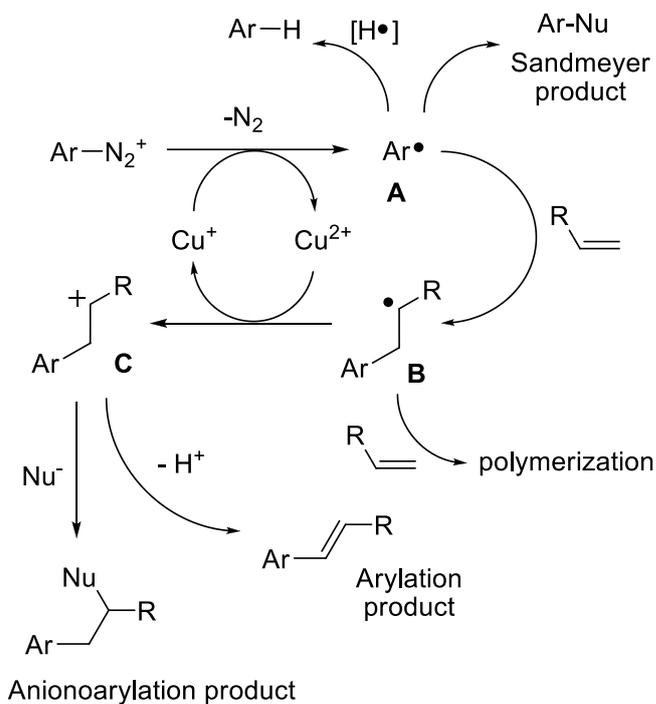


**Photoredox-copper catalyzed Meerwein cyanoarylation of styrenes**

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**Scheme S1**

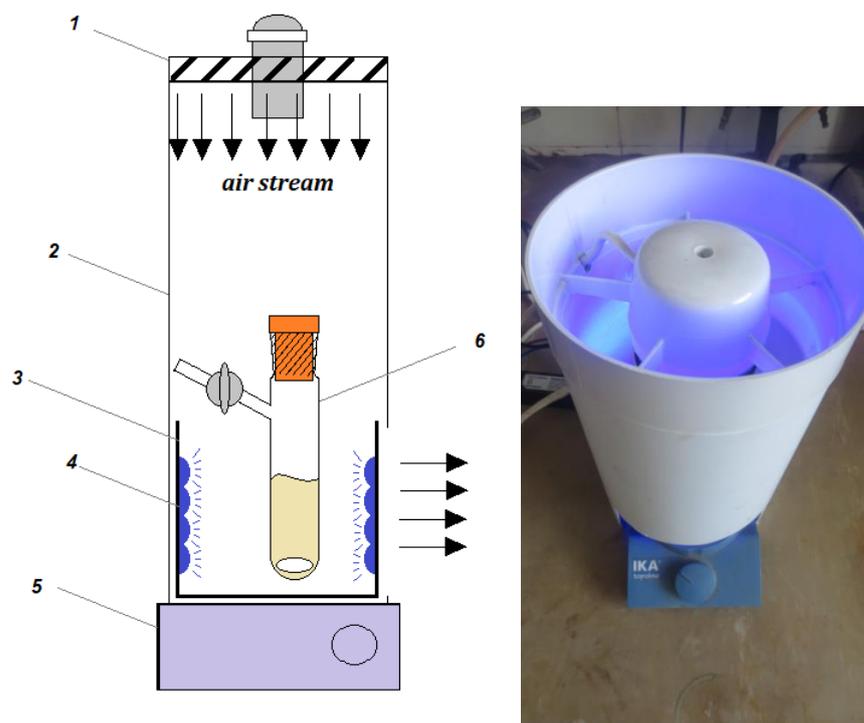
**General mechanism of the Meerwein reaction.** The precise mechanism of the Meerwein reaction has not yet been established, a plausible mechanism (Scheme S1) suggests the reduction of diazonium salt into corresponding aryl radical **A** which undergoes addition to alkene forming dialkyl radical **B**. As the reduction of the arenediazonium salt demands the presence of Cu(I) salts and the Meerwein reaction employs Cu(II) salts,<sup>[S1]</sup> one can suppose that the Cu<sup>I</sup> concentration is governed by the Cu<sup>II</sup>↔Cu<sup>I</sup> equilibrium ( $E = -0.16$  eV). The radical **A** can participate in the Sandmeyer reaction or react with the olefin, thus the Meerwein synthesis demands the control over the aryl radical concentration, olefin excess and its ability to form enough stable radical **B** without tendency to polymerize. Further oxidation of radical **B** with Cu<sup>II</sup> gives carbocation **C** which can either eliminate β-proton to produce the arylation product of the initial olefin or react with a nucleophile giving the difunctionalization product. Due to such competition of two routes the researchers had to precisely select the reagents and adjust the reaction conditions.<sup>[S1,S2]</sup>

## General materials and methods

Unless otherwise noted, all chemicals and starting materials were obtained commercially from Alfa Aesar and Aldrich-Sigma Co. and used without further purification. Aryl diazonium salts were prepared from the corresponding anilines as described<sup>[S3]</sup> and purified by precipitation with diethyl ether from acetone solution. *Caution! Although no problems were experienced, diazonium salts are potentially explosive and should be manipulated with care and used only in very small quantities.* Solvents CH<sub>2</sub>Cl<sub>2</sub> and MeCN were distilled over CaH<sub>2</sub>. All the solvents were degassed using “freeze-pump-thaw” technique in three cycles before use in reactions. Preparative column chromatography was carried out using Silica gel 60 (40×63 μm) from Merck Co.

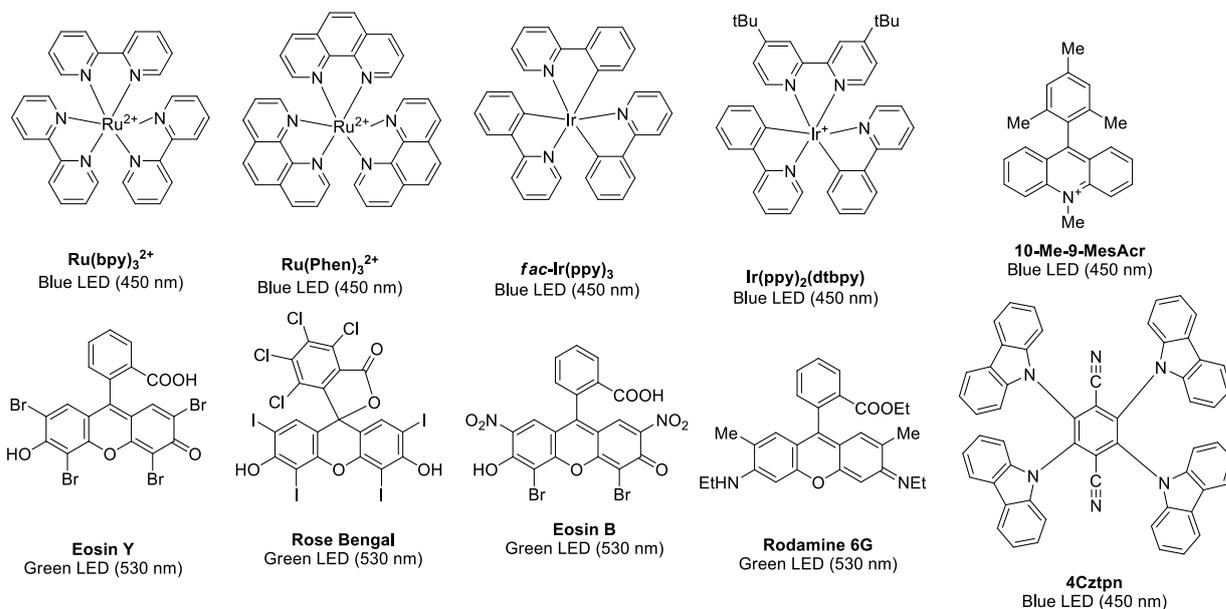
<sup>1</sup>H and <sup>13</sup>C NMR spectra were registered with Bruker Avance-400 spectrometer in CDCl<sub>3</sub>. HRMS ESI mass-spectra were obtained on TripleTOF 5600+ mass-spectrometer (AB Sciex, Canada) with TurboIon Spray ionization source in positive ion mode. FTIR spectra were registered on Nicolet iS 5.

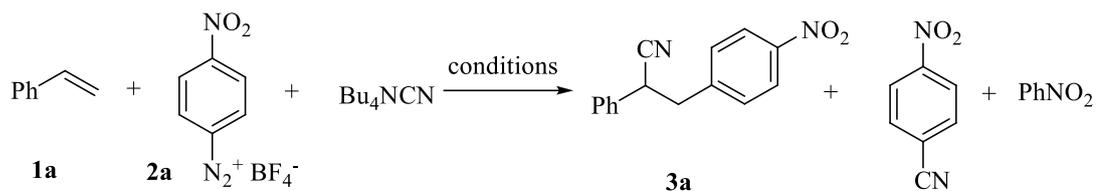
**Cyanoarylation of styrenes with diazonium salts (general procedure).** A Schlenk tube equipped with magnetic stirrer was charged with Eosin Y (10 mg, 0.015 mmol) and Cu(OAc)<sub>2</sub>·H<sub>2</sub>O (6 mg, 0.03 mmol), capped with a rubber septum and filled with dry argon, and deaerated MeCN (1 ml) was syringed. Styrene (1.2 mmol, 4 equiv.) and Bu<sub>4</sub>NCN (96 mg, 0.36 mmol, freshly prepared solution in 1 ml MeCN) were consequently syringed. The mixture was cooled to 0°C in ice bath, and freshly prepared solution of arenediazonium salt (0.3 mmol) in deaerated MeCN (1 ml) was added drop by drop within 1 minute. The vessel was then placed in the photoreactor (Figure S1), and the mixture was stirred at room temperature under green light irradiation for 8 h. The mixture was concentrated under reduced pressure. The residue was taken up in dichloromethane and subjected to column chromatography on silica gel using petroleum ether/dichloromethane mixtures as eluents.



**Figure S1.** Photoreactor setup. **1** – Electric fan (24 W, 185 m<sup>3</sup>/h); **2** – plastic tube (d = 125 mm, l = 500 mm); **3** – aluminum cup (d = 110 mm); **4** – LED strip (LP SMD 5050, 300 Led, IP65, 12V, 14 W, green (530 nm) or blue (455 nm)); **5** – Magnetic stirrer (IKA Topolino); **6** – Schlenk tube capped with a rubber septum.

### The photocatalysts used in the study



**Table S1.** Photoredox-copper catalyzed Meerwein cyanoarylation of styrenes

Entry <sup>a</sup>	Catalyst	Photocatalyst (mol%)	Solvent	Yields, %	
				<b>3a</b>	4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CN
1	-	Ru(bpy) <sub>3</sub> <sup>2+</sup> (2) <sup>b</sup>	DMSO	0	0
2	-	Ru(bpy) <sub>3</sub> <sup>2+</sup> (2) <sup>b</sup>	DMSO	0	0
3	-	Ru(bpy) <sub>3</sub> <sup>2+</sup> (2) <sup>b</sup>	MeCN	0	0
4	-	Ir(ppy) <sub>3</sub> (2) <sup>b</sup>	MeCN	0	0
5	-	Eosin Y (5) <sup>c</sup>	MeCN	0	0
<b>6</b>	<b>Cu(OAc)<sub>2</sub></b>	<b>Ru(bpy)<sub>3</sub><sup>2+</sup> (2)<sup>b</sup></b>	<b>MeCN</b>	<b>57</b>	<b>0</b>
7	CuCN	Ru(bpy) <sub>3</sub> <sup>2+</sup> (2) <sup>b</sup>	MeCN	29	15
8	Cu(MeCN) <sub>4</sub> BF <sub>4</sub>	Ru(bpy) <sub>3</sub> <sup>2+</sup> (2) <sup>b</sup>	MeCN	45	20
10	Cu(OAc) <sub>2</sub>	Ir(ppy) <sub>3</sub> (2) <sup>b</sup>	MeCN	41	6
11	Cu(OAc) <sub>2</sub>	Ir(ppy) <sub>2</sub> (dtbbpy) (2) <sup>b</sup>	MeCN	48	7
12	Cu(OAc) <sub>2</sub>	Ru(Phen) <sub>3</sub> (2) <sup>b</sup>	MeCN	31	4
<b>13</b>	<b>Cu(OAc)<sub>2</sub></b>	<b>Eosin Y (5)<sup>c</sup></b>	<b>MeCN</b>	<b>65</b>	<b>5</b>
14	Cu(OAc) <sub>2</sub>	Rodamine 6G (5) <sup>c</sup>	MeCN	45	8
15	Cu(OAc) <sub>2</sub>	Rose Bengal (5) <sup>c</sup>	MeCN	37	9
16	Cu(OAc) <sub>2</sub>	Eosin B (5) <sup>c</sup>	MeCN	41	8
17	Cu(OAc) <sub>2</sub>	4Cztpn (5) <sup>b</sup>	MeCN	42	12
18	Cu(OAc) <sub>2</sub>	10-Me-9-MesAcr (5) <sup>b</sup>	MeCN	43	10
19	Cu(OAc) <sub>2</sub>	Eosin Y (5) <sup>c</sup>	DMSO	15	5
20	Cu(OAc) <sub>2</sub>	Eosin Y (5) <sup>c</sup>	DMF	17	8
21	Cu(OAc) <sub>2</sub>	Eosin Y (5) <sup>c</sup>	dioxane	12	6
22	Cu(OAc) <sub>2</sub>	Eosin Y (5) <sup>c</sup>	acetone	36	8

<sup>a</sup>Reaction conditions: 0.3 mmol of **2a**, 1.2 mmol of **1a**, 0.36 mmol of  $\text{Bu}_4\text{NCN}$ , 10% of Cu catalyst in 3 ml of MeCN, 8 h, r.t. <sup>b</sup>The reaction was performed under irradiation (450 nm). <sup>c</sup> The reaction was performed under irradiation (530 nm).

## Characterization of the compounds

**3-(4-Nitrophenyl)-2-phenylpropanenitrile (3a)** <sup>[S4]</sup> was prepared according to the general procedure from 4-nitrophenyldiazonium tetrafluoroborate **2a** (71 mg, 0.3 mmol) and styrene **1a** (125 mg, 137  $\mu$ L, 1.2 mmol) and Bu<sub>4</sub>NCN (96 mg, 0.36 mmol). Eluent: petroleum ether-CH<sub>2</sub>Cl<sub>2</sub>, 1:1, 49 mg (65%), yellowish crystalline powder, mp 134-135°C. IR (cm<sup>-1</sup>): 2956 (w), 2920 (m), 2851 (w), 2242 (w), 1597 (m), 1509 (vs), 1489 (s), 1453 (s), 1339 (vs), 1320 (s), 1313 (s), 1285 (m), 1261 (m), 1243 (m), 1178 (m), 1154 (m), 1103 (s), 1075 (m), 1031 (m), 1013 (m), 920 (w), 883 (w), 856 (s), 826 (w), 804 (s), 757 (s), 743 (s), 696 (s), 655 (m), 619 (w). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 3.29 (d, *J* = 7.3 Hz, 2H), 4.09 (t, *J* = 7.3 Hz, 1H), 7.20-7.32 (m, 4H), 7.34-7.42 (m, 3H), 8.15 (d, *J* = 8.6 Hz, 2H). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta$  = 38.9 (1C, CH<sub>2</sub>), 41.5 (1C, CHCN), 119.6 (1C, CN), 123.7 (2C, CH), 127.4 (2C, CH), 128.6 (1C, CH), 129.2 (2C, CH), 130.3 (2C, CH), 134.0 (1C), 143.3 (1C), 147.3 (1C, C-NO<sub>2</sub>). HRMS (ESI): *m/z* [M+Na]<sup>+</sup> calcd for C<sub>15</sub>H<sub>12</sub>N<sub>2</sub>NaO<sub>2</sub>: 275.0796; found: 275.0789

**2,3-Diphenylpropanenitrile (3b)** <sup>[S5]</sup> was prepared according to the general procedure from phenyldiazonium tetrafluoroborate **2b** (58 mg, 0.3 mmol) and styrene **1a** (125 mg, 137  $\mu$ L, 1.2 mmol) and Bu<sub>4</sub>NCN (96 mg, 0.36 mmol). Eluent: petroleum ether-CH<sub>2</sub>Cl<sub>2</sub>, 4:1, 20 mg (32%), yellowish crystalline powder, mp 56-57°C. IR (cm<sup>-1</sup>): 3107 (s), 3087 (s), 3064 (m), 3031 (m), 3012 (s), 2928 (s), 2861 (s), 2241 (s), 1953 (vw), 1879 (vw), 1810 (vw), 1772 (vw), 1750 (vw), 1601 (m), 1520 (s), 1497 (s), 1455 (vs), 1344 (s), 1266 (s), 1207 (s), 1182 (s), 1157 (s), 1074 (s), 1030 (s), 913 (s), 755 (m), 738 (m), 698 (s). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 3.13 (dd, *J* = 13.3 Hz, *J* = 6.5 Hz, 1H), 3.13 (dd, *J* = 13.3 Hz, *J* = 8.5 Hz, 1H), 4.00 (dd, *J* = 8.5 Hz, *J* = 6.5 Hz, 1H), 7.12-7.15 (m, 2H), 7.25-7.38 (m, 8H). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta$  = 39.8 (1C, CH<sub>2</sub>), 42.2 (1C, CHCN), 120.3 (1C, CN), 127.4 (1C, CH), 127.5 (2C, CH), 128.2 (1C, CH), 128.6 (2C, CH), 129.0 (2C, CH), 129.2 (2C, CH), 135.2 (1C), 136.2 (1C). HRMS (ESI): *m/z* [M+Na]<sup>+</sup> calcd for C<sub>15</sub>H<sub>13</sub>NNa: 230.0946 ; found: 230.0942.

**3-(4-Bromophenyl)-2-phenylpropanenitrile (3c)** <sup>[S5]</sup> was prepared according to the general procedure from 4-bromophenyldiazonium tetrafluoroborate **2c** (81 mg, 0.3 mmol) and styrene **1a** (125 mg, 137  $\mu$ L, 1.2 mmol) and Bu<sub>4</sub>NCN (96 mg, 0.36 mmol). Eluent: petroleum ether-CH<sub>2</sub>Cl<sub>2</sub>, 2:1, 32 mg (37%), orange crystalline powder, mp 108-110°C. IR (cm<sup>-1</sup>): 3058 (vw), 3029 (vw), 2934 (vw), 2862 (vw), 2242 (vw), 1906 (vw), 1880 (vw), 1671 (vw), 1598 (vw), 1585 (vw), 1485 (m), 1454 (w), 1443 (w), 1403 (w), 1315 (vw), 1265 (w), 1241 (vw), 1201 (vw), 1177 (vw), 1154 (vw), 1099 (w), 1067 (w), 1030 (vw), 1010 (m), 914 (w), 876 (vw), 848 (w), 839 (w),

832 (w), 798 (m), 783 (m), 753 (m), 738 (s), 695 (vs), 669 (m), 652 (m).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 3.19 (dd,  $J$  = 13.3 Hz,  $J$  = 6.7 Hz, 1H), 3.14 (dd,  $J$  = 13.3 Hz,  $J$  = 7.7 Hz, 1H), 4.09 (dd,  $J$  = 7.7 Hz,  $J$  = 6.7 Hz, 1H), 6.97 (d,  $J$  = 8.3 Hz, 2H), 7.20-7.24 (m, 2H), 7.30-7.37 (m, 3H), 7.40 (d,  $J$  = 8.3 Hz, 2H).  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 39.4 (1C,  $\text{CH}_2$ ), 41.4 (1C,  $\underline{\text{CHCN}}$ ), 120.0 (1C, CN), 121.5 (1C, C-Br), 127.4 (2C, CH), 128.3 (1C, CH), 129.1 (2C, CH), 130.9 (2C, CH), 131.7 (2C, CH), 134.7 (1C), 135.0 (1C). HRMS (ESI):  $m/z$   $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{15}\text{H}_{12}\text{BrNNa}$ : 308.0051; found: 308.0046.

**3-(4-Chlorophenyl)-2-phenylpropanenitrile (3d)** <sup>[S5]</sup> was prepared according to the general procedure from 4-chlorophenyldiazonium tetrafluoroborate **2d** (68 mg, 0.3 mmol) and styrene **1a** (125 mg, 137  $\mu\text{L}$ , 1.2 mmol) and  $\text{Bu}_4\text{NCN}$  (96 mg, 0.36 mmol). Eluent: petroleum ether- $\text{CH}_2\text{Cl}_2$ , 4:1, 36 mg (50%), orange crystalline powder, mp 99-100°C. IR ( $\text{cm}^{-1}$ ): 3059 (w), 3030 (w), 2936 (w), 2242 (w), 1917 (vw), 1880 (vw), 1672 (w), 1598 (w), 1589 (vw), 1491 (m), 1453 (w), 1444 (w), 1409 (w), 1315 (w), 1265 (w), 1240 (w), 1210 (w), 1176 (vw), 1152 (vw), 1087 (m), 1076 (w), 1014 (m), 913 (w), 839 (m), 803 (m), 786 (m), 754 (m), 737 (s), 696 (vs), 665 (m), 622 (w).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 3.12 (dd,  $J$  = 13.5 Hz,  $J$  = 6.5 Hz, 1H), 3.17 (dd,  $J$  = 13.5 Hz,  $J$  = 7.5 Hz, 1H), 4.00 (t,  $J$  = 7.0 Hz, 1H), 7.05 (d,  $J$  = 8.3 Hz, 2H), 7.23-7.28 (m, 4H), 7.32-7.39 (m, 3H).  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 39.5 (1C,  $\text{CH}_2$ ), 41.4 (1C,  $\underline{\text{CHCN}}$ ), 120.0 (1C, CN), 127.4 (2C, CH), 128.3 (1C, CH), 128.7 (2C, CH), 129.1 (2C, CH), 130.6 (2C, CH), 133.7 (1C, C-Cl), 134.5 (1C), 134.7 (1C). HRMS (ESI):  $m/z$   $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{15}\text{H}_{12}\text{ClNNa}$ : 265.0556 ; found: 265.0550.

**3-(4-Fluorophenyl)-2-phenylpropanenitrile (3e)** <sup>[S4]</sup> was prepared according to the general procedure from 4-fluorophenyldiazonium tetrafluoroborate **2e** (63 mg, 0.3 mmol) and styrene **1a** (125 mg, 137  $\mu\text{L}$ , 1.2 mmol) and  $\text{Bu}_4\text{NCN}$  (96 mg, 0.36 mmol). Eluent: petroleum ether- $\text{CH}_2\text{Cl}_2$ , 4:1, 31 mg (46%), yellowish crystalline powder, mp 88-90°C. IR ( $\text{cm}^{-1}$ ): 3061 (vw), 3036 (vw), 3006 (vw), 2959 (vw), 2934 (vw), 2862 (vw), 2242 (w), 1957 (vw), 1898 (vw), 1667 (vw), 1599 (w), 1508 (s), 1455 (m), 1445 (w), 1417 (w), 1218 (m), 1157 (m), 1093 (w), 1078 (w), 1016 (w), 978 (w), 913 (w), 876 (w), 840 (m), 823 (m), 794 (m), 767 (m), 743 (s), 697 (vs), 637 (w).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 3.13 (dd,  $J$  = 13.7 Hz,  $J$  = 6.7 Hz, 1H), 3.18 (dd,  $J$  = 13.7 Hz,  $J$  = 7.5 Hz, 1H), 3.99 (t,  $J$  = 7.1 Hz, 1H), 6.98 (t,  $J$  = 8.7 Hz, 2H), 7.09 (dd,  $J$  = 8.7 Hz,  $J$  = 5.3 Hz, 2H), 7.25 (dd,  $J$  = 7.6 Hz,  $J$  = 1.7 Hz, 2H), 7.32-7.39 (m, 3H).  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 39.8 (1C,  $\text{CH}_2$ ), 41.3 (1C,  $\underline{\text{CHCN}}$ ), 115.5 (d,  $^3J_{\text{C-F}}$  = 21.6 Hz, 2C, CH), 120.2 (1C, CN), 127.4 (2C, CH), 128.3 (1C, CH), 129.0 (2C, CH), 130.8 (d,  $^4J_{\text{C-F}}$  = 7.5 Hz, 2C, CH), 131.8 (1C), 134.8 (1C), 162.1 (1C d,  $^2J_{\text{C-F}}$  = 246.3 Hz).  $^{19}\text{F}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = -115.1 (tt, 1 F,  $^3J_{\text{H-F}}$  = 8.7

Hz,  $^4J_{H-F} = 5.4$  Hz). HRMS (ESI):  $m/z$   $[M+Na]^+$  calcd for  $C_{15}H_{12}FNNa$  : 248.08515; found: 248.0848.

**3-(3-Nitrophenyl)-2-phenylpropanenitrile (3f)** was prepared according to the general procedure from 3-nitrophenyldiazonium tetrafluoroborate **2f** (71 mg, 0.3 mmol) and styrene **1a** (125 mg, 137  $\mu$ L, 1.2 mmol) and  $Bu_4NCN$  (96 mg, 0.36 mmol). Eluent: petroleum ether- $CH_2Cl_2$ , 1:1, 40 mg (53%), beige crystalline powder, mp 117-119°C. IR ( $cm^{-1}$ ): 3389 (vw), 3074 (vw), 2923 (vw), 2236 (vw), 1734 (vw), 1719 (vw), 1684 (vw), 1617 (vw), 1599 (vw), 1582 (vw), 1526 (s), 1497 (w), 1480 (w), 1453 (w), 1349 (s), 1265 (m), 1237 (w), 1206 (w), 1168 (vw), 1160 (vw), 1099 (w), 1076 (w), 1029 (vw), 1002 (vw), 976 (vw), 931 (vw), 919 (vw), 902 (w), 857 (vw), 804 (w), 760 (w), 731 (vs), 701 (s), 687 (s), 671 (s), 618 (w).  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  = 3.29 (d,  $J = 7.3$  Hz, 2H), 4.10 (d,  $J = 7.3$  Hz, 1H), 7.26-7.28 (m, 2H), 7.35-7.40 (m, 3H), 7.50 (d,  $J = 5.2$  Hz, 2H), 7.96 (s, 1H), 8.12-8.17 (m, 1H).  $^{13}C$  NMR (100.6 MHz,  $CDCl_3$ ):  $\delta$  = 39.2 (1C,  $CH_2$ ), 41.5 (1C,  $\underline{C}HCN$ ), 119.6 (1C, CN), 122.6 (1C, CH), 124.1 (1C, CH), 127.4 (2C, CH), 128.6 (1C, CH), 129.2 (2C, CH), 129.6 (1C, CH), 134.1 (1C), 135.5 (1C, CH), 137.9 (1C), 148.2 (1C, C- $NO_2$ ). HRMS (ESI):  $m/z$   $[M+Na]^+$  calcd for  $C_{15}H_{12}N_2NaO_2$ : 275.0796; found: 275.0794.

**3-(3-Bromophenyl)-2-phenylpropanenitrile (3g)** was prepared according to the general procedure from 3-bromophenyldiazonium tetrafluoroborate **2g** (81 mg, 0.3 mmol) and styrene **1a** (125 mg, 137  $\mu$ L, 1.2 mmol) and  $Bu_4NCN$  (96 mg, 0.36 mmol). Eluent: petroleum ether- $CH_2Cl_2$ , 2:1, 39.5 mg (46%), yellowish oil. IR ( $cm^{-1}$ ): 3062 (w), 3032 (w), 2932 (vw), 2241 (w), 1949 (vw), 1875 (vw), 1804 (vw), 1718 (vw), 1676 (vw), 1597 (m), 1568 (m), 1496 (m), 1474 (m), 1454 (m), 1427 (m), 1340 (w), 1301 (w), 1265 (w), 1204 (m), 1169 (w), 1085 (w), 1072 (m), 1030 (w), 997 (m), 911 (w), 889 (w), 852 (w), 836 (w), 774 (m), 753 (s), 738 (m), 706 (m), 695 (vs), 670 (m).  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  = 3.09 (dd,  $J = 13.4$  Hz,  $J = 6.5$  Hz, 1H), 3.14 (dd,  $J = 13.4$  Hz,  $J = 8.2$  Hz, 1H), 3.98 (dd,  $J = 8.2$  Hz,  $J = 6.5$  Hz, 1H), 7.06 (d,  $J = 7.8$  Hz, 1H), 7.16 (d,  $J = 7.8$  Hz, 1H), 7.21-7.25 (m, 3H), 7.33-7.42 (m, 4H).  $^{13}C$  NMR (100.6 MHz,  $CDCl_3$ ):  $\delta$  = 39.5 (1C,  $CH_2$ ), 41.6 (1C,  $\underline{C}HCN$ ), 120.0 (1C, CN), 122.5 (1C, C-Br), 127.4 (2C, CH), 127.9 (1C, CH), 128.4 (1C, CH), 129.1 (2C, CH), 130.1 (1C, CH), 130.5 (1C, CH), 132.2 (1C, CH), 134.7 (1C), 138.4 (1C). HRMS (ESI):  $m/z$   $[M+Na]^+$  calcd for  $C_{15}H_{12}BrNNa$ : 308.0051; found: 308.0055.

**3-(2-Bromophenyl)-2-phenylpropanenitrile (3h)** <sup>[S5]</sup> was prepared according to the general procedure from 2-bromophenyldiazonium tetrafluoroborate **2h** (81 mg, 0.3 mmol) and styrene **1a** (125 mg, 137  $\mu$ L, 1.2 mmol) and  $Bu_4NCN$  (96 mg, 0.36 mmol). Eluent: petroleum ether- $CH_2Cl_2$ ,

4:1, 27 mg (32%), yellowish crystalline powder, mp 83-84°C. IR (cm<sup>-1</sup>): 3057 (w), 3032 (w), 2925 (w), 2851 (vw), 2241 (w), 1681 (vw), 1675 (vw), 1599 (w), 1568 (w), 1496 (w), 1455 (m), 1441 (m), 1205 (w), 1182 (w), 1159 (w), 1116 (w), 1077 (w), 1046 (w), 1026 (s), 975 (w), 944 (w), 912 (w), 737 (vs), 698 (vs), 661 (m). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 3.22 (dd, *J* = 13.4 Hz, *J* = 10.0 Hz, 1H), 3.14 (dd, *J* = 13.4 Hz, *J* = 5.9 Hz, 1H), 4.21 (dd, *J* = 10.0 Hz, *J* = 5.9 Hz, 1H), 7.13-7.20 (m, 1H), 7.20-7.28 (m, 2H), 7.31-7.41 (m, 5H), 7.58 (dd, *J* = 7.8 Hz, *J* = 0.8 Hz, 1H). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>): δ = 37.7 (1C, CH<sub>2</sub>), 42.9 (1C, CHCN), 120.0 (1C, CN), 124.4 (1C, C-Br), 127.3 (2C, CH), 127.8 (1C, CH), 128.3 (1C, CH), 129.1 (2C, CH), 129.3 (1C, CH), 131.9 (1C, CH), 133.0 (1C, CH), 135.2 (1C), 135.8 (1C). HRMS (ESI): *m/z* [M+Na]<sup>+</sup> calcd for C<sub>15</sub>H<sub>12</sub>BrNNa: 308.0051; found: 308.0054;

**3-(2,6-Dichlorophenyl)-2-phenylpropanenitrile (3i)** was prepared according to the general procedure from 2,6-dichlorophenyldiazonium tetrafluoroborate **2i** (78 mg, 0.3 mmol) and styrene **1a** (125 mg, 137 μL, 1.2 mmol) and Bu<sub>4</sub>NCN (96 mg, 0.36 mmol). Eluent: petroleum ether-CH<sub>2</sub>Cl<sub>2</sub>, 4:1, 28 mg (34%), beige crystalline powder, mp 69-70°C. IR (cm<sup>-1</sup>): 3064 (w), 3031 (w), 2949 (w), 2926 (w), 2851 (w), 2242 (w), 1943 (w), 1869 (w), 1690 (w), 1599 (w), 1581 (m), 1561 (m), 1493 (m), 1435 (vs), 1329 (w), 1216 (m), 1162 (m), 1139 (m), 1087 (m), 1031 (w), 1002 (w), 980 (m), 936 (w), 911 (w), 776 (m), 764 (s), 755 (m), 714 (w), 697 (m). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 3.36 (dd, *J* = 13.6 Hz, *J* = 6.8 Hz, 1H), 3.68 (dd, *J* = 13.6 Hz, *J* = 9.7 Hz, 1H), 4.31 (dd, *J* = 9.7 Hz, *J* = 6.8 Hz, 1H), 7.17 (t, *J* = 8.2 Hz, 1H), 7.33 (d, *J* = 7.9 Hz, 2H), 7.35-7.39 (m, 5H). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>): δ = 36.0 (1C, CH<sub>2</sub>), 37.1 (1C, CHCN), 119.7 (1C, CN), 127.3 (2C, CH), 128.4 (1C, CH), 128.6 (2C, CH), 129.1 (2C, CH), 129.3 (1C, CH), 132.6 (2C, C-Cl), 135.0 (1C), 136.0 (1C). HRMS (ESI): *m/z* [M+Na]<sup>+</sup> calcd for C<sub>15</sub>H<sub>11</sub>Cl<sub>2</sub>NNa: 298.0166; found: 298.0168;

**2-(4-tert-Butylphenyl)-3-(4-nitrophenyl)propanenitrile (3j)** was prepared according to the general procedure from 4-nitrophenyldiazonium tetrafluoroborate **2a** (71 mg, 0.3 mmol) and 4-tert-butylstyrene **1b** (192 mg, 220 μL, 1.2 mmol) and Bu<sub>4</sub>NCN (96 mg, 0.36 mmol). Eluent: petroleum ether-CH<sub>2</sub>Cl<sub>2</sub>, 2:1, 45 mg (49%), yellowish crystalline powder, mp 87-88°C. IR (cm<sup>-1</sup>): 2963 (w), 2904 (vw), 2869 (vw), 2242 (vw), 1604 (w), 1517 (s), 1476 (w), 1461 (w), 1447 (vw), 1412 (vw), 1395 (vw), 1343 (vs), 1268 (w), 1202 (vw), 1182 (vw), 1109 (w), 1017 (w), 855 (m), 832 (m), 806 (w), 794 (w), 736 (m), 709 (m), 688 (w), 639 (w). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 1.32 (s, 9H), 3.26 (d, *J* = 7.2 Hz, 2H), 4.05 (t, *J* = 7.2 Hz, 1H), 7.19 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.7 Hz, 2H), 7.40 (d, *J* = 8.3 Hz, 2H), 8.16 (d, *J* = 8.7 Hz, 2H). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>): δ = 31.2 (3C, CH<sub>3</sub>), 34.6 (1C, CMe<sub>3</sub>), 38.6 (1C, CH<sub>2</sub>), 41.6 (CHCN), 119.7 (1C, CN), 123.8 (2C, CH), 126.1 (2C, CH), 127.0 (2C, CH), 130.2 (2C, CH), 131.1 (2C, CH), 143.6 (1C),

147.3 (1C), 151.8 (1C, C-NO<sub>2</sub>). HRMS (ESI):  $m/z$  [M+Na]<sup>+</sup> calcd for C<sub>19</sub>H<sub>20</sub>N<sub>2</sub>NaO<sub>2</sub>: 331.1425; found: 331.1420;

**2-(4-*tert*-Butylphenyl)-3-(3-nitrophenyl)propanenitrile (3k)** was prepared according to the general procedure from 3-nitrophenyldiazonium tetrafluoroborate **2f** (71 mg, 0.3 mmol) and 4-*tert*-butylstyrene **1b** (192 mg, 220  $\mu$ L, 1.2 mmol) and Bu<sub>4</sub>NCN (96 mg, 0.36 mmol). Eluent: petroleum ether-CH<sub>2</sub>Cl<sub>2</sub>, 1:1, 35 mg (38%), yellow crystalline powder, mp 88-89°C. IR (cm<sup>-1</sup>): 3095 (vw), 3060 (vw), 3031 (vw), 2959 (w), 2902 (w), 2865 (w), 2241 (vw), 1529 (s), 1513 (m), 1475 (w), 1445 (w), 1409 (w), 1346 (vs), 1305 (w), 1267 (m), 1241 (w), 1202 (w), 1161 (vw), 1109 (w), 1097 (w), 1082 (w), 1019 (w), 992 (w), 911 (w), 895 (w), 871 (vw), 835 (m), 825 (m), 820 (m), 805 (m), 797 (m), 735 (vs), 710 (s), 679 (m), 672 (s). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.31 (s, 9H), 3.25 (d,  $J$  = 7.2 Hz, 2H), 4.04 (t,  $J$  = 7.2 Hz, 1H), 7.18 (d,  $J$  = 8.3 Hz, 2H), 7.38 (d,  $J$  = 8.4 Hz, 2H), 7.48 (d,  $J$  = 7.5 Hz, 1H), 7.51-7.54 (m, 1H), 7.89 (t,  $J$  = 1.6 Hz, 1H), 8.14 (dt,  $J$  = 8.0 Hz,  $J$  = 1.6 Hz, 1H). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta$  = 31.2 (3C, CH<sub>3</sub>), 34.6 (1C, CMe<sub>3</sub>), 38.8 (1C, CH<sub>2</sub>), 41.5 (CHCN), 119.7 (1C, CN), 122.5 (1C, CH), 124.2 (1C, CH), 126.2 (2C, CH), 127.1 (2C, CH), 131.1 (1C, CH), 135.5 (1C, CH), 138.1 (1C), 138.2 (1C), 151.9 (1C, C-NO<sub>2</sub>). HRMS (ESI):  $m/z$  [M+Na]<sup>+</sup> calcd for C<sub>19</sub>H<sub>20</sub>N<sub>2</sub>NaO<sub>2</sub>: 331.1425; found: 331.1428.

**3-(3-Bromophenyl)-2-(4-*tert*-butylphenyl)propanenitrile (3l)** was prepared according to the general procedure from 3-bromophenyldiazonium tetrafluoroborate **2g** (81 mg, 0.3 mmol) and 4-*tert*-butylstyrene **1b** (192 mg, 220  $\mu$ L, 1.2 mmol) and Bu<sub>4</sub>NCN (96 mg, 0.36 mmol). Eluent: petroleum ether-CH<sub>2</sub>Cl<sub>2</sub>, 1:1, 36 mg (35%), beige crystalline powder, mp 78-80°C. IR (cm<sup>-1</sup>): 3082 (w), 3056 (m), 3033 (w), 2962 (s), 2903 (m), 2868 (m), 2233 (w), 1699 (m), 1684 (m), 1670 (m), 1590 (m), 1568 (m), 1511 (m), 1473 (s), 1427 (m), 1409 (m), 1363 (m), 1266 (m), 1209 (m), 1186 (m), 1109 (m), 1072 (m), 1019 (m), 997 (m), 880 (w), 828 (m), 787 (m), 774 (m), 737 (s), 685 (m). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.32 (s, 9H), 3.07-3.15 (m, 2H), 3.96 (t,  $J$  = 7.5 Hz, 1H), 7.10-7.22 (m, 5H), 7.34-7.42 (m, 2H). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta$  = 31.2 (3C, CH<sub>3</sub>), 34.6 (1C, CMe<sub>3</sub>), 39.1 (1C, CH<sub>2</sub>), 41.7 (CHCN), 120.1 (1C, CN), 122.5 (1C, C-Br), 126.0 (2C, CH), 127.1 (2C, CH), 127.9 (1C, CH), 130.2 (1C, CH), 130.5 (1C, CH), 131.7 (1C), 132.2 (1C, CH), 138.8 (1C), 151.5 (1C). HRMS (ESI):  $m/z$  [M+Na]<sup>+</sup> calcd for C<sub>19</sub>H<sub>20</sub>BrNNa: 364.0676; found: 364.0684;

**2-(4-*tert*-Butylphenyl)-3-(4-iodophenyl)propanenitrile (3m)** was prepared according to the general procedure from 4-iodophenyldiazonium tetrafluoroborate **2j** (95 mg, 0.3 mmol) and 4-*tert*-butylstyrene **1b** (192 mg, 220  $\mu$ L, 1.2 mmol) and Bu<sub>4</sub>NCN (96 mg, 0.36 mmol). Eluent: petroleum ether-CH<sub>2</sub>Cl<sub>2</sub>, 2:1, 32 mg (27%), brown crystalline powder, mp 92-94°C. IR (cm<sup>-1</sup>): 3088 (vw), 3057 (vw), 3029 (w), 2961 (s), 2929 (m), 2904 (m), 2867 (m), 2241 (w), 1588 (w), 1511 (m), 1485 (s), 1461 (m), 1444 (w), 1402 (m), 1364 (m), 1269 (m), 1202 (w), 1109 (m),

1060 (w), 1007 (vs), 828 (s), 799 (m), 717 (w). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 1.31 (s, 9H), 3.06-3.10 (m, 2H), 3.94 (t, *J* = 7.2 Hz, 1H), 6.90 (d, *J* = 8.3 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 8.3 Hz, 2H). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>): δ = 31.2 (3C, CH<sub>3</sub>), 34.6 (1C, CMe<sub>3</sub>), 39.1 (1C, CH<sub>2</sub>), 41.6 (CHCN), 92.9 (1C, C-I), 120.2 (1C, CN), 126.0 (2C, CH), 127.1 (2C, CH), 131.2 (2C, CH), 131.7 (1C), 136.0 (1C), 137.7 (2C, CH), 151.5 (1C). HRMS (ESI): *m/z* [M+Na]<sup>+</sup> calcd for C<sub>19</sub>H<sub>20</sub>INNa: 412.0538; found: 412.0540;

**2-(4-Bromophenyl)-3-(4-nitrophenyl)propanenitrile (3n)** was prepared according to the general procedure from 4-nitrophenyldiazonium tetrafluoroborate **2a** (71 mg, 0.3 mmol) and 4-bromostyrene **1c** (220 mg, 157 μL, 1.2 mmol) and Bu<sub>4</sub>NCN (96 mg, 0.36 mmol). Eluent: petroleum ether-CH<sub>2</sub>Cl<sub>2</sub>, 1:1, 40 mg (40%), beige crystalline powder, mp 126-128°C. IR (cm<sup>-1</sup>): 3111 (vw), 3080 (vw), 3060 (vw), 2926 (vw), 2851 (vw), 2245 (vw), 1600 (w), 1516 (vs), 1488 (m), 1445 (w), 1406 (w), 1343 (vs), 1265 (w), 1182 (w), 1108 (w), 1072 (m), 1011 (m), 855 (m), 820 (m), 791 (m), 735 (s), 720 (m), 698 (m), 631 (w). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 3.27 (d, *J* = 7.1 Hz, 2H), 4.07 (t, *J* = 7.1 Hz, 1H), 7.11 (d, *J* = 8.5 Hz, 2H), 7.28 (d, *J* = 8.8 Hz, 2H), 7.51 (d, *J* = 8.5 Hz, 2H), 8.16 (d, *J* = 8.8 Hz, 2H). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>): δ = 38.4 (1C, CH<sub>2</sub>), 41.3 (1C, CHCN), 119.1 (1C, CN), 122.8 (1C, C-Br), 123.9 (2C, CH), 129.0 (2C, CH), 130.3 (2C, CH), 132.4 (2C, CH), 133.0 (1C), 142.8 (1C), 147.4 (1C, C-NO<sub>2</sub>). HRMS (ESI): *m/z* [M+Na]<sup>+</sup> calcd for C<sub>15</sub>H<sub>11</sub>BrN<sub>2</sub>NaO<sub>2</sub>: 352.9901; found: 352.9911;

**2-(4-Chlorophenyl)-3-(4-nitrophenyl)propanenitrile (3o)** was prepared according to the general procedure from 4-nitrophenyldiazonium tetrafluoroborate **2a** (71 mg, 0.3 mmol) and 4-chlorostyrene **1d** (166 mg, 144 μL, 1.2 mmol) and Bu<sub>4</sub>NCN (96 mg, 0.36 mmol). Eluent: petroleum ether-CH<sub>2</sub>Cl<sub>2</sub>, 1:1, 41 mg (44%), beige crystalline powder, mp 79-80°C. IR (cm<sup>-1</sup>): 3109 (vw), 3080 (vw), 2934 (vw), 2854 (vw), 2243 (vw), 1600 (w), 1515 (s), 1491 (m), 1446 (w), 1410 (w), 1343 (vs), 1316 (w), 1181 (w), 1092 (m), 1014 (m), 855 (m), 827 (m), 793 (m), 735 (m), 724 (m), 700 (m), 686 (m), 631 (w). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 3.27 (d, *J* = 7.4 Hz, 2H), 4.09 (t, *J* = 7.4 Hz, 1H), 7.17 (d, *J* = 8.5 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 8.16 (d, *J* = 8.5 Hz, 2H). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>): δ = 38.3 (1C, CH<sub>2</sub>), 41.3 (1C, CHCN), 119.1 (1C, CN), 123.8 (2C, CH), 128.7 (2C, CH), 129.4 (2C, CH), 130.2 (2C, CH), 132.5 (1C, C-Cl), 134.7 (1C), 142.9 (1C), 147.4 (1C, C-NO<sub>2</sub>). HRMS (ESI): *m/z* [M+Na]<sup>+</sup> calcd for C<sub>15</sub>H<sub>11</sub>ClN<sub>2</sub>NaO<sub>2</sub>: 309.0406; found: 309.0399;

**2-(4-Chlorophenyl)-3-phenylpropanenitrile (3p)** <sup>[S5]</sup> was prepared according to the general procedure from phenyldiazonium tetrafluoroborate **2a** (58 mg, 0.3 mmol) and 4-chlorostyrene **1d** (166 mg, 144 μL, 1.2 mmol) and Bu<sub>4</sub>NCN (96 mg, 0.36 mmol). Eluent: petroleum ether-CH<sub>2</sub>Cl<sub>2</sub>, 4:1, 23 mg (32%), yellowish crystalline powder, mp 78-80°C. IR (cm<sup>-1</sup>): 3085 (vw), 3065 (vw), 3054 (vw), 3028 (vw), 2932 (vw), 2859 (vw), 2242 (w), 1671 (vw), 1601 (vw), 1586 (vw), 1491

(m), 1453 (m), 1442 (w), 1409 (w), 1279 (w), 1266 (w), 1239 (vw), 1209 (vw), 1173 (vw), 1161 (vw), 1149 (vw), 1093 (m), 1073 (w), 1016 (m), 973 (w), 914 (vw), 875 (w), 826 (s), 814 (s), 793 (m), 740 (s), 713 (m), 699 (vs), 688 (s). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 3.10 (dd,  $J$  = 13.7 Hz,  $J$  = 6.7 Hz, 1H), 3.18 (dd,  $J$  = 13.7 Hz,  $J$  = 7.9 Hz, 1H), 3.98 (dd,  $J$  = 7.9 Hz,  $J$  = 6.7 Hz, 1H), 7.09-7.12 (m, 2H), 7.16 (d,  $J$  = 8.4 Hz, 2H), 7.25-7.30 (m, 3H), 7.32 (d,  $J$  = 8.4 Hz, 2H). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta$  = 39.1 (1C, CH<sub>2</sub>), 42.0 (1C, CHCN), 119.9 (1C, CN), 127.5 (1C, CH), 128.7 (2C, CH), 128.9 (2C, CH), 129.2 (4C, CH), 130.6 (2C, CH), 133.6 (1C, C-Cl), 134.2 (1C), 135.7 (1C). HRMS (ESI):  $m/z$  [M+Na]<sup>+</sup> calcd for C<sub>15</sub>H<sub>12</sub>ClNNa: 265.0556 ; found: 265.0551;

**2-(4-Nitrophenyl)-2,3-dihydro-1H-indene-1-carbonitrile (3q)** was prepared according to the general procedure from 4-nitrophenyldiazonium tetrafluoroborate **2a** (71 mg, 0.3 mmol), indene **1e** (139 mg, 140  $\mu$ L, 1.2 mmol) and Bu<sub>4</sub>NCN (96 mg, 0.36 mmol). Eluent: petroleum ether-CH<sub>2</sub>Cl<sub>2</sub>, 2:1, 35 mg (44%), beige crystalline powder, mp 144-146°C. IR (cm<sup>-1</sup>): 3383 (vw), 3111 (vw), 3076 (vw), 3044 (vw), 3027 (vw), 2939 (vw), 2915 (vw), 2851 (vw), 2240 (vw), 1600 (w), 1514 (s), 1496 (w), 1479 (w), 1459 (w), 1442 (w), 1344 (vs), 1311 (m), 1235 (w), 1212 (w), 1181 (w), 1155 (vw), 1108 (w), 1014 (w), 855 (m), 843 (m), 828 (w), 789 (w), 747 (s), 711 (w), 696 (m), 631 (w). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 3.24 (dd,  $J$  = 15.9 Hz,  $J$  = 9.8 Hz, 1H), 3.50 (dd,  $J$  = 15.9 Hz,  $J$  = 8.1 Hz, 1H), 4.04 (q,  $J$  = 9.2 Hz, 1H), 4.23 (dd,  $J$  = 9.8 Hz, 1H), 7.27-7.42 (m, 3H), 7.45-7.50 (m, 1H), 7.58 (d,  $J$  = 8.7 Hz, 2H), 8.26 (d,  $J$  = 8.7 Hz, 2H). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta$  = 39.0 (1C, CH<sub>2</sub>), 42.6 (1C, CHCN), 51.2 (1C, CHCHCN), 119.6 (1C, CN), 124.2 (3C, CH), 124.3 (1C), 124.9 (1C, CH), 128.0 (1C, CH), 128.1 (2C, CH), 129.2 (1C, CH), 136.1 (1C), 140.7 (1C), 147.5 (1C, C-NO<sub>2</sub>). HRMS (ESI):  $m/z$  [M+Na]<sup>+</sup> calcd for C<sub>16</sub>H<sub>12</sub>N<sub>2</sub>NaO<sub>2</sub>: 287.0797; found: 287.0791.

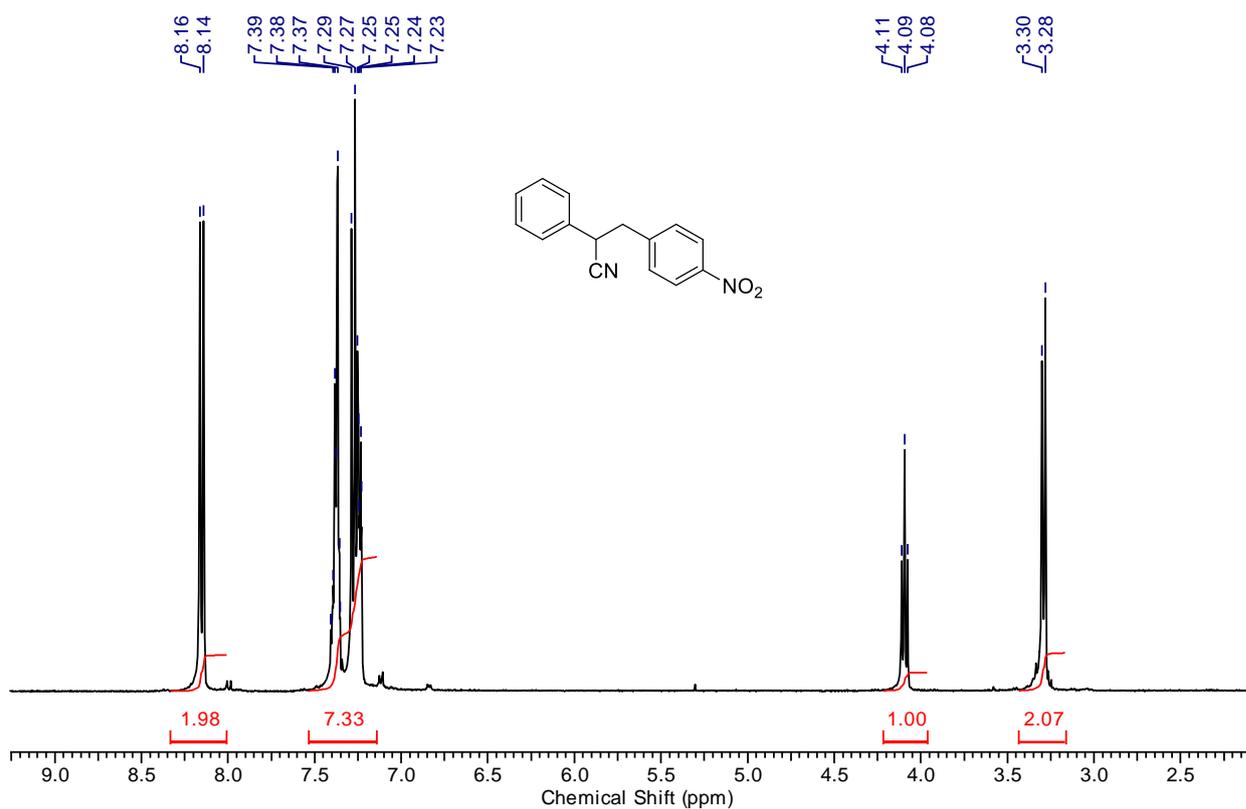
**1-Nitro-4-(2-phenyl-2-thiocyanatoethyl)benzene (4)** was prepared according to the general procedure from 4-nitrophenyldiazonium tetrafluoroborate **2a** (71 mg, 0.3 mmol) and styrene **1a** (125 mg, 137  $\mu$ L, 1.2 mmol) and NH<sub>4</sub>SCN (69 mg, 0.9 mmol) in the presence of Cu(OAc)<sub>2</sub>·H<sub>2</sub>O (6 mg, 0.03 mmol) and Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> (5 mg, 0.006 mmol) under blue LED irradiation. Eluent: petroleum ether-CH<sub>2</sub>Cl<sub>2</sub>, 2:1, 61 mg (72%), beige crystalline powder, mp 97-98°C. IR (cm<sup>-1</sup>): 3103 (vw), 3078 (vw), 3051 (vw), 3031 (vw), 2924 (vw), 2844 (vw), 2147 (m), 1604 (m), 1596 (m), 1510 (s), 1496 (m), 1453 (w), 1441 (w), 1339 (s), 1322 (m), 1259 (m), 1225 (w), 1187 (w), 1180 (w), 1152 (w), 1104 (m), 1080 (w), 1014 (w), 1001 (w), 929 (w), 914 (w), 879 (m), 855 (m), 833 (m), 795 (m), 765 (m), 745 (s), 737 (s), 696 (vs), 668 (m), 656 (m), 622 (m), 605 (m).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 3.52 (dd,  $J$  = 14.0 Hz,  $J$  = 8.6 Hz, 1H), 3.60 (dd,  $J$  = 14.0 Hz,  $J$  = 6.9 Hz, 1H), 4.55 (dd,  $J$  = 8.6 Hz,  $J$  = 6.9 Hz, 1H), 6.97 (d,  $J$  = 8.3 Hz, 2H), 7.20-7.30 (m, 4H), 7.32-7.40 (m, 3H), 8.10 (d,  $J$  = 8.6 Hz, 2H).  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 41.8 (1C,  $\text{CH}_2$ ), 53.9 (1C,  $\underline{\text{C}}\text{HCN}$ ), 111.0 (1C,  $\text{SCN}$ ), 123.8 (2C, CH), 127.5 (2C, CH), 129.3 (2C, CH), 129.5 (1C, CH), 130.1 (2C, CH), 136.6 (1C), 144.0 (1C), 147.2 (1C). HRMS (ESI):  $m/z$   $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{15}\text{H}_{12}\text{N}_2\text{NaO}_2\text{S}$ : 307.0517; found: 307.0472.

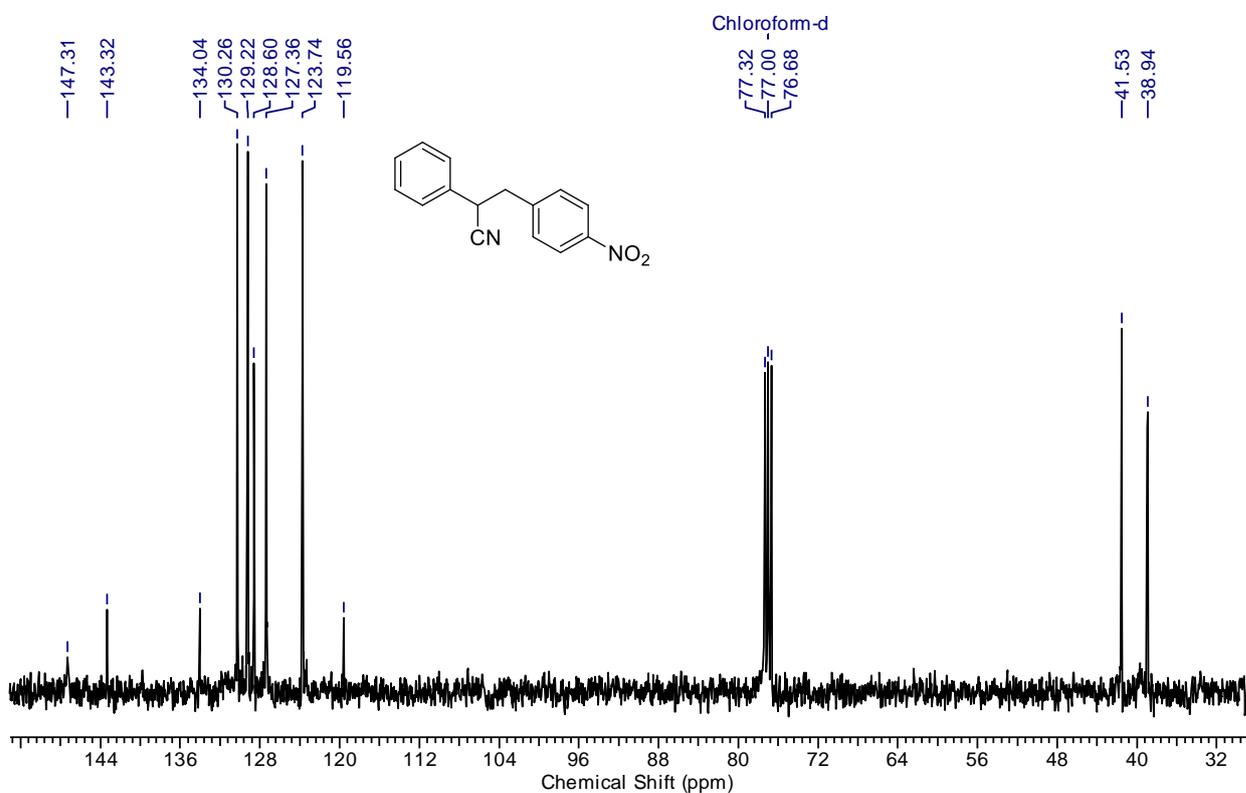
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## NMR spectra



**Figure S2.**  $^1\text{H}$  NMR spectrum of **3a** ( $\text{CDCl}_3$ , 400MHz, 300K).



**Figure S3.**  $^{13}\text{C}$  NMR spectrum of **3a** ( $\text{CDCl}_3$ , 100.6 MHz, 300K).

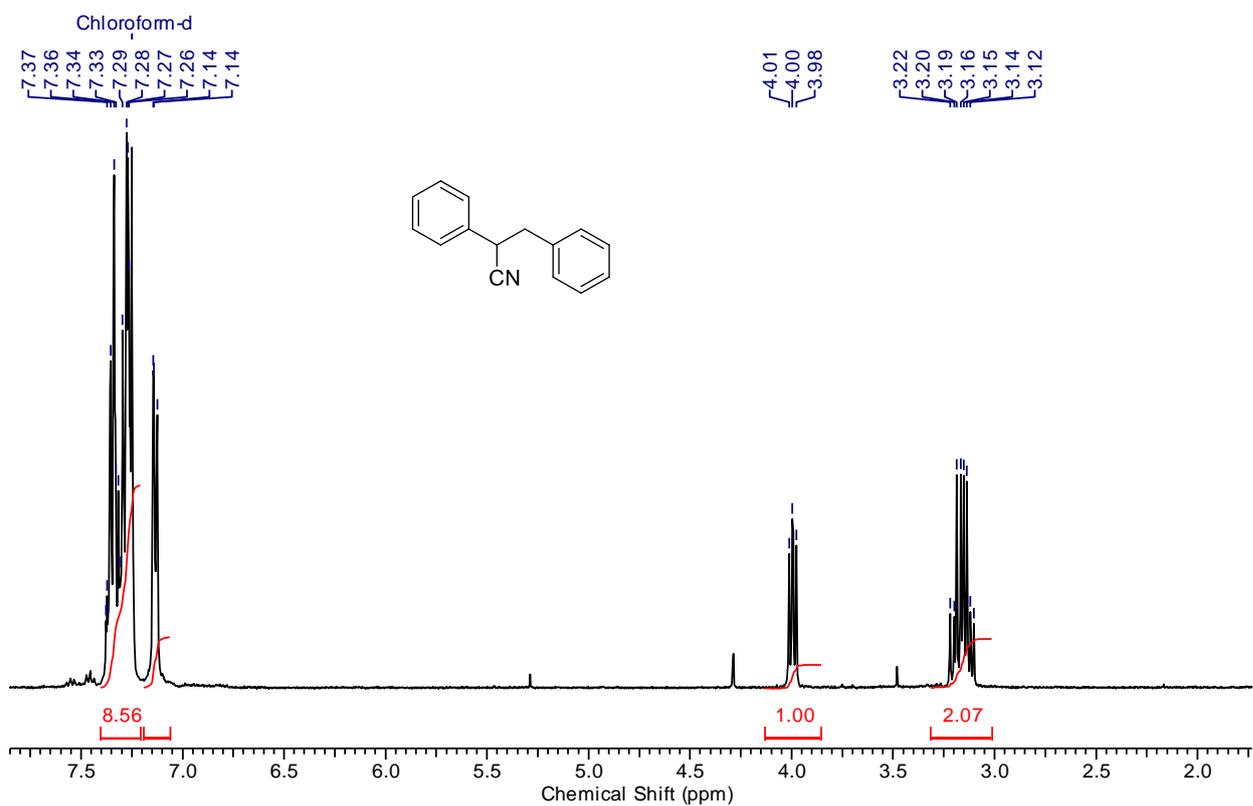


Figure S4. <sup>1</sup>H NMR spectrum of **3b** (CDCl<sub>3</sub>, 400MHz, 300K).

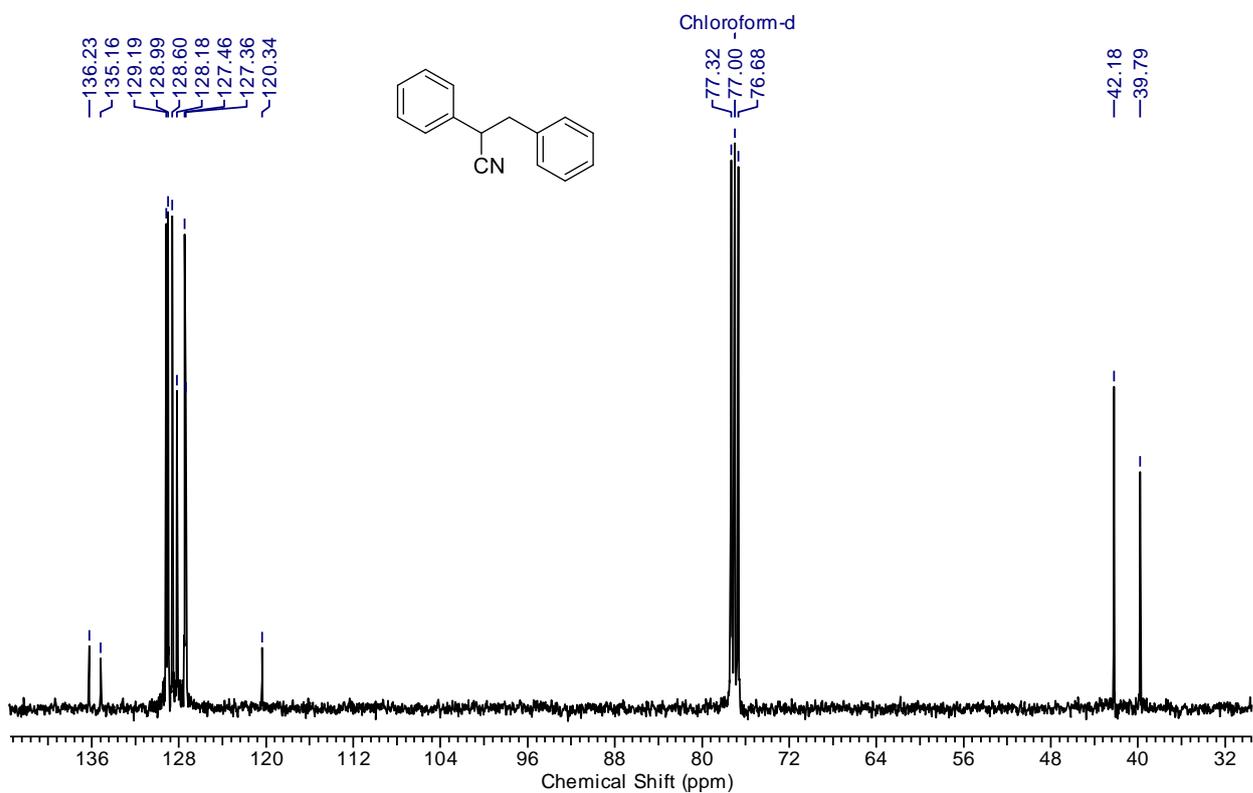
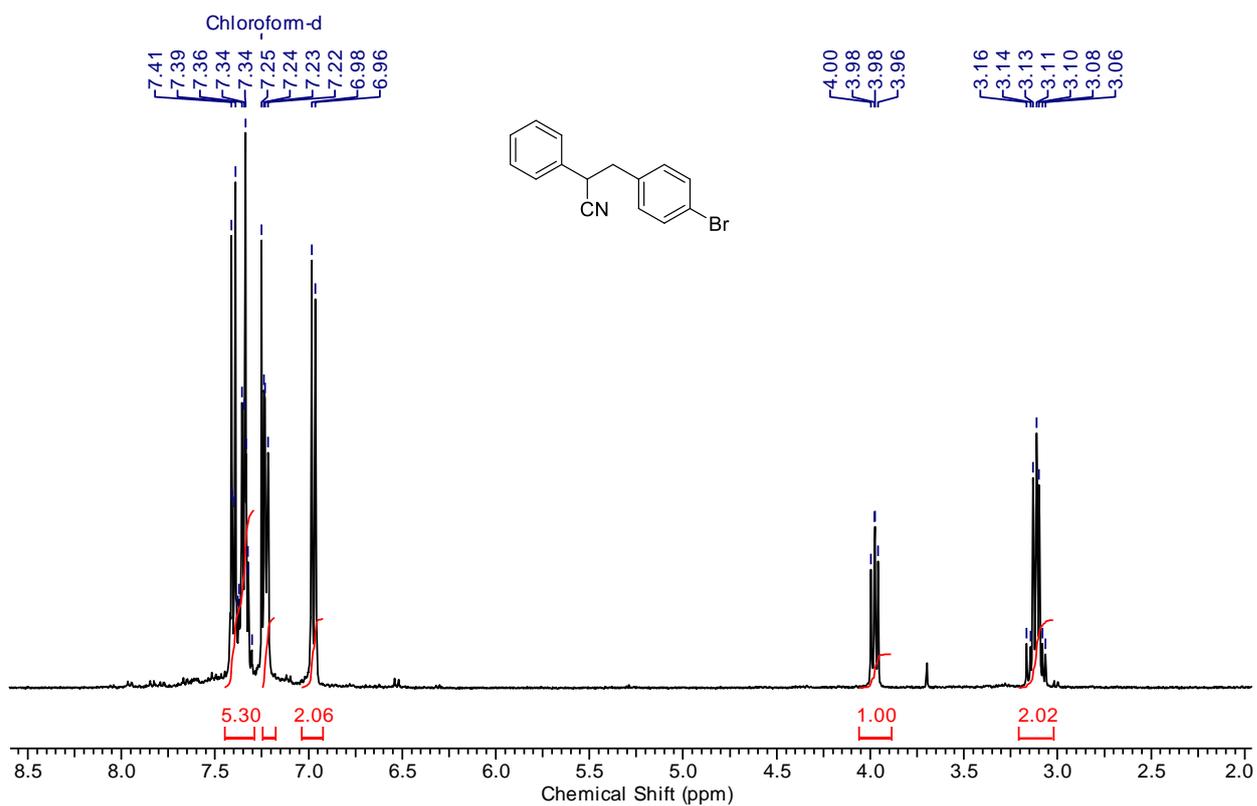
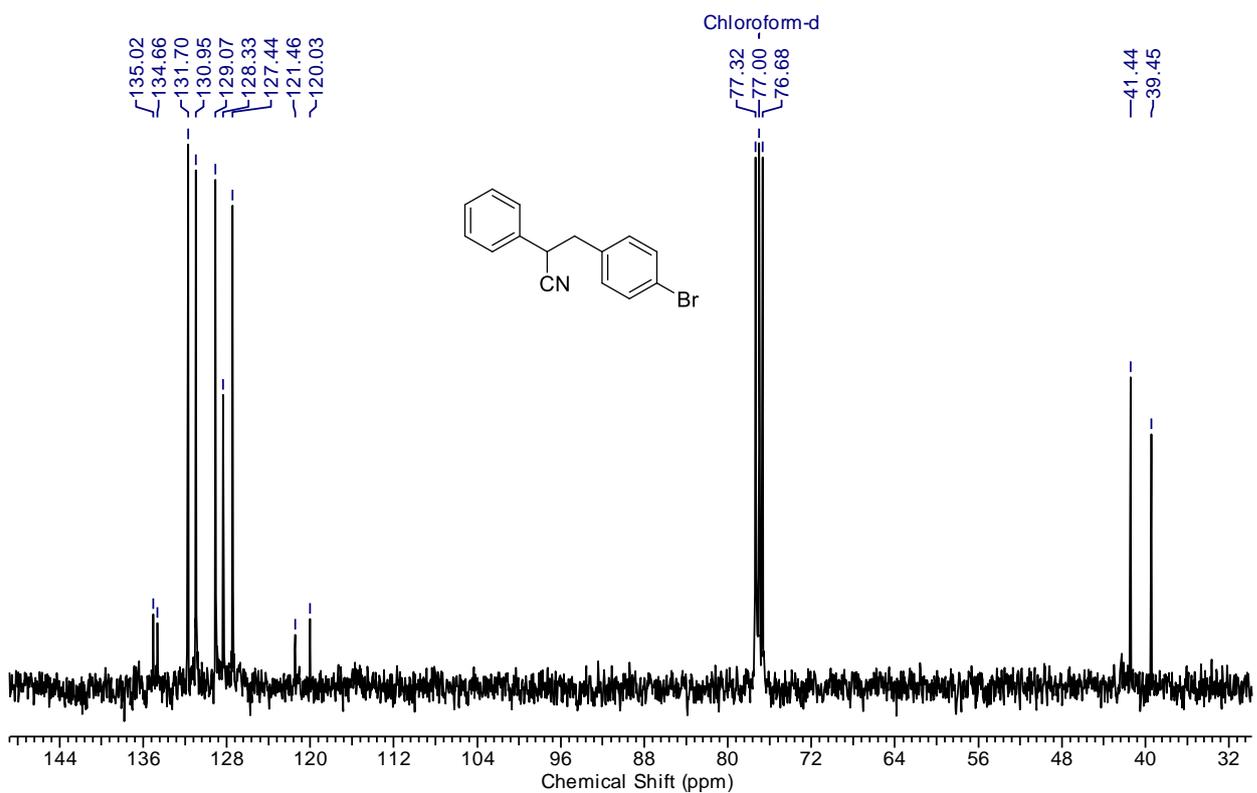


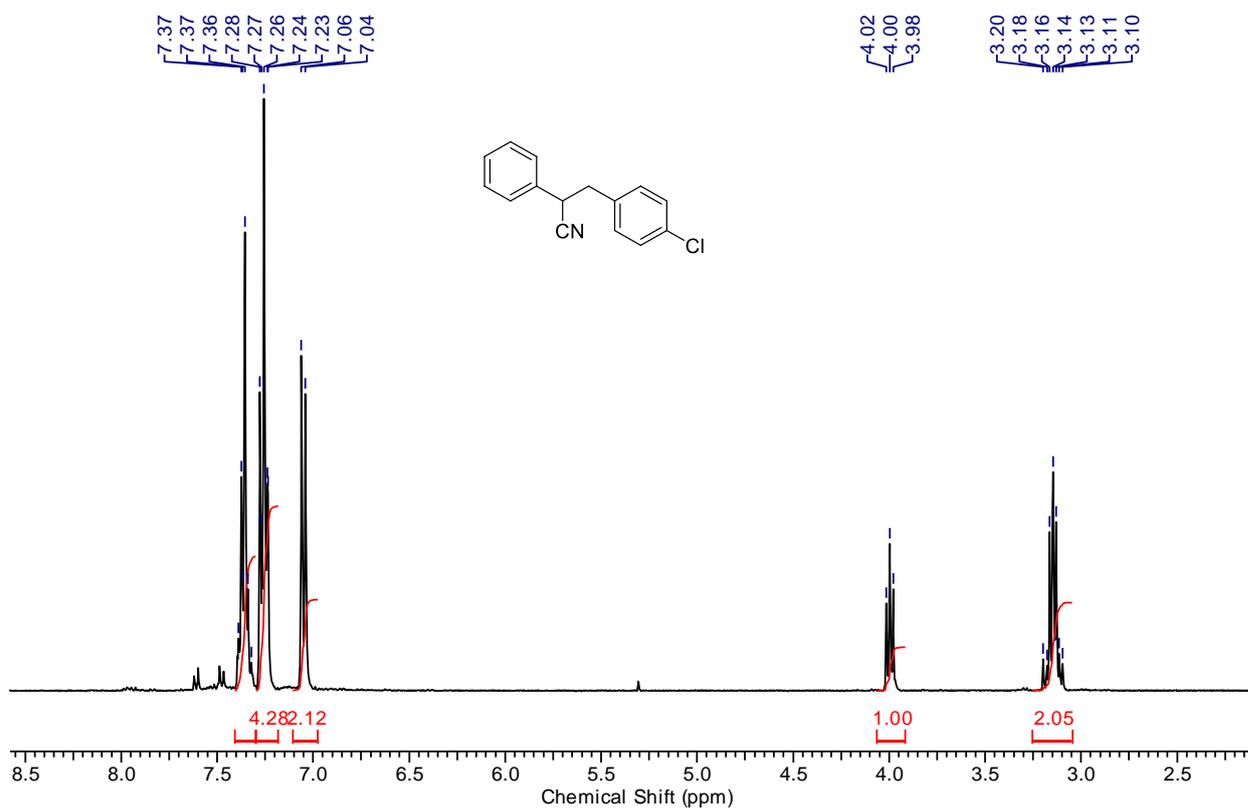
Figure S5. <sup>13</sup>C NMR spectrum of **3b** (CDCl<sub>3</sub>, 100.6 MHz, 300K).



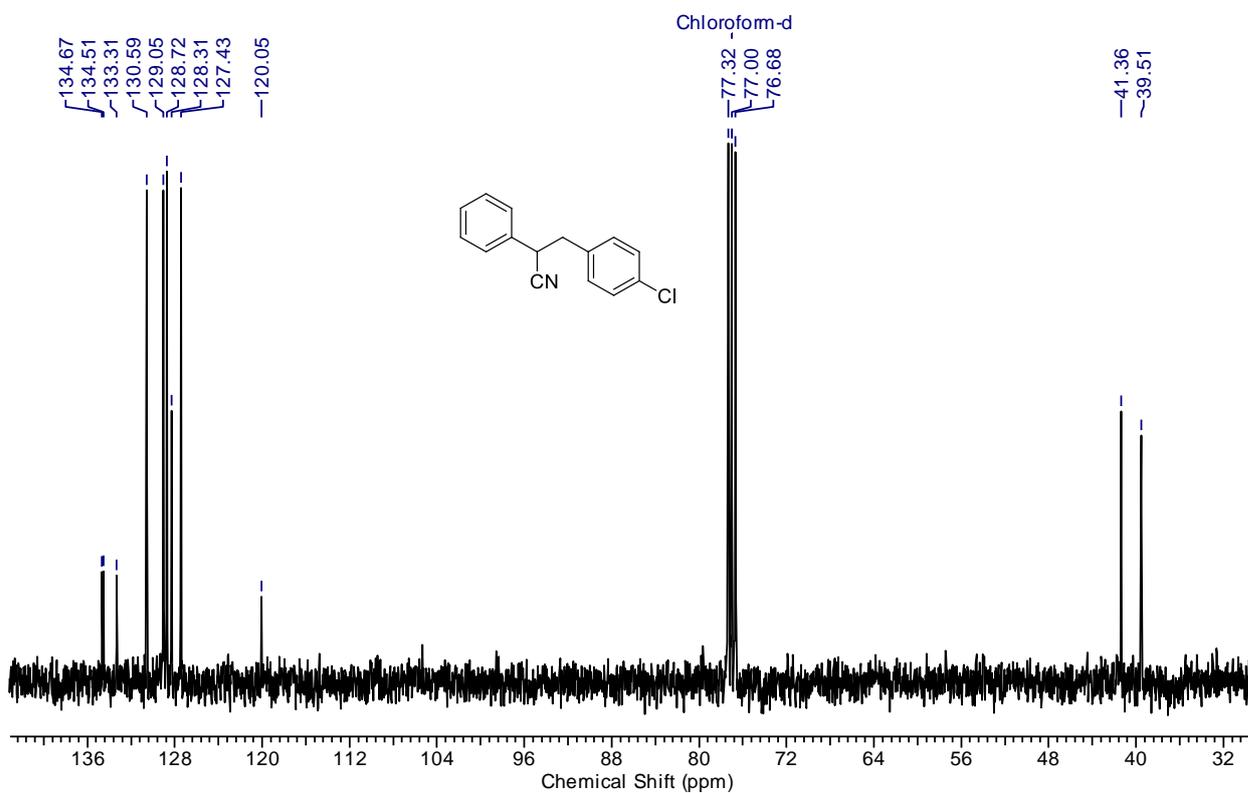
**Figure S6.** <sup>1</sup>H NMR spectrum of **3c** (CDCl<sub>3</sub>, 400MHz, 300K).



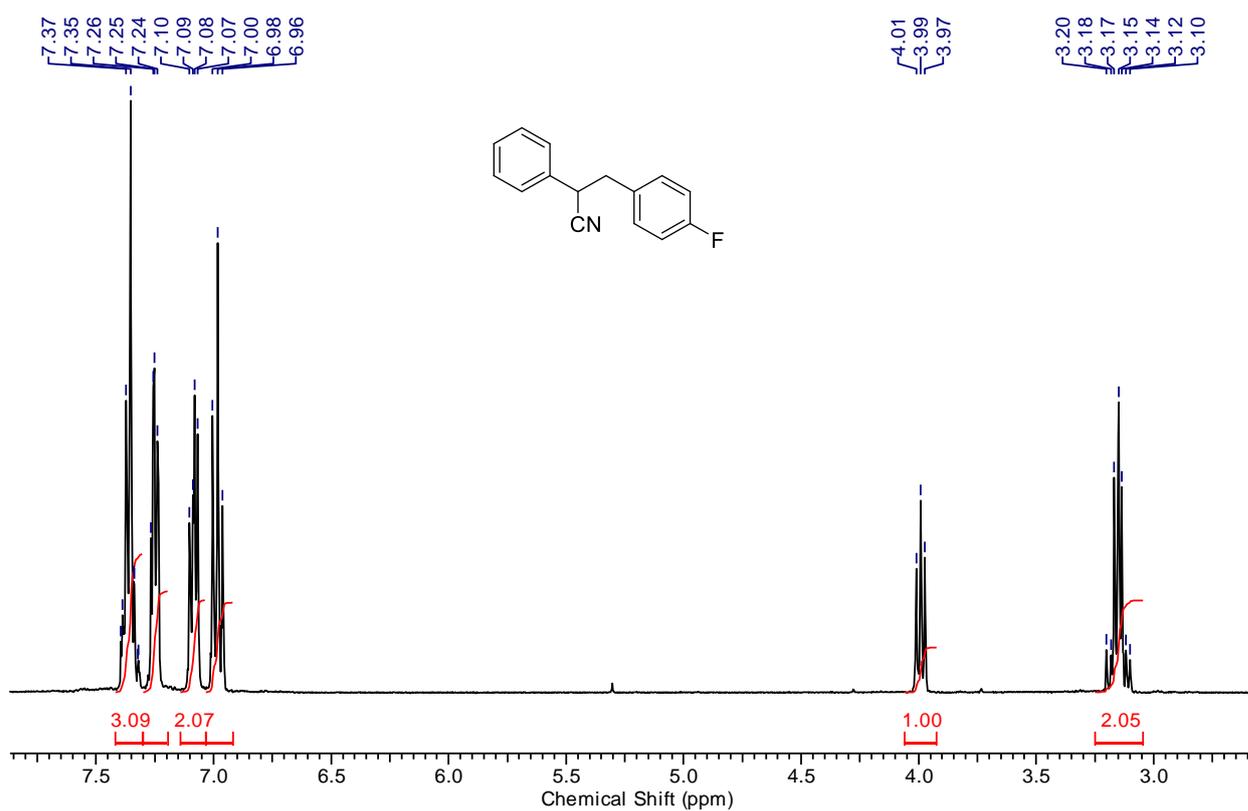
**Figure S7.** <sup>13</sup>C NMR spectrum of **3c** (CDCl<sub>3</sub>, 100.6 MHz, 300K).



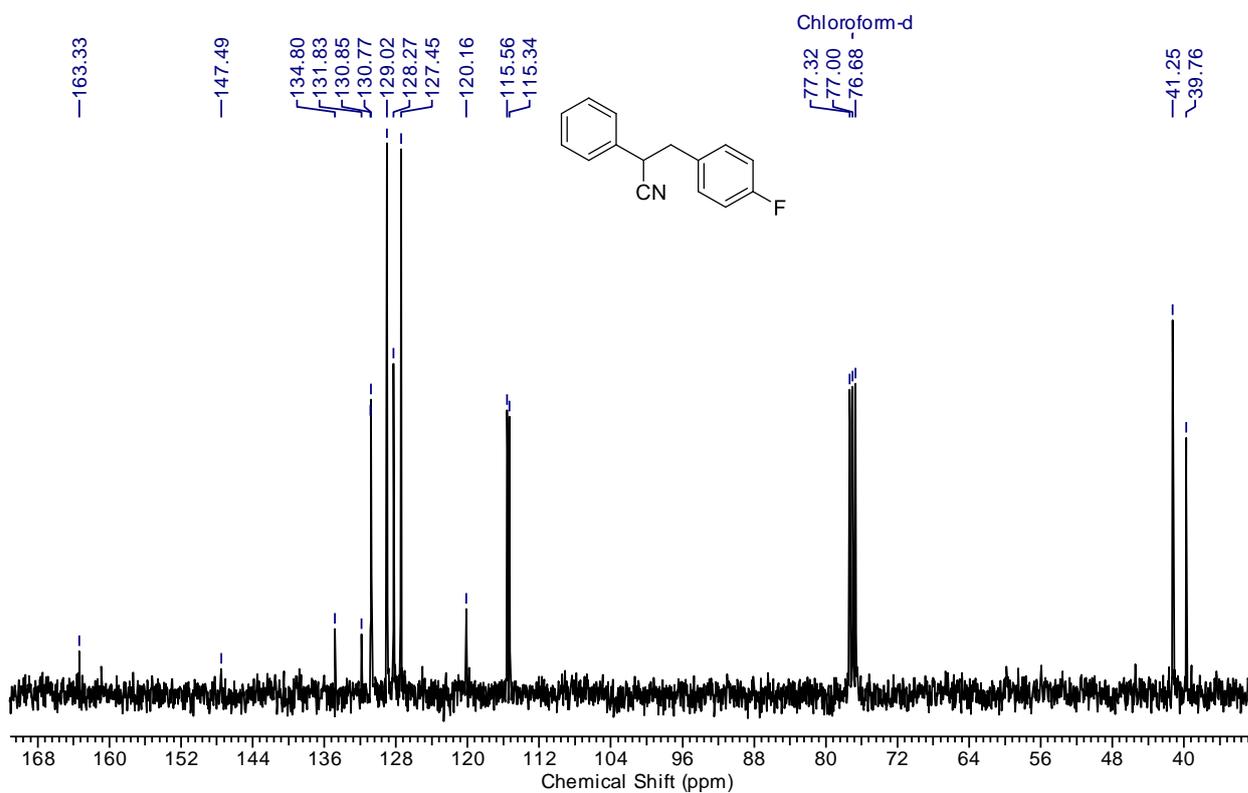
**Figure S8.** <sup>1</sup>H NMR spectrum of **3d** (CDCl<sub>3</sub>, 400MHz, 300K).



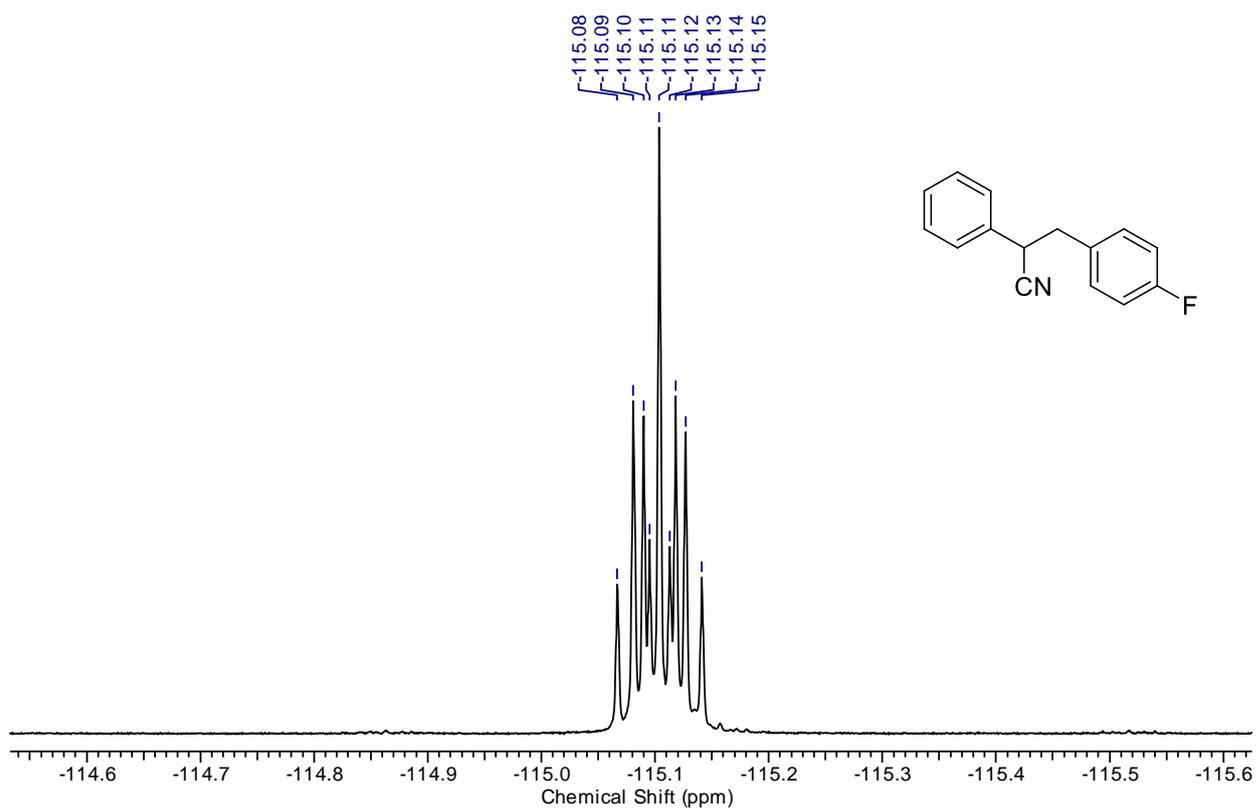
**Figure S9.** <sup>13</sup>C NMR spectrum of **3d** (CDCl<sub>3</sub>, 100.6 MHz, 300K).



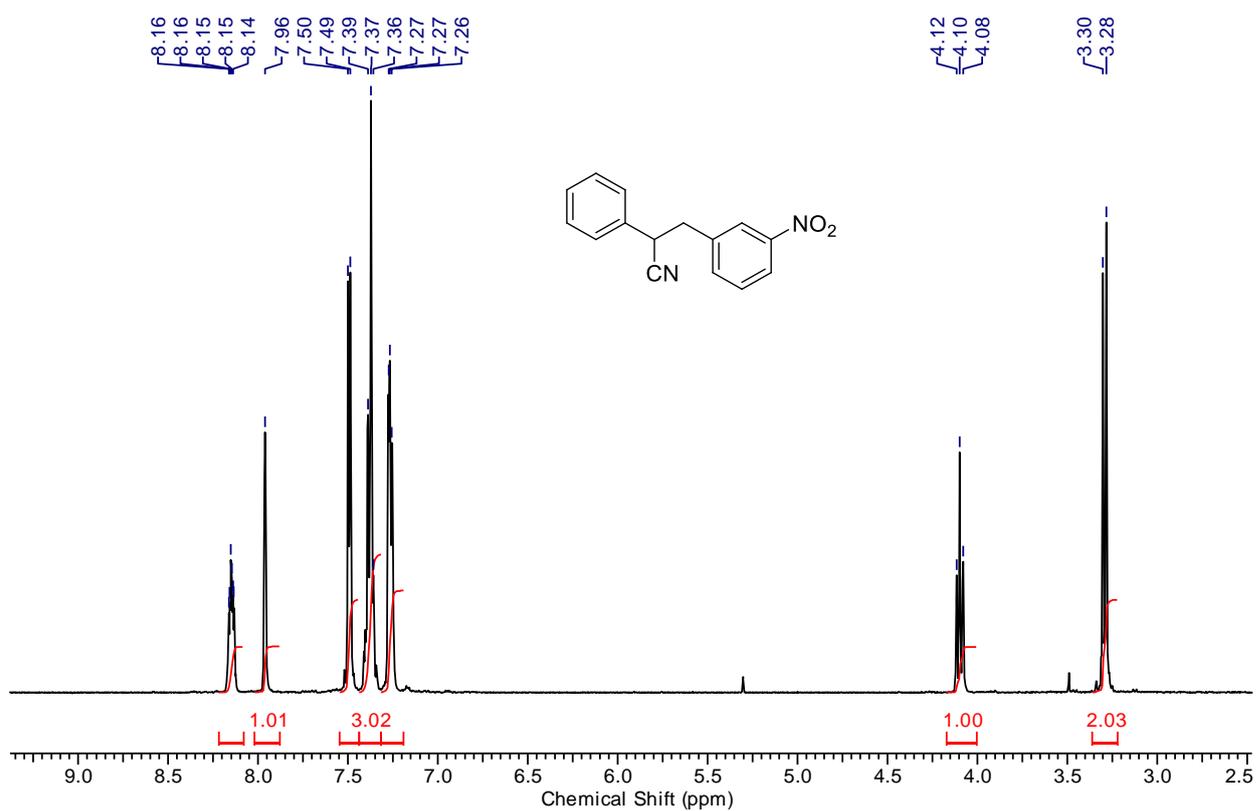
**Figure S10.** <sup>1</sup>H NMR spectrum of **3e** (CDCl<sub>3</sub>, 400MHz, 300K).



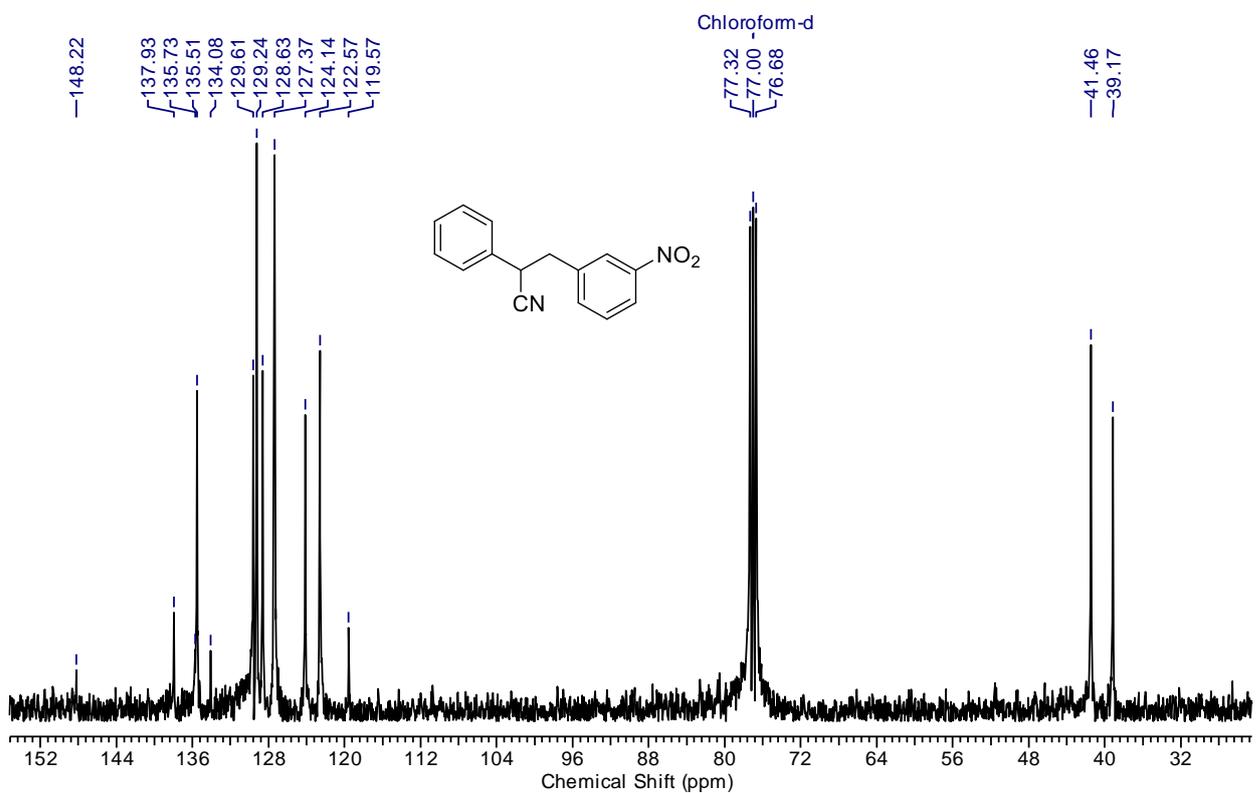
**Figure S11.** <sup>13</sup>C NMR spectrum of **3e** (CDCl<sub>3</sub>, 100.6 MHz, 300K).



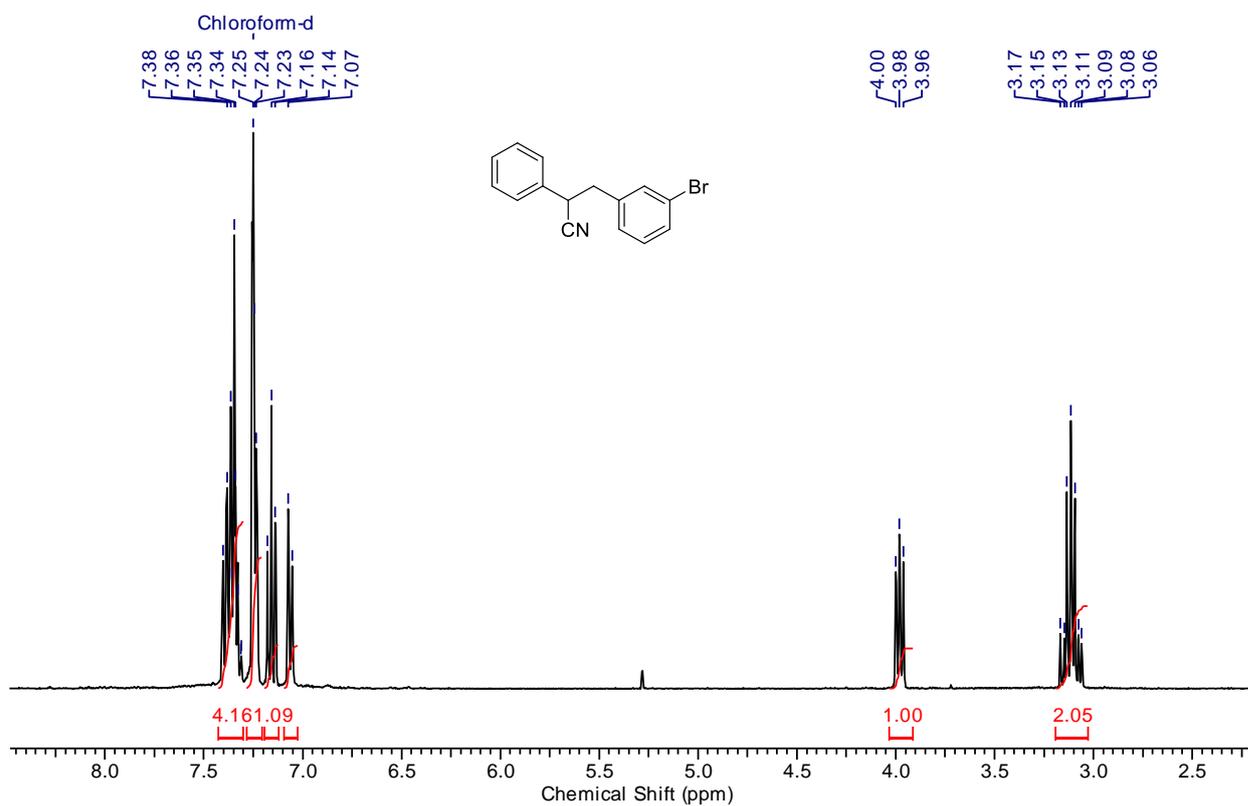
**Figure S12.**  $^{19}\text{F}$  NMR spectrum of **3e** ( $\text{CDCl}_3$ , 400MHz, 300K).



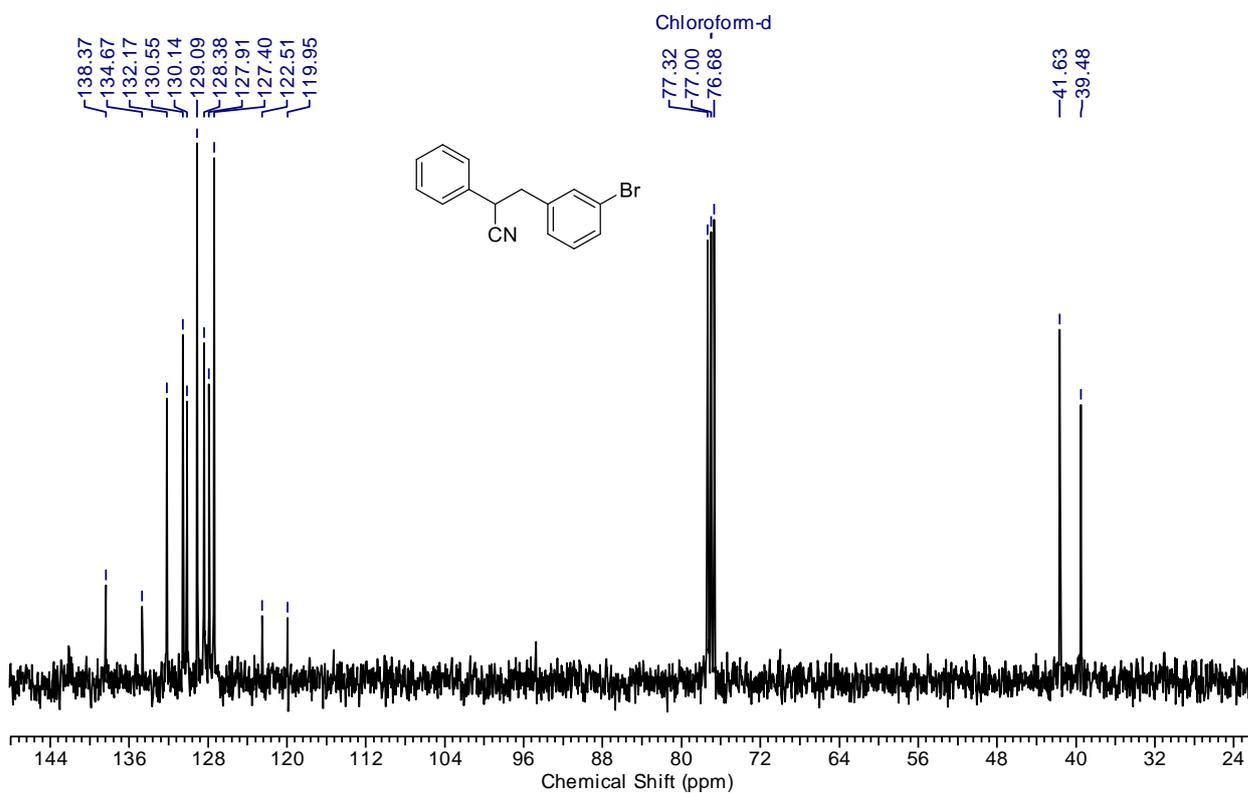
**Figure S13.** <sup>1</sup>H NMR spectrum of **3f** (CDCl<sub>3</sub>, 400MHz, 300K).



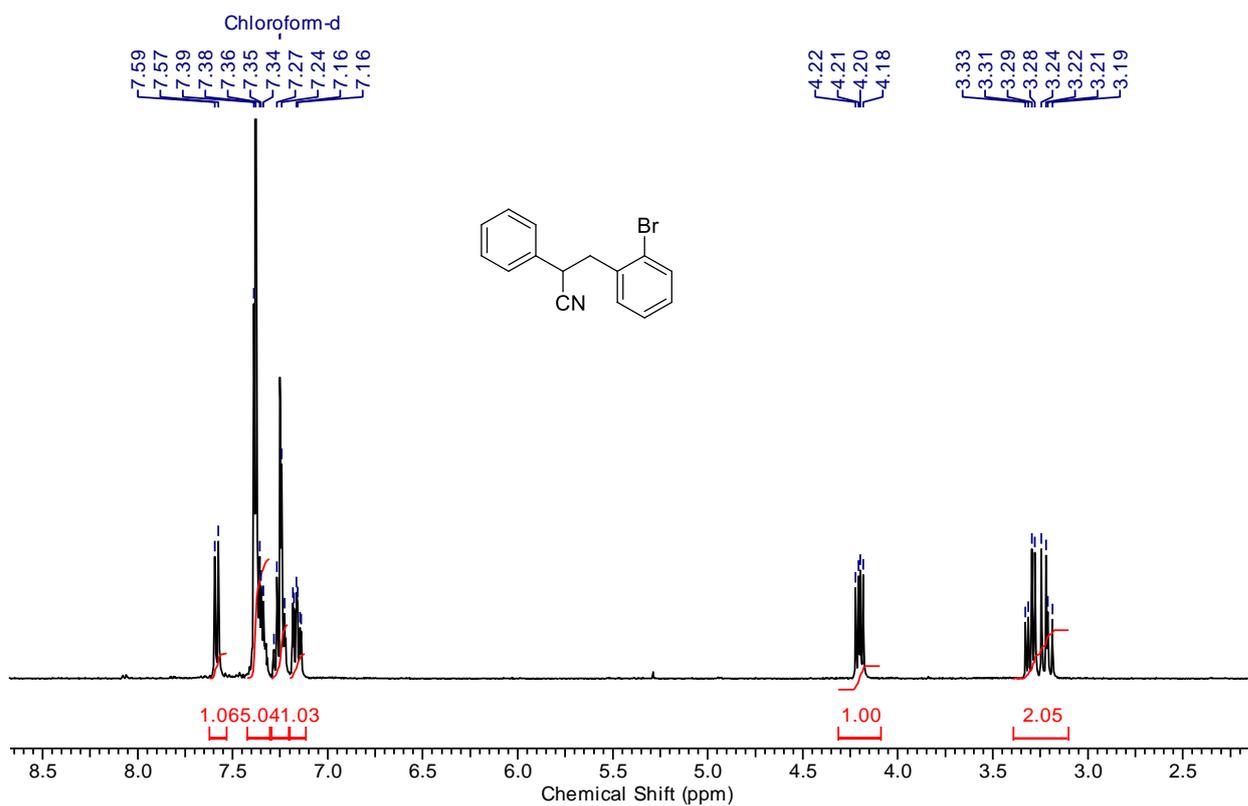
**Figure S14.** <sup>13</sup>C NMR spectrum of **3f** (CDCl<sub>3</sub>, 100.6 MHz, 300K).



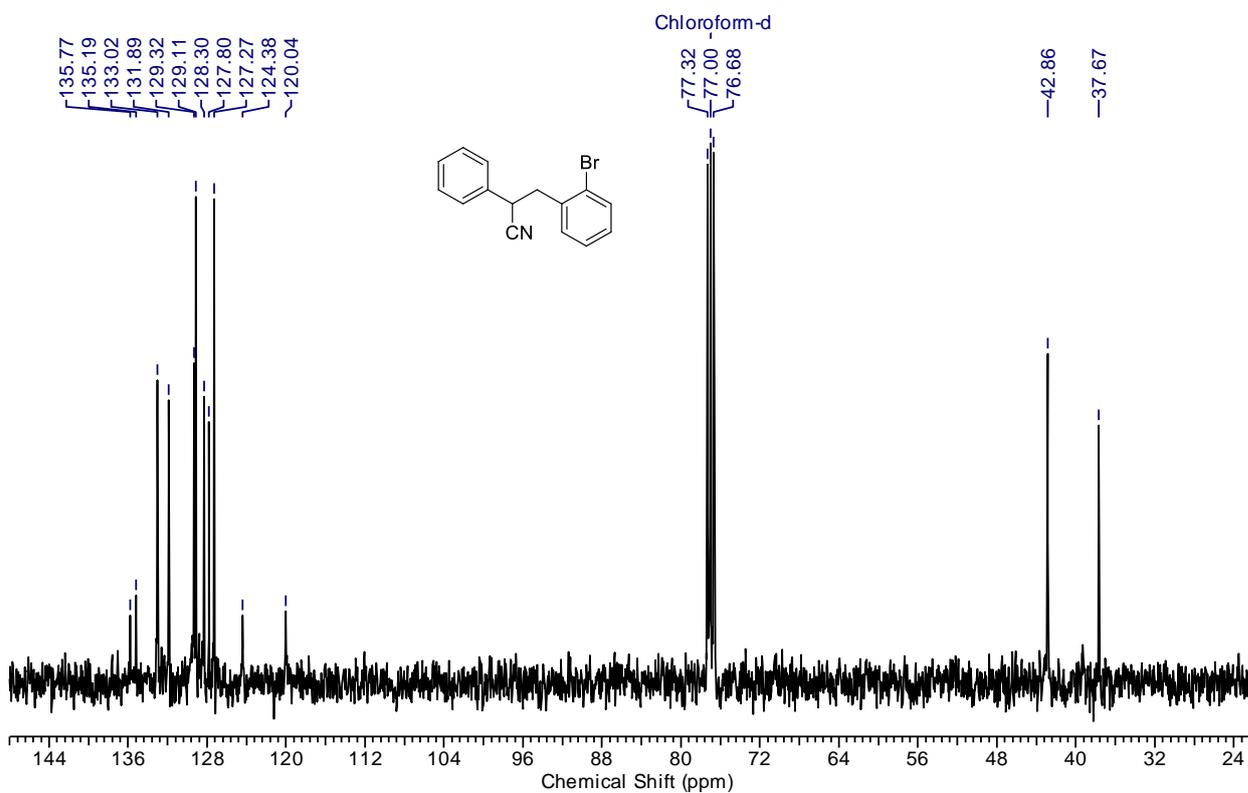
**Figure S15.** <sup>1</sup>H NMR spectrum of **3g** (CDCl<sub>3</sub>, 400MHz, 300K).



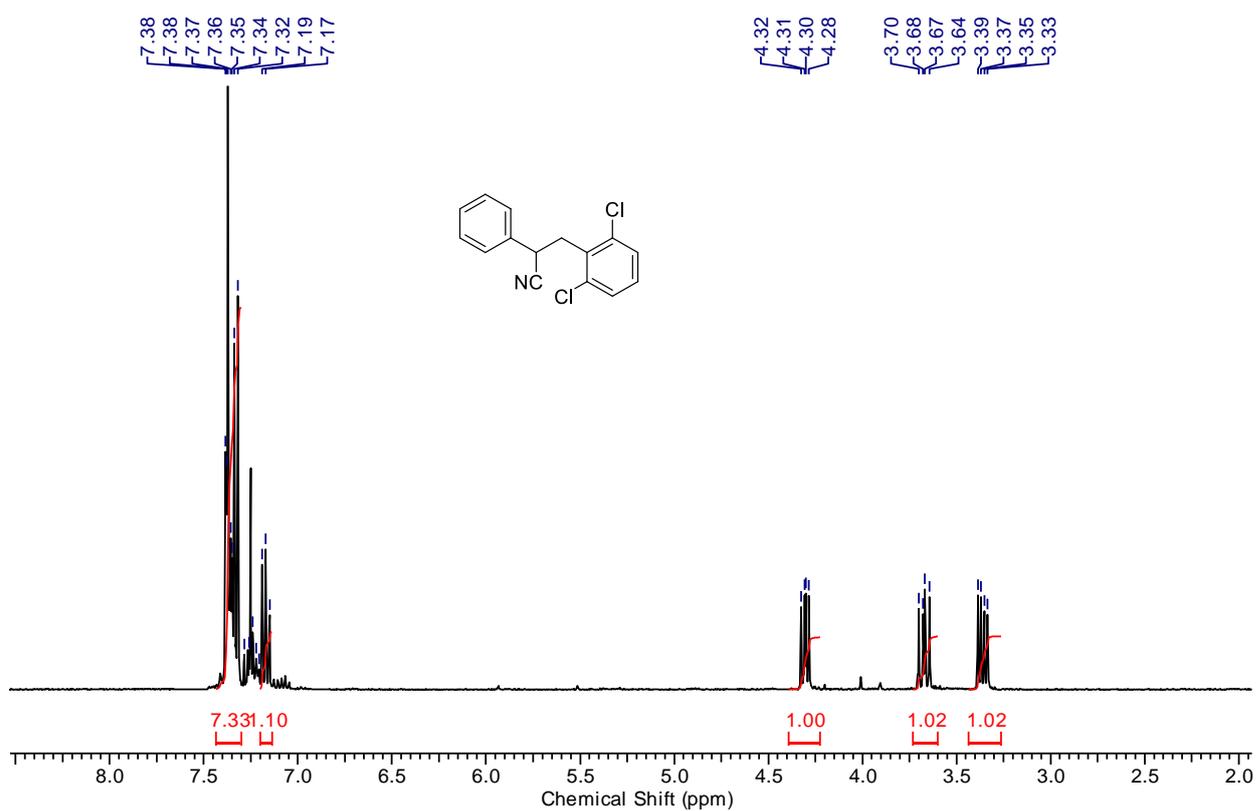
**Figure S16.** <sup>13</sup>C NMR spectrum of **3g** (CDCl<sub>3</sub>, 100.6 MHz, 300K).



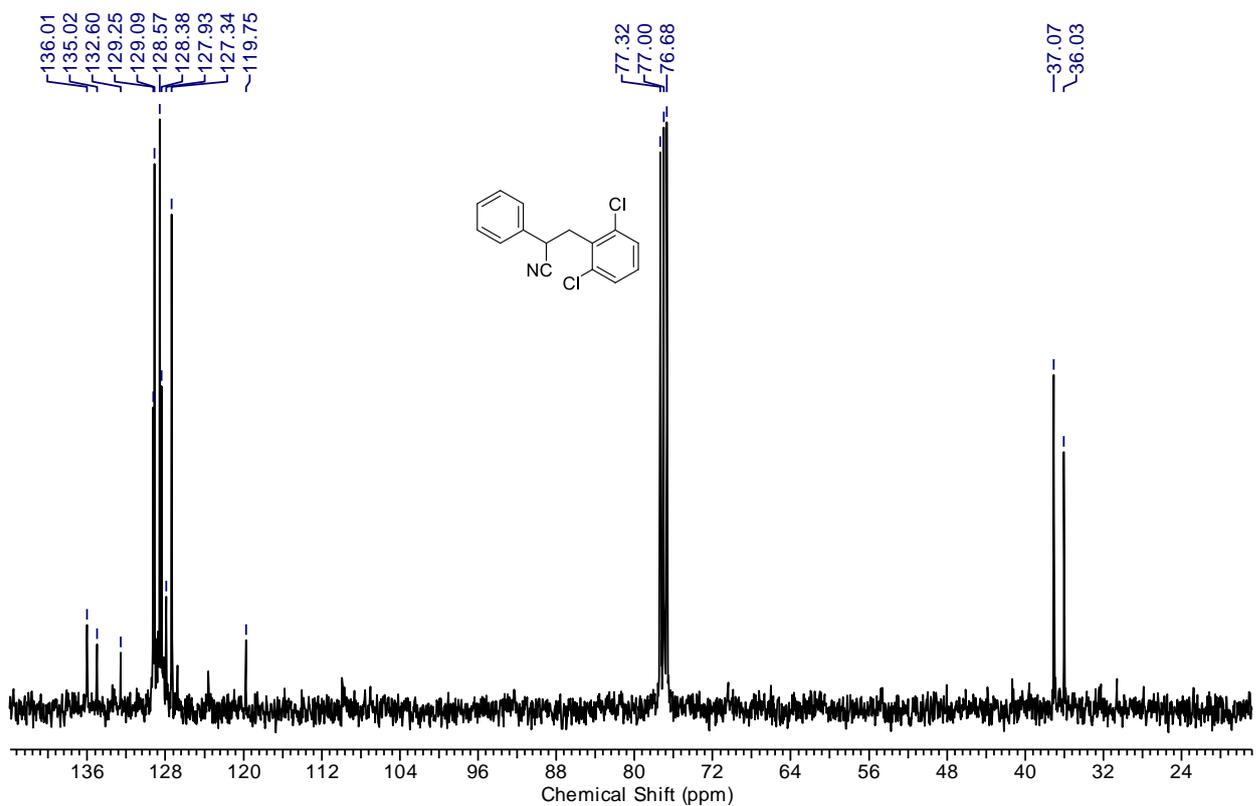
**Figure S17.** <sup>1</sup>H NMR spectrum of **3h** (CDCl<sub>3</sub>, 400MHz, 300K).



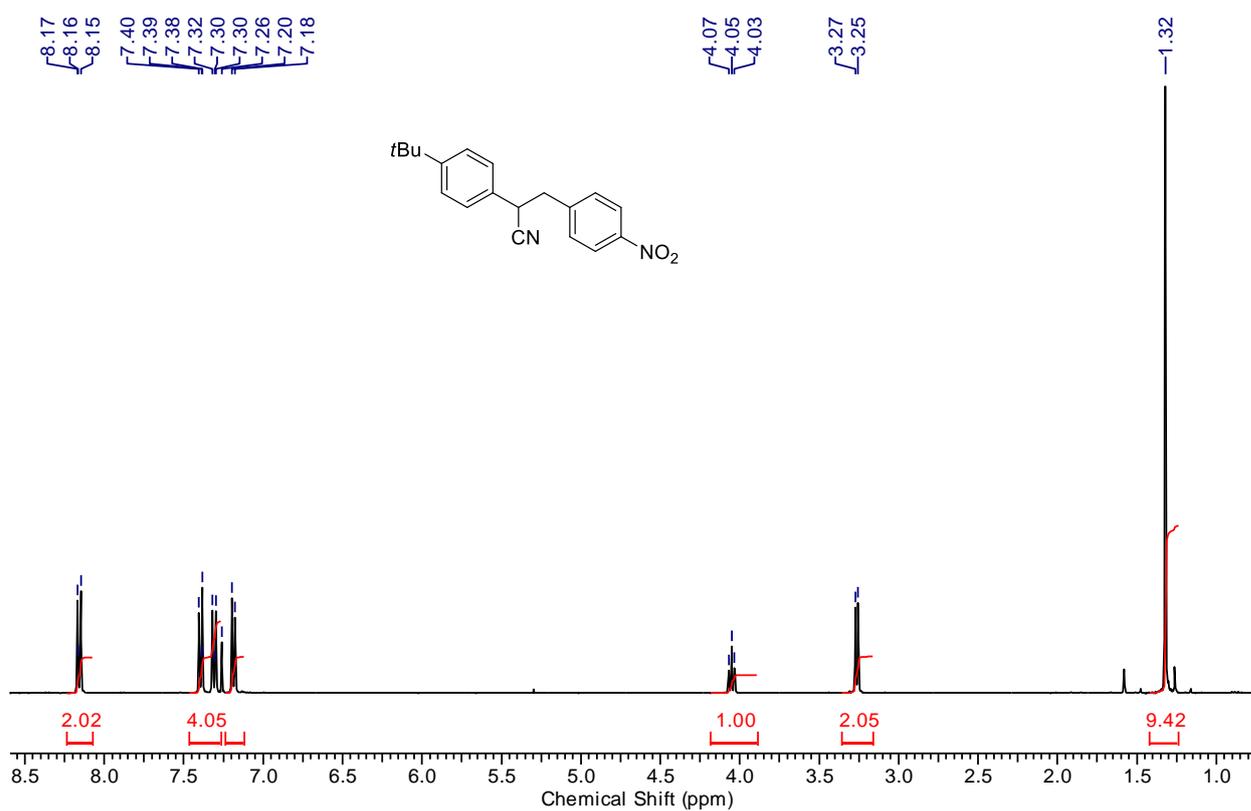
**Figure S18.** <sup>13</sup>C NMR spectrum of **3h** (CDCl<sub>3</sub>, 100.6 MHz, 300K).



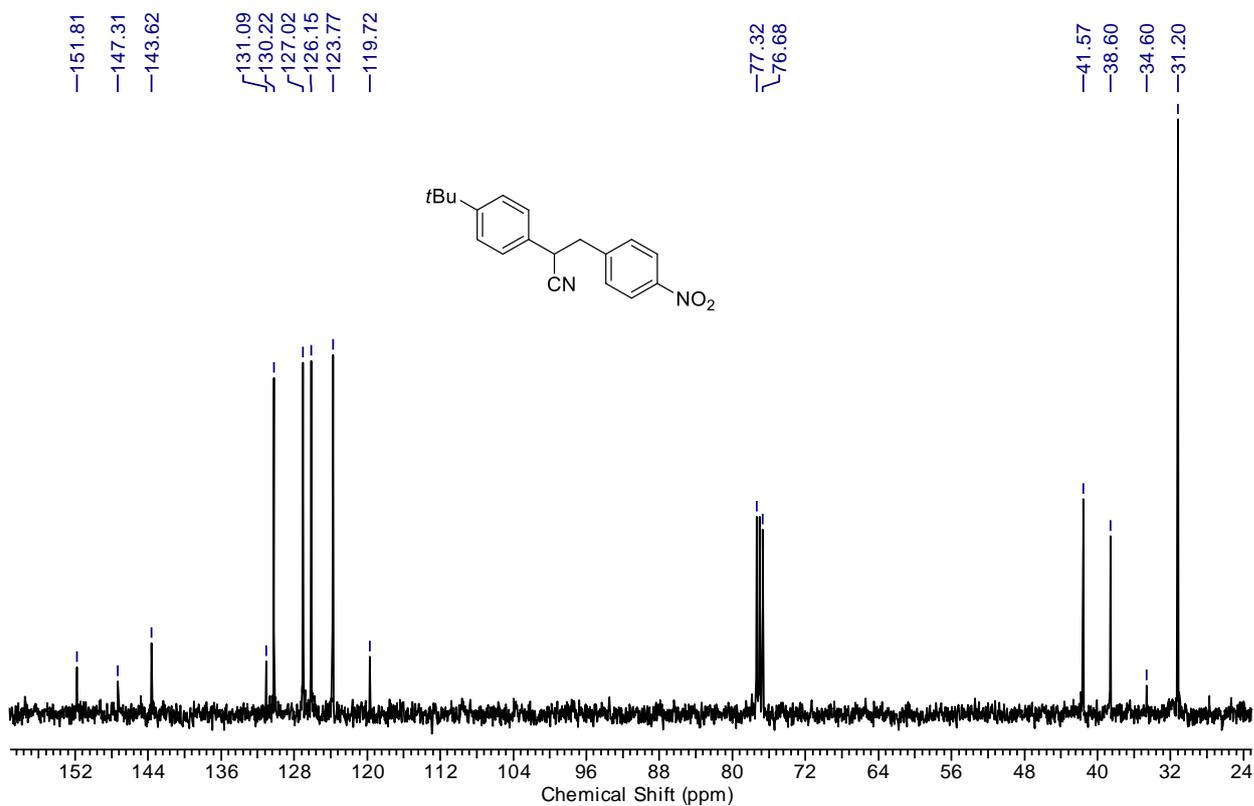
**Figure S19.** <sup>1</sup>H NMR spectrum of **3i** (CDCl<sub>3</sub>, 400MHz, 300K).



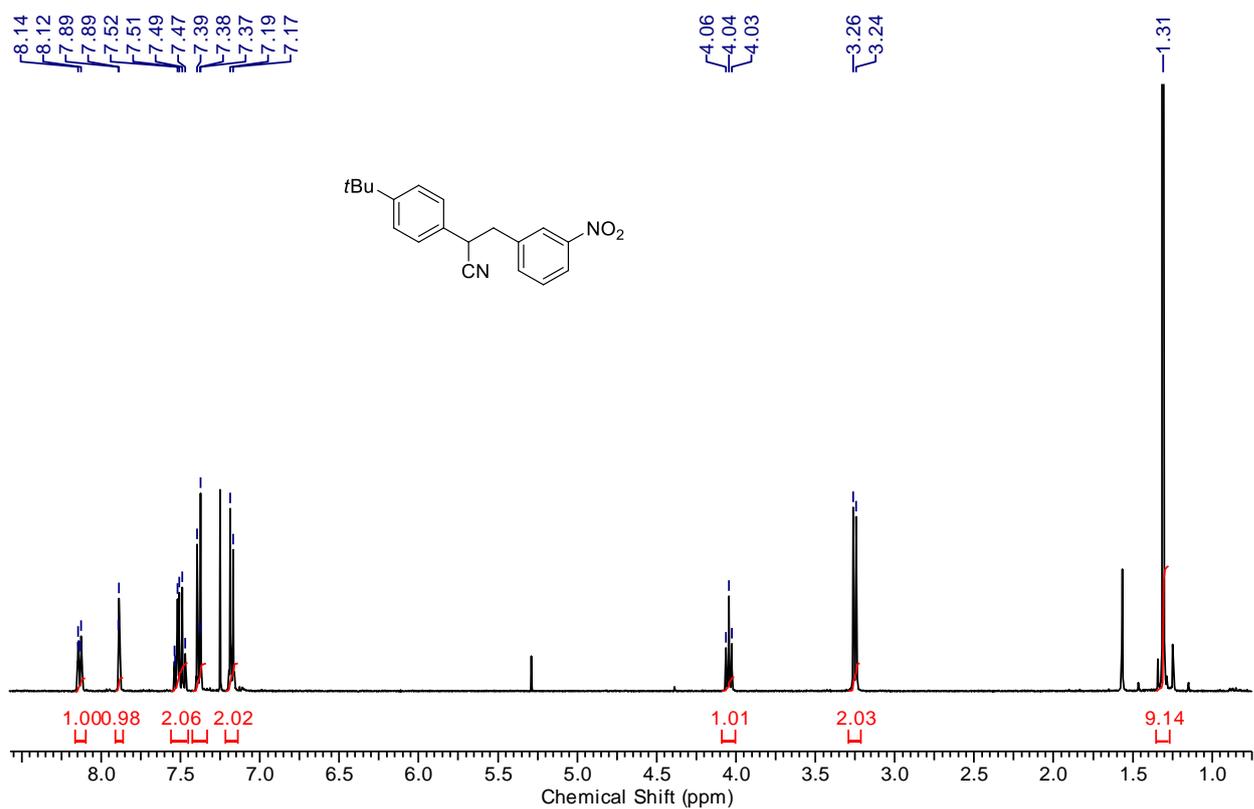
**Figure S20.** <sup>13</sup>C NMR spectrum of **3i** (CDCl<sub>3</sub>, 100.6 MHz, 300K).



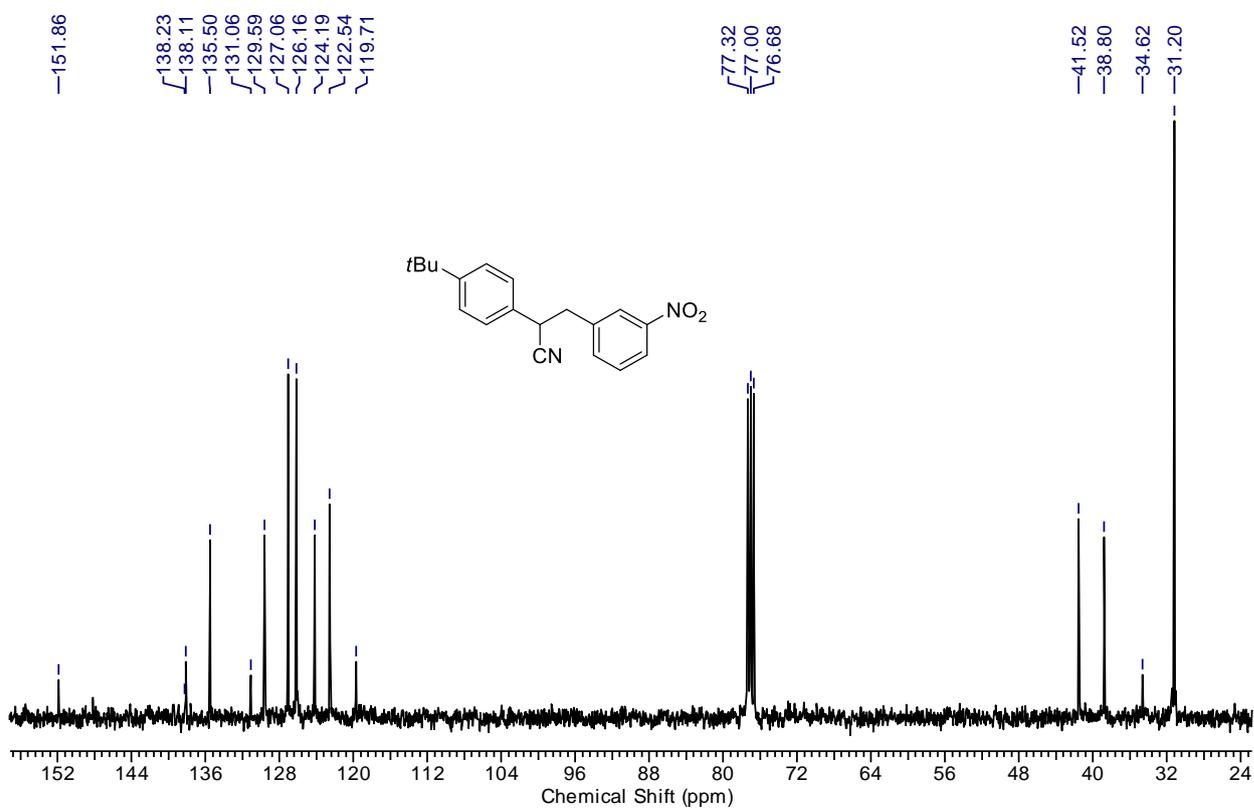
**Figure S21.** <sup>1</sup>H NMR spectrum of **3j** (CDCl<sub>3</sub>, 400MHz, 300K).



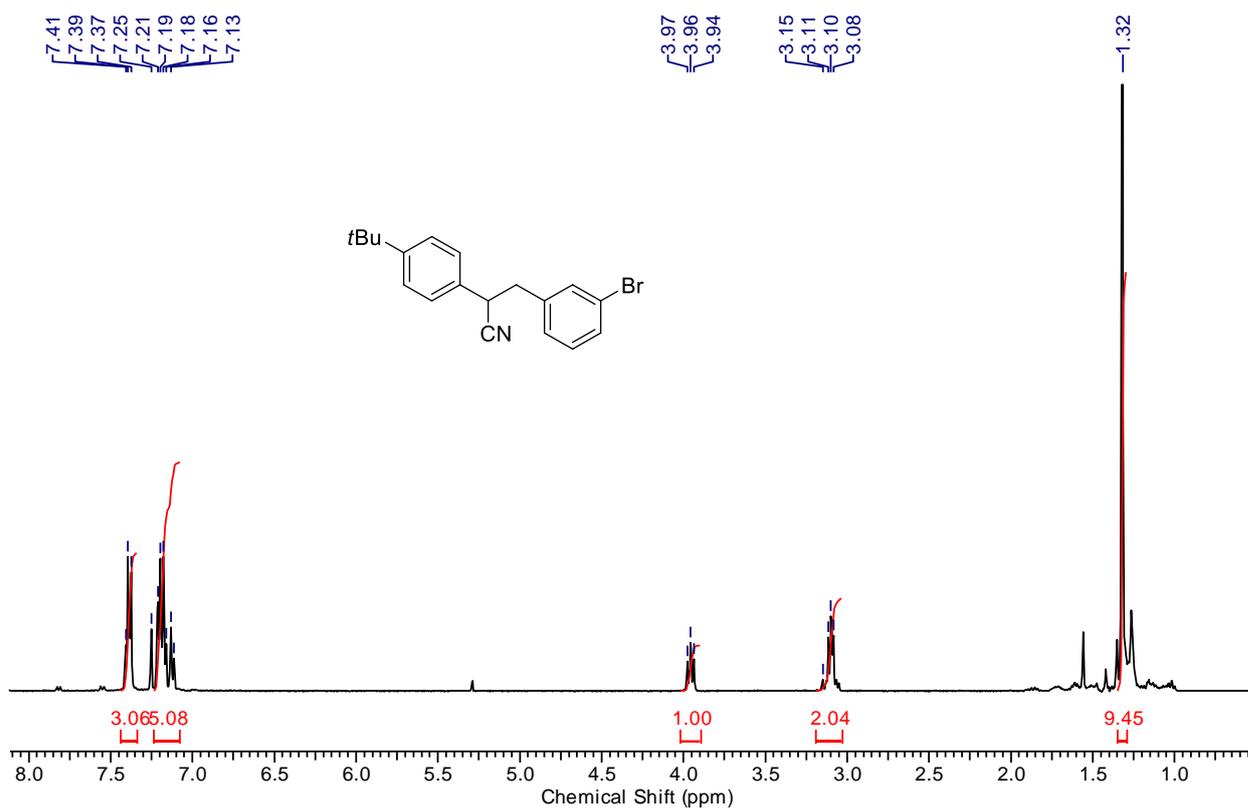
**Figure S22.** <sup>13</sup>C NMR spectrum of **3j** (CDCl<sub>3</sub>, 100.6 MHz, 300K).



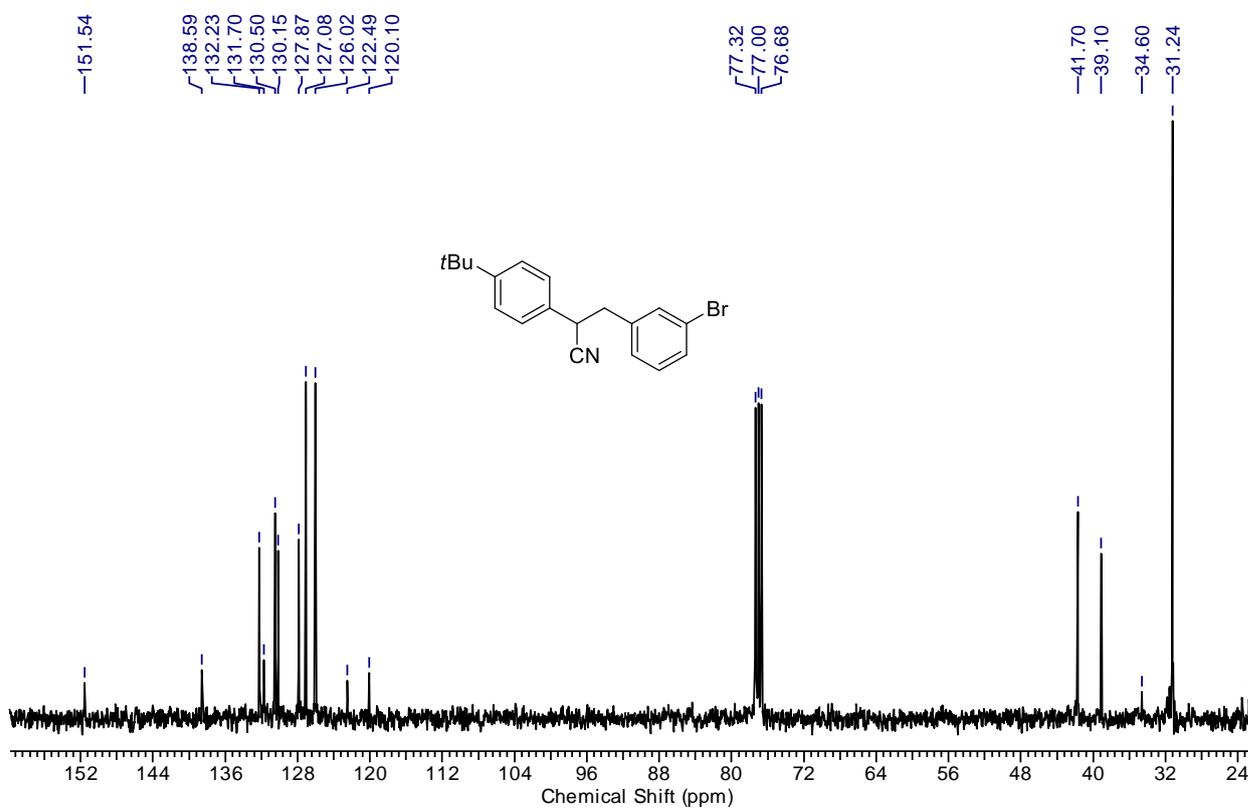
**Figure S23.** <sup>1</sup>H NMR spectrum of **3k** (CDCl<sub>3</sub>, 400 MHz, 300 K).



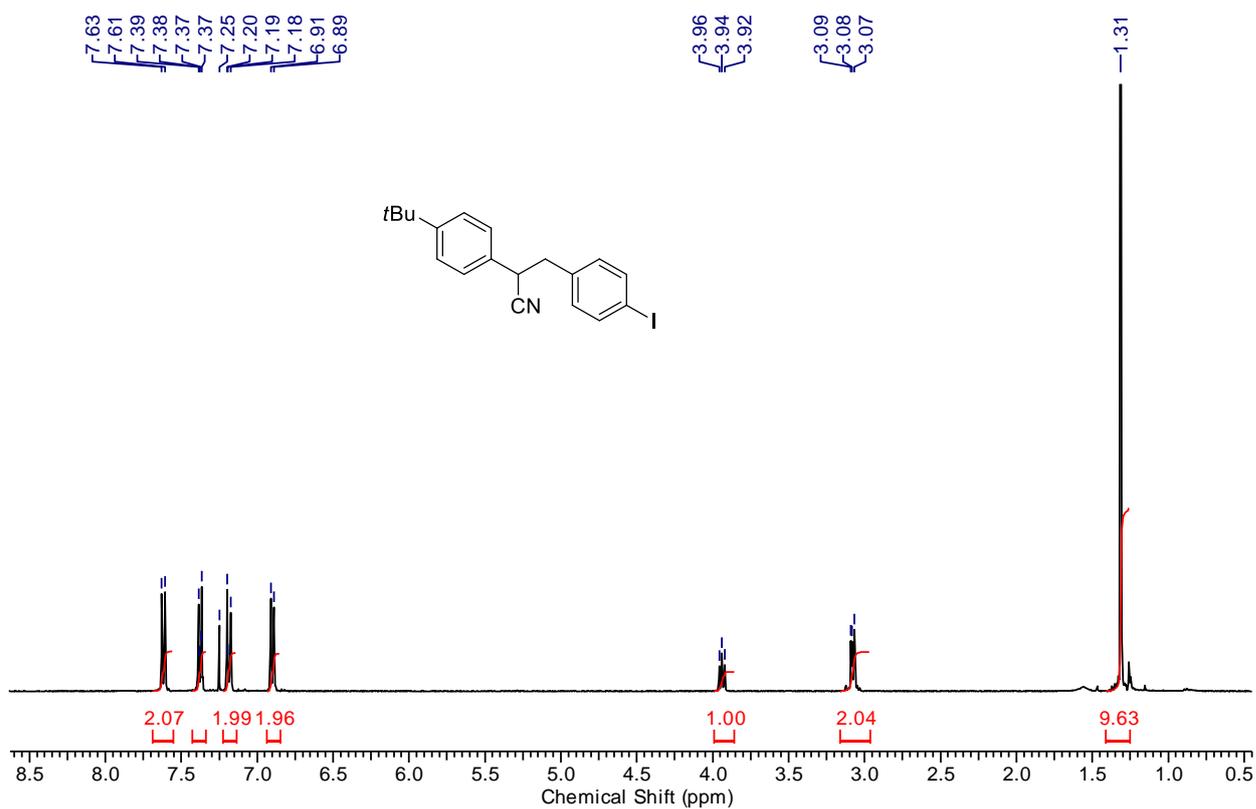
**Figure S24.** <sup>13</sup>C NMR spectrum of **3k** (CDCl<sub>3</sub>, 100.6 MHz, 300 K).



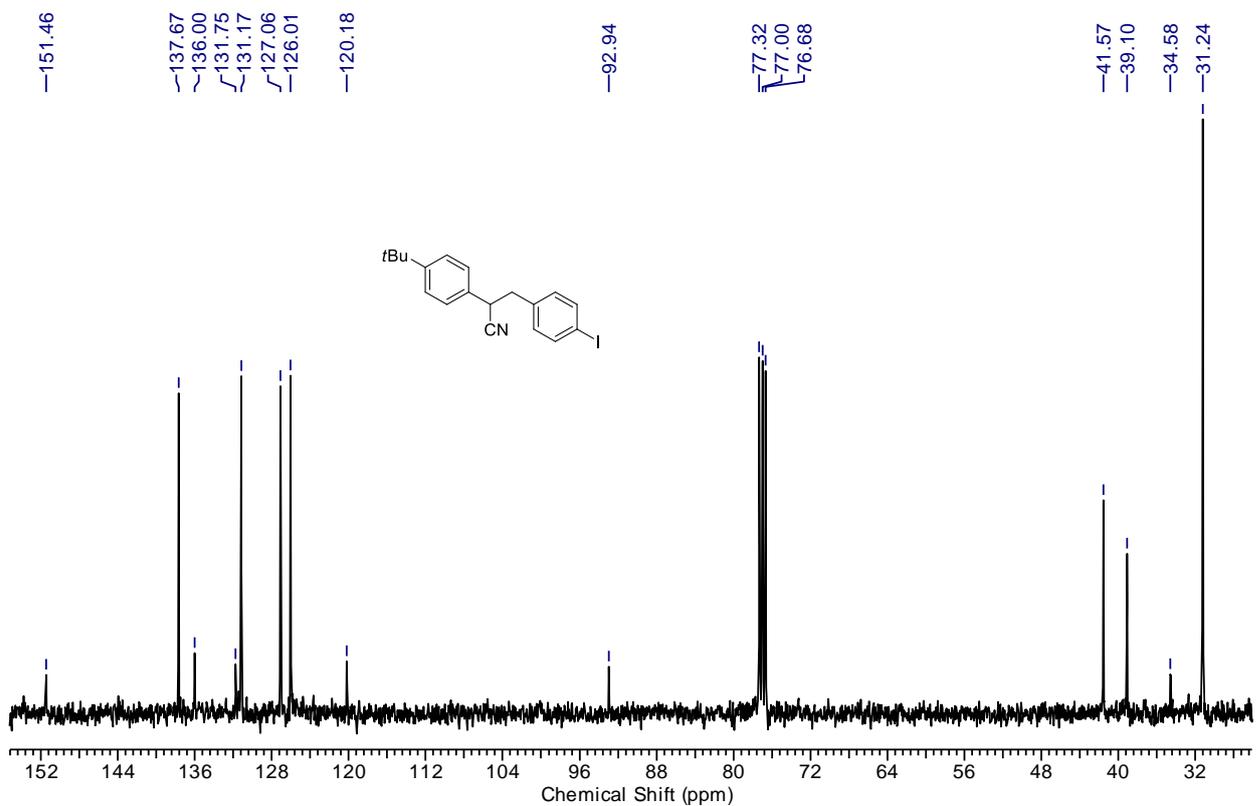
**Figure S25.** <sup>1</sup>H NMR spectrum of **3I** (CDCl<sub>3</sub>, 400MHz, 300K).



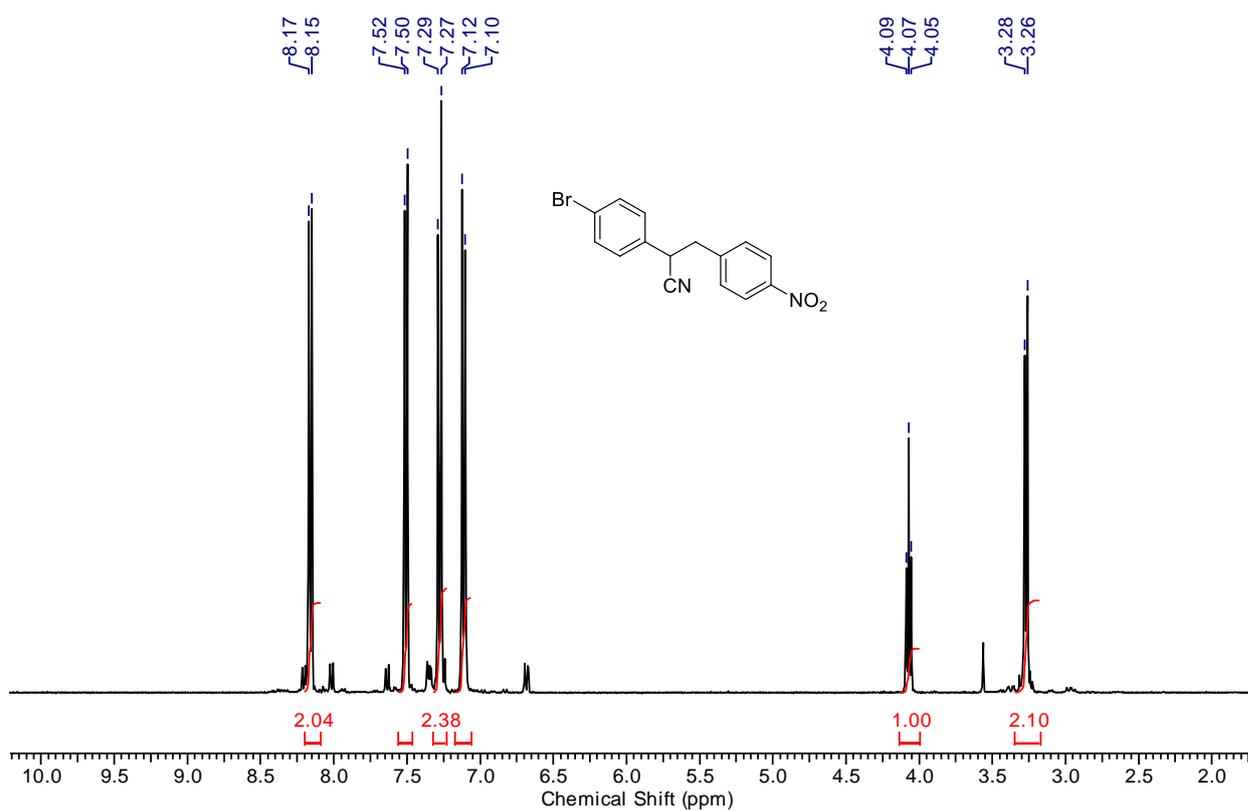
**Figure S26.** <sup>13</sup>C NMR spectrum of **3I** (CDCl<sub>3</sub>, 100.6 MHz, 300K).



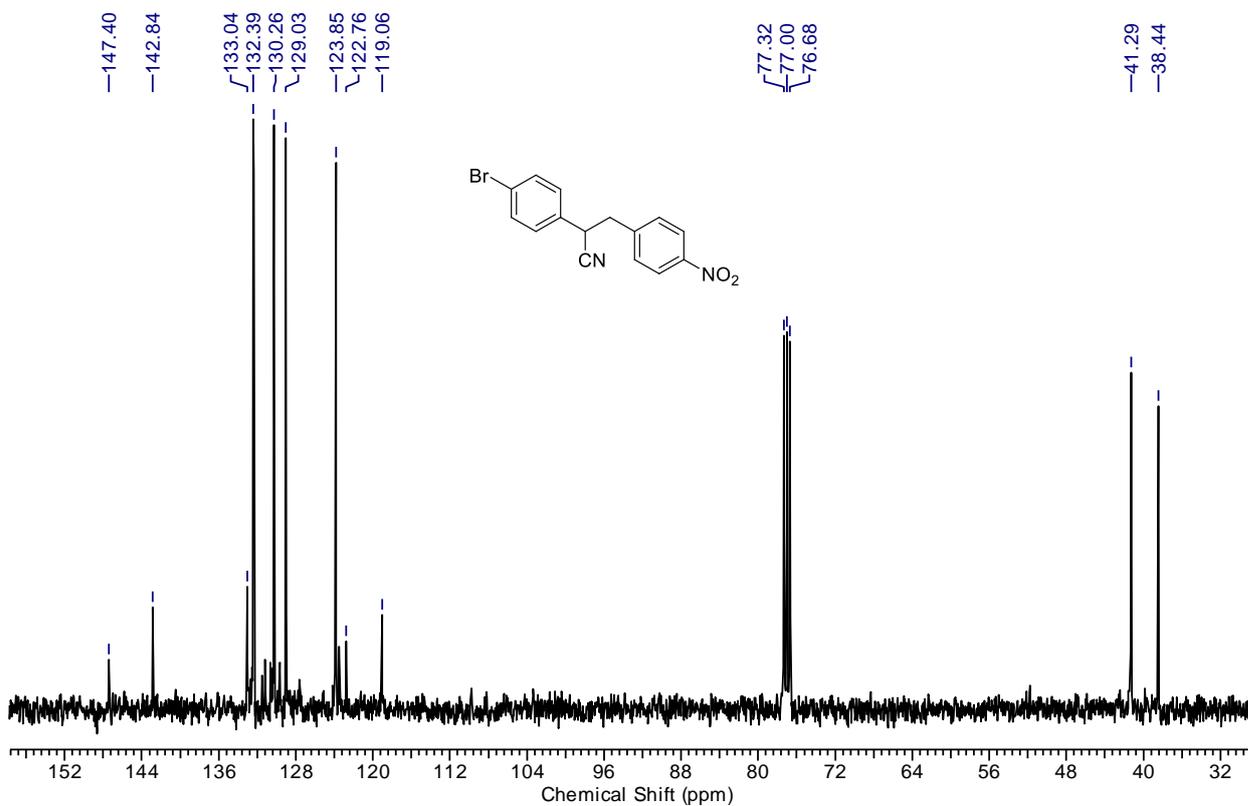
**Figure S27.** <sup>1</sup>H NMR spectrum of **3m** (CDCl<sub>3</sub>, 400MHz, 300K).



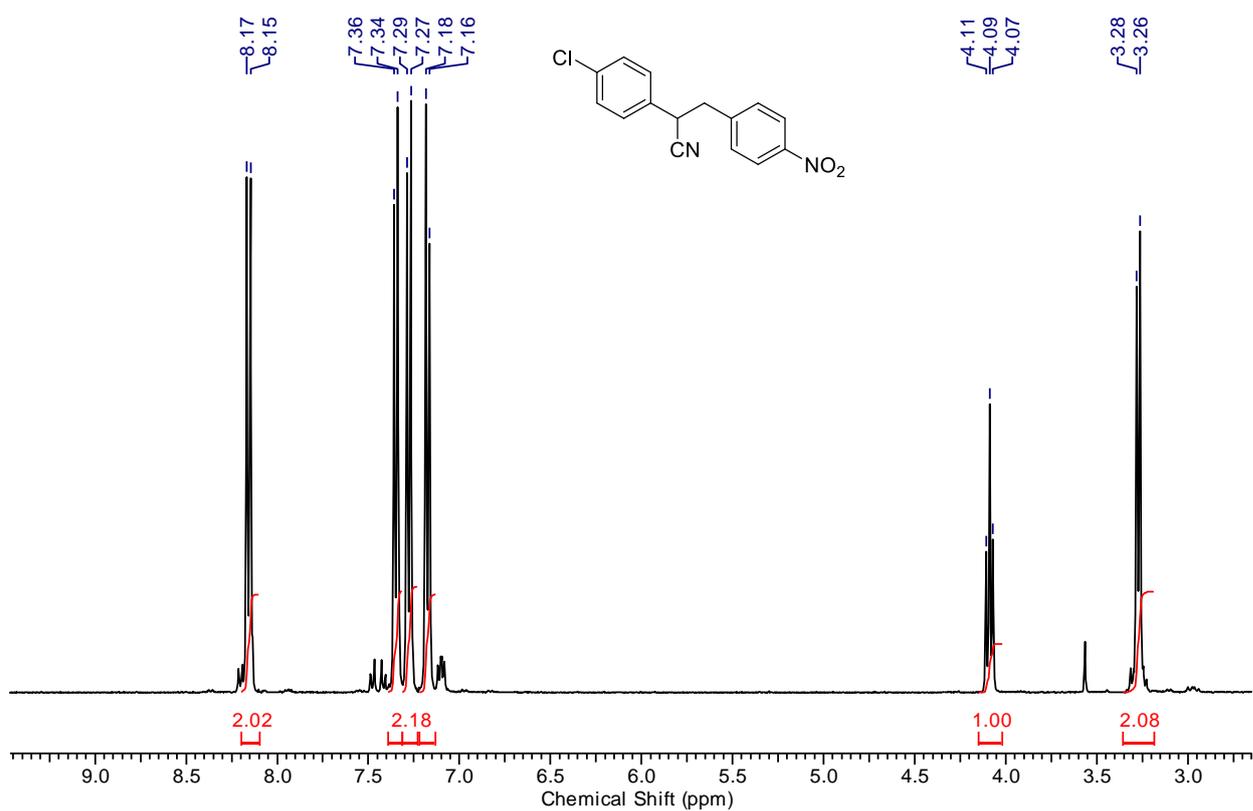
**Figure S28.** <sup>13</sup>C NMR spectrum of **3m** (CDCl<sub>3</sub>, 100.6 MHz, 300K).



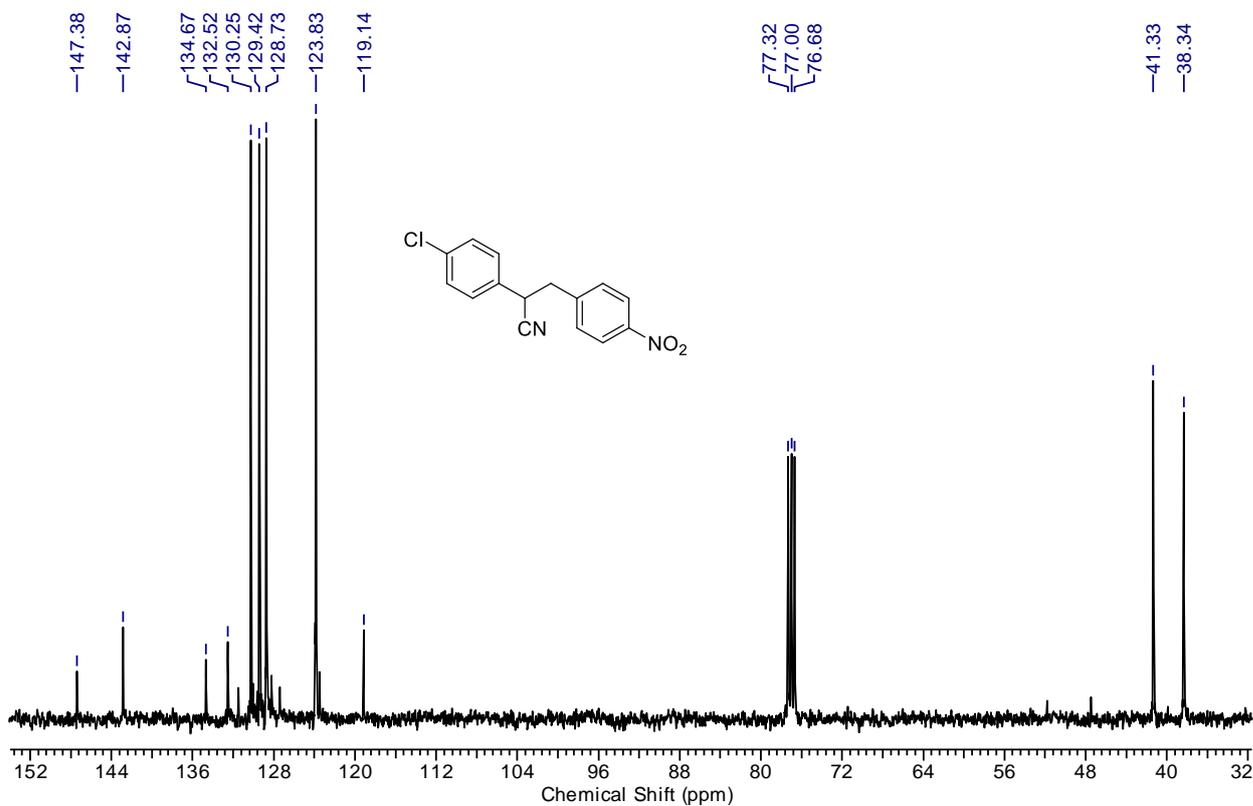
**Figure S29.**  $^1\text{H}$  NMR spectrum of **3n** ( $\text{CDCl}_3$ , 400MHz, 300K).



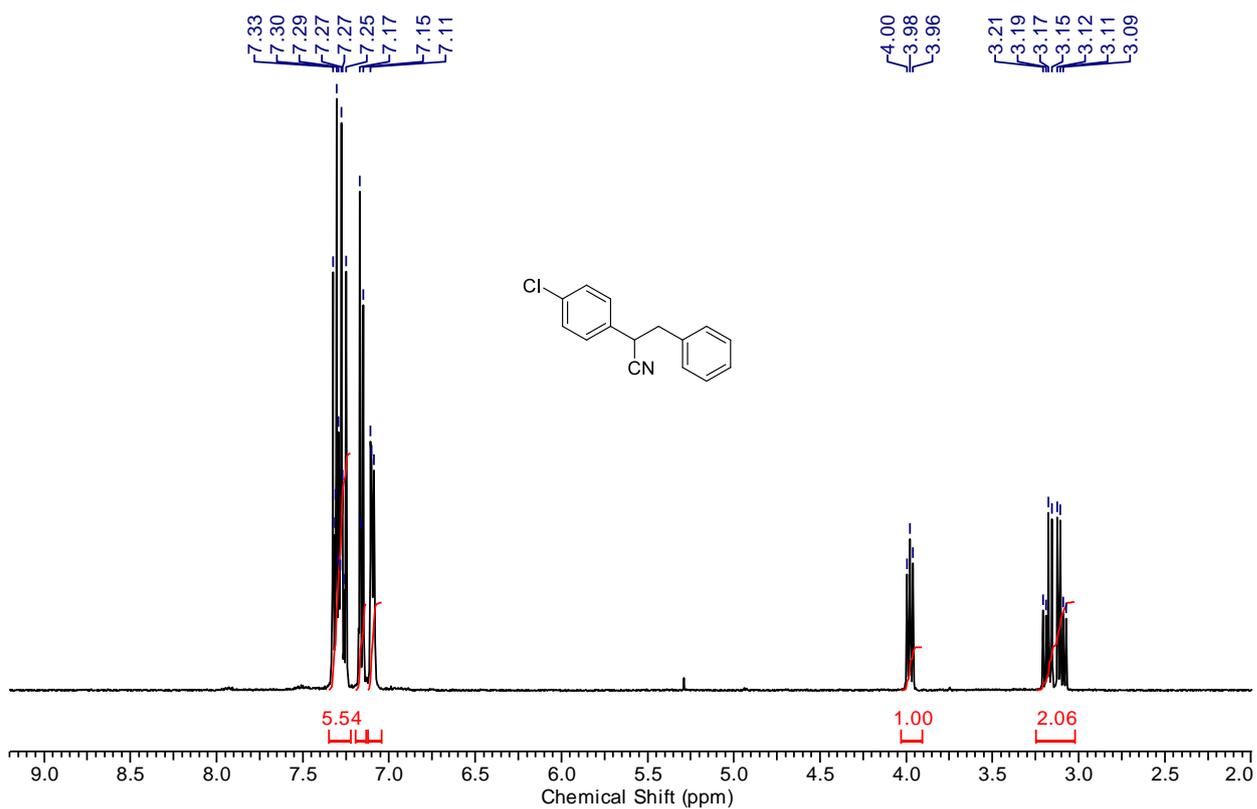
**Figure S30.**  $^{13}\text{C}$  NMR spectrum of **3n** ( $\text{CDCl}_3$ , 100.6 MHz, 300K).



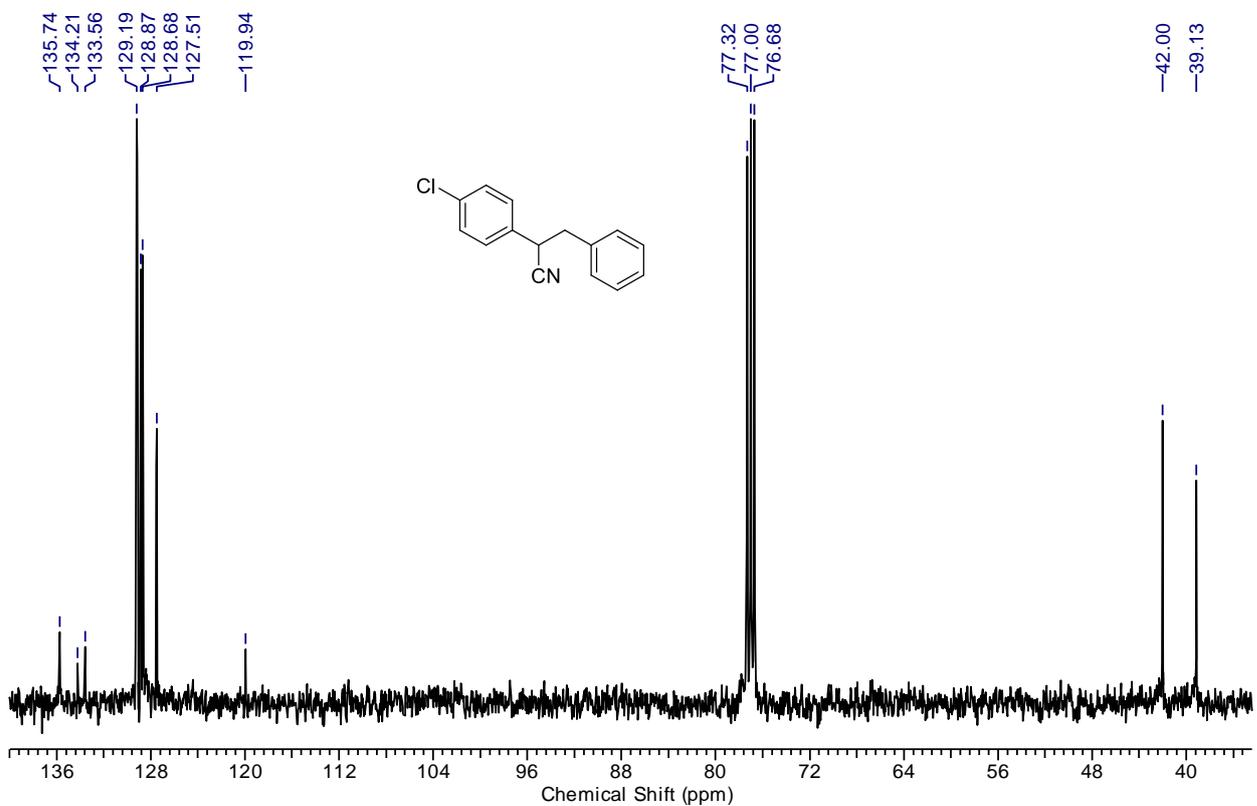
**Figure 31.**  $^1\text{H}$  NMR spectrum of **3o** ( $\text{CDCl}_3$ , 400MHz, 300K).



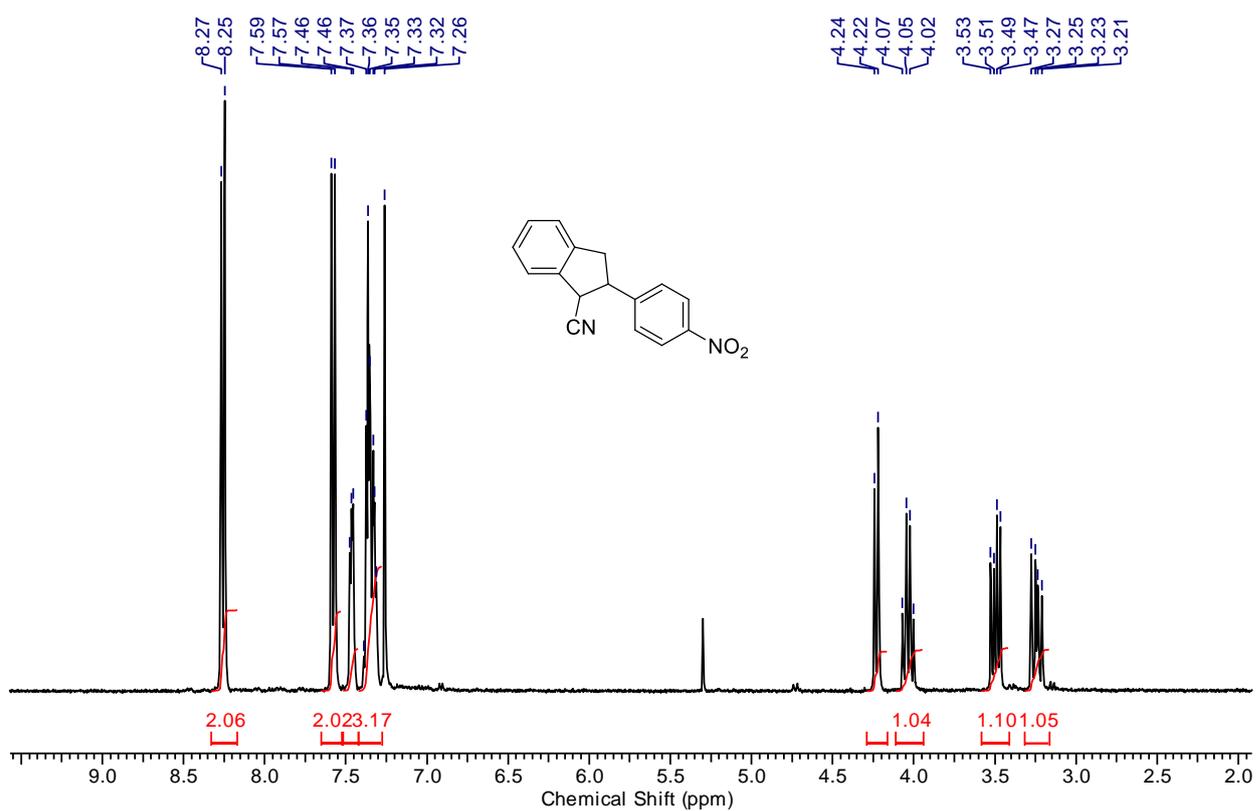
**Figure S32.**  $^{13}\text{C}$  NMR spectrum of **3o** ( $\text{CDCl}_3$ , 100.6 MHz, 300K).



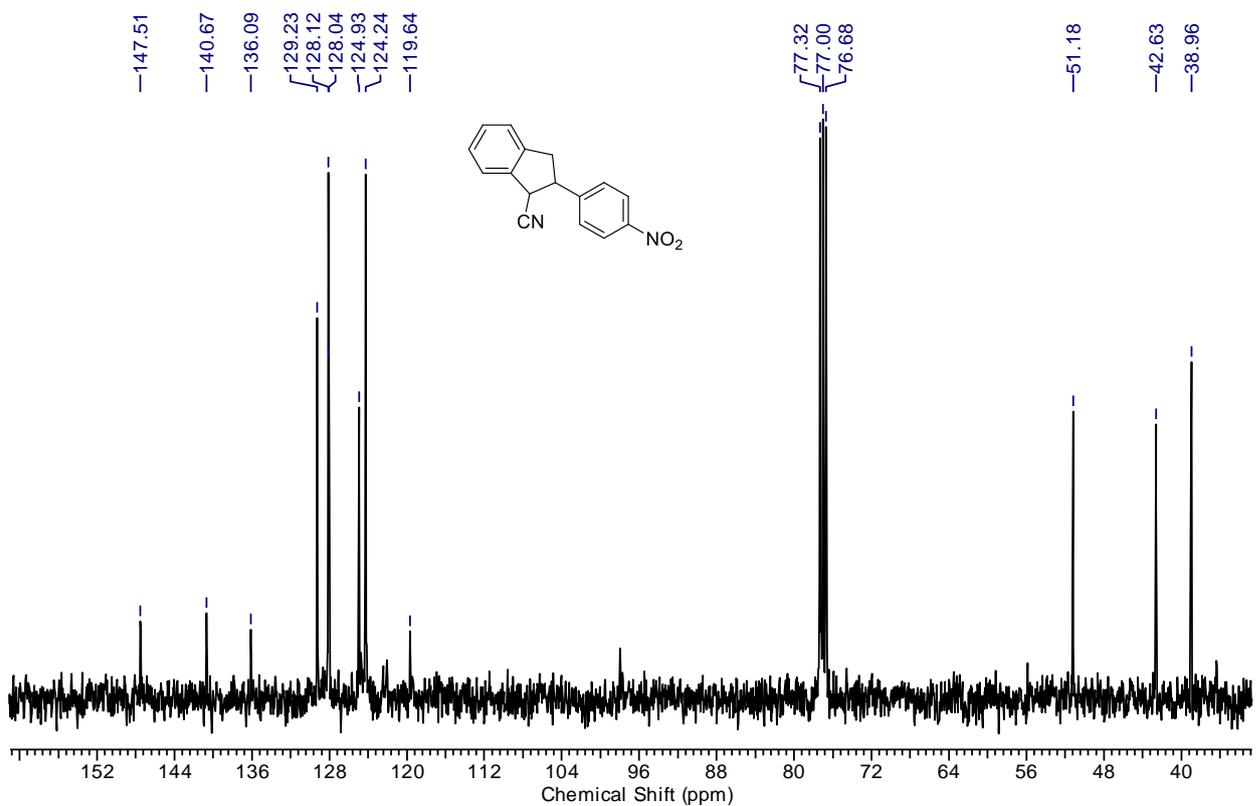
**Figure S33.**  $^1\text{H}$  NMR spectrum of **3p** ( $\text{CDCl}_3$ , 400MHz, 300K).



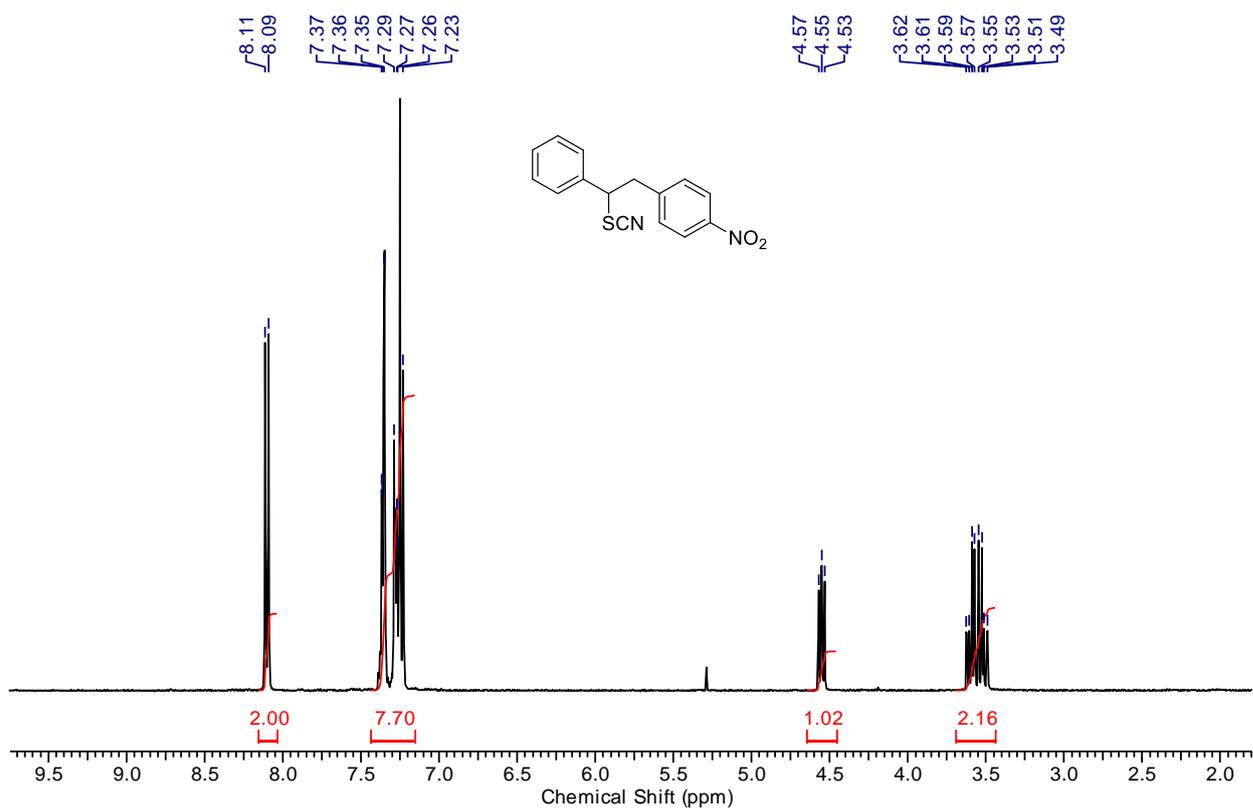
**Figure S34.**  $^{13}\text{C}$  NMR spectrum of **3p** ( $\text{CDCl}_3$ , 100.6 MHz, 300K).



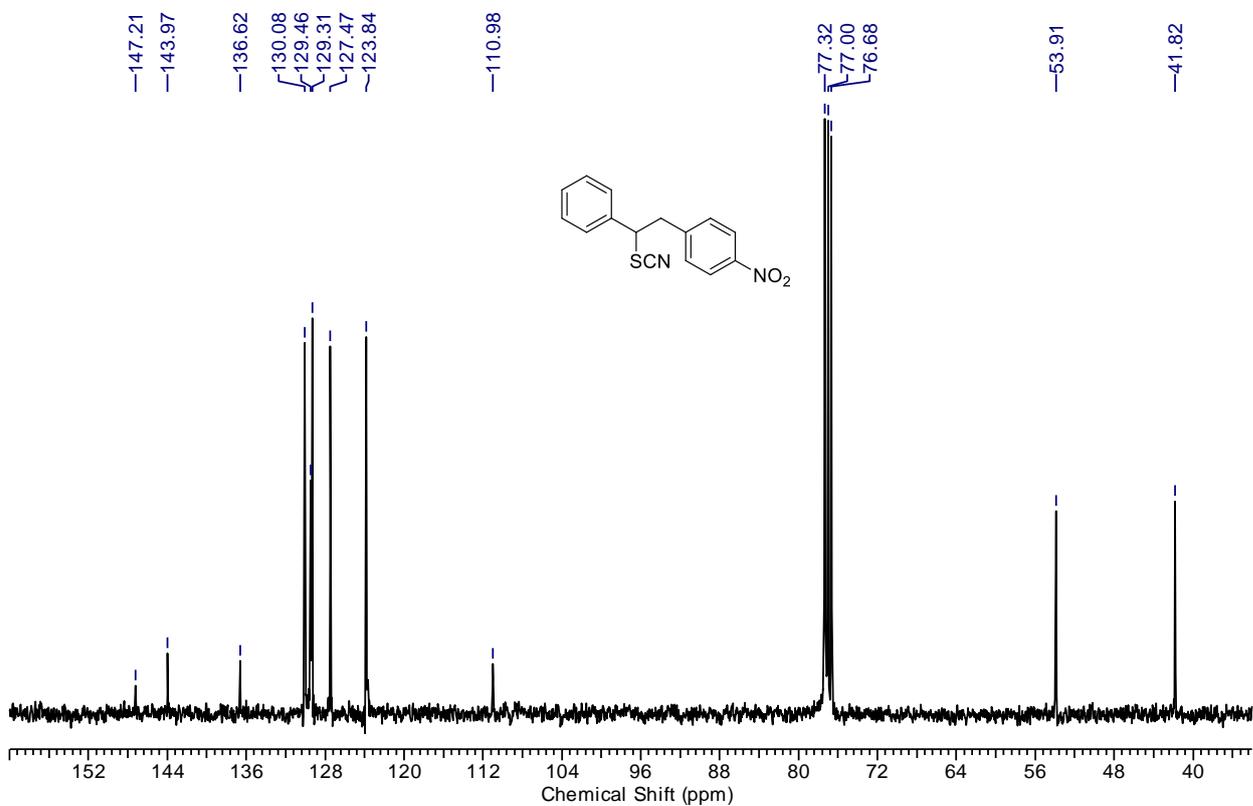
**Figure S35.** <sup>1</sup>H NMR spectrum of **3q** (CDCl<sub>3</sub>, 400MHz, 300K).



**Figure S36.** <sup>13</sup>C NMR spectrum of **3q** (CDCl<sub>3</sub>, 100.6 MHz, 300K).



**Figure S37.** <sup>1</sup>H NMR spectrum of **4** (CDCl<sub>3</sub>, 400MHz, 300K).



**Figure S38.** <sup>13</sup>C NMR spectrum of **4** (CDCl<sub>3</sub>, 100.6 MHz, 300K).