Highly Selective Direct Reductive Amidation of Nitroarenes with Carboxylic Acids using Cobalt(II) Phthalocyanine/PMHS

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Supporting information

Table of Contents

General experimental

Procedure for synthesis of metal phthalocyanines

General experimental procedure for reductive amidation of nitroarenes

Procedure for recyclability of the catalyst

Reductive amidation of nitrobenzene in different solvents using stoichiometric amount of carboxylic acids (Table S1)

Reductive amidation of nitrobenzene in different solvents in the presence of mineral acids using stoichiometric amount of carboxylic acids (Table S2)

Spectral data of isolated compounds

^{1}H and ^{13}C NMR spectra of synthesized compounds

HRMS (ESI) spectra of isolated compounds

Mechanistic investigation

References

General experimental

Metal salts used were purchased from Merck, Germany. Metal phthalocyanines were synthesized by a reported procedure with some modification and characterized by FTIR and UV-VIS spectroscopy. Silica gel (60-120 mesh) used for column chromatography was purchased from Sisco Research Laboratories Pvt. Ltd. India and all other chemicals were purchased from Spectrochem, India, Merck, Germany, and Sigma-Aldrich, USA and were used without further purification. NMR spectra were recorded on Bruker Avance-300/600 spectrometers. Mass spectra were recorded on QTOF-Micro of Waters Micromass and Maxis-Bruker. The GC-MS analysis was carried out on a Shimadzu (QP 2010) series Gas Chromatogram-Mass Spectrometer (Tokyo, Japan), AOC-20i auto-sampler coupled, and a DB-5MS capillary column, (30 m x 0.25 mm i.d., 0.25μm). The initial temperature of column was 70 °C held for 4 min. and was programmed to 230 °C at 4°C/min., then held for 15 min. at 230 °C; the sample injection volume was 2 μL in GC grade dichloromethane. Helium was used as carrier gas at a flow rate of 1.1 ml min^{-1} on split mode (1: 50).

Procedure for synthesis of metal phthalocyanines

Metal phthalocyanines were synthesized by using a reported method with some modification.

Synthesis of Cobalt (II) phthalocyanine

A mixture of phthalimide (26.28 g, 0.18 mol), urea (55.2 g, 0.92 mol), $CoCl_2.6H_2O$ (11.85 g, 0.05 mol) and ammonium molybdate (4.69 g, 0.0038 mol) was heated under microwave irradiation for 3 min. The reaction mixture was cooled to room temperature and in sequence washed with 5% NaOH, distilled water and 2% HCl and finally with distilled water again. After that the resulting solid was dissolved in minimum quantity of concentrated H_2SO_4 and poured in distilled water to precipitate the desired cobalt (II) phthalocyanine, which were then filtered to give 9.5 g (48.5% yield) of cobalt (II) phthalocyanine.

Synthesis of Iron, Nickel and Copper(II) phthalocyanines

Iron, Nickel and Copper(II) phthalocyanines were prepared from $FeSO_4.7H_2O$, $NiCl_2$ and $CuSO_4.7H_2O$ respectively using same procedure as described above.

General experimental procedure for reductive amidation of nitroarenes with carboxylic acids

To a stirred suspension of CoPc (0.01 mmol) in carboxylic acid (2 mL) were added nitroarene (1.0 mmol) and PMHS (4.0 H equiv.) at room temperature and then the temperature was raised to 100 ^oC. On completion of the reaction (as monitored by TLC), reaction mixture was dried under vacuum and the

crude product was analyzed directly by GC-MS. For the purification of desired product column chromatography was carried out (*n*-hexane: ethyl acetate).

Procedure for recyclability of the catalyst

To a stirred suspension of CoPc (0.01 mmol) in acetic acid (2 mL) were added nitrobenzene (1.0 mmol) and PMHS (4.0 H equiv.) at room temperature and then the temperature was raised to 100 ^{o}C. After 12 h, the reaction mixture was analyzed by GC and GC-MS. Further, nitrobenzene (1.0 mmol) and PMHS (4.0 H equiv.) were added to the reaction mixture and stirred at 100 ^{o}C for 12 h. The same procedure was repeated for further cycles and excellent yield of product was observed up to three cycles, whereas in forth cycle the yield was reduced.

Table S1. Reductive amidation of nitrobenzene in different solvents using stoichiometric amount of carboxylic acids[a]

entry	carboxylic acid	solvent	yield (%)[b]
1	AcOH	EtOH	nr
2	AcOH	MeOH	5
3	AcOH	MeCN	nr
4	AcOH	DMSO	nr
5	AcOH	DMF	nr
6	AcOH	Toluene	nr
7	AcOH	PEG-400	nr
8	AcOH	EG	7
9	AcOH	DCE	nr
10	$PhCO_2H$	EG	nr
11	Cinnamic acid	EG	nr

[a]Reaction conditions: nitrobenzene (1.0 mmol), carboxylic acid (5.0 mmol), CoPc (1 mol%), PMHS (4.0 H equiv.), [b]GC yield. DMSO = dimethylsulfoxide, DMF = dimethylformamide, PEG = polyethylene glycol, EG = ethylene glycol, DCE = dichloroethane.

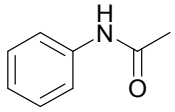
Table S2 Reductive amidation of nitrobenzene in different solvents in the presence of mineral acids using stoichiometric amount of carboxylic acids[a]

entry	solvent	yield (%)[b]
1	EtOH	nr
2	MeOH	6
3	MeCN	nr
4	DMSO	nr
5	DMF	9
6	Toluene	nr
7	PEG-400	18
8	EG	22
9	DCE	10
10	EG	20[c]
11	EG	12[d]
12	EG	24[e]
13	EG	7[f]
14	EG	20[g]

[a]Reaction conditions: nitrobenzene (1.0 mmol), AcOH (3.0 mmol), CoPc (1 mol%), PMHS (4.0 H equiv.), 1M HCl in solvent (2 mL) at 100 ^{o}C for 12h. [b]Isolated yield. [c]1M HBr was used instead of HCl. [d]2.0 mmol AcOH was used. [e]5.0 mmol AcOH was used. [f]0.5M HCl was used. [g]2.0M HCl was used. nr = no reaction, DMSO = dimethylsulfoxide, DMF = dimethylformamide, PEG = polyethylene glycol, EG = ethylene glycol, DCE = dichloroethane.

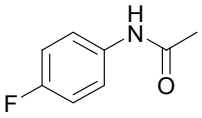
Spectral data of isolated compounds

1. *N*-Acetylaniline (Table 2, entry 1)[1]



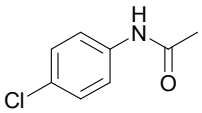
^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.15 (s, 3H), 7.10 (t, 1H, J = 7.3 Hz), 7.28-7.33 (m, 2H), 7.52 (d, 2H, J = 7.7 Hz), 8.01 (brs, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 24.8, 120.5, 124.6, 129.3, 138.4, 169.3; HRESIMS calcd for $C_8H_{10}NO$ $[M+H]^+$ 136.0762, found 136.0734.

2. *N*-Acetyl-4-fluoroaniline (Table 2, entry 2)[2]



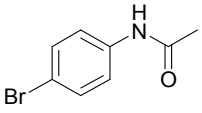
^{1}H NMR (CD_3OD, 300 MHz) δ 2.11 (s, 3H), 7.00-7.06 (m, 2H), 7.50-7.55 (m, 2H); ^{13}C NMR (CD_3OD, 75 MHz) δ 22.6, 115.0, 115.3, 121.9, 122.0, 135.0, 158.0, 161.2, 170.5; HRESIMS calcd for $C_8H_8N_3OS$ $[M+H]^+$ 154.0668, found 154.0631.

3. *N*-Acetyl-4-chloroaniline (Table 2, entry 3)[3]



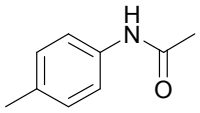
^{1}H NMR (CD_3OD, 300 MHz) δ 2.09 (s, 3H), 7.20 (d, 2H, J = 8.8 Hz), 7.46 (d, 2H, J = 8.8 Hz); ^{13}C NMR (CD_3OD, 75 MHz) δ 23.8, 121.6, 129.0, 129.2, 137.3, 170.4; HRESIMS calcd for C_8H_9ClNO $[M+H]^+$ 170.0373, found 169.0348.

4. *N*-Acetyl-4-bromoaniline (Table 2, entry 4)[4]



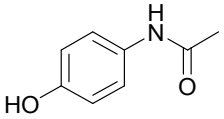
^{1}H NMR (CD_3OD, 300 MHz) δ 2.04 (s, 3H), 7.29-7.38 (m, 4H); ^{13}C NMR (CD_3OD, 75 MHz) δ 23.6, 116.5, 121.5, 131.6, 137.4, 169.8; HRESIMS calcd for $C_9H_9N_2O$ $[M+H]^+$ 213.9868, found 213.9811.

5. 4-(*N*-Acetylamino)toluene (Table 2, entry 5)[5]



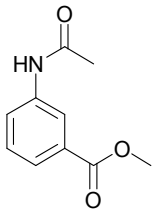
^{1}H NMR (CD_3OD, 300 MHz) δ 2.15 (s, 3H), 2.31 (s, 3H), 7.10 (d, 2H, J = 8.1 Hz), 7.38 (d, 2H, J = 8.1 Hz), 7.69 (brs, 1H); ^{13}C NMR (CD_3OD, 75 MHz) δ 21.2, 24.7, 120.5, 129.8, 134.2, 135.8, 168.9; HRESIMS calcd for $C_9H_{12}NO$ $[M+H]^+$ 150.0919, found 150.0950.

6. 4-(*N*-Acetylamino)phenol (Table 2, entry 6)[5]



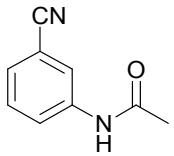
^{1}H NMR (CD_3OD, 300 MHz) δ 2.09 (s, 3H), 6.71-6.76 (m, 2H), 7.28-7.32 (m, 2H); ^{13}C NMR (CD_3OD, 75 MHz) δ 24.2, 116.9, 124.1, 132.4, 156.1, 172.1; HRESIMS calcd for $C_8H_{10}NO_2$ $[M+H]^+$ 152.0712, found 152.0729.

7. Methyl-3-(*N*-acetylamino)benzoate (Table 2, entry 7)[6]



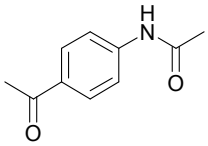
^{1}H NMR (CD_3OD, 300 MHz) δ 2.14 (s, 3H), 3.89 (s, 3H), 7.37-7.42 (m, 1H), 7.71-7.73 (m, 1H), 7.77-7.81 (m, 1H), 8.21 (s, 1H); ^{13}C NMR (CD_3OD, 75 MHz) δ 22.8, 51.6, 120.8, 124.4, 124.8, 128.9, 130.9, 139.3, 167.2, 170.7; HRESIMS calcd for $C_{10}H_{12}NO_3$ $[M+H]^+$ 194.0817, found 194.0809.

8. 3-(*N*-Acetylamino)benzonitrile (Table 2, entry 8)[1]



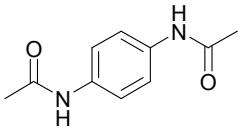
^{1}H NMR ($CDCl_3$, 600 MHz) δ 2.20 (s, 3H), 7.38-7.41 (m, 2H), 7.72 (d, 1H, J = 6.6 Hz), 7.89 (s, 1H), 7.93 (s, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 24.5, 112.8, 118.5, 122.8, 123.9, 127.6, 129.9, 138.8, 168.9; HRESIMS calcd for $C_9H_9N_2O$ $[M+H]^+$ 161.0715, found 161.0704.

9. 4-(*N*-Acetylamino)acetophenone (Table 2, entry 9)[7]



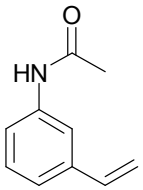
^{1}H NMR (CD_3OD, 300 MHz) δ 2.16 (s, 3H), 2.56 (s, 3H), 7.68-7.71 (m, 2H), 7.94-7.97 (m, 2H); ^{13}C NMR (CD_3OD, 75 MHz) δ 23.0, 25.4, 119.0, 129.6, 132.6 143.7, 170.9, 198.4; HRESIMS calcd for $C_8H_8N_3OS$ $[M+H]^+$ 178.0868, found 178.0851.

10. 1,4-Di-(*N*-acetylamino)benzene (Table 2, entry 10)[5]



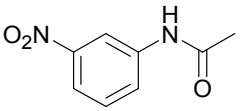
^{1}H NMR (DMSO-d_6, 600 MHz) δ 1.99 (s, 6H), 7.45 (s, 4H), 9.83 (s, 2H); ^{13}C NMR (DMSO-d_6, 150 MHz) δ 24.3, 119.8, 135.0, 168.4; HRESIMS calcd for $C_{10}H_{13}N_2O_2$ $[M+H]^+$ 193.0977, found 193.0942.

11. 3-(*N*-Acetylamino)styrene (Table 2, entry 11)[8]



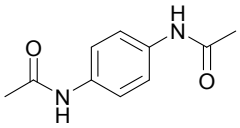
^{1}H NMR (CD_3OD, 300 MHz) δ 2.13 (s, 3H), 5.24 (d, 1H, J = 11.0 Hz), 5.76 (d, 1H, J = 17.5 Hz), 6.66-6.75 (m, 1H), 7.16 (d, 1H, J = 7.6 Hz), 7.26 (m, 1H), 7.43 (d, 1H, J = 8.0 Hz), 7.65 (s, 1H); ^{13}C NMR (CD_3OD, 75 MHz) δ 24.3, 114.8, 119.2, 121.0, 123.5, 130.4, 138.4, 140.1, 140.6, 172.1; HRESIMS calcd for $C_{10}H_{12}NO$ $[M+H]^+$ 162.0919, found 162.0933.

12. *N*-Acetyl-3-nitroaniline (Table 2, entry 12)[9]



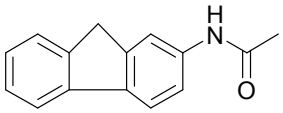
^{1}H NMR (CD_3OD, 600 MHz) δ 2.15 (s, 3H), 7.50 (s, 1H), 7.82 (d, 1H, J = 6.0 Hz), 7.90 (d, 1H, J = 6.0 Hz), 8.57 (s, 1H); ^{13}C NMR (CD_3OD, 150 MHz) δ 24.2, 115.6, 119.6, 126.6, 131.1, 141.6, 150.2, 172.3; HRESIMS calcd for $C_8H_9N_2O_3$ $[M+H]^+$ 181.0613, found 181.0637.

13. 1,4-Di-(*N*-acetylamino)benzene (Table 2, entry 13)[5]



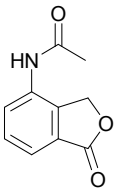
^{1}H NMR (DMSO-d_6, 300 MHz) δ 2.00 (s, 6H), 7.46 (s, 4H), 9.85 (s, 2H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 24.1, 119.6, 134.8, 168.2; HRESIMS calcd for $C_{10}H_{13}N_2O_2$ $[M+H]^+$ 193.0977, found 193.0934.

14. 2-(*N*-Acetylamino)fluorine (Table 2, entry 14)[10]



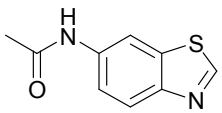
^{1}H NMR (CD_3OD, 300 MHz) δ 2.14 (s, 3H), 3.82 (s, 2H), 7.21-7.26 (m, 1H), 7.29-7.34 (m, 1H), 7.45-7.50 (m, 2H), 7.68-7.73 (m, 2H), 7.80 (s, 1H); ^{13}C NMR (CD_3OD, 75 MHz) δ 24.0, 37.8, 118.2, 120.2, 120.5, 121.0, 126.1, 127.5, 127.9, 138.9, 139.3, 142.7, 144.6, 145.4, 171.7; HRESIMS calcd for $C_{15}H_{14}NO$ $[M+H]^+$ 224.1075, found 224.1021.

15. 4-(*N*-Actylamino)phthalide (Table 2, entry 15)[11]



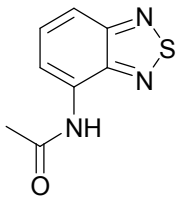
^{1}H NMR (DMSO-d_6, 600 MHz) δ 2.06 (s, 3H), 5.32 (s, 2H), 7.56 (d, 1H, J = 6.0 Hz), 7.75 (d, 1H, J = 6.0 Hz), 8.17 (s, 1H), 10.28 (s, 1H); ^{13}C NMR (DMSO-d_6, 150 MHz) δ 24.1, 69.8, 114.0, 123.3, 125.2, 125.5, 140.1, 141.6, 168.9, 170.7; HRESIMS calcd for $C_{10}H_{10}NO_3$ $[M+H]^+$ 192.0661, found 192.0637.

16. 6-(*N*-Acetylamino)benzothiazole (Table 2, entry 16)[12]



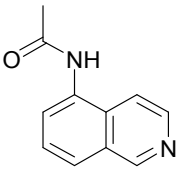
^{1}H NMR (CD_3OD, 300 MHz) δ 2.17 (s, 3H), 7.52 (dd, 1H, J = 1.8, 8.8 Hz), 7.95 (d, 1H, J = 8.8 Hz), 8.47 (d, 1H, J = 1.8 Hz), 9.11 (s, 1H); ^{13}C NMR (CD_3OD, 75 MHz) δ 22.9, 112.5, 119.5, 122.7, 134.6, 137.0, 149.4, 154.9, 170.8; HRESIMS calcd for $C_9H_9N_2OS$ $[M+H]^+$ 193.0436, found 193.0411.

17. 4-(*N*-Acetylamino)-2,1,3-benzothiadiazole (Table 2, entry 17)[13]



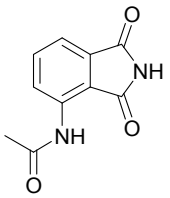
^{1}H NMR (CD_3OD, 300 MHz) δ 2.31 (s, 3H), 7.58-7.63 (m, 1H), 7.68-7.71 (m, 1H), 8.32 (d, 1H, J = 7.1 Hz); ^{13}C NMR (CD_3OD, 75 MHz) δ 24.4, 117.6, 118.3, 132.0, 132.2, 149.9, 156.8, 172.7; HRESIMS calcd for $C_8H_8N_3OS$ $[M+H]^+$ 194.0388, found 194.0345.

18. 5-(*N*-Acetylamino)isoquinoline (Table 2, entry 18)[14]



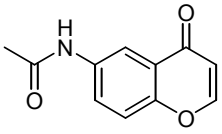
^{1}H NMR (CD_3OD, 300 MHz) δ 2.31 (s, 3H), 7.67-7.31 (m, 1H), 7.93-8.01 (m, 3H), 8.48 (d, 1H, J = 6.0 Hz), 9.26 (s, 1H); ^{13}C NMR (CD_3OD, 75 MHz) δ 23.5, 117.5, 127.1, 128.2, 128.9, 130.8, 132.7, 134.0, 143.1, 153.6, 172.9; HRESIMS calcd for $C_{11}H_{11}N_2O$ $[M+H]^+$ 187.0871, found 187.0886.

19. 4-(*N*-acetylamino)phthalimide (Table 2, entry 19)



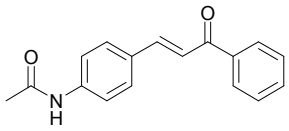
^{1}H NMR (DMSO-d_6, 300 MHz) δ 2.11 (s, 3H), 7.73 (d, 1H, J = 8.1 Hz), 7.80-7.84 (m, 1H), 8.12-8.13 (m, 1H), 10.52 (s, 1H), 11.56 (brs, 1H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 24.1, 112.3, 123.0, 123.9, 126.2, 134.0, 144.6, 168.7, 168.9, 169.1.

20. 6-(*N*-Acetylamino)chromone (Table 2, entry 20)[15]



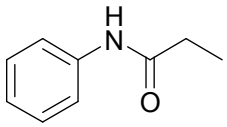
^{1}H NMR (DMSO-d_6, 300 MHz) δ 2.07 (s, 3H), 6.30 (d, 1H, J = 6.0 Hz), 7.58 (d, 1H, J = 9.0 Hz), 7.88-7.92 (m, 1H), 8.24 (d, 1H, J = 6.0 Hz), 8.30 (s, 1H), 10.25 (s, 1H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 24.8, 112.5, 114.0, 119.8, 125.2, 126.4, 137.4, 152.6, 157.5, 169.4, 171.1; HRESIMS calcd for $C_{11}H_{10}NO_3$ $[M+H]^+$ 204.0661, found 204.0643.

21. 4-(*N*-Acetylamino)chalcone (Table 2, entry 21)[16]



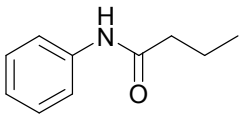
^{1}H NMR (CD_3OD, 600 MHz) δ 2.13 (s, 1H), 7.53 (d, 2H, J = 6.0 Hz), 7.61-7.75 (m, 7H), 8.05 (d, 2H, J = 6.0 Hz); ^{13}C NMR (CD_3OD, 150 MHz) δ 23.9, 120.8, 121.5, 129.5, 129.6, 130.5, 131.6, 134.0, 139.4, 142.3, 145.8, 171.7, 192.2; HRESIMS calcd for $C_{10}H_{12}NO_3$ $[M+H]^+$ 266.1181, found 266.1169.

22. *N*-Phenylpropanamide (Table 3, entry 3)[5]



^{1}H NMR (CD_3OD, 300 MHz) δ 1.20 (t, 3H, J = 7.5 Hz), 2.39 (q, 2H, J = 7.5 Hz), 7.08 (t, 1H, J = 7.4 Hz), 7.27-7.32 (m, 2H), 7.54 (d, 2H, J = 7.7 Hz); ^{13}C NMR (CD_3OD, 75 MHz) δ 9.2, 30.0, 120.2, 124.0, 128.7, 138.9, 174.4; HRESIMS calcd for $C_9H_{12}NO$ $[M+H]^+$ 150.0919, found 150.0922.

23. *N*-Phenylbutanamide (Table 3, entry 4)[17]

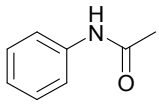


^{1}H NMR (CD_3OD, 600 MHz) δ 0.99-1.00 (m, 3H), 1.71-1.72 (m, 2H), 2.33 (s, 2H), 7.07 (s, 1H), 7.28 (s, 2H), 7.53 (m, 2H); ^{13}C NMR (CD_3OD, 150 MHz) δ 13.8, 20.1, 39.7, 121.1, 124.9, 129.6, 139.7, 174.4; HRESIMS calcd for $C_{10}H_{14}NO$ $[M+H]^+$ 164.1075, found 164.1054.

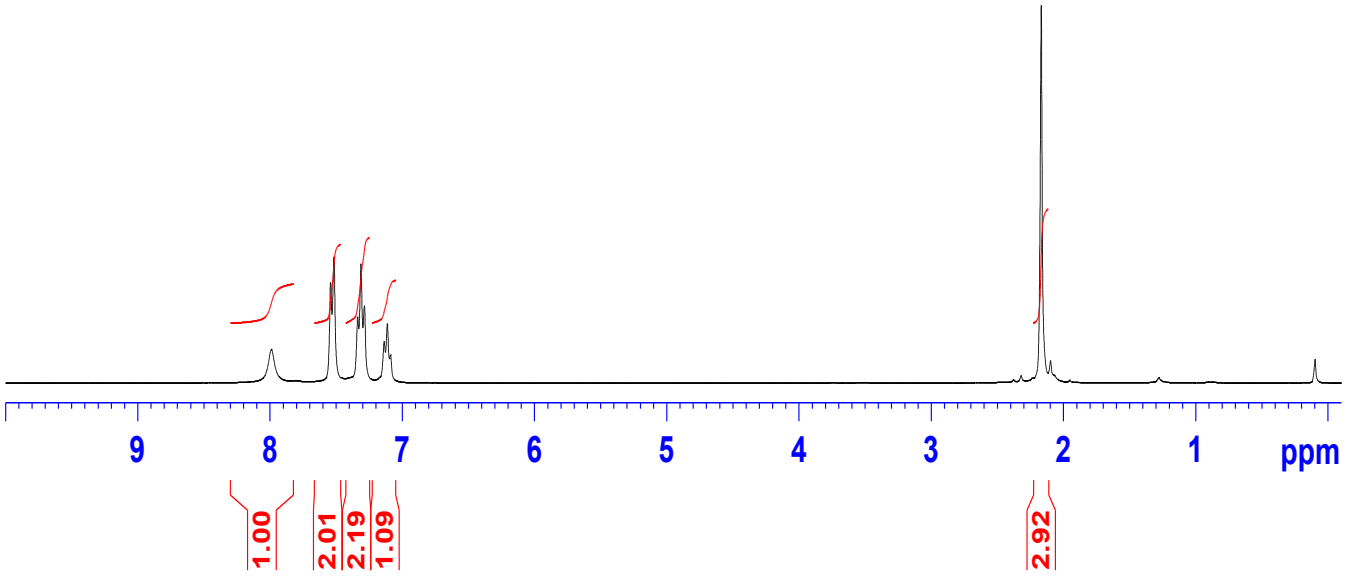
^{1}H and ^{13}C NMR spectra of isolated compounds

In ^{1}H NMR spectra, peaks at δ 3.31 and 4.90 correspond to trace amount of protonated solvent in CD_3OD and peaks at δ 2.50 and 3.34 correspond to trace amount of protonated solvent in DMSO-d_6.

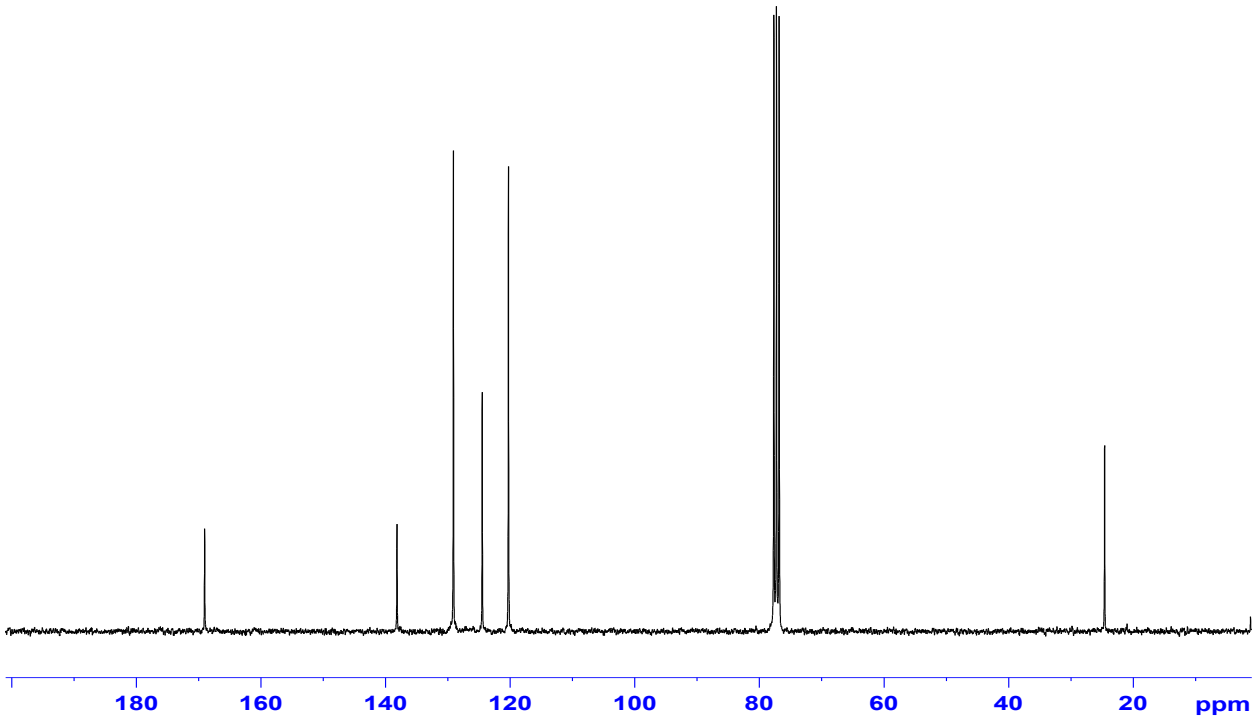
1. *N*-Acetylaniline in $CDCl_3$ (Table 2, entry 1)



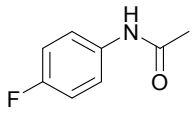
^{1}H NMR



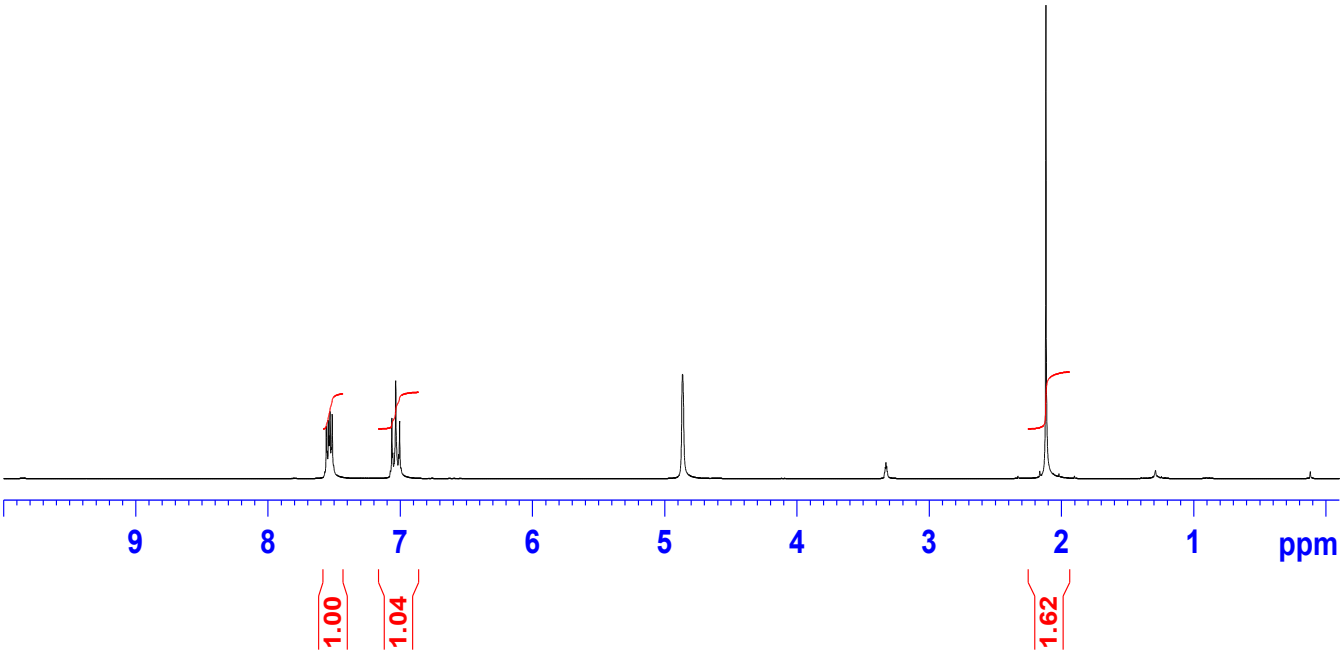
^{13}C NMR



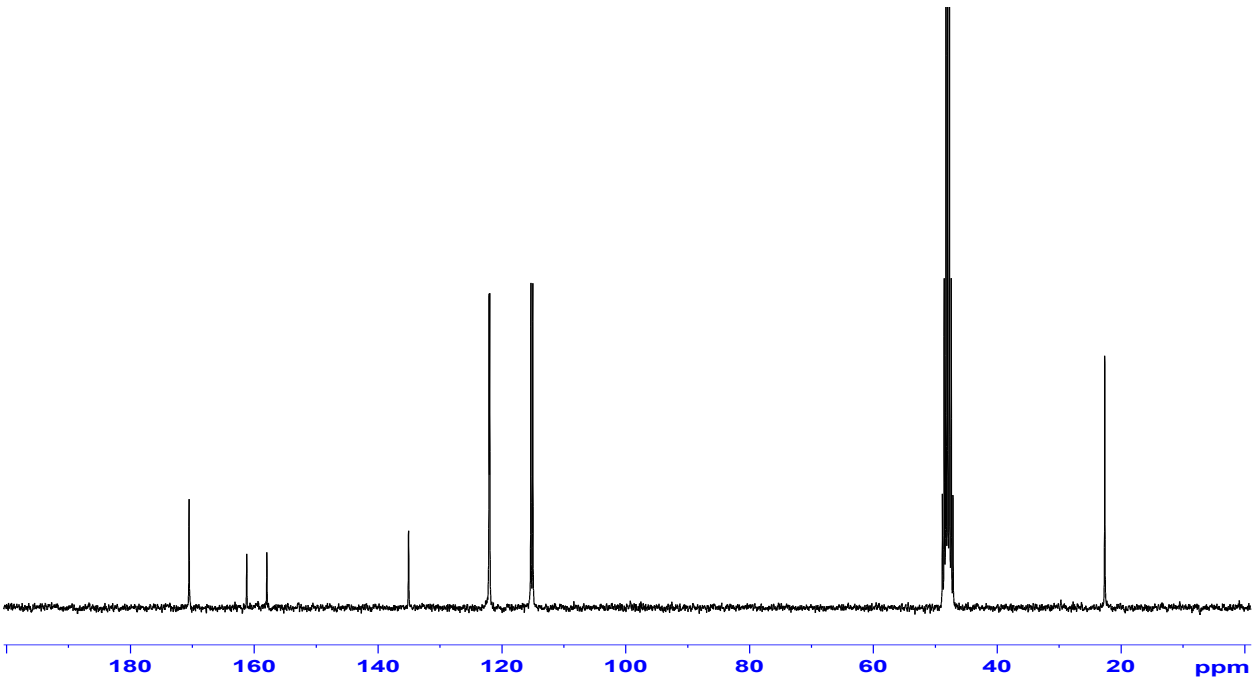
2. *N*-Acetyl-4-fluoroaniline in CD_3OD (Table 2, entry 2)



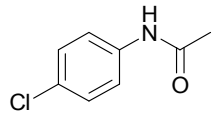
^{1}H NMR



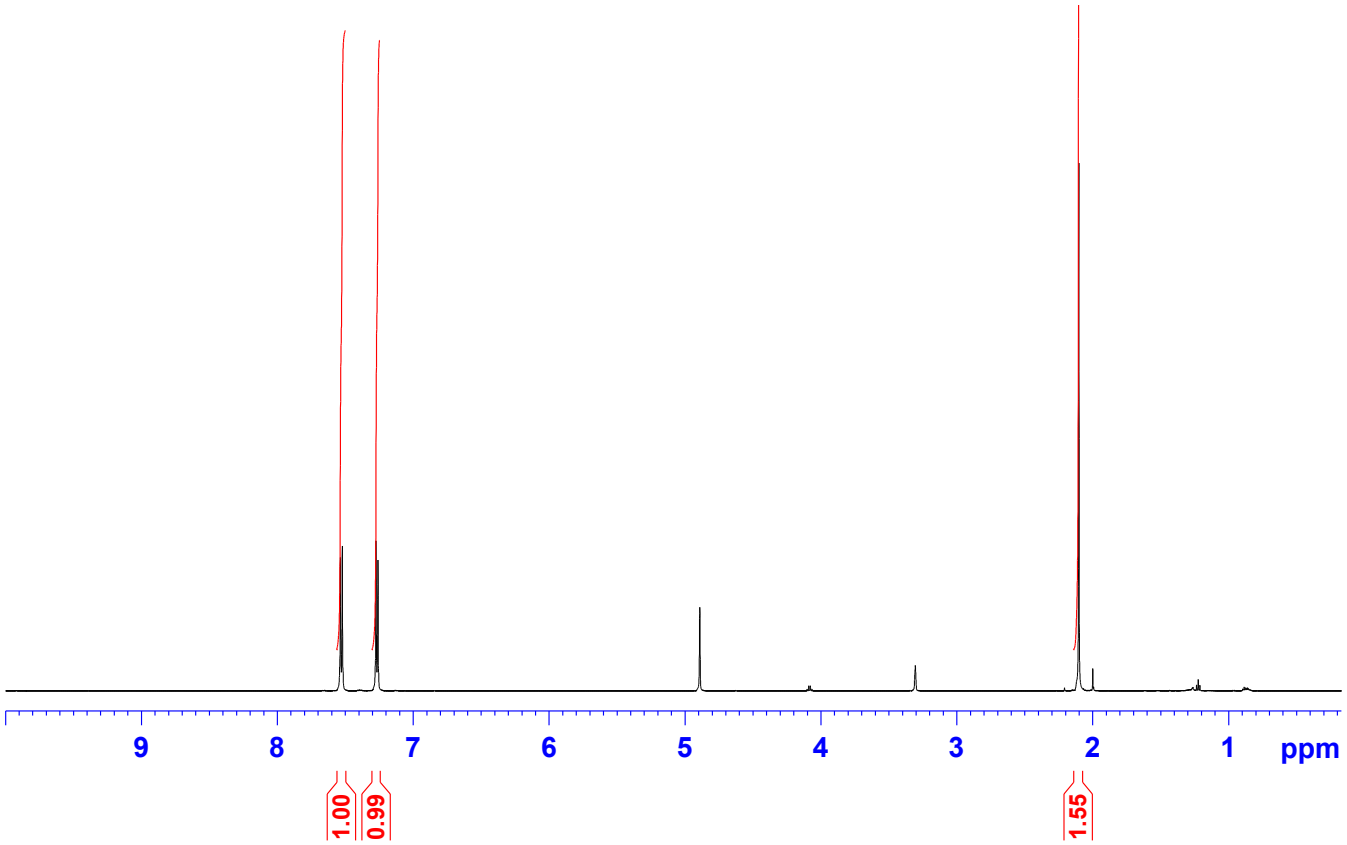
^{13}C NMR



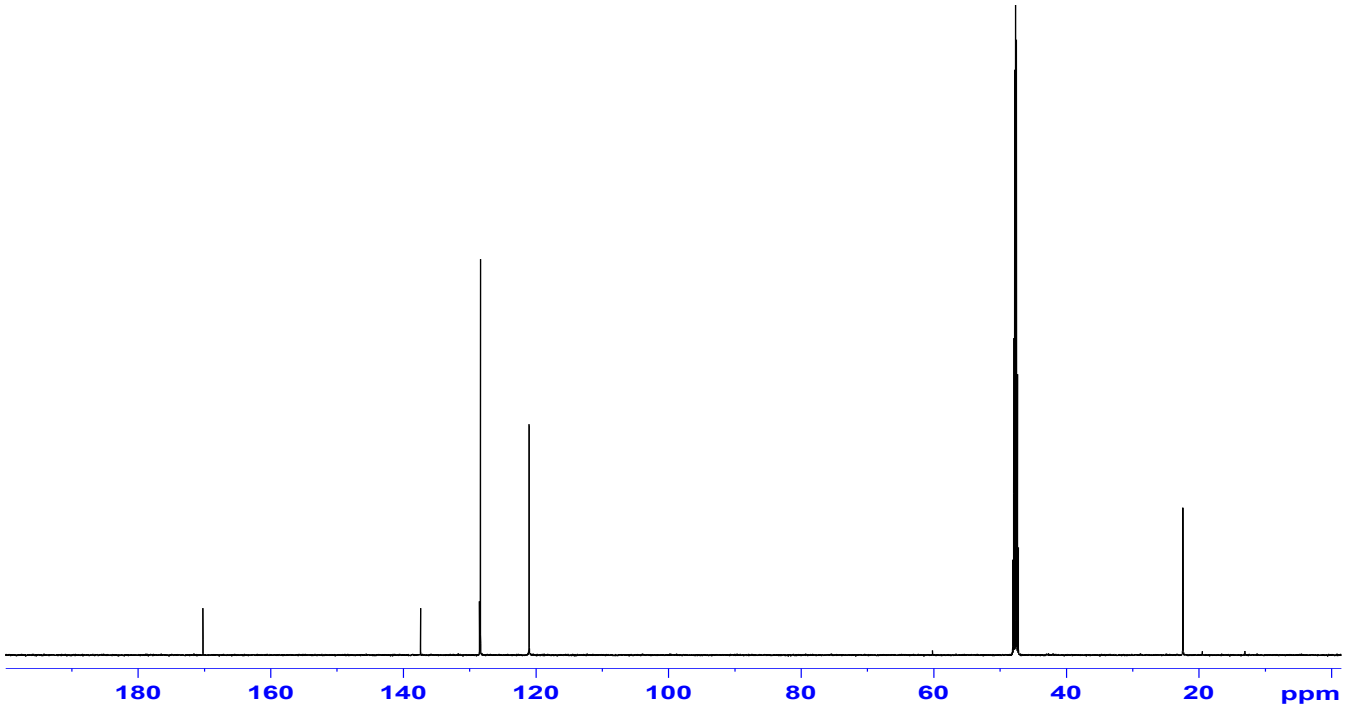
3. *N*-Acetyl-4-chloroaniline in CD_3OD (Table 2, entry 3)



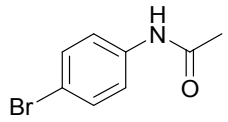
^{1}H NMR



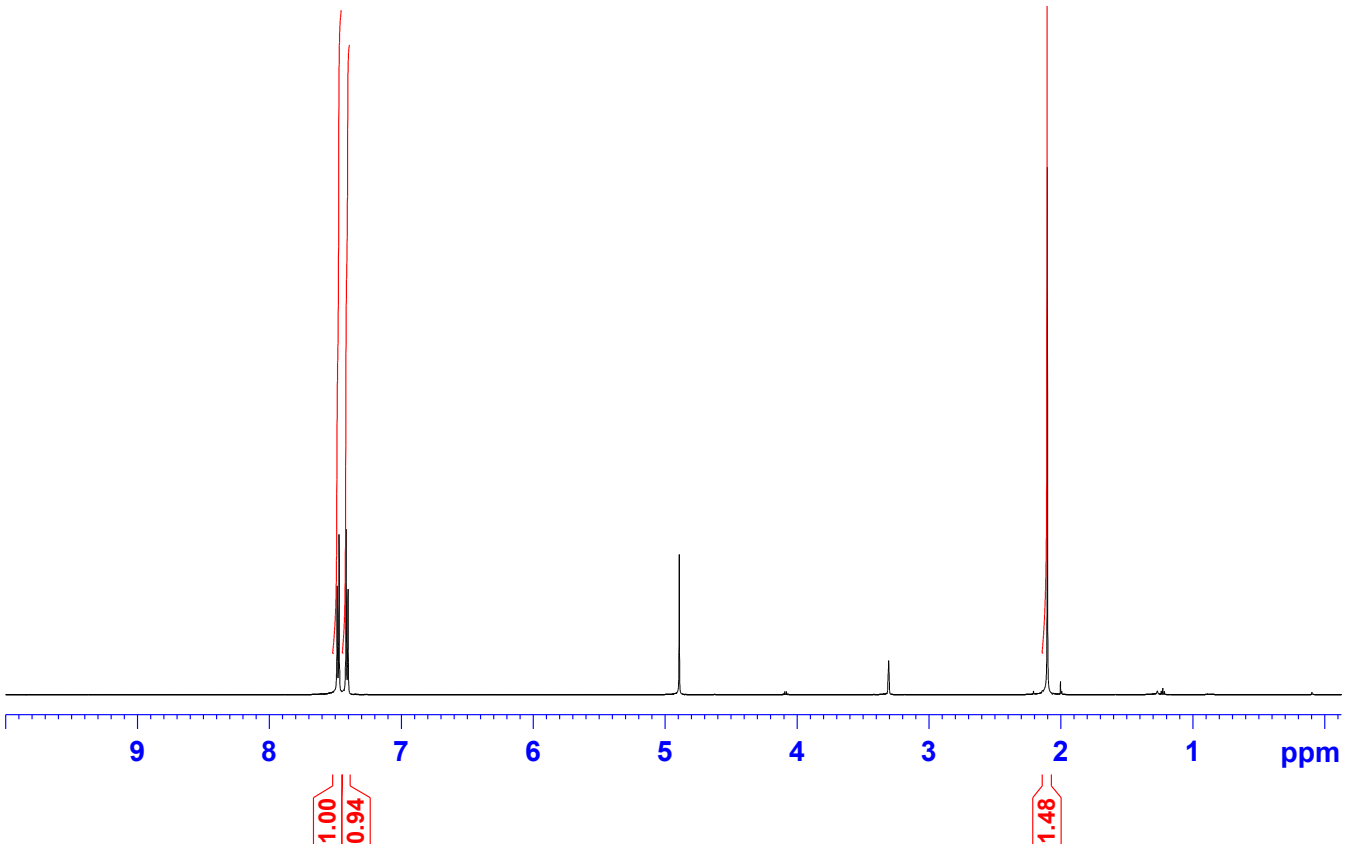
^{13}C NMR



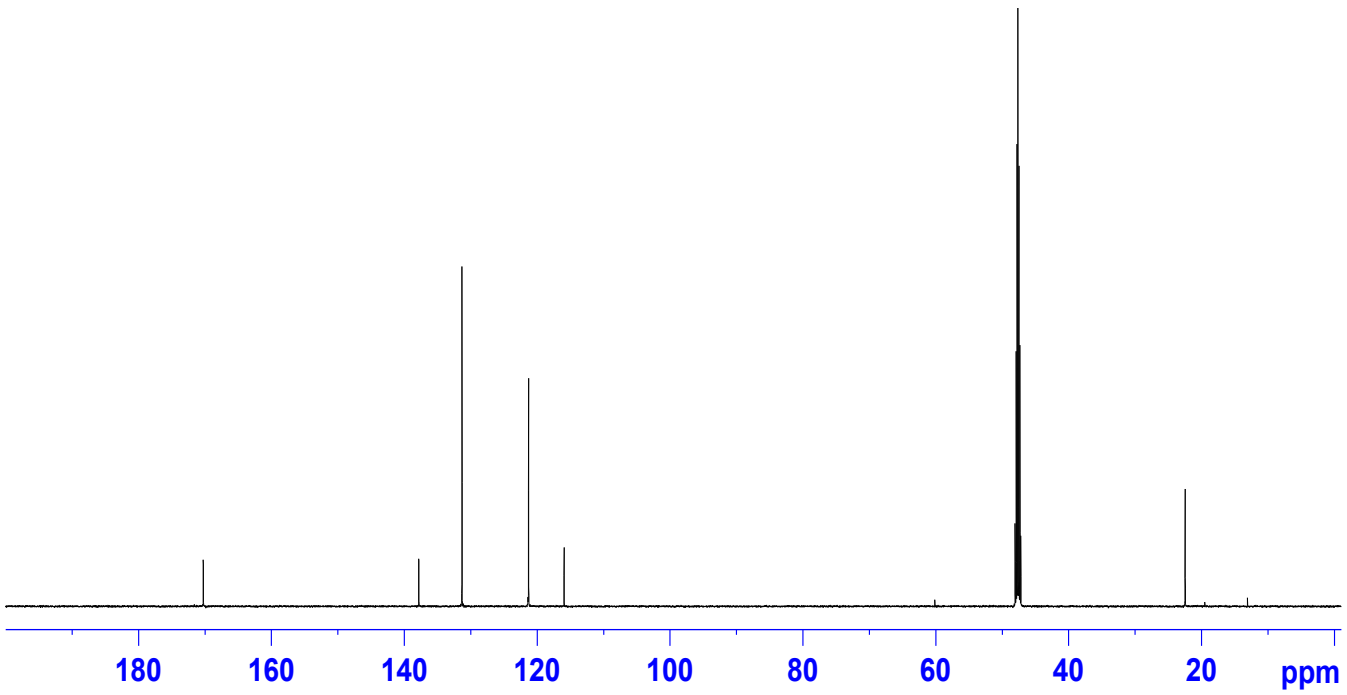
4. *N*-Acetyl-4-bromoaniline in CD_3OD (Table 2, entry 4)



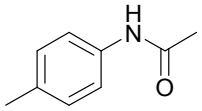
^{1}H NMR



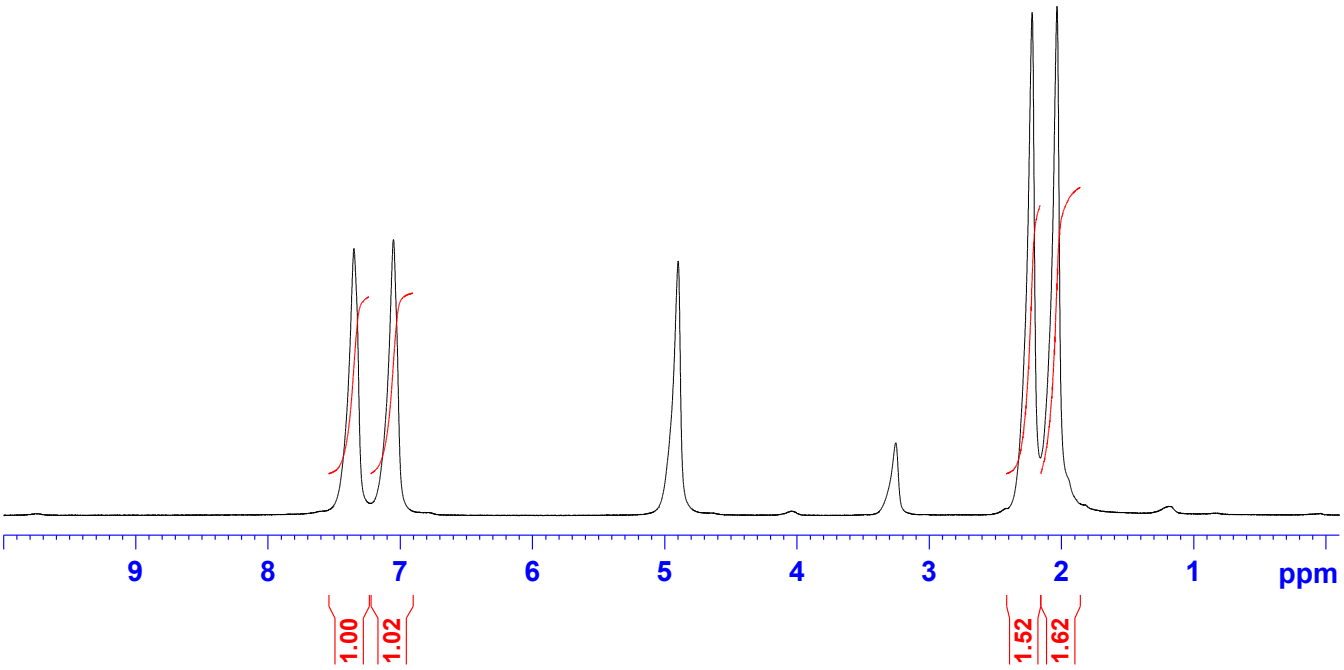
^{13}C NMR



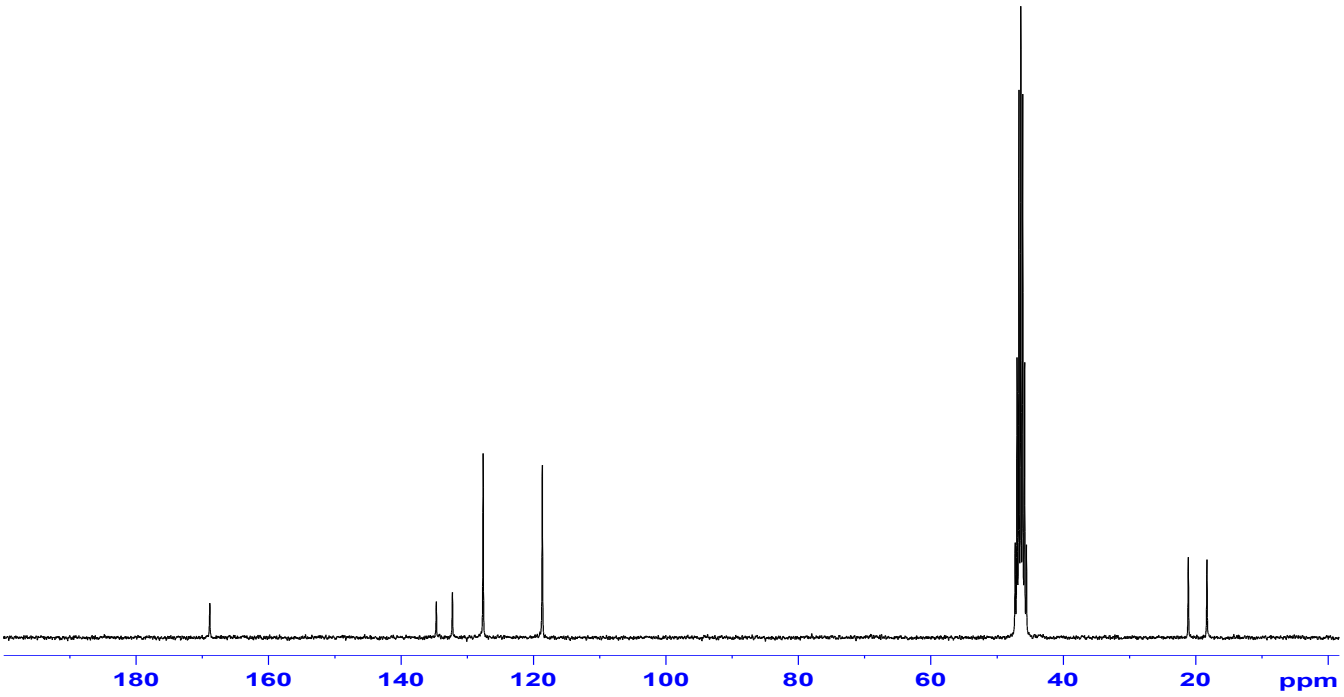
5. 4-(*N*-Acetylamino)toluene in CD_3OD (Table 2, entry 5)



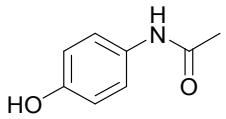
^{1}H NMR



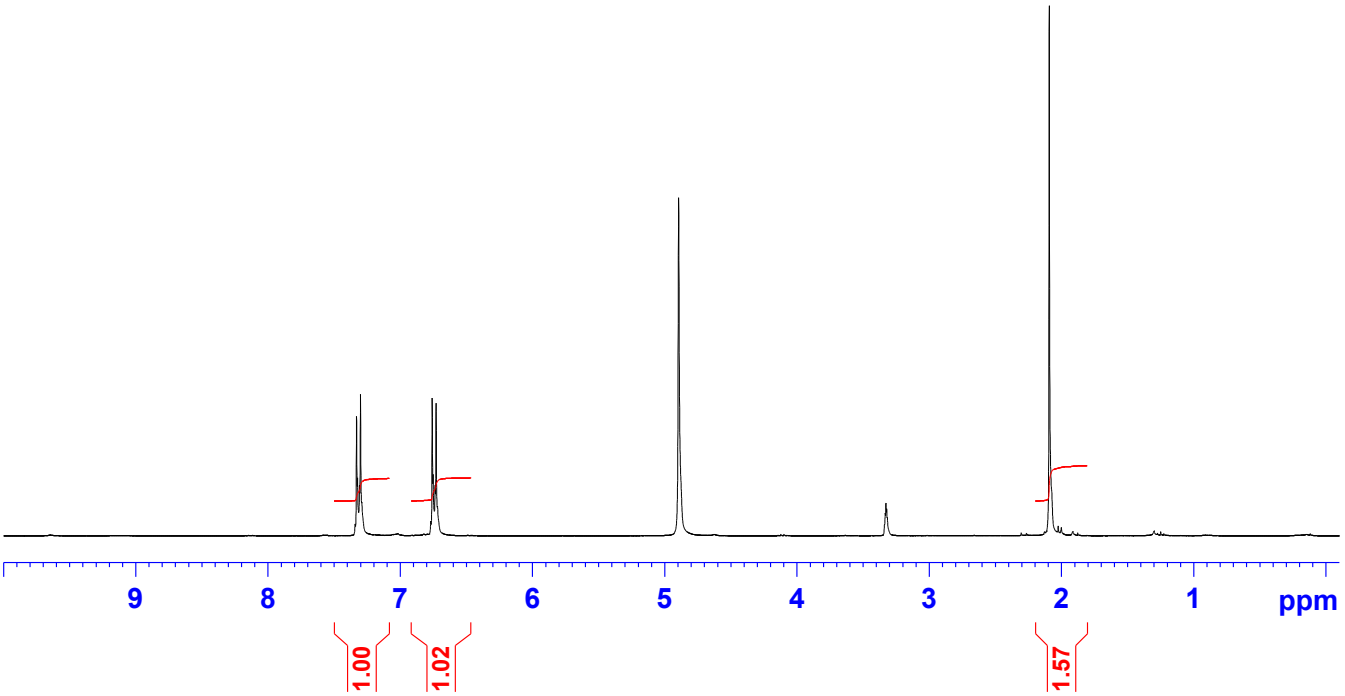
^{13}C NMR



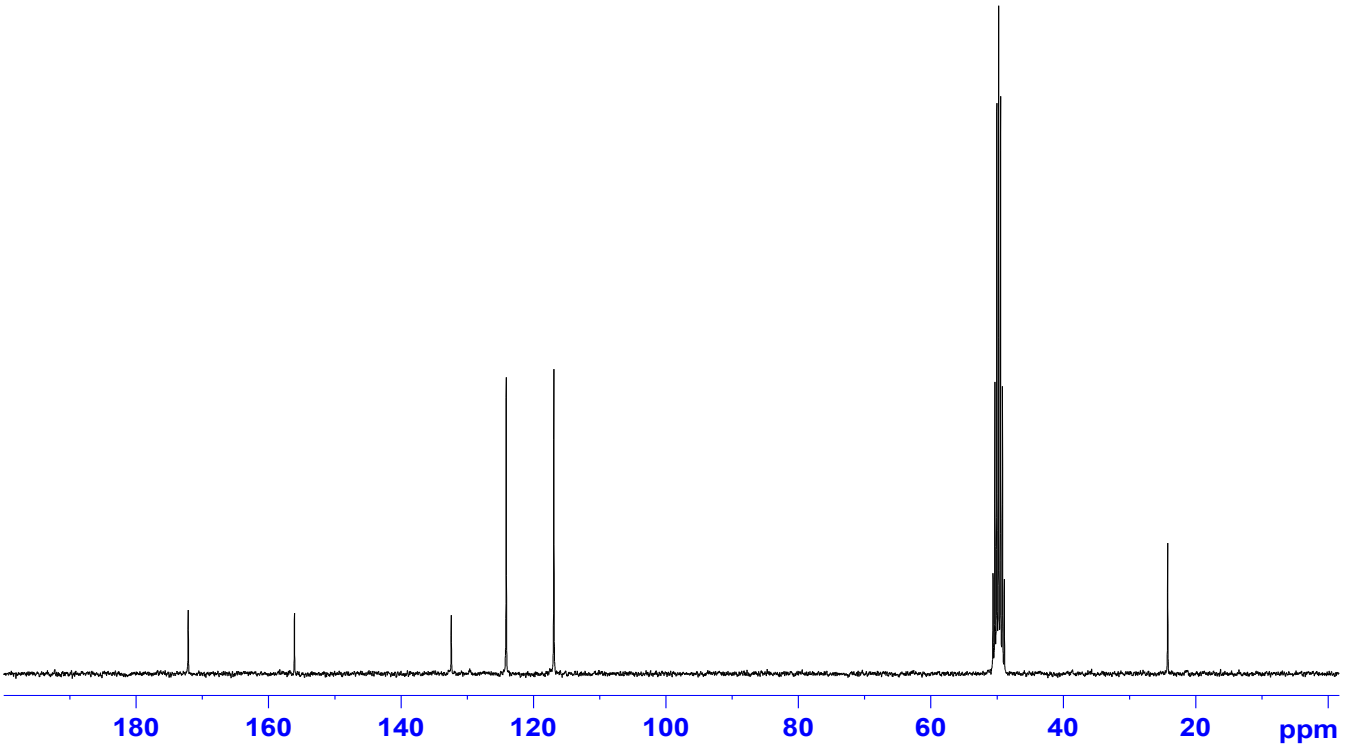
6. 4-(*N*-Acetylamino)phenol in CD_3OD (Table 2, entry 6)



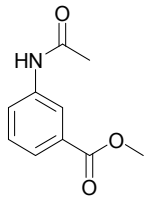
^{1}H NMR



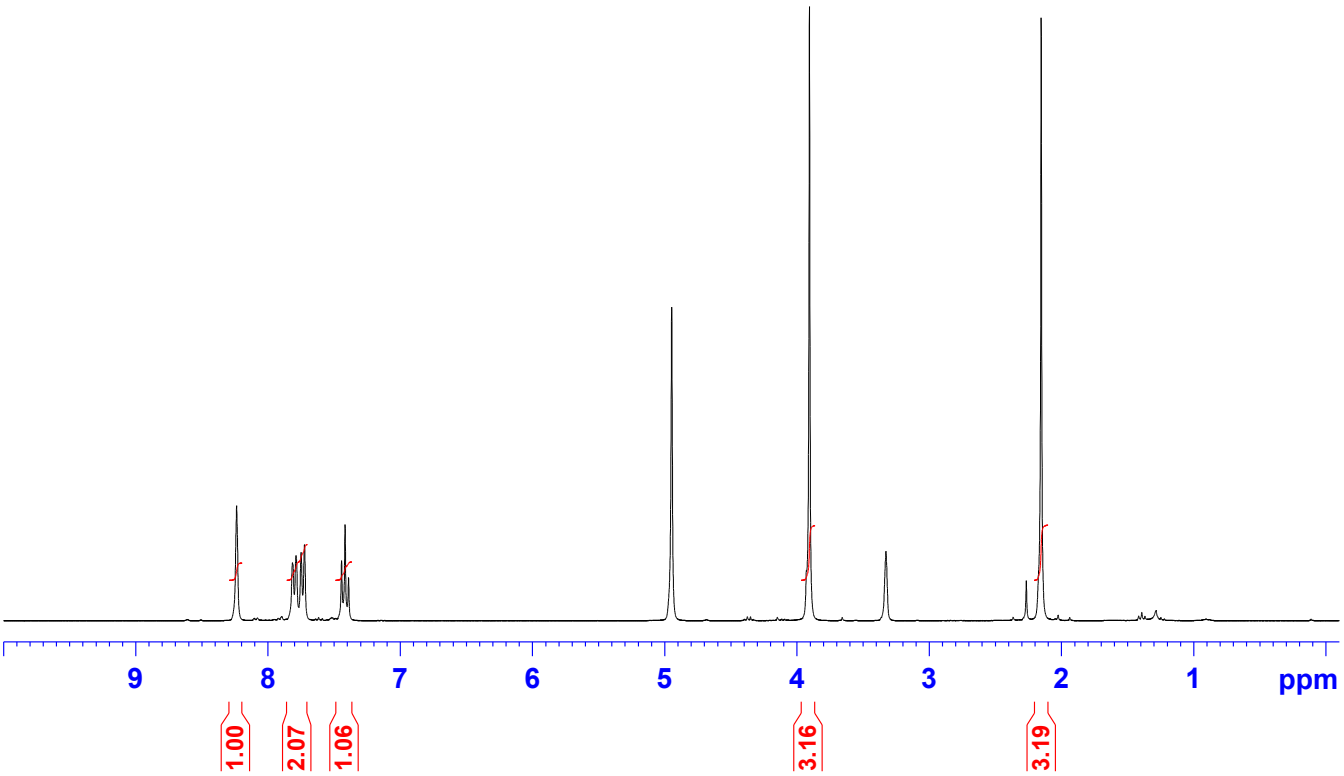
^{13}C NMR



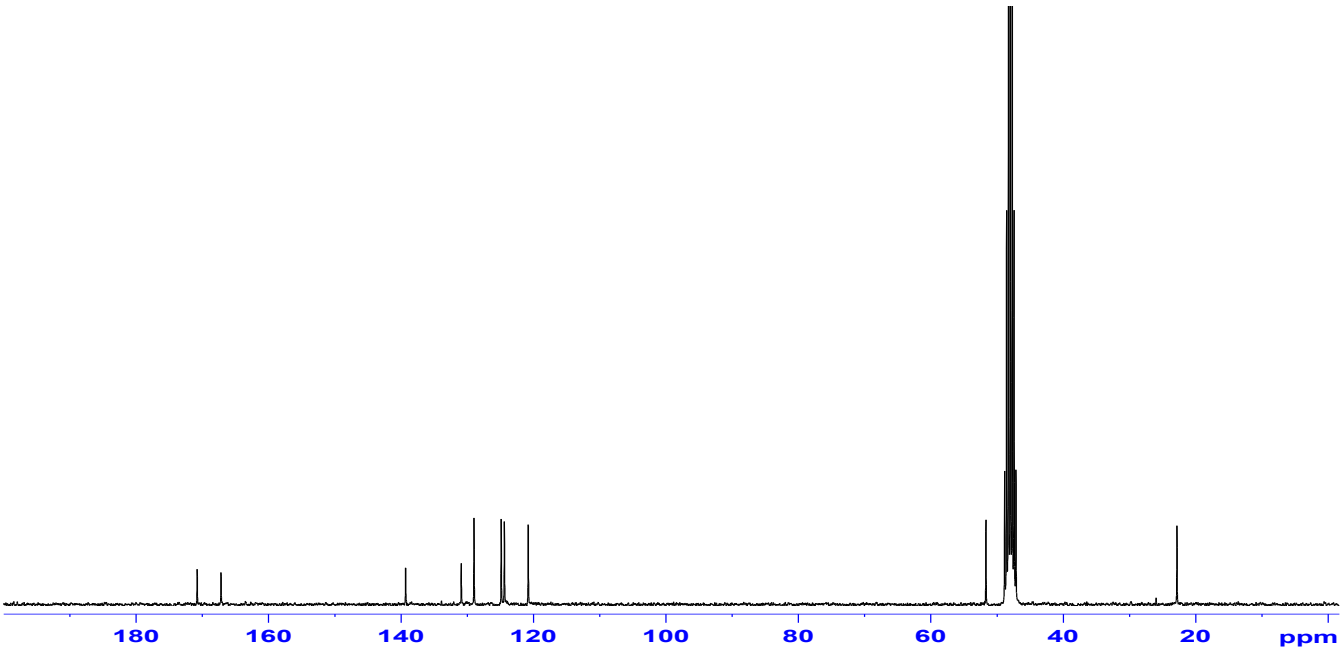
7. Methyl-3-(*N*-acetylamino)benzoate in CD_3OD (Table 2, entry 7)



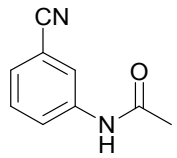
^{1}H NMR



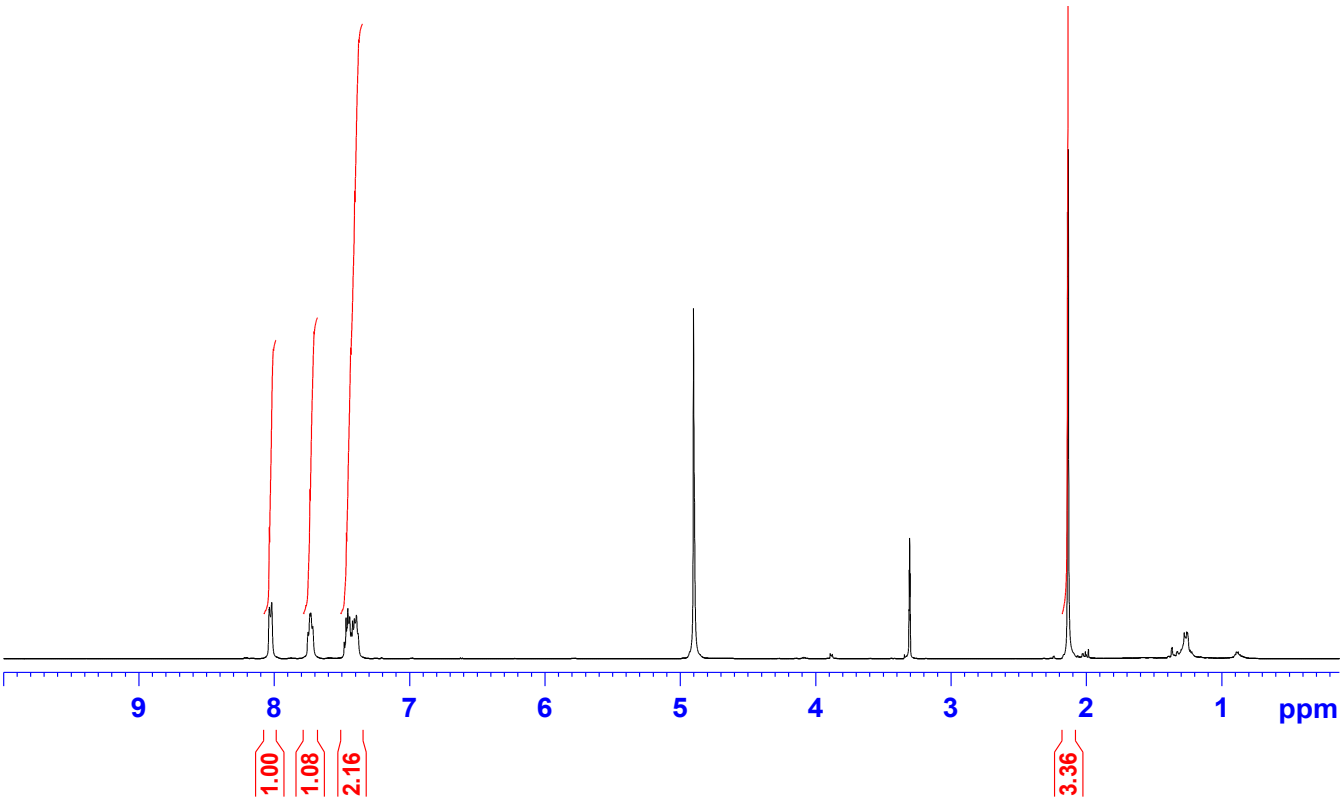
^{13}C NMR



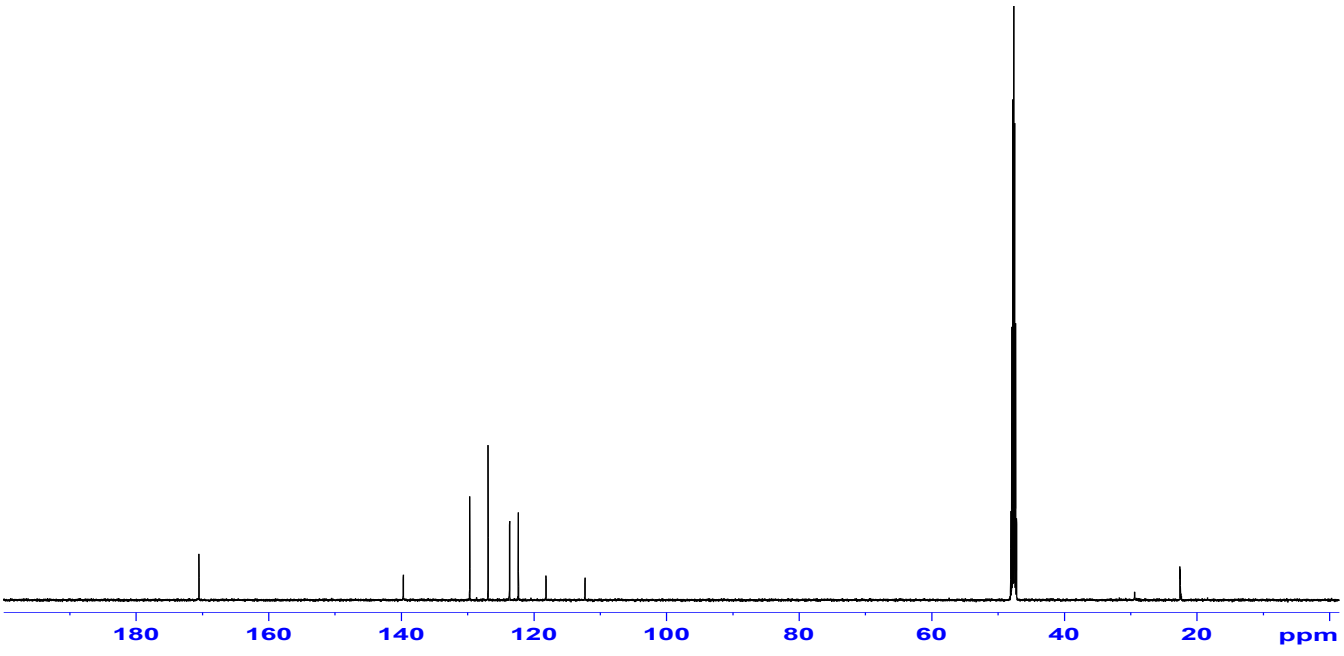
8. 3-(*N*-Acetylamino)benzonitrile in CD_3OD (Table 2, entry 8)



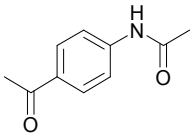
^{1}H NMR



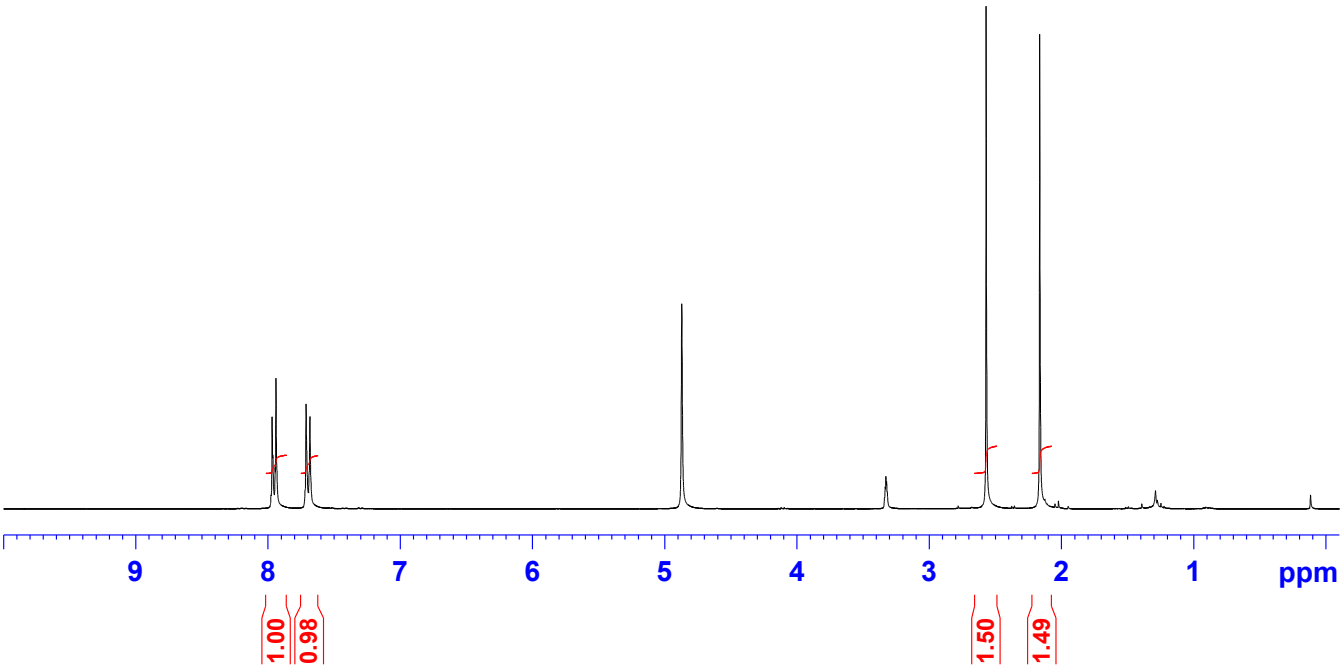
^{13}C NMR



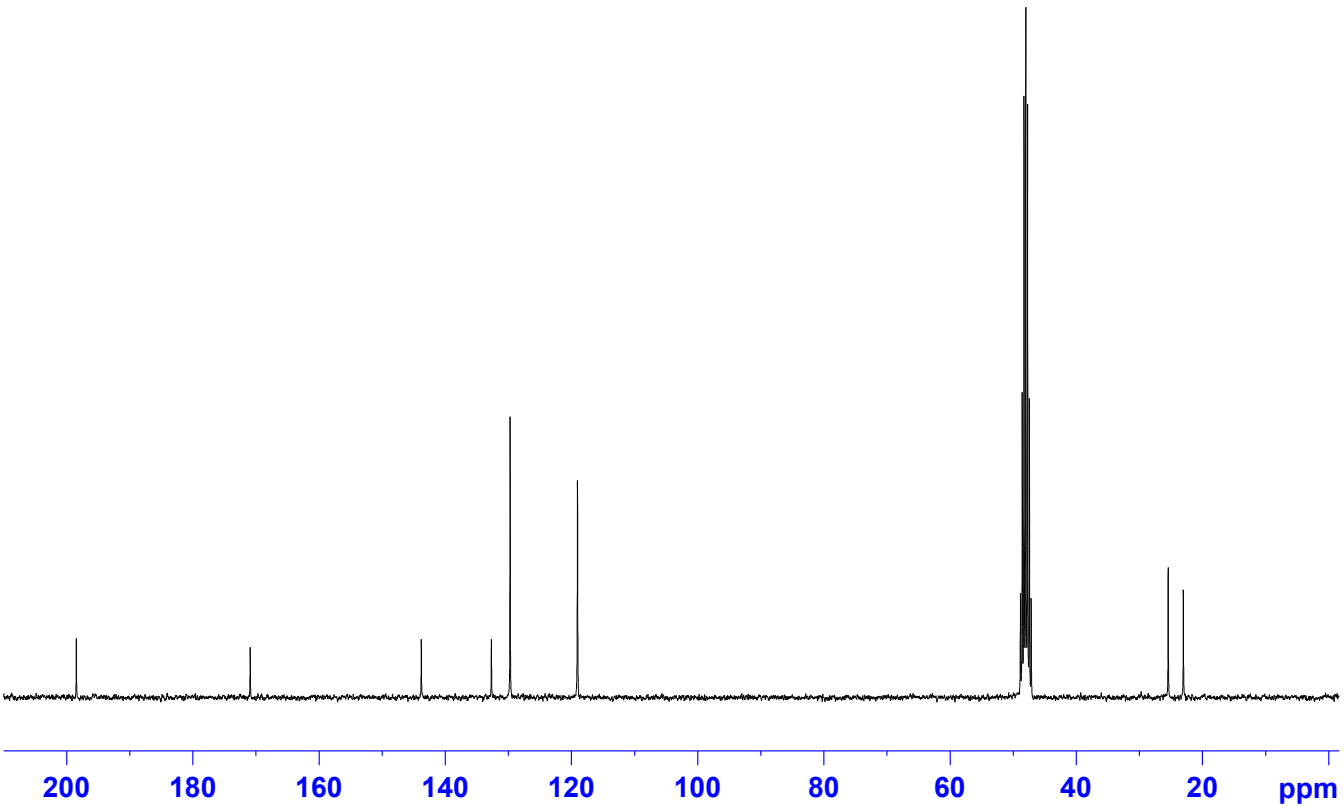
9. 4-(*N*-Acetylamino)acetophenone in CD_3OD (Table 2, entry 9)



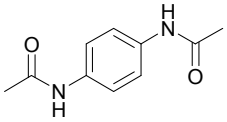
^{1}H NMR



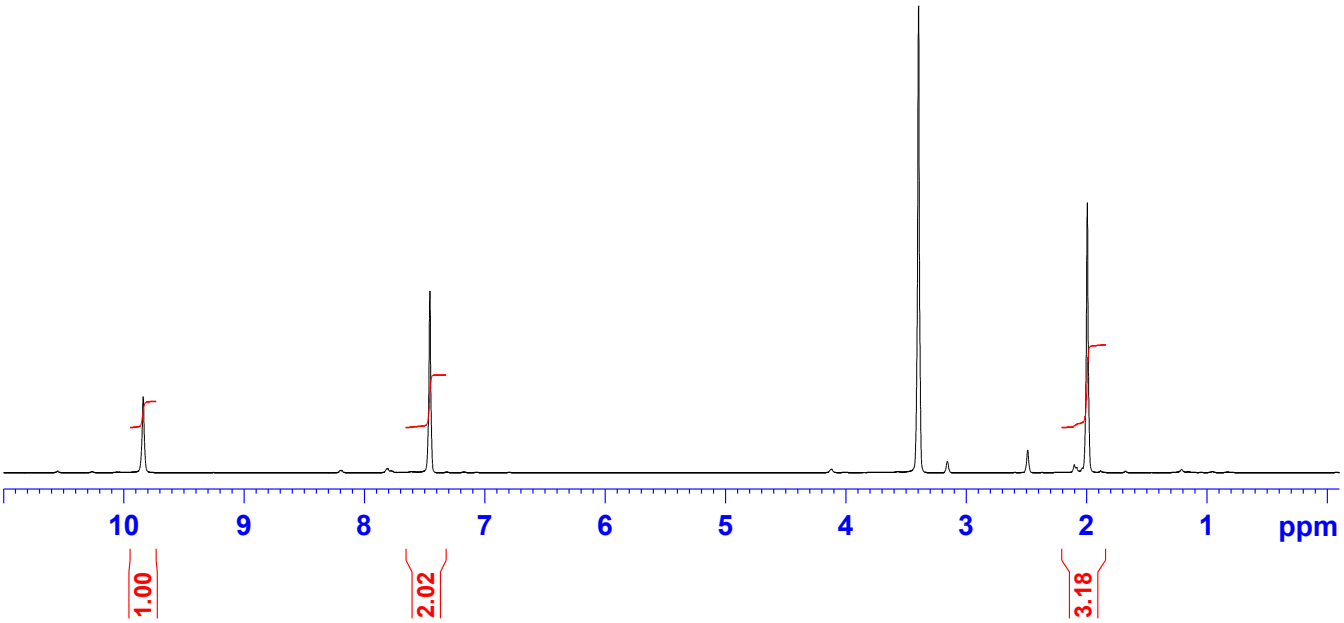
^{13}C NMR



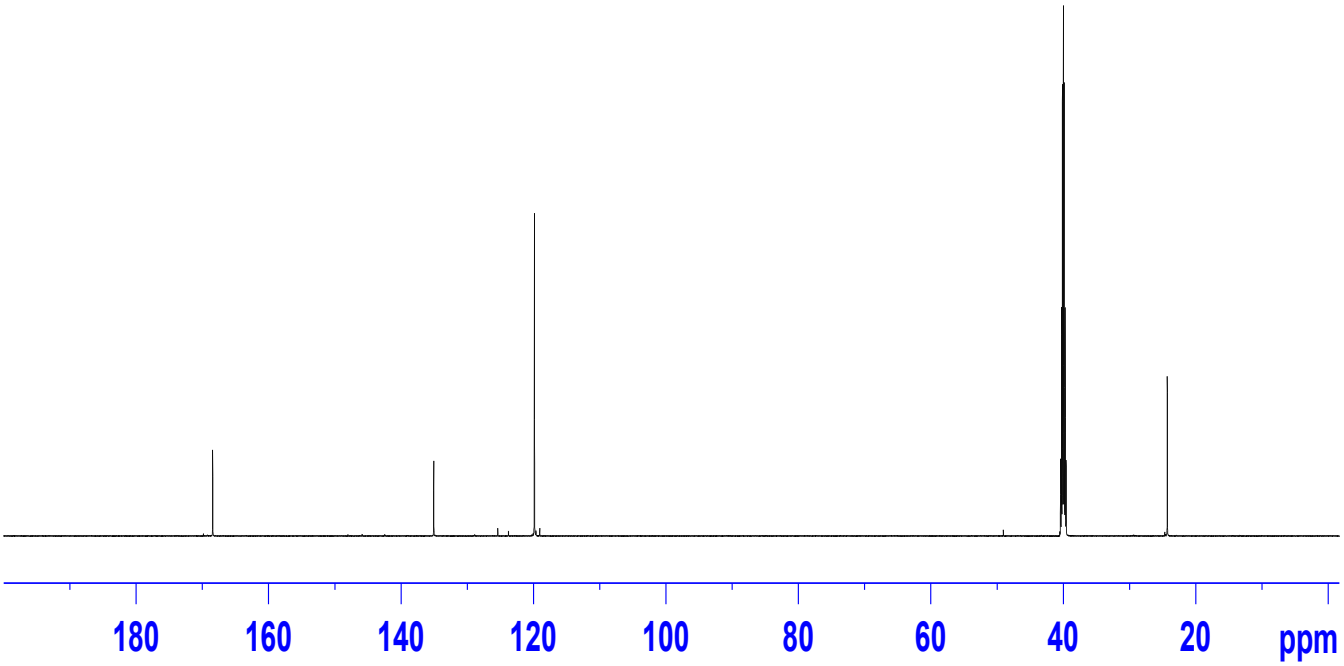
10. 1,4-Di-(*N*-acetylamino)benzene in DMSO-d_6 (Table 2, entry 10)



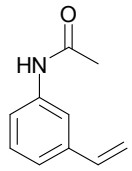
^{1}H NMR



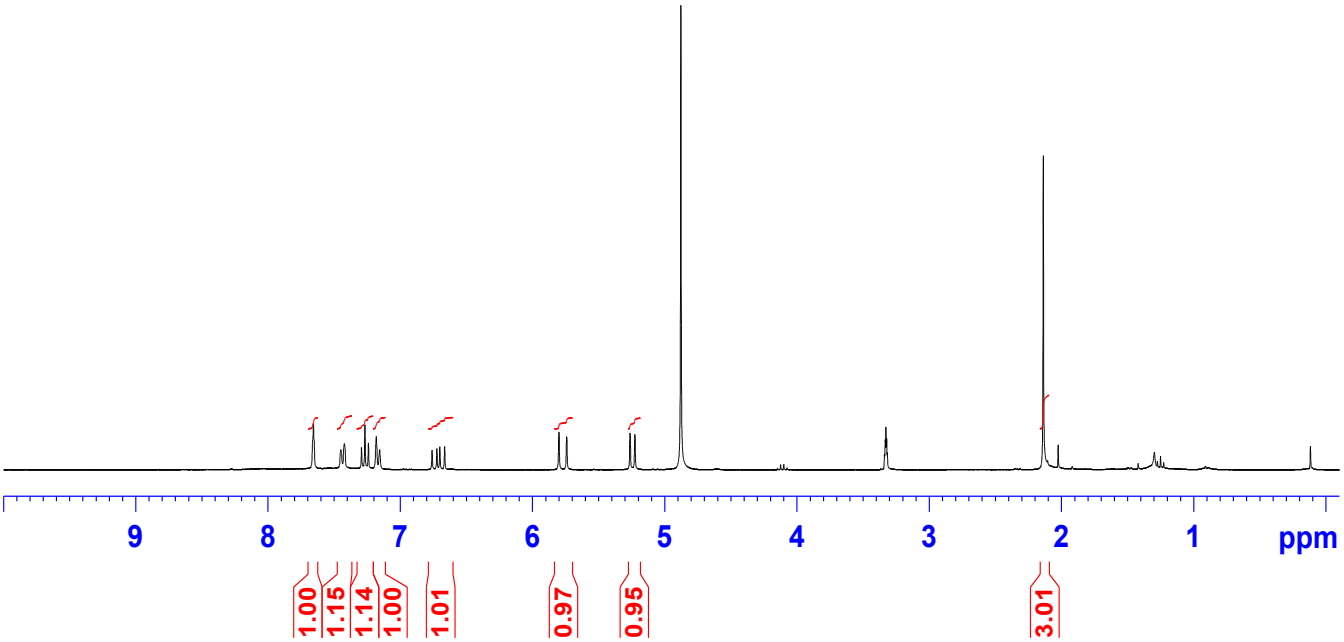
^{13}C NMR



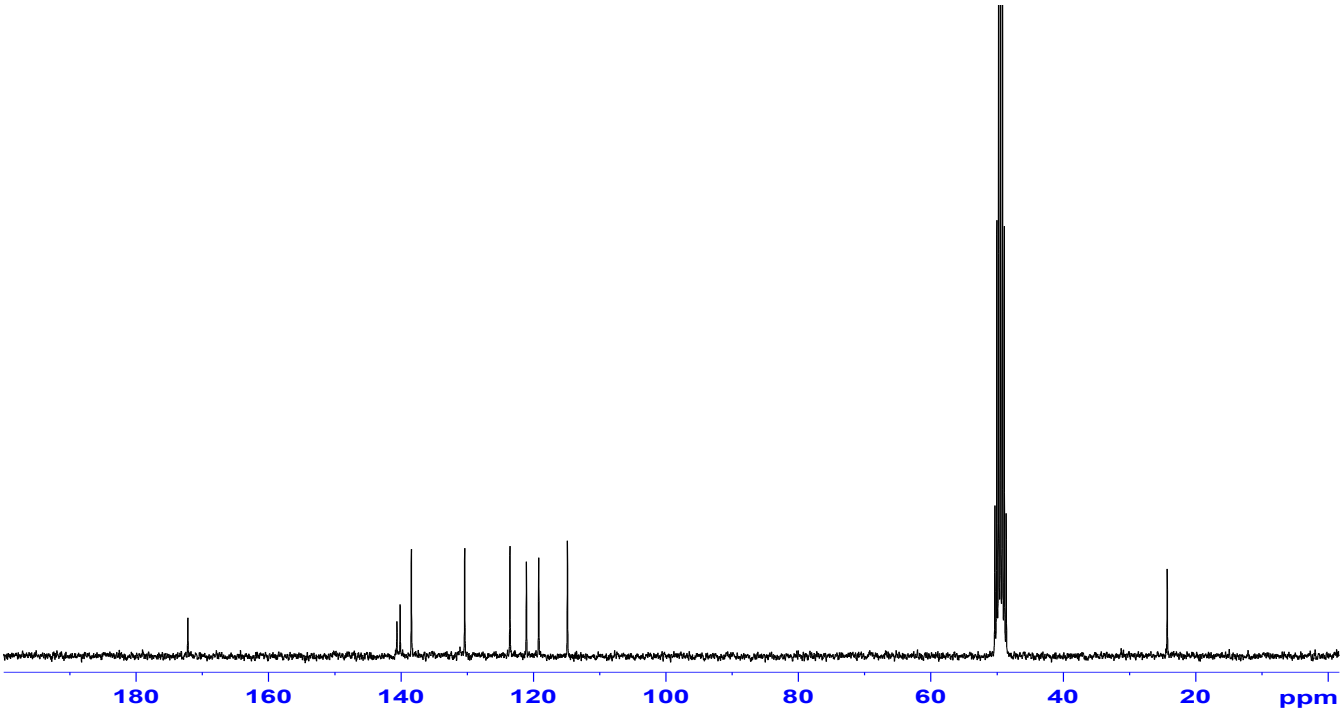
11. 3-(*N*-Acetylamino)styrene in CD_3OD (Table 2, entry 11)



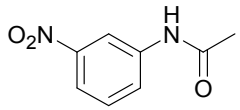
^{1}H NMR



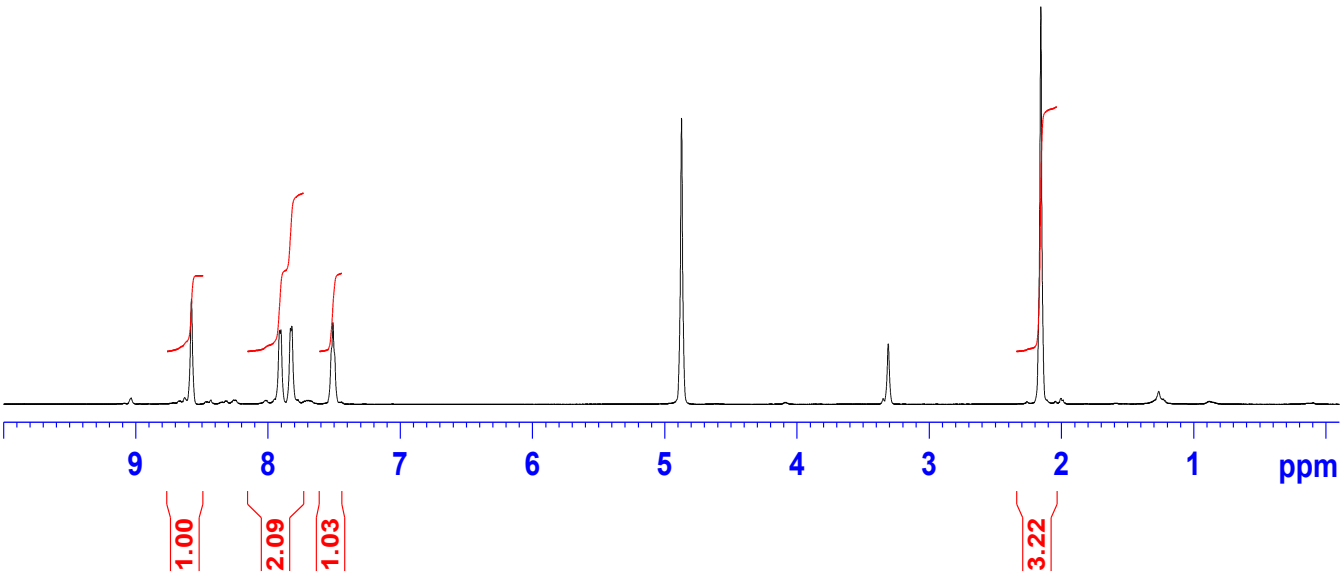
^{13}C NMR



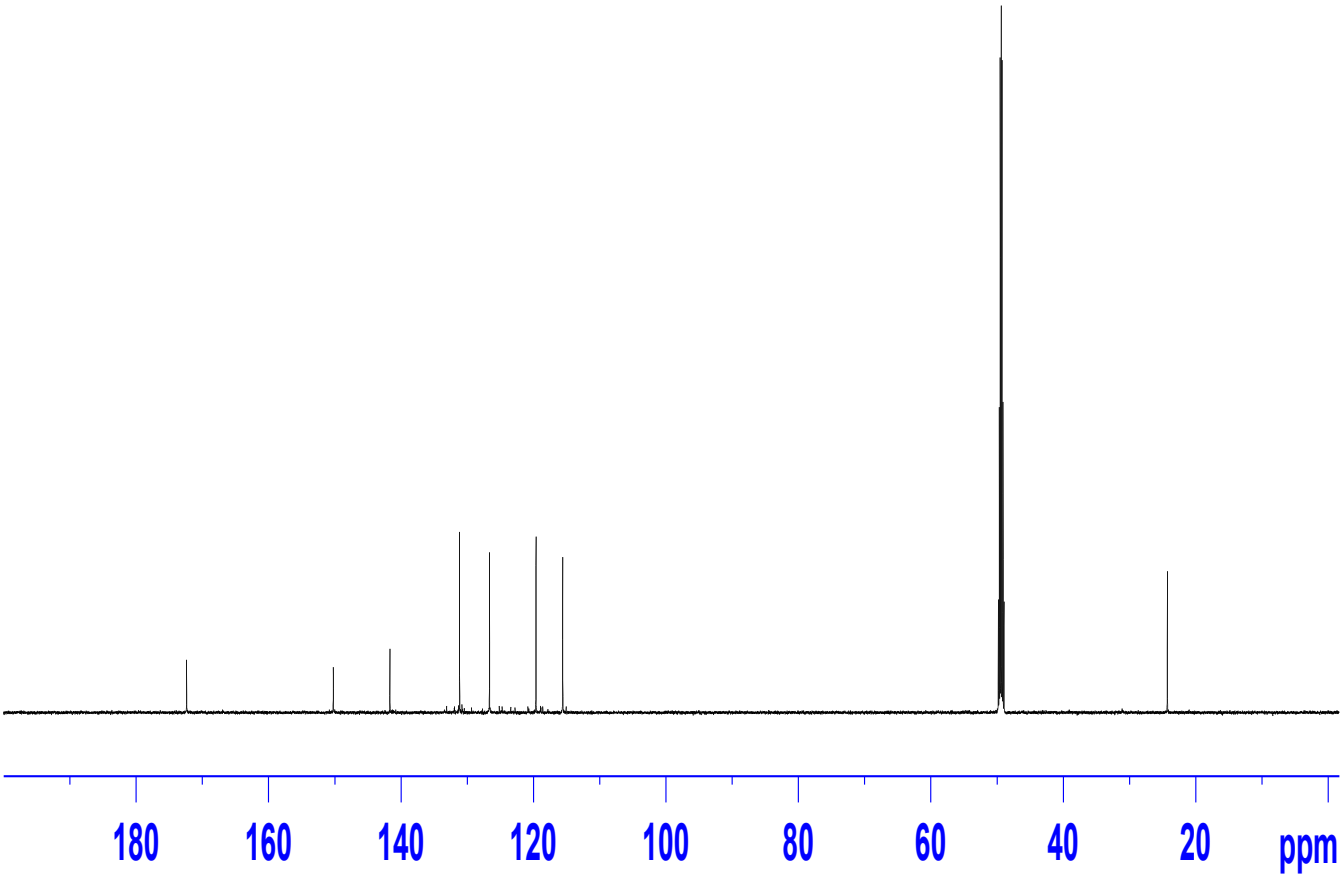
12. *N*-Acetyl-3-nitroaniline in CD_3OD (Table 2, entry 12)



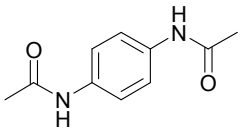
^{1}H NMR



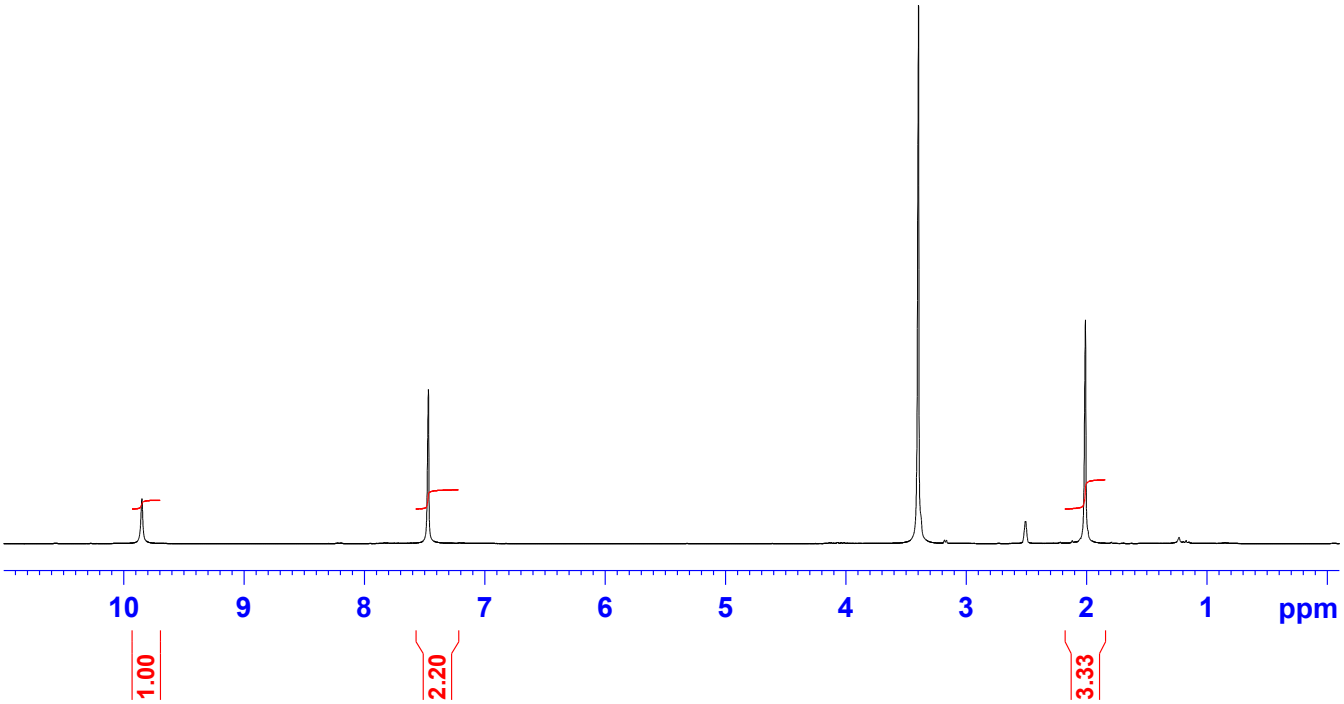
^{13}C NMR



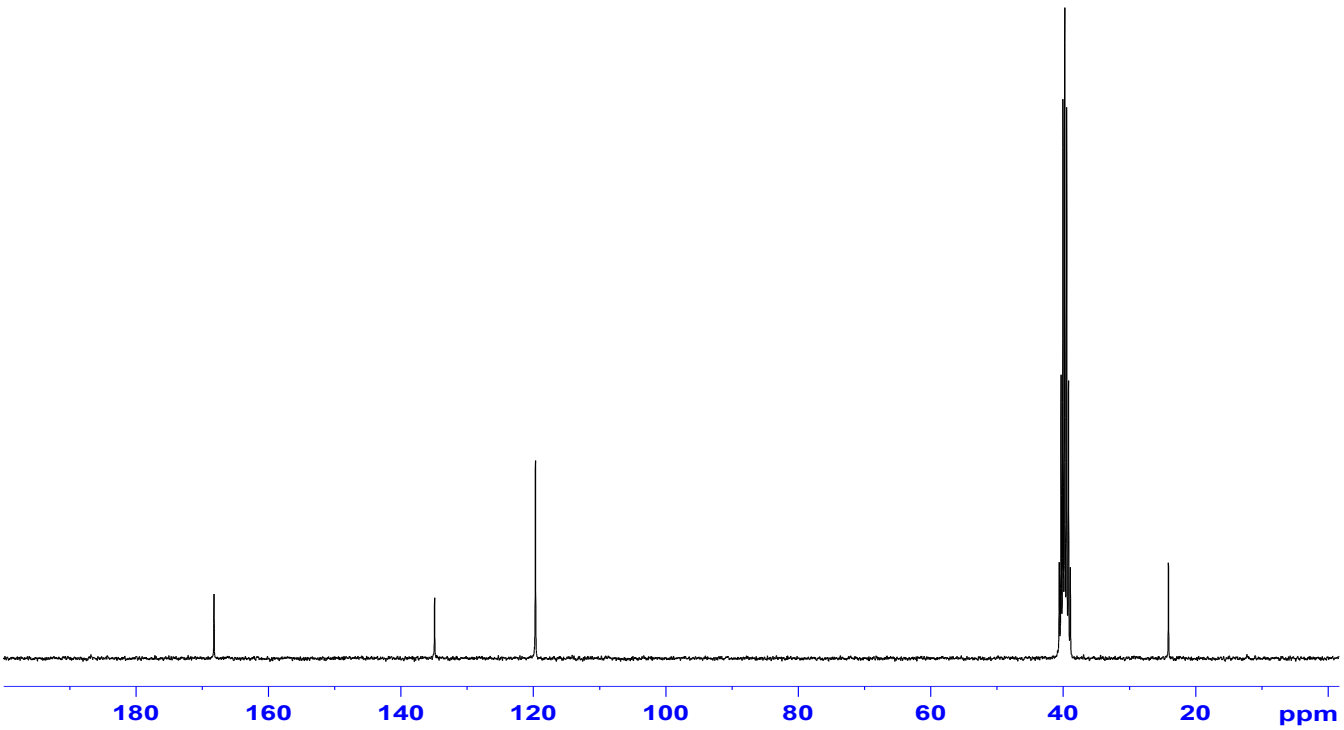
13. 1,4-Di-(*N*-acetylamino)benzene in DMSO-d_6 (Table 2, entry 13)



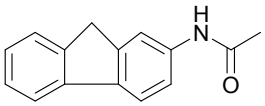
^{1}H NMR



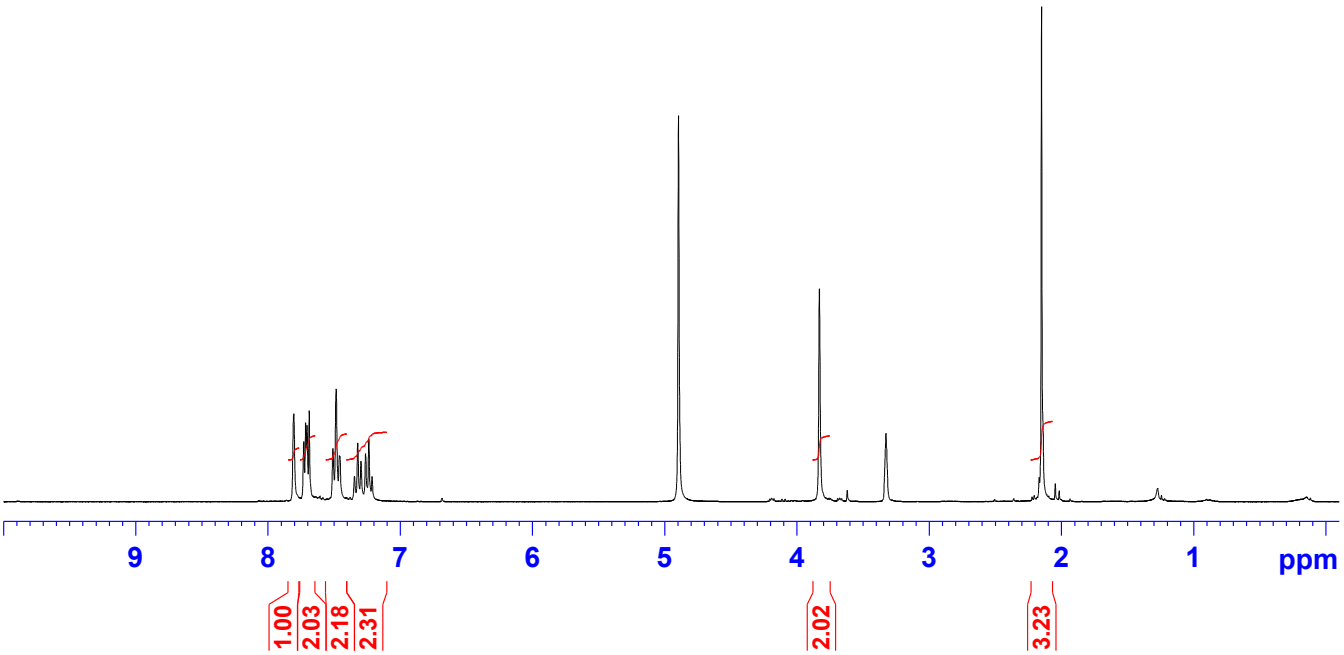
^{13}C NMR



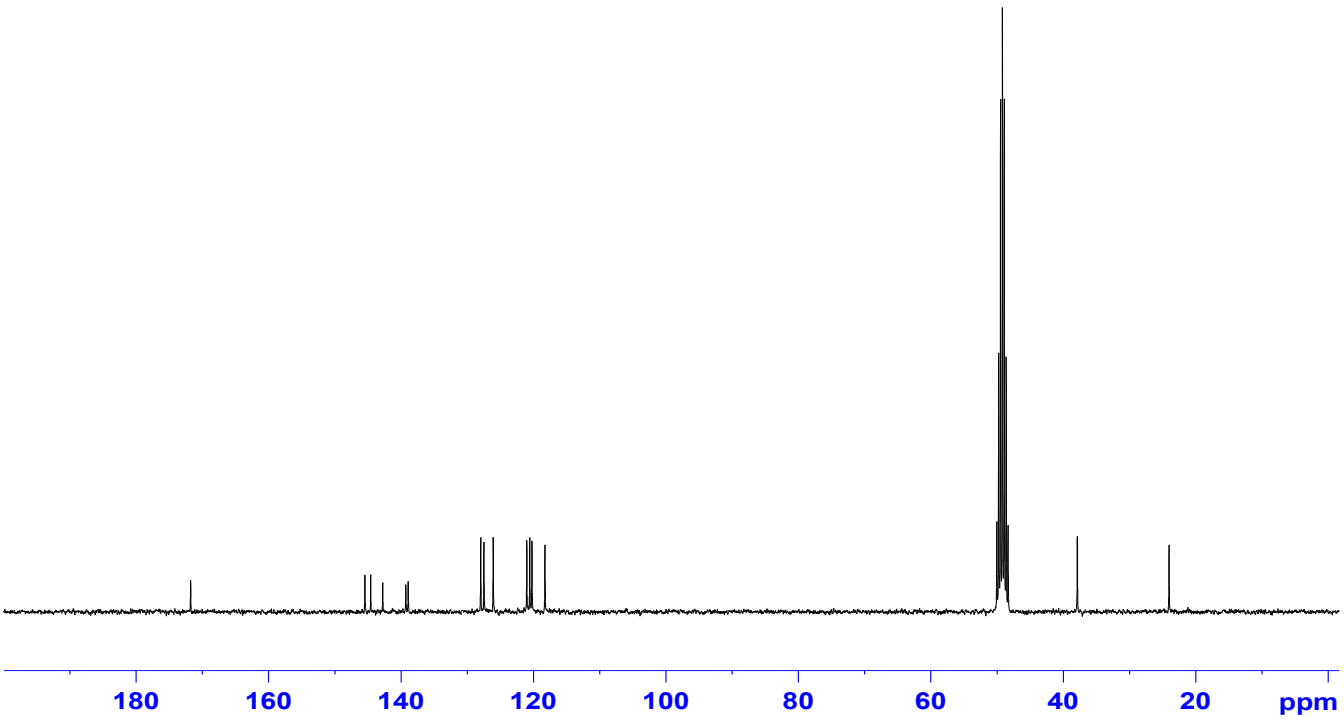
14. 2-(*N*-Acetylamino)fluorine in CD_3OD (Table 2, entry 14)



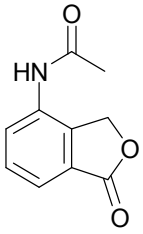
^{1}H NMR



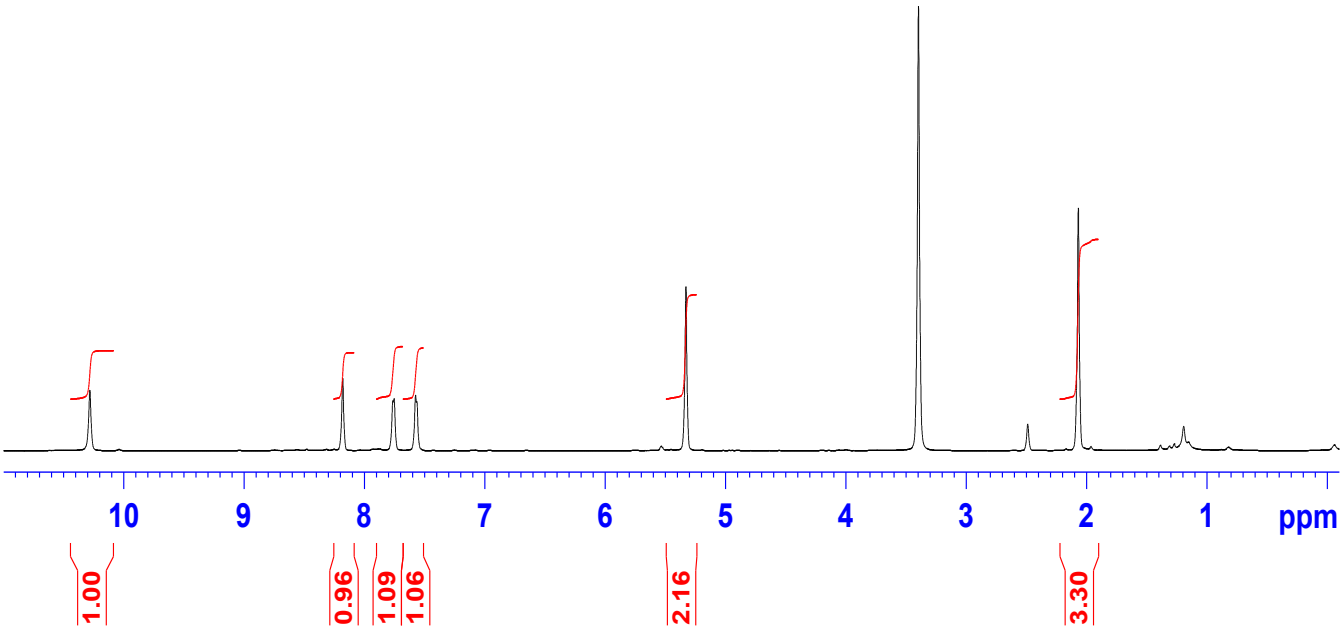
^{13}C NMR



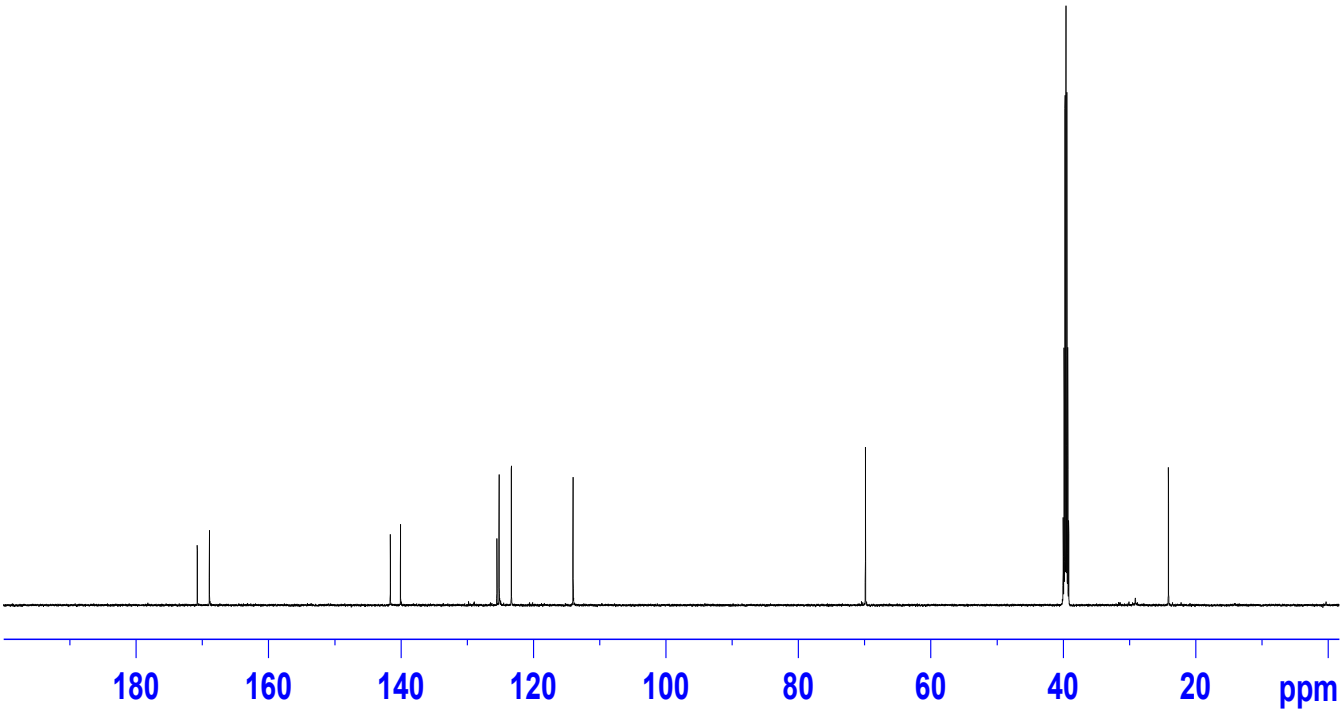
15. 4-(*N*-Actylamino)phthalide in DMSO-d_6 (Table 2, entry 15)



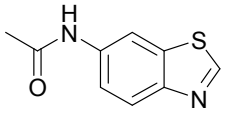
^{1}H NMR



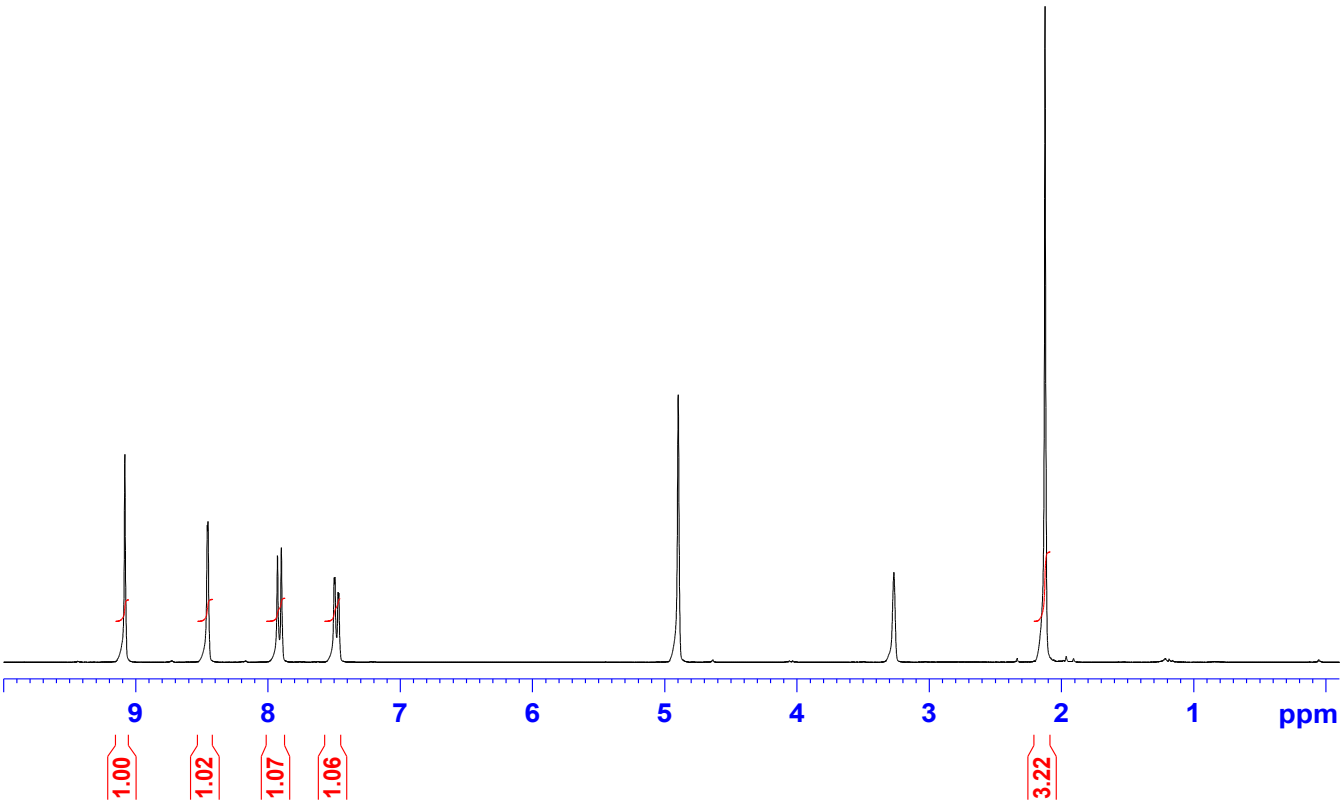
^{13}C NMR



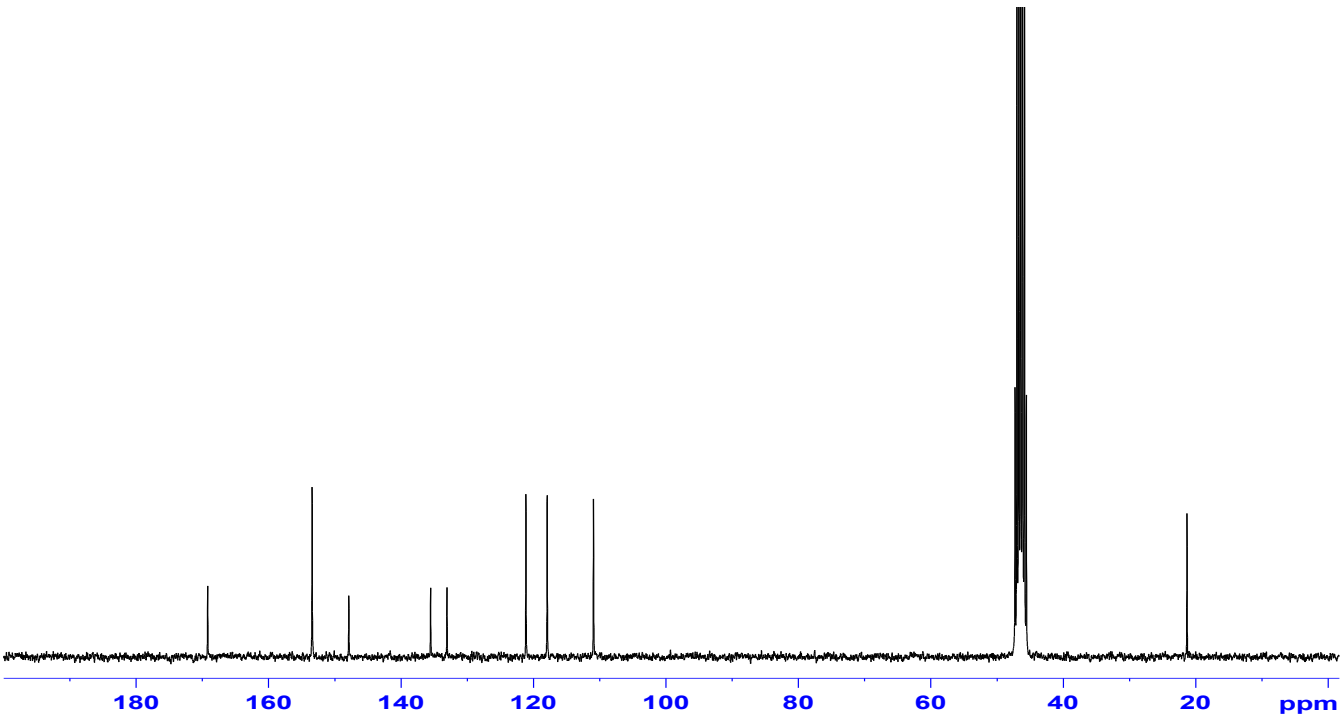
16. 6-(*N*-Acetylamino)benzothiazole in CD_3OD (Table 2, entry 16)



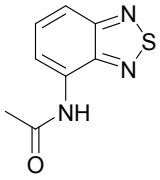
^{1}H NMR



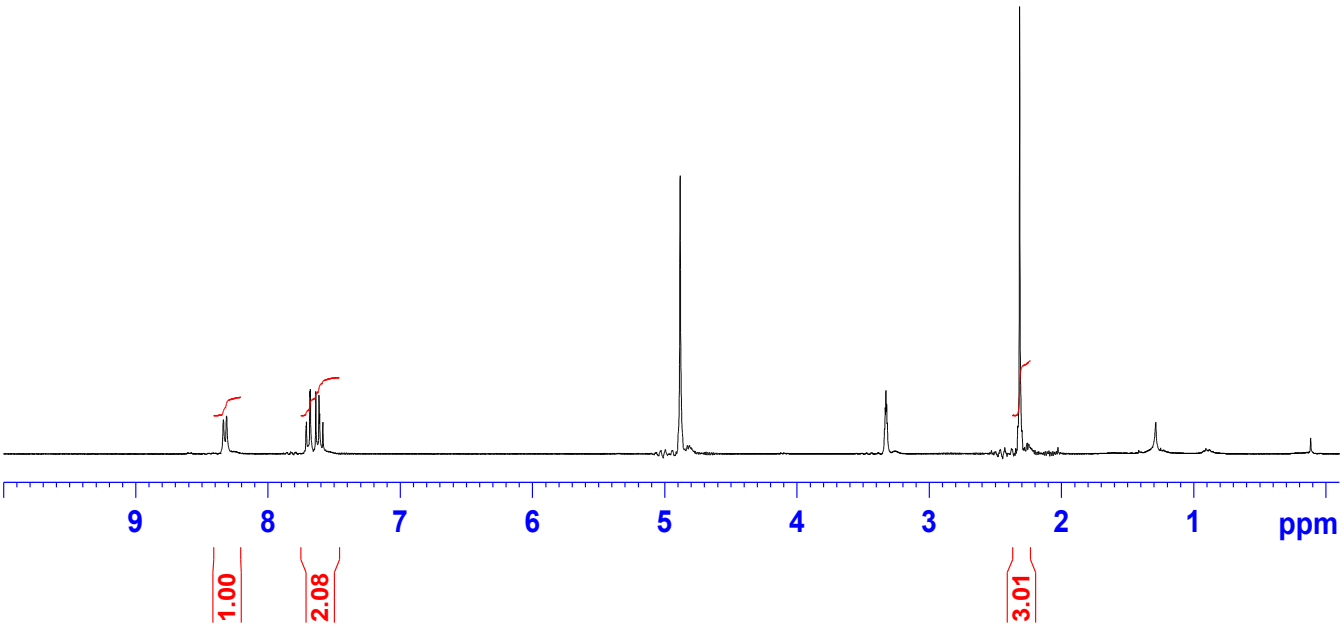
^{13}C NMR



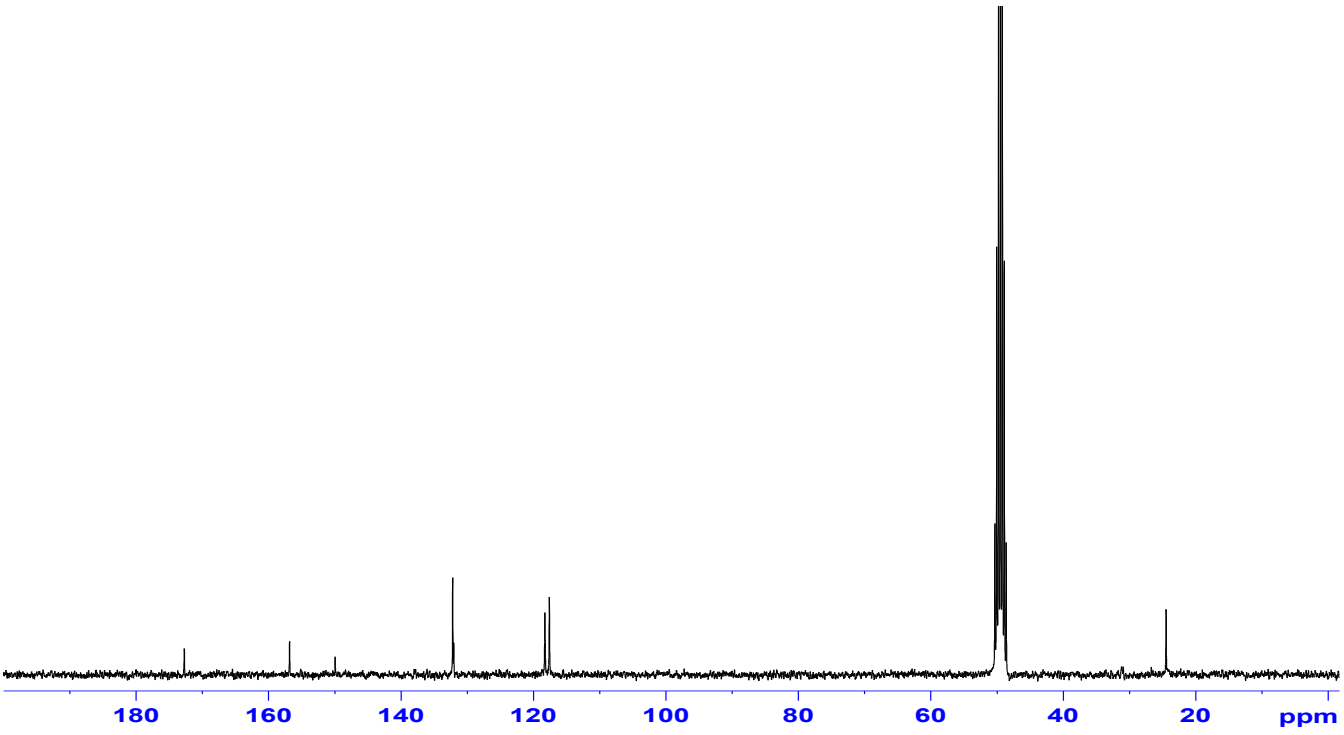
17. 4-(*N*-Acetylamino)-2,1,3-benzothiadiazole in CD_3OD (Table 2, entry 17)



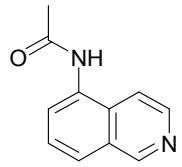
^{1}H NMR



^{13}C NMR



18. 5-(*N*-Acetylamino)isoquinoline in CD_3OD (Table 2, entry 18)



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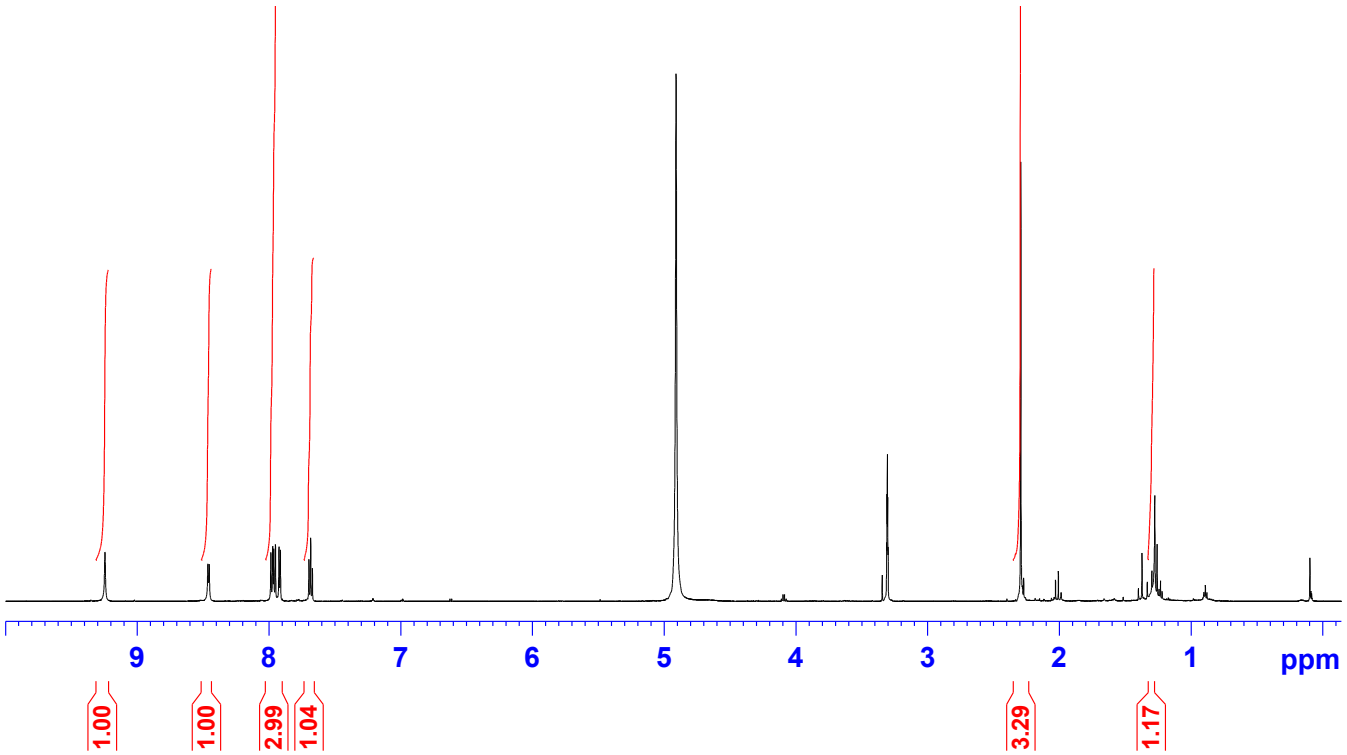
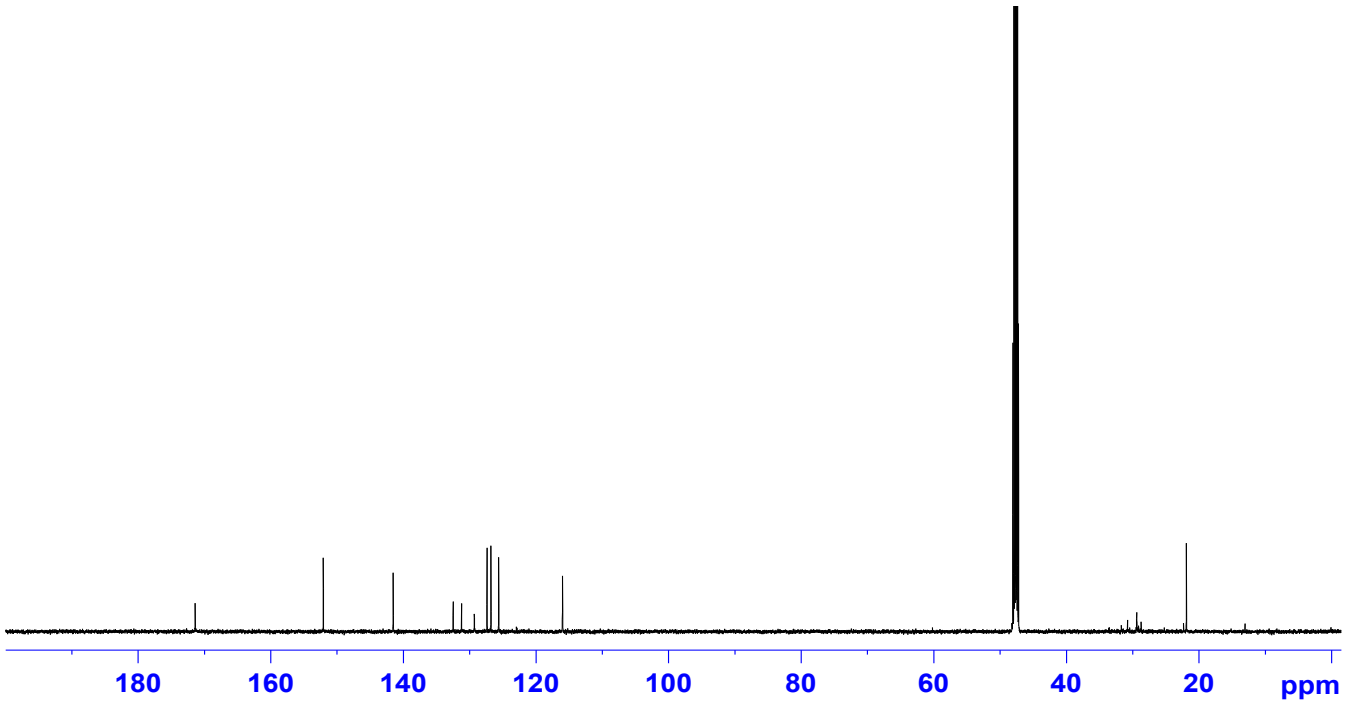
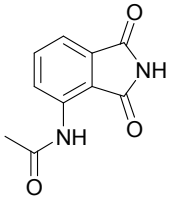


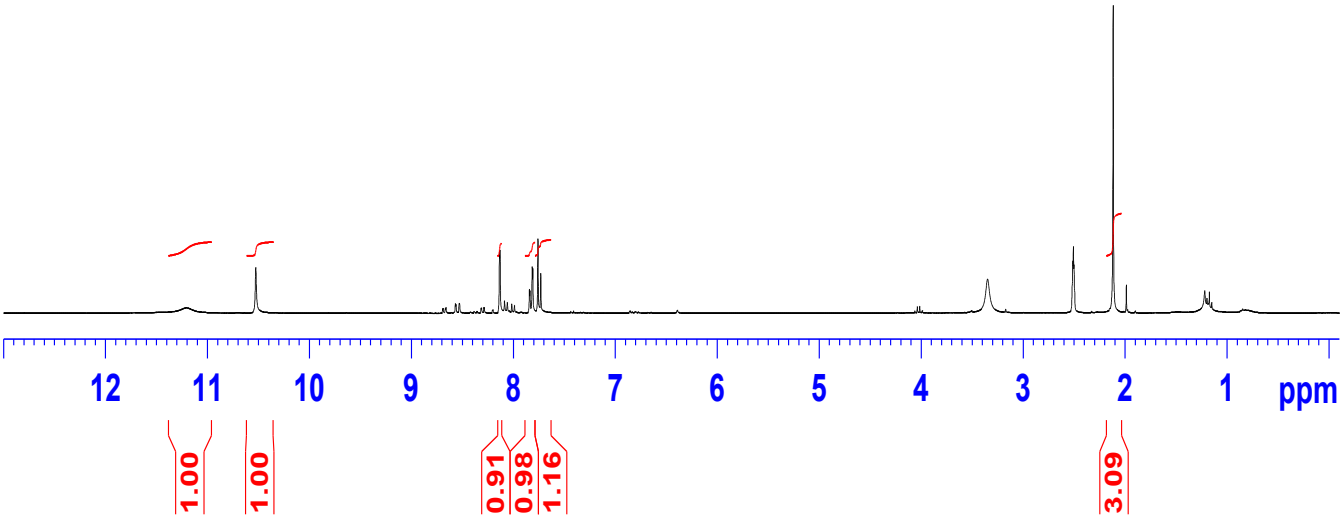
^{13}C NMR



19. 4-(*N*-acetylamino)phthalimide in DMSO-d_6 (Table 2, entry 19)



^{1}H NMR



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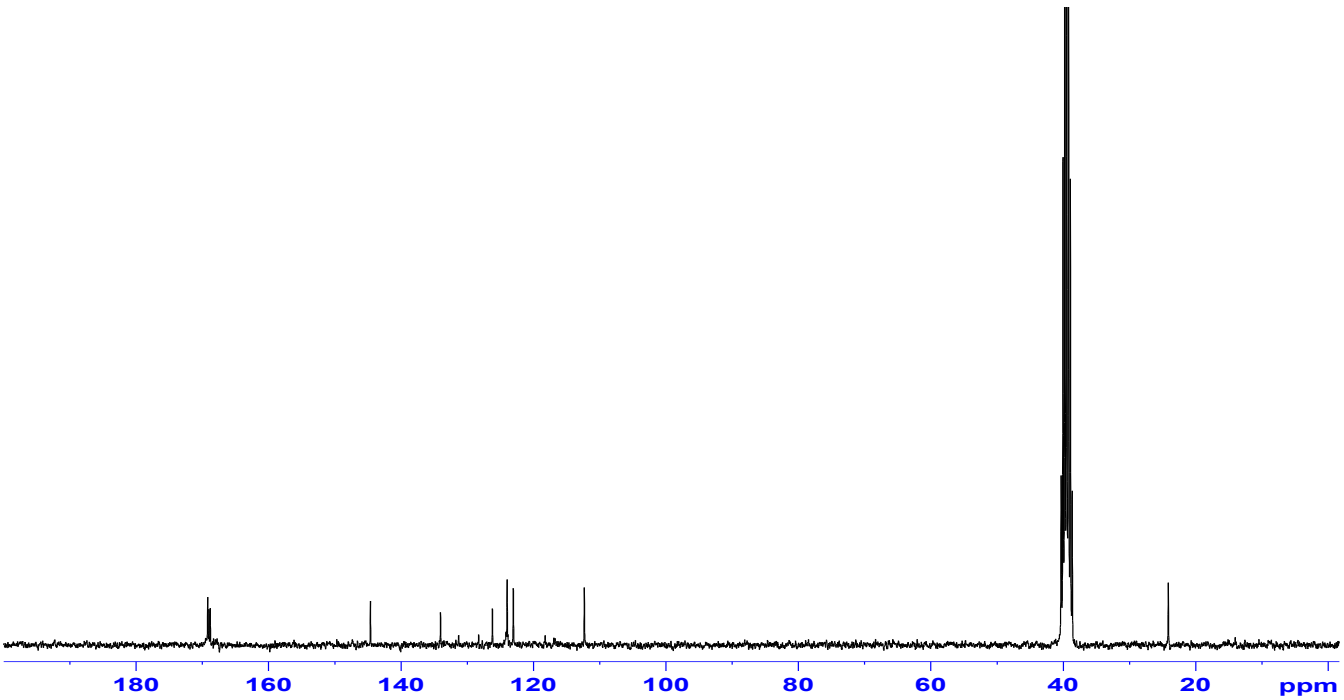
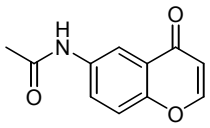
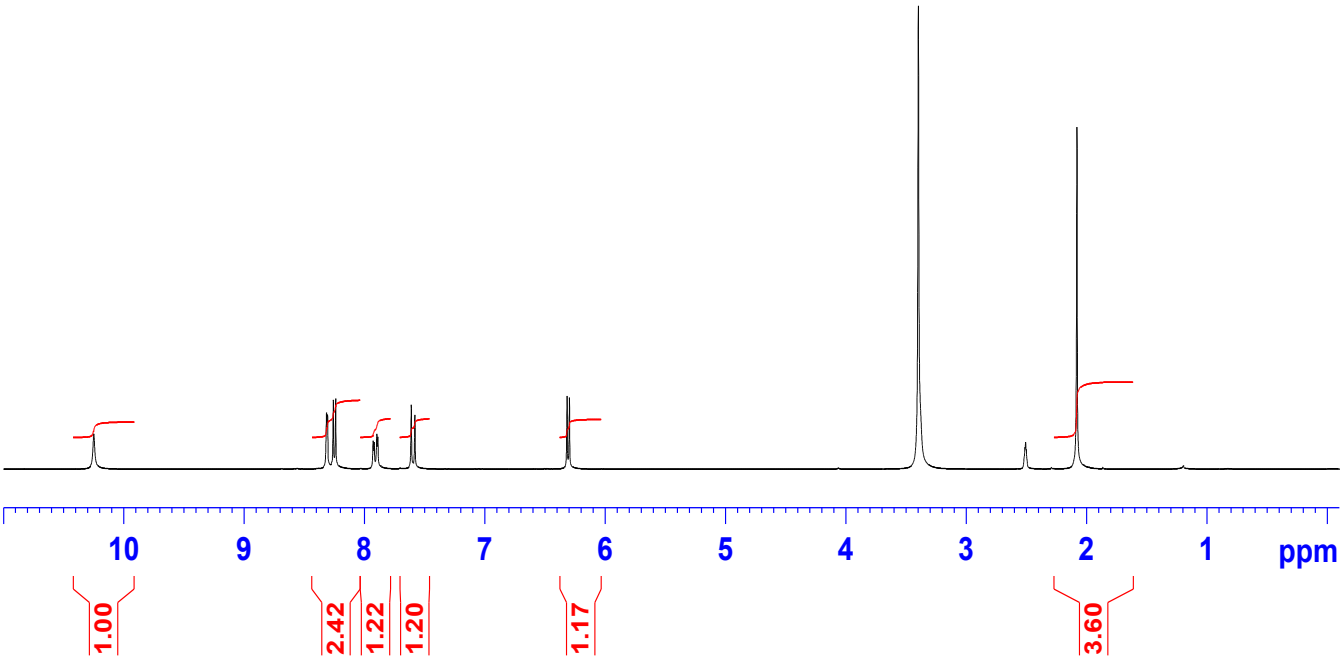


20. 6-(*N*-Acetylamino)chromone in DMSO-d_6 (Table 2, entry 20)



^{1}H NMR



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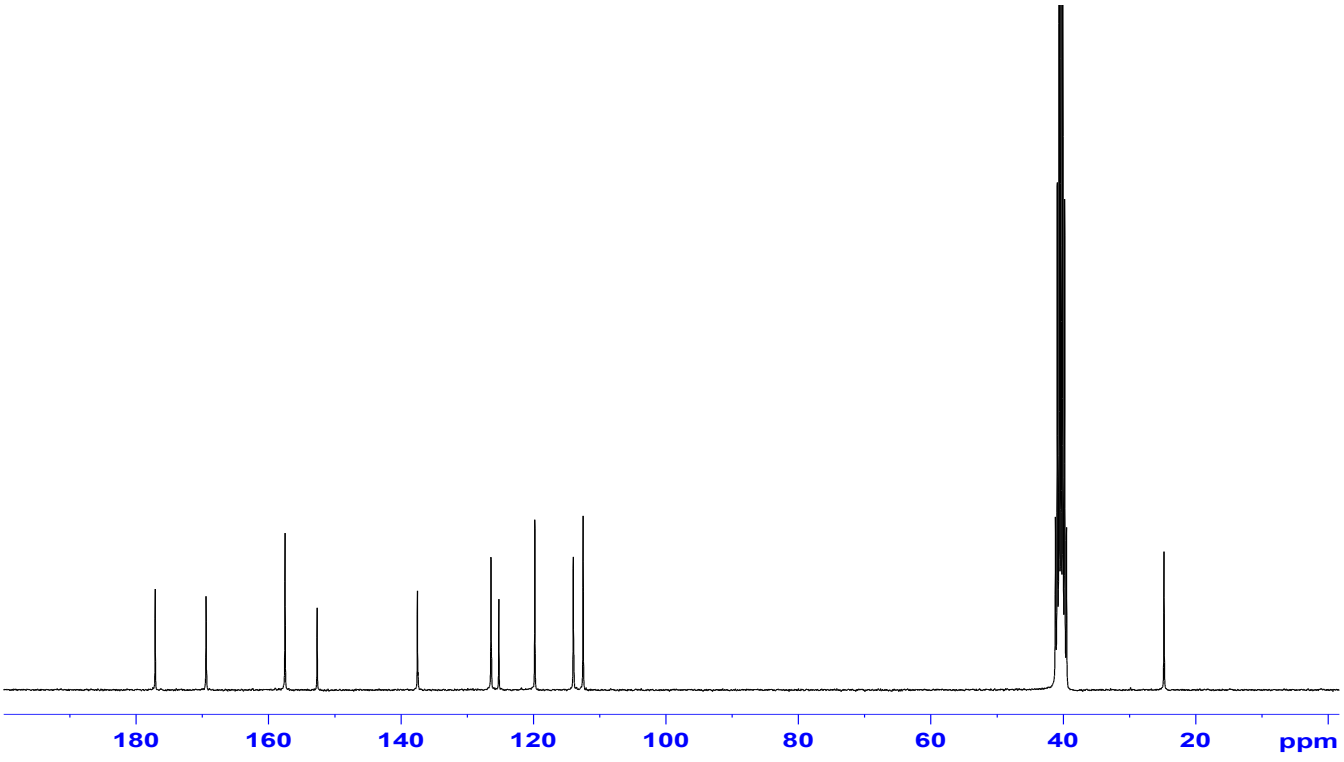
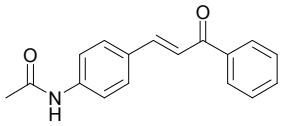


21. 4-(*N*-Acetylamino)chalcone in CD_3OD (Table 2, entry 21)



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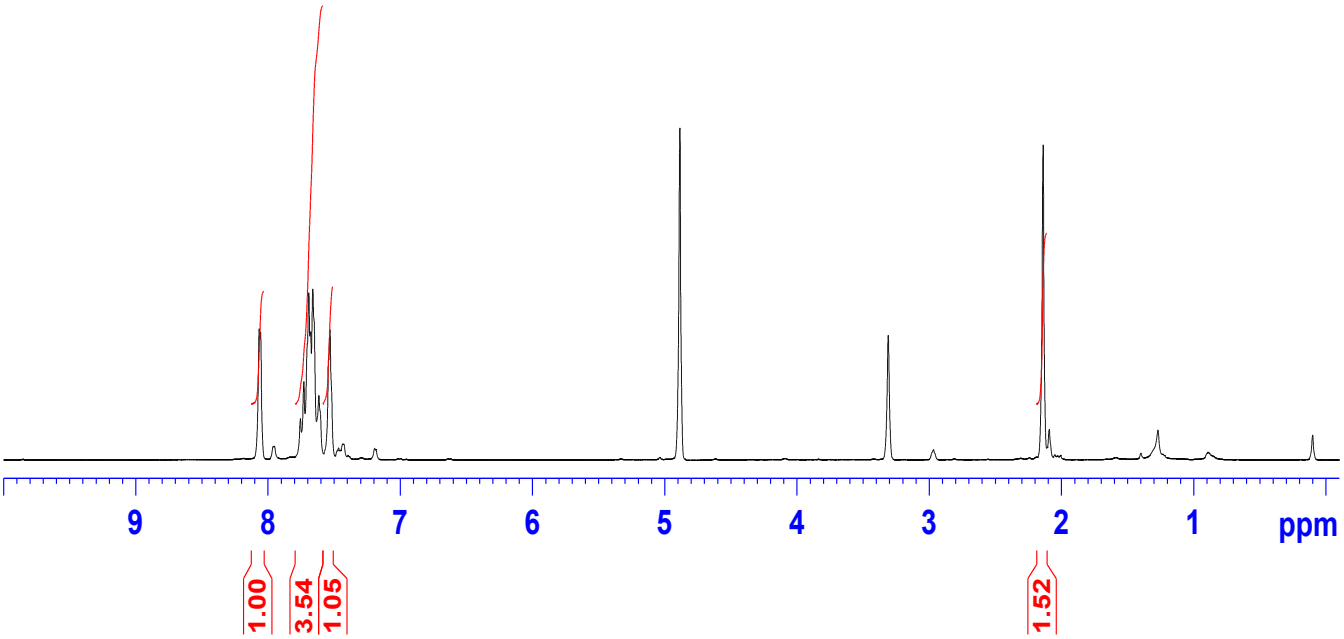

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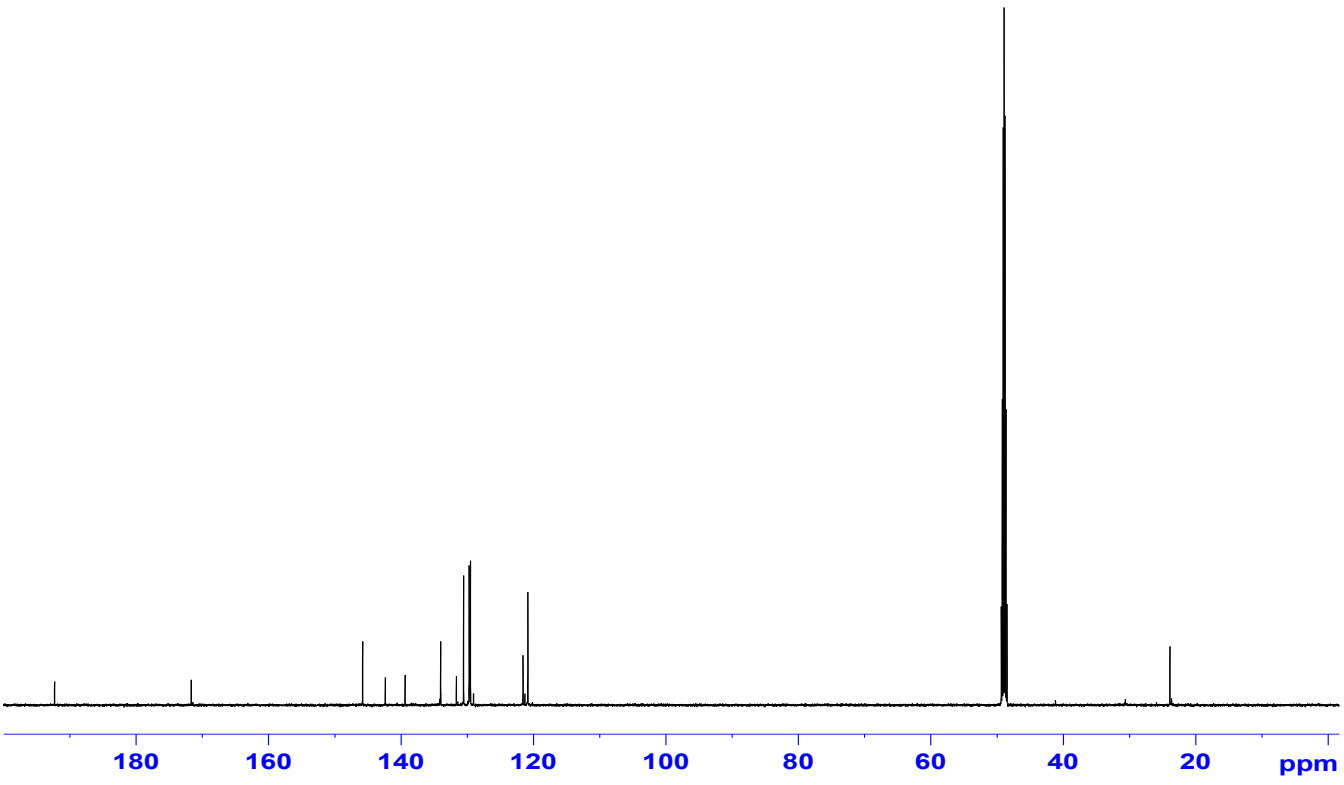
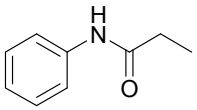


22. *N*-Phenylpropanamide in CD_3OD (Table 3, entry 3)



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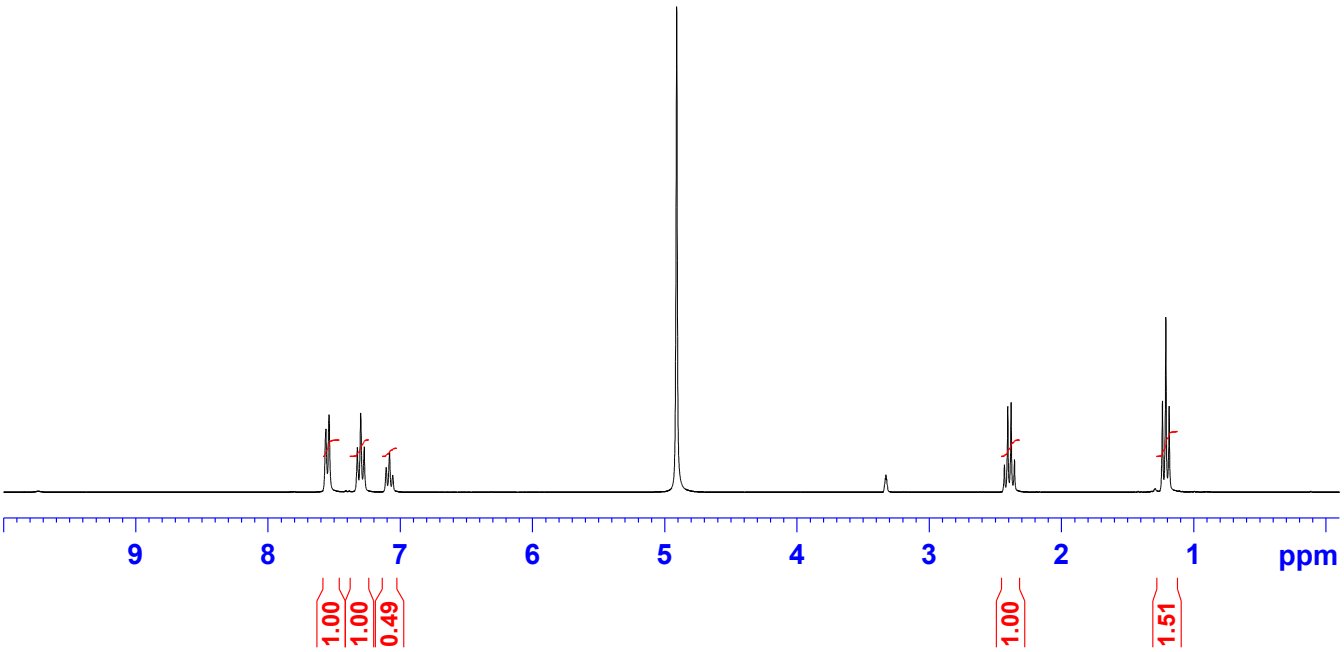

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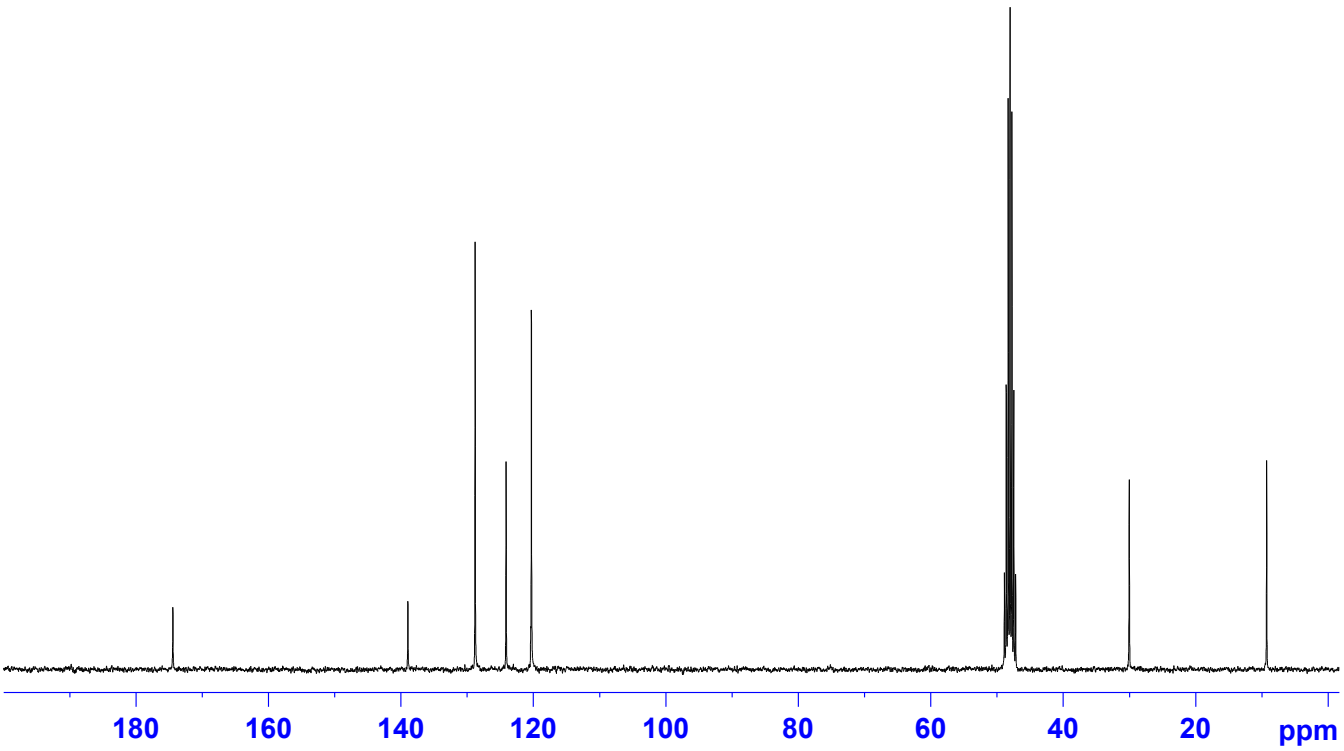
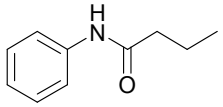


23. *N*-Phenylbutanamide in CD_3OD (Table 3, entry 4)



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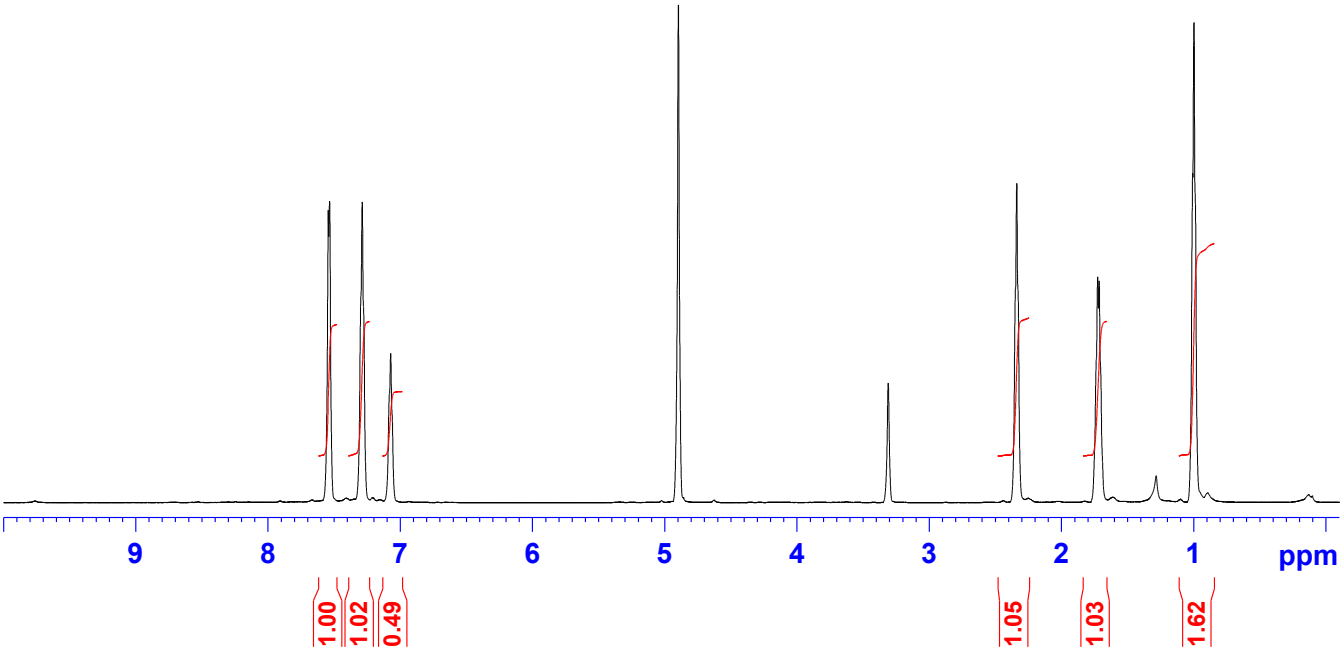

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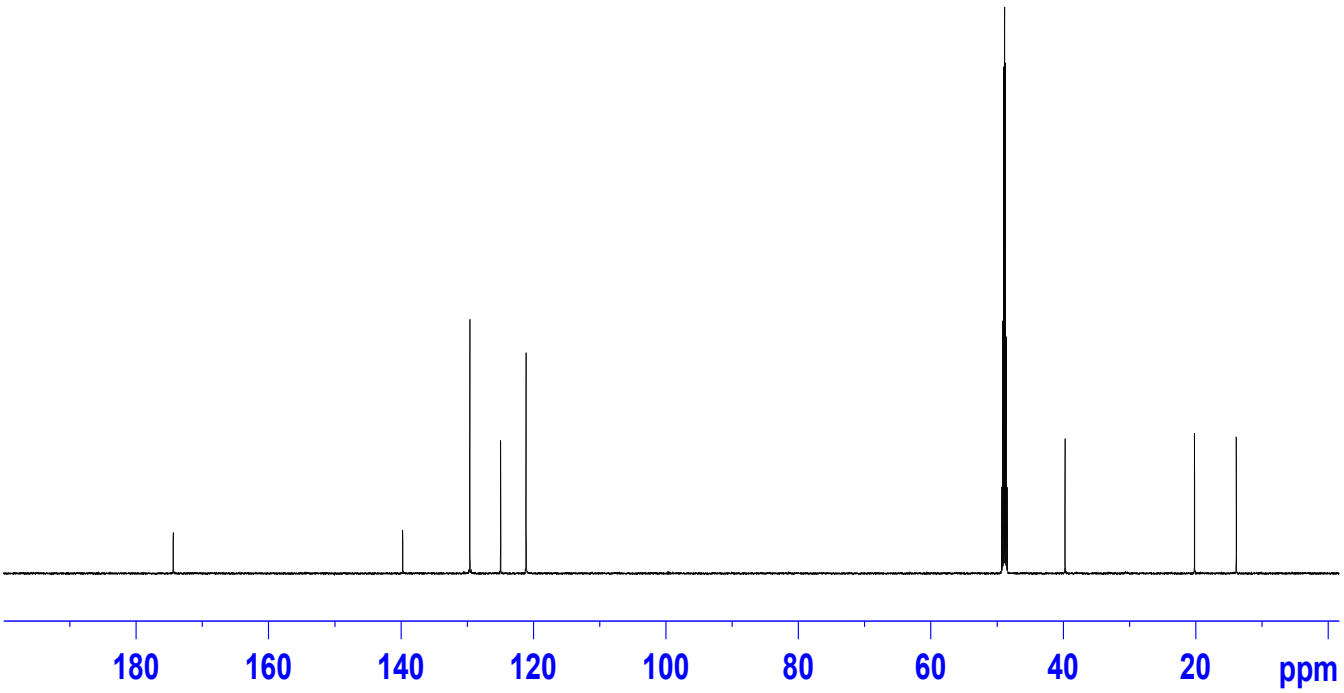
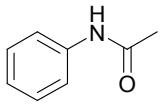
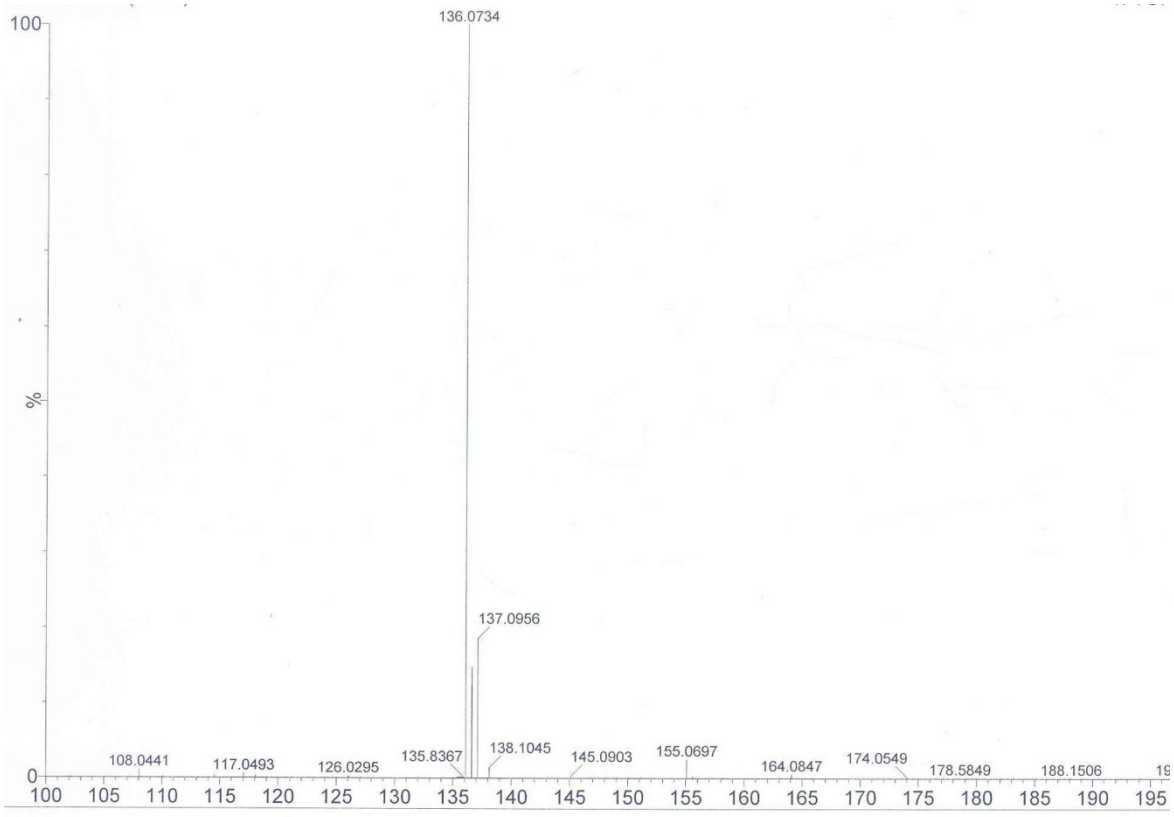


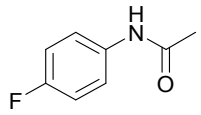
HRMS (ESI) of isolated compounds

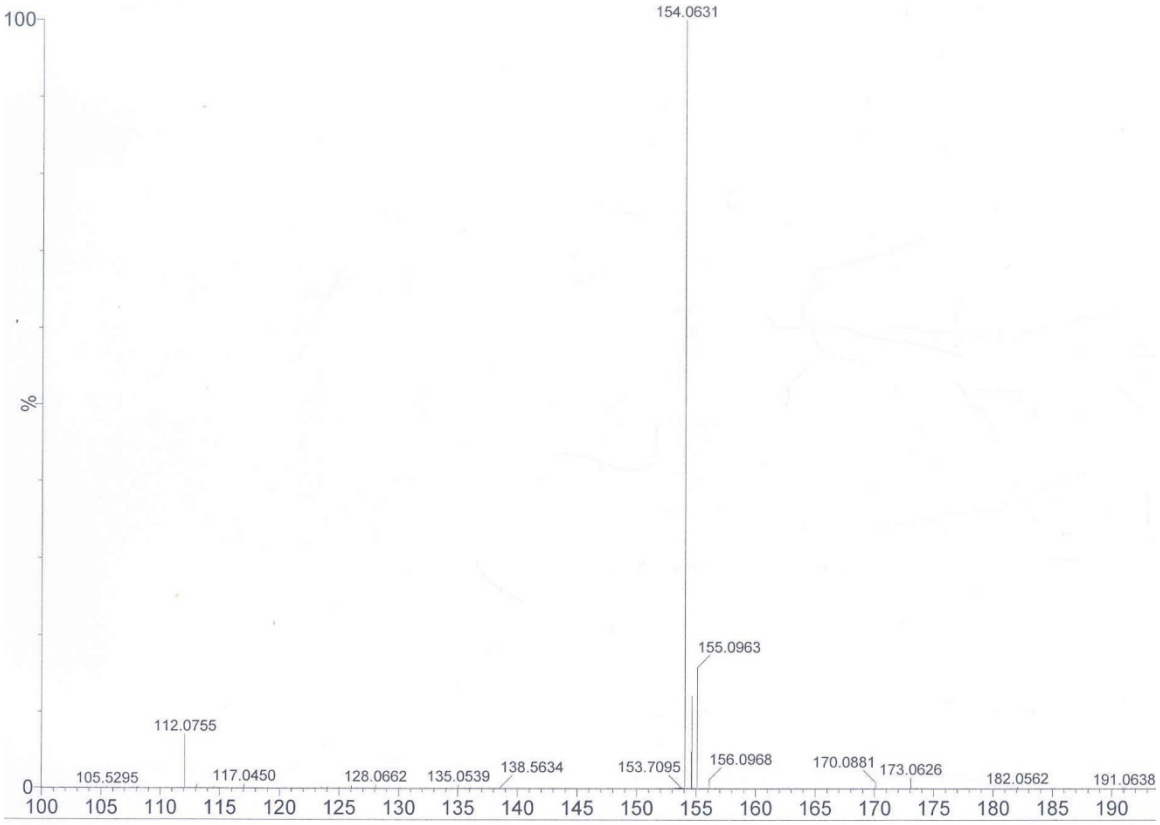
1. *N*-Acetylaniline (Table 2, entry 1)



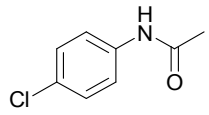


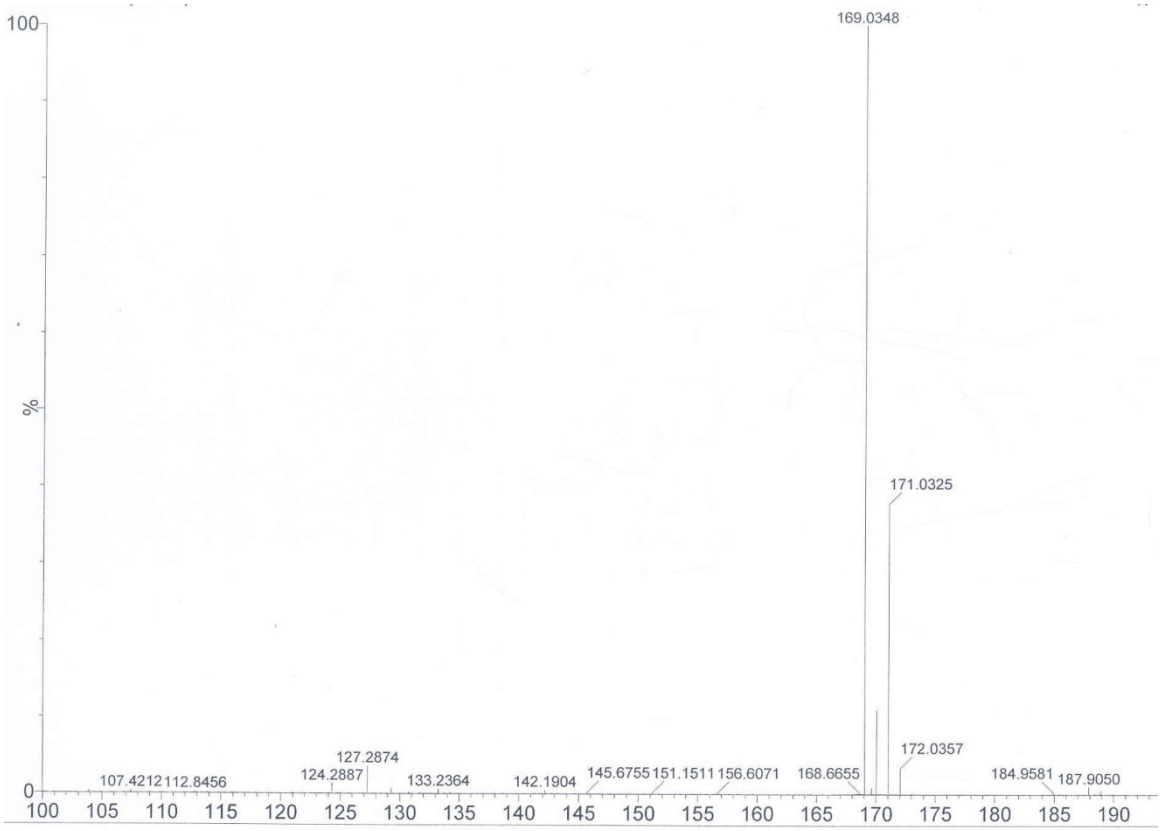
2. *N*-Acetyl-4-fluoroaniline (Table 2, entry 2)



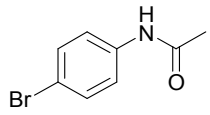


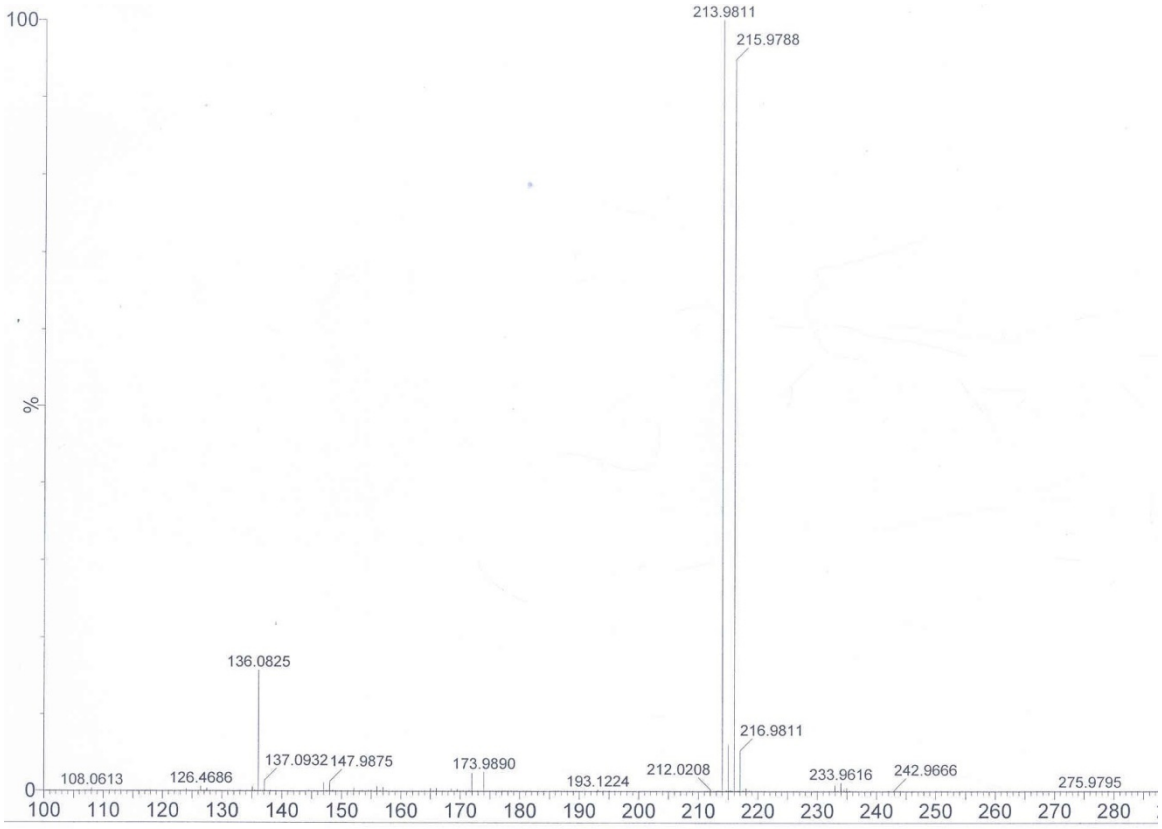
3. *N*-Acetyl-4-chloroaniline (Table 2, entry 3)



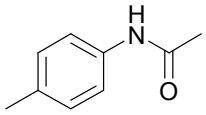


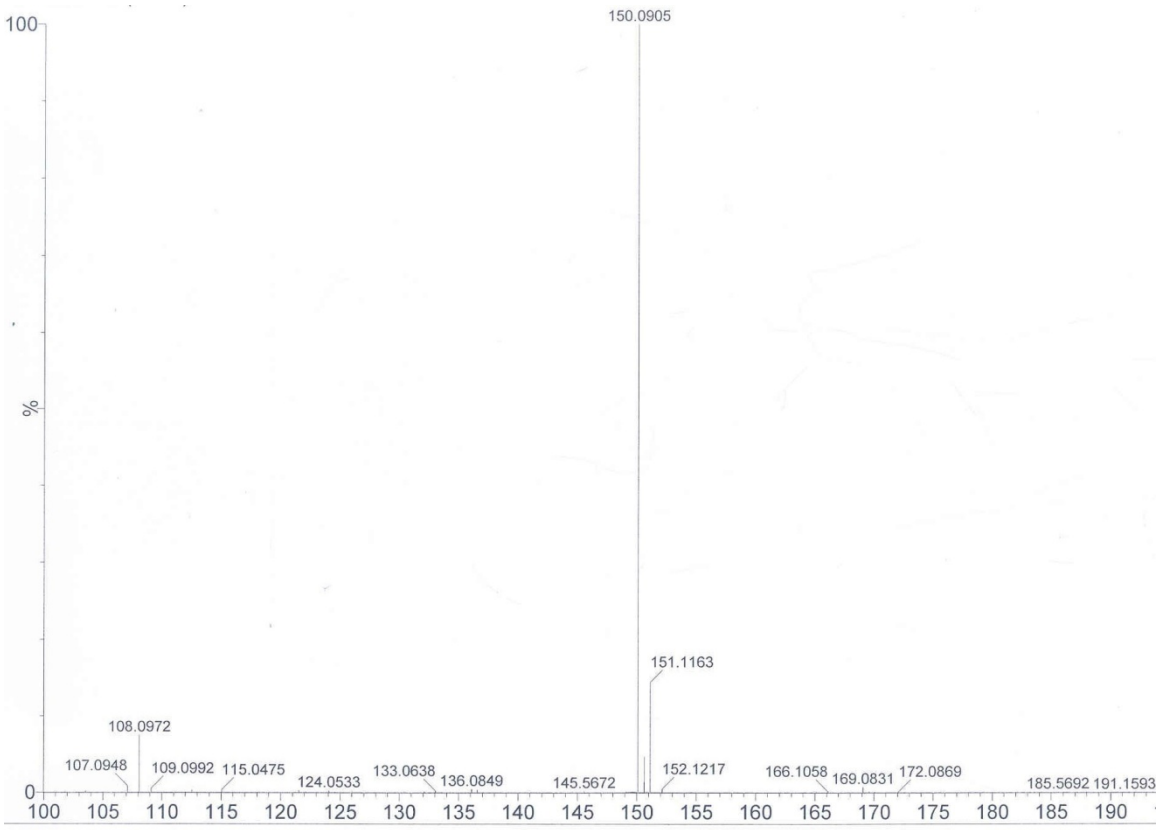
4. *N*-Acetyl-4-bromoaniline (Table 2, entry 4)



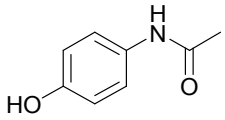


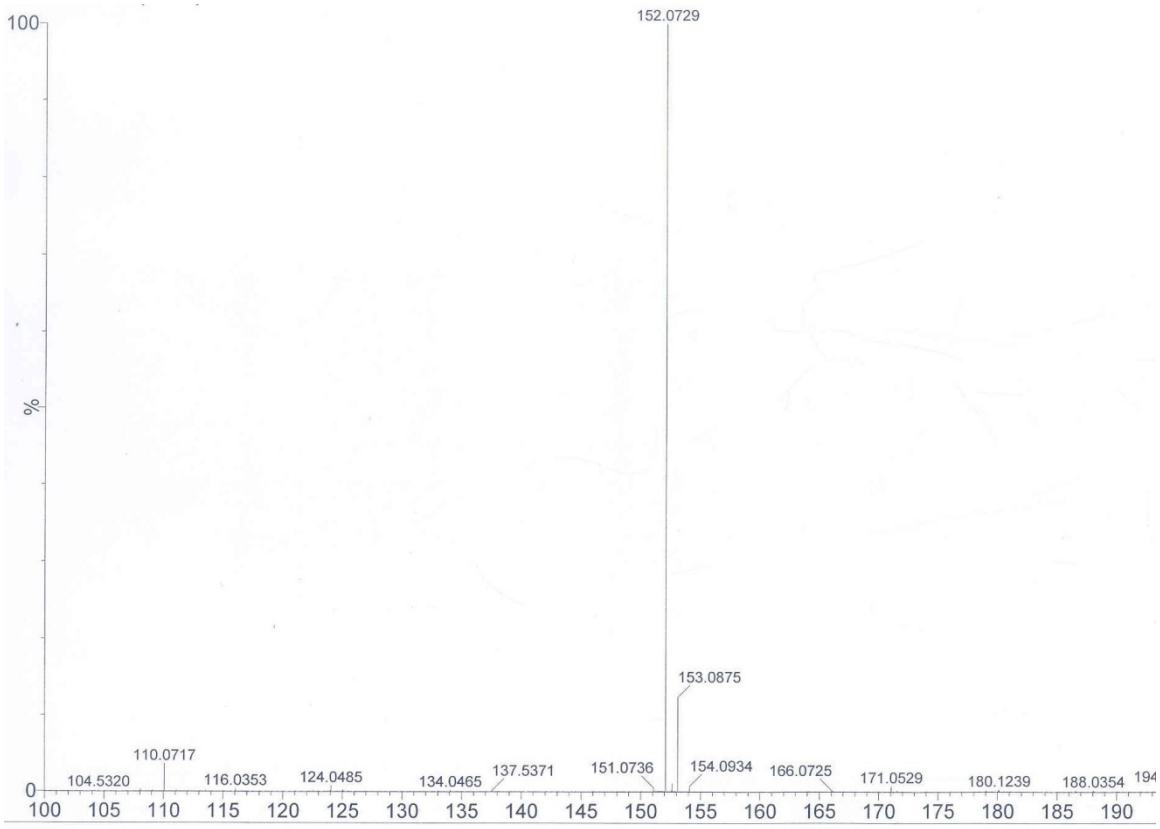
5. 4-(*N*-Acetylamino)toluene (Table 2, entry 5)



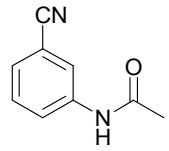


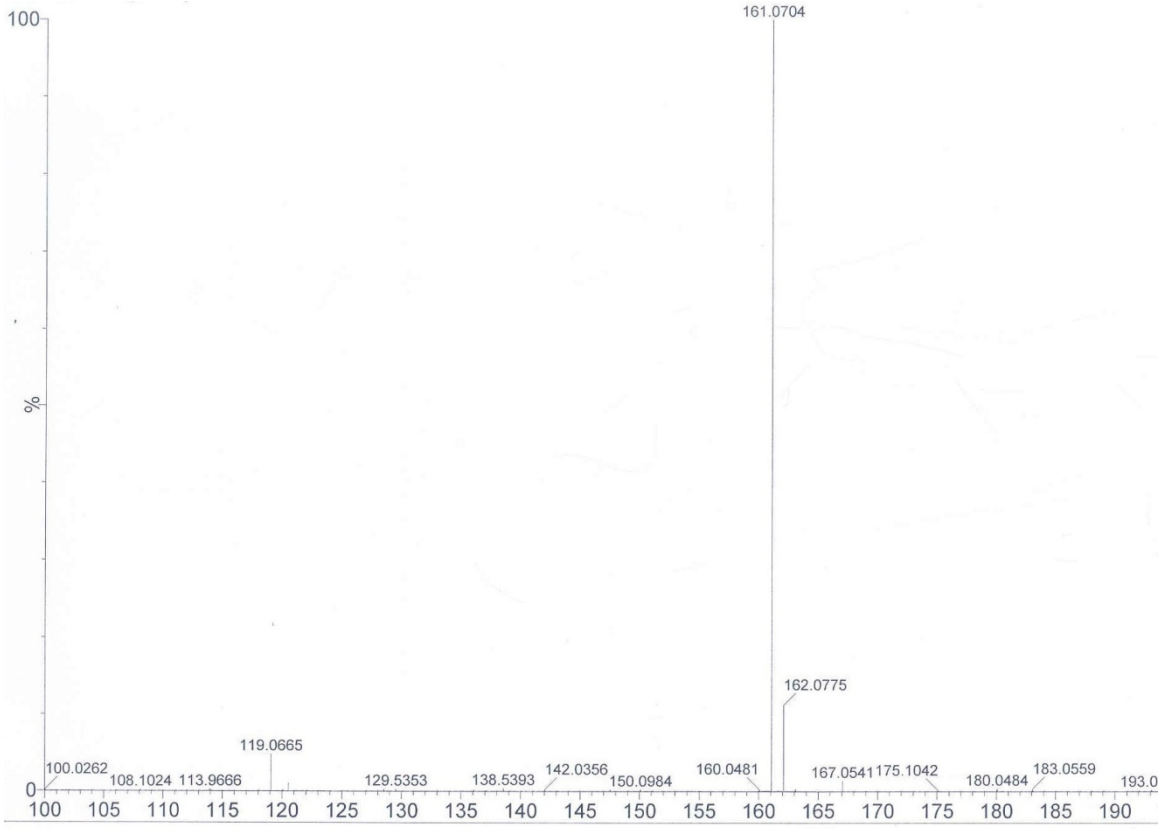
6. 4-(*N*-Acetylamino)phenol (Table 2, entry 6)



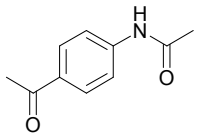


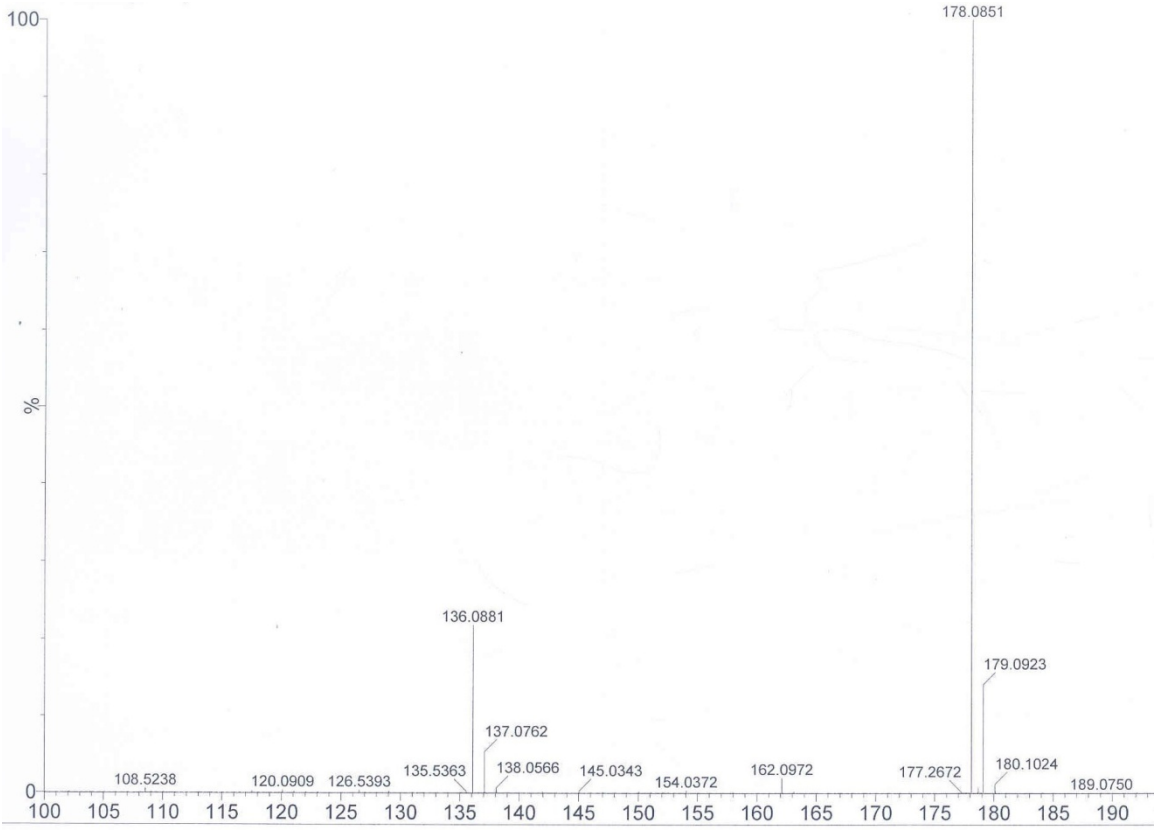
7. 3-(*N*-Acetylamino)benzonitrile (Table 2, entry 8)



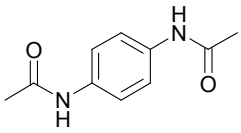


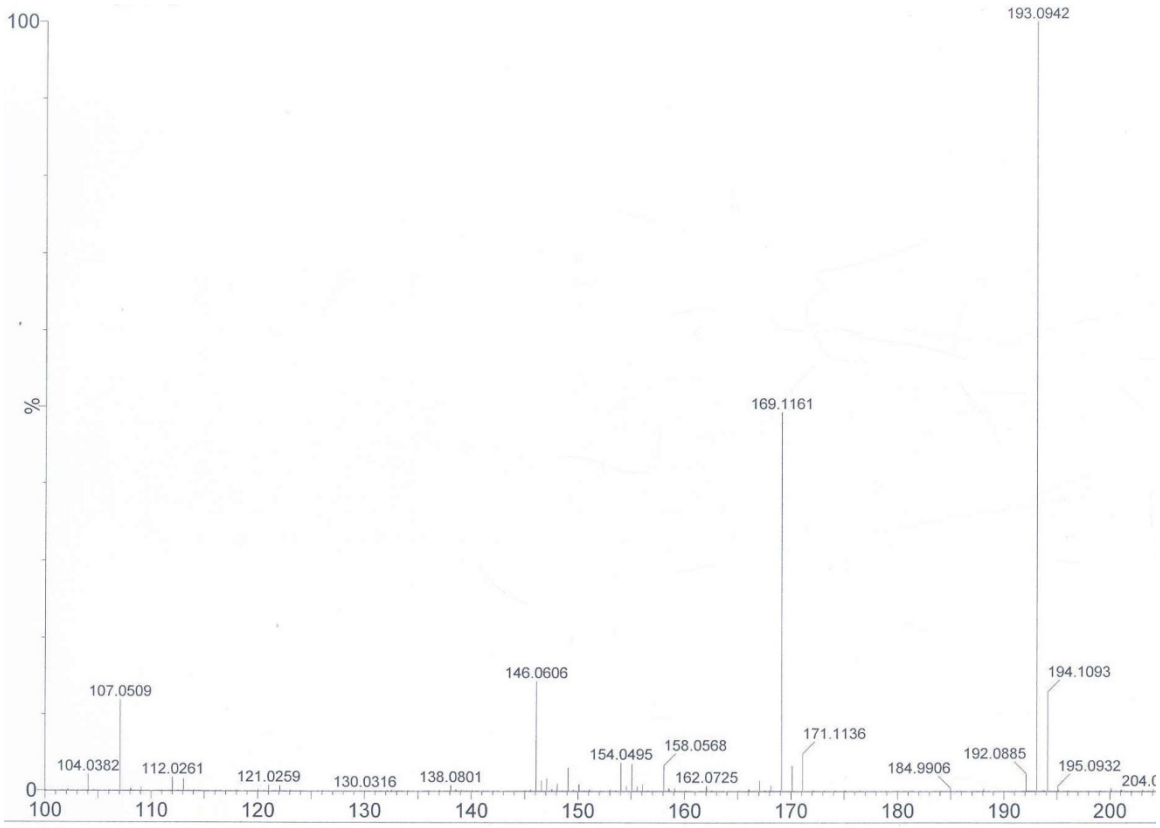
8. 4-(*N*-Acetylamino)acetophenone (Table 2, entry 9)



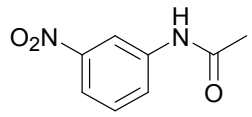


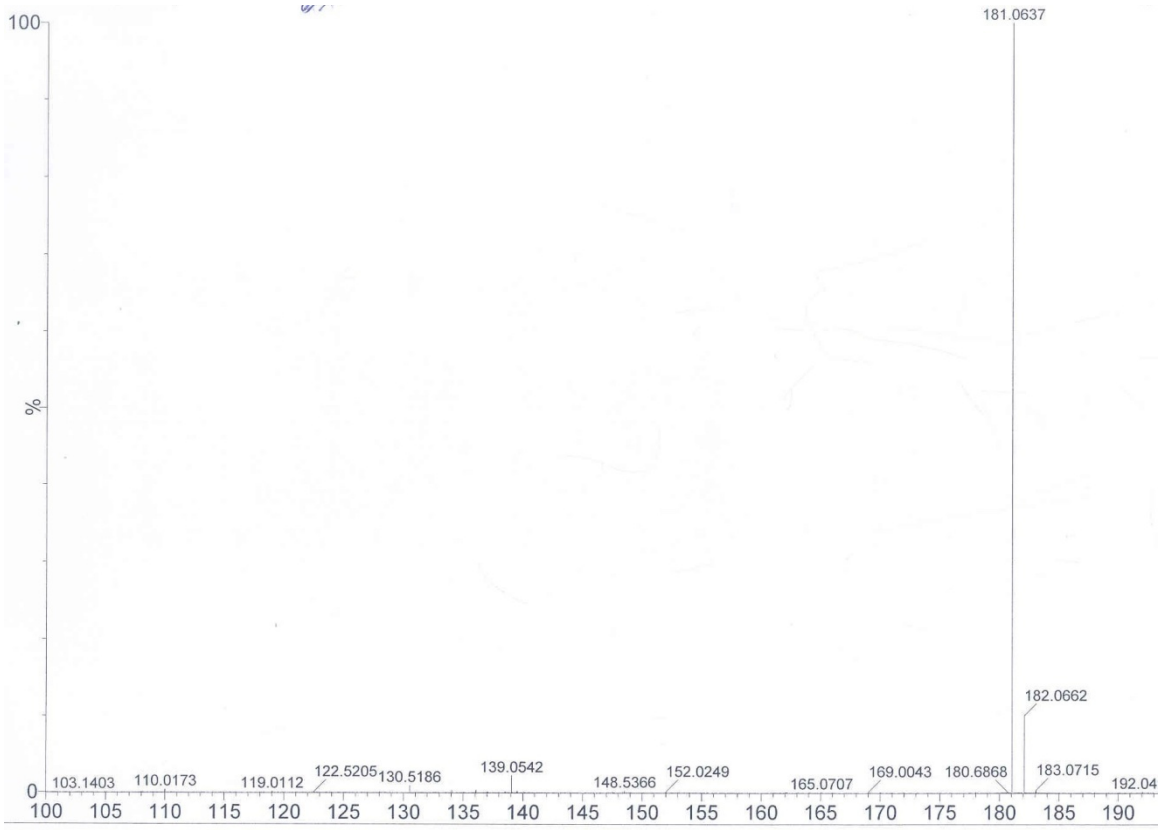
9. 1,4-Di-(*N*-acetylamino)benzene (Table 2, entry 10)



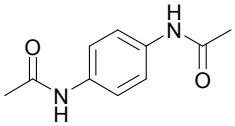


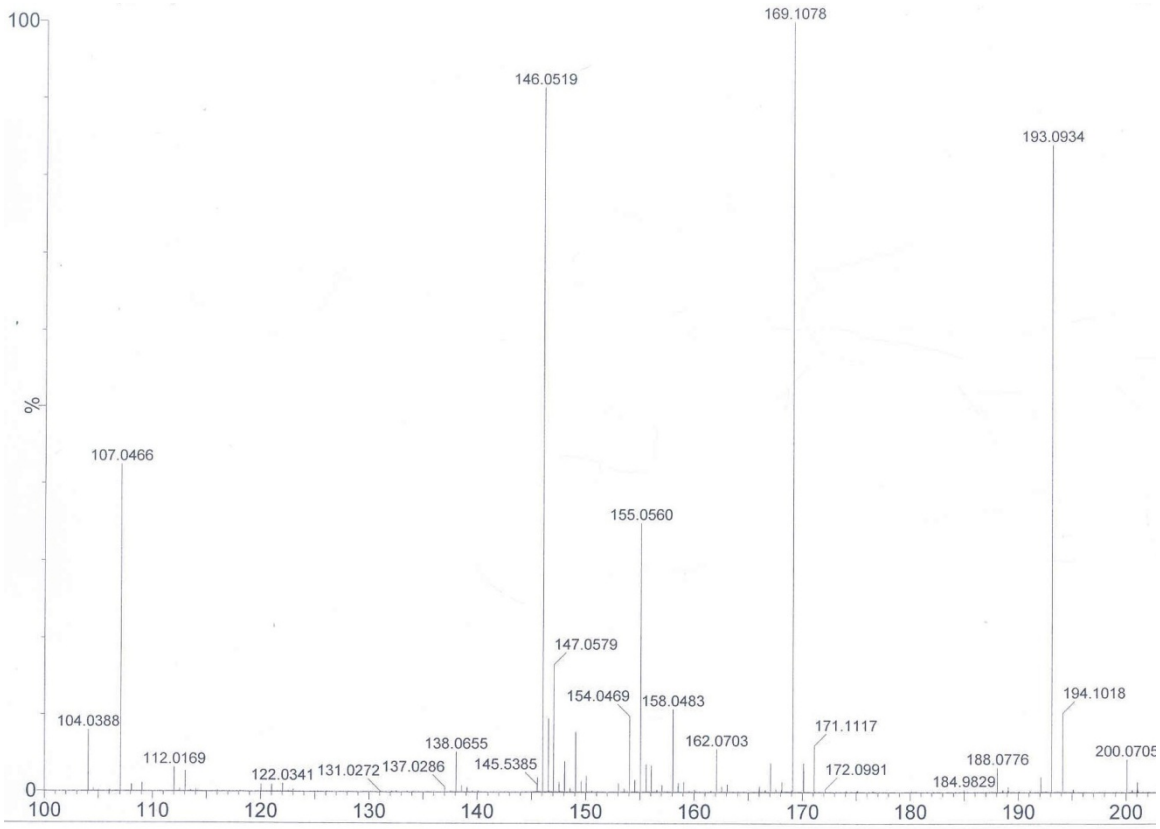
10. *N*-Acetyl-3-nitroaniline (Table 2, entry 12)



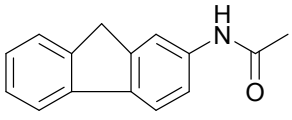


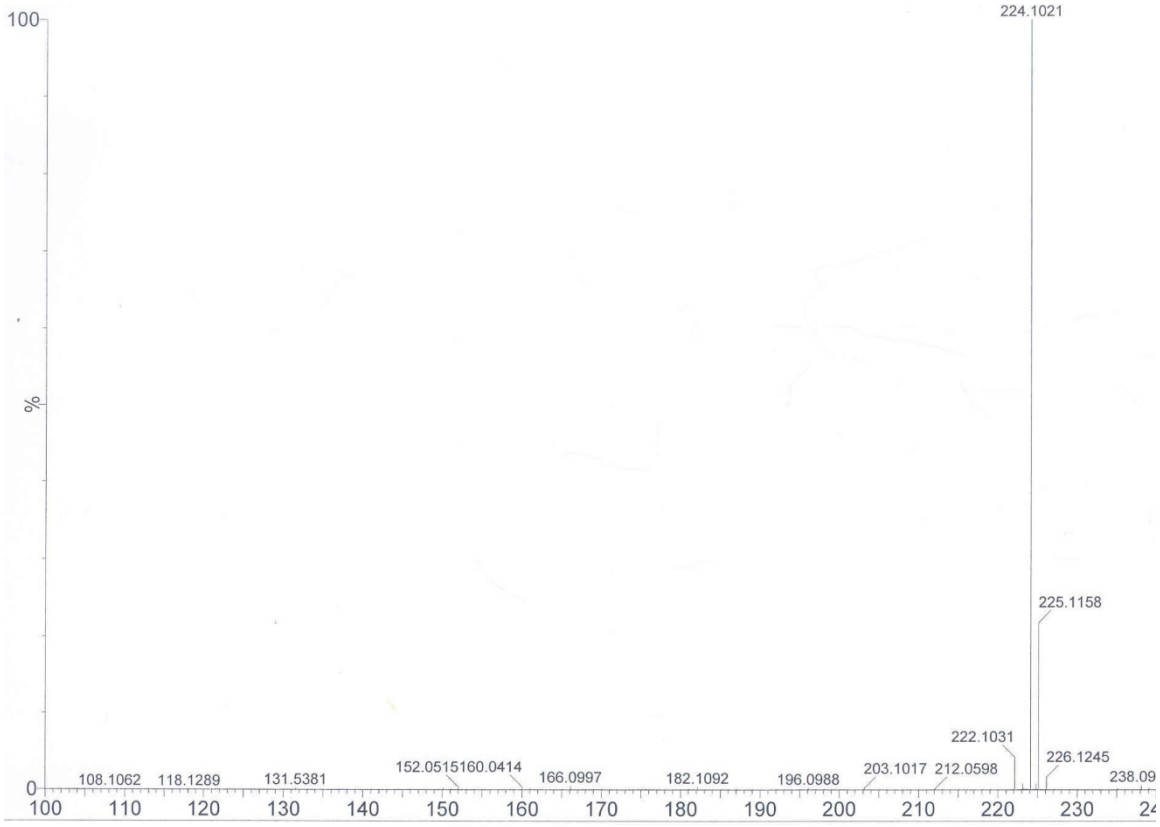
11. 1,4-Di-(*N*-acetylamino)benzene (Table 2, entry 13)



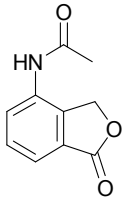


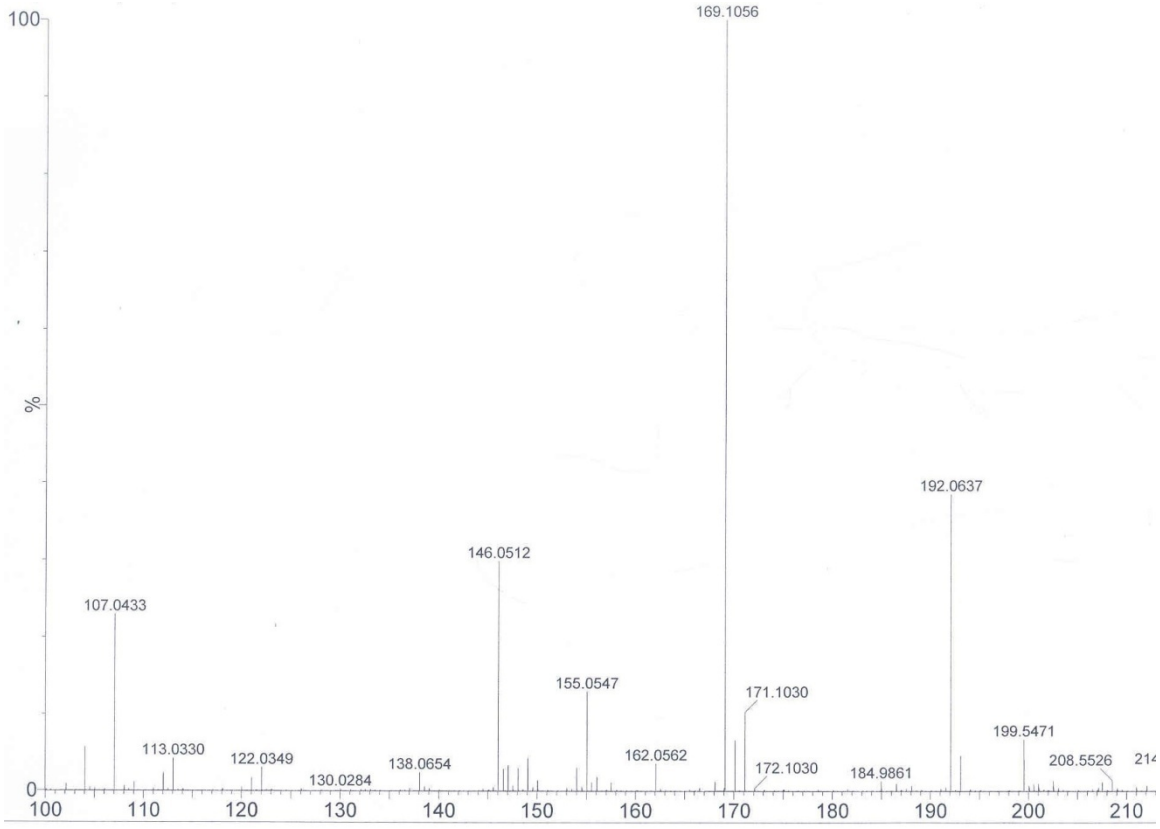
12. 2-(*N*-Acetylamino)fluorine (Table 2, entry 14)



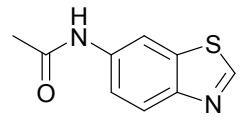


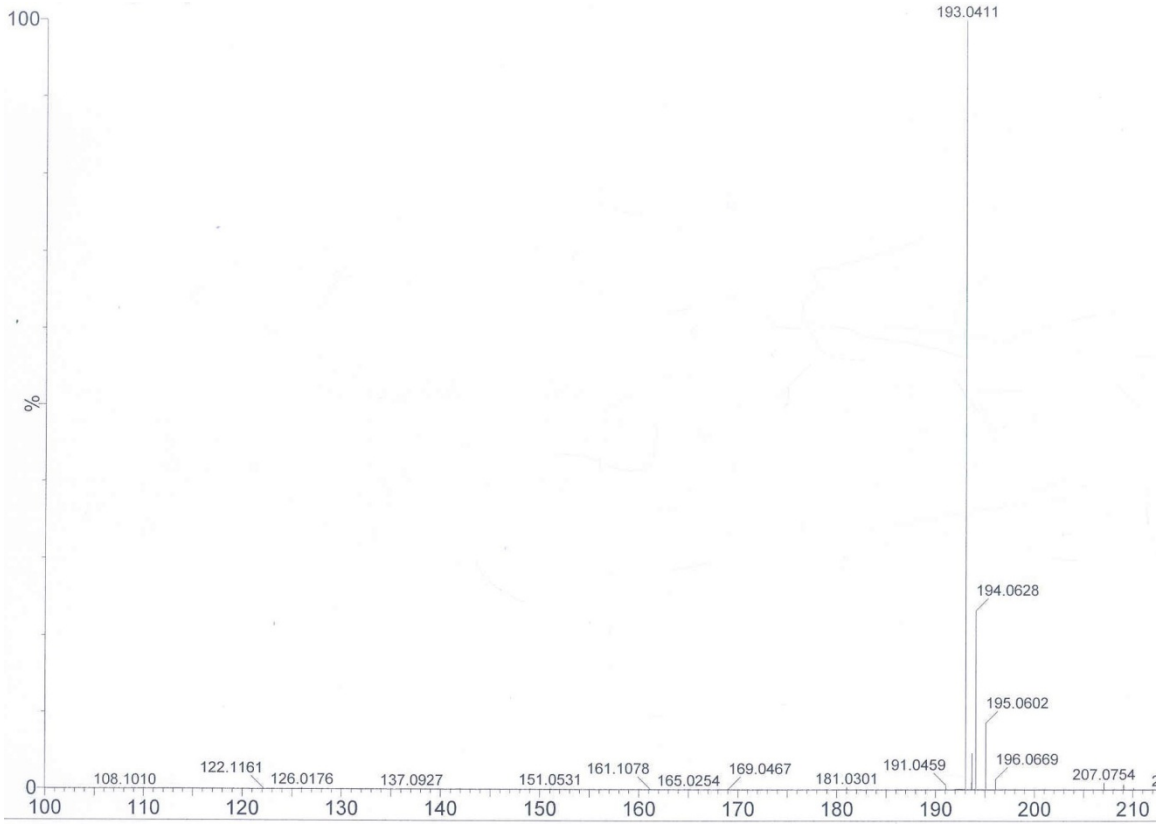
13. 4-(*N*-Actylamino)phthalide (Table 2, entry 15)



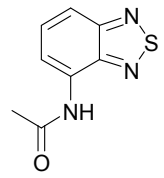


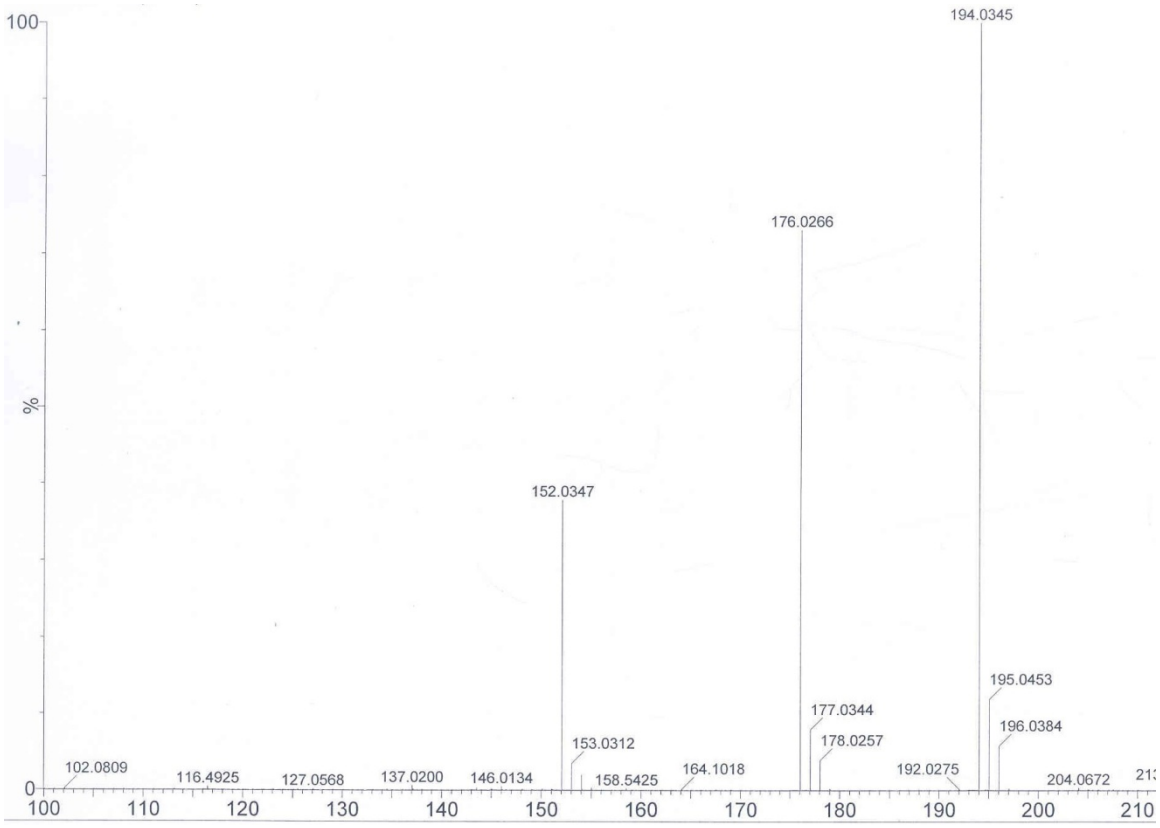
14. 6-(*N*-Acetylamino)benzothiazole (Table 2, entry 16)



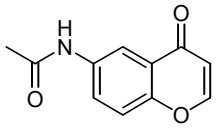


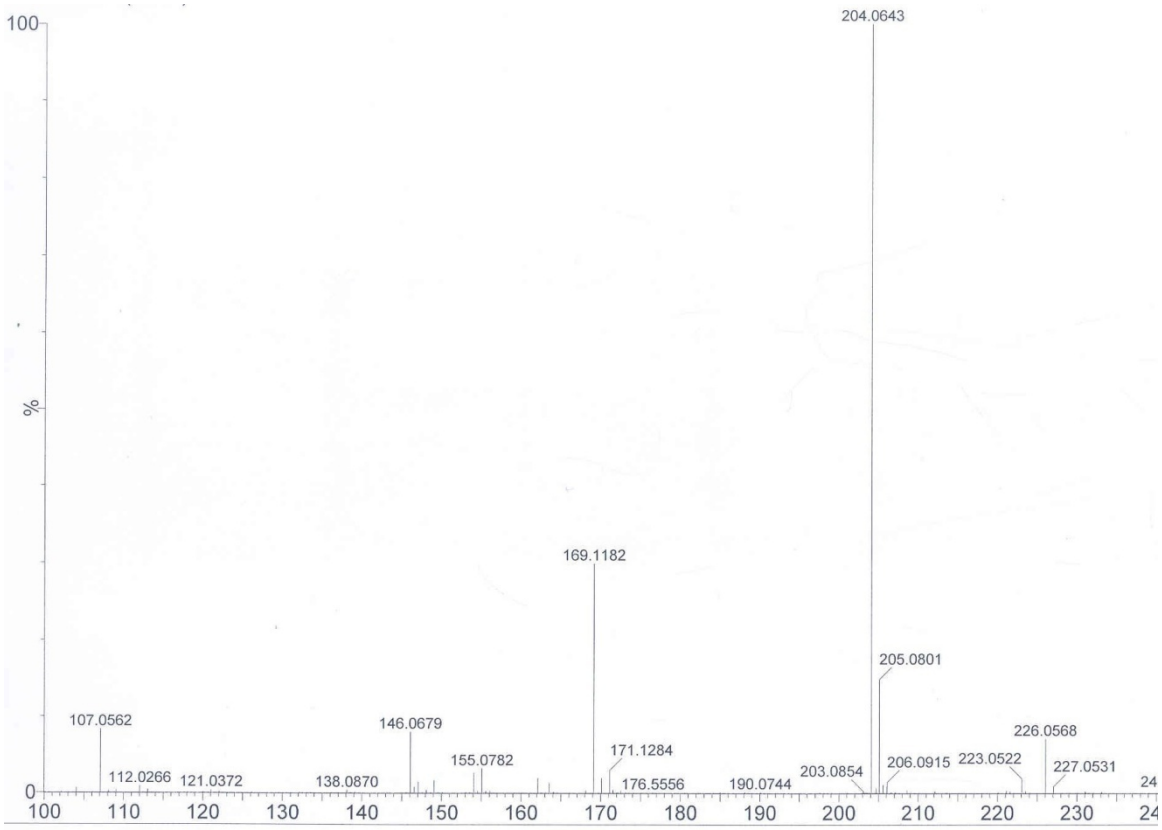
15. 4-(*N*-Acetylamino)-2,1,3-benzothiadiazole (Table 2, entry 17)



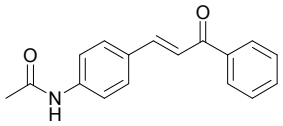


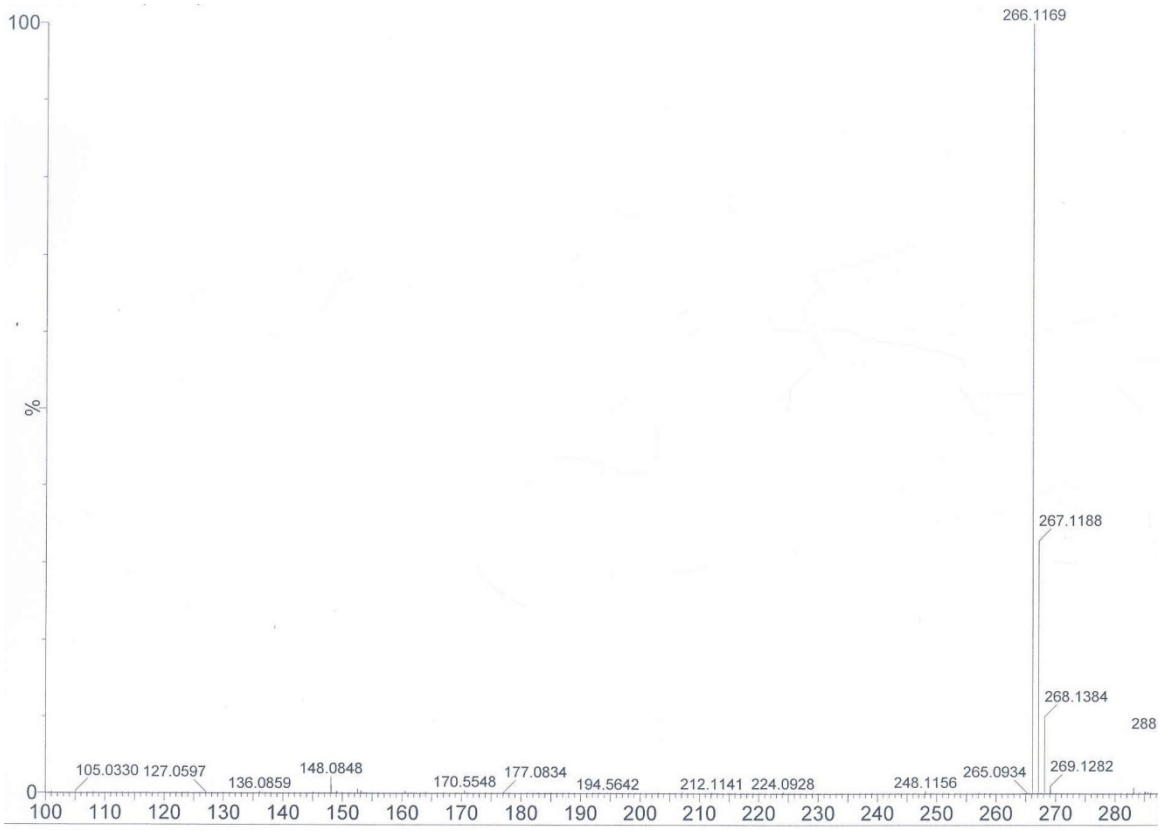
16. 6-(*N*-Acetylamino)chromone (Table 2, entry 20)



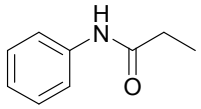


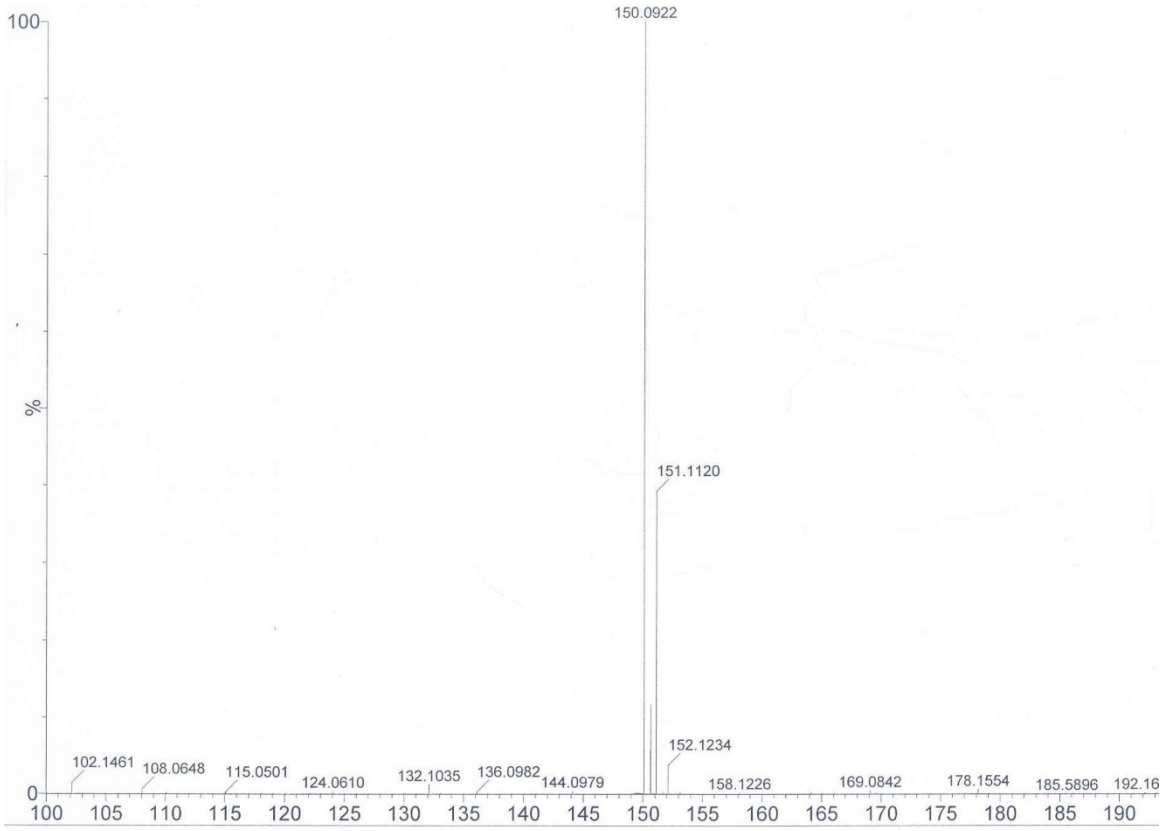
17. 4-(*N*-Acetylamino)chalcone (Table 2, entry 21)



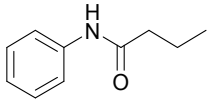


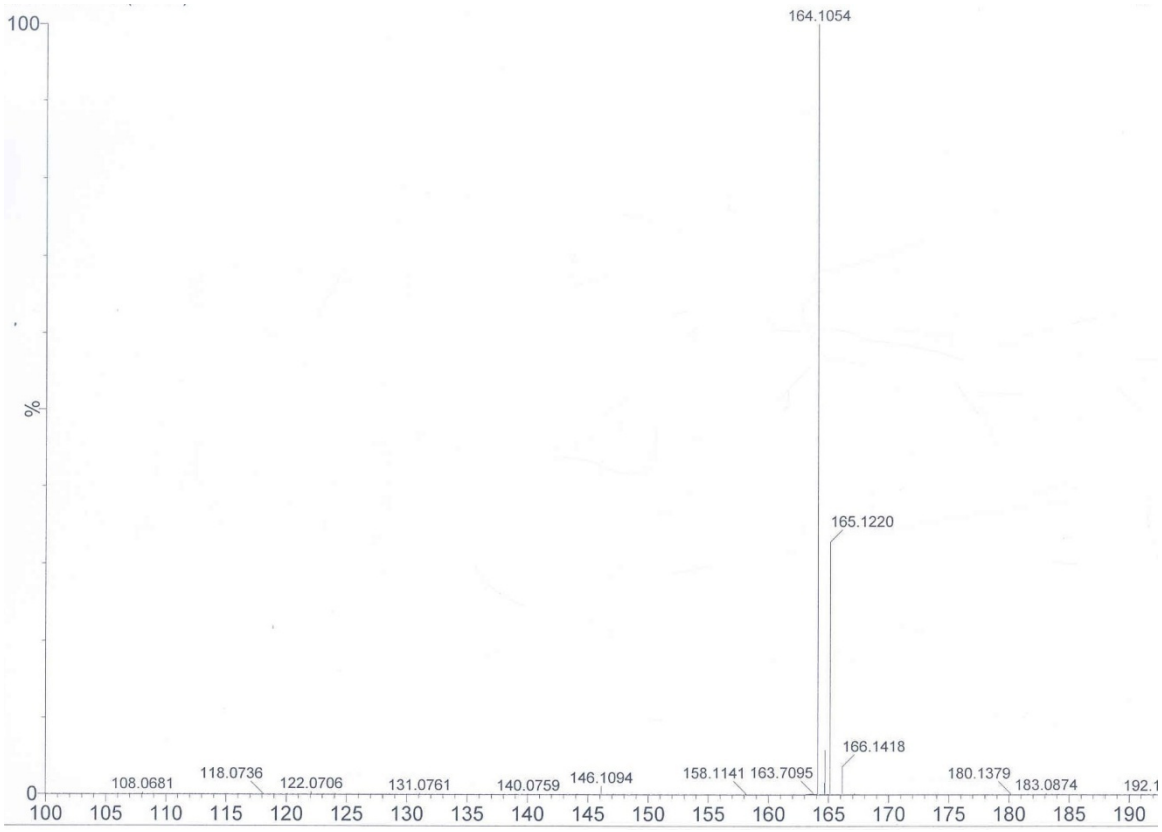
18. *N*-Phenylpropanamide (Table 3, entry 3)





19. *N*-Phenylbutanamide (Table 3, entry 4)





Mechanistic study

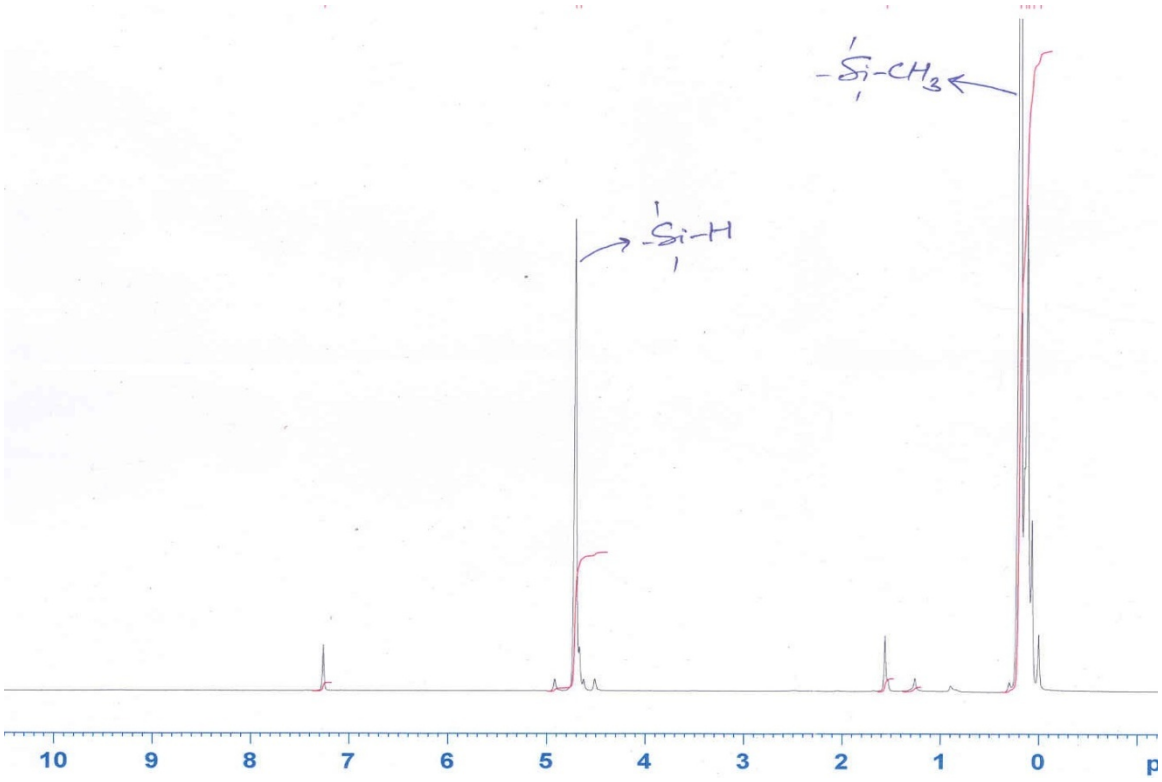
Experimental procedure for reaction of PMHS with AcOH

PMHS (4.0 mmol) was treated with AcOH (2.0 mL) at 100 ^{o}C for 12 h. The solvent was evaporated under reduced pressure and resultant product was dissolved in $CDCl_3$ for NMR analysis.

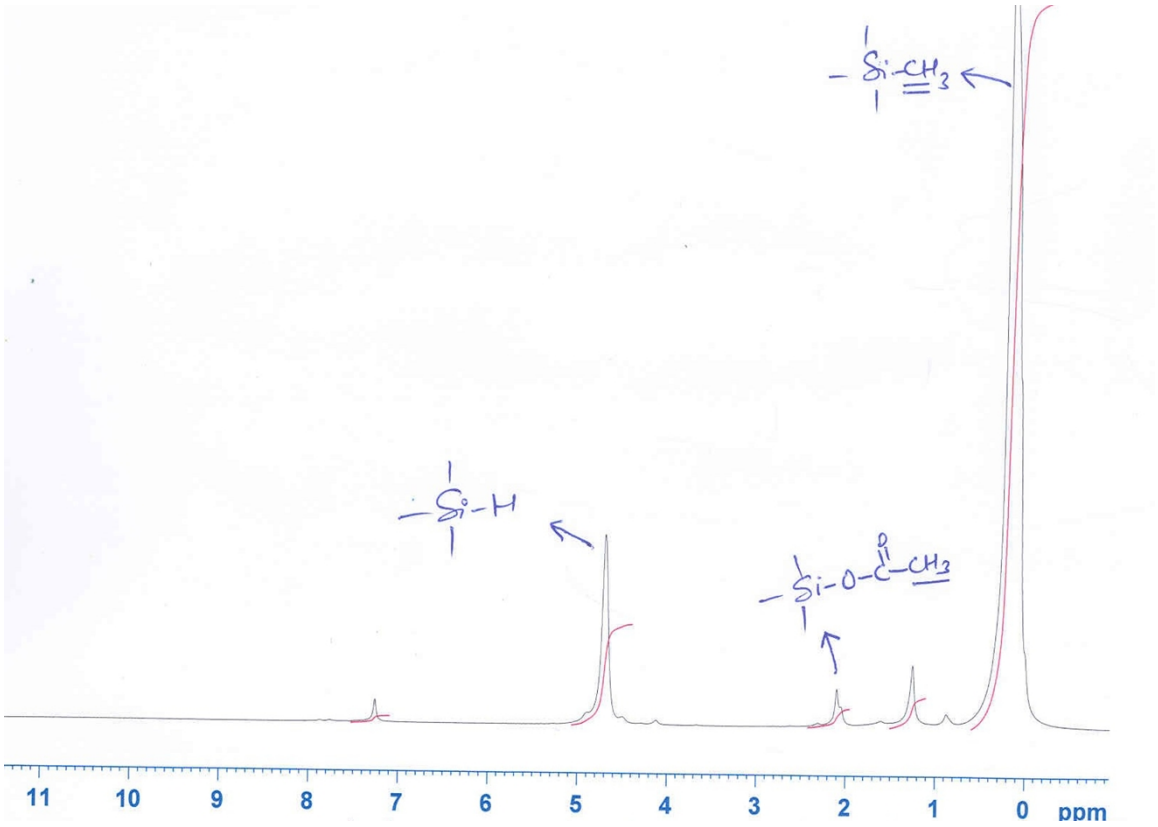
Experimental procedure for reaction of PMHS with CoPc

PMHS (4.0 mmol) was treated with CoPc (1.0 mol%) at 100 ^{o}C for 12 h under solvent free conditions. The resultant product was dissolved in $CDCl_3$ for NMR analysis.

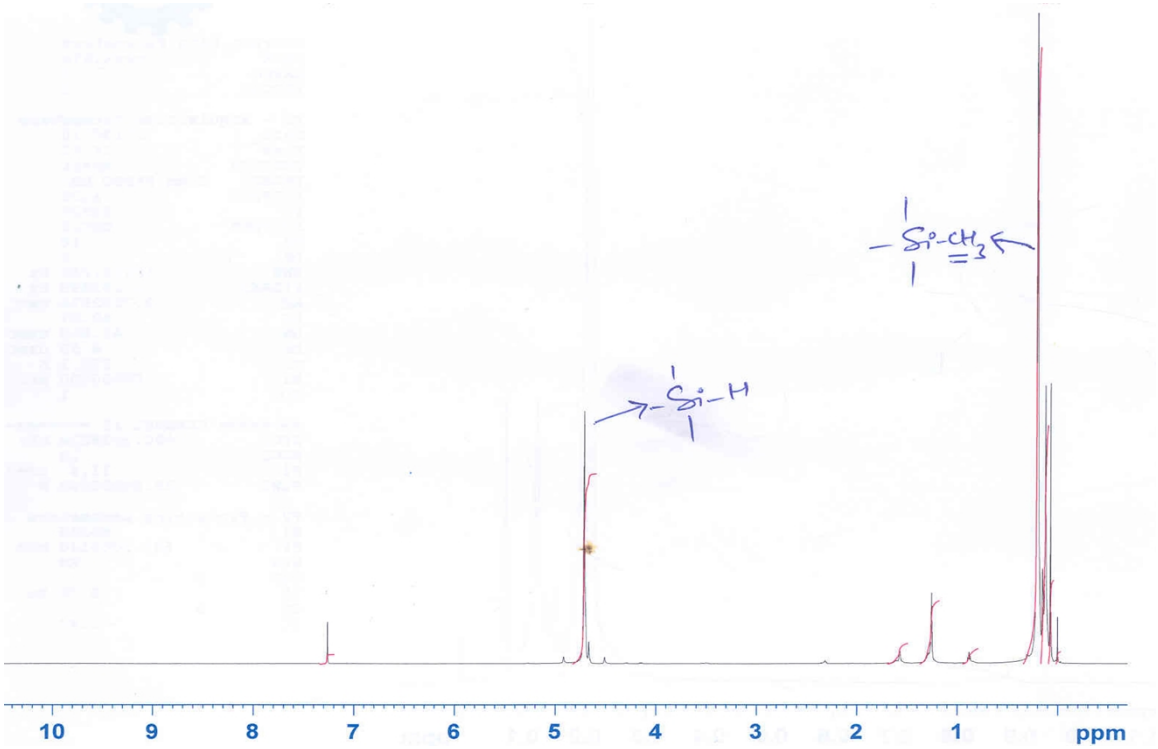
^{1}HNMR spectrum of PMHS in $CDCl_3$



^{1}HNMR spectrum of PMHS + AcOH reaction (600 MHz, $CDCl_3$)



^{1}HNMR spectrum of PMHS + CoPc reaction (600 MHz, $CDCl_3$)



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