Copper-free Sandmeyer Cyanation of Arenediazonium *o*-Benzenedisulfonimides

Margherita Barbero, Silvano Cadamuro and Stefano Dughera*

Dipartimento di Chimica, Università di Torino, C.so Massimo d'Azeglio 48, 10125 Torino, Italy.

Electronic Supplementary Informations

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1. Synthesis of heteroarenediazonium *o*-benzenedisulfonimides 1u-y

According to the procedure previously reported by us[1], diazotization of heteroaromatic amines (2.5 mmol) was carried out in formic acid (10 ml) at 0-5 °C with isopentyl nitrite (0.32 g, 2.75 mmol) in the presence of *o*-benzenedisulfonimide (**6**; 0.66 g, 3 mmol)**.**

[1] M. Barbero, M. Crisma, I. Degani, R. Fochi and P. Perracino, *Synthesis*, 1998, 1171.

2. Physical and spectroscopic data of new heteroarenediazonium *o*-benzenedisulfonimides 1u-y

Thiophene-3-diazonium o-benzenedisulfonimide ***(1u)***. Brown solid; 0.72 g (88%); Found: C 36.38; H 2.12; N 12.67; S 29.50. $C_{10}H_7N_3O_4S_3$ requires: C 36.47; H 2.14; N 12.76; S 29.21%. Dp (decomposition point) 152–153 °C (MeCN/Et_2O). ^{1}H NMR (200 MHz, DMSO-d_6): δ = 9.30 (s, 1H), 8.28–8.19 (m, 2H), 7.76–7.51 (m, 4H); ^{13}C NMR (50 MHz, DMSO-d_6): δ = 147.9, 142.8, 136.4, 132.9, 130.4, 121.3, 109.9.

Pyridine-3-diazonium o-benzenedisulfonimide ***(1v)***. Orange solid; 0.58 g (71%); Found: C 40.65; H 2.54; N 17.21; S 19.64. $C_{11}H_8N_4O_4S_2$ requires: C 40.73; H 2.49; N 17.27; S 19.77%. Dp 75–76 °C (MeCN/Et_2O). ^{1}H NMR (200 MHz,DMSO-d_6): δ = 9.68 (d, *J* = 1.6 Hz, 1H), 9.18 (d, *J* = 4.8 Hz, 1H), 9.00–8.96 (m, 1H), 7.99–7.92 (m, 1H), 7.71–7.60 (m, 4H) ; ^{13}C NMR (50 MHz, DMSO-d6): δ = 157.0, 142.8, 133.4, 132.9, 130.4, 128.7, 121.3, 111.6.

Pyrimidine-2-diazonium o-benzenedisulfonimide ***(1w)***. Yellow solid; 0.59 g (73%); Found: C 36.84; H 2.14; N 21.61; S 19.74. $C_{10}H_7N_5O_4S_2$ requires: C 36.92; H 2.17; N 21.53; S 19.71%. Dp 98–99 °C (MeCN/Et_2O). ^{1}H NMR (200 MHz, DMSO-d6): δ = 9.05 (d, *J* = 4.8 Hz, 2H), 7.68–7.59 (m, 5H) ; ^{13}C NMR (50 MHz, DMSO-d6): δ = 158.0, 147.9, 143.4, 133.3, 130.4, 121.8, 110.6.

Quinoline-3-diazonium o-benzenedisulfonimide ***(1x)***. Pale orange solid; 0.88 g (94%); Found: C 48.18; H 2.63; N 15.00; S 17.07. $C_{15}H_{10}N_4O_4S_2$ requires: C 48.12; H 2.69; N 14.96; S 17.13%. Dp 107–108 °C (MeCN/Et_2O). ^{1}H NMR (200 MHz, DMSO-d_6): δ = 9.88 (d, *J* = 2.2 Hz, 1H), 9.64 (d, *J* = 2.2 Hz, 1H), 8.40–8.36 (m, 1H), 8.25–8.23 (m, 2H), 7.97–7.89 (m, 1H), 7.69–7.58 (m, 4H) ; ^{13}C NMR (50 MHz, DMSO-d_6): δ = 149.5, 147.8, 147.0, 142.8, 139.0, 132.9, 131.6, 131.2, 130.2, 124.9, 121.3, 110.8.

Benzo[d]thiazole-2-diazonium o-benzenedisulfonimide ***(1y)***. Brown solid; 0.87 g (92%); Found: C 40.99; H 2.15; N 14.68; S 25.34. $C_{13}H_8N_4O_4S_3$ requires: C 41.04; H 2.12; N 14.73; S 25.29%. Dp 132–133 °C (MeCN/Et_2O). ^{1}H NMR (200 MHz, CD_3CN): δ = 8.36–8.10 (m, 2H), 7.81–7.67 (m, 4H), 7.57–7.29 (m, 2H) ; ^{13}C NMR (50 MHz, DMSO-d6): δ = 1475, 142.8, 132.9, 130.5, 127.6, 125.9, 123.3, 121.4, 120.3, 114.7.

3. Physical and spectroscopic data of aryl cyanides 3

*4-Methoxybenzonitrile (**3a**)*. White solid; 0.31 g (93%); commercial; mp 57–58 °C (MeOH). R_f = 0.51. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.52 (d, *J* = 8.6 Hz, 2H), 6.89 (d, *J* = 8.6 Hz, 2H), 3.80 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 163.0, 133.1, 119.3, 114.7, 103.8, 55.3; IR (neat; ν CN): 2215 cm^{-1}; MS (*m/z*, EI) = 133 (M^+).

*Benzonitrile (**3b**)*. Pale yellow liquid; 0.23 g (88%); commercial. R_f = 0.64. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.41–7.35 (m, 3H), 7.27–7.21 (m, 2H) ; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 132.9, 132.1, 129.2, 118.9, 112.3, IR (neat; ν CN): 2199 cm^{-1}; MS (*m/z*, EI) = 103 (M^+).*2-Methylbenzonitrile (**3c**)*. Pale yellow liquid; 0.19 g (65%); commercial. R_f = 0.48. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.28–7.17 (m, 2H), 7.04–6.96 (m, 2H), 2.23 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 141.7, 132.7, 132.4, 130.3, 126.3, 118.0, 112.6, 20.3 ; IR (neat; ν CN): 2221 cm^{-1}; MS (*m/z*, EI) = 117 (M^+).

*3-Methylbenzonitrile (**3d**)*. Pale yellow liquid; 0.27 g (92%); commercial. R_f = 0.48. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.41–7.39 (m, 2H), 7.16–7.12 (m, 2H), 2.89 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 139.3, 133.8, 132.4, 129.2, 129.0, 118.9, 112.4, 21.0 ; IR (neat; ν CN): 2234 cm^{-1}; MS (*m/z*, EI) = 117 (M^+).

*4-Methylbenzonitrile (**3e**)*. Pale yellow liquid; 0.28 g (96%); commercial. R_f = 0.48. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.39 (d, *J* = 8.2 Hz, 2H), 7.14 (d, *J* = 8.2 Hz, 2H), 2.29 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 143.9, 132.1, 130.0, 119.3, 109.3, 21.9; IR (neat; ν CN): 2199 cm^{-1}; MS (*m/z*, EI) = 117 (M^+).

*4-Bromobenzonitrile (**3f**)*. White solid; 0.40 g (88%); commercial; mp 112–114 °C (MeOH). R_f = 0.51. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.54 (d, *J* = 8.6 Hz, 2H), 7.43 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 133.6, 132.8, 128.2, 118.2, 111.4; IR (neat; ν CN): 2223 cm^{-1}; MS (*m/z*, EI) = 181 (M^+).

*4-Chlorobenzonitrile (**3g**)*. White solid; 0.28 g (82%); commercial; mp 92–93 °C (MeOH). R_f = 0.55. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.48 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 139.6, 133.6, 129.8, 118.1, 110.9; IR (neat; ν CN): 2229 cm^{-1}; MS (*m/z*, EI) = 137 (M^+).

*4-Iodobenzonitrile (**3h**)*. White solid; 0.49 g (79%); commercial; mp 126–127 °C (MeOH). R_f = 0.58. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 138.7, 133.4, 118.4, 111.9, 100.6; IR (neat; ν CN): 2221 cm^{-1}; MS (*m/z*, EI) = 249 (M^+).

*2-Nitrobenzonitrile (**3i**)*. White solid; 0.23 g (62%); commercial; mp 108–109 °C (MeOH). R_f = 0.38. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.48–8.25 (m, 1H), 7.99–7.88 (m, 1H), 7.85–7.77 (m, 2H), ^{13}C NMR (50 MHz, $CDCl_3$): δ =148.8, 135.8, 134.7, 134.1, 125.8, 115.1, 108.4; IR (neat; ν CN): 2231 cm^{-1}; MS (*m/z*, EI) = 148 (M^+).

*3-Nitrobenzonitrile (**3j**)*. White solid; 0.32 g (87%); commercial; mp 115–116 °C (MeOH). R_f = 0.37. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.43–8.37 (m, 2H), 7.98–7.93 (m, 1H), 7.74–7.66 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 148.4, 137.9, 131.0, 127.8, 127.4, 116.8, 114.0; IR (neat; ν CN): 2239 cm^{-1}; MS (*m/z*, EI) = 148 (M^+).

*4-Nitrobenzonitrile (**3k**)*. White solid; 0.31 g (84%); commercial; mp 145–146 °C (MeOH). R_f = 0.37. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.29 (d, *J* = 8.6 Hz, 2H), 7.82 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 150.2, 133.7, 124.5, 118.5,117.0; IR (neat; ν CN): 2233 cm^{-1}; MS (*m/z*, EI) = 148 (M^+).

*2-Hydroxybenzonitrile (**3l**)*. White solid; 0.16 g (54%); commercial; mp 92–93 °C (MeOH). R_f = 0.20. ^{1}H NMR (200 MHz, DMSO-d_6): δ = 10.99 (br s, 1H), 7.49–7.37 (m, 2H), 6.95–6.76 (m, 2H); ^{13}C NMR (50 MHz, DMSO-d_6): δ = 160.8, 135.2, 133.8, 120.1, 117.7,116.8, 99.5; IR (neat; ν CN): 2245 cm^{-1}; MS (*m/z*, EI) = 119 (M^+).

*4-Hydroxybenzonitrile (**3m**)*. White solid; 0.27 g (90%); commercial; mp 111–112 °C (MeOH). R_f = 0.20. ^{1}H NMR (200 MHz, DMSO-d_6): δ = 10.54 (br s, 1H), 7.52 (d, *J* = 8.6 Hz, 2H), 6.81 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR (50 MHz, DMSO-d_6): δ = 162.0, 135.4, 120.1, 117.0, 101.6; IR (neat; ν CN): 2237 cm^{-1}; MS (*m/z*, EI) = 119 (M^+).

*4-Acetylbenzonitrile (**3n**)*. White solid; 0.30 g (82%); commercial; mp 56–57 °C (MeOH). R_f = 0.35. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 196.7, 139.9, 132.6, 128.8, 118.1, 116.1, 26.9; IR (neat; ν CN): 2230 cm^{-1}; MS (*m/z*, EI) = 145 (M^+).

*Methyl 4-cyanobenzoate (**3o**)*. White solid; 0.31 g, (77%); commercial; mp 66–67 °C (MeOH). R_f = 0.36. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.11 (d, *J* = 8.6 Hz, 2H), 7.75 (d, *J* = 8.6 Hz, 2H), 3.96 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 165.5, 132.6, 132.1, 130.1, 117.3, 116.5, 52.8; IR (neat; ν CN): 2234 cm^{-1}; MS (*m/z*, EI) = 161 (M^+).

*Terephthalonitrile (**3p**)*. White solid; 0.25 g, (78%); commercial; mp 222–223 °C (MeOH). R_f = 0.21. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.57 (s, 4H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 132.2, 117.1, 116.8; IR (neat; ν CN): 2230 cm^{-1}; MS (*m/z*, EI) = 128 (M^+).

*2-Naphthonitrile (**3q**)*. Pale brown solid; 0.31 g, (82%); commercial; mp 66–67 °C (MeOH). R_f = 0.55. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.27 (s, 1H), 7.91–7.87 (m, 3H), 7.55–7.40 (m, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 134.0, 133.9, 132.3, 129.4, 129.2, 129.0, 128.5, 127.4, 126.3, 118.4, 109.4; IR (neat; ν CN): 2225 cm^{-1}; MS (*m/z*, EI) = 153 (M^+).

*2,6-Dimethylbenzonitrile (**3r**)*. White solid; 0.15 g, (45%); commercial; mp 90–91 °C (MeOH). R_f = 0.51. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.50 (t, *J* = 7.4 Hz, 1H), 6.98 (d, *J* = 7.4 Hz, 2H), 2.51(s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 142.2, 132.1, 127.3, 117.2, 113.3, 20.7 ; IR (neat; ν CN): 2221 cm^{-1}; MS (*m/z*, EI) = 131 (M^+).

*2,6-Dichlorobenzonitrile (**3s**)*. White solid; 0.16 g, (37%); commercial; mp 144–145 °C (MeOH). R_f = 0.60. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.48–7.32 (m, 3H), ^{13}C NMR (50 MHz, $CDCl_3$): δ = 138.6, 133.8, 128.1, 114.5, 113.4; IR (neat; ν CN): 2233 cm^{-1}; MS (*m/z*, EI) = 171 (M^+).

*2,6-Dibromobenzonitrile (**3t**)*. White solid; 0.22 g, (34%); mp 154–155 °C (MeOH; lit.[1] mp 155 °C). R_f = 0.65. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.28 (t, *J* = 8.4 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 137.6, 132.3, 128.8, 119.0, 115.4; IR (neat; ν CN): 2230 cm^{-1}; MS (*m/z*, EI) = 259 (M^+).

*Thiophene-3-carbonitrile (**3u**)*.Yellow liquid; 0.22 g, (81%); commercial. R_f = 0.62. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.83–7.78 (m, 1H), 7.32–7.28 (m, 1H), 7.15–7.12 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 135.9, 128.8, 127.7, 115.5, 110.7; IR (neat; ν CN): 2238 cm^{-1}; MS (*m/z*, EI) = 109 (M^+).

Pyridine-3-carbonitrile (**3v**). Pale brown solid; 0.19 g, (73%); commercial; mp 49–50 °C (MeOH). R_f = 0.54. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.78 (d, *J* = 1.6 Hz, 1H), 8.76–8.74 (m, 1H), 7.91–7.88 (m, 1H), 7.45–7.41 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 153.1, 153.0, 139.5, 123.9, 116.5, 110.5; IR (neat; ν CN): 2219 cm^{-1}; MS (*m/z*, EI) = 104 (M^+).

*Pyrimidine-2-carbonitrile (**3w**)*. White solid; 0.18 g, (69%); commercial; mp 44–45 °C (MeOH). R_f = 0.46. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.79 (d, *J* = 5.0 Hz, 2H), 7.50 (t, *J* = 5.0 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 158.3, 145.4, 123.9, 115.8; IR (neat; ν CN): 2194 cm^{-1}; MS (*m/z*, EI) = 105 (M^+).

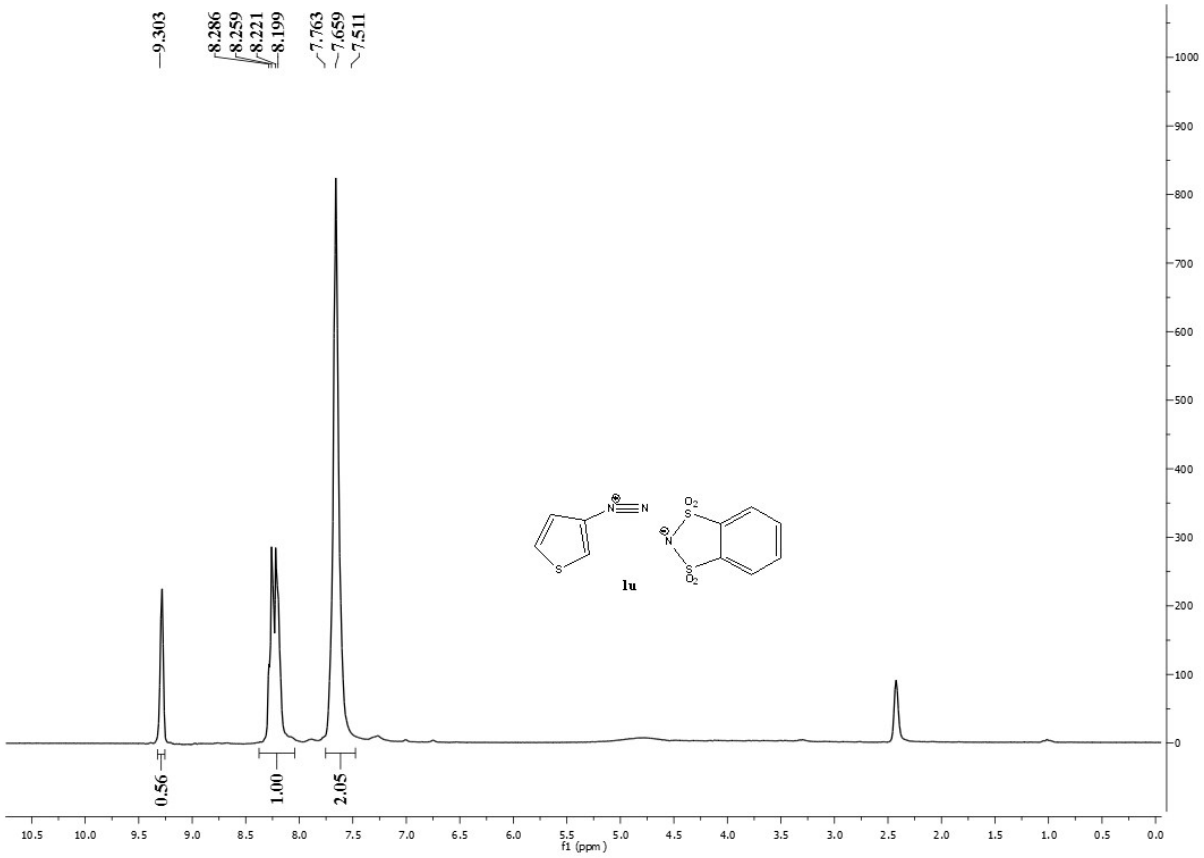
*Quinoline-3-carbonitrile (**3x**)*. White solid; 0.30 g, (78%); mp 105–106 °C (MeOH; lit.[2] 107–108 °C). R_f = 0.41. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 9.00 (d, *J* = 2.8 Hz, 1H), 8.54 (d, *J* = 2.8 Hz, 1H), 8.19–8.17 (m, 1H), 7.92–7.87 (m, 2H), 7.71–7.69 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 150.1, 149.5, 143.3, 133.4, 130.6, 129.4, 129.1, 126.1, 115.1, 107.2; IR (neat; ν CN): 2234 cm^{-1}; MS (*m/z*, EI) = 154 (M^+).

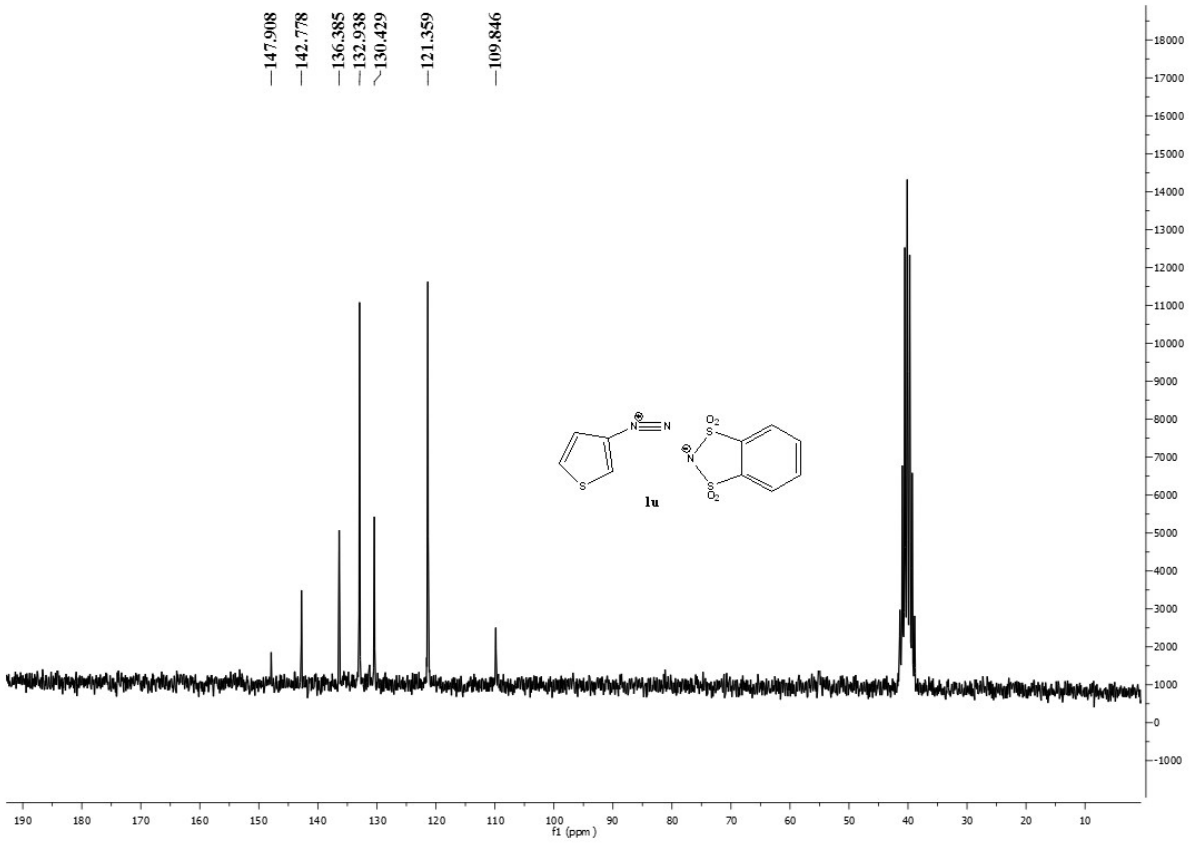
Benzo[d]thiazole-2-carbonitrile ***(3y)***. Pale yellow solid; 0.32 g, (80%); mp 76–77 °C (MeOH; lit.[3] 75–77 °C). R_f = 0.35. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.40–8.32 (m, 1H), 8.22–8.14 (m, 2H), 7.54–7.44 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 152.0, 137.3, 135.7, 129.1, 128.7, 126.1, 122.4, 112.8; IR (neat; ν CN): 2228 cm^{-1}; MS (*m/z*, EI) = 160 (M^+).

References

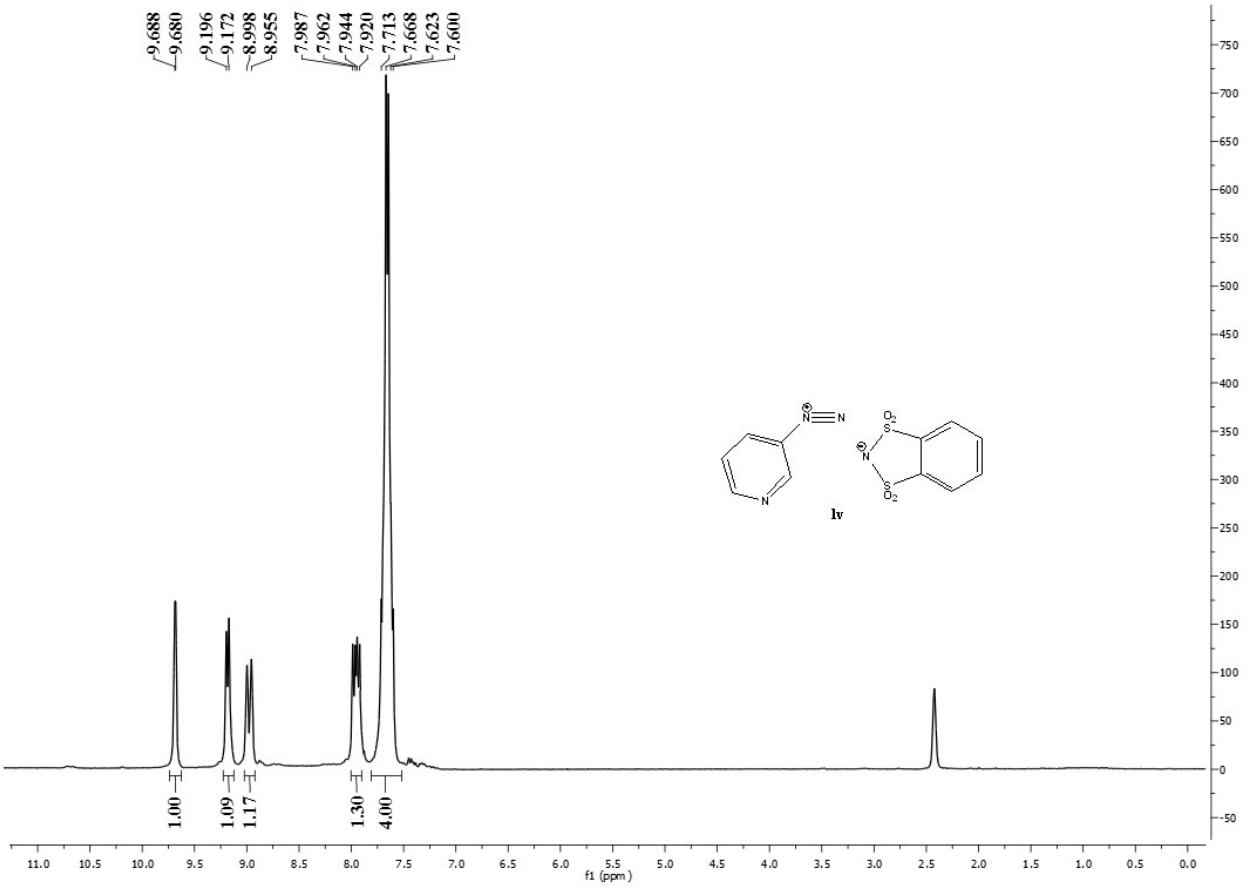
1. K. A. Cirigottis, E Ritchie and W. C. Taylor, *Aust. J. Chem.,* 1974, **27**, 2209.
2. T. D. Senecal, W. Shu and S. L. Buchwald, *Angew. Chem. Int. Ed.*, 2013, **52**, 10035.
3. E. Deau, C. Dubouilh-Benard, V. Levacher and T. Besson, *Tetrahedron,* 2015, **70**, 5532.

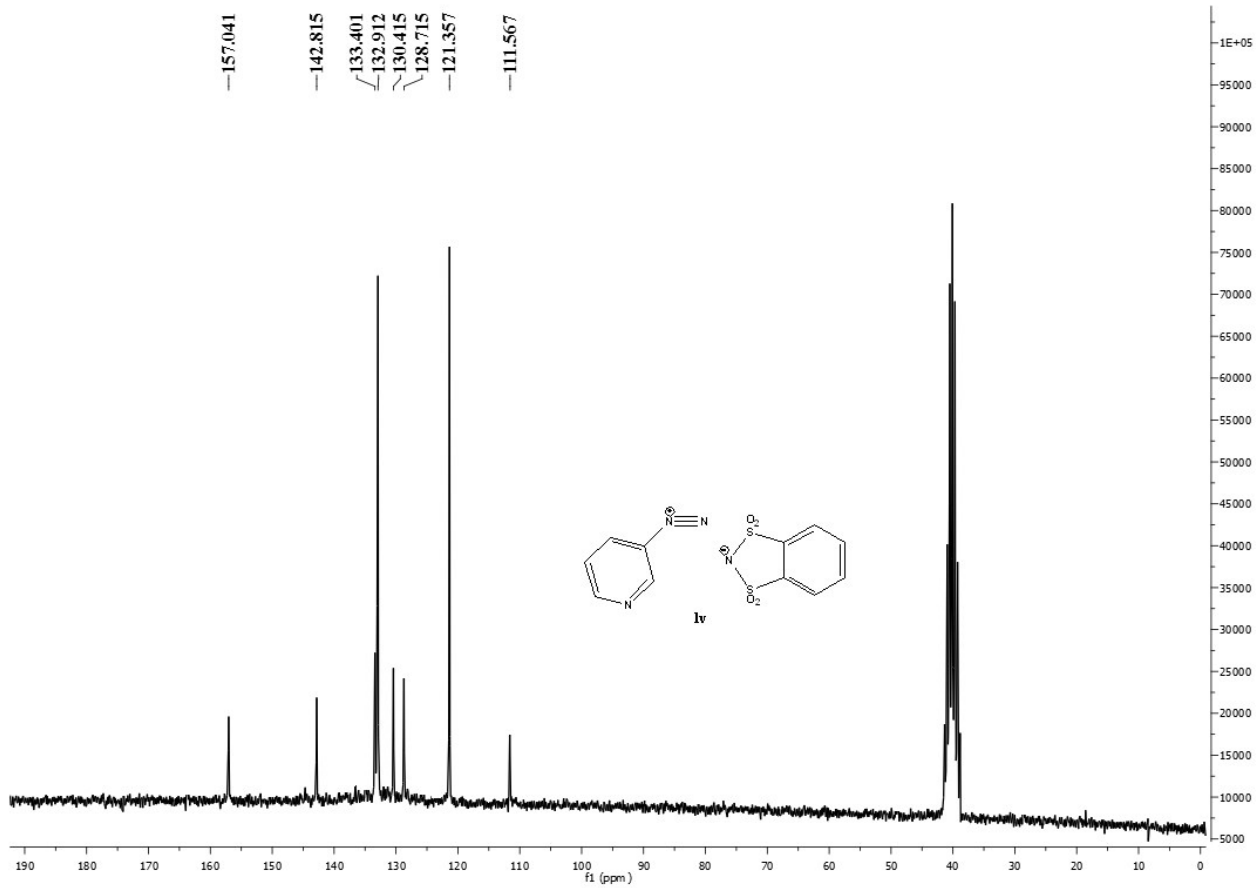
4. NMR spectra of heteroarene diazonium salts 1u-y



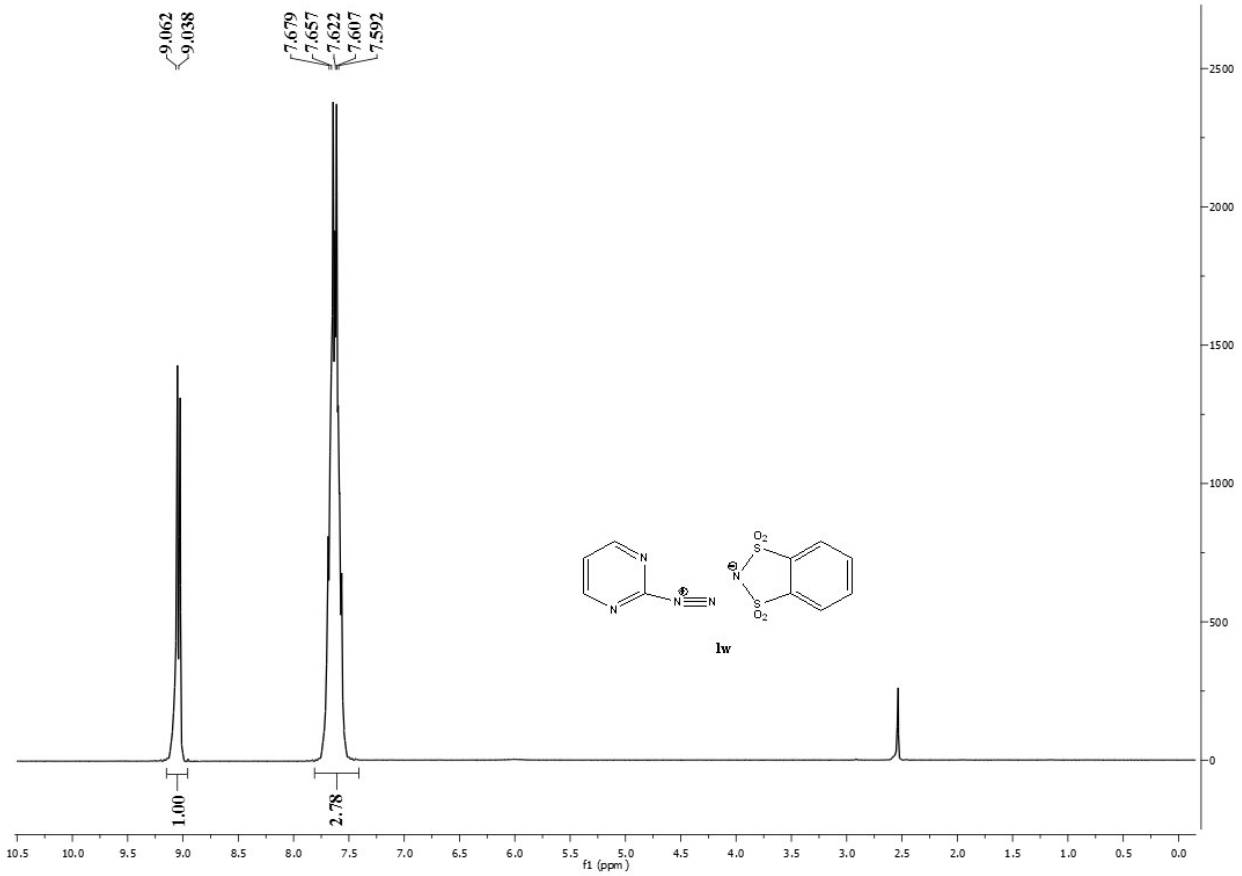


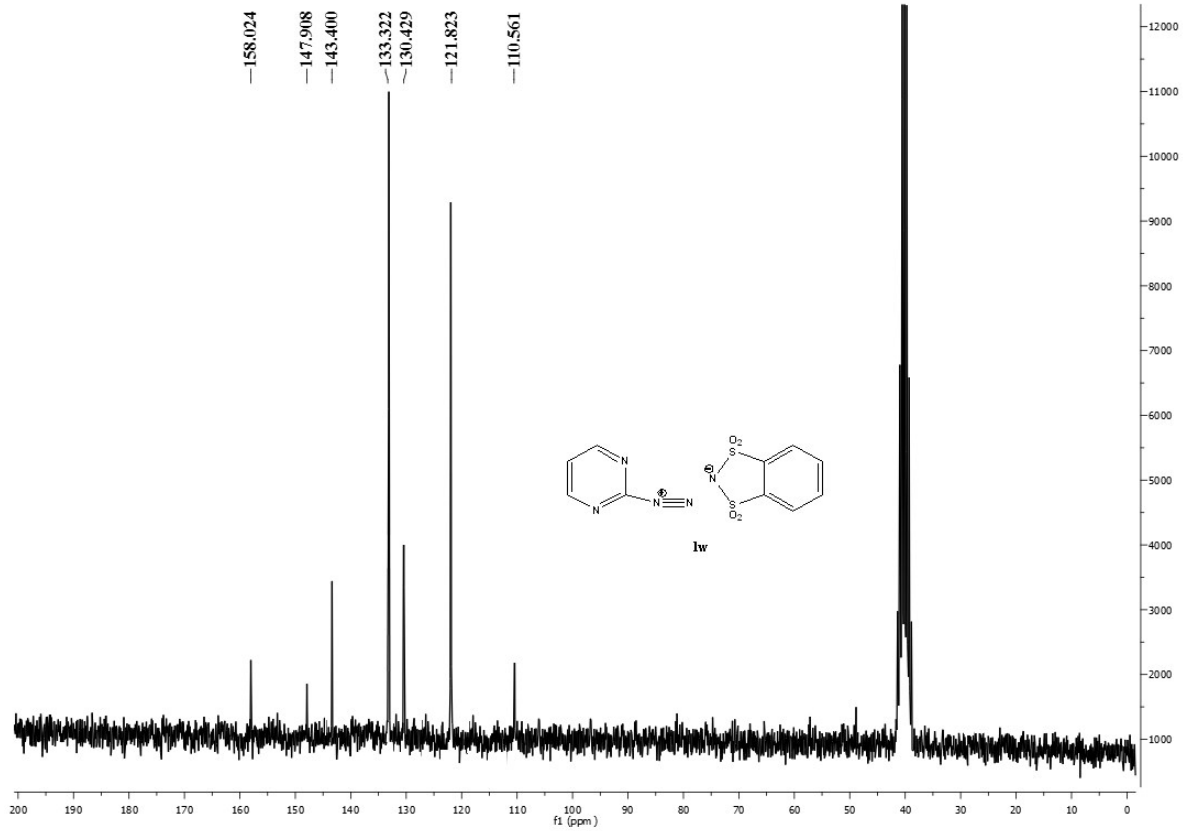
Thiophene-3-diazonium *o*-benzenedisulfonimide (1u)



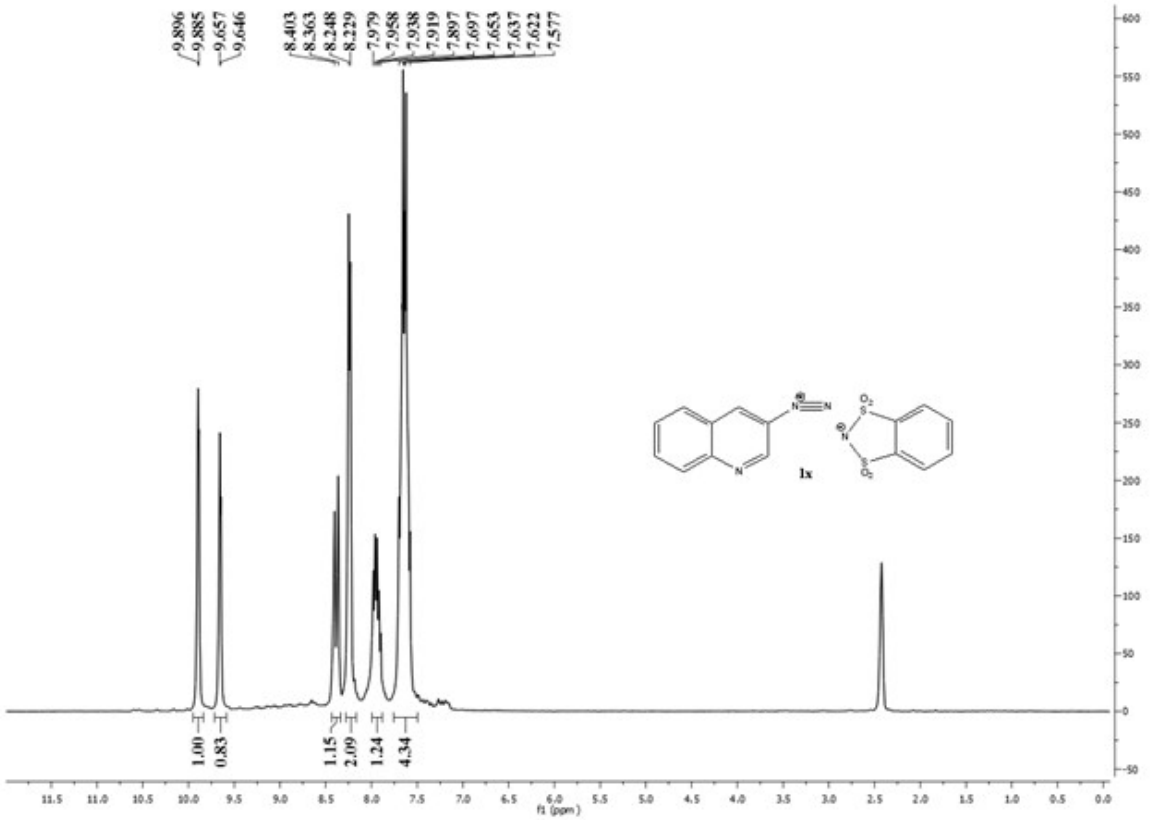


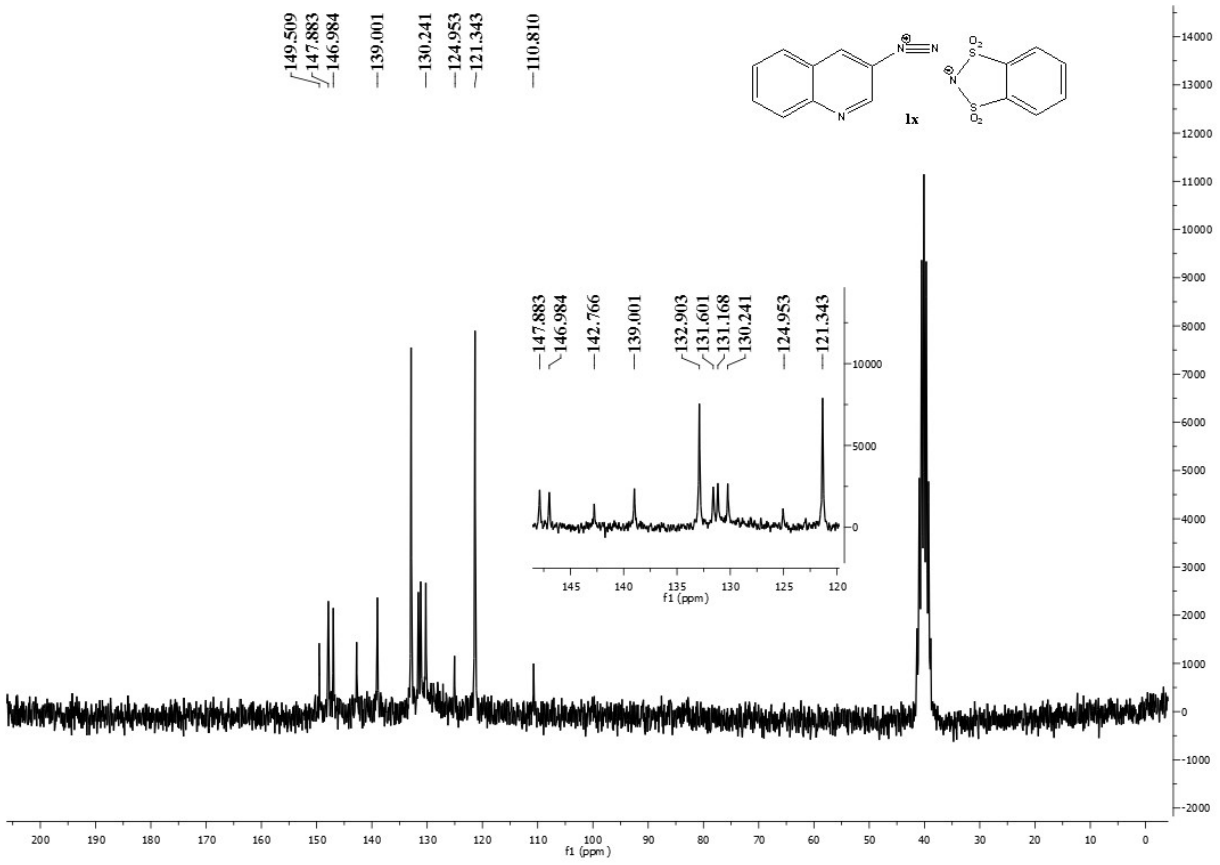
Pyridine-3-diazonium *o*-benzenedisulfonimide (1v)



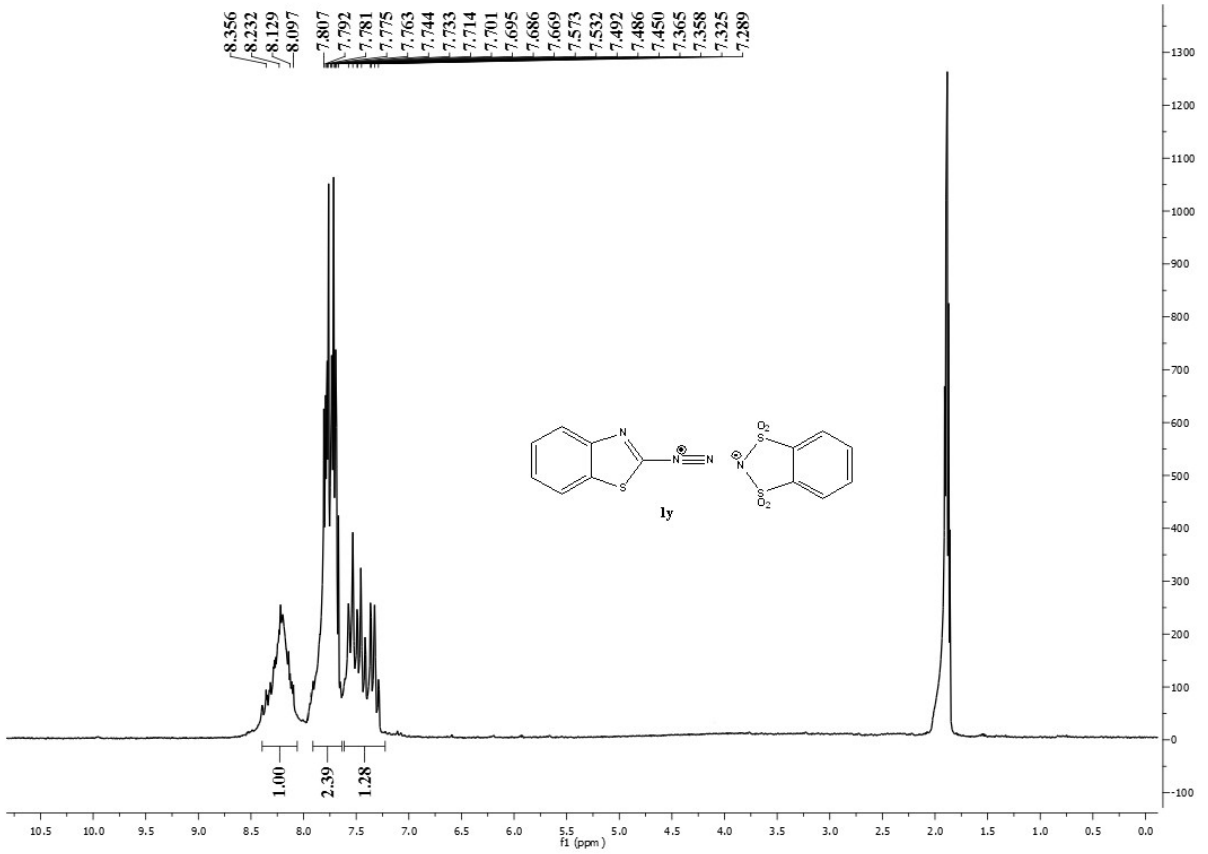


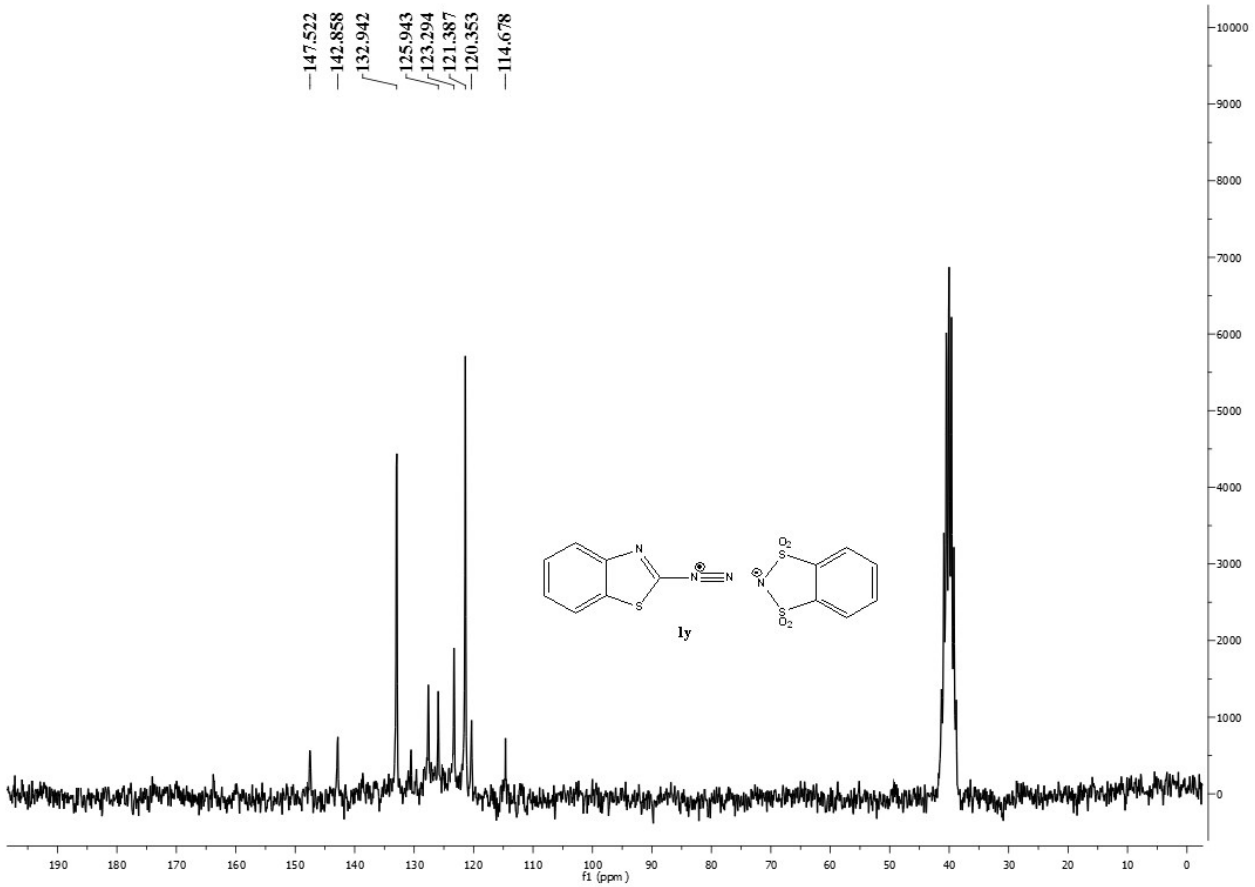
Pyrimidine-2-diazonium *o*-benzenedisulfonimide (1w)





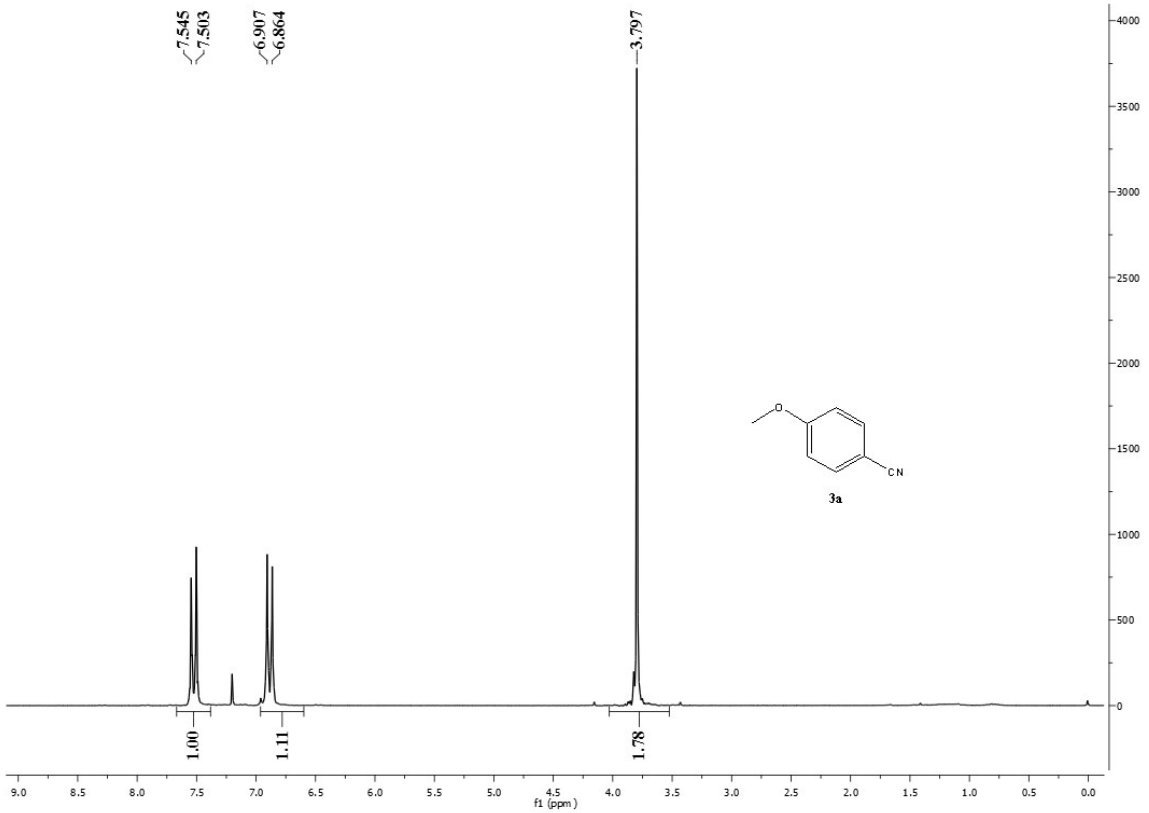
Quinoline-3-diazonium *o*-benzenedisulfonimide (1x)

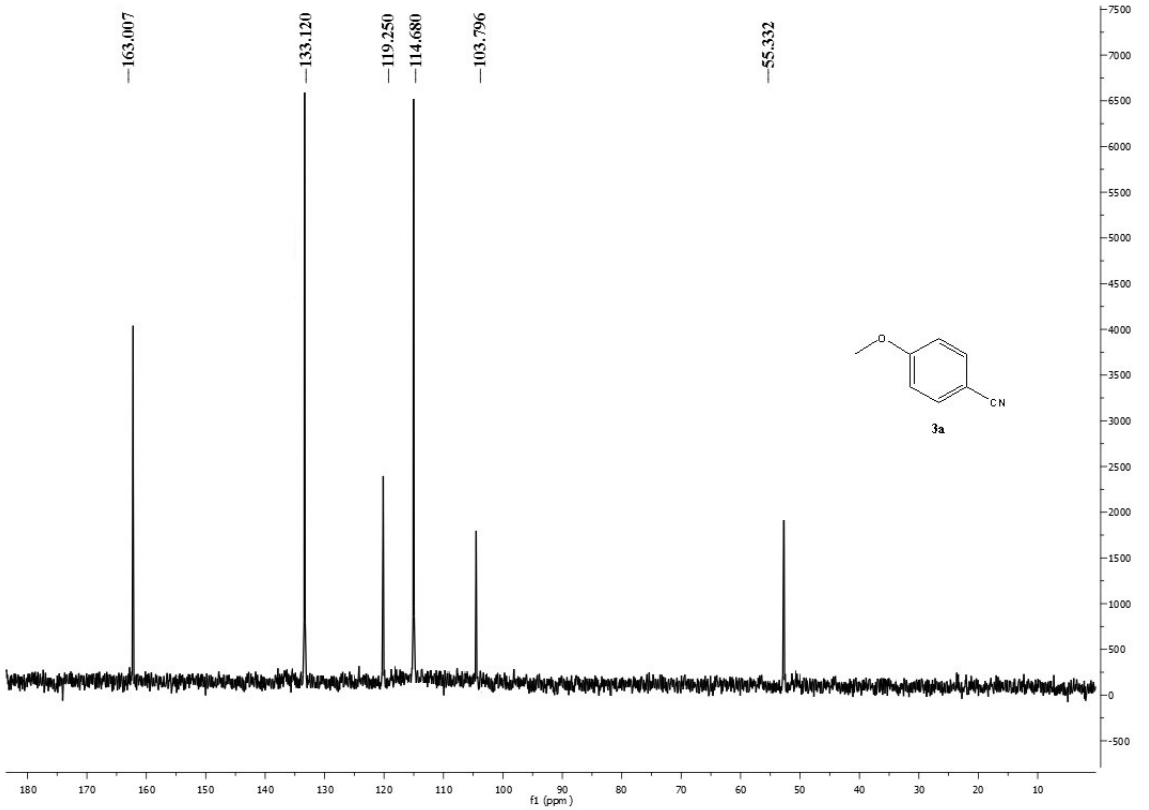




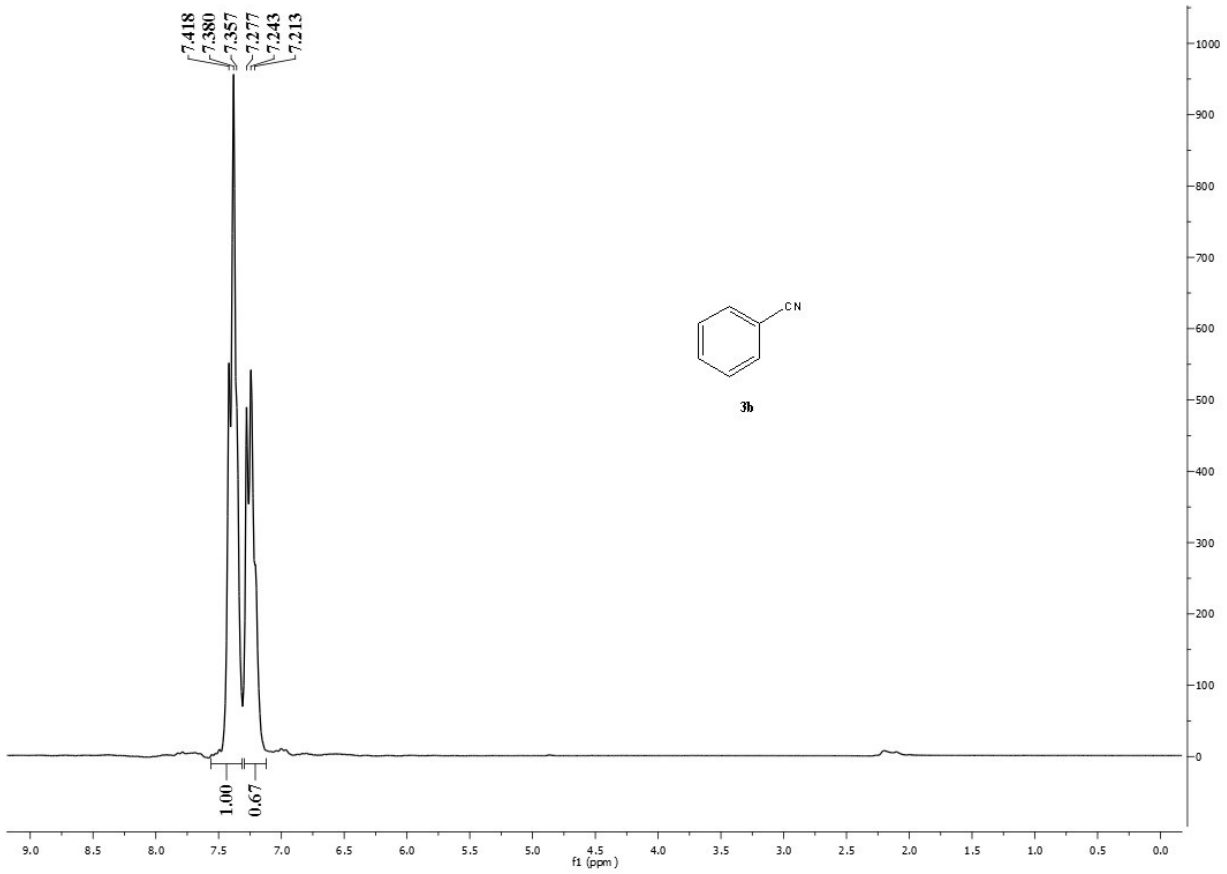
Benzo[*d*]thiazole-2-diazonium *o*-benzenedisulfonimide (1y)

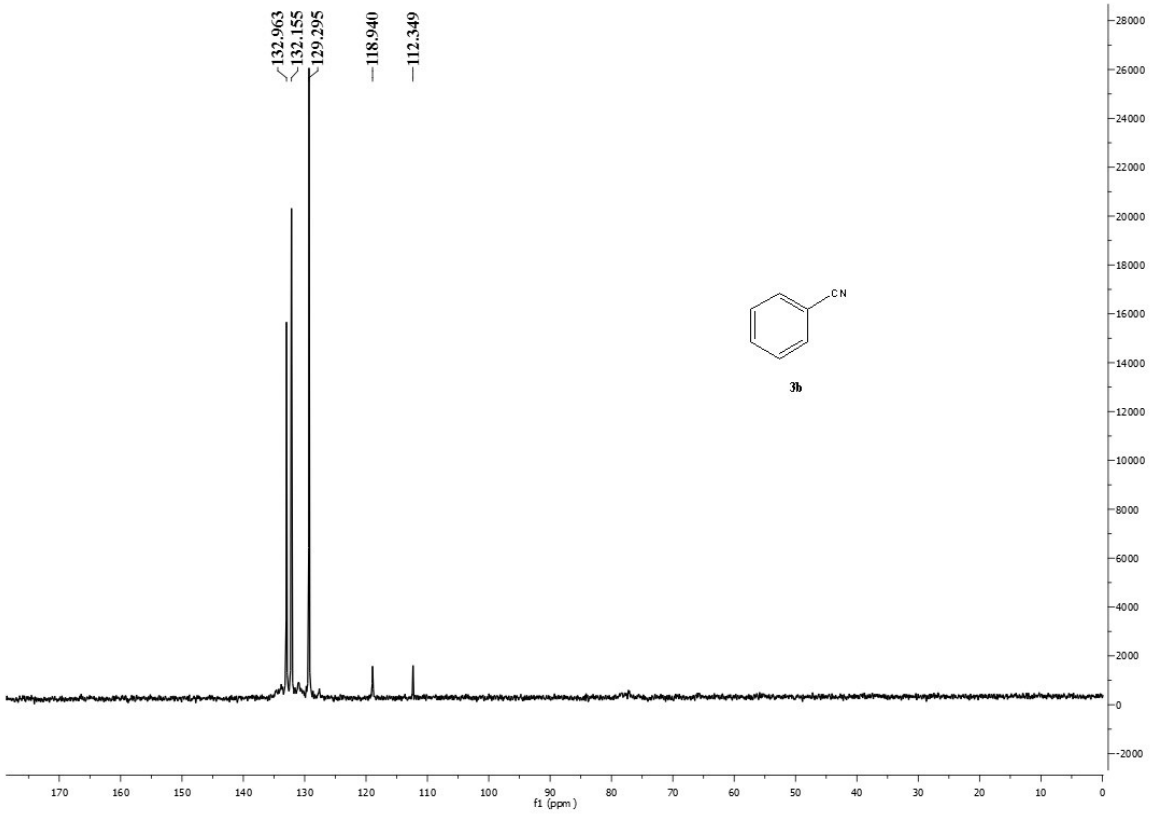
4. NMR Spectra of cyanide 3



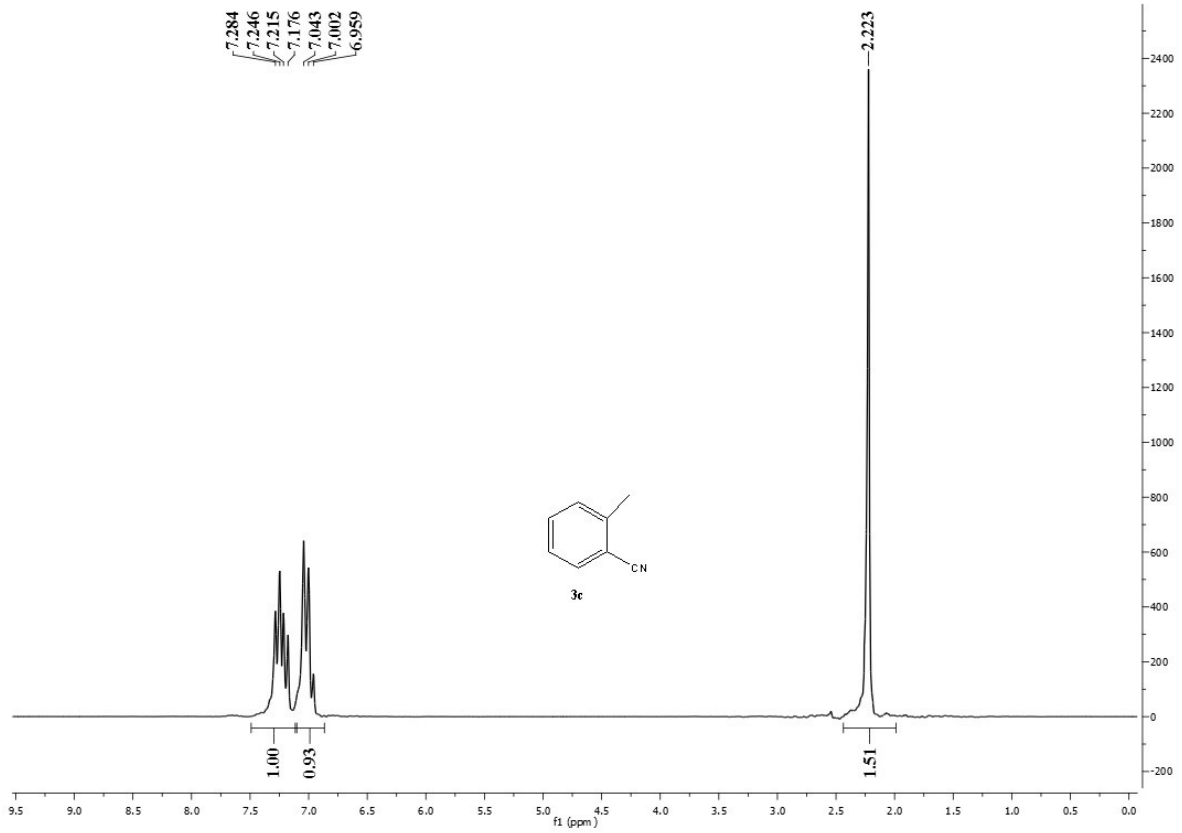


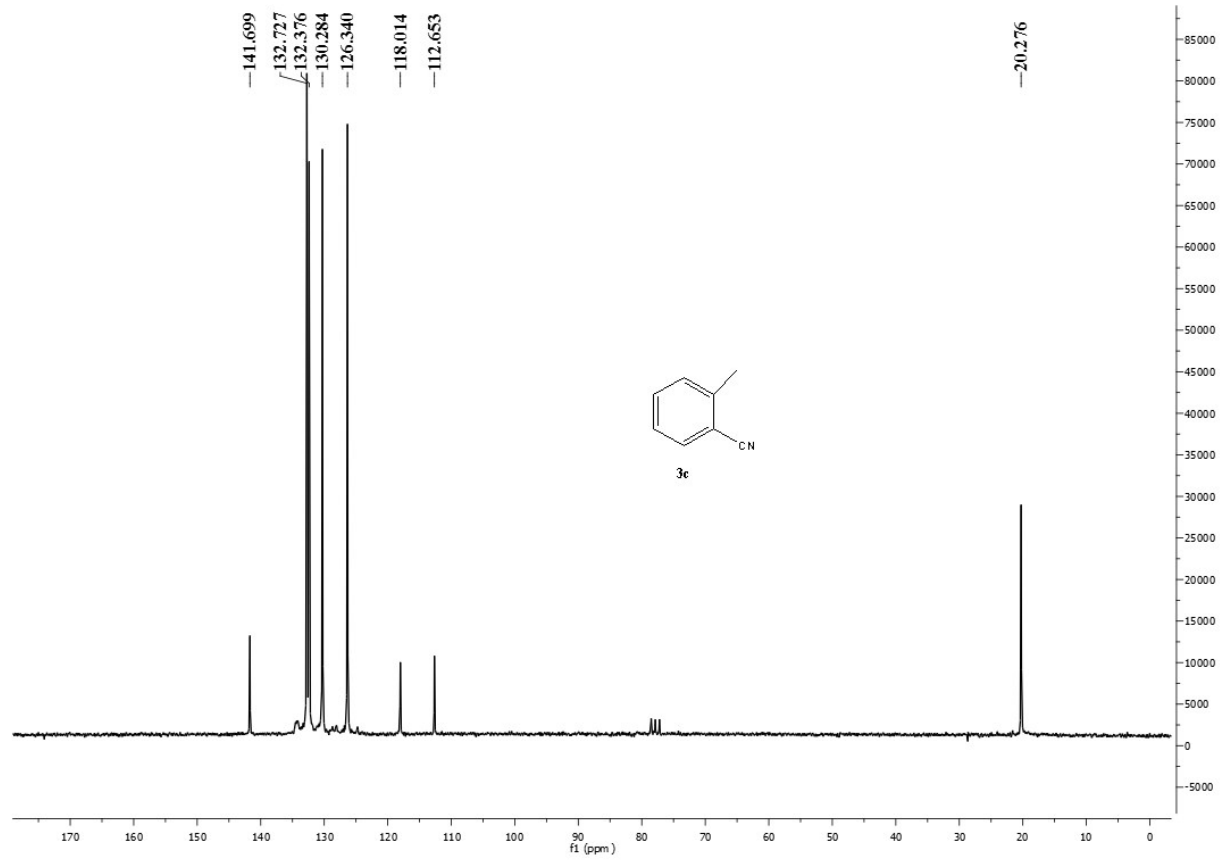
4-Methoxybenzonitrile (3a)



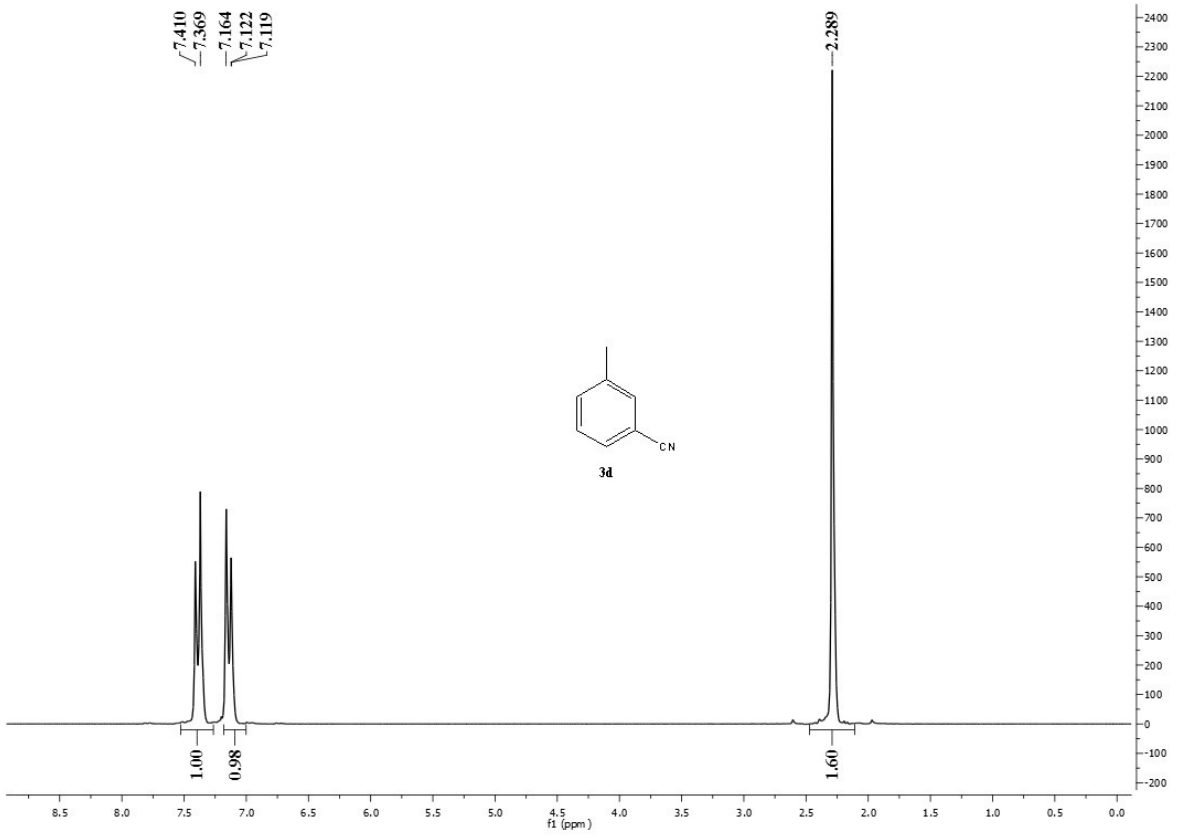


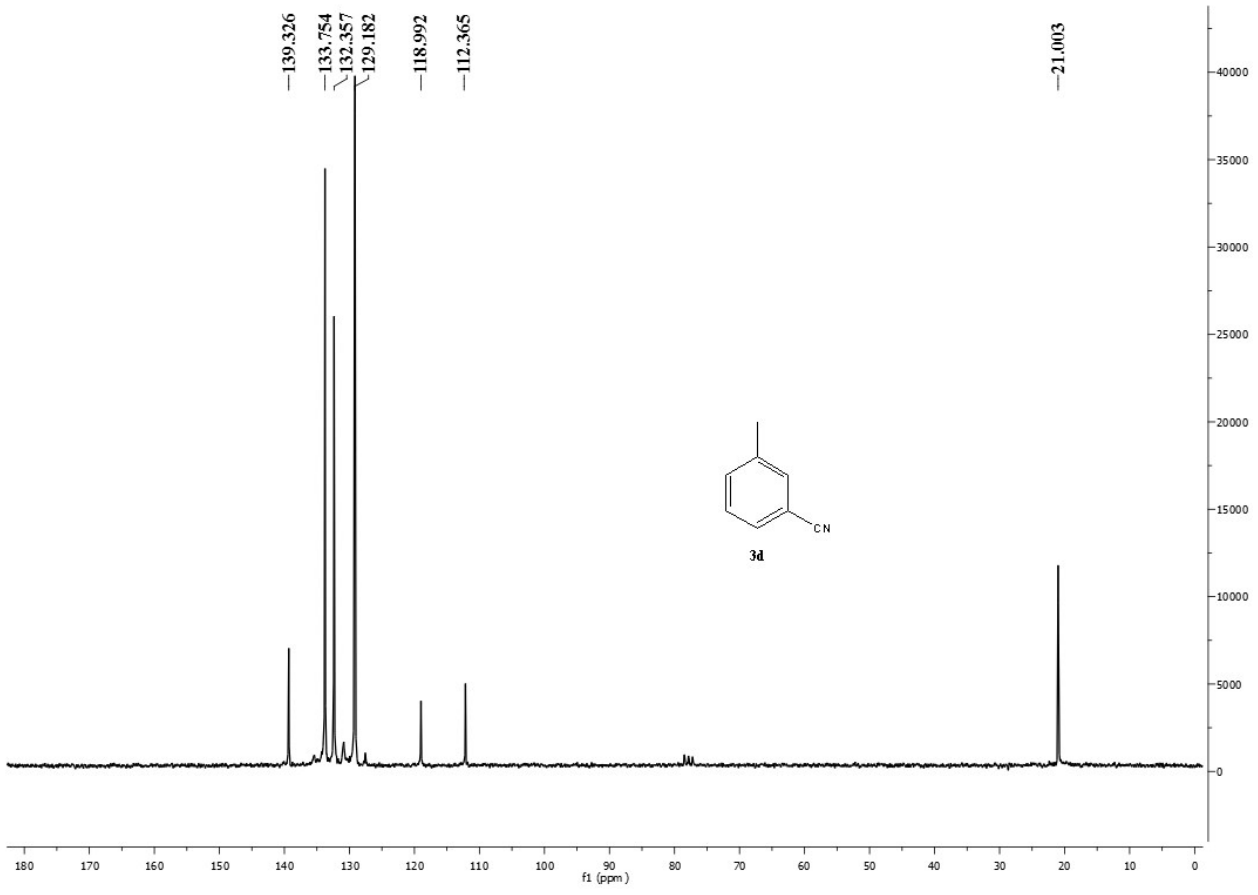
Benzonitrile (3b)



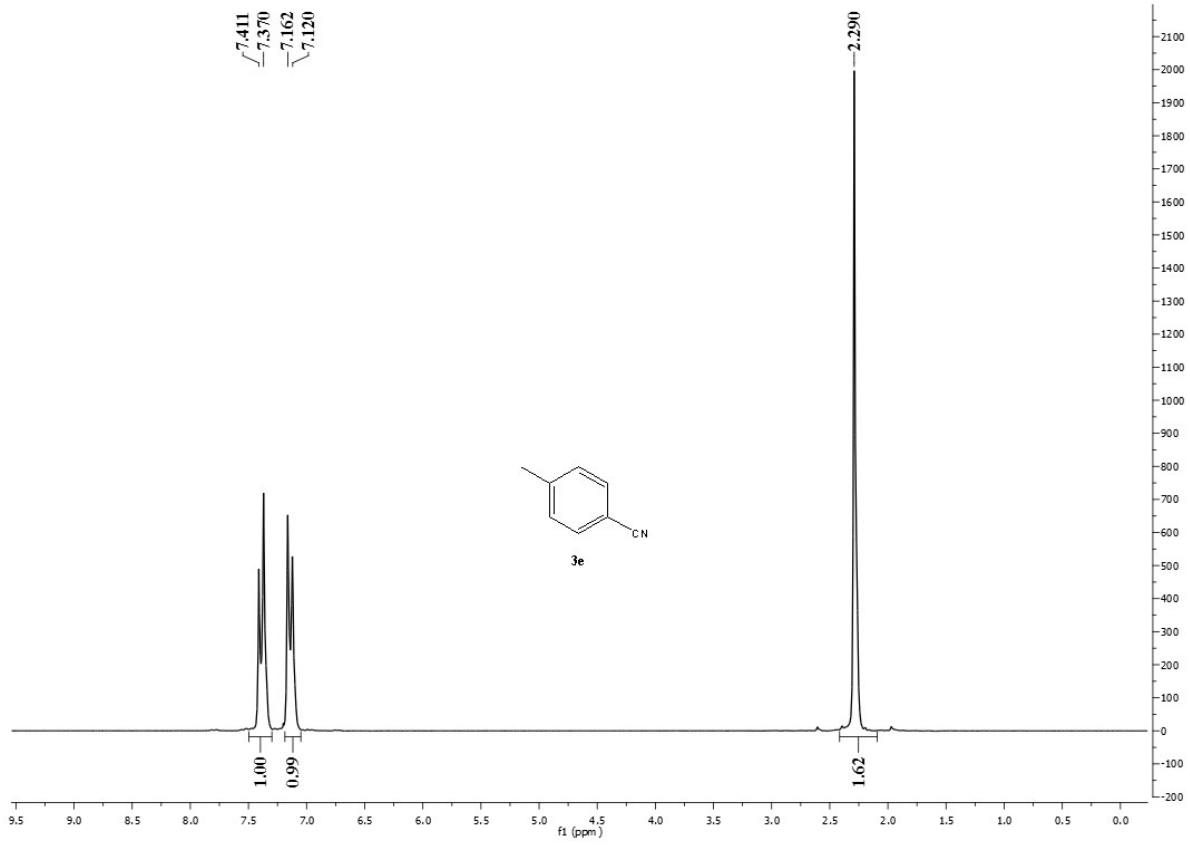


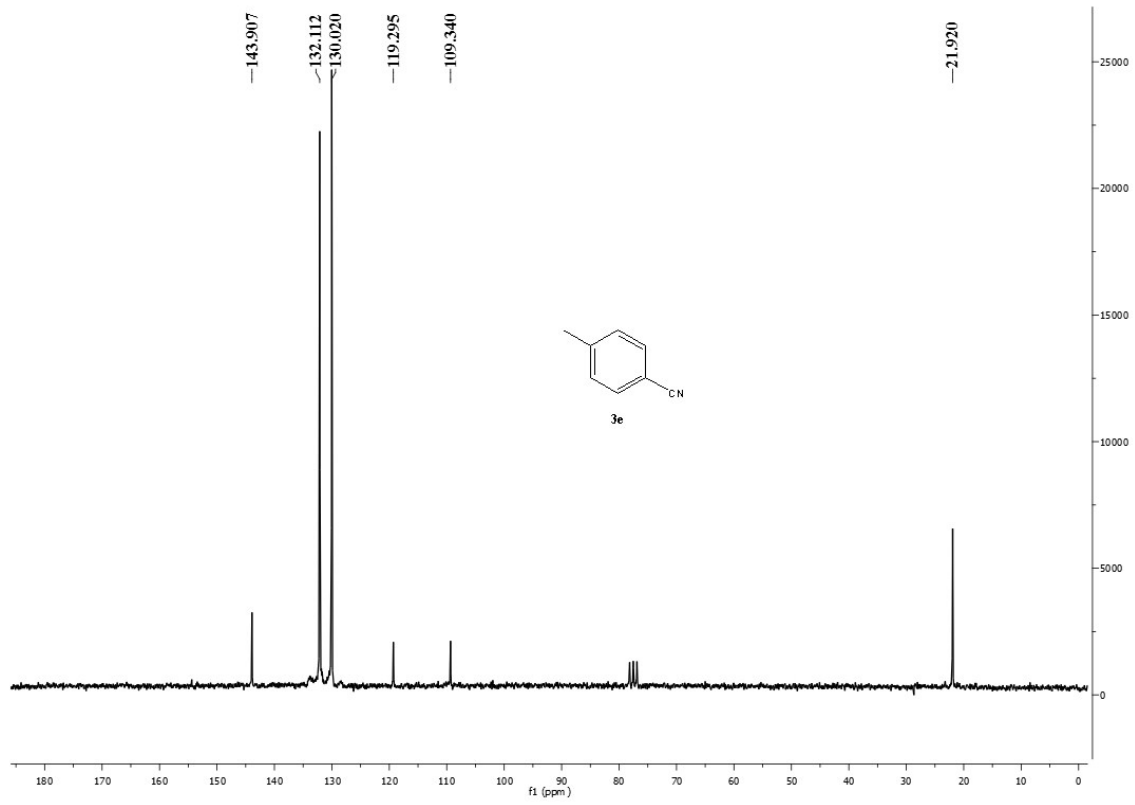
2-Methylbenzonitrile (3c)



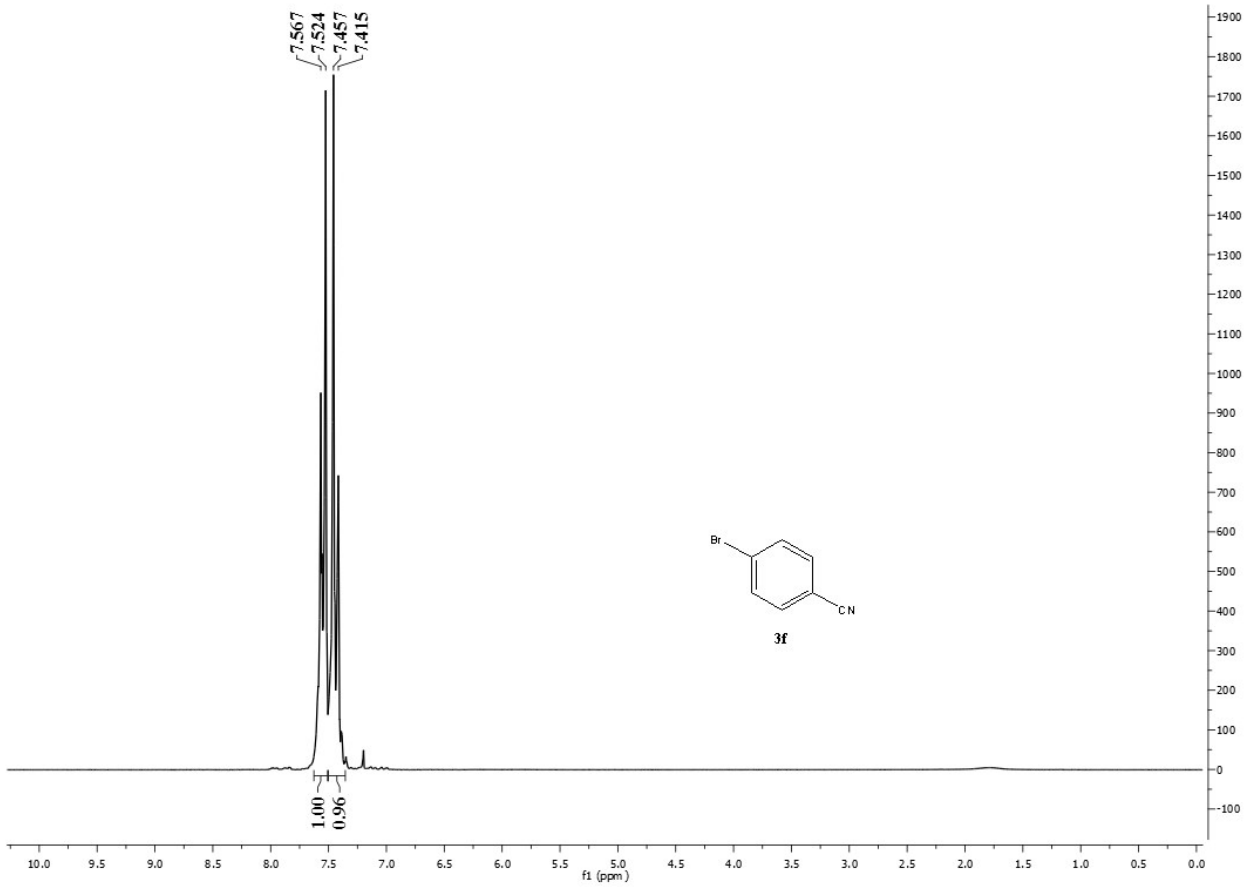


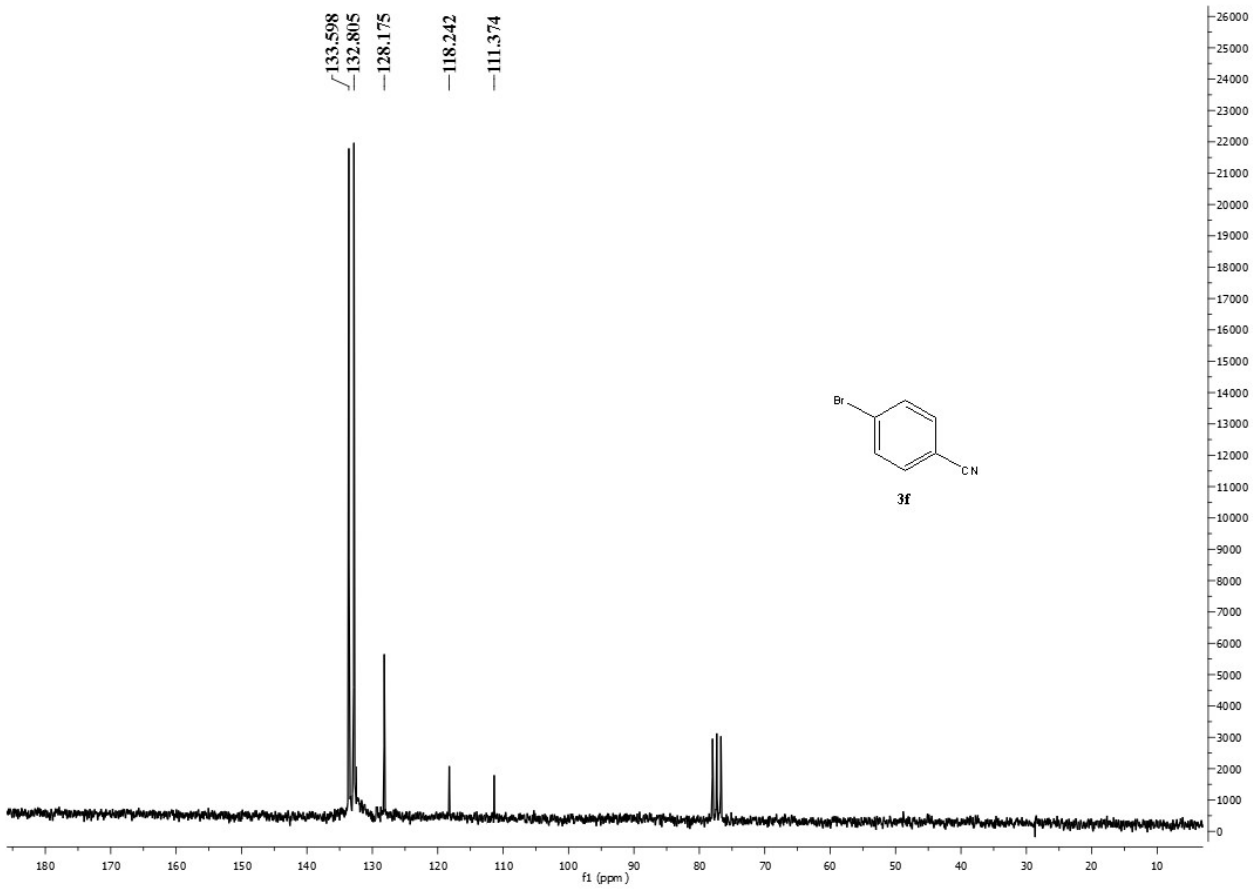
3-Methylbenzonitrile (3d)



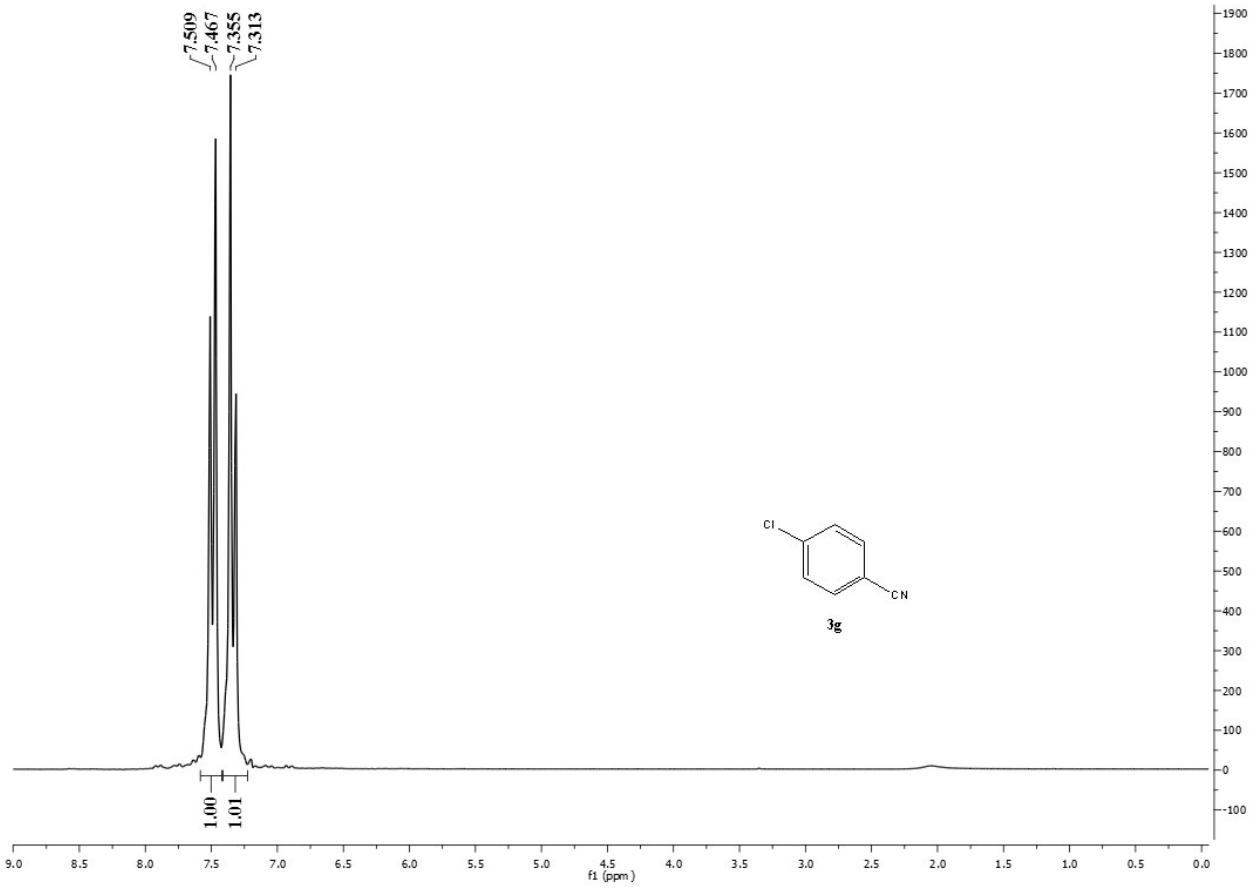


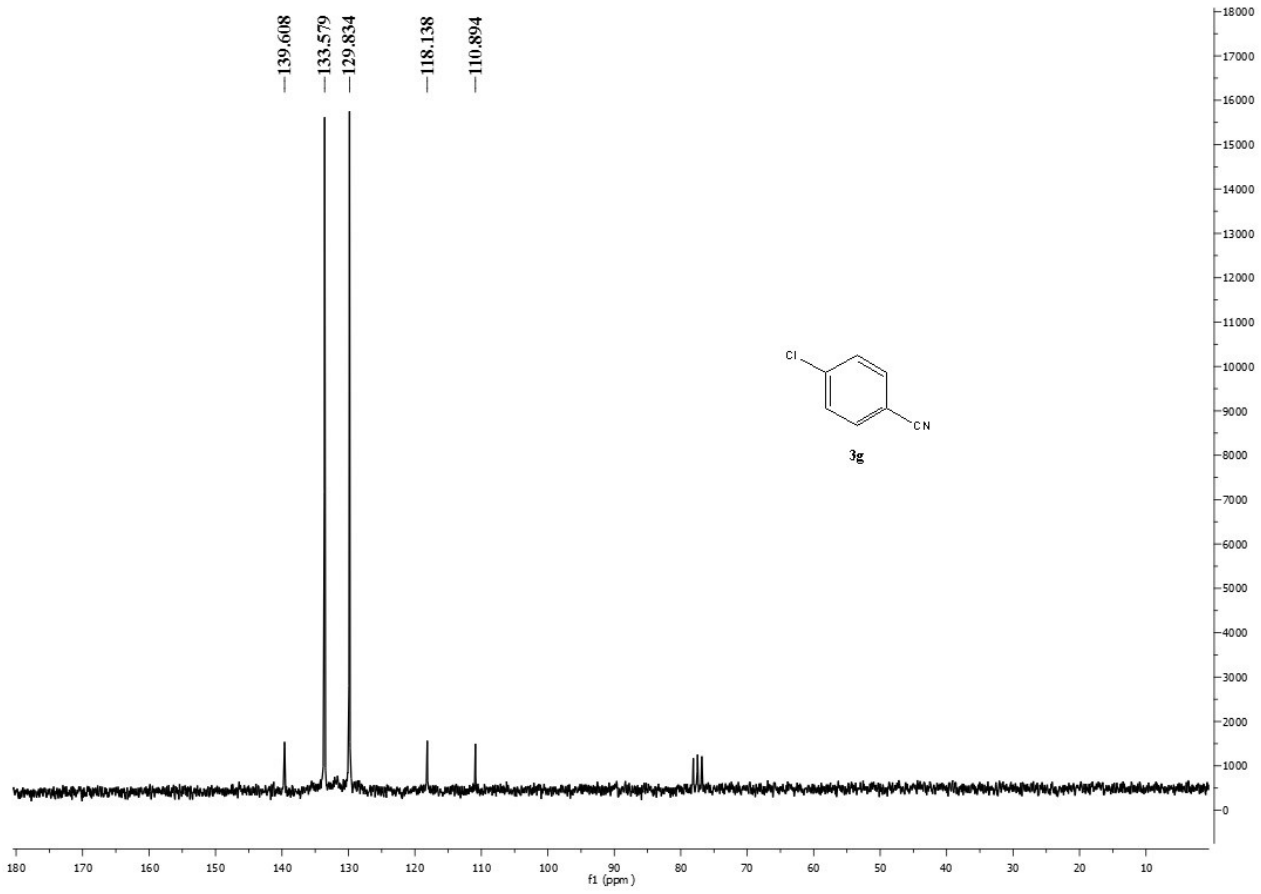
4-Methylbenzonitrile (3e)



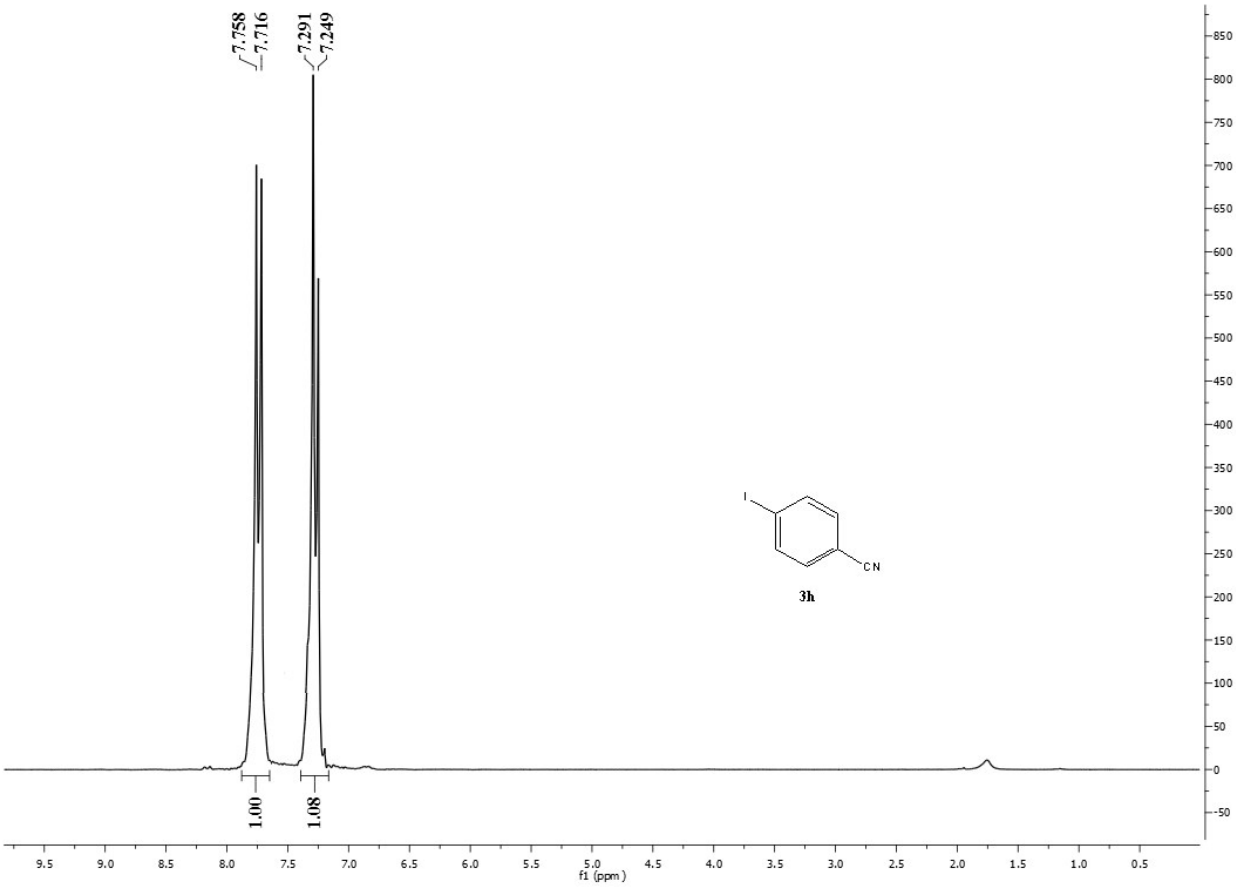


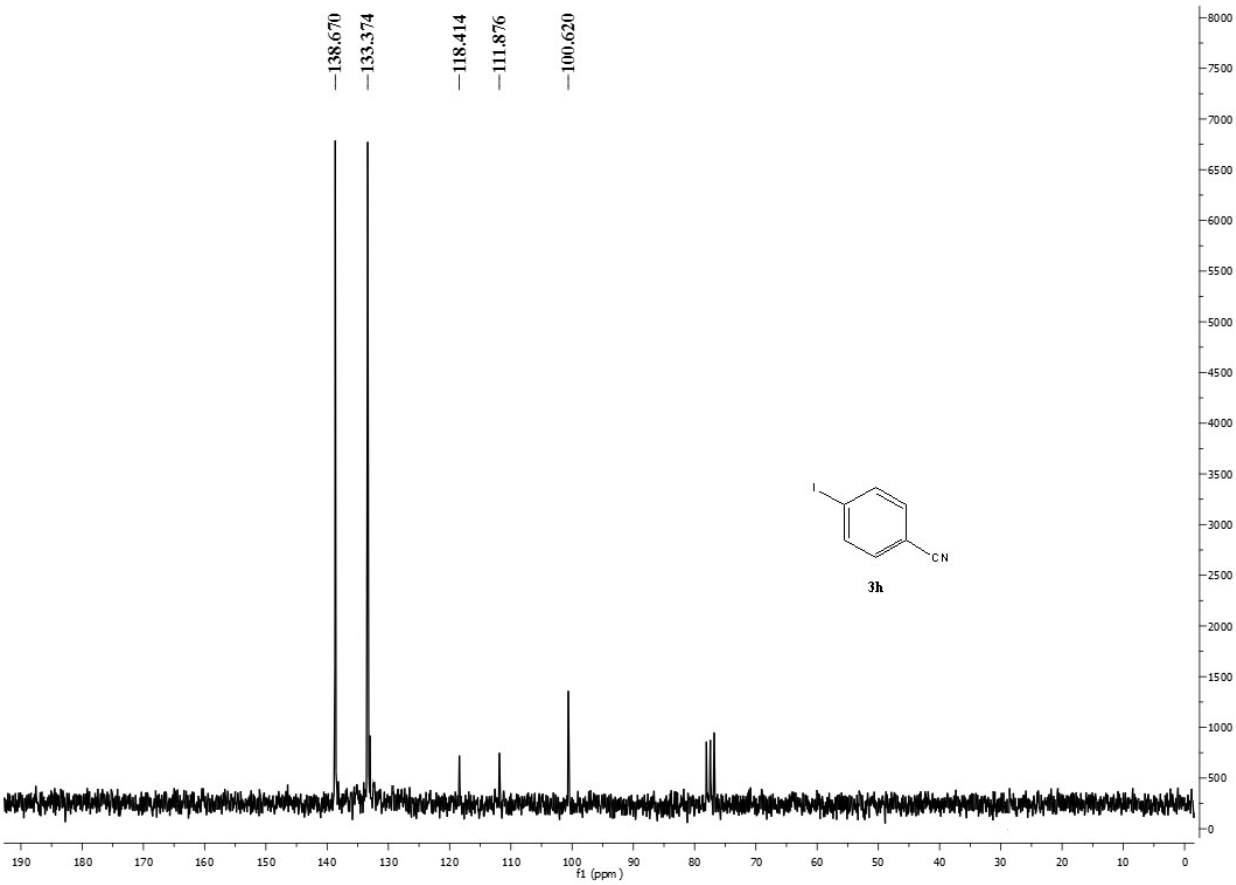
4-Bromobenzonitrile (3f)



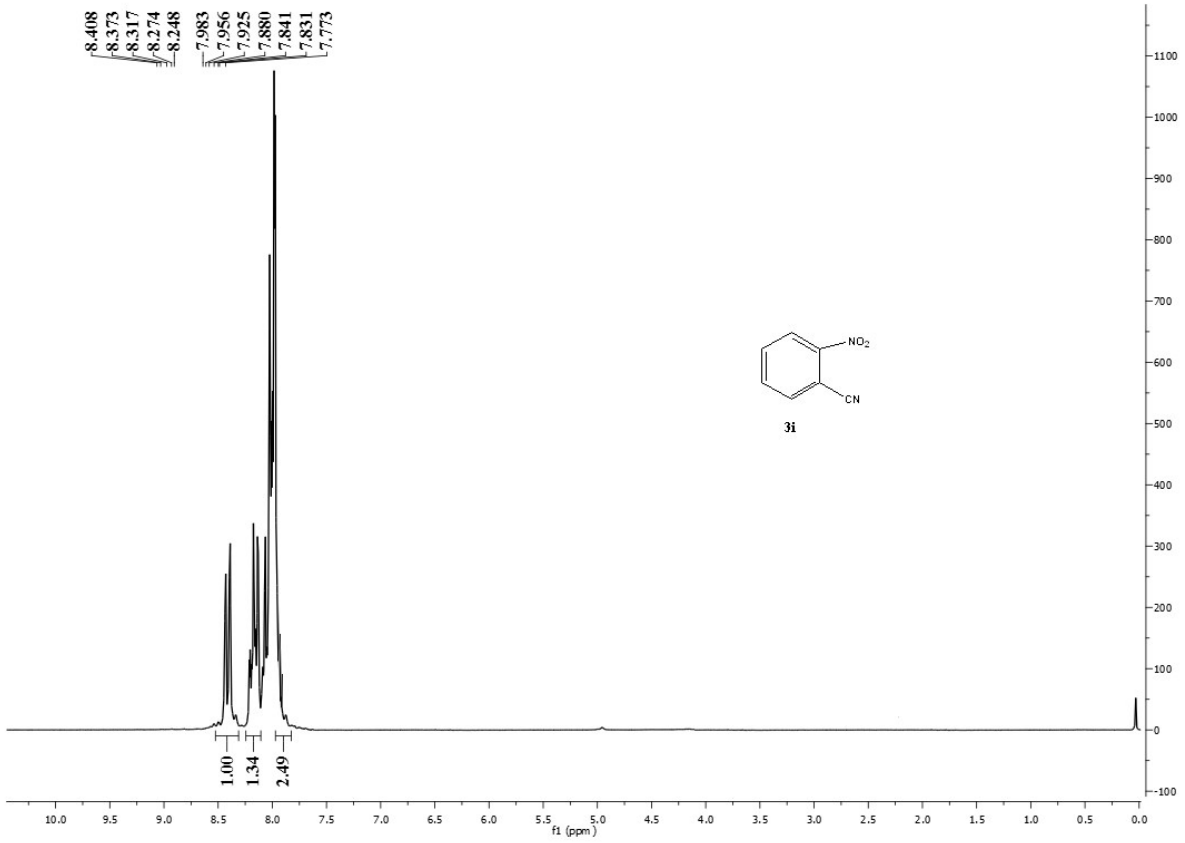


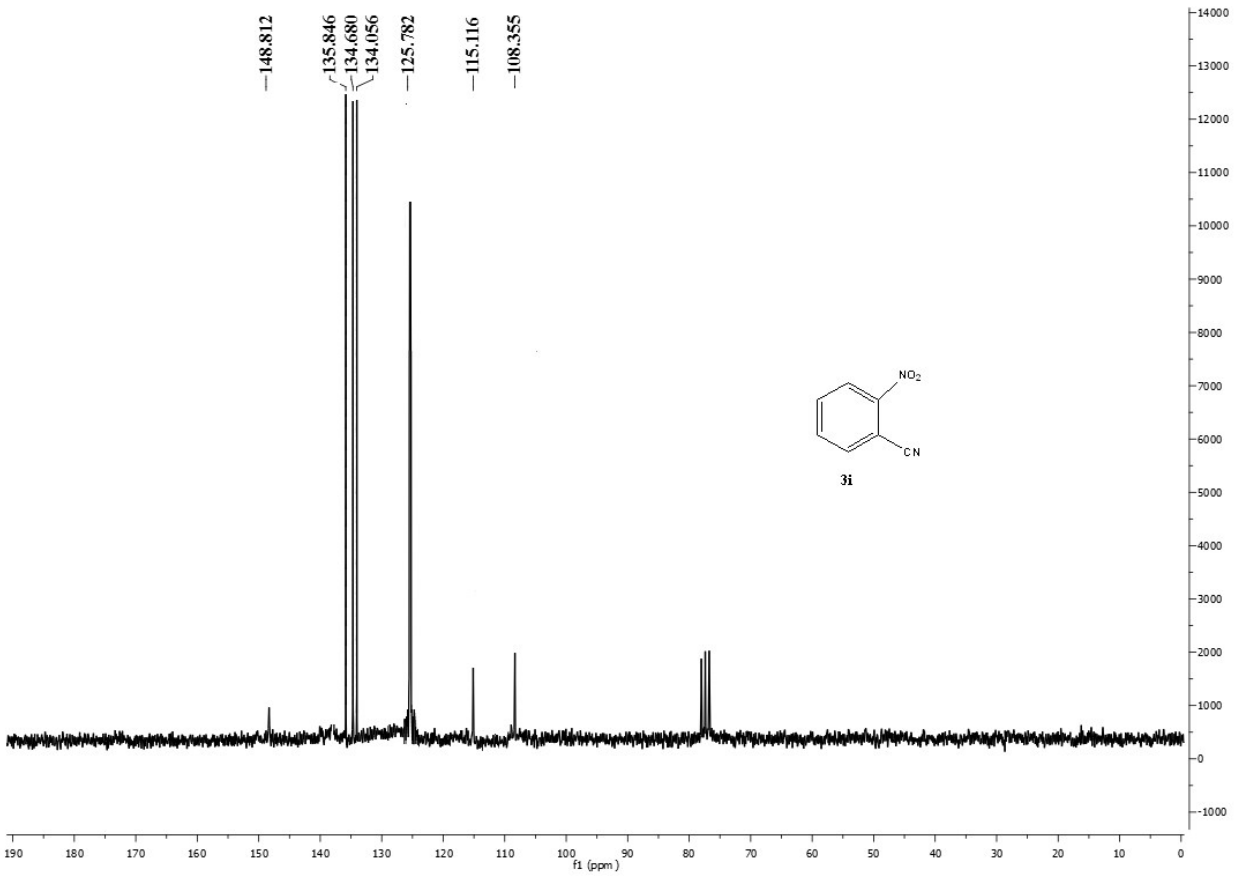
4-Chlorobenzonitrile (3g)



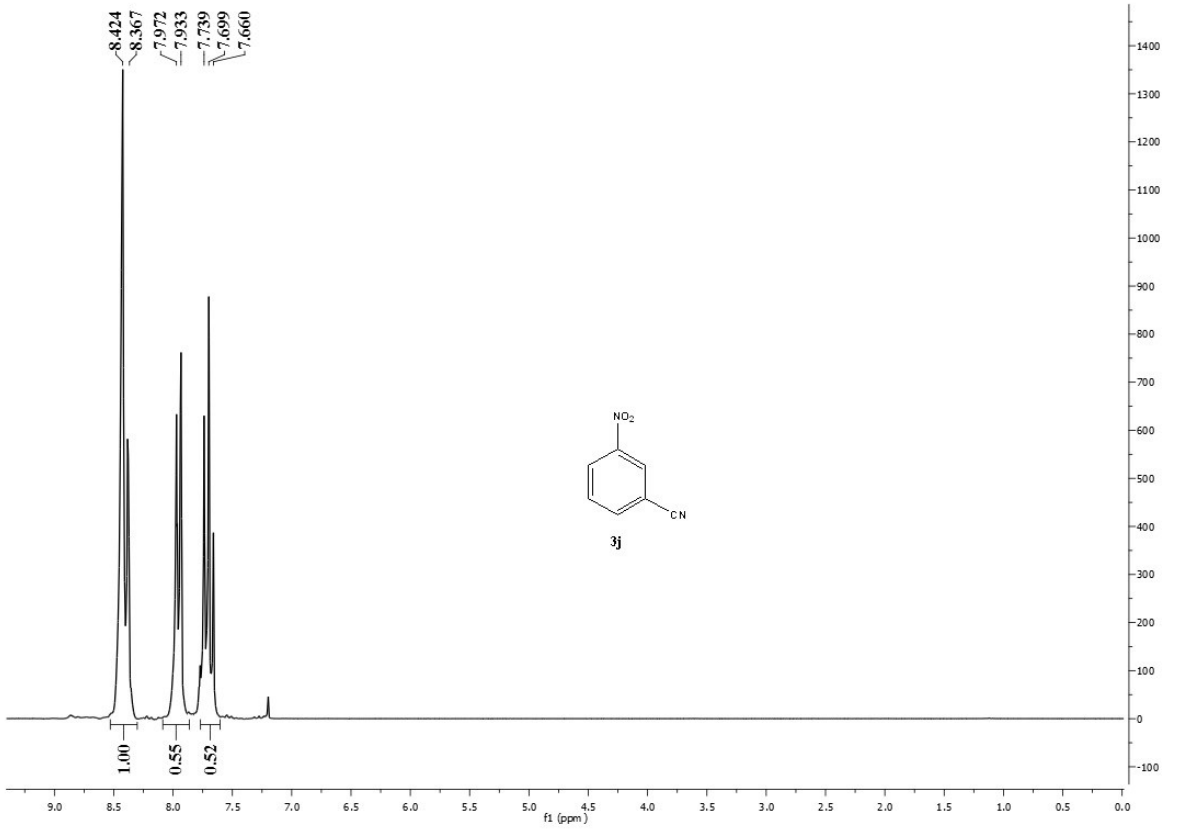


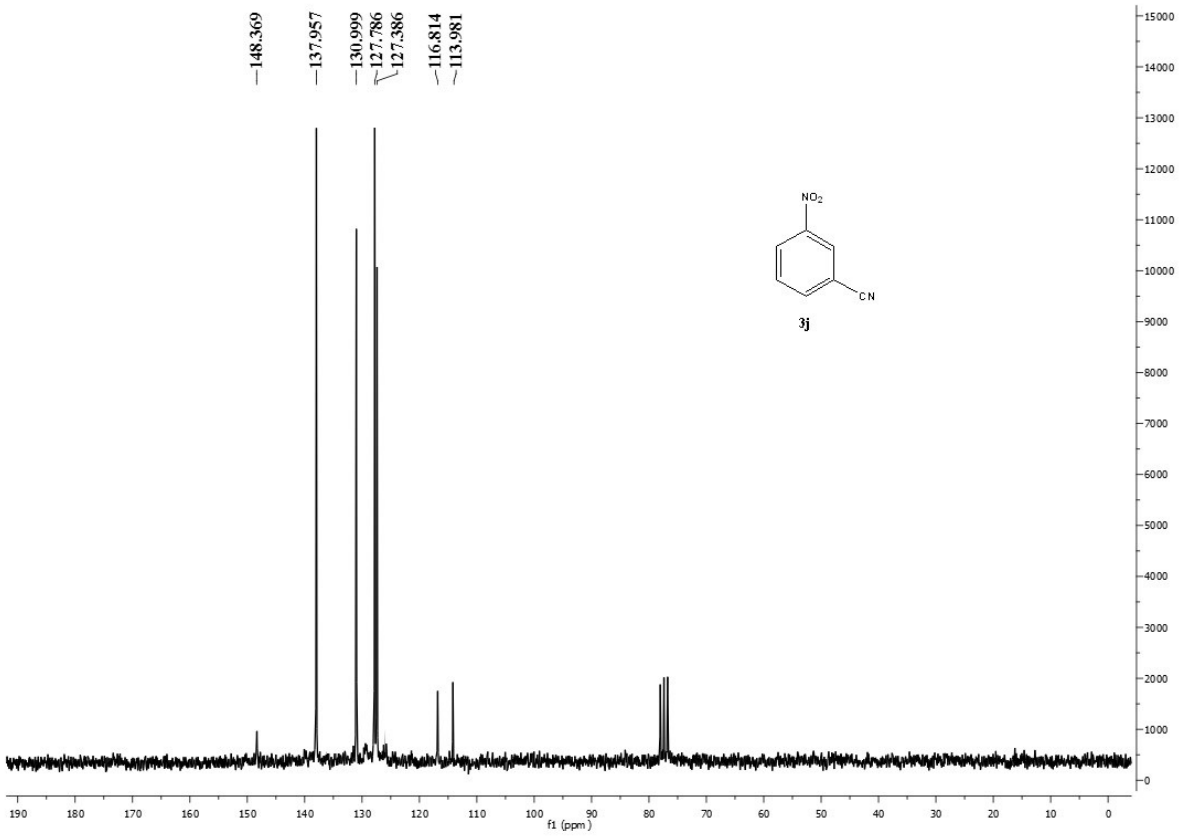
4-Iodobenzonitrile (3h)



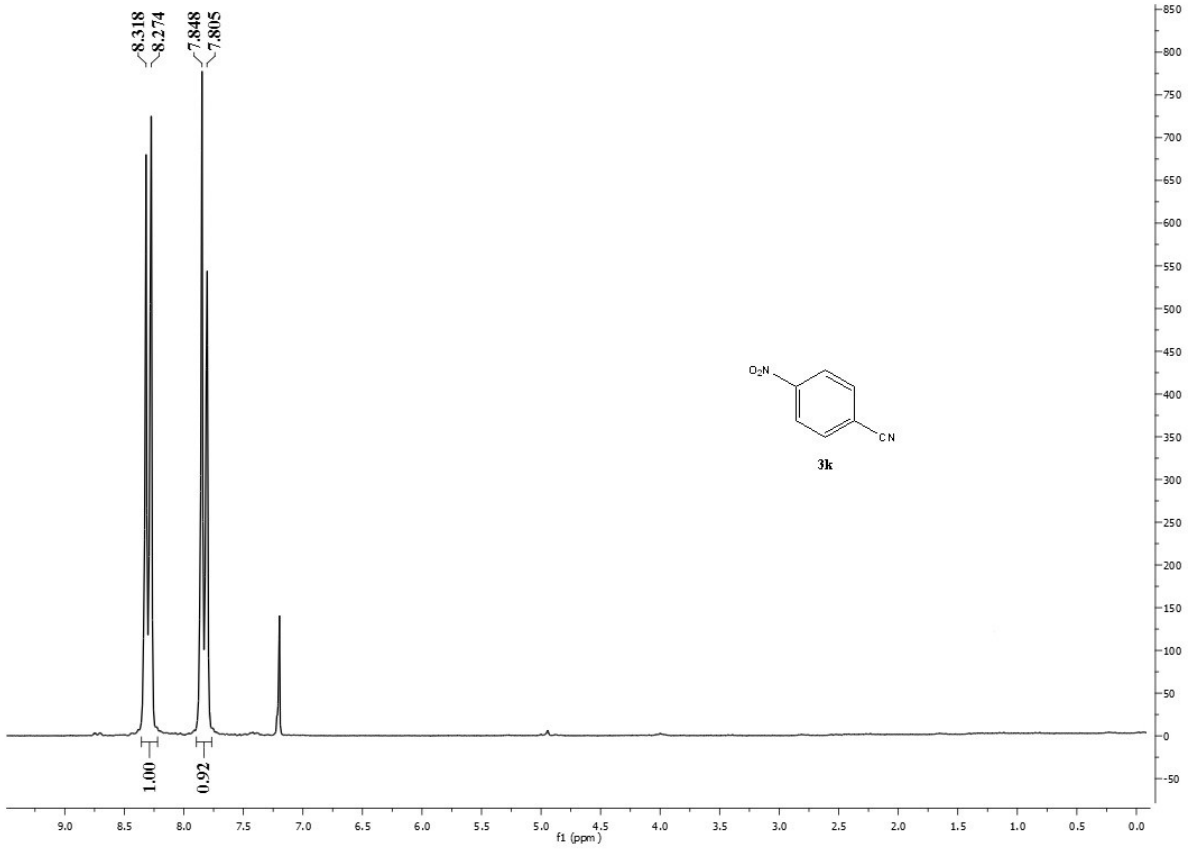


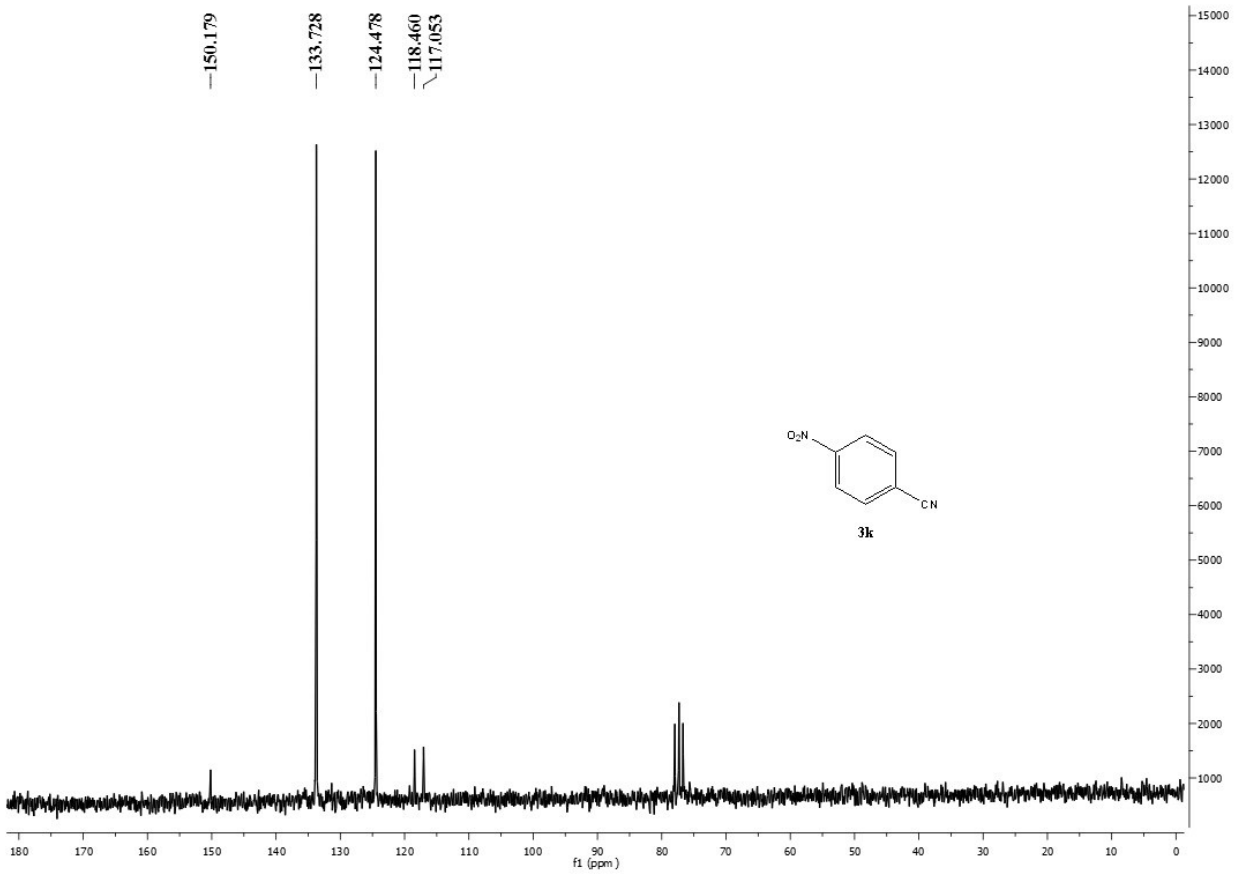
2-Nitrobenzonitrile (3i)



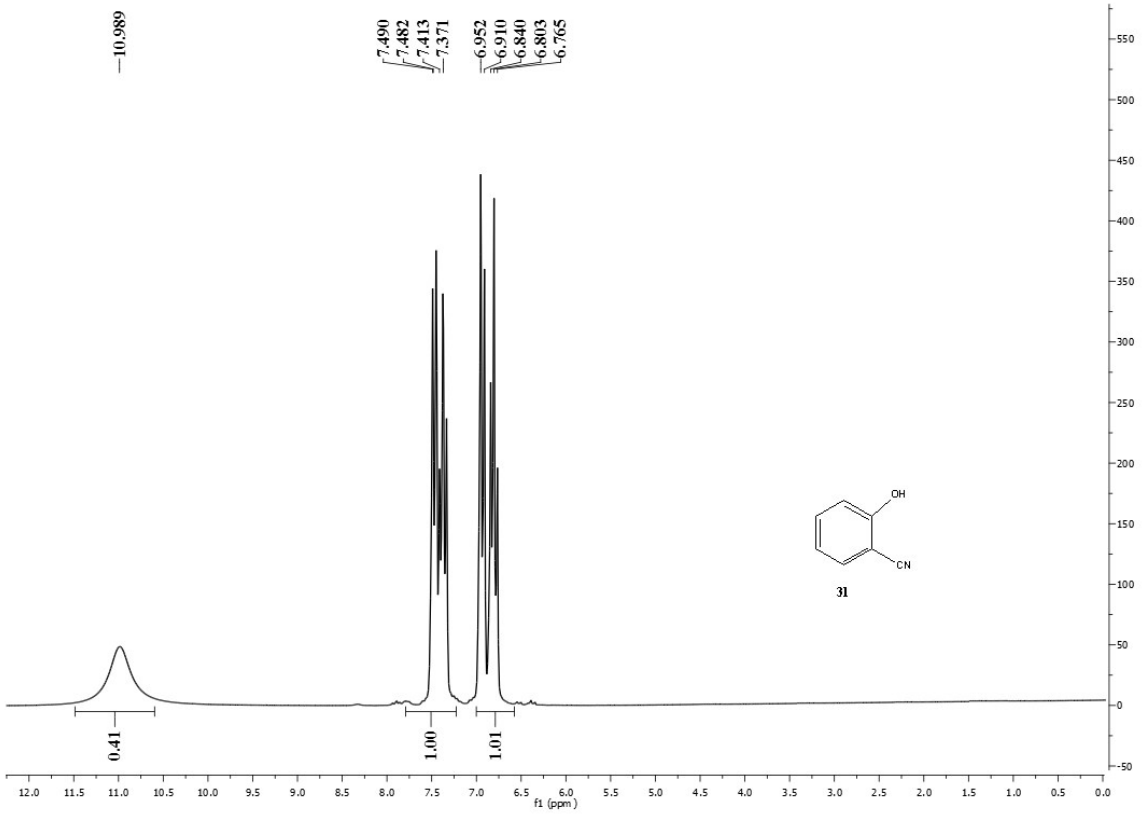


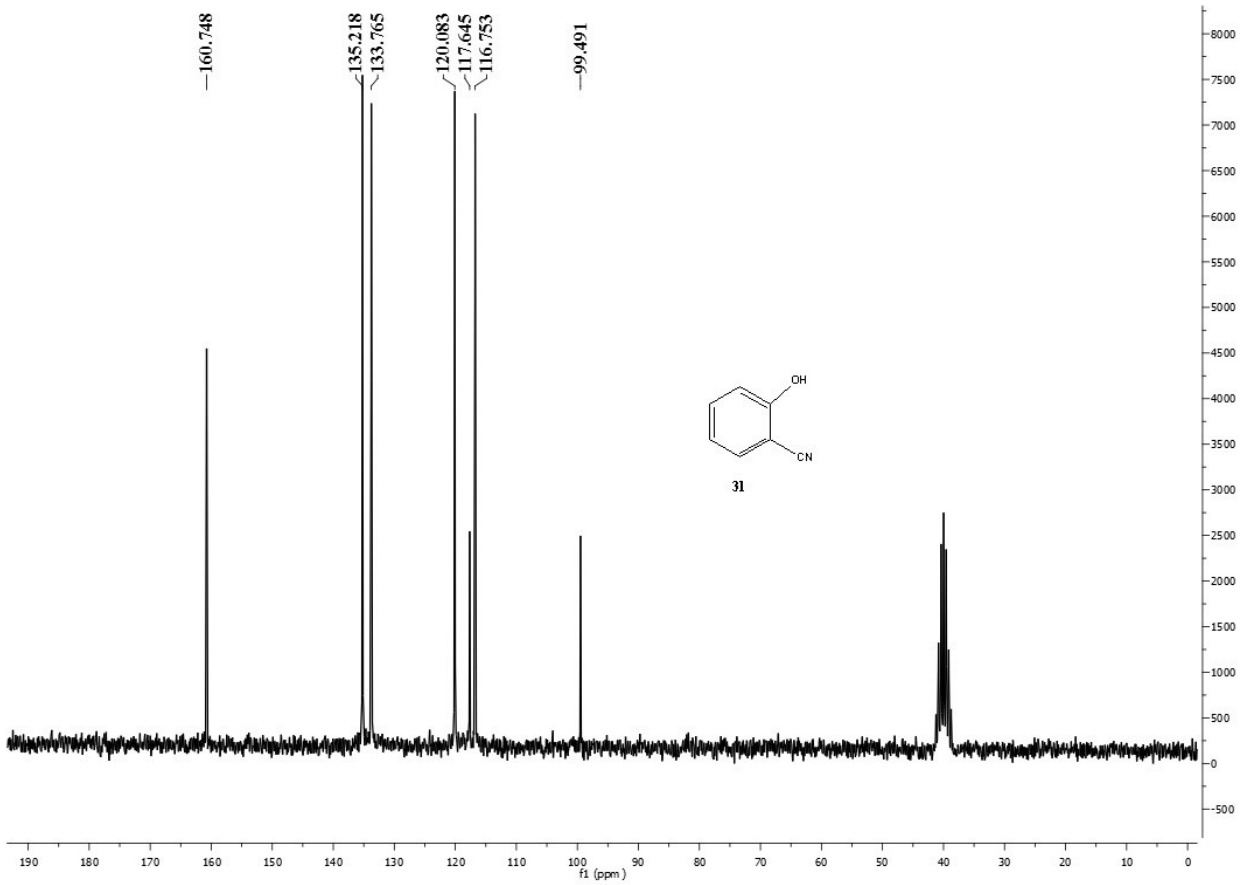
3-Nitrobenzonitrile (3j)



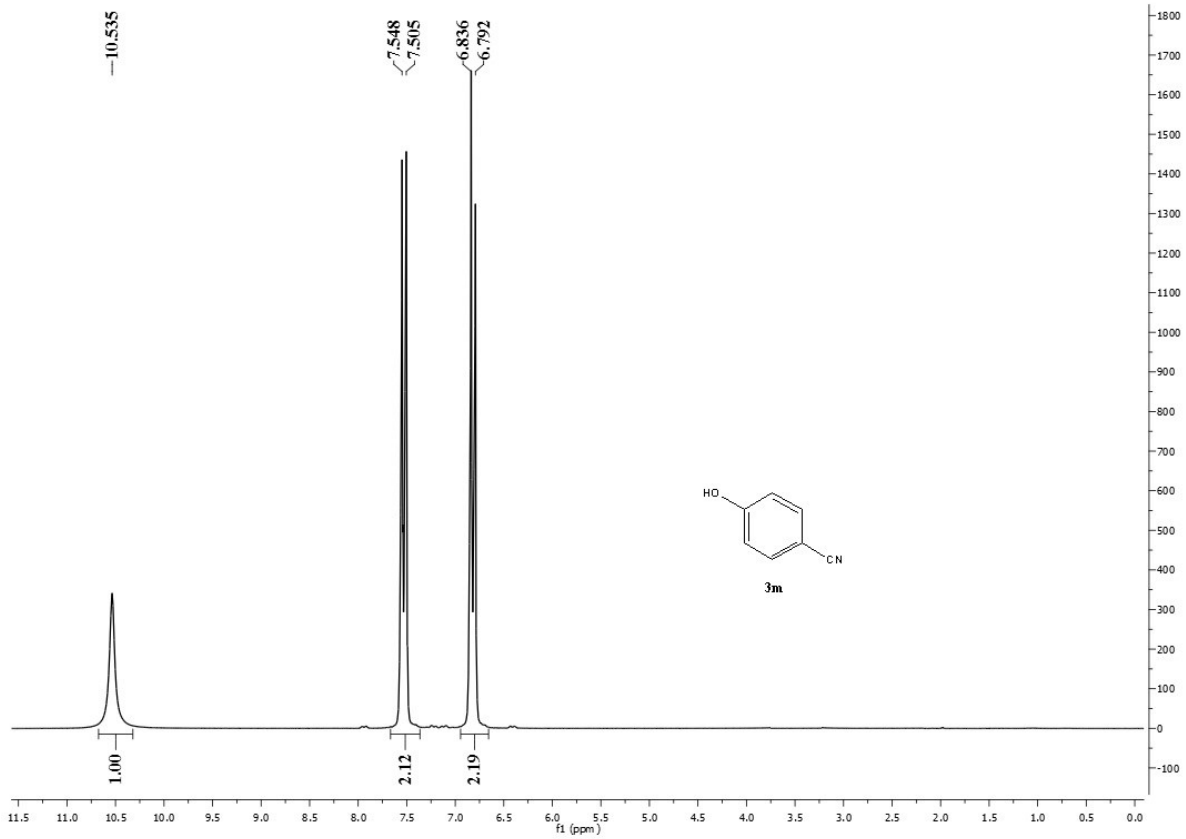


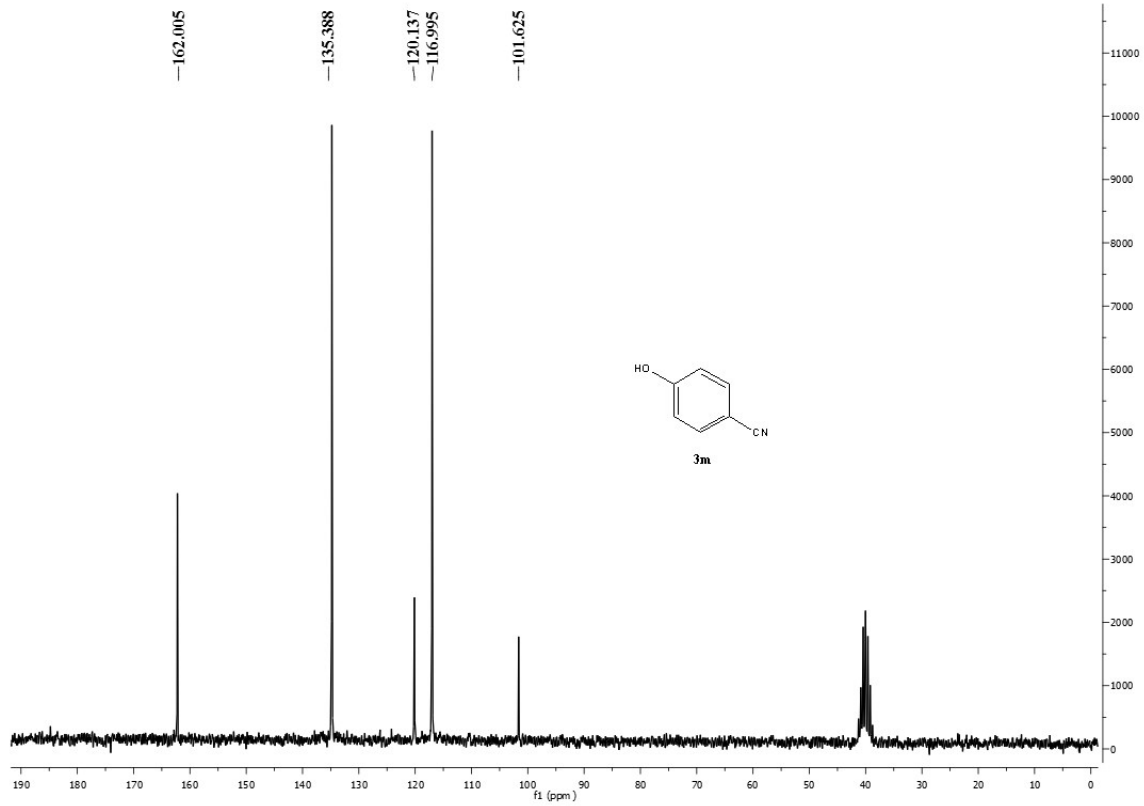
4-Nitrobenzonitrile (3k)



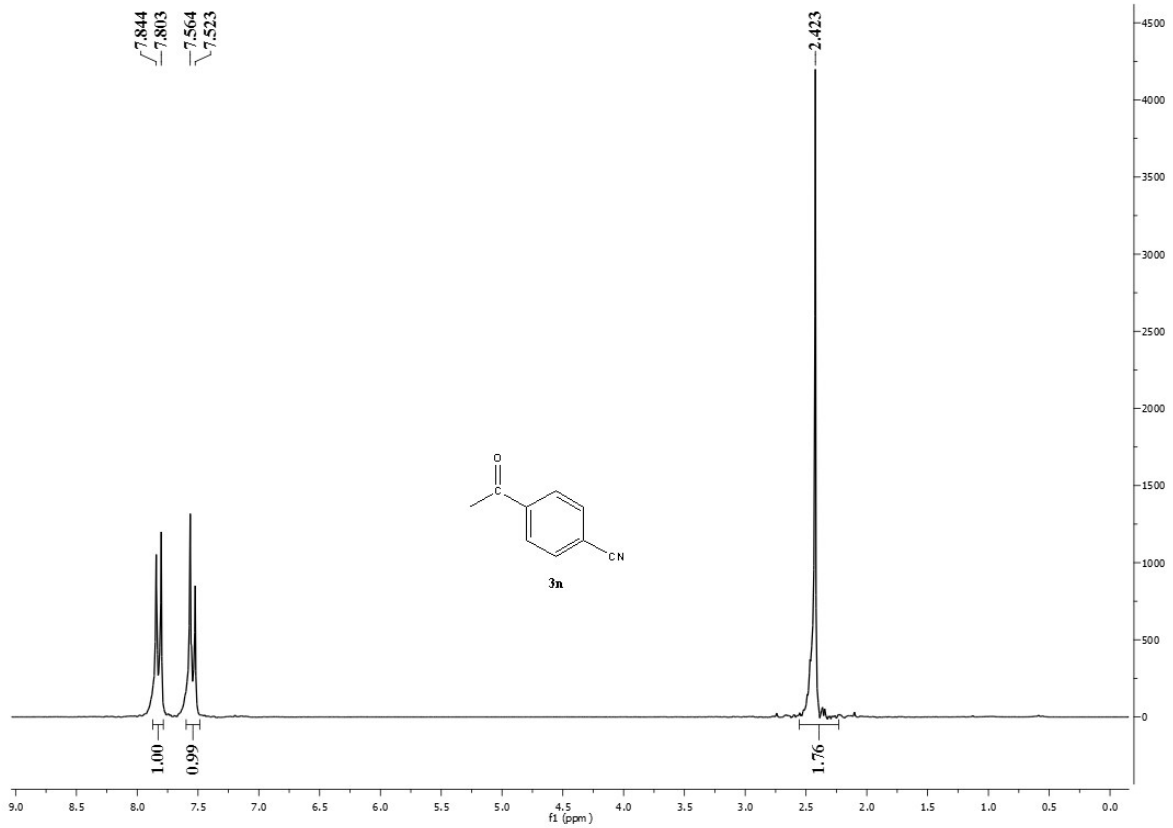


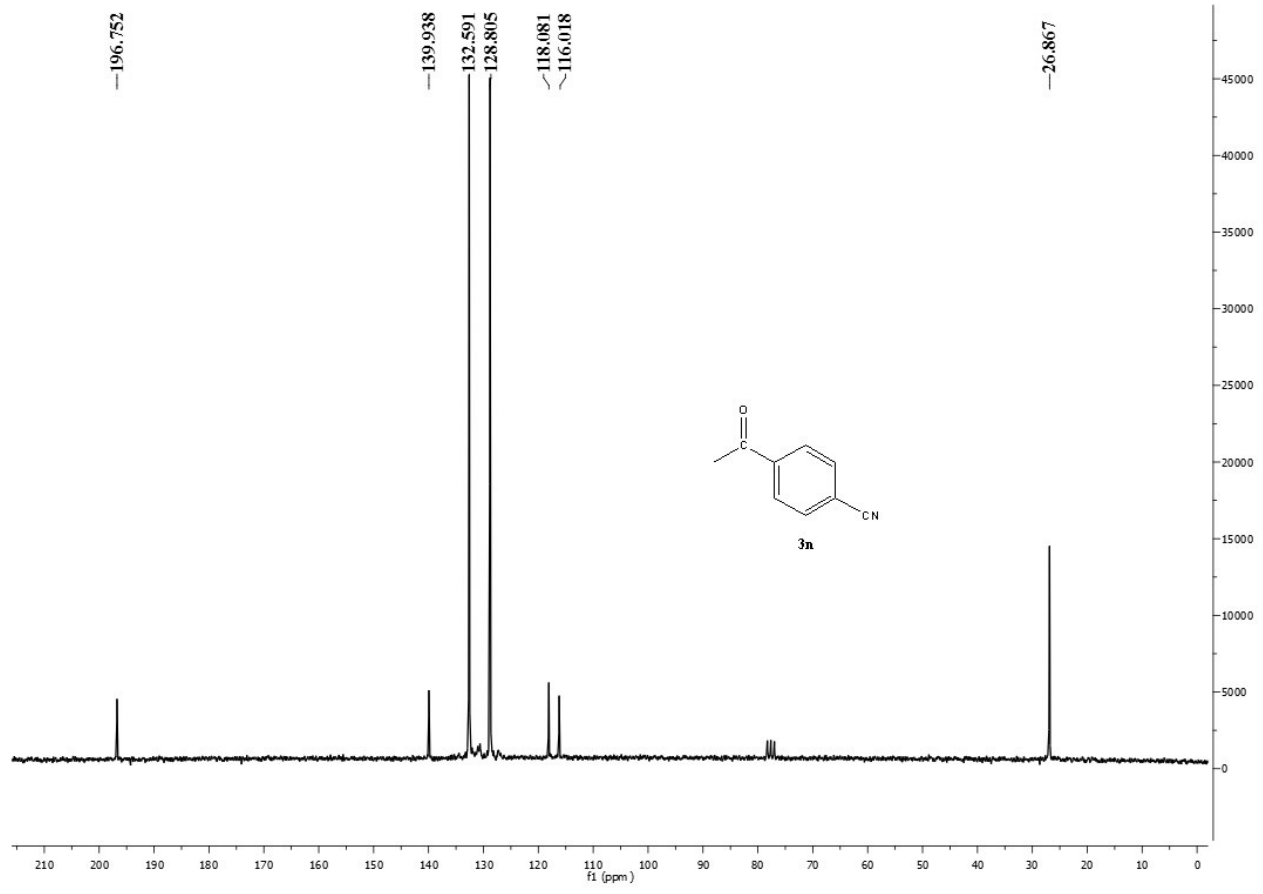
2-Hydroxybenzonitrile (3l)



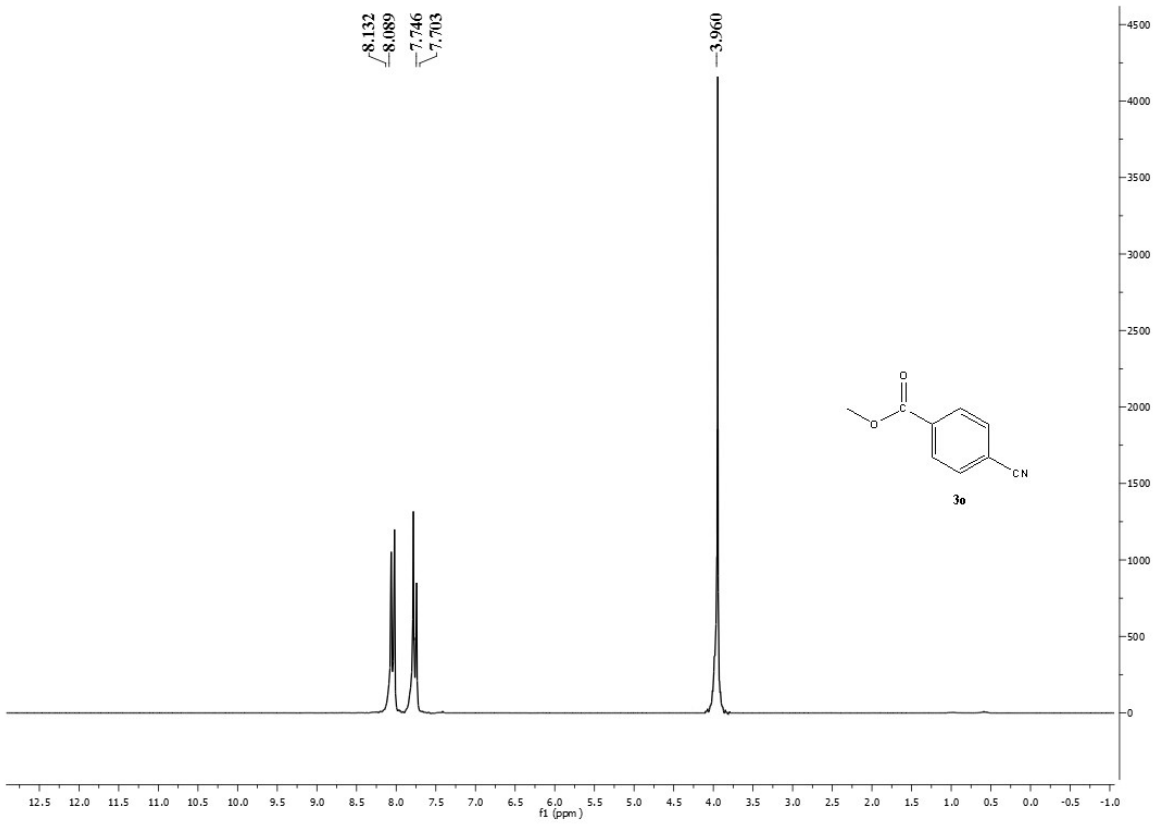


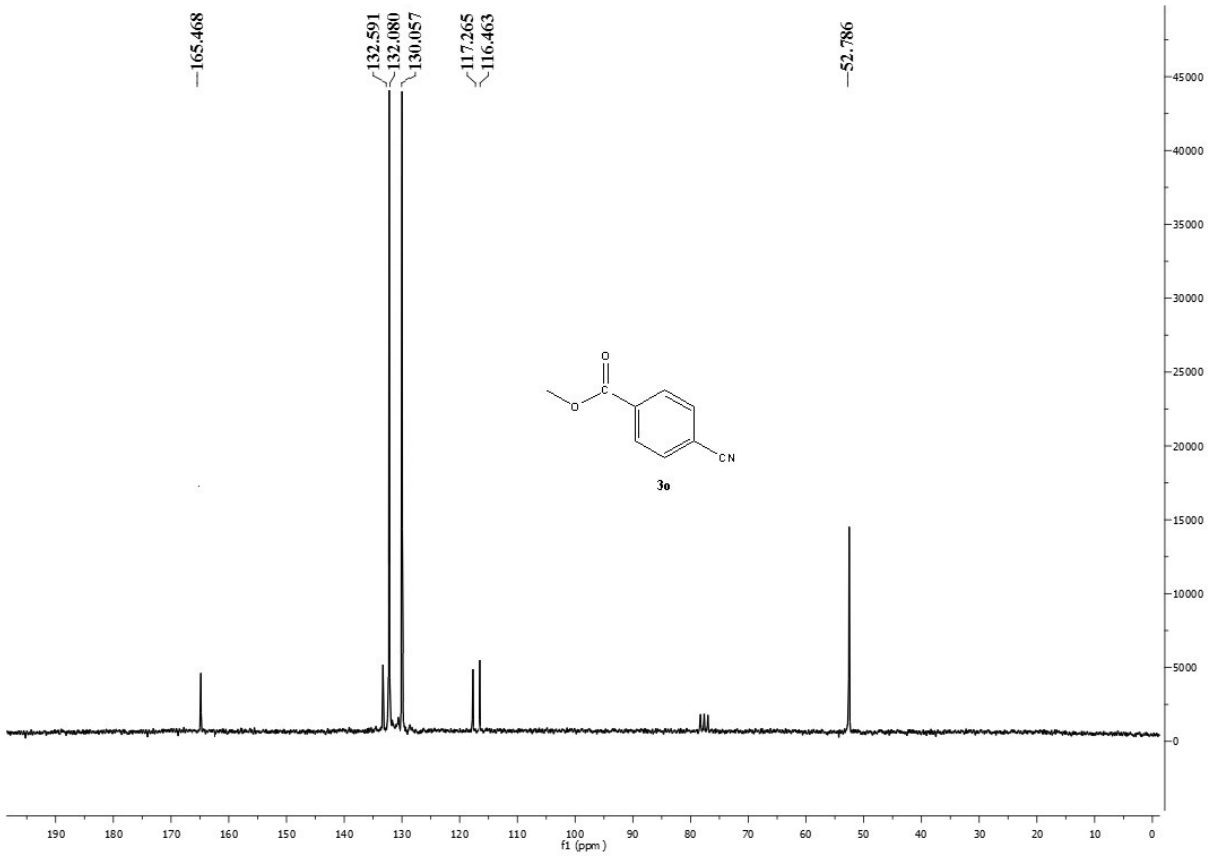
4-Hydroxybenzonitrile (3m)



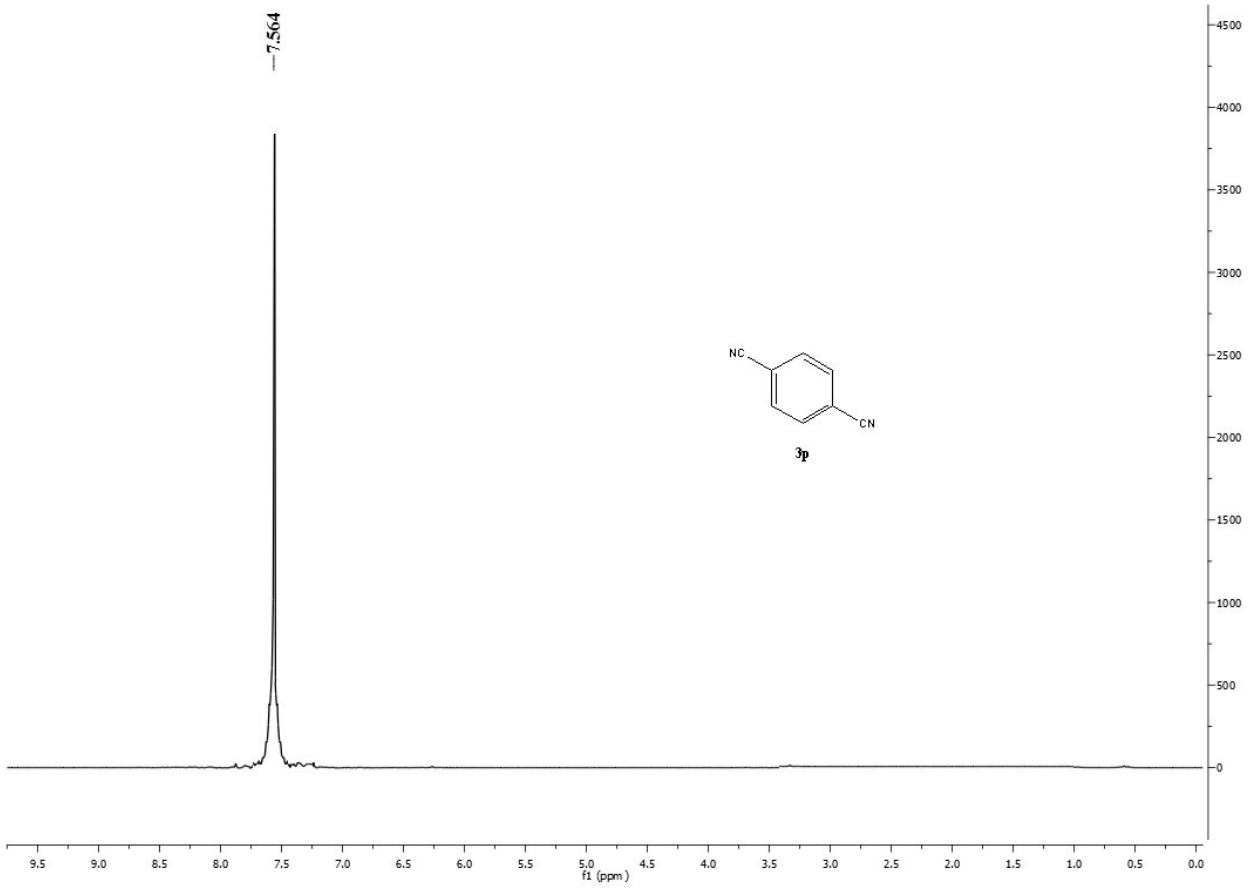


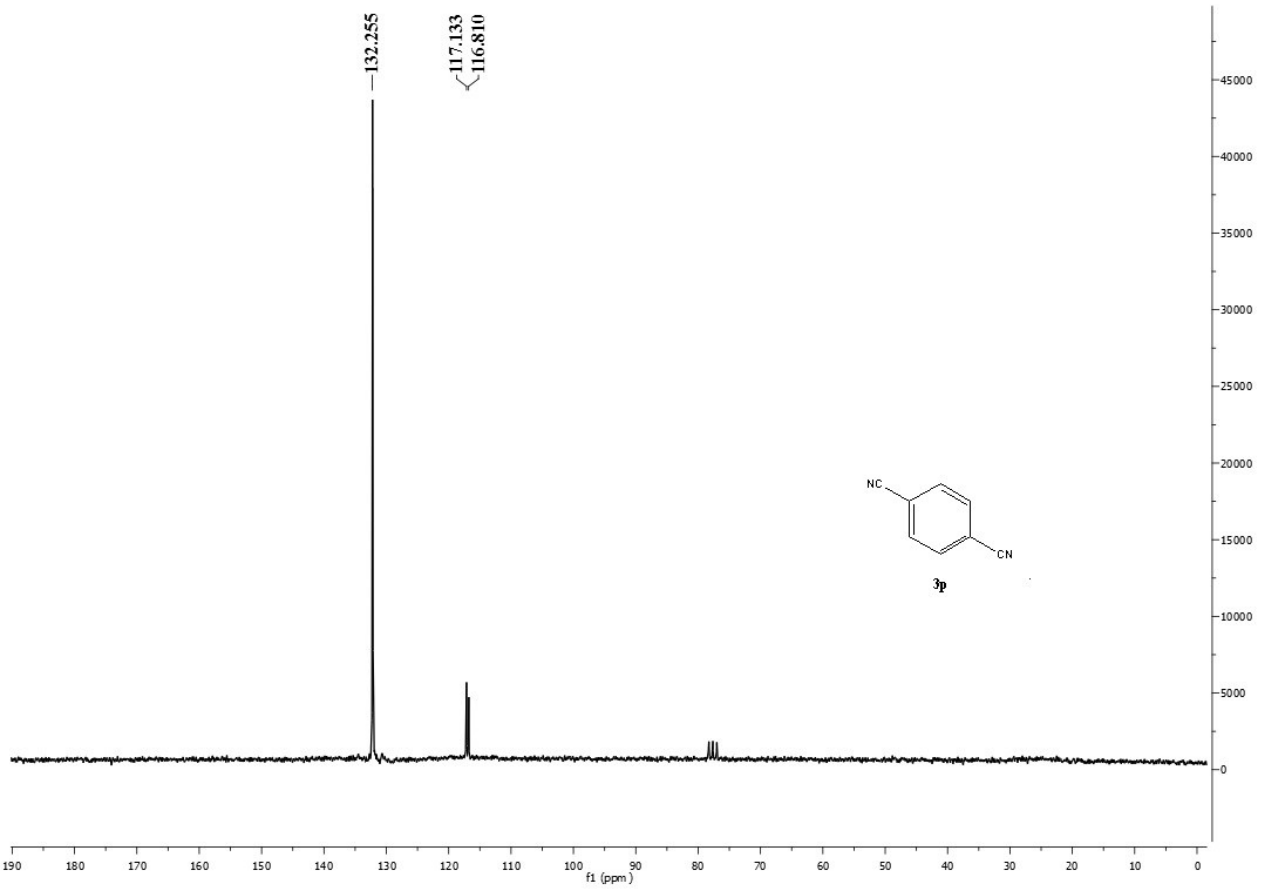
4-Acetylbenzonitrile (3n)



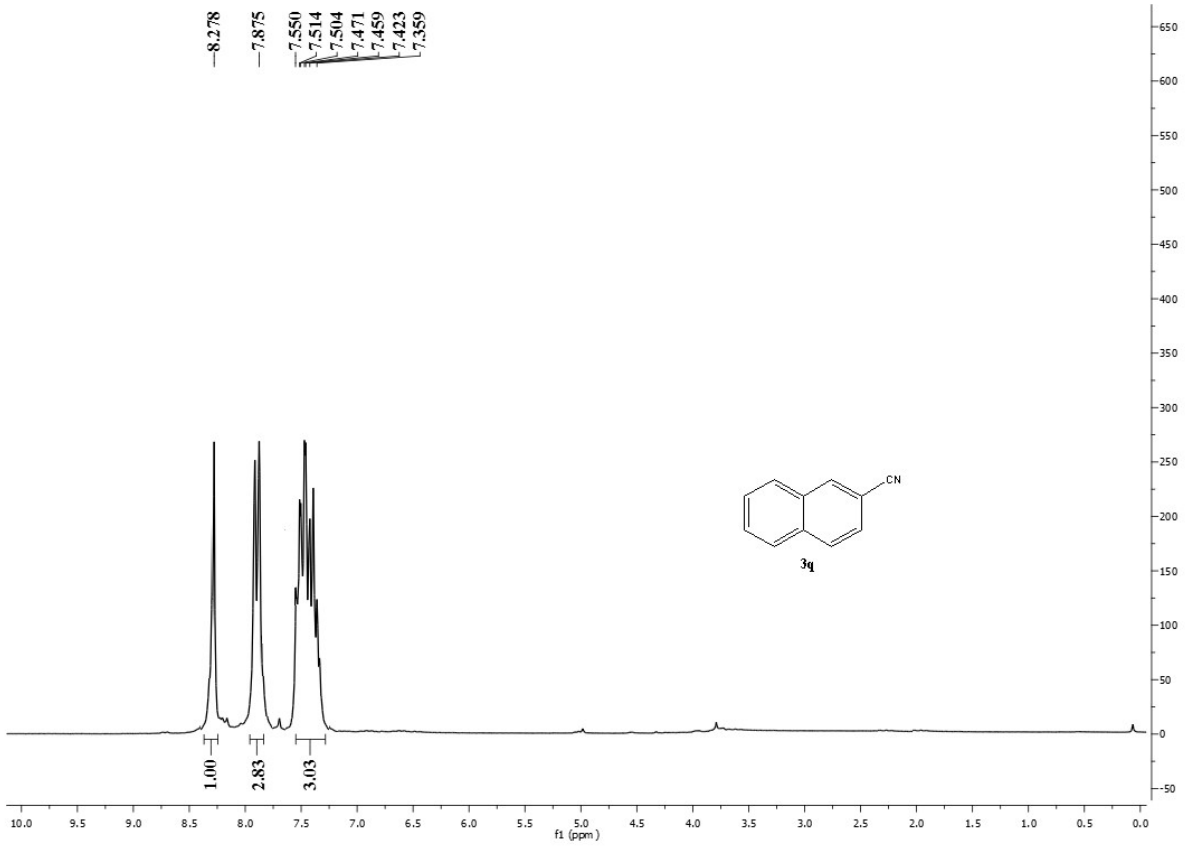


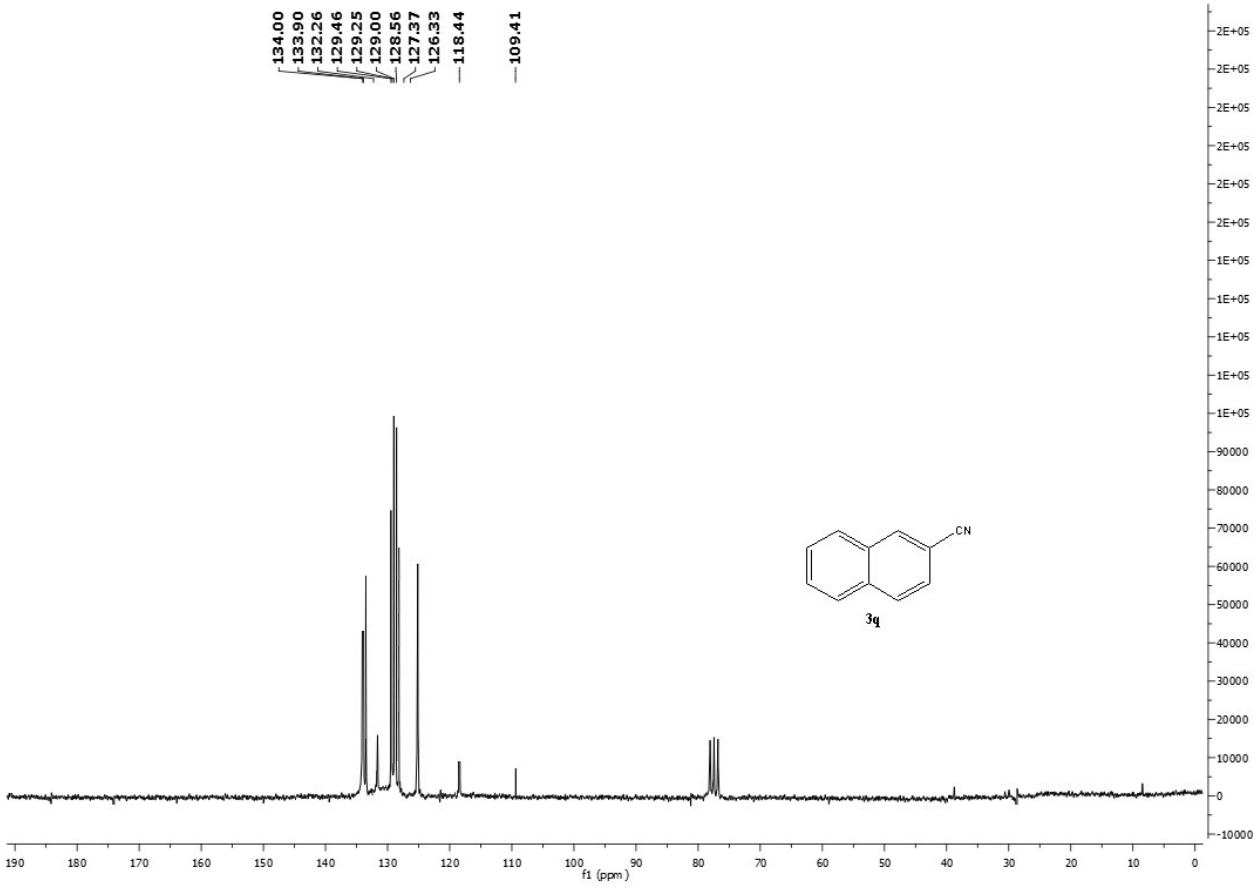
Methyl 4-cyanobenzoate (3o)



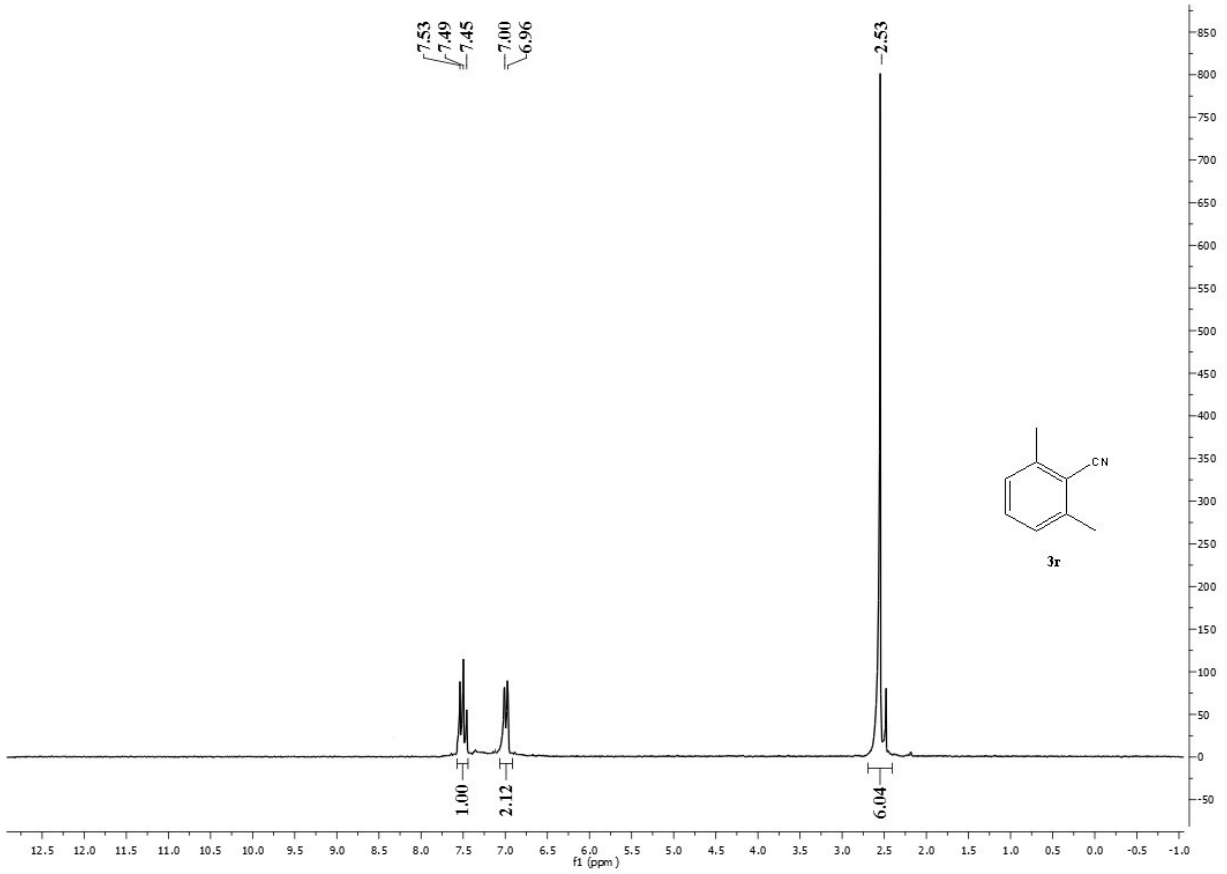


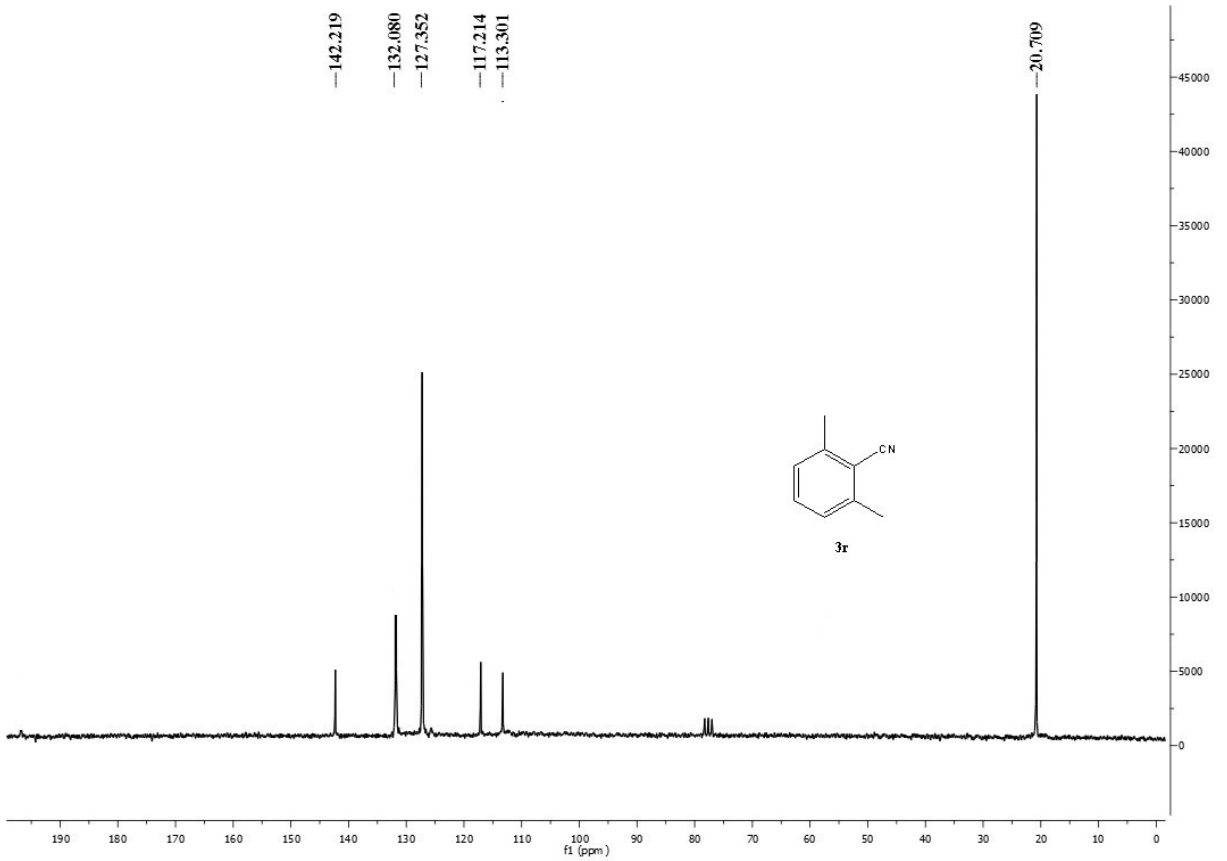
Terephthalonitrile (3p)



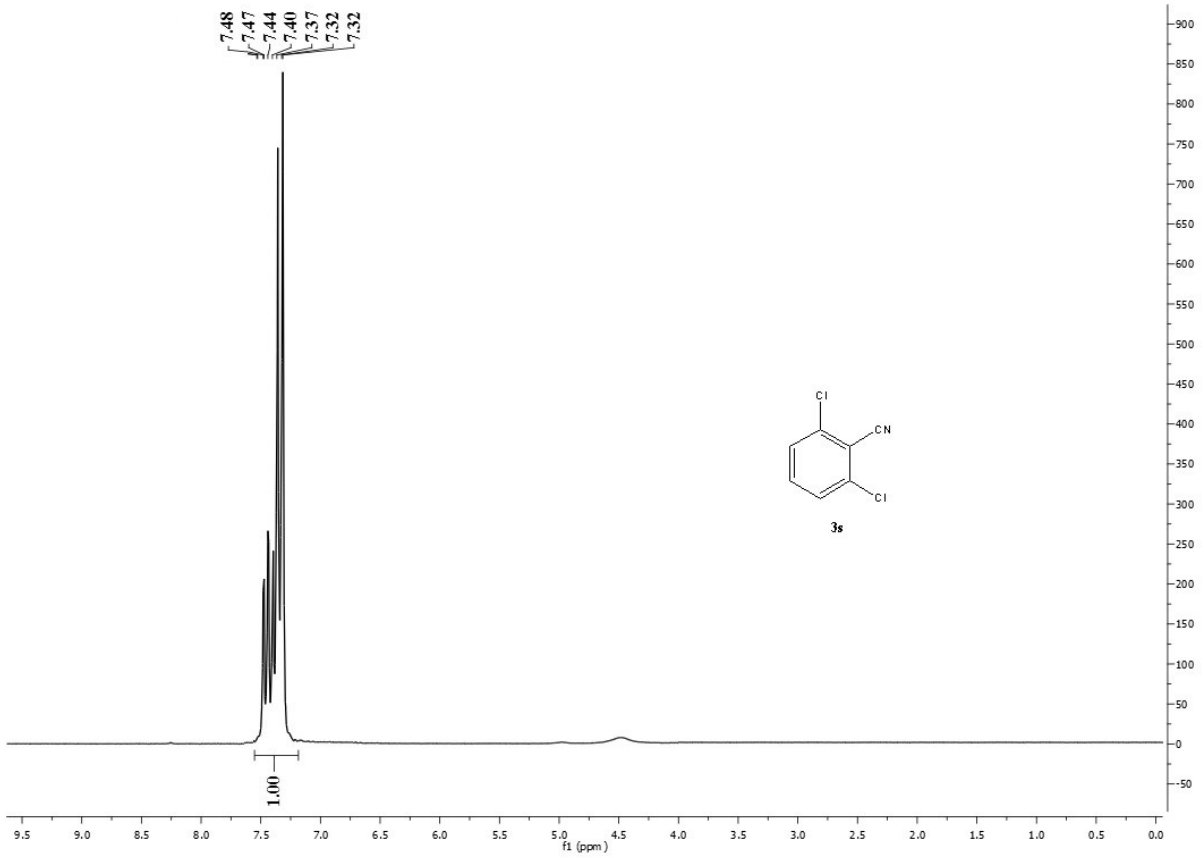


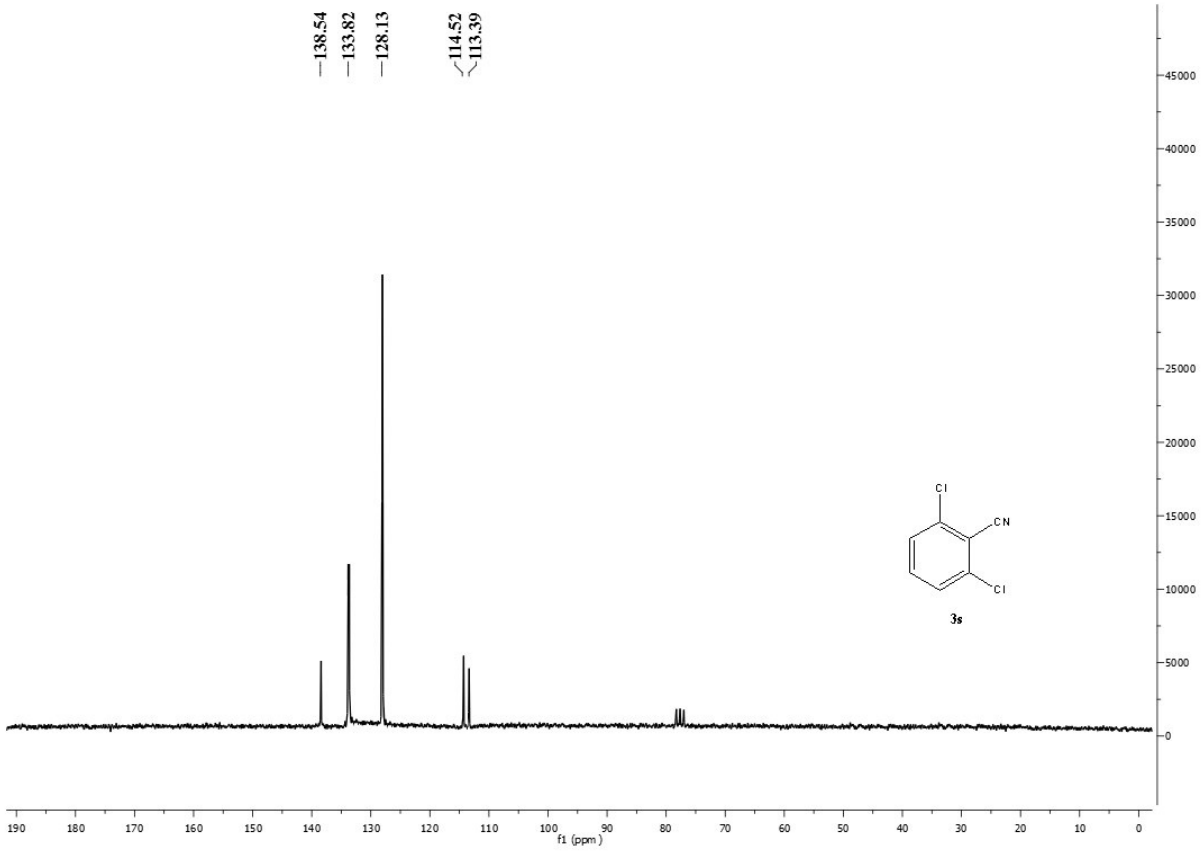
2-Naphthonitrile (3q)



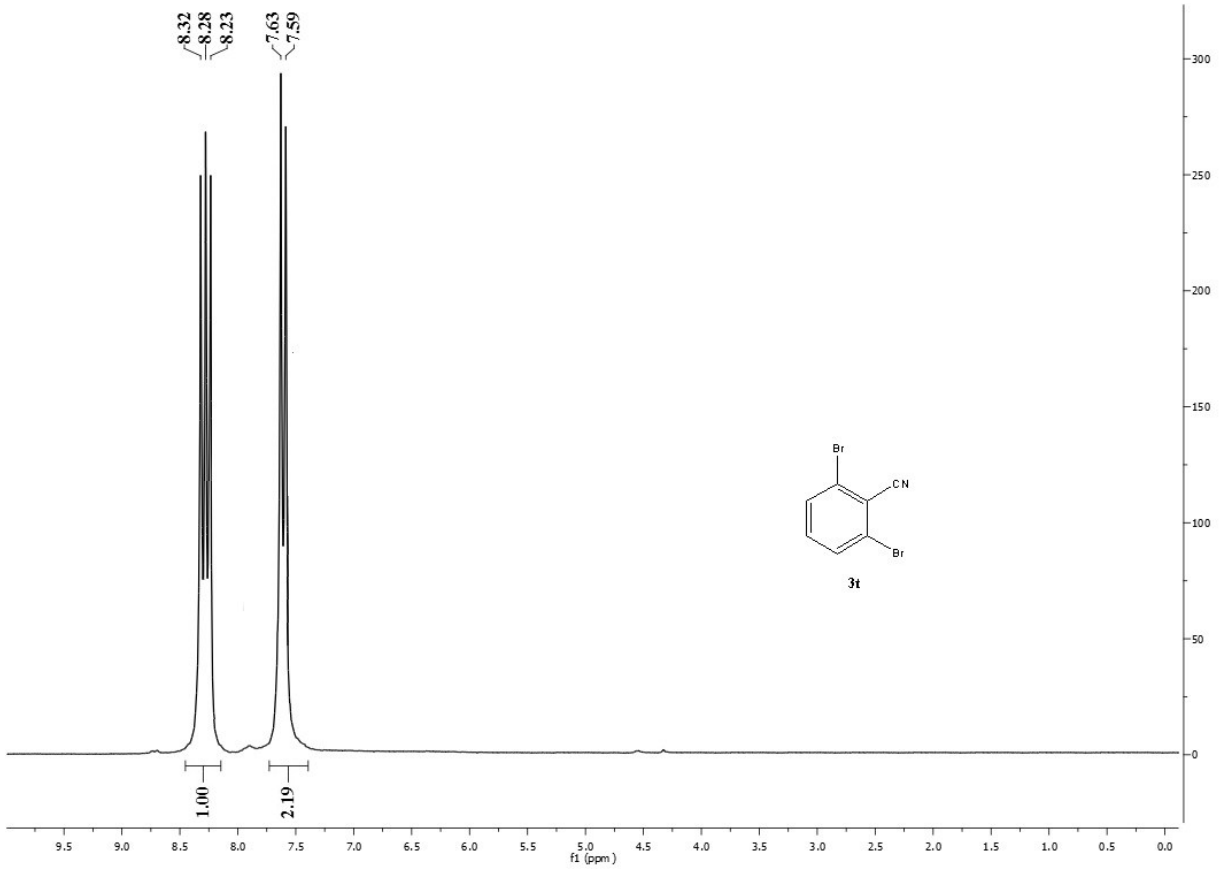


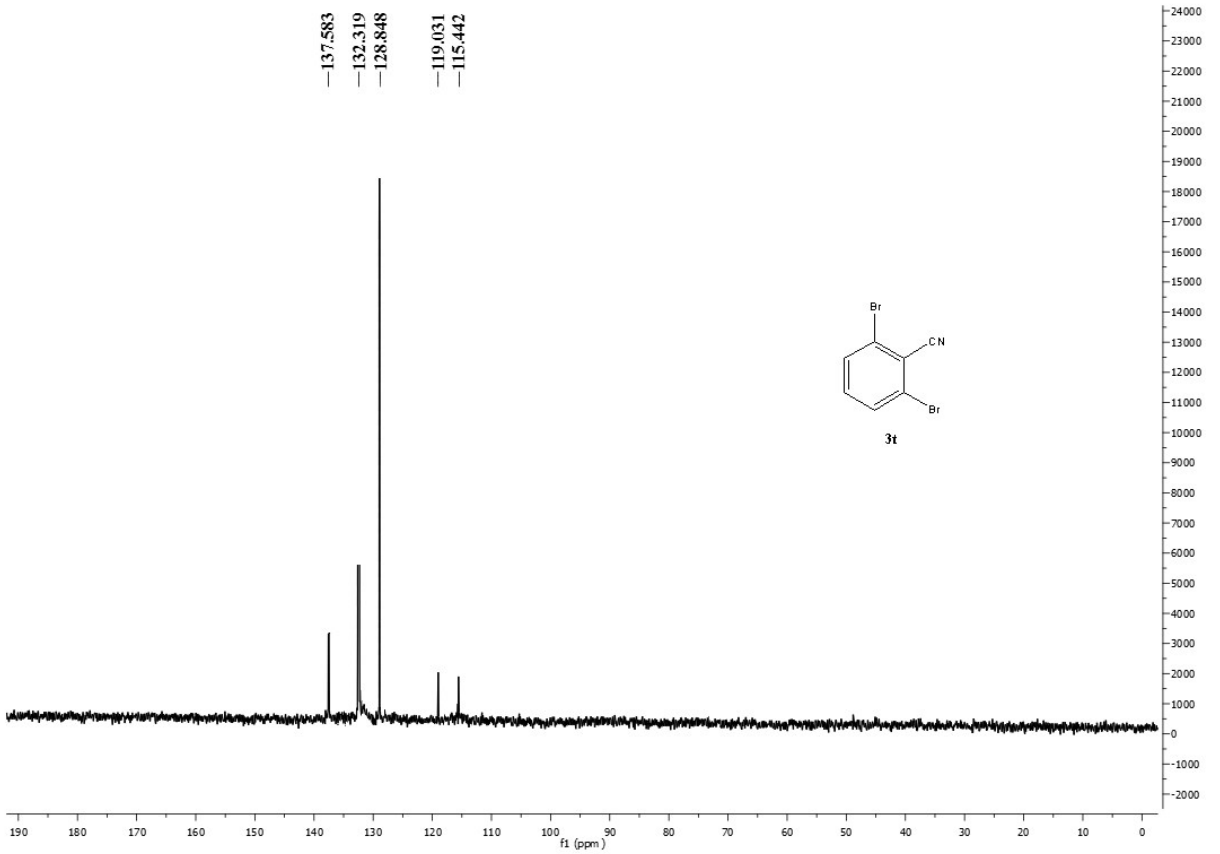
2,6-Dimethylbenzonitrile (3r)



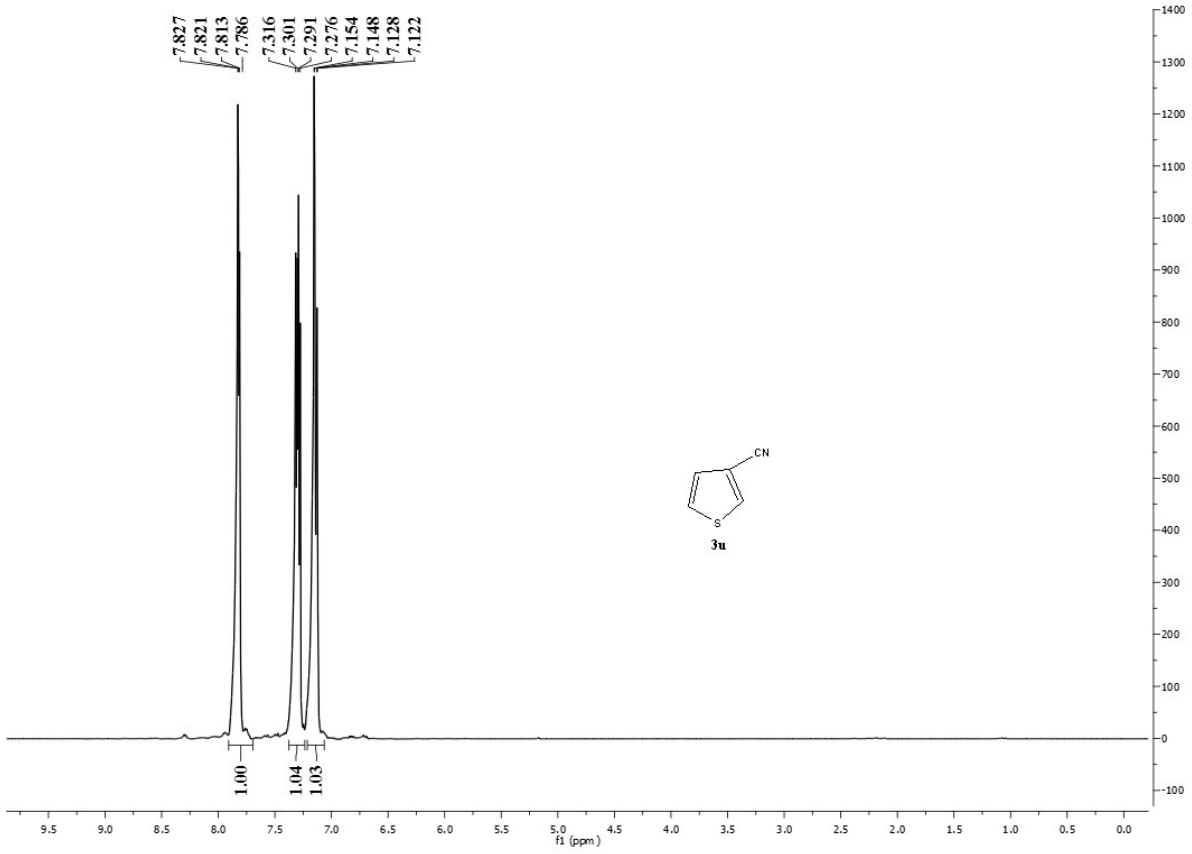


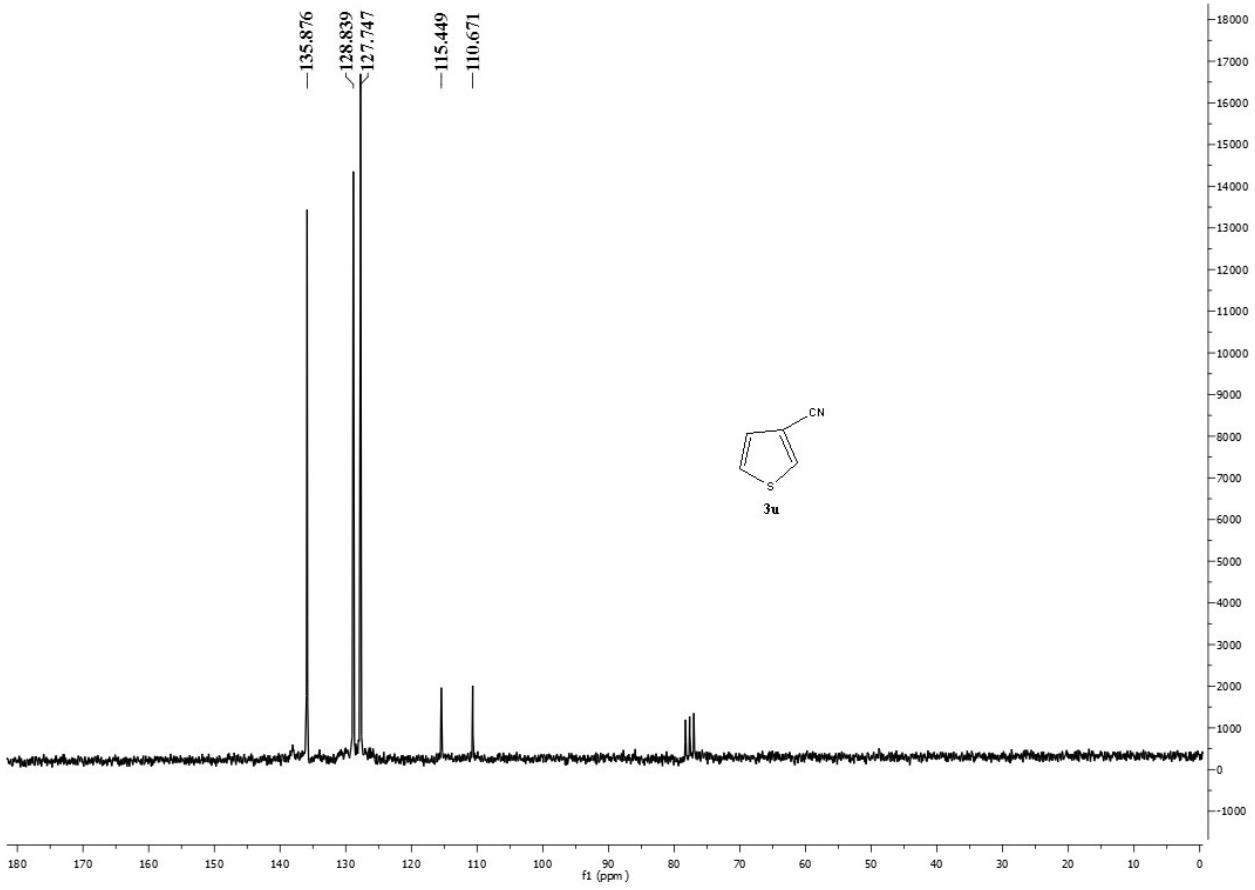
2,6-Dichlorobenzonitrile (3s)



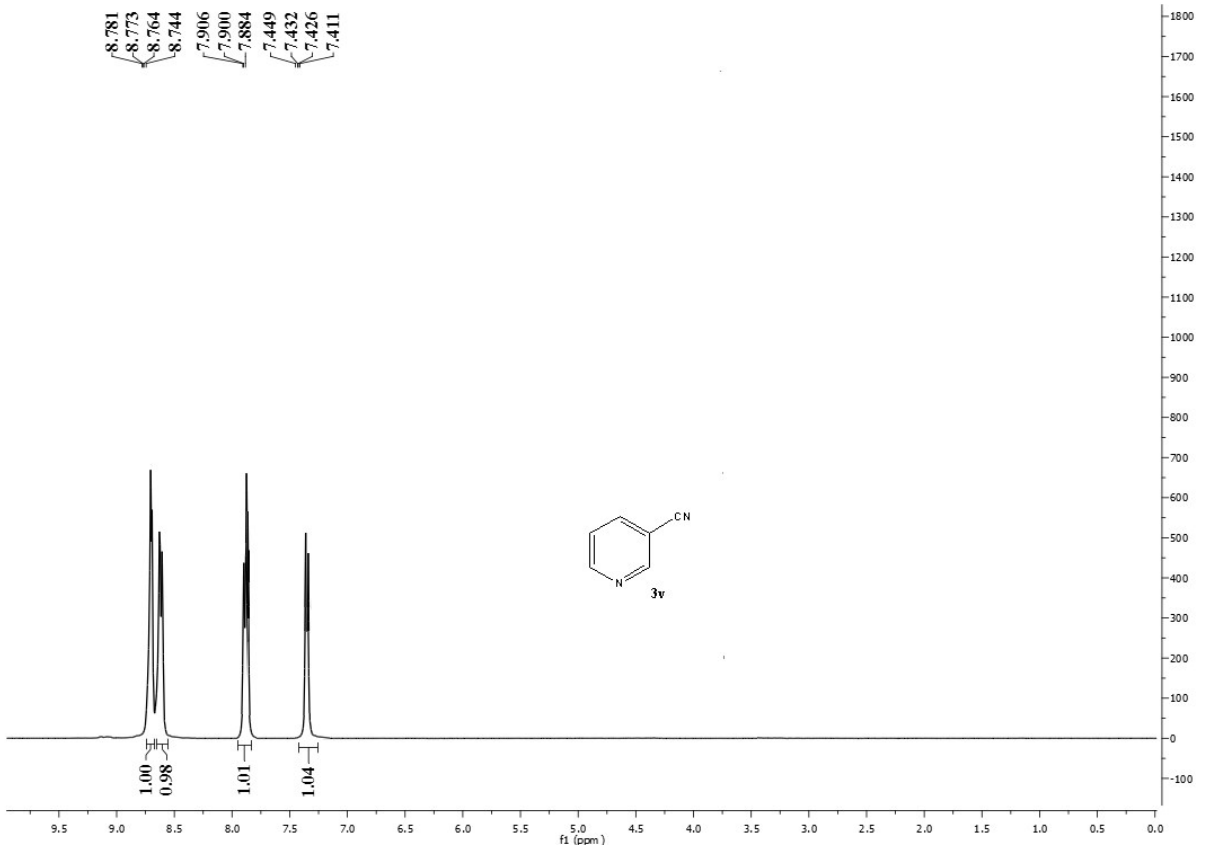


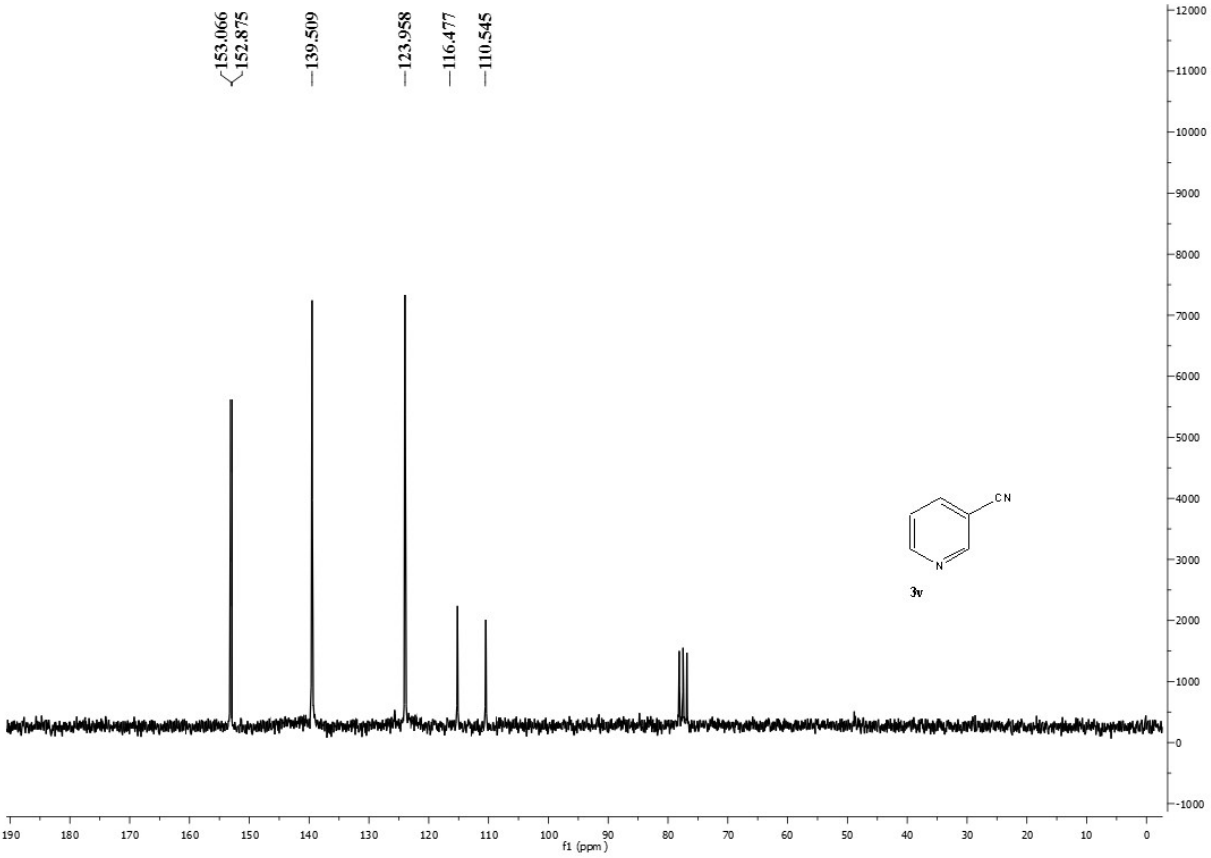
2,6-Dibromobenzonitrile (3t)



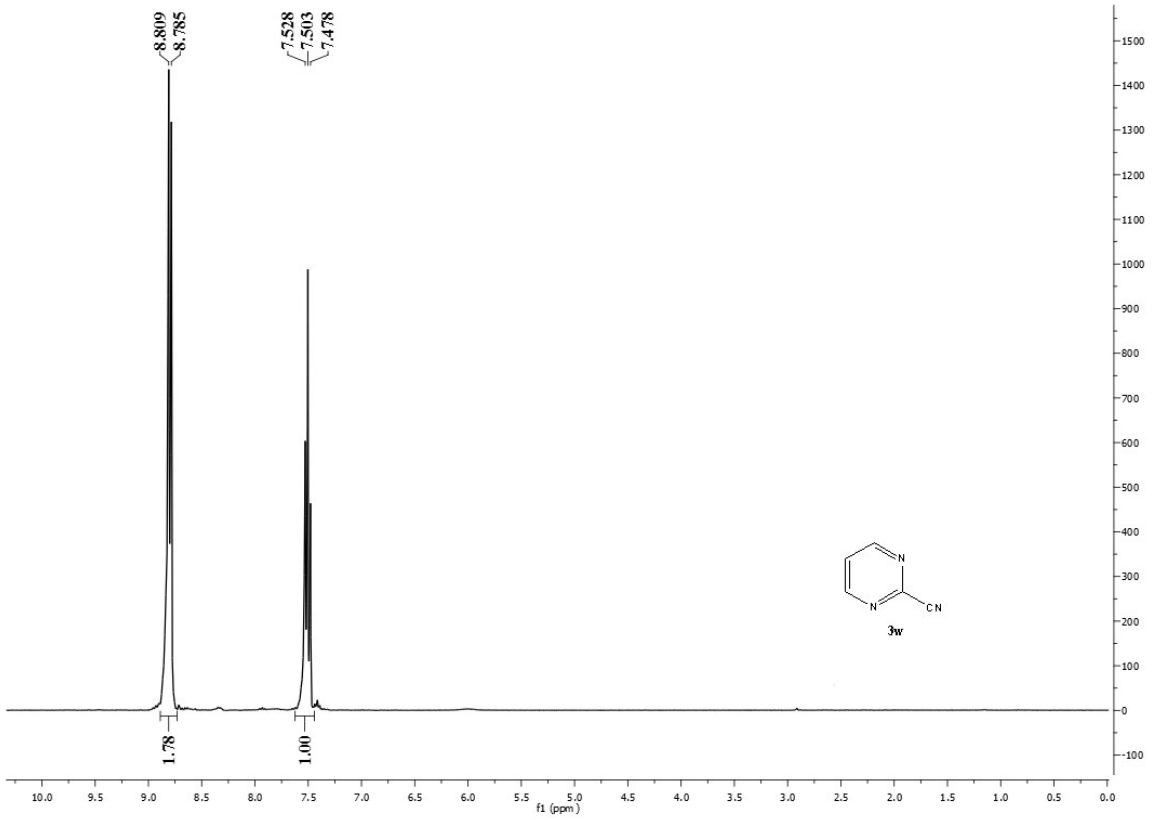


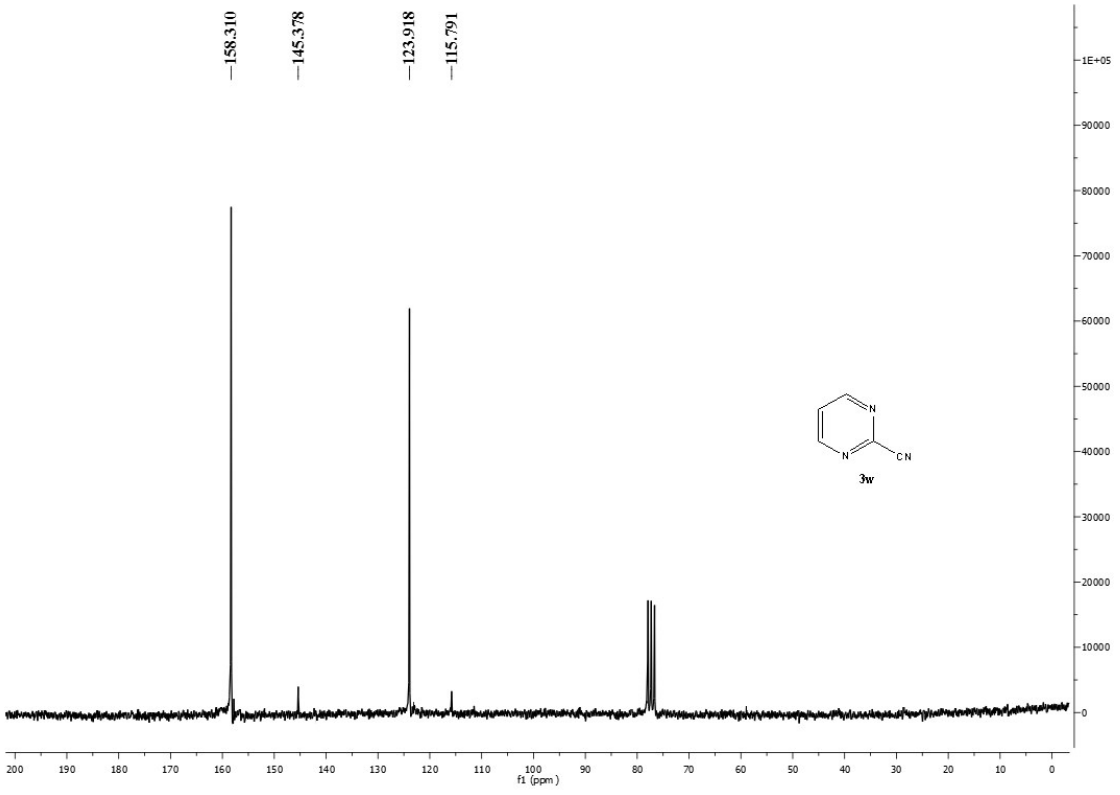
Thiophene-3-carbonitrile (3u)



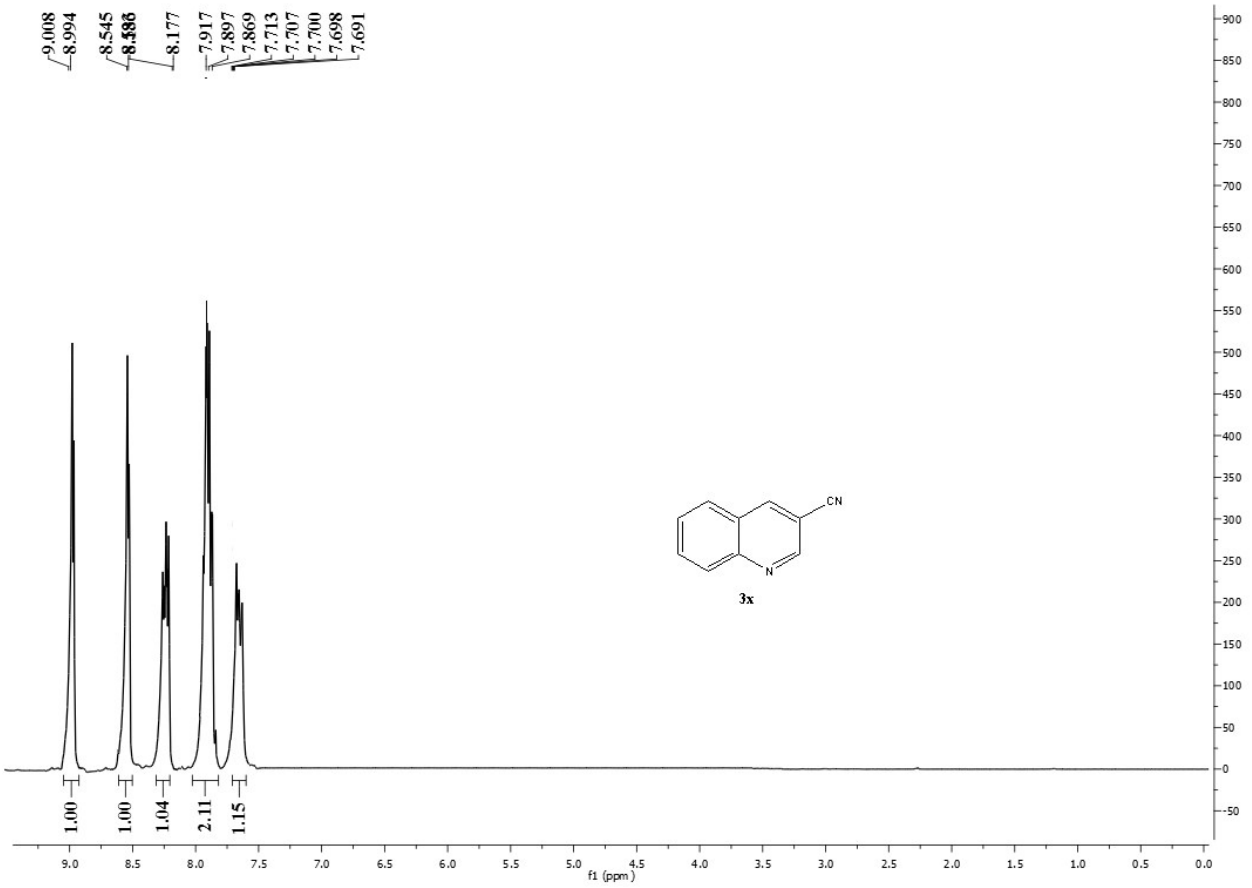


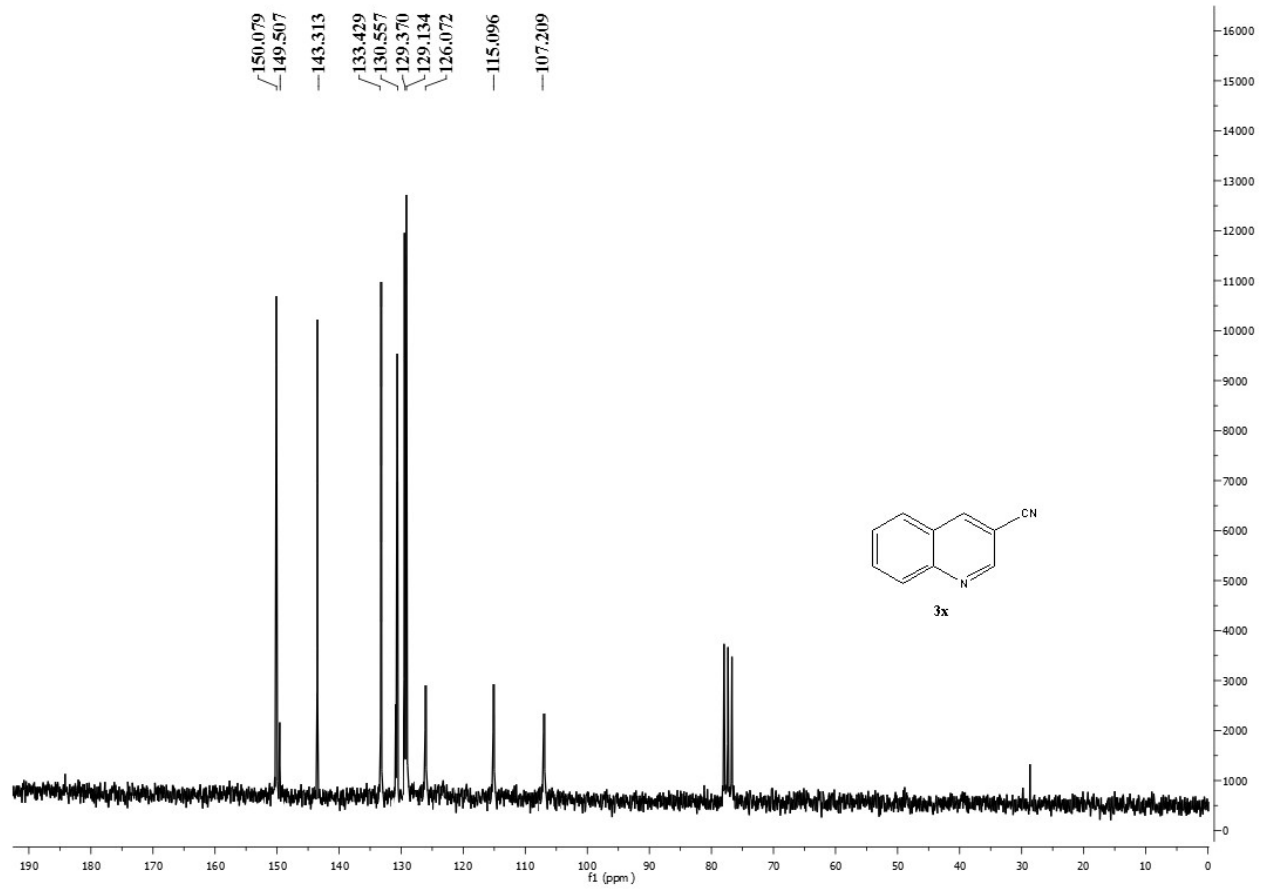
Pyridine-3-carbonitrile (3)



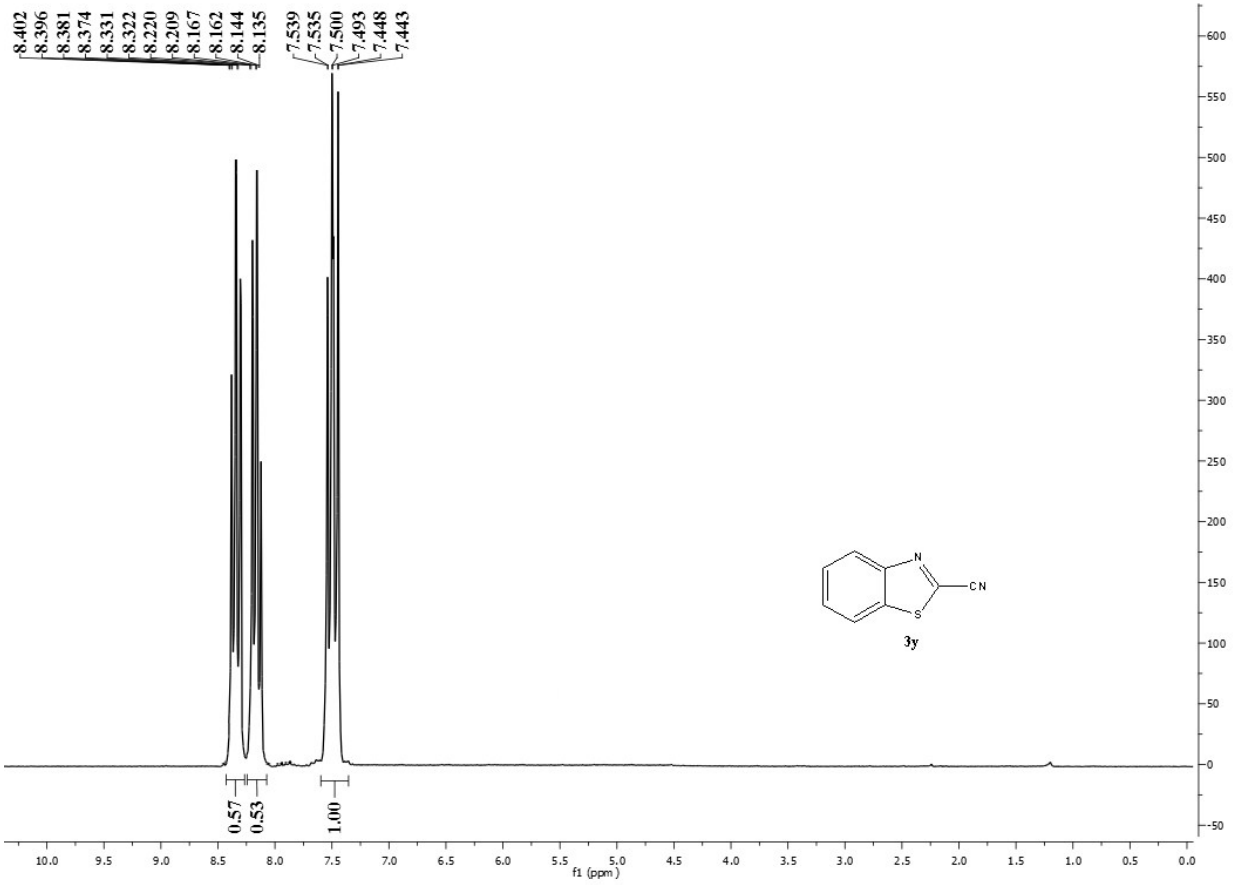


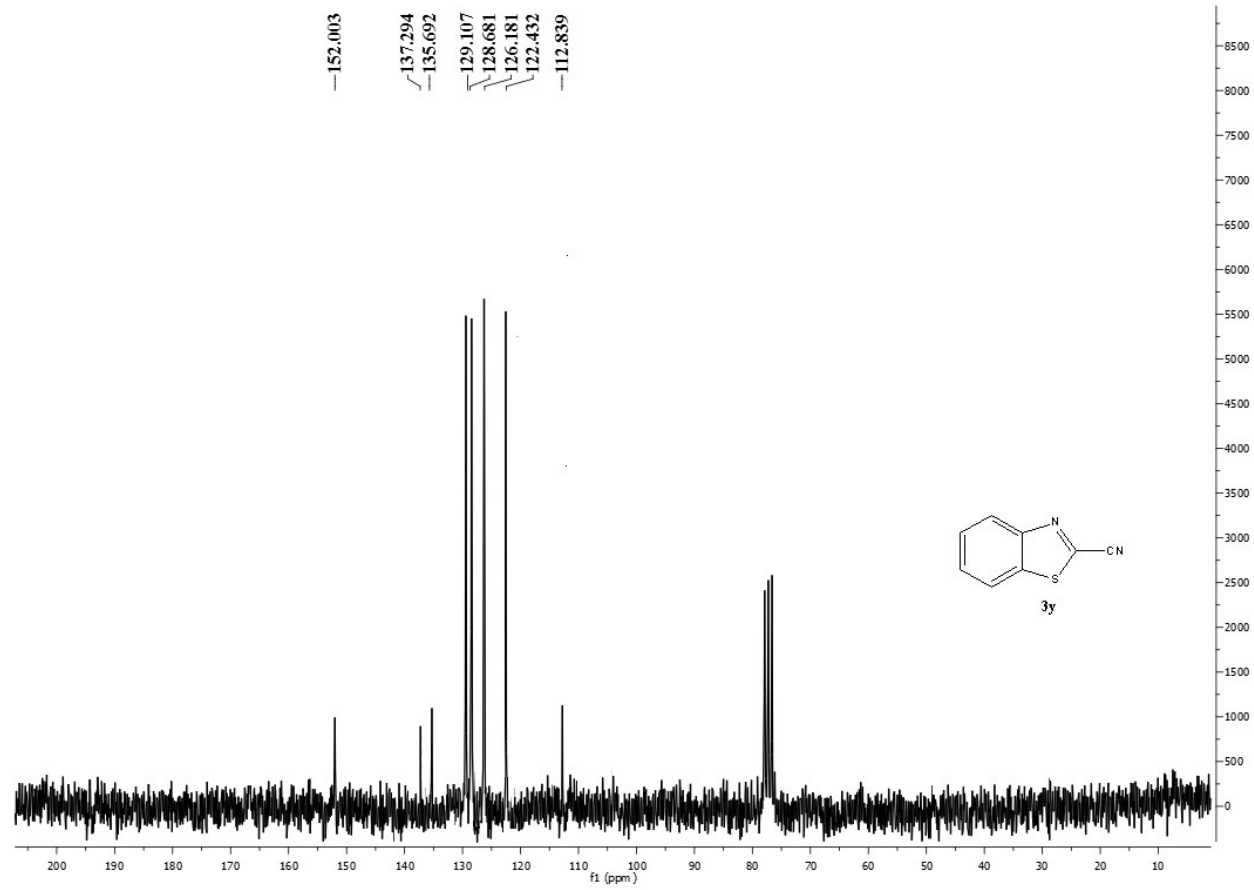
Pyrimidine-2-carbonitrile (3w)





Quinoline-3-carbonitrile (3x)





Benzo[*d*]thiazole-2-carbonitrile (3y)