

Electronic Supplementary Information (ESI)

Visible-light photocatalysed cyanation of benzylic C-H bonds

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1. Experimental Section

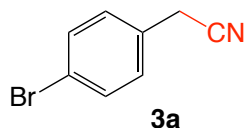
All materials used are commercially available and were purchased from Merck and Pubchem, further used without any additional purification. Melting points were determined by open glass capillary method and are uncorrected. All chemicals used were reagent grade and were used as received. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker AVANCE DPX (400 MHz and 100 MHz) FT spectrometer in CDCl₃ using TMS as an internal reference (chemical shift in δ ppm).

General procedure for the preparation of products (3a-p): The reactions were carried out in a 10 mL glass vial, equipped with a rubber septum and a magnetic stirrer. Substituted benzene (0.2 mmol) (**1a**), *N*-Cyano-*N*-phenyl-*p*-toluenesulfonamide (NCTS) (1.3 equiv) (**2**), and 4-CzIPN (2 mol%), were dissolved in MeCN (4mL) and the mixture was irradiated with a 45W blue-LED under an air atmosphere at 12-24 h at rt. After completion of the reaction (monitored by TLC), the reaction crude was placed into a separatory funnel, water (5 mL) was added and the mixture was extracted with EtOAc (3 × 5 mL). The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (2 x 15 mL). The combined organic extract was dried over anhydrous MgSO₄, filtered and evaporated under reduced pressure. Finally, the products (3a-p) were isolated by column chromatography (silica gel, eluent: 8:2 hexanes/ethyl acetate).

Supplementary Information: ¹H and ¹³C NMR spectra for all synthesized compounds are available in the supplementary material [1-13].

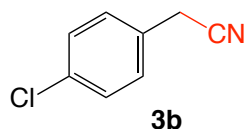
Spectroscopic characterization of all synthesized compounds

2-(4-Bromophenyl)acetonitrile (3a).



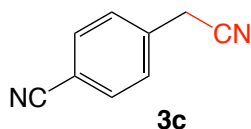
According to the general procedure, compound 3a was achieved as a colourless oil, 91% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.50 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.3 Hz, 2H), 3.70 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 132.3, 129.7, 129.0, 122.2, 117.4, 23.2.

2-(4-Chlorophenyl)acetonitrile (3b).



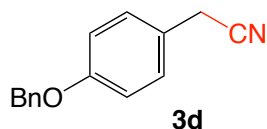
According to the general procedure, compound 3b was achieved as a colourless oil, 82% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.35 (d, $J = 8.5$ Hz, 2H), 7.27 (d, $J = 8.3$ Hz, 2H), 3.73 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 134.0, 129.3, 129.2, 128.5, 117.5, 23.0.

4-(Cyanomethyl)benzonitrile (3c).



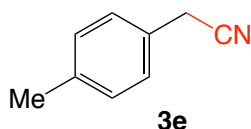
According to the general procedure, compound 3c was achieved as a colourless oil, 68% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.69 (d, $J = 8.3$ Hz, 2H), 7.47 (d, $J = 8.0$ Hz, 2H), 3.84 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 135.2, 133.0, 128.9, 118.2, 116.7, 112.5, 23.9.

2-(4-(Benzyloxy)phenyl)acetonitrile (3d).



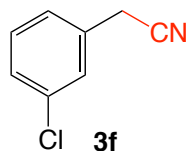
According to the general procedure, compound 3d was achieved as a colourless oil, 92% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.34 – 7.27 (m, 4H), 7.26 – 7.22 (m, 1H), 7.26 (d, $J = 8.6$ Hz, 2H), 7.01 (d, $J = 8.7$ Hz, 2H), 5.09 (s, 2H), 3.69 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 158.5, 136.7, 129.2, 128.7, 128.1, 127.5, 122.1, 118.3, 115.5, 70.1, 22.8.

2-(*p*-Tolyl)acetonitrile (3e).



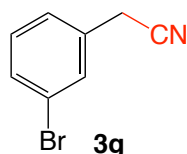
According to the general procedure, compound 3e was achieved as a colourless oil, 94% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.23 – 7.17 (m, 4H), 3.70 (s, 2H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 137.9, 129.8, 127.9, 126.9, 118.2, 23.3, 21.1.

2-(3-Chlorophenyl)acetonitrile (3f).



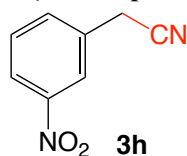
According to the general procedure, compound 3f was achieved as a colourless oil, 80% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.33 – 7.31 (m, 3H), 7.24 – 7.21 (m, 1H), 3.73 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 135.1, 131.8, 130.5, 128.5, 128.2, 126.2, 117.3, 23.4.

2-(3-Bromophenyl)acetonitrile (3g).



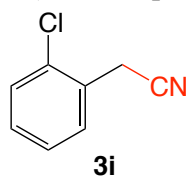
According to the general procedure, compound 3g was achieved as a yellow oil, 88% yield. ^1H NMR (400 MHz, CDCl_3) 7.48 – 7.45 (m, 2H), 7.28 – 7.25 (m, 2H), 3.73 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 132.1, 131.3, 131.0, 130.7, 126.6, 123.0, 117.3, 23.2.

2-(3-Nitrophenyl)acetonitrile (3h).



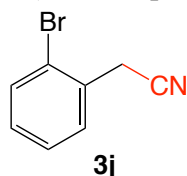
According to the general procedure, compound 3h was achieved as a colourless oil, 63% yield. ^1H NMR (400 MHz, CDCl_3) δ 8.20 – 8.18 (m, 2H), 7.71 (d, $J = 7.7$ Hz, 1H), 7.60 (t, $J = 7.9$ Hz, 1H), 3.91 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 148.5, 134.1, 132.1, 130.4, 123.3, 123.1, 116.8, 23.4.

2-(2-Chlorophenyl)acetonitrile (3i).



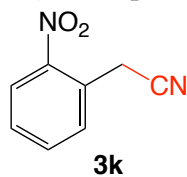
According to the general procedure, compound 3i was achieved as a colourless oil, 78% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.52 – 7.50 (m, 1H), 7.43 – 7.40 (m, 1H), 7.33 – 7.29 (m, 2H), 3.83 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 133.5, 129.81, 129.75, 129.7, 128.2, 127.6, 116.9, 22.2.

2-(2-Bromophenyl)acetonitrile (3j).



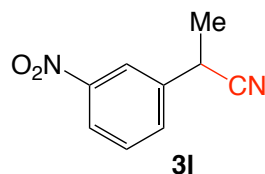
According to the general procedure, compound 3j was achieved as a colourless oil, 86% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.57 (d, $J = 8.0$ Hz, 1H), 7.49 (d, $J = 7.8$ Hz, 1H), 7.33 (t, $J = 7.6$ Hz, 1H), 7.19 (t, $J = 6.9$ Hz, 1H), 3.80 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 133.0, 129.9, 129.8, 129.7, 128.1, 123.5, 116.9, 24.8.

2-(2-Nitrophenyl)acetonitrile (3k).



According to the general procedure, compound 3k was achieved as a colourless oil, 60% yield. ^1H NMR (400 MHz, CDCl_3) δ 8.18 (d, $J = 8.2$ Hz, 1H), 7.72 (d, $J = 4.1$ Hz, 2H), 7.57 (dt, $J = 8.6, 4.2$ Hz, 1H), 4.20 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 147.6, 134.6, 131.3, 129.8, 125.9, 125.8, 116.5, 22.9.

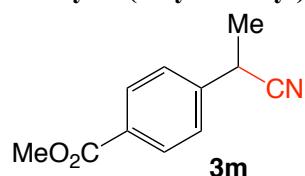
2-(3-Nitrophenyl)propanenitrile (3l).



According to the general procedure, compound 3l was achieved as a colourless oil, 65% yield. ^1H NMR

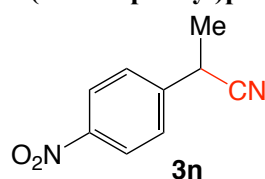
(400 MHz, CDCl₃) δ 8.22 (s, 1H), 8.19 (d, J = 8.2 Hz, 1H), 7.74 (d, J = 7.7 Hz, 1H), 7.60 (t, J = 7.9 Hz, 1H), 4.06 (q, J = 7.3 Hz, 1H), 1.70 (d, J = 7.3 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 148.7, 139.1, 133.0, 130.4, 123.3, 122.0, 120.5, 31.0, 21.2.

Methyl 4-(1-cyanoethyl)benzoate (3m).



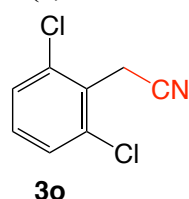
According to the general procedure, compound 3m was achieved as a colourless oil, 71% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.02 (d, J = 8.1 Hz, 2H), 7.41 (d, J = 8.6 Hz, 2H), 3.95 (q, J = 7.4 Hz, 1H), 3.89 (s, 3H), 1.63 (d, J = 7.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 166.4, 141.9, 130.5, 130.0, 126.9, 121.0, 52.3, 31.2, 21.3.

2-(4-Nitrophenyl)propanenitrile (3n).



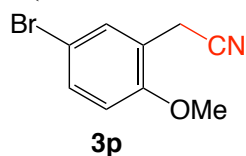
According to the general procedure, compound 3n was achieved as a colourless oil, 70% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.24 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 9.0 Hz, 2H), 4.04 (q, J = 7.3 Hz, 1H), 1.69 (d, J = 7.3 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 147.8, 144.1, 128.0, 124.5, 120.4, 31.2, 21.3.

2-(2,6-dichlorophenyl)acetonitrile (3o).



According to the general procedure, compound 3o was achieved as a pale yellow oil, 74% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.38 – 7.36 (m, 2H), 7.25 (dd, J = 8.8, 7.4 Hz, 1H), 4.01 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 135.7, 130.4, 128.7, 127.2, 115.6, 19.9.

2-(5-bromo-2-methoxyphenyl)acetonitrile (3p).



According to the general procedure, compound 3p was achieved as a white solid, 96% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.46 (d, J = 2.3 Hz, 1H), 7.40 (dd, J = 8.7, 2.5 Hz, 1H), 6.76 (d, J = 8.7 Hz, 1H), 3.84 (s, 3H), 3.64 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 155.9, 132.3, 131.9, 120.8, 117.4, 112.8, 112.2, 55.9, 18.5.

References

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

Figure S1a: ^1H NMR (400 MHz, CDCl_3) of 2-(4-Bromophenyl)acetonitrile (**3a**)

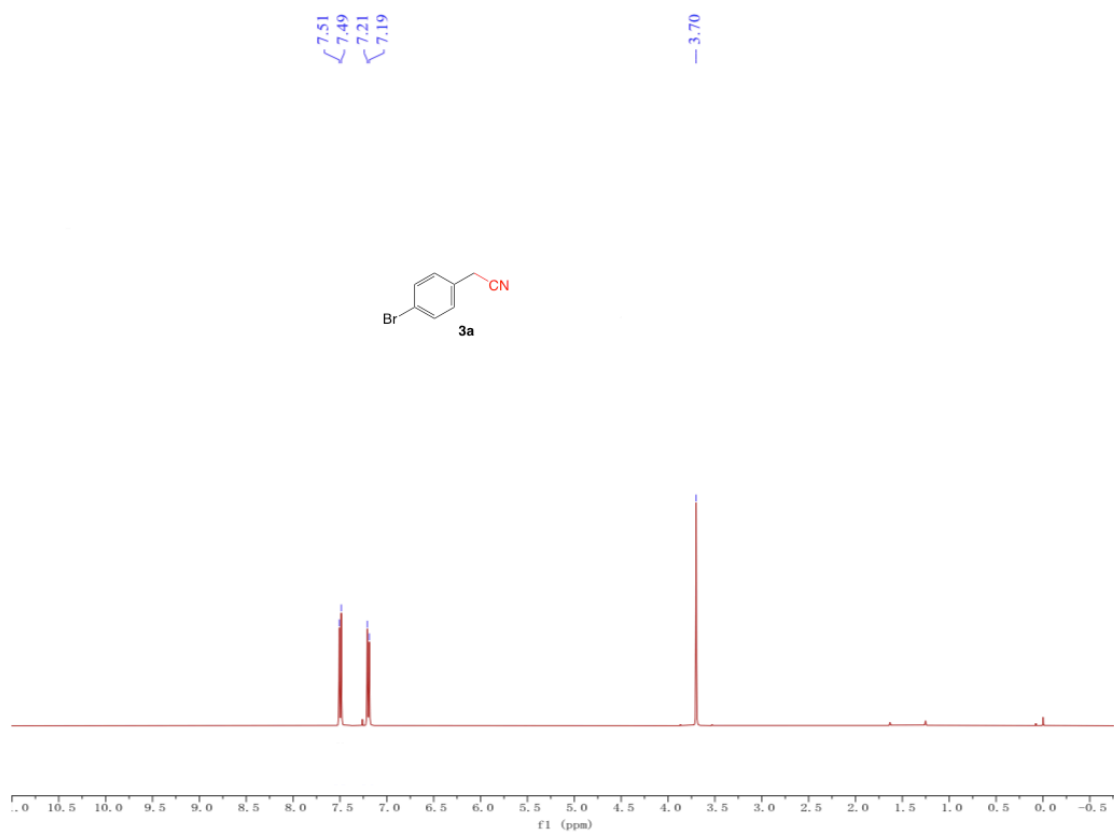


Figure S1b: ^{13}C NMR (100 MHz, CDCl_3) of 2-(4-Bromophenyl)acetonitrile (**3a**)

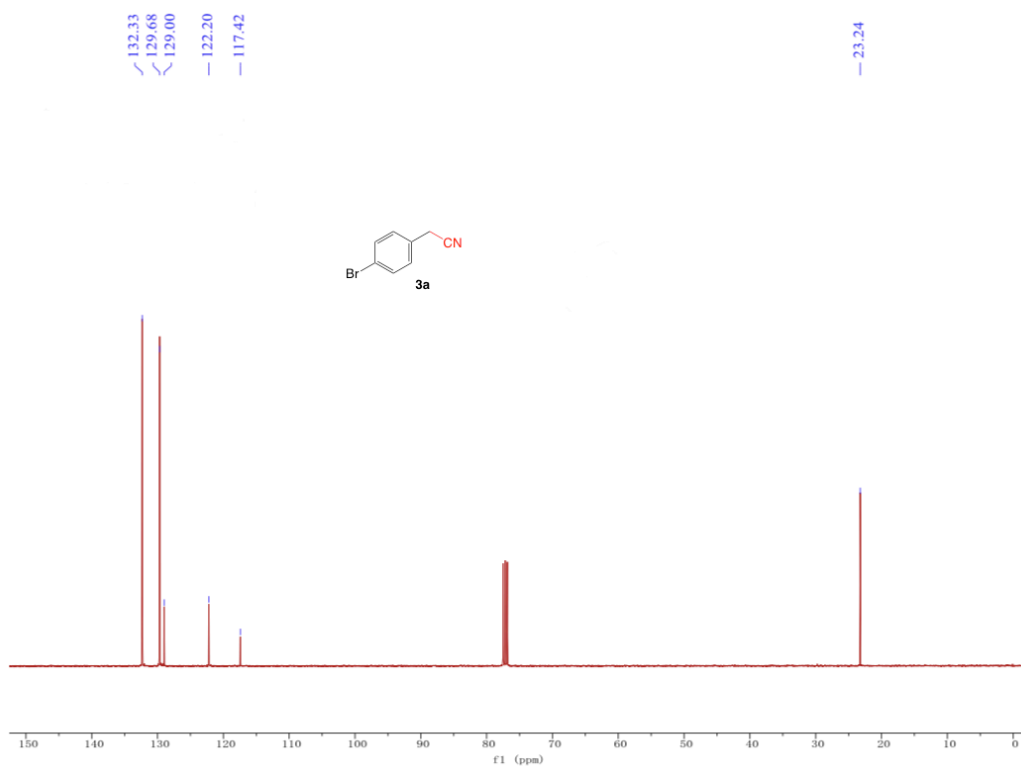


Figure S2a: ^1H NMR (400 MHz, CDCl_3) of 2-(4-Chlorophenyl)acetonitrile (**3b**)

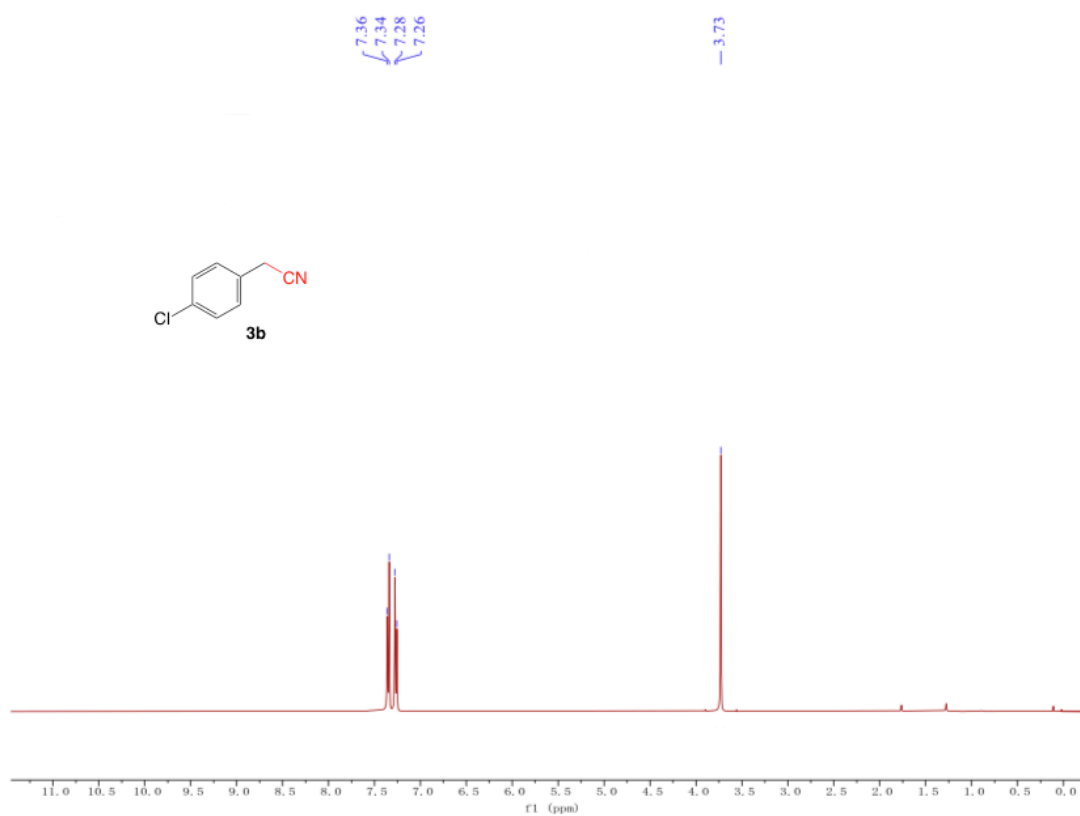


Figure S2b: ^{13}C NMR (100 MHz, CDCl_3) of 2-(4-Chlorophenyl)acetonitrile (**3b**)

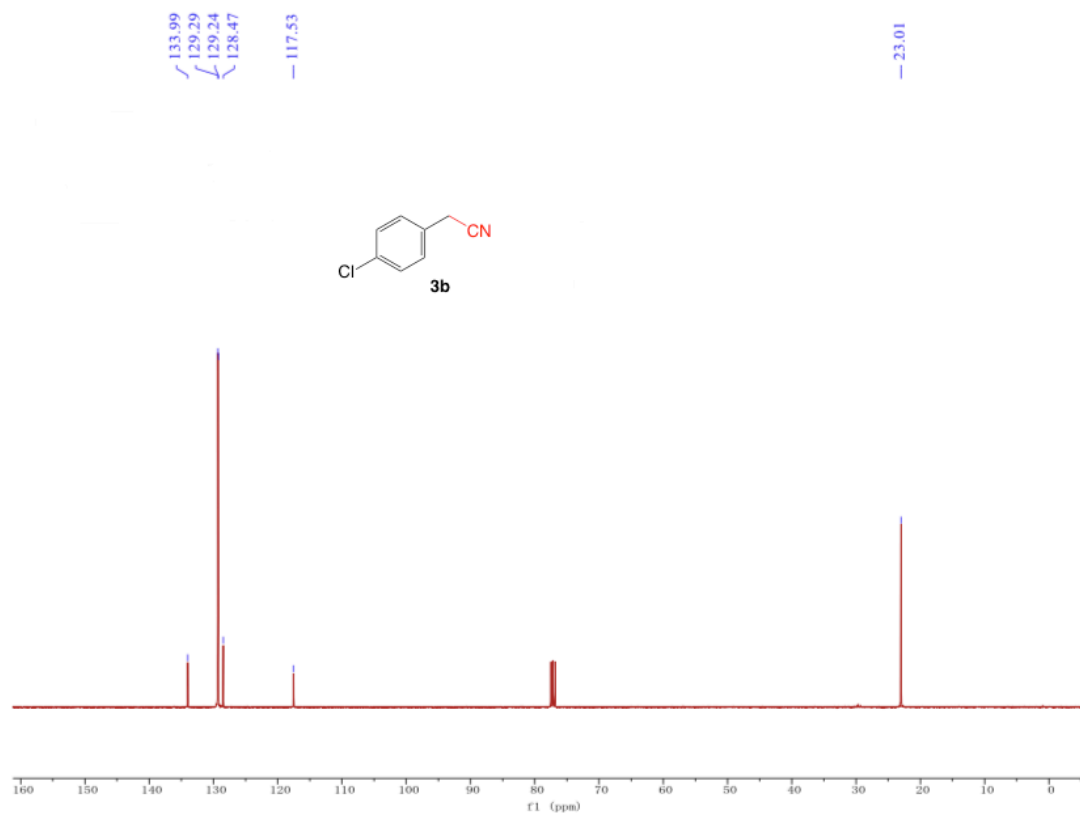


Figure S3a: ^1H NMR (400 MHz, CDCl_3) of 4-(Cyanomethyl)benzonitrile (**3c**)

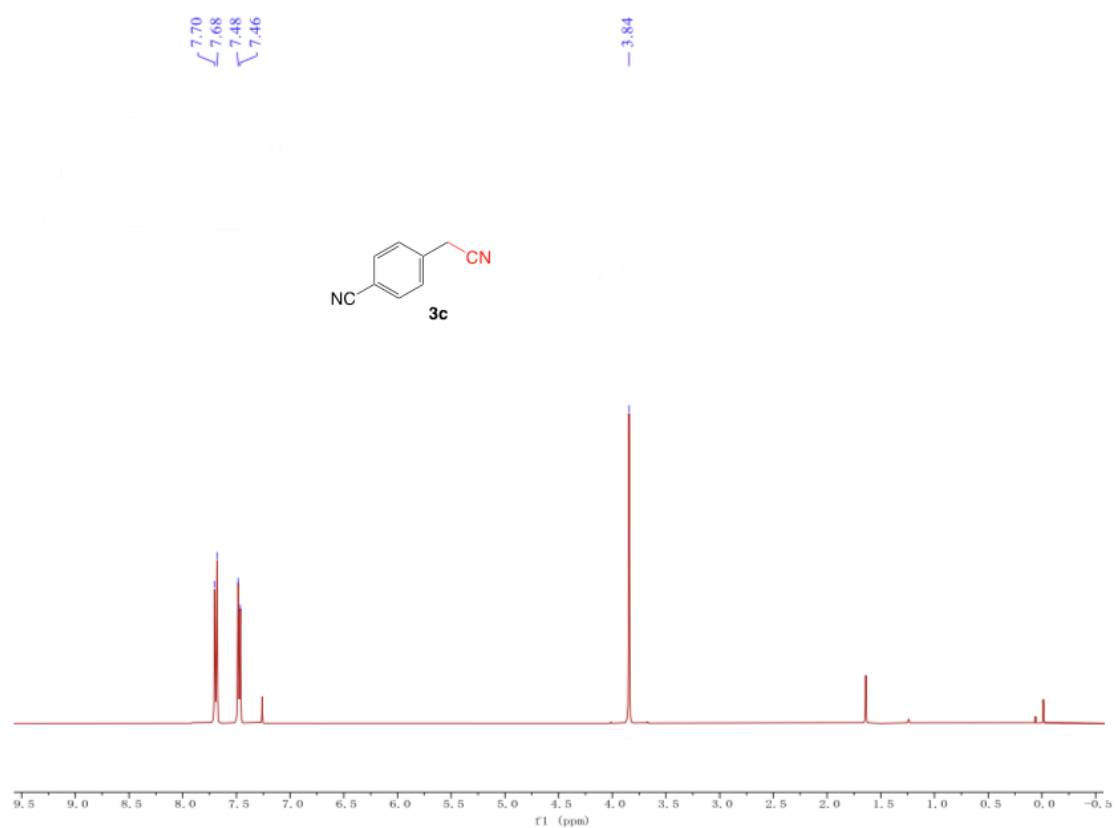


Figure S3b: ^{13}C NMR (100 MHz, CDCl_3) of 4-(Cyanomethyl)benzonitrile (**3c**)

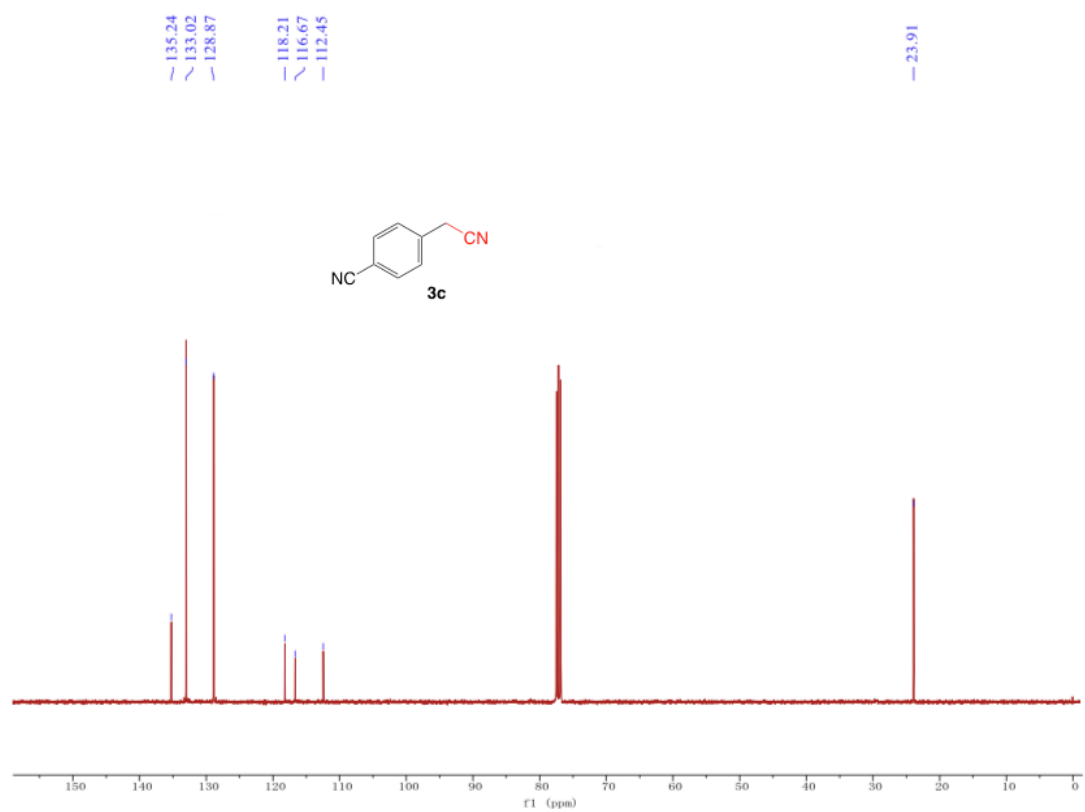


Figure S4a: ^1H NMR (400 MHz, CDCl_3) of 2-(4-(Benzyloxy)phenyl)acetonitrile (**3d**)

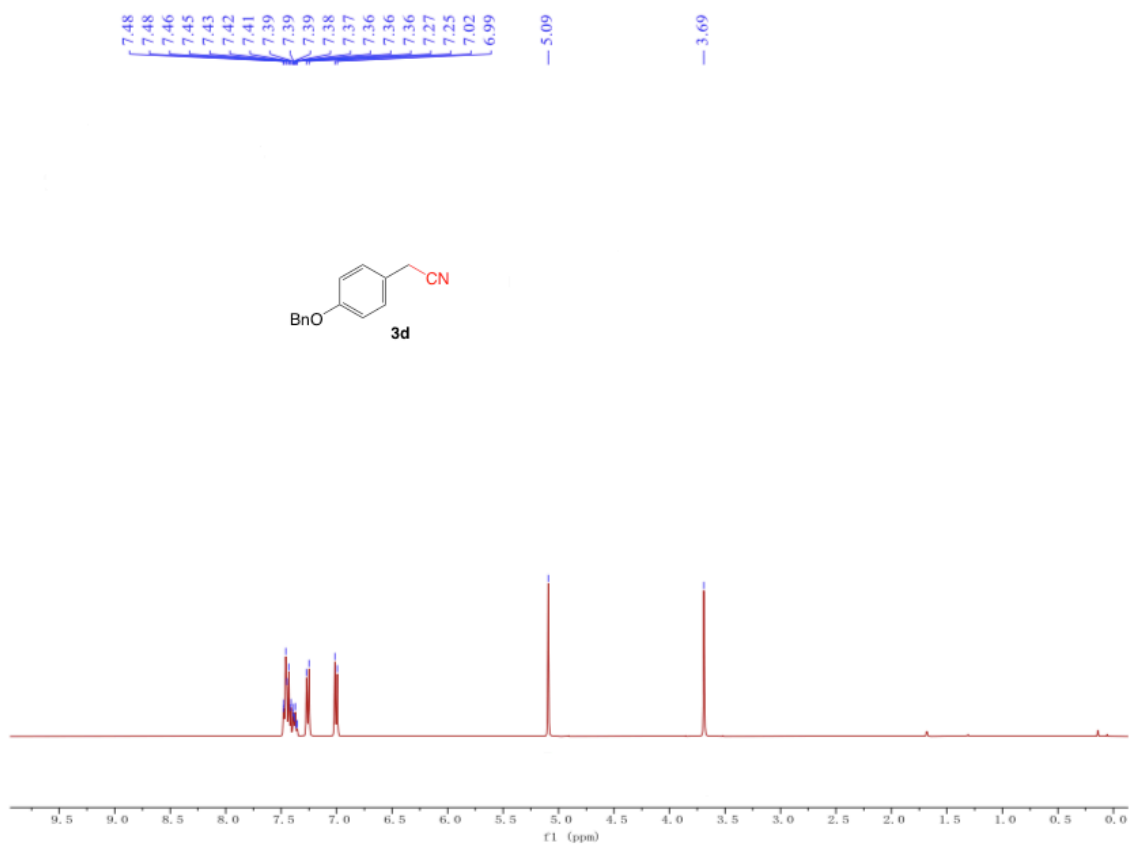


Figure S4b: ^{13}C NMR (100 MHz, CDCl_3) of 2-(4-(Benzyloxy)phenyl)acetonitrile (**3d**)

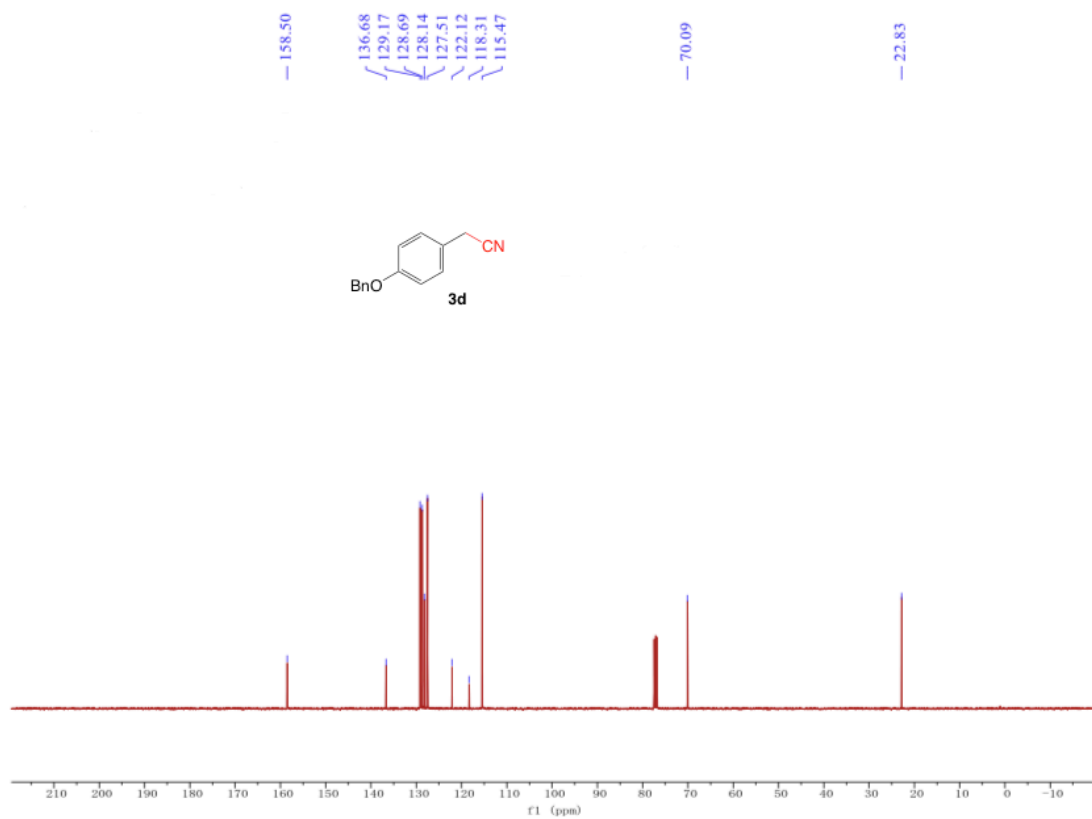


Figure S5a: ^1H NMR (400 MHz, CDCl_3) of 2-(*p*-Tolyl)acetonitrile (**3e**)

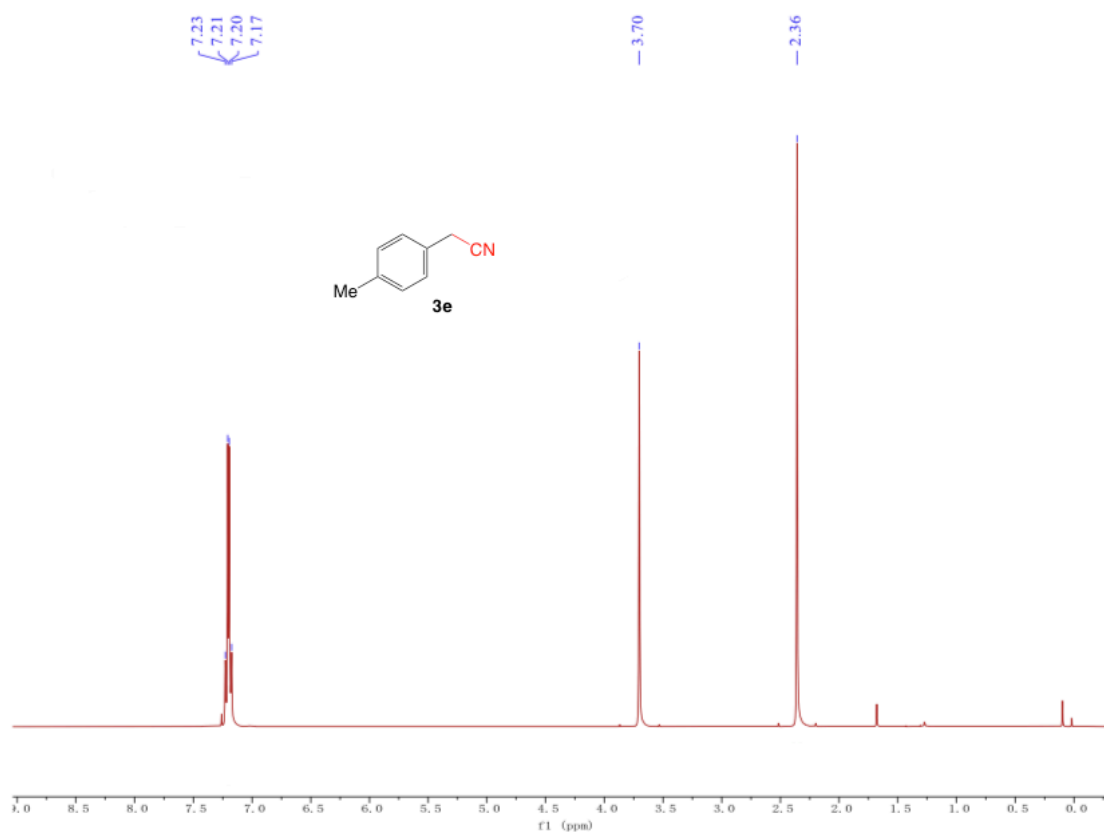


Figure S5b: ^{13}C NMR (100 MHz, CDCl_3) of 2-(*p*-Tolyl)acetonitrile (**3e**)

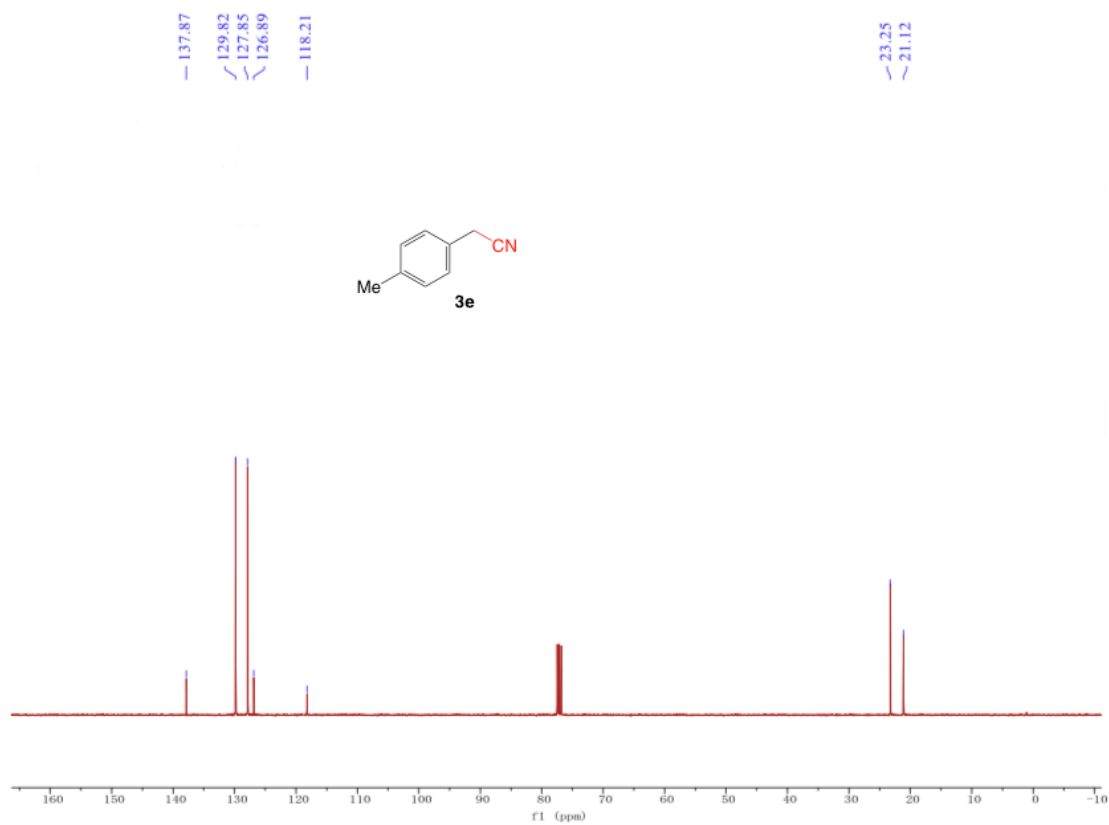


Figure S6a: ^1H NMR (400 MHz, CDCl_3) of 2-(3-Chlorophenyl)acetonitrile (**3f**)

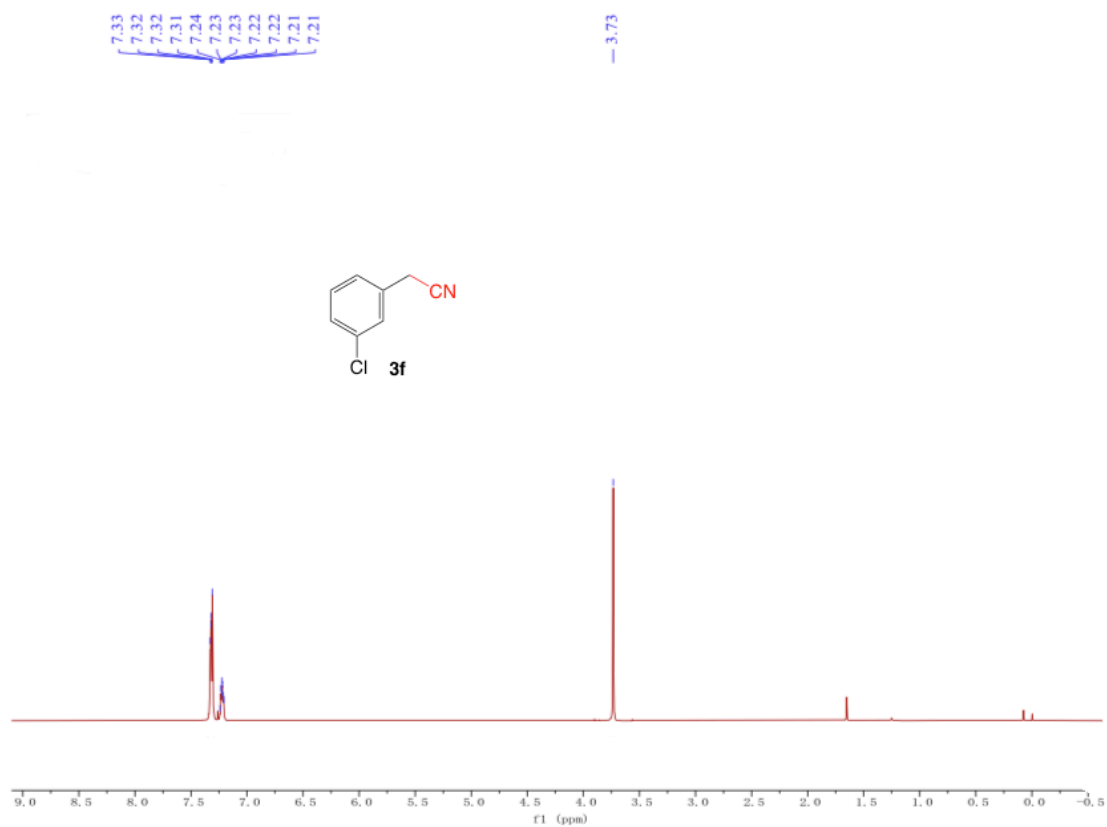


Figure S6b: ^{13}C NMR (100 MHz, CDCl_3) of 2-(3-Chlorophenyl)acetonitrile (**3f**)

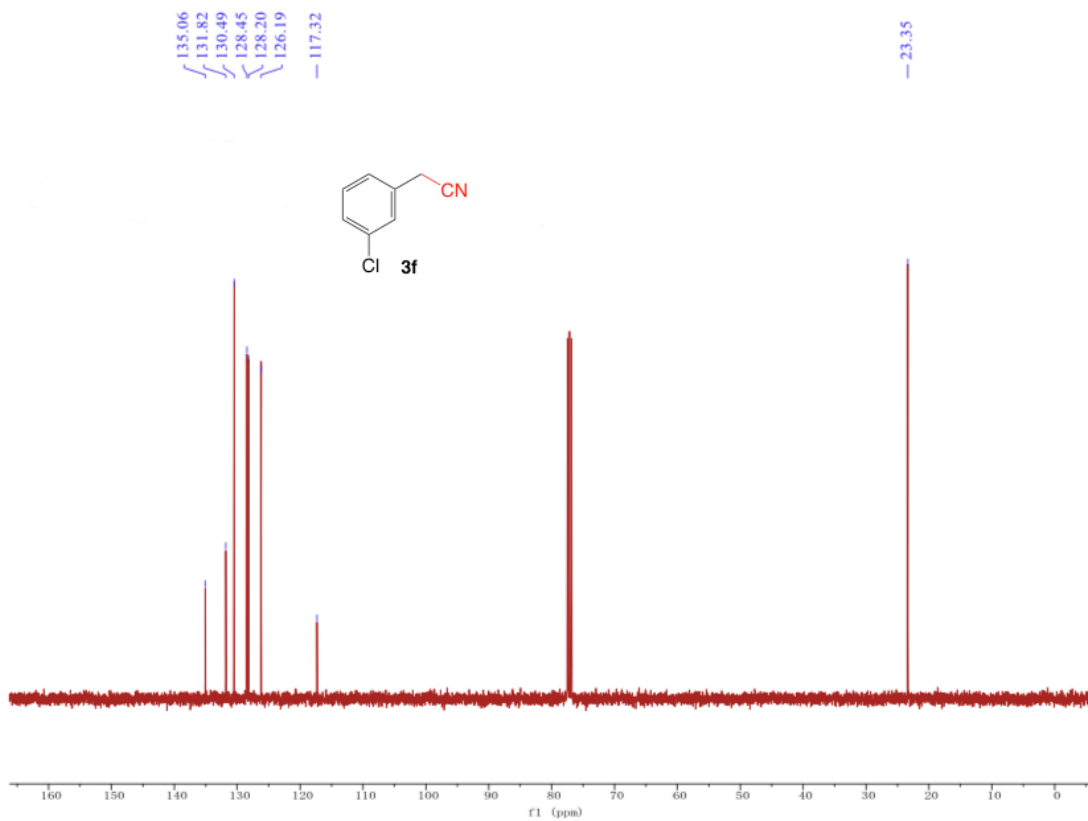


Figure S7a: ^1H NMR (400 MHz, CDCl_3) of 2-(3-Bromophenyl)acetonitrile (**3g**)

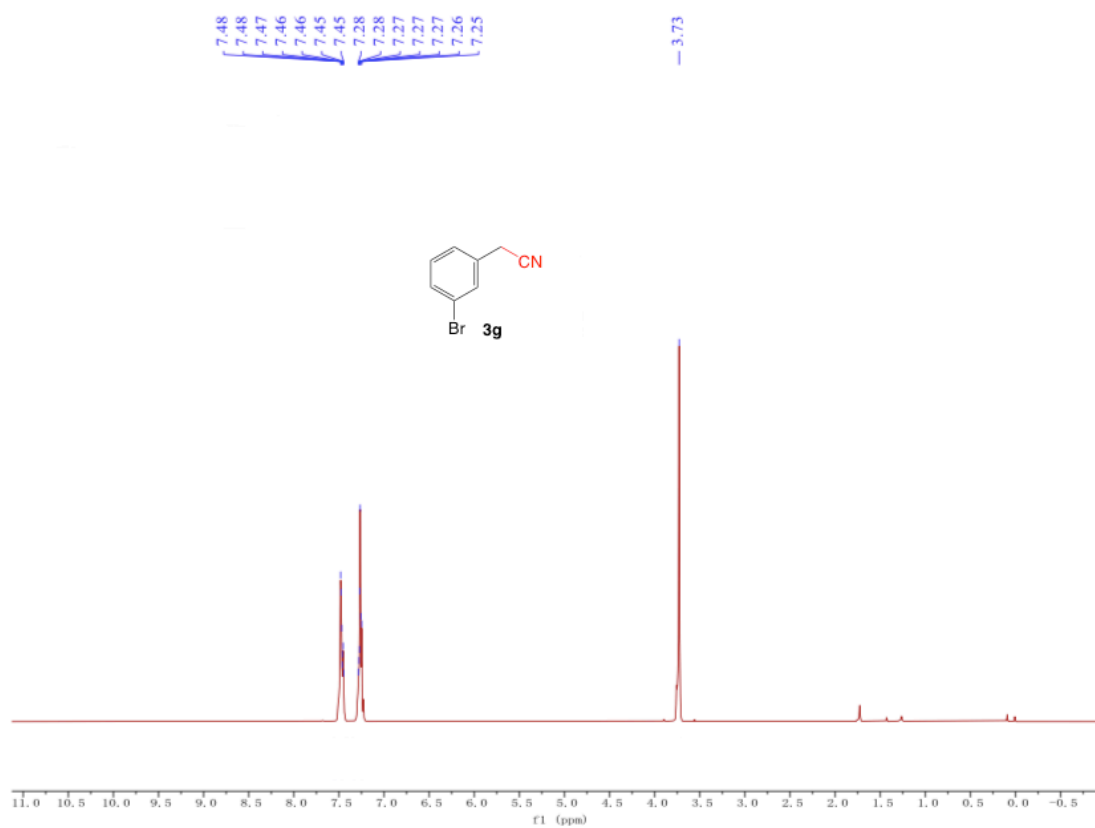


Figure S7b: ^{13}C NMR (100 MHz, CDCl_3) of 2-(3-Bromophenyl)acetonitrile (**3g**)

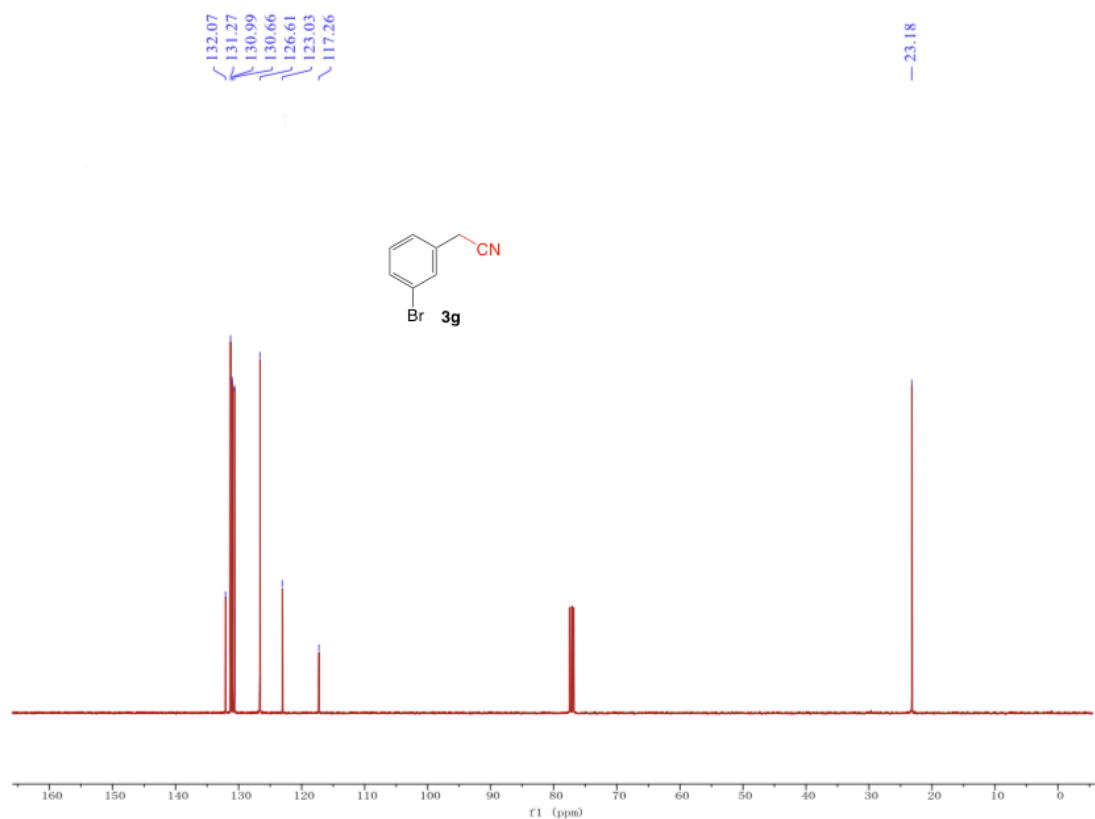


Figure S8a: ^1H NMR (400 MHz, CDCl_3) of 2-(3-Nitrophenyl)acetonitrile (**3h**)

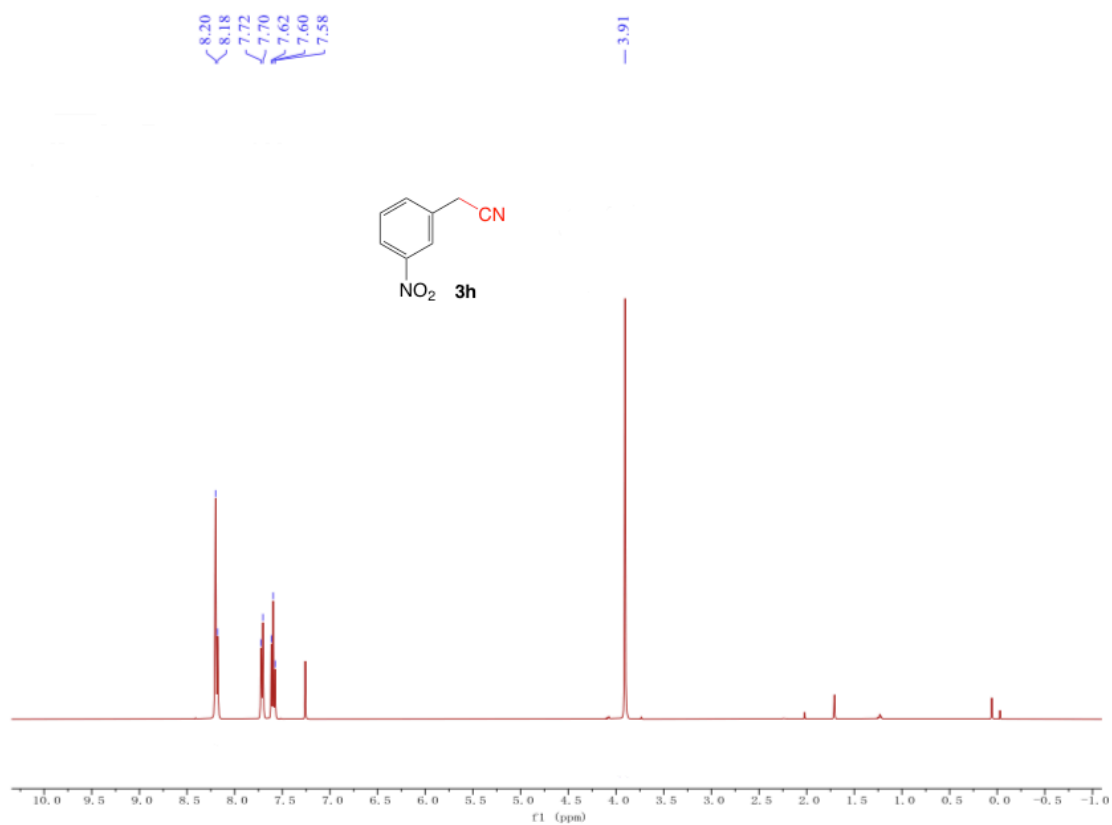


Figure S8b: ^{13}C NMR (100 MHz, CDCl_3) of 2-(3-Nitrophenyl)acetonitrile (**3h**)

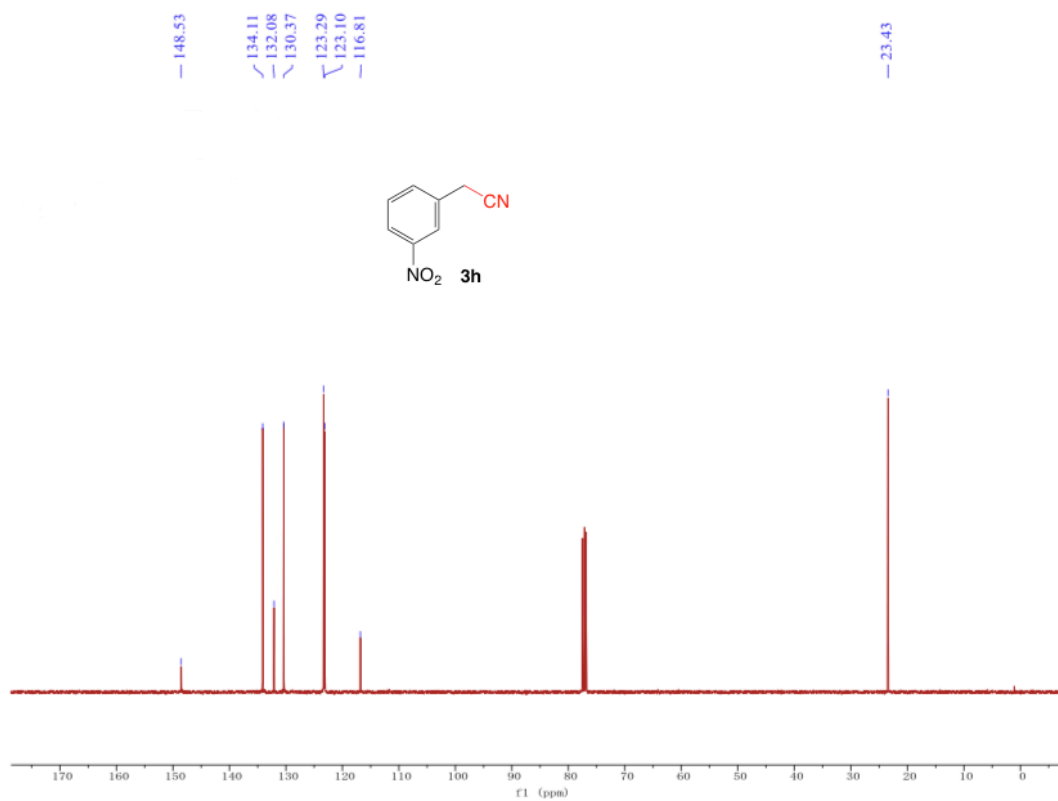


Figure S9a: ^1H NMR (400 MHz, CDCl_3) of 2-(2-Chlorophenyl)acetonitrile (**3i**)

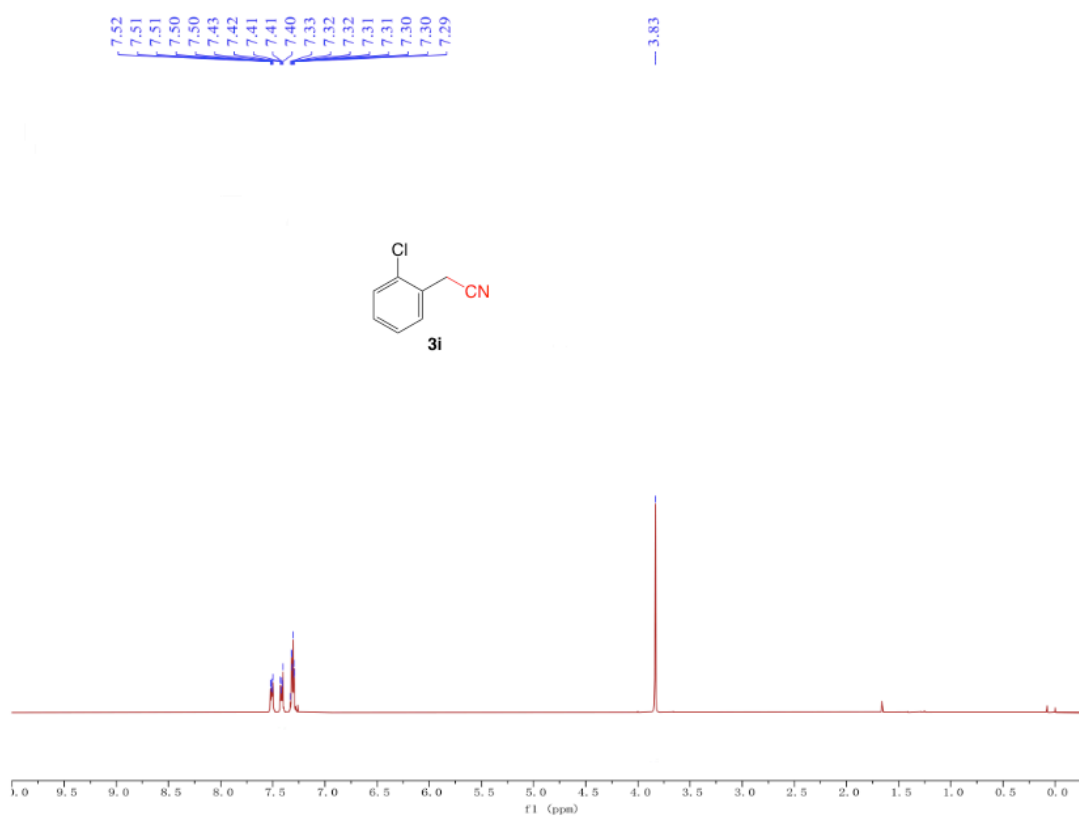


Figure S9b: ^{13}C NMR (100 MHz, CDCl_3) of 2-(2-Chlorophenyl)acetonitrile (**3i**)

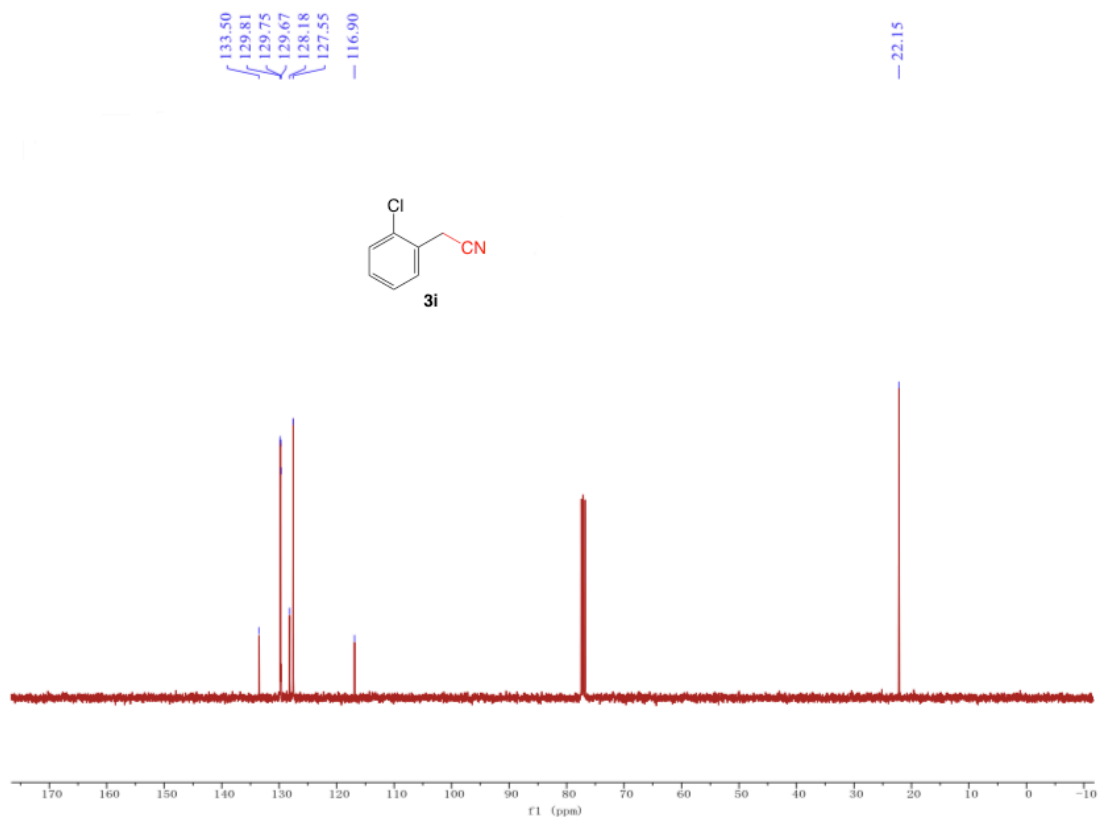


Figure S10a: ^1H NMR (400 MHz, CDCl_3) of 2-(2-Bromophenyl)acetonitrile (**3j**)

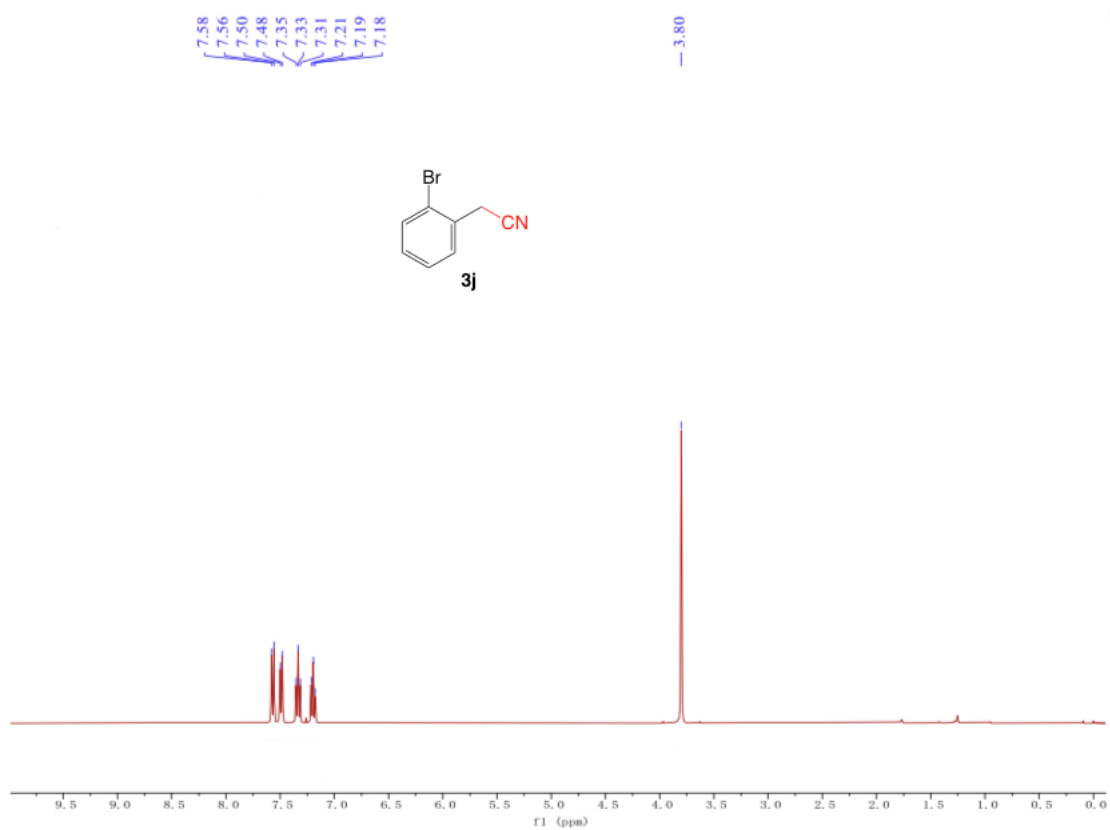


Figure S10b: ^{13}C NMR (100 MHz, CDCl_3) of 2-(2-Bromophenyl)acetonitrile (**3j**)

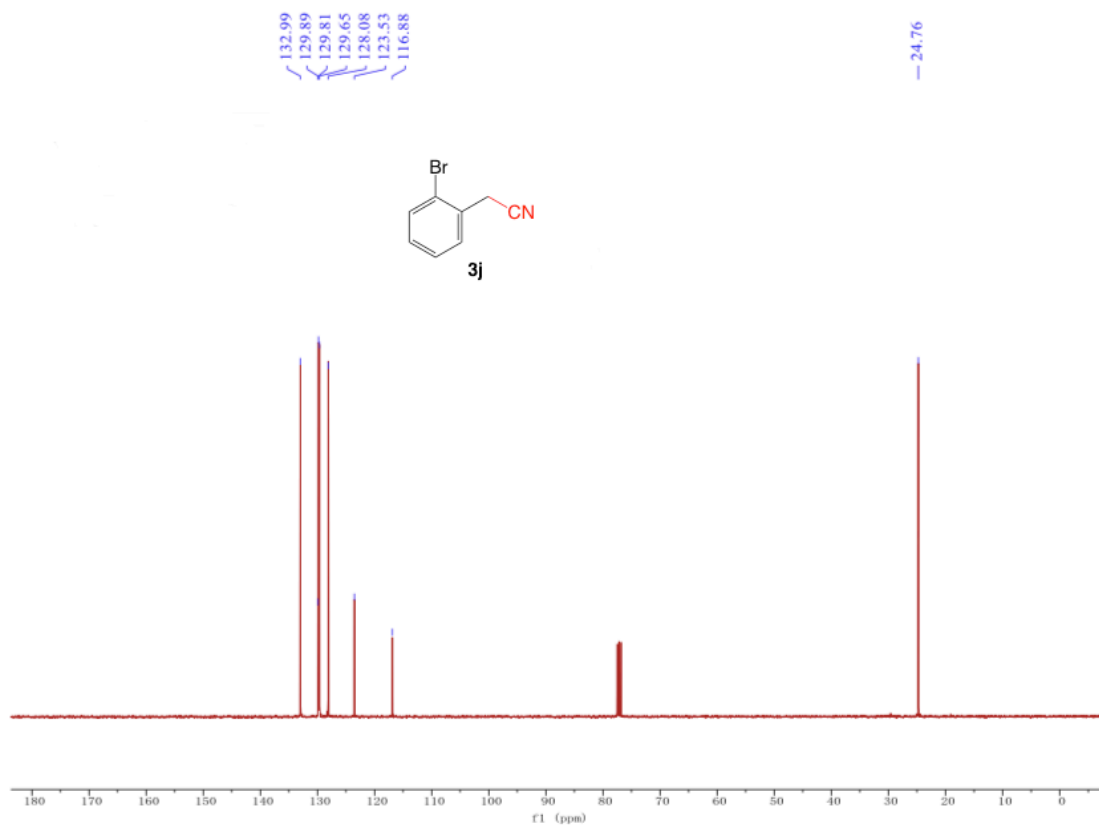


Figure S11a: ^1H NMR (400 MHz, CDCl_3) of 2-(2-Nitrophenyl)acetonitrile (**3k**)

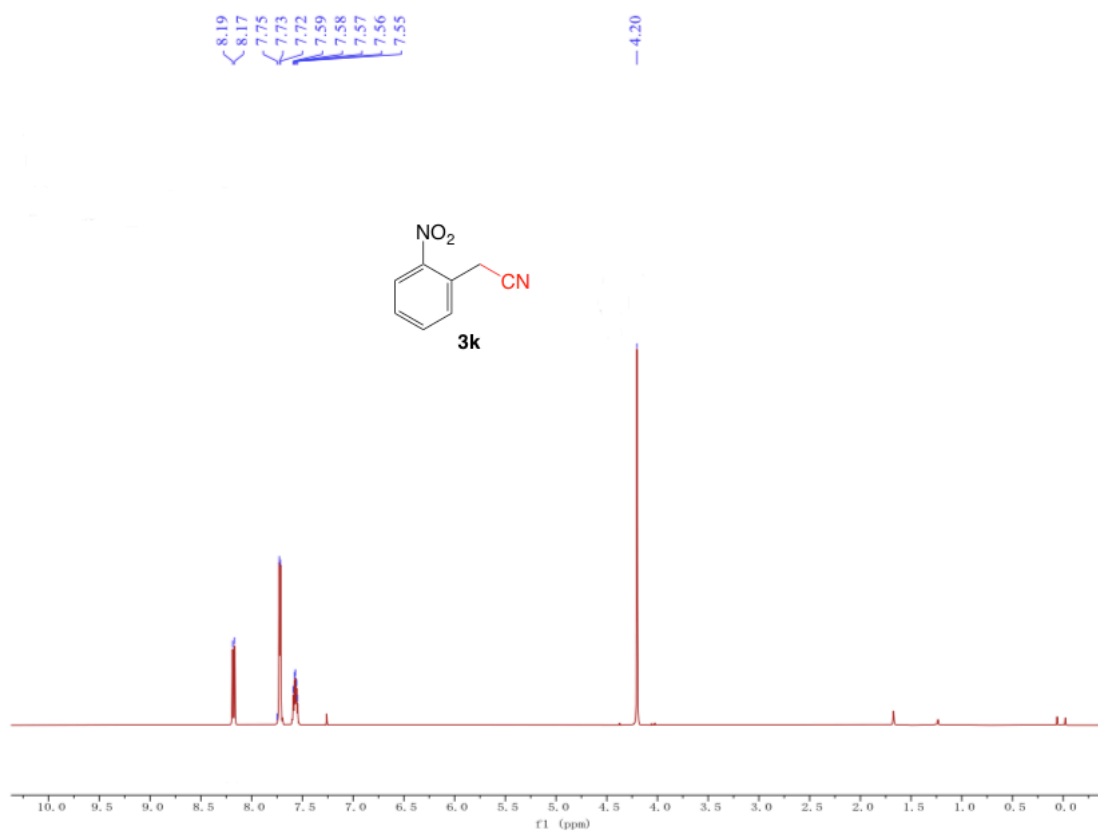


Figure S11b: ^{13}C NMR (100 MHz, CDCl_3) of 2-(2-Nitrophenyl)acetonitrile (**3k**)

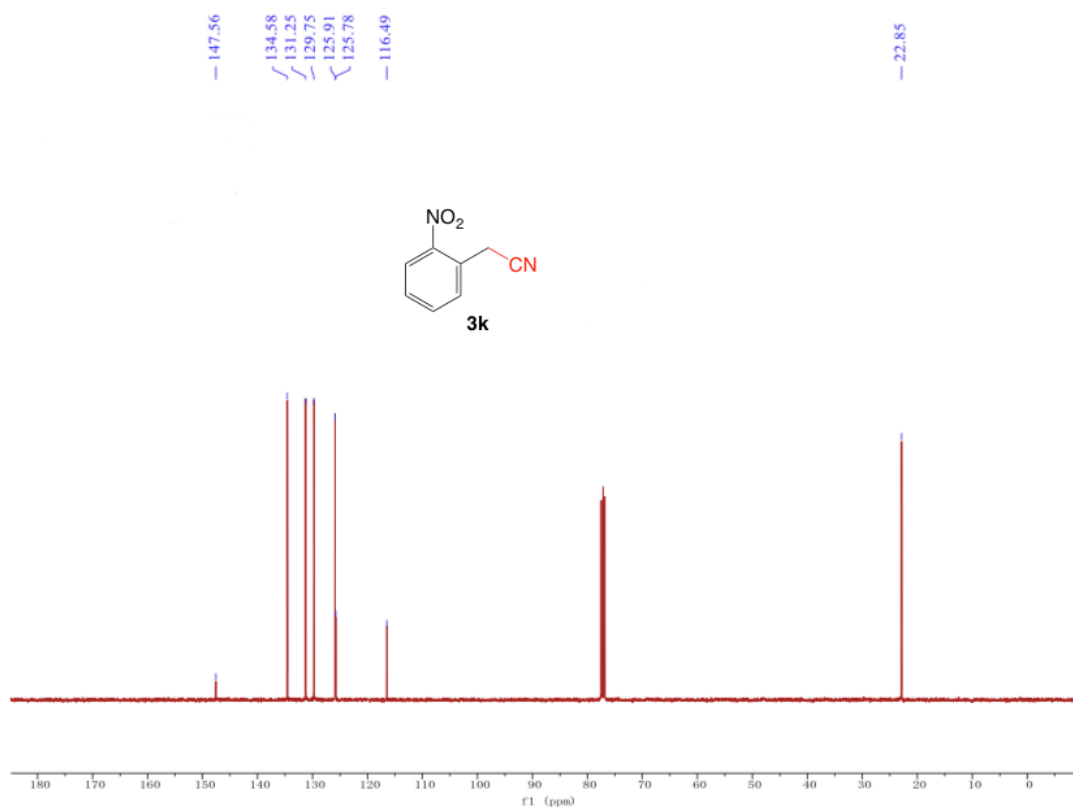


Figure S12a: ^1H NMR (400 MHz, CDCl_3) of 2-(3-Nitrophenyl)propanenitrile (**3I**)

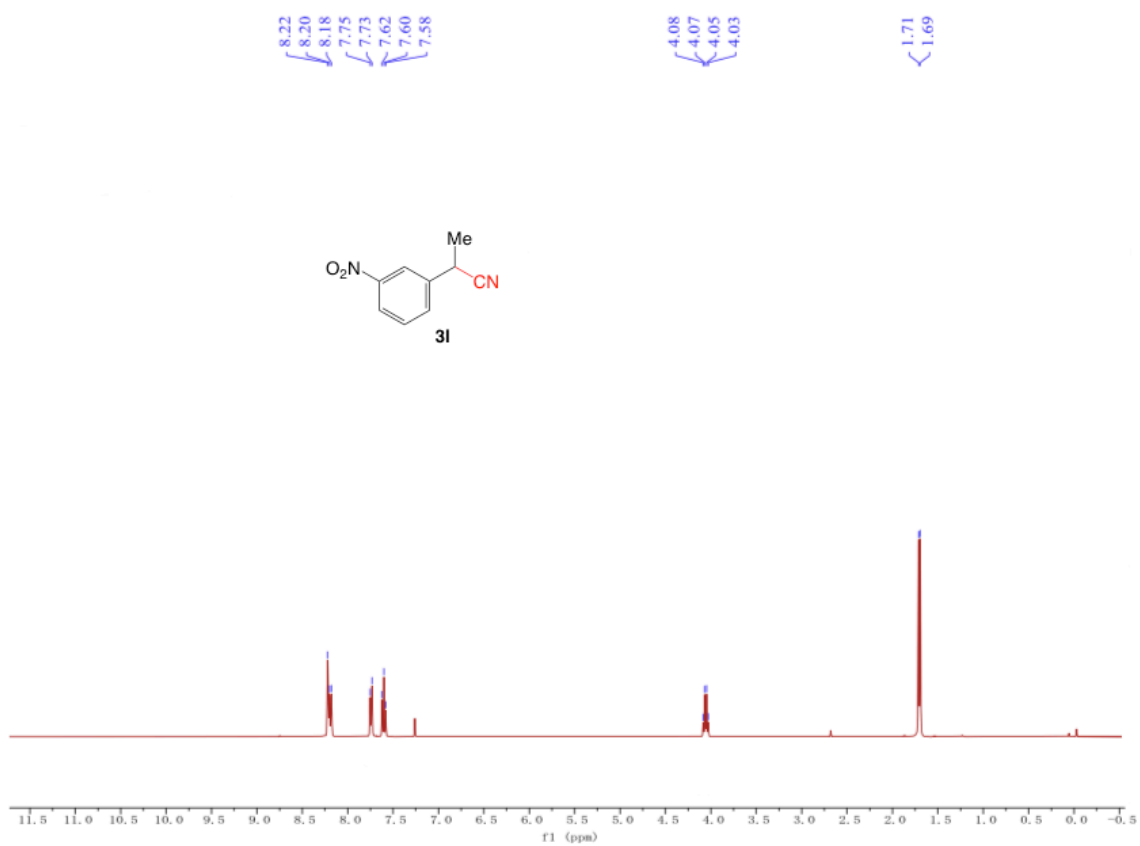


Figure S12b: ^{13}C NMR (100 MHz, CDCl_3) of 2-(3-Nitrophenyl)propanenitrile (**3I**)

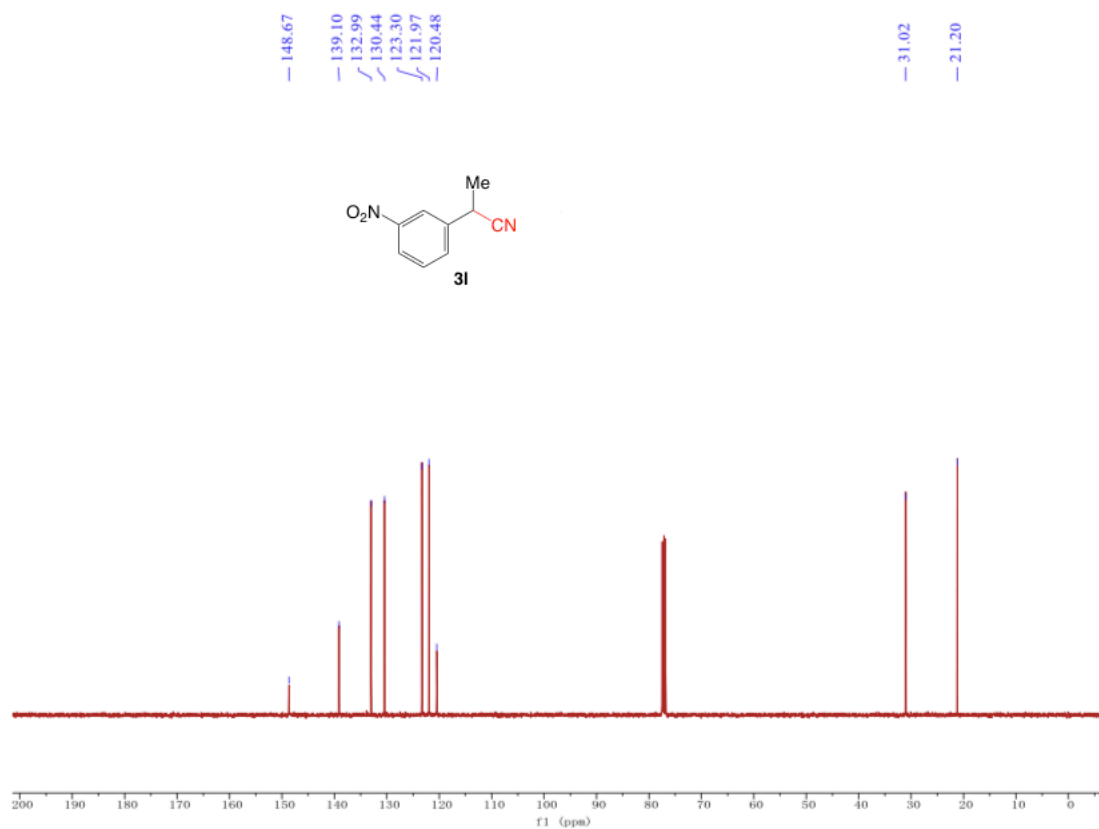


Figure S13a: ^1H NMR (400 MHz, CDCl_3) of Methyl 4-(1-cyanoethyl)benzoate (**3m**)

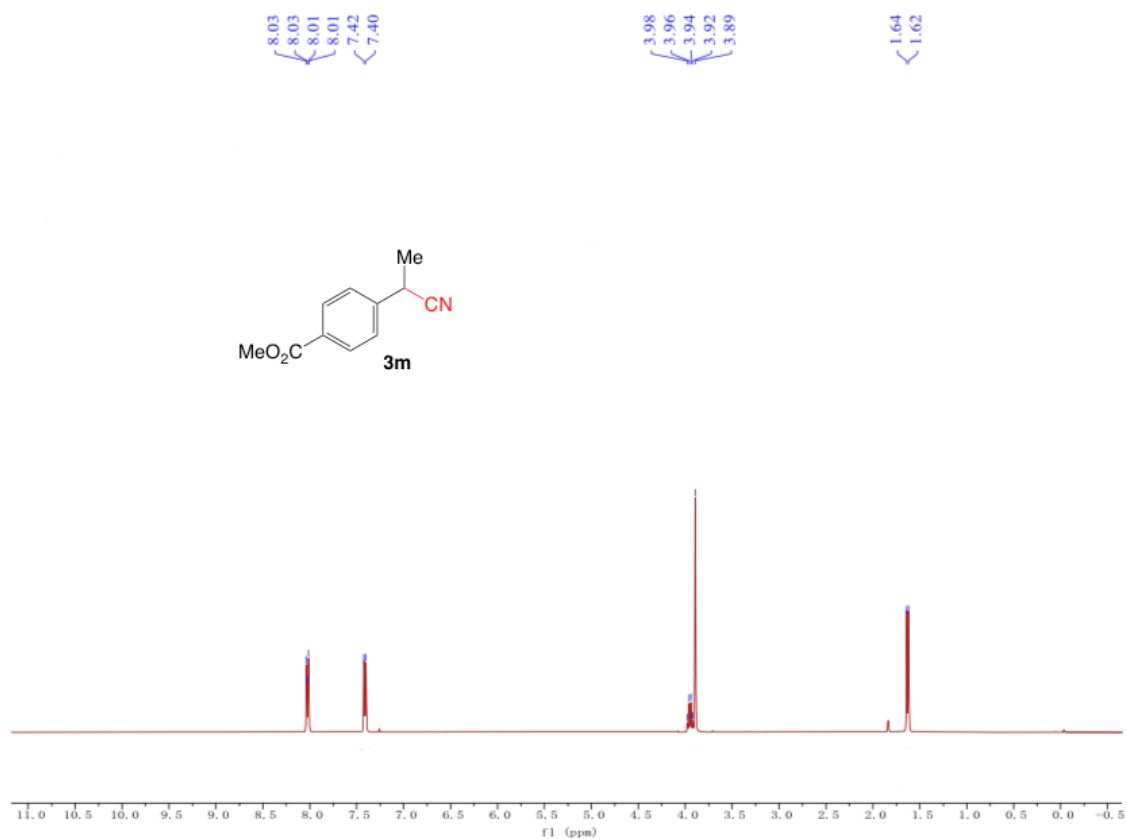


Figure S13b: ^{13}C NMR (100 MHz, CDCl_3) of Methyl 4-(1-cyanoethyl)benzoate (**3m**)

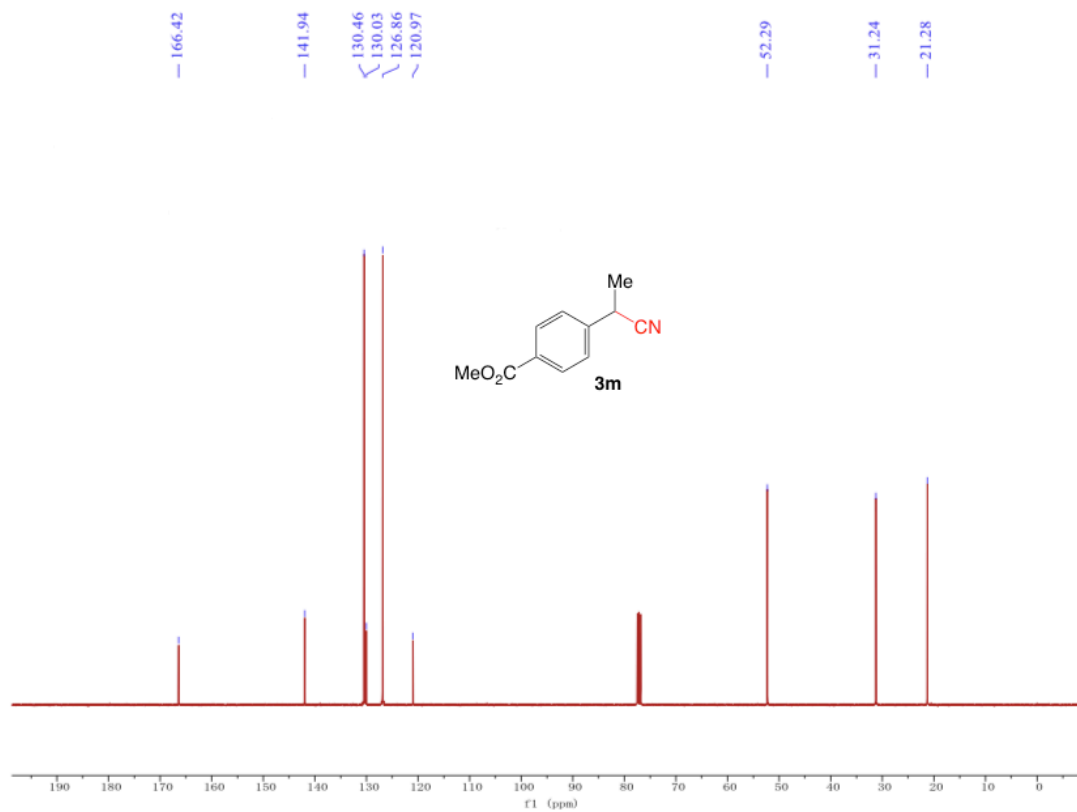


Figure S14a: ^1H NMR (400 MHz, CDCl_3) of 2-(4-Nitrophenyl)propanenitrile (**3n**)

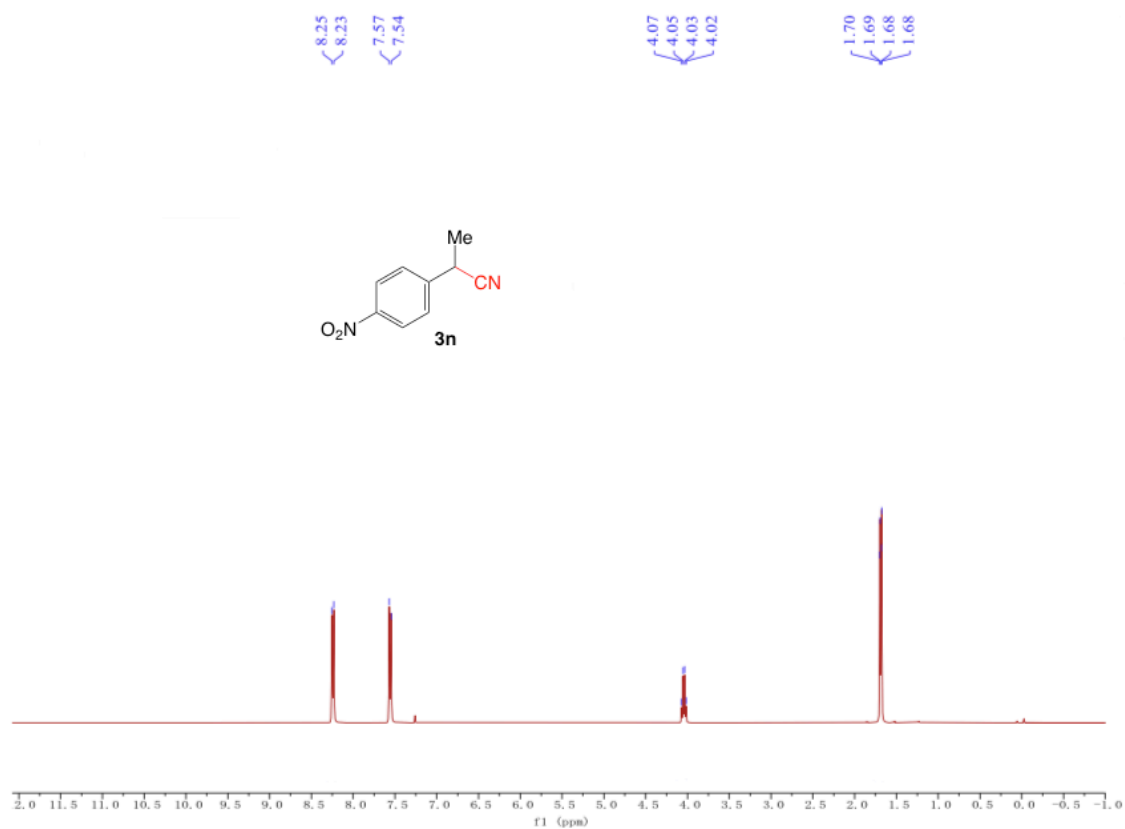


Figure S14b: ^{13}C NMR (100 MHz, CDCl_3) of 2-(4-Nitrophenyl)propanenitrile (**3n**)

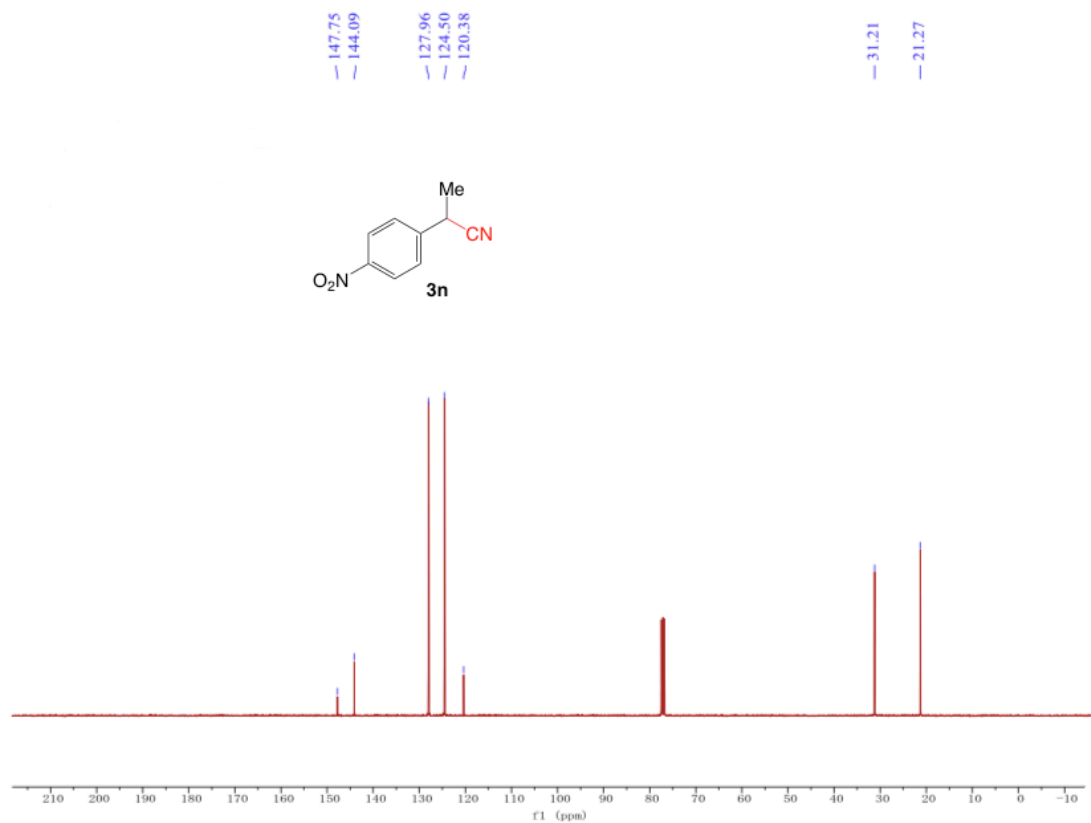


Figure S15a: ^1H NMR (400 MHz, CDCl_3) of 2-(2,6-dichlorophenyl)acetonitrile (**3o**)

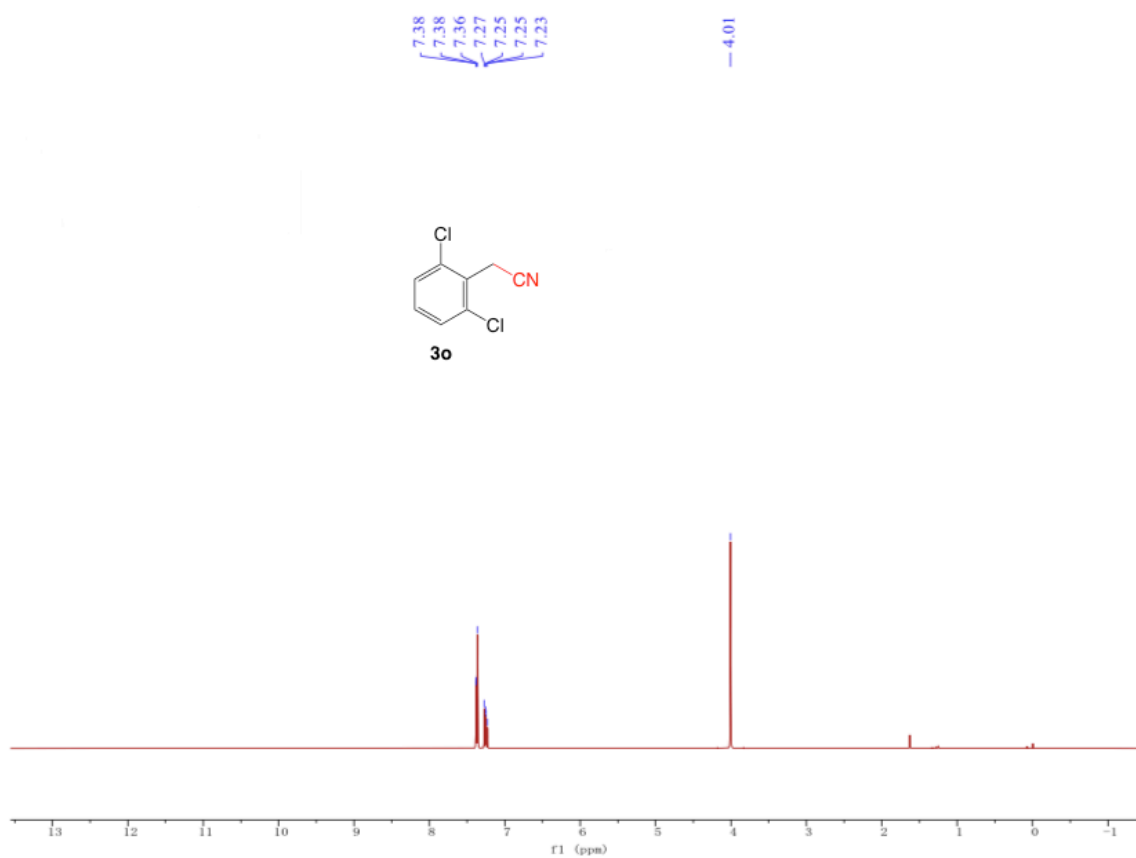


Figure S15b: ^{13}C NMR (100 MHz, CDCl_3) of 2-(2,6-dichlorophenyl)acetonitrile (**3o**)

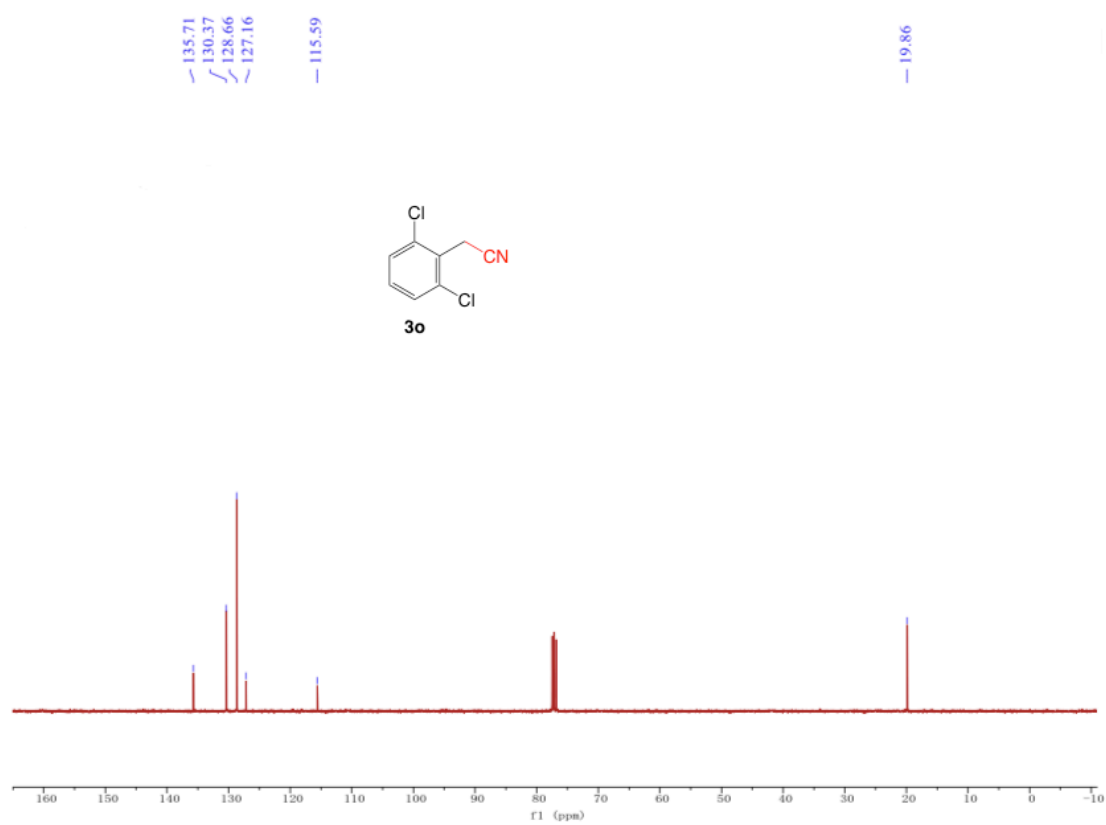


Figure S16a: ^1H NMR (400 MHz, CDCl_3) of 2-(5-bromo-2-methoxyphenyl)acetonitrile (**3p**)

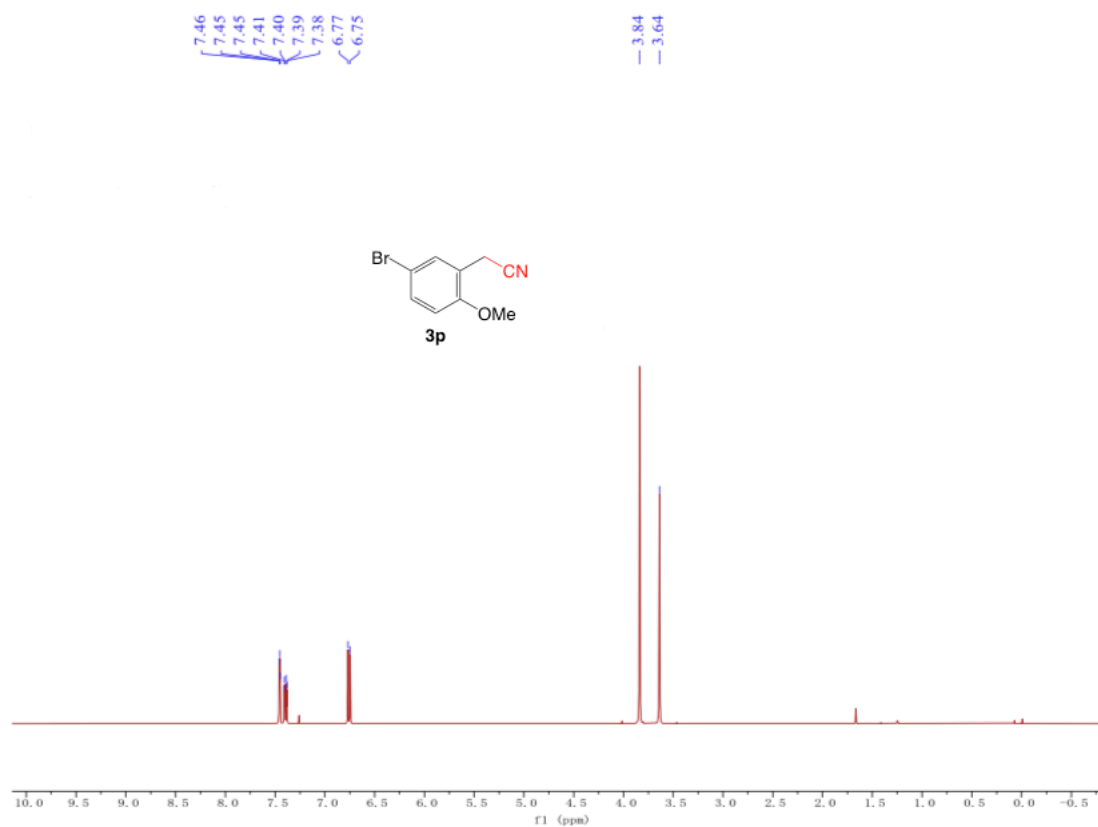


Figure S16b: ^{13}C NMR (100 MHz, CDCl_3) of 2-(5-bromo-2-methoxyphenyl)acetonitrile (**3p**)

