Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

One-step Access to *N*-Enoxyimides by Gold-catalysed Addition of *N*-hydroxyimides to Terminal Alkynes

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Supplementary Information

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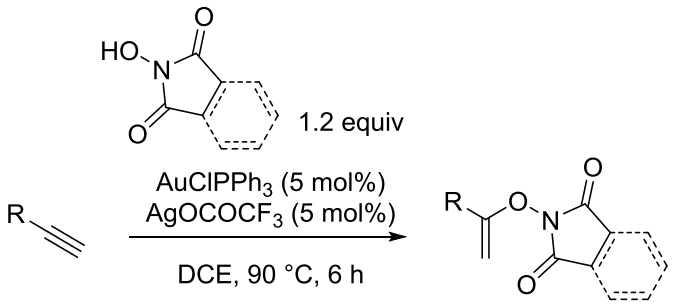
General Methods

Toluene, dichloromethane, tetrahydrofuran, acetonitrile and diethyl ether were purified by an Innovative Technology Solvent Delivery System. Chemicals were used as obtained from the suppliers. Flash chromatography was performed with Silicycle silica gel 60 (0.040-0.063 μm grade). Analytical thin-layer chromatography was performed with commercial glass plates coated with 0.25 mm silica gel (E. Merck, Kieselgel 60 F254). Compounds were either visualised under UV-light at 254 nm or by dipping the plates in an aqueous potassium permanganate solution followed by heating. Proton nuclear magnetic resonance (^{1}H-NMR) data were acquired on a Bruker *AV400* (400 MHz). Chemical shifts (δ) are reported in parts per million (ppm) relative to incompletely deuterated $CDCl_3$ (s, 7.26 ppm). Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; p, pentet; dd, doublet of doublets; qd, quadruplet of dublets; m, multiplet; br, broad. Proton decoupled Carbon-13 nuclear magnetic resonance (^{13}C-NMR) data were acquired on a Bruker *AV400* (100 MHz). Chemical shifts are reported in ppm relative to $CDCl_3$ (77.16 ppm). Proton decoupled Fluorine-19 nuclear magnetic resonance (^{19}F-NMR) were acquired at 376 MHz on a Bruker *AV400* spectrometer. Infrared (IR) data were recorded on an Alpha-P Bruker FT-IR Spectrometer. Absorbance frequencies are reported in reciprocal centimeters (cm^{-1}).

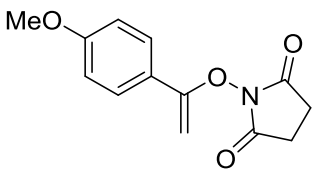
Experimental Section

General procedure for N-Enoxysuccinimide substrates preparation:



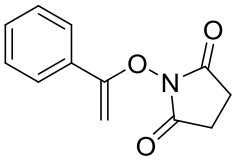
(PPh_3)AuCl (5 mol %) and silver trifluoroacetate (5 mol %) were premixed in 1,2-DCE (1ml) for 10 mins at rt and filtered over a short plug of celite before use. This solution was added in a sealed tube to alkyne (1.0 mmol) in 1,2-DCE (4ml) and *N*-hydroxyimide (1.1 mmol) was then added. The tube was sealed and the reaction was stirred for 6 h at 90 °C. The reaction was diluted with DCM and passed through a short plug of celite. The filtrate was concentrated and the residue purified by column chromatography.

1-((1-(4-methoxyphenyl)vinyl)oxy)pyrrolidine-2,5-dione **3aa**



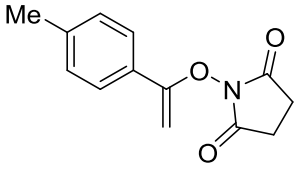
Obtained as a white solid (185 mg, 75 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 – 7.58 (m, 2H), 6.93 – 6.85 (m, 2H), 4.72 (d, *J* = 4.0 Hz, 1H), 4.29 (d, *J* = 4.0 Hz, 1H), 3.83 (s, 3H), 2.85 (s, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.0, 160.9, 159.4, 128.0, 124.7, 113.9, 85.1, 55.5, 25.8; **IR (ATR, cm^{-1}):** ν_{max} = 2955, 1715, 1673, 1599, 1511, 1258, 1209, 1175, 1075, 1026, 837, 653; **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_{13}H_{13}NNaO_4^+$ 270.0737; Found 270.0738; **Rf:** 0.38 (Pentane: EtOAc, 1:1); **m.p.:** 166 °C.

1-((1-phenylvinyl)oxy)pyrrolidine-2,5-dione **3ba**



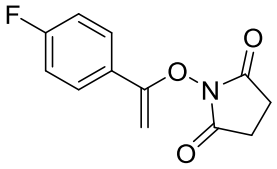
Obtained as a white solid (78 mg, 36 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (m, 2H), 7.38 (m, 3H), 4.84 (d, *J* = 4.1 Hz, 1H), 4.38 (d, *J* = 4.1 Hz, 1H), 2.86 (s, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.9, 159.4, 132.1, 129.9, 128.5, 126.5, 86.6, 25.8; **IR (ATR, cm^{-1}):** ν_{max} = 1731, 1644, 1365, 1264, 1198, 1100; **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_{12}H_{11}NNaO_3^+$ 240.0631; Found 240.0632; **Rf:** 0.45 (Pentane: EtOAc, 1:1); **m.p.:** 148 °C.

1-((1-(p-tolyl)vinyl)oxy)pyrrolidine-2,5-dione **3ca**



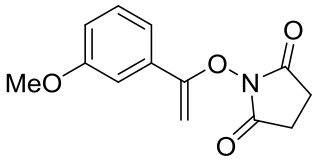
Obtained as a white solid (95 mg, 41 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 4.79 (d, *J* = 4.0 Hz, 1H), 4.33 (d, *J* = 4.0 Hz, 1H), 2.85 (s, 4H), 2.37 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.0, 159.5, 139.9, 129.3, 129.2, 126.4, 85.8, 25.8, 21.5; **IR (ATR, cm^{-1}):** ν_{max} = 1726, 1648, 1369, 1200, 1065, 1064, 911, 821, 646; **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_{13}H_{13}NNaO_3^+$ 254.0788; Found 254.0789; **Rf:** 0.45 (Pentane: EtOAc, 1:1); **m.p.:** 177 °C.

1-((1-(4-fluorophenyl)vinyl)oxy)pyrrolidine-2,5-dione **3da**



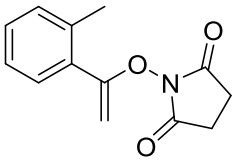
Obtained as a white solid (87 mg, 37 % yield) using 10 mol% catalyst. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 8.8, 5.4 Hz, 2H), 7.07 (t, *J* = 8.7 Hz, 2H), 4.78 (d, *J* = 4.2 Hz, 1H), 4.38 (d, *J* = 4.2 Hz, 1H), 2.86 (s, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.9, 165.0, 162.5, 158.6, 128.6 (d, *J* = 8.6 Hz, 1H), 128.3 (d, *J* = 3.2 Hz, 1H), 115.6 (d, *J* = 22.0 Hz, 1H), 86.7, 25.8; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -111.0; **IR (ATR, cm^{-1}):** ν_{max} = 1728, 1651, 1509, 1370, 1262, 1203, 1092, 1063, 911, 846, 646; **HRMS (APPI/LTQ-Orbitrap) m/z:** $[M + H]^+$ Calcd for $C_{12}H_{11}FNO_3^+$ 236.0717; Found 236.0721; **Rf:** 0.46 (Pentane: EtOAc, 1:1); **m.p.:** 175 °C;

1-((1-(3-methoxyphenyl)vinyl)oxy)pyrrolidine-2,5-dione **3ea**



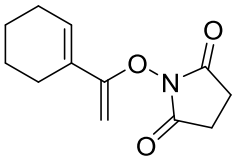
Obtained as a white solid (148 mg, 60 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 – 7.22 (m, 4H), 6.93 (dt, *J* = 6.9, 2.5 Hz, 1H), 4.85 (d, *J* = 4.1 Hz, 1H), 4.40 (d, *J* = 4.1 Hz, 1H), 3.83 (s, 3H), 2.85 (s, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.9, 159.6, 159.3, 133.4, 129.6, 119.1, 115.9, 111.7, 87.0, 55.5, 25.8; **IR (ATR, cm^{-1}):** ν_{max} = 1732, 1581, 1489, 1430, 1277, 1199, 1081, 1043, 647; **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_{13}H_{13}NNaO_4^+$ 270.0737; Found 270.0737; **Rf:** 0.48 (Pentane: EtOAc, 1:1); **m.p.:** 140 °C.

1-((1-(o-tolyl)vinyl)oxy)pyrrolidine-2,5-dione **3fa**



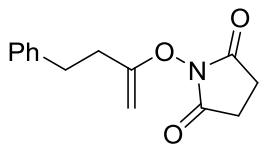
Obtained as a white solid (108 mg, 47 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.6 Hz, 1H), 7.30 (td, *J* = 7.6, 1.2 Hz, 1H), 7.20 (dd, *J* = 15.9, 7.8 Hz, 2H), 4.52 (d, *J* = 3.6 Hz, 1H), 4.47 (d, *J* = 3.6 Hz, 1H), 2.82 (s, 4H), 2.53 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.8, 159.6, 137.9, 132.2, 130.5, 130.4, 129.8, 125.6, 89.1, 25.8, 20.3; **IR (ATR, cm^{-1}):** ν_{max} = 1731, 1655, 1361, 1256, 1197, 1084, 756, 646; **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_{13}H_{13}NNaO_3^+$ 254.0788; Found 254.0783; **Rf:** 0.51 (Pentane: EtOAc, 1:1); **m.p.:** 129 °C.

1-((1-(cyclohex-1-en-1-yl)vinyl)oxy)pyrrolidine-2,5-dione **3ga**



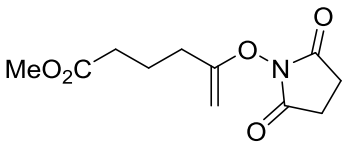
Obtained as a white solid (136 mg, 62 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.47 (s, 1H), 4.37 (d, *J* = 4.0 Hz, 1H), 4.05 (d, *J* = 4.0 Hz, 1H), 2.83 (s, 4H), 2.17 (t, *J* = 4.8 Hz, 4H), 1.72 - 167 (m, 2H), 1.65 – 1.57 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.2, 159.0, 128.2, 128.0, 83.4, 25.7, 25.5, 25.4, 22.5, 21.9; **IR (ATR, cm^{-1}):** ν_{max} = 2934, 1729, 1366, 1237, 1197, 901, 815, 647 cm^{-1}; **HRMS (APCI/QTOF) m/z:** $[M + H]^+$ Calcd for $C_{12}H_{16}NO_3^+$ 222.1125; Found 222.1121; **Rf:** 0.48 (Pentane: EtOAc, 1:1); **m.p.:** 158 °C.

1-((4-phenylbut-1-en-2-yl)oxy)pyrrolidine-2,5-dione **3ha**



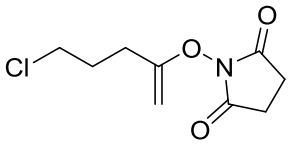
Obtained as a white solid (202 mg, 82 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.23 (m, 4H), 7.23 – 7.17 (m, 1H), 4.13 (d, *J* = 3.8 Hz, 1H), 4.03 (d, *J* = 3.8 Hz, 1H), 2.99 – 2.87 (m, 2H), 2.82 (s, 4H), 2.62 – 2.55 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.9, 160.8, 140.9, 128.7, 128.5, 126.3, 84.9, 33.5, 33.3, 25.7; **IR (ATR, cm^{-1}):** ν_{max} = 1731, 1662, 1367, 1199, 1080, 701, 647; **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_{14}H_{15}NNaO_3^+$ 268.0944; Found 268.0945; **Rf:** 0.62 (Pentane: EtOAc, 1:1); **m.p.:** 106 °C.

methyl 5-((2,5-dioxopyrrolidin-1-yl)oxy)hex-5-enoate **3ia**



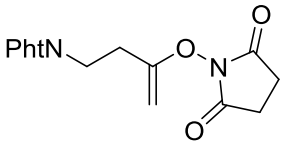
Obtained as a white solid (160 mg, 68 % yield). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 4.18 (d, *J* = 3.8 Hz, 1H), 4.04 (d, *J* = 3.8 Hz, 1H), 3.67 (s, 3H), 2.81 (s, 4H), 2.46 (t, *J* = 7.4 Hz, 2H), 2.36 (t, *J* = 7.3 Hz, 2H), 1.95 (p, *J* = 7.4 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.9, 169.8, 160.5, 85.2, 51.7, 32.8, 30.7, 25.7, 22.1; **IR (ATR, cm^{-1}):** ν_{max} = 1728, 1436, 1368, 1200, 1147; **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_{11}H_{15}NNaO_5^+$ 264.0842; Found 264.0848; **Rf :** 0.37 (Pentane: EtOAc, 1:1); **m.p.:** 69 °C.

1-((5-chloropent-1-en-2-yl)oxy)pyrrolidine-2,5-dione **3ja**



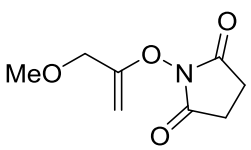
Obtained as a white solid (140 mg, 78 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.25 (d, *J* = 3.8 Hz, 1H), 4.07 (d, *J* = 3.8 Hz, 1H), 3.68 (t, *J* = 6.3 Hz, 2H), 2.81 (s, 4H), 2.50 (t, *J* = 7.1 Hz, 2H), 2.10 (p, *J* = 6.7 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.8, 159.7, 85.8, 43.9, 29.5, 28.7, 25.7; **IR (ATR, cm^{-1}):** ν_{max} = 1730, 1664, 1368, 1199, 1078, 649; **HRMS (APCI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_9H_{12}ClNNaO_3^+$ 240.0398; Found 240.0401; **Rf:** 0.53 (Pentane: EtOAc, 1:1).

2-(3-((2,5-dioxopyrrolidin-1-yl)oxy)but-3-en-1-yl)isoindoline-1,3-dione **3ka**



Obtained as a white solid (185 mg, 59 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (td, *J* = 5.3, 2.1 Hz, 2H), 7.77 – 7.64 (m, 2H), 4.33 (d, *J* = 3.9 Hz, 1H), 4.14 (d, *J* = 3.9 Hz, 1H), 4.04 – 3.94 (m, 2H), 2.79 (s, 4H), 2.77 – 2.71 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.7, 168.3, 158.1, 134.1, 132.3, 123.4, 87.1, 35.9, 30.4, 25.7; **IR (ATR, cm^{-1}):** ν_{max} = 1732, 1710, 1398, 1368, 1200, 1074, 721, 648; **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_{16}H_{14}N_2NaO_5^+$ 337.0795; Found 337.0787; **Rf:** 0.28 (Pentane: EtOAc, 1:1); **m.p.:** 188 °C.

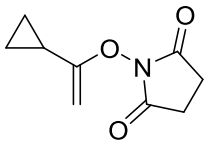
1-((3-methoxyprop-1-en-2-yl)oxy)pyrrolidine-2,5-dione **3la**



Obtained as a white solid (66 mg, 36 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.51 (d, *J* = 3.7 Hz, 1H), 4.33 (d, *J* = 3.7 Hz, 1H), 4.08 (s, 2H), 3.42 (s, 3H), 2.81 (s, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.7, 157.5, 88.8, 69.8, 58.3, 25.7; **IR (ATR, cm^{-1}):** ν_{max} = 1730, 1667, 1197, 1076, 648; **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for

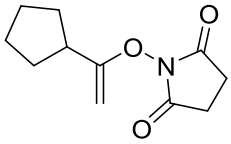
$C_8H_{11}NNaO_4^+$ 208.0580; Found 208.0584; **Rf:** 0.31 (Pentane: EtOAc, 1:1).

1-((1-cyclopropylvinyl)oxy)pyrrolidine-2,5-dione **3ma**



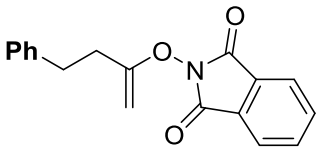
Obtained as a white solid (140 mg, 77 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.19 (d, *J* = 3.6 Hz, 1H), 4.03 (d, *J* = 3.6 Hz, 1H), 2.79 (s, 4H), 1.62-1.58 (m, 1H), 0.85-0.75 (m, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.0, 162.7, 83.7, 25.7, 11.8, 5.8; **IR (ATR, cm^{-1}):** ν_{max} = 1730, 1660, 1370, 1200, 1086, 649; **HRMS (APPI/LTQ-Orbitrap) m/z**: $[M + H]^+$ Calcd for $C_9H_{12}NO_3^+$ 182.0812; Found 182.0815; **Rf:** 0.54 (Pentane: EtOAc, 1:1) ; **m.p.:** 56 °C.

1-((1-cyclopentylvinyl)oxy)pyrrolidine-2,5-dione **3na**



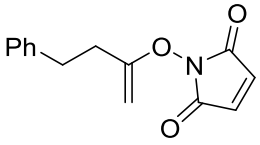
Obtained as a white solid (130 mg, 62 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.17 (d, *J* = 4.4 Hz, 1H), 3.94 (d, *J* = 3.8 Hz, 1H), 2.80 (s, 4H), 2.78 – 2.66 (m, 1H), 1.95 (q, *J* = 10.2, 8.2 Hz, 2H), 1.78 – 1.66 (m, 4H), 1.60 (dd, *J* = 13.3, 9.0 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.0, 165.3, 82.1, 41.6, 30.9, 25.7, 25.5; **IR (ATR, cm^{-1}):** ν_{max} = 1730, 1446, 1229, 1093, 974; **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_8H_{11}NNaO_4^+$ 208.0580; Found 208.0584; **Rf:** 0.59 (Pentane: EtOAc, 1:1) ; **m.p.:** 68 °C.

2-((4-phenylbut-1-en-2-yl)oxy)isoindoline-1,3-dione **3hb**



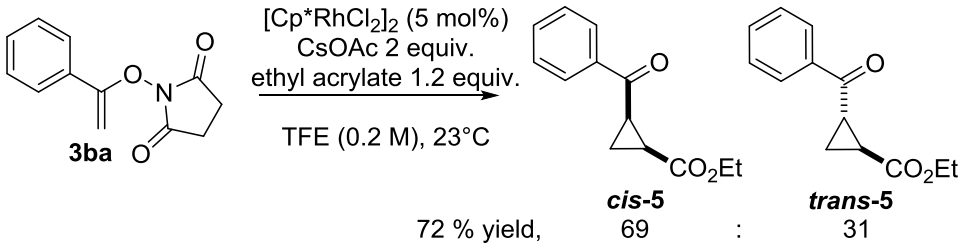
Obtained as a white solid (95 mg, 65 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (td, *J* = 5.2, 2.0 Hz, 2H), 7.80 (td, *J* = 5.2, 2.0 Hz, 2H), 7.31 (m, 4H), 7.21 (ddd, *J* = 8.6, 5.6, 2.3 Hz, 1H), 4.22 (d, *J* = 3.7 Hz, 1H), 4.15 (d, *J* = 3.7 Hz, 1H), 3.05 – 2.96 (m, 2H), 2.71 – 2.59 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.6, 161.9, 141.0, 134.9, 129.0, 128.7, 128.5, 126.3, 124.0, 85.3, 33.6, 33.4; **IR (ATR, cm^{-1}):** ν_{max} = 1794, 1733, 1661, 1367, 1187, 1127, 1080, 976, 876, 670, 518; **HRMS (nanochip-ESI/LTQ-Orbitrap) m/z:** $[M + Na]^+$ Calcd for $C_{18}H_{15}NNaO_3^+$ 316.0944; Found 316.0941.**Rf:** 75 °C (Pentane: EtOAc, 7:3); **m.p.:** 79 °C;

1-((4-phenylbut-1-en-2-yl)oxy)-1H-pyrrole-2,5-dione **3hc**



Obtained as a white solid (44 mg, 32 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.15 (m, 5H), 6.74 (s, 2H), 4.18 (d, *J* = 3.7 Hz, 1H), 4.13 (d, *J* = 3.7 Hz, 1H), 3.04 – 2.90 (m, 2H), 2.64 – 2.51 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.7, 162.0, 140.9, 132.2, 128.7, 128.5, 126.3, 85.3, 33.5, 33.4; **IR (ATR, cm^{-1}):** ν_{max} = 1732, 1663, 1158, 1123, 1041, 811, 748, 811, 747, 698, 669; **HRMS (nanochip-ESI/LTQ-Orbitrap) m/z:** $[M + Na]^+$ Calcd for $C_{14}H_{13}NNaO_3^+$ 266.0788; Found 266.0785; **Rf:** 0.68 (Pentane: EtOAc, 7:3); **m.p.:** 65 °C.

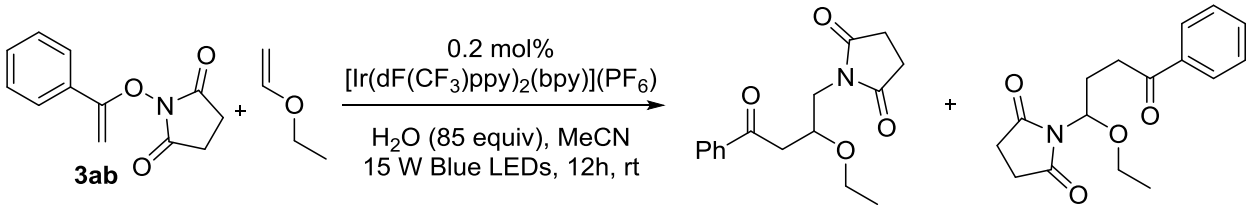
Synthetic transformations of 1-((1-phenylvinyl)oxy)pyrrolidine-2,5-dione ***3ba***



***cis*-5** ***trans*-5**

72 % yield, 69 : 31

Following a procedure published by Rovis and coworkers,[1] $[Cp^*RhCl_2]_2$ (2.15 mg, 5.00 µmol), CsOAc (38.0 mg, 0.12 mmol, 2.0 equiv.) and **3ba** (22.0 mg, 0.10 mmol, 1.00 equiv.) were weighed into a vial equipped with a magnetic stir bar and sealed with a rubber septum. 500 µL of TFE was added and the mixture was stirred at 23°C for 2 mins. Then ethyl acrylate (13 µL, 0.12mmol, 1.20 equiv.) was added and the reaction mixture was stirred for 16 hours. The mixture was concentrated under reduced pressure and the residue was purified further by silica gel column (hexane/EtOAc, 20:1 to 4:1) to afford separately ***cis*-5** (10.4 mg, 48mmol, 48 %) and ***trans*-5** (5.2 mg, 24 mmol, 24 %). ***Cis*-5:** All spectroscopic data were in agreement with those reported in the literature.[1] **R_f:** 0.41 (Pentane: EtOAc, 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.2 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 3.98 (qd, *J* = 7.1, 1.3 Hz, 2H), 2.85 – 2.69 (td, *J* = 8.4, 7.0 Hz, 1H), 2.39 – 2.24 (td, *J* = 8.4, 6.4 Hz, 1H), 1.92 (td, *J* = 6.6, 4.9 Hz, 1H), 1.36 (td, *J* = 8.3, 4.8 Hz, 1H), 1.05 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 194.7, 170.2, 137.3, 133.3, 128.7, 128.5, 61.0, 26.4, 23.2, 14.1, 11.8; ***Trans*-5:** All spectroscopic data were in agreement with those reported in the literature[2]; **R_f:** 0.71 (Pentane: EtOAc, 9:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.4 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.4 Hz, 2H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.19 (ddd, *J* = 8.7, 5.8, 3.9 Hz, 1H), 2.38 (ddd, *J* = 8.7, 5.9, 3.8 Hz, 1H), 1.57-1.31 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.2, 172.5, 137.2, 133.5, 128.8, 128.4, 61.3, 26.1, 24.9, 18.1, 14.4.



6 **6'**

52 % 5 : 1

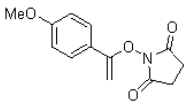
Following procedure published by Fend and coworkers,[3] a stock solution of photocatalyst was prepared by dissolving $[Ir(dF(CF_3)ppy)_2(bpy))](PF_6)$ (10.1mg) in MeCN (50 mL). A 10 ml Schlenk tube charged with **3ba** (22mg, 0.1 mmol, 1.0 equiv) was evacuated with pump and refilled with N_2 for three times, then ethyl vinyl ether (62 µL, 0.65 mmol, 6.5 equiv), prepared stock solution of photocatalyst (1.0 mL, 0.2mg/mL), H_2O (8.5 mmol, 85 equiv, 155 µL) were introduced in sequence. The reaction tube was sealed, and the resulting mixture was irradiated under 15W blue LEDs at rt for 12 h. The reaction mixture was filtered through a short pad of silica gel and further rinsed with EtOAc. The filtrate collected was

concentrated under reduced pressure and purified by silica gel column chromatography using hexane/ethyl acetate to give a mixture of **6** and **6'** in a 5:1 ratio (15 mg, 52 mmol, 52 %) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (t, *J* = 8.4 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.45 (d, *J* = 15.2 Hz, 2H), 5.36 (dd, *J* = 8.5, 5.3 Hz, 0H), 4.22 (p, *J* = 6.3 Hz, 1H), 3.82 – 3.65 (m, 2H), 3.61 – 3.39 (m, 1H), 3.29 (dd, *J* = 17.3, 6.9 Hz, 1H), 3.16 – 2.99 (m, 1H), 2.81 – 2.61 (m, 5H), 2.41 – 2.22 (m, 0H), 1.18 (t, *J* = 7.0 Hz, 1H), 1.11 (t, *J* = 7.0 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.9, 198.1, 177.5, 177.0, 137.1, 136.8, 133.3, 133.3, 128.7, 128.2, 128.2, 82.0, 72.8, 65.8, 65.0, 43.1, 41.5, 34.4, 29.7, 28.3, 26.7, 15.5, 15.0; **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_{16}H_{19}NNaO_4^+$ 312.1206; Found 312.1208; **Rf:** 0.22 (Pentane: EtOAc, 9:1).

References

1. T. Piou, F. Romanov-Michailidis, M. A. Ashley, M. Romanova-Michaelides and T. Rovis, *J. Am. Chem. Soc.*, 2018, **140**, 9587-9593.
2. M. P. Doyle, R. L. Dorow and W. H. Tamblyn, *J. Org. Chem.*, 1982, **47**, 4059-4068.
3. Y. Zhang, H. Liu, L. Tang, H.-J. Tang, L. Wang, C. Zhu and C. Feng, *J. Am. Chem. Soc.*, 2018, **140**, 10695-10699.

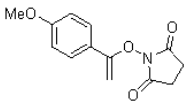
NMR spectra



3aa

^{1}H NMR - 400MHz

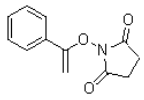
$CDCl_3$



3aa

^{13}C NMR - 101MHz

$CDCl_3$



3ba

^{1}H NMR - 400MHz

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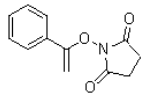

3ba

^{13}C NMR - 101MHz

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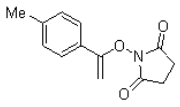
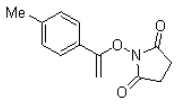


3ca

^{1}H NMR - 400MHz

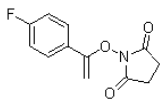
$CDCl_3$



3ca

^{13}C NMR - 101MHz

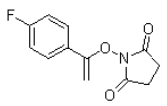
$CDCl_3$



3da

^{1}H NMR - 400MHz

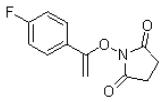
$CDCl_3$



3da

^{13}C NMR - 101MHz

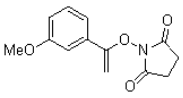
$CDCl_3$



3da

^{19}F NMR - 376MHz

$CDCl_3$



3ea

^{1}H NMR - 400MHz

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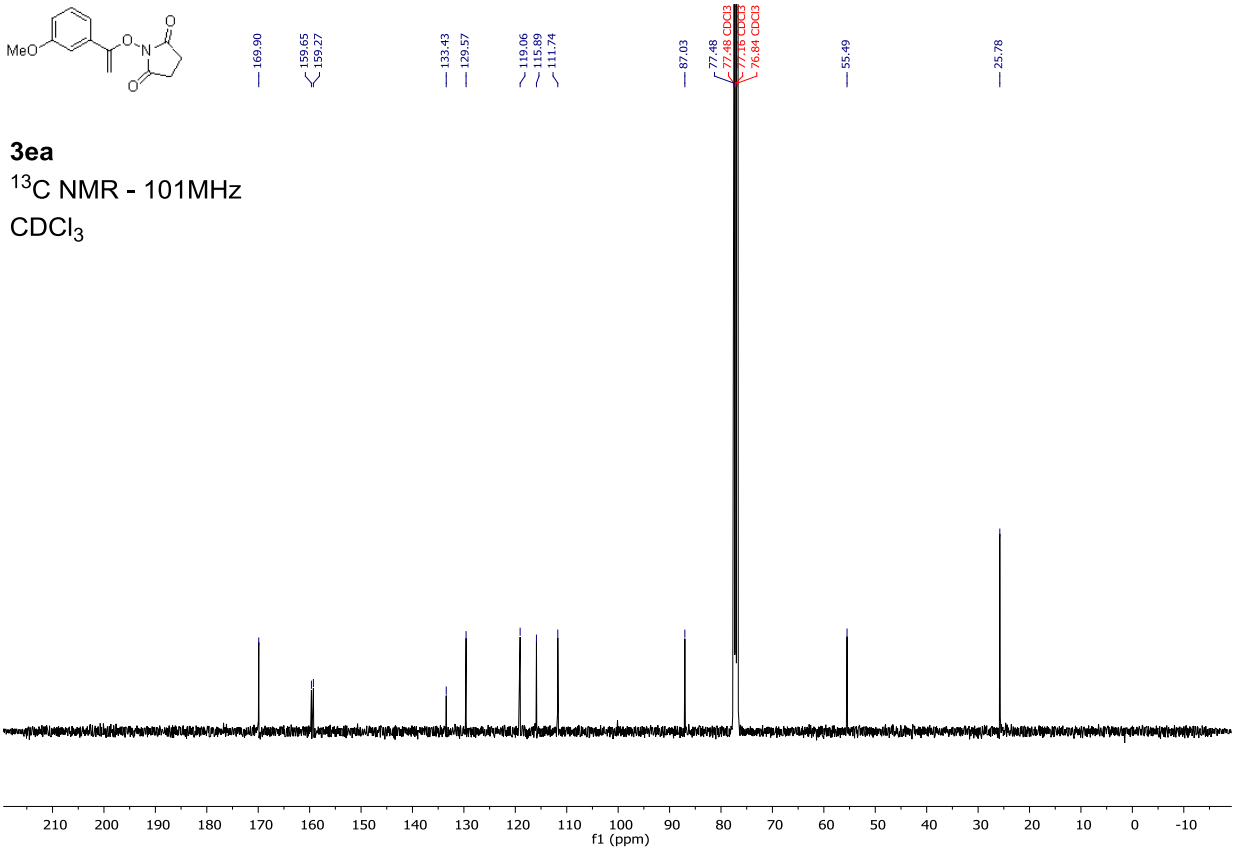

3ea

^{13}C NMR - 101MHz

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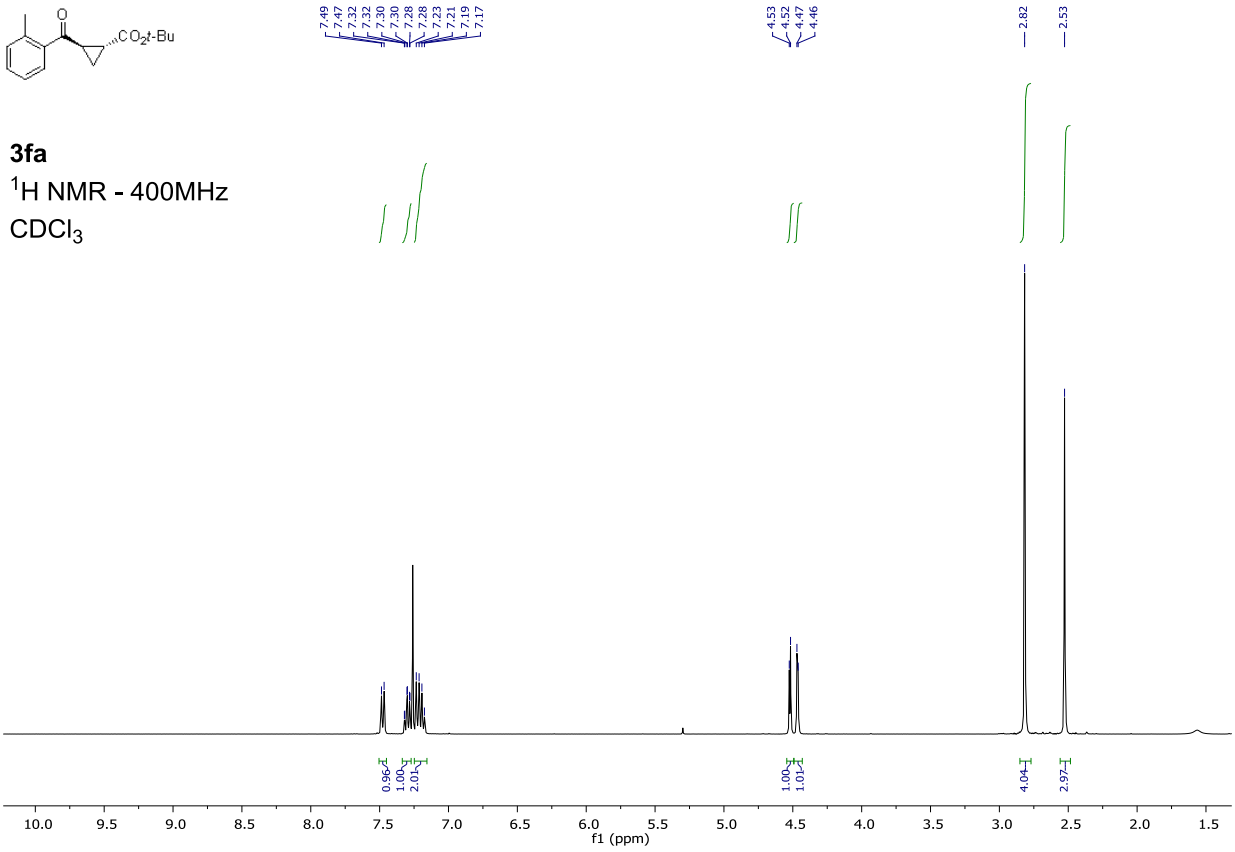
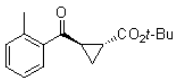


3fa

^{1}H NMR - 400MHz

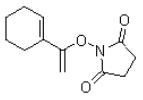
$CDCl_3$



3fa

^{13}C NMR - 101MHz

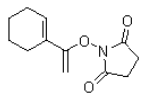
$CDCl_3$



3ga

^{1}H NMR - 400MHz

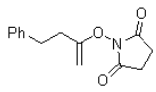
$CDCl_3$



3ga

^{13}C NMR - 101MHz

$CDCl_3$



3ha

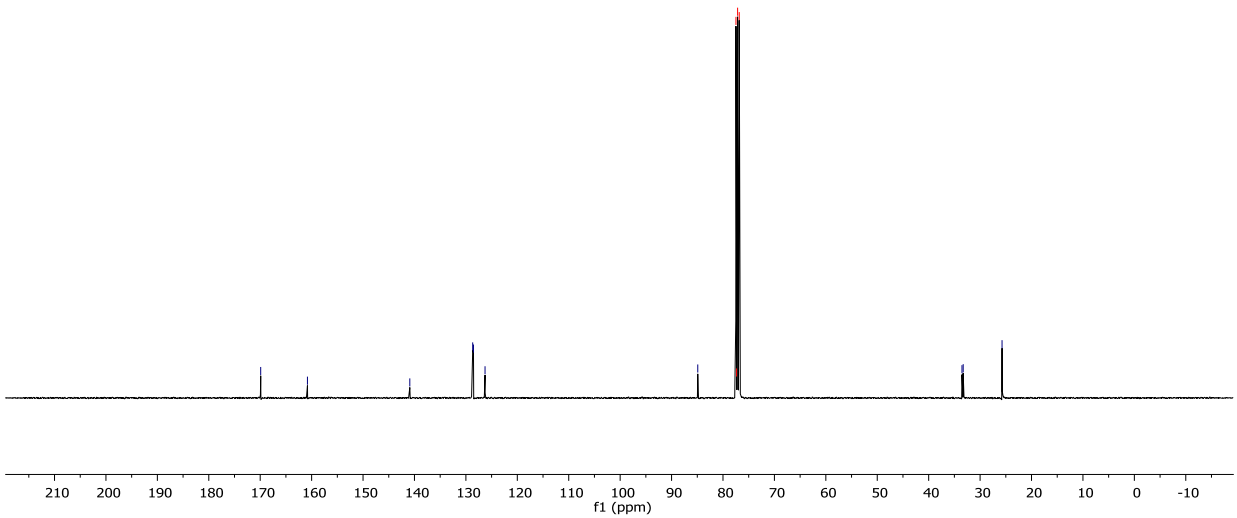
^{1}H NMR - 400MHz

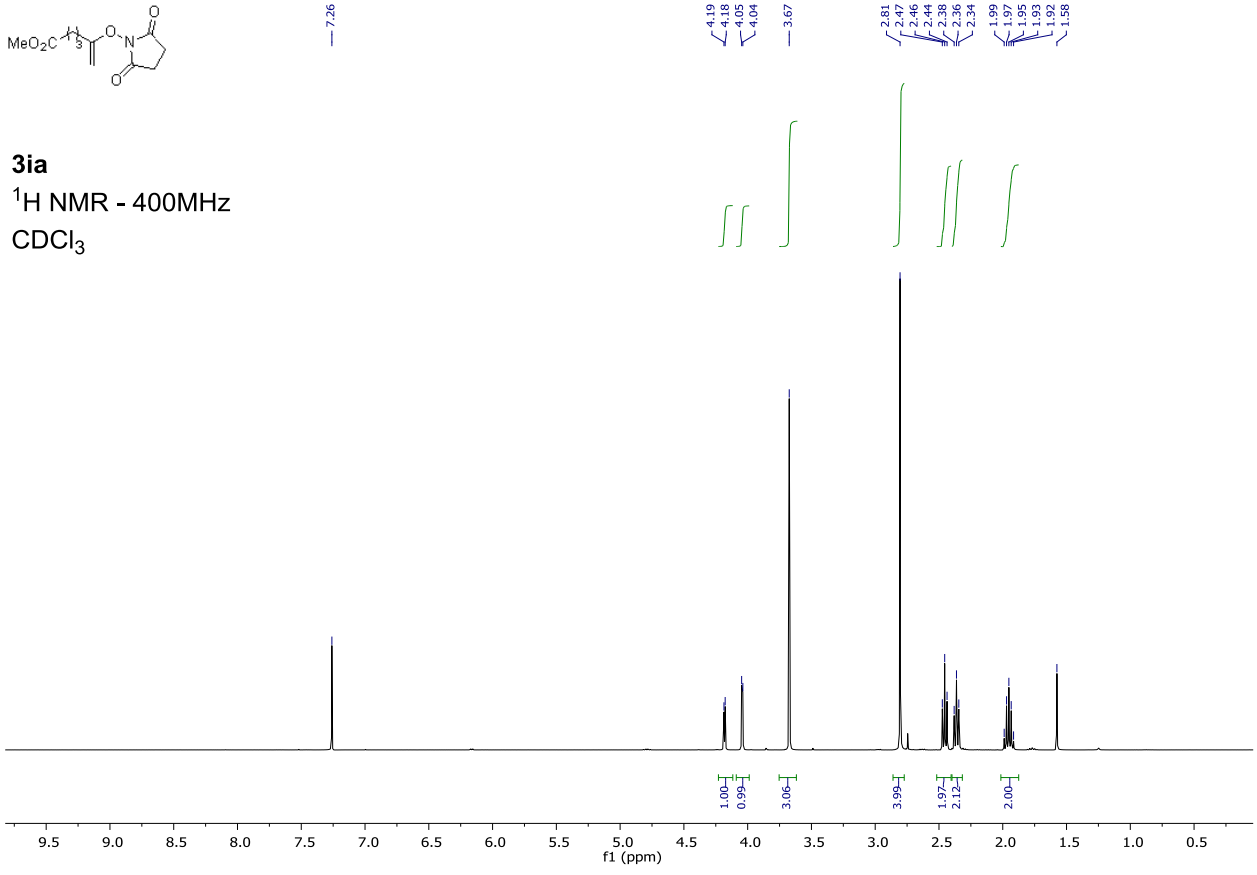
$CDCl_3$

3ha

^{13}C NMR - 101MHz

$CDCl_3$

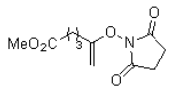




3ia

^{1}H NMR - 400MHz

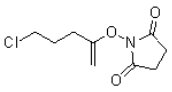
$CDCl_3$



3ia

^{13}C NMR - 101MHz

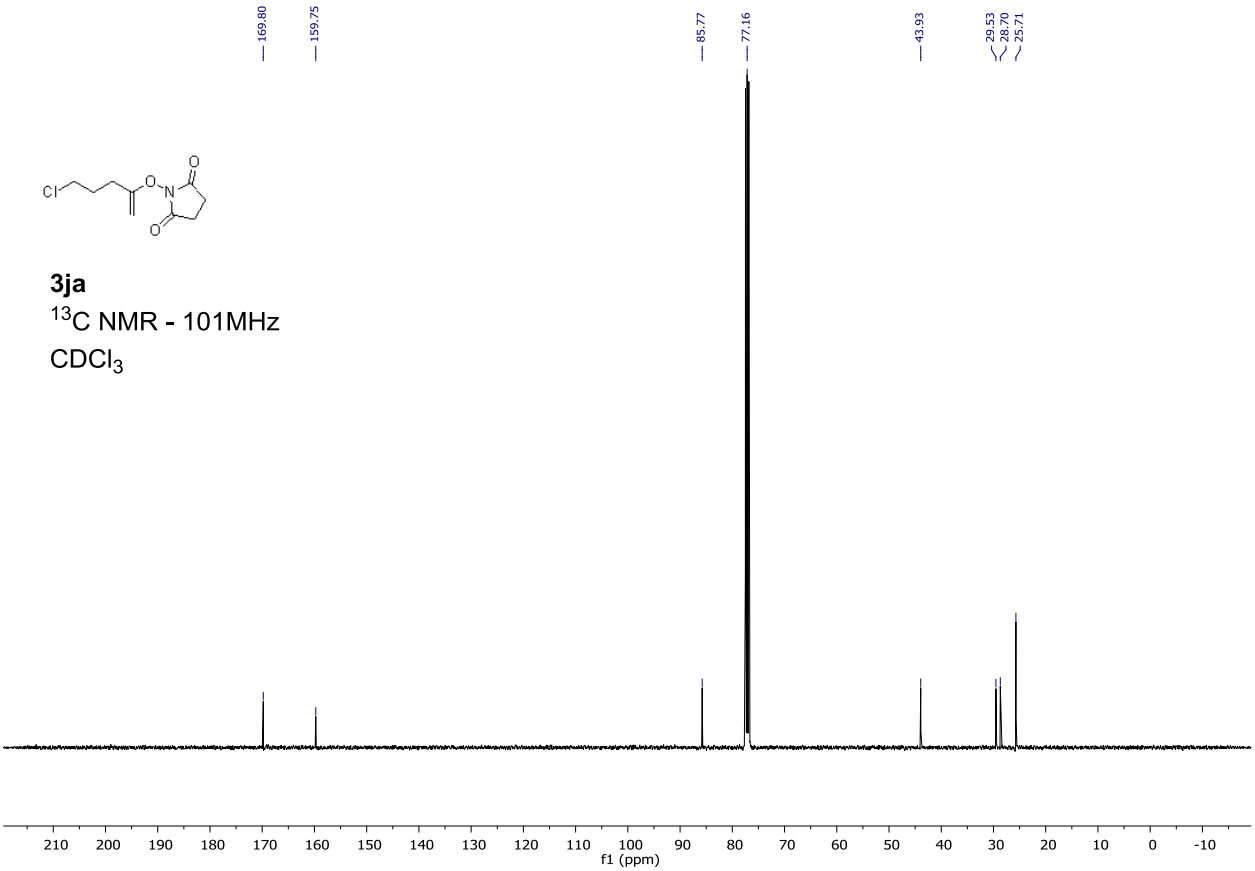
$CDCl_3$

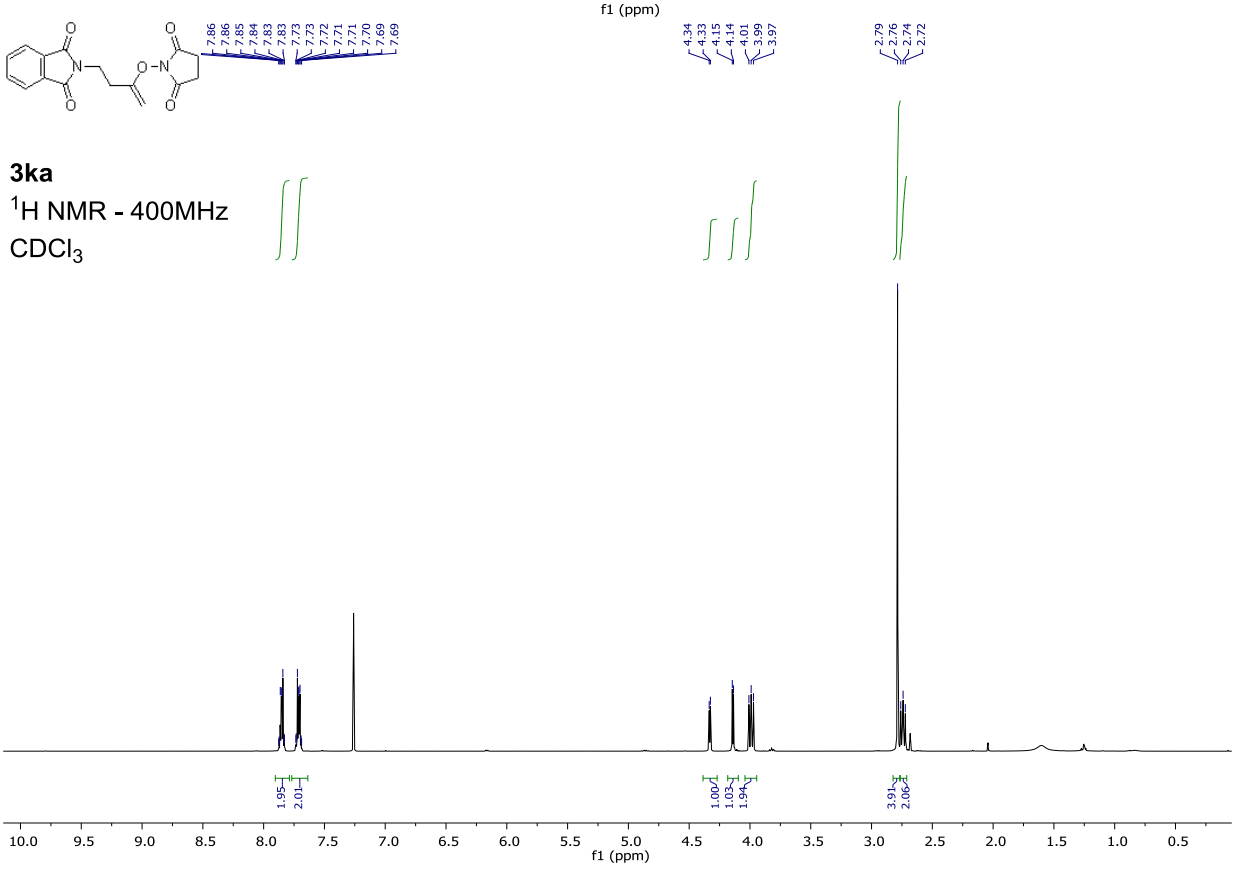


3ja

^{1}H NMR - 400MHz

$CDCl_3$


169.80
159.75
85.77
77.16
43.93
29.53
28.70
25.71
Cl
O
N
O
O
3ja
13C NMR - 101MHz
CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.86
7.86
7.85
7.84
7.83
7.83
7.73
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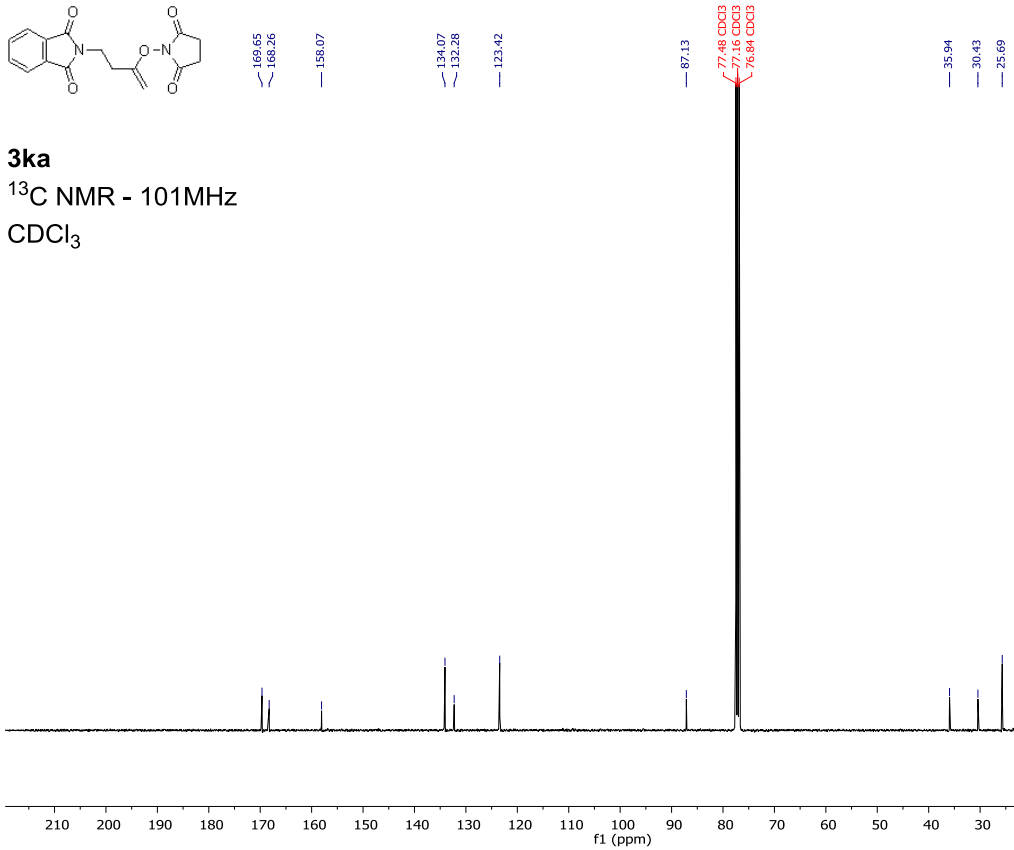
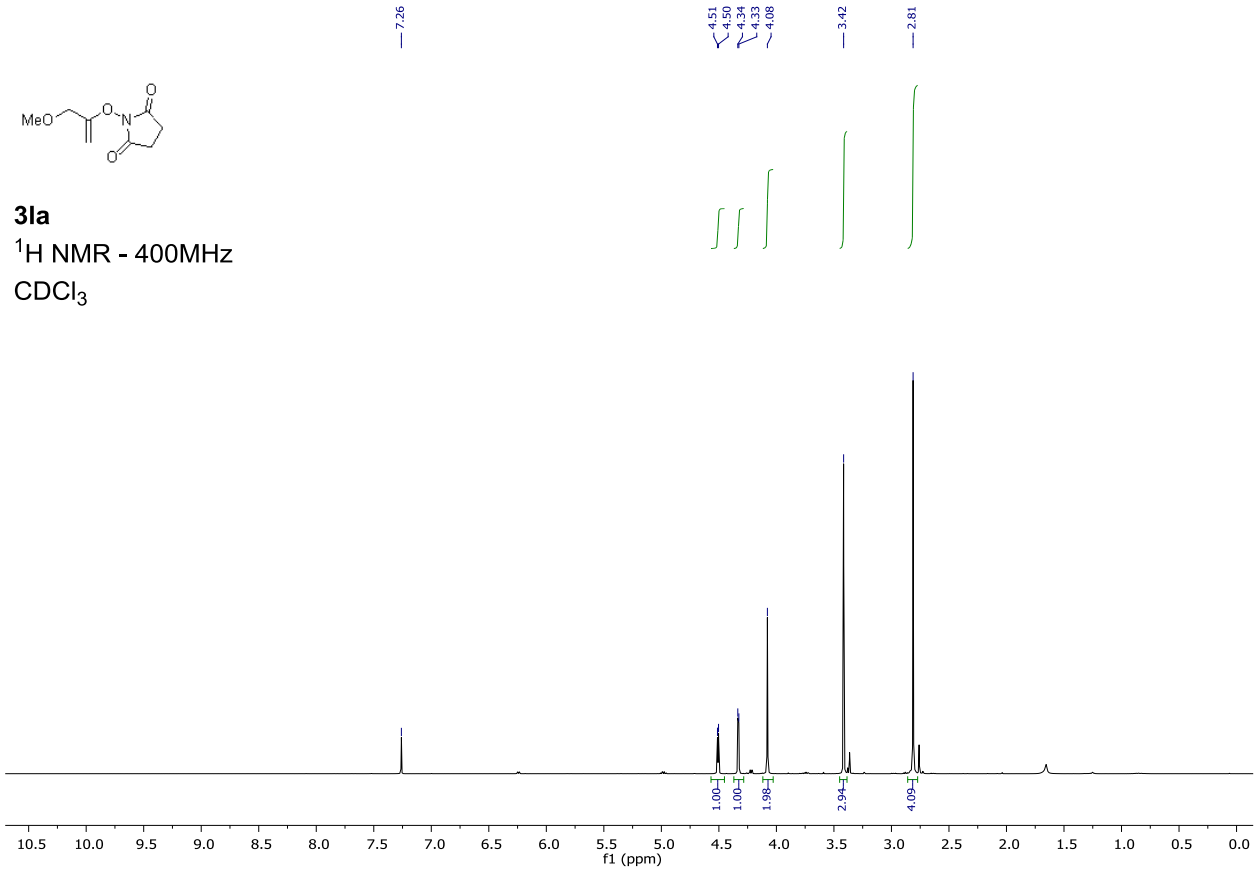
7.69
4.34
4.33
4.15
4.14
4.01
3.99
3.97
2.79
2.76
2.74
2.72
O
N
O
O
3ka
1H NMR - 400MHz
CDCl3
1.95
2.01
1.00
1.03
1.94
3.91
2.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)



3ka

^{13}C NMR - 101MHz

$CDCl_3$



3la

^{1}H NMR - 400MHz

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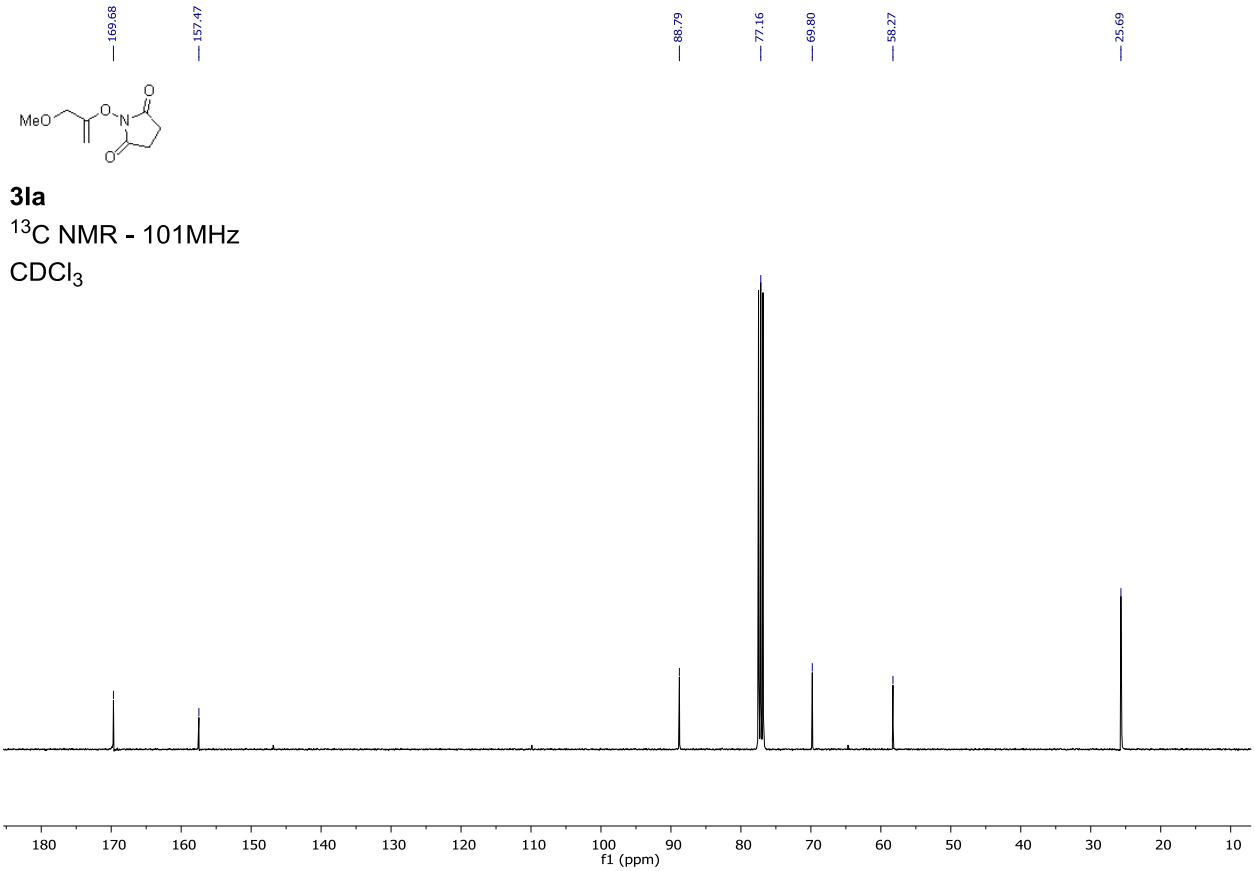

3la

^{13}C NMR - 101MHz

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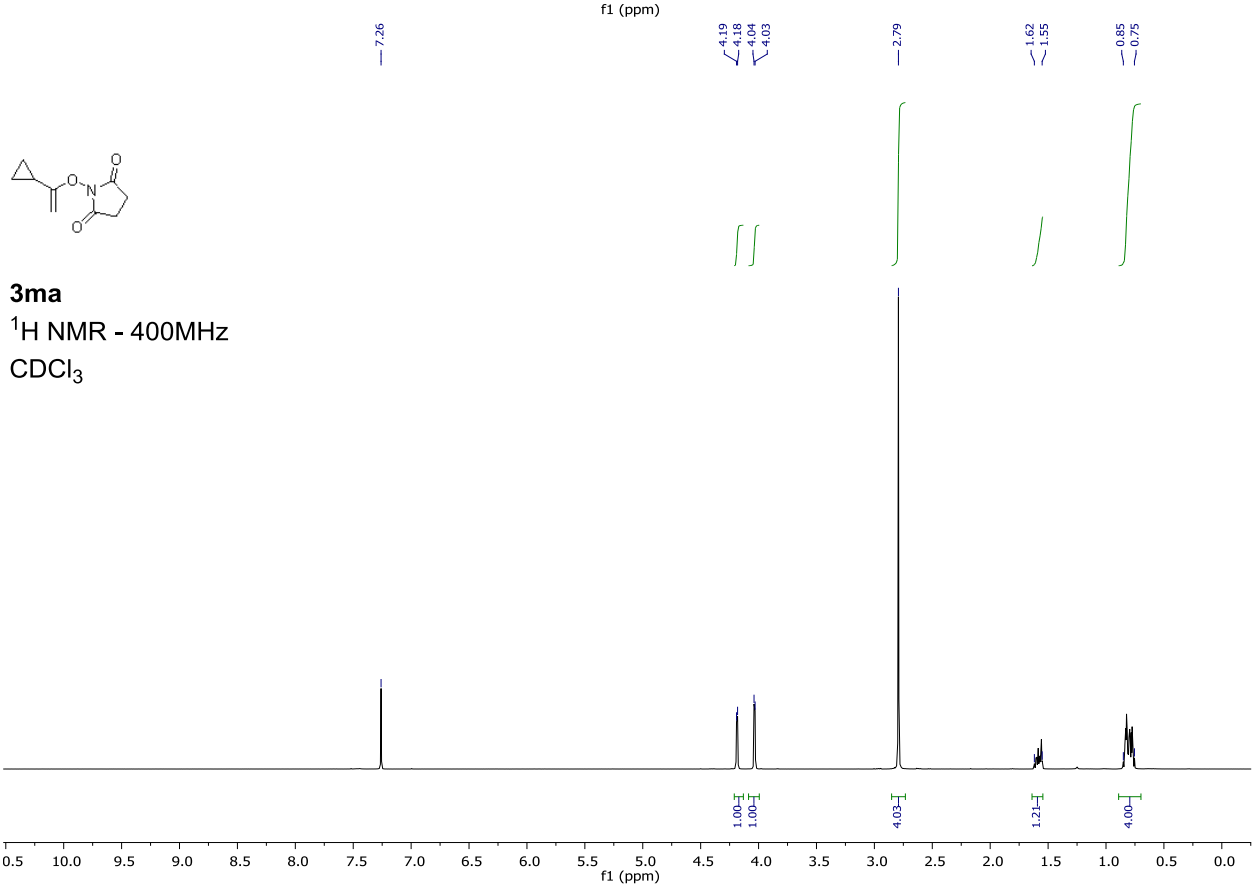
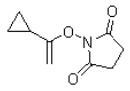


3ma

^{1}H NMR - 400MHz

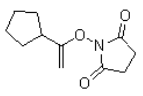
$CDCl_3$



3ma

^{13}C NMR - 101MHz

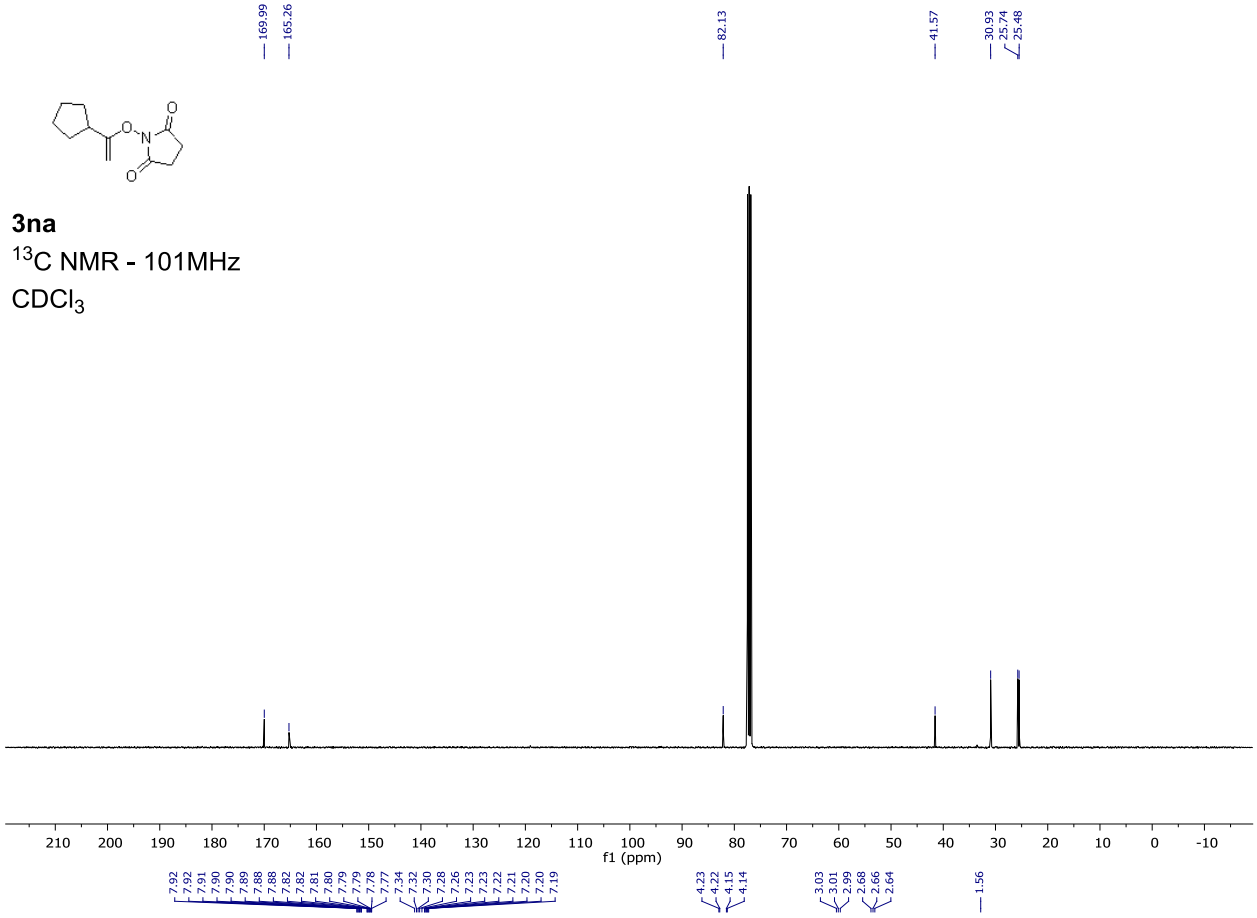
$CDCl_3$



3na

^{1}H NMR - 400MHz

$CDCl_3$



3na

^{13}C NMR - 101MHz

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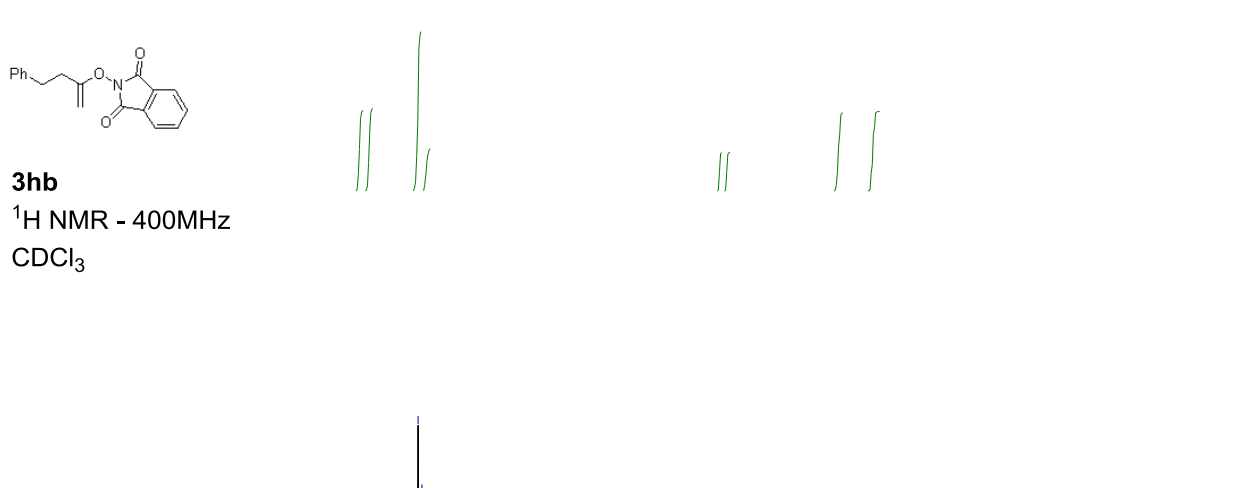

3hb

^{1}H NMR - 400MHz

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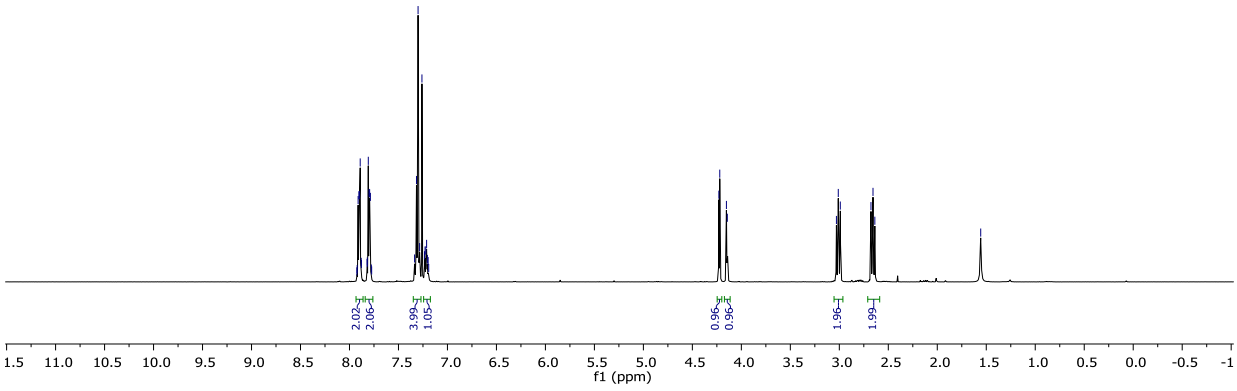
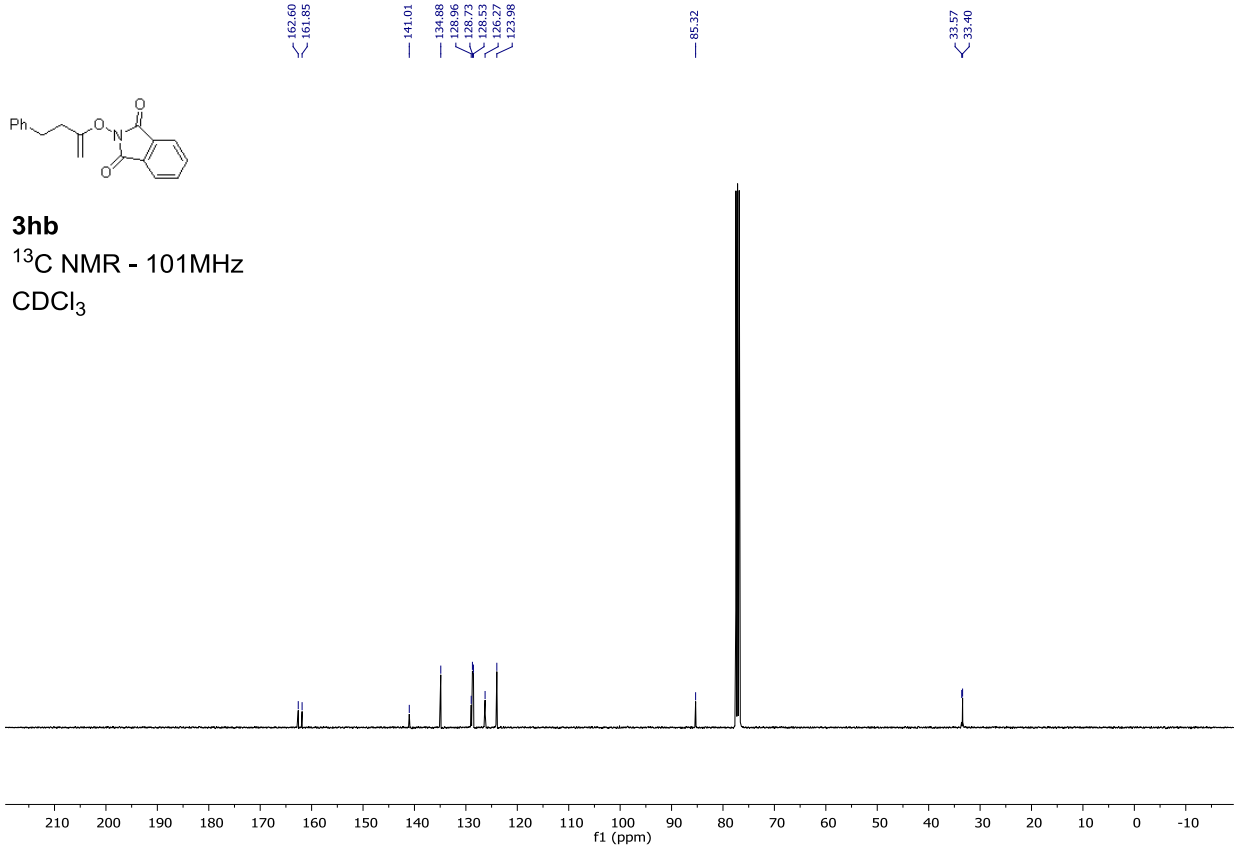
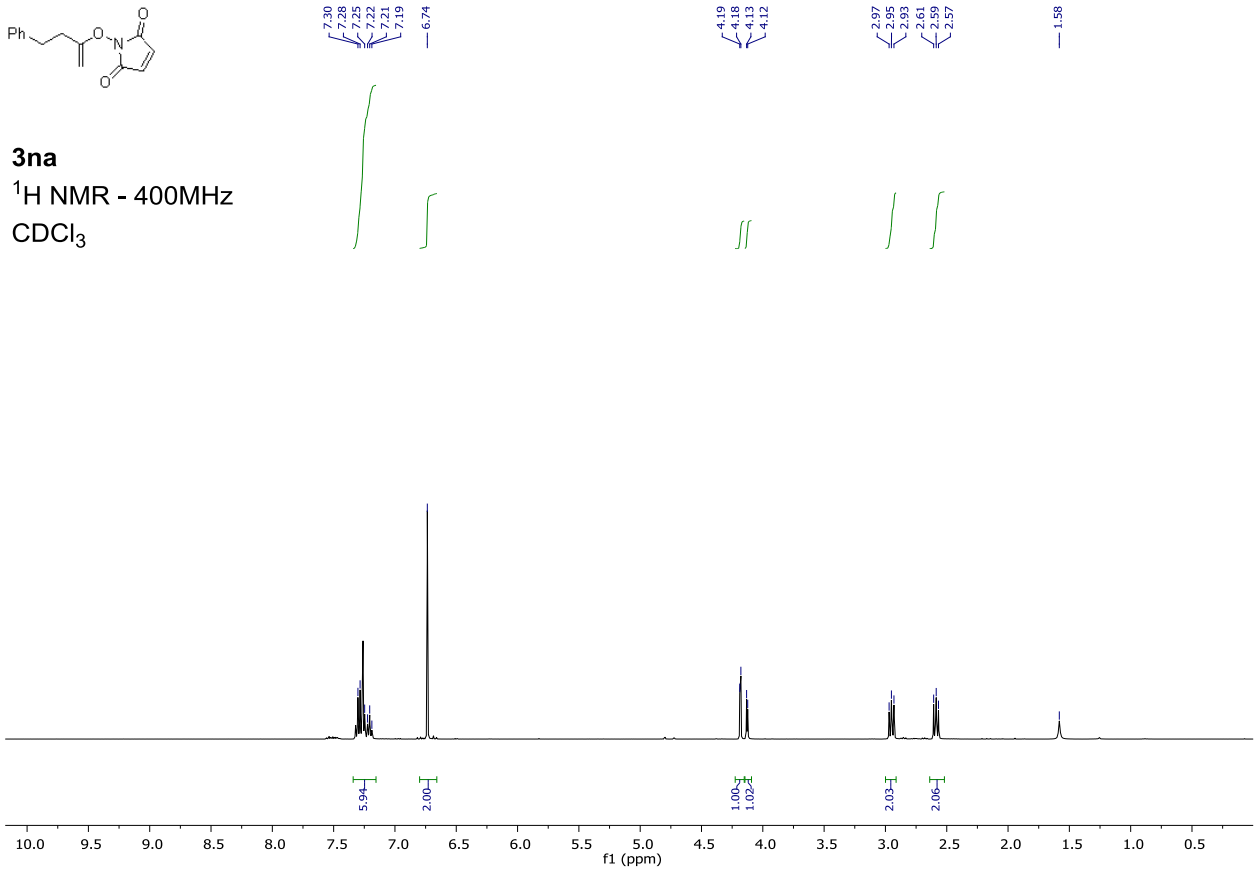




3hb

^{13}C NMR - 101MHz

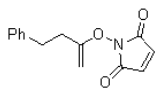
$CDCl_3$



3na

^{1}H NMR - 400MHz

$CDCl_3$



3na

^{13}C NMR - 101MHz

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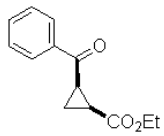
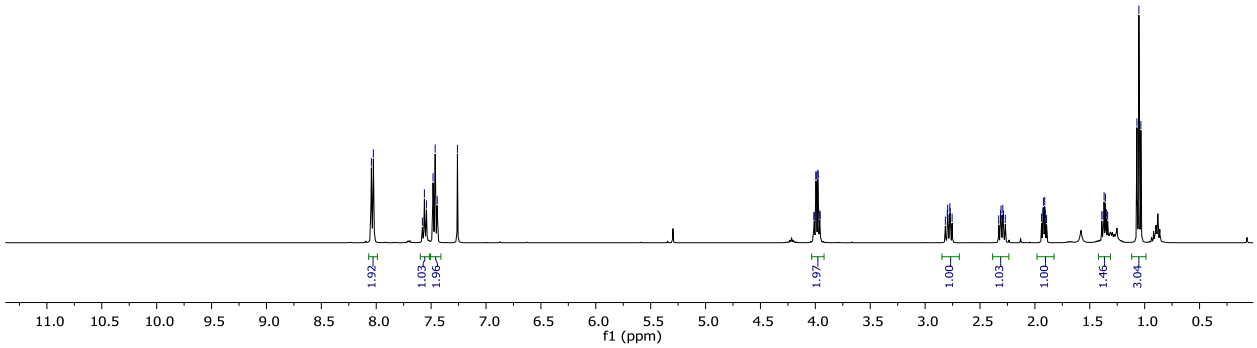
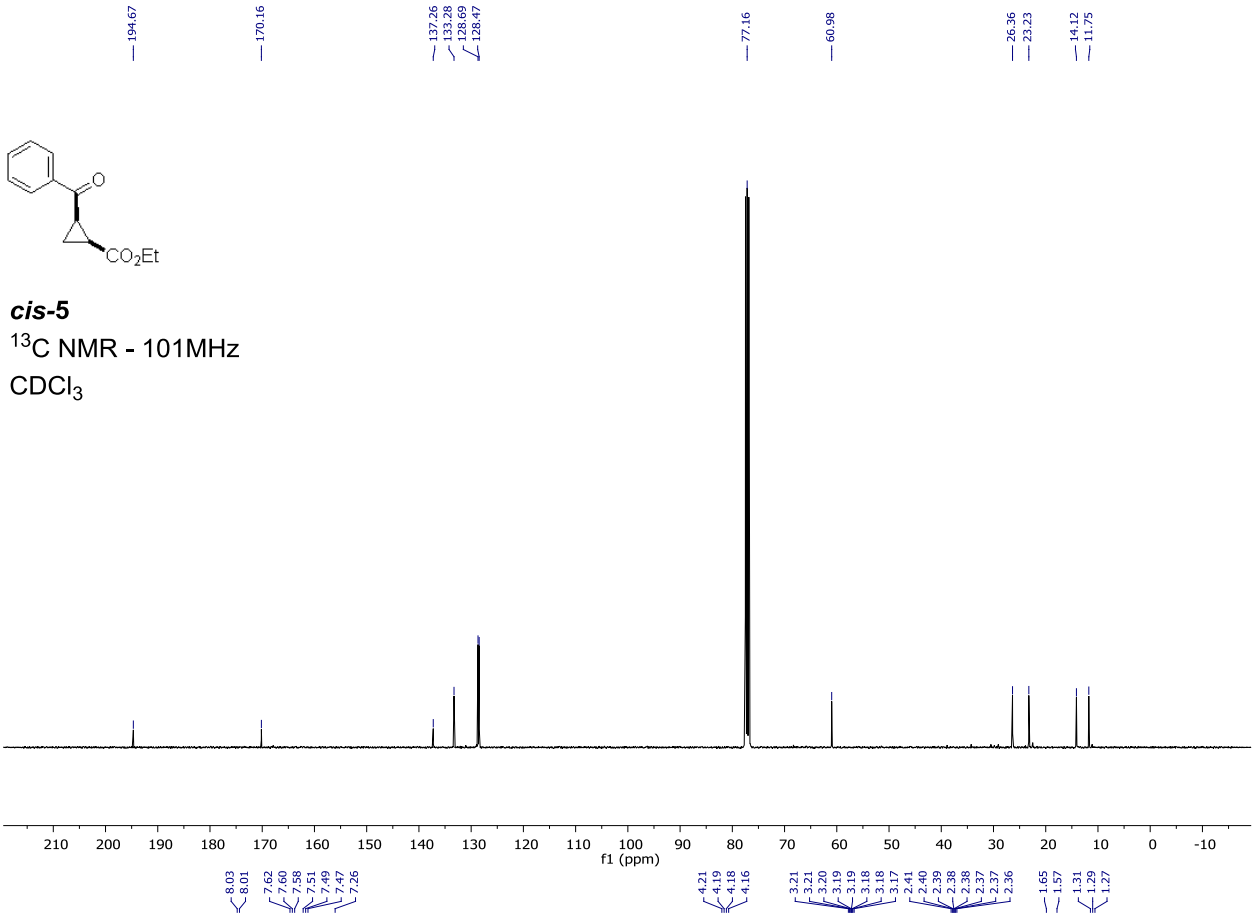


***cis*-5**

^{1}H NMR - 400MHz

$CDCl_3$

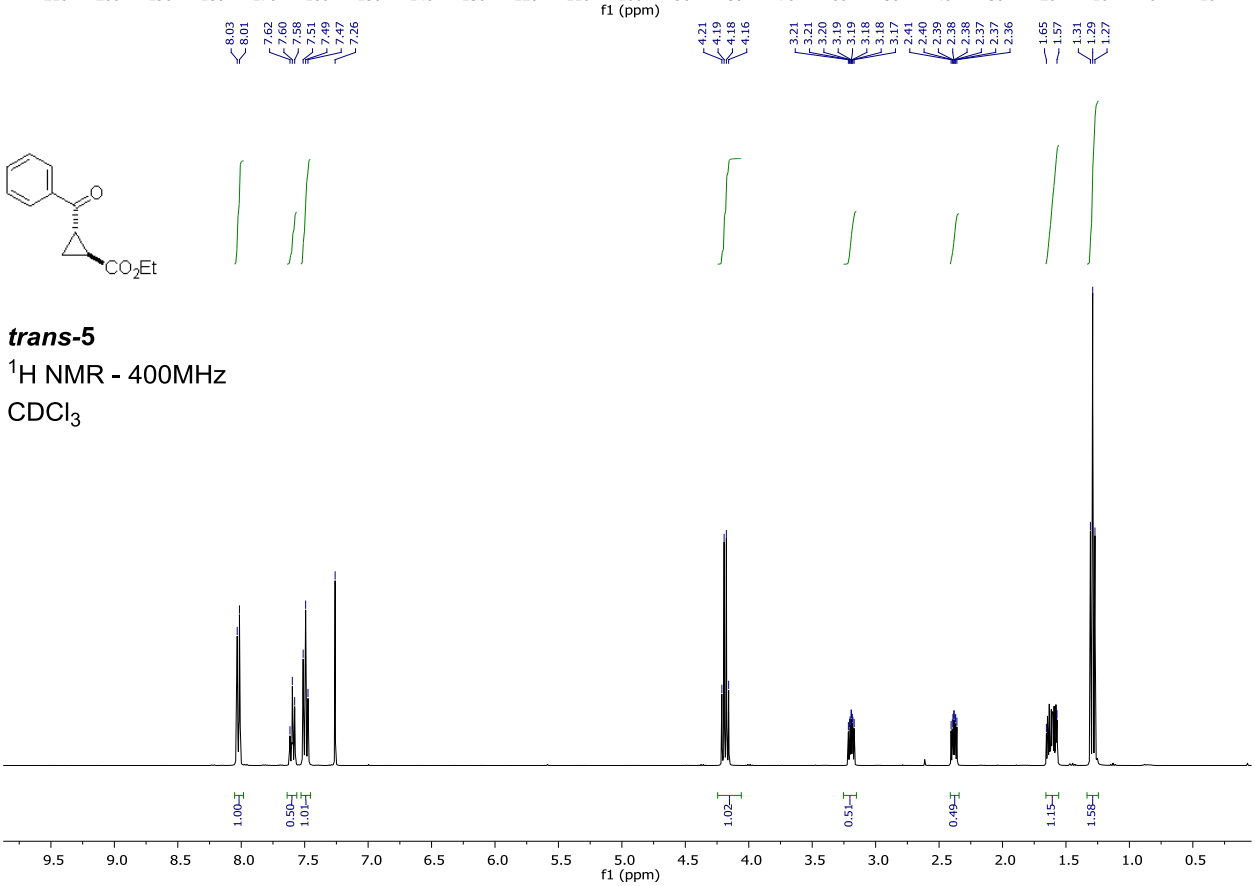




***cis*-5**

^{13}C NMR - 101MHz

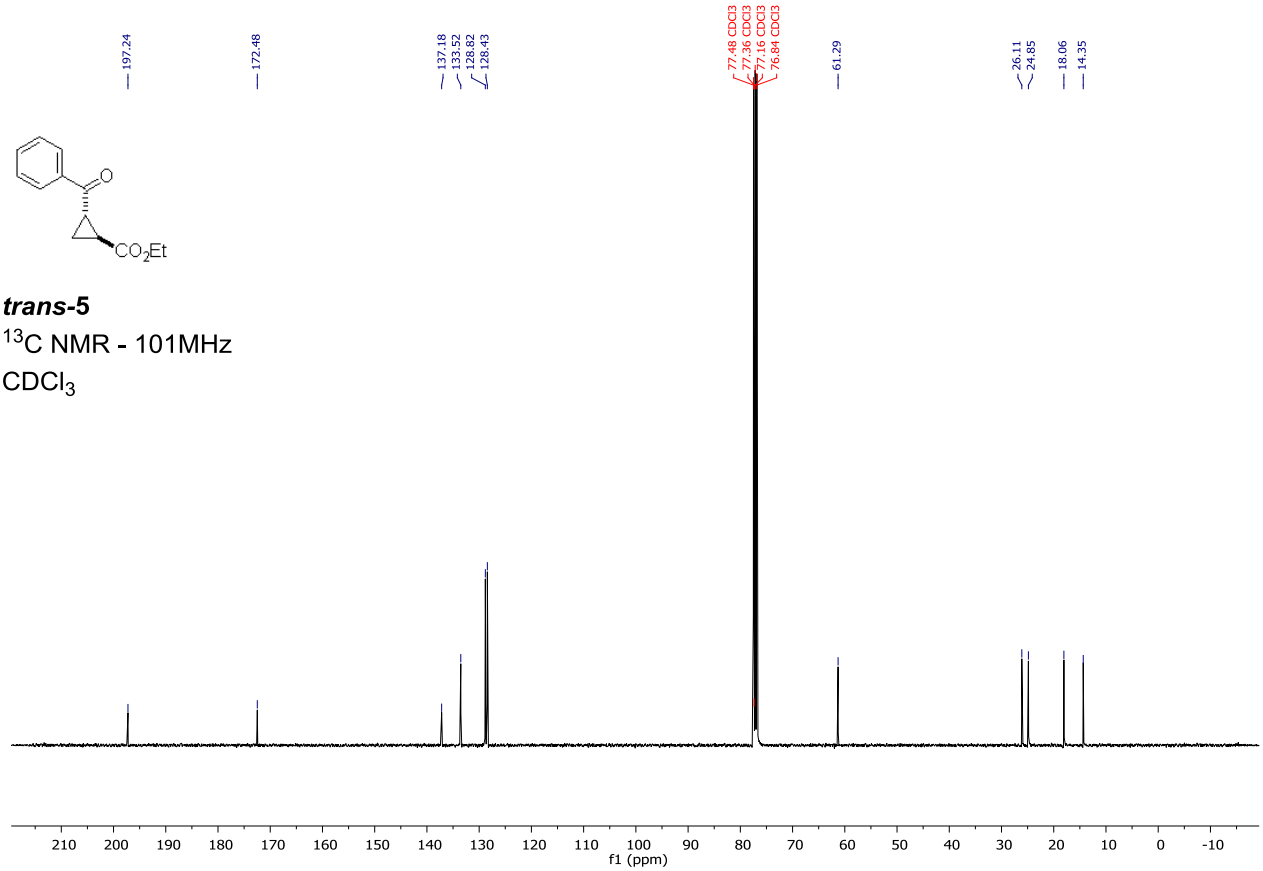
$CDCl_3$



***trans*-5**

^{1}H NMR - 400MHz

$CDCl_3$



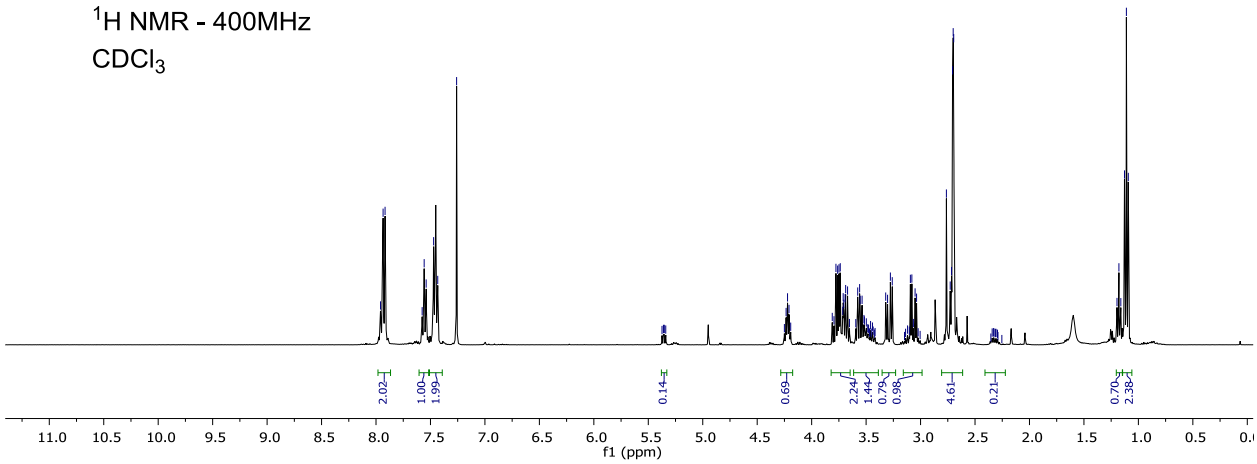
***trans*-5**

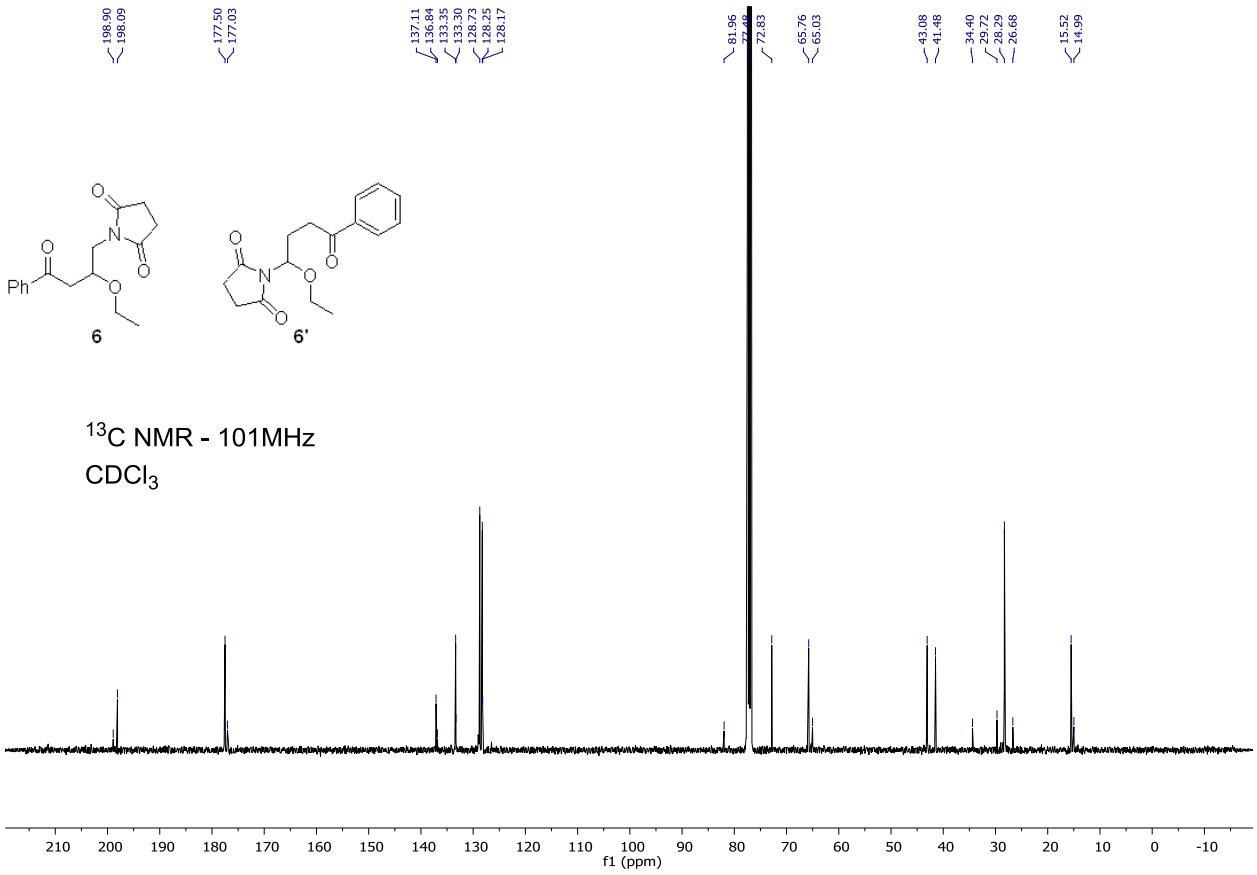
^{13}C NMR - 101MHz

$CDCl_3$

^{1}H NMR - 400MHz

$CDCl_3$




198.90
198.09
177.50
177.03
137.11
136.84
133.35
133.30
128.73
128.25
128.17
81.96
72.83
65.76
65.03
43.08
41.48
34.40
29.72
28.29
26.68
15.52
14.99
Ph
6
6'
13C NMR - 101MHz
CDCl3
f1 (ppm)