Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

In situ generated aminodiborane as a reagent for deoxygenative reduction of carboxamides to amines

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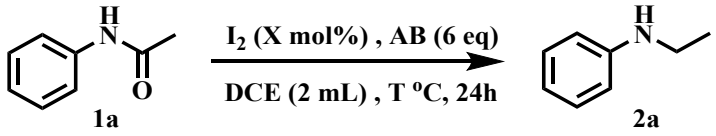
Contents

A. General Information

All the reactions and manipulations were performed under atmospheric conditions except for the synthesis of $NH_2B_2H_5$.THF (using the protocol of Shore & co-workers) [1]. Schlenk or glovebox techniques [GP(Concept)-T2, Jacomex] were used for the synthesis of $NH_2B_2H_5$.THF. ^1H, ^{13}C, ^{19}F and ^{11}B NMR spectra were recorded on a Bruker Ascend 500 NMR spectrometer and Bruker Ascend 400 NMR. All chemical shifts (δ) are reported in ppm. All chemical shifts are related to residual solvent peaks [$CDCl_3$: 7.26 (^1H), 77.16 (^{13}C)]. All amide derivatives were purchased from commercial sources. Ammonia-borane was synthesised by the literature procedure.[2] Mass Spectra were recorded on a Bruker Micro-TOF QII quadrupole time-of-flight (Q-TOF) mass spectrometer.

B. Optimization of reaction conditions:

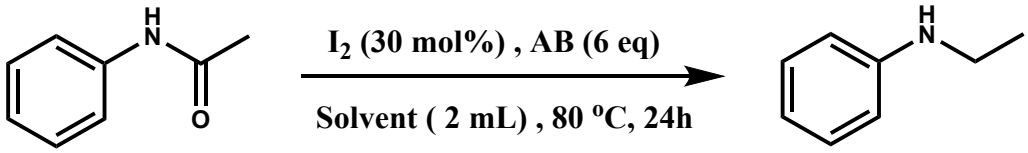
Table S1: Optimization of promoter and temperature for reduction of acetanilide



S. No.	Promoter (X mol%)	Temperature (°C)	(%) of Yield[a]
1	-	50	0
2	KI (30 mol%)	50	0
3	NIS (30 mol%)	50	0
4	NBS (30 mol%)	50	0
5	Br_2 (30 mol%)	50	27
6	I_2 (5 mol%)	50	15
7	I_2 (30 mol%)	50	41
8	I_2 (30 mol%)	60	55
9	I_2 (30 mol%)	70	76
10	I_2 (30 mol%)	80	94
11	I_2 (30 mol%)	90	95

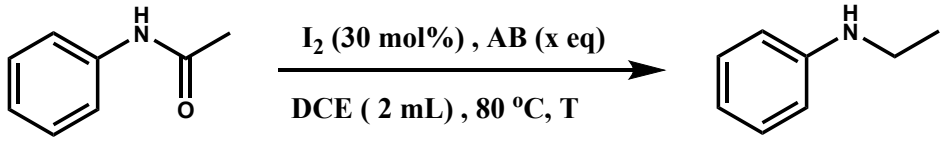
[a] Conditions: 1a (0.37 mmol), I_2 (as indicated), AB (6 eq.), DCE as solvent, 24h

Table S2: Effect of solvent for reduction of secondary amides



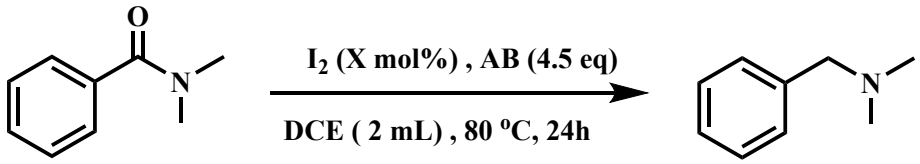
S. No.	Solvent	Percentage Yield (%)
1.	H_2O	0
2.	CH_3CN - H_2O	0
3.	CH_3CN	67
4.	toluene	80
5.	DCE	94
6.	THF	82

Table S3: Effect of amount of ammonia-borane and time for reduction of secondary amides



S. No.	Ammonia-borane (eq.)	Time	Percentage Yield (%)
1.	6	24h	94
2.	5	24h	93
3.	4	24h	94
4.	3	24h	78
5.	4	20h	92
6.	4	18h	93
7.	4	15h	82

Table S4: Effect of amount of iodine for reduction of tertiary amides

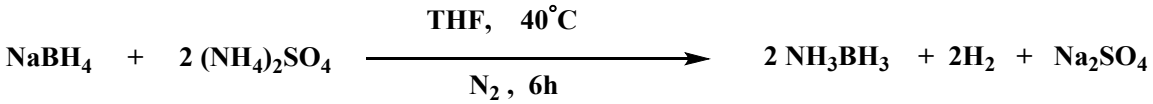


S. No.	Iodine (X mol%)	(%) of Yield[a]
1	30	80
2	60	91
3	100	98

a. All the reactions were carried out using 50 mg of N-methyl benzamide

C. General procedure for the synthesis of ammonia-borane

Ammonia-borane was prepared according to the literature procedure.[2] In a 250 ml two-neck round bottom flask, sodium borohydride (1g, 26.3 mmol) and powdered ammonium sulfate (3.48g, 26.3 mmol) were added in 125 ml THF. One neck through a condenser is fitted to nitrogen cylinder and second neck is fitted with a connecting tube. The connecting tube was vented via an oil bubbler to the hood exhaust. The contents were vigorously stirred at 40 °C. After 6h, the reaction mixture was cooled to room temperature (RT) and filtered. The filtrate was concentrated under vacuum to obtain ammonia-borane (AB). The product AB was obtained as a white powder: ^{11}B NMR ($CDCl_3$, 160 MHz) δ: -22.1 (q) (Figure S1).



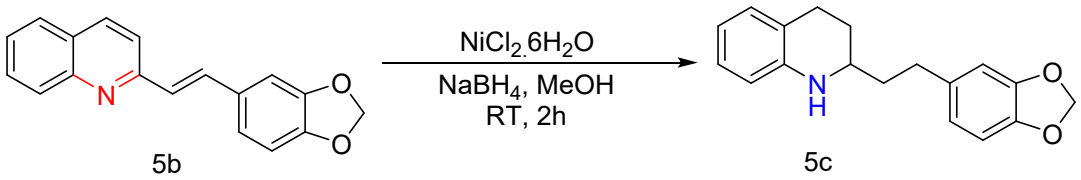
Scheme S1: Ammonia-borane preparation using sodium borohydride and ammonium sulfate

D. General procedure for the reaction

1. **For secondary amides**: A 10 mL T-23 pressure tube was charged with a magnetic bead, acetanilide (100mg, 0.74mmol), iodine (14mg, 30 mol%), ammonia-borane (92mg, 2.95 mmol) and 2 mL DCE. This reaction was carried out at 80°C for 24 h. After the reaction, ethyl acetate and water were added to the reaction mixture. Ethyl acetate

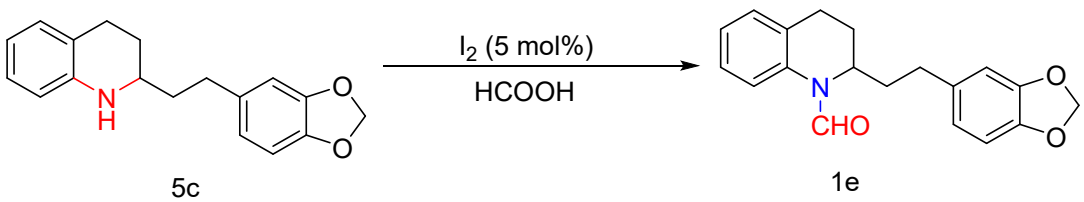
layer was concentrated using a rotavapor. After evaporation, the crude mixture was purified by silica gel column chromatography using EtOAc and hexane (10:90) as eluent. The product was characterized by ^{1}H NMR, ^{13}C NMR and HRMS.

2. **For tertiary amides:** A 10 mL T-23 pressure tube was charged with a magnetic bead, N, N-dimethylbenzamide (100mg, 0.67mmol), iodine (163mg, 1 eq.), ammonia-borane (83mg, 2.68 mmol) and 2 mL DCE. This reaction was carried out at 80°C for 24 h. After the reaction, ethyl acetate and water were added to the reaction mixture. Ethyl acetate layer was concentrated using a rotavapor. After evaporation, the crude mixture was purified by silica gel column chromatography using EtOAc and hexane (10:90) as eluent The product was characterized by ^{1}H NMR, ^{13}C NMR and HRMS.
3. **Total Synthesis of (±)-galipinine**



5b 5c

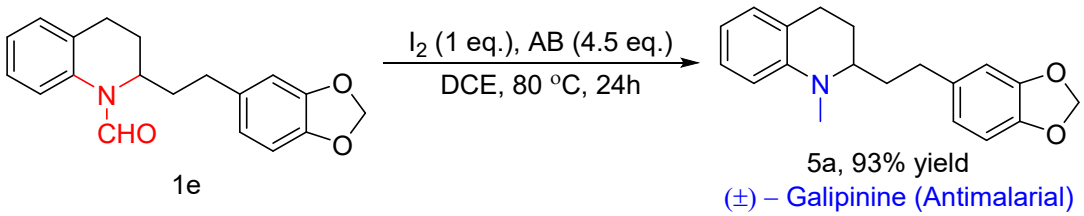
Compound 5b was synthesized using the literature procedure.[3] Compound 5b (70 mg, 0.25 mmol) and $NiCl_2.6H_2O$ (0.05 mmol, 20 mol%) were taken in a 100 mL RB and dissolved in 10 mL of methanol. Then $NaBH_4$ (1 mmol, 4 equiv.) was added in portion at 0°C and stirred at RT for 2h. Afterwards, excess methanol was evaporated, and black ppt. was dissolved in 10% aq. HCl, the acidic solution was basified by adding conc. ammonium hydroxide solution and then extracted with ether. The organic layer was dried over anhydrous Na_2SO_4. After evaporation of the solvent, the crude mixture was purified by silica gel column chromatography using EtOAc and hexane (10:90) as eluent to yield the desired product 5c as yellow oil (64 mg, 90% yield).



5c 1e

A mixture of 5c (0.23 mmol), formic acid (99% purity, 0.4mL), and iodine (4 mg, 5 mol %) was stirred at 70 °C. After completion of the reaction as monitored by TLC (42 h), the mixture was diluted with DCM (10 mL), washed with sat. $Na_2S_2O_3$ (5 mL), sat. $NaHCO_3$ (5 mL), and brine (5 mL), and then dried over anhydrous Na_2SO_4. After

filtration and evaporation of the solvent, the residue was purified by column chromatography (petroleum ether: ethyl acetate = 2:1 or 5:1) on silica gel to give the formylated product 1e (65 mg, 93% yield).



Compound 1e (65mg, 0.21mmol), iodine (54mg, 1 eq.), ammonia-borane (26mg, 0.84 mmol) and 2 mL DCE. This reaction was carried out at 80˚C for 24 h. After the reaction, ethyl acetate and water were added to the reaction mixture. Ethyl acetate layer was concentrated using a rotavapor. The product 5a was characterized by ^{1}H NMR,^{13}C NMR and HRMS.

E. ^{11}B NMR Spectra:

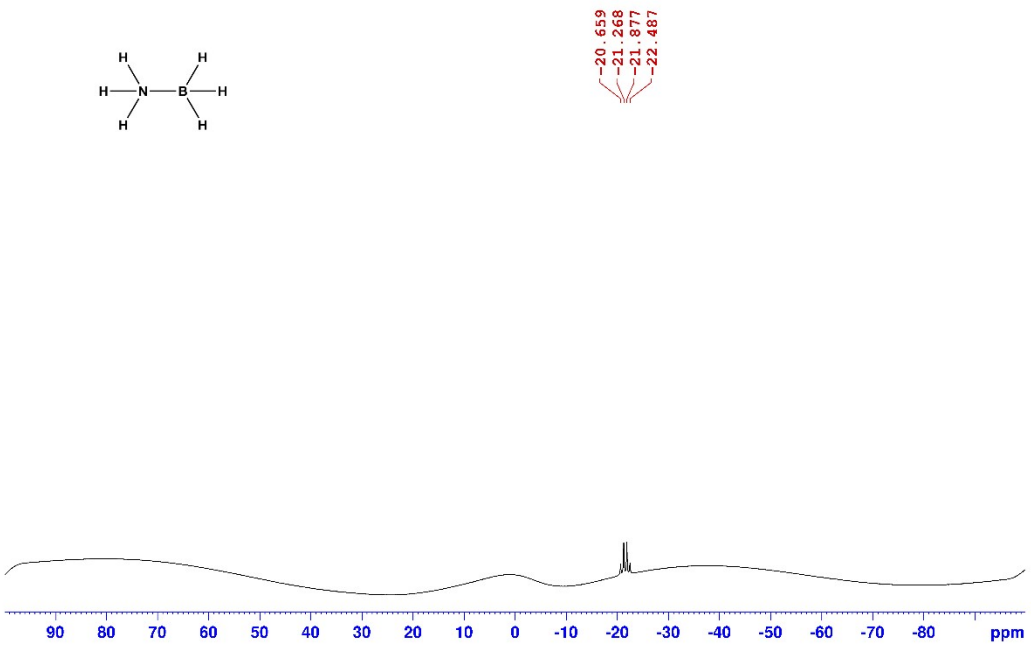


Figure S1. ^{11}B NMR spectra of NH_3BH_3 (in $CDCl_3$)

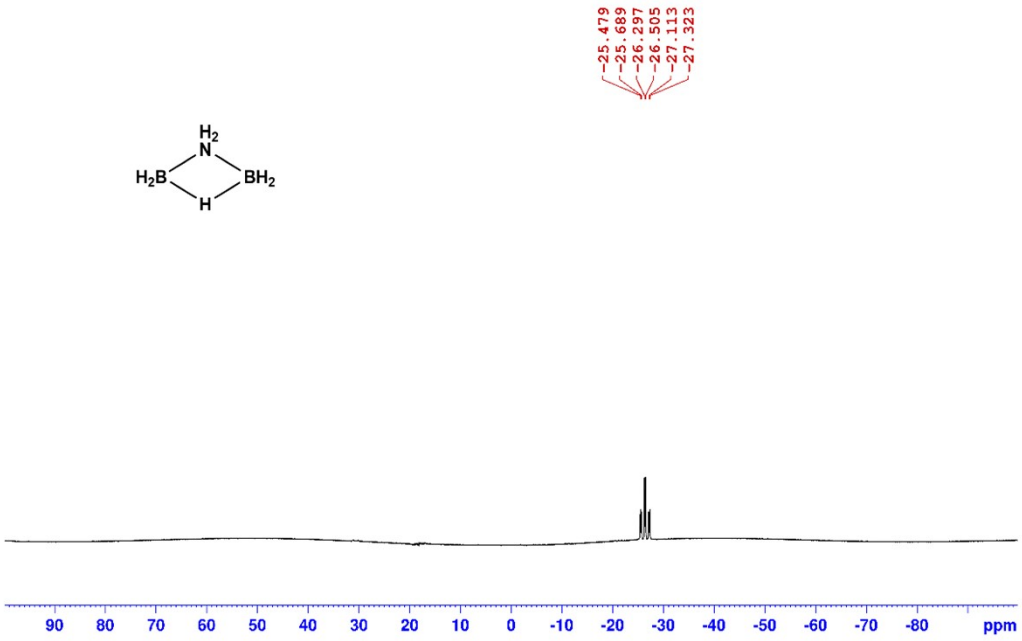


Figure S2. ^{11}B NMR spectra of $NH_2B_2H_5$ (in $CDCl_3$)

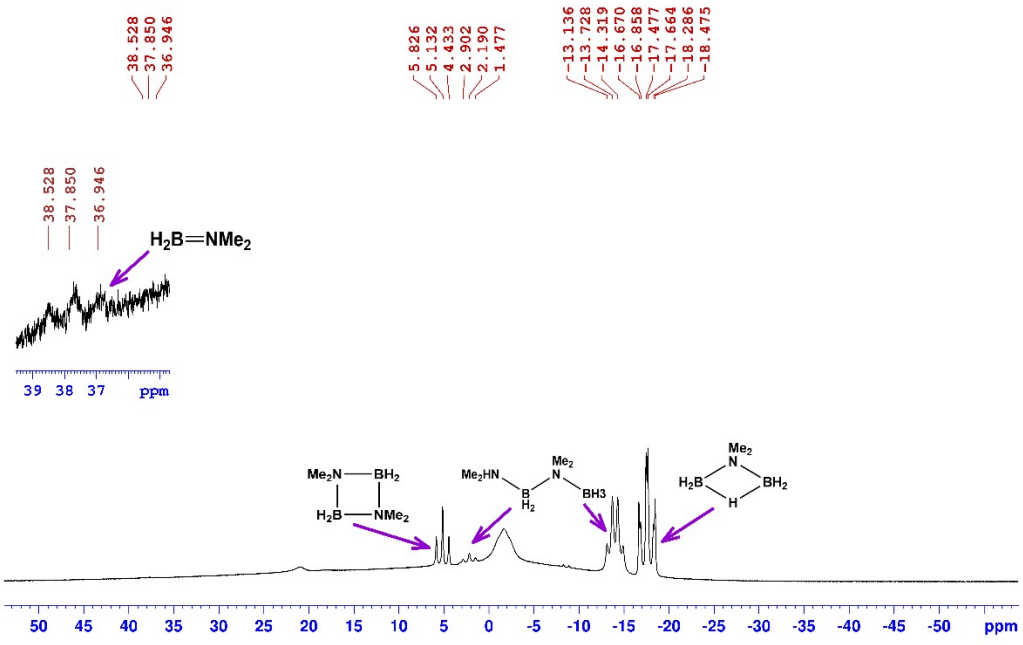


Figure S3: ^{11}B NMR spectra (in $CDCl_3$) of reaction mixture of dimethylamine-borane with iodine.

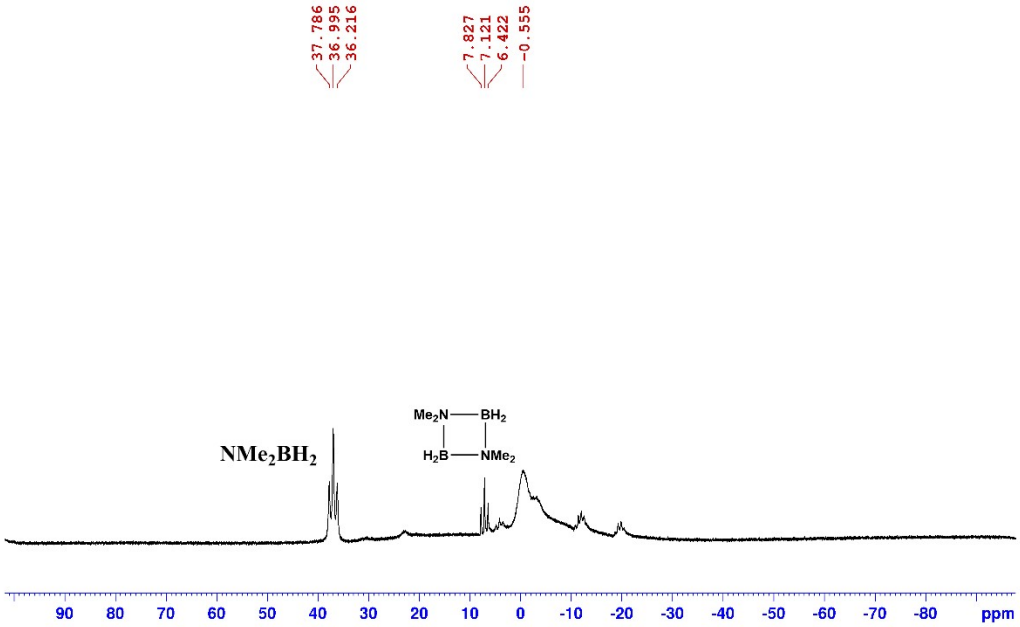


Figure S4: ^{11}B NMR spectra (in $CDCl_3$) of NMe_2BH_2 reaction mixture (prepared by protocol reported by Ramachandran and co-workers).

F. Detailed procedure for detection of H_2 gas:

To detect the H_2 gas, first 1.0 equiv. of NH_3BH_3 and 2mL DCE were taken in a 10mL round bottomed flask equipped with a stirring bar. A PVC tube of small diameter was taken, and one end of the tube was attached to an aspiration needle. The NMR tube filled with 0.6 ml of C_6D_6 was taken and the tip of the needle was immersed into the C_6D_6. The other end of the tube was kept ready to be sealed on the mouth of the 10 ml round bottomed flask. I_2 (7.5 mol%) was then added to the reaction mixture in the flask and the free end of the tube was firmly inserted on the mouth of the round bottomed flask. The reaction was stirred for 15 min at 80°C and the gas generated from the reaction was found to bubble in the C_6D_6 taken in the NMR tube. When the bubbles stopped, the NMR tube was capped and the spectra of the solution was recorded. In the ^1H NMR, a peak at 4.47 ppm was observed which indicated the presence of H_2 in the C_6D_6.

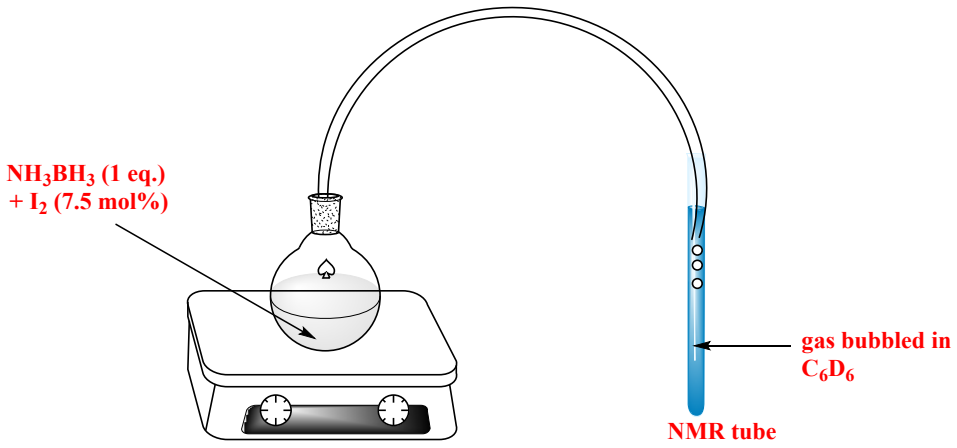
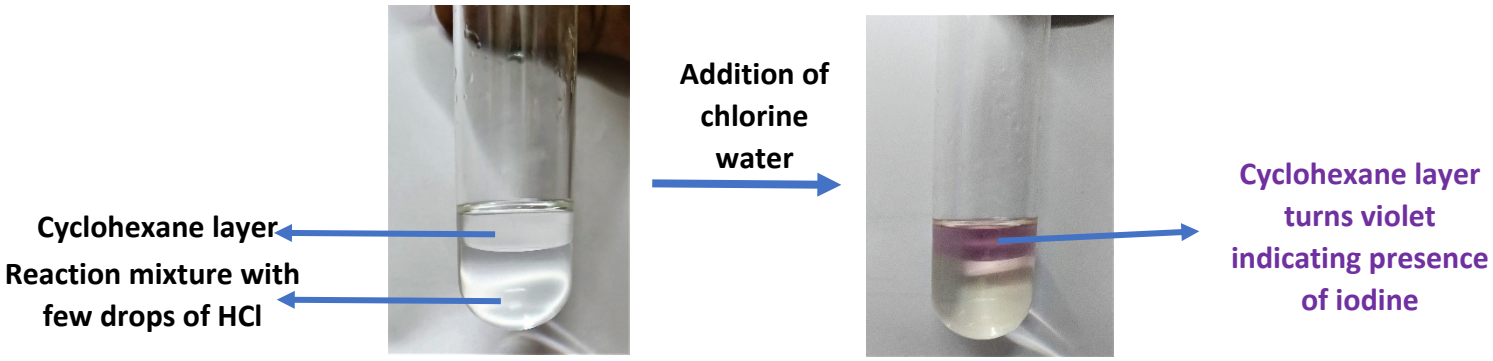


Figure S5: Pictorial diagram of detection of H_2 gas

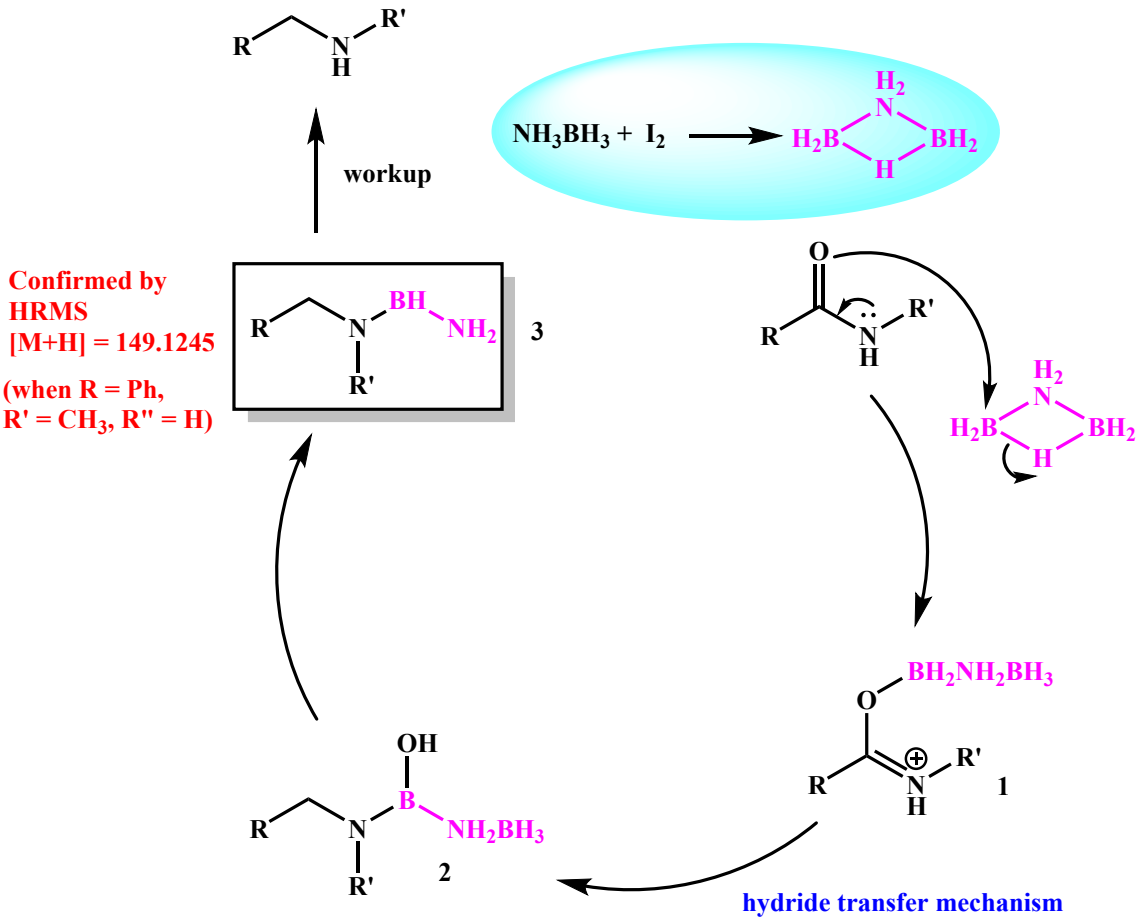
G. Chlorine Water Test:



$$I^- + Cl_2 \longrightarrow I_2 + Cl^-$$

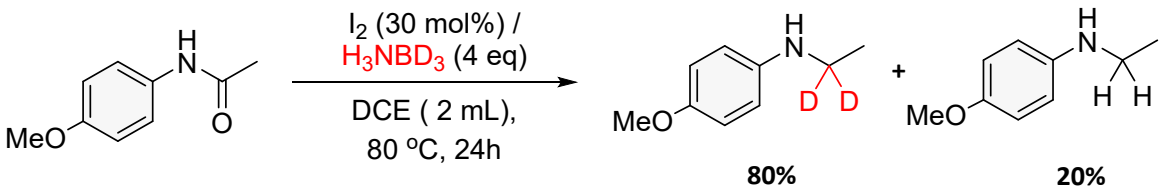
Figure S6: Chlorine water test of the final reaction mixture in water medium.

H. Probable mechanism for the reduction of secondary amides to amines



Scheme S2: Probable mechanism for reduction of secondary amides to amines.

I. Deuterium Incorporation Studies



Scheme S3: Reaction of NH_3BD_3 and iodine with acetanilide.

^{1}H NMR of spectra of deuterated mixture of N-(ethyl) 4-methoxyaniline

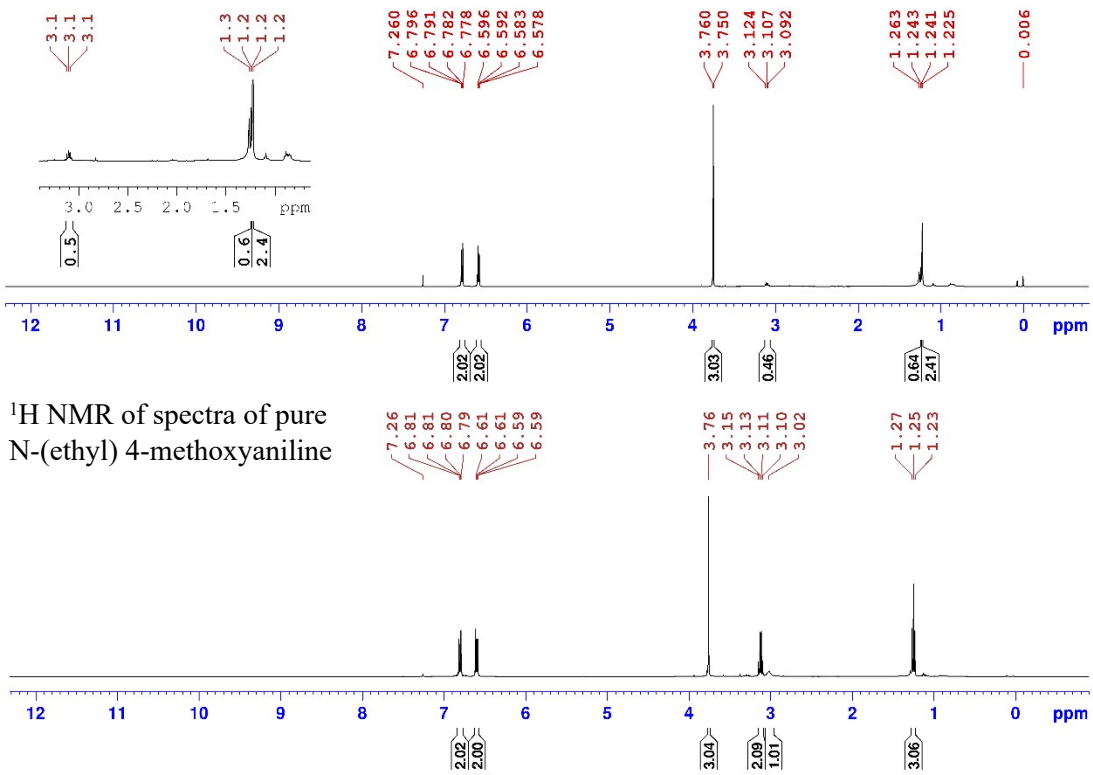
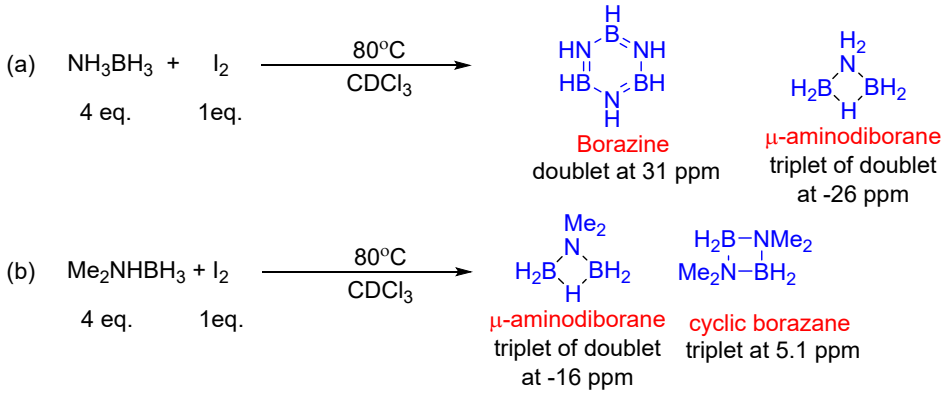


Figure S7: ^{1}H NMR comparison of deuterated mixture of N-(ethyl) 4-methoxyaniline and pure N-(ethyl) 4-methoxyaniline.

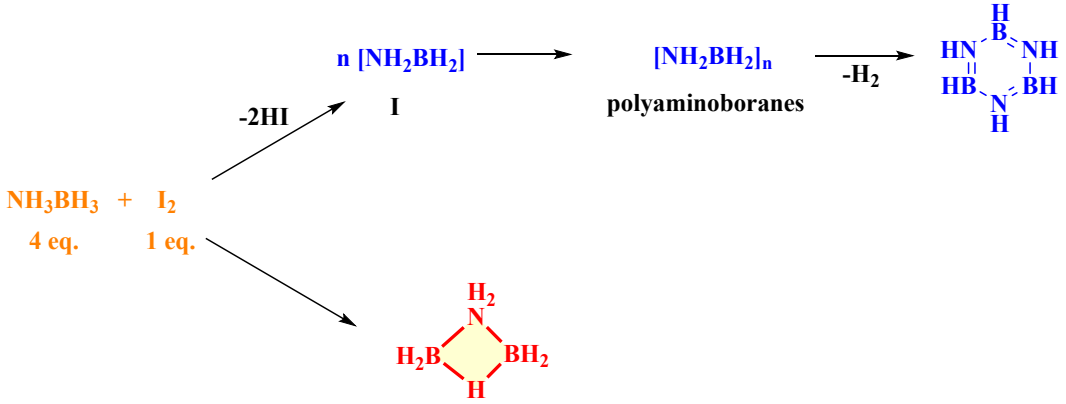
J. Mechanistic pathway using 1 eq. Iodine and ammonia borane for tertiary amides



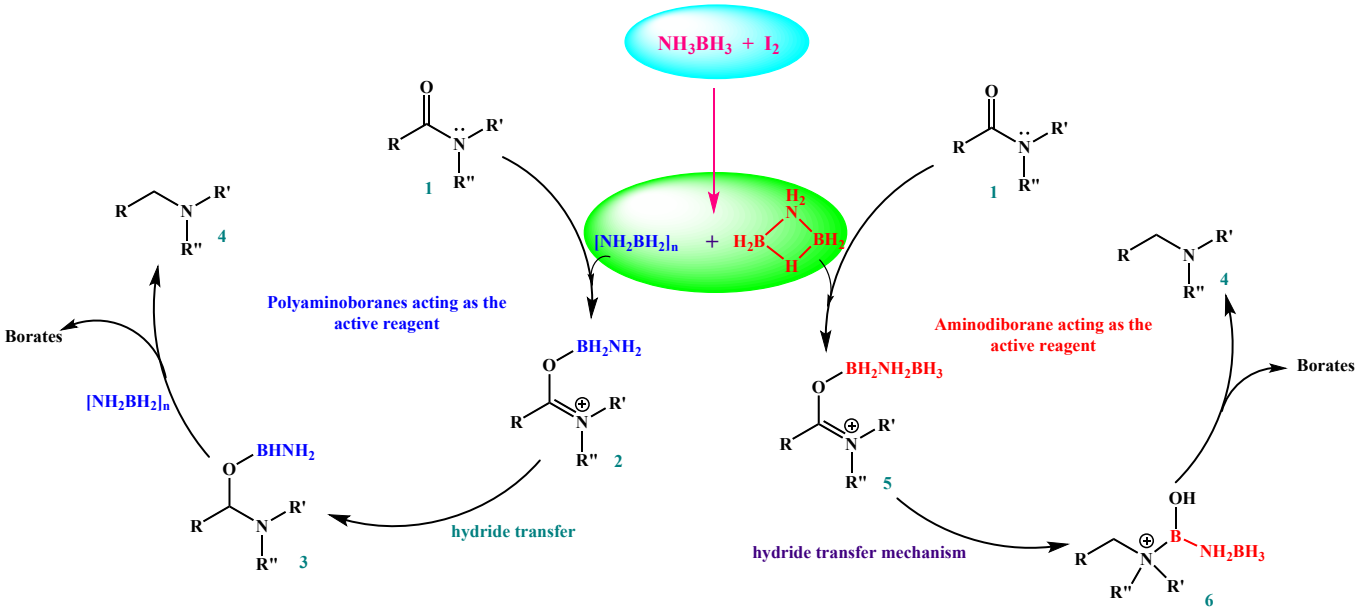
Scheme S4: Control experiments involving 4 eq. Amine-borane with 1 eq. I_2.

Based on the control experiments (Scheme S4) and literature studies,[4] the plausible pathway for the dehydrogenation of ammonia borane using 1eq. of iodine is as follows: AB undergoes dehydrogenation to form NH_2BH_2 (I). Characteristic peak for Me_2NBH_2 was found in ^{11}B

NMR (Figure S3) confirming the formation of NH_2BH_2 in the reaction mechanism. NH_2BH_2 further undergoes oligomerization to form polyaminoboranes and finally generating borazine (Scheme S5). There is also a possibility that HI which is released during the process can undergo acid-initiated ammonia-borane dehydrogenation reaction.[5]

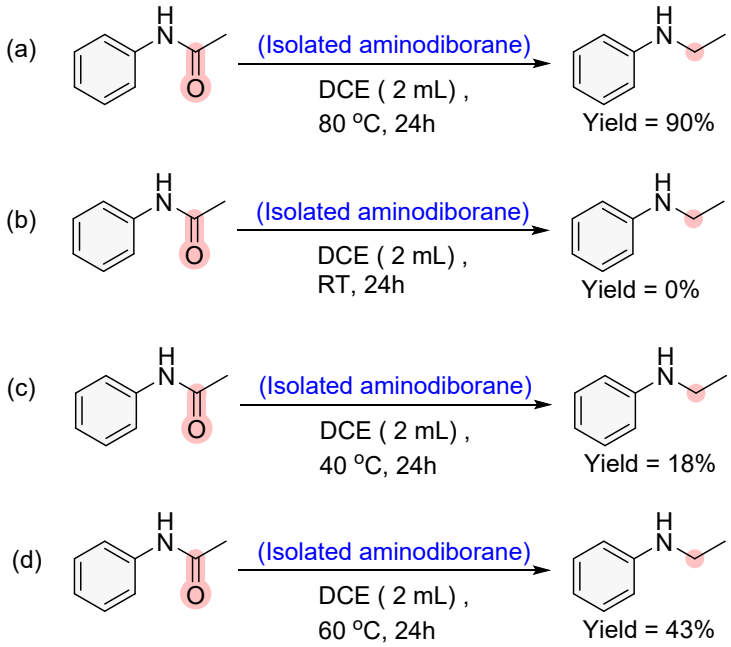


Scheme S5: Plausible pathways for dehydrogenation of ammonia borane using stoichiometric amount of iodine and ammonia borane



Scheme S6: Probable mechanism for reduction of tertiary amides to amines.

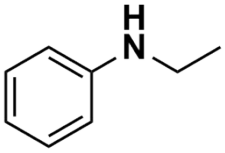
K. Control Study involving the reaction of aminodiborane with amide at different temperature conditions



Scheme S7: Reaction of aminodiborane with amide at different temperature conditions.

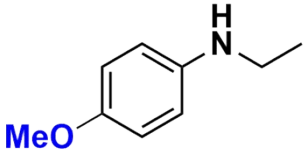
L. Identification of products

Compound **2a**[6a]



2a; ^{1}H NMR ($CDCl_3$, 400MHz, ppm): 7.08 (m, 2H), 6.61 (t, J = 7.6Hz, 1H), 6.52 (d, J = 7.6Hz, 2H), 3.06 (q, J = 7.2 Hz, 2H), 1.16 (t, J = 7.2Hz, 3H). ^{13}C NMR ($CDCl_3$, 125MHz, ppm) 148.6, 129.3, 117.3, 112.9, 38.6, 15.0. HRMS ($[M + H]^+$) m/z, calcd for $C_8H_{12}N$ 122.0964, found 122.0968.

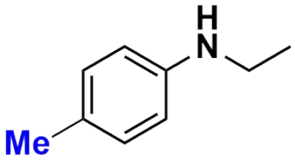
Compound **2b**[6a]



2b; ^{1}H NMR ($CDCl_3$, 400MHz, ppm): 6.81-6.79 (m, 2H), 6.58-6.61 (m, 2H), 3.76 (s, 3H), 3.11 (q, J= 7.2Hz, 2H), 3.02 (s, br, 1H), 1.25 (t, J = 7.2Hz, 3H). ^{13}C NMR ($CDCl_3$, 125MHz, ppm):

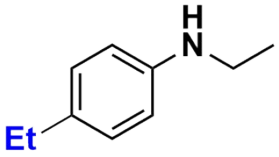
152.1, 142.8, 114.9, 114.1, 55.8, 39.5, 15.0. HRMS ([M + H]$^+$) m/z, calcd for $C_9H_{14}NO$ 152.1070, found 152.1065.

Compound **2c**[6a]



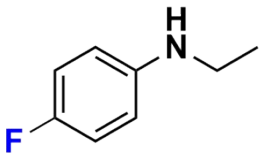
2c; ^{1}H NMR ($CDCl_3$, 500MHz, ppm): 7.01 (d, J = 8Hz, 2H), 6.57 (d, J = 8Hz, 2H), 3.15 (q, J = 7.1 Hz, 2H), 2.26 (s, 3H), 1.26 (t, J =+ 7.2Hz, 3h). ^{13}C NMR ($CDCl_3$, 125MHz, ppm): 146.3, 129.8, 126.5, 113.1, 38.9, 20.5, 15.0. HRMS ([M + H]$^+$) m/z, calcd for $C_9H_{14}N$ 136.1126, found 136.1120.

Compound **2d**[6b]



2d; ^{1}H NMR ($CDCl_3$, 400MHz, ppm): 7.01(d, J = 8.4Hz, 2H), 6.56 (d, J = 8.4Hz, 2H), 3.1 (q, J = 7.2Hz 2H), 2.55 (q, J = 7.6Hz, 2H), 1.25 (t, J = 7.2Hz, 3H), 1.19 (t, J = 7.6Hz, 3H). ^{13}C NMR ($CDCl_3$, 125MHz, ppm): 146.6, 133.2, 128.6, 113.0, 38.9, 28.0, 16.1, 15.1. HRMS ([M + H]$^+$) m/z, calcd for $C_{10}H_{16}N$ 150.1277, found 150.1272.

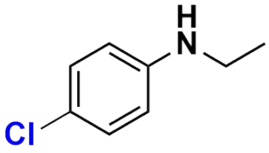
Compound **2e**[6a]



2e; ^{1}H NMR ($CDCl_3$, 500MHz, ppm): 6.87-6.90 (m, 2H), 6.52-6.55 (m, 2H), 3.09-3.13 (q, J = 7Hz, 2H), 1.23-1.26 (t, J = 7Hz, 3H). ^{13}C NMR ($CDCl_3$, 125MHz, ppm): 155.9 (d, J = 233 Hz),

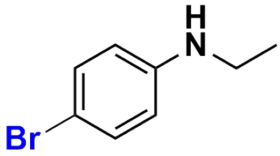
144.9, 115.7 (d, J = 22 Hz), 113.6 (d, J = 7.4 Hz), 39.2, 15.0. ^{19}F NMR ($CDCl_3$, 470.6, ppm): -128.4.

Compound **2f**[6a]



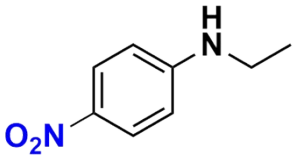
2f; ^{1}H NMR ($CDCl_3$, 400MHz, ppm): 7.12-7.10 (m, 2H), 6.52-6.50 (m, 2H), 3.12 (q, J = 7.2Hz, 2H), 1.25 (t, J = 7.2Hz, 3H). ^{13}C NMR ($CDCl_3$, 125MHz, ppm): 147.1, 129.1, 121.8, 113.9, 38.7, 14.8. HRMS ($[M + H]^+$) m/z, calcd for $C_8H_{11}ClN$ 156.0575, found 156.0575.

Compound **2g**[6a]



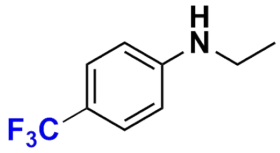
2g; ^{1}H NMR ($CDCl_3$, 400MHz, ppm): 7.12-7.15 (m, 2H), 6.41-6.38 (m, 2H), 3.05 (q, J = 7.2Hz, 2H), 1.17 (t, J = 7.2Hz, 3H). ^{13}C NMR ($CDCl_3$, 125MHz, ppm): 147.5, 132.0, 114.4, 108.8, 38.6, 14.8. HRMS ($[M + H]^+$) m/z, calcd for $C_8H_{11}BrN$ 200.0069, found 200.0075.

Compound **2h**[6c]



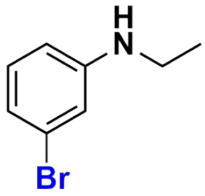
2h; ^{1}H NMR ($CDCl_3$, 400MHz, ppm): 8.06 (d, J = 9.2Hz, 2H), 6.51 (d, J = 9.2 Hz, 2H), 4.50 (s, br, 1H), 3.27-3.25 (m, 2H), 1.29 (t, J = 7.2Hz, 3H). ^{13}C NMR ($CDCl_3$, 125MHz, ppm): 153.5, 137.9, 126.6, 111.0, 38.1, 14.5. HRMS ($[M + Na]^+$) m/z, calcd for $C_8H_{10}N_2NaO_2$ 189.0634, found 189.0632.

Compound **2i**[6a]



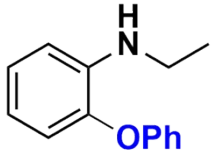
2i; ^{1}H NMR ($CDCl_3$, 500MHz, ppm): 7.40 (d, J = 8.5Hz, 2H), 6.60 (d, J = 8.5 Hz, 2H), 3.91 (s, br, 1H), 3.19 (q, J = 7Hz, 2H), 1.28 (t, J = 7Hz, 3H). ^{13}C NMR ($CDCl_3$, 125MHz, ppm): 150.9, 126.7 (q, J = 3.9 Hz), 125.3 (q, J = 268.3 Hz), 118.6 (q, J = 25 Hz), 111.8, 38.1, 14.7. ^{19}F NMR ($CDCl_3$, 470.6, ppm) : -60.9. HRMS ($[M + H]^+$) m/z, calcd for $C_9H_{11}F_3N$ 190.0838, found 190.0843.

Compound **2j**[6e]



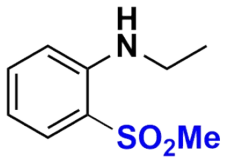
2j; ^{1}H NMR ($CDCl_3$, 400MHz, ppm) : 7.03 (t, J = 8Hz, 1H), 6.78 (d, J = 0.8Hz, 1H), 6.73 (t, J = 2Hz, 1H), 6.49-6.51 (m, 1H), 3.62 (s, br, 1H), 3.12 (q, J = 7.2Hz, 2H), 1.23 (t, J = 7.2 Hz, 3H).^{13}C NMR ($CDCl_3$, 125MHz, ppm): 149.8, 130.5, 123.4, 119.9, 115.2, 111.6, 38.4, 14.8. HRMS ($[M + H]^+$) m/z, calcd for $C_8H_{11}BrN$ 200.0075, found 200.0076.

Compound **2k**



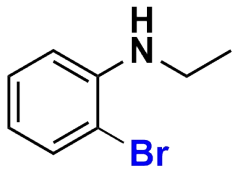
2k; ^{1}H NMR ($CDCl_3$, 400MHz, ppm): 7.34-7.29 (m, 2H), 7.06-7.05 (m, 2H), 7.00-6.98 (m, 2H), 6.86-6.85 (m, 1H), 6.83-6.72 (m, 1H), 6.64-6.63 (m, 1H), 4.02 (s, br, 1H), 3.20 (q, J = 7.2Hz, 2H), 1.24 (t, J = 7.2 Hz, 3H).^{13}C NMR ($CDCl_3$, 125MHz, ppm): 157.7, 143.0, 140.8, 129.8, 125.0, 122.8, 119.3, 117.5, 116.6, 111.5, 38.2, 14.9. HRMS ($[M + H]^+$) m/z, calcd for $C_{14}H_{16}NO$ 214.1232, found 214.1222.

Compound **2l**



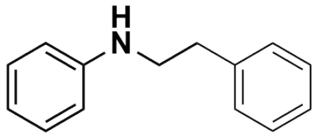
2l; ^{1}H NMR ($CDCl_3$, 400MHz, ppm): 7.73-7.75 (m, 1H), 7.42 (m, 1H), 6.73-6.76 (m, 2H), 5.99 (s, br, 1H), 3.18-3.21 (m, 2H), 3.02 (s, 3H), 1.24 (t, J = 7.2Hz, 3H). ^{13}C NMR ($CDCl_3$, 125MHz, ppm): 147.2, 135.6, 129.9, 121.3, 116.2, 112.4, 42.3, 37.9, 14.5. HRMS ($[M + Na]^+$) m/z, calcd for $C_9H_{13}NNaO_2S$ 222.0559, found 222.00559.

Compound **2m**[6d]



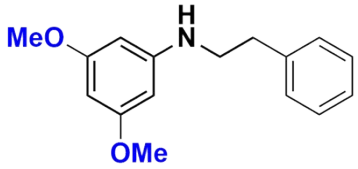
2m; ^{1}H NMR ($CDCl_3$, 500MHz, ppm): 7.40-7.42 (m, 1H), 7.16-7.19 (m, 1H), 6.62-6.64 (m, 1H), 6.54-6.57 (m, 1H), 4.21 (s, br, 1H), 3.20 (q, J = 7Hz, 2H), 1.29-1.32 (t, J = 7Hz, 3H).^{13}C NMR ($CDCl_3$, 125MHz, ppm): 145.2, 132.4, 128.6, 117.6, 111.3, 109.6, 38.5, 14.8. HRMS ($[M + H]^+$) m/z, calcd for $C_8H_{11}BrN$ 200.0069, found 200.0061.

Compound **2n**[6a]



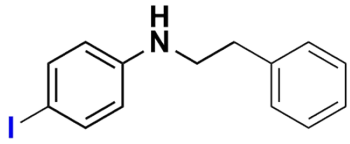
2n; ^{1}H NMR ($CDCl_3$, 400MHz, ppm): 7.25-7.24 (m, 2H), 7.19-7.09 (m, 5H), 6.64-6.62 (m, 1H), 6.56-6.53 (m, 2H), 3.61 (s, br, 1H), 3.34 (t, J = 7.2Hz, 2H), 2.85 (t, J = 7.2Hz, 2H).^{13}C NMR ($CDCl_3$, 125MHz, ppm): 148.1, 139.4, 129.4, 128.9, 128.7, 126.5, 117.6, 113.1, 45.1, 35.6. HRMS ($[M + H]^+$) m/z, calcd for $C_{14}H_{16}N$ 198.1283, found 198.1281.

Compound **2o**[6f]



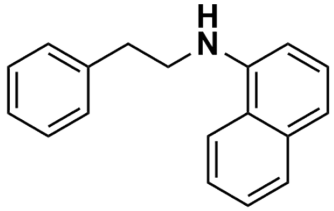
2o; ^{1}H NMR ($CDCl_3$, 500MHz, ppm):7.33-7.31 (m, 2H), 7.24-7.22 (m, 3H), 5.89 (s, 1H), 5.81 (s, 2H), 3.75 (s, 6H), 3.38 (t, J = 7.2Hz, 2H), 2.93 (t, J = 7.2Hz, 2H).^{13}C NMR ($CDCl_3$, 125MHz, ppm): 161.9, 150.0, 139.4, 128.9, 128.7, 126.6, 91.9, 89.9, 55.3, 45.1, 35.6. HRMS ($[M + H]^+$) m/z, calcd for $C_{16}H_{20}NO_2$ 258.1489, found 258.1496.

Compound **2p**[6g]



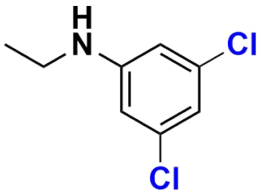
2q; ^{1}H NMR ($CDCl_3$, 400MHz, ppm): 7.34-7.32 (m, 2H), 7.24-7.11 (m, 5H), 6.31 (d, J = 8.8Hz, 1H), 3.63 (s, br, 1H), 3.28 (t, J = 6.8Hz, 2H), 2.82 (t, J = 6.8Hz, 2H).^{13}C NMR ($CDCl_3$, 125MHz, ppm): 147.7, 139.1, 137.9, 128.9, 128.7, 126.7, 115.3, 44.9, 35.4. HRMS ($[M + H]^+$) m/z, calcd for $C_{14}H_{15}IN$ 324.0244, found 324.0245.

Compound **2q**[6g]



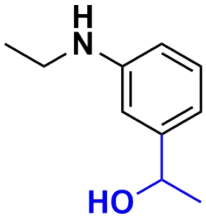
2q; ^{1}H NMR ($CDCl_3$, 500MHz, ppm): 7.82 (d, J = 7.5Hz, 1H), 7.71 (d, J = 5H, 1H), 7.47-7.27 (m, 9H), 6.70 (d, 8Hz, 1H), 4.43 (s, br, 1H), 3.60 (t, J = 7Hz, 2H), 3.12 (t, J = 7Hz, 2H).^{13}C NMR ($CDCl_3$, 125MHz, ppm): 143.3, 139.4, 134.5, 128.9, 128.8, 128.7, 126.7, 126.6, 125.8, 124.8, 123.6, 119.9, 117.6, 104.6, 45.3, 35.5. HRMS ($[M + H]^+$) m/z, calcd for $C_{18}H_{18}N$ 248.1434, found 248.1429.

Compound **2r**[6h]



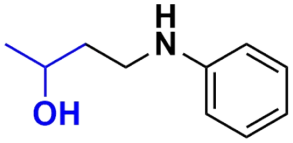
2r; ^{1}H NMR ($CDCl_3$, 400MHz, ppm): 6.64 (t, J = 2Hz, 1H), 6.36-6,35 (d, J = 2Hz, 2H), 3.73 (s, br, 1H), 3.14-3.08 (m, 2H), 1.24 (t, J = 7.2 Hz, 3H).^{13}C NMR ($CDCl_3$, 125MHz, ppm): 150.0, 135.5, 116.8, 110.8, 38.3, 14.7. HRMS ($[M + H]^+$) m/z, calcd for $C_8H_{10}Cl_2N$ 190.0185, found 190.0184.

Compound **2s**



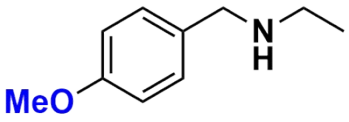
2s; ^{1}H NMR ($CDCl_3$, 400MHz, ppm): 7.15 (t, J = 6.4Hz, 1H), 6.68 (d, J = 6Hz, 1H), 6.62 (s, 1H), 6.52-6.50 (m, 1H), 4.78 (q, J = 6.4Hz, 1H), 3.16 (q, J = 5.6Hz, 2H), 1.47 (d, J = 4.8Hz, 3H), 1.25 (t, J = 5.6Hz, 3H).^{13}C NMR ($CDCl_3$, 125MHz, ppm): 148.7, 147.2, 129.4, 114.4, 111.9, 109.9, 38.6, 25.0, 14.9. HRMS ($[M + H]^+$) m/z, calcd for $C_{10}H_{16}NO$ 166.1226, found 166.1228.

Compound **2t**[6i]



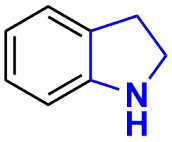
2t; ^{1}H NMR ($CDCl_3$, 500MHz, ppm): 7.20 (t, J = 7.5Hz, 2H), 6.74 (t, J = 7Hz, 1H), 6.67 (d, J = 8.5Hz, 2H), 4.012-3.98(m, 1H), 3.30-3.23 (m, 2H), 1.79-1.76 (m, 1H), 1.75-1.71 (m, 1H), 1.25 (d, J = 6Hz).^{13}C NMR ($CDCl_3$, 125MHz, ppm): 148.4, 129.3, 117.8, 113.4, 67.4, 43.9, 38.1, 23.9. HRMS ($[M + H]^+$) m/z, calcd for $C_{10}H_{16}NO$ 166.1226, found 166.1226.

Compound **2u**[6j]



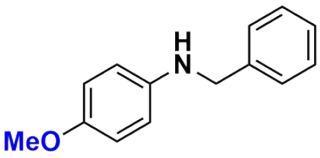
2u; ^{1}H NMR ($CDCl_3$, 500MHz, ppm): 7.24-7.22 (d, J = 8.5Hz, 2H), 6.86-6.84 (d, J = 8.5Hz, 2H), 3.78(s, 1H), 3.73 (s, 2H), 2.68 (q, J = 7Hz, 2H), 1.13 (t, J = 7.5Hz, 3H).^{13}C NMR ($CDCl_3$, 125MHz, ppm): 158.8, 131.9, 129.6, 113.9, 55.3, 53.1, 43.4, 14.9. HRMS ([M + H]$^{+}$) m/z, calcd for $C_{10}H_{16}NO$ 166.1226, found 166.1222.

Compound **2v**[6k]



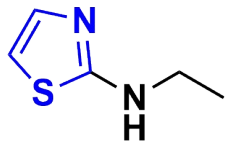
2v; ^{1}H NMR ($CDCl_3$, 500MHz, ppm): 7.13 (d, J = 7.5Hz, 1H), 7.01 (t, J = 7.5Hz, 1H), 6.72 (t, J = 7.5 Hz, 1H), 6.66 (d, J = 8 Hz, 1H), 3.56 (t, J = 8.5Hz, 2H), 3.42 (s, 1H), 3.04 (t, J = 8.5Hz, 2H).^{13}C NMR ($CDCl_3$, 125MHz, ppm): 151.7, 129.4, 127.3, 124.7, 118.8, 109.6, 47.4, 29.9. HRMS ([M + H]$^{+}$) m/z, calcd for $C_8H_{10}N$ 120.0808, found 120.0808.

Compound **2w**[6b]



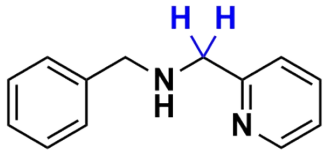
2w; ^{1}H NMR ($CDCl_3$, 500MHz, ppm): 7.33 (d, J = 8.5Hz, 2H), 7.22 (t, J = 7.5Hz, 2H), 6.93 (d, J = 8.5Hz, 2H), 6.77 (t, J = 7.5Hz, 1H), 6.68 (d, J = 8Hz, 2H), 3.84 (s, 3H).^{13}C NMR ($CDCl_3$, 125MHz, ppm): 158.9, 148.3, 131.5, 129.3, 128.9, 117.5, 114.1, 112.9, 55.3, 47.8. HRMS ([M + H]$^{+}$) m/z, calcd for $C_{14}H_{16}NO$ 214.1226, found 214.1225.

Compound **2x**



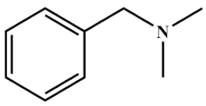
2x; ^{1}H NMR ($CDCl_3$, 500MHz, ppm): 7.11 (d, J = 3.5Hz, 1H), 6.47 (d, J = 3.5Hz, 1H), 5.65 (s, br, 1H), 3.30 (q, J = 7Hz, 2H), 1.29 (t, J = 7Hz, 3H). ^{13}C NMR ($CDCl_3$, 125MHz, ppm): 170.8, 139.1, 106.3, 40.9, 14.7. LRMS ($[M + H]^+$) m/z, calcd for $C_5H_9N_2S$ 129.04, found 129.04.

Compound **2y**[6l]



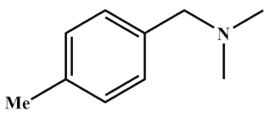
2y; ^{1}H NMR ($CDCl_3$, 500MHz, ppm): 8.58-8.57 (m, 1H), 7.66 (t, J = 8.5Hz, 1H), 7.38-7.32 (m, 6H), 7.29-7.27 (m, 2H), 7.20-7.18 (m, 1H), 3.96 (s, 2H), 3.87 (s, 2H). ^{13}C NMR ($CDCl_3$, 125MHz, ppm): 159.3, 149.3, 139.7, 136.5, 128.4, 128.3, 127.1, 122.5, 122.1. HRMS ($[M + H]^+$) m/z, calcd for $C_{13}H_{15}N_2$ 199.1229, found 199.1226.

Compound **3a**[6a]



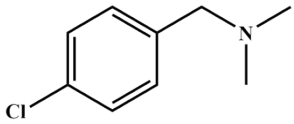
3a; ^{1}H NMR ($CDCl_3$, 500MHz, ppm): 7.42-7.40 (m, 3H), 7.36-7.34 (m, 2H), 4.05 (s, 2H), 2.53 (s, 6H); ^{13}C NMR ($CDCl_3$, 125MHz, ppm): 132.5, 129.9, 129.5, 128.7, 63.7, 46.3. HRMS ($[M + Na]^+$) m/z, calcd for $C_9H_{13}NNa$ 158.0940, found 158.0940.

Compound **3b**[6m]



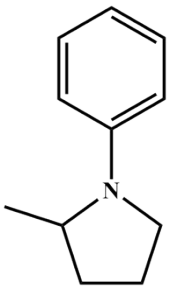
3b; ^{1}H NMR ($CDCl_3$, 500MHz, ppm): 7.26-7.22 (m, 4H), 4.02 (s, 2H), 2.52 (s, 6H), 2.38 (s, 3H); ^{13}C NMR ($CDCl_3$, 125MHz, ppm): 139.6, 132.4, 129.4, 126.9, 63.5, 46.2, 21.3. HRMS ($[M + Na]^+$) m/z, calcd for $C_{10}H_{15}NNa$ 172.1097, found 172.1093.

Compound **3c**[6m]



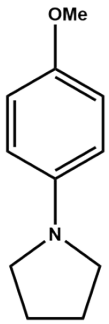
3c; ^{1}H NMR ($CDCl_3$, 500MHz, ppm): 7.38 (d, J = 8.5 Hz, 2H), 7.28 (d, J = 8 Hz, 2H), 3.94 (s, 2H), 2.50 (s, 6H); ^{13}C NMR ($CDCl_3$, 125MHz, ppm): 135.5, 133.6, 129.8, 128.8, 66.9, 50.0. HRMS ($[M + H]^+$) m/z, calcd for $C_9H_{13}ClN$ 170.0731, found 170.0731.

Compound **3d**[6n]



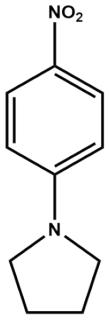
3d; ^{1}H NMR ($CDCl_3$, 500MHz, ppm): 7.25-7.22 (m, 2H), 6.65 (t, J = 7 Hz, 1H), 6.61 (d, J = 8Hz, 2H), 3.90-3.87 (m, 1H), 3.45-3.41 (m, 1H), 3.18-3.16 (m, 1H), 2.08-2.07 (m, 2H), 2.07-2.05 (m, 1H), 1.99-1.97 (m, 1H), 1.20 (d, J = 6.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125MHz, ppm): 147.3, 129.2, 115.2, 111.8, 53.7, 48.2, 33.2, 23.4, 19.5. HRMS ($[M + H]^+$) m/z, calcd for $C_{11}H_{16}N$ 162.1277, found 162.1274.

Compound **3e**[6o]



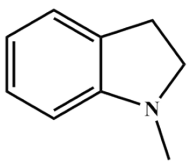
3e; ^{1}H NMR ($CDCl_3$, 500MHz, ppm): 6.88-6.86 (m, 2H), 6.57-6.55 (m, 2H), 3.78 (s, 3H), 3.26-3.24 (m, 4H), 2.02-1.99 (m, 4H); ^{13}C NMR ($CDCl_3$, 125MHz, ppm): 150.8, 143.3, 115.1, 112.6, 56.0, 48.3, 25.4. HRMS ($[M + H]^+$) m/z, calcd for $C_{11}H_{16}NO$ 178.1232, found 178.1226.

Compound **3f**[6o]



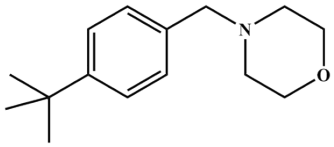
3f; ^{1}H NMR ($CDCl_3$, 500MHz, ppm): 8.11-8.08 (m, 2H), 6.47-6.44 (m, 2H), 3.41-3.38 (m, 4H), 2.08-2.05 (m, 4H); ^{13}C NMR ($CDCl_3$, 125MHz, ppm): 151.9, 136.6, 126.4, 110.5, 48.0, 25.5. HRMS ($[M + Na]^+$) m/z, calcd for $C_{10}H_{12}N_2NaO_2$ 215.0791, found 215.0787.

Compound **3g**[6p]



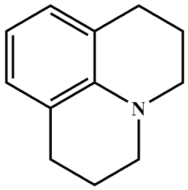
3g; ^{1}H NMR ($CDCl_3$, 500MHz, ppm): 7.09-7.08 (m, 2H), 6.69 (t, J = 7Hz, 1H), 6.51 (d, J = 10 Hz, 1H), 3.2 (t, J = 8.5, 2H), 2.95 (t, J = 8.5 Hz, 2H), 2.76 (s, 3H); ^{13}C NMR ($CDCl_3$, 125MHz, ppm): 153.5, 130.4, 127.4, 124.4, 117.9, 107.3, 56.3, 36.4, 28.9. HRMS ($[M + H]^+$) m/z, calcd for $C_9H_{12}N$ 134.0970, found 134.0966.

Compound **3h**[6q]



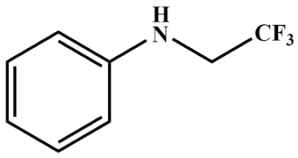
3h; ^{1}H NMR ($CDCl_3$, 500MHz, ppm): 7.16 (d, J = 8.5 Hz, 2H), 7.08-7.07 (m, 2H), 3.54 (t, J = 4.5 Hz, 4H), 3.3 (s, 2H), 2.27 (m, 4H), 1.14 (s, 9H); ^{13}C NMR ($CDCl_3$, 125MHz, ppm): 150.2, 134.4, 129.1, 125.2, 67.0, 63.1, 53.6, 34.5, 31.5. HRMS ($[M + H]^+$) m/z, calcd for $C_{15}H_{24}NO$ 234.1852, found 234.1844.

Compound **3i**[6r]



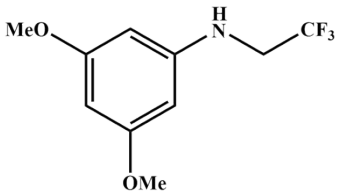
3i; ^{1}H NMR ($CDCl_3$, 500MHz, ppm): 6.83 (d, J = 7.5 Hz, 2H), 6.56 (t, J = 7Hz, 1H), 3.16 (t, J = 5.5 Hz, 4H), 2.05-2.04 (m, 4H); ^{13}C NMR ($CDCl_3$, 125MHz, ppm): 142.5, 127.1, 122.1, 116.4, 50.3, 27.6, 22.1. HRMS ($[M + H]^+$) m/z, calcd for $C_{12}H_{16}N$ 174.1277, found 174.1277.

Compound **4a**[6a]



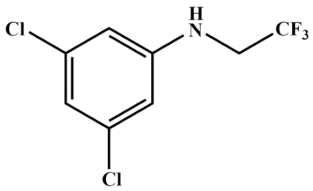
4a; ^{1}H NMR ($CDCl_3$, 500MHz, ppm): 7.22 (t, J = 8 Hz, 2H), 6.81 (t, J = 8Hz, 1H), 6.70 (d, J = 8 Hz, 2H), 3.92 (s, br, 1H), 3.80-3.74 (m, 2 H); ^{13}C NMR ($CDCl_3$, 125MHz, ppm): 146.4, 129.5, 125.2 (q, J = 278.4 Hz), 119.2, 113.3, 46.1 (q, J = 33.2 Hz). ^{19}F NMR ($CDCl_3$, 470.385, ppm): -72.3.

Compound **4b**[6s]



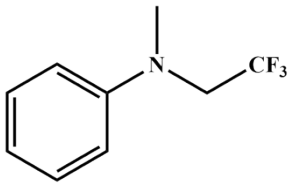
4b; ^{1}H NMR ($CDCl_3$, 500MHz, ppm): 5.99 (s, 1H), 5.89 (s, 2H), 3.90 (m, 1H), 3.78 (s, 6H), 3.77-3.75 (m, 2 H); ^{13}C NMR ($CDCl_3$, 125MHz, ppm): 161.9, 148.3, 125.0 (q, 278.1 Hz), 92.3, 91.3, 55.3, 46.1 (q, J = 33.5 Hz). ^{19}F NMR ($CDCl_3$, 470.6, ppm): -72.3. HRMS ($[M + H]^+$) m/z, calcd for $C_{10}H_{13}F_3NO_2$ 286.0893, found 236.0893.

Compound **4c**



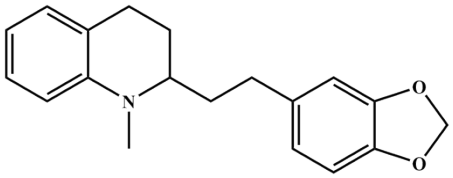
4c; ^{1}H NMR ($CDCl_3$, 500MHz, ppm): 6.78 (s, 1H), 6.55 (s, 2H), 4.10 (m, 1H), 3.77-3.70 (m, 2 H); ^{13}C NMR ($CDCl_3$, 125MHz, ppm): 148.0, 135.9, 124.7 (q, J = 278.1), 119.2, 111.6, 45.7 (q, J = 34 Hz). ^{19}F NMR ($CDCl_3$, 470.6 MHz, ppm): -72.2. LRMS ($[M + H]^+$) m/z, calcd for $C_8H_7Cl_2F_3N$ 243.99, found 243.99.

Compound **4d**[6t]



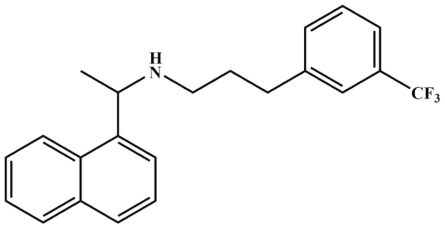
4d; ^{1}H NMR ($CDCl_3$, 500MHz, ppm): 7.30 (t, J = 8.5 Hz, 2H), 6.84 (m, 3H), 3.87 (q, 2H), 3.06 (s, 3H); ^{13}C NMR ($CDCl_3$, 125MHz, ppm): 148.8, 129.4, 125.8 (q, J = 287.5 Hz), 118.4, 112.9, 54.5 (q, J = 32.4 Hz), 39.2. ^{19}F NMR ($CDCl_3$, 470.385 MHz, ppm): -70.5. LRMS ($[M]^+$) m/z, calcd for $C_9H_{10}F_3N$ 189.07, found 189.07.

Compound **5a**[6a]



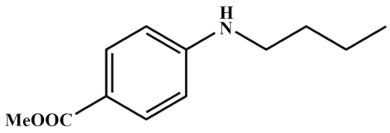
5a; ^{1}H NMR ($CDCl_3$, 500MHz, ppm): 7.09 (t, J = 7.6 Hz, 1H), 6.98 (d, J = 6.8Hz, 1H), 6.74-6.69 (m, 2H), 6.64-6.63 (m, 2H), 6.63-6.61 (m, 1H), 5.92 (s, 2H), 3.28-3.27 (m, 1H), 2.92 (s, 3H), 2.82-2.80 (m, 1H), 2.71-2.62 (m, 2H), 2.55-2.51 (m, 1H), 1.95-1.92 (m, 3H), 1.71-1.69 (m, 1H), 0.94 (t, J = 7.5Hz, 3H); ^{13}C NMR ($CDCl_3$, 125MHz, ppm): 147.8, 145.8, 145.4, 135.9, 128.8, 127.2, 122.1, 121.0, 115.6, 110.8, 108.8, 108.3, 100.9, 58.4, 38.2, 33.3, 32.2, 24.5, 23.7. HRMS ($[M+H]^+$) m/z, calcd for $C_{19}H_{22}NO_2$ 296.1645, found 296.1632.

Compound **6a**[6a]



6a; ^{1}H NMR ($CDCl_3$, 500MHz, ppm): 8.09 (d, J = 8Hz, 1H), 7.90-7.88 (m, 2H), 7.80 (d, 1H), 7.54-7.48 (m, 3H), 7.35-7.26 (m, 2H), 7.24-7.22 (m, 2H), 4.90-4.89 (m, 1H), 2.74-2.56 (m, 4H), 2.02-2.01 (m, 2H), 1.73 (d, J = 6Hz, 3H); ^{13}C NMR ($CDCl_3$, 125MHz, ppm): 142.1, 137.1, 134.0, 131.8, 131.1, 130.7 (q, J = 32.1 Hz), 129.3, 128.8, 128.4, 126.6, 125.9, 125.8, 125.0 (q, J = 3.6 Hz), 124.2 (q, J = 272.3 Hz), 123.9, 122.9 (q, J = 3.5 Hz), 122.3, 54.0, 46.7, 33.1, 29.8, 22.5. ^{19}F NMR ($CDCl_3$, 470.6 MHz, ppm): -62.4. HRMS ($[M+H]^+$) m/z, calcd for $C_{22}H_{23}F_3N$ 358.1777, found 358.1769.

Compound **7a**[6a]

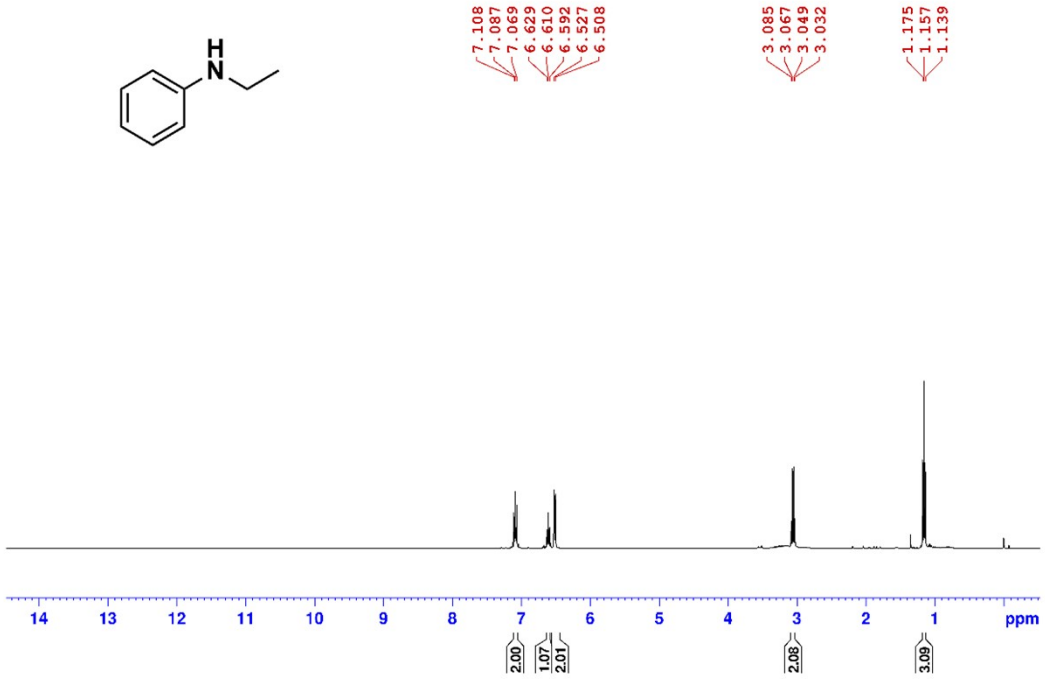


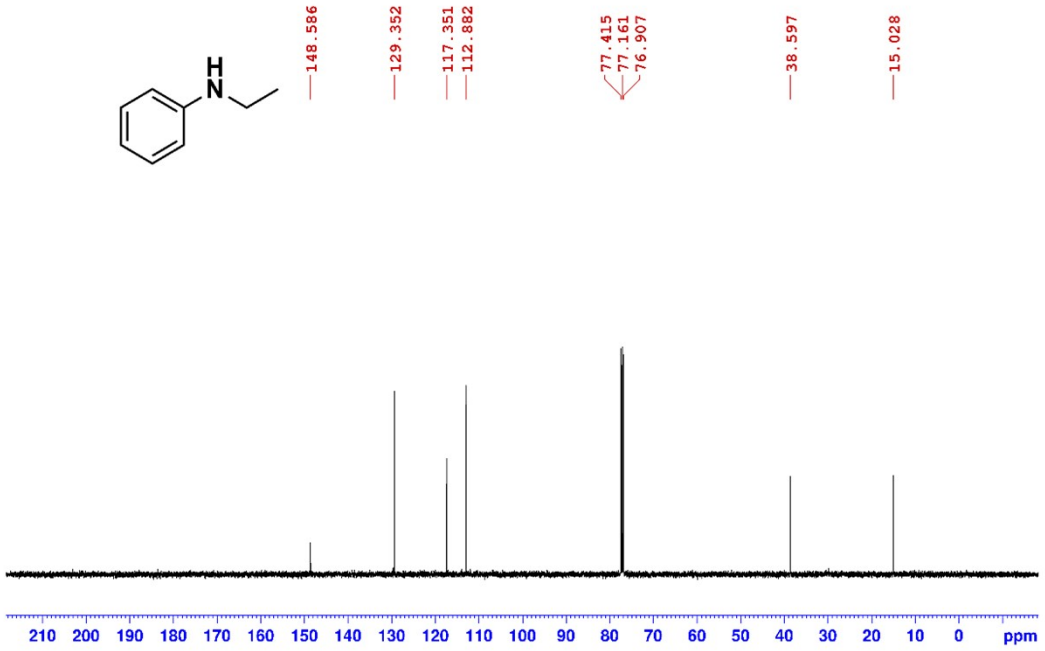
7a; ^{1}H NMR ($CDCl_3$, 500MHz, ppm): 7.84 (d, J = 9 Hz, 2H), 6.52 (d, J = 8.5Hz, 2H), 4.23 (s, 1H), 3.83 (s, 3H), 3.14-3.11 (m, 2H), 1.59-1.56 (m, 2H), 1.42-1.38 (m, 2H), 0.94 (t, J = 7.5Hz,

3H); ^{13}C NMR ($CDCl_3$, 125MHz, ppm): 167.4, 152.3, 131.7, 117.7, 111.2, 51.4, 43.0, 31.3, 20.2, 13.8. HRMS ([M+Na]$^+$) m/z, calcd for $C_{12}H_{17}NNaO_2$ 230.1151, found 230.1142.

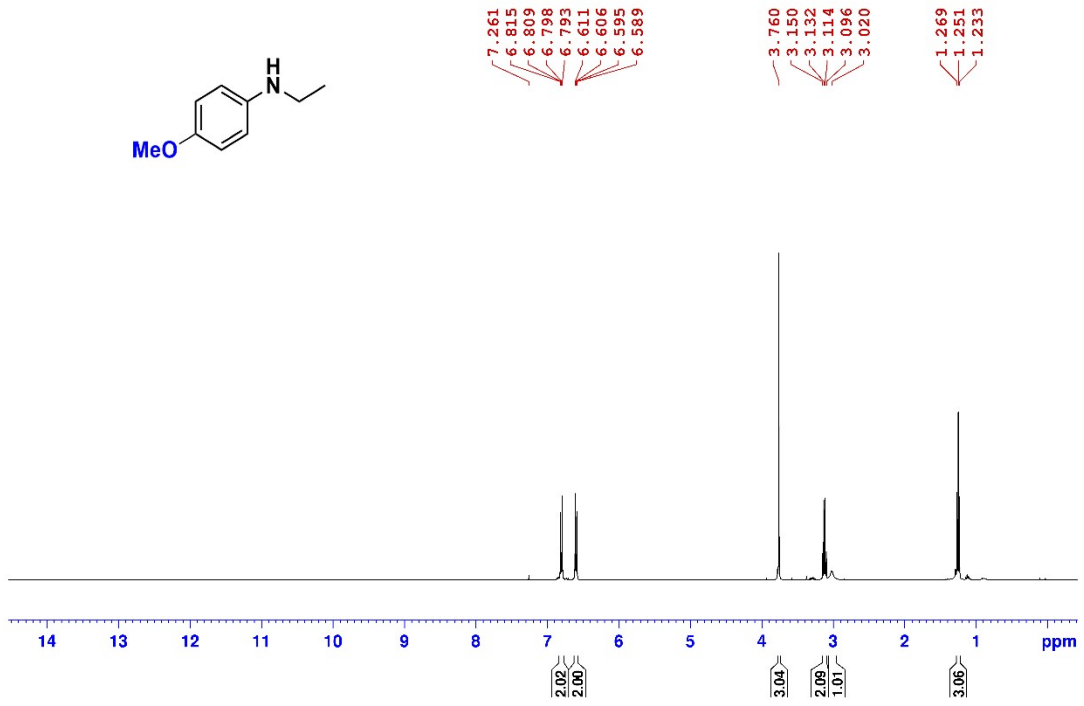
M. Representative NMR Spectra:

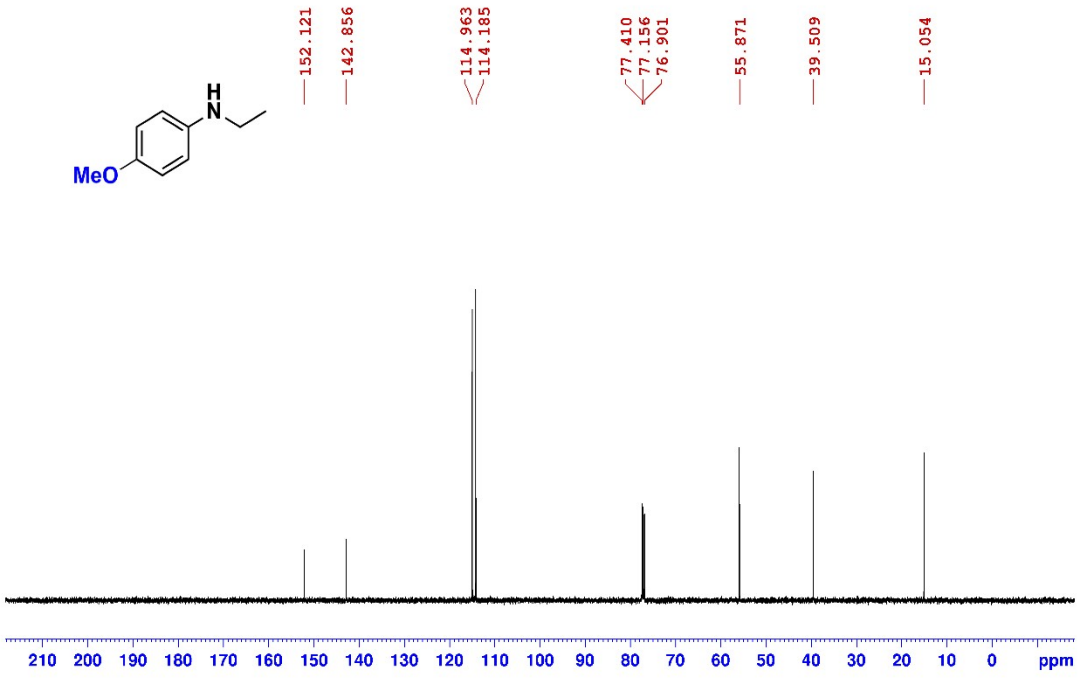
^1H-NMR & $^{13}C\{^1H\}$ (in $CDCl_3$) spectra of compound **2a**



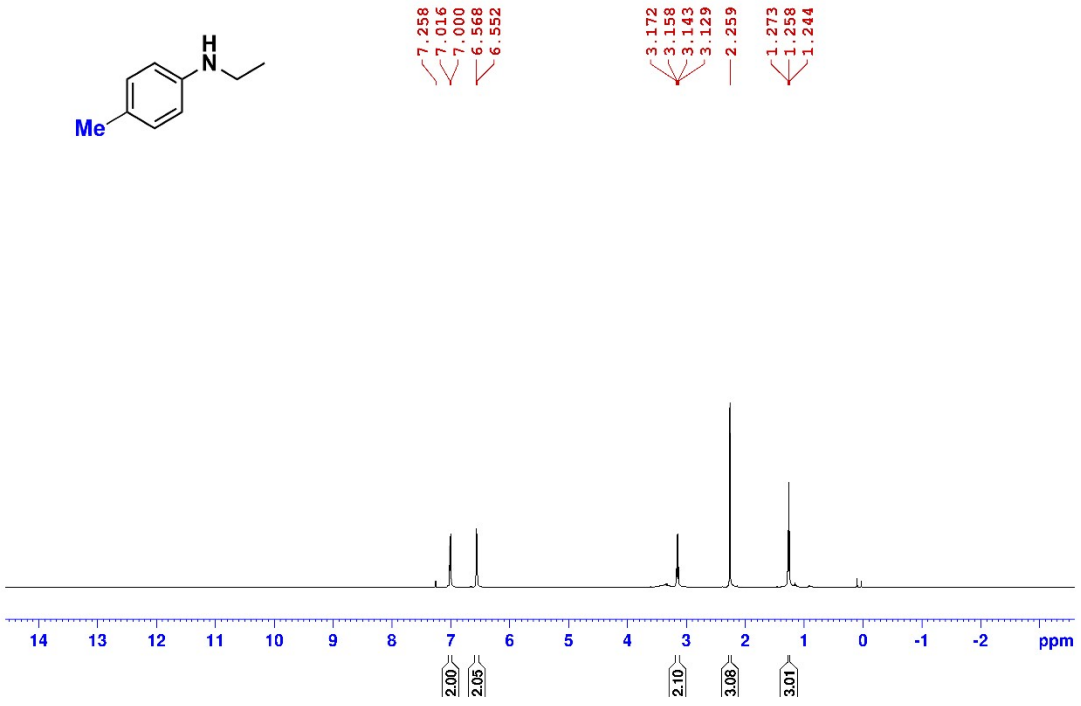


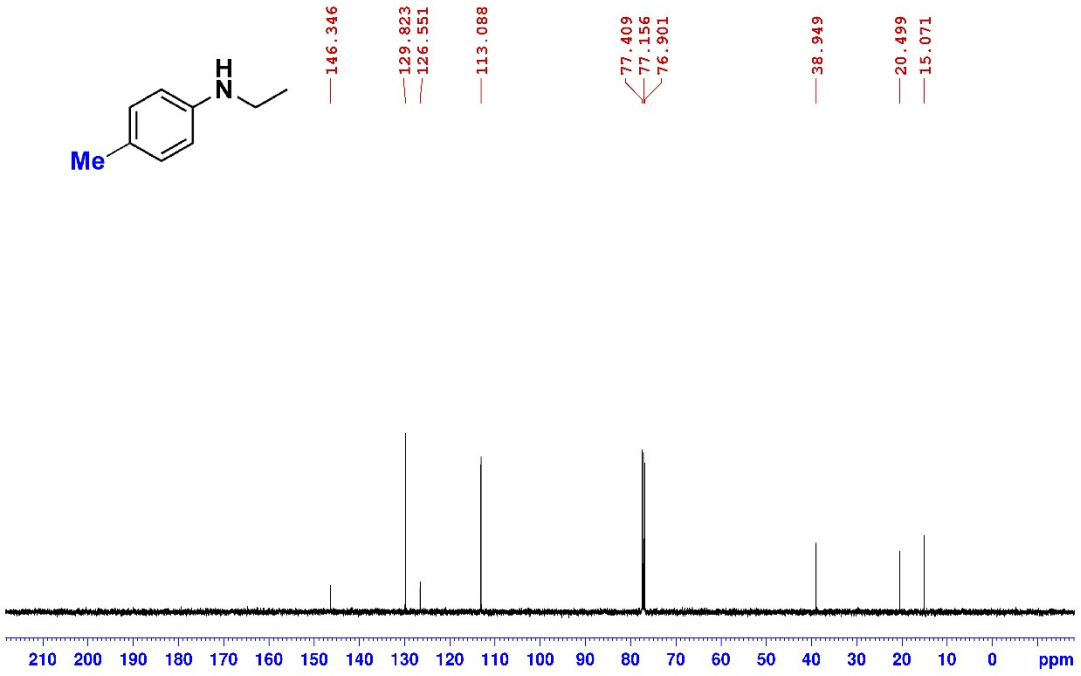
^{1}H-NMR & ^{13}C{^{1}H} (in $CDCl_3$) spectra of compound **2b**



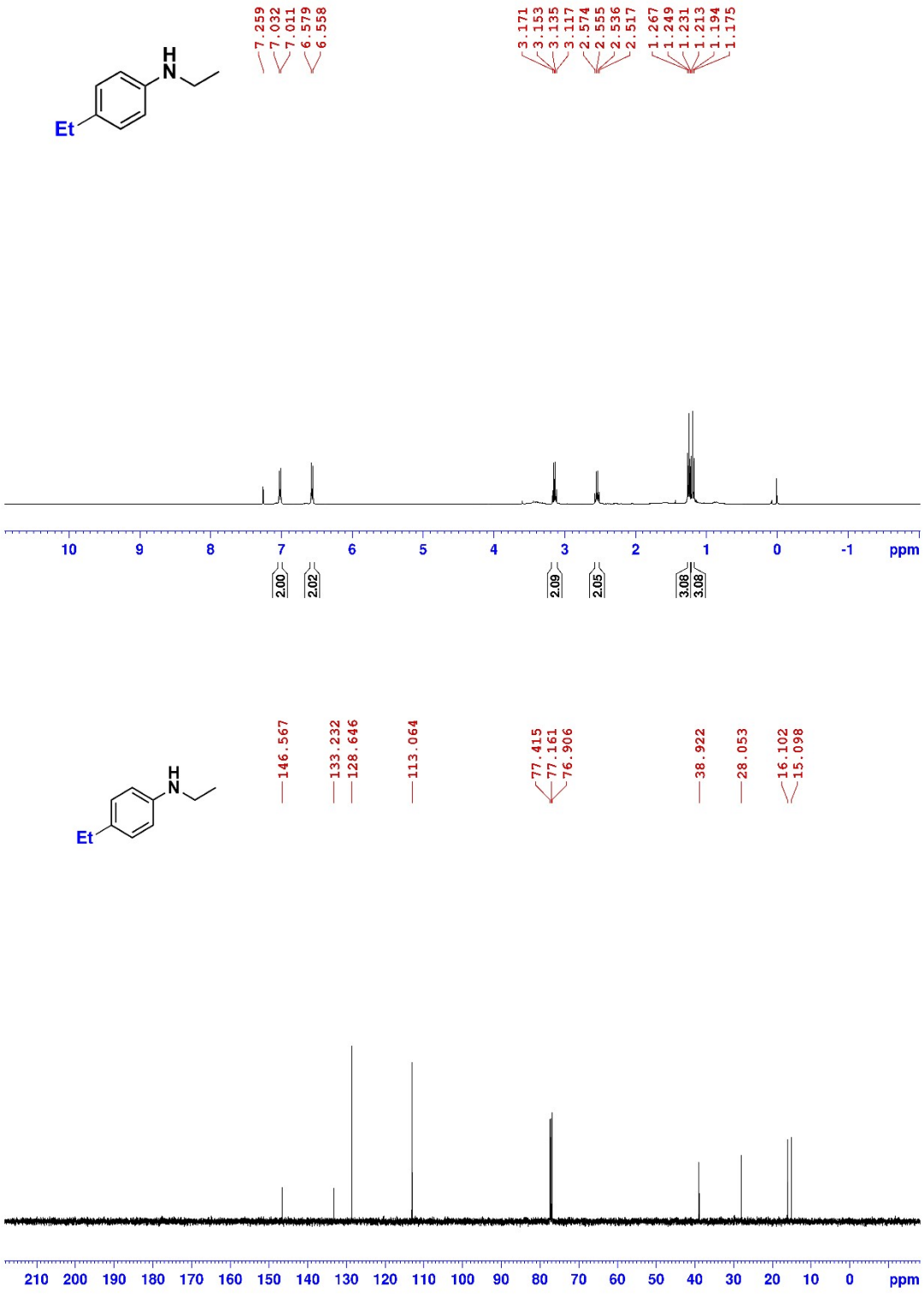


^{1}H-NMR & ^{13}C{^{1}H} (in $CDCl_3$) spectra of compound **2c**

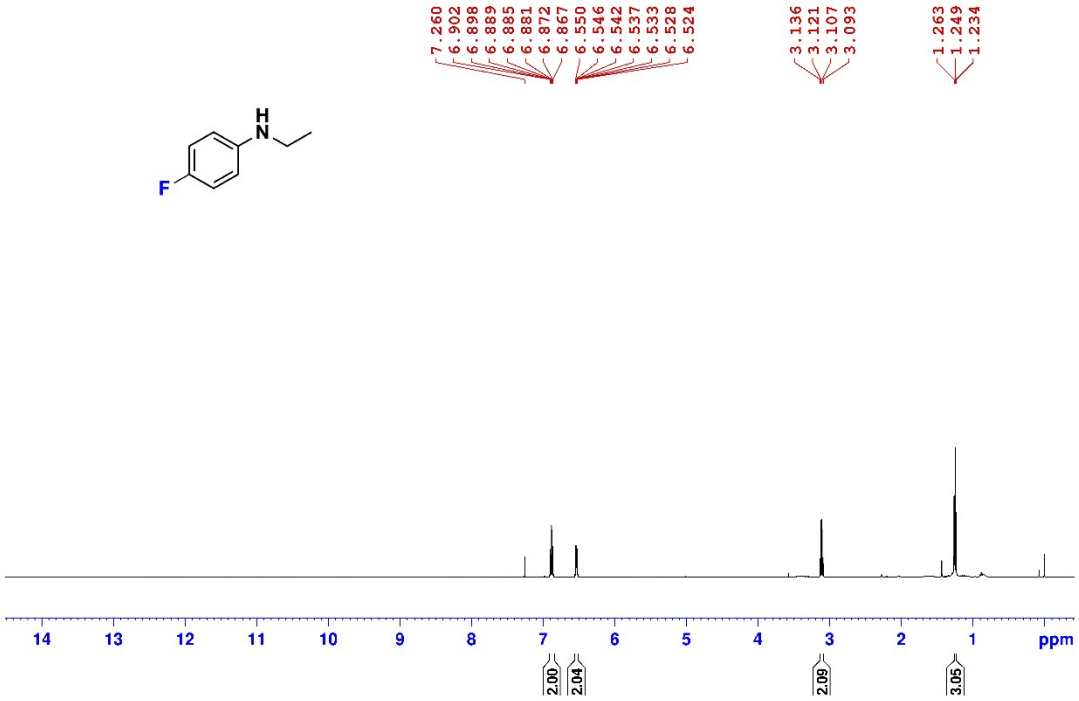


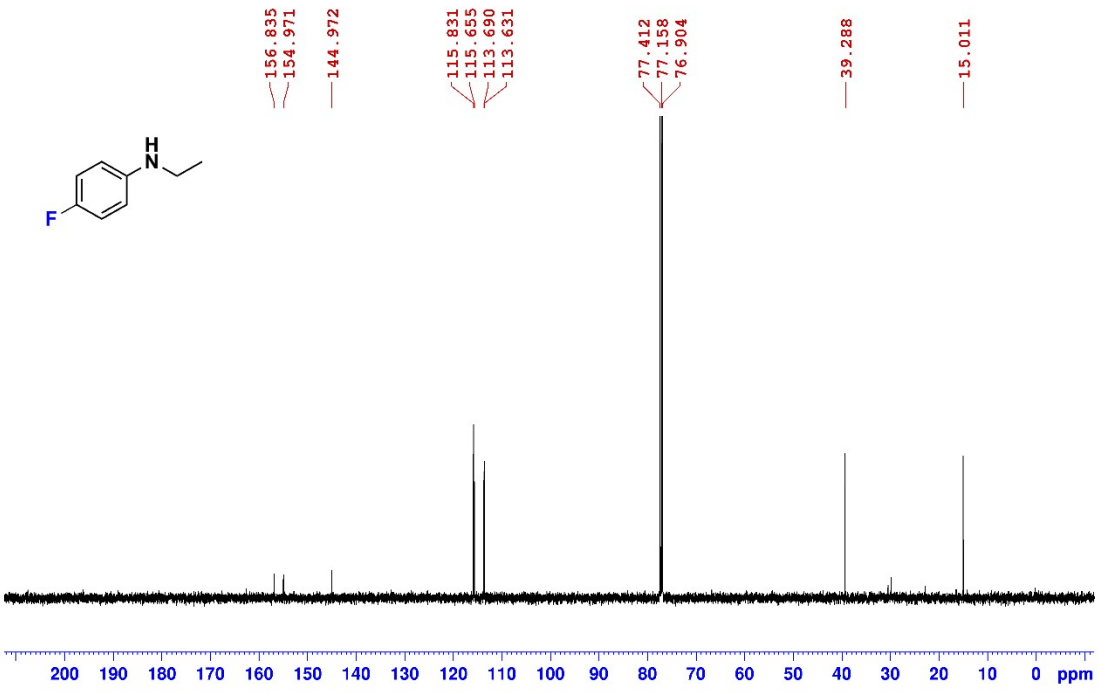


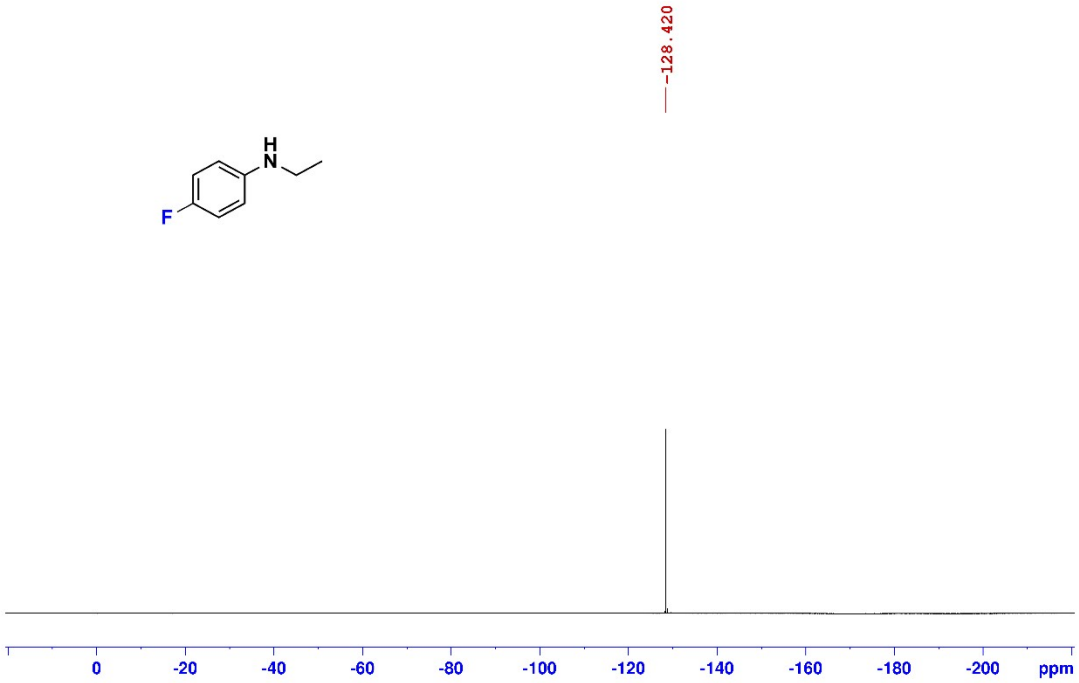
^{1}H-NMR & ^{13}C{^{1}H} (in $CDCl_3$) spectra of compound **2d**



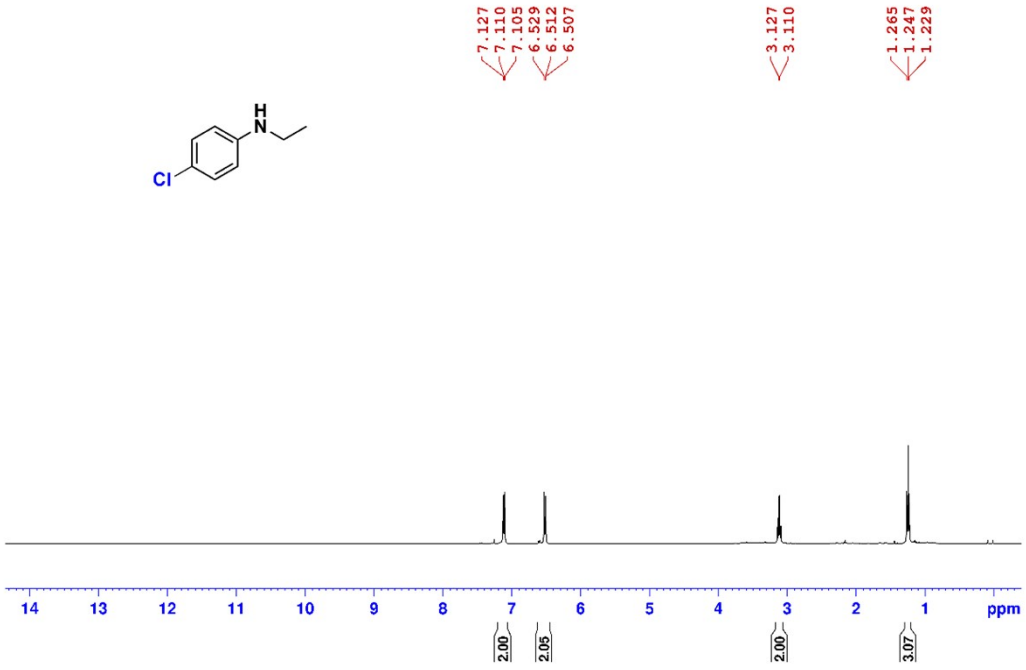
^{1}H-NMR, ^{13}C{^{1}H} & ^{19}F{^{1}H} (in $CDCl_3$) spectra of compound **2e**

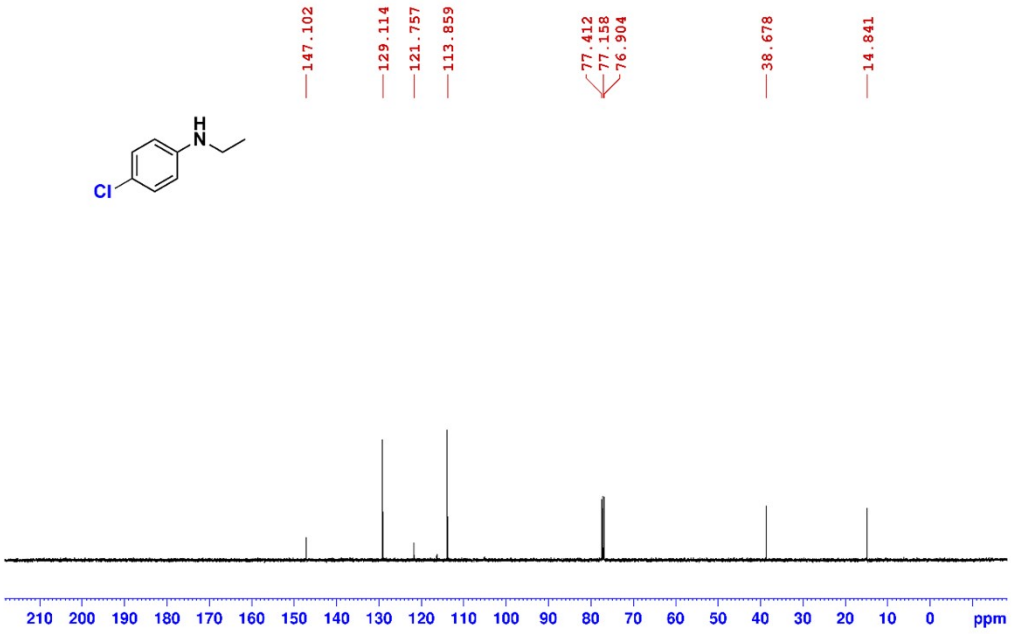

7.260
6.902
6.898
6.889
6.885
6.881
6.872
6.867
6.550
6.546
6.542
6.537
6.533
6.528
6.524
3.136
3.121
3.107
3.093
1.263
1.249
1.234
H
N
F
14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
2.00
2.04
2.09
3.05


156.835
154.971
144.972
115.831
115.655
113.690
113.631
77.412
77.158
76.904
39.288
15.011
H
N
F
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

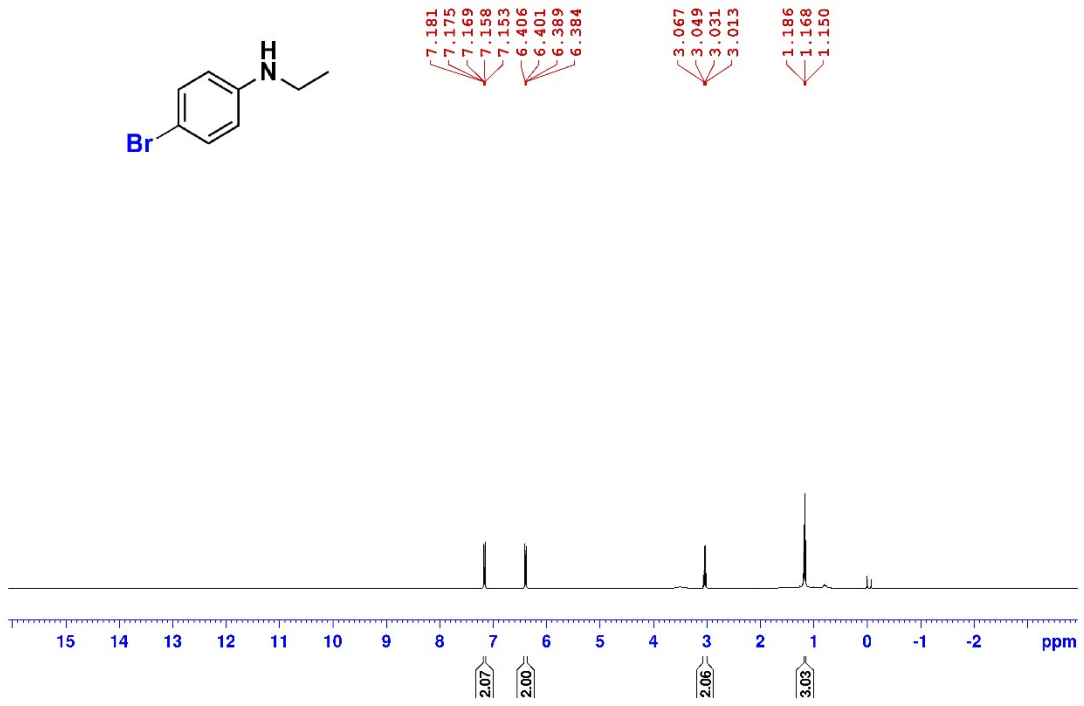


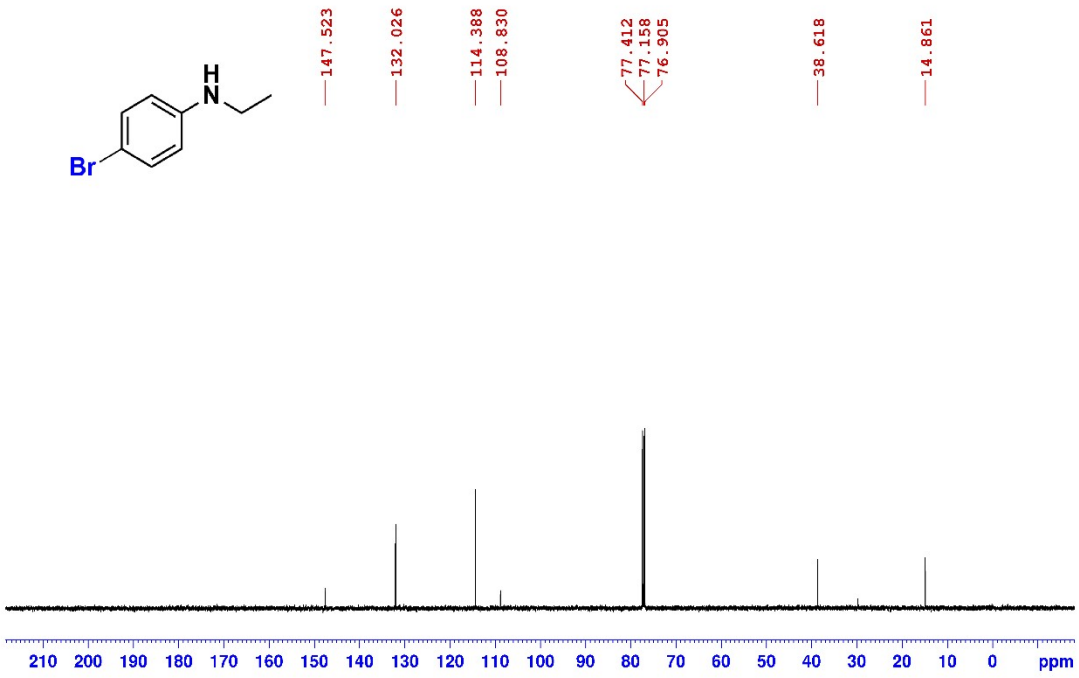
^{1}H-NMR & ^{13}C{^{1}H} (in $CDCl_3$) spectra of compound **2f**



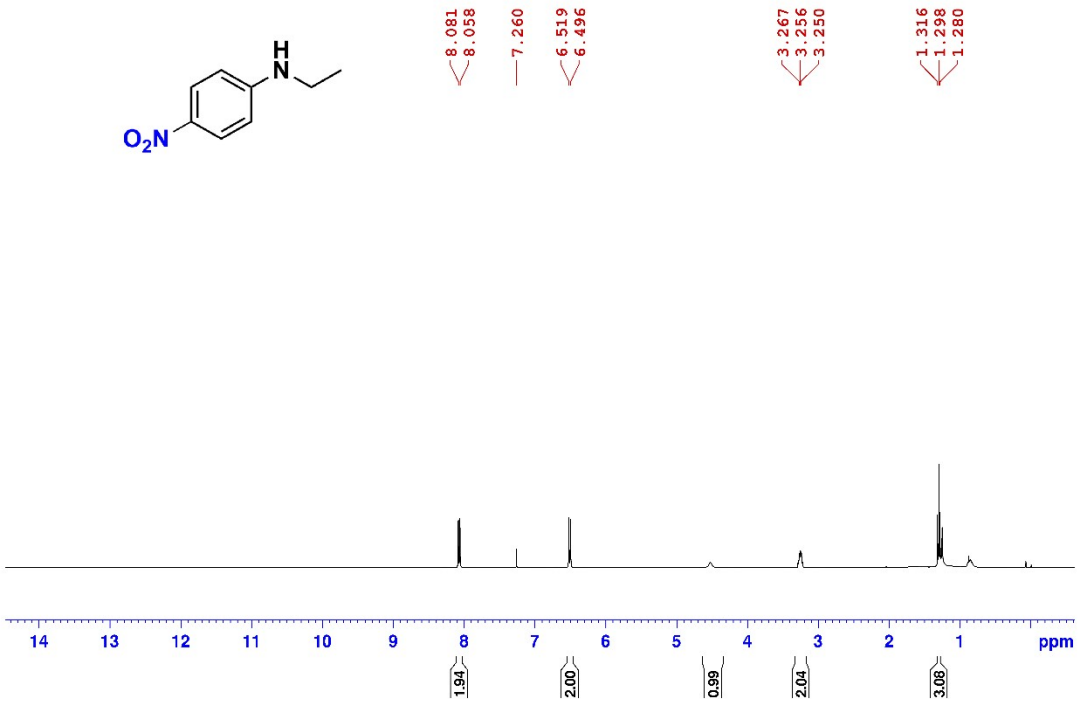


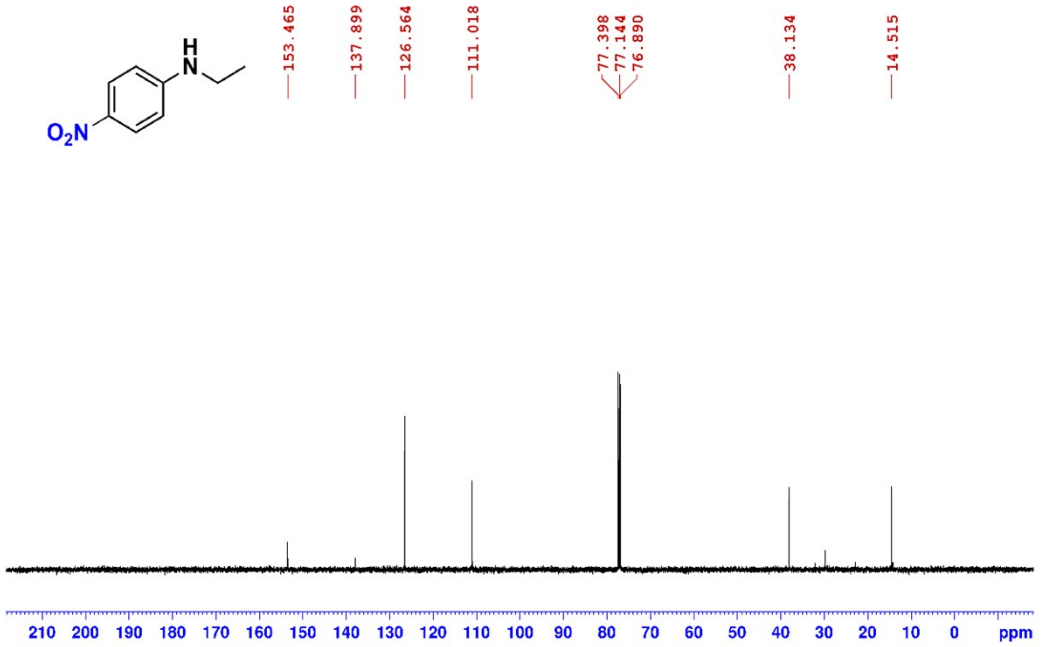
^{1}H-NMR & ^{13}C{^{1}H} (in $CDCl_3$) spectra of compound **2g**



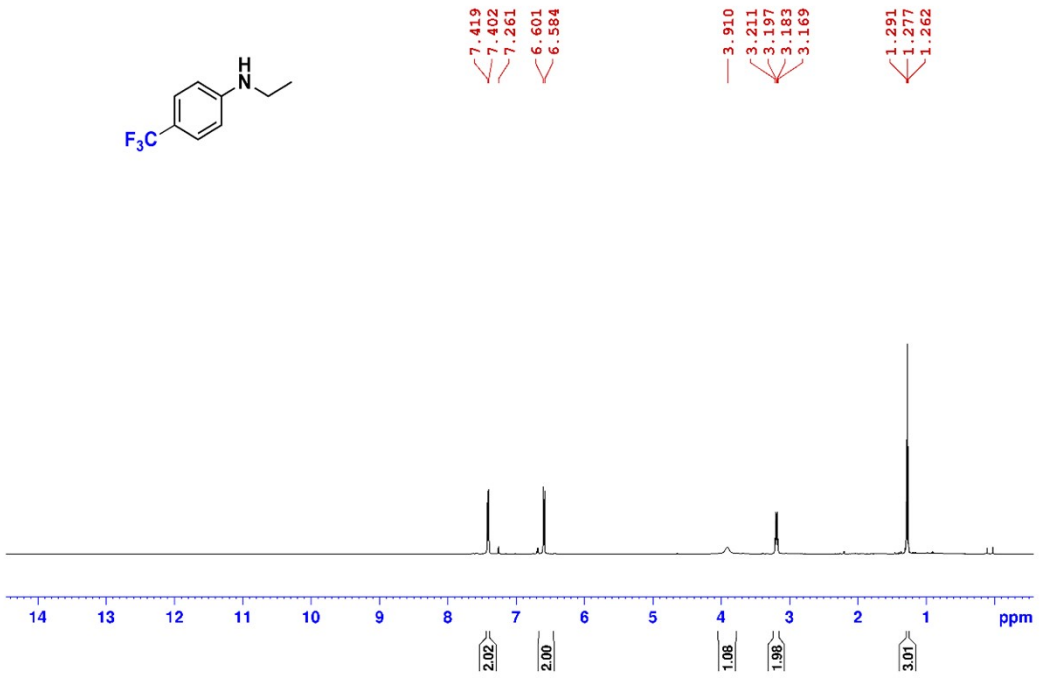


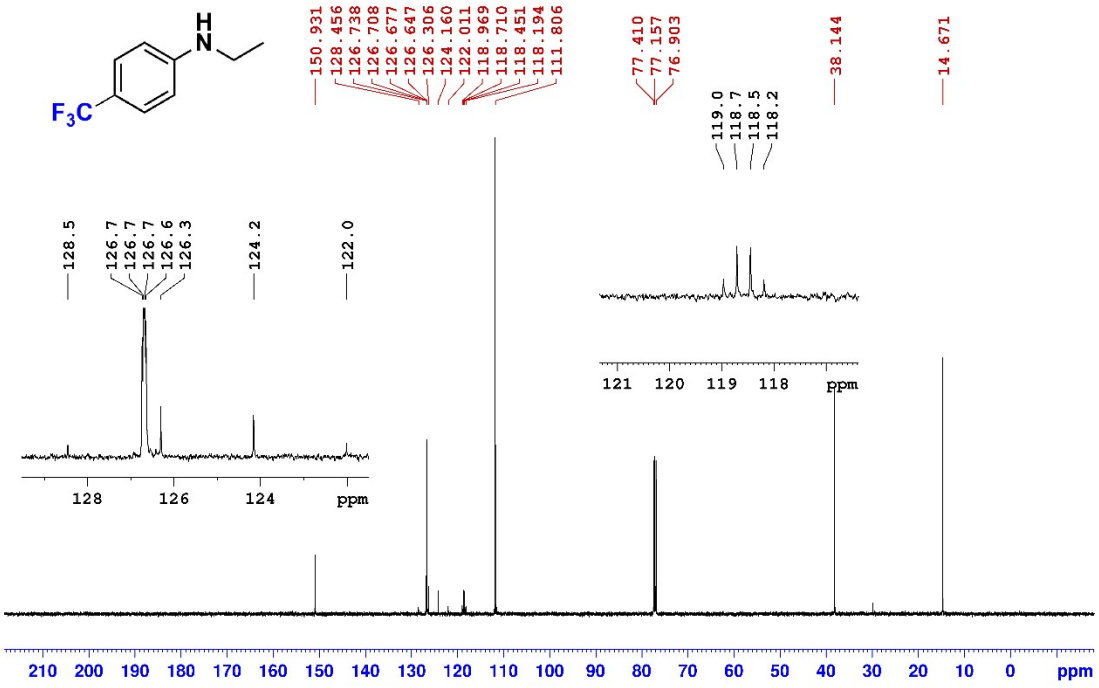
^{1}H-NMR & $^{13}C\{^{1}H\}$ (in $CDCl_3$) spectra of compound **2h**





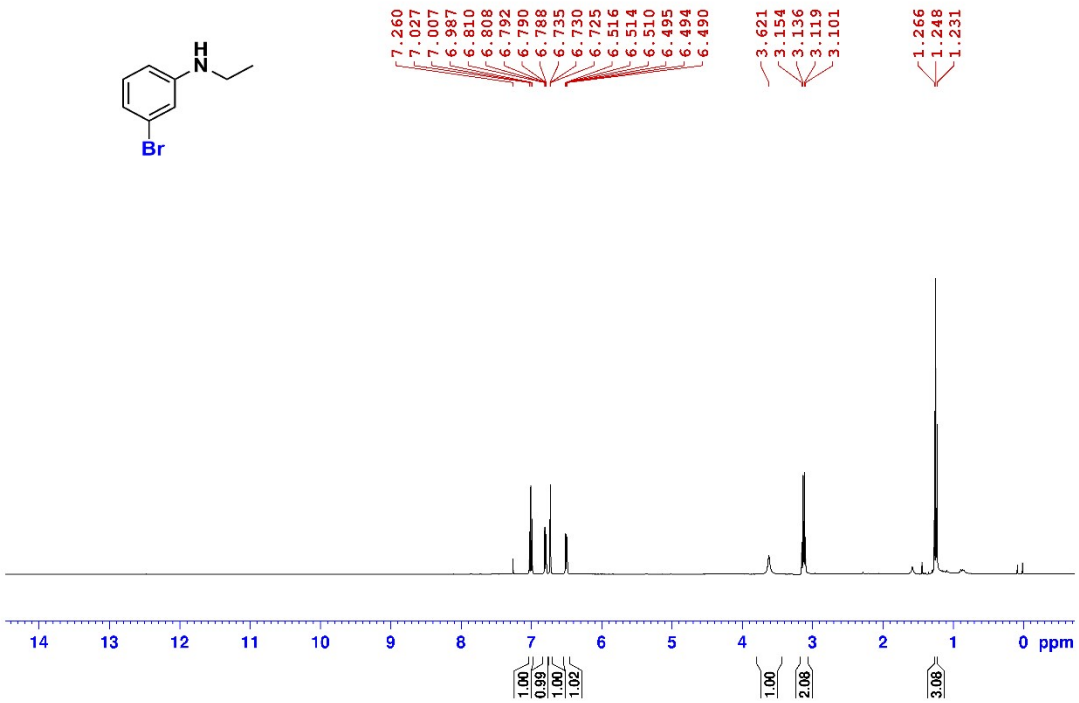
^{1}H-NMR, ^{13}C{^{1}H} & ^{19}F{^{1}H} (in $CDCl_3$) spectra of compound **2i**

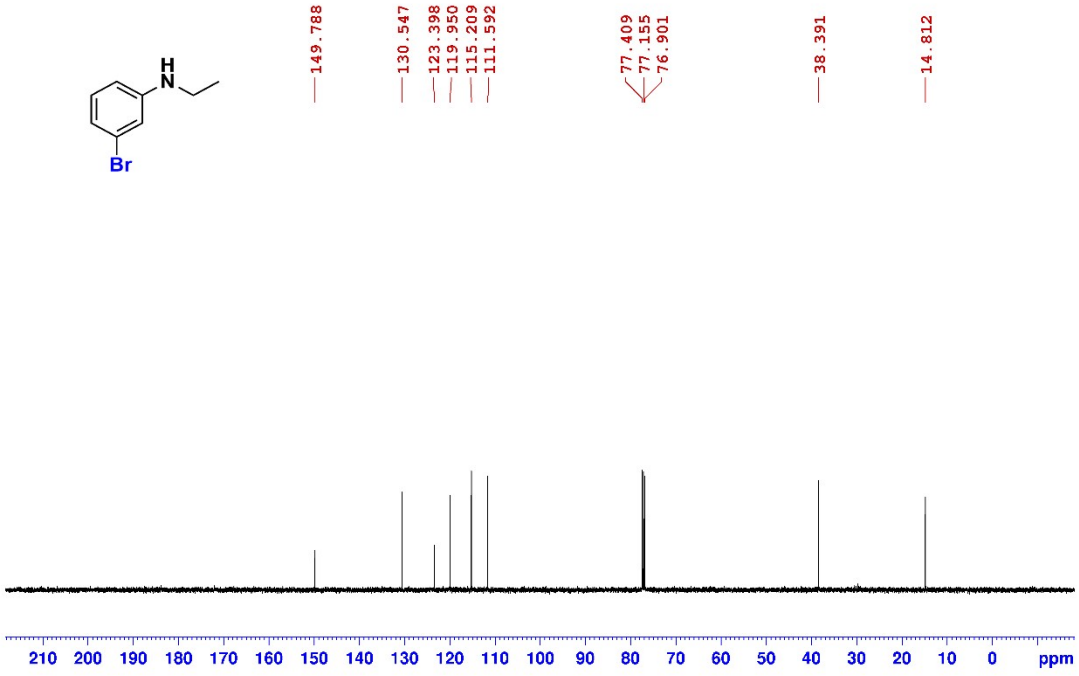



150.931
128.456
126.738
126.708
126.677
126.647
126.306
124.160
122.011
118.969
118.710
118.451
118.194
111.806
77.410
77.157
76.903
119.0
118.7
118.5
118.2
38.144
14.671
128.5
126.7
126.7
126.7
126.6
126.3
124.2
122.0
128
126
124
ppm
121
120
119
118
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

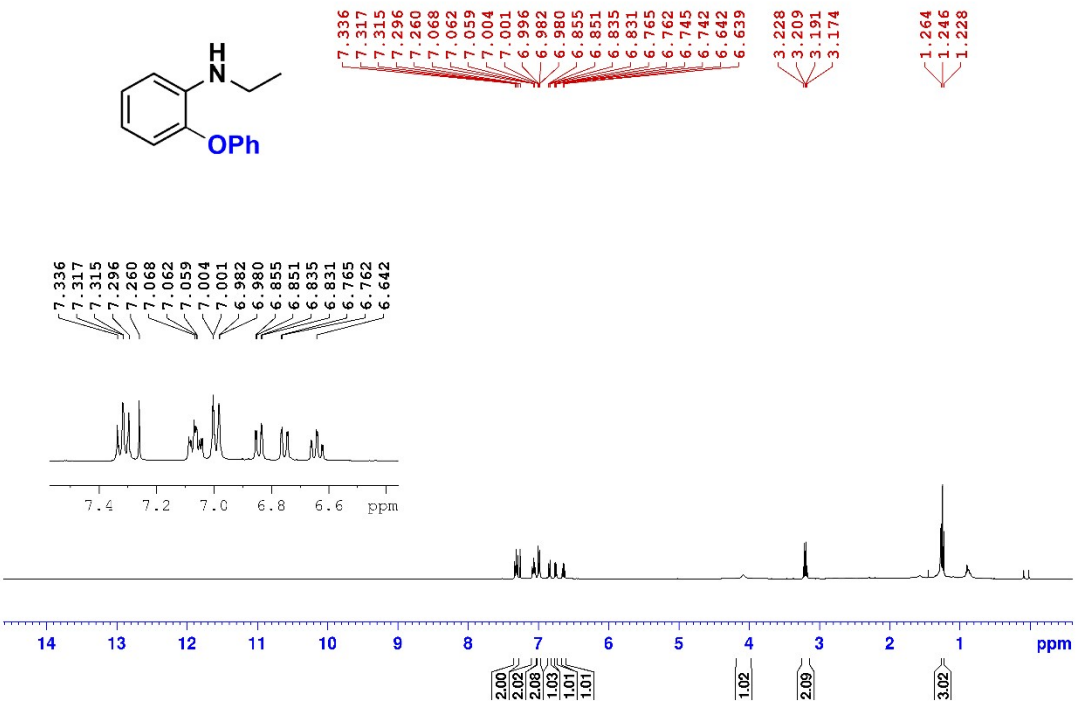

-60.925
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm

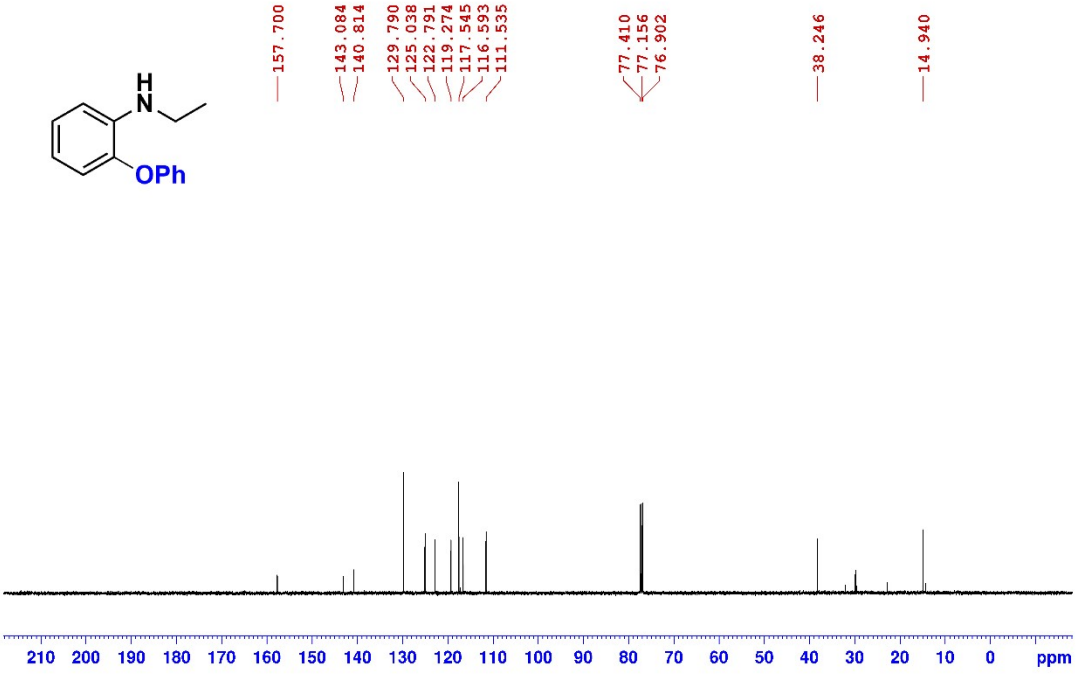
^{1}H-NMR & ^{13}C{^{1}H} (in $CDCl_3$) spectra of compound **2j**



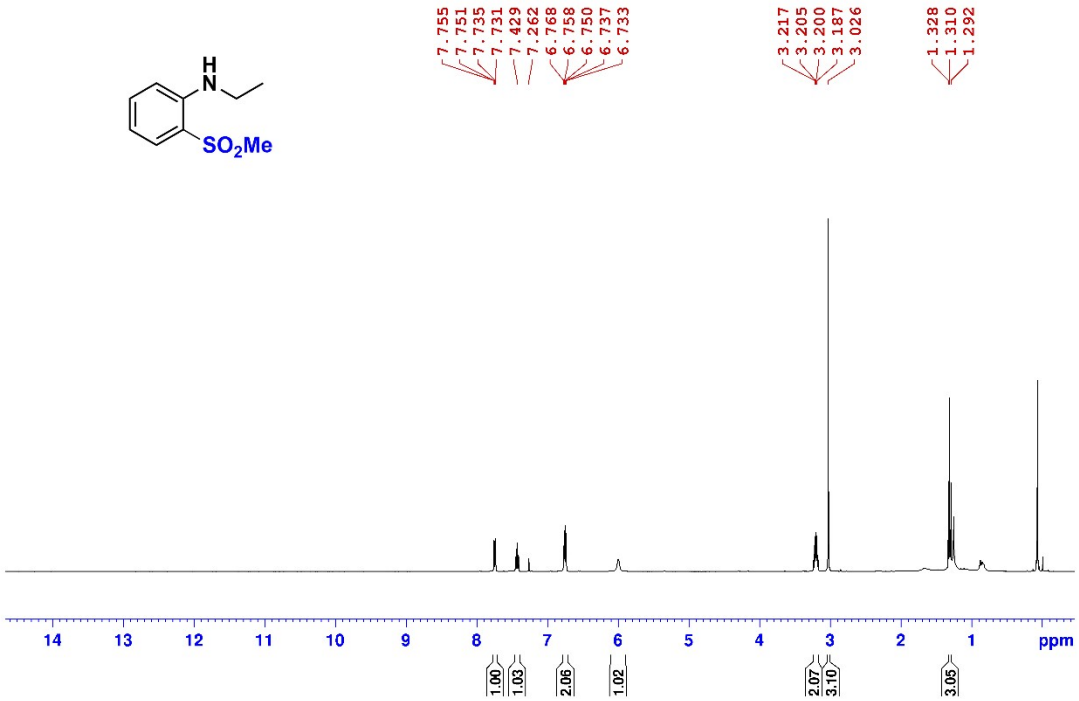


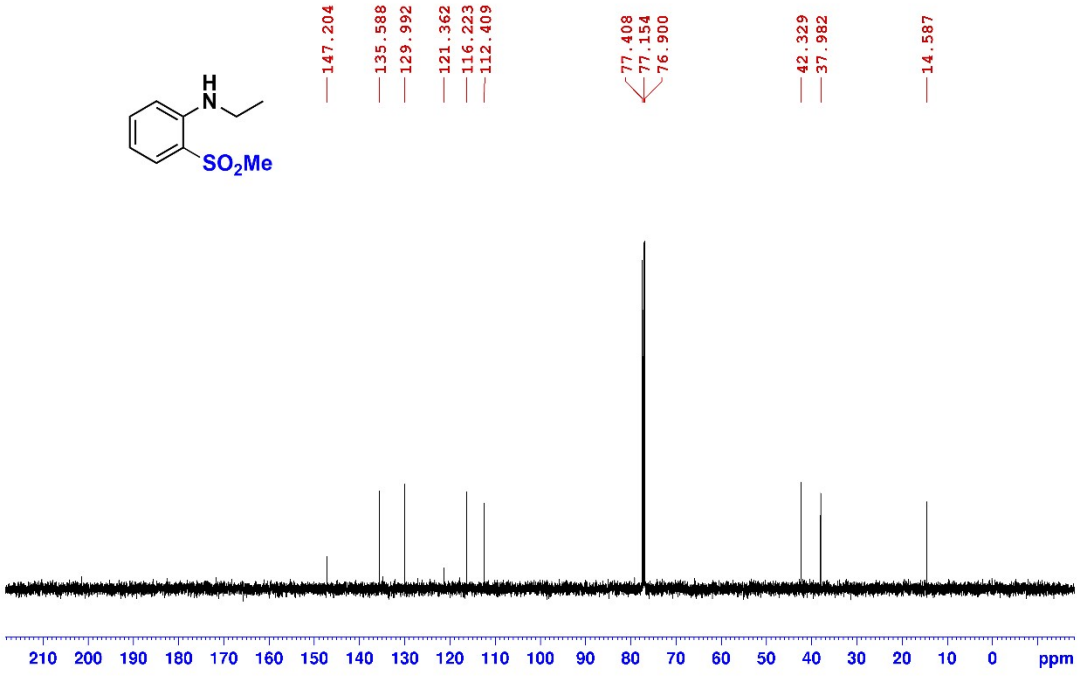
^{1}H-NMR & ^{13}C{^{1}H} (in $CDCl_3$) spectra of compound **2k**



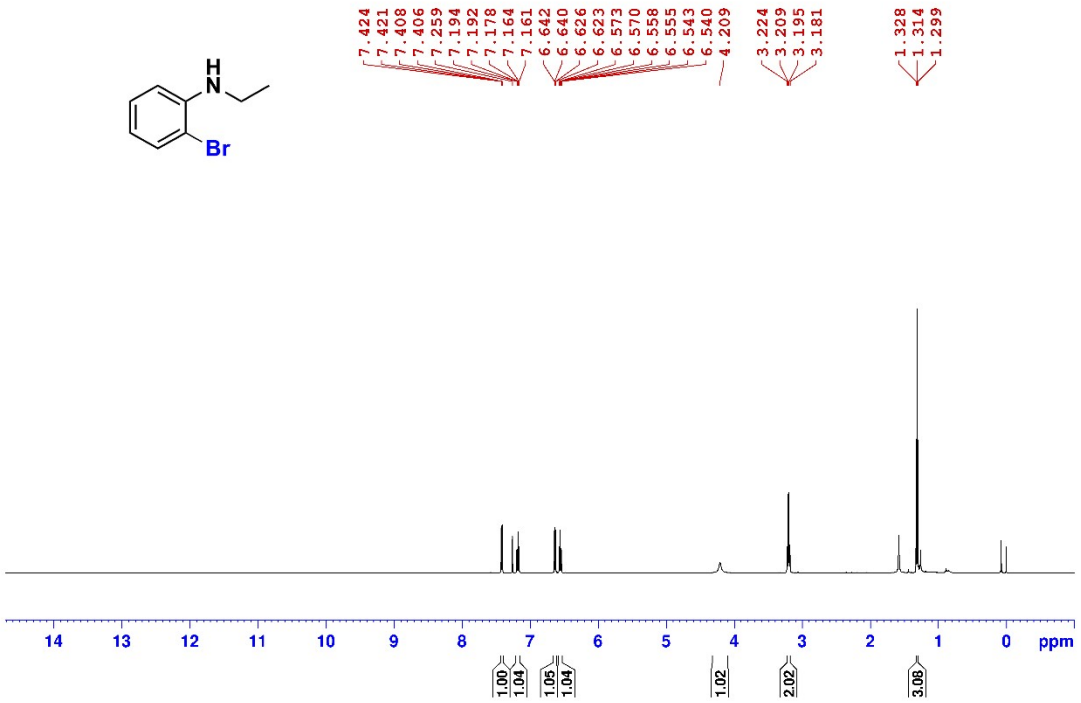


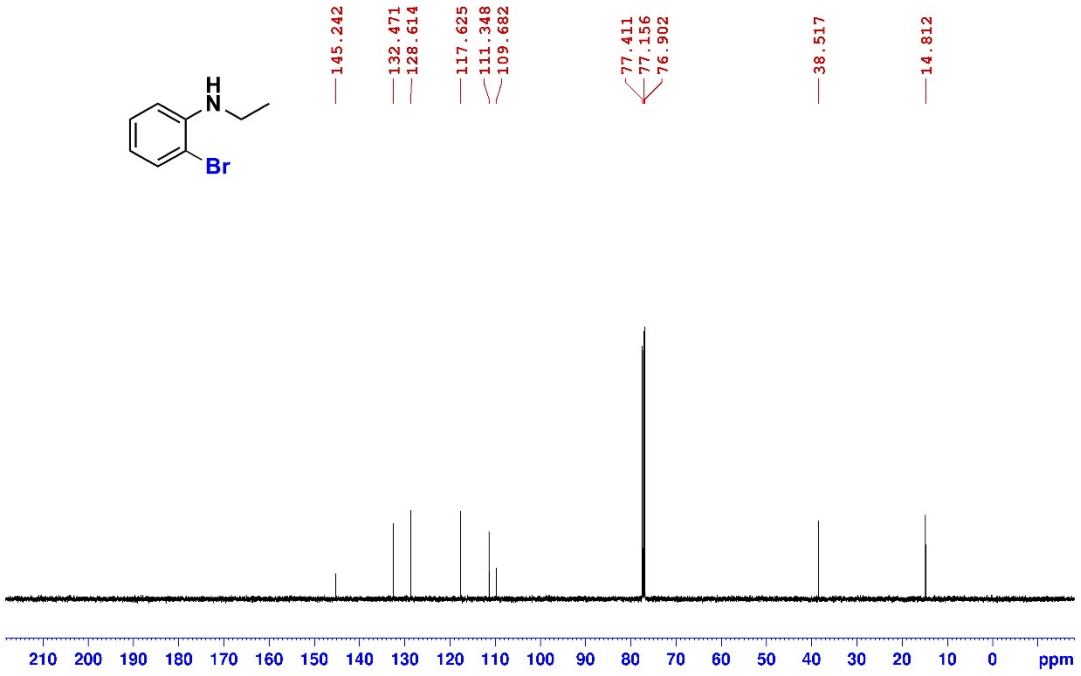
^{1}H-NMR & ^{13}C{^{1}H} (in $CDCl_3$) spectra of compound **2l**



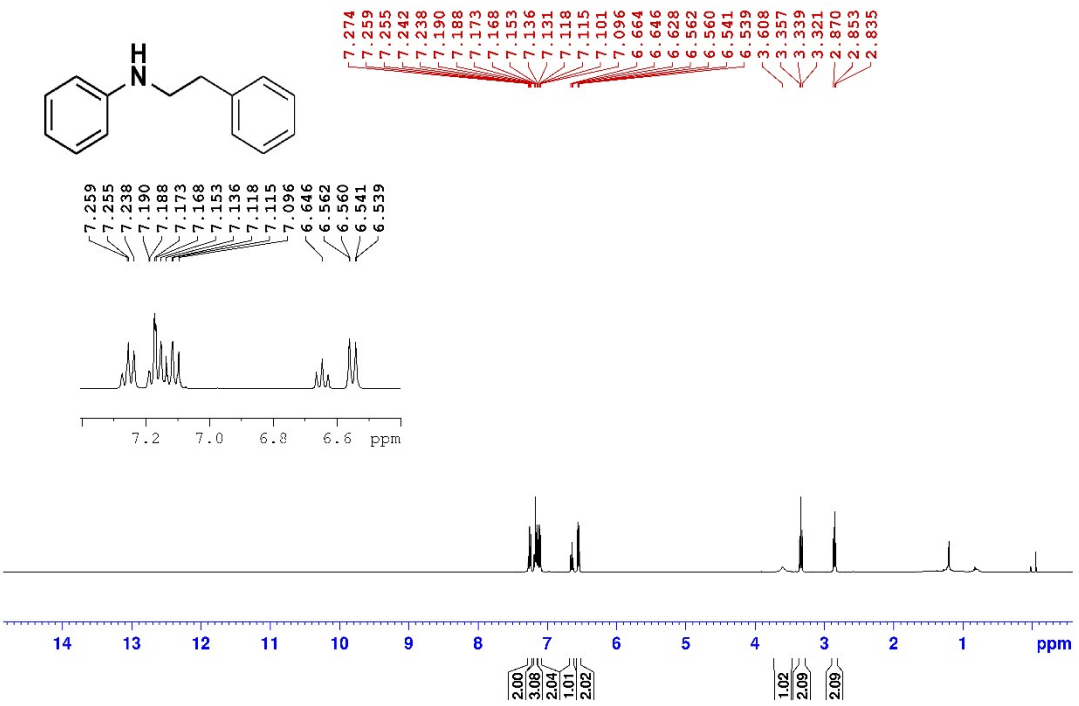


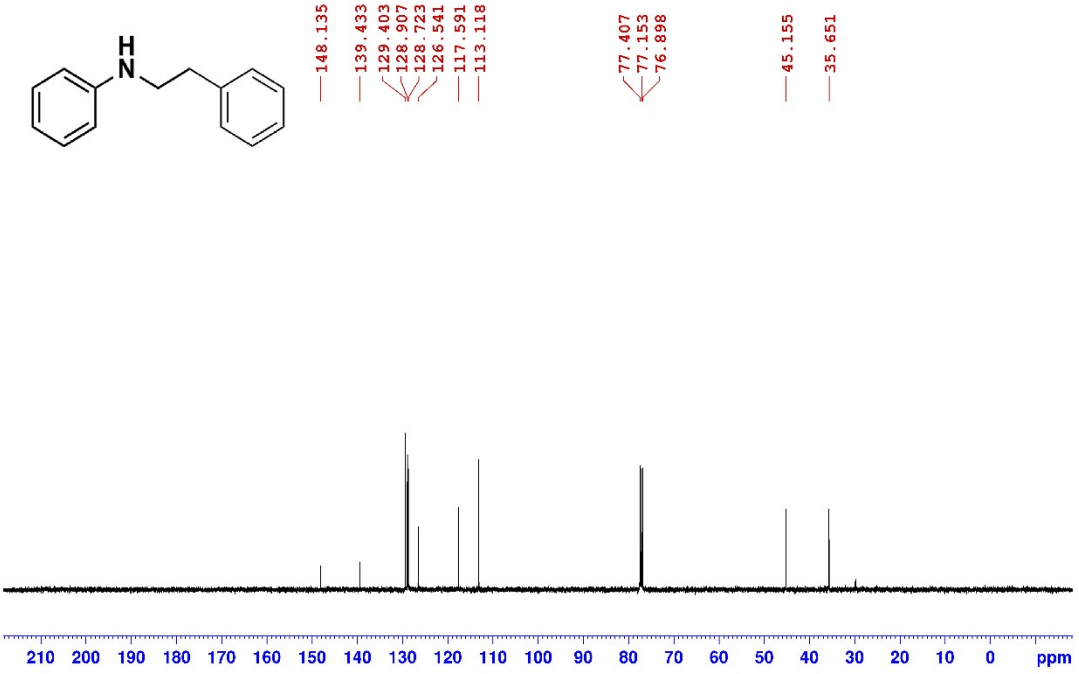
^{1}H-NMR & ^{13}C{^{1}H} (in $CDCl_3$) spectra of compound **2m**



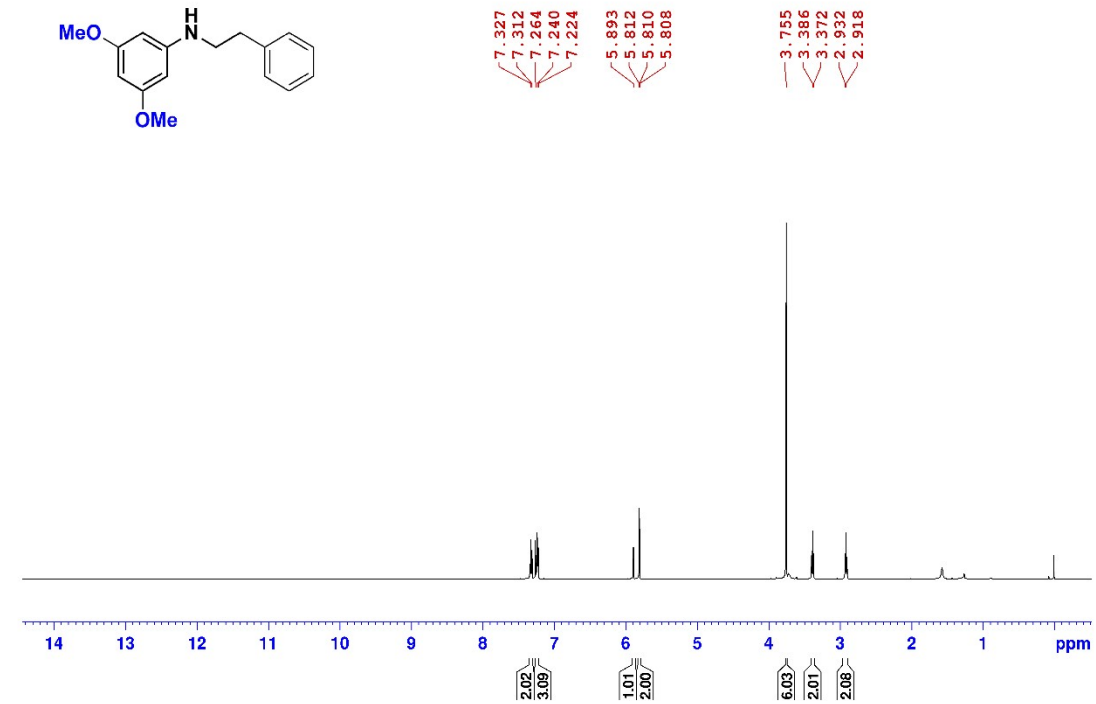


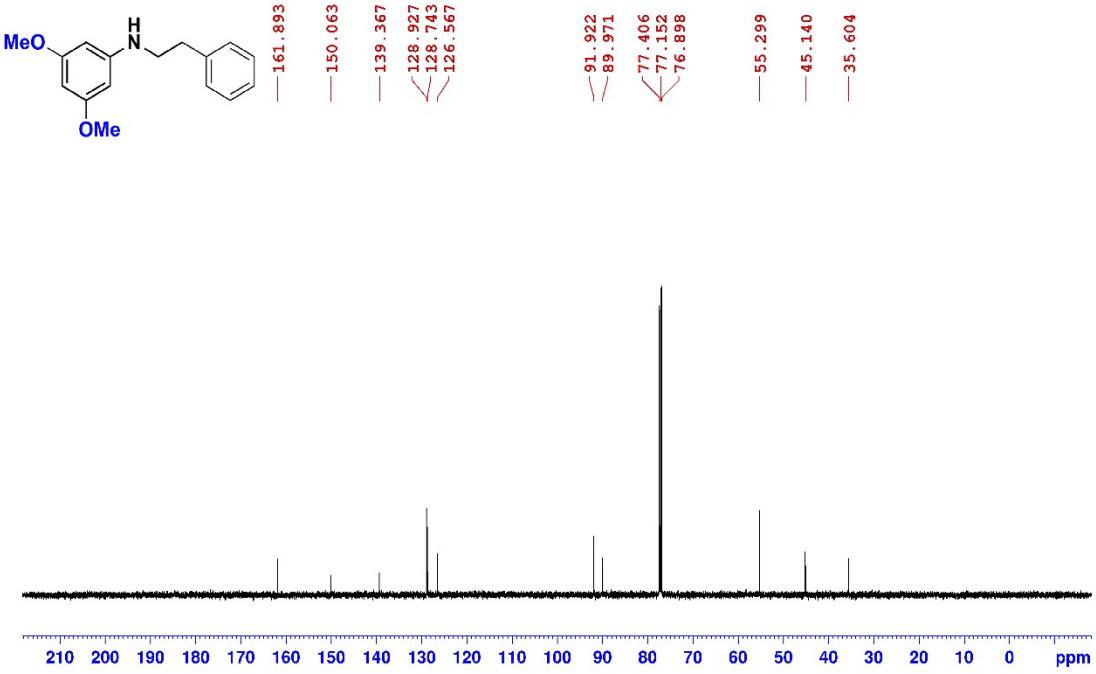
^{1}H-NMR & ^{13}C{^{1}H} (in $CDCl_3$) spectra of compound **2n**



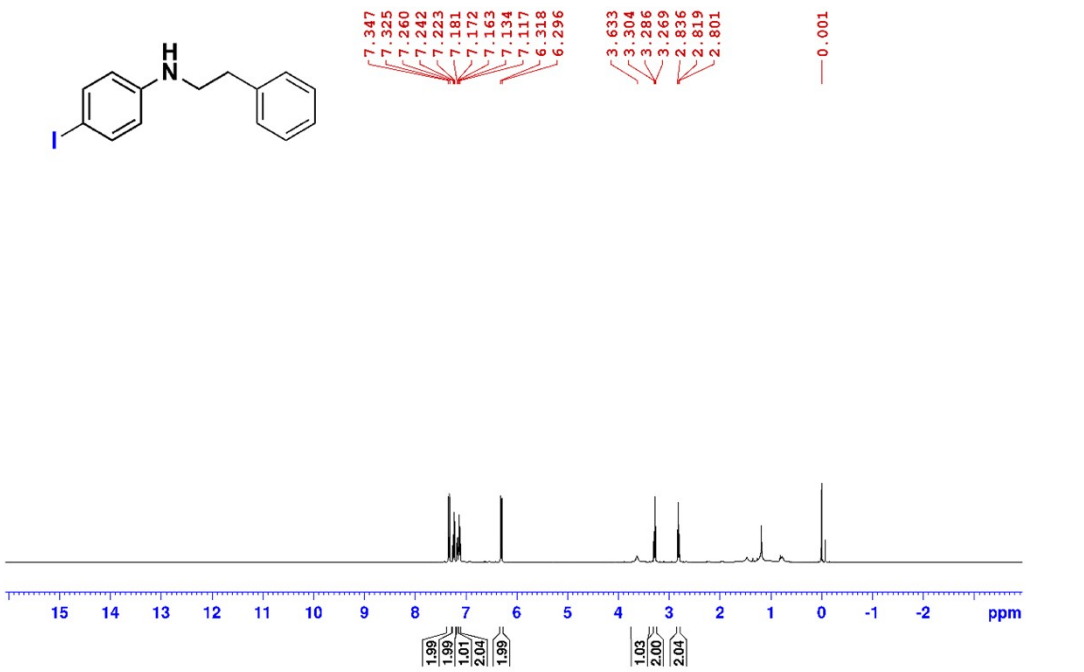


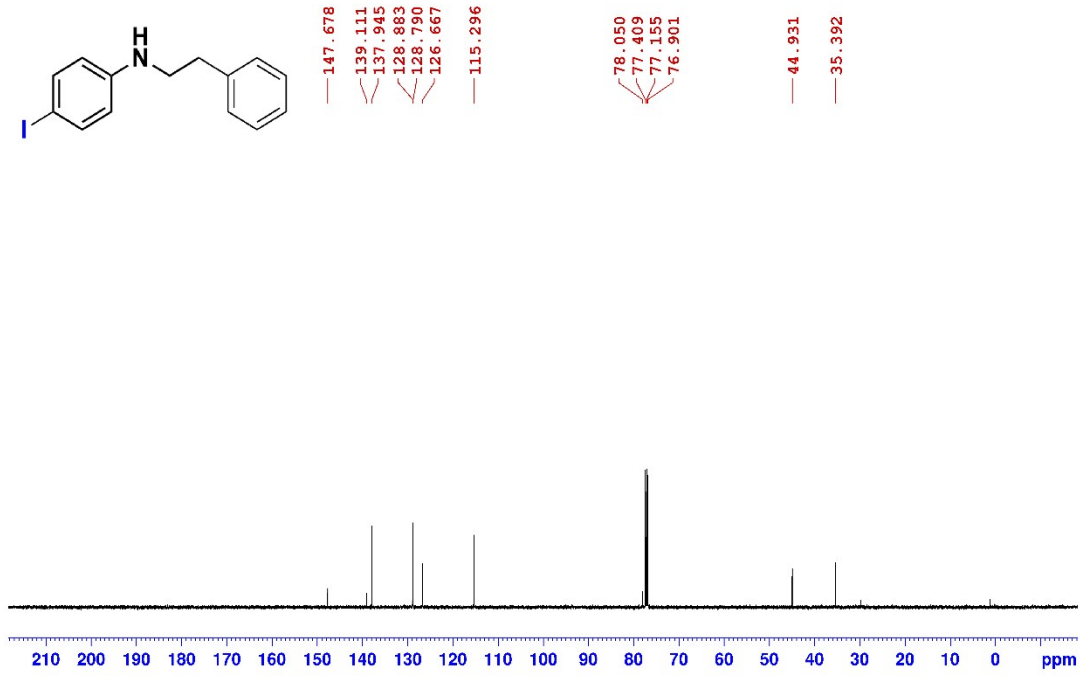
^{1}H-NMR & ^{13}C{^{1}H} (in $CDCl_3$) spectra of compound **2o**



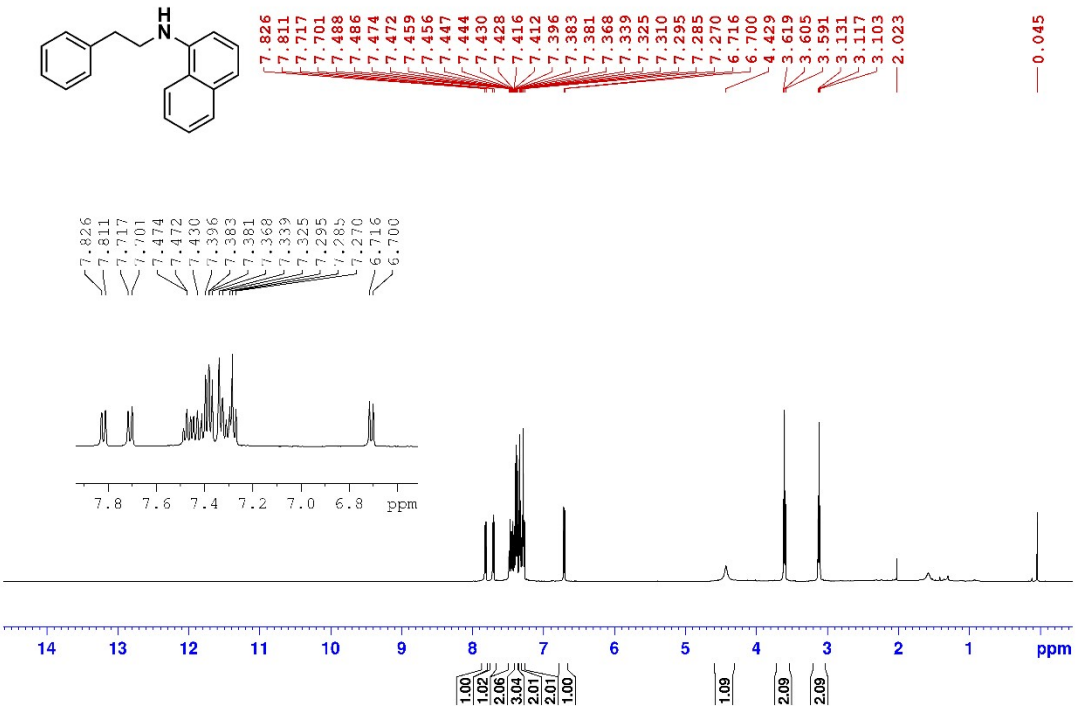


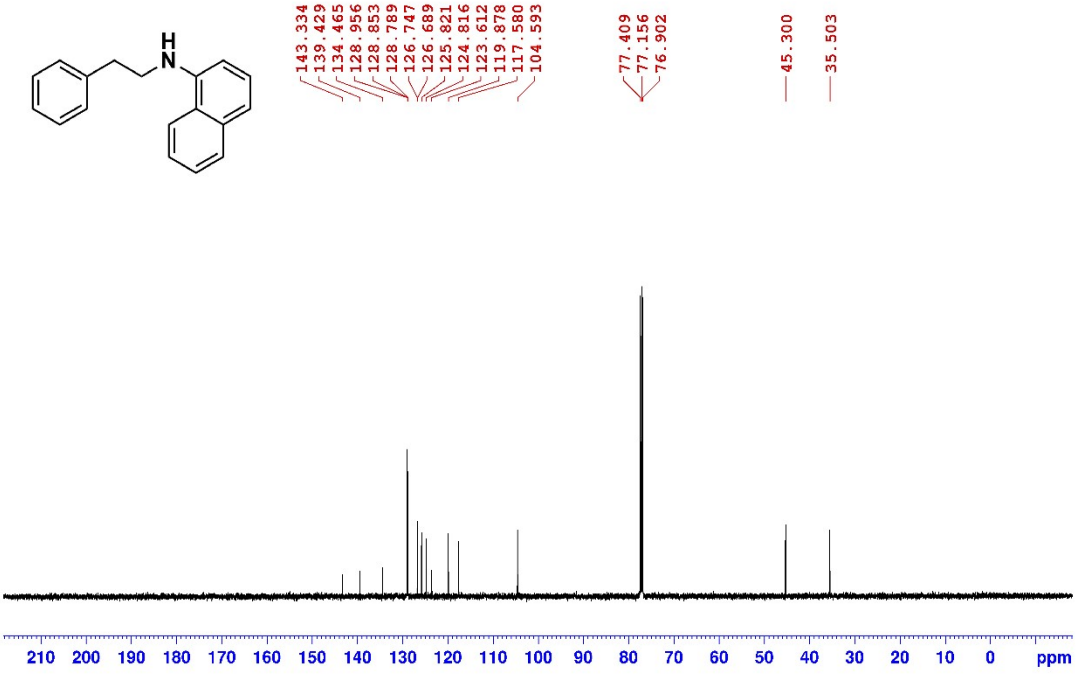
^{1}H-NMR & ^{13}C{^{1}H} (in $CDCl_3$) spectra of compound **2p**



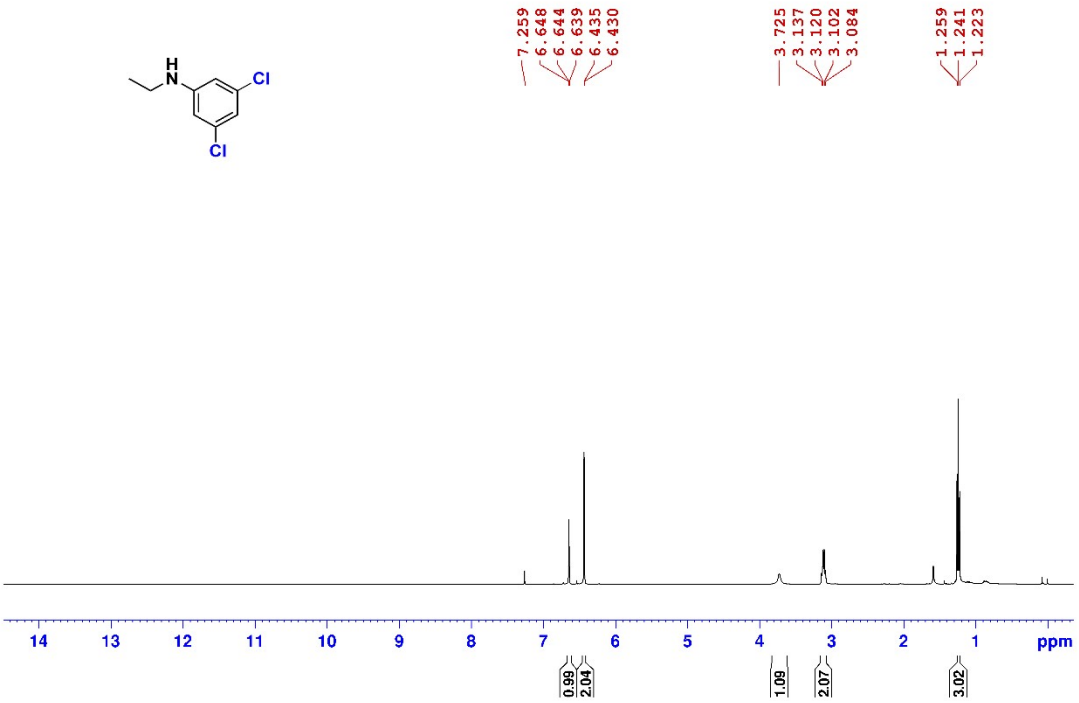


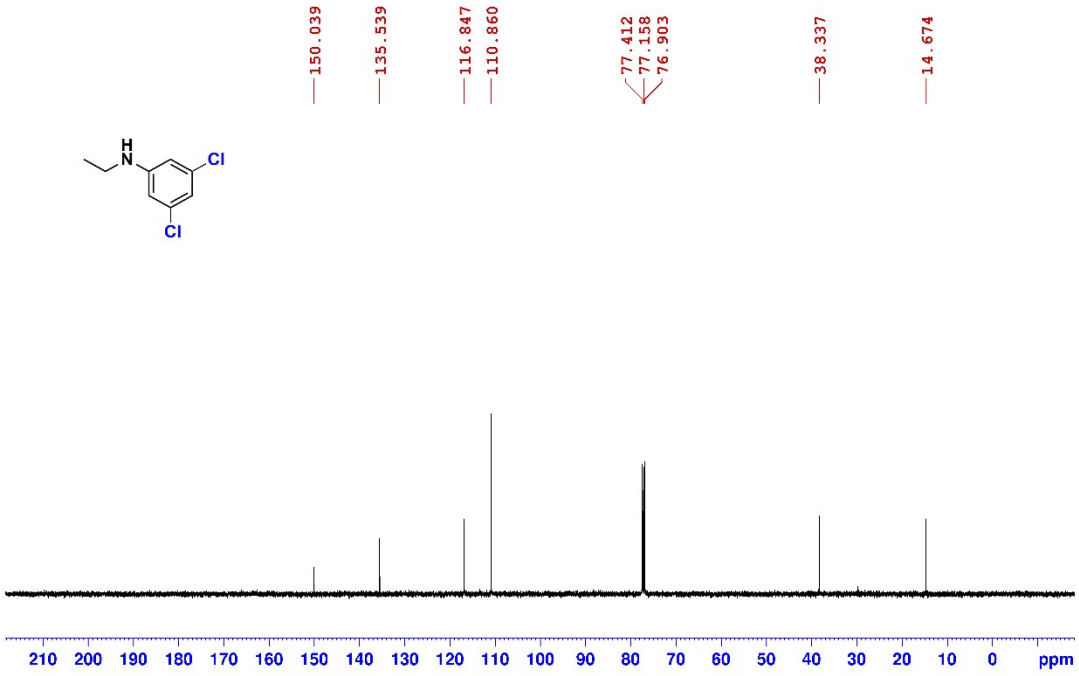
^{1}H-NMR & ^{13}C{^{1}H} (in $CDCl_3$) spectra of compound **2q**



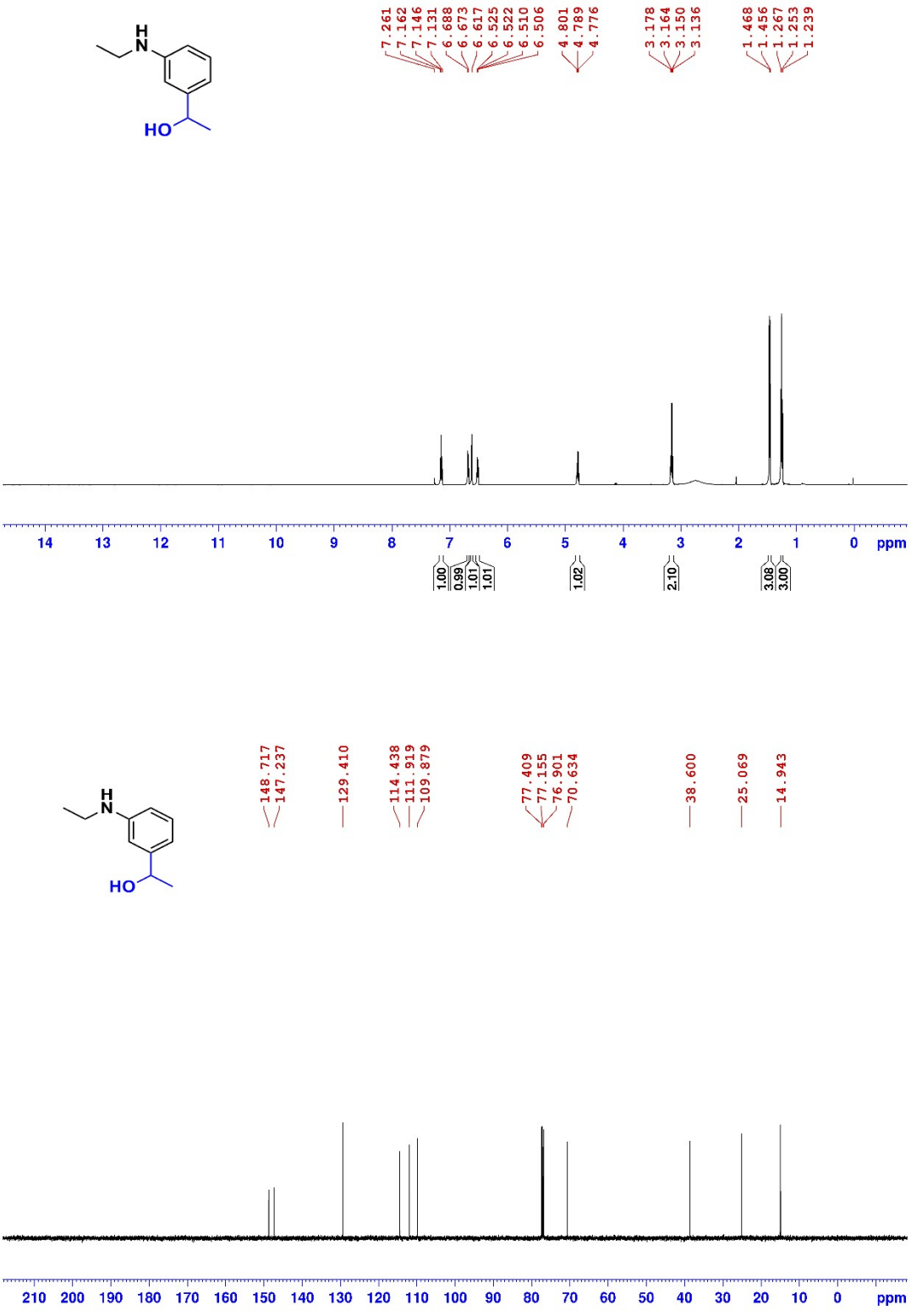


^{1}H-NMR & ^{13}C{^{1}H} (in $CDCl_3$) spectra of compound **2r**

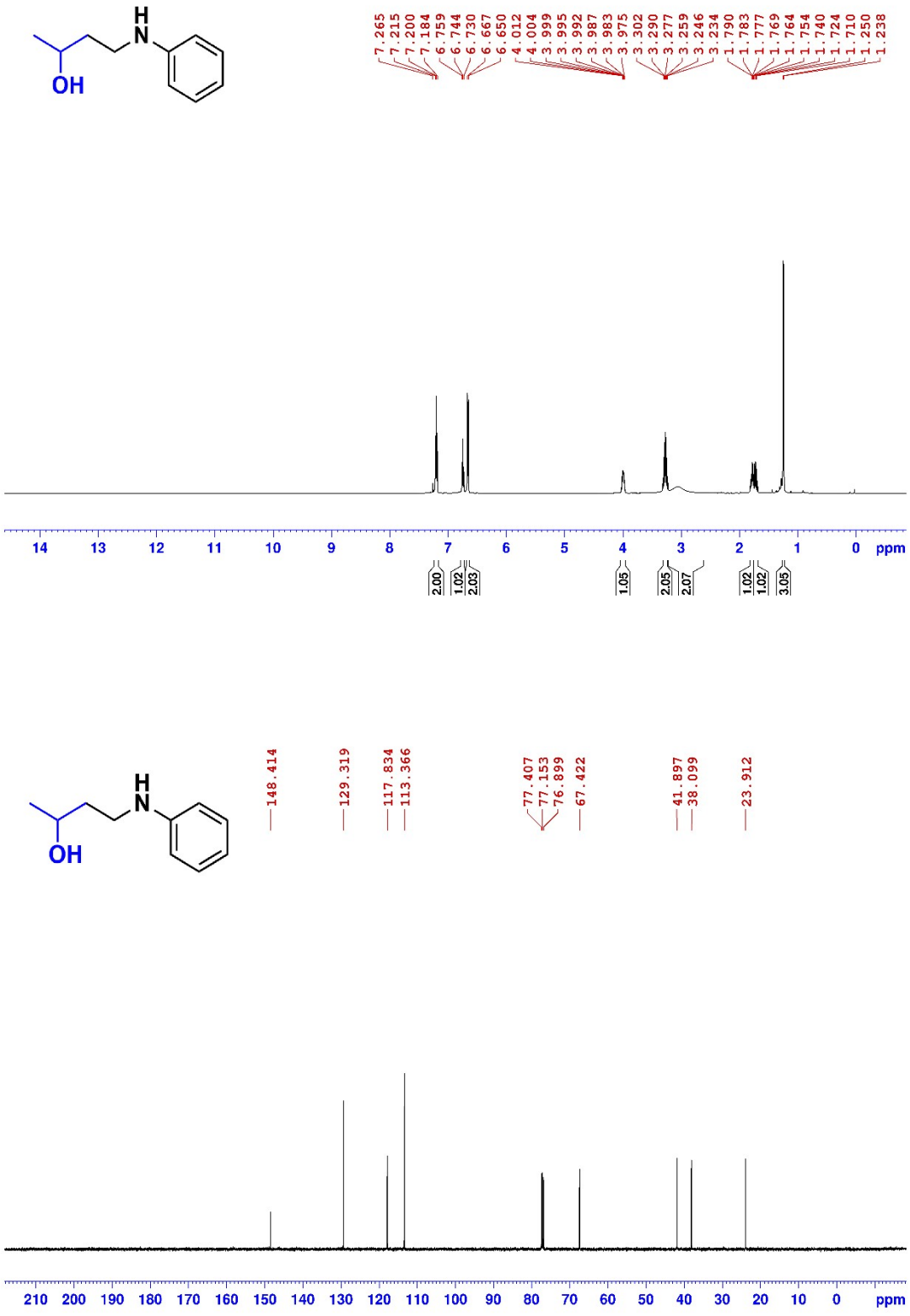




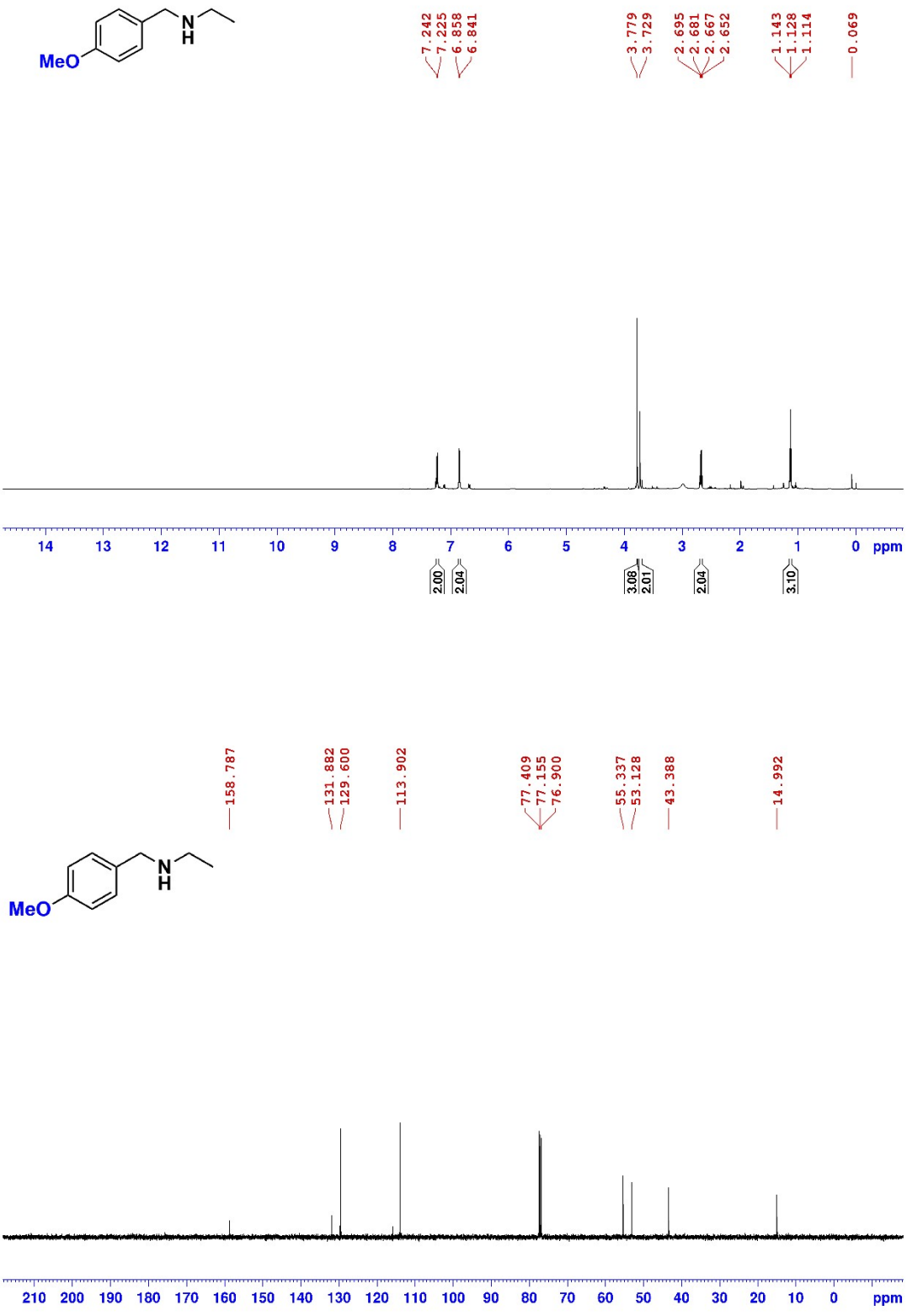
^{1}H-NMR & ^{13}C{^{1}H} (in $CDCl_3$) spectra of compound **2s**



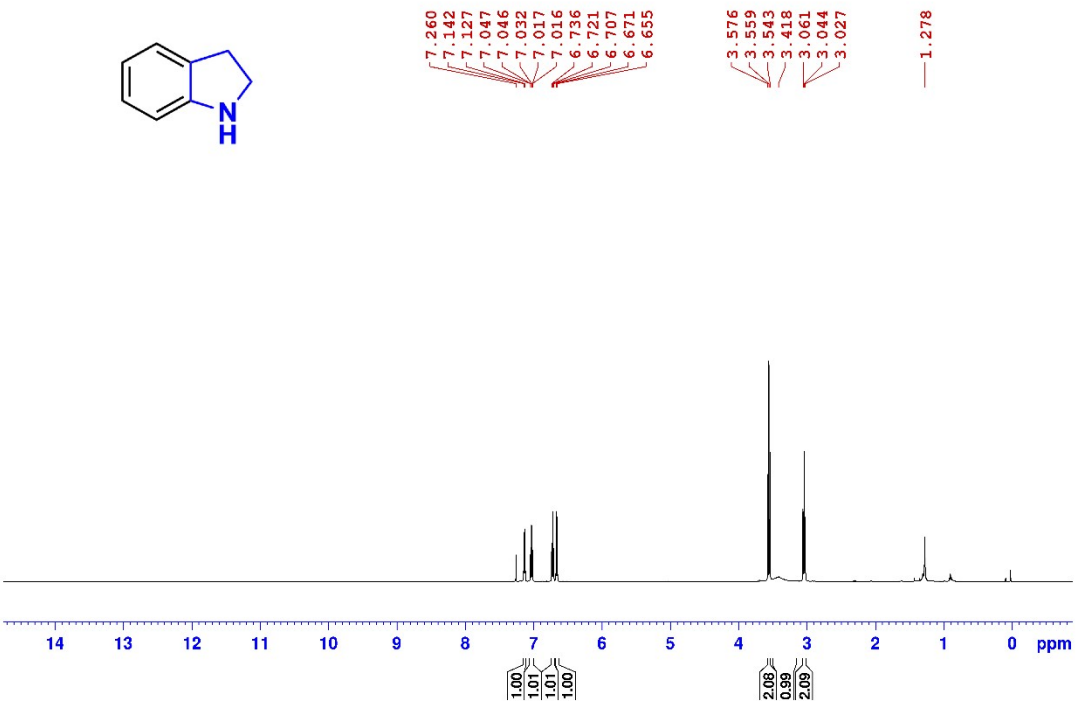
^{1}H-NMR & ^{13}C{^{1}H} (in $CDCl_3$) spectra of compound **2t**

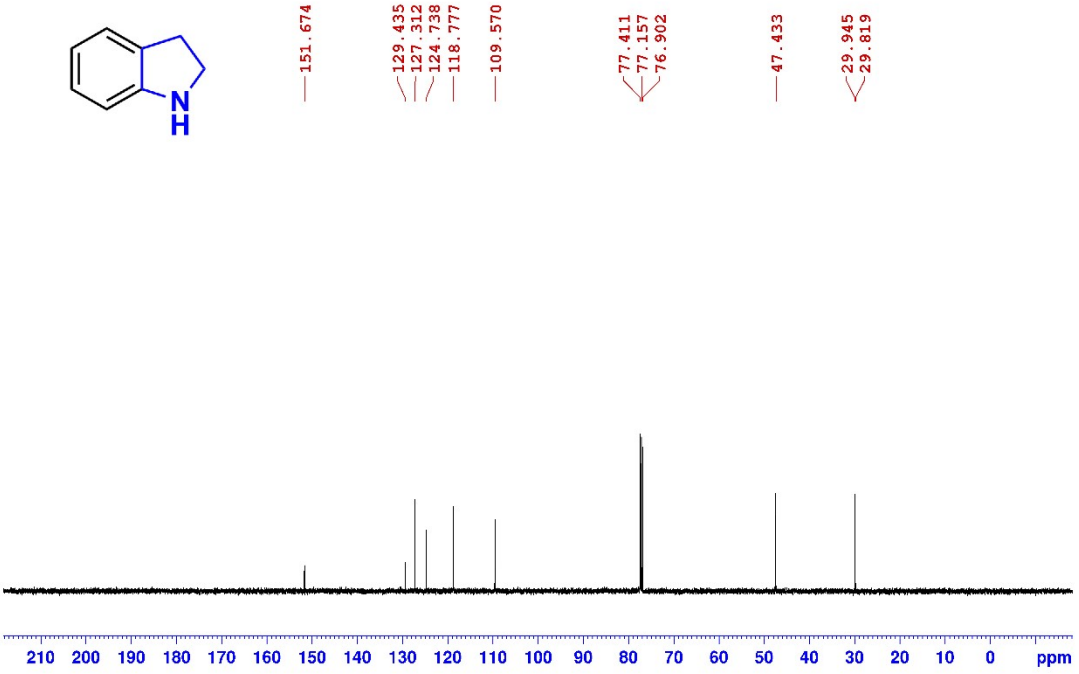


^{1}H-NMR & ^{13}C{^{1}H} (in $CDCl_3$) spectra of compound **2u**

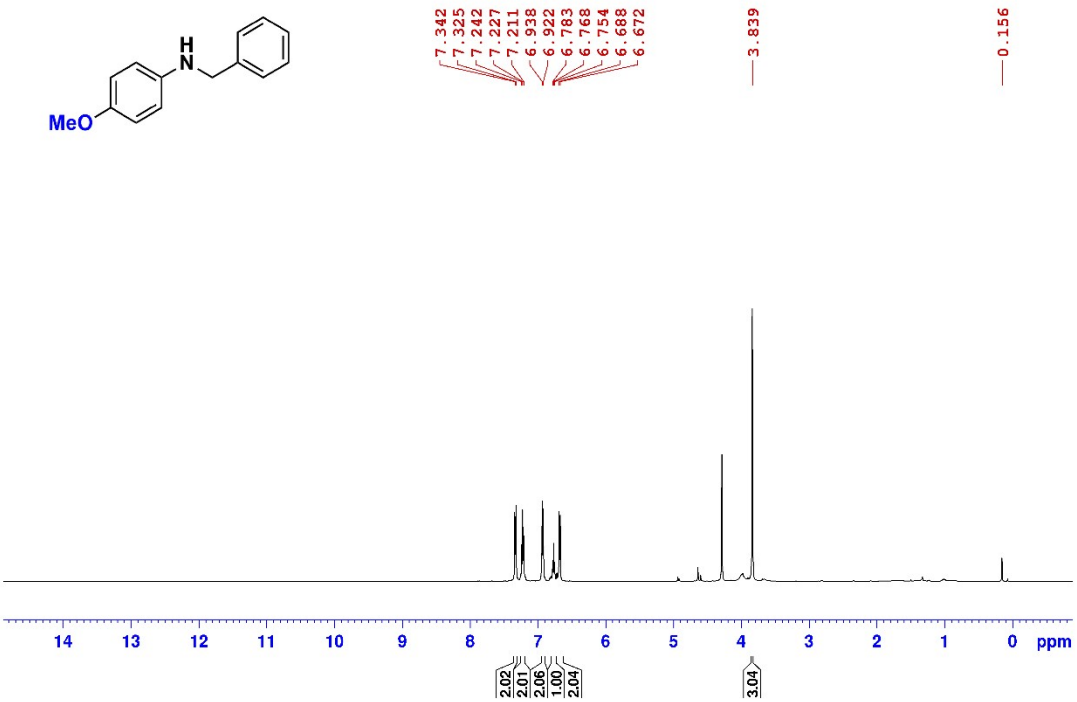


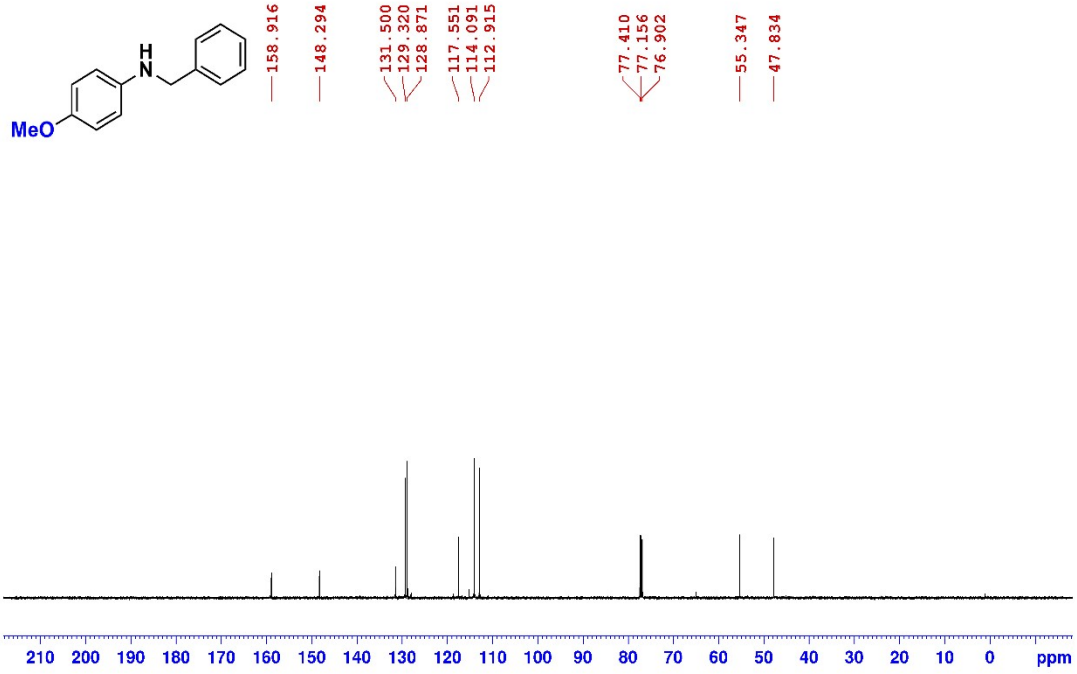
^{1}H-NMR & ^{13}C{^{1}H} (in $CDCl_3$) spectra of compound **2v**



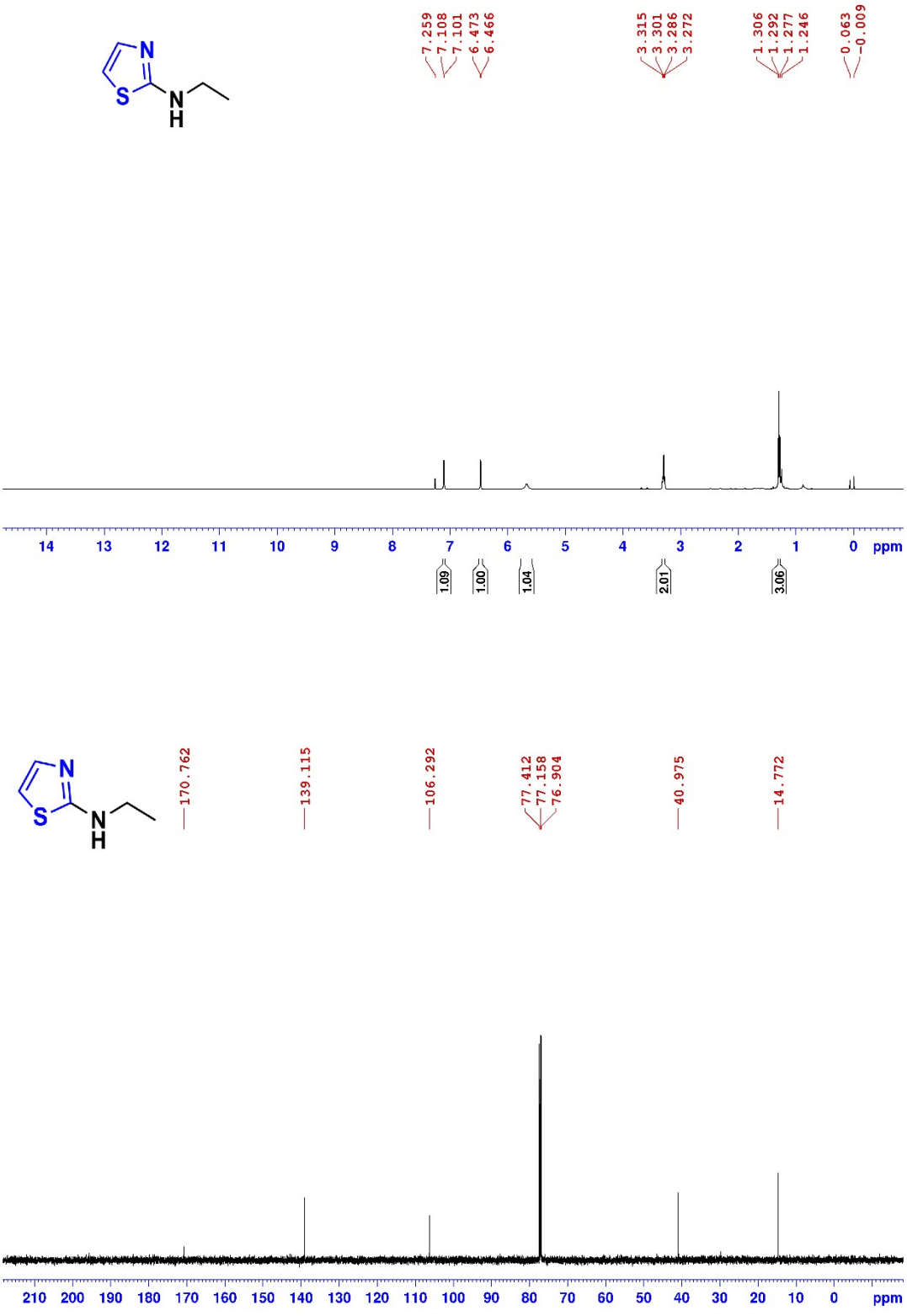


^{1}H-NMR & ^{13}C{^{1}H} (in $CDCl_3$) spectra of compound **2w**

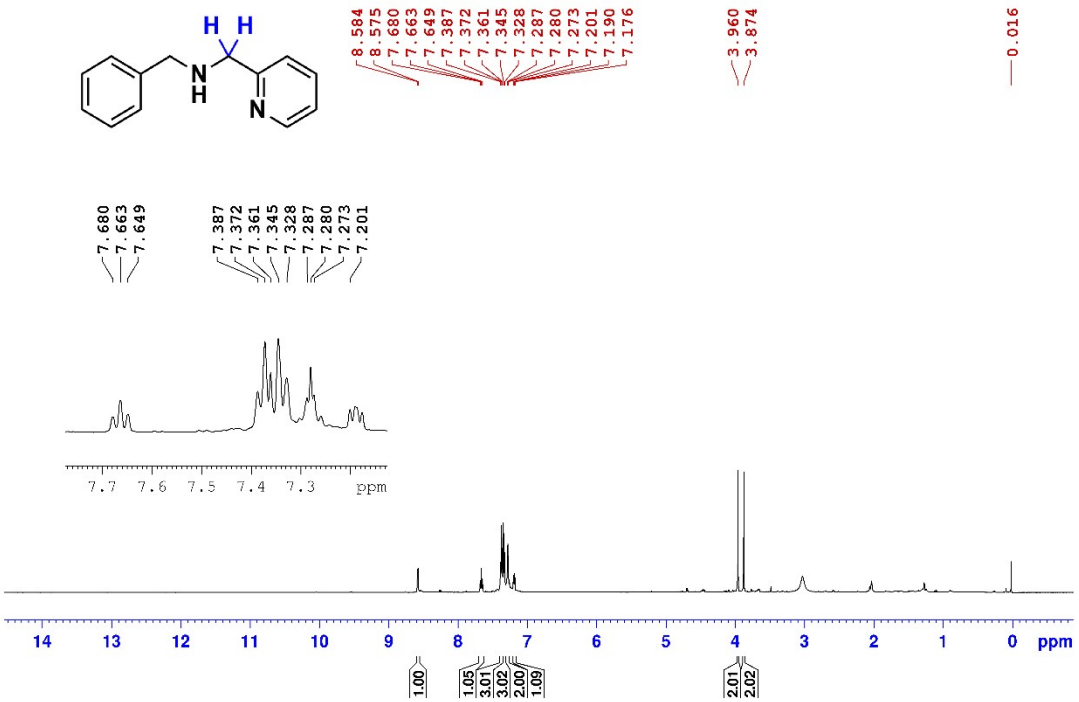


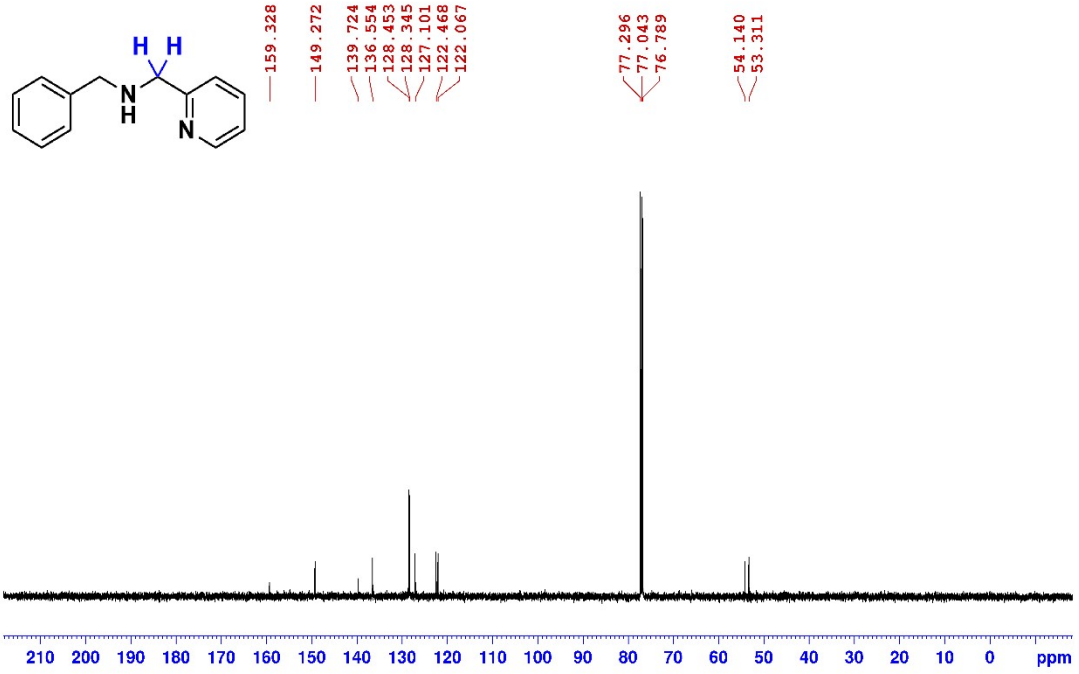


^{1}H-NMR & ^{13}C{^{1}H} (in $CDCl_3$) spectra of compound **2x**

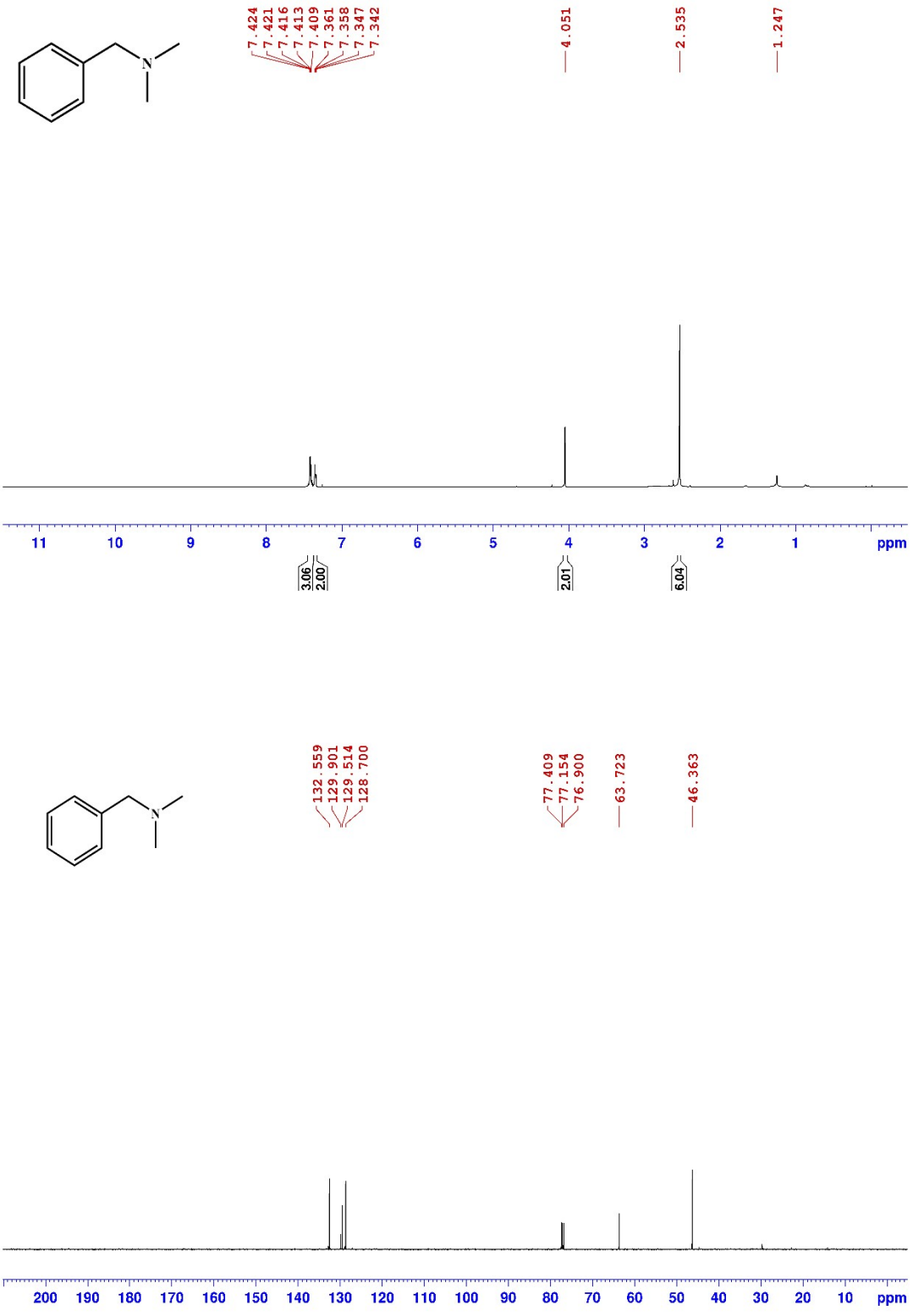


^{1}H-NMR & ^{13}C{^{1}H} (in $CDCl_3$) spectra of compound **2y**

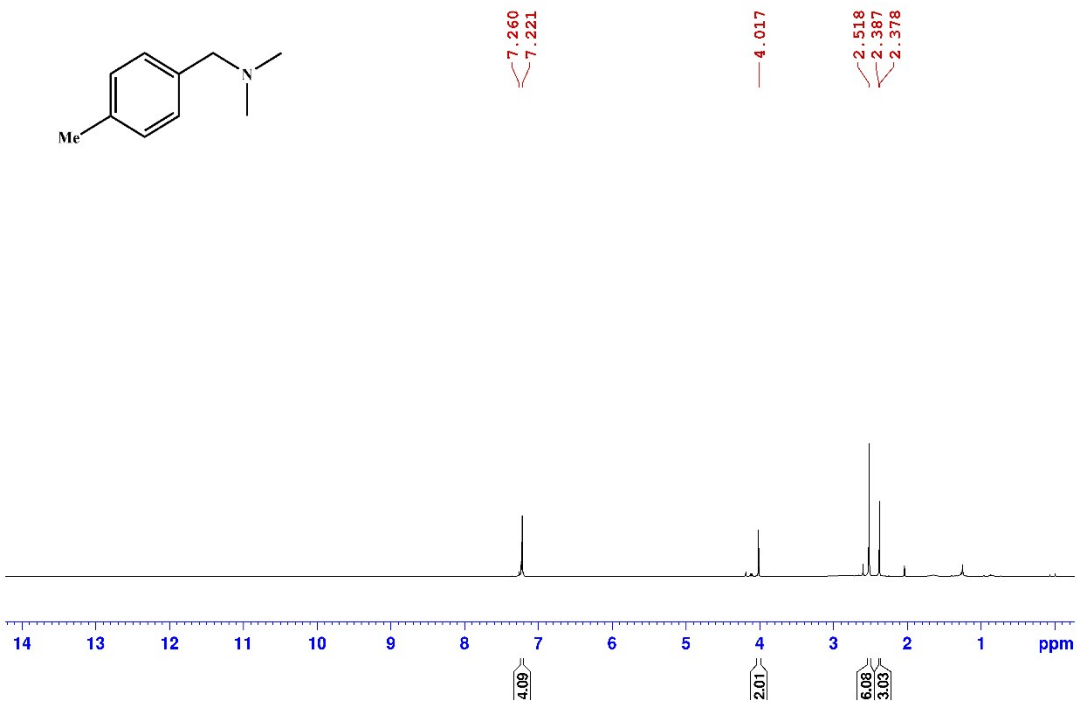


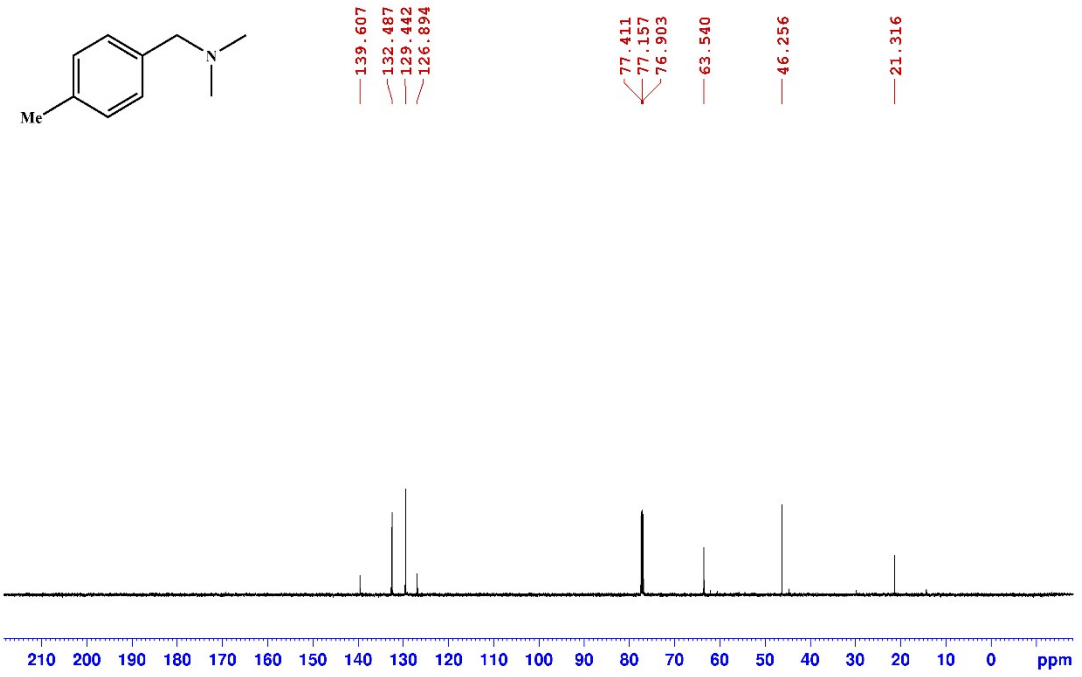


^{1}H-NMR & ^{13}C{^{1}H} (in $CDCl_3$) spectra of compound **3a**

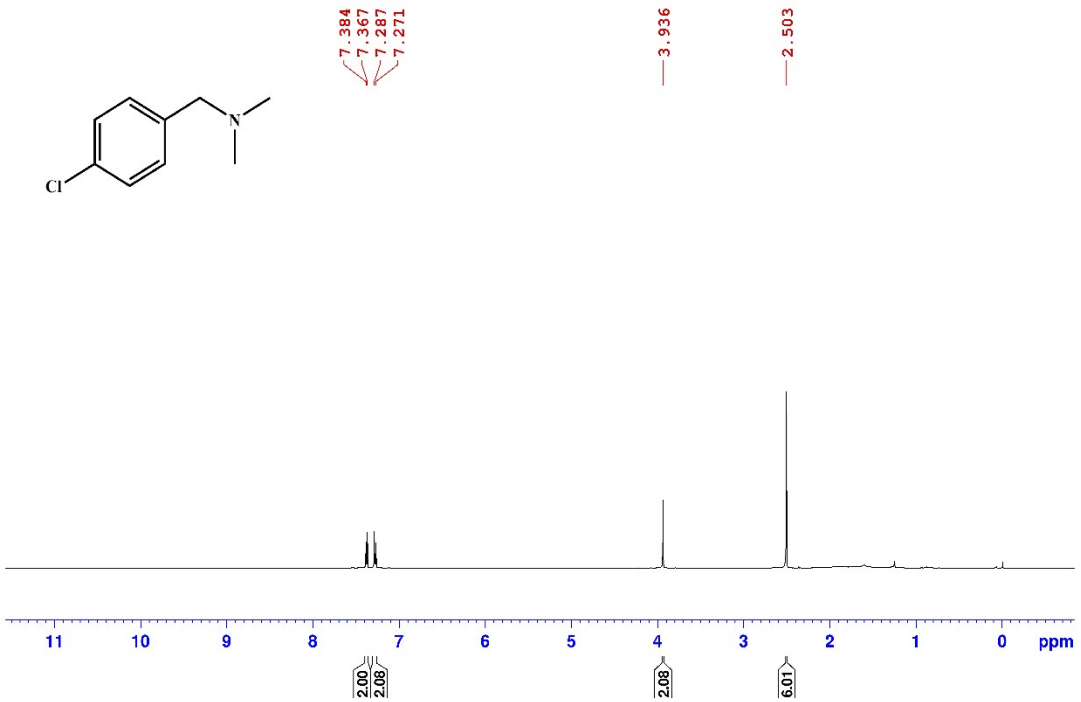


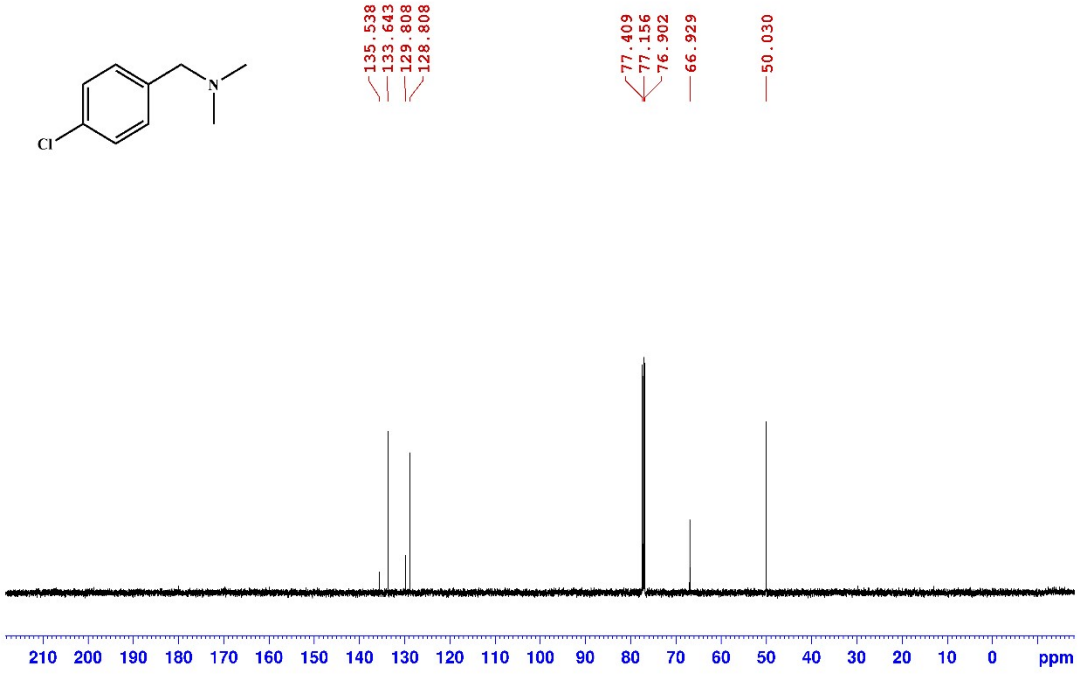
^{1}H-NMR & ^{13}C{^{1}H} (in $CDCl_3$) spectra of compound **3b**



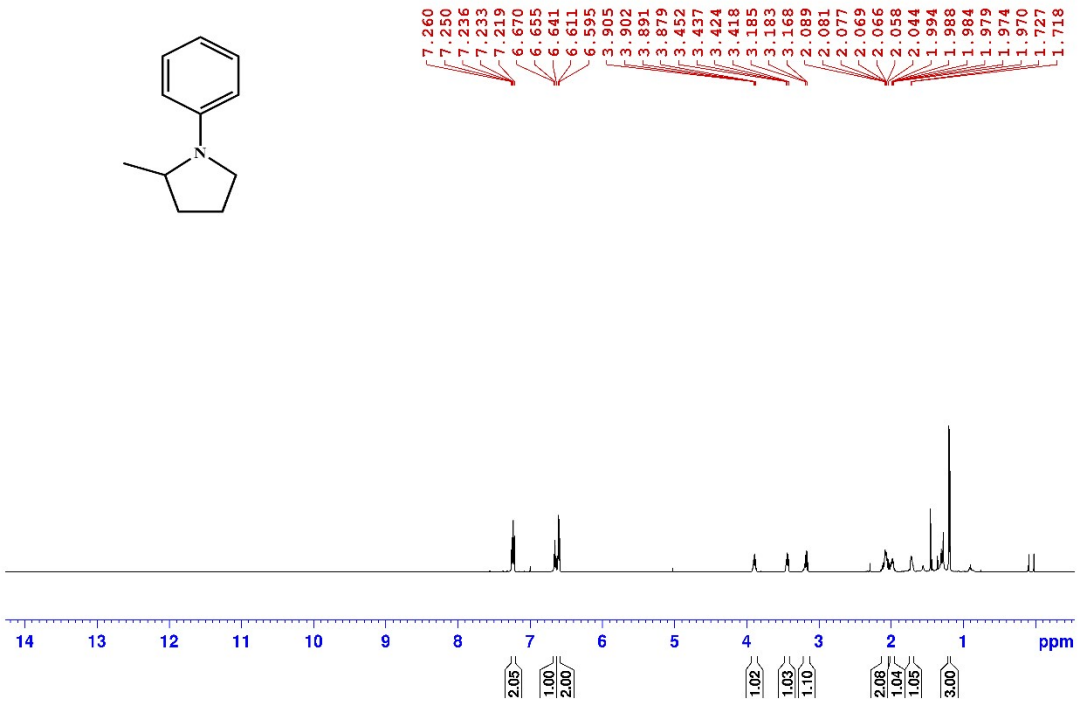


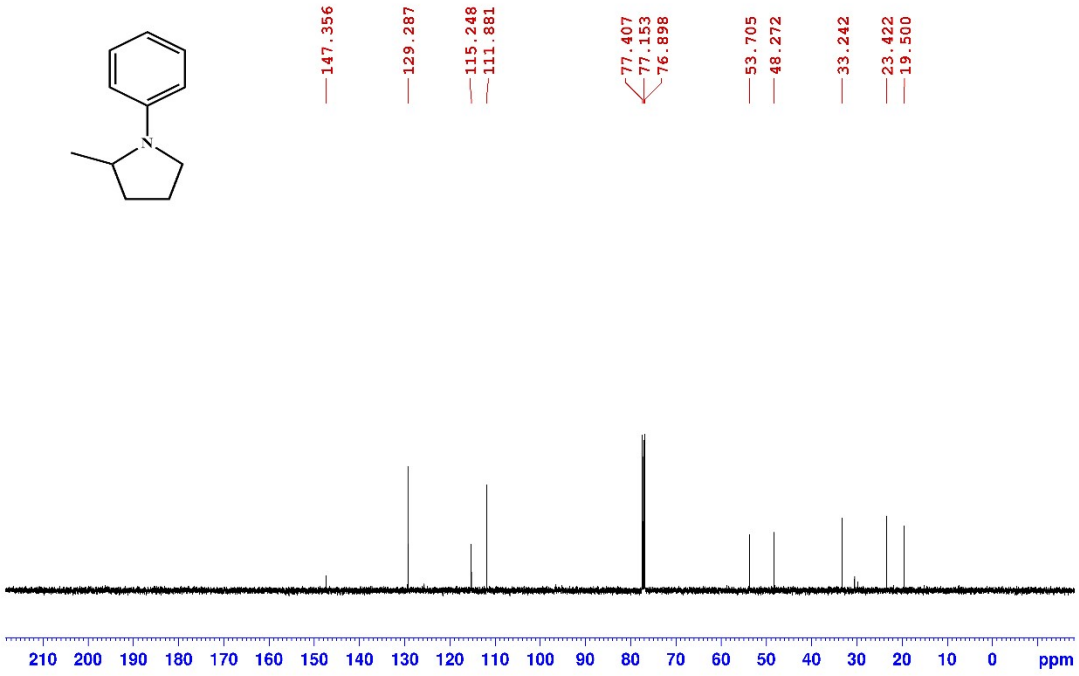
^{1}H-NMR & ^{13}C{^{1}H} (in $CDCl_3$) spectra of compound **3c**



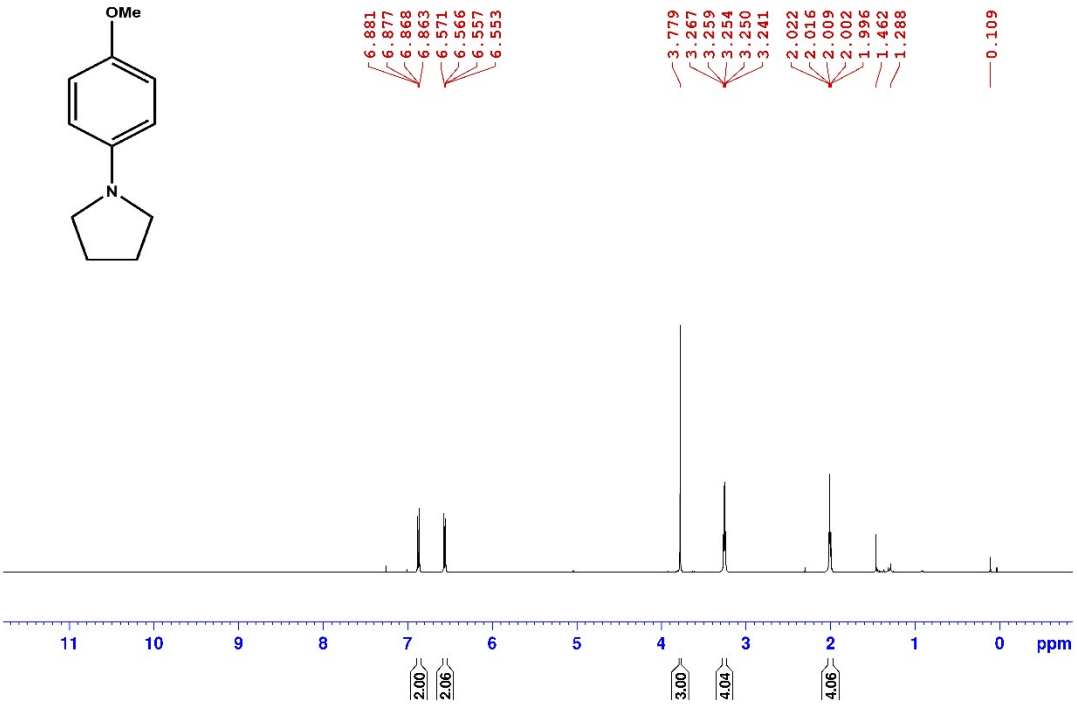


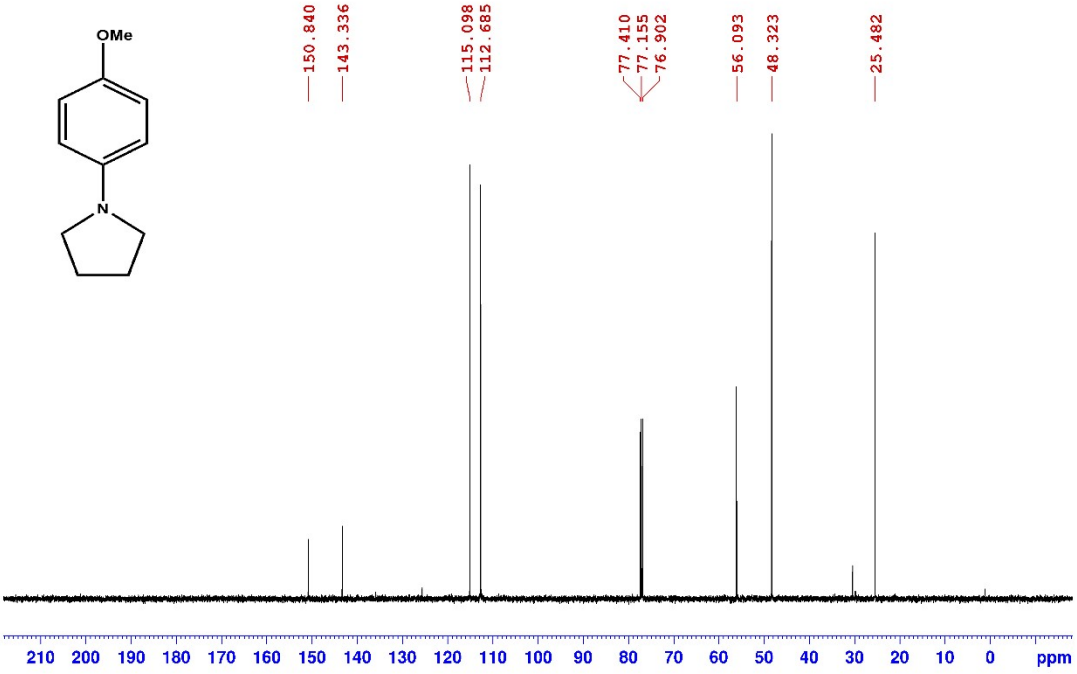
^{1}H-NMR & ^{13}C{^{1}H} (in $CDCl_3$) spectra of compound **3d**



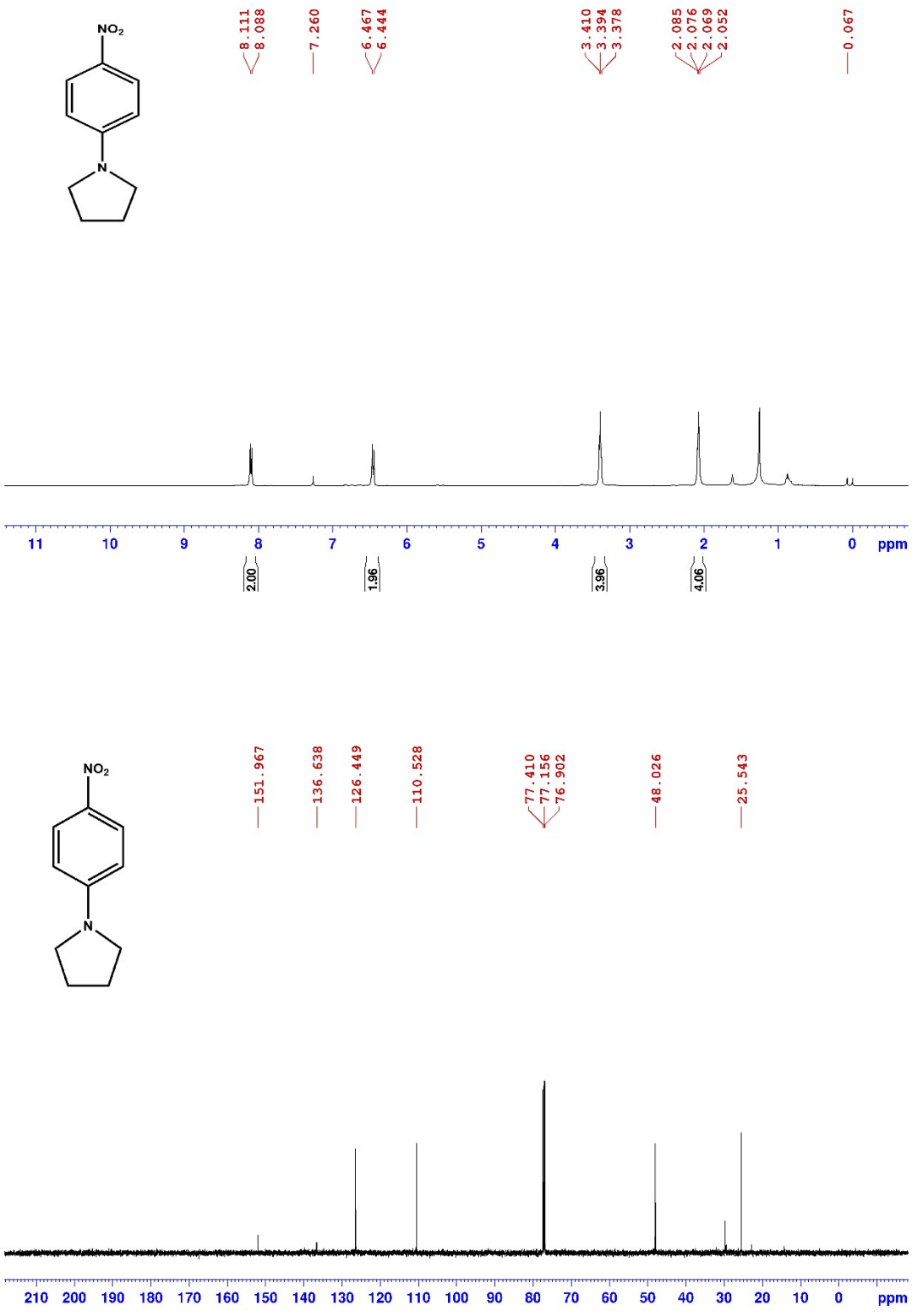


^{1}H-NMR & ^{13}C{^{1}H} (in $CDCl_3$) spectra of compound **3e**

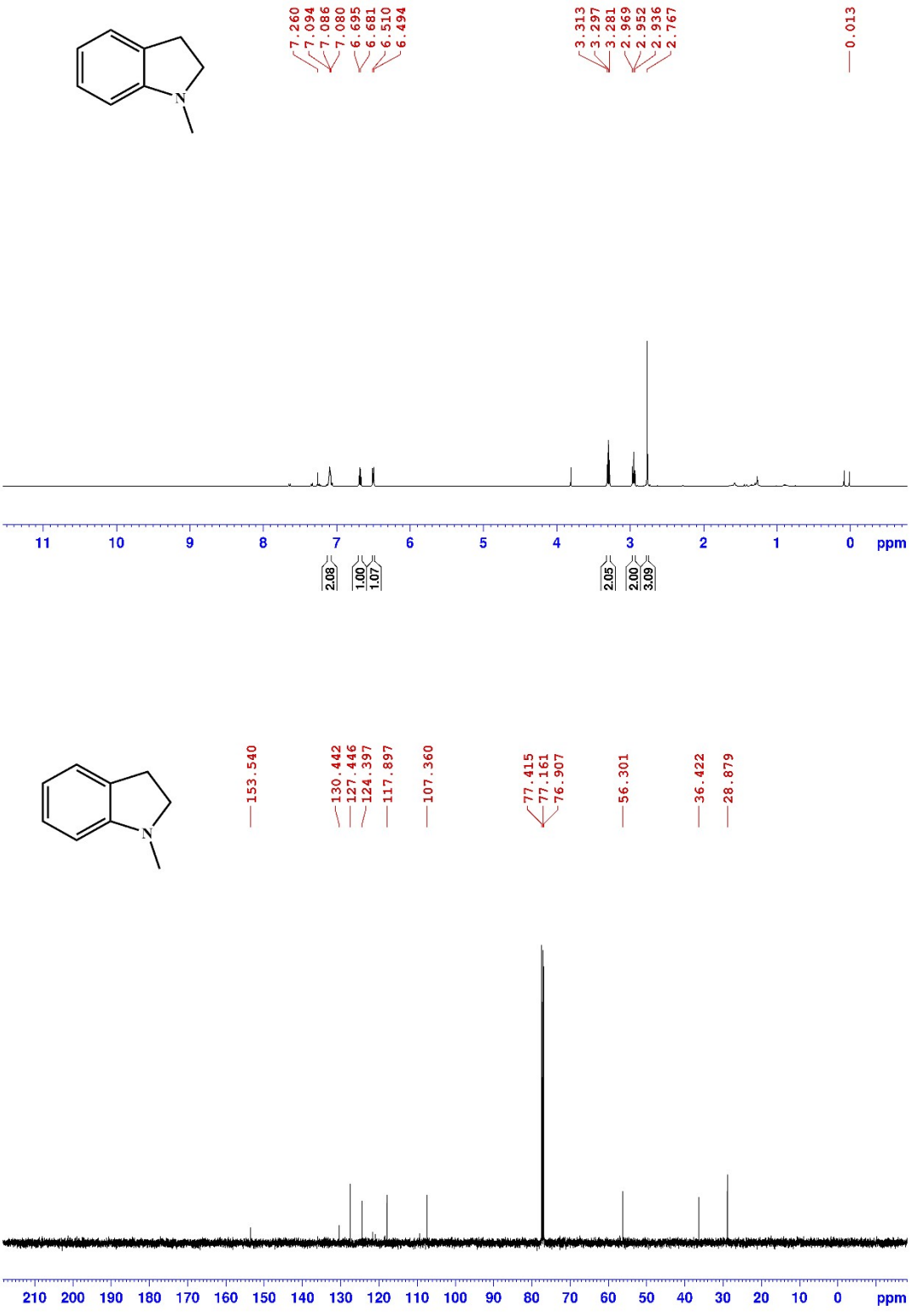




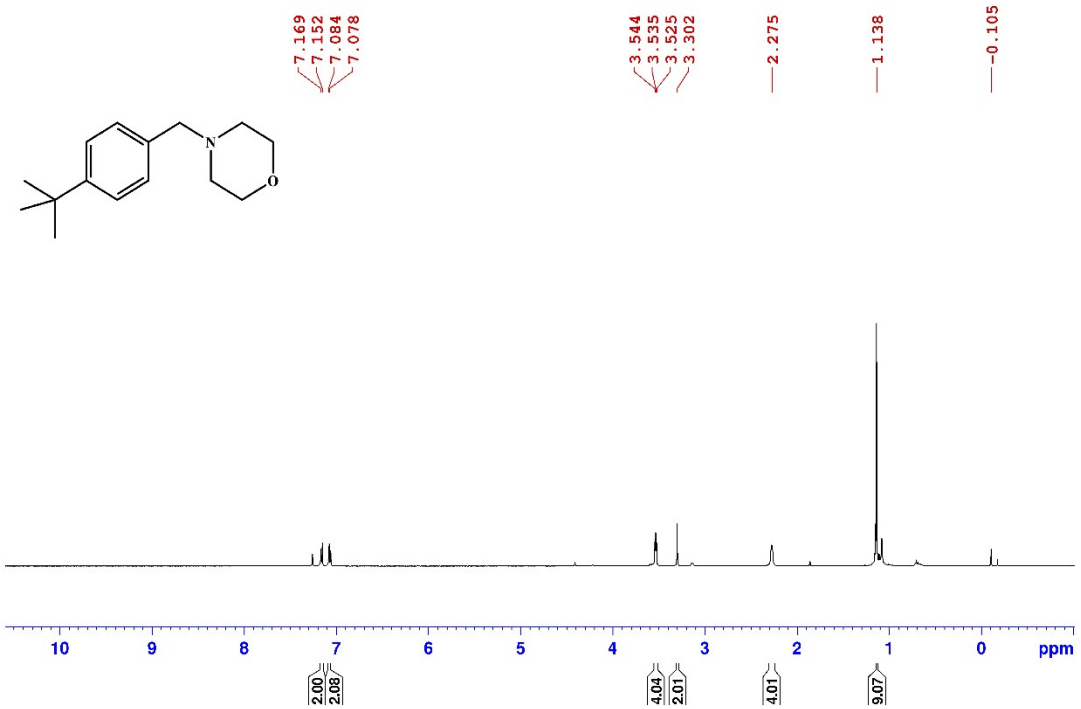
^{1}H-NMR & $^{13}C\{^{1}H\}$ (in $CDCl_3$) spectra of compound **3f**

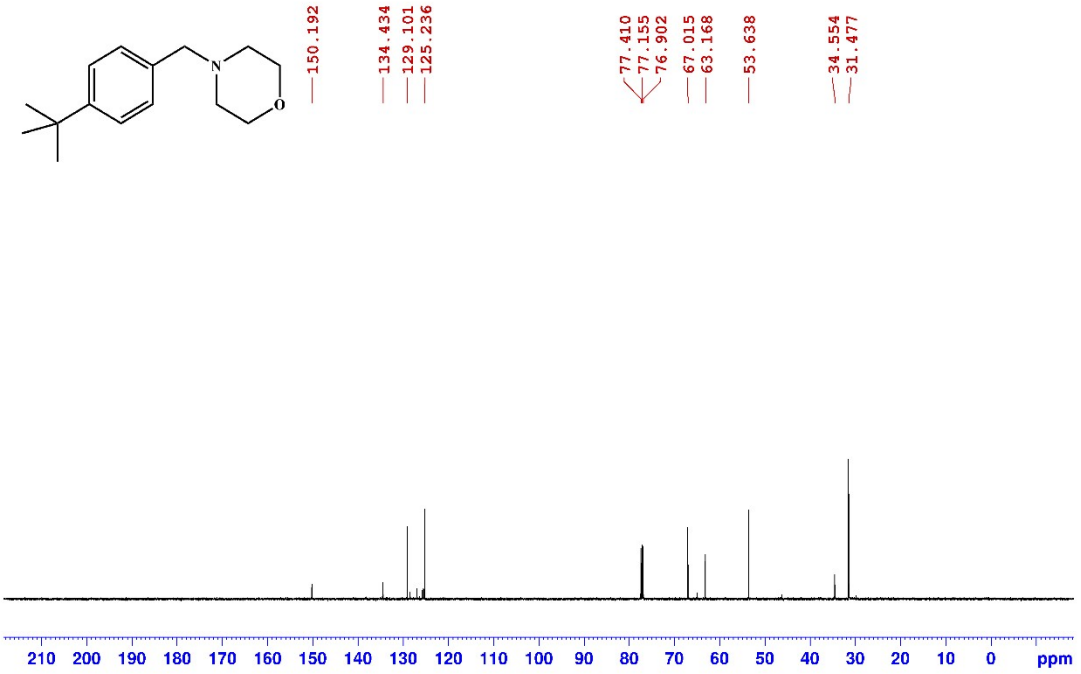


^{1}H-NMR & ^{13}C{^{1}H} (in $CDCl_3$) spectra of compound **3g**

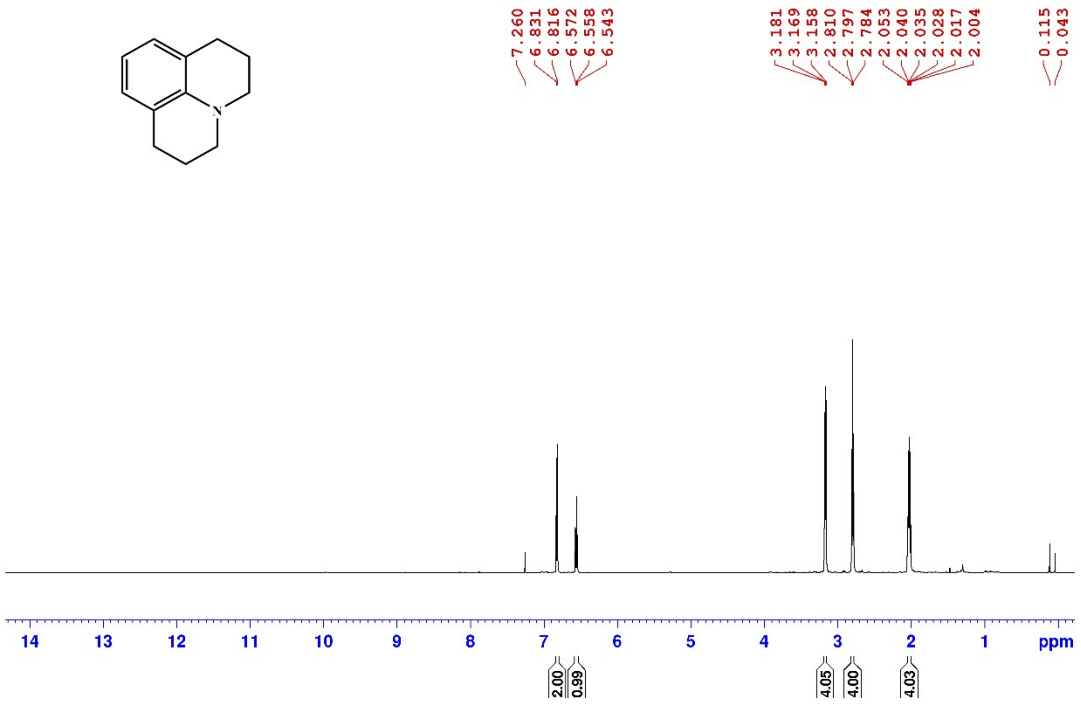


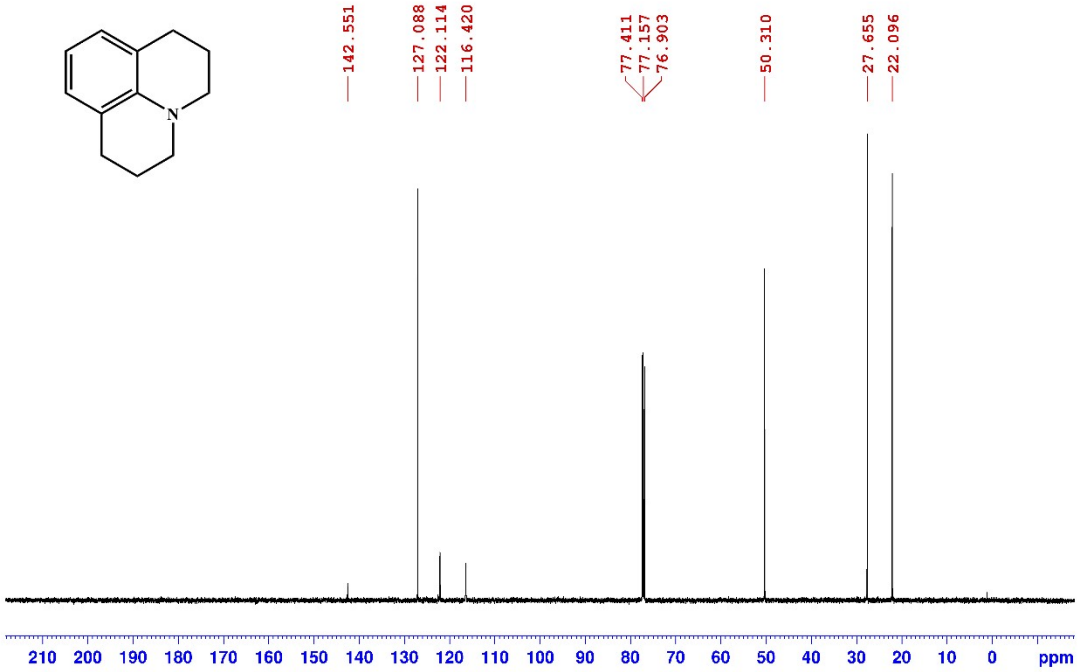
^{1}H-NMR & ^{13}C{^{1}H} (in $CDCl_3$) spectra of compound **3h**



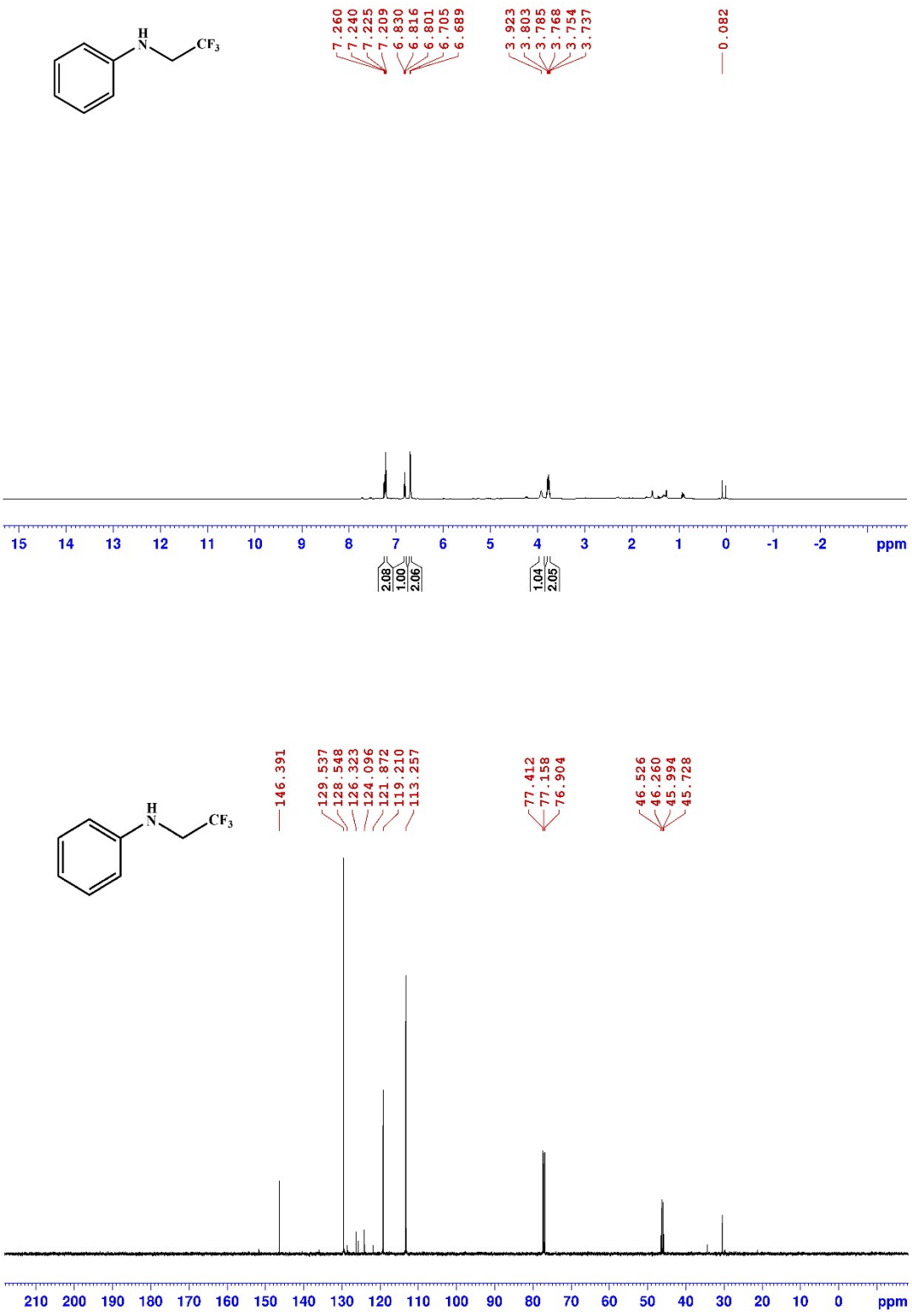


^{1}H-NMR & ^{13}C{^{1}H} (in $CDCl_3$) spectra of compound **3i**

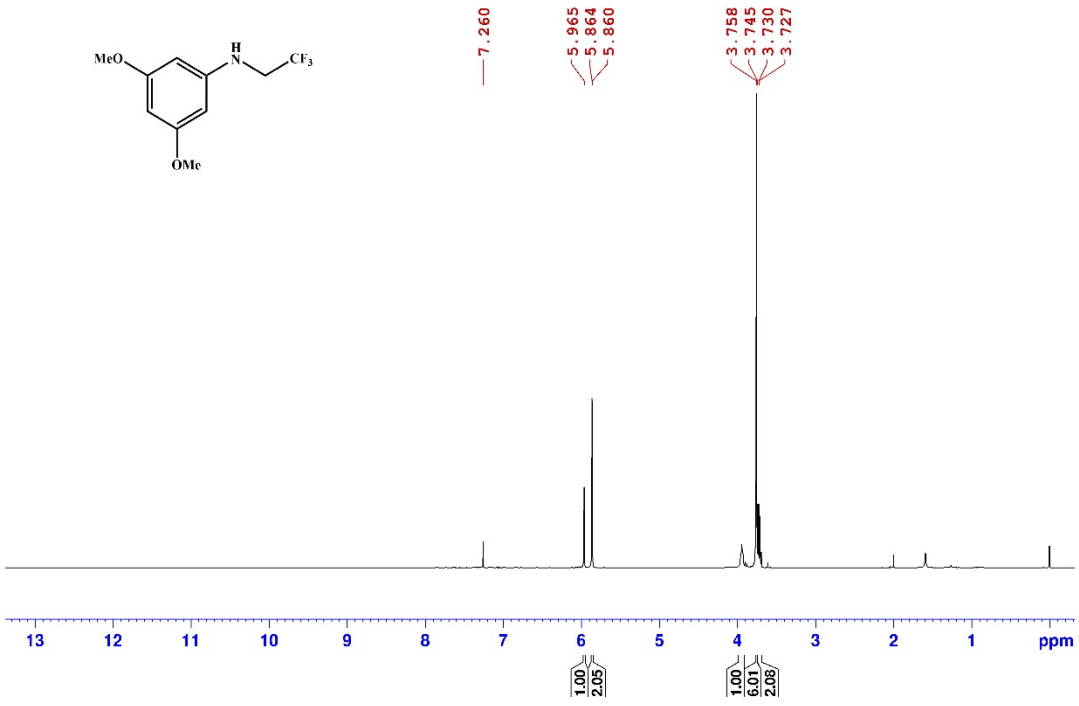


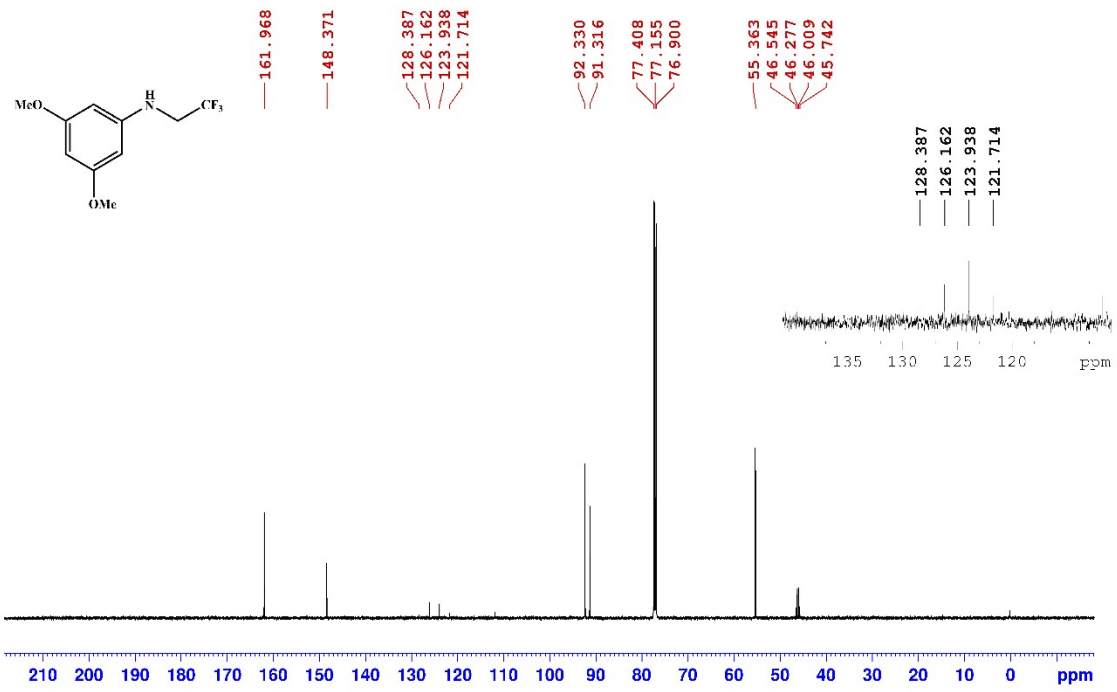


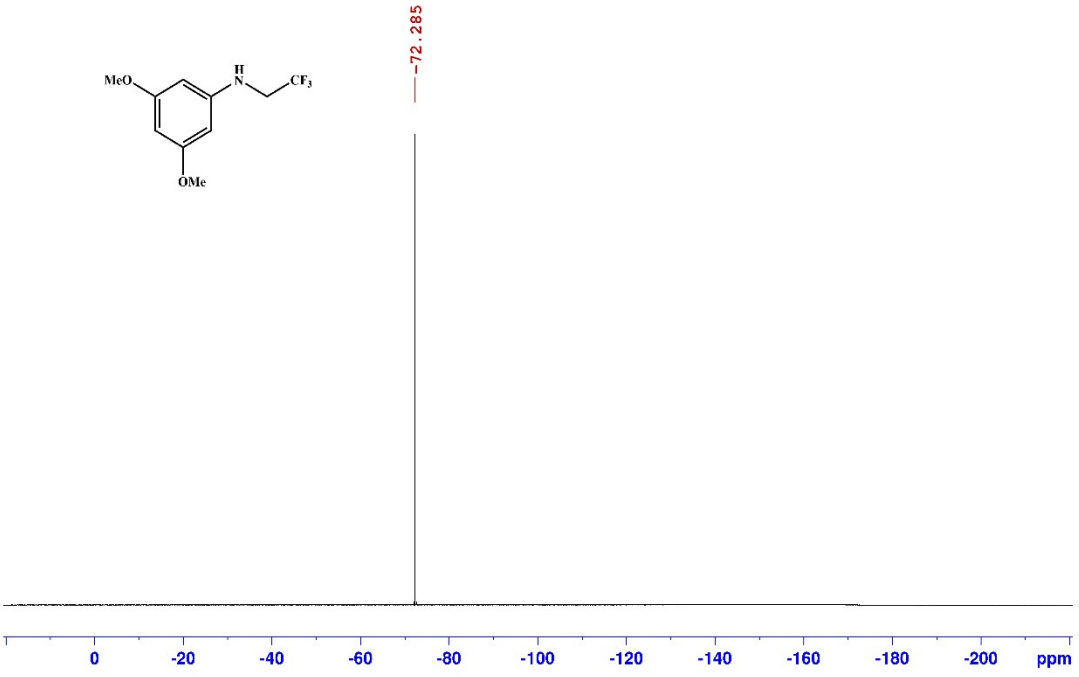
^{1}H-NMR, ^{13}C{^{1}H} & ^{19}F{^{1}H} (in $CDCl_3$) spectra of compound **4a**



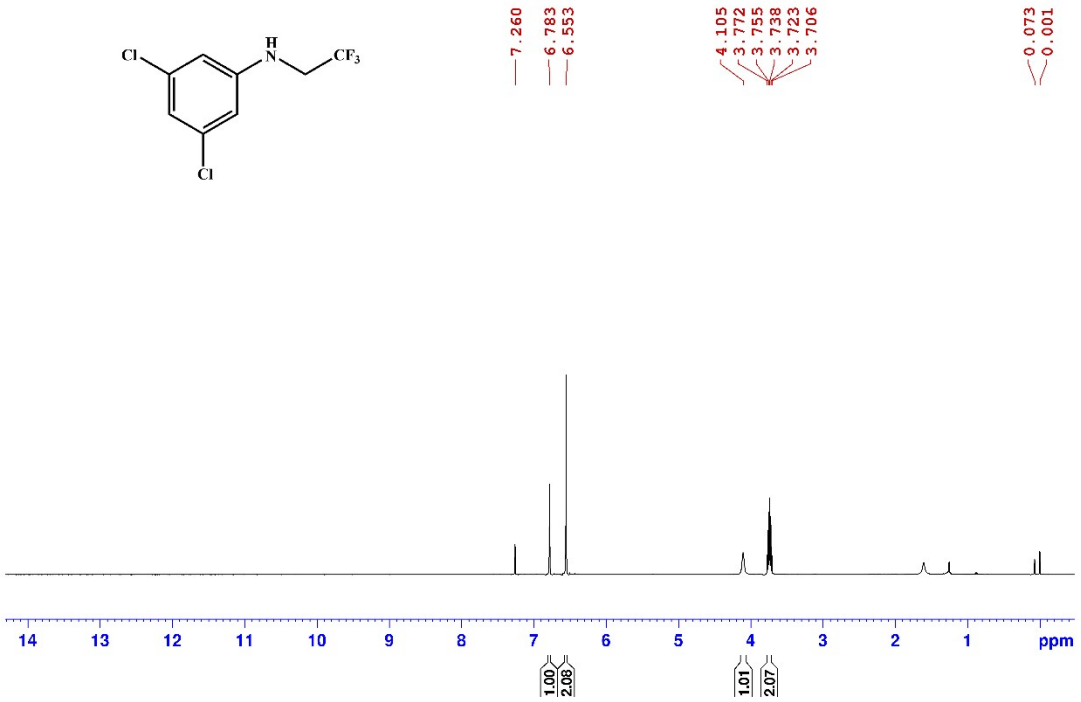
^{1}H-NMR, ^{13}C{^{1}H} & ^{19}F{^{1}H} (in $CDCl_3$) spectra of compound **4b**

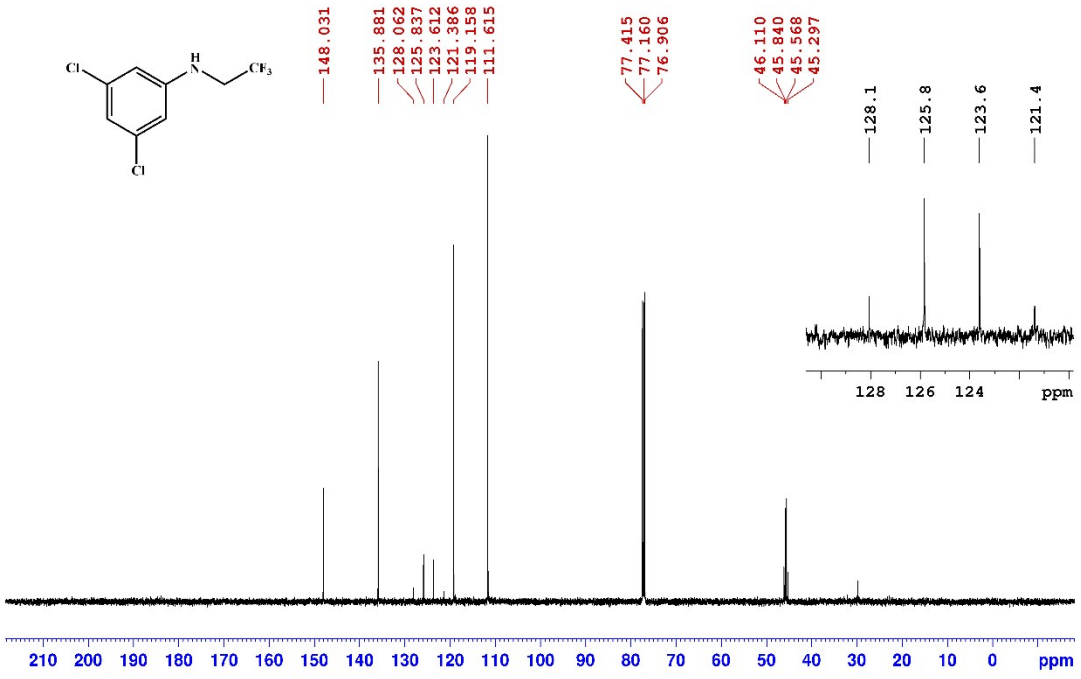


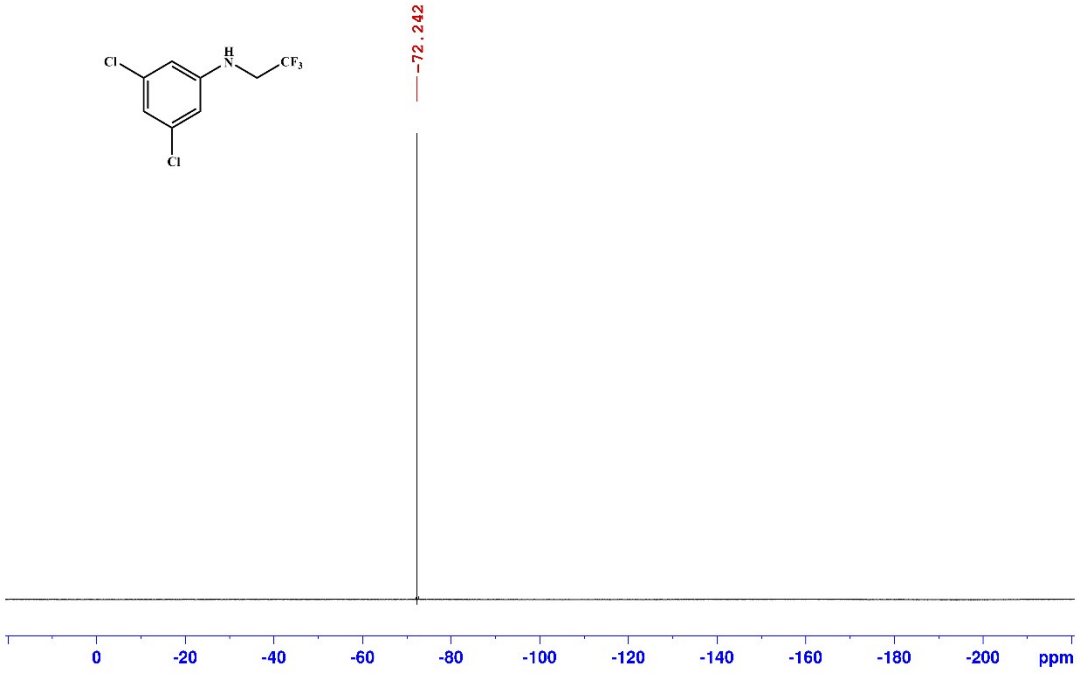

MeO
H
N
CF3
OMe
161.968
148.371
128.387
126.162
123.938
121.714
92.330
91.316
77.408
77.155
76.900
55.363
46.545
46.277
46.009
45.742
128.387
126.162
123.938
121.714
135 130 125 120 ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


MeO
H
N
CF3
OMe
-72.285
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm

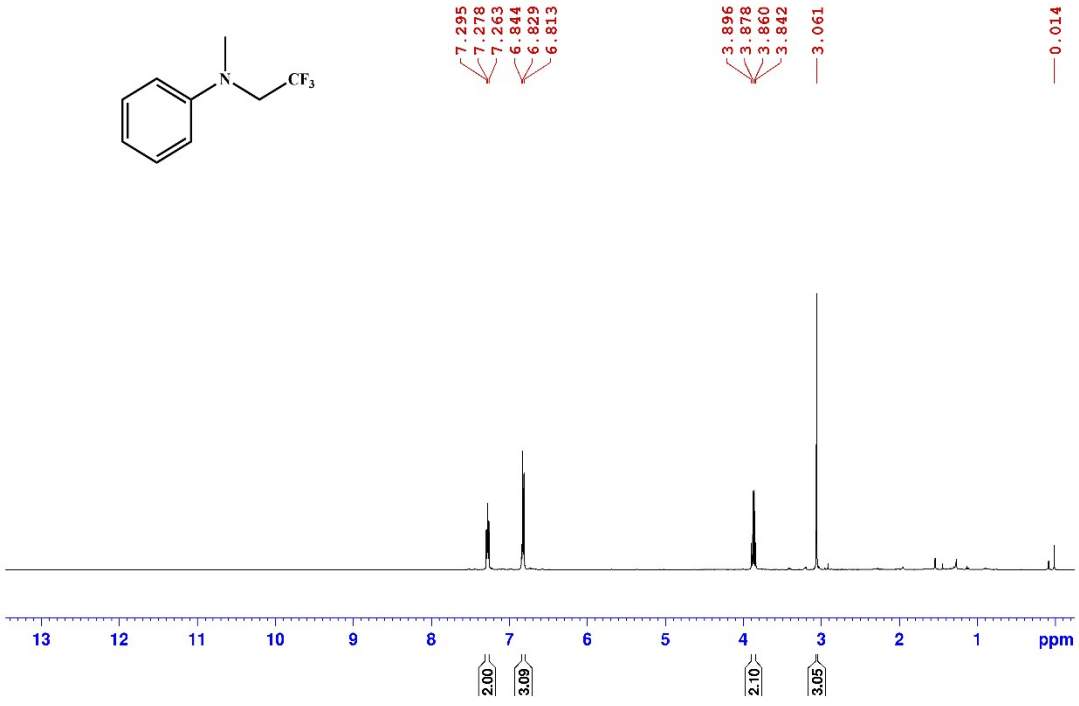
^{1}H-NMR, ^{13}C{^{1}H} & ^{19}F{^{1}H} (in $CDCl_3$) spectra of compound **4c**

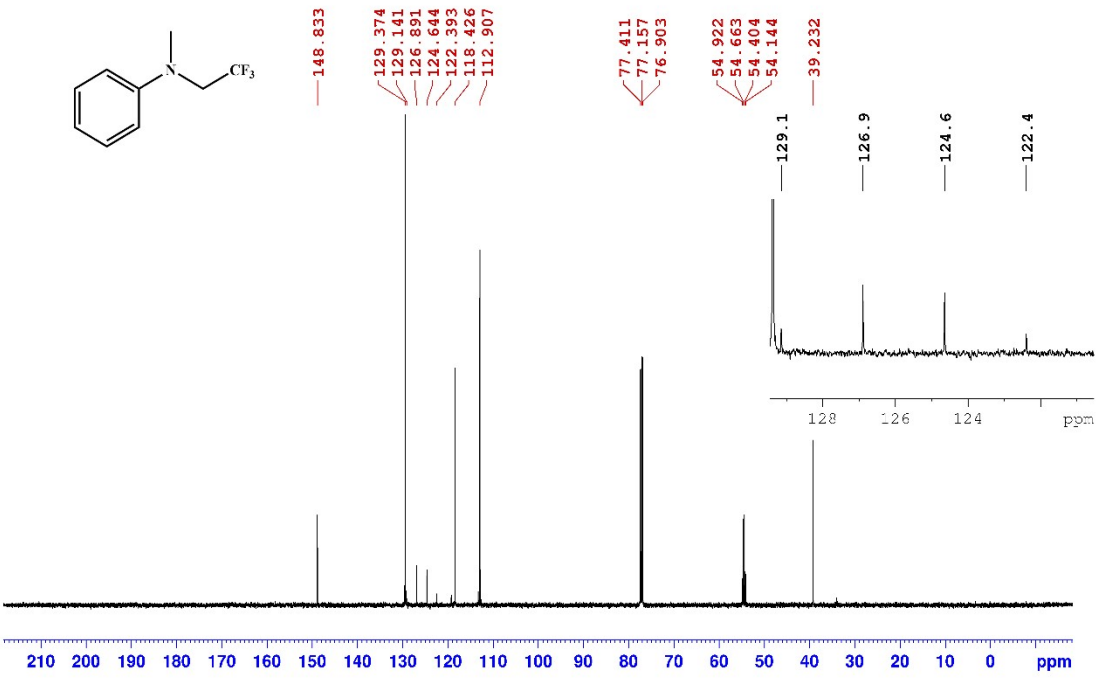






^{1}H-NMR, ^{13}C{^{1}H} & ^{19}F{^{1}H} (in $CDCl_3$) spectra of compound **4d**

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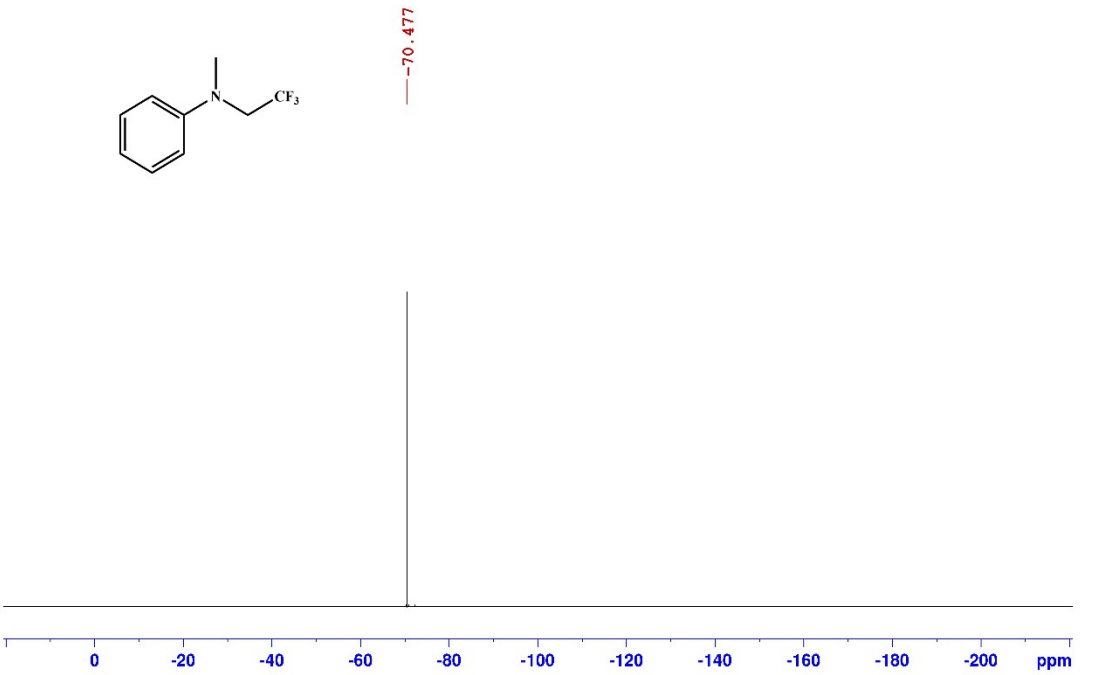
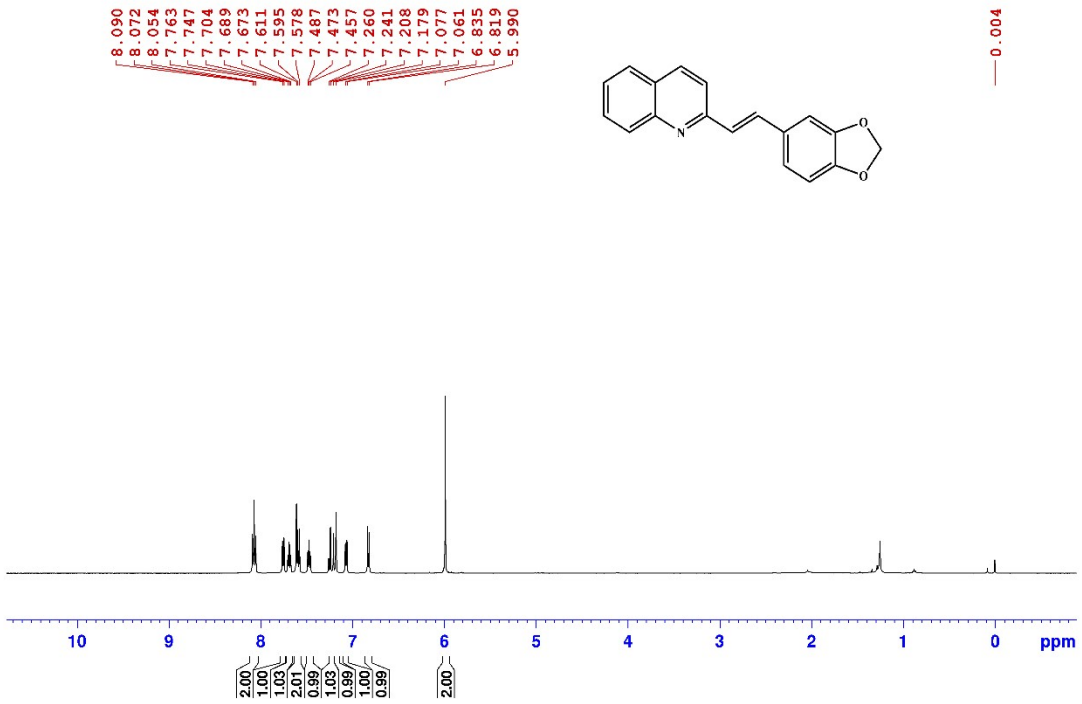
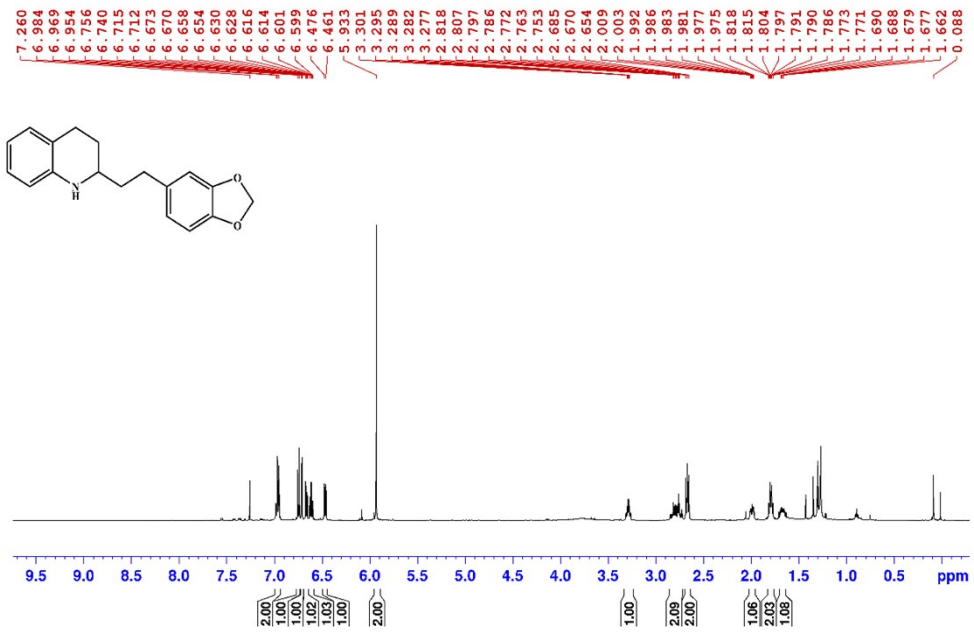
129.374
129.141
126.891
124.644
122.393
118.426
112.907
77.411
77.157
76.903
54.922
54.663
54.404
54.144
39.232
129.1
126.9
124.6
122.4
128
126
124
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


-70.477
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm

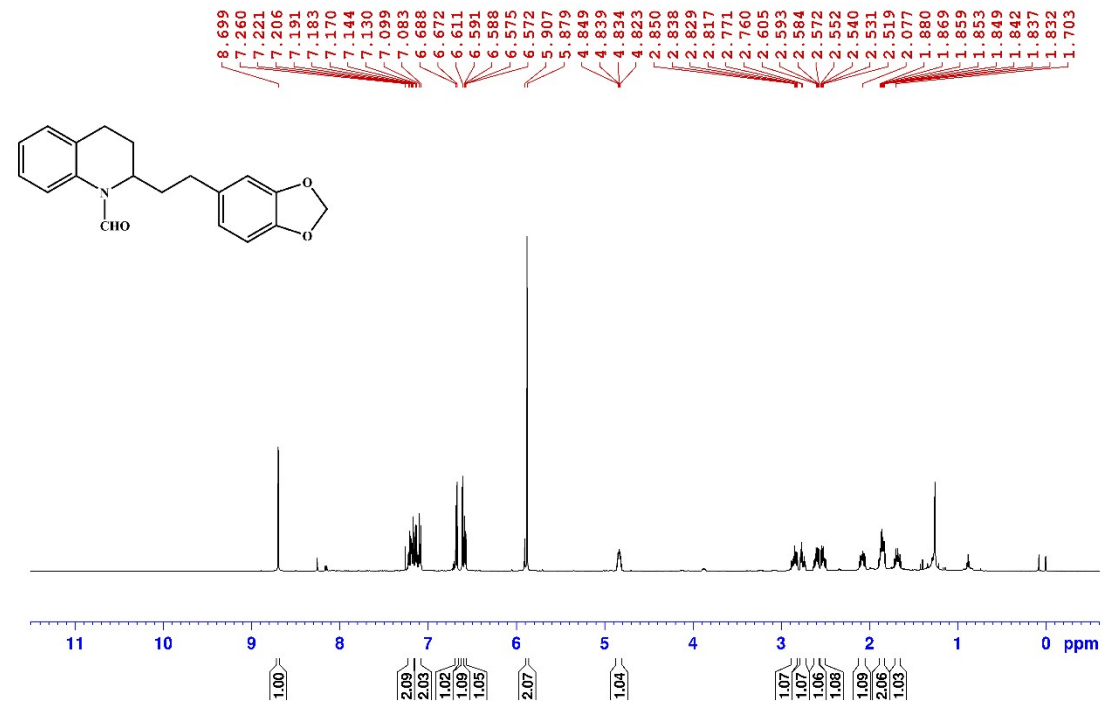
^{1}H-NMR (in $CDCl_3$) spectra of compound **5b**

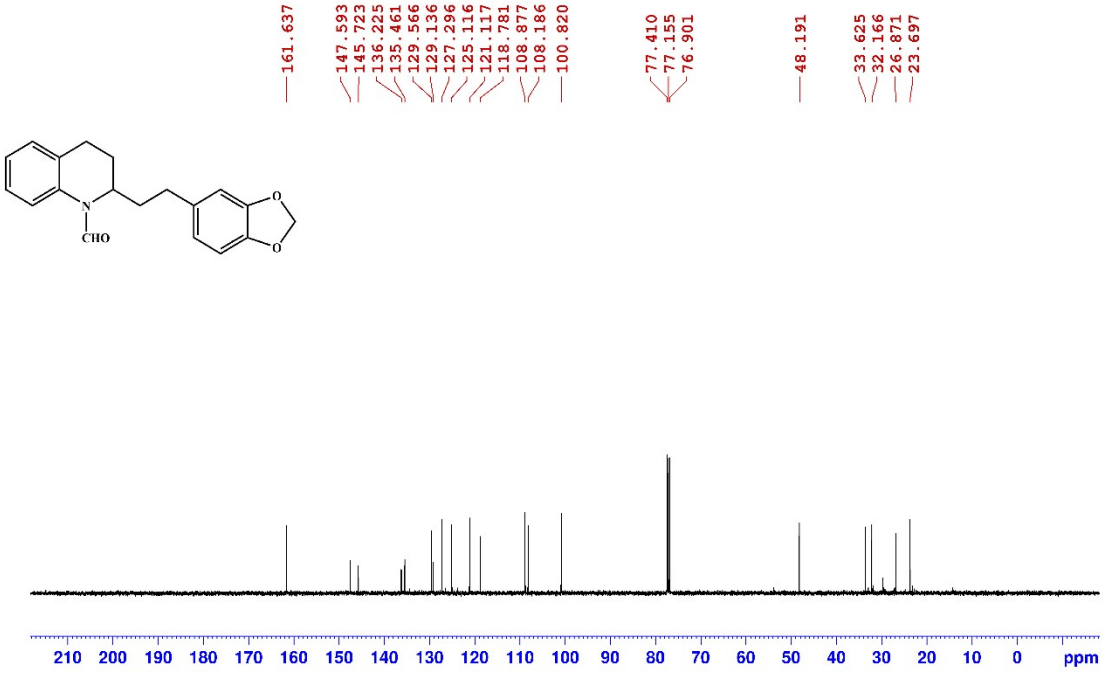


^{1}H-NMR (in $CDCl_3$) spectra of compound **5c**

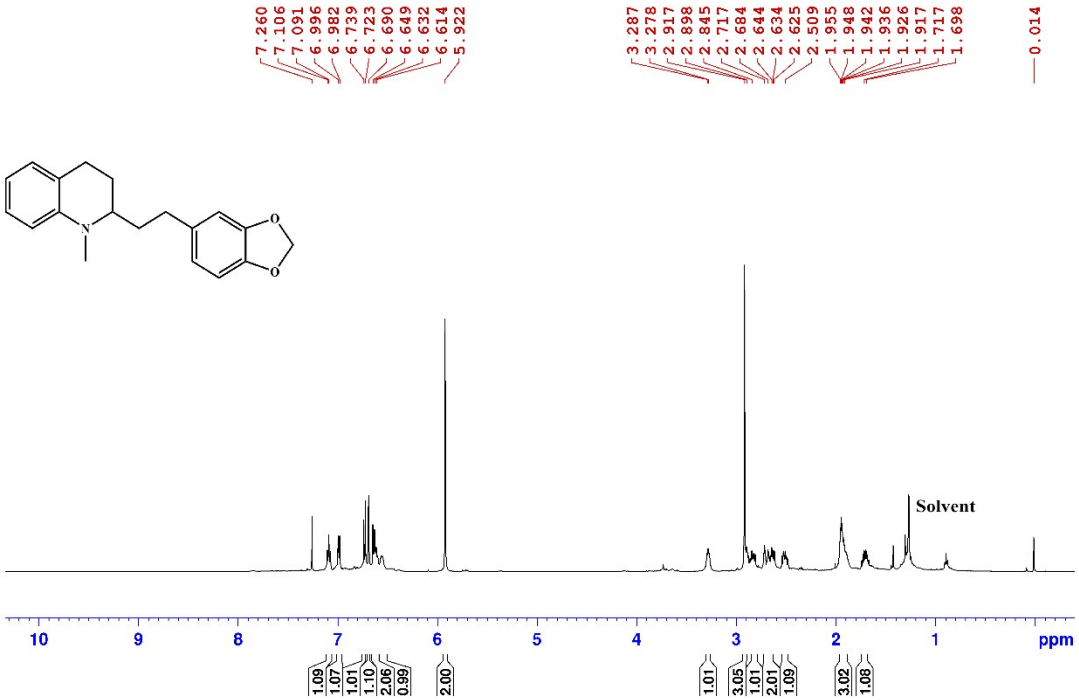


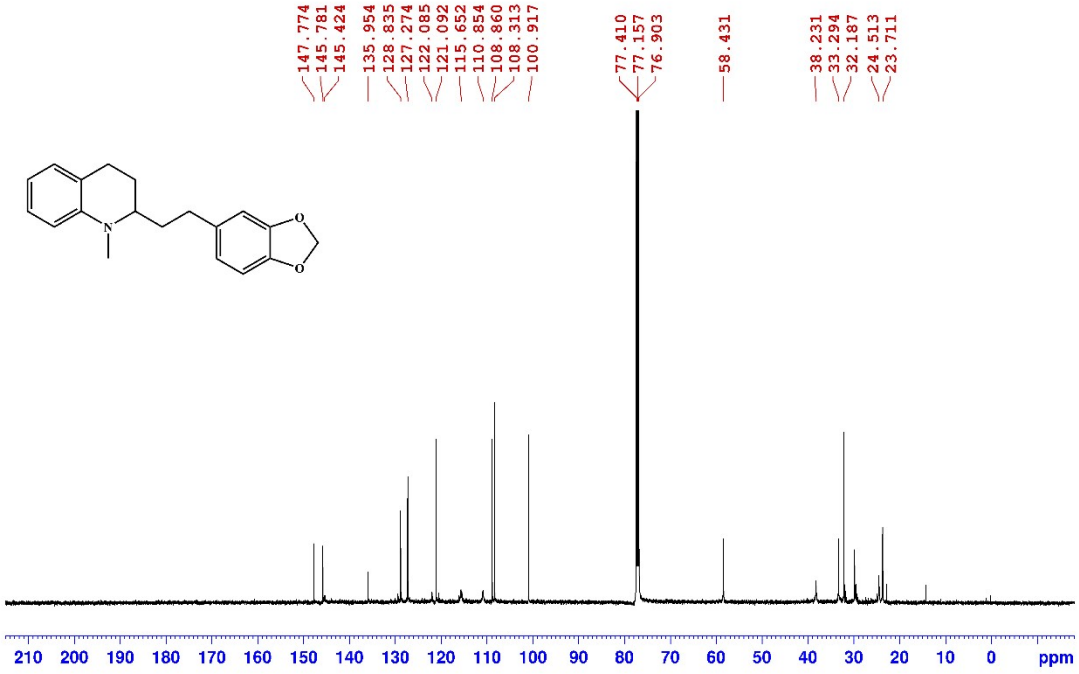
^{1}H-NMR & ^{13}C{^{1}H} (in $CDCl_3$) spectra of compound **1e**



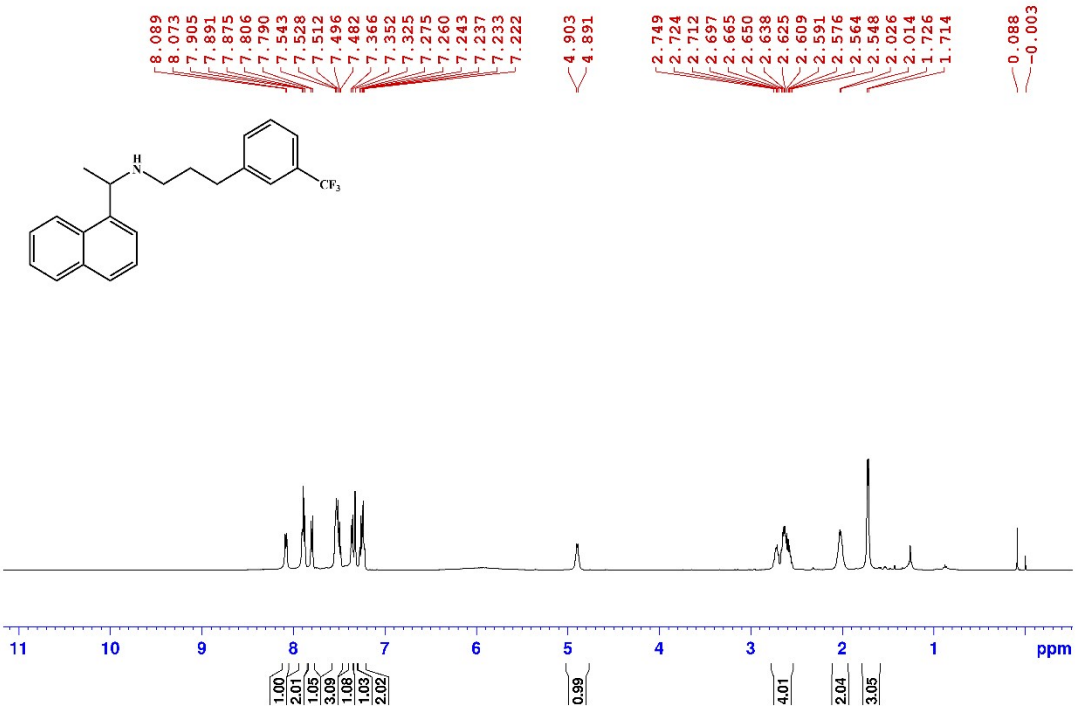


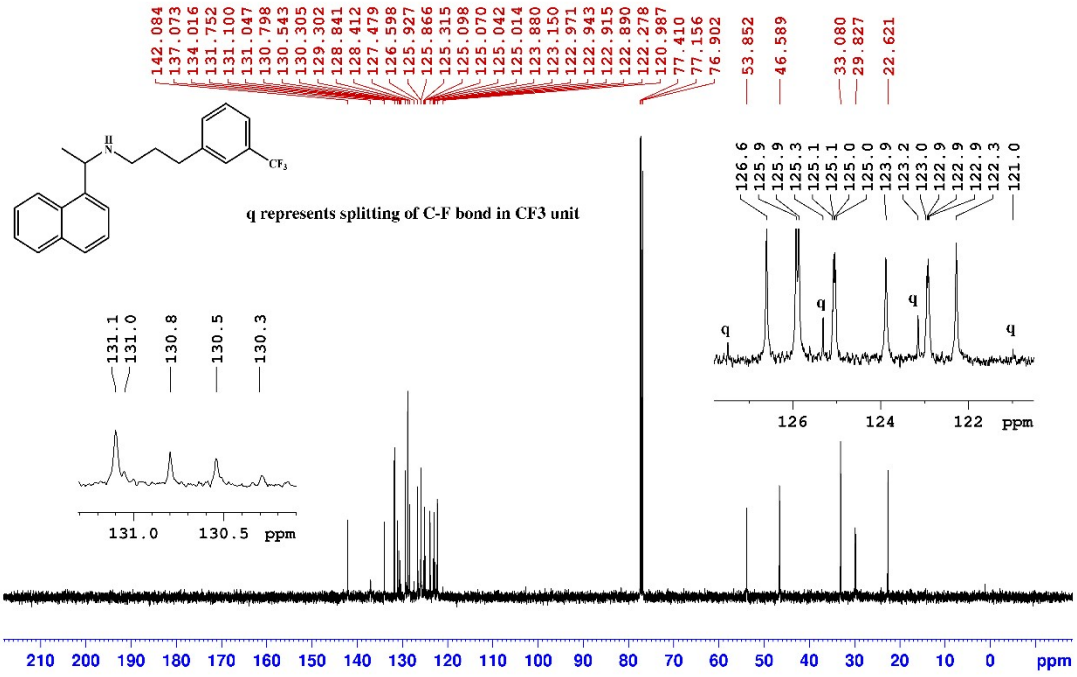
^{1}H-NMR & ^{13}C{^{1}H} (in $CDCl_3$) spectra of compound **5a**

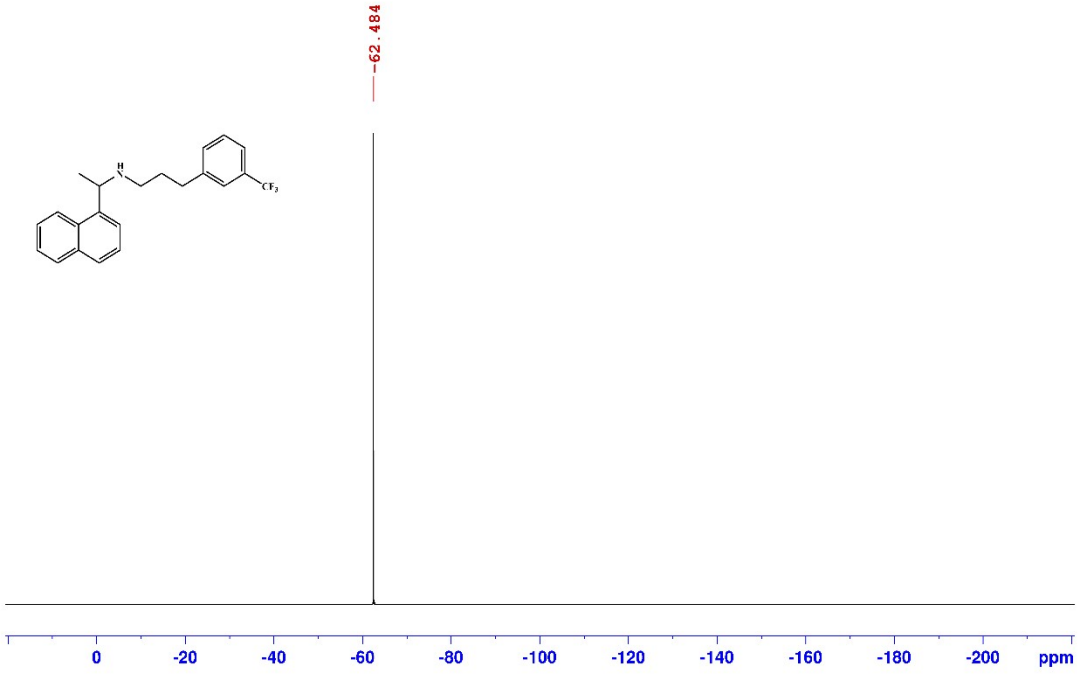




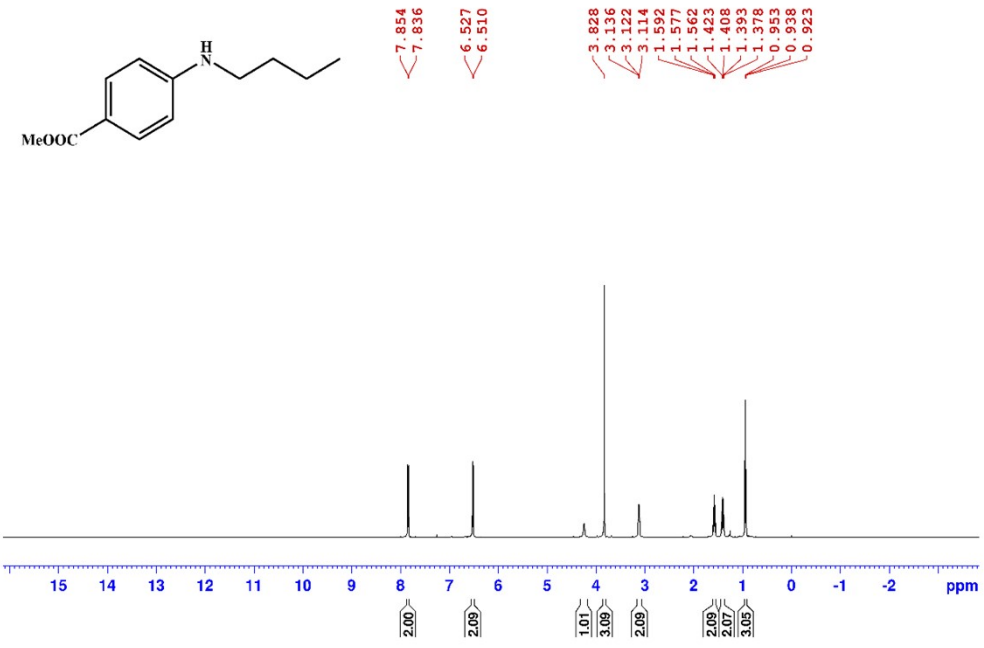
^{1}H-NMR, ^{13}C{^{1}H} & ^{19}F{^{1}H} (in $CDCl_3$) spectra of compound **6a**

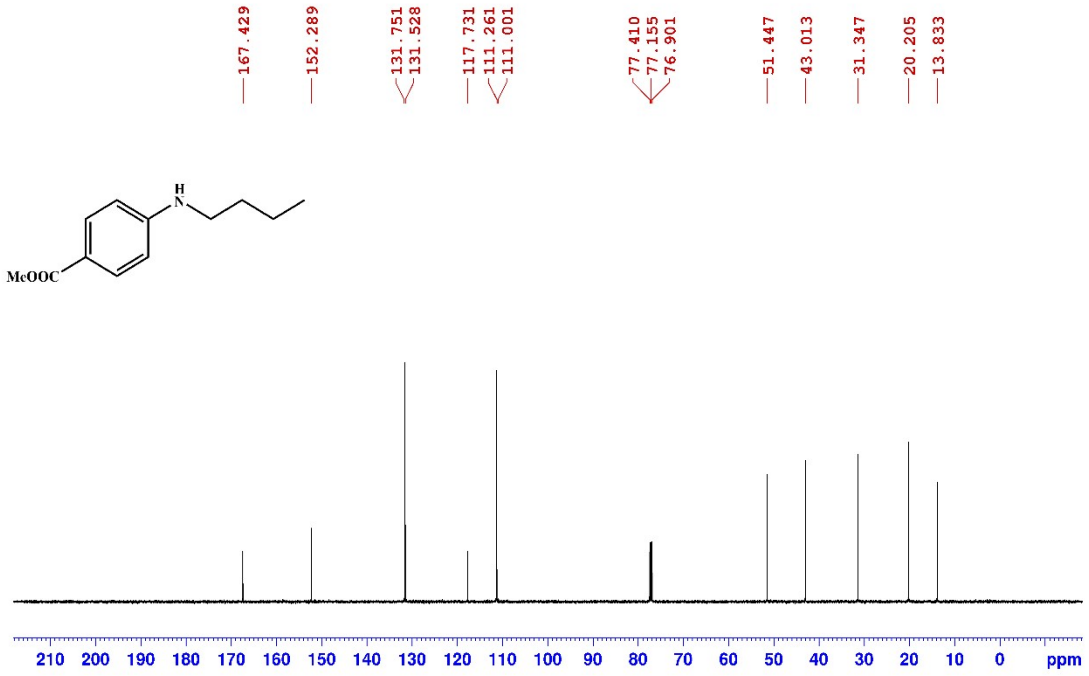






^{1}H-NMR & ^{13}C{^{1}H} (in $CDCl_3$) spectra of compound **7a**





N. Computational details

All the density functional theory (DFT) calculations were performed using *Gaussian 09 Revision D.01*.[6] The geometry optimisation of all the stationary points in gas phase was performed using M06-2X[7] functional with a combination of a LanL08(d)[8] basis set for iodine (I) consisting of a single polarization and diffusion function and a Pople type basis set with single polarisation 6-31g(d)[9] for all other atoms. To confirm the nature of the stationary points, the harmonic vibrational frequencies of normal modes were computed using the same level of theory. From the vibrational frequency analysis, it was confirmed that all the intermediates are at minimum with no imaginary frequencies, whereas all the transition states were accompanied with exactly one imaginary frequency. Additionally, the intrinsic reaction coordinates (IRC)[10] was followed to verify the energy profiles connecting the key transition structures to the correct associated local minima. Further, the single point energies were calculated using LanL08(d) basis set for iodine (I) and a higher basis set 6-31g++(d, p) consisting of double polarisation and diffusion function was used for other atoms. To incorporate the effect of solvent, a continuum solvation model SMD[11] was used with DCE as the solvent where the continuous quantum mechanical charge density of the solute serves as the basis for this model. All the 3D structures were illustrated using CYLview[12] software.

Coordinates for optimised structure

Ammonia borane (NH_3BH_3)

Zero-point correction= 0.071075 (Hartree/Particle)

Thermal correction to Energy= 0.074883

Thermal correction to Enthalpy= 0.075827

Thermal correction to Gibbs Free Energy= 0.048639

Sum of electronic and zero-point Energies= -83.084153

Sum of electronic and thermal Energies= -83.080346

Sum of electronic and thermal Enthalpies= -83.079401

Sum of electronic and thermal Free Energies= -83.106589

Cartesian coordinates

N	0.00000000	0.00000000	0.72827700
H	0.84461000	0.43869500	1.09220900
H	-0.04238400	-0.95080100	1.09220900
H	-0.80222600	0.51210600	1.09220900
B	0.00000000	0.00000000	-0.93298100
H	0.05263500	1.16903700	-1.23655200
H	0.98609800	-0.63010200	-1.23655200
H	-1.03873300	-0.53893500	-1.23655200

Ammonia borane (NH_3BH_3) + Iodine (I_2)

Zero-point correction= 0.072331 (Hartree/Particle)

Thermal correction to Energy= 0.080286

Thermal correction to Enthalpy= 0.081230

Thermal correction to Gibbs Free Energy= 0.035859

Sum of electronic and zero-point Energies= -105.784650

Sum of electronic and thermal Energies= -105.776695

Sum of electronic and thermal Enthalpies= -105.775751

Sum of electronic and thermal Free Energies= -105.821122

Cartesian coordinates

N	-3.74687800	1.30052700	-0.07845100
H	-4.45058400	1.86394900	0.39877000
H	-3.83648000	1.46998100	-1.08059900
H	-2.82452800	1.63366800	0.21144400
B	-3.94585300	-0.28893300	0.28328300
H	-3.79650600	-0.38207700	1.47411500
H	-5.03495800	-0.59677100	-0.12878200
H	-3.07537800	-0.87529400	-0.36049400
I	-0.66658900	-0.43694800	-0.05955800
I	1.96802000	0.23369300	0.03348800

TS_1

Zero-point correction= 0.068680 (Hartree/Particle)

Thermal correction to Energy= 0.075618

Thermal correction to Enthalpy= 0.076563

Thermal correction to Gibbs Free Energy= 0.033660

Sum of electronic and zero-point Energies= -105.725905

Sum of electronic and thermal Energies= -105.718967

Sum of electronic and thermal Enthalpies= -105.718023

Sum of electronic and thermal Free Energies= -105.760926

Cartesian coordinates

N	-0.18732900	2.68687800	-0.54460700
H	-0.73428900	3.54943500	-0.49703200
H	-0.86509100	1.89640800	-0.57998600
H	0.34101700	2.69214700	-1.41894300
B	0.73507500	2.52035200	0.73592800
H	1.79478000	3.05572900	0.60359700
H	0.09060100	2.60288200	1.74010200
H	1.01093500	1.21064800	0.71094800
I	-1.65265900	-0.37300900	0.02973200
I	1.57714900	-0.50278700	-0.03777100

Int_1

Zero-point correction= 0.062207 (Hartree/Particle)

Thermal correction to Energy= 0.072054

Thermal correction to Enthalpy= 0.072999

Thermal correction to Gibbs Free Energy= 0.021235

Sum of electronic and zero-point Energies= -105.787915

Sum of electronic and thermal Energies= -105.778068

Sum of electronic and thermal Enthalpies= -105.777124

Sum of electronic and thermal Free Energies= -105.828887

Cartesian coordinates

N	-0.51514600	3.03382500	-0.10423900
H	-1.20469700	3.14769600	0.62678900
H	-1.14328000	0.83582400	-0.08532200
H	-0.89106000	3.15919400	-1.03454800
B	0.85601800	2.92411400	0.15566800
H	1.61461000	2.89691300	-0.76565900
H	1.22468700	2.86567200	1.28845700
H	1.19008700	-1.75556300	0.15809400
I	-2.15667300	-0.44011800	0.00586800
I	2.12904200	-0.44680900	-0.01033000

Int_1 + Ammonia borane (NH_3BH_3)

Zero-point correction= 0.144345 (Hartree/Particle)

Thermal correction to Energy= 0.156951

Thermal correction to Enthalpy= 0.157895

Thermal correction to Gibbs Free Energy= 0.101100

Sum of electronic and zero-point Energies= -188.922150

Sum of electronic and thermal Energies= -188.909544

Sum of electronic and thermal Enthalpies= -188.908600

Sum of electronic and thermal Free Energies= -188.965395

Cartesian coordinates

H	2.71088800	2.22851600	-0.82806600
H	-0.65247900	-1.17124100	-0.00093700
I	2.13872200	-0.87817300	0.00029600

I	-2.26447000	-0.89806300	-0.00018200
N	2.11209100	2.26498600	-0.00150400
H	1.59465100	3.15874300	-0.00228600
H	2.71092400	2.23004900	0.82509500
B	1.02239300	1.09859400	-0.00045000
H	0.39747200	1.17280300	1.02128000
H	0.39671400	1.17173900	-1.02178700
B	-0.49679300	4.21222600	0.00021000
H	0.14997100	4.03631300	1.01621300
H	0.14862400	4.03591400	-1.01660100
H	-1.07649200	5.26807400	0.00034600
N	-1.63496700	3.04075500	0.00117200
H	-1.21524600	2.10539900	0.00135700
H	-2.23371500	3.10529100	0.82448700
H	-2.23452600	3.10460000	-0.82160600

TS_2

Zero-point correction= 0.143013 (Hartree/Particle)

Thermal correction to Energy= 0.154701

Thermal correction to Enthalpy= 0.155645

Thermal correction to Gibbs Free Energy= 0.101187

Sum of electronic and zero-point Energies= -188.894056

Sum of electronic and thermal Energies= -188.882368

Sum of electronic and thermal Enthalpies= -188.881424

Sum of electronic and thermal Free Energies= -188.935882

Cartesian coordinates

H	2.43858600	2.03904800	-0.60320900
H	-0.11757000	-0.98758700	-0.01944500
I	2.07065500	-0.64274200	-0.01402100
I	-1.85794300	-1.12880800	-0.00221500
N	1.80147400	2.66147600	-0.09064800
H	1.46884400	3.40708300	-0.70967700
H	2.31976000	3.07617000	0.68564800
B	0.57844300	1.77297400	0.38332700
H	0.47424100	1.52152400	1.53363100
H	-0.08850800	1.39585400	-0.51439000
B	-1.17822600	3.71146600	-0.05295100
H	-0.33154800	3.23080700	0.71366500
H	-0.75317200	3.80537000	-1.18097000
H	-1.58832600	4.73739700	0.42236500
N	-2.38484600	2.63691600	-0.05059300
H	-2.08058200	1.68481900	-0.30051100
H	-2.81198700	2.56381800	0.87425900
H	-3.12095600	2.90691600	-0.70405900

Int_2

Zero-point correction= 0.144491 (Hartree/Particle)

Thermal correction to Energy= 0.156111

Thermal correction to Enthalpy= 0.157055

Thermal correction to Gibbs Free Energy= 0.103115

Sum of electronic and zero-point Energies= -188.924194

Sum of electronic and thermal Energies= -188.912575

Sum of electronic and thermal Enthalpies= -188.911631

Sum of electronic and thermal Free Energies= -188.965571

Cartesian coordinates

H	-0.54040400	1.70767000	1.23151100
H	-0.91439500	-0.61511300	-0.13390600
I	-2.43050400	0.20016400	-0.14808200
I	1.19555800	-1.46155700	0.11532000
N	0.48275100	1.82879800	1.22981300
H	0.86940400	0.86714600	1.16494800
H	0.76111900	2.23554400	2.12412000
B	0.86249000	2.71006300	-0.02155200
H	0.43092200	3.81943700	0.07757300
H	0.65751400	2.11885700	-1.03974600
B	3.17940400	2.25697800	0.09122900
H	2.13398600	3.02878000	0.04385600
H	3.20316200	1.70162700	1.14975000
H	4.00655900	3.09468300	-0.11704600
N	3.12553700	1.20569200	-1.09138300
H	2.46997500	0.41969200	-0.88645200
H	2.85783100	1.61732100	-1.98722000

H	4.04898700	0.78153200	-1.20838500

Int_3

Zero-point correction= 0.123919 (Hartree/Particle)

Thermal correction to Energy= 0.133820

Thermal correction to Enthalpy= 0.134764

Thermal correction to Gibbs Free Energy= 0.084959

Sum of electronic and zero-point Energies= -187.787426

Sum of electronic and thermal Energies= -187.777525

Sum of electronic and thermal Enthalpies= -187.776580

Sum of electronic and thermal Free Energies= -187.826385

Cartesian coordinates

N	0.55037100	2.17671400	-0.98687300
H	0.82594300	1.18491100	-1.00703900
H	-0.08404100	2.39477200	-1.74936200
B	1.70569600	3.15375100	-0.66538200
H	1.70038300	4.18363300	-1.25848000
H	1.15273700	3.57197000	0.55661000
B	0.15393800	2.75924700	0.37840900
H	-0.82934300	3.42364800	0.42266600
H	2.70424700	2.61367300	-0.30800600
N	0.26900900	1.69861800	1.52952700
H	-0.59955900	1.13508100	1.52830800
H	1.03462900	1.01146000	1.37683400

H	0.37699400	2.12053300	2.45377800
H	-0.35349100	-0.85388500	-0.08350700
I	-2.10710000	-0.36711600	-0.07688700
I	1.71158400	-1.09473500	-0.00416100

TS_3

Zero-point correction= 0.196067 (Hartree/Particle)

Thermal correction to Energy= 0.210916

Thermal correction to Enthalpy= 0.211861

Thermal correction to Gibbs Free Energy= 0.149715

Sum of electronic and zero-point Energies= -270.887009

Sum of electronic and thermal Energies= -270.872160

Sum of electronic and thermal Enthalpies= -270.871215

Sum of electronic and thermal Free Energies= -270.933361

Cartesian coordinates

N	-0.64712300	2.15547600	-0.16348900
H	-0.64231600	1.15702700	0.07590200
H	-0.29071400	2.67895400	0.63308100
B	-1.98086400	2.60428700	-0.70951300
H	-2.28473100	3.74079700	-0.57787700
H	-0.94464100	2.95143100	-2.22696900
B	-0.00162000	2.53674400	-1.55634300
H	0.87073900	3.34652400	-1.46398700
H	-2.62877500	1.77761500	-1.26184100

N	0.51933000	1.20242100	-2.24849900
H	1.37281700	0.86782100	-1.77875100
H	-0.15928700	0.42407900	-2.18726200
H	0.74137000	1.36018900	-3.23268900
H	0.89483000	-0.80180700	0.22147500
I	2.39929000	-0.02891100	0.62000300
I	-1.09536500	-1.48739900	-0.55311300
B	-2.78839300	1.62023800	2.12079100
H	-3.40616700	2.09710400	3.03923900
H	-1.59272300	1.56055700	2.31942600
H	-3.06609600	2.16780300	1.06301400
N	-3.28968200	0.07905700	1.95444700
H	-2.78932100	-0.40512100	1.19670100
H	-3.11816800	-0.45017200	2.80963600
H	-4.28813000	0.02660500	1.75381100

Int_4

Zero-point correction= 0.198982 (Hartree/Particle)

Thermal correction to Energy= 0.213554

Thermal correction to Enthalpy= 0.214498

Thermal correction to Gibbs Free Energy= 0.154159

Sum of electronic and zero-point Energies= -270.903284

Sum of electronic and thermal Energies= -270.888712

Sum of electronic and thermal Enthalpies= -270.887768

Sum of electronic and thermal Free Energies= -270.948108

Cartesian coordinates

N	0.68993100	1.96461200	0.68342700
H	0.78765100	1.00030600	0.34136400
H	-0.14079500	2.34281700	0.22351800
B	1.95963100	2.77147700	0.29690400
H	1.88936700	3.93042200	0.57988300
H	1.55822300	1.76390700	2.79976800
B	0.50035500	1.94256100	2.25943900
H	-0.10390200	2.91635900	2.61900700
H	2.97203500	2.18903500	0.56910300
N	-0.40687600	0.63727400	2.57895200
H	-1.32444200	0.65641100	2.11950400
H	0.06229400	-0.22585800	2.26543900
H	-0.55897200	0.56321000	3.58564200
H	-0.85390400	-0.75427100	-0.32843200
I	-2.35222000	0.09917400	-0.50084600
I	1.16383200	-1.64783700	0.17438900
B	1.91389100	2.10411300	-2.00261500
H	2.33956100	2.76846900	-2.90241000
H	0.78857200	1.70490300	-2.08666000
H	1.98712200	2.94934400	-1.04016700
N	2.90514100	0.88677800	-1.71991800
H	2.53630100	0.21392800	-1.02443700

H	3.03323000	0.35379800	-2.58325700
H	3.82542800	1.19498900	-1.40154500

TS_4

Zero-point correction= 0.193301 (Hartree/Particle)

Thermal correction to Energy= 0.209254

Thermal correction to Enthalpy= 0.210198

Thermal correction to Gibbs Free Energy= 0.145726

Sum of electronic and zero-point Energies= -270.850152

Sum of electronic and thermal Energies= -270.834200

Sum of electronic and thermal Enthalpies= -270.833255

Sum of electronic and thermal Free Energies= -270.897728

Cartesian coordinates

N	0.53972500	1.95957200	0.68571200
H	0.60582800	0.94786900	0.51498500
H	-0.43873900	2.23757700	0.67649900
B	1.55774500	2.87111800	0.00380500
H	2.29835100	3.18415700	0.98954000
H	2.15009400	1.58857800	2.29430100
B	1.36255000	2.38713400	1.89960000
H	0.94761100	3.29384500	2.54509100
H	2.47922500	2.17987300	-0.56967000
N	-0.65219400	0.52303900	2.90858900
H	-1.61825500	0.27511300	2.70055400

H	-0.09596800	-0.29937700	2.67218600
H	-0.59228200	0.62827400	3.91910900
H	-0.97310500	-0.72812900	-0.26814500
I	-2.42758200	0.09073900	-0.54591100
I	1.19607000	-1.58706600	0.23350600
B	2.28340500	1.95333600	-1.87509200
H	2.96544800	2.77139500	-2.41016600
H	1.13343000	1.86865000	-2.17215400
H	1.19993000	3.84857500	-0.56141200
N	2.95542700	0.51362500	-1.90096500
H	2.45385800	-0.16844800	-1.28281600
H	2.89380600	0.13852600	-2.85092000
H	3.94168000	0.50727300	-1.63445100

Int_5

Zero-point correction= 0.194261 (Hartree/Particle)

Thermal correction to Energy= 0.210069

Thermal correction to Enthalpy= 0.211013

Thermal correction to Gibbs Free Energy= 0.146811

Sum of electronic and zero-point Energies= -270.858978

Sum of electronic and thermal Energies= -270.843171

Sum of electronic and thermal Enthalpies= -270.842226

Sum of electronic and thermal Free Energies= -270.906429

Cartesian coordinates

N	-0.89470200	2.22716300	-0.57925400
H	-0.94751900	1.20342300	-0.54550000
H	-0.09583200	2.52898800	-1.18587400
B	-1.01816500	2.96959100	0.74230700
H	-2.24785100	3.36566400	0.67844200
H	-3.20167800	2.10807500	-0.58028500
B	-2.29164100	2.86936800	-0.67016000
H	-2.36260800	3.89370500	-1.27312400
H	-1.26231600	2.19894300	1.74416000
N	1.52189000	2.68434600	-1.99793800
H	2.07889500	3.49766200	-1.74649800
H	2.02334600	1.86275900	-1.65755200
H	1.51695000	2.62795100	-3.01382800
H	0.36698200	-1.04879700	-0.25967400
I	2.10133200	-0.64609300	0.02781100
I	-1.70693300	-1.33322000	-0.35728700
B	-0.13402500	1.83527800	2.38699200
H	-0.28681000	2.39190200	3.42990700
H	0.86439000	2.03486900	1.77475500
H	-0.34705200	3.92378900	0.94709700
N	-0.40482400	0.27279200	2.48662500
H	-0.88185000	-0.13980000	1.65493400
H	0.49972700	-0.21211900	2.53051600
H	-0.95730800	0.00529200	3.30302600

TS_5

Zero-point correction= 0.193726 (Hartree/Particle)

Thermal correction to Energy= 0.209012

Thermal correction to Enthalpy= 0.209956

Thermal correction to Gibbs Free Energy= 0.146755

Sum of electronic and zero-point Energies= -270.852541

Sum of electronic and thermal Energies= -270.837255

Sum of electronic and thermal Enthalpies= -270.836311

Sum of electronic and thermal Free Energies= -270.899512

Cartesian coordinates

N	-3.58828300	0.67267800	-0.91860400
H	-2.83368000	-0.01604500	-0.82021500
H	-3.88133900	0.76399300	-1.88510800
B	-3.42978400	1.98923100	-0.13887400
H	-4.39395300	1.82790000	0.73205600
H	-4.46996100	-0.15624800	1.04589400
B	-4.70042800	0.60192200	0.15757400
H	-5.80502700	0.79812500	-0.24209000
H	-2.45860500	1.98096100	0.60937600
N	1.35308800	3.35369400	-0.30364200
H	1.07694300	4.20441300	-0.79044800
H	2.15101200	3.59890500	0.28122900
H	1.71133600	2.70875500	-1.00761300

H	1.00422200	-0.86812100	-0.11851000
I	2.61750500	-0.10072100	-0.09834000
I	-0.96710500	-1.65091200	0.05410800
B	-0.96078900	2.57158000	0.21080600
H	-1.19352300	3.67101600	0.58338700
H	-0.93400600	2.21418500	-0.91958600
H	-3.66436800	3.00050400	-0.71802200
N	-0.32247100	1.58408000	1.23598100
H	-0.64044200	0.60302600	1.08730300
H	0.69166800	1.58320500	1.04899400
H	-0.47275800	1.83512600	2.21401400

$BH_2(NH_3)_2^+$ HI_2^-

Zero-point correction= 0.110917 (Hartree/Particle)

Thermal correction to Energy= 0.120251

Thermal correction to Enthalpy= 0.121195

Thermal correction to Gibbs Free Energy= 0.073325

Sum of electronic and zero-point Energies= -162.350337

Sum of electronic and thermal Energies= -162.341003

Sum of electronic and thermal Enthalpies= -162.340059

Sum of electronic and thermal Free Energies= -162.387929

Cartesian coordinates

H	-0.00015900	-0.73091400	-0.00015700
I	1.93149800	-0.60230100	-0.00001500

I	-1.93143800	-0.60242500	0.00002300
B	-0.00056900	3.11304800	-0.00006200
H	-1.01726200	3.74918300	-0.00008900
H	1.01528600	3.75051800	-0.00009300
N	-0.00006900	2.14388100	-1.27697800
H	0.82395900	1.52410200	-1.29969100
H	-0.82389600	1.52382100	-1.29966400
N	0.00018900	2.14396800	1.27699600
H	0.82429200	1.52429200	1.29942700
H	0.00038800	2.70278200	2.13179800
H	-0.00020000	2.70260400	-2.13184500
H	-0.82357400	1.52390500	1.30003700

Aminodiborane

Zero-point correction= 0.085178 (Hartree/Particle)

Thermal correction to Energy= 0.089122

Thermal correction to Enthalpy= 0.090066

Thermal correction to Gibbs Free Energy= 0.060316

Sum of electronic and zero-point Energies= -108.550557

Sum of electronic and thermal Energies= -108.546614

Sum of electronic and thermal Enthalpies= -108.545669

Sum of electronic and thermal Free Energies= -108.575419

Cartesian coordinates

N	-0.00013600	0.78836400	0.00005400

H	-0.00013100	1.36009900	0.83592300
H	-0.00006900	1.36010000	-0.83581800
B	-0.95768700	-0.44120700	0.00002000
H	-1.52023000	-0.61183300	-1.03783000
H	0.00027500	-1.38021900	-0.00029600
B	0.95775700	-0.44111800	-0.00009300
H	1.52004400	-0.61127000	-1.03818300
H	-1.51937800	-0.61209700	1.03830600
H	1.52008500	-0.61170900	1.03789000

H_2

Zero-point correction= 0.010319 (Hartree/Particle)

Thermal correction to Energy= 0.012680

Thermal correction to Enthalpy= 0.013624

Thermal correction to Gibbs Free Energy= -0.001153

Sum of electronic and zero-point Energies= -1.153393

Sum of electronic and thermal Energies= -1.151033

Sum of electronic and thermal Enthalpies= -1.150088

Sum of electronic and thermal Free Energies= -1.164866

Cartesian coordinates

H	0.00000000	0.00000000	0.36849600
H	0.00000000	0.00000000	-0.36849600

O. References:

1. X. Chen, J.-C. Zhao and S. G. Shore, *J. Am. Chem. Soc.,* 2010, **132**, 10658– 10659.
2. P. V. Ramachandran and P.D. Gagare, *Inorg. Chem.* 2007, **46**, 7810– 7817.

3. S. Hazra, V. Tiwari, A. Verma, P. Dolui and A. J. Elias, *Org. Lett.*, 2020, **22**, 5496-5501.

4. (a) I. Bhattacharjee, M. Sultana, S. Bhunya and A. Paul, *Chem. Commun*., 2022, **58**, 1672–1684. (b) H. A. Kalviri, F. Gärtner, G. Ye, I. Korobkov, R. T. Baker, *Chem. Sci.* 2015, **6**, 618. (c) N. E. Stubbs, A. Schafer, A. P. M. Robertson, E. M. Leitao, T. Jurca, H. A. Sparkes, C. H. Woodall, M. F. Haddow, and I. Manners, *Inorg. Chem*. 2015, **54**, 10878−10889 (d) P. M. Zimmerman, A. Paul, Z. Zhang, C. B. Musgrave, *Inorg. Chem*. 2009, **48**, 1069– 1081. (e) U. B. Demirci, *Inorg. Chem. Front.,* 2021, **8**, 1900 —1930. (f) S. Bhunya, P. M. Zimmerman and A. Paul, *ACS Catal.,* 2015, **5**, 3478–3493.

5. F. H. Stephens, R. T. Baker, M. H. Matus, D. J. Grant and D. A. Dixon, *Angew. Chem. Int., Ed.* 2007, **46**, 746– 749.

6. (a) Y. X. Pan, Z. L. Luo, J. H. Han, X. Xu, C. J. Chen, H. Q. Zhao, L. J. Xu, Q. H. Fan and J. L. Xiao, *Adv. Synth. Catal.,* 2019, **361**, 2301– 2308. (b) Y. Wei, Q. Xuan, Y. Zhou, Q. Song, *Org. Chem. Front*., 2018, **5**, 3510-3514. (c) C. Yang, F. Zhang, G.-J. Deng, H. Gong, *J. Org. Chem*., 2019, **84**, 181-190. (d) D. Wang, K. Zhao, C. Xu, H. Miao, Y. Ding, *ACS Catal*., 2014, **4**, 3910-3918. (e) S. Radl, M. Blahovcova, M. Tkadlecova, J. Havlicek, *Heterocycles*, 2010, **80**, 1359-1379. (f) P. Li, B. C. Lee, X. Zhang, M. J. Koh, *Synthesis*, 2022, **54**, 1566-1576. (g) S. Xu, H. Guo, Y. Li, W. Chang, J. Feng, X. He, Z. Zhang, *Org. Lett*., 2022, **24**, 5546-5551. (h) M. Kawasaki, Y. Suzuki, S. Terashima, *Chem. Pharm. Bull*., 1985, **33**, 52-60. (i) K. O. Marichev, J. M. Takacs, *ACS Catal.,* 2016, **6**, 2205-2210. (j) X. Jv, S. Sun, Q. Zhang, M. Du, L. Wang and B. Wang, *ACS Sustainable Chem. Eng.,* 2020, **8**, 1618-1626. (k) F. Xu, B. Simmons, R. A. Reamer, E. Corley, J. Murry and D. Tschaen, *J. Org. Chem*., 2008, **73**, 312-315. (l) E. Dorko, M. Szabo, B. Kotai, I. Papai, A. Domjan and T. Soos, *Angew. Chem. Int. Ed.,* 2017, 5**6**, 9512-9516. (m) Z. Liu, Z. Yang, X. Yu, H. Zhang, B. Yu, Y. Zhao and Z. Liu, *Adv. Synth. Catal*., 2017, **359**, 4278-4283. (n) D. Wei, C. Netkaew, C. Darcel, *Adv. Synth. Catal.,* 2019, **361**, 1781-1786. (o) Y. Wang, J. Ling, Y. Zhang, A. Zhang, Q. Yao, *Eur. J. Org. Chem.*, 2015, 4153-4161. (p) Y. Li, I. Sorribes, T. Yan, K. Junge and M. Beller, *Angew. Chem. Int. Ed.,* 2013, **52**, 12156-12160. (q) C. Houle, P. R. Savoie, C. Davies, D. Jardel, P. A. Champagne, B. Bibal, J. F. Paquin, *Chem. Eur. J*. 2020, **26**, 10620-10625. (r) J. Shao, S. Ji, X. Li, J. Zhou and H. Guo, *Eur. J. Org. Chem*.,

2011, **2011**, 6100. (s) S. Chen, H. Wang, W. Jiang, P. X. Rui, X. G. Hu, *Org. Biomol. Chem*., 2019, **17**, 9799-9807. (t) F. Haghighi, F. Panahi, M. G. Haghighi and A. K. Nezhad, *Chem. Commun*. 2017, **53**, 12650-12653.

7. M. J. Frisch et. al. Gaussian 09, Revision D.01, Gaussian, Inc., Wallingford, CT, 2013.
8. Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.,* **2008**, *120*, 215–241.
9. L. E. Roy, P. J. Hay, and R. L. Martin. *J. Chem. Theory Comput*., **2008**, *4*, 1029–1031.
10. (a) P. C. Hariharan and J. A. Pople. *Theoret. Chimica. Acta* **1973**, *28*, 213. (b) V. Rassolov, J. A. Pople, M. Ratner and T. L. Windus, *J. Chem. Phys.,* **1998**, *109*, 1223–1229.
11. C. Gonzalez and H. B. Schlegel. *J. Phys. Chem.,* **1990**, *94*, 5523.
12. A. V. Marenich, C. J. Cramer and D. G. Truhlar. *J. Phys. Chem. B.* **2009**, *113*, 6378.
13. CYLview20; Legault, C. Y., Université de Sherbrooke, 2020.