Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

Perfluorobutyliodide-assisted direct cyanomethylation of azoles and phenols with acetonitrile

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General experimental procedures

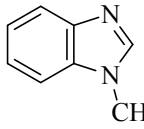
All reagents were of analytical grade, and obtained from commercial suppliers and used without further purification. CH_3CN was dried by standard method prior to use. Melting points were measured in an open capillary using Büchi melting point B-540 apparatus and are uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded on a 400 spectrometer (400 MHz for ^1H and 100 MHz for ^{13}C) using TMS as internal standard. The ^{19}F NMR spectra were obtained using a 400 spectrometer (376 MHz). $CDCl_3$ or DMSO-d_6 was used as the NMR solvents. The GC and GC-MS were calibrated by authentic standards. High-resolution mass spectra (HRMS) were acquired in the electron-impact mode (EI) using a TOF mass analyzer.

General procedure for synthesis of 3a–t

A solution of azoles **2a–j** or phenols **2k–t** (1.0 mmol) and NaH (72.0 mg, 3.0 mmol) in CH_3CN (10 mL) was stirred at 50 °C for 30 min. Subsequently, *n*-C_4F_9I (415.2 mg, 1.2 mmol) was added dropwise to the mixture via a syringe. Stirring was continued at 50 °C for 12–24 h (monitored by TLC). After the completion of reaction, the reaction mixture was quenched with H_2O (20 mL) and extracted with ethyl acetate (3×10 mL). The organic layer was separated and dried over Na_2SO_4, filtered and evaporated under vacuum. The crude product was purified by column chromatography on silica gel using *n*-hexane /ethyl acetate (2/3) [*n*-hexane /dichloromethane (3/1) for **3k–3t**] as eluent to afford the pure target compounds **3a–3t**.

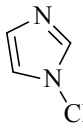
Spectral and analytical data of compounds 3

1*H*-Benzimidazole-1-acetonitrile (3a, CAS: 4414-74-8):[1] Light yellow solid. Yield: 86%, mp 133.5–134.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (s, 1H), 7.85 (d, *J* = 7.6 Hz, 1H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.43–7.36 (m, 2H), 5.08 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.7, 142.0, 132.8, 124.3, 123.5, 121.0, 113.3, 109.2, 32.7 ppm.



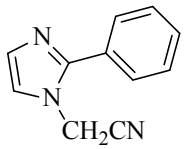
3a

Imidazol-1-yl-acetonitrile (3b, CAS: 98873-55-3):[2] Light yellow liquid. Yield: 87%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (s, 1H), 7.14 (s, 1H), 7.06 (s, 1H), 4.95 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.1, 130.9, 119.0, 113.7, 34.4 ppm.



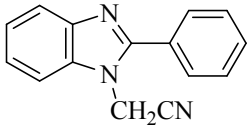
3b

2-(2-Phenyl-1*H*-imidazol-1-yl)acetonitrile (3c): Yellow liquid. Yield: 70%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59–7.56 (m, 2H), 7.53–7.48 (m, 3H), 7.21 (d, *J* = 1.2 Hz, 1H), 7.16 (d, *J* = 1.2 Hz, 1H), 4.89 (s, 2H) ppm; ^{13}C NMR (100MHz, $CDCl_3$): δ 148.2, 130.0, 129.9, 129.1, 128.9, 128.8, 120.6, 114.2, 34.8 ppm; HRMS (EI): calcd for $C_{11}H_9N_3$ $[M–H]^+$: 182.0718, found: 182.0720.



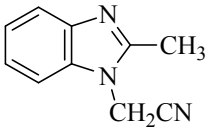
3c

2-(2-Phenyl-1*H*-benzol[d]imidazol-1-yl)acetonitrile (3d): White solid. Yield: 68%, mp 151.0–152.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86–7.84 (m, 1H), 7.74–7.71 (m, 2H), 7.57–7.55 (m, 3H), 7.49–7.46 (m, 1H), 7.42–7.37 (m, 2H), 5.02 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.1, 142.9, 134.9, 130.7, 129.3, 129.2, 128.6, 124.1, 123.8, 120.6, 113.9, 109.4, 33.1 ppm; HRMS (EI): calcd for $C_{15}H_{11}N_3$ $[M–H]^+$: 232.0875, found: 232.0879.



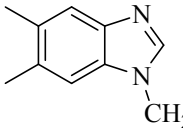
3d

2-(2-Methyl-1*H*-benzol[d]imidazol-1-yl)acetonitrile (3e, CAS: 54980-87-9):[3] White solid. Yield: 75%, mp 145.6–146.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73–7.71 (m, 1H), 7.34–7.29 (m, 3H), 4.96 (s, 2H), 2.66 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.6, 142.5, 134.1, 123.4, 123.2, 119.8, 113.3, 108.5, 31.4, 13.7 ppm.



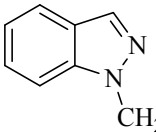
3e

2-(5,6-Dimethyl-1*H*-benzo[d]imidazol-1-yl)acetonitrile (3f): Light yellow solid. Yield: 80%, mp 133.5–134.8 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.18 (s, 1H), 7.50 (s, 1H), 7.47 (s, 1H), 5.60 (s, 2H), 2.36 (s, 3H), 2.32 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 142.8, 141.8, 132.0, 131.5, 130.9, 119.8, 115.9, 110.1, 32.3, 20.1, 19.8 ppm; HRMS (EI): calcd for $C_{11}H_{11}N_3$ [M]$^+$: 185.0953, found: 185.0954.



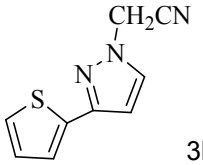
3f

2-(1*H*-Indazol-1-yl)acetonitrile (3g): Light yellow solid. Yield: 62%, mp 60.2–61.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (s, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.50–7.45 (m, 2H), 7.26–7.23 (m, 1H), 5.29 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.5, 135.7, 127.7, 124.8, 122.0, 121.7, 113.9, 108.5, 37.0 ppm; HRMS (EI): calcd for $C_9H_7N_3$ [M]$^+$: 157.0640, found: 157.0639.



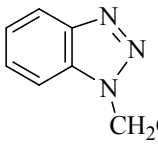
3g

2-(3-(Thiophen-2-yl)-1*H*-pyrazol-1-yl)acetonitrile (3h): Light yellow solid. Yield: 58%, mp 102.5–103.5 °C.^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, J = 2.4 Hz, 1H), 7.33 (d, J = 2.8 Hz, 1H), 7.27 (d, J = 5.2 Hz, 1H), 7.07–7.05 (m, 1H), 6.55 (d, J = 2.4 Hz, 1H), 5.06 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.6, 135.4, 131.2, 127.6, 125.3, 124.6, 113.8, 105.0, 39.6 ppm; HRMS (EI): calcd for $C_9H_7N_3S$ [M]$^+$: 189.0361, found: 189.0362.



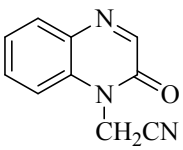
3h

2-(1*H*-Benzo[d][1,2,3]triazol-1-yl)acetonitrile (3i, CAS: 111198-08-4):[4] Light yellow solid. Yield: 40%, mp 84.0–85.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, J = 8.8 Hz, 1H), 7.69–7.61 (m, 2H), 7.50–7.46 (m, 1H), 5.63 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.1, 132.3, 129.0, 125.0, 120.6, 112.6, 108.8, 35.7 ppm.



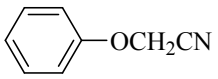
3i

2-(2-Oxoquinoxalin-1(2*H*)-yl)acetonitrile (3j): Light yellow solid. Yield: 60%, mp 60.2–61.2 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.45 (s, 1H), 8.20 (dd, J = 8.0, 1.2 Hz, 1H), 7.92–7.88 (m, 1H), 7.73 (d, J = 8.0 Hz, 1H), 7.64–7.60 (m, 1H), 5.13 (s, 2H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 159.7, 147.6, 146.8, 135.0, 127.6, 127.4, 126.0, 121.1, 115.6, 34.3 ppm; HRMS (EI): calcd for $C_{10}H_7N_3O$ [M]$^+$:185.0589, found:185.0590.



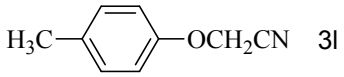
3j

2-Phenoxyacetonitrile (3k, CAS: 3598-14-9):[5] Light yellow liquid. Yield: 82%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38–7.34 (m, 2H), 7.09 (t, *J* = 8.0 Hz, 1H), 7.00–6.98 (m, 2H), 4.76 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.6, 129.9, 123.2, 115.2, 115.0, 53.6 ppm.



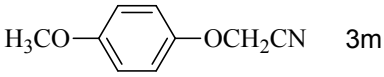
3k

2-(*p*-Tolyloxy)acetonitrile (3l, CAS: 33901-44-9):[5] Light yellow liquid. Yield: 90%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 2H), 4.70 (s, 2H), 2.30 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.6, 132.7, 130.3, 115.3, 115.1, 54.0, 20.5 ppm.



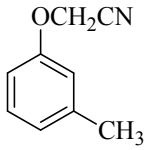
3l

2-(4-Methoxyphenoxy)acetonitrile (3m, CAS: 22446-12-4):[5] Light yellow liquid. Yield: 93%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.96–6.92 (m, 2H), 6.89–6.85 (m, 2H), 4.69 (s, 2H), 3.78 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.7, 150.7, 116.8, 115.4, 115.0, 55.7, 55.0 ppm.



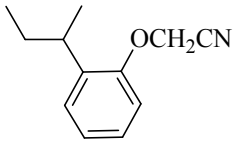
3m

2-(*m*-Tolyloxy)acetonitrile(3n, CAS: 50635-22-8):[5] Light yellow liquid. Yield: 85%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (t, *J* = 8.0 Hz, 1H), 6.89 (d, *J* = 8.0 Hz, 1H), 6.78–6.75 (m, 2H), 4.70 (s, 2H), 2.34 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.6, 140.2, 129.6, 124.0, 115.9, 115.4, 111.8, 53.6, 21.5 ppm.



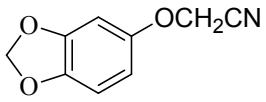
3n

2-(2-(*sec*-Butyl)phonoxy)acetonitrile (3o): Light yellow liquid. Yield: 70%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23–7.16 (m, 2H), 7.07–7.03 (m, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 4.73 (s, 2H), 3.12–3.03 (m, 1H), 1.65–1.52 (m, 2H), 1.20 (d, *J* = 6.8 Hz, 3H), 0.83 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.2, 137.0, 127.6, 126.8, 123.2, 115.5, 112.1, 54.0, 33.6, 30.0, 20.7, 12.2 ppm; HRMS (EI): calcd for $C_{12}H_{15}NO$ $[M]^+$: 189.1154, found: 189.1156.



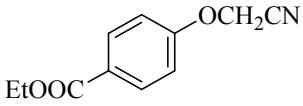
3o

2-(Benzo[d][1,3]doaxol-5-yloxy)acetonitrile (3p): Yellow solid. Yield: 76%, mp 44.0–45.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.74 (d, *J* = 8.4 Hz, 1H), 6.56 (d, *J* = 2.4 Hz, 1H), 6.42 (dd, *J* = 8.4, 2.4 Hz, 1H), 5.95(s, 2H), 4.68 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.9, 148.6, 143.7, 115.2, 108.1, 107.0, 101.6, 99.2, 55.1 ppm; HRMS (EI): calcd for $C_9H_7NO_3$ $[M]^+$: 177.0426, found: 177.0425.



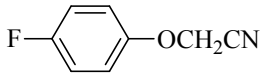
3p

Ethyl 4-(cyanomethoxy)benzoate (3q): White solid. Yield: 60%, mp 71.0–72.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08–8.04 (m, 2H), 7.02–6.99 (m, 2H), 4.83 (s, 2H)，4.36 (q, J = 7.2 Hz, 2H), 1.39 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8, 159.8, 131.8, 125.4, 114.6, 114.4, 61.0, 53.3, 14.3 ppm; HRMS (EI): calcd for $C_{11}H_{11}NO_3[M]^+$: 205.0739, found: 205.0740.



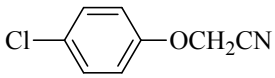
3q

2-(4-Fluorophenoxy)acetonitrile (3r, CAS: 24115-20-6):[5] Light yellow liquid. Yield: 72%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.07–7.01 (m, 2H), 6.98–6.93 (m, 2H), 4.73 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.6 (d, $^1J_{CF}$ = 240.2 Hz), 152.7 (d, $^4J_{CF}$ = 2.3 Hz), 116.7 (d, $^3J_{CF}$ = 8.2 Hz), 116.4 (d, $^2J_{CF}$ = 23.4 Hz), 115.0, 54.6 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ –120.2 to –120.3 (m, 1F) ppm.



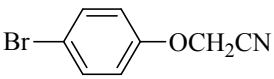
3r

2-(4-Chlorophenoxy)acetonitrile (3s, CAS: 3598-13-8):[5] White solid. Yield: 85%, mp 45.5–46.5 °C.^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32–7.28 (m, 2H), 6.94–6.90 (m, 2H), 4.73 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.1, 129.8, 128.3, 116.4, 114.9, 53.9 ppm.



3s

2-(4-Bromophenoxy)acetonitrile (3t, CAS: 39489-67-3):[5] White solid. Yield: 63%, mp 46.5–47.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47–7.43 (m, 2H), 6.89–6.85 (m, 2H), 4.73 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.6, 132.8, 116.9, 115.7, 114.8, 53.8 ppm.



3t

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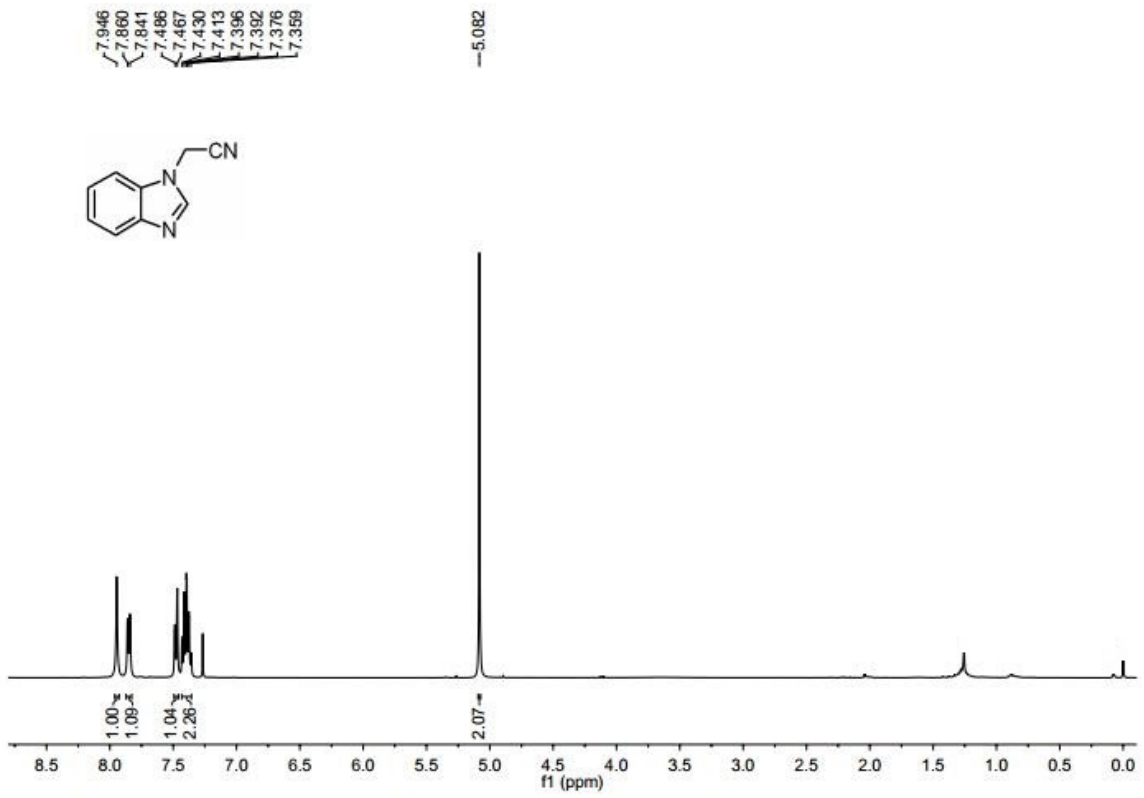
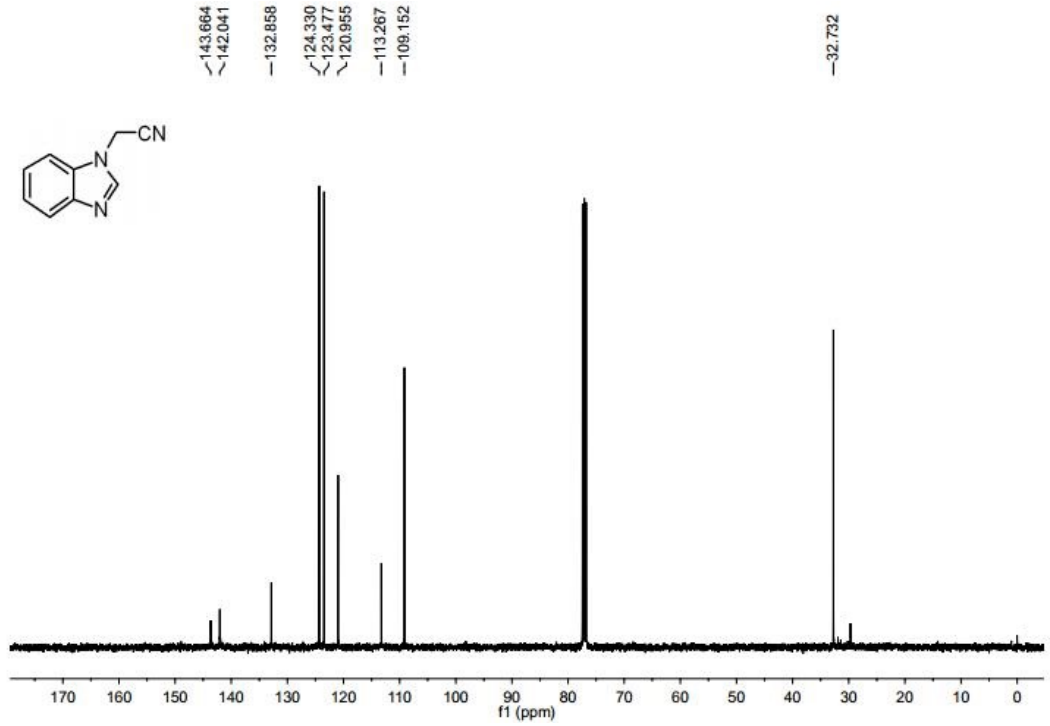
^{1}H, ^{13}C, ^{19}F NMR and HRMS (EI) spectra of compounds 3

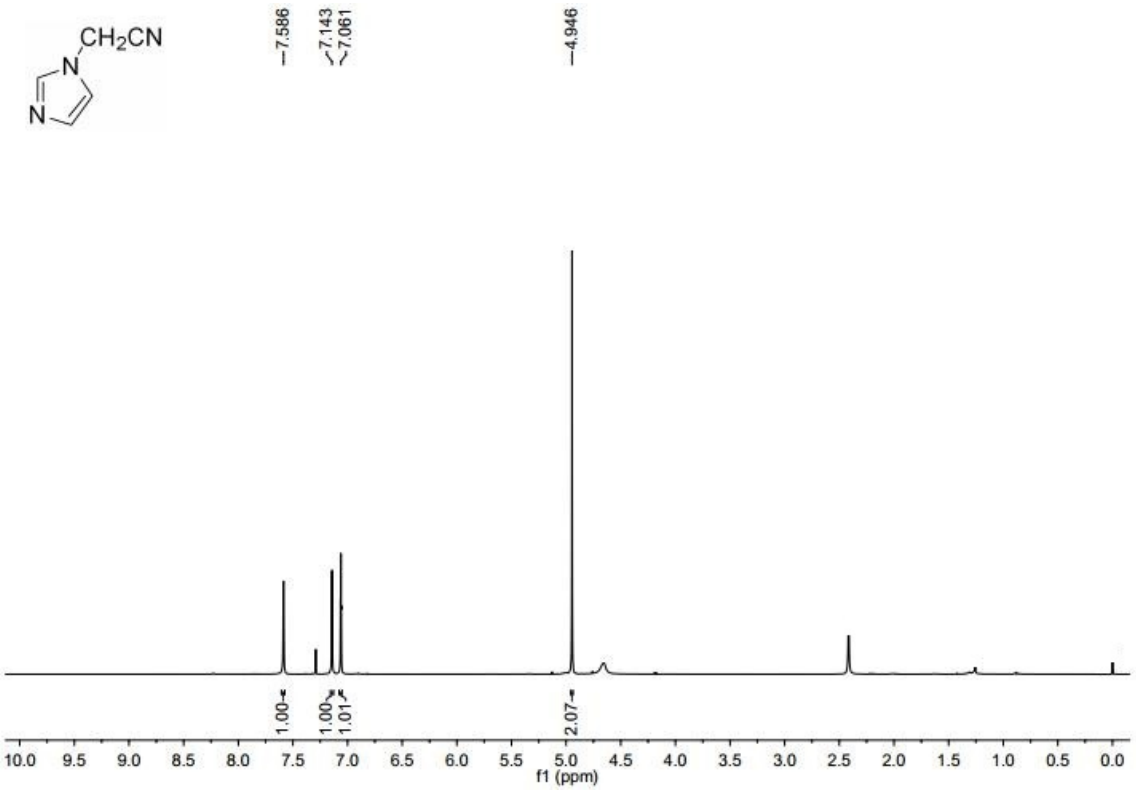
^{1}H NMR spectrum of 3a



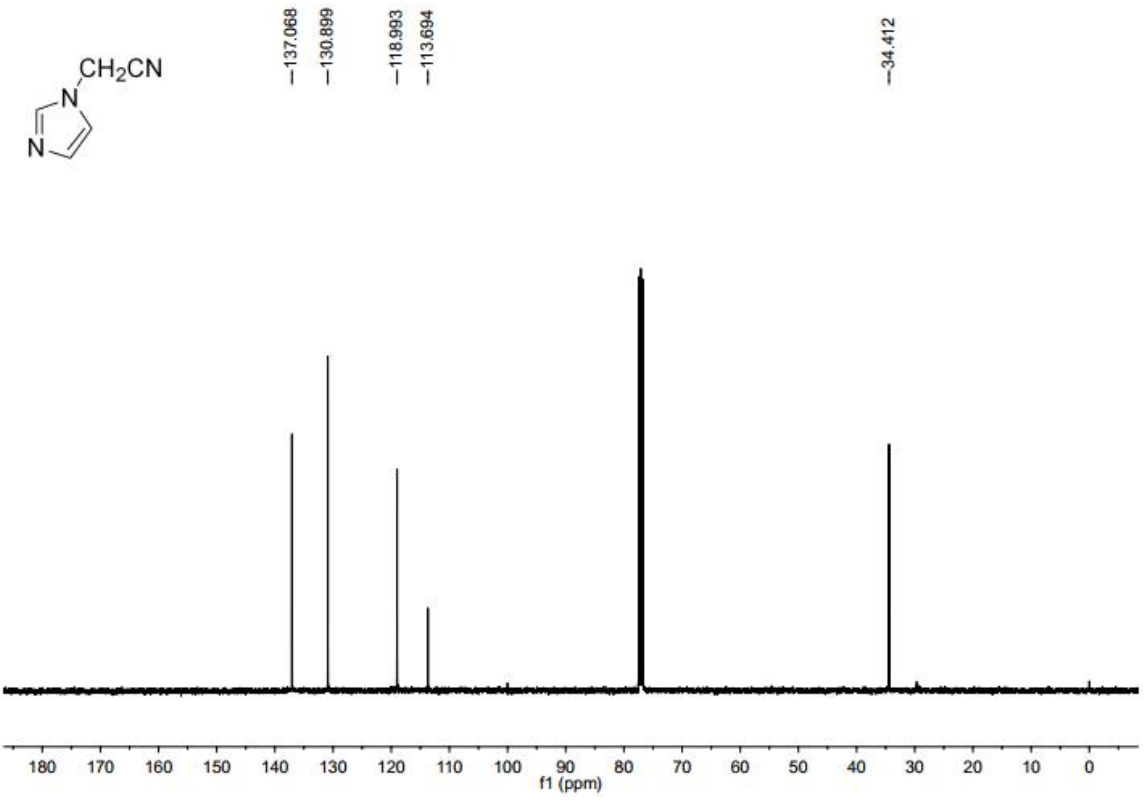
^{13}C NMR spectrum of 3a



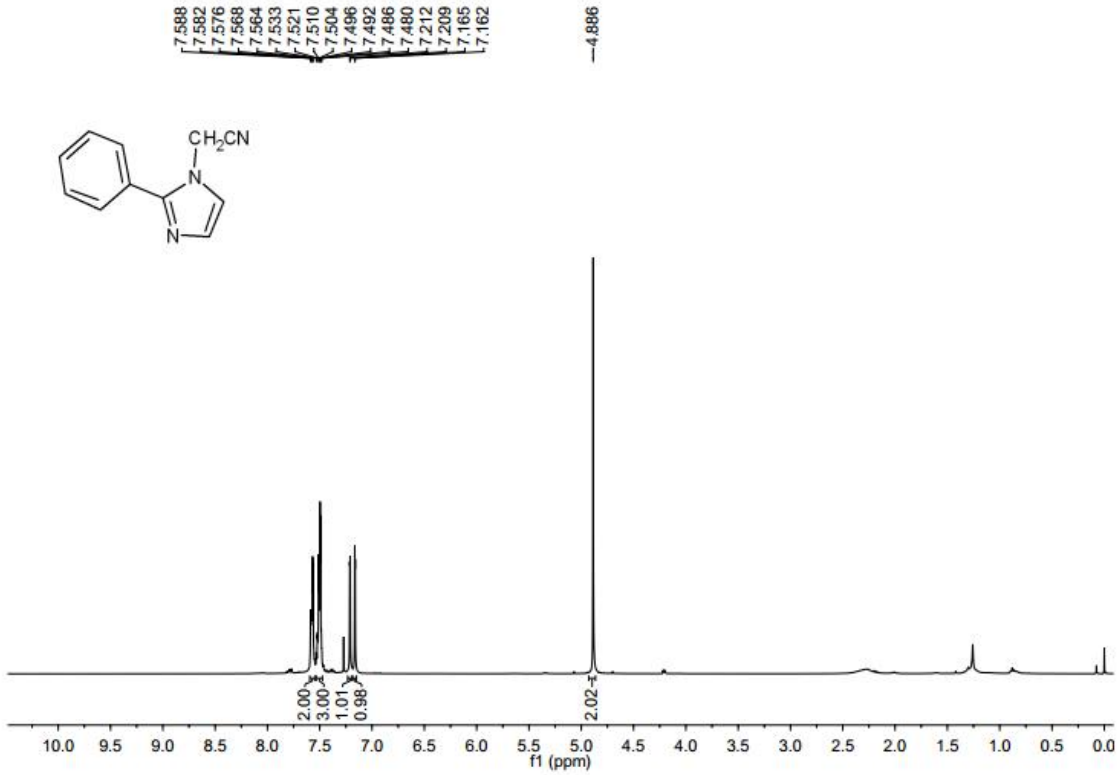
^{1}H NMR spectrum of 3b



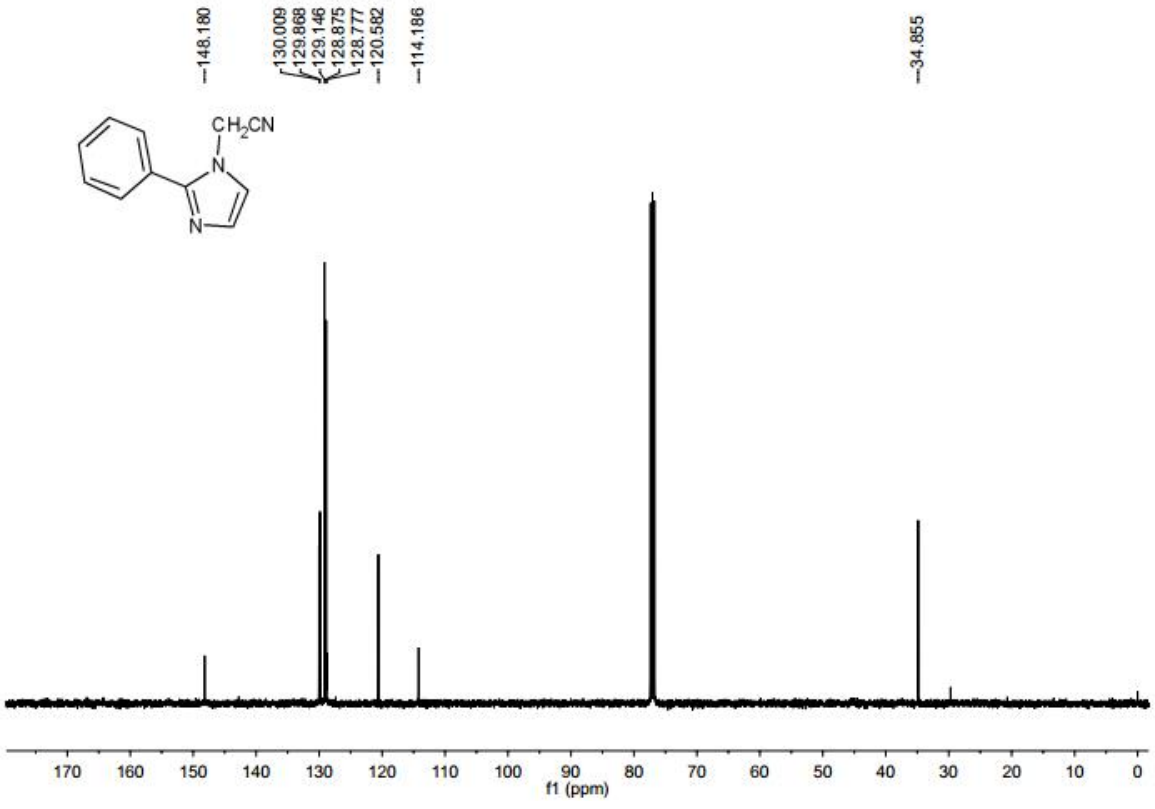
^{13}C NMR spectrum of 3b



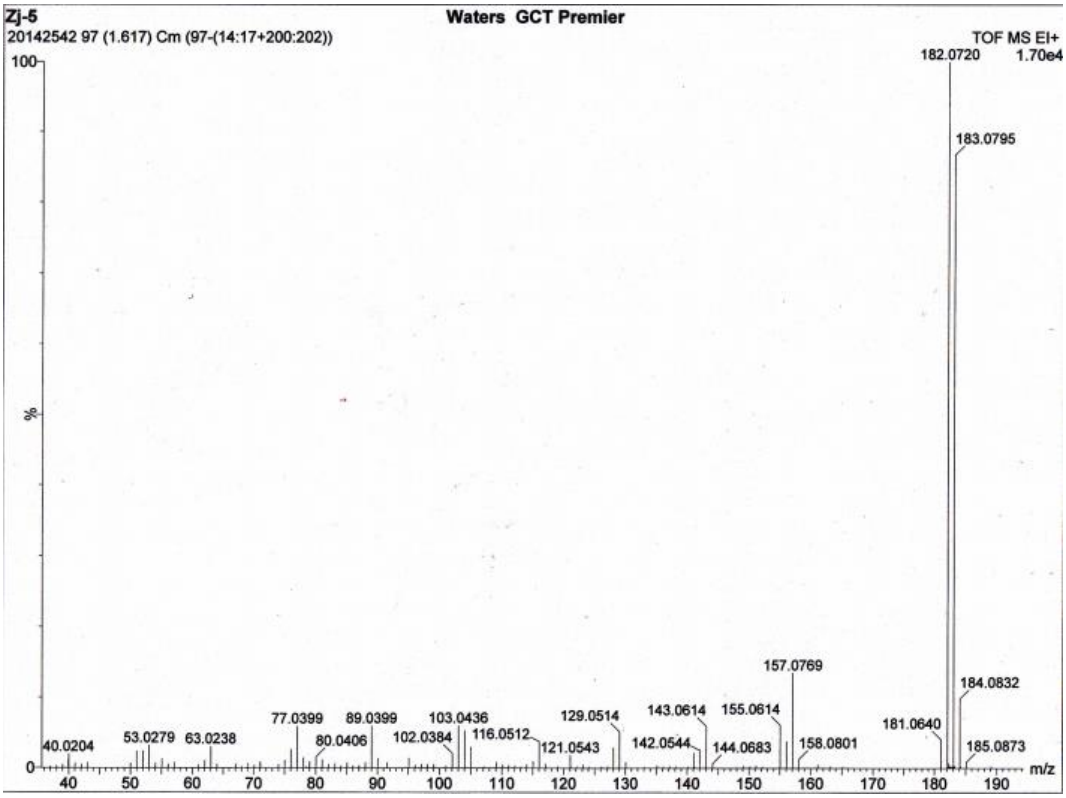
^{1}H NMR spectrum of 3c



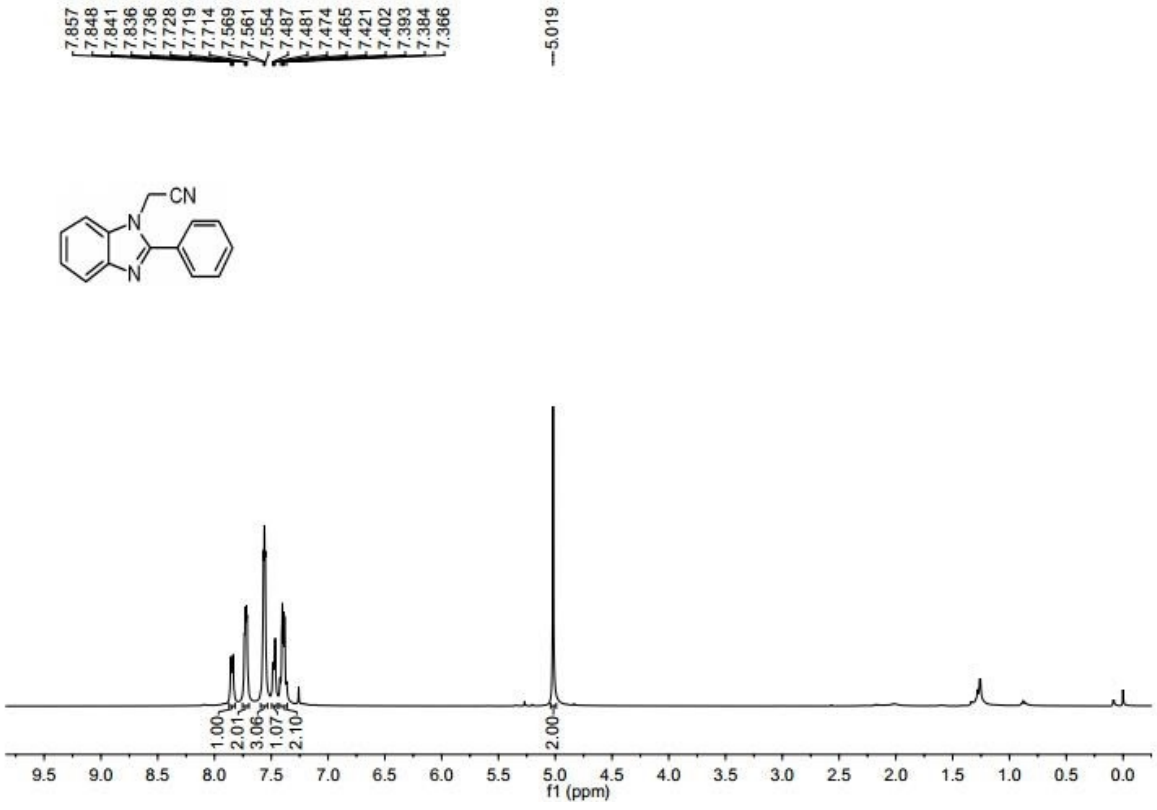
^{13}C NMR spectrum of 3c



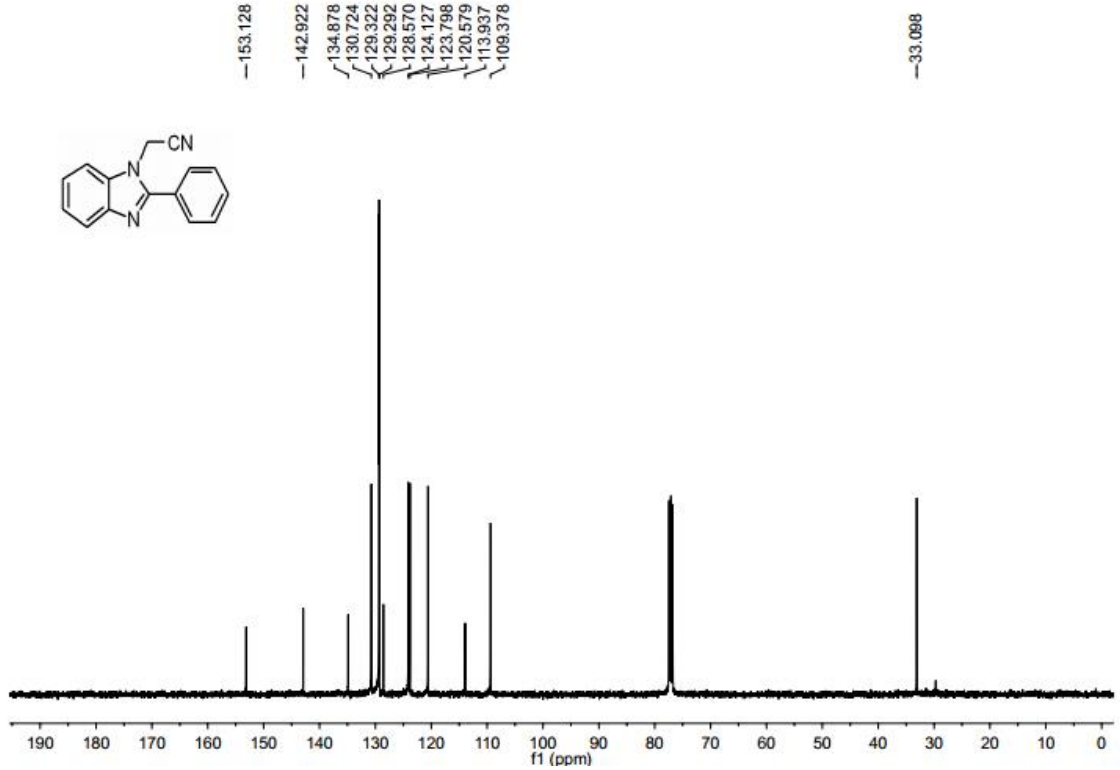
HRMS (EI) spectrum of 3c



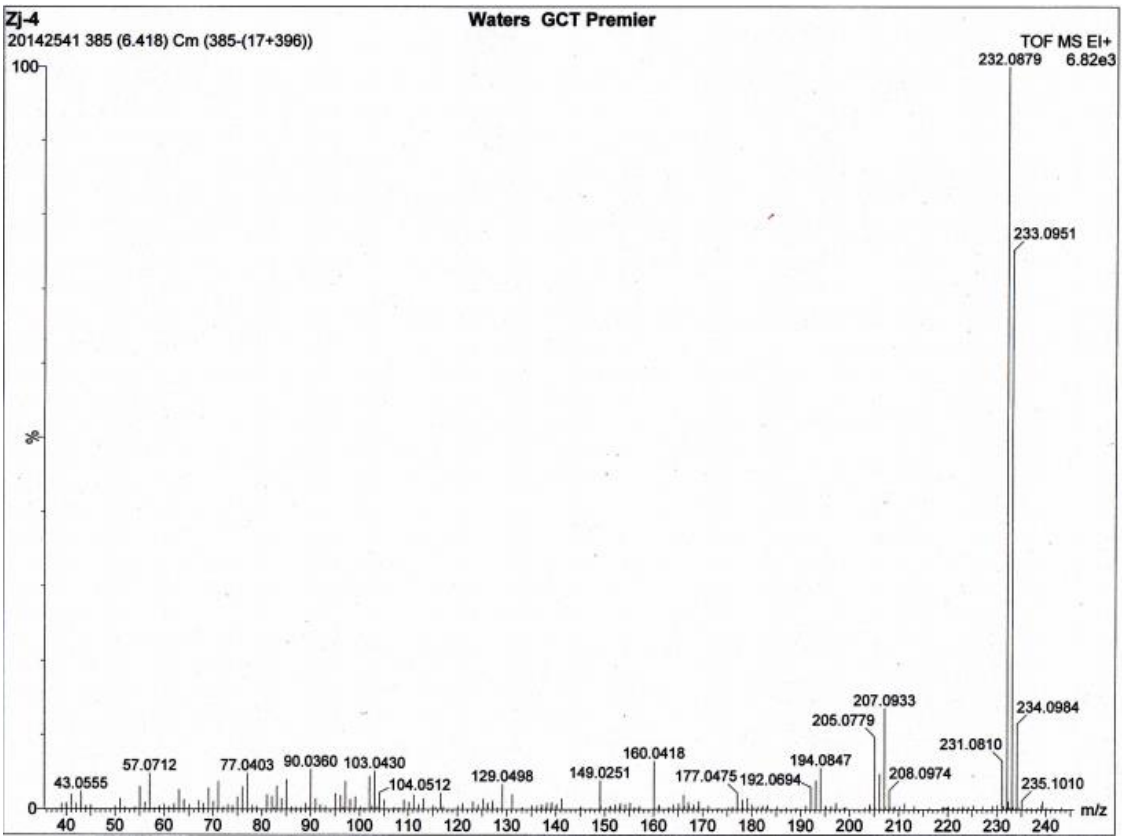
^{1}H NMR spectrum of 3d



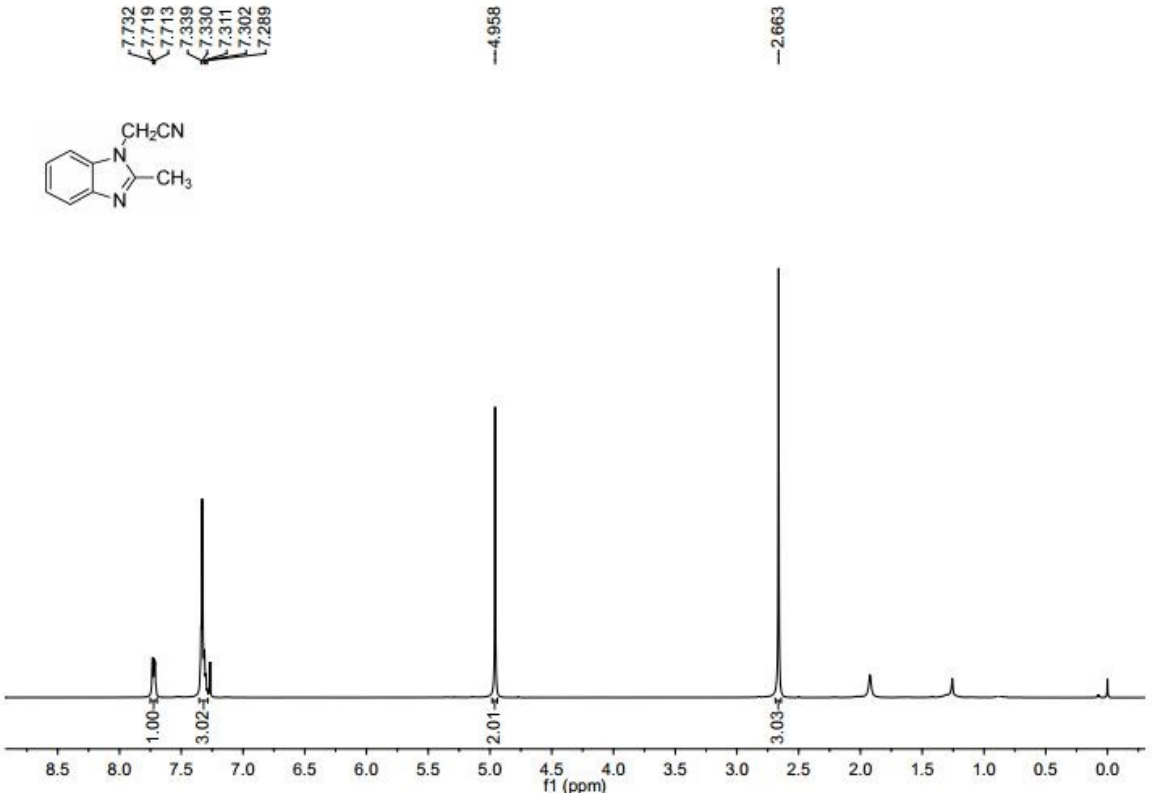
^{13}C NMR spectrum of 3d



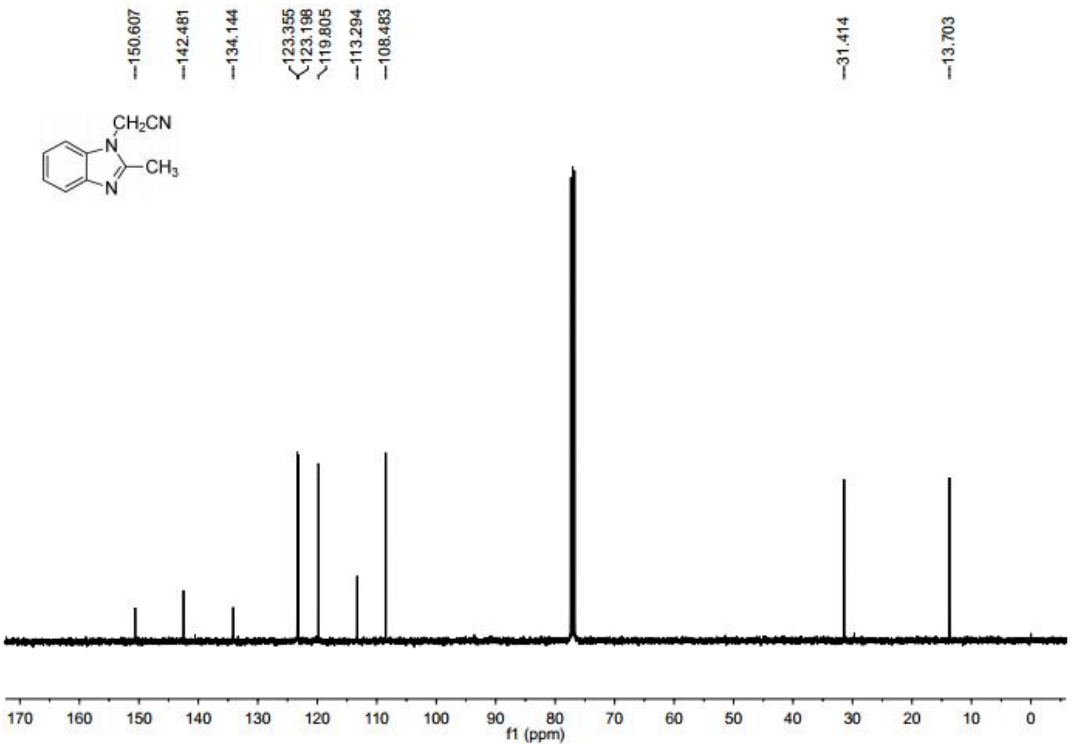
HRMS (EI) spectrum of 3d



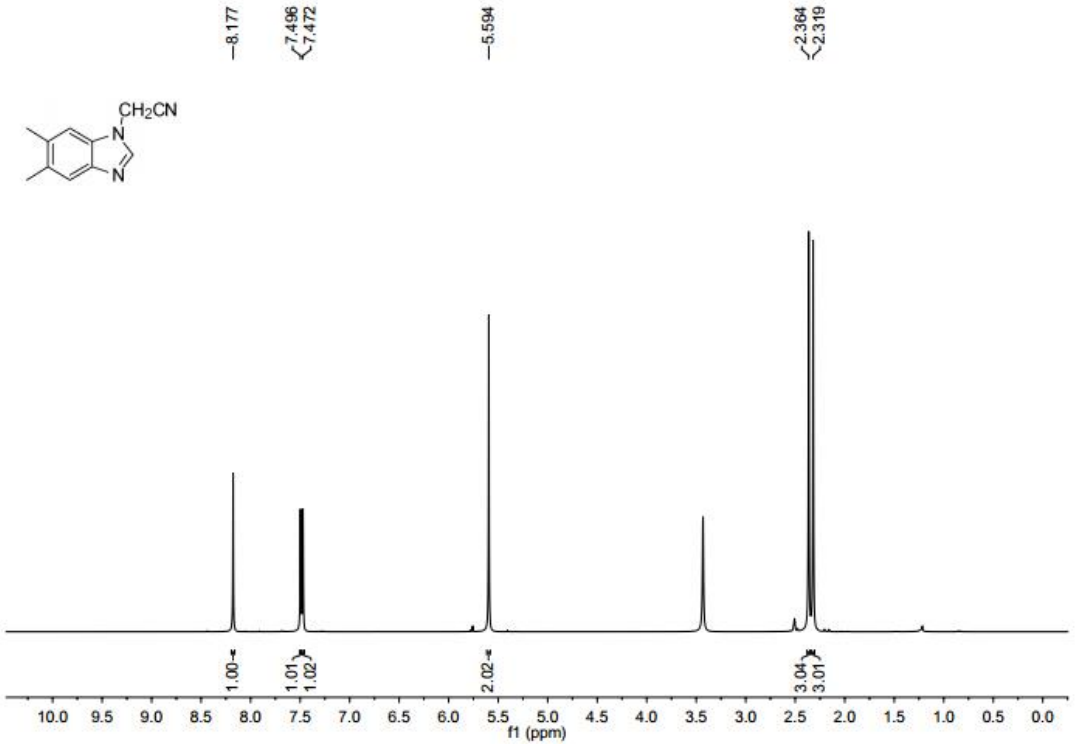
^{1}H NMR spectrum of 3e



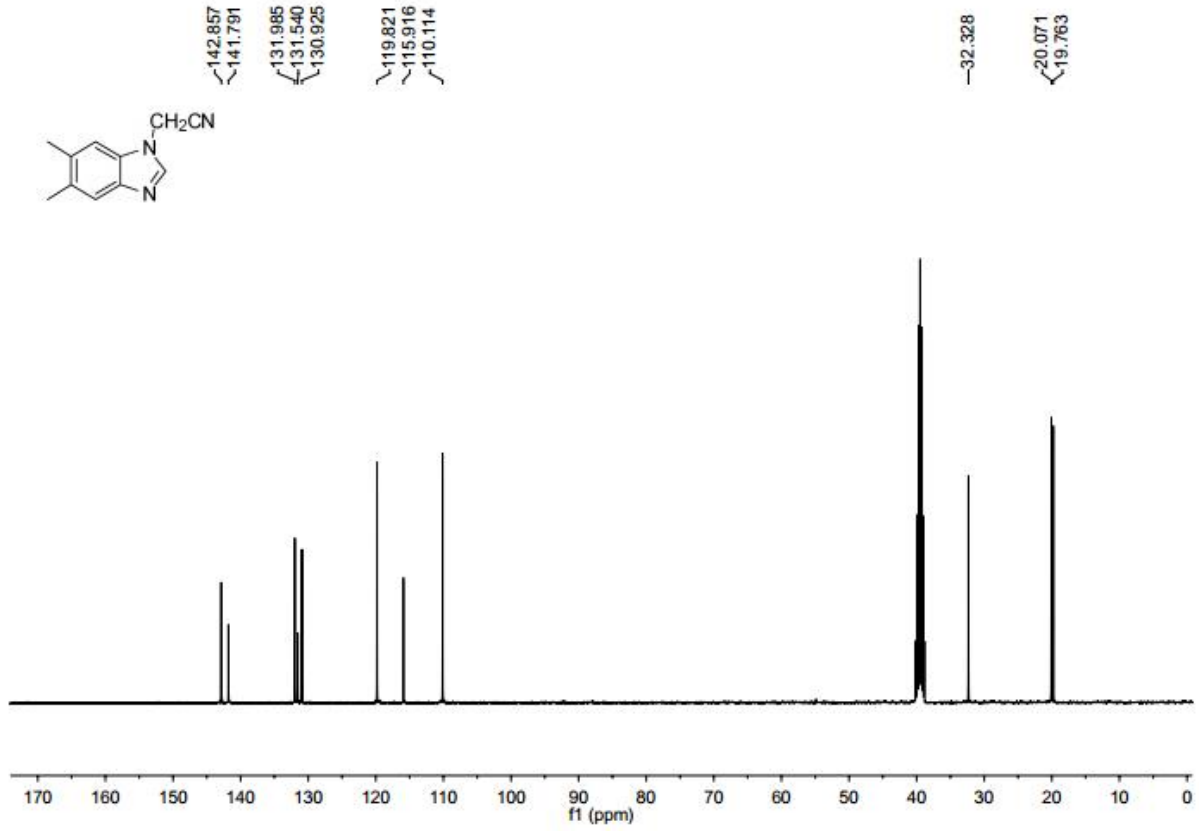
^{13}C NMR spectrum of 3e



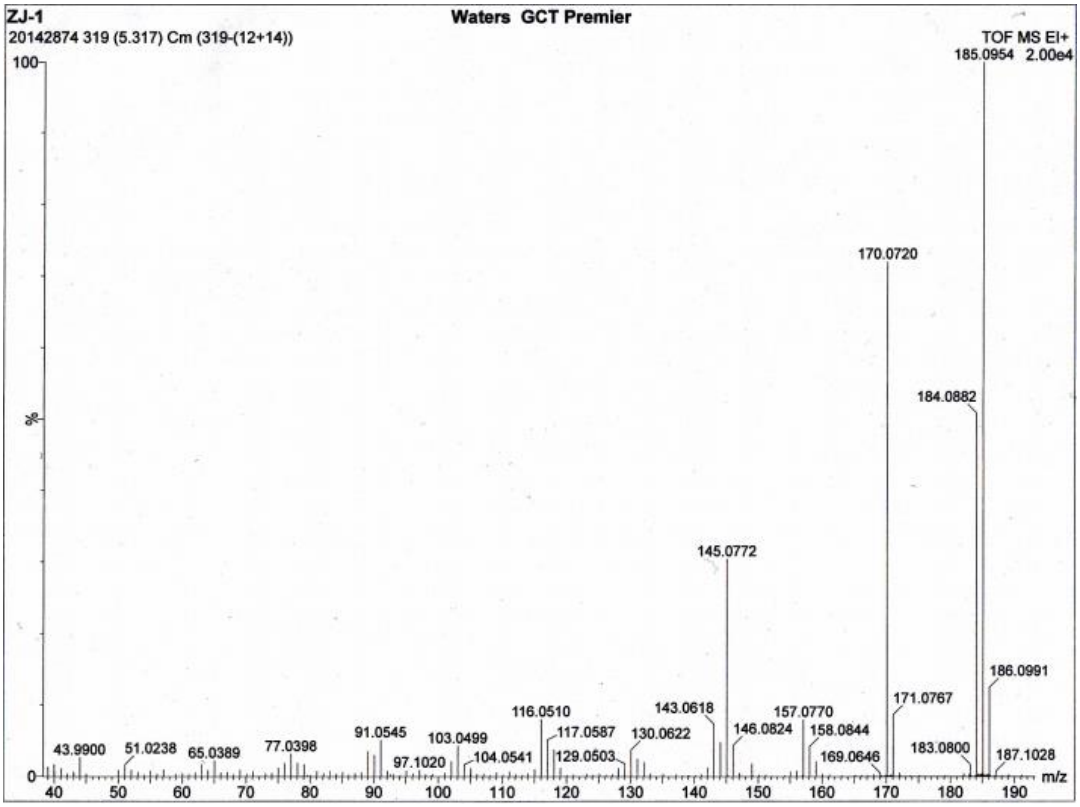
^{1}H NMR spectrum of 3f



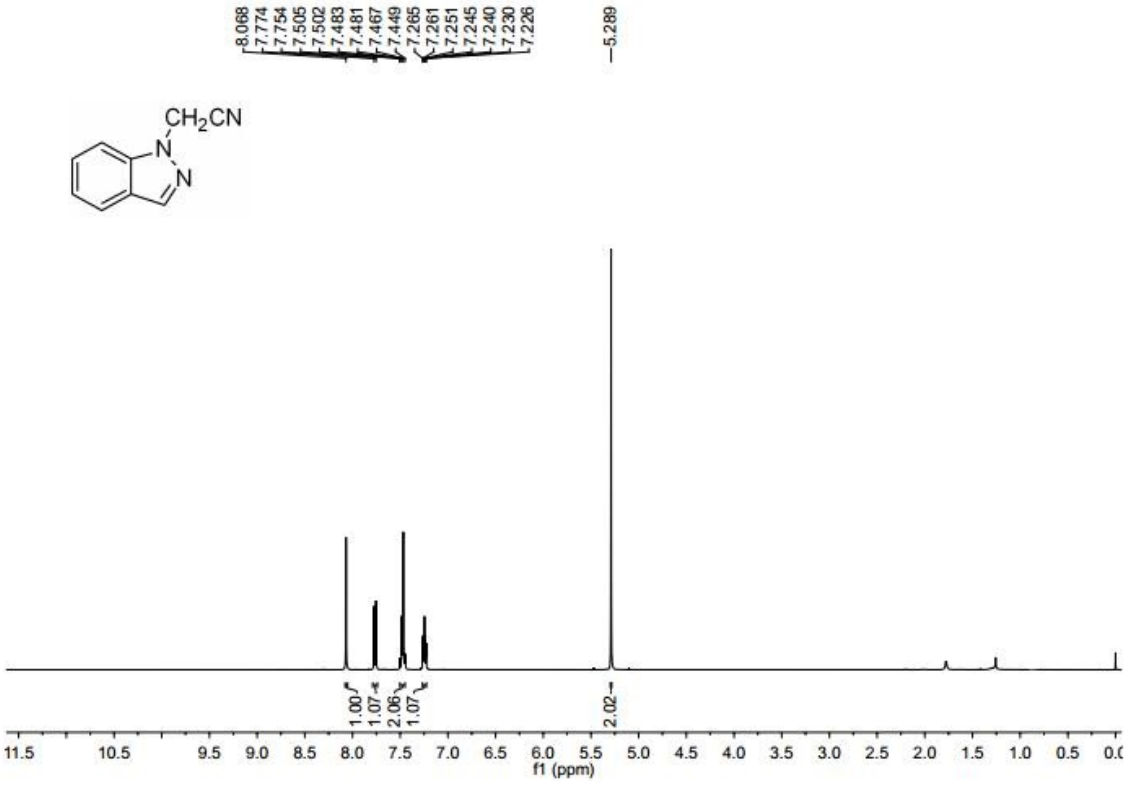
^{13}C NMR spectrum of 3f



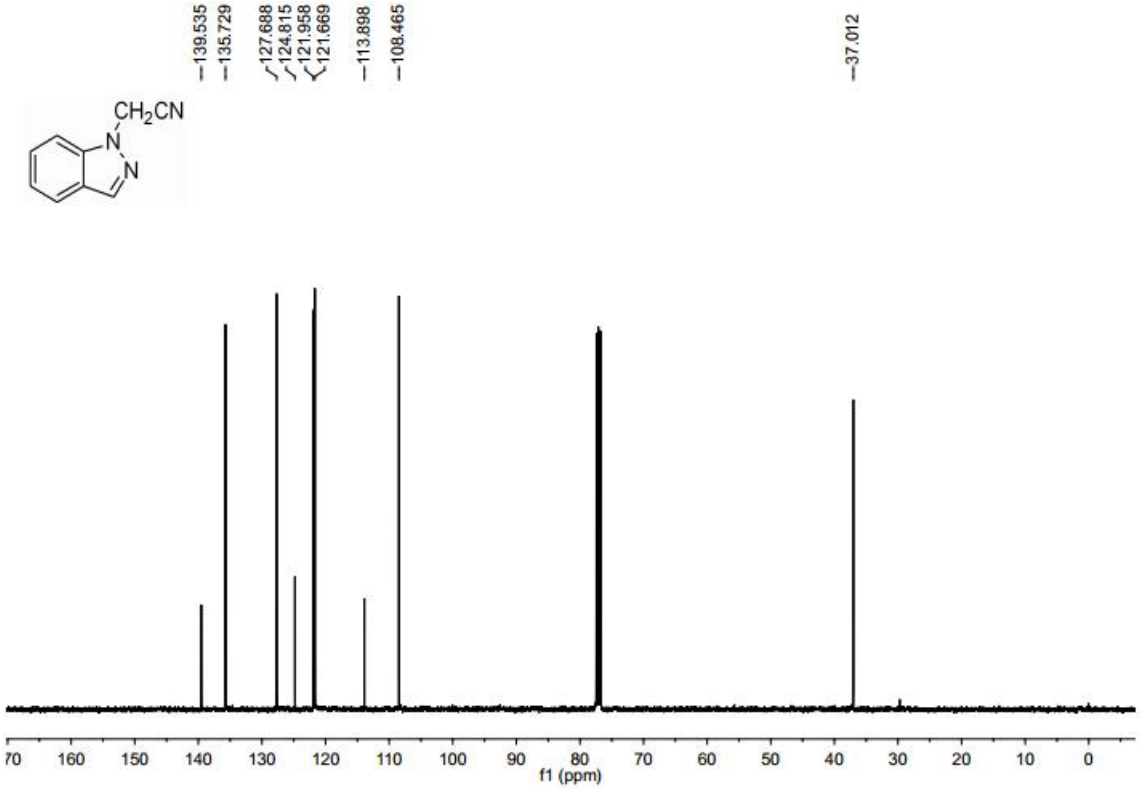
HRMS (EI) spectrum of 3f



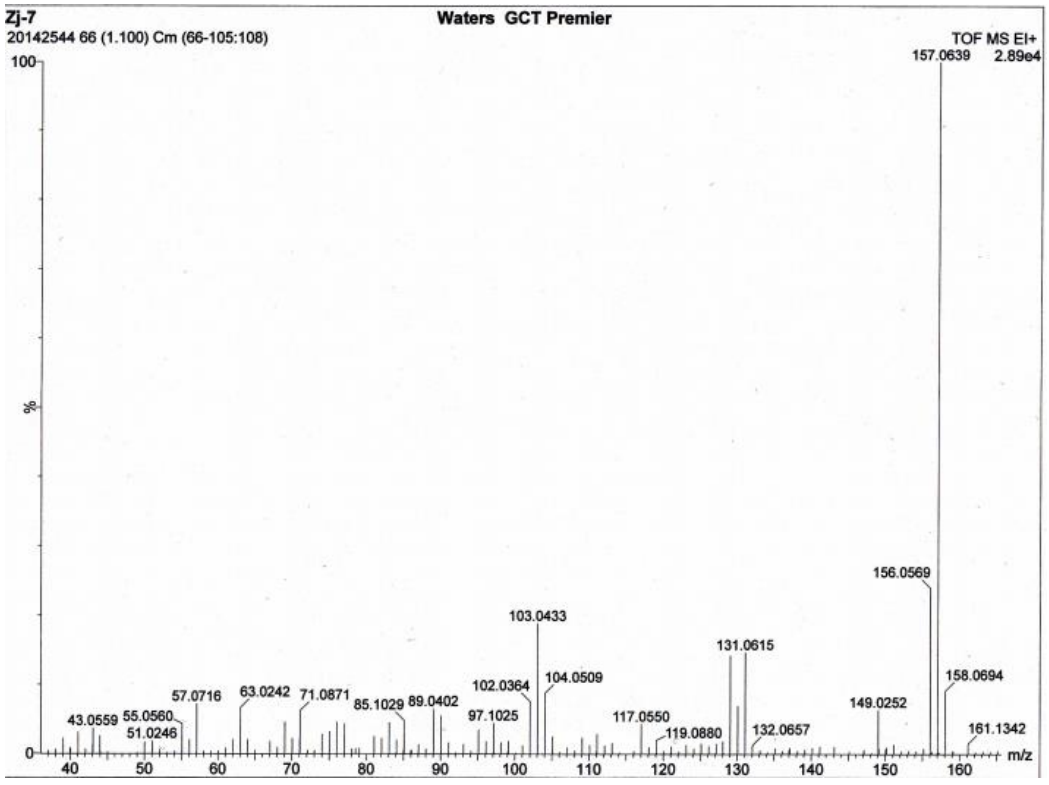
^{1}H NMR spectrum of 3g



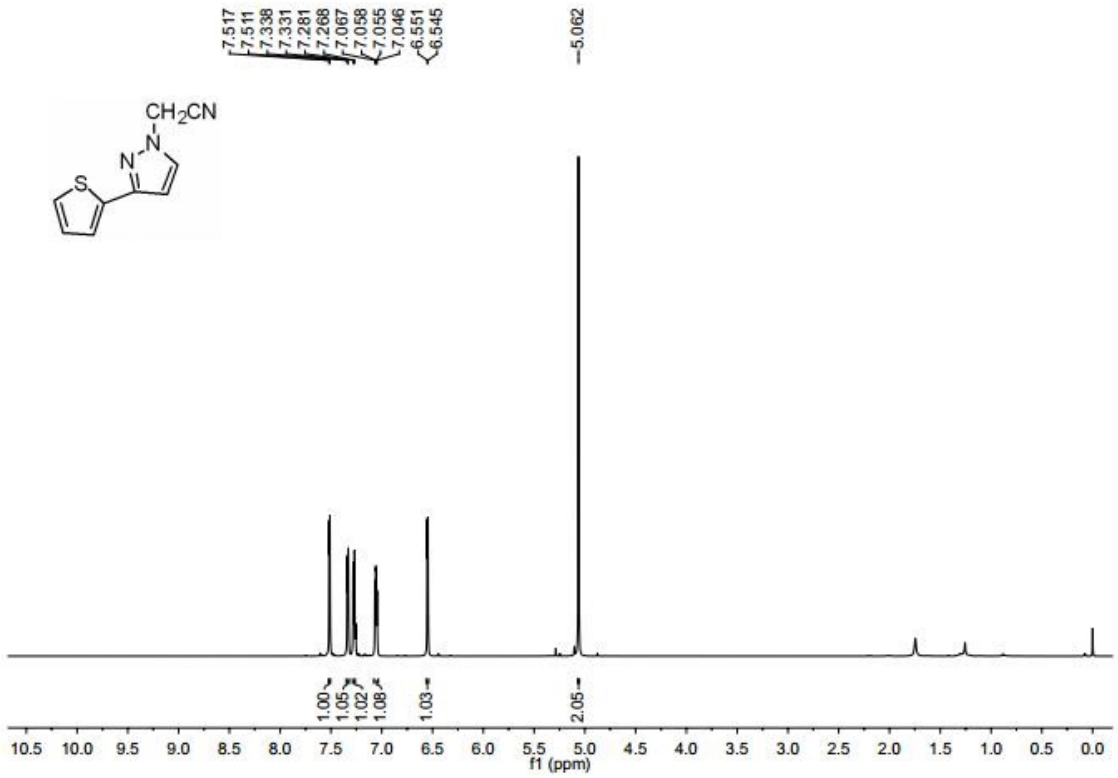
^{13}C NMR spectrum of 3g



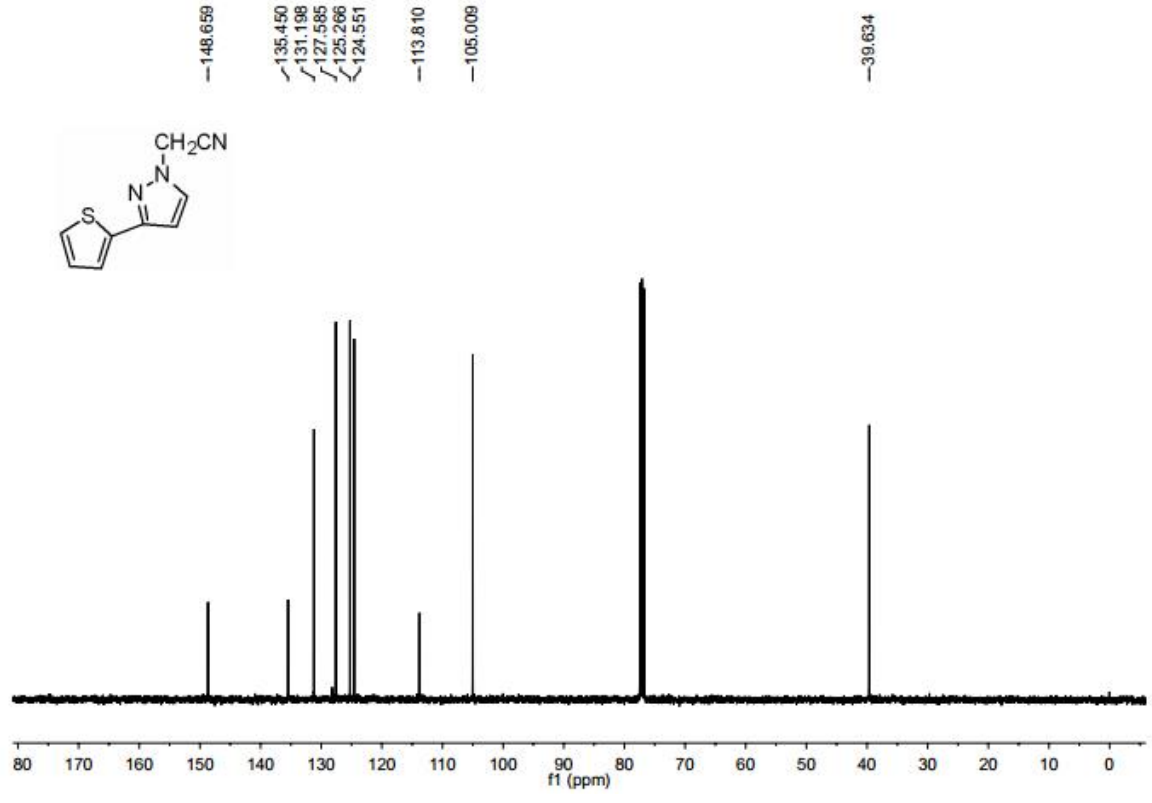
HRMS (EI) spectrum of 3g



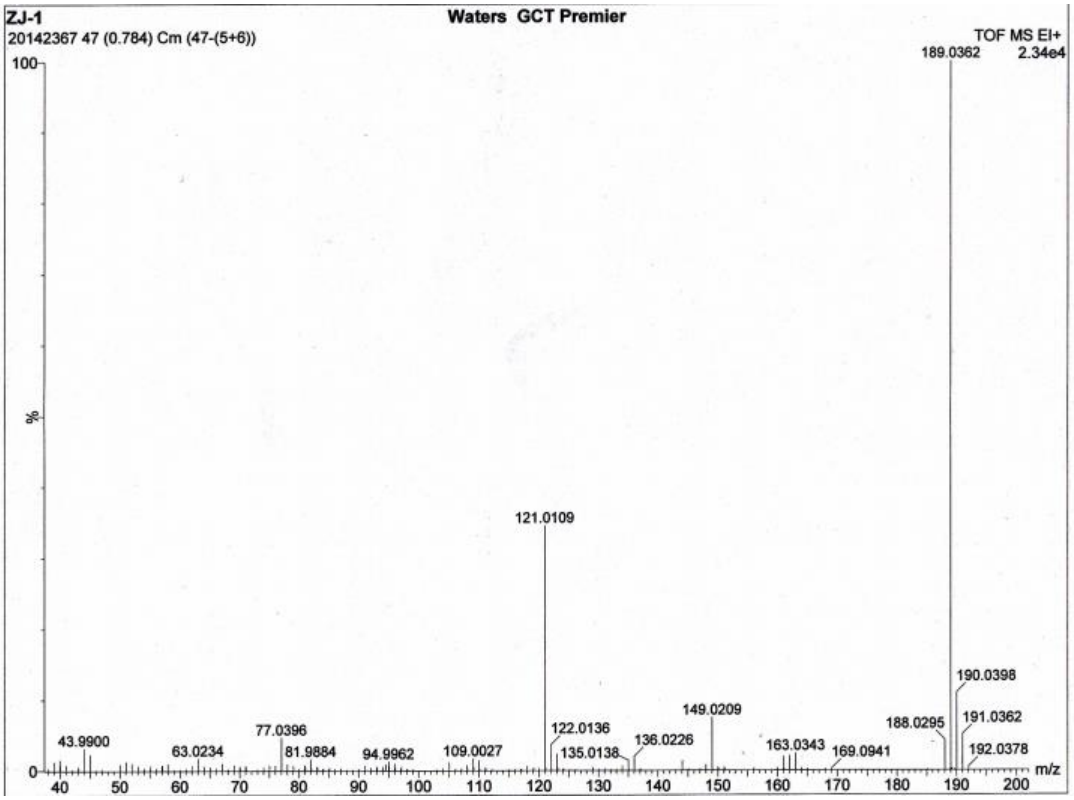
[1]H NMR spectrum of 3h



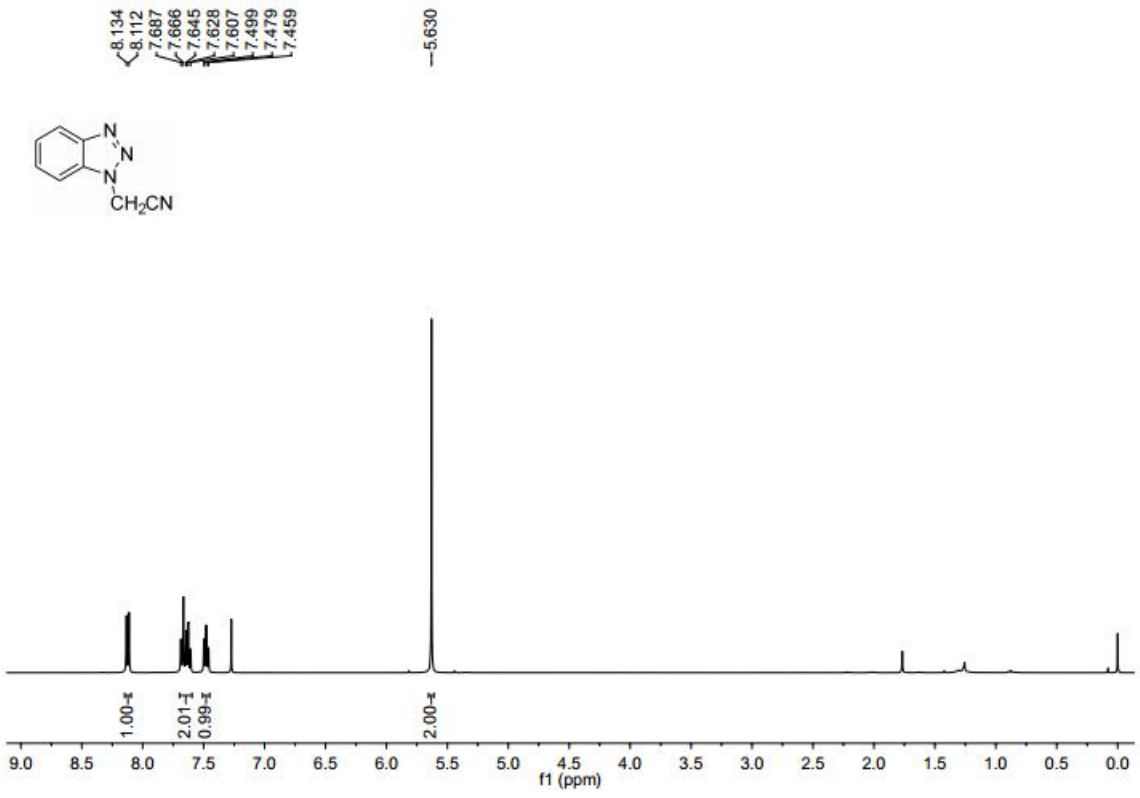
[13]C NMR spectrum of 3h



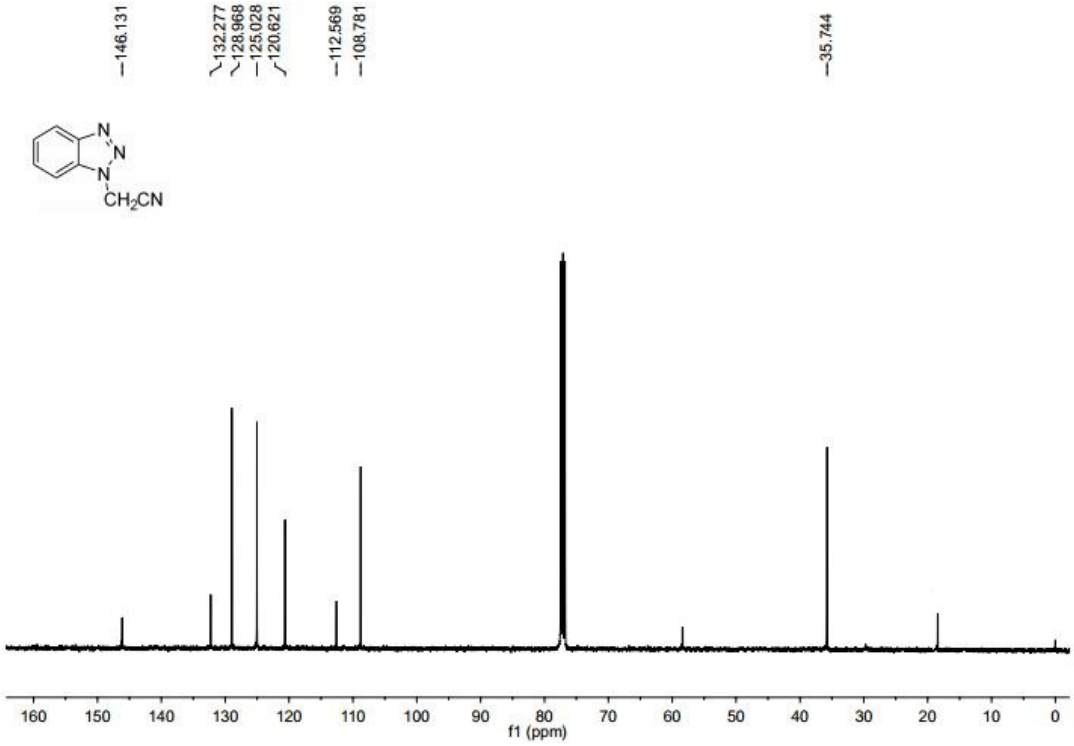
HRMS (EI) spectrum of 3h



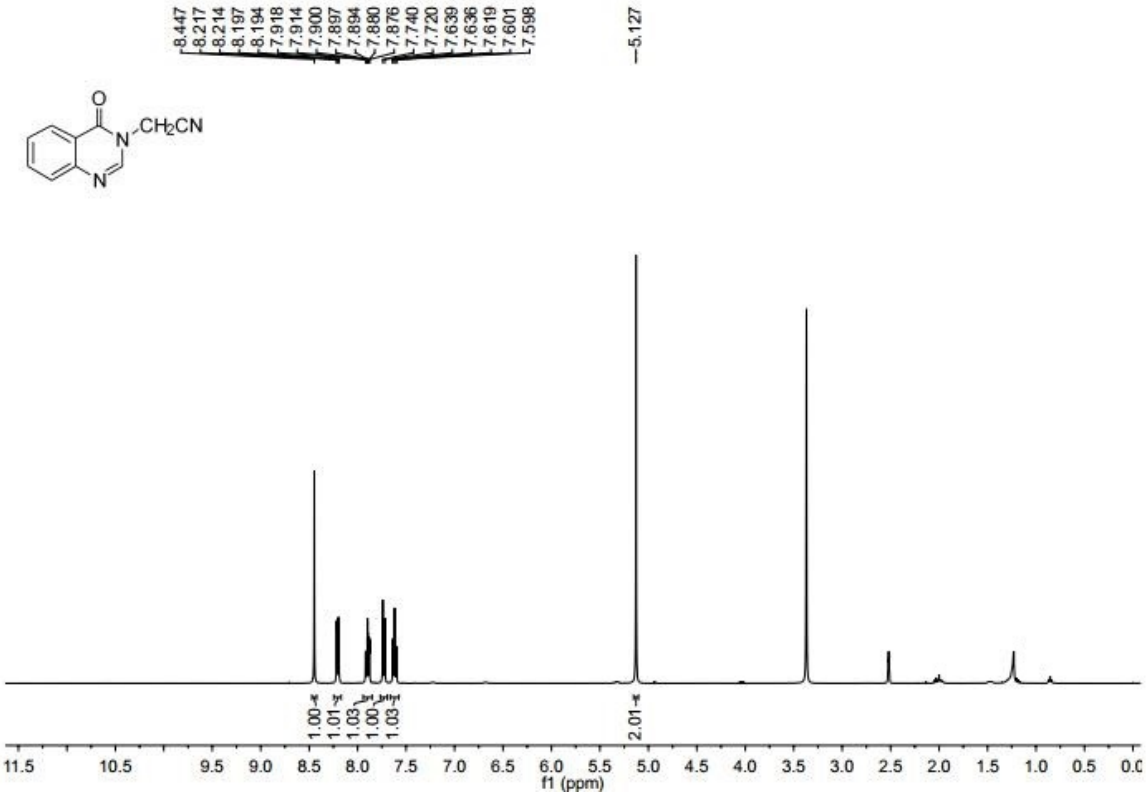
^{1}H NMR spectrum of 3i



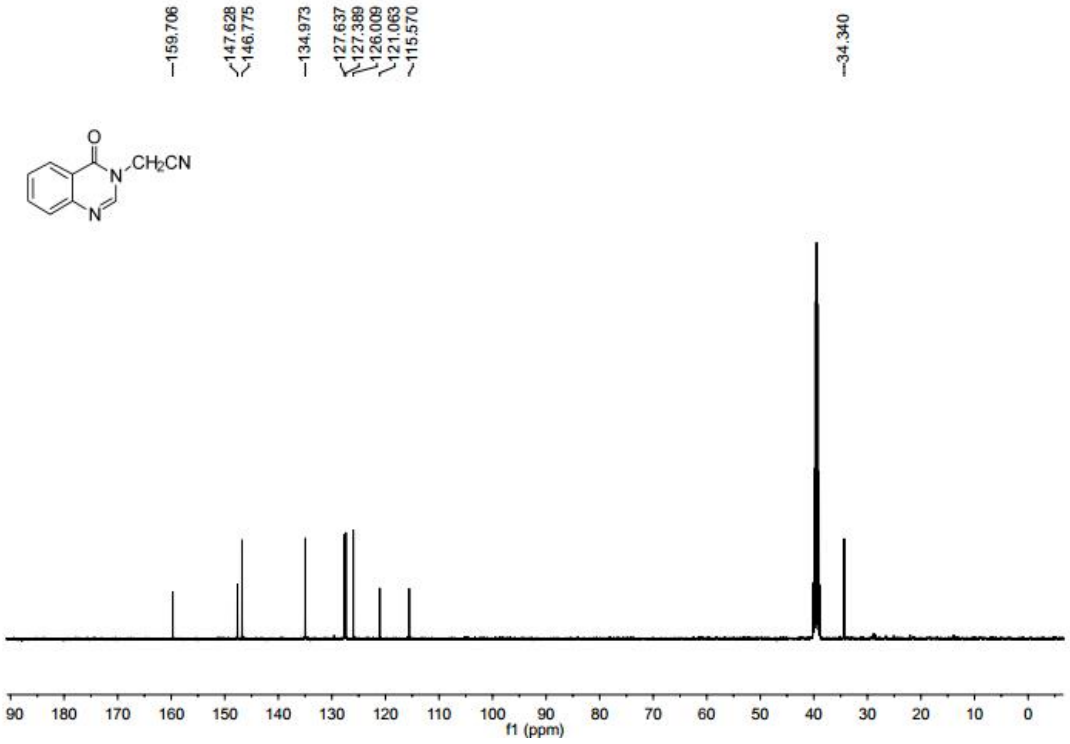
^{13}C NMR spectrum of 3i



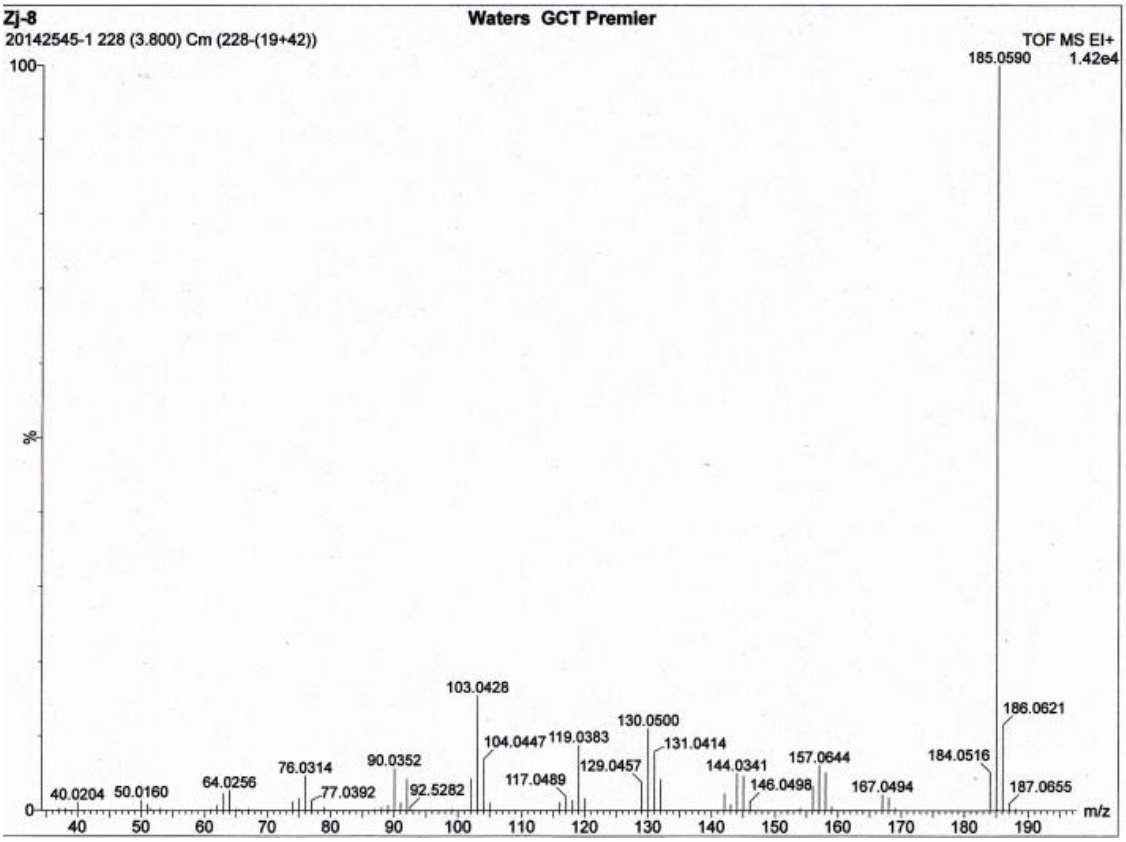
^{1}H NMR spectrum of 3j



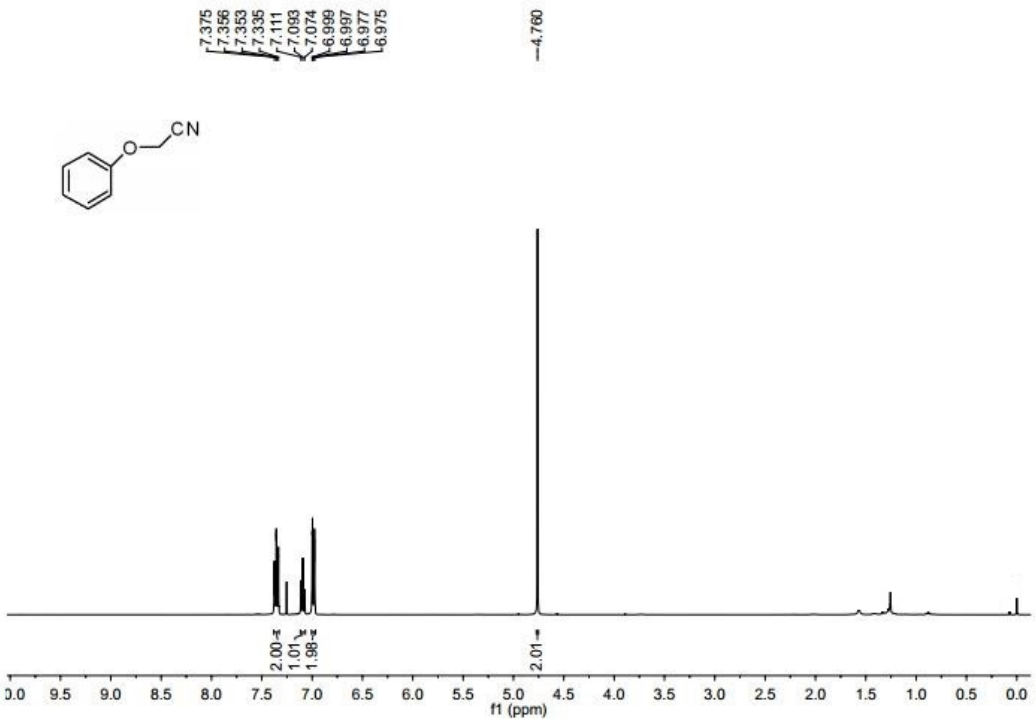
^{13}C NMR spectrum of 3j



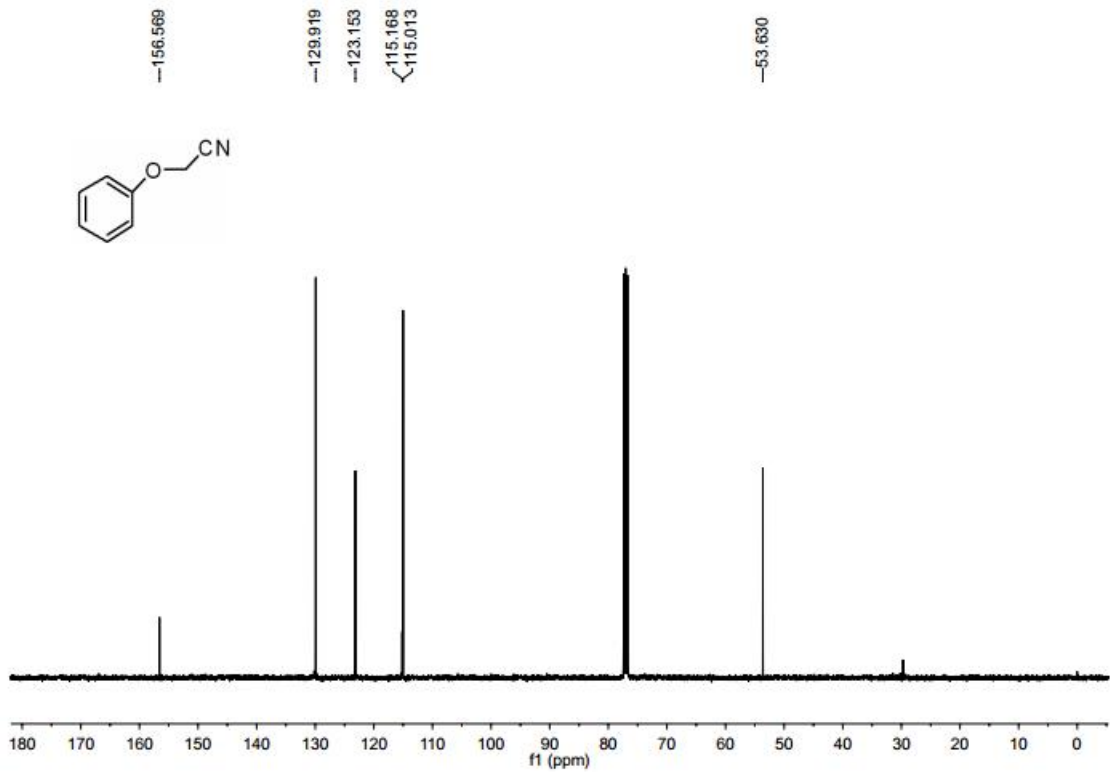
HRMS (EI) spectrum of 3j



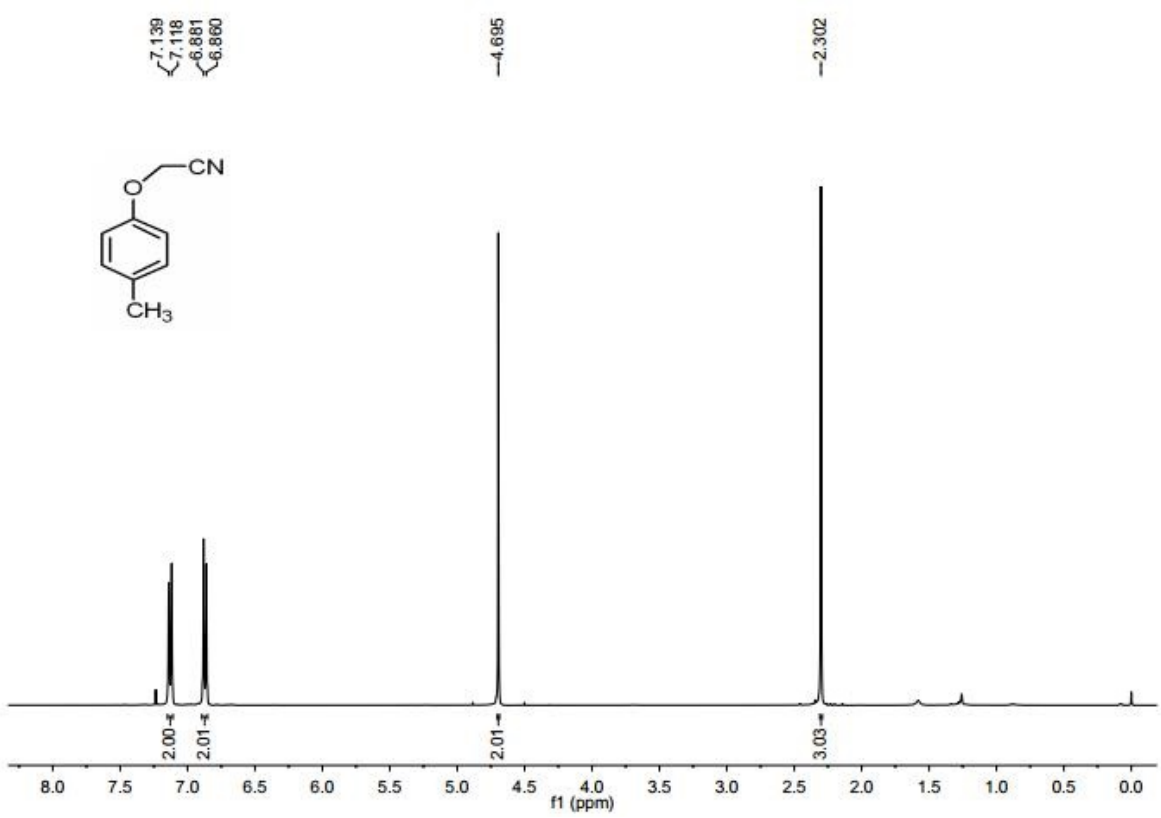
^{1}H NMR spectrum of 3k



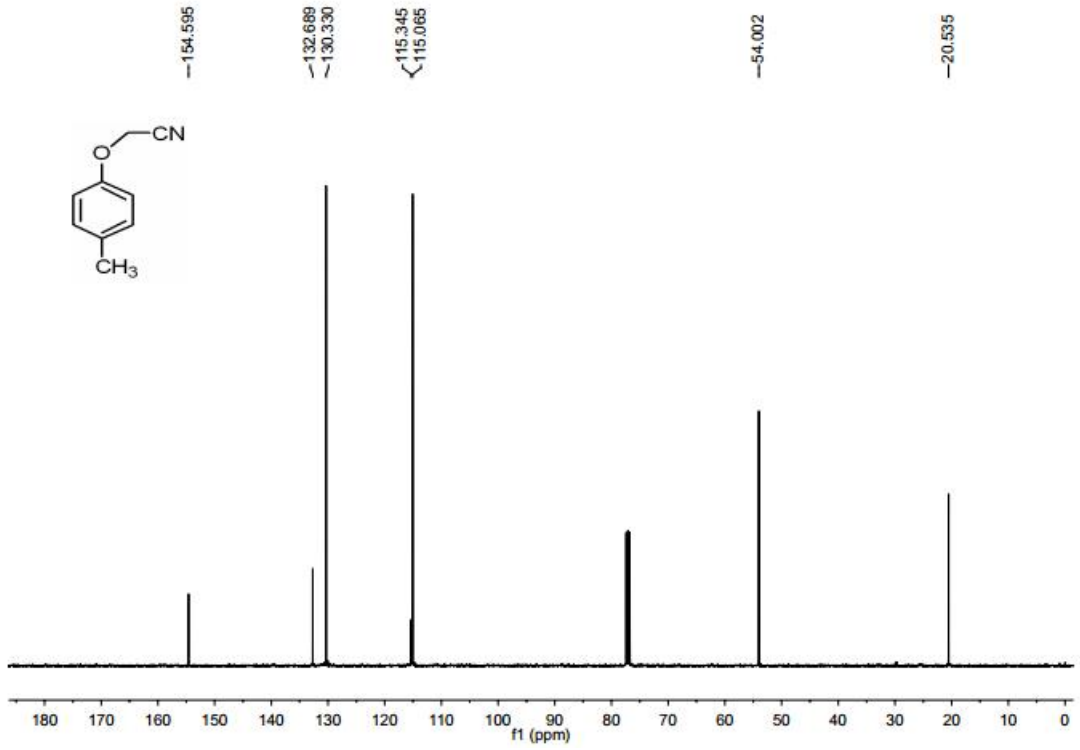
^{13}C NMR spectrum of 3k



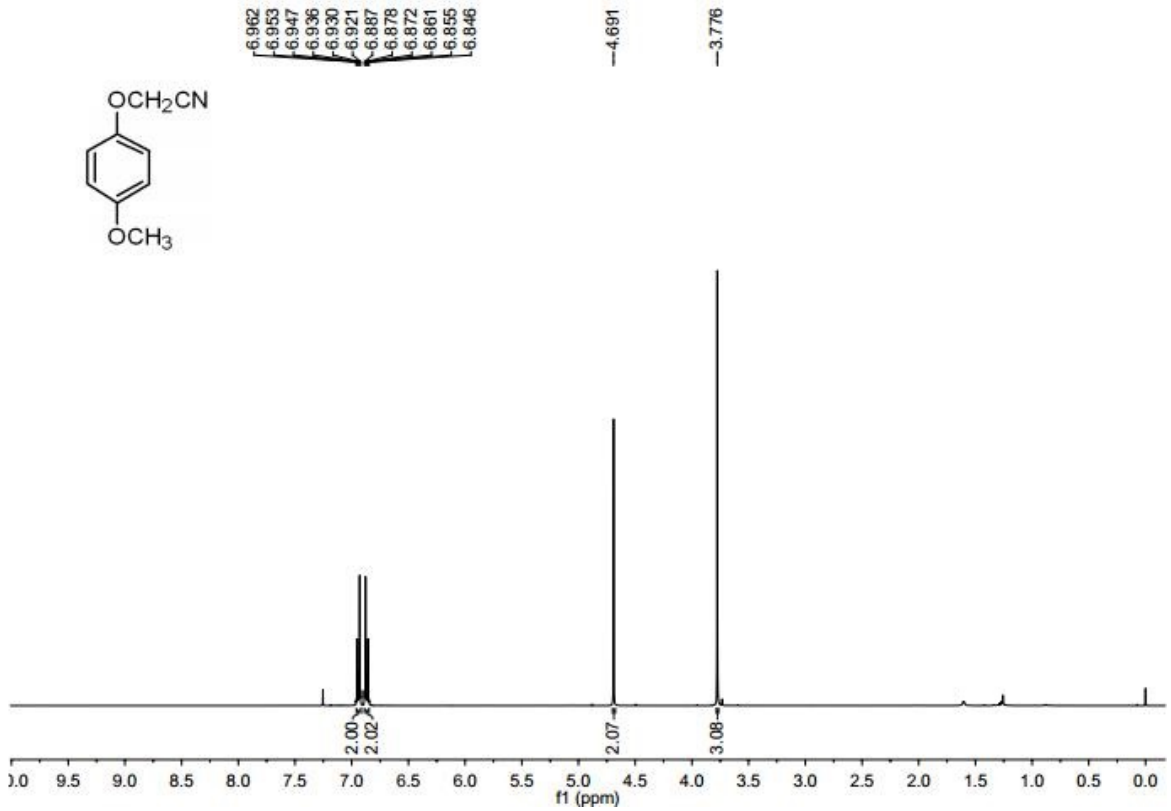
^{1}H NMR spectrum of 3l



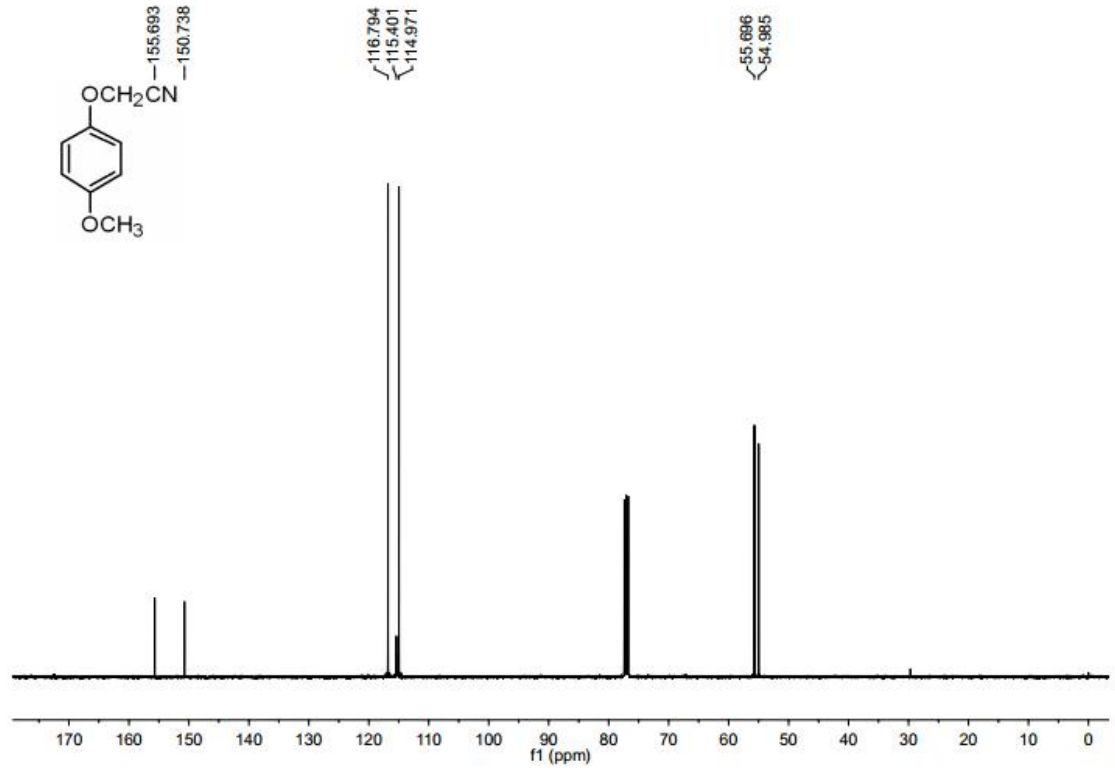
^{13}C NMR spectrum of 3l



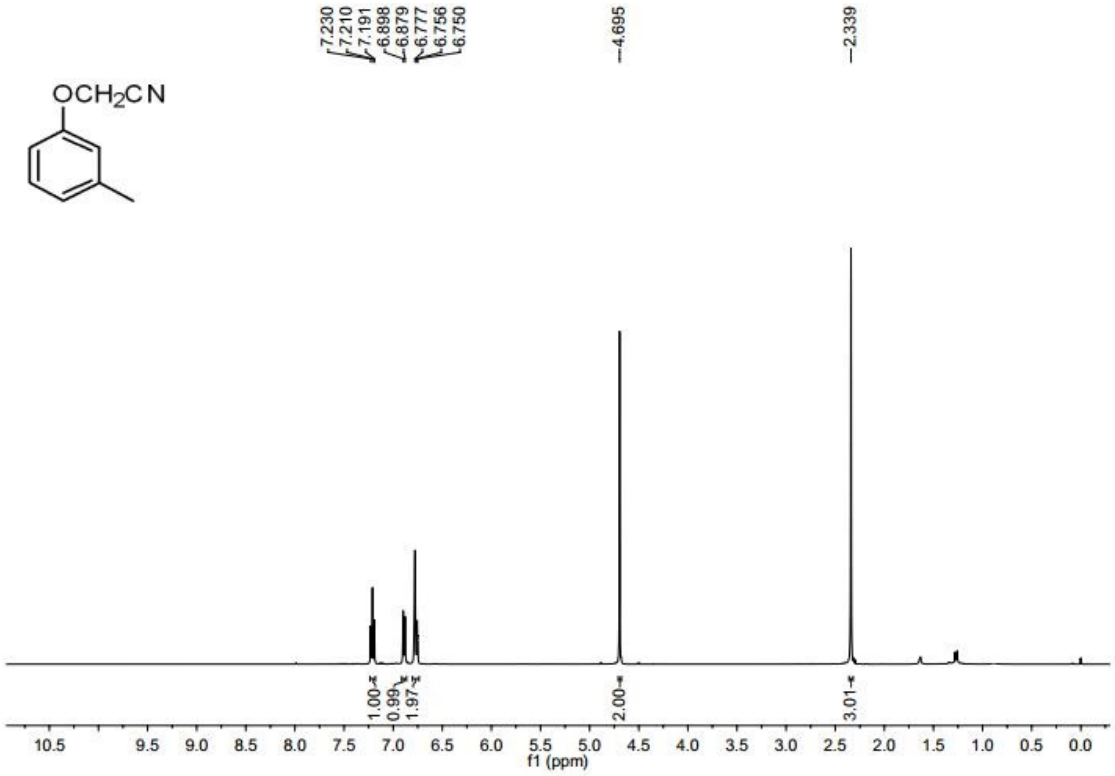
^{1}H NMR spectrum of 3m



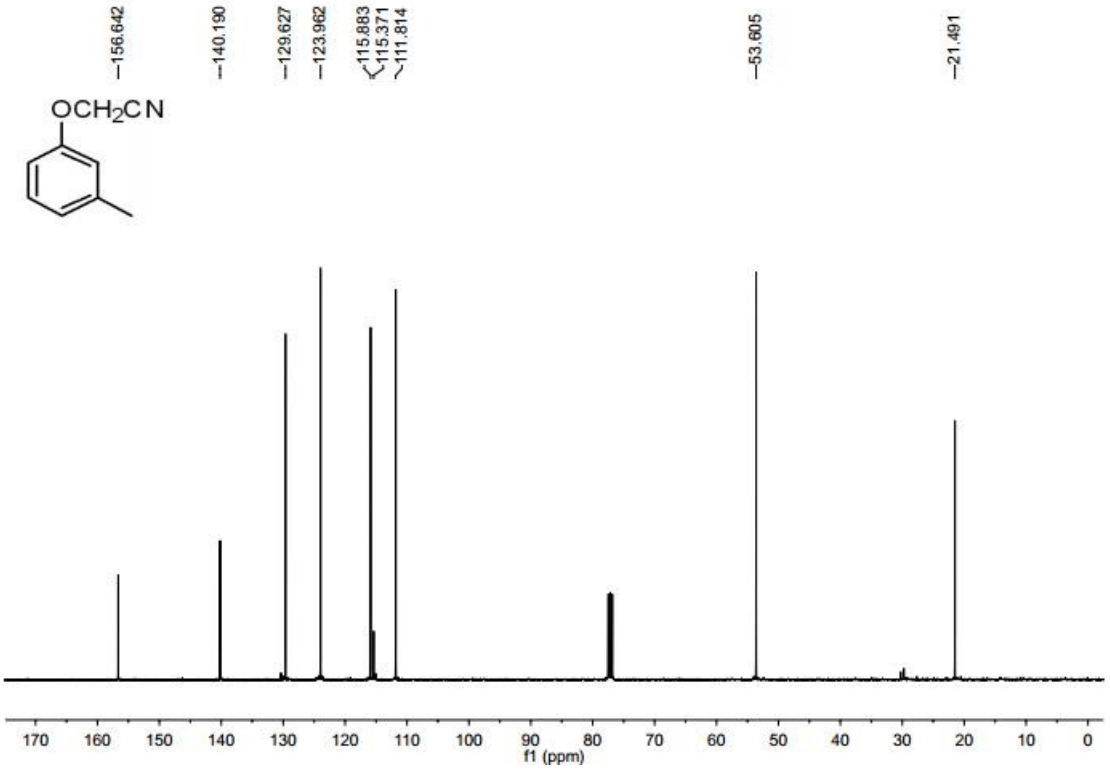
^{13}C NMR spectrum of 3m



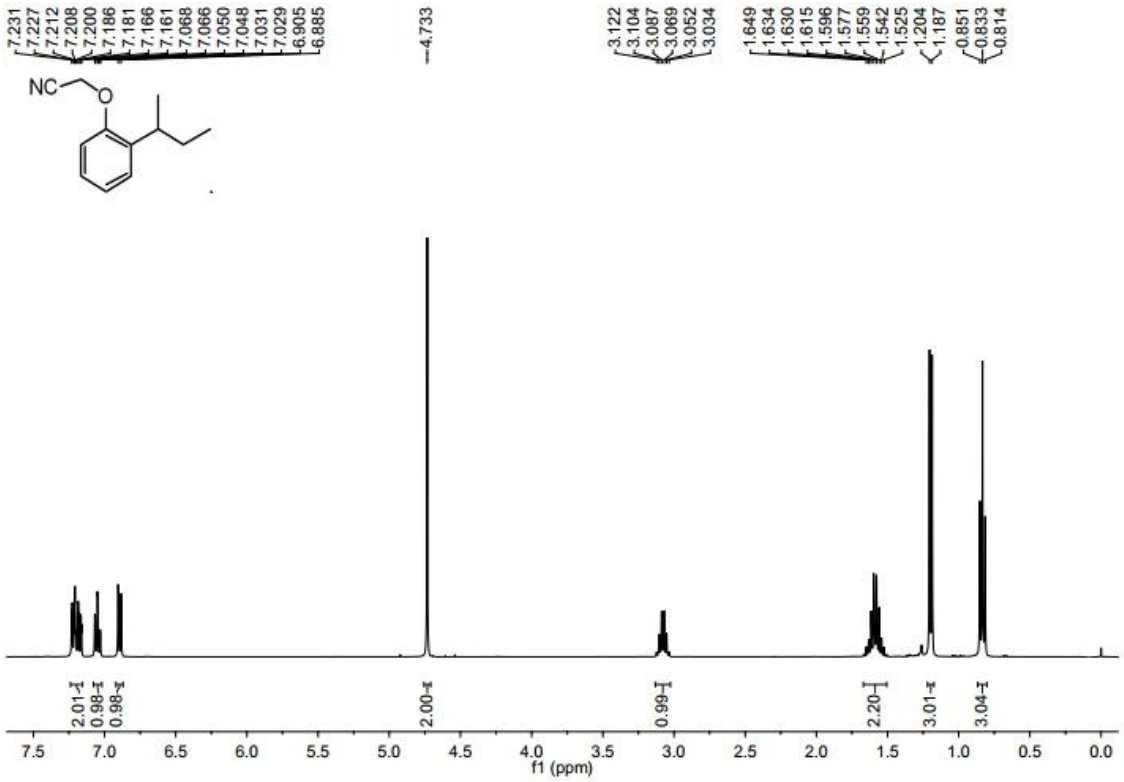
^{1}H NMR spectrum of 3n



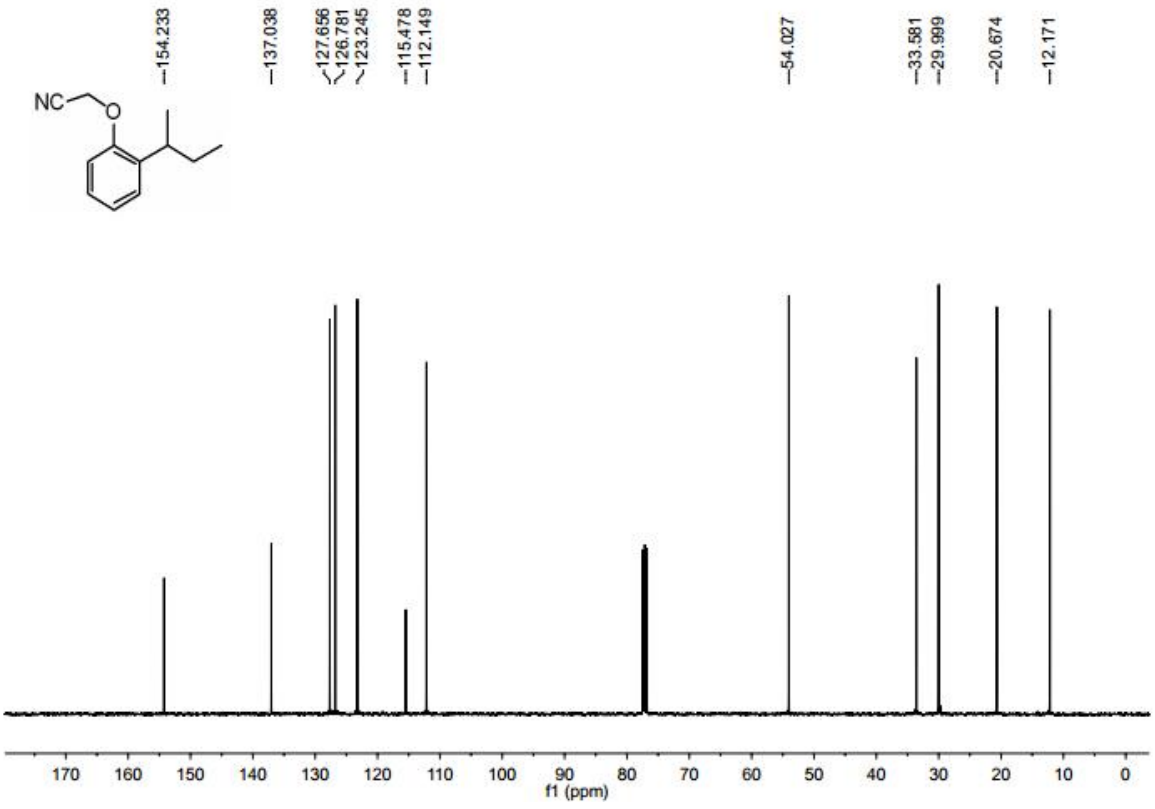
^{13}C NMR spectrum of 3n



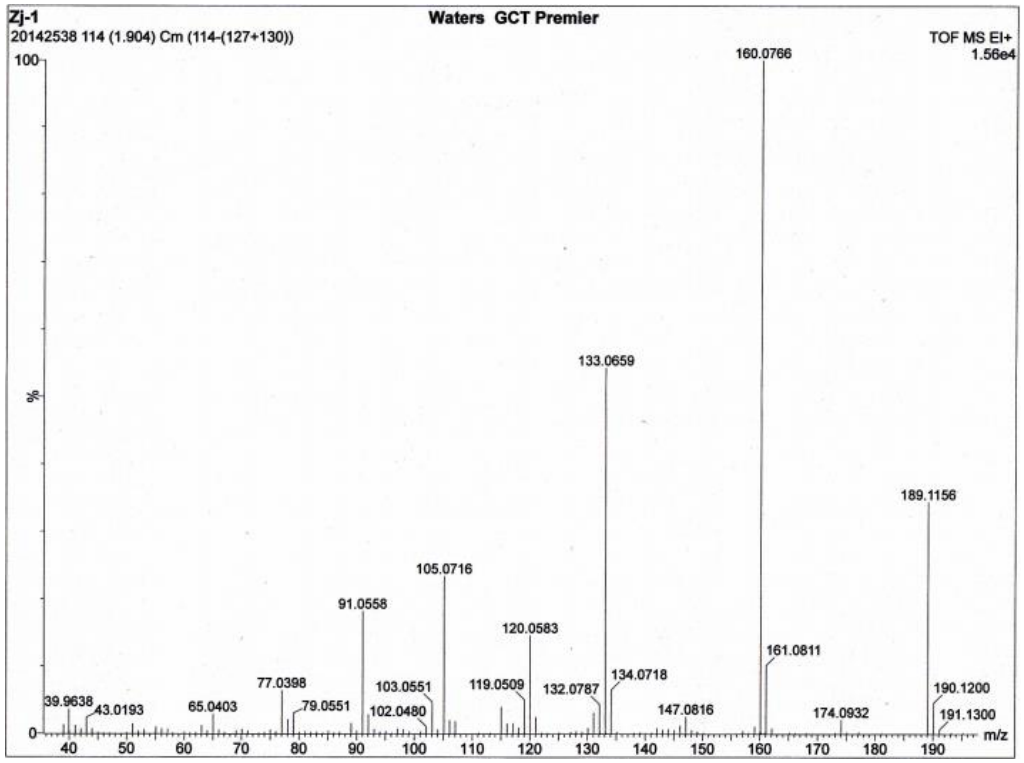
^{1}H NMR spectrum of 3o



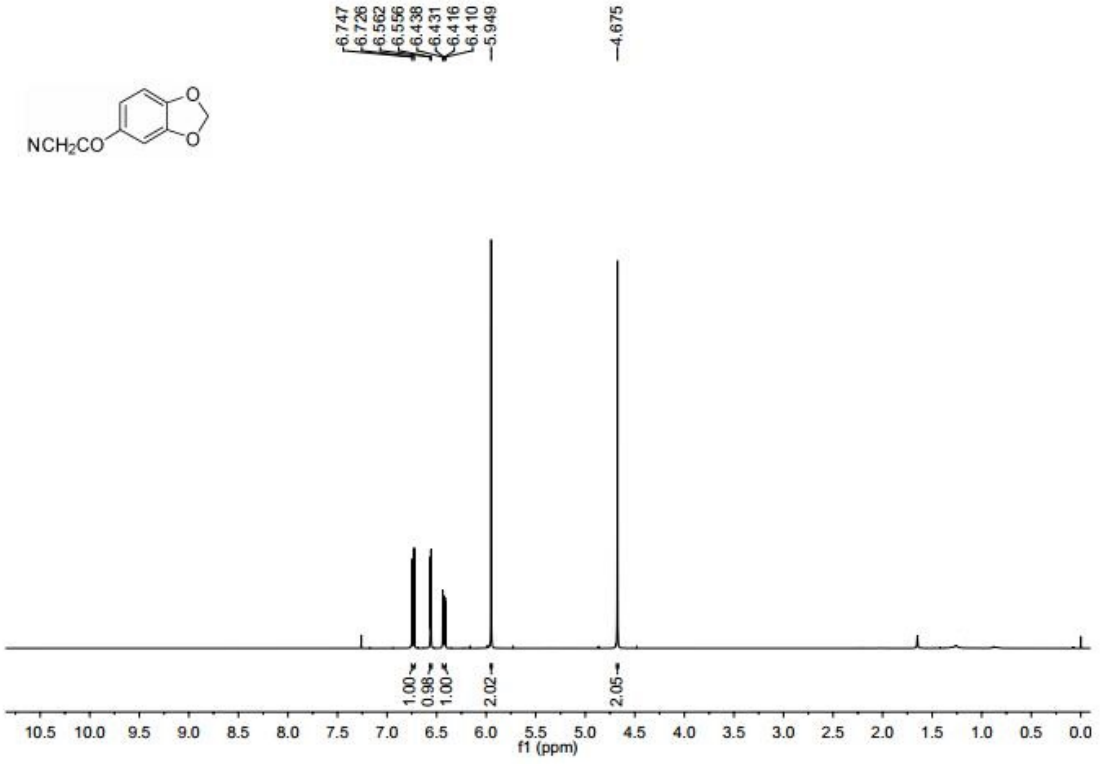
^{13}C NMR spectrum of 3o



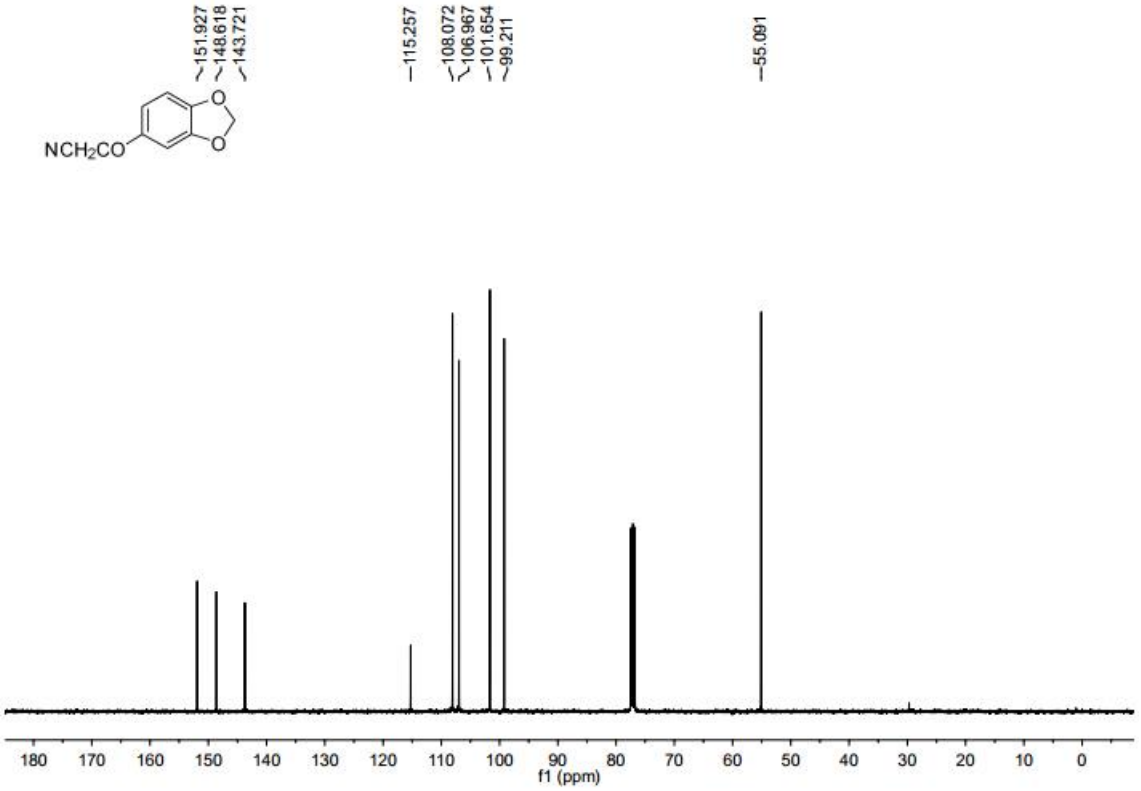
HRMS (EI) spectrum of 3o



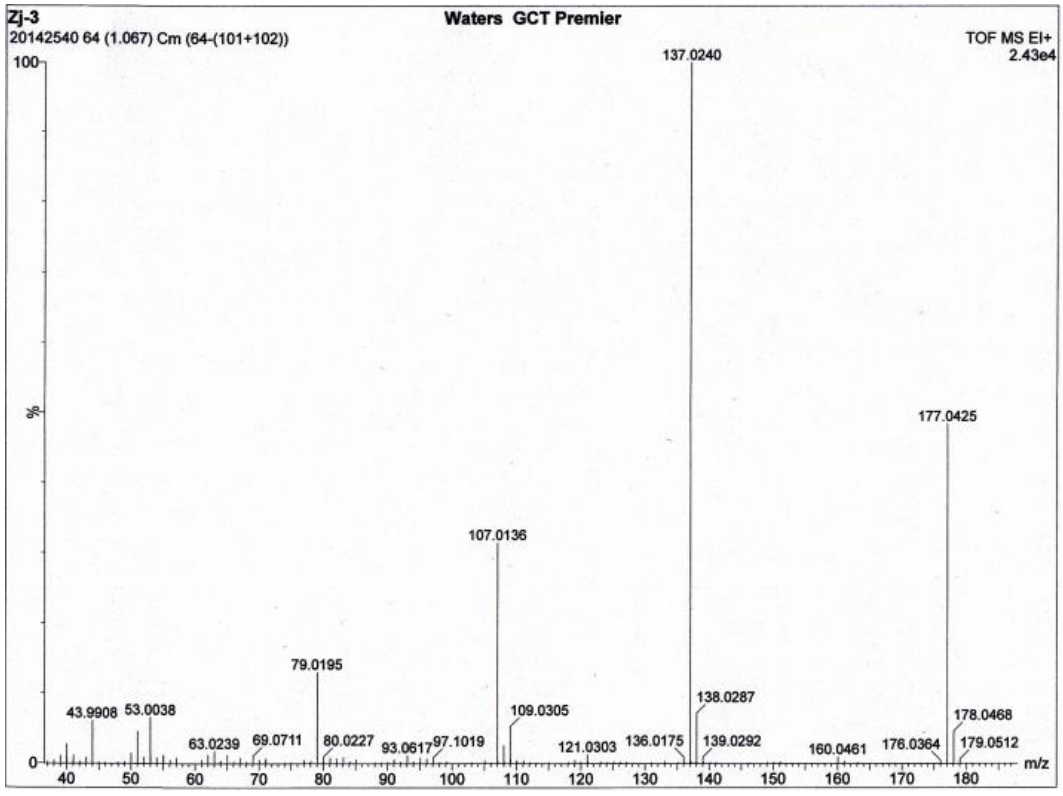
^{1}H NMR spectrum of 3p



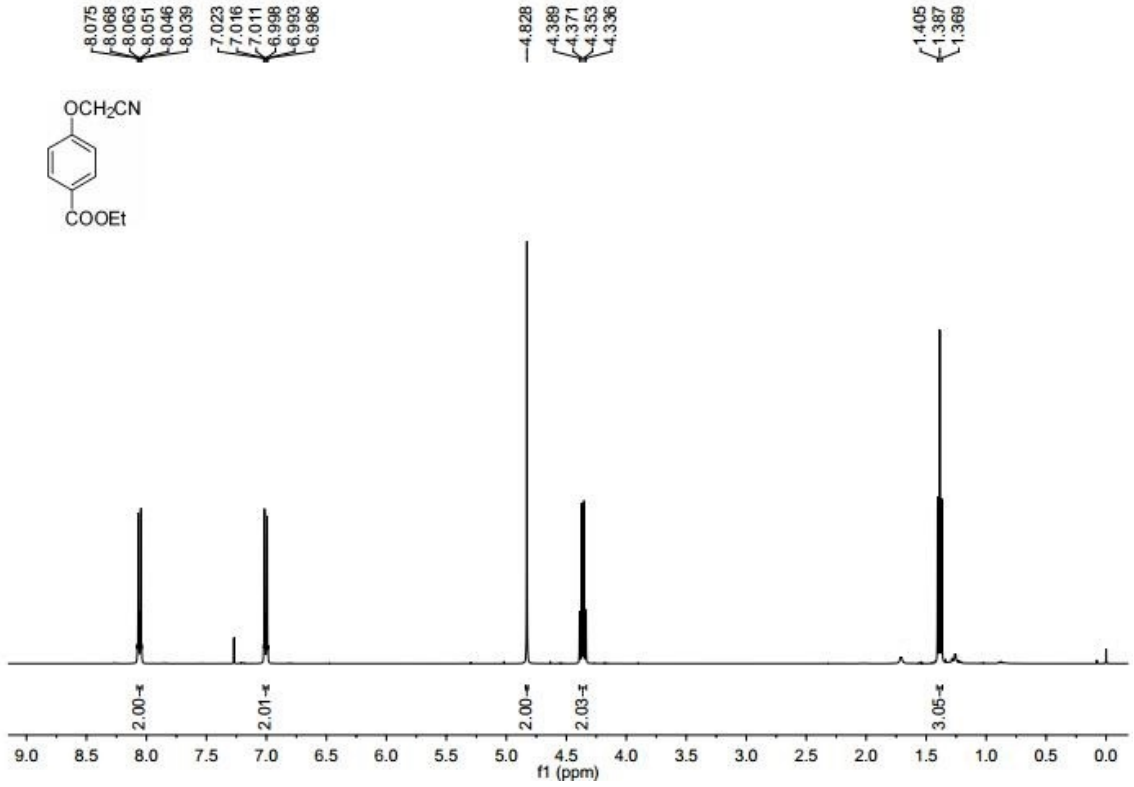
^{13}C NMR spectrum of 3p



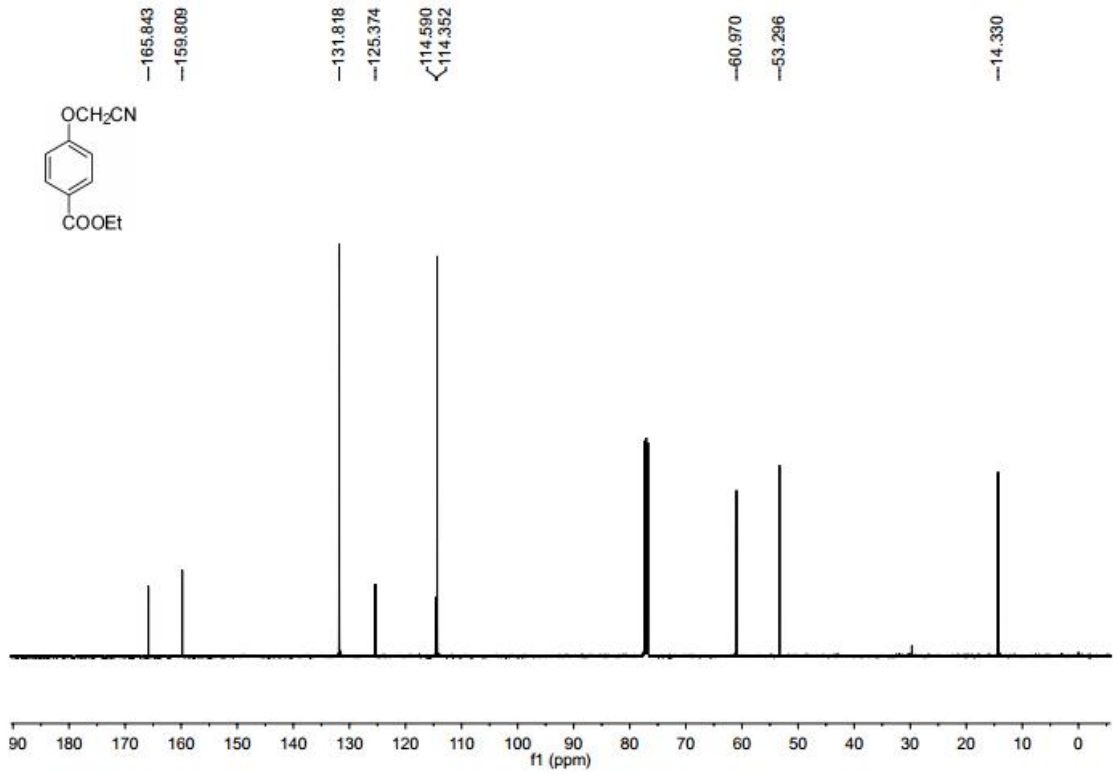
HRMS (EI) spectrum of 3p



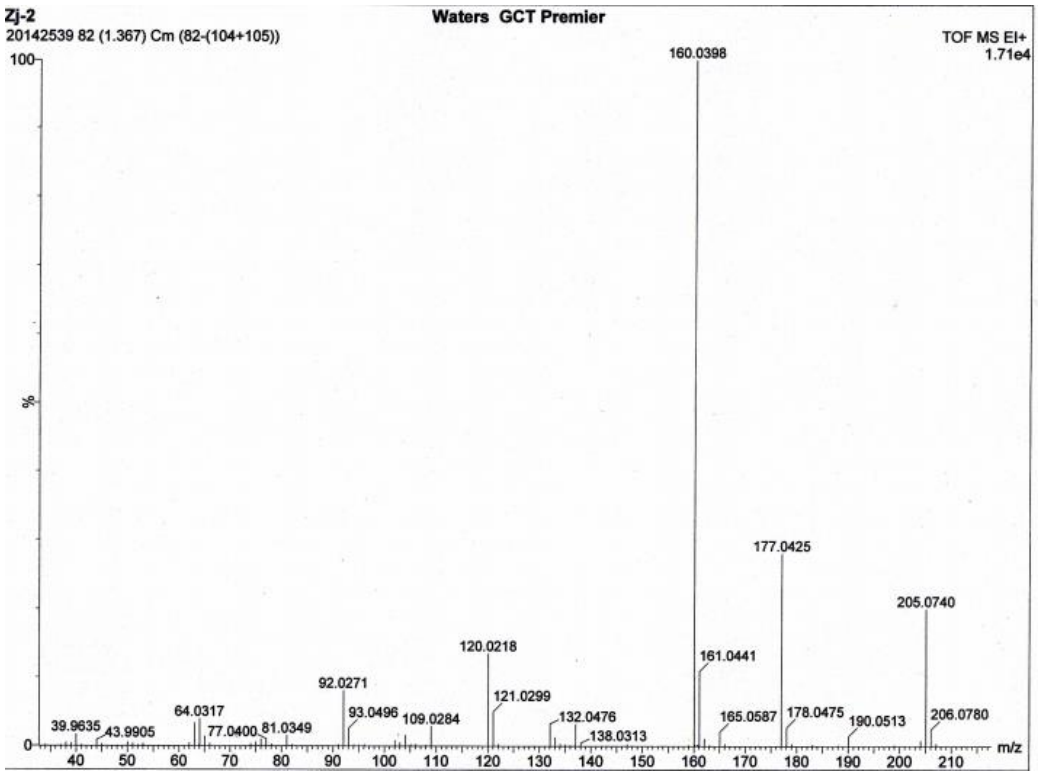
^{1}H NMR spectrum of 3q



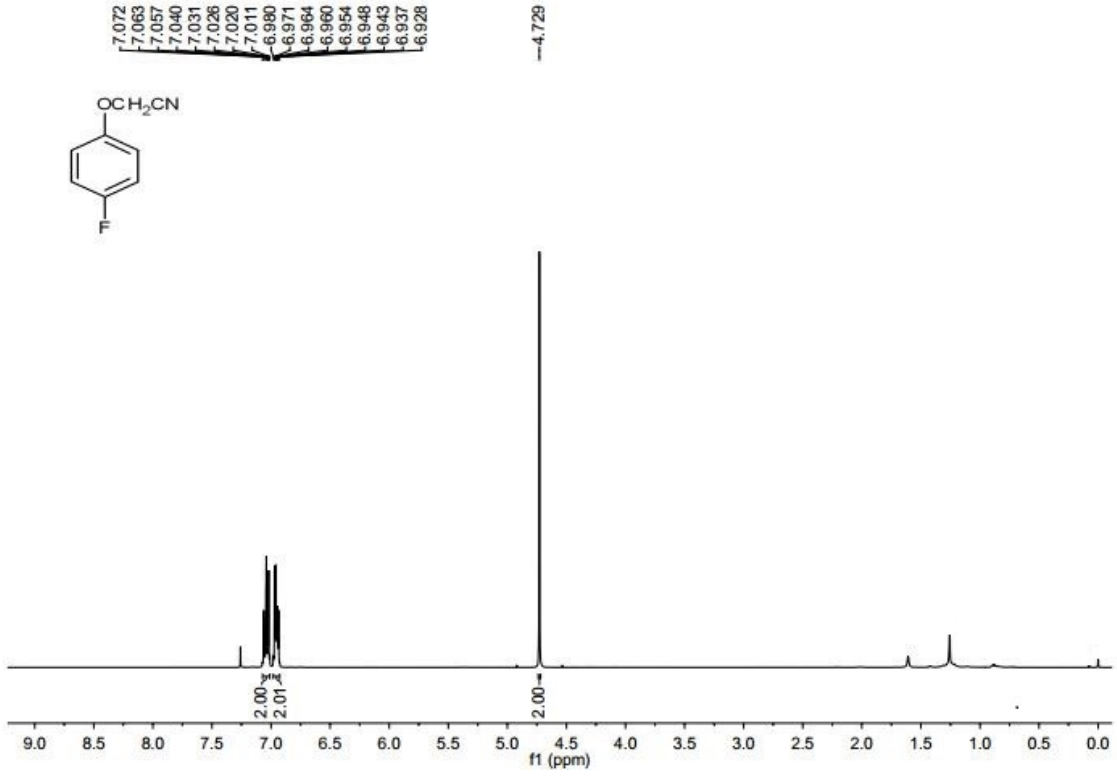
^{13}C NMR spectrum of 3q



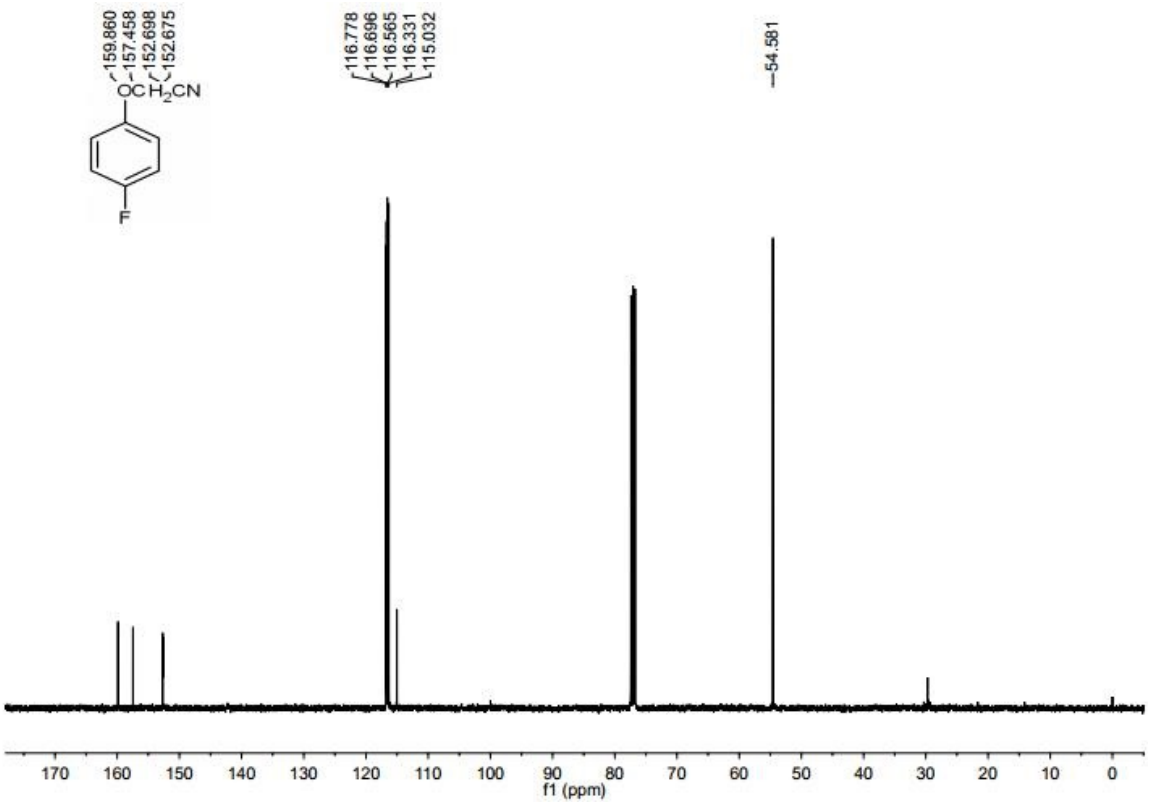
HRMS (EI) spectrum of 3q



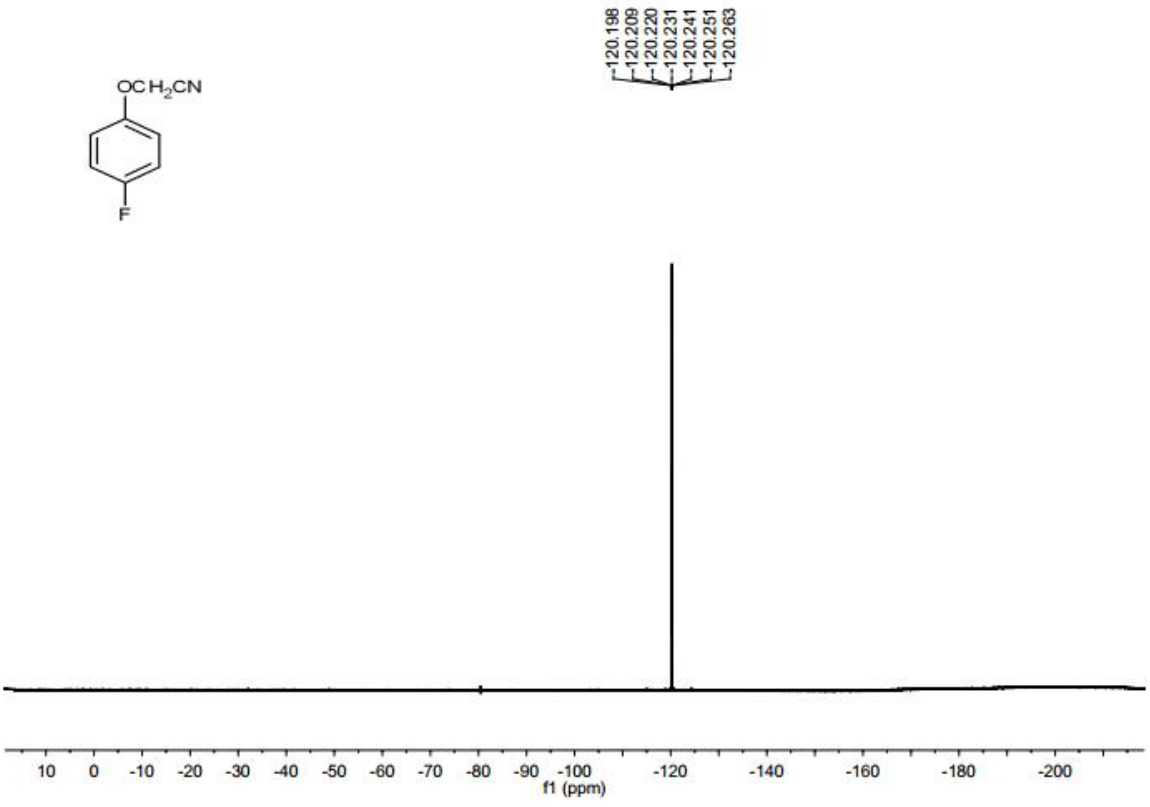
^{1}H NMR spectrum of 3r



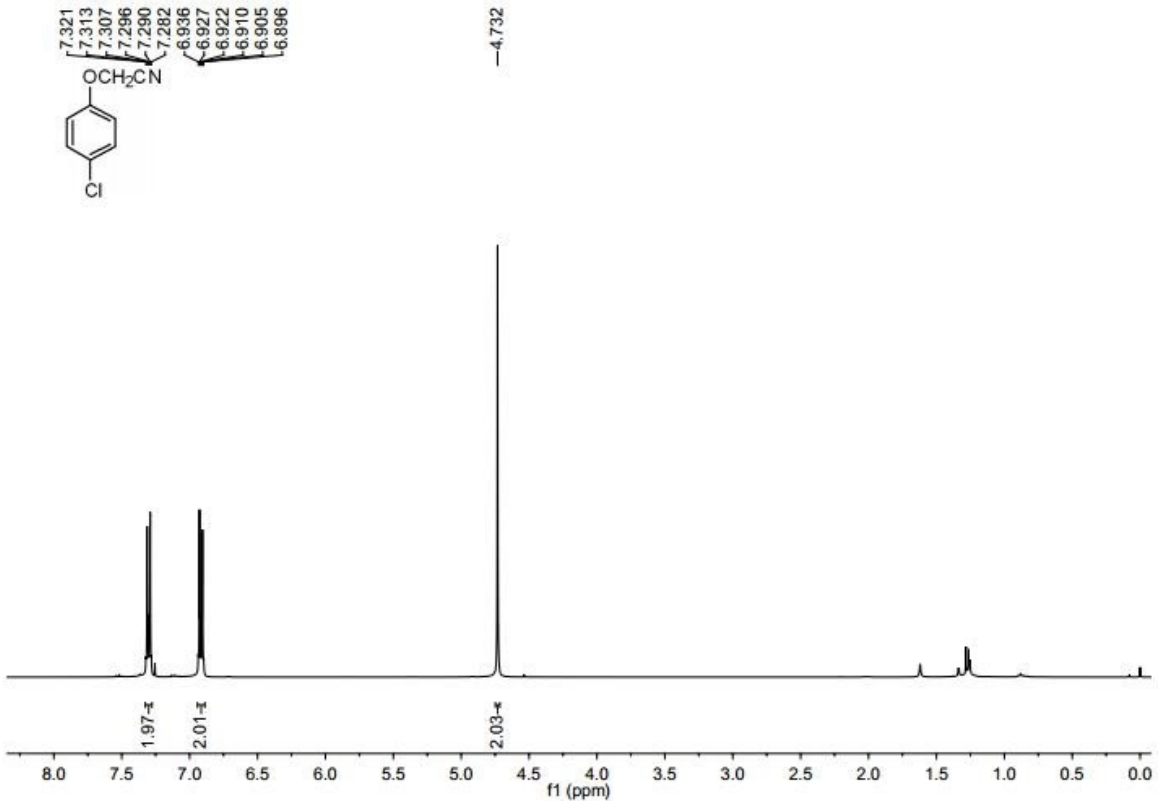
^{13}C NMR spectrum of 3r



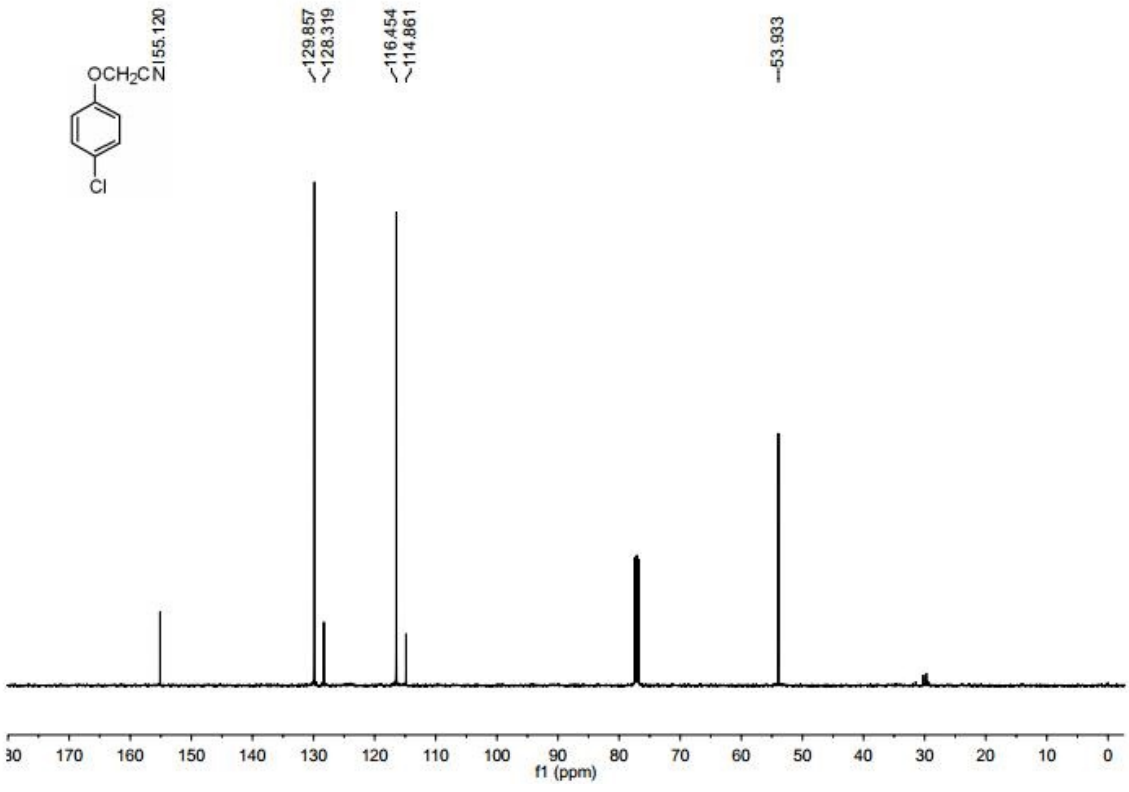
^{19}F NMR spectrum of 3r



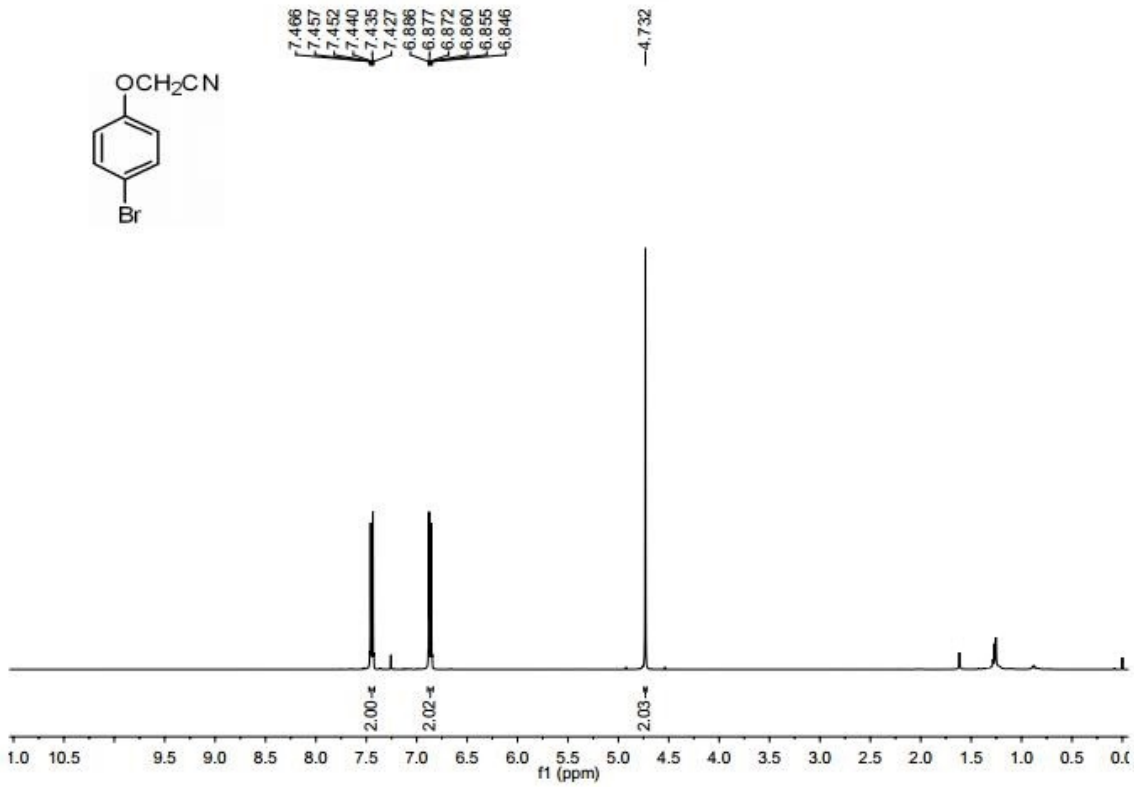
^{1}H NMR spectrum of 3s



^{13}C NMR spectrum of 3s



^{1}H NMR spectrum of 3t



^{13}C NMR spectrum of 3t