Catalytic Alkene Carboaminations Enabled by Oxidative Proton-Coupled Electron Transfer

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Supporting Information

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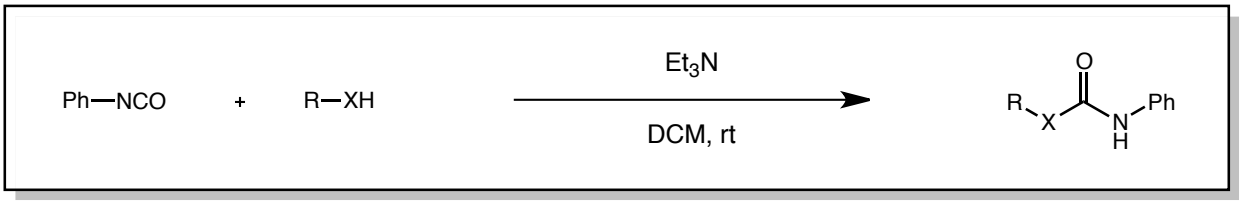
General Information

Commercial reagents were purified prior to use following the guidelines of Perrin and Armarego.[1] All solvents were purified according to the method of Grubbs.[2] Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. Chromatographic purification of products was accomplished by flash chromatography on Silicycle F60 silica gel or Sorbent Technologies neutral alumina according to the method of Still.[3] All reactions were carried out in well ventilated fume hoods. Thin-layer chromatography (TLC) was performed on Silicycle 250 μm silica gel plates or Sorbent Technologies 250 μm neutral alumina plates. Visualization of the developed chromatogram was performed by irradiation with UV light or treatment with a solution of potassium permanganate or ceric ammonium molybdate stain followed by heating. Yields refer to purified compounds unless otherwise noted.

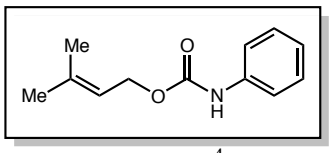
^{1}H and ^{13}C NMR spectra were recorded on a Bruker 500 (500 and 126 MHz) instrument, and are internally referenced to residual solvent signals, $CDCl_3$ referenced at δ 7.26 and 77.16 ppm. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz) and assignment. Data for ^{13}C NMR are reported in terms of chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz) and no special nomenclature is used for equivalent carbons. IR spectra were recorded on a Perkin Elmer Paragon 1000 spectrometer and are reported in terms of frequency of absorption (cm^{-1}). High-resolution mass spectra were obtained at Princeton University mass spectrometry facilities using an Agilent 6210 TOF LC/MS. Gas chromatography-mass spectrometry (GC-MS) was performed on an Agilent 6890 GC-5975C MSD. Gas chromatography (GC) was performed on an Agilent Technologies 7890A GC system equipped with a split-mode capillary injection system and flame ionization detectors. Stern-Volmer experiments were conducted on an Agilent Technologies Cary Eclipse Fluorescence Spectrophotometer.

Synthesis and Characterization of Substrates



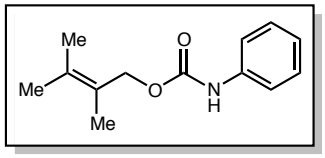
Phenyl Carbamate/Urea Synthesis General Procedure

A flame-dried round-bottomed flask was degassed, flushed with argon, and charged with phenyl isocyanate (10 mmol, 1 equiv), DCM (20 mL), Et_3N (4.18 mL, 30 mmol, 1.1 equiv) and alcohol/amine (10 mmol, 1 equiv). The reaction mixture was stirred at room temperature until the alcohol/amine was fully consumed by TLC. The reaction mixture was then diluted with DCM (20 mL), washed with 1M HCl (3 x 20 mL), water (20 mL), and brine (20 mL), and then dried (Na_2SO_4) and concentrated. The crude product was purified by silica gel column chromatography (gradient 100% hexanes to 5% EtOAc/hexanes) to afford the desired product.



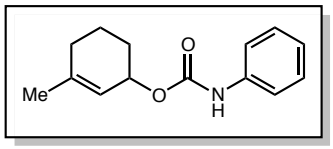
3-Methylbut-2-en-1-yl phenylcarbamate

Followed general phenyl carbamate synthesis procedure with commercially available 3-methyl-2-buten-1-ol to give 1.2 g (88% yield) of the title compound. Spectra are consistent with reported literature values.[4]



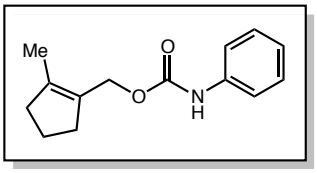
2,3-Dimethylbut-2-en-1-yl phenylcarbamate

Followed general phenyl carbamate synthesis procedure with 2,3-dimethyl-2-buten-1-ol[5] to give 920 mg (85% yield) of the title compound. IR (neat): 3317, 2993, 2917, 1700, 1599, 1531, 1500, 1442, 1312, 1214, 1049, 1025, 750, 691 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, J = 8.0 Hz, 2H), 7.30 (t, J = 7.8 Hz, 2H), 7.05 (t, J = 7.4 Hz, 1H), 6.63 (s, 1H), 4.70 (s, 2H), 1.80 (s, 3H), 1.74 (d, J = 10.4 Hz, 6H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.92, 138.12, 132.43, 129.17, 123.43, 122.96, 118.64, 66.53, 21.08, 20.42, 16.93.; HRMS (ESI) exact mass calculated for $[M+Na]^+$ ($C_{13}H_{17}NO_2$) requires *m/z* 219.12593, found *m/z* 219.12591, difference 0.09 ppm.



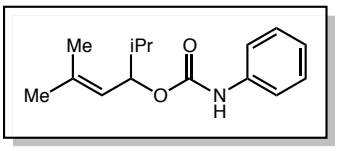
3-Methylcyclohex-2-en-1-yl phenylcarbamate

Followed general phenyl carbamate synthesis procedure with commercially available 3-methyl-2-cyclohexen-1-ol to give 770 mg (83% yield) of the title compound. IR (neat): 3316, 2936, 1694, 1599, 1532, 1501, 1442, 1378, 1312, 1223, 1165, 1050, 1027, 931, 751, 692 cm^{-1}; ^1H NMR (501 MHz, $CDCl_3$) δ 7.37 (d, J = 8.1 Hz, 2H), 7.30 (t, J = 7.8 Hz, 2H), 7.05 (t, J = 7.3 Hz, 1H), 6.56 (s, 1H), 5.56 (d, J = 4.0 Hz, 1H), 5.27 (t, J = 4.7 Hz, 1H), 2.06 – 1.91 (m, 2H), 1.88 – 1.74 (m, 3H), 1.73 (s, 3H), 1.71 – 1.61 (m, 1H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ .; HRMS (ESI) exact mass calculated for $[M+Na]^+$ ($C_{14}H_{17}NO_2$) requires *m/z* 231.12593, found *m/z* 231.12554, difference 1.7 ppm.



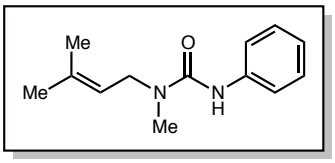
(2-Methylcyclopent-1-en-1-yl)methyl phenylcarbamate

Followed general phenyl carbamate synthesis procedure with (2-methylcyclopent-1-en-1-yl)methanol[7,8] to give 640 mg (85% yield) of the title compound. IR (neat): 3318, 3059, 2938, 2844, 1703, 1600, 1537, 1501, 1444, 1313, 1220, 1083, 1047, 1027, 752, 692 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.0 Hz, 2H), 7.30 (t, *J* = 7.9 Hz, 2H), 7.06 (t, *J* = 7.3 Hz, 1H), 6.57 (s, 1H), 4.73 (s, 2H), 2.47 – 2.39 (m, 2H), 2.36 (t, *J* = 7.7 Hz, 2H), 1.83 (p, *J* = 7.6 Hz, 2H), 1.75 (s, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.82, 139.27, 138.08, 129.84, 129.18, 123.46, 118.71, 61.83, 38.86, 34.69, 21.66, 14.13.; HRMS (ESI) exact mass calculated for $[M+Na]^+$ ($C_{14}H_{17}NO_2$) requires *m/z* 231.12593, found *m/z* 231.12619, difference 1.11 ppm.



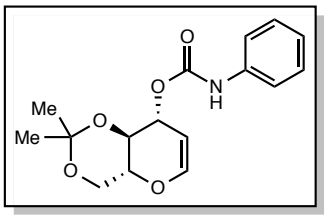
2,5-dimethylhex-4-en-3-yl phenylcarbamate

Followed general phenyl carbamate synthesis procedure with 2,5-dimethylhex-4-en-3-ol[9] to give 550 mg (79% yield) of the title compound. IR (neat): 3319, 2964, 2932, 2874, 1698, 1600, 1529, 1501, 1442, 1382, 1312, 1220, 1047, 1026, 967, 949, 858, 752, 691 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.0 Hz, 2H), 7.25 – 7.20 (m, 2H), 6.99 – 6.94 (m, 1H), 6.46 (s, 1H), 5.20 (dd, *J* = 9.5, 6.8 Hz, 1H), 5.08 (dp, *J* = 9.4, 1.4 Hz, 1H), 1.81 (h, *J* = 6.8 Hz, 1H), 1.69 (dd, *J* = 8.9, 1.4 Hz, 6H), 0.86 (dd, *J* = 20.0, 6.8 Hz, 6H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.45, 138.32, 138.07, 129.13, 123.26, 122.09, 118.63, 32.87, 26.09, 18.78, 18.50, 18.06.; HRMS (ESI) exact mass calculated for $[M+Na]^+$ ($C_{15}H_{21}NO_2$) requires *m/z* 247.15723, found *m/z* 247.15752, difference 1.17 ppm.



1-Methyl-1-(3-methylbut-2-en-1-yl)-3-phenylurea

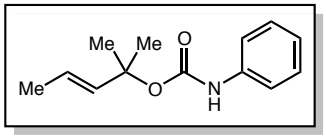
Followed general phenyl carbamate synthesis procedure with N-methyl-N-(3-methyl-2-buten-1-yl)amine[10] to give 720 mg (86% yield) of the title compound. IR (neat): 3318, 3054, 2969, 2920, 1637, 1594, 1528, 1498, 1478, 1439, 1376, 1305, 1240, 1192, 1142, 1025, 882, 750, 693 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.7 Hz, 2H), 7.30 – 7.25 (m, 3H), 7.01 (t, *J* = 7.3 Hz, 1H), 6.36 (s, 1H), 5.27 (t, *J* = 7.1 Hz, 1H), 3.94 (d, *J* = 6.8 Hz, 2H), 2.99 (s, 3H), 1.78 (d, *J* = 15.6 Hz, 5H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.72, 139.42, 136.35, 128.95, 122.84, 120.39, 119.68, 46.96, 34.68, 25.93, 17.99.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{13}H_{18}N_2O$) requires *m/z* 218.14191, found *m/z* 218.14226, difference 1.57 ppm.



2,2-Dimethyl-4,4a,8,8a-tetrahydropyrano[3,2-*d*][1,3]dioxin-8-ylphenylcarbamate

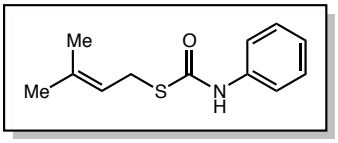
Followed general phenyl carbamate synthesis procedure with commercially available 4,6-O-isopropylidene-D-glucal to give 1.2 g (72% yield) of the title compound. IR (neat): 3325, 2994, 2894, 1729, 1640, 1601, 1537, 1501, 1444, 1378, 1313,1269, 1217, 1168, 1111, 1091, 1052, 1015, 869, 753, 692 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.1 Hz, 2H), 7.30 (t, *J* = 7.9 Hz, 2H), 7.06 (t, *J* = 7.4 Hz, 1H), 6.75 (s, 1H), 6.37 (d, *J* = 6.1 Hz, 1H), 5.38 (d, *J* = 7.8 Hz, 1H), 4.89 (dd, *J* = 6.3, 2.2 Hz, 1H), 4.11 – 4.04 (m, 1H), 4.04 – 3.95 (m, 1H), 3.92 – 3.81 (m, 2H), 1.55 (s, 3H), 1.44 (s, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.99, 145.37, 137.82, 129.17, 123.63, 118.70, 101.39, 100.06, 70.42, 69.91, 61.67, 29.06, 19.10.; HRMS (ESI) exact

mass calculated for $[M+H]^+$ ($C_{16}H_{19}NO_5$) requires *m/z* 305.12632, found *m/z* 305.12692, difference 1.96 ppm.



(*E*)-2-Methylpent-3-en-2-yl phenylcarbamate

A flame dried round-bottomed flask was charged with NaH (575 mg, 24.0 mmol) and degassed and backfilled with argon. THF (30 mL) was added followed by *(E)*-2-methylpent-3-en-2-ol[6] (1.44 g, 14.4 mmol). The reaction mixture was stirred at room temperature for 30 minutes. Phenyl isocyanate (1.57 mL, 14.4 mmol) was then added and the reaction was stirred at room temperature for 1 hour or until complete consumption of the alcohol was seen by TLC. The reaction was quenched with sat. NH_4Cl solution and extracted with Et_2O three times. The combined organic layers were washed with brine, dried with Na_2SO_4, and concentrated to yield the crude product, which was then purified by silica gel column chromatography to give the 1.6 g (52% yield) of the pure product. IR (neat): 3327, 2977, 2936, 1701, 1599, 1528, 1500, 1440, 1380, 1365, 1313, 1223, 1193, 1127, 1082, 1046, 1027, 996, 966, 898, 832, 750, 692 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.0 Hz, 2H), 7.32 – 7.22 (m, 2H), 7.02 (t, *J* = 7.3 Hz, 1H), 6.49 (s, 1H), 5.84 (d, *J* = 15.6 Hz, 1H), 5.69 (dq, *J* = 14.3, 6.4 Hz, 1H), 1.72 (d, *J* = 6.7 Hz, 3H), 1.57 (s, 6H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.53, 138.40, 135.55, 129.13, 124.45, 123.16, 118.60, 81.02, 27.26, 17.99.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{13}H_{17}NO_2$) requires *m/z* 219.12593, found *m/z* 219.12571, difference 1 ppm.



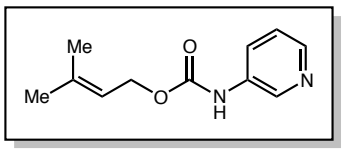
***S*-(3-Methylbut-2-en-1-yl)phenylcarbamothioate**

A flame dried round-bottomed flask was charged with dry, oil-free KH (672 mg, 16.75 mmol) inside a glove box. THF (20 mL) was added and the suspension was cooled to 0 ºC. 2-methyl-3-buten-2-ol (1.75 mL, 16.75 mmol) was added and the reaction mixture was allowed to warm to room temperature and stirred for 30 minutes. Phenyl isothiocyanate (2 mL, 16.75 mmol) was then added and the reaction was stirred for 6 hours or until complete consumption of alcohol was seen by TLC. The reaction was quenched with sat. NH_4Cl solution and extracted with Et_2O three times. The combined organic layers were then washed with brine, dried with Na_2SO_4, and concentrated to yield the crude product, which was then purified by recrystallization from petroleum ether and ethyl acetate to give 1.2 g (44% yield) of the title compound. IR (neat): 3291, 3059, 2970, 2921, 1656, 1599, 1529, 1498, 1439, 1376, 1308, 1237, 1148, 1106, 1078, 1027, 879, 841, 808, 750, 691 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.0 Hz, 2H), 7.31 (t, *J* = 7.8 Hz, 2H), 7.11 (t, *J* = 7.4 Hz, 1H), 7.06 (s, 1H), 5.30 (t, *J* = 8.0 Hz, 1H), 3.64 (d, *J* = 7.8 Hz, 2H), 1.72 (d, *J* = 8.7 Hz, 6H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.84, 136.88, 129.37, 129.26, 125.43, 124.54, 119.28, 28.60, 25.84, 17.99.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{12}H_{15}NOS$) requires *m/z* 221.08743, found *m/z* 221.08725, difference 0.86 ppm.

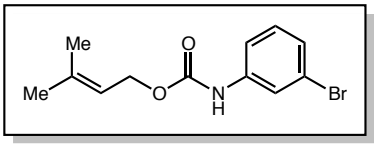
Aryl Carbamate Synthesis General Procedure

A flame dried round-bottomed flask was degassed, flushed with argon, and charged with triphosgene (1.49 g, 5.0 mmol) in THF (10 mL). Then, a solution of substituted aniline (5.0 mmol) dissolved in THF (40 mL) was slowly dripped into the triphosgene solution. NEt_3 (1.5

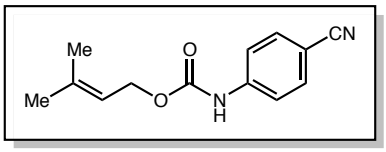
mL, 10.5 mmol) was then added slowly to the reaction mixture after the aniline was added. The reaction mixture was stirred at room temperature for 2 hours. The reaction mixture was then concentrated and the flask containing the resulting residue was degassed and acetonitrile (80 mL), NEt_3 (1.5 mL, 10.5 mmol), and 3-methyl-2-buten-1-ol were added (0.61 mL, 6.0 mmol). The reaction mixture was then stirred at 70 ºC for 8 hours. The reaction mixture was concentrated and the crude residue was purified by alumina column chromatography (gradient 100% hexanes to 20% EtOAc/hexanes) to yield the pure aryl carbamate product.



3-Methylbut-2-en-1-yl pyridin-3-ylcarbamate
Followed general aryl carbamate synthesis procedure from commercially available 3-aminopyridine to give 880 mg (62% yield) of the title compound. IR (neat): 3238, 3184, 2975, 2913, 1728, 1610, 1550, 1484, 1424, 1379, 1331, 1303, 1225, 1126, 1062, 1028, 978, 859, 801, 766, 705 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.39 (s, 1H), 8.21 (d, *J* = 4.6 Hz, 1H), 7.92 (d, *J* = 8.5 Hz, 1H), 7.20 – 7.13 (m, 1H), 7.11 (s, 1H), 5.30 (t, *J* = 7.4 Hz, 1H), 4.59 (d, *J* = 7.3 Hz, 2H), 1.66 (d, *J* = 16.4 Hz, 6H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.81, 144.48, 140.29, 139.92, 135.18, 125.85, 123.84, 118.50, 62.50, 25.94, 18.21.; HRMS (ESI) exact mass calculated for $[M+Na]^+$ ($C_{11}H_{14}N_2O_2$) requires *m/z* 206.10553, found *m/z* 206.10576, difference 1.1 ppm.



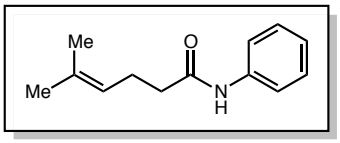
3-Methylbut-2-en-1-yl (3-bromophenyl)carbamate
Followed general aryl carbamate synthesis procedure from commercially available 3-bromoaniline to give 720 mg (74% yield) of the title compound. IR (neat): 3312, 2973, 2934, 1700, 1589, 1526, 1479, 1421, 1380, 1304, 1274, 1214, 1167, 1094, 1072, 1054, 994, 871, 771, 679 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.64 (t, *J* = 2.0 Hz, 1H), 7.25 – 7.23 (m, 1H), 7.20 – 7.12 (m, 2H), 6.56 (s, 1H), 5.39 (tdq, *J* = 7.2, 2.8, 1.4 Hz, 1H), 4.67 (d, *J* = 7.3 Hz, 2H), 1.77 (dd, *J* = 15.9, 1.3 Hz, 6H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.41, 139.91, 139.42, 130.42, 126.44, 122.88, 121.57, 118.56, 117.13, 62.39, 25.95, 18.21.; HRMS (ESI) exact mass calculated for $[M+Na]^+$ ($C_{12}H_{14}BrNO_2$) requires *m/z* 283.02079, found *m/z* 283.02126, difference 1.67 ppm.



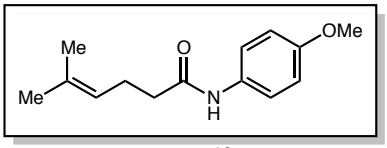
3-Methylbut-2-en-1-yl (4-cyanophenyl)carbamate
Followed general aryl carbamate synthesis procedure from commercially available 4-aminobenzonitrile to give 820 mg (79% yield) of the title compound. IR (neat): 3322, 3104, 2978, 2936, 2225, 1731, 1708, 1608, 1591, 1524, 1412, 1316, 1215, 1177, 1053, 975, 835, 767 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.62 – 7.45 (m, 4H), 6.90 (s, 1H), 5.38 (t, *J* = 7.5 Hz, 1H), 4.68 (d, *J* = 7.3 Hz, 2H), 1.76 (d, *J* = 15.6 Hz, 6H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.07, 142.30, 140.29, 133.47, 119.09, 118.32, 118.23, 106.23, 62.69, 25.95, 18.21.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{13}H_{14}N_2O_2$) requires *m/z* 230.10553, found *m/z* 230.10572 difference 0.85 ppm.

Aryl Amide Synthesis General Procedure
A flame dried round-bottomed flask was degassed, flushed with argon, and charged with 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide, EDC (2.5 g, 13 mmol) and DMAP (1.7 g, 14 mmol)

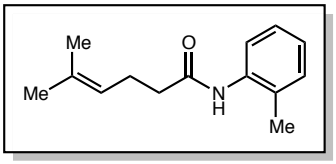
in DCM (25 mL). Then, 5-methylhex-4-enoic acid (1.3 g, 10 mmol) was added followed by the substituted aniline (12 mmol). The reaction mixture was stirred until TLC showed complete consumption of the carboxylic acid. The reaction mixture was then diluted with Et_2O (150 mL) and washed with 1M HCl solution (30 mL). The aqueous layer was then extracted twice with Et_2O (100 mL). The combined organic layers were then dried with Na_2SO_4 and concentrated to yield the crude amide, which was then purified by silica gel column chromatography (gradient 10% EtOAc/hexanes to 40% EtOAc/hexanes) in order to afford the pure amide.



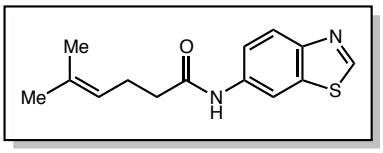
5-Methyl-N-phenylhex-4-enamide
Followed aryl amide synthesis general procedure from commercially available aniline to give 1.7 g (84% yield) of the title compound. Spectra are consistent with reported literature values.[11]



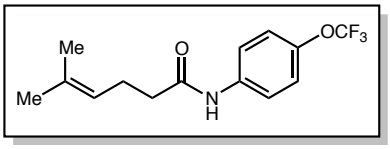
N-(4-methoxyphenyl)-5-methylhex-4-enamide
Followed aryl amide synthesis general procedure from commercially available *p*-anisidine to give 1.8 g (77% yield) of the title compound. Spectra are consistent with reported literature values.[12]



5-Methyl-N-(*o*-tolyl)hex-4-enamide
Followed aryl amide synthesis general procedure from commercially available *o*-toluidine to give 1.4 g (64% yield) of the title compound. IR (neat): 3266, 2971, 2924, 2858, 1644, 1587, 1530, 1456, 1366, 1366, 1352, 1305, 1288, 1263, 1202, 1143, 864, 842, 756, 734 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, J = 8.0 Hz, 1H), 7.25 – 7.14 (m, 2H), 7.07 (t, J = 7.5 Hz, 1H), 7.01 (s, 1H), 5.19 (d, J = 7.1 Hz, 1H), 2.44 (m, 4H), 2.24 (s, 3H), 1.69 (d, J = 29.7 Hz, 6H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.13, 135.90, 134.09, 130.56, 126.92, 125.18, 123.21, 122.75, 37.84, 25.93, 24.45, 18.01, 17.88.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{14}H_{19}NO$) requires *m/z* 217.14666, found *m/z* 217.14687, difference 0.96 ppm.



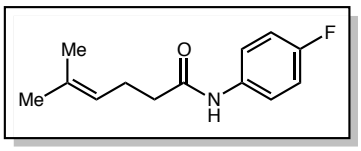
N-(Benzo[*d*]thiazol-6-yl)-5-methylhex-4-enamide
Followed aryl amide synthesis general procedure from commercially available 6-aminobenzothiazole to give 0.6 g (69% yield) of the title compound. IR (neat): 3289, 2919, 2348, 1663, 1605, 1576, 1531, 1475, 1447, 1399, 1246, 1195, 833 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.90 (s, 1H), 8.57 (s, 1H), 8.00 (d, J = 8.7 Hz, 1H), 7.80 (s, 1H), 7.32 – 7.27 (m, 1H), 5.16 (s, 1H), 2.43 (m, 4H), 1.67 (d, J = 33.4 Hz, 6H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.53, 153.47, 149.89, 135.93, 134.93, 134.07, 123.58, 122.54, 118.97, 112.59, 37.84, 25.89, 24.29, 17.92.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{14}H_{16}N_2OS$) requires *m/z* 260.09833, found *m/z* 260.09875, difference 1.61 ppm.



5-Methyl-*N*-(4-(trifluoromethoxy)phenyl)hex-4-enamide

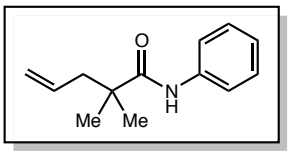
Followed aryl amide synthesis general procedure from commercially available 4-(trifluoromethoxy)aniline to give 0.72 g (76% yield) of the title compound. IR (neat): 3300, 2966, 2918, 1665, 1612, 1543, 1507, 1408, 1260, 1247, 1219, 1200, 1162, 1107, 1015, 907, 837, 731

cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.7 Hz, 2H), 7.42 (s, 1H), 7.16 (d, *J* = 8.5 Hz, 2H), 5.22 – 5.10 (m, 1H), 2.40 (d, *J* = 4.4 Hz, 4H), 1.68 (d, *J* = 33.9 Hz, 6H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.30, 145.27, 136.75, 134.14, 122.53, 121.88, 121.62, 120.98, 37.75, 25.88, 24.23, 17.92.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{14}H_{16}F_3NO_2$) requires *m/z* 287.11331, found *m/z* 287.11315, difference 0.59 ppm.

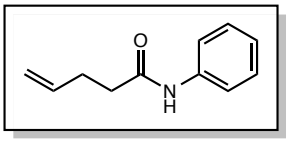


***N*-(4-Fluorophenyl)-5-methylhex-4-enamide**
Followed aryl amide synthesis general procedure from commercially available 4-fluoroaniline to give 0.63 g (75% yield) of the title compound. IR (neat): 3279, 2966, 2921, 1649, 1611, 1528, 1508, 1447, 1406, 1349, 1307, 1291, 1214, 1154, 1095, 1012, 973, 829, 785, 711 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 8.8, 4.8 Hz, 2H), 7.32 (s, 1H), 6.99 (t, *J* = 8.7 Hz, 2H), 5.16 (t, *J* = 6.6 Hz, 1H), 2.39 (p, *J* = 6.5 Hz, 4H), 1.68 (d, *J* = 33.9 Hz, 6H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.16, 160.35, 158.42, 134.09, 134.07, 133.99, 122.63, 121.71, 121.67, 115.81, 115.63, 37.69, 25.89, 24.29, 17.92.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{13}H_{16}FNO$) requires *m/z* 221.12159, found *m/z* 221.12160, difference 0.05 ppm.

Phenyl Amide Synthesis General Procedure
Three flame-dried round-bottomed flasks were degassed, flushed with argon, and charged with Et_2O (16 mL). Ester (5.26 mmol, 1 equiv) was added to one flask. Aniline (10.51 mmol, 2 equiv) was added to a separated flask. Methylmagnesium bromide (3.0 M in Et_2O, 10.5 mmol, 2 equiv) was added to the third flask. The aniline solution was added slowly to the methylmagnesium bromide solution. Once the reaction subsided, the ester solution was added to the reaction flask. The reaction was let stir at room temperature for 2 hours. The reaction was quenched with 1 M HCl and diluted with EtOAc. The aqueous layer was extracted three times with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated. The crude product was purified by recrystallization from 50% EtOAc/Hexanes to give the phenyl amide product.



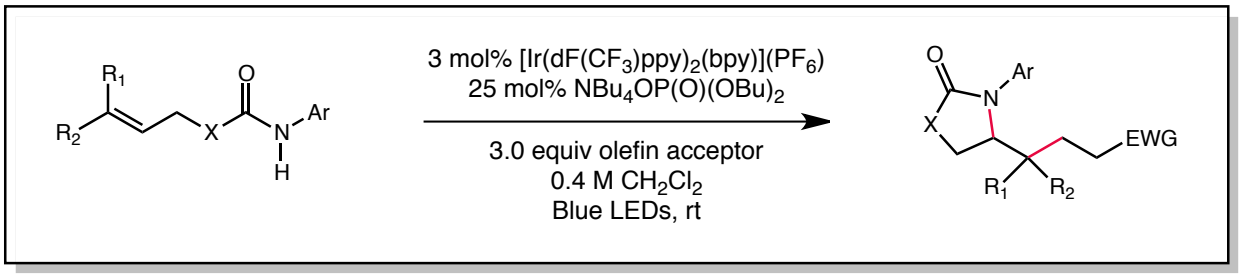
2,2-Dimethyl-N-phenylpent-4-enamide
Followed phenyl amide synthesis general procedure from commercially available methyl 3,3-dimethyl-4-pentenoate to give 2.2 g (87% yield) of the title compound. Spectra are consistent with reported literature values.[11]



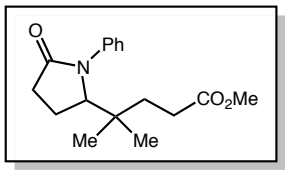
N-Phenylpent-4-enamide
Followed phenyl amide synthesis general procedure from commercially available methyl 4-pentenoate to give 2.8 g (94% yield) of the title compound. Spectra are consistent with reported literature values.[13]

Synthesis and Characterization of Products

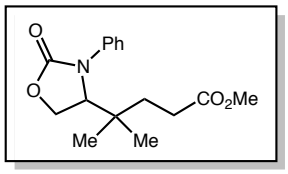
General Procedure for Photocatalytic Amidoalkylation via PCET



A screw cap test tube was charged with starting material (0.5 mmol, 1 equiv), $[Ir(dF(CF_3)ppy)_2(bpy)](PF_6)$[14] (0.015 mmol, 3 mol%), tetrabutylammonium dibutyl phosphate (0.125 mmol, 25 mol%), the acceptor (1.5 mmol, 3 equiv) and flushed with argon. 1.25 mL degassed anhydrous DCM was added, the reaction was irradiated with blue LEDs, and let stir at room temperature. Upon complete consumption of the starting material, the reaction was concentrated then purified by alumina column chromatography (gradient 100% hexanes to 50% EtOAc/hexanes) to obtain the named product.

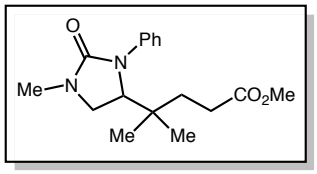


Methyl 4-methyl-4-(5-oxo-1-phenylpyrrolidin-2-yl)pentanoate (2)
Followed general procedure with 5-methyl-N-phenylhex-4-enamide (102 mg, 0.5 mmol) and methyl acrylate for 20 hours and purified using alumina column chromatography (gradient 100% hexanes to 50% EtOAc/hexanes) to give 137 mg (95% yield) of the title compound. IR (neat): 2956, 1733, 1691, 1596, 1497, 1391, 1291, 1263, 1219, 1169, 761, 696 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.37 (t, *J* = 7.7 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 2H), 7.21 (t, *J* = 7.3 Hz, 1H), 4.15 (dd, *J* = 9.2, 2.5 Hz, 1H), 3.62 (s, 3H), 2.64 (dt, *J* = 17.4, 9.8 Hz, 1H), 2.48 (ddd, *J* = 17.4, 10.6, 3.3 Hz, 1H), 2.27 (dq, *J* = 13.4, 9.6 Hz, 1H), 2.22 – 2.12 (m, 2H), 2.08 (ddt, *J* = 13.1, 9.8, 3.0 Hz, 1H), 1.60 – 1.47 (m, 2H), 0.76 (d, *J* = 17.8 Hz, 6H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.47, 174.14, 140.12, 129.10, 126.44, 125.71, 68.07, 51.82, 39.22, 33.52, 31.53, 31.46, 28.96, 24.53, 23.41, 20.77.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{17}H_{23}NO_3$) requires *m/z* 289.16779, found 289.16748, difference 1.1 ppm.



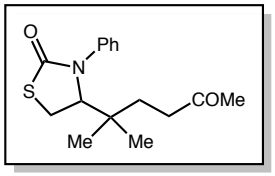
Methyl 4-methyl-4-(2-oxo-3-phenyloxazolidin-4-yl)pentanoate (3)
Followed general procedure with 3-methylbut-2-en-1-yl phenylcarbamate (103 mg, 0.5 mmol) and methyl acrylate for 21 hours and purified using alumina column chromatography (gradient 100% hexanes to 33% EtOAc/hexanes) to give 127 mg (87% yield) of the title compound. IR (neat): 2959, 1735, 1597, 1500, 1405, 1291, 1272, 1203, 1170, 1124, 1058, 764, 696, 675 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.36 (m, 4H), 7.25 – 7.20 (m, 1H), 4.45 (t, *J* = 9.0 Hz, 1H), 4.36 (dd, *J* = 9.3, 3.7 Hz, 1H), 4.28 (dd, *J* = 8.9, 3.7 Hz, 1H), 3.63 (s, 3H), 2.24 – 2.17 (m, 2H), 1.56 – 1.48 (m, 2H), 0.80 (d, *J* = 19.7 Hz, 6H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.82, 157.04, 138.85, 129.34, 126.47, 124.68, 64.36, 64.21, 51.91, 38.27, 32.63, 28.77, 23.30,

22.31.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{16}H_{21}NO_4$) requires *m/z* 291.14706, found 291.14719, difference 0.44 ppm.



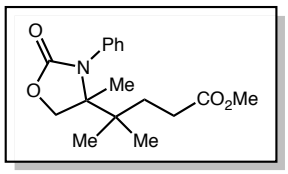
Methyl 4-methyl-4-(1-methyl-2-oxo-3-phenylimidazolidin-4-yl)pentanoate (4)

Followed general procedure with 1-methyl-1-(3-methylbut-2-en-1-yl)-3-phenylurea (109 mg, 0.5 mmol) and methyl acrylate for 45 hours and purified using alumina column chromatography (gradient 100% hexanes to 50% EtOAc/hexanes) to give 96 mg (63% yield) of the title compound. IR (neat): 2943, 1735, 1701, 1597, 1499, 1434, 1404, 1369, 1261, 761, 695 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 4H), 7.16 – 7.11 (m, 1H), 4.15 (dd, *J* = 9.7, 4.6 Hz, 1H), 3.63 (s, 3H), 3.52 (t, *J* = 9.5 Hz, 1H), 3.32 (dd, *J* = 9.4, 4.6 Hz, 1H), 2.85 (s, 3H), 2.21 (dd, *J* = 9.0, 7.5 Hz, 2H), 1.55 (q, *J* = 8.4, 7.1 Hz, 2H), 0.76 (d, *J* = 10.9 Hz, 6H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.25, 159.64, 141.24, 128.95, 125.24, 124.96, 61.46, 51.85, 47.13, 38.48, 32.66, 31.05, 28.98, 23.85, 22.73.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{17}H_{24}N_2O_3$) requires *m/z* 304.17869, found 304.17843, difference 0.85 ppm.



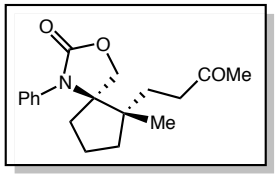
4-(2-Methyl-5-oxohexan-2-yl)-3-phenylthiazolidin-2-one (5)

Followed general procedure with *S*-(3-Methylbut-2-en-1-yl)phenylcarbamothioate (111 mg, 0.5 mmol) and methyl vinyl ketone for 72 hours and purified using alumina column chromatography (gradient 100% hexanes to 33% EtOAc/hexanes) to give 105 mg (72% yield) of the title compound. IR (neat): 2963, 1711, 1662, 1593, 1492, 1470, 1455, 1375, 1264, 1183, 1091, 1042, 1000, 848, 755, 736, 695, 660 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.32 (m, 4H), 7.23 (t, *J* = 7.1 Hz, 1H), 4.32 (dd, *J* = 9.1, 2.6 Hz, 1H), 3.67 (dd, *J* = 11.7, 9.1 Hz, 1H), 3.28 (dd, *J* = 11.7, 2.6 Hz, 1H), 2.26 (dd, *J* = 9.9, 6.4 Hz, 2H), 2.02 (s, 3H), 1.57 – 1.50 (m, 2H), 0.86 (d, *J* = 14.2 Hz, 6H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.17, 172.31, 140.59, 129.26, 126.93, 126.32, 68.36, 39.94, 38.23, 32.46, 29.96, 27.31, 24.71, 23.79.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{16}H_{21}NO_2S$) requires *m/z* 291.12930, found 291.12952, difference 0.74 ppm.



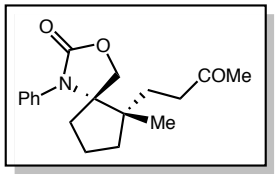
Methyl 4-methyl-4-(4-methyl-2-oxo-3-phenyloxazolidin-4-yl)pentanoate (6)

Followed general procedure with 2,3-dimethylbut-2-en-1-yl phenylcarbamate (103 mg, 0.5 mmol) and methyl acrylate for 45 hours and purified using alumina column chromatography (gradient 100% hexanes to 33% EtOAc/hexanes) to give 122 mg (80% yield) of the title compound. IR (neat): 2968, 1736, 1492, 1404, 1390, 1345, 1204, 1163, 1132, 1119, 1071, 765, 701 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.38 (m, 2H), 7.36 – 7.30 (m, 3H), 4.53 (d, *J* = 9.0 Hz, 1H), 4.02 (d, *J* = 9.1 Hz, 1H), 3.64 (s, 3H), 2.23 (t, *J* = 8.2 Hz, 2H), 1.62 (s, 3H), 0.84 (s, 3H), 0.78 (s, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.05, 157.92, 137.92, 129.36, 128.10, 71.77, 69.09, 51.87, 40.58, 31.09, 29.25, 22.82, 21.29, 20.99.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{17}H_{23}NO_4$) requires *m/z* 305.16271, found 305.16315, difference 1.44 ppm.



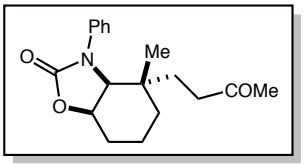
Trans-6-methyl-6-(3-oxobutyl)-1-phenyl-3-oxa-1-azaspiro[4.4]nonan-2-one (7)

Followed general procedure with (2-methylcyclopent-1-en-1-yl)methyl phenylcarbamate (103 mg, 0.5 mmol) and methyl vinyl ketone for 48 hours and purified using alumina column chromatography (gradient 100% hexanes to 33% EtOAc/hexanes) to give 124 mg (82% yield) of the title compound as a 6:1 mixture of diastereomers. Major diastereomer: IR (neat): 2955, 1745, 1713, 1596, 1492, 1453, 1391, 1353, 1311, 1215, 1169, 1140, 1058, 766, 702 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.37 (m, 2H), 7.33 (d, *J* = 7.1 Hz, 3H), 4.55 (d, *J* = 9.0 Hz, 1H), 4.11 (d, *J* = 9.1 Hz, 1H), 2.56 – 2.44 (m, 2H), 2.37 (dt, *J* = 16.7, 7.9 Hz, 1H), 2.17 (s, 3H), 1.99 – 1.90 (m, 1H), 1.72 – 1.64 (m, 2H), 1.55 (p, *J* = 7.7, 7.2 Hz, 2H), 1.43 (dt, *J* = 13.3, 7.9 Hz, 1H), 1.26 – 1.15 (m, 1H), 0.80 (s, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.27, 157.95, 137.51, 129.63, 129.27, 128.22, 74.99, 71.43, 47.18, 39.26, 34.69, 34.12, 30.22, 29.04, 20.20, 17.57.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{18}H_{23}NO_3$) requires *m/z* 301.16779, found *m/z* 301.16831, difference 1.7 ppm.



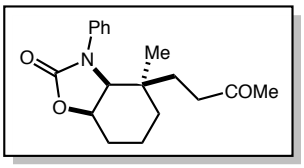
Cis-6-methyl-6-(3-oxobutyl)-1-phenyl-3-oxa-1-azaspiro[4.4]nonan-2-one (7)

Minor diastereomer: IR (neat): 2964, 1746, 1713, 1595, 1494, 1397, 1379, 1352, 1219, 1155, 1138, 1078, 1004, 961, 766, 702, 670 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 4.4 Hz, 4H), 7.44 – 7.27 (m, 1H), 4.49 (d, *J* = 9.1 Hz, 1H), 4.20 (d, *J* = 9.1 Hz, 1H), 2.58 – 2.45 (m, 2H), 2.33 (ddd, *J* = 16.5, 10.7, 5.2 Hz, 1H), 2.16 (s, 3H), 2.20 – 2.07 (m, 1H), 1.90 (ddd, *J* = 15.6, 10.8, 5.2 Hz, 1H), 1.76 (ddd, *J* = 14.0, 10.6, 5.5 Hz, 1H), 1.62 (m, *J* = 8.5 Hz, 1H), 1.42 (dtdd, *J* = 13.6, 10.1, 6.4, 3.0 Hz, 1H), 1.38 – 1.26 (m, 1H), 1.19 (ddd, *J* = 13.1, 10.5, 8.1 Hz, 1H), 0.95 (s, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.27, 157.87, 137.81, 129.53, 129.38, 128.28, 76.18, 69.87, 47.88, 39.38, 35.81, 35.54, 30.06, 28.47, 21.84, 18.69.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{18}H_{23}NO_3$) requires *m/z* 301.16779, found *m/z* 301.1673, difference 1.64 ppm.



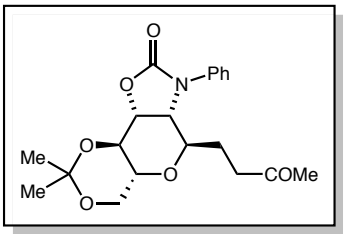
Trans-4-methyl-4-(3-oxobutyl)-3-phenylhexahydrobenzo[*d*]oxazol-2(3*H*)-one (8)

Followed general procedure with 3-methylcyclohex-2-en-1-yl phenylcarbamate (116 mg, 0.5 mmol) and methyl vinyl ketone for 48 hours and purified using alumina column chromatography (gradient 100% hexanes to 33% EtOAc/hexanes) to give 130 mg (86% yield) of the title compound as a 8:1 mixture of diastereomers. Major diastereomer: IR (neat): 2935, 1740, 1710, 1597, 1497, 1456, 1392, 1356, 1293, 1206, 1187, 1148, 1120, 1062, 1003, 980, 911, 822, 762, 696, 678 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 7.4, 1.7 Hz, 2H), 7.40 – 7.34 (m, 2H), 7.17 (t, *J* = 7.4 Hz, 1H), 4.71 (ddd, *J* = 6.2, 3.9, 2.0 Hz, 1H), 4.08 (d, *J* = 6.3 Hz, 1H), 2.32 – 2.23 (m, 1H), 2.23 – 2.12 (m, 2H), 1.96 (s, 3H), 1.74 – 1.60 (m, 2H), 1.51 (dt, *J* = 11.4, 3.5 Hz, 1H), 1.45 (ddt, *J* = 13.4, 4.1, 2.0 Hz, 1H), 1.35 – 1.23 (m, 2H), 1.09 (td, *J* = 12.9, 3.2 Hz, 1H), 1.00 (s, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.17, 156.49, 138.60, 129.26, 125.64, 123.20, 75.04, 63.39, 38.33, 37.64, 36.60, 33.71, 29.82, 26.66, 20.22, 15.73.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{18}H_{23}NO_3$) requires *m/z* 301.16779, found *m/z* 301.16748, difference 1.05 ppm.



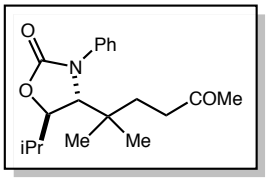
Cis-4-methyl-4-(3-oxobutyl)-3-phenylhexahydrobenzo[*d*]oxazol-2(3*H*)-one (8)

Minor diastereomer: IR (neat): 2940, 1746, 1713, 1595, 1494, 1457, 1397, 1352, 1311, 1260, 1189, 1155, 1138, 1078, 1004, 961, 766, 702, 670 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.0 Hz, 2H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.17 (t, *J* = 7.4 Hz, 1H), 4.70 (ddd, *J* = 6.0, 2.0 Hz, 1H), 4.12 (d, *J* = 6.4 Hz, 1H), 2.32 – 2.24 (m, 1H), 2.20 – 2.09 (m, 2H), 2.07 (s, 3H), 1.91 (ddd, *J* = 13.9, 11.1, 5.5 Hz, 1H), 1.81 – 1.72 (m, 1H), 1.69 – 1.72 (m, 1 H), 1.63 – 1.55 (m, 1H), 1.55 – 1.48 (m, 1H), 1.11 – 1.02 (m, 1H), 0.70 (s, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.16, 156.40, 138.64, 129.20, 125.52, 123.33, 74.77, 66.00, 38.05, 37.75, 32.95, 29.78, 27.93, 26.63, 26.39, 15.75.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{18}H_{23}NO_3$) requires *m/z* 301.16779, found *m/z* 301.16837, difference 1.91 ppm.



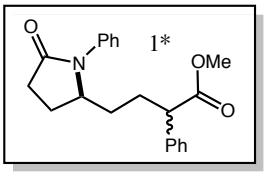
Trans-2,2-dimethyl-6-(3-oxobutyl)-7-phenylhexahydro-[1,3]dioxino[4',5':5,6]pyrano[3,4-*d*]oxazol-8(6*H*)-one (9)

Followed general procedure with 2,2-dimethyl-4,4a,8,8a-tetrahydropyrano[3,2-*d*][1,3]dioxin-8-ylphenylcarbamate (153 mg, 0.5 mmol) and 1.1 equivalents of methyl vinyl ketone for 48 hours and purified using alumina column chromatography (gradient 100% hexanes to 50% EtOAc/hexanes) to give 232 mg (63% yield) of the title compound as a >20:1 mixture of diastereomers. Major diastereomer: IR (neat): 2994, 2943, 1760, 1712, 1598, 1501, 1456, 1384, 1302, 1264, 1200, 1169, 1107, 1090, 1022, 953, 917, 854, 765, 733, 697, 671 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (t, *J* = 7.8 Hz, 2H), 7.34 – 7.21 (m, 3H), 4.67 (t, *J* = 7.8 Hz, 1H), 4.35 (d, *J* = 7.7 Hz, 1H), 4.05 – 3.95 (m, 2H), 3.82 (dd, *J* = 10.8, 5.4 Hz, 1H), 3.71 (t, *J* = 10.4 Hz, 1H), 3.38 (td, *J* = 10.1, 5.5 Hz, 1H), 2.55 – 2.38 (m, 2H), 2.11 (s, 3H), 2.18 – 2.00 (m, 1H), 1.69 (dtd, *J* = 14.7, 7.3, 3.9 Hz, 1H), 1.54 (s, 3H), 1.44 (s, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.14, 156.23, 136.10, 129.61, 127.06, 124.42, 100.39, 73.41, 72.22, 70.93, 62.49, 62.43, 60.31, 38.89, 30.26, 29.14, 24.79, 19.25.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{20}H_{26}NO_6$) requires *m/z* 375.16819, found *m/z* 375.16865, difference 1.23 ppm.



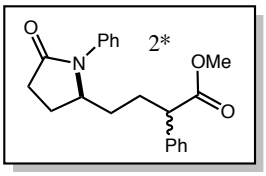
Trans-methyl 4-(5-isopropyl-2-oxo-3-phenyloxazolidin-4-yl)-4-methylpentanoate (10)

Followed general procedure with 2,5-dimethylhex-4-en-3-yl phenylcarbamate (124 mg, 0.5 mmol) and methyl acrylate for 21 hours and purified using alumina column chromatography (gradient 100% hexanes to 33% EtOAc/hexanes) to give 123 mg (77% yield) of the title compound as a >20:1 mixture of diastereomers. Major diastereomer: IR (neat): 2966, 2878, 1741, 1711, 1598, 1501, 1468, 1402, 1368, 1216, 1128, 1012, 766, 734, 695, 677 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.34 (m, 4H), 7.19 (t, *J* = 7.3 Hz, 1H), 4.21 (dd, *J* = 5.3, 2.2 Hz, 1H), 3.93 (d, *J* = 2.3 Hz, 1H), 2.33 – 2.25 (m, 2H), 2.02 (s, 3H), 1.91 (dq, *J* = 13.0, 6.6 Hz, 1H), 1.50 – 1.36 (m, 2H), 1.12 – 1.01 (m, 6H), 0.79 (d, *J* = 4.7 Hz, 6H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.04, 156.48, 139.06, 129.25, 126.08, 123.91, 79.53, 67.05, 38.44, 38.12, 33.38, 31.35, 29.93, 23.27, 22.58, 18.23, 16.38.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{19}H_{27}NO_4$) requires *m/z* 317.19909, found *m/z* 317.19931, difference 0.69 ppm.



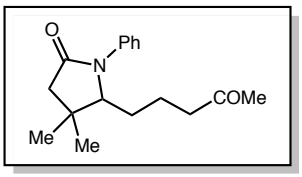
Methyl 4-methyl-4-(5-oxo-1-phenylpyrrolidin-2-yl)-2-phenylpentanoate – 1st diastereomer (11)

Followed general procedure with N-phenylpent-4-enamide (88 mg, 0.5 mmol) and 1.1 equivalents of methyl 2-phenylacrylate[15] for 48 hours and purified using alumina column chromatography (gradient 100% hexanes to 33% EtOAc/hexanes) to give 152 mg (90% yield) of the title compound as a 1:1 mixture of inseparable diastereomers. First diastereomer: IR (neat): 2951, 1732, 1694, 1597, 1497, 1455, 1393, 1294, 1220, 1165, 760, 696 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.33 (m, 2H), 7.33 – 7.27 (m, 4H), 7.25 – 7.14 (m, 4H), 4.15 (tdd, *J* = 8.2, 5.2, 3.0 Hz, 1H), 3.59 (s, 3H), 3.42 (dd, *J* = 8.7, 6.6 Hz, 1H), 2.63 (ddd, *J* = 16.6, 9.8, 6.5 Hz, 1H), 2.53 (ddd, *J* = 17.1, 9.8, 6.8 Hz, 1H), 2.36 – 2.26 (m, 1H), 2.10 (dddd, *J* = 13.2, 11.2, 8.7, 4.6 Hz, 1H), 1.91 – 1.83 (m, 1H), 1.73 – 1.64 (m, 1H), 1.60 (ddt, *J* = 13.8, 8.8, 2.7 Hz, 1H), 1.56 (s, 3H), 1.40 (dddd, *J* = 13.6, 11.4, 8.9, 4.5 Hz, 1H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.35, 174.00, 138.76, 137.56, 129.16, 128.91, 127.80, 127.64, 125.98, 124.09, 59.49, 52.23, 51.41, 31.50, 31.38, 28.80, 23.85.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{23}H_{27}NO_3$) requires *m/z* 365.19909, found *m/z* 337.16837, difference 1.72 ppm.



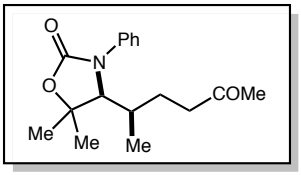
Methyl 4-methyl-4-(5-oxo-1-phenylpyrrolidin-2-yl)-2-phenylpentanoate – 2nd diastereomer (11)

Second diastereomer: IR (neat): 3030, 2950, 1731, 1692, 1597, 1497, 1454, 1434, 1391, 1294, 1220, 1165, 1118, 1070, 1030, 903, 760, 734, 696, 672 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 6H), 7.26 – 7.13 (m, 4H), 4.23 (td, *J* = 11.6, 10.0, 5.6 Hz, 1H), 3.60 (s, 3H), 3.45 – 3.37 (m, 1H), 2.68 – 2.59 (m, 1H), 2.59 – 2.47 (m, 1H), 2.36 – 2.27 (m, 1H), 2.05 – 1.96 (m, 1H), 1.83 – 1.75 (m, 1H), 1.73 – 1.60 (m, 1H), 1.59 (s, 3H), 1.34 – 1.24 (m, 1H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.34, 174.31, 174.16, 173.99, 138.75, 138.34, 137.56, 137.48, 129.15, 129.14, 128.90, 127.86, 127.79, 127.63, 127.61, 125.97, 125.91, 124.08, 123.98, 77.41, 77.16, 76.91, 59.49, 59.19, 52.24, 52.23, 51.40, 51.23, 31.50, 31.40, 31.38, 30.98, 28.79, 28.14, 23.84, 23.75.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{23}H_{27}NO_3$) requires *m/z* 365.19909, found *m/z* 337.16830, difference 1.51 ppm.



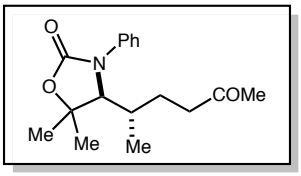
4,4-Dimethyl-5-(4-oxopentyl)-1-phenylpyrrolidin-2-one (12)

Followed general procedure with 2,2-dimethyl-N-phenylpent-4-enamide (102 mg, 0.5 mmol) and methyl vinyl ketone for 18 hours and purified using alumina column chromatography (gradient 100% hexanes to 33% EtOAc/hexanes) to give 103 mg (76% yield) of the title compound. IR (neat): 2959, 1694, 1597, 1499, 1456, 1397, 1383, 1370, 1311, 1266, 1217, 1178, 1129, 760, 694 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.37 (m, 4H), 7.21 (tt, *J* = 5.9, 3.0 Hz, 1H), 3.74 (dd, *J* = 6.6, 4.2 Hz, 1H), 2.50 (d, *J* = 16.5 Hz, 1H), 2.32 (t, *J* = 6.5 Hz, 2H), 2.27 (d, *J* = 16.5 Hz, 1H), 2.03 (s, 3H), 1.60 – 1.37 (m, 4H), 1.23 (d, *J* = 43.9 Hz, 6H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.19, 173.39, 138.52, 129.22, 126.05, 124.30, 69.68, 46.74, 43.61, 36.39, 30.01, 29.93, 29.43, 22.93, 20.69.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{17}H_{23}NO_2$) requires *m/z* 273.17288, found 273.17319, difference 1.15 ppm.



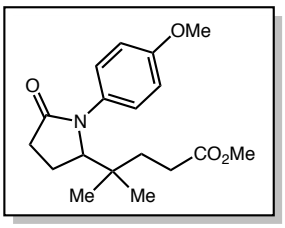
Trans-5,5-dimethyl-4-(5-oxohexan-2-yl)-3-phenyloxazolidin-2-one (13)

Followed general procedure with (*E)*-2-Methylpent-3-en-2-yl phenylcarbamate (110 mg, 0.5 mmol) and methyl vinyl ketone for 48 hours and purified using alumina column chromatography (gradient 100% hexanes to 33% EtOAc/hexanes) to give 110 mg (76% yield) of the title compound as a 5:1 mixture of diastereomers. Major diastereomer: IR (neat): 2973, 1739, 1713, 1598, 1502, 1457, 1400, 1373, 1294, 1277, 1223, 1170, 1118, 1003, 983, 958, 797, 761, 697, 683 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.8 Hz, 2H), 7.41 – 7.35 (m, 2H), 7.22 – 7.16 (m, 1H), 4.04 (d, *J* = 1.6 Hz, 1H), 2.35 – 2.21 (m, 2H), 2.02 (s, 3H), 1.83 (dqdt, *J* = 8.4, 6.6, 4.6, 2.3 Hz, 1H), 1.52 (d, *J* = 32.2 Hz, 6H), 1.44 (ddd, *J* = 15.0, 7.2, 4.7 Hz, 1H), 1.09 – 1.01 (m, 1H), 0.99 (d, *J* = 6.7 Hz, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.12, 155.43, 138.55, 129.25, 125.88, 123.67, 80.70, 69.37, 41.52, 35.10, 30.00, 29.74, 29.68, 21.73, 14.00.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{17}H_{23}NO_3$) requires *m/z* 289.16779, found *m/z* 298.16763, difference 0.58 ppm.



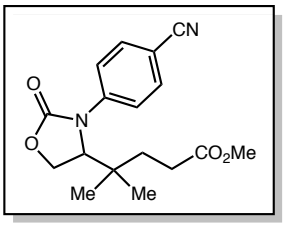
Cis-5,5-dimethyl-4-(5-oxohexan-2-yl)-3-phenyloxazolidin-2-one (13)

Minor diastereomer: IR (neat): 2971, 1740, 1714, 1598, 1502, 1457, 1401, 1279, 1222, 1172, 1118, 1004, 984, 797, 761, 696 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.43 (m, 2H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.19 (q, *J* = 6.7, 6.2 Hz, 1H), 4.05 – 4.00 (m, 1H), 2.49 (dt, *J* = 17.5, 6.8 Hz, 1H), 2.41 – 2.34 (m, 1H), 2.11 (s, 3H), 1.85 (s, 1H), 1.56 (d, *J* = 9.4 Hz, 6H), 1.45 (q, *J* = 5.9 Hz, 1H), 1.09 – 1.00 (m, 1H), 0.81 (d, *J* = 7.0 Hz, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.14, 155.27, 138.13, 129.27, 125.57, 123.19, 80.85, 77.41, 77.16, 76.91, 70.06, 41.45, 34.29, 30.16, 30.14, 25.32, 22.19, 16.63.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{18}H_{23}NO_3$) requires *m/z* 289.16779, found *m/z* 289.16784, difference 0.16 ppm.



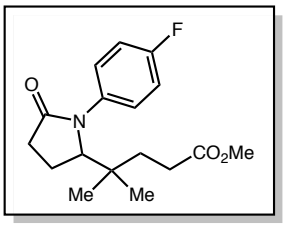
Methyl 4-(1-(4-methoxyphenyl)-5-oxopyrrolidin-2-yl)-4-methylpentanoate (14)

Followed general procedure with N-(4-methoxyphenyl)-5-methylhex-4-enamide (117 mg, 0.5 mmol) and methyl acrylate for 12 hours and purified using alumina column chromatography (gradient 100% hexanes to 50% EtOAc/hexanes) to give 127 mg (78% yield) of the title compound. IR (neat): 2956, 1734, 1689, 1510, 1472, 1439, 1392, 1288, 1246, 1172, 1116, 1032, 833 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.5 Hz, 2H), 6.89 (d, *J* = 8.5 Hz, 2H), 4.05 (d, *J* = 8.5 Hz, 1H), 3.79 (s, 3H), 3.62 (s, 3H), 2.61 (dt, *J* = 18.6, 9.6 Hz, 1H), 2.51 – 2.40 (m, 1H), 2.21 (dddd, *J* = 25.0, 21.3, 14.6, 8.2 Hz, 3H), 2.09 – 1.99 (m, 1H), 1.53 (tt, *J* = 10.7, 5.2 Hz, 2H), 0.75 (d, *J* = 13.2 Hz, 6H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.74, 174.19, 157.91, 132.93, 127.01, 114.38, 68.33, 55.55, 51.81, 38.93, 33.47, 31.25, 28.96, 24.59, 23.47, 20.76.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{18}H_{25}NO_4$) requires *m/z* 319.17836, found 319.17817, difference 0.6 ppm.



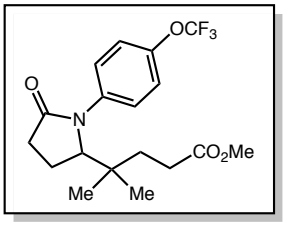
Methyl 4-(3-(4-cyanophenyl)-2-oxooxazolidin-4-yl)-4-methylpentanoate (15)

Followed general procedure with 3-methylbut-2-en-1-yl (4-cyanophenyl)carbamate (115 mg, 0.5 mmol) and methyl acrylate for 45 hours and purified using alumina column chromatography (gradient 100% hexanes to 50% EtOAc/hexanes) to give 149 mg (94% yield) of the title compound. IR (neat): 2961, 2226, 1739, 1603, 1510, 1400, 1359, 1293, 1276, 1198, 1128, 1110, 1059, 841, 756, 732 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.6 Hz, 2H), 7.61 (d, *J* = 8.6 Hz, 2H), 4.50 – 4.40 (m, 2H), 4.35 (dd, *J* = 8.5, 2.8 Hz, 1H), 3.65 (s, 3H), 2.25 (t, *J* = 8.1 Hz, 2H), 1.57 (d, *J* = 7.9 Hz, 2H), 0.82 (d, *J* = 30.9 Hz, 6H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.62, 155.97, 143.05, 133.27, 123.68, 118.47, 109.10, 64.35, 63.63, 52.03, 38.94, 32.59, 28.70, 23.51, 22.23.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{17}H_{20}N_2O_4$) requires *m/z* 316.14231, found 316.14281, difference 1.59 ppm.



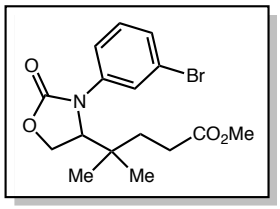
Methyl 4-(1-(4-fluorophenyl)-5-oxopyrrolidin-2-yl)-4-methylpentanoate (16)

Followed general procedure with *N*-(4-Fluorophenyl)-5-methylhex-4-enamide (111 mg, 0.5 mmol) and methyl acrylate for 45 hours and purified using alumina column chromatography (gradient 100% hexanes to 50% EtOAc/hexanes) to give 133 mg (86% yield) of the title compound. IR (neat): 2959, 1734, 1692, 1602, 1509, 1474, 1436, 1421, 1391, 1293, 1265, 1224, 1171, 1112, 1014, 838, 814, 658 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.26 (m, 2H), 7.06 (t, *J* = 8.4 Hz, 2H), 4.09 (d, *J* = 8.7 Hz, 1H), 3.63 (s, 3H), 2.63 (dt, *J* = 18.7, 9.7 Hz, 1H), 2.54 – 2.41 (m, 1H), 2.27 (dt, *J* = 13.4, 9.7 Hz, 1H), 2.18 (h, *J* = 7.9 Hz, 2H), 2.08 (dd, *J* = 13.1, 9.8 Hz, 1H), 1.53 (t, *J* = 8.4 Hz, 2H), 0.75 (d, *J* = 14.5 Hz, 6H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.61, 174.06, 161.75, 159.79, 136.10, 136.08, 127.42, 127.39, 116.08, 115.90, 68.32, 51.84, 39.16, 33.49, 31.25, 28.92, 24.53, 23.44, 20.75.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{17}H_{22}FNO_3$) requires *m/z* 307.15837, found 307.15855, difference 0.57 ppm.



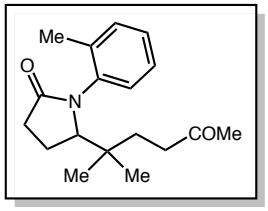
Methyl 4-methyl-4-(5-oxo-1-(4-(trifluoromethoxy)phenyl)pyrrolidin-2-yl)pentanoate (17)

Followed general procedure with 5-Methyl-*N*-(4-(trifluoromethoxy)phenyl)hex-4-enamide (144 mg, 0.5 mmol) and methyl acrylate for 45 hours and purified using alumina column chromatography (gradient 100% hexanes to 50% EtOAc/hexanes) to give 131 mg (70% yield) of the title compound. IR (neat): 2962, 1735, 1694, 1508, 1474, 1437, 1390, 1251, 1219, 1201, 1160, 1116, 1017, 921, 850, 809, 660 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ .; ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.49, 174.00, 146.96, 138.66, 126.87, 121.66, 68.11, 51.85, 39.37, 33.56, 31.34, 28.95, 24.53, 23.45, 20.74.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{18}H_{22}F_3NO_4$) requires *m/z* 373.15009, found 373.14939, difference 1.89 ppm.



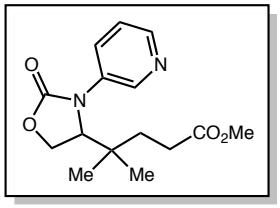
Methyl 4-(3-(3-bromophenyl)-2-oxooxaazolidin-4-yl)-4-methylpentanoate (18)

Followed general procedure with 3-methylbut-2-en-1-yl (3-bromophenyl)carbamate (142 mg, 0.5 mmol) and methyl acrylate for 45 hours and purified using alumina column chromatography (gradient 100% hexanes to 50% EtOAc/hexanes) to give 154 mg (82% yield) of the title compound. IR (neat): 2960, 1740, 1590, 1479, 1434, 1402, 1266, 1202, 1171, 1126, 1060, 996, 781, 710 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (t, *J* = 2.1 Hz, 1H), 7.36 (ddd, *J* = 12.1, 8.1, 1.9 Hz, 2H), 7.27 – 7.24 (m, 1H), 4.44 (t, *J* = 9.0 Hz, 1H), 4.37 (dd, *J* = 9.3, 3.4 Hz, 1H), 4.26 (dd, *J* = 8.8, 3.4 Hz, 1H), 3.64 (s, 3H), 2.26 – 2.20 (m, 2H), 1.59 – 1.46 (m, 2H), 0.81 (d, *J* = 20.7 Hz, 6H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.71, 156.56, 140.22, 130.55, 129.38, 127.29, 123.04, 122.72, 64.25, 64.17, 51.96, 38.46, 32.58, 28.73, 23.42, 22.27.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{17}H_{20}N_2O_4$) requires *m/z* 316.14231, found 369.05704, difference 1.44 ppm.



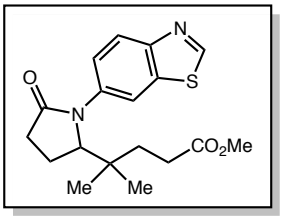
5-(2-Methyl-5-oxohexan-2-yl)-1-(*o*-tolyl)pyrrolidin-2-one (19)

Followed general procedure with 5-Methyl-N-(*o*-tolyl)hex-4-enamide (109 mg, 0.5 mmol) and methyl vinyl ketone for 45 hours and purified using alumina column chromatography (gradient 100% hexanes to 50% EtOAc/hexanes) to give 86 mg (60% yield) of the title compound as a mixture of rotamers (~2:1). IR (neat): 2958, 1691, 1603, 1581, 1494, 1461, 1390, 1367, 1295, 1278, 1259, 1218, 1162, 1137, 1047, 885, 843, 804, 783, 762, 728, 663 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$, major rotamer) δ 7.28 – 7.22 (m, 2H), 7.22 – 7.17 (m, 1H), 7.17 – 7.12 (m, 1H), 4.10 (dd, *J* = 9.3, 2.7 Hz, 1H), 2.71 – 2.60 (m, 1H), 2.55 – 2.43 (m, 1H), 2.36 (s, 3H), 2.35 – 2.28 (m, 1H), 2.28 – 2.22 (m, 2H), 2.19 – 2.08 (m, 1H), 2.01 (s, 3H), 1.48 – 1.40 (m, 2H), 0.81 (d, *J* = 22.7 Hz, 6H).; ^{13}C NMR (126 MHz, $CDCl_3$, major rotamer) δ 208.50, 175.33, 139.55, 136.22, 131.78, 127.23, 126.40, 124.66, 69.40, 38.21, 38.11, 32.46, 31.34, 29.90, 23.93, 23.33, 21.67, 19.29.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{18}H_{26}NO_2$) requires *m/z* 287.18853, found 287.18834, difference 0.64 ppm.



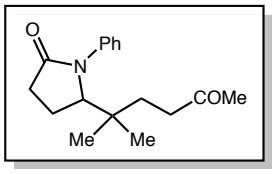
Methyl 4-methyl-4-(2-oxo-3-(pyridin-3-yl)oxazolidin-4-yl)pentanoate (20)

Followed general procedure with 3-methylbut-2-en-1-yl (3-bromophenyl)carbamate (102 mg, 0.5 mmol) and methyl acrylate for 24 hours and purified using alumina column chromatography (gradient 100% hexanes to 50% EtOAc/hexanes) to give 116 mg (70% yield) of the title compound. IR (neat): 2961, 1737, 1582, 1482, 1434, 1404, 1372, 1288, 1206, 1128, 1057, 1025, 990, 958, 808, 762, 711, 697 cm^{-1}; ^{1}H NMR (501 MHz, $CDCl_3$) δ 8.68 (d, *J* = 2.7 Hz, 1H), 8.47 (d, *J* = 4.6 Hz, 1H), 7.86 (dt, *J* = 8.3, 1.9 Hz, 1H), 7.36 (dd, *J* = 8.2, 4.7 Hz, 1H), 4.50 (t, *J* = 9.1 Hz, 1H), 4.42 (dd, *J* = 9.4, 3.4 Hz, 1H), 4.35 (dd, *J* = 8.7, 3.3 Hz, 1H), 3.64 (s, 3H), 2.27 – 2.20 (m, 2H), 1.63 – 1.49 (m, 2H), 0.82 (d, *J* = 26.1 Hz, 6H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.66, 156.73, 147.08, 145.23, 135.83, 123.92, 64.51, 64.01, 52.00, 38.47, 32.58, 28.69, 23.56, 22.36.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{15}H_{20}N_2O_4$) requires *m/z* 292.14231, found *m/z* 292.14276, difference 1.53 ppm.



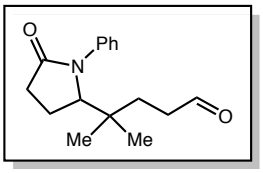
Methyl 4-(1-(benzo[*d*]thiazol-6-yl)-5-oxopyrrolidin-2-yl)-4-methylpentanoate (21)

Followed general procedure with N-(Benzo[*d*]thiazol-6-yl)-5-methylhex-4-enamide (130 mg, 0.5 mmol) and methyl acrylate (5 equiv.) in 1.25 mL DCM (0.4 M) for 36 hours and purified using alumina column chromatography (gradient 100% hexanes to 50% EtOAc/hexanes) to give 110 mg (63% yield) of the title compound. IR (neat): 2958, 1732, 1690, 1599, 1556, 1472, 1446, 1389, 1292, 1221, 1171, 1117, 841, 807, 731 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.98 (s, 1H), 8.12 (d, *J* = 8.7 Hz, 1H), 7.98 (d, *J* = 2.1 Hz, 1H), 7.45 (dd, *J* = 8.7, 2.1 Hz, 1H), 4.24 (dd, *J* = 9.2, 2.4 Hz, 1H), 3.57 (s, 3H), 2.69 (dt, *J* = 17.5, 9.8 Hz, 1H), 2.52 (ddd, *J* = 17.5, 10.6, 3.1 Hz, 1H), 2.32 (dq, *J* = 13.6, 9.9 Hz, 1H), 2.26 – 2.09 (m, 3H), 1.62 – 1.50 (m, 2H), 0.77 (d, *J* = 18.8 Hz, 6H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.68, 174.01, 154.55, 151.52, 137.81, 134.44, 123.92, 123.86, 119.42, 68.54, 51.82, 39.40, 33.47, 31.43, 28.95, 24.72, 23.47, 20.80.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{18}H_{23}N_2O_3S$) requires *m/z* 346.13511, found 346.13504, difference 0.2 ppm.



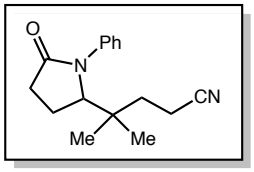
5-(2-methyl-5-oxohexan-2-yl)-1-phenylpyrrolidin-2-one (22)

Followed general procedure with 5-Methyl-N-phenylhex-4-enamide (102 mg, 0.5 mmol) and methyl vinyl ketone for 15 hours and purified using alumina column chromatography (gradient 100% hexanes to 50% EtOAc/hexanes) to give 131 mg (94% yield) of the title compound. IR (neat): 2963, 1690, 1596, 1497, 1474, 1394, 1368, 1291, 1264, 1221, 1163, 1111, 881, 843, 799, 762, 723, 696, 659 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (t, *J* = 7.7 Hz, 2H), 7.31 (d, *J* = 7.7 Hz, 2H), 7.21 (t, *J* = 7.3 Hz, 1H), 4.14 (dd, *J* = 9.2, 2.4 Hz, 1H), 2.64 (dt, *J* = 17.4, 9.8 Hz, 1H), 2.47 (ddd, *J* = 17.4, 10.6, 3.2 Hz, 1H), 2.35 – 2.20 (m, 3H), 2.08 (ddt, *J* = 13.1, 9.9, 2.9 Hz, 1H), 2.02 (s, 3H), 1.45 (dp, *J* = 13.4, 6.9, 6.5 Hz, 2H), 0.76 (d, *J* = 20.8 Hz, 6H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.51, 175.51, 140.19, 129.10, 126.51, 125.79, 68.02, 39.12, 38.31, 32.50, 31.47, 29.95, 24.52, 23.49, 20.86.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{17}H_{23}NO_2$) requires *m/z* 273.17288, found 273.17259, difference 1.06 ppm.

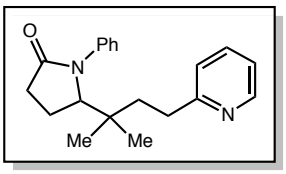


4-Methyl-4-(5-oxo-1-phenylpyrrolidin-2-yl)pentanal (23)

Followed general procedure with 5-methyl-N-phenylhex-4-enamide (102 mg, 0.5 mmol) and acrolein for 6 hours and purified using silica column chromatography (gradient 100% hexanes to 50% EtOAc/hexanes) to give 65 mg (50% yield) of the title compound. IR (neat): 2957, 2835, 1720, 1689, 1596, 1498, 1474, 1399, 1292, 1263, 1224, 1112, 843, 763, 697 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.57 (s, 1H), 7.42 – 7.34 (m, 2H), 7.31 (d, *J* = 7.8 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 1H), 4.17 (dd, *J* = 9.2, 2.5 Hz, 1H), 2.65 (dt, *J* = 17.4, 9.8 Hz, 1H), 2.49 (ddd, *J* = 17.4, 10.6, 3.2 Hz, 1H), 2.36 – 2.22 (m, 3H), 2.08 (ddt, *J* = 13.1, 9.8, 3.0 Hz, 1H), 1.48 (dddd, *J* = 23.4, 14.1, 9.5, 6.3 Hz, 2H), 0.78 (d, *J* = 9.8 Hz, 6H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.94, 175.46, 140.11, 129.16, 126.61, 125.78, 67.82, 39.14, 38.78, 31.44, 30.63, 24.39, 23.66, 20.84.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{16}H_{21}NO_2$) requires *m/z* 259.15723, found *m/z* 259.15745, difference 0.85 ppm.

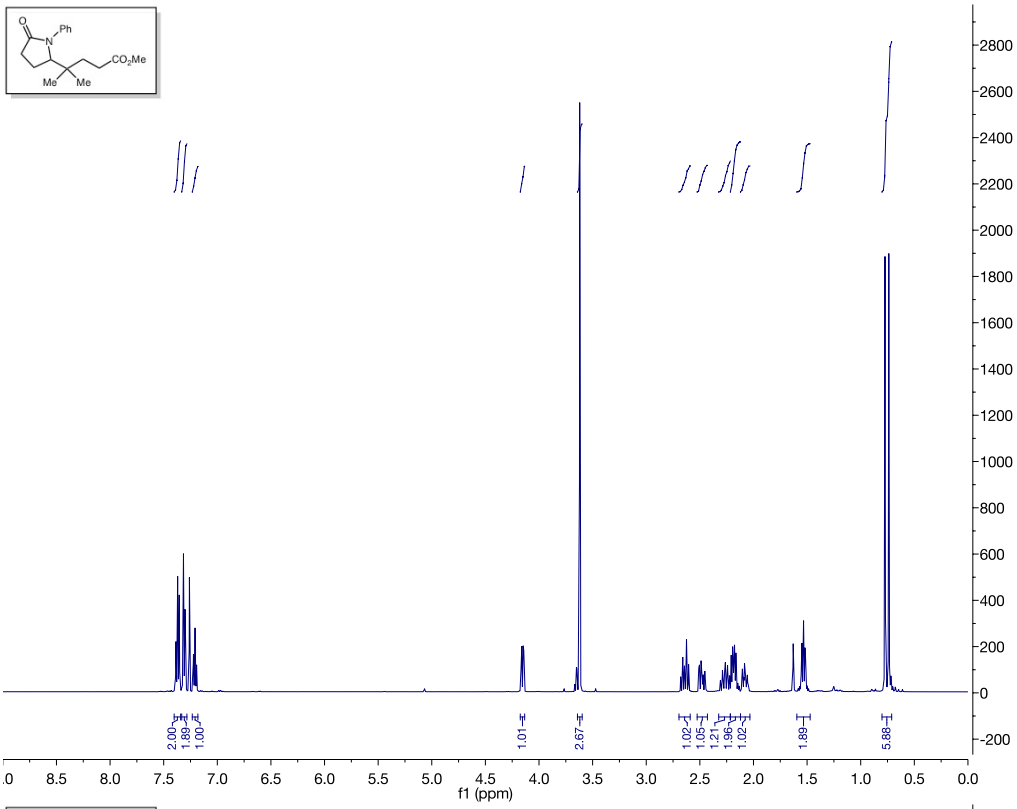


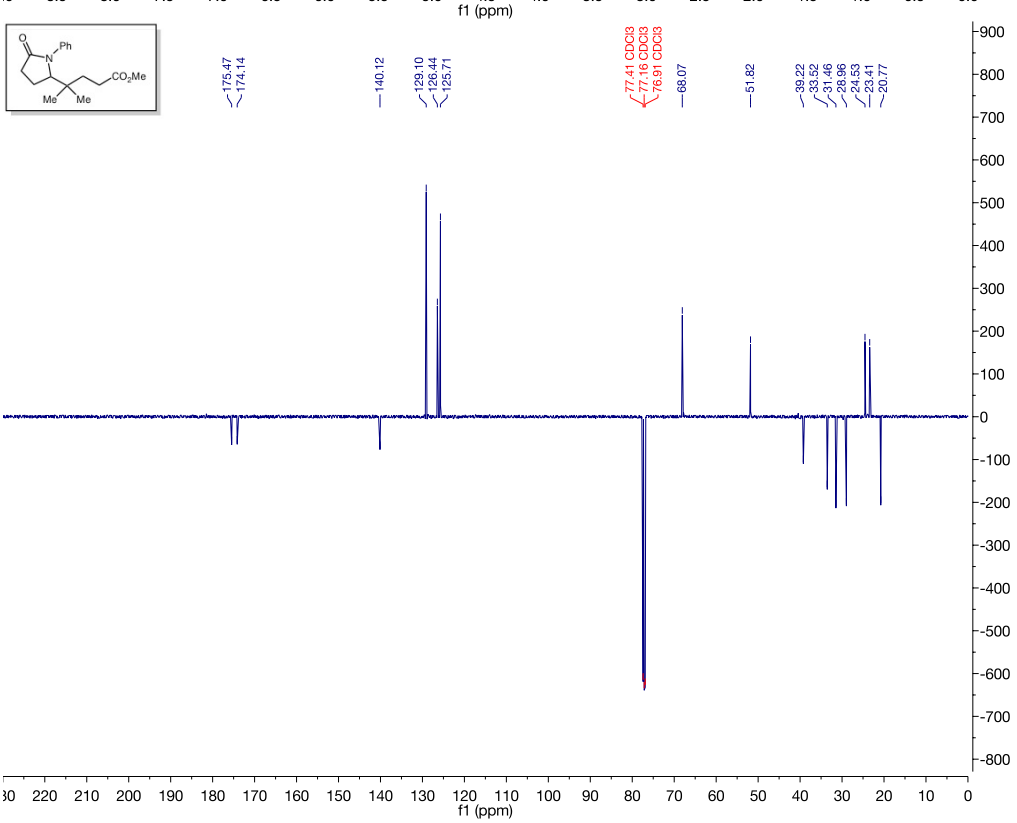
4-Methyl-4-(5-oxo-1-phenylpyrrolidine-2-yl)pentanenitrile (24)
Followed general procedure with 5-methyl-N-phenylhex-4-enamide (102 mg, 0.5 mmol) and acrylonitrile for 45 hours and purified using alumina column chromatography (gradient 100% hexanes to 50% EtOAc/hexanes) to give 100 mg (78% yield) of the title compound. IR (neat): 2954, 2244, 1688, 1596, 1497, 1474, 1392, 1292, 1222, 1112, 762, 697 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (t, *J* = 7.9 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 2H), 7.24 (m, 1H), 4.16 (dd, *J* = 9.1, 2.6 Hz, 1H), 2.64 (dt, *J* = 17.4, 9.7 Hz, 1H), 2.51 (ddd, *J* = 17.5, 10.6, 3.4 Hz, 1H), 2.32 (dq, *J* = 13.6, 9.8 Hz, 1H), 2.24 – 2.12 (m, 2H), 2.06 (ddt, *J* = 13.2, 9.9, 3.1 Hz, 1H), 1.64 – 1.49 (m, 3H), 0.83 (d, *J* = 6.2 Hz, 6H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.29, 139.84, 129.33, 126.85, 125.64, 119.91, 67.50, 39.44, 34.50, 31.26, 23.69, 23.36, 20.76, 12.23.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{16}H_{20}N_2O$) requires *m/z* 256.15756, found 256.15711, difference 1.78 ppm.

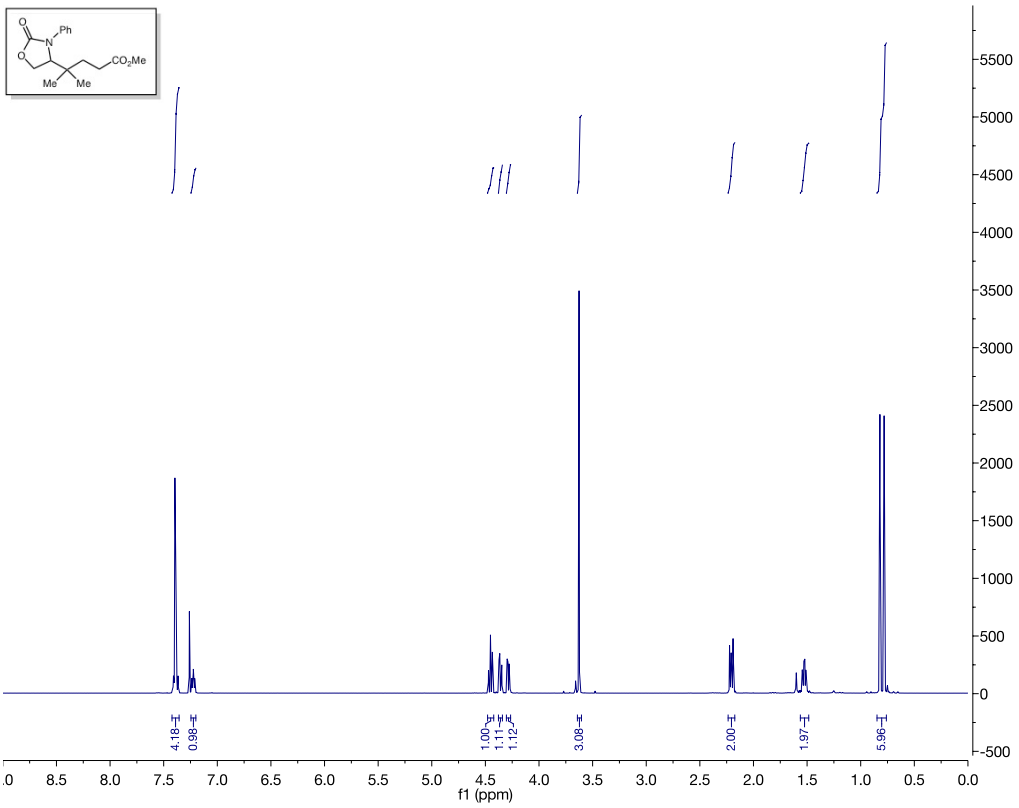


4-Methyl-4-(5-oxo-1-phenylpyrrolidin-2-yl)pentanal (25)
Followed general procedure with 5-methyl-N-phenylhex-4-enamide (102 mg, 0.5 mmol) and 2-vinylpyridine for 72 hours and purified using alumina column chromatography (gradient 100% hexanes to 75% EtOAc/hexanes) to give 117 mg (76% yield) of the title compound. IR (neat): 3458, 3063, 2962, 1588, 1591, 1568, 1497, 1473, 1433, 1392, 1291, 1263, 1220, 1111, 1051, 993, 758, 695, 659 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47 (d, *J* = 5.0 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.40 – 7.30 (m, 4H), 7.19 (t, *J* = 7.0 Hz, 1H), 7.07 (dd, *J* = 7.5, 5.0 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 4.25 (d, *J* = 8.4 Hz, 1H), 2.65 (tdd, *J* = 19.4, 13.6, 9.1 Hz, 4H), 2.46 (ddd, *J* = 17.4, 10.5, 3.1 Hz, 1H), 2.32 – 2.20 (m, 1H), 2.17 – 2.08 (m, 1H), 1.65 – 1.53 (m, 2H), 0.85 (d, *J* = 25.8 Hz, 6H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.54, 162.15, 149.30, 140.29, 136.45, 129.03, 126.31, 125.79, 122.51, 121.14, 68.10, 39.71, 39.27, 32.85, 31.55, 25.00, 23.84, 20.81.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{20}H_{24}N_2O$) requires *m/z* 308.18886, found *m/z* 308.18842, difference 1.43 ppm.

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



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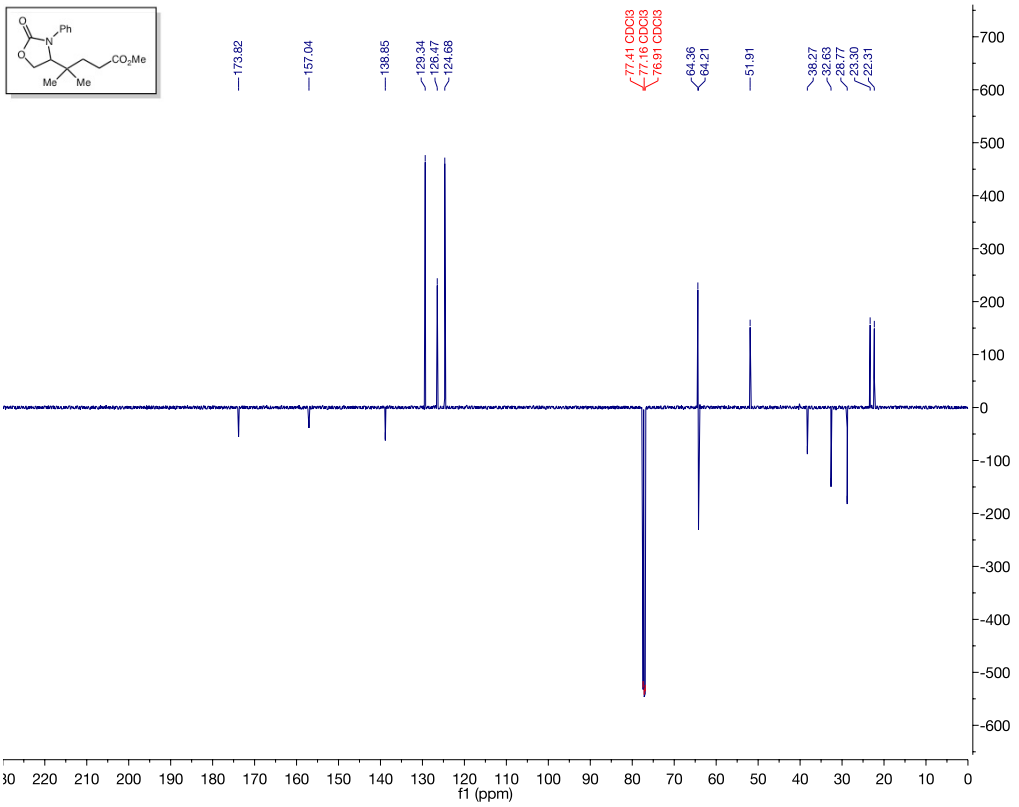
2.00
1.97
5.96
f1 (ppm)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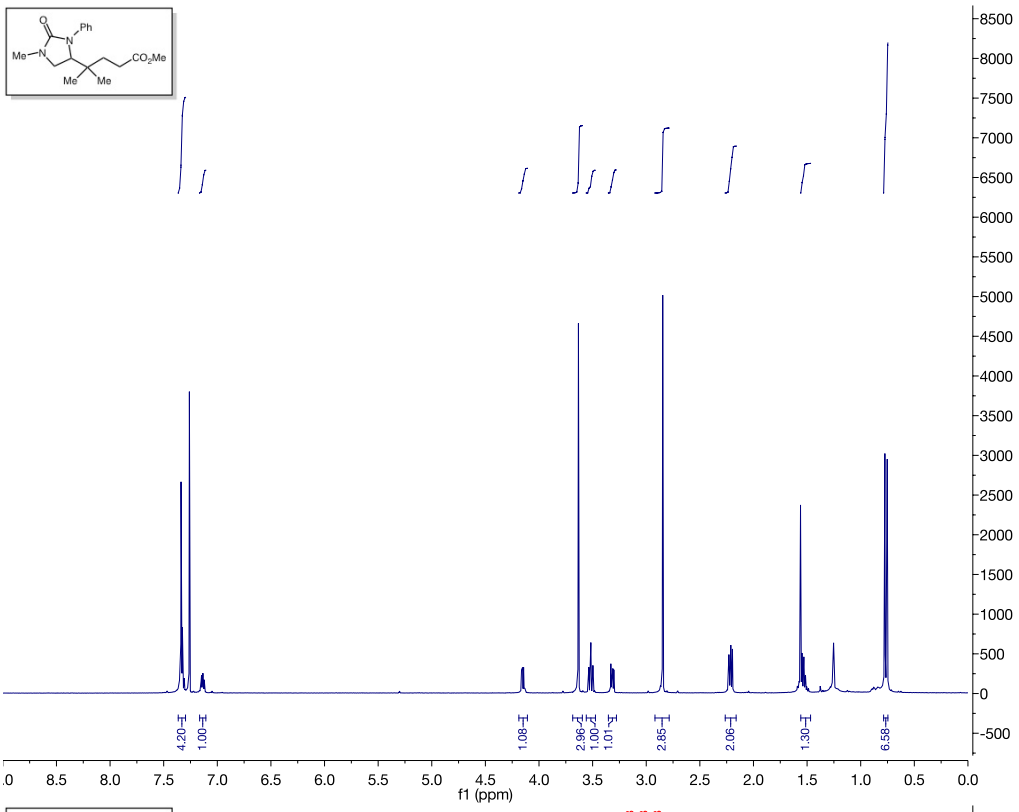
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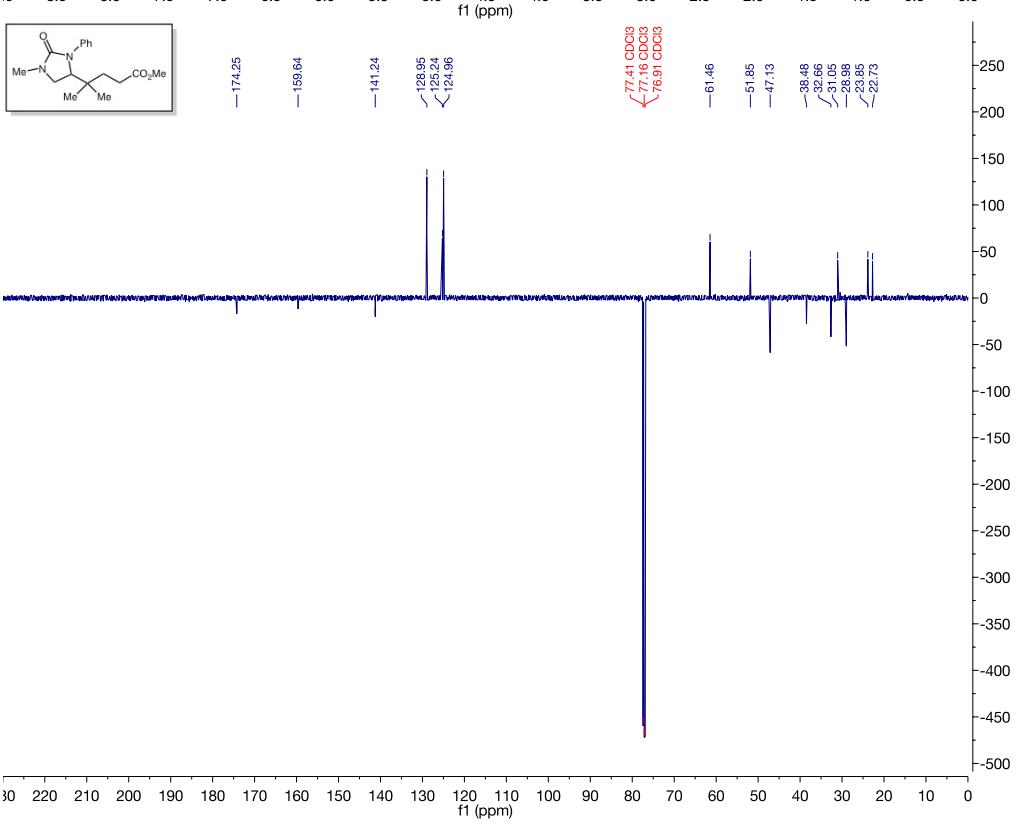
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22.73
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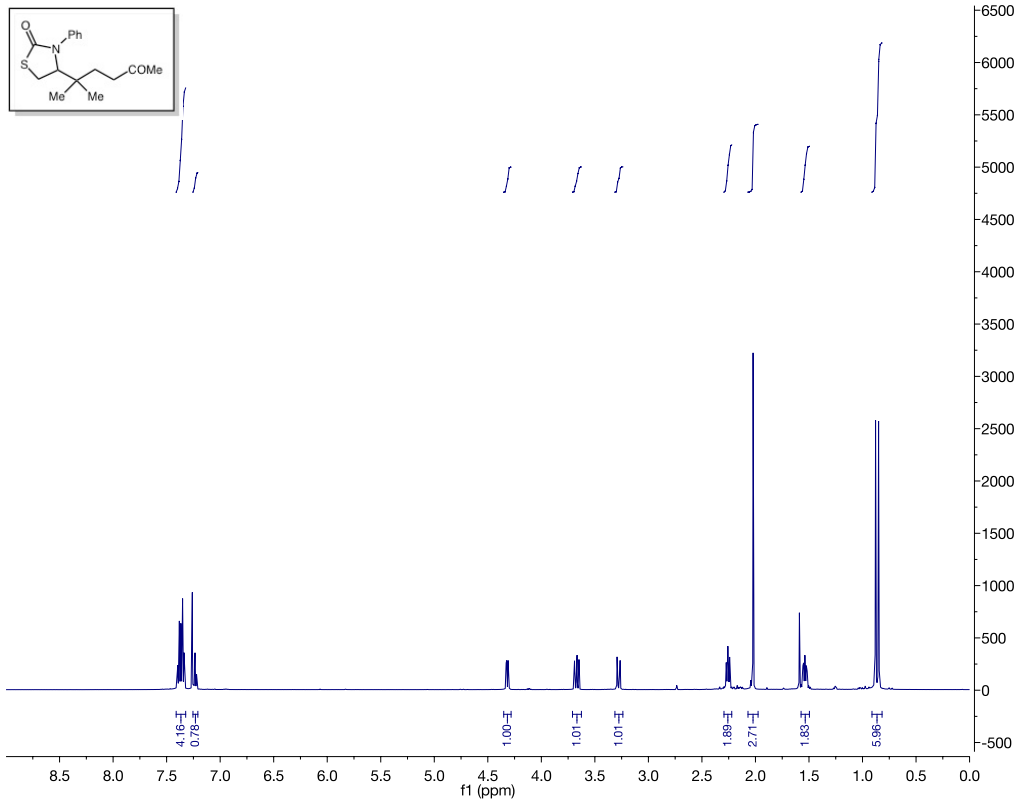
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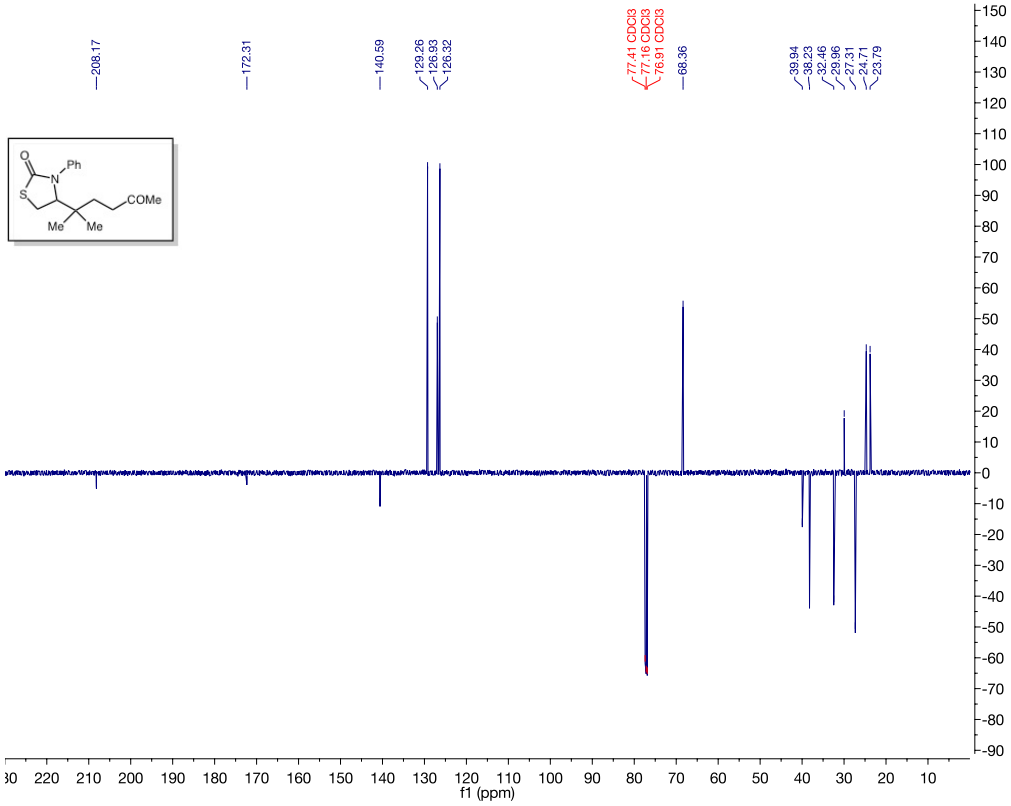
f1 (ppm)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S
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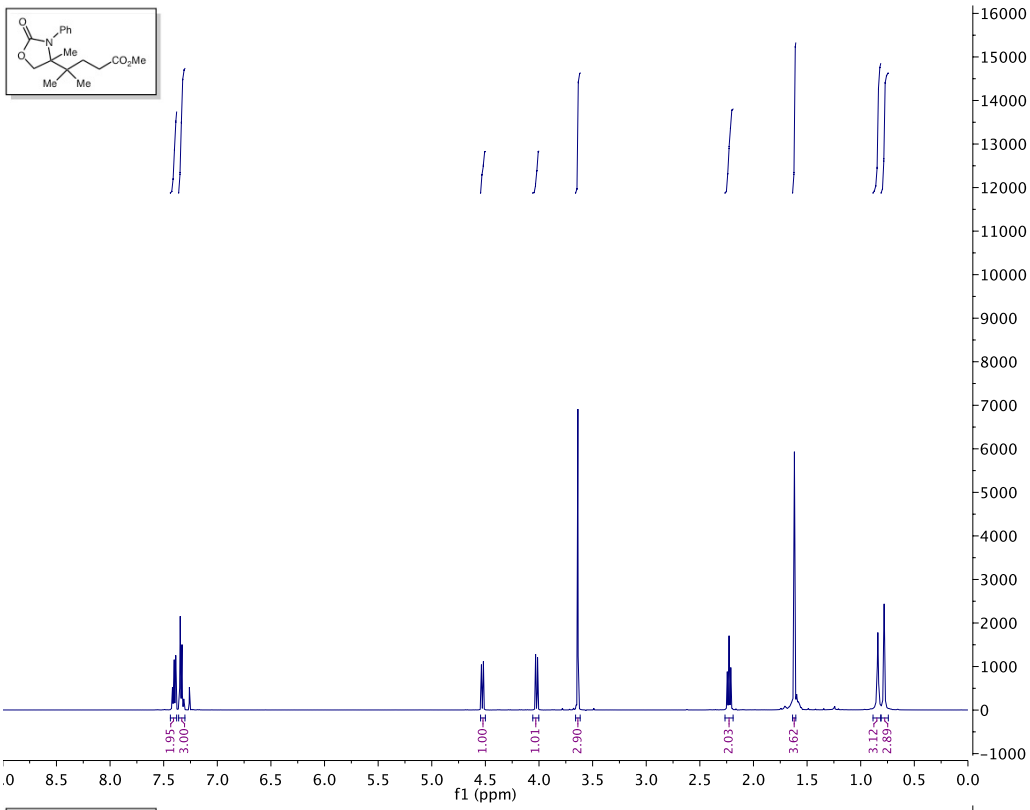
COMe
Me
Me
f1 (ppm)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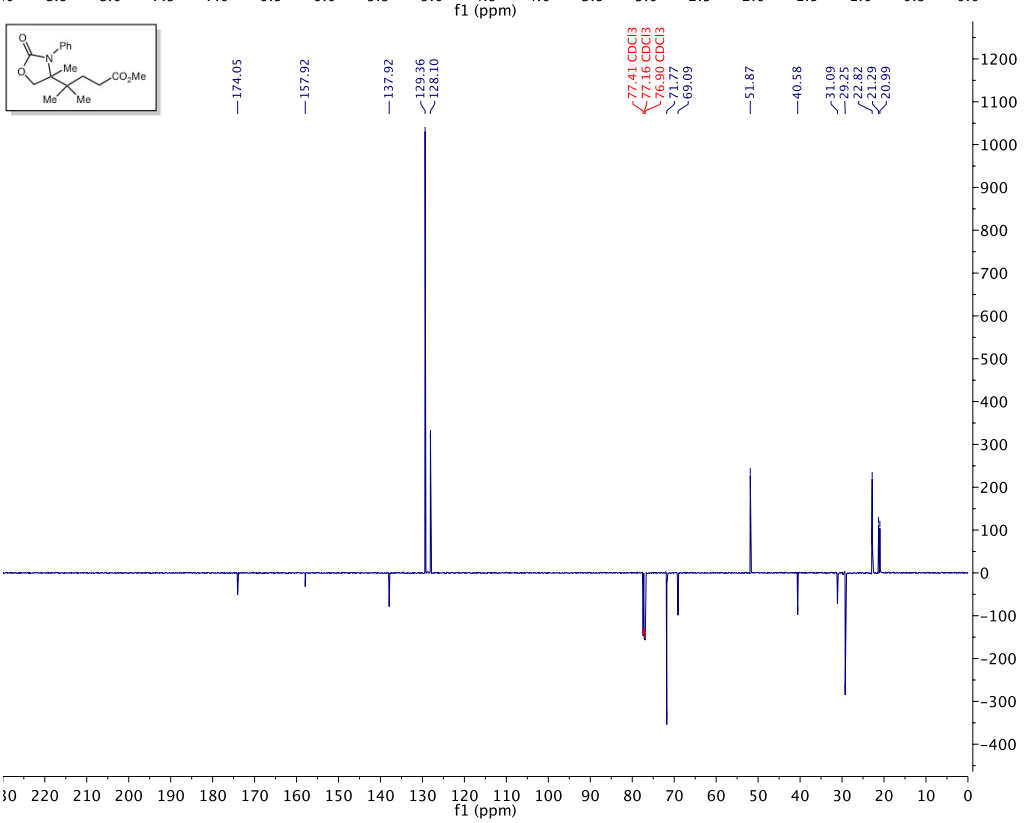
f1 (ppm)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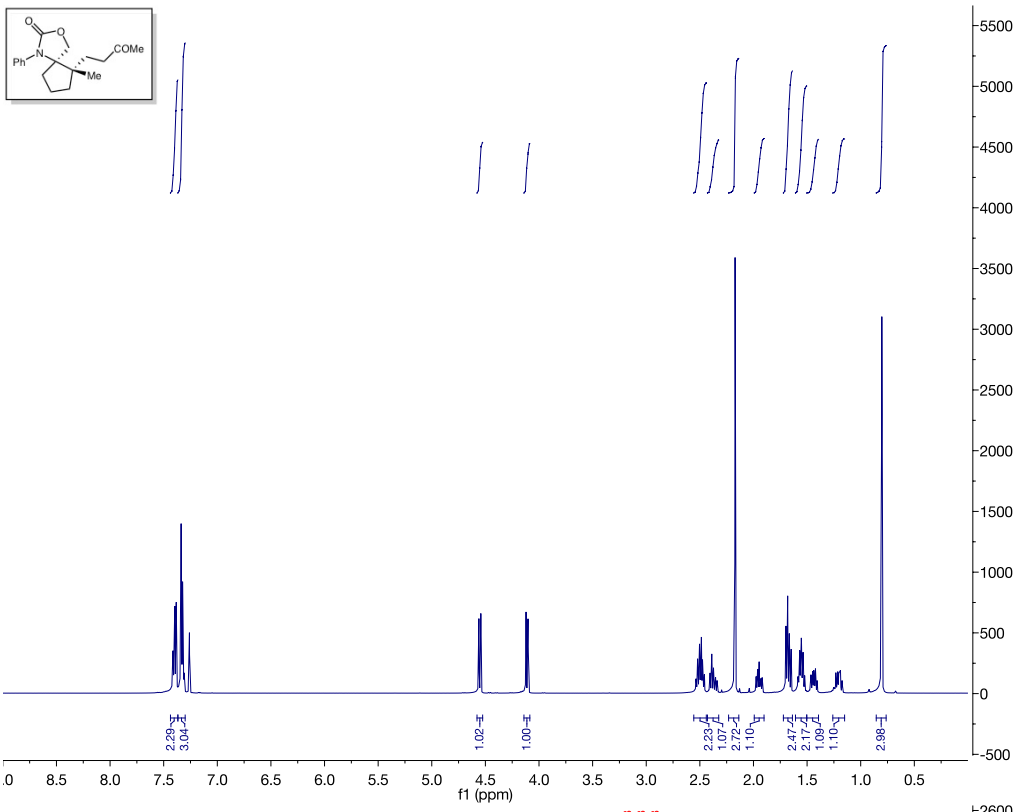
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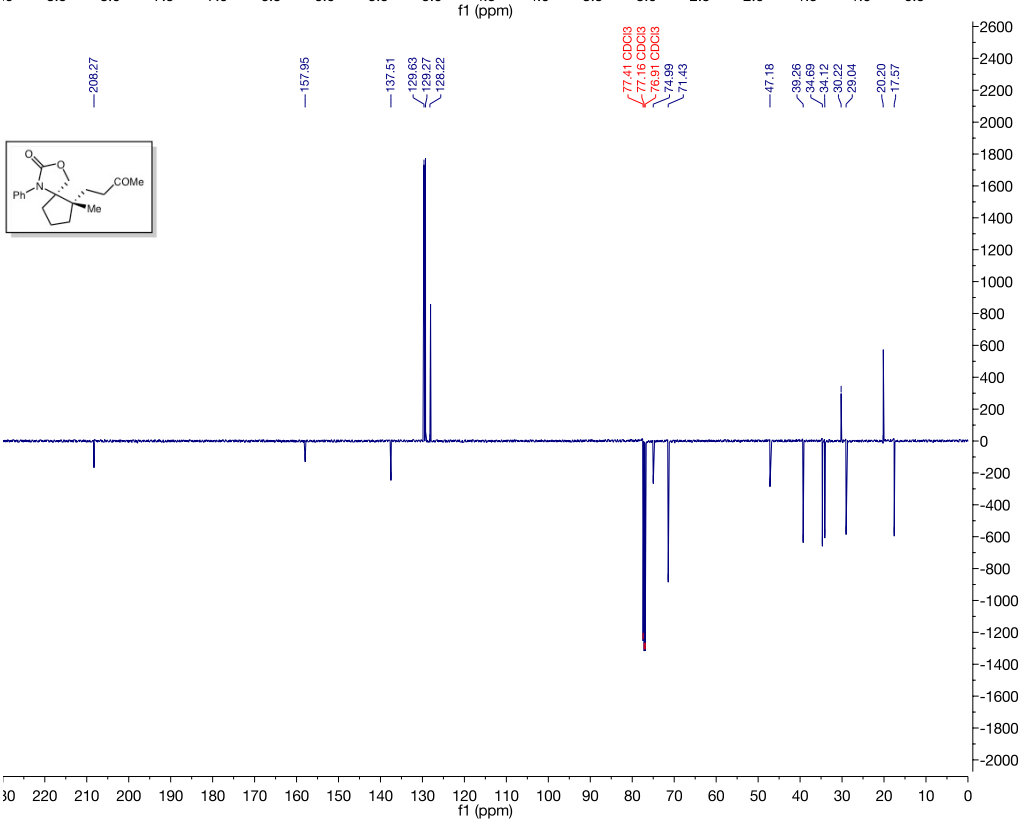
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129.27
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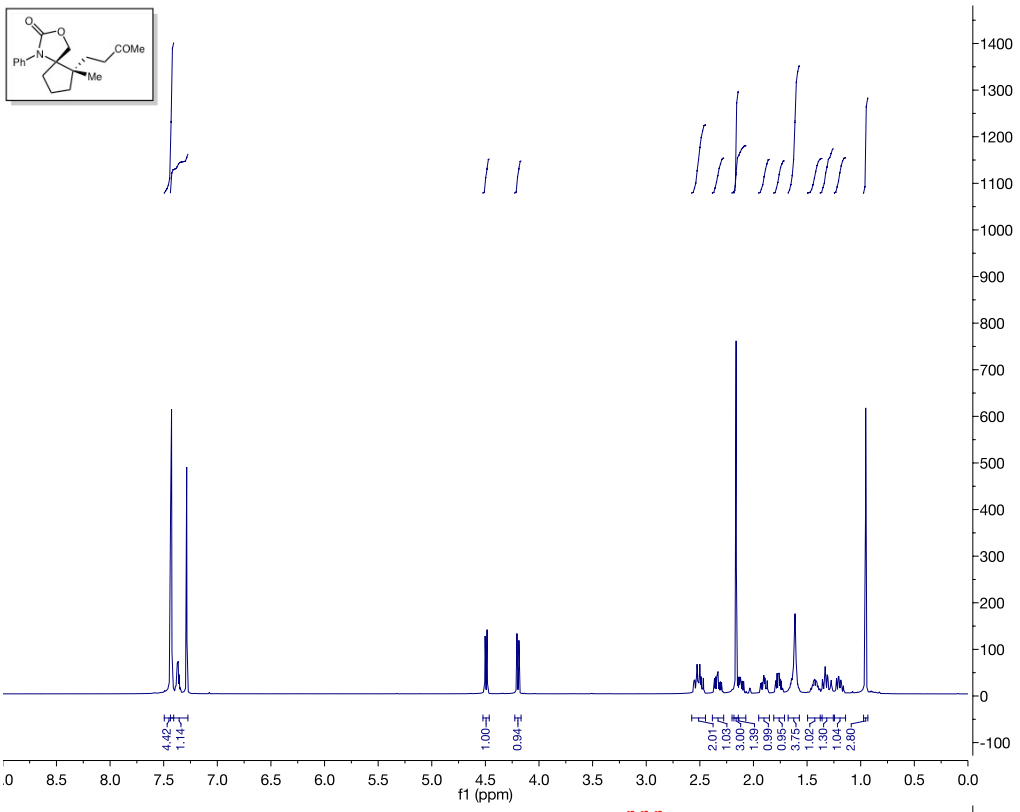
30.22
29.04
20.20
17.57
COMe
Ph
Me
f1 (ppm)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1.30
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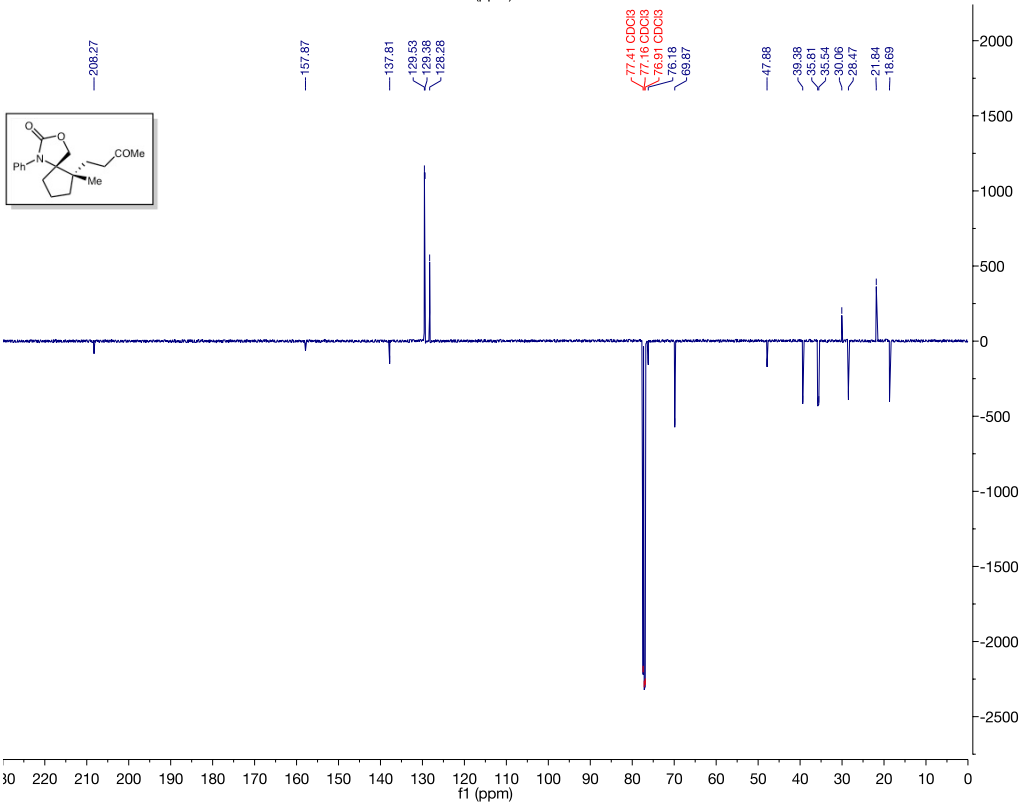
2.80
f1 (ppm)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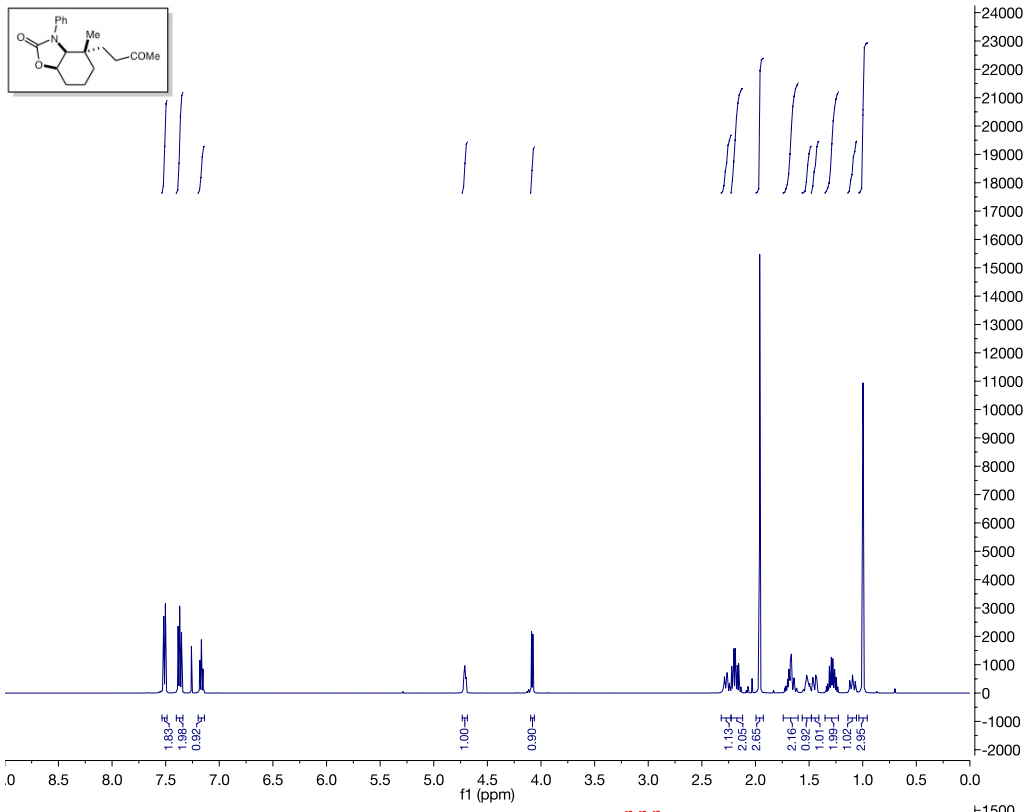
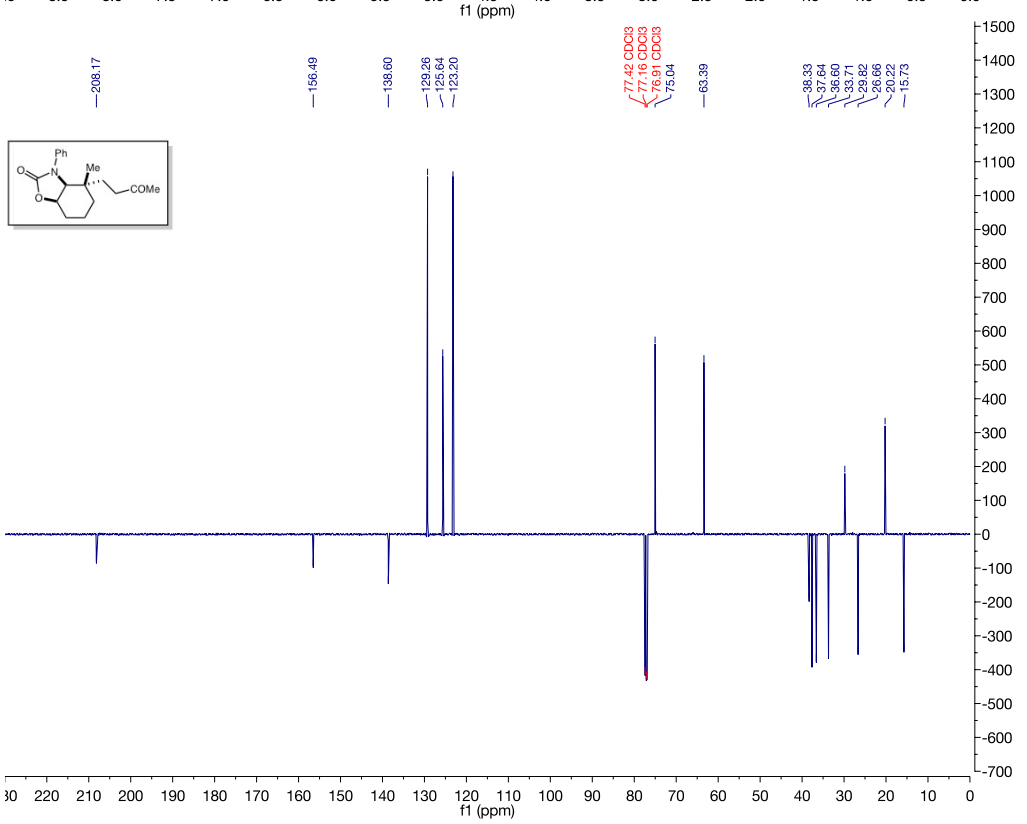
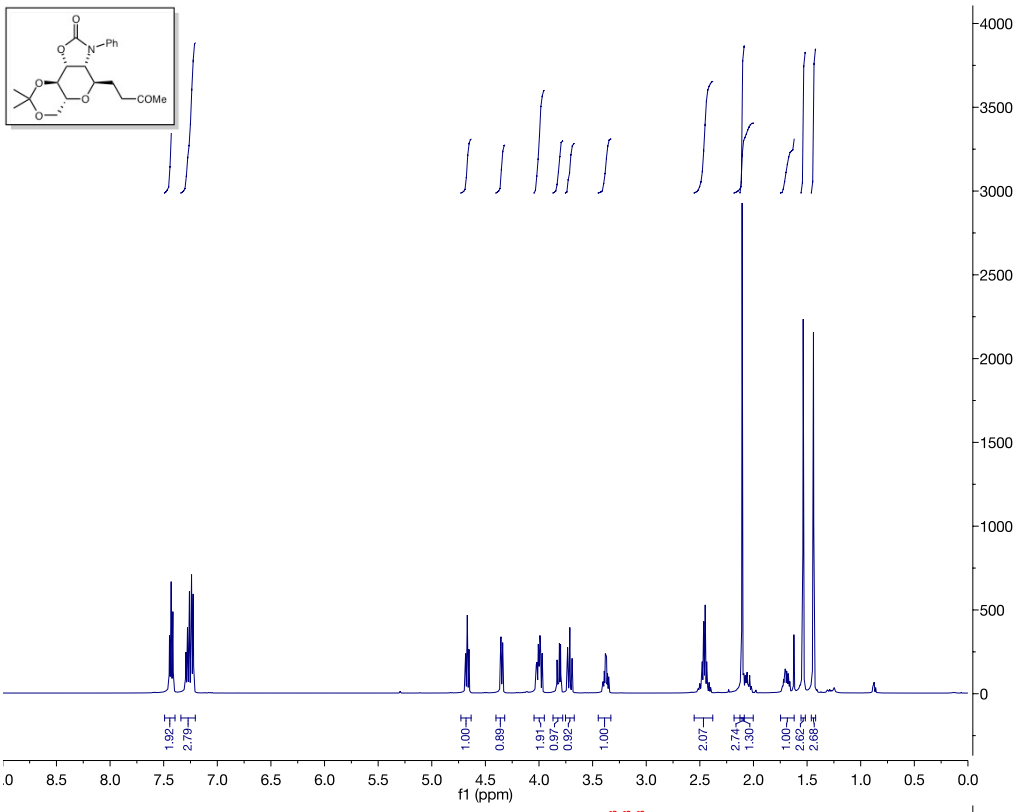
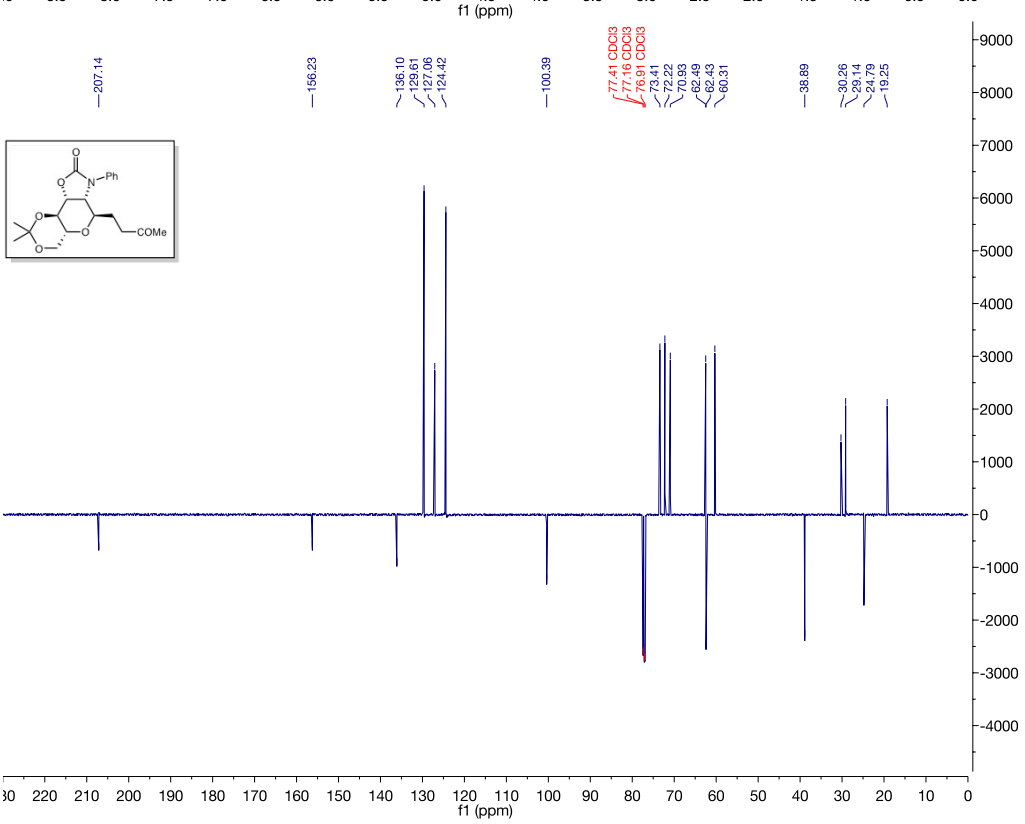
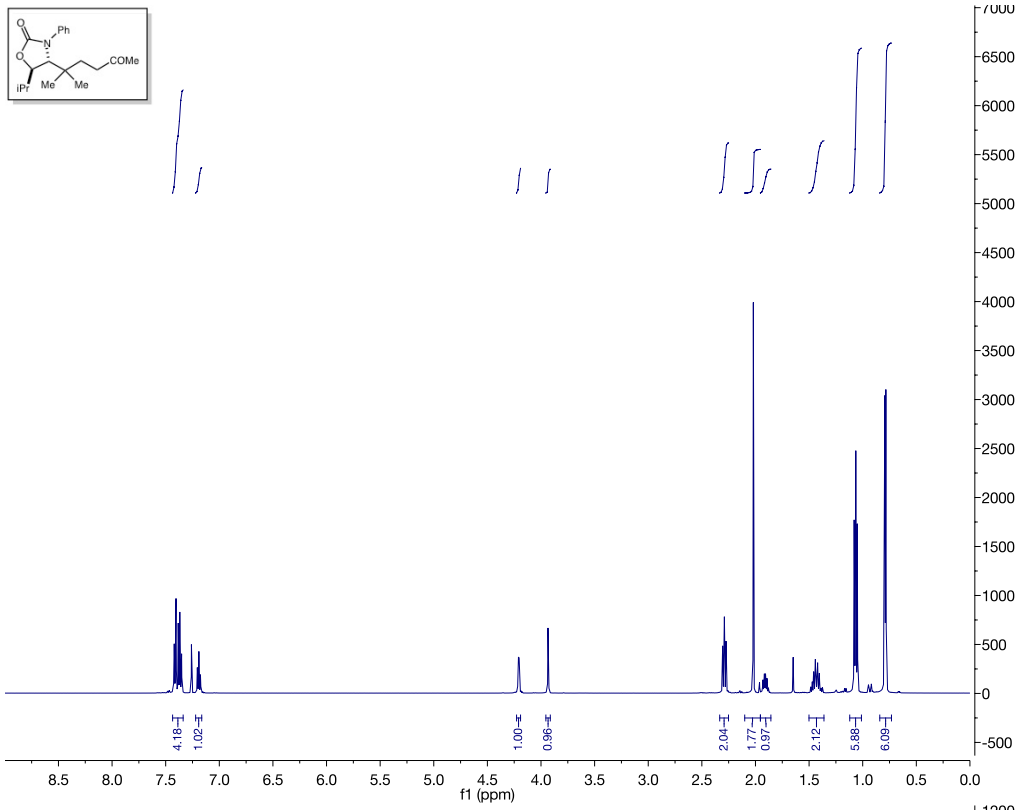
137.81
129.53
129.38
128.28
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
76.18
69.87
47.88
39.38
35.81
35.54
30.06
28.47
21.84
18.69
Ph
N
O
O
COMe
Me
f1 (ppm)

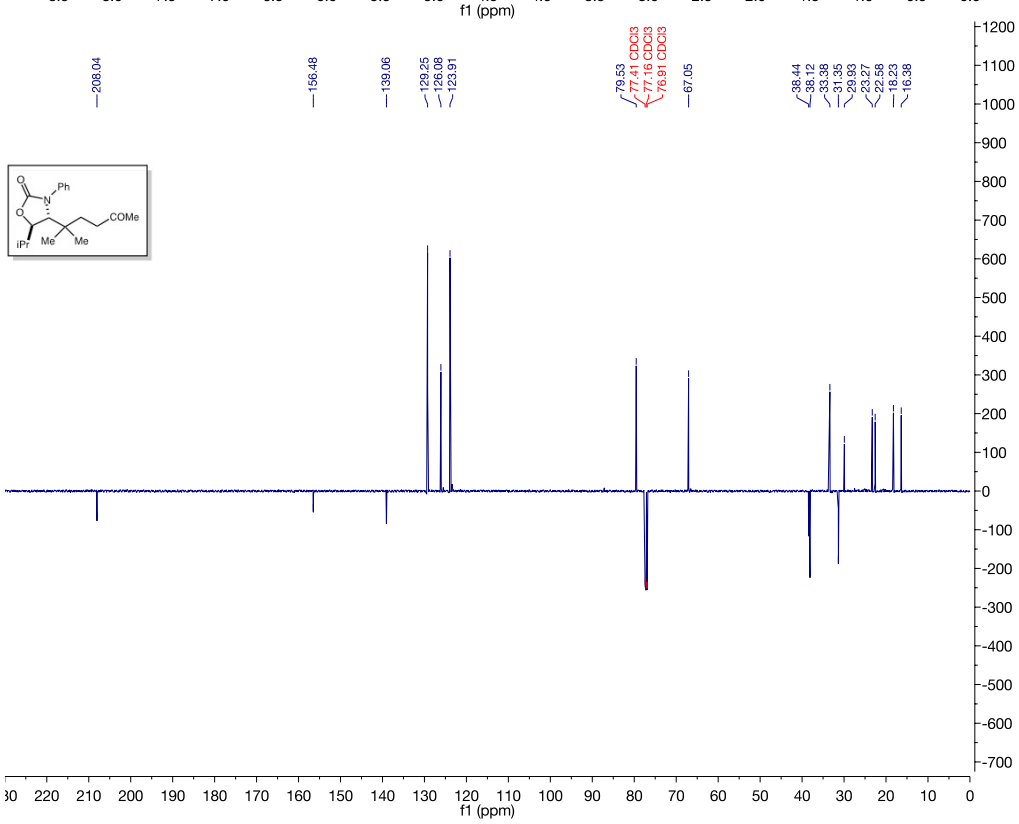

Ph
Me
COMe
1.83
1.98
0.92
1.00
0.90
1.13
2.05
2.65
2.16
0.92
1.01
1.99
1.02
2.95
f1 (ppm)

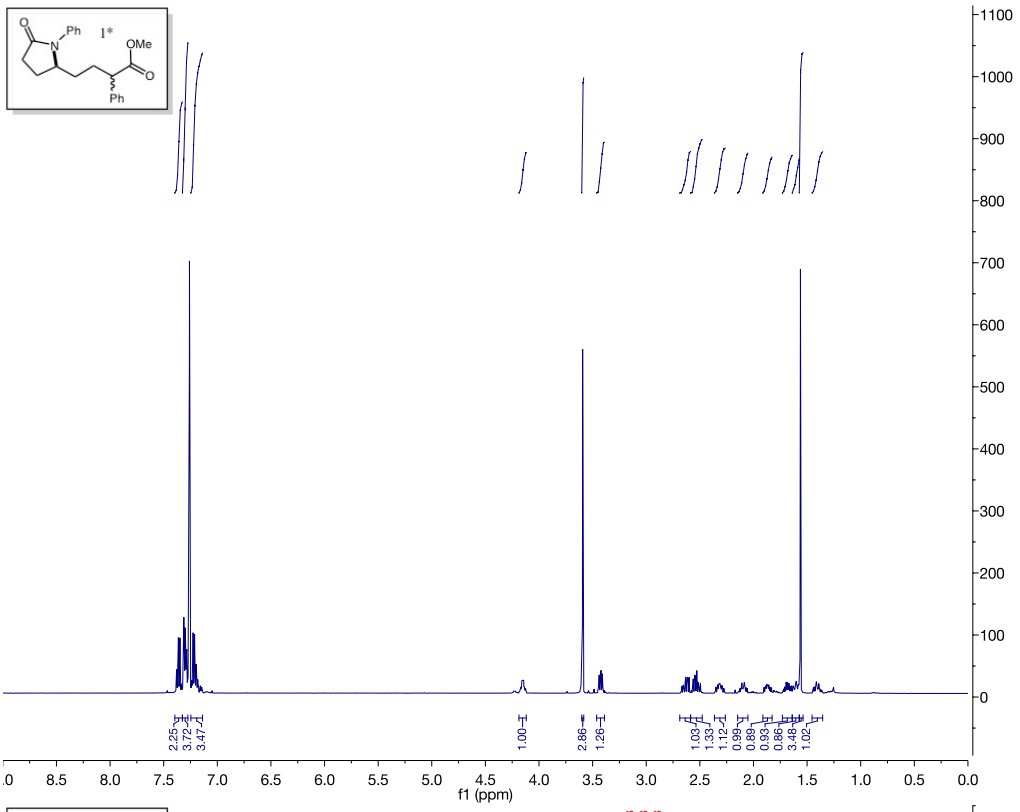

208.17
156.49
138.60
129.26
125.64
123.20
77.42 CDCl3
77.16 CDCl3
76.91 CDCl3
75.04
63.39
38.33
37.64
36.60
33.71
29.82
26.86
20.22
15.73
Ph
Me
COMe
f1 (ppm)

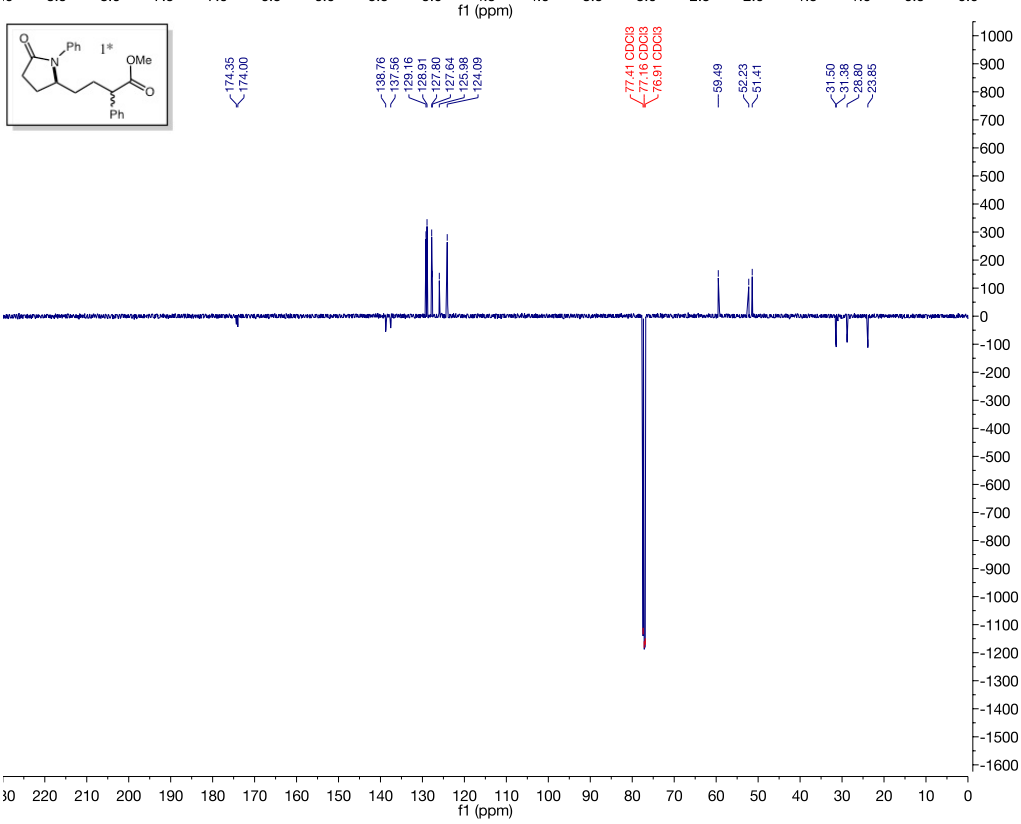

COMe
Ph
1.92
2.79
1.00
0.89
1.91
0.97
0.92
1.00
2.07
2.74
1.30
1.00
2.62
2.68
f1 (ppm)

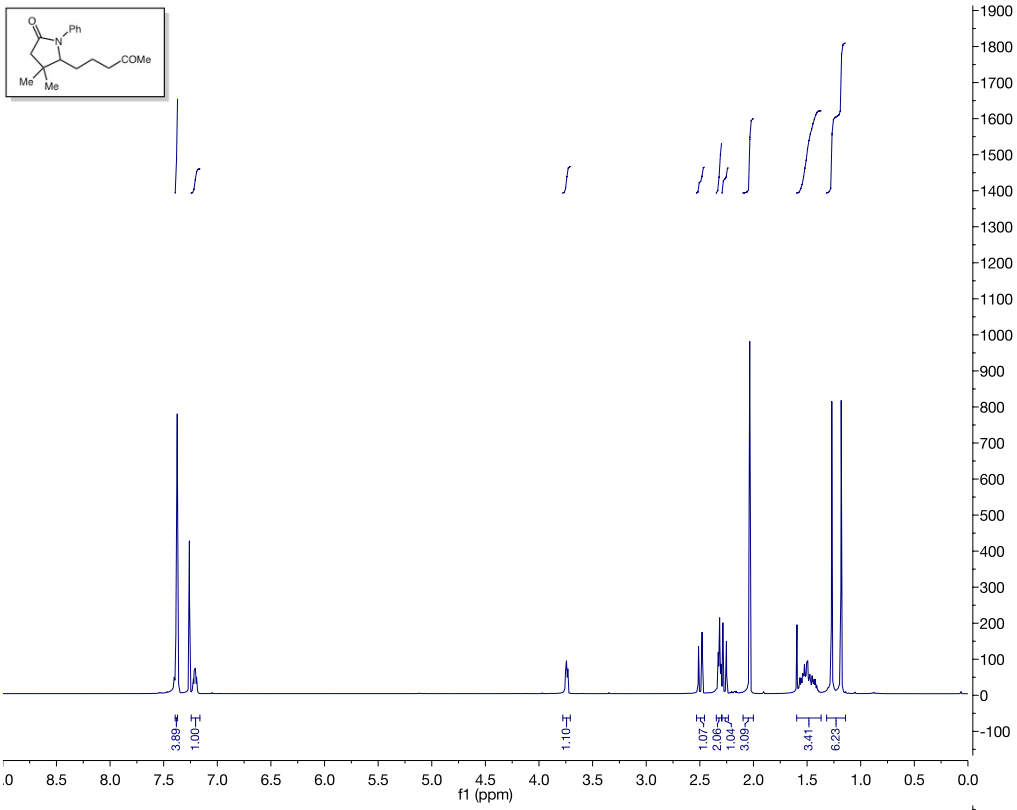

207.14
156.23
136.10
129.61
127.06
124.42
100.39
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
73.41
72.22
70.93
62.49
62.43
60.31
38.89
30.26
29.14
24.79
19.25
COMe
Ph
f1 (ppm)

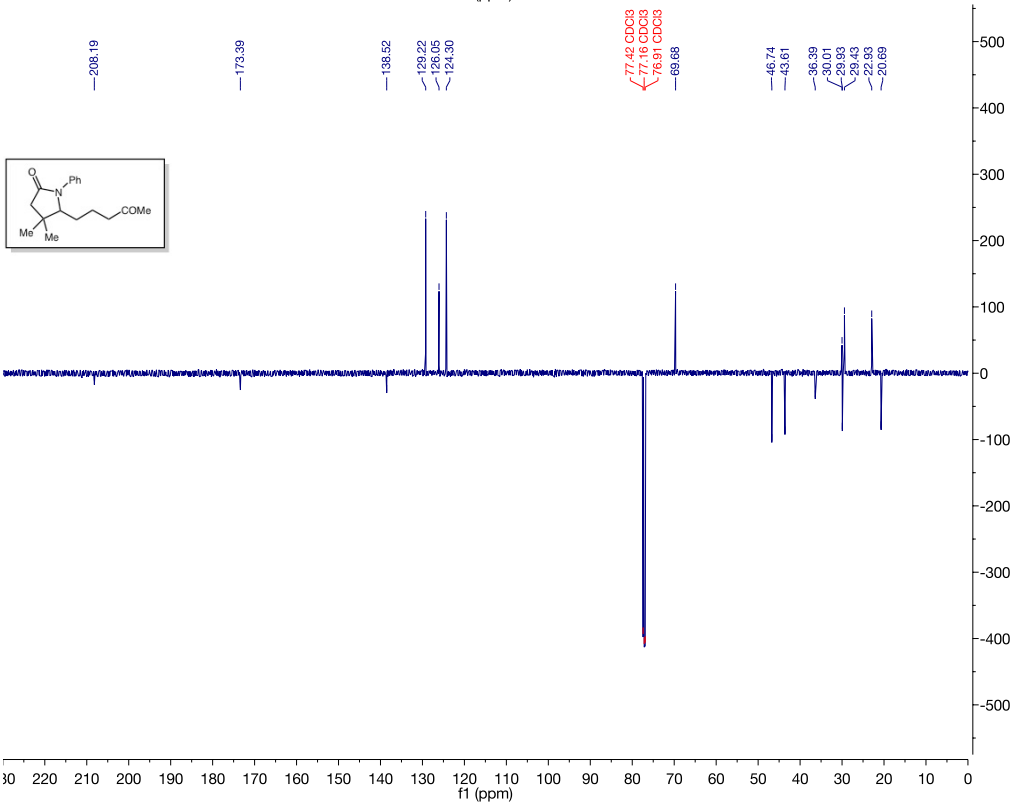

Ph
COMe
iPr
Me
Me
4.18
1.02
1.00
0.96
2.04
1.77
0.97
2.12
5.88
6.09
f1 (ppm)

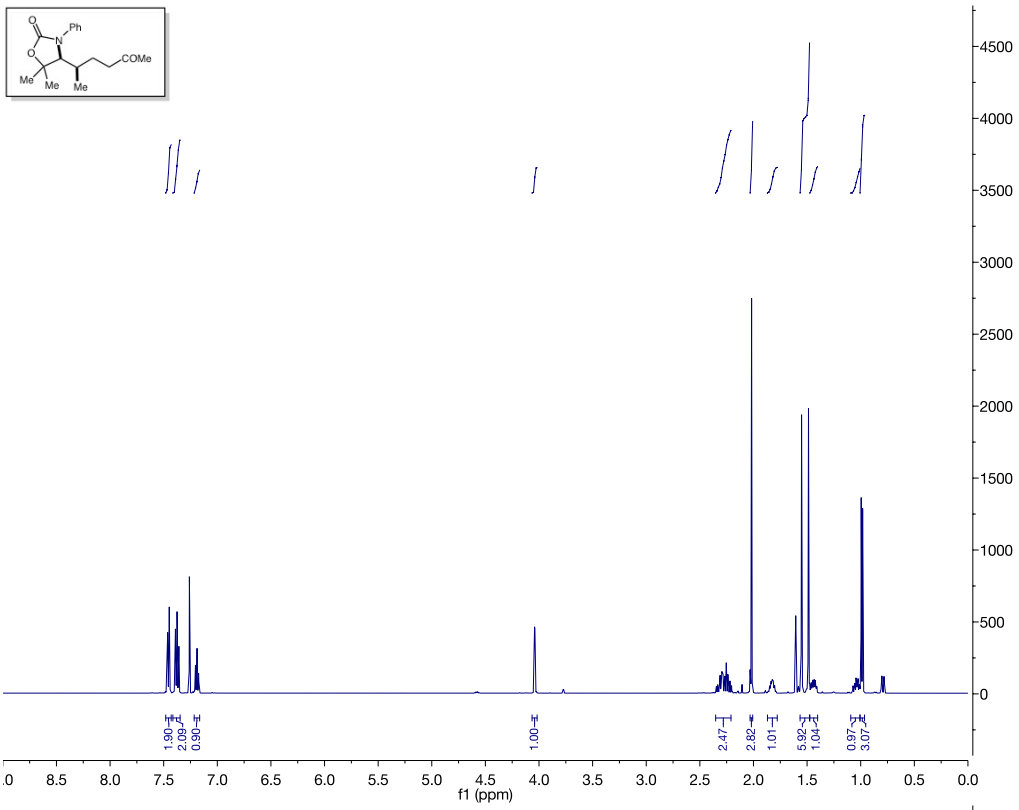

208.04
156.48
139.06
129.25
126.08
123.91
79.53
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
67.05
38.44
38.12
33.38
31.35
29.93
23.27
22.58
18.23
16.38
Ph
COMe
iPr
Me
Me
f1 (ppm)

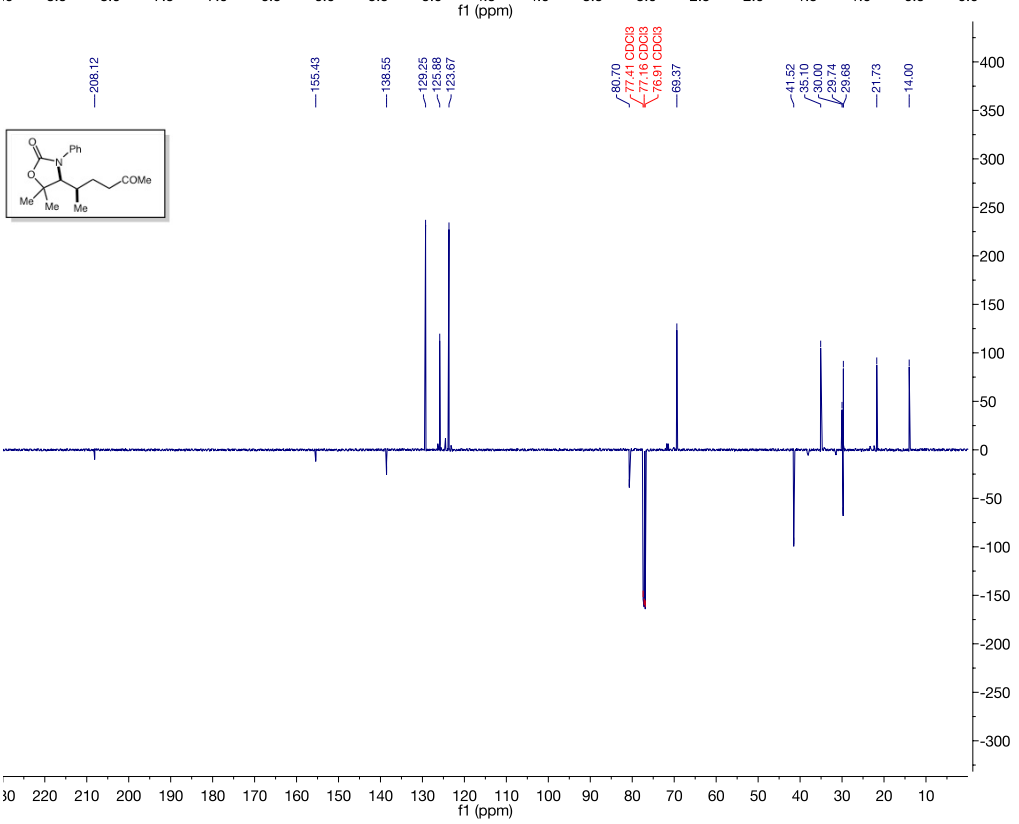

1*
OMe
Ph
Ph
2.25
3.72
3.47
1.00
2.86
1.26
1.03
1.33
1.12
0.99
0.89
0.93
0.86
3.48
1.02
f1 (ppm)

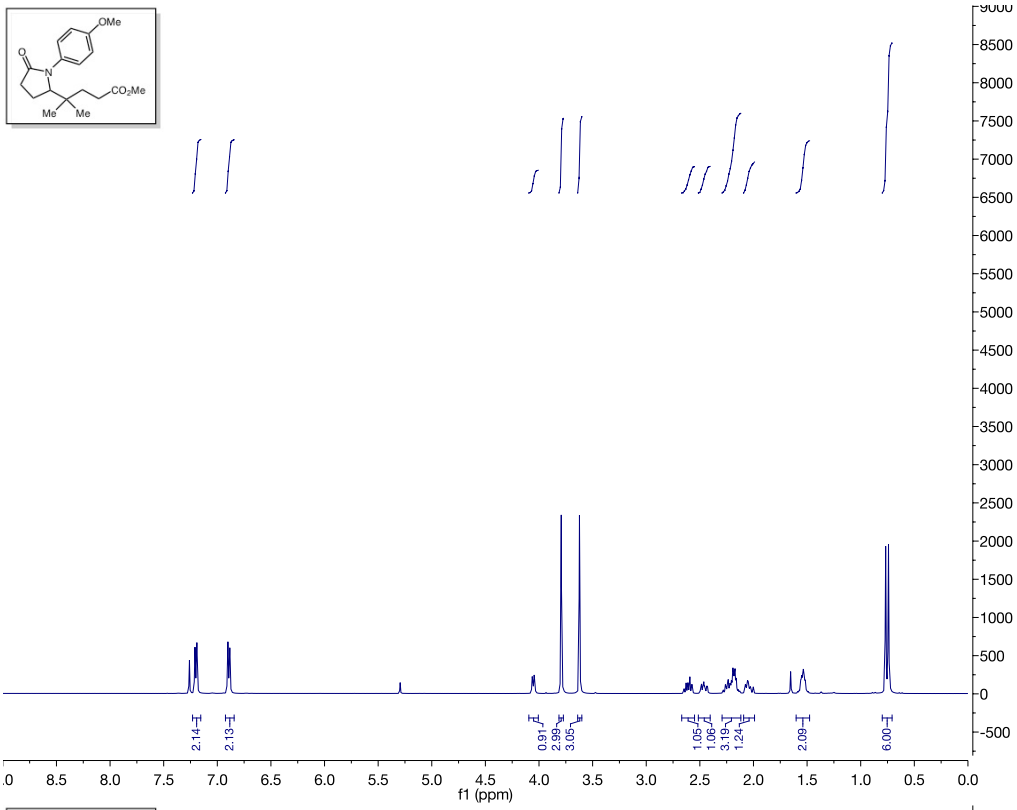

1*
OMe
Ph
Ph
174.35
174.00
138.76
137.56
129.16
128.91
127.80
127.64
125.98
124.09
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
59.49
52.23
51.41
31.50
31.38
28.80
23.85
f1 (ppm)

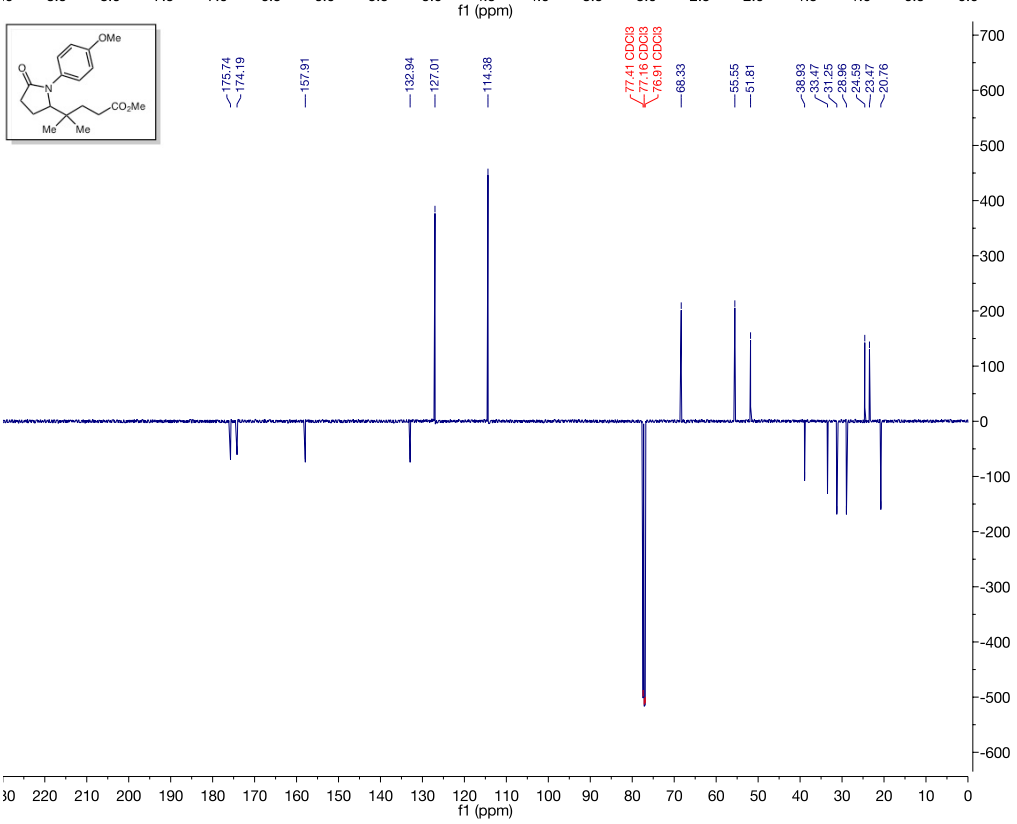

Ph
N
O
COMe
Me
Me
3.89
1.00
1.10
1.07
2.06
1.04
3.09
3.41
6.23
f1 (ppm)

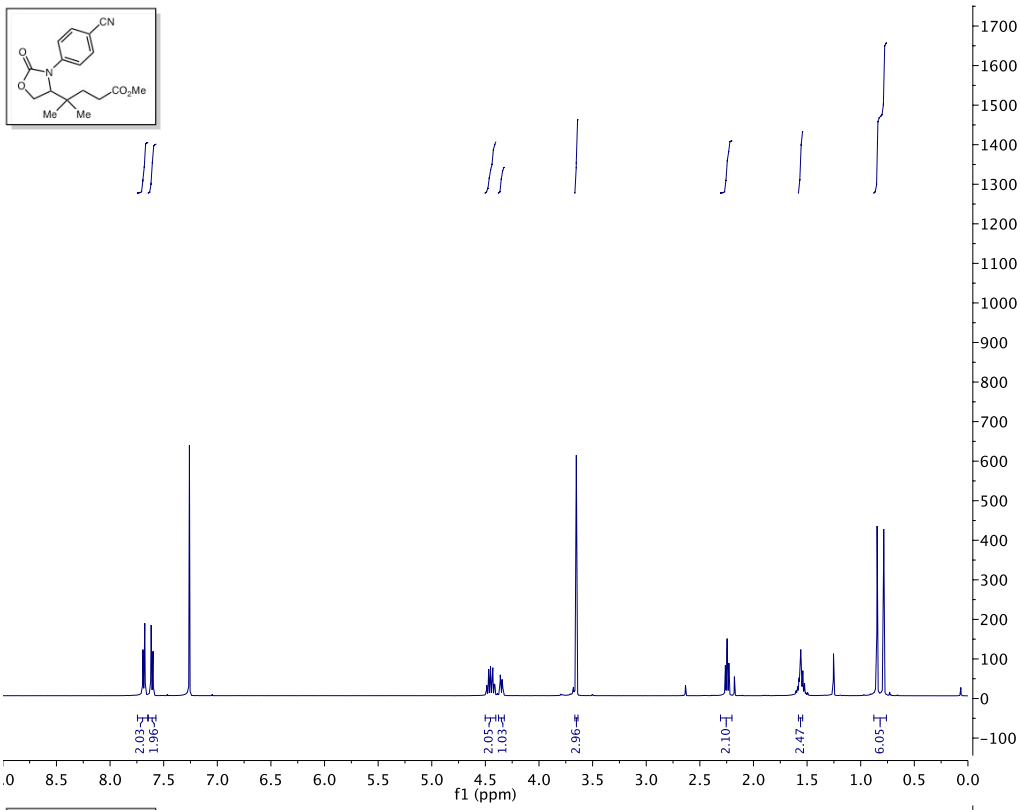

208.19
173.39
138.52
129.22
126.05
124.30
77.42 CDCl3
77.16 CDCl3
76.91 CDCl3
69.68
46.74
43.61
36.39
30.01
29.93
29.43
22.93
20.69
Ph
N
O
COMe
Me
Me
f1 (ppm)

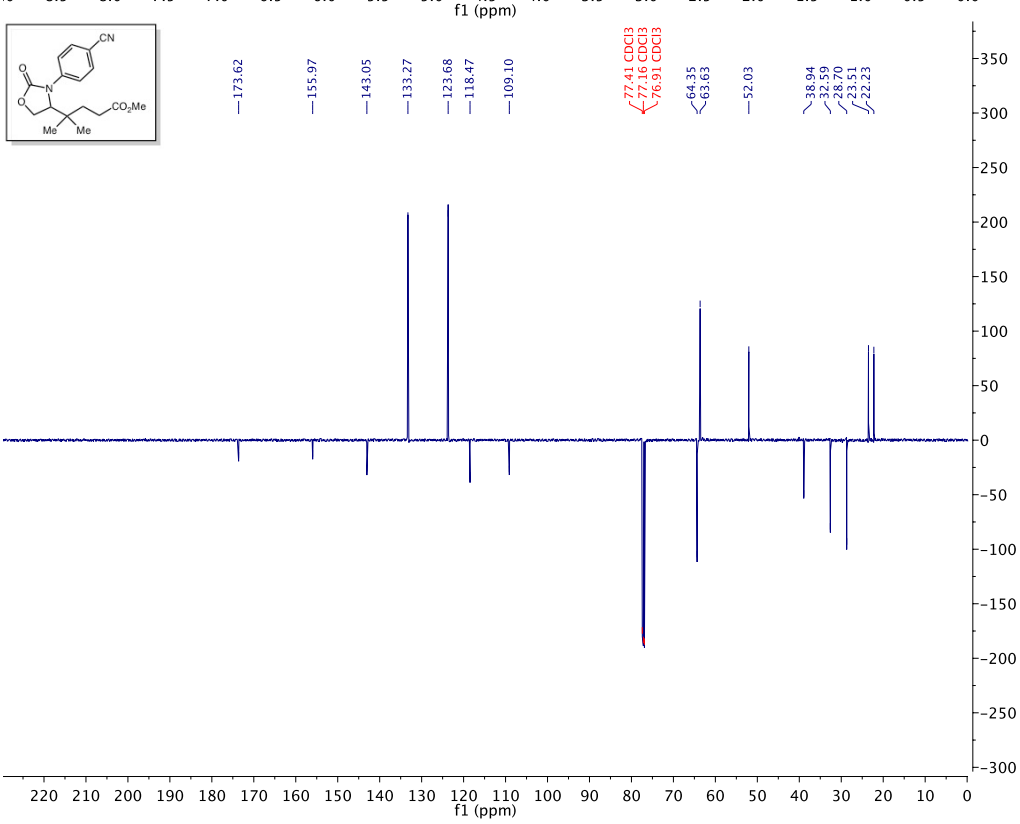

Ph
COMe
Me
Me
Me
1.90
2.09
0.90
1.00
2.47
2.82
1.01
5.92
1.04
0.97
3.07
f1 (ppm)

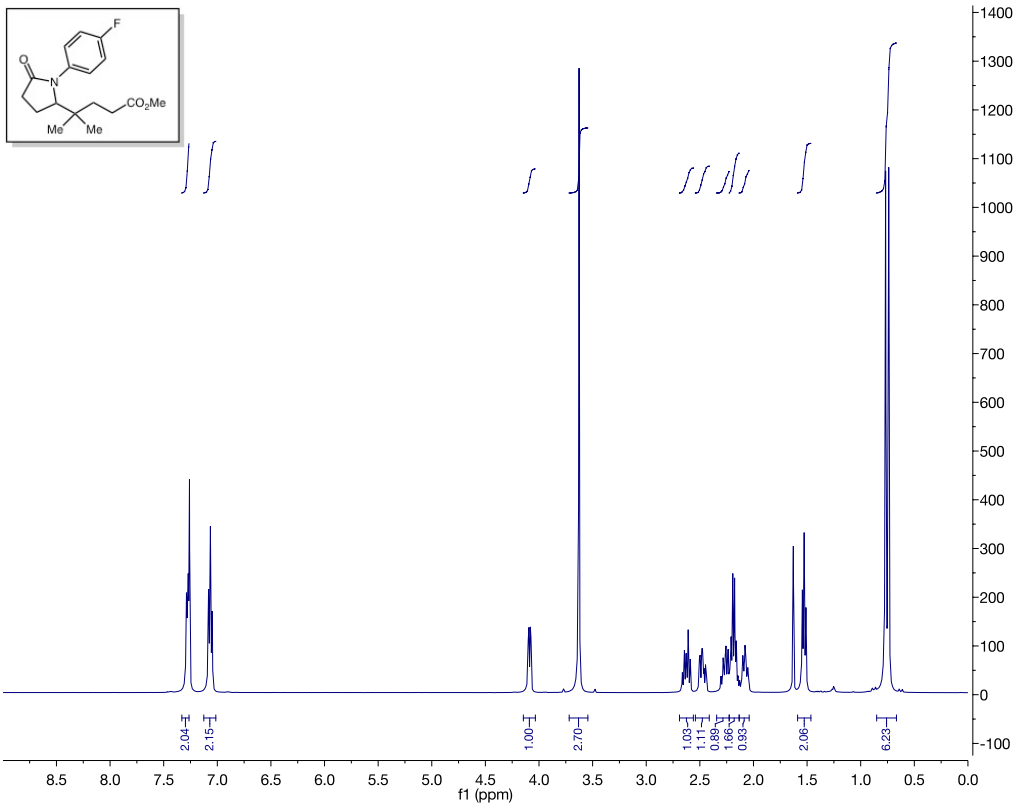

208.12
155.43
138.55
129.25
125.88
123.67
80.70
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
69.37
41.52
35.10
30.00
29.74
29.68
21.73
14.00
Ph
COMe
Me
Me
Me
f1 (ppm)

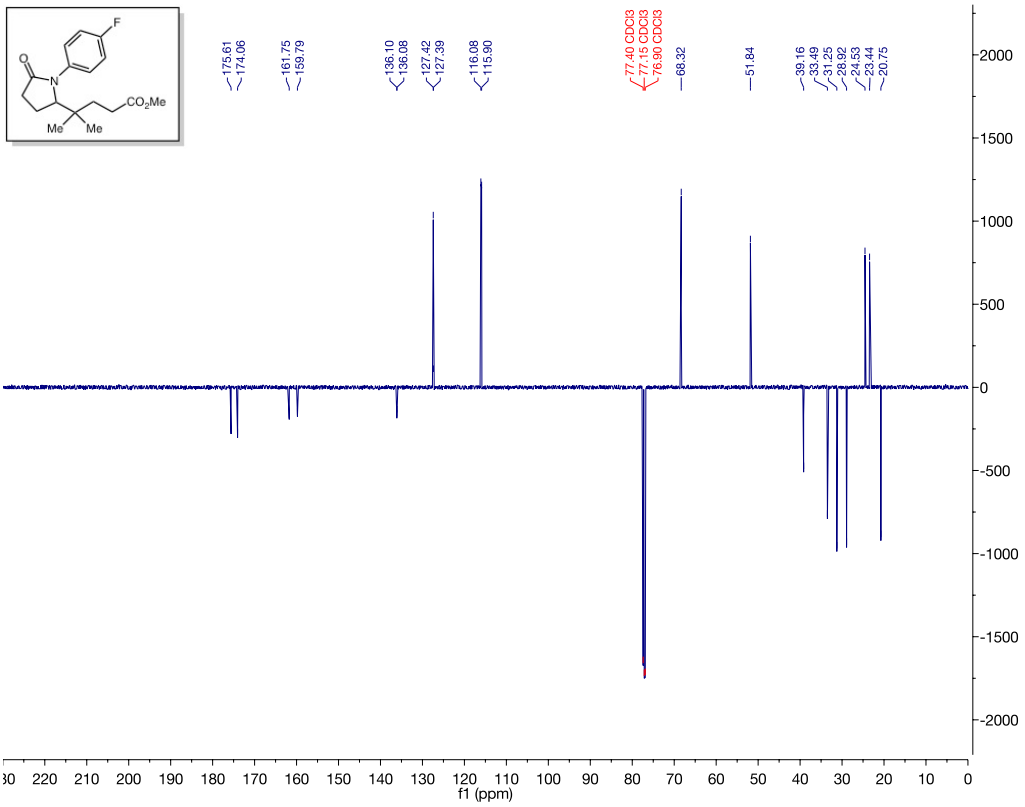

OMe
O
N
CO2Me
Me
Me
2.14
2.13
0.91
2.99
3.05
1.05
1.06
3.19
1.24
2.09
6.00
f1 (ppm)

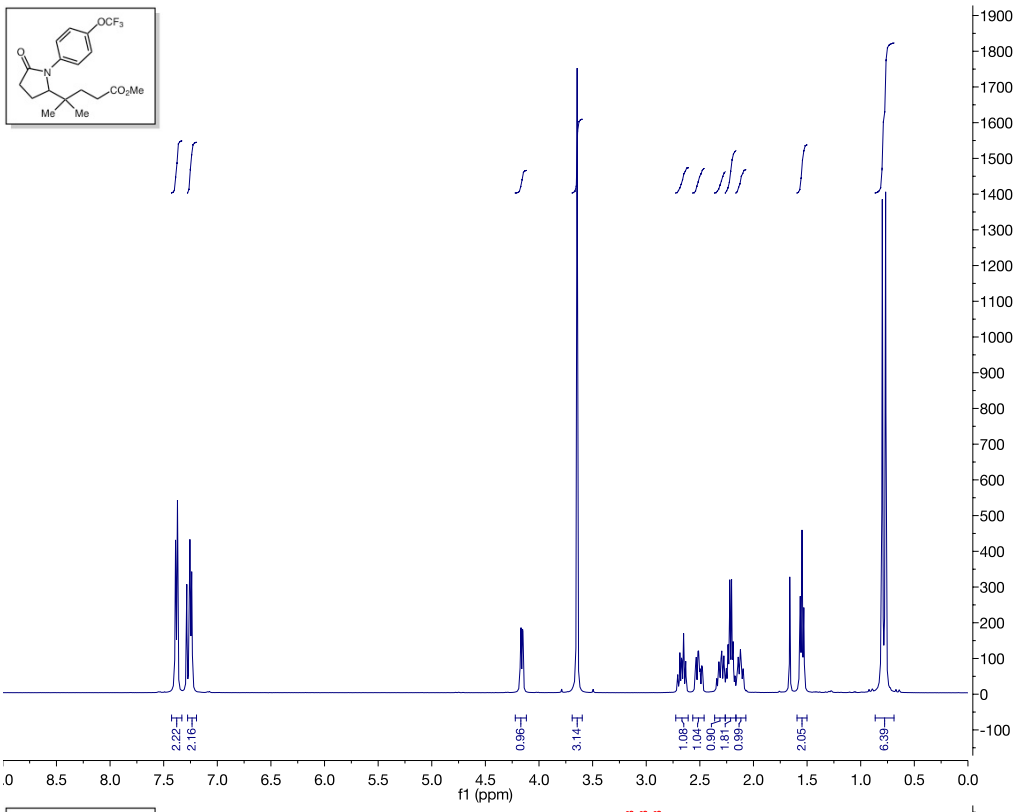

OMe
O
N
CO2Me
Me
Me
175.74
174.19
157.91
132.94
127.01
114.38
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
68.33
55.55
51.81
38.93
33.47
31.25
28.96
24.59
23.47
20.76
f1 (ppm)

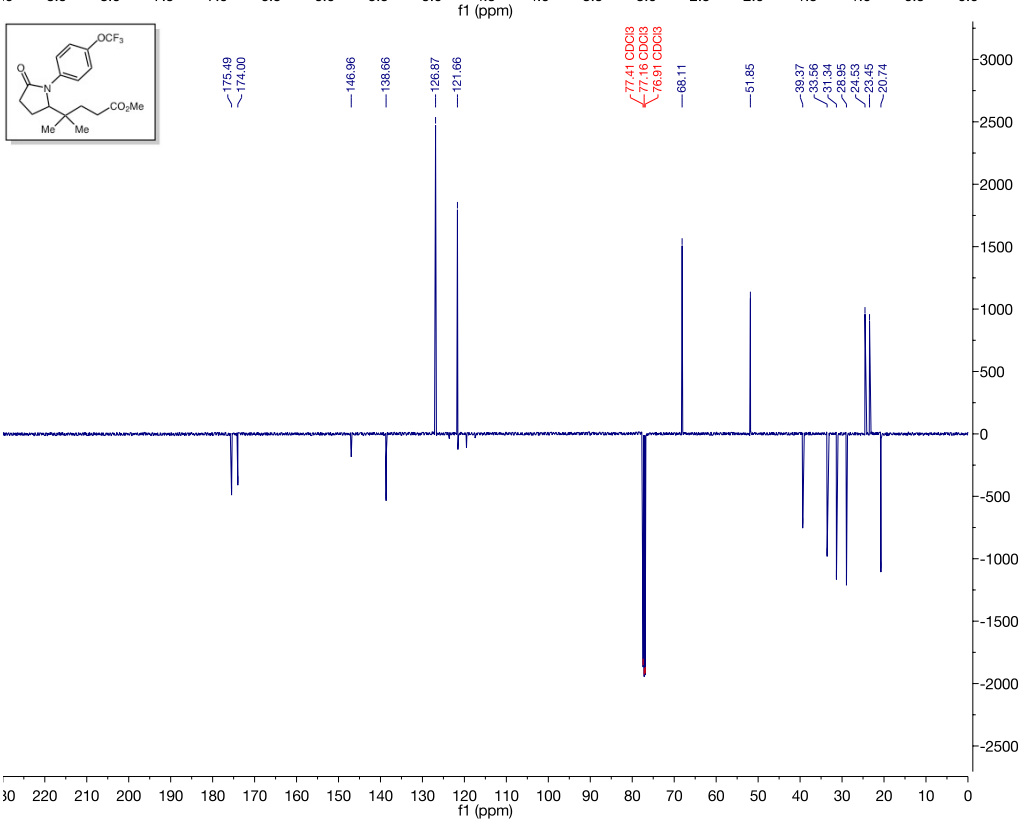

CN
O
N
O
CO2Me
Me
Me
2.03
1.96
2.05
1.03
2.96
2.10
2.47
6.05
f1 (ppm)

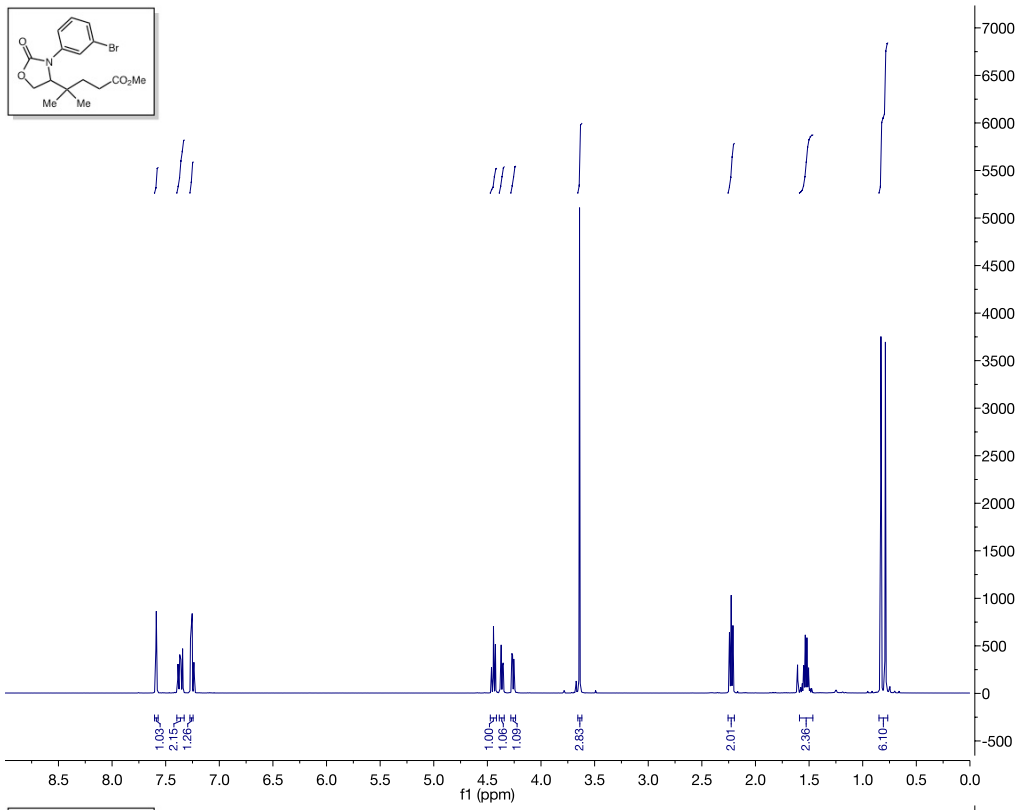

CN
O
N
O
CO2Me
Me
Me
173.62
155.97
143.05
133.27
123.68
118.47
109.10
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
64.35
63.63
52.03
38.94
32.59
28.70
23.51
22.23
f1 (ppm)

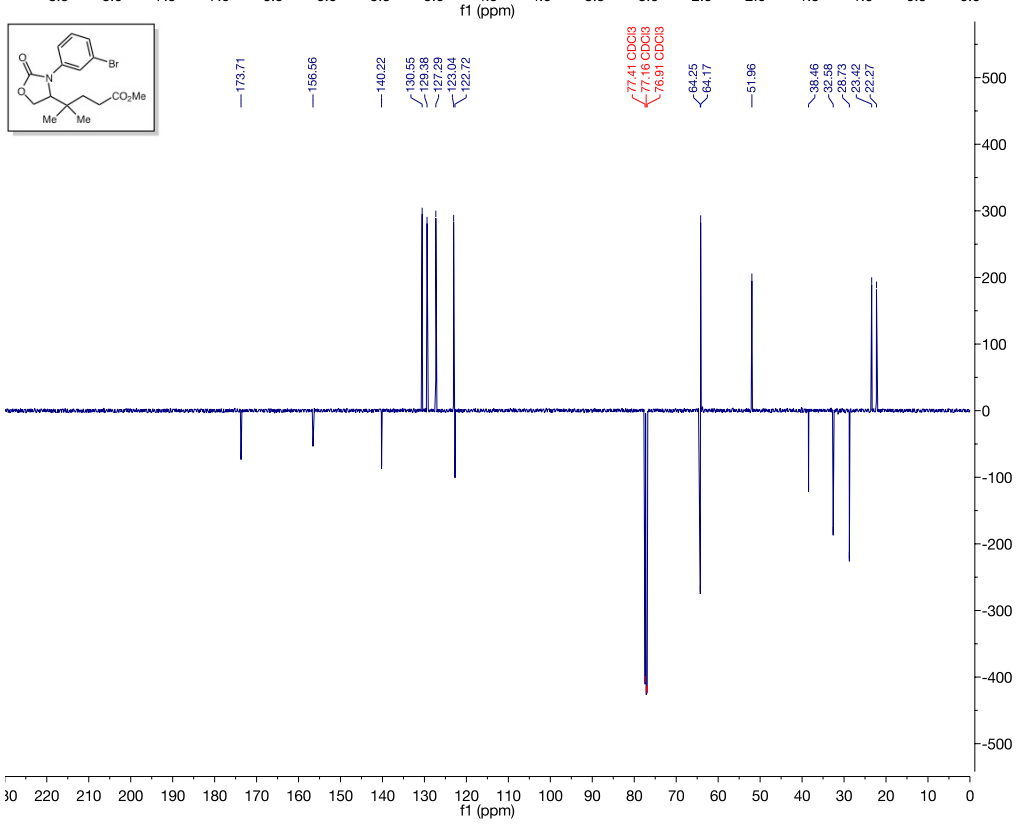

F
O
N
CO2Me
Me
Me
2.04
2.15
1.00
2.70
1.03
1.11
0.89
1.66
0.93
2.06
6.23
f1 (ppm)

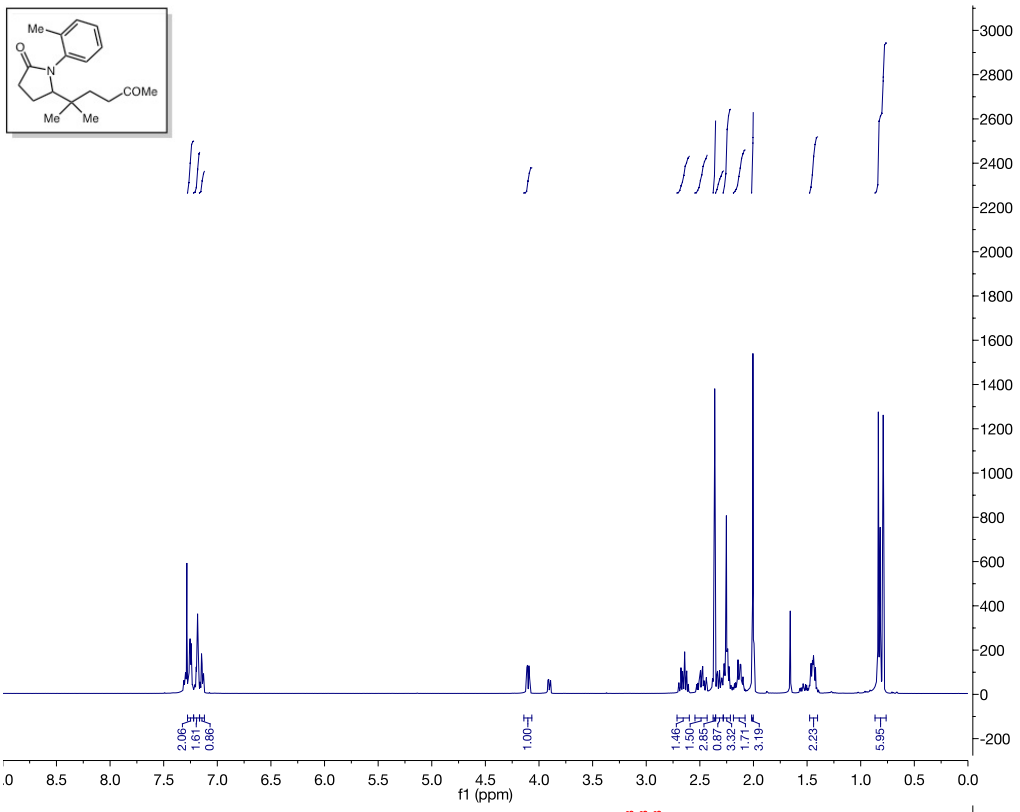

F
O
N
CO2Me
Me
Me
175.61
174.06
161.75
159.79
136.10
136.08
127.42
127.39
116.08
115.90
77.40 CDCl3
77.15 CDCl3
76.90 CDCl3
68.32
51.84
39.16
33.49
31.25
28.92
24.53
23.44
20.75
f1 (ppm)

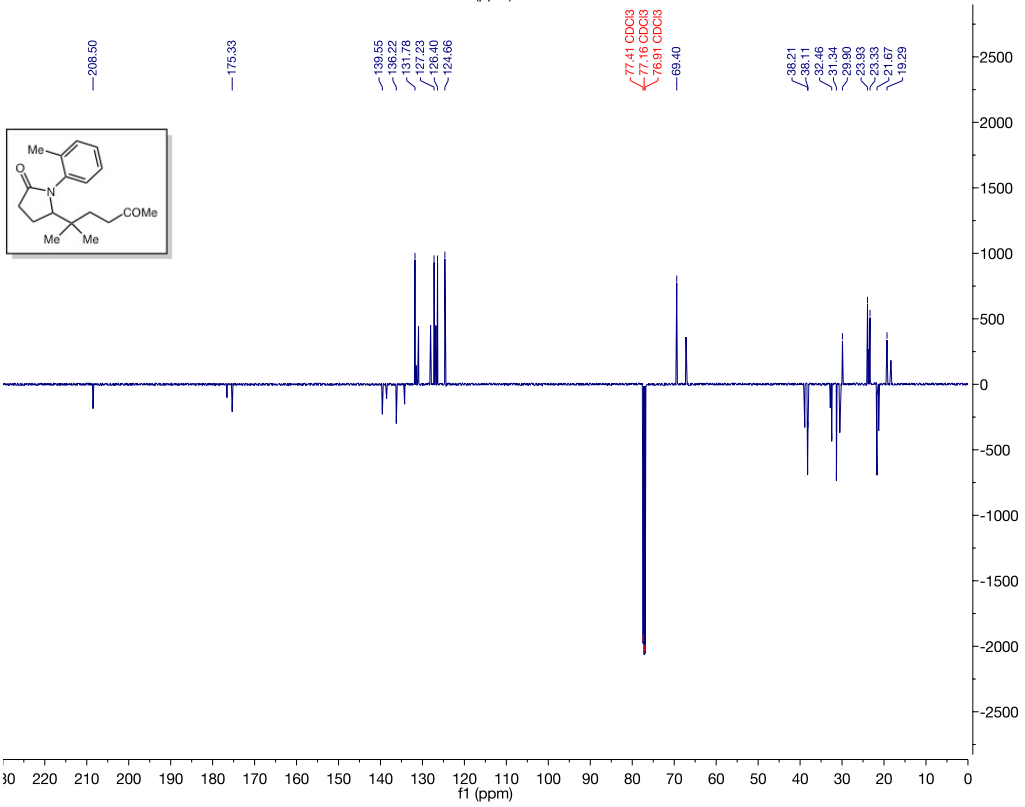

OCF3
CO2Me
Me
Me
2.22
2.16
0.96
3.14
1.08
1.04
0.90
1.81
0.99
2.05
6.39
f1 (ppm)

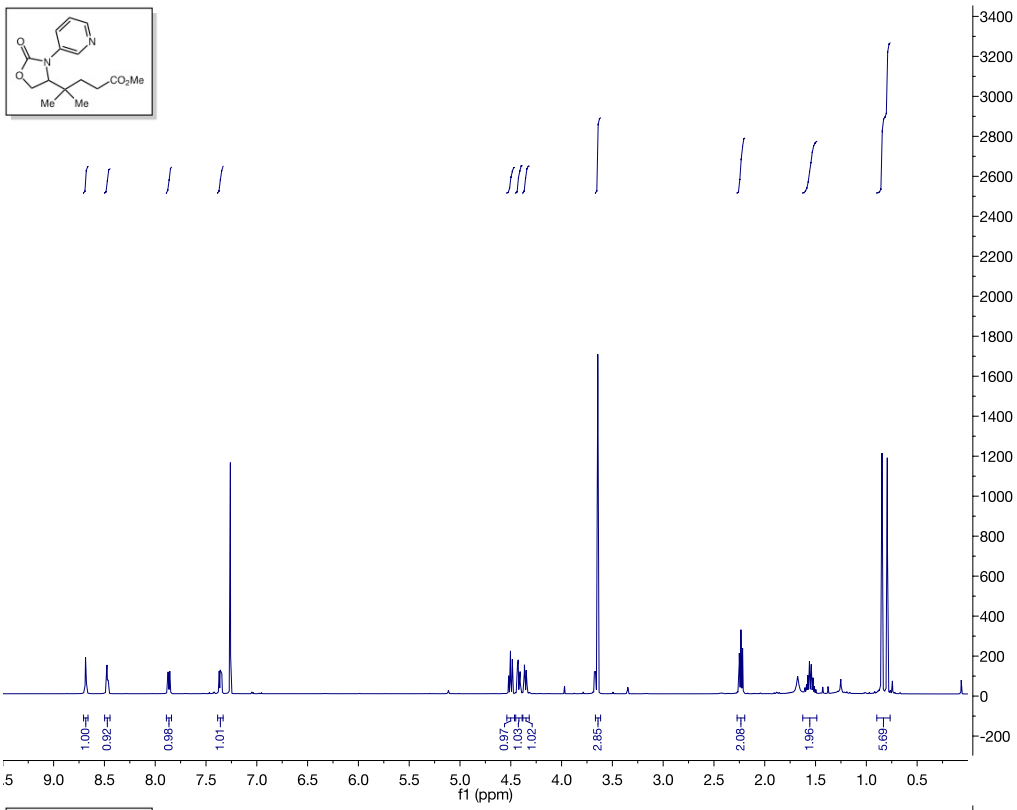

OCF3
CO2Me
Me
Me
175.49
174.00
146.96
138.66
126.87
121.66
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
68.11
51.85
39.37
33.56
31.34
28.95
24.53
23.45
20.74
f1 (ppm)

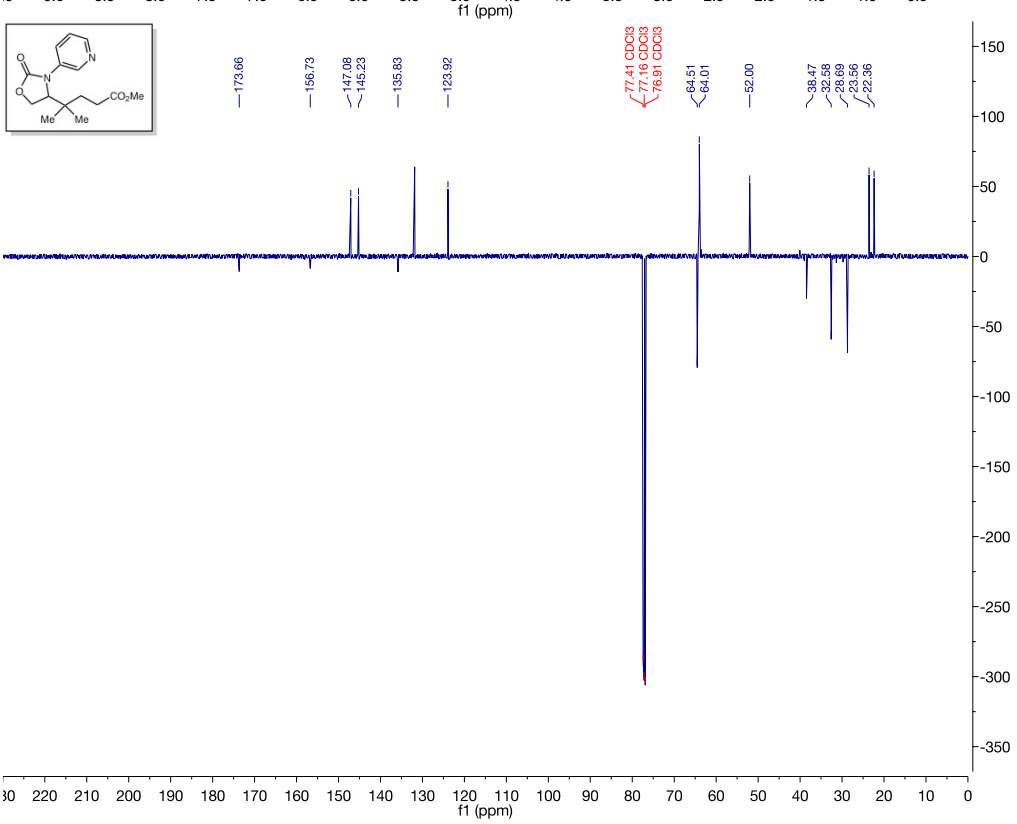

Br
CO2Me
Me
Me
1.03
2.15
1.26
1.00
1.06
1.09
2.83
2.01
2.36
6.10
f1 (ppm)


Br
CO2Me
Me
Me
173.71
156.56
140.22
130.55
129.38
127.29
123.04
122.72
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
64.25
64.17
51.96
38.46
32.58
28.73
23.42
22.27
f1 (ppm)


Me
O
N
COMe
Me
Me
2.06
1.61
0.86
1.00
1.46
1.50
2.85
0.87
3.32
1.71
3.19
2.23
5.95
f1 (ppm)


208.50
175.33
139.55
136.22
131.78
127.23
126.40
124.66
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
69.40
38.21
38.11
32.46
31.34
29.90
29.89
23.33
21.67
19.29
Me
O
N
COMe
Me
Me
f1 (ppm)


1.00
0.92
0.98
1.01
0.97
1.03
1.02
2.85
2.08
1.96
5.69
f1 (ppm)


173.66
156.73
147.08
145.23
135.83
123.92
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
64.51
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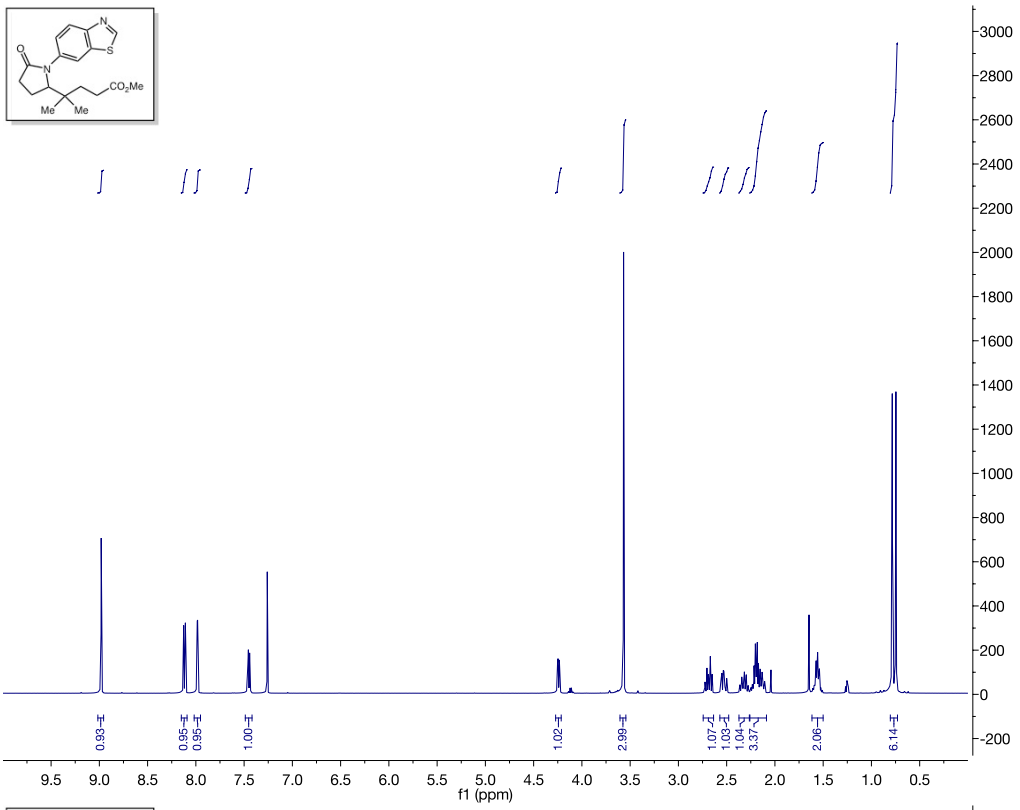
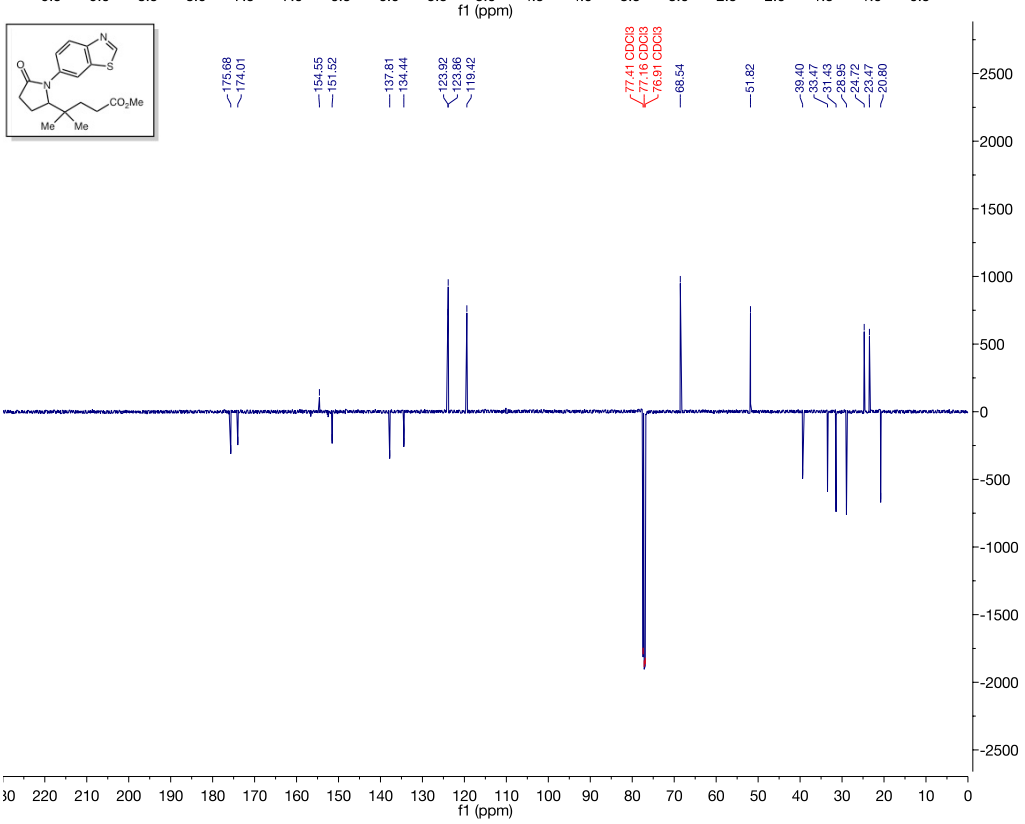
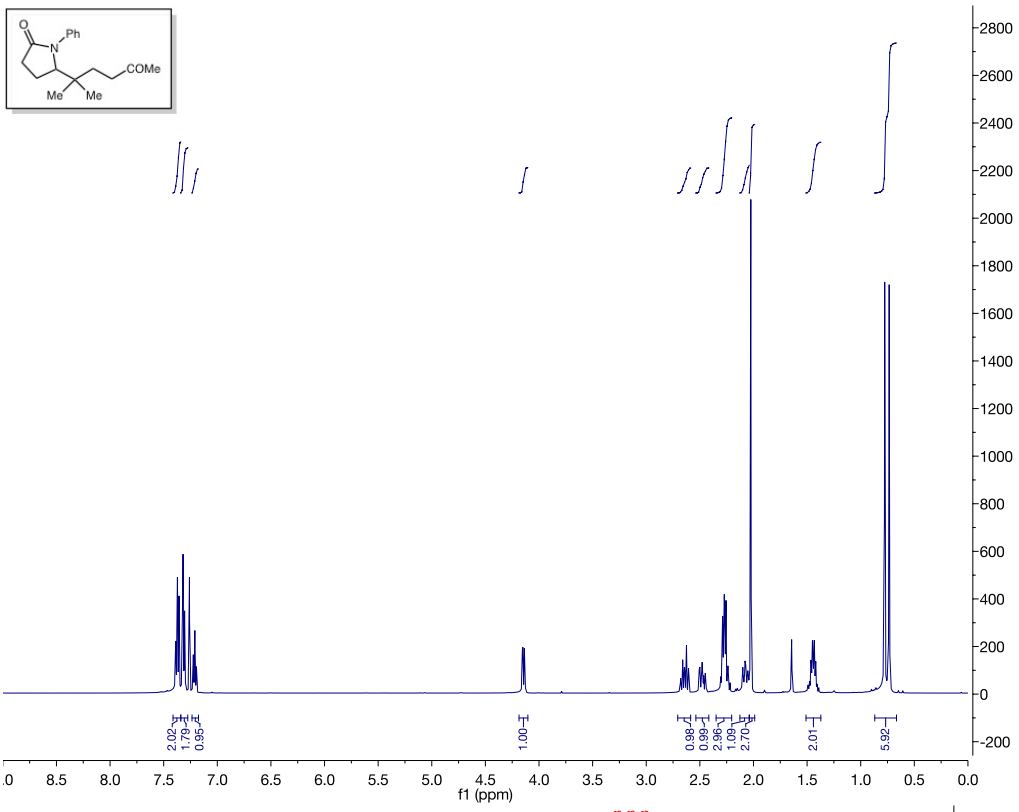
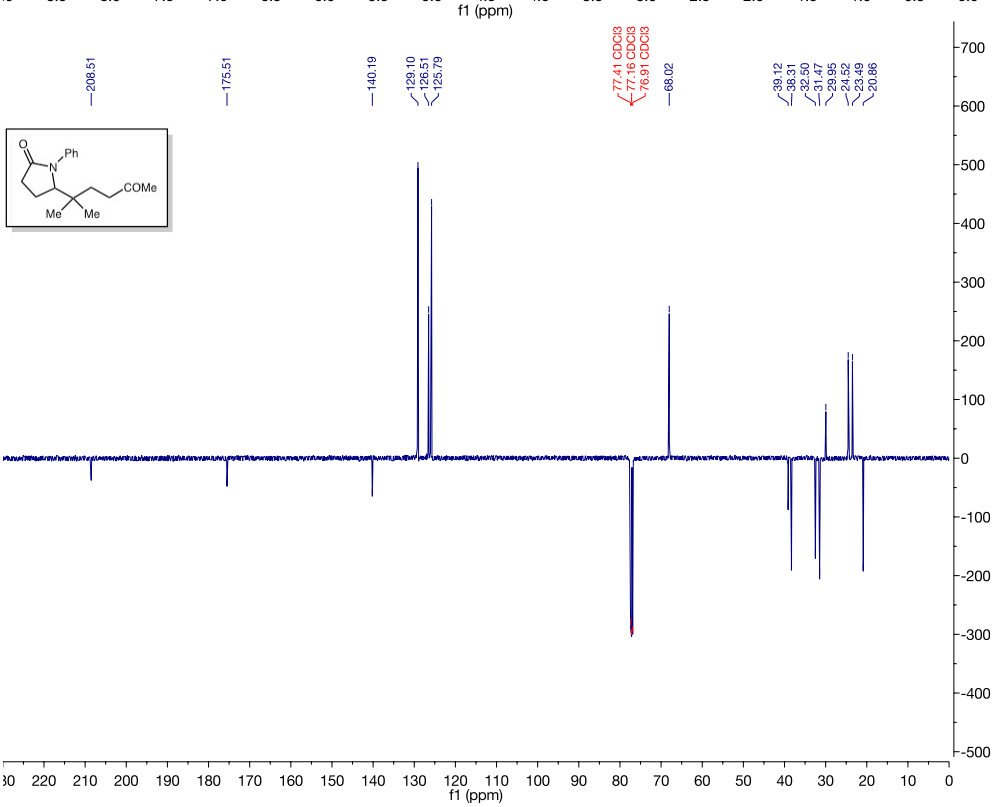
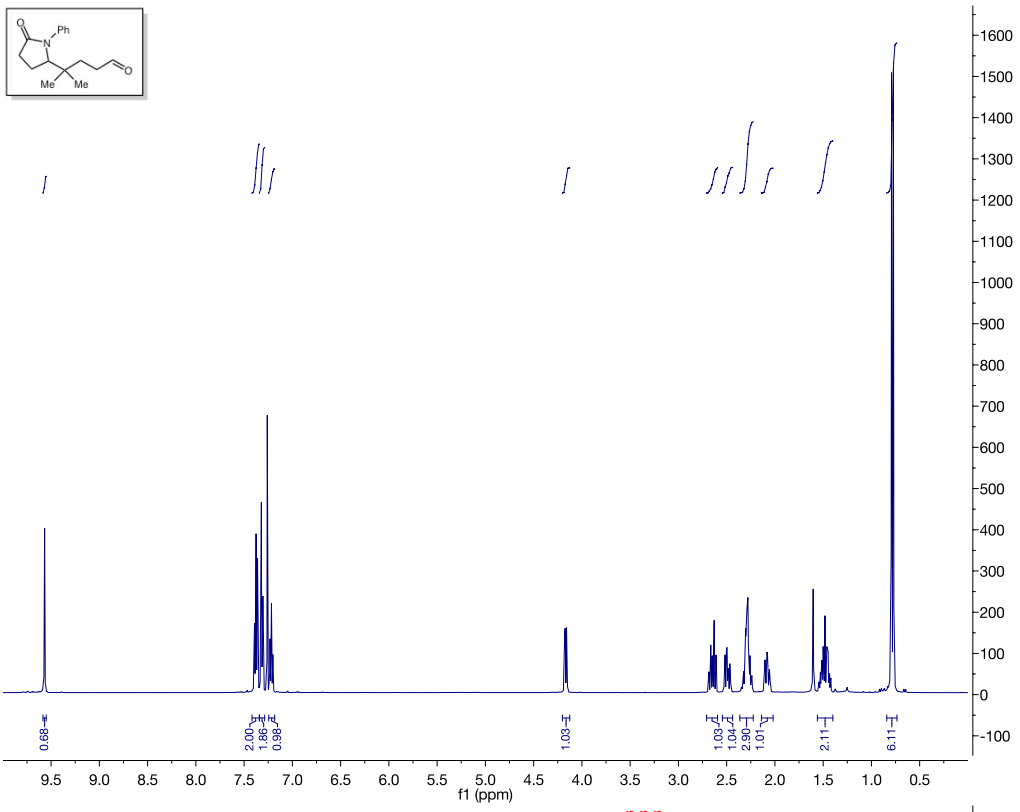
38.47
32.58
28.69
23.56
22.36
f1 (ppm)

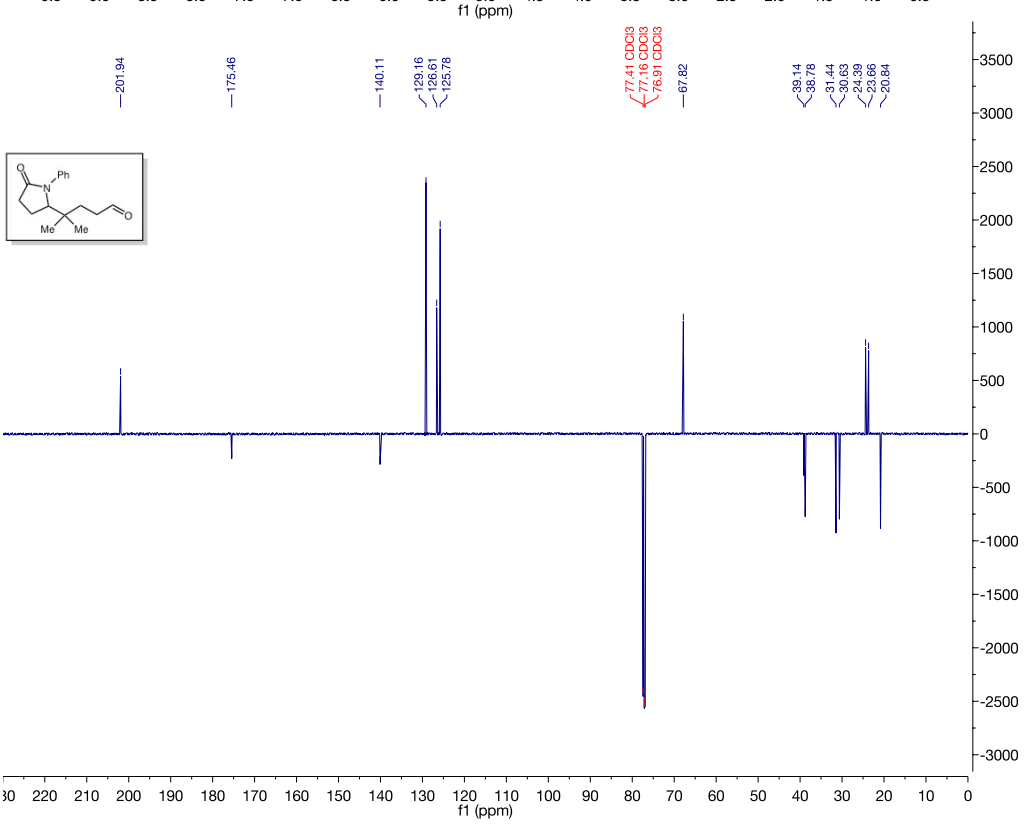

0.93
0.95
0.95
1.00
1.02
2.99
1.07
1.03
1.04
3.37
2.06
6.14
f1 (ppm)

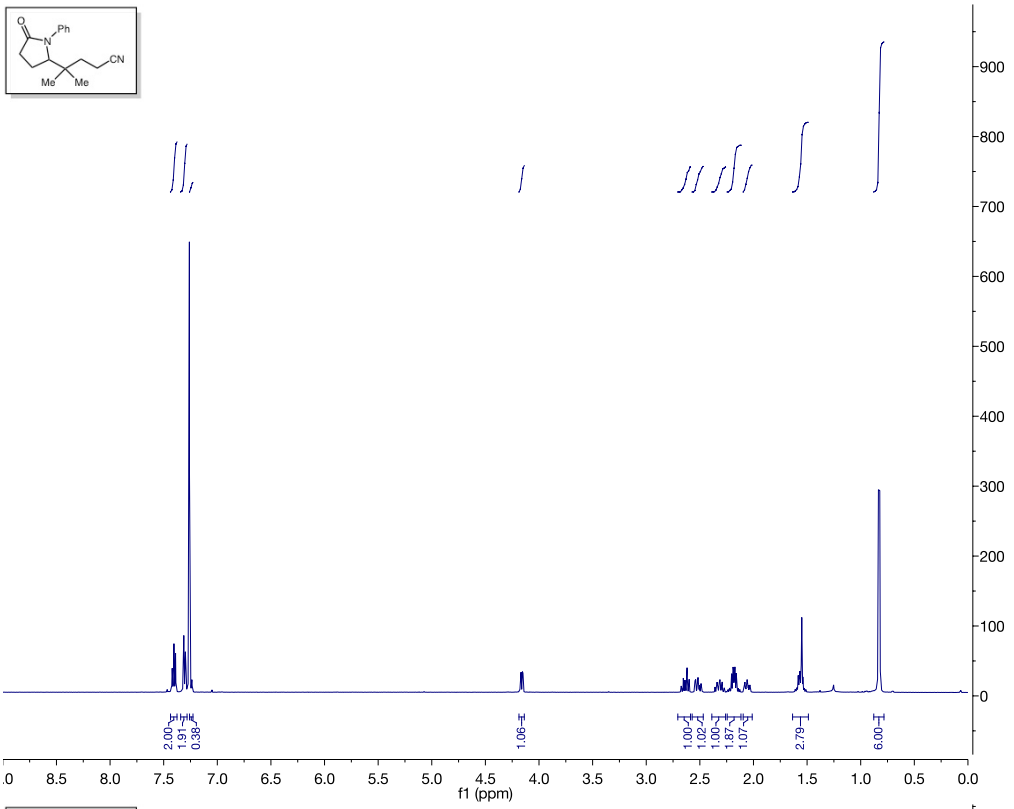

175.68
174.01
154.55
151.52
137.81
134.44
123.92
123.86
119.42
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
68.54
51.82
39.40
33.47
31.43
28.95
24.72
23.47
20.80
f1 (ppm)

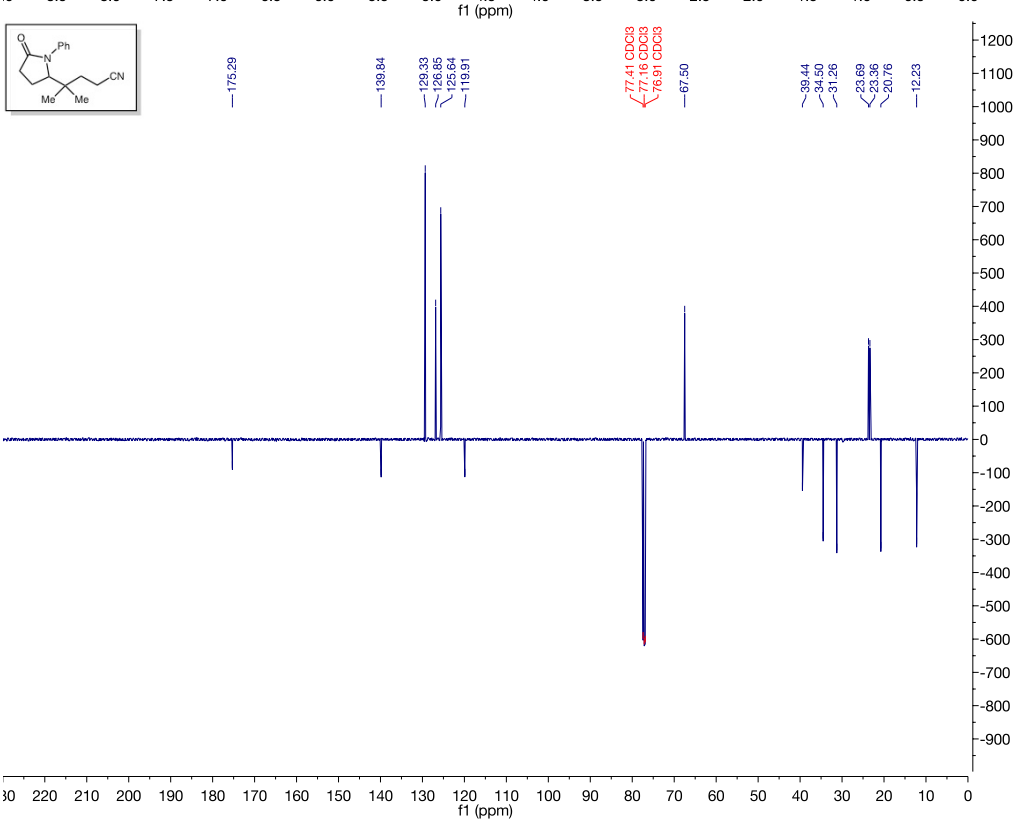

Ph
N
O
COMe
Me
Me
2.02
1.79
0.95
1.00
0.98
0.99
2.96
1.09
2.70
2.01
5.92
f1 (ppm)

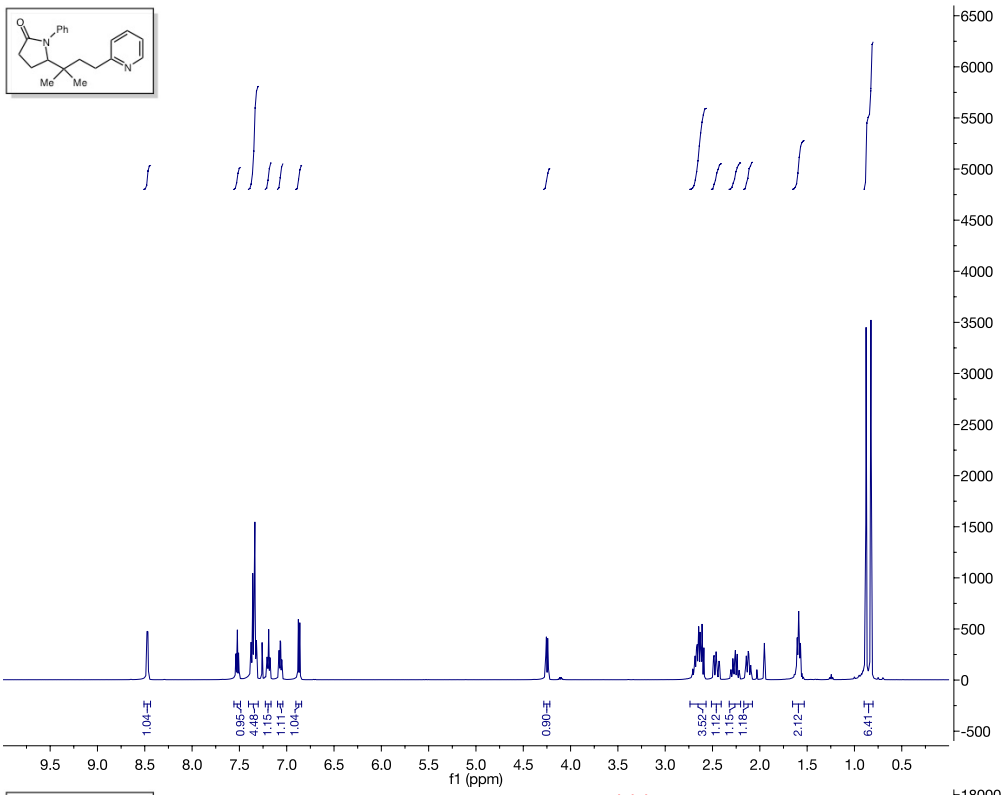

208.51
175.51
140.19
129.10
126.51
125.79
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
68.02
39.12
38.31
32.50
31.47
29.95
24.52
23.49
20.86
Ph
N
O
COMe
Me
Me
f1 (ppm)

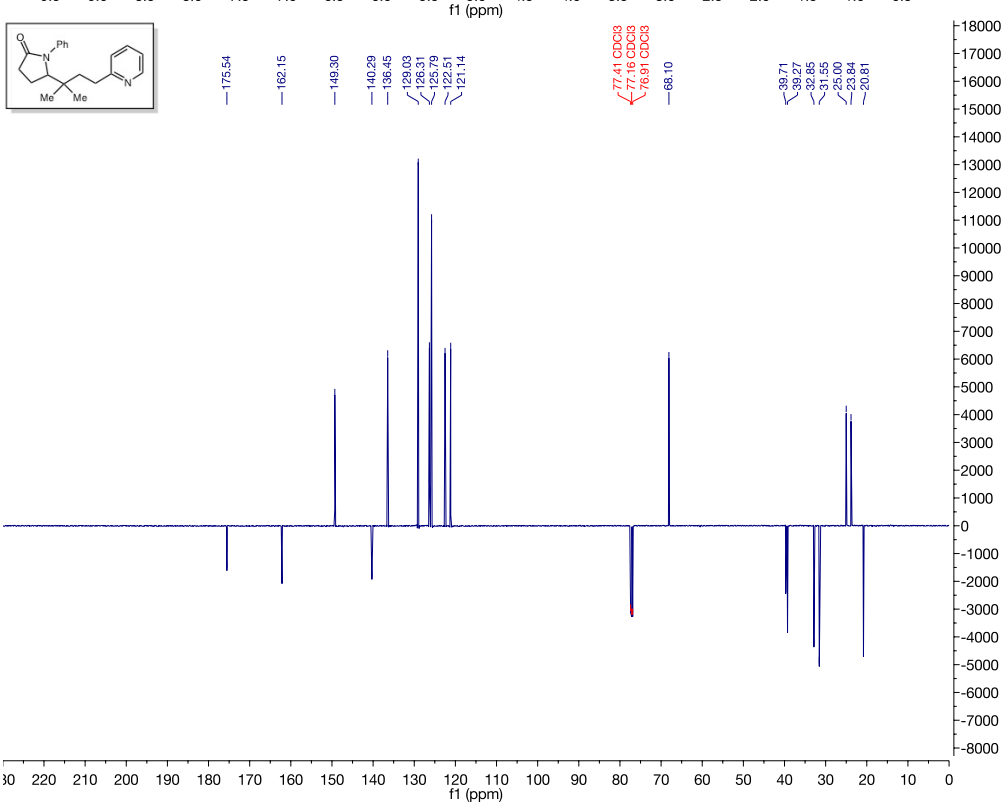

Ph
N
O
Me
Me
O
0.68
2.00
1.86
0.98
1.03
1.03
1.04
2.90
1.01
2.11
6.11
f1 (ppm)


201.94
175.46
140.11
129.16
126.61
125.78
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
67.82
39.14
38.78
31.44
30.63
24.39
23.66
20.84
Ph
N
O
Me
Me
O
f1 (ppm)


Ph
CN
Me
Me
2.00
1.91
0.38
1.06
1.00
1.02
1.00
1.87
1.07
2.79
6.00
f1 (ppm)

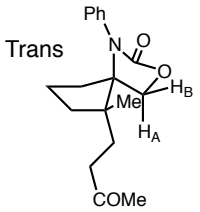

Ph
CN
Me
Me
175.29
139.84
129.33
126.85
125.64
119.91
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
67.50
39.44
34.50
31.26
23.69
23.36
20.76
12.23
f1 (ppm)

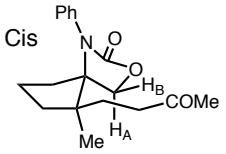

1.04
0.95
4.48
1.15
1.11
1.04
0.90
3.52
1.12
1.15
1.18
2.12
6.41
f1 (ppm)


175.54
162.15
149.30
140.29
136.45
129.03
126.31
125.79
122.51
121.14
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
68.10
39.71
39.27
32.85
31.55
25.00
23.84
20.81
f1 (ppm)

Diastereomer Identification

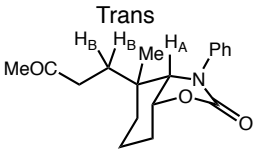
6-Methyl-6-(3-oxobutyl)-1-phenyl-3-oxa-1-azaspiro[4.4]nonan-2-one (**7**):

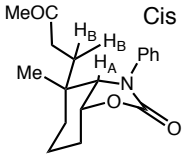




	NOE?	NOE?
H_A-Me	weak	strong
Me-Ph	strong	none
H_B-(CO)Me	none	strong

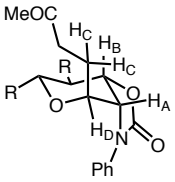
4-Methyl-4-(3-oxobutyl)-3-phenylhexahydrobenzo[*d*]oxazol-2(3*H*)-one (**8**):





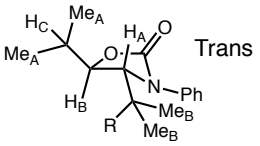
	NOE?	NOE?
H_A-Me	weak	strong
H_A-H_B	strong	weak

2,2-dimethyl-6-(3-oxobutyl)-7-phenylhexahydro-[1,3]dioxino[4',5':5,6]pyrano[3,4-*d*]oxazol-8(6*H*)-one (**9**):



	NOE?
H_A-H_C	strong
H_B-H_C	weak
H_D-Ph	medium
H_C-Ph	none

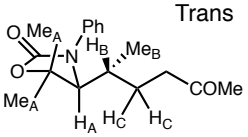
Methyl 4-(5-isopropyl-2-oxo-3-phenyloxazolidin-4-yl)-4-methylpentanoate (**10**):



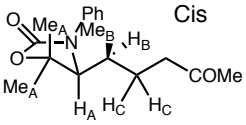
	NOE?
H_A-Me	strong
H_A-H_C	medium
Me_A-Me_B	none

5,5-dimethyl-4-(5-oxohexan-2-yl)-3-phenyloxazolidin-2-one (**13**):

Major



Minor



*Me_A and H_C protons are not equivalent but exact assignment is not necessary for analysis

	NOE?	NOE?
H_A-H_B	Medium	Strong
H_A-H_C	None	Weak
H_A-Me_A	Strong	Strong
H_A-Me_B	Weak	Medium
H_A-Ph	Strong	Medium
H_B-Me_A	Strong	Strong
H_B-Ph	Weak	Weak
H_C-Me_A	Weak	None
H_C-Ph	Weak	Weak
Me_A-Me_B	Weak	Medium
Me_B-Ph	Medium	Weak

Stern-Volmer Experiments

Stern-Volmer experiments were conducted on an Agilent Technologies Cary Eclipse Fluorescence Spectrophotometer using the Cary Eclipse Scan Application. Stern-Volmer luminescence quenching experiments were run with freshly prepared solutions of 1.0 X 10^{-5} M $[Ir(dF(CF_3)ppy)_2(bpy)](PF_6)$ in acetonitrile at room temperature under an inert atmosphere. The solutions were irradiated at 412 nm and luminescence was measured at 490 nm. The data summarized in the table is the fluorescence intensity measured three times for each sample. The data shown in the graph is the average of three experiments.

Experiment	Vial	1	2	3	Avg	I0/I	Amide [M]
Run 1	0	948.55	955.18	951.11	951.61	1.00	0
	1	964.00	976.41	976.85	972.42	0.98	0.002
	2	970.89	973.17	972.77	972.28	0.98	0.004
	3	952.86	949.03	949.68	950.52	1.00	0.006
	4	983.11	984.50	986.35	984.66	0.97	0.008

Table S1. Fluorescence quenching data with $[Ir(dF(CF_3)ppy)_2(bpy)]PF_6$ and acetanilide. See Fig. S1.

Experiment	Vial	1	2	3	Avg	I0/I	Amide [M]
Run 1	0	968.93	970.43	966.30	968.56	1.00	0
	1	433.85	434.92	432.25	433.68	2.23	0.002
	2	320.05	319.79	319.08	319.64	3.03	0.004
	3	251.32	251.06	251.22	251.20	3.86	0.006
	4	214.25	214.48	213.54	214.09	4.52	0.008
Run 2	0	973.73	972.50	970.07	972.10	1.00	0
	1	467.45	475.84	469.79	471.03	2.06	0.002
	2	334.40	328.81	331.81	331.67	2.93	0.004
	3	261.63	263.35	259.72	261.57	3.72	0.006
	4	213.41	213.68	213.34	213.48	4.55	0.008
Run 3	0	980.19	979.15	979.47	979.60	1.00	0
	1	498.47	498.02	498.79	498.43	1.97	0.002
	2	326.04	326.98	327.32	326.78	3.00	0.004
	3	254.18	256.11	255.53	255.27	3.84	0.006
	4	215.61	215.47	216.88	215.99	4.54	0.008

Table S2. Fluorescence quenching data with $[Ir(dF(CF_3)ppy)_2(bpy)]PF_6$, 0.015 M $NBu_4(BuO)_2PO_2$ and variable protiated acetanilide. See Fig. S1.

Experiment	Vial	1	2	3	Avg	I0/I	Amide [M]
Run 1	0	792.82	798.77	791.37	794.32	1.00	0
	1	430.83	427.71	423.42	427.32	1.86	0.002
	2	302.16	299.67	299.27	300.37	2.64	0.004
	3	236.63	235.84	234.03	235.50	3.37	0.006
	4	192.80	193.19	192.42	192.80	4.12	0.008
Run 2	0	820.78	814.01	812.65	815.81	1.00	0
	1	422.84	421.73	417.90	420.82	1.94	0.002
	2	300.03	299.51	301.03	300.19	2.72	0.004
	3	235.66	236.12	237.11	236.30	3.45	0.006
	4	200.57	200.64	200.85	200.69	4.07	0.008
Run 3	0	827.21	832.90	824.32	828.14	1.00	0
	1	411.16	409.38	410.25	410.26	2.02	0.002
	2	311.95	312.82	313.98	312.91	2.65	0.004
	3	236.99	236.79	235.97	236.58	3.50	0.006
	4	202.45	202.26	202.00	202.24	4.09	0.008

Table S3. Fluorescence quenching data with $[Ir(dF(CF_3)ppy)_2(bpy)]PF_6$, 0.015 M $NBu_4(BuO)_2PO_2$ and variable deuterated acetanilide. See Fig. S1.

Experiment	Vial	1	2	3	Avg	I0/I	Base [M]
Run 1	0	894.53	899.16	903.85	899.18	1.00	0
	1	886.50	878.07	887.58	884.05	1.02	0.0003
	2	846.15	847.24	868.79	854.06	1.05	0.0012
	3	799.01	794.81	793.25	795.69	1.13	0.003
	4	752.89	747.38	758.05	752.77	1.19	0.0048
Run 2	0	905.18	905.33	912.70	907.74	1.00	0
	1	899.79	894.43	890.41	894.88	1.01	0.0003
	2	871.79	870.39	870.09	870.76	1.04	0.0012
	3	805.35	803.14	801.79	803.42	1.13	0.003
	4	757.85	761.14	765.42	761.47	1.19	0.0048
Run 3	0	893.05	889.57	886.27	889.63	1.00	0
	1	878.07	871.02	885.77	878.28	1.01	0.0003
	2	852.32	857.24	848.70	852.75	1.04	0.0012
	3	777.22	789.35	783.47	783.35	1.14	0.003
	4	752.58	744.81	742.95	746.78	1.19	0.0048

Table S4. Fluorescence quenching data with $[Ir(dF(CF_3)ppy)_2(bpy)]PF_6$ and $NBu_4(BuO)_2PO_2$. See Fig. S2.

Experiment	Vial	1	2	3	Avg	I0/I	Base [M]
Run 1	0	961.91	969.62	968.77	966.76	1.00	0
	1	710.80	709.34	711.09	710.41	1.36	0.0003
	2	440.09	441.88	439.54	440.50	2.19	0.0012
	3	278.55	278.84	278.54	278.64	3.47	0.003
	4	225.95	225.94	225.05	225.65	4.28	0.0048
Run 2	0	880.30	879.25	880.14	879.90	1.00	0
	1	646.47	646.79	649.00	647.42	1.36	0.0003
	2	400.99	401.96	399.57	400.84	2.20	0.0012
	3	260.56	259.07	260.03	259.89	3.39	0.003
	4	206.86	206.50	205.81	206.39	4.26	0.0048
Run 3	0	900.77	902.08	899.23	900.69	1.00	0
	1	660.78	660.33	661.04	660.72	1.36	0.0003
	2	409.57	409.07	409.33	409.32	2.20	0.0012
	3	264.93	263.84	266.51	265.09	3.40	0.003
	4	207.37	212.95	209.35	209.89	4.29	0.0048

Table S5. Fluorescence quenching data with $[Ir(dF(CF_3)ppy)_2(bpy)]PF_6$ and **1.** See Fig. S2.

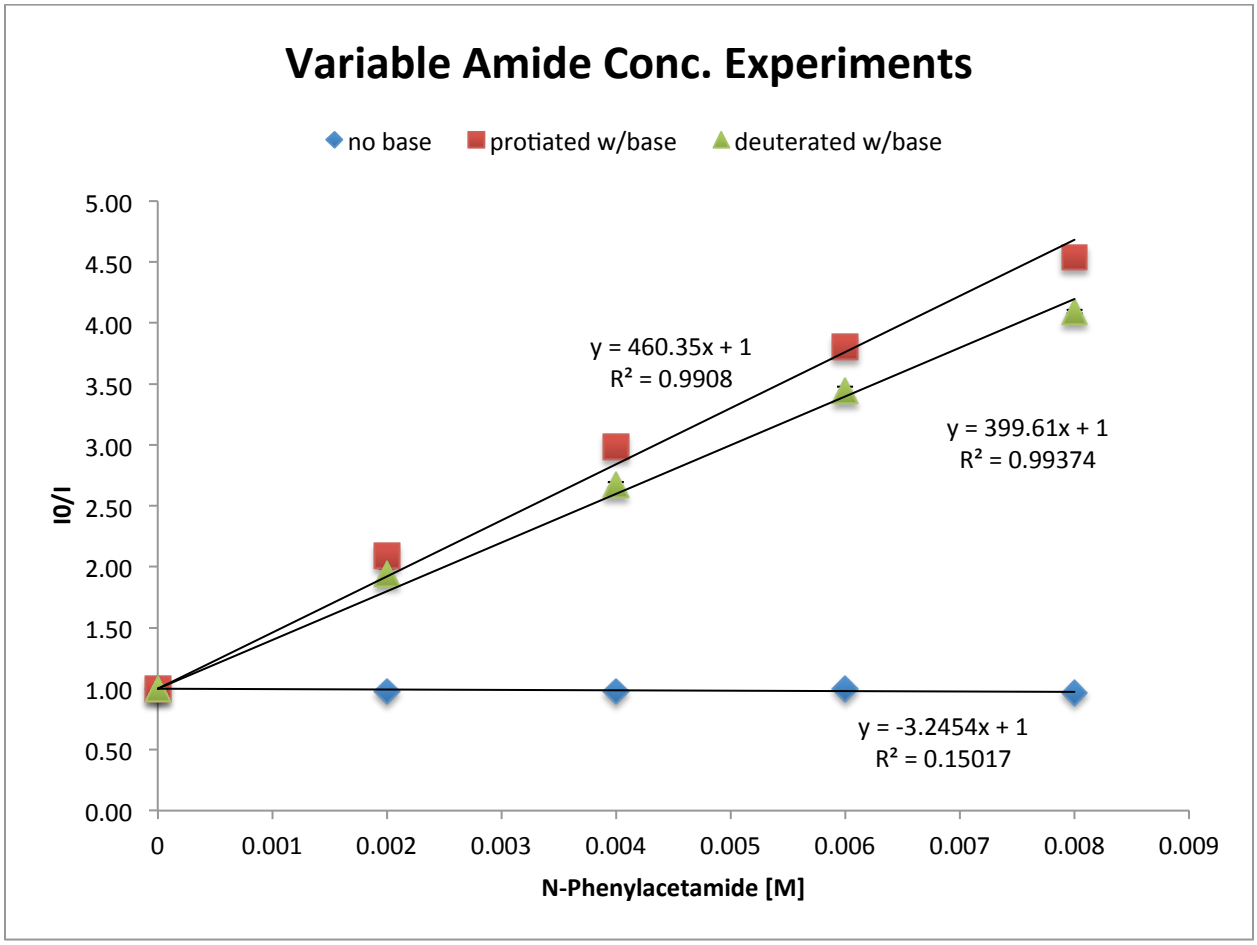


Fig. S1. Stern-Volmer plot of $[Ir(dF(CF_3)ppy)_2(bpy)]PF_6$, $NBu_4(BuO)_2PO_2$, and variable acetanilide. The error in the slope was calculated (from LINEST analysis) to be 460.3 ± 12.2 for protiated acetanilide and 399.6 ± 8.8 for deuterated acetanilide.

k_H/k_D = 460.3 ± 12.2 / 399.6 ± 8.8 = 1.15 ± 0.04

Note: The error in the H/D isotope effect measurement was determined through propagation of error in the slopes of the Stern-Volmer plots for quenching runs carried out in the presence of either protiated or deuterated acetanilide.

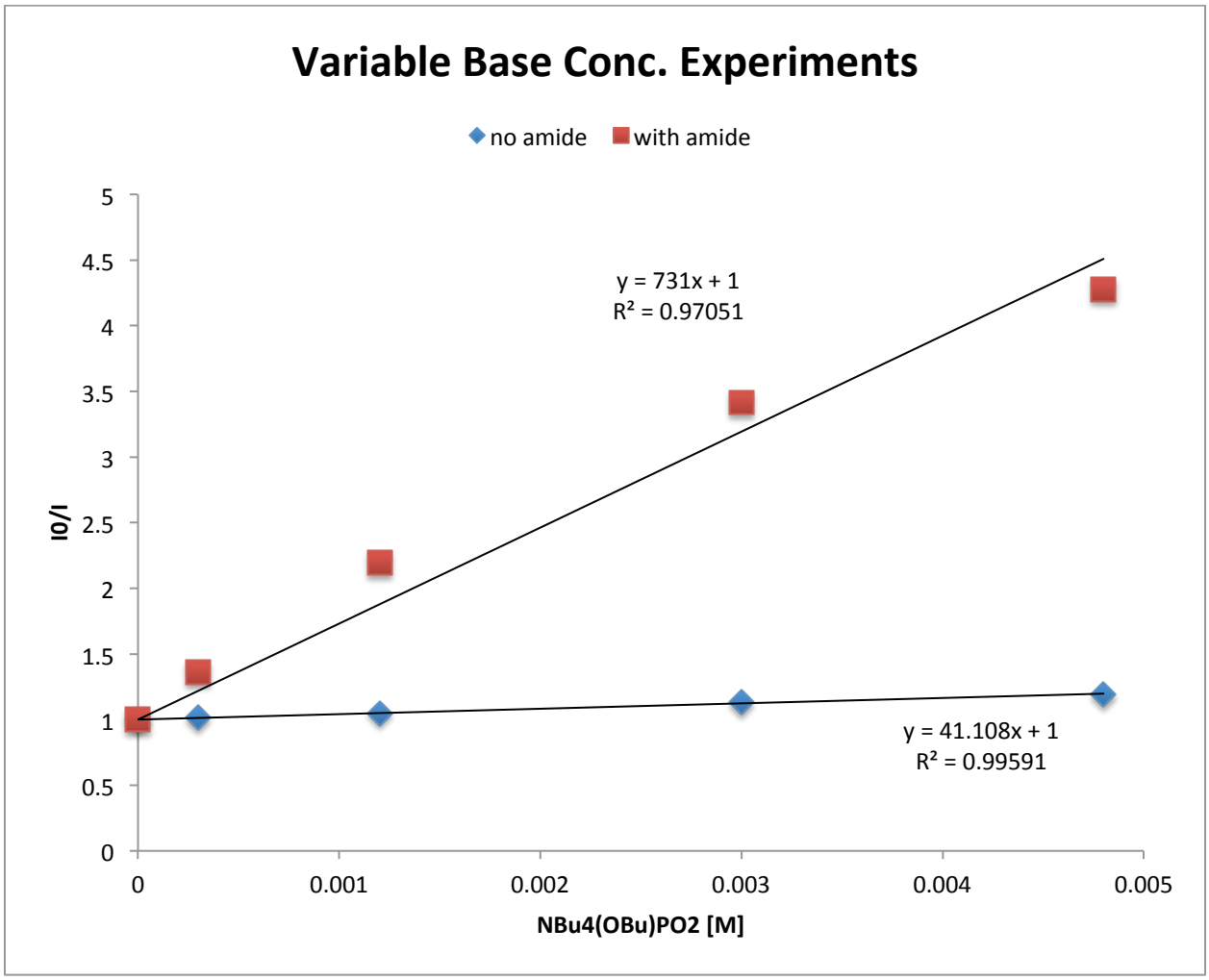


Fig. S2. Stern-Volmer plot of $[Ir(dF(CF_3)ppy)_2(bpy)]PF_6$, 0.01 M acetanilide, and variable $NBu_4(BuO)_2PO_2$.

CV Data

Cyclic voltammograms were taken on a CH Instruments 600E potentiostat using a glassy carbon working electrode, a Ag/Ag^+ or saturated calomel (SCE) reference electrode, and a Pt mesh counter electrode. The pH was not adjusted and voltammograms were taken at 23 ºC in a 0.1 M MeCN or DCM solution of tetrabutylammonium hexafluorophosphate containing 1 mM solution of substrate and 1 mM of ferrocene as an internal standard (for voltammograms with the Ag/Ag^+ reference electrode). The scan rate was 0.1 V/s. The Fc/Fc^+ couple is 380 mV less positive than SCE.

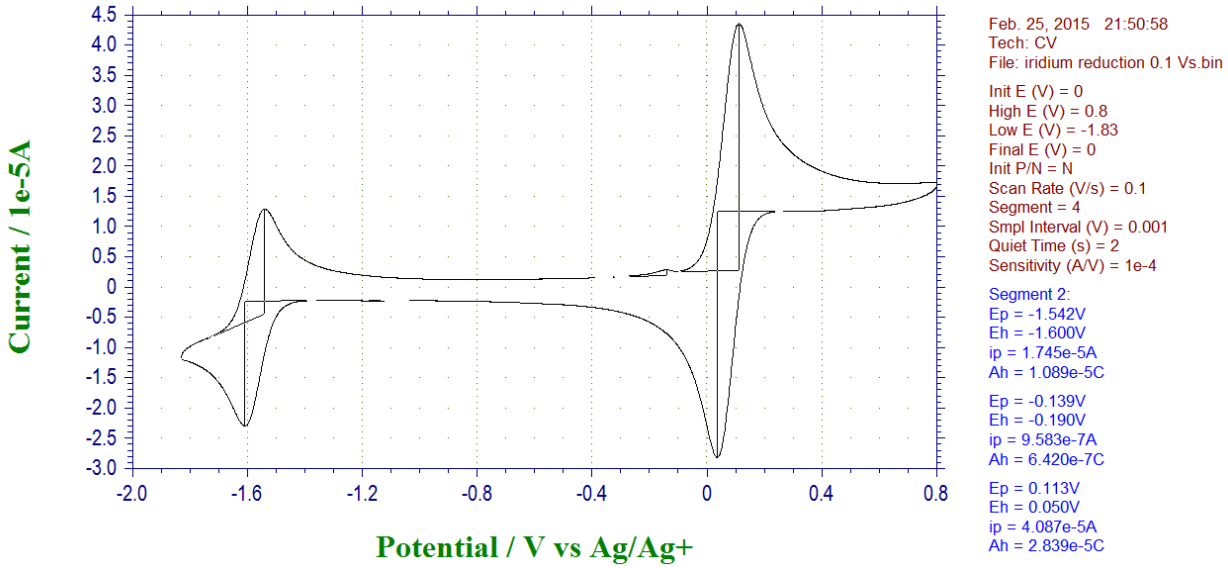


Fig. S3. Cyclic voltammogram of $[Ir(dF(CF_3)ppy)_2(bpy)]PF_6$ in MeCN.
$E(L/L^-)$ = -1.65 V vs. Fc/Fc^+

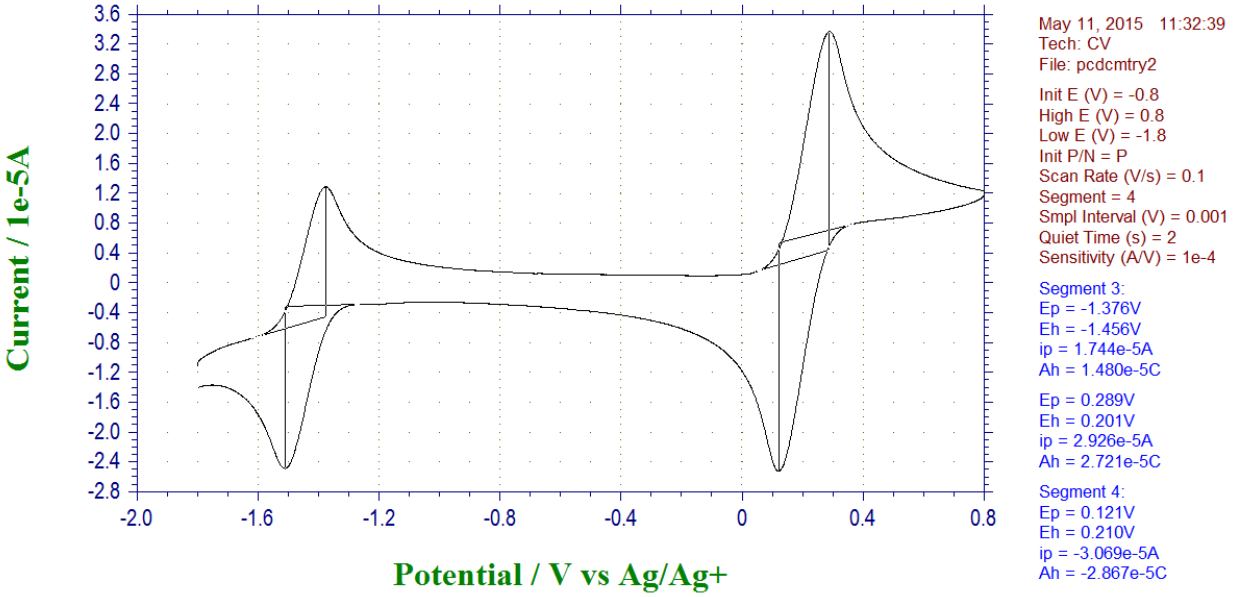


Fig. S4. Cyclic voltammogram of $[Ir(dF(CF_3)ppy)_2(bpy)]PF_6$ in DCM.
$E(L/L^-)$ = -1.58 V vs. Fc/Fc^+

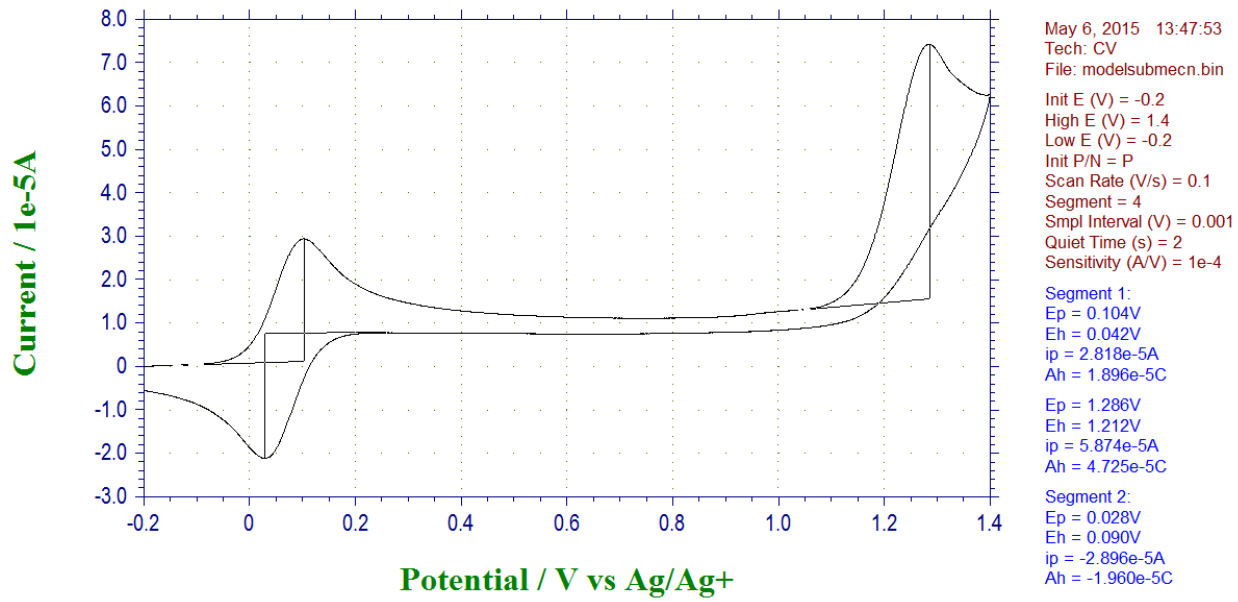


Fig. S5. Cyclic voltammogram of **1** in MeCN.
E_p = 1.23 V vs. Fc/Fc$^+$

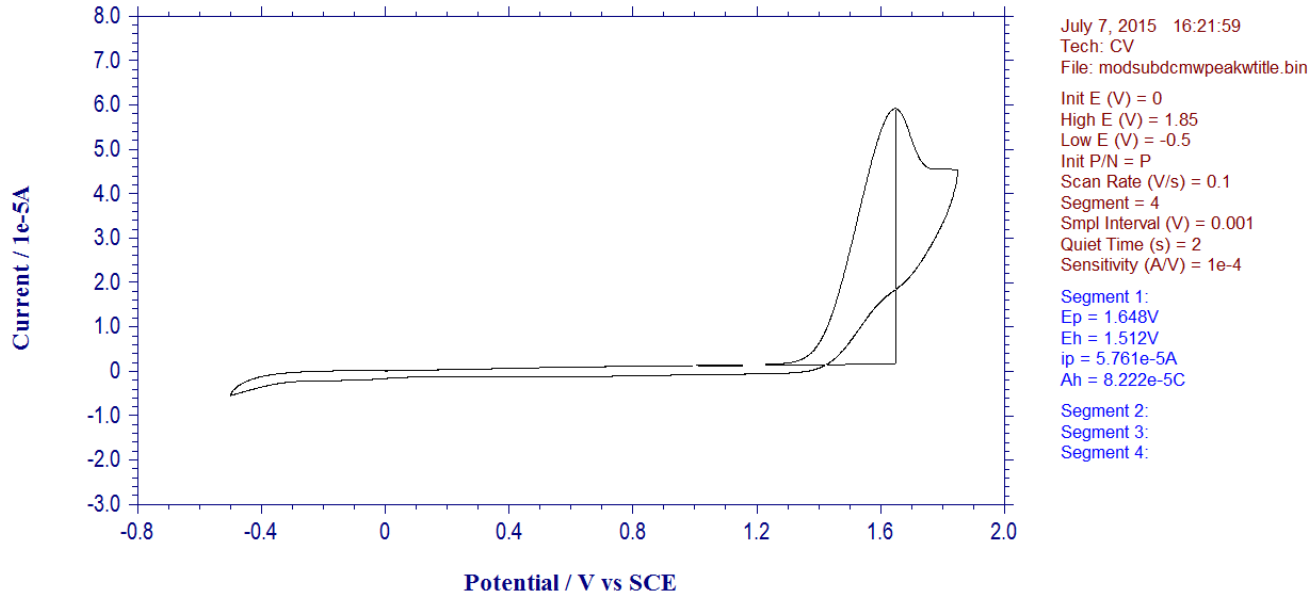
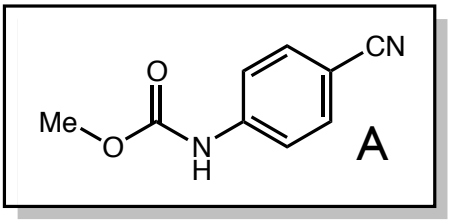


Fig. S6. Cyclic voltammogram of **1** in DCM.
E_p = 1.19 V vs. Fc/Fc$^+$



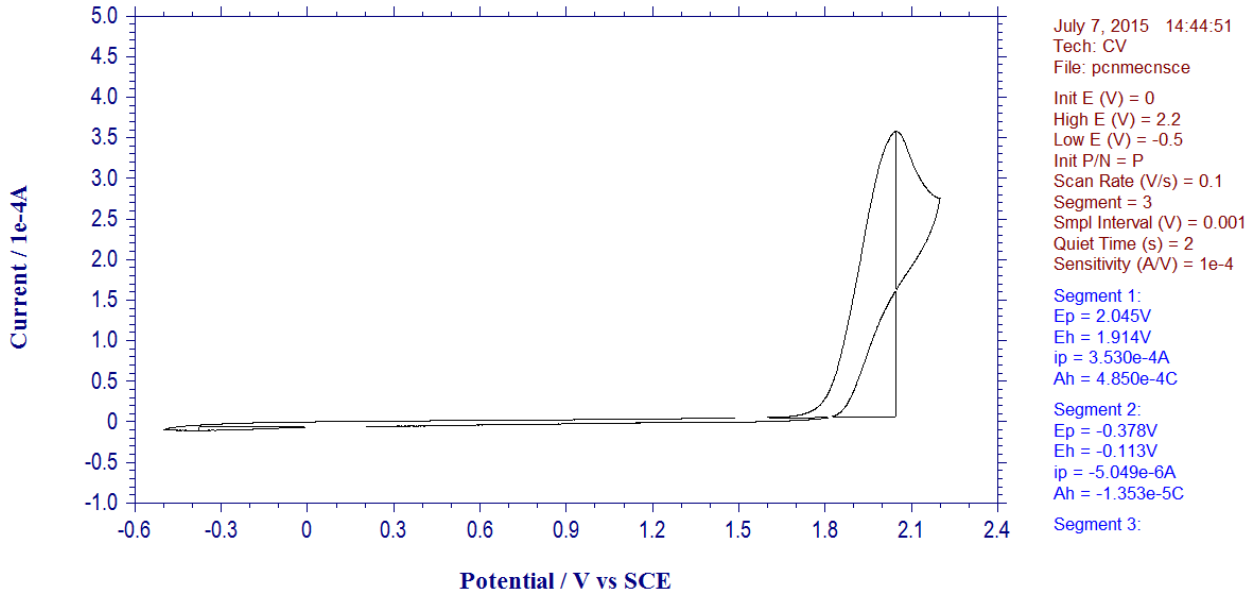


Fig. S7. Cyclic voltammogram of **A** in MeCN.
E_p = 1.64 V vs. Fc/Fc$^+$

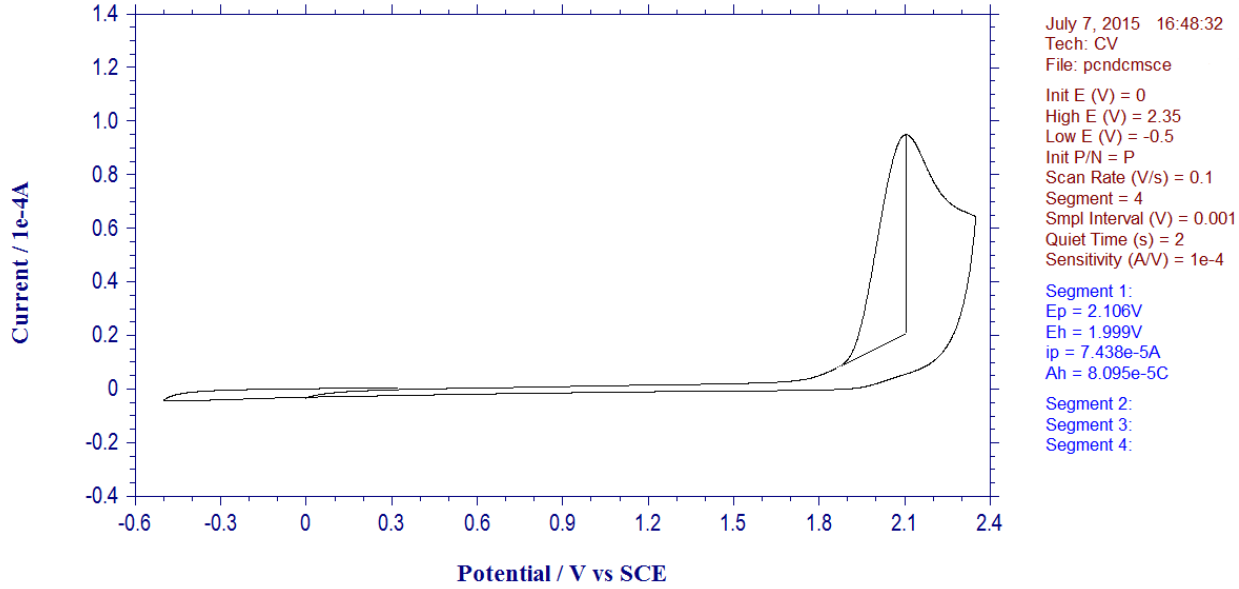
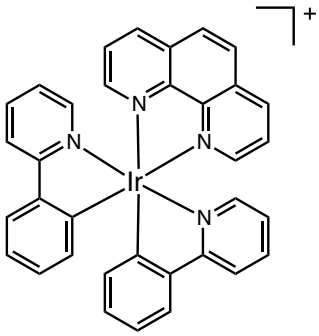
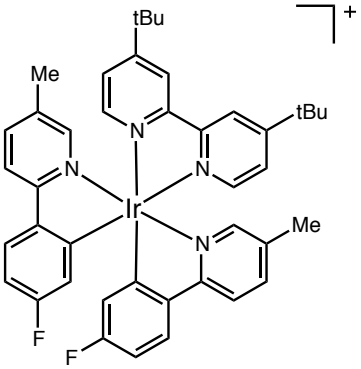


Fig. S8. Cyclic voltammogram of **A** in DCM.
E_p = 1.65 V vs. Fc/Fc$^+$

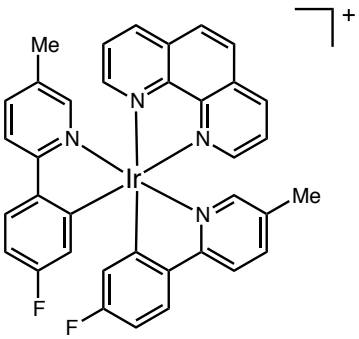
Photocatalyst Structures



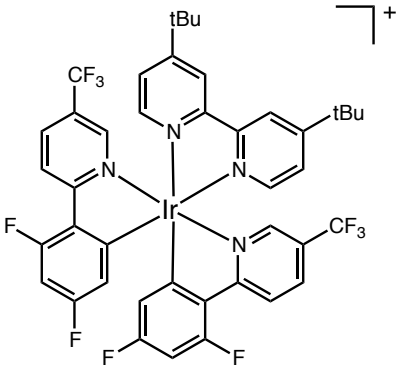
$Ir(ppy)_2(phen)^+$



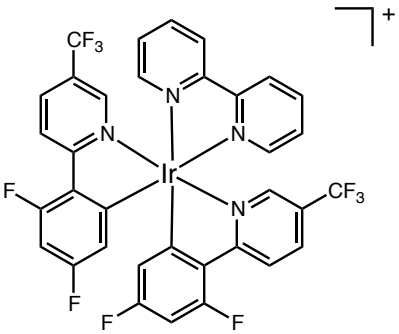
$Ir(Fmppy)_2(dtbbpy)^+$



$Ir(Fmppy)_2(phen)^+$



$Ir(dF(CF_3)ppy)(dtbbpy)^+$



$Ir(dF(CF_3)ppy)_2(bpy)^+$

Figure S9. Structures of photocatalysts utilized in Table 1.

Formal Bond Dissociation Free Energy Calculations (Table 2)

Formal BDFE (kcal/mol) = 2.3RTpK_a +23.06E + 54.9 (MeCN)

entry	oxidant	base	pKa (MeCN)	E^o (vs FC)	BDFE (MeCN)
1	*[Ir(ppy)2(phen)]+	NBu4OP(O)(OBu)2	13	0.32	80
2	*[Ir(ppy)2(phen)]+	lutidine	14.1	0.32	82
3	*[Ir(Fmppy)2(dtbbpy)]+	NBu4OP(O)(OBu)2	13	0.39	82
4	*[Ir(Fmppy)2(dtbbpy)]+	lutidine	14.1	0.39	83
5	*[Ir(Fmppy)2(phen)]+	NBu4OP(O)(OBu)2	13	0.45	83
6	*[Ir(Fmppy)2(phen)]+	lutidine	14.1	0.45	85
7	*[Ir(ppy)2(phen)]+	DMAP	18	0.32	87
8	*[Ir(Fmppy)2(dtbbpy)]+	DMAP	18	0.39	89
9	*[Ir(Fmppy)2(phen)]+	DMAP	18	0.45	90
10	*[Ir(ppy)2(phen)]+	NBu4OBz	21.5	0.32	92
11	*[Ir(dF(CF3)ppy)2(dtbbpy)]+	NBu4OP(O)(OBu)2	13	0.83	92
12	*[Ir(dF(CF3)ppy)2(dtbbpy)]+	lutidine	14.1	0.83	93
13	*[Ir(Fmppy)2(dtbbpy)]+	NBu4OBz	21.5	0.39	93
14	*[Ir(Fmppy)2(phen)]+	NBu4OBz	21.5	0.45	95
15	*[Ir(dF(CF3)ppy)2(bpy)]+	NBu4OP(O)(OBu)2	13	1.04	97
16	*[Ir(dF(CF3)ppy)2(bpy)]+	lutidine	14.1	1.04	98
17	*[Ir(dF(CF3)ppy)2(dtbbpy)]+	DMAP	18	0.83	99
18	*[Ir(dF(CF3)ppy)2(bpy)]+	DMAP	18	1.04	103
19	*[Ir(dF(CF3)ppy)2(dtbbpy)]+	NBu4OBz	21.5	0.83	104
20	*[Ir(dF(CF3)ppy)2(bpy)]+	NBu4OBz	21.5	1.04	108

Table S6. BDFE calculations from pK_a and E^0 values in MeCN.

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