Supporting Information

Solvent-Controlled Silver Catalyzed Radical Transformation of α-Imino-Oxy Acids with Cyclic Aldimines

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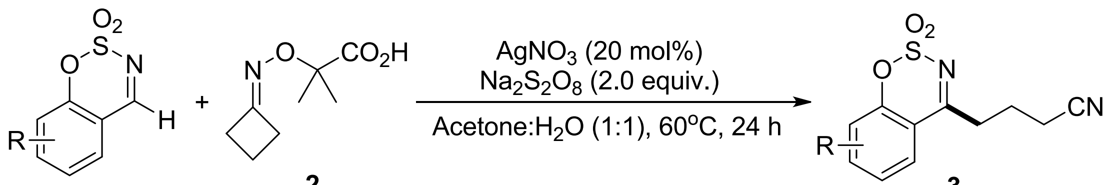
General information:

^{1}H, and ^{13}C were recorded at Bruker 400 MHz (^{1}H NMR) and 100 MHz (^{13}C NMR). Chemical shifts were reported in ppm from the solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm, 77.0 ppm). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), br (broad). Coupling constants were reported in Hertz (Hz). Melting points were measured with a XT-4 melting point apparatus without correction. X-ray structural analysis was conducted on the XtaLAB mini.

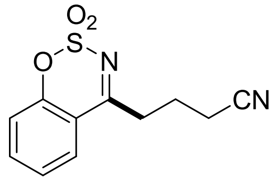
Materials: All commercially available reagents and solvent were used without further purification. Analytical thin layer chromatography was performed on 0.25 mm silica gel plates. Silica gel (200-300 mesh) was used for flash chromatography. α-Imino-oxy acids[1] and cyclic aldimines[2] were prepared according to the literatures.

General Procedure for the Cyanoalkylation of α-Imino-Oxy Acids with Cyclic Aldimines:



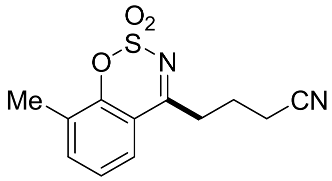
To a 10 mL Schlenk charged with cyclic aldimines **1** (0.2 mmol), α-imino-oxy acids **2** (0.4 mmol), $AgNO_3$ (6.8 mg, 0.04 mmol), and $Na_2S_2O_8$ (96 mg, 0.4 mmol) were added acetone (1.0 mL) and distilled H_2O (1.0 mL) *via* a syringe. Then, the reaction mixture was vigorously stirred at 60 °C for 24 h. After the reaction was complete, the mixture was diluted with water (5 mL) and extracted with ethyl acetate (3 × 5 mL). The organic layers were combined and washed with saturated brine (10 mL), dried anhydrous $MgSO_4$, and then concentrated in vacuo. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc as the eluent) to afford the desired products **3**.

4-(2,2-dioxidobenzo[e][1,2,3]oxathiazin-4-yl)butanenitrile (3a)



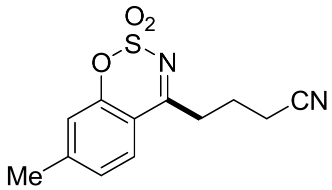
White solid, 80% yield, mp 108–109 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.20–2.27 (m, 2H), 2.60 (t, *J* = 6.8 Hz, 2H), 3.27 (t, *J* = 6.8 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.74 (t, *J* = 7.6 Hz, 1H), 7.83 (d, *J* = 7.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.6, 153.4, 137.3, 127.5, 126.1, 119.3, 118.7, 115.9, 33.3, 20.3, 16.4.

4-(8-methyl-2,2-dioxidobenzo[e][1,2,3]oxathiazin-4-yl)butanenitrile (3b)



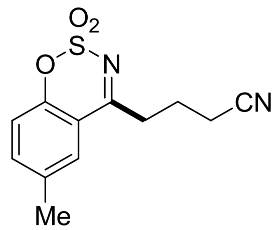
White solid, 67% yield, mp 104–105 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.19–2.26 (m, 2H), 2.40 (s, 3H), 2.60 (t, *J* = 6.8 Hz, 2H), 3.25 (t, *J* = 6.8 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.58 (d *J* = 7.6 Hz, 1H), 7.66 (d, *J* = 7.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.9, 151.8, 138.6, 129.1, 125.3, 125.1, 118.8, 115.7, 33.4, 20.4, 16.4, 14.9.

4-(7-methyl-2,2-dioxidobenzo[e][1,2,3]oxathiazin-4-yl)butanenitrile (3c)



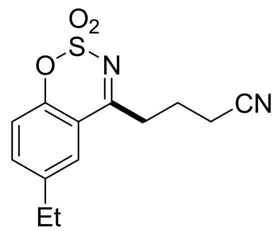
Viscous oil, 66% yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.18–2.25 (m, 2H), 2.48 (s, 3H), 2.59 (t, *J* = 6.8 Hz, 2H), 3.22 (t, *J* = 6.8 Hz, 2H), 7.11 (s, 1H), 7.21 (dd, *J* = 8.0 Hz, 0.8 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.5, 153.5, 149.8, 127.4, 127.0, 119.3, 118.8, 113.5, 33.2, 22.0, 20.4, 16.3.

4-(6-methyl-2,2-dioxidobenzo[e][1,2,3]oxathiazin-4-yl)butanenitrile (3d)



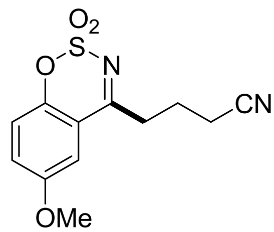
White solid, 65% yield, mp 84–85 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.18–2.25 (m, 2H), 2.44 (s, 3H), 2.59 (t, *J* = 6.8 Hz, 2H), 3.24 (t, *J* = 6.8 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.60 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.7, 151.3, 138.0, 136.2, 127.4, 118.9, 115.6, 33.2, 20.8, 20.2, 16.3.

4-(6-ethyl-2,2-dioxidobenzo[e][1,2,3]oxathiazin-4-yl)butanenitrile (3e)



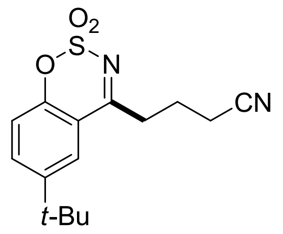
White solid, 68% yield, mp 88–89 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.28 (t, *J* = 7.6 Hz, 3H), 2.20–2.26 (m, 2H), 2.61 (t, *J* = 6.8 Hz, 2H), 2.73 (q, *J* = 7.6 Hz, 2H), 3.26 (t, *J* = 6.8 Hz, 2H), 7.23 (d, *J* = 8.8 Hz, 1H), 7.56 (dd, *J* = 8.4 Hz, 2.0 Hz, 1H), 7.60 (d, *J* = 1.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.7, 151.5, 142.5, 137.0, 126.3, 119.0, 118.9, 115.7, 33.2, 28.2, 20.3, 16.4, 15.4.

4-(6-methoxy-2,2-dioxidobenzo[e][1,2,3]oxathiazin-4-yl)butanenitrile (3f)



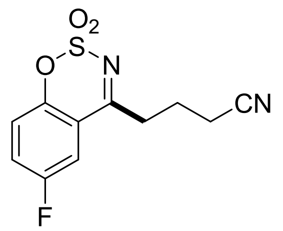
White solid, 57% yield, mp 101–102 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.19–2.26 (m, 2H), 2.60 (t, *J* = 6.8 Hz, 2H), 3.23 (t, *J* = 6.8 Hz, 2H), 3.88 (s, 3H), 7.21–7.23 (m, 1H), 7.25–2.29 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.5, 156.9, 147.1, 123.5, 120.2, 118.9, 116.3, 110.8, 56.1, 33.3, 20.3, 16.3.

4-(6-(tert-butyl)-2,2-dioxidobenzo[e][1,2,3]oxathiazin-4-yl)butanenitrile (3g)



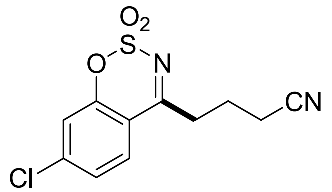
White solid, 71% yield, mp 102–103 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.35 (m, 9H), 2.18–2.25 (m, 2H), 2.60 (t, *J* = 6.8 Hz, 2H), 3.27 (t, *J* = 6.8 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 1H), 7.75–7.78 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.1, 151.1, 149.5, 134.9, 123.7, 118.9, 118.6, 115.3, 34.8, 33.1, 31.0, 20.4, 16.3.

4-(6-fluoro-2,2-dioxidobenzo[e][1,2,3]oxathiazin-4-yl)butanenitrile (3h)



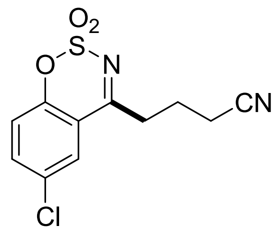
White solid, 53% yield, mp 94–95 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.18–2.25 (m, 2H), 2.59 (t, *J* = 6.8 Hz, 2H), 3.22 (t, *J* = 6.8 Hz, 2H), 7.32 (dd, *J* = 8.8 Hz, 4.4 Hz, 1H), 7.46 (dt, *J* = 8.8 Hz, 2.4 Hz, 1H), 7.52 (dd, *J* = 7.6 Hz, 2.4 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.9, 159.0 (d, J_{C-F} = 247.6 Hz), 149.3, 124.5 (d, J_{C-F} = 23.8 Hz), 121.1 (d, J_{C-F} = 8.0 Hz), 118.7, 116.5 (d, J_{C-F} = 7.5 Hz), 113.2 (d, J_{C-F} = 25.1 Hz), 33.4, 20.0, 16.2; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -112.57 (s, 1F).

4-(7-chloro-2,2-dioxidobenzo[e][1,2,3]oxathiazin-4-yl)butanenitrile (3i)



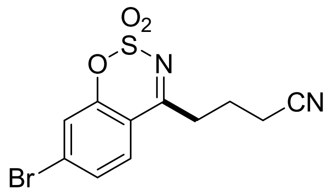
White solid, 51% yield, mp 95–96 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.18–2.25 (m, 2H), 2.60 (t, *J* = 6.8 Hz, 2H), 3.24 (t, *J* = 6.8 Hz, 2H), 7.34 (s, 1H), 7.40 (d, *J* = 8.4 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.8, 153.8, 143.5, 128.5, 126.6, 119.7, 118.7, 114.3, 33.3, 20.2, 16.3.

4-(6-chloro-2,2-dioxidobenzo[e][1,2,3]oxathiazin-4-yl)butanenitrile (3j)



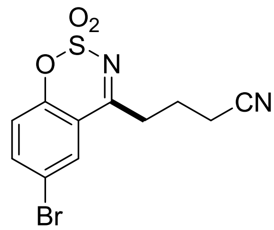
White solid, 62% yield, mp 97–99 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.21–2.28 (m, 2H), 2.62 (t, *J* = 6.8 Hz, 2H), 3.25 (t, *J* = 6.8 Hz, 2H), 7.29 (d, *J* = 8.8 Hz, 1H), 7.69 (dd, *J* = 8.8 Hz, 2.4 Hz, 1H), 7.79 (d, *J* = 2.4 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.4, 151.8, 137.0, 131.6, 127.1, 120.8, 118.6, 116.7, 33.3, 20.0, 16.3.

4-(7-bromo-2,2-dioxidobenzo[e][1,2,3]oxathiazin-4-yl)butanenitrile (3k)



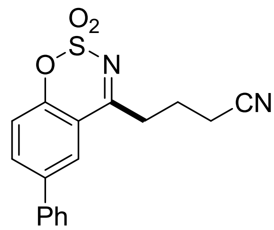
White solid, 40% yield, mp 107–108 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.18–2.26 (m, 2H), 2.60 (t, *J* = 6.8 Hz, 2H), 3.24 (t, *J* = 6.8 Hz, 2H), 7.51 (d, *J* = 2.0 Hz, 1H), 7.56 (dd, *J* = 8.8 Hz, 2.0 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.0, 153.6, 131.8, 129.6, 128.3, 122.7, 118.7, 114.6, 33.3, 20.2, 16.3.

4-(6-bromo-2,2-dioxidobenzo[e][1,2,3]oxathiazin-4-yl)butanenitrile (3l)



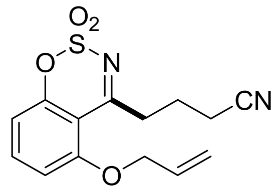
White solid, 52% yield, mp 113–115 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.21–2.28 (m, 2H), 2.62 (t, *J* = 6.8 Hz, 2H), 3.25 (t, *J* = 6.8 Hz, 2H), 7.23 (d, *J* = 8.8 Hz, 1H), 7.83 (dd, *J* = 8.4 Hz, 2.4 Hz, 1H), 7.93 (d, *J* = 2.4 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.3, 152.3, 139.9, 130.1, 121.0, 118.8, 118.7, 117.1, 33.3, 20.0, 16.3.

4-(2,2-dioxido-6-phenylbenzo[e][1,2,3]oxathiazin-4-yl)butanenitrile (3m)



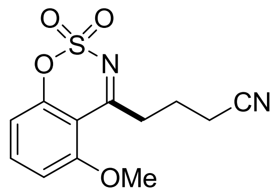
White solid, 44% yield, mp 103–105 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.23–2.30 (m, 2H), 2.62 (t, J = 6.8 Hz, 2H), 3.33 (t, J = 6.8 Hz, 2H), 7.39 (d, J = 8.4 Hz, 1H), 7.43–7.47 (m, 1H), 7.49–7.56 (m, 4H), 7.91 (d, J = 2.0 Hz, 1H), 7.93–7.95 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.6, 152.6, 139.8, 138.2, 136.0, 129.2, 128.6, 127.1, 125.8, 119.6, 118.8, 116.1, 33.3, 20.3, 16.4.

4-(5-(allyloxy)-2,2-dioxidobenzo[e][1,2,3]oxathiazin-4-yl)butanenitrile (3n)



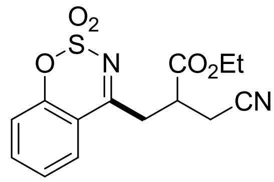
White solid, 36% yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.10–2.16 (m, 2H), 2.52 (t, J = 6.8 Hz, 2H), 3.36 (t, J = 6.8 Hz, 2H), 4.73 (d, J = 5.2 Hz, 2H), 5.42–5.49 (m, 2H), 6.05–6.15 (m, 1H), 6.88 (d, J = 8.4 Hz, 2H), 7.59 (t, J = 8.4 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 179.2, 158.5, 154.4, 137.1, 131.0, 120.4, 119.0, 111.2, 109.9, 108.0, 70.7, 38.5, 21.2, 16.4.

4-(5-methoxy-2,2-dioxidobenzo[e][1,2,3]oxathiazin-4-yl)butanenitrile (3o)



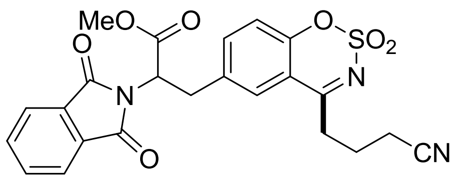
Viscous oil, 68% yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.11–2.18 (m, 2H), 2.55 (t, J = 6.8 Hz, 2H), 3.35 (t, J = 7.2 Hz, 2H), 4.02 (s, 3H), 6.90 (d, J = 8.4 Hz, 2H), 7.62 (t, J = 8.4 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 179.2, 159.5, 154.4, 137.3, 119.1, 111.2, 108.8, 107.9, 56.6, 38.4, 21.3, 16.5.

Ethyl 3-cyano-2-((2,2-dioxidobenzo[e][1,2,3]oxathiazin-4-yl)methyl)propanoate (3p)



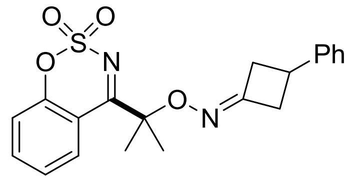
Viscous oil, 25% yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.27 (t, *J* = 7.2 Hz, 3H), 2.88–3.00 (m, 2H), 3.37–3.43 (m, 1H), 3.48–3.54 (m, 1H), 3.70–3.79 (m, 1H), 4.24 (q, *J* = 7.2 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.76 (t, *J* = 7.6 Hz, 1H), 7.87 (d, *J* = 7.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.1, 170.5, 153.5, 137.5, 127.6, 126.1, 119.3, 117.0, 115.8, 62.3, 37.1, 34.8, 19.2, 13.9.

methyl 3-(4-(3-cyanopropyl)-2,2-dioxidobenzo[e][1,2,3]oxathiazin-6-yl)-2-(1,3-dioxoisoindolin-2-yl)propanoate (3q)



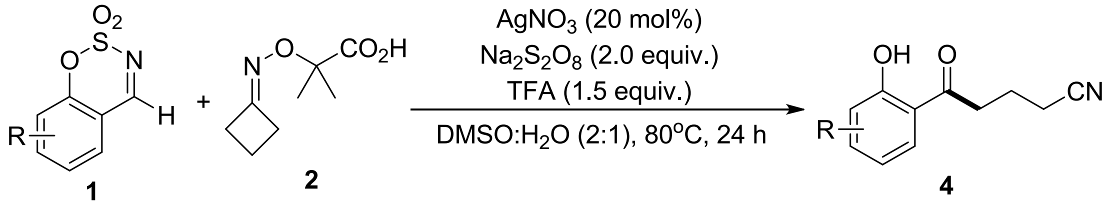
Viscous oil, 37% yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.10–2.17 (m, 2H), 2.55 (t, *J* = 6.8 Hz, 2H), 3.04–3.12 (m, 1H), 3.14–3.23 (m, 1H), 3.60 (dd, *J* = 14.8 Hz, 10.8 Hz, 1H), 3.68 (dd, *J* = 14.8 Hz, 5.6 Hz, 1H), 3.77 (s, 3H), 5.20 (dd, *J* = 10.8 Hz, 5.6 Hz, 1H), 7.12 (d, *J* = 8.8 Hz, 1H), 7.52 (dd, *J* = 8.8 Hz, 2.0 Hz, 1H), 7.68 (d, *J* = 1.6 Hz, 1H), 7.71–7.74 (m, 2H), 7.77–7.81 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.5, 168.5, 167.3, 152.1, 137.7, 135.0, 134.5, 131.1, 127.6, 123.7, 119.3, 118.8, 115.5, 53.1, 52.0, 33.9, 33.3, 20.4, 16.2.

4-(2-(((3-phenylcyclobutylidene)amino)oxy)propan-2-yl)benzo[e][1,2,3]oxathiazine 2,2-dioxide (3r)



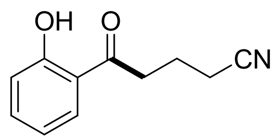
Viscous oil, 21% yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.25 (s, 6H), 2.86 (dd, *J* = 5.2 Hz, 1H), 2.97 (dd, *J* = 6.8 Hz, 1H), 3.48 (dd, J = 5.6 Hz, 1H), 3.61 (dd, J = 8.0 Hz, 1H), 3.79–3.85 (m, 1H), 7.29–7.40 (m, 1H), 7.72 (d, *J* = 7.6 Hz, 1H), 7.78 (t, *J* = 7.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.7, 153.5, 139.9, 137.3, 129.2, 128.2, 127.6, 127.0, 126.0, 119.3, 117.7, 116.0, 101.7, 39.5, 37.5, 29.6, 24.0.

General Procedure for the Opening-ring of α-Imino-Oxy Acids with Cyclic Aldimines:



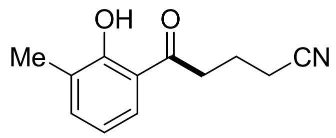
To a 10 mL Schlenk charged with cyclic aldimines **1** (0.2 mmol), α-imino-oxy acids **2** (0.4 mmol), $AgNO_3$ (6.8 mg, 0.04 mmol), $Na_2S_2O_8$ (96 mg, 0.4 mmol), and trifluoroacetic acid (35 mg, 0.3 mmol) were added DMSO (1.0 mL) and distilled H_2O (0.5 mL) *via* a syringe. Then, the reaction mixture was vigorously stirred at 80 °C for 24 h. After the reaction was complete, the mixture was diluted with water (5 mL) and extracted with ethyl acetate (3 × 5 mL). The organic layers were combined and washed with saturated brine (10 mL), dried anhydrous $MgSO_4$, and then concentrated in vacuo. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc as the eluent) to afford the desired products **4**.

5-(2-hydroxyphenyl)-5-oxopentanenitrile (4a)



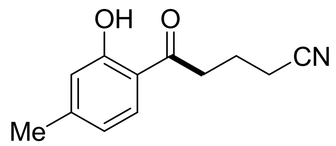
White solid, 78% yield, mp 42–43 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.09–2.16 (m, 2H), 2.53 (t, J = 6.8 Hz, 2H), 3.22 (t, J = 6.8 Hz, 2H), 6.92 (dt, J = 8.0 Hz, 0.8 Hz, 1H), 6.99 (dd, J = 8.4 Hz, 0.8 Hz, 1H), 7.49 (dt, J = 8.4 Hz, 1.6 Hz, 1H), 7.76 (dd, J = 8.0 Hz, 1.6 Hz, 1H), 12.08 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 204.0, 162.3, 136.7, 129.6, 119.1, 119.0, 118.6, 35.9, 19.5, 16.6.

5-(2-hydroxy-3-methylphenyl)-5-oxopentanenitrile (4b)



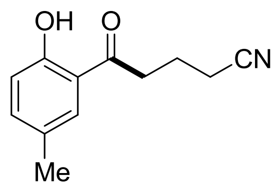
White solid, 48% yield, mp 62–63 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.10–2.14 (m, 2H), 2.26 (s, 3H), 2.53 (t, *J* = 6.8 Hz, 2H), 3.22 (t, *J* = 6.8 Hz, 2H), 6.82 (t, *J* = 7.6 Hz, 1H), 7.36 (d, *J* = 6.4 Hz, 1H), 7.61 (d, *J* = 7.6 Hz, 1H), 12.39 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 204.2, 160.8, 137.4, 127.7, 127.1, 119.1, 118.4, 118.3, 36.0, 19.6, 16.6, 15.5.

5-(2-hydroxy-4-methylphenyl)-5-oxopentanenitrile (4c)



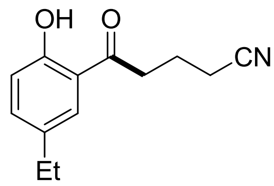
White solid, 56% yield, mp 70–71 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.07–2.14 (m, 2H), 2.35 (s, 3H), 2.52 (t, *J* = 6.8 Hz, 2H), 3.17 (t, *J* = 6.8 Hz, 2H), 6.72 (d, *J* = 8.0 Hz, 1H), 6.79 (s, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 12.10 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 203.3, 162.5, 148.4, 129.4, 120.4, 119.1, 118.5, 116.8, 35.8, 21.9, 19.6, 16.6.

5-(2-hydroxy-5-methylphenyl)-5-oxopentanenitrile (4d)



White solid, 45% yield, mp 55–56 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.08–2.15 (m, 2H), 2.31 (s, 3H), 2.53 (t, *J* = 6.8 Hz, 2H), 3.20 (t, *J* = 6.8 Hz, 2H), 6.89 (d, *J* = 8.4 Hz, 1H), 7.30 (dd, *J* = 8.4 Hz, 1.6 Hz, 1H), 7.52 (s, 1H), 11.91 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 203.8, 160.2, 137.7, 129.2, 128.2, 119.2, 118.6, 118.3, 35.9, 20.4, 19.5, 16.6.

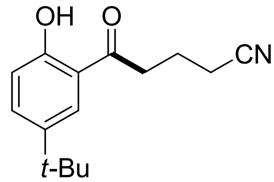
5-(5-ethyl-2-hydroxyphenyl)-5-oxopentanenitrile (4e)



Viscous oil, 58% yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.23 (t, *J* = 7.6 Hz, 3H), 2.08–

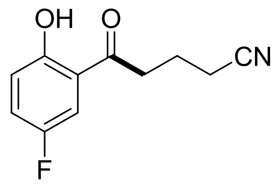
2.15 (m, 2H), 2.54 (t, J = 6.8 Hz, 2H), 2.61 (q, J = 7.6 Hz, 2H), 3.22 (t, J = 6.8 Hz, 2H), 6.92 (d, J = 8.4 Hz, 1H), 7.34 (dd, J = 8.8 Hz, 2.0 Hz, 1H), 7.53 (d, J = 2.0 Hz, 1H), 11.93 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 203.9, 160.4, 136.7, 134.8, 128.1, 119.2, 118.7, 118.4, 35.9, 27.9, 19.5, 16.6, 15.7.

5-(5-(tert-butyl)-2-hydroxyphenyl)-5-oxopentanenitrile (4f)



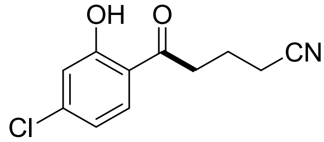
Viscous oil, 76% yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.32 (s, 9H), 2.09–2.16 (m, 2H), 2.54 (t, J = 6.8 Hz, 2H), 3.23 (t, J = 6.8 Hz, 2H), 6.94 (d, J = 8.8 Hz, 1H), 7.56 (dd, J = 8.8 Hz, 2.4 Hz, 1H), 7.69 (d, J = 2.4 Hz, 1H), 11.95 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 204.0, 160.2, 141.8, 134.5, 125.2, 119.2, 118.3, 118.2, 35.8, 34.1, 31.2, 19.6, 16.6.

5-(5-fluoro-2-hydroxyphenyl)-5-oxopentanenitrile (4g)



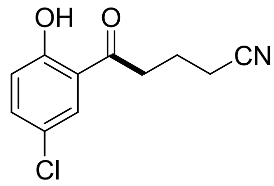
White solid, 49% yield, mp 49–50 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.08–2.15 (m, 2H), 2.53 (t, J = 6.8 Hz, 2H), 3.16 (t, J = 6.8 Hz, 2H), 6.97 (dd, J = 9.2 Hz, 4.4 Hz, 1H), 7.21–7.25 (m, 1H), 7.41 (dd, J = 8.8 Hz, 3.2 Hz, 1H), 11.79 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 203.2, 158.5, 154.8 (d, J_{C-F} = 237.8 Hz), 124.4 (d, J_{C-F} = 23.6 Hz), 120.0 (d, J_{C-F} = 7.2 Hz), 118.9, 118.4 (d, J_{C-F} = 6.2 Hz), 114.4 (d, J_{C-F} = 23.3 Hz), 36.1, 19.3, 16.5; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -123.38 (s, 1F).

5-(4-chloro-2-hydroxyphenyl)-5-oxopentanenitrile (4h)



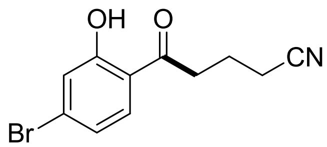
White solid, 52% yield, mp 76–77 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.08–2.15 (m, 2H), 2.53 (t, J = 6.8 Hz, 2H), 3.18 (t, J = 6.8 Hz, 2H), 6.90 (dd, J = 8.4 Hz, 1.2 Hz, 1H), 7.01 (s, 1H), 7.68 (dd, J = 8.4 Hz, 1H), 12.20 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 203.3, 163.0, 142.5, 130.5, 119.8, 119.0, 118.6, 117.6, 36.0, 19.3, 16.5.

5-(5-chloro-2-hydroxyphenyl)-5-oxopentanenitrile (4i)



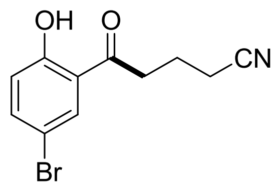
White solid, 53% yield, mp 67–68 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.09–2.15 (m, 2H), 2.31 (s, 3H), 2.53 (t, J = 6.8 Hz, 2H), 3.18 (t, J = 6.8 Hz, 2H), 6.95 (d, J = 8.8 Hz, 1H), 7.43 (dd, J = 8.8 Hz, 2.4 Hz, 1H), 7.71 (d, J = 2.4 Hz, 1H), 11.94 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 203.2, 160.8, 136.6, 128.8, 123.8, 120.3, 119.5, 118.9, 36.1, 19.3, 16.5.

5-(4-bromo-2-hydroxyphenyl)-5-oxopentanenitrile (4j)



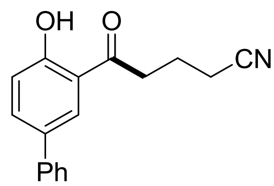
White solid, 50% yield, mp 42–43 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.07–2.14 (m, 2H), 2.31 (s, 3H), 2.53 (t, J = 6.8 Hz, 2H), 3.17 (t, J = 6.8 Hz, 2H), 7.05 (dd, J = 8.8 Hz, 2.0 Hz, 1H), 7.18 (d, J = 1.6 Hz, 1H), 7.59 (d, J = 8.4 Hz, 1H), 12.15 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 203.5, 162.7, 131.1, 130.5, 122.6, 121.8, 119.0, 117.8, 36.0, 19.3, 16.5.

5-(5-bromo-2-hydroxyphenyl)-5-oxopentanenitrile (4k)



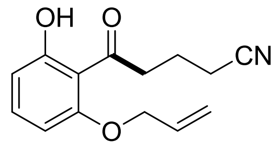
White solid, 43% yield, mp 80–81 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.08–2.15 (m, 2H), 2.31 (s, 3H), 2.53 (t, J = 6.8 Hz, 2H), 3.18 (t, J = 6.8 Hz, 2H), 6.90 (d, J = 9.2 Hz, 1H), 7.56 (d, J = 8.8 Hz, 1H), 7.84 (s, 1H), 11.95 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 203.1, 161.2, 139.3, 131.8, 120.7, 120.2, 118.9, 110.7, 36.1, 19.3, 16.5.

5-(4-hydroxy-[1,1'-biphenyl]-3-yl)-5-oxopentanenitrile (4l)



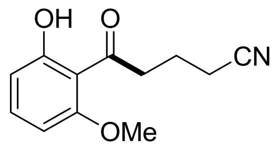
White solid, 46% yield, mp 69–70 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.12–2.19 (m, 2H), 2.55 (t, *J* = 6.8 Hz, 2H), 3.29 (t, *J* = 6.8 Hz, 2H), 7.08 (d, *J* = 8.8 Hz, 1H), 7.36 (t, *J* = 7.2 Hz, 1H), 7.46 (t, *J* = 8.0 Hz, 2H), 7.52–7.55 (m, 2H), 7.73 (dd, *J* = 8.8 Hz, 2.4 Hz, 1H), 7.92 (d, *J* = 2.0 Hz, 1H), 12.08 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 204.1, 161.7, 139.7, 135.6, 132.6, 128.9, 127.8, 127.3, 126.7, 119.1, 119.0, 36.0, 19.5, 16.6.

5-(2-(allyloxy)-6-hydroxyphenyl)-5-oxopentanenitrile (4m)



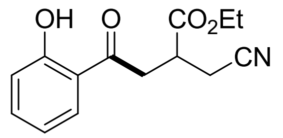
White solid, 41% yield, mp 49–50 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.02–2.09 (m, 2H), 2.48 (t, *J* = 7.2 Hz, 2H), 3.27 (t, *J* = 6.8 Hz, 2H), 4.63 (d, *J* = 6.0 Hz, 1H), 5.37 (dd, *J* = 10.4 Hz, 1.2 Hz, 1H), 5.43 (dd, *J* = 17.2 Hz, 1.2 Hz, 1H), 6.38 (d, *J* = 8.4 Hz, 1H), 6.57 (d, *J* = 8.4 Hz, 1H), 7.33 (t, *J* = 8.0 Hz, 1H), 13.03 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 205.1, 164.6, 160.3, 136.2, 132.1, 119.4, 119.2, 111.1, 111.0, 102.3, 43.0, 20.0, 16.6.

5-(2-hydroxy-6-methoxyphenyl)-5-oxopentanenitrile (4n)



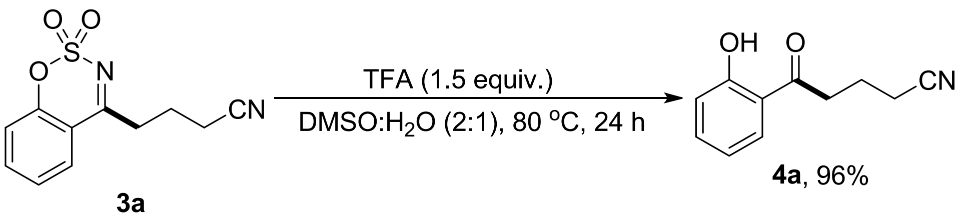
Viscous oil, 62% yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.02–2.09 (m, 2H), 2.50 (t, *J* = 7.2 Hz, 2H), 3.25 (t, *J* = 6.8 Hz, 2H), 3.92 (s, 3H), 6.40 (d, *J* = 8.0 Hz, 1H), 6.58 (dd, *J* = 8.4 Hz, 0.8 Hz, 1H), 7.36 (t, *J* = 8.4 Hz, 1H), 13.07 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 205.1, 164.7, 161.3, 136.3, 119.5, 110.9, 110.8, 101.2, 55.7, 42.8, 20.1, 16.7.

Ethyl 2-(cyanomethyl)-4-(2-hydroxyphenyl)-4-oxobutanoate (4o)



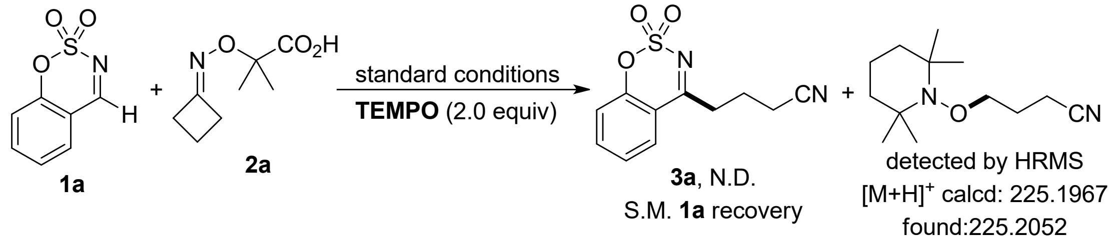
Viscous oil, 27% yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.27 (t, *J* = 6.8 Hz, 3H), 2.87–2.89 (m, 2H), 3.30–3.36 (m, 1H), 3.41–3.48 (m, 1H), 3.64–3.70 (m, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 6.94 (t, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.78 (dd, *J* = 8.0 Hz, 0.8 Hz, 1H), 11.84 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 201.2, 170.3, 161.3, 136.0, 128.6, 118.2, 117.8, 117.6, 116.4, 60.9, 37.0, 35.5, 18.1, 13.0.

The procedure for the hydrolysis of product 3a:



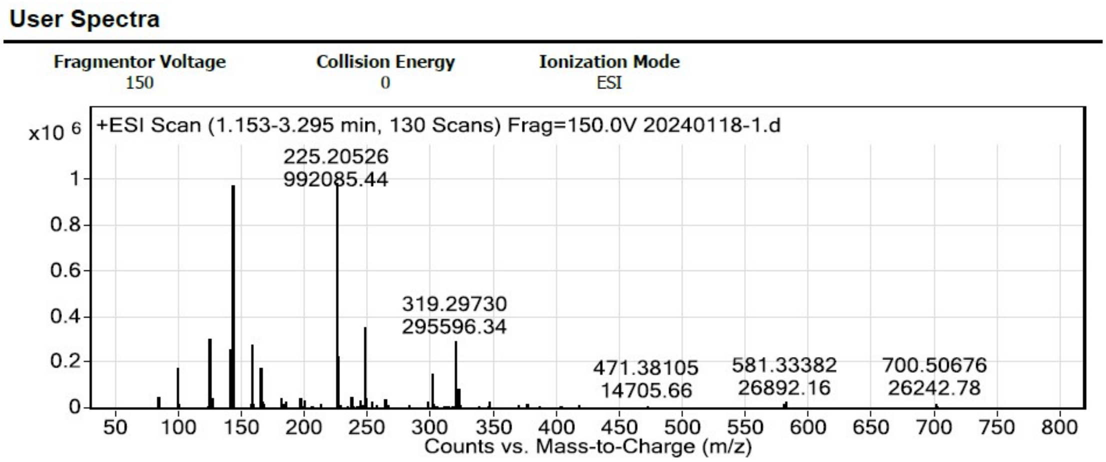
To a 10 mL Schlenk charged with the compound **3a** (0.2 mmol) and trifluoroacetic acid (35 mg, 0.3 mmol) were added DMSO (1.0 mL) and distilled H_2O (0.5 mL) *via* a syringe. Then, the reaction mixture was vigorously stirred at 80 °C for 24 h. After the reaction was complete, the mixture was diluted with water (5 mL) and extracted with ethyl acetate (3 × 5 mL). The organic layers were combined and washed with saturated brine (10 mL), dried anhydrous $MgSO_4$, and then concentrated in vacuo. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc as the eluent) to afford the desired products **4** in 96% yield as white solid.

The Procedure for the radical inhibition experiment:



To a 10 mL Schlenk charged with cyclic aldimines **1a** (0.2 mmol), α-imino-oxy acids

2a (0.4 mmol), $AgNO_3$ (6.8 mg, 0.04 mmol), $Na_2S_2O_8$ (96 mg, 0.4 mmol) and TEMPO (62.5 mg, 0.4 mmol) were added acetone (1.0 mL) and distilled H_2O (1.0 mL) *via* a syringe. Then, the reaction mixture was vigorously stirred at 60 ^oC for 24 h. After the reaction was complete, the mixture was diluted with water (5 mL) and extracted with ethyl acetate (3 × 5 mL). The organic layers were combined and washed with saturated brine (10 mL), dried anhydrous $MgSO_4$, and then concentrated in vacuo. The target product **2a** was not detected by TLC. The mass spectrometry data of possible intermediates and TEMPO radical trapped species were observed in the reaction system.

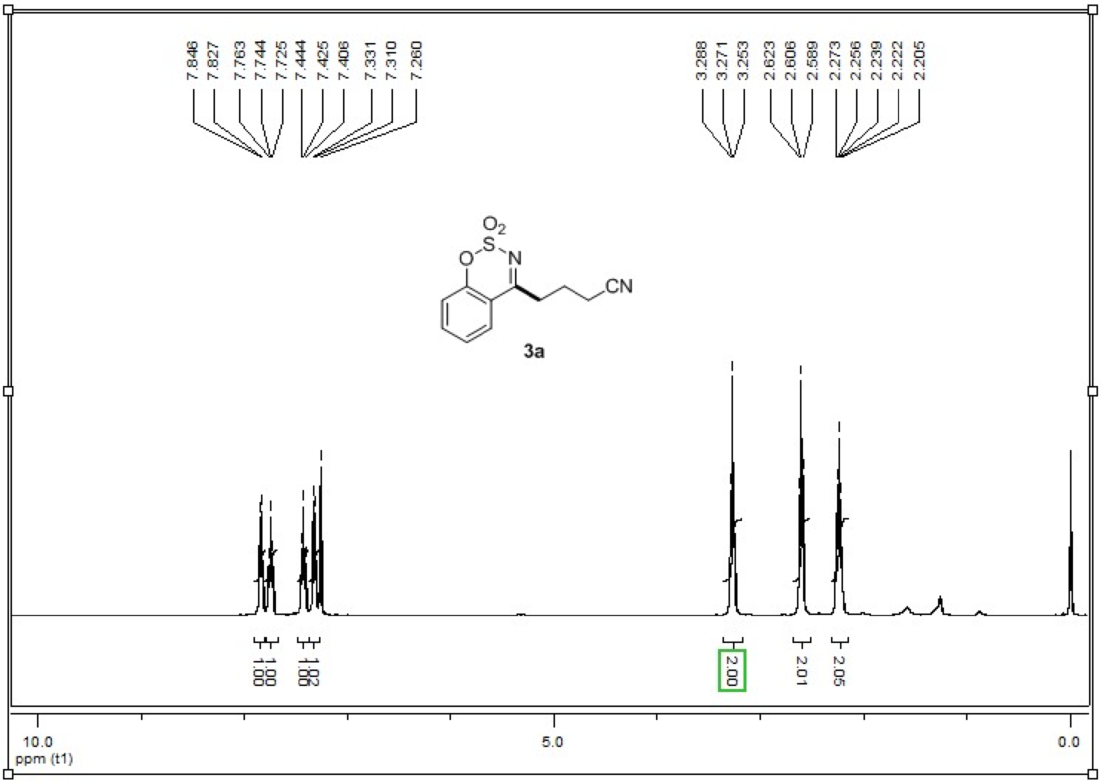


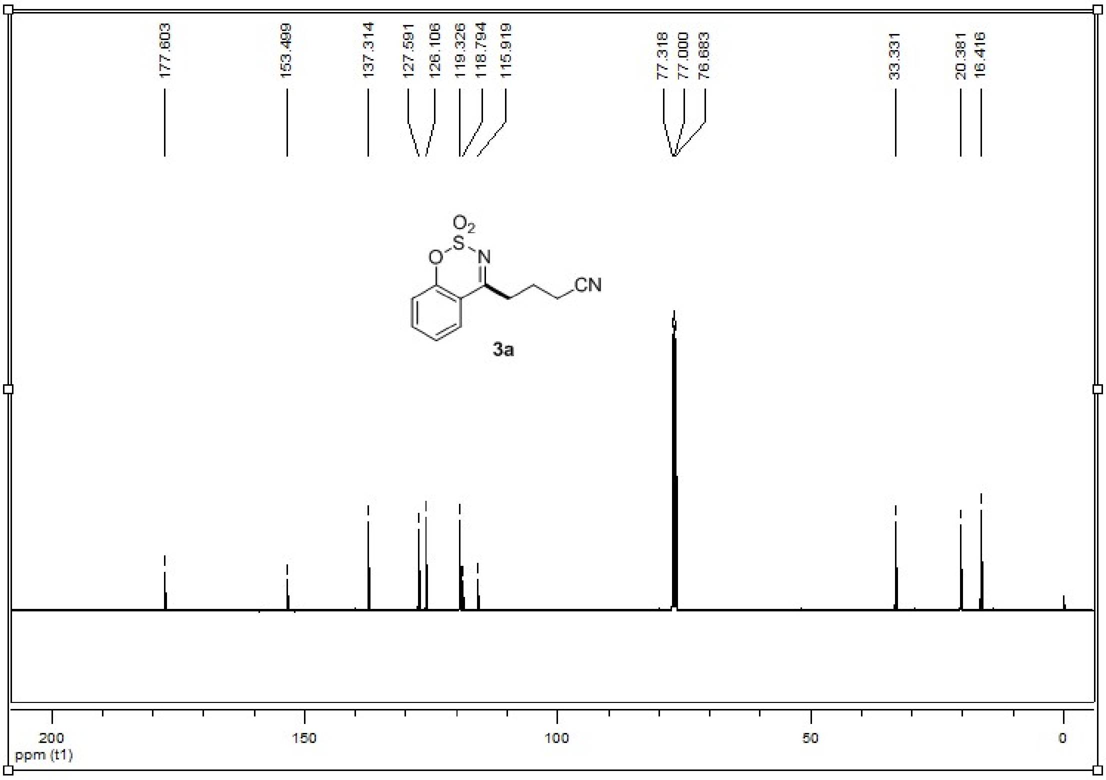
Reference:

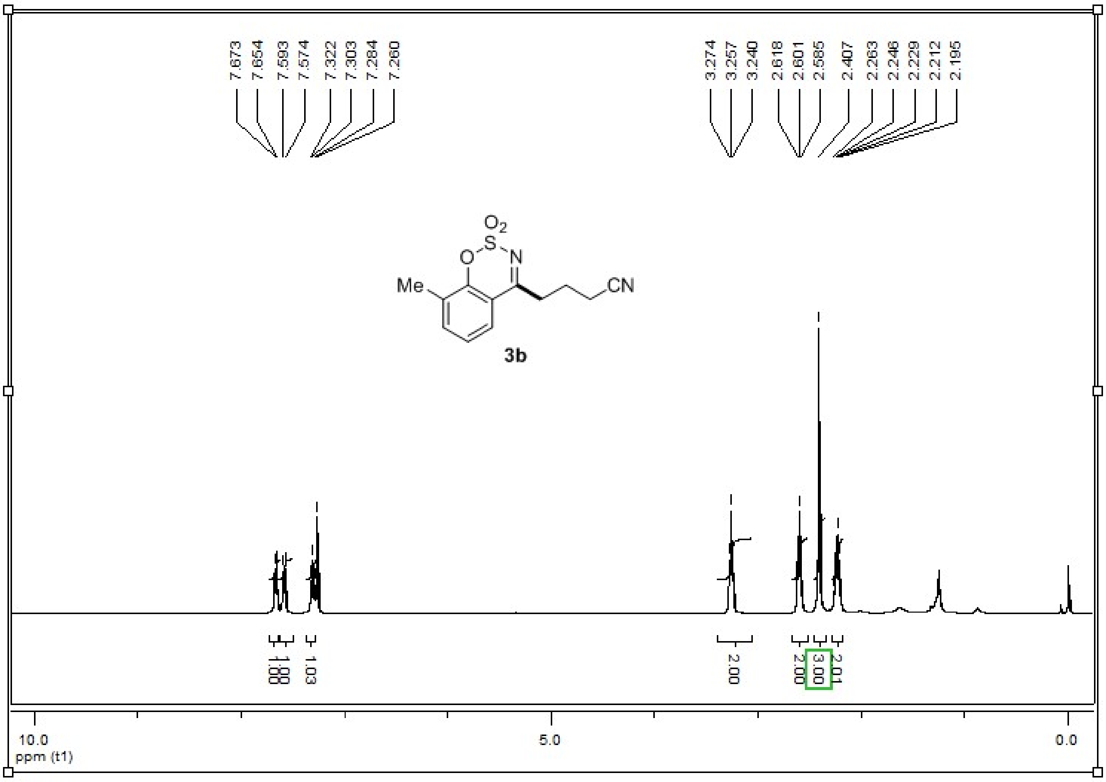
[1] F. Le Vaillant, M. Garreau, S. Nicolai, G. Gryn'ova, C. Corminboeuf and J. Waser, *Chem. Sci.*, **2018**, *9*, 5883.

[2] (a) N. D. Litvinas, B. H. Brodsky, J. D. Bois, *Angew. Chem. Int. Ed.*, **2009**, *48*, 4513; (b) H. Yu, L. Zhang, Z. Yang, Z. Li, Y. Zhao, Y. Xiao, H. Guo, *J. Org. Chem.*, **2013**, *78*, 8427.

Copies of NMR spectra of the products:



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3.240
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2.585
2.407
2.263
2.246
2.229
2.212
2.195
O2
S
O
N
Me
CN
3b
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1.88
1.03
2.00
2.00
3.00
2.01
10.0
5.0
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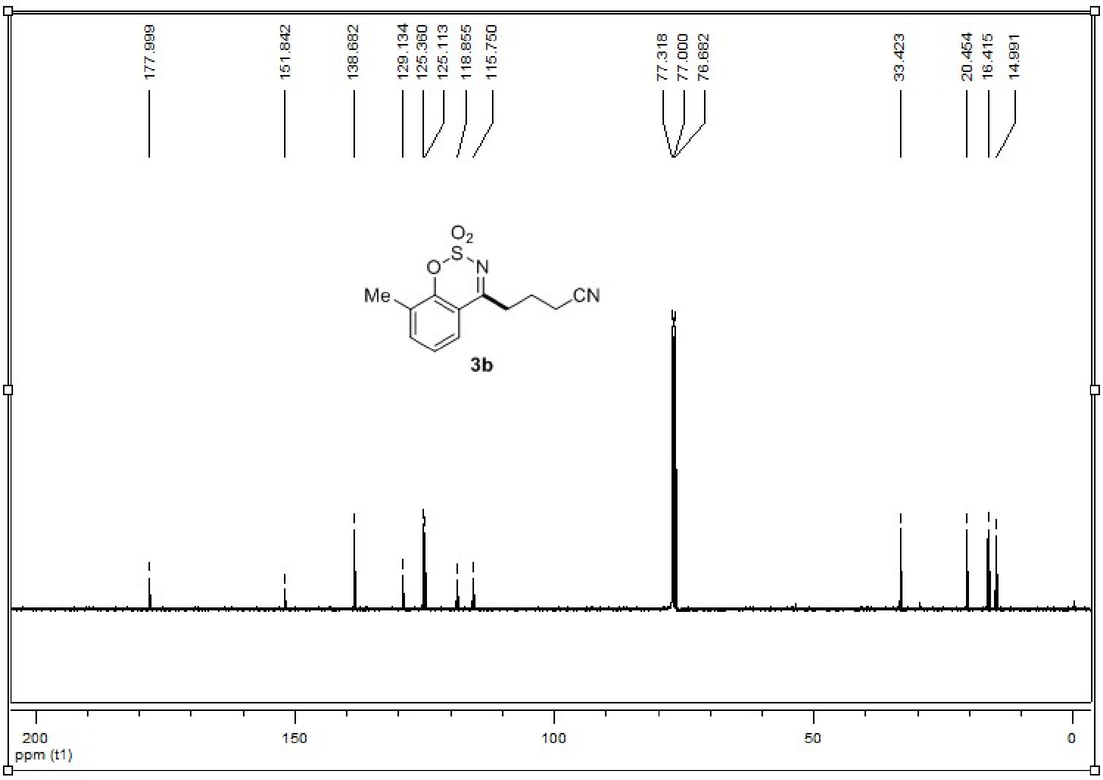
ppm (t1)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O
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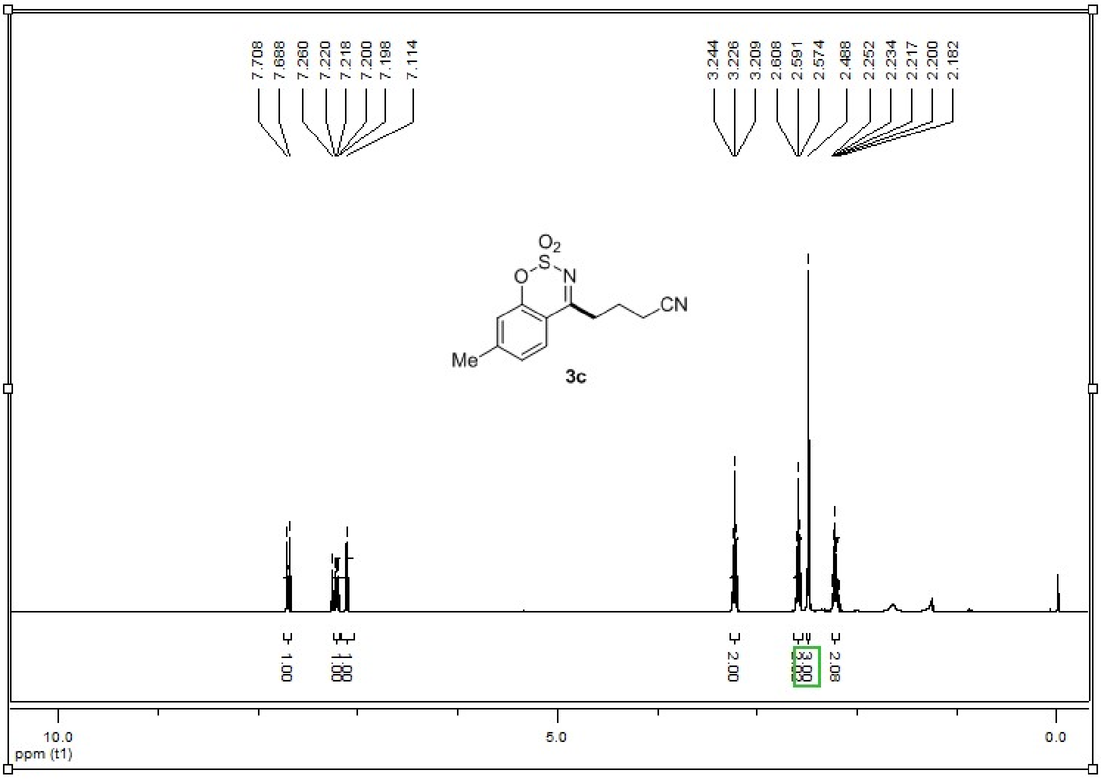
Me
CN
3b
200
150
100
50
0
ppm (t1)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2.234
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2.200
2.182
O2
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2.00
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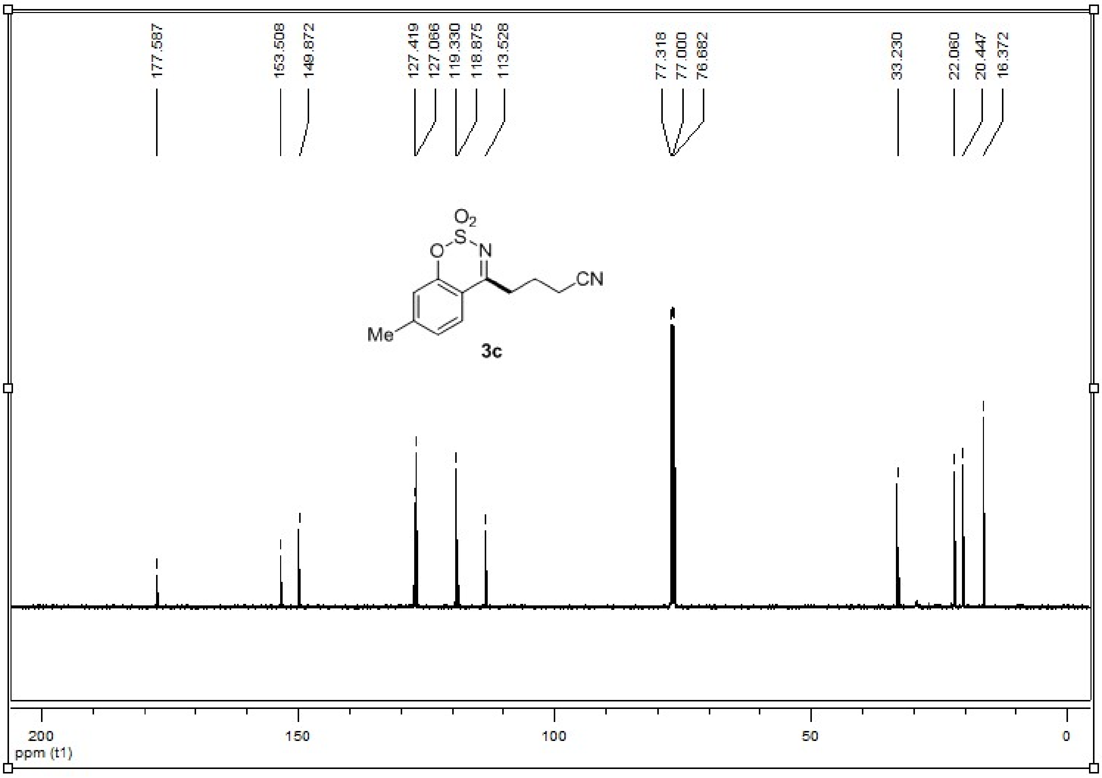
ppm (t1)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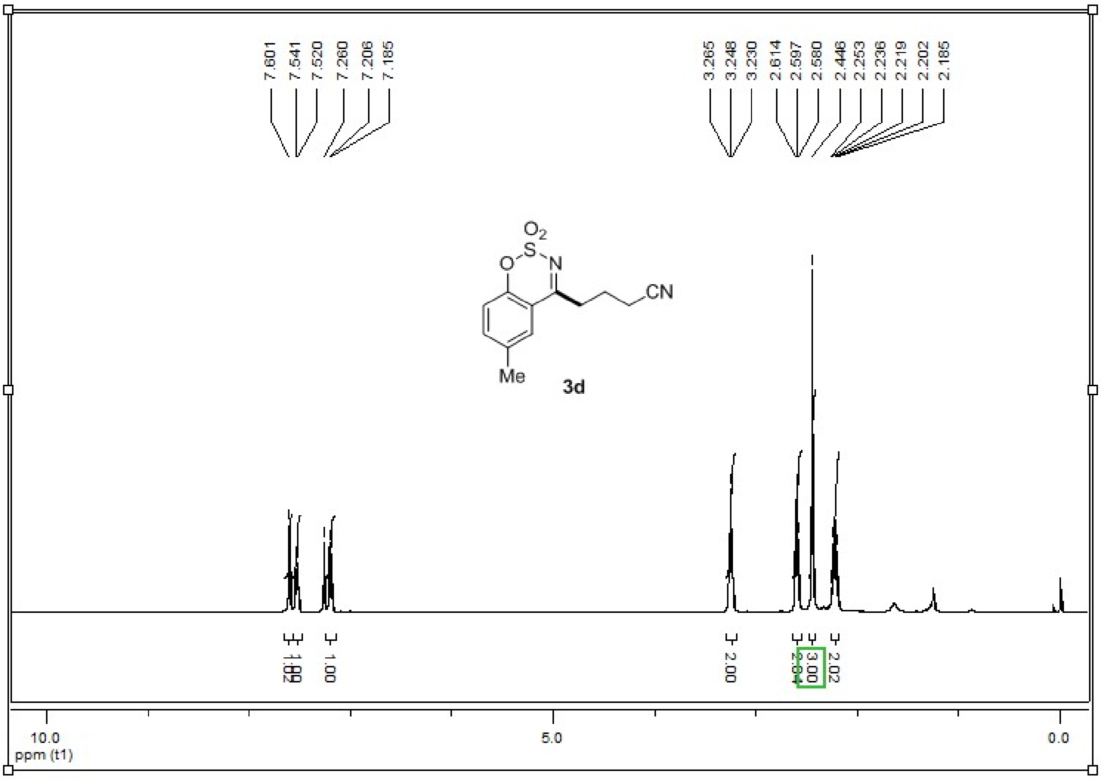
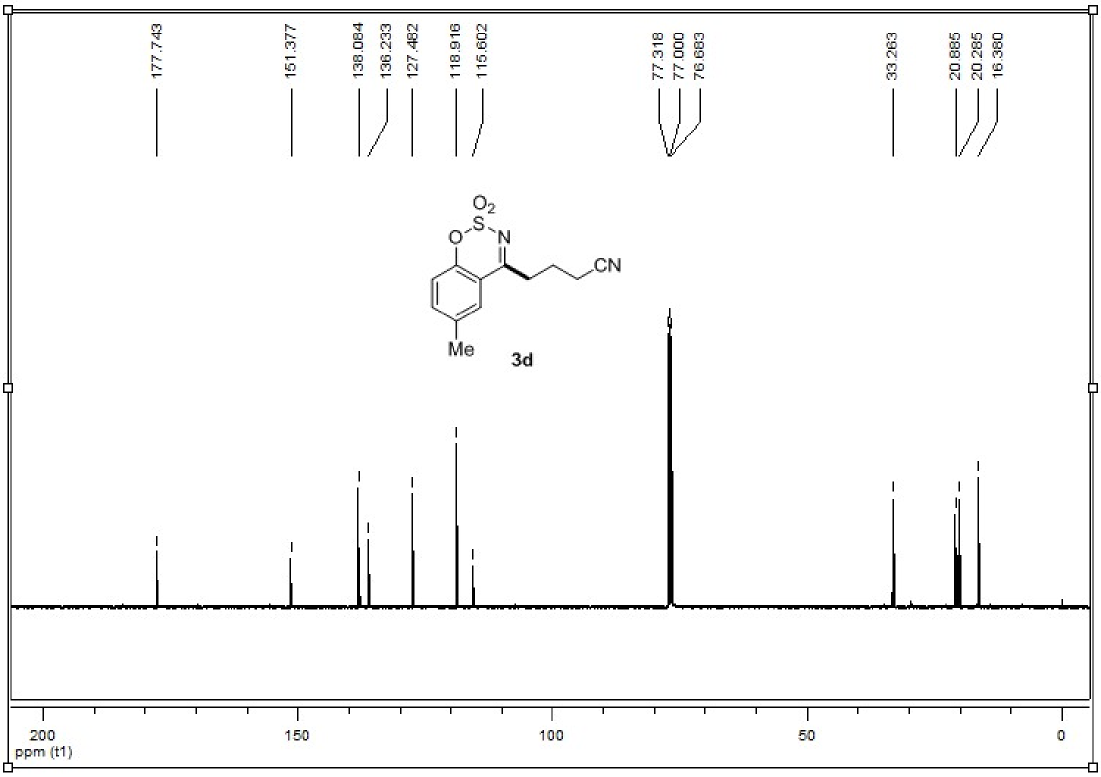
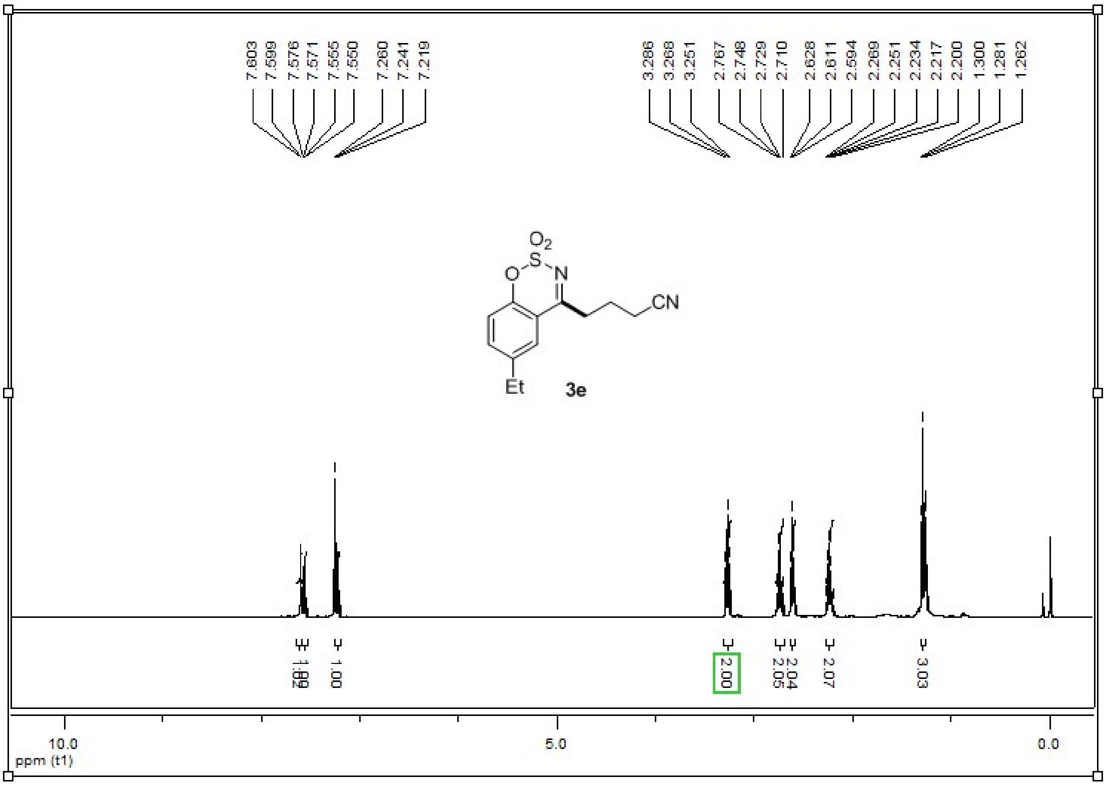
ppm (t1)



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2.729
2.710
2.628
2.611
2.594
2.269
2.251
2.234
2.217
2.200
1.300
1.281
1.262
O2
S
O
N
CN
Et
3e
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2.00
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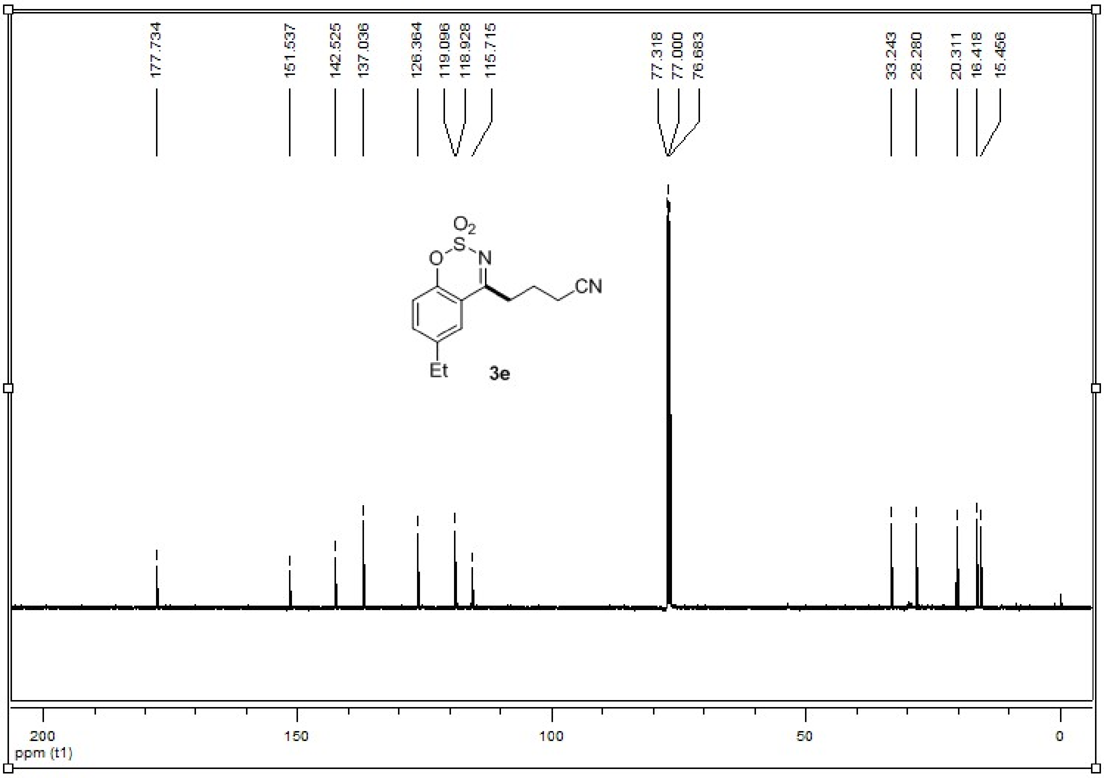
2.04
2.07
3.03
10.0
5.0
0.0
ppm (t1)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77.000
76.683
33.243
28.280
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15.456
O2
S
O
N
CN
Et
3e
200
150
100
50
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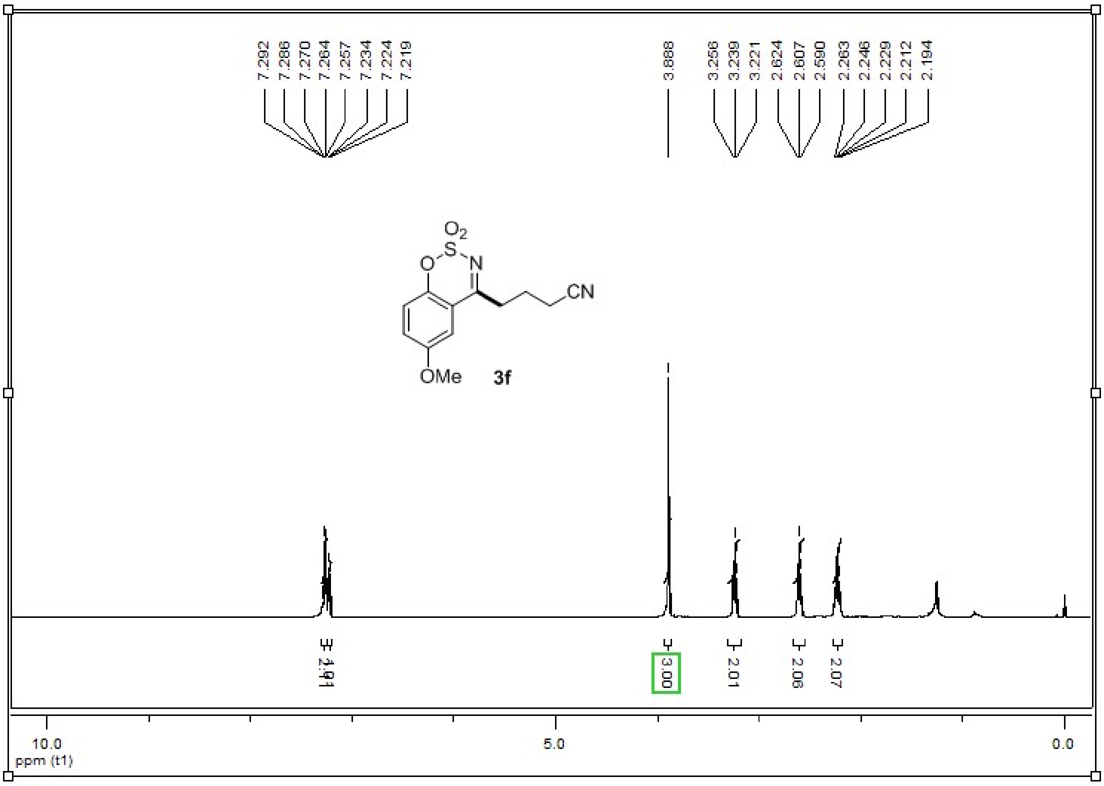
ppm (t1)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7.224
7.219
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3.256
3.239
3.221
2.624
2.607
2.590
2.263
2.246
2.229
2.212
2.194
O2
S
O
N
CN
OMe
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3.00
2.01
2.06
2.07
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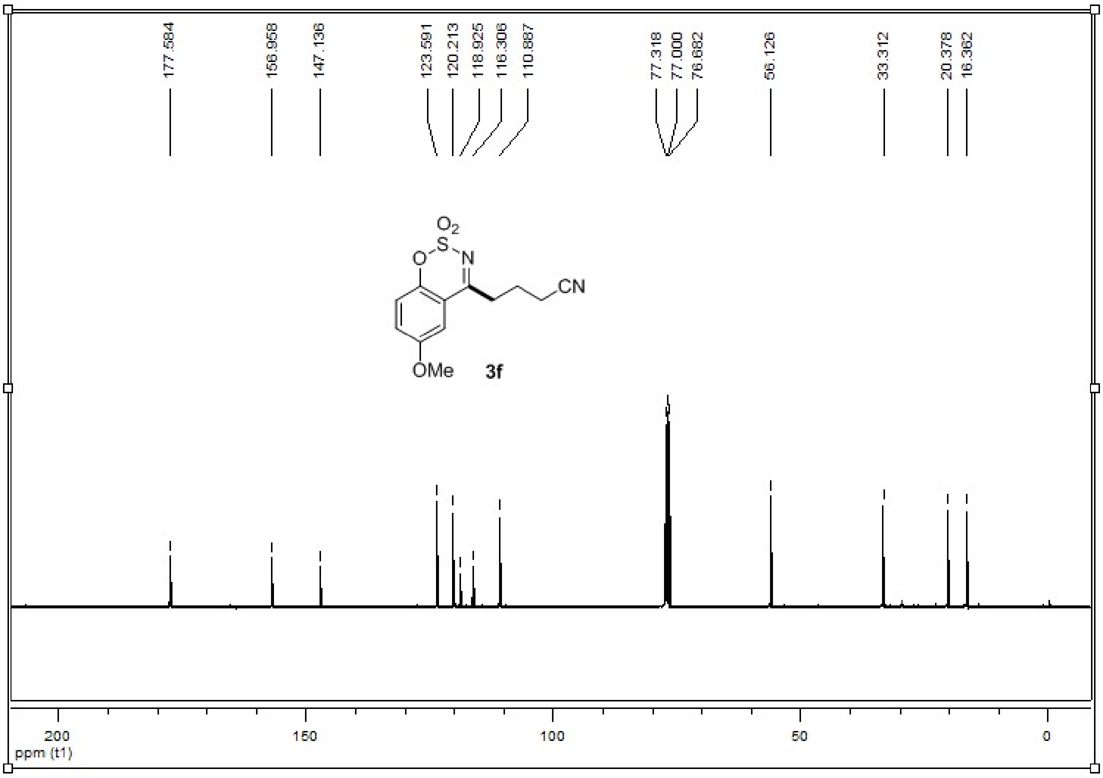
ppm (t1)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110.887
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77.000
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56.126
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S
O
N
CN
OMe
3f
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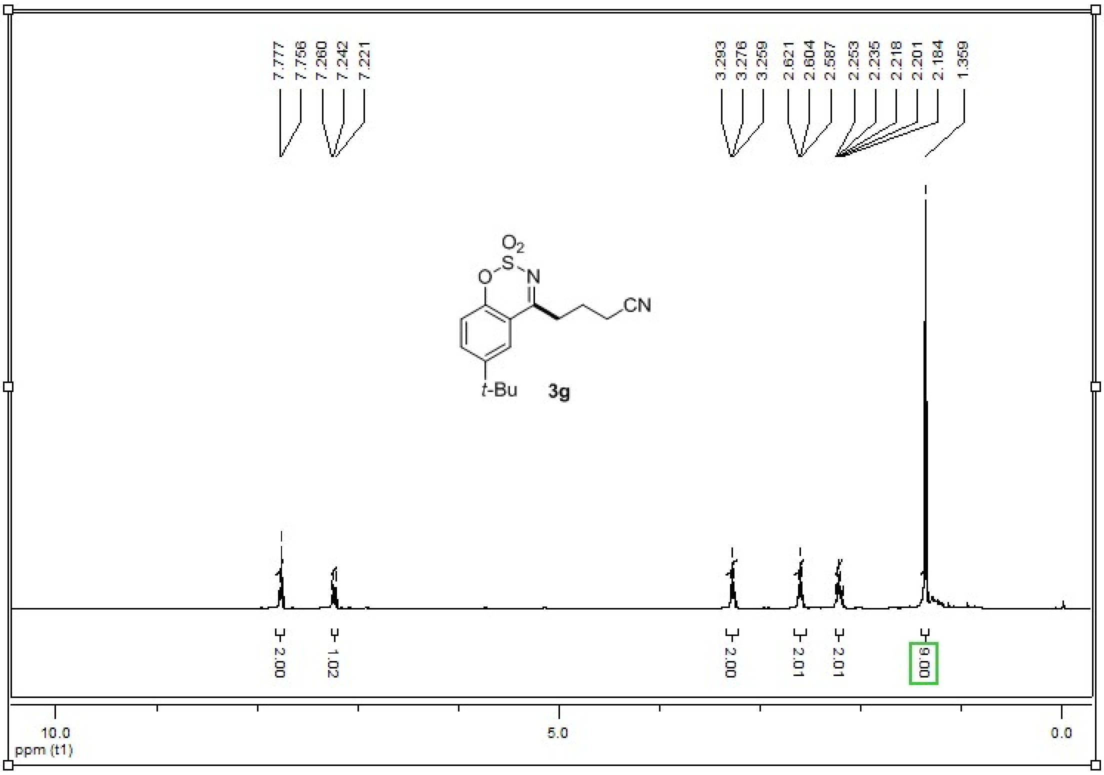
100
50
0
ppm (t1)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7.221
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3.276
3.259
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2.587
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2.235
2.218
2.201
2.184
1.359
O2
S
O
N
CN
t-Bu
3g
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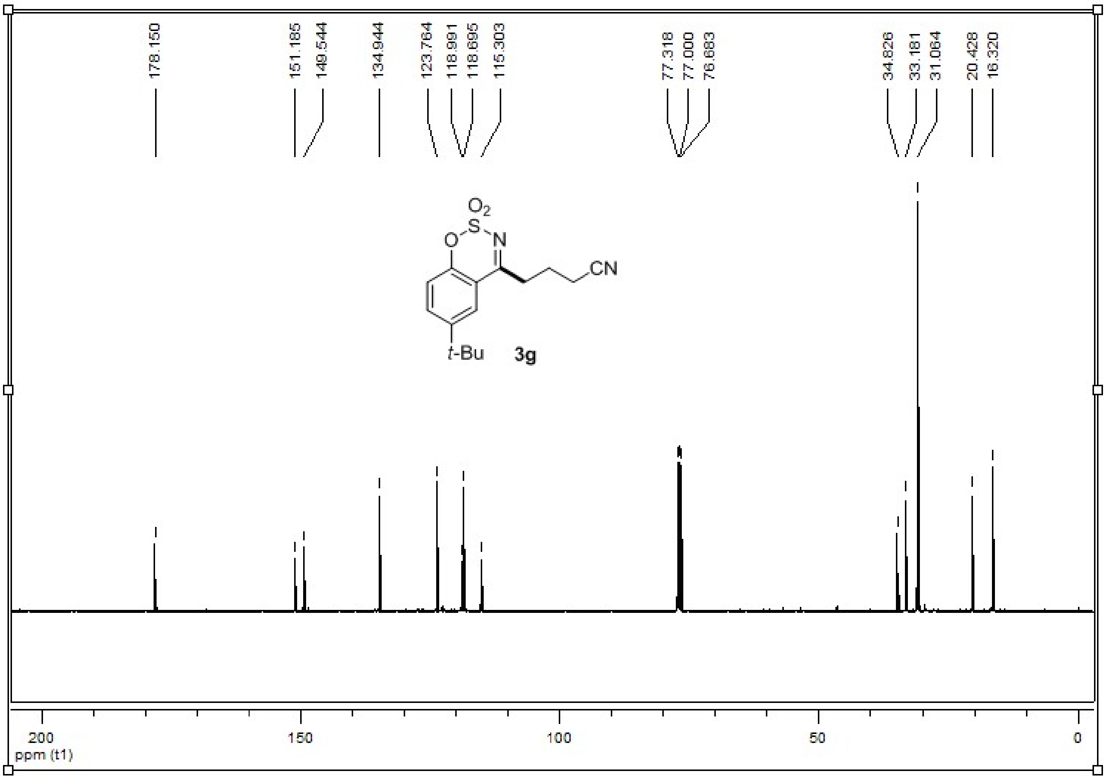
5.0
0.0
ppm (t1)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33.181
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N
CN
t-Bu
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50
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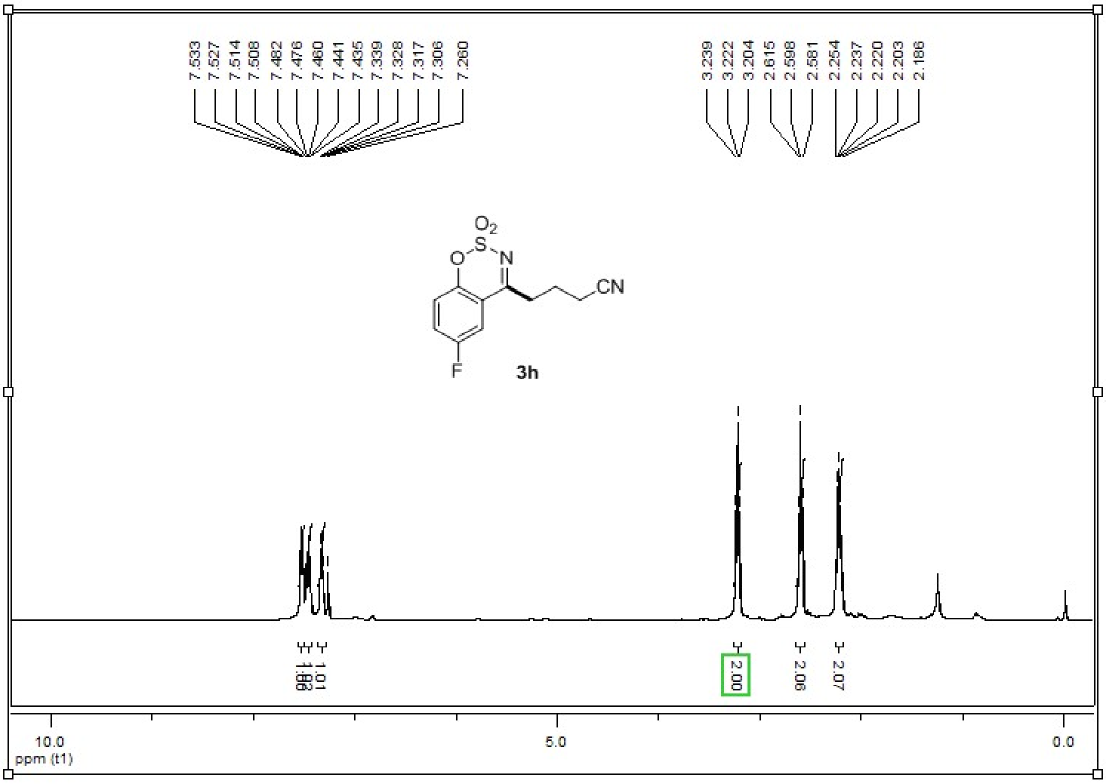
ppm (t1)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7.441
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7.339
7.328
7.317
7.306
7.260
3.239
3.222
3.204
2.615
2.598
2.581
2.254
2.237
2.220
2.203
2.186
O2
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O
N
CN
F
3h
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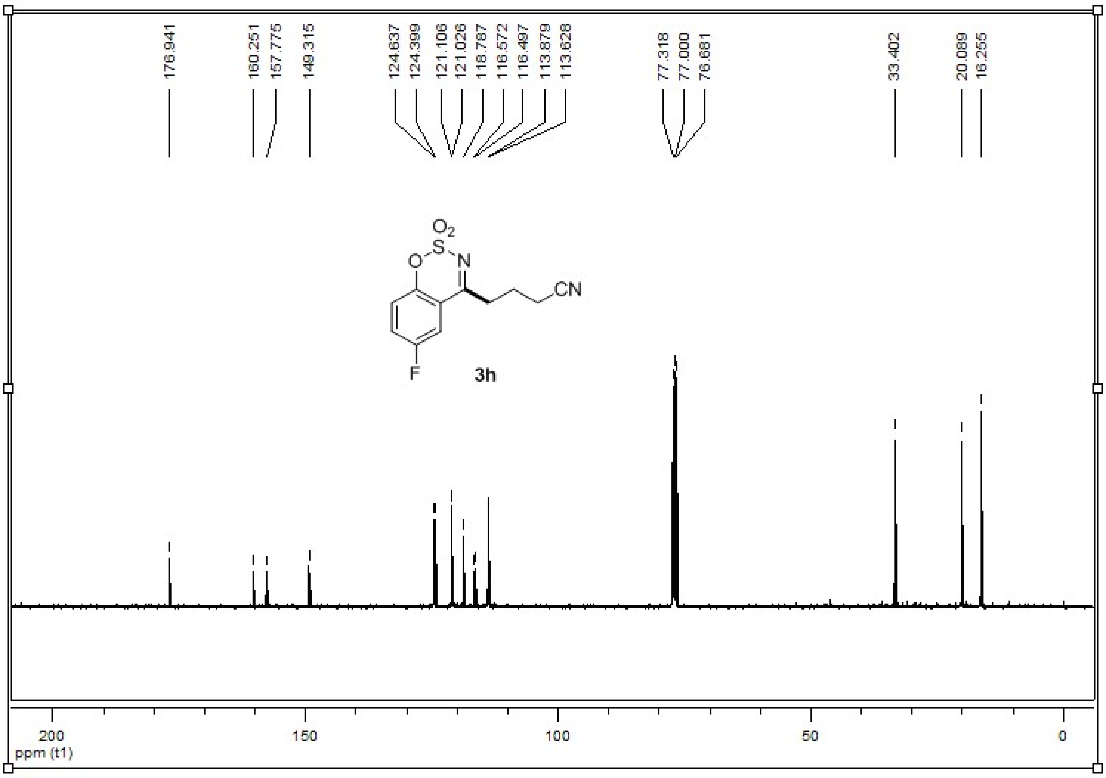
5.0
0.0
ppm (t1)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77.000
76.681
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O2
S
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N
CN
F
3h
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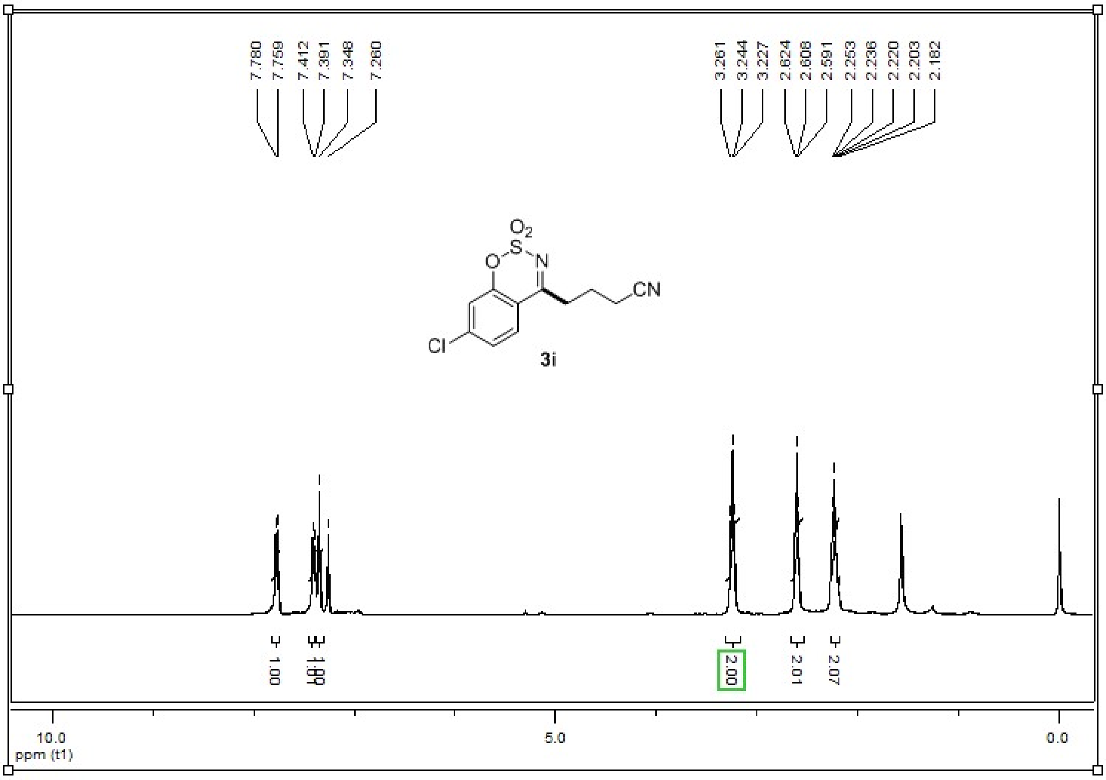
100
50
0
ppm (t1)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7.348
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3.244
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2.608
2.591
2.253
2.236
2.220
2.203
2.182
O2
S
O
N
CN
Cl
3i
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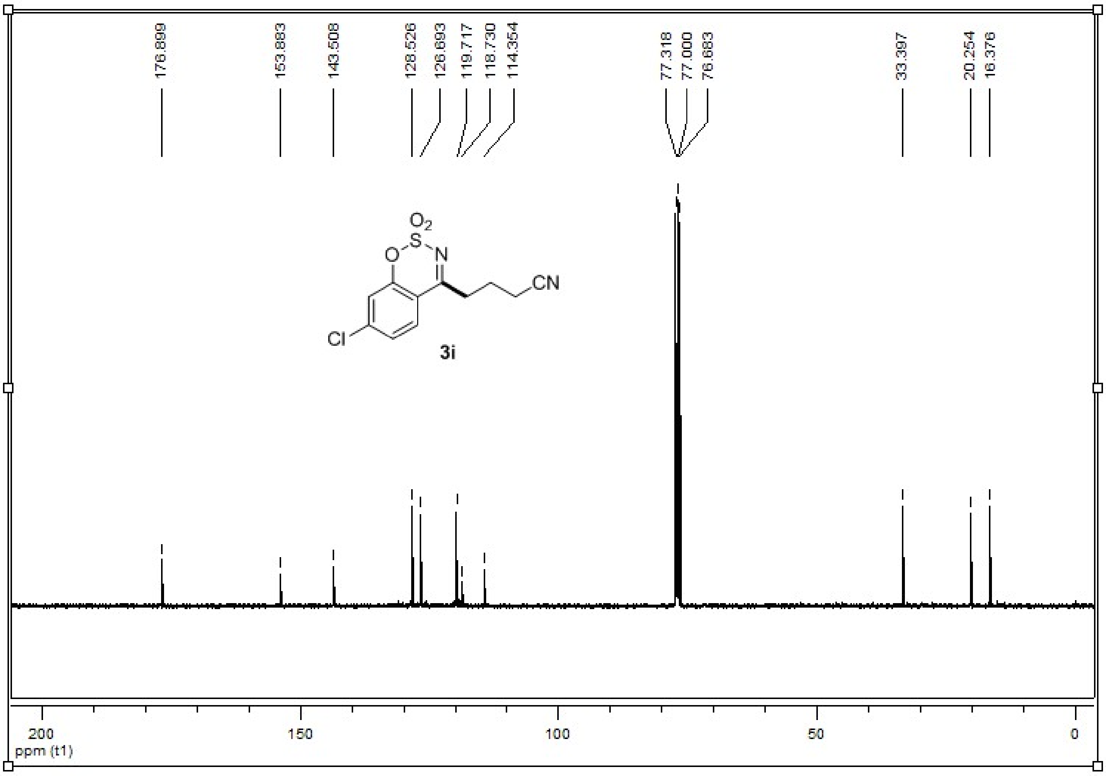
5.0
0.0
ppm (t1)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114.354
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77.000
76.683
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N
CN
Cl
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100
50
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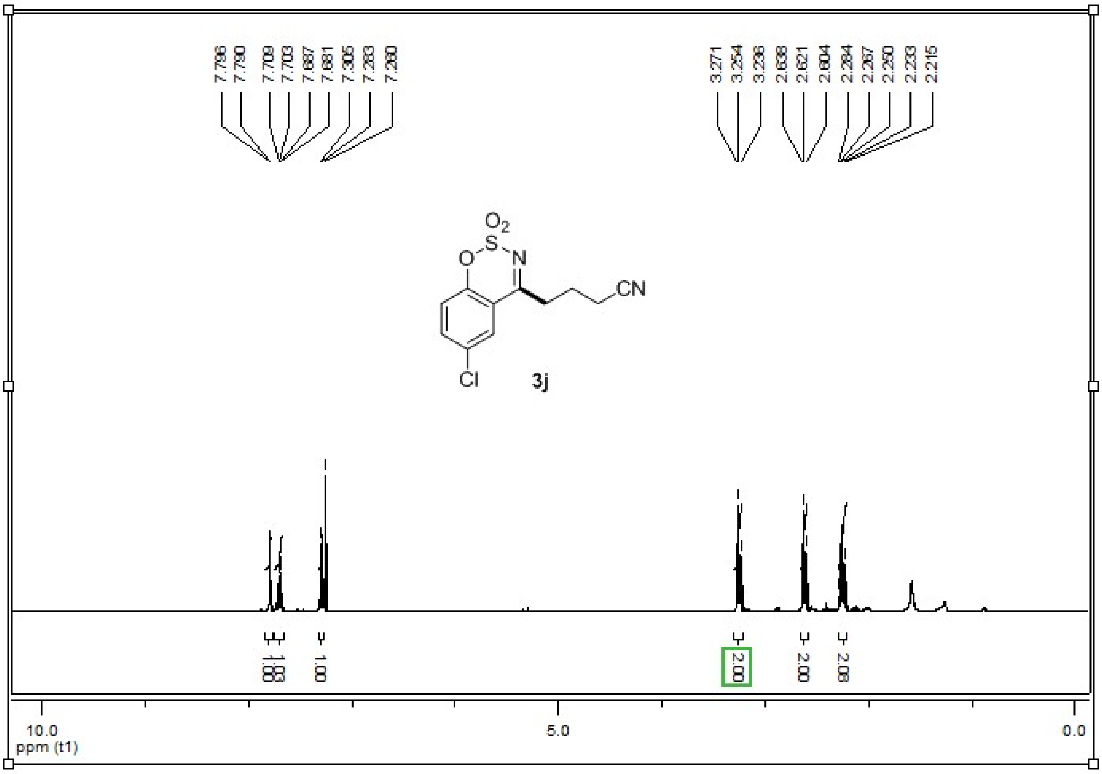
ppm (t1)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7.283
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3.254
3.236
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2.621
2.604
2.284
2.267
2.250
2.233
2.215
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O
S
N
CN
Cl
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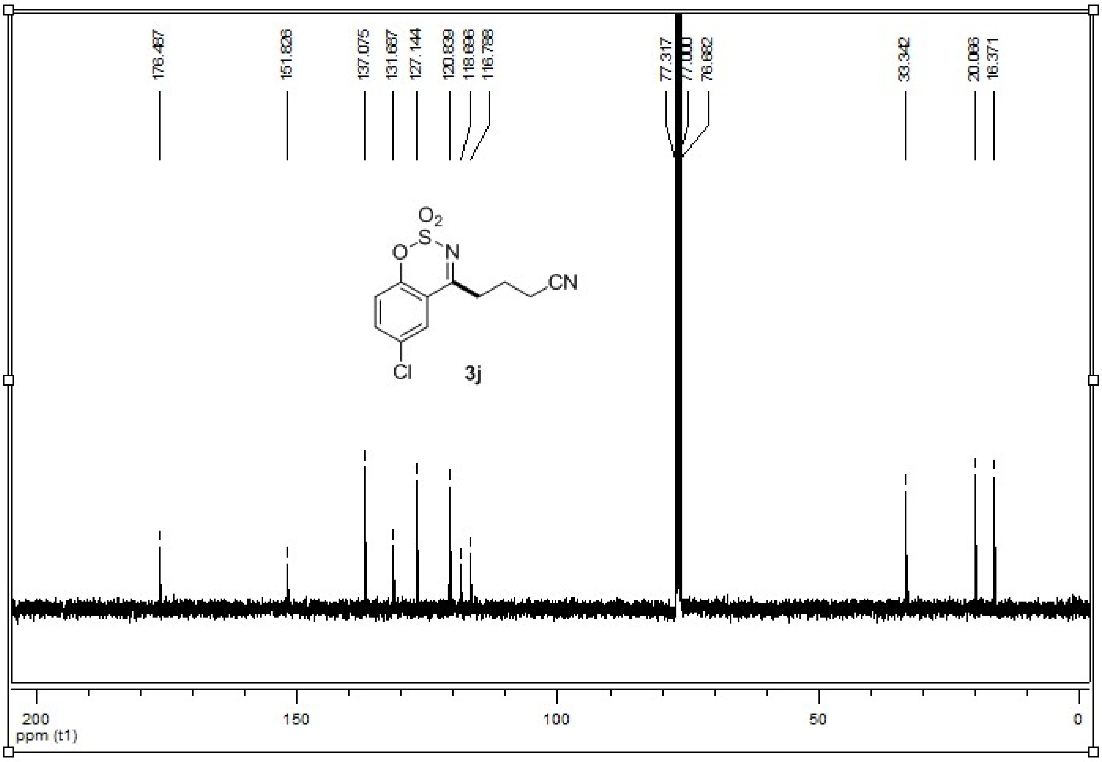
1.03
1.00
2.00
2.00
2.08
10.0
ppm (t1)
5.0
0.0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116.788
77.317
77.000
76.682
33.342
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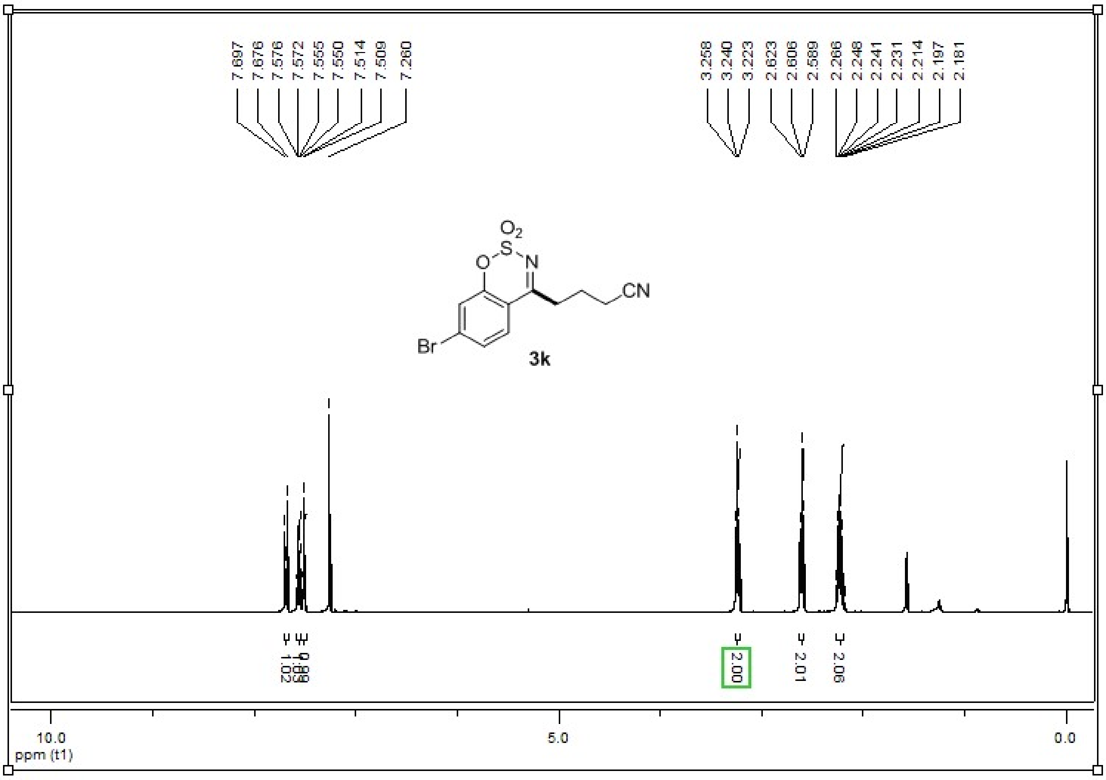
O2
O
S
N
CN
Cl
3j
200
ppm (t1)
150
100
50
0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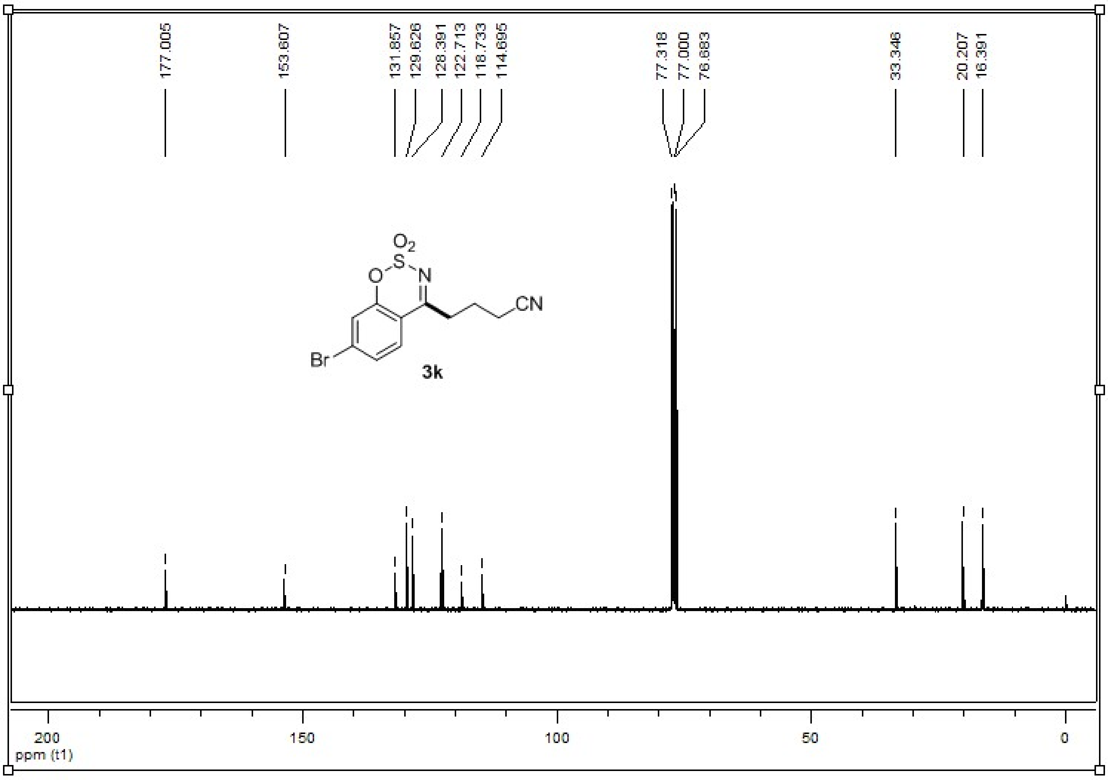
7.514
7.509
7.260
3.258
3.240
3.223
2.623
2.606
2.589
2.266
2.248
2.241
2.231
2.214
2.197
2.181
O2
S
O
N
CN
Br
3k
1.02
2.00
2.01
2.06
10.0
5.0
0.0
ppm (t1)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114.695
77.318
77.000
76.683
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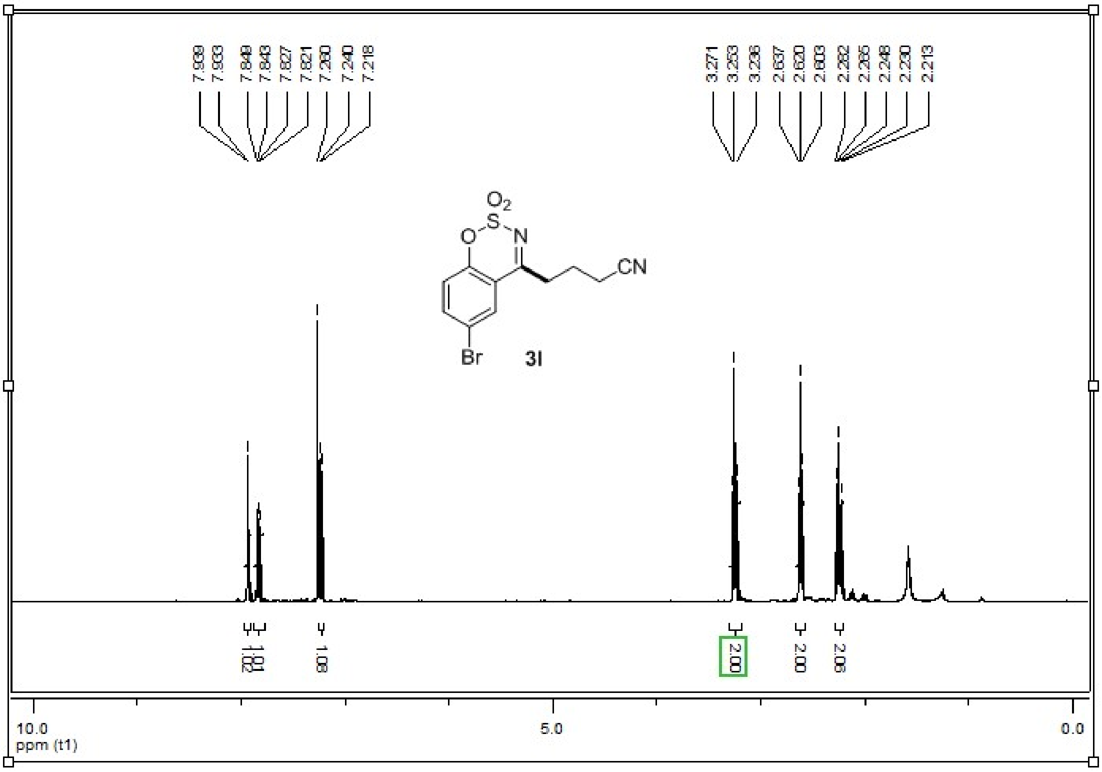
16.391
O2
S
O
N
CN
Br
3k
200
150
100
50
0
ppm (t1)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7.843
7.827
7.821
7.260
7.240
7.218
3.271
3.253
3.236
2.637
2.620
2.603
2.282
2.265
2.248
2.230
2.213
O2
S
O
N
CN
Br
3l
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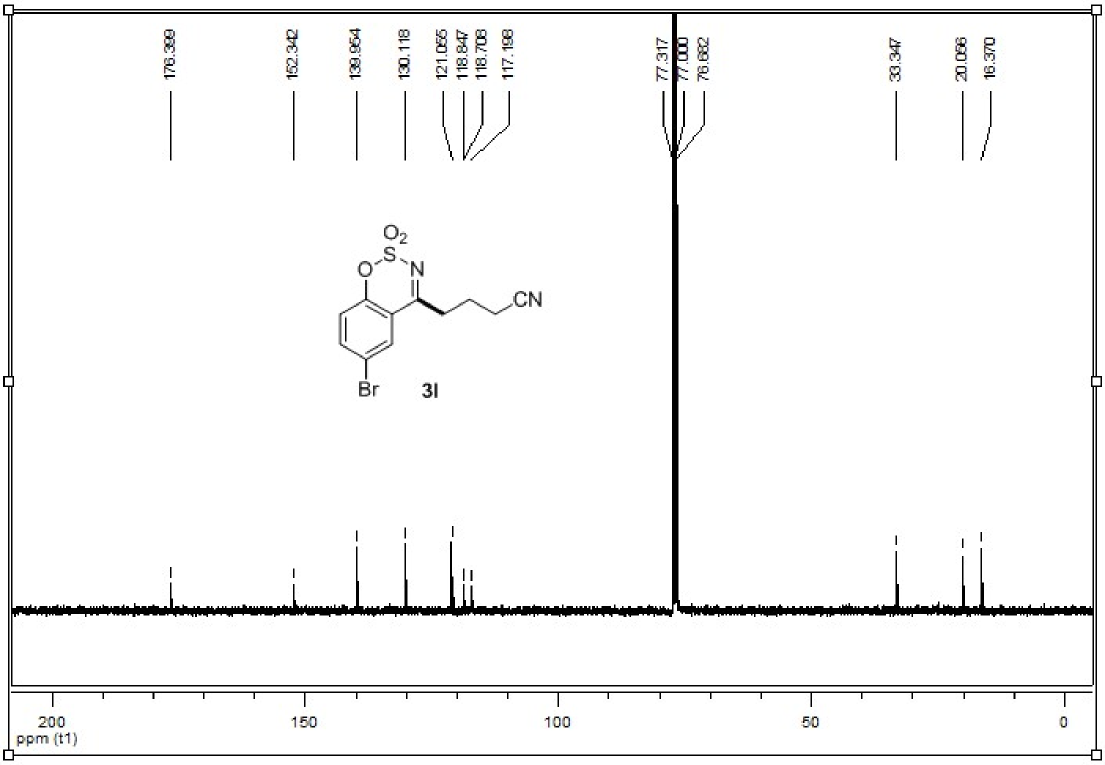
1.01
1.08
2.00
2.00
2.06
10.0
5.0
0.0
ppm (t1)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139.954
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121.055
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77.000
76.682
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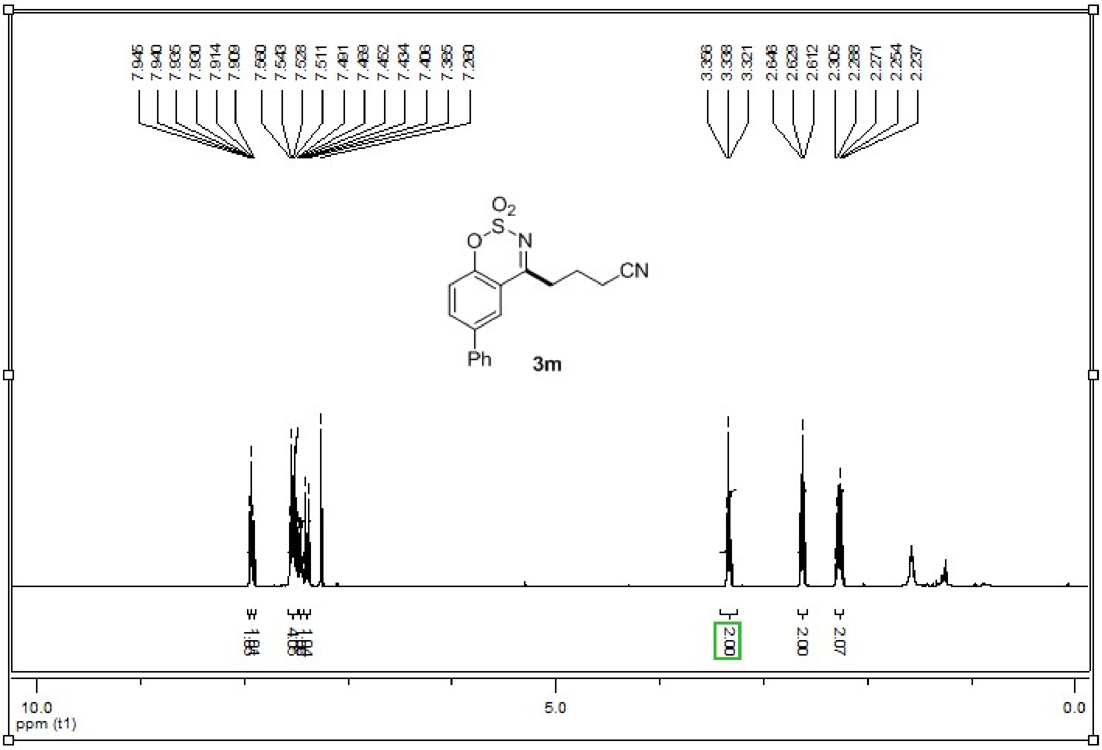
O2
S
O
N
CN
Br
3l
200
150
100
50
0
ppm (t1)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7.511
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7.489
7.462
7.434
7.406
7.385
7.260
3.356
3.338
3.321
2.646
2.629
2.612
2.305
2.288
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2.237
3m
Ph
CN
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2.00
2.07
10.0
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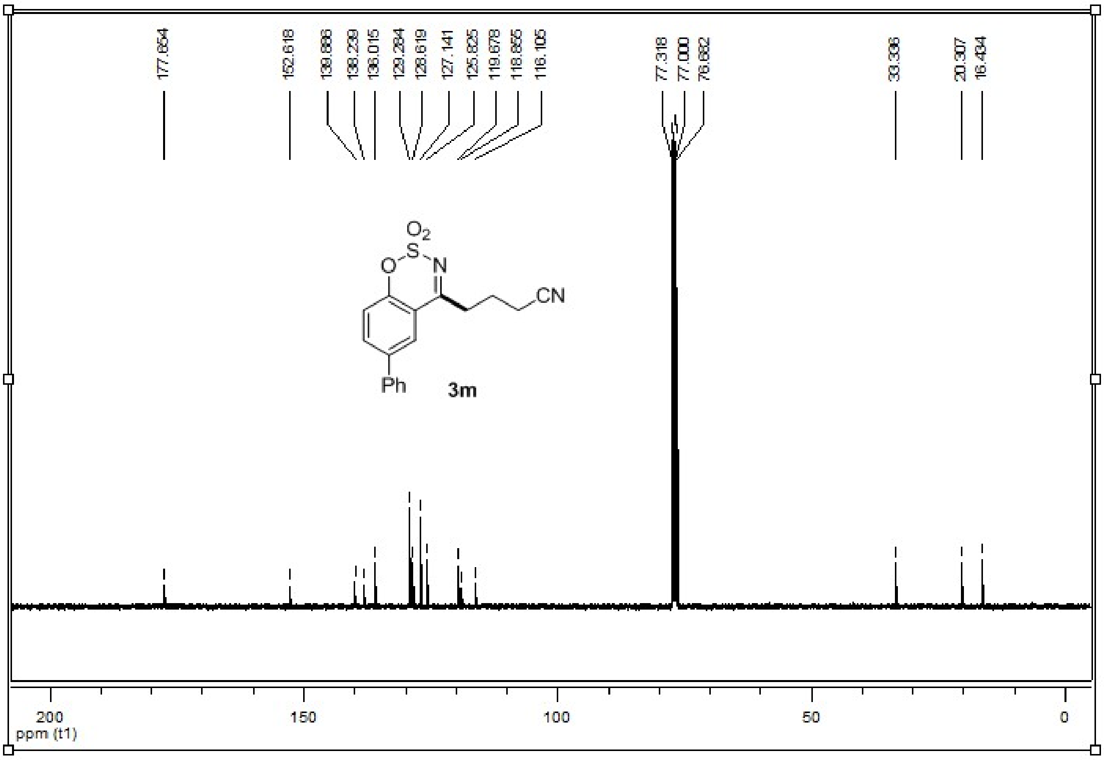
0.0
ppm (t1)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127.141
125.825
119.678
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Ph
CN
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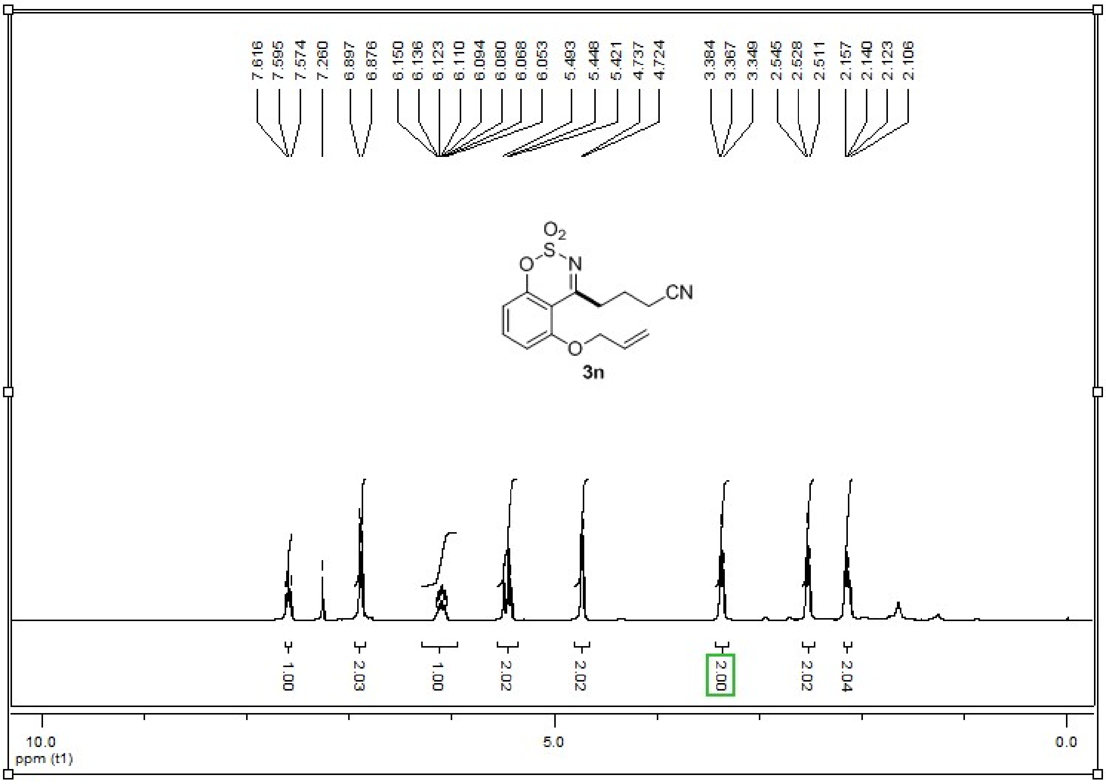
150
100
50
0
ppm (t1)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O2
S
O
N
CN
O
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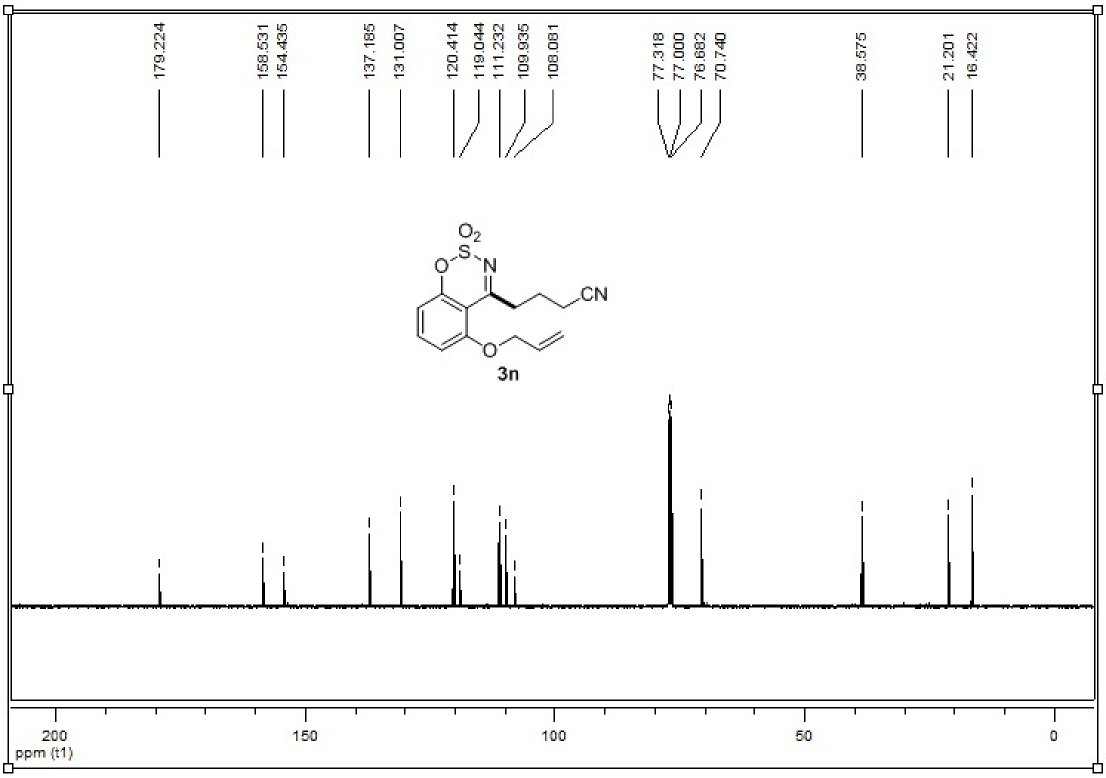
1.00 2.03 1.00 2.02 2.02 2.00 2.02 2.04
10.0
5.0
0.0
ppm (t1)


179.224 158.531 154.435 137.185 131.007 120.414 119.044 111.232 109.935 108.081 77.318 77.000 76.682 70.740 38.575 21.201 16.422
O2
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O
N
CN
O
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50
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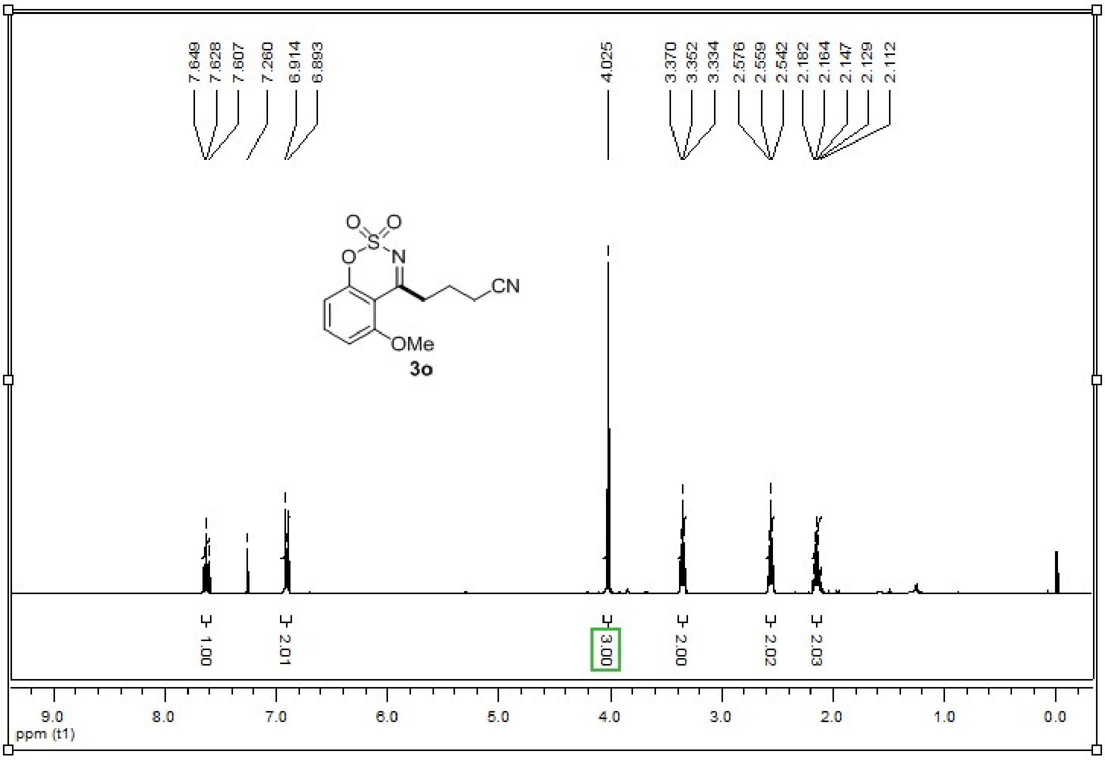
ppm (t1)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2.542
2.182
2.164
2.147
2.129
2.112
CN
OMe
3o
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2.01
3.00
2.00
2.02
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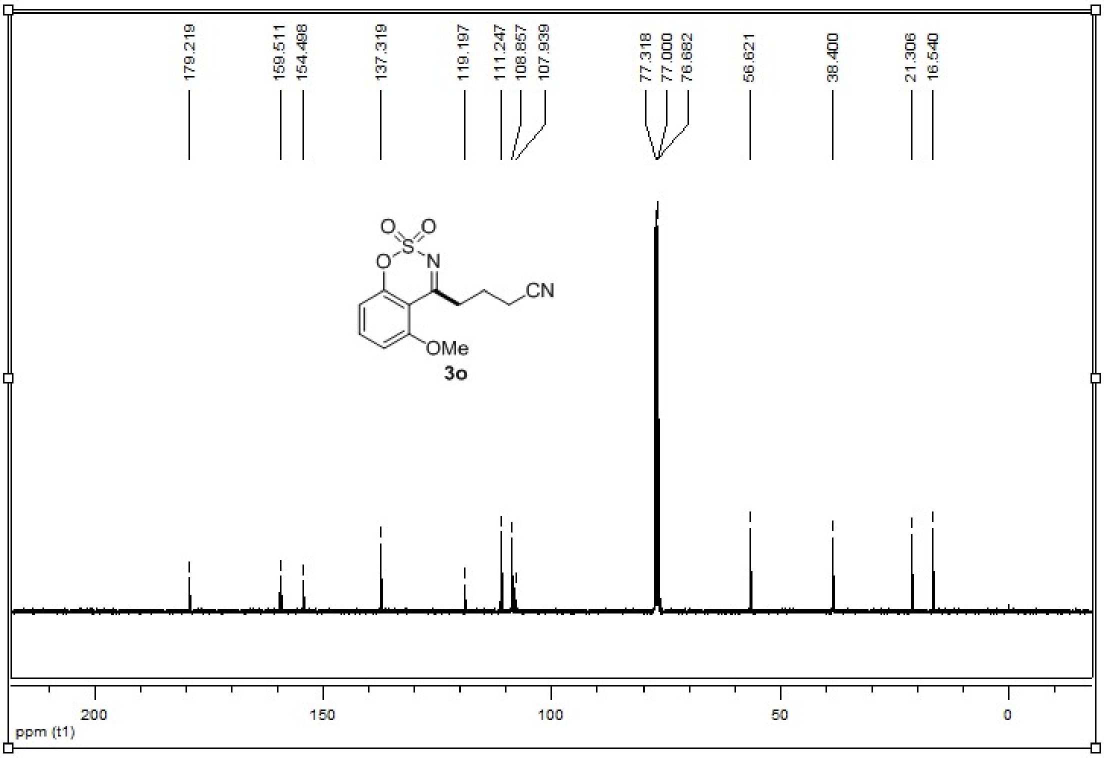
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77.000
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OMe
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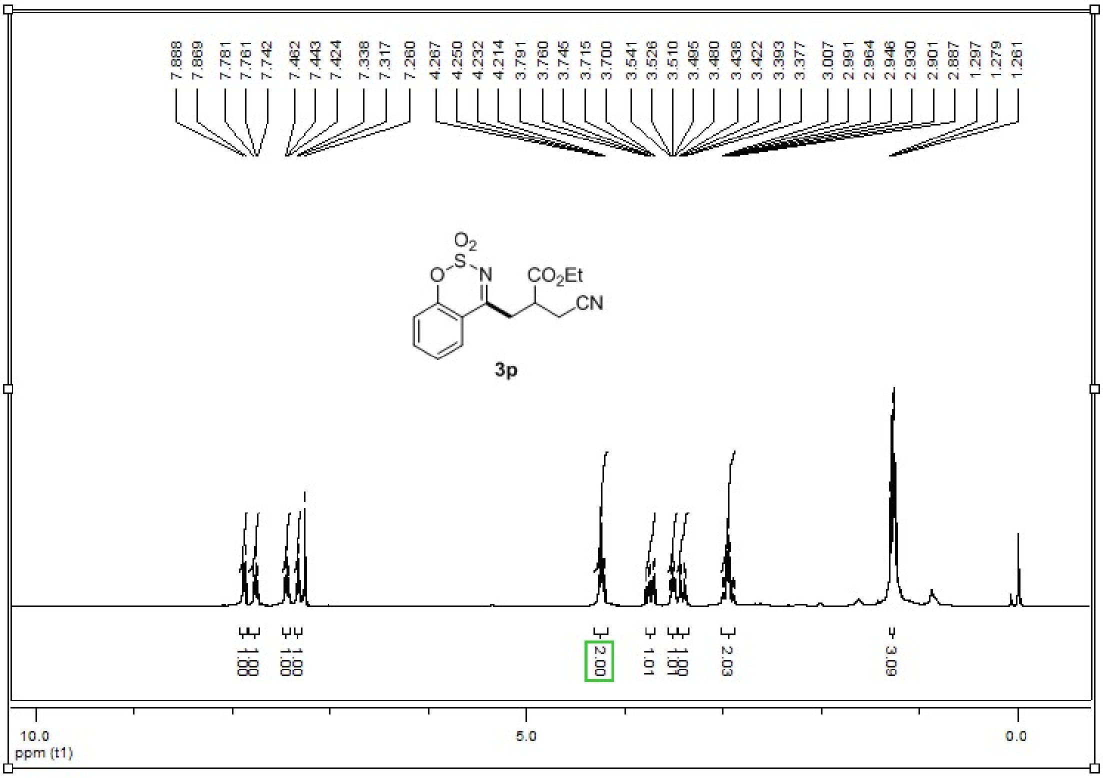
ppm (t1)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4.267
4.250
4.232
4.214
3.791
3.760
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3.715
3.700
3.541
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3.510
3.495
3.480
3.438
3.422
3.393
3.377
3.007
2.991
2.964
2.946
2.930
2.901
2.887
1.297
1.279
1.261
O2
S
O
N
CO2Et
CN
3p
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1.01
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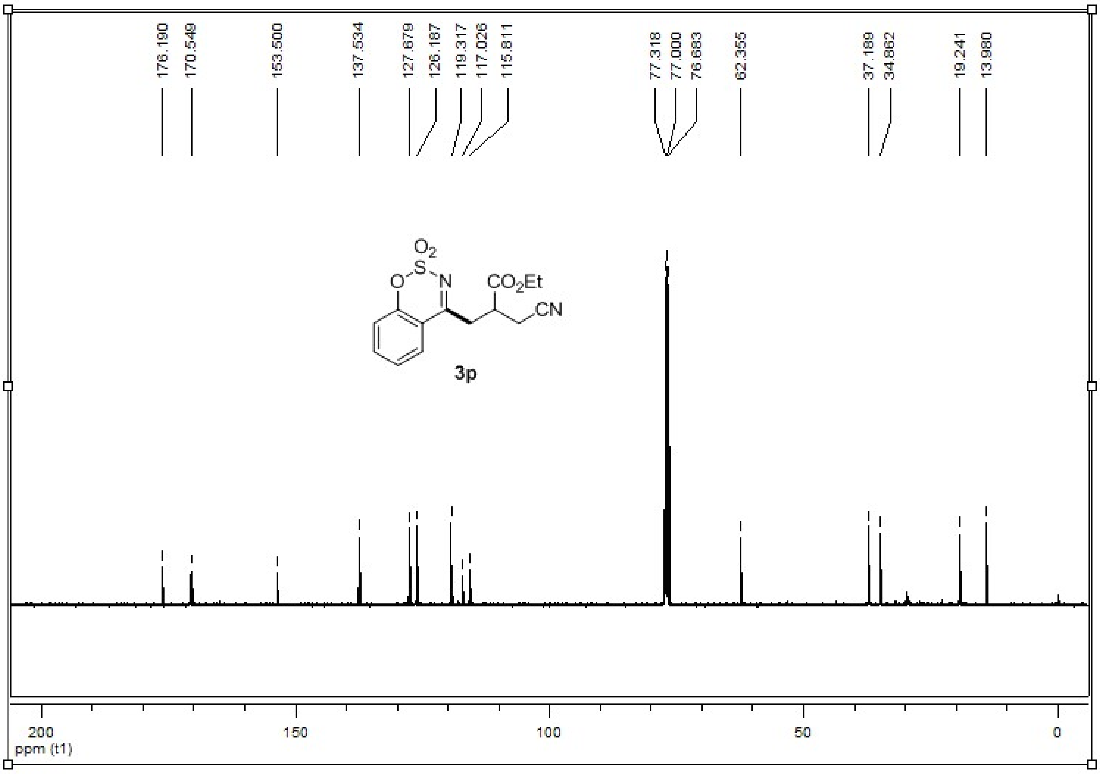
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37.189
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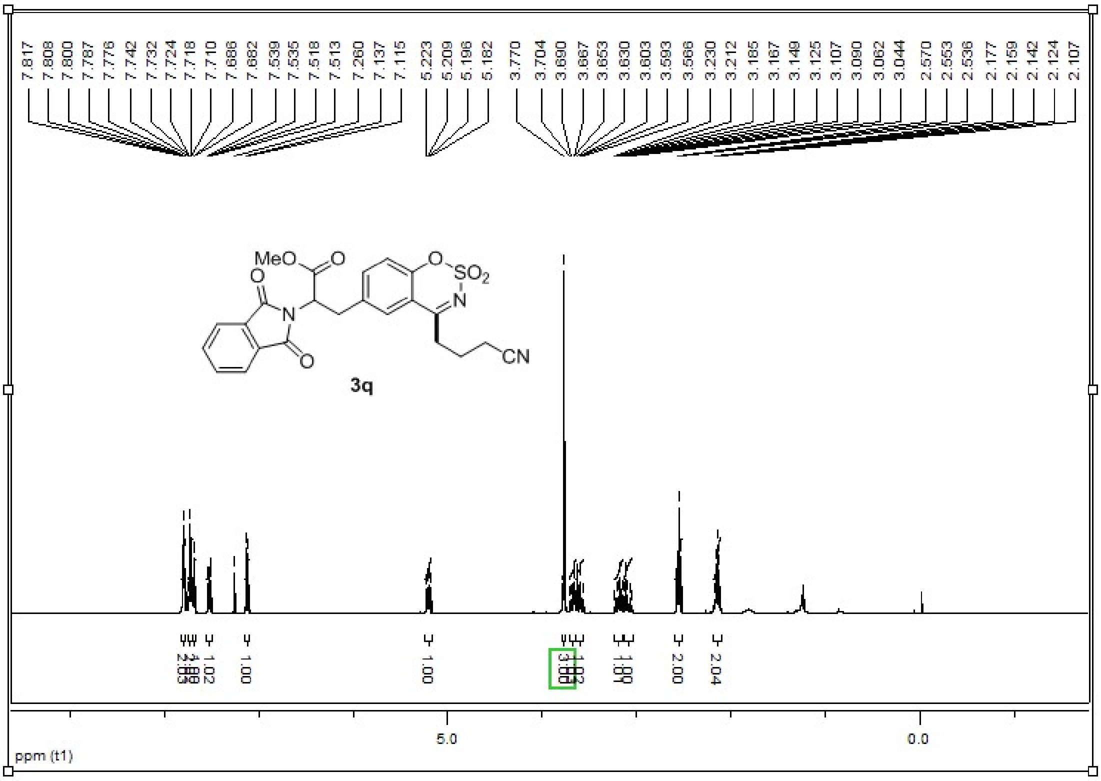
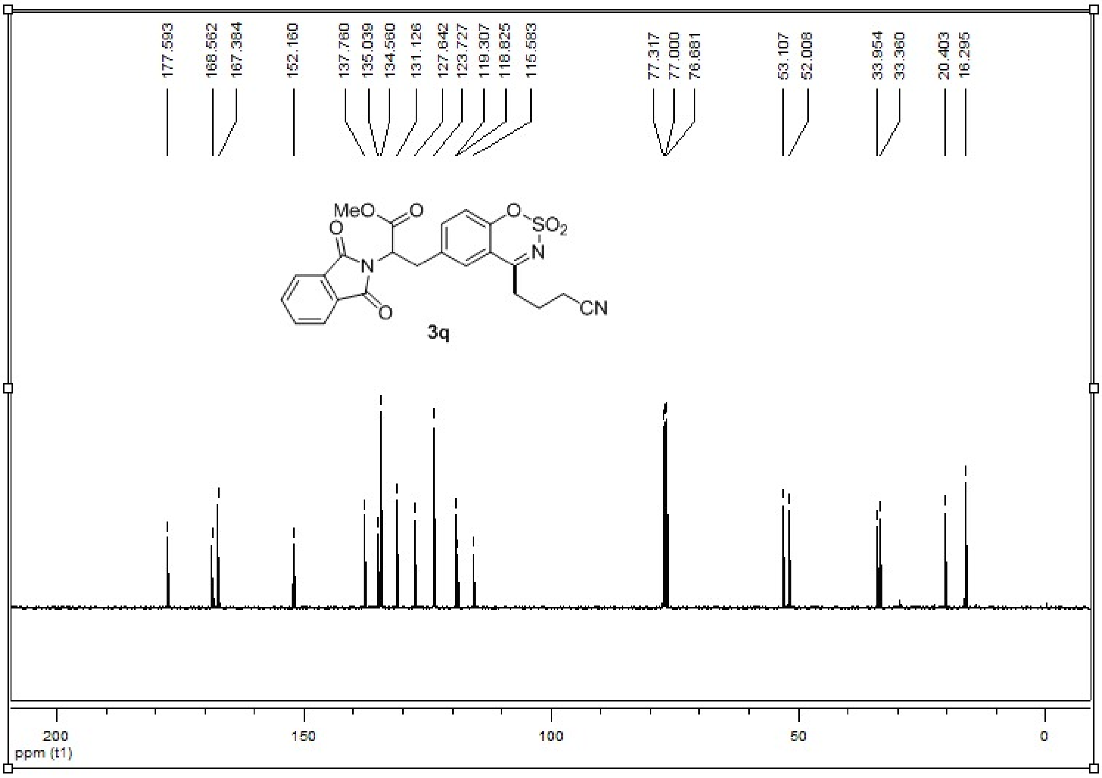
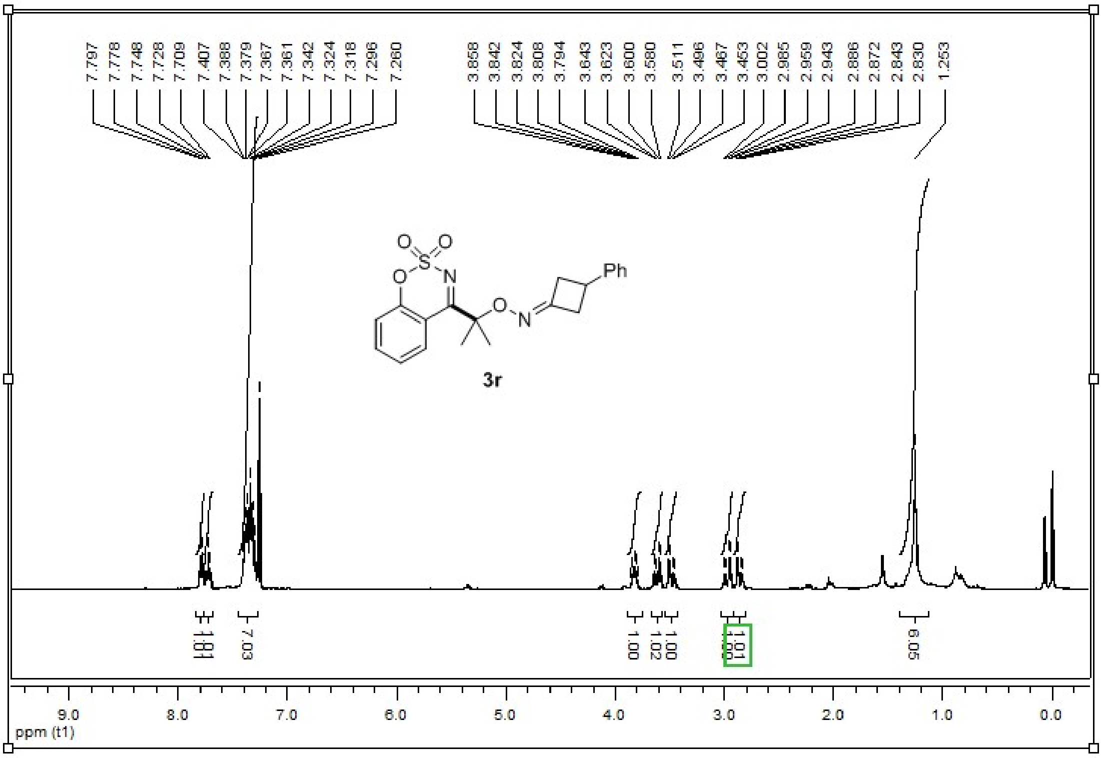
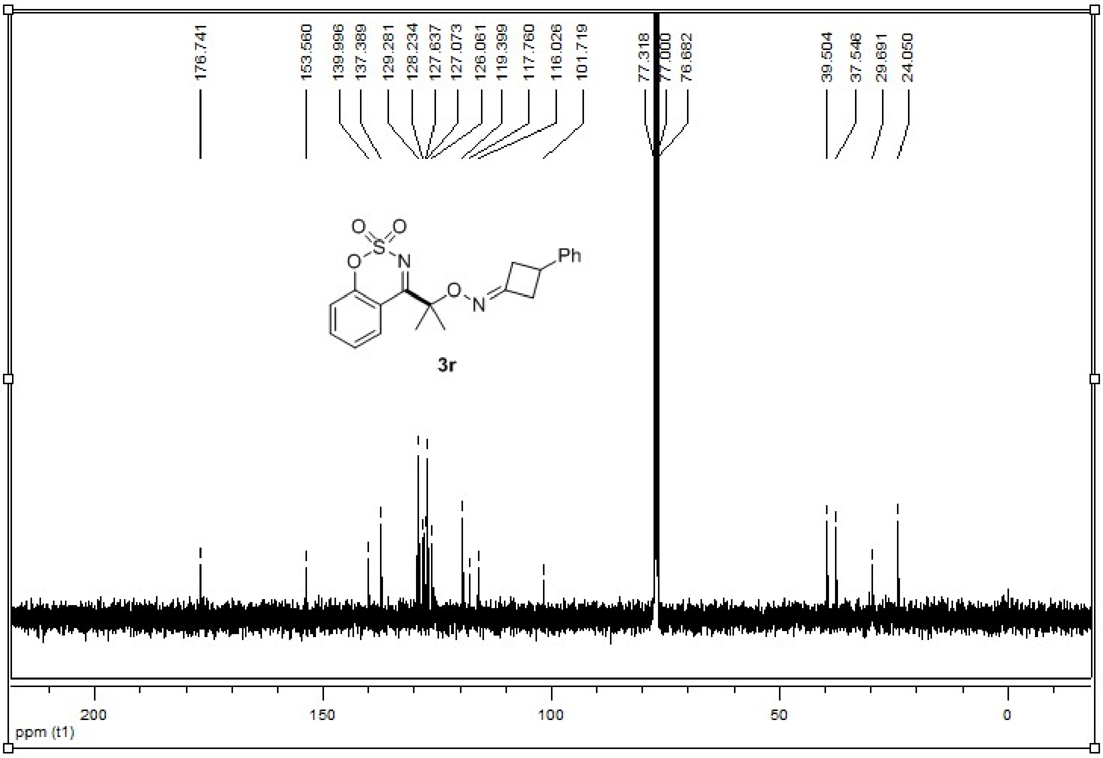
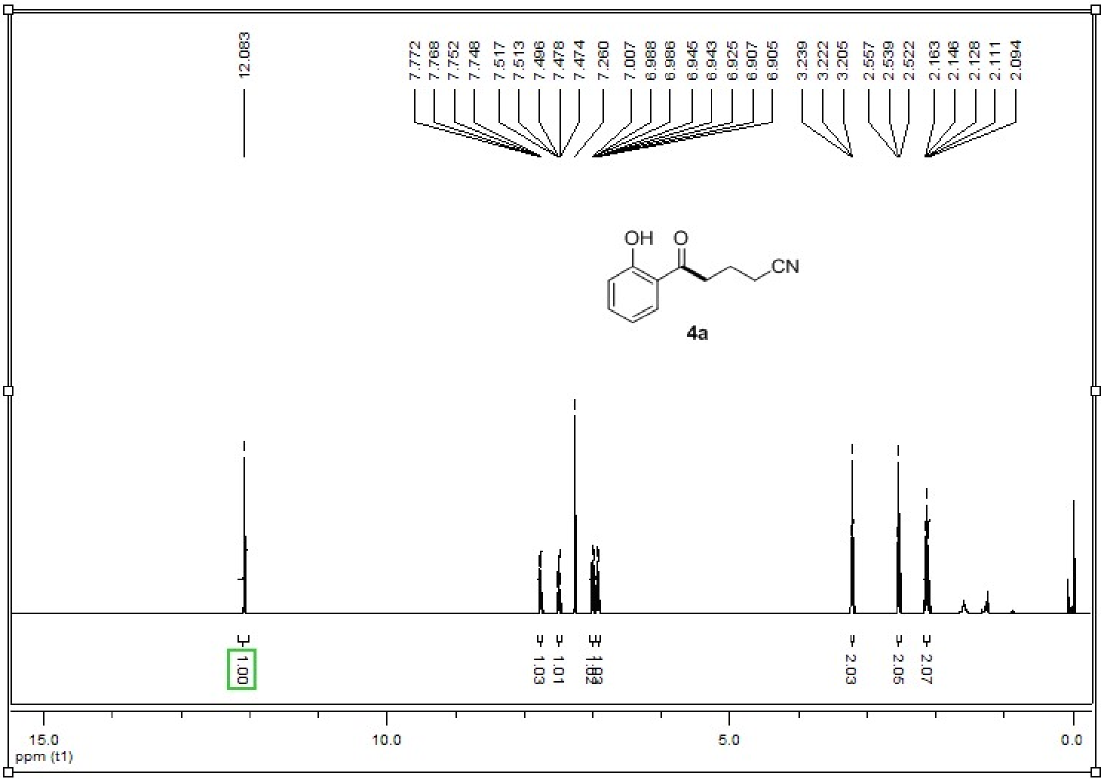
13.980
O2
S
O
N
CO2Et
CN
3p
200
ppm (t1)
150
100
50
0







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6.986
6.945
6.943
6.925
6.907
6.905
3.239
3.222
3.205
2.557
2.539
2.522
2.163
2.146
2.128
2.111
2.094
OH
O
CN
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2.03
2.05
2.07
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10.0
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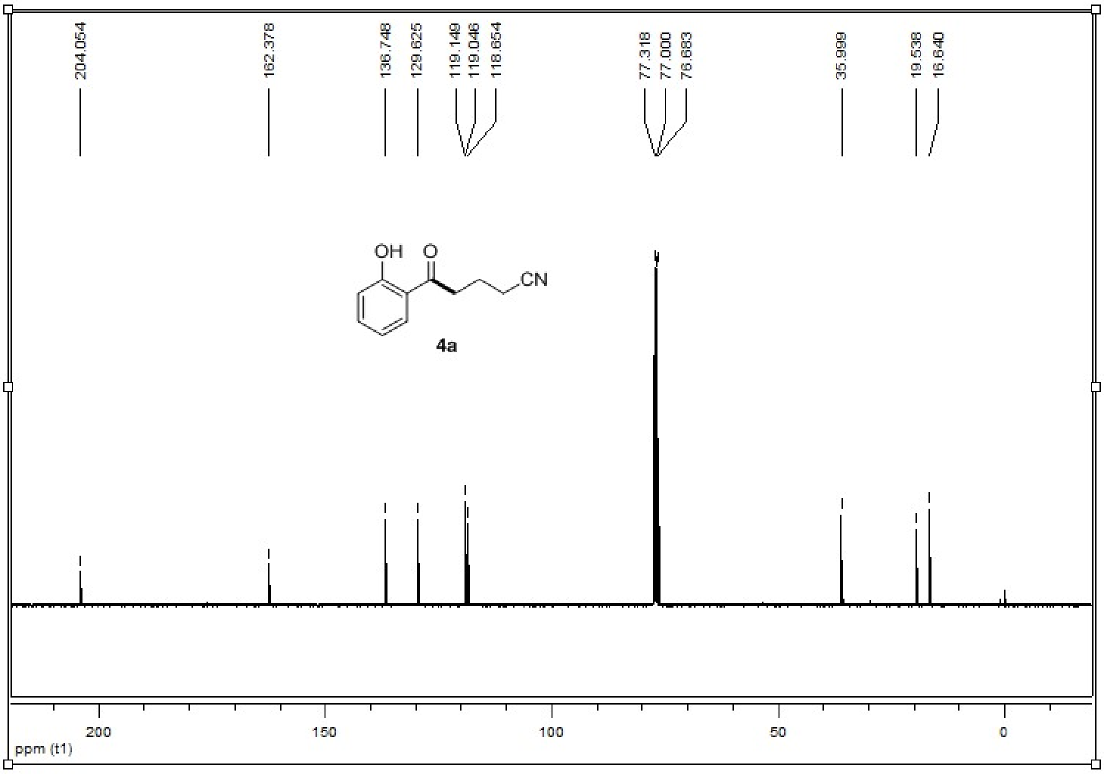
ppm (t1)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77.318
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O
CN
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100
50
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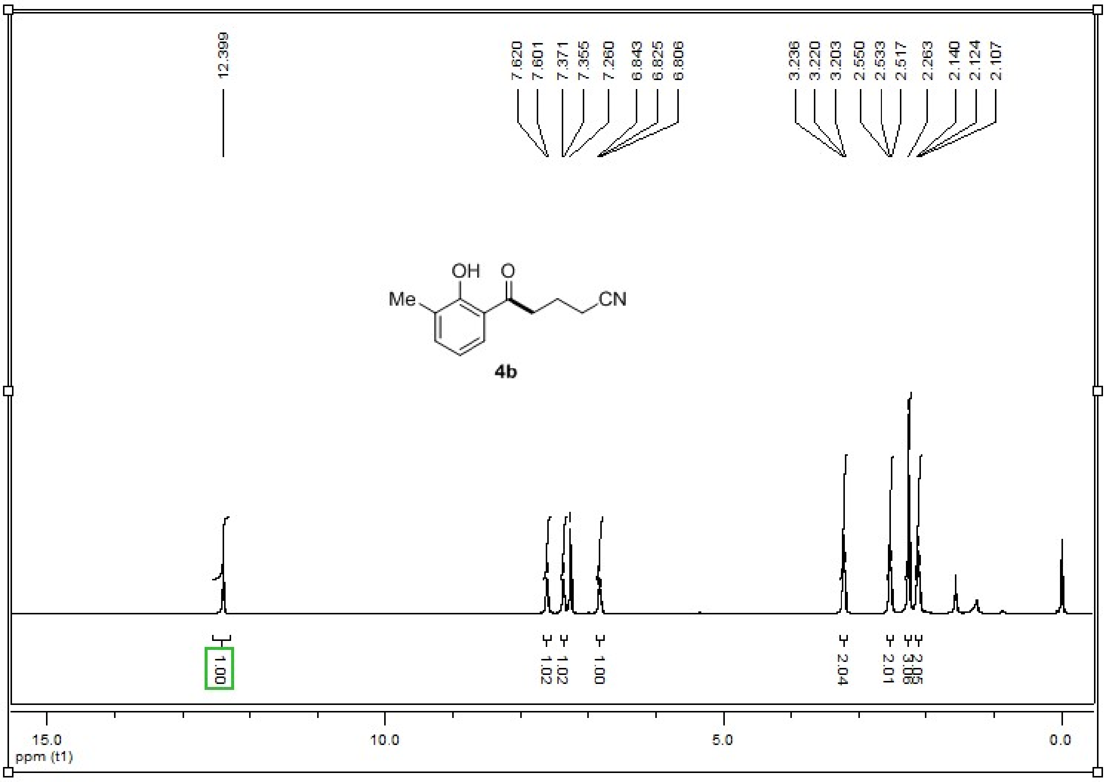
ppm (t1)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3.220
3.203
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2.533
2.517
2.263
2.140
2.124
2.107
OH
O
Me
CN
4b
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2.05
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10.0
5.0
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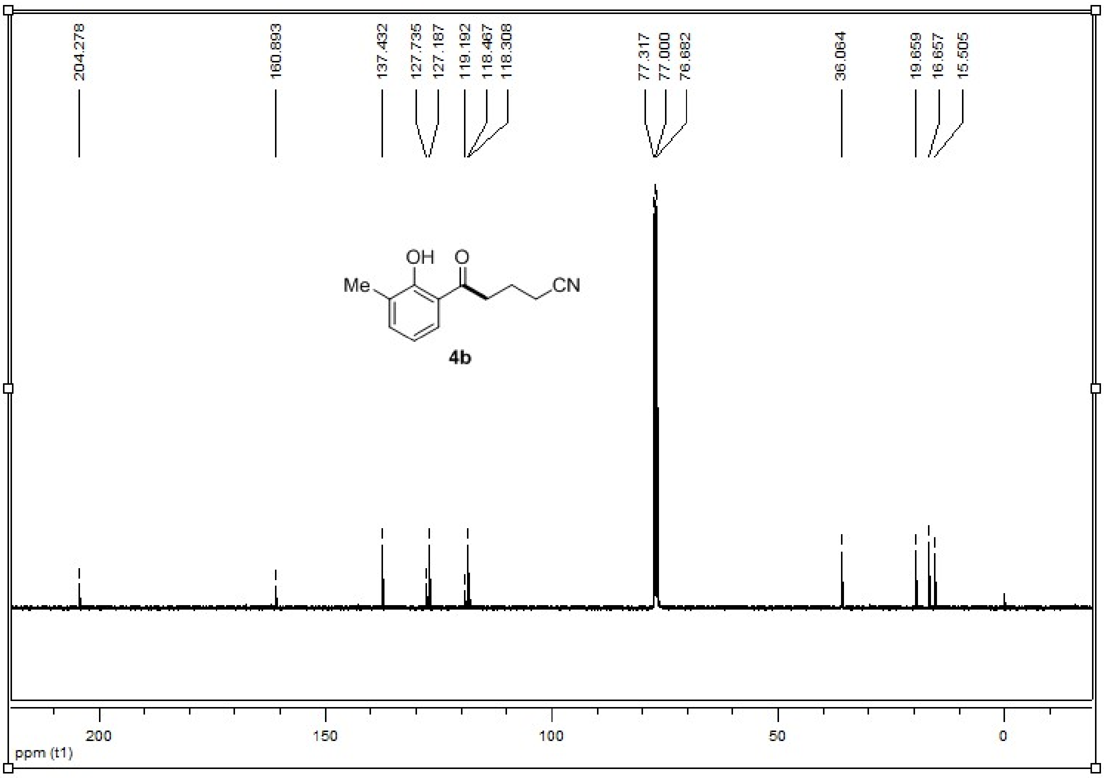
ppm (t1)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119.192
118.467
118.308
77.317
77.000
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16.657
15.505
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O
Me
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150
100
50
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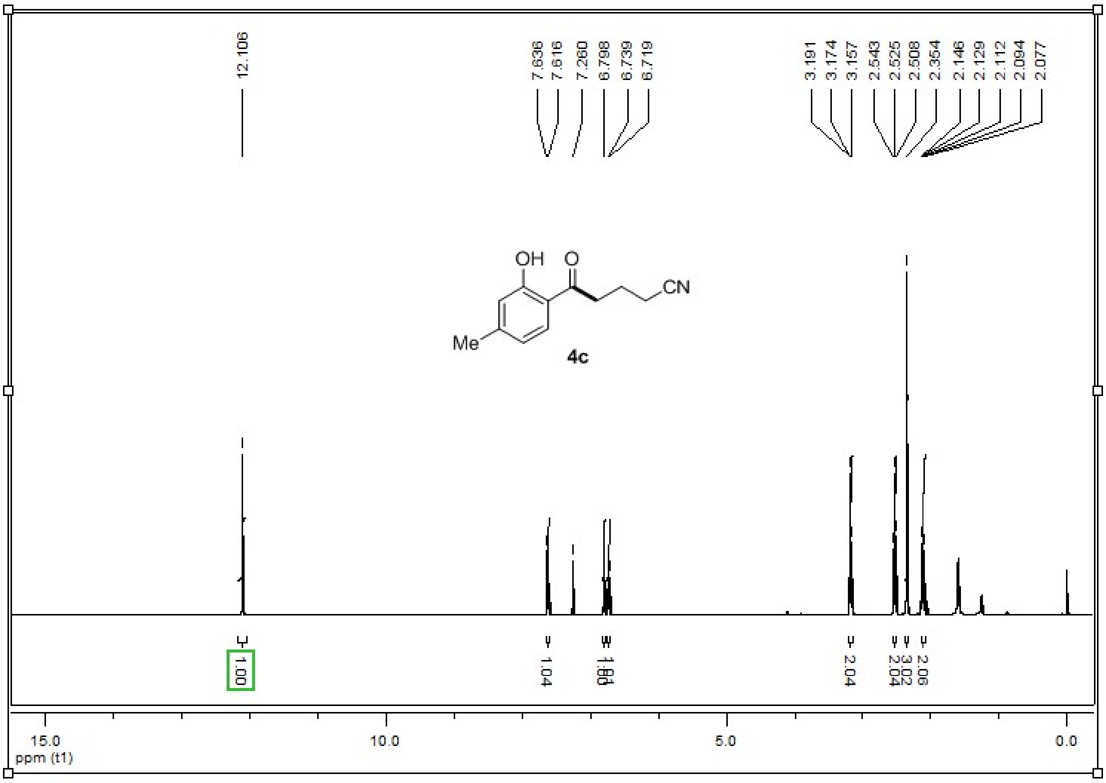
ppm (t1)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2.508
2.354
2.146
2.129
2.112
2.094
2.077
OH
O
CN
Me
4c
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1.04
2.04
3.02
2.06
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10.0
5.0
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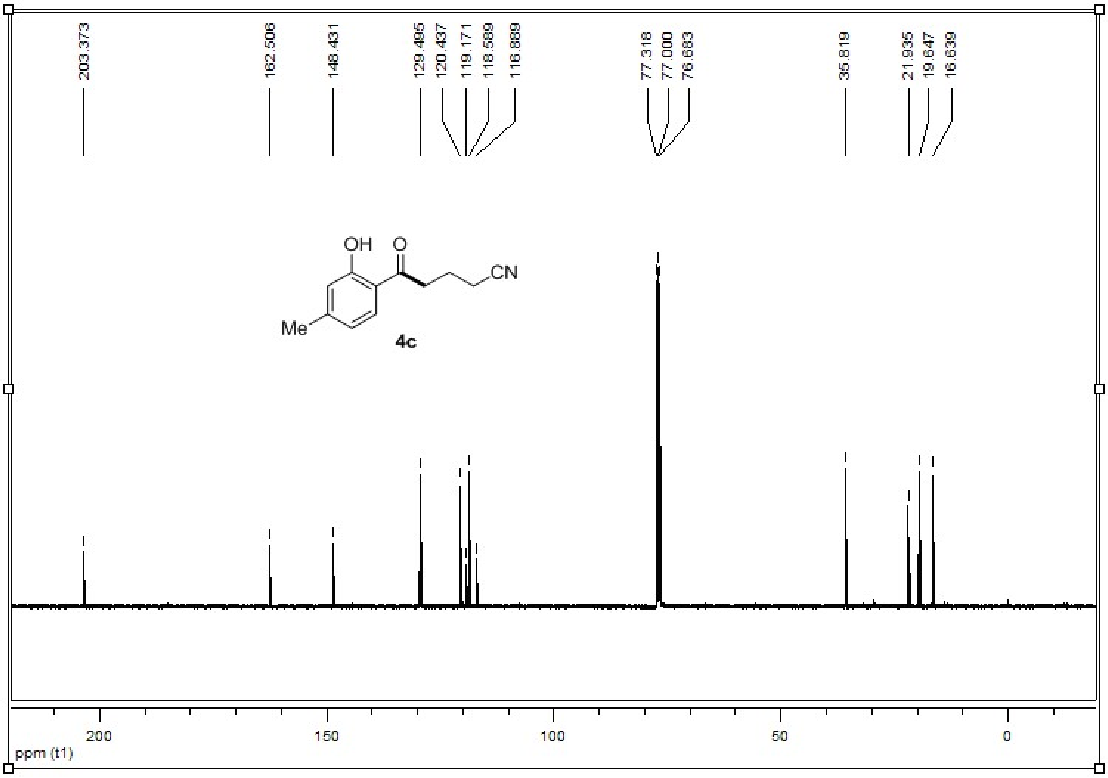
ppm (t1)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77.000
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19.647
16.639
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O
CN
Me
4c
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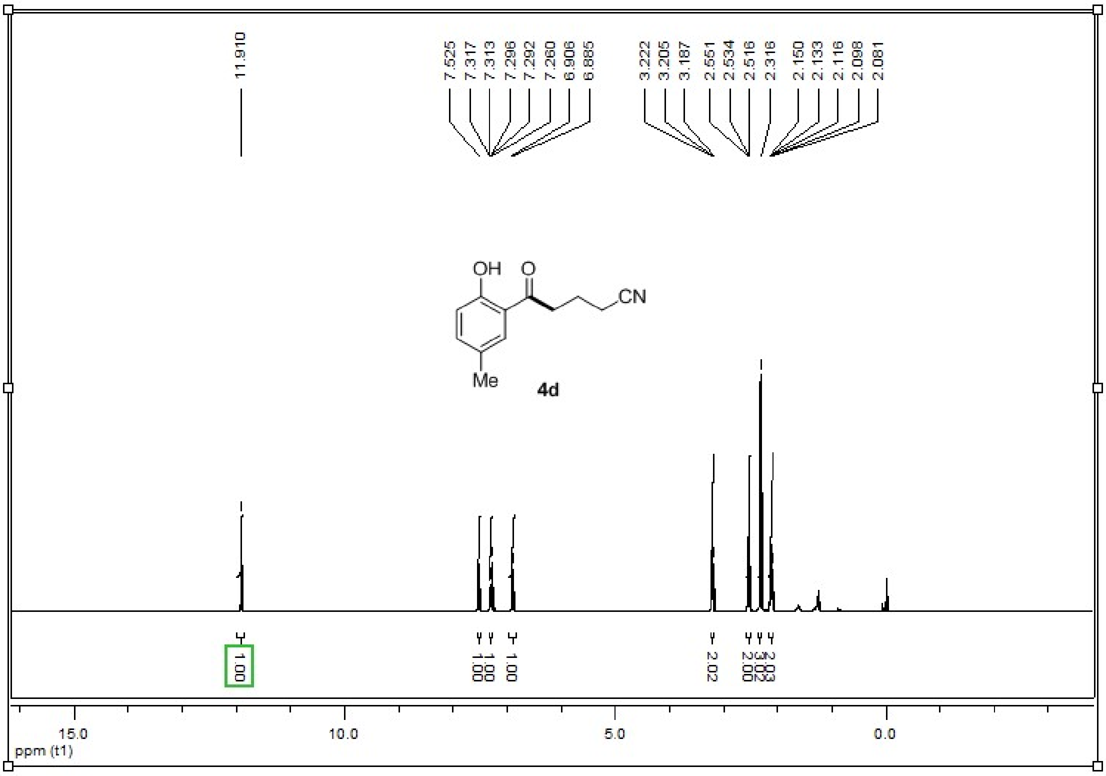
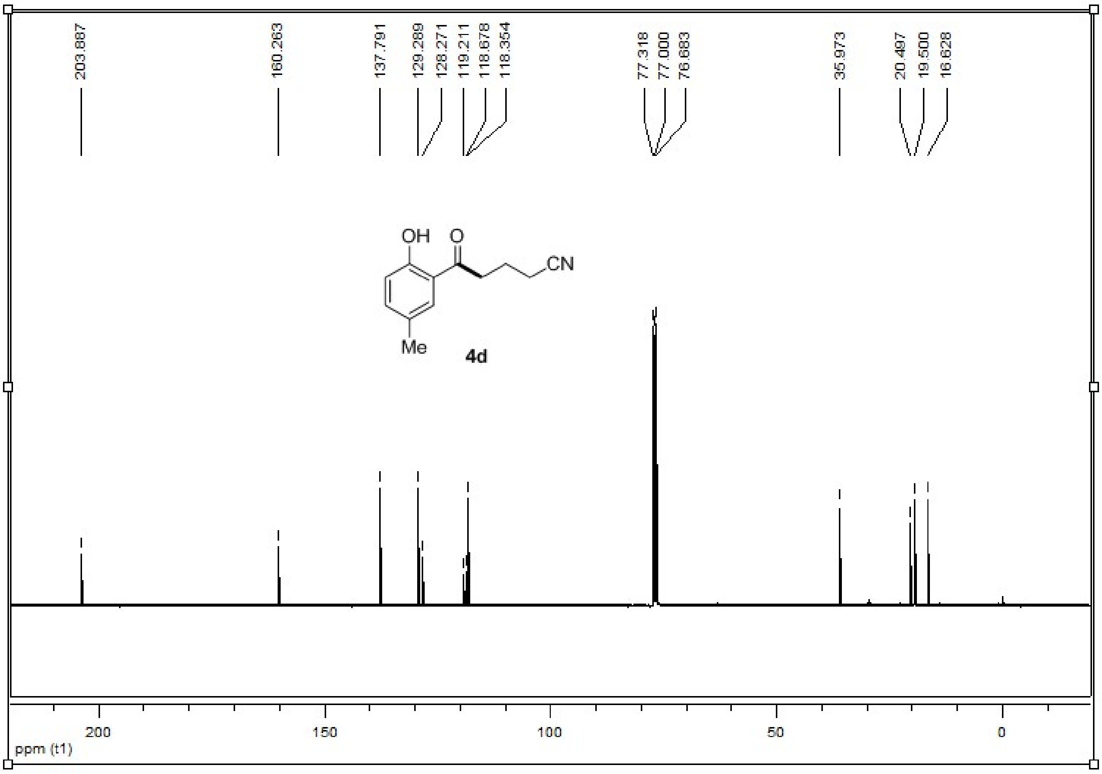
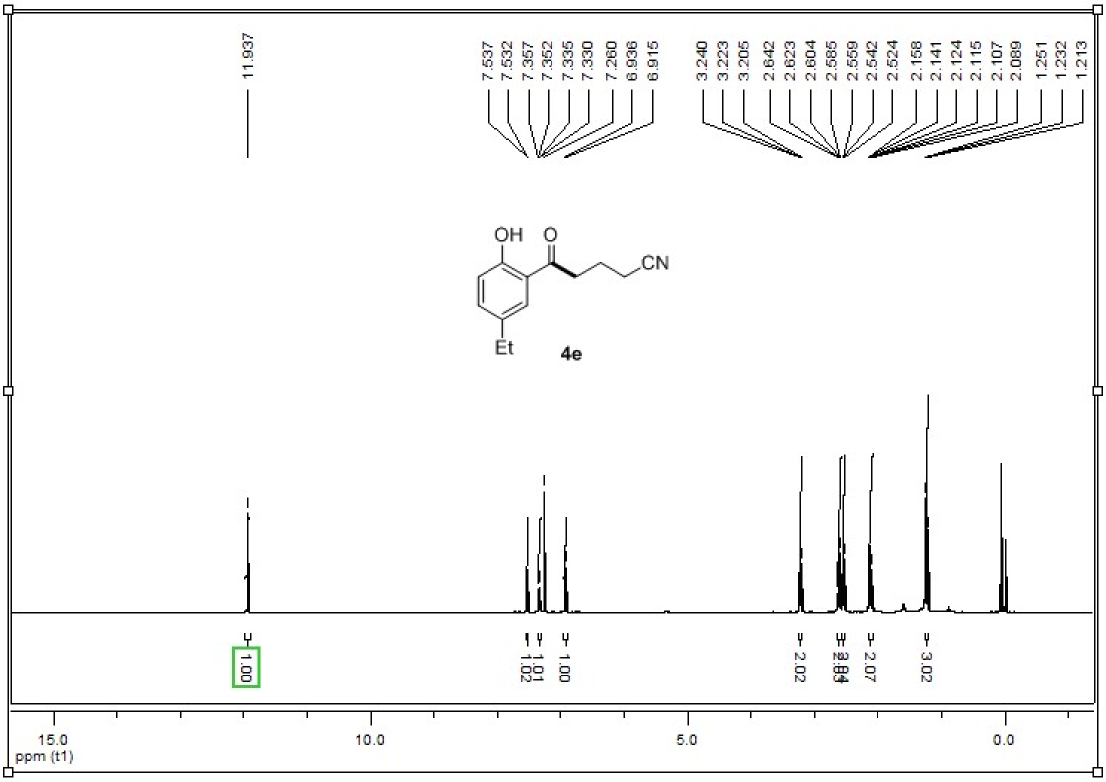
100
50
0
ppm (t1)



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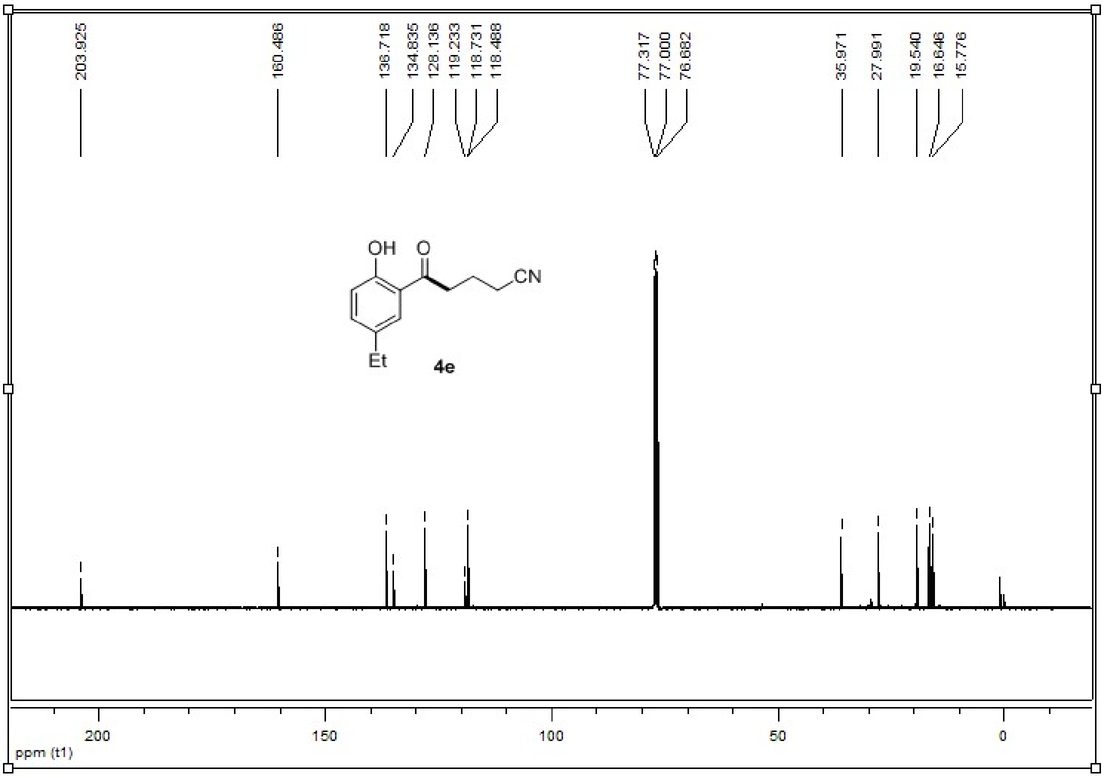
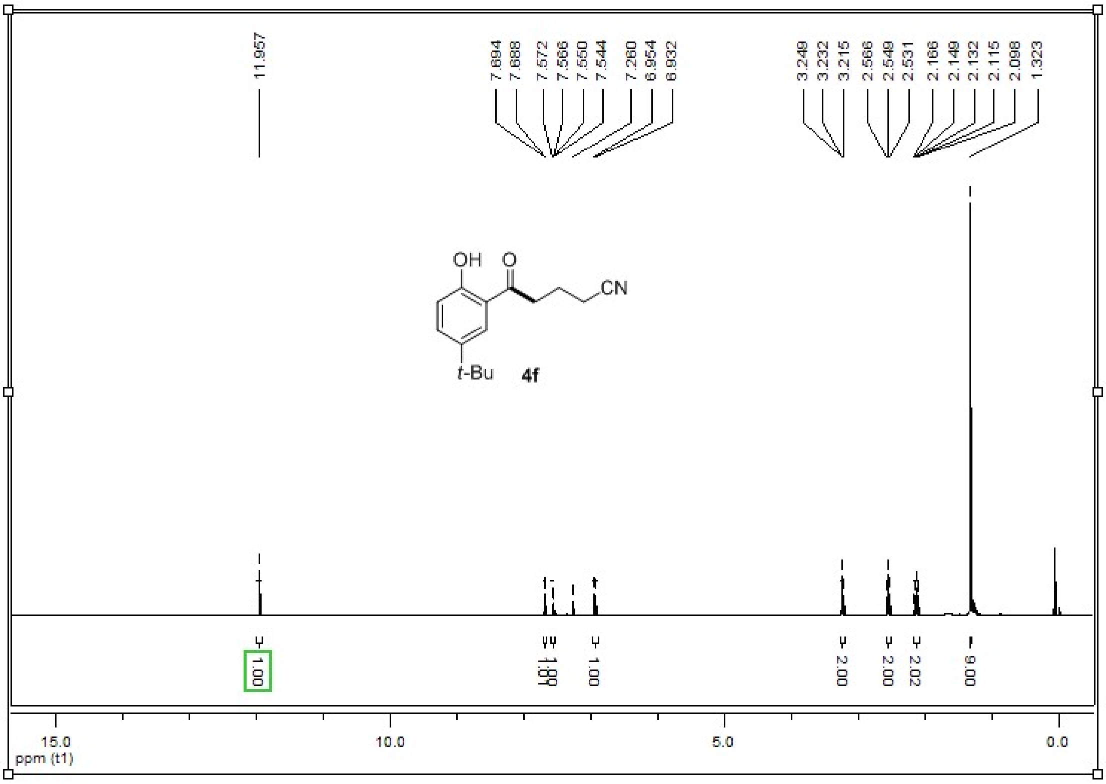
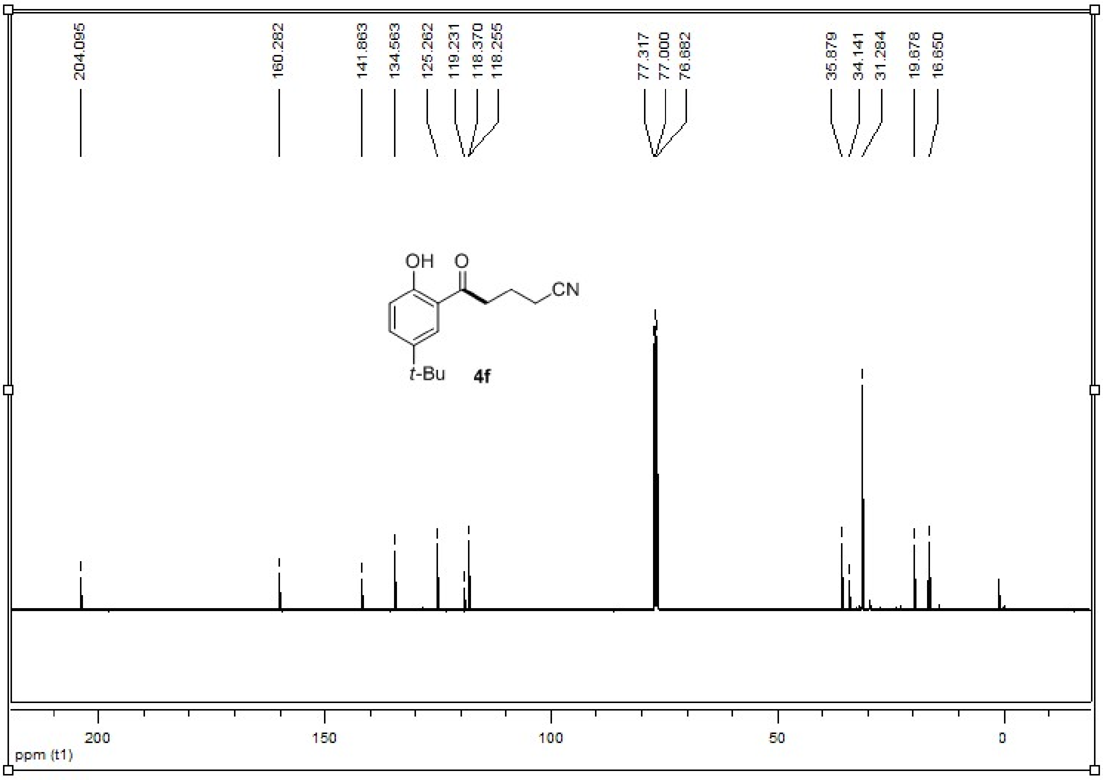
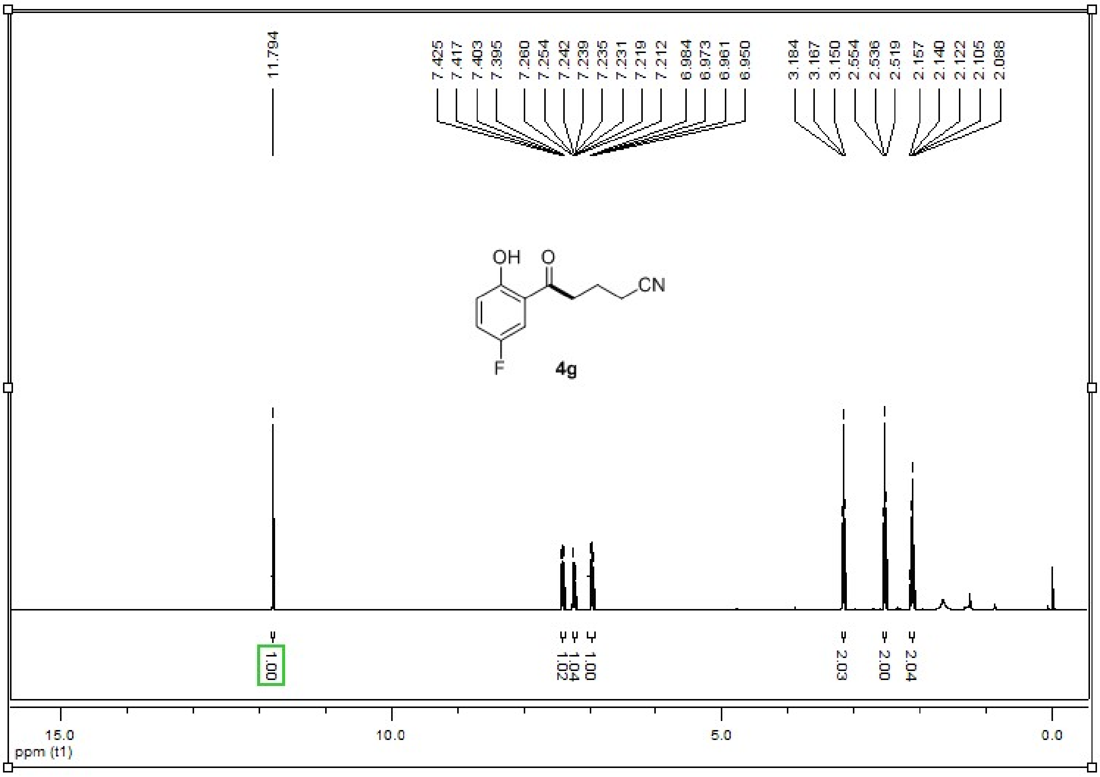
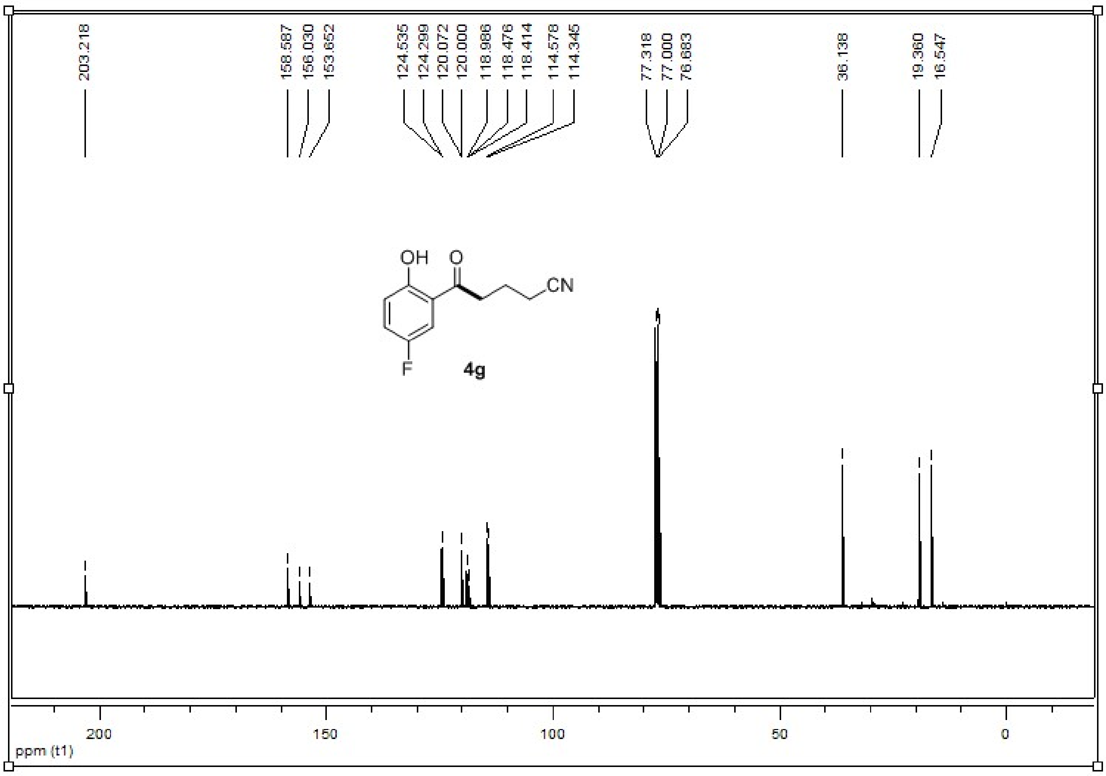
7.335
7.330
7.260
6.936
6.915
3.240
3.223
3.205
2.642
2.623
2.604
2.585
2.559
2.542
2.524
2.158
2.141
2.124
2.115
2.107
2.089
1.251
1.232
1.213
OH
O
CN
Et
4e
1.00
1.02
1.01
1.00
2.02
2.07
3.02
15.0
10.0
5.0
0.0
ppm (t1)

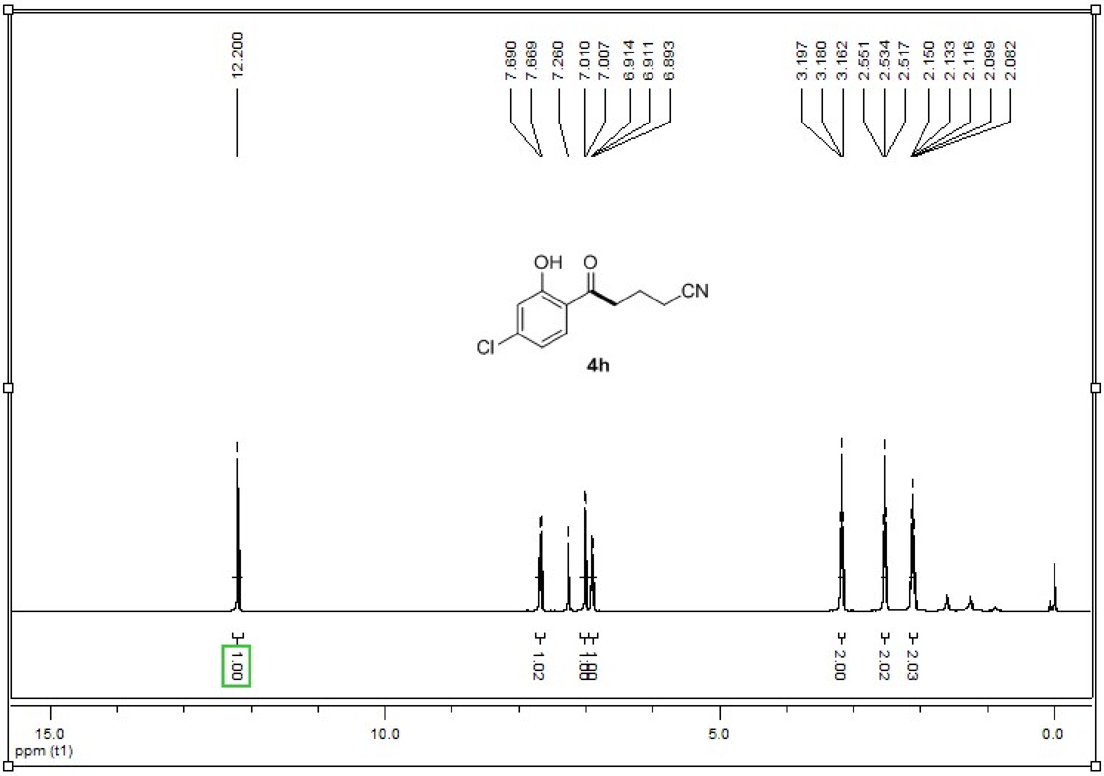

203.925
160.486
136.718
134.835
128.136
119.233
118.731
118.488
77.317
77.000
76.682
35.971
27.991
19.540
16.646
15.776
OH
O
CN
Et
4e
200
150
100
50
0
ppm (t1)

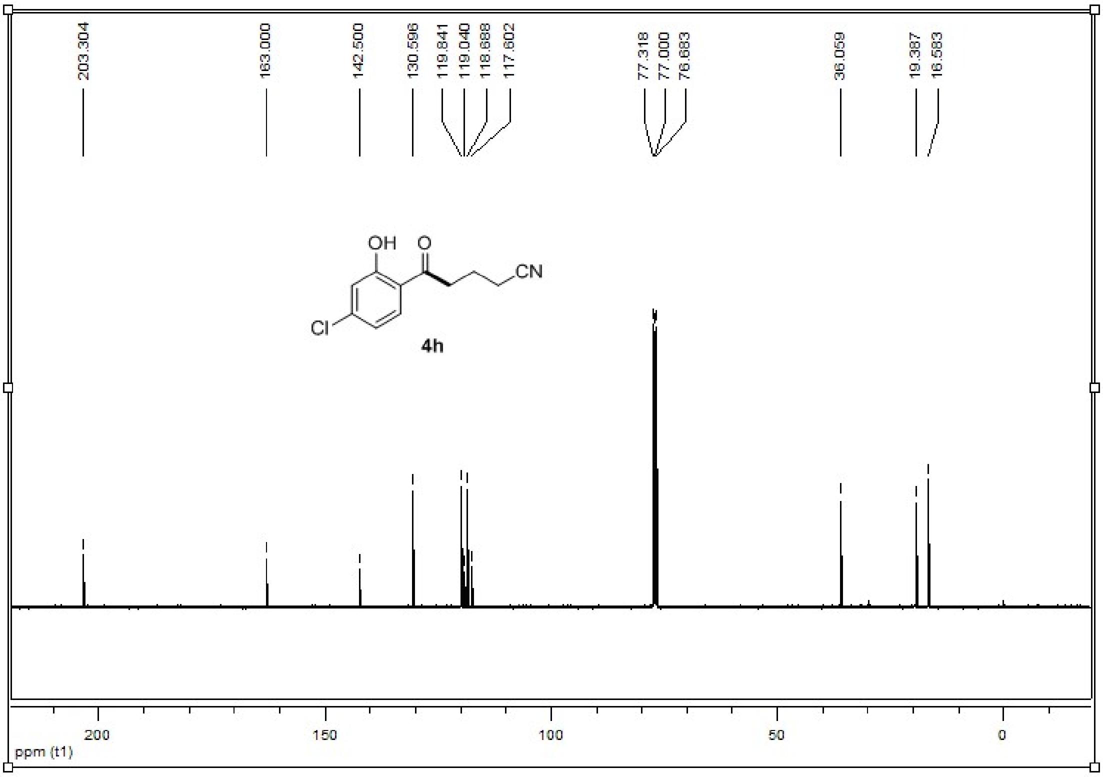

11.957
7.694
7.688
7.572
7.566
7.550
7.544
7.260
6.954
6.932
3.249
3.232
3.215
2.566
2.549
2.531
2.166
2.149
2.132
2.115
2.098
1.323
OH
O
CN
t-Bu
4f
1.00
1.00
2.00
2.00
2.02
9.00
15.0
10.0
5.0
0.0
ppm (t1)

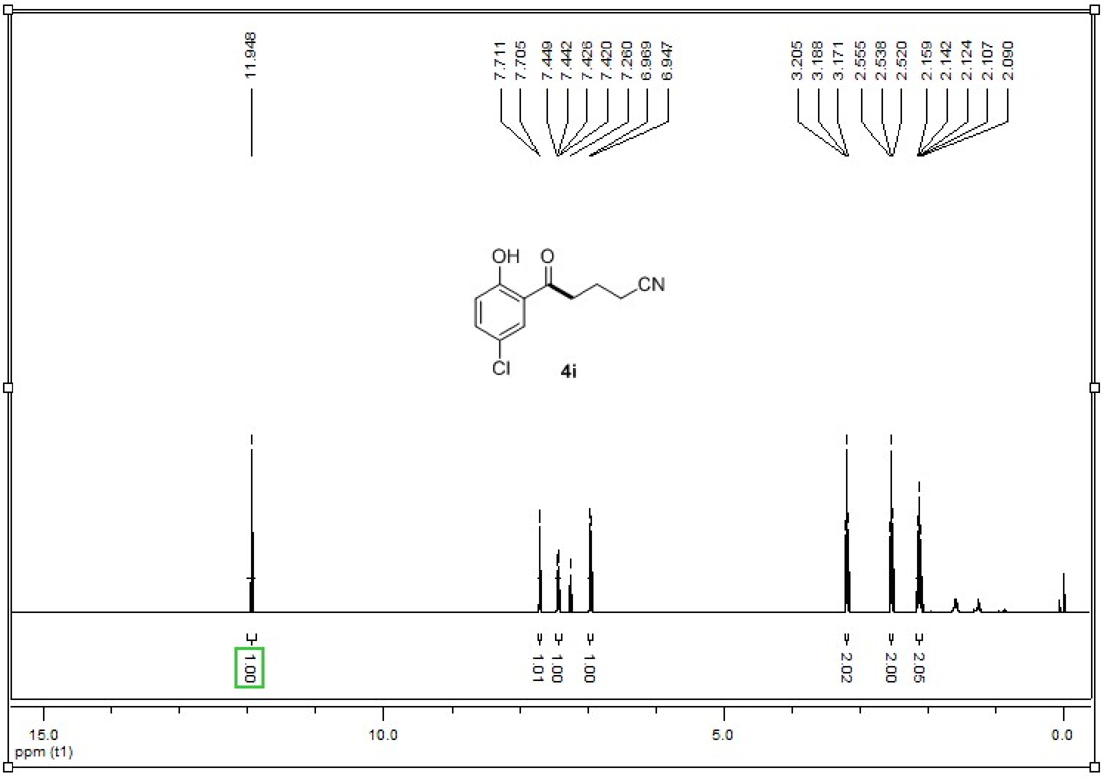

204.095
160.282
141.863
134.563
125.262
119.231
118.370
118.255
77.317
77.000
76.682
35.879
34.141
31.284
19.678
16.650
OH
O
CN
t-Bu
4f
200
150
100
50
0
ppm (t1)






12.200
7.690
7.669
7.260
7.010
7.007
6.914
6.911
6.893
3.197
3.180
3.162
2.551
2.534
2.517
2.150
2.133
2.116
2.099
2.082
OH
O
CN
Cl
4h
1.00
1.02
1.88
2.00
2.02
2.03
15.0
10.0
5.0
0.0
ppm (t1)


203.304
163.000
142.500
130.596
119.841
119.040
118.688
117.602
77.318
77.000
76.683
36.059
19.387
16.583
OH
O
CN
Cl
4h
200
150
100
50
0
ppm (t1)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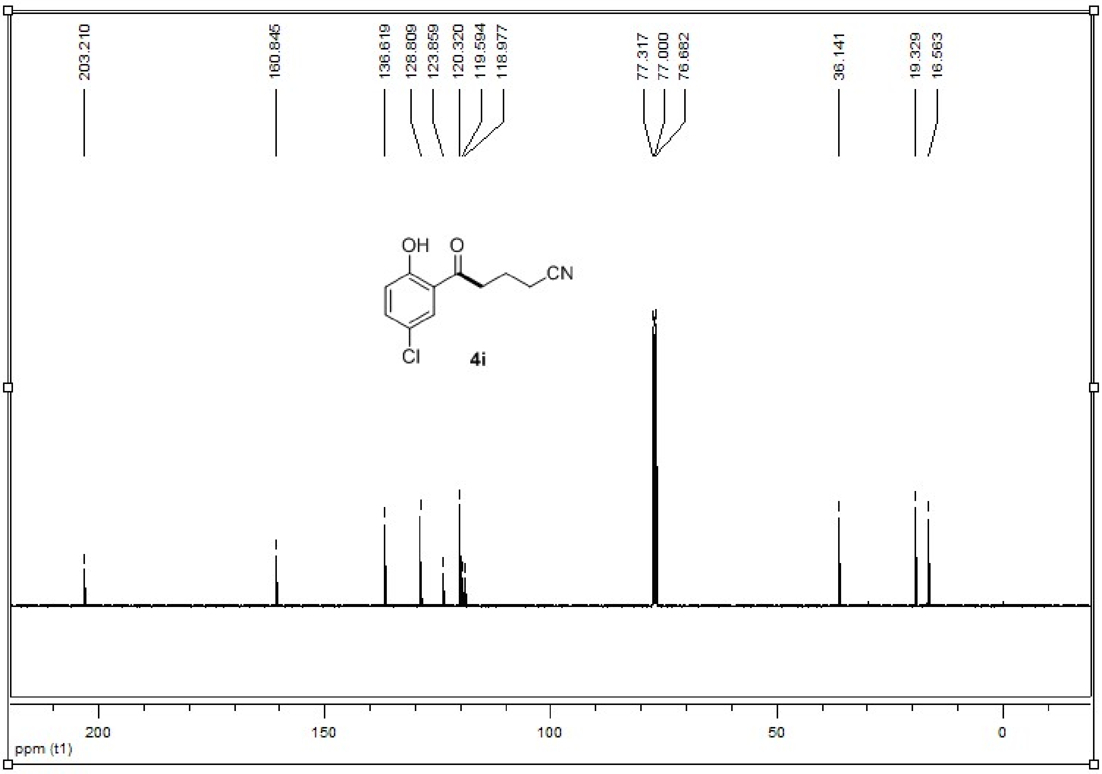
7.711
7.705
7.449
7.442
7.426
7.420
7.260
6.969
6.947
3.205
3.188
3.171
2.555
2.538
2.520
2.159
2.142
2.124
2.107
2.090
OH
O
CN
Cl
4i
1.00
1.01
1.00
1.00
2.02
2.00
2.05
15.0
10.0
5.0
0.0
ppm (t1)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160.845
136.619
128.809
123.859
120.320
119.594
118.977
77.317
77.000
76.682
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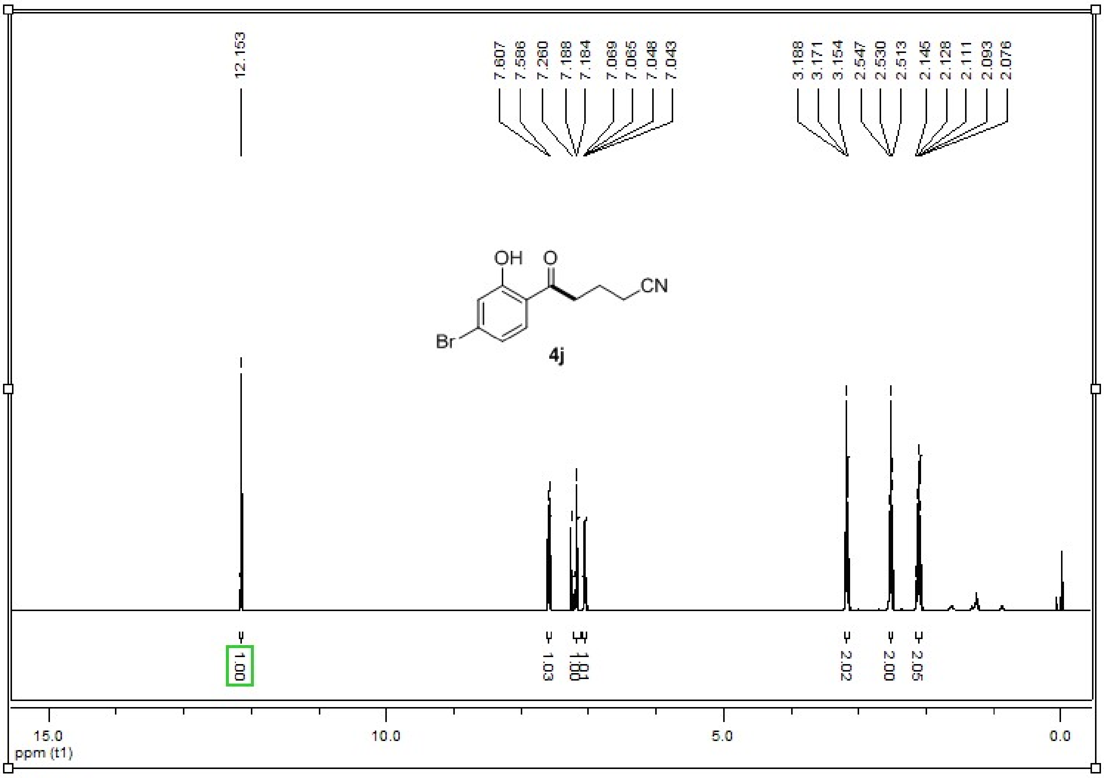
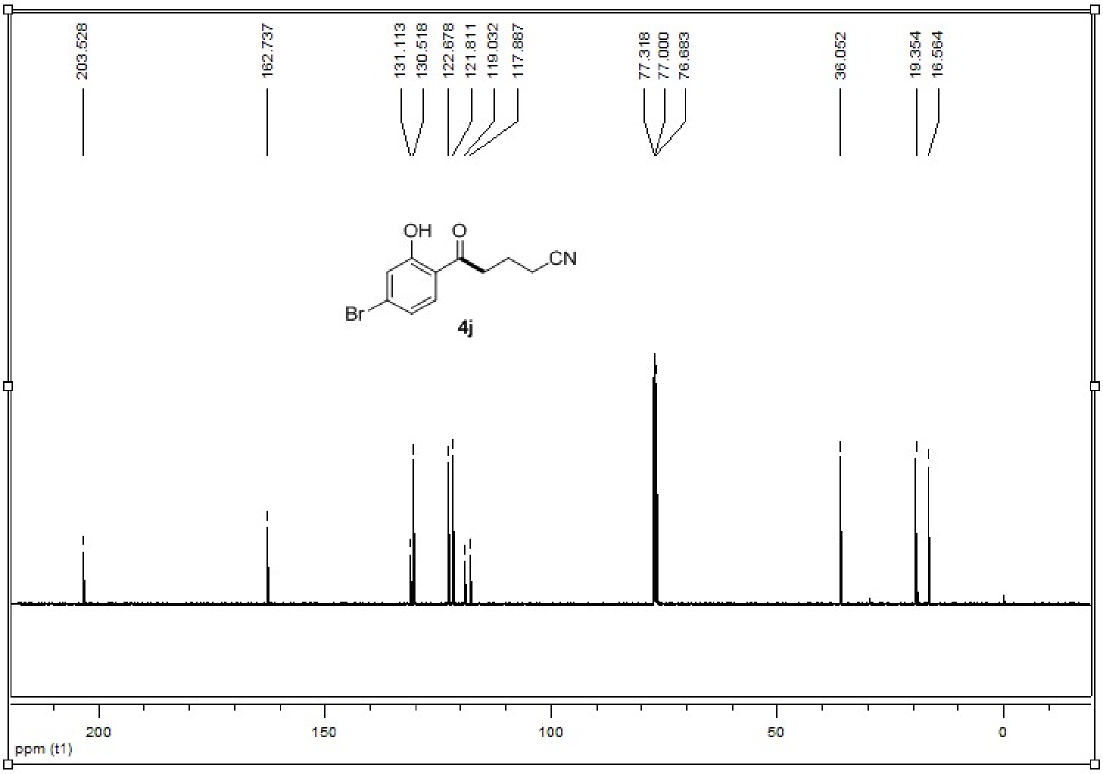
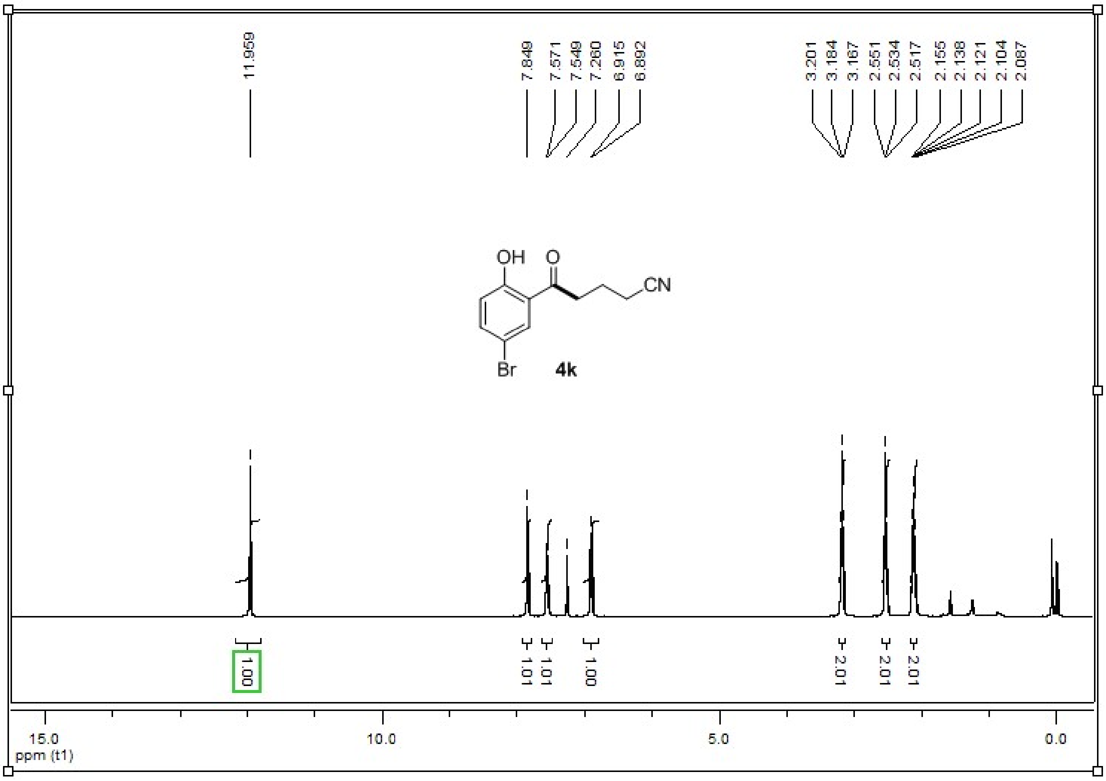
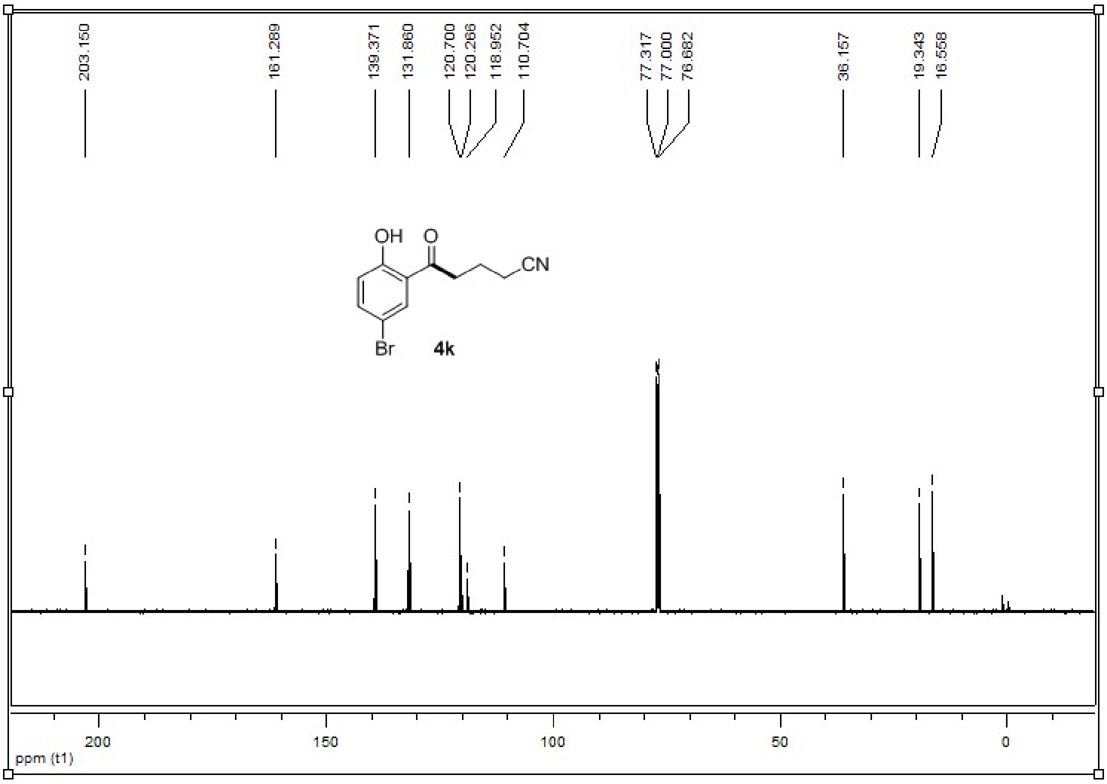
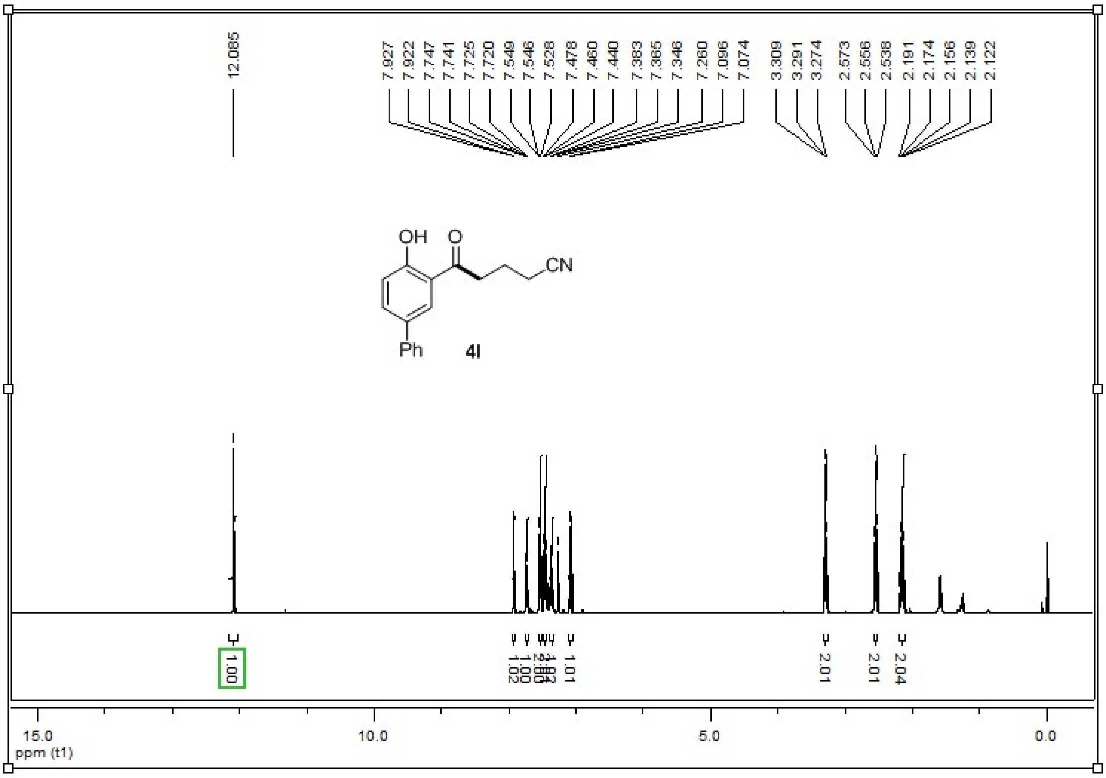
19.329
16.563
OH
O
CN
Cl
4i
200
150
100
50
0
ppm (t1)

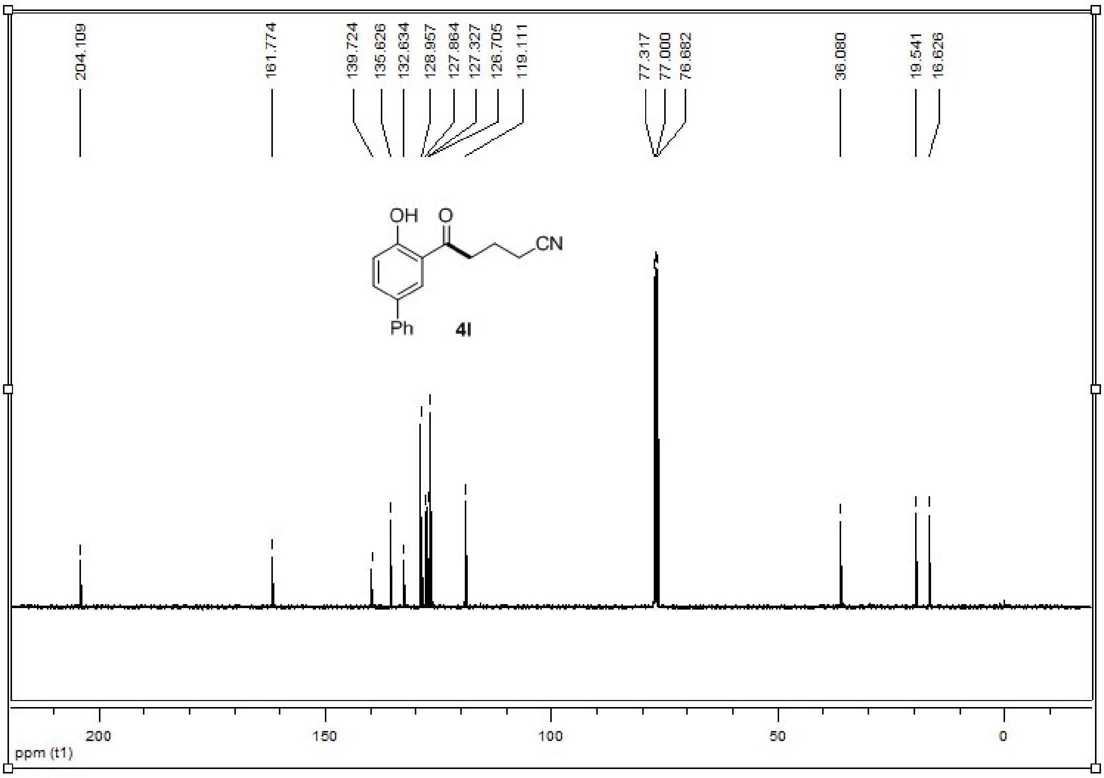

12.153
7.607
7.586
7.260
7.188
7.184
7.069
7.065
7.048
7.043
3.188
3.171
3.154
2.547
2.530
2.513
2.145
2.128
2.111
2.093
2.076
OH
O
CN
Br
4j
1.00
1.03
1.01
1.01
2.02
2.00
2.05
15.0
10.0
5.0
0.0
ppm (t1)

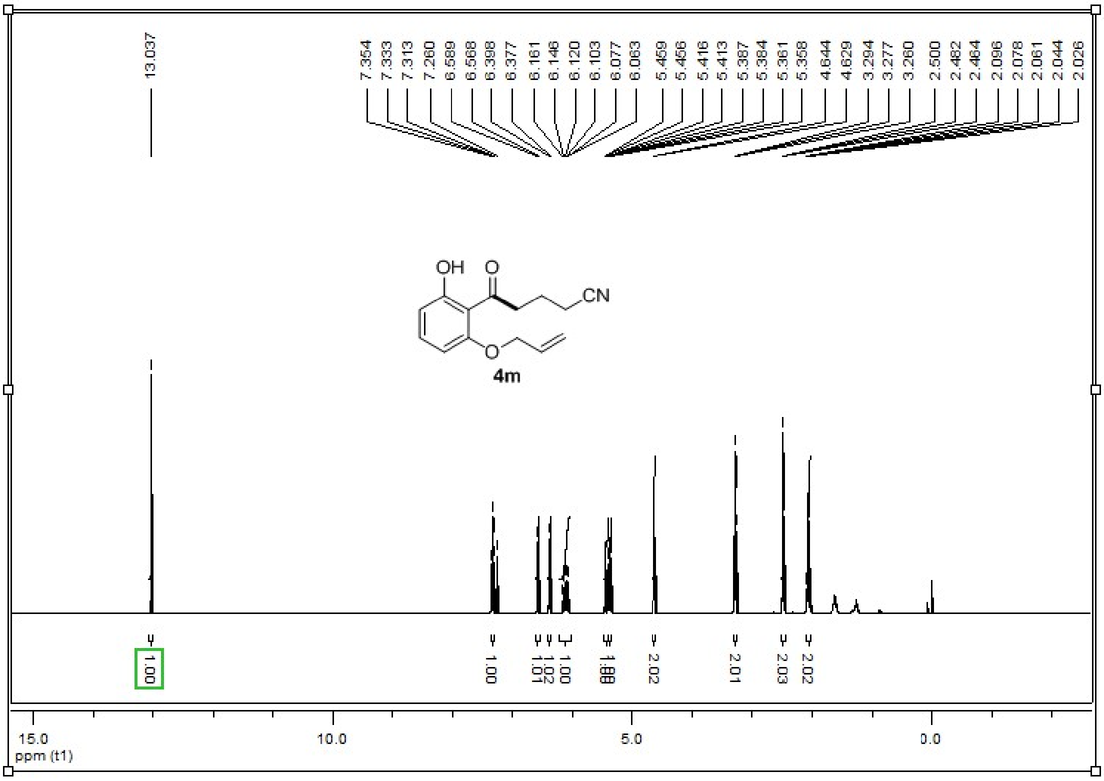

203.528
162.737
131.113
130.518
122.678
121.811
119.032
117.887
77.318
77.000
76.683
36.052
19.354
16.564
OH
O
CN
Br
4j
200
150
100
50
0
ppm (t1)

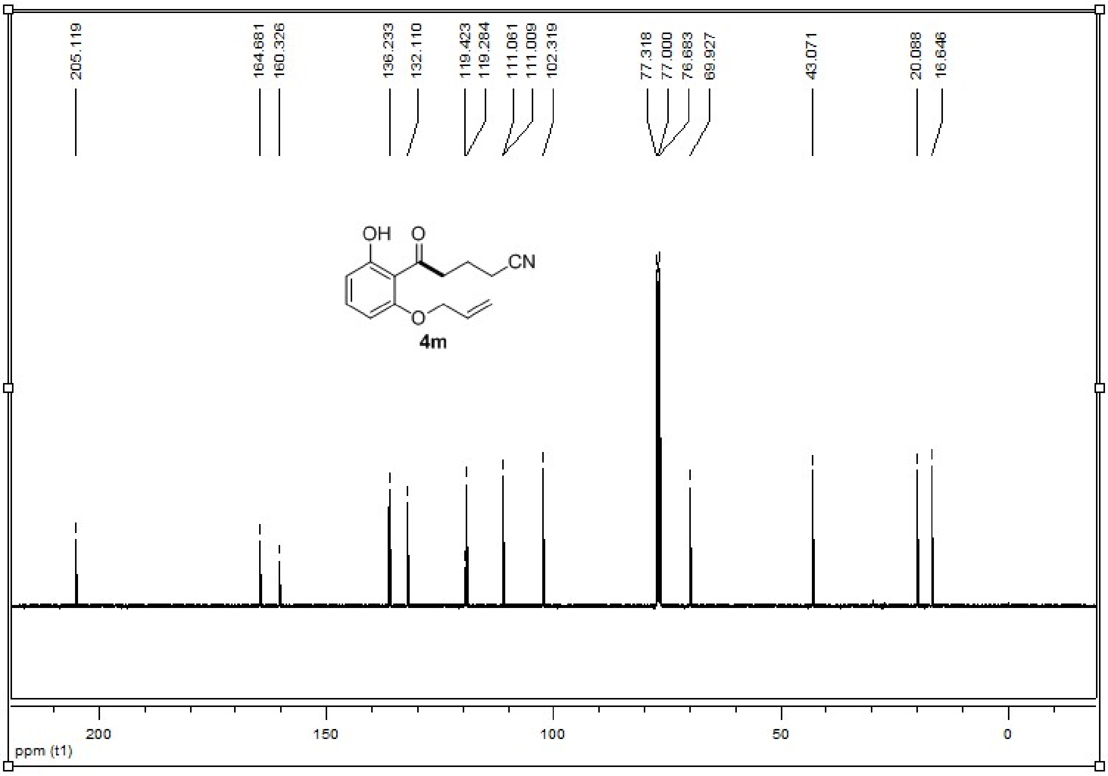

11.959
7.849
7.571
7.549
7.260
6.915
6.892
3.201
3.184
3.167
2.551
2.534
2.517
2.155
2.138
2.121
2.104
2.087
OH
O
CN
Br
4k
1.00
1.01
1.01
1.00
2.01
2.01
2.01
15.0
10.0
5.0
0.0
ppm (t1)

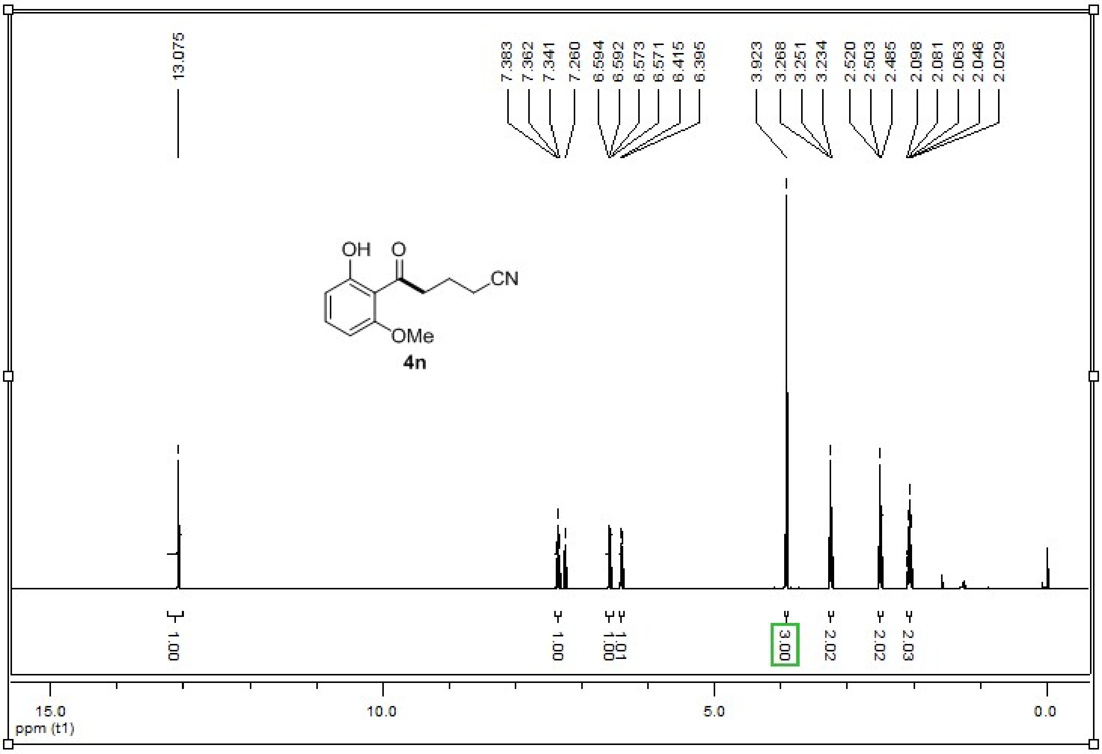

203.150
161.289
139.371
131.860
120.700
120.266
118.952
110.704
77.317
77.000
76.682
36.157
19.343
16.558
OH
O
CN
Br
4k
200
150
100
50
0
ppm (t1)

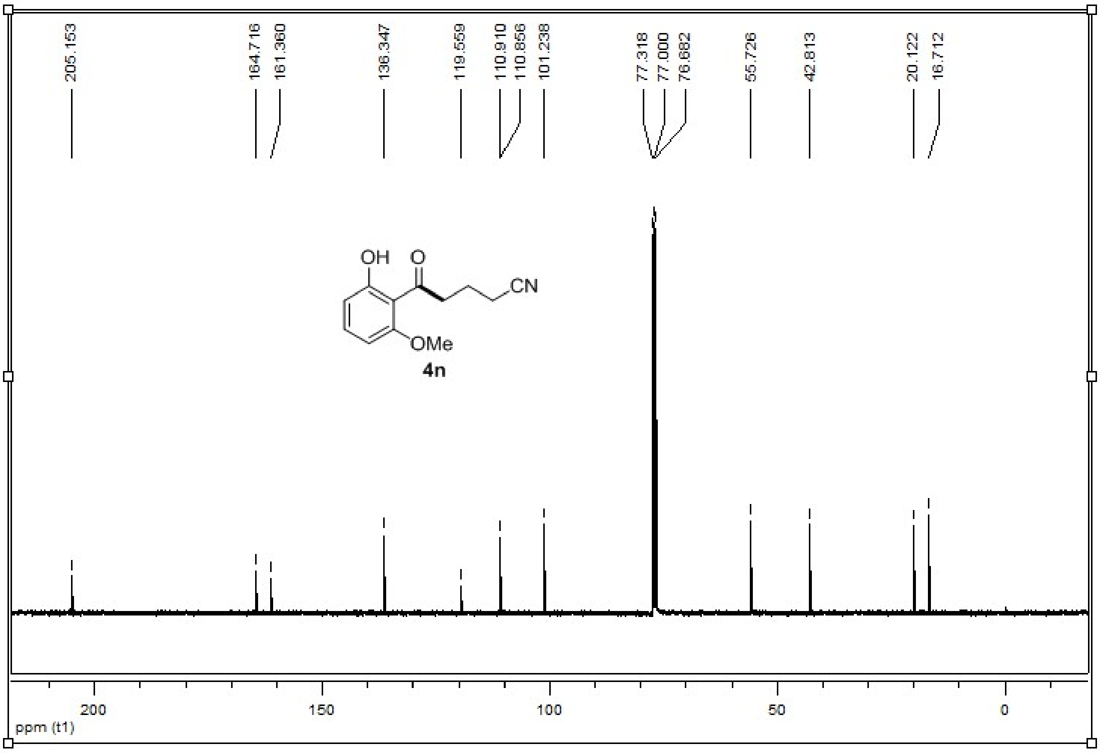

12.085
7.927 7.922 7.747 7.741 7.725 7.720 7.549 7.546 7.528 7.478 7.460 7.440 7.383 7.365 7.346 7.260 7.096 7.074
3.309 3.291 3.274 2.573 2.556 2.538 2.191 2.174 2.156 2.139 2.122
OH O
CN
Ph
4l
1.00
1.02
1.00
1.01
2.01
2.01
2.04
15.0
10.0
5.0
0.0
ppm (t1)

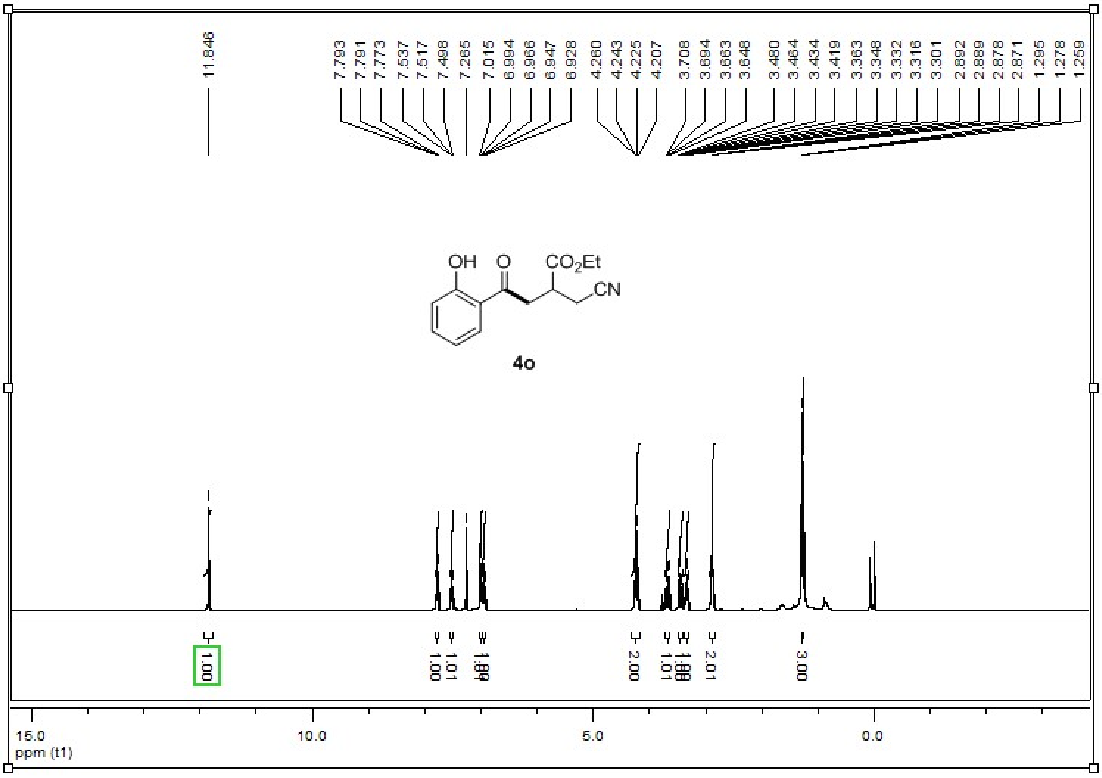

204.109
161.774
139.724 135.626 132.634 128.957 127.864 127.327 126.705 119.111
77.317 77.000 76.682
36.080
19.541 16.626
OH O
CN
Ph
4l
200
150
100
50
0
ppm (t1)

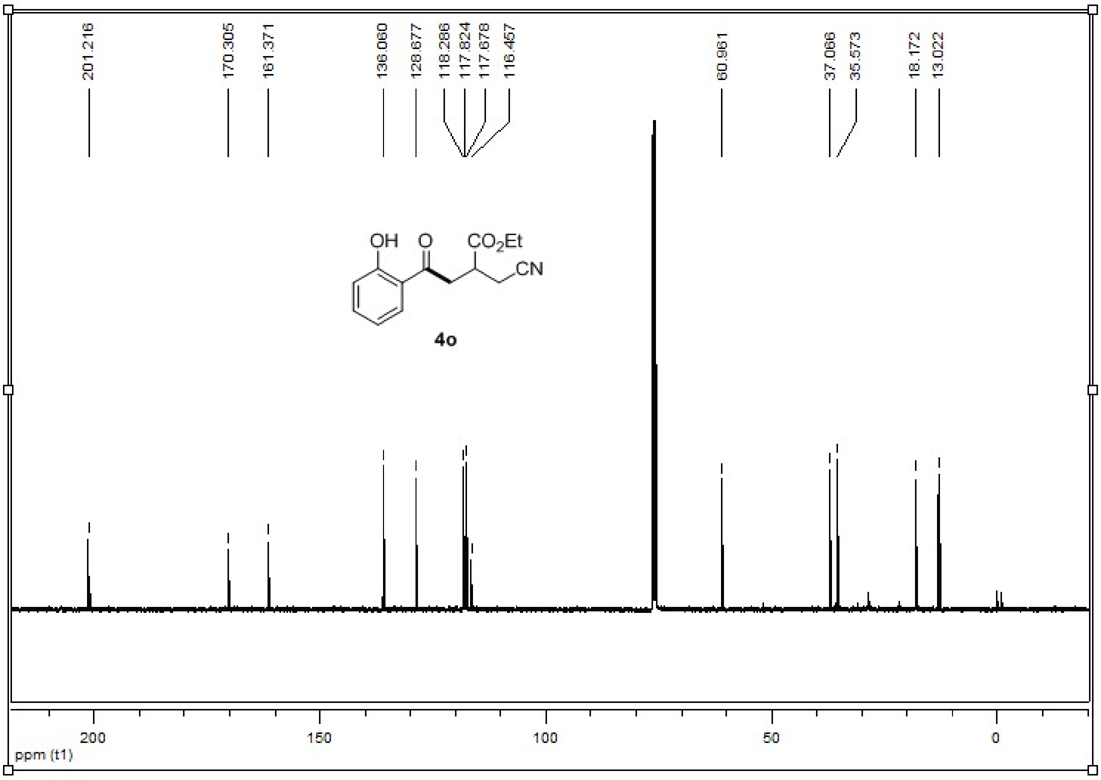

13.037
7.354 7.333 7.313 7.260 6.589 6.568 6.398 6.377 6.161 6.146 6.120 6.103 6.077 6.063 5.459 5.456 5.416 5.413 5.387 5.384 5.361 5.358 4.644 4.629 3.294 3.277 3.260 2.500 2.482 2.464 2.096 2.078 2.061 2.044 2.026
OH
O
CN
O
4m
1.00
1.00
1.01
1.02
1.00
2.02
2.01
2.03
2.02
15.0
10.0
5.0
0.0
ppm (t1)


205.119
164.681 160.326
136.233 132.110
119.423 119.284 111.061 111.009 102.319
77.318 77.000 76.683 69.927
43.071
20.088 16.646
OH
O
CN
O
4m
200
150
100
50
0
ppm (t1)


13.075
7.383
7.362
7.341
7.260
6.594
6.592
6.573
6.571
6.415
6.395
3.923
3.268
3.251
3.234
2.520
2.503
2.485
2.098
2.081
2.063
2.046
2.029
OH
O
CN
OMe
4n
1.00
1.00
1.00
1.01
3.00
2.02
2.02
2.03
15.0
10.0
5.0
0.0
ppm (t1)


205.153
164.716
161.360
136.347
119.559
110.910
110.856
101.238
77.318
77.000
76.682
55.726
42.813
20.122
16.712
OH
O
CN
OMe
4n
200
150
100
50
0
ppm (t1)





Crystallographic data for the product 3d and 4k:

(1) CCDC 2353287 contains the supplementary crystallographic data for the product **3d**. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

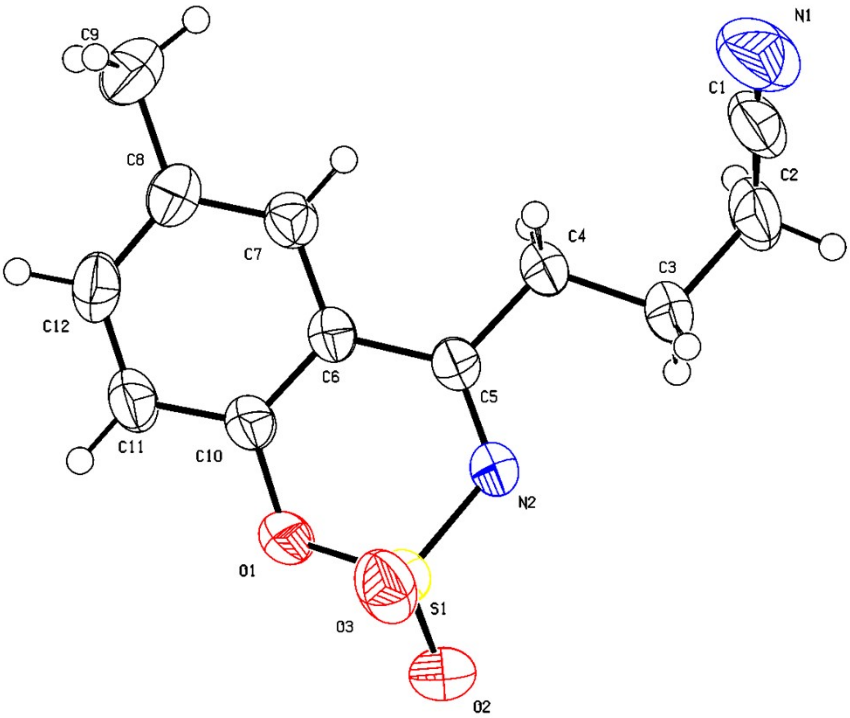


Table 1. Crystal data and structure refinement for 1.

Empirical formula	C12 H12 N2 O3 S
Formula weight	264.30
Temperature	300(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 7.7907(5) A alpha = 106.943(2) deg. b = 9.2425(6) A beta = 105.014(2) deg. c = 9.6790(5) A gamma = 96.858(3) deg.
Volume	629.44(7) Å ^{3}
Z, Calculated density	2, 1.394 Mg/m ^{3}
Absorption coefficient	0.259 mm $^{-1}$
F(000)	276
Crystal size	0.24 x 0.21 x 0.06 mm
Theta range for data collection	2.69 to 26.00 deg.

Limiting indices	-9<=h<=9, -11<=k<=11, -11<=l<=11
Reflections collected / unique	11872 / 2441 [R(int) = 0.0287]
Completeness to theta = 25.03	99.0%
Max. and min. transmission	0.9841 and 0.9403
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2441 / 0 / 164
Goodness-of-fit on F^2	1.088
Final R indices [I>2sigma(I)]	R1 = 0.0432, wR2 = 0.1072
R indices (all data)	R1 = 0.0503, wR2 = 0.1118
Largest diff. peak and hole	0.221 and -0.337 e.A^{-3}

(2) CCDC 2353284 contains the supplementary crystallographic data for the product **4k**. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

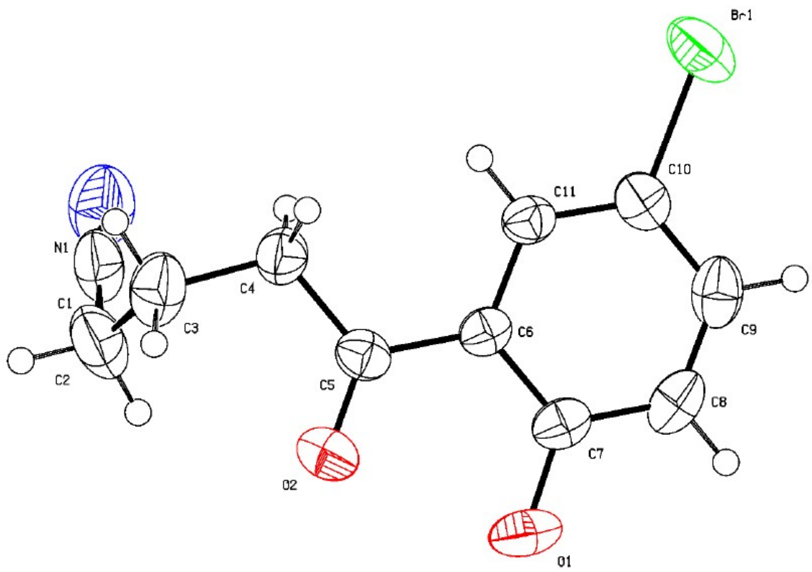


Table 1. Crystal data and structure refinement for 1.

Empirical formula	C11 H9 Br N O2
Formula weight	267.10
Temperature	295(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 6.7614(19) A alpha = 82.509(18) deg. b = 7.298(2) A beta = 89.624(18) deg. c = 11.361(3) A gamma = 84.148(19)

	deg.
Volume	552.9(3) Å ^{3}
Z, Calculated density	2, 1.604 Mg/m^3
Absorption coefficient	3.695 mm^{-1}
F(000)	266
Crystal size	0.31 x 0.21 x 0.07 mm
Theta range for data collection	2.83 to 27.51 deg.
Limiting indices	-8<=h<=8, -9<=k<=9, -14<=l<=14
Reflections collected / unique	16439 / 2529 [R(int) = 0.0759]
Completeness to theta = 25.03	99.3%
Max. and min. transmission	0.7846 and 0.3918
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2529 / 0 / 136
Goodness-of-fit on F^2	1.058
Final R indices [I>2sigma(I)]	R1 = 0.0431, wR2 = 0.0953
R indices (all data)	R1 = 0.0648, wR2 = 0.1045
Largest diff. peak and hole	0.549 and -0.805 e.A^{-3}