Supporting Information For

Transition-metal-free catalytic hydroborative reduction of amides to amines

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1. General considerations

1.1 Materials

All manipulations were carried out using standard Schlenk, high vacuum, and glovebox techniques. Glassware was dried in a 140 ºC oven over 4 h prior to use. KO*t*Bu (95%), BEt_3 (1M solution in THF), $KBEt_3H$ (1M solution in THF) and $B(C_6F_5)_3$ (97%) were purchased from Aladdin and used as received. BPh_3 (96%) and HBpin (97%) were purchased from Alfa and used as received. Flash colum chromatography was performed on silica gel (particle size 300-400 mesh ASTM), purchased from Yantai, China. The other bases and aldehydes were obtained from commerical sources and used as received. All solvents were obtained from commercial sources and dried and degassed according to standard procedures. Secondary and tertiary aromatic amides are all known compounds, and are synthesized according to literature procedures.[1] All heating reactions were performed on the IKA RCT Basic magnetic stirring apparatus with an oil bath.

1.2 Analytical Methods

NMR spectra data were obtained on Avance (III) HD 400 MHz instruments. ^{1}H NMR and ^{13}C NMR spectra were referenced to residual protic solvent peaks or TMS signal (0 ppm). ^{19}F NMR chemical shifts were externally referenced to CCl_3F (0 ppm). Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, coupling constant (s) in Hz, integration). Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). GC was performed on a Shimadzu GC-2010 plus spectrometer. GC/MS was performed on a Shimadzu GCMS-QP2010 Plus spectrometer. The photophysical measurements were performed on the U-5100 spectrophotometer (HITACHI) and FLS980 fluorescence spectrophotometer (Edinburgh). Melting points were determined on a microscopic apparatus and were uncorrected. High-resolution mass spectra (HRMS) analyses were performed on Waters SYNAPT G2-Si mass spectrometer.

2. The typical reaction procedures

2.1 Hydroboration of primary amides

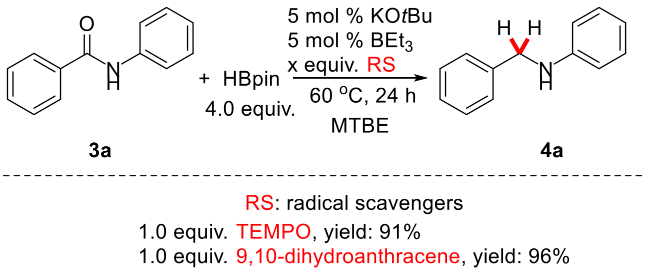
In an argon filled glovebox, a 10 mL dried Schlenk tube equipped with a magnetic stir bar was charged with KO*t*Bu (5 mol %), BEt_3 (5 mol %), amide (0.5 mmol), HBpin (4.0 equiv.), MTBE (2.0 mL). The tube was then sealed with a Teflon plug under an argon atmosphere, and removed from the glovebox. Then, the solution was stirred at 25 °C for 48 h. After that, the residue was filtrated though Celite. The filtrate was collected and the corresponding reduced amines were concentrated in vacuum. Consequently, 2.0 mL 1 M aqueous HCl was added to the concentrated amines followed by addition of 10 mL Et_2O, stirring at 25 °C for 6 h. The corresponding amine hydrochloride salt was purified by washing with Et_2O. Isolated amine hydrochlorides were characterized through NMR spectroscopy in DMSO-*d6*.

2.2 Hydroboration of secondary and tertiary amines

In an argon filled glovebox, a 10 mL dried Schlenk tube equipped with a magnetic stir bar was charged with KO*t*Bu (5 mol %), BEt_3 (5 mol %), amide (0.5 mmol), HBpin (4.0 equiv.), MTBE (2.0 mL). The tube was then sealed with a Teflon plug under an argon atmosphere, and removed from the glovebox. Then, the solution was stirred at 60 °C for 24 h. After this time, the reaction mixture was cooled to room temperature, and quenched by the addition of 1 mL of water. The crude mixture was extracted with ethyl acetate and the combined organic layers were dried over $MgSO_4$. The crude product was purified by silica gel column chromatography using the ethyl acetate/petroleum ether mixture.

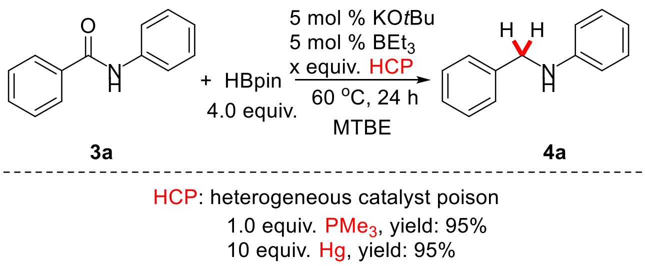
3. The mechanism studies

3.1 The free radical experiment



Addition of typical radical scavengers, such as TEMPO and 9,10-dihydroanthracene, did not obviously effect the reduction transformations, rendering a free radical mechanism unlikely to be operative.

3.2 The homogeneous test



Addition of commonly used heterogeneous catalyst poison PMe_3 or Hg showed no adverse effect on the yield of **4a**, which indicated that the combined KO*t*Bu/BEt_3 catalyst was likely to be homogeneous under current conditions.

3.3 The kinetic studies

a. General procedure for typical reaction kinetics

For the reaction of *N,N*-dimethylbenzamide (0.50 mmol), pinacolborane (2.0 mmol) with KO*t*Bu/BEt₃ (0.025 mmol) in 2 ml MTBE:

In a glovebox, KO*t*Bu/BEt_3 (2.80 mg, 0.025 mmol) was added to a Schlenk tube equipped with a magnetic stirring bar and a Teflon cap. Then, a mixture of *N,N*-dimethylbenzamide (74.60 mg, 0.50 mmol) and pinacolborane (256.0 mg, 2.0 mmol) in 2 mL MTBE was added. The sealed tube was taken out from the glovebox, and was stirred at 60 °C taken out at 5, 10, 15, 20, 25, 30, 40, 60, 90, 120, 180 minutes. The sample was analyzed by GC. The percentage yields of the product **4n** were calculated by mesitylene as an internal standard, which were then converted to molar concentrations. A duplicate reaction was also run under otherwise identical conditions and an average value was taken for each time point. The yields in molar concentrations are presented in

Table S1. The molar concentrations of the product **4n** were plotted against the reaction time to obtain a typical reaction kinetic profile.

Table S1. The molar concentration of product **3n** at different time interval

Time (s)	Yield of **4n** (M)
0	0
300	0.01928
600	0.02881
900	0.03122
1200	0.03306
1500	0.03328
1800	0.03842
2400	0.04275
3600	0.04992
5400	0.05778
7200	0.07045
10800	0.07530

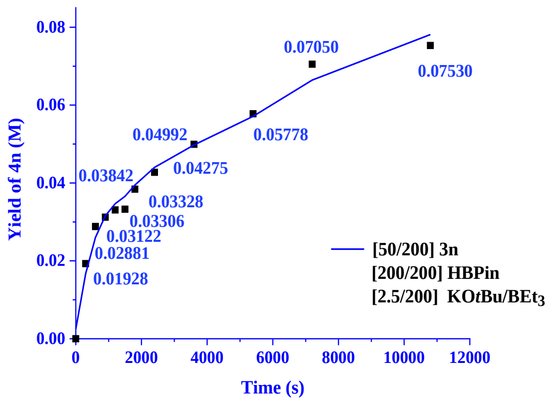


Figure S1. Plot of the rise of product **4n** from the reaction of *N,N*-dimethylbenzamide (0.50 mmol), pinacolborane (2.00 mmol) with KO*t*Bu/BEt_3 (0.025 mmol) in 2 ml MTBE. The reaction in different time interval at 60 °C.

b. General procedure to determine the dependence of reaction rate on the concentration of pinacolborane

For the reaction of *N,N*-dimethylbenzamide (0.50 mmol), pinacolborane (2.00 mmol) with KO*t*Bu/BEt_3 (0.025 mmol) in 2 ml MTBE:

In a glovebox, KO*t*Bu/BEt_3 (2.80 mg, 0.025 mmol) was added to a Schlenk tube equipped with a magnetic stirring bar and a Teflon cap. Then, a mixture of *N,N*-dimethylbenzamide (74.60mg, 0.50 mmol) and pinacolborane (256.0 mg, 2.0 mmol) in 2 mL MTBE was added. The sealed tube was taken out from the glovebox, and was stirred at 60 °C taken out at 30, 60, 90, 120 minutes. The sample was analyzed by GC. The percentage yields of the product **4n** were calculated by mesitylene as an internal standard, which were then converted to molar concentrations. A duplicate reaction was also run under otherwise identical conditions and an average value was taken for each time point. The yields in molar concentrations are presented in Table S2. The molar concentrations of the product **4n** were plotted against the reaction time to obtain a typical reaction kinetic profile.

For the reaction of *N,N*-dimethylbenzamide (0.50 mmol), pinacolborane (1.80 mmol) with KO*t*Bu/BEt$_3$ (0.025 mmol) in 2 ml MTBE: The procedure for this reaction was the same as above but instead of pinacolborane (2.00 mmol), pinacolborane (1.80 mmol) were added in the reaction.

For the reaction of *N,N*-dimethylbenzamide (0.50 mmol), pinacolborane (1.60 mmol) with KO*t*Bu/BEt$_3$ (0.025 mmol) in 2 ml MTBE: The procedure for this reaction was the same as above but instead of pinacolborane (2.00 mmol), pinacolborane (1.60 mmol) were added in the reaction.

For the reaction of *N,N*-dimethylbenzamide (0.50 mmol), pinacolborane (1.40 mmol) with KO*t*Bu/BEt$_3$ (0.025 mmol) in 2 ml MTBE: The procedure for this reaction was the same as above but instead of pinacolborane (2.00 mmol), pinacolborane (1.40 mmol) were added in the reaction.

The percentage yields of the product **4n** were calculated by mesitylene as an internal standard, which were then converted to molar concentrations. A duplicate reaction was also run under otherwise identical conditions and an average value was taken for each time point. The molar concentration of product **4n** was plotted against the reaction time and the slope of linear portion of the curve was used to determine the initial rates of the reaction. The Table S3 showing molar concentration of product **4n** in different concentration of pinacolborane, graph showing the rate at different concentration of pinacolborane, table with k_{in} in value and the graph showing k_{in} in versus [HBpin] are shown below.

Table S2. The molar concentration of product **4n** in different concentration of pinacolborane at different time interval

Time (s)	HBPin [20/20 M]	HBPin [18/20 M]	HBPin [16/20 M]	HBPin [14/20 M]
1800	0.03842	0.03350	0.03069	0.02755
3600	0.04992	0.03992	0.03765	0.03068
5400	0.05778	0.05044	0.04305	0.03741
7200	0.07045	0.05752	0.04929	0.04038

Table S3. The K_{in} value of product **4n** in different concentration of pinacolborane

HBPin (M)	K_{in} M s^{-1}
20/20	5.7829×10^{-6}
18/20	4.5871×10^{-6}
16/20	3.3997×10^{-6}
14/20	2.5110×10^{-6}

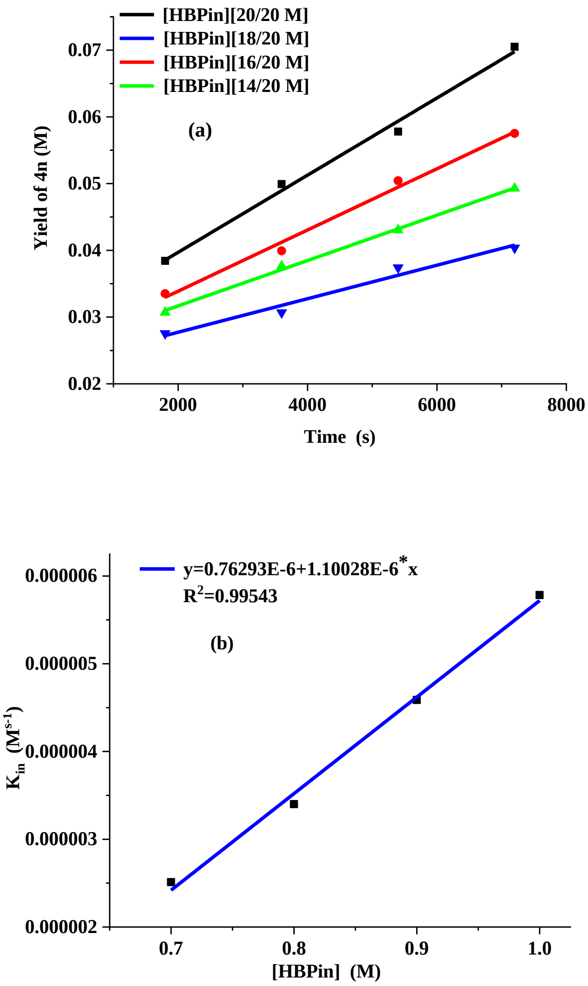


Figure S2. (a) Plot of the rise of product **4n** from the reaction of **3n** (0.5 mmol), KO*t*Bu/BEt_3 (0.025 mmol) with 1.40 mmol, 1.60 mmol, 1.80 mmol and 2.00 mmol of pinacolborane in 2 mL MTBE at different time. (b) Plot of K_{in} versus [HBPin] from the reaction of **3n** (0.5 mmol), KO*t*Bu/BEt_3 (0.025 mmol) with 1.40 mmol, 1.60 mmol, 1.80 mmol and 2.00 mmol of pinacolborane in 2 mL MTBE.

c. General procedure to determine the dependence of reaction rate on the concentration of 3n (*N,N*-dimethylbenzamide)

For the reaction of *N,N*-dimethylbenzamide (0.50 mmol), pinacolborane (2.00 mmol) with KO*t*Bu/BEt_3 (0.025 mmol) in 2 ml MTBE:

In a glovebox, KO*t*Bu/BEt_3 (2.80 mg, 0.025 mmol) was added to a Schlenk tube equipped with a magnetic stirring bar and a Teflon cap. Then, a mixture of *N,N*-dimethylbenzamide (74.60 mg, 0.50 mmol) and pinacolborane (256.0 mg, 2.0 mmol) in 2 mL MTBE was added. The sealed tube was taken out from the glovebox, and was stirred at 60 °C taken out at 30, 60, 90, 120 minutes. The sample was analyzed by GC. The percentage yields of the product **4n** were calculated by mesitylene as an internal standard, which were then converted to molar concentrations. A duplicate reaction was also run under otherwise identical conditions and an average value was taken for each time point. The yields in molar concentrations are presented in Table S4. The molar concentrations of the product **4n** were plotted against the reaction time to obtain a typical reaction kinetic profile.

For the reaction of *N,N*-dimethylbenzamide (0.40 mmol), pinacolborane (2.00 mmol) with KO*t*Bu/BEt$_3$ (0.025 mmol) in 2 ml MTBE: The procedure for this reaction was the same as above but instead of *N,N*-dimethylbenzamide (0.50 mmol), *N,N*-dimethylbenzamide (0.40 mmol) were added in the reaction.

For the reaction of *N,N*-dimethylbenzamide (0.30 mmol), pinacolborane (2.00 mmol) with KO*t*Bu/BEt$_3$ (0.025 mmol) in 2 ml MTBE: The procedure for this reaction was the same as above but instead of *N,N*-dimethylbenzamide (0.50 mmol), *N,N*-dimethylbenzamide (0.30 mmol) were added in the reaction.

For the reaction of *N,N*-dimethylbenzamide (0.20 mmol), pinacolborane (2.00 mmol) with KO*t*Bu/BEt$_3$ (0.025 mmol) in 2 ml MTBE: The procedure for this reaction was the same as above but instead of *N,N*-dimethylbenzamide (0.50 mmol), *N,N*-dimethylbenzamide (0.20 mmol) were added in the reaction.

The percentage yields of the product **4n** were calculated by mesitylene as an internal standard, which were then converted to molar concentrations. A duplicate reaction was also run under otherwise identical conditions and an average value was taken for each time point. The molar concentration of product **4n** was plotted against the reaction time and the slope of linear portion of the curve was used to determine the initial rates of the reaction. The Table S5 showing molar concentration of product **4n** in different concentration of *N,N*-dimethylbenzamide, graph showing the rate at different concentration of *N,N*-dimethylbenzamide, table with k_{in} in value and the graph showing k_{in} in versus [*N,N*-dimethylbenzamide] are shown below.

Table S4. The molar concentration of product **4n** in different concentration of *N,N*-dimethylbenzamide (**3n**) at different time interval

Time (s)	**3n**[5/20 M]	**3n**[4/20 M]	**3n**[3/20 M]	**3n**[2/20 M]
1800	0.03842	0.02591	0.01638	0.00951
3600	0.04992	0.03498	0.01980	0.01292
5400	0.05778	0.04038	0.02527	0.01496
7200	0.07045	0.04523	0.03065	0.01875

Table S5. The K_{in} value of product **3n** in different concentration of *N,N*-dimethylbenzamide

3n (M)	K_{in} Ms^{-1}
2/20	1.6531×10^{-6}
3/20	2.6816×10^{-6}
4/20	3.5213×10^{-6}
5/20	5.7829×10^{-6}

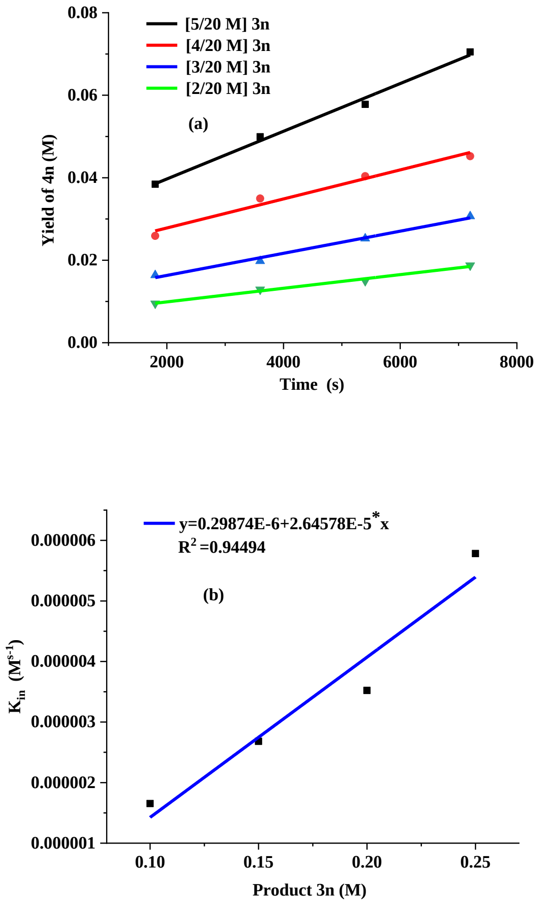


Figure S3. (a) Plot of the rise of product **4n** from the reaction of pinacolborane (2.00 mmol) with KO*t*Bu/BEt_3 (0.025 mmol) with 0.20 mmol, 0.30 mmol, 0.40 mmol and 0.50 mmol of *N,N*-dimethylbenzamide (**3n**) in 2 mL MTBE at different time interval. (b) Plot of K_{in} versus [*N,N*-dimethylbenzamide] from the reaction of pinacolborane (2.00 mmol), KO*t*Bu/BEt_3 (0.025 mmol) with 0.20 mmol, 0.30 mmol, 0.40 mmol and 0.50 mmol of *N,N*-dimethylbenzamide in 2 mL MTBE.

d. General procedure to determine the dependence of reaction rate on the concentration of catalyst

For the reaction of *N,N*-dimethylbenzamide (0.50 mmol), pinacolborane (2.00 mmol) with KO*t*Bu/BEt_3 (0.025 mmol) in 2 ml MTBE:

In a glovebox, KO*t*Bu/BEt_3 (2.80 mg, 0.025 mmol) was added to a Schlenk tube equipped with a magnetic stirring bar and a Teflon cap. Then, a mixture of *N,N*-dimethylbenzamide (74.60 mg, 0.50 mmol) and pinacolborane (256.0 mg, 2.0 mmol) in 2 mL MTBE was added.The sealed tube was taken out from the glovebox, and was stirred at 60 °C taken out at 30, 60, 90, 120 minutes. the sample was analyzed by GC. The percentage yields of the product **4n** were calculated by mesitylene as an internal standard, which were then converted to molar concentrations. A duplicate reaction was also run under otherwise identical conditions and an average value was taken for each time point. The yields in molar concentrations are presented in Table S6. The molar concentrations of the product **4n** were plotted against the reaction time to obtain a typical reaction kinetic profile.

For the reaction of *N,N*-dimethylbenzamide (0.50 mmol), pinacolborane (2.00 mmol) with KO*t*Bu/BEt$_3$ (0.020 mmol) in 2 ml MTBE: The procedure for this reaction was the same as above but instead of KO*t*Bu/BEt$_3$ (0.025 mmol), KO*t*Bu/BEt$_3$ (0.020 mmol) were added in the reaction.

For the reaction of *N,N*-dimethylbenzamide (0.50mmol), pinacolborane (2.00 mmol) with KO*t*Bu/BEt$_3$ (0.015 mmol) in 2 ml MTBE: The procedure for this reaction was the same as above but instead of KO*t*Bu/BEt$_3$ (0.025 mmol), KO*t*Bu/BEt$_3$ (0.015 mmol) were added in the reaction.

For the reaction of *N,N*-dimethylbenzamide (0.50mmol), pinacolborane (2.00 mmol) with KO*t*Bu/BEt$_3$ (0.010 mmol) in 2 ml MTBE: The procedure for this reaction was the same as above but instead of KO*t*Bu/BEt$_3$ (0.025 mmol), KO*t*Bu/BEt$_3$ (0.010mol) were added in the reaction.

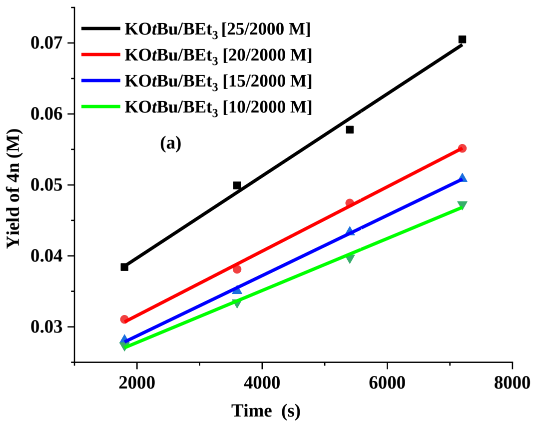
The percentage yields of the product **4n** were calculated by mesitylene as an internal standard, which were then converted to molar concentrations. A duplicate reaction was also run under otherwise identical conditions and an average value was taken for each time point. The molar concentration of product **4n** was plotted against the reaction time and the slope of linear portion of the curve was used to determine the initial rates of the reaction. The Table S7 showing molar concentration of product **4n** in different concentration of pinacolborane, graph showing the rate at different concentration of KO*t*Bu/BEt$_3$, table with k_{in} in value and the graph showing k_{in} in versus KO*t*Bu/BEt$_3$ are shown below.

Table S6. The molar concentration of product **4n** in different concentration of KO*t*Bu/BEt$_3$ at different time interval

Time (s)	KO*t*Bu/BEt$_3$ [25/3000M]	KO*t*Bu/BEt$_3$ [20/3000M]	KO*t*Bu/BEt$_3$ [15/3000M]	KO*t*Bu/BEt$_3$ [10/3000 M]
1800	0.03842	0.03104	0.02811	0.02738
3600	0.04992	0.03811	0.03507	0.03343
5400	0.05778	0.04743	0.04334	0.03972
7200	0.07045	0.05515	0.05085	0.04727

Table S7. The K_{in} value of product **4n** in different concentration of KO*t*Bu/BEt$_3$

KO*t*Bu/BEt$_3$ (M)	K_{in} Ms^{-1}
10/3000	3.6642×10^{-6}
15/3000	4.2495×10^{-6}
20/3000	4.5362×10^{-6}
25/3000	5.7829×10^{-6}



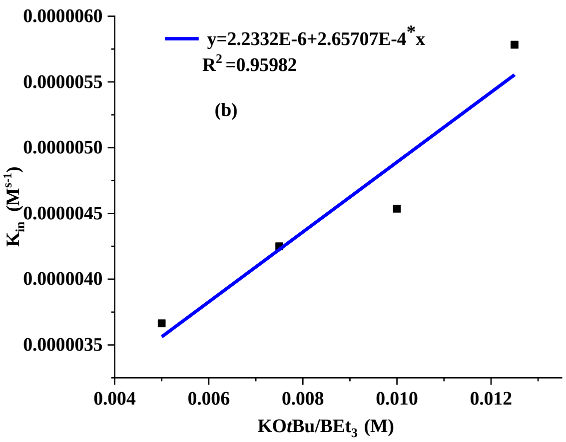
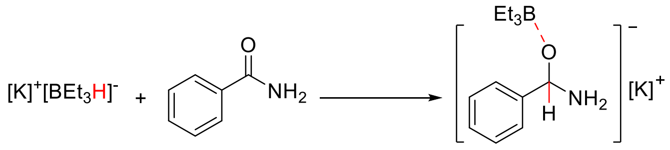


Figure S4. (a) Plot of the rise of product **4n** from the reaction of **3n** (0.5 mmol), pinacolborane (2.0 with 0.01mmol, 0.015mmol, 0.020mmol and 0.025mmol concentration of KO*t*Bu/BEt_3 respectively in different time interval. (b) Plot of K_{in} versus KO*t*Bu/BEt_3 from the reaction of **3n** (0.5 mmol), pinacolborane (2.0 mmol) with 0.01mmol, 0.015mmol, 0.020mmol and 0.025mmol of KO*t*Bu/BEt_3 in 2mL MTBE.

3.4 The DFT calculations

(1)



A B C

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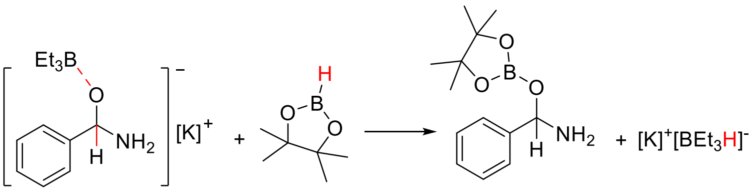

C D E A

Table S8 The calculated gibbs free energies of reactions by DFT/B3LYP/6-311+G*

Eq (1)	G_A/a.u.	G_B/a.u.	G_C/a.u.		$\Delta G_{eq\,(1)}$ (a.u.)	$\Delta G_{eq\,(1)}$ (kcal/mol)	$\Delta G_{eq\,(1)}$ (kJ/mol)
	-862.8889	-400.8579	-1263.7552		-0.0084	-5.2711	-22.03
Eq (2)	G_C/a.u.	G_D/a.u.	G_E/a.u.	G_A/a.u.	$\Delta G_{eq\,(2)}$ (a.u.)	$\Delta G_{eq\,(2)}$ (kcal/mol)	$\Delta G_{eq\,(2)}$ (kJ/mol)
	-1263.7552	-411.6966	-812.5606	-862.8889	0.0023	1.4433	6.03

1 a.u. = 627.5095 kcal/mol 1 kcal/mol = 4.18 kJ/mol

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G_A = -862.8889 a.u.

Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
1	5	-0.021270705	-0.011873266	-0.002129049
2	6	-0.004405418	0.009734887	0.000647107
3	6	0.013841113	0.002893197	-0.004982339
4	6	0.002556609	0.011955923	-0.005996825
5	6	0.009330507	-0.004863058	0.007574435
6	6	0.004357375	0.012444893	-0.002024044
7	6	0.010124115	-0.009039381	0.000374515
8	1	0.006424519	0.006422577	-0.002483950
9	1	-0.002109879	0.003884438	0.001407329
10	1	-0.002912116	-0.002655493	-0.000234681
11	1	-0.002712822	0.000660726	-0.001843345

12	1	-0.004609519	0.002725645	-0.002098600
13	1	-0.006908579	-0.001601944	0.003758998
14	1	0.001557662	0.001327046	0.004931252
15	1	-0.000666562	-0.010083028	0.003873379
16	1	0.002521225	-0.000967290	0.003814903
17	1	-0.002956992	-0.002211083	0.000700762
18	1	-0.003488140	0.006587726	0.010355252
19	1	-0.002438767	-0.006909759	0.003225381
20	1	0.001891971	-0.003298874	-0.003895321
21	1	0.003328174	-0.003330329	-0.001348346
22	1	-0.001296200	-0.003750876	-0.012269964
23	1	-0.002997163	-0.002089684	0.000612218
24	19	0.002839591	0.004037007	-0.001969068

Cartesian Forces: Max 0.021270705 RMS 0.005960533

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G_B = -400.8579 a.u.

Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
1	6	-0.000027588	0.000084037	-0.000055662
2	6	0.000162392	-0.000082937	-0.000048217
3	7	-0.000003442	0.000012552	0.000036577
4	8	-0.000082414	0.000094405	0.000044226
5	6	-0.000058941	-0.000011711	0.000046449
6	6	0.000041309	-0.000029143	-0.000015876
7	6	-0.000009903	0.000037246	-0.000021365
8	6	-0.000046759	-0.000032626	-0.000004934
9	6	0.000044003	-0.000053097	0.000030937
10	1	-0.000031908	-0.000021935	-0.000008994
11	1	-0.000004530	-0.000011790	-0.000008808
12	1	0.000009136	-0.000006863	-0.000010188
13	1	-0.000003156	-0.000005482	-0.000003659
14	1	-0.000009054	-0.000000418	0.000007289
15	1	0.000006503	0.000006311	0.000001253
16	1	0.000014352	0.000021452	0.000010973

Cartesian Forces: Max 0.000162392 RMS 0.000042886

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G_C = -1263.7552 a.u.

Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
1	6	0.015303753	-0.020955657	-0.010760326
2	7	-0.007038576	0.003529487	-0.008086987
3	8	0.005220515	0.010884585	0.012569632
4	6	-0.002534776	0.000770277	-0.012958708
5	6	-0.002646893	-0.006820690	-0.001688298
6	6	0.005092101	-0.003612063	0.001925035
7	6	0.007663878	0.001318343	0.002702965
8	6	0.003038327	0.006525058	-0.002145991
9	6	-0.001332874	0.003830188	-0.005011623
10	5	-0.010124567	0.007351992	-0.000573922
11	6	-0.015549298	-0.000658379	0.005252277
12	6	-0.008173087	0.001083519	-0.015523552
13	6	0.003568524	0.012430495	0.003484609
14	6	-0.007830734	-0.007478355	0.005699206
15	6	-0.002741263	-0.010894440	0.008395441
16	6	0.001143012	0.008866318	-0.005369859
17	1	0.007893032	-0.013110903	0.015910453
18	1	0.005519164	-0.000794140	-0.002079141
19	1	0.009088654	0.005358559	-0.003901521
20	1	-0.000730727	0.011098987	0.000848915
21	1	-0.003671334	0.003991055	-0.001007010
22	1	-0.004338425	-0.001199781	-0.001568381
23	1	-0.002439158	-0.005088555	0.001252404
24	1	0.012829460	-0.013389999	0.009376095
25	1	0.003365232	-0.001957232	0.003468385
26	1	0.000960368	-0.001051703	0.002040114
27	1	0.008847377	0.009740732	0.006586763
28	1	0.003532689	0.000968848	0.007378052
29	1	-0.001895427	0.002347209	0.002826110
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31	1	-0.002277256	-0.004926705	-0.003042162
32	1	0.000056781	-0.003200471	0.001543351
33	1	0.002067199	-0.007788379	-0.007274345

34	1	-0.004003173	-0.000112210	0.002085366
35	1	0.002424651	0.000929325	-0.003778656
36	1	-0.004970843	0.005744445	-0.003750247
37	1	0.002499700	0.002360408	0.000306264
38	1	-0.008855507	0.004931158	0.000663821
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Cartesian Forces: Max 0.020955657 RMS 0.006545053

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2	6	0.007969577	-0.016748527	0.000001313
3	6	-0.007968637	-0.016751353	-0.000000311
4	8	0.007345890	0.027151144	0.000000491
5	5	-0.000002108	-0.004531253	-0.000000414
6	6	0.007066697	-0.002833520	0.009665700
7	6	0.007068759	-0.002835549	-0.009666408
8	6	-0.007065567	-0.002835088	0.009667416
9	6	-0.007067506	-0.002835000	-0.009666493
10	1	0.000000651	0.003208902	0.000000134
11	1	-0.000149010	0.001302544	-0.000295011
12	1	0.000359235	-0.002764821	-0.005067997
13	1	-0.005515592	-0.000573674	-0.003611383
14	1	-0.000148295	0.001303450	0.000295379
15	1	-0.005515402	-0.000572110	0.003610780
16	1	0.000356939	-0.002765480	0.005066870
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18	1	-0.000359063	-0.002766232	-0.005067519
19	1	0.000148688	0.001303073	-0.000294580
20	1	0.005514769	-0.000570204	0.003610124
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22	1	-0.000356026	-0.002767352	0.005066853

Cartesian Forces: Max 0.027151144 RMS 0.006988128

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G_E = -812.5606 a.u.

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3	7	0.006847642	0.002303078	0.007456424
4	8	0.020764180	0.004249355	0.007083517
5	5	-0.009494641	0.007309173	-0.004697825
6	8	-0.022162354	-0.014959119	0.004078386
7	6	0.018368576	0.008209621	-0.002024304
8	6	0.018582577	-0.008691910	0.004428472
9	8	-0.025357036	0.017704274	-0.006393251
10	6	0.005124686	0.008760306	0.007228156
11	6	0.002393568	0.003592459	-0.010863275
12	6	0.000732163	-0.002951864	0.011406218
13	6	0.004562902	0.006402087	-0.000348370
14	6	-0.001843339	0.002173366	-0.000121495
15	6	-0.004401806	0.002007560	-0.000034440
16	6	-0.003056978	-0.002374015	0.000151731
17	6	-0.001645478	-0.002690238	0.000488610
18	1	-0.004465357	0.001051888	-0.017107128
19	1	-0.005096965	-0.001737883	0.005064942
20	1	-0.005843979	0.000758719	0.002217201
21	1	-0.000830803	0.000313262	-0.000422321
22	1	0.002954176	-0.002343753	-0.005467265

23	1	-0.000412988	-0.006267586	-0.001707925
24	1	-0.001376203	-0.000620481	0.000192316
25	1	0.000720032	-0.004589028	0.005433236
26	1	0.002177796	0.001411980	0.003597678
27	1	0.001783862	0.003729620	-0.004972828
28	1	0.002547645	-0.001867159	-0.003518153
29	1	-0.001596770	0.000609028	-0.000605661
30	1	-0.007827062	-0.007523543	0.000864156
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32	1	0.003477470	-0.001343545	-0.000052275
33	1	0.002871403	0.002460653	-0.000240775
34	1	-0.000126049	0.006467521	-0.000539429
35	6	0.005452817	-0.008903814	-0.006205994
36	1	-0.001491573	-0.000227481	0.000296537
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Cartesian Forces: Max 0.025357036 RMS 0.006731461

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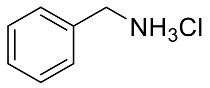
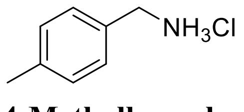
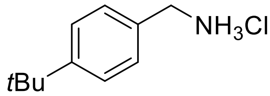
4. NMR spectra data



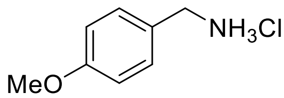
Phenylmethanamine hydrochloride (2'a), white solid, 0.057 g, 80%. ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) δ 8.35 (s, 3H), 7.49 (s, 2H), 7.40 (d, J = 7.1 Hz, 3H), 3.99 (s, 2H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6, 20 ºC) δ 134.2, 129.0, 128.5, 128.4, 42.1. These spectroscopic data correspond to reported data.[2]



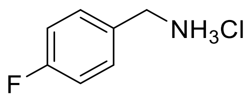
4-Methylbenzylamine hydrochloride (2'b), white solid, 0.066 g, 83%. ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) δ 8.38 (s, 3H), 7.37 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 7.8 Hz, 2H), 3.95 (q, J = 5.7 Hz, 2H), 2.31 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6, 20 ºC) δ 137.8, 131.0, 129.1, 128.9, 41.9, 20.7. These spectroscopic data correspond to reported data.[2]



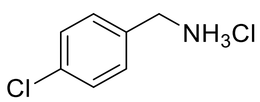
(4-(Tert-butyl)phenyl)methanamine hydrochloride (2'c), white solid, 0.085 g, 85%. ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) δ 8.50 (s, 3H), 7.42 (s, 4H), 3.95 (s, 2H), 1.27 (s, 9H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6, 20 ºC) δ 150.9, 131.1, 128.7, 125.3, 41.8, 34.3, 31.0. These spectroscopic data correspond to reported data.[2]



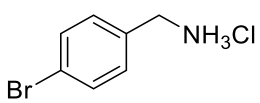
4-Methoxybenzylamine hydrochloride (2'd), white solid, 0.061 g, 70%. ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) δ 8.29 (s, 3H), 7.41 (d, J = 8.6 Hz, 2H), 6.97 (d, J = 8.6 Hz, 2H), 3.93 (q, J = 5.7 Hz, 2H), 3.76 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6, 20 ºC) δ 159.4, 130.5, 125.9, 113.9, 55.2, 41.7. These spectroscopic data correspond to reported data.[2]



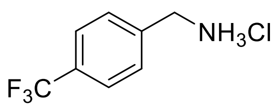
4-Fluorobenzylamine hydrochloride (2'e), white solid, 0.075 g, 92%. ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) δ 8.52 (s, 3H), 7.56 (dd, J = 8.3 Hz, J = 5.7 Hz, 2H), 7.25 (t, J = 8.9 Hz, 2H), 4.00 (s, 2H). ^{19}F NMR (377 MHz, $CDCl_3$, 20 ºC) δ -113.69. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6, 20 ºC) δ 163.3, 160.8, 131.3 (d, J = 8.4 Hz), 130.4 (d, J = 3.1 Hz), 115.4, 115.2, 41.4. These spectroscopic data correspond to reported data.[3]



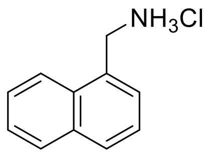
4-Chlorobenzylamine hydrochloride (2'f), white solid, 0.079 g, 90%. ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) δ 8.60 (s, 3H), 7.55 (d, J = 7.9 Hz, 2H), 7.47 (d, J = 7.9 Hz, 2H), 4.00 (s, 2H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6, 20 ºC) δ 133.2, 133.1, 131.0, 128.5, 41.4. These spectroscopic data correspond to reported data.[3]



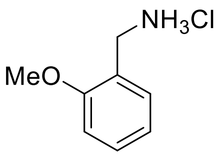
4-Bromobenzylamine hydrochloride (2'g), white solid, 0.097 g, 88%. ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) δ 8.63 (s, 3H), 7.59 (d, J = 8.3 Hz, 2H), 7.49 (d, J = 8.3 Hz, 2H), 3.96 (s, 2H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6, 20 ºC) δ 133.6, 131.4, 121.6, 41.4. These spectroscopic data correspond to reported data.[3]



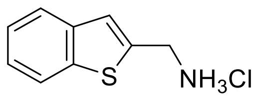
(4-(Trifluoromethyl)phenyl)methanamine (2'h), white solid, 0.054 g, 51%. ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) δ 8.89 (s, 3H), 7.75 (q, *J* = 8.2 Hz, 4H), 4.10 (s, 2H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6, 20 ºC) δ 138.9, 130.0, 129.0 (q, *J* = 31.8 Hz), 128.3, 125.6, 125.4 (d, *J* = 3.7 Hz), 122.9, 120.2, 41.7. ^{19}F NMR (377 MHz, $CDCl_3$, 20 ºC) δ -61.17. These spectroscopic data correspond to reported data.[2]



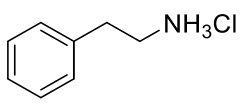
Naphthalen-1-ylmethanamine hydrochloride (2'i), white solid, 0.02 g, 21%. ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) δ 8.52 (s, 3H), 8.15 (d, *J* = 8.2 Hz, 1H), 8.00 (t, *J* = 9.1 Hz, 2H), 7.69-7.51 (m, 4H), 4.52 (d, *J* = 5.6 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6, 20 ºC) δ 133.2, 130.7, 130.2, 128.9, 128.7, 127.3, 126.8, 126.2, 125.4, 123.5. These spectroscopic data correspond to reported data.[3]



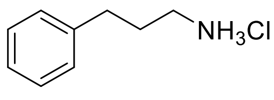
(2-Methoxyphenyl)methanamine hydrochloride (2'j), white solid, 0.053 g, 36%. ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) δ 8.33 (s, 3H), 7.39 (dd, *J* = 11.6 Hz, *J* = 7.6 Hz, 2H), 7.07 (d, *J* = 8.2 Hz, 1H), 6.98 (t, *J* = 7.4 Hz, 1H), 3.95 (q, *J* = 5.6 Hz, 2H), 3.83 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6, 20 ºC) δ 157.2, 130.3, 130.2, 121.7, 120.3, 110.9, 55.5 37.6. These spectroscopic data correspond to reported data.[3]



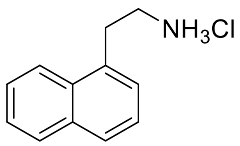
Benzo[b]thiophen-2-ylmethanamine hydrochloride (2'k), white solid, 0.077 g, 77%. ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) δ 8.77 (s, 3H), 7.98 (d, *J* = 8.1 Hz, 1H), 7.94-7.76 (m, 1H), 7.58 (s, 1H), 7.41-7.35 (m, 2H), 4.33 (s, 2H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6, 20 ºC) δ 139.6, 139.0, 136.6, 125.4, 124.8, 124.7, 123.8, 122.6, 37.5. These spectroscopic data correspond to reported data.[3]



Phenylethylamine hydrochloride (2'l), white solid, 0.071 g, 90%. ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) δ 8.37 (s, 3H), 7.35-7.27 (m, 2H), 7.26-7.19 (m, 3H), 2.94 (s, 4H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6, 20 ºC) δ 137.7, 128.6, 126.7, 32.8. These spectroscopic data correspond to reported data.[3]

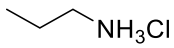


Phenylethylamine hydrochloride (2'm), white solid, 0.079 g, 93%. ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) δ 8.03 (s, 3H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.25-7.13 (m, 2H), 2.76 (dd, *J* = 13.4 Hz, *J* = 6.4 Hz, 2H), 2.64 (t, *J* = 7.7 Hz, 2H), 1.93-1.72 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6, 20 ºC) δ 140.9, 128.4, 128.2, 126.0, 38.3, 31.8, 28.7. These spectroscopic data correspond to reported data.[3]

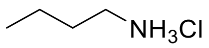


2-(Naphthalen-1-yl)ethan-1-amine hydrochloride (2'n), white solid, 0.039 g, 38%. ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) δ 8.21 (d, *J* = 11.4 Hz, 3H), 8.18 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 7.9 Hz, 1H), 7.86 (d, *J* = 7.9 Hz, 1H), 7.58 (dt, *J* = 14.7 Hz, *J* = 6.9 Hz, 2H), 7.51-7.40 (m, 2H), 3.46-3.29 (m, 2H), 3.22-2.96 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6, 20 ºC) δ 133.5, 133.4, 131.3, 128.7, 127.4, 126.9, 126.4, 125.8, 125.7, 123.5, 30.2. These spectroscopic data correspond to reported data.[3]

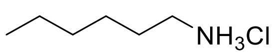
Ethylamine hydrochloride (2'o), white solid, 0.037 g, 91%. ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) δ 7.84 (s, 3H), 2.77 (dd, *J* = 14.0 Hz, *J* = 6.9 Hz, 2H), 1.15 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6, 20 ºC) δ 34.0, 12.5. These spectroscopic data correspond to reported data.[3]



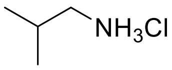
***n*-Propylamine hydrochloride (2'p)**, white solid, 0.044 g, 92%. ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) δ 8.09 (s, 3H), 2.70 (t, *J* = 7.5 Hz, 2H), 1.57 (dd, *J* = 15.0 Hz, *J* = 7.5 Hz, 2H), 0.89 (t, *J* = 7.5 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6, 20 ºC) δ 40.3, 20.4, 10.9. These spectroscopic data correspond to reported data.[3]



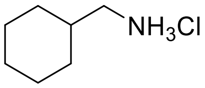
***n*-Butylamine hydrochloride (2'q)**, white solid, 0.042 g, 76%. ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) δ 8.03 (s, 3H), 2.90-2.63 (m, 2H), 1.53 (dt, *J* = 15.2 Hz, *J* = 7.6 Hz, 2H), 1.41-1.19 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6, 20 ºC) δ 38.4, 29.0, 19.2, 13.5. These spectroscopic data correspond to reported data.[3]



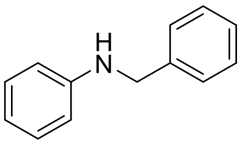
Hexylamine hydrochloride (2'r), white solid, 0.054 g, 78%. ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) δ 8.22 (s, 3H), 2.69 (t, *J* = 7.5 Hz, 2H), 1.63-1.46 (m, 2H), 1.28 (dd, *J* = 14.5 Hz, *J* = 7.7 Hz, 6H), 0.85 (t, *J* = 6.7 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6, 20 ºC) δ 30.8, 26.8, 25.6, 22.0, 13.9. These spectroscopic data correspond to reported data.[3]



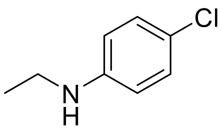
Isobutylamine hydrochloride (2's), white solid, 0.078 g, 71%. ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) δ 8.11 (s, 3H), 2.59 (s, 2H), 1.93-1.83 (m, 1H), 0.91 (d, J = 6.7 Hz, 6H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6, 20 ºC) δ 45.6, 26.3, 19.8. These spectroscopic data correspond to reported data.[3]



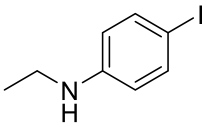
Cyclohexanemethylamine hydrochloride (2't), white solid, 0.066 g, 87%. ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) δ 8.08 (s, 3H), 2.60 (s, 2H), 1.70 (dd, J = 24.2 Hz, J = 12.6 Hz, 4H), 1.65-1.47 (m, 2H), 1.24-1.05 (m, 3H), 1.02-0.74 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6, 20 ºC) δ 44.3, 35.4, 29.8, 25.6, 25.0. These spectroscopic data correspond to reported data.[3]



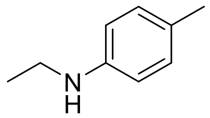
***N*-benzylaniline (4a)**. Purification by silica gel column chromatography using petroleum ether/ethyl acetate gave white solid, 0.087 g, 95%. ^{1}H NMR (400 MHz, $CDCl_3$, 20 ºC) δ 7.44-7.34 (m, 4H), 7.31 (dd, J = 8.1 Hz, J = 5.5 Hz, 1H), 7.21 (dd, J = 8.5 Hz, J = 7.4 Hz, 2H), 6.76 (t, J = 7.3 Hz, 1H), 6.67 (dd, J = 8.5 Hz, J = 0.9 Hz, 2H), 4.36 (s, 2H), 4.04 (s, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 20 ºC) δ 148.3, 139.6, 129.4, 128.8, 127.6, 127.4, 117.7, 113.0, 48.5. These spectroscopic data correspond to reported data.[4]



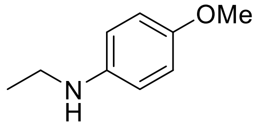
4-Chloro-N-ethylaniline (4b). Purification by silica gel column chromatography using petroleum ether/ethyl acetate gave yellow oil, 0.071 g, 91%. ^{1}H NMR (400 MHz, $CDCl_3$, 20 ºC) δ 7.11 (d, J = 8.8 Hz, 2H), 6.53 (d, J = 8.8 Hz, 2H), 3.12 (q, J = 7.1 Hz, 2H), 1.30-1.06 (m, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 20 ºC) δ 147.0, 129.2, 122.0, 114.0, 38.8, 29.9. These spectroscopic data correspond to reported data.[4]



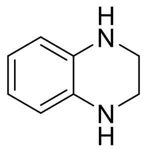
***N*-ethyl-4-iodoaniline (4c)**. Purification by silica gel column chromatography using petroleum ether/ethyl acetate gave pale yellow solid, 0.12 g, 98%. ^{1}H NMR (400 MHz, $CDCl_3$, 20 ºC) δ 7.41 (d, J = 8.6 Hz, 2H), 6.38 (d, J = 8.6 Hz, 2H), 3.59 (s, 1H), 3.12 (q, J = 7.1 Hz, 2H), 1.25 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 20 ºC) δ 148.0, 137.8 , 115.0, 77.6, 38.4, 14.8. These spectroscopic data correspond to reported data.[4]



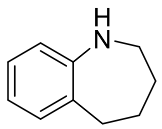
***N*-ethyl-4-methylaniline (4d)**. Purification by silica gel column chromatography using petroleum ether/ethyl acetate gave colorless oil, 0.066 g, 97%. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C) δ 7.02 (d, *J* = 8.2 Hz, 2H), 6.57 (d, *J* = 8.2 Hz, 2H), 3.40 (s, 1H), 3.16 (q, *J* = 7.1 Hz, 2H), 2.27 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 20 °C) δ 146.4, 129.8, 126.6, 113.1, 39.0, 20.5, 15.1. These spectroscopic data correspond to reported data.[4]



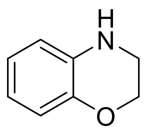
***N*-ethyl-4-methoxyaniline (4e)**. Purification by silica gel column chromatography using petroleum ether/ethyl acetate gave pale yellow oil, 0.072 g, 95%. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C) δ 6.80 (d, *J* = 8.9 Hz, 2H), 6.60 (d, *J* = 8.9 Hz, 2H), 3.76 (s, 3H), 3.12 (q, *J* = 7.1 Hz, 2H), 2.99 (s, 1H), 1.25 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 20 °C) δ 152.2, 142.9, 115.0, 114.2, 55.9, 39.6, 15.1. These spectroscopic data correspond to reported data.[4]



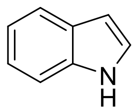
1,2,3,4-Tetrahydroquinoxaline (4f). Purification by silica gel column chromatography using petroleum ether/ethyl acetate gave brown solid, 0.052 g, 78%. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C) δ 6.63-6.54 (m, 2H), 6.54-6.46 (m, 2H), 3.42 (s, 4H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 20 °C) δ 133.8, 118.9, 114.9, 41.5. These spectroscopic data correspond to reported data.[5]



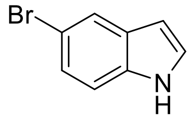
2,3,4,5-tetrahydro-1H-benzo[b]azepine (4g). Purification by silica gel column chromatography using petroleum ether/ethyl acetate gave white solid, 0.071 g, 97%. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C) δ 7.11 (d, *J* = 7.4 Hz, 1H), 7.04 (td, *J* = 7.6 Hz, *J* = 1.4 Hz, 1H), 6.83 (td, *J* = 7.4 Hz, *J* = 1.0 Hz, 1H), 6.74 (d, *J* = 7.7 Hz, 1H), 3.12-2.98 (m, 2H), 2.82-2.70 (m, 2H), 1.80 (ddd, *J* = 7.9 Hz, *J* = 6.9 Hz, *J* = 4.4 Hz, 2H), 1.69-1.57 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 20 °C) δ 150.5, 133.9, 130.9, 126.7, 120.9, 119.5, 49.0, 36.2, 32.1, 27.0.These spectroscopic data correspond to reported data.[5]



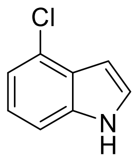
3,4-dihydro-2H-benzo[b][1,4]oxazine (4h). Purification by silica gel column chromatography using petroleum ether/ethyl acetate gave colorless oil, 0.064 g, 95%. ^{1}H NMR (400 MHz, $CDCl_3$, 20 ºC) δ 7.45-7.34 (m, 4H), 7.31 (t, J = 6.8 Hz, 1H), 7.21 (dd, J = 8.5 Hz, J = 7.4 Hz, 2H), 6.76 (t, J = 7.3 Hz, 1H), 6.67 (dd, J = 8.5 Hz, J = 0.9 Hz, 2H), 4.36 (s, 2H), 4.04 (s, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 20 ºC) δ 148.3, 139.6, 129.4, 128.8, 127.6, 127.4, 117.7, 113.0, 48.5. These spectroscopic data correspond to reported data.[5]



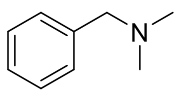
Indole (4k). Purification by silica gel column chromatography using petroleum ether/ethyl acetate gave white solid, 0.064 g, 69%. ^{1}H NMR (400 MHz, $CDCl_3$, 20 ºC) δ 8.02 (s, 1H), 7.65 (d, J = 7.8 Hz, 1H), 7.35 (d, J = 8.1 Hz, 1H), 7.24-7.05 (m, 3H), 6.54 (d, J = 0.8 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 20 ºC) δ 135.9, 127.9, 124.3, 122.1, 120.8, 119.9, 111.2, 102.7. These spectroscopic data correspond to reported data.[6]



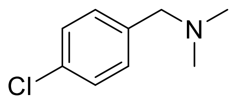
5-Bromo-indole (4l). Purification by silica gel column chromatography using petroleum ether/ethyl acetate gave white solid, 0.084 g, 86%. ^{1}H NMR (400 MHz, $CDCl_3$, 20 ºC) δ 8.20 (s, 1H), 7.78 (s, 1H), 7.32-7.23 (m, 2H), 7.21 (t, J = 2.8 Hz, 1H), 6.57-6.36 (m, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 20 ºC) δ 134.5, 129.8, 125.5, 125.0, 123.4, 113.2, 112.6, 102.4. These spectroscopic data correspond to reported data.[6]



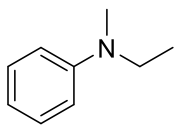
4-Chloro-indole (4m). Purification by silica gel column chromatography using petroleum ether/ethyl acetate gave pale yellow oil, 0.049 g, 65%. ^{1}H NMR (400 MHz, $CDCl_3$, 20 ºC) δ 8.26 (s, 1H), 7.30 (d, J = 7.2 Hz, 1H), 7.30 (d, J = 7.2 Hz, 1H), 7.18-7.09 (m, 2H), 6.68 (d, J = 2.3 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 20 ºC) δ 136.6, 126.9, 126.2, 124.8, 122.7, 119.7, 109.8, 101.4. These spectroscopic data correspond to reported data.[6]



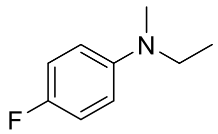
***N,N*-dimethyl-1-phenylmethanamine (4n)**. Purification by silica gel column chromatography using petroleum ether/ethyl acetate gave colorless oil, 0.048 g, 72%. ^{1}H NMR (400 MHz, $CDCl_3$, 20 ºC) δ 7.46-7.12 (m, 5H), 3.42 (s, 2H), 2.24 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 20 ºC) δ 138.8, 129.2, 128.3, 127.1, 64.4, 45.4. These spectroscopic data correspond to reported data.[7]



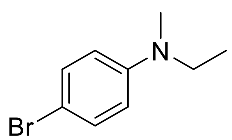
***N,N*-dimethyl-1-phenylmethanamine (4o)**. Purification by silica gel column chromatography using petroleum ether/ethyl acetate gave colorless oil, 0.048 g, 70%. ^{1}H NMR (400 MHz, $CDCl_3$, 20 ºC) δ 7.29 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 8.3 Hz, 2H), 3.37 (s, 2H), 2.22 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 20 ºC) δ 137.5, 132.8, 130.5, 128.5, 63.7, 45.4. These spectroscopic data correspond to reported data.[7]



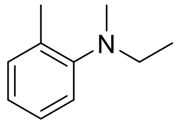
***N*-ethyl-N-methylaniline (4p)**. Purification by silica gel column chromatography using petroleum ether/ethyl acetate gave pale yellow oil, 0.042 g, 62%. ^{1}H NMR (400 MHz, $CDCl_3$, 20 ºC) δ 7.26 (dd, J = 8.4 Hz, J = 7.7 Hz, 2H), 6.72 (dd, J = 15.0 Hz, J = 7.7 Hz, 3H), 3.43 (q, J = 7.1 Hz, 2H), 2.93 (s, 3H), 1.14 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 20 ºC) δ 149.2, 129.3, 116.1, 112.5, 46.9, 37.6, 11.3. These spectroscopic data correspond to reported data.[8]



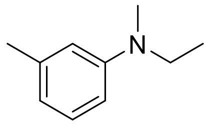
***N*-ethyl-4-fluoro-N-methylaniline (4q)**. Purification by silica gel column chromatography using petroleum ether/ethyl acetate gave pale yellow oil, 0.056 g, 73%. ^{1}H NMR (400 MHz, $CDCl_3$, 20 ºC) δ 6.98-6.89 (m, 2H), 6.66 (ddd, J = 10.7 Hz, J = 5.4 Hz, J = 3.2 Hz, 2H), 3.35 (q, J = 7.1 Hz, 2H), 2.86 (s, 3H), 1.10 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 20 ºC) δ 156.6, 154.3, 146.2, 115.6 (d, J = 21.9 Hz), 114.0 (d, J = 7.3 Hz), 47.7, 38.1, 11.1. These spectroscopic data correspond to reported data.[8]



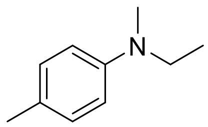
4-Bromo-N-ethyl-N-methylaniline (4r). Purification by silica gel column chromatography using petroleum ether/ethyl acetate gave yellow oil, 0.066 g, 62%. ^{1}H NMR (400 MHz, $CDCl_3$, 20 ºC) δ 7.29 (d, *J* = 9.1 Hz, 2H), 6.57 (d, *J* = 9.0 Hz, 2H), 3.37 (q, *J* = 7.1 Hz, 2H), 2.88 (s, 3H), 1.11 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 20 ºC) δ 148.1, 131.9, 114.0, 107.9, 47.0, 37.6, 11.1. These spectroscopic data correspond to reported data.[8]



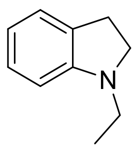
***N*-ethyl-N,2-dimethylaniline (4s)**. Purification by silica gel column chromatography using petroleum ether/ethyl acetate gave pale yellow oil, 0.052 g, 70%. ^{1}H NMR (400 MHz, $CDCl_3$, 20 ºC) δ 7.24-7.15 (m, 2H), 7.08 (d, *J* = 7.1 Hz, 1H), 6.99 (td, *J* = 7.3 Hz, *J* = 1.2 Hz, 1H), 2.95 (q, *J* = 7.1 Hz, 2H), 2.72 (s, 3H), 2.35 (s, 3H), 1.14 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 20 ºC) δ 152.3, 133.2, 131.1, 126.4, 122.8, 119.9, 50.6, 41.0, 18.4, 13.0. These spectroscopic data correspond to reported data.[8]



***N*-ethyl-*N*, 3-dimethylaniline (4t)**. Purification by silica gel column chromatography using petroleum ether/ethyl acetate gave yellow oil, 0.067 g, 90%. ^{1}H NMR (400 MHz, $CDCl_3$, 20 ºC) δ 7.14 (t, *J* = 8.1 Hz, 1H), 6.59 (s, 3H), 3.39 (q, *J* = 7.1 Hz, 2H), 2.91 (s, 3H), 2.32 (s, 3H), 1.13 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 20 ºC) δ 149.3, 138.9, 129.2, 117.2, 113.3, 109.8, 47.0, 37.6, 22.1, 11.4. These spectroscopic data correspond to reported data.[8]

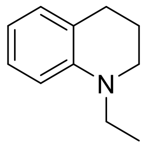


N-ethyl-N,4-dimethylaniline (4u). Purification by silica gel column chromatography using petroleum ether/ethyl acetate gave pale yellow oil, 0.060 g, 81%. ^{1}H NMR (400 MHz, $CDCl_3$, 20 ºC) δ 7.06 (d, *J* = 8.3 Hz, 2H), 6.68 (d, *J* = 8.6 Hz, 2H), 3.38 (q, *J* = 7.1 Hz, 2H), 2.88 (s, 3H), 2.27 (s, 3H), 1.11 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 20 ºC) δ 147.4, 129.8, 125.6, 113.1, 47.3, 37.8, 20.4, 11.2. These spectroscopic data correspond to reported data.[8]

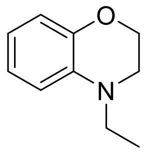


1-Ethylindoline (4v). Purification by silica gel column chromatography using petroleum ether/ethyl acetate gave yellow oil, 0.070 g, 95%. ^{1}H NMR (400 MHz,

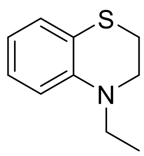
$CDCl_3$, 20 ºC) δ 7.08 (t, *J* = 7.7 Hz, 2H), 6.71-6.61 (m, 1H), 6.50 (d, *J* = 7.7 Hz, 1H), 3.88 (q, *J* = 7.0 Hz, 1H), 3.34 (t, *J* = 8.3 Hz, 2H), 3.15 (q, *J* = 7.2 Hz, 2H), 2.97 (t, *J* = 8.2 Hz, 2H), 1.26 (t, *J* = 7.0 Hz, 1H), 1.21 (t, *J* = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 20 ºC) δ 152.5, 130.4, 127.4, 124.5, 117.6, 107.3, 52.4, 43.3, 28.6, 12.1. These spectroscopic data correspond to reported data.[8]



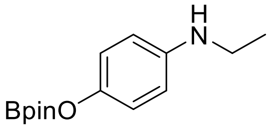
1-Ethyl-1,2,3,4-tetrahydroquinoline (4w). Purification by silica gel column chromatography using petroleum ether/ethyl acetate gave pale yellow oil, 0.052 g, 65%. ^1H NMR (400 MHz, $CDCl_3$, 20 ºC) δ 7.07 (t, *J* = 7.7 Hz, 1H), 6.96 (d, *J* = 7.3 Hz, 1H), 6.62 (d, *J* = 8.2 Hz, 1H), 6.57 (t, *J* = 7.3 Hz, 1H), 3.36 (q, *J* = 7.1 Hz, 2H), 3.33-3.24 (m, 2H), 2.77 (t, *J* = 6.4 Hz, 2H), 2.05-1.82 (m, 2H), 1.16 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 20 ºC) δ 145.1, 129.3, 127.2, 122.6, 115.5, 110.7, 48.5, 45.4, 28.3, 22.4, 10.9. These spectroscopic data correspond to reported data.[8]



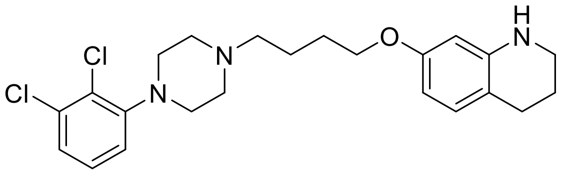
4-Ethyl-3,4-dihydro-2H-benzo[b][1,4]oxazine (4x). Purification by silica gel column chromatography using petroleum ether/ethyl acetate gave pale yellow oil, 0.061 g, 75%. ^1H NMR (400 MHz, $CDCl_3$, 20 ºC) δ 6.84 (td, *J* = 8.1 Hz, *J* = 1.5 Hz, 1H), 6.78 (dd, *J* = 7.9 Hz, *J* = 1.4 Hz, 1H), 6.70 (dd, *J* = 8.0 Hz, *J* = 1.1 Hz, 1H), 6.61 (td, *J* = 7.9 Hz, *J* = 1.4 Hz, 1H), 4.39-4.19 (m, 2H), 3.34 (dt, *J* = 8.8 Hz, *J* = 5.8 Hz, 4H), 1.16 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 20 ºC) δ 144.3, 135.0, 121.7, 117.4, 116.4, 112.3, 64.7, 46.1, 45.0, 10.7. These spectroscopic data correspond to reported data.[8]



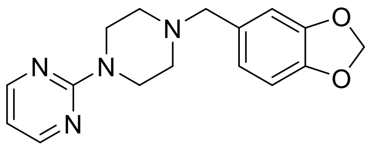
4-Ethyl-3,4-dihydro-2H-benzo[b][1,4]thiazine (4y). Purification by silica gel column chromatography using petroleum ether/ethyl acetate gave yellow oil, 0.074 g, 83%. ^1H NMR (400 MHz, $CDCl_3$, 20 ºC) δ 7.03 (dd, *J* = 7.0 Hz, *J* = 5.5 Hz, 1H), 6.98 (dd, *J* = 6.9 Hz, *J* = 1.3 Hz, 1H), 6.70 (d, *J* = 7.6 Hz, 1H), 6.60 (t, *J* = 6.6 Hz, 1H), 3.60 (dd, *J* = 6.0 Hz, *J* = 4.2 Hz, 2H), 3.48-3.27 (m, 2H), 3.05 (dd, *J* = 5.9 Hz, *J* = 4.4 Hz, 2H), 1.19 (t, *J* = 7.0 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 20 ºC) δ 143.3, 128.1, 126.1, 117.8, 117.1, 112.6, 49.1, 46.6, 26.1, 11.3. These spectroscopic data correspond to reported data.[8]



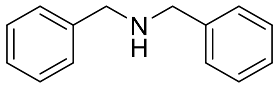
N-ethyl-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)aniline (4ab). Purification by silica gel column chromatography using petroleum ether/ethyl acetate gave white solid, 0.079 g, 60%. mp: 89-92 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 20 ºC) δ 6.69 (d, *J* = 8.6 Hz, 2H), 6.54 (d, *J* = 8.7 Hz, 2H), 4.31 (s, 1H), 3.10 (q, *J* = 7.1 Hz, 2H), 1.25 (t, *J* = 8.0 Hz, 12H), 1.22 (d, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 20 ºC) δ 148.2, 142.6, 116.3, 114.8, 83.3, 75.4, 39.9, 25.0, 24.7, 15.1. HRMS (ESI/TOF) Calcd for $C_{14}H_{23}NO_3B$ [$(M+H)^+$]: 264.1771; found: 264.1773.



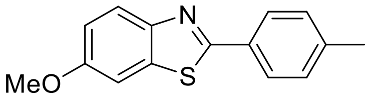
7-(4-(4-(2,3-dichlorophenyl)piperazin-1-yl)butoxy)-1,2,3,4-tetrahydroquinoline (4ac). Purification by silica gel column chromatography using petroleum ether/ethyl acetate gave colorless oil, 0.17 g, 81%. ^{1}H NMR (400 MHz, $CDCl_3$, 20 ºC) δ 7.19-7.09 (m, 2H), 6.96 (dd, *J* = 6.4 Hz, *J* = 3.0 Hz, 1H), 6.83 (d, *J* = 8.2 Hz, 1H), 6.19 (dd, *J* = 8.2, 2.3 Hz, 1H), 6.04 (d, *J* = 2.2 Hz, 1H), 3.92 (t, *J* = 6.2 Hz, 2H), 3.33-3.22 (m, 2H), 3.07 (s, 4H), 2.68 (dd, *J* = 15.0 Hz, *J* = 8.6 Hz, 6H), 2.52-2.40 (m, 2H), 1.97-1.86 (m, 2H), 1.79 (dt, *J* = 13.1 Hz, *J* = 6.4 Hz, 2H), 1.68 (dt, *J* = 9.4 Hz, *J* = 7.0 Hz, 2H), 1.26 (s, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 20 ºC) δ 158.4, 151.5, 145.6, 134.1, 130.2, 127.6, 127.5, 124.6, 118.7, 114.1, 103.6, 100.3, 100.1, 67.7, 58.4, 53.4, 51.4, 42.0, 27.5, 26.4, 23.6, 22.6. HRMS (ESI/TOF) Calcd for $C_{23}H_{30}N_3O\ Cl_2$ [$(M+H)^+$]: 434.1766; found: 434.1759.



2-(4-(benzo[d][1,3]dioxol-5-ylmethyl)piperazin-1-yl)pyrimidine (4ad). Purification by silica gel column chromatography using petroleum ether/ethyl acetate gave white solid 0.086 g, 61%. ^{1}H NMR (400 MHz, $CDCl_3$, 20 ºC) δ 8.28 (d, *J* = 4.7 Hz, 2H), 6.88 (s, 1H), 6.81-6.70 (m, 2H), 6.45 (t, *J* = 4.7 Hz, 1H), 5.94 (s, 2H), 3.83 (dd, *J* = 21.3 Hz, *J* = 16.3 Hz, 4H), 3.44 (s, 2H), 2.63-2.32 (m, 4H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 20 ºC) δ 161.8, 157.8, 147.8, 146.7, 132.0, 122.3, 109.8, 109.6, 108.0, 101.0, 63.0, 52.9, 43.8. These spectroscopic data correspond to reported data.[9]



Dibenzylamine (5). Purification by silica gel column chromatography using petroleum ether/ethyl acetate gave colorless oil, 0.069 g, 70%. ^{1}H NMR (400 MHz, $CDCl_3$, 20 ºC) δ 7.32 (dd, *J* = 8.2 Hz, *J* = 5.5 Hz, 8H), 7.29-7.21 (m, 2H), 3.80 (s, 4H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 20 ºC) δ 140.5, 128.5, 128.3, 127.1, 53.30. These spectroscopic data correspond to reported data.[9]



6-Methoxy-2-(p-tolyl)benzo[d]thiazole (6). Purification by silica gel column chromatography using petroleum ether/ethyl acetate gave yellow solid, 0.084 g, 66%. ^1H NMR (400 MHz, $CDCl_3$, 20 ºC) δ 7.97-7.84 (m, 3H), 7.33 (d, *J* = 2.3 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.07 (dd, *J* = 8.9 Hz, *J* = 2.4 Hz, 1H), 3.87 (s, 3H), 2.41 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 20 ºC) δ 165.9, 157.8, 148.8, 141.0, 136.4, 131.2, 129.8, 127.3, 123.6, 115.6, 104.3, 55.9, 21.6. These spectroscopic data correspond to reported data.[10]

5. References

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6. NMR spectra

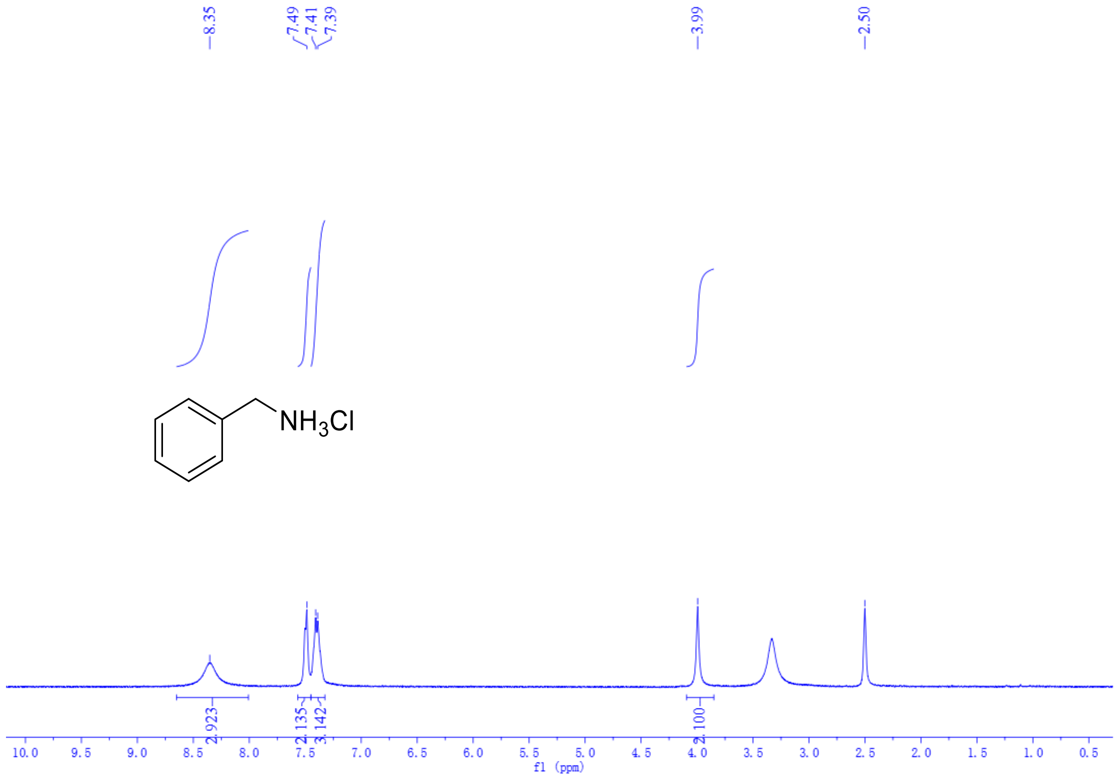

Figure S5. ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) of **2'a**

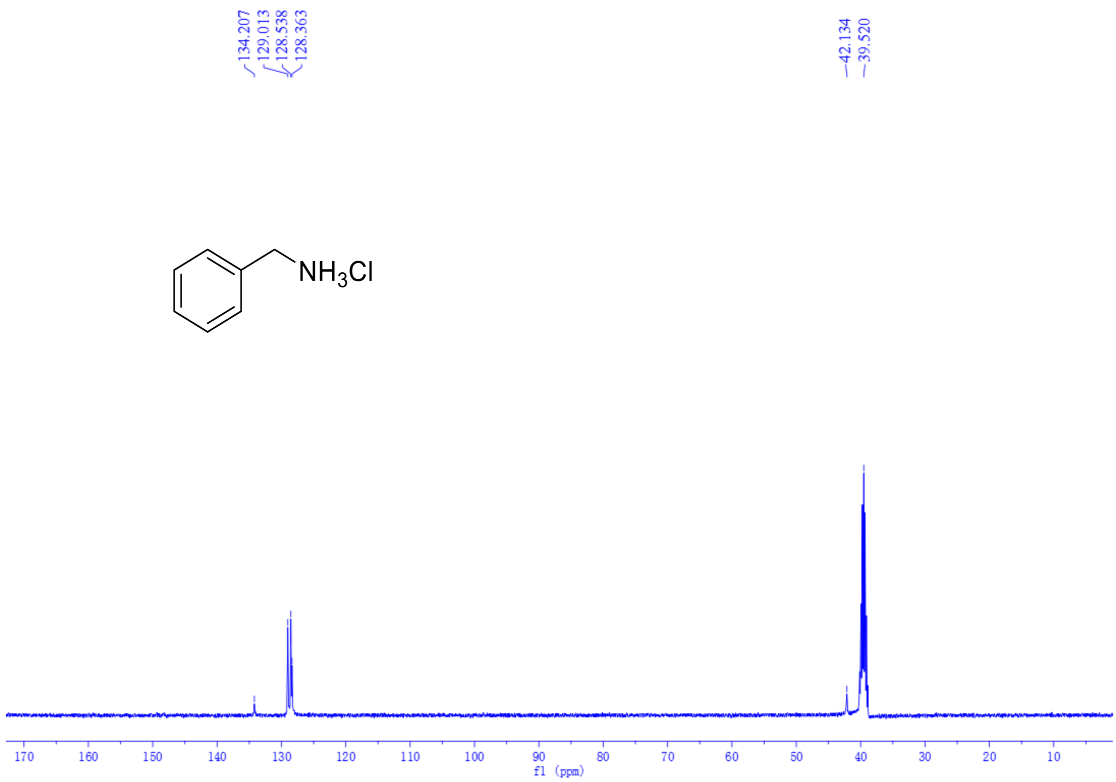

Figure S6. $^{13}C\{^{1}H\}$ (101 MHz, DMSO-d_6, 20 ºC) of **2'a**

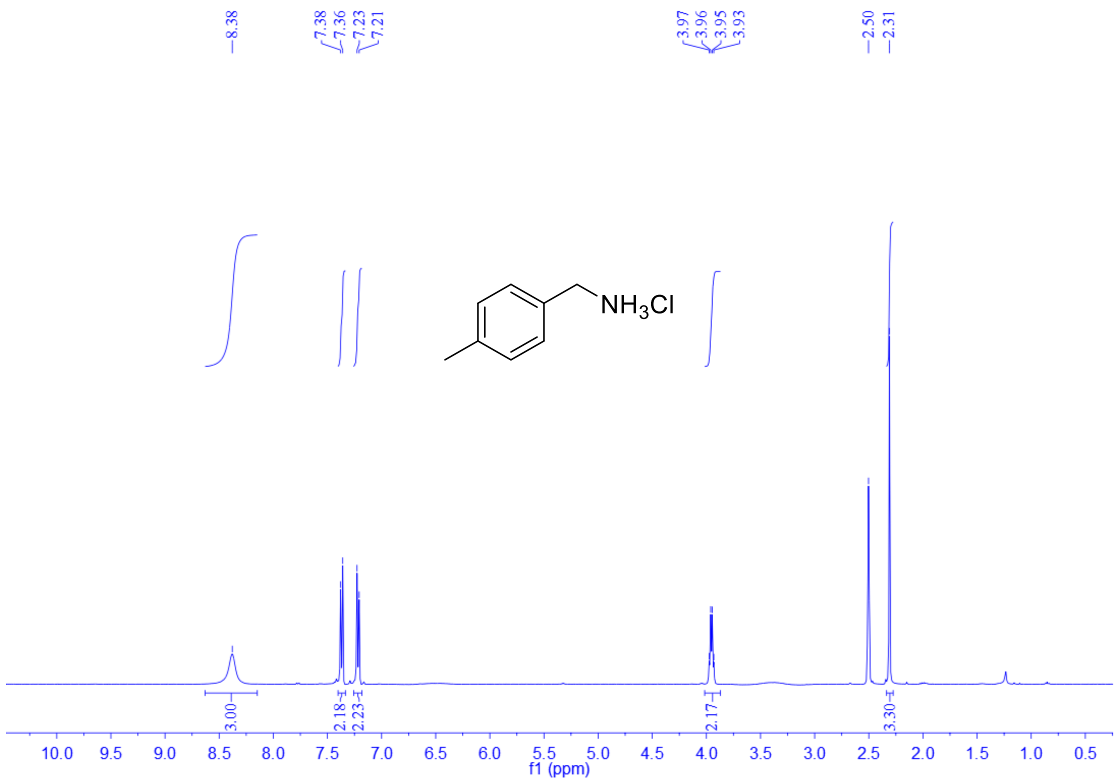

Figure S7. ^{1}H NMR (400 MHz, DMSO-d_6, 20 °C) of **2'b**

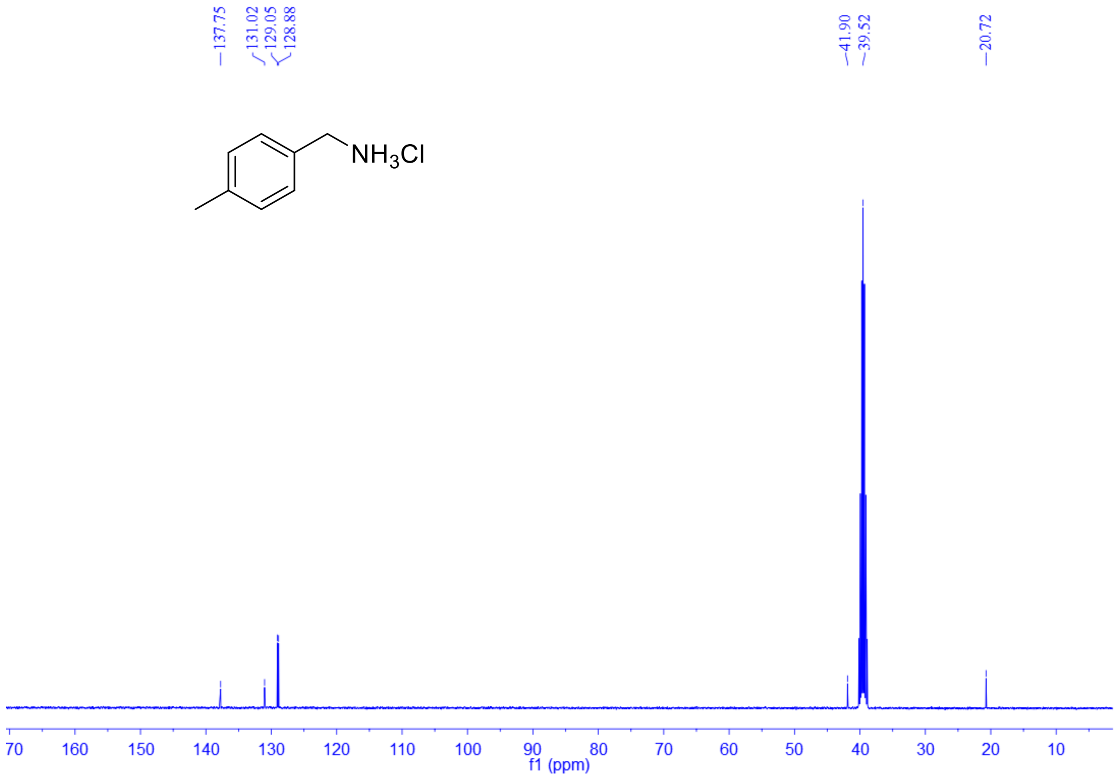

Figure S8. $^{13}C\{^{1}H\}$ (101 MHz, DMSO-d_6, 20 °C) of **2'b**

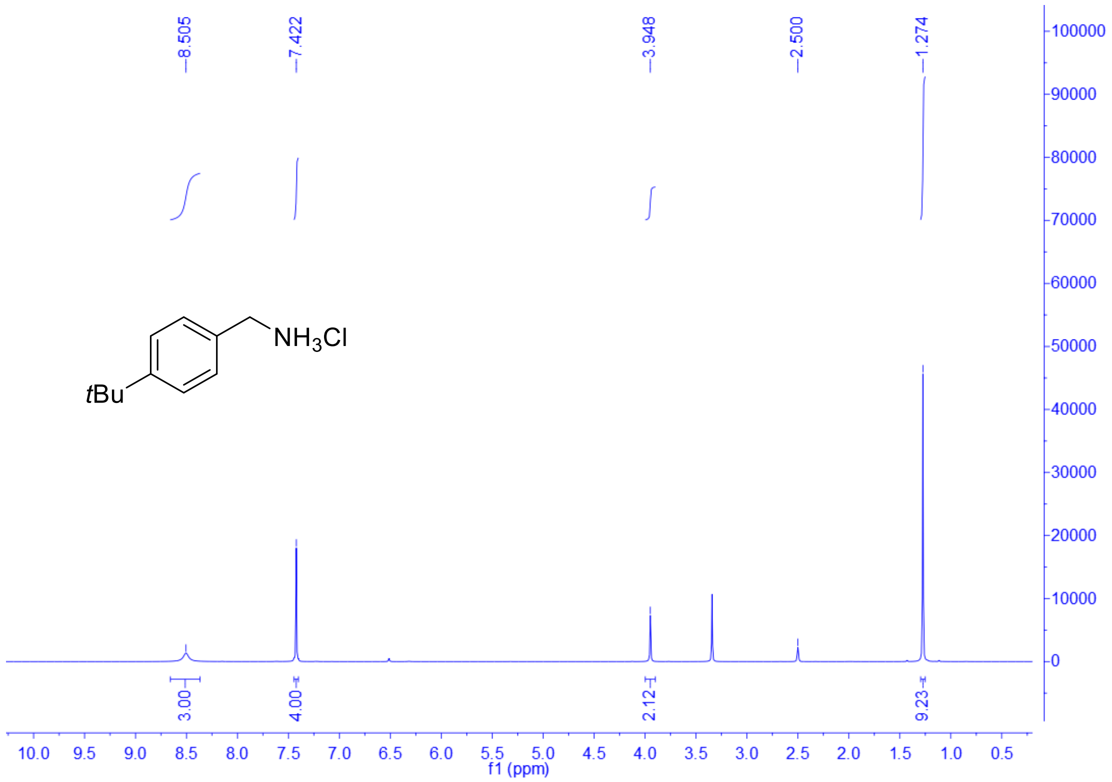

Figure S9. ^{1}H NMR (400 MHz, DMSO-d_6, 20 °C) of **2'c**

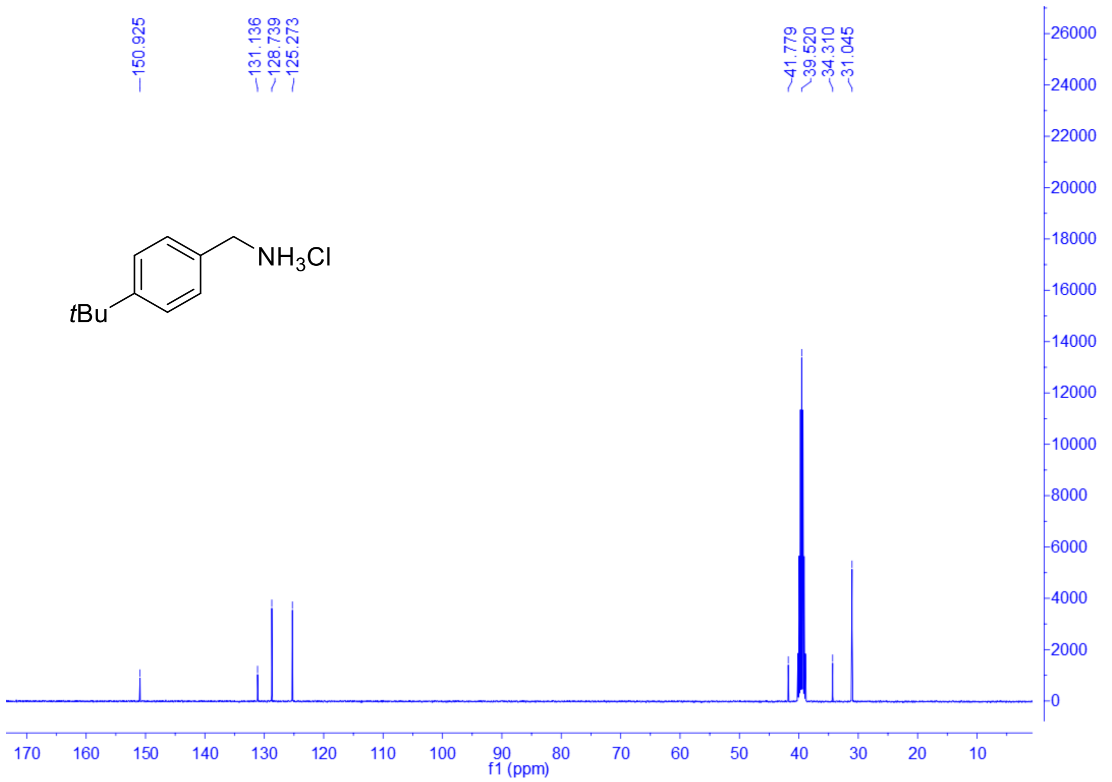

Figure S10. $^{13}C\{^{1}H\}$ (101 MHz, DMSO-d_6, 20 °C) of **2'c**

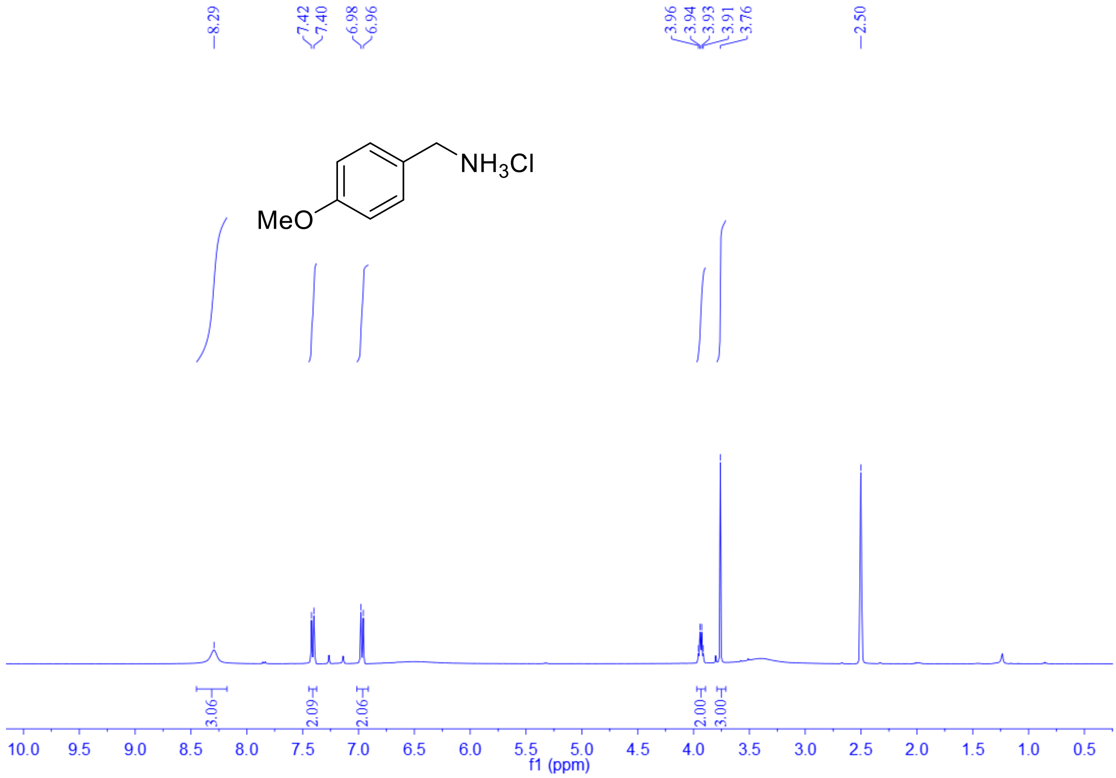

Figure S11. ^{1}H NMR (400 MHz, DMSO-d_6, 20 °C) of **2'd**

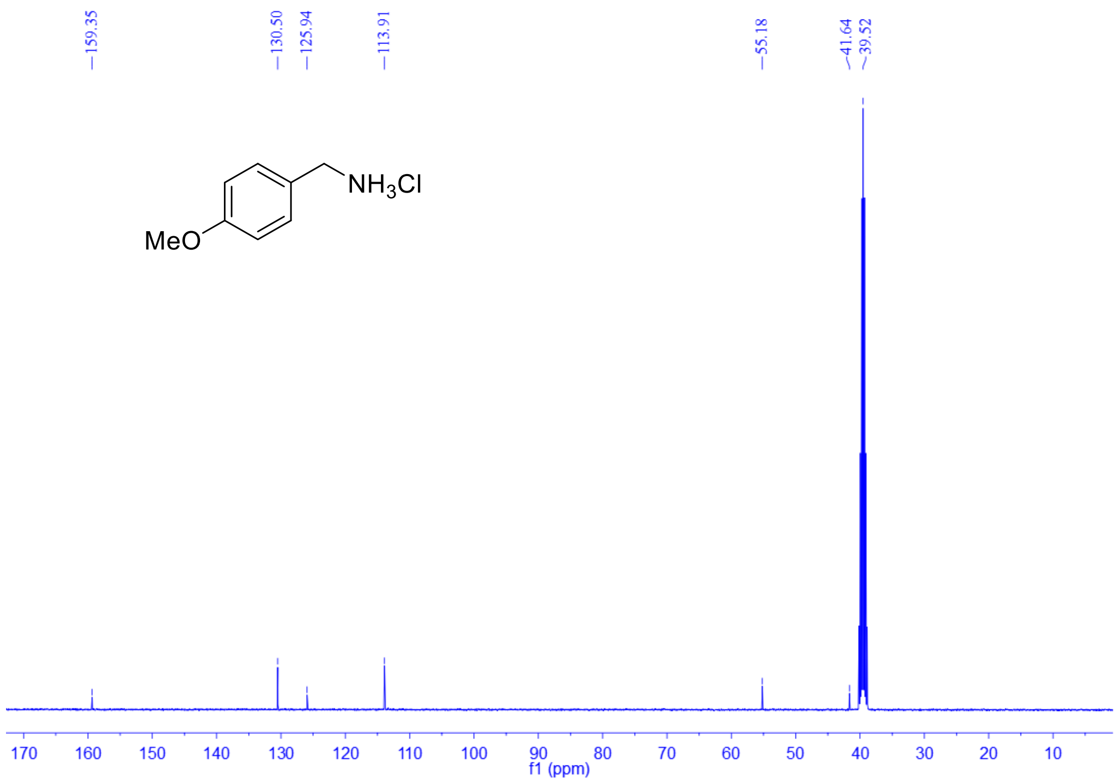

Figure S12. ^{13}C{^{1}H} (101 MHz, DMSO-d_6, 20 °C) of **2'd**

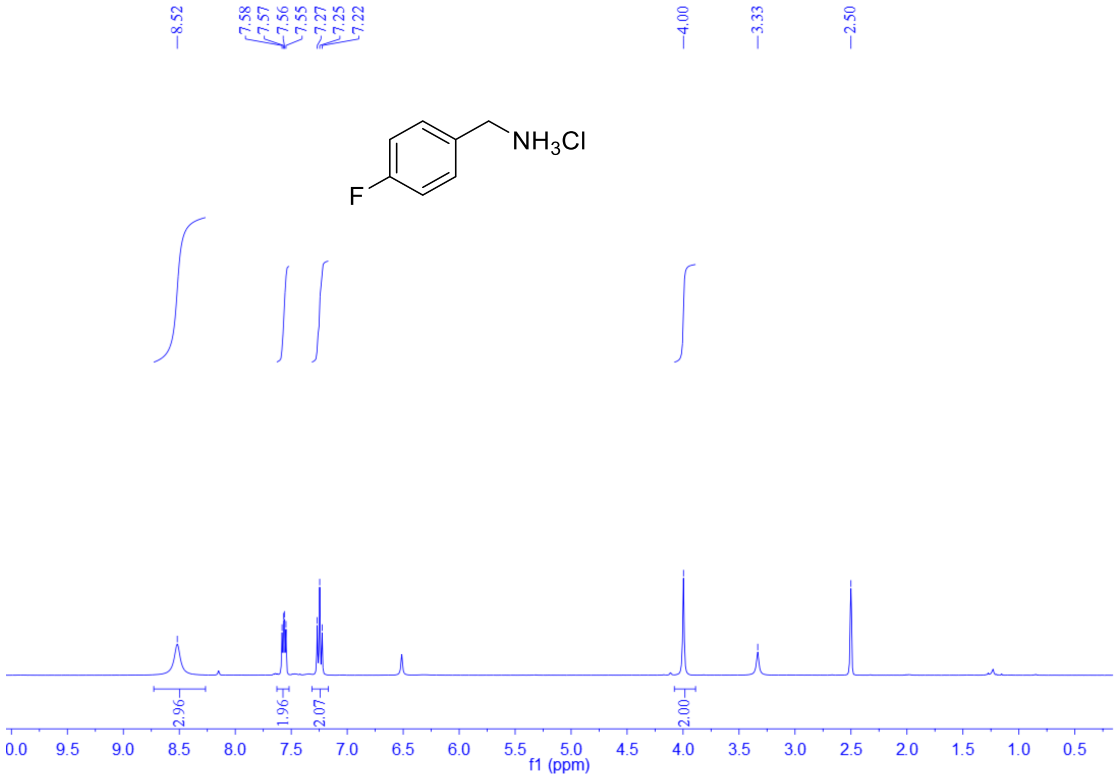

Figure S13. ^{1}H NMR (400 MHz, DMSO-d_6, 20 °C) of **2'e**

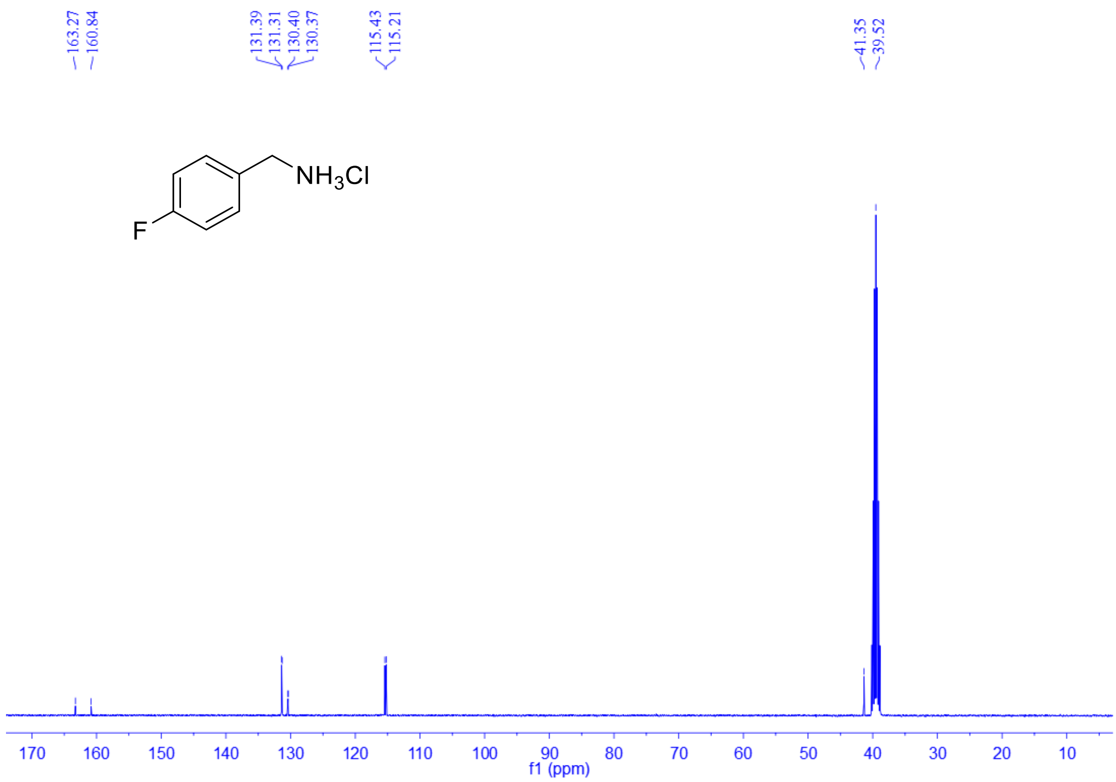

Figure S14. ^{13}C{^{1}H} (101 MHz, DMSO-d_6, 20 °C) of **2'e**

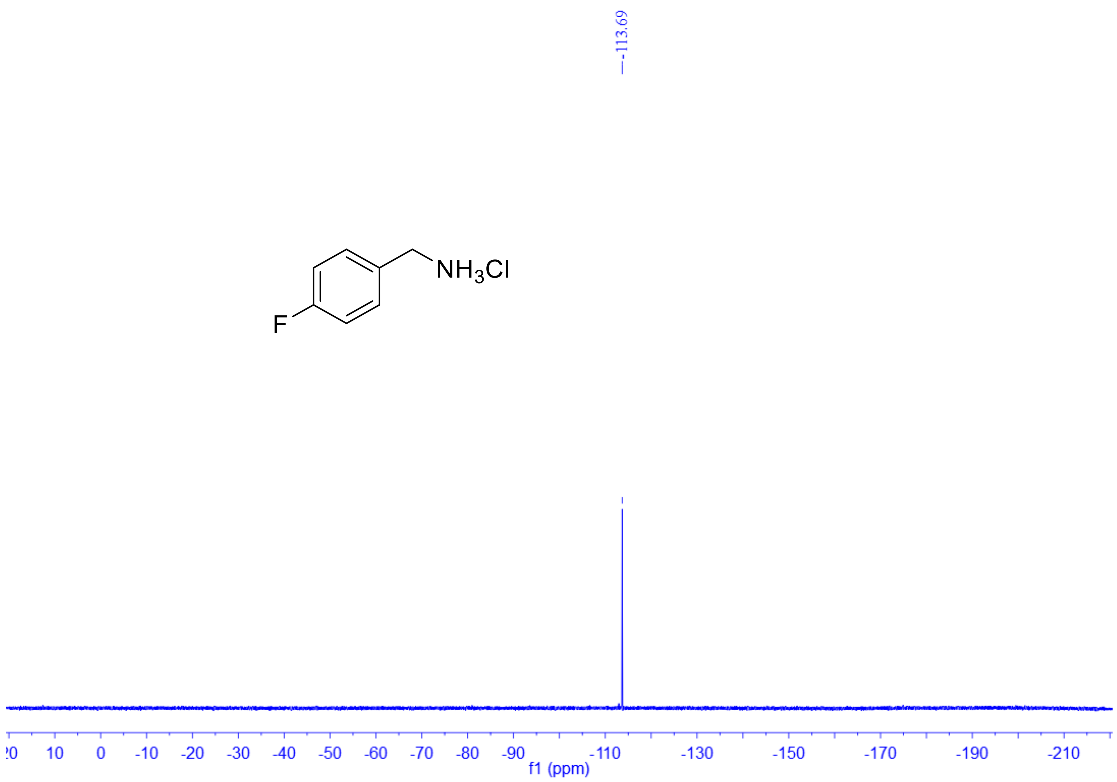

Figure S15. ^{19}F NMR (377 MHz, DMSO-d_6, 20 °C) of **2'e**

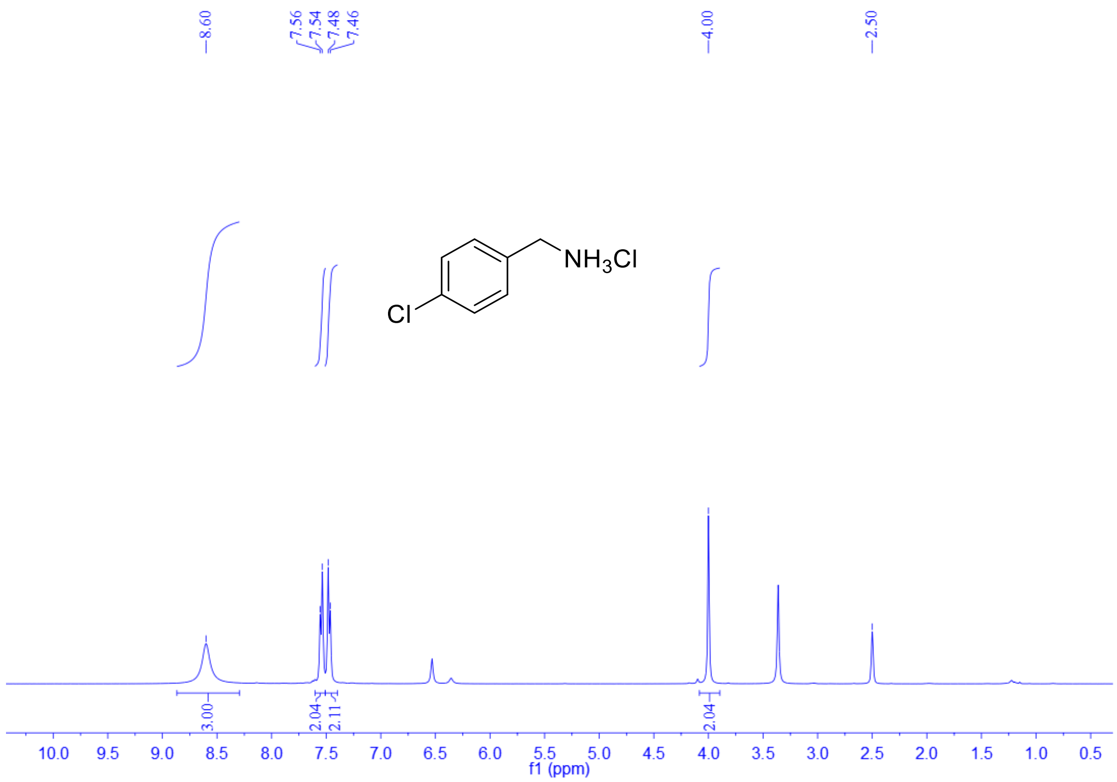

Figure S16. ^{1}H NMR (400 MHz, DMSO-d_6, 20 °C) of **2'f**

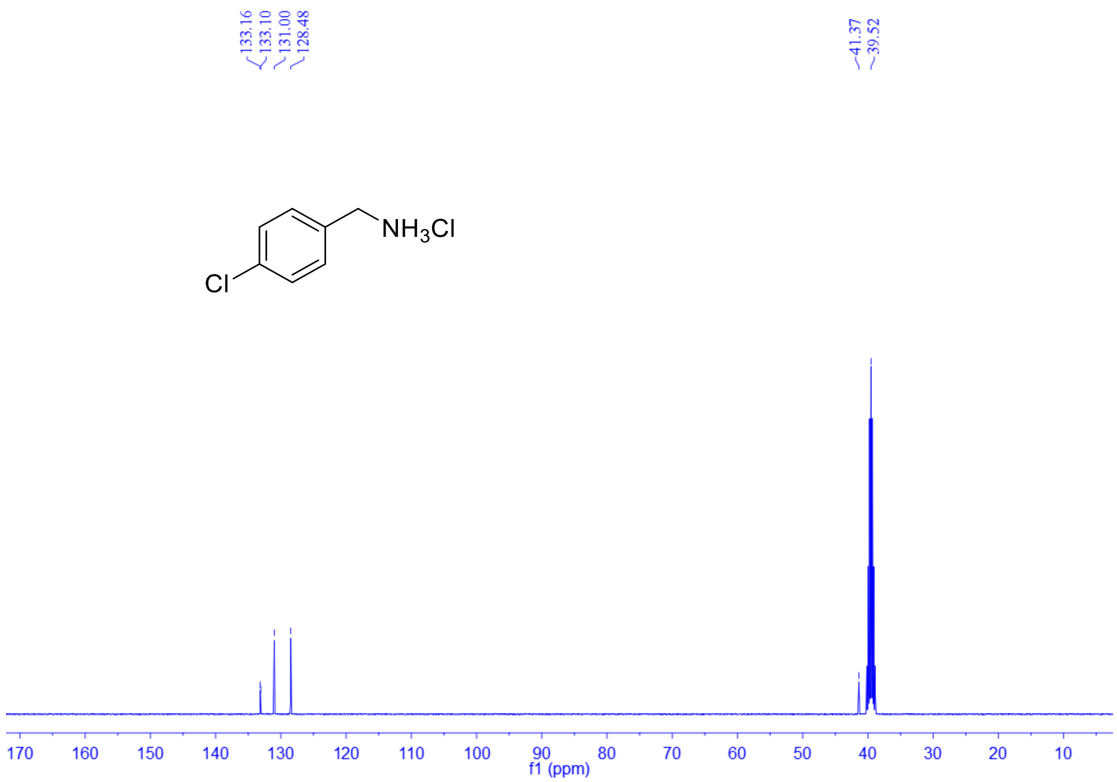

Figure S17. $^{13}C\{^{1}H\}$ (101 MHz, DMSO-d_6, 20 ºC) of **2'f**

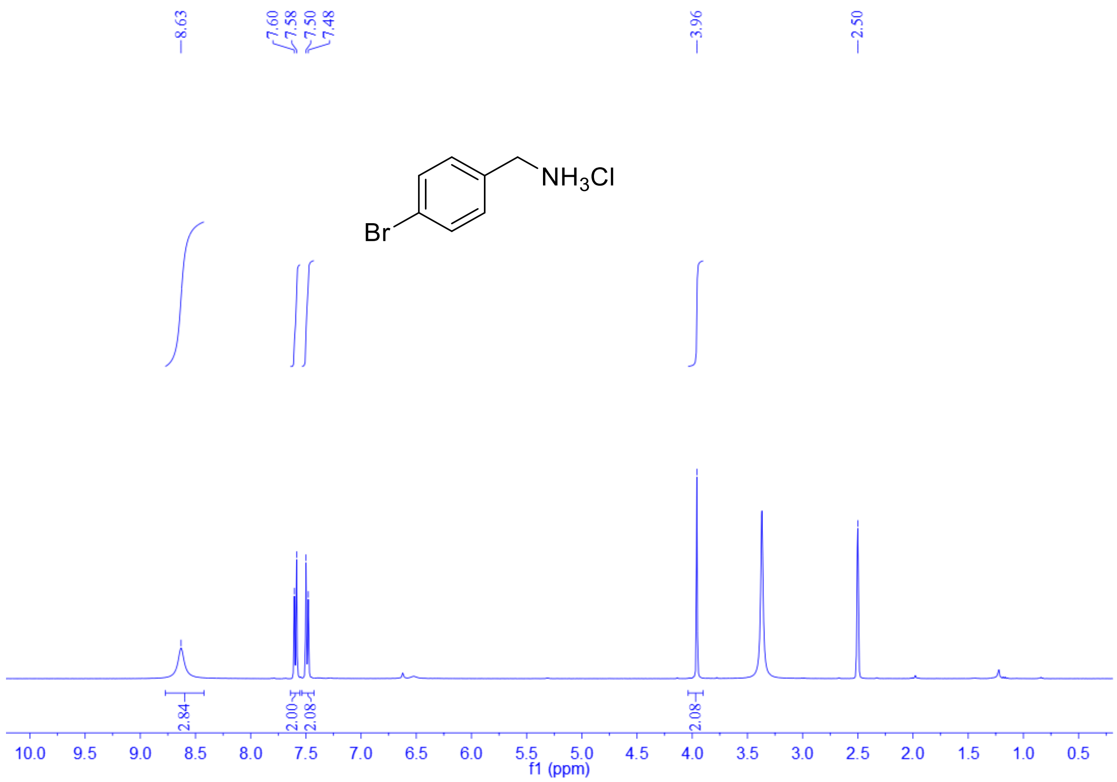

Figure S18. ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) of **2'g**

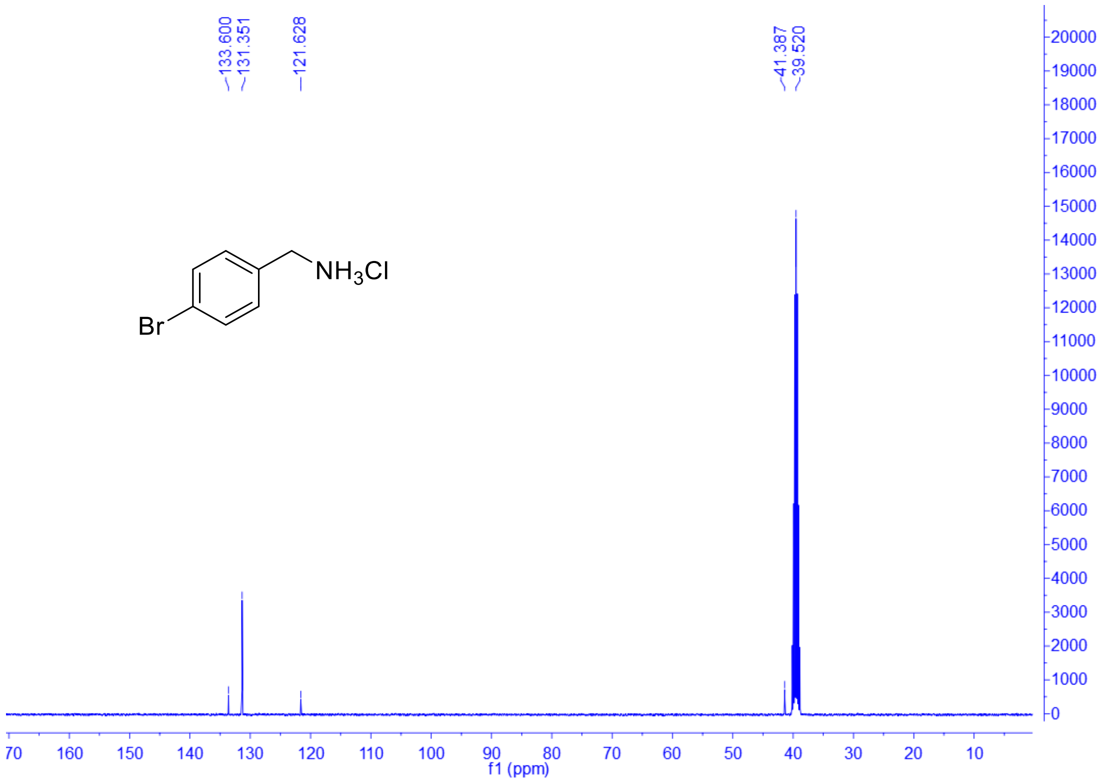

Figure S19. $^{13}C\{^{1}H\}$ (101 MHz, DMSO-d_6, 20 ºC) of **2'g**

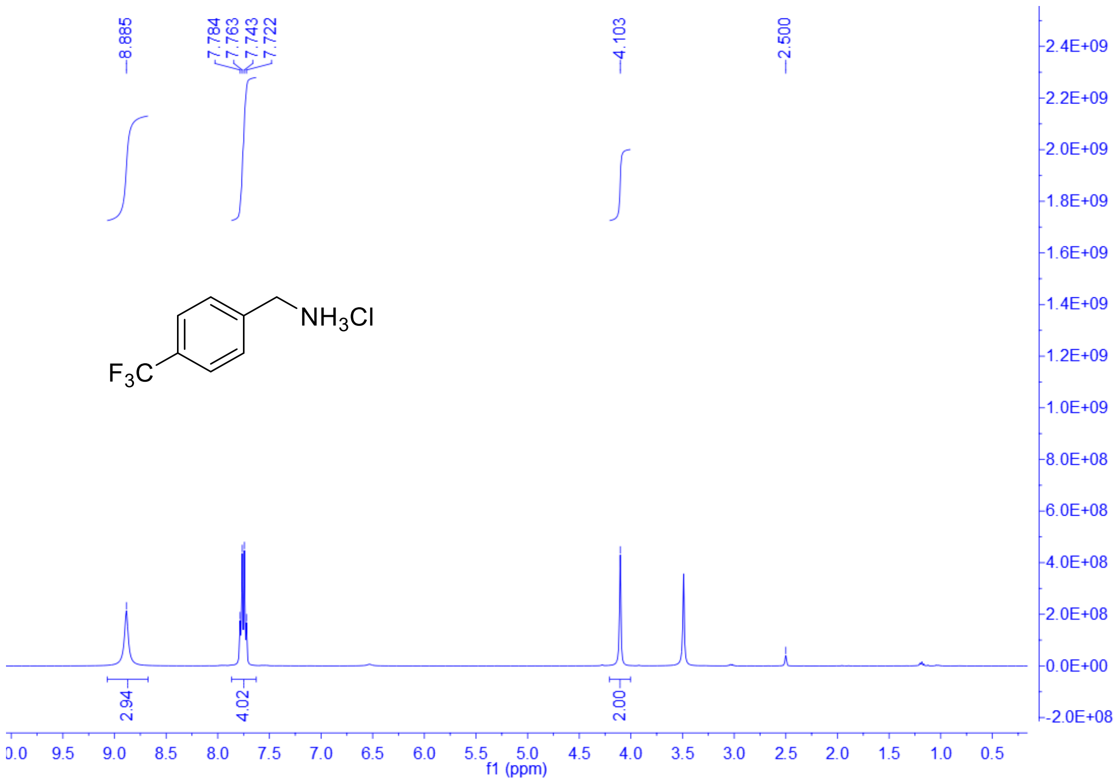

Figure S20. ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) of **2'h**

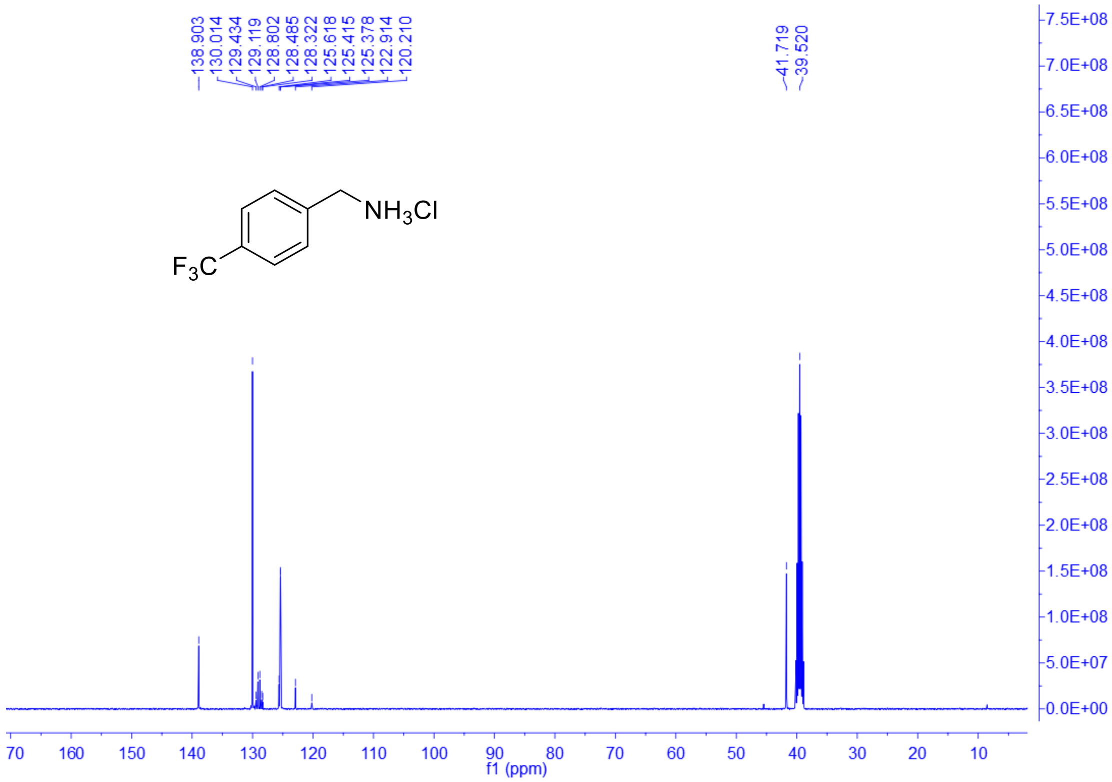

Figure S21. $^{13}C\{^{1}H\}$ (101 MHz, DMSO-d_6, 20 ºC) of **2'h**

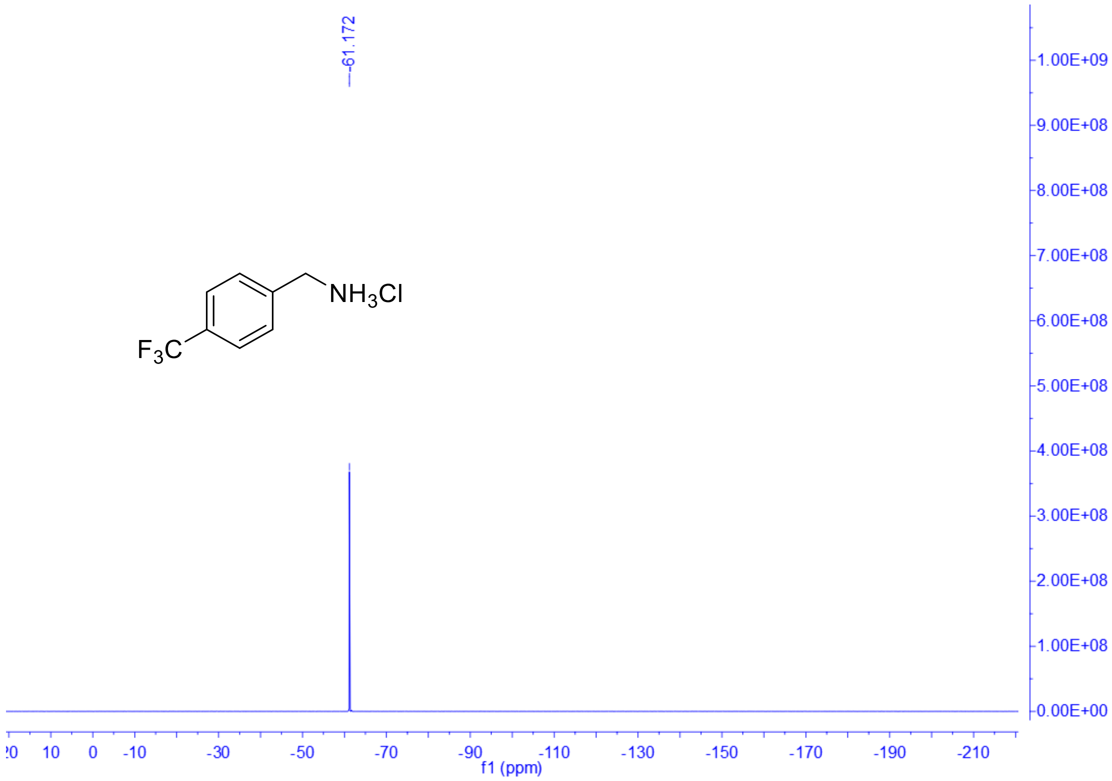

Figure S22. ^{19}F NMR (377 MHz, DMSO-d_6, 20 ºC) of **2'h**

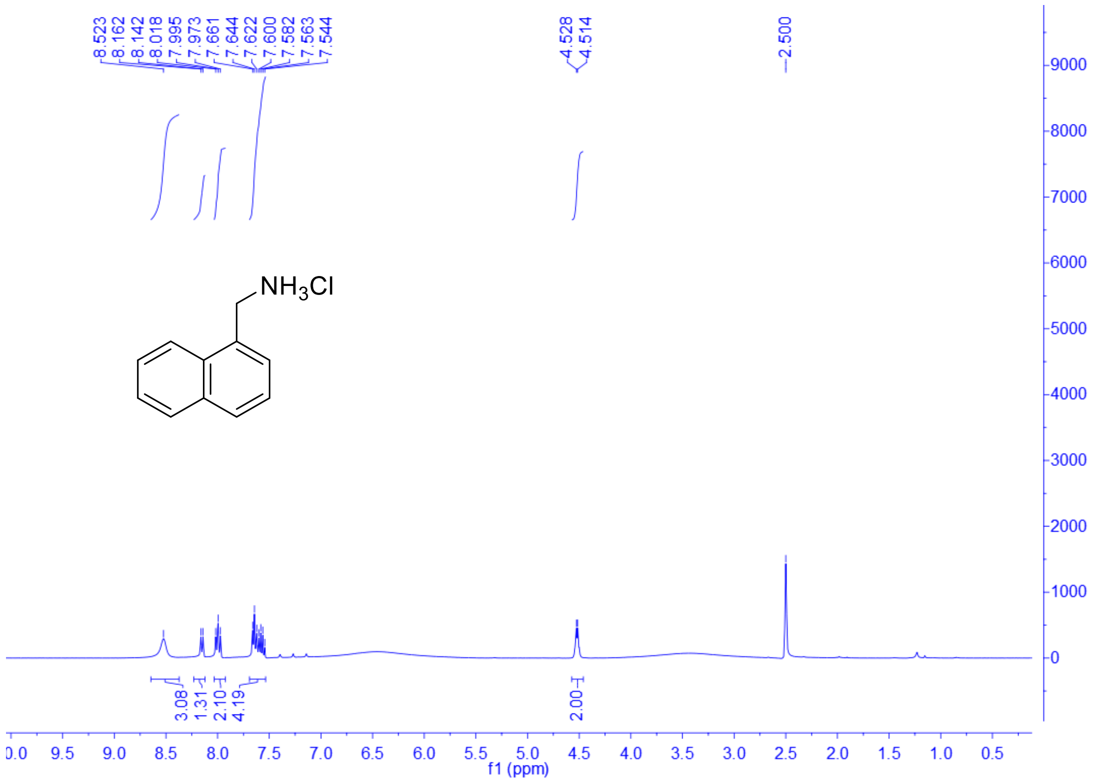

Figure S23. ^{1}H NMR (400 MHz, DMSO-d_6, 20 °C) of **2'i**

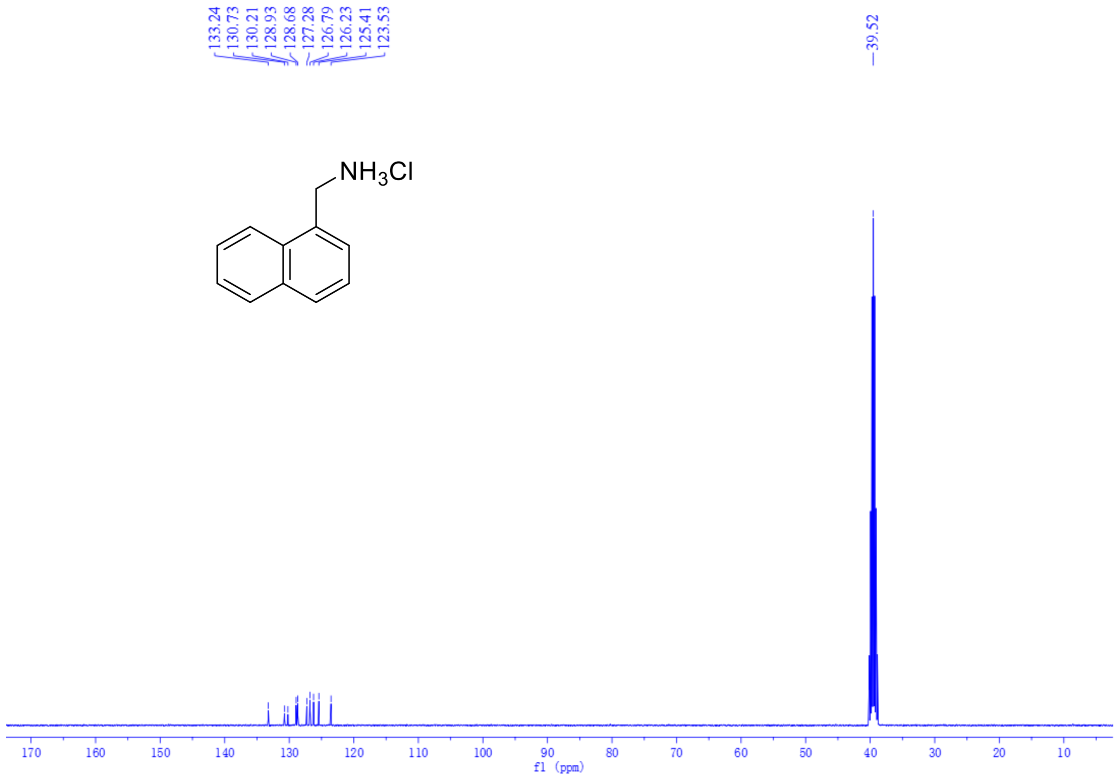

Figure S24. $^{13}C\{^{1}H\}$ (101 MHz, DMSO-d_6, 20 °C) of **2'i**

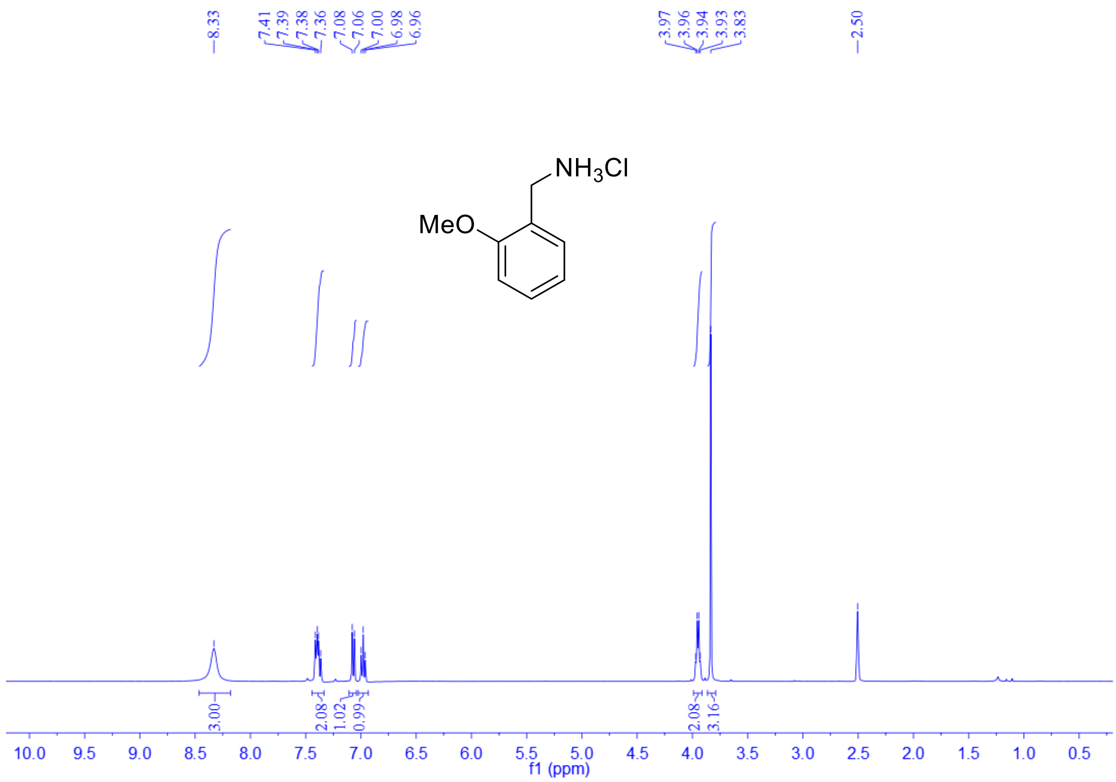

Figure S25. ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) of **2'j**

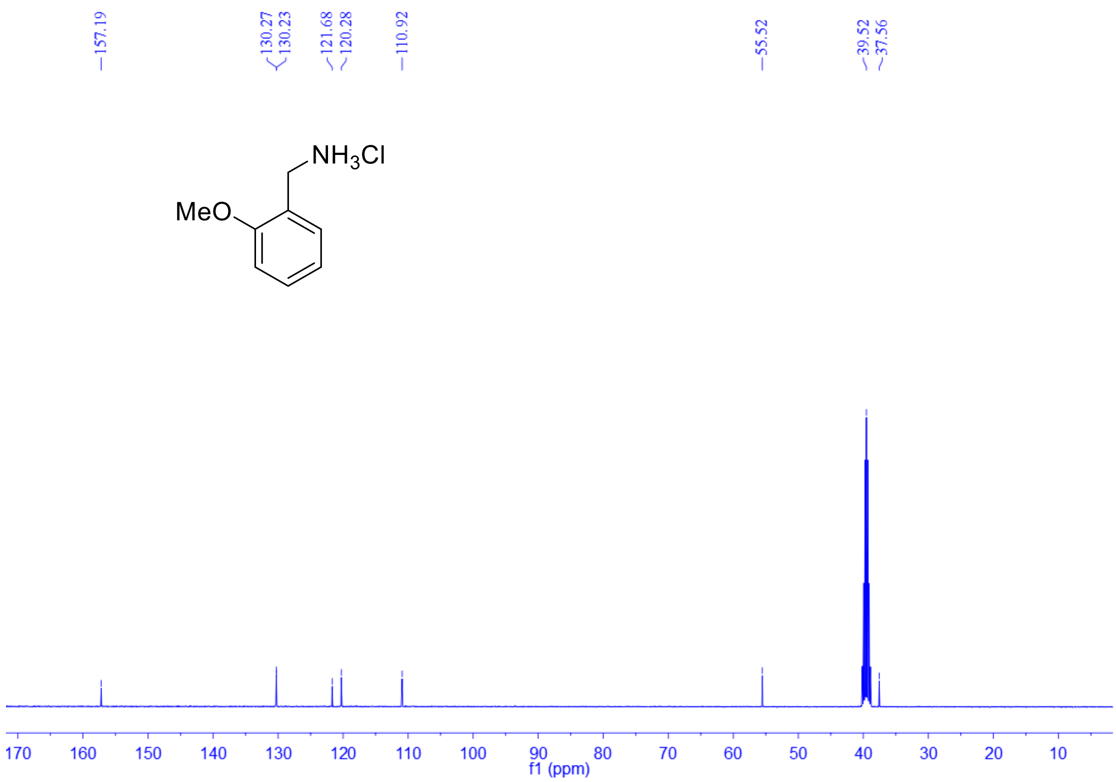

Figure S26. $^{13}C\{^{1}H\}$ (101 MHz, DMSO-d_6, 20 ºC) of **2'j**

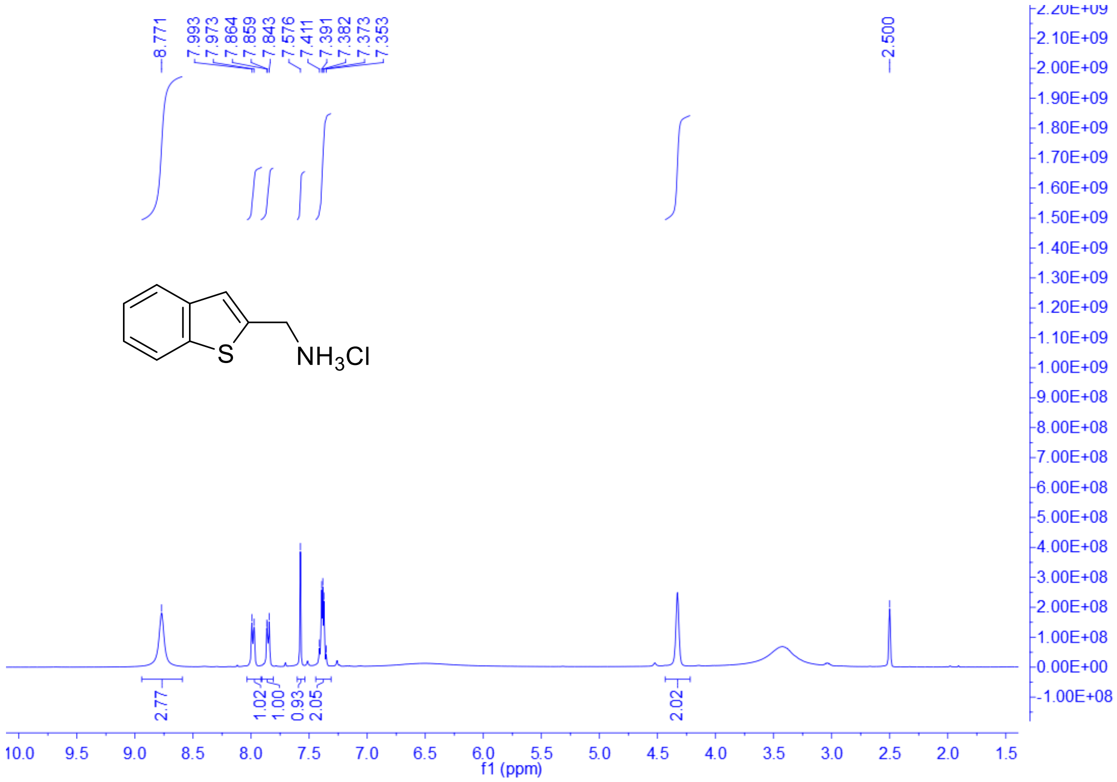

Figure S27. ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) of **2'k**

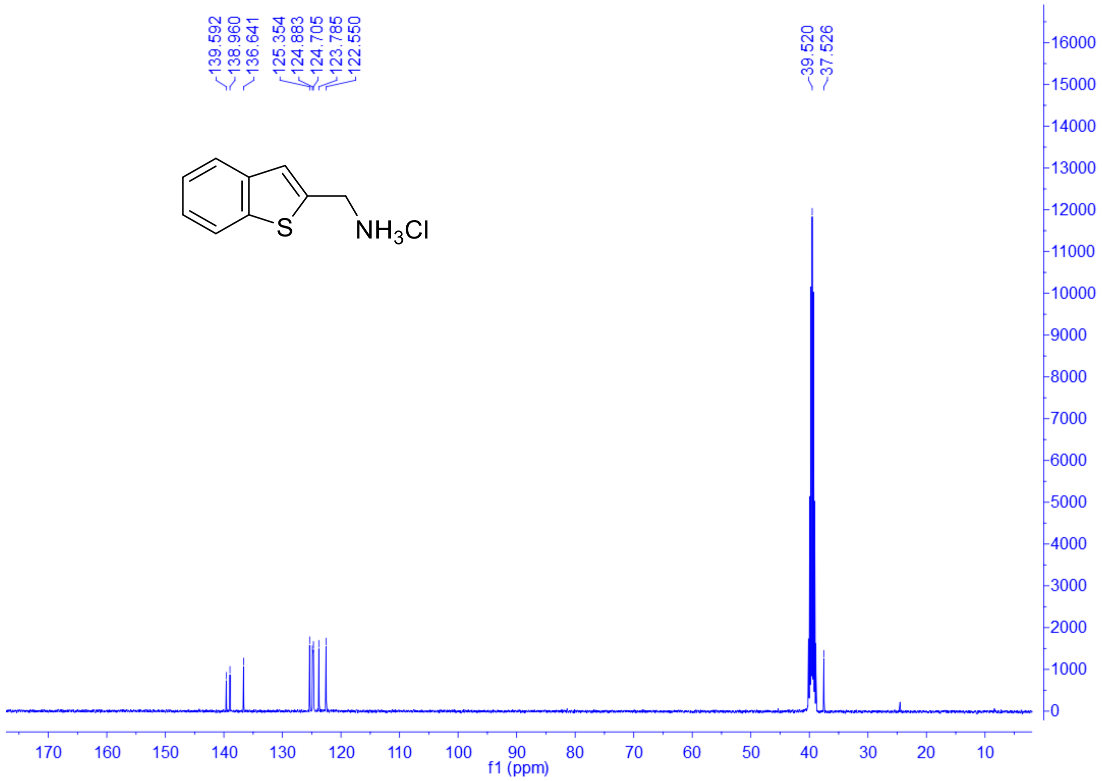

Figure S28. $^{13}C\{^{1}H\}$ (101 MHz, DMSO-d_6, 20 ºC) of **2'k**

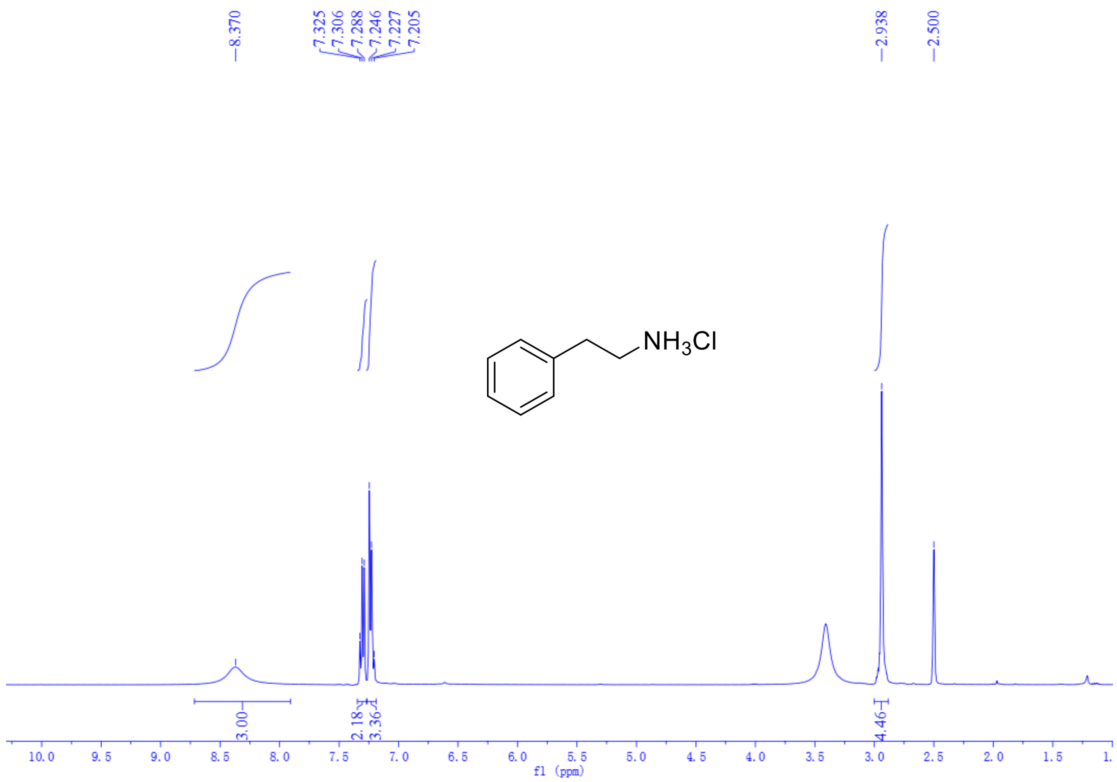

Figure S29. ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) of **2'l**

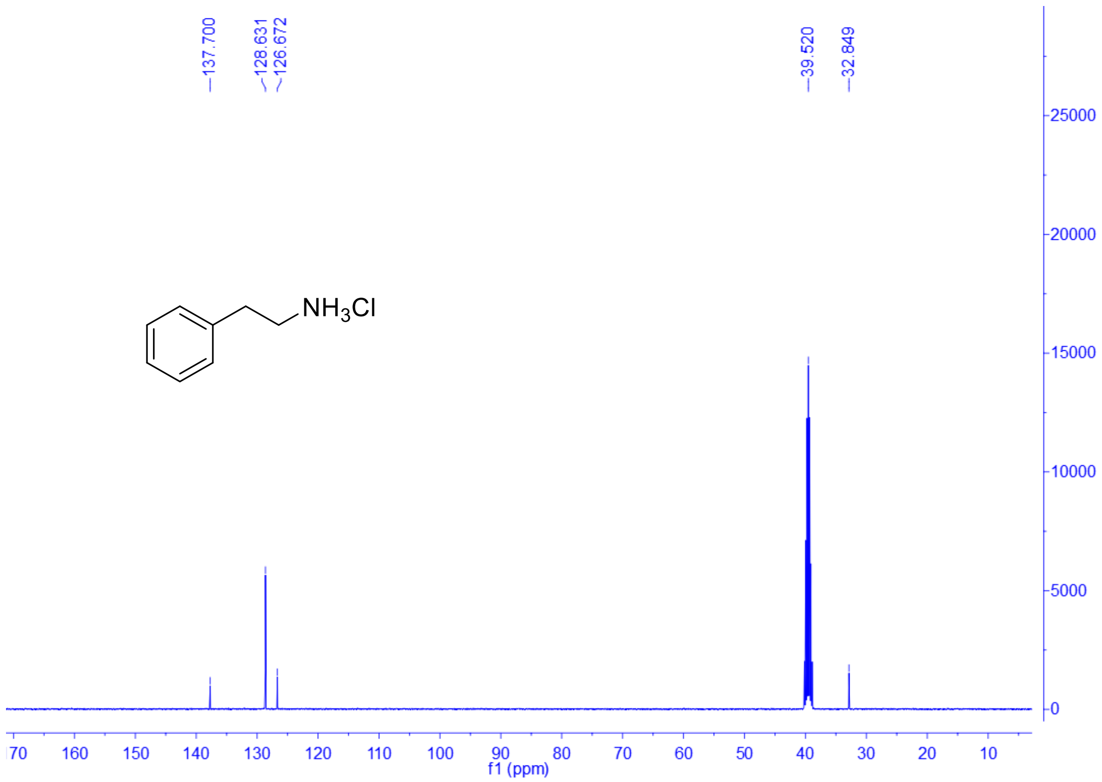

Figure S30. $^{13}C\{^{1}H\}$ (101 MHz, DMSO-d_6, 20 ºC) of **2'l**

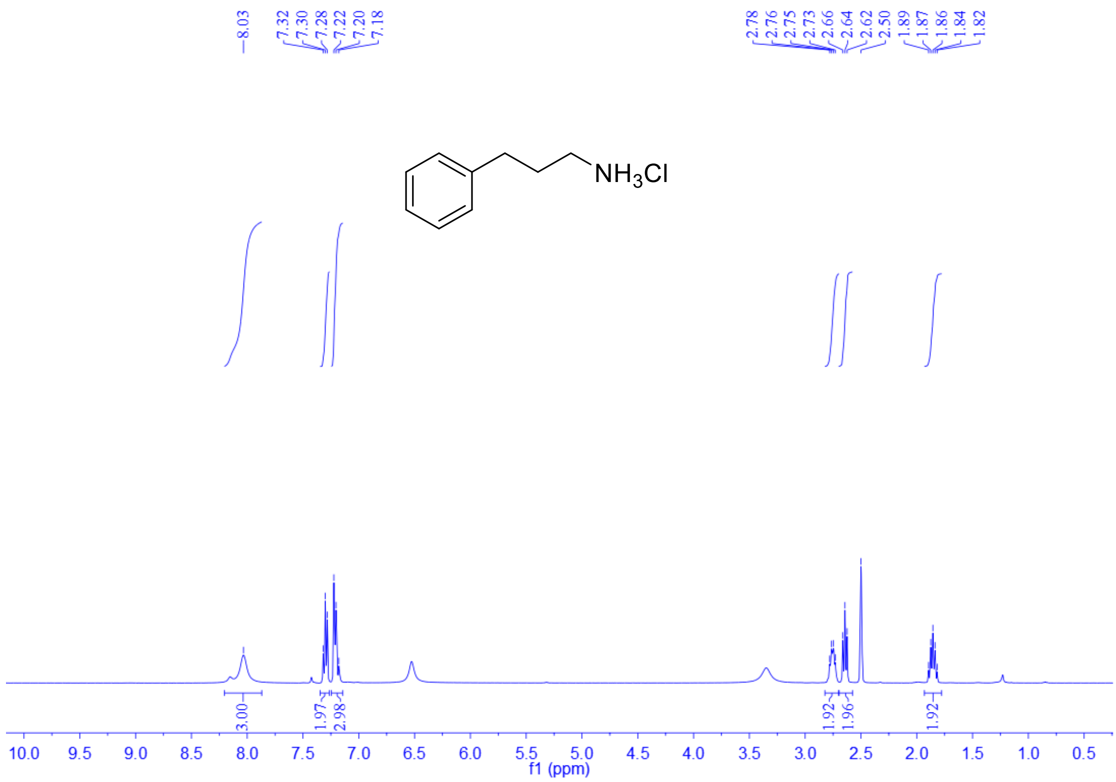

Figure S31. ^{1}H NMR (400 MHz, DMSO-d_6, 20 °C) of **2'm**

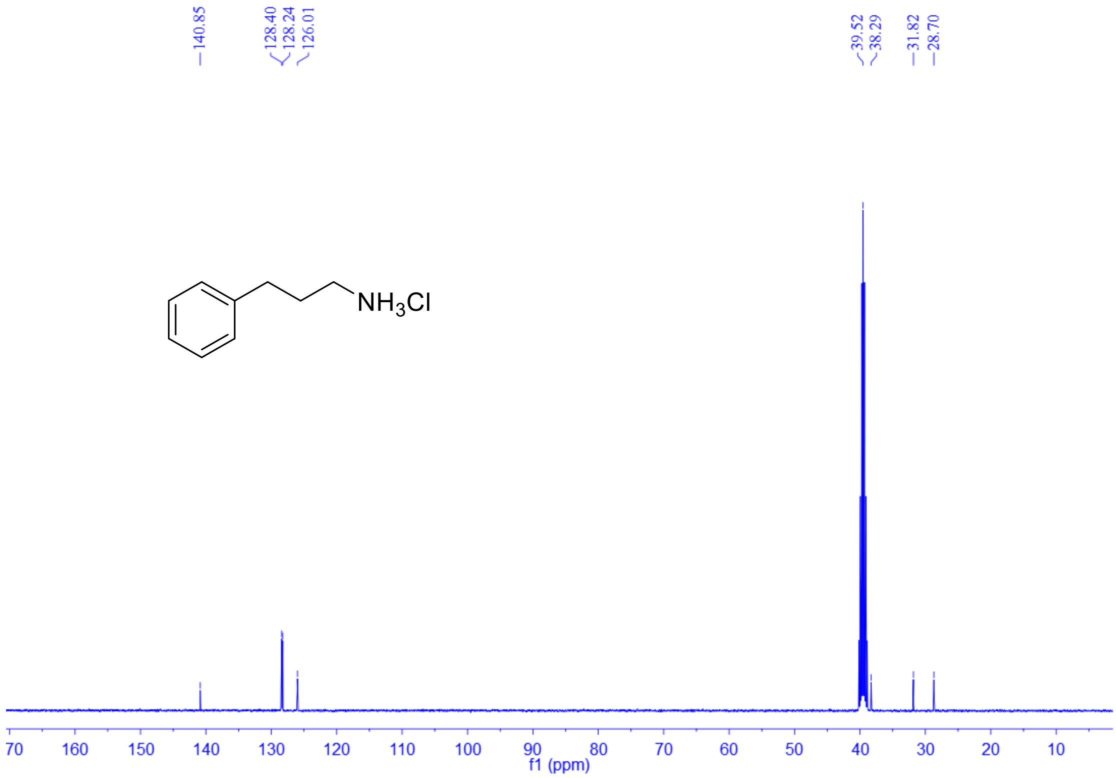

Figure S32. $^{13}C\{^{1}H\}$ (101 MHz, DMSO-d_6, 20 °C) of **2'm**

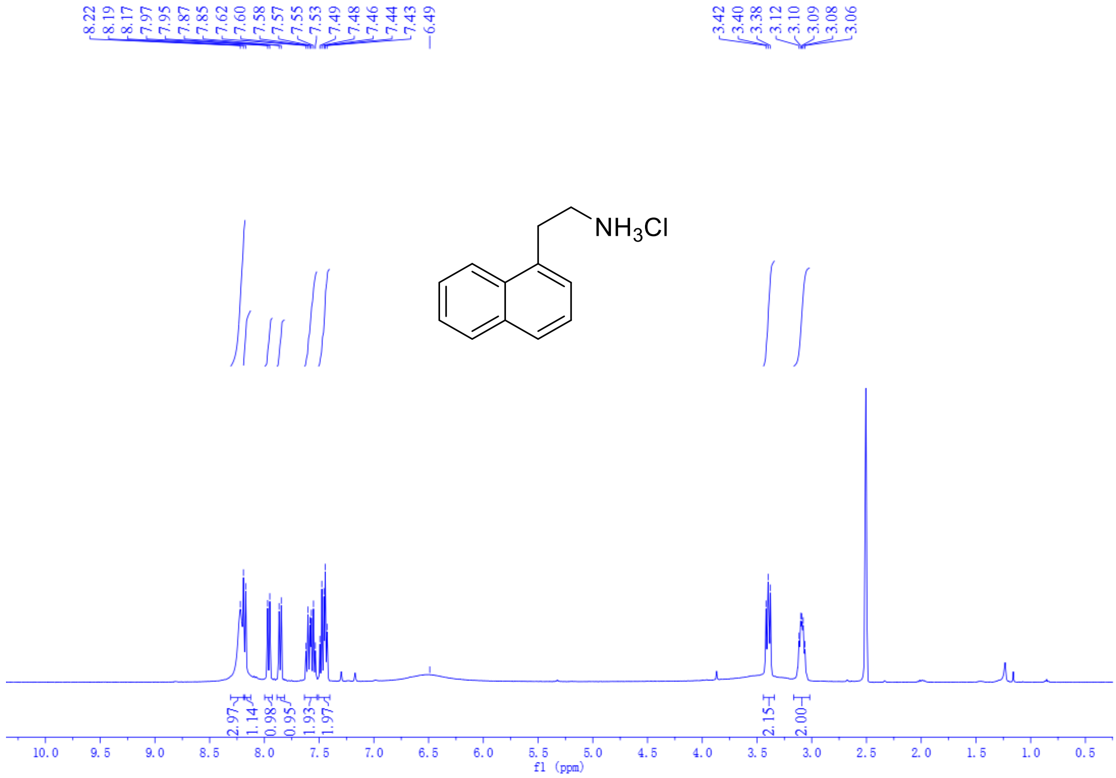

Figure S33. ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) of **2'n**

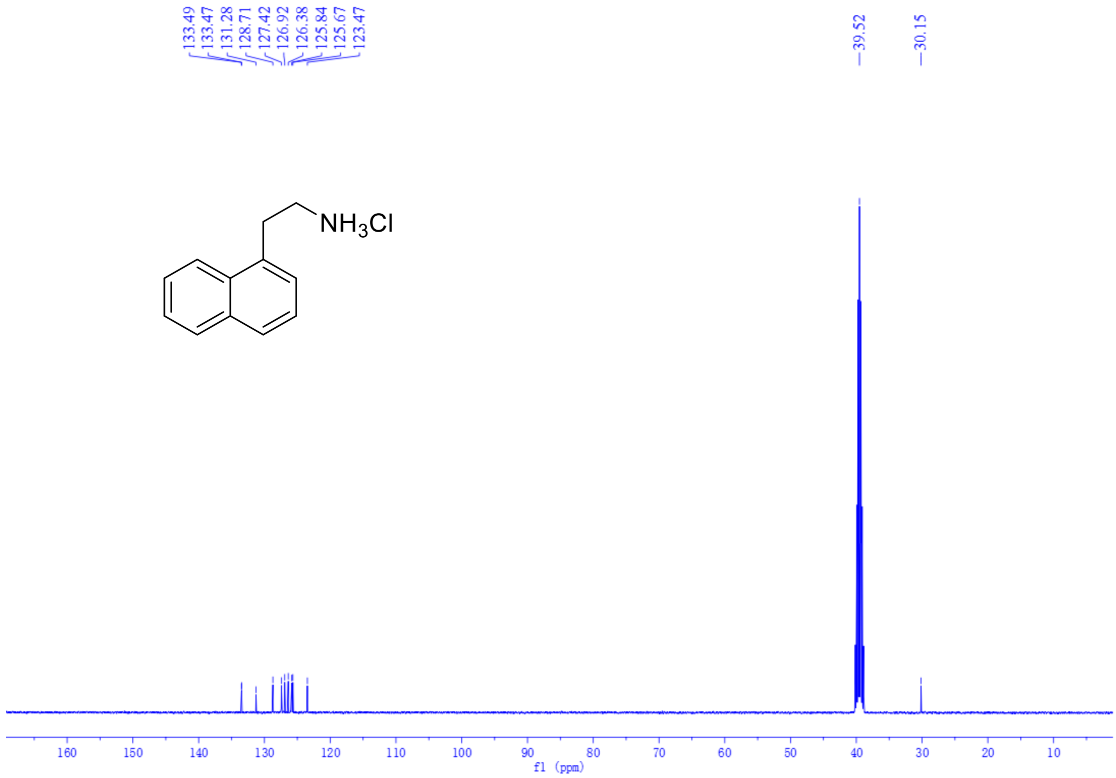

Figure S34. $^{13}C\{^{1}H\}$ (101 MHz, DMSO-d_6, 20 ºC) of **2'n**

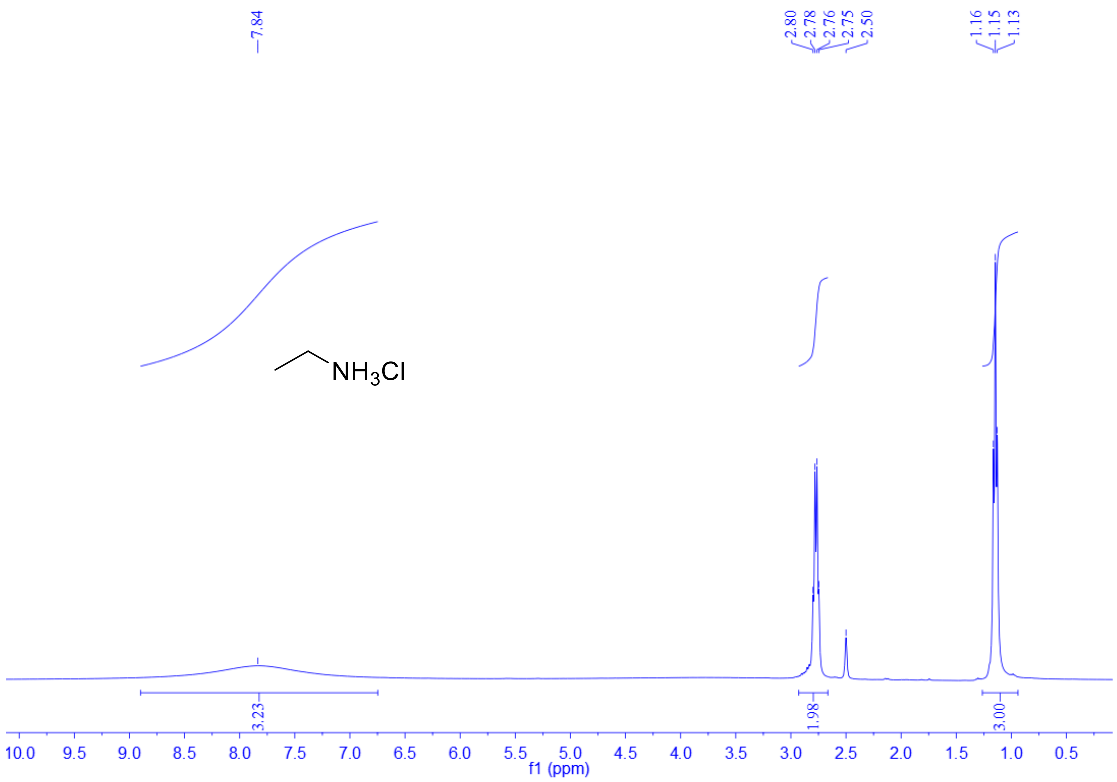

Figure S35. ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) of **2'o**

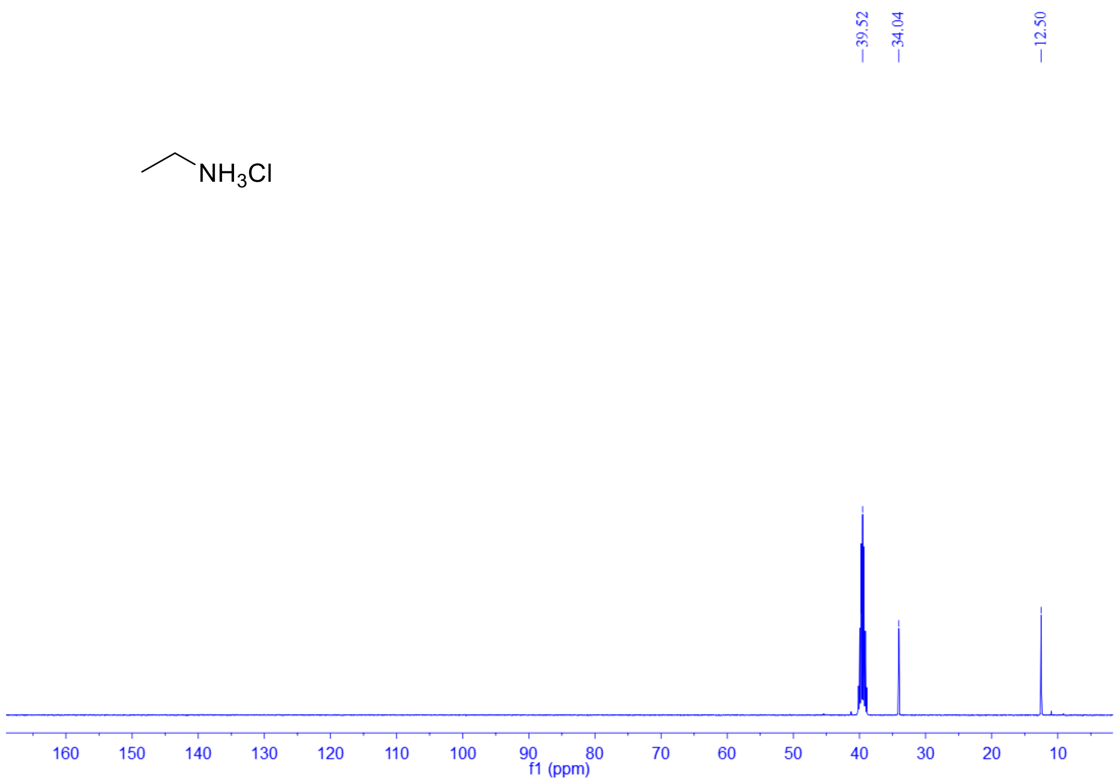

Figure S36. $^{13}C\{^{1}H\}$ (101 MHz, DMSO-d_6, 20 ºC) of **2'o**

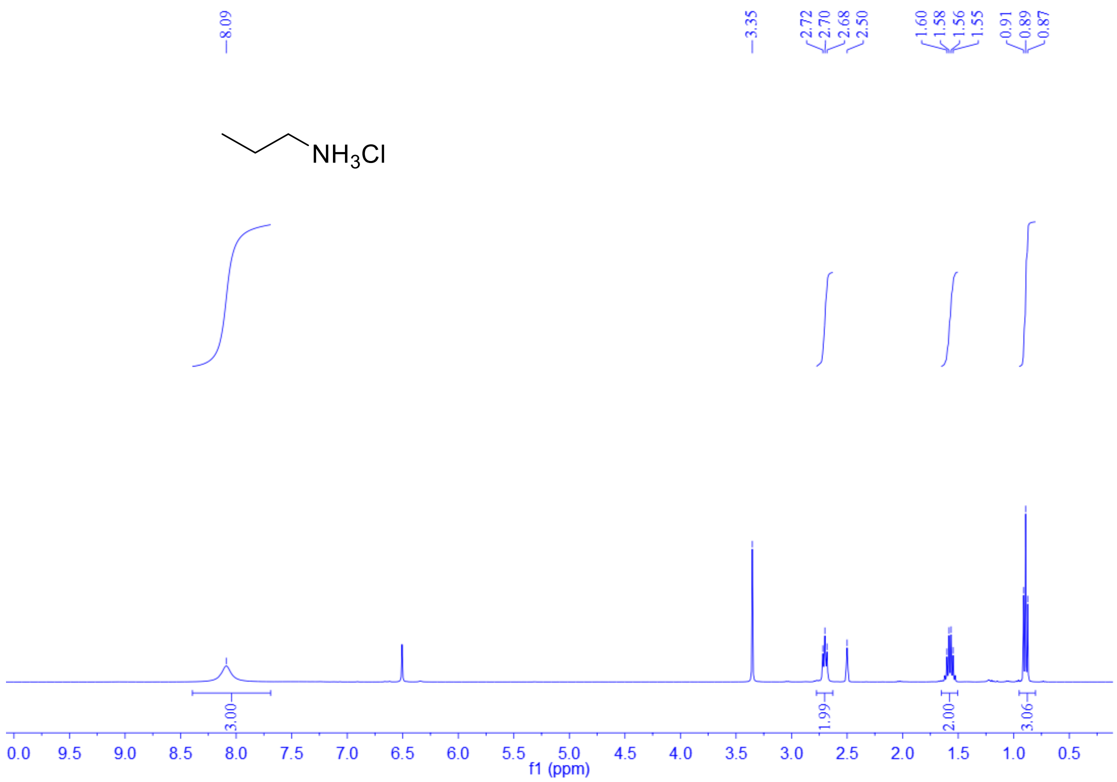

Figure S37. ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) of **2'p**

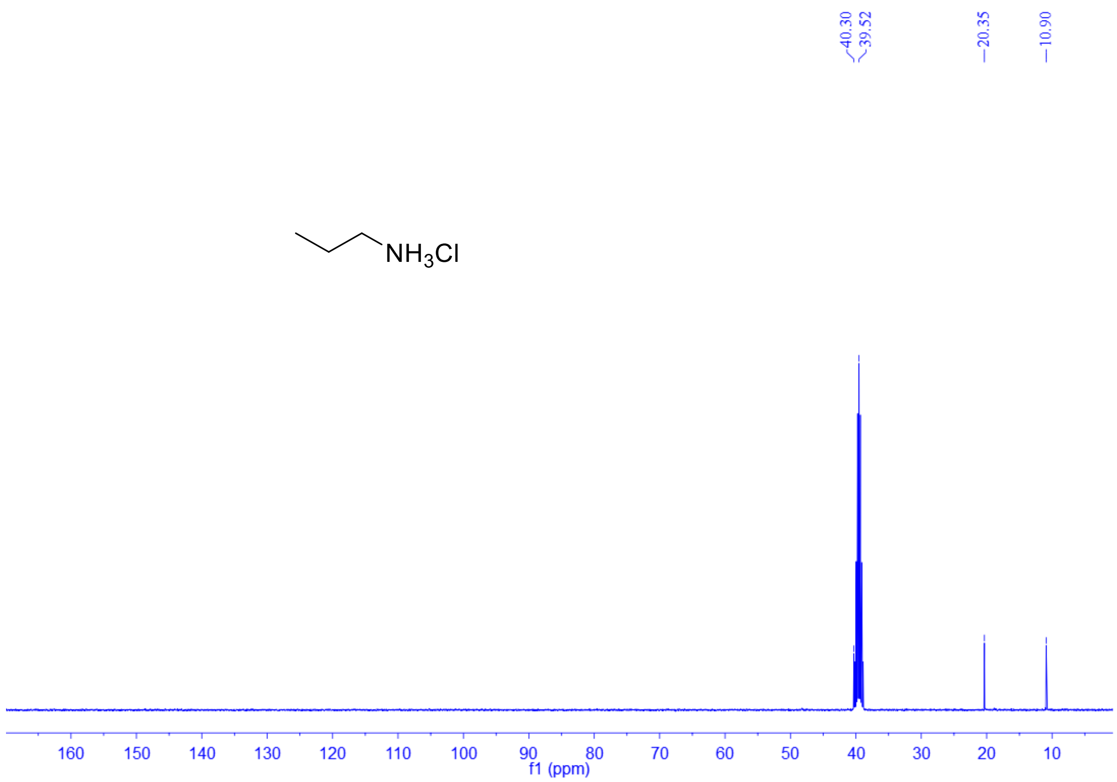

Figure S38. ^{13}C{^{1}H} (101 MHz, DMSO-d_6, 20 ºC) of **2'p**

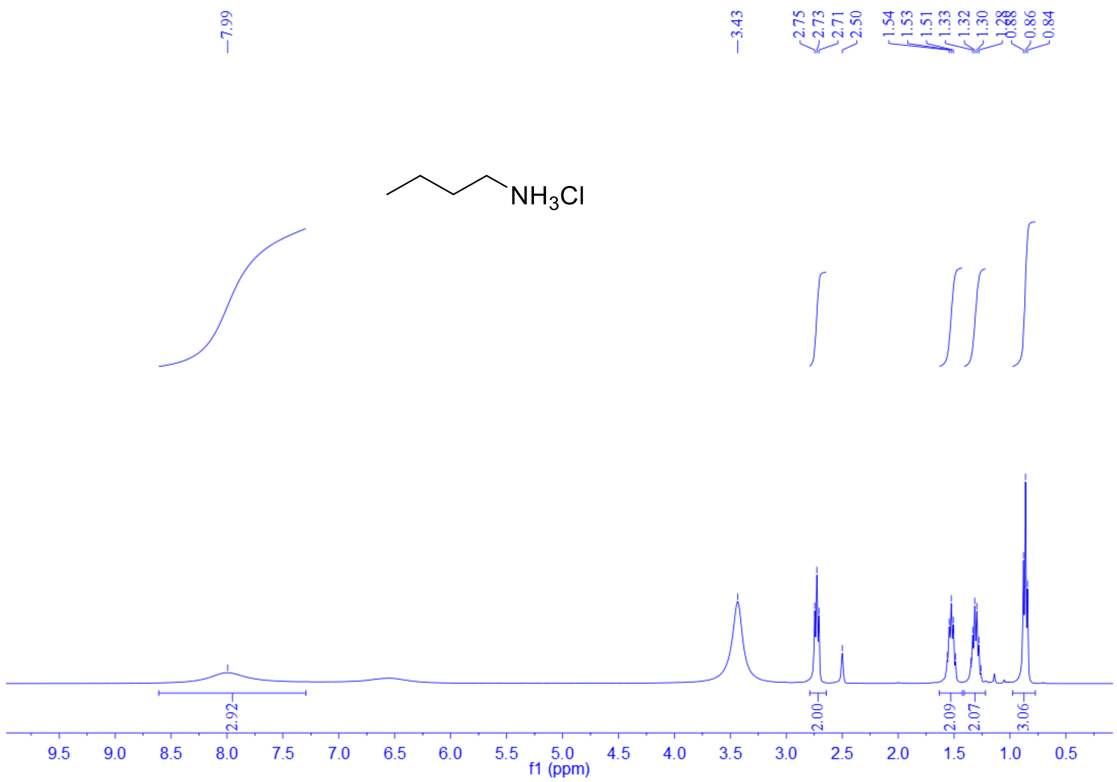

Figure S39. ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) of **2'q**

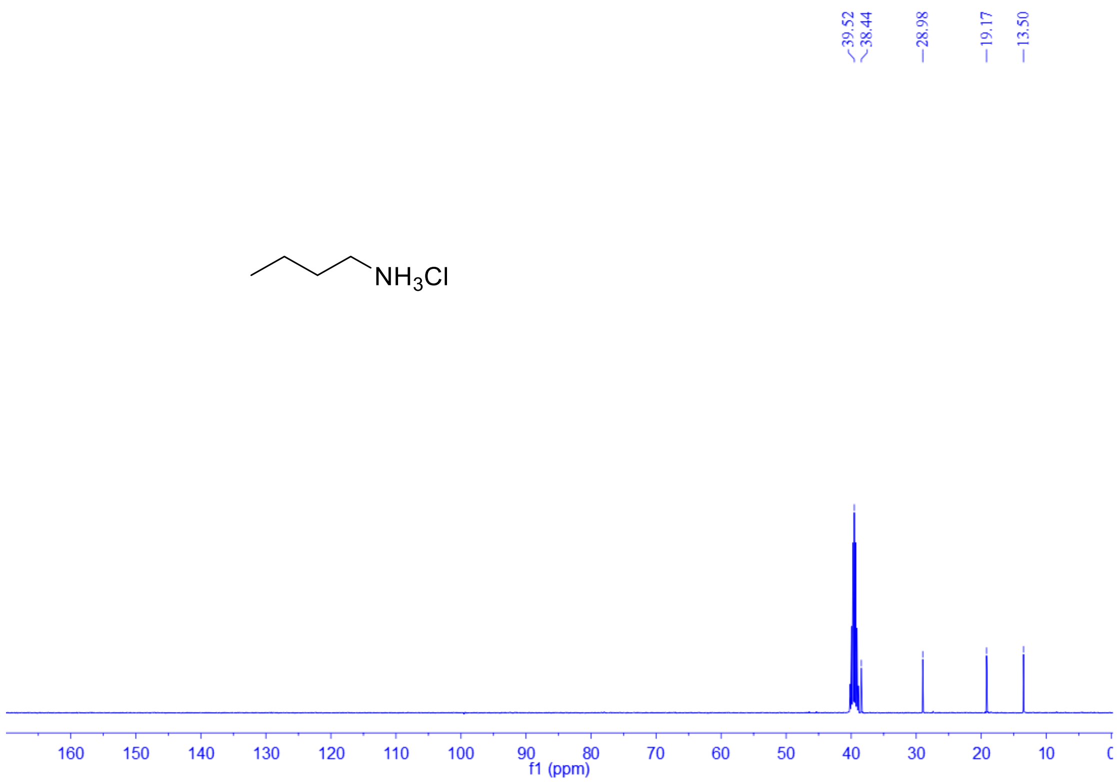

Figure S40. $^{13}C\{^{1}H\}$ (101 MHz, DMSO-d_6, 20 ºC) of **2'q**

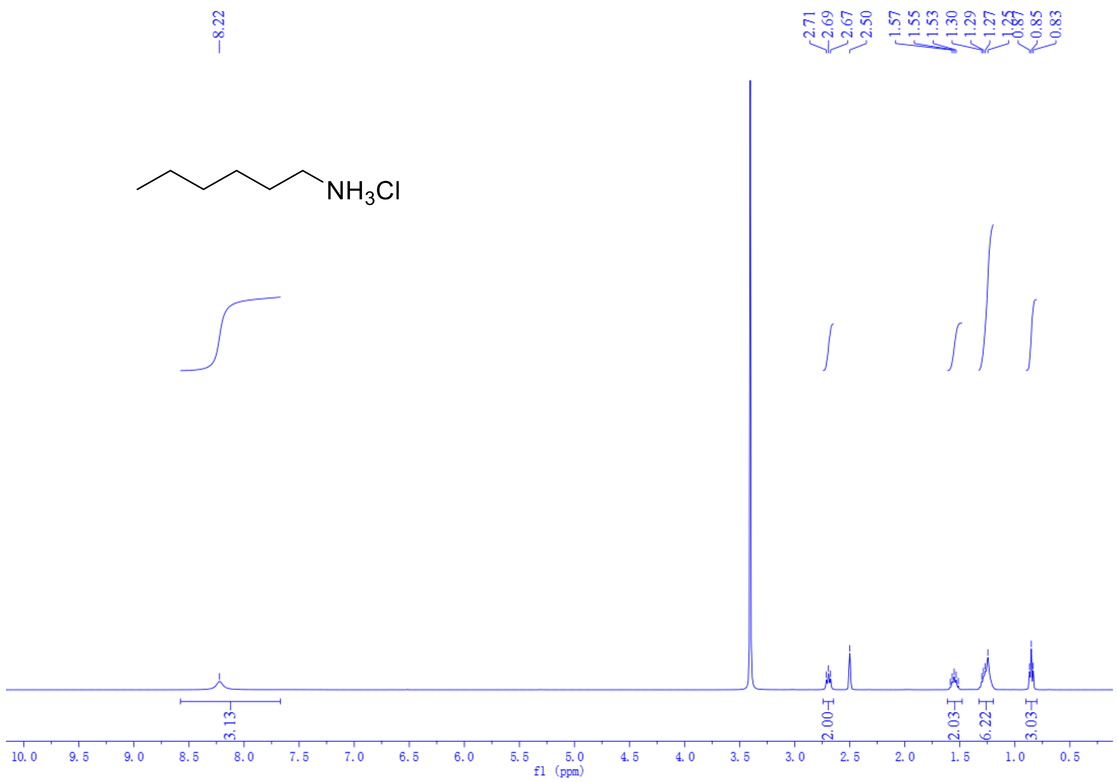

Figure S41. ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) of **2'r**

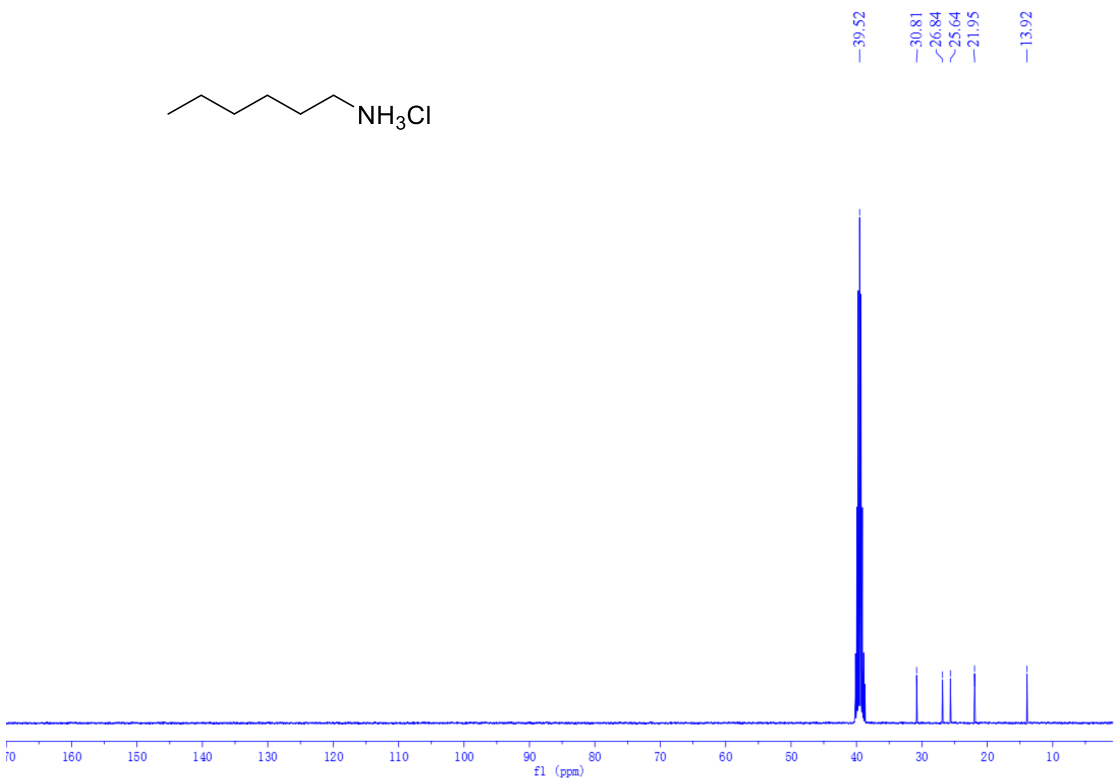

Figure S42. $^{13}C\{^{1}H\}$ (101 MHz, DMSO-d_6, 20 ºC) of **2'r**

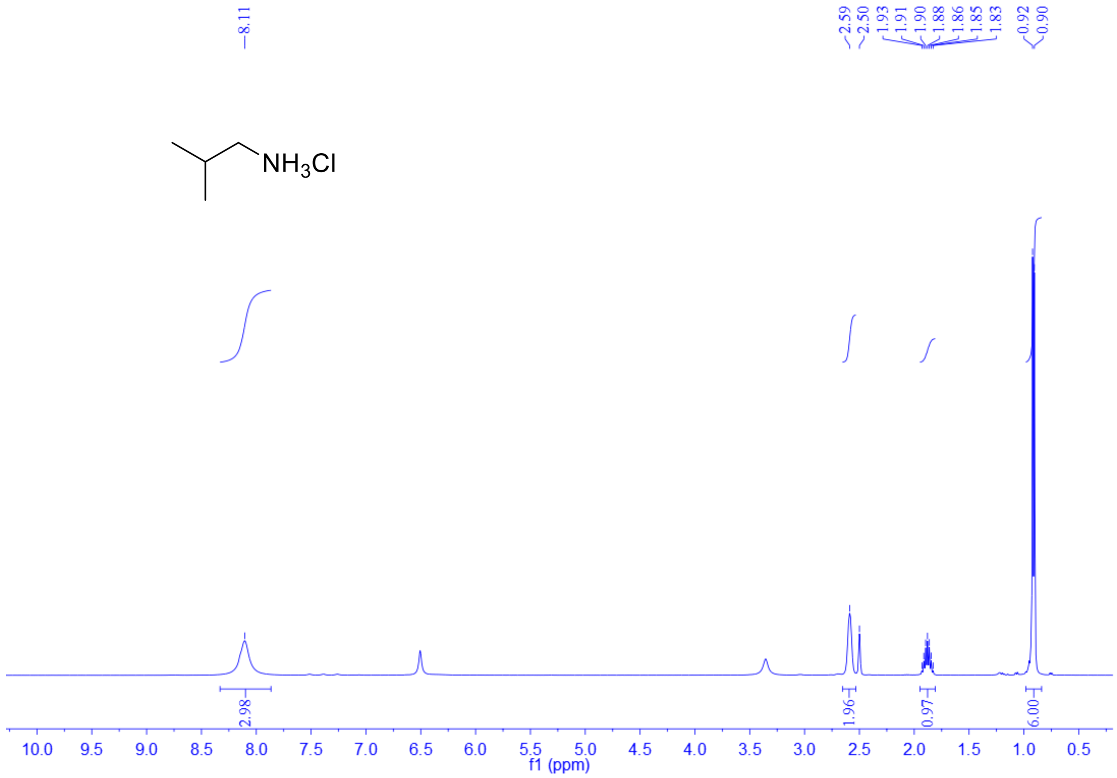

Figure S43. ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) of **2's**

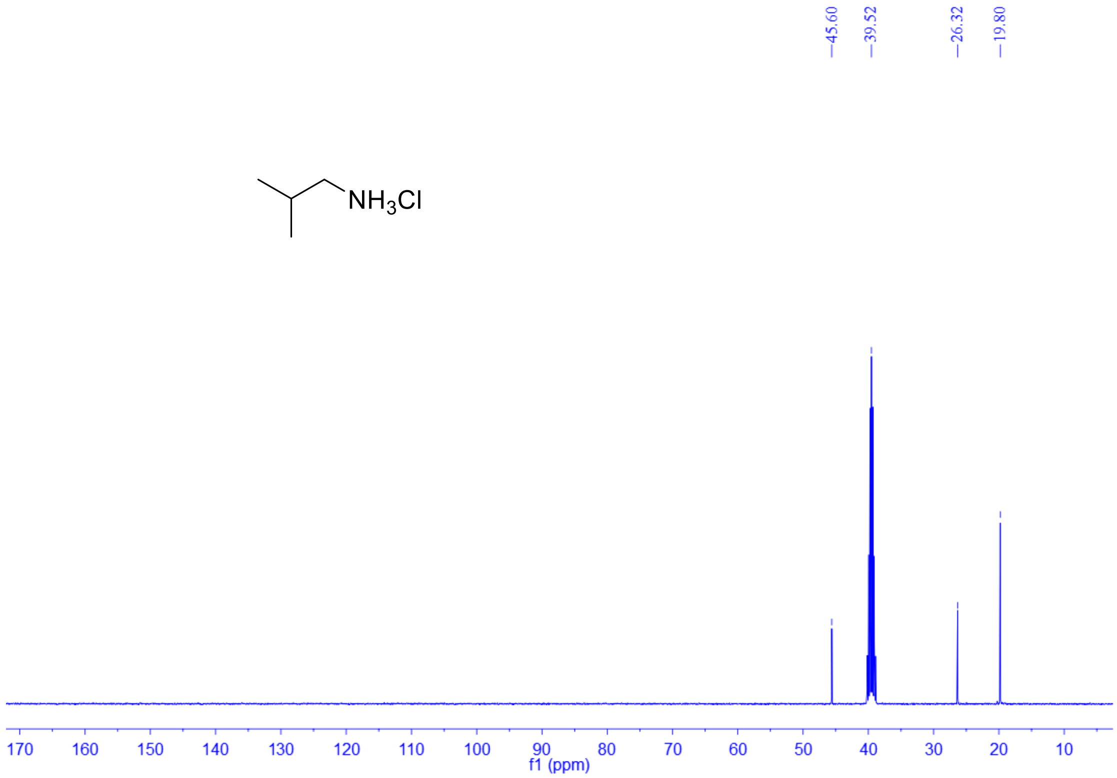

Figure S44. $^{13}C\{^{1}H\}$ (101 MHz, DMSO-d_6, 20 ºC) of **2's**

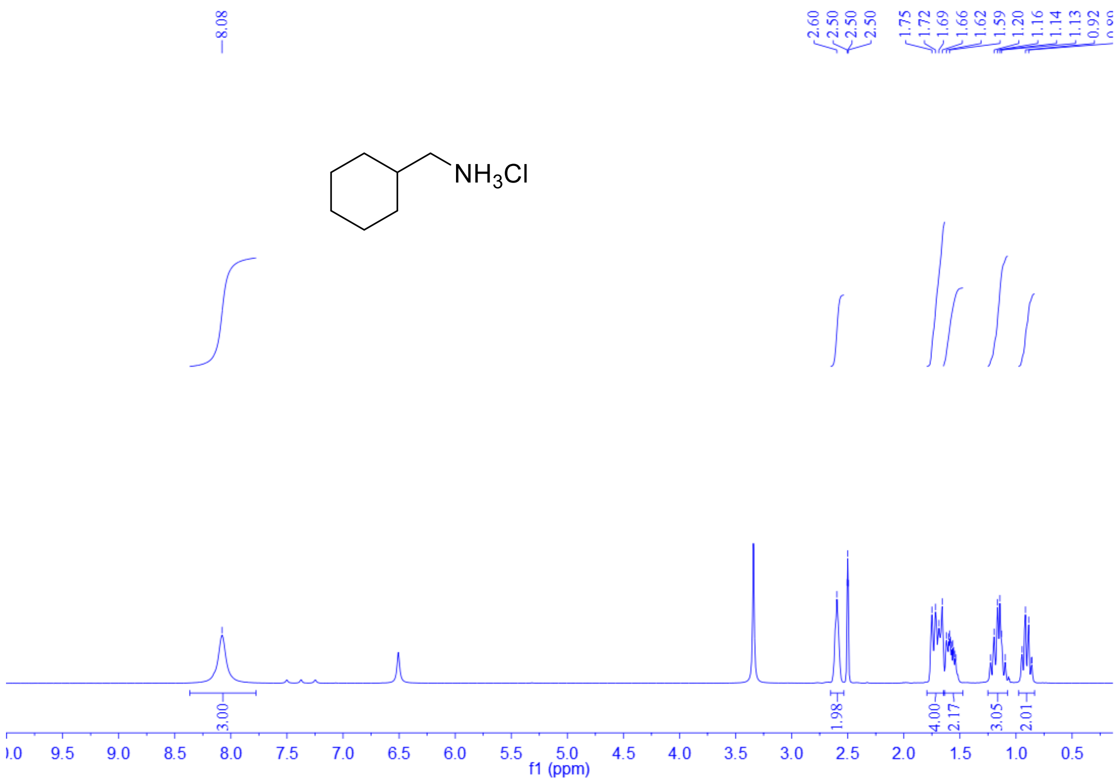

Figure S45. ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) of **2't**

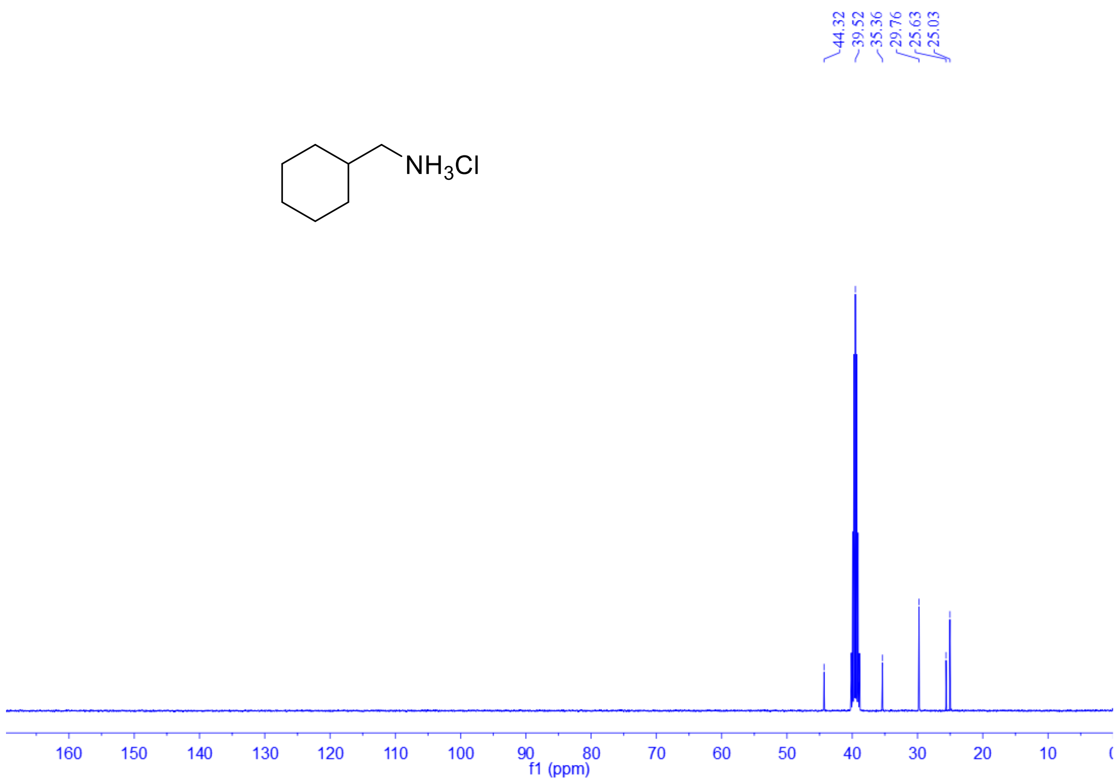

Figure S46. ^{13}C{^{1}H} (101 MHz, DMSO-d_6, 20 ºC) of **2't**

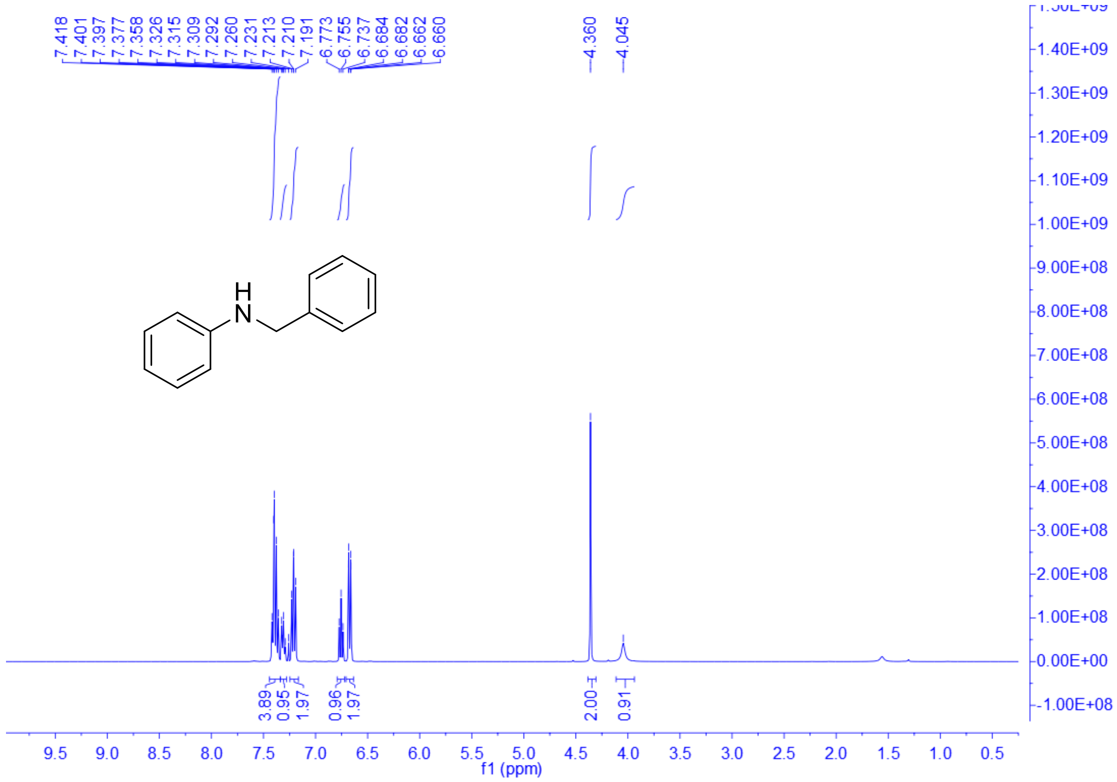

Figure S47. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C) of **4a**

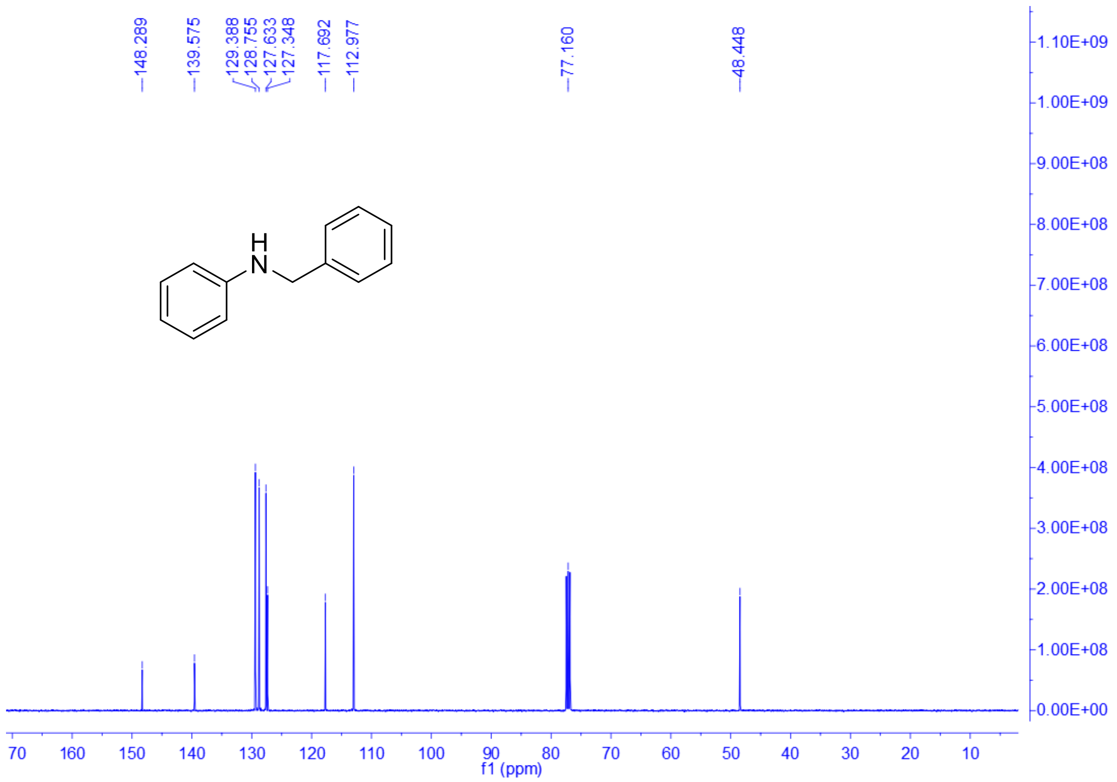

Figure S48. $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$, 20 °C) of **4a**

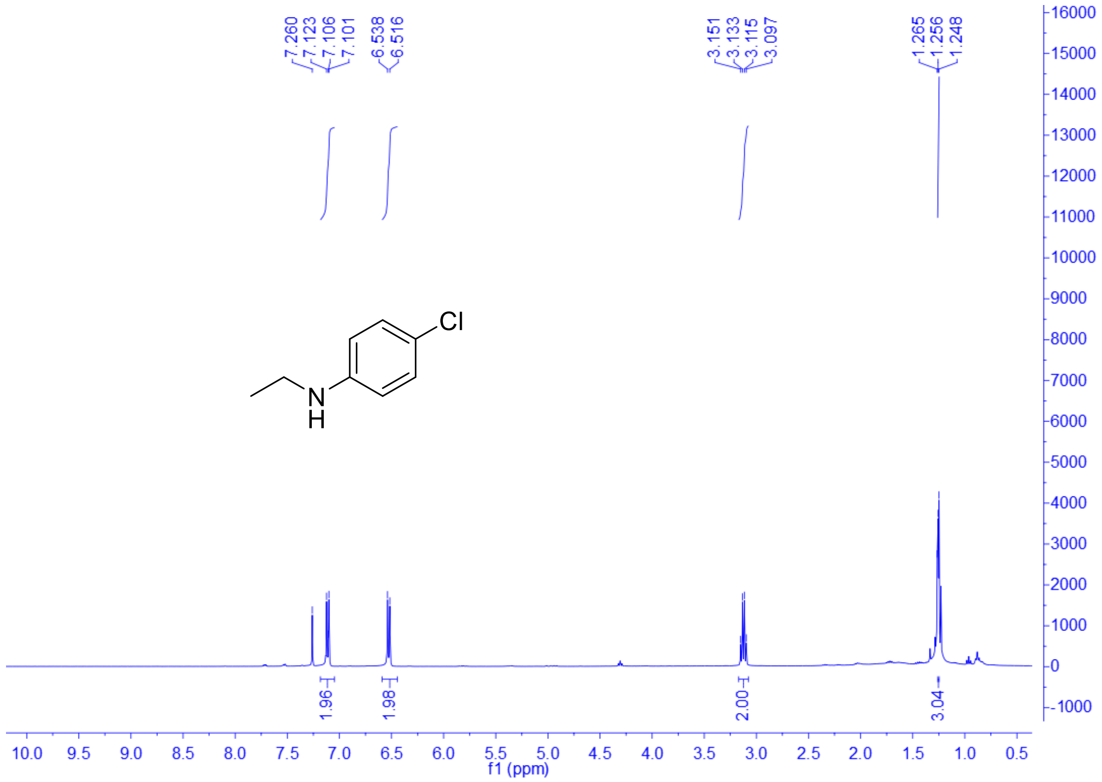

Figure S49. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C) of **4b**

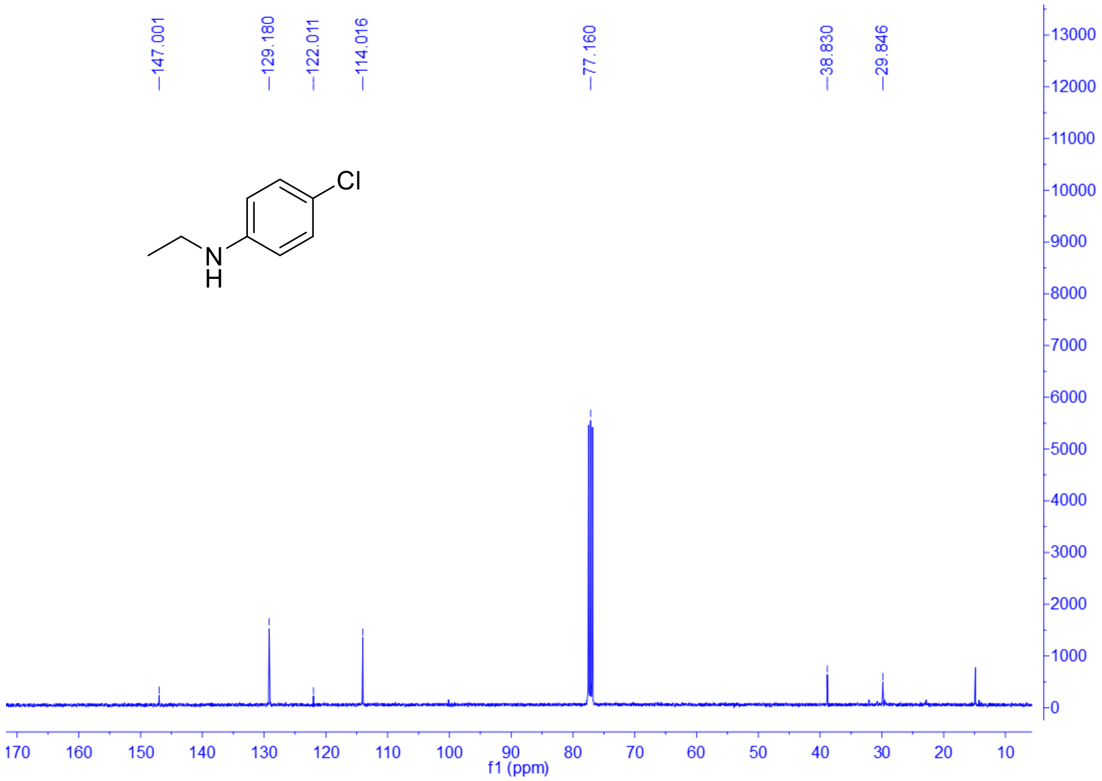

Figure S50. $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$, 20 °C) of **4b**

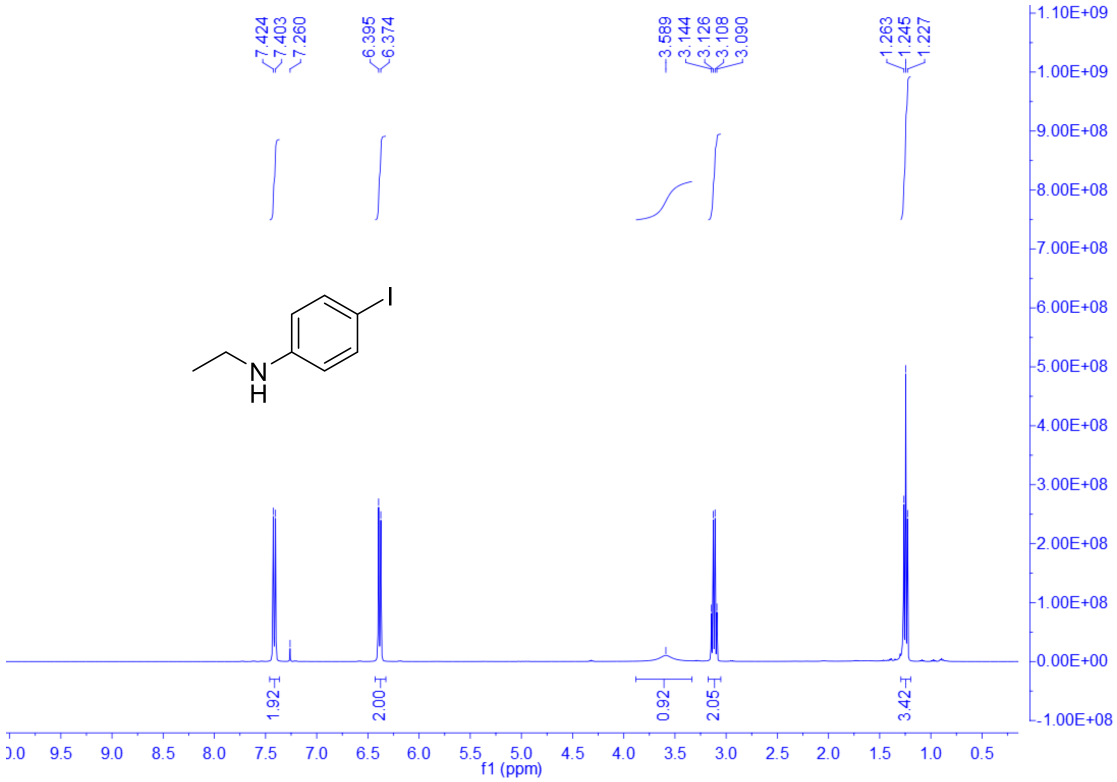

Figure S51. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C) of **4c**

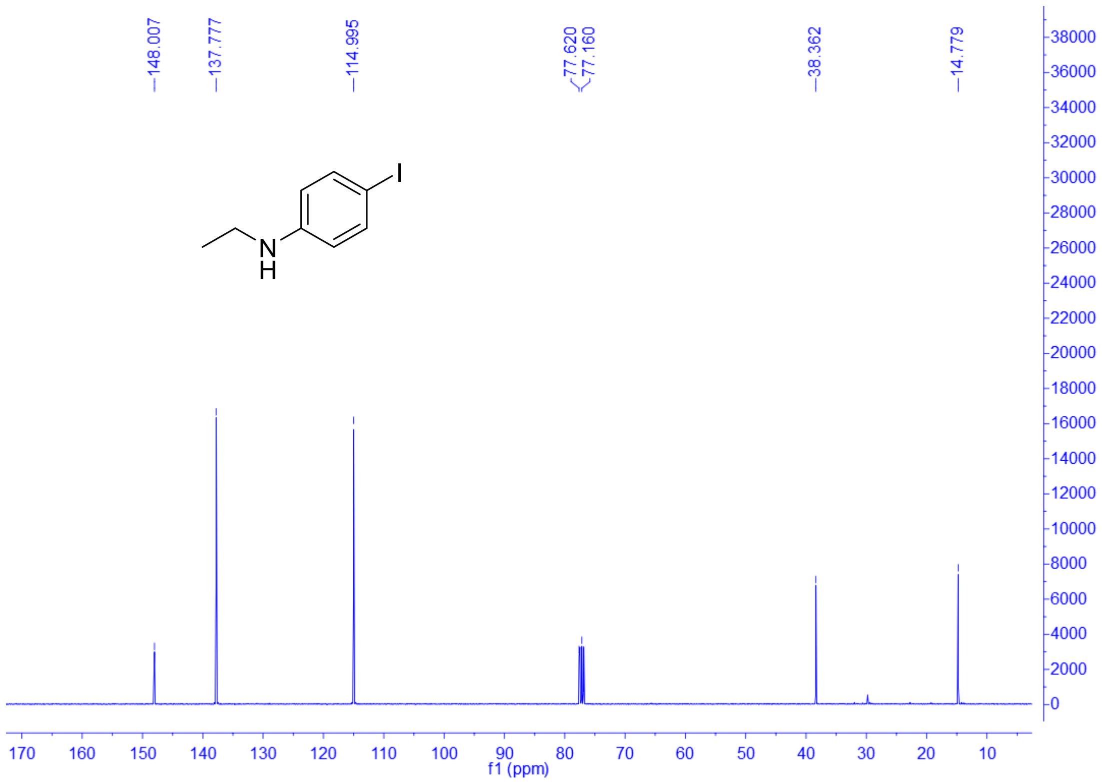

Figure S52. $^{13}C\{^1H\}$ (101 MHz, $CDCl_3$, 20 °C) of **4c**

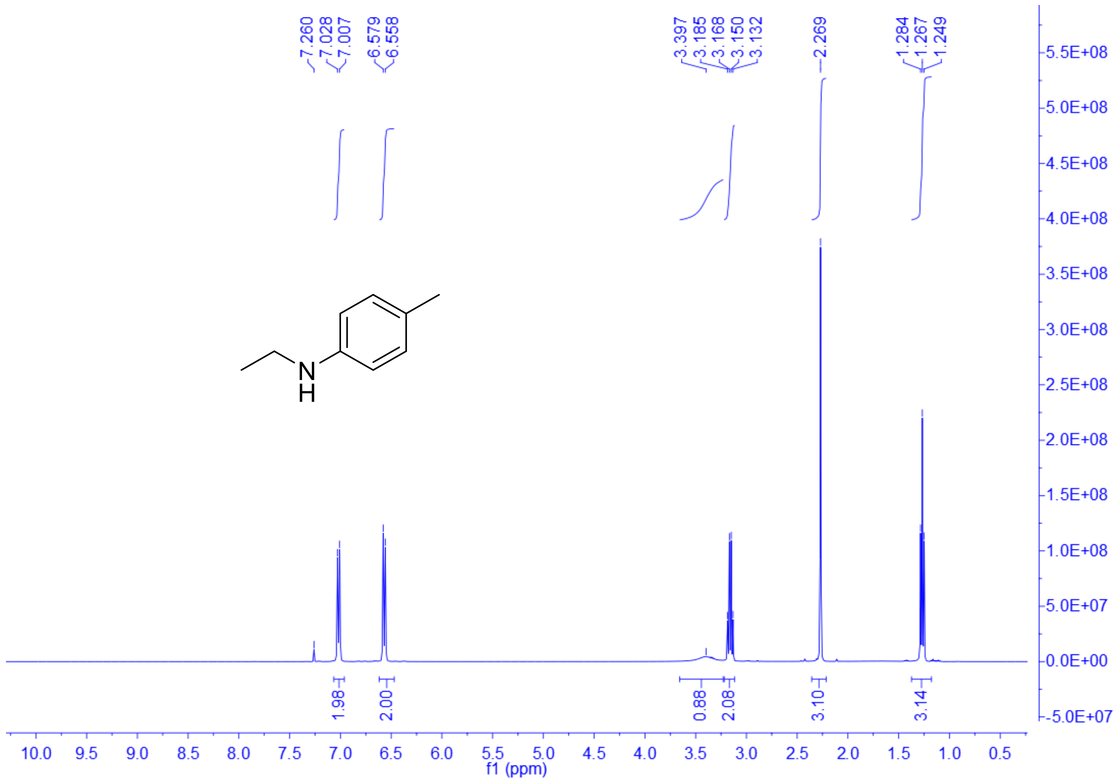

Figure S53. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C) of **4d**

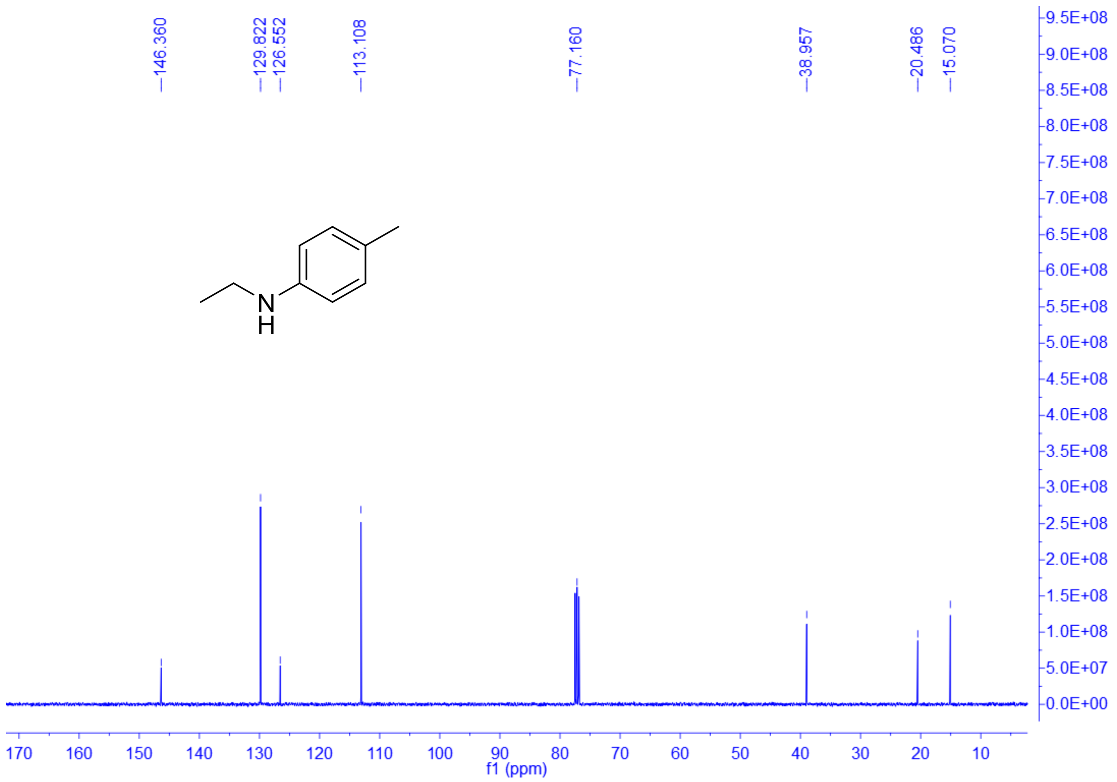

Figure S54. $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$, 20 °C) of **4d**

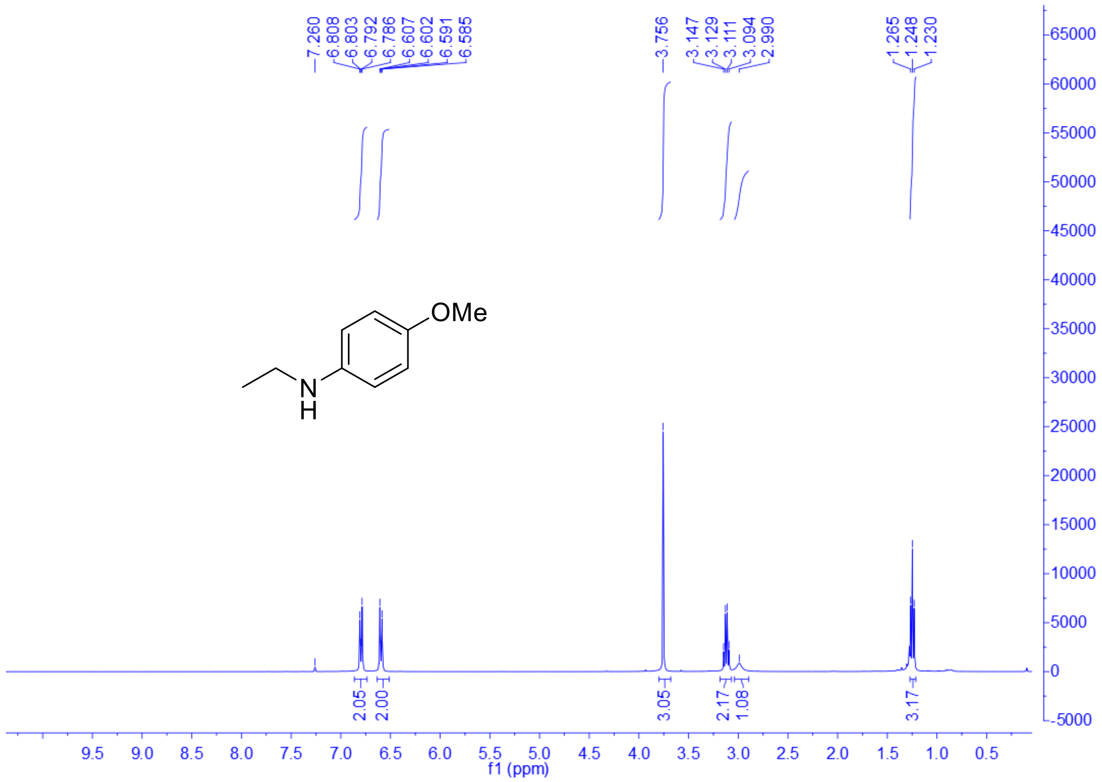

Figure S55. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C) of **4e**

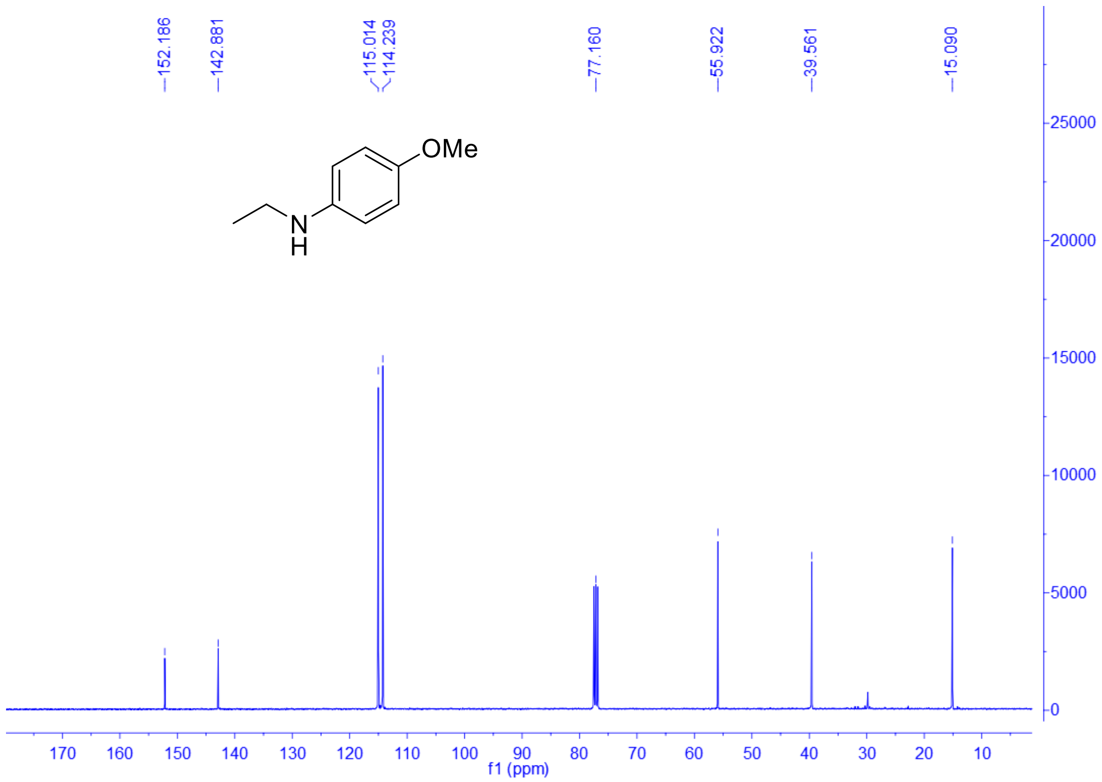

Figure S56. $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$, 20 °C) of **4e**

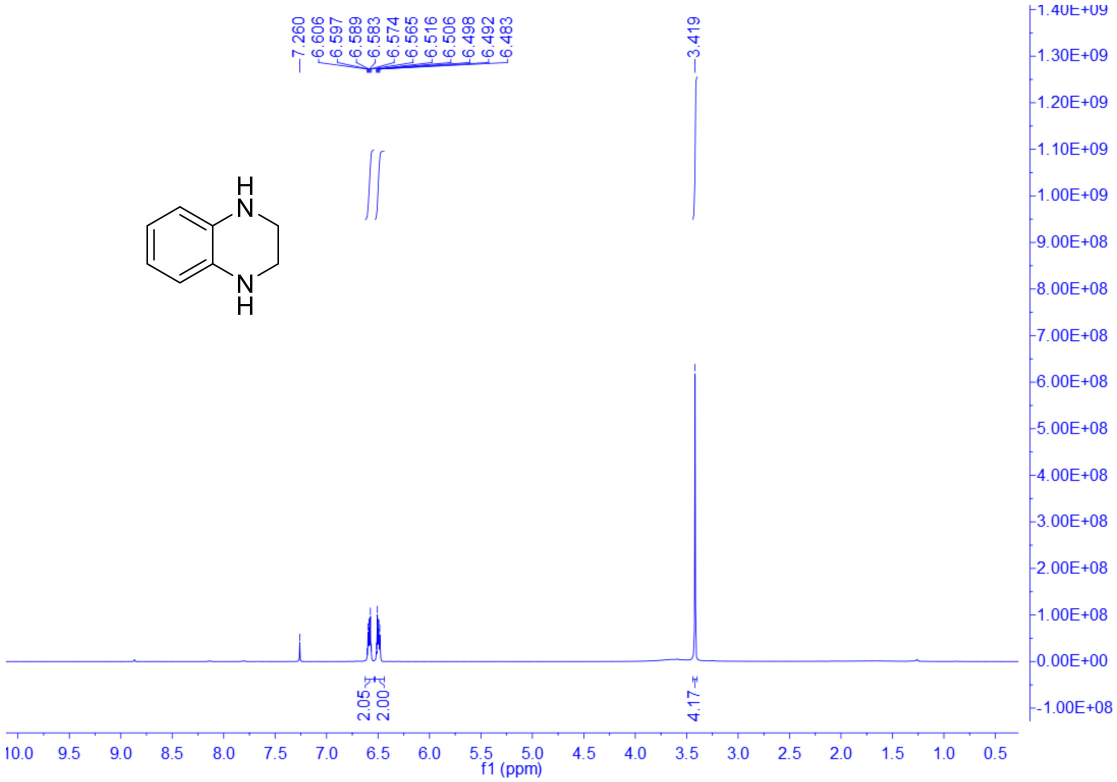

Figure S57. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C) of **4f**

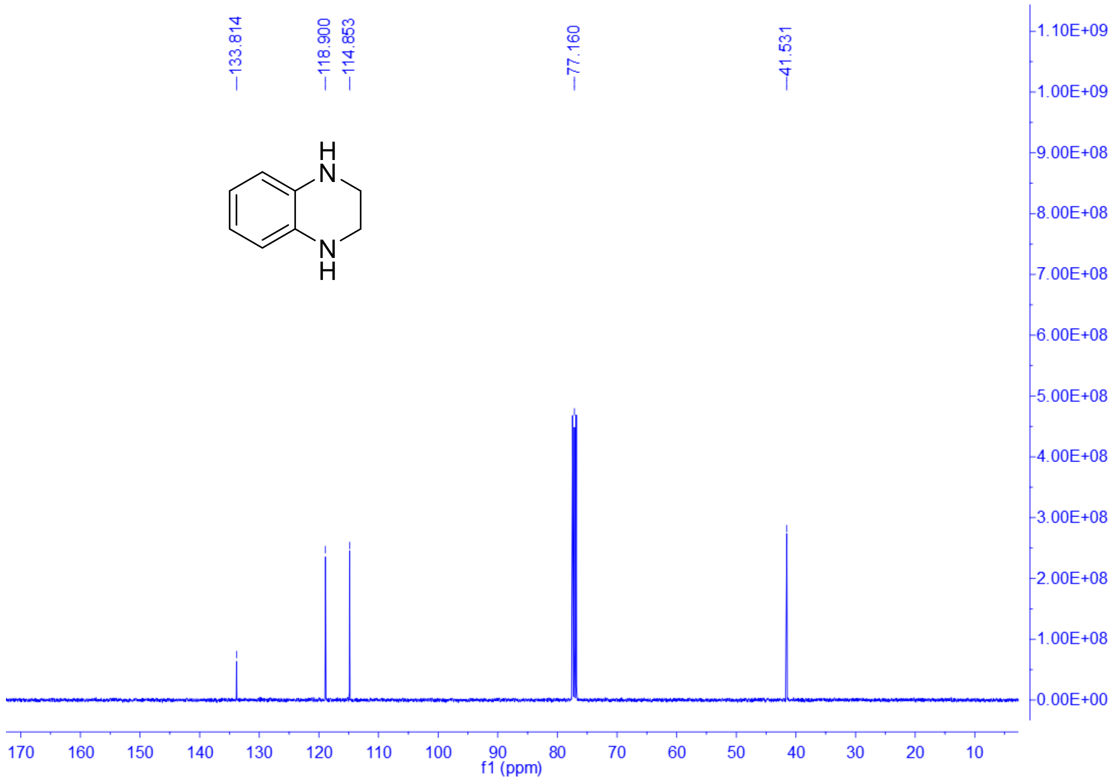

Figure S58. $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$, 20 °C) of **4f**

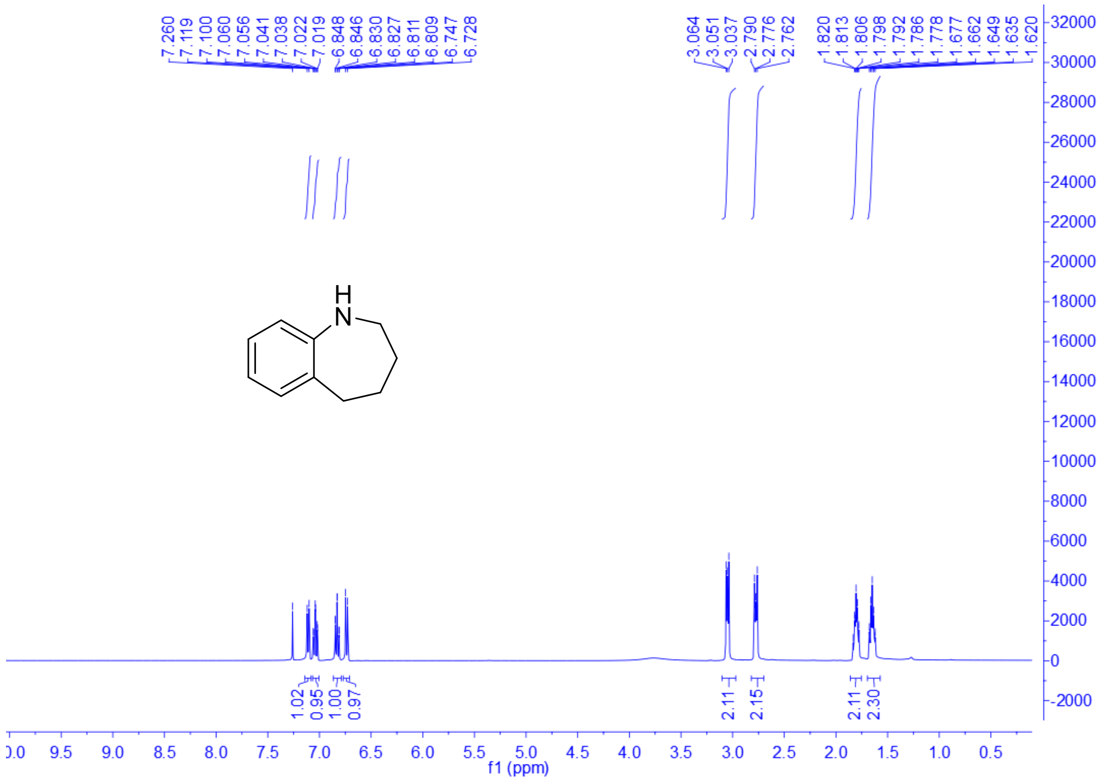

Figure S59. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C) of **4g**

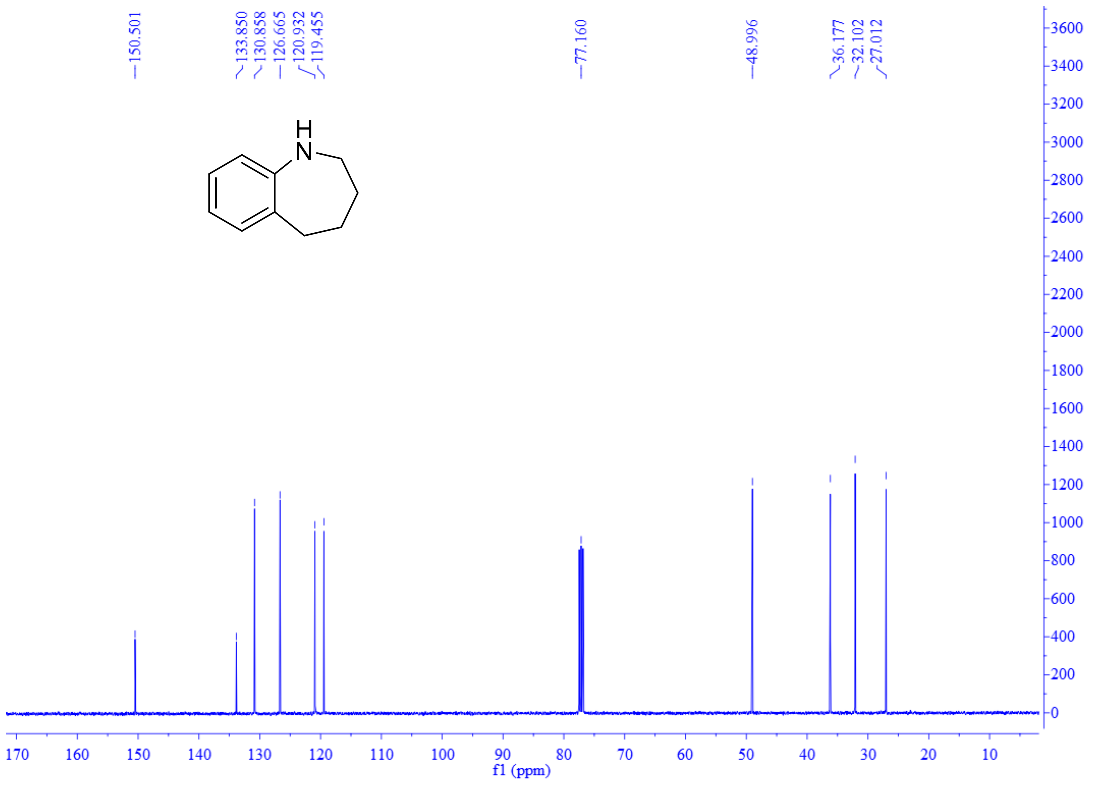

Figure S60. $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$, 20 °C) of **4g**

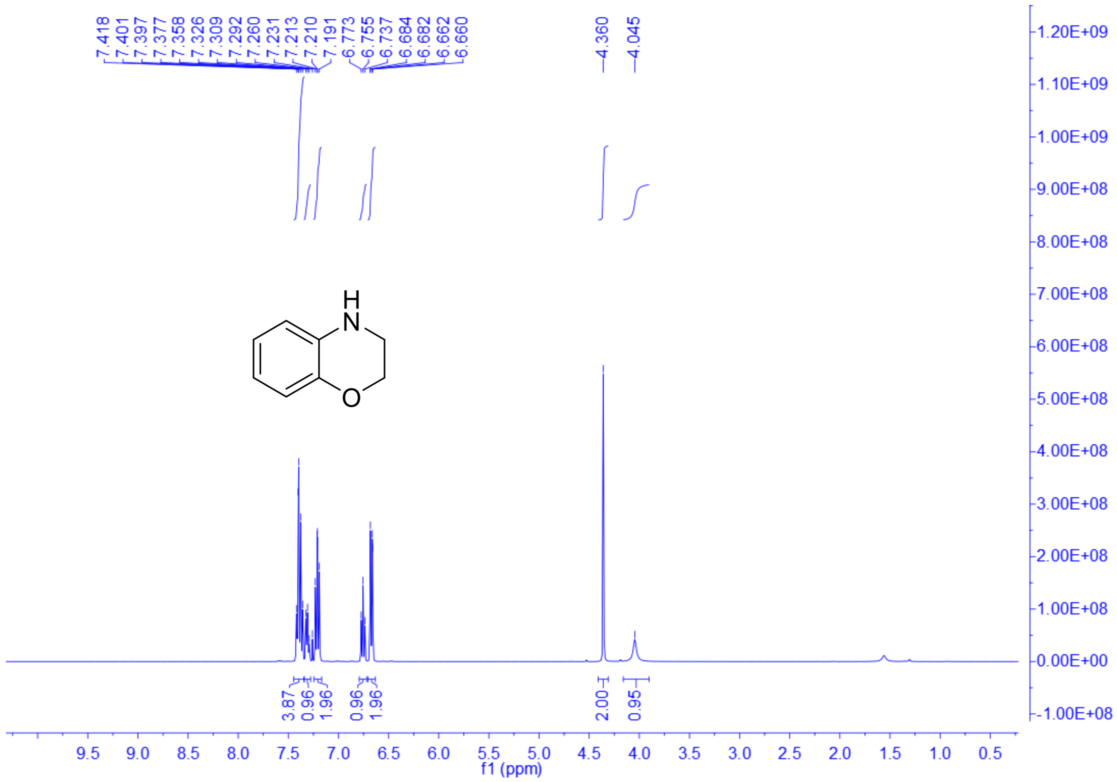

Figure S61. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C) of **4h**

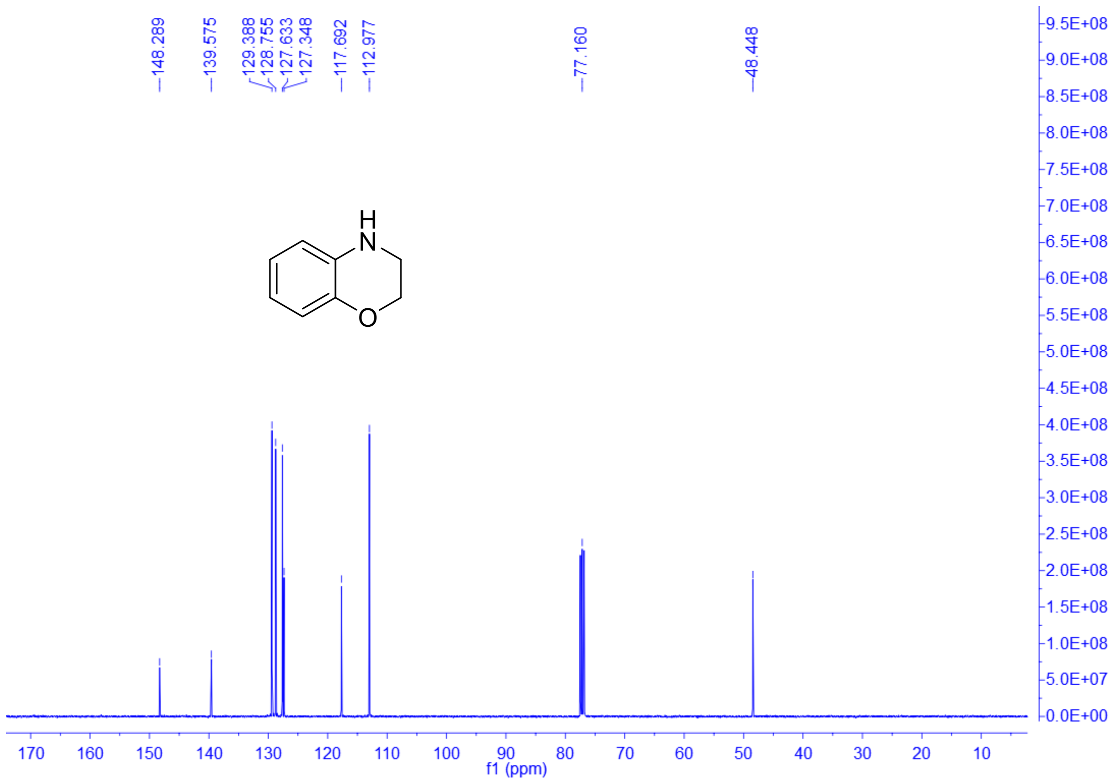

Figure S62. $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$, 20 °C) of **4h**

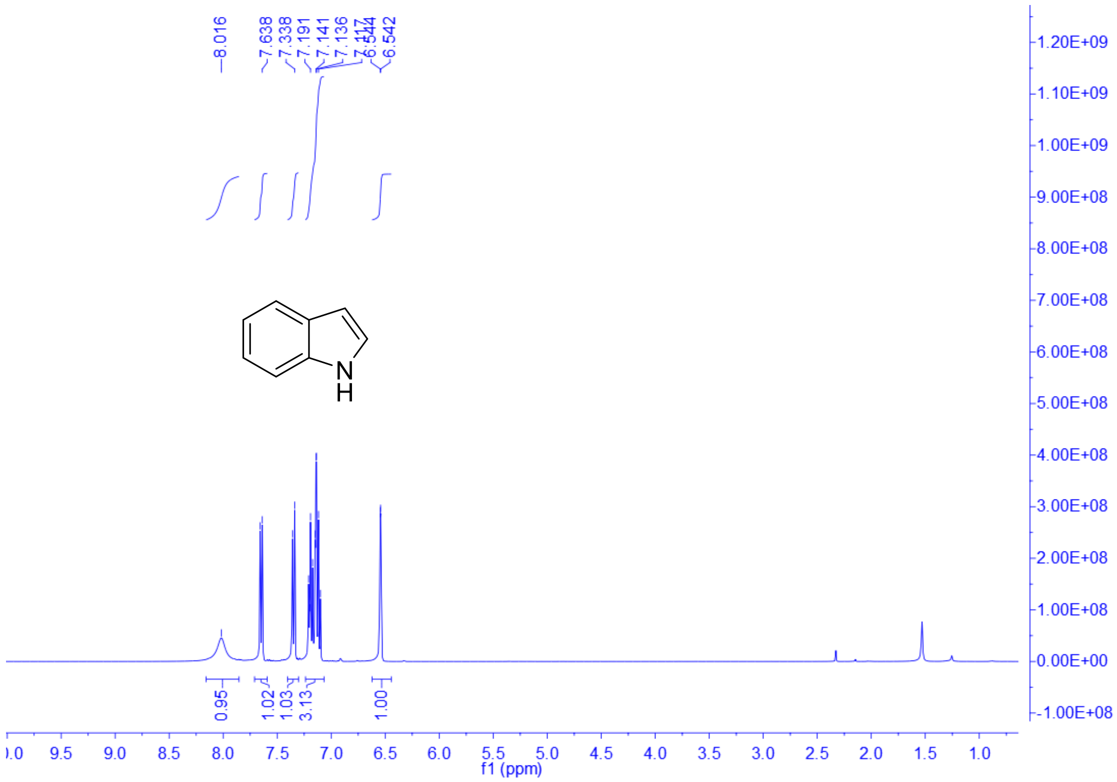

Figure S63. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C) of **4k**

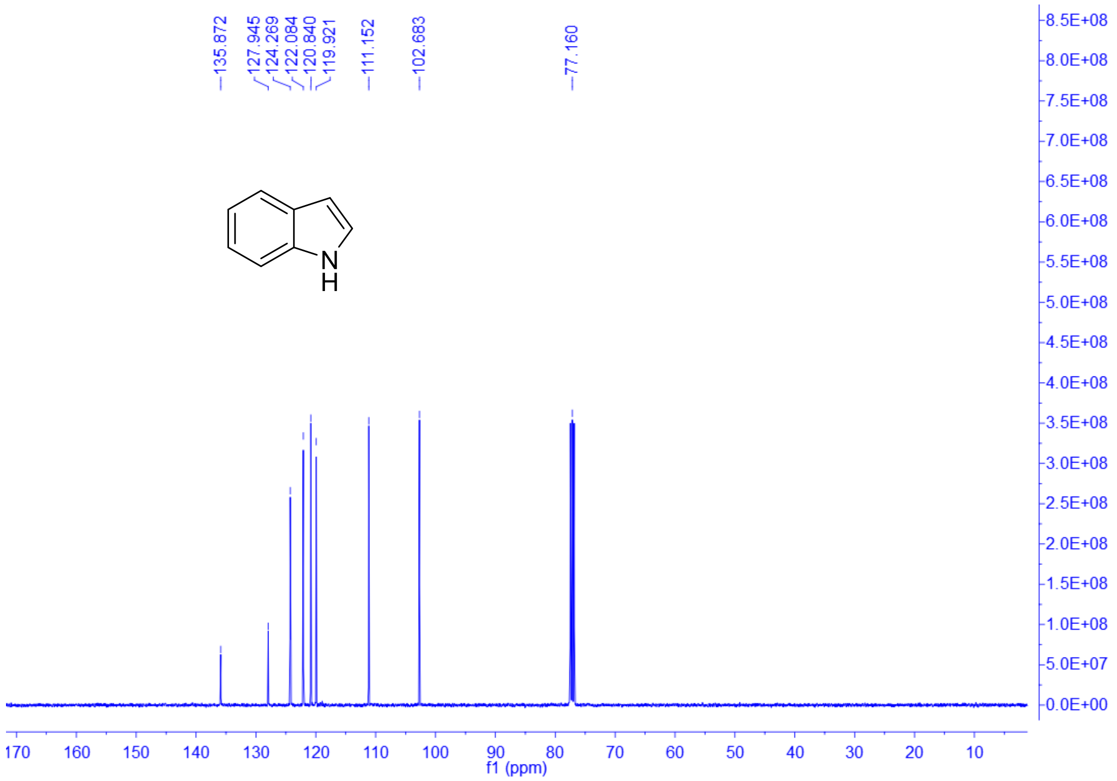

Figure S64. $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$, 20 °C) of **4k**

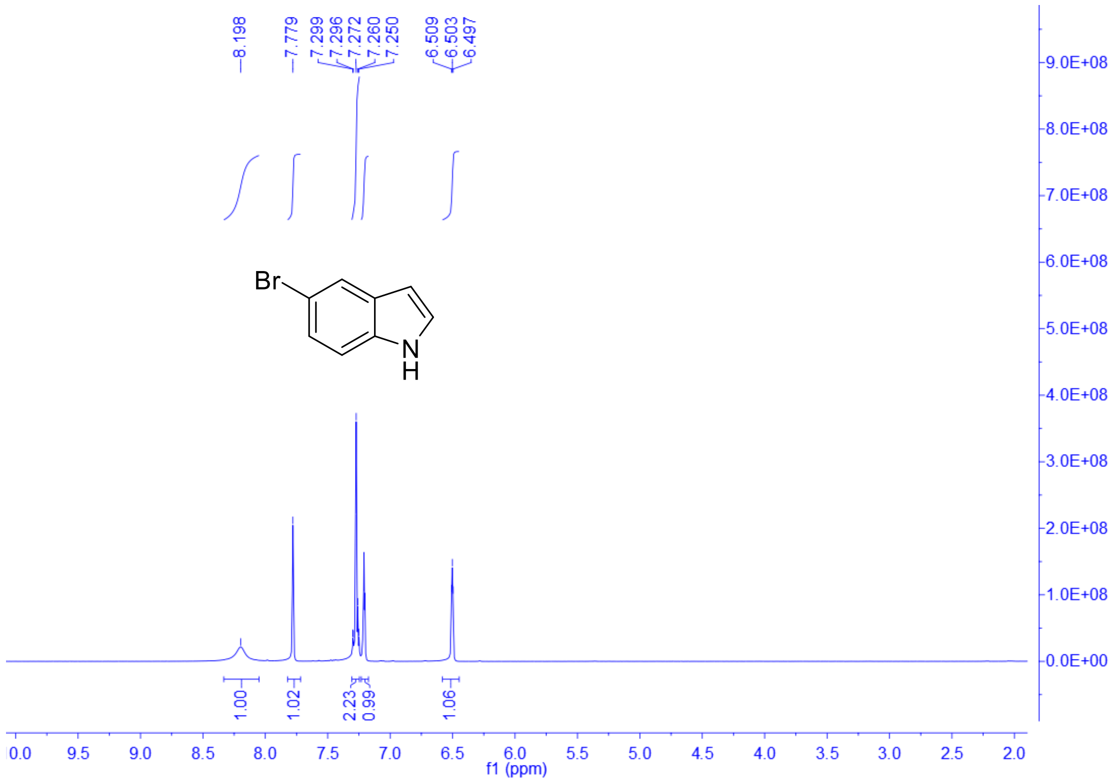

Figure S65. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C) of **4l**

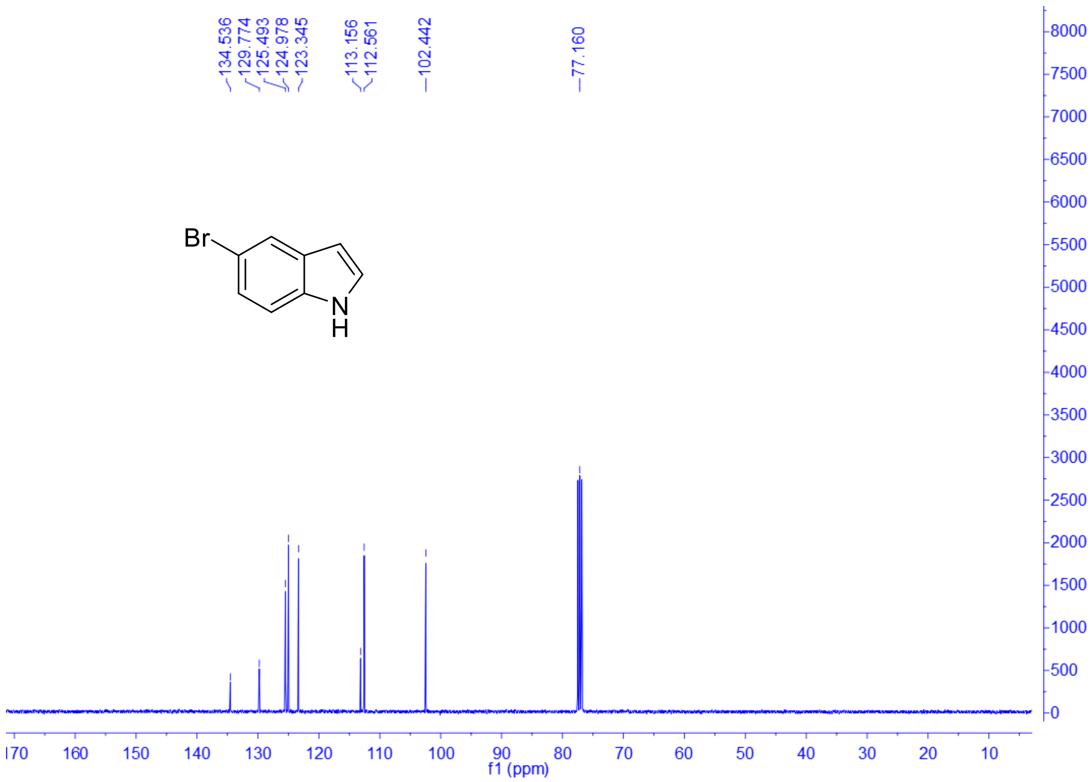

Figure S66. $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$, 20 °C) of **4l**

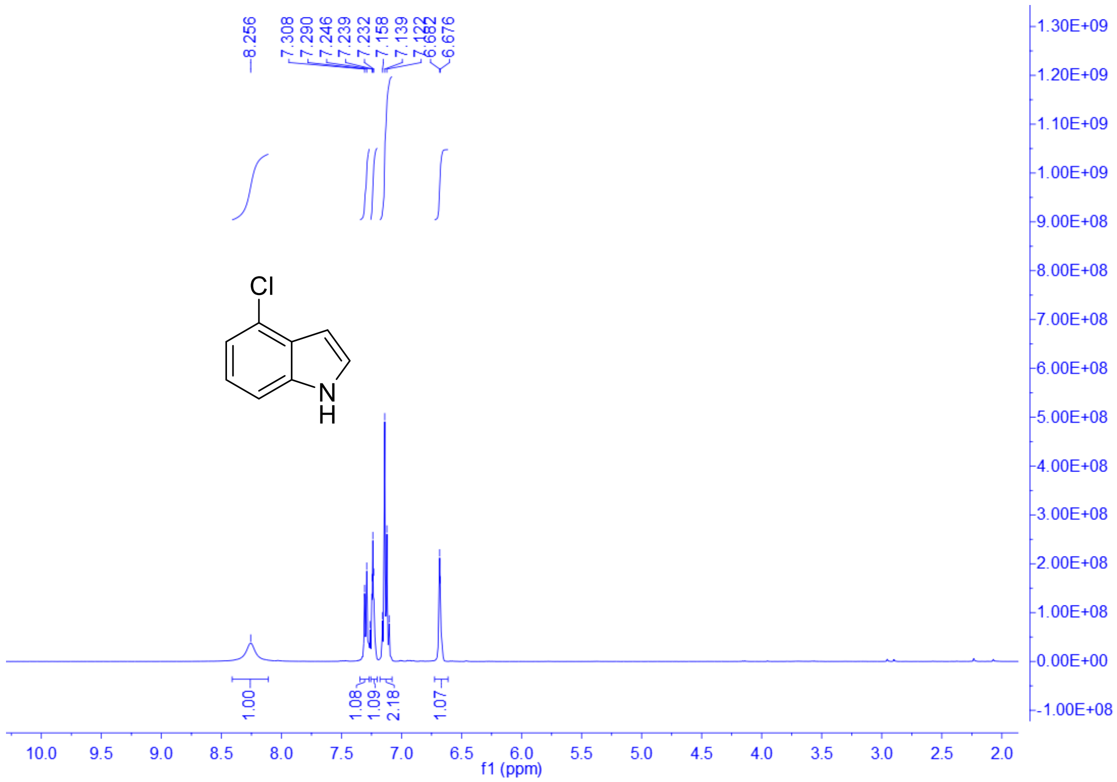

Figure S67. ^{1}H NMR (400 MHz, $CDCl_3$, 20 ºC) of **4m**

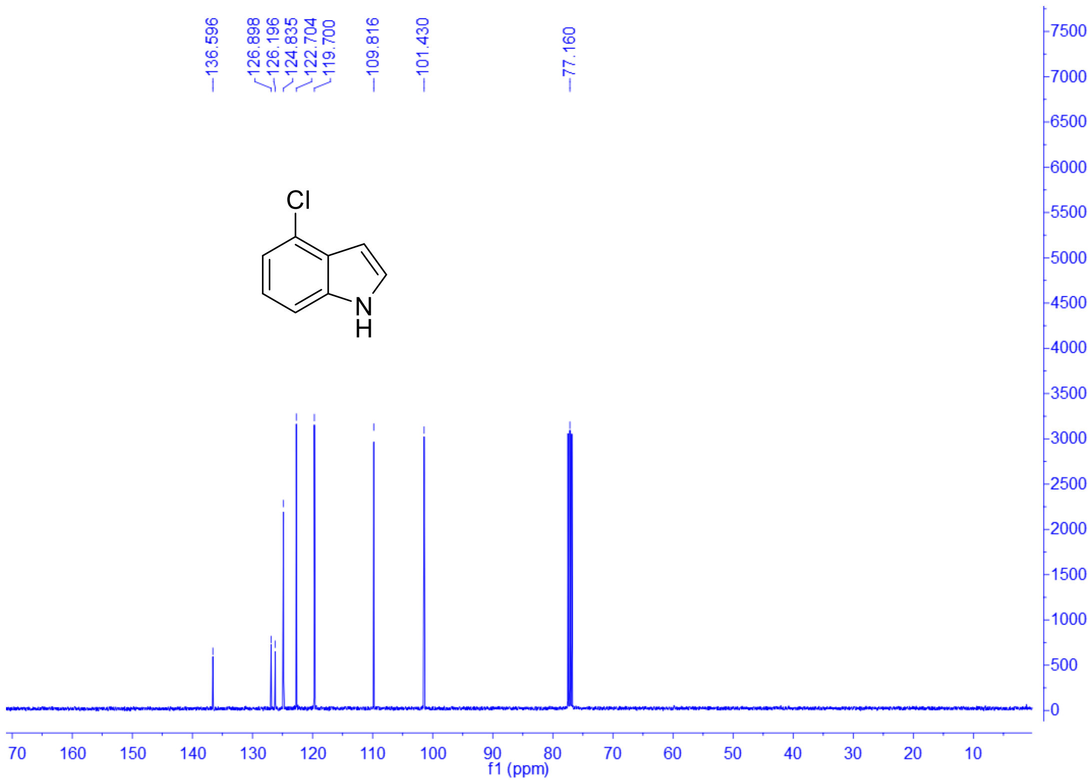

Figure S68. $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$, 20 ºC) of **4m**

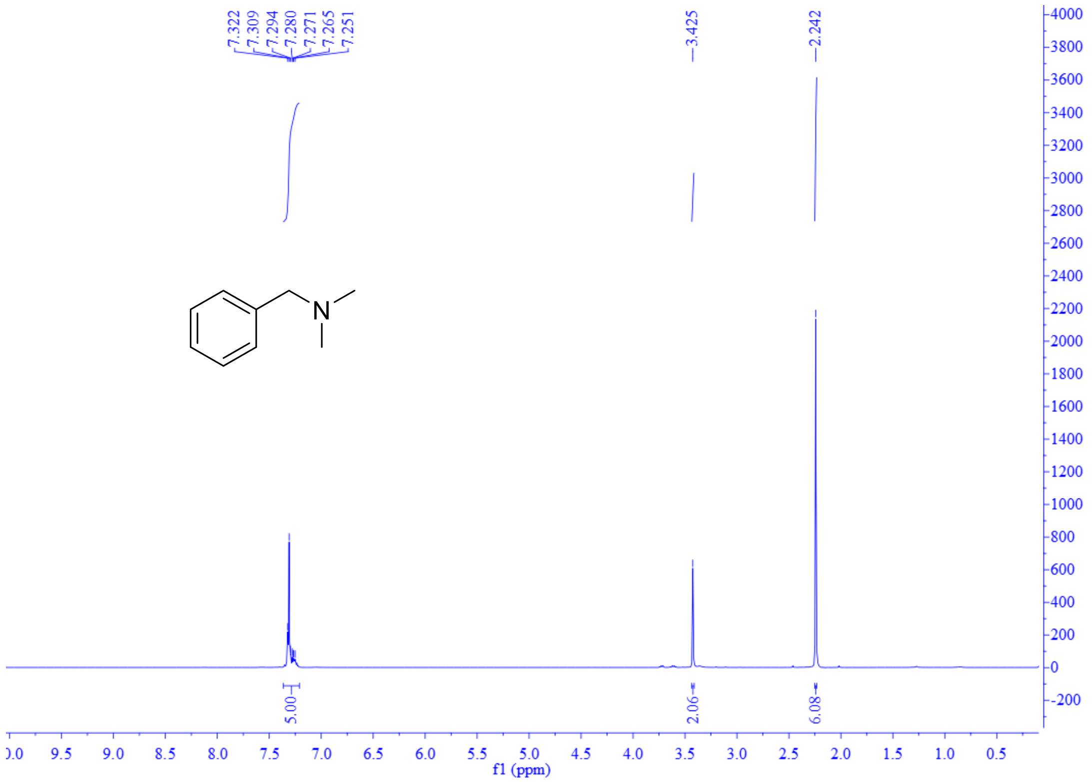

Figure S69. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C) of **4n**

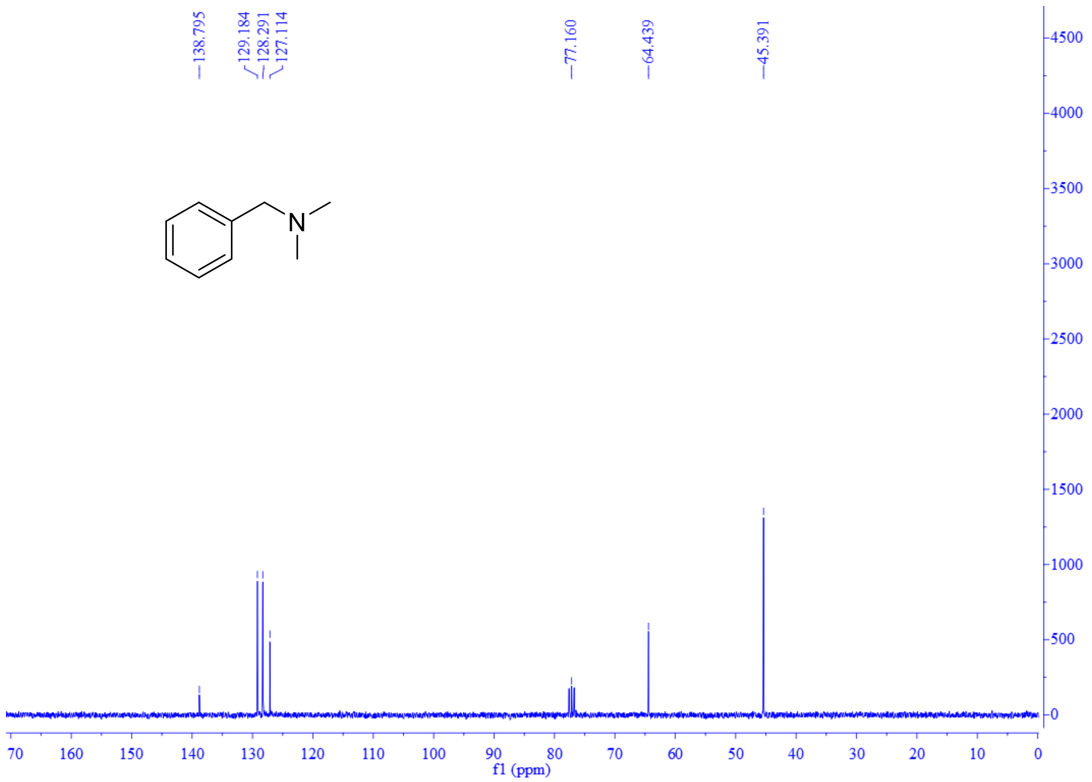

Figure S70. $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$, 20 °C) of **4n**

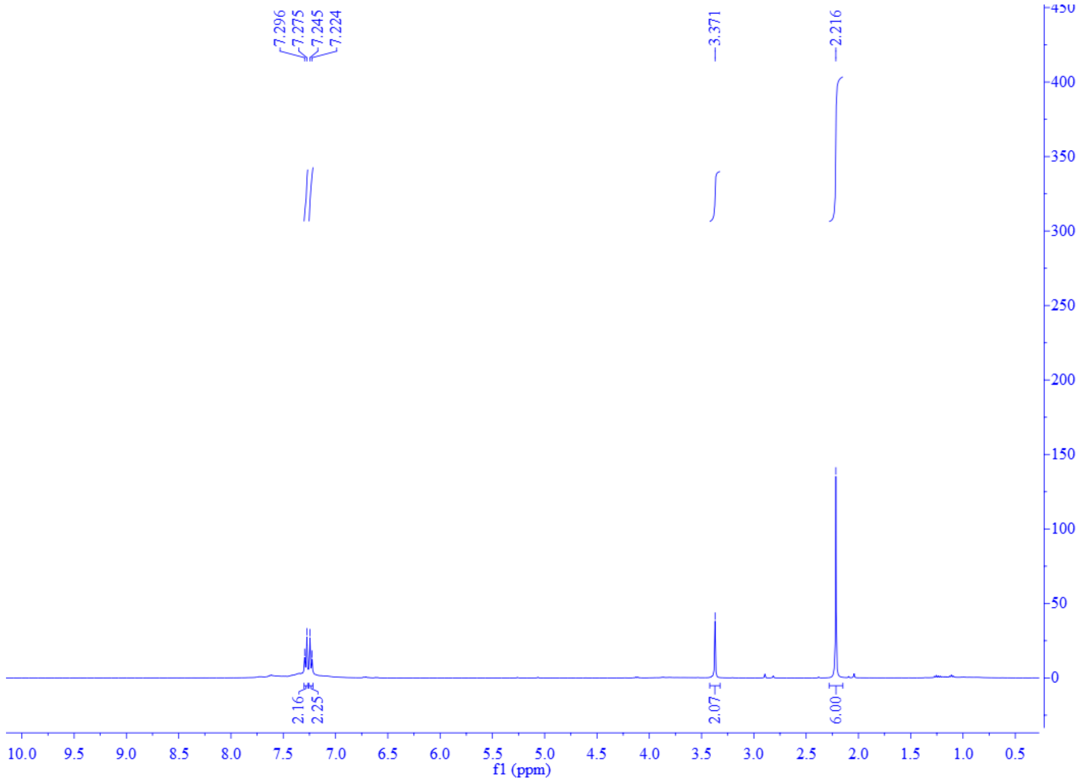

Figure S71. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C) of **4o**

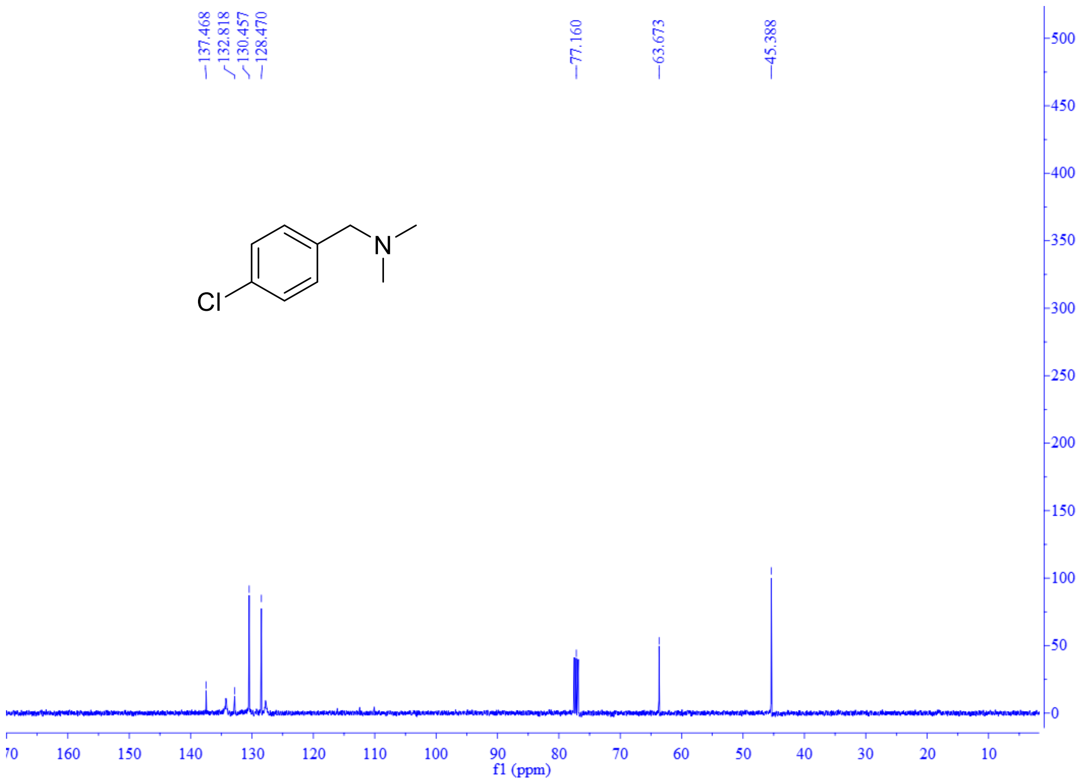

Figure S72. $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$, 20 °C) of **4o**

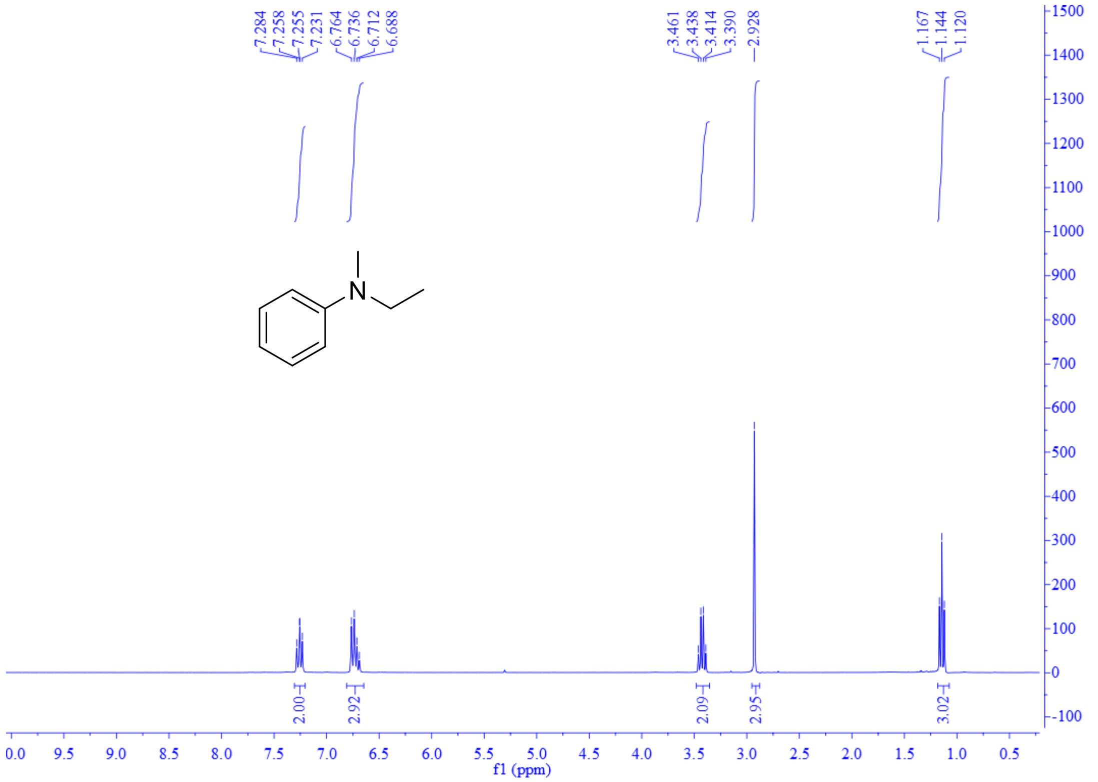

Figure S73. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C) of **4p**

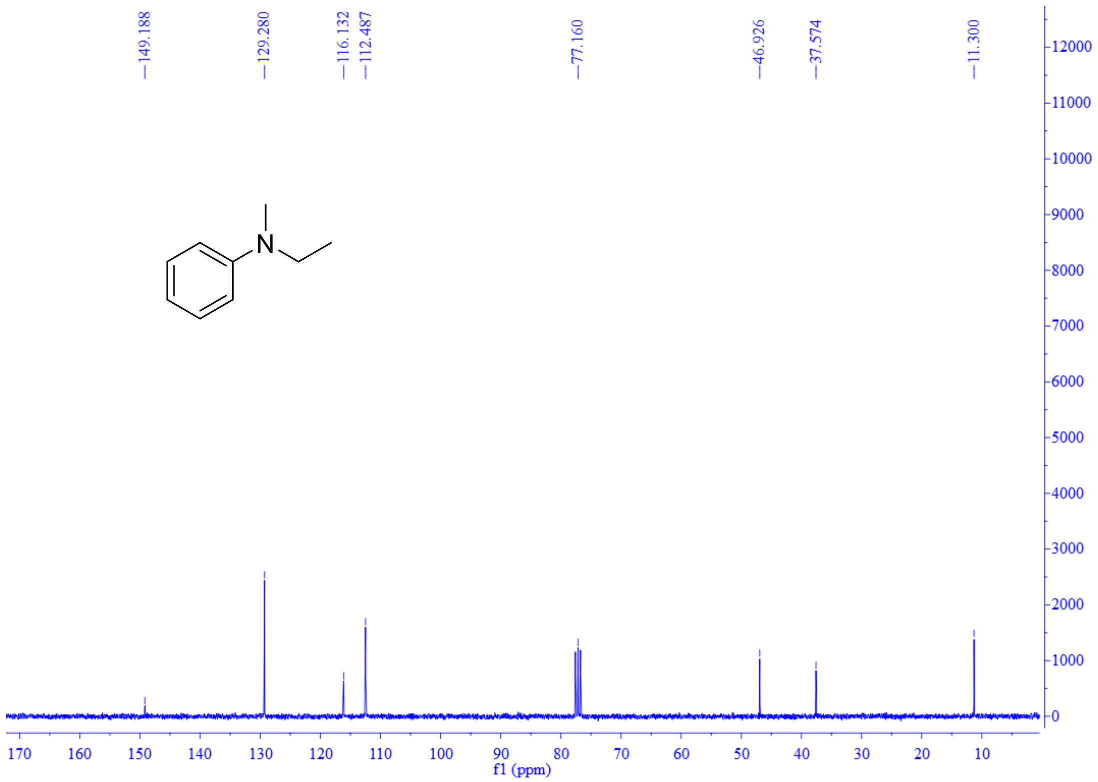

Figure S74. $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$, 20 °C) of **4p**

Figure S75. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C) of **4q**

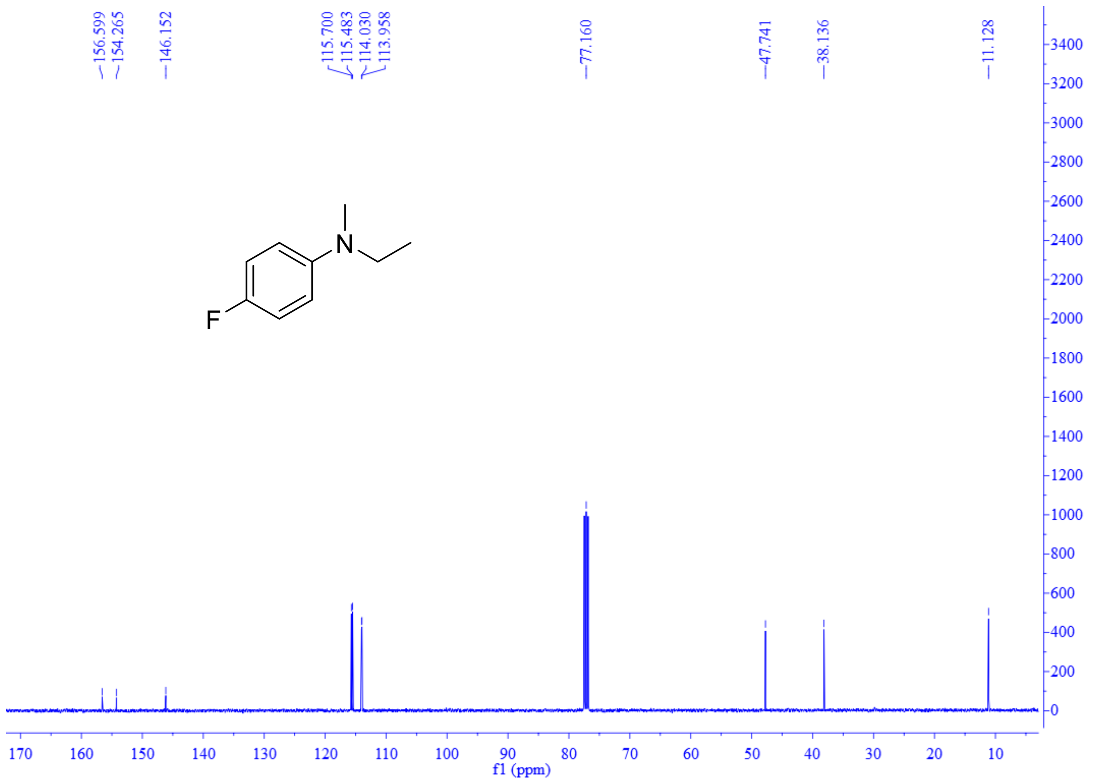

Figure S76. $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$, 20 °C) of **4q**

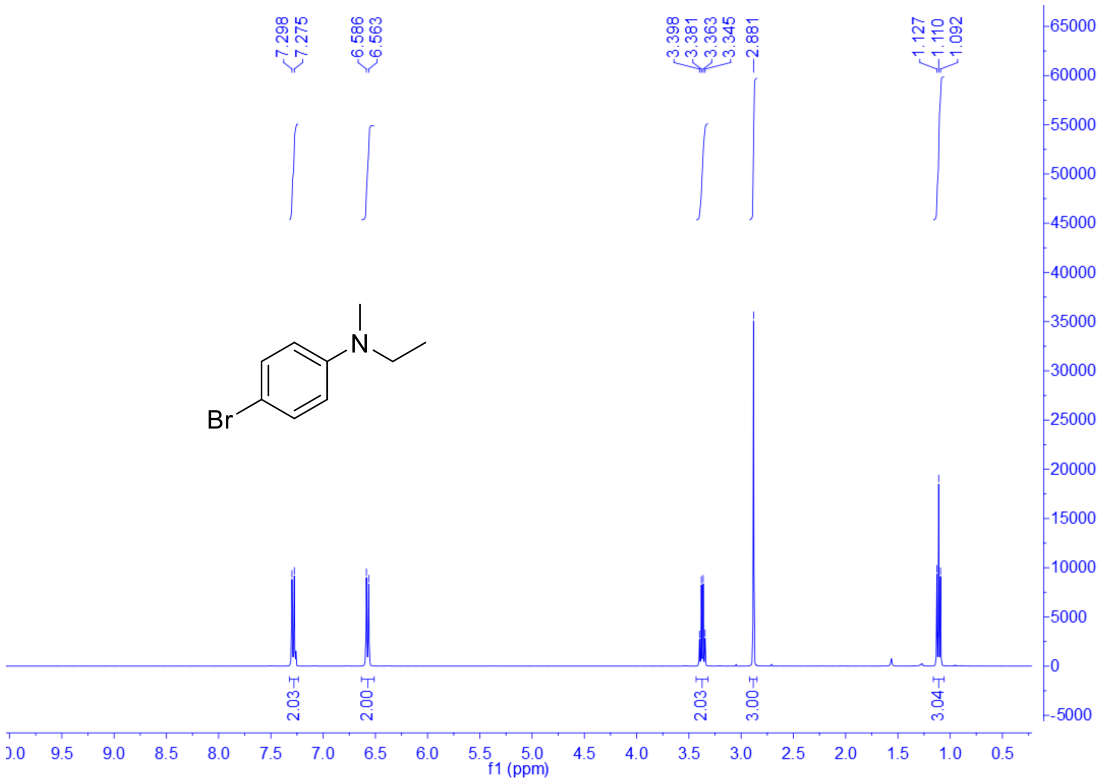

Figure S77. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C) of **4r**

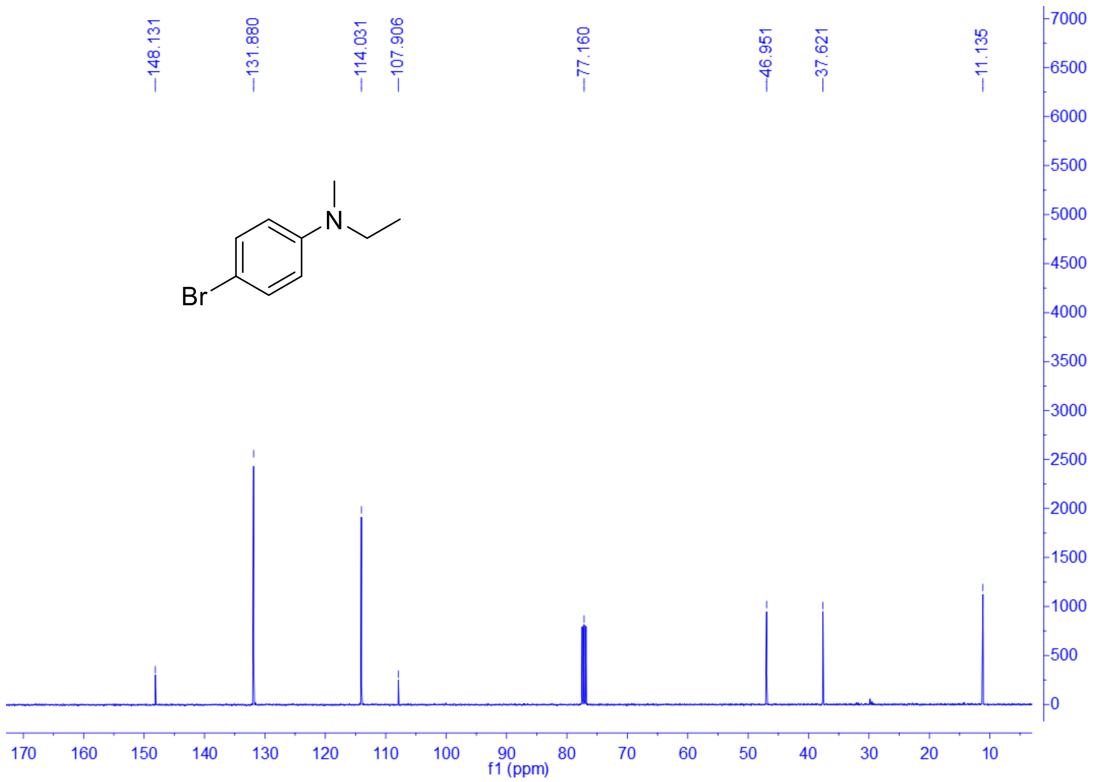

Figure S78. $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$, 20 °C) of **4r**

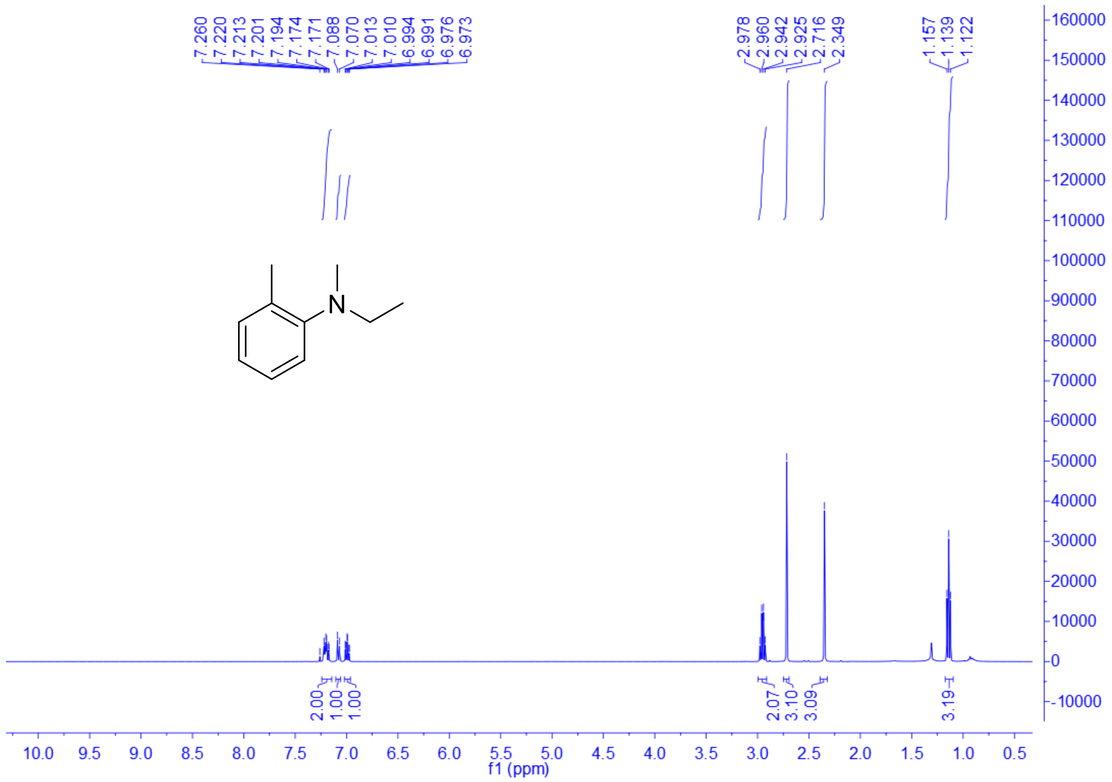

Figure S79. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C) of **4s**

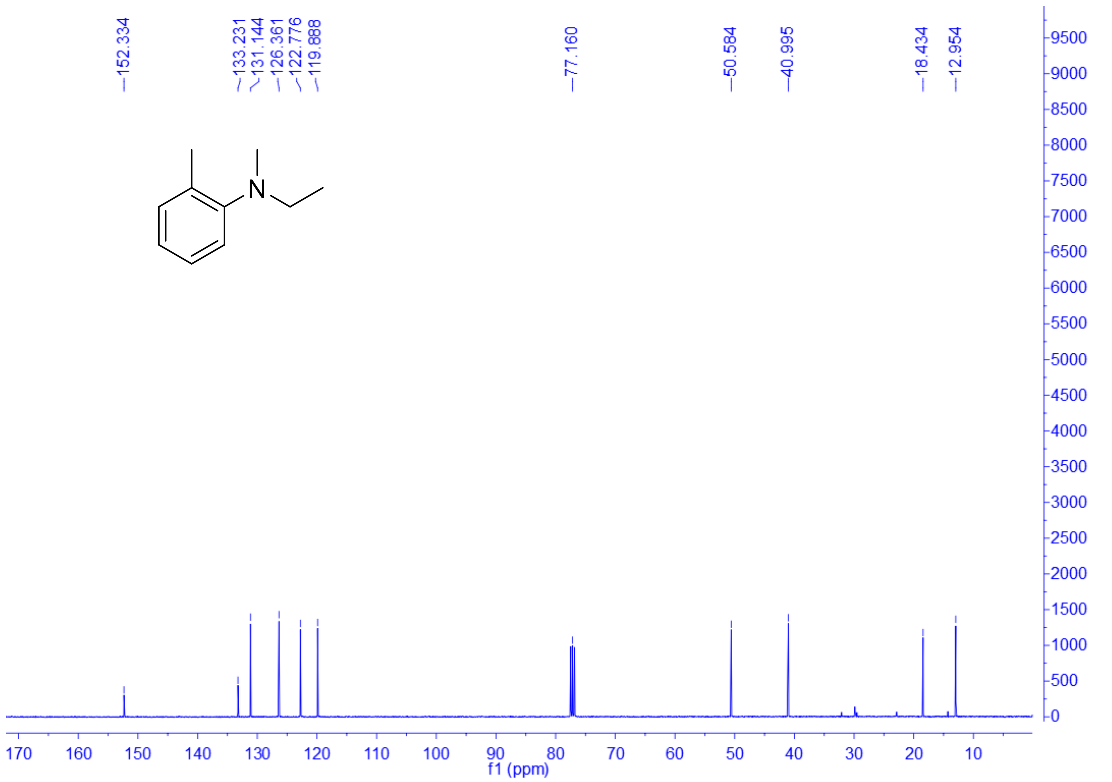

Figure S80. $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$, 20 °C) of **4s**

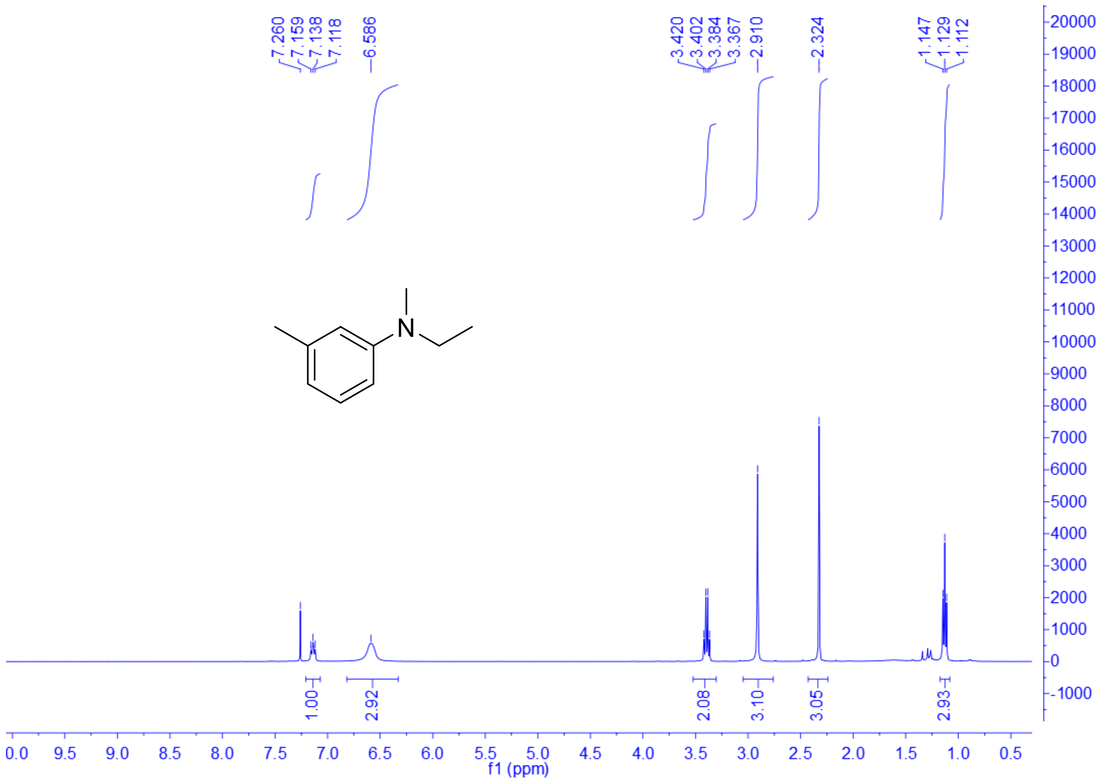

Figure S81. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C) of **4t**

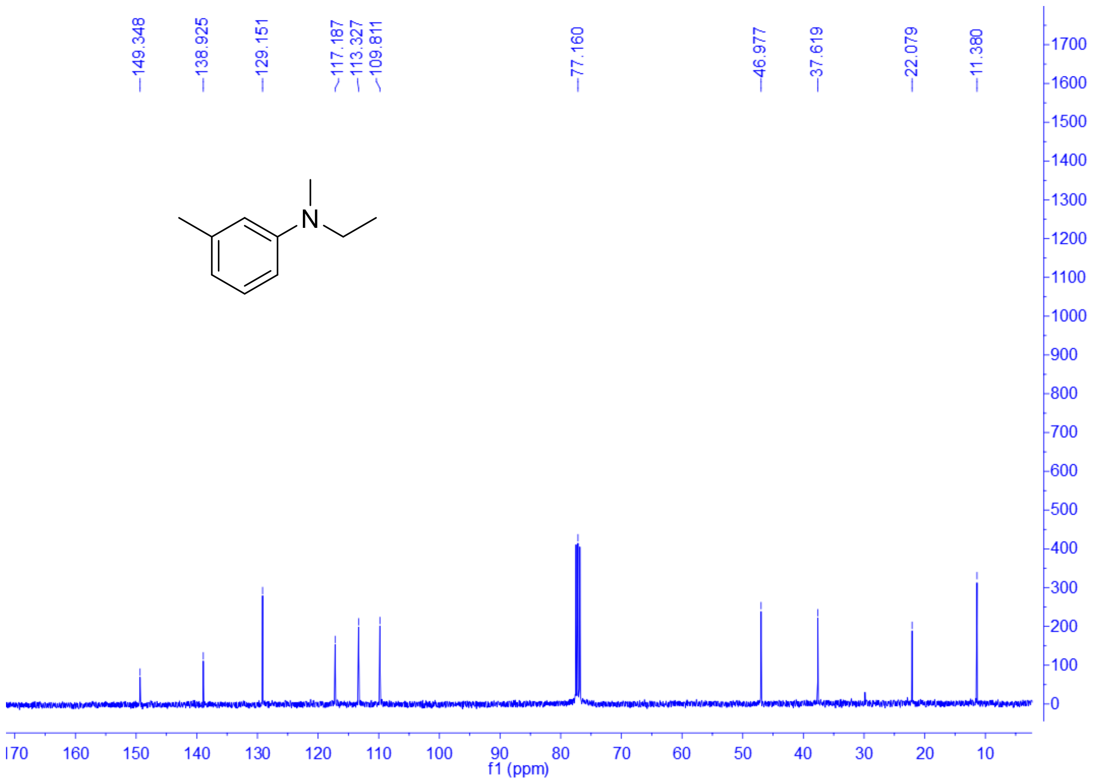

Figure S82. $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$, 20 °C) of **4t**

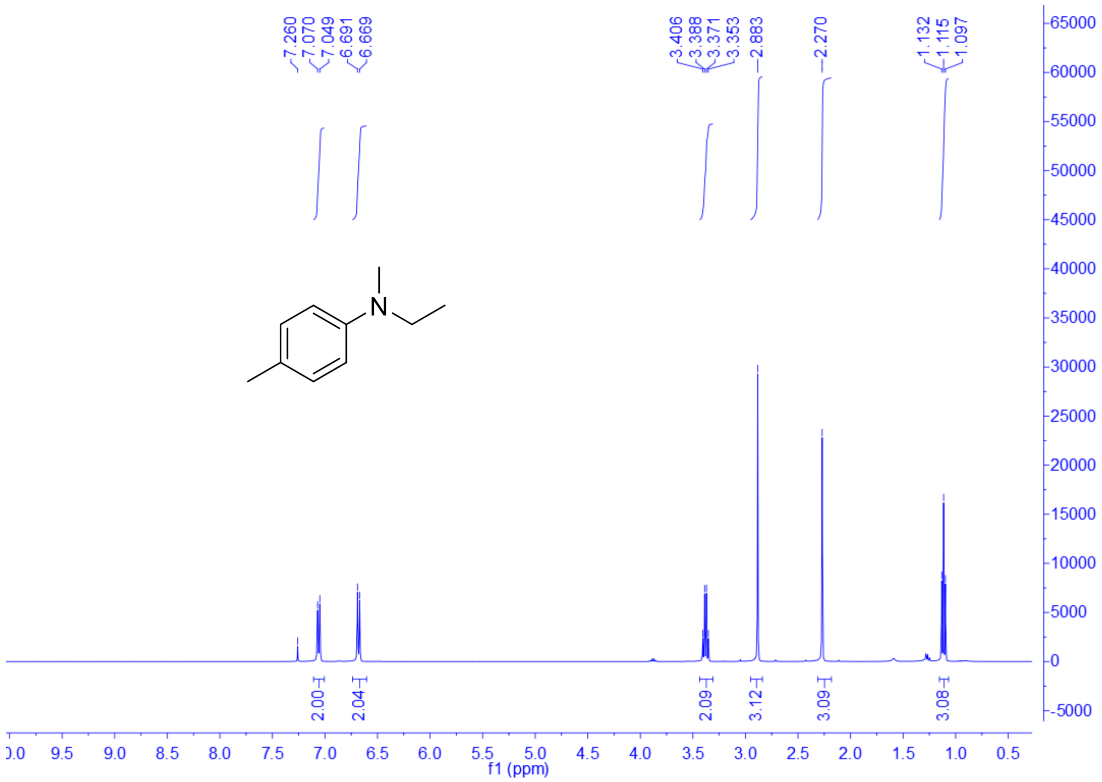

Figure S83. ^{1}H NMR (400 MHz, $CDCl_3$, 20 ºC) of **4u**

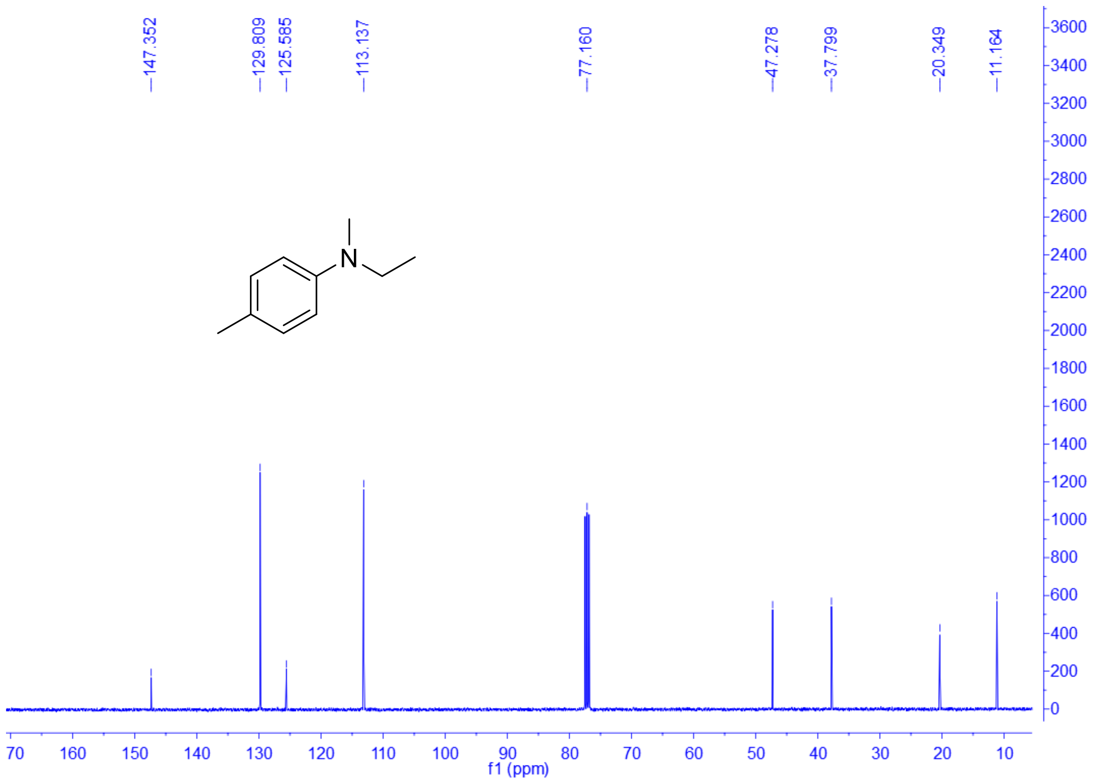

Figure S84. $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$, 20 ºC) of **4u**

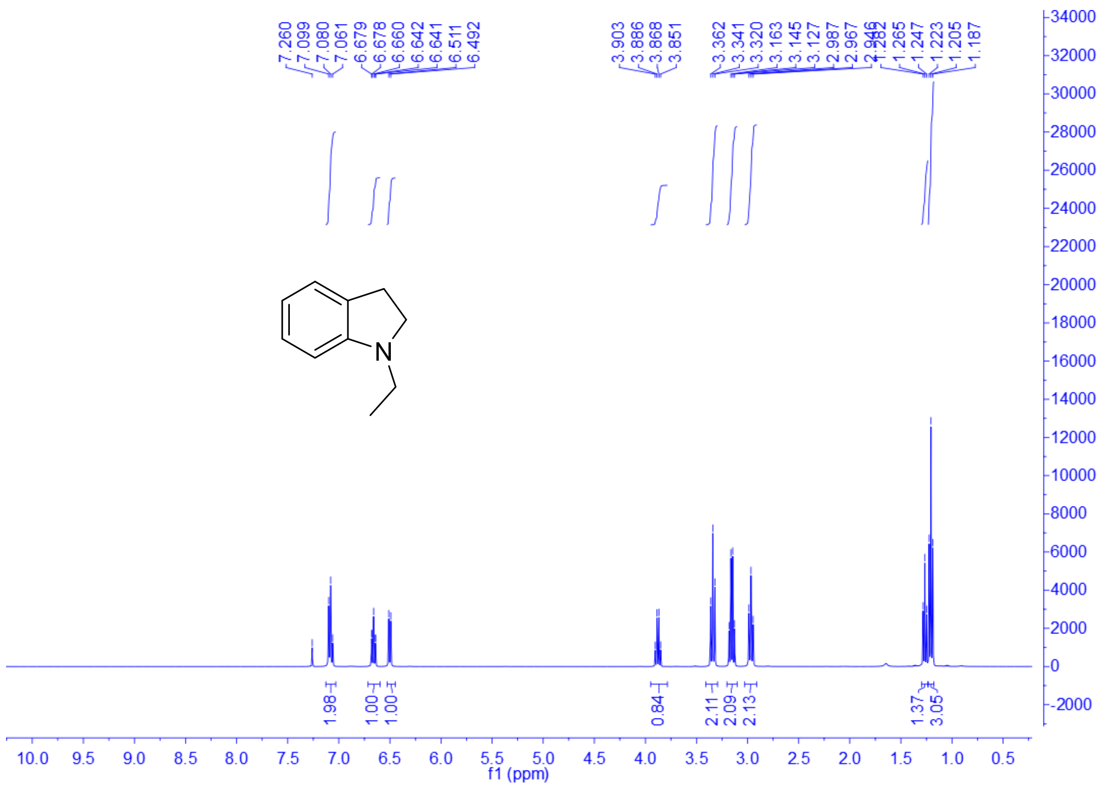

Figure S85. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C) of **4v**

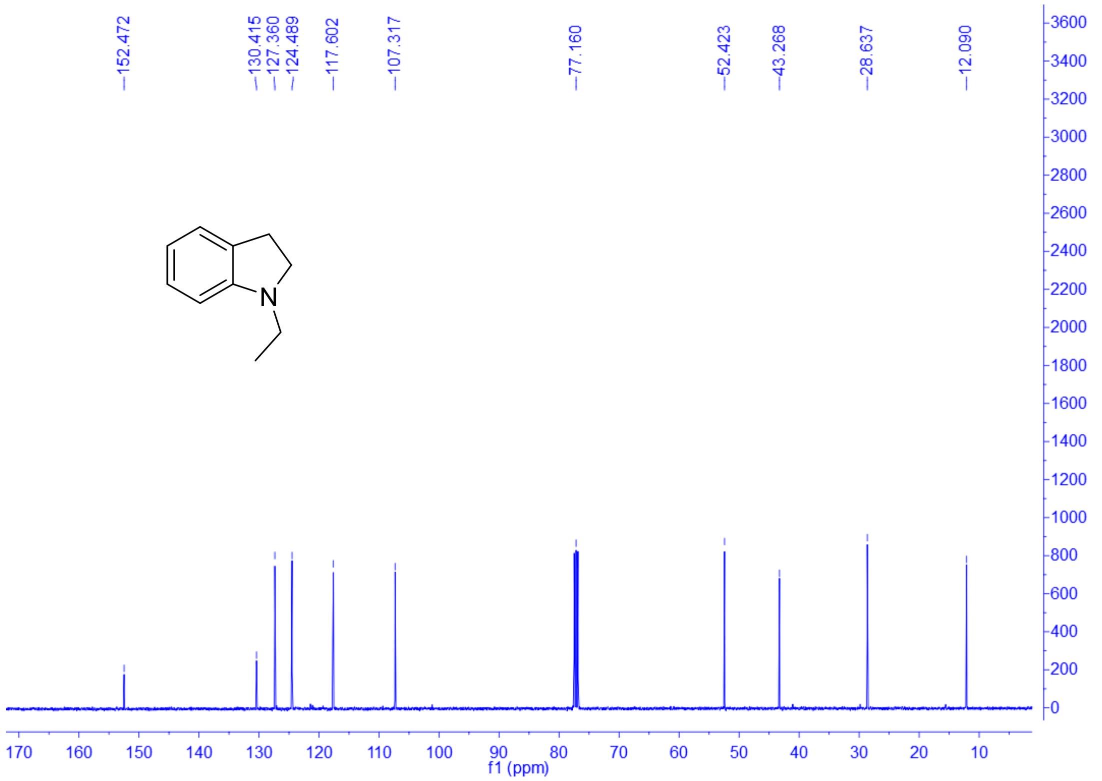

Figure S86. $^{13}C\{^1H\}$ (101 MHz, $CDCl_3$, 20 °C) of **4v**

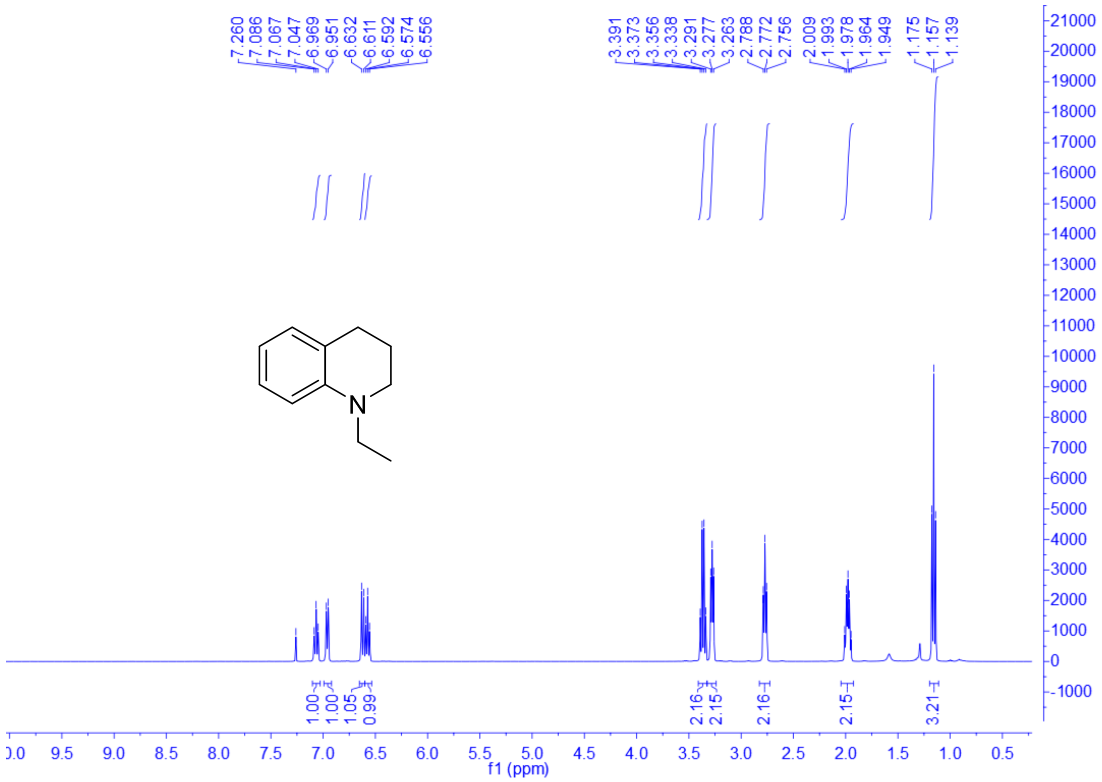

Figure S87. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C) of **4w**

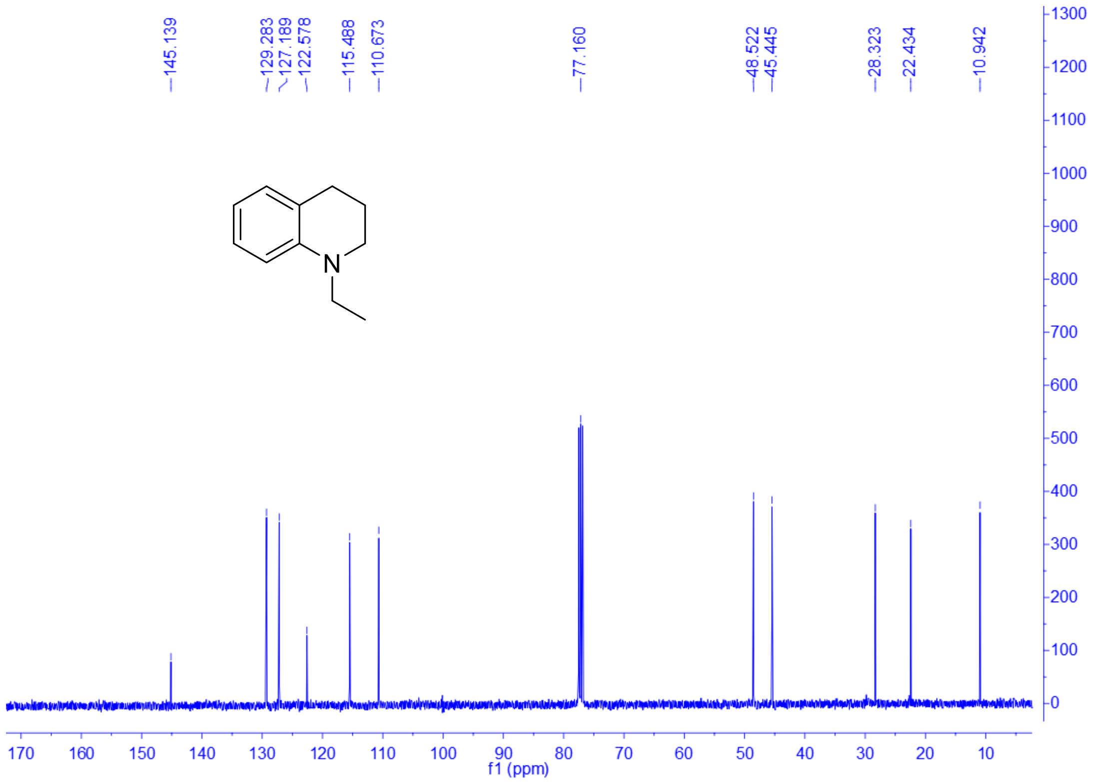

Figure S88. $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$, 20 °C) of **4w**

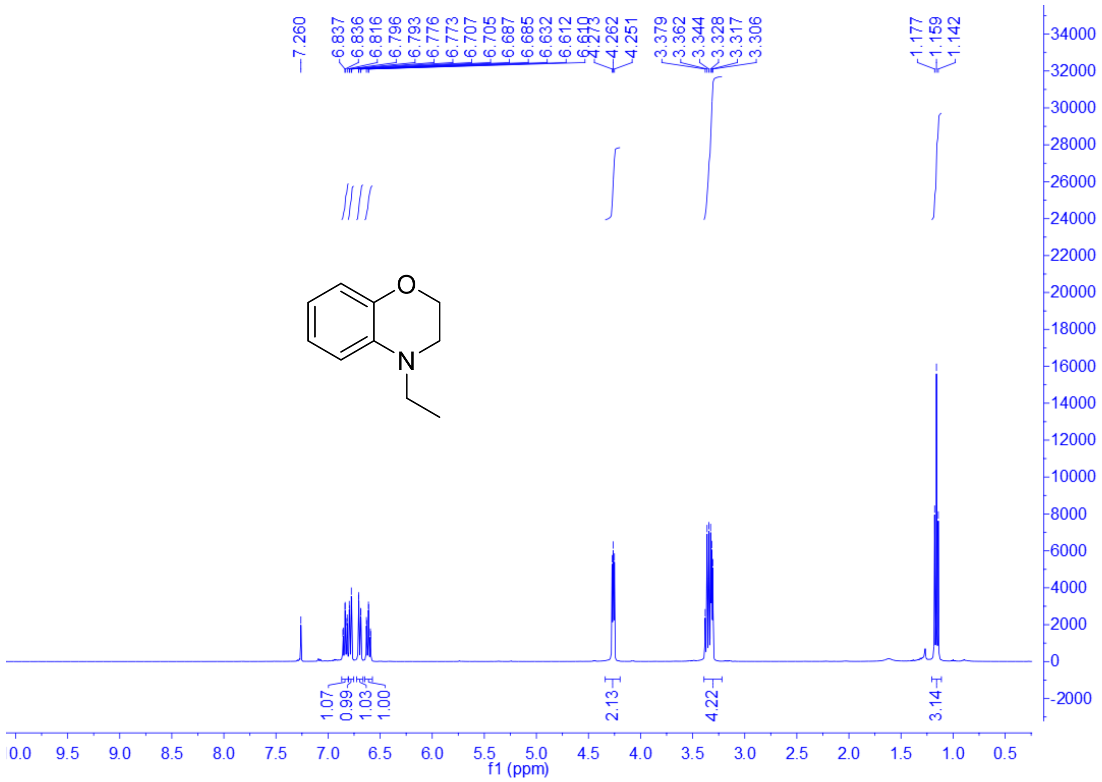

Figure S89. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C) of **4x**

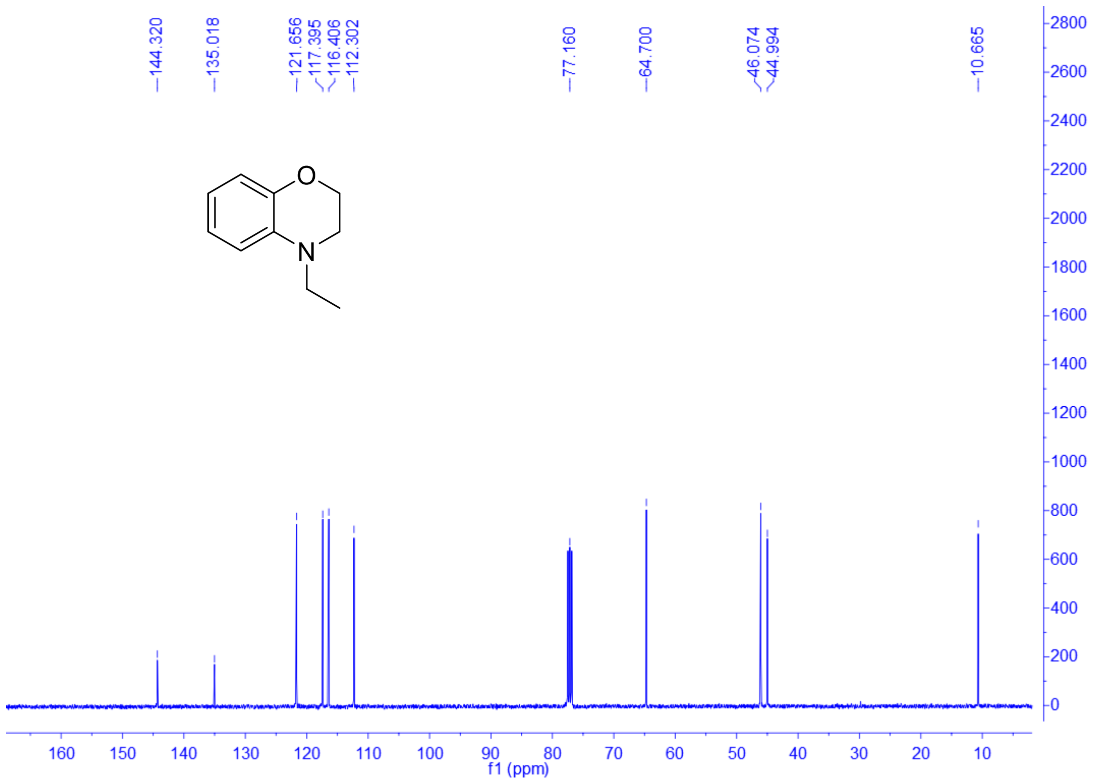

Figure S90. $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$, 20 °C) of **4x**

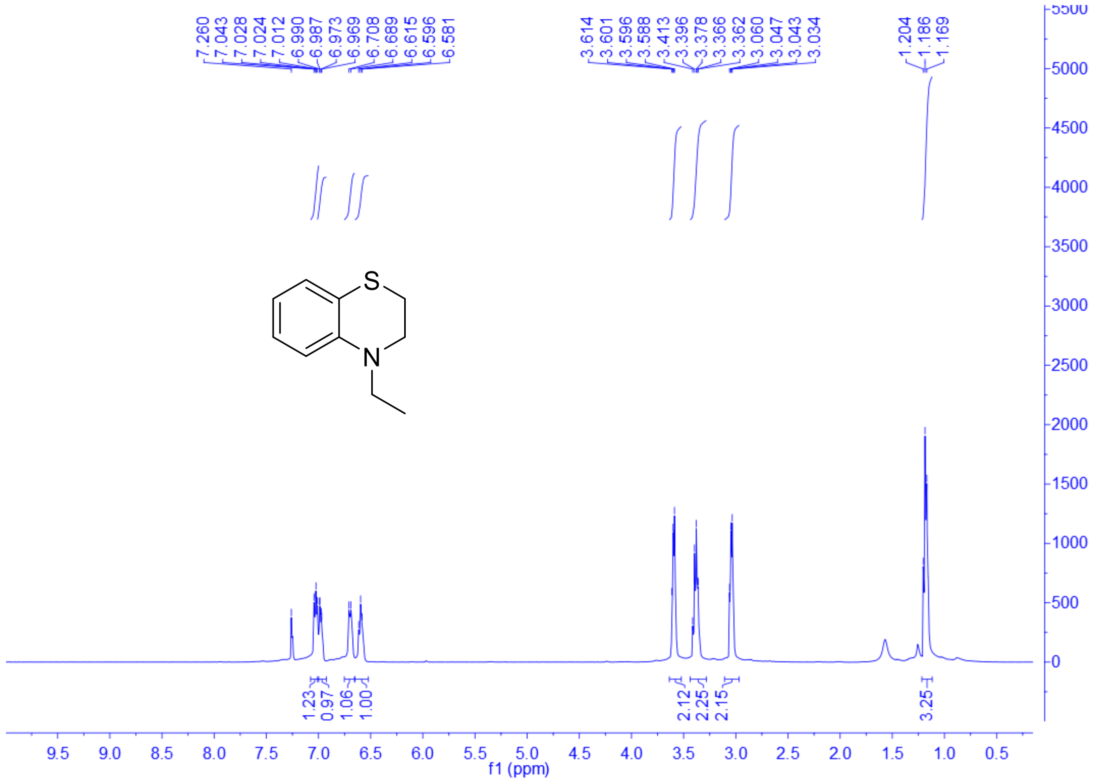

Figure S91. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C) of **4y**

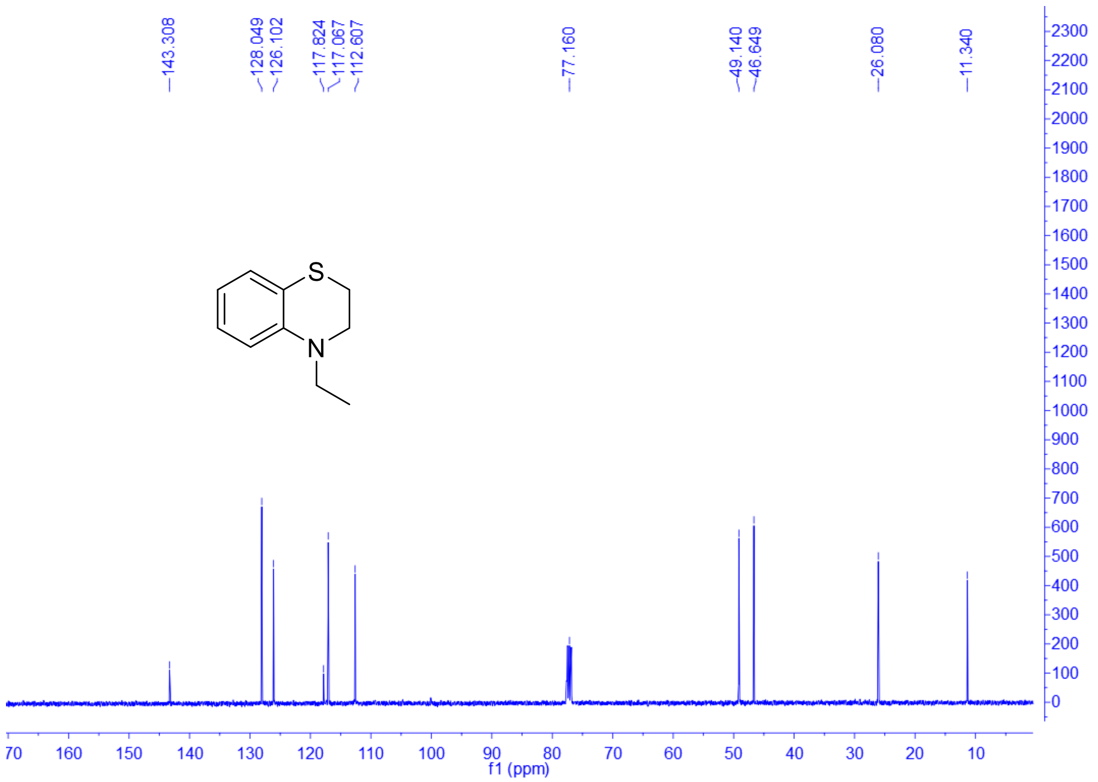

Figure S92. $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$, 20 °C) of **4y**

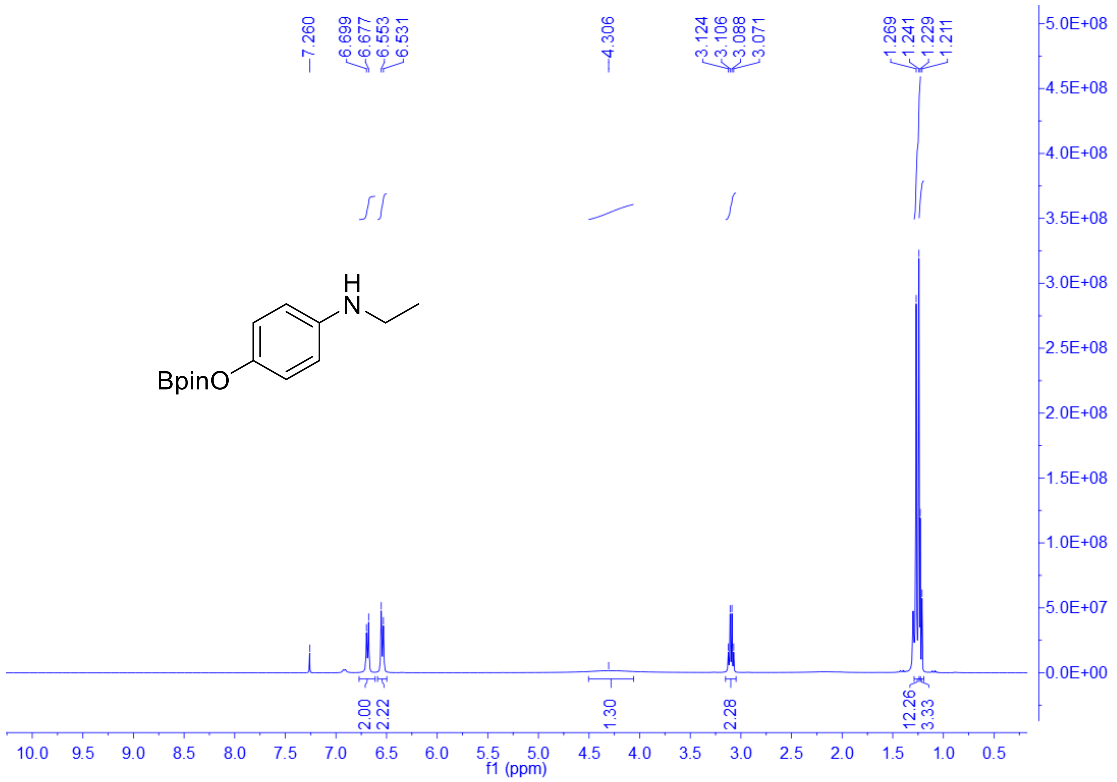

Figure S93. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C) of **4ab**

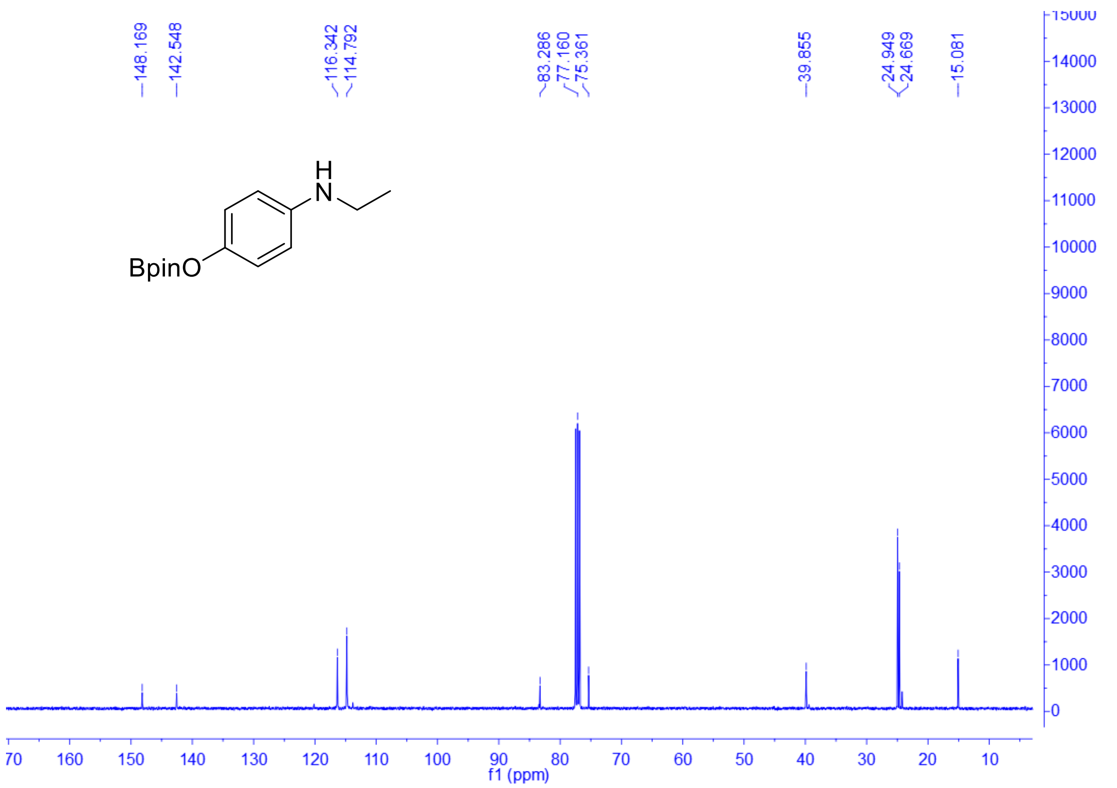

Figure S94. $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$, 20 °C) of **4ab**

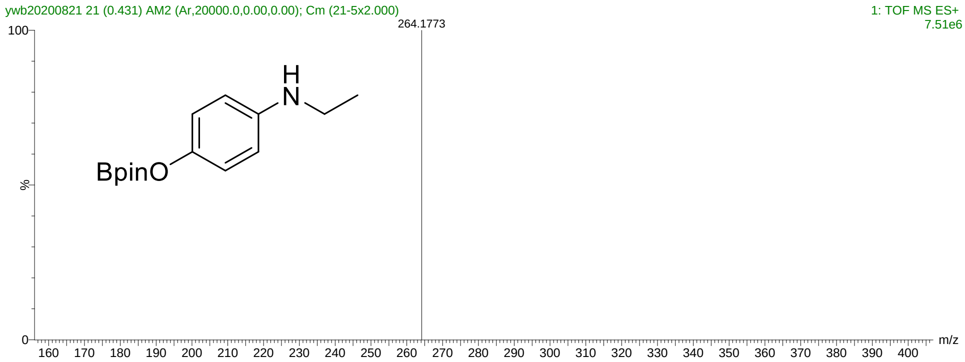

Figure S95. HR MS of **4ab**

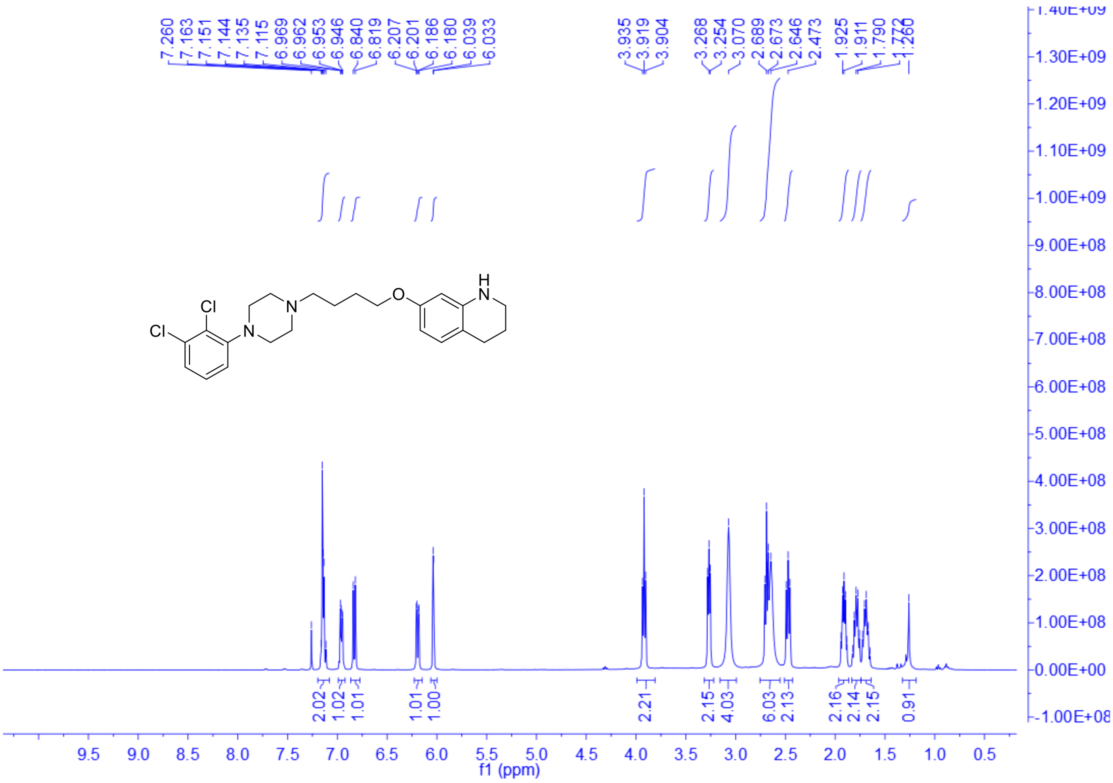

Figure S96. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C) of **4ac**

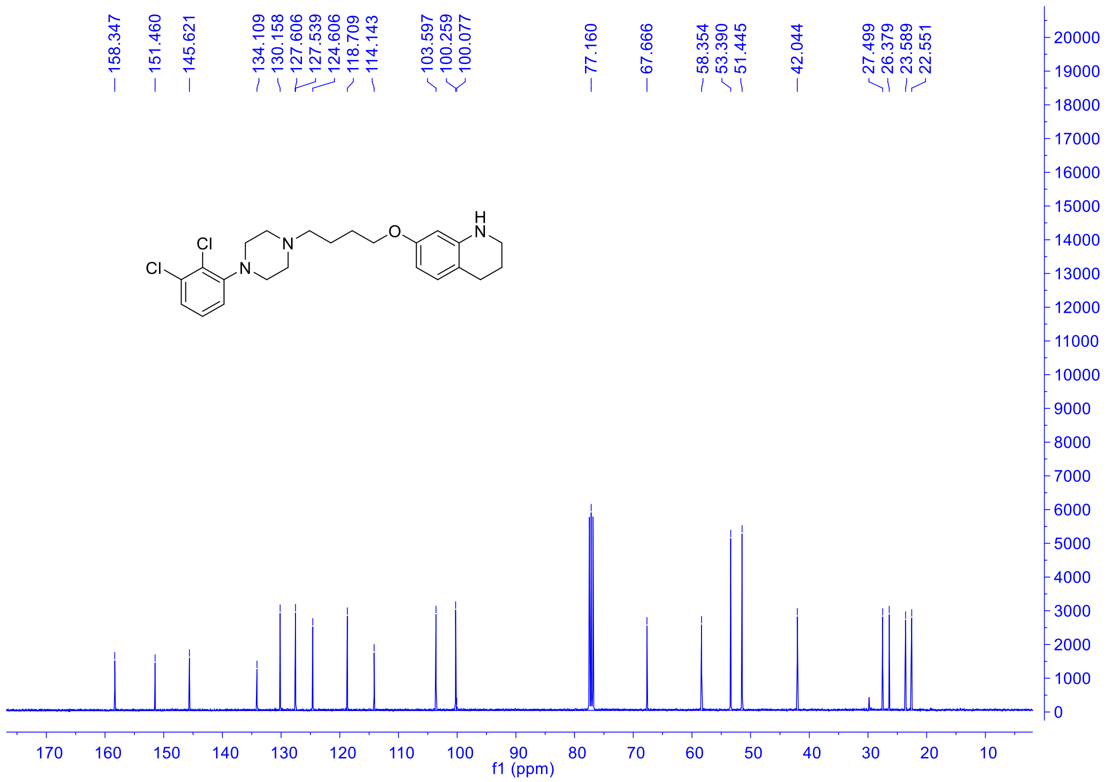

Figure S97. $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$, 20 °C) of **4ac**

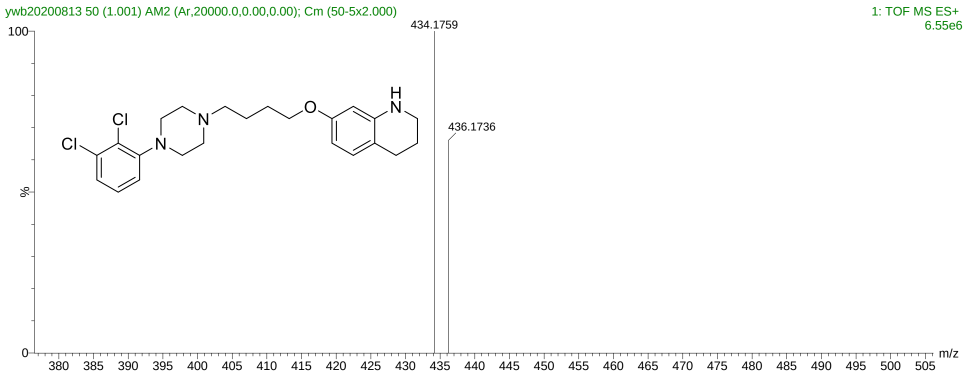

Figure S98. HR MS of **4ac**

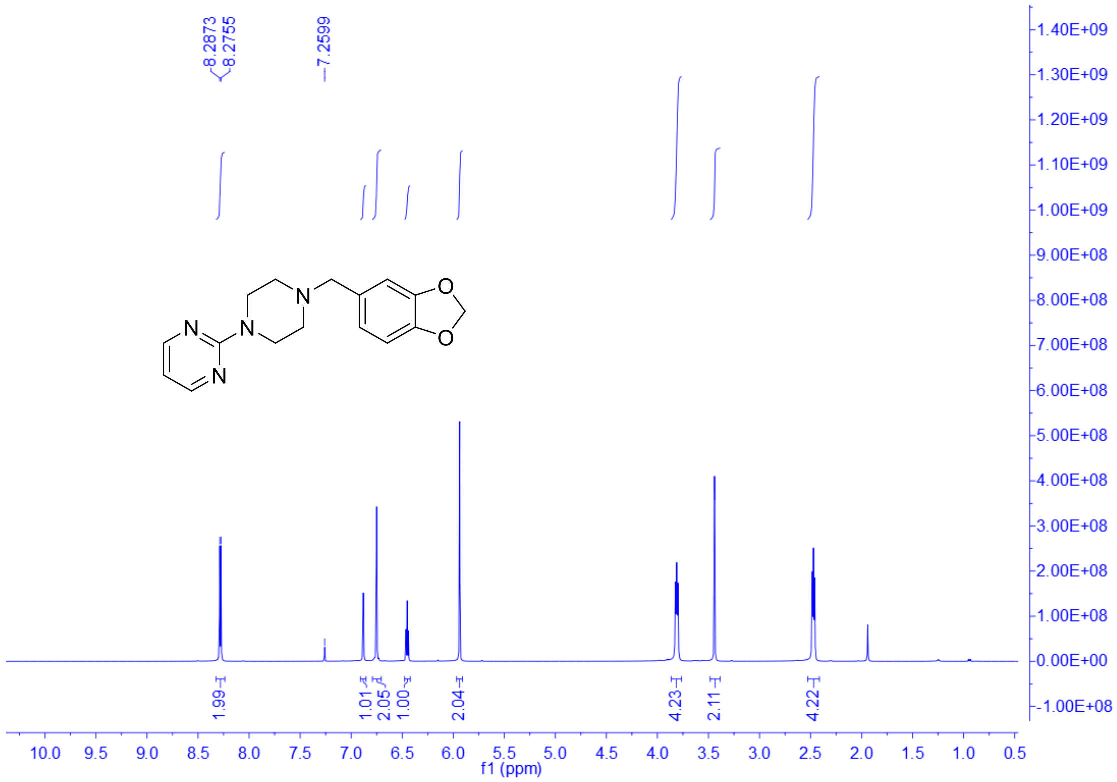

Figure S99. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C) of **4ad**

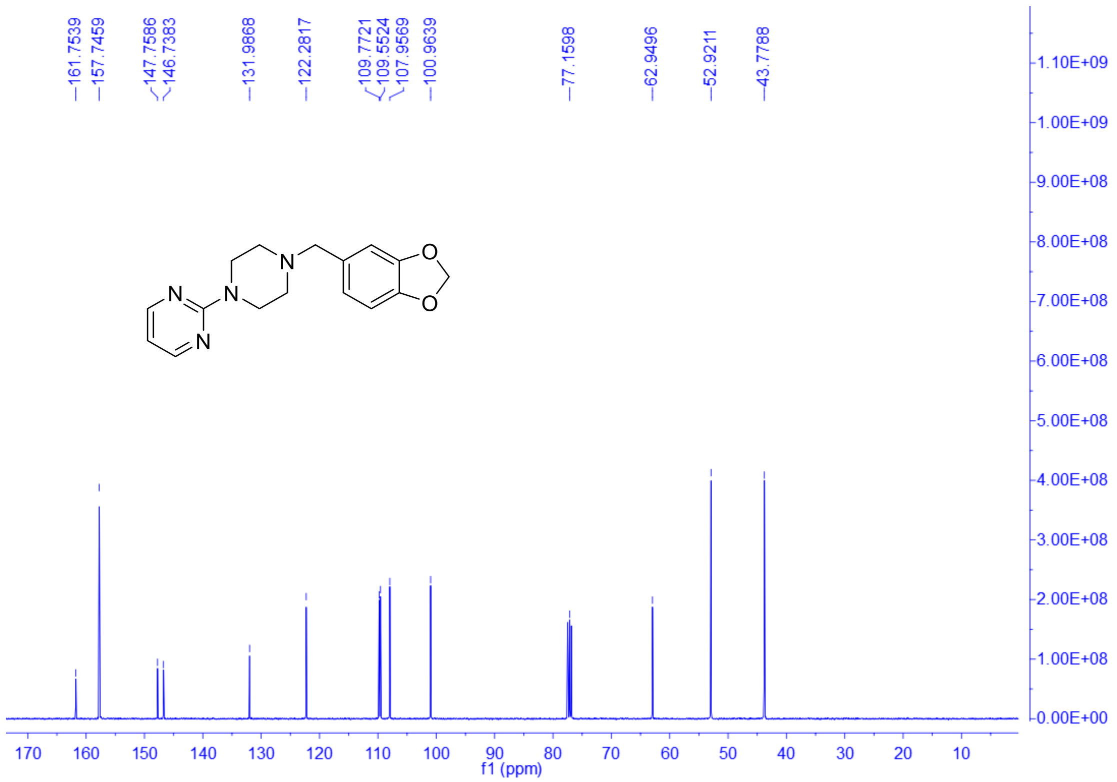

Figure S100. $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$, 20 °C) of **4ad**

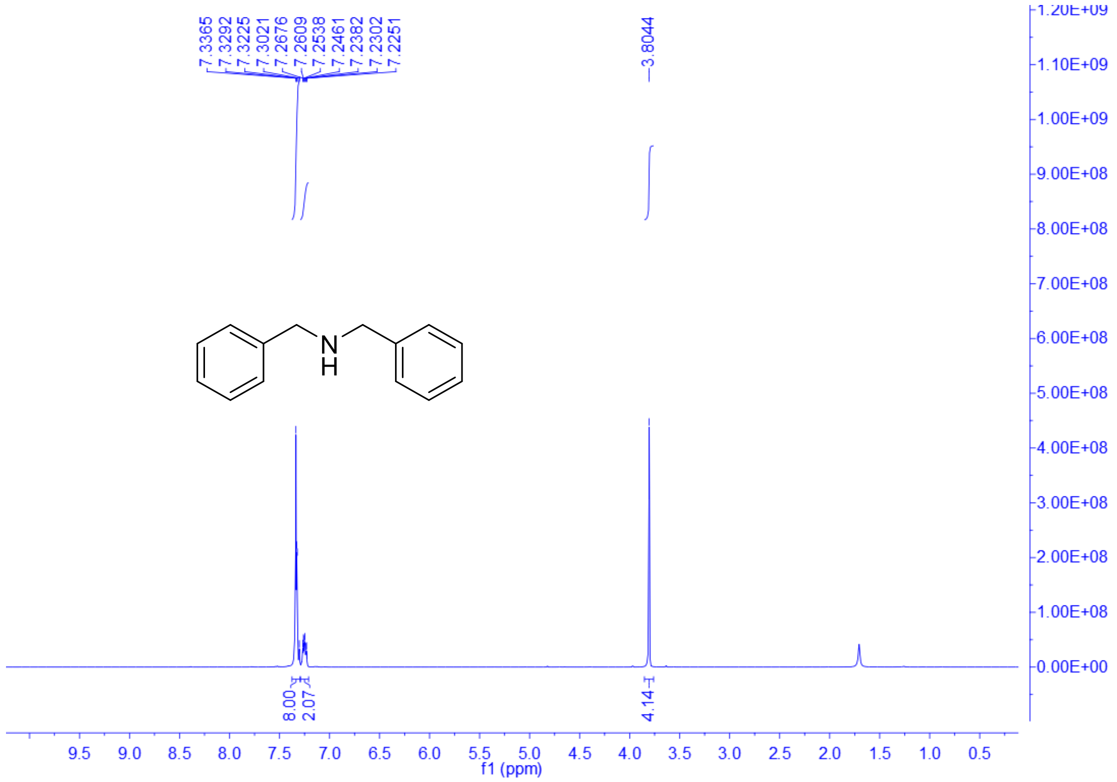

Figure S101. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C) of **5**

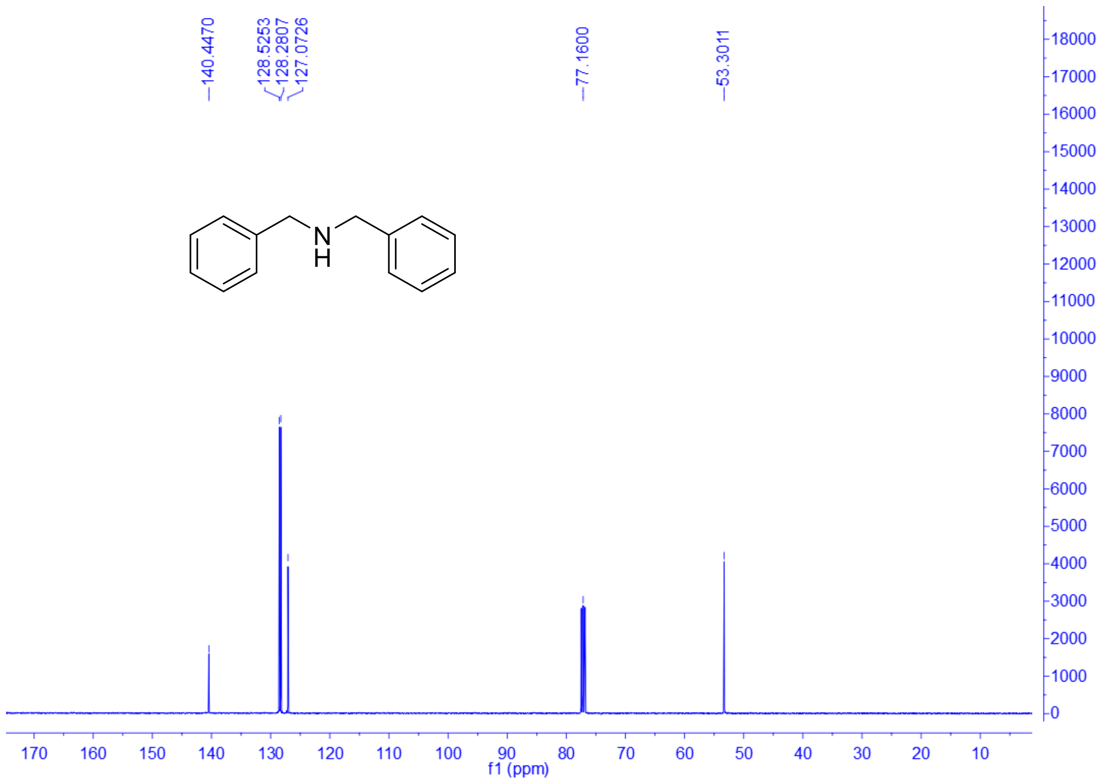

Figure S102. $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$, 20 °C) of **5**

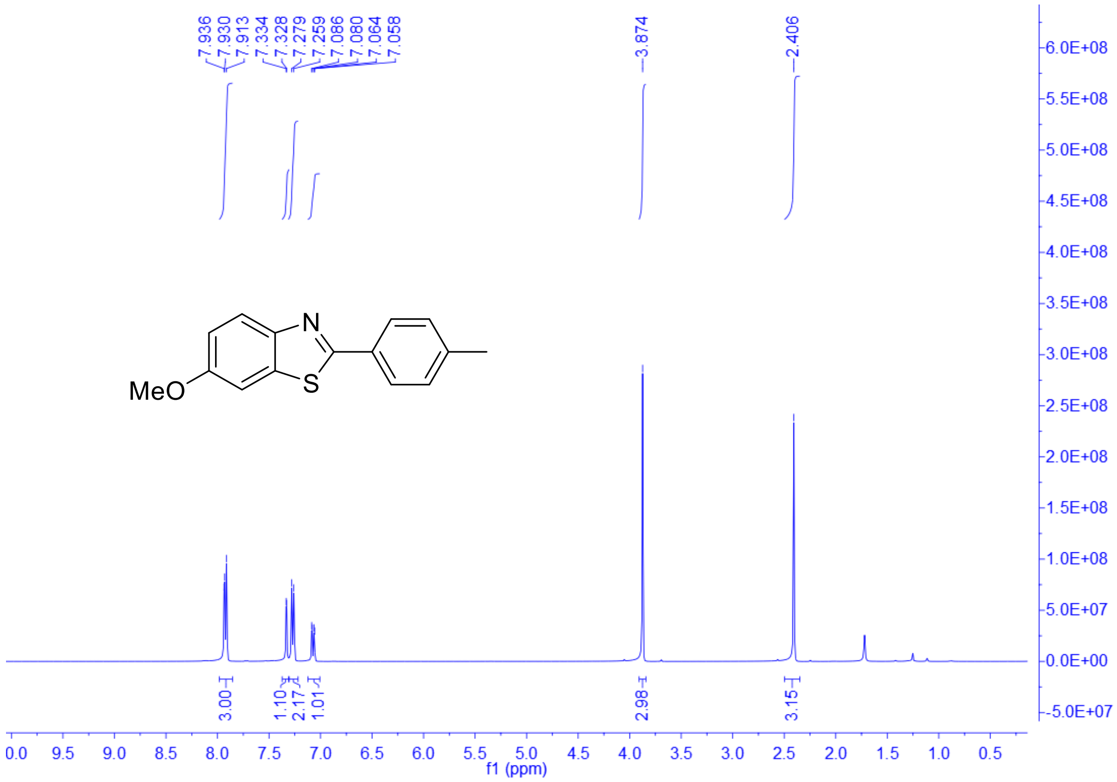

Figure S103. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C) of **6**

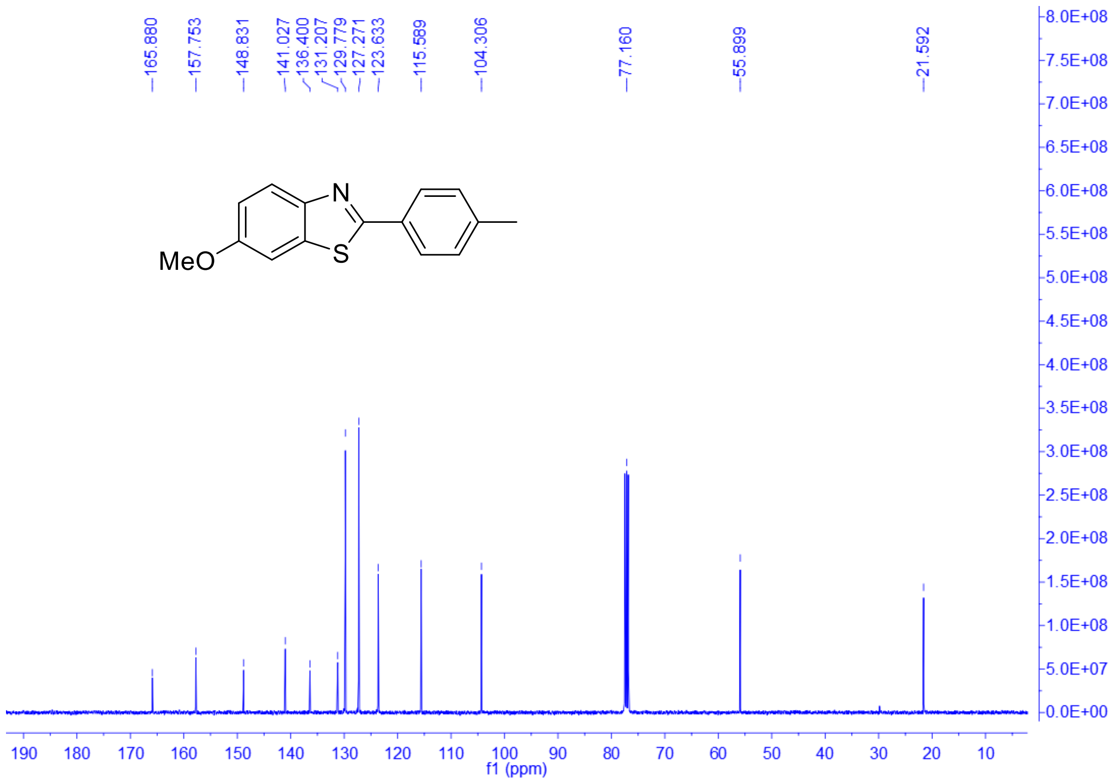

Figure S104. $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$, 20 °C) of **6**