Enantioselective allylic amination of MBH carbonates catalyzed by new chiral 4-dimethylaminopyridine catalysts

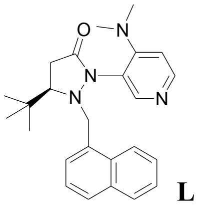
Supporting Information

1. General

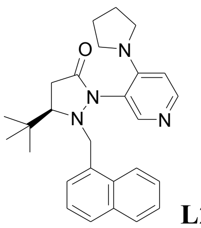
All solvents were dried and degassed by standard methods and stored under nitrogen. Flash chromatography was performed using EM Science silica gel 60 (230-400 mesh). Melting points were measured with a Fisher-Johns melting points apparatus and are uncorrected. ^{1}H NMR spectra were recorded on Varian Unity/Inova-400 NB (400 MHz) spectrometer. ^{13}C NMR spectra were recorded on Varian Unity/Inova-400 NB (100 MHz) spectrometer. HPLC analyses were carried out with Waters 515 HPLC pumps and a 2487 dual wavelength absorbance detector connected to a PC with Empower workstation. Rotations were recorded on a JASCO-DIP-370 polarimeter. FT-IR spectra were recorded on a Bruker Optics Vertex 70 FTIR. High resolution mass spectra were obtained at a Bruker Daltronics BioTOF HRMS spectrometer.

2. Experimental details and characterization

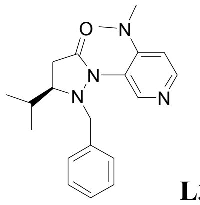
The chiral pyrazolidinone-DMAP catalysts were prepared according to the procedure reported in the literature.[1]



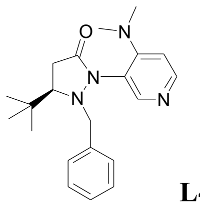
L1 mp. 198-199 °C; $[\alpha]_D^{25}$ -133.3 (*c* 0.53, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.46 (s, 9H), 2.46 (dd, *J* = 17.2, 1.6 Hz, 1H), 3.00 (s, 6H), 3.11 (dd, *J* = 10.0, 1.6 Hz, 1H), 3.27-3.23 (m, 1H), 4.11 (d, *J* = 11.6 Hz, 1H), 4.89 (d, *J* = 12.0 Hz, 1H), 6.67 (d, *J* = 6.0 Hz, 1H), 7.35-7.44 (m, 4H), 7.76-7.82 (m, 3H), 8.20 (d, *J* = 5.6 Hz, 1H), 8.80 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 25.7, 31.5, 34.6, 41.3, 59.7, 66.4, 111.7, 121.5, 121.6, 124.3, 124.9, 126.2, 126.6, 128.6, 129.1, 129.4, 132.1, 132.8, 133.8, 148.8, 149.9, 153.0, 169.9; IR (NaCl) *v* 1697, 1591 cm^{-1}; ESI-HRMS *m/z* calcd. for $(C_{25}H_{30}N_4ONa)^+$ 425.2312; found 425.2305.



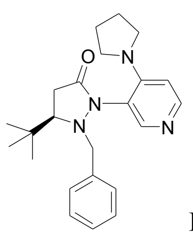
L2 mp. 104-107 °C; $[\alpha]_D^{25}$ -193.6 (*c* 0.50, $CHCl_3$); ^{1}H NMR (DMSO-d6, 400 MHz, 78 ^{o}C) δ 0.45 (s, 9H), 1.88 (m, 4H), 2.32 (m, 1H), 3.05 (m, 4H), 3.13 (m, 1H), 3.38 (m, 2H), 4.31 (d, *J* = 12.4 Hz,, 1H), 4.71 (d, *J* = 12.0 Hz,, 1H), 6.58 (d, *J* = 6.0 Hz, 1H), 7.28-7.32 (m, 2H), 7.52-7.54 (m, 1H), 7.74-7.84 (m, 3H), 8.03 (d, *J* = 5.6 Hz, 1H), 8.45 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 25.7, 25.8, 31.8, 34.7, 49.2, 59.8, 66.3, 110.2, 119.0, 124.5, 124.9, 126.1, 126.6, 128.6, 129.1, 129.4, 132.1, 132.8, 133.8, 148.7, 150.0, 170.5; IR (NaCl) *v* 1693, 1592 cm^{-1}; ESI-HRMS *m/z* calcd. for $(C_{23}H_{24}ClN_3O_2Na)^+$ 432.1449; found 432.1450.



L3 mp. 106-108 °C; $[\alpha]_D^{25}$ -54.3 (*c* 0.65, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ 0.72-0.80 (m, 6H), 1.67-1.72 (m, 1H), 2.37-2.41 (m, 1H), 2.89 (s, 6H), 2.89-3.05 (m, 2H), 3.76 (d, *J* = 12.8 Hz, 1H), 4.05 (d, *J* = 12.4 Hz, 1H), 6.41-6.43 (m, 1H), 7.10-7.14 (m, 5H), 8.02 (dd, *J* = 5.6, 2.8 Hz, 1H), 8.29 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 18.2, 19.6, 31.0, 32.9, 41.4, 60.9, 66.1, 111.0, 127.6, 128.2, 129.4, 136.6, 149.1, 151.7, 153.5, 170.8; IR (NaCl) *v* 1698, 1591 cm^{-1}; ESI-HRMS *m/z* calcd. for $(C_{20}H_{26}N_4ONa)^+$ 361.1999; found 361.2009.



L4 mp. 140-142 °C; $[\alpha]_D^{25}$ -4.6 (*c* 0.41, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ 0.71 (s, 9H), 2.45 (dd, *J* = 16.8, 2.0 Hz, 1H), 2.93 (s, 6H), 2.98 (dd, *J* = 9.6, 2.0 Hz, 1H), 3.20 (dd, *J* = 17.2, 9.6 Hz, 1H), 3.84 (d, *J* = 12.0 Hz, 1H), 4.23 (d, *J* = 12.0 Hz, 1H), 6.54 (d, *J* = 6.0 Hz, 1H), 7.20-7.23 (m, 5H), 8.07 (d, *J* = 6.0 Hz, 1H), 8.76 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 26.0, 31.8, 34.8, 40.9, 61.9, 67.0, 111.5, 121.5, 128.0, 128.4, 130.0, 136.3, 148.3, 148.8, 152.2, 169.1; IR (NaCl) *v* 1691, 1191 cm^{-1}; ESI-HRMS: *m/z* calcd. for $(C_{21}H_{28}N_4ONa)^+$ 375.2155; found 375.2185.

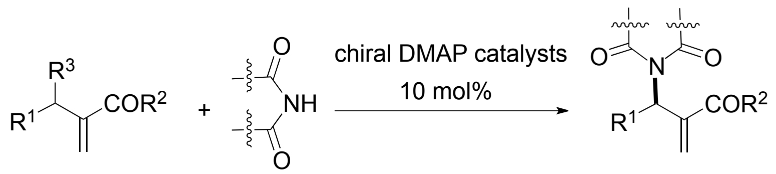


L5 mp. 180-182 °C; $[\alpha]_D^{25}$ -106.7 (*c* 0.63, $CHCl_3$); ^1H NMR (DMSO-d6, 400 MHz, 78 ^oC) δ 0.73 (s, 9H), 1.87 (m, 4H), 2.36 (d, *J* = 2.8 Hz, 1H), 2.37 (d, *J* = 2.4 Hz, 1H), 3.05 (m, 4H), 4.03 (d, *J* = 12 Hz, 1H), 4.16 (d, *J* = 13.6 Hz, 1H), 6.4 (d, *J* = 6.0 Hz, 1H), 7.15-7.19 (m, 5H), 7.88 (d, *J* = 6.0 Hz, 1H), 8.38 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 25.7, 26.0, 32.0, 34.9, 48.9, 62.2, 67.0, 110.0, 119.6, 128.0, 128.2, 130.1, 136.3, 148.2, 149.0, 149.4, 170.1; IR (NaCl) *v* 1695, 1592 cm^{-1};

ESI-HRMS *m/z* calcd. for $(C_{19}H_{22}ClN_3O_2Na)^+$ 382.1293; found 382.1296.

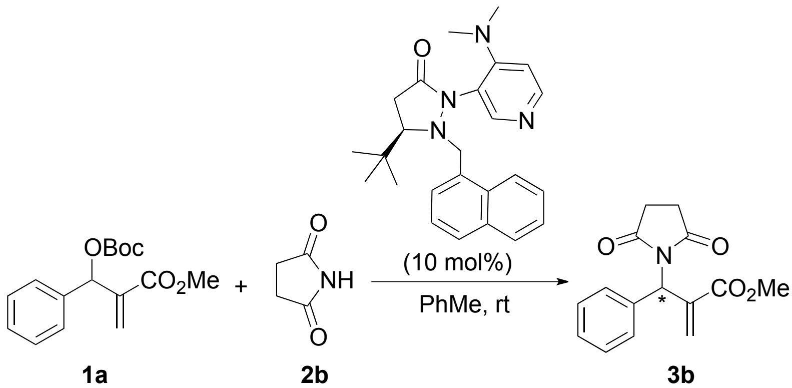
The Morita–Baylis–Hillman carbonates were prepared according to the literature reported.[2, 3]

General Procedure for the allylic nucleophilic substitution of Morita–Baylis–Hillman carbonates.



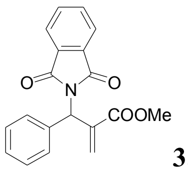
Under an argon atmosphere, a solution of MBH carbonate (1 equiv.), succinimide (1.5 equiv.) and chiral DMAP catalyst (10 mol%) in toluene was stirred at the given temperature. Once the reaction was judged complete (TLC), the solvent was removed under reduced pressure, and the residue was chromatographed on silica gel (elution with ethyl acetate / hexane 1:5–1:2) to provide the product.

Table **S1** Solvents screening

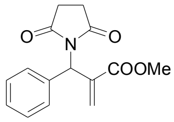


Entry	Solvents	Time	Yield (%)[b]	ee (%)[c]
1	THF	24	62	35
2	DCM	24	80	17
3	PhMe	24	75	39
4	MeOH	48	45	29

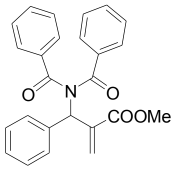
[a] Reaction conditions: the reaction were performed with 1 equiv. of **1a**, 1.5 equiv. of **2b** and 10 mol% of catalyst in the given solvents at room temp. [b] Isolated yield. [c] Determined by chiral HPLC analysis.



3a Enantiomeric excess was determined by HPLC with a Chiralcel OD column (90:10 hexane:2-propanol, 0.5 mL/min, 254 nm); minor enantiomer t_1 = 19.2 min, major enantiomer t_2 = 42.6 min; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.67 (s, 3H), 5.6 (d, *J* = 1.6 Hz, 1H), 6.37 (s, 1H), 6.53 (d, *J* = 1.2 Hz, 1H), 7.27-7.34 (m, 3H), 7.41 (d, *J* = 7.2 Hz, 2H), 7.67-7.69 (m, 2H), 7.79-7.81 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 52.4, 54.8, 123.6, 123.8, 128.3, 128.8, 129.9, 132, 134.3, 134.5, 137.2, 137.8, 166.3, 168.1; IR (neat) *v* 3198, 1753, 1387, 1140, 1054 cm^{-1}; ESI-HRMS *m/z* calcd. for $(C_{19}H_{15}NO_4Na)^+$ 344.0893; found 344.0902.

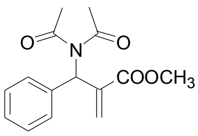


3b Enantiomeric excess was determined by HPLC with a Chiralcel OD column (90:10 hexane:2-propanol, 0.5 mL/min, 254 nm); minor enantiomer t_1 = 33.4 min, major enantiomer t_2 = 50.4 min; $[\alpha]_D^{25}$ -121.1 (*c* 0.58, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.65-2.66 (m, 4H), 3.7 (s, 3H); 5.45 (d, *J* = 2 Hz, 1H), 6.1 (t, *J* = 2 Hz, 1H), 6.45(d, *J* = 2 Hz, 1H), 6.45(d, *J* = 2 Hz, 1H), 7.27-7.37 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 28.3, 52.3, 55.8, 128.5, 128.9, 129, 129.8, 136.8, 137.3, 166.2, 177.1; IR (neat) *v* 2923, 1704, 1388, 1178 cm^{-1}; ESI-HRMS *m/z* calcd. for $(C_{15}H_{15}NO_4Na)^+$ 296.0893; found 296.0893.

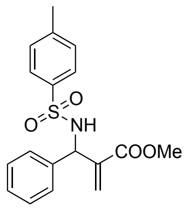


3c Enantiomeric excess was determined by HPLC with a Chiralcel OD-3 column (97:3 hexane:2-propanol, 1.0 mL/min, 254 nm); minor enantiomer t_1 = 15.7 min, major enantiomer t_2 = 32.9 min; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.7 (s, 3H), 5.68 (d, *J* = 1.6 Hz, 1H), 6.52(m, 1H), 6.9 (s, 1H), 7.06(t, *J* = 7.6 Hz, 4H), 7.13-7.18 (m, 2H), 7.23-7.28(m, 1H), 7.32-7.36 (m, 2H), 7.55(d, *J* = 7.6 Hz, 2H); ^{13}C NMR

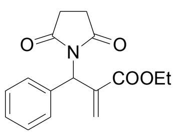
(CDCl$_3$, 100 MHz) δ 52.4, 61.8, 128.2, 128.3, 128.9, 129.1, 129.3, 129.7, 131.9, 137.6, 137.9, 139.3, 166.7, 173.7; IR (neat) *v* 2924, 1656, 1322, 1237, 1132 cm^{-1}; ESI-HRMS *m/z* calcd. for $(C_{25}H_{21}NO_4Na)^+$ 422.1363; found 422.1362.



3d Enantiomeric excess was determined by HPLC with a Chiralcel OD-3 column (98:2 hexane:2-propanol, 0.5 mL/min, 254 nm); minor enantiomer t_1 = 25.1 min, major enantiomer t_2 = 27.8 min; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 2.32 (s, 6H), 3.74 (s, 3H); 5.61 (d, *J* = 1.6 Hz, 1H), 6.26 (s, 1H), 6.49(d, *J* = 1.6 Hz, 1H), 7.18-7.21(m, 2H), 7.25-7.35(m, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 27, 52.5, 60.7, 127.9, 128.1, 128.6, 128.8, 129.6, 137.2, 138.4, 166.9, 174.4; IR (neat) *v* 2924, 1704, 1645, 1496, 1375, 1152 cm^{-1}; ESI-HRMS *m/z* calcd. for $(C_{15}H_{17}NO_4Na)^+$ 298.1050; found 298.1044.

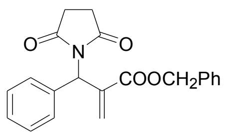


3e Enantiomeric excess was determined by HPLC with a Chiralcel OD-3 column (99:1 hexane:2-propanol, 0.7 mL/min, 254 nm); minor enantiomer t_1 = 112.4 min, major enantiomer t_2 = 117.1 min; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 2.38 (s, 3H), 3.57 (s, 3H), 5.28(d, *J* = 8.8 Hz, 1H), 5.64 (d, *J* = 8.8 Hz, 1H), 5.8 (s, 1H), 6.19 (s, 1H), 7.1-7.13 (m, 2H), 7.17-7.24 (m, 5H), 7.65 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 21.7, 52.2, 59.2, 126.6, 127.4, 127.9, 128.1, 128.8, 129.7, 137.8, 138.7, 138.8, 143.6, 166; IR (neat) *v* 2921, 1716, 1437, 1327, 1159 cm^{-1}; ESI-HRMS *m/z* calcd. for $(C_{18}H_{19}SNO_4Na)^+$ 368.0927; found 368.0924.

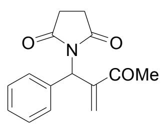


3f Enantiomeric excess was determined by HPLC with a Chiralcel

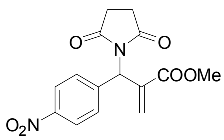
OD-3 column (90:10 hexane:2-propanol, 0.5 mL/min, 254 nm); minor enantiomer t_1 = 26.7 min, major enantiomer t_2 = 37.4 min; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.21 (t, *J* = 7.2 Hz, 3H), 2.65 (m, 4H), 4.10-4.2 (m, 2H), 5.41-5.42 (m, 1H), 6.1 (d, *J* = 1.6 Hz, 1H), 6.45 (m, 1H), 7.23-7.33 (m, 3H), 7.37 (d, *J* = 8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.2, 28.3, 55.9, 61.2, 128.5, 128.9, 129.0, 129.5, 137, 137.6, 165.8, 177.1, 134, 136.6, 166.3, 177.2; IR (neat) *v* 2982, 1706, 1363, 1179 cm^{-1}; ESI-HRMS *m/z* calcd. for $(C_{16}H_{17}NO_4Na)^+$ 310.1050; found 310.1055.



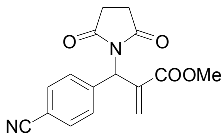
3g Enantiomeric excess was determined by HPLC with a Chiralcel OD-3 column (95:5 hexane:2-propanol, 1.0 mL/min, 254 nm); minor enantiomer t_1 = 49.6 min, major enantiomer t_2 = 56.7 min; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.43 (s, 4H), 5.02 (d, *J* = 12 Hz, 1H), 5.29 (d, *J* = 12 Hz, 1H), 5.41 (d, *J* = 2 Hz, 1H), 6.08 (t, *J* = 2 Hz, 1H), 6.51 (d, *J* = 2 Hz, 1H), 7.27-7.38 (m, 10H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 28.2, 55.9, 66.9, 128.5, 128.6, 128.8, 129, 129.1, 130.2, 135.8, 136.9, 137.5, 165.5, 177; IR (neat) *v* 3033, 1704, 1360, 1204 cm^{-1}; ESI-HRMS *m/z* calcd. for $(C_{21}H_{19}NO_4Na)^+$ 372.1206; found 372.1198.



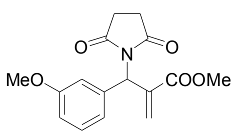
3h Enantiomeric excess was determined by HPLC with a Chiralcel AD-3 column (96:4 hexane:2-propanol, 1.0 mL/min, 254 nm); minor enantiomer t_1 = 36.1 min, major enantiomer t_2 = 63.9 min; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.36 (s, 3H), 2.63 (m, 4H), 5.51 (d, *J* = 2 Hz, 1H), 6.06 (t, *J* = 1.6 Hz, 1H), 6.23 (d, *J* = 2 Hz, 1H), 7.23-7.33 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.3, 28.3, 55.9, 61.2, 128.5, 128.9, 129, 129.5, 136.9, 137.6, 165.8, 177, 198.8; IR (neat) *v* 2923, 1703, 1388, 1179 cm^{-1}; ESI-HRMS *m/z* calcd. for $(C_{15}H_{15}NO_3Na)^+$ 280.0944; found 280.0950.



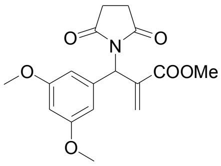
3i Enantiomeric excess was determined by HPLC with a Chiralcel OD-3 column (70:30 hexane:2-propanol, 0.5 mL/min, 254 nm); minor enantiomer t_1 = 42.9 min, major enantiomer t_2 = 75.2 min; $[\alpha]_D^{25}$ -34.4372 (*c* 0.77, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ 2.7-2.71 (m, 4H), 3.7 (s, 3H), 5.47 (d, *J* = 2 Hz, 1H), 6.24 (s, 1H), 6.5 (d, *J* = 2 Hz, 1H), 7.52 (d, *J* = 8.8 Hz, 2H), 8.18 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 28.3, 52.6, 54.8, 124.1, 129.9, 130.1, 136.1, 143.8, 147.9, 165.7, 176.8; IR (neat) *v* 2922, 1707, 1521, 1348, 1177, 1144 cm^{-1}; ESI-HRMS *m/z* calcd. for $(C_{15}H_{14}N_2O_6Na)^+$ 341.0744; found 341.0749.



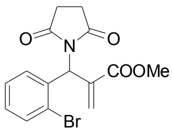
3j Enantiomeric excess was determined by HPLC with a Chiralcel AD-3 column (95:5 hexane:2-propanol, 1.0 mL/min, 254 nm); minor enantiomer t_1 = 71.6 min, major enantiomer t_2 = 102.9 min; $[\alpha]_D^{25}$ -37.7187 (*c* 1.03, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ 2.69-2.7 (m, 4H), 3.7 (s, 3H), 5.45 (d, *J* = 2 Hz, 1H), 6.18 (s, 1H), 6.5 (d, *J* = 2 Hz, 1H), 7.47 (d, *J* = 8 Hz, 1H), 7.6 (d, *J* = 8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 28.3, 52.4, 55.1, 115.7, 115.9, 129.5, 131, 132.6, 132.7, 137.2, 161.5, 164, 166.1, 177; IR (neat) *v* 2923, 1705, 1437, 1264, 1179 cm^{-1}; ESI-HRMS *m/z* calcd. for $(C_{16}H_{14}N_2O_4Na)^+$ 321.0846; found 321.0838.



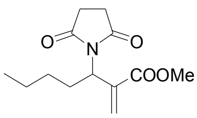
3k Enantiomeric excess was determined by HPLC with a Chiralcel AD-3 column (95:5 hexane:2-propanol, 1.0 mL/min, 254 nm); minor enantiomer t_1 = 31.1 min, major enantiomer t_2 = 47.0 min; $[\alpha]_D^{25}$ -101.9 (*c* 1.22, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ 2.65-2.66 (m, 4H), 3.71 (s, 3H), 3.75 (s, 3H), 5.5 (d, *J* = 2 Hz, 1H), 6.07 (s, 1H), 6.46 (d, *J* = 2 Hz, 1H), 6.82 (dd, *J* = 8, 2.8 Hz, 1H), 6.92-6.96 (m, 2H), 7.23(t, *J* = 8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 28.3, 52.4, 55.4, 55.8, 113.9, 114.7, 121.3, 129.91, 129.94, 137.1, 138.3, 160, 166.2, 177; IR (neat) *v* 2952, 1704, 1437, 1184 cm^{-1}; ESI-HRMS *m/z* calcd. for $(C_{16}H_{17}NO_5Na)^+$ 326.0999; found 326.1002.



3l Enantiomeric excess was determined by HPLC with a Chiralcel AD-3 column (95:5 hexane:2-propanol, 1.0 mL/min, 254 nm); minor enantiomer t_1 = 39.1 min, major enantiomer t_2 = 66.7 min; $[\alpha]_D^{25}$ -116.5304 (*c* 1.02, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ 2.65-2.66 (m, 4H), 3.7 (s, 3H); 3.73 (s, 6H), 5.54(d, *J* = 2.4 Hz, 1H), 6.01 (s, 1H), 6.37 (t, *J* = 2.4 Hz, 1H), 6.45 (d, *J* = 1.6 Hz, 1H), 6.53 (d, *J* = 2.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 28.3, 52.3, 55.6, 55.9, 100.3, 107.1, 130, 137, 139.1, 161.1, 166.2, 177; IR (neat) *v* 2952, 1705, 1355, 1155, 1066 cm^{-1}; ESI-HRMS *m/z* calcd. for $(C_{17}H_{19}NO_6Na)^+$ 356.1105; found 356.1110.



3m Enantiomeric excess was determined by HPLC with a Chiralcel AD-3 column (95:5 hexane:2-propanol, 1.0 mL/min, 254 nm); minor enantiomer t_1 = 29.2 min, major enantiomer t_2 = 37.9 min; $[\alpha]_D^{25}$ -13.9 (*c* 1.27, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ 2.7 (m, 4H), 3.7 (s, 1H), 5.42 (d, *J* = 1.6 Hz, 1H), 6.47 (s, 1H), 6.5 (d, *J* = 1.6 Hz, 1H), 7.15 (td, *J* = 8, 1.6 Hz, 1H), 7.26 (td, *J* = 8, 1.2 Hz, 2H), 7.4 (dd, *J* = 8, 1.6 Hz, 1H), 7.54 (dd, *J* = 8, 1.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 28.3, 52.5, 55.5, 124.1, 127.7, 129.2, 130, 130.5, 133.3, 135.82, 135.84, 165.8, 176.8; IR (neat) *v* 2952, 1708, 1388, 1180, 1145 cm^{-1}; ESI-HRMS *m/z* calcd. for $(C_{15}H_{14}BrNO_4Na)^+$ 373.9998; found 373.9971.



3n Enantiomeric excess was determined by HPLC with a Chiralcel OD-3 column (95:5 hexane:2-propanol, 1.0 mL/min, 254 nm); minor enantiomer t_1 = 17.9 min, major enantiomer t_2 = 26.1 min; $[\alpha]_D^{25}$ -15.8 (*c* 0.58, $CHCl_3$); ^1H NMR

($CDCl_3$, 400 MHz) δ 0.85 (t, *J* = 7.2 Hz, 3H), 1.13-1.35 (m, 4H), 1.82-1.89 (m, 1H), 2.09-2.18 (m, 1H), 2.63 (m, 4H), 3.7 (s, 3H), 5.04 (q, *J* = 4.4 Hz, 1H), 5.99(d, *J* = 1.6 Hz, 1H), 6.48(m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.1, 22.5, 28.2, 28.7, 29.1, 50.4, 52.3, 128.8, 136.8, 166.5, 177.1; IR (neat) *v* 2956, 1700, 1635, 1361, 1183, 1154 cm^{-1}; ESI-HRMS *m/z* calcd. for $(C_{13}H_{19}NO_4Na)^+$ 276.1206; found 276.1204.

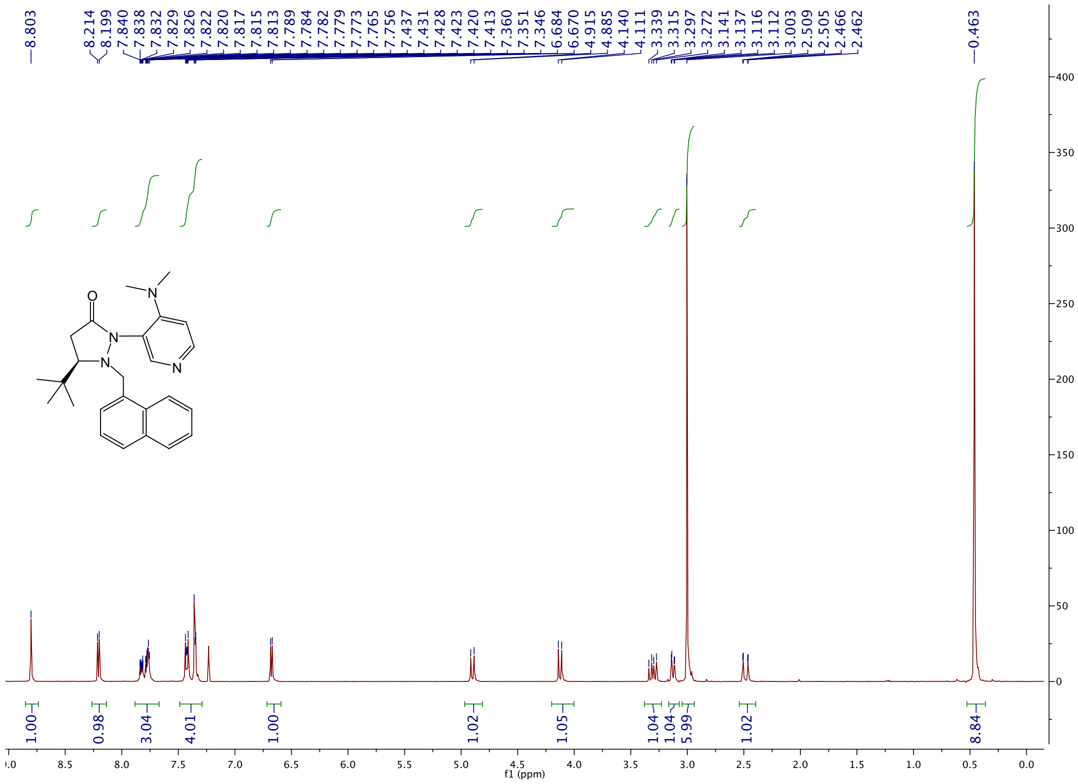
3. References

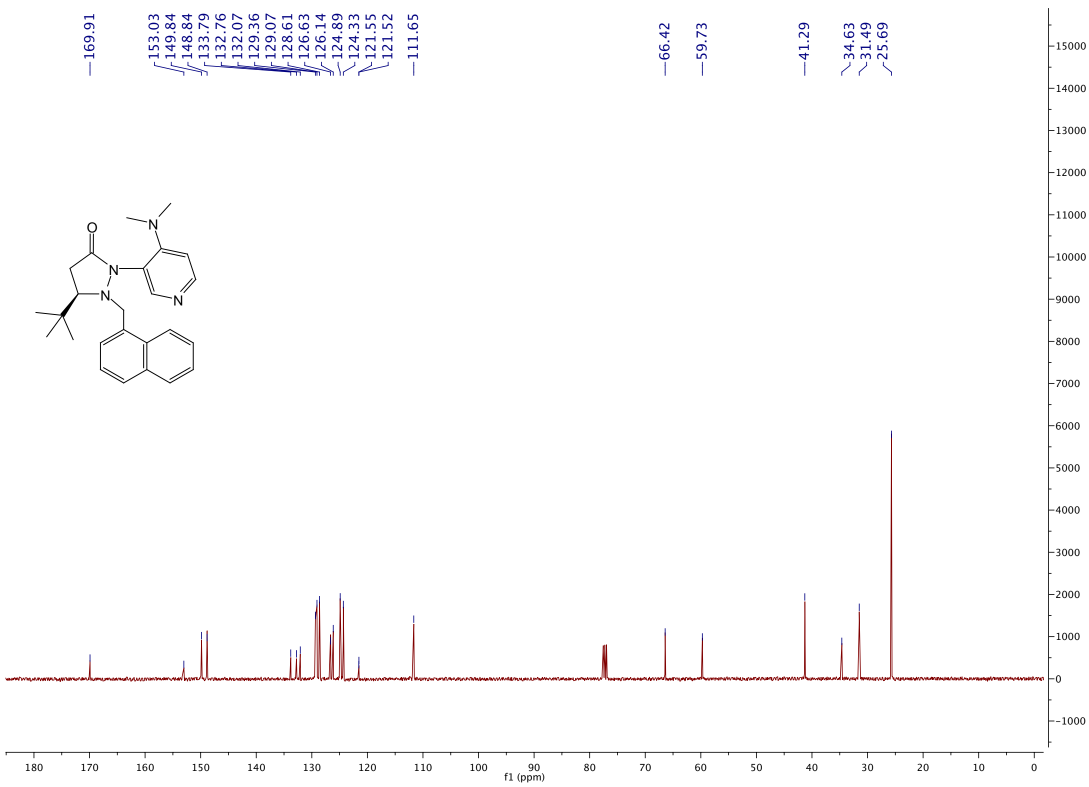
1. G. Ma, J. Deng and M. P. Sibi, *Angew. Chem. Int. Ed.*, 2014, DOI: 10.1002/anie.201406684 and 10.1002/ange.201406684. In press.

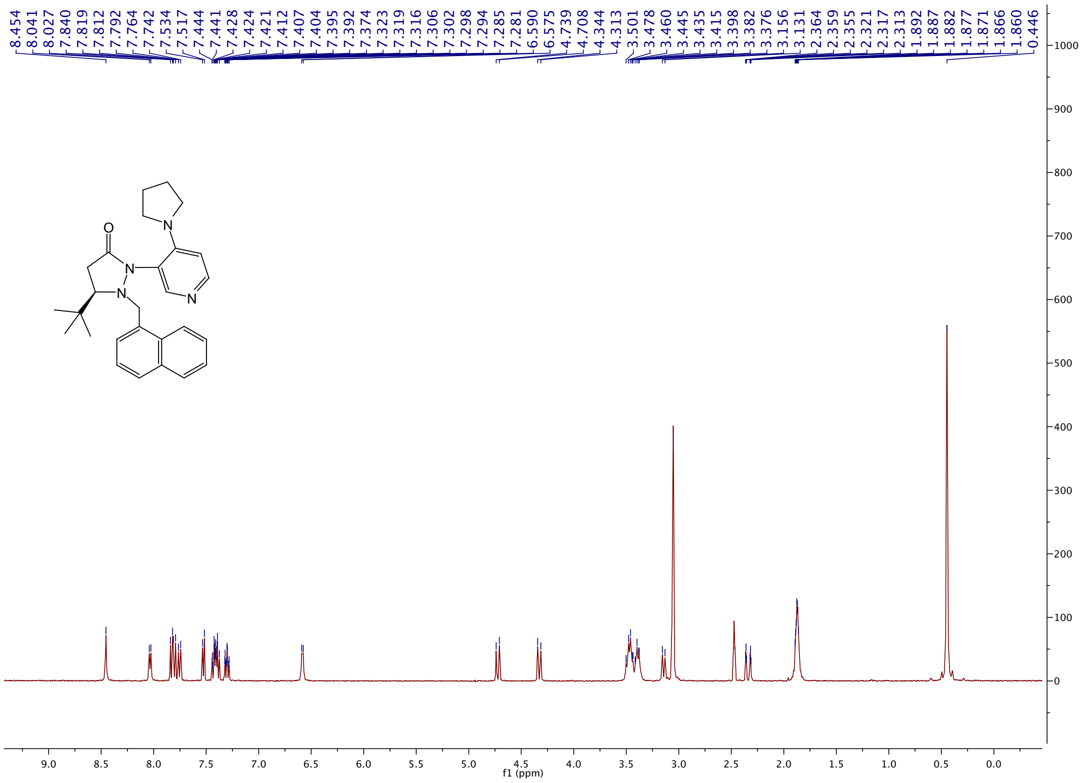
2. H. M. R. Hoffmann and J. Rabe, *J. Org. Chem.*, 1985, **50**, 3849.

3. J. Feng, X. Lu, A. Kong and X. Han, *Tetrahedron*, 2007, **63**, 6035.

4. NMR spectra



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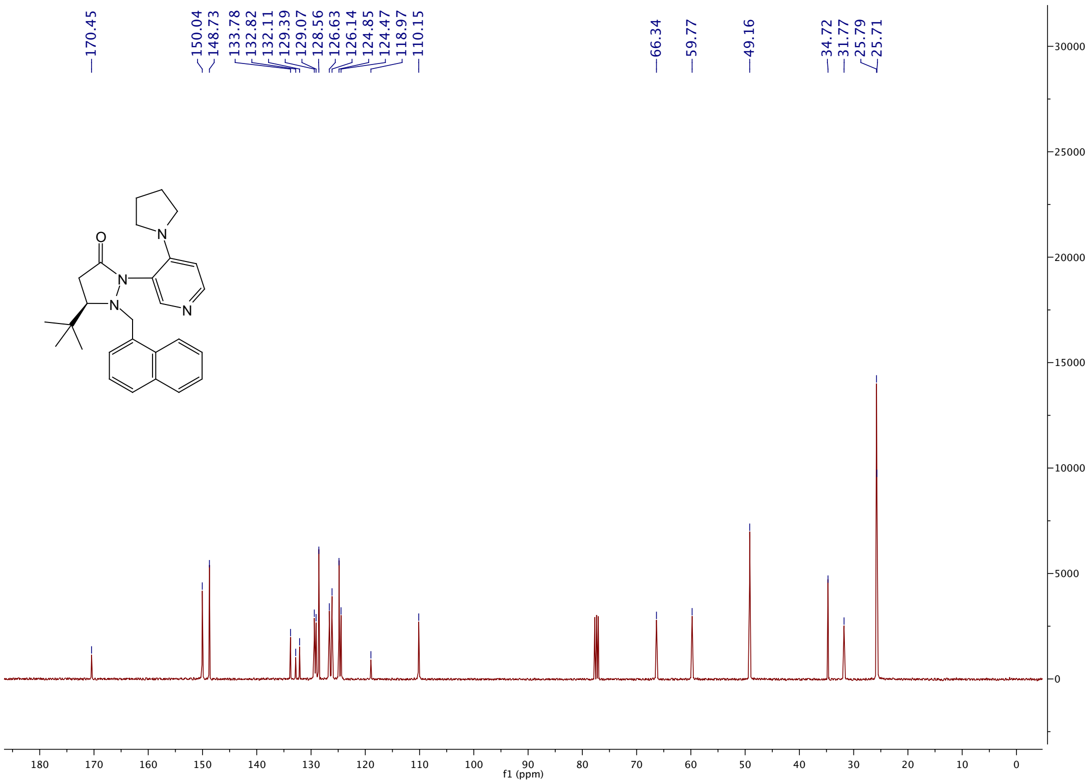
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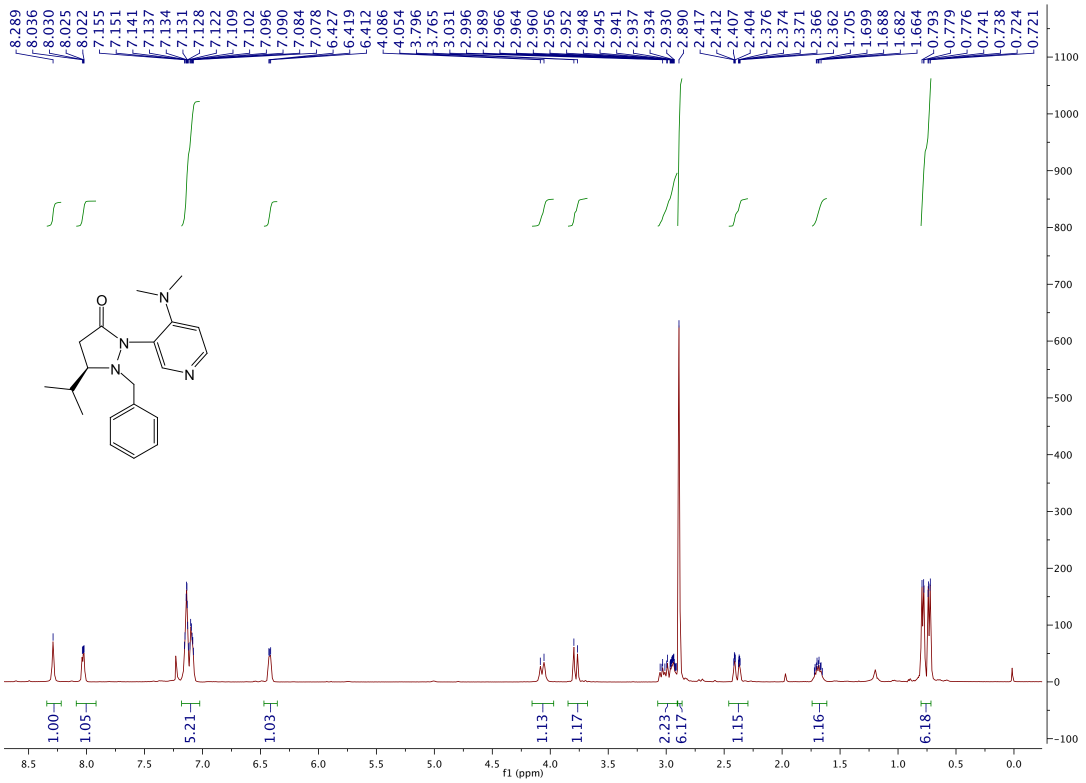

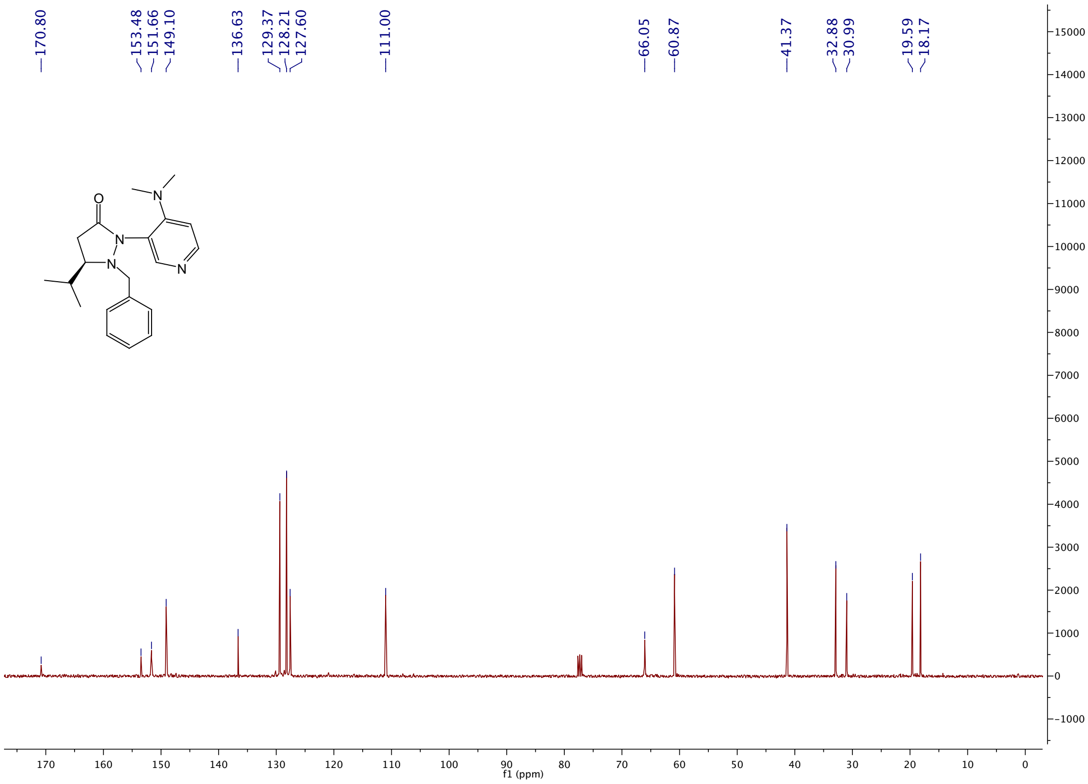

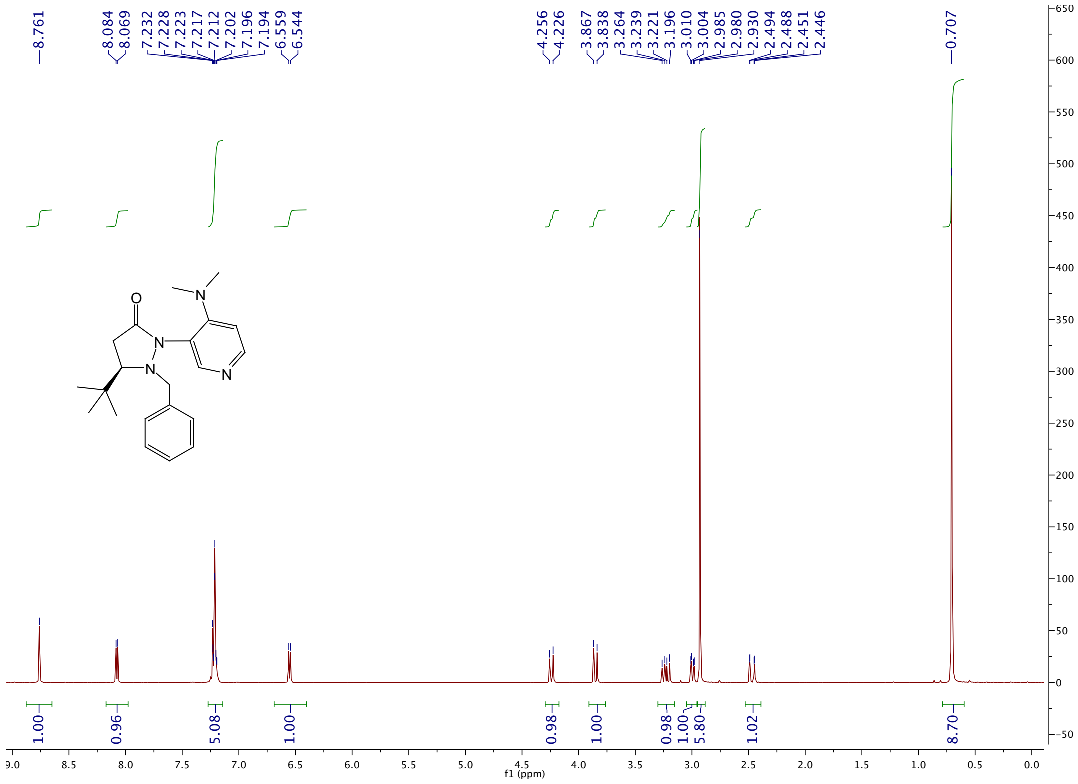
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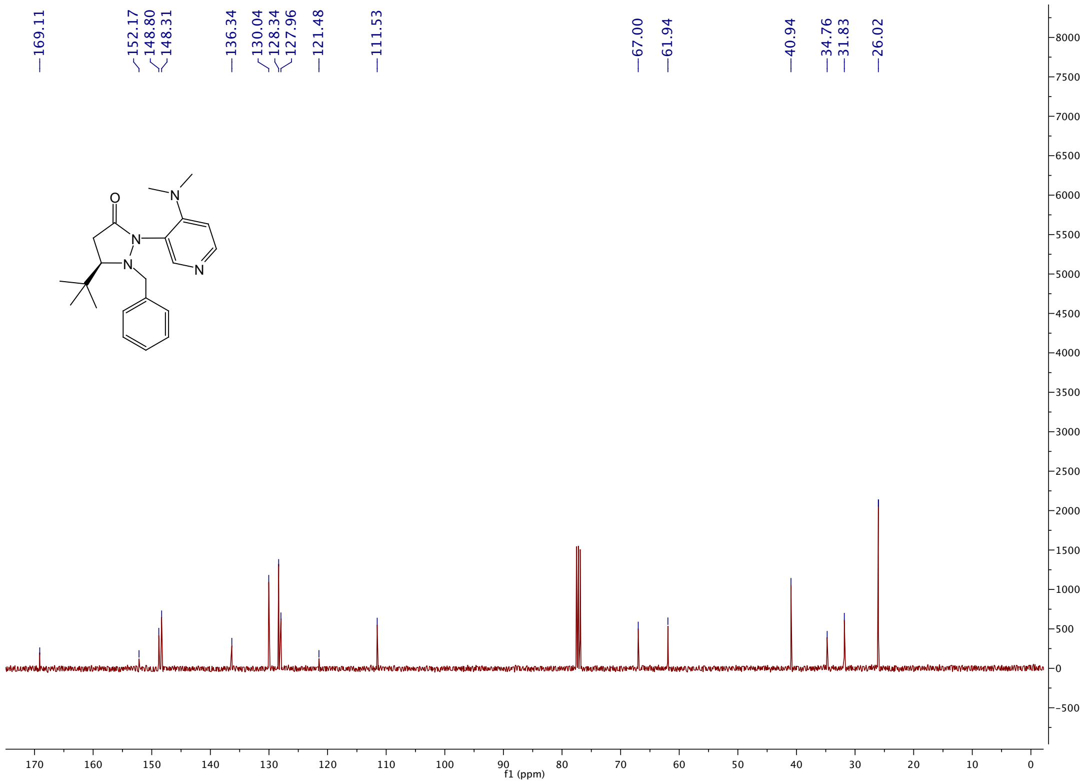
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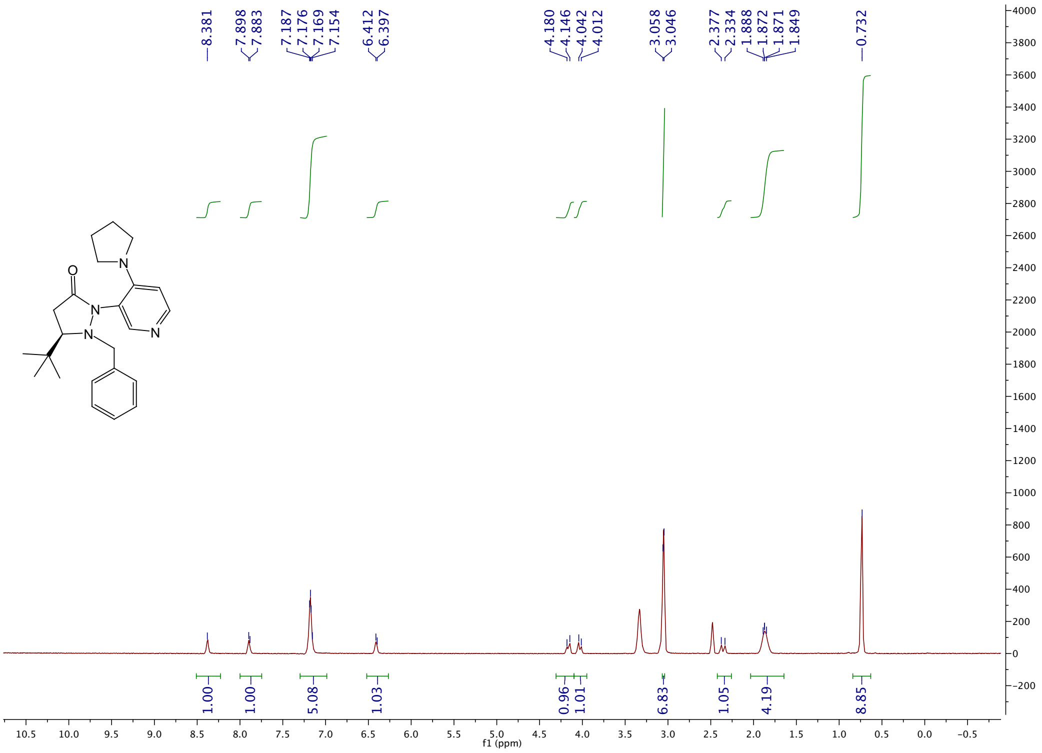
N
f1 (ppm)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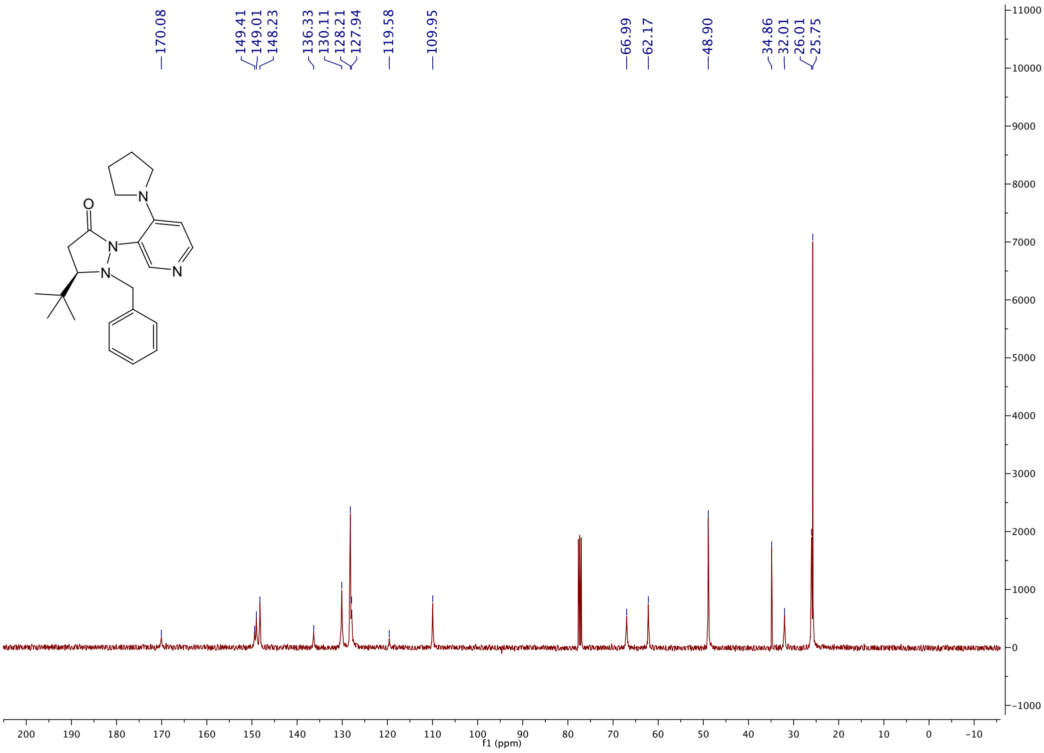
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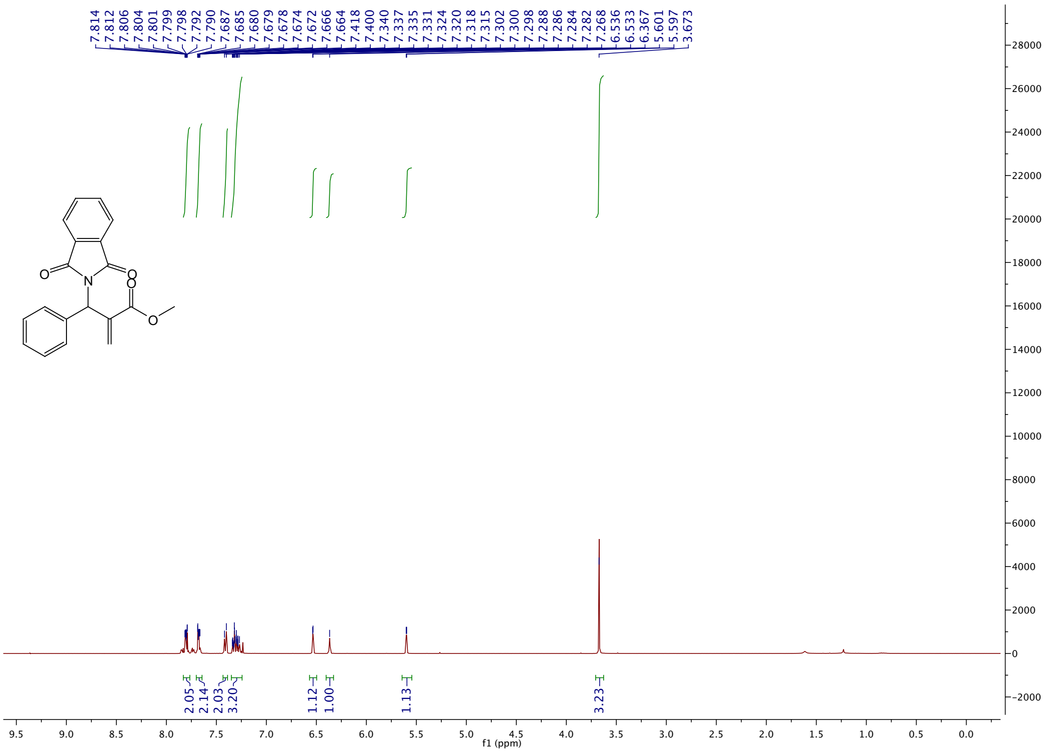
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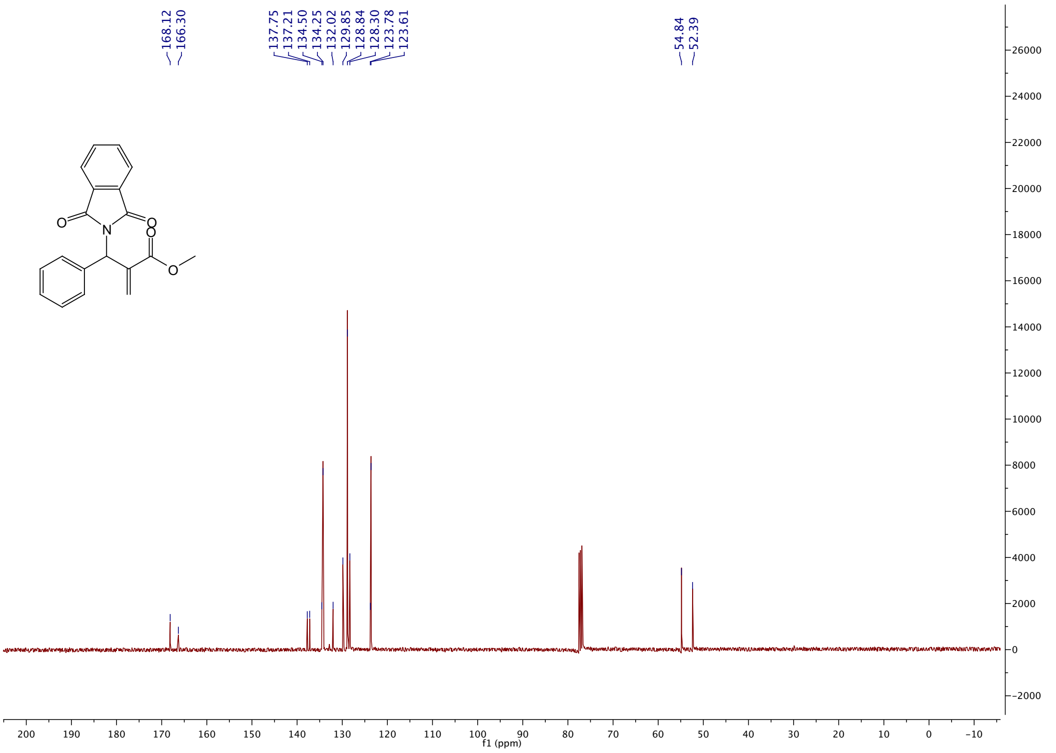
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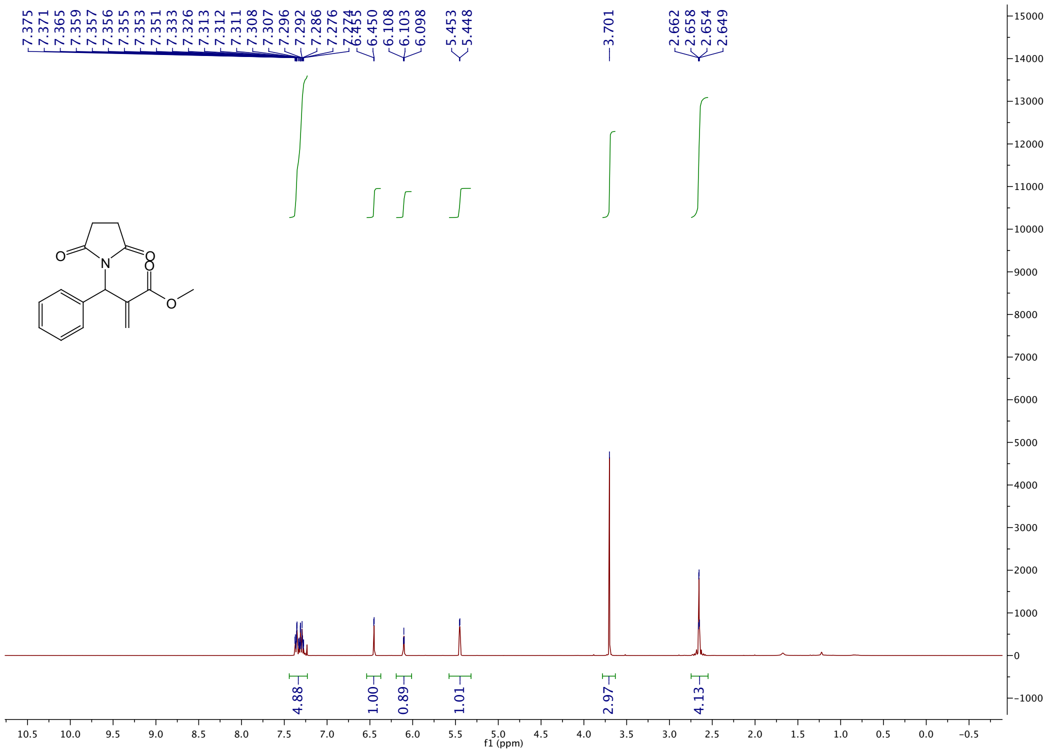

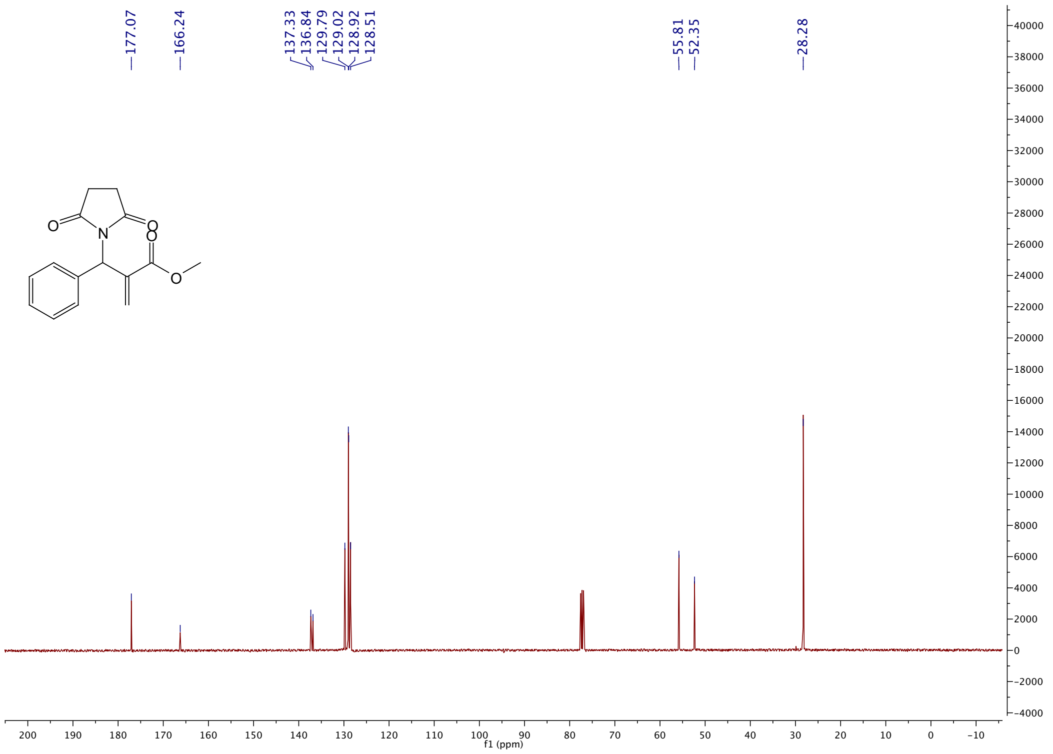

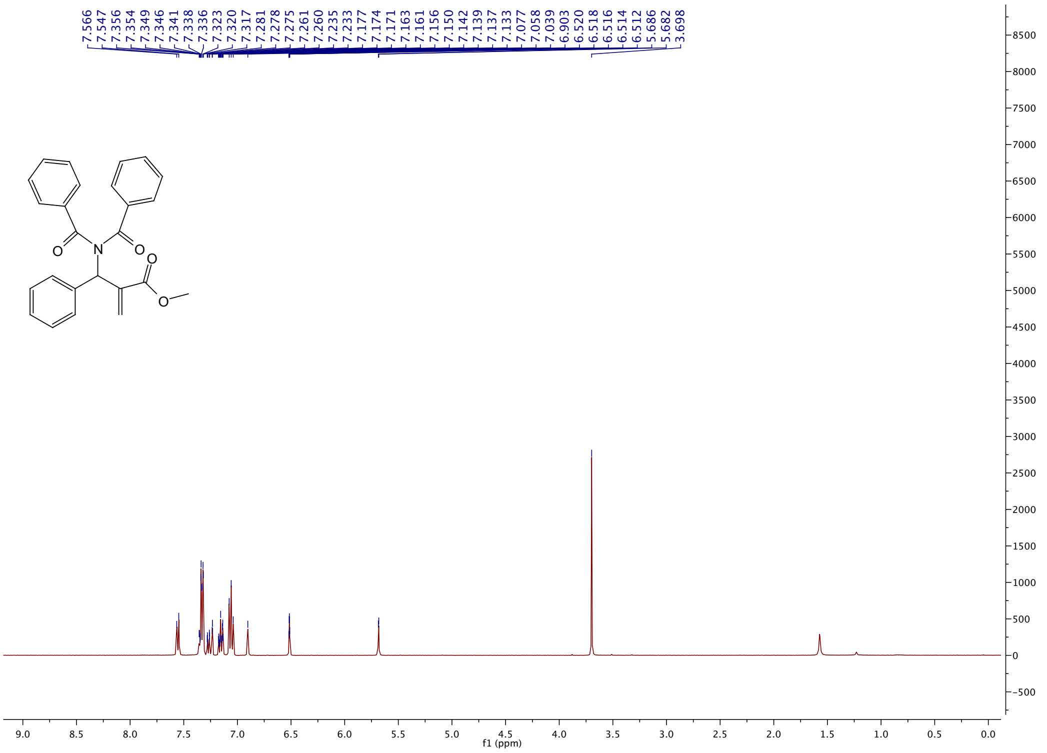
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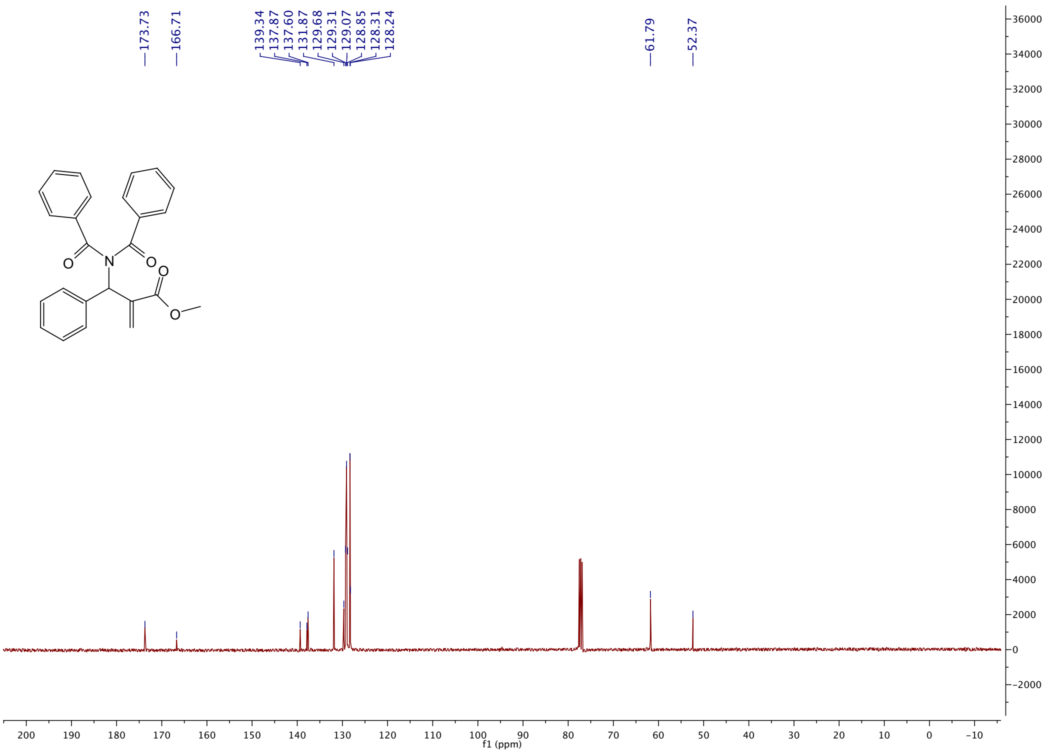
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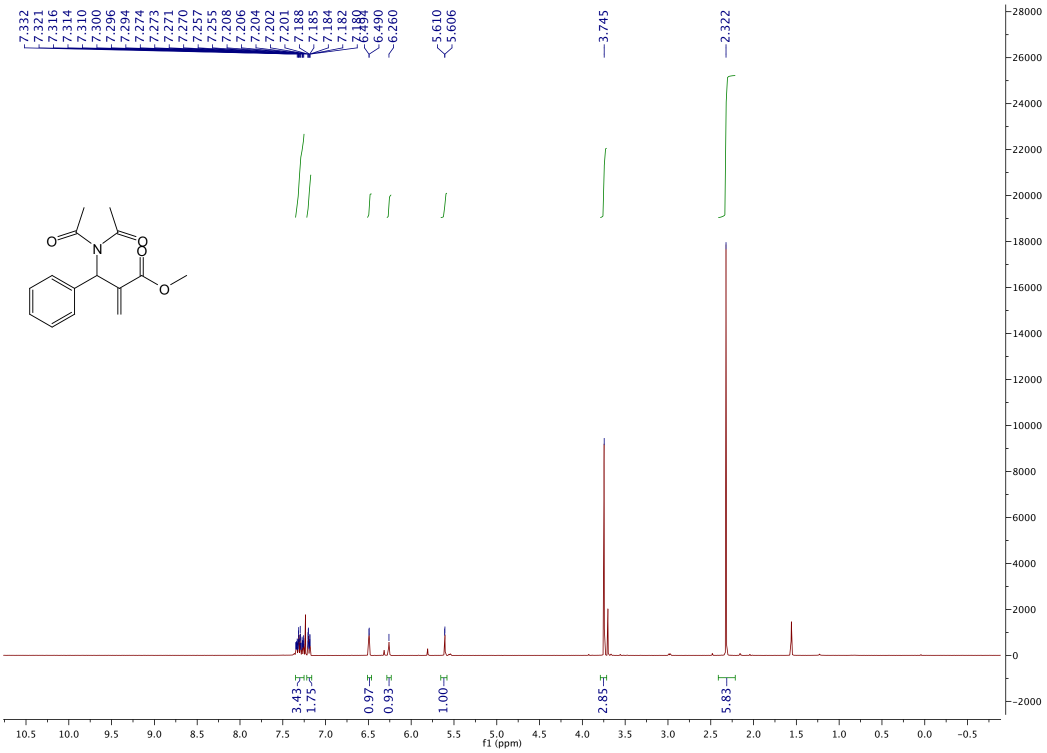
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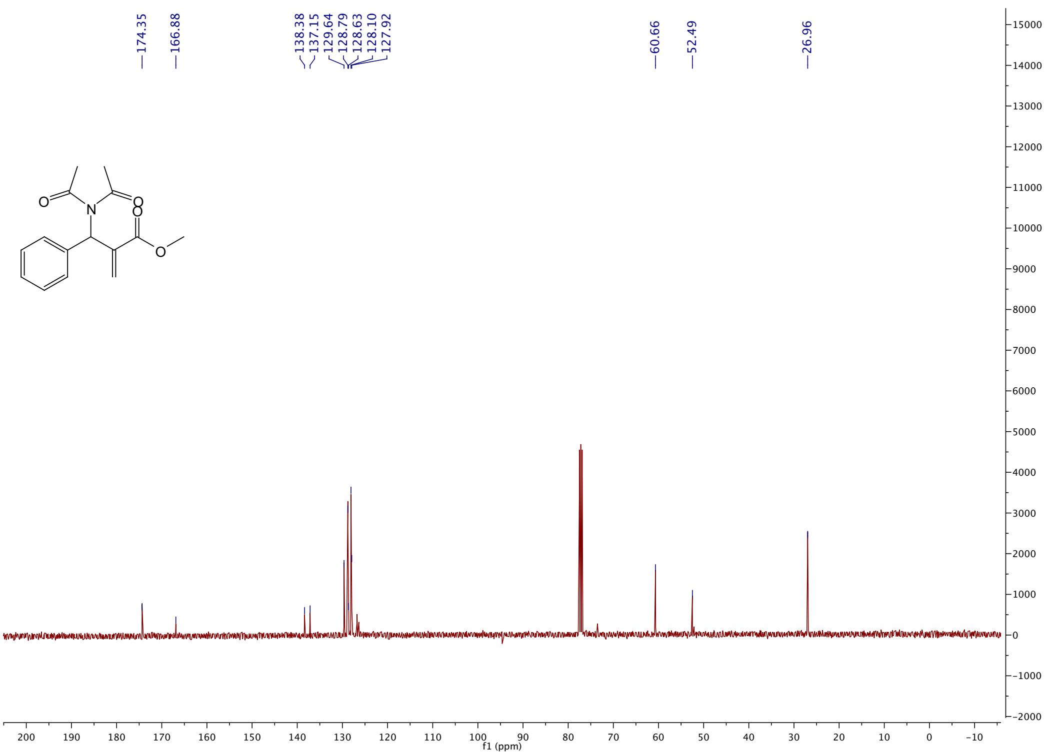
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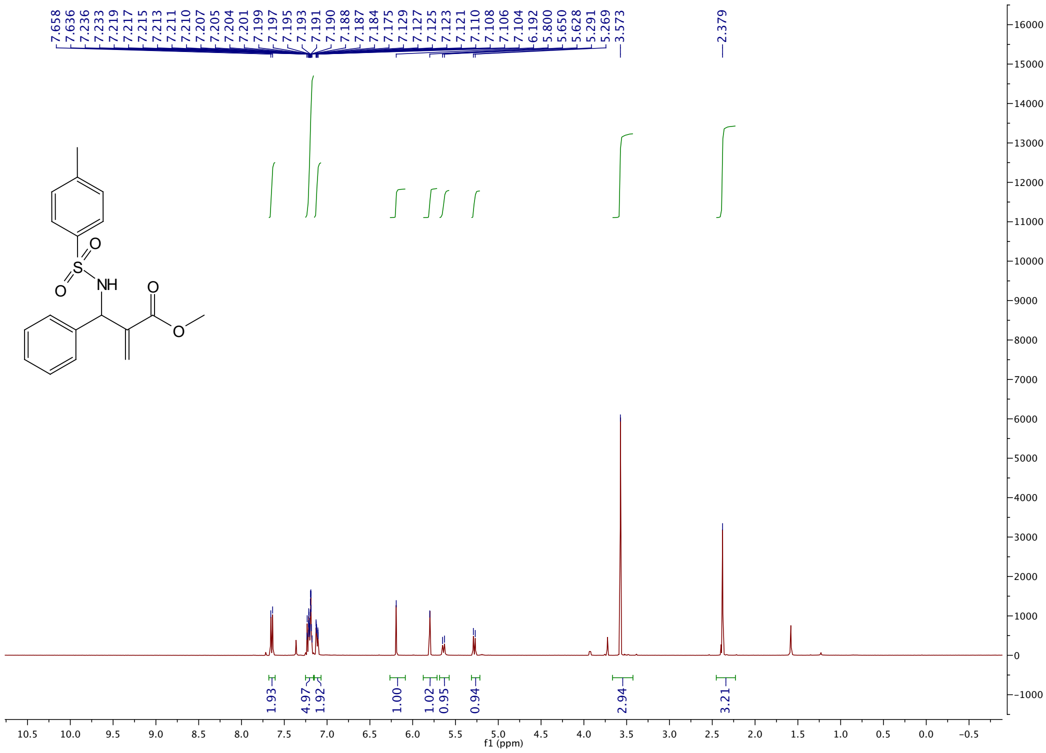

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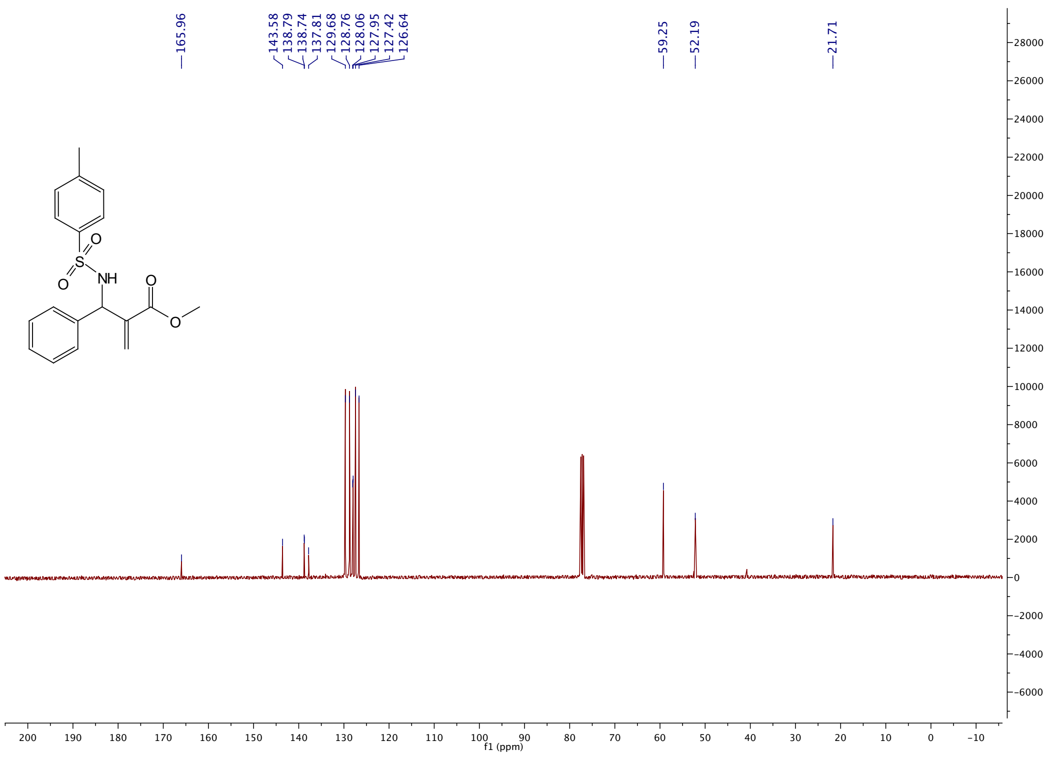

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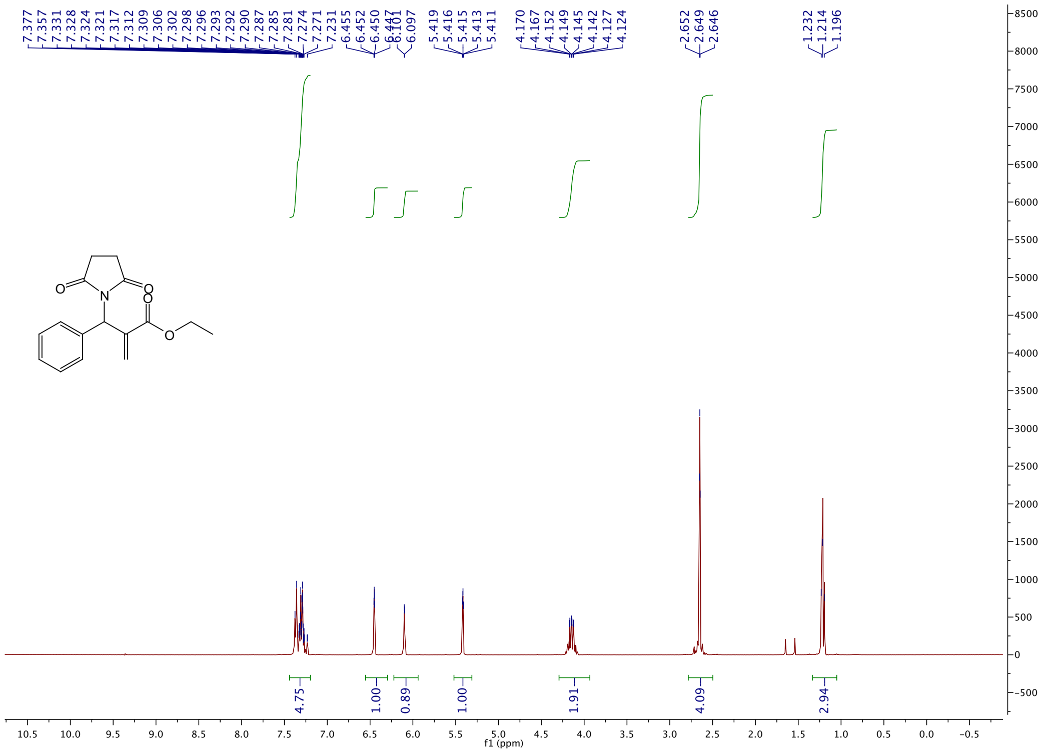
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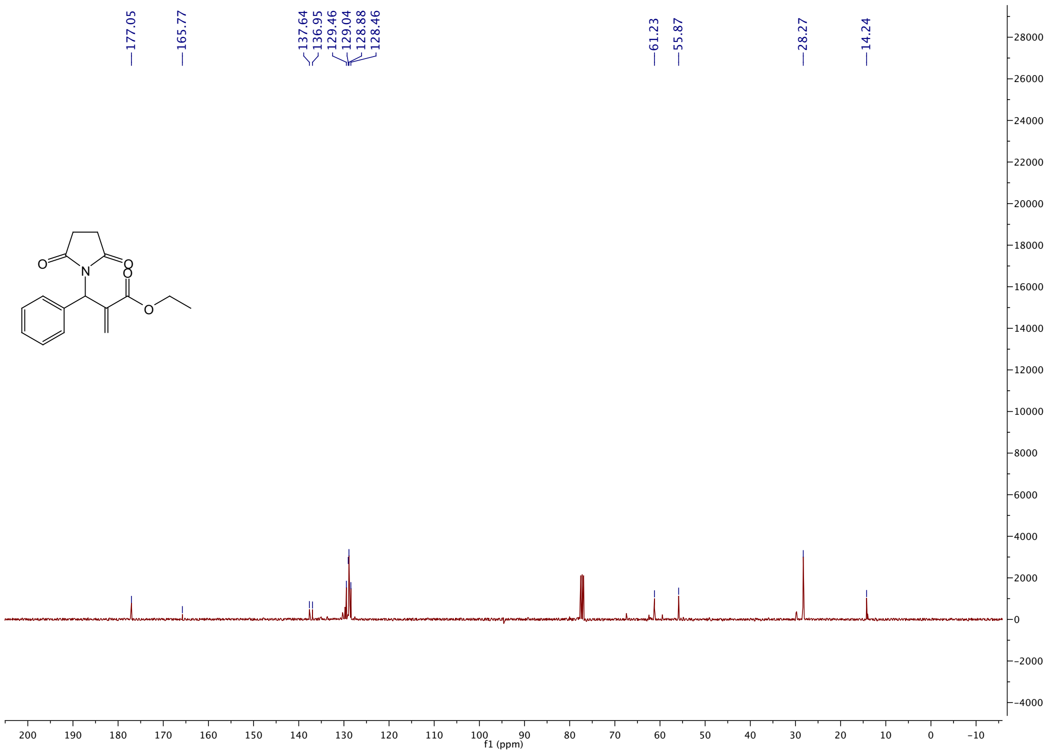
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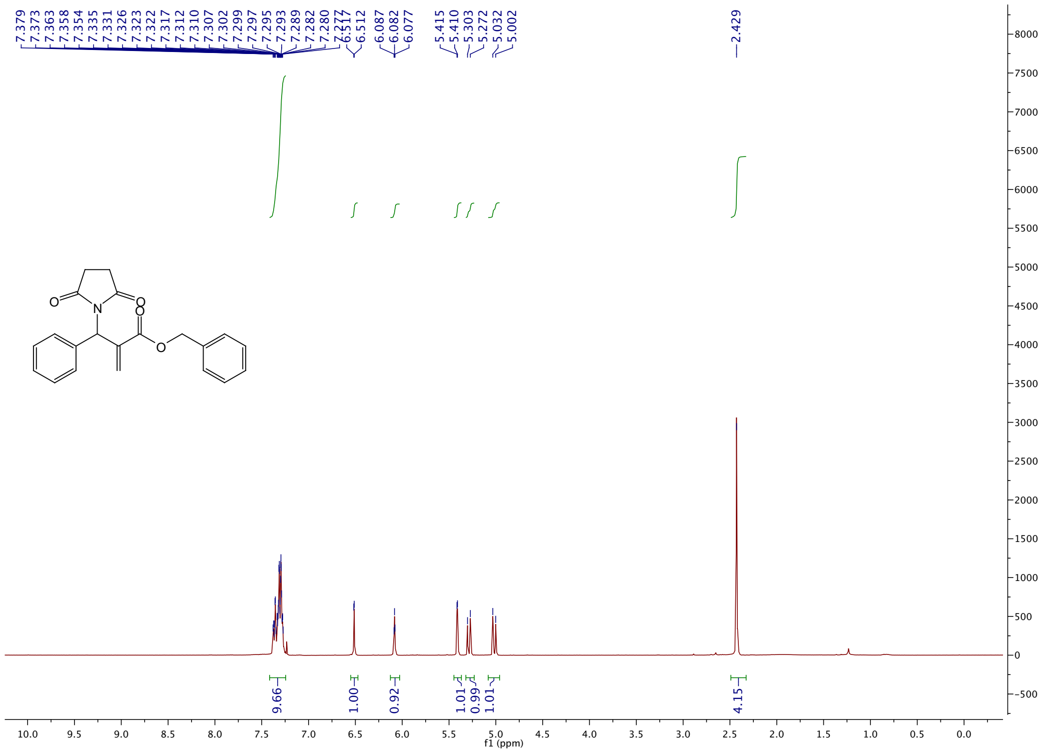

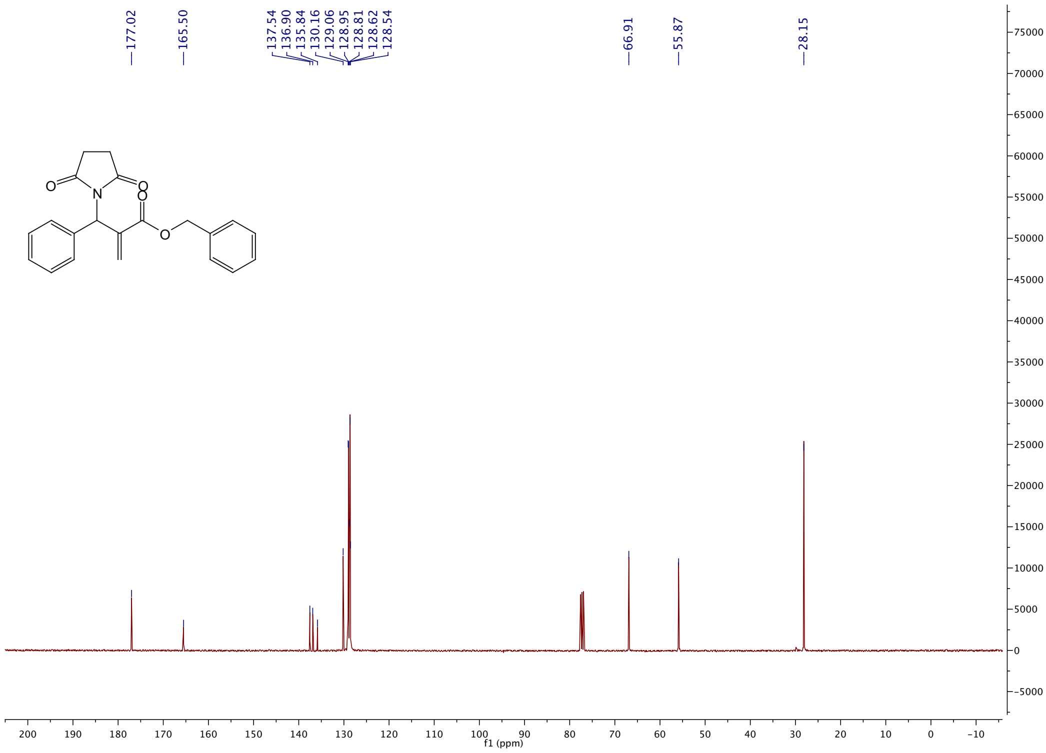

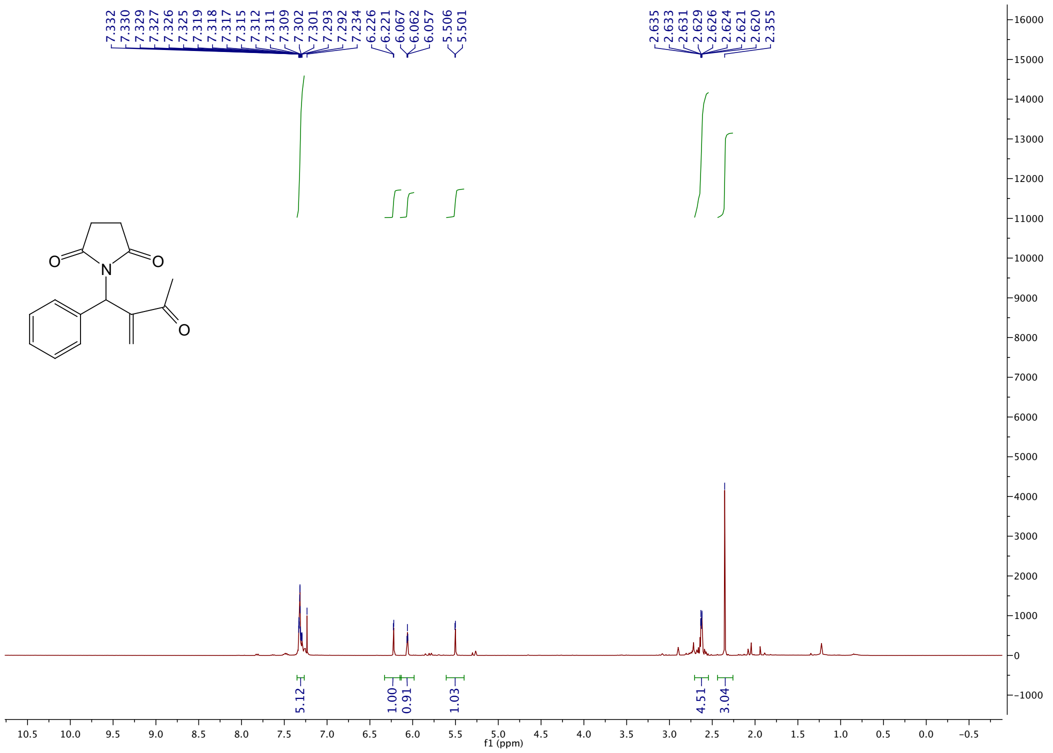

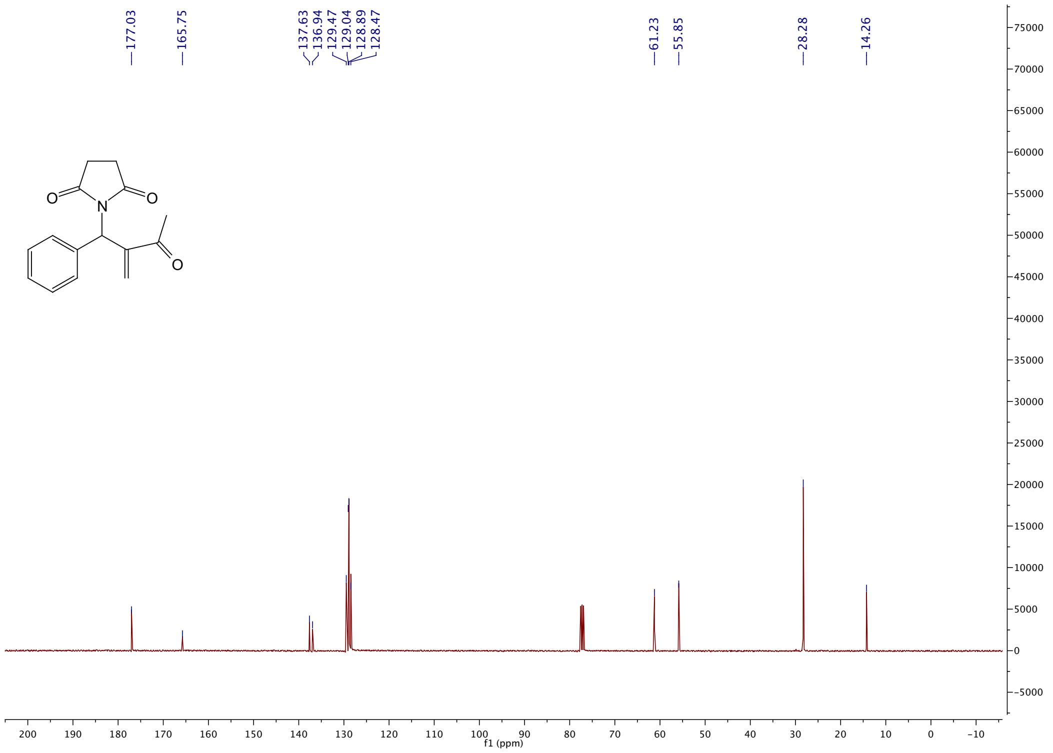

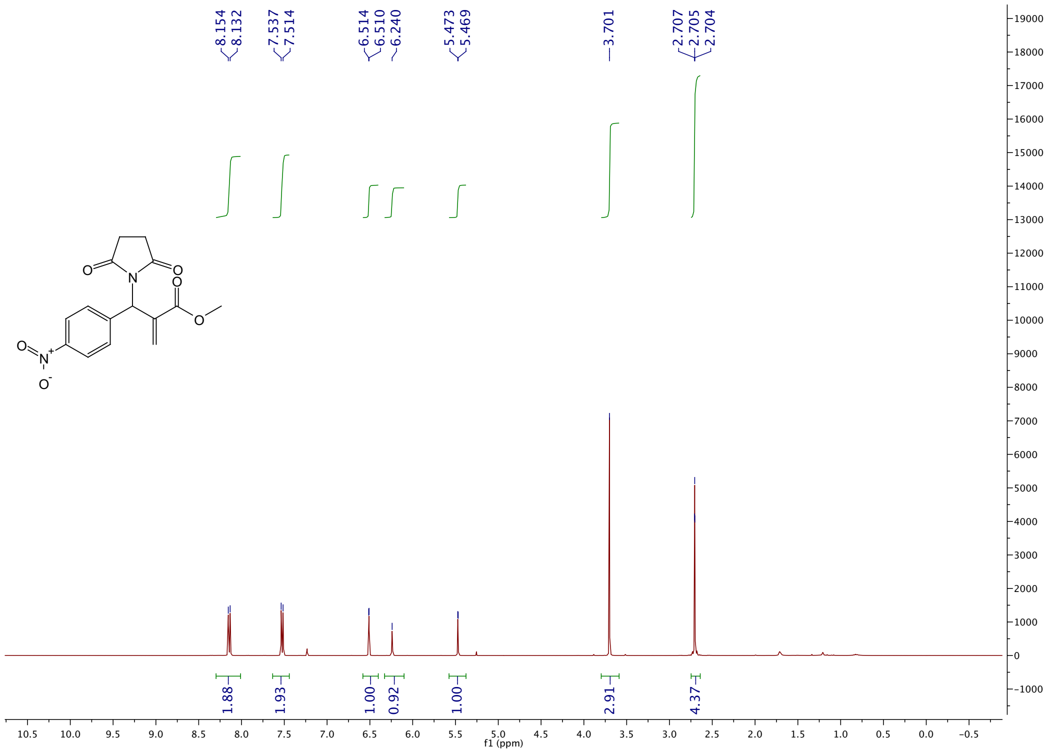
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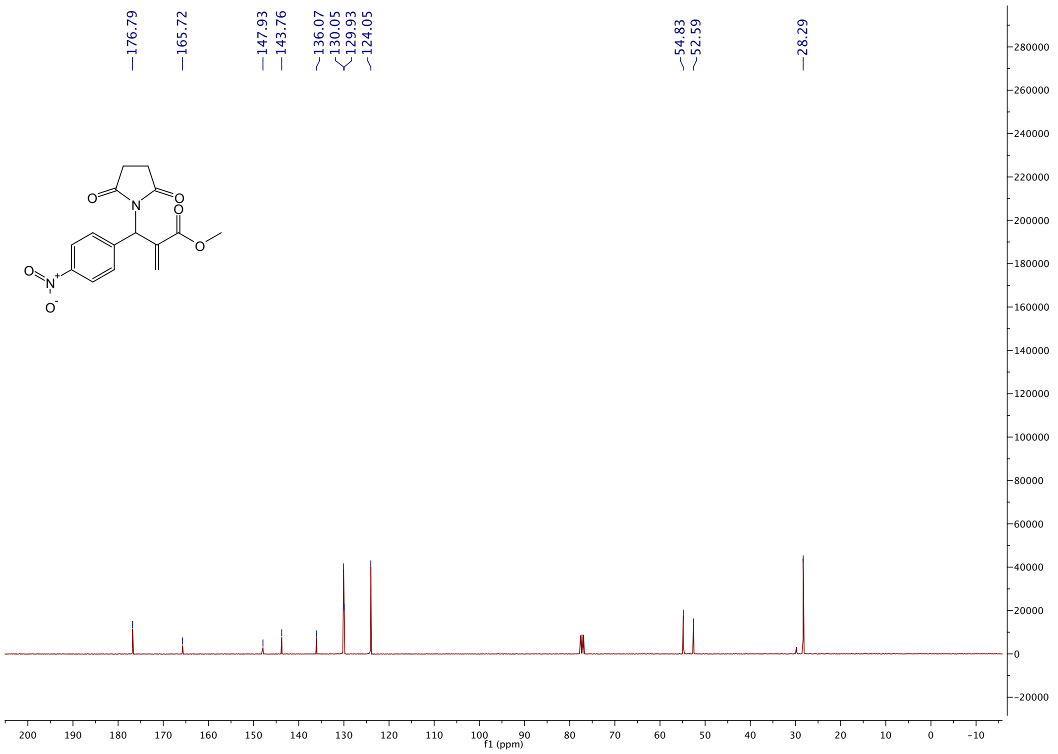
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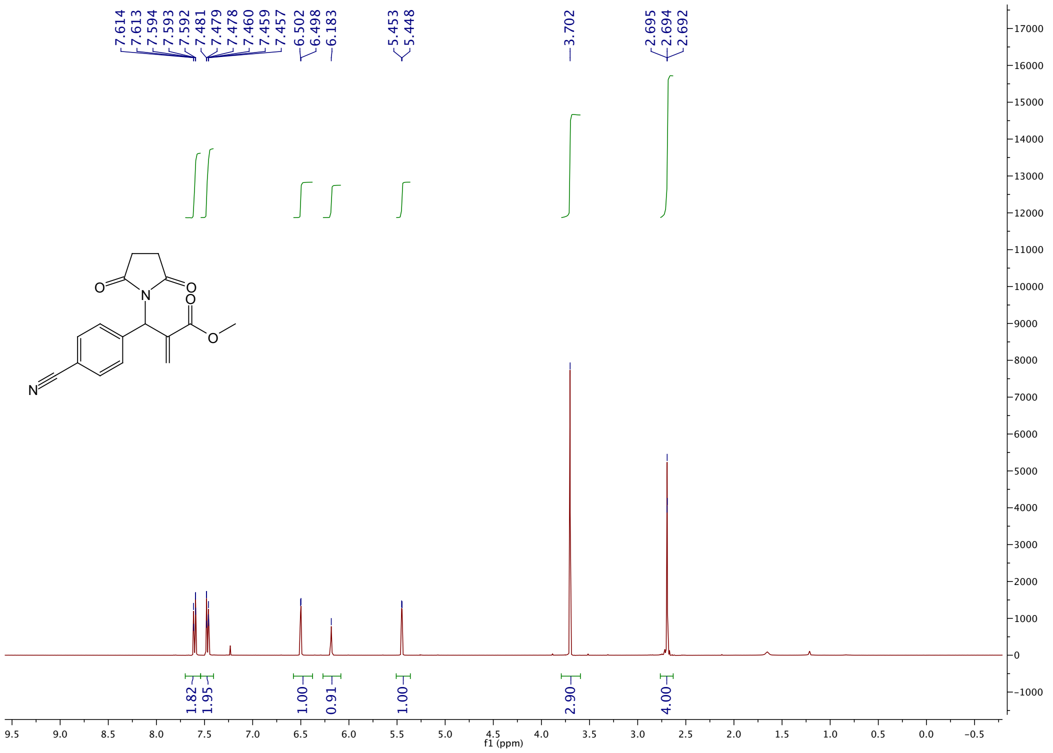

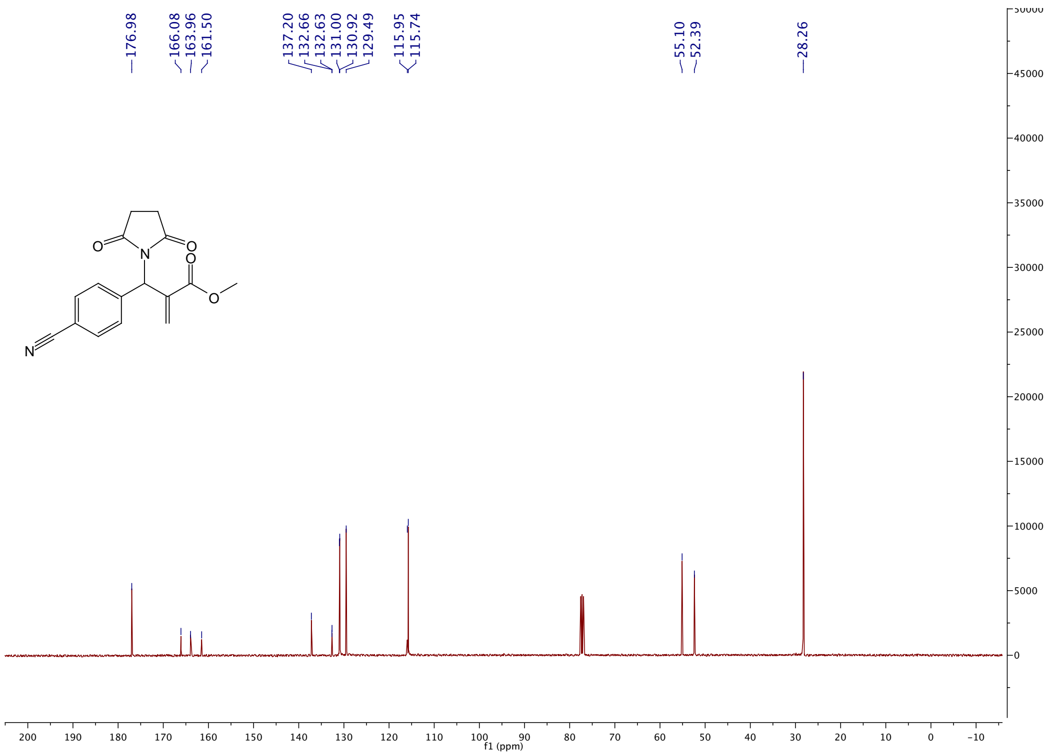

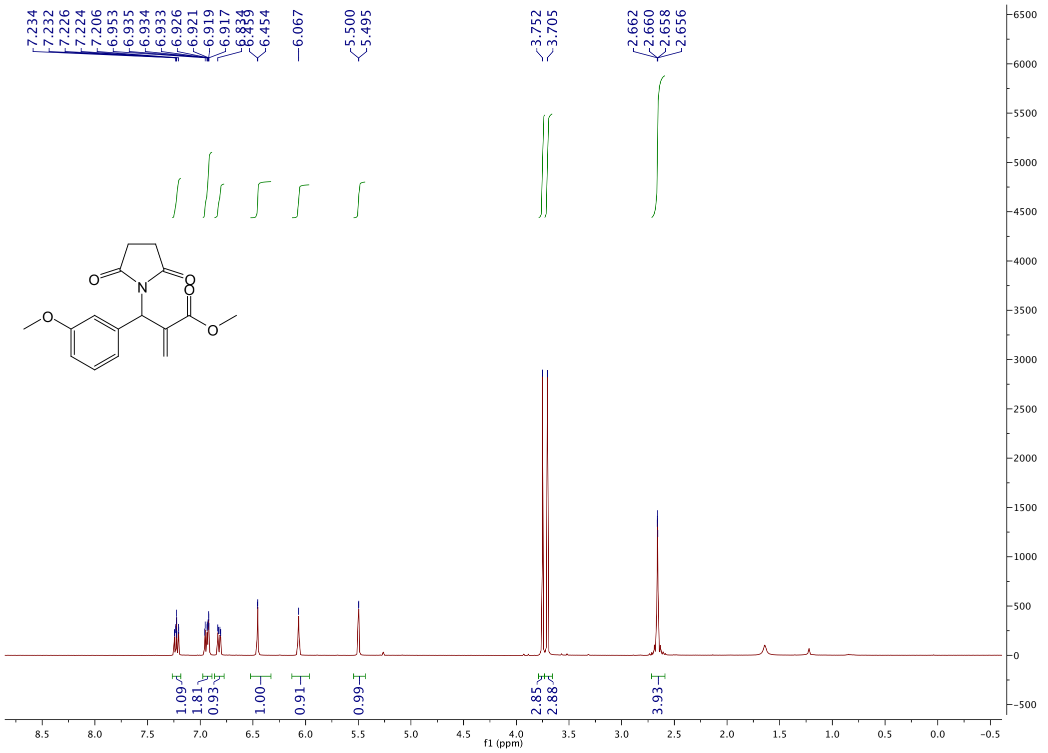

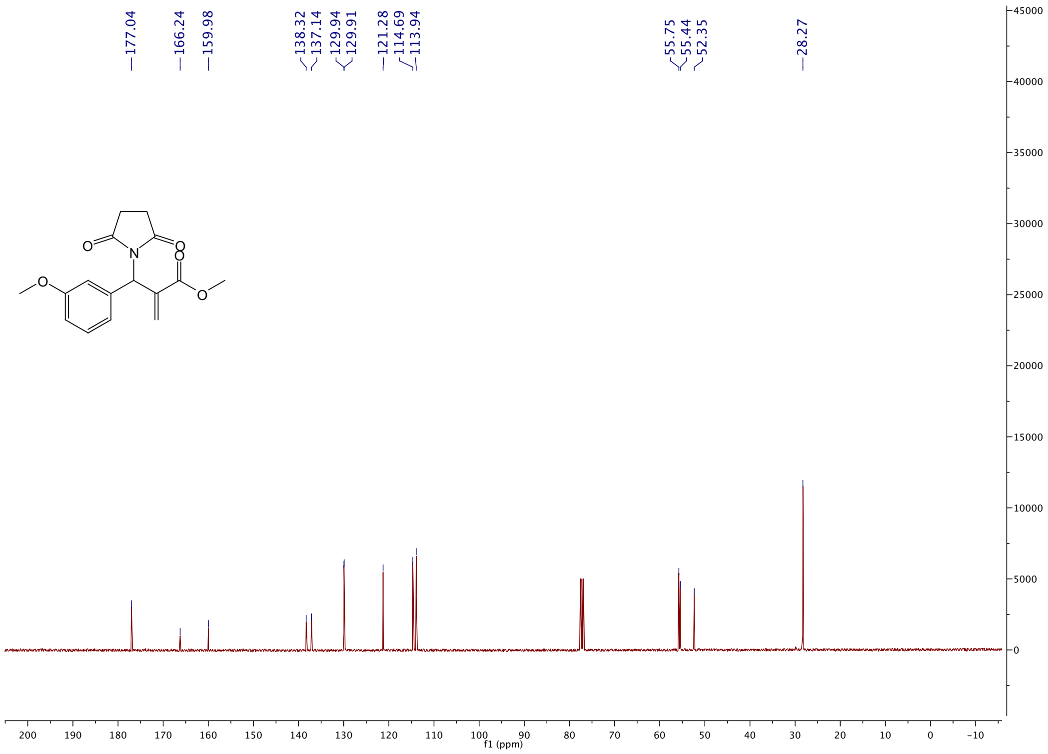

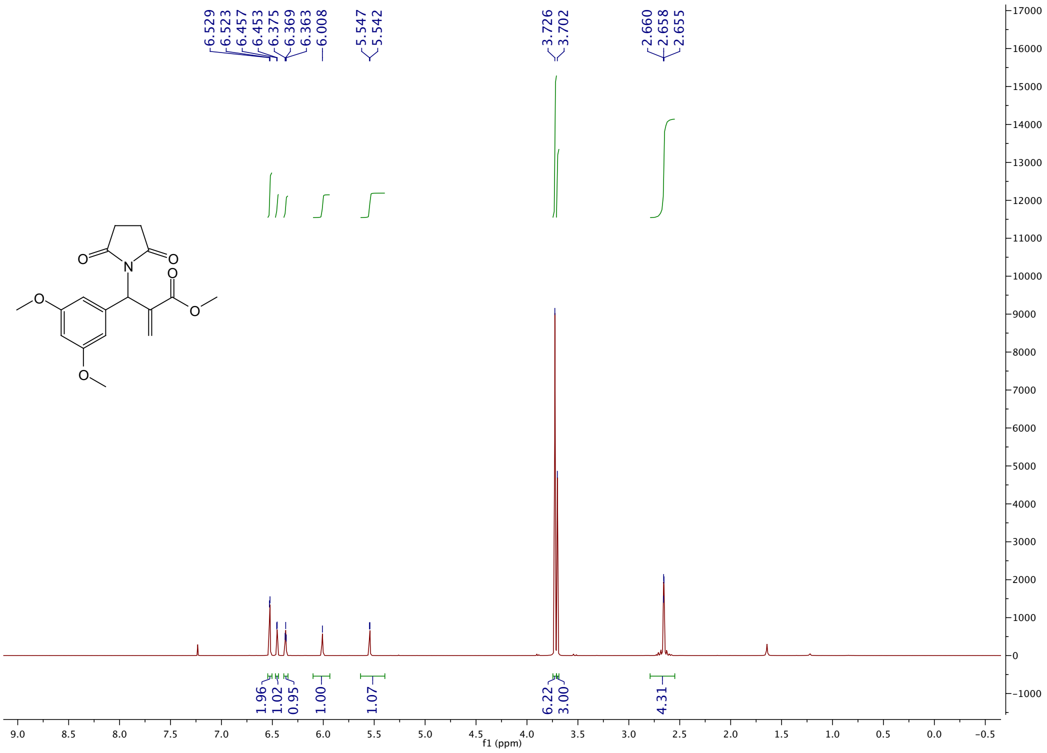
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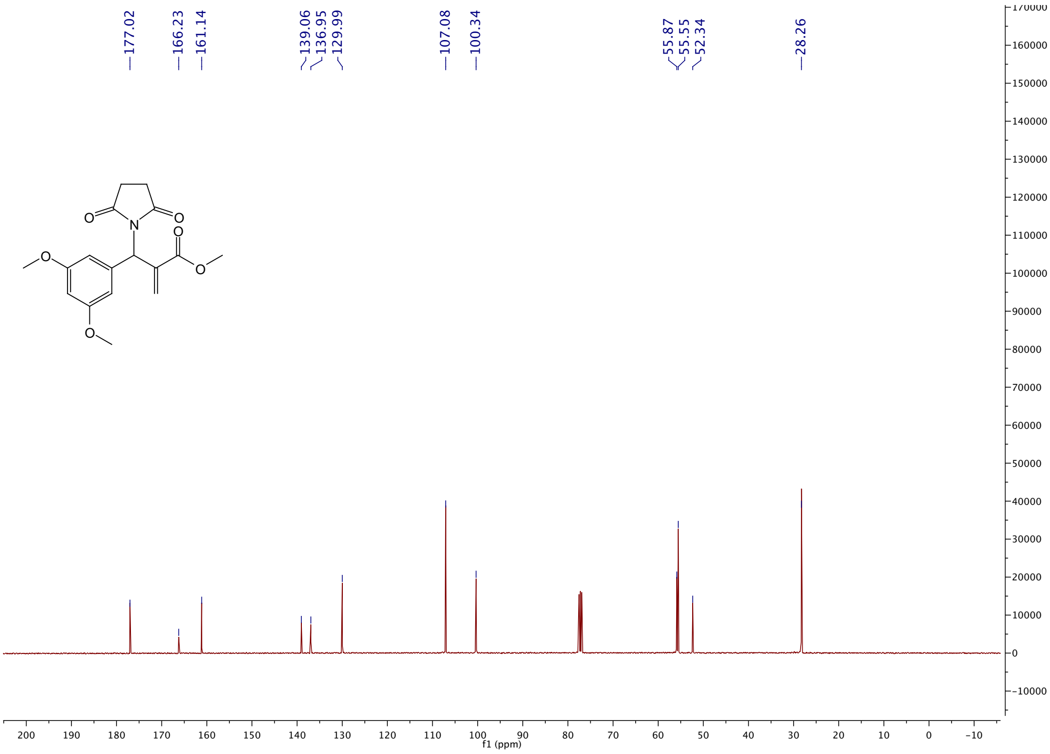
6.523
6.457
6.453
6.375
6.369
6.363
6.008
5.547
5.542
3.726
3.702
2.660
2.658
2.655
1.96
1.02
0.95
1.00
1.07
6.22
3.00
4.31
f1 (ppm)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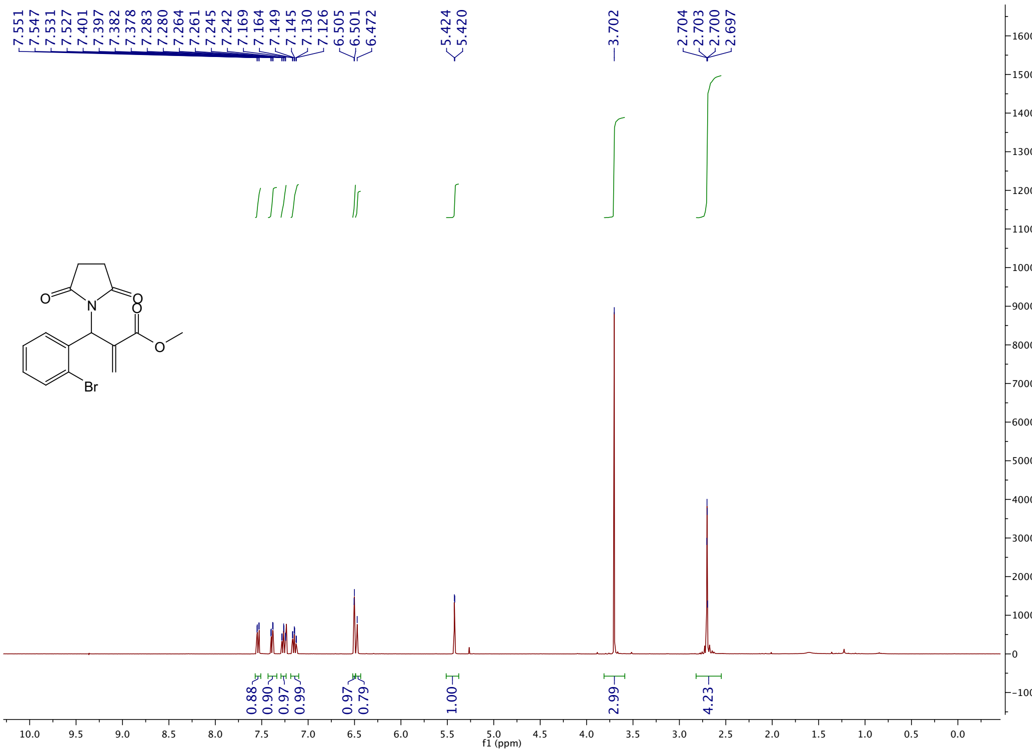
166.23
161.14
139.06
136.95
129.99
107.08
100.34
55.87
55.55
52.34
28.26
f1 (ppm)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7.547
7.531
7.527
7.401
7.397
7.382
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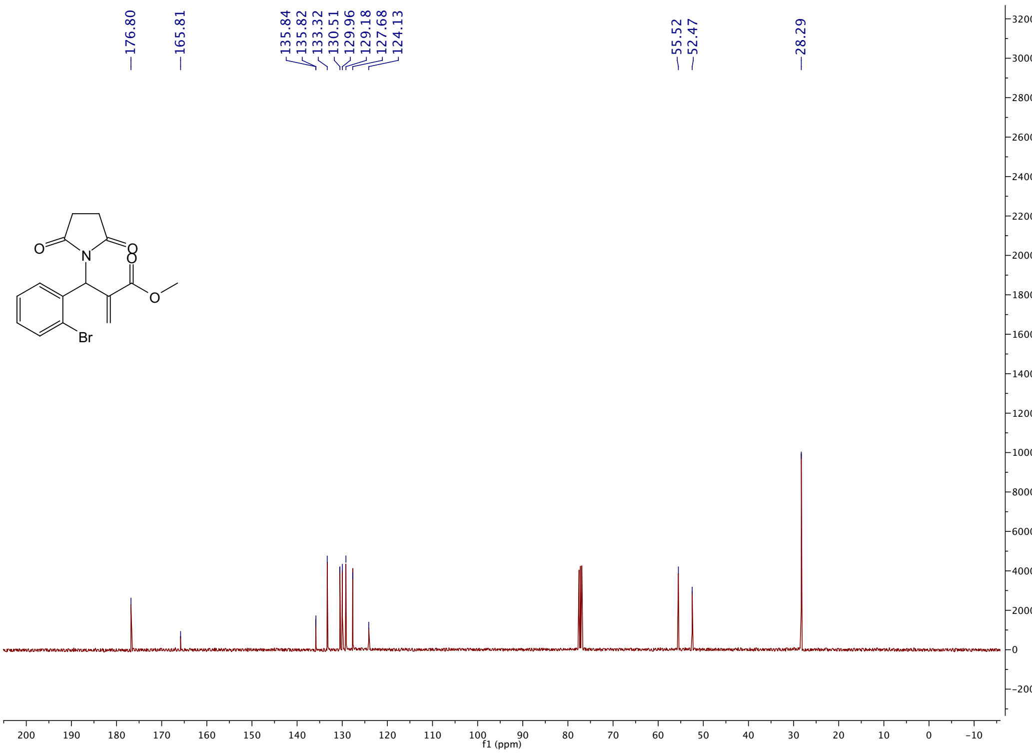
7.261
7.245
7.242
7.169
7.164
7.149
7.145
7.130
7.126
6.505
6.501
6.472
5.424
5.420
3.702
2.704
2.703
2.700
2.697
O
N
O
O
O
Br
0.88
0.90
0.97
0.99
0.97
0.79
1.00
2.99
4.23
f1 (ppm)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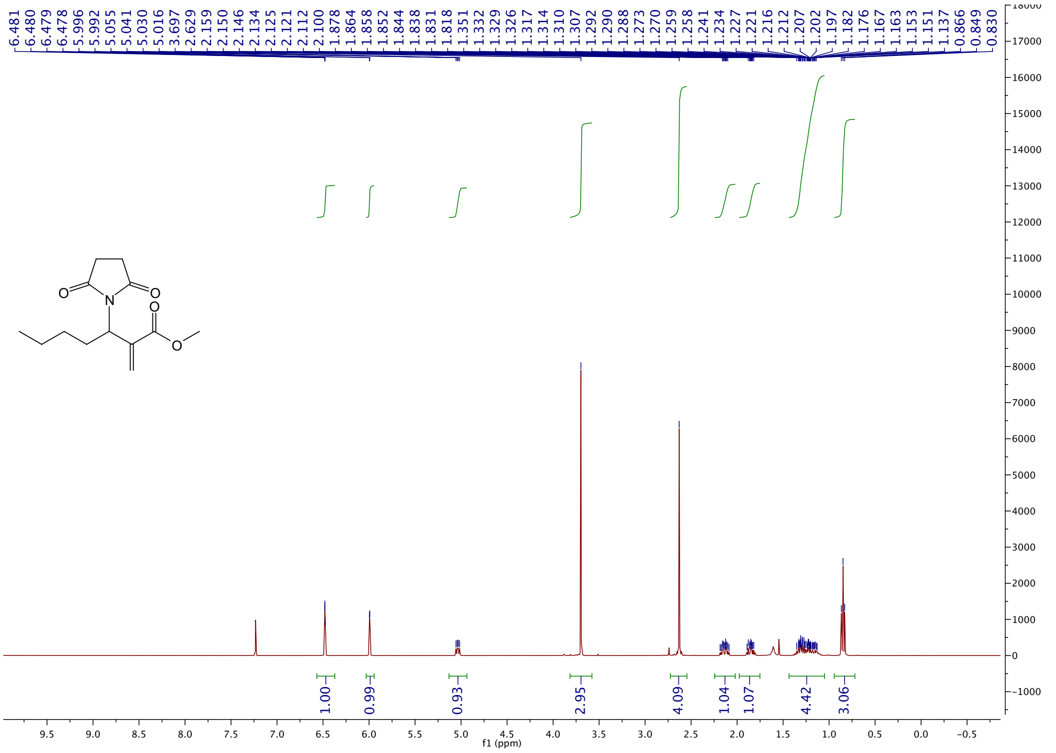
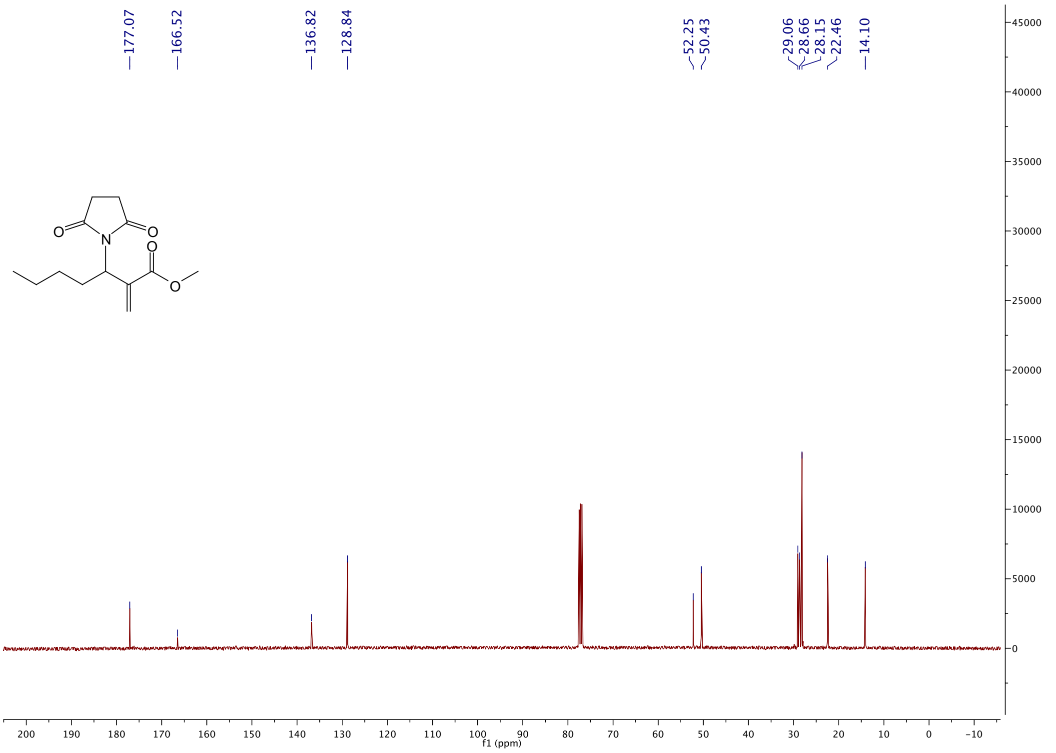
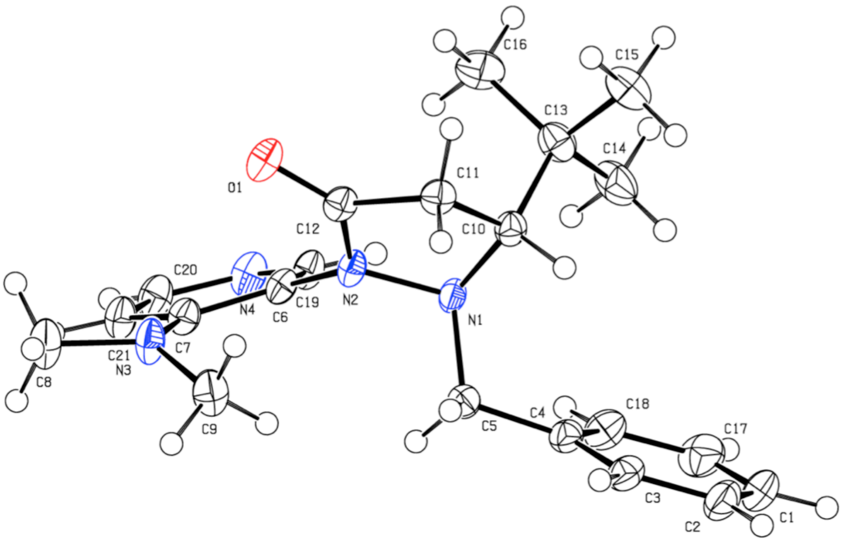
165.81
135.84
135.82
133.32
130.51
129.96
129.18
127.68
124.13
55.52
52.47
28.29
O
N
O
O
O
Br
f1 (ppm)


6.481 6.480 6.479 6.478 5.996 5.992 5.055 5.041 5.030 5.016 3.697 2.629 2.159 2.150 2.146 2.134 2.125 2.121 2.112 2.100 1.878 1.864 1.858 1.852 1.844 1.838 1.831 1.818 1.351 1.332 1.329 1.326 1.317 1.314 1.310 1.307 1.292 1.290 1.288 1.283 1.273 1.270 1.259 1.258 1.241 1.234 1.227 1.221 1.216 1.212 1.207 1.202 1.197 1.182 1.176 1.167 1.163 1.153 1.151 1.137 0.866 0.849 0.830
1.00 0.99 0.93 2.95 4.09 1.04 1.07 4.42 3.06
f1 (ppm)


177.07 166.52 136.82 128.84 52.25 50.43 29.06 28.66 28.15 22.46 14.10
f1 (ppm)

5. X-ray data



X-ray Structure determination: Single crystal X-ray diffraction data of **L4** was collected on a Bruker APEX-II CCD diffractometer. The crystal was kept at 99.99K during data collection. Cu radiation was used for the sample. Using Olex2, the structure was solved with the ShelXS structure solution program using Direct Methods and refined with the XL refinement package using Least Squares minimization. Basic information pertaining to crystal parameters and structure refinement is summarized in Table **S2**.

Table S2 Crystal data and structure refinement

Empirical formula	$C_{21}H_{28}N_4O$
Formula weight	352.47
Temperature	99.99K
Crystal system	trigonal
space group	$P3_2$
a/Å	13.2040(2)
b/Å	13.2040(2)
c/Å	11.5028(10)
α, deg	90
β, deg	90

γ, deg	120
V, Å^3	1736.78(5)
Z	3
d_{calcd}, g.cm^{-3}	1.011
μ, mm^{-1}	0.501
F(000)	570.0
Crystal size/mm^3	0.22 × 0.137 × 0.065
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection	7.732 to 133.186
Index ranges	$-15 \le h \le 15, -15 \le k \le 15, -13 \le l \le 13$
Reflections collected	18957
Independent reflections	3975 [R_{int} = 0.0240, R_{sigma} = 0.0162]
Data/restraints/parameters	3975/1/241
GOOF on F^2	1.056
Final R indexes [I>=2σ (I)]	R_1 = 0.0226, wR_2 = 0.0579
Final R indexes [all data]	R_1 = 0.0230, wR_2 = 0.0582
Largest diff. peak/hole/e Å^{-3}	0.09/-0.13
Flack parameter	0.1(2)