Humic Acid: A Green Acid Catalyzed by Acylation of Amine, Phenol, and Thiols Derivatives under Solvent-Free Conditions

Experimental Section

Spectral data:

^{1}H-NMR

^{13}C-NMR

Reference

Recyclable study of humic acid analyzed using FT-IR spectroscopy

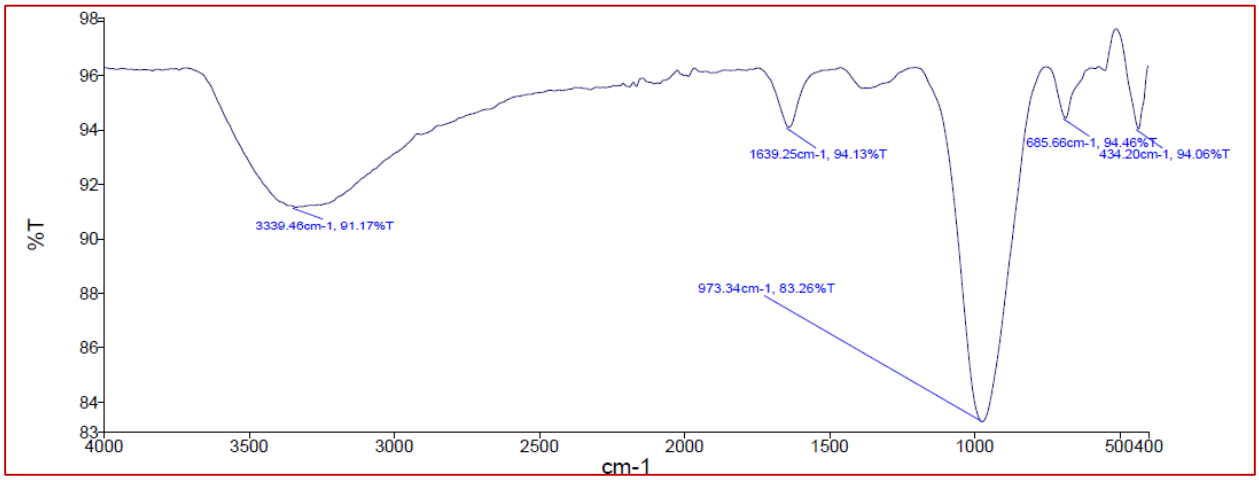


Figure 1. FT-IR spectra of Humic acid Before use in acylation reaction

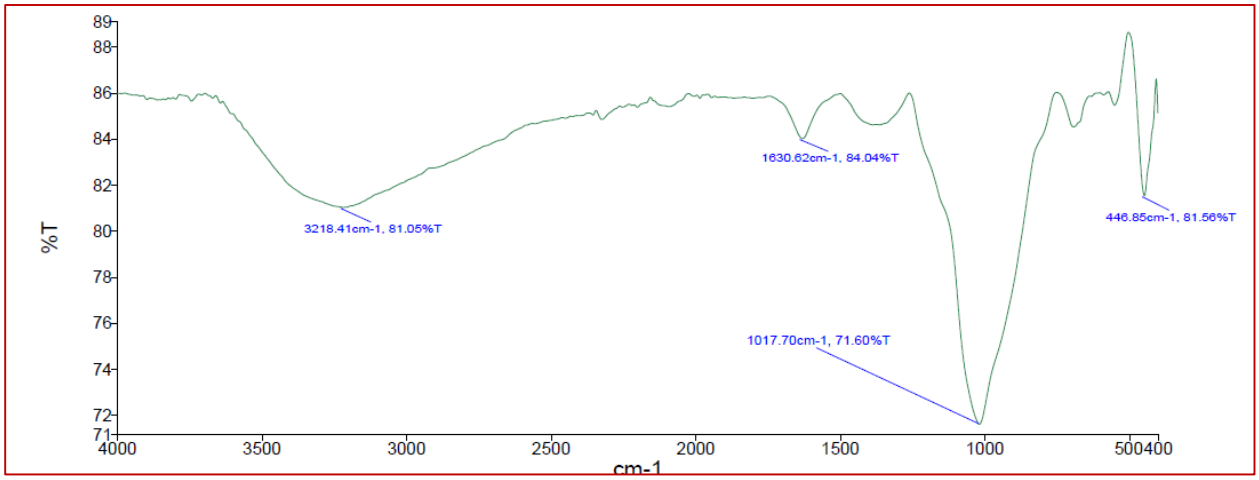


Figure 1. FT-IR spectra of Humic acid after use in acylation reaction

Experimental Section

Material methods

All the chemicals were given from commercial chemical suppliers and used directly in the reaction. Chromatographic techniques purified all the prepared compounds on a 60-120 mesh silica powder. The reaction progress was monitored on Merck plates (F254 coated with silica gel 60). The prepared compounds were characterized using ^{1}H-NMR and ^{13}C-NMR at 450 MHz Bruker AV 400 NMR spectrometer.

General procedure for the acylation of aniline derivative

A mixture of aniline (10 mmol, 0.93 mL), acetic anhydride (10 mmol, 1 mL), and humic acid catalyst (15 mg) was stirred at room temperature for 10 minutes under the solvent-free condition. The reaction was monitored on TLC in n-hexane and ethyl acetate (9:1) ratio. After the complete reaction, the mixture was extracted with diethyl ether (10 mL). Then filter the reaction mixture to separate humic acid. The ether layer was evaporated at room temperature to form white solid crude product.

General procedure for the acylation of Phenol derivative

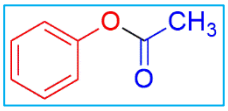
A mixture of phenol (10 mmol, 0.94 mL), acetic anhydride (10 mmol, 1 mL), and humic acid catalyst (15 mg) was stirred at room temperature for 10 minutes under the solvent-free condition. The reaction was monitored on TLC in n-hexane and ethyl acetate (9:1) ratio. After the complete reaction, the mixture was extracted with diethyl ether (10 mL). Then filter the reaction mixture to separate humic acid. The ether layer was evaporated at room temperature to form colorless liquid product.

General procedure for the acylation of Thiol derivative

A mixture of thiophenol (10 mmol, 1.10 mL), acetic anhydride (10 mmol, 1 mL), and humic acid catalyst (15 mg) was stirred at room temperature for 10 minutes under the solvent-free condition. The reaction was monitored on TLC in n-hexane and ethyl acetate (9:1) ratio. After the complete reaction, the mixture was extracted with diethyl ether (10 mL). Then filter the reaction mixture to separate humic acid. The ether layer was evaporated at room temperature to form yellow liquid product.

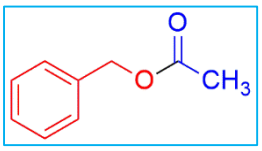
Spectral data:

1. **Phenyl acetate[10]:**



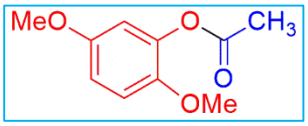
Colorless liquid (Yield-97%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ = 7.31-7.27 (m, 2H), 7.06-7.09 (m, 1H), 6.89-6.85 (m, 2H), 2.20 (s, 3H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$) δ = 169.49, 150.72, 129.46, 126.88, 121.59, 21.88 ppm.

2. **Benzyl acetate[8]:**



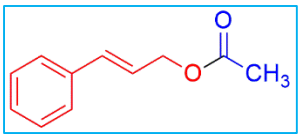
Colorless liquid (Yield-98%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ = 7.30-7.19 (m, 5H), 5.10 (s, 2H), 2.13 (s, 3H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$) δ = 170.79, 136.10, 128.59, 128.11, 128.19, 66.28, 21.11 ppm.

3. **2,5-dimethoxybenzyl acetate[7]:**



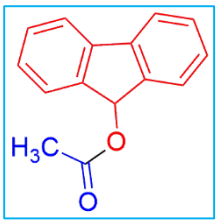
Colorless liquid (Yield-97%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ = 6.88 (s, 1H), 6.79-6.76 (m, 2H), 5.09 (s, 2H), 3.82 (s, 3H), 3.80 (s, 3H), 2.08 (s, 3H) ppm. ^{13}C-NMR (151 MHz, $CDCl_3$) δ = 170.98, 153.39, 151.59, 125.09, 115.67, 114.01, 111.78, 61.55, 56.09, 55.68, 20.09 ppm.

4. **Cinnamyl acetate[8]:**



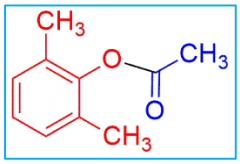
Colorless liquid (Yield-94%). ^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.39-7.36 (m, 2H), 7.40-7.37 (m, 2H), 7.32-7.30 (m, 1H), 6.70 (d, *J* = 16.4 Hz, 1H), 6.36-6.32 (m, 1H), 4.80 (d, *J* = 6.8 Hz, 2H), 2.09 (s, 3H) ppm. ^{13}C-NMR (151 MHz, $CDCl_3$) δ = 171.01, 136.19, 134.12, 128.58, 128.03, 126.58, 123.13, 65.01, 21.22 ppm.

5. **9*H*-fluoren-9-yl acetate[9]:**



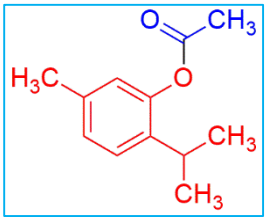
Colorless liquid (Yield-95%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ = 7.49 (d, *J* = 7.2 Hz, 2H), 7.39 (d, *J* = 7.2 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 2H), 7.20 (t, *J* = 7.2 Hz, 2H), 6.70 (s, 1H), 2.10 (s, 3H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$) δ = 172.01, 142.09, 141.08, 129.15, 128.01, 126.02, 119.98, 75.08, 21.03 ppm.

6. **2, 6-dimethylphenyl acetate[13]:**



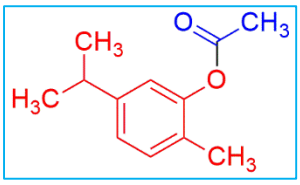
Colorless liquid (Yield-91%). ^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.20-7.17 (m, 3H), 2.39 (s, 3H), 2.19 (s, 6H) ppm. ^{13}C-NMR (151 MHz, $CDCl_3$) δ = 168.88, 148.23, 130.19, 128.59, 126.01, 20.03, 16.04 ppm.

7. **2-isopropyl-5-methylphenyl acetate[12]:**



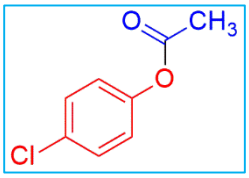
Colorless liquid (Yield-91%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ = 7.21 (d, *J* = 8.2 Hz, 1H), 7.01 (d, *J* = 8.2 Hz, 1H), 6.69 (s, 1H), 2.88-2.84 (m, 1H), 2.20 (s, 3H), 2.19 (s, 3H), 1.08 (d, *J* = 7.0 Hz, 6H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$) δ = 169.78, 148.01, 137.10, 136.56, 127.12, 126.49, 122.91, 27.09, 23.06, 21.12, 20.89 ppm.

8. **5-isopropyl-2-methylphenyl acetate[11]:**



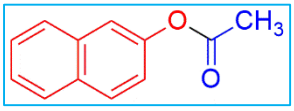
Colorless liquid (Yield-92%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ = 7.20 (d, *J* = 7.4 Hz, 1H), 7.10 (d *J* = 7.4 Hz, 1H), 6.89 (s, 1H), 2.94-2.87 (m, 1H), 2.36 (s, 3H), 2.22 (s, 3H), 1.30 (d, *J* = 6.4 Hz, 6H) ppm. ^{13}C- NMR (101 MHz, $CDCl_3$) δ =170.01, 150.04, 148.09, 131.01, 127.32, 124.42, 120.01, 33.89, 23.79, 20.08, 15.10 ppm.

9. **4-Chlorophenyl acetate[10]:**



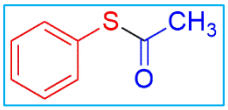
A colorless liquid, (Yield-94%), ^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.29 (d, J=9.2 Hz, 2H), 7.11 (d, J= 9.2 Hz, 2H), 2.29 (s, 3H) ppm; ^{13}C-NMR (151 MHz, $CDCl_3$) δ = 170.01, 150.02, 130.98, 130.06, 123.32, 21.12 ppm.

10. **Naphthalen-6-yl acetate[10]:**



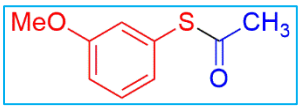
Colorless liquid (Yield-92%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ = 7.70-7.59 (m, 3H), 7.39 (s, 1H), 7.29-7.22 (m, 2H), 7.08-7.05 (m, 1H), 2.20 (s, 3H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$) δ = 170.01, 148.44, 133.89, 131.09, 130.01, 128.06, 128.06, 126.12, 126.01, 121.05, 118.11, 21.19 ppm.

11. **S-Phenyl thioacetate[14]:**



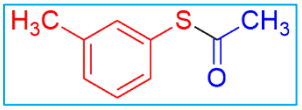
Yellow liquid (Yield-90%) ^{1}H-NMR: (600 MHz, C_6D_6): δ (ppm) = 1.78 (s, 3H), 6.88-7.10 (m, 3H), 7.30-7.34 (m, 2H); ^{13}C-NMR: (151 MHz, C_6D_6): δ (ppm) = 29.09, 128.07, 129.02, 134.59, 191.58 ppm.

12. S-(3-Methoxy phenyl)thioacetate[14]:



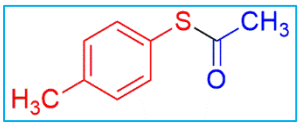
Yellow oil; (Yield-93%), ^{1}H-NMR: (600 MHz, C_6D_6): δ (ppm) = 1.91 (s, 3H), 3.33 (s, 3H), 6.90-6.76 (ddd, J = 8.2, 2.8, 1.4 Hz, 1H), 6.89-7.10 (m, 2H), 7.11 (dd, J = 2.4, 1.4 Hz, 1H); ^{13}C-NMR: (151 MHz, C_6D_6): δ (ppm) = 29.03, 54.11, 115.06, 119.12, 126.67, 129.59, 130.10, 160.23, 192.11 ppm.

13. S-(3-Methyl phenyl) thioacetate[14]:



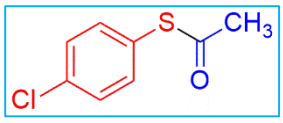
Yellow oil; (Yield-92%), ^{1}H-NMR: (600 MHz, C_6D_6): δ (ppm) = 1.88 (s, 3H), 1.96 (s, 3H), 6.90-6.97 (m, 1H), 7.11 (t, J=7.6 Hz, 1H), 7.22-7.30 (m, 2H); ^{13}C-NMR: (151 MHz, C_6D_6): δ (ppm) = 20.05, 29.21, 128.05, 128.17, 129.26, 131.31, 135.11, 138.04, 192.11 ppm.

14. S-(4-Methylphenyl) thioacetate[14]:



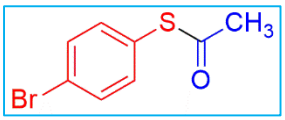
Pale yellow oil; (Yield-91%), ^{1}H-NMR: (600 MHz, C_6D_6): δ (ppm) = 1.90 (s, 3H), 2.01 (s, 3H), 6.84-6.90 (m, 2H), 7.22-7.32 (m, 2H); ^{13}C-NMR: (151 MHz, C_6D_6): δ (ppm) = 20.08, 29.15, 125.09, 129.22, 134.61, 139.44, 192.23 ppm.

15. S-(4-Chorophenyl)thioacetate[14]:



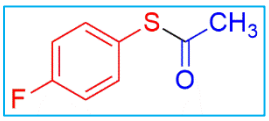
Pale yellow oil; (Yield-88%), ^{1}H-NMR: (600 MHz, C_6D6): δ (ppm) = 1.80 (s, 3H), 6.90-6.96 (m, 2H), 7.01-7.14 (m, 2H); ^{13}C-NMR: (151 MHz, C6D6): δ (ppm) = 30.01, 127.02, 130.05, 135.15, 135.17, 191.22 ppm.

16. S-(4-Bromophenyl)thioacetate[14]:



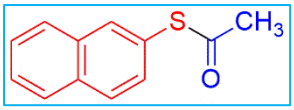
Yellow Solid; (Yield-89%) M. P. 50-51 ˚C; ^{1}H-NMR: (600 MHz, C_6D_6): δ (ppm) = 1.80 (s, 3H), 6.90-6.95 (m, 2H), 7.09-7.12 (m, 2H); ^{13}C-NMR: (151 MHz, C_6D_6): δ (ppm) = 29.12, 123.07, 127.09, 132.07, 135.12, 191.09 ppm.

17. S-(4-Fluorophenyl) thioacetate[14]:



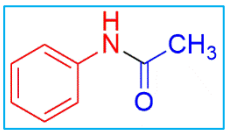
Yellow oil; (Yield-87%), ^{1}H-NMR: (600 MHz, C_6D_6): δ (ppm) = 1.77 (s, 3H), 6.71 (t, J=8.4 Hz, 2H), 7.10-7.21 (m, 2H); ^{13}C-NMR: (151 MHz, C_6D_6): δ (ppm) = 29.5, 116.11 (d, J=22.2 Hz), 123.52 (d, J=3.6 Hz), 136.51 (d, J=8.6 Hz), 163.56 (d, J=248.3 Hz), 192.08 ppm.

18. S-Naphthalene-2-yl thioacetate[14]:



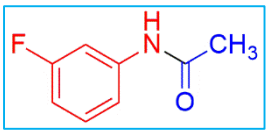
Pale Yellow semi-solid, (Yield-95%), ^{1}H-NMR: (600 MHz, C_6D_6): δ (ppm) = 1.89 (s, 3H), 7.20-7.26 (m, 2H), 7.45–7.60 (m, 4H), 7.90 (dd, J = 1.6, 0.8 Hz, 1H); ^{13}C-NMR: (151 MHz, C_6D_6): δ (ppm) = 29.99, 125.03, 126.65, 126.81, 127.80, 128.41, 128.88, 131.29, 133.81, 134.65, 192.09 ppm.

19. *N*-phenyl acetamide[1]:



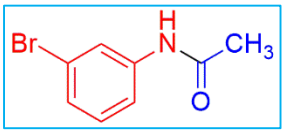
White solid (Yield-97%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ = 8.51 (br. s, 1H), 7.63 (d, *J* = 8.2 Hz, 2H), 7.26-7.19 (m, 2H), 7.06-6.91 (m, 1H), 2.11 (s, 3H) ppm. ^{13}C-NMR (151 MHz, $CDCl_3$) δ = 169.52, 138.21, 128.96, 124.36, 120.28, 24.39 ppm.

20. *N*-(3-fluorophenyl) acetamide[1]:



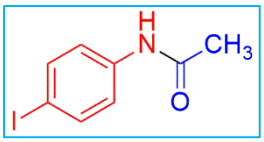
White solid (Yield-94%). ^{1}H-NMR (600 MHz, $CDCl_3$) δ = 8.89 (br. s, 1H), 7.49-7.39 m, 1H), 7.19- 7.09 (m, 2H), 6.80 -6.78 (m, 1H), 2.20 (s, 3H) ppm. ^{13}C-NMR (151 MHz, $CDCl_3$) δ = 169.78, 169.02, 163.66, 162.05, 139.66, 139.58, 130.11, 130.01, 115.55, 110.99, 111.01, 108.01, 107.05, 24.09 ppm.

21. *N*-(3-bromophenyl) acetamide[6]:



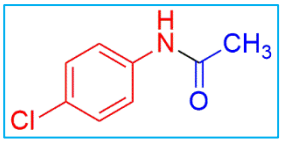
White solid (Yield-92%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ = 8.58 (br. s, 1H), 7.80 (s, 1H), 7.40 (d, *J* = 8.2 Hz, 1H), 7.21 (d, *J* = 8.2 Hz, 1H), 7.09 (t, *J* = 8.2 Hz, 1H), 2.20 (s, 3H) ppm. ^{13}C-NMR (151 MHz, $CDCl_3$) δ = 169.58, 139.28, 130.19, 127.29, 123.19, 122.49, 118.68, 24.38 ppm.

22. *N*-(4-iodophenyl) acetamide[5]:



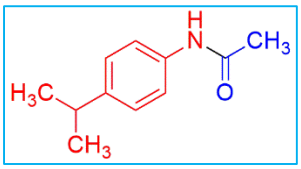
White solid (Yield-93%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ = 7.59 (d, *J* = 8.7 Hz, 2H), 7.51 (br. s, 1H), 7.30 (d, *J* = 8.2 Hz, 2H), 2.20 (s, 3H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$) δ = 168.59, 137.88, 137.58, 121.78, 87.62, 24.70 ppm.

23. *N*-(4-chlorophenyl) acetamide[1]:



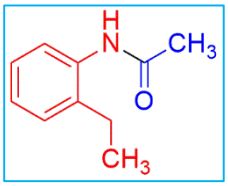
White solid (Yield-94%). ^{1}H-NMR (600 MHz, DMSO-d_6) δ = 10.12 (br. s, 1H), 7.59 (d, *J* = 8.8 Hz, 2H), 7.29 (d, *J* = 8.8 Hz, 2H), 2.10 (s, 3H). ppm. ^{13}C-NMR (151 MHz, DMSO-d_6) δ = 168.89, 138.17, 129.11, 126.15, 120.89, 24.14 ppm.

24. *N*-(4-isopropylphenyl) acetamide[3]:



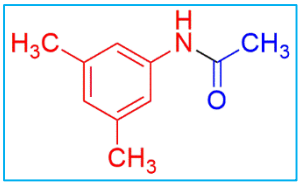
White solid (Yield-95%). ^{1}H-NMR (600 MHz, $CDCl_3$) δ = 8.20 (br. s, 1H), 7.39-7.35 (m, 2H), 7.11-7.07 (m, 2H), 2.90-2.86 (m, 1H), 2.08 (s, 3H), 1.18 (d, *J* = 7.1 Hz, 6H) ppm. ^{13}C-NMR (151 MHz, $CDCl_3$) δ = 169.19, 145.02, 135.78, 126.79, 120.49, 33.58, 24.29, 24.08 ppm.

25. *N*-(2-ethylphenyl)acetamide[3]:



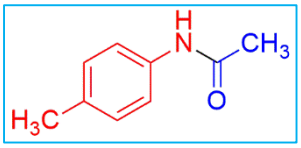
White solid (Yield- 96%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ = 7.61-7.49 (m, 1H), 7.30 (br. s, 1H), 7.22-7.05 (m, 3H), 2.51 (q, *J* = 7.6 Hz, 2H), 2.11 (s, 3H), 1.05 (t, *J* = 7.6 Hz, 3H) ppm. ^{13}C-NMR (151 MHz, $CDCl_3$) δ = 169.18, 136.26, 134.88, 128.48, 126.49, 126.11, 124.88, 24.19, 23.89, 14.06 ppm.

26. *N*-(3,5-dimethylphenyl)acetamide[2]:



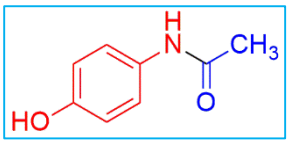
White solid (Yield-96%). ^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.69 (br. s, 1H), 7.09 (s, 2H), 6.79 (s, 1H), 2.30 (s, 6H), 2.20 (s, 3H) ppm. ^{13}C-NMR (151 MHz, $CDCl_3$) δ = 168.68, 138.70, 137.85, 126.16, 117.78, 24.49, 21.38 ppm.

27. *N*-*p*-tolyl acetamide[1]:



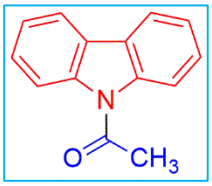
White solid (Yield-97%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ = 7.87 (br. s, 1H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 2.27 (s, 3H), 2.20 (s, 3H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$) δ = 168.77, 135.36, 134.13, 129.38, 120.28, 24.29, 20.87 ppm.

28. *N*-(4-hydroxyphenyl)acetamide[1]:



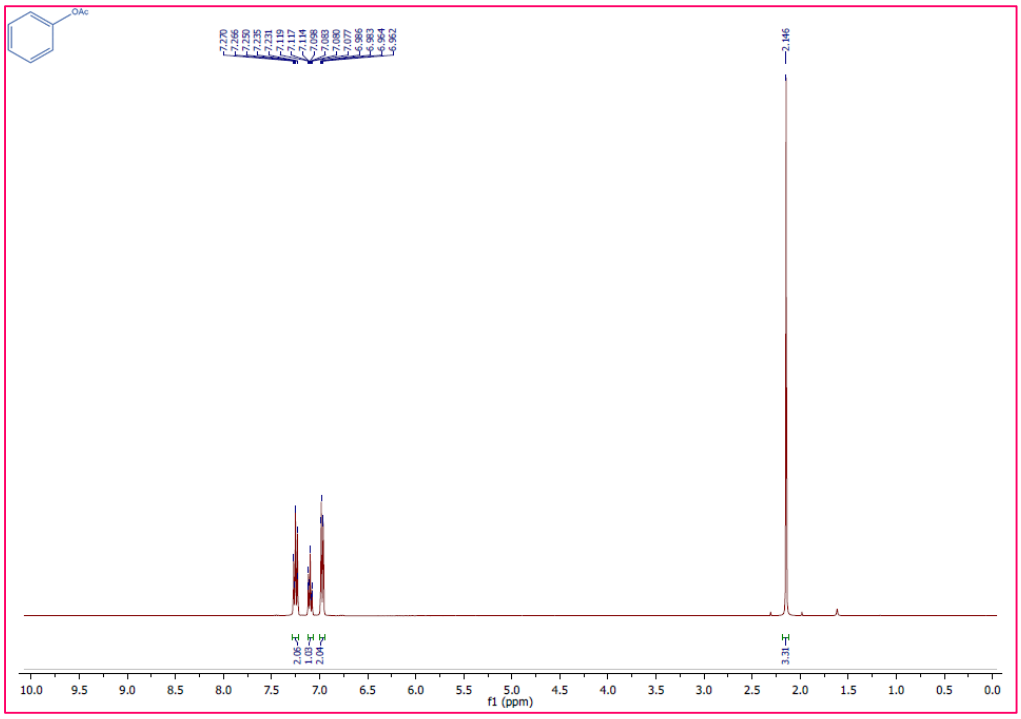
White solid (Yield-96%). ^{1}H-NMR (400 MHz, DMSO-d$_6$) δ = 9.40 (br. s, 1H), 9.01 (br. s, 1H), 6.99 (d, *J* = 8.8 Hz, 2H), 6.38 (d, *J* = 8.78 Hz, 2H), 1.81 (s, 3H) ppm. ^{13}C-NMR (101 MHz, DMSO-d$_6$) δ = 168.19, 153.58, 131.38, 121.39, 115.44, 24.09 ppm.

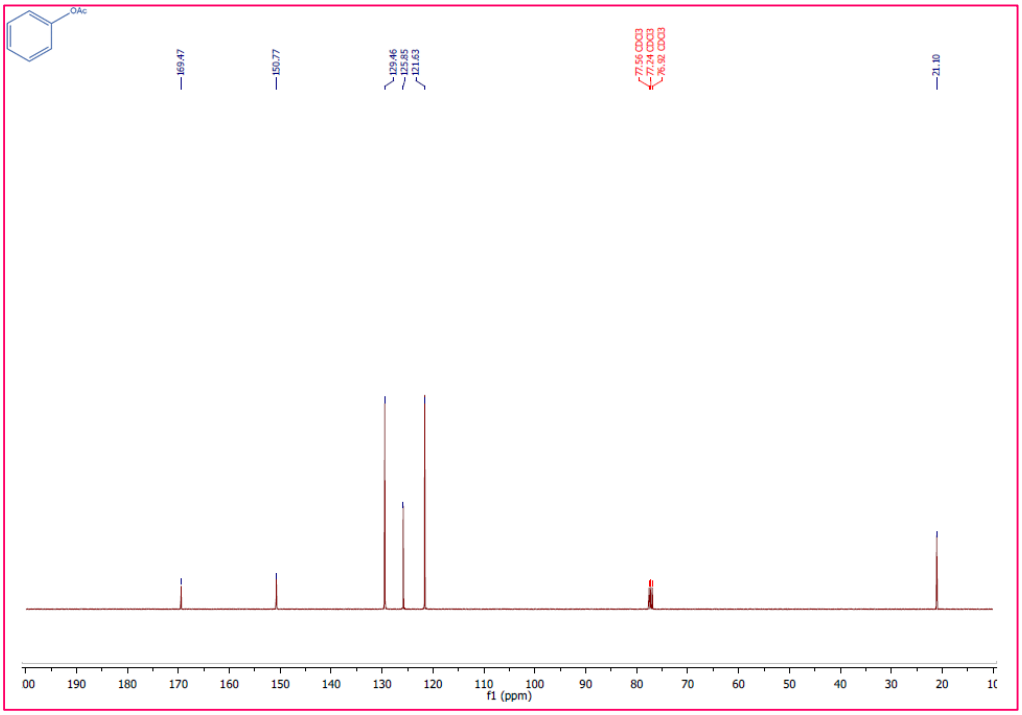
29. 1-(acridin-10(*9H*)-yl)ethanone[4]:



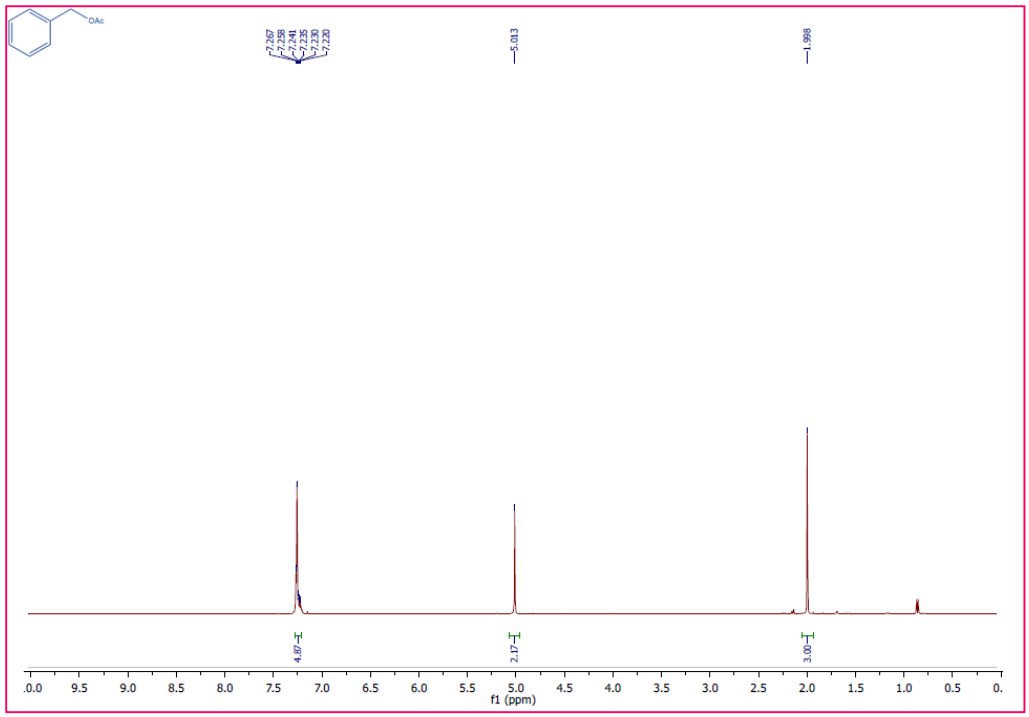
White solid (Yield-95%). ^{1}H-NMR (600 MHz, CDCl$_3$) δ = 7.90 (d, *J* = 8.2 Hz, 2H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.20-7.15 (m, 2H), 7.09-6.99 (m, 2H), 2.90 (s, 3H) ppm. ^{13}C-NMR (151 MHz, CDCl$_3$) δ = 171.01, 138.59, 127.38, 126.42, 123.69, 120.01, 116.28, 27.78 ppm.

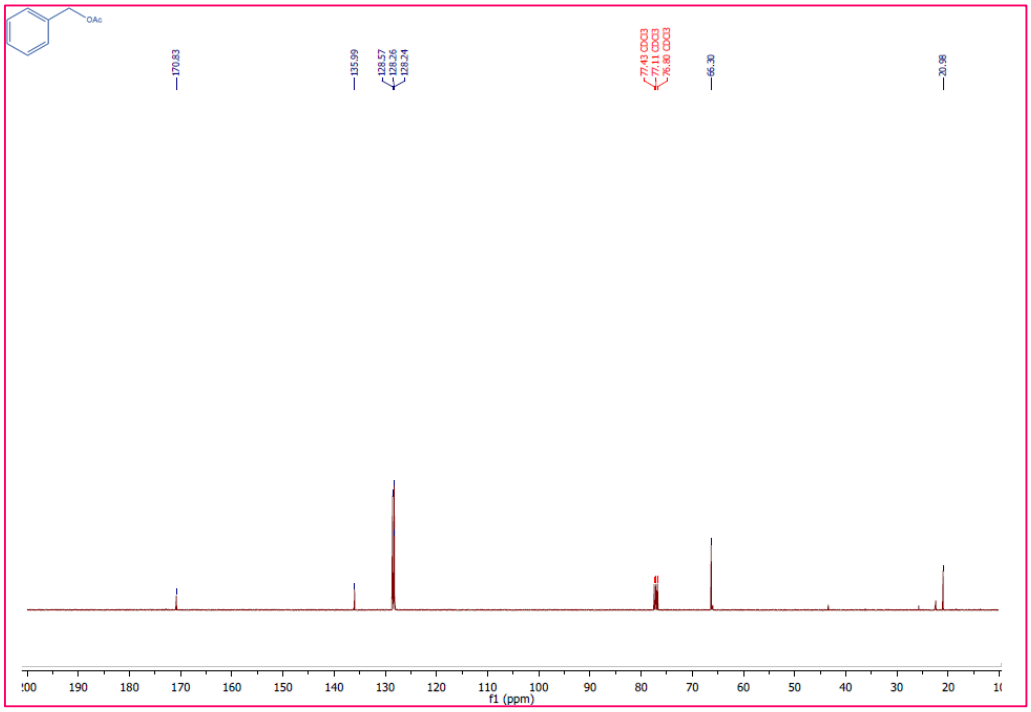
1. Phenyl acetate[10]:



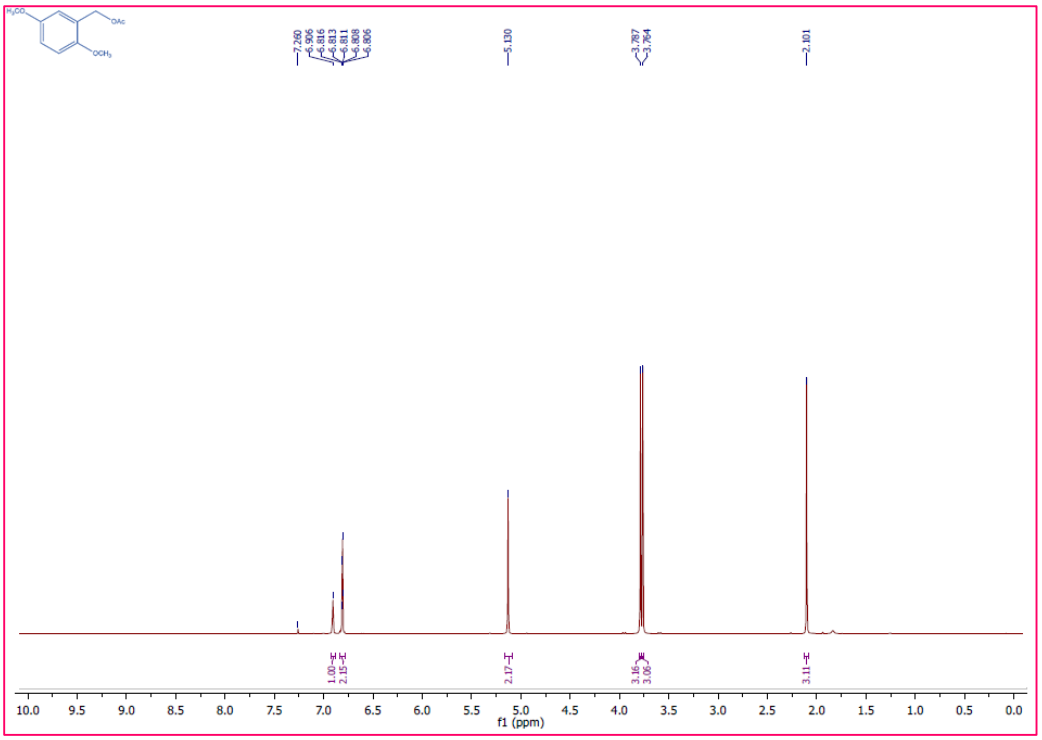


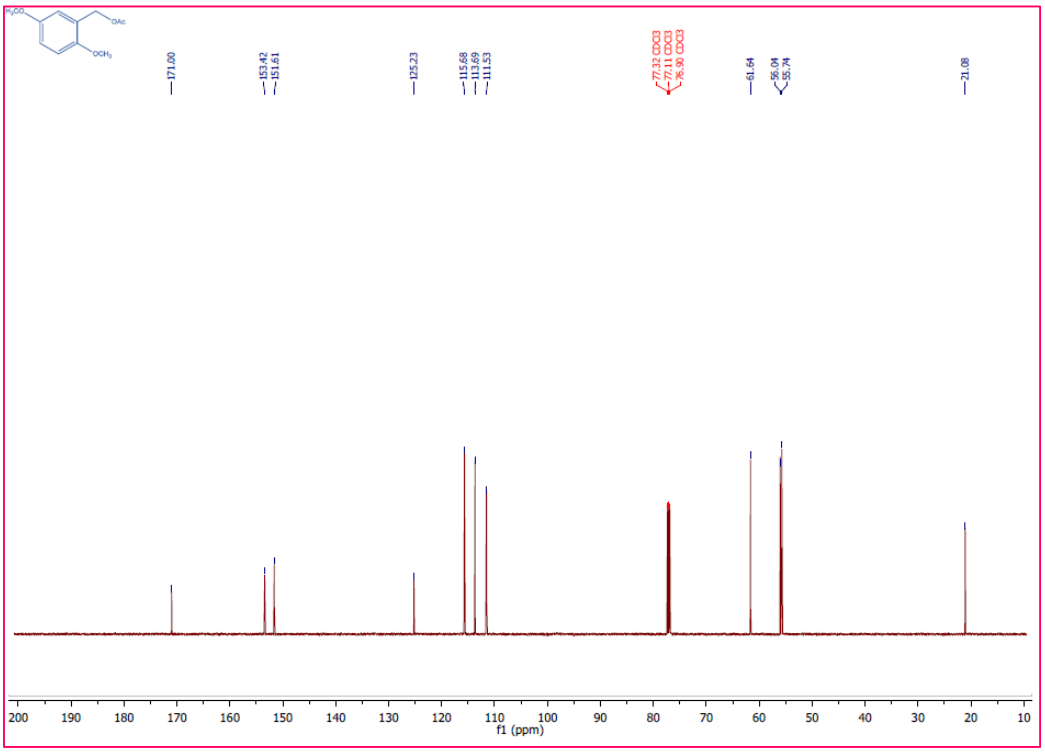
2. Benzyl acetate[8]:



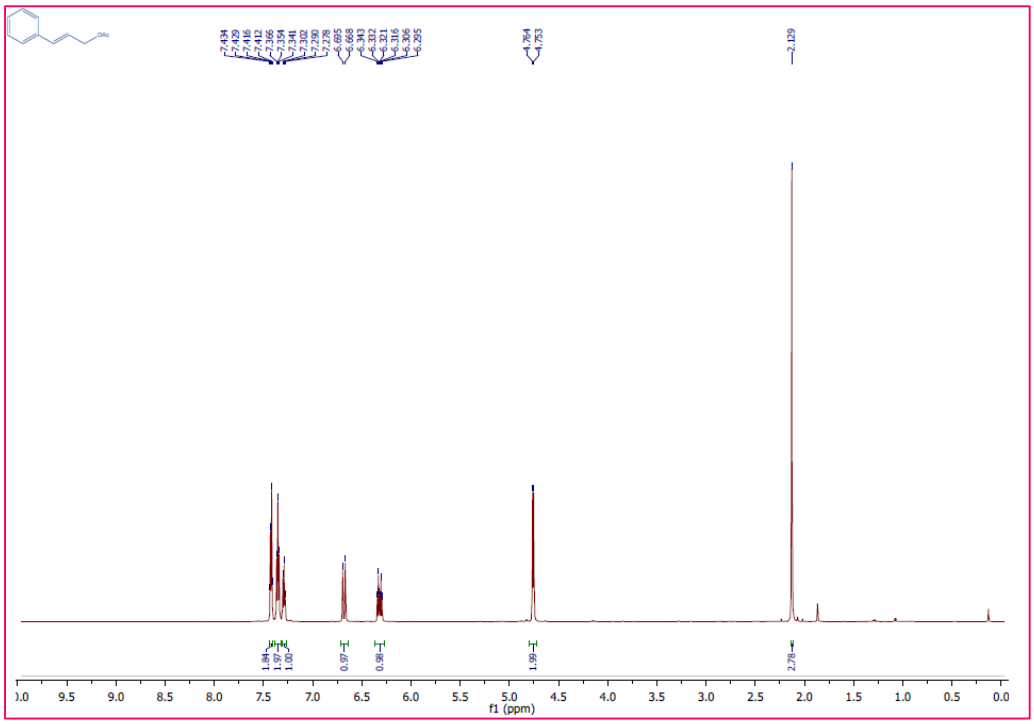


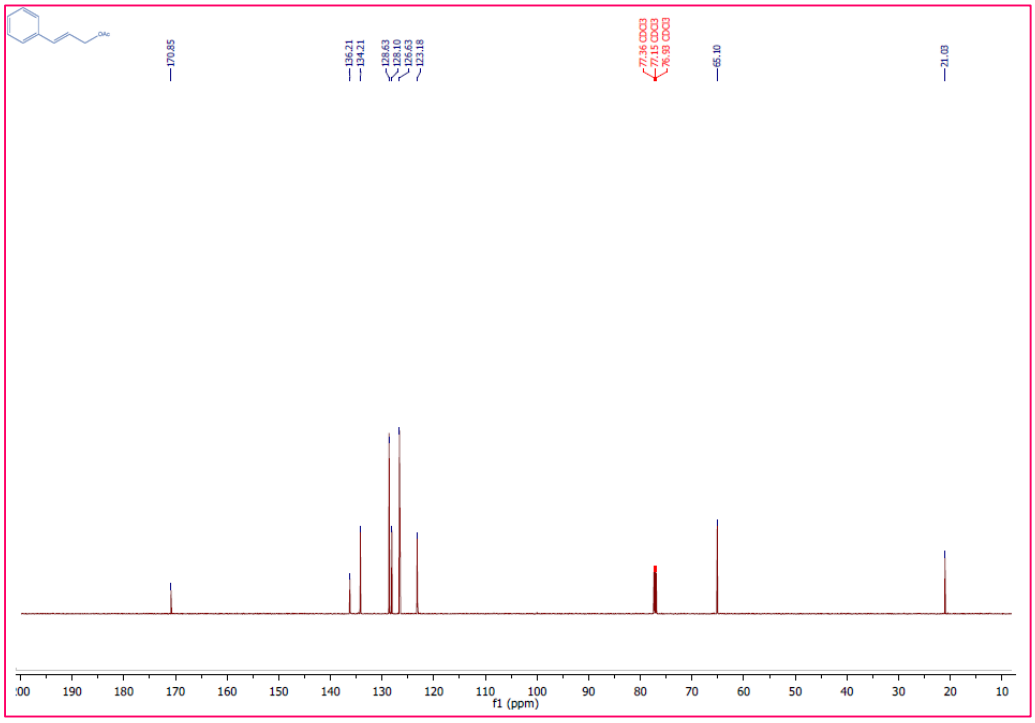
3. 2,5-dimethoxybenzyl acetate[7]:



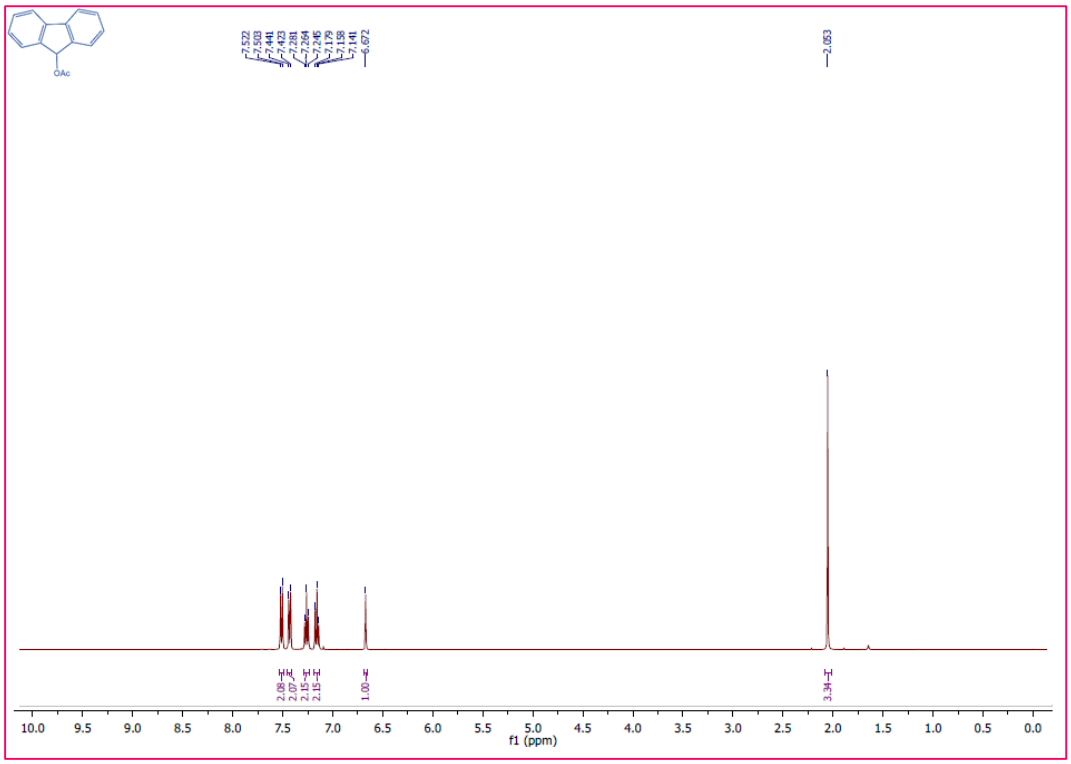


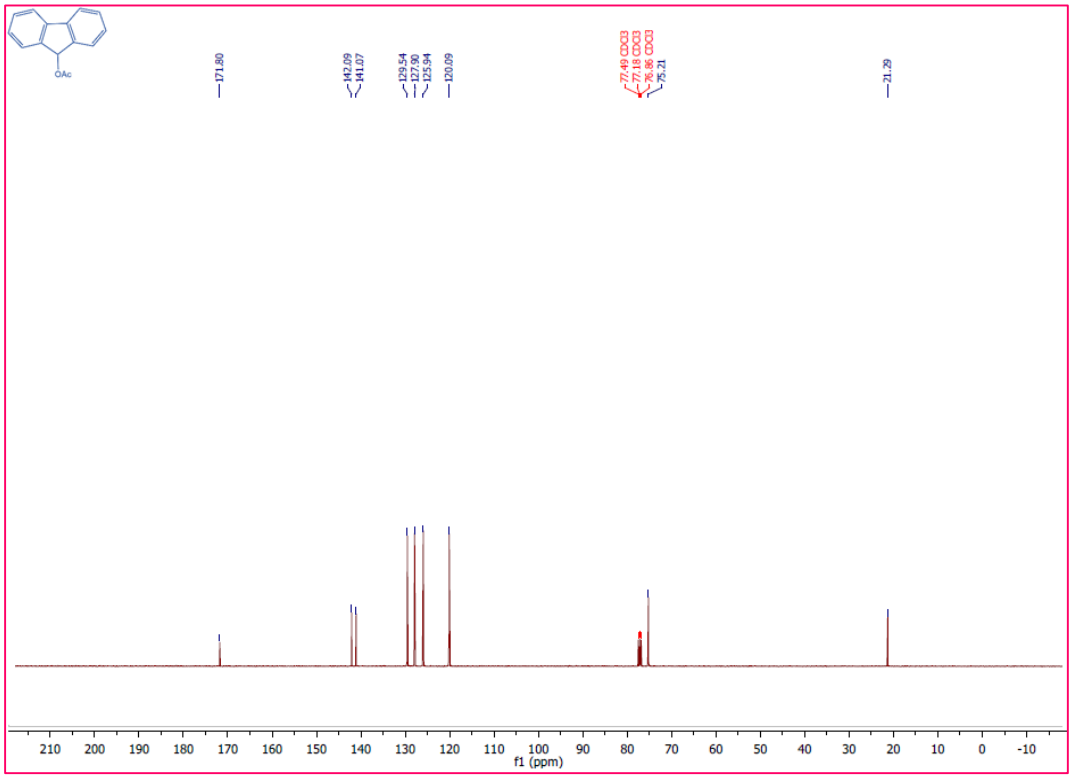
4. Cinnamyl acetate[8]:



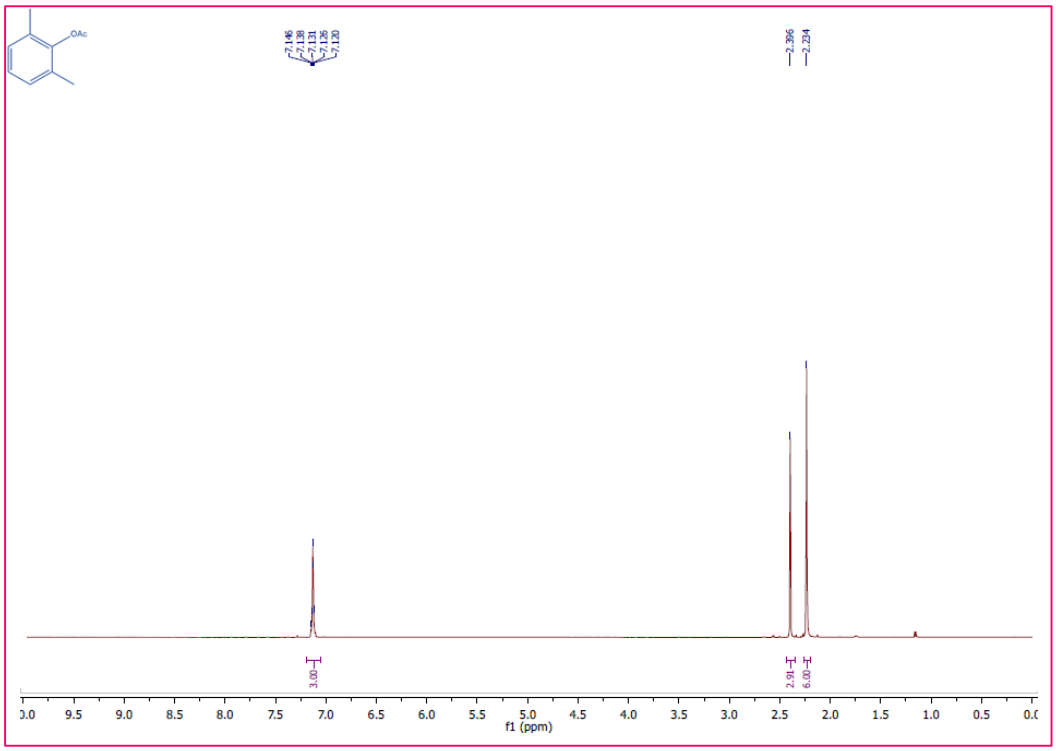


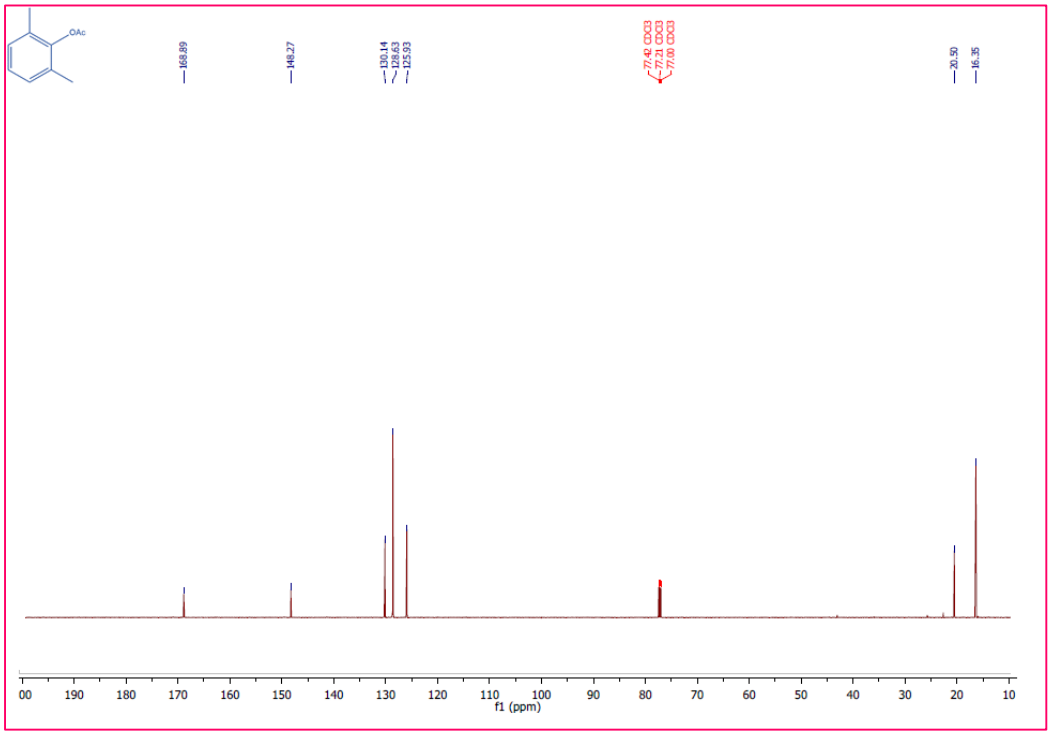
5. 9*H*-fluoren-9-yl acetate[9]:



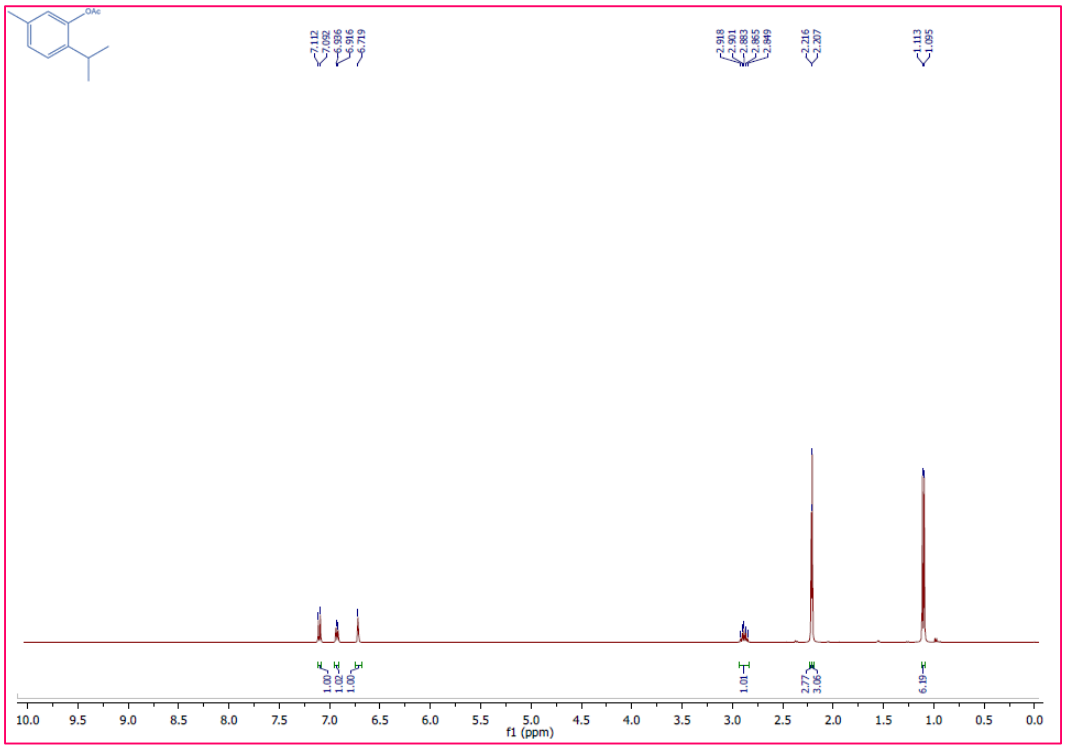


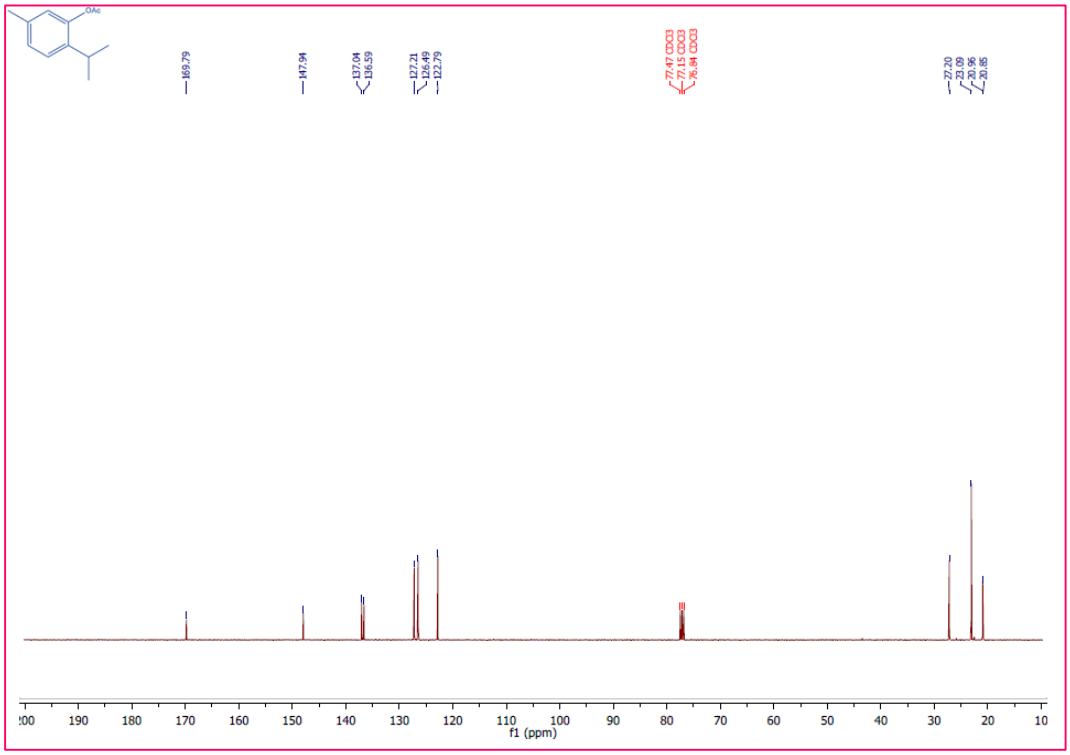
6. 2, 6-dimethylphenyl acetate[13]:



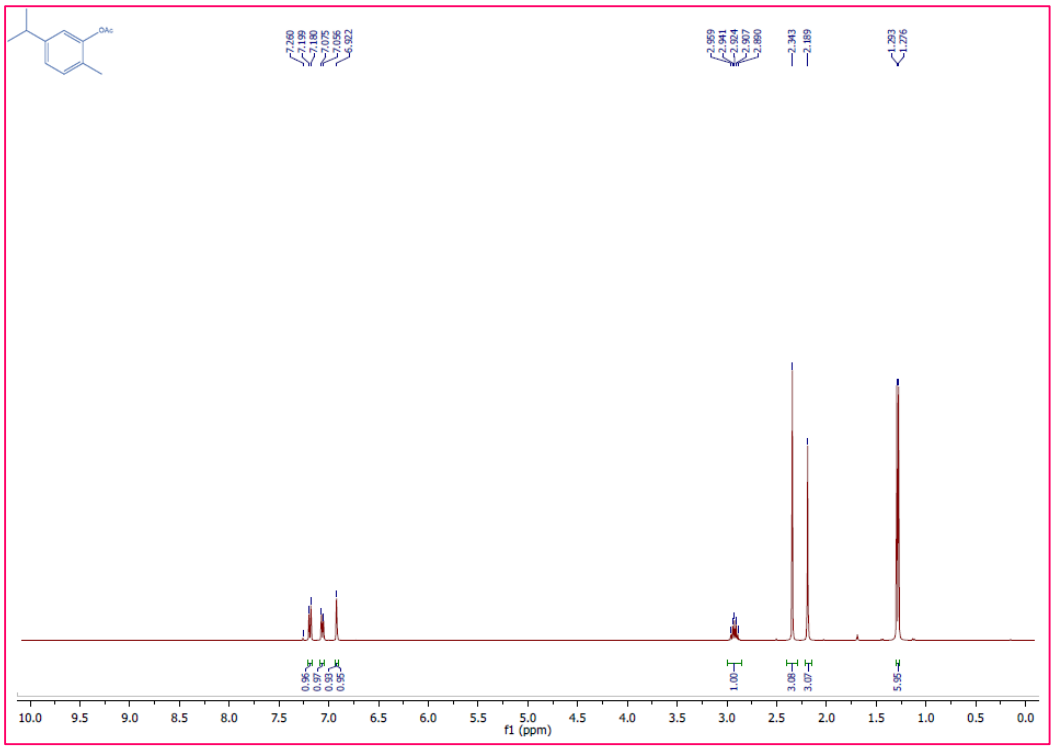


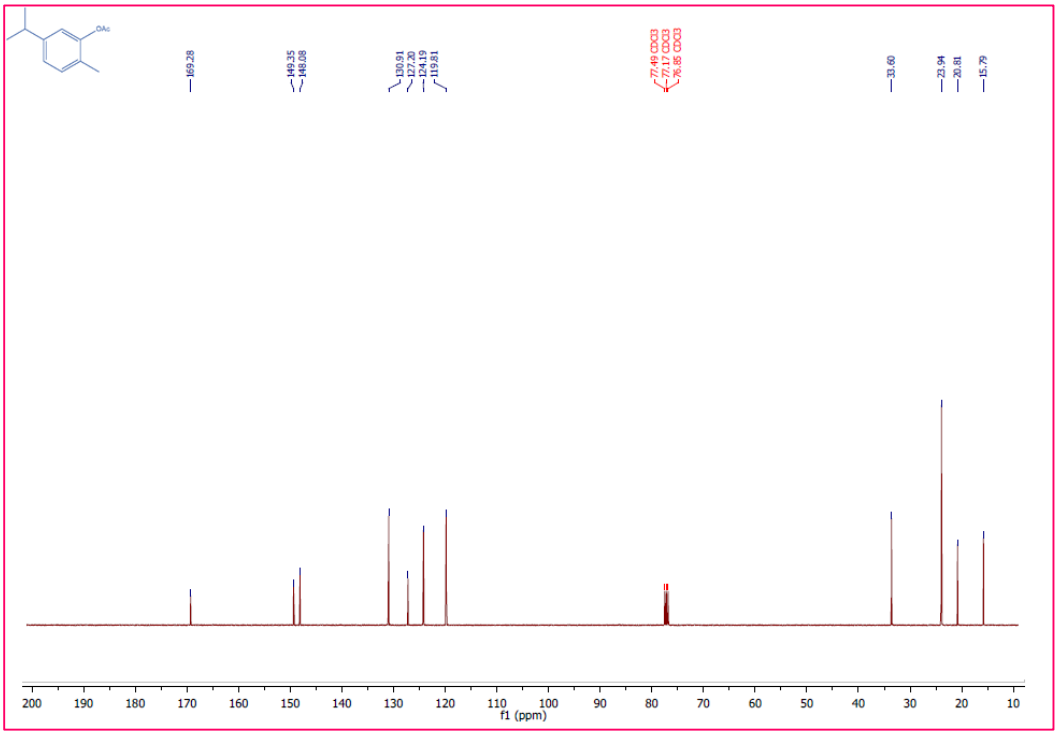
7. 2-isopropyl-5-methylphenyl acetate[12]:



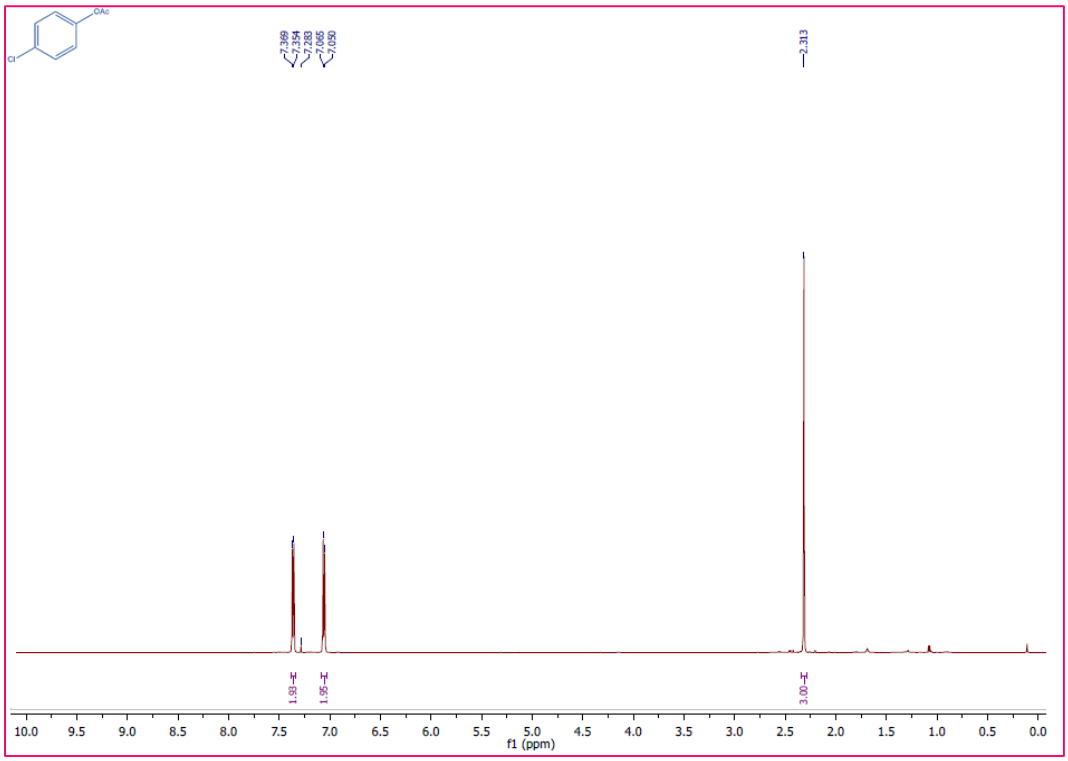


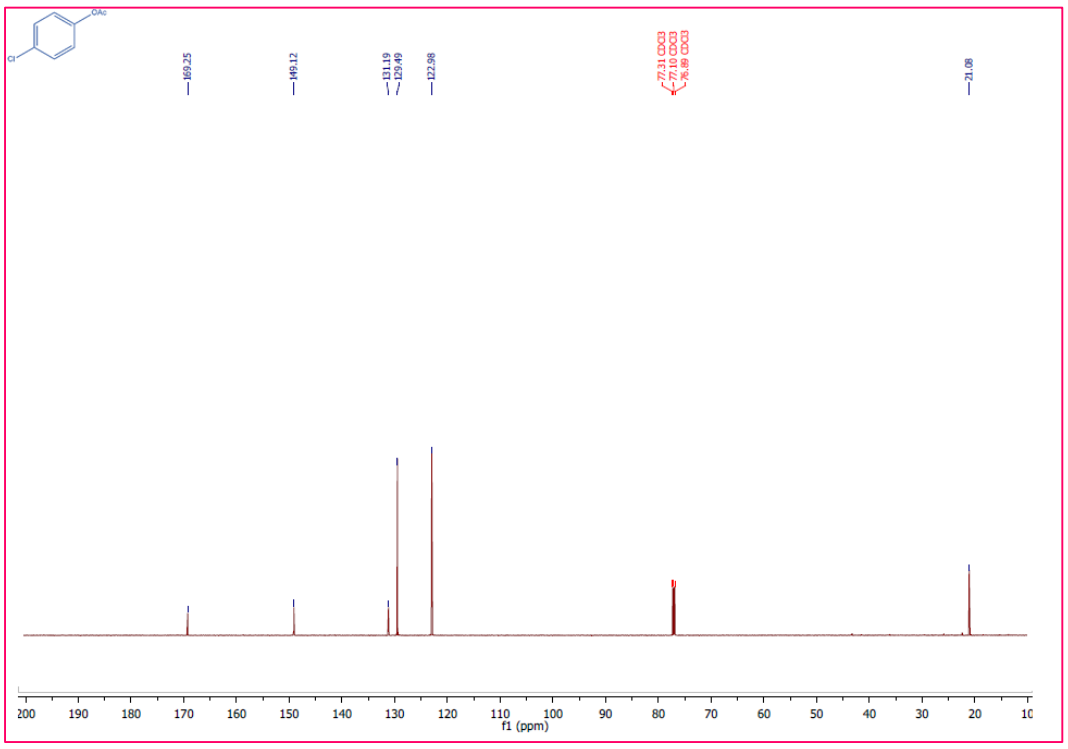
8. 5-isopropyl-2-methylphenyl acetate[11]:



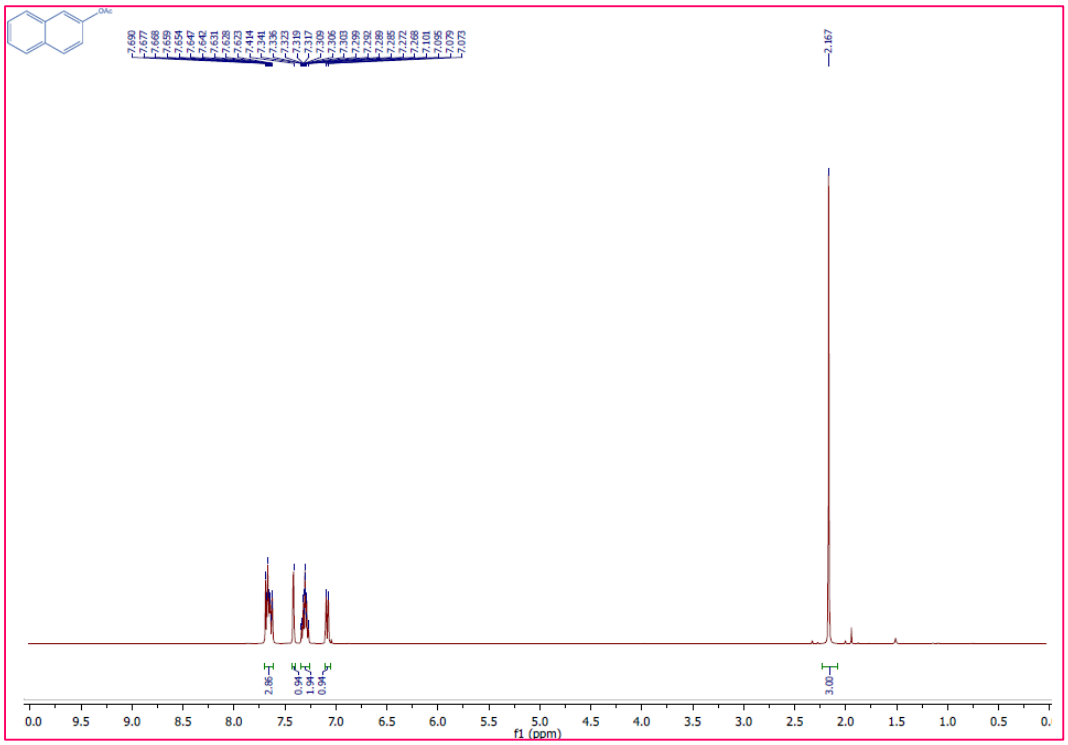


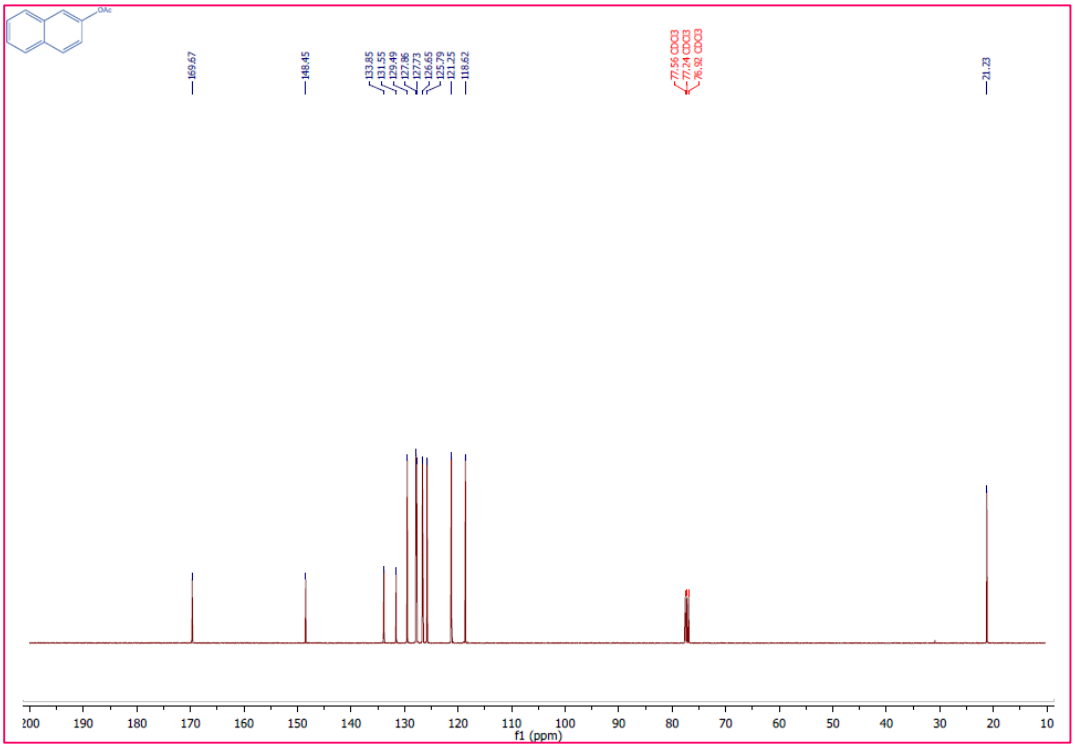
9. 4-Chlorophenyl acetate[10]:



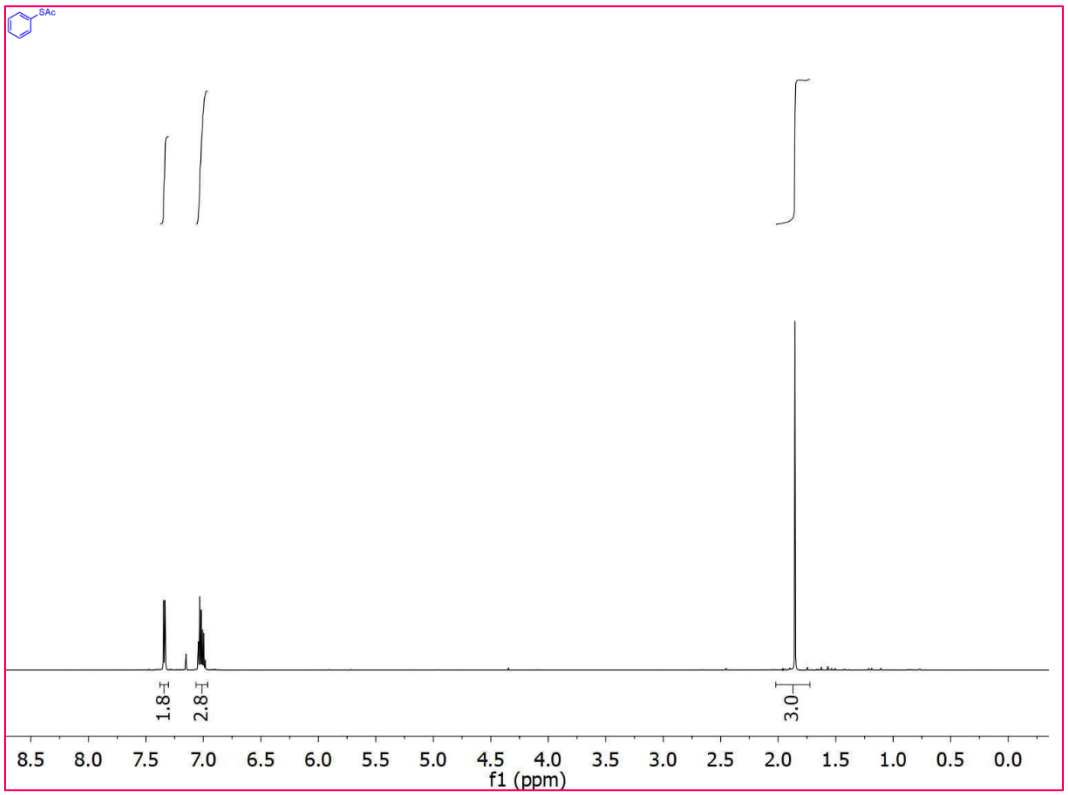


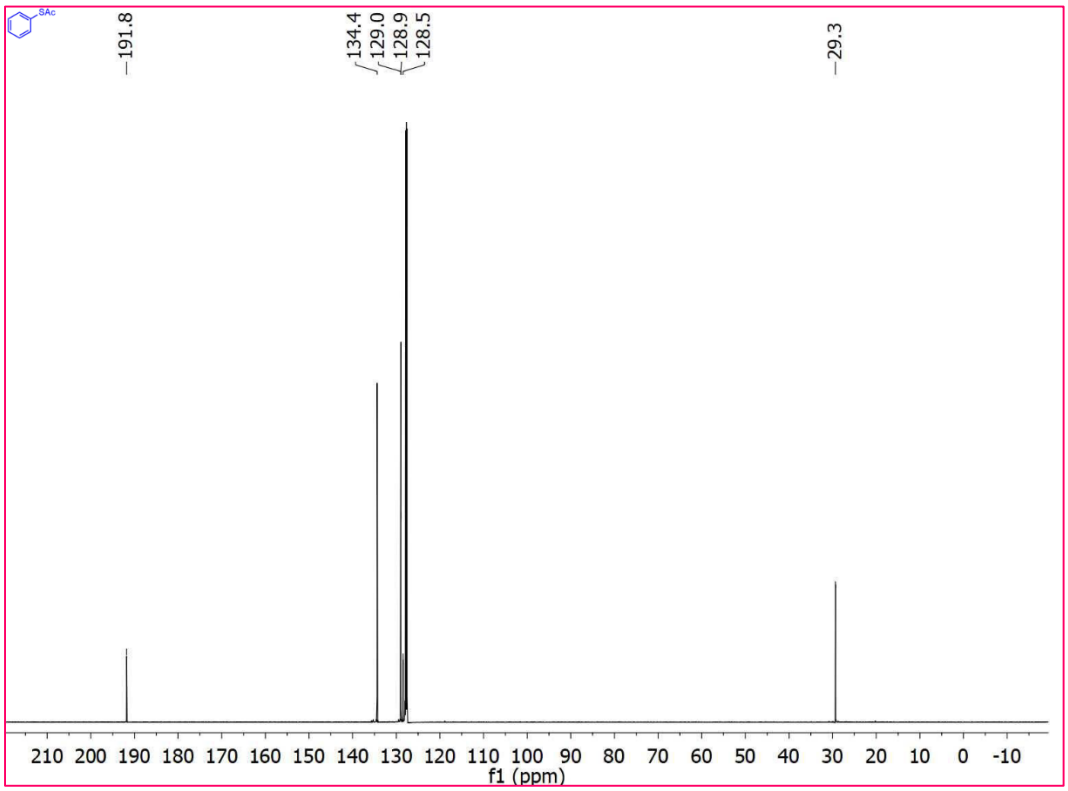
10. Naphthalen-6-yl acetate[10]:



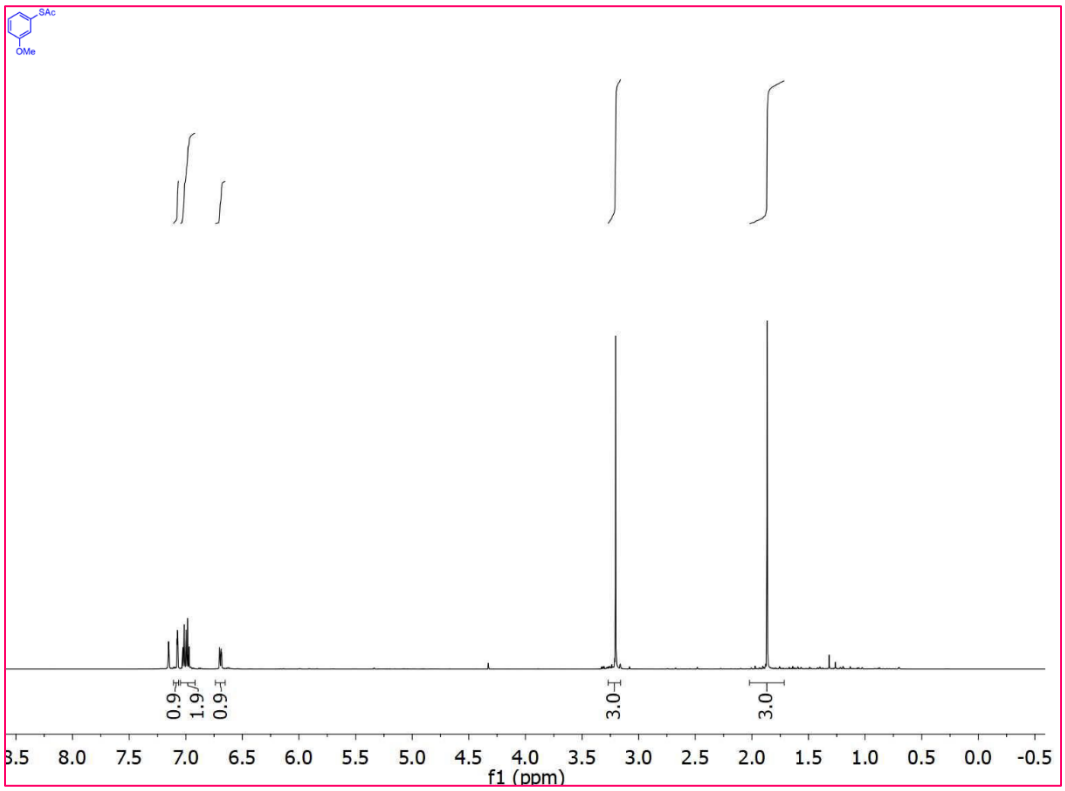


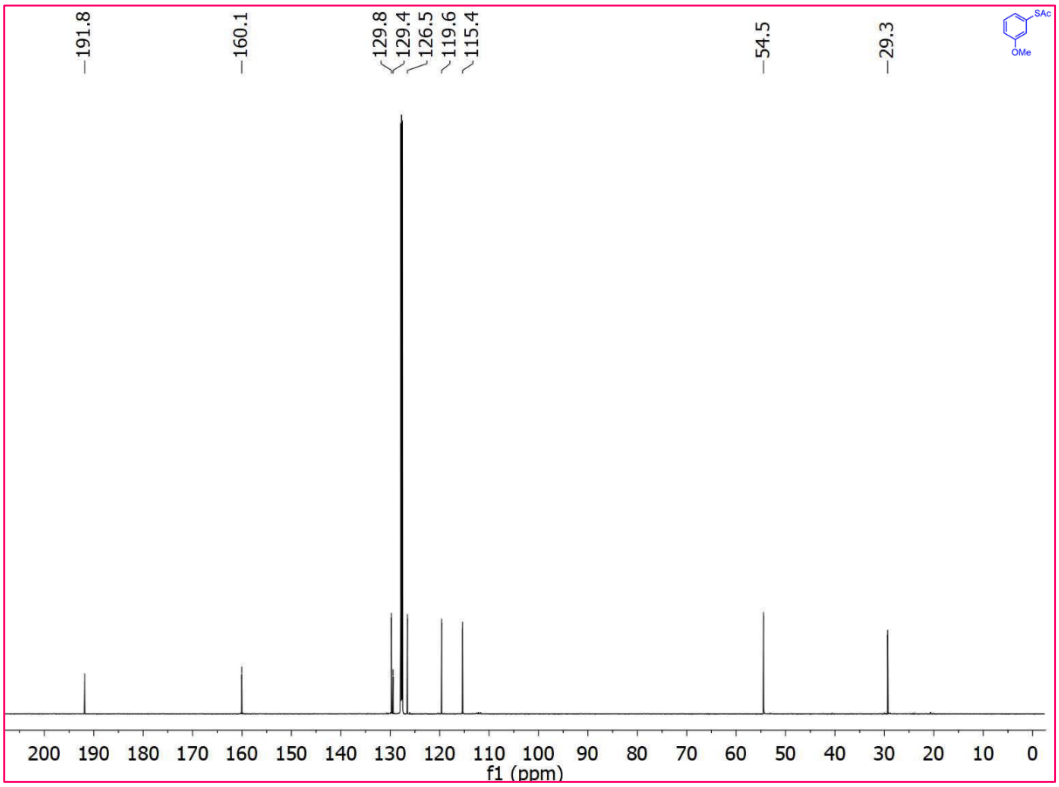
11. S-Phenyl thioacetate[14]:



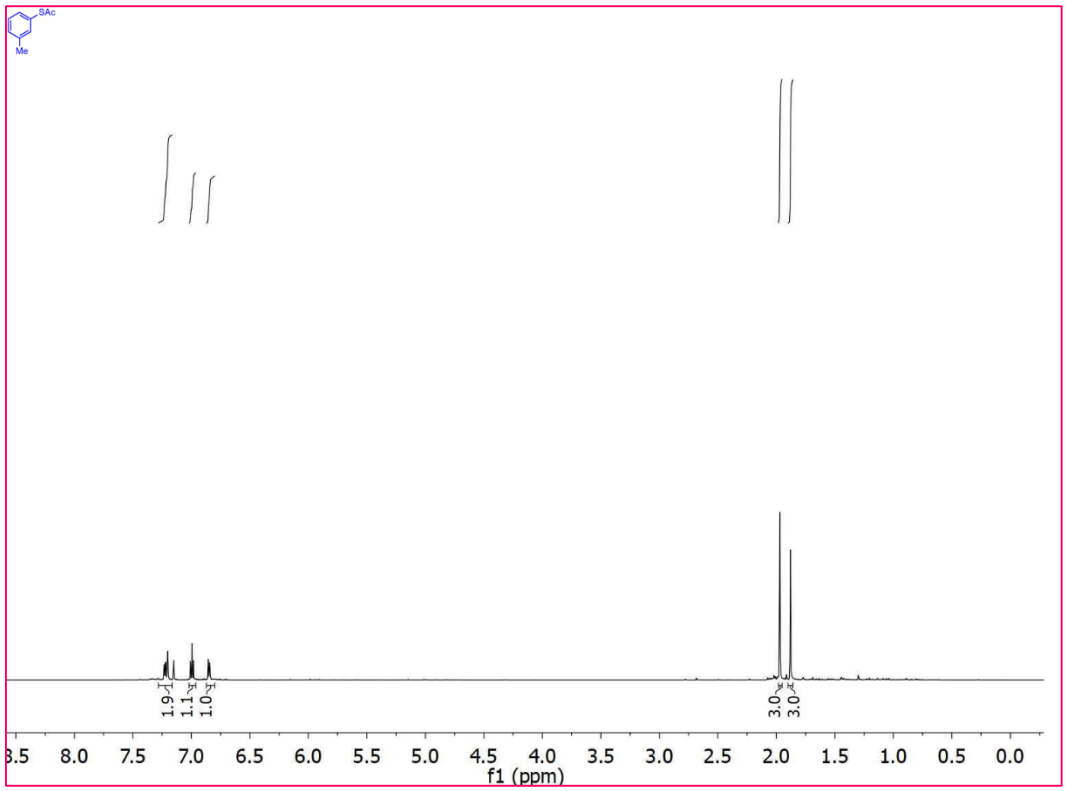


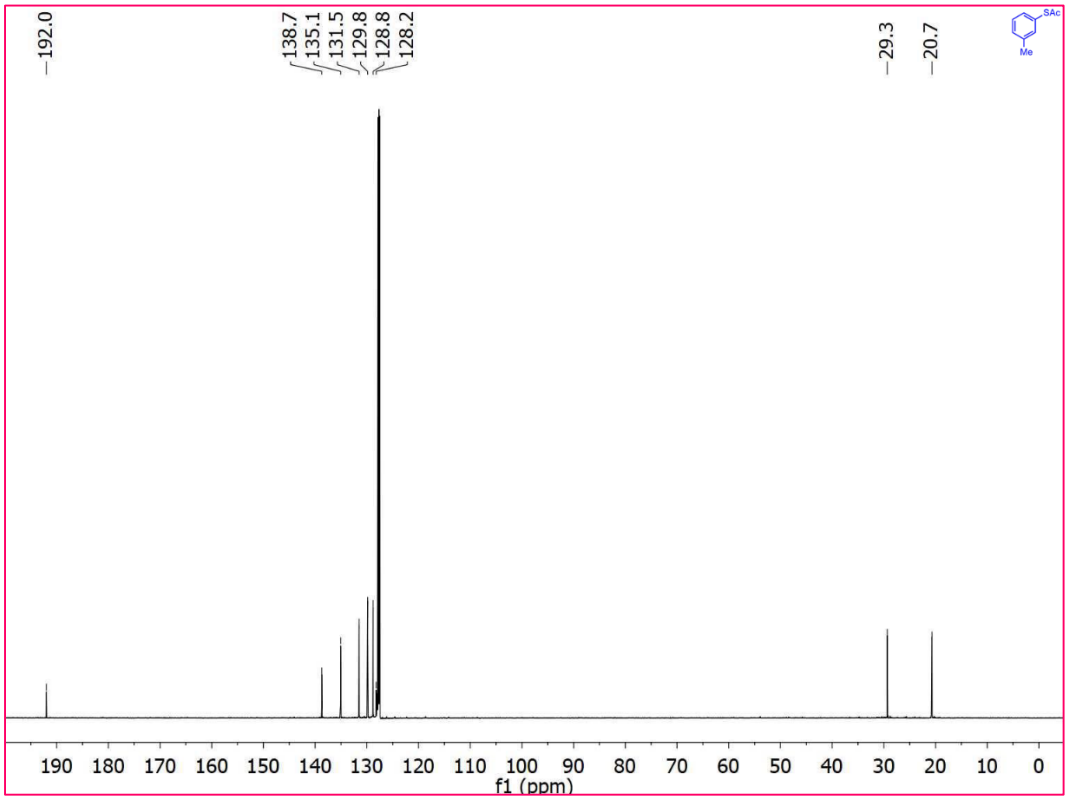
12. S-(3-Methoxy phenyl)thioacetate[14]:



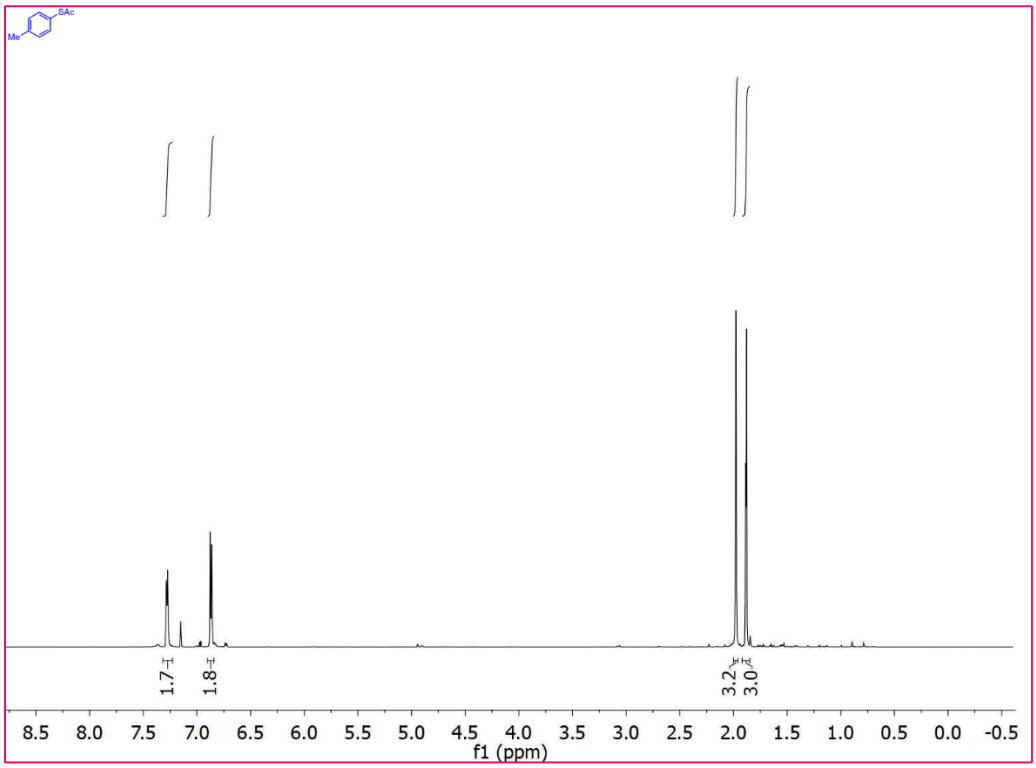


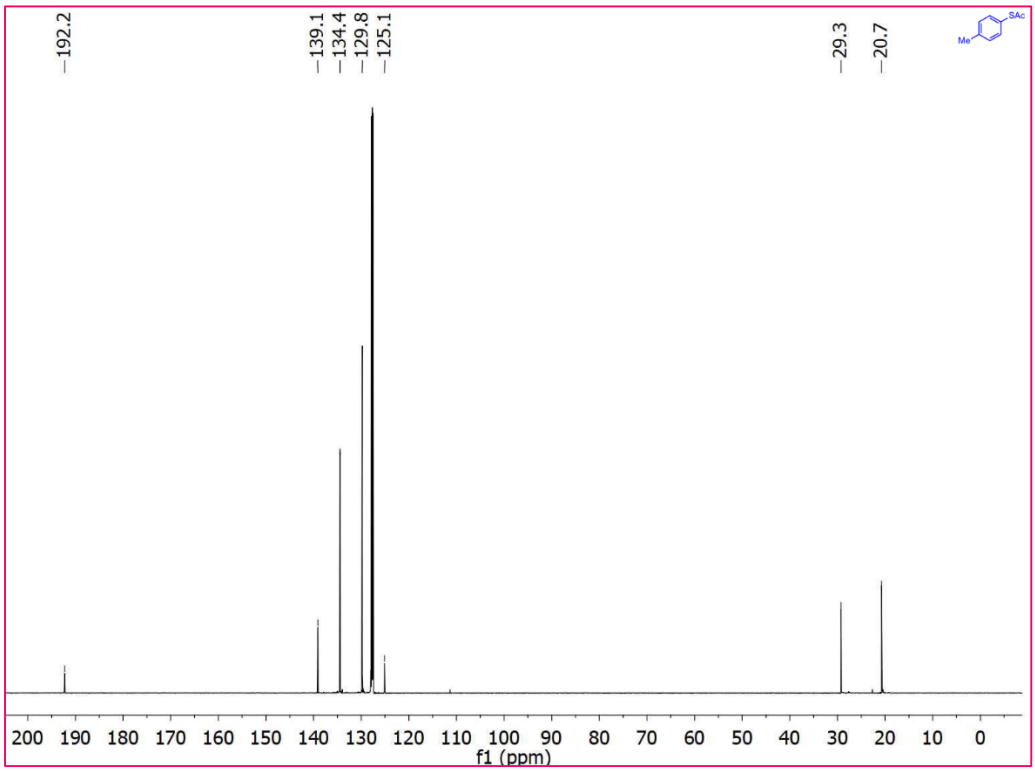
13. S-(3-Methyl phenyl) thioacetate[14]:



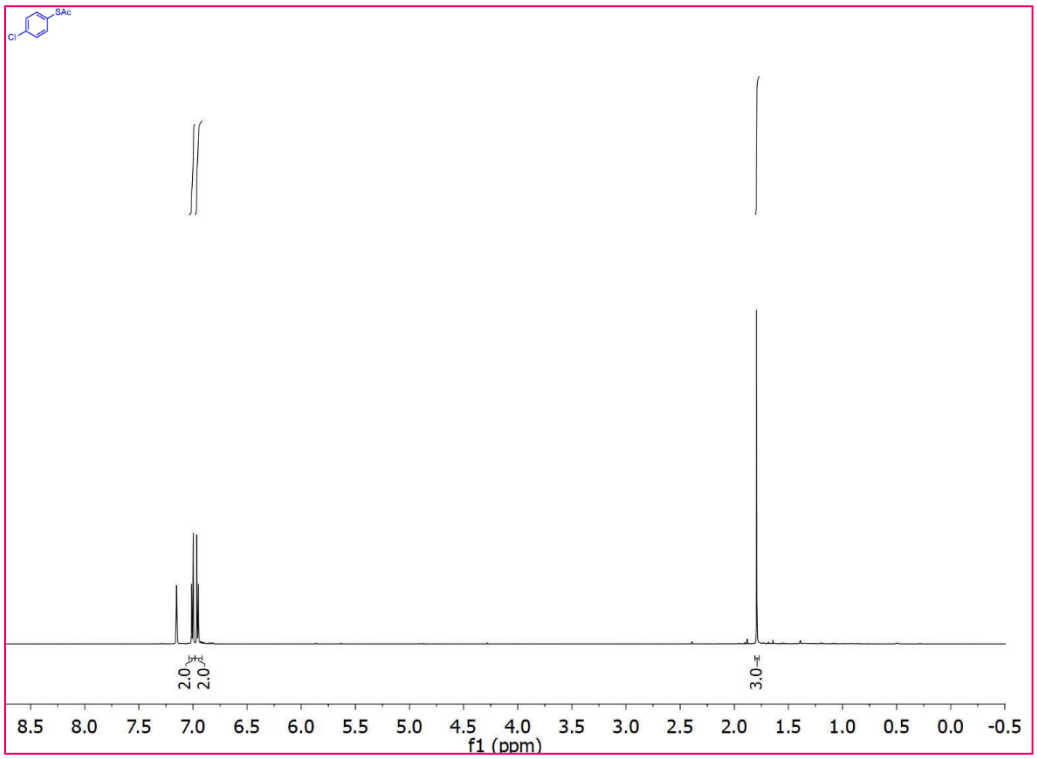


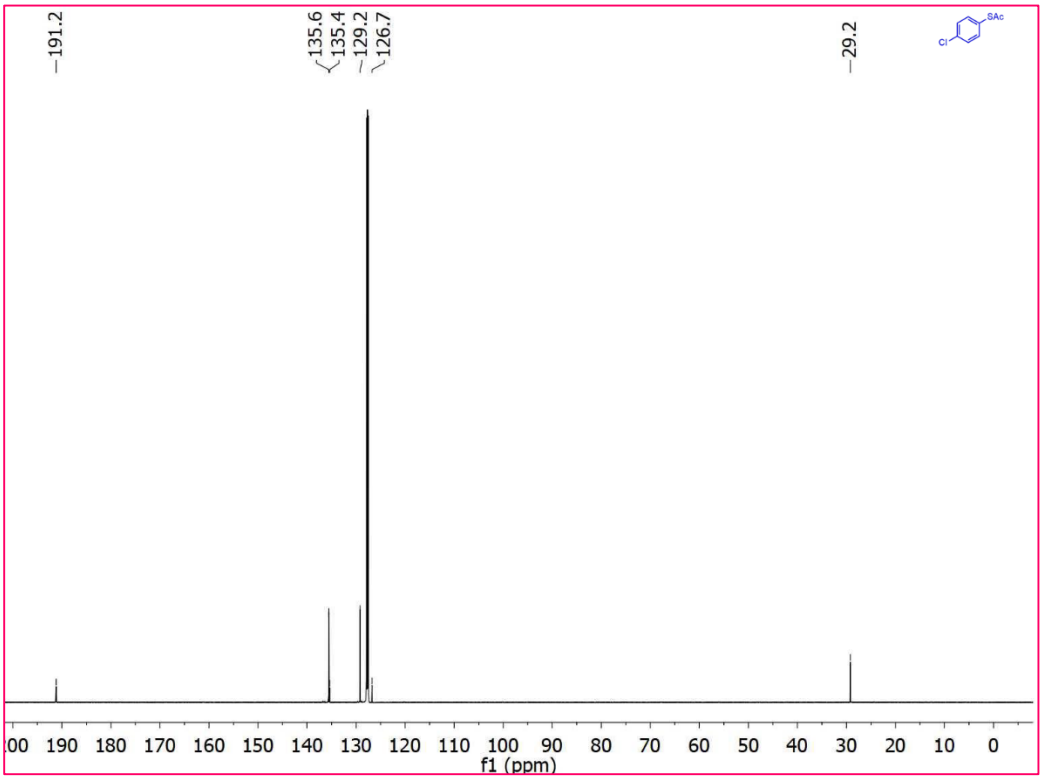
14. S-(4-Methylphenyl) thioacetate[14]:



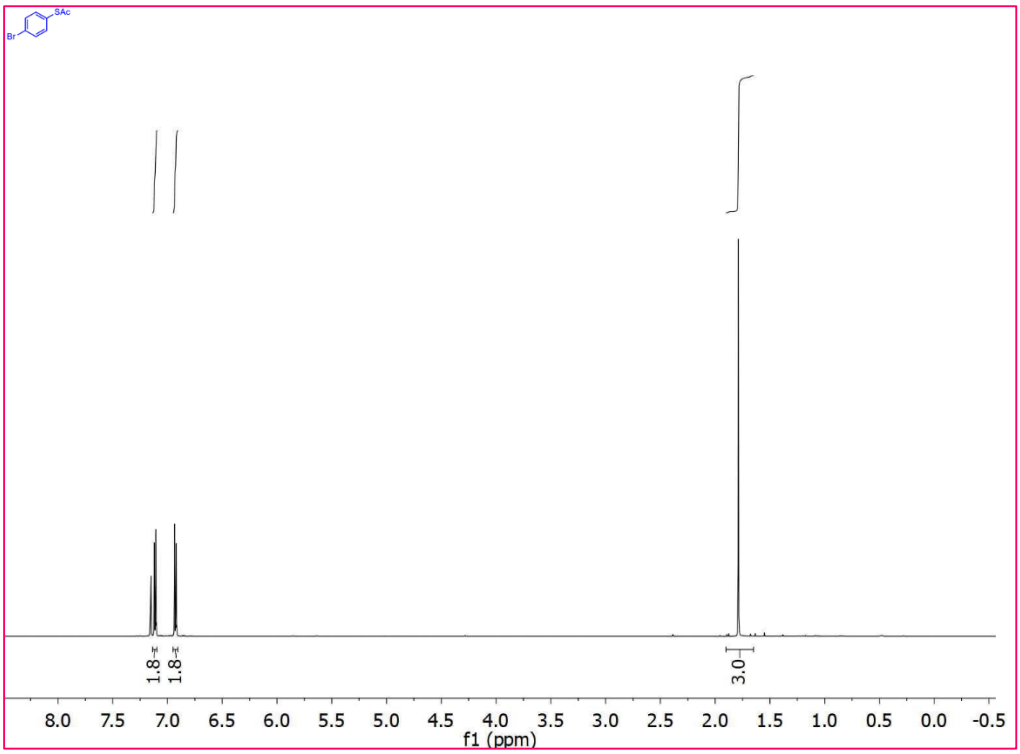


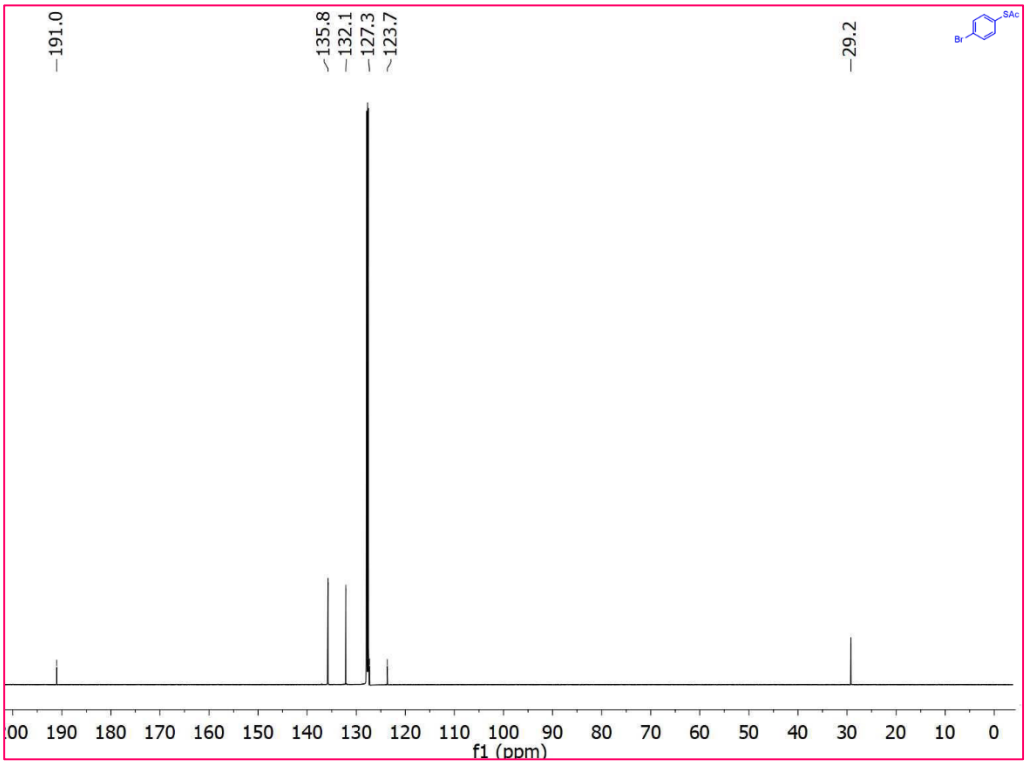
15. S-(4-Chorophenyl)thioacetate[14]:



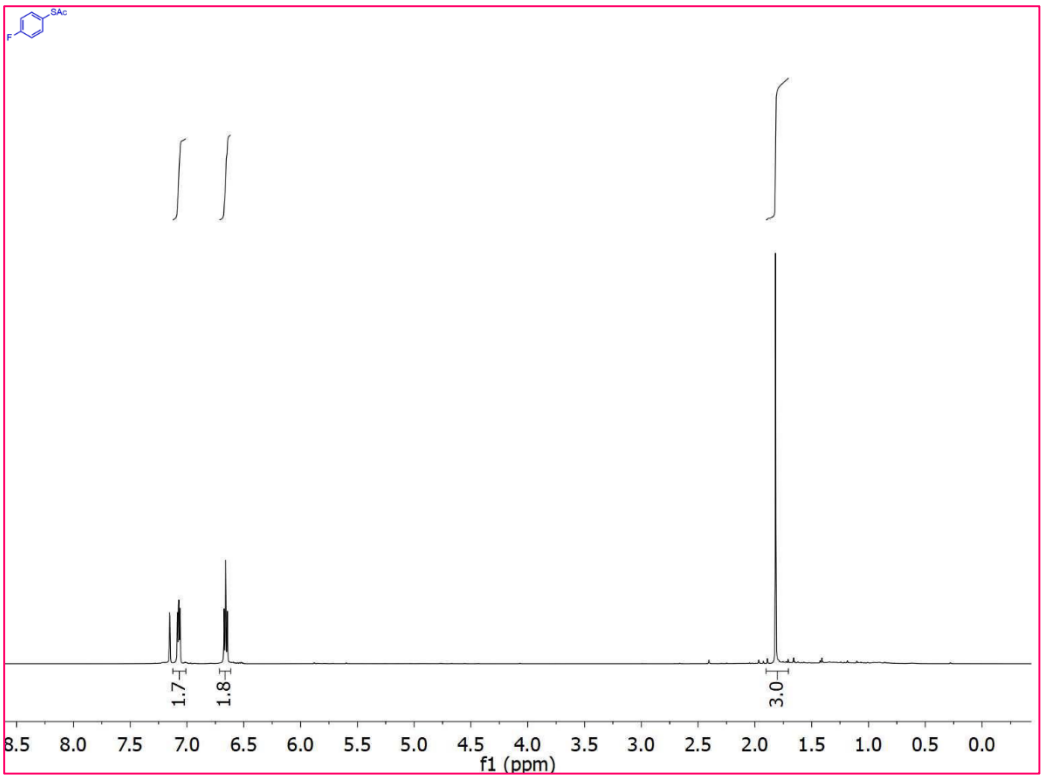


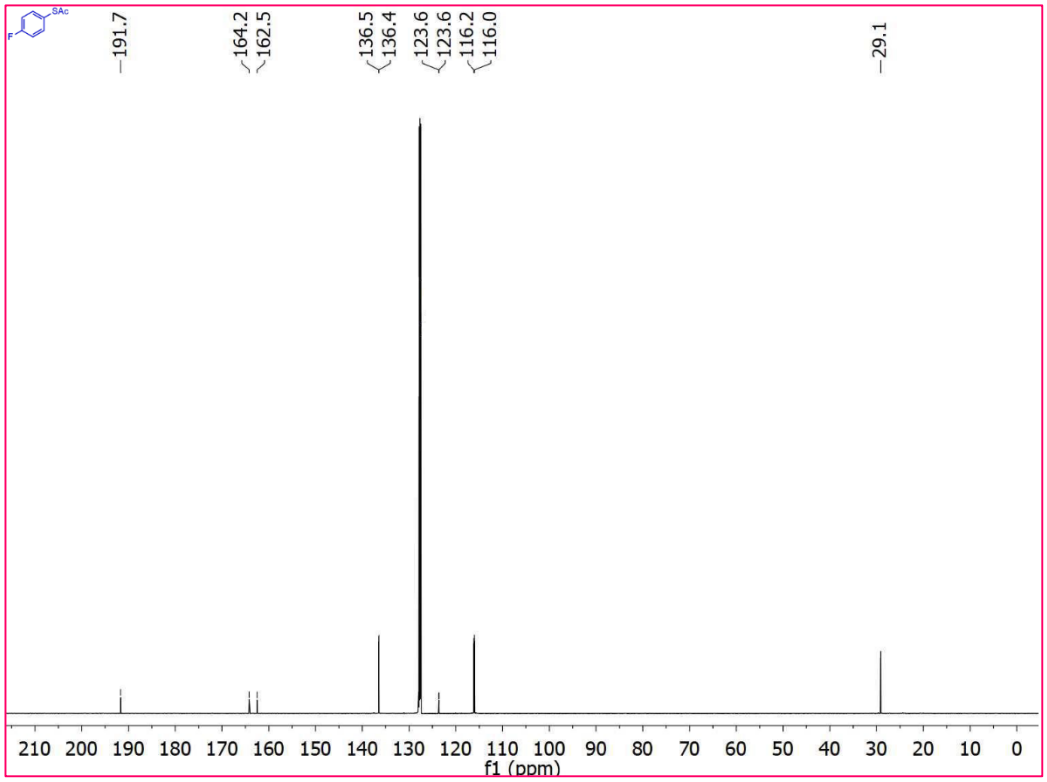
16. S-(4-Bromophenyl)thioacetate[14]:



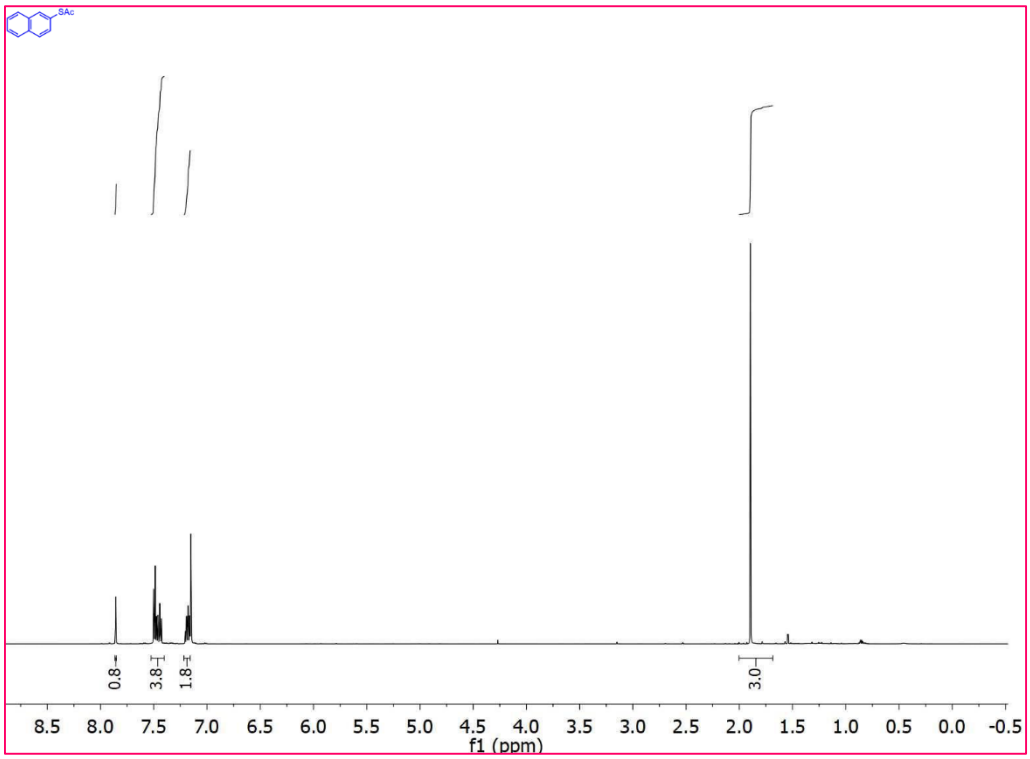


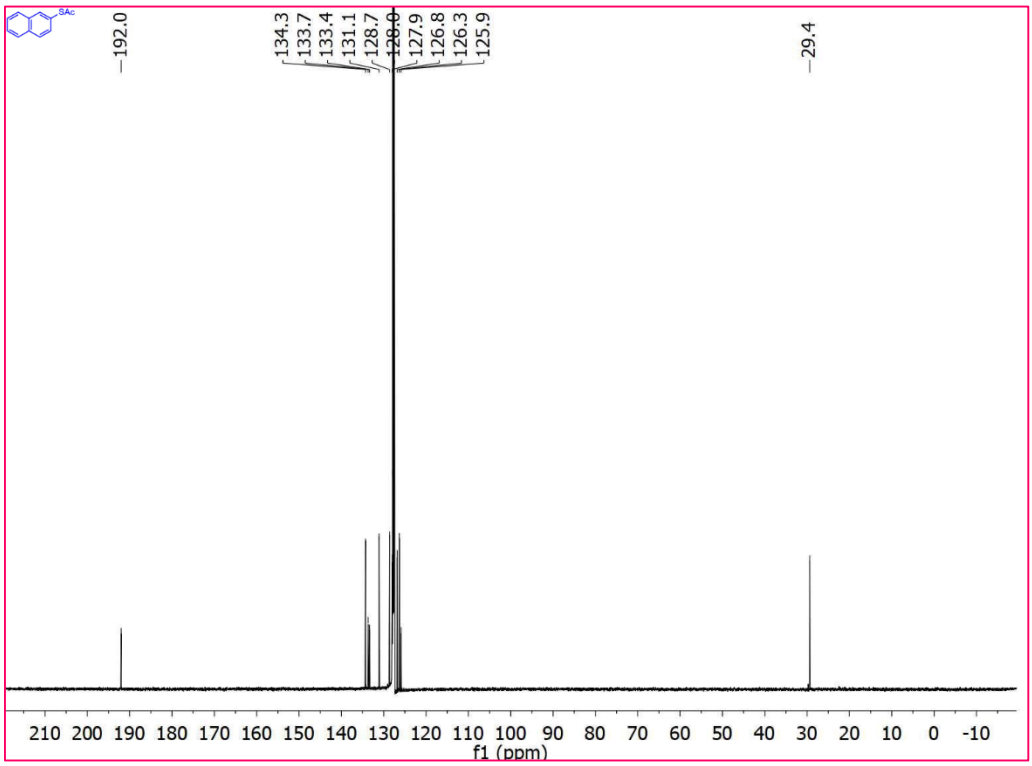
17. S-(4-Fluorophenyl) thioacetate[14]:



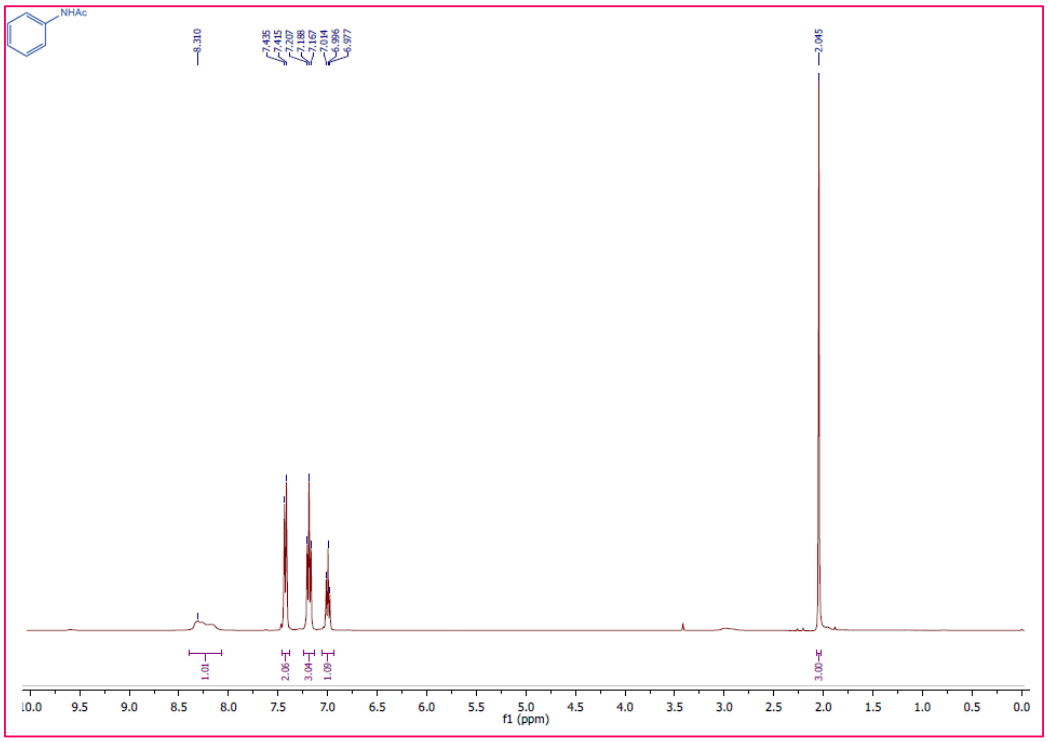


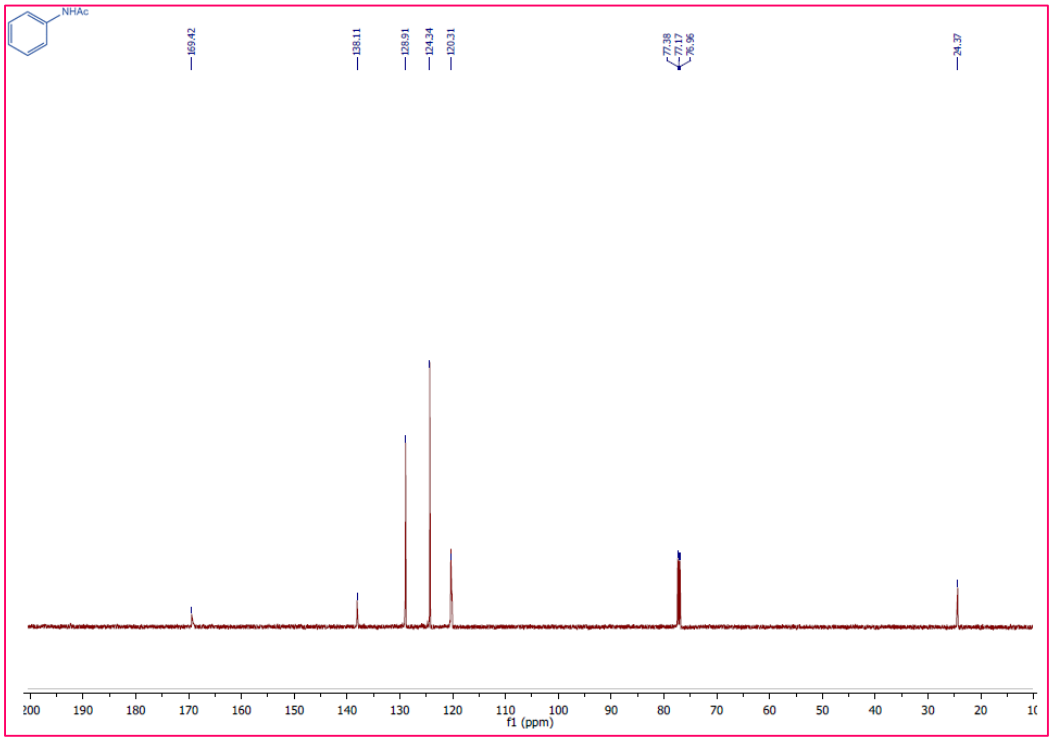
18. S-Naphthalene-2-yl thioacetate[14]:



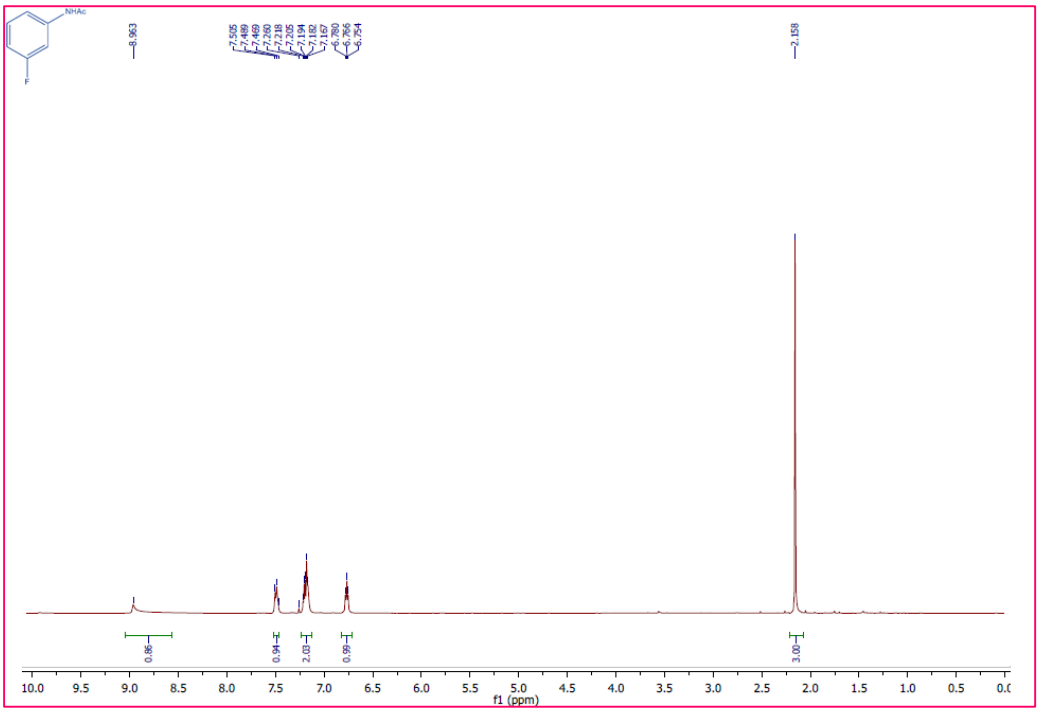


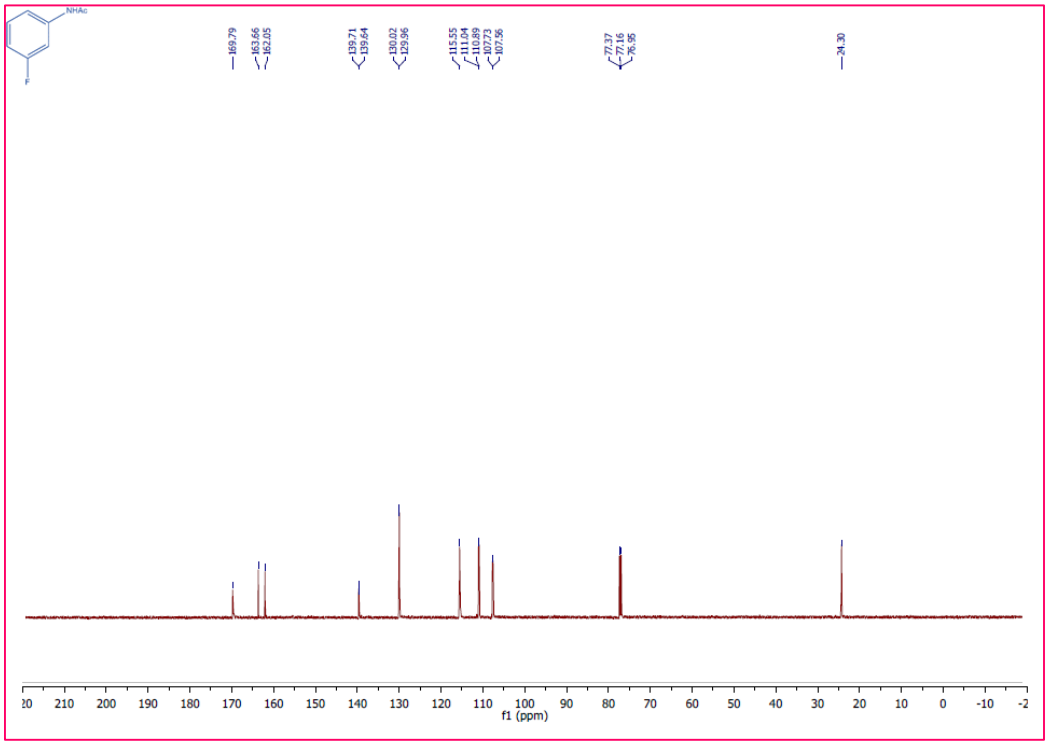
19. *N*-phenyl acetamide[1]:



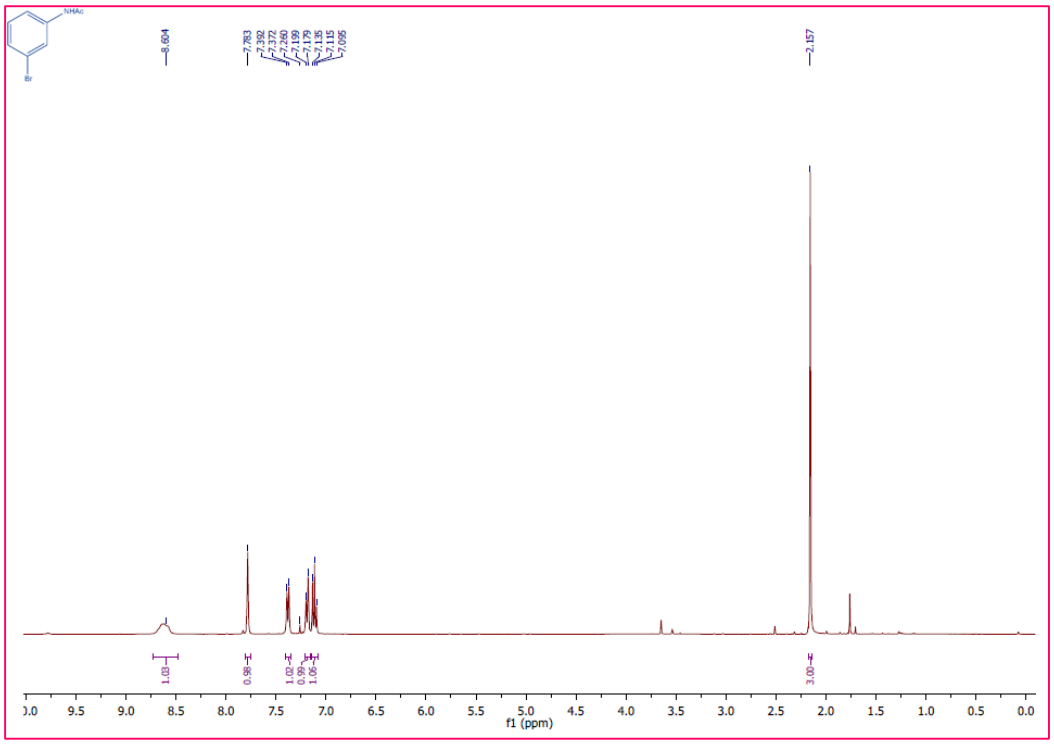


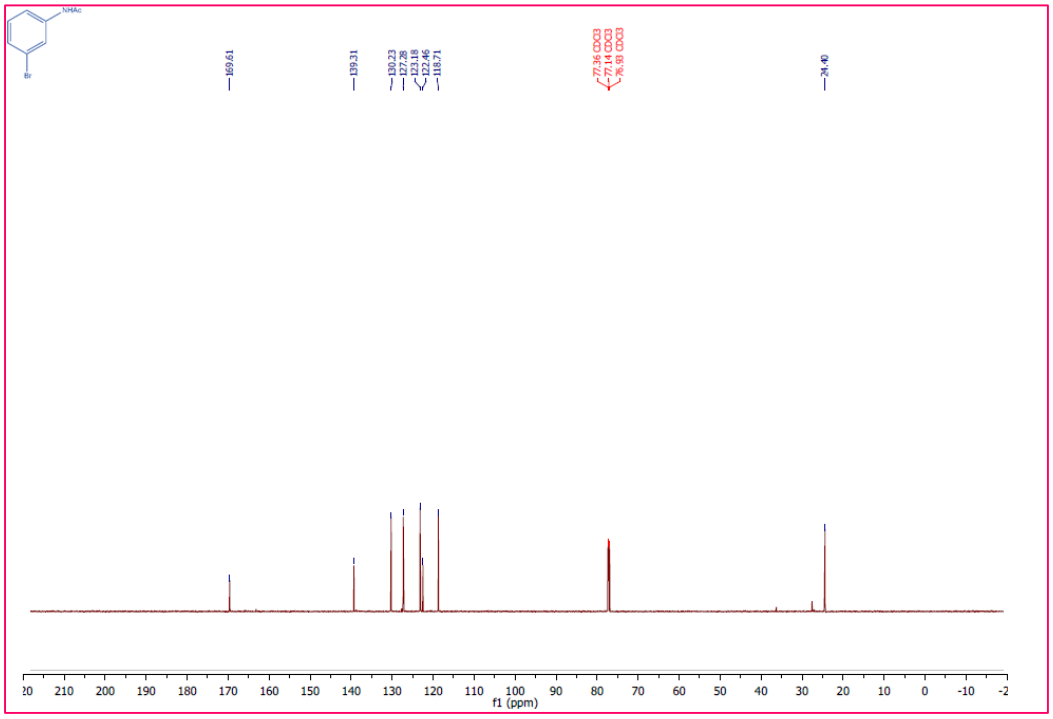
20. *N*-(3-fluorophenyl) acetamide[1]:



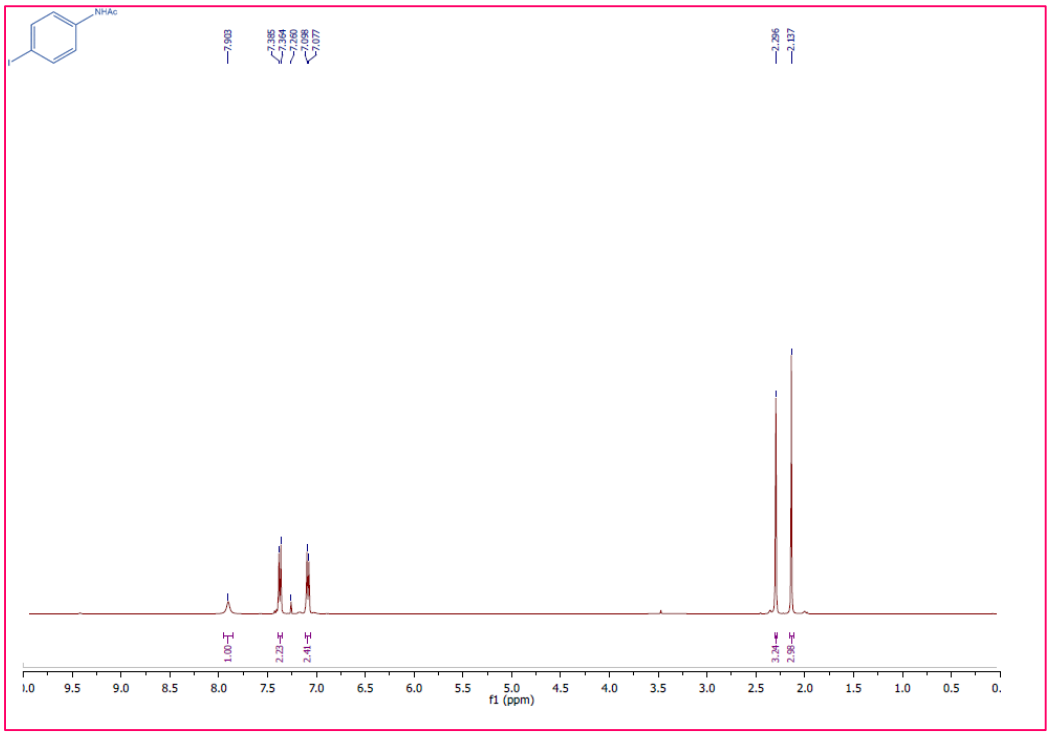


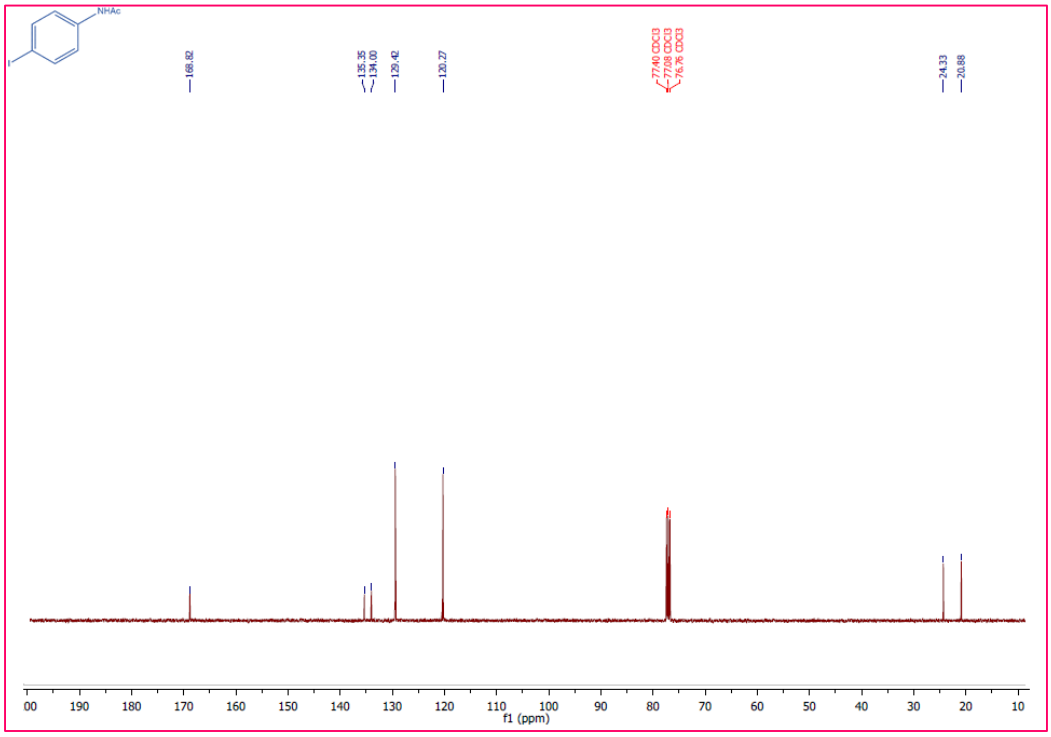
21. *N*-(3-bromophenyl) acetamide[6]:



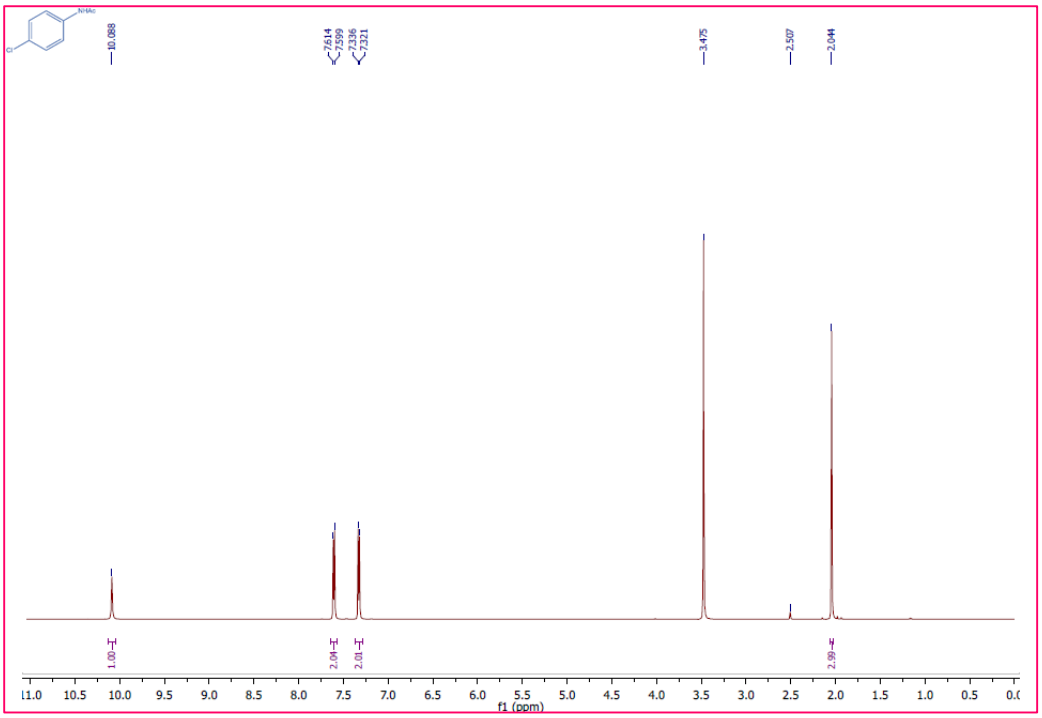


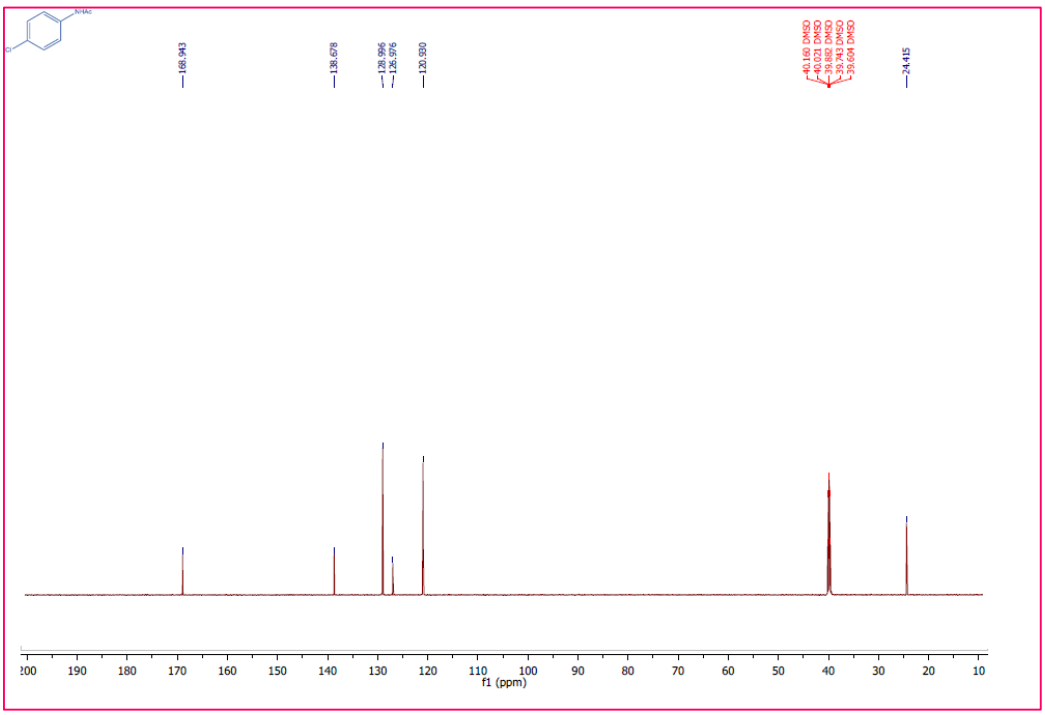
22. *N*-(4-iodophenyl) acetamide[5]:



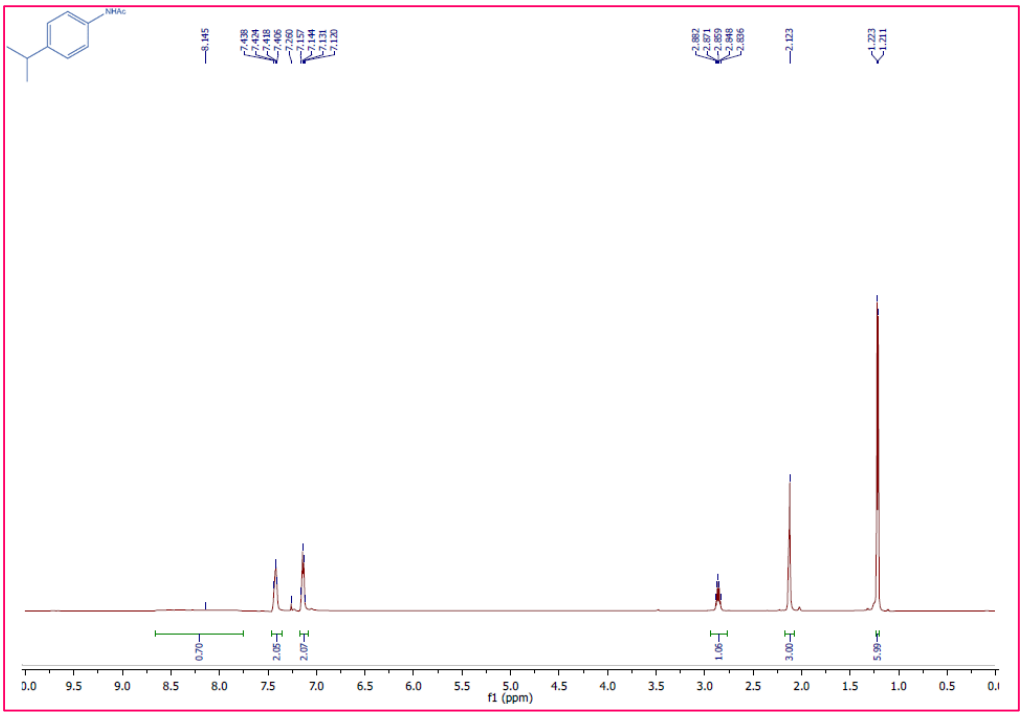


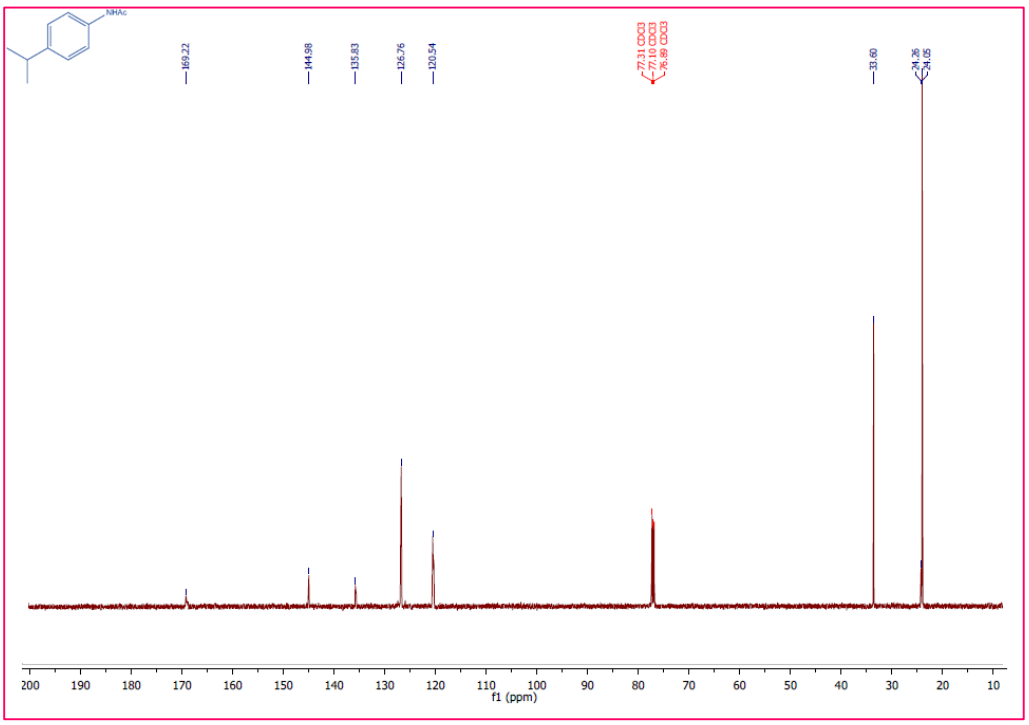
23. *N*-(4-chlorophenyl) acetamide[1]:



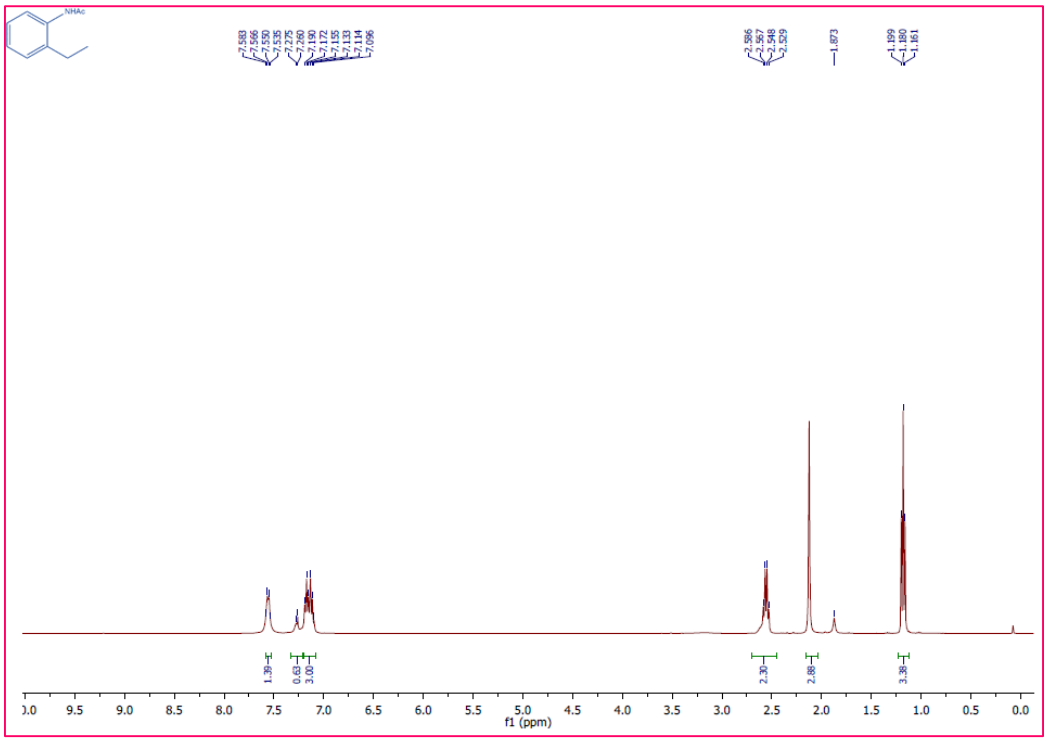


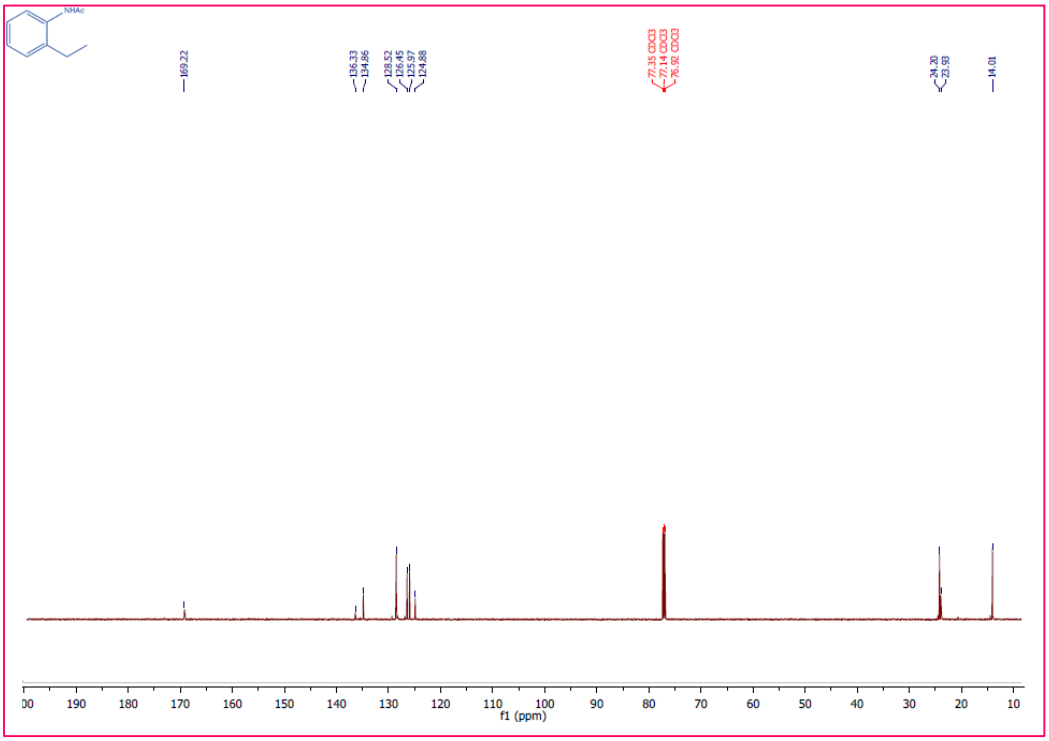
24. *N*-(4-isopropylphenyl) acetamide[3]:



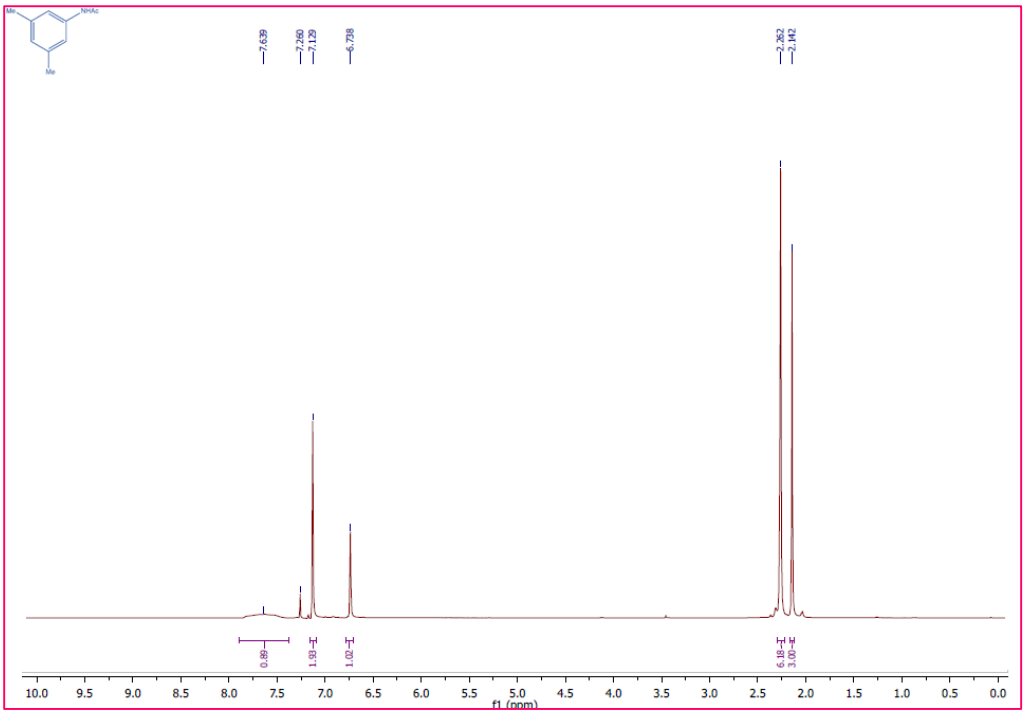


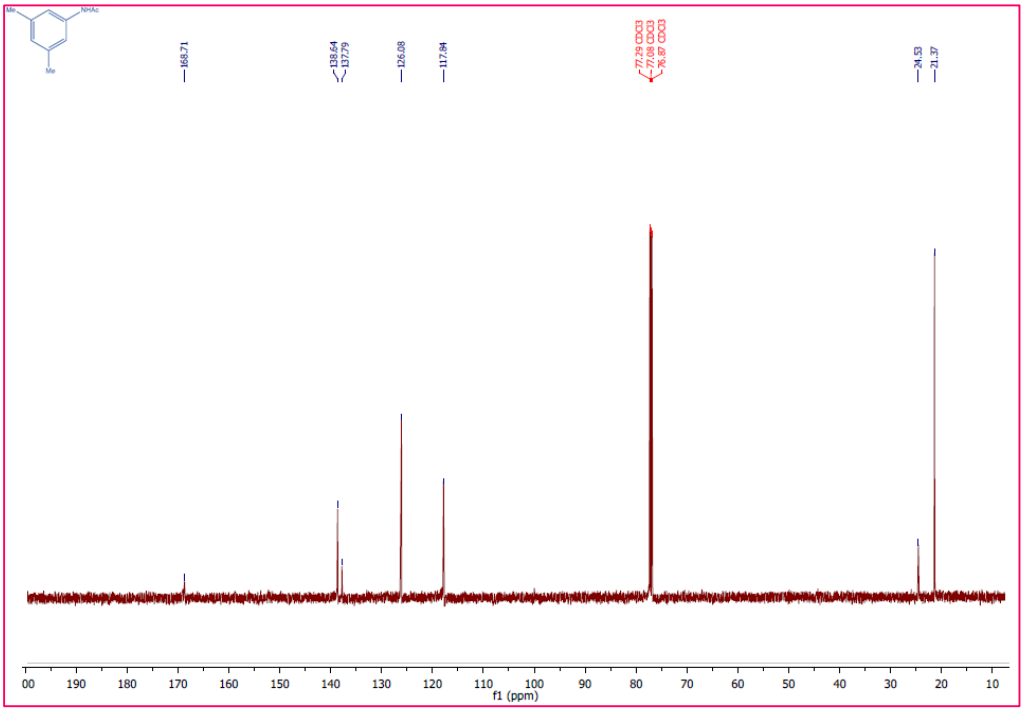
25. *N*-(2-ethylphenyl)acetamide[3]:



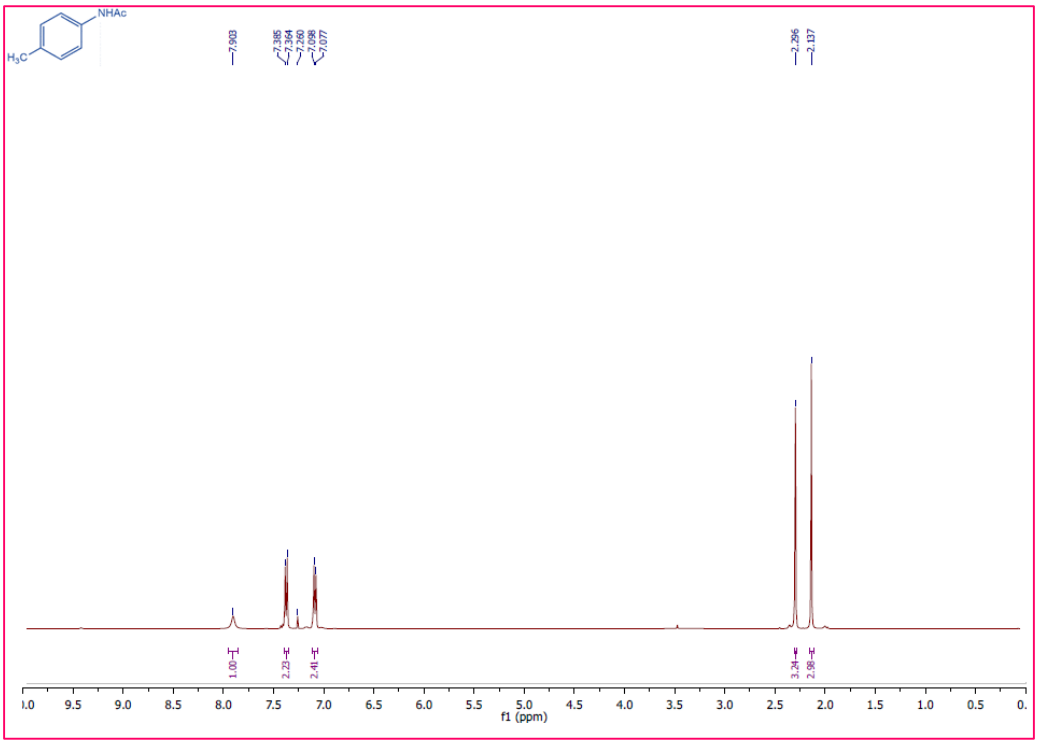


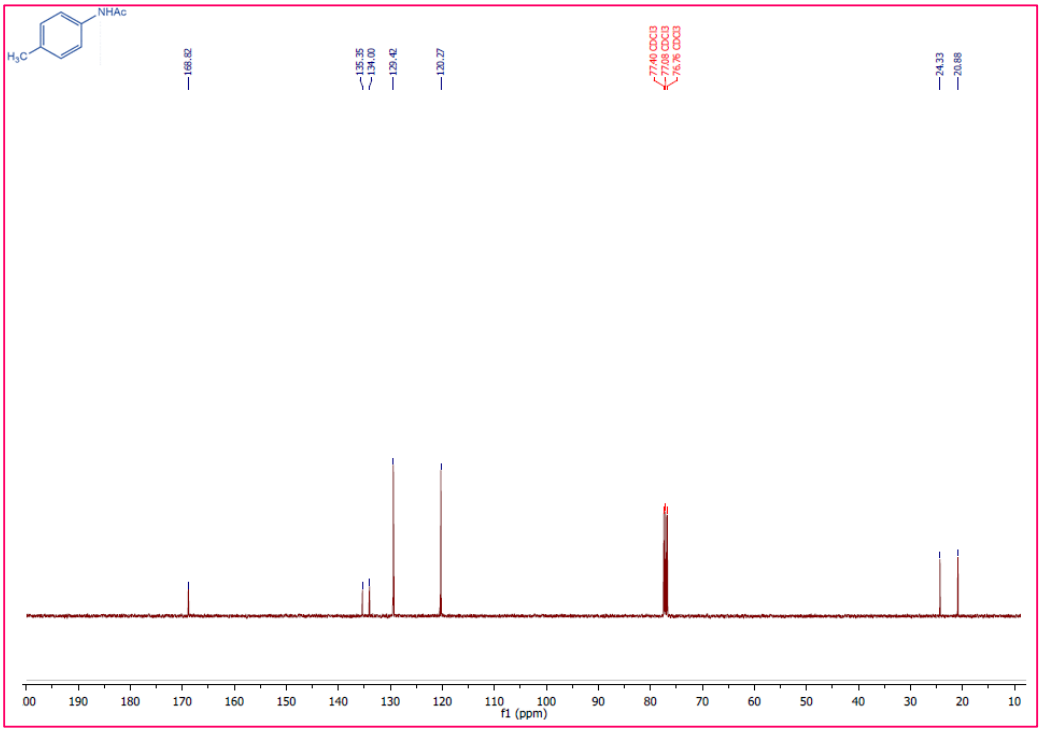
26. *N*-(3,5-dimethylphenyl)acetamide[2]:



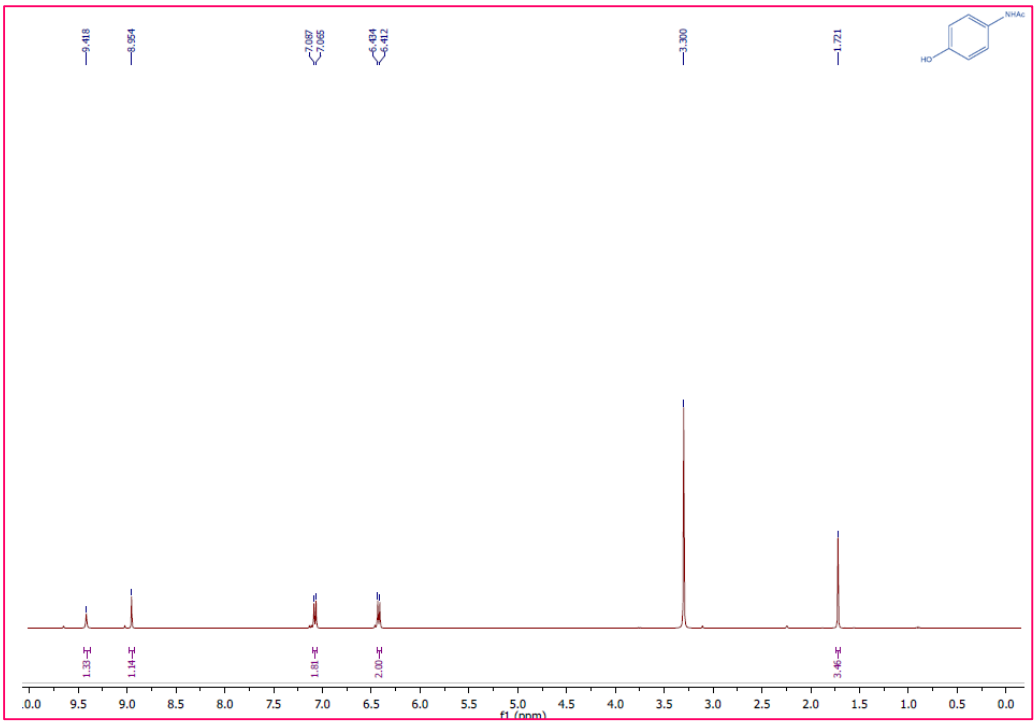


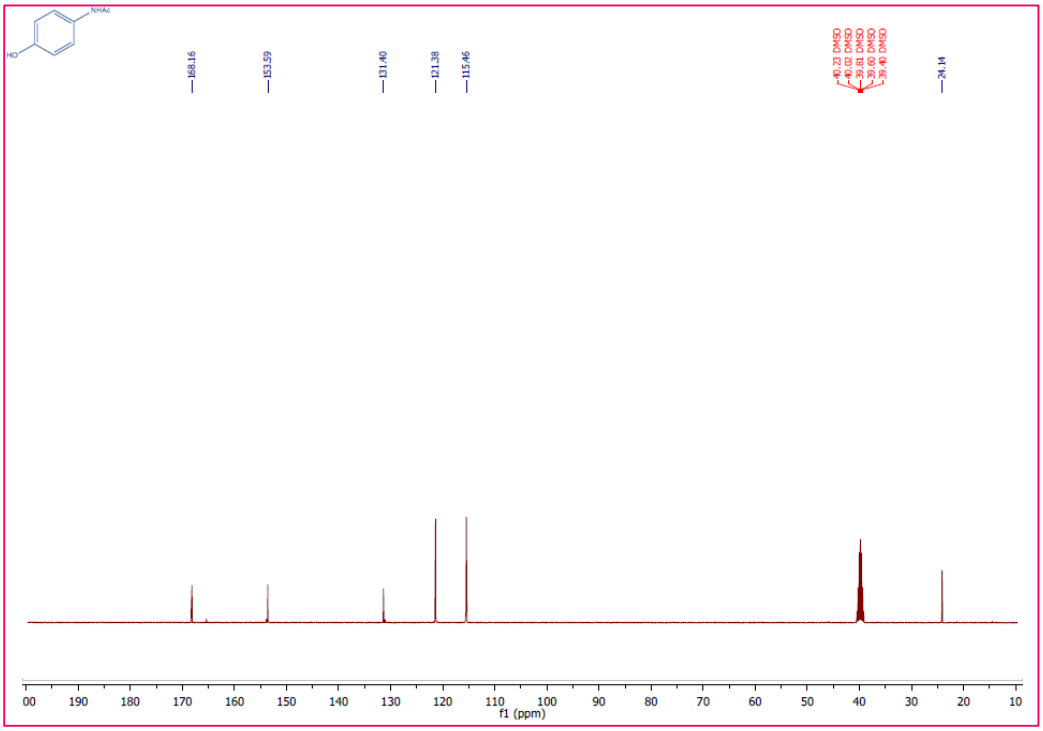
27. *N*-*p*-tolyl acetamide[1]:



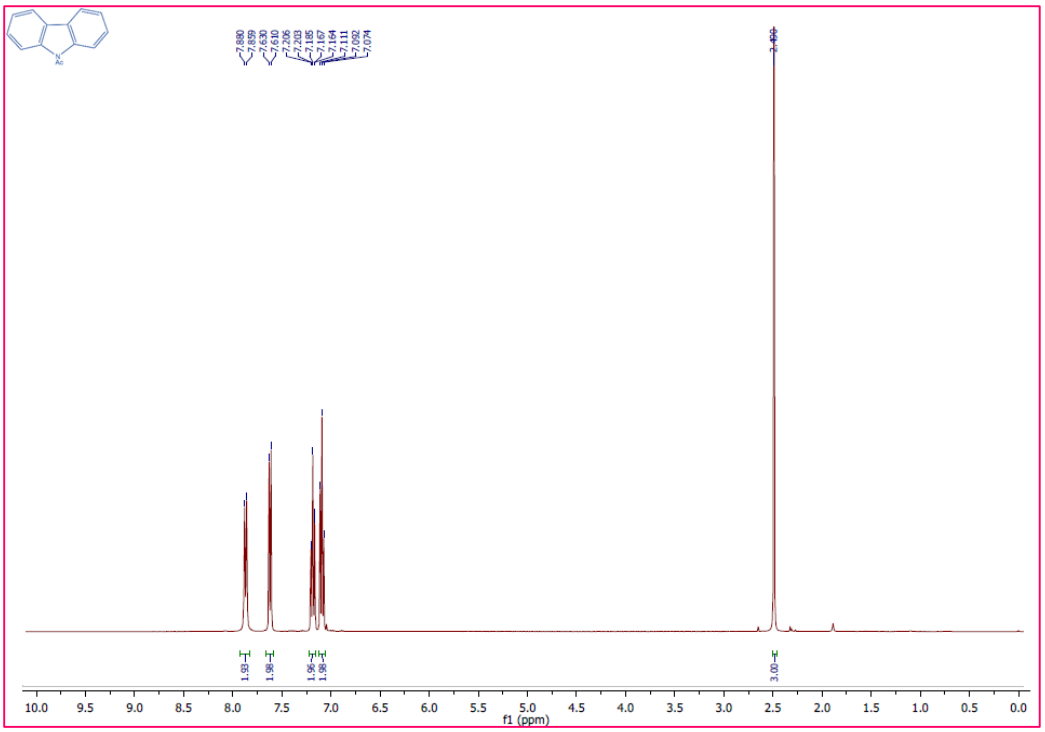


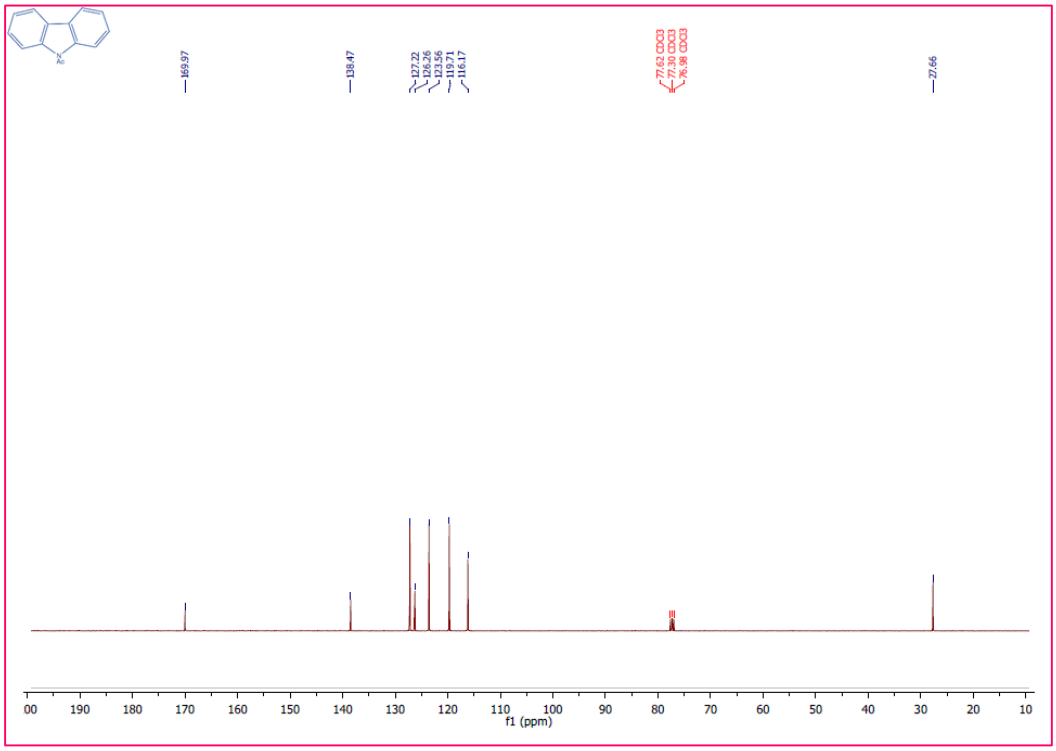
28. *N*-(4-hydroxyphenyl)acetamide[1]:





29. 1-(acridin-10(*9H*)-yl)ethanone[4]:





References

1. R. B. Sonawane, N. K. Rasal and S. V. Jagtap, Org. Lett., 2017, 19, 2078.
2. G. Zhang, Y. Zhao, L. Xuan and C. Ding, Eur. J. Org. Chem, 2019, 30, 4911.
3. B. P. Fors Karin, D. Qingle, Z. Stephen and L. Buchwald, Tetrahedron, 2009, 65, 6576.
4. V. Arumugam, W. Kaminsky and D. Nallasamy, Green Chem., 2016, 18, 3295.
5. K. Iida, S. Ishida, T. Watanabe and T. Arai, J. Org. Chem., 2019, 84, 7411.
6. M. D. H. Bhuiyan, A. B. Mahon, P. Jensen, J. K. Clegg and A. C. Try, Eur. J. Org. Chem., 2009, 5, 687.
7. U. Mandi, A. S. Roy, B. Banerjee and Sk. M. Islam, RSC Adv. 2014, 4, 42670.
8. M. J. Dur´an-Pe˜na, J. M. Botubol-Ares, J. R. Hanson, R. Hernandez-Galan and I. G. Collado, J. Am. Chem. Soc. 2014, 136, 1062.
9. A. Correa, T. Leon and R. Martin, J. Am. Chem. Soc., 2014, 136, 1062.
10. M. Kumar, S. Bagchi and A. Sharma, New J. Chem., 2015, 39, 8329.
11. H. P. Narkhede, U. B. More, D. S. Dalal and P. P. Mahulikar, Synth. Commun, 2008, 38, 2413.
12. S. M. D. Morais, N. S. Vila-Nova, C. M. L. Bevilaqua, F. C. Rondon, C. H. Lobo, A. A. A. N. Moura, A. D. Sales, A. P. R. Rodrigues, J. R. de Figuereido, C. C. Campello, M. E. Wilson and H. F. de Andrade Jr, Bioorg. Med. Chem., 2014, 22, 6250.
13. R. Das and D. Chakraborty, Synthesis, 2011, 10, 1621.
14. K. Kucinski and G. Hreczycho, Org. Process Res. Dev., 2018, 22(4), 489.