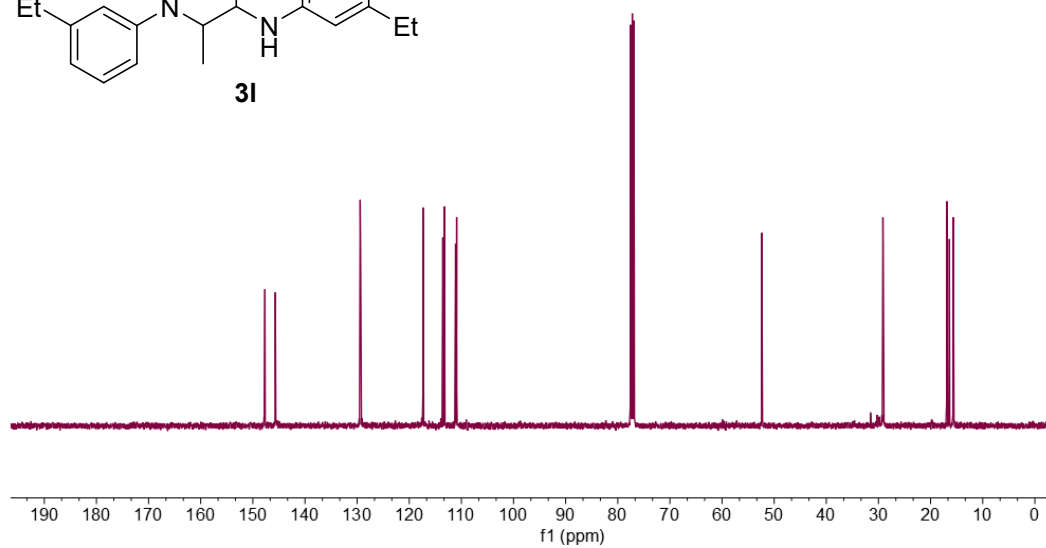
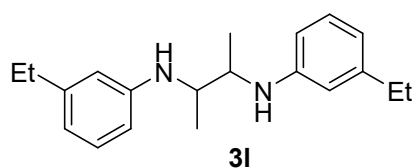
7.12, 7.10, 7.09, 7.08, 7.07, 7.06, 7.05, 6.56, 6.54, 6.50, 6.49, 6.48, 6.47, 6.46, 6.44, 6.42, 6.41, 3.73, 3.71, 3.71, 3.61, 3.60, 3.59, 3.59, 3.58, 3.57, 2.60, 2.58, 2.56, 2.55, 2.54, 2.54, 2.52, 2.50, 1.24, 1.22, 1.20, 1.19, 1.18, 1.16



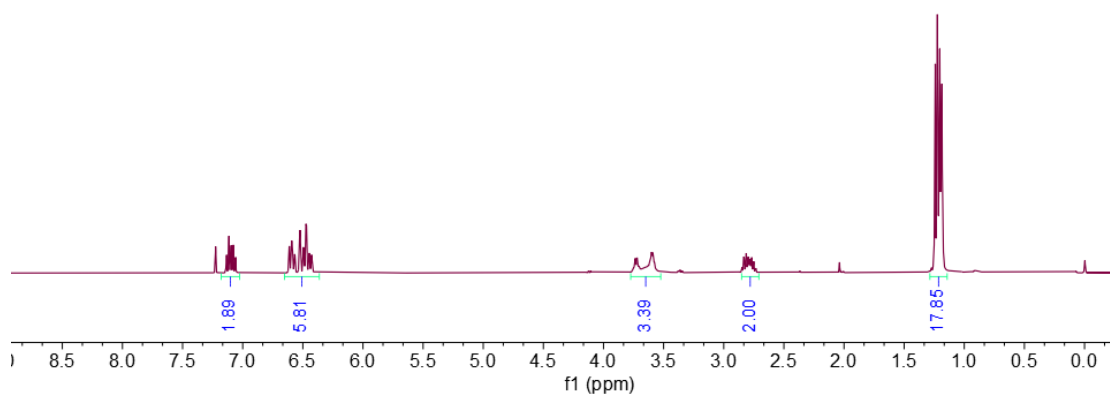
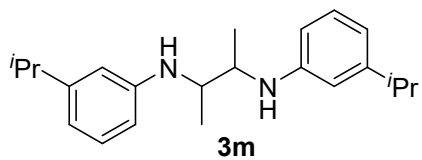
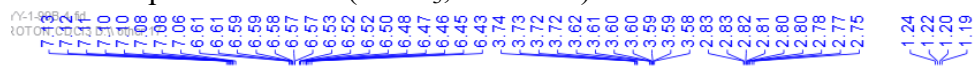
¹³C-NMR spectrum of **31** (CDCl₃, 100 MHz)

MYY-2-47A.4.fid
C13CPD CDCl3 D:\other19

147.8, 147.7, 145.7, 145.6, 129.4, 129.3, 117.4, 117.3, 113.6, 113.3, 111.1, 110.9, 52.4, 52.3, 29.1, 29.1, 16.9, 16.4, 15.7, 15.6

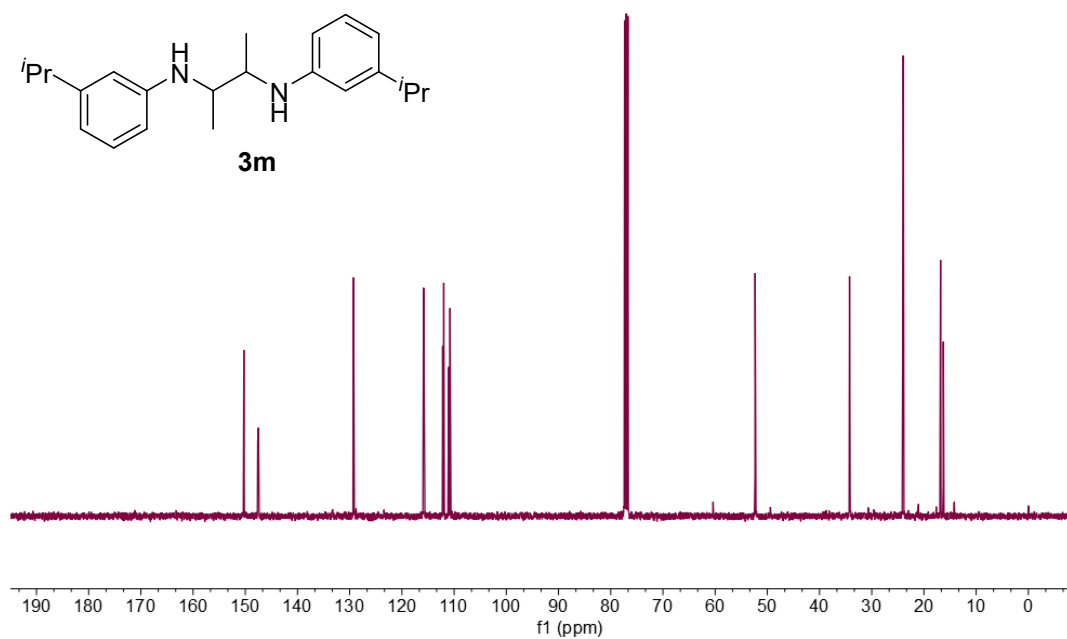
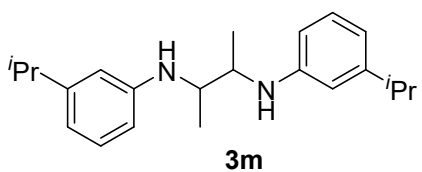


¹H-NMR spectrum of **3m** (CDCl₃, 400 MHz)

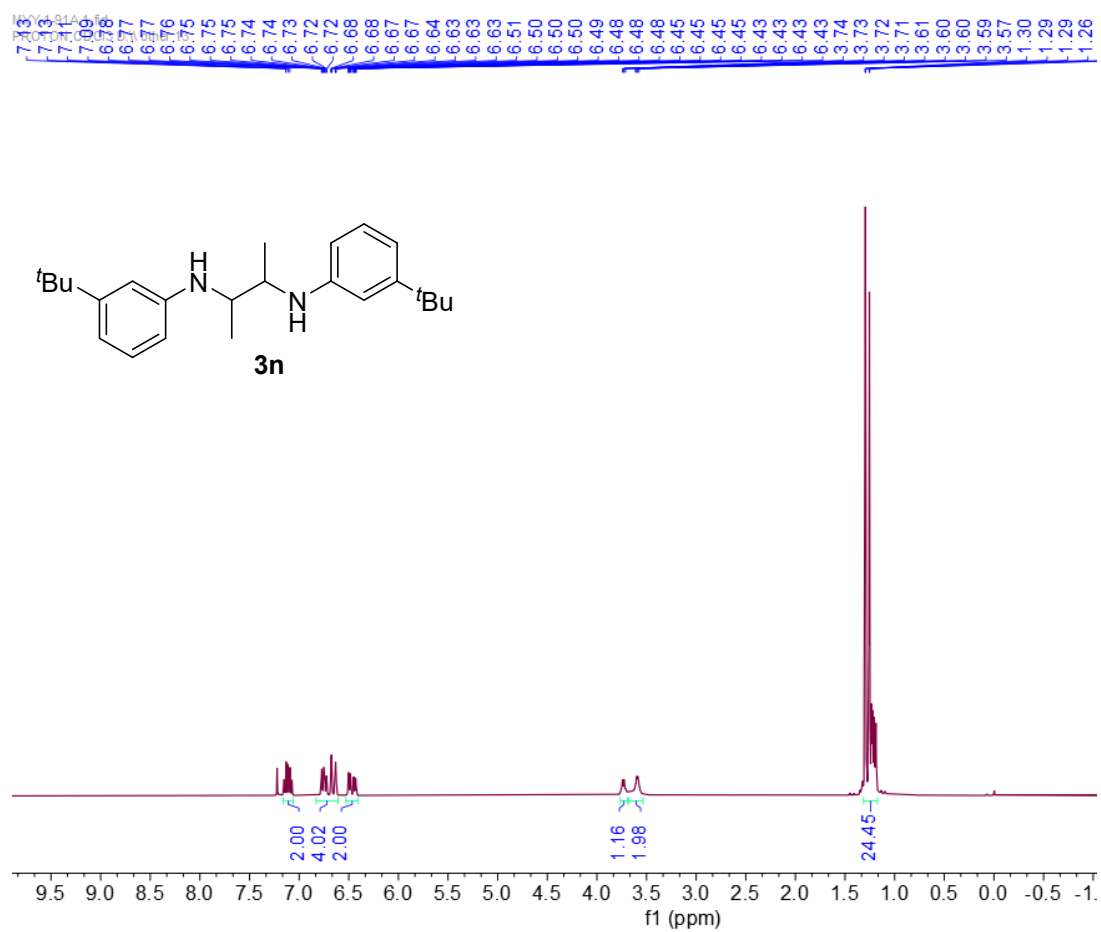


¹³C-NMR spectrum of **3m** (CDCl₃, 100 MHz)

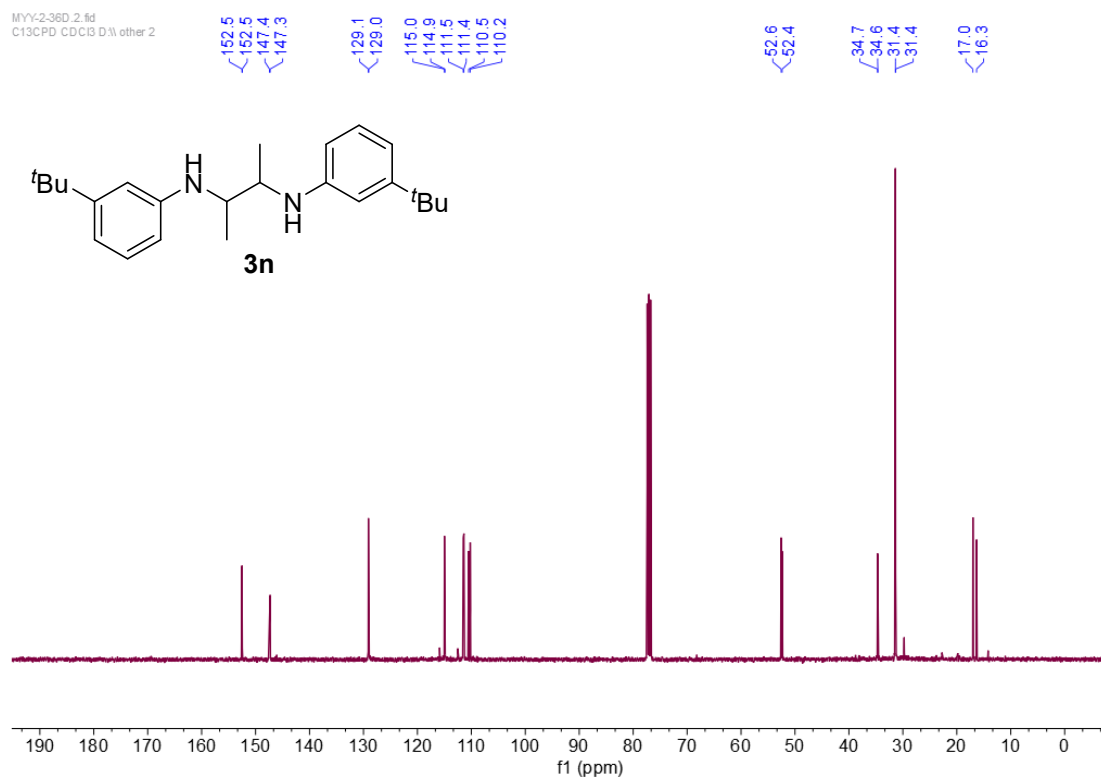
MY-1-99B 7.fid
C13CPD CDCB.D\ other 1



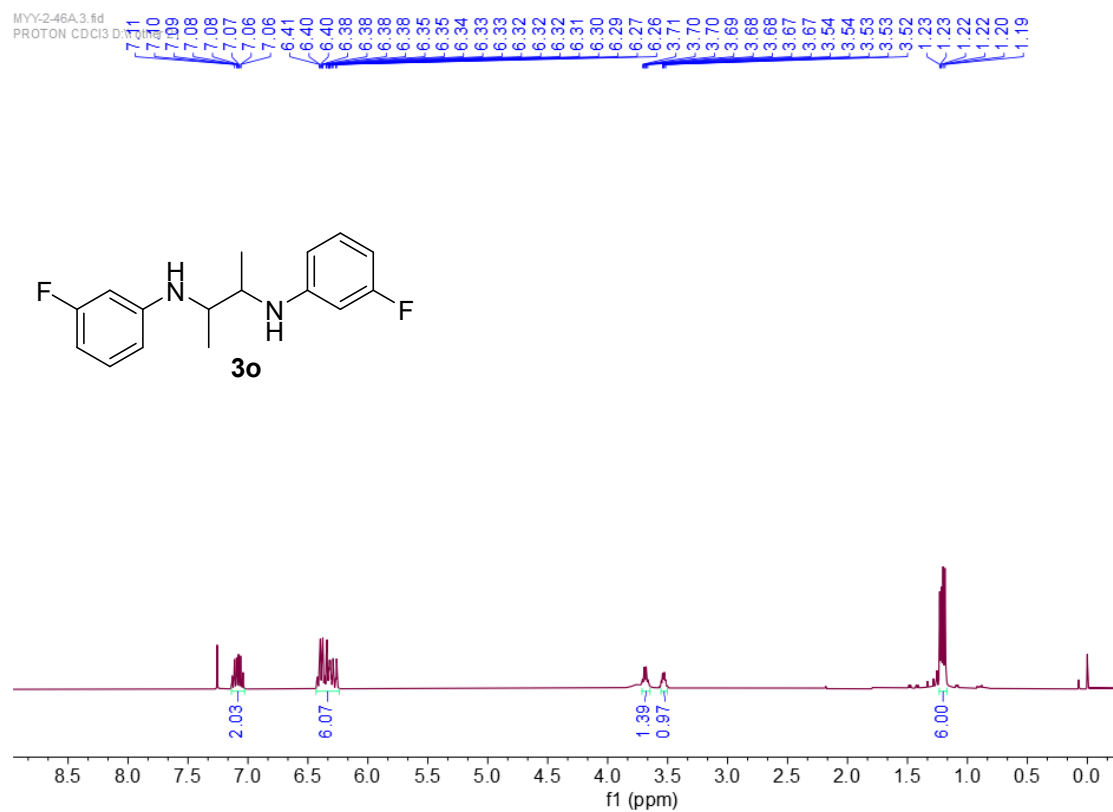
$^1\text{H-NMR}$ spectrum of **3n** (CDCl_3 , 400 MHz)



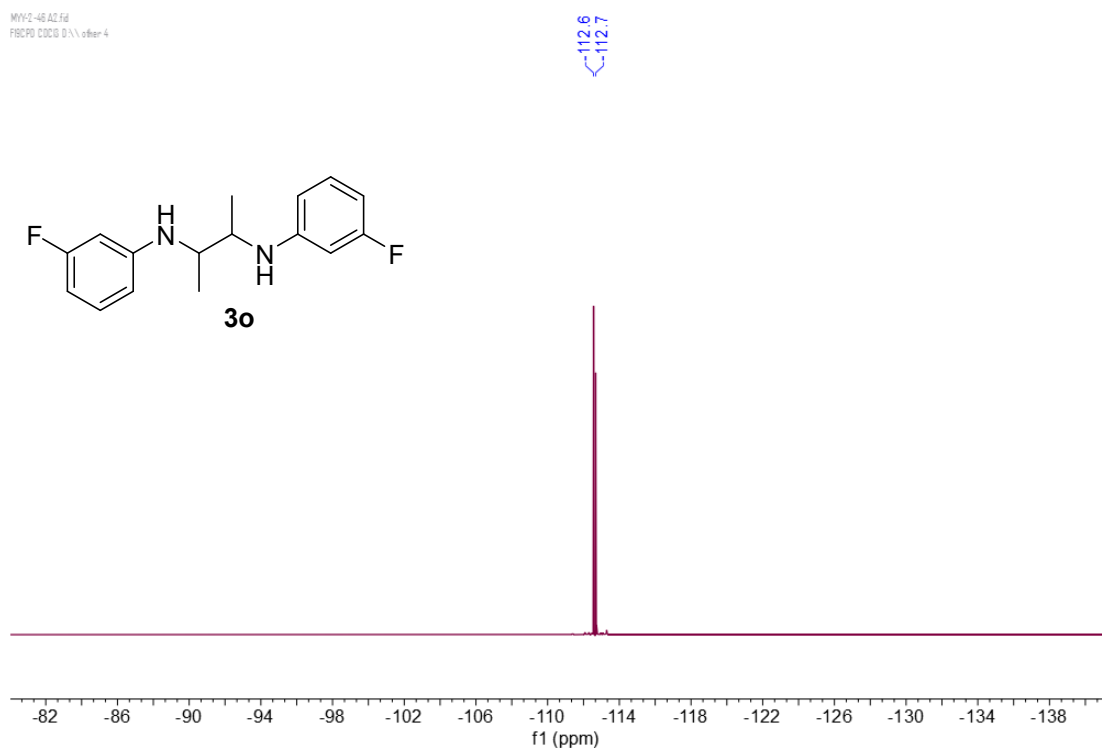
$^{13}\text{C-NMR}$ spectrum of **3n** (CDCl_3 , 100 MHz)



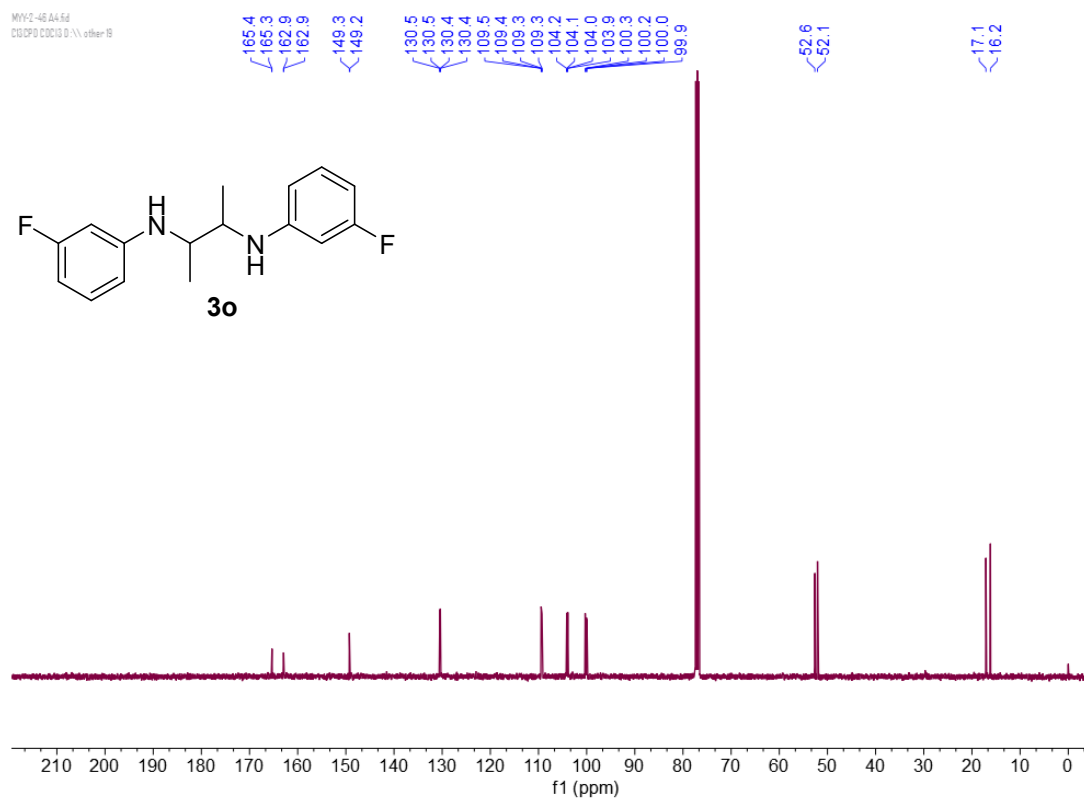
¹H-NMR spectrum of **3o** (CDCl₃, 400 MHz)



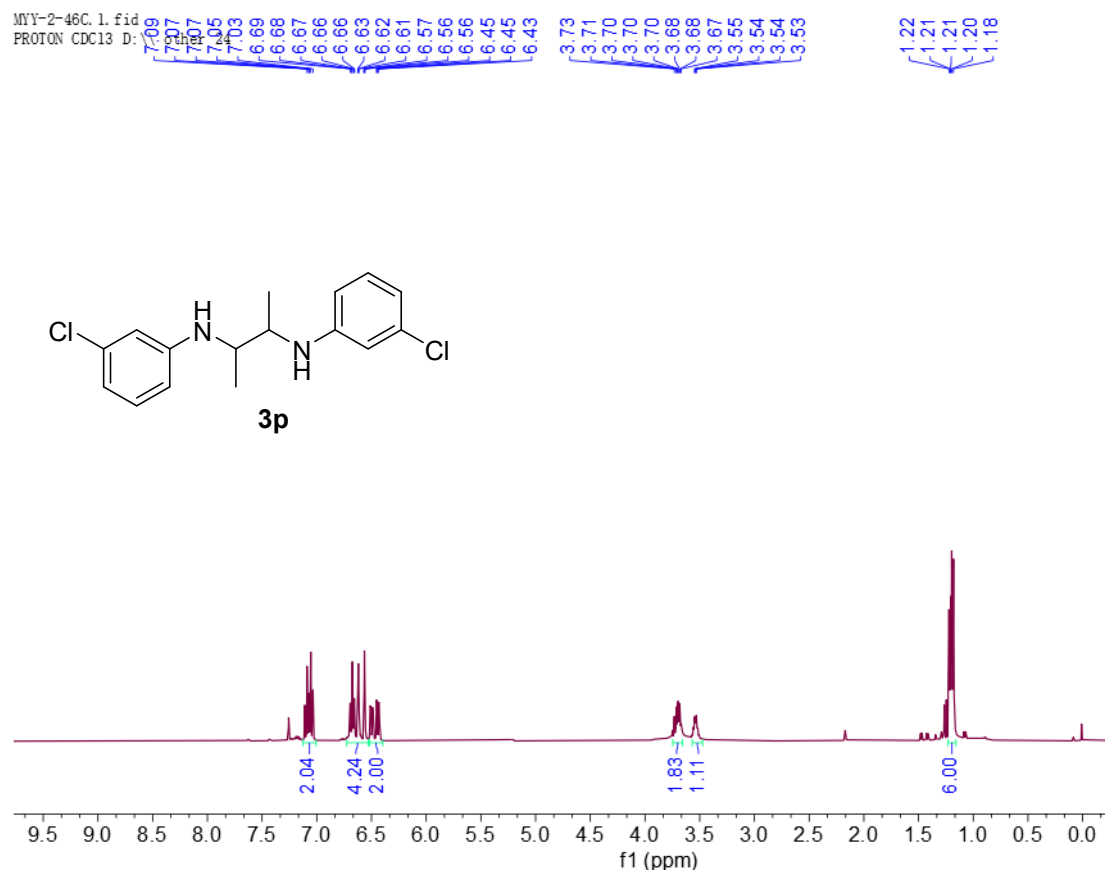
¹⁹F-NMR spectrum of **3o** (CDCl₃, 376 MHz)



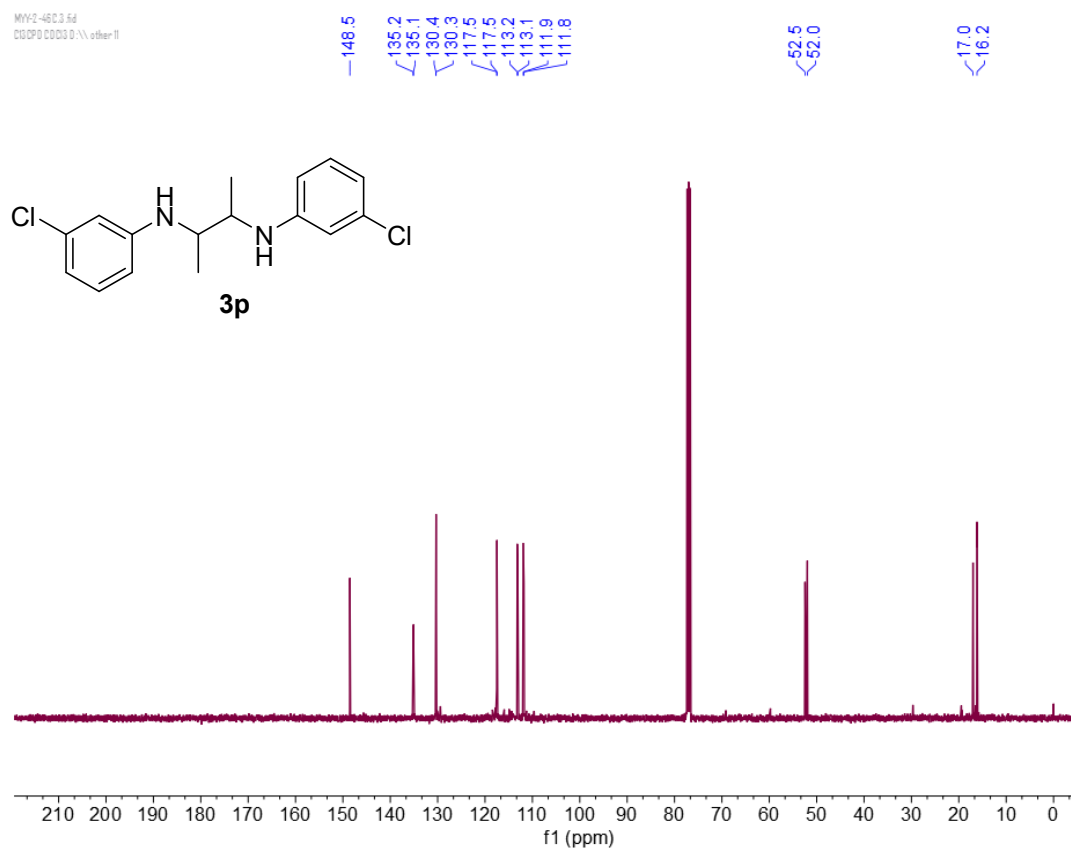
^{13}C -NMR spectrum of **3o** (CDCl_3 , 100 MHz)



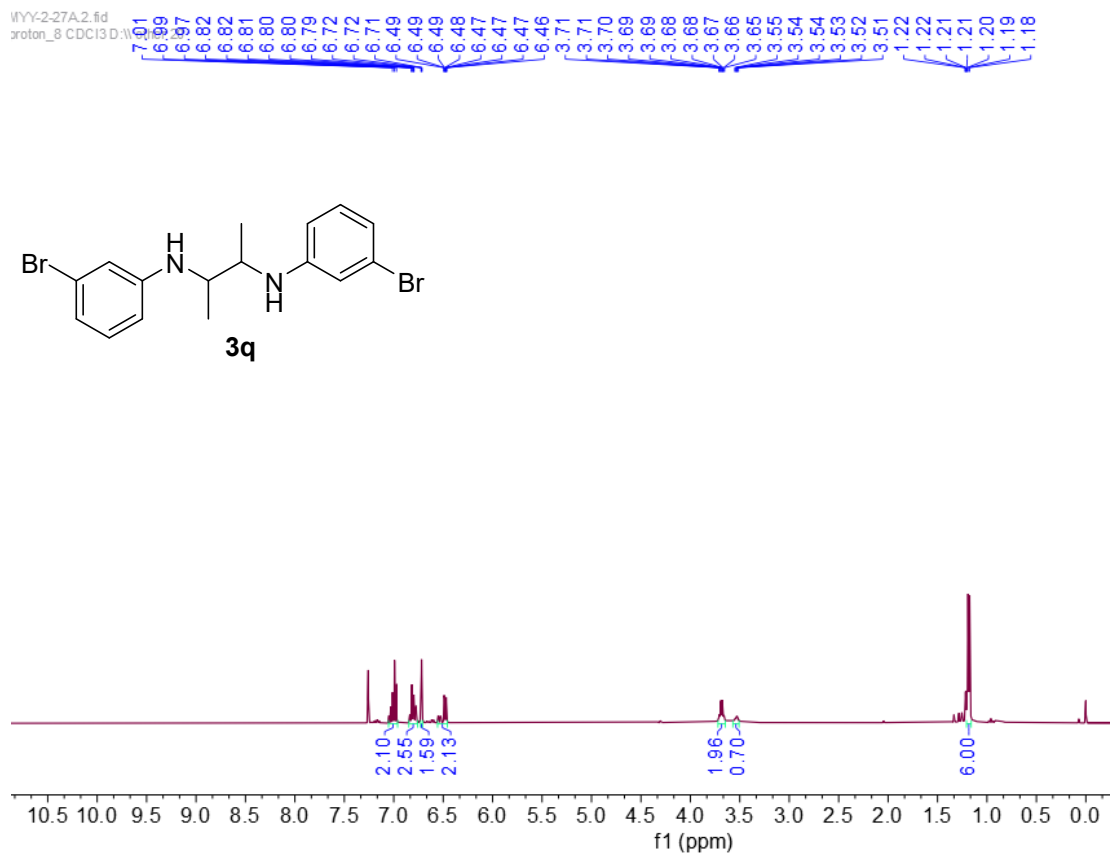
^1H -NMR spectrum of **3p** (CDCl_3 , 400 MHz)



^{13}C -NMR spectrum of **3p** (CDCl_3 , 100 MHz)

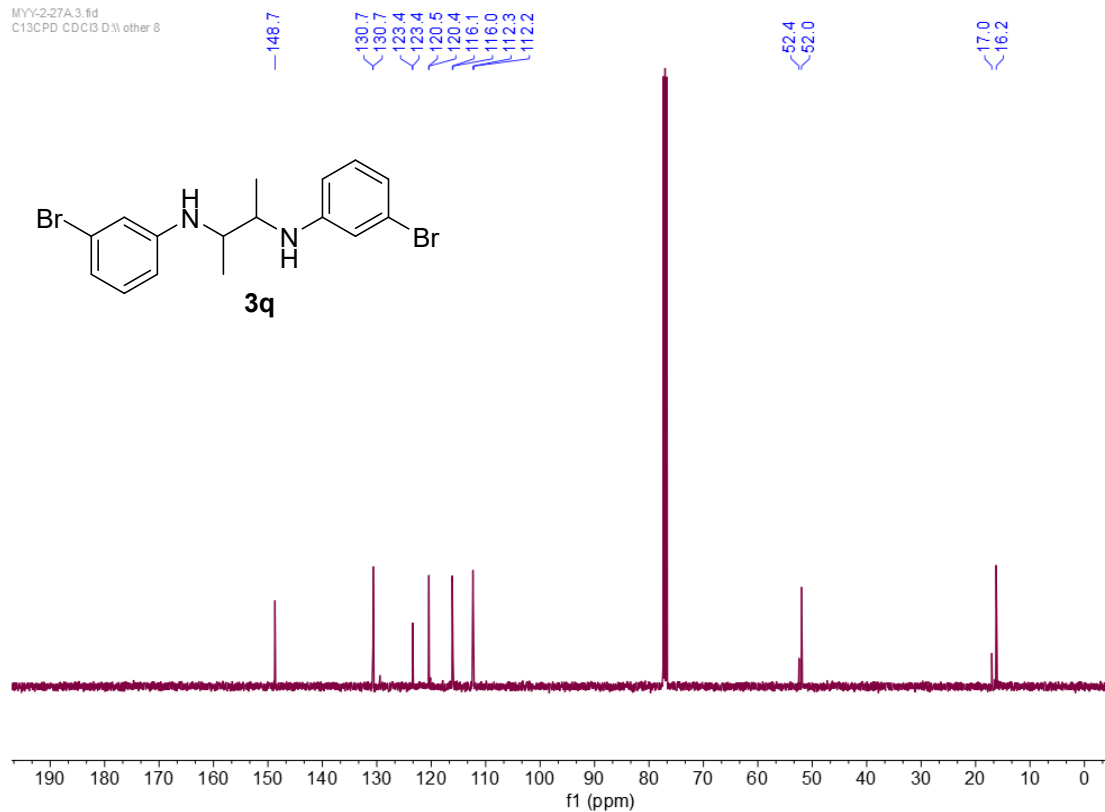


^1H -NMR spectrum of **3q** (CDCl_3 , 400 MHz)



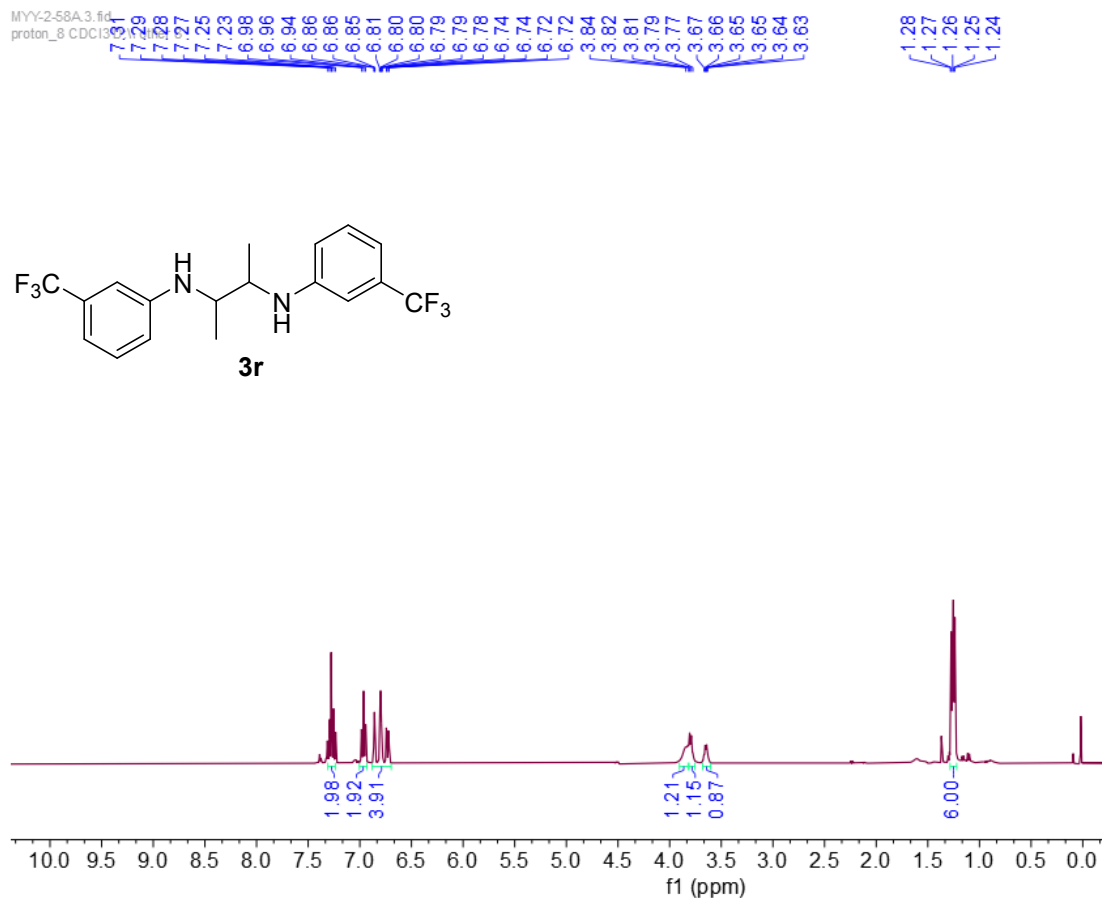
¹³C-NMR spectrum of **3q** (CDCl₃, 100 MHz)

MY-2-27A.3.fid
C13CPD CDCl3.D\\ other 8



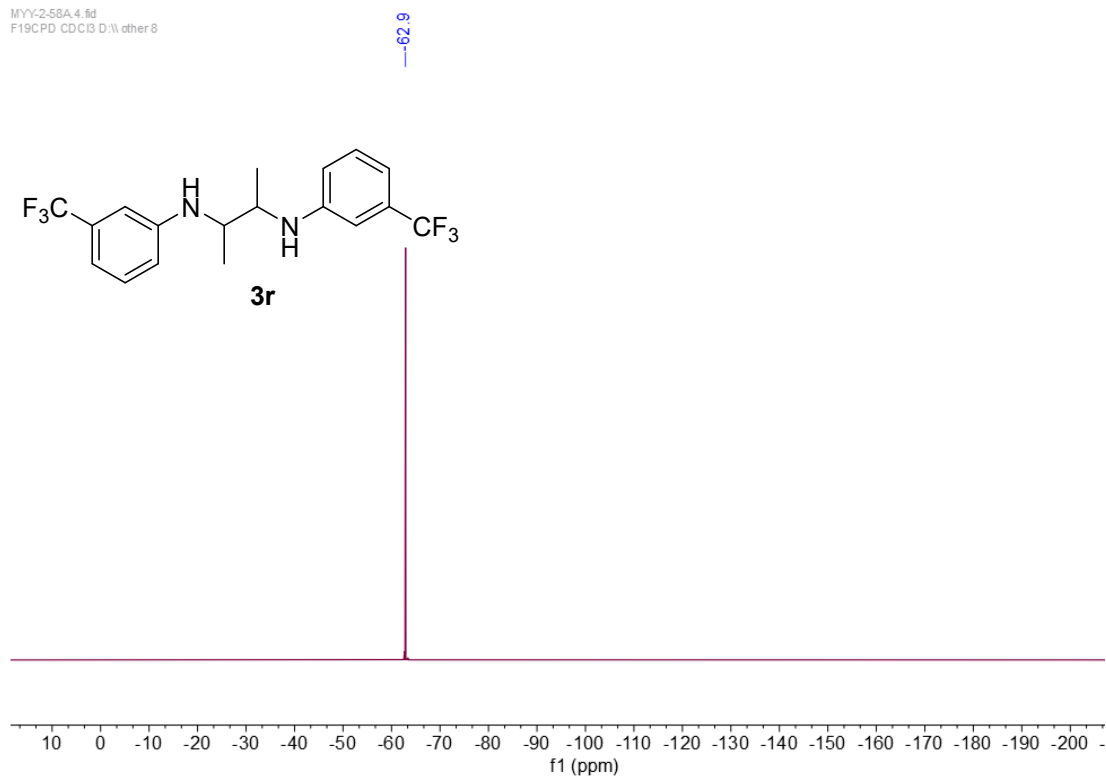
¹H-NMR spectrum of **3r** (CDCl₃, 400 MHz)

MY-2-58A.3.fid
proton_8 CDCl3



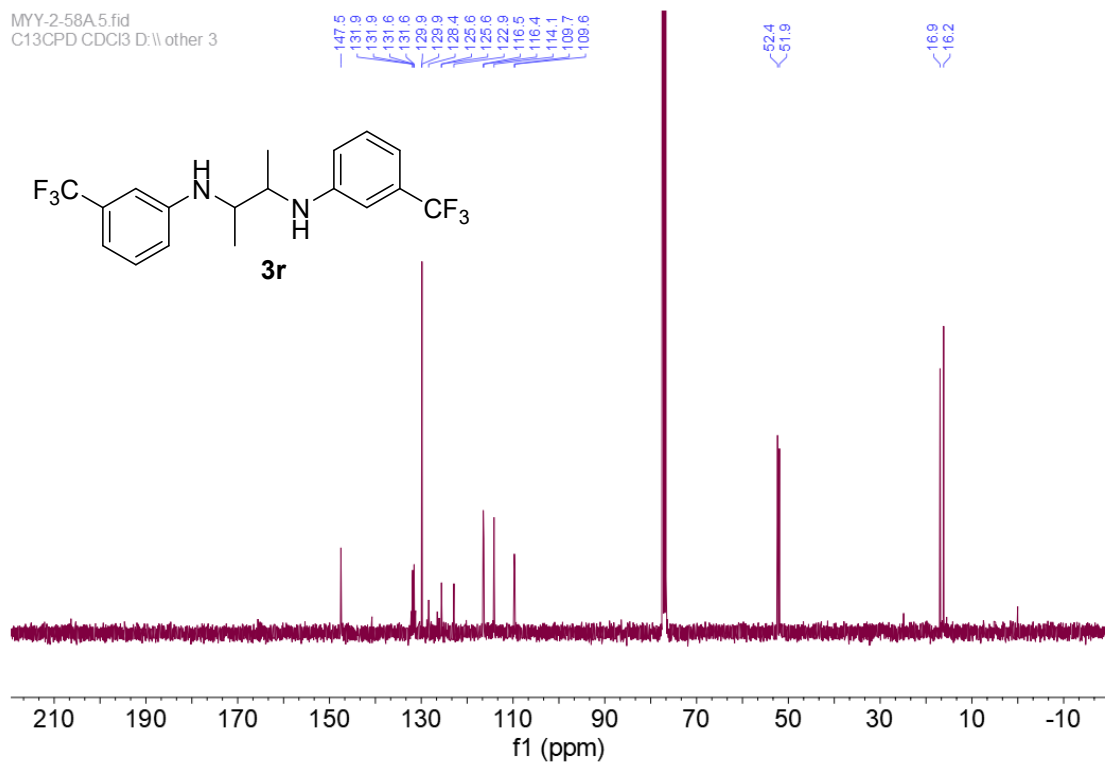
^{19}F -NMR spectrum of **3r** (CDCl_3 , 376 MHz)

MYY-2-58A.4.fid
F19CPD CDC13 D:\other 8

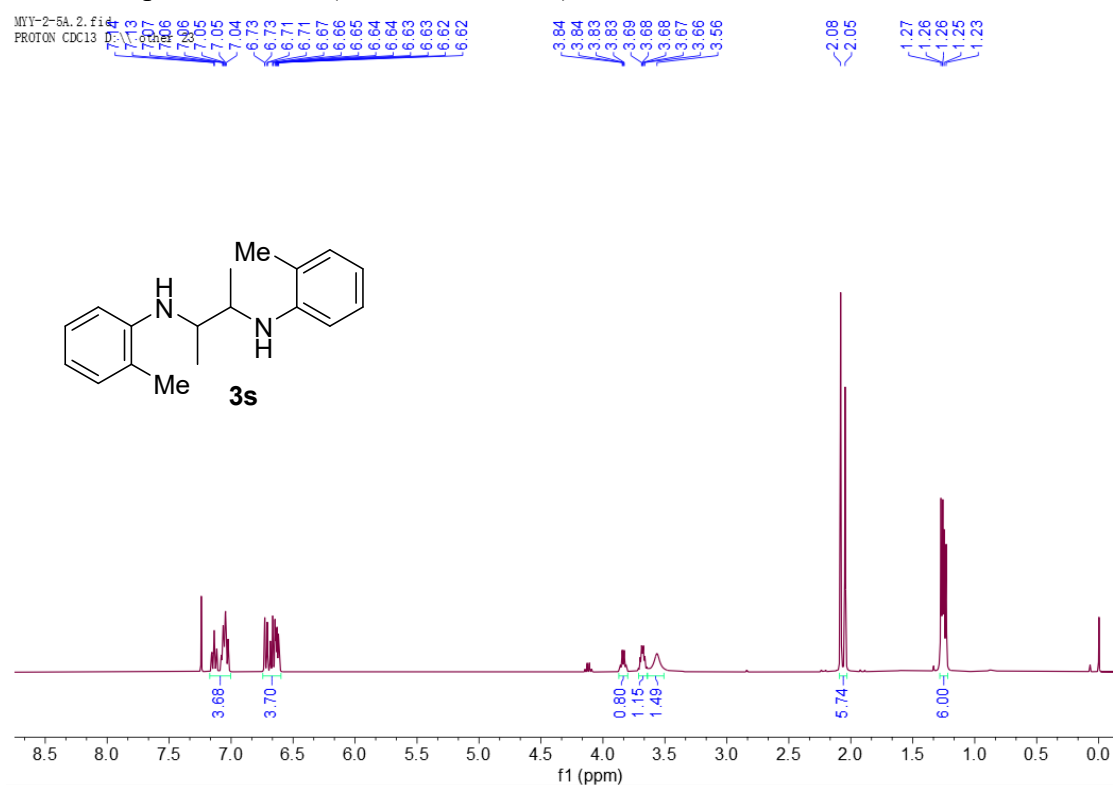


^{13}C -NMR spectrum of **3r** (CDCl_3 , 100 MHz)

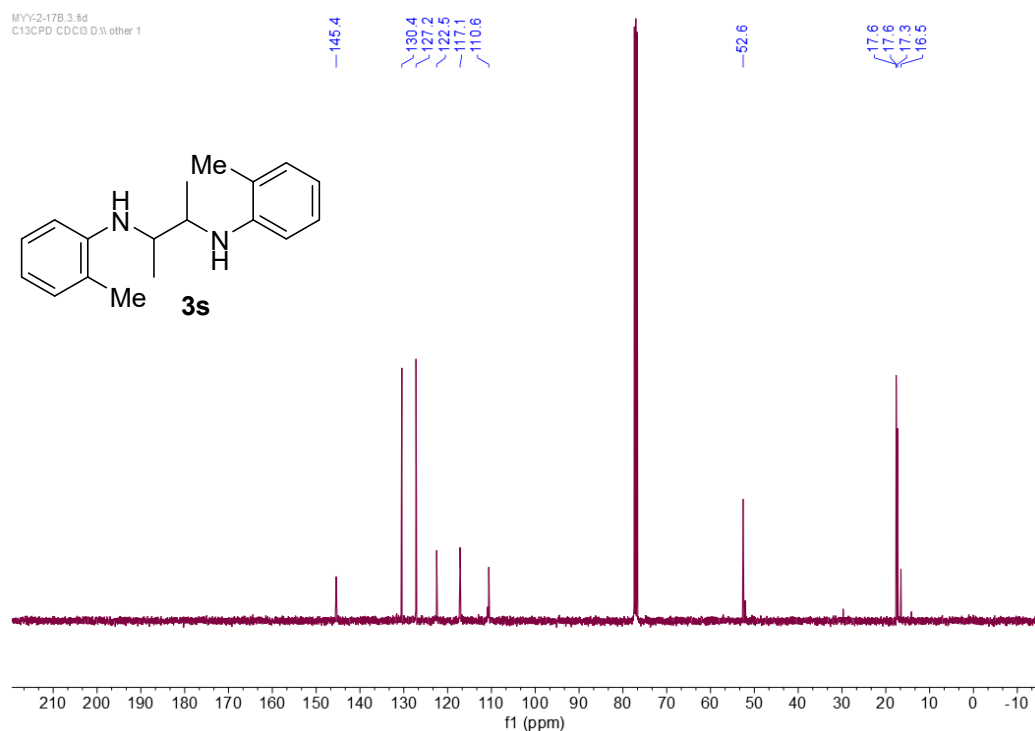
MYY-2-58A.5.fid
C13CPD CDC13 D:\other 3



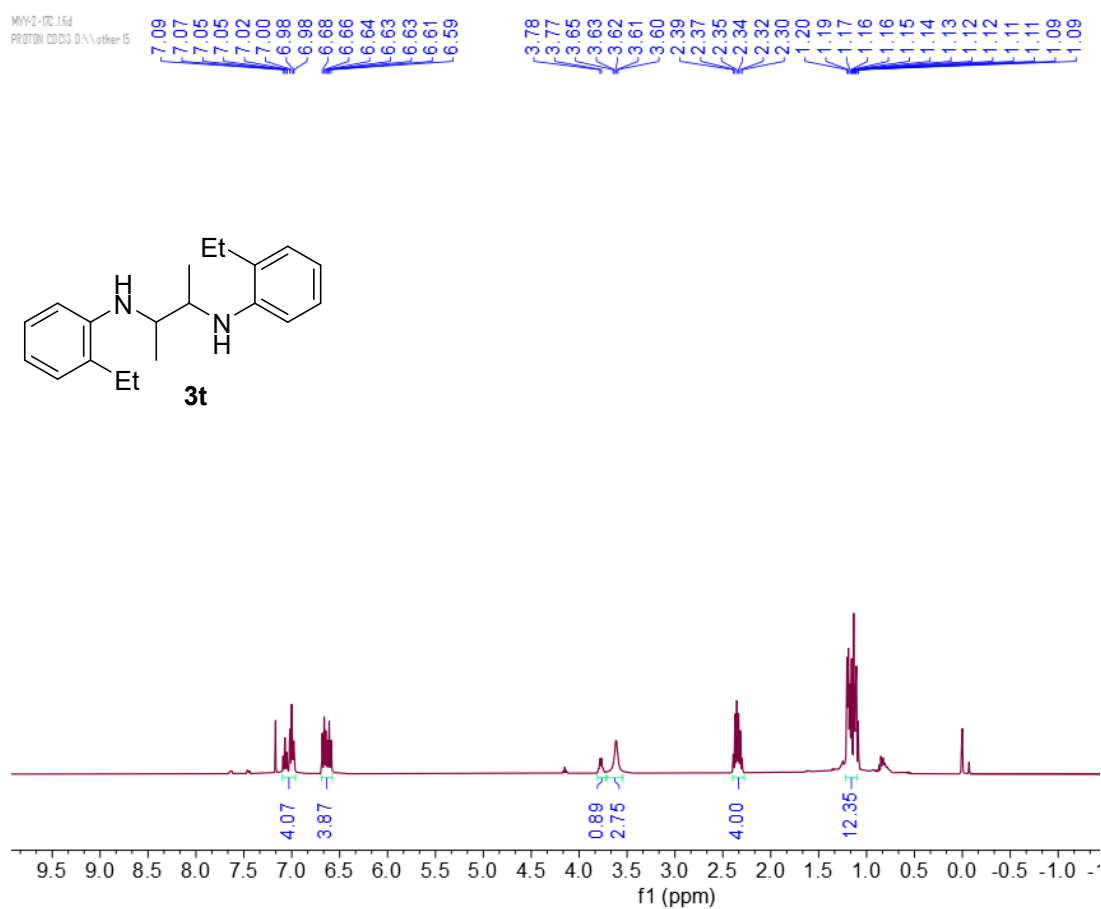
$^1\text{H-NMR}$ spectrum of **3s** (CDCl_3 , 400 MHz)



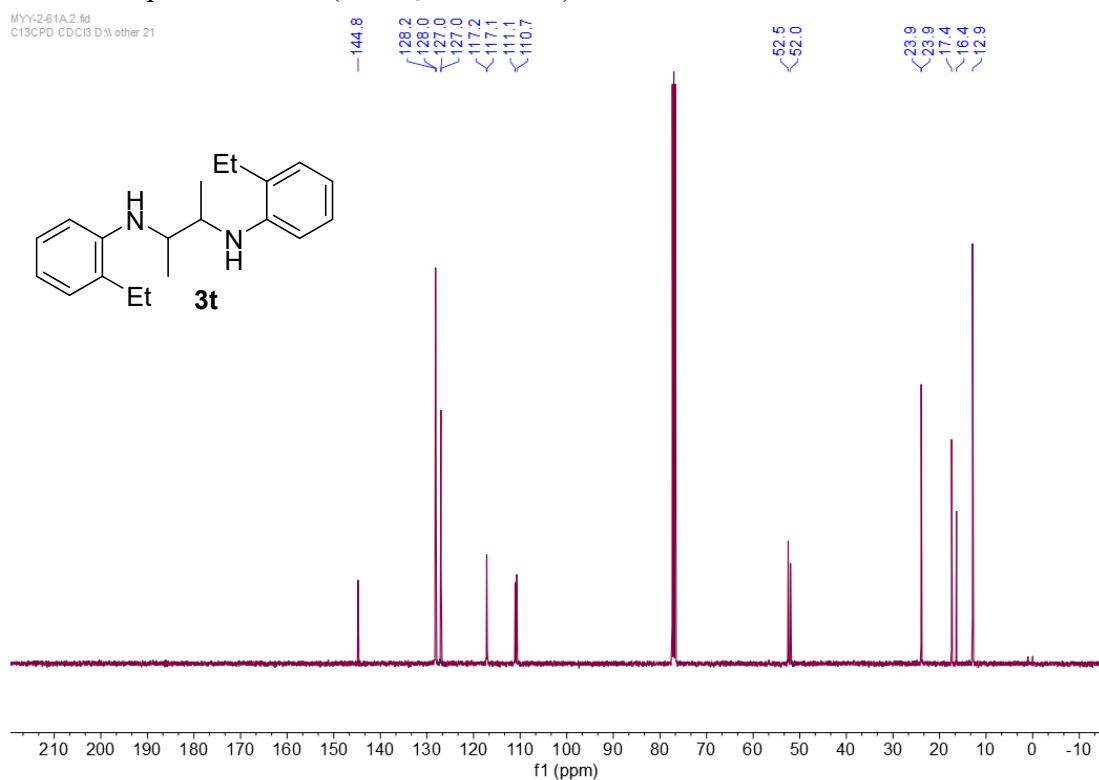
$^{13}\text{C-NMR}$ spectrum of **3s** (CDCl_3 , 100 MHz)



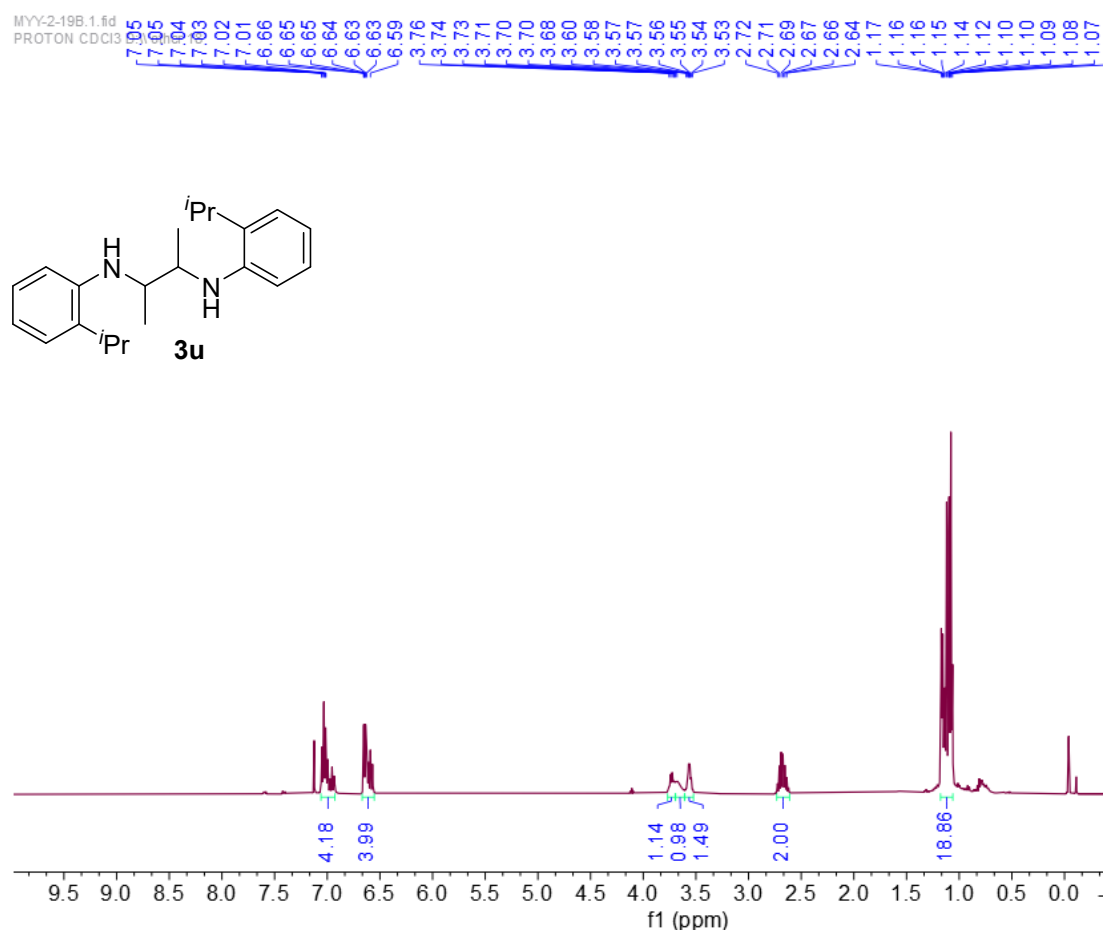
$^1\text{H-NMR}$ spectrum of **3t** (CDCl_3 , 400 MHz)



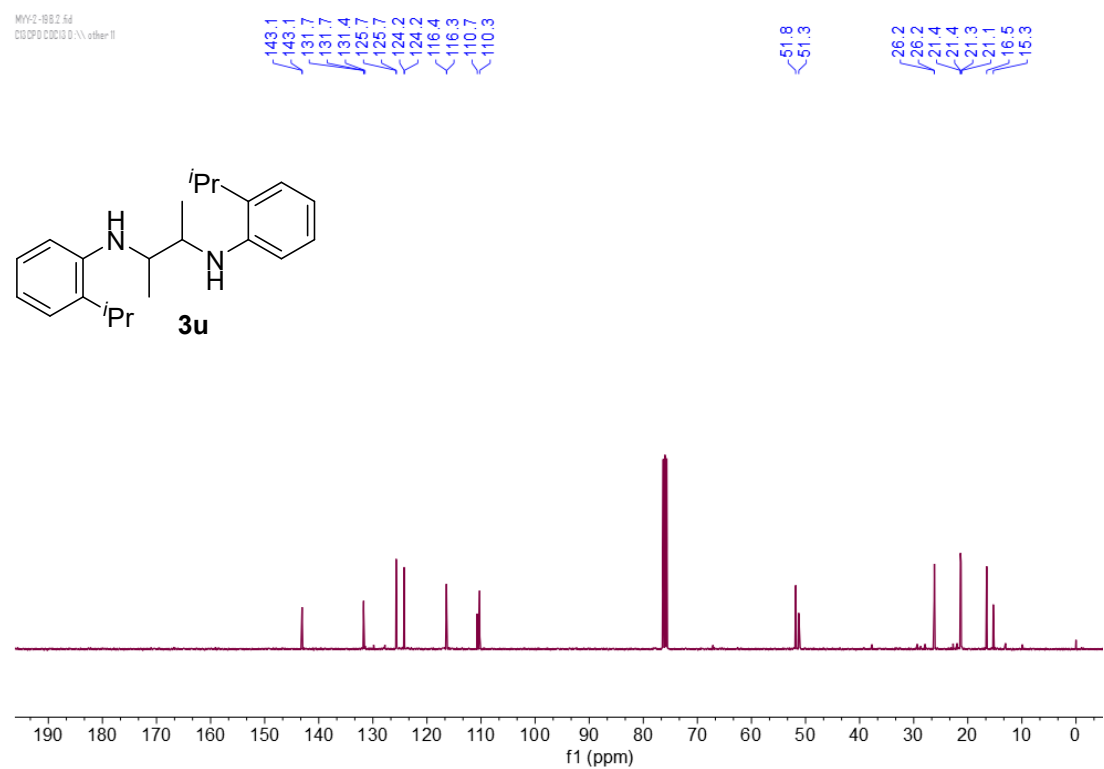
$^{13}\text{C-NMR}$ spectrum of **3t** (CDCl_3 , 100 MHz)



$^1\text{H-NMR}$ spectrum of **3u** (CDCl_3 , 400 MHz)

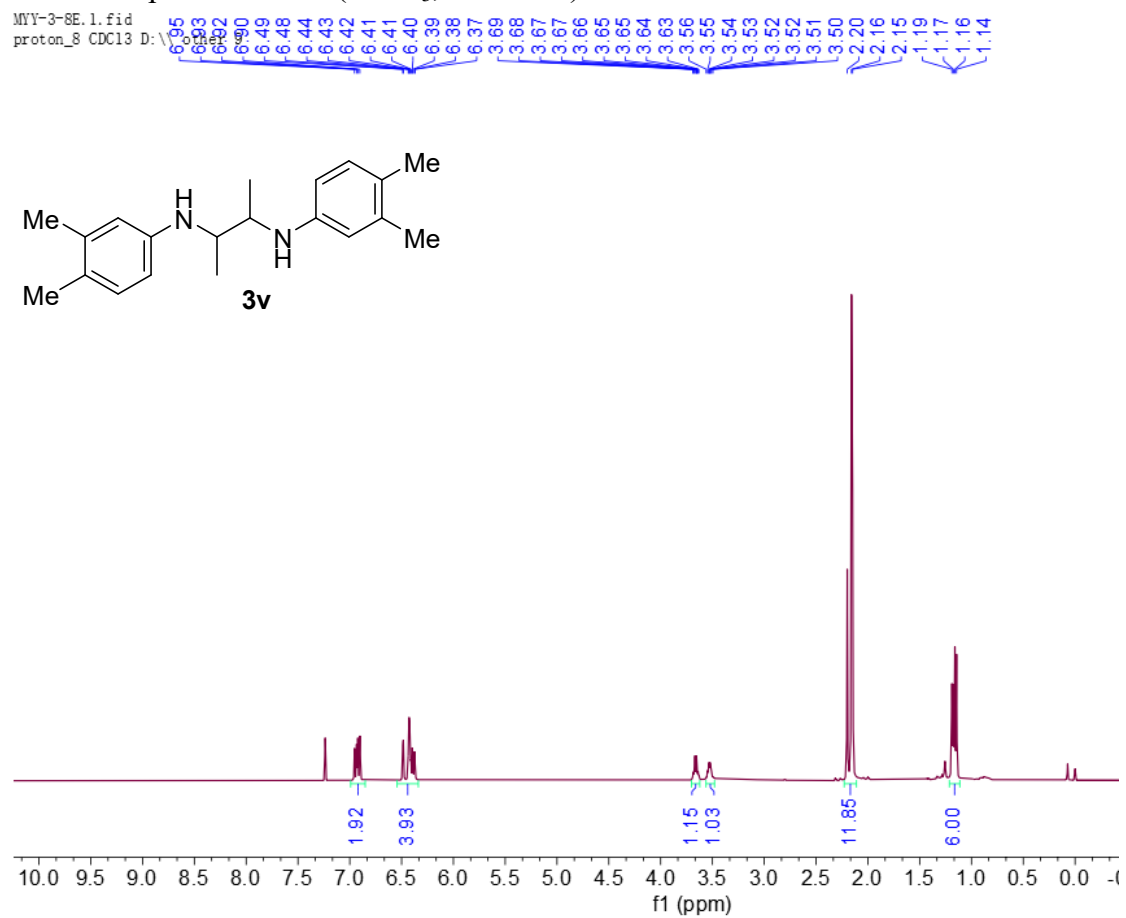


$^{13}\text{C-NMR}$ spectrum of **3u** (CDCl_3 , 100 MHz)



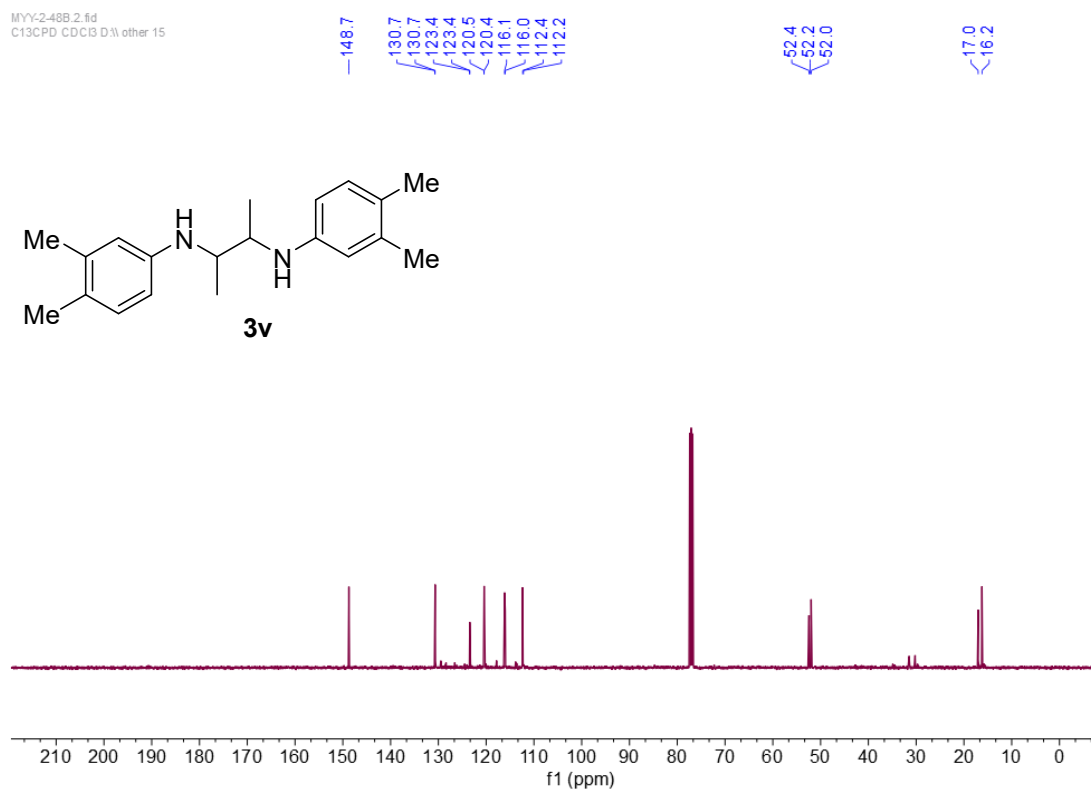
¹H-NMR spectrum of **3v** (CDCl₃, 400 MHz)

MYY-3-8E.1.fid
proton_8 CDCl3 D:\



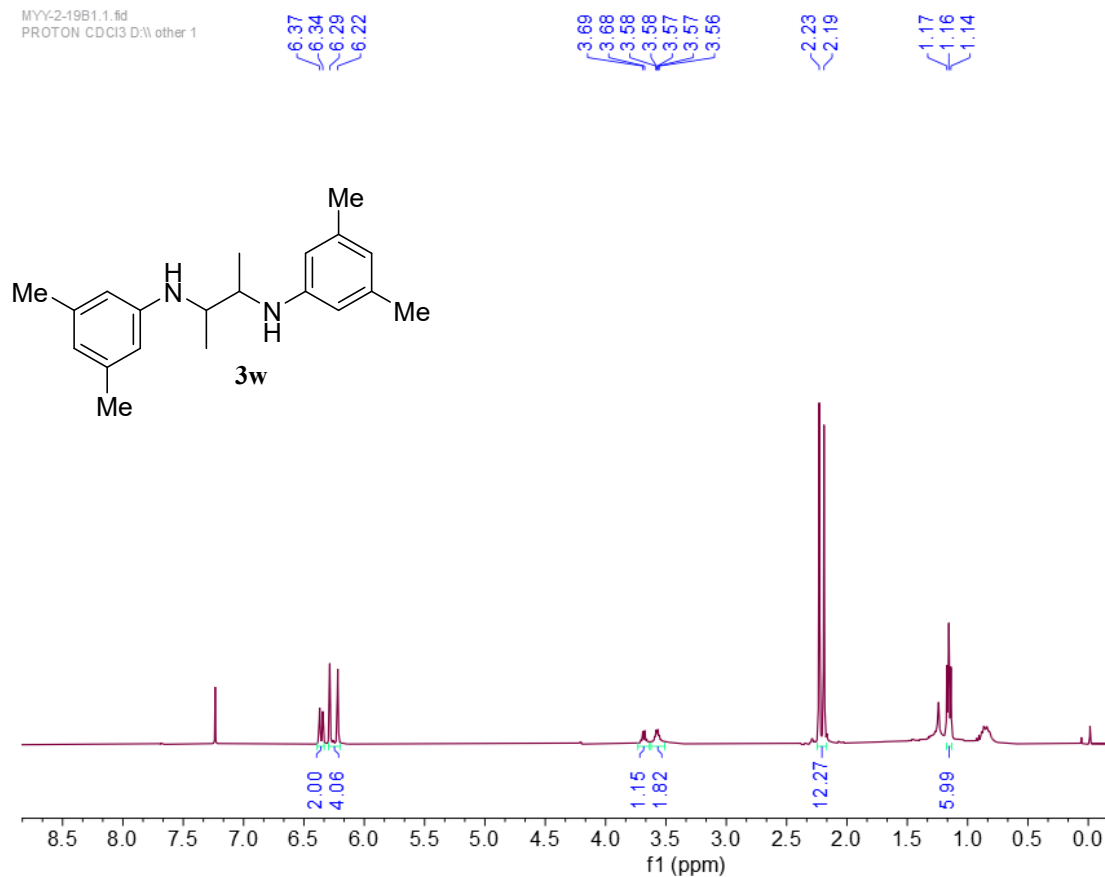
¹³C-NMR spectrum of **3v** (CDCl₃, 100 MHz)

MYY-2-48B.2.fid
C13CPD CDCl3 D:\other 15



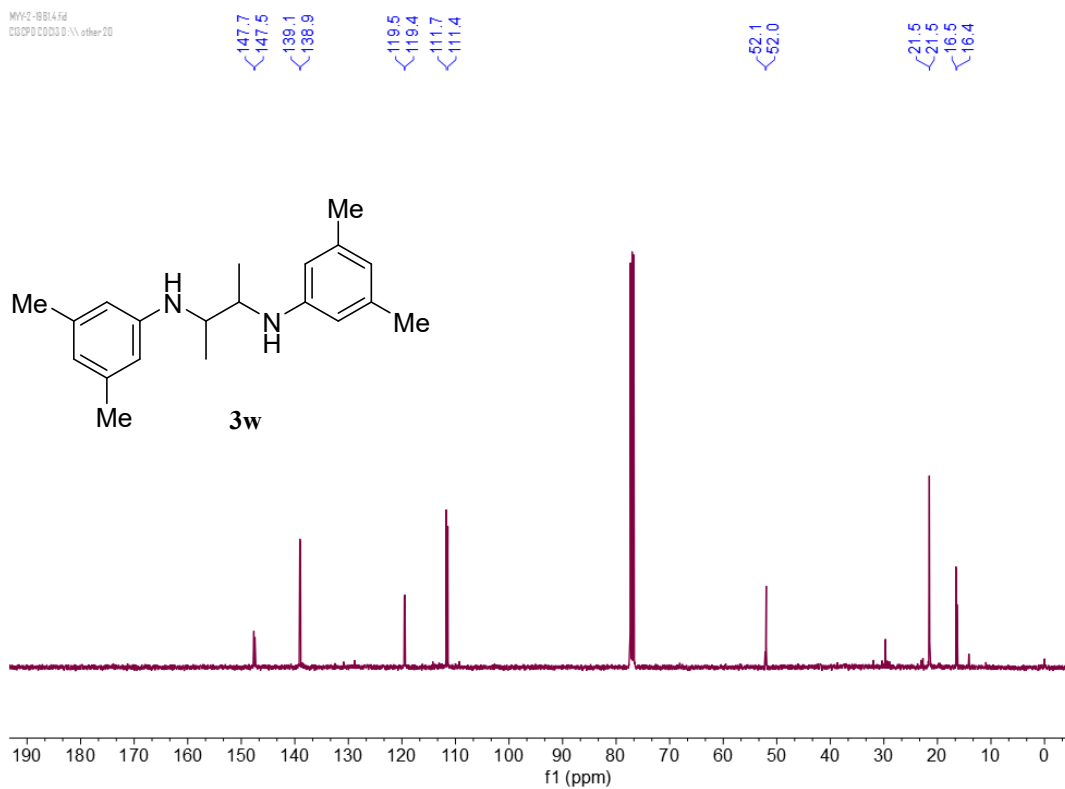
¹H-NMR spectrum of **3w** (CDCl₃, 400 MHz)

MYY-2-19B1.1.fid
PROTON CDCl3 D:\other 1

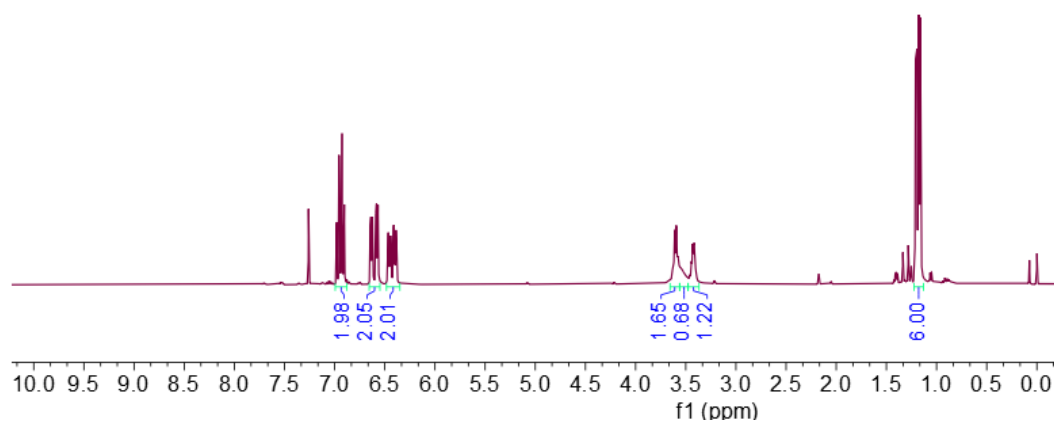
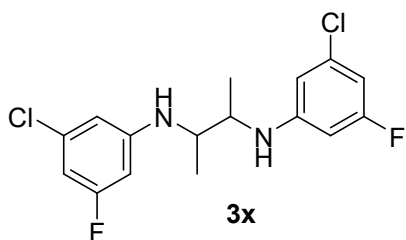
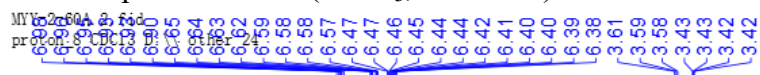


¹³C-NMR spectrum of **3w** (CDCl₃, 100 MHz)

MW2-18B14.fid
CDCl3 CDCl3 D:\other 20

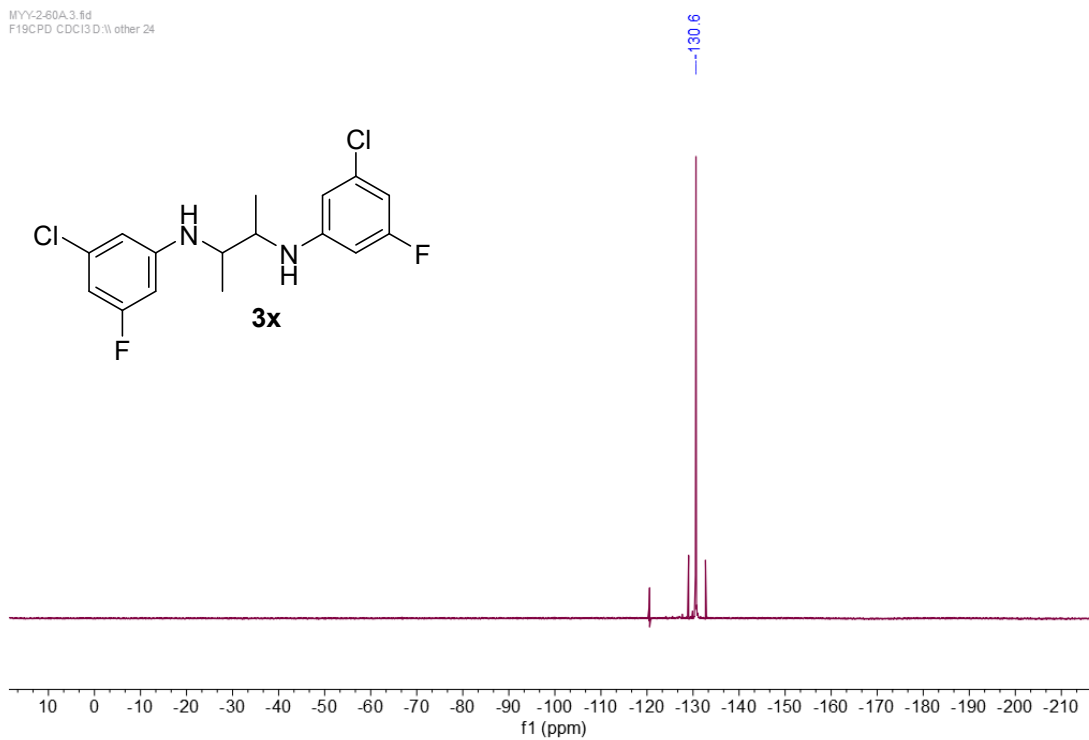
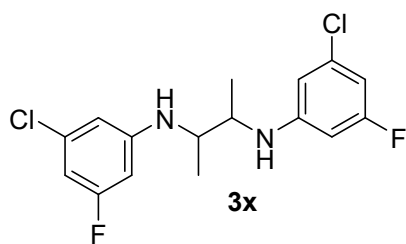


¹H-NMR spectrum of **3x** (CDCl₃, 400 MHz)



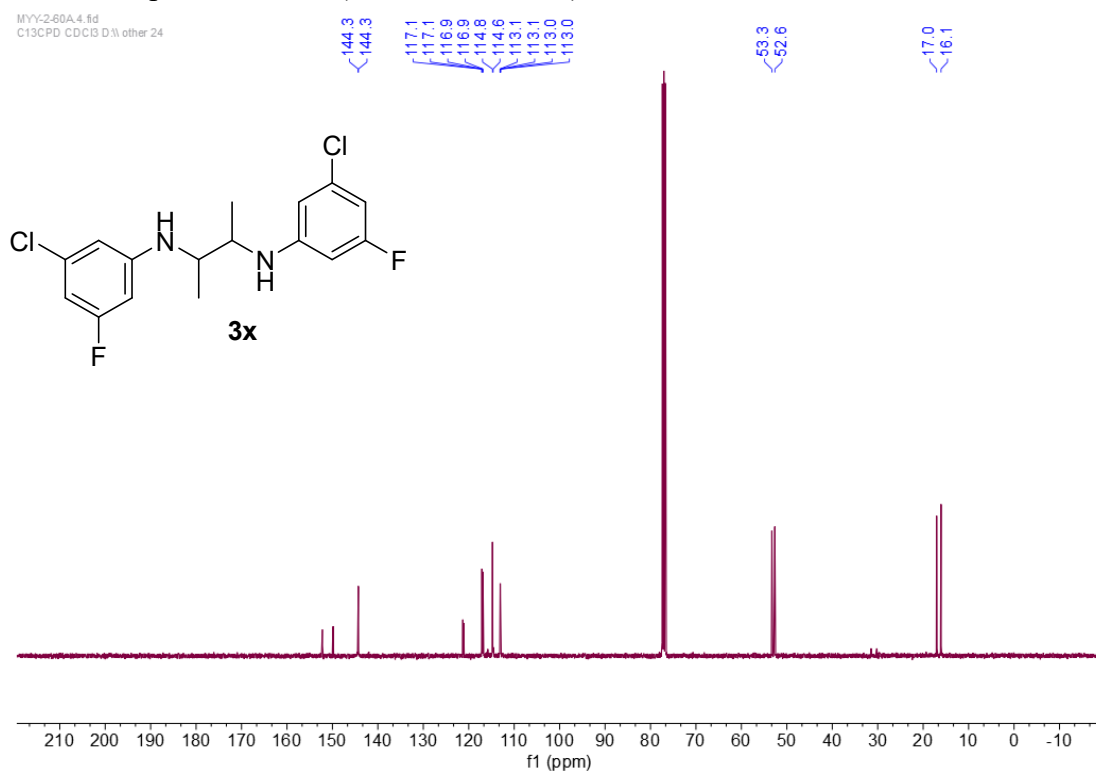
¹⁹F-NMR spectrum of **3x** (CDCl₃, 376 MHz)

MY-2-60A-3.fid
F19CPD CDCl3.D:\other 24



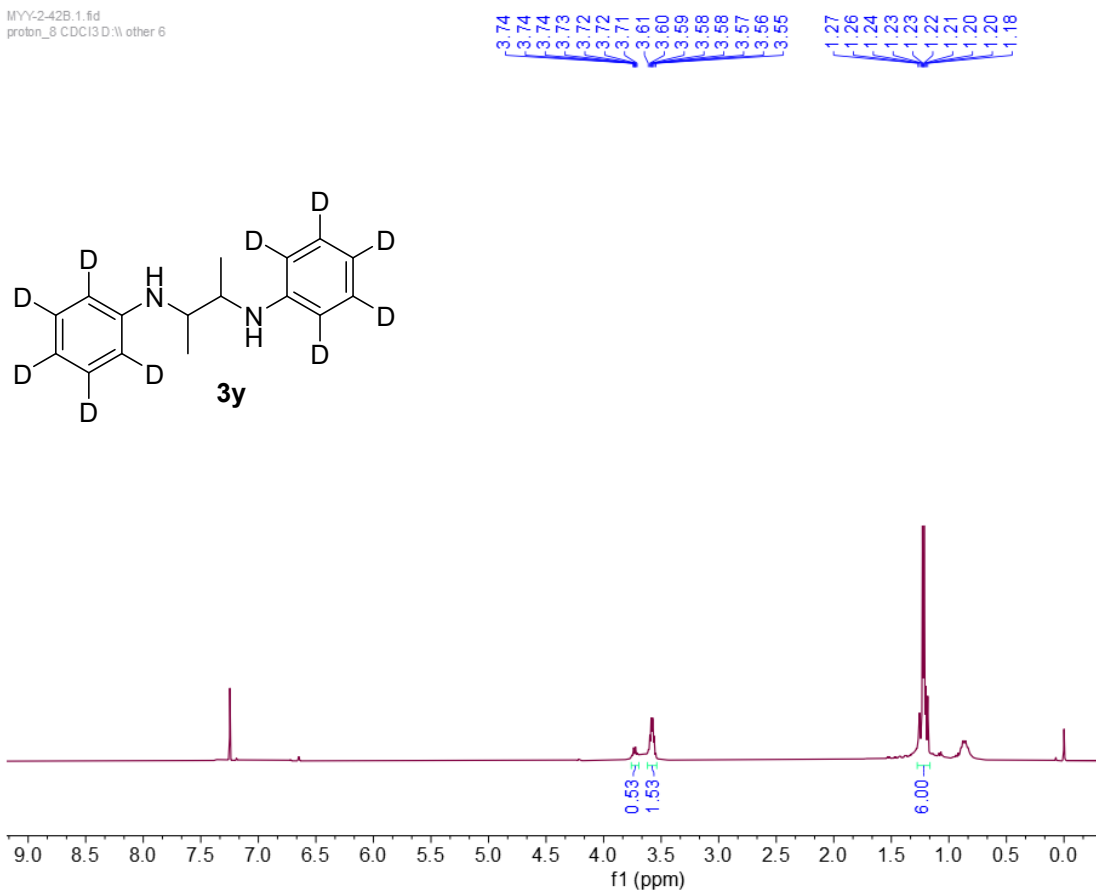
^{13}C -NMR spectrum of **3x** (CDCl_3 , 100 MHz)

MYY-2-60A-4.fid
C13CPD CDCl3 D:\other 24



^1H -NMR spectrum of **3y** (CDCl_3 , 400 MHz)

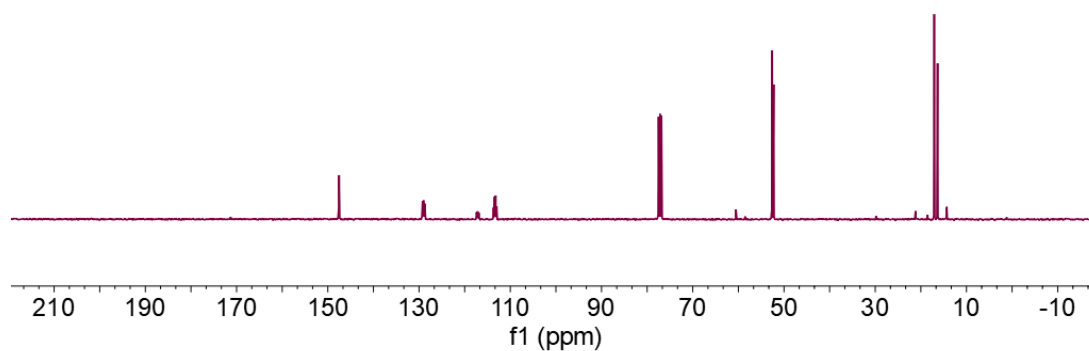
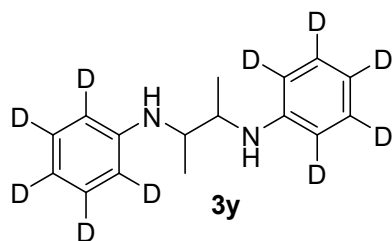
MYY-2-42B-1.fid
probin_8 CDCl3 D:\other 6



¹³C-NMR spectrum of **3y** (CDCl₃, 100 MHz)

MYY-3-37B.11.fid
MYY-3-37B

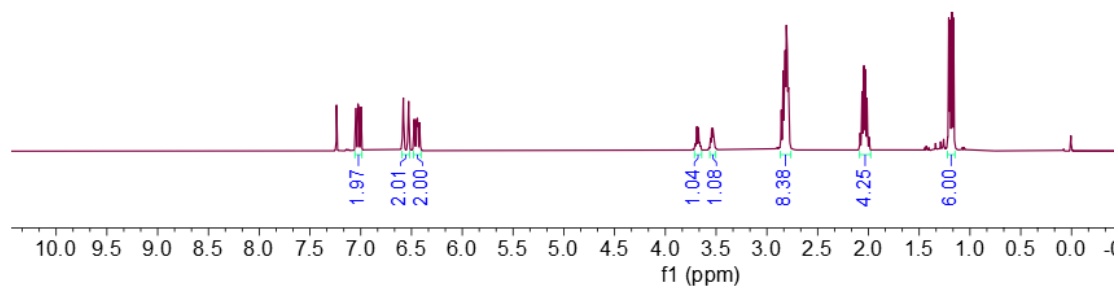
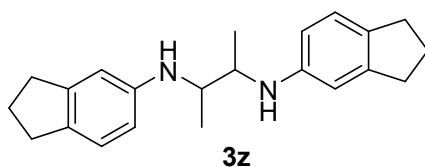
147.6
147.5
129.2
129.0
128.9
128.8
117.4
117.1
116.9
113.7
113.4
113.2
113.0
52.6
52.3
17.1
16.3



¹H-NMR spectrum of **3z** (CDCl₃, 400 MHz)

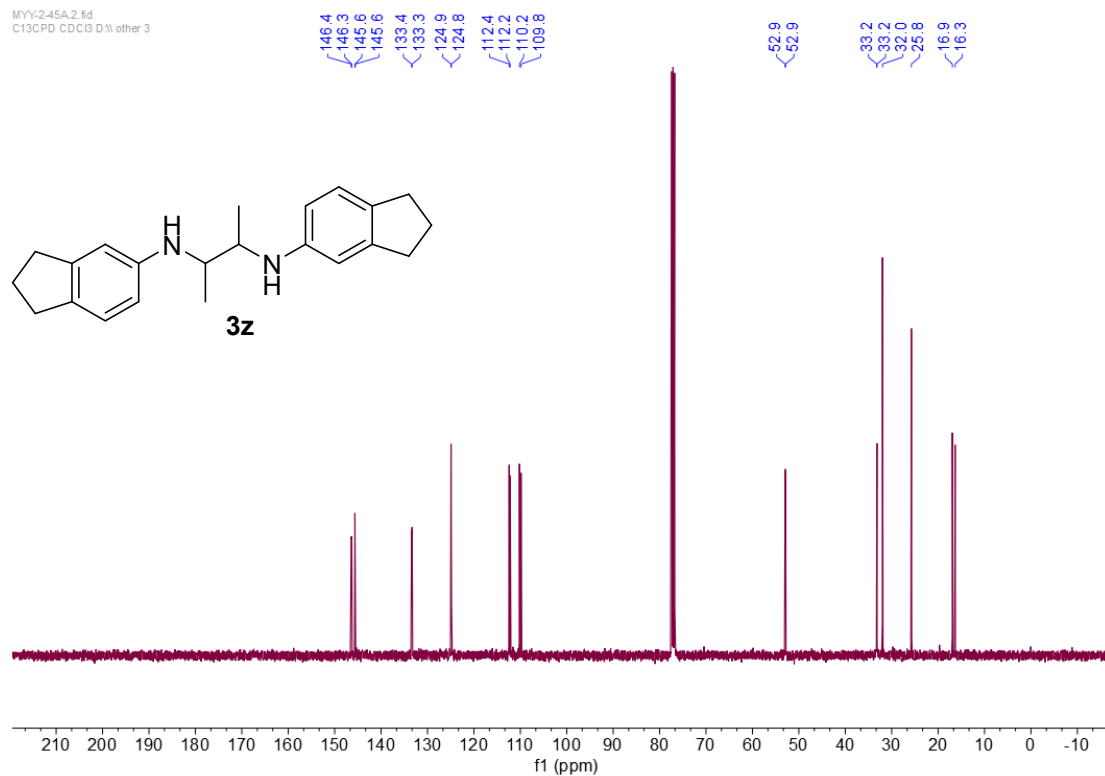
MYY-2-45A.1.fid
proton_8 CDCl3 D:\w other 22

7.05
7.03
7.03
7.02
7.00
6.59
6.58
6.53
6.53
6.47
6.45
6.45
6.44
6.44
6.42
6.42
3.69
3.69
3.68
3.68
3.67
3.67
3.54
3.54
3.53
3.53
3.53
2.84
2.83
2.82
2.81
2.80
2.79
2.78
2.06
2.05
2.04
2.03
2.03
2.01
1.21
1.19
1.18
1.16



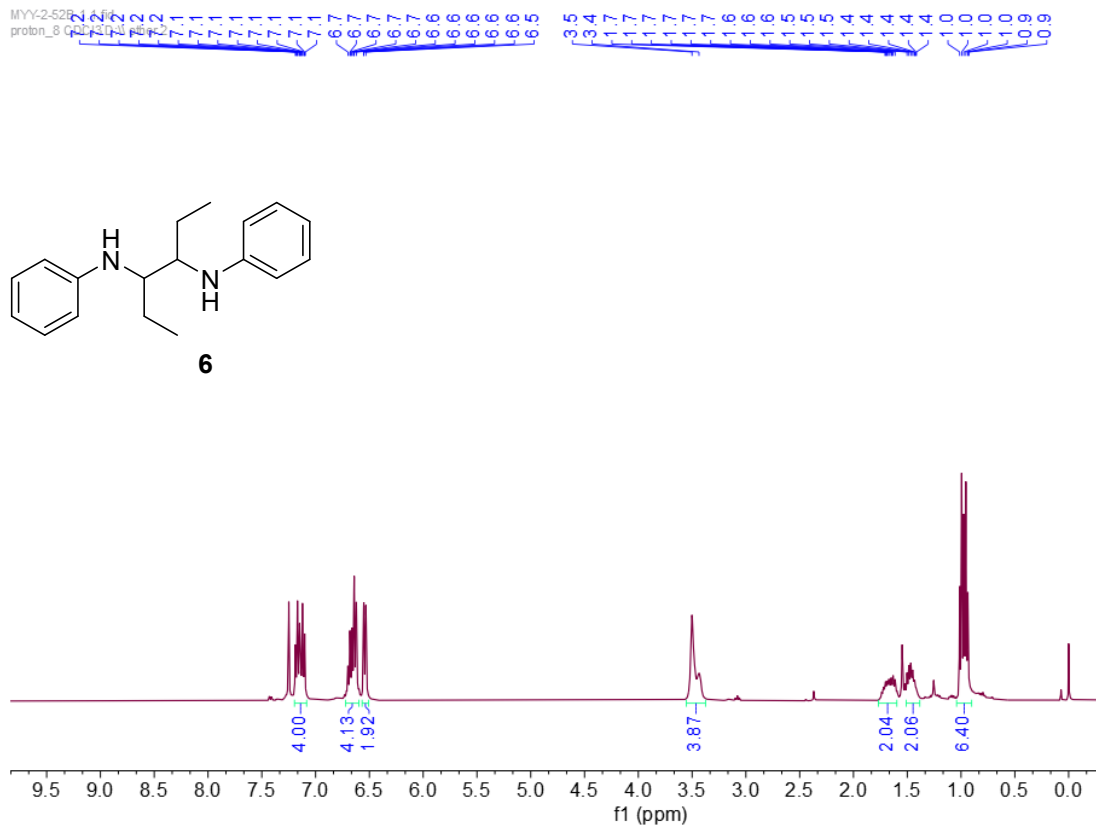
¹³C-NMR spectrum of **3z** (CDCl₃, 100 MHz)

MYY-2-45A.2.fid
C13CPD CDCl3 D:\other 3



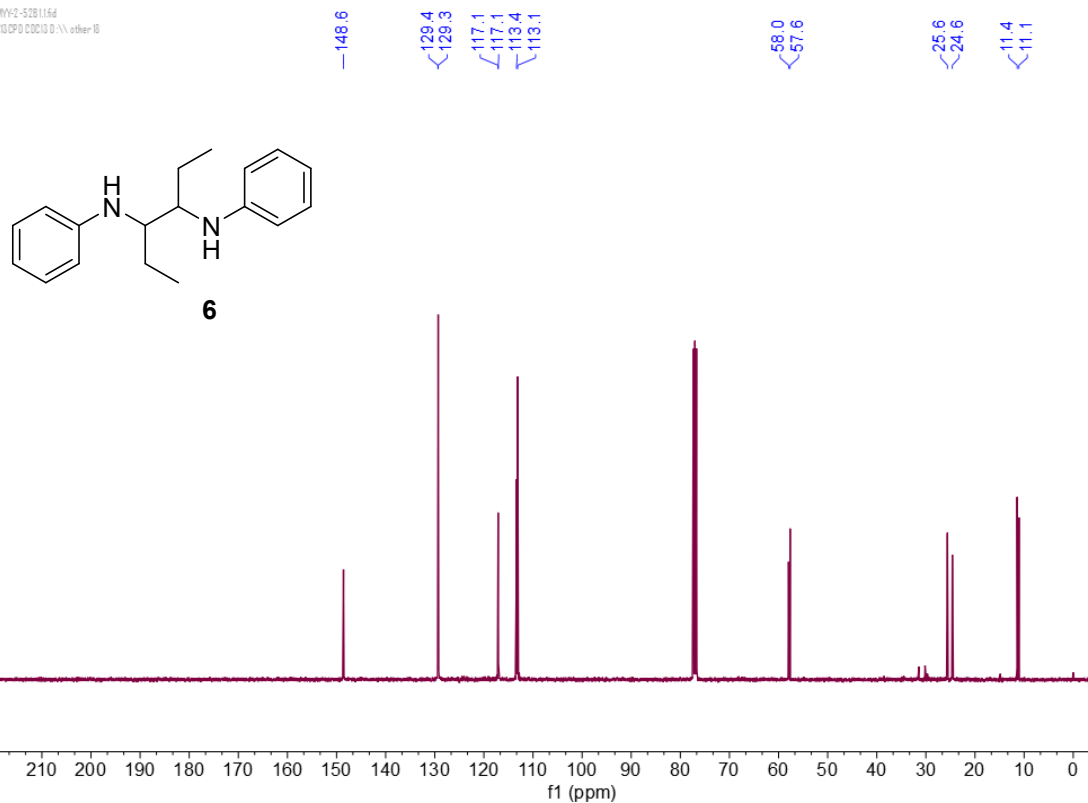
¹H-NMR spectrum of **6** (CDCl₃, 400 MHz)

MYY-2-52B.1.fid
proton_8 CDCl3 D:\other 2



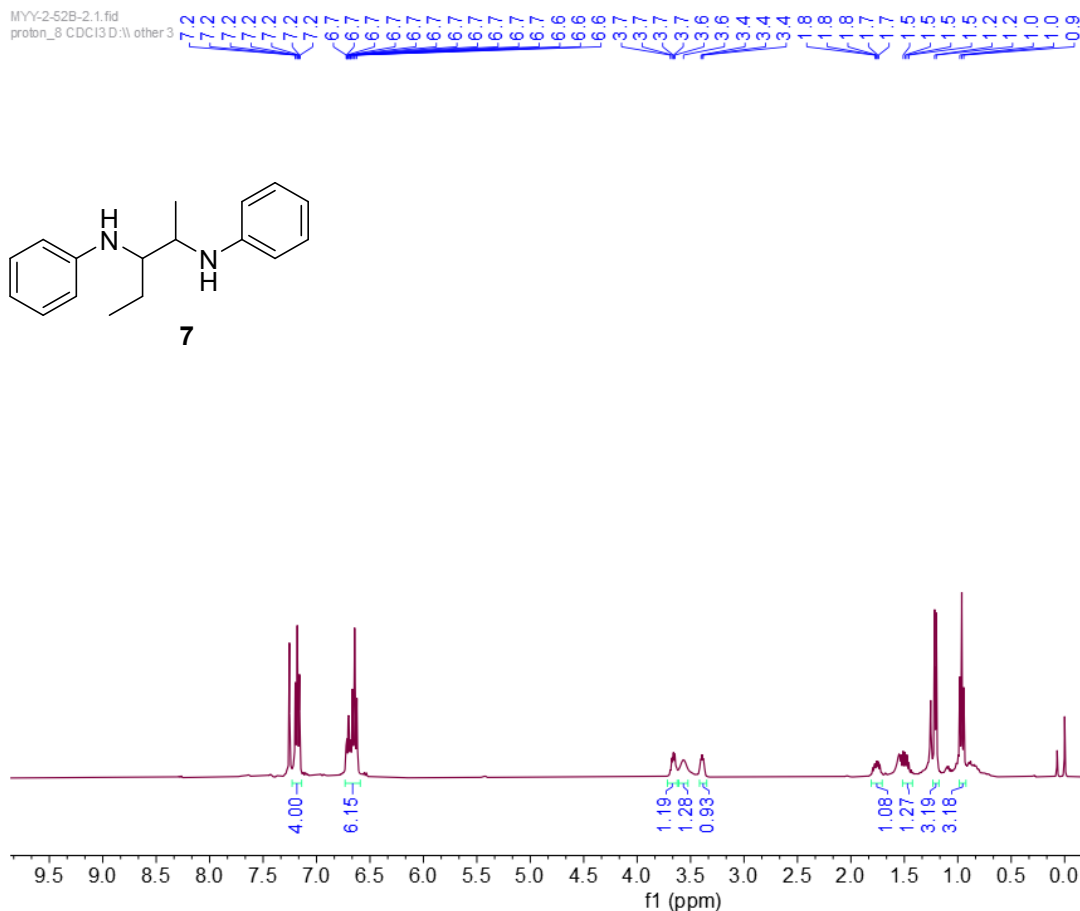
¹³C-NMR spectrum of **6** (CDCl₃, 100 MHz)

MY2-52B164
CDCl₃ CDCl₃D:\other\B



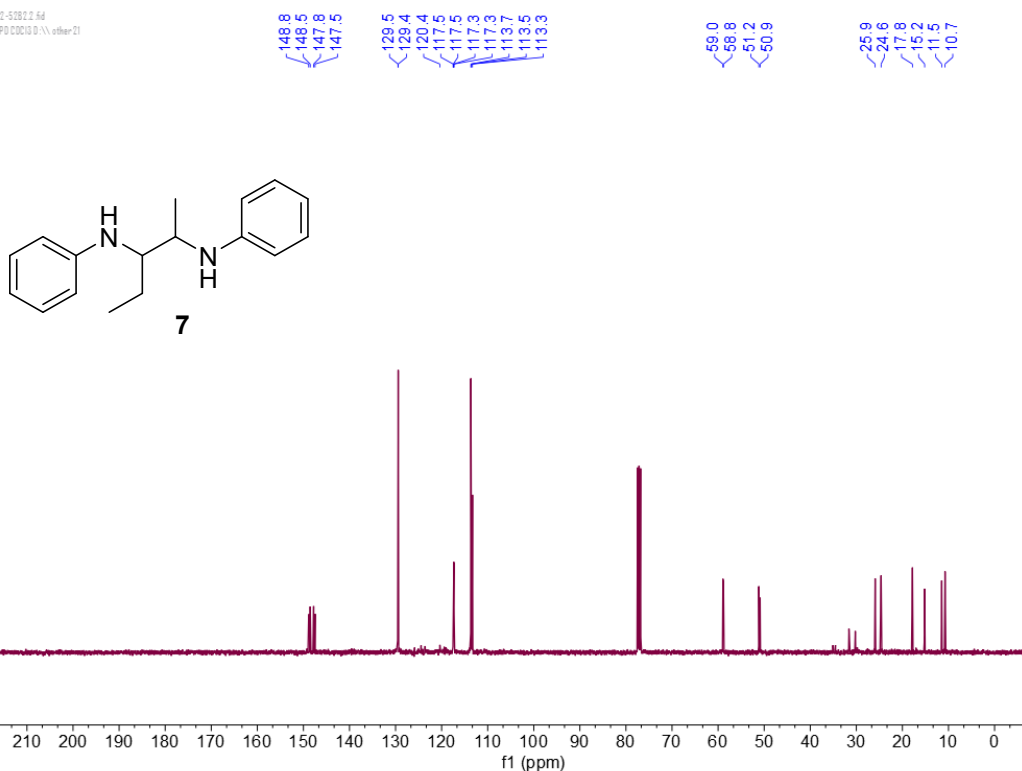
¹H-NMR spectrum of **7** (CDCl₃, 400 MHz)

MY2-52B-2.1.fid
proton_8 CDCl₃D:\other\3



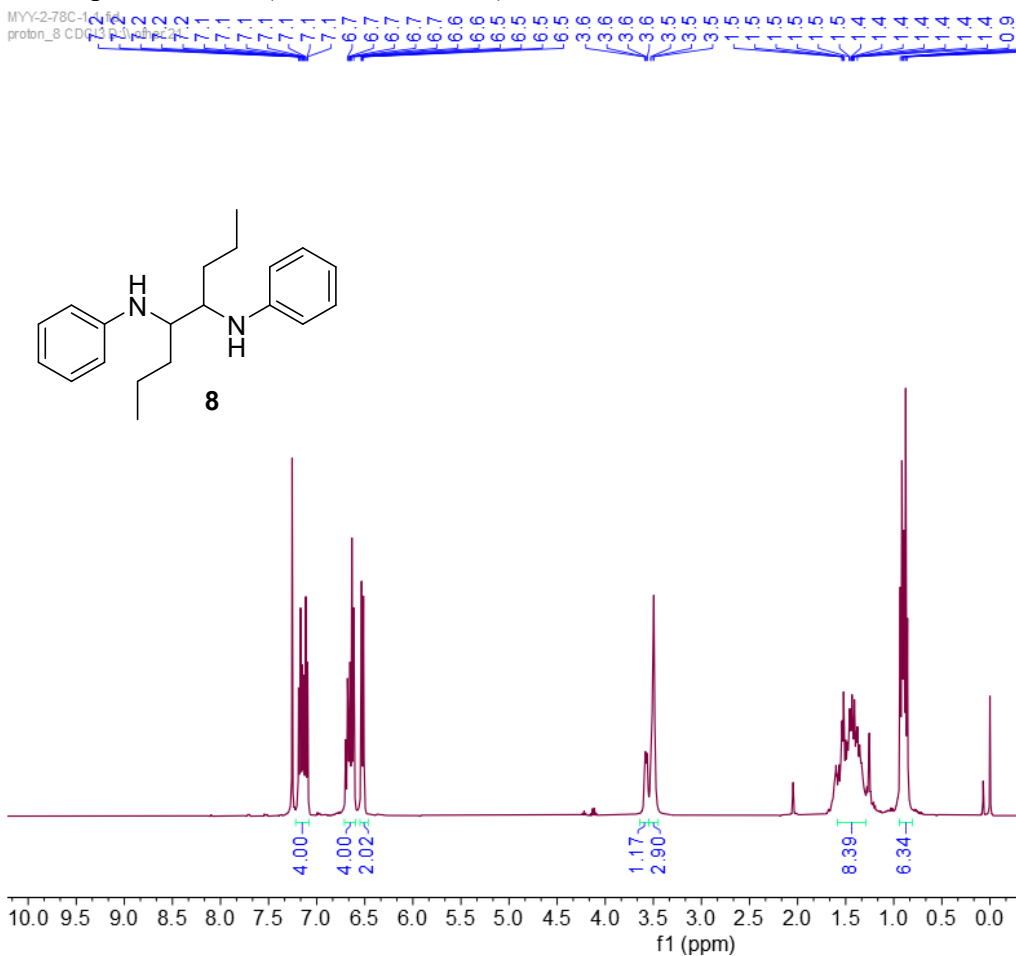
¹³C-NMR spectrum of **7** (CDCl₃, 100 MHz)

MW2-53212.64
CDCl₃ CDCl₃ ether21



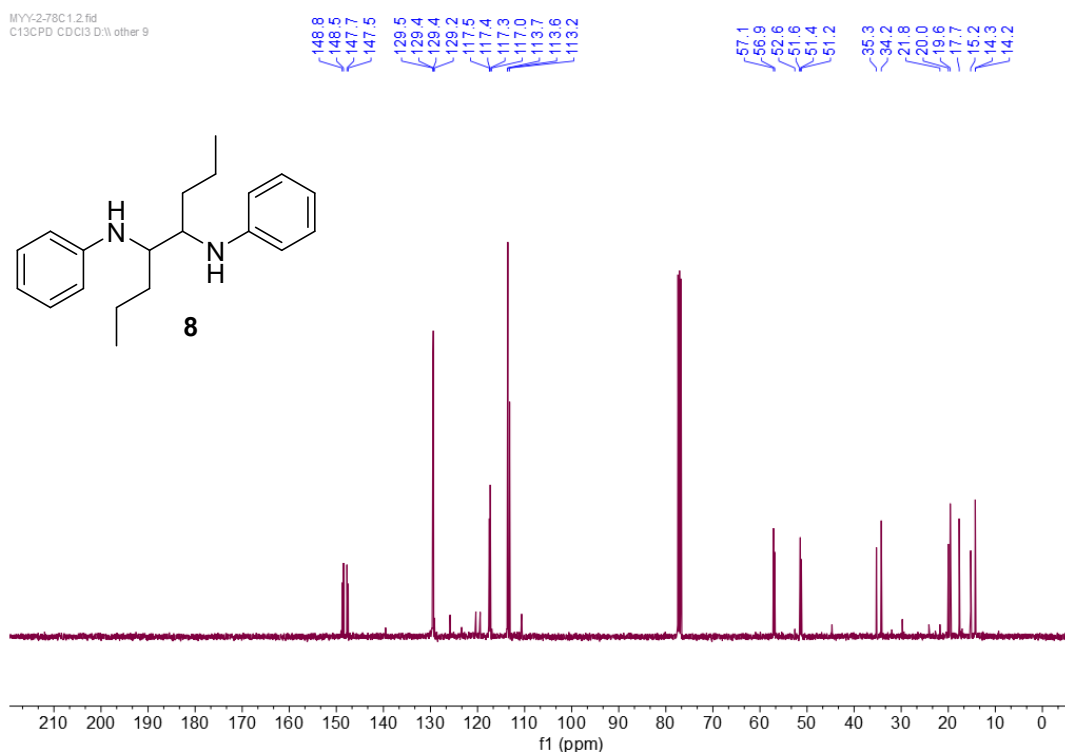
¹H-NMR spectrum of **8** (CDCl₃, 400 MHz)

MYY-2-78C-14.64
proton_8 CDCl₃ ether21



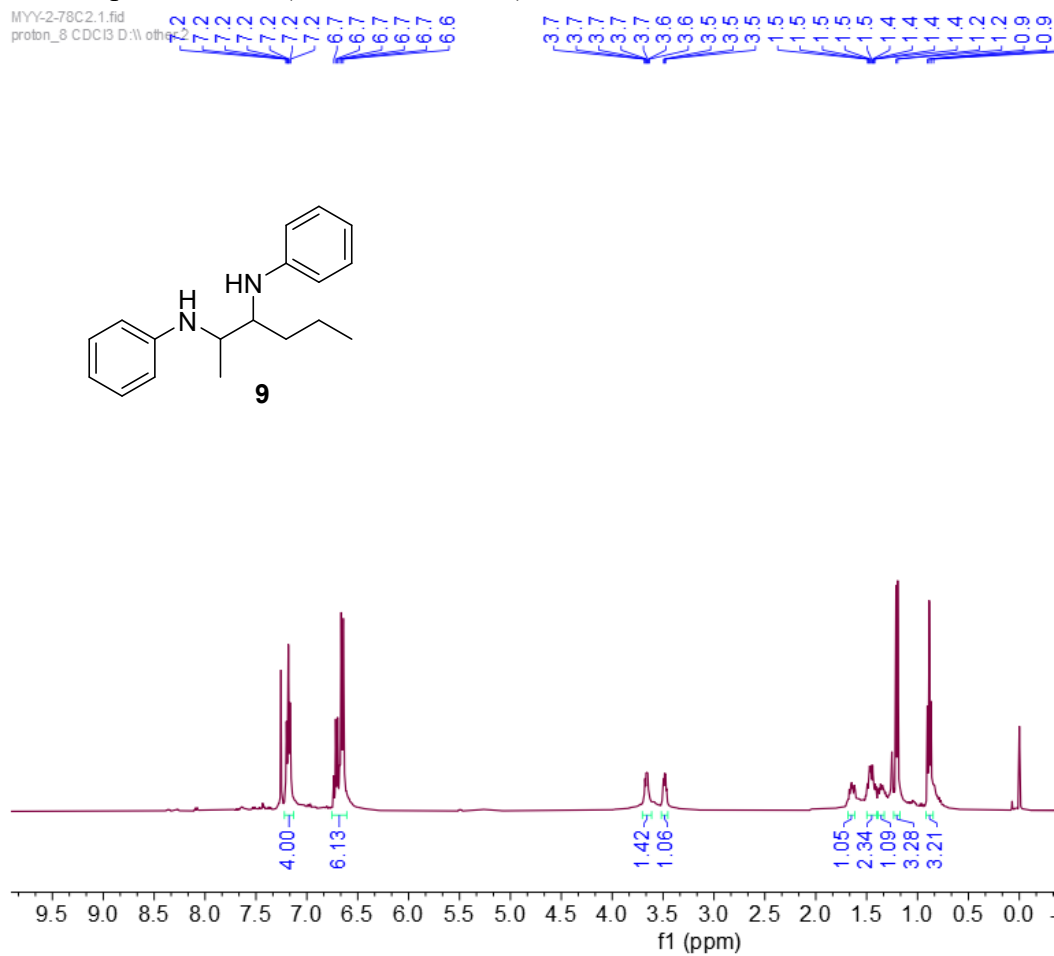
^{13}C -NMR spectrum of **8** (CDCl_3 , 100 MHz)

MY-2-78C1.2.fid
C13CPD CDCl3 D:\other 9



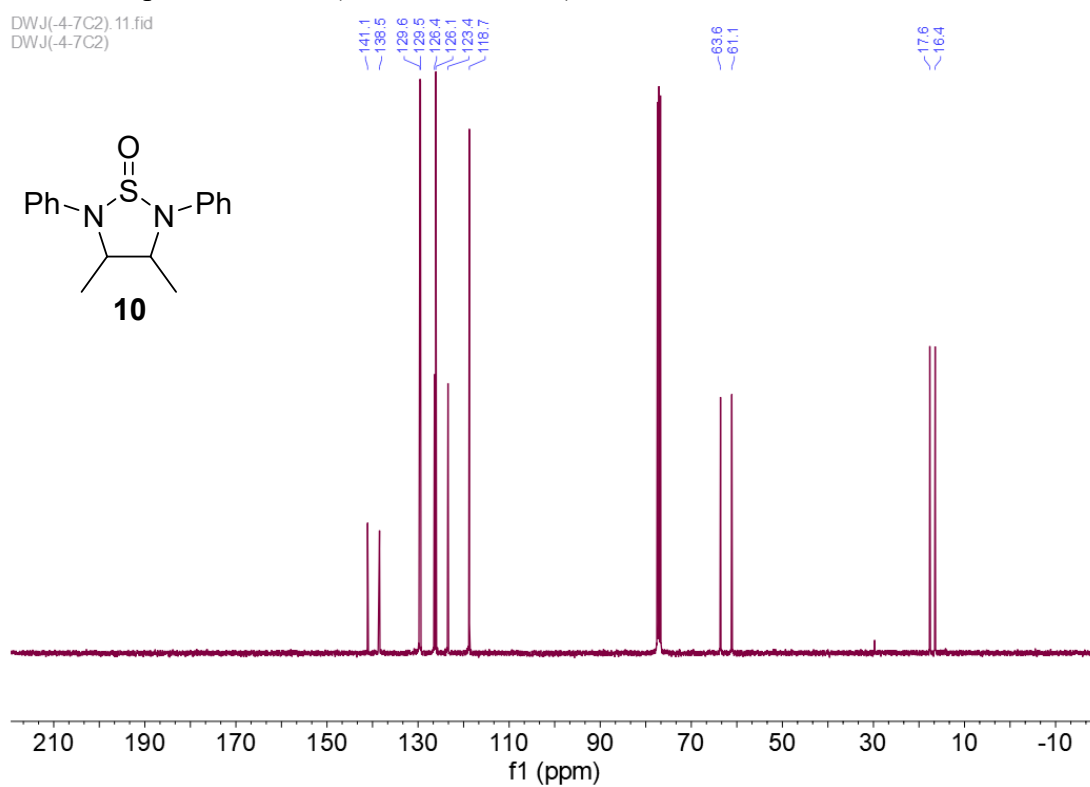
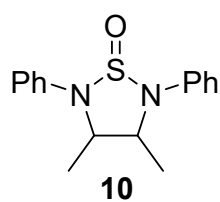
^1H -NMR spectrum of **9** (CDCl_3 , 400 MHz)

MY-2-78C2.1.fid
proton_8 CDCl3 D:\other 2



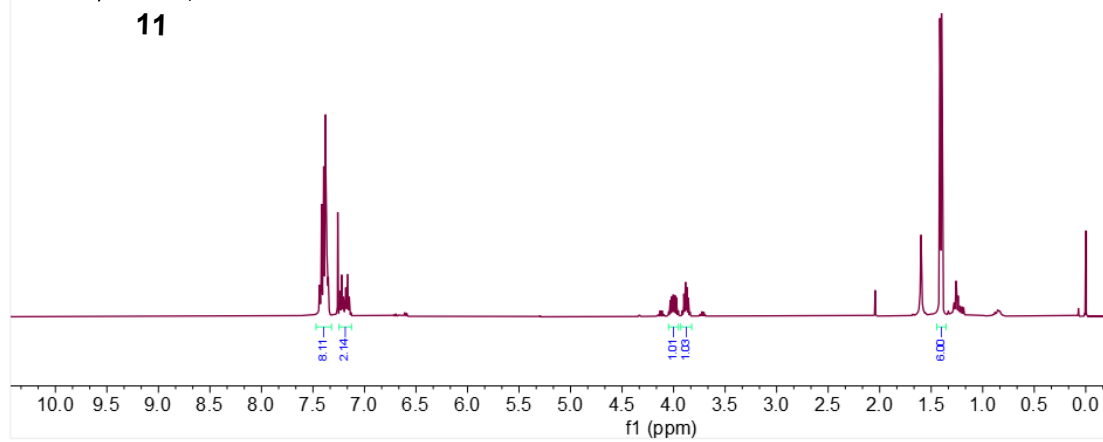
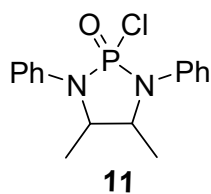
¹³C-NMR spectrum of **10** (CDCl₃, 100 MHz)

DWJ(-4-7C2).11.fid
DWJ(-4-7C2)



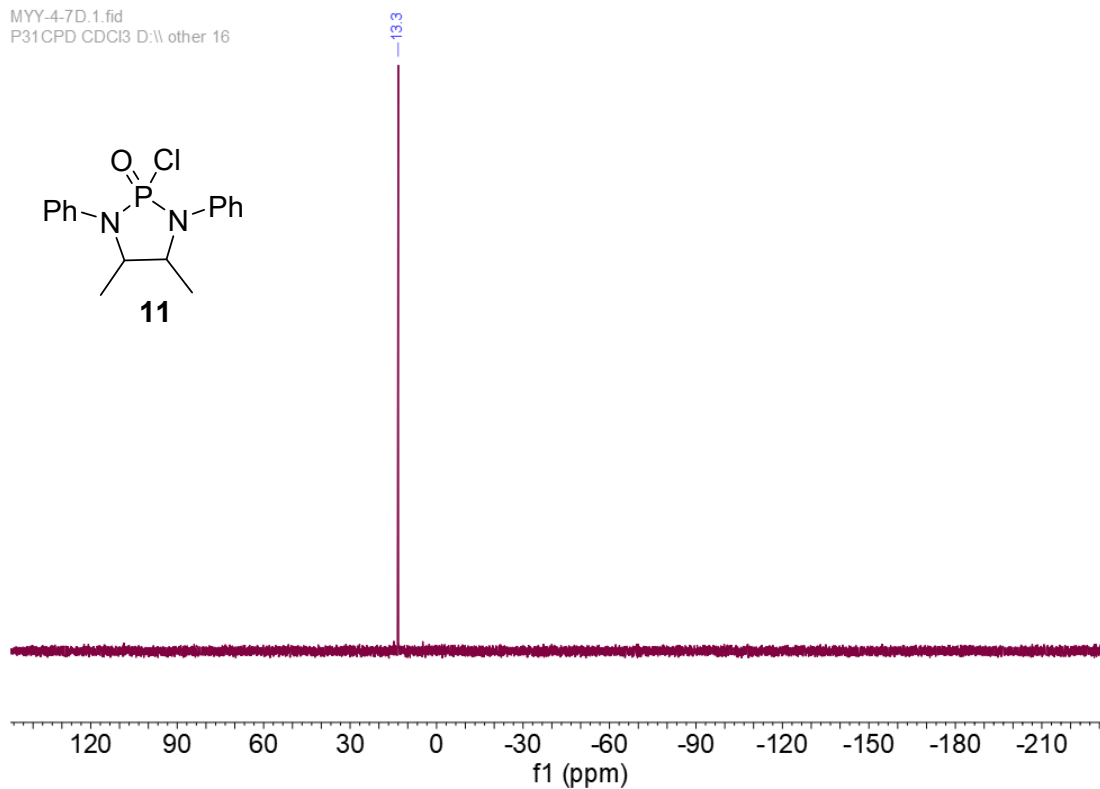
¹H-NMR spectrum of **11** (CDCl₃, 400 MHz)

MYY-4-7D.2.fid
proton_8 CDCl3.D:\ other 6



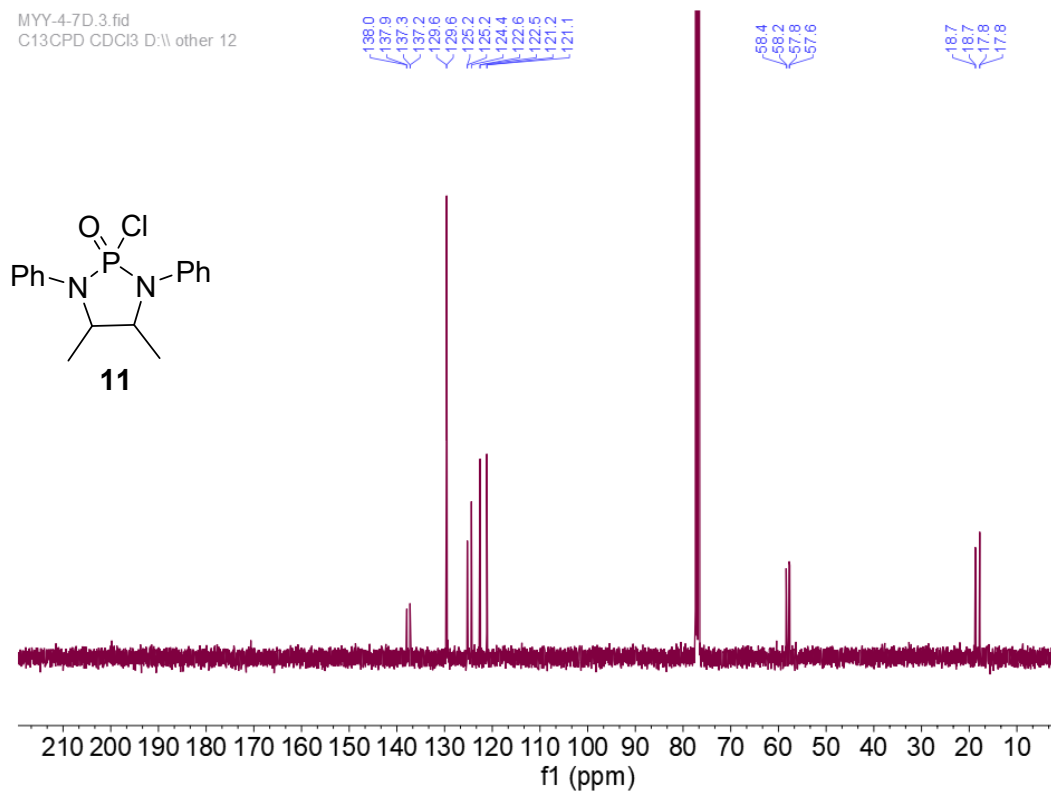
³¹P-NMR spectrum of **11** (CDCl₃, 162 MHz)

MYY-4-7D.1.fid
P31CPD CDCl3 D:\ other 16



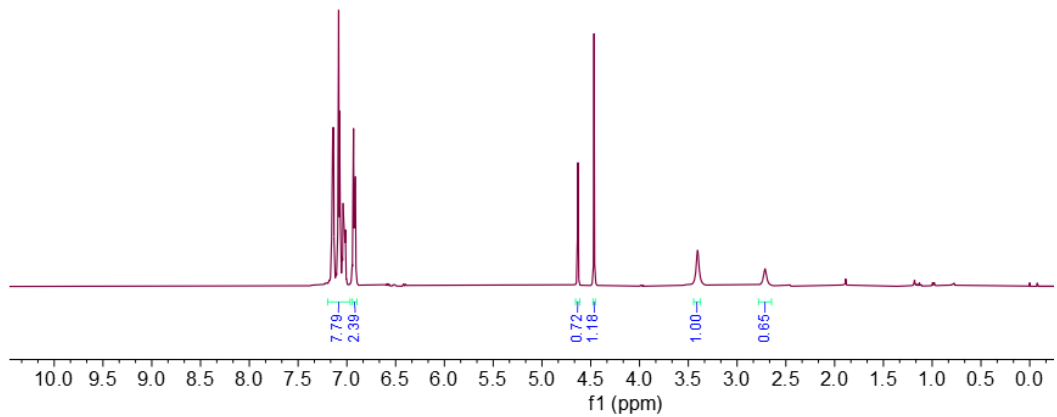
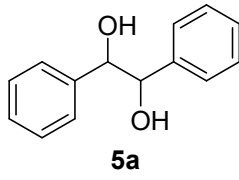
¹³C-NMR spectrum of **11** (CDCl₃, 100 MHz)

MYY-4-7D.3.fid
C13CPD CDCl3 D:\ other 12



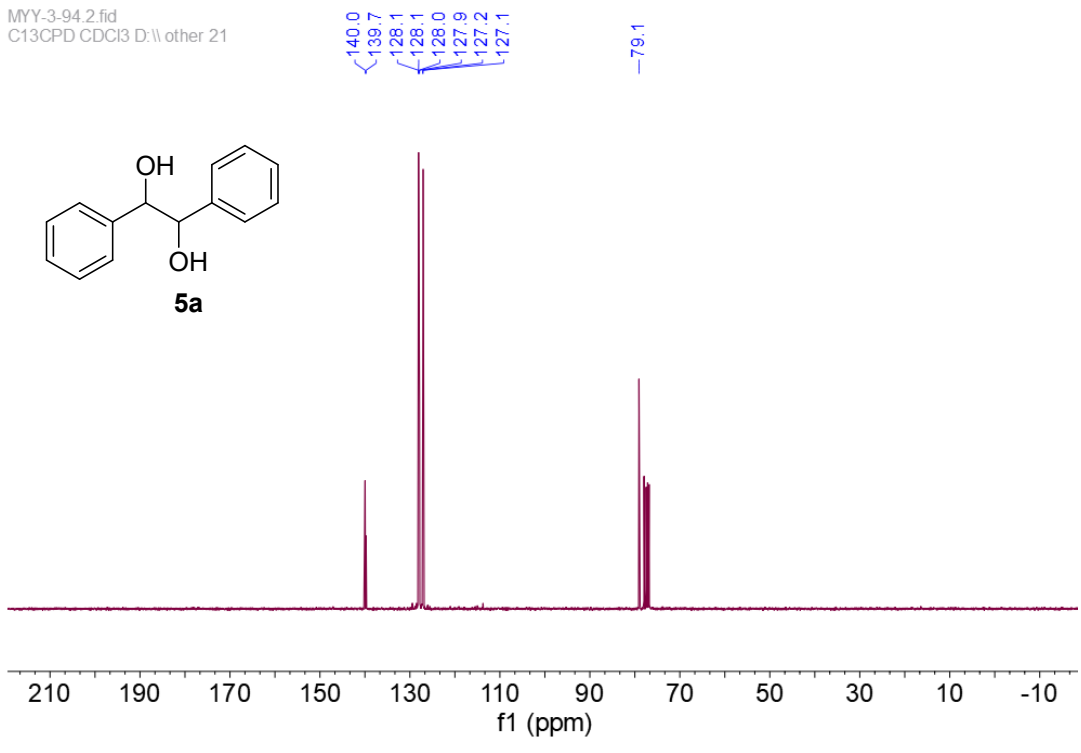
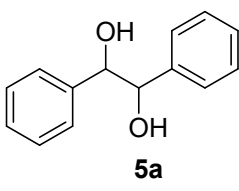
¹H-NMR spectrum of **5a** (CDCl₃, 400 MHz)

MYY-3-94.1.fid
 protn_8 CDCl3 D:\other 21



¹³C-NMR spectrum of **5a** (CDCl₃, 100 MHz)

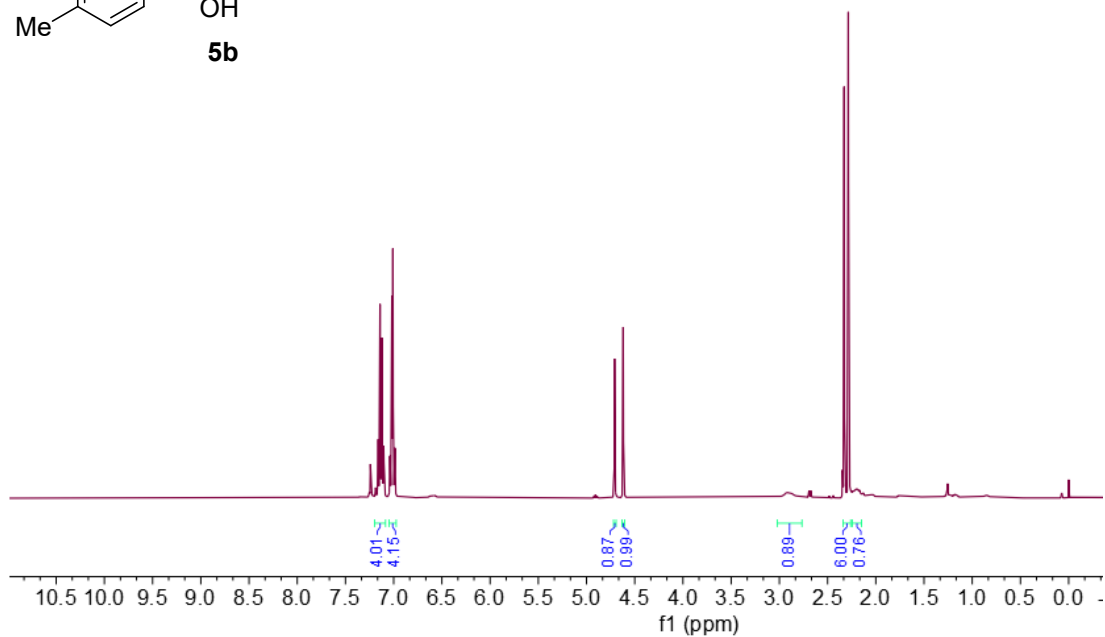
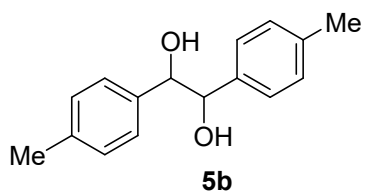
MYY-3-94.2.fid
 C13CPD CDCl3 D:\other 21



¹H-NMR spectrum of **5b** (CDCl₃, 400 MHz)

MYY-3-90A.1.fid
proton_8 CDCl3 D:\other 1

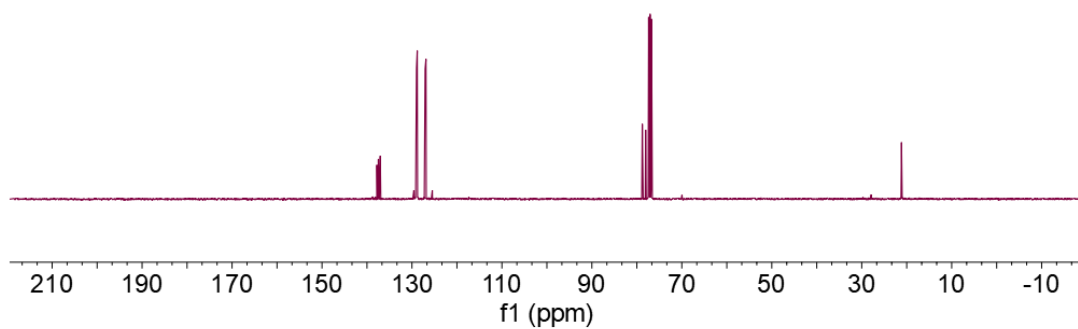
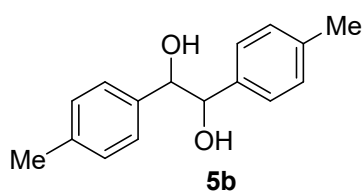
7.2
7.2
7.2
7.1
7.1
7.1
7.1
7.0
7.0
7.0
7.0
7.0
7.0
7.0
4.7
4.6
-2.9
2.3
2.3
2.2



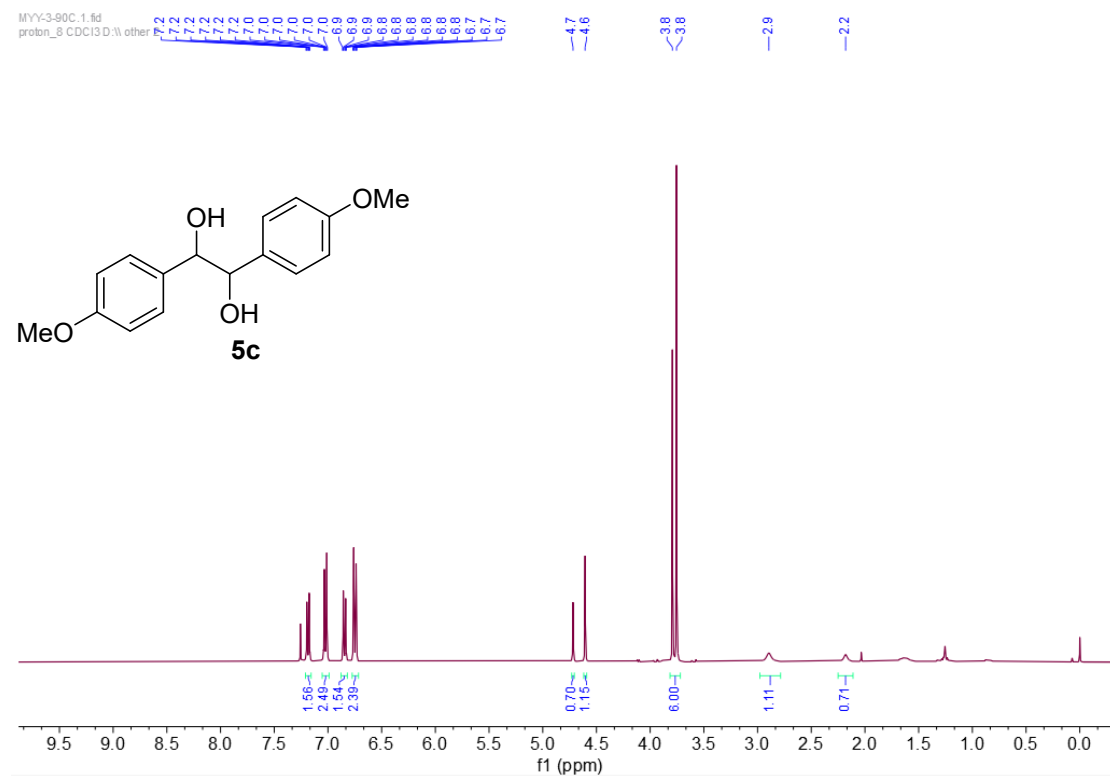
¹³C-NMR spectrum of **5b** (CDCl₃, 100 MHz)

MYY-3-90A.2.fid
C13CPD CDCl3 D:\other 22

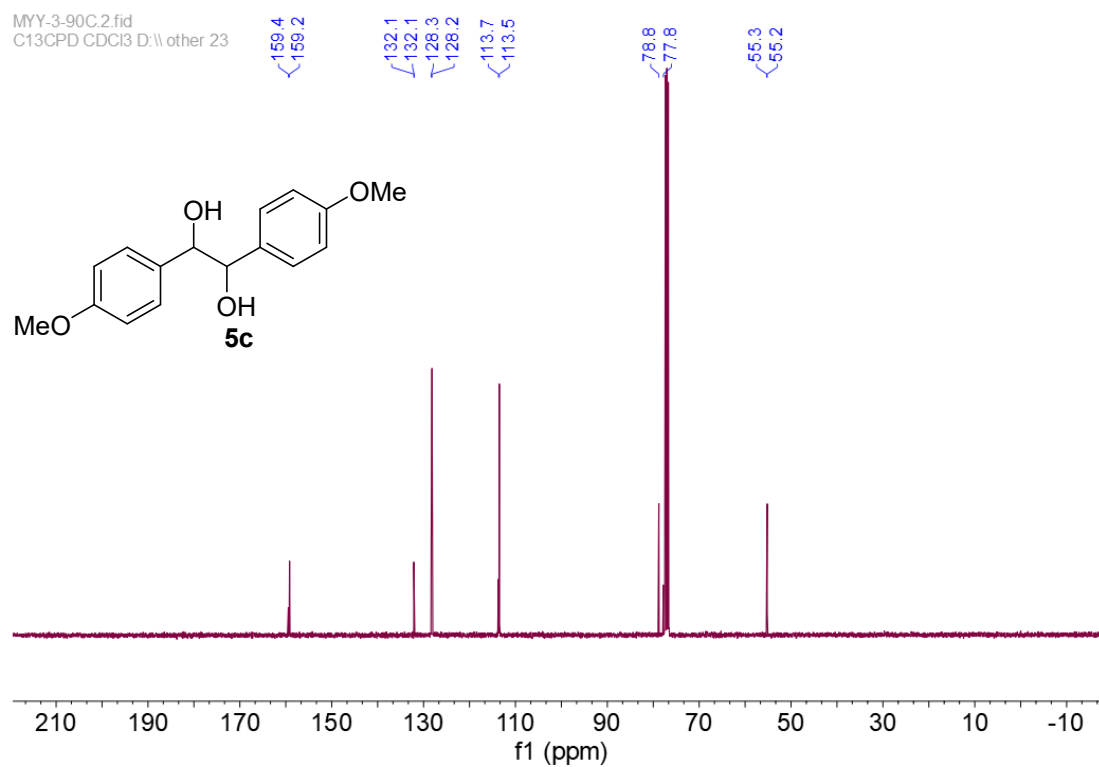
137.8
137.5
137.0
137.0
129.0
128.8
127.1
126.9
78.8
78.0
21.2
21.2



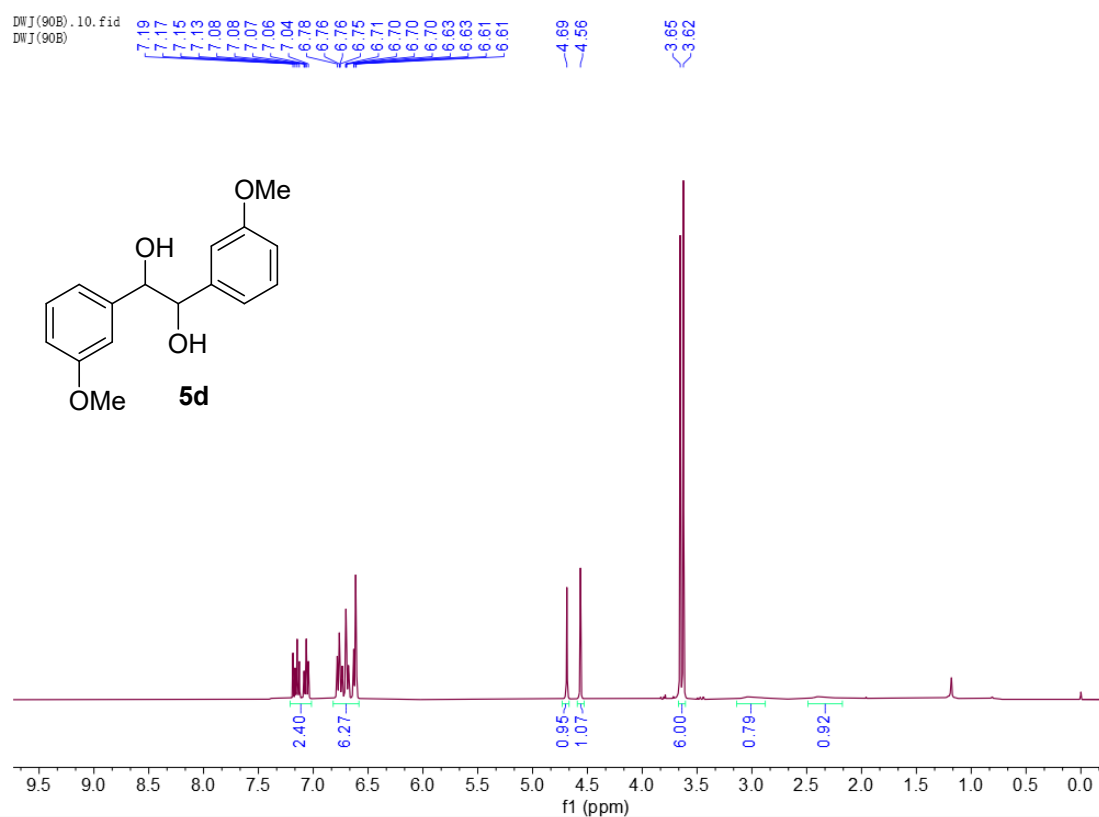
¹H-NMR spectrum of **5c** (CDCl₃, 400 MHz)



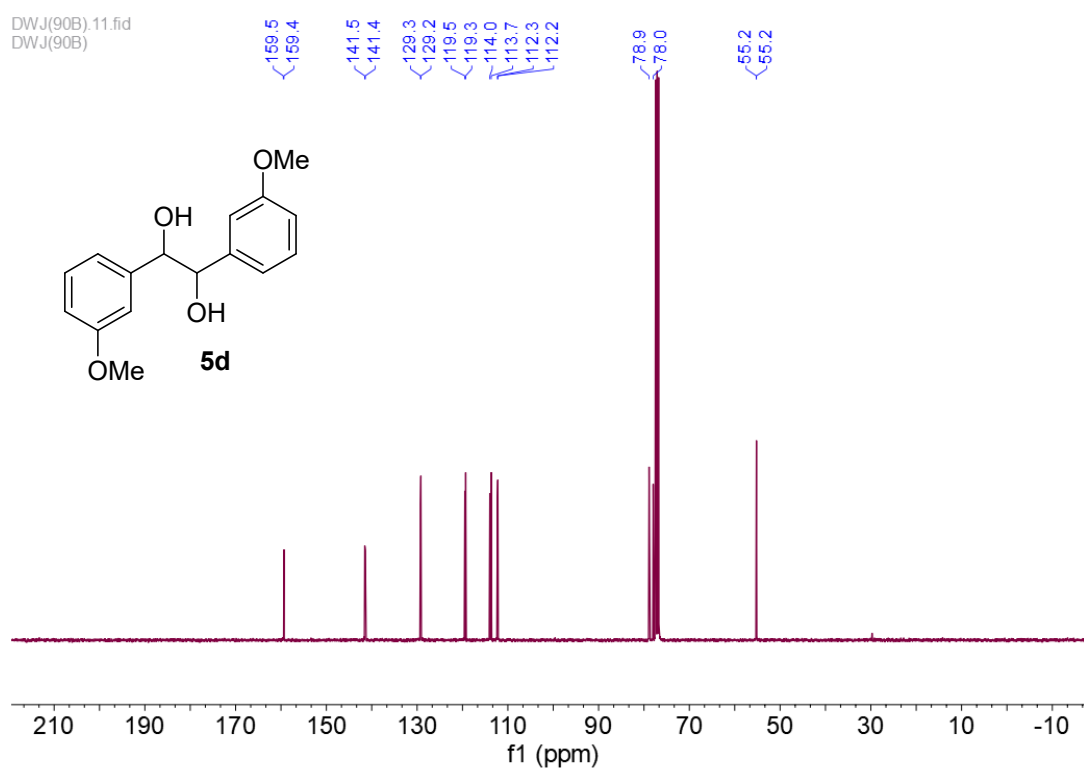
¹³C-NMR spectrum of **5c** (CDCl₃, 100 MHz)



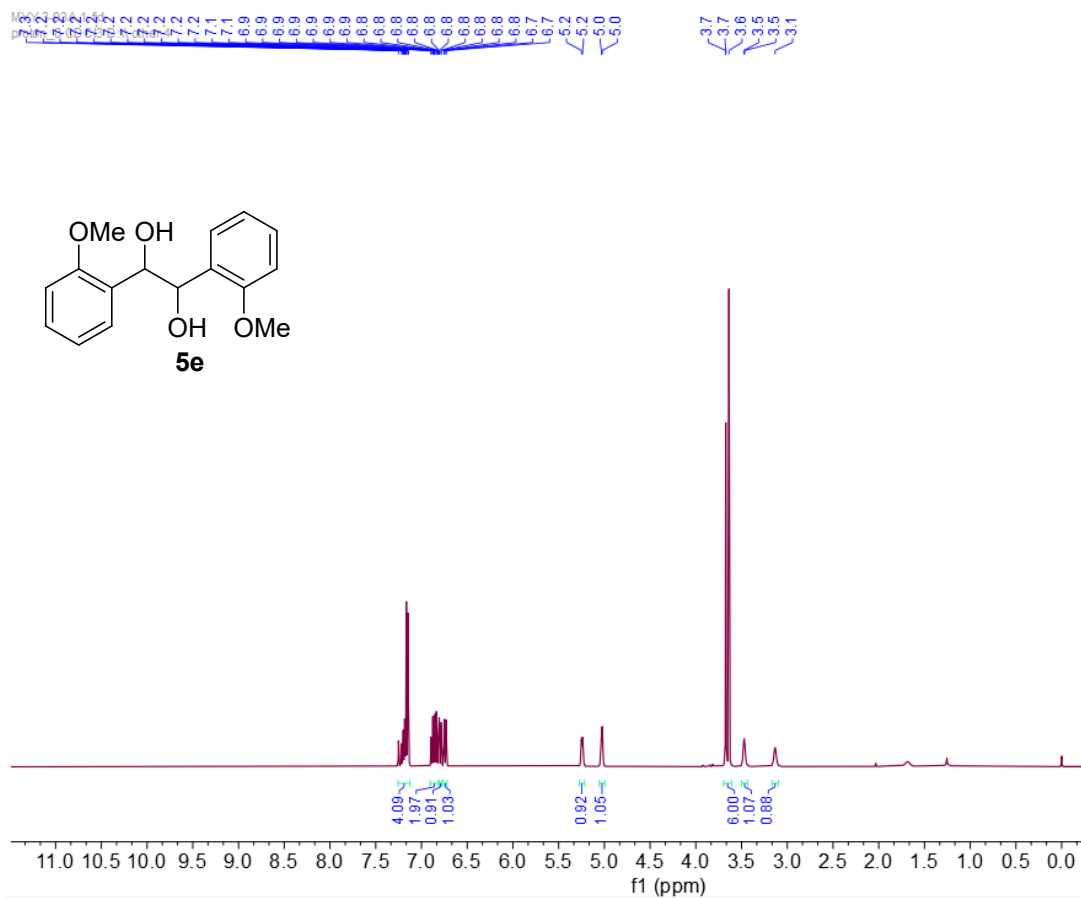
¹H-NMR spectrum of **5d** (CDCl₃, 400 MHz)



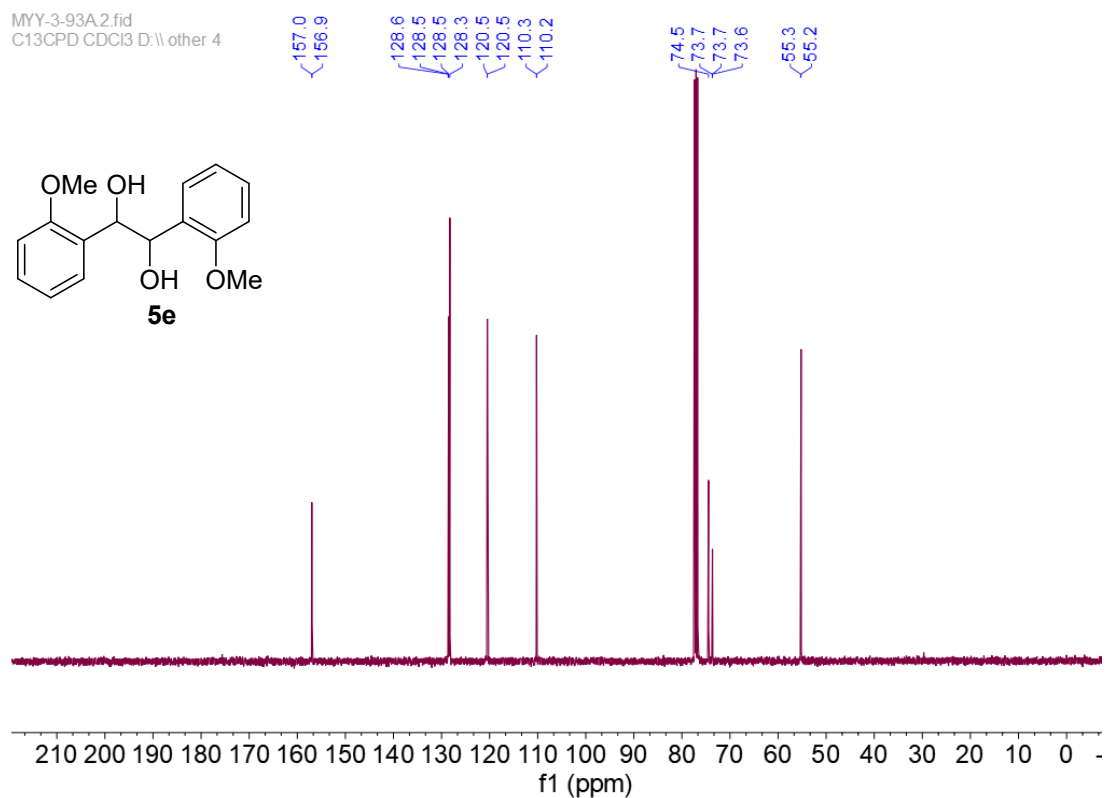
¹³C-NMR spectrum of **5d** (CDCl₃, 100 MHz)



¹H-NMR spectrum of **5e** (CDCl₃, 400 MHz)



¹³C-NMR spectrum of **5e** (CDCl₃, 100 MHz)



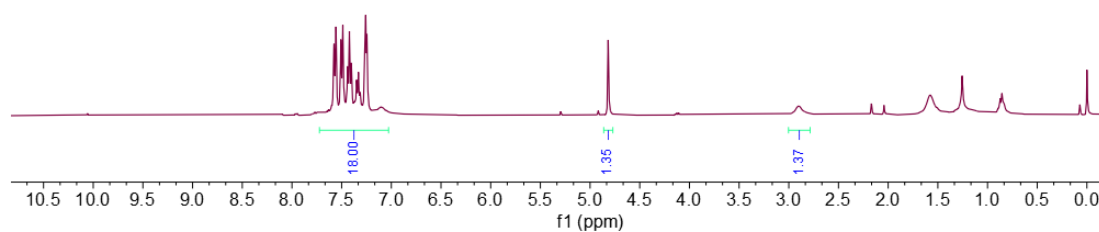
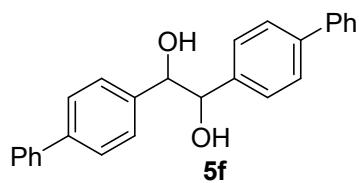
$^1\text{H-NMR}$ spectrum of **5f** (CDCl_3 , 400 MHz)

MYY-3-91B.2.fid
proton_8_CDCl3 D:\other 18

7.6
7.6
7.5
7.5
7.4
7.4
7.3
7.3
7.3
7.2

—4.8

—2.9

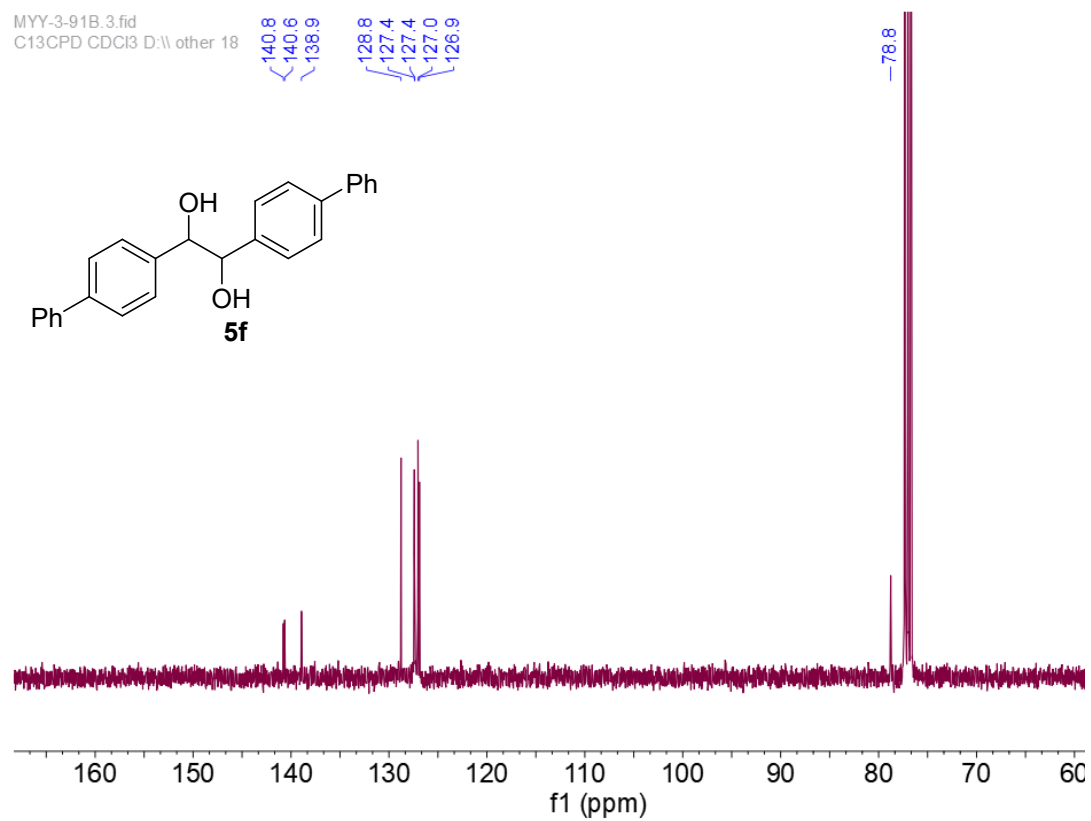
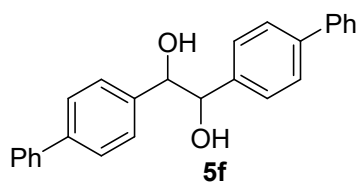


$^{13}\text{C-NMR}$ spectrum of **5f** (CDCl_3 , 100 MHz)

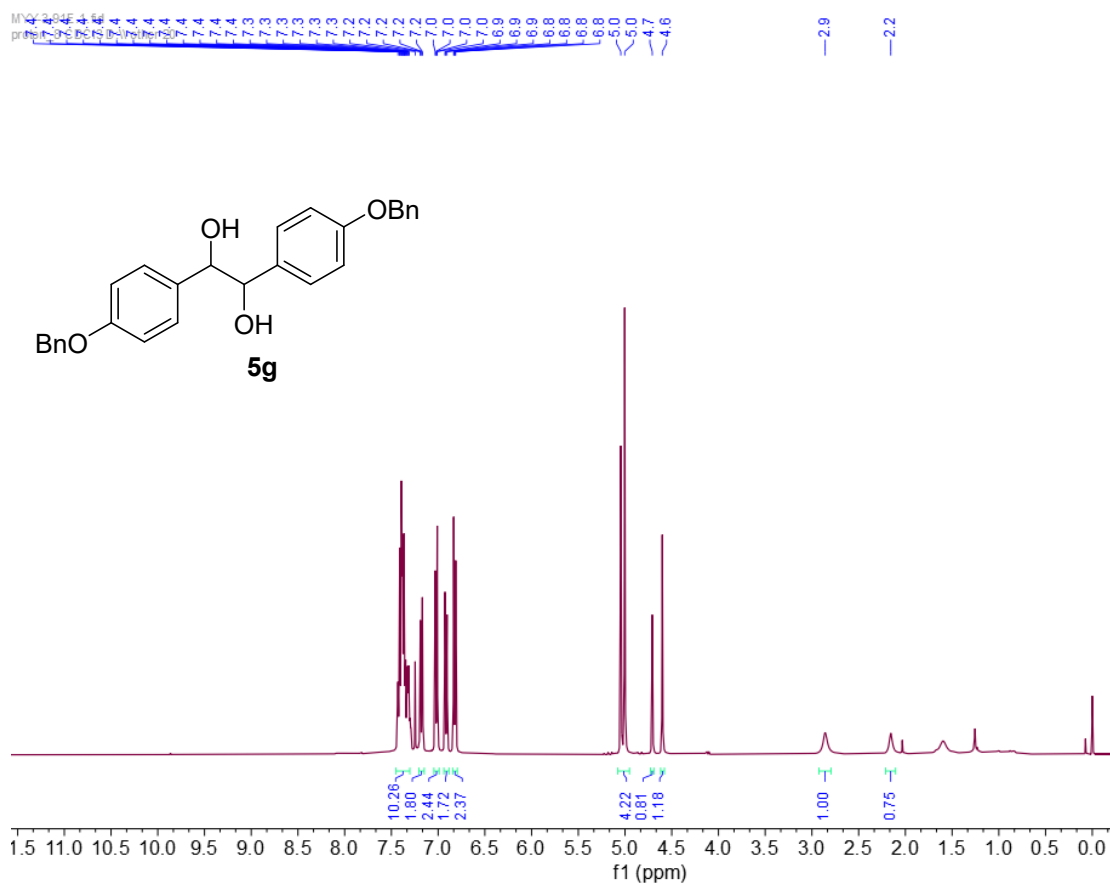
MYY-3-91B.3.fid
C13CPD CDCl3 D:\other 18

140.8
140.6
138.9
128.8
127.4
127.4
127.0
126.9

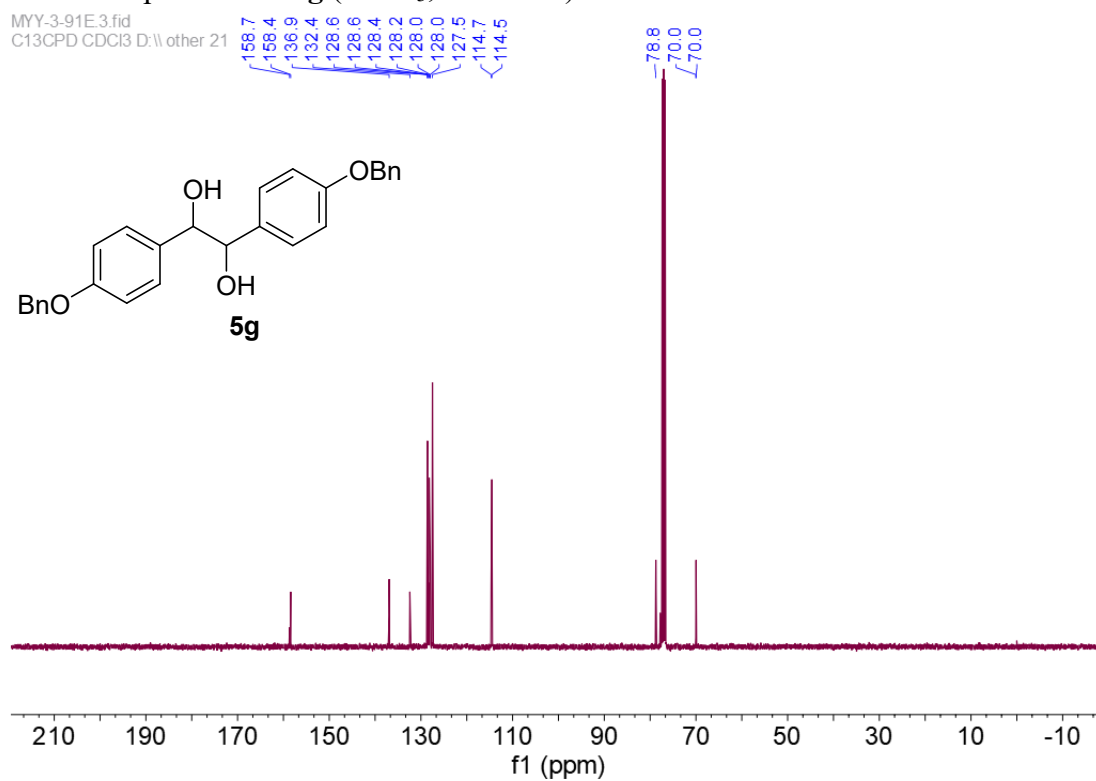
—78.8



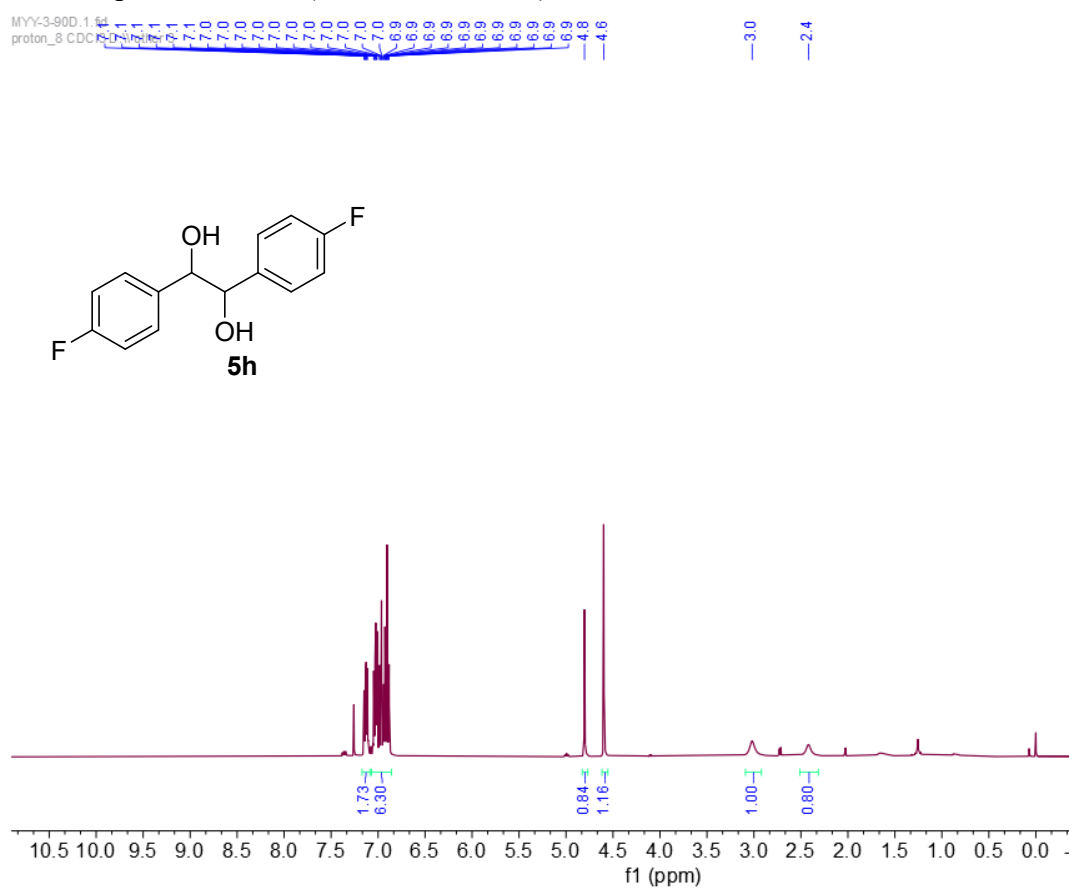
¹H-NMR spectrum of **5g** (CDCl₃, 400 MHz)



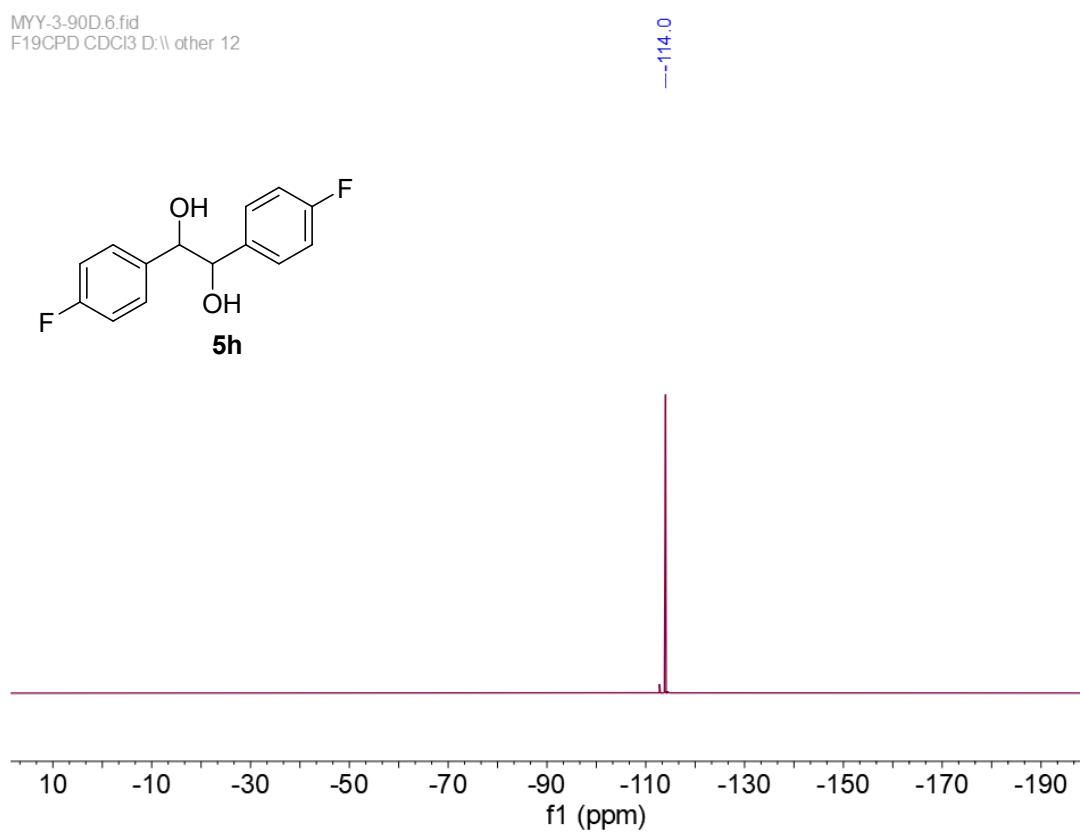
¹³C-NMR spectrum of **5g** (CDCl₃, 100 MHz)



¹H-NMR spectrum of **5h** (CDCl₃, 400 MHz)

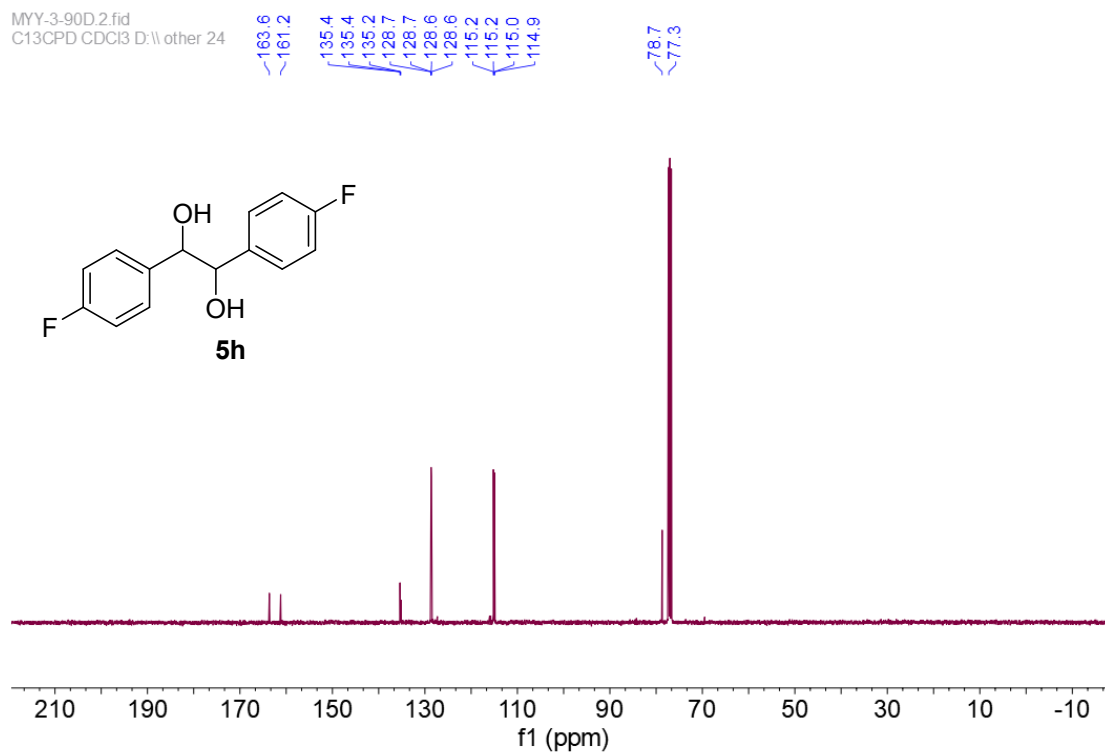


¹⁹F-NMR spectrum of **5h** (CDCl₃, 376 MHz)



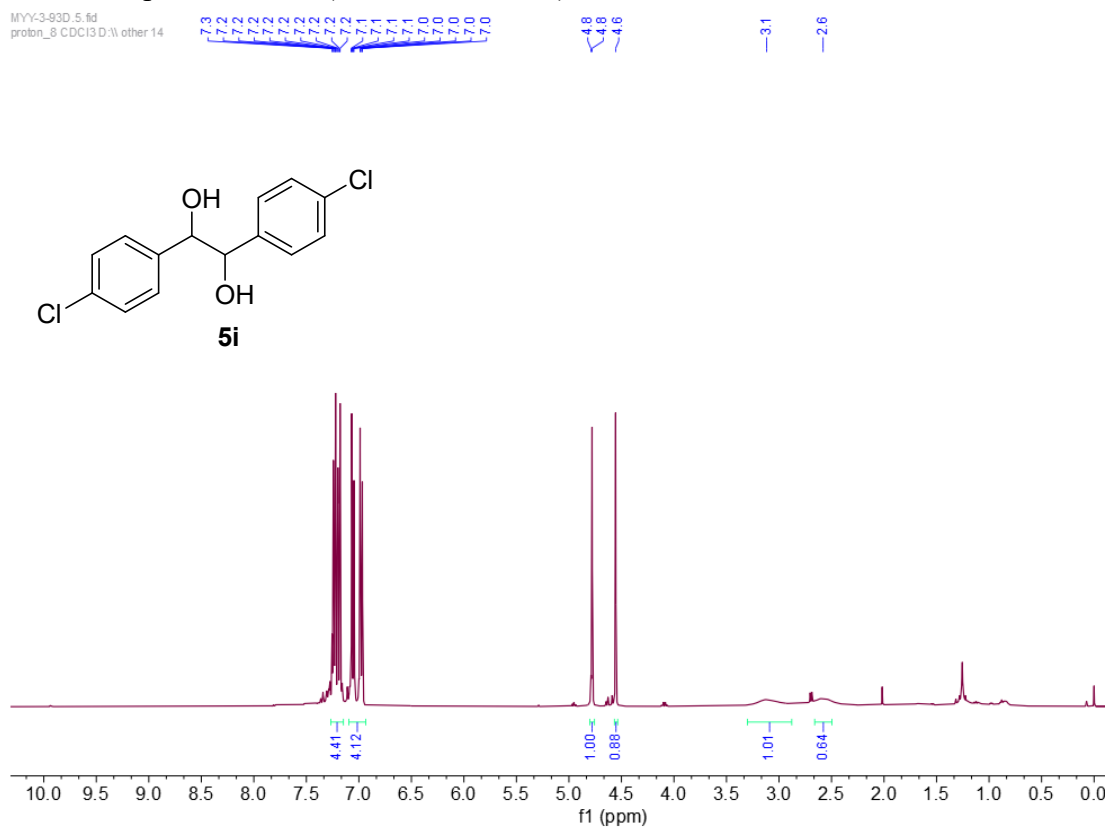
^{13}C -NMR spectrum of **5h** (CDCl_3 , 100 MHz)

MYY-3-90D.2.fid
C13CPD CDC13 D:\other 24



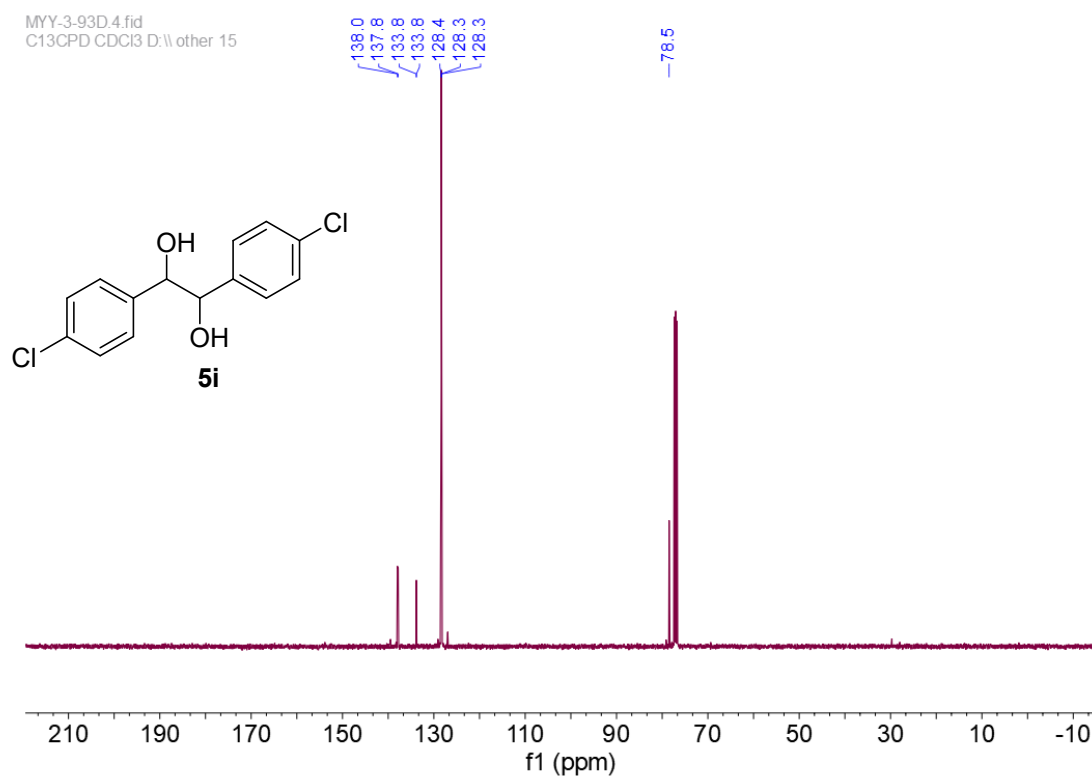
^1H -NMR spectrum of **5i** (CDCl_3 , 400 MHz)

MYY-3-93D.5.fid
proton_8 CDC13 D:\other 14



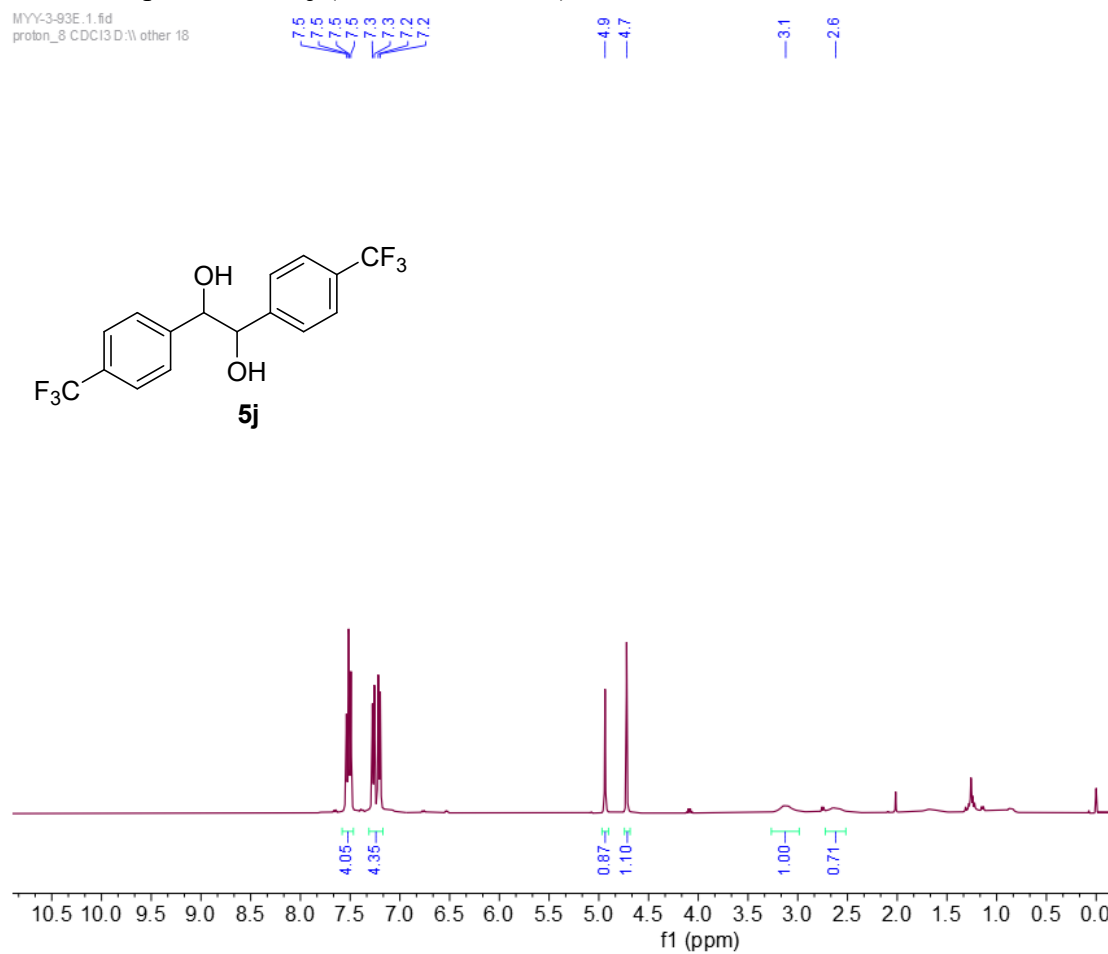
¹³C-NMR spectrum of **5i** (CDCl₃, 100 MHz)

MYY-3-93D.4.fid
C13CPD CDCl3 D:\other 15

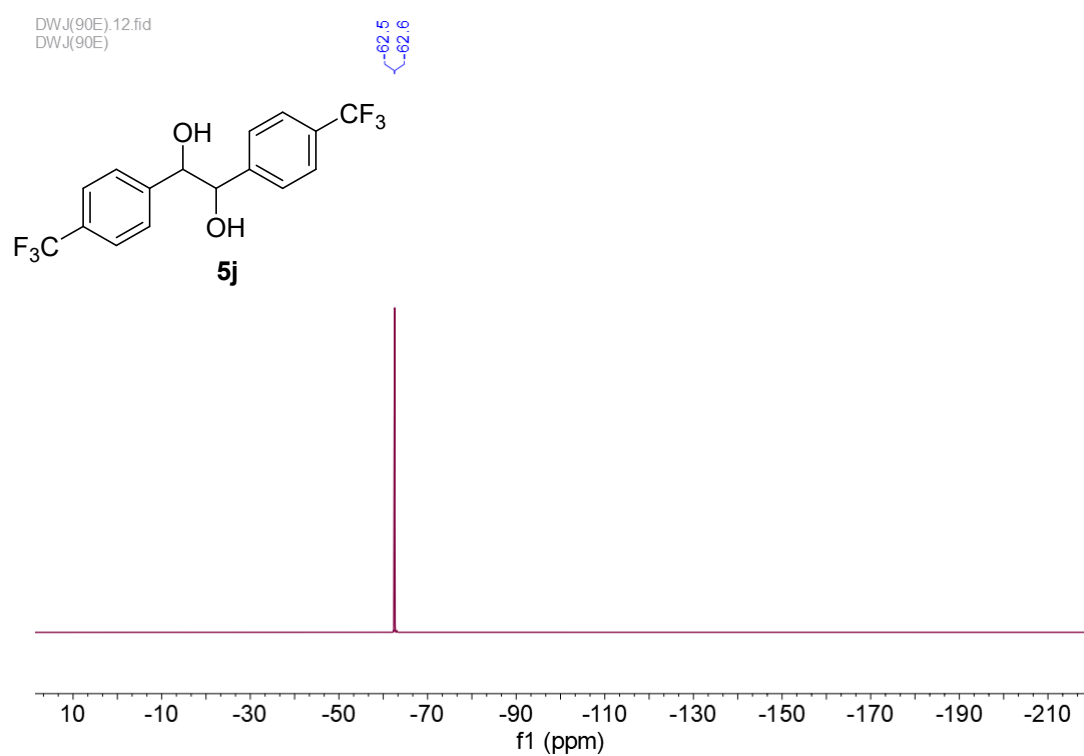


¹H-NMR spectrum of **5j** (CDCl₃, 400 MHz)

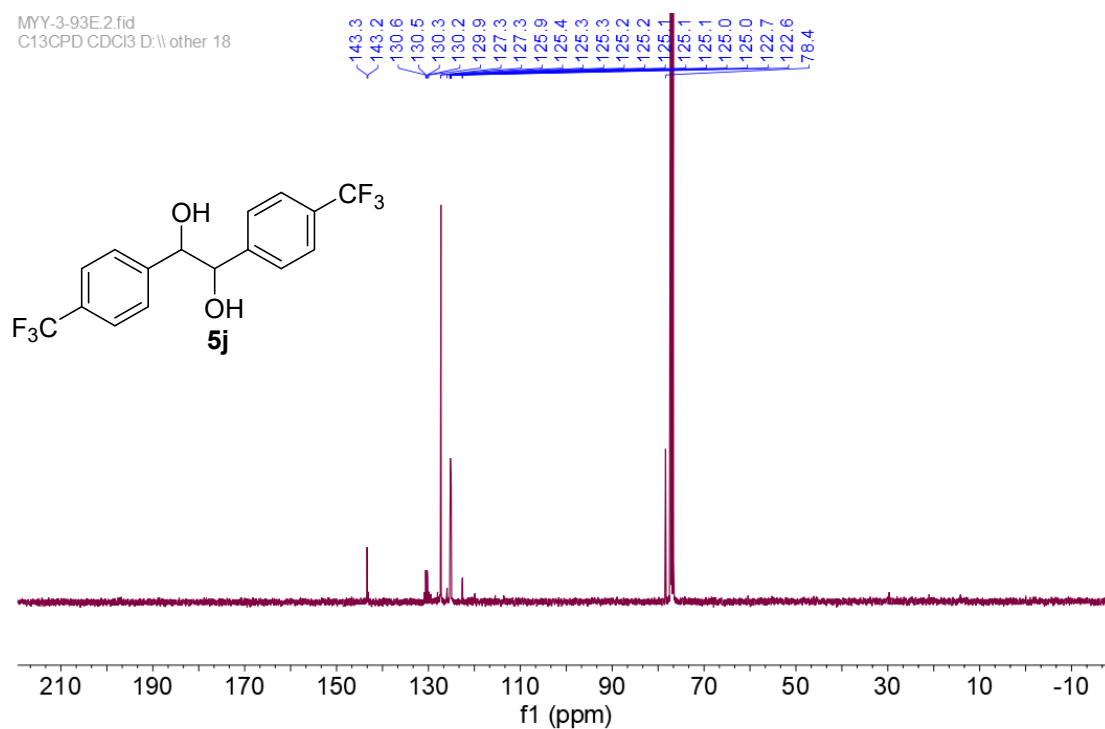
MYY-3-93E.1.fid
proton_8 CDCl3 D:\other 18



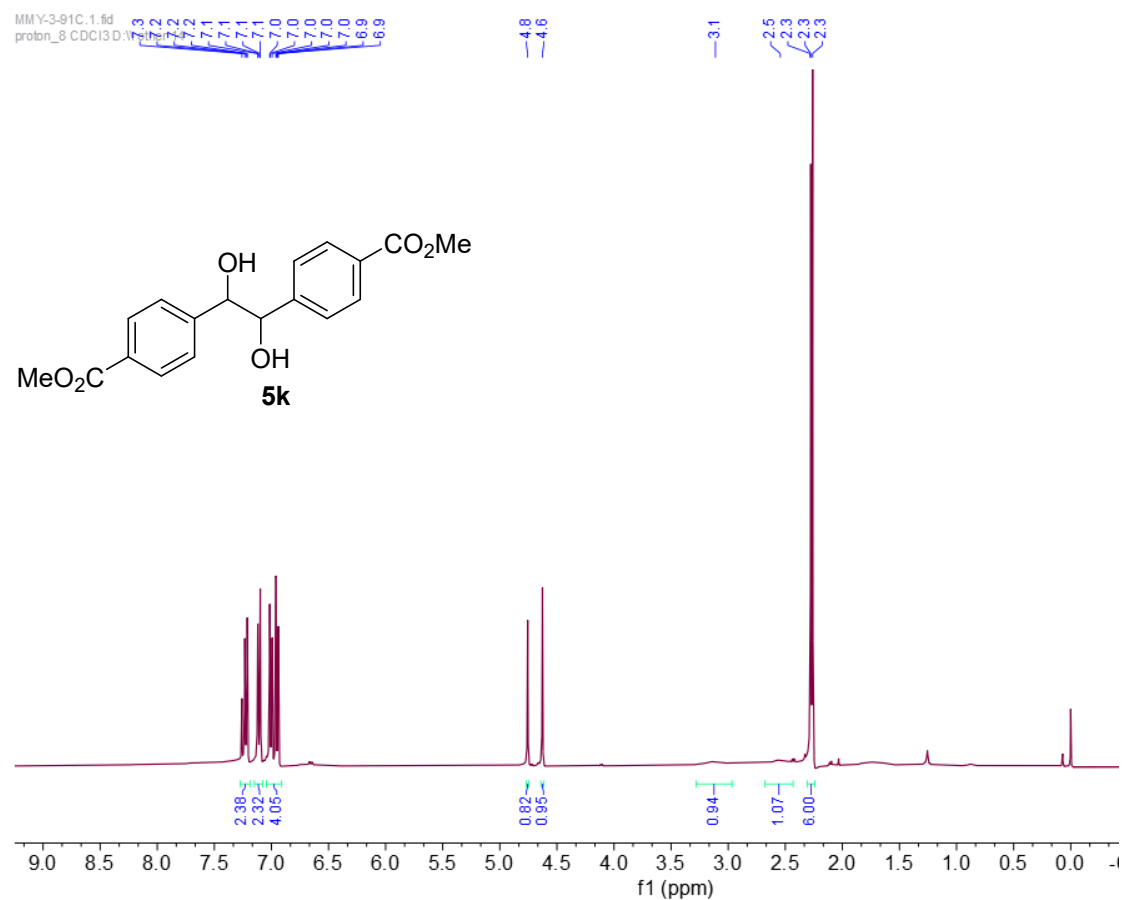
¹⁹F-NMR spectrum of **5j** (CDCl₃, 376 MHz)



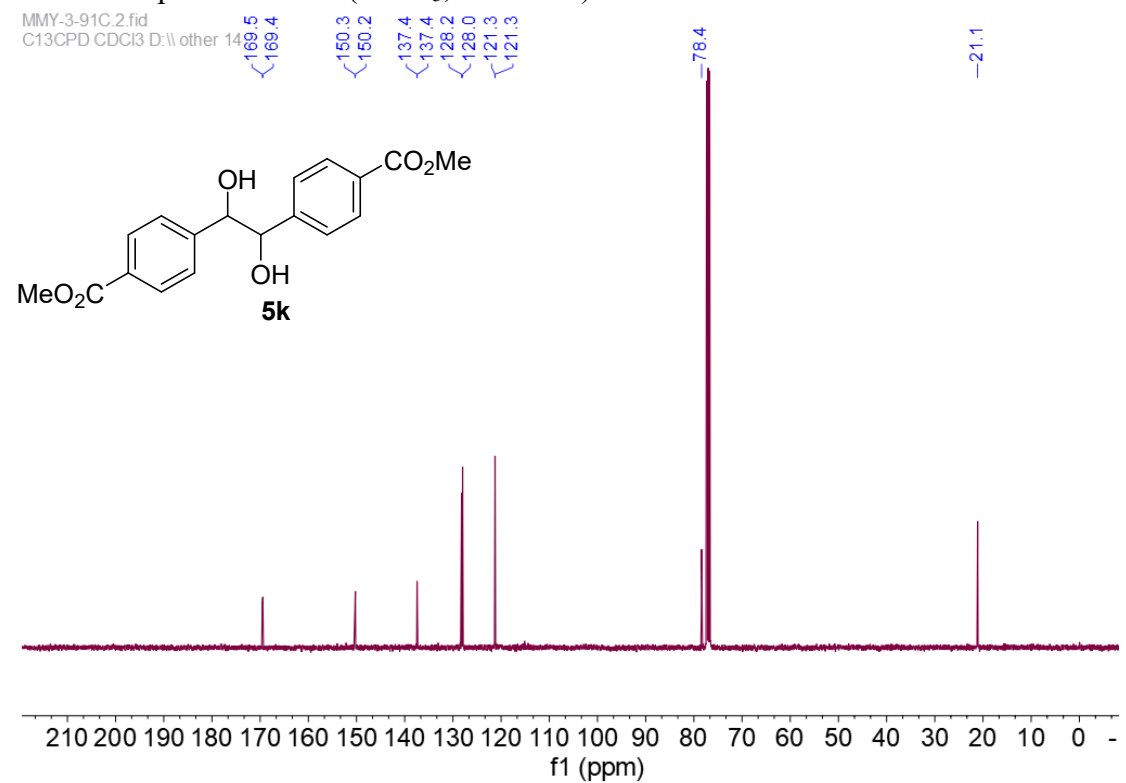
¹³C-NMR spectrum of **5j** (CDCl₃, 100 MHz)



¹H-NMR spectrum of **5k** (CDCl₃, 400 MHz)

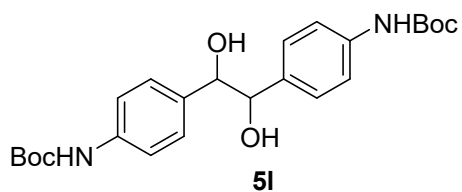
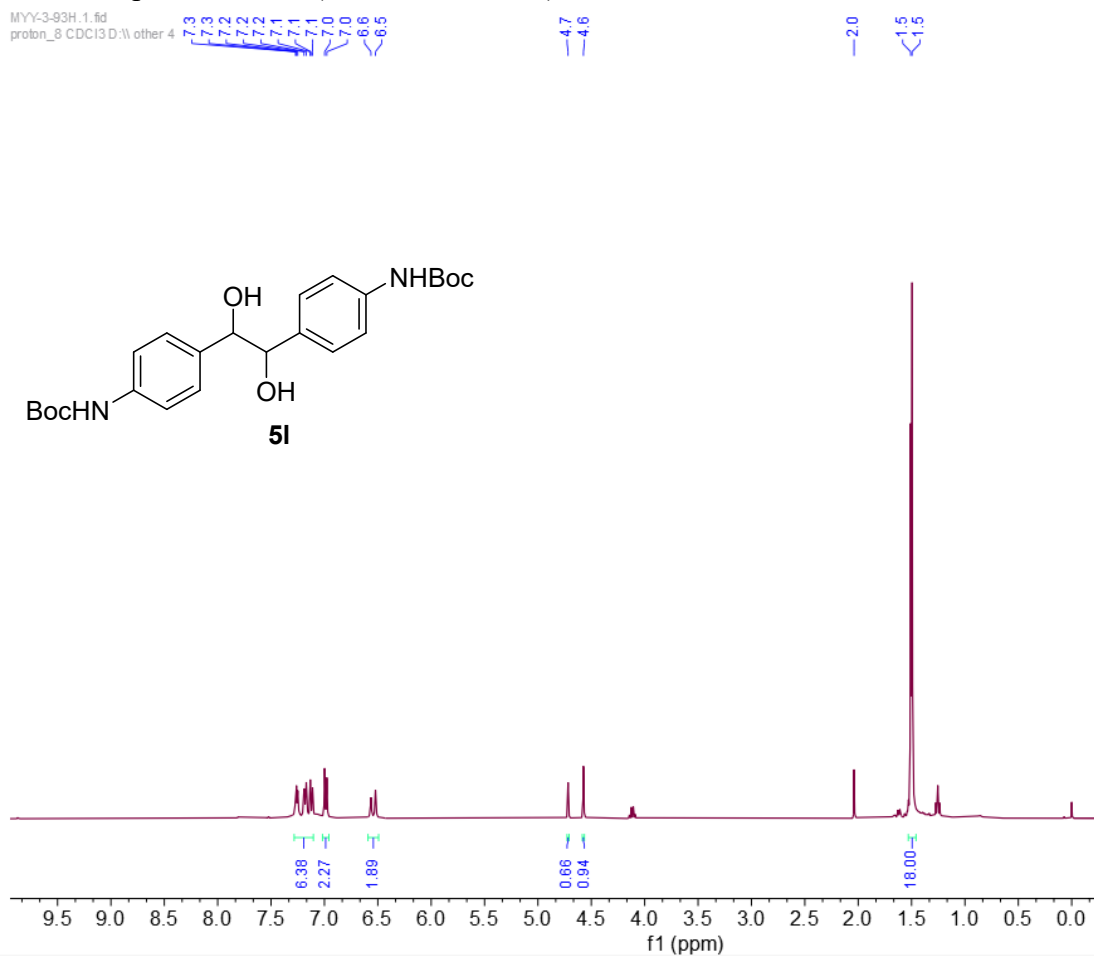


¹³C-NMR spectrum of **5k** (CDCl₃, 100 MHz)



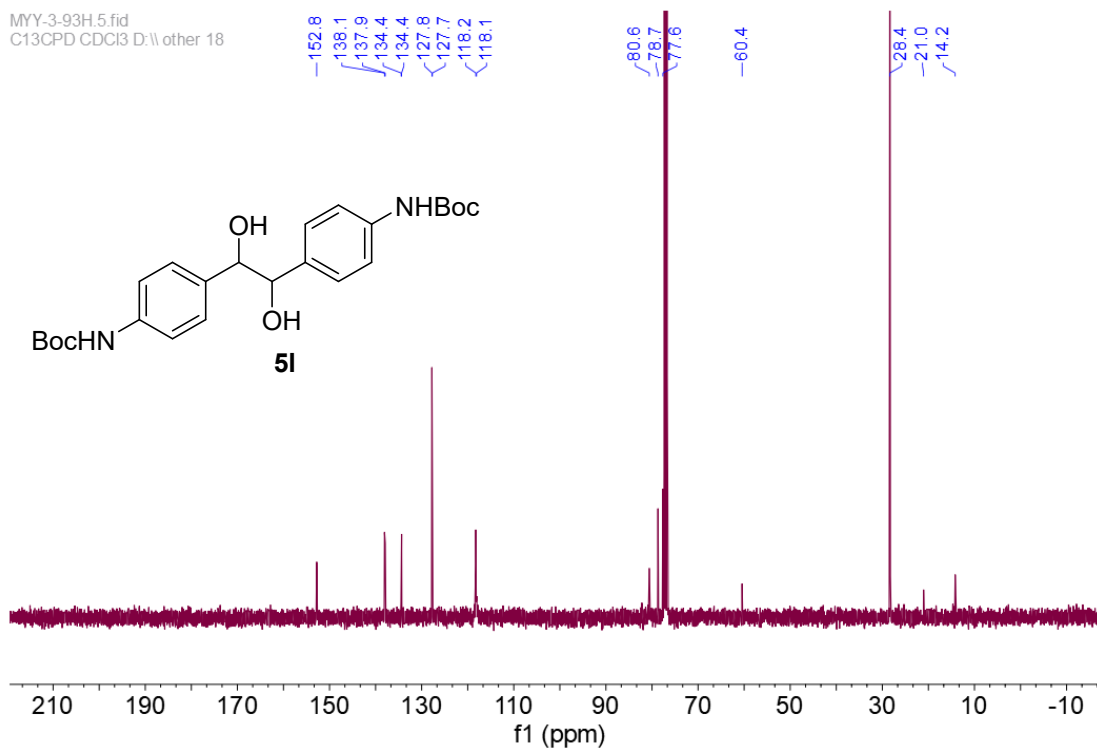
¹H-NMR spectrum of **5I** (CDCl₃, 400 MHz)

MYY-3-93H.1.fid
proton_8 CDCl3 D:\other 4

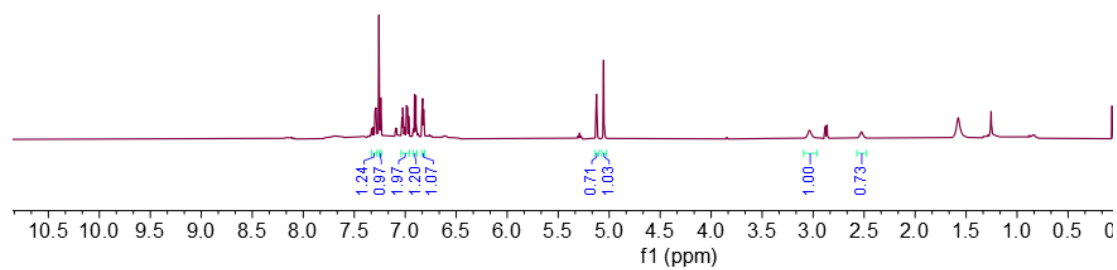
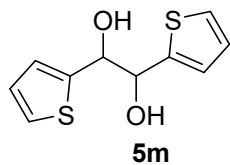


¹³C-NMR spectrum of **5I** (CDCl₃, 100 MHz)

MYY-3-93H.5.fid
C13CPD CDCl3 D:\other 18

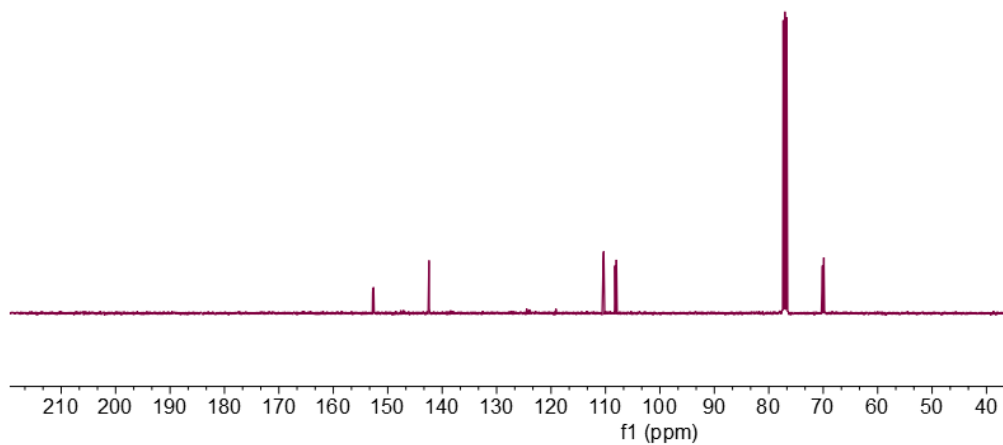
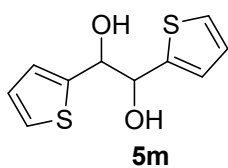


¹H-NMR spectrum of **5m** (CDCl₃, 400 MHz)

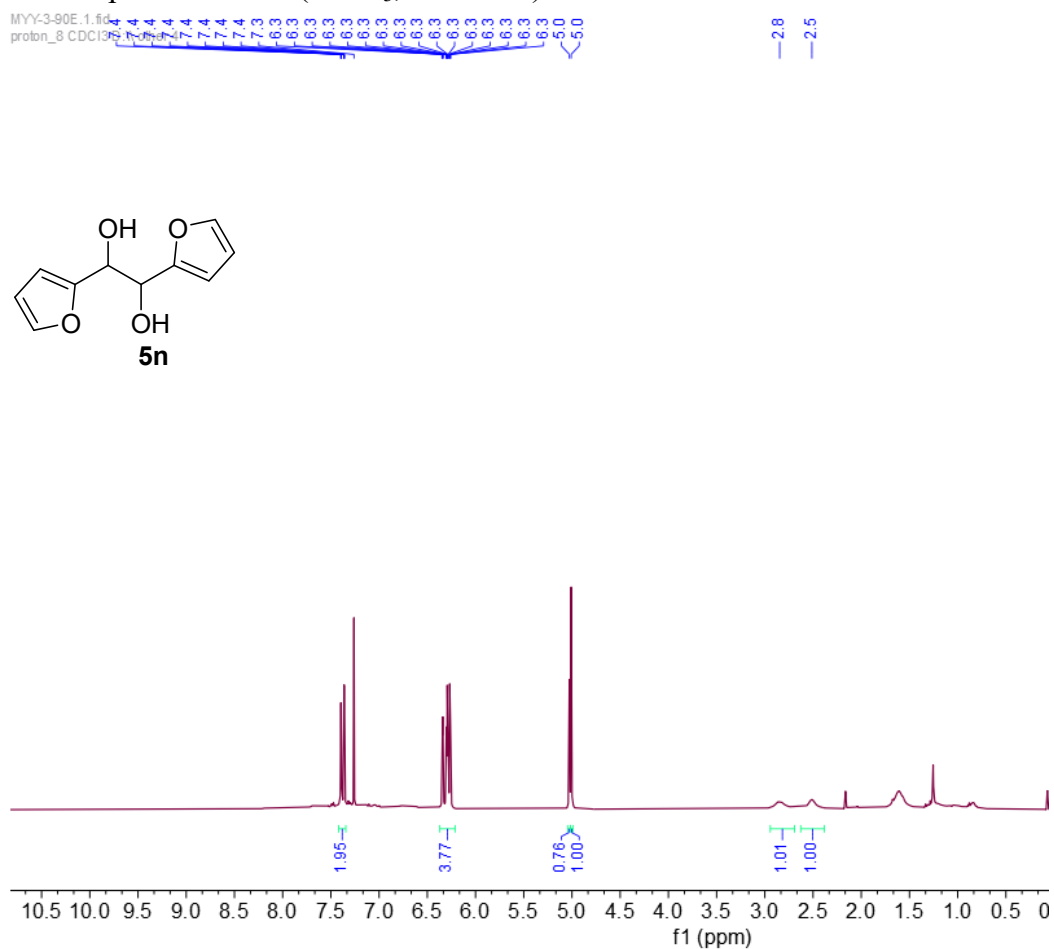


¹³C-NMR spectrum of **5m** (CDCl₃, 100 MHz)

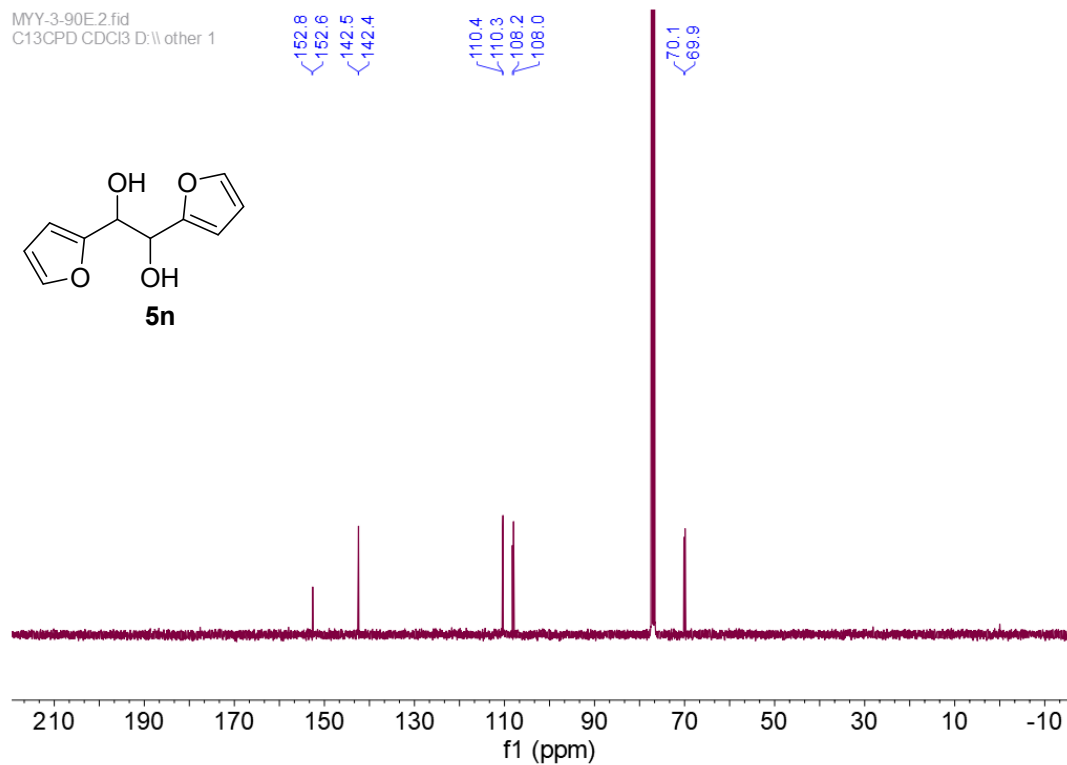
MY4-S.4.fid
 C13CPD CDCl3.D:\other 7



¹H-NMR spectrum of **5n** (CDCl₃, 400 MHz)



¹³C-NMR spectrum of **5n** (CDCl₃, 100 MHz)



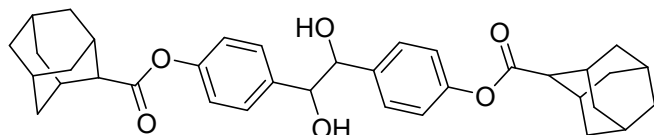
¹H-NMR spectrum of **5o** (CDCl₃, 400 MHz)

MYY-3-95A.2.fid
proton_8 CDCl3 D:\other 13

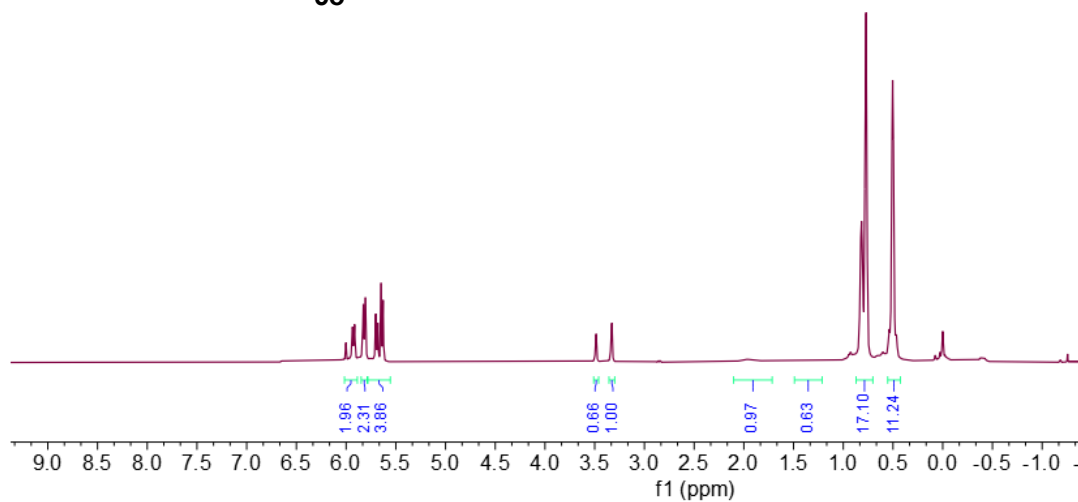
6.0
5.9
5.9
5.8
5.8
5.7
5.7
5.6

3.5
3.5
3.3
3.3

1.9
1.4
0.8
0.8
0.8
0.8
0.5
0.5



5o



¹³C-NMR spectrum of **5o** (CDCl₃, 100 MHz)

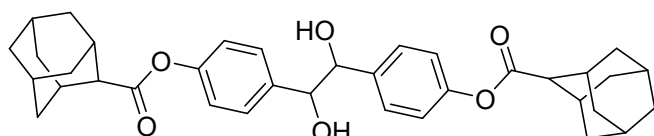
MYY-3-95A.1.fid
C13CPD CDCl3 D:\other 10

176.2

137.1
128.1
128.0
121.3

78.5

41.0
41.0
38.7
36.5
27.9



5o

