Supporting Information

Chemoselective Photoredox Synthesis of Unprotected Primary Amines Using Ammonia

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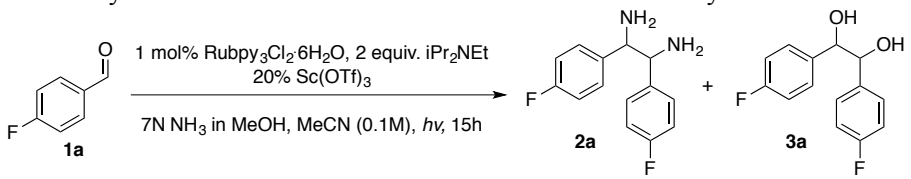
I. General Information

Chemicals and solvents were purchased from commercial suppliers and used as received. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a 400, 100, and 376 MHz Varian, 400, 100, and 376 MHz Bruker, 600, 151, 564 MHz Varian or NMR 700, 176, 659 MHz Bruker spectrometer. Chemical shifts were calibrated using residual undeuterated solvent as an internal reference ($CDCl_3$: 7.26 ppm ^{1}H NMR, 77.0 ppm ^{13}C NMR). Multiplicity is indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), br s (broad singlet). High-resolution mass spectral data were obtained using a HR-EI-MS (Waters Autospec Premier). The Blue LED strips (2 M, 12 W) and white LED strips (3 M, 18 W) were purchased from Tween Light (No: 22517610) with LED RGB controller (Model No: MY960R5). Cyclic voltammetry measurements were performed on a CHI 600E electrochemical analyzer equipped with a glassy carbon working electrode, a platinum wire counter electrode, and a Ag/AgCl reference electrode (CH Instruments, Inc.). Silica 60 M (0.04-0.063 mm) silica gel (Macherey-Nagel) was used for the column chromatography. The solvents were dried over molecular sieves (4 Å, 0.4 nm, type 514, pearls, Carl Roth).

II. Reaction optimization

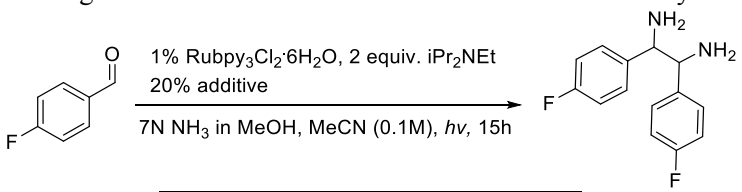
Table S1. Control study for the reductive dimerization of 4-fluorobenzaldehyde.



Entry	2a(%)[b]	3a(%)[c]	Comment
1	0	-	No NH_3
2	0	0	Without **PC1**
3	0	0	Without light
4	15	0	Under air
5	55	0	Wet solvent

[a] Reactions were carried out with **1a** (0.2 mmol), following typical procedure III. [b] Yields were determined after work up by 1H NMR spectra using 1,3,5-Trimethoxybenzene as internal standard. [c] Yields were determined by ^{19}F NMR spectra using Trifluorotoluene as an internal standard.

Table S2. Additive screening for the reductive dimerization of 4-fluorobenzaldehyde.

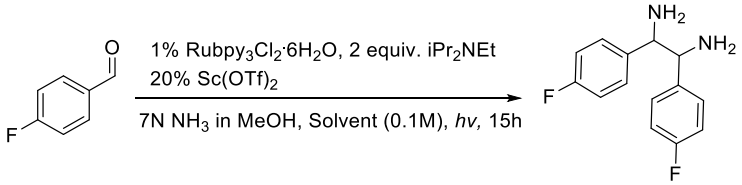


Entry[a]	Additive	Imino pinacol coupling (%)[b]
1	$Sc(OTf)_3$	79
2	$Sm(OTf)_3$	15
3	$Yb(OTf)_3$	23
4	$Gd(OTf)_3$	18
5	$Eu(OTf)_3$	14
6	$La(OTf)_3$	19
7	$In(OTf)_3$	55
8	$Al(OTf)_3$	20

9	$Zn(OTf)_2$	0
10	$Cu(OTf)_2$	6
11	$LiBF_4$	0
12	$(PhO)_2POOH$	0
13	Oxalic acid	0
14	Li_2CO_3	12
15[c]	$Sc(OTf)_3$	46
16[d]	$Sc(OTf)_3$	14

[a] Reactions were carried out with **1a** (0.2 mmol), following typical procedure III. [b] Yields were determined after work up by 1H NMR spectra using 1,3,5-Trimethoxybenzene as internal standard. [c] 10% $Sc(OTf)_3$ [d] 5% $Sc(OTf)_3$

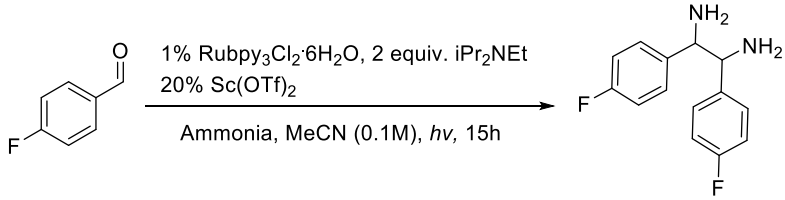
Table S3. Solvent screening for the reductive dimerization of 4-fluorobenzaldehyde.



Entry[a]	Solvent	Yield(%)[b]
1	MeCN	79
2	DMF	57
3	DMAC	27
4	DMSO	23
5	DCM	49
6	Me-THF	60
7	MTBE	67
8	Acetone	messy
9	Toluene	44
10	DME	57
11	Dioxane	messy
12	MeOH	0

[a] Reactions were carried out with **1a** (0.2 mmol), following typical procedure III. [b] Yields were determined after work up by 1H NMR spectra using 1,3,5-Trimethoxybenzene as internal standard.

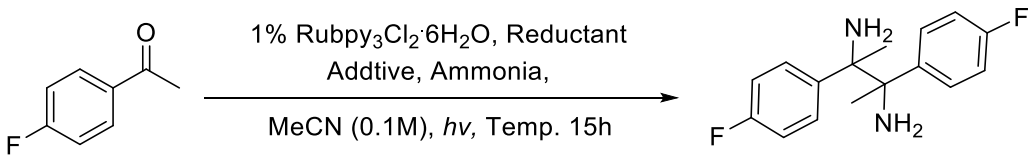
Table S4. Ammonia source screening for the reductive dimerization of 4-fluorobenzaldehyde.



Entry[a]	Ammonia source	Equiv. of NH_3	Yield(%)[b]
1	NH_3 in MeOH	10	79
2	NH_3 in MeOH	3	78
3	NH_3 in MeOH	2	32
4	NH_3 in Dioxane	3	29
5	NH_3 in water	10	63
6	NH_4OAC	3	0
7	NH_4OOCH	3	8
8	NH_4Cl	3	12
9	NH_4BF_4	3	0
10	$(NH_4)_2CO_3$	3	12

[a] Reactions were carried out with **1a** (0.2 mmol), following typical procedure III. [b] Yields were determined after work up by 1H NMR spectra using 1,3,5-Trimethoxybenzene as internal standard.

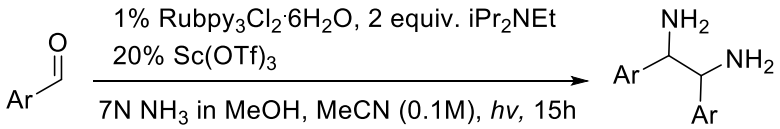
Table S5. Reoptimization of reductive dimerization conditions for ketones.



Entry[a]	Ammonia source	Temp.	Reductant	Additive	Conv.[b]
1	NH_3 in MeOH	RT	iPr_2NEt	20% $Sc(OTf)_3$	0
2	NH_3 in MeOH	RT	HE	20% $Sc(OTf)_3$	0
3[c]	NH_3 in MeOH	RT	iPr_2NEt	20% $Sc(OTf)_3$	0[d]
4	NH_3 gas	RT	iPr_2NEt	20% $Sc(OTf)_3$	0
5	NH_3 gas	60 °C	iPr_2NEt	20% $Sc(OTf)_3$	100%
6	NH_3 gas	60 °C	HE	20% $Sc(OTf)_3$	100%
7	NH_3 gas	60 °C	HE	20% $(PhO)_2POOH$	64%
8	NH_3 gas	60 °C	HE	20% $LiBF_4$	0
9	NH_3 gas	60 °C	HE	20% $Al(OTf)_3$	81%
10	NH_3 gas	60 °C	HE	1 equiv. TFA	100%
11	NH_3 gas	60 °C	HE	$Sm(OTf)_3$	100%
12	NH_3 gas	60 °C	HE	$In(OTf)_3$	84%
13	NH_3 gas	60 °C	HE	20% Oxalic acid	0
14	NH_3 gas	60 °C	HE	1 equiv. CH_3COOH	10%
15	NH_3 gas	60 °C	HE	1 equiv. MsOH	23%
16	NH_3 gas	60 °C	iPr_2NEt	1 equiv. TFA	0
17	NH_3 gas	60 °C	iPr_2NEt	$Sm(OTf)_3$	0

[a] Reactions were carried out with **4b** (0.2 mmol), following typical procedure III or IV. [b] Conversions were determined by 1H NMR spectra. [c] **PC2** ($Ir(dtbbpy)ppy_2PF_6$) instead of **PC1** ($Ru(bpy)_3Cl_2 \cdot 6H_2O$) was used. [d] full conversion to diol.

III. Typical Procedure for synthesis of unprotected vicinal diamines from aldehydes



Using iPr_2NEt as reductant:

To a 10 mL tube equipped with a magnetic stir bar was added Scandium(III) triflate (49.3 mg, 0.1 mmol, 0.2 equivalent), $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (3.8 mg, 0.005 mmol, 0.01 equivalent), aldehydes (1 equivalent), and anhydrous MeCN (5 mL). The solution was sealed with a septum, cooled to 0 °C and bubbled with argon via a balloon for 10 min. Then the ammonia solution (0.8 mL, 5 mmol, 10 equivalents) and iPr_2NEt (0.18 mL, 1 mmol, 2 equivalents) were added. After that the reaction was placed in photoreactor A (Figure S1) and irradiated at 25 °C for 15 hrs. The reaction mixture was transferred to a separation funnel, diluted with DCM and extracted with 1M HCl solution (40 mL). The aqueous layer was then washed with DCM for 3 times before adding 2M NaOH solution until pH 10. The aqueous phase was extracted with ether and concentrated under vacuum. The crude product was solubilized in MTBE and added to a 2M HCl solution at 40 °C stirring for 1h. The mixture was washed with DCM and basified with NaOH to pH 10. Then the aqueous phase was extracted with ether. The product was obtained after evaporation of the solvents with the presence of trace amount of Ru, which was subsequently removed by passing through a 2 cm silica gel plug with eluent of hexane : Etyl acetate : $iPrNH_2$ = 7:2:1.

Using Hantzsch ester as reductant:

To a 10 mL tube equipped with a magnetic stir bar was added Hantzsch ester (140 mg, 0.55 mmol, 1.1 equivalent), Scandium(III) triflate (49.3 mg, 0.1 mmol, 0.2 equivalent), $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (3.8 mg, 0.005 mmol, 0.01 equivalent), and anhydrous MeCN (5 mL). The solution was sealed with a septum, cooled to 0 °C and bubbled with argon via a balloon for 10 min. Then the aldehyde (0.5 mmol, 1 equivalent) and ammonia solution (0.8 mL, 5 mmol, 10 equivalents) were added. After that the reaction was placed in photoreactor A (Figure S1) and irradiated at 25 °C for 15 hrs. The reaction mixture was transferred to a separation funnel, diluted with DCM and extracted with 1M HCl solution (40 mL). The aqueous layer was then washed with

DCM for 3 times before adding 2M NaOH solution until pH 10. The aqueous phase was extracted with ether. The product was obtained after evaporation of the solvents with the presence of trace amount of Ru, which was subsequently removed by passing through a 2 cm silica gel plug with eluent of hexane : Etyl acetate : $iPrNH_2$ = 7:2:1.

Photoreactor A setup:
A flexible 2-meter, blue 12 W LED band was wrapped around a 115 mm borosilicate evaporating dish which was placed inside of a cardboard syringe box lined with aluminum foil (Figure S1) and the box was placed on a stirring plate. The evaporating dish was filled with H_2O and compressed was air flowed over the top to maintain a bath temperature around 20 °C. The reaction tube was placed in the reactor and stirred rapidly (1000 rpm).

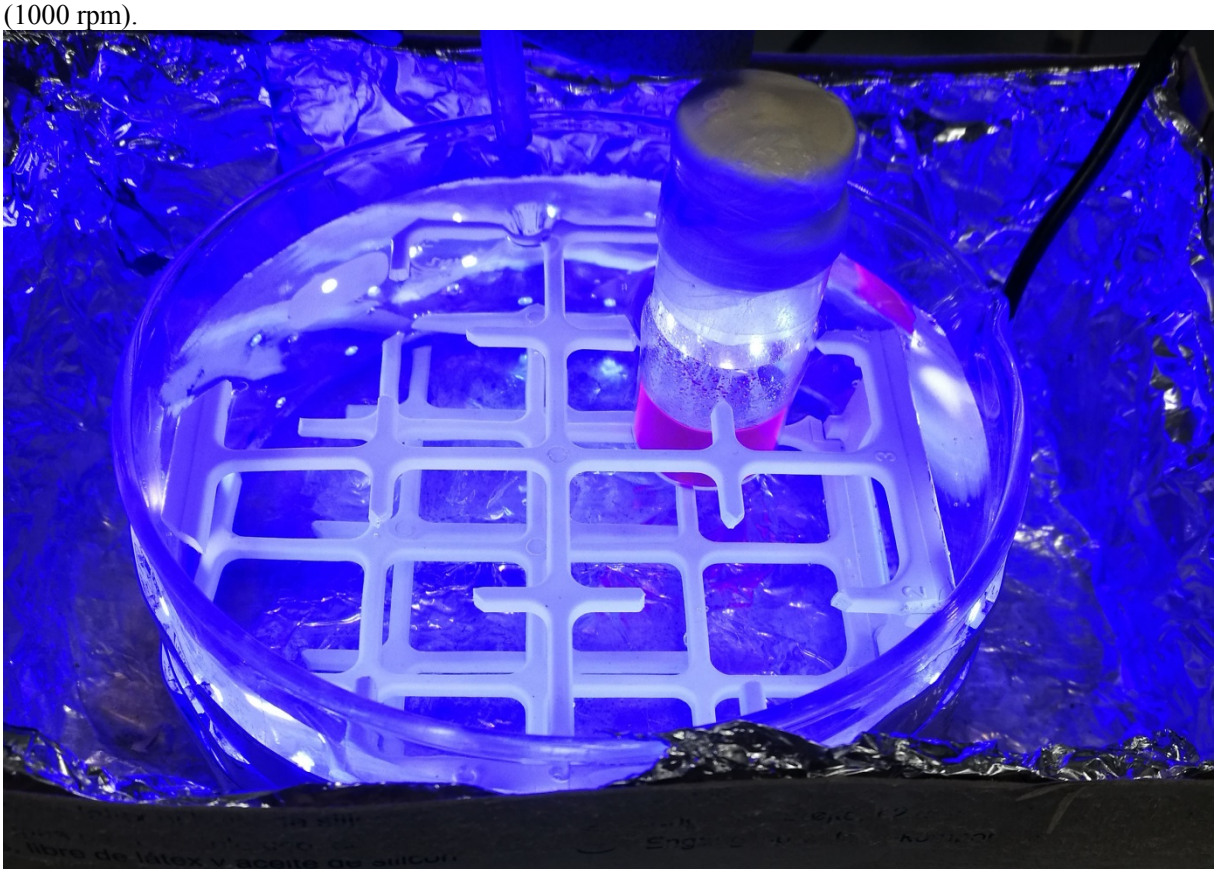


Figure S1 Typical photoreactor setup for typical procedure III

IV. Mid-scale batch synthesis of unprotected vicinal diamine from aldehyde

To a 20 mL tube equipped with a magnetic stir bar was added Scandium(III) triflate (98.6 mg, 0.2 mmol, 0.2 equivalent), $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (7.6 mg, 0.01 mmol, 0.01 equivalent), 4-fluorobenzaldehyde (124 mg, 1 mmol, 1 equivalent), and anhydrous MeCN (10 mL). The solution was sealed with a septum, cooled to 0 °C and bubbled with argon via a balloon for 10 min. Then the ammonia solution (1.6 mL, 10 mmol, 10 equivalents) and iPr_2NEt (0.36 mL, 2 mmol, 2 equivalents) were added. After that the reaction was placed in photoreactor A (Figure S1) and irradiated at 25 °C for 15 hrs. The reaction mixture was transferred to a separation funnel, diluted with DCM and extracted with 1M HCl solution (80 mL). The aqueous layer was then washed with DCM for 3 times before adding 2M NaOH solution until pH 10. The aqueous phase was extracted with ether and concentrated under vacuum. A yield of 70% was calculated by ^{1}H NMR using 1,3,5-trimethoxybenzene as internal standard.

V. Typical Procedure for synthesis of unprotected vicinal diamines from ketones

To a 10 mL tube equipped with a magnetic stir bar was added Hantzsch ester (154 mg, 0.6 mmol, 1.2 equivalent), $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (3.8 mg, 0.005 mmol, 0.01 equivalent), and anhydrous MeCN (5 mL). The solution was sealed with a septum and bubbled with gaseous NH_3 for 10 min. Then the ketone (0.5 mmol, 1 equivalent) and TFA (40 µL, 0.5 mmol, 1 equivalent) were added. After that the reaction was placed in the photoreactor B (Figure S2) with a NH_3 balloon and irradiated at 60 ^oC for 15 hrs. The reaction mixture was transferred to a separation funnel, diluted with DCM and extracted with 1M HCl solution (40 mL). The aqueous layer was then washed with DCM for 3 times before adding 2M NaOH solution until pH 10. The aqueous phase was extracted with ether. Aft The product was obtained after evaporation of the solvents with the presence of trace amount of Ru, which was subsequently removed by passing through a 2 cm silica gel plug with eluent of hexane : Etyl acetate : $iPrNH_2$ = 7:2:1. A common separable byproduct in this reaction is that of the reductive amination.

Photoreactor B setup:
A flexible 3-meter, blue 18 W LED band was wrapped around a 115 mm borosilicate evaporating dish filled with Ethylene glycol, which was placed on a heated stirring plate. The reaction tube was placed in the reactor and stirred rapidly (1000 rpm).

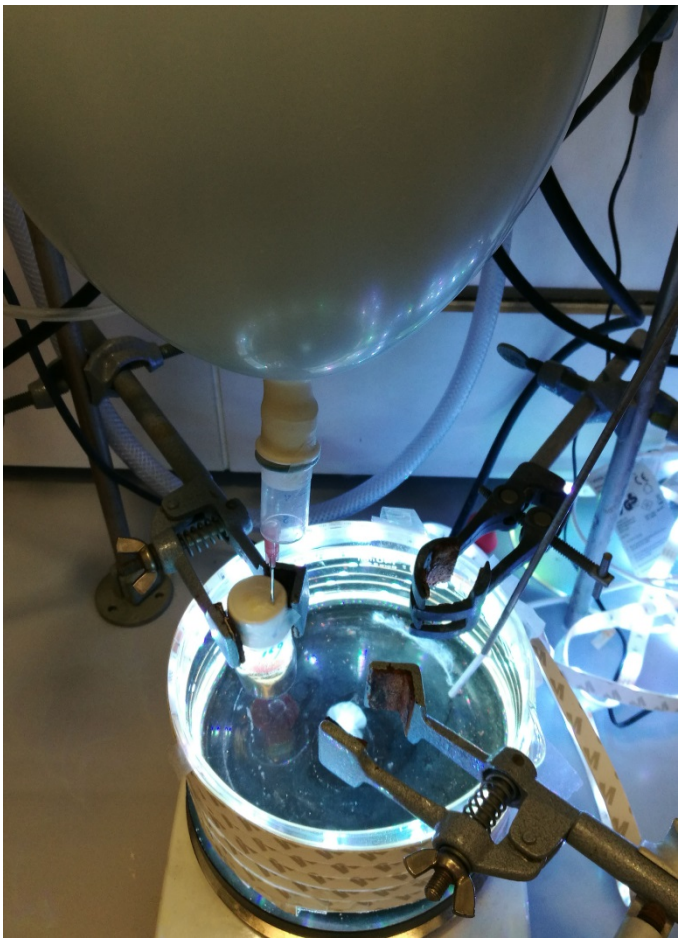


Figure S2 Photoreactor B setup for typical procedure IV, V and VI

VI. Typical Procedure for reductive amination

To a 10 mL tube equipped with a magnetic stir bar was added Hantzsch ester (154 mg, 0.6 mmol, 1.2 equivalent), $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (3.8 mg, 0.005 mmol, 0.01 equivalent), and anhydrous MeCN (5 mL). The solution was sealed with a septum and bubbled with gaseous NH_3 for 10 min. Then the ketone (0.5 mmol, 1 equivalent), PhSH (10µL diluted in 30 µL MeCN, 0.1 mmol, 0.2 equivalent), and TFA (40 µL, 0.5 mmol, 1 equivalent) were added. After that the reaction was placed in the photoreactor B (Figure S2) with a NH_3

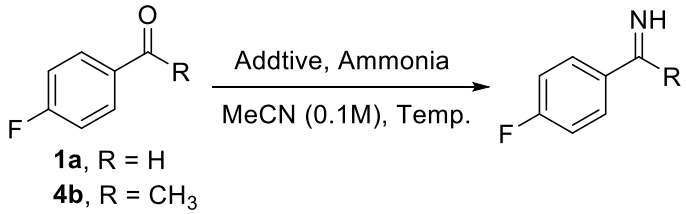
balloon and irradiated at 40 °C for 15 hrs. The reaction mixture was transferred to a separation funnel, diluted with DCM and extracted with 1M HCl solution (40 mL). The aqueous layer was then washed with DCM for 3 times before adding 2M NaOH solution until pH 10. The aqueous phase was extracted with DCM. The product was obtained after evaporation of the solvents.

VII. Typical Procedure for arylation

To a 10 mL tube equipped with a magnetic stir bar was added Hantzsch ester (256 mg, 1 mmol, 2 equivalent), 4-cyanopyridine (104 mg, 1 mmol, 2 equivalent), $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (3.8 mg, 0.005 mmol, 0.01 equivalent), and anhydrous MeCN (5 mL). The solution was sealed with a septum and bubbled with gaseous NH_3 for 10 min. Then the ketone (0.5 mmol, 1 equivalent) and TFA (40 µL, 0.5 mmol, 1 equivalent) were added. After that, the reaction was placed in the photoreactor B (Figure S2) with a NH_3 balloon and irradiated at 60 °C for 15 hrs. The reaction mixture was transferred to a separation funnel, diluted with DCM and extracted with 1M HCl solution (40 mL). The aqueous layer was then washed with DCM for 3 times before adding 2M NaOH solution until pH 10. The aqueous phase was extracted with DCM. After evaporation of solvents, the crude product was purified by column chromatography with silica gel and 10% $iPrNH_2$ in hexane as eluent.

VIII. N-H imine formation experiment

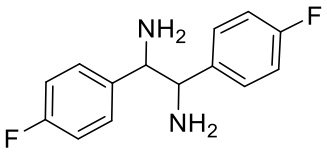
Table S6: Effect of additive, ammonia source, time, and temperature on the percent imine formation from 4-fluorobenzaldehyde and 4-fluoroacetophenone.



Entry	SM	Additive	Ammonia	Time	Temp.	Yield[c]
1[a]	**1a**	-	10 equiv. NH_3/MeOH	2h	RT	11%
2[a]	**1a**	20% $Sc(OTf)_3$	10 equiv. NH_3/MeOH	2h	RT	61%
3[a]	**1a**	100% TFA	10 equiv. NH_3/MeOH	2h	RT	59%
4[a]	**4b**	-	10 equiv. NH_3/MeOH	6h	RT	0%
5[b]	**4b**	-	NH_3 Gas	6h	60 °C	0%
6[b]	**4b**	20% $Sc(OTf)_3$	NH_3 Gas	6h	60 °C	15%
7[b]	**4b**	100% TFA	NH_3 Gas	6h	60 °C	23%

[a] Reactions were carried out with **1a** (0.2 mmol), following typical procedure III. [b] Reactions were carried out with **4b** (0.2 mmol), following typical procedure IV. [c] Isolated yield.

IX. Product characterization, reported as an ~1:1 mixture of diasteriomers

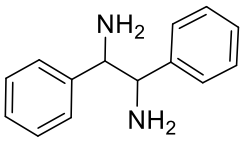


1,2-bis(4-fluorophenyl)ethane-1,2-diamine, **2a**

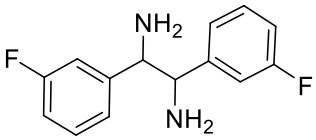
Following the typical procedure **III** with 4-fluorobenzaldehyde **1a** (62 mg, 0.5 mmol), the product **2a** (48 mg) was obtained in 77% yield as light yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 – 7.28 (m, 4H), 7.17 – 7.12 (m, 4H), 7.03 – 6.98 (m, 4H), 6.94 – 6.89 (m,

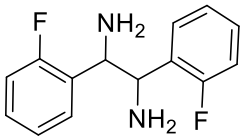
4H), 3.98 (s, 2H), 3.97 (s, 2H), 1.53 (s, 8H).
^{19}F NMR (564 MHz, $CDCl_3$) δ -114.95 (m), -115.60 (m).
^{13}C NMR (151 MHz, $CDCl_3$) δ 162.19 (d, *J* = 245.8 Hz), δ 161.79 (d, *J* = 245.2 Hz), 138.83 (d, *J* = 3.2 Hz), 138.25 (d, *J* = 3.4 Hz), 129.01 (d, *J* = 8.0 Hz), 128.38 (d, *J* = 7.9 Hz), 115.18 (d, *J* = 21.4 Hz), 114.96 (d, *J* = 21.3 Hz), 61.98, 61.61.
HRMS-ESI $[M-NH_2]^+$ Calcd for $C_{14}H_{12}F_2N$ 232.0932, found 232.0945.



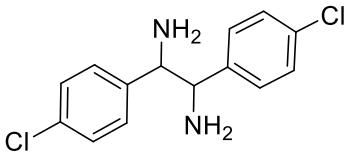
1,2-diphenylethane-1,2-diamine, **2b**
Following the typical procedure **III** with benzaldehyde **1b** (53.1 mg, 0.5 mmol), the product **2b** (41 mg) was obtained in 77% yield as white solid.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 – 7.12 (m, 20H), 4.09 (s, 2H), 4.01 (s, 2H), 1.57 (s, 8H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 143.30, 142.83, 128.41, 128.18, 127.56, 126.98, 126.86, 62.76, 61.84.
HRMS-ESI $[M-NH_2]^+$ Calcd for $C_{14}H_{14}N$ 196.1121, found 196.1130.



1,2-bis(3-fluorophenyl)ethane-1,2-diamine, **2c**
Following the typical procedure **III** with 3-fluorobenzaldehyde **1c** (62 mg, 0.5 mmol), the product **2c** (51 mg) was obtained in 77% yield as white solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.18 (m, 4H), 7.14 – 7.05 (m, 4H), 7.03 – 6.87 (m, 8H), 4.06 (s, 2H), 4.00 (s, 2H), 1.62 (s, 8H).
^{19}F NMR (376 MHz, $CDCl_3$) δ -112.79 (m), -113.02 (m).
^{13}C NMR (101 MHz, $CDCl_3$) δ 162.85 (d, *J* = 246.3 Hz), 162.76 (d, *J* = 245.9 Hz), 145.75 (d, *J* = 6.7 Hz), 145.15 (d, *J* = 6.6 Hz), 129.83 (d, *J* = 8.1 Hz), 129.73 (d, *J* = 8.2 Hz), 123.27 (d, *J* = 2.8 Hz), 122.49 (d, *J* = 2.7 Hz), 114.58 (d, *J* = 21.2 Hz), 114.25 (d, *J* = 21.7 Hz), 144.04(d, *J* = 21.5 Hz), 113.74 (d, *J* = 21.7 Hz), 62.15 (d, *J* = 1.8 Hz), 61.43 (d, *J* = 1.8 Hz).
HRMS-ESI $[M-NH_2]^+$ Calcd for $C_{14}H_{12}F_2N$ 232.0932, found 232.0948.

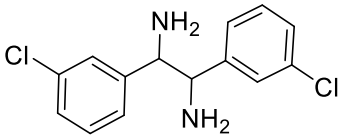


1,2-bis(2-fluorophenyl)ethane-1,2-diamine, **2d**
Following the typical procedure **III** with 2-fluorobenzaldehyde **1d** (62 mg, 0.5 mmol), the product **2d** (51 mg) was obtained in 82% yield as white solid.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 (dt, *J* = 19.1, 7.4 Hz, 4H), 7.24 – 7.18 (m, 2H), 7.14 – 7.07 (m, 4H), 7.03 – 6.95 (m, 4H), 6.89 (t, *J* = 9.4 Hz, 2H), 4.42 (s, 2H), 4.40 (s, 2H), 1.68 (s, 8H).
^{19}F NMR (564 MHz, $CDCl_3$) δ -118.01 (m), -118.18 (m).
^{13}C NMR (151 MHz, $CDCl_3$) δ δ 160.94 (d, *J* = 245.4 Hz), δ 160.40 (d, *J* = 245.9 Hz), 130.36 (d, *J* = 13.2 Hz), 129.96 (d, *J* = 13.3 Hz), δ 128.76 (d, *J* = 8.4 Hz), δ 128.50 (d, *J* = 8.0 Hz), 128.44 (d, *J* = 4.8 Hz), 124.19 (d, *J* = 3.5 Hz), 123.92 (d, *J* = 2.2 Hz), δ 115.41 (d, *J* = 22.6 Hz), δ 115.29 (d, *J* = 21.9 Hz), 55.53, 55.11.
HRMS-ESI $[M-NH_2]^+$ Calcd for $C_{14}H_{12}F_2N$ 232.0932, found 232.0947.

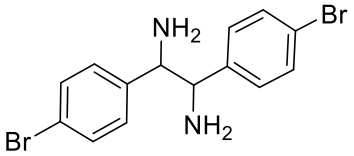


1,2-bis(4-chlorophenyl)ethane-1,2-diamine, **2e**
Following the typical procedure **III** with 4-chlorobenzaldehyde **1e** (70 mg, 0.5 mmol), the product **2d** (56

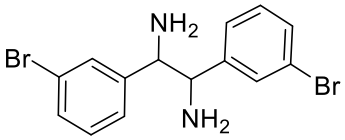
mg) was obtained in 80% yield as light yellow solid.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (d, J = 8.4 Hz, 4H), 7.24 (d, J = 8.5 Hz, 4H), 7.22 (d, J = 8.2 Hz, 4H), 7.13 (d, J = 8.1 Hz, 4H), 3.99 (s, 2H), 3.97 (s, 2H), 1.54 (s, 8H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 141.49, 140.90, 133.32, 132.81, 128.86, 128.52, 128.37, 128.27, 61.94, 61.48.
HRMS-ESI $[M-NH_2]^+$ Calcd for $C_{14}H_{12}Cl_2N$ 264.0341, found 264.0354.



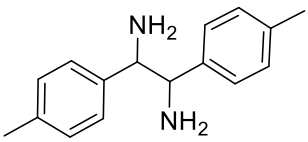
1,2-bis(3-chlorophenyl)ethane-1,2-diamine, **2f**
Following the typical procedure **III** with 3-chlorobenzaldehyde **1f** (70 mg, 0.5 mmol), the product **2f** (49 mg) was obtained in 70% yield as white solid.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (s, 2H), 7.29 (s, 2H), 7.28 – 7.24 (m, 5H), 7.22 – 7.17 (m, 5H), 7.14 – 7.08 (m, 2H), 4.03 (s, 2H), 3.97 (s, 2H), 1.46 (s, 8H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 145.23, 144.66, 134.41, 134.26, 129.63, 129.53, 127.89, 127.62, 127.36, 127.01, 125.86, 125.11, 62.24, 61.37.
HRMS-ESI $[M-NH_2]^+$ Calcd for $C_{14}H_{12}Cl_2N$ 264.0341, found 264.0357.



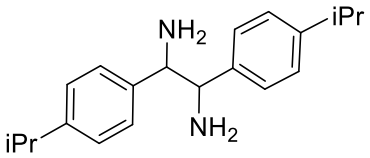
1,2-bis(4-bromophenyl)ethane-1,2-diamine, **2g**
Following the typical procedure **III** with 4-bromobenzaldehyde **1g** (95 mg, 0.5 mmol), the product **2g** (53 mg) was obtained in 57% yield as light yellow solid.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (d, J = 8.4 Hz, 4H), 7.38 (d, J = 8.4 Hz, 4H), 7.19 (d, J = 8.4 Hz, 4H), 7.09 (d, J = 8.4 Hz, 4H), 3.99 (s, 2H), 3.96 (s, 2H), 1.53 (s, 8H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 141.96, 141.41, 131.48, 131.35, 129.25, 128.65, 121.47, 120.97, 61.96, 61.44.
HRMS-ESI $[M-NH_2]^+$ Calcd for $C_{14}H_{12}Br_2N$ 351.9331, found 351.9343.



1,2-bis(3-bromophenyl)ethane-1,2-diamine, **2h**
Following the typical procedure **III** with 3-bromobenzaldehyde **1h** (92.5 mg, 0.5 mmol), the product **2h** (51 mg) was obtained in 55% yield as light yellow solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 2H), 7.49 (s, 2H), 7.46 (dt, J = 7.6, 1.7 Hz, 2H), 7.42 – 7.36 (m, 2H), 7.32 – 7.15 (m, 8H), 4.07 (s, 2H), 3.99 (s, 2H), 1.56 (s,8H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 145.42, 144.90, 130.92, 130.58, 130.38, 130.02, 129.97, 129.91, 126.41, 125.64, 122.72, 122.58, 62.26, 61.32.
HRMS-ESI $[M-NH_2]^+$ Calcd for $C_{14}H_{12}Br_2N$ 351.9331, found 351.9341.



1,2-di-p-tolylethane-1,2-diamine, **2i**
Following the typical procedure **III** with 4-methylbenzaldehyde **1i** (61 mg, 0.5 mmol), the product **2i** (70 mg) was obtained in 80% yield as white solid.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (d, J = 8.0 Hz, 4H), 7.18 – 7.15 (m, 8H), 7.09 (d, J = 7.7 Hz, 4H), 4.07 (s, 2H), 3.96 (s, 2H), 2.35 (s, 6H), 2.31 (s, 6H), 1.60 (s, 8H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 140.28, 139.95, 137.14, 136.47, 129.10, 128.86, 127.44, 126.74, 62.51, 61.34, 21.06, 21.00.
HRMS-ESI $[M-NH_2]^+$ Calcd for $C_{16}H_{18}N$ 224.1434, found 224.1446.



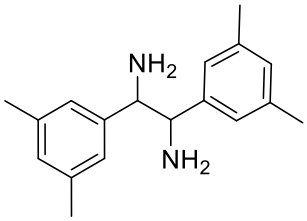
1,2-bis(4-isopropylphenyl)ethane-1,2-diamine, **2j**

Following the typical procedure **III** with 4-*iso*-propylbenzaldehyde **1j** (74 mg, 0.5 mmol), the product **2j** (40 mg) was obtained in 54% yield as white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (d, J = 8.1 Hz, 4H), 7.25 (d, J = 8.0 Hz, 4H), 7.22 (d, J = 7.9 Hz, 4H), 7.17 (d, J = 7.8 Hz, 4H), 4.11 (s, 2H), 3.95 (s, 2H), 2.90 (m, 4H), 1.59 (s, 8H), 1.26 (d, J = 6.9 Hz, 12H), 1.24 (d, J = 7.2 Hz, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 148.23, 147.57, 140.75, 140.42, 127.52, 126.73, 126.52, 126.25, 62.66, 61.15, 33.78, 33.70, 24.02, 23.98.

HRMS-ESI $[M-NH_2]^+$ Calcd for $C_{20}H_{26}N$ 280,2060, found 280,2071.



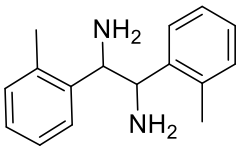
1,2-bis(3,5-dimethylphenyl)ethane-1,2-diamine, **2k**

Following the typical procedure **IV** with 3,5-dimethyl benzaldehyde **1k** (68 mg, 0.5 mmol), the product **2k** (42 mg) was obtained as white solid in 63% yield as white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (s, 4H), 6.96 (d, *J* = 6.7 Hz, 6H), 6.88 (s, 2H), 4.09 (s, 2H), 3.89 (s, 2H), 2.33 (s, 12H), 2.30 (s, 12H), 1.66 (s, 8H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.09, 142.99, 138.11, 137.77, 129.34, 128.67, 125.46, 124.64, 62.88, 60.97, 21.40, 21.35.

HRMS-ESI $[M-NH_2]^+$ Calcd for $C_{18}H_{22}N$ 252.1747, found 252.1759.



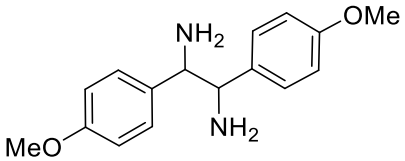
1,2-di-o-tolylethane-1,2-diamine, **2l**

Following the typical procedure **III** with 2-methylbenzaldehyde **1l** (61 mg, 0.5 mmol), the product **2l** (47 mg) was obtained in 78% yield as white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.8 Hz, 2H), 7.38 (d, *J* = 7.6 Hz, 2H), 7.25 – 7.11 (m, 8H), 7.08 (t, *J* = 7.4 Hz, 2H), 7.00 (d, *J* = 7.6 Hz, 2H), 4.43 (s, 2H), 4.34 (s, 2H), 2.30 (s, 6H), 2.09 (s, 6H), 1.68 (s, 8H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 141.47, 141.17, 136.58, 135.21, 130.26, 126.94, 126.77, 126.65, 126.23, 126.15, 125.92, 56.94, 55.76, 19.56, 19.49.

HRMS-ESI $[M-NH_2]^+$ Calcd for $C_{16}H_{18}N$ 224.1434, found 224.1441.



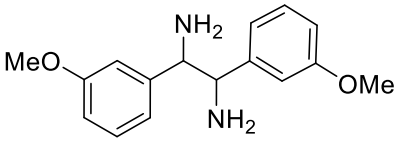
1,2-bis(4-methoxyphenyl)ethane-1,2-diamine, **2m**

Following the typical procedure **III** with 4-methoxybenzaldehyde **1m** (68 mg, 0.5 mmol), the product **2m** (42 mg) was obtained in 62% yield as white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.7 Hz, 4H), 7.14 (d, *J* = 8.6 Hz, 4H), 6.88 (d, *J* = 8.6 Hz, 4H), 6.79 (d, *J* = 8.6 Hz, 4H), 4.00 (s, 2H), 3.92 (s, 2H), 3.80 (s, 6H), 3.76 (s, 6H), 1.54 (s, 8H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.01, 158.51, 135.40, 135.01, 128.57, 127.92, 113.81, 113.54, 62.22, 61.31, 55.26, 55.20.

HRMS-ESI $[M-NH_2]^+$ Calcd for $C_{16}H_{18}O_2N$ 256.1332, found 256.1347.



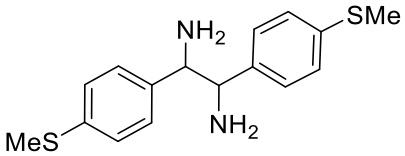
1,2-bis(3-methoxyphenyl)ethane-1,2-diamine, **2n**

Following the typical procedure **III** with 3-methoxybenzaldehyde **1n** (68 mg, 0.5 mmol), the product **2n** (56 mg) was obtained in 82% yield as white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 (t, *J* = 7.9 Hz, 2H), 7.21 (t, *J* = 7.9 Hz, 2H), 6.98 (d, *J* = 7.6, Hz, 2H), 6.96 – 9.94 (m, 2H), 6.88 (d, *J* = 7.6, Hz, 2H), 6.86 – 6.84 (m, 2H), 6.83 (dd, *J* = 2.6, 0.9 Hz, 2H), 6.77 (dd, *J* = 2.6, 0.9 Hz, 1H), 6.76 (dd, *J* = 2.7, 0.9 Hz, 1H), 4.08 (s, 2H), 3.98 (s, 2H), 3.80 (s, 6H), 3.77 (s, 6H), 1.63 (s, 8H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.74, 159.53, 145.08, 144.59, 129.40, 129.21, 120.00, 119.23, 113.38, 112.76, 112.51, 112.48, 62.79, 61.69, 55.23, 55.19.

HRMS-ESI $[M-NH_2]^+$ Calcd for $C_{16}H_{18}O_2N$ 256.1332, found 256.1346.



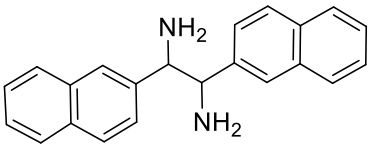
1,2-bis(4-(methylthio)phenyl)ethane-1,2-diamine, **2o**

Following the typical procedure **III** with 4-methylthio benzaldehyde **1o** (76 mg, 0.5 mmol), the product **2o** (55 mg) was obtained in 72% yield as white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.1 Hz, 4H), 7.21 (d, *J* = 8.3 Hz, 4H), 7.15 (s, 8H), 4.01 (s, 2H), 3.94 (s, 2H), 2.47 (s, 6H), 2.44 (s, 6H), 1.59 (s, 8H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 140.12, 139.63, 137.58, 136.91, 128.06, 127.44, 126.60, 126.50, 62.25, 61.40, 15.92, 15.87.

HRMS-ESI $[M-NH_2]^+$ Calcd for $C_{16}H_{18}S_2N$ 288.0875, found 288.0889.



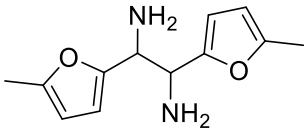
1,2-di(naphthalen-2-yl)ethane-1,2-diamine, **2p**

Following the typical procedure **III** with 2-naphthaldehyde **1q** (78 mg, 0.5 mmol), the product **2q** (48 mg) was obtained in 62% yield as white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 2H), 7.92 – 7.77 (m, 14H), 7.63 (dd, *J* = 8.5, 1.6 Hz, 2H), 7.59 – 7.44 (m, 10H), 4.46 (s, 2H), 4.34 (s, 2H), 1.84 (s, 8H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.57, 140.24, 133.33, 133.30, 133.15, 132.72, 128.38, 128.03, 127.94, 127.70, 127.62, 126.88, 126.20, 126.09, 125.92, 125.73, 125.53, 125.41, 125.35, 62.86, 61.42.

HRMS-ESI $[M-NH_2]^+$ Calcd for $C_{22}H_{18}N$ 296.1434, found 296.1446.



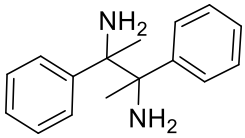
1,2-bis(5-methylfuran-2-yl)ethane-1,2-diamine, **2q**

Following the typical procedure **III** with 1-(5-methylfuran-2-yl)ethan-1-one **1q** (55 mg, 0.5 mmol), the product **2q** (40 mg) was obtained after flushing through a silica gel column with the eluent (hexane : ethyl acetate : iPr_2NH_2 = 10:2:1) in 73% yield as white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.08 (d, *J* = 3.0 Hz, 2H), 6.03 (d, *J* = 3.1 Hz, 2H), 5.89 – 5.82 (m, 4H), 4.20 (s, 2H), 4.07 (s, 2H), 2.25 (s, 6H), 2.24 (s, 6H), 1.69 (s, 8H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.29, 153.68, 151.46, 151.04, 107.62, 106.55, 105.94, 105.91, 54.98, 53.93, 13.58, 13.54.

HRMS-ESI $[M-NH_2]^+$ Calcd for $C_{12}H_{14}O_2N$ 204.1019, found 204.1030.



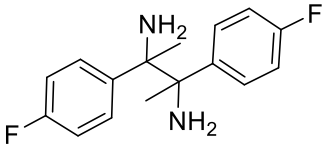
2,3-diphenylbutane-2,3-diamine, **5a**

Following the typical procedure **IV** with acetophenone **4a** (61 mg, 0.5 mmol), the product (60 mg) **5a** was obtained as white solid in quantitative yield as white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.7 Hz, 4H), 7.30 (t, *J* = 7.5 Hz, 4H), 7.24 (d, *J* = 7.1 Hz, 2H), 7.21 (s, 10H), 1.62 (s, 8H), 1.53 (s, 6H), 1.45 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.37, 145.34, 127.79, 127.72, 127.26, 127.01, 126.44, 126.34, 60.59, 60.23, 27.16, 26.73.

HRMS-ESI $[M-NH_2]^+$ Calcd for $C_{16}H_{18}N$ 224.1434, found 224.1446.



2,3-bis(4-fluorophenyl)butane-2,3-diamine, **5b**

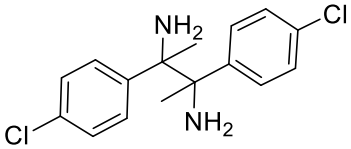
Following the typical procedure **IV** with 4-fluoro acetophenone **4b** (70 mg, 0.5 mmol), the product **5b** (70 mg) was obtained as white solid in quantitative yield.

^{1}H NMR (700 MHz, $CDCl_3$) δ 7.39 (t, *J* = 6.8 Hz, 4H), 7.17 (t, *J* = 6.8 Hz, 4H), 7.03 – 6.98 (m, 4H), 6.94 – 6.87 (m, 4H), 1.67 (s, 8H), 1.56 (s, 6H), 1.46 (s, 6H).

^{19}F NMR (659 MHz, $CDCl_3$) δ -116.80 (m), -116.84 (m).

^{13}C NMR (176 MHz, $CDCl_3$) δ 161.65 (d, *J* = 245.7 Hz), 161.59 (d, *J* = 245.6 Hz), 140.90, 140.86, 129.42 (d, *J* = 7.1 Hz), 129.38 (d, *J* = 7.2 Hz), 114.00 (d, *J* = 20.8 Hz), 113.75 (d, *J* = 20.8 Hz), 60.39, 60.08, 27.20, 26.86.

HRMS-ESI $[M-NH_2]^+$ Calcd for $C_{16}H_{16}F_2N$ 260.1245, found 260.1237.



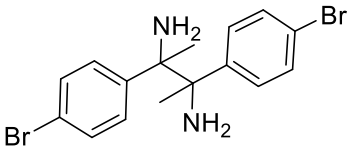
2,3-bis(4-chlorophenyl)butane-2,3-diamine, **5c**

Following the typical procedure **IV** with 4-Chloro acetophenone **4c** (77.3 mg, 0.5 mmol), the product **5c** (76 mg) was obtained as white crystal in 98% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.6 Hz, 4H), 7.25 (d, *J* = 7.0 Hz, 4H), 7.18 (d, *J* = 8.8 Hz, 4H), 7.12 (d, *J* = 8.3 Hz, 4H), 1.55 (s, 8H), 1.50 (s, 6H), 1.41 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 143.69, 143.66, 132.60, 132.50, 129.22, 129.19, 127.36, 127.14, 60.35, 60.06, 27.02, 26.76.

HRMS-ESI $[M-NH_2]^+$ Calcd for $C_{12}H_{14}O_2N$ 292.0654, found 292.0667.



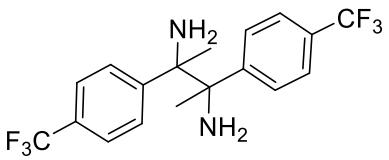
2,3-bis(4-bromophenyl)butane-2,3-diamine, **5d**

Following the typical procedure **IV** with 4-bromo acetophenone **4d** (100 mg, 0.5 mmol), the product **5d** (101 mg) was obtained as white solid in quantitative yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.2 Hz, 4H), 7.33 (d, *J* = 8.2 Hz, 4H), 7.26 (d, *J* = 8.2 Hz, 4H), 7.06 (d, *J* = 8.2 Hz, 4H), 1.54 (s, 8H), 1.49 (s, 6H), 1.40 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 144.22, 144.19, 130.34, 130.12, 129.62, 129.60, 120.82, 120.74, 60.36, 60.07, 26.97, 26.74.

HRMS-ESI $[M-NH_2]^+$ Calcd for $C_{16}H_{16}Br_2N$ 379.9644, found 379.9655.



2,3-bis(4-(trifluoromethyl)phenyl)butane-2,3-diamine, **5e**

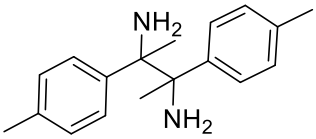
Following the typical procedure **IV** with 4-trifluoro acetophenone **4e** (90 mg, 0.5 mmol), the product **5e** (65 mg) was obtained as white crystal in 69% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 (s, 8H), 7.47 (d, *J* = 8.1 Hz, 4H), 7.35 (d, *J* = 8.1 Hz, 4H), 1.59 (s, 8H), 1.55 (s, 6H), 1.46 (s, 6H).

^{19}F NMR (564 MHz, $CDCl_3$) δ -62.47, -62.50.

^{13}C NMR (151 MHz, $CDCl_3$) δ 149.17, 149.10, 128.97 (q, *J* = 32.5 Hz), 128.89 (q, *J* = 32.4 Hz), 128.16, 128.12, 124.23 (q, *J* = 3.7 Hz), 124.01 (q, *J* = 3.6 Hz), 124.15 (q, *J* = 271.9 Hz), 60.65, 60.35, 27.08, 26.91.

HRMS-ESI $[M-NH_2]^+$ Calcd for $C_{18}H_{16}F_6N$ 360.1181, found 360.1198.



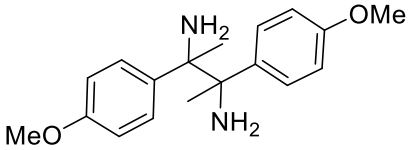
2,3-di-p-tolylbutane-2,3-diamine, **5f**

Following the typical procedure **IV** with 4-methyl acetophenone **4f** (68 mg, 0.5 mmol), the product **5f** (50 mg) was obtained as white solid in 75% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.0 Hz, 4H), 7.11 (dd, *J* = 9.8, 7.9 Hz, 8H), 7.03 (d, *J* = 8.0 Hz, 4H), 2.33 (s, 6H), 2.32 (s, 6H), 1.56 (s, 8H), 1.50 (s, 6H), 1.42 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 142.50, 142.44, 135.87, 135.78, 127.94, 127.71, 127.68, 60.34, 60.00, 27.24, 26.92, 20.86.

HRMS-ESI $[M-NH_2]^+$ Calcd for $C_{18}H_{22}N$ 252.1747, found 252.1760.



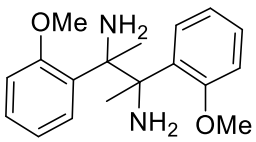
2,3-bis(4-(methoxy)phenyl)butane-2,3-diamine, **5g**

Following the typical procedure **IV** with 4-methoxy acetophenone **4g** (76 mg, 0.5 mmol), the product **5g** (40 mg) was obtained as light yellow crystal in 53% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.3 Hz, 4H), 7.11 (d, *J* = 8.2 Hz, 4H), 6.82 (d, *J* = 8.4 Hz, 4H), 6.74 (d, *J* = 8.3 Hz, 4H), 3.80 (s, 6H), 3.78 (s, 6H), 1.58 (s, 8H), 1.49 (s, 6H), 1.41 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.06, 157.99, 137.60, 137.56, 128.86, 128.85, 112.51, 112.25, 60.24, 59.94, 55.19, 55.17, 27.22, 26.88.

HRMS-ESI $[M-NH_2]^+$ Calcd for $C_{18}H_{22}O_2N$ 284.1645, found 284.1659.



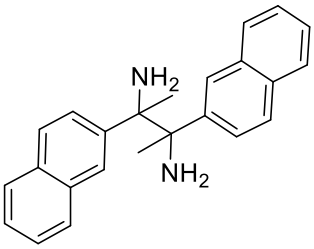
2,3-bis(2-(methoxy)phenyl)butane-2,3-diamine, **5h**

Following the typical procedure **IV** with 2-methoxy acetophenone **4h** (75 mg, 0.5 mmol), the product **5h** (59 mg) was obtained as colorless oil in 79% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.19 – 7.09 (m, 8H), 6.88 – 6.77 (m, 6H), 6.73 (d, *J* = 8.1 Hz, 2H), 3.62 (s, 6H), 3.51 (s, 6H), 2.30 (s, 8H), 1.52 (s, 6H), 1.47 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.54, 158.41, 133.30, 133.19, 130.75, 130.49, 127.77, 127.69, 119.82, 119.59, 111.69, 111.38, 64.42, 64.34, 55.09, 54.91, 27.67, 27.18.

HRMS-ESI $[M-NH_2]^+$ Calcd for $C_{18}H_{22}O_2N$ 284.1645, found 284.1660.



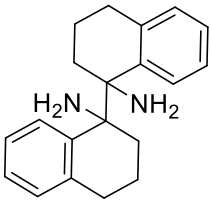
2,3-di(naphthalen-2-yl)butane-2,3-diamine, **5i**

Following the typical procedure **IV** with 2-Acetonaphthone **4i** (85 mg, 0.5 mmol), the product **5i** (81 mg) was obtained as white crystal in 95% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 2H), 7.89 – 7.71 (m, 12H), 7.66 (d, *J* = 8.7 Hz, 2H), 7.60 (dd, *J* = 8.7, 2.0 Hz, 2H), 7.53 – 7.43 (m, 8H), 7.37 – 7.30 (m, 2H), 1.87 (s, 8H), 1.70 (s, 6H), 1.62 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.98, 142.91, 132.71, 132.57, 132.09, 132.05, 128.32, 128.28, 127.31, 127.27, 126.75, 126.69, 126.59, 126.42, 126.42, 126.33, 125.94, 125.87, 125.84, 125.80, 61.02, 60.73, 27.56, 27.23.

HRMS-ESI $[M-NH_2]^+$ Calcd for $C_{14}H_{22}N$ 324.1747, found 324.1760.



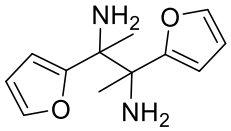
3,3',4,4'-tetrahydro-[1,1'-binaphthalene]-1,1'(2H,2'H)-diamine, **5j**

Following the typical procedure **IV** with alpha-Tetralone **4j** (74 mg, 0.5 mmol), after a fast flash column with hexane : iPe_2NH_2 = 10:1 as eluent, the product **5j** (54 mg) was obtained as white crystal in 74% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.36 (d, *J* = 8.1Hz, 1H), 7.19 (d, *J* = 7.4Hz, 2H), 7.12 (td, *J* = 7.4, 1.4 Hz, 2H), 7.04 (d, *J* = 7.6 Hz, 2H), 2.71 – 2.65 (m, 2H), 2.61 – 2.54 (m, 2H), 2.09 (s, 4H), 1.72 – 1.65 (m, 2H), 1.52 (qt, *J* = 12.9, 3.6 Hz, 2H), 1.34 (td, *J* = 13.8, 3.5 Hz, 2H), 1.31 – 1.22 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 144.62, 137.37, 129.09, 128.60, 125.96, 125.86, 59.70, 38.14, 31.65, 20.51.

HRMS-ESI $[M-NH_2]^+$ Calcd for $C_{20}H_{22}N$ 276.1747, found 276.1737.



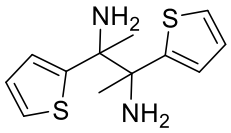
2,3-di(furan-2-yl)butane-2,3-diamine, **5k**

Following the typical procedure **IV** with 1-(furan-2-yl)ethan-1-one **4k** (56 mg, 0.5 mmol), the product **5k** (50 mg) was obtained as colorless oil in 91% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (s, 2H), 7.24 (s, 2H), 6.29 (s, 2H), 6.24 (s, 2H), 6.12 (d, *J* = 3.1 Hz, 2H), 5.99 (d, *J* = 3.1 Hz, 2H), 1.82 (s, 8H), 1.45 (s, 6H), 1.38 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.80, 159.23, 141.08, 140.87, 110.04, 109.92, 106.36, 105.69, 59.20, 58.92, 24.36, 23.47.

HRMS-ESI $[M-NH_2]^+$ Calcd for $C_{12}H_{14}N$ 204.1019, found 204.1029.



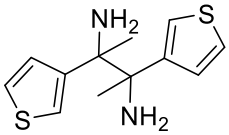
2,3-di(thiophen-2-yl)butane-2,3-diamine, **5l**

Following the typical procedure **IV** with 1-(thiophen-2-yl)ethan-1-one **4l** (63 mg, 0.5 mmol), the product **5l** (48 mg) was obtained as white crystal in 76% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (dd, *J* = 5.1, 1.3 Hz, 2H), 7.16 (dd, *J* = 5.1, 1.2 Hz, 2H), 6.97 (dd, *J* = 5.1, 3.6 Hz, 2H), 6.95 – 6.91 (m, 4H), 6.79 (dd, *J* = 3.6, 1.2 Hz, 2H), 1.96 (s, 8H), 1.64 (s, 6H), 1.58 (s, 6H).

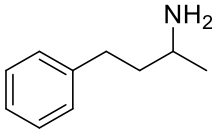
^{13}C NMR (101 MHz, $CDCl_3$) δ 151.58, 151.01, 126.34, 126.32, 125.35, 125.03, 124.27, 124.10, 60.64, 60.52, 27.99, 27.94.

HRMS-ESI $[M-NH_2]^+$ Calcd for $C_{12}H_{14}S_2N$ 236.0562, found 236.0562.

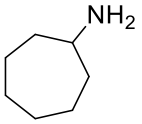


2,3-di(thiophen-3-yl)butane-2,3-diamine, **5m**
Following the typical procedure **IV** with 1-(thiophen-3-yl)ethan-1-one **4m** (63 mg, 0.5 mmol), the product **5m** (46 mg) was obtained as white crystal in 73% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (dd, *J* = 5.0, 3.0 Hz, 2H), 7.16 – 7.11 (m, 4H), 7.03 (dd, *J* = 5.0, 1.4 Hz, 2H), 6.92 (dd, *J* = 3.1, 1.4 Hz, 2H), 6.76 (dd, *J* = 5.1, 1.4 Hz, 2H), 1.90 (s, 8H), 1.52 (s, 6H), 1.45 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 147.75, 147.29, 128.12, 128.02, 124.15, 123.81, 121.88, 121.67, 59.93, 59.74, 27.05, 26.44.
HRMS-ESI $[M-NH_2]^+$ Calcd for $C_{12}H_{14}S_2N$ 236.0562, found 236.0575.

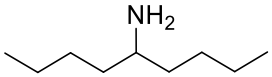
diethyl 2,3-diamino-2,3-dimethylsuccinate, **5n**
Following the typical procedure **IV** with ethyl pyruvate **4n** (59 mg, 0.5 mmol), the product **5n** (24 mg) was obtained as colorless oil in 41% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.28 – 4.11 (m, 4H), 1.96 (s, 4H), 1.42 (d, *J* = 12.1 Hz, 6H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.30 (t, *J* = 7.1 Hz, 3H),
^{13}C NMR (101 MHz, $CDCl_3$) δ 176.15, 175.71, 62.92, 62.81, 61.31, 22.06, 22.04, 14.12, 14.10.
HRMS-ESI $[M+Na]^+$ Calcd for $C_{10}H_{20}N_2NaO_4$ 255.1315 found 255.1327.



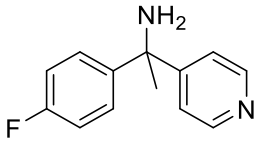
4-phenylbutan-2-amine, **7a**
Following the typical procedure **V** with benzyl acetone **6a** (70 mg, 0.5 mmol), the product **7a** (60 mg) was obtained in 80% yield.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 2H), 7.21 – 7.14 (m, 3H), 2.91 (h, *J* = 6.3 Hz, 1H), 2.73 – 2.58 (m, 2H), 1.72 – 1.56 (m, 2H), 1.44 (s, 2H), 1.10 (d, *J* = 6.3 Hz, 3H).
This data is in accordance with that published in literature.[1]



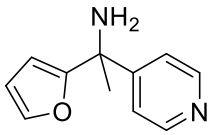
Cycloheptanamine, **7b**
Following the typical procedure **V** with cycloheptanone **6b** (62 mg, 0.5 mmol), the product **7b** (55 mg) was obtained in 96% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.03 – 2.91 (m, 1H), 1.93 – 1.77 (m, 2H), 1.74 – 1.31 (m, 12H).
This data is in accordance with that published in literature.[2]



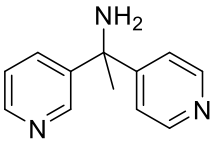
nonan-5-amine, **7c**
Following the typical procedure **V** with 5-nonanone **6c** (71 mg, 0.5 mmol), the product **7c** (51 mg) was obtained in 71% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.68 – 2.56 (m, 1H), 1.43 – 1.08 (m, 14H), 0.85 (t, *J* = 6.5 Hz, 6H).
This data is in accordance with that published in literature.[3]



1-(4-fluorophenyl)-1-(pyridin-4-yl)ethan-1-amine, **8a**
Following the typical procedure **VI** with 4-fluoro acetophenone **4a** (70 mg, 0.5 mmol), the product **8a** (106 mg) was obtained as light yellow oil in 99% yield.
^{1}H NMR (700 MHz, $CDCl_3$) δ 8.51 (d, *J* = 4.9 Hz, 2H), 7.34 – 7.30 (m, 2H), 7.28 (d, *J* = 4.7 Hz, 2H), 7.03 – 6.94 (m, 2H), 1.86 (s, 2H), 1.81 (s, 3H).
^{19}F NMR (659 MHz, $CDCl_3$) δ -115.94 (m).
^{13}C NMR (176 MHz, $CDCl_3$) δ 161.59 (d, *J* = 246.2 Hz), 158.34, 149.84, 143.92 (d, *J* = 3.3 Hz), 127.79 (d, *J* = 7.8 Hz), 121.15, 115.09 (d, *J* = 21.1 Hz), 57.66, 31.38.
HRMS-ESI $[M-NH_2]^+$ Calcd for $C_{13}H_{11}FN$ 200.0870, found 200.0870.

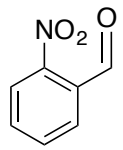
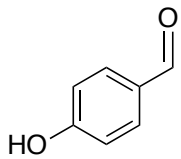
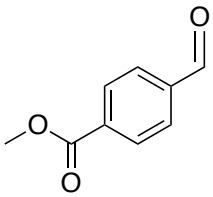
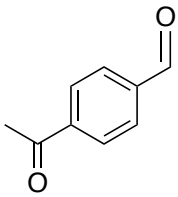


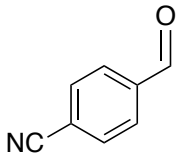
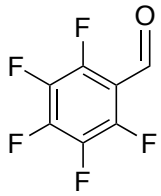
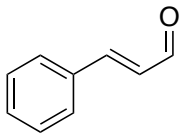
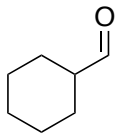
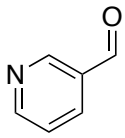
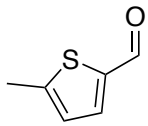
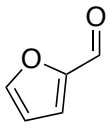
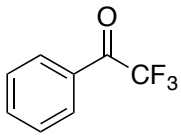
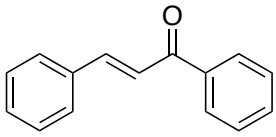
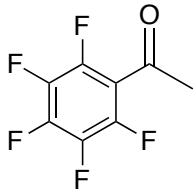
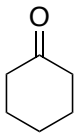
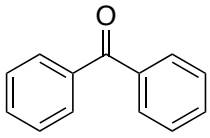
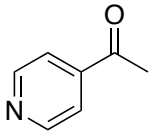
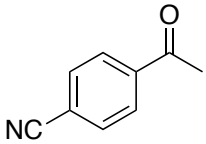
1-(furan-2-yl)-1-(pyridin-4-yl)ethan-1-amine, **8b**
Following the typical procedure **VI** with 1-(furan-2-yl)ethan-1-one **4l** (56 mg, 0.5 mmol), the product **8b** (75 mg) was obtained as colorless oil in 80% yield.
^{1}H NMR (700 MHz, $CDCl_3$) δ 8.55 – 8.53 (m, 2H), 7.35 (s, 1H), 7.33 – 7.30 (m, 2H), 6.36 – 6.32 (m, 1H), 6.24 (s, 1H), 1.98 (s, 2H), 1.74 (s, 3H).
^{13}C NMR (176 MHz, $CDCl_3$) δ 159.95, 155.69, 149.81, 142.02, 120.81, 110.08, 105.24, 55.21, 29.55.
HRMS-ESI $[M-NH_2]^+$ Calcd for $C_{11}H_{10}NO$ 172.0757, found 172.0754.



1-(pyridin-3-yl)-1-(pyridin-4-yl)ethan-1-amine, **8c**
Following the typical procedure **VI** with 3-Acetylpyridine **4o** (61 mg, 0.5 mmol), the product **8c** (72 mg) was obtained as light yellow oil in 72% yield.
^{1}H NMR (700 MHz, Chloroform-*d*) δ 8.65 (s, 1H), 8.54 (d, *J* = 4.4 Hz, 2H), 8.49 (d, *J* = 4.7 Hz, 1H), 7.70 – 7.65 (m, 1H), 7.29 (d, *J* = 4.9, Hz, 2H), 7.26 – 7.21 (m, 1H), 1.94 (s, 2H), 1.87 (s, 3H).
^{13}C NMR (176 MHz, $CDCl_3$) δ 157.31, 150.03, 148.30, 147.87, 143.31, 133.80, 123.18, 121.08, 56.95, 31.01.
HRMS-ESI $[M-NH_2]^+$ Calcd for $C_{12}H_{11}N_2$ 183.0917, found 183.0921.

X. Substrates examined for the dimerization studies which did not give the desired vicinyl diamine, were highly unselective, or gave the desired product but as an inseparable mixture with an undetermined co-eluting byproduct.

Entry	Substrate	Comment	Entry	Substrate	Comment
1		No conversion	2		Messy reaction
3		Messy reaction	4		Messy reaction

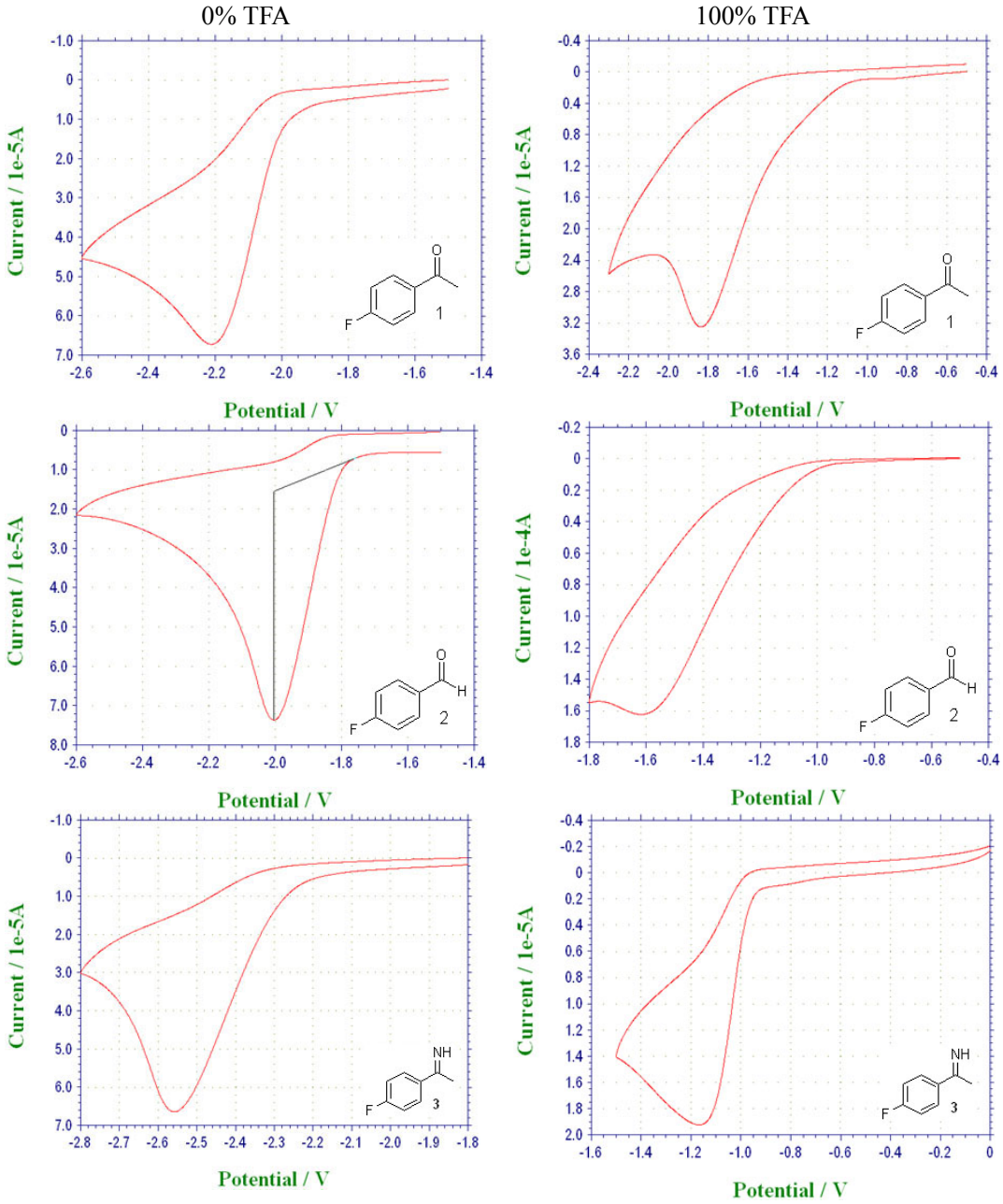
5		Messy reaction	6		Messy reaction
7		Messy reaction	8		Trimerize
9		Unable to purify product	10		Unable to purify product
11		Unable to purify product	12		Messy reaction
13		Messy reaction	14		Messy reaction
15		Messy reaction	16		No Conversion
17		Only reductive amination product	18		A mixture of dimerization and reductive amination product

XI. Cyclic voltammetry studies

Cyclic Voltammetry was performed using a CHI 600E electrochemical analyzer at a rate of 0.1 V/s in acetonitrile. Polished glassy carbon, platinum wire and Ag/AgCl were used as the working, counter and reference electrodes, respectively. Different carbonyl compounds (0.05 mmol) were solubilized in acetonitrile (5 mL) respectively containing tetra-*n*-butylammonium hexafluorophosphate (0.1 M) as electrolyte with or without the presence of TFA. The solution was degassed with Argon for 10 min before measurement.

Table S7: Cyclic voltammetry measured for 4-fluorobenzaldehyde, 4-fluoroacetophenone, 1-(4-fluorophenyl)ethan-1-imine in the absence and presence of trifluoroacetic acid.

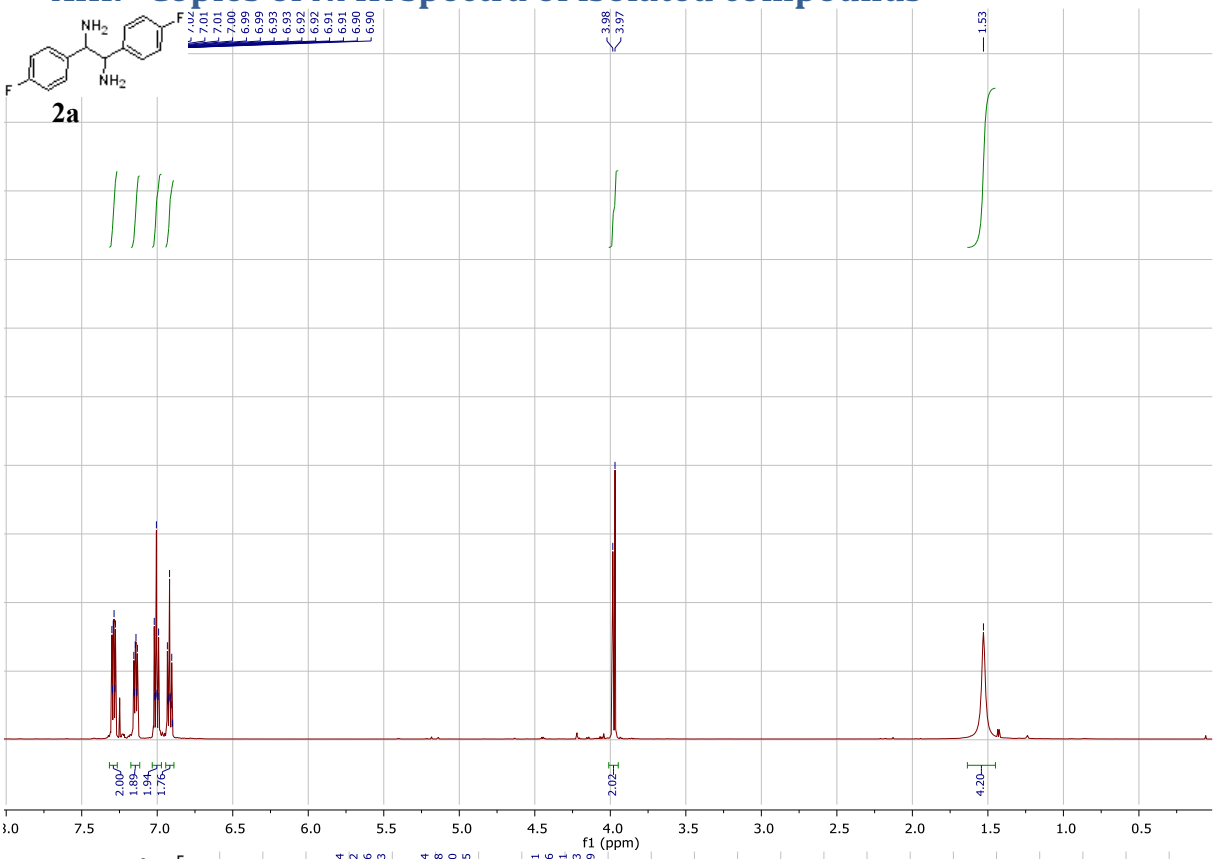
Entry	Substrate	TFA	$E_{1/2}$ (V)
1	1	0 equiv.	-2.088
2	2	0 equiv.	-1.898
3	3	0 equiv.	-2.384
4	1	1 equiv. (0.05 mmol)	-1.586
5	2	1 equiv. (0.05 mmol)	-1.352
6	3	1 equiv. (0.05 mmol)	-1.052

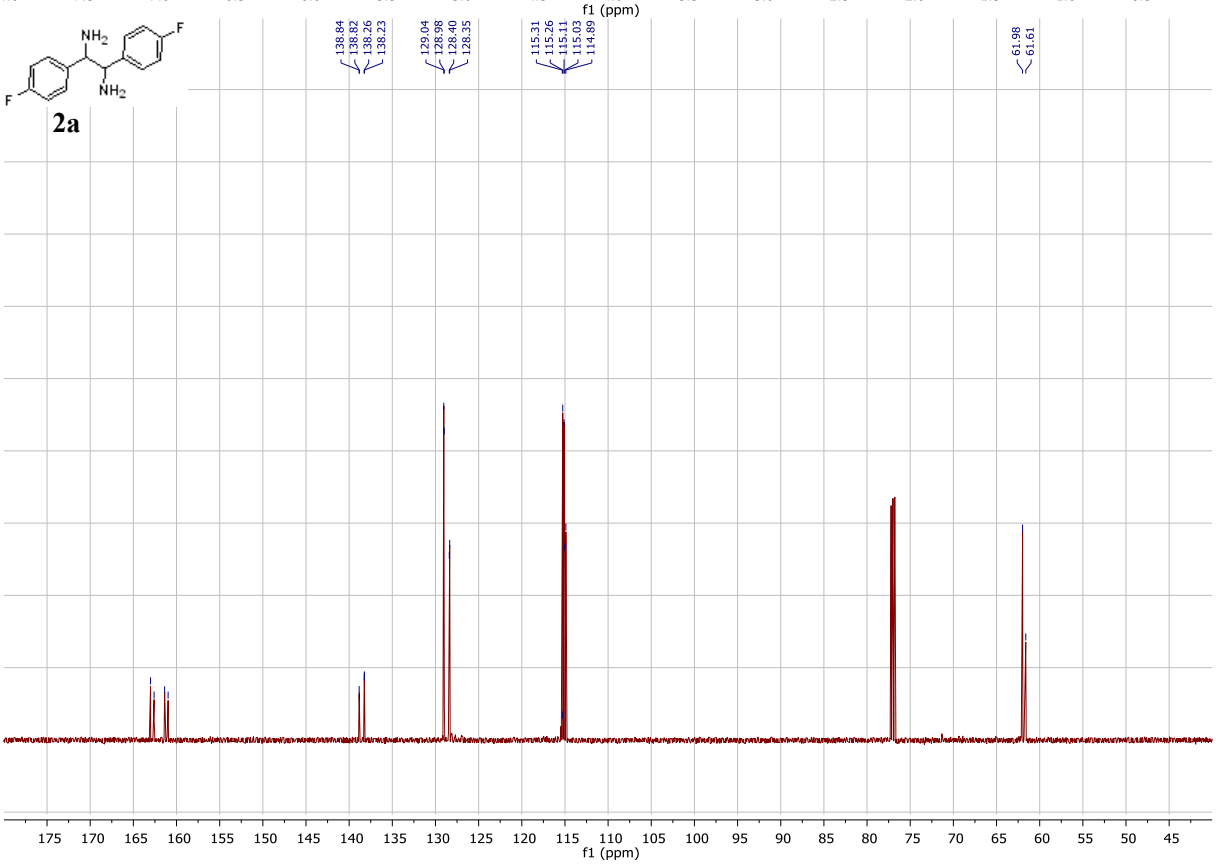


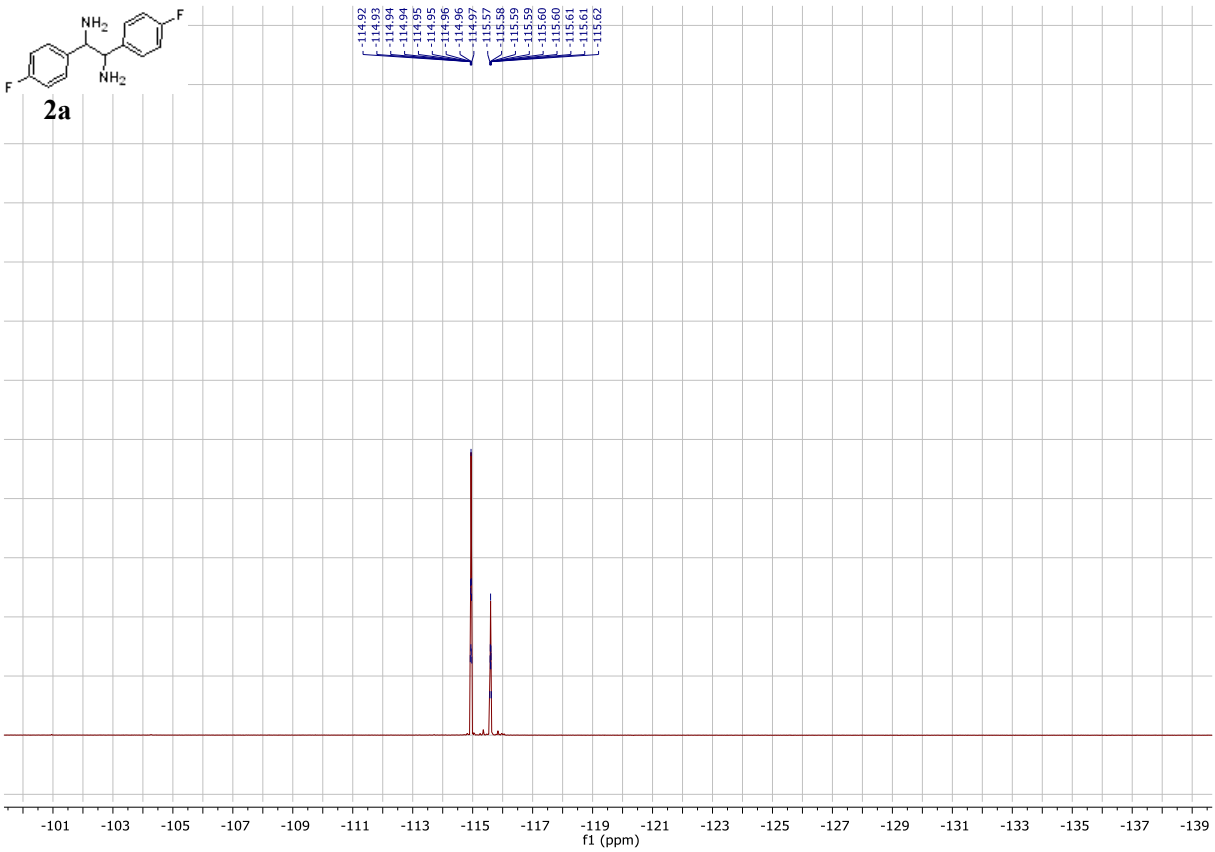
XII. References

1. Waser, J.; Gaspar, B.; Nambu, H.; Carreira, E. M. *J. Am. Chem. Soc.* **2006**, *128*, 11693.
2. ACD-A: Sigma-Aldrich (Spectral data were obtained from Advanced Chemistry Development, Inc.)
3. Boobalan, G.; Mohamed Imran, P.; Nagarajan, S. *J. Electron. Mater.* **2011**, *40*, 2392.

XIII. Copies of NMR spectra of isolated compounds



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NH2
F
F
2a
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-114.93
-114.94
-114.94
-114.94
-114.95
-114.95
-114.96
-114.96
-114.97
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-115.58
-115.59
-115.59
-115.60
-115.60
-115.61
-115.61
-115.62
-101
-103
-105
-107
-109
-111
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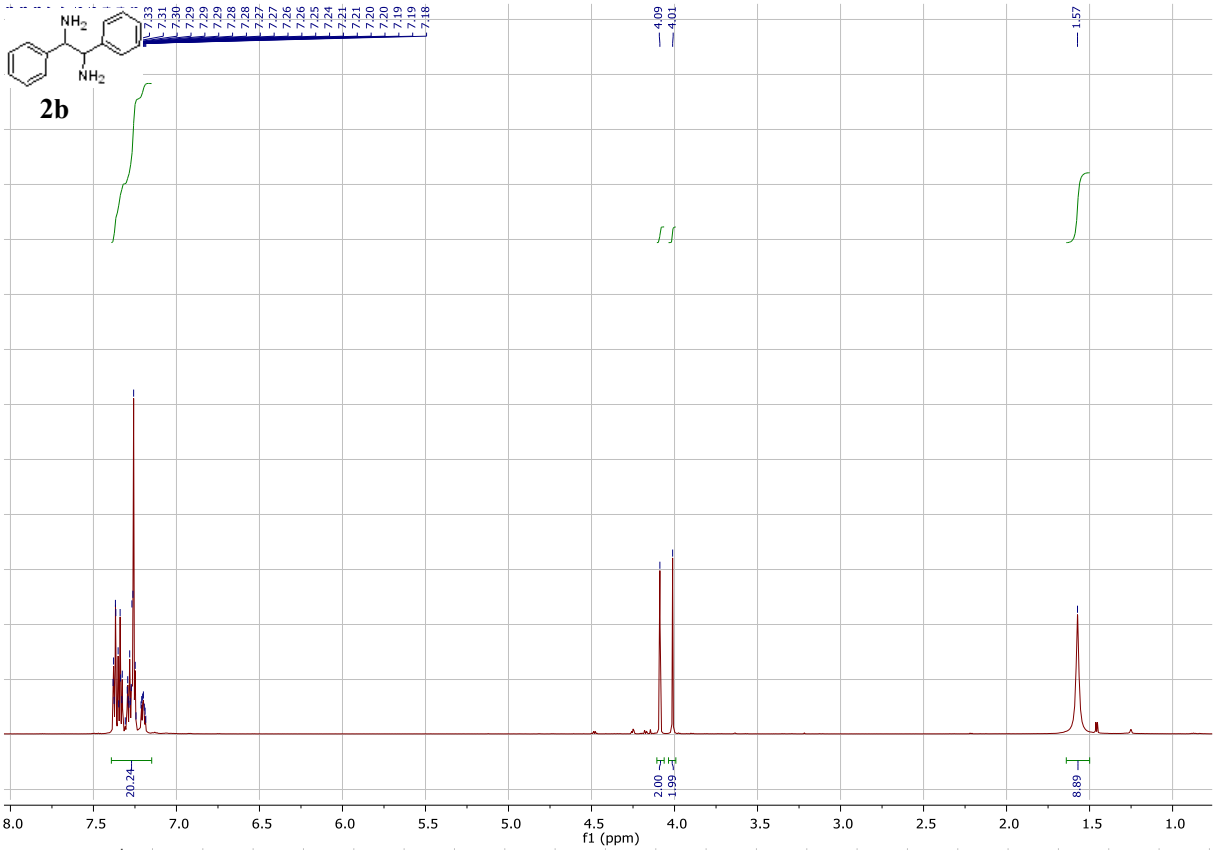
-131
-133
-135
-137
-139
f1 (ppm)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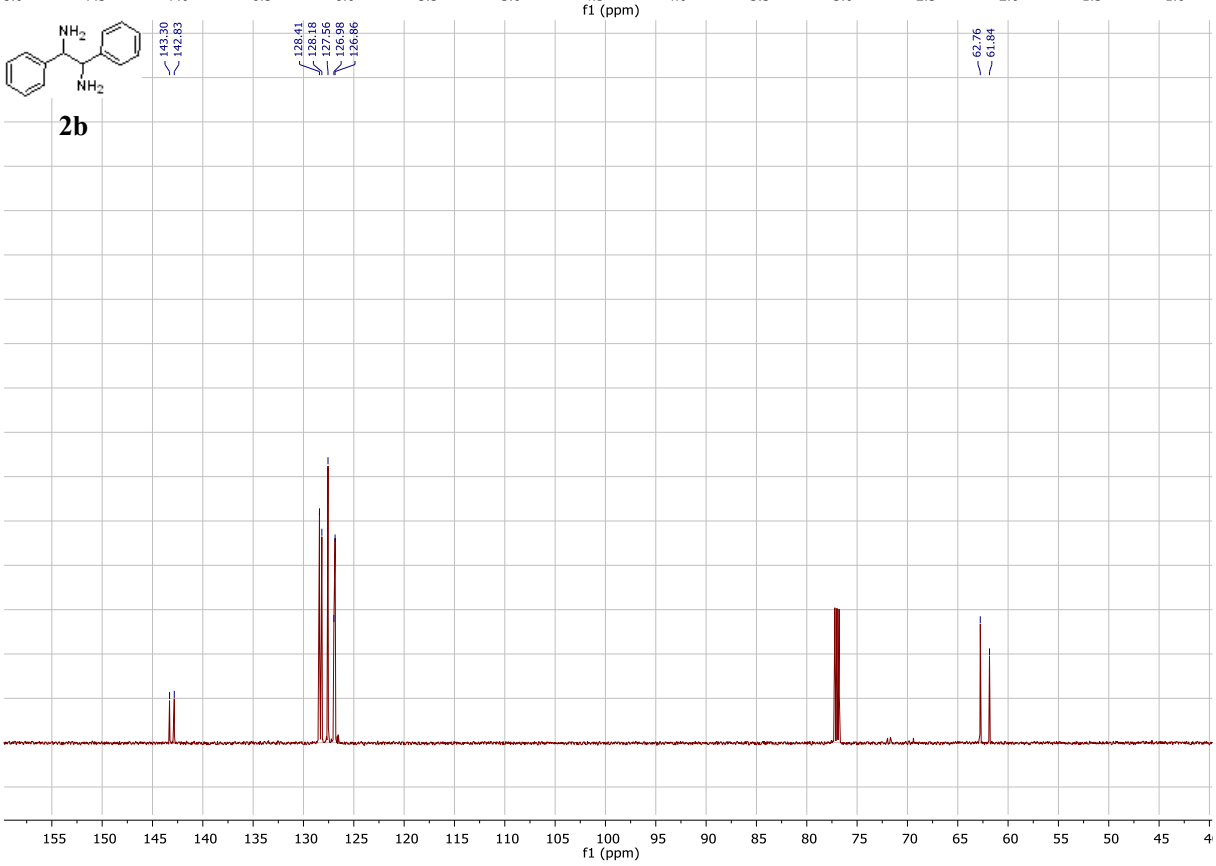
7.33
7.31
7.30
7.29
7.29
7.29
7.28
7.28
7.27
7.27
7.26
7.26
7.25
7.24
7.21
7.21
7.20
7.20
7.19
7.19
7.18
4.09
4.01
1.57
20.24
2.00
1.99
8.89
f1 (ppm)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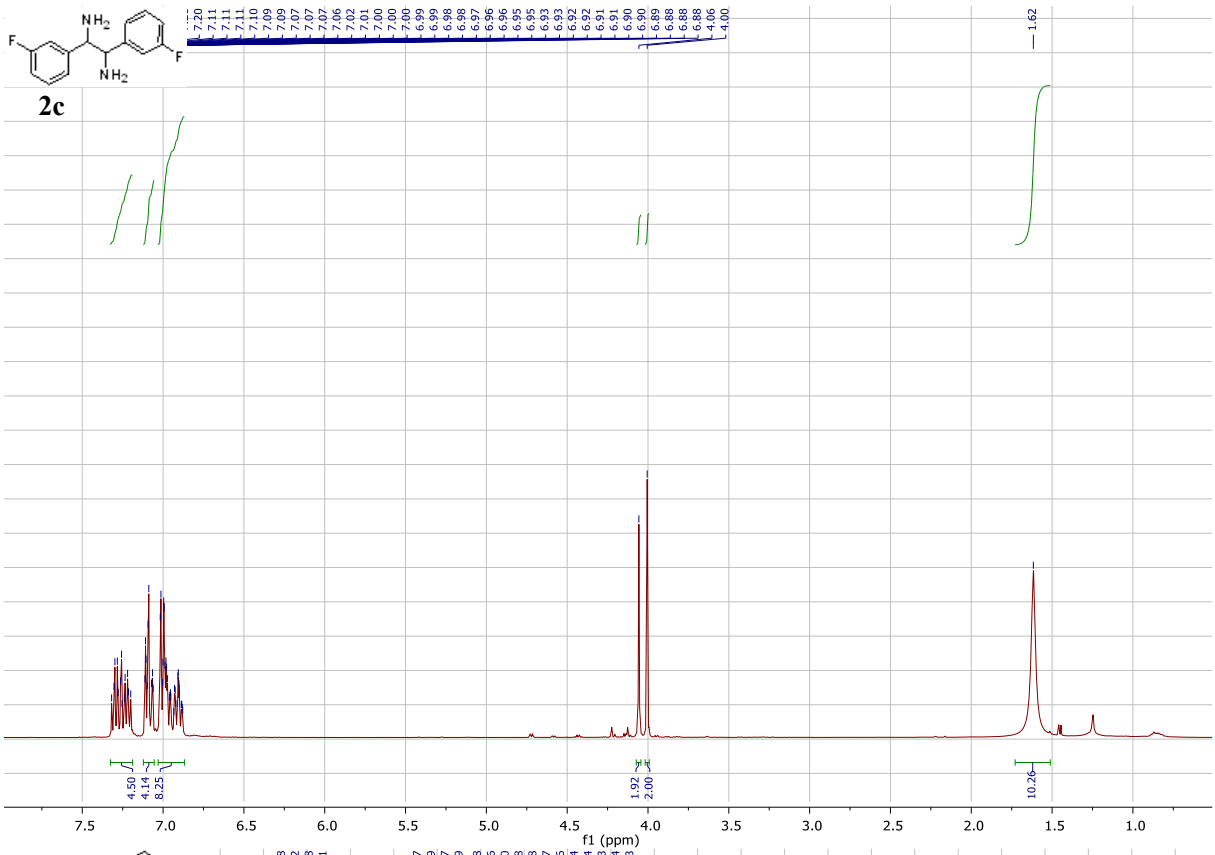
127.56
126.98
126.86
62.76
61.84
f1 (ppm)


2c
7.20
7.11
7.11
7.11
7.10
7.09
7.09
7.07
7.07
7.07
7.06
7.02
7.01
7.00
7.00
7.00
6.99
6.99
6.98
6.98
6.97
6.96
6.96
6.95
6.95
6.93
6.93
6.92
6.92
6.91
6.91
6.90
6.90
6.89
6.88
6.88
6.88
6.86
4.00
1.62
4.50
4.14
8.25
1.92
2.00
10.26
7.5
7.0
6.5
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4.5
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3.5
3.0
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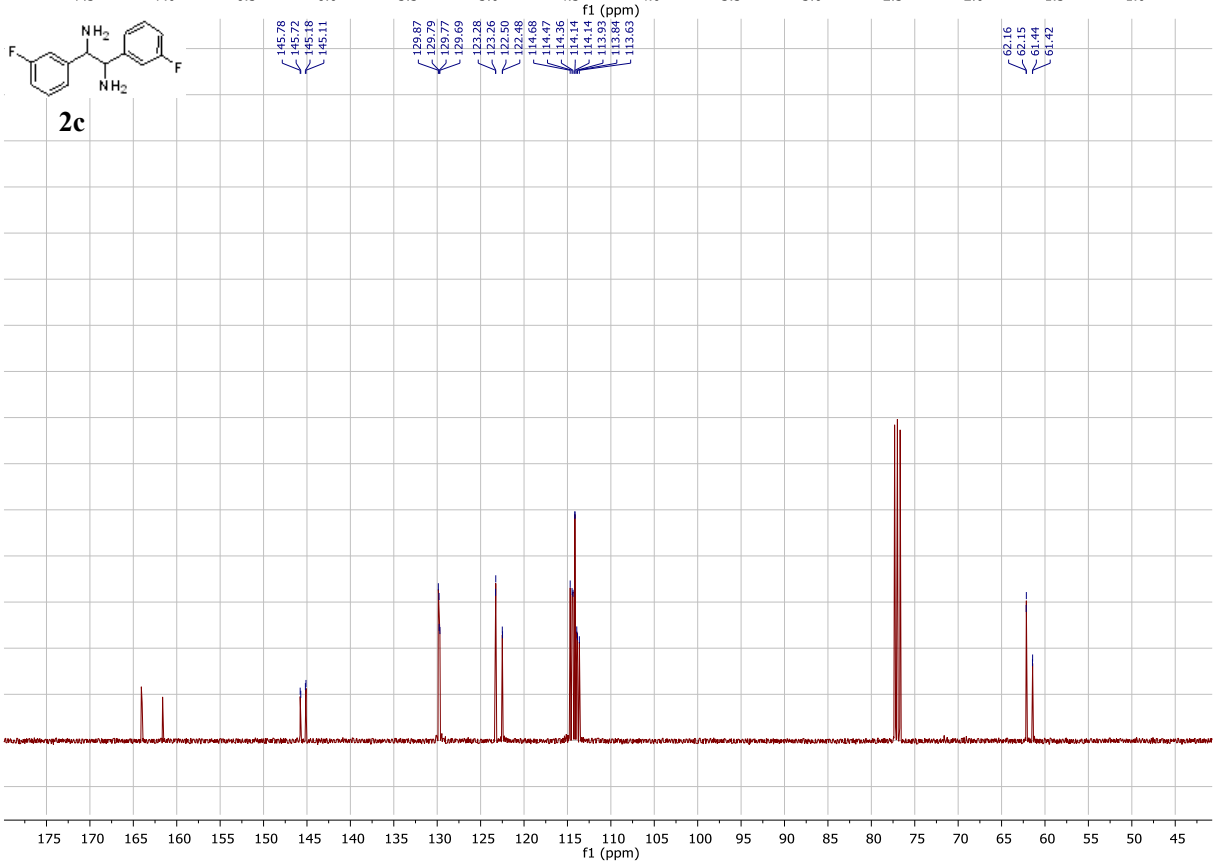
1.0
f1 (ppm)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145.18
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129.87
129.79
129.77
129.69
123.28
123.26
122.50
122.48
114.68
114.47
114.36
114.14
114.14
113.93
113.84
113.63
62.16
62.15
61.44
61.42
175
170
165
160
155
150
145
140
135
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110
105
100
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90
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70
65
60
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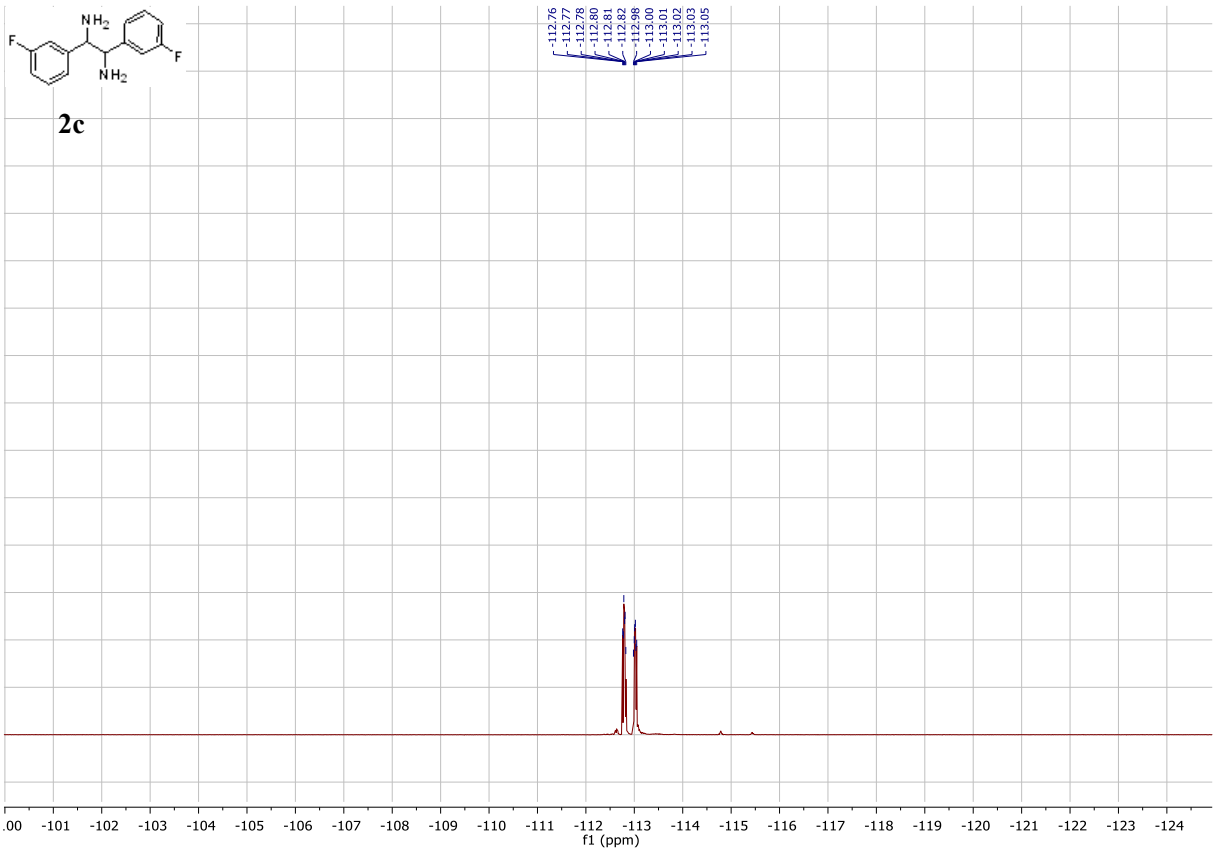
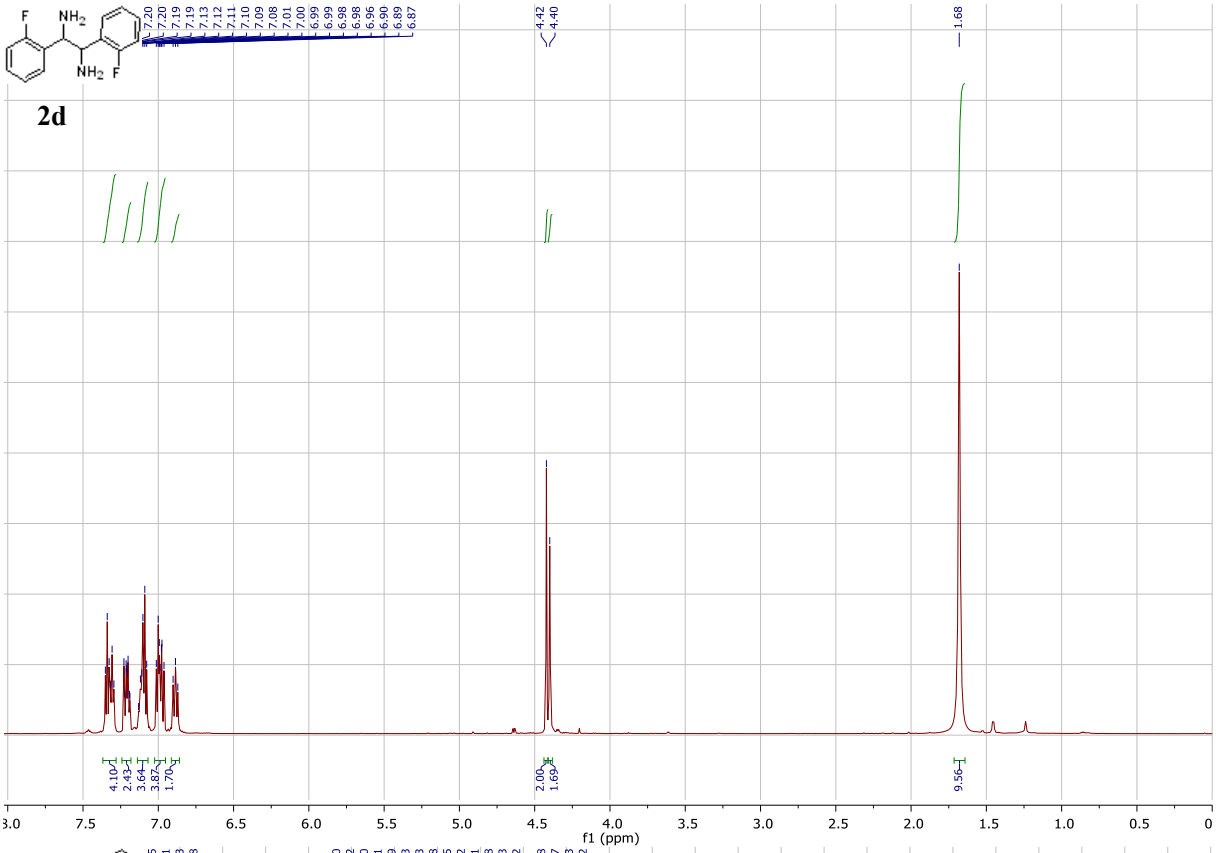
50
45
f1 (ppm)


NH2
NH2
F
F
2c
-112.76
-112.77
-112.78
-112.80
-112.81
-112.82
-112.98
-113.00
-113.01
-113.02
-113.03
-113.05
.00 -101 -102 -103 -104 -105 -106 -107 -108 -109 -110 -111 -112 -113 -114 -115 -116 -117 -118 -119 -120 -121 -122 -123 -124
f1 (ppm)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7.20
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7.11
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7.08
7.01
7.00
6.99
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6.98
6.98
6.96
6.90
6.89
6.87
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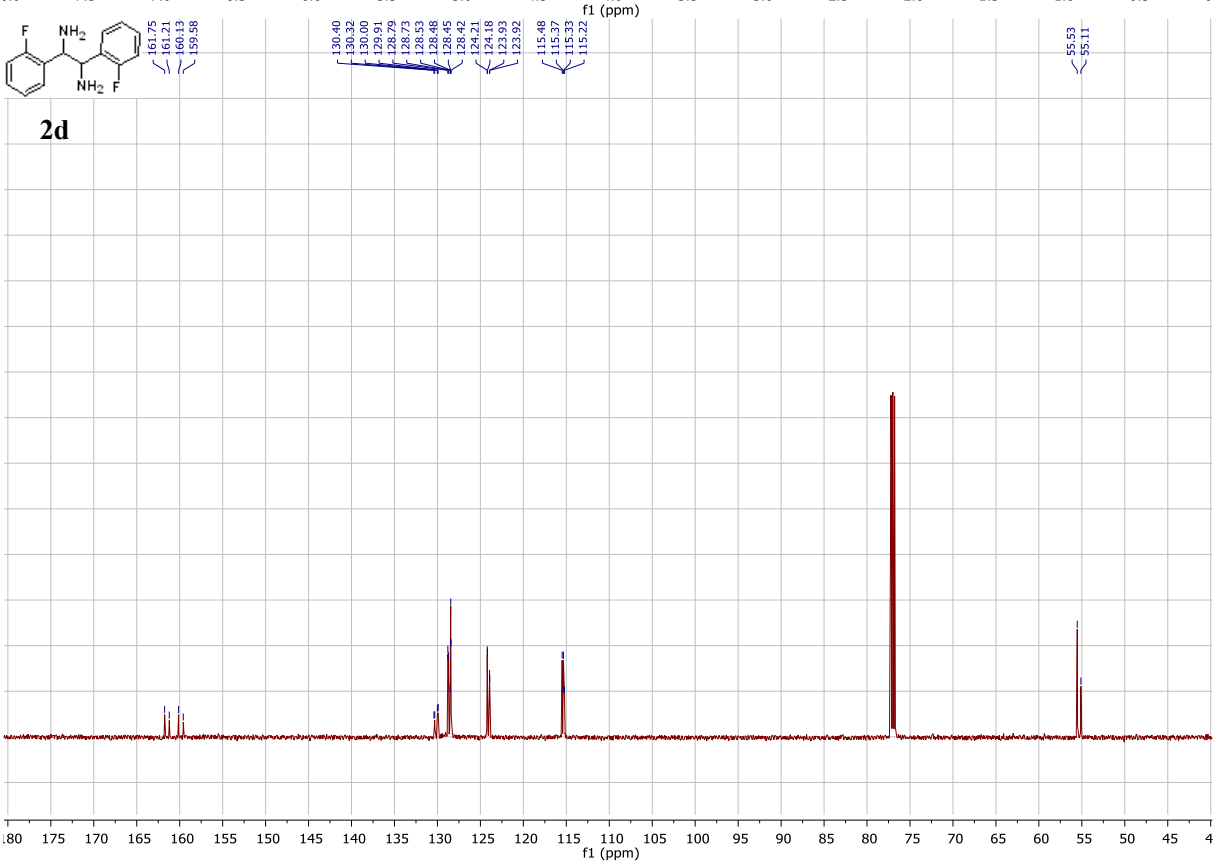
2.00
1.69
9.56
f1 (ppm)


2d
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130.32
130.00
129.91
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128.73
128.53
128.48
128.45
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123.93
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115.33
115.22
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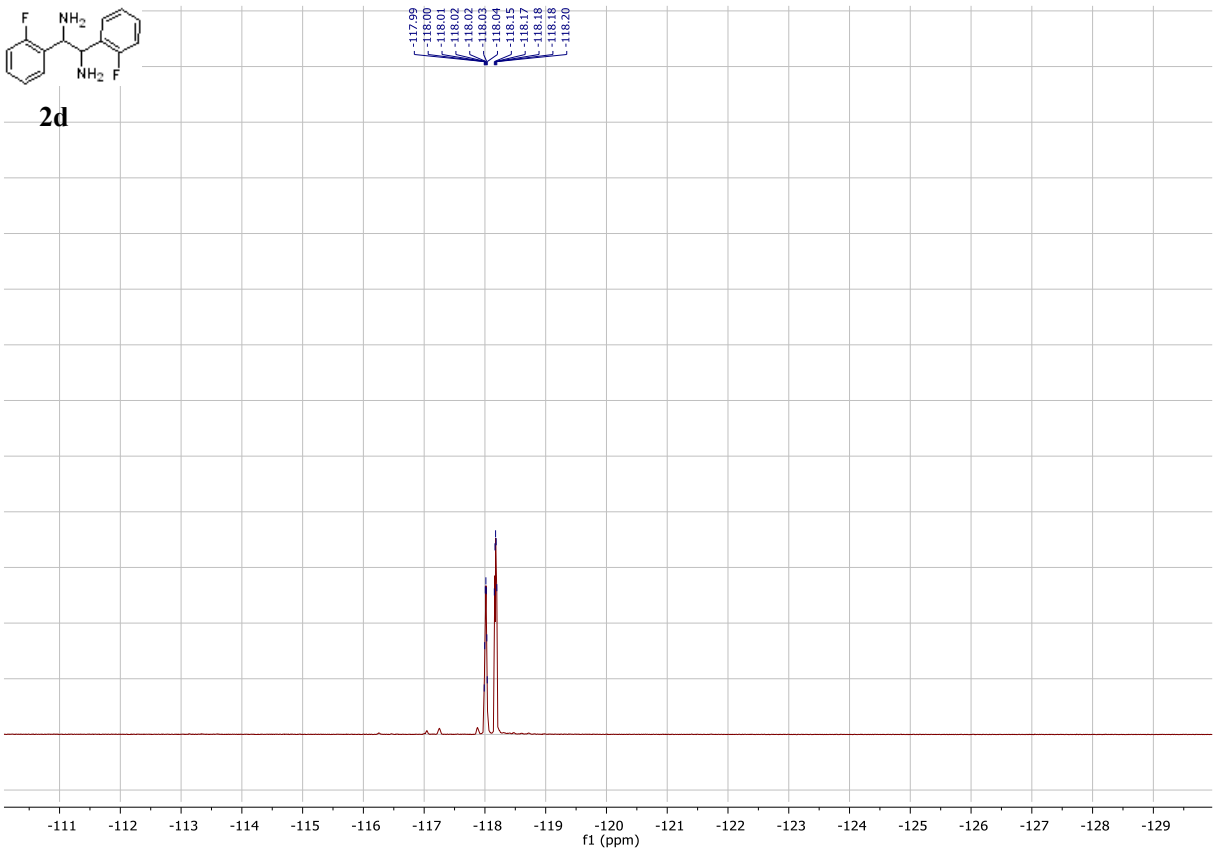
55.11
f1 (ppm)


F
NH2
NH2
F
2d
-117.99
-118.00
-118.01
-118.02
-118.02
-118.03
-118.04
-118.15
-118.17
-118.18
-118.18
-118.20
-111
-112
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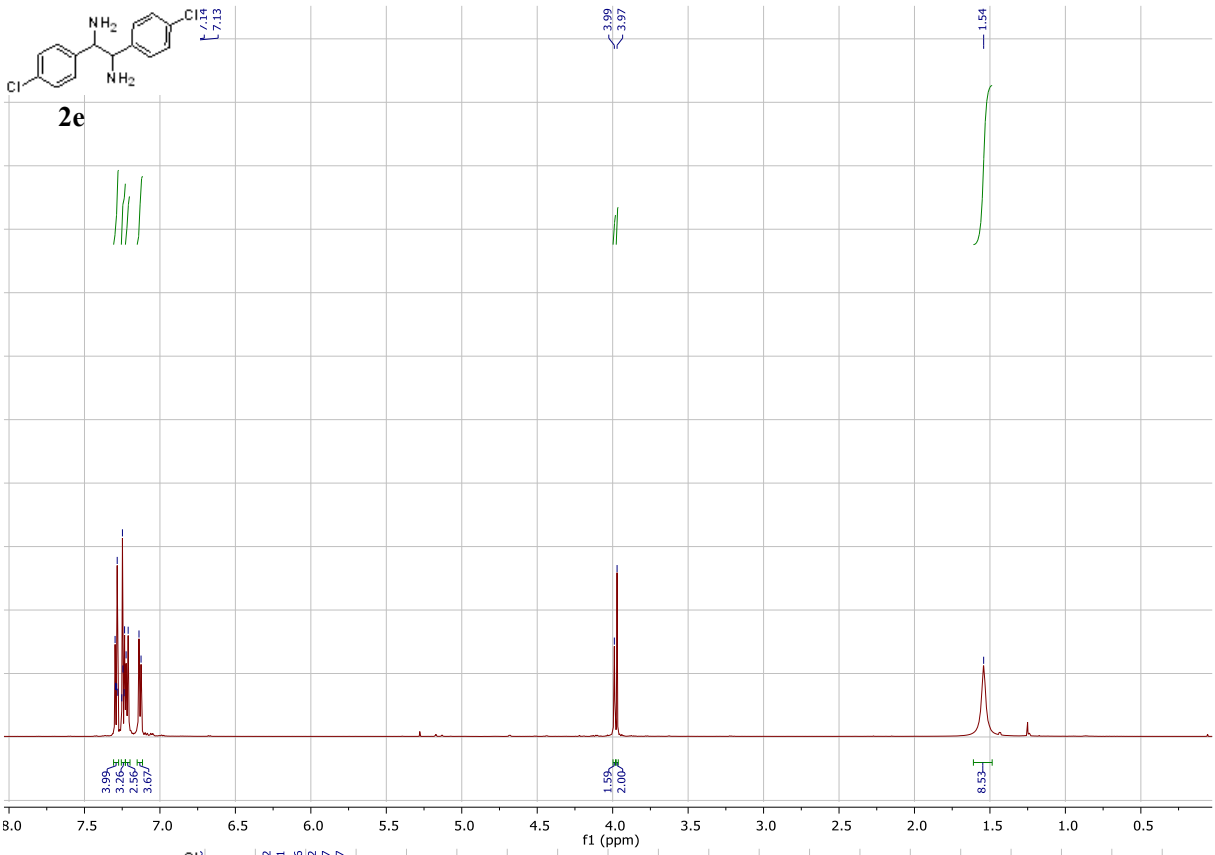
-129
f1 (ppm)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NH2
Cl
Cl
2e
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1.54
3.99
3.26
2.56
3.67
1.59
2.00
8.53
8.0
7.5
7.0
6.5
6.0
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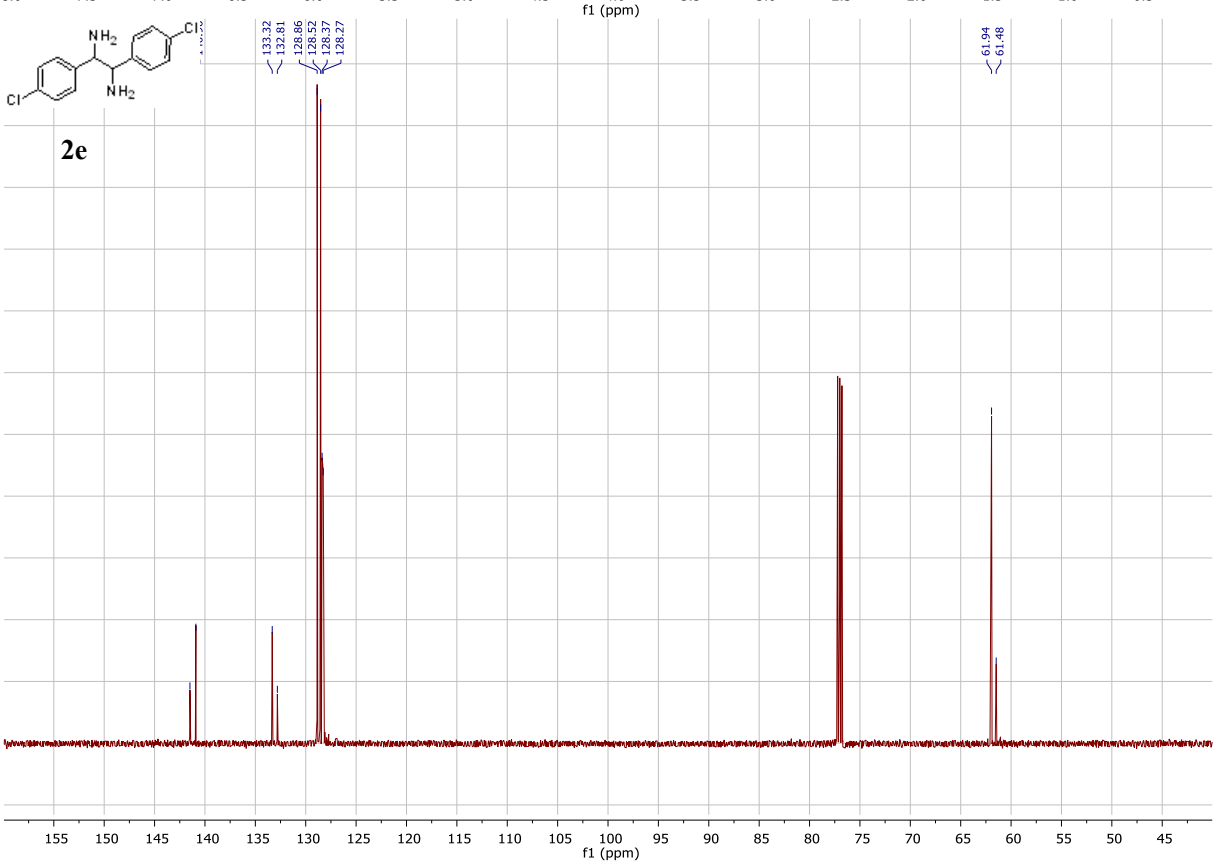
f1 (ppm)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NH2
Cl
Cl
2e
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128.52
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128.27
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61.48
155
150
145
140
135
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70
65
60
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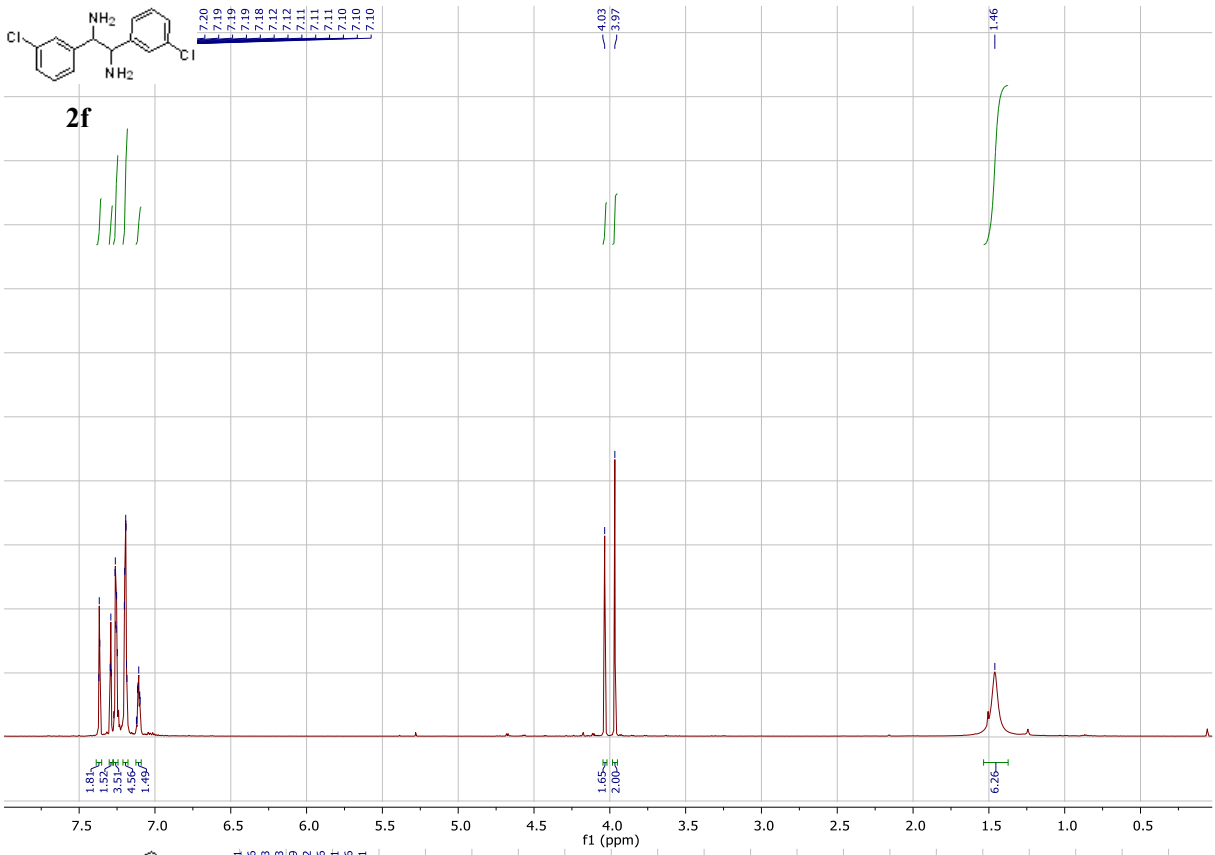
50
45
f1 (ppm)


NH2
Cl
Cl
NH2
2f
7.20
7.19
7.19
7.19
7.18
7.12
7.12
7.11
7.11
7.11
7.10
7.10
7.10
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6.5
6.0
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1.5
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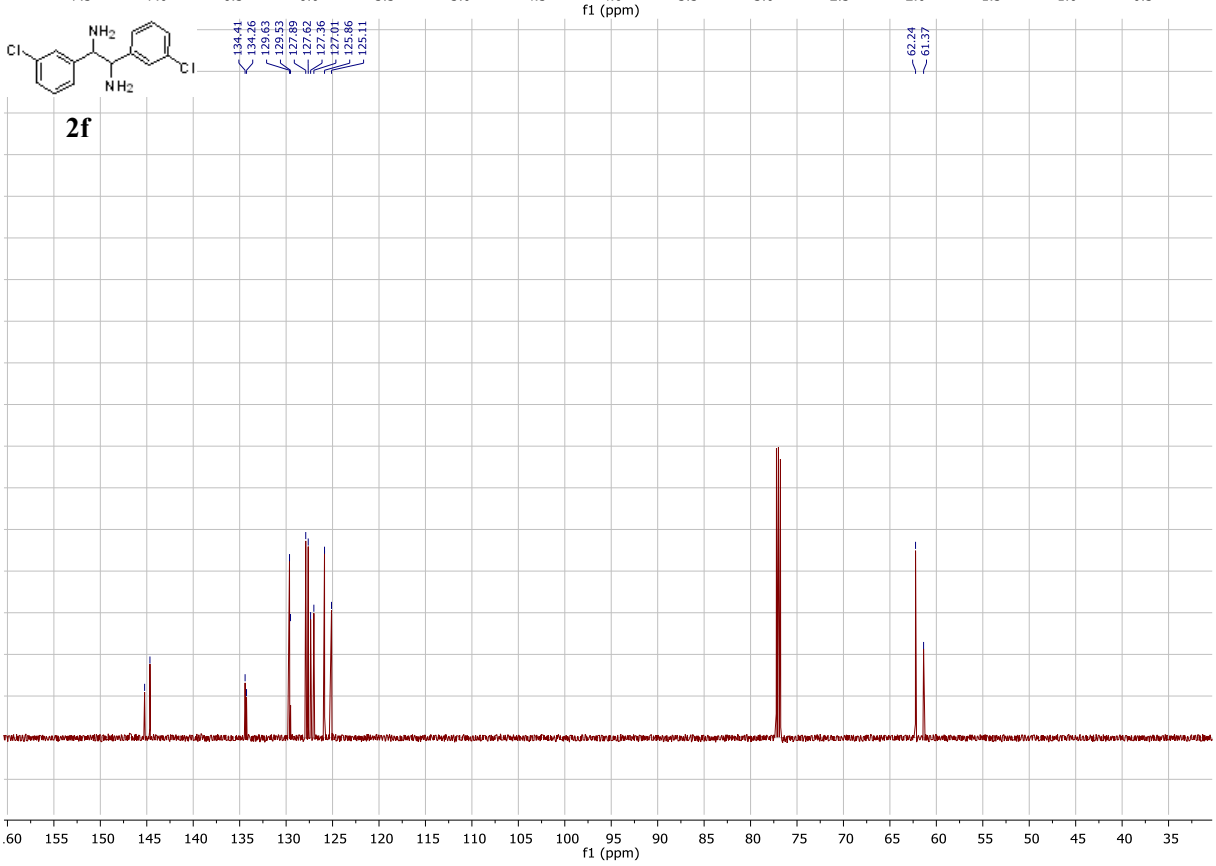
0.5
f1 (ppm)


NH2
Cl
Cl
NH2
2f
134.41
134.26
129.63
129.53
127.89
127.62
127.36
127.01
125.86
125.11
62.24
61.37
155
150
145
140
135
130
125
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115
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80
75
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60
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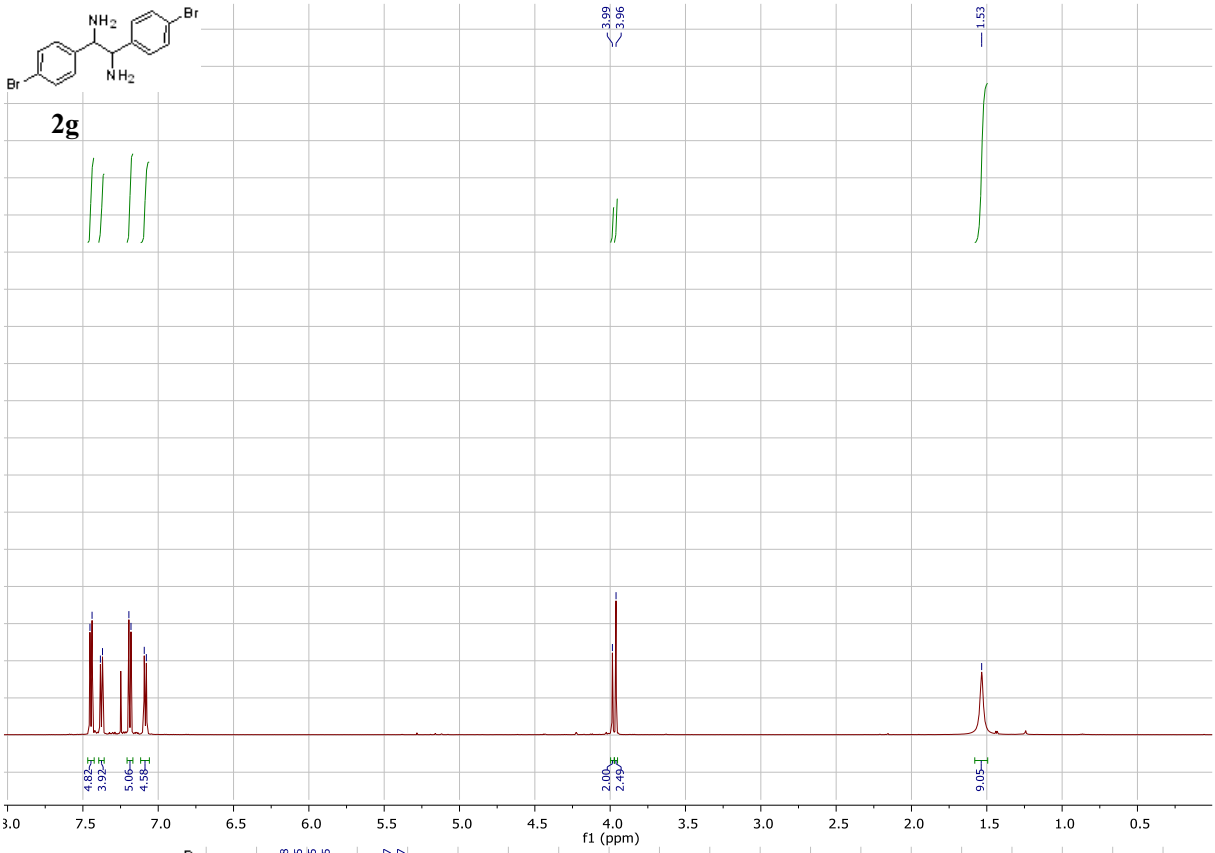
50
45
40
35
f1 (ppm)


NH2
Br
Br
NH2
2g
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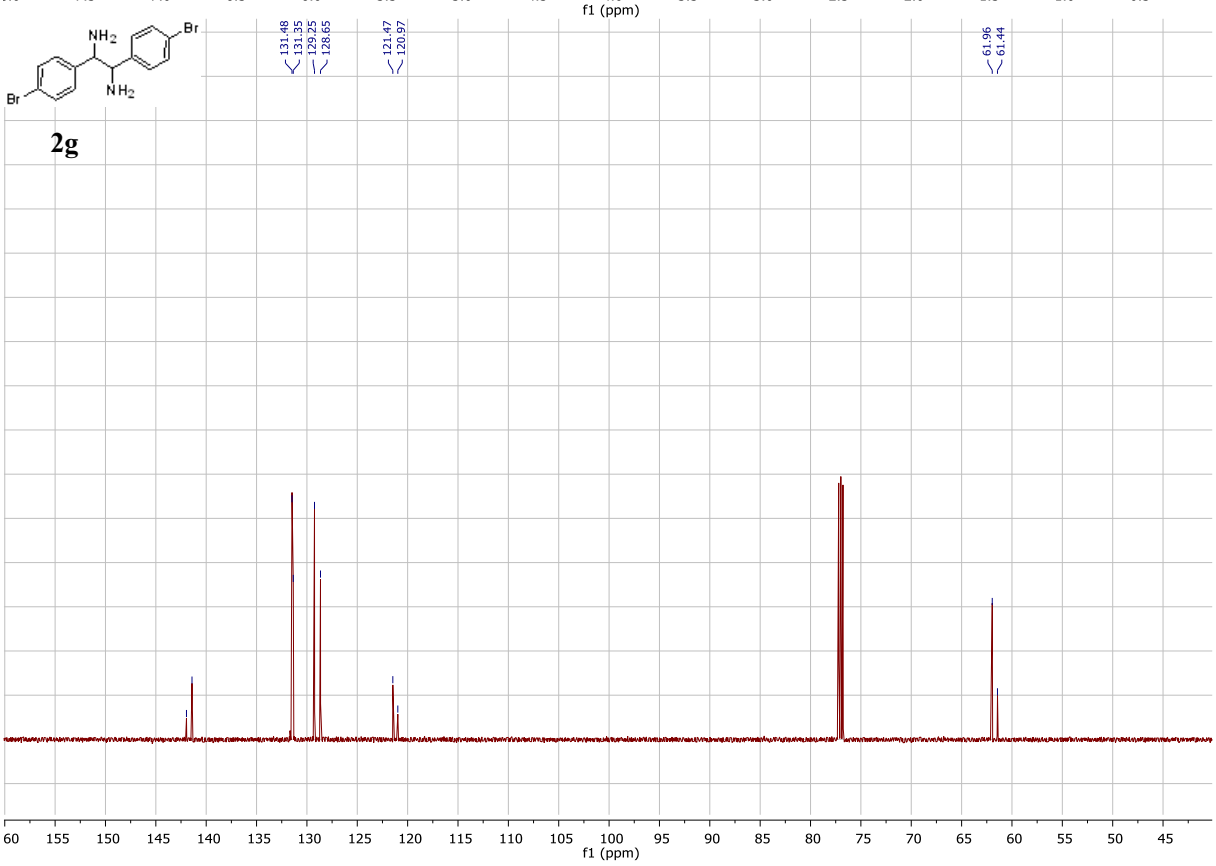
5.06
4.58
2.00
2.49
9.05
f1 (ppm)


NH2
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Br
NH2
2g
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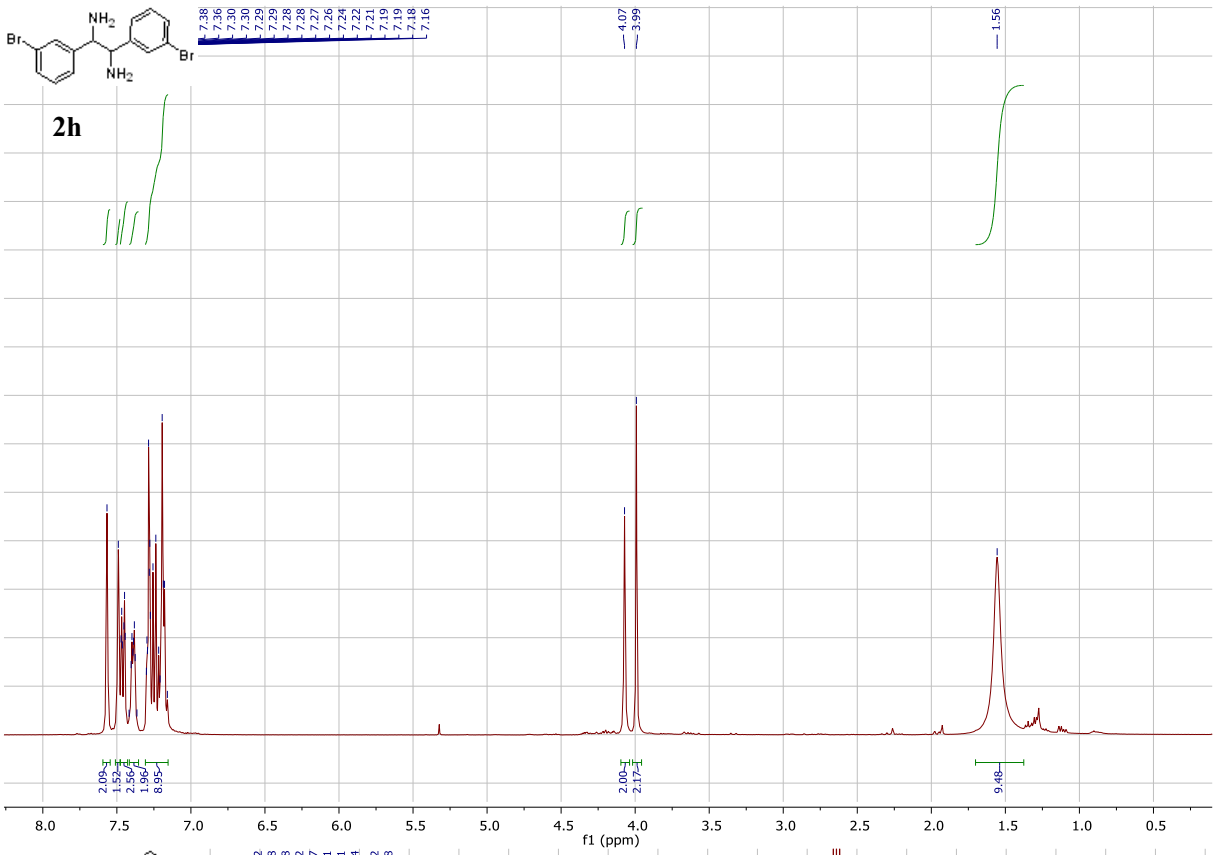
129.25
128.65
121.47
120.97
61.96
61.44
f1 (ppm)


2h
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7.29
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7.28
7.27
7.26
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7.22
7.21
7.19
7.19
7.18
7.16
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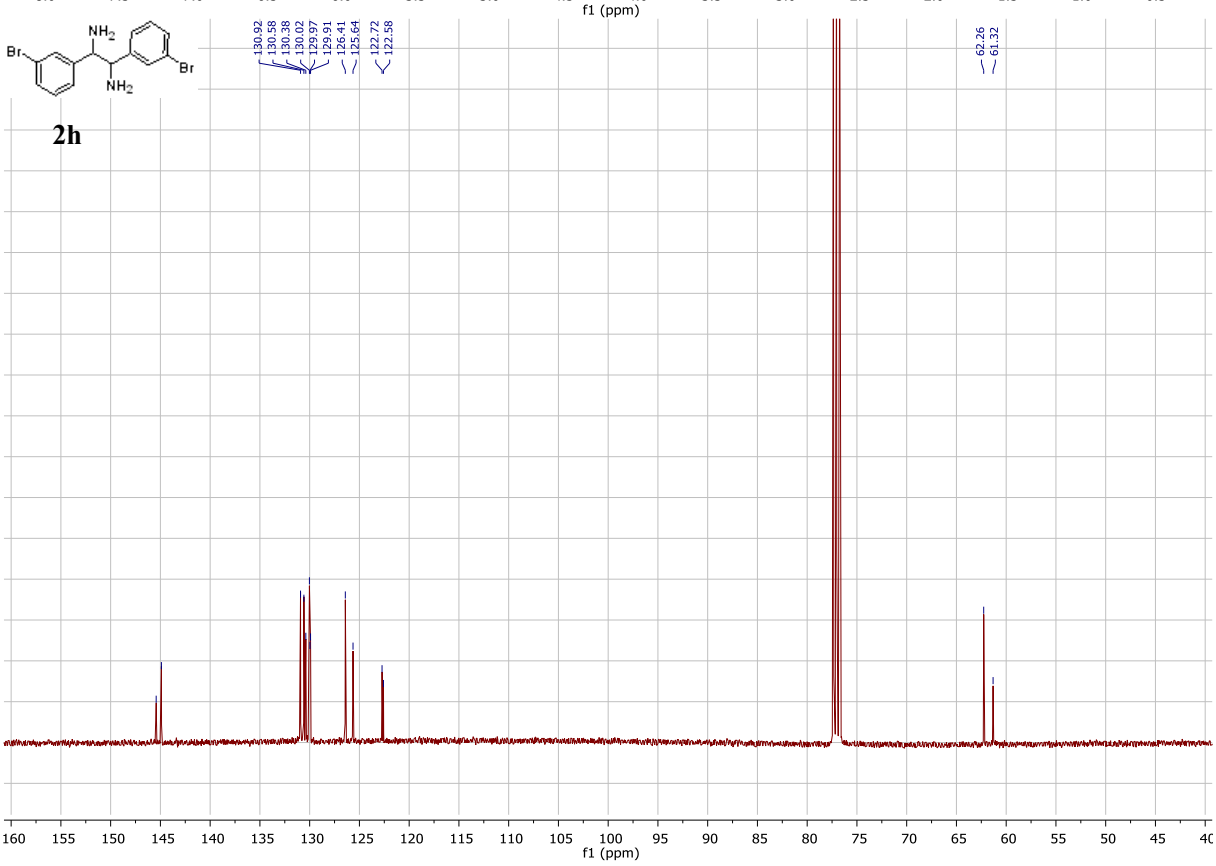
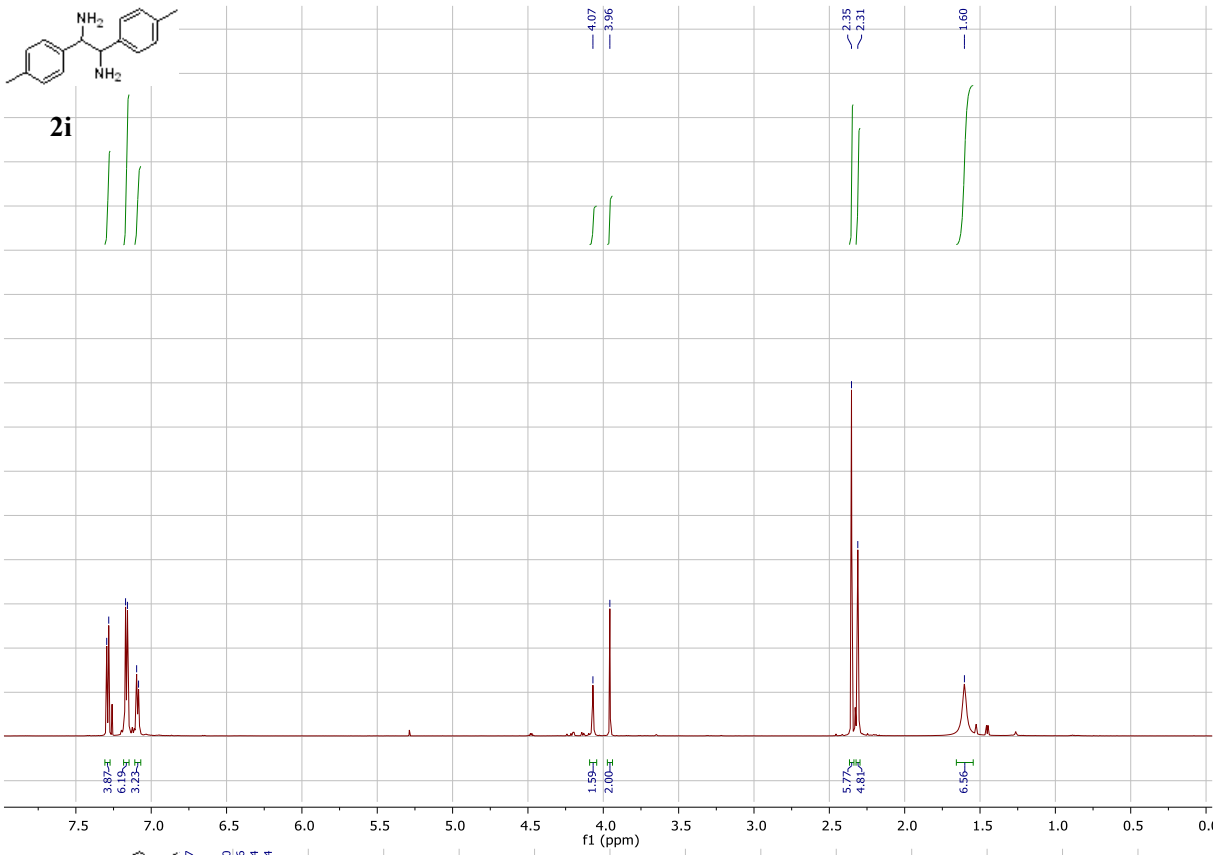
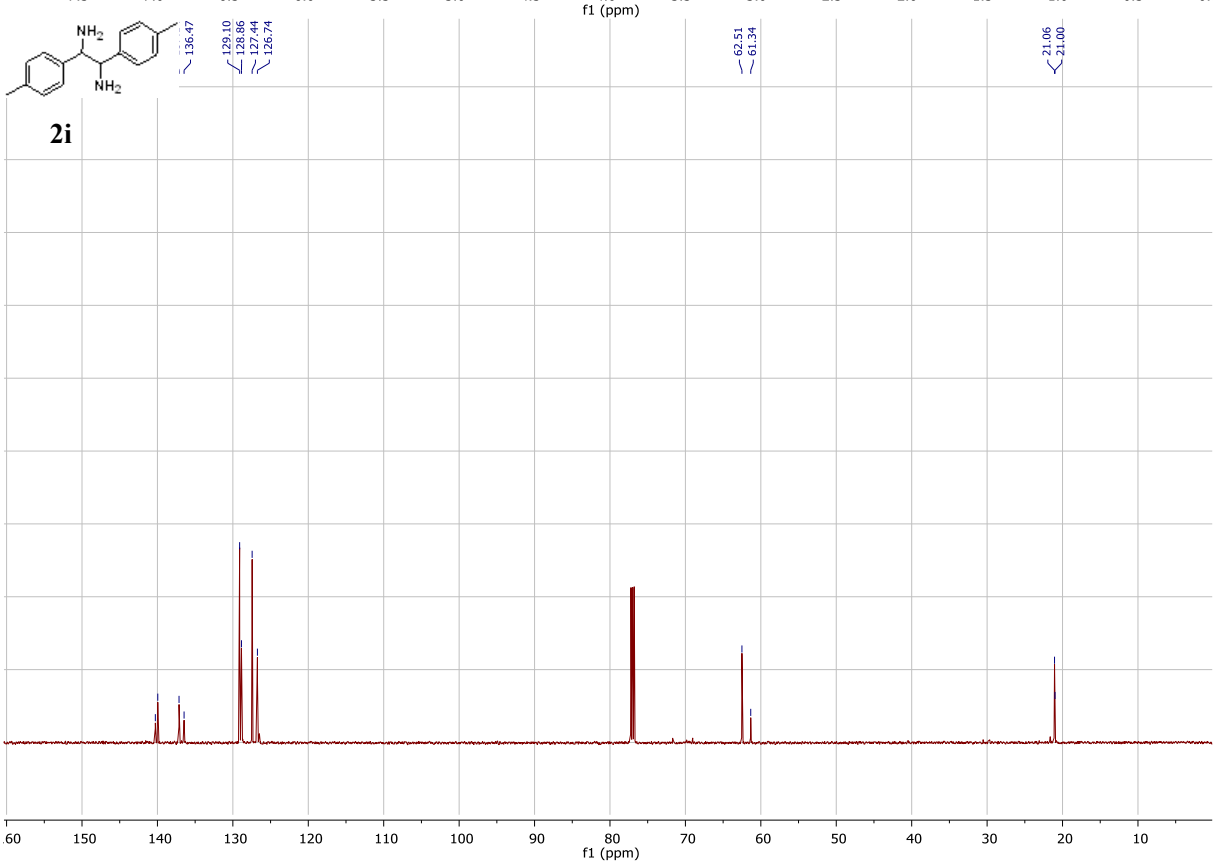
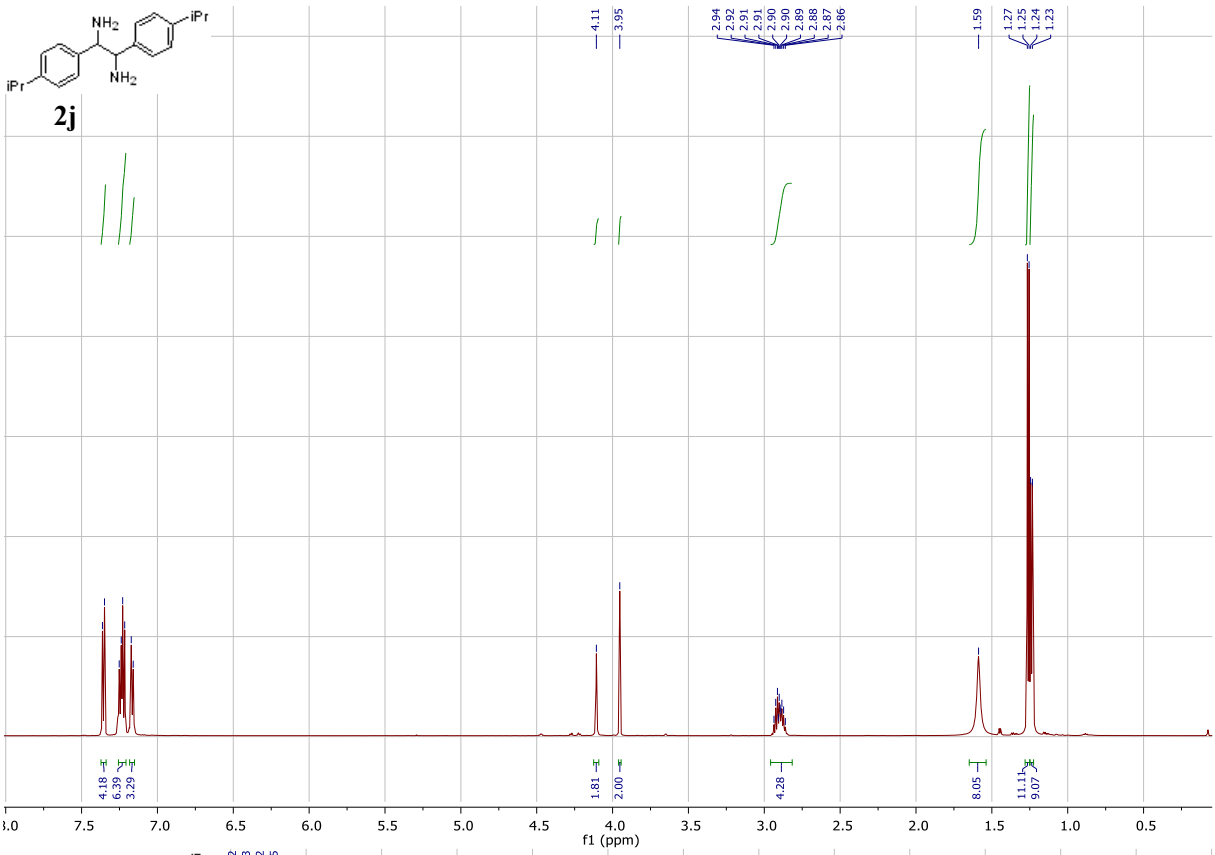
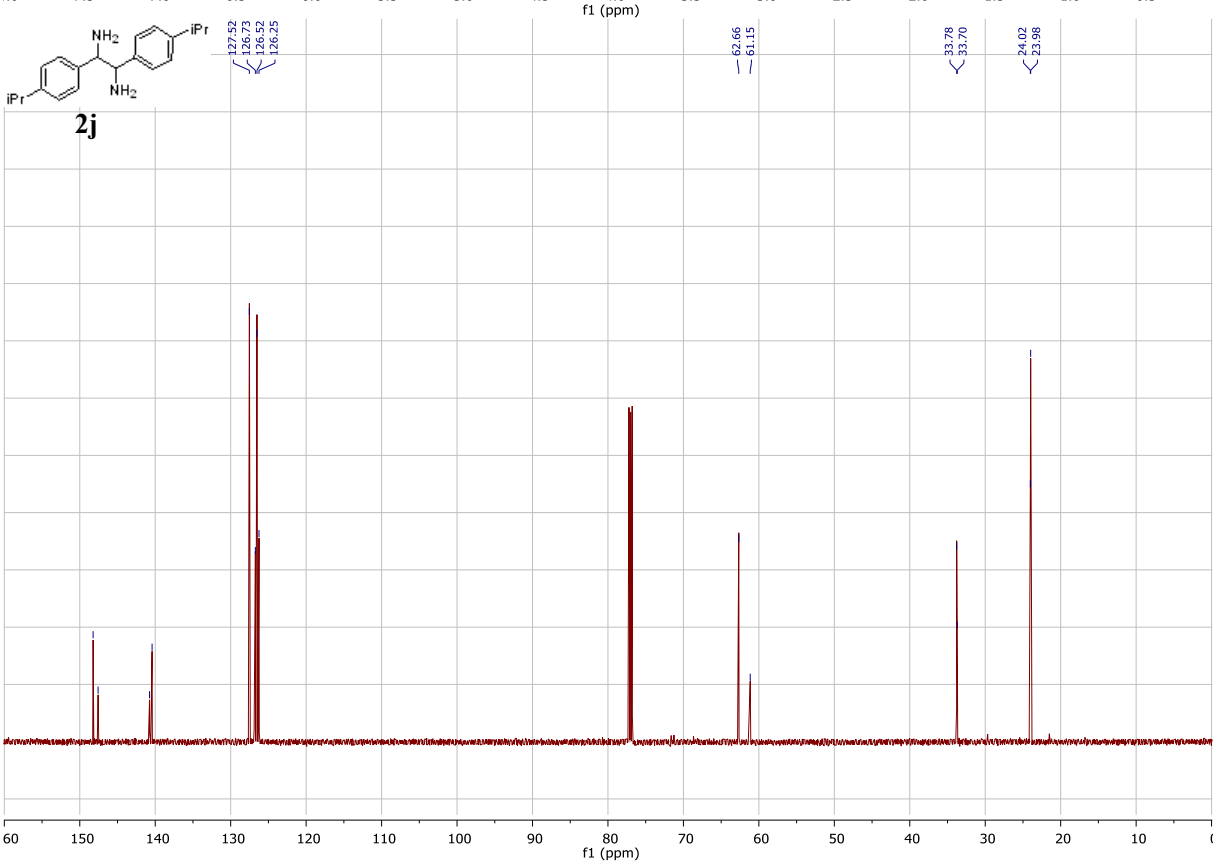
f1 (ppm)

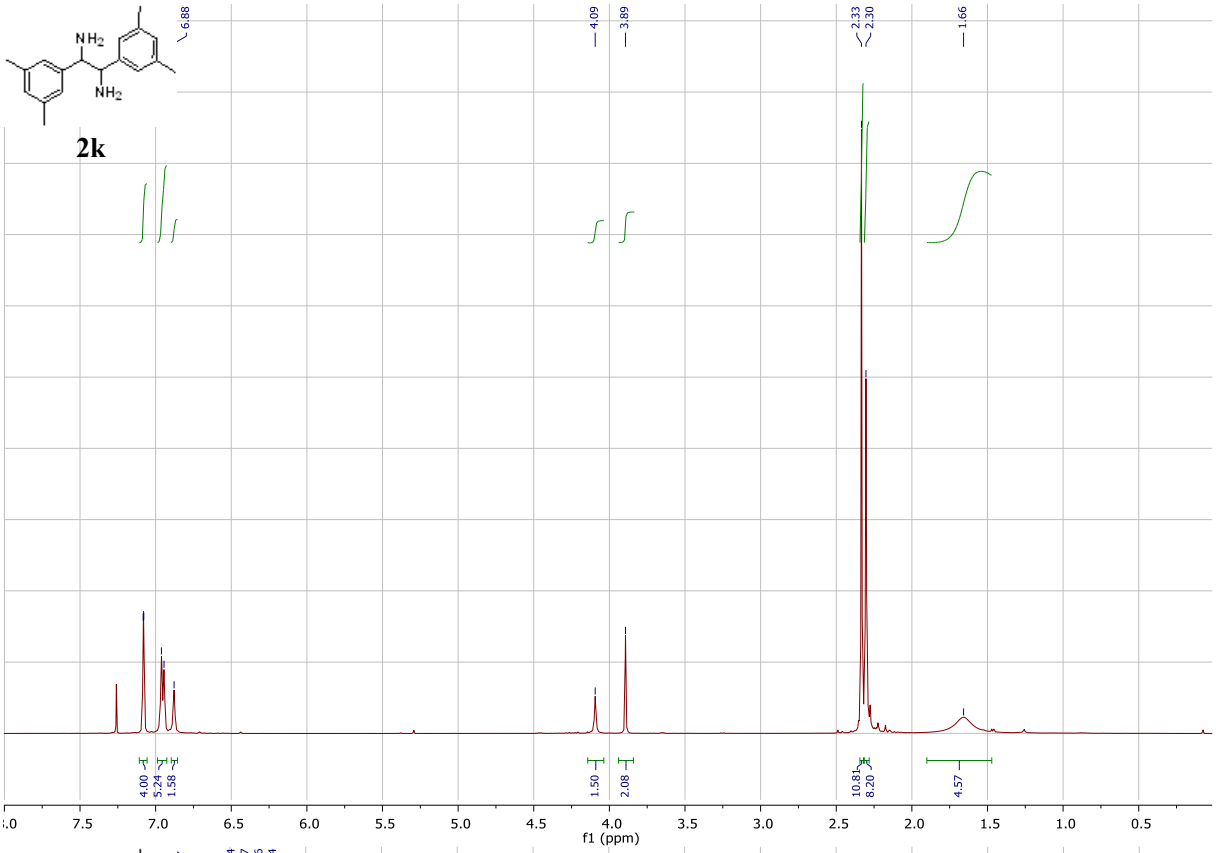

2h
130.92
130.58
130.38
130.02
129.97
129.91
126.41
125.64
122.72
122.58
62.26
61.32
f1 (ppm)

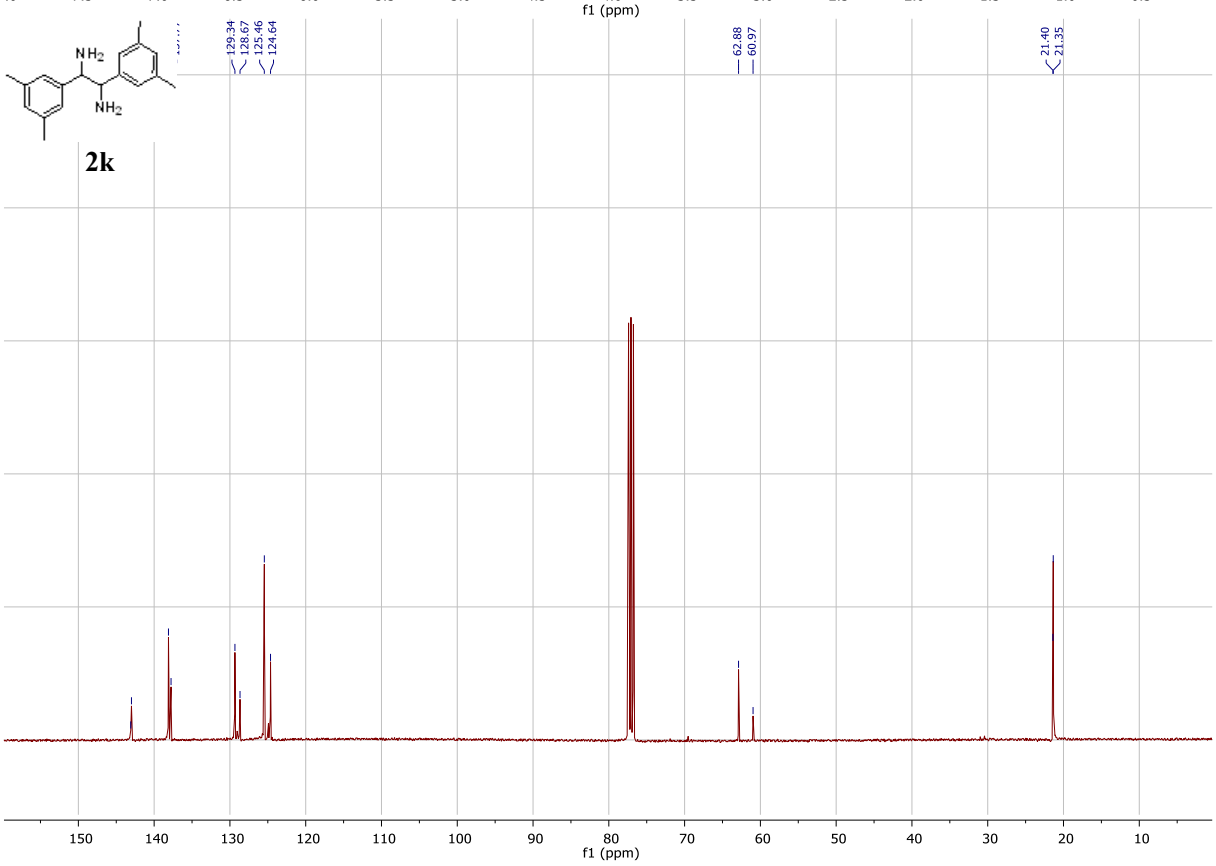

2i
4.07
3.96
2.35
2.31
1.60
3.87
6.19
3.23
1.59
2.00
5.77
4.81
6.56
f1 (ppm)

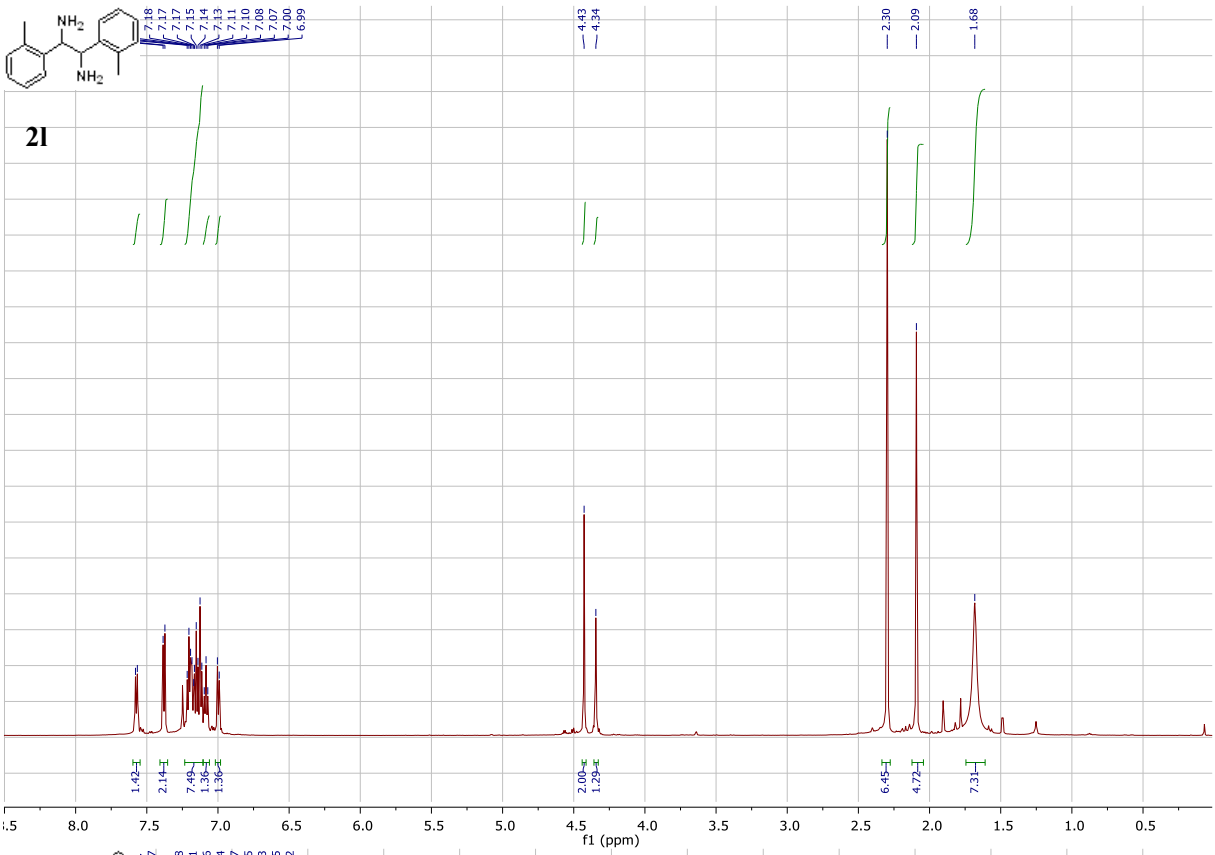

2i
136.47
129.10
128.86
127.44
126.74
62.51
61.34
21.06
21.00
f1 (ppm)

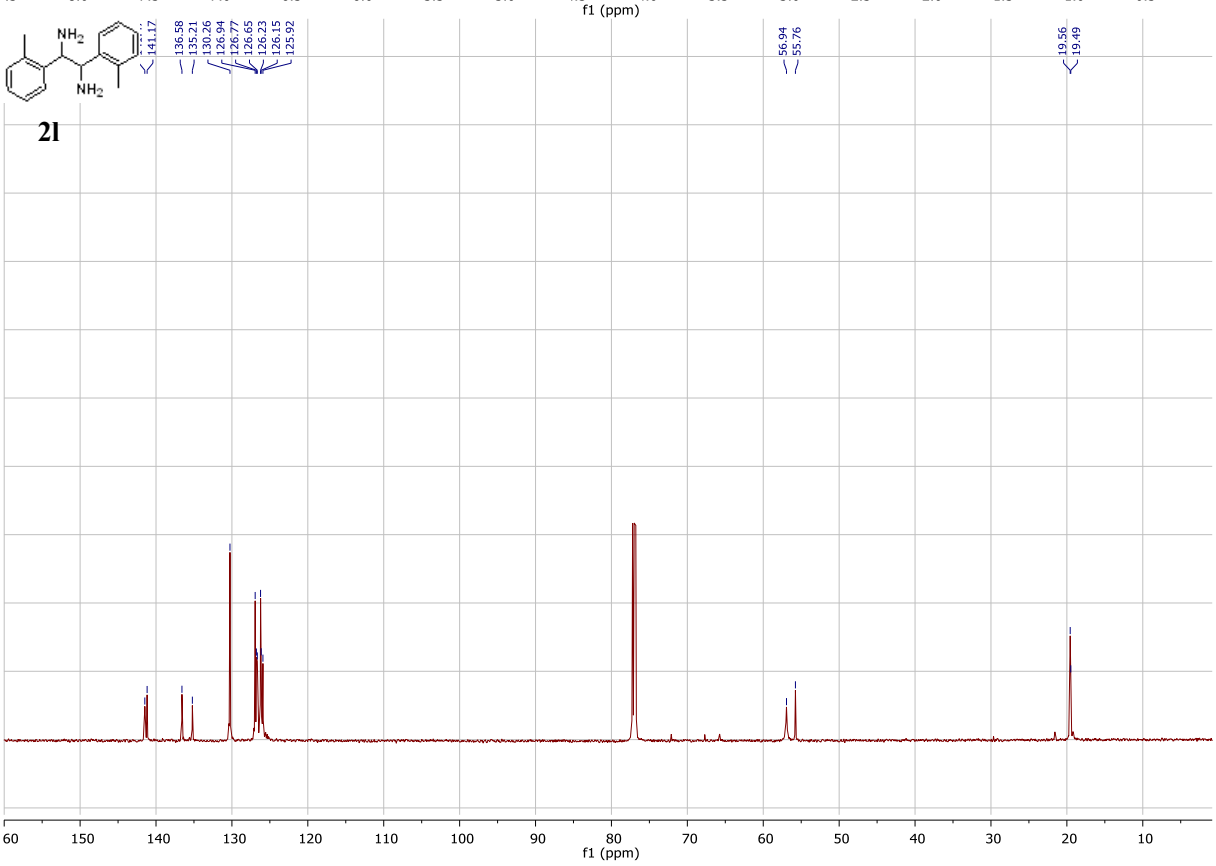

NH2
iPr
iPr
NH2
2j
4.11
3.95
2.94
2.92
2.91
2.91
2.90
2.90
2.89
2.88
2.87
2.86
1.59
1.27
1.25
1.24
1.23
4.18
6.39
3.29
1.81
2.00
4.28
8.05
11.11
9.07
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

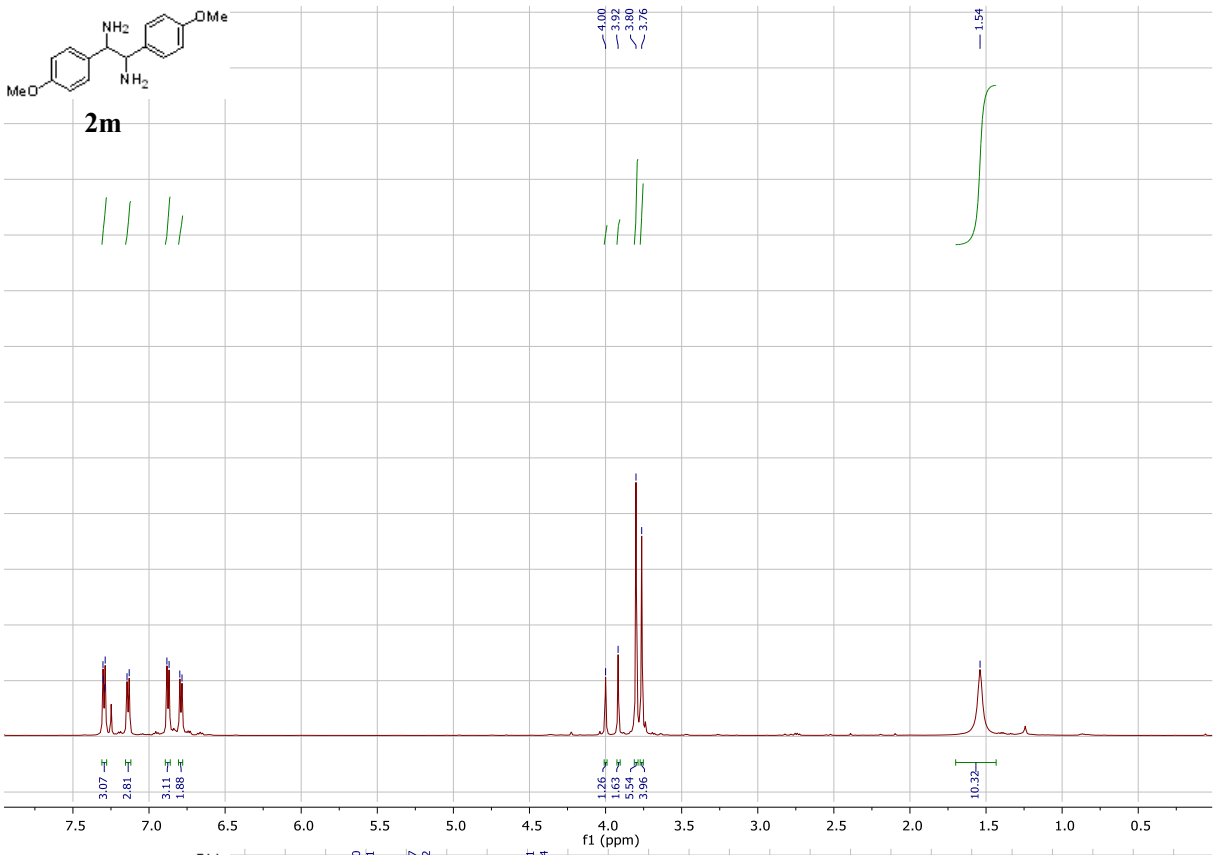

NH2
iPr
iPr
NH2
2j
127.52
126.73
126.52
126.25
62.66
61.15
33.78
33.70
24.02
23.98
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

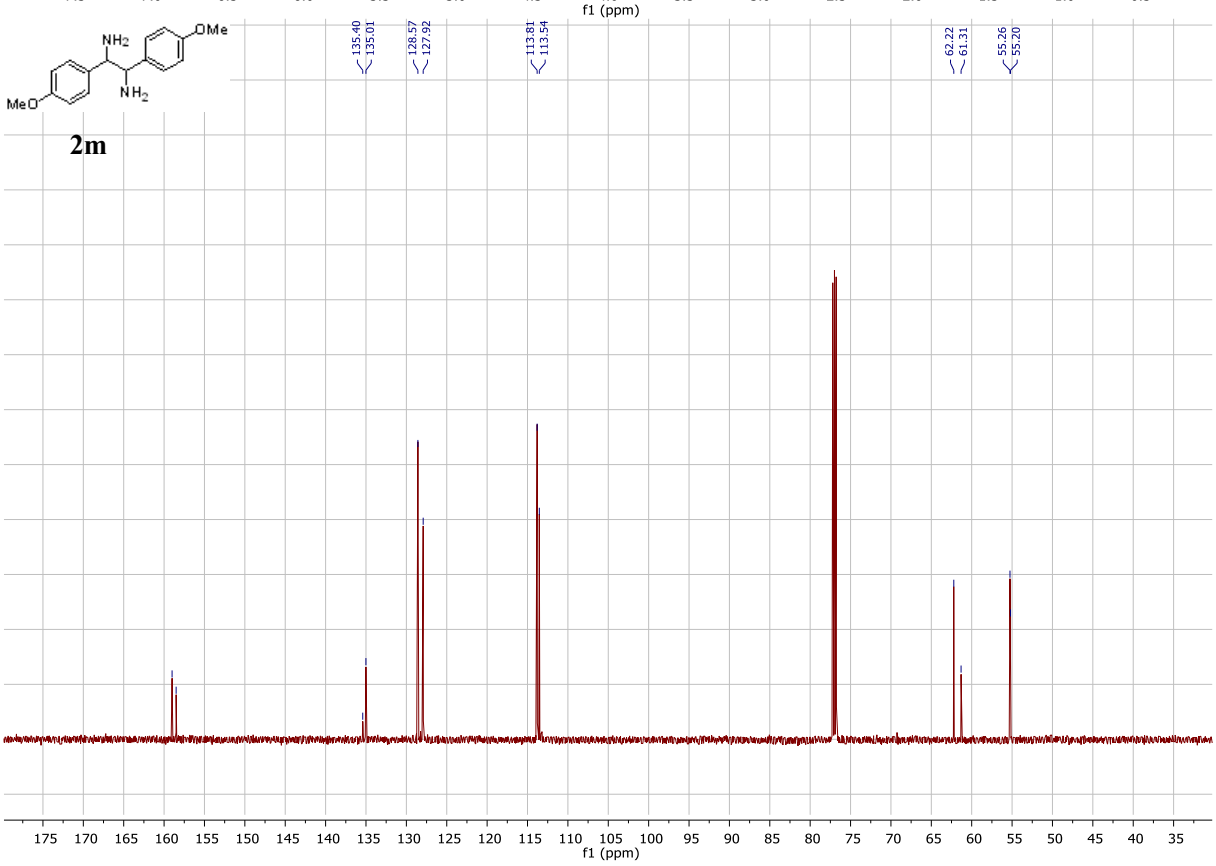

NH2
NH2
2k
6.88
4.09
3.89
2.33
2.30
1.66
4.00
5.24
1.58
1.50
2.08
10.81
8.20
4.57
f1 (ppm)

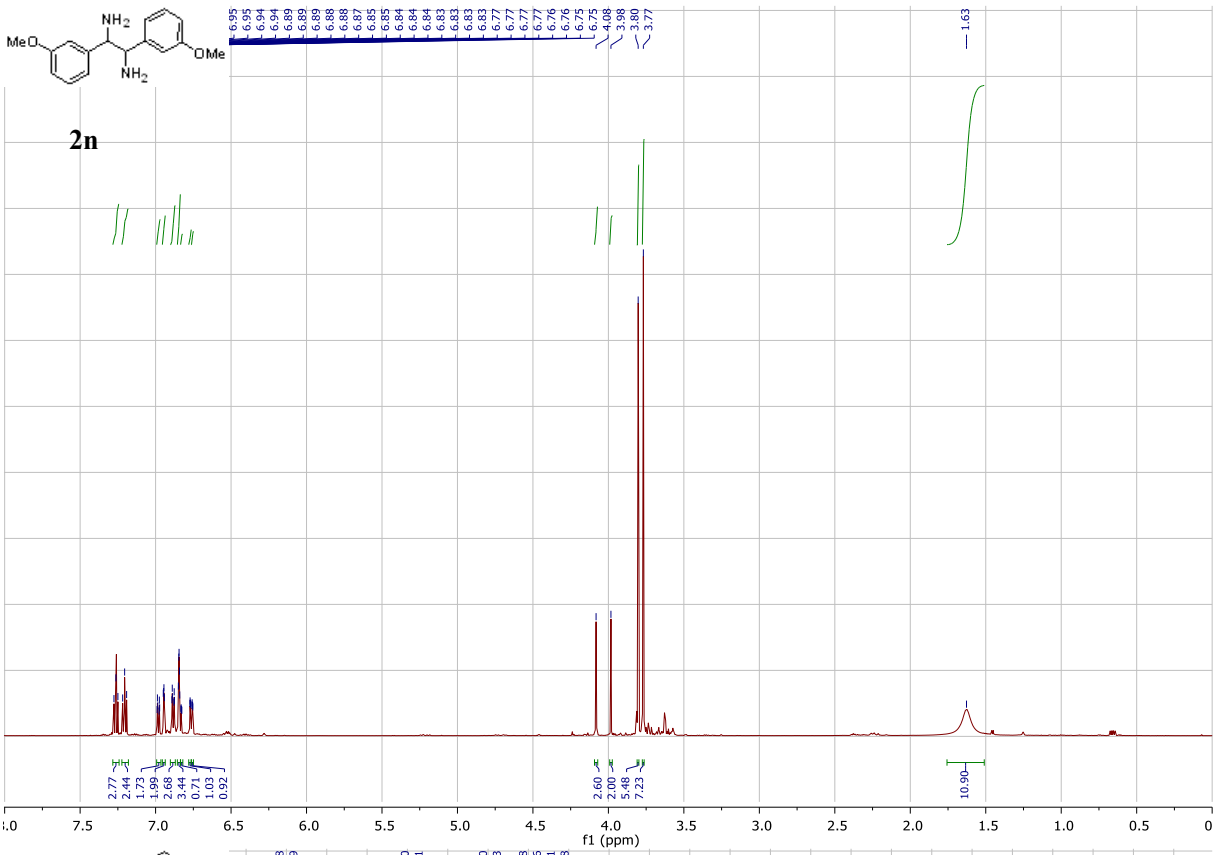

NH2
NH2
2k
129.34
128.67
125.46
124.64
62.88
60.97
21.40
21.35
f1 (ppm)

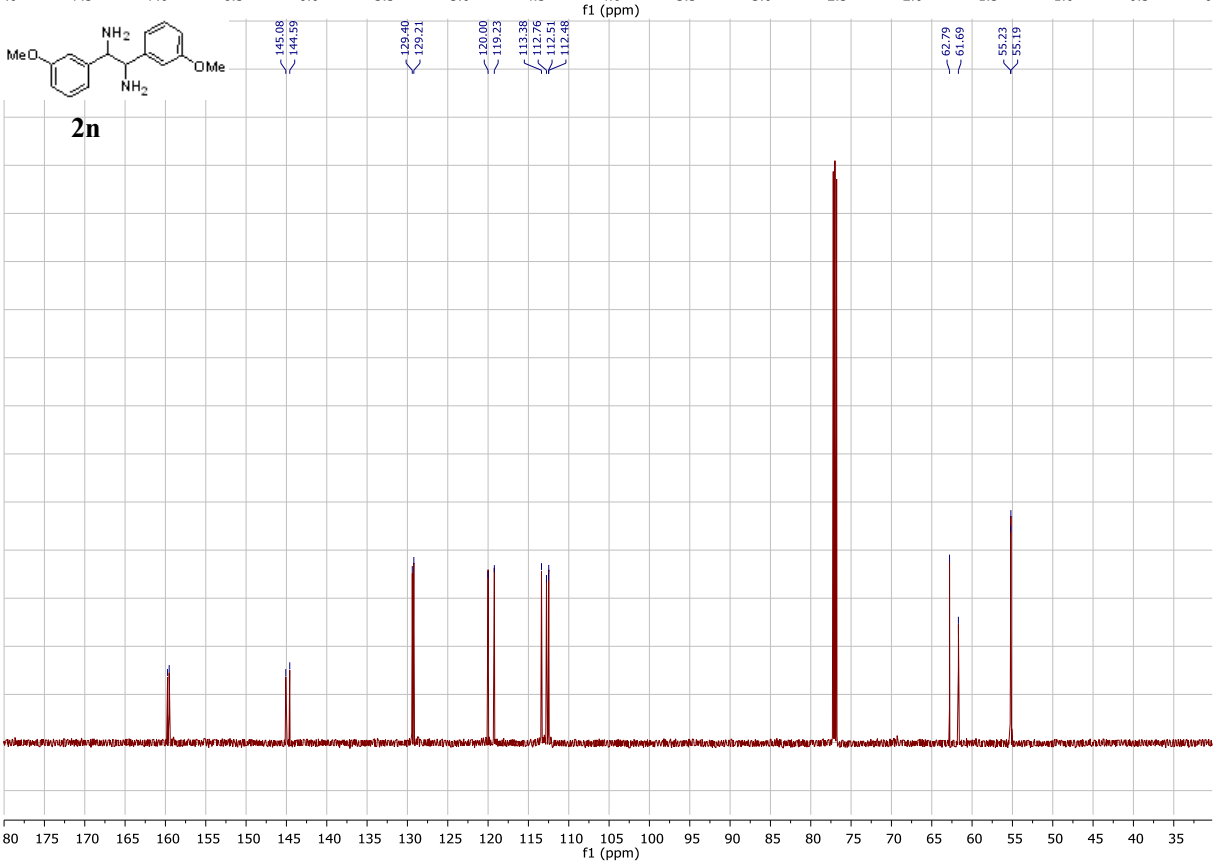

NH2
NH2
2l
7.18
7.17
7.17
7.15
7.14
7.13
7.11
7.10
7.08
7.07
7.00
6.99
4.43
4.34
2.30
2.09
1.68
1.42
2.14
7.49
1.36
1.36
2.00
1.29
6.45
4.72
7.31
f1 (ppm)

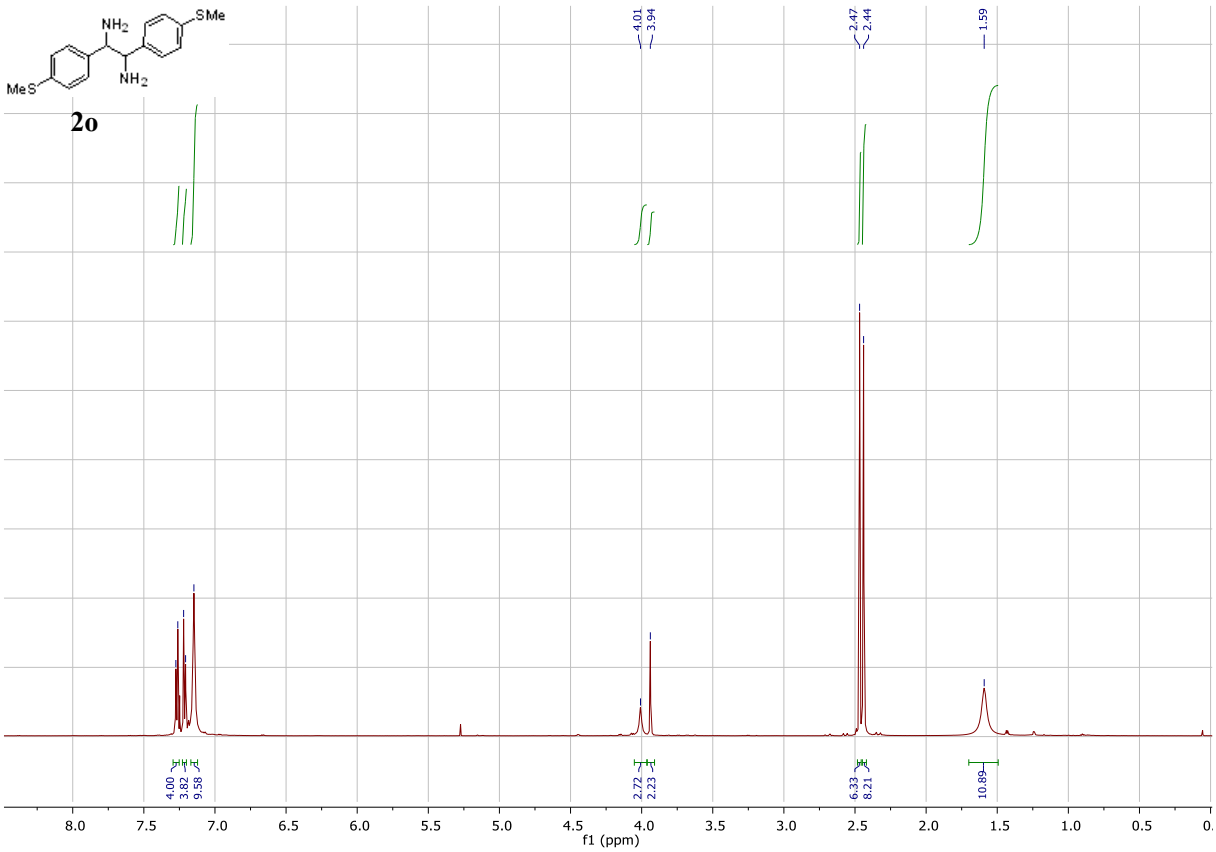

NH2
NH2
2l
141.17
136.58
135.21
130.26
126.94
126.77
126.65
126.23
126.15
125.92
56.94
55.76
19.56
19.49
f1 (ppm)

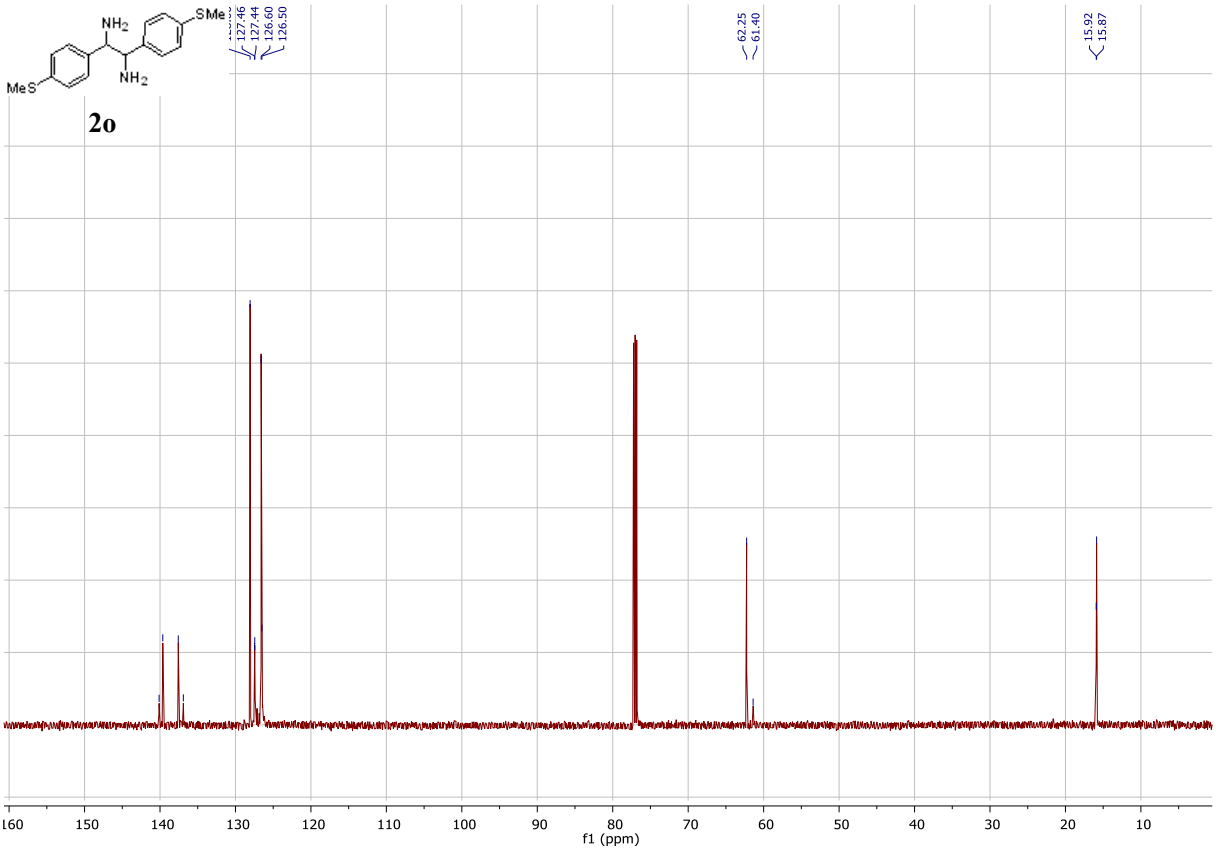

NH2
OMe
MeO
NH2
2m
4.00
3.92
3.80
3.76
1.54
3.07
2.81
3.11
1.88
1.26
1.63
5.54
3.96
10.32
f1 (ppm)

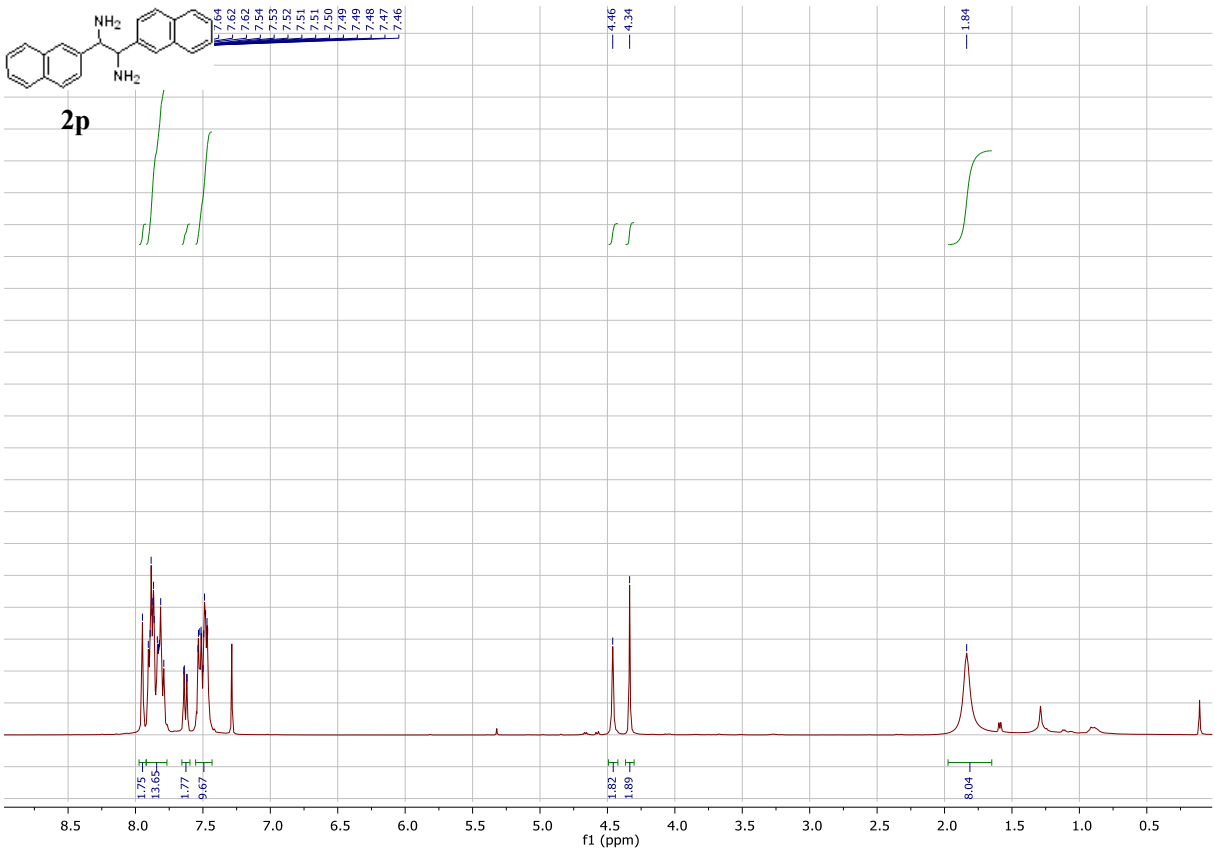

NH2
OMe
MeO
NH2
2m
135.40
135.01
128.57
127.92
113.81
113.54
62.22
61.31
55.26
55.20
f1 (ppm)

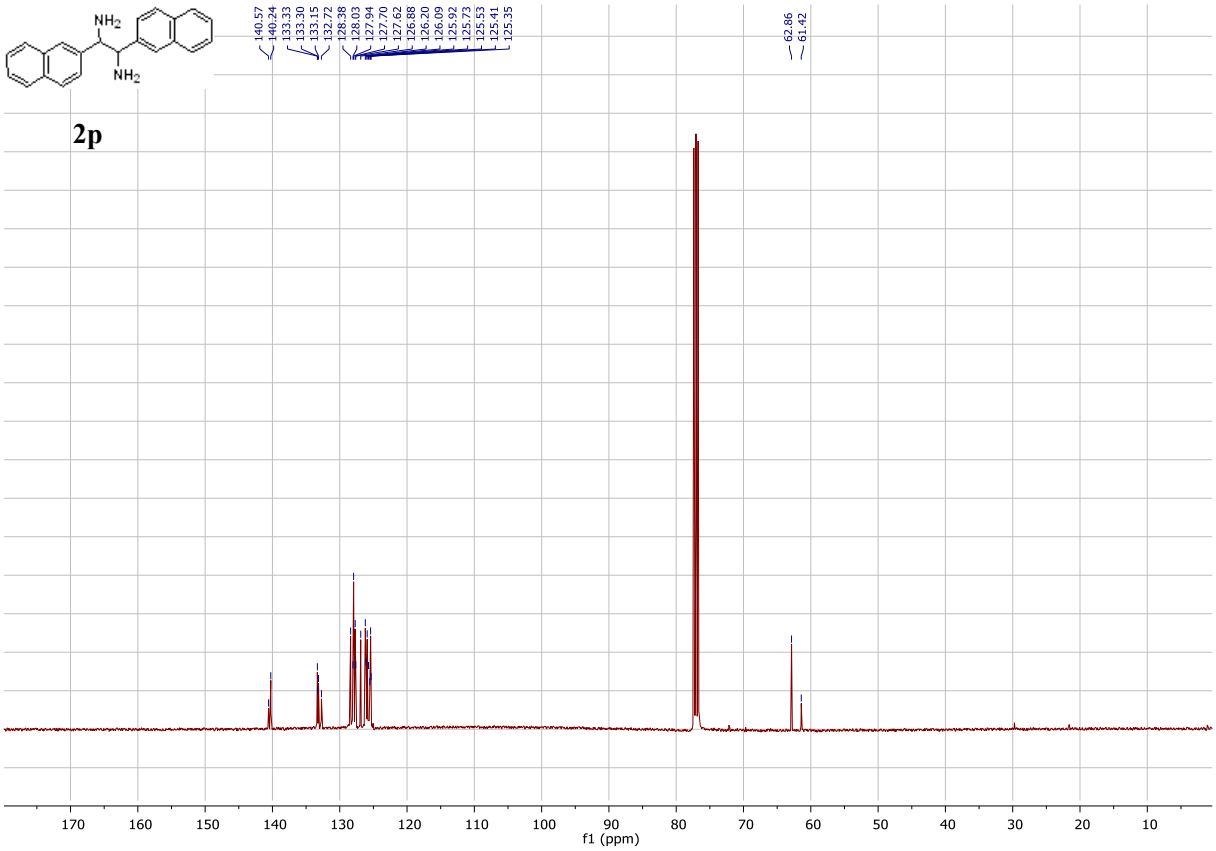

MeO
NH2
NH2
OMe
2n
6.95 6.95 6.94 6.94 6.89 6.89 6.89 6.88 6.88 6.87 6.85 6.85 6.84 6.84 6.84 6.83 6.83 6.83 6.77 6.77 6.77 6.76 6.76 6.75 6.75 4.08 3.98 3.80 3.77
1.63
2.77 2.44 1.73 1.99 2.68 3.44 0.71 1.03 0.92
2.60 2.00 5.48 7.23
10.90
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)

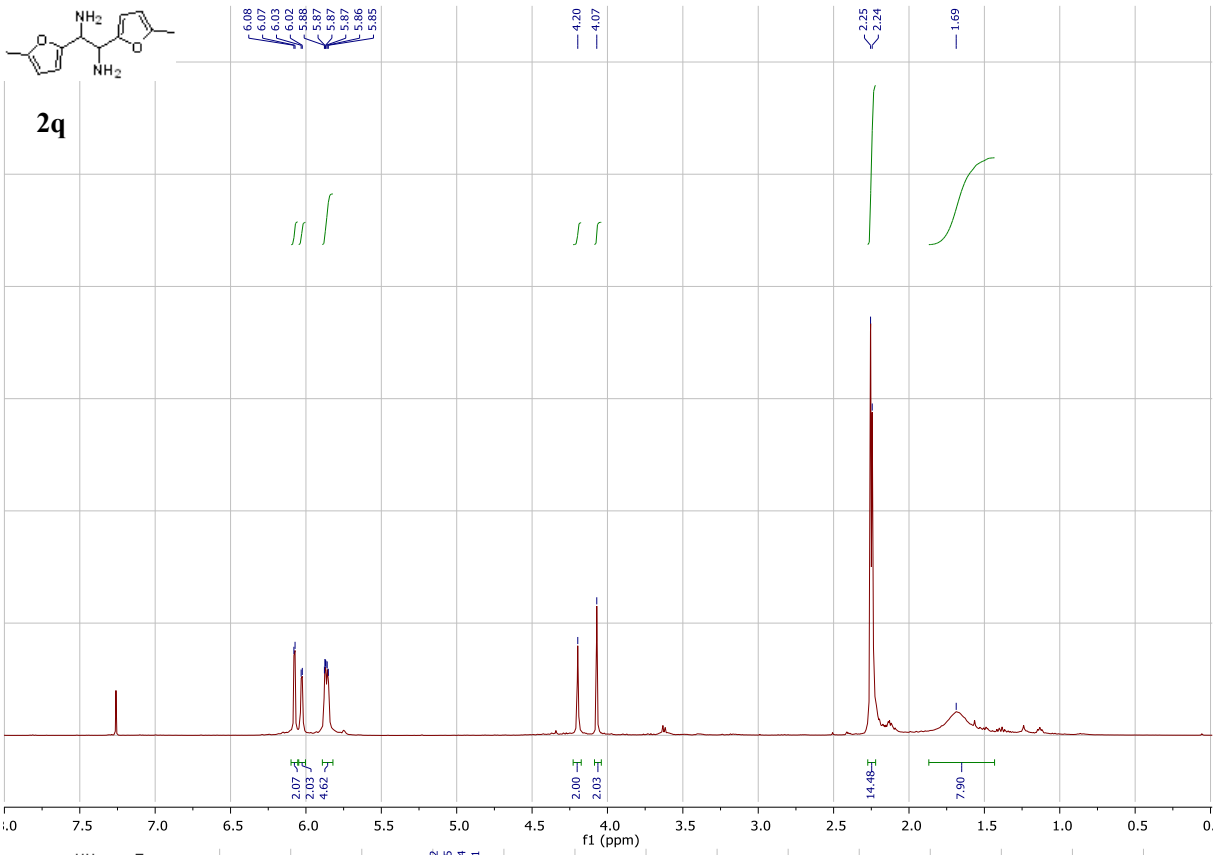

MeO
NH2
NH2
OMe
2n
145.08 144.59
129.40 129.21
120.00 119.23
113.38 112.76 112.51 112.48
62.79 61.69
55.23 55.19
175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35
f1 (ppm)

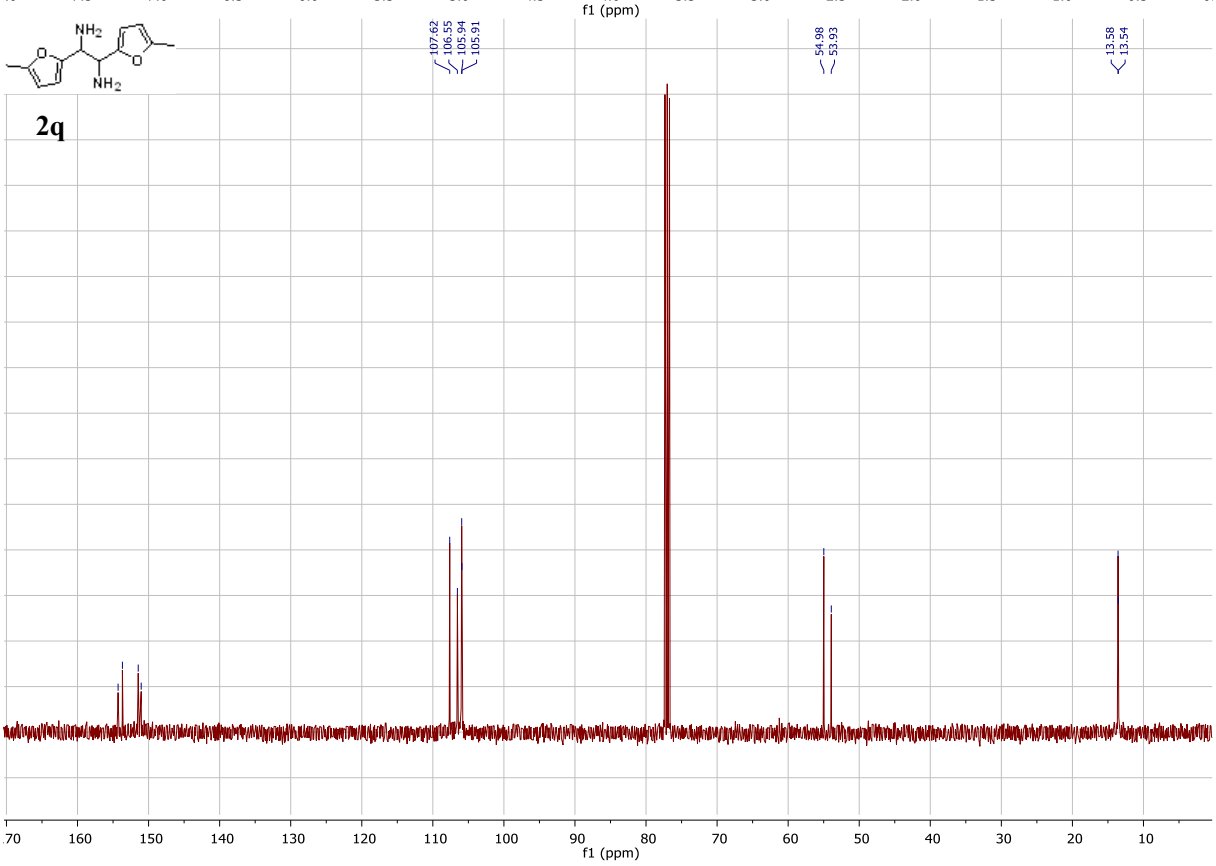

NH2
SMe
MeS
NH2
2o
4.01
3.94
2.47
2.44
1.59
4.00
3.82
9.58
2.72
2.23
6.33
8.21
10.89
f1 (ppm)

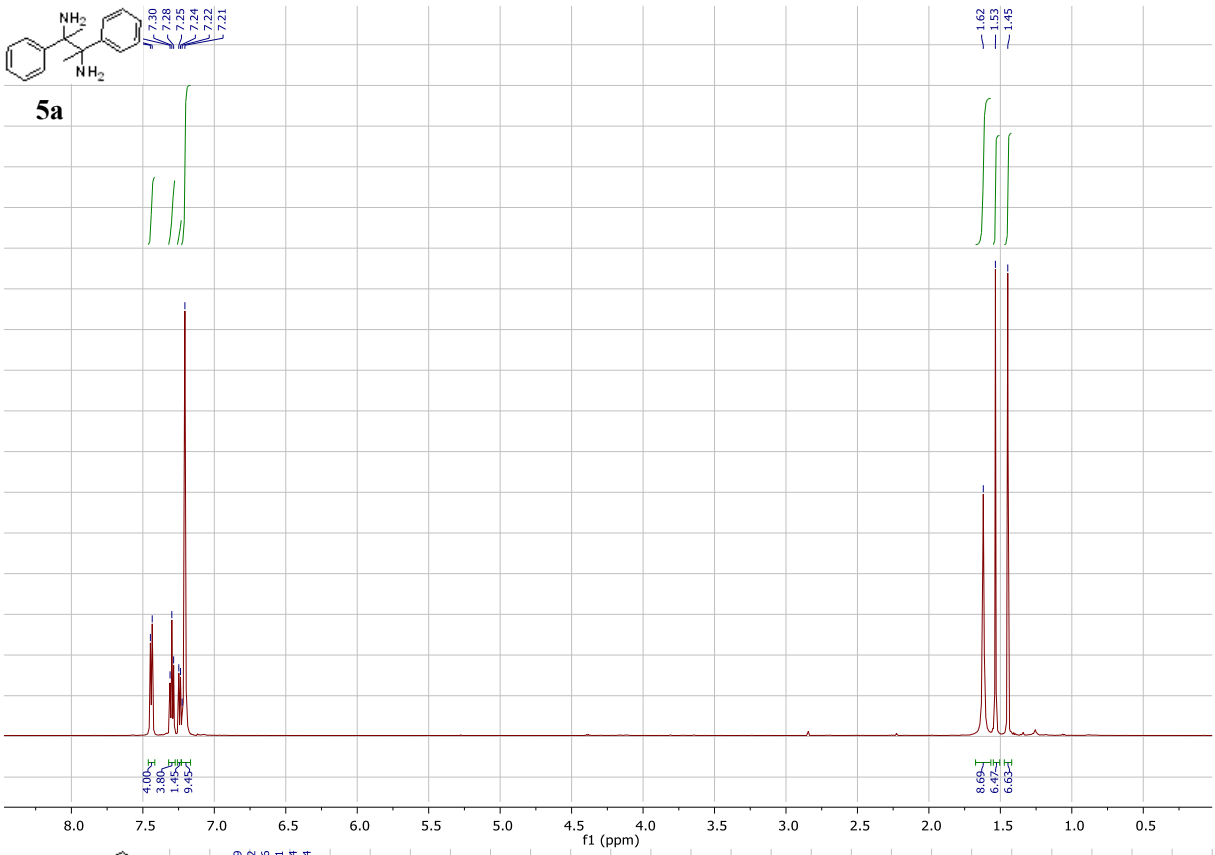

NH2
SMe
MeS
NH2
2o
127.46
127.44
126.60
126.50
62.25
61.40
15.92
15.87
f1 (ppm)

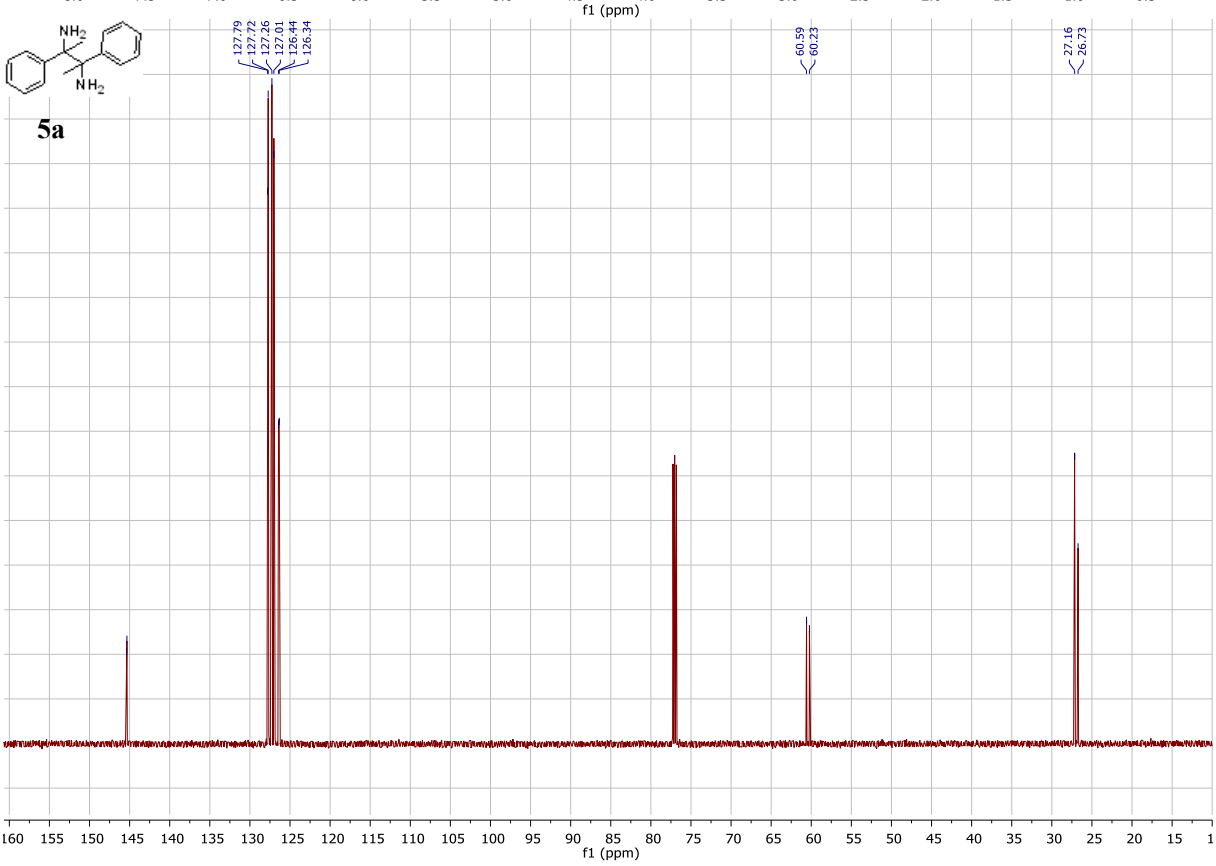

NH2
NH2
2p
7.64
7.62
7.62
7.54
7.53
7.52
7.51
7.51
7.50
7.49
7.49
7.48
7.47
7.46
4.46
4.34
1.84
1.75
13.65
1.77
9.67
1.82
1.89
8.04
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

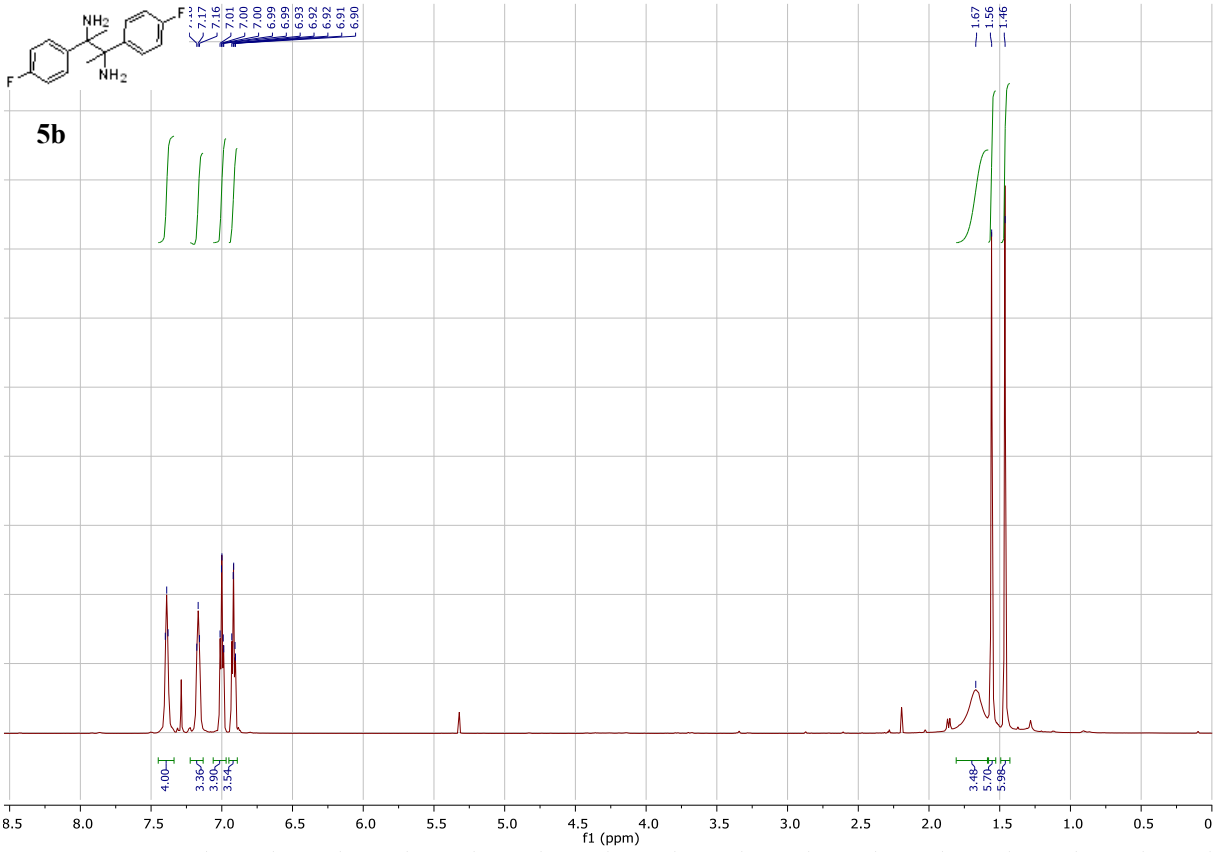

NH2
NH2
2p
140.57
140.24
133.33
133.30
133.15
132.72
128.38
128.03
127.94
127.70
127.62
126.88
126.20
126.09
125.92
125.73
125.53
125.41
125.35
62.86
61.42
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

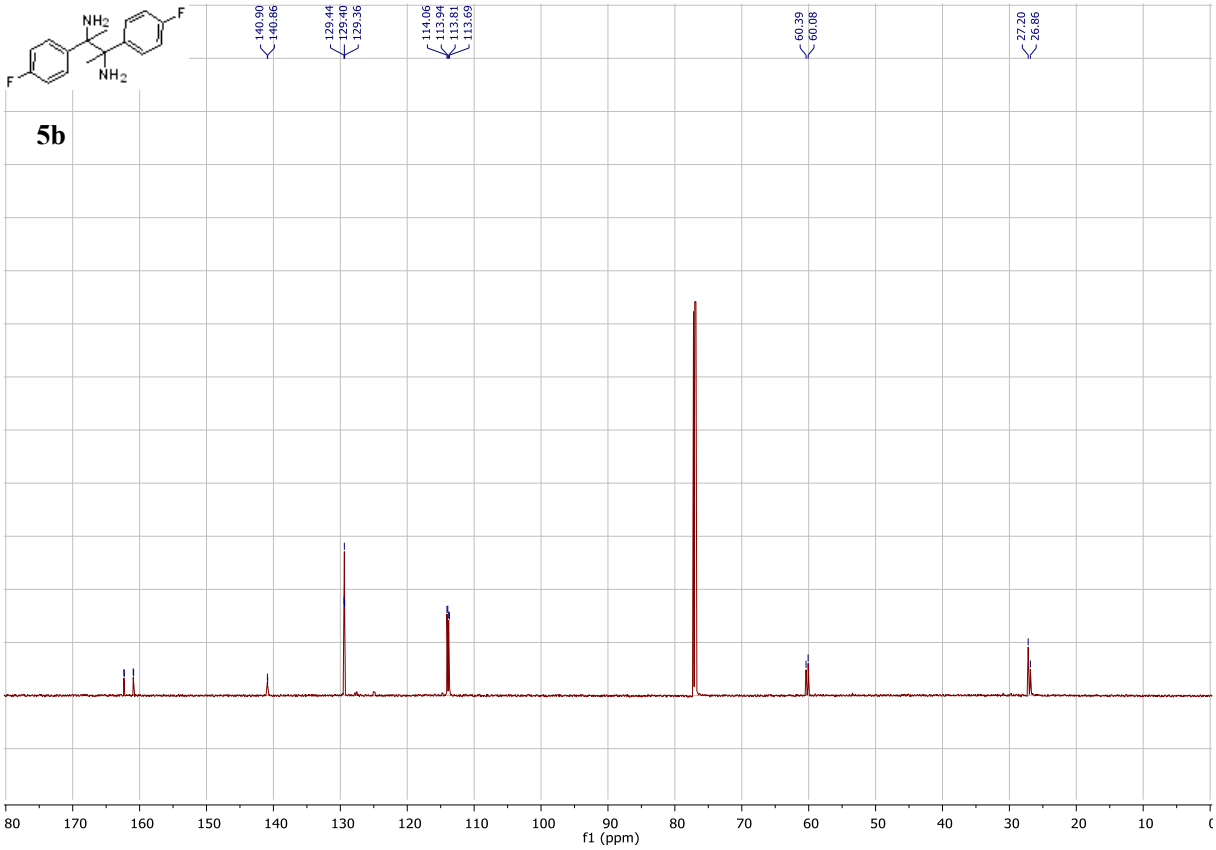

2q
6.08
6.07
6.03
6.02
5.88
5.87
5.87
5.87
5.86
5.85
4.20
4.07
2.25
2.24
1.69
2.07
2.03
4.62
2.00
2.03
14.48
7.90
f1 (ppm)

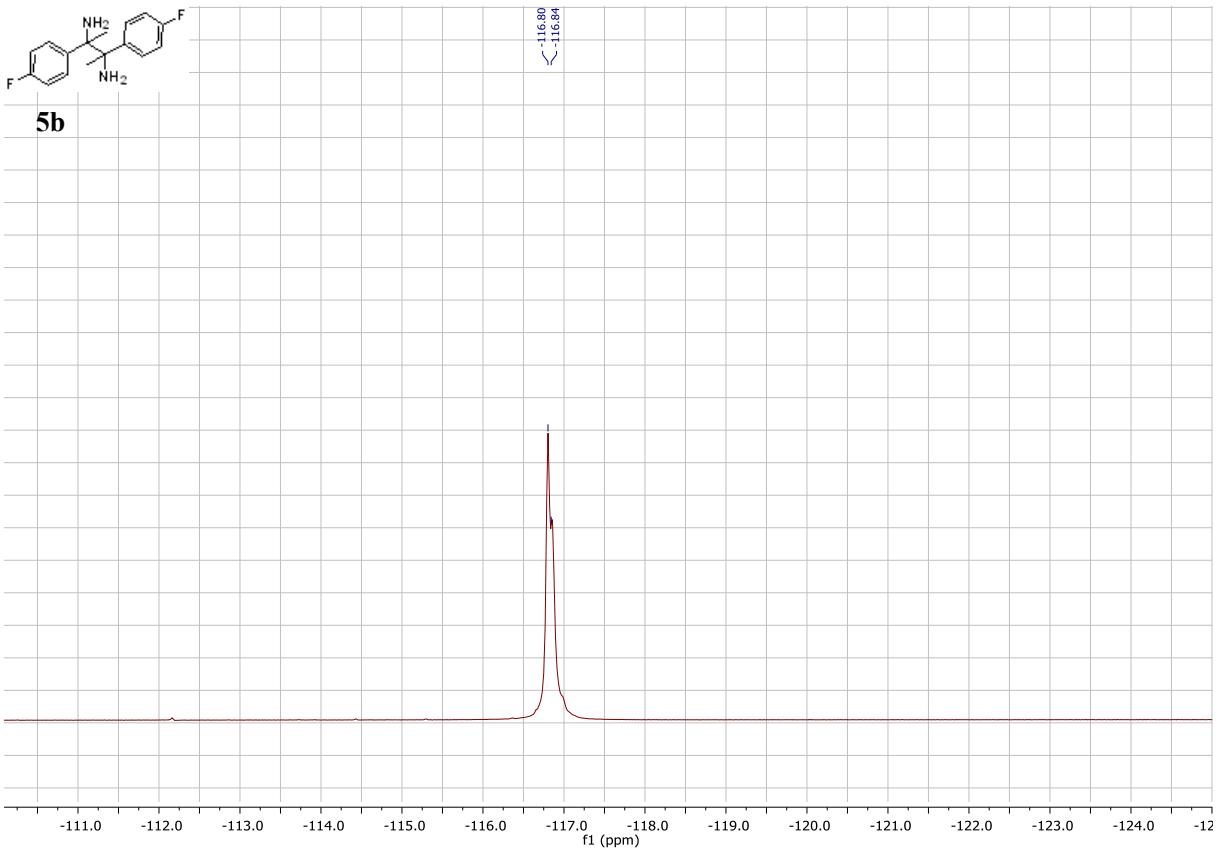

2q
107.62
106.55
105.94
105.91
54.98
53.93
13.58
13.54
f1 (ppm)

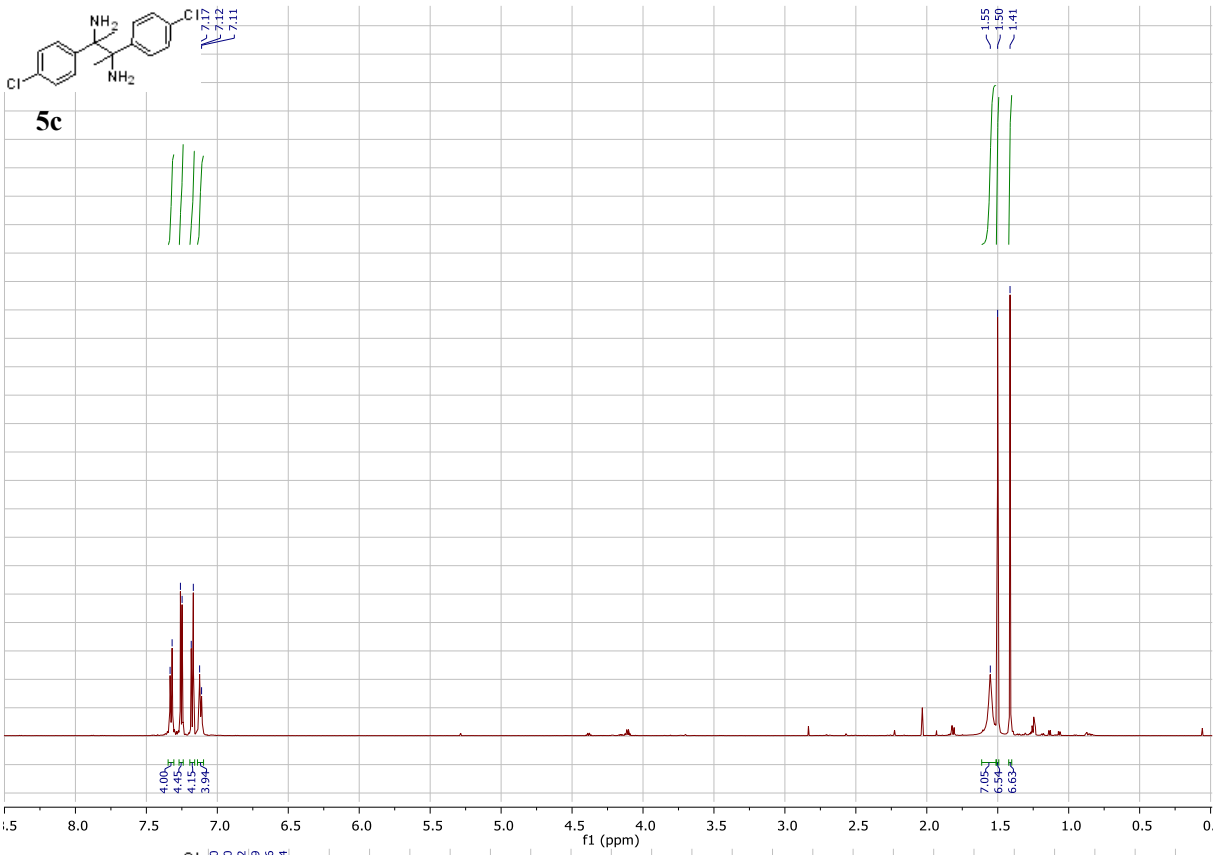

5a
7.30
7.28
7.25
7.24
7.22
7.21
1.62
1.53
1.45
4.00
3.80
1.45
9.45
8.69
6.47
6.63
f1 (ppm)

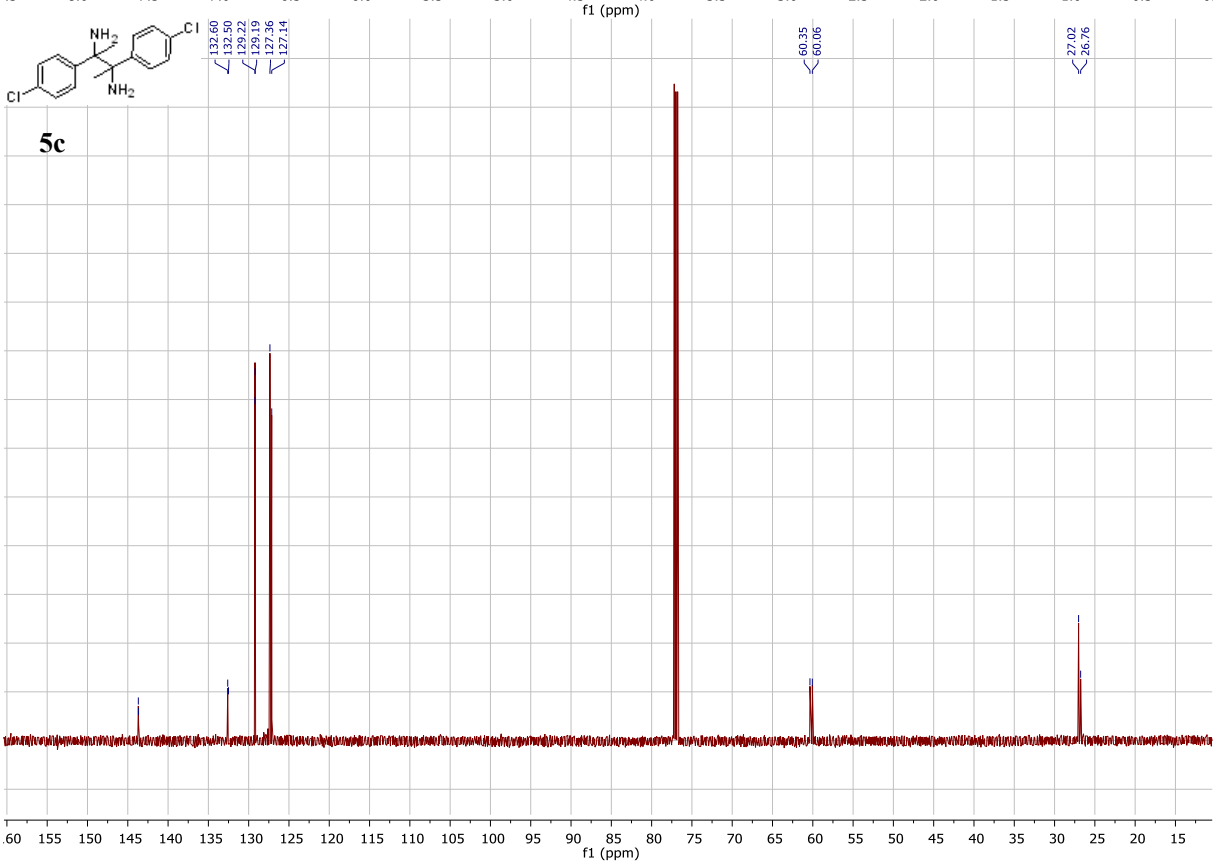

5a
127.79
127.72
127.26
127.01
126.44
126.34
60.59
60.23
27.16
26.73
f1 (ppm)

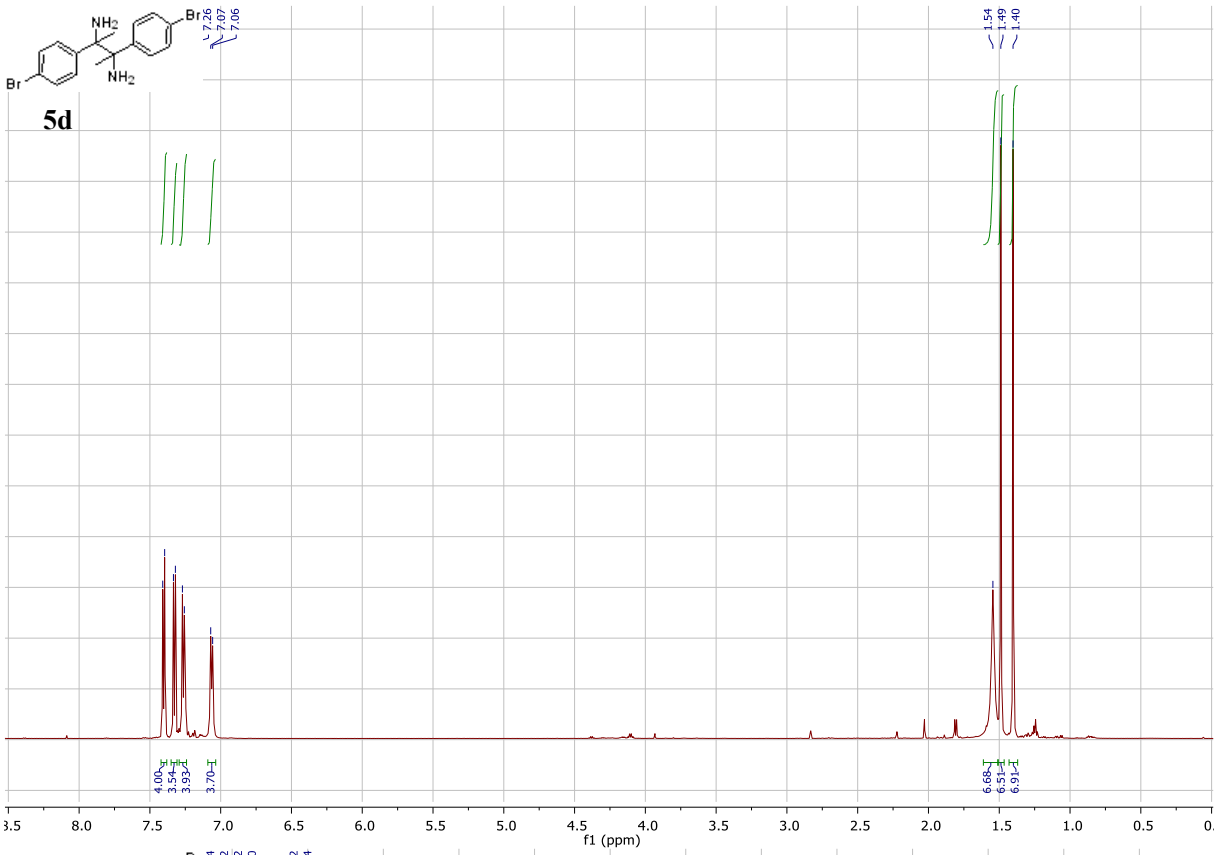

5b
7.17
7.16
7.01
7.00
7.00
6.99
6.99
6.93
6.92
6.92
6.91
6.90
1.67
1.56
1.46
4.00
3.36
3.90
3.54
3.48
5.70
5.98
f1 (ppm)

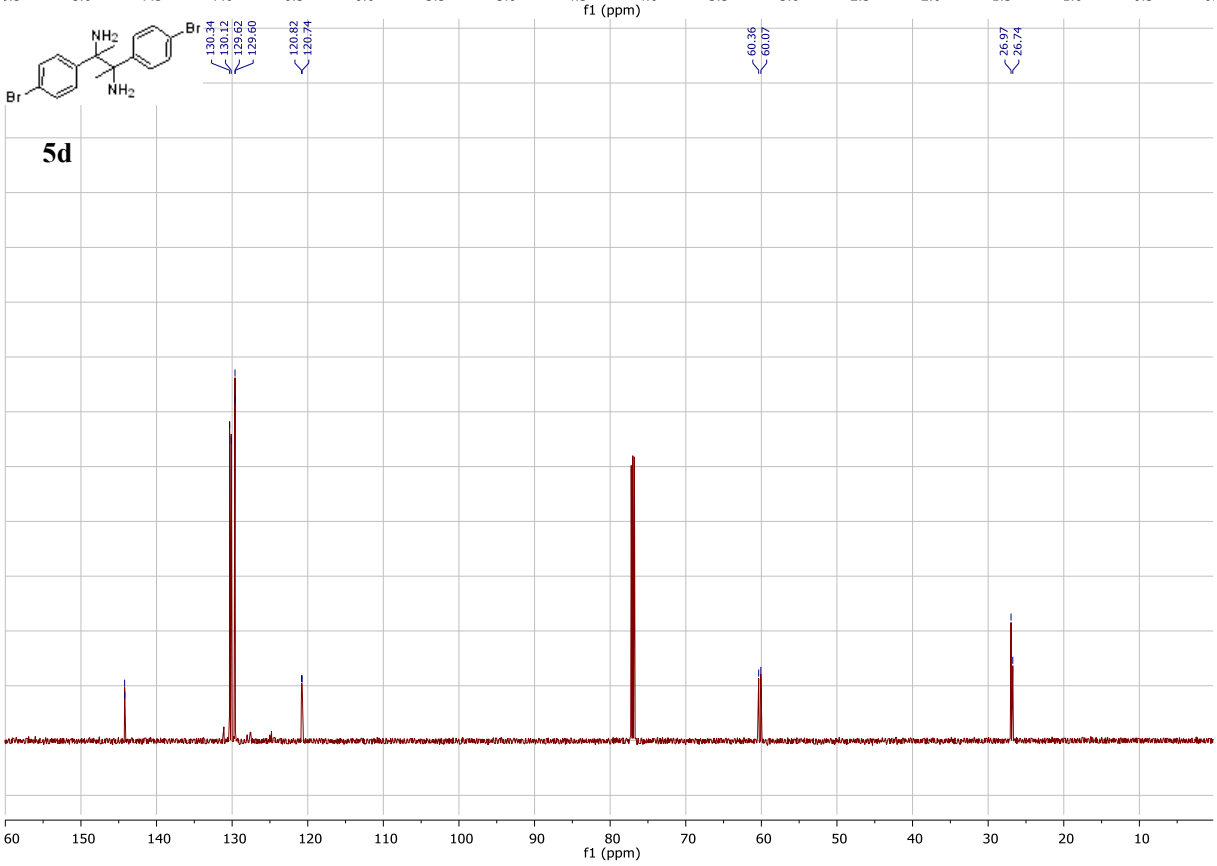

5b
140.90
140.86
129.44
129.40
129.36
114.06
113.94
113.81
113.69
60.39
60.08
27.20
26.86
f1 (ppm)

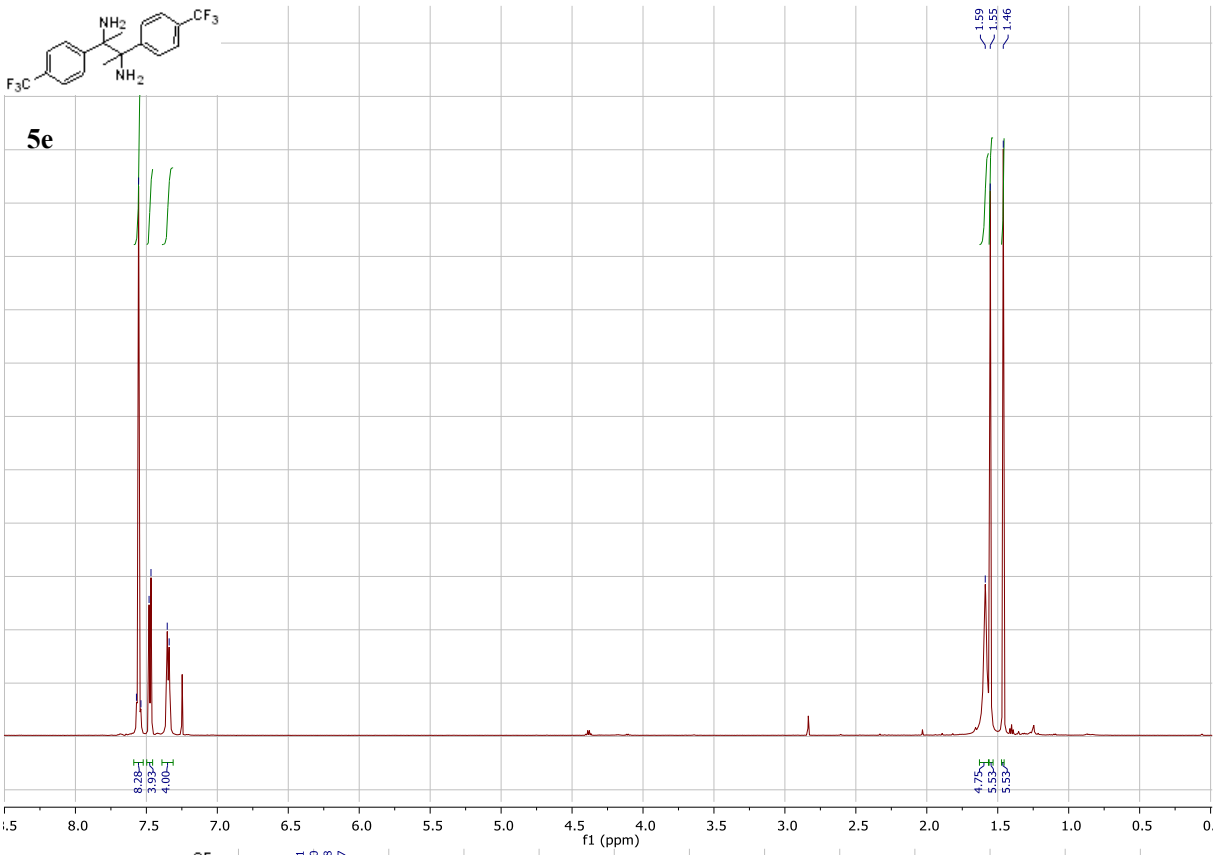

NH2
NH2
F
F
5b
-116.80
-116.84
-111.0
-112.0
-113.0
-114.0
-115.0
-116.0
-117.0
-118.0
-119.0
-120.0
-121.0
-122.0
-123.0
-124.0
f1 (ppm)

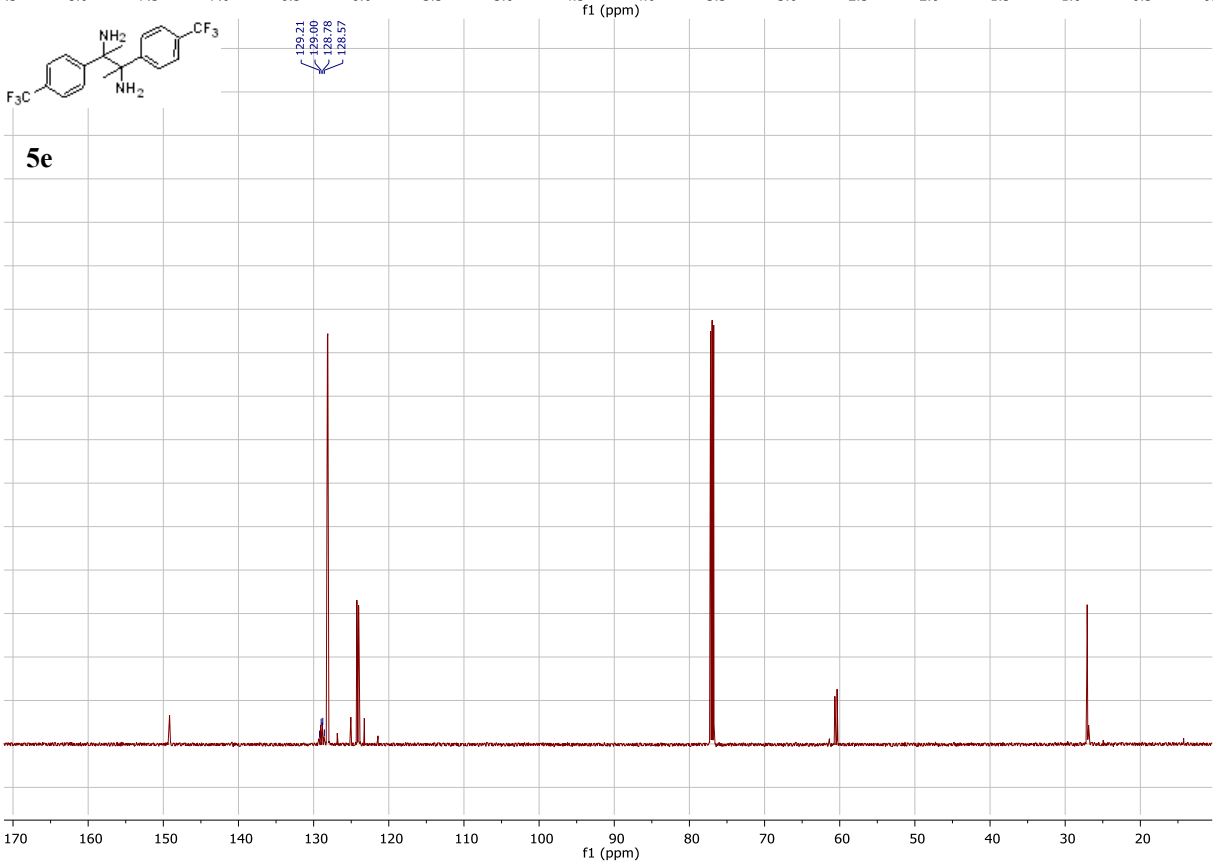

5c
7.17
7.12
7.11
1.55
1.50
1.41
4.00
4.45
4.15
3.94
7.05
6.54
6.63
f1 (ppm)

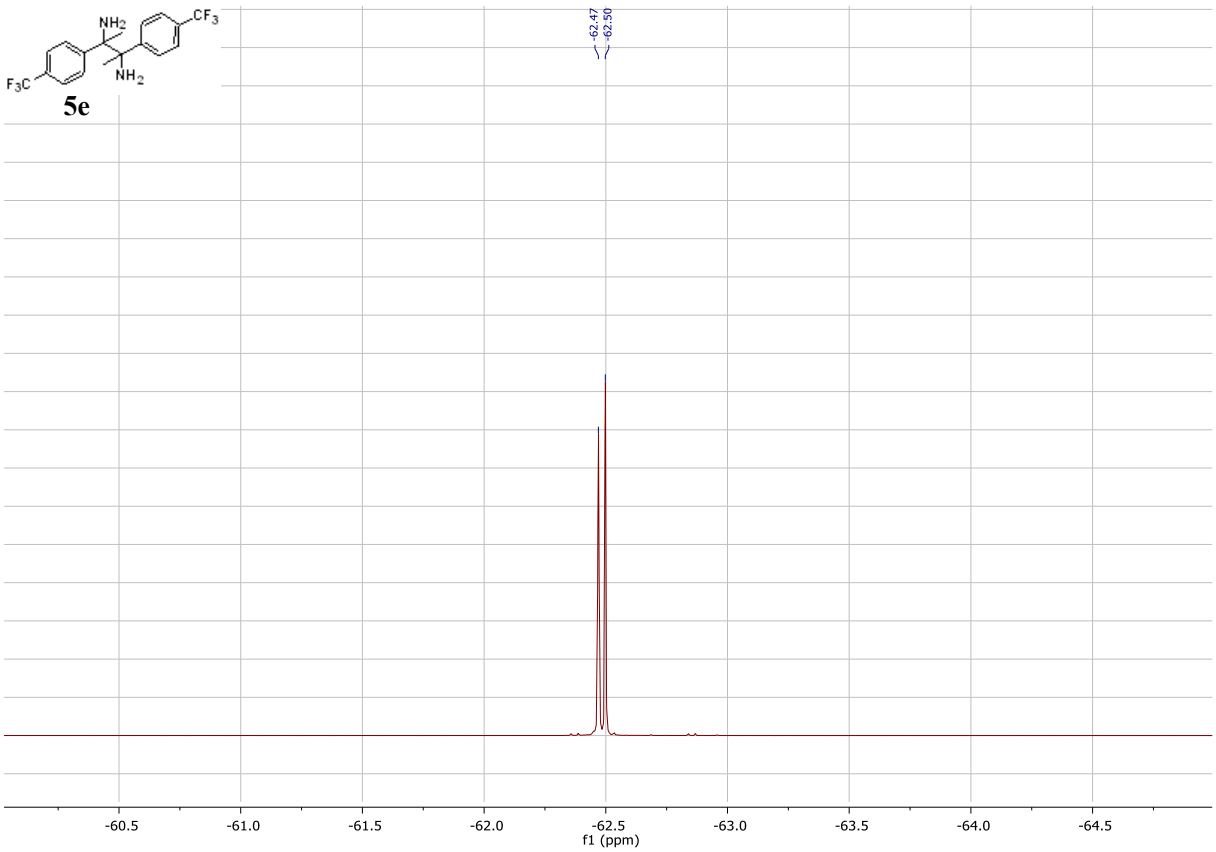

5c
132.60
132.50
129.22
129.19
127.36
127.14
60.35
60.06
27.02
26.76
f1 (ppm)

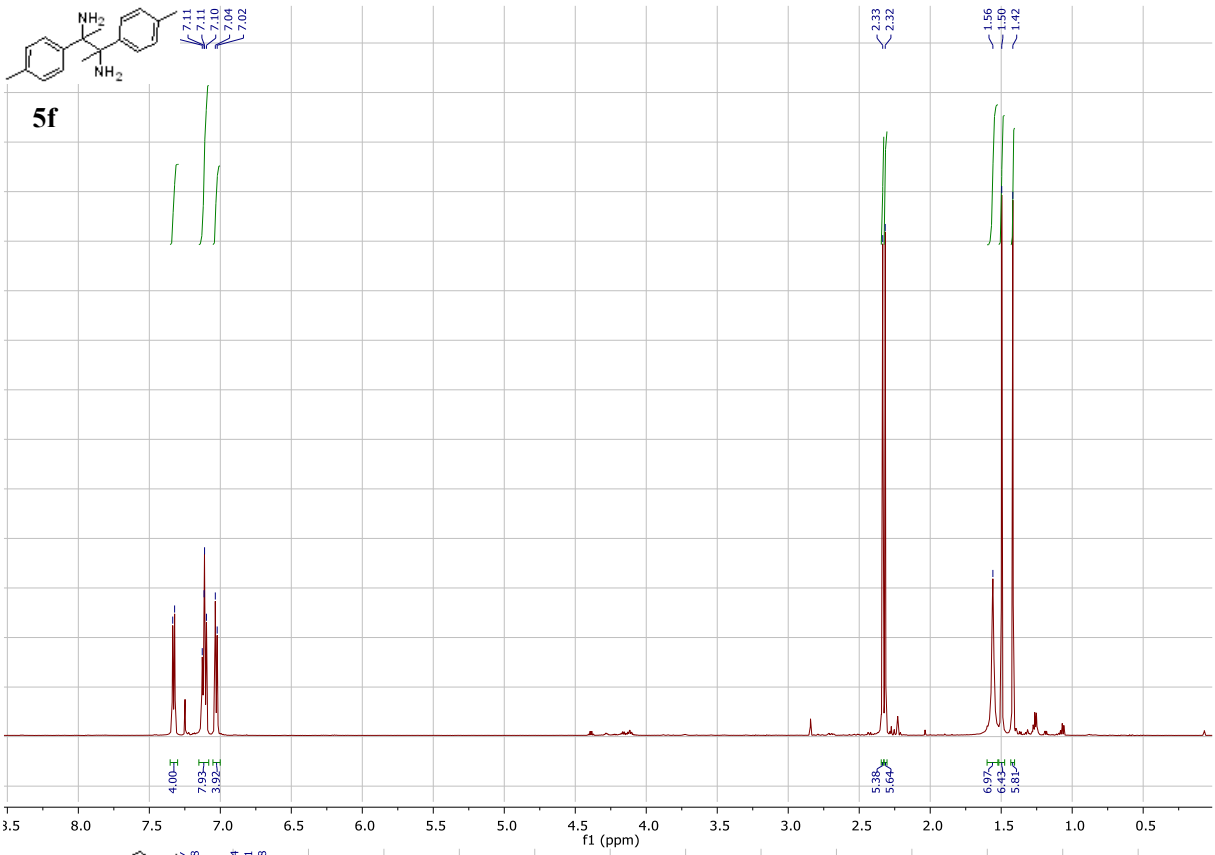

5d
7.26
7.07
7.06
1.54
1.49
1.40
4.00
3.54
3.93
3.70
6.68
6.51
6.91
f1 (ppm)

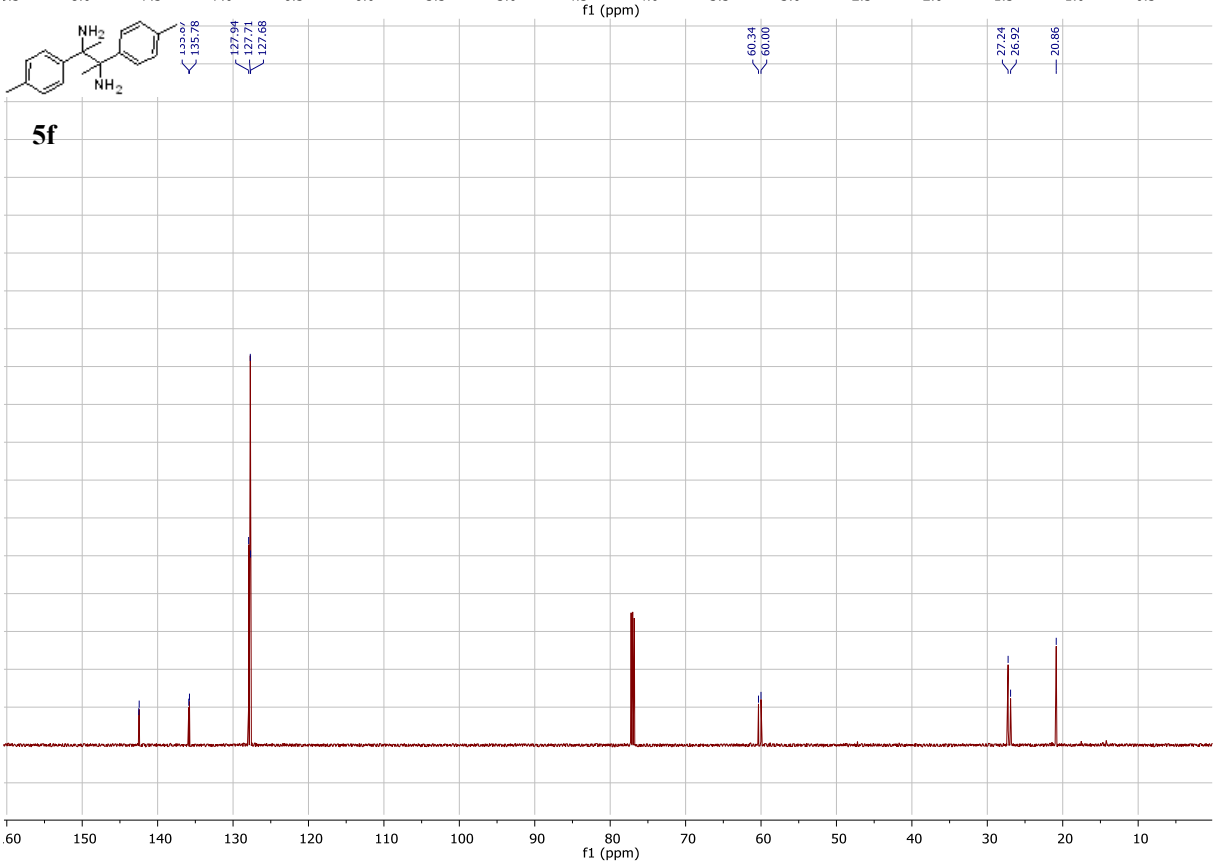

5d
130.34
130.12
129.62
129.60
120.82
120.74
60.36
60.07
26.97
26.74
f1 (ppm)

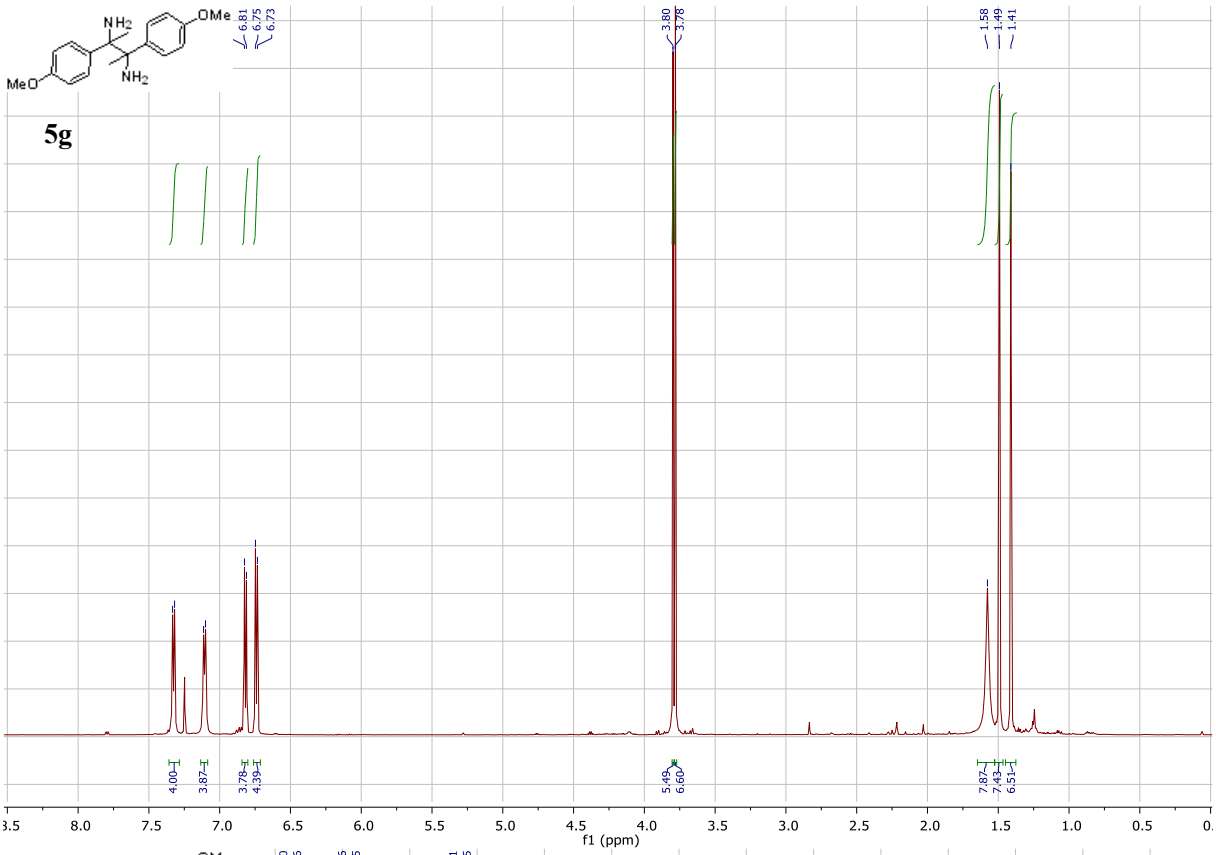

5e
1.59
1.55
1.46
8.28
3.93
4.00
4.75
5.53
5.53
f1 (ppm)

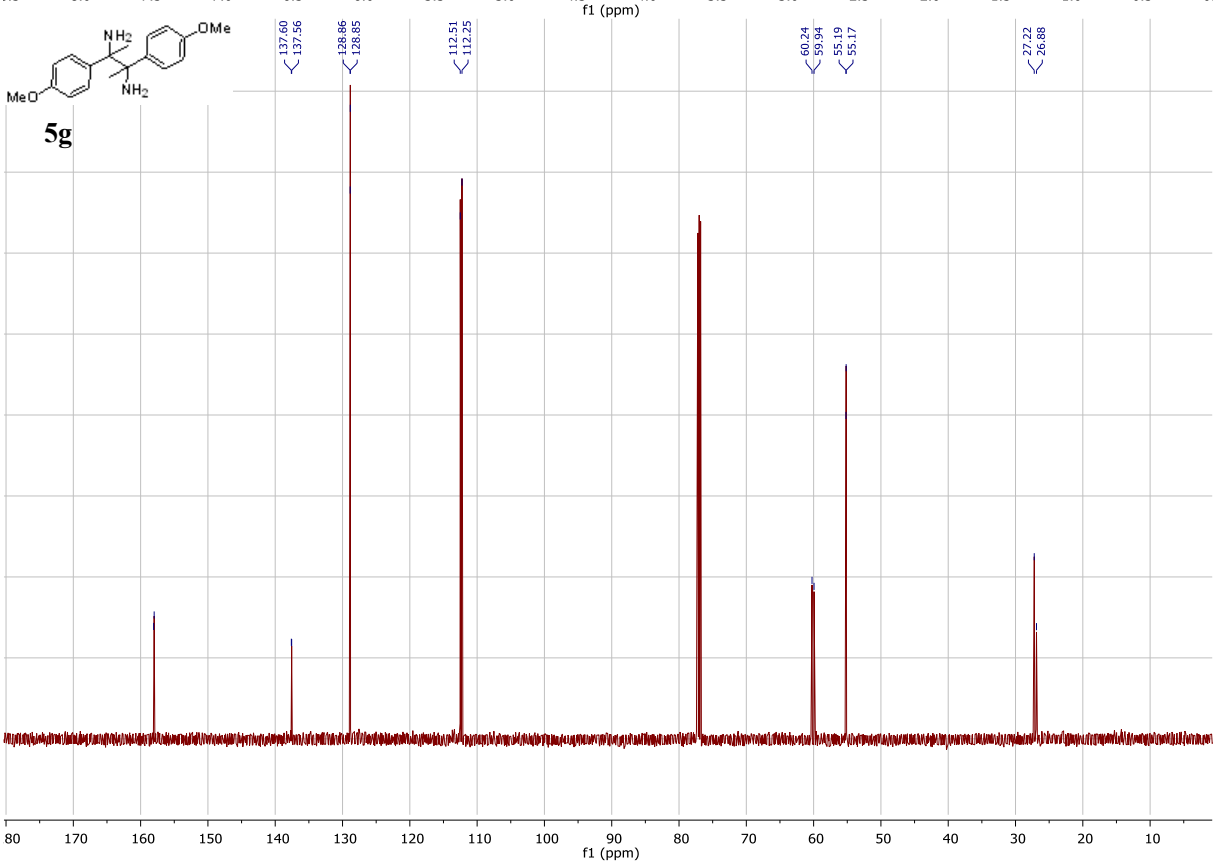

5e
129.21
129.00
128.78
128.57
f1 (ppm)

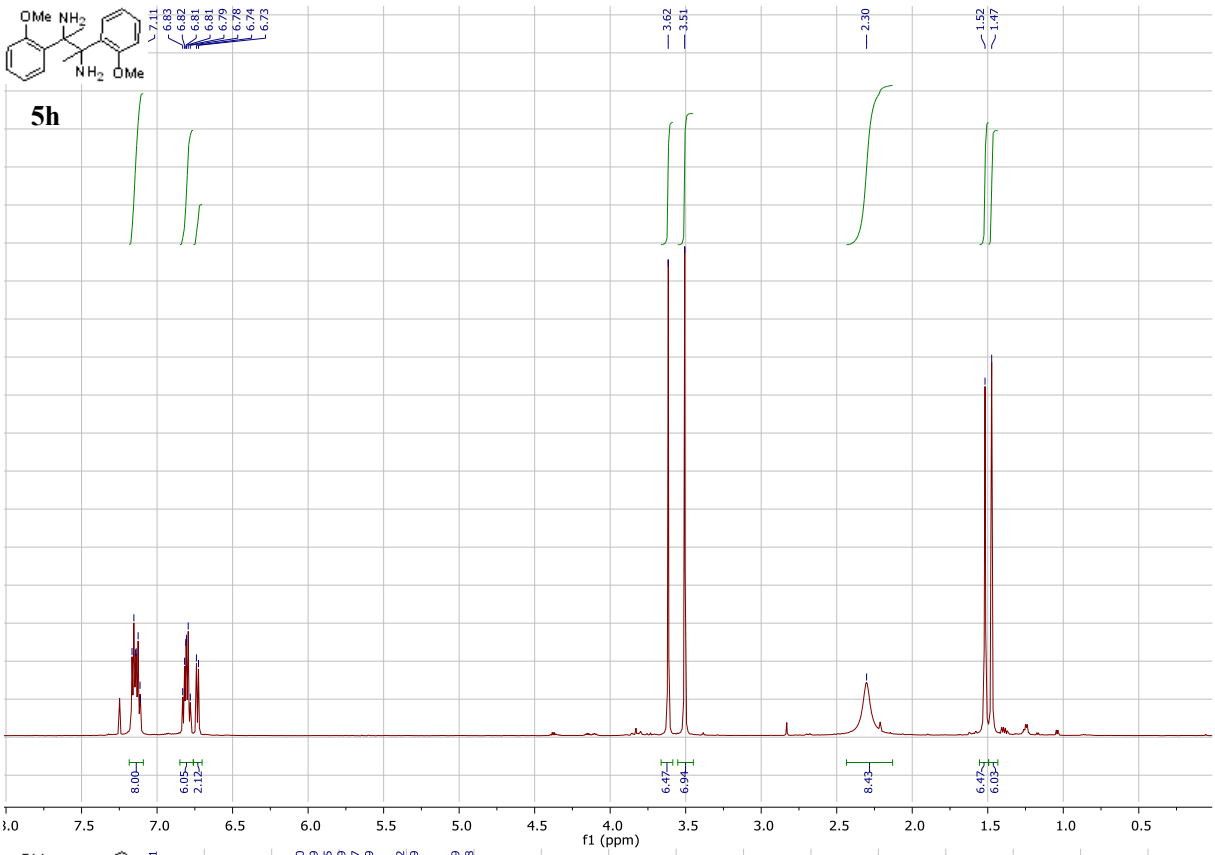

NH2
CF3
F3C
NH2
5e
-62.47
-62.50
-60.5
-61.0
-61.5
-62.0
-62.5
-63.0
-63.5
-64.0
-64.5
f1 (ppm)

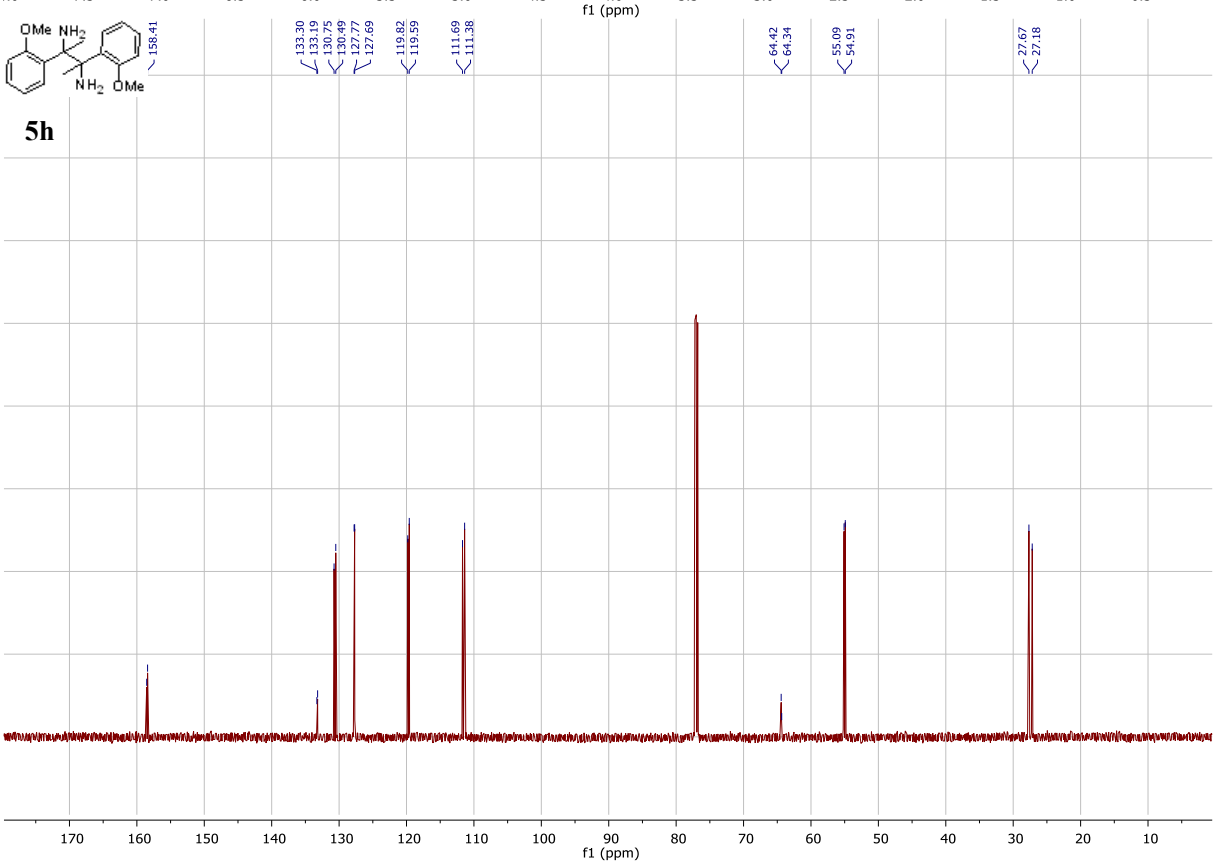

5f
7.11
7.11
7.10
7.04
7.02
2.33
2.32
1.56
1.50
1.42
4.00
7.93
3.92
5.38
5.64
6.97
6.43
5.81
f1 (ppm)

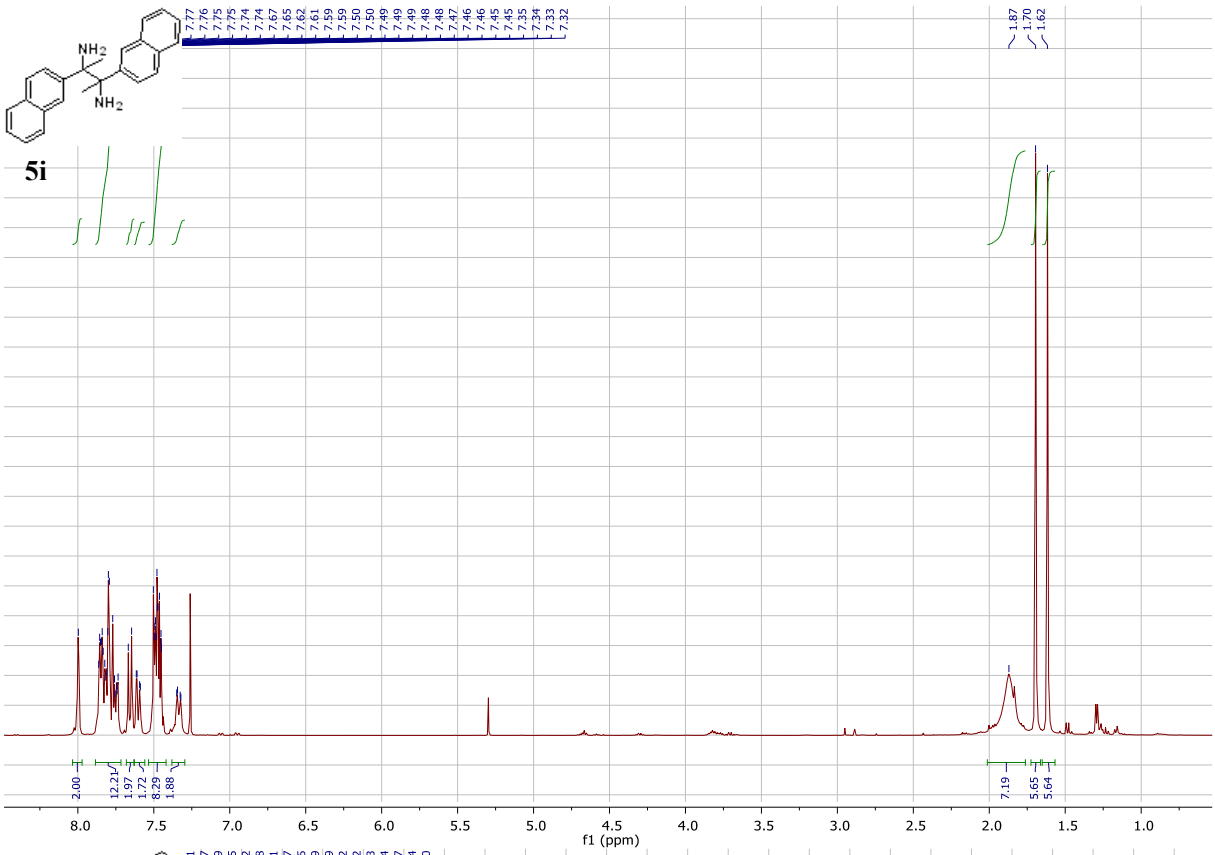

5f
135.78
127.94
127.71
127.68
60.34
60.00
27.24
26.92
20.86
f1 (ppm)

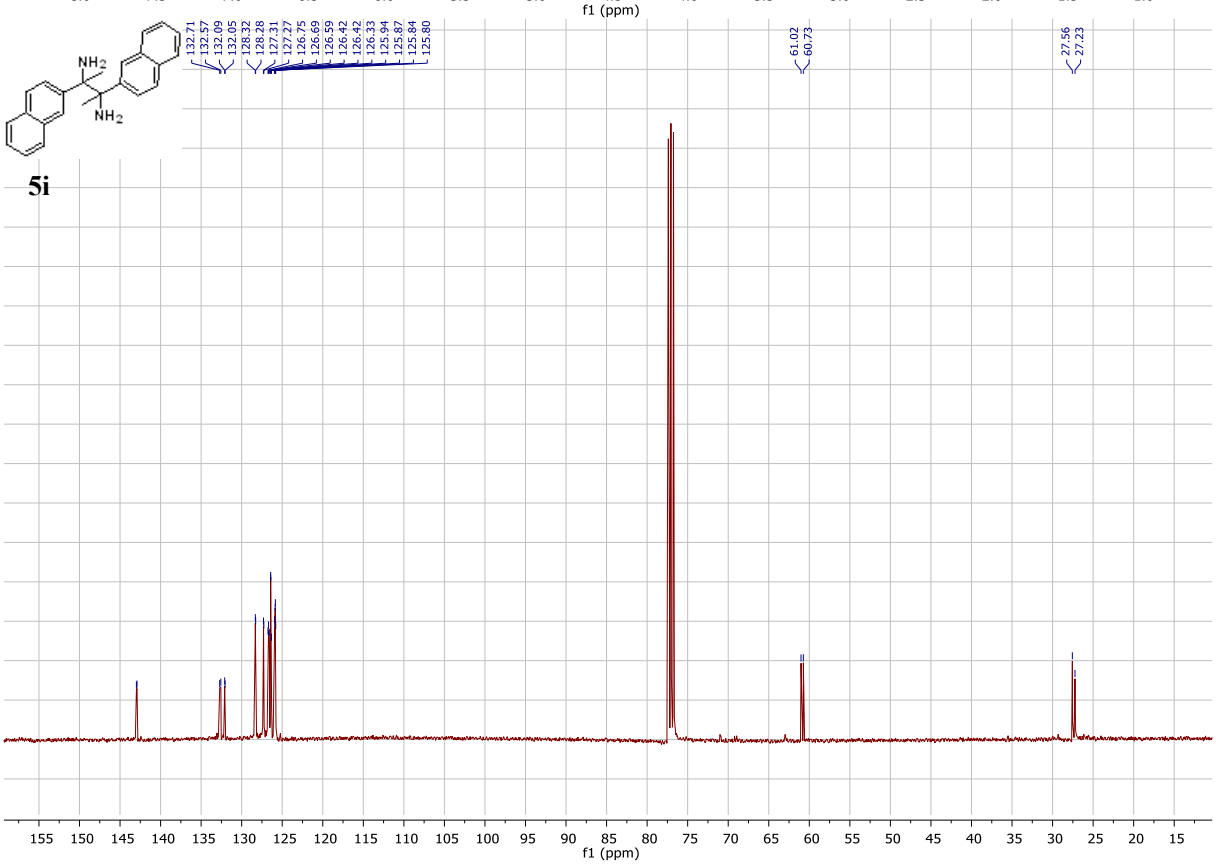

5g
6.81
6.75
6.73
3.80
3.78
1.58
1.49
1.41
4.00
3.87
3.78
4.39
5.49
6.60
7.87
7.43
6.51
f1 (ppm)

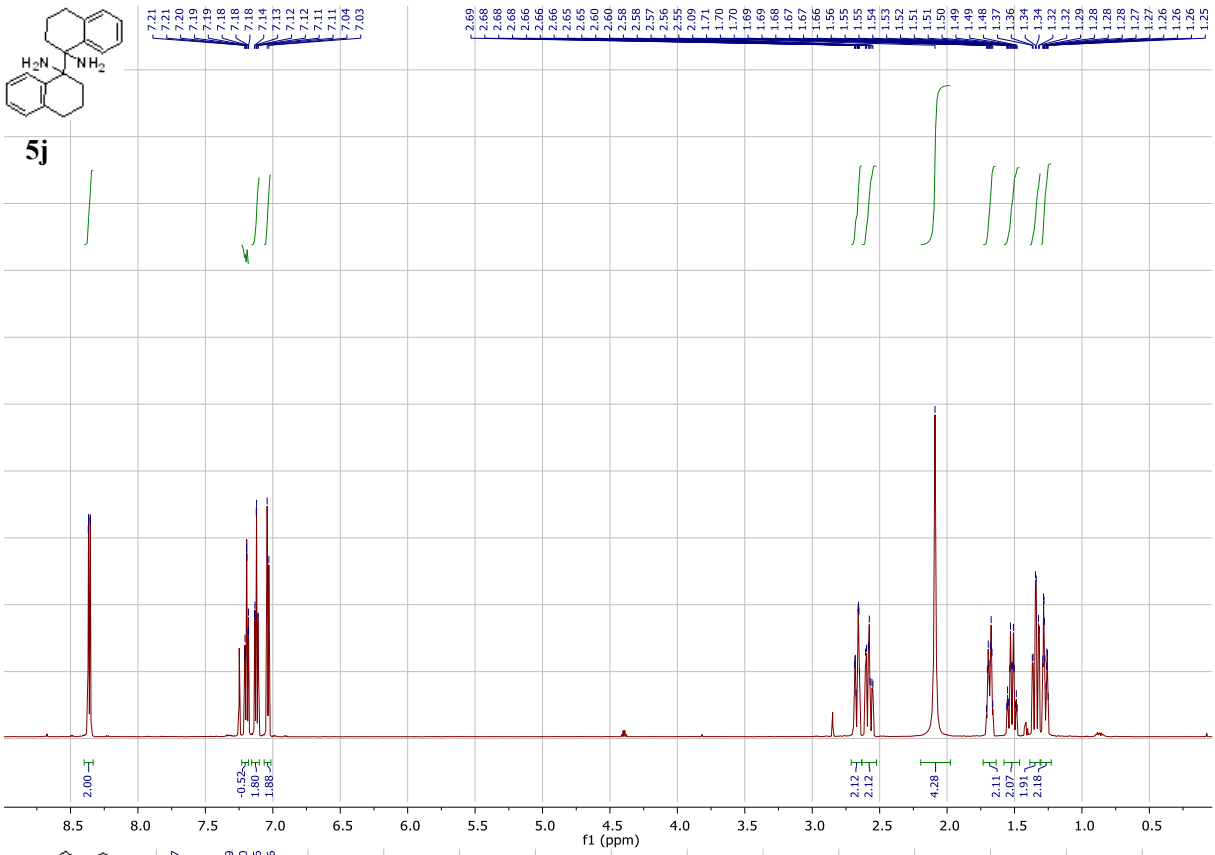

5g
137.60
137.56
128.86
128.85
112.51
112.25
60.24
59.94
55.19
55.17
27.22
26.88
f1 (ppm)

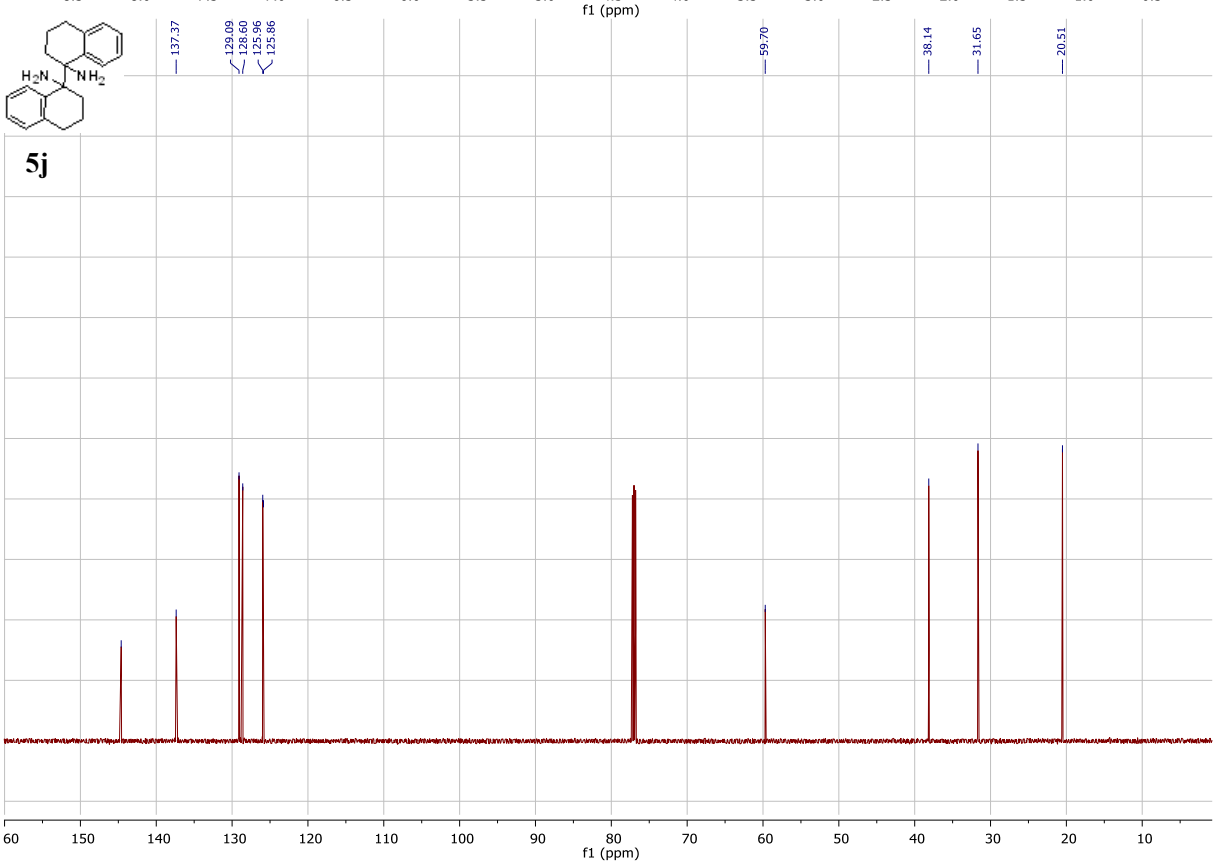

5h
7.11
6.83
6.82
6.81
6.81
6.79
6.78
6.74
6.73
3.62
3.51
2.30
1.52
1.47
8.00
6.05
2.12
6.47
6.94
8.43
6.47
6.03
f1 (ppm)

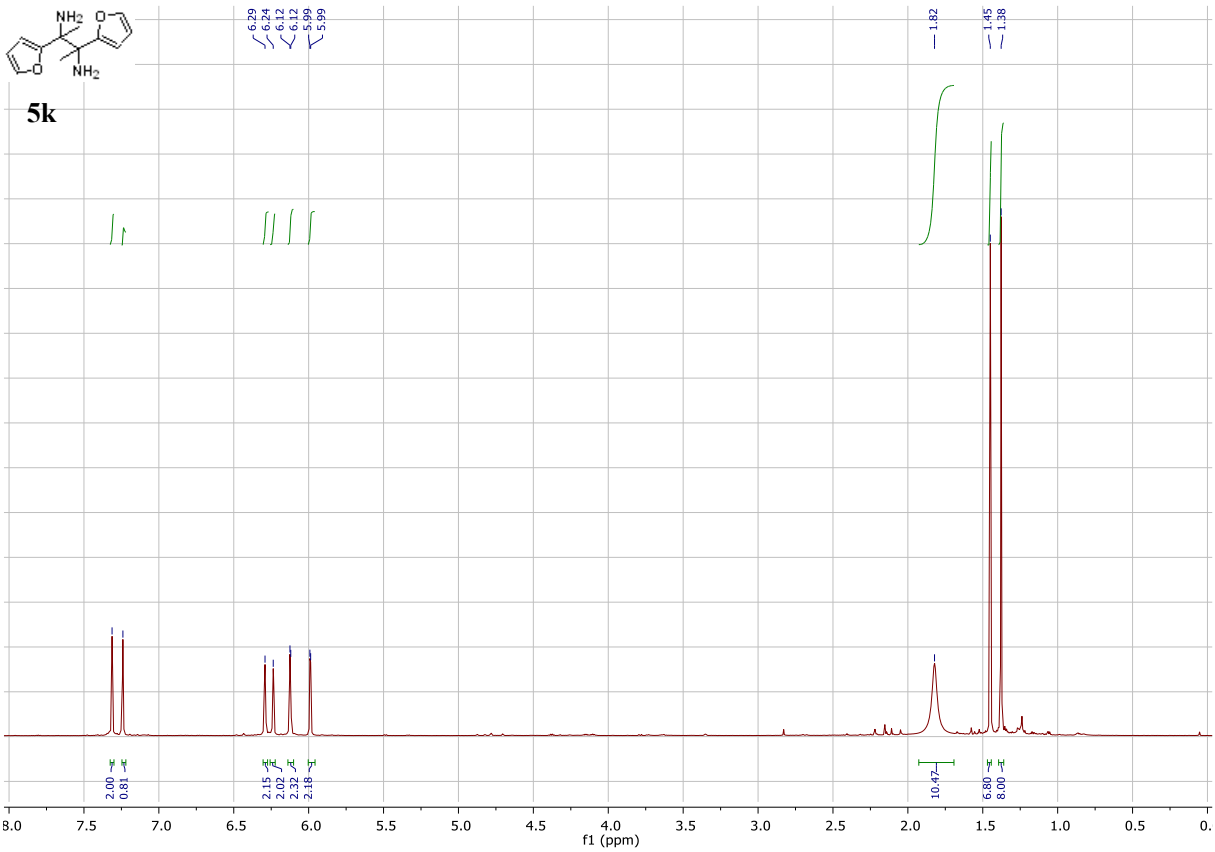

5h
158.41
133.30
133.19
130.75
130.49
127.77
127.69
119.82
119.59
111.69
111.38
64.42
64.34
55.09
54.91
27.67
27.18
f1 (ppm)

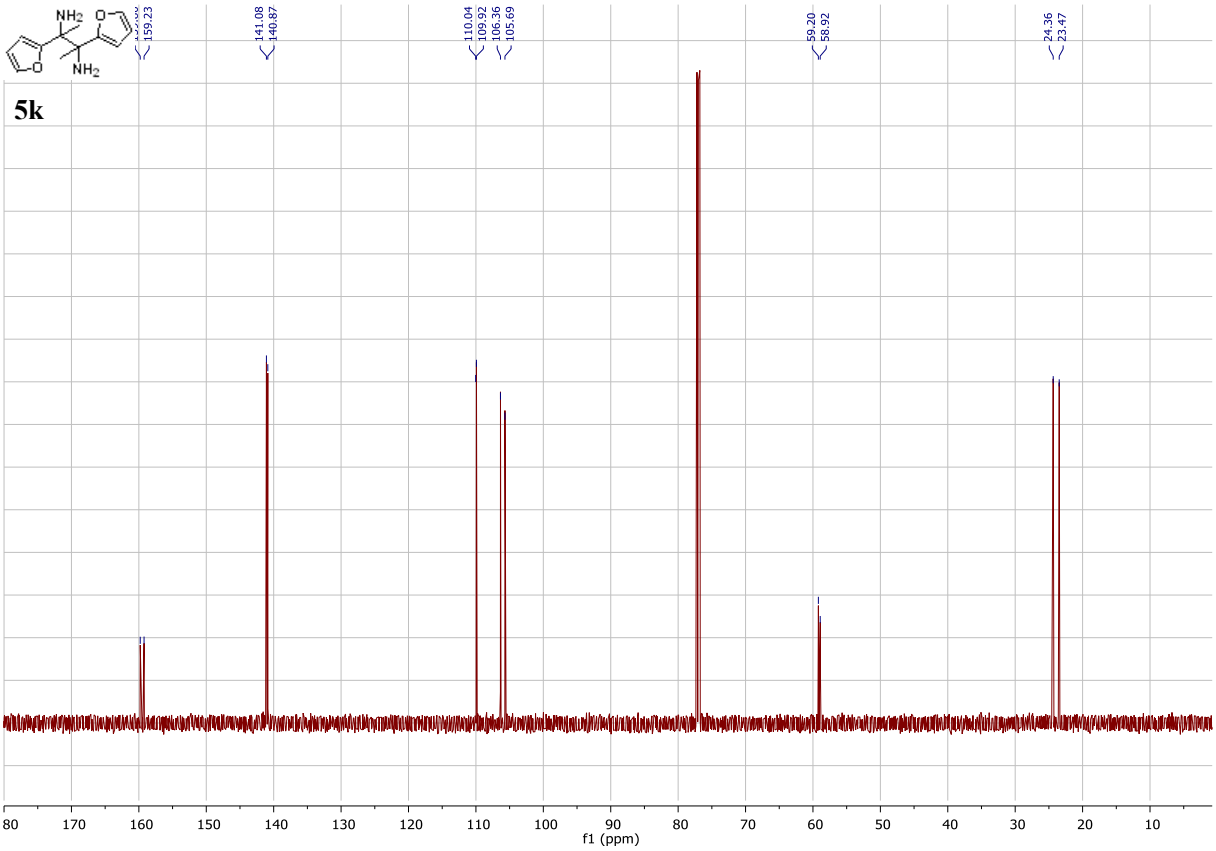

5i
NH2
NH2
7.77
7.76
7.75
7.75
7.74
7.74
7.67
7.65
7.62
7.61
7.59
7.59
7.50
7.50
7.49
7.49
7.49
7.48
7.48
7.47
7.46
7.46
7.45
7.45
7.35
7.34
7.33
7.32
1.87
1.70
1.62
2.00
12.21
1.97
1.72
8.29
1.88
7.19
5.65
5.64
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

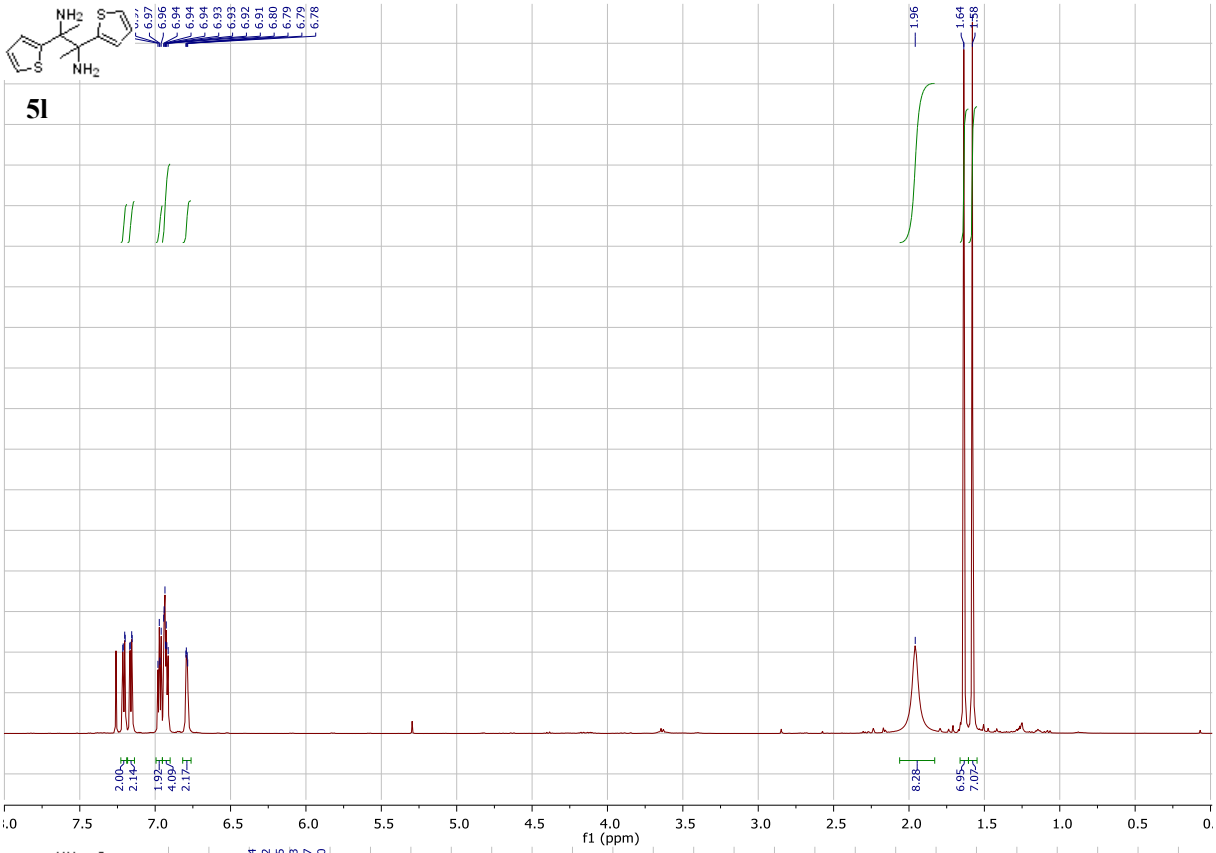

5i
NH2
NH2
132.71
132.57
132.09
132.05
128.32
128.28
127.31
127.27
126.75
126.69
126.59
126.42
126.33
125.94
125.87
125.84
125.80
61.02
60.73
27.56
27.23
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
f1 (ppm)

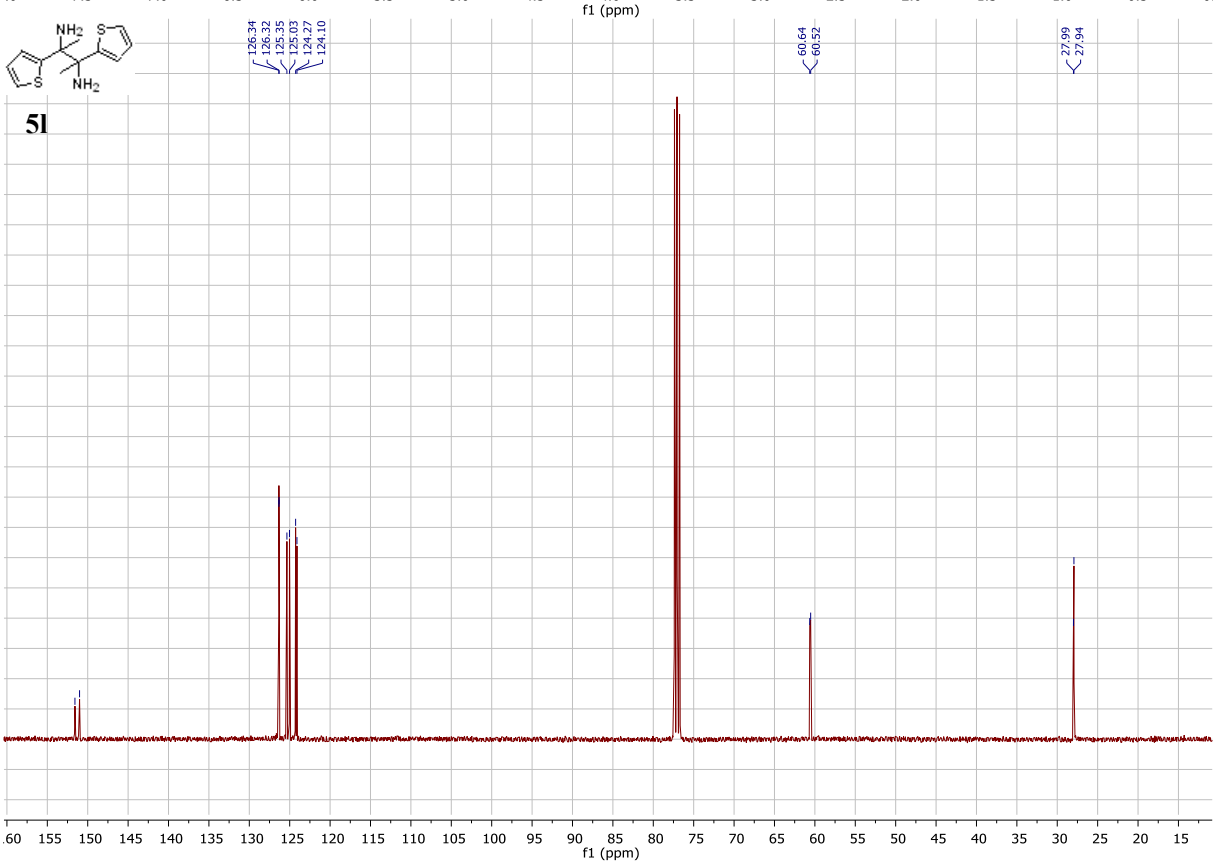

5j
7.21 7.21 7.20 7.19 7.19 7.18 7.18 7.18 7.14 7.13 7.12 7.12 7.11 7.11 7.04 7.03
2.69 2.68 2.68 2.68 2.66 2.66 2.65 2.65 2.60 2.60 2.58 2.58 2.57 2.56 2.55 2.09 1.71 1.70 1.70 1.69 1.69 1.68 1.67 1.67 1.66 1.56 1.55 1.55 1.54 1.53 1.52 1.51 1.51 1.50 1.49 1.49 1.48 1.37 1.36 1.34 1.34 1.32 1.32 1.29 1.28 1.28 1.28 1.27 1.27 1.26 1.26 1.26 1.25
2.00
0.52 1.80 1.88
2.12 2.12
4.28
2.11 2.07 1.91 2.18
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

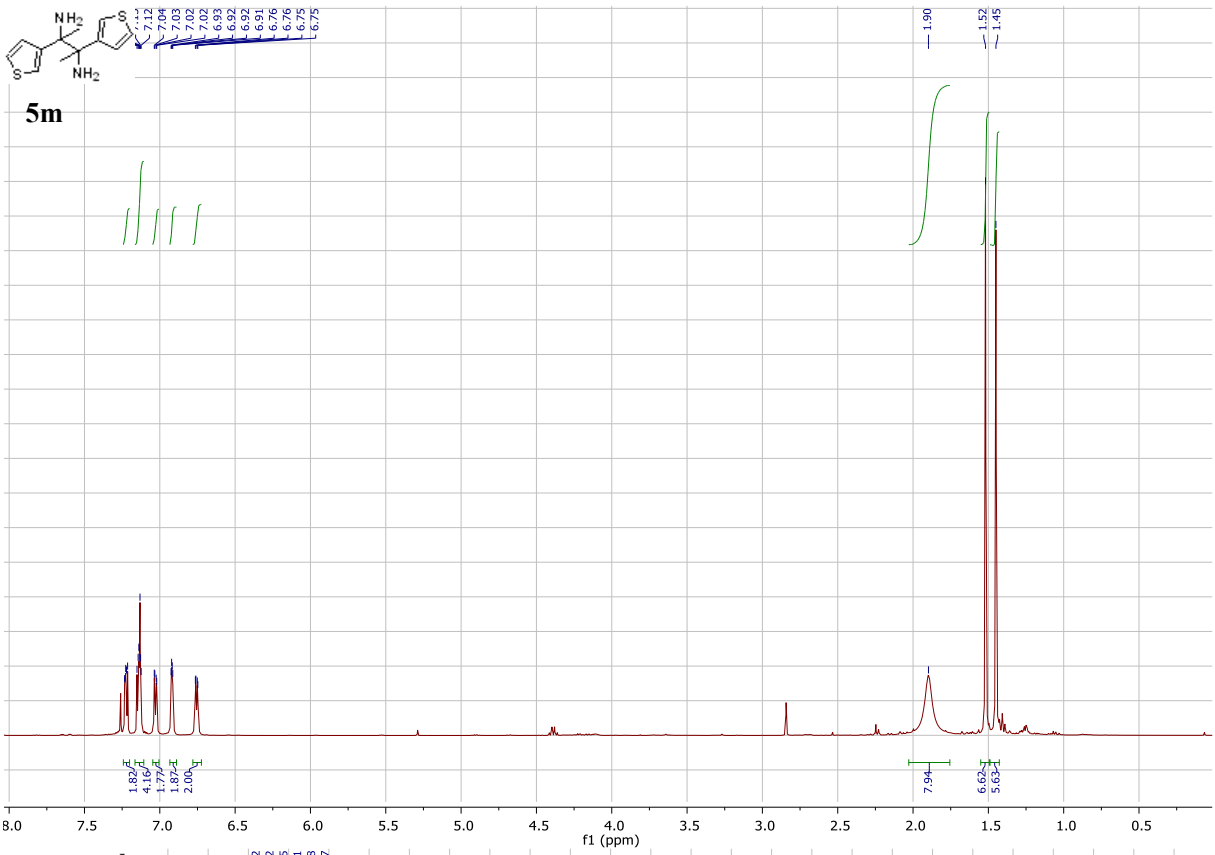

5j
137.37
129.09 128.60 125.96 125.86
59.70
38.14
31.65
20.51
60 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

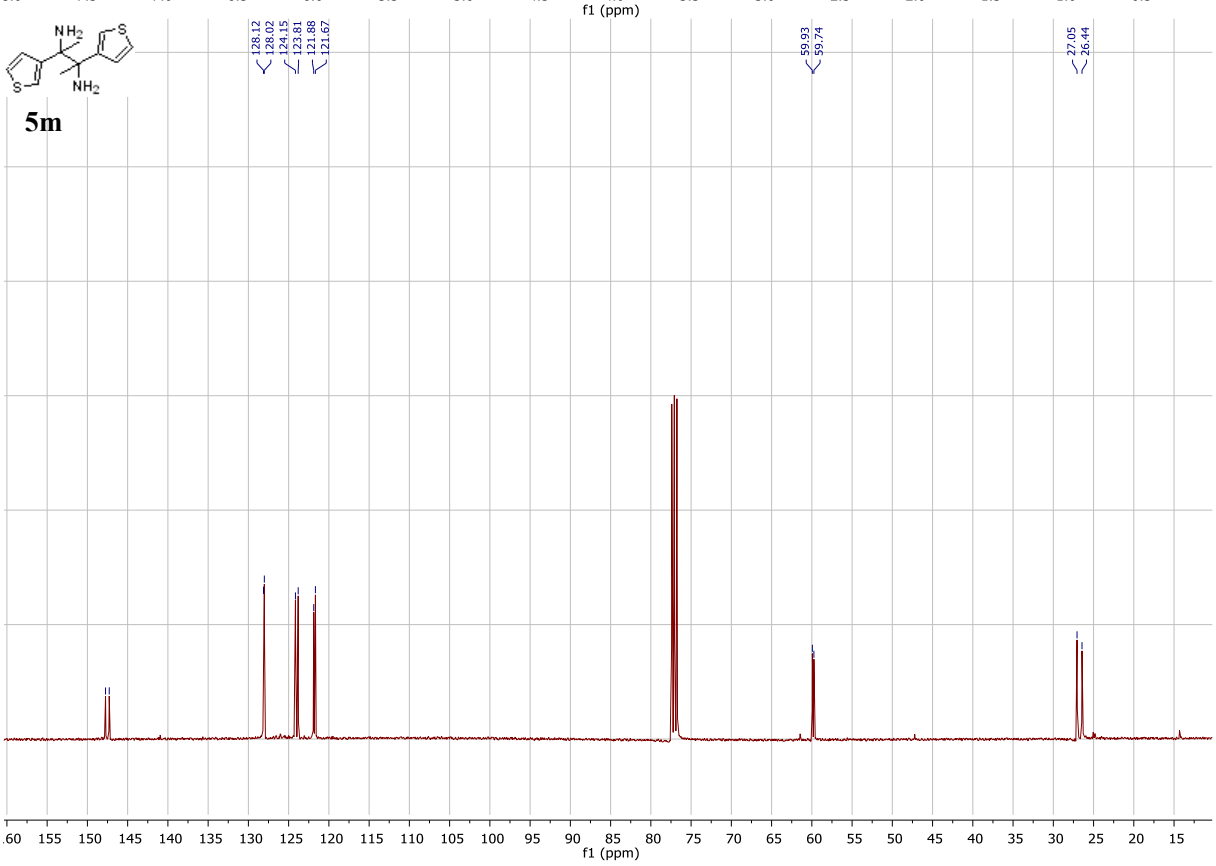

5k
6.29
6.24
6.12
6.12
5.99
5.99
1.82
1.45
1.38
2.00
0.81
2.15
2.02
2.32
2.18
10.47
6.80
8.00
f1 (ppm)


5k
159.23
141.08
140.87
110.04
109.92
106.36
105.69
59.20
58.92
24.36
23.47
f1 (ppm)

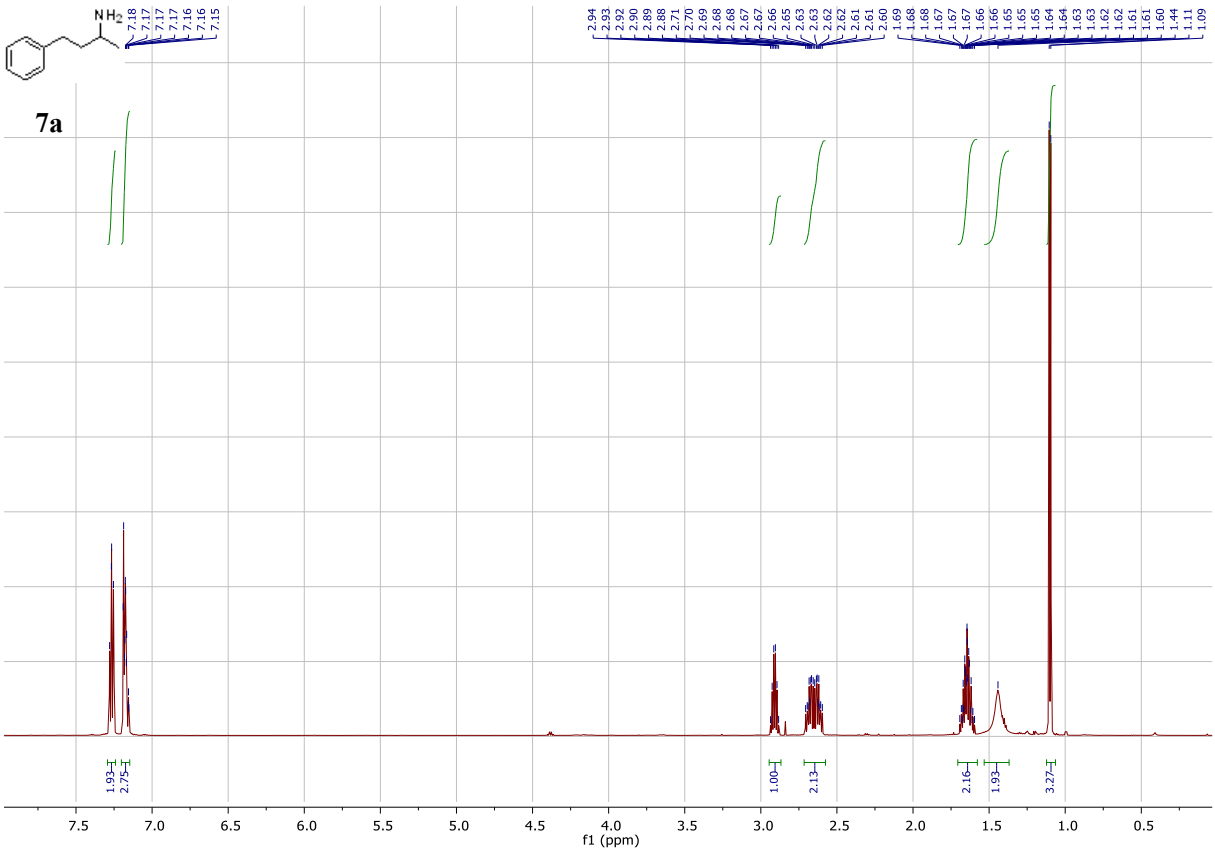

5l
f1 (ppm)

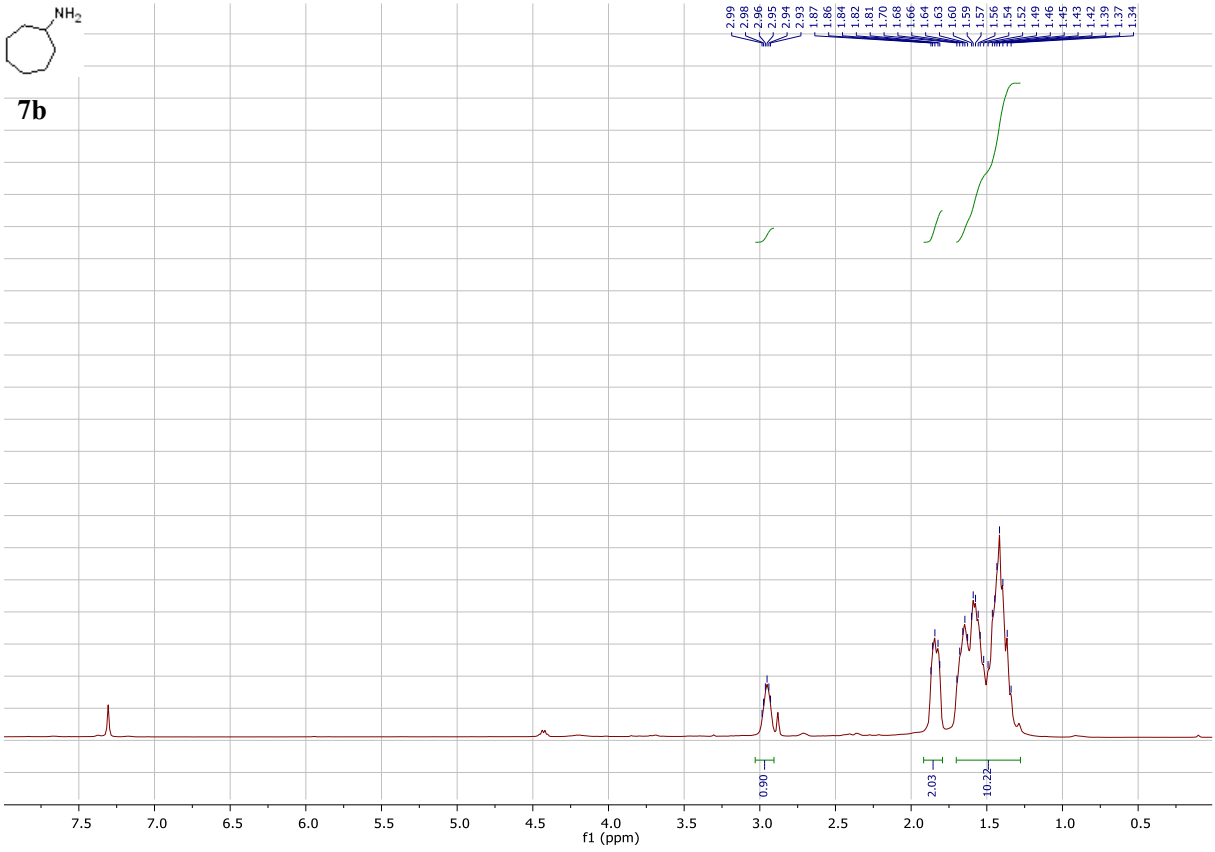

5l
f1 (ppm)

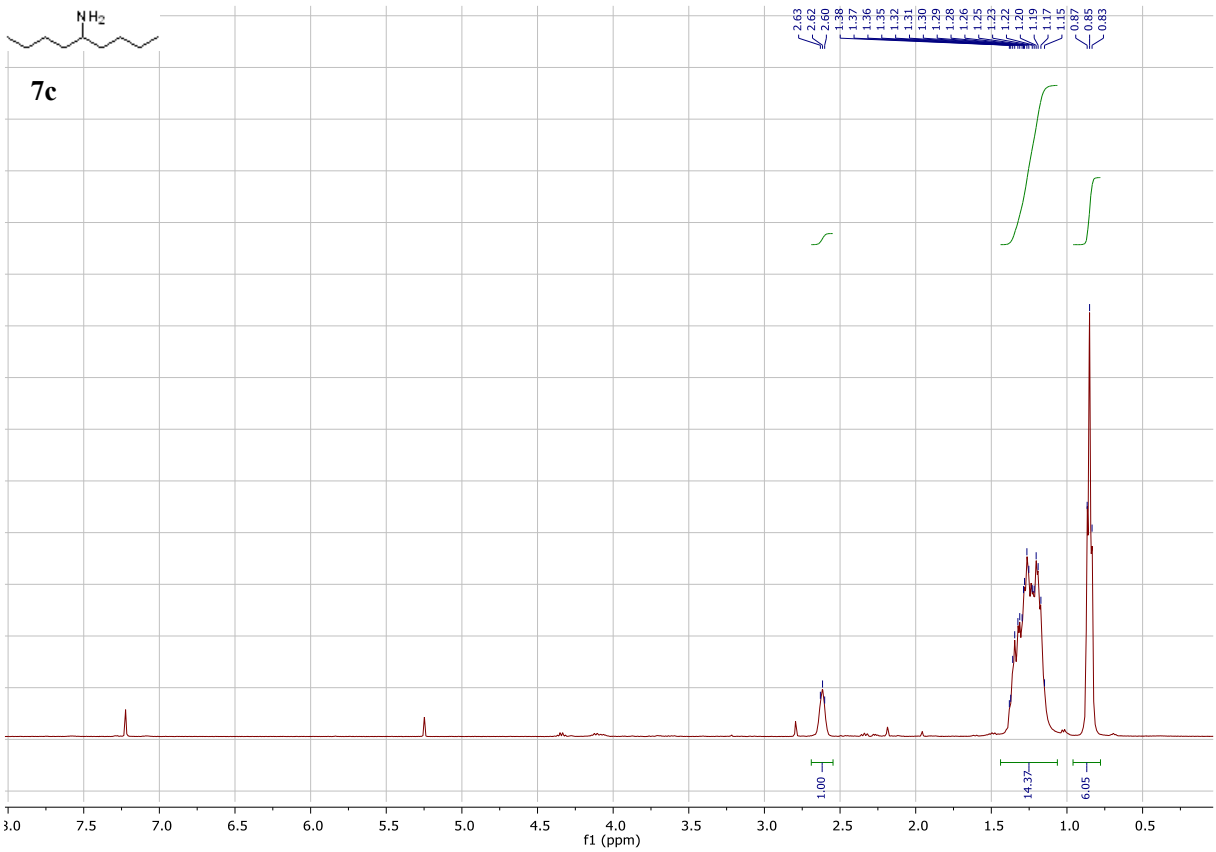

5m
7.12
7.04
7.03
7.02
7.02
6.93
6.92
6.92
6.91
6.76
6.76
6.75
6.75
1.90
1.52
1.45
1.82
4.16
1.77
1.87
2.00
7.94
6.62
5.63
f1 (ppm)

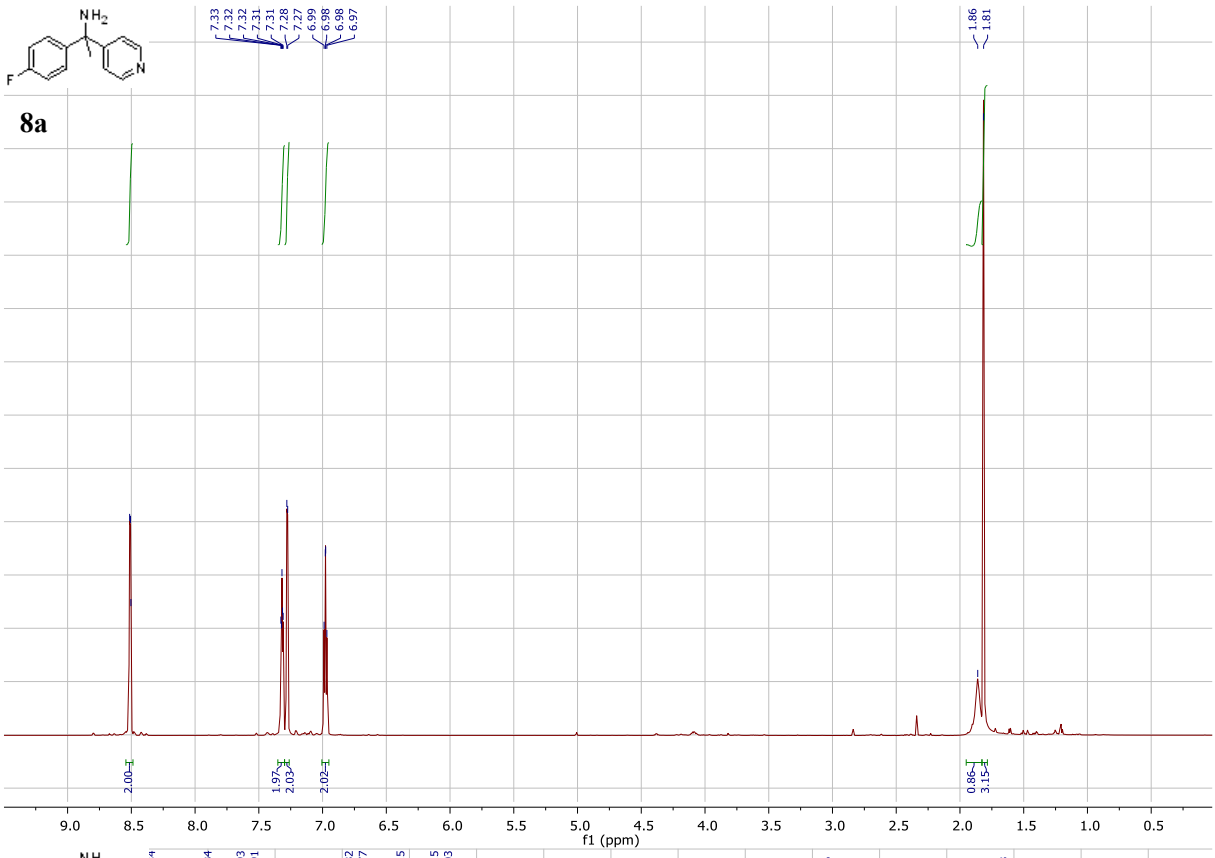

5m
128.12
128.02
124.15
123.81
121.88
121.67
59.93
59.74
27.05
26.44
f1 (ppm)

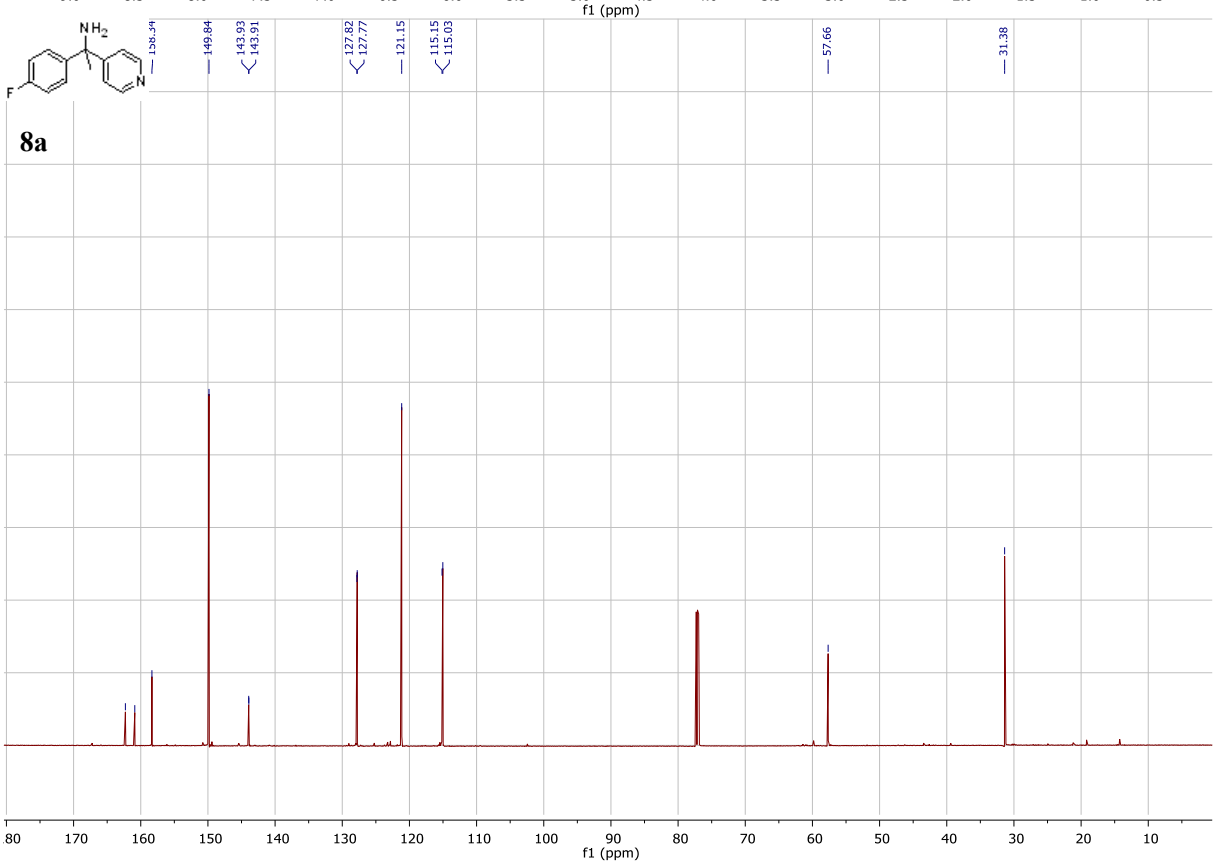
5n

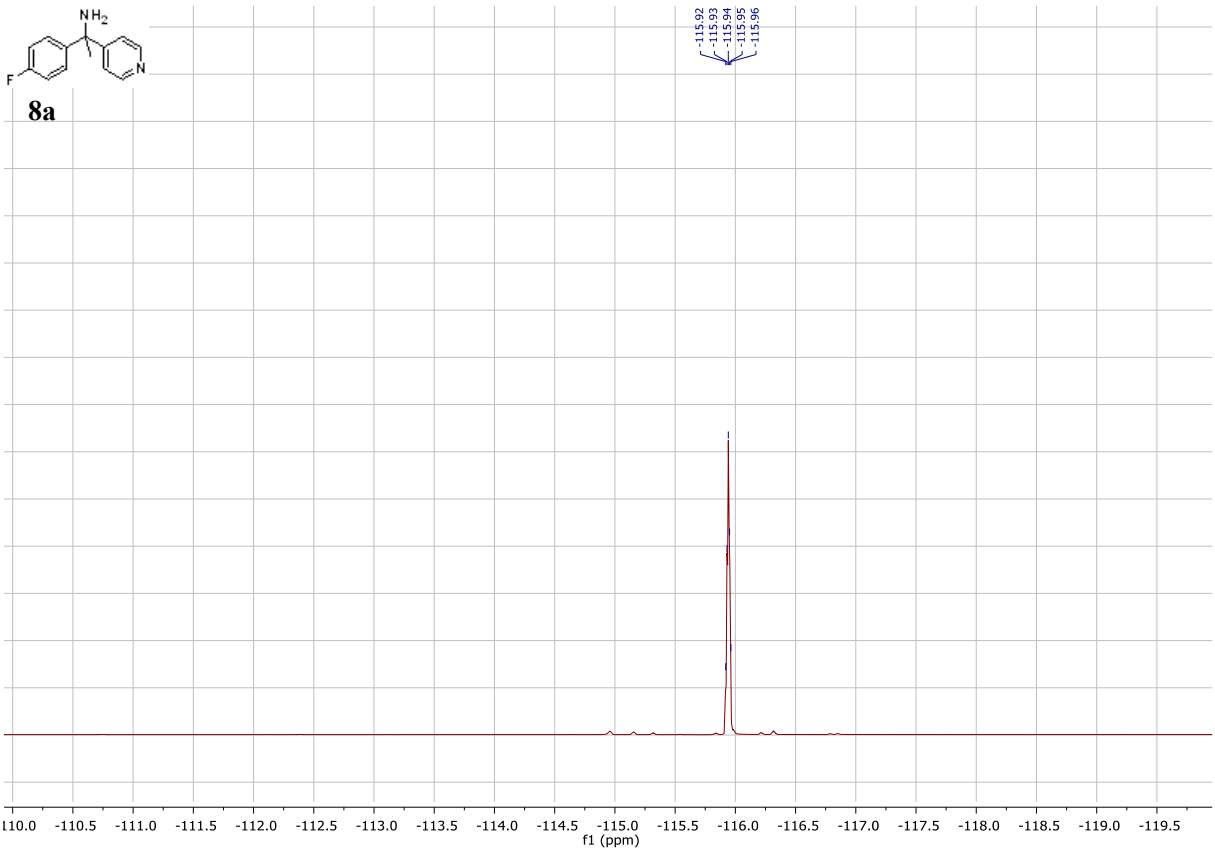

7a
NH2
7.18 7.17 7.17 7.17 7.16 7.15
2.94 2.93 2.92 2.90 2.89 2.88 2.71 2.70 2.69 2.68 2.68 2.67 2.67 2.66 2.65 2.63 2.63 2.62 2.62 2.61 2.61 2.60
1.69 1.68 1.68 1.67 1.67 1.66 1.66 1.65 1.65 1.65 1.64 1.64 1.63 1.63 1.62 1.62 1.61 1.61 1.60 1.44 1.11 1.09
1.93 2.75 1.00 2.13 2.16 1.93 3.27
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

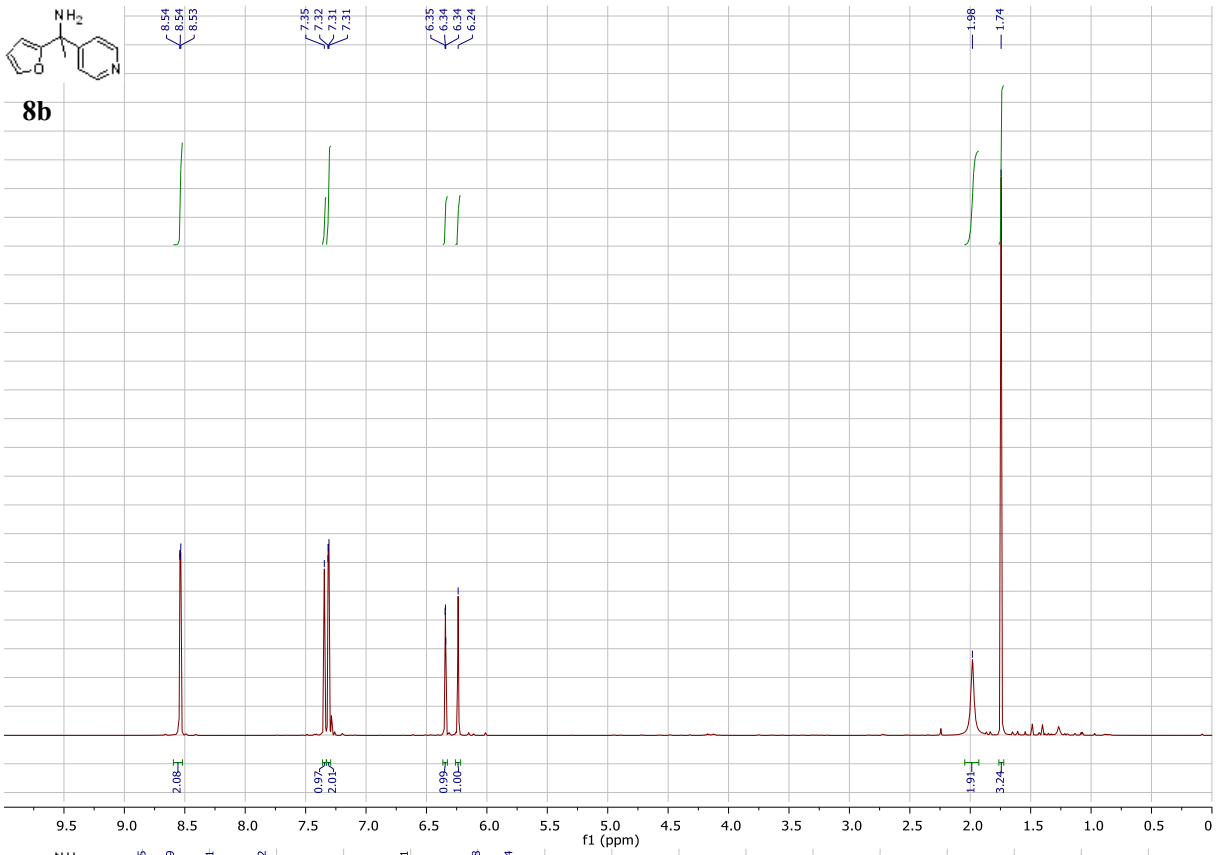

7b
NH2
2.99 2.98 2.96 2.95 2.94 2.93 1.87 1.86 1.84 1.82 1.81 1.70 1.68 1.66 1.64 1.63 1.60 1.59 1.57 1.56 1.54 1.52 1.49 1.46 1.45 1.43 1.42 1.39 1.37 1.34
0.90 2.03 10.22
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

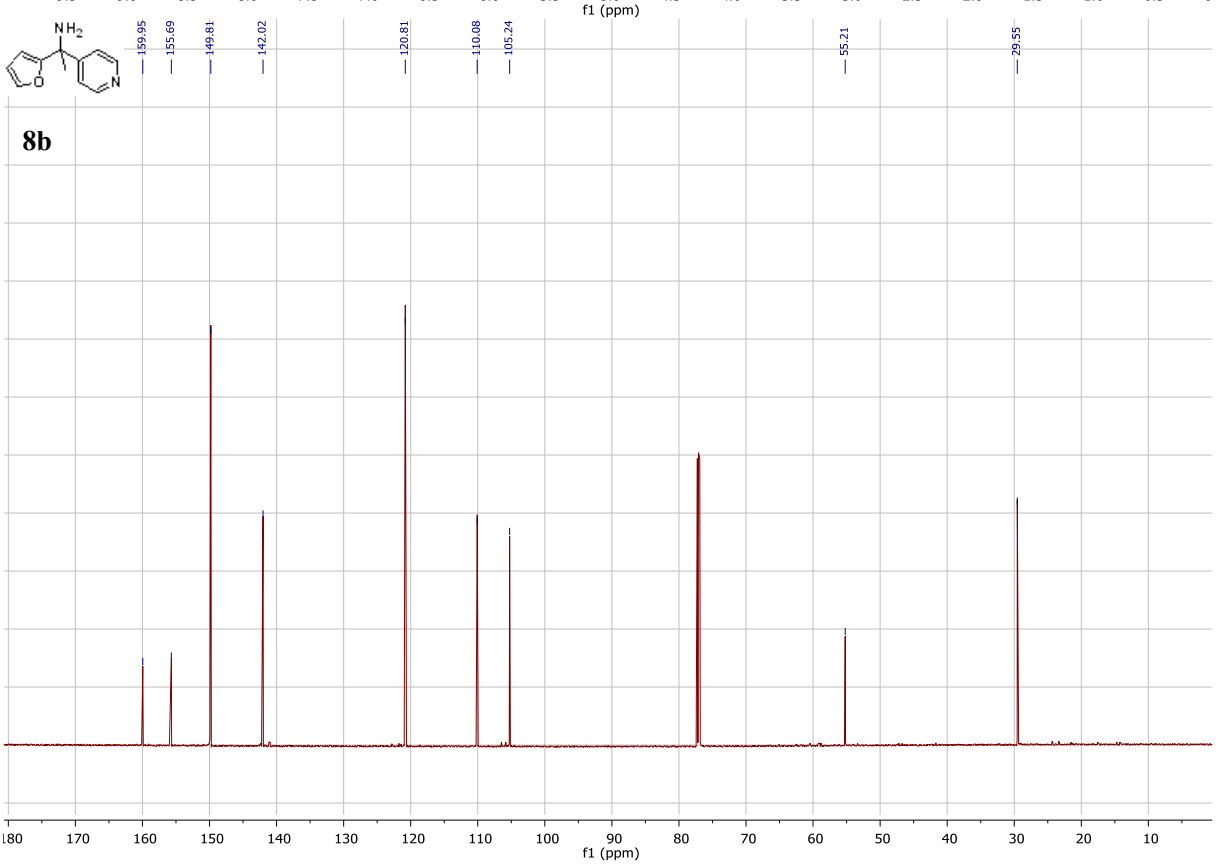

NH2
7c
2.63
2.62
2.60
1.38
1.37
1.36
1.35
1.32
1.31
1.30
1.29
1.28
1.26
1.25
1.23
1.22
1.20
1.19
1.17
1.15
0.87
0.85
0.83
1.00
14.37
6.05
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

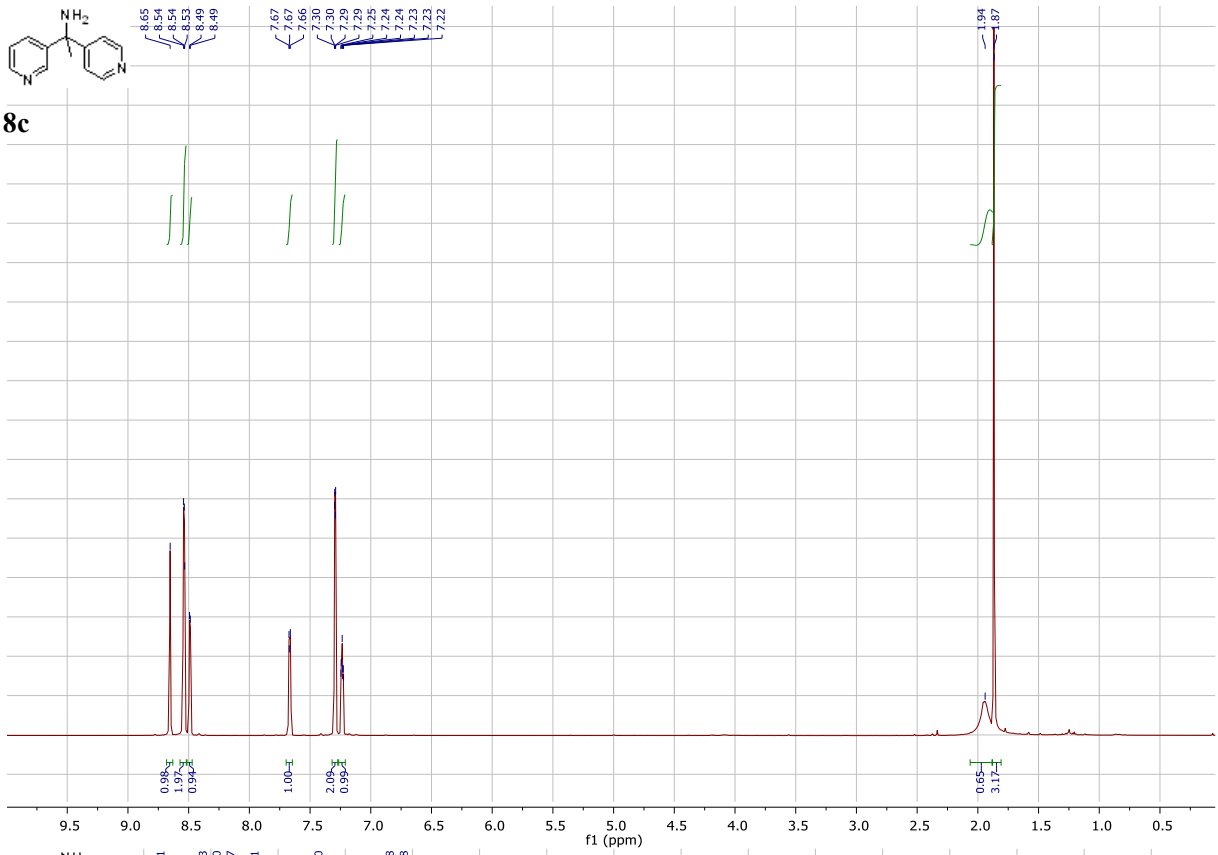

8a
7.33
7.32
7.32
7.31
7.31
7.28
7.27
6.99
6.98
6.98
6.97
1.86
1.81
2.00
1.97
2.03
2.02
0.86
3.15
f1 (ppm)

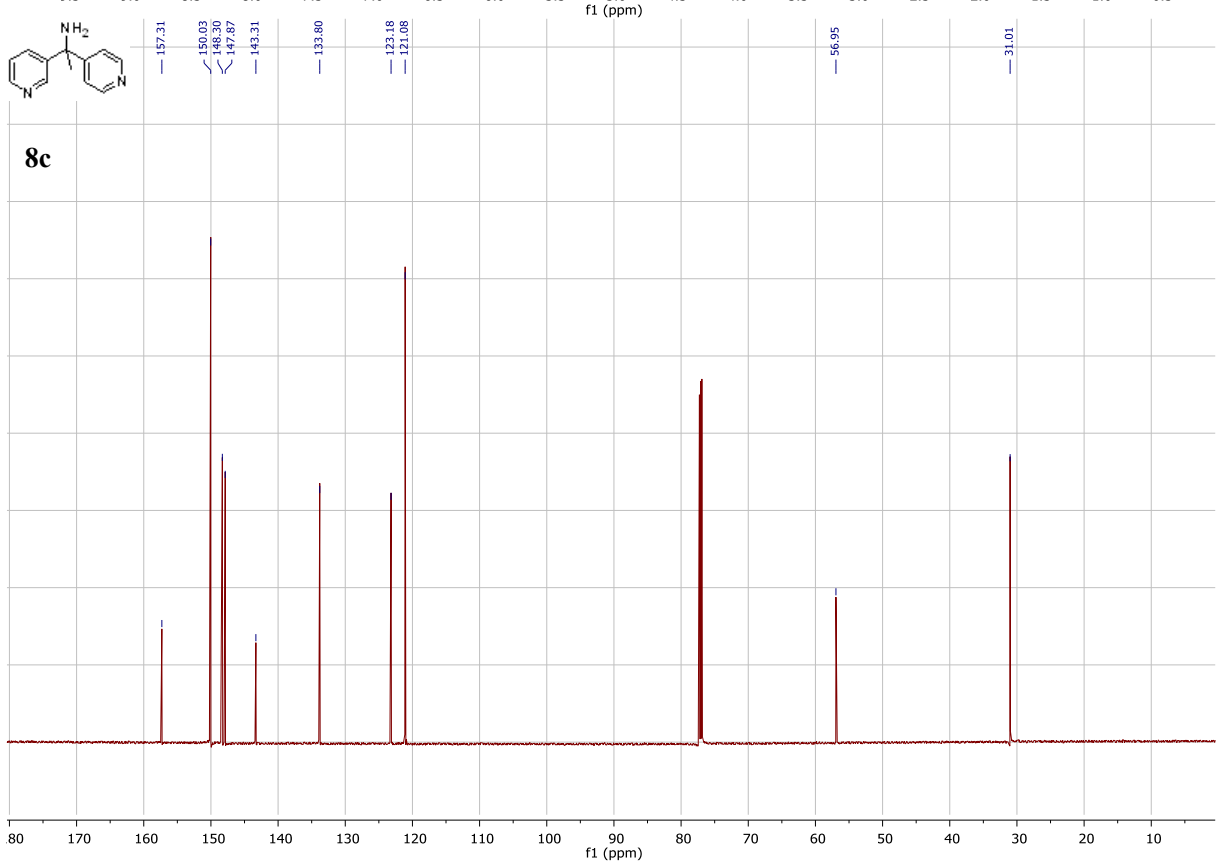

8a
149.84
143.93
143.91
127.82
127.77
121.15
115.15
115.03
57.66
31.38
f1 (ppm)


NH2
F
N
8a
-115.92
-115.93
-115.94
-115.95
-115.96
-110.0 -110.5 -111.0 -111.5 -112.0 -112.5 -113.0 -113.5 -114.0 -114.5 -115.0 -115.5 -116.0 -116.5 -117.0 -117.5 -118.0 -118.5 -119.0 -119.5
f1 (ppm)


8b
8.54
8.54
8.53
7.35
7.32
7.31
7.31
6.35
6.34
6.34
6.24
1.98
1.74
2.08
0.97
2.01
0.99
1.00
1.91
3.24
f1 (ppm)


8b
159.95
155.69
149.81
142.02
120.81
110.08
105.24
55.21
29.55
f1 (ppm)


8c
8.65
8.54
8.54
8.53
8.49
8.49
7.67
7.67
7.66
7.30
7.30
7.29
7.29
7.25
7.24
7.24
7.23
7.23
7.22
1.94
1.87
0.98
1.97
0.94
1.00
2.09
0.99
0.65
3.17
f1 (ppm)


8c
157.31
150.03
148.30
147.87
143.31
133.80
123.18
121.08
56.95
31.01
f1 (ppm)