Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Reduction of esters to alcohols and iodides using aminodiborane (μ-$NH_2B_2H_5$): Scope and mechanistic investigations

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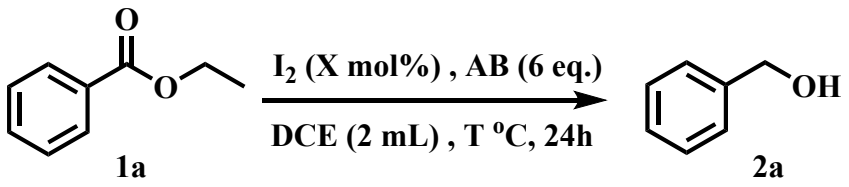
A. General Information

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. 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 ester 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:

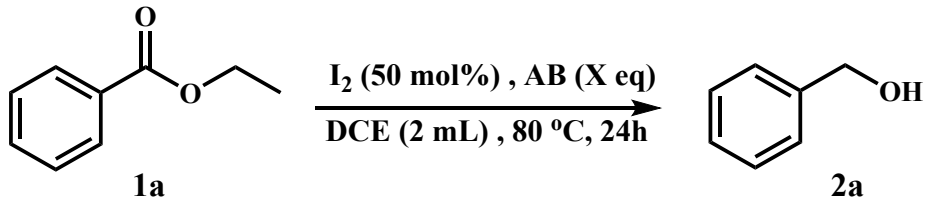
Table S1: Optimization of promoter and temperature for reduction of ethyl benzoate



S. No.	Promoter (X mol%)	Temperature (°C)	(%) of Yield[a]
1	-	60	5
2	KI (30 mol%)	60	0
3	Br_2 (30 mol%)	60	55
4	I_2 (30 mol%)	60	62
5	I_2 (50 mol%)	60	72
6	I_2 (50 mol%)	80	95
7	I_2 (30 mol%)	80	83
8	I_2 (50 mol%)	100	94

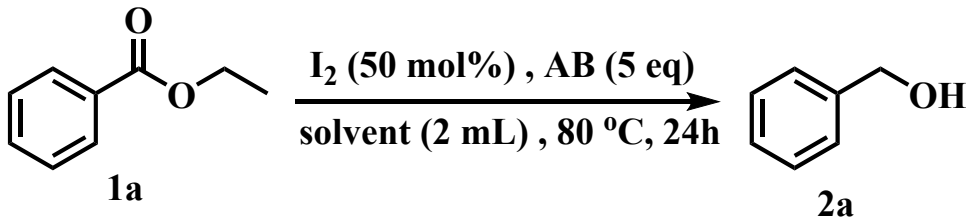
[a] Conditions: 1a (0.37 mmol), I_2 (as indicated), AB (6 eq.), DCE as solvent, 24h

Table S2: Effect of amount of ammonia-borane and time for reduction of esters



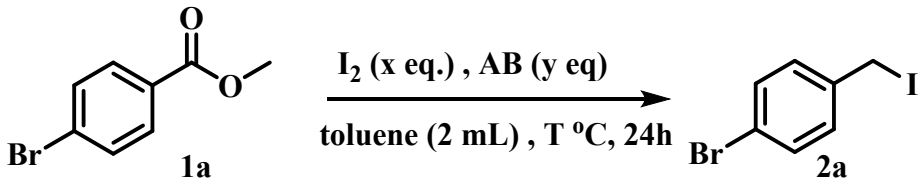
S. No.	Ammonia-borane (eq.)	Time	Percentage Yield (%)
1.	6	24h	95
2.	5	24h	93
3.	4	24h	88
4	3	24h	76
5.	2	24h	70
6.	5	20h	70

Table S3: Effect of solvent for reduction of ethyl benzoate



S. No.	Solvent	Percentage Yield (%)
1.	H_2O	0
2.	CH_3CN - H_2O	0
3.	CH_3CN	75
4.	toluene	96
5.	DCE	94
6.	THF	62

Table S4: Effect of temperature, amount of iodine and ammonia borane for the reduction of methyl 4-bromobenzoate



S. No.	I_2 (x eq.)	NH_3BH_3 (y eq.)	Temperature (°C)	(%) of Yield[a]
1	1	5	80	51
2	1.5	5	80	72
3	2	5	80	96
4	2	4	80	62
5	2	3	80	72
6	2	5	60	95

[a] Conditions: 1a (0.37 mmol), I_2 (as indicated), AB (as indicated), toluene as solvent, 24h

C. General procedure for the reaction

1. **For the reduction of esters to alcohols**: A 10 mL T-23 pressure tube was charged with a magnetic bead, Ethylbenzoate (100mg, 0.67mmol), iodine (85mg, 50 mol%), ammonia-borane (92mg, 3.35 mmol) and 2 mL toluene. This reaction was carried out at 80°C for 24 h. After the reaction, 4-5 mL water was added to the reaction mixture and stirred for 5 mins. 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 (20:80) as eluent. The product was characterized by ^{1}H NMR and ^{13}C NMR.

2. **For conversion of esters to iodides:** A 10 mL T-23 pressure tube was charged with a magnetic bead, methyl 4-bromobenzoate (100mg, 0.47mmol), iodine (236mg, 2 eq.), ammonia-borane (72mg, 2.33 mmol) and 2 mL toluene. This reaction was carried out at 80°C for 24 h. After the reaction, ethyl acetate and water were added to the reaction

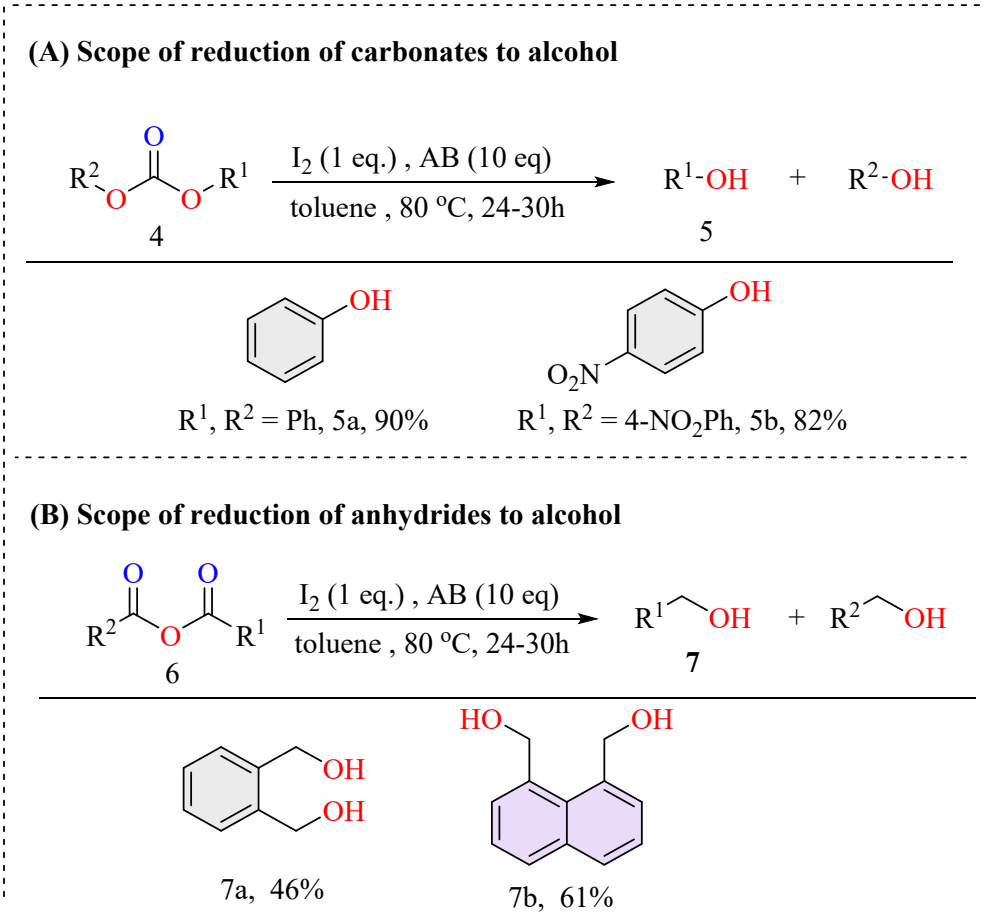
mixture. Ethyl acetate layer was concentrated using a rotavapor. After evaporation, the crude mixture was purified by silica gel column chromatography using hexane as eluent The product was characterized by ^{1}H NMR and ^{13}C NMR.

3. **For the reduction of carbonates and anhydrides to alcohols**: A 10 mL T-23 pressure tube was charged with a magnetic bead, carbonate or anhydride (100mg, 1 eq.), iodine (1 eq.), ammonia-borane (10 eq.) and 2 mL toluene. This reaction was carried out at 80°C for 24 h. After the reaction, 4-5 mL water was added to the reaction mixture and stirred for 5 mins. 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 as eluent. The product was characterized by ^{1}H NMR and ^{13}C NMR.

D. Substrate Scope:

Unsubstituted aromatic esters were reduced to the corresponding benzyl alcohols with yields up to 86% (2a-2c). The reduction of aromatic esters to alcohols, especially those having electron-donating and electron-withdrawing groups at the ortho, meta, and para positions, gave more than 60% yield of the corresponding alcohols (2d-2m). Methyl 4-acetylbenzoate underwent the reduction of both ketone and ester functional groups, giving the corresponding diol compound in good yield (2n). When 3-methylisobenzofuran-1-one was employed, 30% of the diol product (2o) was obtained. Diethyl terephthalate was reduced to 1,4-benzenedimethanol (2p) with 41% yield. The reduction of methyl 2-phenylacetate was also carried out, resulting in 58% yield of 2-phenylethan-1-ol (2q). Ethyl thiophene-3-carboxylate resulted in 90% yield of 3-thiophenemethanol (2s), while 0% yield of 2t was observed with ethyl isonicotinate. Aliphatic esters such as dimethyl succinate and ethyl levulinate gave moderate to low yields of corresponding alcohols, 2u & 13, respectively (see manuscript, Scheme 4).

To determine the substrate scope of benzyl and alkyl halides, ester substrates were reacted resulting in good to moderate yields of iodides (3a-3j) (see manuscript, Scheme 5). Diphenyl carbonate (4a) and bis(4-nitrophenyl) carbonate (4b) resulted in good yields of phenol compounds (Scheme S1A). Phthalic anhydride (6a) and naphthoic anhydride (6b) were reduced to diol compounds with moderate yields (Scheme S1B).



Scheme S1 : (A) Substrate scope for the reduction of carbonates to alcohols. Conditions: 4 (0.37 mmol), I_2 (1 eq.), AB (10 eq.), 80 °C, toluene as solvent, 24h. (B) Substrate scope for the reduction of anhydrides to alcohols. Conditions: 6 (0.37 mmol), I_2 (1 eq.), AB (10 eq.), 80 °C, toluene as solvent, 24h.

E. ^{11}B NMR Spectra:

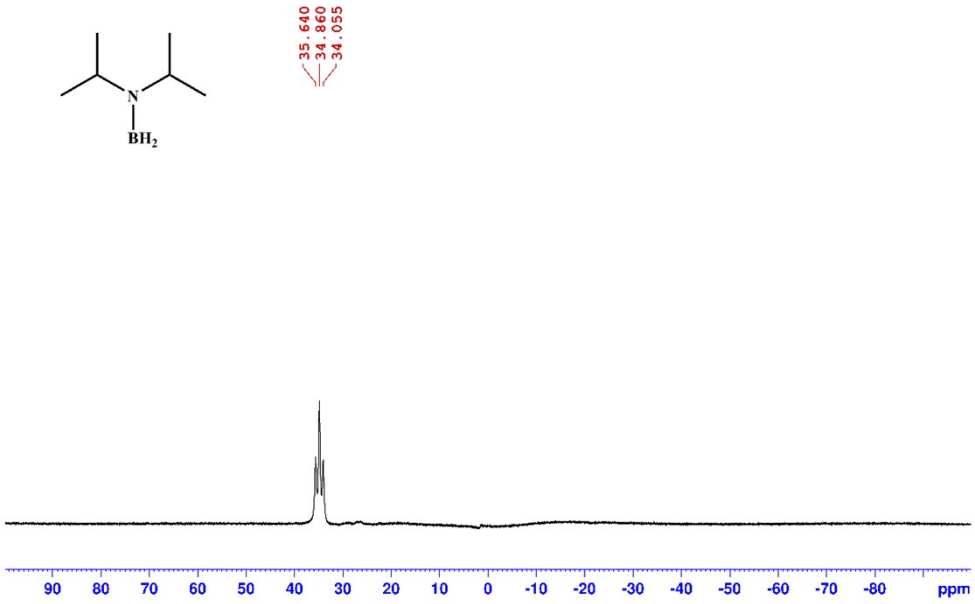


Figure S1. ^{11}B NMR spectra of diisopropylaminoborane (in $CDCl_3$) (prepared by protocol reported by Ramachandran and co-workers).

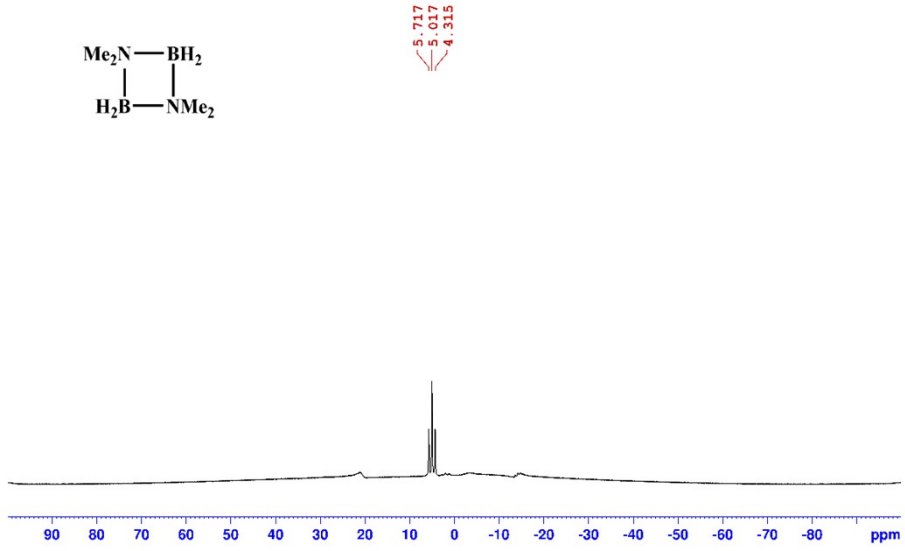
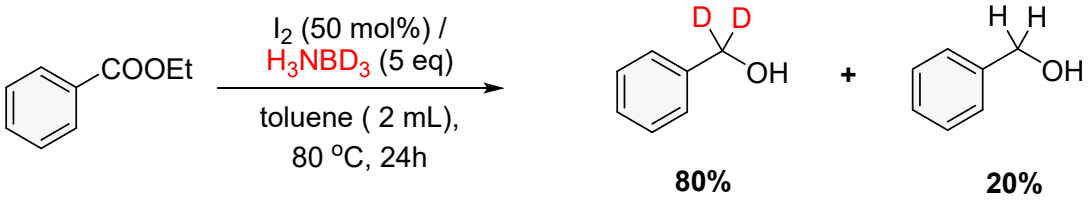


Figure S2. ^{11}B NMR spectra of dimethylaminoborane (in $CDCl_3$) (prepared by protocol reported by Ramachandran and co-workers).

F. Deuterium Incorporation Studies



Scheme S2: Reaction of NH_3BD_3 and iodine with ethylbenzoate.

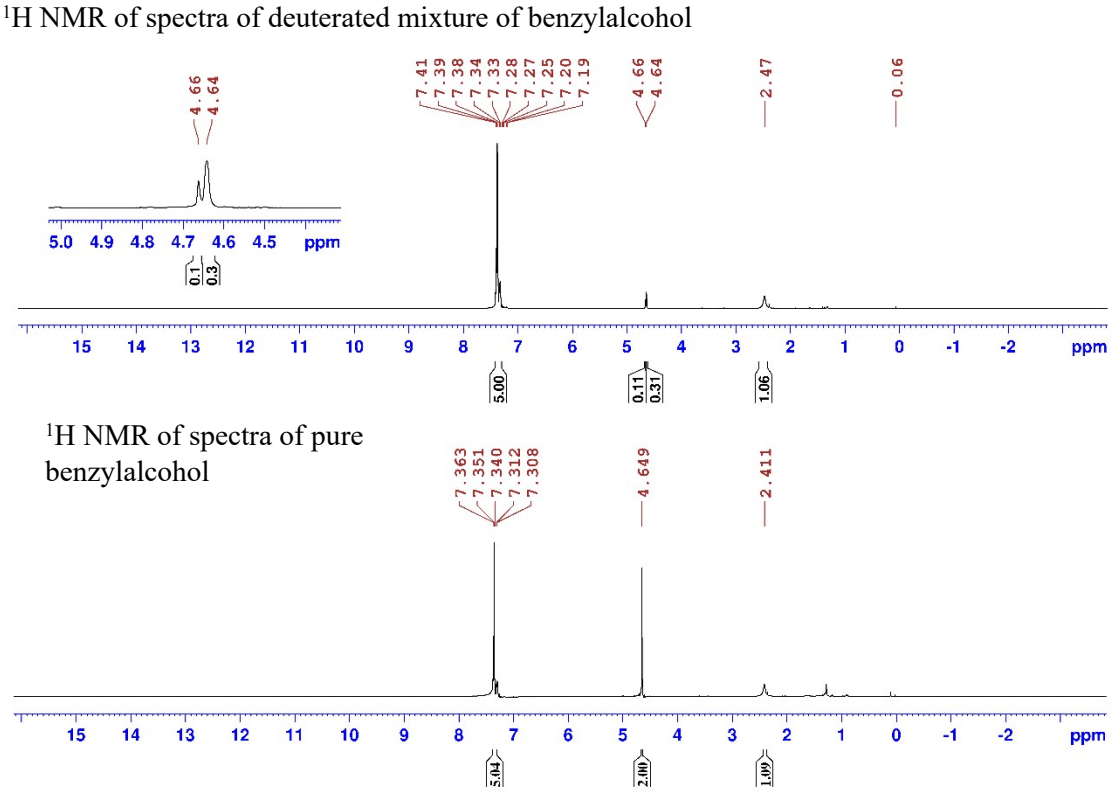
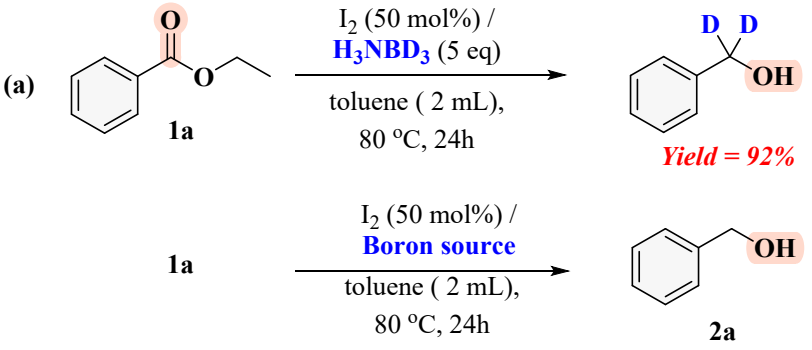


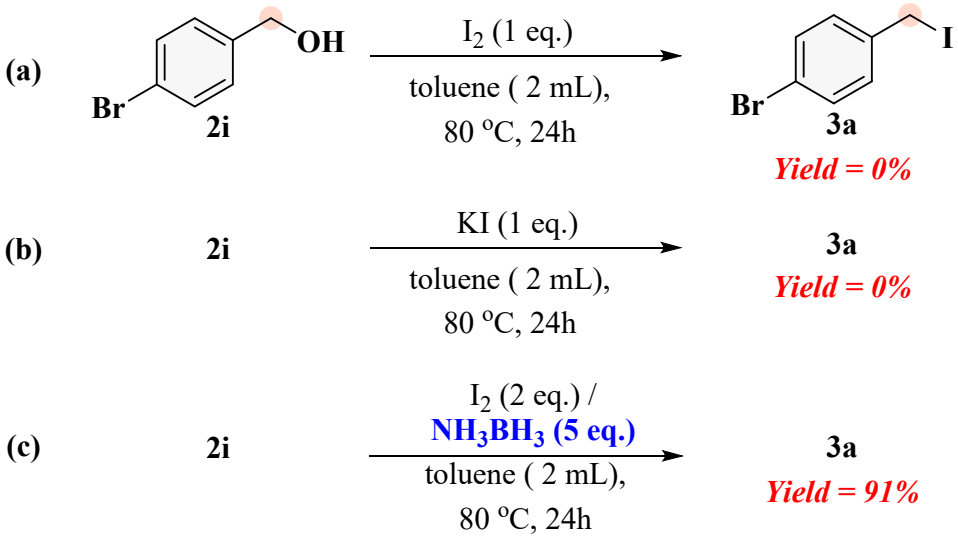
Figure S3: ^{1}H NMR comparison of deuterated mixture of benzylalcohol and pure benzylalcohol.

G. Control Experiments

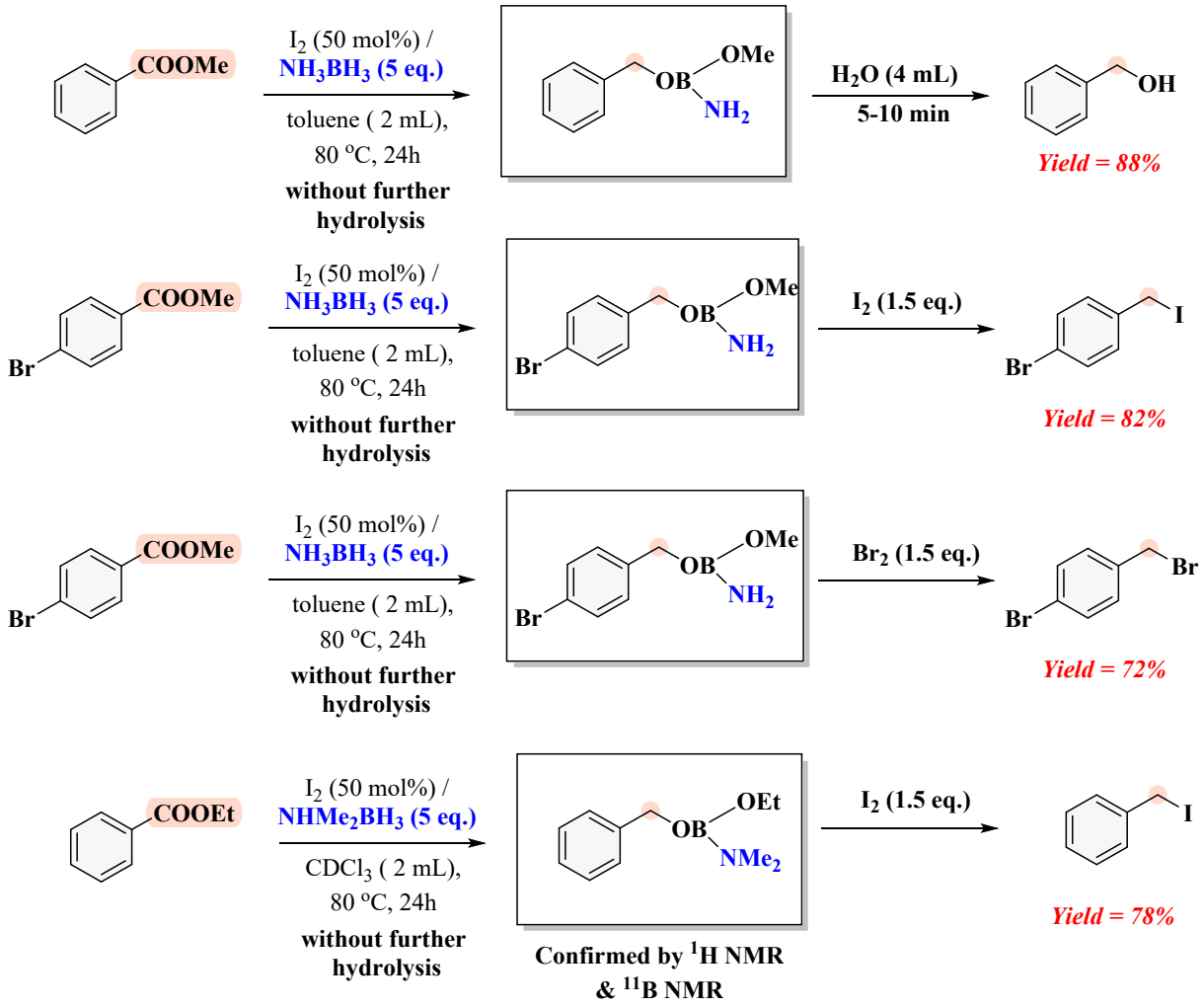


	Boron Source	Yield
(b)	$(CH_3)_3NBH_3$ (5 eq.)	*38%*
(c)	$(CH_3)_2NHBH_3$ (5 eq.)	*90%*
(d)	In situ generated borazine[a]	*0%*
(e)	(iPr_2NBH_2 monomer reaction mixture)[b]	*20%*
(f)	NMe_2BH_2 dimer reaction mixture)[b]	*30%*
(g)	Isolated aminodiborane[c]	*94%*

Scheme S3: Control studies for the reduction of ethyl benzoate to benzyl alcohol. [a]Borazine was prepared by reacting 1 eq. I_2 and 4 eq. NH_3BH_3 at 60°C. [b]Isolated iPr_2NBH_2 and NMe_2BH_2 was synthesised by employing protocol of Ramachandran and co-workers. [c]Aminodiborane was synthesised by employing protocol of Shore and co-workers.



Scheme S4: Control studies for the reductive iodination of 4-bromo benzyl alcohol



Scheme S5: Control studies for the determination of **Int_6**.

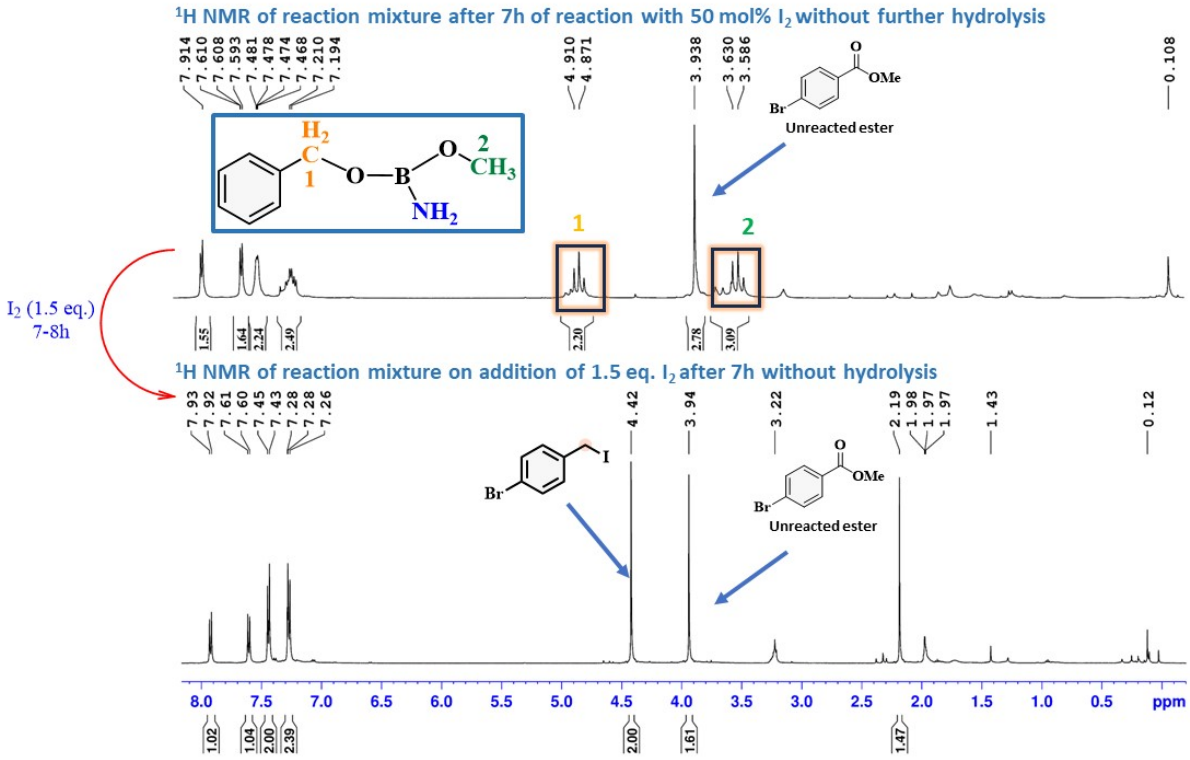
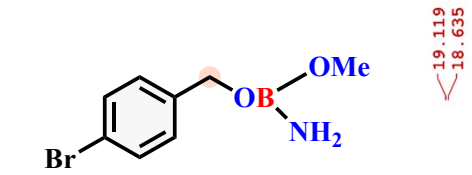


Figure S4: ^{1}H NMR study comparison of reaction mixture without any hydrolysis using NH_3BH_3.



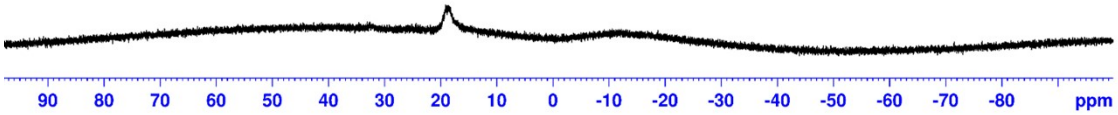


Figure S5: ^{11}B NMR of reaction mixture using ammonia borane.

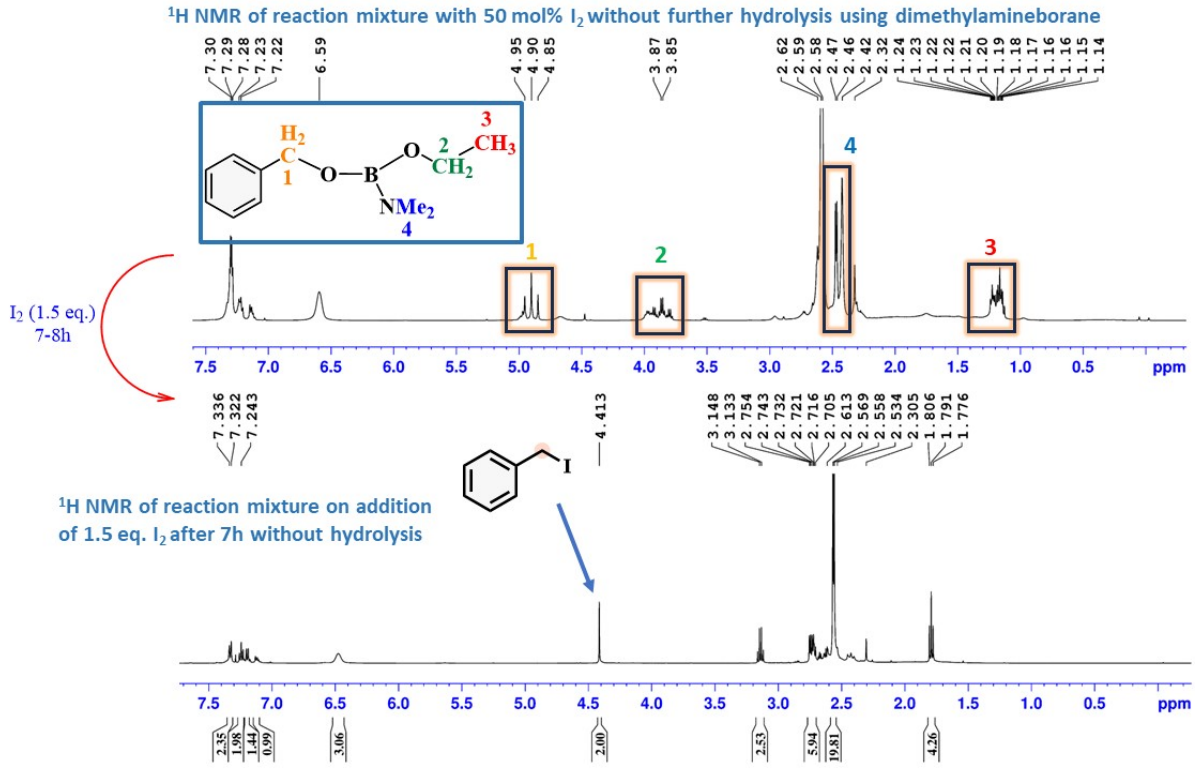


Figure S6: ^{1}H NMR study comparison of reaction mixture without any hydrolysis using $NHMe_2BH_3$.

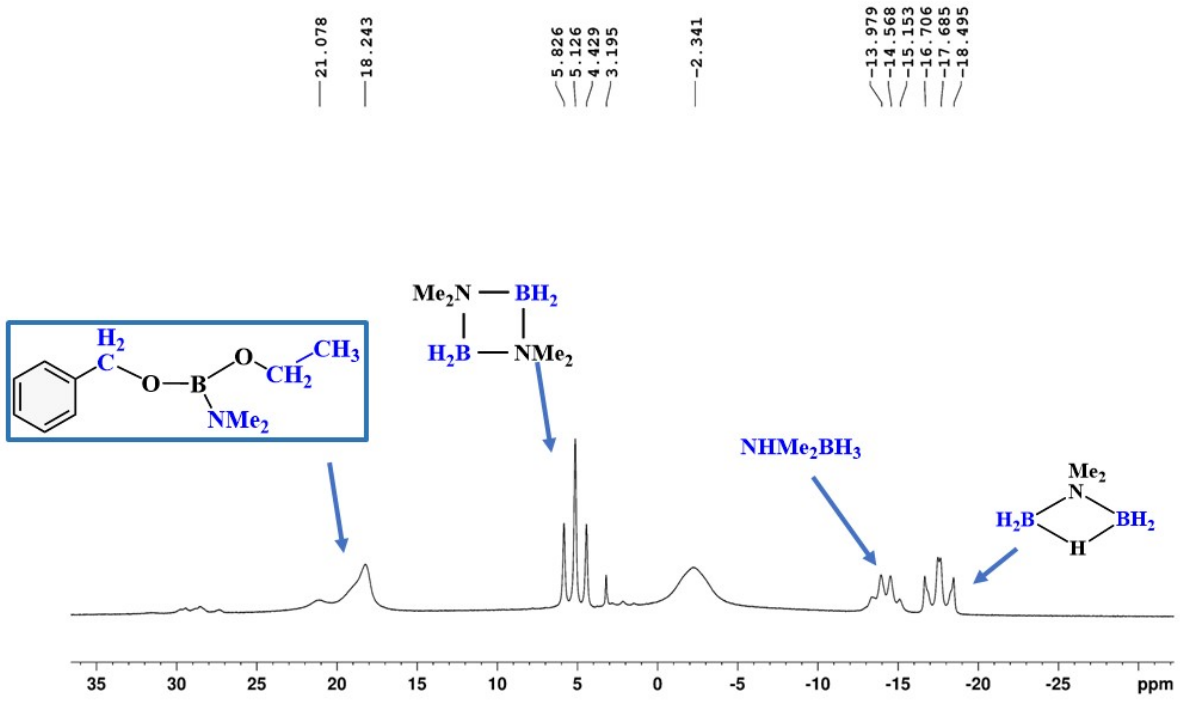


Figure S7: ^{11}B NMR of reaction mixture using dimethylamineborane.

H. All the possible mechanistic pathways

Here we have compared various possible pathways of ester reduction in the presence of iodine (I_2) and ammonia borane (AB). AB reacts with I_2 to give exclusively aminodiborane (ADB). Other possible active reagents which may be formed during the reaction are NH_2BH_2 and NH_3BH_2I. We have not considered NH_3BH_2I, due to its high reactivity with AB giving ADB ($NH_2B_2H_5$), which has been reported previously.[3] Both ADB and NH_2BH_2 reacts with ester to give the Int_2 (Figure S8A). The highest $\Delta G^{\ddagger}$ for reaction of ester with ADB is lower (33.4 Kcal/mol) compared with NH_2BH_2 (35.9 Kcal/mol), suggesting that pathway involving ADB is more favourable. Further Int_2 reacts via various pathways to give the corresponding products (Figure S8B). The most favourable pathway having lowest energy barriers is shown in green coloured dotted lines.

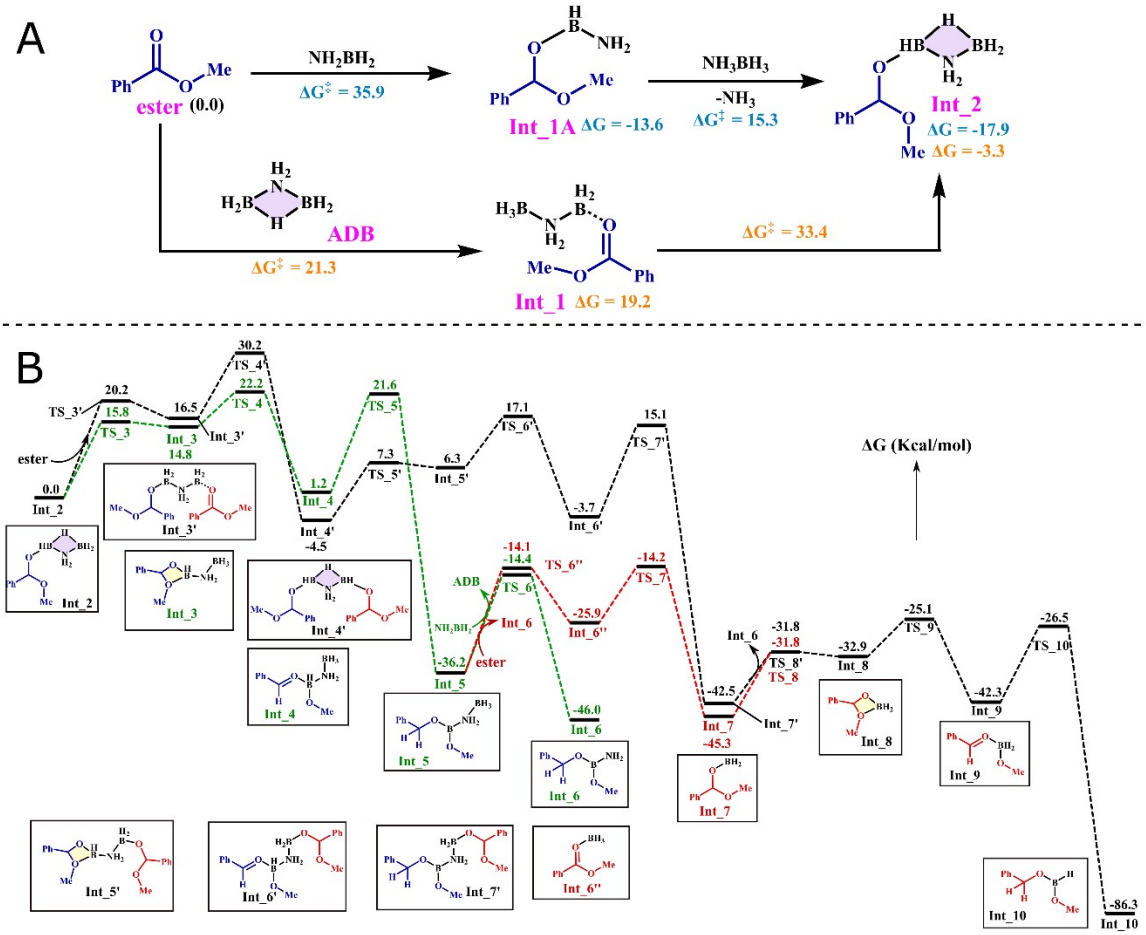


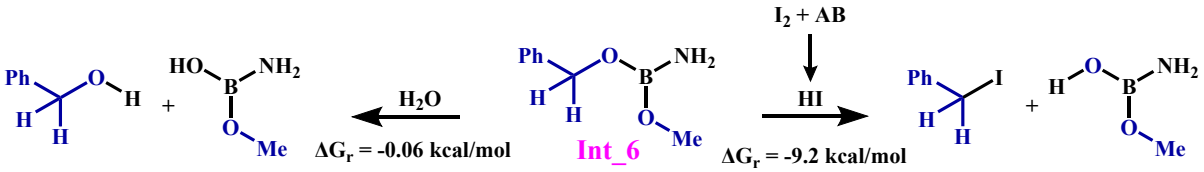
Figure S8: A) Reaction of ester with ADB and NH_2BH_2 to form Int_2. B) Various pathways for the reduction of esters in the presence of I_2/NH_3BH_3 using DFT calculations. The Gibbs free energy (ΔG) values are indicated in Kcal/mol. The most favourable pathway is shown in green colour.

I. Formation of product after hydrolysis and iodination

Int_6 undergoes hydrolysis in the presence of water, leading to the formation of benzyl alcohols as products. The reaction is thermodynamically favorable, as indicated by a ΔG_r value of -0.06 kcal/mol. This suggests that both the reactant and the product have similar stabilities. Experimental observations have also confirmed the difficulty and time-consuming nature of the hydrolysis of Int_6.

Alternatively, in the presence of an excess of iodine, benzyl iodide is formed as the product. The excess iodide reacts with ammonia borane (AB) to generate hydrogen iodide (HI). Subsequently, HI reacts with Int_6 to yield benzyl iodide. This reaction exhibits a significantly more negative ΔG_r value of -9.2 kcal/mol, indicating that the equilibrium is strongly shifted towards the formation of the product.

In both cases, the byproduct generated is a borate species.



Scheme S6: Gibbs free energy of reaction (ΔG_r) for hydrolysis and iodination of Int_6 to give benzyl alcohol and benzyl iodide respectively.

J. DFT calculated energy profile for the most favourable pathway

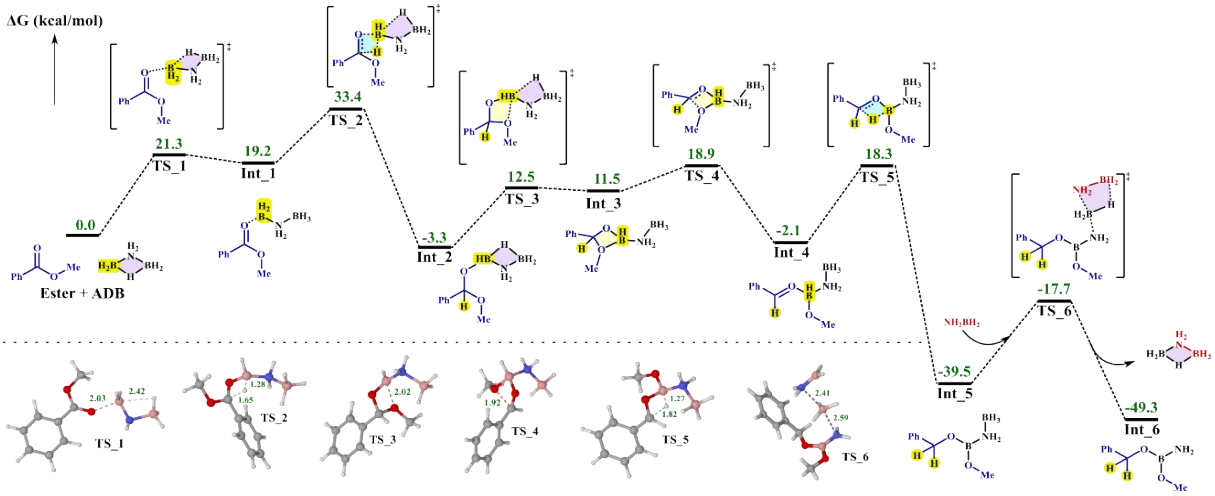


Figure S9 DFT calculations on reduction of esters in presence of ADB. Level of theory: M06-2X/6–311++G**(SMD=Toluene)//M06-2X/6-31+G*

K. ^{11}B NMR comparison study with different amounts of iodine

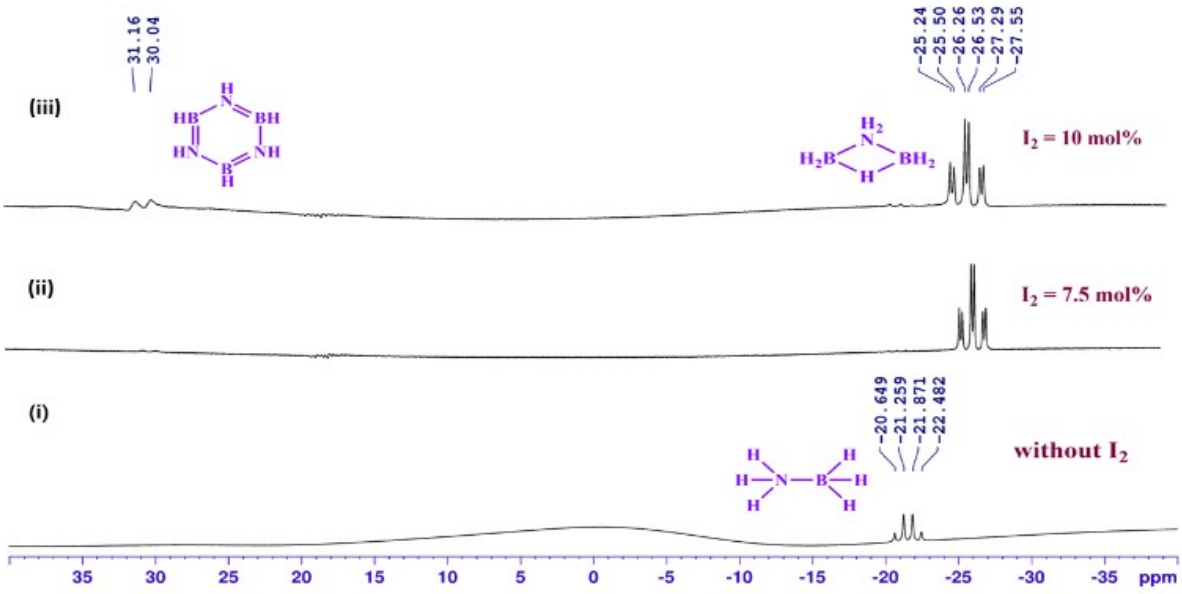
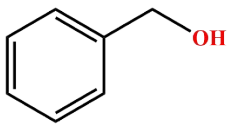


Figure S10. Comparison of ^{11}B NMR spectra of reaction of ammonia borane with different amounts of iodine.

L. Identification of products

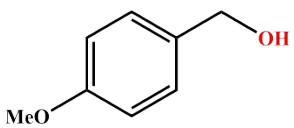
Compound **2a**



2a; (69mg, 96%) ^{1}H-NMR ($CDCl_3$, 500 MHz, ppm): 7.36-7.30 (5H, m), 4.65 (2H, s), 2.41 (1H, s, br).

^{13}C-NMR ($CDCl_3$, 125 MHz, ppm): 140.92, 128.61, 127.68, 127.09, 65.24

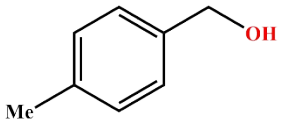
Compound **2d**



2d; (73mg, 88%) ^{1}H-NMR ($CDCl_3$, 500 MHz, ppm): 7.29 (2H, d, J= 8.5 Hz), 6.89 (2H, d, J= 8.5 Hz), 4.61 (2H, s), 3.80 (3H, s), 1.70 (1H, s, br)

^{13}C-NMR ($CDCl_3$, 125 MHz, ppm): 159.34, 133.24, 128.78, 114.09, 65.17, 55.43

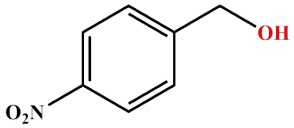
Compound **2e**



2e; (71mg, 95%) ^{1}H-NMR ($CDCl_3$, 500 MHz, ppm): 7.25 (2H, d, J= 8.0 Hz), 7.18 (2H, d, J= 8.0 Hz), 4.61 (2H, s), 2.37 (3H, s), 2.35 (1H, s, br)

^{13}C-NMR ($CDCl_3$, 125 MHz, ppm): 138.00, 137.37, 129.27, 127.19, 65.16, 21.22

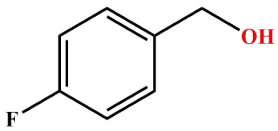
Compound **2f**



2f; (51mg, 60%) ^{1}H-NMR ($CDCl_3$, 500 MHz, ppm): 8.17 (2H, d, J= 8.0 Hz), 7.51 (2H, d, J= 8.0 Hz), 4.81 (2H, d, J= 4.5 Hz), 2.33 (1H, s, br)

^{13}C-NMR ($CDCl_3$, 125 MHz, ppm): 148.37, 147.30, 127.09, 123.80, 64.04.

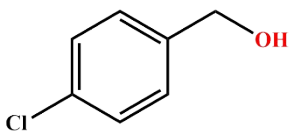
Compound **2g**



2g; (62mg, 82%) ^{1}H-NMR ($CDCl_3$, 500 MHz, ppm): 7.308 (2H, t, J= 8.0 Hz, 7.03 (2H, t, J= 8.0 Hz), 4.62, (2H, s), 2.09 (1H, s, br)

^{13}C-NMR ($CDCl_3$, 125 MHz, ppm): 162.40 (d, J= 243.75 Hz), 136.7, 128.63 (d, J=8.12 Hz), 115.47 (d, J=21.5 Hz), 64.66

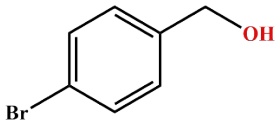
Compound **2h**



2h; (71mg, 92%) ^{1}H-NMR ($CDCl_3$, 500 MHz, ppm): 7.31 (2H, d, J=8.5 Hz), 7.26 (2H, d, J= 8.5 Hz), 4.63 (2H, s), 2.20 (1H, s, br)

^{13}C-NMR ($CDCl_3$, 125 MHz, ppm): 139.35, 133.42, 128.75, 128.39, 64.56

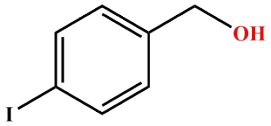
Compound **2i**



2i; (54mg, 62%) ^{1}H-NMR ($CDCl_3$, 500 MHz, ppm): 7.46 (2H, d, J=8.0 Hz), 7.24 (2H, d, J= 8.0 Hz), 4.61 (2H, s), 2.09 (1H, s, br)

^{13}C-NMR ($CDCl_3$, 125 MHz, ppm): 139.85, 131.71, 128.69, 121.53, 64.60.

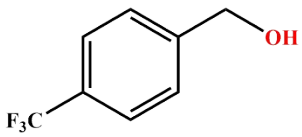
Compound **2j**



2j; (71mg, 84%) ^{1}H-NMR ($CDCl_3$, 500 MHz, ppm): 7.62 (2H, d, J= 8.25 Hz), 7.12 (2H, d, J= 8.25 Hz), 4.38 (2H, s).

^{13}C-NMR ($CDCl_3$, 125 MHz, ppm): 140.53, 137.69, 128.92, 93.09, 64.70.

Compound **2k**

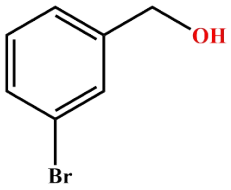


2k; (61mg, 75%) ^{1}H-NMR ($CDCl_3$, 500 MHz, ppm): 7.60 (2H, d, J= 8.0 Hz), 7.45 (2H, d, J= 8.0 Hz), 4.7 (2H, s), 2.16 (1H, s, br).

^{13}C-NMR ($CDCl_3$, 125 MHz, ppm): 144.85, 129.87 (q, J= 32.5 Hz), 126.94, 124.28 (q, J=127.2 Hz), 64.51.

^{19}F NMR ($CDCl_3$, 470.6, ppm) : -62.5.

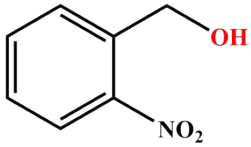
Compound **2l**



2l; (84mg, 96%) ^{1}H-NMR ($CDCl_3$, 500 MHz, ppm): 7.48 (1H, s), 7.39 (1H, d, J= 7.5 Hz), 7.23-7.18 (2H, m), 4.59 (2H, s).

^{13}C-NMR ($CDCl_3$, 125 MHz, ppm): 143.13, 130.65, 130.17, 129.92, 125.40, 122.66, 64.32.

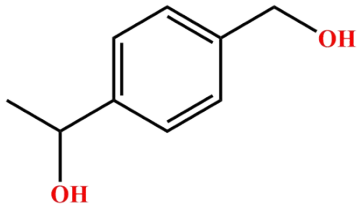
Compound **2m**



2m; (42mg, 50%) ^{1}H-NMR ($CDCl_3$, 500 MHz, ppm): 8.07 (1H, d, J=8.5 Hz), 7.32 (1H, d, J= 8.5 Hz), 7.65 (1H, t, J= 7.5 Hz), 7.45 (1H, t, J= 7.5 Hz), 4.95 (2H, s), 2.84 (1H, s, br).

^{13}C-NMR ($CDCl_3$, 125 MHz, ppm): 147.65, 136.97, 134.22, 129.92, 128.53, 125.07, 62.51.

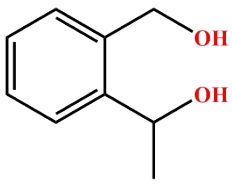
Compound **2n**



2n; (55mg, 65%) ^{1}H-NMR ($CDCl_3$, 500 MHz, ppm): 7.31-7.26 (4H, m), 4.83 (1H, q, J= 7.5 Hz), 4.59 (2H, s), 2.25 (1H, s, br), 1.45 (3H, t, J= 7.5 Hz)

^{13}C-NMR ($CDCl_3$, 125 MHz, ppm): 145.26, 140.13, 127.22, 125.66, 70.15, 64.91, 25.24

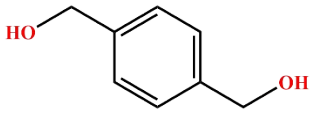
Compound **2o**



2o; (30mg, 30%) ^{1}H-NMR ($CDCl_3$, 500 MHz, ppm): 7.46 (1H, d, J= 7.5Hz), 7.34 (1H, t. J= 7.5 Hz), 7.30-7.27 (2H, m), 5.12 (1H, q, J=6.5 Hz), 4.75 (1H, d, J= 12.5 Hz), 4.59 (1H, d, J= 12.5 Hz), 3.42 (2H, s, br), 1.55 (3H, d, J=6.5 Hz)

^{13}C-NMR ($CDCl_3$, 125 MHz, ppm): 143.41, 138.07, 129.96, 128.67, 127.95, 125.95, 67.05, 63.72, 22.88

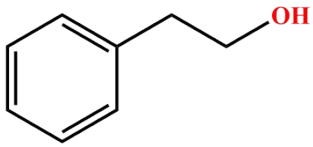
Compound **2p**



2p; (29mg, 41%) ^{1}H-NMR ($CDCl_3$, 500 MHz, ppm): 7.29 (4H, s), 4.60 (4H, s), 3.96 (2H, s, br).

^{13}C-NMR ($CDCl_3$, 125 MHz, ppm): 139.40, 129.73, 128.57, 63.95.

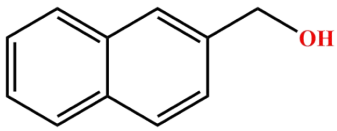
Compound **2q**



2q; (47mg, 58%) ^{1}H-NMR ($CDCl_3$, 500 MHz, ppm): 7.34 (2H, t, J= 7.5 Hz), 7.25 (3H, t, J= 7.5 Hz), 3.83 (2H, t, J=6.5 Hz), 2.868 (2H, t, J= 6.5 Hz), 2.36 (1H, s, br).

^{13}C-NMR ($CDCl_3$, 125 MHz, ppm): 138.62, 129.06, 128.55, 126.42, 63.58, 39.17.

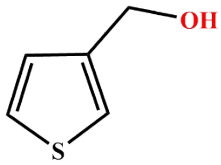
Compound **2r**



2r; (76mg, 90%) ^{1}H-NMR ($CDCl_3$, 500 MHz, ppm): 7.85-7.76 (4H, m), 7.50-7.43 (3H, m), 4.79 (2H, s), 2.51 (1H, s, br)

^{13}C-NMR ($CDCl_3$, 125 MHz, ppm): 133.41, 132.96, 128.34, 127.96, 127.77, 126.22, 125.94, 125.47, 125.24, 65.34

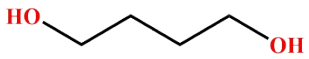
Compound **2s**



2s; (65mg, 90%) ^{1}H-NMR ($CDCl_3$, 500 MHz, ppm): 7.31 (1H, q, J= 2.5 Hz), 7.21 (1H, s), 7.08 (1H, d, J=5.0 Hz), 4.67 (2H, s), 2.12 (1H, s, br).

^{13}C-NMR ($CDCl_3$, 125 MHz, ppm): 142.33, 126.89, 126.39, 122.08, 60.74.

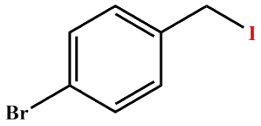
Compound **2u**



2u; (14mg, 21%) ^{1}H-NMR ($CDCl_3$, 500 MHz, ppm): 3.68 (4H, t, J= 6.0 Hz), 2.32 (1H, s, br), 1.68 (4H, qu, J= 3.0 Hz).

^{13}C-NMR ($CDCl_3$, 125 MHz, ppm): 62.83, 30.00.

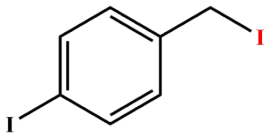
Compound **3a**



3a (132mg, 96%) ^{1}H-NMR ($CDCl_3$, 500 MHz, ppm): 7.44 (2H, d, J=8Hz), 7.27 (2H, d, J=8Hz), 4.42 (2H, s).

^{13}C-NMR ($CDCl_3$, 125 MHz, ppm): 138.49, 132.09, 130.47, 121.85, 4.29.

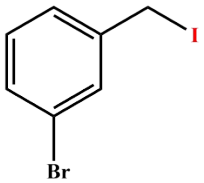
Compound **3b**



3b; (76mg, 61%) ^{1}H-NMR ($CDCl_3$, 500 MHz, ppm): 7.20 (2H, d, J= 8 Hz), 7.12 (2H, d, J= 8 Hz), 4.38 (2H, s).

^{13}C-NMR ($CDCl_3$, 125 MHz, ppm): 139.15, 138.10, 130.67, 93.44, 4.37.

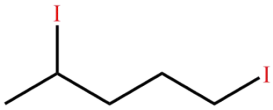
Compound **3c**



3c; (132mg, 96%) ^{1}H-NMR ($CDCl_3$, 500 MHz, ppm): 7.52 (1H, s), 7.37 (1H, d, J=8 Hz), 7.30 (1H, d, J=8 Hz), 7.16 (1H, t, J= 8 Hz), 4.38 (2H, s).

^{13}C-NMR ($CDCl_3$, 125 MHz, ppm): 141.59, 131.82, 131.10, 130.46, 127.52, 122.64, 3.69.

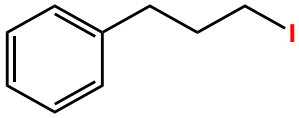
Compound **3d**



3d; (146mg, 65%) ^{1}H-NMR ($CDCl_3$, 500 MHz, ppm): 4.15 (1H, q, J=6.5Hz), 3.19 (2H, q, J= 6.5 Hz), 2.04(1H, qu, J= 3.0 Hz), 1.94-1.87 (5H, m), 1.76 (1H, qu, J=4.5 Hz).

^{13}C-NMR ($CDCl_3$, 125 MHz, ppm): 43.27, 33.45, 29.08, 28.18, 5.47.

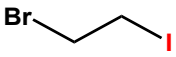
Compound **3e**



3e; (83mg, 60%) ^{1}H-NMR ($CDCl_3$, 500 MHz, ppm): 7.29 (2H, t, J=7.5Hz), 7.22-7.05 (3H, m), 3.18 (2H, t, J= 7 Hz), 2.74 (2H, t, J= 7Hz), 2.17-2.11(2H, m).

^{13}C-NMR ($CDCl_3$, 125 MHz, ppm): 140.56, 128.69, 128.64, 126.32, 36.37, 35.04, 6.41.

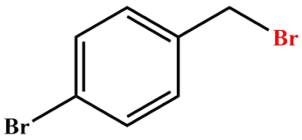
Compound **3g**



3g; (54mg, 35%) ^{1}H-NMR ($CDCl_3$, 500 MHz, ppm): 3.19 (2H, t, J=5.5Hz), 1.95 (2H, t, J=3Hz).

^{13}C-NMR ($CDCl_3$, 125 MHz, ppm): 33.99, 4.92.

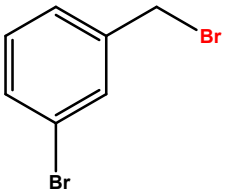
Compound **3h**



3e; (111mg, 96%) ^{1}H-NMR ($CDCl_3$, 500 MHz, ppm): 7.47 (2H, d, J=8.0 Hz), 7.64 (2H, d, J= 8.0 Hz), 4.43 (2H, s).

^{13}C-NMR ($CDCl_3$, 125 MHz, ppm): 136.90, 132.09, 130.79, 122.58, 32.51.

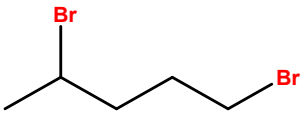
Compound **3i**



3i; (88mg, 81%) ^{1}H-NMR ($CDCl_3$, 500 MHz, ppm): 7.55 (1H, s), 7.43 (1H, d, J= 8 Hz), 7.31 (1H, d, J= 8Hz), 7.23-7.19 (1H, m), 4.42 (2H, s).

^{13}C-NMR ($CDCl_3$, 125 MHz, ppm): 140.01, 132.17, 131.63, 130.44, 127.75, 122.70, 32.12.

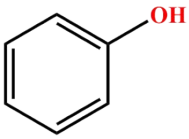
Compound **3j**



3j; (87mg, 55%) ^{1}H-NMR ($CDCl_3$, 500 MHz, ppm): 4.16-4.10 (1H, m), 3.44 (1H, t, J= 6.5 Hz), 2.14-2.09(1H, m), 2.02-1.96 (3H, m), 1.73 (3H, d, J=6.5 Hz).

^{13}C-NMR ($CDCl_3$, 125 MHz, ppm): 50.32, 39.49, 32.96, 31.00, 26.71.

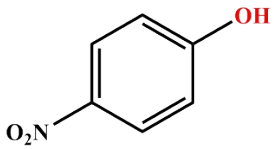
Compound **5a**



5a; (79mg, 90%) ^{1}H-NMR ($CDCl_3$, 500 MHz, ppm): 7.25 (2H, t, J= 7.5 Hz), 6.96-6.93 (1H, m), 6.85 (2H, d, J= 7.5 Hz), 5.21 (1H, s, br).

^{13}C-NMR ($CDCl_3$, 125 MHz, ppm): 155.53, 129.81, 120.93, 115.45.

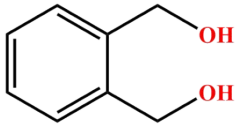
Compound **5b**



5b; (75mg, 82%) ^{1}H NMR ($CDCl_3$, 500MHz, ppm): 8.17 (2H, d, J=8.5Hz), 6.93 (2H, d, J = 8.5Hz), 5.87 (1H, s, br).

^{13}C NMR ($CDCl_3$, 125MHz, ppm): 161.48. 141.83, 126.45, 115.87.

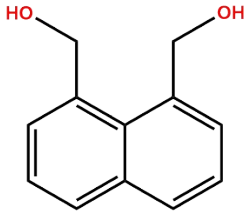
Compound **7a**



7a; (43mg, 46%) ^{1}H-NMR ($CDCl_3$, 500 MHz, ppm): 7.29 (4H, s), 4.60 (4H, s), 3.96 (2H, s, br).

^{13}C-NMR ($CDCl_3$, 125 MHz, ppm): 139.40, 129.73, 128.57, 63.95.

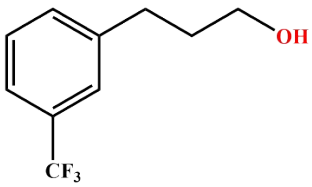
Compound **7b**



7b; (58mg, 61%) ^{1}H NMR ($CDCl_3$, 500MHz, ppm): 7.51(2H, d, J=8.5Hz), 7.45(2H, m), 7.18(2H, d, J=8.5Hz).

^{13}C NMR ($CDCl_3$, 125MHz, ppm): 132.99, 132.71, 126.91, 126.49, 125.75, 120.09, 69.51.

Compound **9**

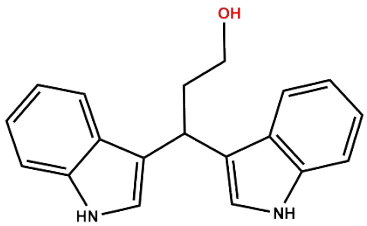


9; (75mg, 91%) ^{1}H-NMR ($CDCl_3$, 500 MHz, ppm): 7.45 (2H, d, J= 5.5 Hz), 7.39 (2H, d, J= 5.5Hz), 3.68 (2H, t, J= 6.5 Hz), 2.77 (2H, t, J= 7.5 Hz), 1.90 (2H, qu, J= 6.5 Hz), 1.70 (1H, s, br)

^{13}C-NMR ($CDCl_3$, 125 MHz, ppm): 142.86, 131.99, 130.80 (q, J=127.5Hz), 128.91, 125.22 (q, J=15 Hz), 124.27 (q, J= 1082.5 Hz), 122.98 (q, J= 15Hz), 62.00, 34.06, 31.96

^{19}F NMR ($CDCl_3$, 470.6, ppm) : -62.57.

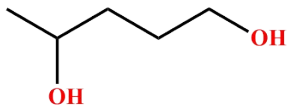
Compound **11**



11; (61mg, 81%) ^{1}H-NMR ($CDCl_3$, 500 MHz, ppm): 7.93 (2H, s), 7.61 (2H, d, J= 8.0 Hz), 7.31 (2H, d, J= 8.0 Hz), 7.15 (2H, t, J= 7.5 Hz), 7.04 (2H, t, J= 7.5 Hz), 6.98 (2H, s), 4.69 (1H, t, J= 7.5 Hz), 3.73 (2H, t, J= 6.5Hz), 2.49 (2H, q, J= 6.5 Hz), 1.64 (1H, s, br).

^{13}C-NMR ($CDCl_3$, 125 MHz, ppm): 136.73, 127.05, 122.01, 121.67, 119.76, 119.73, 119.27, 111.27, 61.87, 38.49, 30.70.

Compound **13**

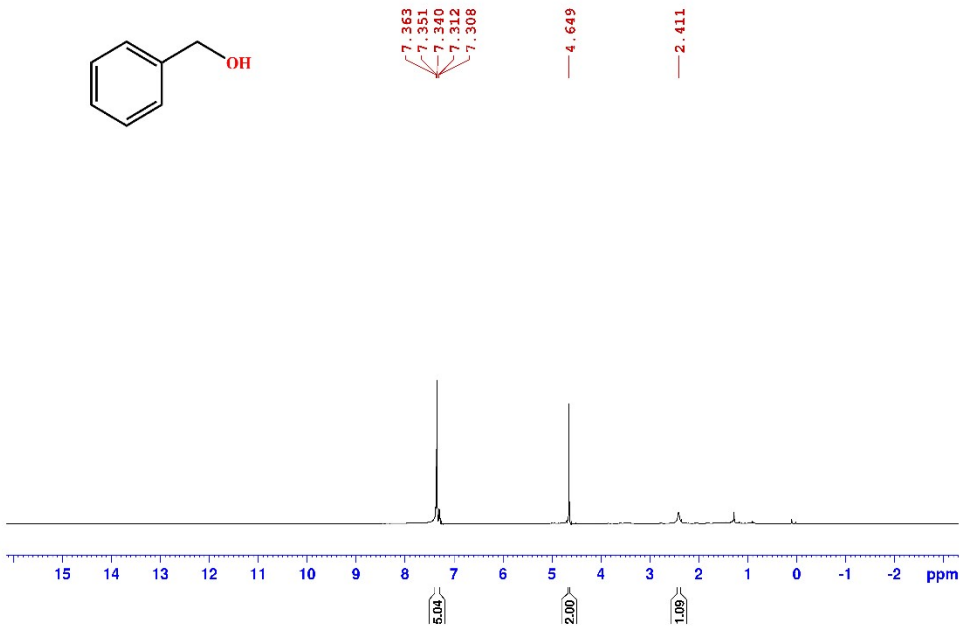


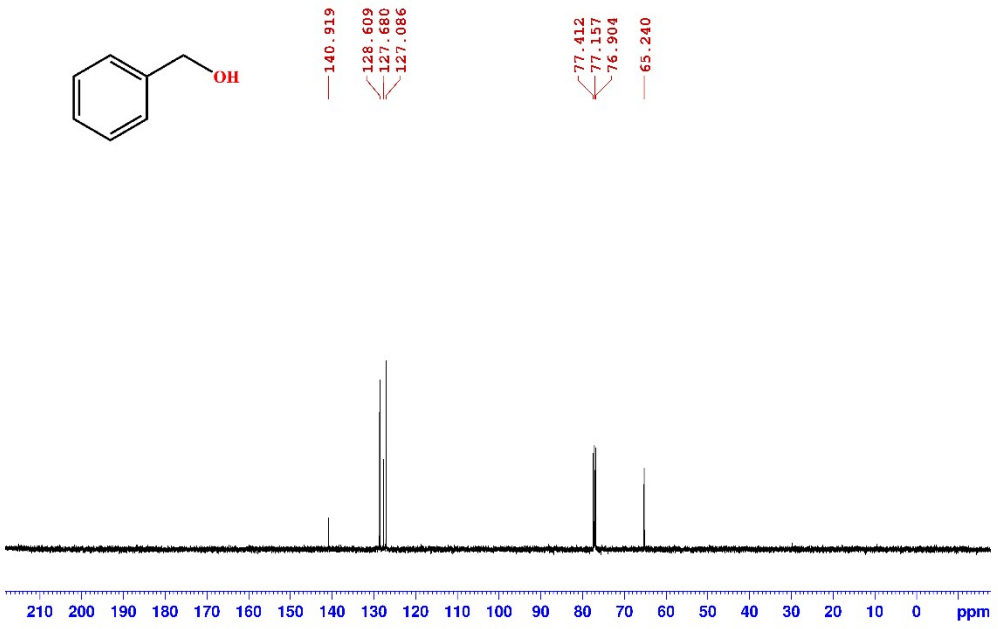
13; (51mg, 70%) ^{1}H-NMR ($CDCl_3$, 500 MHz, ppm): 3.81 (2H, s), 3.63 (2H, d, J= 19Hz), 3.15 (2H, s, br), 1.67-1.58 (2H, m), 1.49 (2H, t, J= 6.75 Hz), 1.18 (3H, d, J= 6.75 Hz).

^{13}C-NMR ($CDCl_3$, 125 MHz, ppm): 67.95, 62.82, 36.30, 29.16, 23.58.

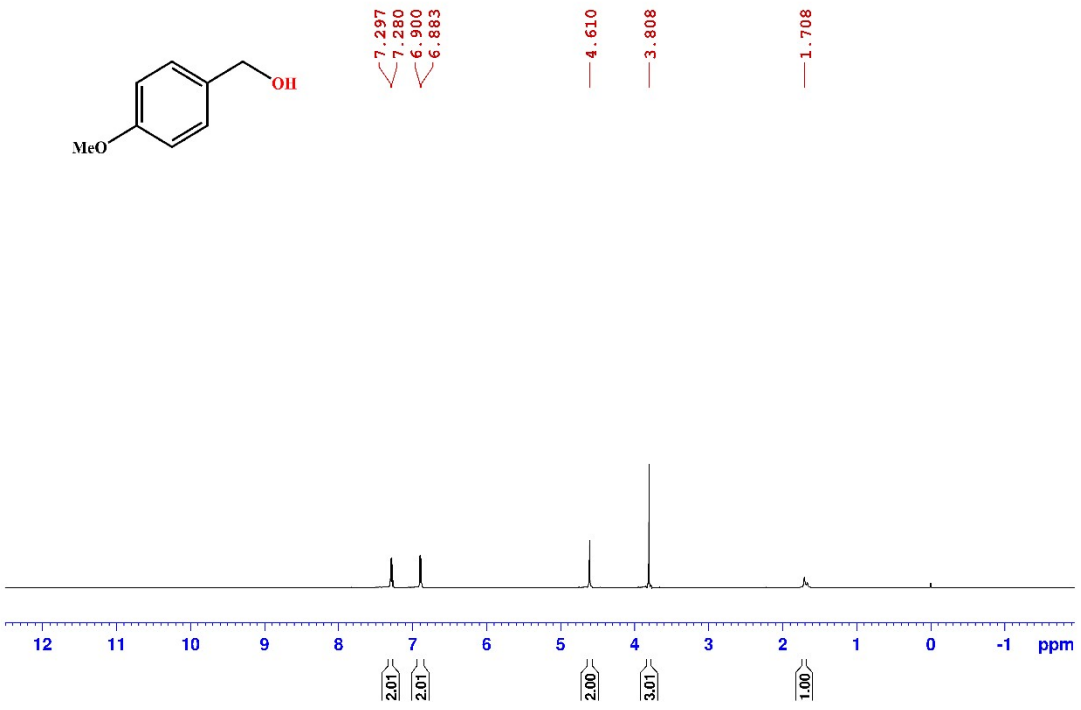
M. Representative NMR Spectra:

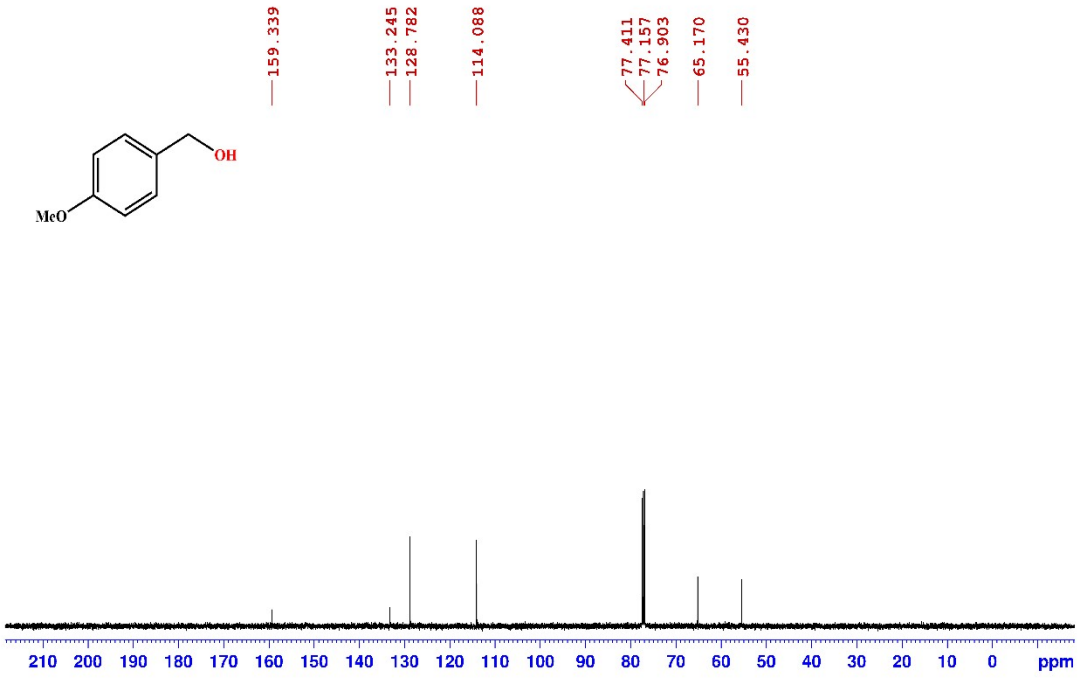
^{1}H-NMR & $^{13}C\{^{1}H\}$ (in $CDCl_3$) spectra of compound **2a**



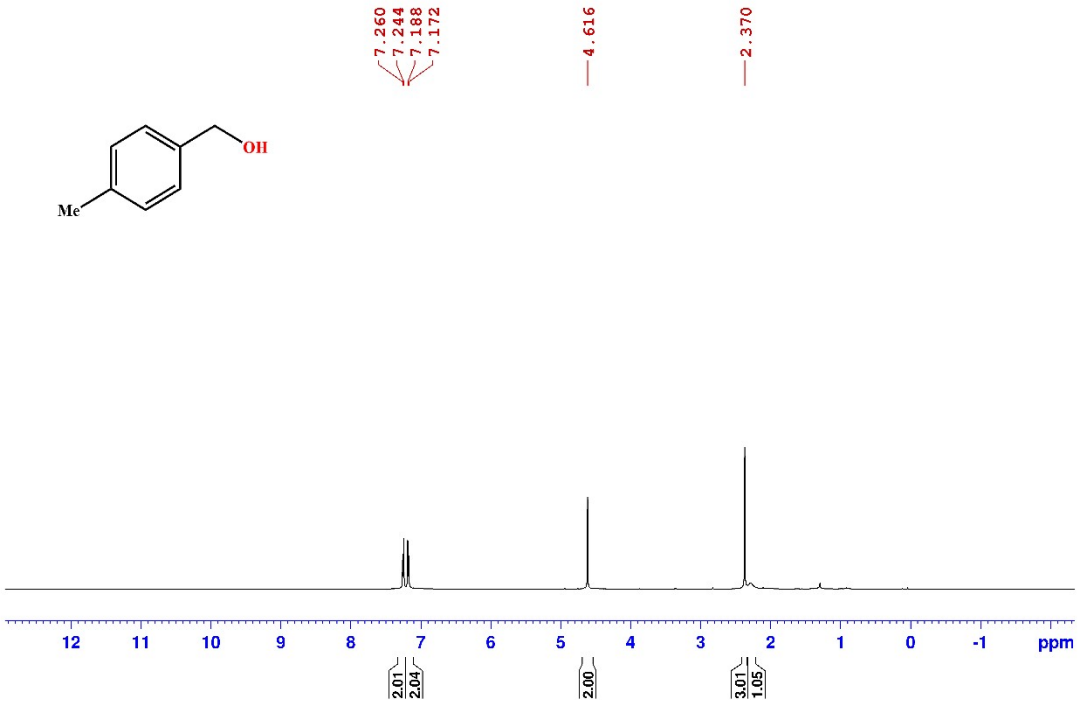


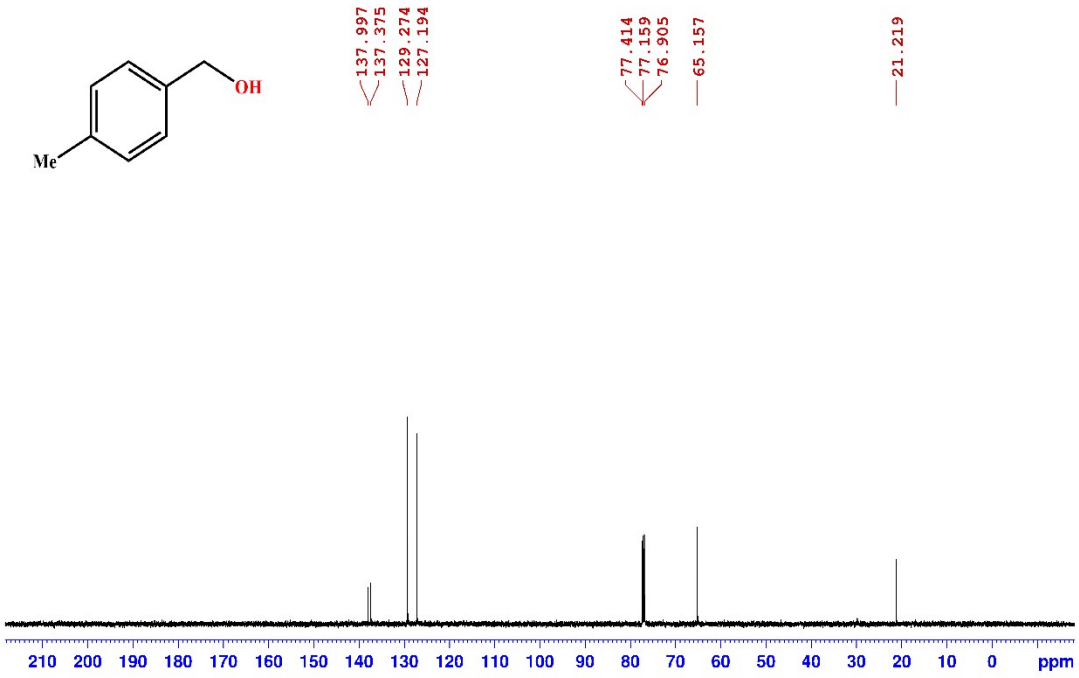
^{1}H-NMR & ^{13}C{^{1}H} (in $CDCl_3$) spectra of compound **2d**



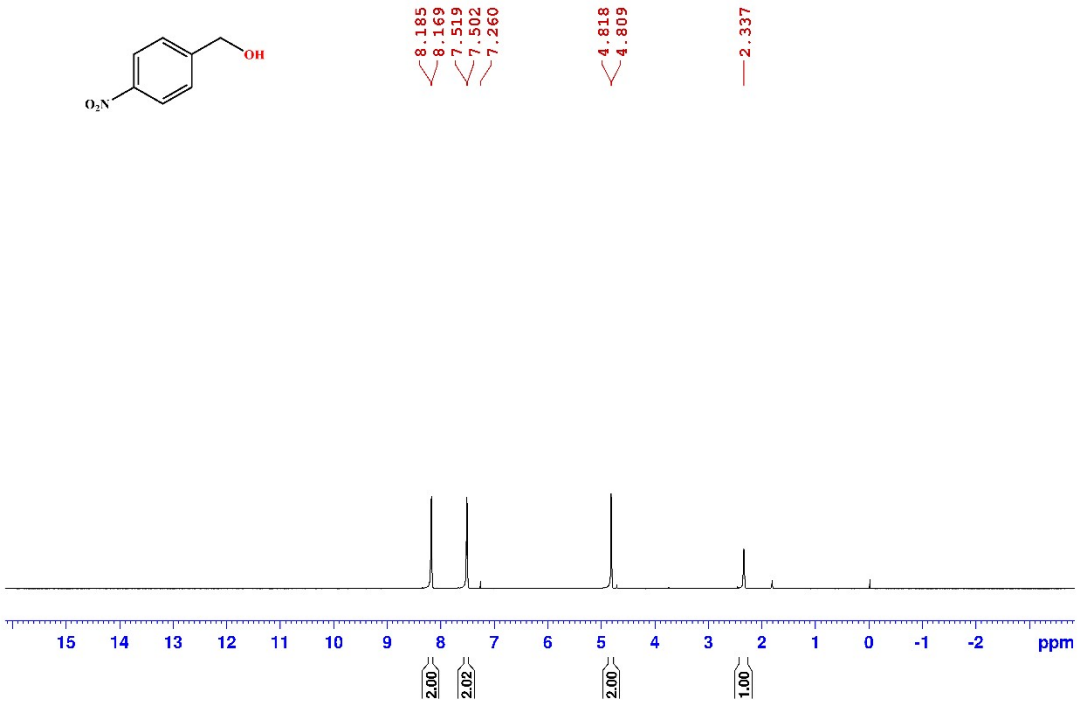


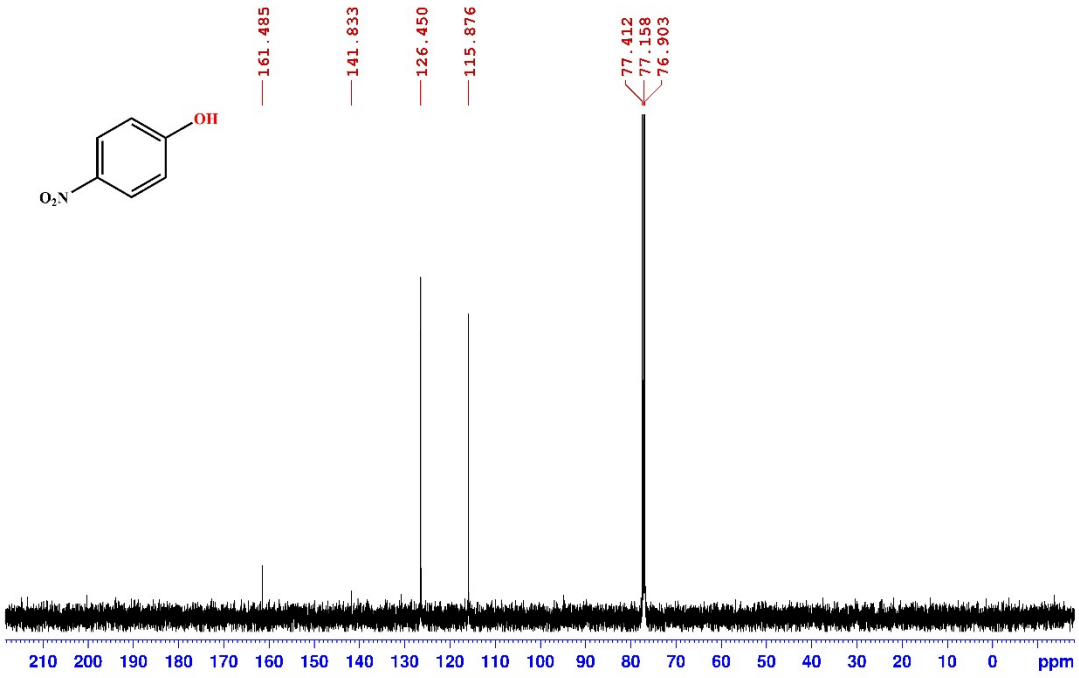
^{1}H-NMR & $^{13}C\{^{1}H\}$ (in $CDCl_3$) spectra of compound **2e**



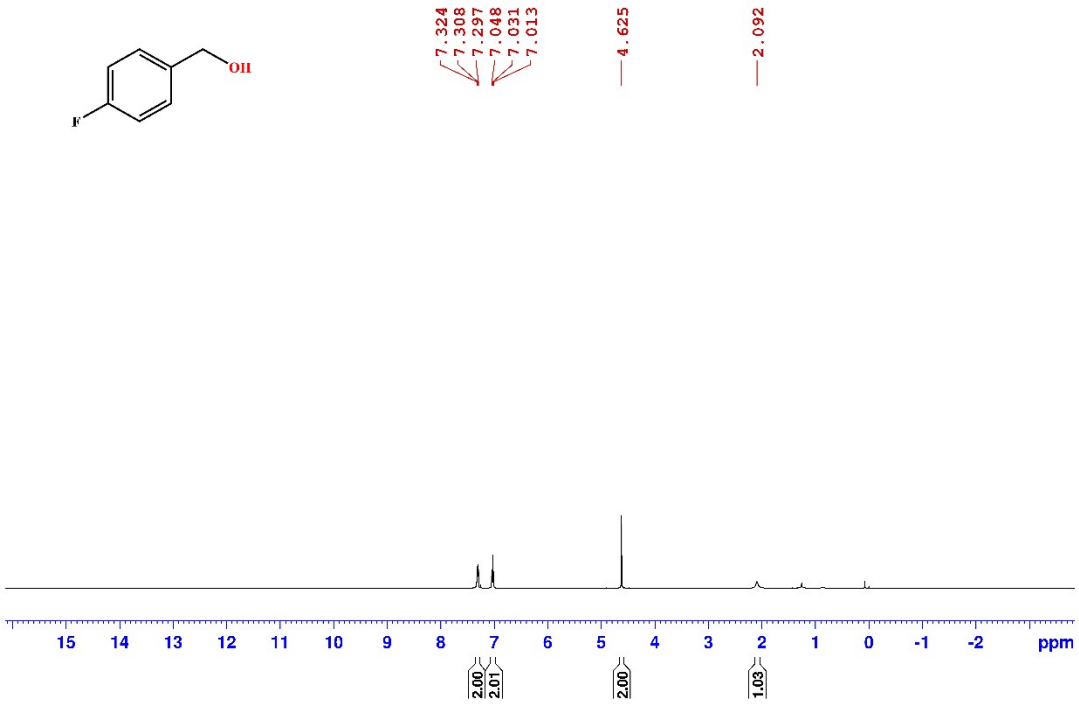


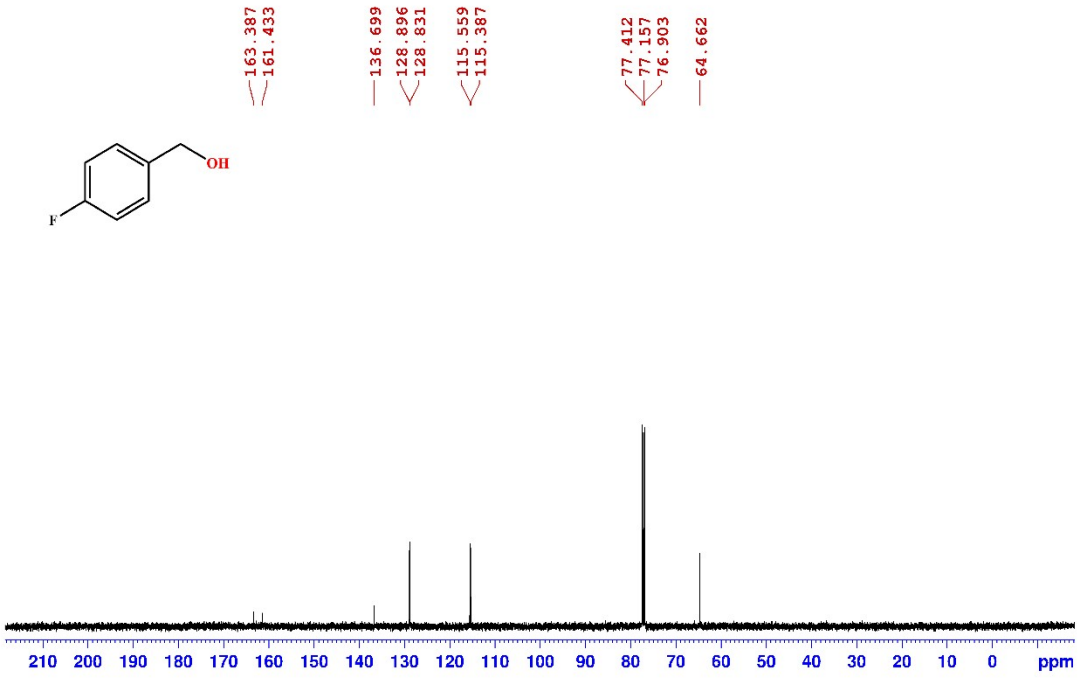
^{1}H-NMR & ^{13}C{^{1}H} (in $CDCl_3$) spectra of compound **2f**

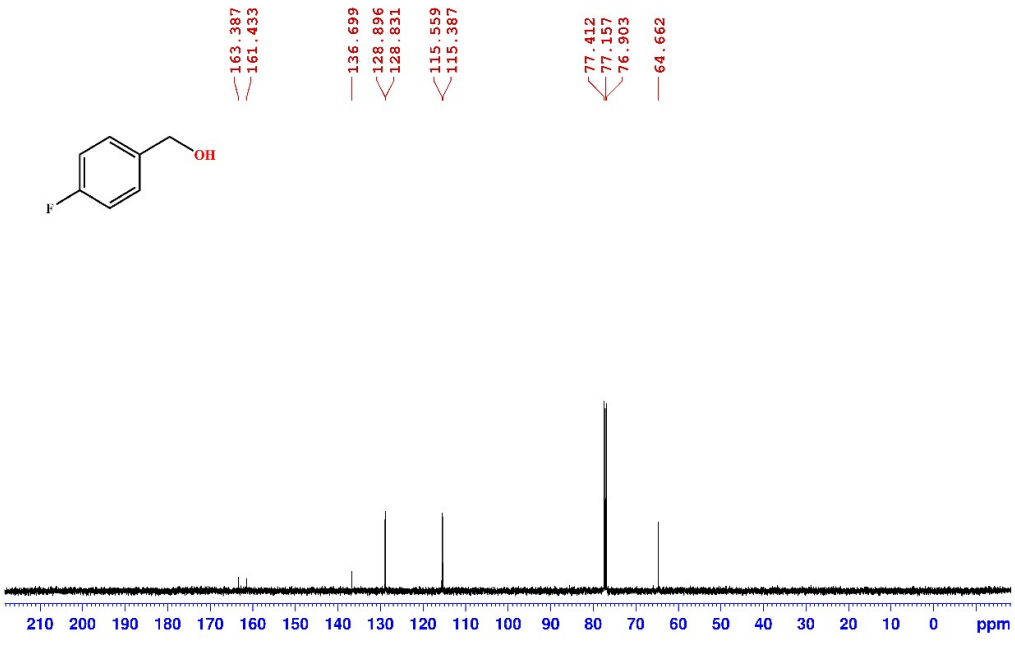




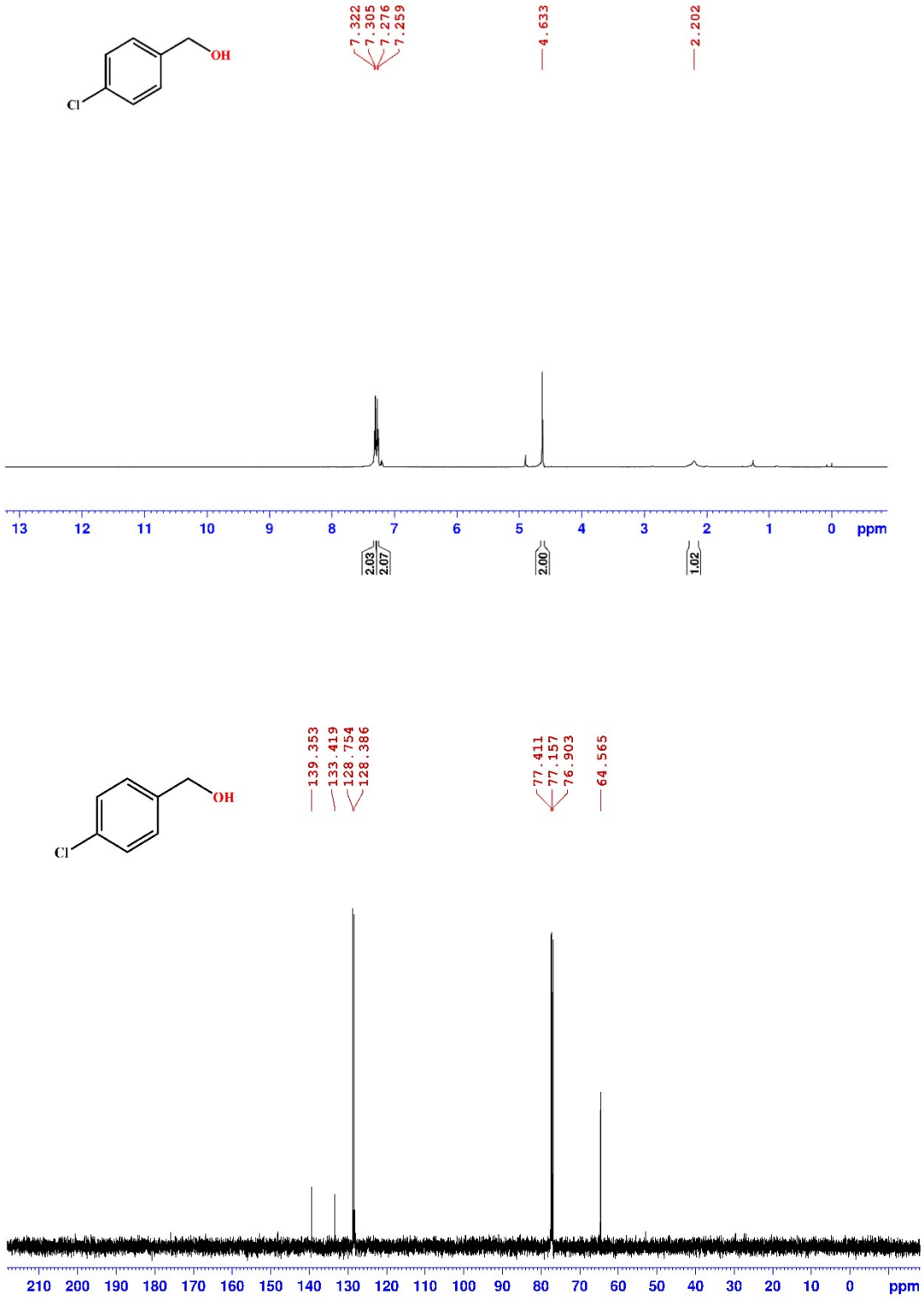
^{1}H-NMR, ^{13}C{^{1}H} & ^{19}F{^{1}H} (in $CDCl_3$) spectra of compound **2g**



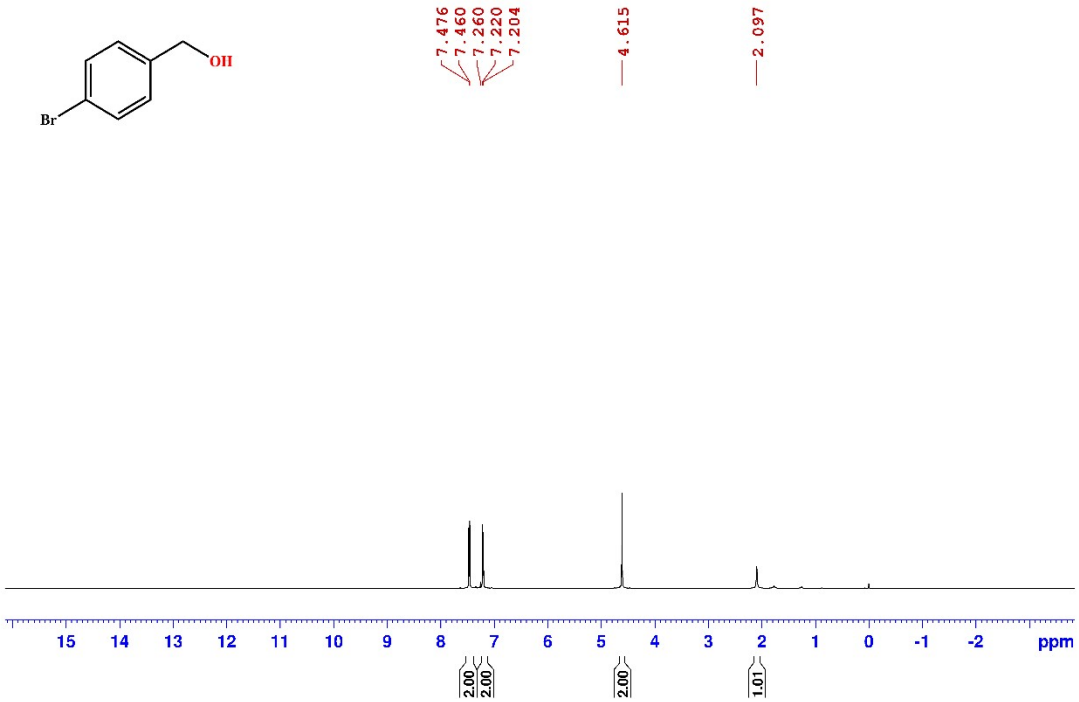


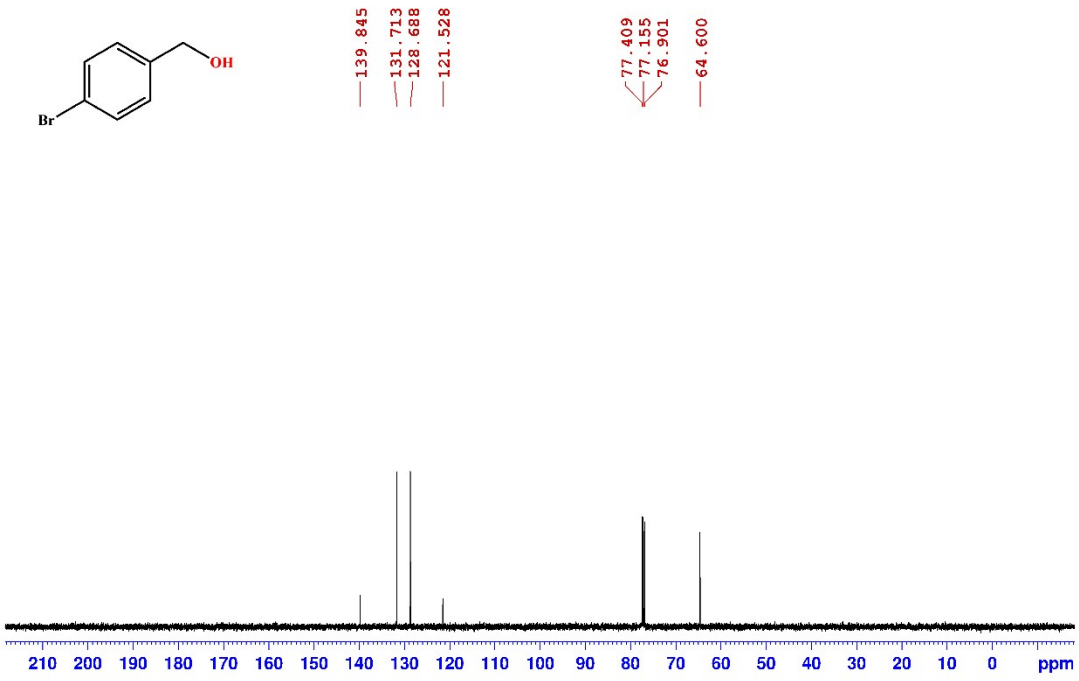


^{1}H-NMR & ^{13}C{^{1}H} (in $CDCl_3$) spectra of compound **2h**

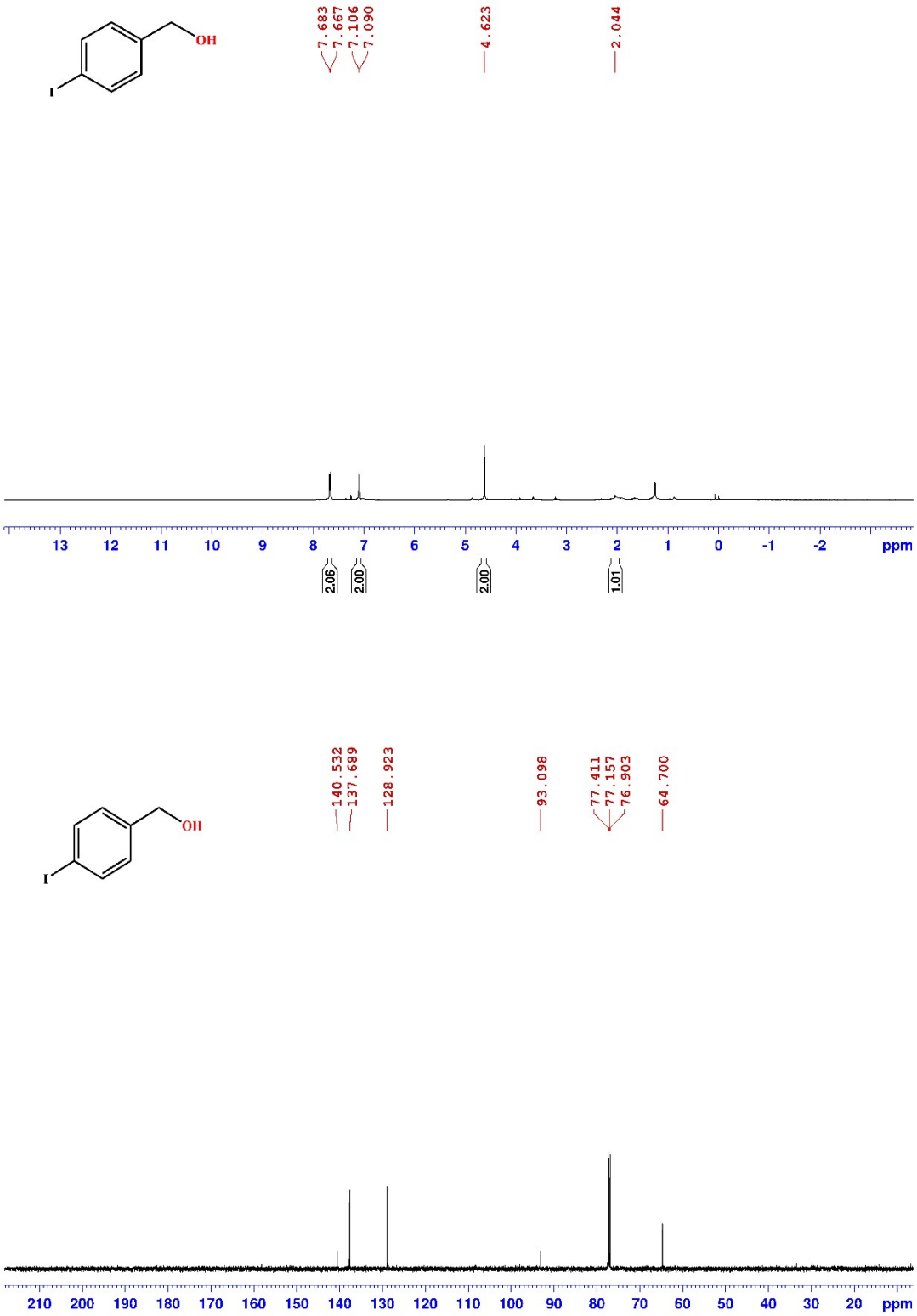


^{1}H-NMR & ^{13}C{^{1}H} (in $CDCl_3$) spectra of compound **2i**

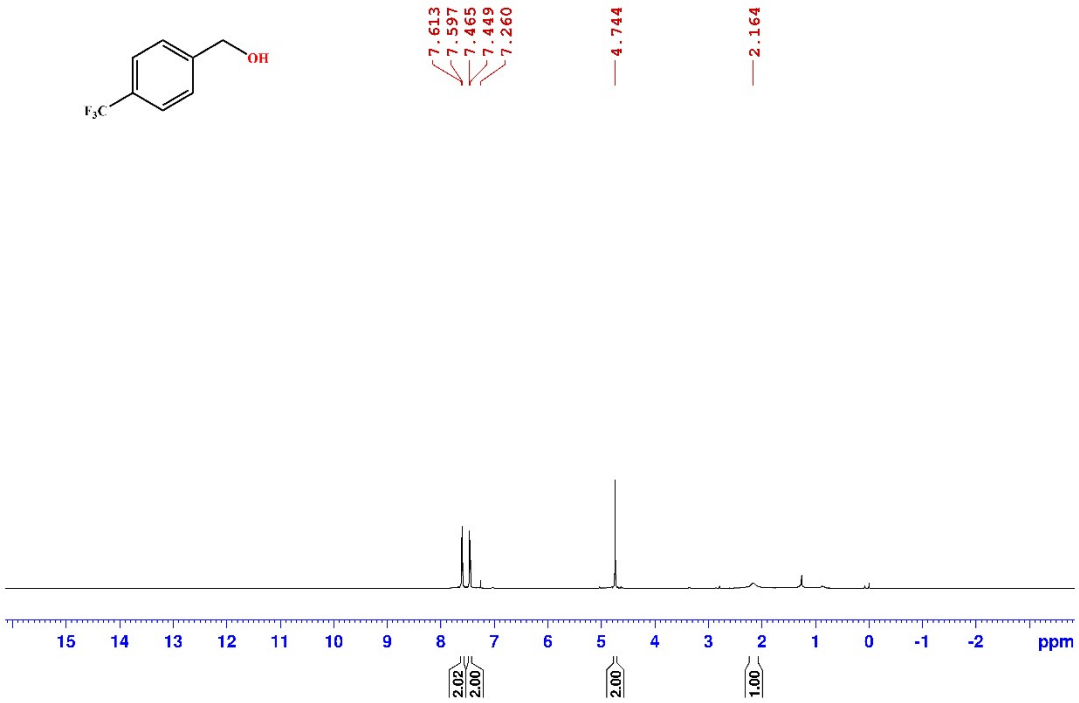




^{1}H-NMR & ^{13}C{^{1}H} (in $CDCl_3$) spectra of compound **2j**



^{1}H-NMR, ^{13}C{^{1}H} & ^{19}F{^{1}H} (in $CDCl_3$) spectra of compound **2k**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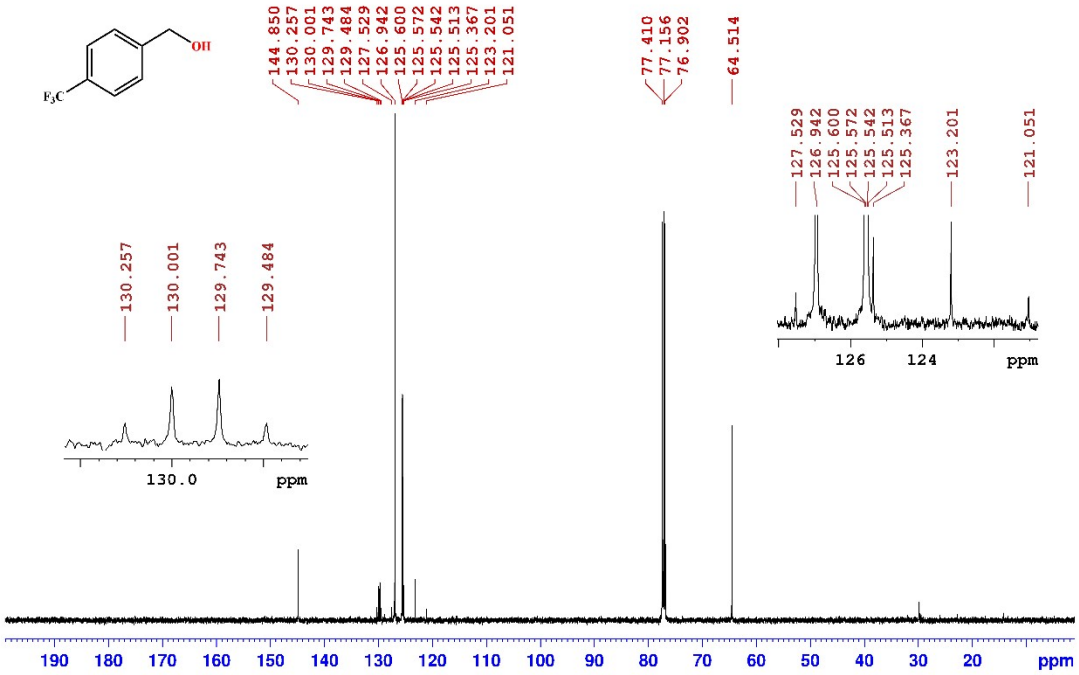
F3C
7.613
7.597
7.465
7.449
7.260
4.744
2.164
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 ppm
2.02
2.00
2.00
1.00


OH
F3C
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130.257
130.001
129.743
129.484
127.529
126.942
125.600
125.572
125.542
125.513
125.367
123.201
121.051
77.410
77.156
76.902
64.514
130.257
130.001
129.743
129.484
130.0 ppm
127.529
126.942
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125.572
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125.513
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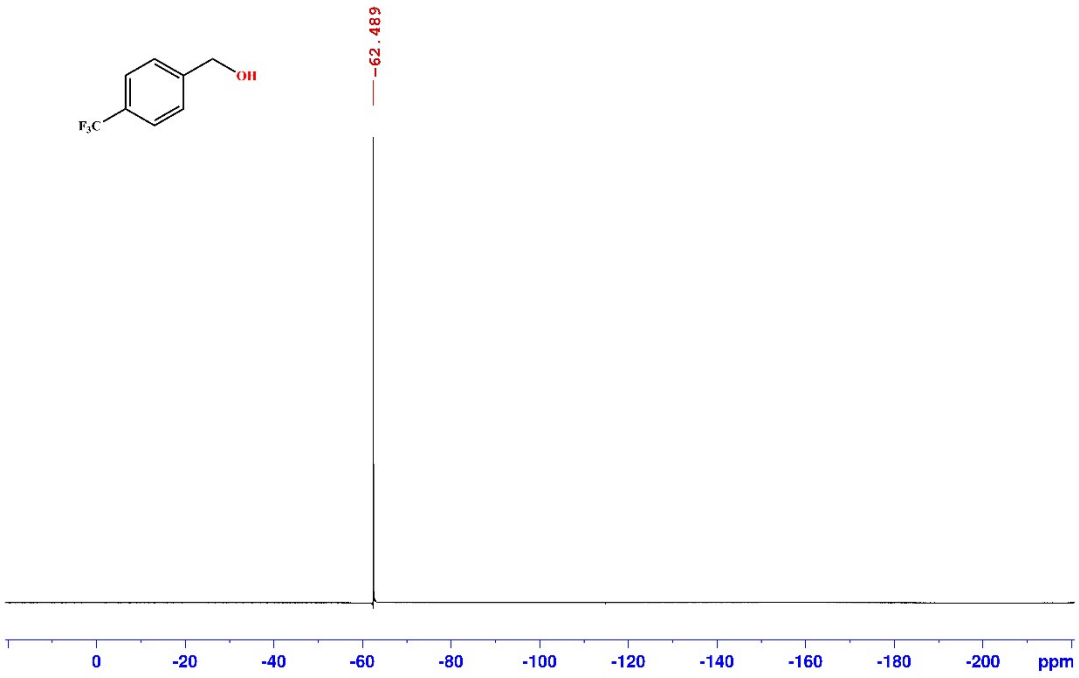
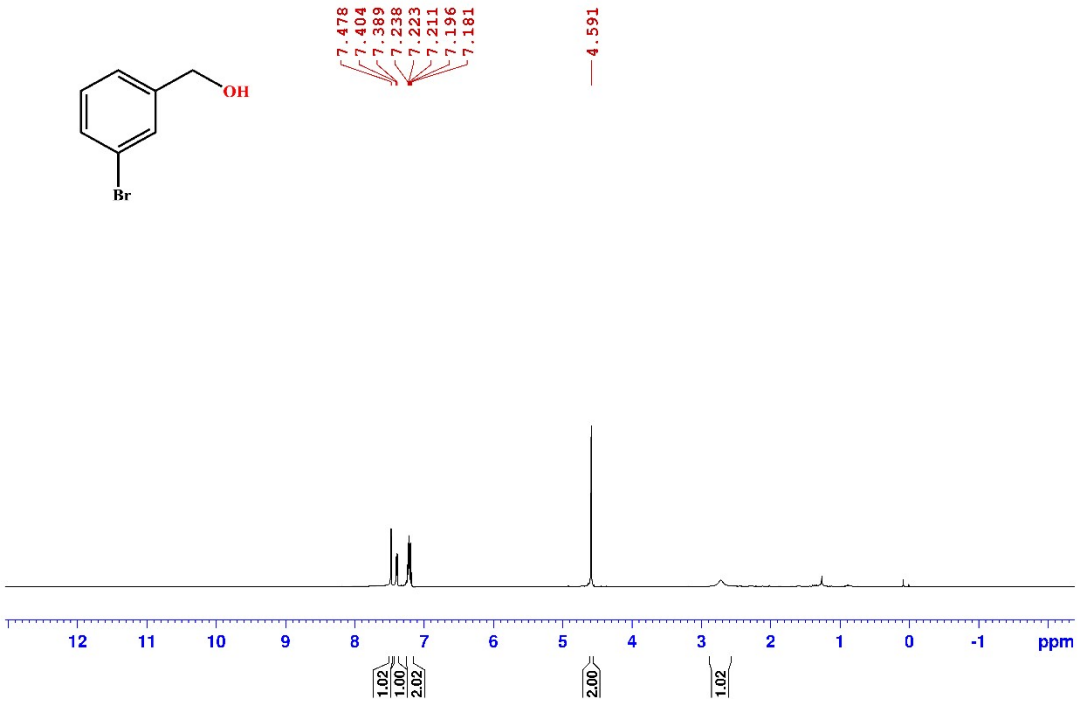
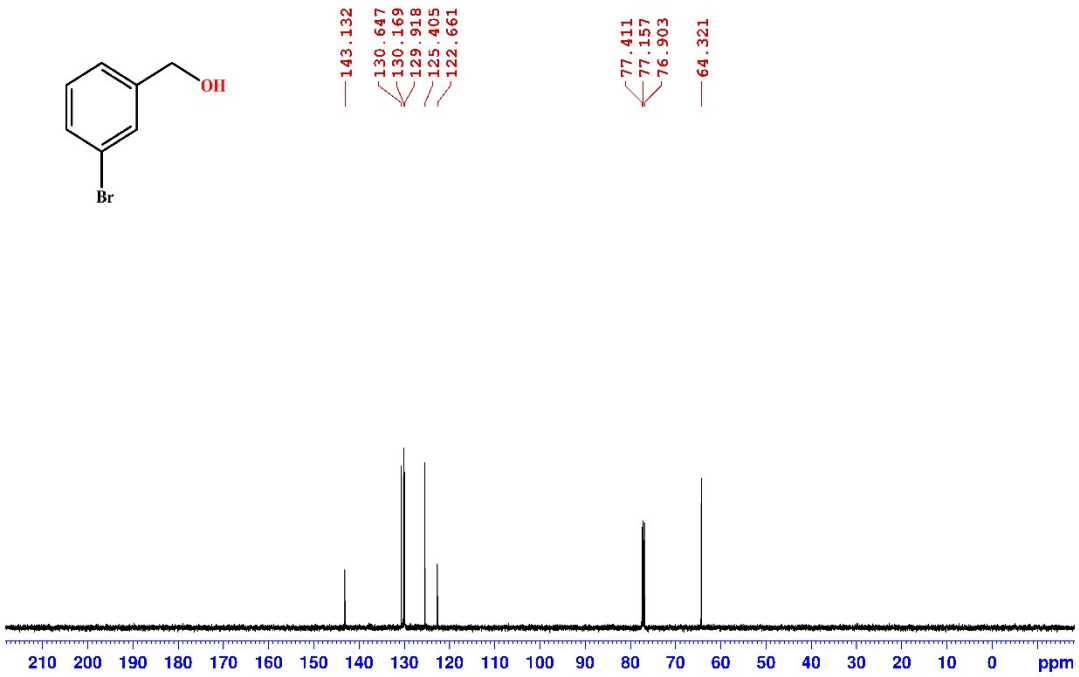
123.201
121.051
126 124 ppm
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

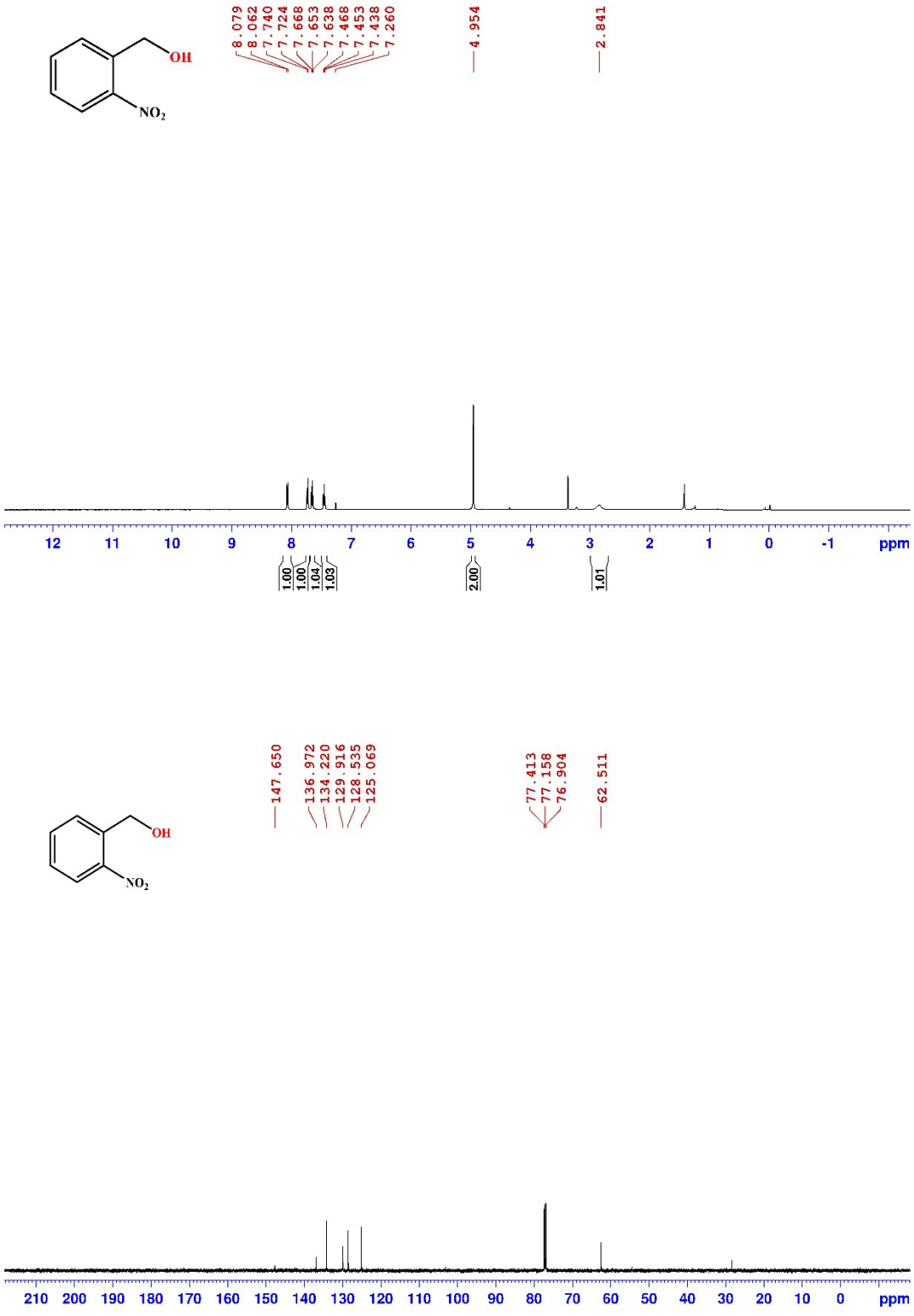


^{1}H-NMR & ^{13}C{^{1}H} (in $CDCl_3$) spectra of compound **2l**

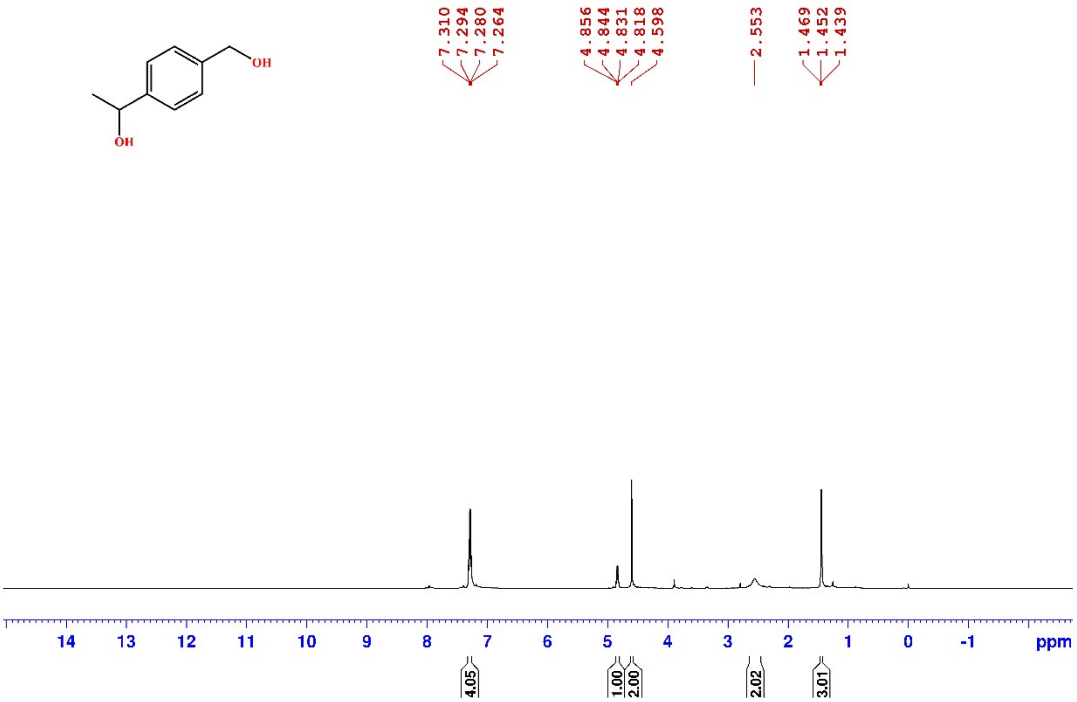


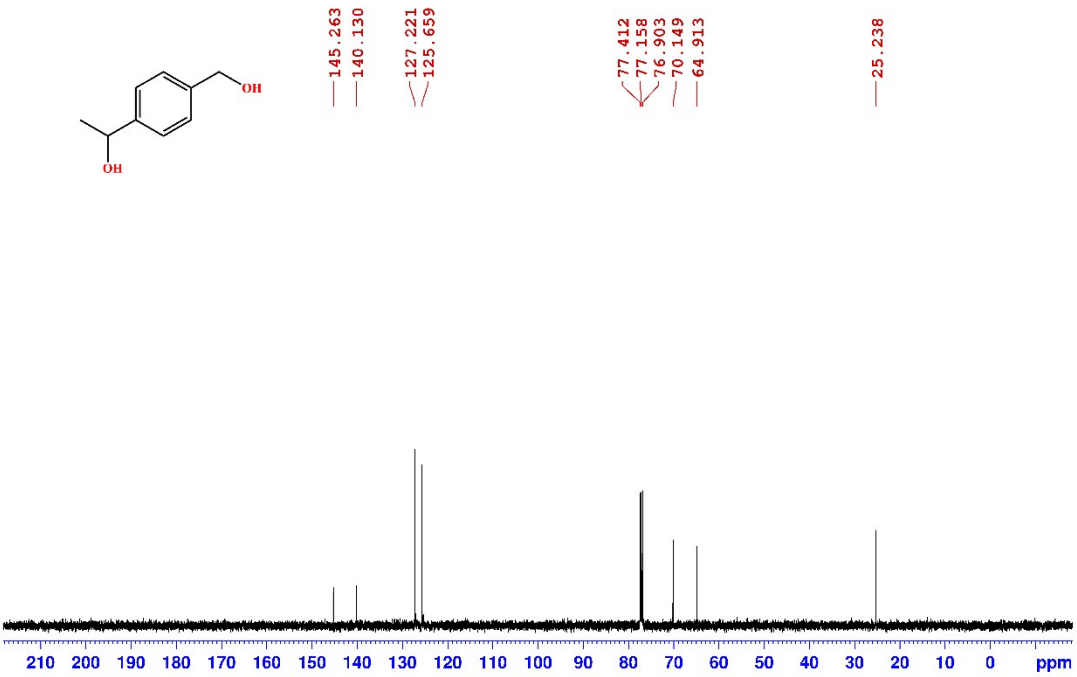


^{1}H-NMR & ^{13}C{^{1}H} (in $CDCl_3$) spectra of compound **2m**

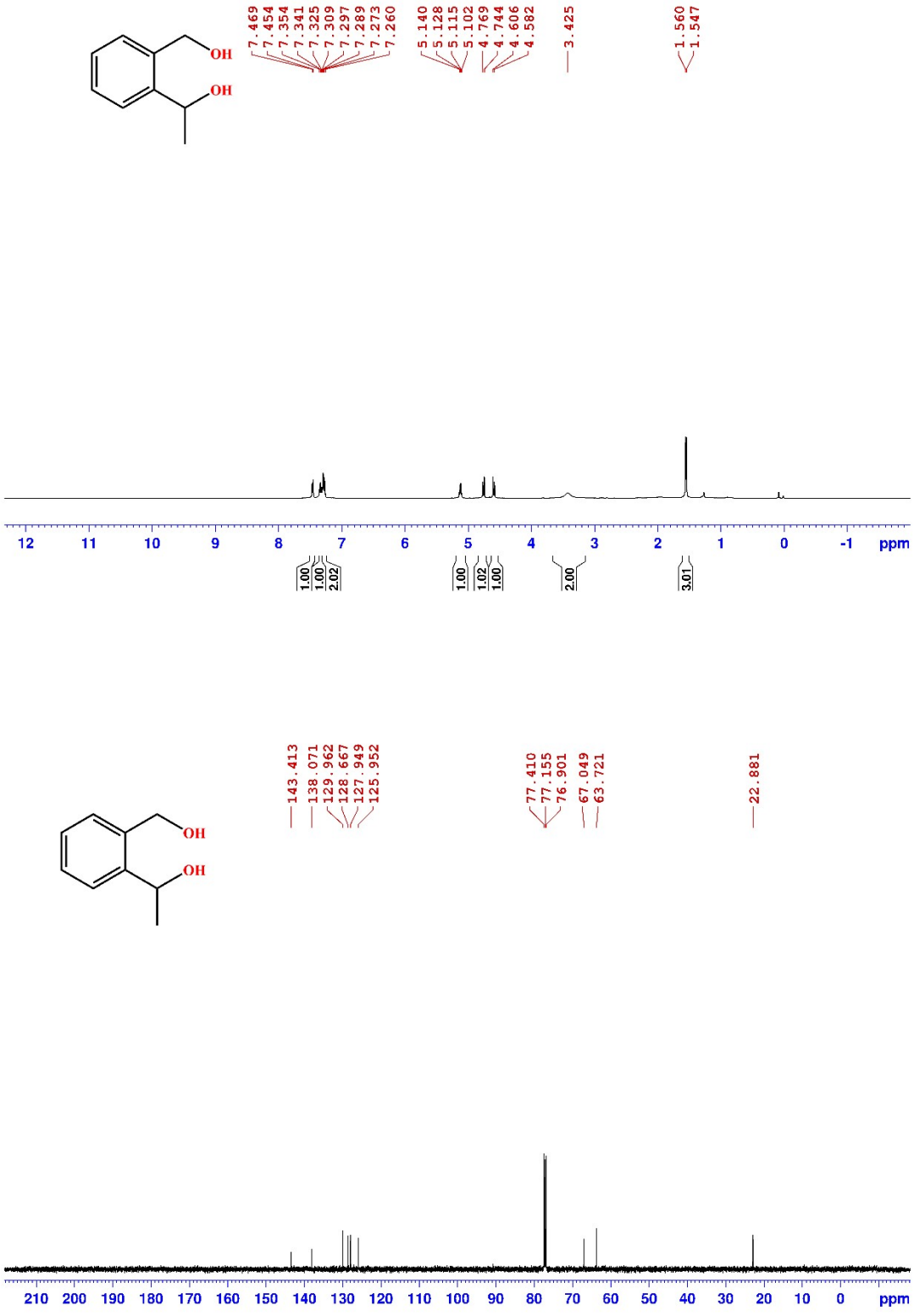


^{1}H-NMR & ^{13}C{^{1}H} (in $CDCl_3$) spectra of compound **2n**

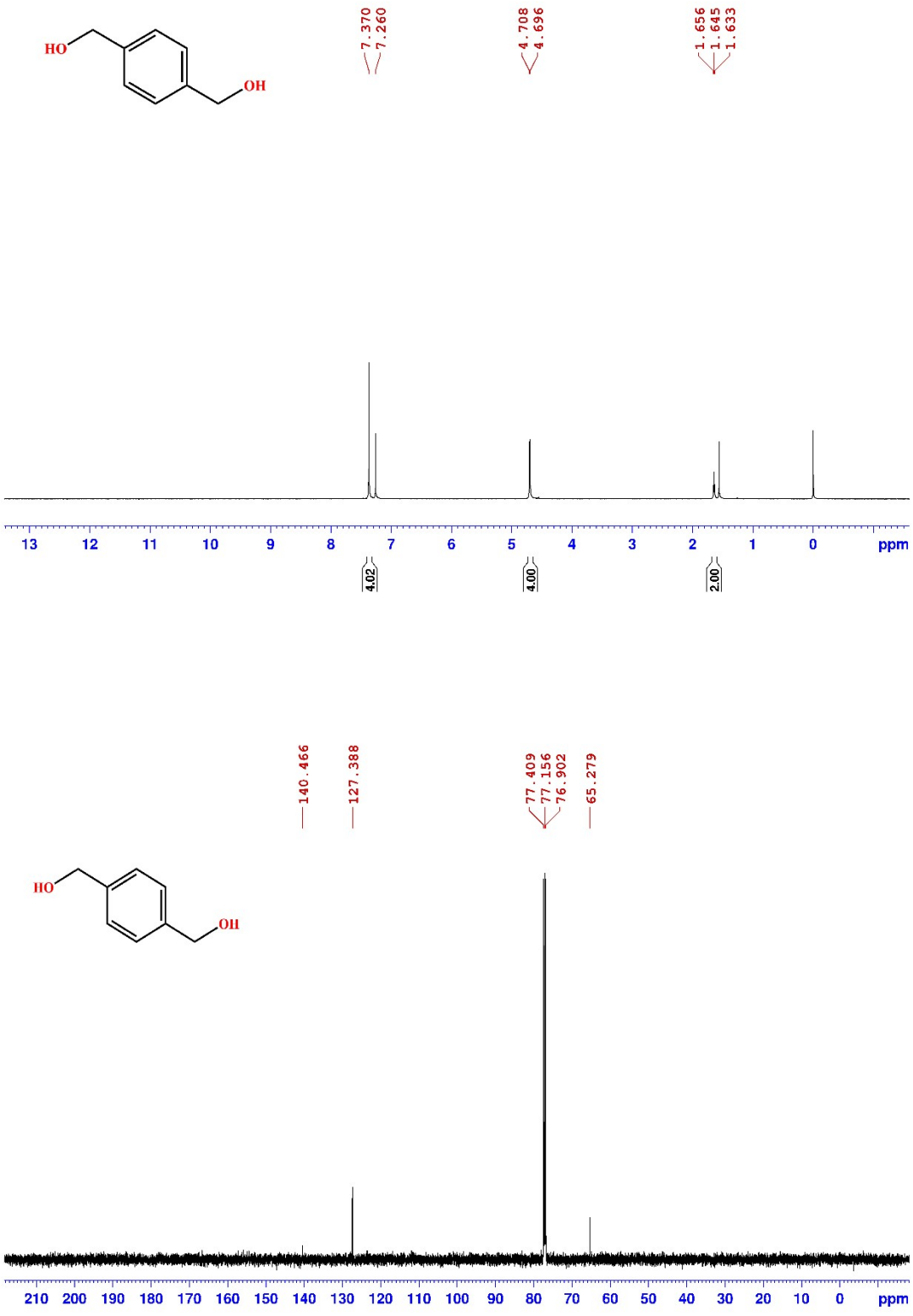




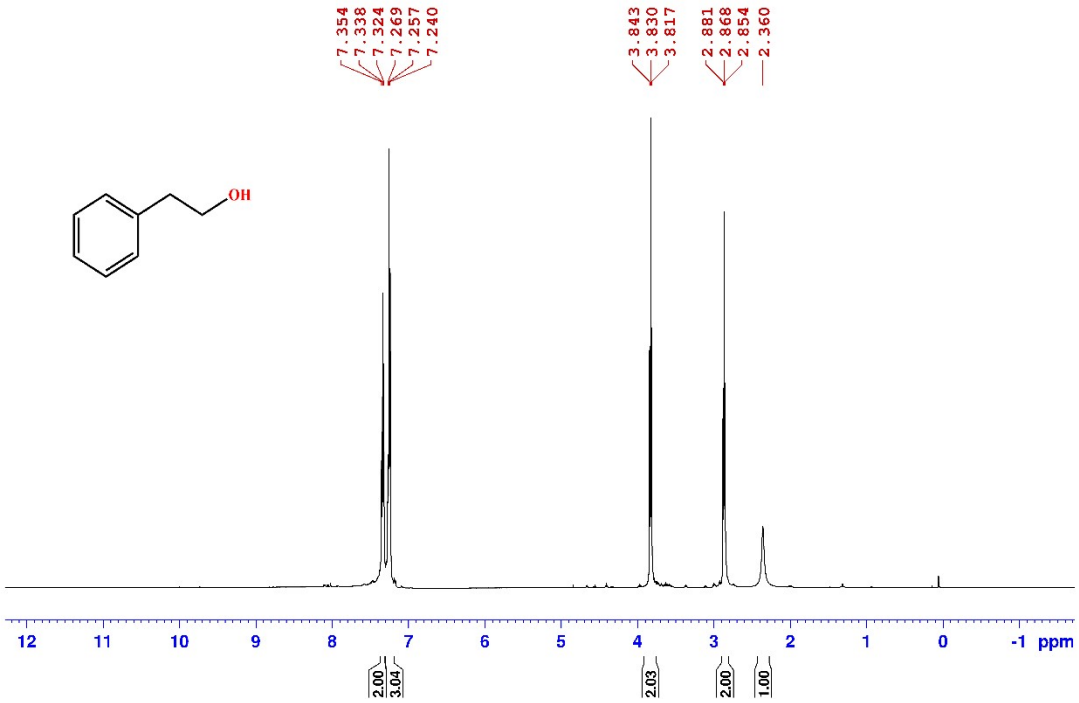
^{1}H-NMR & ^{13}C{^{1}H} (in $CDCl_3$) spectra of compound **2o**

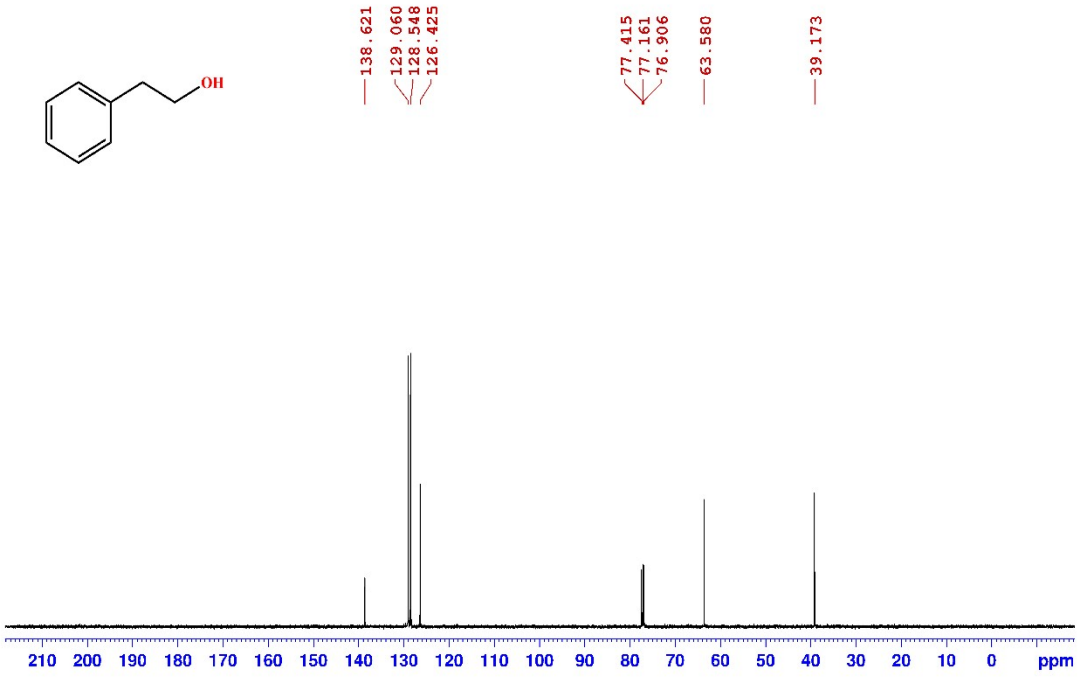


^{1}H-NMR & ^{13}C{^{1}H} (in $CDCl_3$) spectra of compound **2p**

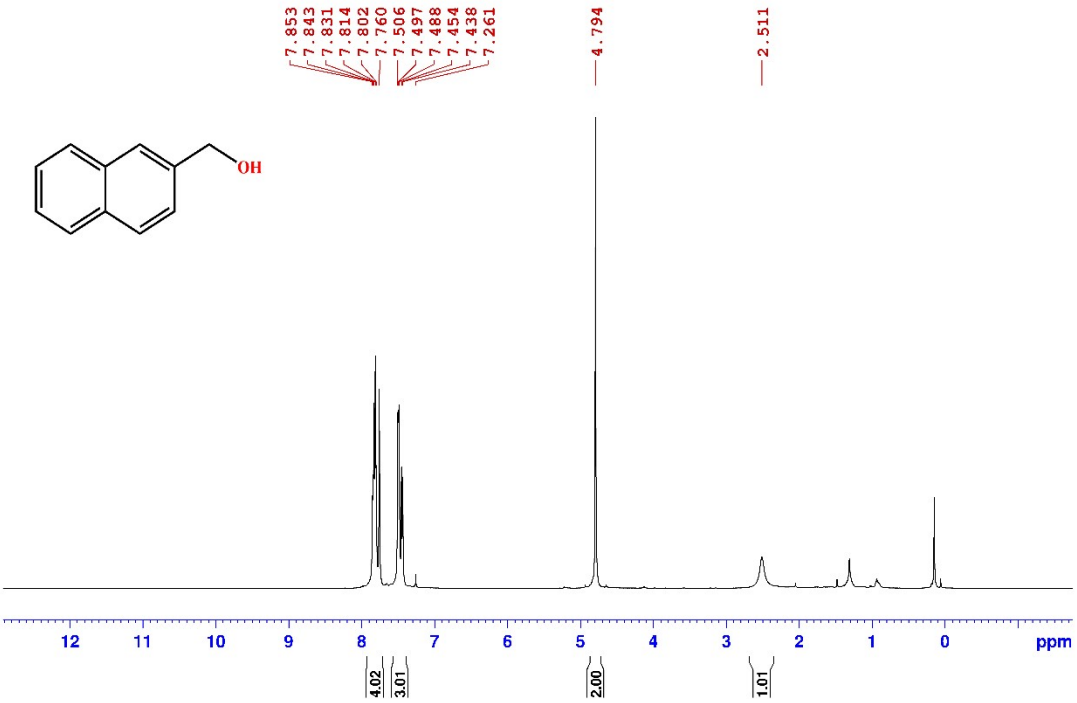


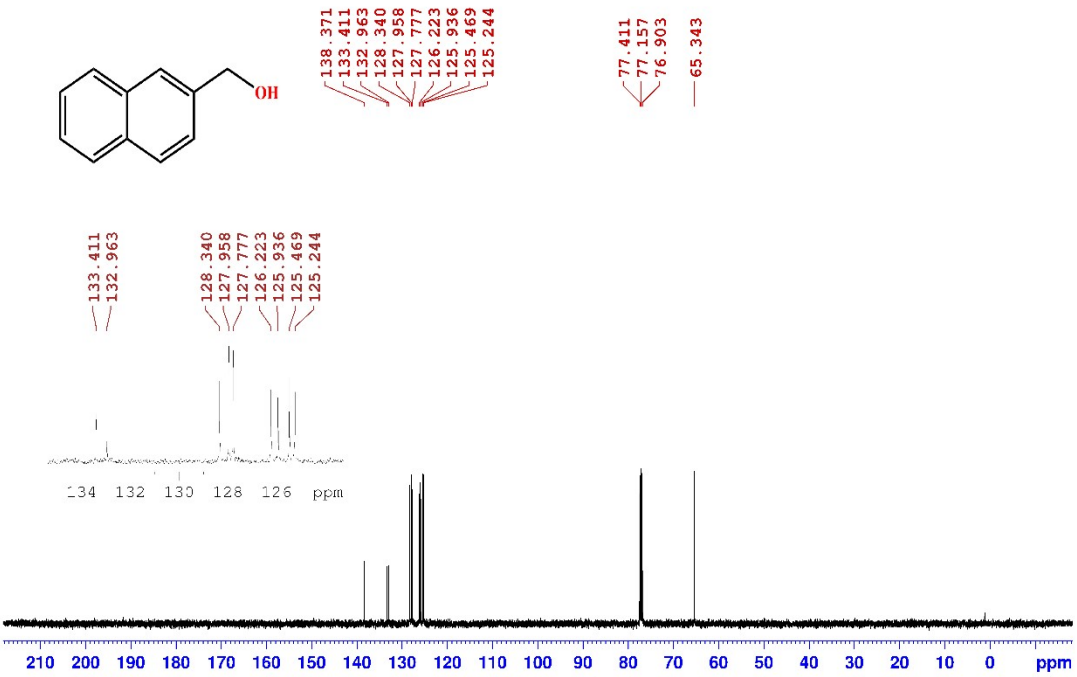
^{1}H-NMR & $^{13}C\{^{1}H\}$ (in $CDCl_3$) spectra of compound **2q**



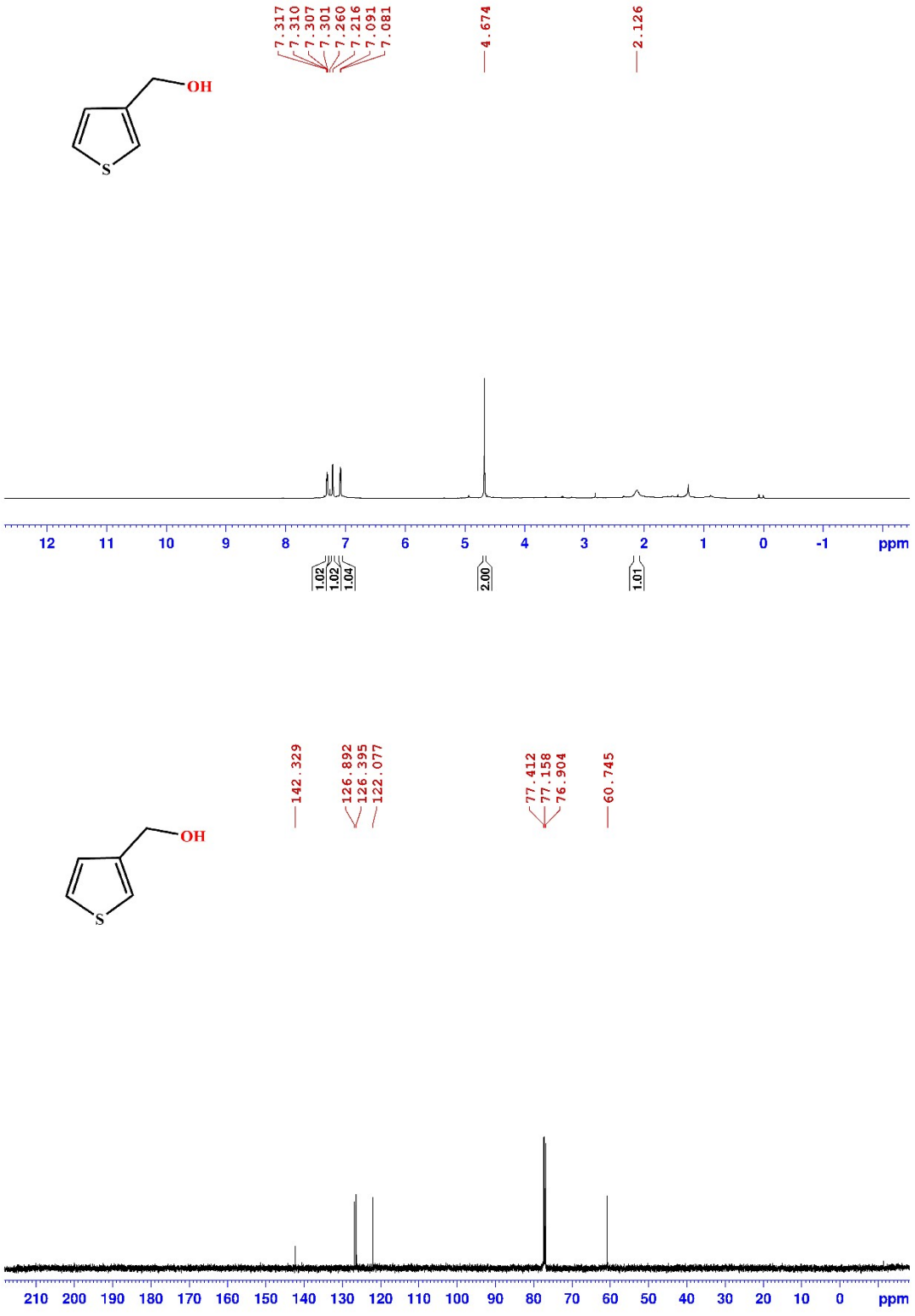


^{1}H-NMR & $^{13}C\{^{1}H\}$ (in $CDCl_3$) spectra of compound **2r**

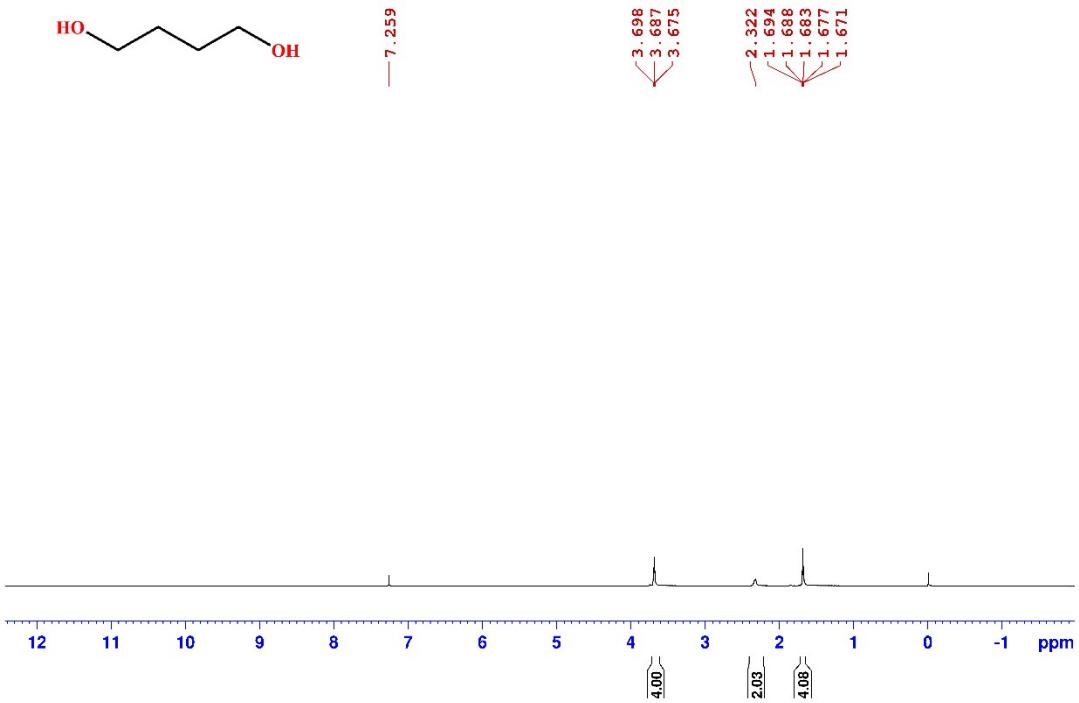


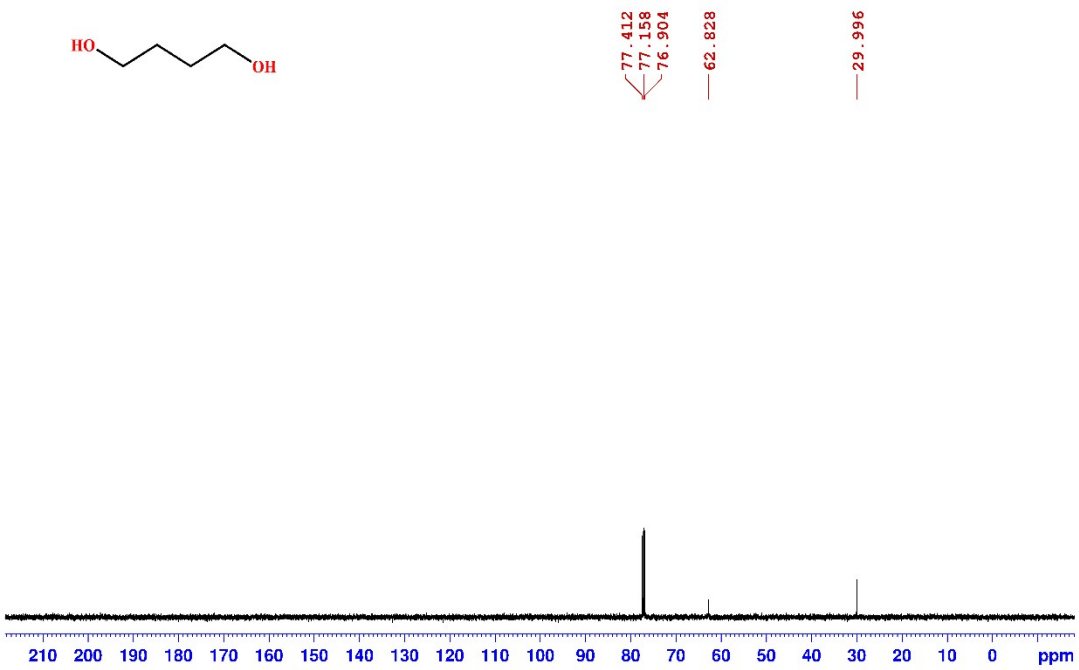


^{1}H-NMR & ^{13}C{^{1}H} (in $CDCl_3$) spectra of compound **2s**

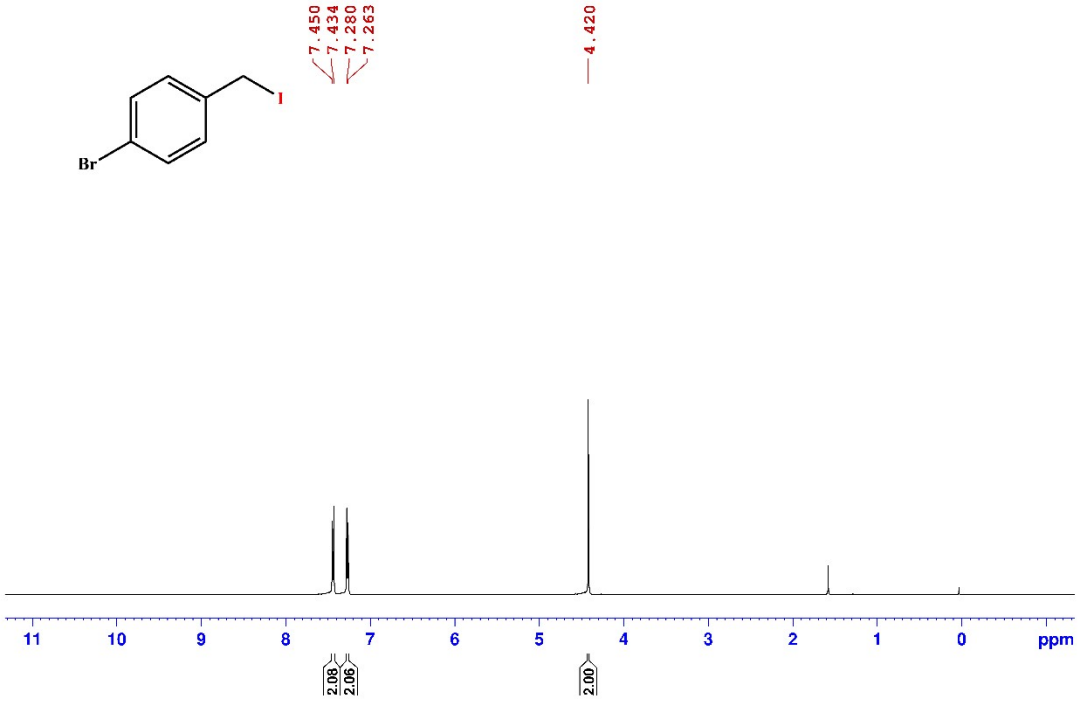


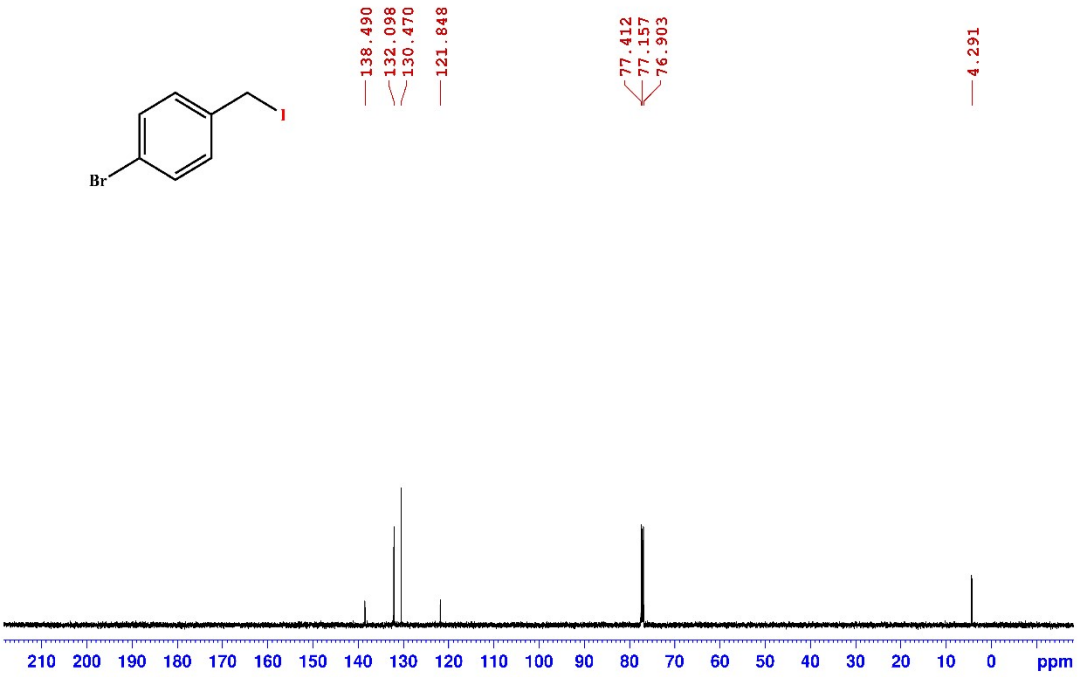
^{1}H-NMR & $^{13}C\{^{1}H\}$ (in $CDCl_3$) spectra of compound **2u**



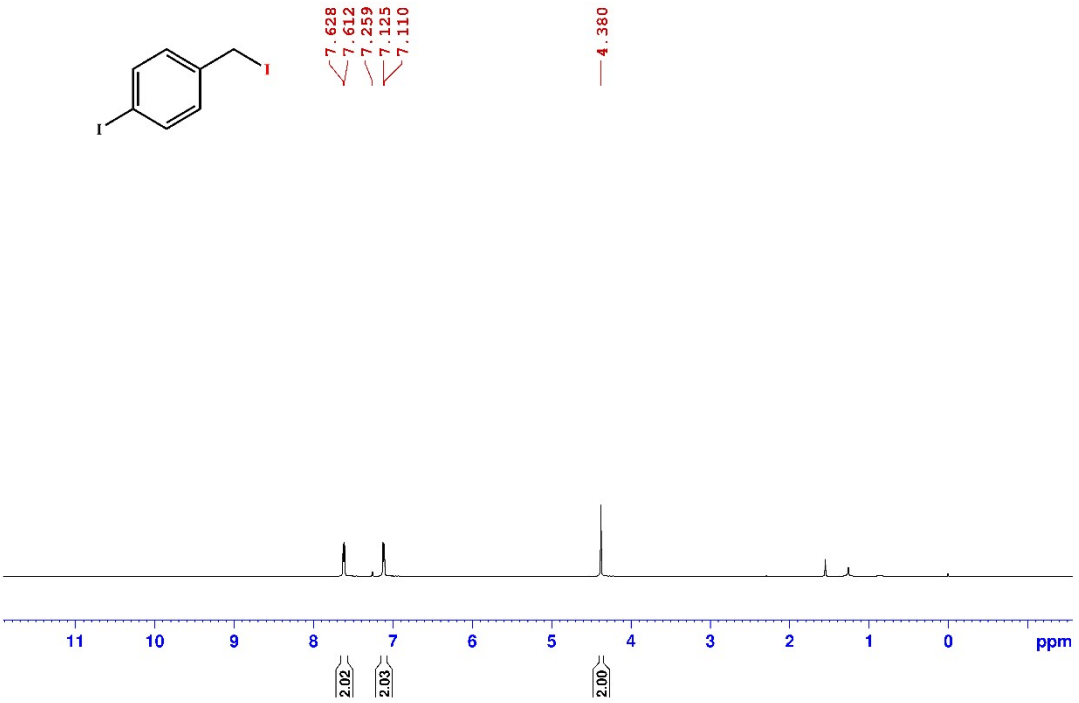


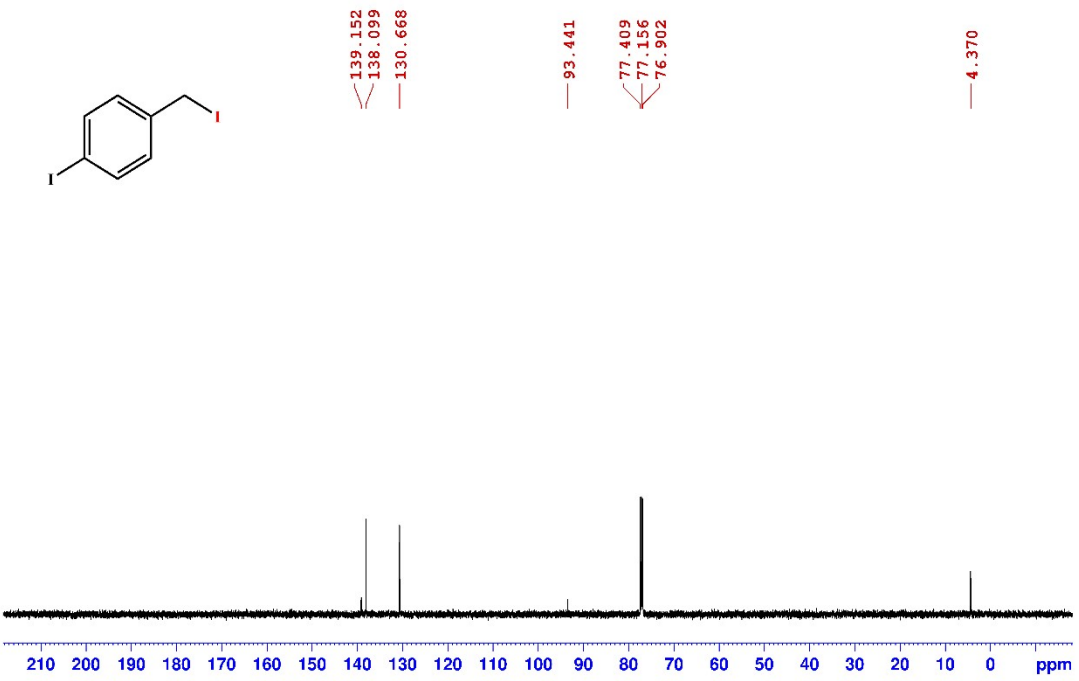
^{1}H-NMR & ^{13}C{^{1}H} (in $CDCl_3$) spectra of compound **3a**



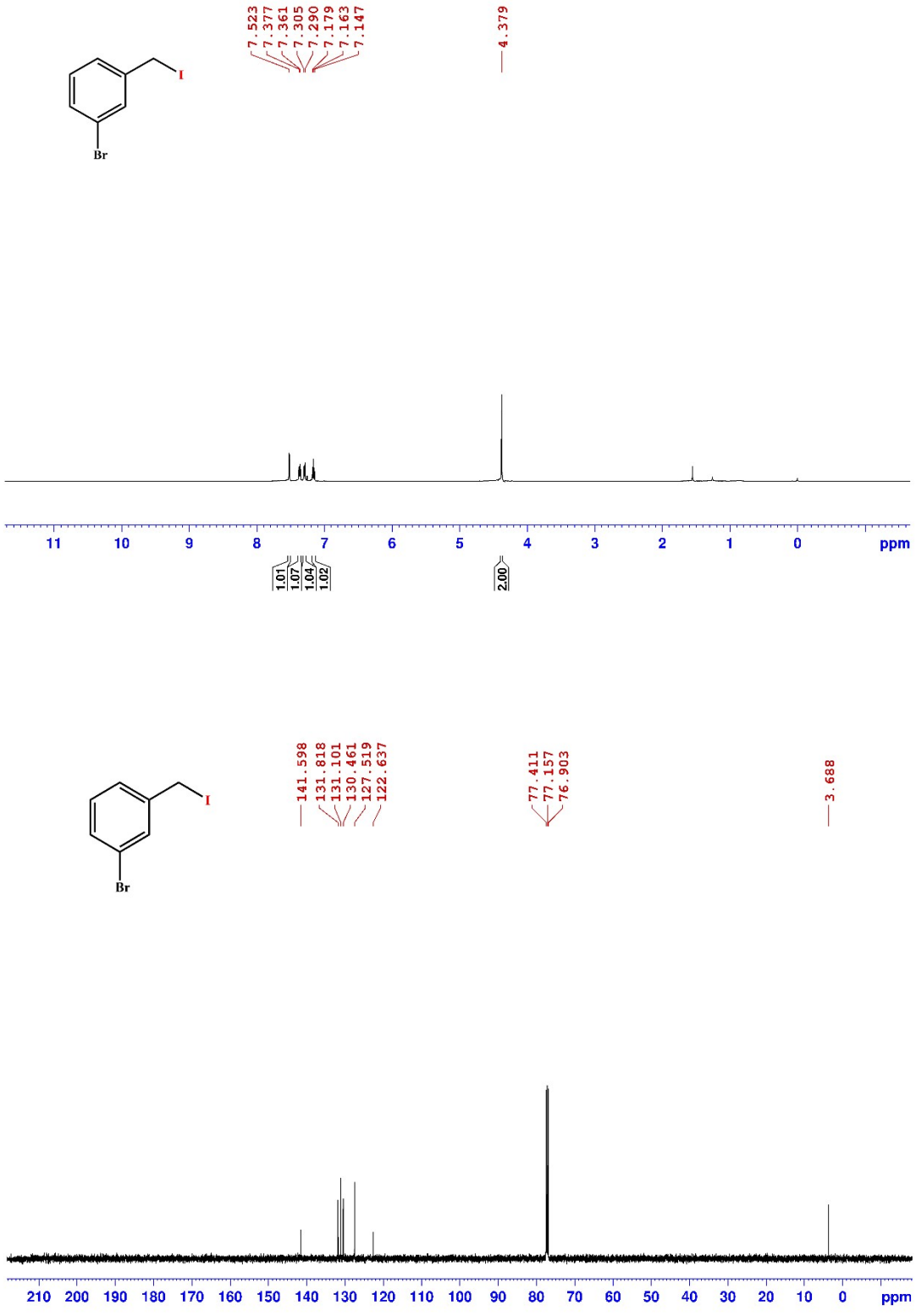


^{1}H-NMR & $^{13}C\{^{1}H\}$ (in $CDCl_3$) spectra of compound **3b**

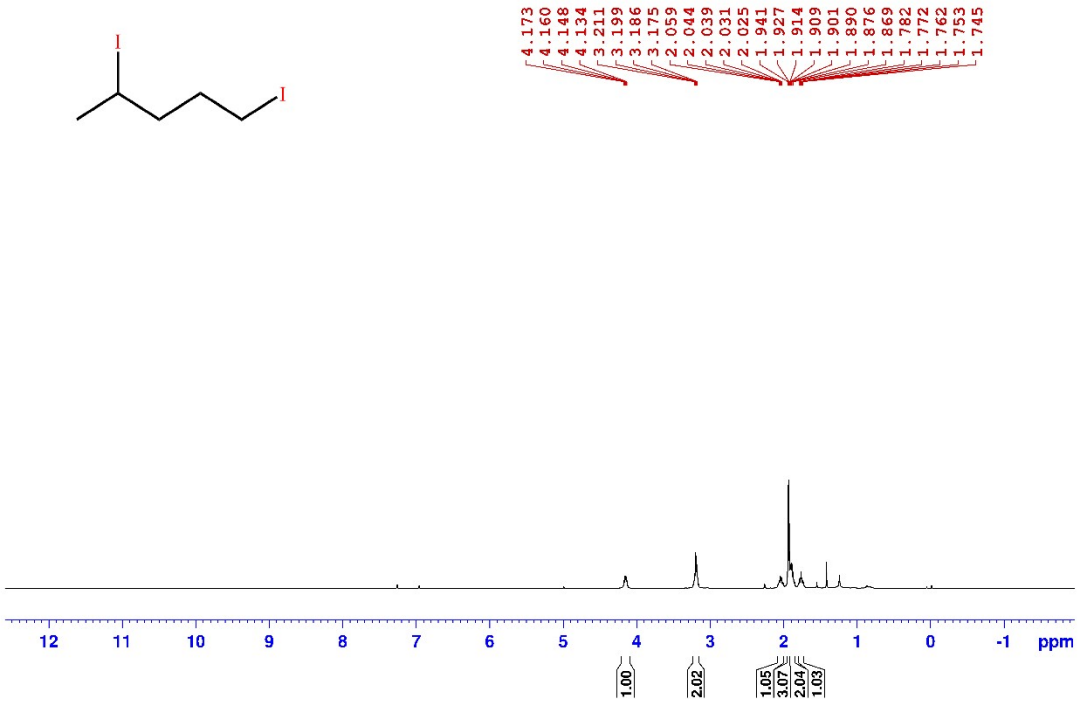


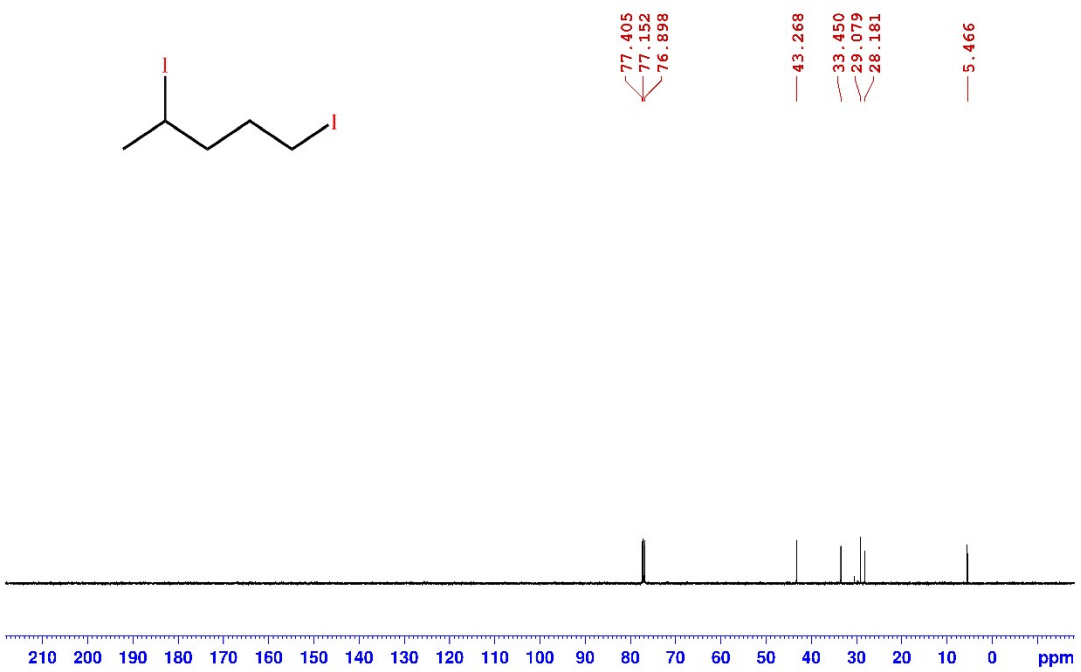


^{1}H-NMR & $^{13}C\{^{1}H\}$ (in $CDCl_3$) spectra of compound **3c**

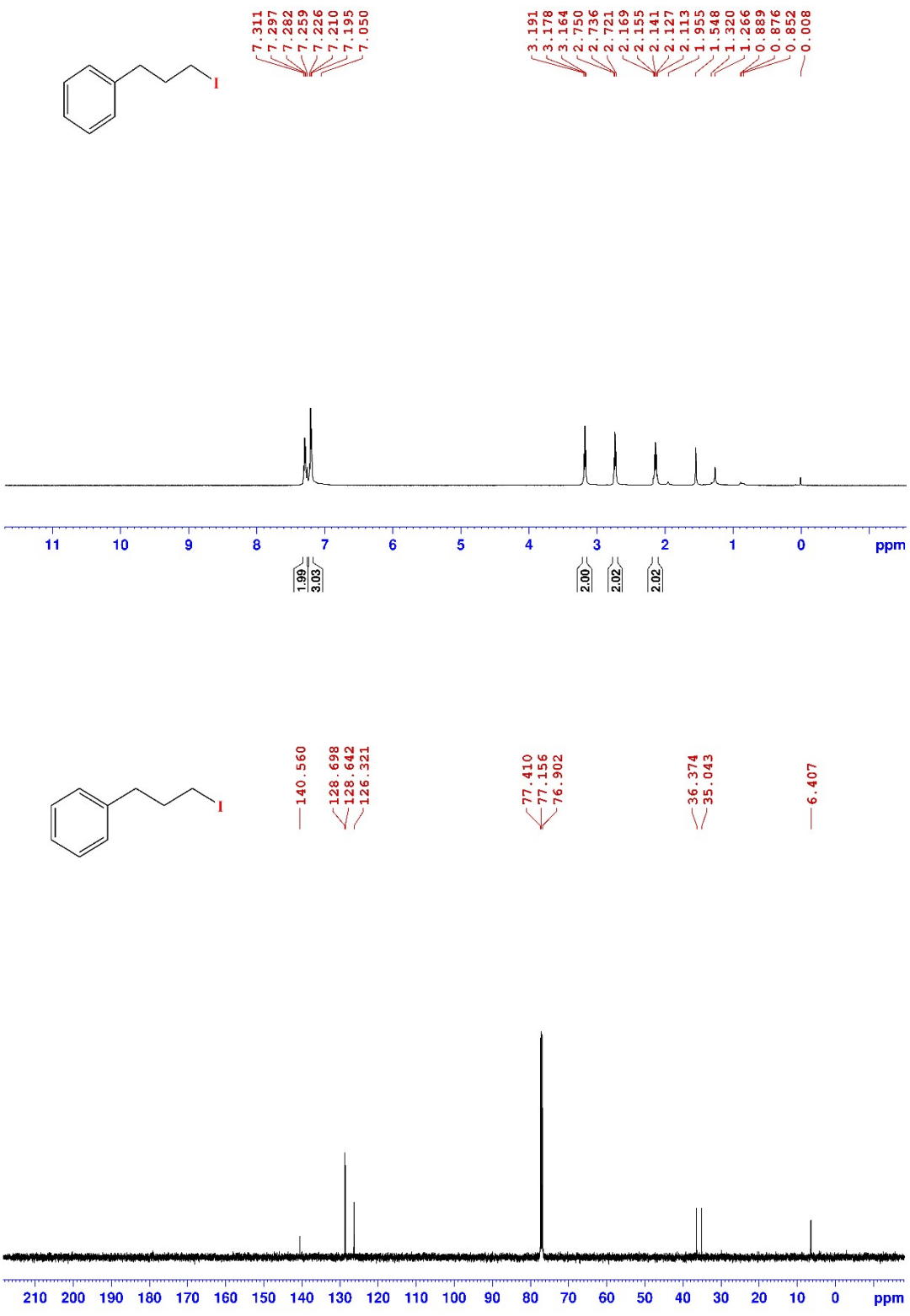


^{1}H-NMR & $^{13}C\{^{1}H\}$ (in $CDCl_3$) spectra of compound **3d**

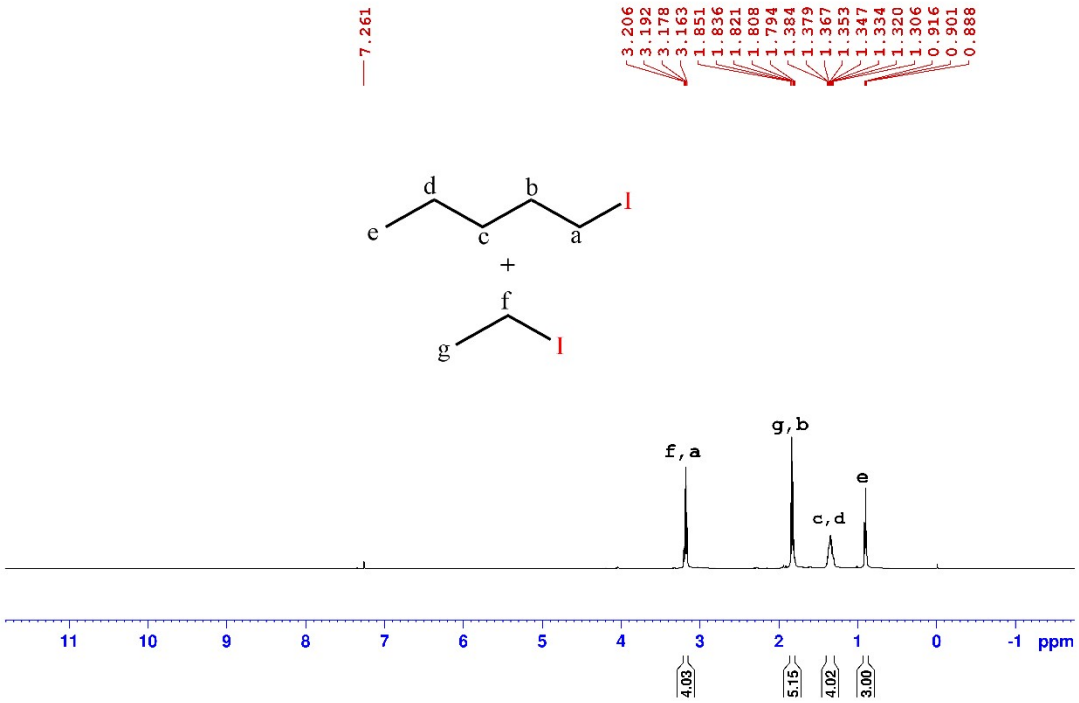


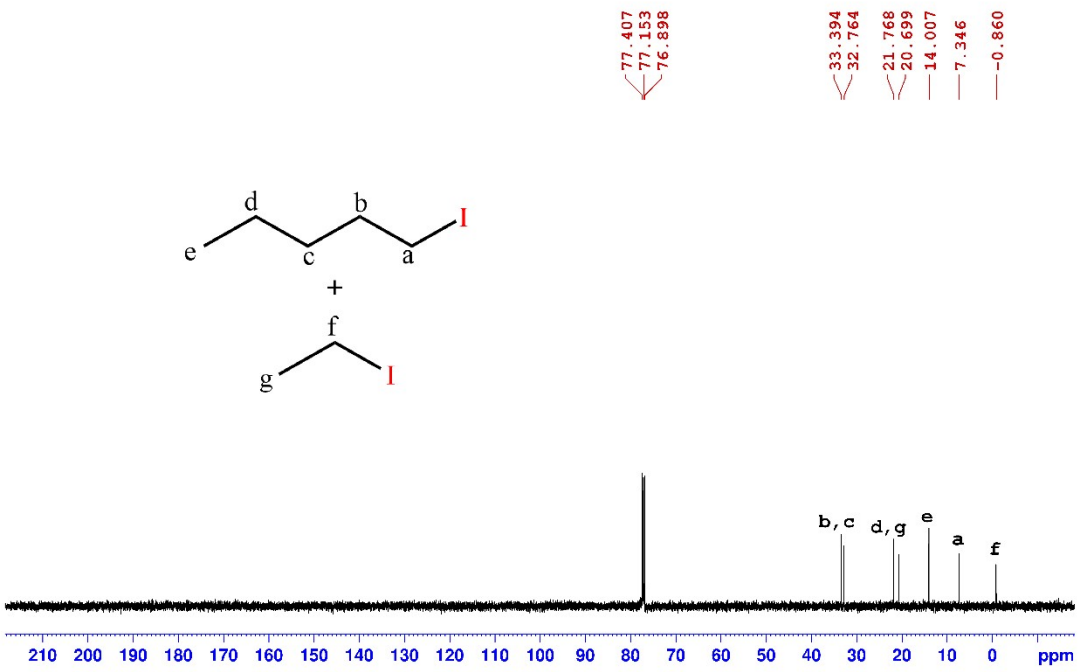


^{1}H-NMR & $^{13}C\{^{1}H\}$ (in $CDCl_3$) spectra of compound **3e**

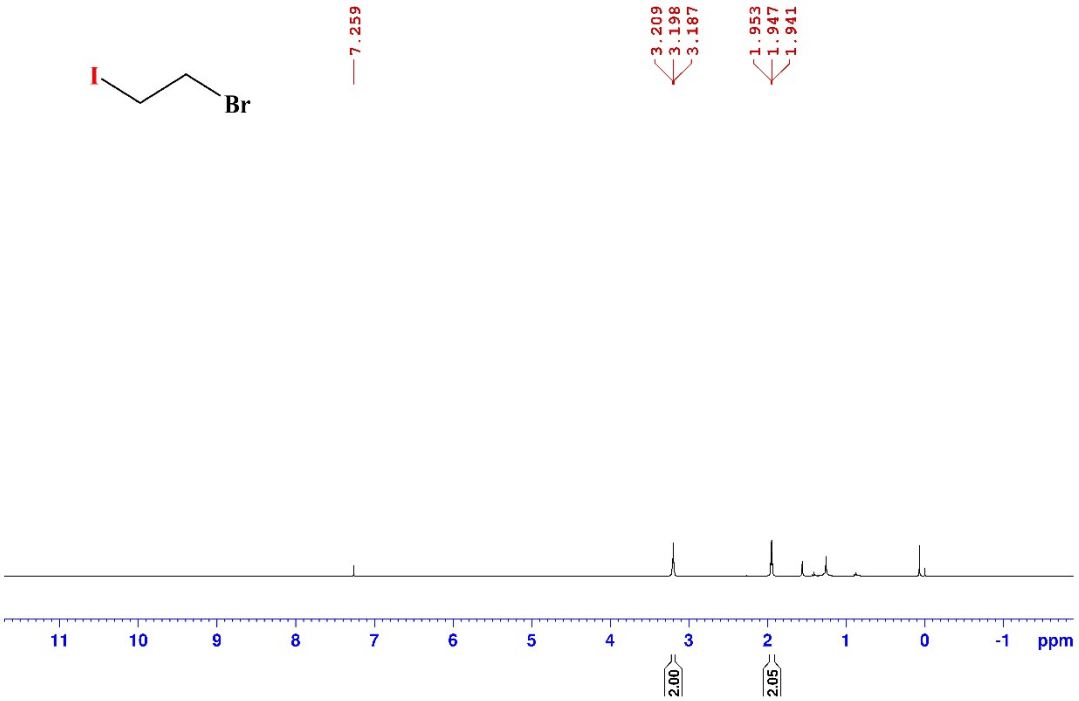


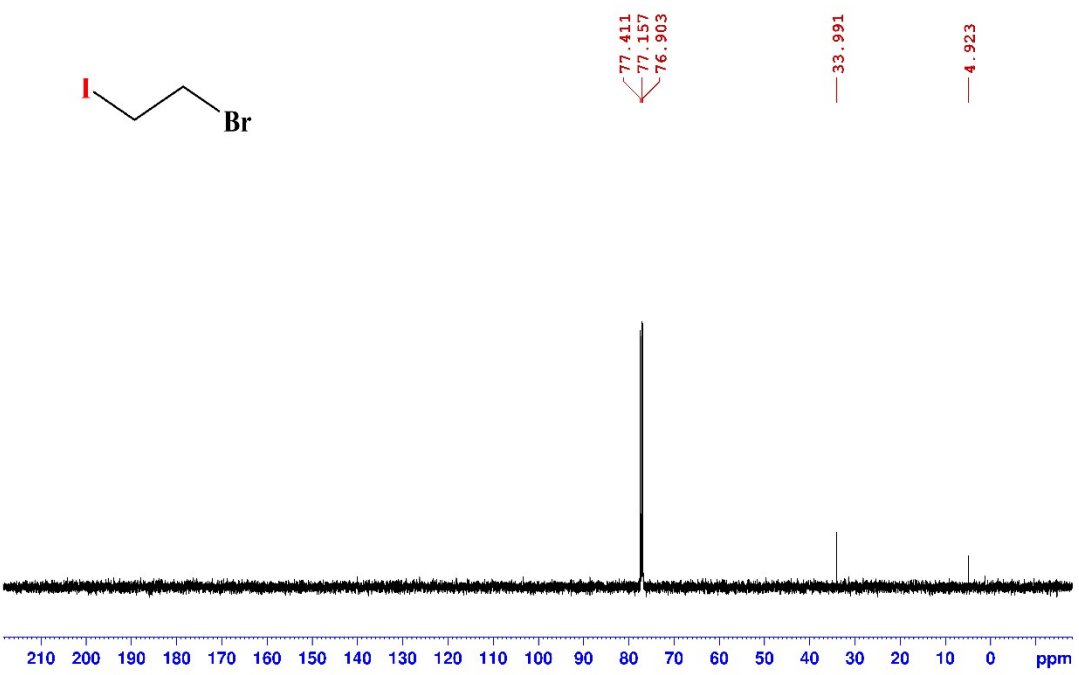
^{1}H-NMR & $^{13}C\{^{1}H\}$ (in $CDCl_3$) spectra of compound **3f** and C_2H_5I



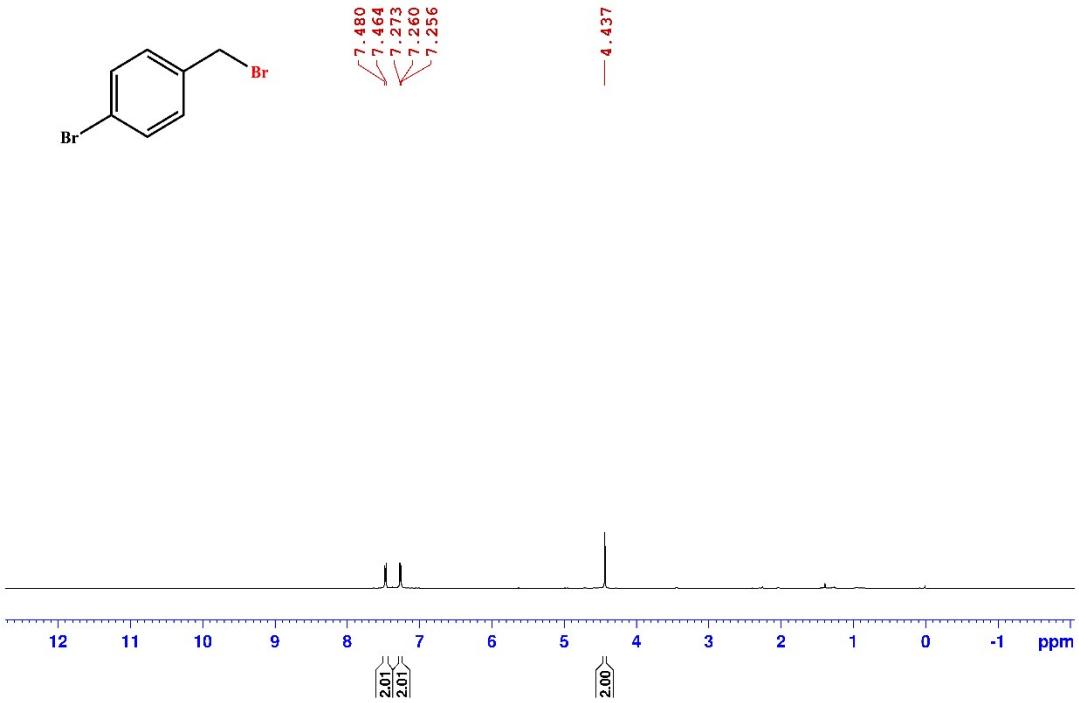


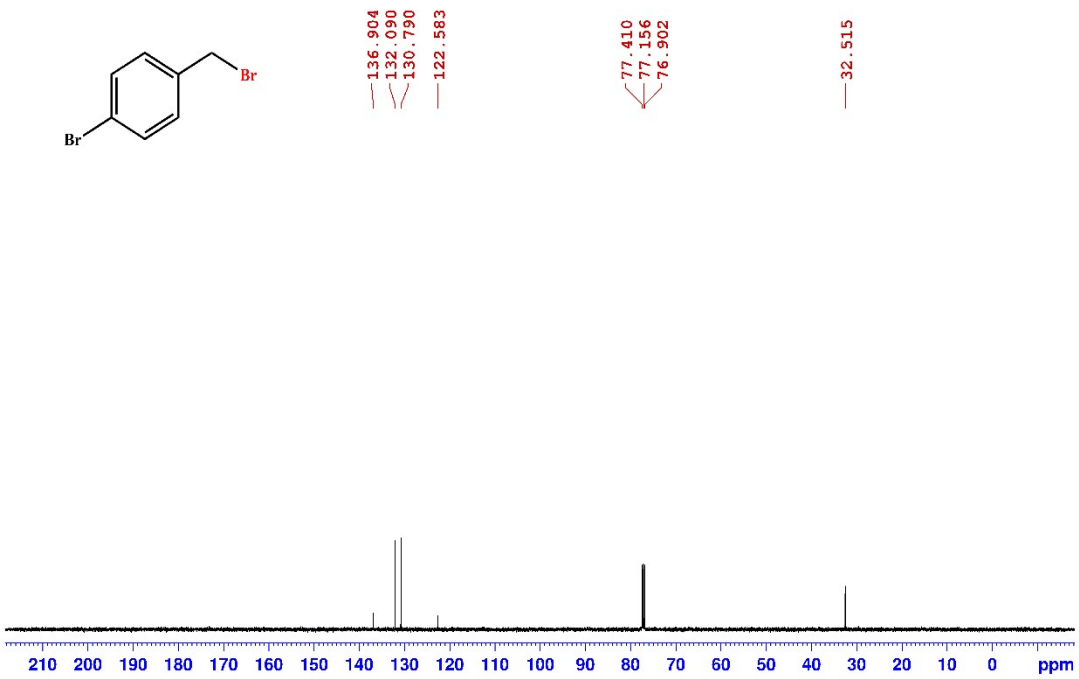
^{1}H-NMR & ^{13}C{^{1}H} (in $CDCl_3$) spectra of compound **3g**



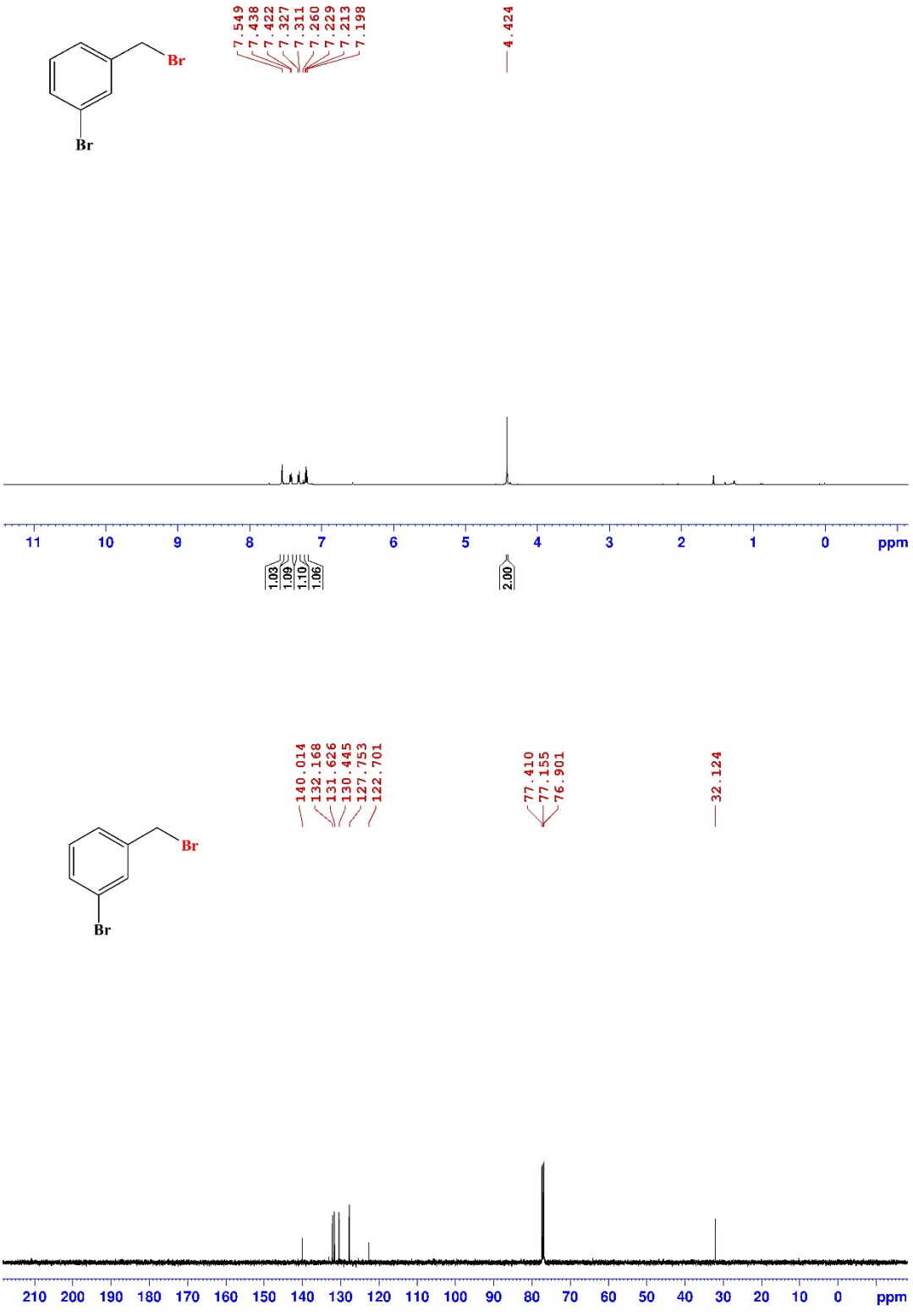


^{1}H-NMR & ^{13}C{^{1}H} (in $CDCl_3$) spectra of compound **3h**

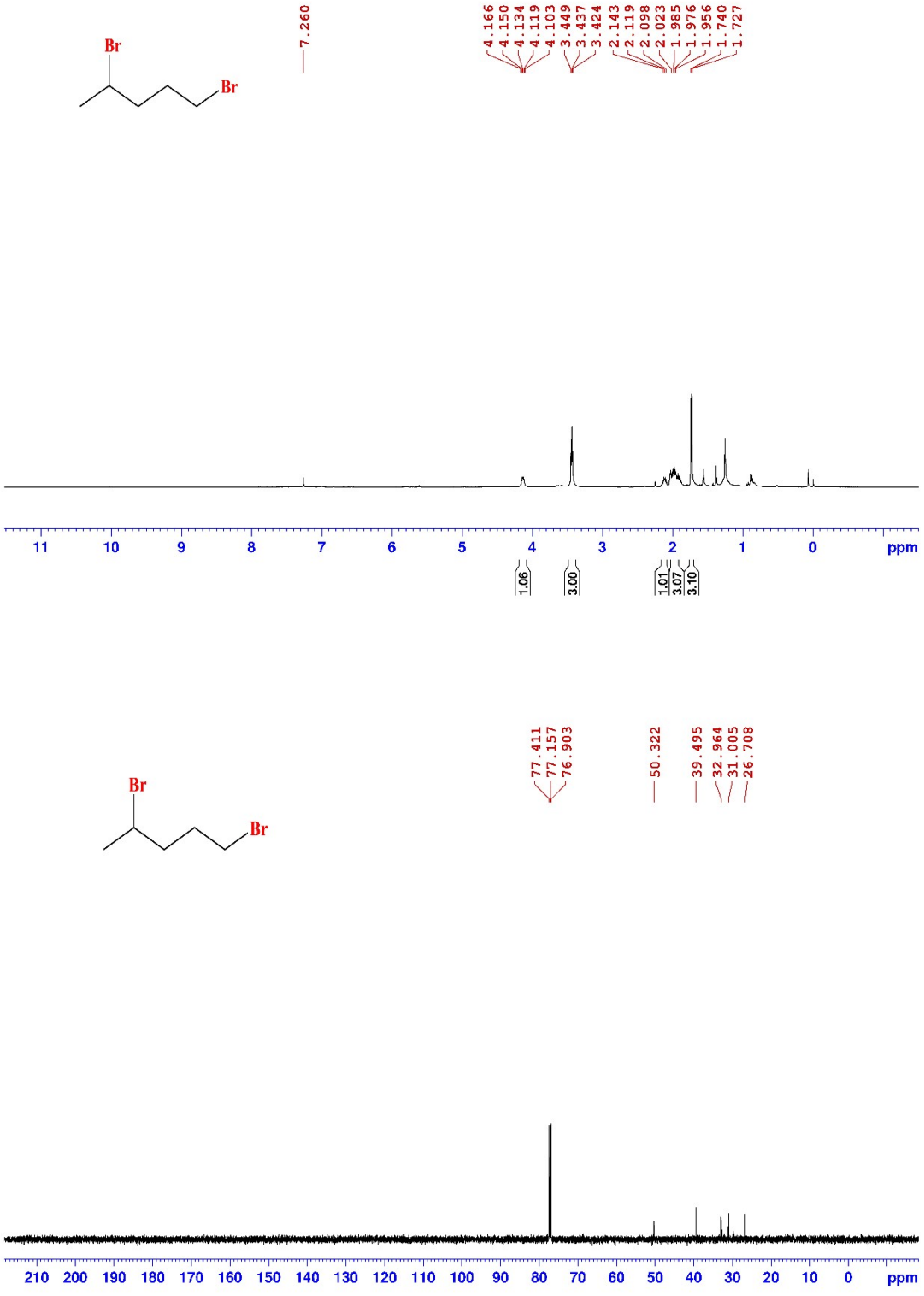




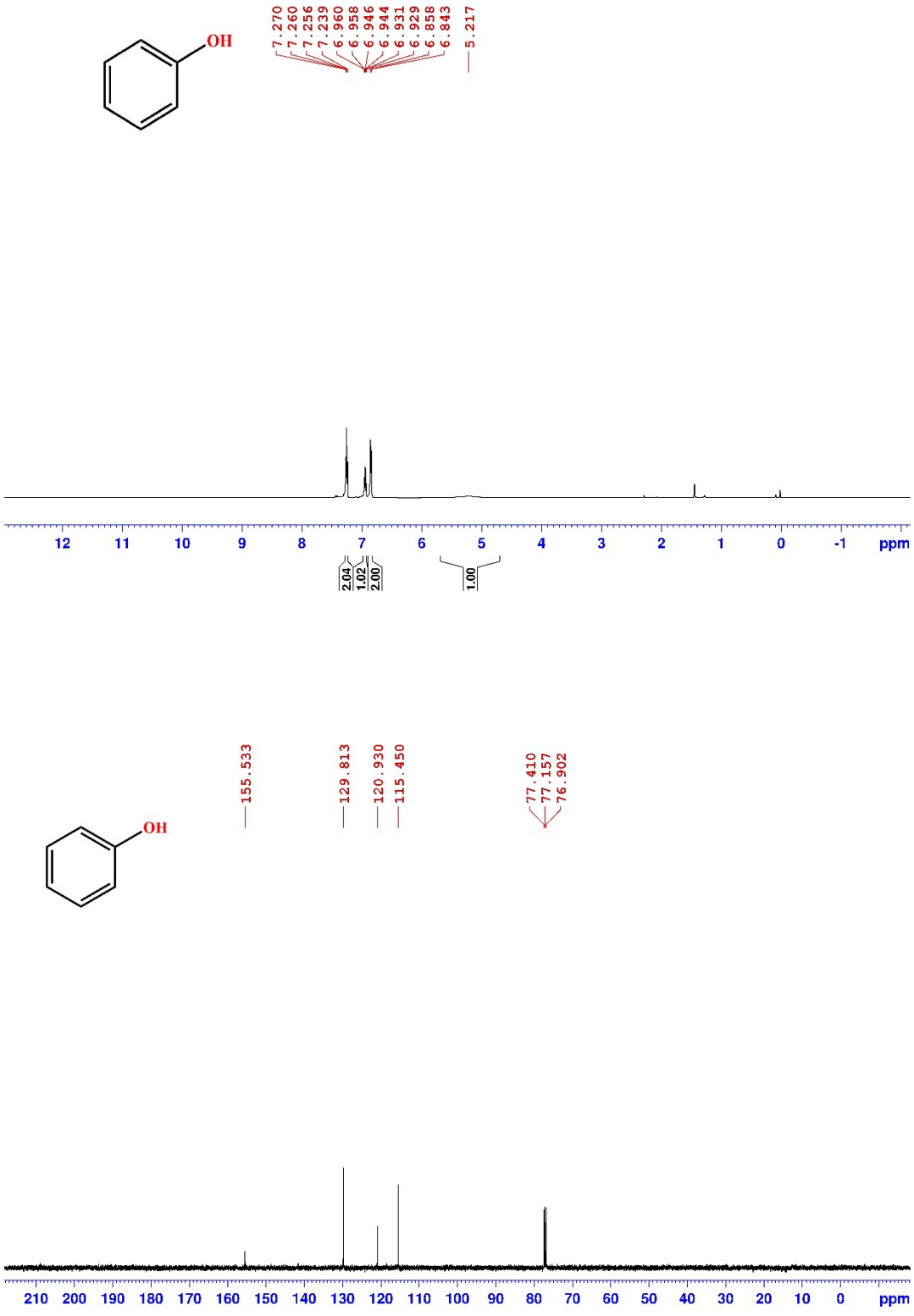
^{1}H-NMR & $^{13}C\{^{1}H\}$ (in $CDCl_3$) spectra of compound **3i**



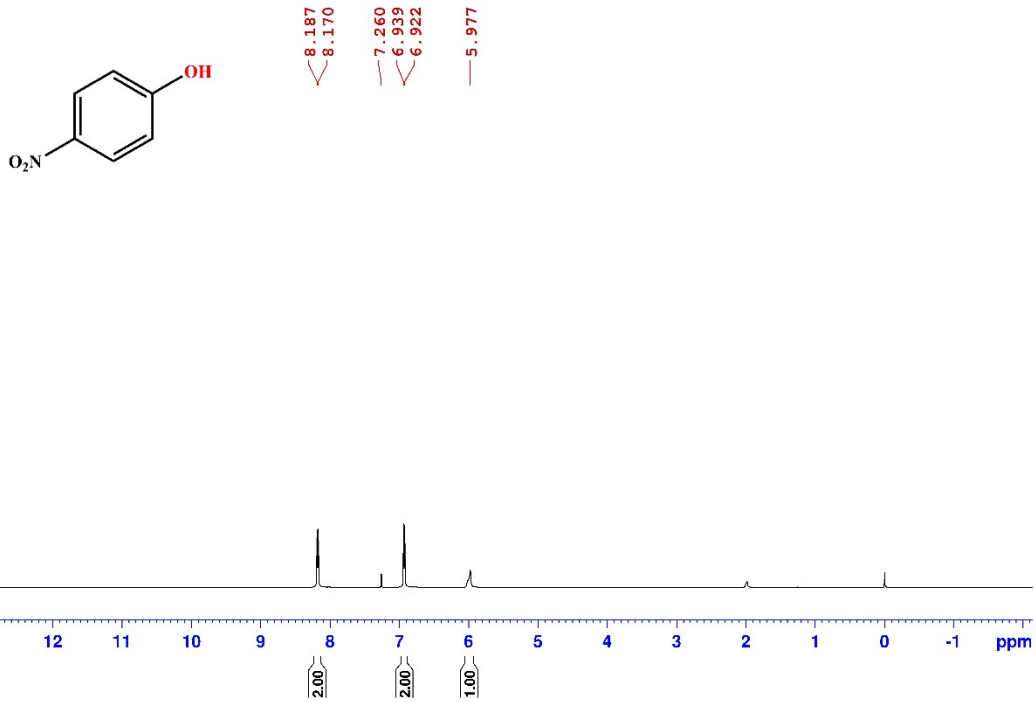
^{1}H-NMR & ^{13}C{^{1}H} (in $CDCl_3$) spectra of compound **3j**



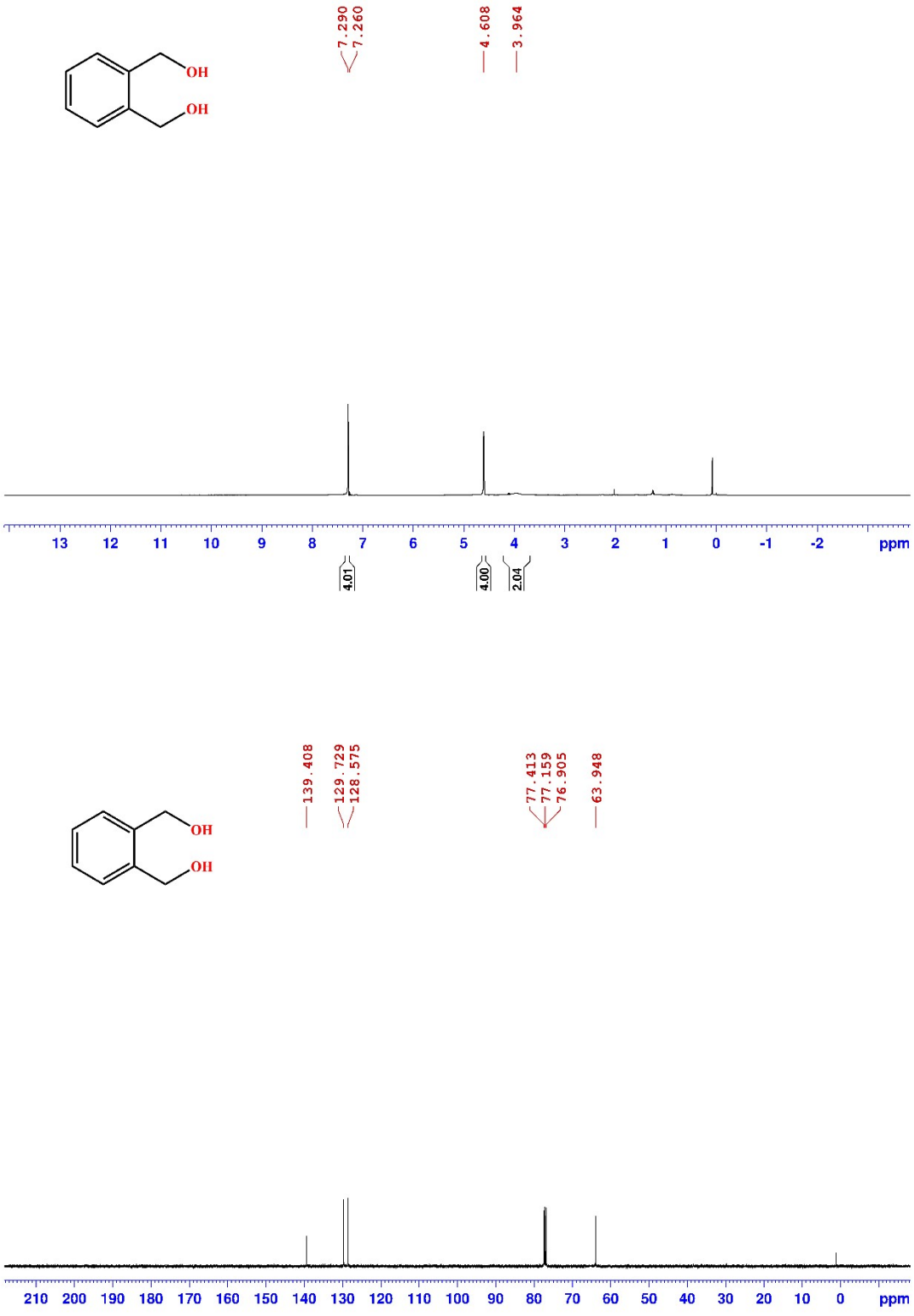
^{1}H-NMR & $^{13}C\{^{1}H\}$ (in $CDCl_3$) spectra of compound **5a**



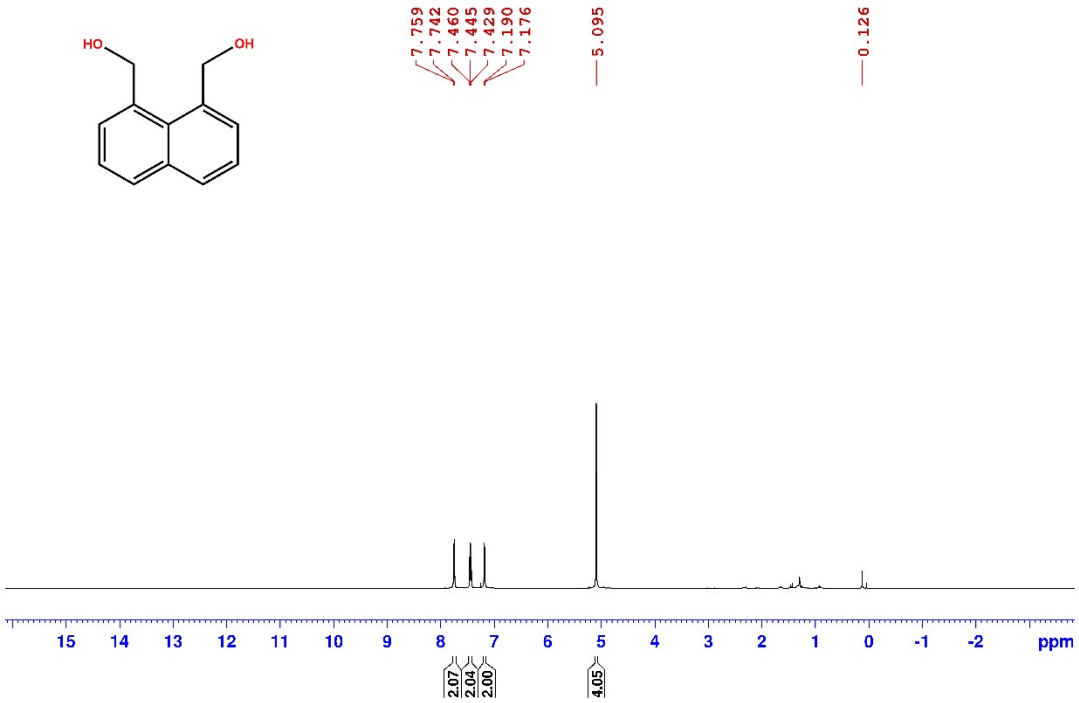
^{1}H-NMR & ^{13}C{^{1}H} (in $CDCl_3$) spectra of compound **5b**

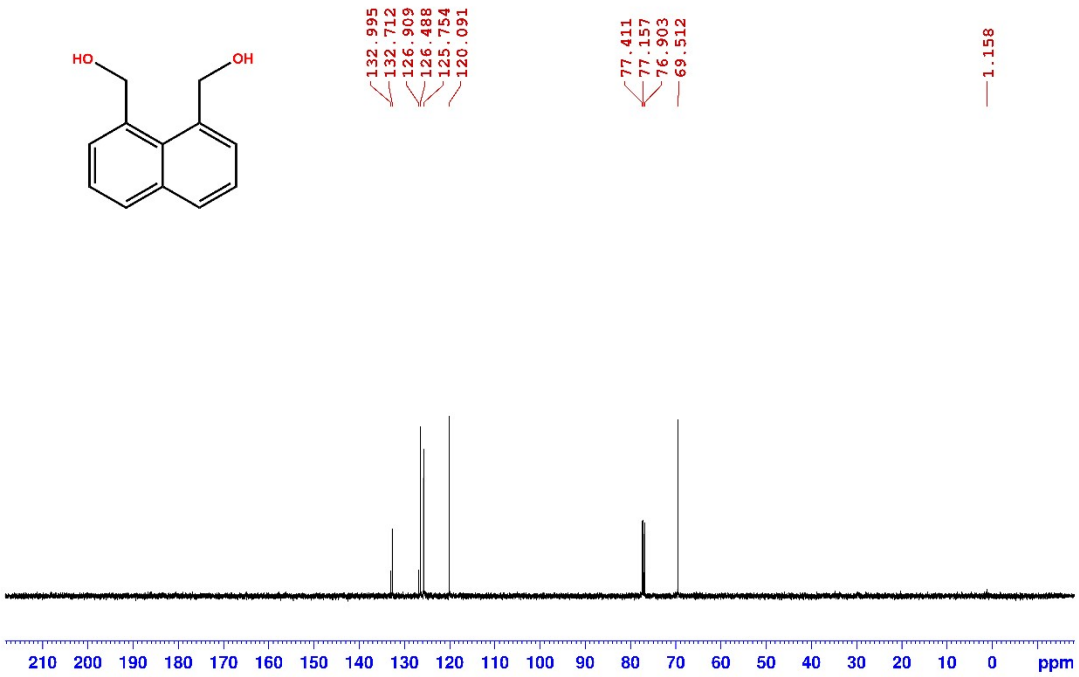


^{1}H-NMR & $^{13}C\{^{1}H\}$ (in $CDCl_3$) spectra of compound **7a**

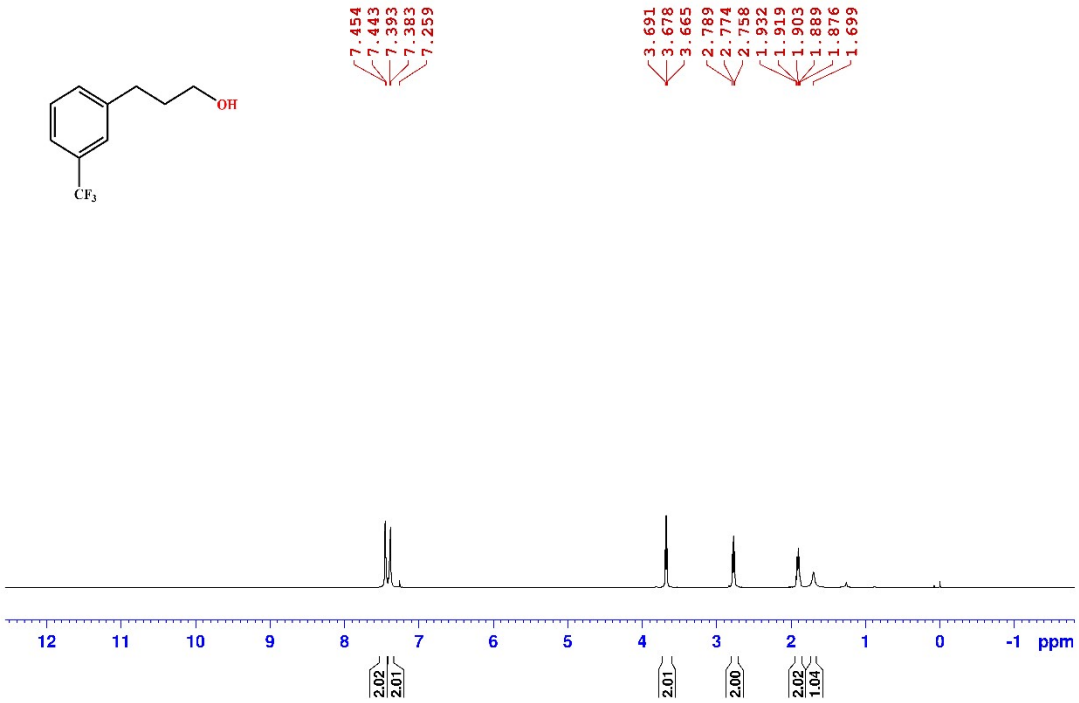


^{1}H-NMR & $^{13}C\{^{1}H\}$ (in $CDCl_3$) spectra of compound **7b**





^{1}H-NMR, ^{13}C{^{1}H} & ^{19}F{^{1}H} (in $CDCl_3$) spectra of compound **9**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OH
CF3
12 11 10 9 8 7 6 5 4 3 2 1 0 -1 ppm
2.02
2.01
2.01
2.00
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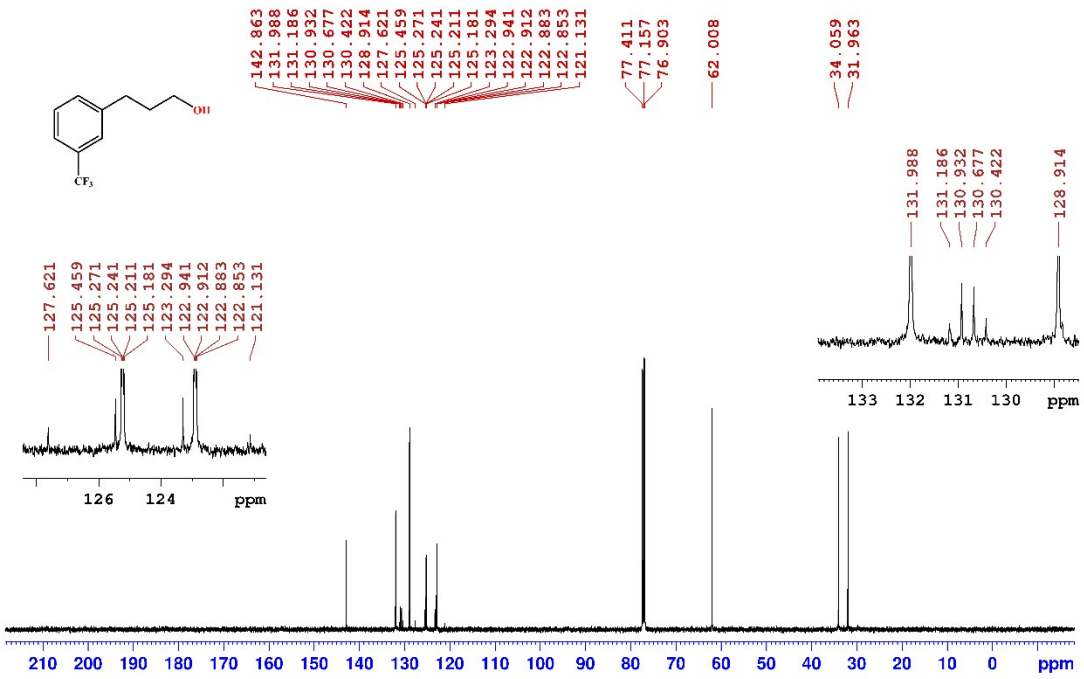
1.04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127.621
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125.181
123.294
122.941
122.912
122.883
122.853
121.131
77.411
77.157
76.903
62.008
34.059
31.963
OH
CF3
127.621
125.459
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125.241
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125.181
123.294
122.941
122.912
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121.131
126 124 ppm
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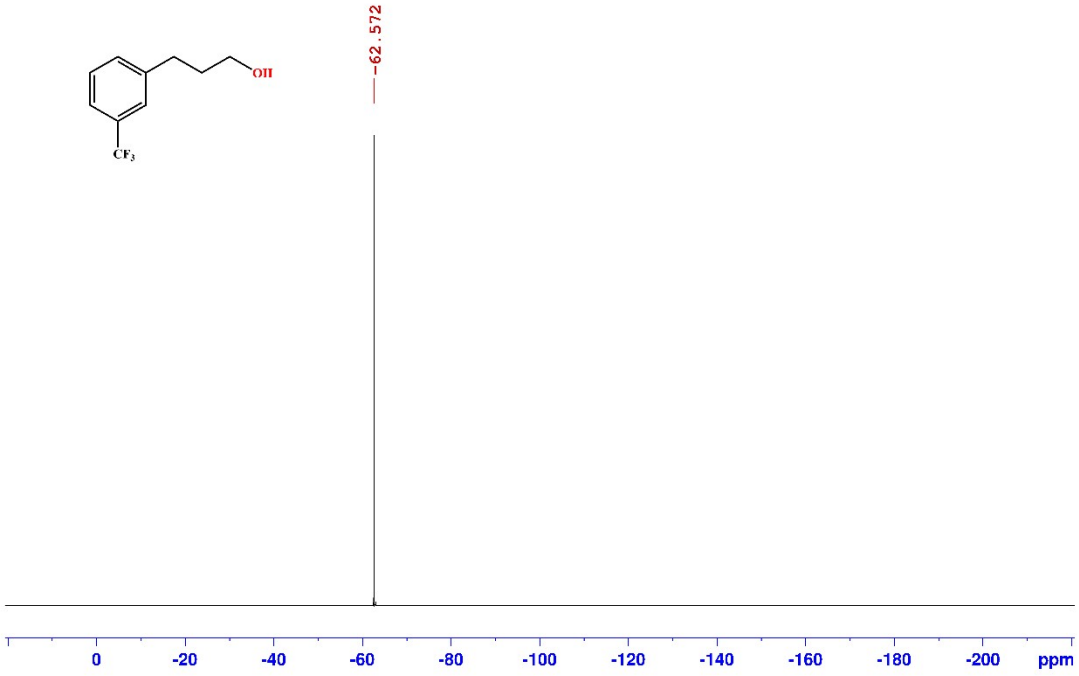
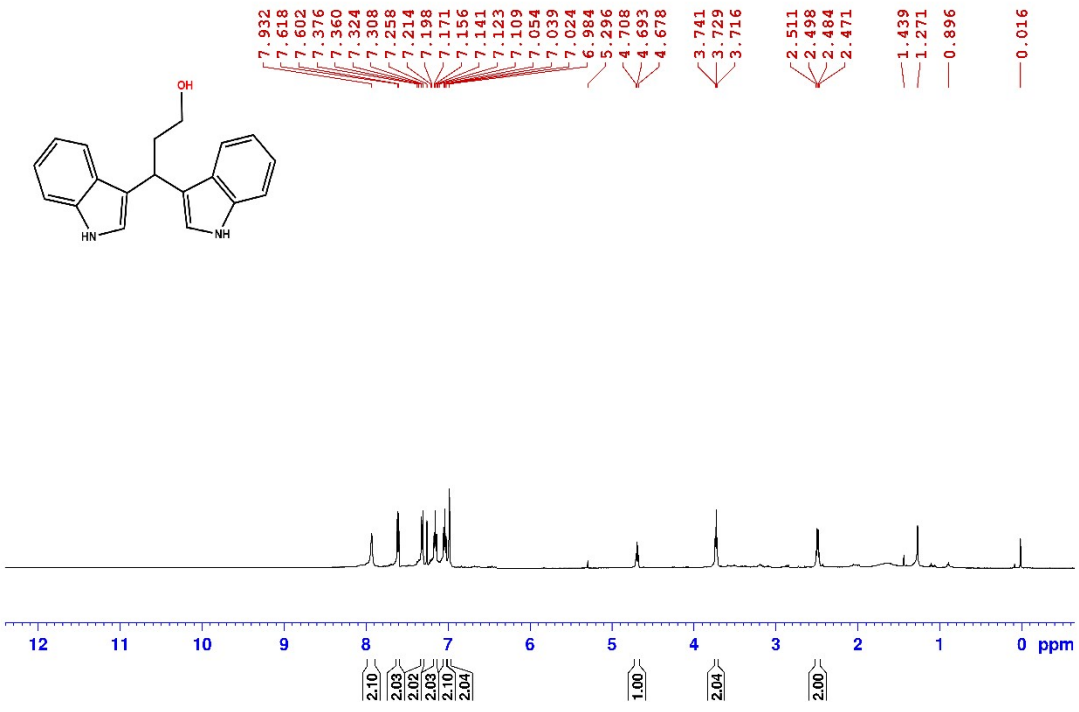
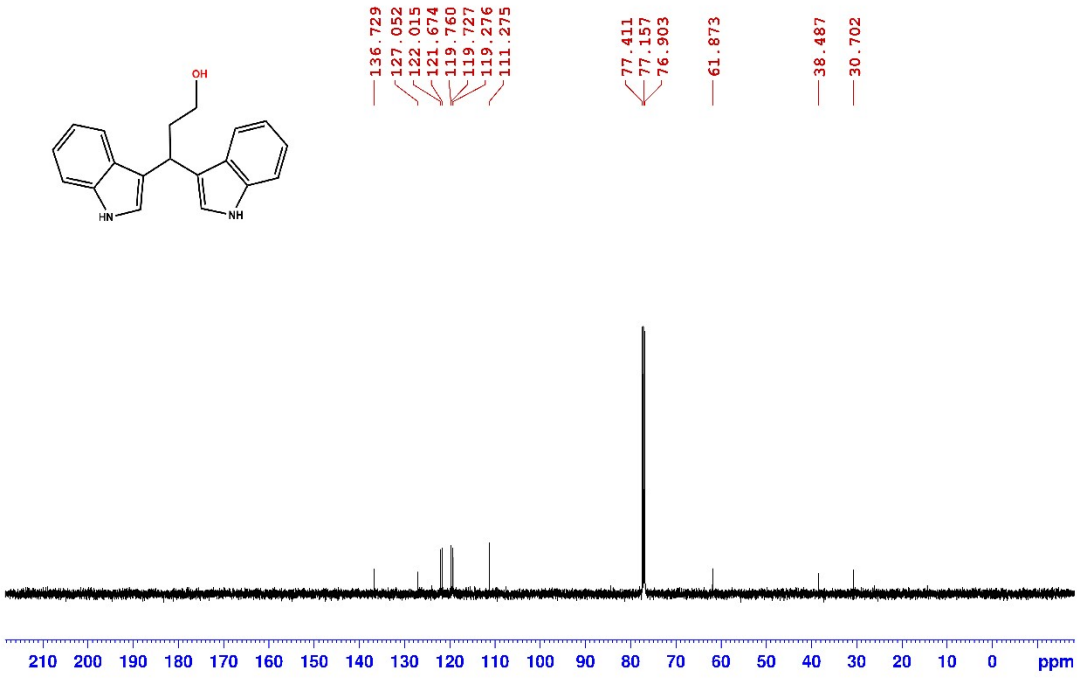
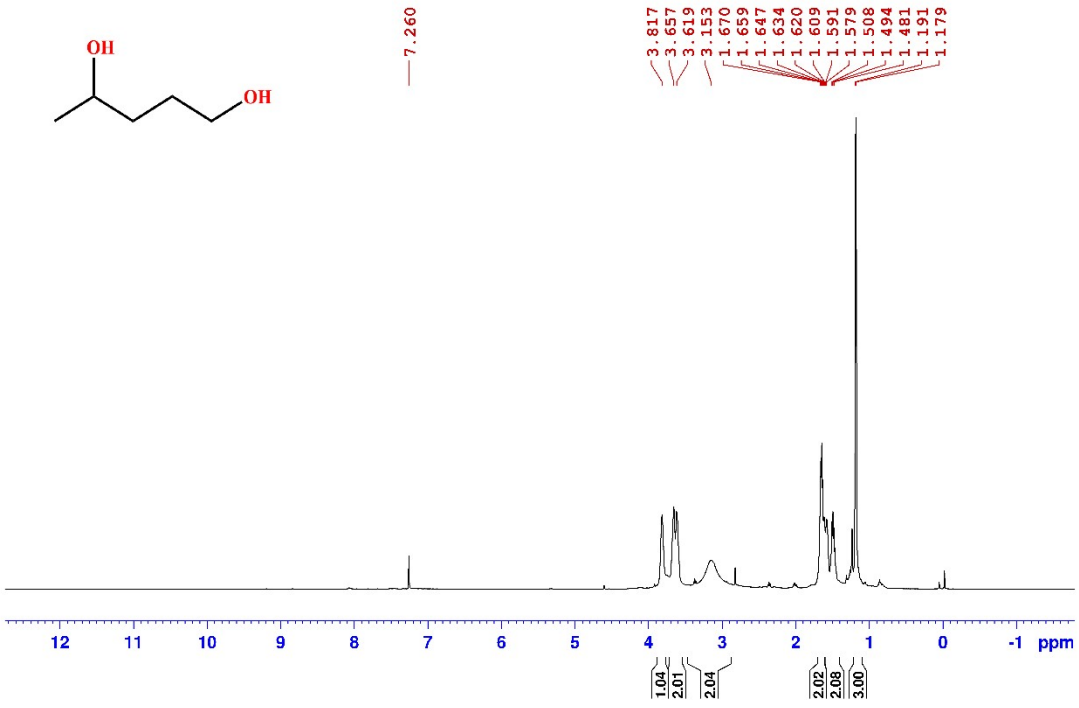


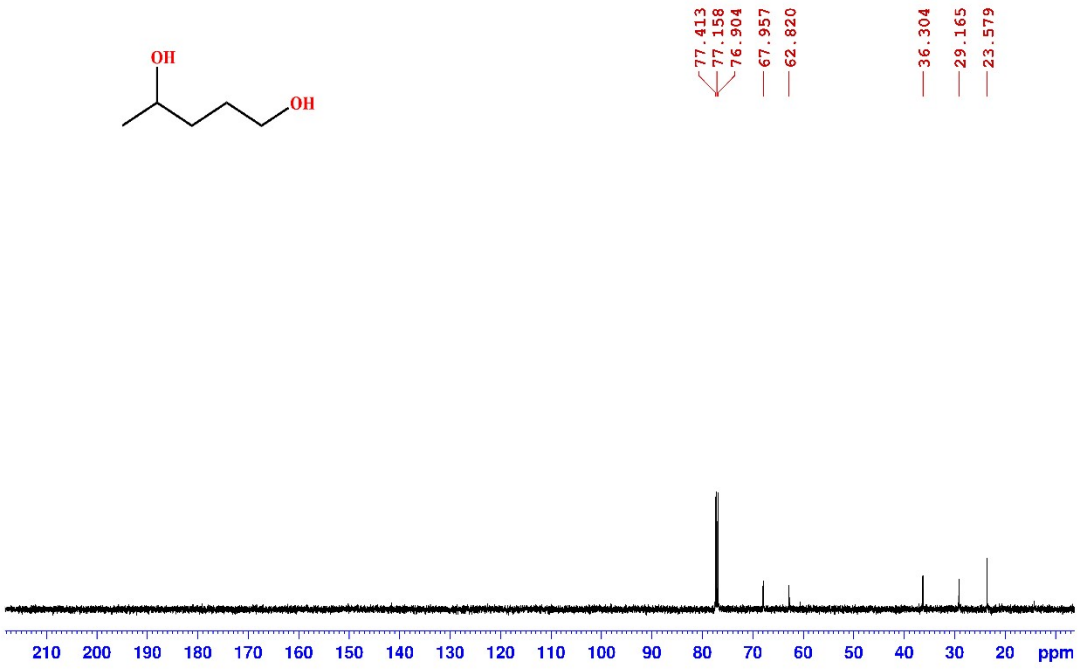
^{1}H-NMR & ^{13}C{^{1}H} (in $CDCl_3$) spectra of compound **11**





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





N. Computational Studies

All density functional theory (DFT) calculations were carried out using Gaussian 16 Revision C.01.4 software[4] package. The geometry optimization of all the stationary points was performed in the gas phase using the M06-2X[5] functional. The iodine (I) atoms were described using a Stuttgart-Dresden Effective Core Potential (SDD)[6] basis set, while a Pople-type basis set 6-31+g(d)[7] was used for all other atoms.

To confirm the nature of the stationary points, the harmonic vibrational frequencies of the normal modes were computed at the same level of theory. The vibrational frequency analysis revealed that all the intermediates corresponded to minima, exhibiting no imaginary frequencies. On the other hand, the transition states were characterized by exactly one imaginary frequency, confirming their nature as transition states. Additionally, the Intrinsic Reaction Coordinates (IRC)[8] were followed to validate the energy profiles connecting the key transition structures to the associated local minima.

To obtain more accurate single-point energies, the calculations were performed using a SDD basis set for iodine (I) and a higher-level basis set 6-311g++(d, p) for the remaining atoms. This basis set includes double polarization and diffusion functions to capture electron correlation effects. In order to account for the influence of the solvent, a continuum solvation model known as the Solvent Model based on Density (SMD)[9] was employed. Toluene was chosen as the solvent, and

the continuous quantum mechanical charge density of the solute was used as the basis for this model. The three-dimensional structures of the molecules were visualized using CYLview10 software[10].

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Coordinates for optimised structures of the ADB mechanism

Ester

C	1.23452200	0.38716900	0.00000100
O	1.72803800	1.49170700	-0.00000600
O	1.96700000	-0.73972100	0.00001000
C	-0.23272500	0.11954900	-0.00000100
C	-0.74823800	-1.17929600	-0.00001000
C	-1.09410100	1.21948900	0.00000400
C	-2.12727200	-1.37319400	-0.00001400
H	-0.06992500	-2.02580700	-0.00001400
C	-2.47108500	1.02092300	0.00000100
H	-0.66696700	2.21766700	0.00000900
C	-2.98780000	-0.27541200	-0.00000800
H	-2.53112900	-2.38115700	-0.00002200
H	-3.14185100	1.87475700	0.00000500
H	-4.06297600	-0.43025400	-0.00001100
C	3.38101900	-0.54423900	0.00001700
H	3.81515200	-1.54281900	0.00006600
H	3.68574600	0.01085500	-0.89003900
H	3.68572900	0.01093500	0.89002800

ADB

N	0.00001600	0.78926300	0.00002300
H	0.00000700	1.36278100	0.83526300
H	0.00001600	1.36283400	-0.83518100
B	0.95709400	-0.44165200	-0.00000800
H	-0.00003200	-1.38015900	-0.00010400
H	1.52053800	-0.61343500	-1.03848300
B	-0.95710300	-0.44164100	-0.00002100

H	-1.52048100	-0.61348200	1.03848100
H	1.52043600	-0.61353700	1.03850500
H	-1.52055000	-0.61337900	-1.03850200

NH_2BH_2

B	0.00000000	0.00000000	-0.78168300
N	0.00000000	0.00000000	0.61303100
H	0.00000000	-0.84465000	1.16819100
H	0.00000000	1.04528500	-1.35959100
H	0.00000000	0.84465000	1.16819100
H	0.00000000	-1.04528500	-1.35959100

TS_1

C	-0.02775800	0.72644600	-0.07554600
O	1.00893200	0.08600800	-0.20684200
O	-0.07732700	2.04370700	0.02649400
B	2.99216900	0.11770900	0.20520300
H	3.33253400	0.85722700	-0.66062900
N	3.24794500	-1.33514600	-0.02761000
H	2.81723700	-1.93871300	0.66822300
H	2.88239500	0.46154300	1.33930700
H	2.97470400	-1.66613600	-0.94940100
B	4.91195200	-1.43250900	0.09701700
H	5.23489100	-0.53611100	0.85465000
H	5.15185800	-2.52856500	0.55199200
H	5.32756200	-1.25808400	-1.02638800
C	-1.36244500	0.07678100	-0.02880800
C	-1.42251300	-1.31745900	-0.10473000
C	-2.53473700	0.82986500	0.08824600
C	-2.65528600	-1.95923400	-0.06289000
H	-0.50017200	-1.88196100	-0.19693800
C	-3.76554700	0.18208600	0.13019700
H	-2.47684000	1.91130600	0.14616500
C	-3.82613100	-1.20946700	0.05473900

H	-2.70455100	-3.04194700	-0.12160800
H	-4.67812600	0.76270500	0.22153400
H	-4.78867100	-1.71128600	0.08778100
C	1.15789900	2.76895400	-0.08004300
H	0.87549600	3.81884700	-0.03620000
H	1.81818300	2.51032800	0.74812000
H	1.64355100	2.53531700	-1.02864900

Int_1

C	0.04481900	0.70575400	-0.09385200
O	1.04483400	0.02441700	-0.36583400
O	0.05118800	1.99113700	0.14534400
B	2.66570000	0.12683800	0.03244400
H	3.16233800	0.82260300	-0.80641600
N	3.12587000	-1.32510400	-0.06483400
H	2.59708400	-1.93819400	0.55454500
H	2.64921200	0.53020400	1.16415500
H	3.01949600	-1.69570400	-1.00855800
B	4.71745800	-1.49794100	0.34381100
H	4.80963300	-1.12577300	1.49585500
H	4.95839100	-2.68377500	0.21416000
H	5.34209800	-0.80606100	-0.43378300
C	-1.29186100	0.07899700	-0.03314800
C	-1.38671800	-1.31024000	-0.16711800
C	-2.44077300	0.85487300	0.15673400
C	-2.63323000	-1.92260700	-0.11199100
H	-0.48397500	-1.89401700	-0.31444200
C	-3.68405400	0.23479900	0.21250900
H	-2.35416100	1.93101400	0.25973400
C	-3.78002900	-1.15069900	0.07815400
H	-2.71150200	-3.00007400	-0.21503200
H	-4.57866400	0.83123800	0.35992600
H	-4.75293200	-1.63110800	0.12203000
C	1.22449900	2.79121400	-0.12350000

H	0.86655800	3.81809300	-0.08999800
H	1.98054400	2.61238300	0.63797100
H	1.61491000	2.54342300	-1.11038500

TS_2

C	-0.90008700	-0.65146200	-0.25310400
O	-1.56885700	0.01584200	-1.15855900
O	-1.37464400	-1.78797300	0.22965400
B	-1.87180900	1.02179700	-0.03317300
H	-1.37367800	0.37565800	0.94883300
C	0.57646600	-0.52559900	-0.15280500
C	1.26978400	0.10579200	-1.18575000
C	1.25249900	-1.02187300	0.96364300
C	2.65274900	0.24553600	-1.09812000
H	0.72581500	0.46246100	-2.05596800
C	2.63091800	-0.87203000	1.04835800
H	0.69336200	-1.49706800	1.76374300
C	3.32988800	-0.23727900	0.01974400
H	3.19921400	0.73230200	-1.89971900
H	3.16152800	-1.23900100	1.92105800
H	4.40651000	-0.11661300	0.09313200
C	-2.79695700	-1.97314000	0.19825000
H	-2.95777800	-3.00913600	0.48877200
H	-3.25790600	-1.29498500	0.92166100
H	-3.18437500	-1.77945700	-0.80237700
N	-1.07708600	2.32206100	-0.16065400
H	-1.65295500	3.04372300	-0.59427700
H	-0.25649900	2.21494900	-0.75769700
B	-0.55322700	2.88295500	1.30011300
H	-1.53162900	2.90532400	2.01929400
H	0.27719600	2.06913000	1.66371400
H	-0.08281800	3.98409100	1.09905400
H	-3.04476200	1.12780500	0.17059900

Int_2

C	0.39304900	0.45341900	0.47805900
O	1.23721600	-0.63699300	0.54317300
O	0.84878700	1.26452100	-0.60332200
B	2.59849900	-0.35827700	0.84667700
H	0.45589300	1.06106900	1.40108500
C	0.15083100	2.48527600	-0.72948900
H	0.66050600	3.06446700	-1.50104500
H	-0.89253800	2.32188600	-1.02590200
H	0.16954500	3.04836400	0.21507400
N	3.46520400	-0.07031400	-0.41917800
H	4.15965800	0.66423300	-0.34797600
H	2.88083500	0.31036200	1.80243300
H	2.88672600	0.04783200	-1.24661700
B	3.87851900	-1.51127700	-0.00179900
H	4.98412100	-1.59108800	0.44263700
H	3.13006700	-1.56524600	1.11149500
H	3.42943100	-2.37021900	-0.69668000
C	-1.03017300	-0.00858500	0.25927400
C	-2.06490600	0.46849600	1.05940900
C	-1.31259500	-0.89565300	-0.78222700
C	-3.38041400	0.06251000	0.82710200
H	-1.84309400	1.15774900	1.87196800
C	-2.62220600	-1.30250900	-1.01519400
H	-0.49587400	-1.26727500	-1.39483600
C	-3.65900700	-0.82273300	-0.21065900
H	-4.18272900	0.43566700	1.45693100
H	-2.83869300	-1.99678100	-1.82204000
H	-4.68086300	-1.14260500	-0.39312500

TS_3

B	3.86958000	0.72419200	-0.29659500
N	3.43857000	-0.90052500	-0.34526300
H	4.17815800	-1.41336600	0.13164700

H	4.98446100	0.75656600	-0.76545400
H	3.46728700	-1.14339300	-1.33652000
B	2.07760400	-1.17979900	0.21912300
H	3.82334900	1.04887300	0.86920900
H	2.01704700	-1.76813200	1.25414400
O	1.01813600	-1.11336300	-0.70397600
C	0.38755300	0.10824300	-0.44342800
H	0.64890500	0.85072700	-1.21296900
C	1.04494900	1.84160400	1.11960600
H	0.01678500	2.17295700	1.30396500
H	1.63818500	1.93550200	2.02797700
H	1.50931200	2.42517200	0.31876500
O	1.03749900	0.46141400	0.78084500
C	-1.10321500	-0.00688300	-0.27949600
C	-1.63197300	-0.98263600	0.56910000
C	-1.95320600	0.87813000	-0.93766500
C	-3.00694400	-1.06997900	0.75359600
H	-0.95717800	-1.66895200	1.07425800
C	-3.33422400	0.79276500	-0.75183500
H	-1.53670000	1.63338700	-1.60098400
C	-3.85954600	-0.18100000	0.09284100
H	-3.41920100	-1.83021800	1.41042200
H	-3.99500200	1.48266500	-1.26806100
H	-4.93363800	-0.25194400	0.23745300
H	3.04687600	1.28598700	-0.99092100

Int_3

C	0.12494700	-0.49644300	-1.61768800
O	0.04916900	0.56449800	-2.27824700
O	-0.84141100	-1.36084600	-1.50143900
B	-1.15537700	1.56532800	-2.38089100
H	-1.47220500	1.61518900	-3.54592600
N	-0.54373900	2.91791000	-1.88508500
H	0.09861900	3.28652600	-2.58651400

H	-2.02917900	1.22266800	-1.63138500
H	-1.31560100	3.58489500	-1.85453300
B	0.22225900	2.94424000	-0.42477500
H	-0.27805900	3.84655500	0.22304100
H	1.39783700	3.15264800	-0.69063600
C	1.38448200	-0.89497400	-0.97434900
C	2.36981000	0.07437700	-0.76366700
C	1.57638400	-2.21658000	-0.55532700
C	3.55497900	-0.28720200	-0.13335300
H	2.17998000	1.10165000	-1.05666600
C	2.76590200	-2.56948100	0.07071600
H	0.79231200	-2.95020800	-0.71114200
C	3.75250900	-1.60450000	0.28205000
H	4.31878700	0.46243800	0.04740700
H	2.92367600	-3.59243300	0.39787800
H	4.67832500	-1.88090000	0.77867600
C	-2.02294900	-1.31262400	-2.32291800
H	-2.25740100	-2.35562900	-2.53445200
H	-2.82310900	-0.84572100	-1.75262400
H	-1.82588900	-0.75777500	-3.24092200
O	0.04798200	1.63476300	0.20733900
C	-0.54541900	1.47404800	1.44723000
O	0.40187400	1.42383900	2.48796800
C	-1.28253700	0.14904100	1.45614800
H	-1.24067100	2.31232200	1.64020300
C	1.17882200	2.59659200	2.59751200
C	-0.61838400	-1.03052500	1.79817200
C	-2.61375700	0.08981600	1.04306600
H	1.81443400	2.47008200	3.47618000
H	1.80185700	2.74553900	1.70782600
H	0.54005100	3.48083100	2.73332100
C	-1.27513700	-2.25619200	1.70883600
H	0.41427200	-0.97343400	2.13036000
C	-3.27626300	-1.13510300	0.96285400

H	-3.13291000	1.00991400	0.78242300
C	-2.60451400	-2.31326300	1.28854200
H	-0.75038800	-3.17031600	1.97567200
H	-4.31800600	-1.16934000	0.65345000
H	-3.11913100	-3.26865900	1.23038500

TS_4

B	3.16151400	0.93425400	-1.40033000
N	3.27454900	-0.35793500	-0.39805400
H	3.96793300	-0.13903200	0.32131600
H	4.29512400	1.20069700	-1.73989600
H	3.71831200	-1.09813200	-0.94581900
B	2.03309200	-1.01003400	0.29731500
H	2.65214800	1.84677700	-0.77289400
H	2.33766400	-2.02485400	0.87325800
O	0.89462800	-1.21178200	-0.67372700
C	0.29657900	-0.05996100	-0.54427100
H	0.79068600	0.83582700	-0.92696500
C	1.87514600	0.96054200	1.93386500
H	1.08876200	1.55409500	2.40574100
H	2.44708300	0.44918400	2.71902500
H	2.53194500	1.61557300	1.35279100
O	1.25956500	-0.01307700	1.11503700
C	-1.14355400	-0.01024000	-0.32689600
C	-1.84358400	-1.16482300	0.04437000
C	-1.81059500	1.20952700	-0.48741900
C	-3.21539800	-1.09396500	0.24867900
H	-1.29714000	-2.09525100	0.16364200
C	-3.18428600	1.27587900	-0.27938700
H	-1.24995000	2.09478400	-0.77812300
C	-3.88186900	0.12427900	0.08740100
H	-3.77019500	-1.98207900	0.53442600
H	-3.71095500	2.21650800	-0.40470400
H	-4.95489300	0.17501200	0.24859500

H	2.47043000	0.58679400	-2.33747300

Int_4

C	-2.53218100	-0.56494100	-0.55766900
O	-1.68701500	-1.32620300	0.24103900
O	-3.85112300	-0.96919500	-0.28939200
B	-1.37336100	-2.63401500	-0.19054500
H	-2.31527600	-0.73946800	-1.63027100
C	-4.79045300	-0.43262800	-1.19598800
H	-5.76049300	-0.85505900	-0.93117900
H	-4.83916000	0.66222900	-1.12609300
H	-4.54388600	-0.71392100	-2.22997900
N	-0.33655200	-3.29445700	0.73945900
H	-0.50225000	-4.24450200	1.05119500
H	-2.19523600	-3.35640700	-0.67496900
H	-0.01988500	-2.67861100	1.49278000
B	0.53671200	-3.09017000	-0.56164900
H	0.74962700	-4.10425000	-1.15631700
H	-0.46976800	-2.51183300	-1.26285700
C	-2.29355300	0.89489600	-0.22632500
C	-1.50766700	1.69023400	-1.05720800
C	-2.79750800	1.42150000	0.96464700
C	-1.20633300	3.00412000	-0.69375100
H	-1.12091000	1.27900900	-1.98837100
C	-2.50037600	2.73222100	1.32757800
H	-3.41240800	0.78958100	1.60030700
C	-1.69923800	3.52400300	0.50114600
H	-0.59116400	3.62011600	-1.34391900
H	-2.88971700	3.13918300	2.25642700
H	-1.46582800	4.54555600	0.78676700
O	1.61391900	-2.18102900	-0.46502000
C	1.42811300	-0.89761500	0.01848900
O	1.13182500	-1.00251500	1.40960700
H	0.56396800	-0.41103400	-0.46874000

C	2.67645900	-0.07527800	-0.21040400
C	0.71714000	0.22273600	1.98777900
C	2.57647100	1.24801500	-0.63439200
C	3.93295000	-0.62667400	0.04841800
H	0.35318100	-0.00846100	2.99031800
H	1.55459600	0.92742200	2.05742800
H	-0.09675500	0.67355800	1.40475400
C	3.72521600	2.02262100	-0.80362300
H	1.59375600	1.67554700	-0.82852900
C	5.07954400	0.14310500	-0.12213200
H	3.99747400	-1.66185400	0.37100400
C	4.97751500	1.46951600	-0.54834500
H	3.64112300	3.05348700	-1.13571800
H	6.05652100	-0.28953700	0.07383500
H	5.87415300	2.06792400	-0.68232100

TS_5

B	3.11723800	-2.15323200	0.03550600
N	3.23140300	-0.52337100	-0.07052500
H	3.82020500	-0.29923600	-0.87426200
H	4.24788500	-2.58760700	0.01596600
H	3.74244700	-0.18146200	0.74665100
B	1.93722600	0.28789900	-0.19698500
H	2.46589900	-2.50786700	-0.93342900
O	1.07321700	0.04950400	1.09893700
C	0.31594400	-0.74435500	0.42000200
H	0.68027200	-1.75609700	0.20317200
C	-1.09870900	-0.46332800	0.20485500
C	-1.85783800	-1.37368300	-0.54132800
C	-1.69470900	0.67093700	0.77163500
C	-3.21332100	-1.13871900	-0.73893300
H	-1.37740400	-2.25203200	-0.96603200
C	-3.05219800	0.89375800	0.58189600
H	-1.08610300	1.34629800	1.36477200

C	-3.80582100	-0.00624000	-0.17704800
H	-3.80870700	-1.83420300	-1.32142600
H	-3.52839700	1.76334000	1.02350900
H	-4.86644100	0.17422800	-0.32621500
C	1.05671300	2.49081100	-0.65911000
H	0.35808700	2.04274200	-1.38147700
H	0.51552900	2.69816300	0.27266300
H	1.42665400	3.43512800	-1.06545200
O	2.16025300	1.65142800	-0.42736000
H	1.19716800	-0.24101500	-1.08821400
H	2.55264000	-2.39266100	1.08641700

Int_5

B	1.97358900	2.26639700	0.68381500
N	2.67556900	1.29920900	-0.50290700
H	3.68547500	1.32869900	-0.36570100
H	2.73125000	3.19280000	0.84380400
H	2.47196200	1.70106000	-1.41625600
B	2.18513800	-0.09655500	-0.27316400
H	1.88260200	1.54285300	1.65511900
O	0.97262200	-0.54363000	-0.66042200
C	-0.04436700	0.21673900	-1.31026800
H	-0.15500800	-0.17982800	-2.32453500
C	-1.34475700	0.09257500	-0.55843000
C	-2.49423200	-0.36538800	-1.20059700
C	-1.40691900	0.45385900	0.79119300
C	-3.70165000	-0.45934400	-0.50742600
H	-2.44742500	-0.65422800	-2.24839700
C	-2.60916900	0.35373200	1.48490000
H	-0.51229700	0.81986800	1.28957200
C	-3.75920500	-0.10156400	0.83693100
H	-4.59167500	-0.81762100	-1.01643100
H	-2.65172600	0.63712400	2.53248600
H	-4.69655100	-0.17666300	1.38052000

C	2.64341100	-2.19656200	0.78792000
H	2.33378300	-2.80283100	-0.06772100
H	3.49558200	-2.66212000	1.28348400
H	1.80765700	-2.11346900	1.48807900
O	3.06223900	-0.90475600	0.36227800
H	0.25109600	1.27033600	-1.36805300
H	0.89510900	2.59315500	0.24093900

TS_6

B	0.27865500	2.06105700	-0.23066800
N	2.46576800	1.19714600	-1.31481100
H	3.16800700	1.91882600	-1.21813100
H	0.57738900	3.21697200	-0.16981800
H	2.06794100	1.15905700	-2.24133600
B	2.51188700	0.09514800	-0.40487300
H	0.55131300	1.33452000	0.67668400
O	1.70959500	-1.02096600	-0.47977700
C	0.62016400	-1.16438100	-1.35956900
H	0.74620000	-2.11954500	-1.88432400
C	-0.70482700	-1.16535400	-0.62515300
C	-1.88985500	-0.99819800	-1.34703800
C	-0.77116000	-1.34507800	0.75576400
C	-3.12443000	-1.01348600	-0.70005800
H	-1.84674700	-0.84127700	-2.42339600
C	-2.00554200	-1.35778000	1.40696300
H	0.15128600	-1.46095300	1.31624500
C	-3.18566800	-1.19318000	0.68322000
H	-4.03706800	-0.87822100	-1.27343200
H	-2.04447300	-1.49743300	2.48382800
H	-4.14564300	-1.20004500	1.19082400
C	3.37436300	-0.77899000	1.66617000
H	3.44739900	-1.79892000	1.27602800
H	4.22322900	-0.57747900	2.32212500
H	2.44694300	-0.68647100	2.24305200

O	3.41145500	0.17525300	0.62253300
H	0.60394300	-0.37139600	-2.11756000
H	-0.22257600	1.63294900	-1.22544600
N	-1.92474500	2.14575100	0.73103600
H	-2.22531100	1.38669800	0.12771600
H	-1.68164300	1.82447200	1.65941600
B	-2.03984700	3.50454800	0.39635800
H	-1.76030600	4.32369100	1.21712400
H	-2.40718200	3.79488300	-0.70109300

Int_6

N	3.06064000	-0.88101700	0.84813300
H	3.74482700	-0.32653300	1.33855500
H	3.16096600	-1.87604200	0.98641500
B	2.07007600	-0.36774400	-0.02763000
O	1.24452500	-1.26785200	-0.66190100
C	0.16063900	-0.79146900	-1.43383600
H	-0.13113500	-1.61739900	-2.09183100
C	-1.02369900	-0.37163700	-0.58818500
C	-2.00838400	0.45133700	-1.14047700
C	-1.17126100	-0.81695000	0.72575800
C	-3.12596900	0.81986700	-0.39583500
H	-1.89451900	0.81337500	-2.16059300
C	-2.28736400	-0.44474500	1.47538500
H	-0.40716600	-1.45568500	1.15970700
C	-3.26848700	0.37232100	0.91776200
H	-3.88188400	1.46318000	-0.83739800
H	-2.38995100	-0.79585600	2.49845300
H	-4.13676600	0.66208200	1.50236700
C	2.69772000	1.92707200	0.38663600
H	3.75673000	1.80552300	0.12525200
H	2.36979300	2.91736900	0.06576800
H	2.58254300	1.85384400	1.47516300
O	1.89751400	0.97254300	-0.27330300

H 0.47622200 0.04967700 -2.06225400

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. A. Nair, V. Tiwari, A. Verma, P. Saini and A. J. Elias, *Org. Chem. Front.*, 2023, **10**, 327-334.
4. M. J. Frisch et. al. Gaussian 09, Revision D.01, Gaussian, Inc., Wallingford, CT, 2013.
5. Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.,* **2008**, *120*, 215–241.
6. K. L. Schuchardt, B.T. Didier, T. Elsethagen, L. Sun, V. Gurumoorthi , J. Chase, J. Li, and T.L. Windus, J. Chem. Inf. Model., **2007**, *47*, 1045.
7. (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.
8. C. Gonzalez and H. B. Schlegel. *J. Phys. Chem.,* **1990**, *94*, 5523.
9. A. V. Marenich, C. J. Cramer and D. G. Truhlar. *J. Phys. Chem. B.* **2009**, *113*, 6378.
10. CYLview20; Legault, C. Y., Université de Sherbrooke, 2020.