Catalytic Olefin Hydroamidation Enabled by Proton-Coupled Electron Transfer

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Supporting Information

Table of Contents **Page**

General Information

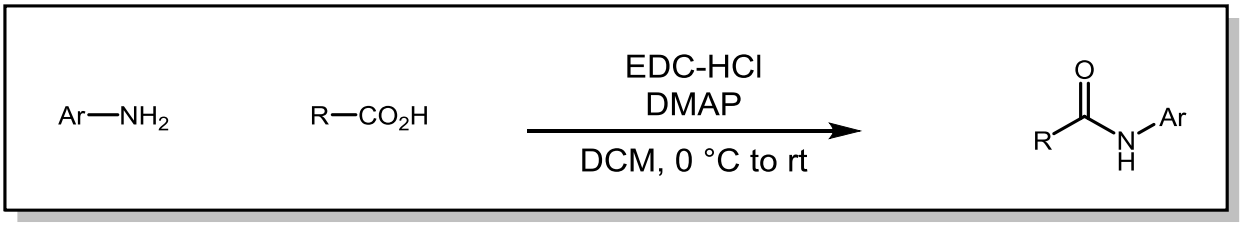
Commercial reagents were purified prior to use following the guidelines of Perrin and Armarego.[1] All solvents were purified according to the method of Grubbs.[2] Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. Chromatographic purification of products was accomplished 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 for ^{1}H and ^{13}C respectively) instrument, and are internally referenced to residual solvent signals, $CDCl_3$ referenced at δ 7.26 and 77.16 ppm and DMSO-d_6 referenced at δ 2.50 and 39.52 ppm. ^{19}F NMR spectra were recorded on a Bruker AVANCE 300 (282 MHz) instrument and are referenced to $CFCl_3$ at δ 0.0 ppm. For high temperature NMR data, ^{1}H and ^{13}C spectra were recorded on either a Bruker 500 (500 and 126 MHz for ^{1}H and ^{13}C respectively) or Bruker 300 (300 and 75 MHz for ^{1}H and ^{13}C respectively). Data for ^{1}H is reported as follows: chemical shift (δ ppm), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), broad peaks (br), coupling constant (Hz) and assignment. Data for ^{13}C and ^{19}F 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.

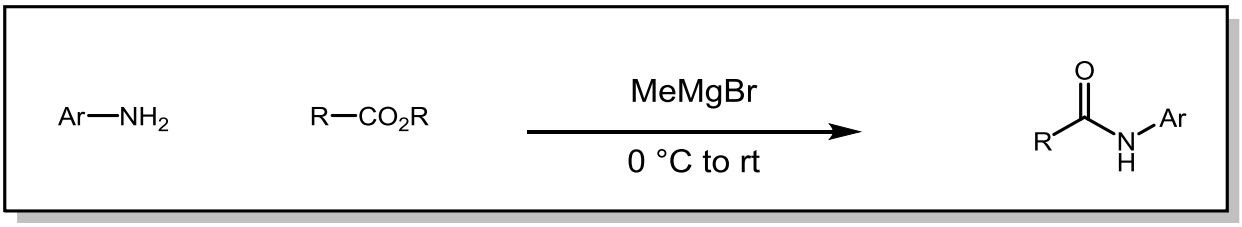
Synthesis and Characterization of Substrates

General Procedures for Substrate Synthesis

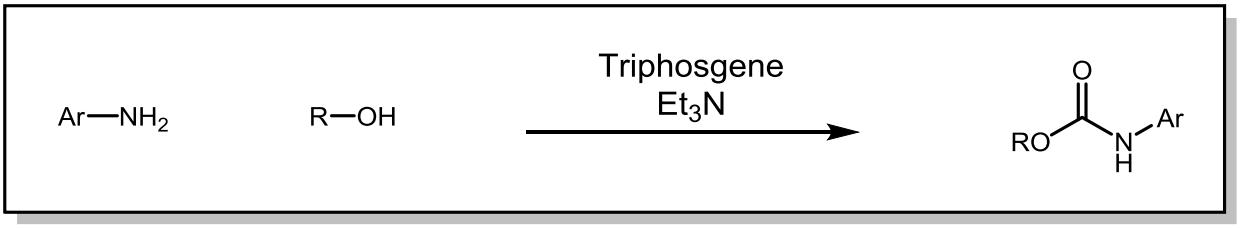
General Procedure A: Phenyl Carbamate/Urea Synthesis General Procedure
This protocol is used as reported using prior disclosed conditions.[4] A flame-dried round-bottomed flask was degassed, flushed with argon, and charged with phenyl isocyanate (10 mmol, 1 equiv), DCM (10 mL, 1.0 M), Et_3N (30 mmol, 3.0 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 either silica gel column chromatography or recrystallization to afford the desired product.



General Procedure B: Amide Synthesis General Procedure by Amide Coupling
This protocol is adapted from prior disclosed conditions.[5] A flame-dried round-bottomed flask was degassed, flushed with argon, and charged with DCM (25 mL, 0.4 M), EDC-HCl (1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride, 13 mmol, 1.3 equiv), and DMAP (14 mmol, 1.4 eqiuv). The reaction flask was cooled to zero degrees in an ice bath and the carboxylic acid (10 mmol, 1.0 equiv) was added. After five minutes of stirring, the substituted aniline (12 mmol, 1.2 equiv) was added. The ice bath was then removed and the reaction allowed to stir for 24 hours at RT or until starting material was consumed by TLC. The reaction was quenched with 1M HCl (25 mL) and the organics separated. The aqueous layer was then extracted with DCM (2 x 25 mL). The organic layers were combined and dried over Na_2SO_4 and concentrated. The crude product was purified by either silica gel column chormatography or recrystallization to afford the desired product.

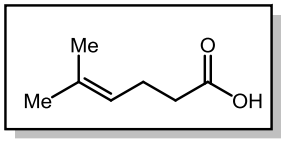


General Procedure C: Amide Synthesis General Procedure by Substitution of Esters
This protocol is used as reported using prior disclosed conditions.[6] Three flame-dried round-bottomed flasks were flushed with argon and charged with Et_2O (16 mL, total reaction concentration 0.1 M). The ester (5.26 mmol, 1 equiv) was added to one flask. The substituted aniline (10.51 mmol, 2 equiv) was added to a separated flask. Methylmagnesium bromide (3.0 M in Et2O, 10.5 mmol, 2 equiv) was added to the third flask. The aniline solution was added slowly to the methylmagnesium bromide solution. When evolution of gas ceased and 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 (50 mL) and diluted with EtOAc (50 mL). The organics were separated and the aqueous layer was extracted with EtOAc (3 x 25 mL). The combined organic layers were washed with brine (25 mL), dried over Na_2SO_4, and concentrated. The crude product was purified by either silica gel column chromatography or recrystallization to afford the desired product.



General Procedure D: Carbamate Synthesis by Sequential Addition to Triphosgene

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 alcohol were added (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.

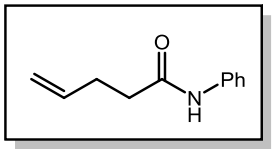


5-Methylhex-4-enoic acid

5-methylhex-4-enoic acid was synthesized as outlined by Shannon.[7] It is a common intermediate to a number of substrates in the table.

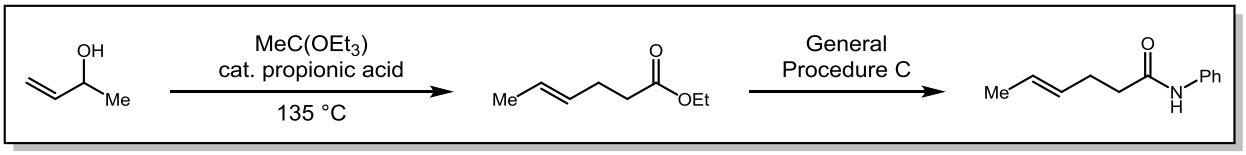
Substrate Syntheses

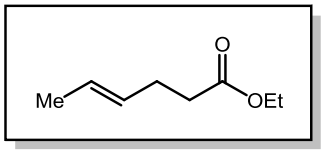
Substrates are presented in the order their corresponding products appear in the substrate table.



***N*-Phenylpent-4-enamide (1)**

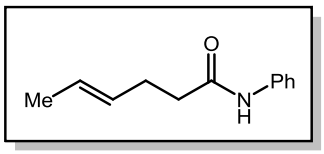
Synthesized using General Procedure B starting from pent-4-enoic acid and aniline on a 40 mmol scale with respect to the carboxylic acid. The product was purified by recrystallization from a mixture of hexanes and ethyl acetate to yield 6.44 g (92% yield) of the title compound as white, glittery flakes. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, J = 8.0 Hz, 2H), 7.44 (br s, 1H), 7.30 (t, J = 7.8 Hz, 2H), 7.10 (t, J = 7.4 Hz, 1H), 5.88 (ddt, J = 16.7, 10.4, 6.0 Hz, 1H), 5.12 (d, J = 16.9 Hz, 1H), 5.05 (d, J = 10.1 Hz, 1H), 2.47 (h, J = 6.2 Hz, 4H). Spectral data in consistent with reported literature values.[8]





Ethyl (*E*)-hex-4-enoate

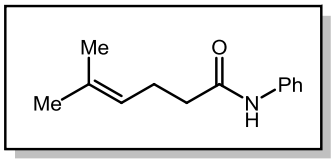
Synthesized using a protocol modified from a literature prep.[9] Glassware is neither flame nor oven-dried prior to the reaction. To a distillation setup with one collection bulb under inert atmosphere, but-3-en-2-ol (5.05 g, 70 mmol, 1 equiv), triethyl orthoacetate (17.03 g, 105 mmol, 1.5 equiv), and propionic acid (0.14 g, 1.9 mmol, 0.03 equiv) were mixed together. The solution was heated to 120 degrees until ethanol distillation ceases. The distillation head was then replaced with a reflux condenser and the solution heated to vigorous reflux (135 degrees) for 6 hours Upon cooling, volatiles are removed on the rotovap (60 torr, 35 degree water bath). The product was distilled to yield 4.80 g (48% yield) of the product as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.58 – 5.37 (m, 2H), 4.12 (q, J = 7.1 Hz, 2H), 2.38 – 2.26 (m, 4H), 1.64 (m, 3H), 1.25 (t, J = 7.1 Hz, 3H). Spectral data is consistent with the reported literature spectra.[9]



(*E*)-*N*-Phenylhex-4-enamide

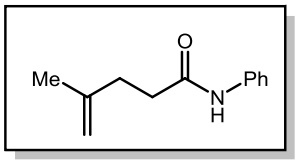
Synthesized using General Procedure C starting from Ethyl (*E*)-hex-4-enoate and aniline on a 5.63 mmol scale with respect to the ester. The product was purified by recrystallization from a mixture of hexanes and ethyl acetate to yield 777 mg (73% yield) of the title compound as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, J = 8.0 Hz, 2H), 7.32 (t, J = 7.9 Hz, 2H), 7.21 (br s, 1H), 7.10 (t, J = 7.4 Hz, 1H), 5.64 – 5.41 (m, 2H), 2.50 – 2.34 (m, 4H), 1.67 (d, J = 6.0 Hz, 3H).

Spectral data in consistent with the reported literature spectra.[10]



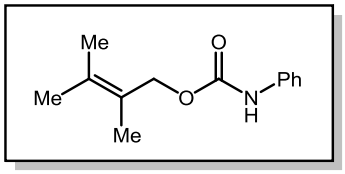
5-Methyl-*N*-phenylhex-4-enamide

Synthesized using General Procedure B starting from 5-methylhex-4-enoic acid and aniline on a 6.81 mmol scale with respect to the carboxylic acid. The product was purified by recrystallization from a mixture of hexanes and ethyl acetate to yield 770 mg (56% yield) of the title compound as a white solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 8.0 Hz, 2H), 7.32 (t, *J* = 7.8 Hz, 2H), 7.17 (br s, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 5.18 (t, *J* = 6.6 Hz, 1H), 2.45 – 2.36 (m, 4H), 1.72 (s, 3H), 1.66 (s, 3H). Spectral data is consistent with the reported literature spectra.[10]



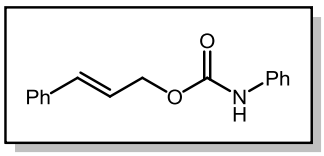
4-Methyl-*N*-phenylpent-4-enamide

Synthesized using General Procedure C starting from ethyl 4-methylpent-4-enoate and aniline on a 5.82 mmol scale with respect to the ester. The crude product is purified by recrystallization from a mixture of hexanes and ethyl acetate to yield 611 mg (56% yield) of the title compound as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.8 Hz, 2H), 7.31 (t, *J* = 7.9 Hz, 2H), 7.10 (t, *J* = 7.4 Hz, 1H), 4.81 (s, 1H), 4.77 (s, 1H), 2.57 – 2.39 (m, 4H), 1.79 (s, 3H). Spectral data is consistent with the reported literature spectra.[11]



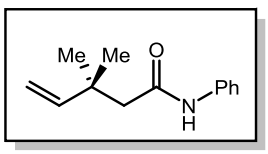
2,3-Dimethylbut-2-en-1-yl phenylcarbamate

Synthesized using General Procedure A from 2,3-dimethyl-2-buten-1-ol[4] on a 4.94 mmol scale with respect to the alcohol component. The crude product is purified by silica gel chromatography (grandient from 0% EtOAc in Hexanes to 10% EtOAc in Hexanes) to give 920 mg (85% yield) of the title compound. ^{1}H 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). Spectral data is consistent with the reported literature spectra.[4]



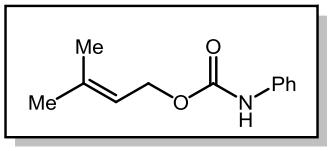
Cinnamyl phenylcarbamate

Synthesized using General Procedure A starting with cinnamyl alcohol on a 8.12 mmol scale with respect to cinnamyl alcohol. The title compound was purified by recrystallization from a mixture of hexanes and ethyl acetate to furnish 1.27 g (62% yield) of the titled compound as a white solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.44 – 7.29 (m, 9H), 7.10 – 7.03 (m, 1H), 6.70 (d, *J* = 15.9 Hz, 1H), 6.34 (dt, *J* = 15.9, 6.4 Hz, 1H), 4.83 (d, *J* = 6.5 Hz, 2H). Spectral data is consistent with the reported literature spectra.[12]



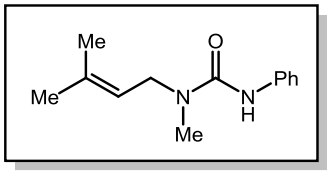
3,3-Dimethyl-*N*-phenylpent-4-enamide

Synthesized using General Procedure C starting from methyl 3,3-dimethylpent-4-enoate and aniline on a 5.90 mmol scale with respect to the ester. The product is purified by recrystallization from a mixture of hexanes and ethyl acetate to afford 770 mg (64% yield) of the title compound as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, J = 7.6 Hz, 2H), 7.31 (t, J = 7.8 Hz, 2H), 7.23 (br s, 1H), 7.09 (t, J = 7.4 Hz, 1H), 6.01 (dd, J = 17.8, 10.4 Hz, 1H), 5.16 – 5.09 (m, 2H), 2.37 (s, 2H), 1.20 (s, 6H). Spectral data is consistent with the reported literature spectra.[10]



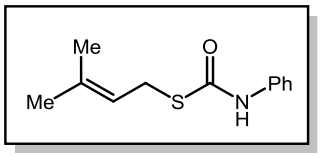
3-Methylbut-2-en-1-yl phenylcarbamate

Synthesized using General Procedure A starting from prenol on a 6.64 mmol scale with respect to prenol. The title compound was purified by silica gel column chromatography (gradient from 10% DCM in Hexanes to 33% DCM in Hexanes) followed by recrystallization from a solution of hexanes and ethyl acetate to yield 1.20 g (88% yield) of the title compound as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, J = 8.0 Hz, 2H), 7.30 (dd, J = 8.6, 7.2 Hz, 2H), 7.05 (tt, J = 7.3, 1.2 Hz, 1H), 6.57 (br s, 1H), 5.47 – 5.34 (m, 1H), 4.67 (d, J = 7.2 Hz, 2H), 1.78 (s, 4H), 1.75 (s, 1H). Spectral data is consistent with the reported literature spectra.[13]



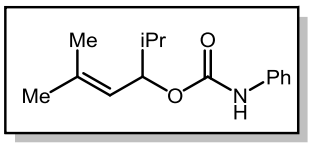
Methyl-1-(3-methylbut-2-en-1-yl)-3-phenylurea

Synthesized using General Procedure A using N-methyl-N-(3-methyl-2-buten-1-yl)amine[4] on a 3.84 mmol scale with respect to the amide. The crude product is purified by silica gel column chromtography (gradient from 0% EtOAc in Hexanes to 33% EtOAc in Hexnaes) to give 720 mg (86% yield) of the title compound as a white solid. ^{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). Spectral data is consistent with the reported literature spectra.[4]



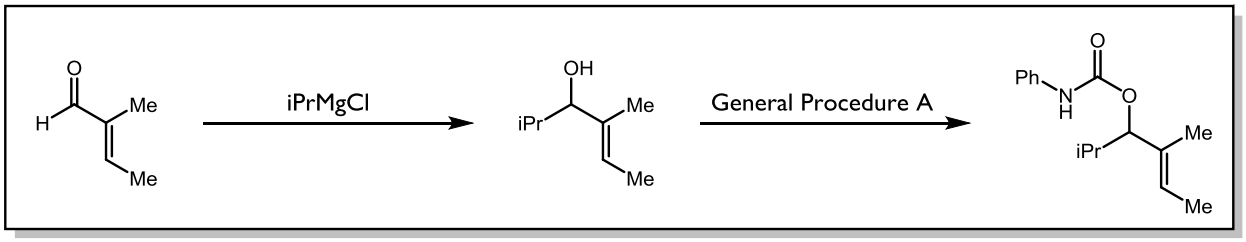
***S*-(3-Methylbut-2-en-1-yl) phenylcarbamothioate**

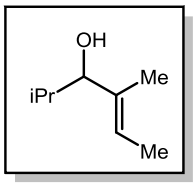
A flame dried round-bottomed flask was charged with dry, oil-free KH (672 mg, 16.75 mmol) inside a glove box. THF (20 mL) was added and the suspension was cooled to 0 ºC. 2-methyl-3-buten-2-ol (1.75 mL, 16.75 mmol) was added and the reaction mixture was allowed to warm to room temperature and stirred 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. ^{1}H 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). Spectral data is consistent with the reported literature spectra.[4]



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

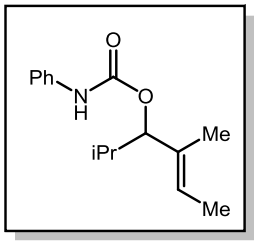
Synthesized using General Procedure A using 2,5-dimethylhex-4-en-3-ol[14] on a 2.84 mmol scale with respect to the alcohol. The crude product is purified by silica gel column chromatography to give 550 mg (79% yield) of the title compound. IR (neat): 3319, 2964, 2932, 2874, 1698, 1600, 1529, 1501, 1442, 1382, 1312, 1220, 1047, 1026, 967, 949, 858, 752, 691 cm^{-1}; ^1H 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.





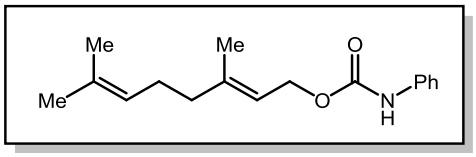
***(E)*-2,4-Dimethylhex-4-en-3-ol**

To a solution of tiglic aldehyde (1.3 g, 15.5 mmol) in diethyl ether (31 mL) at 0 ºC was added a solution of isopropylmagnesium chloride in diethyl ether (10.9 mL, 2 M, 21.7 mmol). The reaction mixture was stirred for 2 h at 0 ºC and then sat. NH_4Cl was added. The mixture was extracted with diethyl ether 3 times, and the organic layer was washed with water and brine, dried over sodium sulfate, and concentrated. The crude product was purified by column chromatography to afford 1.8 g (90% yield) of the pure alcohol. IR (neat): 3382, 2956, 2921, 2870, 1460, 1380, 1296, 1249, 1169, 1124, 1080, 1007, 971, 955, 914, 854, 818 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.43 (q, *J* = 6.7 Hz, 1H), 3.57 (d, *J* = 8.3 Hz, 1H), 1.80 – 1.71 (m, 1H), 1.61 (d, *J* = 6.8 Hz, 3H), 1.58 (s, 3H), 0.98 (d, *J* = 6.6 Hz, 3H), 0.76 (d, *J* = 6.8 Hz, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.38, 121.94, 84.39, 31.26, 19.55, 18.85, 14.27, 13.14.; MS (ESI) exact mass calculated for $[M]^+$ ($C_8H_{16}O$) requires *m/z* 128.1, found *m/z* 128.1.



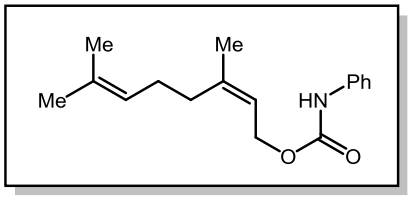
***(E)*-2,4,-Dimethylhex-4-en-3-yl phenylcarbamate**

Synthesized using General Procedure A using *(E)*-2,4-dimethylhex-4-en-3-ol on a 10.4 mmol scale with respect to the alcohol component. The crude product is purified by silica gel column chromatography to give 2.10 g (82% yield) of the title compound. IR (neat): 3315, 2962, 2927, 2873, 1699, 1600, 1534, 1501, 1442, 1383, 1327, 1311, 1222, 1178, 1082, 1048, 1027, 997, 966, 950, 823, 753, 692 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 9.2 Hz, 2H), 7.29 (t, *J* = 8.2 Hz, 2H), 7.07 – 7.00 (m, 1H), 5.56 (q, *J* = 7.2 Hz, 1H), 4.79 (d, *J* = 9.4 Hz, 1H), 2.01 – 1.89 (m, 1H), 1.63 (s, 3H), 1.61 (s, 3H), 0.97 (d, *J* = 6.8 Hz, 3H), 0.83 (d, *J* = 7.1 Hz, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.36, 138.29, 133.09, 129.14, 124.19, 123.28, 86.24, 30.07, 19.18, 18.89, 13.23, 11.68.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{15}H_{21}NO_2$) requires *m/z* 247.15723, found *m/z* 247.15763, difference 1.62 ppm.



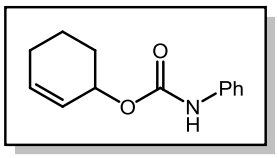
(*E*)-3,7-Dimethylocta-2,6-dien-1-yl phenylcarbamate

Synthesized using General Procedure A starting with geraniol on a 11.0 mmol scale with respect to geraniol. The title compound was purified by silica gel chromatography (gradient from 0% EtOAc in Hexanes to 5% EtOAc in Hexanes) to yield 1.8 g (60% yield) of the title compound as a clear oil. IR (neat) 3323, 2968, 2921, 1706, 1601, 1537, 1501, 1444, 1378, 1313, 1221, 1082, 1053, 1028, 754, 692 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.0 Hz, 2H), 7.34 – 7.26 (m, 2H), 7.09 – 7.01 (m, 1H), 6.61 (br s, 1H), 5.42 – 5.37 (m, 1H), 5.09 (ddt, *J* = 7.0, 5.4, 1.5 Hz, 1H), 4.69 (d, *J* = 7.2 Hz, 2H), 2.15 – 2.04 (m, 4H), 1.74 (s, 3H), 1.69 (s, 3H), 1.61 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.72, 142.75, 138.09, 132.02, 129.17, 123.84, 123.46, 118.72, 118.47, 62.15, 39.69, 26.44, 25.83, 17.84, 16.66; HRMS (ESI) exact mass calculated for $[M+Na]^+$ ($C_{17}H_{23}NO_2$) requires *m/z* 273.17288, found *m/z* 273.17302 difference 0.53 ppm.



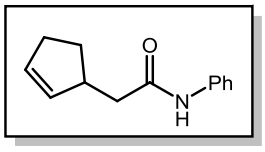
(*Z*)-3,7-Dimethylocta-2,6-dien-1-yl phenylcarbamate

Synthesized using General Procedure A starting with nerol on a 7.32 mmol scale with respect to nerol. The title compound was purified by silica gel chromatography (gradient from 0% EtOAc in Hexanes to 8% EtOAc in Hexanes) to yield 676 mg (34% yield) of the title compound as a colorless oil. IR (neat) 3322, 2969, 2924, 1706, 1601, 1537, 1501, 1444, 1378, 1313, 1220, 1084, 1055, 1027, 753, 692 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.0 Hz, 2H), 7.30 (dd, *J* = 8.6, 7.2 Hz, 2H), 7.09 – 7.02 (m, 1H), 6.57 (br s, 1H), 5.41 (td, *J* = 7.3, 1.7 Hz, 1H), 5.13 – 5.08 (m, 1H), 4.66 (d, *J* = 6.7 Hz, 2H), 2.19 – 2.05 (m, 4H), 1.79 (s, 3H), 1.69 (s, 3H), 1.61 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.66, 143.04, 138.07, 132.38, 129.18, 123.68, 123.47, 119.38, 118.69, 61.89, 32.34, 26.83, 25.86, 23.70, 17.83; HRMS (ESI) exact mass calculated for $[M+Na]^+$ ($C_{17}H_{23}NO_2$) requires *m/z* 273.17288, found *m/z* 273.17244 difference 1.6 ppm.



Cyclohex-2-en-1-yl phenylcarbamate

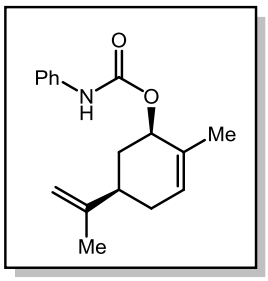
Synthesized using General Procedure A starting with 2-cyclohexen-1-ol on a 10.0 mmol scale with respect to the alcohol component. The title compound was purified by recrystallization from a mixture of hexanes and ethyl acetate to furnish 1.56 g (72% yield) of the title compound as a white solid. ^1H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.5 Hz, 2H), 7.30 (t, *J* = 7.8 Hz, 2H), 7.07 – 7.03 (m, 1H), 6.56 (br s, 1H), 5.99 (dt, *J* = 10.4, 3.9 Hz, 1H), 5.79 (dd, *J* = 10.2, 3.2 Hz, 1H), 5.28 (d, *J* = 5.0 Hz, 1H), 2.17 – 1.88 (m, 3H), 1.85 – 1.62 (m, 3H). Spectral data is consistent with the reported literature spectra.[10]



2-(Cyclopent-2-en-1-yl)-*N*-phenylacetamide

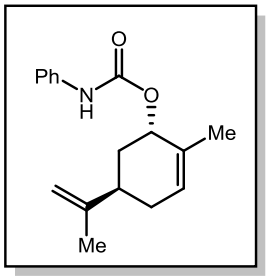
Synthesized using General Procedure B starting with 2-(cyclopent-2-en-1-yl)acetic acid and aniline on a 5.57 mmol scale with respect to the

carboxylic acid. The title compound was purified by recrystallization from a mixture of hexanes and ethyl acetate to afford 878 mg (78% yield) of the title compound as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.0 Hz, 2H), 7.32 (t, *J* = 7.9 Hz, 2H), 7.11 (d, *J* = 7.7 Hz, 1H), 5.78 (m, 1H), 3.29 – 3.15 (m, 1H), 2.45 – 2.32 (m, 4H), 2.20 (m, 1H), 1.58 – 1.49 (m, 1H). Spectral data is consistent with the reported literature spectra.[15]



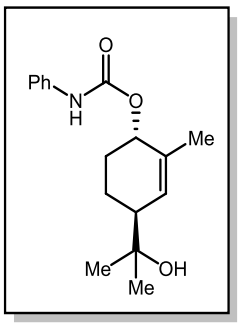
(1R,5R)-2-Methyl-5-(prop-1-en-2-yl)cyclohex-2-en-1-yl phenylcarbamate

Synthesized using General Procedure A starting with (-)-cis-carveol[16] on a 5.14 mmol scale with respect to the alcohol. The title compound was purified by silica gel column chromatography to yield 1.2 g (86% yield) of the title compound. IR (neat): 3319, 2967, 2918, 1695, 1645, 1600, 1532, 1501, 1442, 1374, 1312, 1217, 1179, 1157, 1087, 1048, 1026, 999, 968, 890, 816, 752, 691 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.9 Hz, 2H), 7.31 (t, *J* = 7.8 Hz, 2H), 7.07 (t, *J* = 7.4 Hz, 1H), 6.67 (s, 1H), 5.62 (d, *J* = 5.1 Hz, 1H), 5.46 (t, *J* = 8.4 Hz, 1H), 4.73 (d, *J* = 5.9 Hz, 2H), 2.40 – 2.26 (m, 2H), 2.16 – 2.06 (m, 1H), 2.03 – 1.92 (m, 1H), 1.73 (s, 3H), 1.71 (s, 3H), 1.56 (q, *J* = 11.6 Hz, 1H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.63, 148.38, 138.07, 133.20, 129.19, 126.08, 123.50, 118.65, 109.47, 74.31, 40.40, 34.49, 30.89, 20.68, 19.01.; HRMS (ESI) exact mass calculated for $[M+Na]^+$ ($C_{17}H_{21}NO_2$) requires *m/z* 271.15723, found *m/z* 271.15674, difference 1.8 ppm.



(1R,5S)-2-Methyl-5-(prop-1-en-2-yl)cyclohex-2-en-1-yl phenylcarbamate

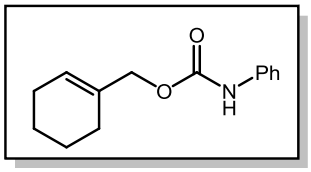
Synthesized using General Procedure A starting with (+)-trans-carveol[17] on a 4.05 mmol scale with respect to the alcohol. The crude compound was purified by silica gel column chromatography to give 880 mg (80% yield) of the title compound. IR (neat): 3322, 2966, 2916, 1697, 1644, 1600, 1529, 1501, 1442, 1375, 1312, 1216, 1168, 1156, 1082, 1043, 1026, 997, 962, 937, 922, 889, 811, 753, 691 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.0 Hz, 2H), 7.34 – 7.28 (m, 2H), 7.09 – 7.03 (m, 1H), 6.62 (s, 1H), 5.79 – 5.73 (m, 1H), 5.29 – 5.23 (m, 1H), 4.79 – 4.70 (m, 2H), 2.38 – 2.30 (m, 1H), 2.26 – 2.18 (m, 1H), 2.12 – 2.06 (m, 1H), 1.89 (dddd, *J* = 17.9, 11.4, 4.3, 2.3 Hz, 1H), 1.76 (d, *J* = 2.4 Hz, 3H), 1.74 (s, 3H), 1.73 – 1.65 (m, 1H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.51, 148.79, 138.11, 131.15, 129.20, 128.10, 123.45, 118.58, 109.45, 71.76, 35.96, 33.94, 31.06, 21.00, 20.84.; HRMS (ESI) exact mass calculated for $[M+Na]^+$ ($C_{17}H_{21}NO_2$) requires *m/z* 271.15723, found *m/z* 271.15749, difference 0.98 ppm.



4-(2-Hydroxypropan-2-yl)-2-methylcyclohex-2-en-1-yl phenyl carbamate

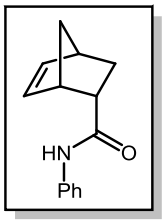
Synthesized using General Procedure A starting from *trans*-sobrerol on a 7.05 mmol scale with respect to the alcohol component. The product is purified by silica gel column chromatography (gradient from 0% EtOAc in Hexanes to 25% EtOAc in Hexanes) to afford 690 mg (34% yield) of the title compound as a white solid. IR (neat) 3316, 2970, 1701, 1602, 1539, 1502, 1444, 1383, 1314, 1226, 1163, 1083, 1044, 1029, 998, 926, 880, 810, 754, 734, 693; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.0 Hz, 2H), 7.31

(dd, *J* = 8.7, 7.3 Hz, 2H), 7.06 (t, *J* = 7.3, 1H), 6.61 (br s, 1H), 5.77 – 5.72 (m, 1H), 5.27 (m, 1H), 2.17 (m, 2H), 1.89 – 1.79 (m, 1H), 1.78 – 1.70 (m, 1H), 1.76 (obscured s, 3H), 1.54 – 1.46 (m, 1H), 1.21 (s, 3H), 1.18 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.52, 138.13, 131.19, 129.22, 128.07, 123.45, 118.55, 72.23, 71.84, 39.57, 30.22, 27.69, 27.03, 26.80, 20.83; HRMS (ESI) exact mass calculated for $[M+Na]^+$ ($C_{17}H_{23}NO_3$) requires *m/z* 289.16779, found *m/z* 289.16783 difference 0.13 ppm.



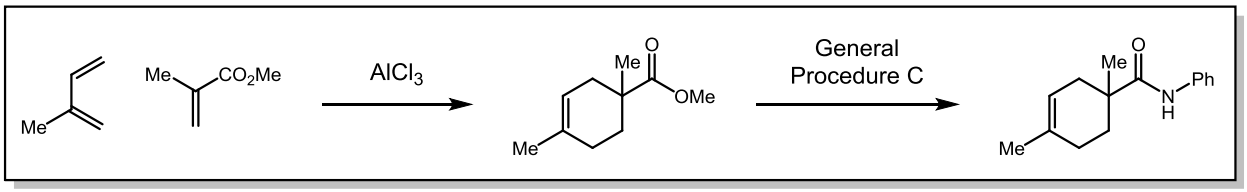
Cyclohex-1-en-ylmethyl phenylcarbamate

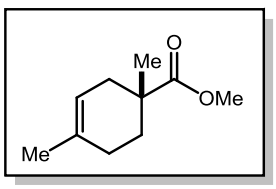
Synthesized using General Procedure A starting with hydroxymethylcyclohexene[11] on a 6.69 mmol scale with respect to the alcohol. The product is purified by silica gel column chromatography to give 1.3 g (84% yield) of the title compound. Spectra are consistent with reported literature values.[18]



Endo-*N*-phenylbicyclo[2.2.1]hept-5-ene-2-carboxamide

Synthesized using General Procedure B starting with racemic 5-norbornene-2-carboxylic acid (ca. 2:1 endo/exo) and aniline on a 5.73 mmol scale with respect to the carboxylic acid. The shown diastereomer of the title compound can be purified by silica gel column chromatography (gradient from 0% EtOAc in Hexanes to 10% EtOAc in Hexanes) to yield 644 mg (53% yield) of the title compound as a white solid. A stereochemical assignment can be made based on the similarity of the coupling constants to the corresponding methyl ester of said compound.[19] IR (neat) 3276, 3187, 3059, 2973, 2940, 2867, 1658, 1597, 1535, 1501, 1489, 1442, 1391, 1337, 1308, 1246, 1196, 1157, 1134, 1029, 991, 929, 905, 874, 843, 920, 754, 697 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.0 Hz, 2H), 7.30 (dd, *J* = 8.5, 7.2 Hz, 2H), 7.08 (br m, 2H), 6.31 (dd, *J* = 5.7, 3.1 Hz, 1H), 6.06 (dd, *J* = 5.7, 2.8 Hz, 1H), 3.24 (s, 1H), 3.03 (dt, *J* = 9.3, 4.0 Hz, 1H), 2.99 (s, 1H), 2.03 (ddd, *J* = 12.7, 9.4, 3.7 Hz, 1H), 1.50 (m, 2H), 1.37 (d, *J* = 8.2 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.59, 138.23, 138.18, 132.21, 129.11, 124.11, 119.70, 50.34, 46.67, 46.12, 43.01, 30.17; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{14}H_{15}NO$) requires *m/z* 213.11536, found *m/z* 213.11567 difference 1.45 ppm.

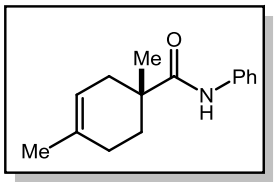




Methyl 1,4-dimethylcyclohex-3-ene-1-carboxylate

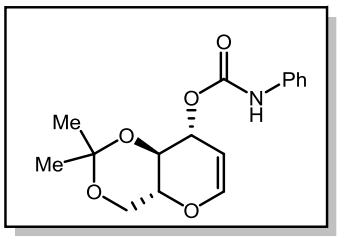
Synthesized as outlined by Fukumoto.[20] To a flame-dried roundbottom under inert atmosphere: $AlCl_3$ (500 mg, 3.75 mmol, 0.09 equiv) is suspended in benzene (25 mL, 1.60 M). Methyl methacrylate (4.00 g, 40 mmol, 1 equiv) was added dropwise. Afterwards, isoprene was added dropwise while cooling the flask in a water bath. The reaction was allowed to stir for fourteen

hours. To quench, 5 mL of concentrated HCl was added to ca. 30 mL of ice and the reaction mixture poured over the ice, rinsing the flask with ethyl acetate. When the ice melts, the aqueous layer was separated and the organic layer was washed with 1M HCl (1 x 30 mL) and brine (1 x 30 mL) prior to drying over Na_2SO_4. Solvent is removed on the rotovap to yield 5.20 g (77% yield) of the title compound as a colorless oil. The crude product is carried forward without purification. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.22 (m, 1H), 3.56 (s, 3H), 2.44 – 2.34 (m, 1H), 1.91 – 1.72 (m, 4H), 1.53 (s, 3H) 1.50 – 1.43 (m, 1H), 1.08 (s, 3H). Spectral data is consistent with the reported literature spectra.[21]



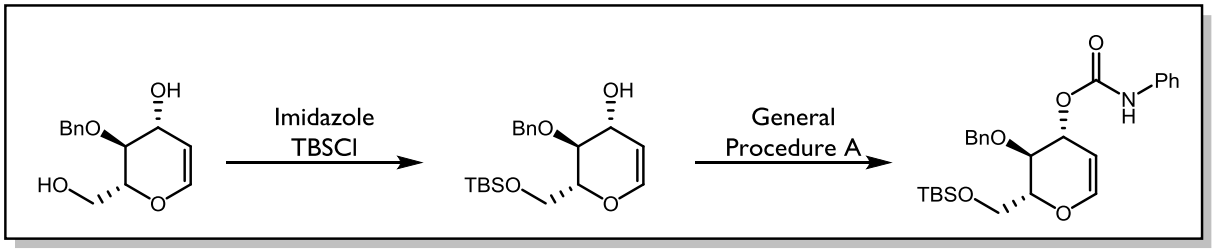
1,4,-Dimethyl-*N*-phenylcyclohex-3-ene-1-carboxamide

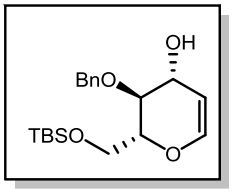
Synthesized using General Procedure C starting with methyl 1,4-dimethylcyclohex-3-ene-1-carboxylate and aniline on a 6.00 mmol scale with respect to the ester. The crude product was purified by recrystallization from a mixture of hexanes and ethyl acetate to afford 817 (59% yield) of the title compound as a white solid. IR (neat) 3312, 3016, 2966, 2918, 1650, 1598, 1532, 1503, 1490, 1436, 1381, 1315, 1245, 1160, 1116, 1062, 1030, 960, 903, 807, 789, 753, 733, 710, 694 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (br s, 1H), 7.48 (d, *J* = 7.5 Hz, 2H), 7.31 (dd, *J* = 8.5, 7.3 Hz, 2H), 7.09 (t, *J* = 7.4 Hz, 1H), 5.51 – 5.44 (m, 1H), 2.55 – 2.47 (m, 1H), 2.14 – 1.97 (m, 4H), 1.71 (s, 3H), 1.70 – 1.63 (m, 1H), 1.30 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) 175.97, 138.24, 135.45, 129.09, 124.23, 120.03, 118.89, 41.46, 34.97, 32.88, 27.98, 25.37, 23.54; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{15}H_{19}NO$) requires *m/z* 229.14666, found *m/z* 229.14680 difference 0.61 ppm.



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

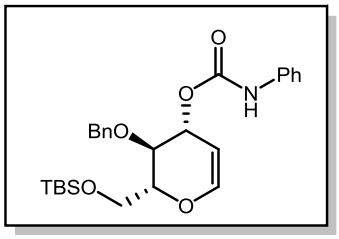
Synthesized using General Procedure A with commercially available 4,6-O-isopropylidene-D-glucal on a 5.46 mmol scale with respect to the glucal component. The crude compound is purified by silica gel column chromatography to give 1.2 g (72% yield) of the title compound. IR (neat): 3325, 2994, 2894, 1729, 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.





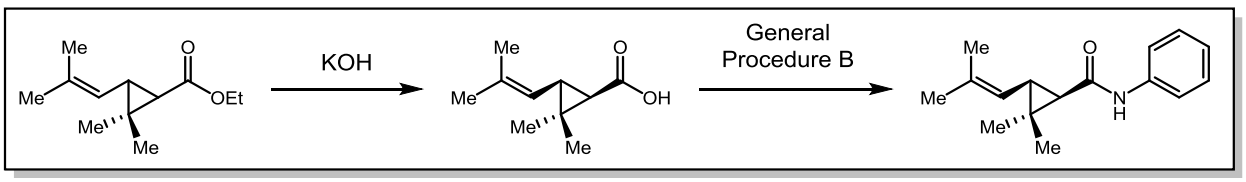
4-*O*-Benzyl-6-*O*-*tert*-butyldimethylsilyl-D-(-)-glucal

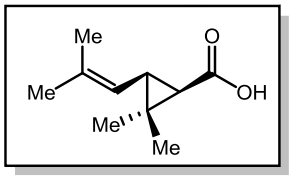
To a solution of commercially available 4-O-benzyl-D-glucal (1.1 g, 4.7 mmol) and imidazole (730 mg, 10.8 mmol) in DMF (4 mL) at 0 ºC was added a solution of *tert*-butylchlorodimethylsilane (740 mg, 4.9 mmol) in DMF (2 mL). The reaction mixture was stirred for 6 h at 0 ºC and then phosphate buffer (pH = 7) was added. The mixture was extracted with diethyl ether, and the organic layer was washed with water and brine, dried over sodium sulfate, and concentrated. The crude product was purified by column chromatography to afford 1.1 g (67% yield) of the pure product. Spectra are consistent with reported literature values.[22]



4-*O*-Benzyl-6-*O*-*tert*-butyldimethylsilyl-D-(-)-glucal phenyl carbamate

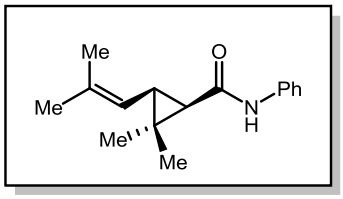
Synthesized using General Procedure A with 4-*O*-Benzyl-6-*O*-*tert*-butyldimethylsilyl-D-(-)-glucal on a 2.49 mmol scale with respect to the glucal component. The crude compound is purified by silica gel column chromatography to give 0.9 g (77% yield) of the title compound. IR (neat): 3331, 2952, 2928, 2883, 2856, 1711, 1650, 1601, 1526, 1501, 1443, 1388, 1360, 1312, 1212, 1149, 1103, 1051, 1028, 937, 883, 835, 813, 776, 748, 693, 674 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 – 7.16 (m, 9H), 6.98 (t, *J* = 7.3 Hz, 1H), 6.32 (d, *J* = 6.0 Hz, 1H), 6.24 (s, 1H), 5.32 (d, *J* = 3.9 Hz, 1H), 4.71 (dd, *J* = 6.3, 2.7 Hz, 1H), 4.66 (s, 2H), 3.94 – 3.78 (m, 4H), 0.83 (s, 9H), 0.00 (s, 6H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.93, 145.92, 138.44, 137.83, 129.19, 128.49, 128.39, 127.83, 123.59, 118.62, 99.33, 78.27, 73.76, 72.95, 71.81, 61.39, 26.04, 18.48, -4.98, -5.21.; HRMS (ESI) exact mass calculated for $[M+Na]^+$ ($C_{26}H_{35}NO_5Si$) requires *m/z* 469.22845, found *m/z* 469.22803, difference 0.9 ppm.





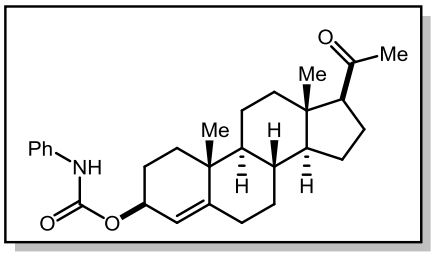
***cis*-Chrysanthemic acid**

To a roundbottom flask equipped with a reflux condenser open to air with no precautions against moisture, ethyl chrysanthemate (ca. 1.6:1 trans/cis as provided by Sigma Aldrich; 27.2 g, 138 mmol, 1 equiv) and KOH (12.0 g, 215 mmol, 1.55 equiv) were dissolved in ethanol (120 mL, 1.15 M). The resultant solution was brought to reflux and allowed to stir for four hours. Upon cooling, the reaction was stripped of ethanol. The resulting residue was dissolved in 100 mL water and extracted with ether (3 x 50 mL). Afterwards, the aqueous layer was acidified with concentrated HCl to pH = 1 and extracted three times with DCM (3 x 50 mL). The combined organics are dried over Na_2SO_4 and are concentrated to yield a crude mixture of the *cis* and *trans* chrysanthemic acid. The residue was brought up in ethyl acetate (ca. 1 mL per gram of raw material) and stored in the freezer until crystallization deposited 4.8 g of crystals with 2.5:1 *cis*:*trans* isomer ratio. The solid was continually recrystallized until 1.66 g (7% yield) of pure *cis*-Chrysanthemic acid was isolated. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.35 (dp, *J* = 8.6, 1.5 Hz, 1H), 1.96 (t, *J* = 8.6 Hz, 1H), 1.75 (s, 3H), 1.70 (d, *J* = 1.4 Hz, 3H), 1.65 (d, *J* = 8.7 Hz, 1H), 1.25 (s, 3H), 1.21 (s, 3H). Spectral data is consistent with the reported literature spectra.[23]



cis-_N_-Phenyl chrysanthemamide

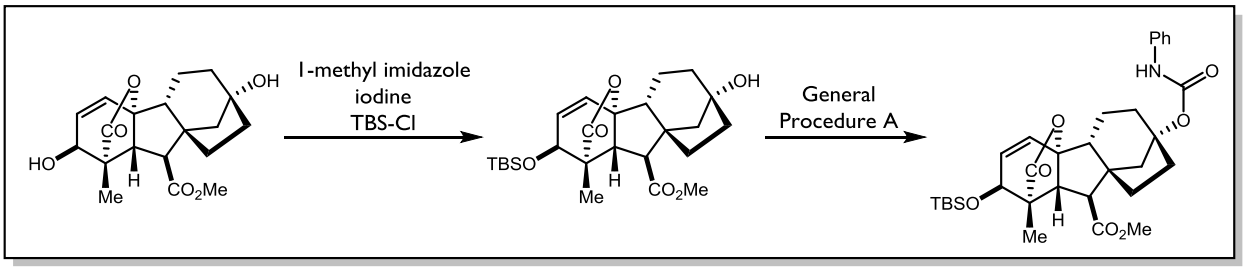
Synthesized using General Procedure B using *cis*-chrysanthemic acid and aniline on a 8.92 mmol scale with respect to the carboxylic acid. The crude product was purified by recrystallization from a mixture of hexanes and ethyl acetate to yield 1.84 g (85% yield) of the title compound as a white solid in >20:1 d.r. Peaks and splitting patterns are identical to that of the corresponding carboxylic acid, indicative of the *cis* geometry of the amide and prenyl groups. IR (neat) 3300, 3058, 2920, 1657, 1599, 1538, 1499, 1441, 1416, 1386, 1375, 1306, 1250, 1193, 1146, 1120, 1074, 1058, 981, 899, 857, 751, 692 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.9 Hz, 2H), 7.41 – 7.36 (br s, 1H), 7.29 (dd, *J* = 8.5, 7.3 Hz, 2H), 7.06 (t, *J* = 7.5 Hz, 1H), 5.47 – 5.41 (m, 1H), 1.82 (s, 3H), 1.76 (s, 3H), 1.58 (d, *J* = 8.7 Hz, 1H), 1.25 (d, *J* = 8.5 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.06, 138.30, 136.48, 129.07, 123.93, 119.63, 118.67, 34.36, 30.62, 29.05, 26.04, 25.12, 18.70, 15.54; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{16}H_{21}NO$) requires *m/z* 243.16231, found *m/z* 243.16198 difference 1.39 ppm.

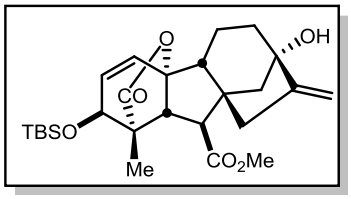


(3*S*,8*S*,9*S*,10*R*,13*S*,14*S*,17*S*)-17-Acetyl-10,13-dimethyl-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopentaphenanthren-3-yl phenylcarbamate

Synthesized using General Procedure A with 3B-Hydroxy-pregn-4-en-20-one[24] on a 2.30 mmol scale with respect to the alcohol. The title compound is purified by silica gel column chromatography to give 2.0 g (87% yield) of the title compound. IR (neat): 3330, 2936, 2875, 2850, 1725, 1694, 1600, 1535, 1501, 1442, 1382, 1357, 1312, 1217, 1154, 1109, 1082, 1050, 1028, 997, 977, 952, 911, 845, 751, 733, 693, 679 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.0 Hz, 2H), 7.23 (t, *J* = 7.8 Hz, 2H), 6.98 (t, *J* = 7.3 Hz, 1H), 6.53 (s, 1H), 5.27 (s, 1H), 5.18 (dd, *J* = 9.7, 6.2 Hz, 1H), 2.46 (t, *J* = 9.0 Hz, 1H), 2.21 – 2.07 (m, 2H), 2.05 (s, 3H), 2.03 – 1.93

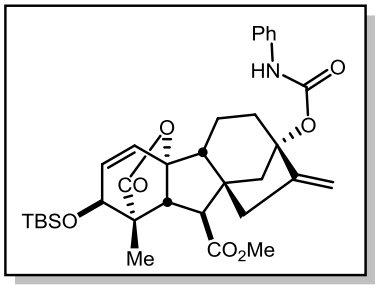
(m, 3H), 1.74 – 1.66 (m, 2H), 1.66 – 1.47 (m, 4H), 1.46 – 1.25 (m, 4H), 1.24 – 1.12 (m, 1H), 1.12 – 1.03 (m, 1H), 1.01 (s, 3H), 0.92 – 0.81 (m, 1H), 0.81 – 0.73 (m, 1H), 0.57 (s, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.72, 153.48, 149.36, 138.12, 129.17, 123.42, 119.53, 118.65, 71.74, 63.80, 56.41, 54.15, 44.22, 38.98, 37.47, 36.00, 35.08, 32.97, 32.25, 31.69, 25.50, 24.54, 22.92, 21.12, 18.99, 13.52.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{28}H_{37}NO_3$) requires *m/z* 435.27734, found *m/z* 435.27714, difference 0.46 ppm.





(1*S*,2*S*,4a*R*,4b*R*,7*S*,9a*S*,10*S*,10a*R*)-Methyl 2-((*tert* butyldimethylsilyl)oxy)-7-hydroxy-1-methyl-8-methylene-13-oxo-1,2,4b,5,6,7,8,9,10,10a-decahydro-4a,1-(epoxymethano)-7,9a-methanobenzo[*a*]azulene-10-carboxylate

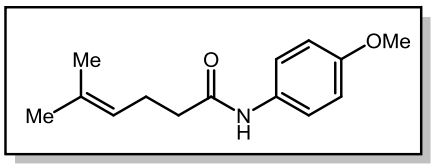
To a solution of gibberellic acid methyl ester[25] (1.2 g, 3.3 mmol), 1-methylimidazole (0.8 mL, 10 mmol), and iodine (2.1 g, 8.3 mmol) in THF (10 mL) was added a solution of *tert*-butylchlorodimethylsilane (550 mg, 3.7 mmol) in THF (2 mL). The reaction mixture was stirred at room temperature for 24 hours or until full consumption of the starting material was seen by TLC. The reaction mixture was concentrated, redissolved in EtOAc and washed with aq. $Na_2S_2O_3$. The organic layer was concentrated and purified by column chromatography on neutral alumina to afford 1.3 g (82% yield) of the pure product. IR (neat): 3451, 2953, 2933, 2858, 1775, 1736, 1457, 1389, 1328, 1252, 1196, 1160, 1073, 1023, 1004, 973, 945, 895, 866, 838, 778, 670 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.21 (d, *J* = 9.3 Hz, 1H), 5.74 (dd, *J* = 9.3, 3.7 Hz, 1H), 5.27 (t, *J* = 2.3 Hz, 1H), 4.95 (s, 1H), 4.10 (d, *J* = 3.6 Hz, 1H), 3.72 (s, 3H), 3.33 (d, *J* = 10.9 Hz, 1H), 2.77 (d, *J* = 10.9 Hz, 1H), 2.24 (dd, *J* = 15.6, 2.5 Hz, 1H), 2.15 (dt, *J* = 15.8, 3.1 Hz, 1H), 2.11 – 2.00 (m, 2H), 1.94 – 1.87 (m, 2H), 1.85 – 1.76 (m, 1H), 1.74 (d, *J* = 11.0 Hz, 1H), 1.71 – 1.62 (m, 1H), 1.16 (s, 3H), 0.91 (s, 9H), 0.09 (d, *J* = 3.1 Hz, 6H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.06, 172.44, 157.36, 133.18, 131.59, 107.61, 90.87, 78.34, 70.13, 54.28, 52.97, 52.12, 51.12, 50.84, 50.55, 44.96, 43.15, 38.41, 25.84, 18.20, 17.18, 15.19, -3.97, -4.71.; HRMS (ESI) exact mass calculated for $[M+Na]^+$ ($C_{26}H_{38}O_6Si$) requires *m/z* 474.24377, found *m/z* 474.24429, difference 1.11 ppm.



(1*S*,2*S*,4a*R*,4b*R*,7*S*,9a*S*,10*S*,10a*R*)-Methyl 2-((*tert*-butyldimethylsilyl)oxy)-1-methyl-8-methylene-13-oxo-7-((phenylcarbamoyl)oxy)-1,2,4b,5,6,7,8,9,10,10a-decahydro-

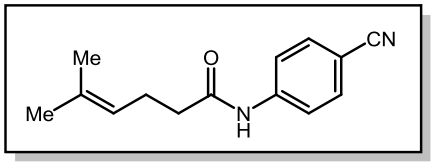
4a,1-(epoxymethano)-7,9a-methanobenzo[*a*]azulene-10-carboxylate

A flame-dried round-bottomed flask was degassed, flushed with argon, and charged with DMAP (67 mg, 0.55 mmol, 0.2 equiv), THF (7 mL), Et_3N (0.38 mL, 2.7 mmol, 1 equiv), (1*S*,2*S*,4a*R*,4b*R*,7*S*,9a*S*,10*S*,10a*R*)-methyl 2-((*tert*-butyldimethylsilyl)oxy)-7-hydroxy-1-methyl-8-methylene-13-oxo-1,2,4b,5,6,7,8,9,10,10a-decahydro-4a,1-(epoxymethano)-7,9a-methanobenzo[*a*]azulene-10-carboxylate (1.3 g, 2.7 mmol, 1 equiv), and then phenyl isocyanate (0.33 mL, 3.0 mmol, 1.1 equiv). The reaction mixture was stirred at room temperature until the starting tertiary alcohol was fully consumed by TLC. The reaction mixture was then concentrated and the crude reaction mixture was purified by silica gel column chromatography (gradient 100% hexanes to 30% Et_2O/hexanes) to afford 1.2 g (73% yield) of the title compound. IR (neat): 3348, 2953, 2857, 1774, 1731 1601, 1529, 1502, 1441, 1375, 1313, 1252, 1220, 1161, 1092, 1075, 1026, 1004, 974, 945, 896, 867, 838, 777, 756, 733, 693, 670 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.0 Hz, 2H), 7.29 (t, *J* = 7.9 Hz, 2H), 7.05 (t, *J* = 7.3 Hz, 1H), 6.58 (s, 1H), 6.22 (d, *J* = 9.3 Hz, 1H), 5.75 (dd, *J* = 9.3, 3.7 Hz, 1H), 5.22 (s, 1H), 5.03 (s, 1H), 4.10 (d, *J* = 3.7 Hz, 1H), 3.73 (s, 3H), 3.35 (d, *J* = 11.0 Hz, 1H), 2.79 (d, *J* = 11.0 Hz, 1H), 2.44 (t, *J* = 9.7 Hz, 2H), 2.34 (d, *J* = 10.9 Hz, 1H), 2.31 – 2.19 (m, 2H), 2.03 – 1.97 (m, 1H), 1.95 (dd, *J* = 12.0, 5.4 Hz, 1H), 1.88 – 1.78 (m, 1H), 1.76 – 1.67 (m, 1H), 1.16 (s, 3H), 0.91 (s, 9H), 0.09 (d, *J* = 3.5 Hz, 6H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.94, 172.35, 153.92, 137.94, 133.21, 131.59, 129.17, 123.55, 120.77, 108.28, 90.74, 70.11, 66.02, 54.28, 53.05, 52.25, 51.22, 50.93, 50.64, 42.90, 40.43, 36.92, 25.85, 18.20, 17.04, 15.18, -3.97, -4.70.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{33}H_{43}NO_7Si$) requires *m/z* 593.28088, found *m/z* 593.28193, difference 1.76 ppm.



***N*-(4-Methoxyphenyl)-5-methylhex-4-enamide**

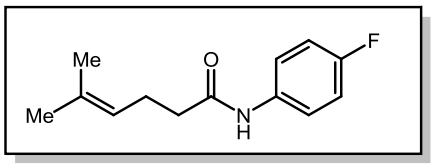
Synthesized using General Procedure B starting from 5-methylhex-4-enoic acid and 4-methoxyaniline on a 10.0 mmol scale with respect to the carboxylic acid. The product was purified by recrystallization from a mixture of hexanes and ethyl acetate to yield 1.8 g (77% yield) of the title compound as a white solid. ^1H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 9.0 Hz, 2H), 7.11 (br s, 1H), 6.85 (d, *J* = 8.9 Hz, 2H), 5.19-5.17 (m, 1H), 3.79 (s, 3H), 2.45 – 2.32 (m, 4H), 1.72 (s, 3H), 1.65 (s, 3H). Spectral data is consistent with the reported literature spectra.[26]



***N*-(4-Cyanophenyl)-5-methylhex-4-enamide**

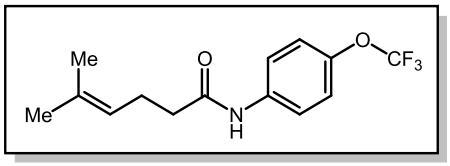
Synthesized using General Procedure B starting from 5-methylhex-4-enoic acid and 4-cyanoaniline on a 2.76 mmol scale with respect to the carboxylic acid. The product was purified by recrystallization from a mixture of hexanes and ethyl acetate to yield 510 mg (81% yield) of the title compound as a white solid. IR (neat): 3320, 3107, 2969, 2918, 2226, 1675, 1594, 1519, 1408, 1311, 1255, 1176, 839 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.8 Hz, 2H), 7.60 (d, *J* = 8.8 Hz, 2H), 5.16 (m, 1H), 2.43 (m, 4H), 1.72 (s, 3H), 1.65 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.55, 142.15, 134.43, 133.44, 122.34, 119.50, 119.01, 110.05, 107.05, 37.90, 25.90, 24.06, 17.95; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{14}H_{16}N_2O$)

requires *m/z* 228.12626, found *m/z* 228.12583 difference 1.88 ppm.



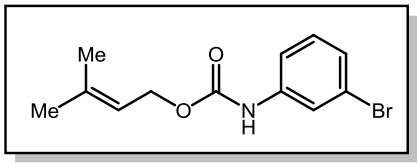
_N_-(4-Fluorophenyl)-5-methylhex-4-enamide

Synthesized using General Procedure B starting from 5-methylhex-4-enoic acid and 4-fluoroaniline on a 6.24 mmol scale with respect to the carboxylic acid. The product was purified by recrystallization from a mixture of hexanes and ethyl acetate to yield 710 mg (52% yield) of the title compound as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 9.0, 4.7 Hz, 2H), 7.18 (br s, 1H), 7.01 (t, *J* = 8.7 Hz, 2H), 5.20 – 5.14 (m, 1H), 2.39 (m, 4H), 1.72 (s, 3H), 1.65 (s, 3H). Spectral data is consistent with the reported literature spectra.[4]



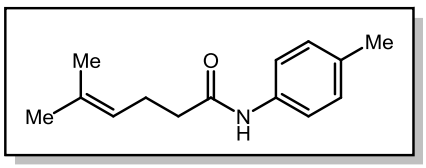
_N_-(4-(Trifluoromethoxy)-phenyl)5-methylhex-4-enamide

Synthesized using General Procedure B starting from 5-methylhex-4-enoic acid and 4-trifluoromethoxyaniline on a 6.24 mmol scale with respect to the carboxylic acid. The product was purified by recrystallization from a mixture of hexanes and ethyl acetate to yield 921 mg (51% yield) of the title compound as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 9.0 Hz, 2H), 7.30 (br s, 1H), 7.17 (d, *J* = 8.6 Hz, 2H), 5.21 – 5.13 (m, 1H), 2.41 (m, 4H), 1.72 (s, 3H), 1.65 (s, 3H). Spectral data is consistent with the reported literature spectra.[4]



3-Methylbut-2-en-1-yl (3-bromophenyl)carbamate

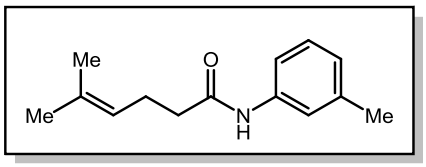
Synthesized using General Procedure D starting from commercially available 3-bromoaniline on a 3.41 mmol scale with respect to prenol and the carbamate. The crude comound is purified by silica gel column chromatography to give 720 mg (74% yield) of the title compound. IR (neat): 3312, 2973, 2934, 1700, 1589, 1526, 1479, 1421, 1380, 1304, 1274, 1214, 1167, 1094, 1072, 1054, 994, 871, 771, 679 cm^{-1}; ^{1}H 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.



5-Methyl-_N_-(p-tolyl)hex-4-enamide

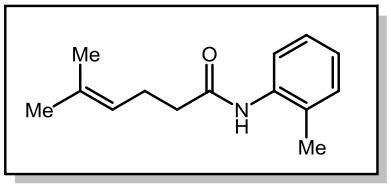
Synthesized using General Procedure B starting from 5-methylhex-4-enoic acid and p-toluidine on a 2.76 mmol scale with respect to the carboxylic acid. The product was purified by recrystallization from a mixture of hexanes and ethyl acetate to yield 372 mg (62% yield) of the title compound as a white solid. IR (neat) 3292, 2358, 3195, 3130, 2962, 2925, 1660, 1604, 1535, 1511, 1448, 1402, 1377, 1351, 1312, 1246, 1190, 1120, 1109, 989, 960, 858, 821, 742 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.1 Hz, 2H), 5.22 – 5.13 (m, 1H), 2.39 (m, 4H), 2.31 (s, 3H), 1.72 (s, 3H), 1.65 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ;

HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{14}H_{19}NO$) requires *m/z* 217.14666, found *m/z* 217.14627 difference 1.82 ppm.



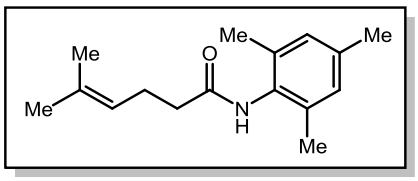
5-Methyl-*N*-(m-tolyl)hex-4-enamide

Synthesized using General Procedure B starting from 5-methylhex-4-enoic acid and m-toluidine on a 2.76 mmol scale with respect to the carboxylic acid. The product was purified by silica gel chromatography (gradient from 0% EtOAc in Hexanes to 15% EtOAc in Hexanes) to afford the 452 mg (75% yield) of the title compound as a colorless oil. IR (neat) 3294, 2968, 2919, 1658, 1614, 1595, 1551, 1490, 1441, 1376, 1345, 1306, 1262, 1209, 1145, 780, 691 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.38 (s, 1H), 7.25 (m, 1H), 7.19 (t, *J* = 7.7 Hz, 1H), 7.14 (s, 1H), 6.91 (d, *J* = 7.4 Hz, 1H), 5.17 (m, 1H), 2.39 (m, 4H), 2.33 (s, 3H), 1.72 (s, 3H), 1.65 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.06, 139.07, 138.01, 133.93, 128.94, 125.09, 122.74, 120.50, 116.86, 37.93, 25.90, 24.32, 21.65, 17.94; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{14}H_{19}NO$) requires *m/z* 217.14666, found *m/z* 217.14656 difference 0.48 ppm.



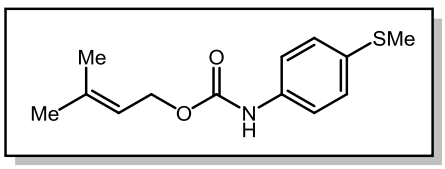
5-Methyl-*N*-(o-tolyl)hex-4-enamide

Synthesized using General Procedure B starting from 5-methylhex-4-enoic acid and o-toluidine on a 3.68 mmol scale with respect to the carboxylic acid. The product was purified by recrystallization from a mixture of hexanes and ethyl acetate to furnish the 500 mg (63% yield) of the title compound as a white solid. ^1H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.0 Hz, 1H), 7.25 – 7.13 (m, 2H), 7.07 (t, *J* = 7.7 Hz, 1H), 6.99 (br s, 1H), 5.20 (m, 1H), 2.44 (m, 4H), 2.24 (s, 3H), 1.72 (s, 3H), 1.66 (s, 3H). Spectral data is consistent with the reported literature spectra.[4]



***N*-Mesityl-5-methylhex-4-enamide**

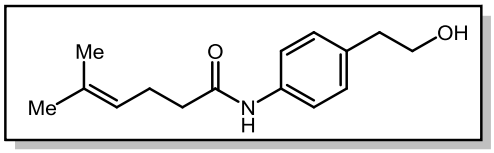
Synthesized using General Procedure B starting from 5-methylhex-4-enoic acid and 2,4,6-trimethylaniline on a 6.05 mmol scale with respect to the carboxylic acid. The product was purified by recrystallization from a mixture of hexanes and ethyl acetate to furnish 1.12 g (75%) of the title compound as a white solid. IR (neat) 3257, 2976, 2921, 2858, 1650, 1609, 1522, 1451, 1376, 1350, 1309, 1264, 1231, 1196, 1107, 1039, 988, 848, 741, 720; N.B. product is a 3:1 mixture of rotamers at RT in $CDCl_3$ and was characterized at high temperature in DMSO, ^1H NMR (500 MHz, DMSO-d_6 at 50 °C) δ 8.96 (s, 1H), 6.85 (s, 2H), 5.18 (m, 1H), 2.31 (m, 4H), 2.22 (s, 3H), 2.09 (s, 6H), 1.68 (s, 3H), 1.62 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6 at 50 °C) δ 170.20, 134.89, 134.66, 132.61, 131.24, 127.92, 123.33, 35.44, 25.24, 24.04, 20.23, 17.70, 17.34; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{16}H_{23}NO$) requires *m/z* 245.17796, found *m/z* 245.17771 difference 1.06 ppm.



3-Methylbut-2-en-1-yl (4-(methylthio)phenyl)carbamate

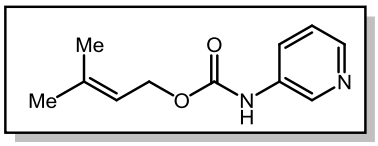
Synthesized using a slight modification of General

Procedure A starting from prenol and 4-(methylthio)phenylisocyanate (in place of phenyl isocyanate) on a 9.85 mmol scale with respect to the prenol and the isocyanate. The crude compound is purified by recrystallization from a mixture of hexanes and ethyl acetate to furnish 1.70 g (69% yield) of the title compound as a white solid. IR (neat) 3325, 2971, 2913, 1698, 1585, 1517, 1495, 1441, 1401, 1380, 1326, 1306, 1282, 1228, 1123, 1094, 1066, 1015, 980, 967, 860, 816, 788, 765, 747; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.3 Hz, 2H), 7.22 (d, *J* = 8.6 Hz, 2H), 6.69 (br s, 1H), 5.38 (m, 1H), 4.65 (d, *J* = 7.3 Hz, 2H), 2.44 (s, 3H), 1.77 (s, 3H), 1.73 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.72, 139.52, 135.88, 132.40, 128.50, 119.41, 118.73, 62.71, 25.90, 18.16, 17.06; HRMS (ESI) exact mass calculated for $[M+Na]^+$ ($C_{13}H_{17}NO_2S$) requires *m/z* 251.09800, found *m/z* 251.09757 difference 1.7 ppm.



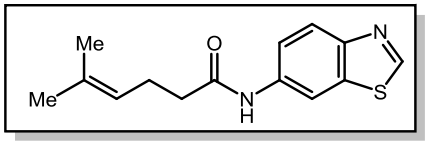
_N_-(4-(2-Hydroxyethyl)phenyl)-5-methylhex-4-enamide

Synthesized using General Procedure B starting from 5-methylhex-4-enoic acid and 2-(4-aminophenyl)ethan-1-ol on a 5.30 mmol scale with respect to the carboxylic acid. The product was purified by recrystallization from a mixture of hexanes and ethyl acetate to furnish 836 mg (64% yield) of the title compound as an off-white solid. IR (neat) 3293, 3035, 2967, 2915, 2877, 1657, 1594, 1526, 1452, 1411, 1375, 1347, 1308, 1277, 1248, 1182, 1111, 1047, 1023, 986, 967, 826; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.3 Hz, 2H), 7.24 (br s, 1H), 7.17 (d, *J* = 8.3 Hz, 2H), 5.17 (m, 1H), 3.83 (t, *J* = 6.5 Hz, 2H), 2.83 (t, *J* = 6.5 Hz, 2H), 2.44 – 2.34 (m, 4H), 1.72 (s, 3H), 1.65 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.14, 136.52, 134.47, 133.95, 129.67, 122.71, 120.24, 63.79, 38.72, 37.82, 25.90, 24.33, 17.94; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{15}H_{21}NO_2$) requires *m/z* 247.15723, found *m/z* 247.15717 difference 0.22 ppm.



3-Methylbut-2-en-1-yl pyridin-3-ylcarbamate

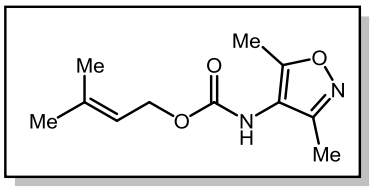
Synthesized using General Procedure D from prenol and 3-aminopyridine on a 6.89 mmol scale with respect to the aniline component. The crude product is purified by silica gel column chromatography to give 880 mg (62% yield) of the title compound. IR (neat): 3238, 3184, 2975, 2913, 1728, 1610, 1550, 1484, 1424, 1379, 1331, 1303, 1225, 1126, 1062, 1028, 978, 859, 801, 766, 705 cm^{-1}; ^{1}H 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.



N-(Benzo[*d*]thiazol-6-yl)-5-methylhex-4-enamide

Synthesized using General Procedure B using 6-aminobenzothiazole on a 3.34 mmol scale with respect to the aniline. The crude product is purified by silica gel column chromatography 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}; ^{1}H 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.



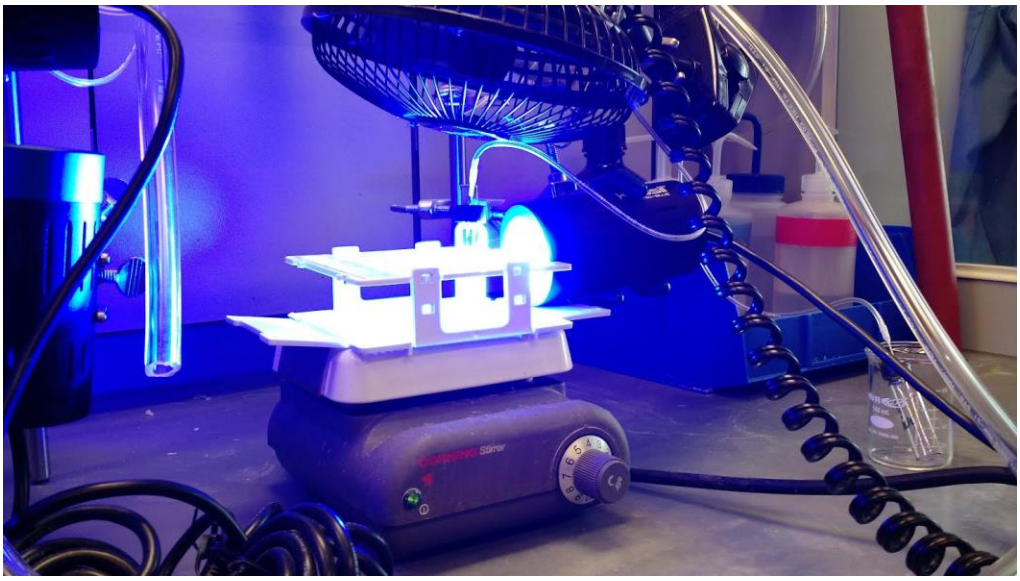
3-Methylbut-2-en-1-yl (3,5-dimethylisoxazol-4-yl)carbamate

Synthesized using a slight modification of General Procedure A using 4-isocyanato-3,5-dimethylisoxale (in place of phenyl isocyanate) and prenol on a 6.94 mmol scale with respect to the isocyanate and alcohol components. The crude compound is recrystallized from a mixture of hexanes and ethyl acetate to afford 1.29 g (83% yield) of the title compound as a white solid. IR (neat) 3276, 2975, 2932, 1729, 1703, 1657, 1521, 1442, 1382, 1345, 1309, 1242, 1125, 1061, 1035, 979, 881, 848, 775, 756; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.12 (br s, 1H), 5.34 (m, 1H), 4.61 (m, 2H), 2.29 (s, 3H), 2.16 (s, 3H), 1.75 (s, 3H), 1.70 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) 163.97, 158.02, 155.06, 139.61, 118.47, 113.62, 62.73, 25.86, 18.12, 11.00, 9.62; HRMS (ESI) exact mass calculated for $[M+H]^+$ requires *m/z* 224.11609, found *m/z* 224.11577 difference 1.42 ppm.

Synthesis and Characterization of Products

General Information and Setup

All reactions were done on a 1.0 mmol scale with respect to substrate. Reactions were run in 2 dram borosilicate vials equipped with a screwcap and teflon septa under inert atmosphere. Reactions were irradiated with a commercially available 34W Kessil KSH150B Blue LED lamp with a fan positioned such that the vial was kept at room temperature throughout irradiation and stirring. As a caution, the light from the lamps is very bright and appropriate safety precautions should be taken. Example reaction setups are demonstrated below.



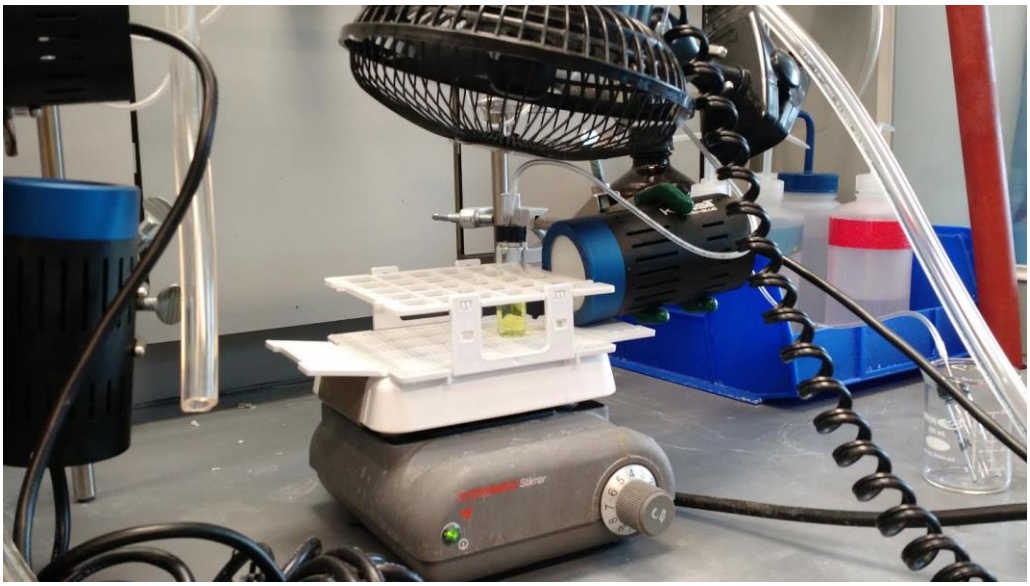
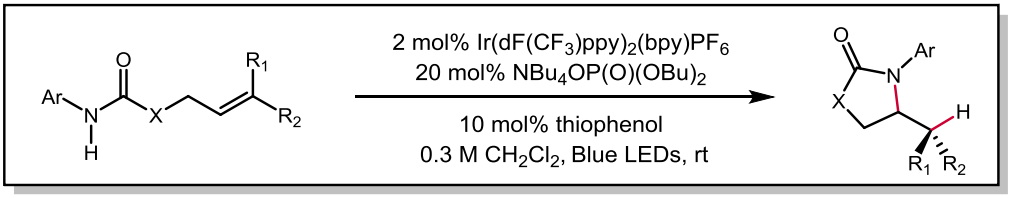
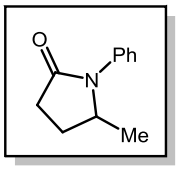


Figure S.1: Sample reaction setup.

General Procedure for Photocatalytic Hydroamination via PCET

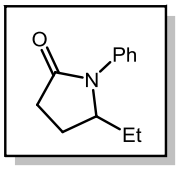


A screw cap dram vial with a teflon septa was charged with starting material (1.0 mmol, 1 equiv), $[Ir(dF(CF_3)ppy)_2(bpy)](PF_6)$[27] (20.2 mg, 0.02 mmol, 2 mol%), and tetrabutylammonium dibutyl phosphate (90.0 mg, 0.2 mmol, 20 mol%) and purged with nitrogen. 3.3 mL of degassed, anhydrous DCM (0.3 M reaction concentration) was added followed by thiophenol (11.0 mg, 0.1 mmol, 10 mol%). The reaction was irradiated with blue LEDs and allowed to stir at room temperature until complete conversion of the starting material was observed by TLC. Upon completion, the reaction mixtures were concentrated. The product was purified from the crude residue by silica gel column chromatography to yield the titled compounds.



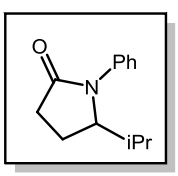
5-Methyl-1-phenylpyrrolidin-2-one (2)

Synthesized using the general procedure, stiring with irradiation for 72 hours. The product is purified by silica gel column chromatography (gradient from 0% EtOAc in Hexanes to 35% EtOAc in Hexanes) to afford 149 mg (85% yield) of the title compound as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.33 (m, 4H), 7.21 (tt, *J* = 6.7, 1.9 Hz, 1H), 4.30 (dp, *J* = 7.4, 6.1 Hz, 1H), 2.69 – 2.50 (m, 2H), 2.38 (dddd, *J* = 13.2, 9.5, 7.4, 6.0 Hz, 1H), 1.76 (dddd, *J* = 12.9, 9.5, 7.3, 5.7 Hz, 1H), 1.21 (d, *J* = 6.2 Hz, 3H). Spectral data is consistent with the reported literature spectra.[28]



5-Ethyl-1-phenylpyrrolidin-2-one (3)

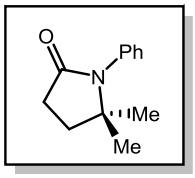
Synthesized using the general procedure, stirring with irradiation for 12 hours. The product is purified by silica gel column chromatography (gradient from 0% EtOAc in Hexanes to 35% EtOAc in Hexanes) to afford 166 mg (88%) of the title compound as a clear oil. IR (neat) 2961, 2934, 2878, 1693, 1597, 1542, 1498, 1461, 1392, 1294, 1222, 1176, 1131, 760, 695 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.32 (m, 4H), 7.24 – 7.18 (m, 1H), 4.17 (tdd, *J* = 8.3, 5.3, 3.0 Hz, 1H), 2.69 – 2.48 (m, 2H), 2.31 (dddd, *J* = 12.8, 9.8, 7.8, 6.5 Hz, 1H), 1.91 – 1.77 (m, 1H), 1.69 (dqd, *J* = 13.7, 7.5, 3.1 Hz, 1H), 1.50 – 1.33 (m, 1H), 0.86 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.53, 137.79, 129.12, 125.94, 124.32, 60.96, 31.51, 26.20, 23.41, 8.81; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{12}H_{15}NO$) requires *m/z* 189.11536, found *m/z* 189.11512 difference 1.27 ppm.



5-Isopropyl-1-phenylpyrrolidin-2-one (4)

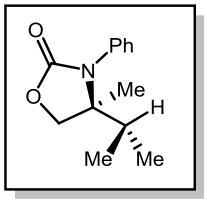
Synthesized using the general procedure, stirring with irradiation for 12 hours. The product is purified by silica gel column chromatography (gradient from 0%

EtOAc in Hexanes to 20% EtOAc in Hexanes) to afford 182 mg (90% yield) of the title compound as a white solid. IR (neat) 2962, 1692, 1598, 1498, 1468, 1394, 1323, 1292, 1224, 1162, 1105, 762, 695 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.34 (m, 4H), 7.20 (tt, *J* = 7.3, 1.7 Hz, 1H), 4.23 (ddd, *J* = 8.6, 5.0, 3.6 Hz, 1H), 2.67 – 2.47 (m, 2H), 2.12 (dddd, *J* = 13.2, 10.2, 8.6, 7.1 Hz, 1H), 2.00 (heptet of doublets, *J* = 6.9, 3.6 Hz, 1H), 1.90 (dddd, *J* = 13.2, 9.9, 6.5, 5.0 Hz, 1H), 0.89 (d, *J* = 7.0 Hz, 3H), 0.75 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.69, 137.74, 129.12, 126.02, 124.61, 64.41, 31.76, 28.47, 18.59, 17.80, 14.39; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{13}H_{17}NO$) requires *m/z* 203.13101, found *m/z* 203.13138 difference 1.81 ppm.



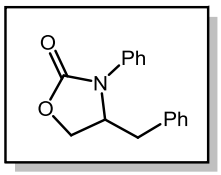
5,5-Dimethyl-1-phenylpyrrolidin-2-one (5)

Synthesized using the general procedure, stirring with irratiation for 12 hours. The product is purified by silica gel column chromatography (gradient from 0% EtOAc in Hexanes to 40% EtOAc in Hexanes) to afford 165 mg (87% yield) of the title compound as a white solid. IR (neat) 3057, 2966, 1683, 1596, 1499, 1463, 1390, 1377, 1325, 1255, 1236, 1225, 1202, 1163, 1117, 1062, 1028, 887, 756, 704, 660; ^1H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.39 (m, 2H), 7.37 – 7.33 (m, 1H), 7.13 (m, 2H), 2.60 (t, *J* = 8.0 Hz, 2H), 2.07 (t, *J* = 8.0 Hz, 2H), 1.26 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.95, 136.42, 129.61, 129.31, 128.07, 62.57, 34.96, 30.32, 27.75; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{12}H_{15}NO$) requires *m/z* 189.11536, found *m/z* 189.11521 difference 0.80 ppm.



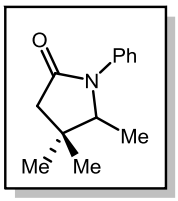
4-Isopropyl-4-methyl-3-phenyloxazolidin-2-one (6)

Synthesized using the general procedure, stirring with irradiation for 14 hours. The product is purified by silica gel column chromatography (gradient from 0% EtOAc in Hexanes to 25% EtOAc in Hexanes) to afford 194 mg (89% yield) of the title comppound as a clear oil. IR (neat) 2973, 1748, 1598, 1499, 1454, 1402, 1386, 1366, 1319, 1235, 1195, 1176, 1143, 1104, 1064, 1012, 966, 763, 720, 699, 682 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.39 (m, 2H), 7.36 – 7.31 (m, 1H), 7.30 – 7.27 (m, 2H), 4.38 (d, *J* = 8.8 Hz, 1H), 3.99 (d, *J* = 8.8 Hz, 1H), 1.90 (heptet, *J* = 6.9 Hz, 1H), 1.38 (s, 3H), 1.09 (d, *J* = 6.8 Hz, 3H), 0.89 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.49, 135.56, 129.41, 128.55, 127.97, 69.77, 65.95, 34.47, 25.37, 17.17, 17.15; HRMS (ESI) exact mass calculated for $[M+H]^+$ requires *m/z* 219.12593, found *m/z* 219.12580 difference 0.57 ppm.



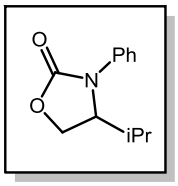
4-Benzyl-3-phenyloxazolidin-2-one (7)

Synthesized using a modification of the general procedure in which the loading of thiophenol is increased to 30 mol%. The reaction is irradiated with stirring for 72 hours. The product is purified by silica gel column chromatography (gradient from 0% EtOAc in Hexanes to 25% EtOAc in Hexanes) to afford 205 mg (81% yield) of the title compound as a white soild. ^1H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.46 (m, 2H), 7.39 – 7.34 (m, 2H), 7.27 – 7.22 (m, 2H), 7.21 – 7.18 (m, 1H), 7.17 – 7.12 (m, 1H), 7.08 – 7.03 (m, 2H), 4.59 (m, 1H), 4.27 (t, *J* = 8.5 Hz, 1H), 4.13 (dd, *J* = 8.8, 4.8 Hz, 1H), 3.07 (dd, *J* = 13.9, 3.5 Hz, 1H), 2.70 (dd, *J* = 13.9, 9.4 Hz, 1H). Spectral data is consistent with the reported literature spectra.[29]



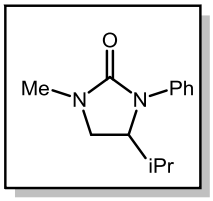
4,4,5-Trimethyl-1-phenylpyrrolidin-2-one (8)

Synthesized using the general procedure, stirring with irradiation for 12 hours. The product is purified by silica gel column chromatography (gradient from 0% EtOAc in Hexanes to 20% EtOAc in Hexanes) to afford 184 mg (91% yield) of the title compound as a white solid. IR (neat) 3064, 2963, 2872, 1690, 1597, 1498, 1394, 1373, 1306, 1268, 1237, 1213, 1136, 1117, 1095, 1075, 987, 966, 953, 834, 755, 693, 665 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.35 (m, 4H), 7.20 (m, 1H), 3.85 (q, *J* = 6.6 Hz, 1H), 2.45 (d, *J* = 16.5 Hz, 1H), 2.31 (d, *J* = 16.4 Hz, 1H), 1.23 (s, 3H), 1.10 (s, 3H), 1.08 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.45, 138.04, 129.07, 125.83, 124.20, 65.25, 46.29, 35.94, 27.91, 22.82, 14.43; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{13}H_{17}NO$) requires *m/z* 203.13101, found *m/z* 203.13063 difference 1.89 ppm.



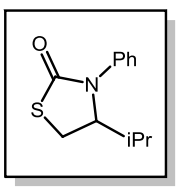
4-Isopropyl-3-phenyloxazolidin-2-one (9)

Synthesized using the general procedure, stirring with irradiation for 12 hours. The product is purified by silica gel column chromatography (gradient from 0% EtOAc in Hexanes to 25% EtOAc in Hexanes) to afford 183 mg (89% yield) of the title compound as a colorless oil. IR (neat) 3065, 2964, 2877, 1743, 1598, 1501, 1458, 1501, 1405, 1392, 1309, 1211, 1148, 1119, 1056, 1003, 995, 959, 760, 694, 676; ^1H NMR (500 MHz, $CDCl_3$) δ 7.49 – 7.43 (m, 2H), 7.42 – 7.37 (m, 2H), 7.19 (tt, *J* = 7.3, 1.2 Hz, 1H), 4.47 – 4.38 (m, 2H), 4.28 – 4.20 (m, 1H), 2.13 (m, 1H), 0.91 (d, *J* = 7.1 Hz, 3H), 0.85 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.18, 136.83, 129.31, 125.44, 122.40, 62.61, 60.64, 27.70, 17.83, 14.34; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{12}H_{15}NO_2$) requires *m/z* 205.11028, found *m/z* 205.11000 difference 1.35 ppm.



4-Isopropyl-1-methyl-3-phenylimidazolidin-2-one (10)

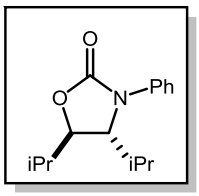
Followed general procedure with 1-methyl-1-(3-methylbut-2-en-1-yl)-3-phenylurea (218 mg, 1 mmol) for 45 hours and purified using alumina column chromatography (gradient 100% hexanes to 33% EtOAc/hexanes) to give 197 mg (90% yield) of the title compound. IR (neat): 2954, 2914, 2870, 1683, 1599, 1494, 1457, 1430, 1402, 1387, 1343, 1322, 1277, 1262, 1214, 1110, 985, 904, 802, 757, 714, 695 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.0 Hz, 2H), 7.33 (t, *J* = 7.8 Hz, 2H), 7.07 (t, *J* = 7.3 Hz, 1H), 4.29 – 4.22 (m, 1H), 3.41 (t, *J* = 9.3 Hz, 1H), 3.21 (dd, *J* = 9.0, 5.7 Hz, 1H), 2.86 (s, 3H), 2.19 – 2.11 (m, 1H), 0.89 (d, *J* = 6.9 Hz, 3H), 0.76 (d, *J* = 6.8 Hz, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.64, 138.94, 128.88, 123.67, 121.81, 57.46, 44.95, 31.04, 27.46, 18.05, 14.34.; HRMS (ESI) exact mass calculated for $[M+Na]^+$ ($C_{13}H_{18}N_2O$) requires *m/z* 218.14191, found *m/z* 218.14226, difference 1.59 ppm.



4-Isopropyl 3-phenylthiazolidin-2-one (11)

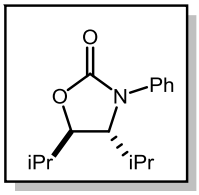
Synthesized using the general procedure, stirring with irradiation for 12 hours.

The product is purified by silica gel column chromatography (gradient from 0% EtOAc in Hexanes to 10% EtOAc in Hexanes) to afford 161 mg (73% yield) of the title compound as a white solid. IR (neat) 3061, 2965, 2932, 2914, 2877, 1652, 1593, 1493, 1965, 1453, 1392, 1379, 1322, 1296, 1248, 1210, 1183, 1155, 1097, 1079, 993, 946, 922, 841, 766, 755, 710, 694, 662 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (m, 2H), 7.30 – 7.27 (m, 2H), 7.27 – 7.24 (m, 1H), 4.37 (ddd, *J* = 8.5, 6.8, 3.7 Hz, 1H), 3.37 (dd, *J* = 11.2, 8.5 Hz, 1H), 3.20 (dd, *J* = 11.2, 6.8 Hz, 1H), 2.02 (ddt, *J* = 10.2, 6.9, 3.2 Hz, 1H), 0.90 (t, *J* = 6.9 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.09, 138.19, 129.38, 127.04, 126.12, 65.63, 28.95, 25.25, 18.32, 14.68; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{12}H_{15}NOS$) requires *m/z* 221.08743, found *m/z* 221.08710 difference 1.52 ppm.



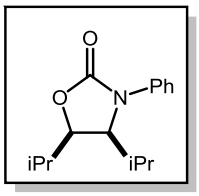
4,5-Diisopropyl-3-phenyloxazolidin-2-one (12)

Followed general procedure with 2,5-dimethylhex-4-en-3-yl phenylcarbamate (248 mg, 1 mmol) and methyl acrylate for 21 hours and purified using alumina column chromatography (gradient 100% hexanes to 33% EtOAc/hexanes) to give 202 mg (82% yield) of the title compound as a 10:1 mixture of diastereomers.



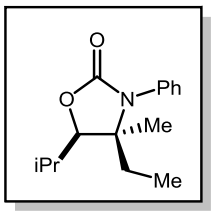
Trans-4,5-Diisopropyl-3-phenyloxazolidin-2-one (12 major)
Major diastereomer:

IR (neat): 2963, 2877, 1742, 1599, 1502, 1462, 1407, 1392, 1314, 1280, 1215, 1181, 1146, 1120, 1034, 1013, 977, 947, 803, 761, 693, 678 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.0 Hz, 2H), 7.38 (t, *J* = 7.9 Hz, 2H), 7.17 (t, *J* = 7.4 Hz, 1H), 4.10 (dd, *J* = 5.3, 3.0 Hz, 1H), 4.05 (t, *J* = 3.2 Hz, 1H), 2.14 – 2.04 (m, 1H), 1.96 – 1.86 (m, *J* = 6.8 Hz, 1H), 1.05 (dd, *J* = 6.8, 3.0 Hz, 6H), 0.90 (d, *J* = 7.1 Hz, 3H), 0.86 (d, *J* = 6.9 Hz, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.62, 137.07, 129.33, 125.19, 122.04, 78.16, 63.41, 33.18, 28.38, 17.83, 17.80, 16.50, 15.08.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{15}H_{21}NO_2$) requires *m/z* 247.15723, found *m/z* 247.15763, difference 1.63 ppm.



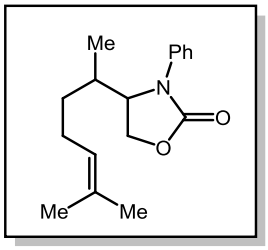
Cis-4,5-Diisopropyl-3-phenyloxazolidin-2-one (12 minor)
Minor diastereomer:

IR (neat): 2964, 2928, 2875, 1727, 1600, 1504, 1468, 1412, 1397, 1324, 1274, 1218, 1151, 1118, 1016, 982, 825, 763, 691, 677 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.0 Hz, 2H), 7.37 (t, *J* = 7.8 Hz, 2H), 7.17 (t, *J* = 7.4 Hz, 1H), 4.34 (d, *J* = 6.6 Hz, 1H), 4.17 (dd, *J* = 11.1, 6.6 Hz, 1H), 2.18 – 2.05 (m, 2H), 1.17 (d, *J* = 6.4 Hz, 3H), 1.04 (d, *J* = 6.7 Hz, 3H), 0.99 (d, *J* = 6.5 Hz, 3H), 0.69 (d, *J* = 7.3 Hz, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.17, 138.86, 129.16, 125.44, 123.35, 84.37, 64.26, 29.36, 27.27, 22.40, 20.00, 19.06, 16.77.; HRMS (ESI) exact mass calculated for $[M+Na]^+$ ($C_{15}H_{21}NO_2$) requires *m/z* 247.15723, found *m/z* 247.15677, difference 1.84 ppm.



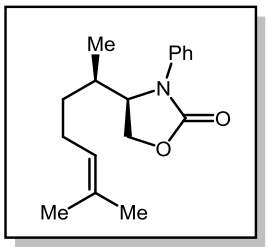
4-Ethyl-5-isopropyl-4-methyl-3-phenyloxazolidin-2-one (13)

Followed general procedure with (*E*)-2,4,-Dimethylhex-4-en-3-yl phenylcarbamate (247 mg, 1 mmol) for 24 hours and purified using silica column chromatography (gradient 100% hexanes to 20% EtOAc/hexanes) to give 179 mg (72% yield) of the title compound as a 4:1 mixture of inseparable diastereomers. Diastreomeric assignments based on allylic strain considerations. IR (neat): 2972, 2880, 1749, 1598, 1499, 1473, 1378, 1285, 1224, 1166, 1071, 1035, 1006, 969, 766, 724, 698 cm^{-1}; Major diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (t, *J* = 7.7 Hz, 2H), 7.33 (q, *J* = 7.4 Hz, 1H), 7.25 (d, *J* = 8.3 Hz, 2H), 3.91 (d, *J* = 9.5 Hz, 1H), 2.25 – 2.14 (m, 1H), 1.82 – 1.63 (m, 2H), 1.29 (s, 3H), 1.18 (d, *J* = 6.6 Hz, 3H), 1.09 (t, *J* = 7.5 Hz, 3H), 1.06 (d, *J* = 6.6 Hz, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.13, 135.46, 129.39, 128.46, 127.79, 90.72, 66.03, 28.35, 28.12, 26.20, 20.31, 20.08, 9.36.; Minor diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (t, *J* = 7.7 Hz, 2H), 7.33 (q, *J* = 7.4 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 4.11 (d, *J* = 7.3 Hz, 1H), 2.10 – 2.00 (m, 1H), 1.73 – 1.64 (m, 1H), 1.60 – 1.52 (m, 1H), 1.24 (s, 2H), 1.15 (d, *J* = 6.7 Hz, 3H), 1.05 (d, *J* = 5.5 Hz, 3H), 1.02 (t, *J* = 7.4 Hz, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.41, 135.34, 129.12, 128.07, 127.79, 84.79, 66.13, 31.72, 29.10, 20.17, 19.94, 18.97, 8.33.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{15}H_{21}NO_2$) requires *m/z* 247.15723, found *m/z* 247.15811, difference 1.1 ppm.



4-(6-Methylhept-5-en-2-yl)-3-phenyloxazolidin-2-one (14)

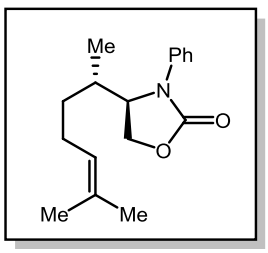
Synthesized using the general procedure, stirring with irradiation for 12 hours. The product is purified by silica gel column chromatography (gradient from 0% EtOAc in Hexanes to 10% EtOAc in Hexanes) to afford the title compound as a 1:1 mixture of diastereomers. For the nerol-derived substrate, the yield was 233 mg (85% yield). For the geraniol-derived substrate, the yield was 246 mg (90% yield).



<u>Top Diastereomer</u>

The diastereomer with a higher Rf in 10% EtOAc in Hexanes is a colorless oil.

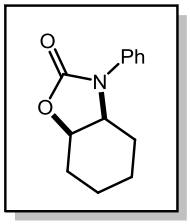
IR (neat) 2966, 2920, 1753, 1696, 1502, 1457, 1406, 1304, 1212, 1129, 1052, 958, 758, 694, 675 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.43 (m, 2H), 7.39 (dd, *J* = 8.7, 7.2 Hz, 2H), 7.19 (tt, *J* = 7.2, 1.3 Hz, 1H), 5.04 (m, 1H), 4.51 (ddd, *J* = 8.8, 5.2, 3.4 Hz, 1H), 4.40 (t, *J* = 8.9 Hz, 1H), 4.23 (dd, *J* = 8.8, 5.1 Hz, 1H), 2.13 – 1.89 (m, 3H), 1.69 (s, 3H), 1.59 (s, 3H), 1.33 – 1.18 (m, 2H), 0.84 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.16, 136.73, 132.63, 129.30, 125.31, 123.64, 122.13, 62.48, 59.24, 32.51, 25.85, 25.71, 17.91, 12.08; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{17}H_{23}NO_2$) requires *m/z* 273.17288, found *m/z* 273.17288 difference 0.01 ppm.



<u>Bottom Diastereomer</u>

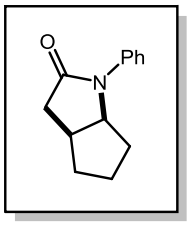
The diastereomer with a lower Rf in 10% EtOAc in Hexanes is a white solid.

IR (neat) 2967, 2922, 1751, 1600, 1503, 1457, 1407, 1311, 1213, 1130, 1054, 989, 959, 759, 694, 675 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.36 (m, 4H), 7.19 (tt, *J* = 7.1, 1.5 Hz, 1H), 4.79 (ddt, *J* = 7.9, 6.4, 1.5 Hz, 1H), 4.47 – 4.40 (m, 2H), 4.26 – 4.17 (m, 1H), 2.01 – 1.83 (m, 2H), 1.74 (m, 1H), 1.54 (s, 3H), 1.48 (s, 3H), 1.40 (m, 1H), 1.10 (m, 1H), 0.90 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) 156.33, 136.82, 132.37, 129.27, 125.58, 123.64, 122.78, 63.46, 60.84, 32.43, 28.83, 25.72, 25.31, 17.71, 15.15; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{17}H_{23}NO_2$) requires *m/z* 273.17288, found *m/z* 273.17331 difference 1.57 ppm.



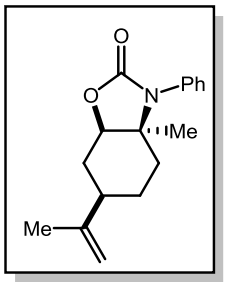
3-Phenylhexahydrobenzo[d]oxazol-2(3H)-one (15)

Synthesized using the general procedure, stirring with irradiation for 12 hours. The product is purified by silica gel column chromatography (gradient from 0% EtOAc in Hexanes to 25% EtOAc in Hexanes) to afford 191 mg (88% yield) of the title compound in >20:1 diastereoselectivity as a white solid. Major diastereomer: ^1H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.0 Hz, 2H), 7.37 (t, *J* = 7.8 Hz, 2H), 7.15 (t, *J* = 7.4 Hz, 1H), 4.67 (m, 1H), 4.27 (q, *J* = 6.6 Hz, 1H), 2.18 – 2.08 (m, 1H), 2.08 – 1.96 (m, 1H), 1.81 (ddt, *J* = 15.1, 10.1, 4.9 Hz, 1H), 1.67 – 1.51 (m, 4H), 1.29 (m, 1H). Spectral data is consistent with the reported literature spectra.[28]



1-Phenylhexahydrocyclopenta[b]pyrrol-2(1*H*)-one (16)

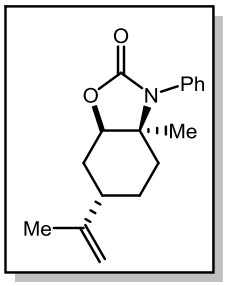
Synthesized using the general procedure, stirring with irradiation for 12 hours. The product is purified by silica gel column chromatography (gradient from 0% EtOAc in Hexanes to 20% EtOAc in Hexanes) to afford 179 mg (89% yield) of the title compound in >20:1 diastereoselectivity as a white solid. Major diastereomer: IR (neat) 2955, 2867, 1691, 1598, 1498, 1387, 1309, 1295, 1282, 1231, 759, 694 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.0 Hz, 2H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.17 (t, *J* = 7.4 Hz, 1H), 4.64 (m, 1H), 2.92 – 2.77 (m, 2H), 2.36 (dd, *J* = 17.1, 2.9 Hz, 1H), 1.91 (m, 1H), 1.76 – 1.69 (m, 2H), 1.68 – 1.60 (m, 2H), 1.57 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.15, 138.34, 129.01, 125.28, 122.80, 65.19, 39.53, 34.33, 34.24, 32.40, 24.15; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{13}H_{15}NO$) requires *m/z* 201.11536, found *m/z* 201.11497 difference 1.98 ppm.



(3a*S*,6*R*,7a*R*)-3a-Methyl-3-phenyl-6-(prop-1-en-2-yl)hexahydrobenzo[*d*]oxazol-2(3*H*)-one (17)

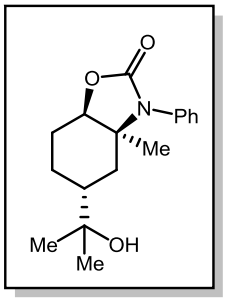
Followed general procedure with (1R,5R)-2-Methyl-5-(prop-1-en-2-yl)cyclohex-2-en-1-yl phenylcarbamate (272 mg, 1 mmol) for 18 hours and purified using silica column chromatography (gradient 100% hexanes to 33% EtOAc/hexanes) to give 240 mg (88% yield) of the title compound as a >20:1 mixture of diastereomers. Major diastereomer: IR (neat): 3071, 2934, 2860, 1742, 1645, 1597, 1496, 1453, 1440, 1366, 1339, 1266, 1223, 1193, 1163, 1147, 1062, 1005, 966, 889, 873, 764, 697, 685 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.42 (t, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.23 (d, *J* = 7.7 Hz, 2H), 4.76 (d, *J* = 10.5 Hz, 2H), 4.36 (dd, *J* = 9.9, 6.6 Hz, 1H), 2.29 – 2.21 (m, 1H), 2.02 – 1.92 (m, 2H), 1.75 (s, 3H), 1.68 – 1.60 (m, 2H), 1.50 – 1.40 (m,

2H), 1.36 (s, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.44, 147.96, 135.07, 129.43, 128.82, 128.06, 109.91, 80.52, 62.18, 40.68, 34.24, 32.44, 26.67, 26.48, 20.86.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{17}H_{21}NO_2$) requires *m/z* 251.15273, found *m/z* 271.15736, difference 0.48 ppm.



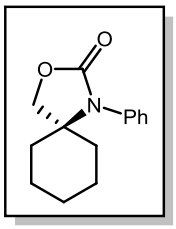
(3a*S*,6*S*,7a*R*)-3a-Methyl-3-phenyl-6-(prop-1-en-2-yl)hexahydrobenzo[*d*]oxazol-2(3*H*)-one (18)

Followed general procedure with (1R,5S)-2-Methyl-5-(prop-1-en-2-yl)cyclohex-2-en-1-yl phenylcarbamate (272 mg, 1 mmol) for 18 hours and purified using silica column chromatography (gradient 100% hexanes to 33% EtOAc/hexanes) to give 255 mg (94% yield) of the title compound as a >20:1 mixture of diastereomers. Major diastereomer: IR (neat): 2935, 2861, 1748, 1644, 1596, 1498, 1453, 1369, 1350, 1269, 1229, 1203, 1180, 1128, 1064, 1025, 977, 964, 888, 763, 697, 683 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (t, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.25 (d, *J* = 7.9 Hz, 2H), 4.76 (d, *J* = 17.5 Hz, 2H), 4.41 – 4.36 (m, 1H), 2.38 – 2.28 (m, 2H), 1.95 – 1.84 (m, 2H), 1.82 – 1.76 (m, 1H), 1.75 (s, 3H), 1.67 – 1.58 (m, 1H), 1.31 (s, 3H), 1.24 – 1.13 (m, 1H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.19, 148.30, 135.49, 129.29, 128.11, 127.71, 109.64, 80.94, 62.12, 38.16, 34.89, 30.78, 26.36, 21.94, 21.08.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{17}H_{21}NO_2$) requires *m/z* 251.15273, found *m/z* 271.15705, difference 0.67 ppm.



5-(2-Hydroxypropan-2-yl)-3a-methyl-3-phenylhexahydrobenzo[d]oxazol-2(3H)-one (19)

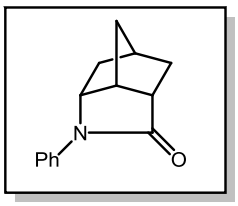
Synthesized using the general procedure, stirring with irradiation for 18 hours. The product is purified by silica gel column chromatography (gradient from 10% EtOAc in Hexanes to 70% EtOAc in Hexanes) to afford 267 mg (92% yield) of the title compound in >20:1 d.r. as a white solid. IR (neat) 3450, 2971, 1739, 1597, 1499, 1455, 1382, 1268, 1210, 1156, 1119, 1066, 972, 946, 837, 766, 699; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.38 (m, 2H), 7.34 – 7.29 (m, 1H), 7.24 (m, 2H), 4.42 (t, *J* = 3.1 Hz, 1H), 2.36 – 2.29 (m, 1H), 1.89 – 1.79 (m, 3H), 1.74 (m, 1H), 1.57 (m, 1H), 1.30 (s, 3H), 1.22 (d, *J* = 4.2 Hz, 6H), 1.19 – 1.07 (m, 1H), ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.20, 135.52, 129.33, 128.16, 127.75, 81.15, 72.23, 62.06, 41.37, 34.37, 27.59, 27.24, 26.68, 22.55, 21.85; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{17}H_{23}NO_3$) requires *m/z* 289.16779, found *m/z* 289.16795 difference 0.55 ppm.



1-Phenyl-3-oxa-1-azaspiro[4.5]decan-2-one (20)

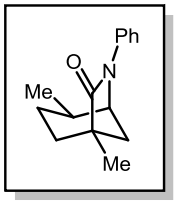
Followed general procedure, stirring for irradiation (232 mg, 1 mmol) for 18 hours and purified using silica column chromatography (gradient 100% hexanes to 33% EtOAc/hexanes) to give 200 mg (86% yield) of the title compound. IR (neat): 2933, 2858, 1752, 1701, 1596, 1543, 1497, 1452, 1394, 1340, 1311, 1285, 1220, 1168, 1130, 1060, 1037, 1009, 985, 956, 761, 728, 699, 684 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.40 (m, 2H), 7.40 – 7.35 (m, 1H), 7.23 – 7.17 (m, 2H), 4.29 (s, 2H), 1.91 – 1.84 (m, 2H), 1.77 (dt, *J* = 14.2, 3.5 Hz, 2H), 1.60 (dd, *J* = 12.9, 3.9 Hz, 1H), 1.47 (td, *J* = 13.2, 4.0 Hz, 2H), 1.28 (qt, *J* = 13.4, 3.5 Hz, 2H), 1.01 – 0.89 (m, 1H).; ^{13}C NMR (126 MHz,

$CDCl_3$) δ 157.42, 134.75, 130.18, 129.37, 128.53, 72.33, 63.15, 35.05, 24.38, 22.95.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{14}H_{17}NO_2$) requires *m/z* 231.12593, found *m/z* 231.12626, difference 1.44 ppm.



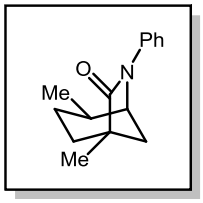
1-Phenylhexahydro-3,5-methanocyclopenta[b]pyrrol-2(1*H*)-one (21)

Synthesized using the general procedure, stirring with irradiation for 12 hours. The product is purified by silica gel column chromatography (gradient from 0% EtOAc in Hexanes to 20% EtOAc in Hexanes) to yield 194 mg (91% yield) of the title compound as a white solid in >20:1 diastereoselectivity. Major diastereomer: IR (neat) 2959, 2871, 1700, 1598, 1495, 1386, 1321, 1304, 1287, 1259, 1221, 1171, 1117, 1073, 1038, 758, 693 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 8.7, 1.1 Hz, 1H), 7.35 (dd, *J* = 8.7, 7.3 Hz, 2H), 7.10 (tt, *J* = 7.2, 1.0 Hz, 1H), 4.12 (m, 1H), 3.08 (m, 1H), 2.61 (ddt, *J* = 11.1, 4.6, 1.7 Hz, 1H), 2.51 (m, 1H), 1.94 (dddd, *J* = 12.8, 11.1, 3.9, 2.8 Hz, 1H), 1.83 (dddd, *J* = 12.5, 8.2, 3.9, 2.7 Hz, 1H), 1.71-1.65 (m, 1H), 1.64 – 1.57 (m, 2H), 1.55 – 1.50 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.59, 139.29, 129.00, 123.98, 119.46, 60.79, 44.37, 44.34, 37.51, 37.41, 37.20, 34.75; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{14}H_{15}NO$) requires *m/z* 213.11536, found *m/z* 213.11525 difference 0.54 ppm.



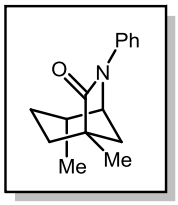
1,4-Dimethyl-6-phenyl-6-azabicyclo[3.2.1]octan-7-one (22)

Synthesized using the general procedure, stirring with irradiation for 16 hours. The product is purified by silica gel column chromatography (gradient from 0% EtOAc in Hexanes to 10% EtOAc in Hexanes) to afford 200 mg (87% yield) of the title compound as a white solid as a 5:1 mixture of diastereomers. N.B., *trans*- and *cis*- labels refer to the relative stereochemistry of the methyl groups on the cyclohexane core respectively.



Trans-1,4-dimethyl-6-phenyl-6-azabicyclo[3.2.1]octan-7-one (22 major)
Major Diastereomer:

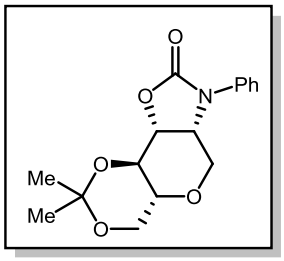
IR (neat) 3064, 2961, 2927, 2871, 1684, 1595, 1503, 1491, 1456, 1397, 1378, 1342, 1323, 1307, 1296, 1272, 1255, 1213, 1157, 1113, 1091, 1061, 1039, 910, 781, 763, 745, 694, 669 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 8.8, 1.1 Hz, 2H), 7.36 – 7.31 (m, 2H), 7.10 (tt, *J* = 7.4, 1.1 Hz, 1H), 4.28 (d, *J* = 5.8 Hz, 1H), 2.18 (ddd, *J* = 10.8, 5.9, 2.6 Hz, 1H), 1.85 – 1.72 (m, 3H), 1.68 (d, *J* = 10.7 Hz, 1H), 1.53 – 1.35 (m, 2H), 1.17 (s, 3H), 0.69 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.53, 140.11, 128.99, 124.58, 122.00, 61.23, 44.47, 44.14, 34.76, 34.57, 28.29, 21.23, 20.54; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{15}H_{19}NO$) requires *m/z* 229.14666, found *m/z* 229.14634 difference 1.40 ppm.



Cis-1,4-dimethyl-6-phenyl-6-azabicyclo[3.2.1]octan-7-one (22 minor)
Minor Diastereomer:

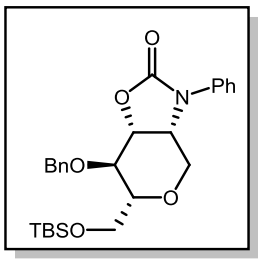
IR (neat) 2960, 2928, 2870, 1699, 1598, 1495, 1457, 1386, 1320, 1259, 1236, 1211, 1151, 1109, 1087, 1062, 993, 911, 879, 765, 754, 691; ^1H NMR (500 MHz,

$CDCl_3$) δ 7.69 (dd, *J* = 8.8, 1.2 Hz, 2H), 7.35 (dd, *J* = 8.7, 7.3 Hz, 2H), 7.13 – 7.08 (m, 1H), 4.13 – 4.02 (m, 1H), 2.20 (pd, *J* = 7.1, 3.3 Hz, 1H), 1.97 (d, *J* = 11.2 Hz, 1H), 1.90 – 1.83 (m, 1H), 1.79 – 1.67 (m, 1H), 1.61 – 1.52 (m, 2H), 1.46 – 1.39 (m, 1H), 1.18 (s, 3H), 1.09 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.52, 138.84, 129.14, 124.14, 120.06, 61.01, 44.86, 36.74, 30.42, 26.72, 25.35, 21.59, 17.01; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{15}H_{19}NO$) requires *m/z* 229.14666, found *m/z* 229.14643 difference 1.03 ppm.



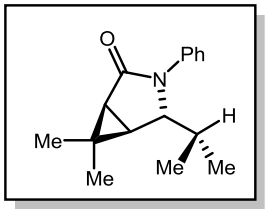
(4a*R*,6a*R*,9a*R*,9b*S*)-2,2-Dimethyl-7-phenylhexahydro-[1,3]dioxino[4',5':5,6]pyrano[3,4-*d*]oxazol-8(6*H*)-one (23)

Followed general procedure with 2,2-Dimethyl-4,4a,8,8a-tetrahydropyrano[3,2-*d*][1,3]dioxin-8-ylphenylcarbamate (305 mg, 1 mmol) for 18 hours and purified using silica column chromatography (gradient 100% hexanes to 33% EtOAc/hexanes) to give 232 mg (78% yield) of the title compound as a >20:1 mixture of diastereomers. Major diastereomer: IR (neat): 2995, 2890, 1764, 1749, 1597, 1504, 1492, 1453, 1383, 1328, 1317, 1275, 1263, 1201, 1168, 1123, 1103, 1085, 1043, 1025, 996, 977, 952, 920, 845, 794, 767, 754, 732, 695, 661 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (t, *J* = 7.7 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.25 (d, *J* = 7.9 Hz, 2H), 4.65 (t, *J* = 7.6 Hz, 1H), 4.41 (dd, *J* = 7.6, 2.7 Hz, 1H), 4.15 (d, *J* = 13.8 Hz, 1H), 4.02 – 3.96 (m, 1H), 3.94 (dd, *J* = 10.9, 5.5 Hz, 1H), 3.76 (t, *J* = 10.5 Hz, 1H), 3.68 (dd, *J* = 13.9, 2.9 Hz, 1H), 3.20 (td, *J* = 10.1, 5.5 Hz, 1H), 1.55 (s, 3H), 1.45 (s, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.68, 135.68, 129.68, 127.33, 125.18, 100.37, 74.16, 72.83, 70.37, 64.57, 62.01, 57.66, 29.14, 19.24.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{20}H_{26}NO_6$) requires *m/z* 305.12632, found *m/z* 305.12625, difference 0.23 ppm.



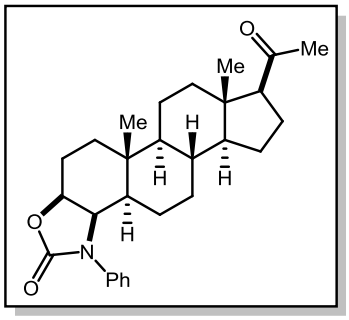
(3a*R*,6*R*,7*S*,7a*R*)-7-(Benzyloxy)-6-(((*tert*-butyldimethylsilyl)oxy)methyl)-3-phenylhexahydro-2*H*-pyrano[3,4-*d*]oxazol-2-one (24)

Followed general procedure with (2*R*,3*S*,4*R*)-3-(benzyloxy)-2-(((*tert*-butyldimethylsilyl)oxy)methyl)-3,4-dihydro-2*H*-pyran-4-yl phenylcarbamate (470 mg, 1 mmol) for 18 hours and purified using silica column chromatography (gradient 100% hexanes to 33% EtOAc/hexanes) to give 440 mg (94% yield) of the title compound as a >20:1 mixture of diastereomers. Major diastereomer: IR (neat): 2952, 2928, 2856, 1755, 1599, 1502, 1471, 1456, 1388, 1340, 1254, 1207, 1155, 1099, 1042, 1004, 974, 945, 835, 814, 775, 755, 695, 671 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.8 Hz, 2H), 7.27 – 7.19 (m, 7H), 7.19 – 7.12 (m, 1H), 4.75 (dd, *J* = 8.1, 5.5 Hz, 1H), 4.71 (d, *J* = 11.3 Hz, 1H), 4.60 (d, *J* = 11.3 Hz, 1H), 4.34 (d, *J* = 7.8 Hz, 1H), 3.91 (d, *J* = 13.4 Hz, 1H), 3.83 (t, *J* = 6.1 Hz, 1H), 3.72 (d, *J* = 4.6 Hz, 2H), 3.56 (dd, *J* = 13.5, 2.5 Hz, 1H), 3.41 (q, *J* = 4.8 Hz, 1H), 0.80 (s, 9H), -0.03 (d, *J* = 3.0 Hz, 6H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.05, 137.78, 135.94, 129.54, 128.64, 128.10, 127.99, 126.52, 123.91, 79.20, 75.63, 74.22, 73.34, 63.30, 63.12, 56.71, 26.05, 18.50, -5.08, -5.18.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{26}H_{35}NO_5Si$) requires *m/z* 469.22845, found *m/z* 469.22794, difference 1.09 ppm.



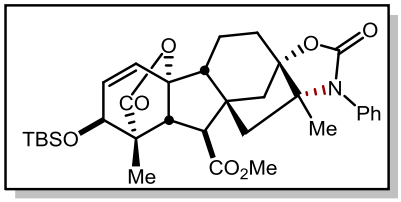
4-Isopropyl-6,6-dimethyl-3-phenyl-3-azabicyclo[3.1.0]hexan-2-one (25)

Synthesized using the general procedure, stirring with irradiation for 16 hours. The product is purified by silica gel column chromatography (gradient from 0% EtOAc in Hexanes to 15% EtOAc in Hexanes) to afford 165 mg (68%) of the title compound as a white solid in >20:1 diastereoselectivity. IR (neat) 3044, 2960, 2928, 2875, 1687, 1599, 1498, 1458, 1385, 1354, 1319, 1290, 1216, 1195, 1150, 1120, 1074, 1039, 1018, 992, 949, 901, 875, 857, 832, 809, 759, 695, 681 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.31 (m, 4H), 7.16 (tt, *J* = 6.8, 1.9 Hz, 1H), 3.95 – 3.92 (m, 1H), 1.99 (m, 1H), 1.95 (dd, *J* = 6.6, 1.9 Hz, 1H), 1.48 (d, *J* = 6.5 Hz, 1H), 1.17 (s, 3H), 1.16 (s, 3H), 0.96 (d, *J* = 7.1 Hz, 3H), 0.83 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.16, 137.25, 129.05, 125.56, 123.81, 62.91, 134.32, 28.62, 26.18, 25.00, 22.06, 18.06, 15.11, 14.59; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{16}H_{22}NO$) requires *m/z* 243.16231, found *m/z* 243.16273 difference 1.7 ppm.



(3a*S*,5a*R*,5b*S*,7a*S*,8*S*,10a*S*,10b*R*,12b*R*)-8-Acetyl-5a,7a-dimethyl-1-phenylhexadecahydro-1*H*-cyclopenta[7,8]phenanthro[1,2-*d*]oxazol-2(12b*H*)-one (26)

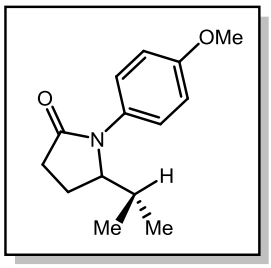
Followed general procedure with (3*S*,8*S*,9*S*,10*R*,13*S*,14*S*,17*S*)-17-acetyl-10,13-dimethyl-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopentaphenanthren-3-yl phenylcarbamate (436 mg, 1 mmol) for 18 hours and purified using silica column chromatography (gradient 100% hexanes to 33% EtOAc/hexanes) to give 410 mg (94% yield) of the title compound as a >20:1 mixture of diastereomers. Major diastereomer: IR (neat): 2938, 2871, 1749, 1700, 1597, 1498, 1454, 1401, 1382, 1355, 1314, 1293, 1199, 1152, 1113, 1082, 1056, 1005, 969, 941, 787, 762, 734, 713, 696, 666 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.39 (t, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.9 Hz, 3H), 4.66 – 4.60 (m, 1H), 4.47 (dd, *J* = 7.3, 3.6 Hz, 1H), 2.47 (t, *J* = 8.7 Hz, 1H), 2.15 – 2.05 (m, 2H), 2.09 (s, 3H), 2.03 – 1.89 (m, 2H), 1.83 (dt, *J* = 13.9, 4.5 Hz, 1H), 1.62 – 1.50 (m, 4H), 1.43 – 1.32 (m, 2H), 1.32 – 1.24 (m, 1H), 1.20 (qd, *J* = 12.2, 10.8, 3.7 Hz, 1H), 1.14 – 1.02 (m, 4H), 1.07 (s, 3H), 0.86 (qd, *J* = 13.1, 3.7 Hz, 1H), 0.75 – 0.60 (m, 2H), 0.54 (s, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.58, 159.09, 139.63, 129.24, 127.60, 126.77, 73.96, 63.78, 61.97, 56.52, 54.87, 47.74, 44.18, 38.97, 35.42, 35.29, 34.26, 32.79, 31.62, 27.42, 24.96, 24.36, 22.86, 20.78, 14.28, 13.50.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{28}H_{37}NO_3$) requires *m/z* 435.27734, found *m/z* 435.27763, difference 0.65 ppm.



Methyl (3a*S*,4a*S*,5*S*,5a*R*,6*S*,7*S*,9a*R*,9b*R*,11a*S*)- 7-((tert-butyldimethylsilyl)oxy)-3a,6-dimethyl-2,14-dioxo-3-phenyl-2,3,3a,4,5,5a,6,7,9b,10-decahydro-11H-9a,6-(epoxymethano)-4a,11a-methanobenzo[1,2]azuleno[5,6-d]oxazole-5-carboxylate (27)

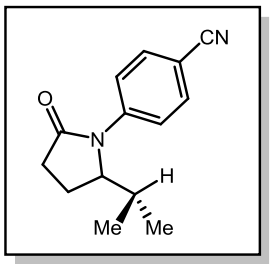
Followed general procedure with (1*S*,2*S*,4a*R*,4b*R*,7*S*,9a*S*,10*S*,10a*R*)-methyl 2-((*tert*-butyldimethylsilyl)oxy)-1-methyl-8-methylene-13-oxo-7-((phenylcarbamoyl)oxy)-1,2,4b,5,6,7,8,9,10,10a-decahydro-4a,1-(epoxymethano)-7,9a-methanobenzo[*a*]azulene-10-carboxylate (594 mg, 1 mmol) for 36 hours and purified using alumina column chromatography (gradient 100% hexanes to 33% EtOAc/hexanes) to give 403 mg (68% yield) of the title compound as a >20:1 mixture of diastereomers. Major diastereomer: IR (neat): 2954, 2885,

2858, 2253, 1739, 1598, 1500, 1454, 1374, 1356, 1329, 1256, 1222, 1203, 1160, 1143, 1134, 1070, 1044, 1024, 1003, 987, 972, 944, 910, 865, 837, 805, 778, 760, 727, 697, 669 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.38 (t, *J* = 7.7 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 1H), 7.24 (d, *J* = 7.9 Hz, 2H), 6.20 (d, *J* = 9.4 Hz, 1H), 5.76 (dd, *J* = 9.3, 3.8 Hz, 1H), 4.08 (d, *J* = 3.8 Hz, 1H), 3.64 (s, 3H), 3.28 (d, *J* = 11.3 Hz, 1H), 2.84 (d, *J* = 11.3 Hz, 1H), 2.30 – 2.17 (m, 3H), 2.17 – 2.07 (m, 1H), 2.07 – 1.97 (m, 2H), 1.91 (d, *J* = 13.1 Hz, 1H), 1.81 (td, *J* = 8.2, 4.2 Hz, 1H), 1.50 (dd, *J* = 13.1, 2.6 Hz, 1H), 1.39 (s, 3H), 1.13 (s, 3H), 0.89 (s, 9H), 0.07 (d, *J* = 4.9 Hz, 6H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.36, 171.80, 155.07, 135.98, 133.49, 131.14, 129.51, 127.55, 127.04, 90.48, 87.01, 69.93, 69.82, 54.32, 52.43, 52.23, 51.29, 51.13, 50.80, 47.61, 42.06, 25.74, 25.55, 23.78, 18.11, 16.26, 15.23, -4.00, -4.80.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{33}H_{43}NO_7Si$) requires *m/z* 593.28088, found *m/z* 593.28102, difference 0.24 ppm.



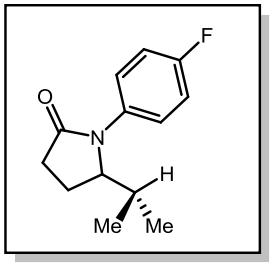
5-Isopropyl-1-(4-methoxyphenyl)pyrrolidin-2-one (28)

Synthesized using the general procedure, stirring with irradiation for 12 hours. The product is purified by silica gel column chromatography (gradient from 0% EtOAc in Hexanes to 35% EtOAc in Hexanes) to yield 203 mg (87% yield) of the title compound as a white solid. IR (neat) 2961, 1688, 1610, 1512, 1466, 1443, 1398, 1328, 1291, 1247, 1179, 1102, 1033, 832 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.26 – 7.22 (m, 2H), 6.95 – 6.87 (m, 2H), 4.12 (ddd, *J* = 8.6, 5.0, 3.4 Hz, 1H), 3.79 (s, 3H), 2.62 – 2.45 (m, 2H), 2.10 (dddd, *J* = 13.3, 10.0, 8.6, 7.3 Hz, 1H), 1.95 (m, 1H), 1.88 (m, 1H), 0.88 (d, *J* = 7.0 Hz, 3H), 0.75 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.79, 157.72, 130.55, 126.25, 114.44, 64.88, 55.56, 31.54, 28.51, 18.57, 17.87, 14.37; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{14}H_{19}NO_2$) requires *m/z* 233.14158, found *m/z* 233.14137 difference 0.90 ppm.



4-(2-Isopropyl-5-oxopyrrolidin-1-yl)benzonitrile (29)

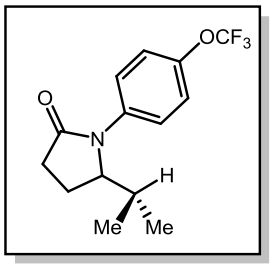
Synthesized using the general procedure, stirring with irradiation for 36 hours. The product is purified by silica gel column chromatography (gradient from 0% EtOAc in Hexanes to 35% EtOAc in Hexanes) to yield 183 mg (80% yield) of the title compound as a white solid. IR (neat) 2964, 2225, 1698, 1602, 1508, 1469, 1420, 1384, 1357, 1322, 1296, 1220, 1179, 1163, 1097, 1015, 962, 905, 841, 668 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.70 – 7.64 (m, 2H), 7.61 – 7.57 (m, 2H), 4.36 – 4.29 (m, 1H), 2.73 – 2.51 (m, 2H), 2.15 (m, 1H), 2.07 (m, 1H), 1.94 (m, 1H), 4.34 – 4.30 (m, 1H), 0.94 (d, *J* = 7.0 Hz, 3H), 0.72 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.90, 141.96, 133.10, 123.50, 118.82, 108.47, 63.47, 31.87, 28.43, 18.59, 17.60, 14.42; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{14}H_{16}N_2O$) requires *m/z* 228.12626, found *m/z* 228.12631 difference 0.20 ppm.



1-(4-Fluorophenyl)-5-isopropylpyrrolidin-2-one (30)

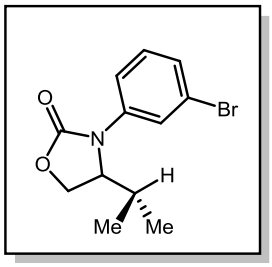
Synthesized using the general procedure, stirring with irradiation for 12 hours. The product is purified by silica gel column chromatography (gradient from 0% EtOAc in Hexanes to 25% EtOAc in Hexanes) to yield

195 mg (88% yield) of the title compound as a white solid. IR (neat) 2963, 2876, 1689, 1601, 1507, 1468, 1422, 1392, 1326, 1293, 1229, 1216, 1159, 1110, 1094, 1014, 961, 905, 835, 815, 728 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.29 (m, 2H), 7.12 – 7.04 (m, 2H), 4.17 (ddd, *J* = 8.6, 5.1, 3.6 Hz, 1H), 2.63 – 2.47 (m, 2H), 2.12 (dddd, *J* = 13.3, 10.0, 8.5, 7.1 Hz, 1H), 2.02 – 1.85 (m, 2H), 0.89 (d, *J* = 7.0 Hz, 3H), 0.74 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.78 , 160.54 (d, *J* = 245.6 Hz), 133.69 (d, *J* = 3.1 Hz), 126.39 (d, *J* = 8.3 Hz), 115.98 (d, *J* = 22.5 Hz), 64.63, 31.54, 28.45, 18.54, 17.84, 14.36; ^{19}F NMR (282 MHz, $CDCl_3$) -116.43 (m); HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{13}H_{16}FNO$) requires *m/z* 221.12159, found *m/z* 221.12131 difference 1.26 ppm.



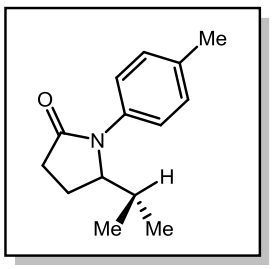
5-Isopropyl-1-(4-(trifluoromethoxyl)phenyl)pyrrolidin-2-one (31)

Synthesized using the general procedure, stirring with irradiation for 12 hours. The product is purified by silica gel column chromatography (gradient from 0% EtOAc in Hexanes to 25% EtOAc in Hexanes) to yield 260 mg (91% yield) of the title compound as a white solid. IR (neat) 2966, 1695, 1608, 1509, 1469, 1426, 1392, 1328, 1253, 1221, 1162, 1115, 1017, 922, 906, 851, 809, 663 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.37 (m, 2H), 7.25 – 7.21 (m, 2H), 4.23 (ddd, *J* = 8.6, 5.0, 3.6 Hz, 1H), 2.64 – 2.49 (m, 2H), 2.13 (dddd, *J* = 13.4, 10.4, 8.6, 7.1 Hz, 1H), 2.01 (ddq, *J* = 10.5, 6.9, 3.5 Hz, 1H), 1.92 (dddd, *J* = 13.5, 10.0, 6.5, 5.0 Hz, 1H), 0.91 (d, *J* = 7.1 Hz, 3H), 0.74 (d, *J* = 6.9 Hz, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.64, 146.46 (q, *J* = 1.9 Hz), 136.19, 125.45, 121.62, 120.44 (q, *J* = 257.2 Hz), 64.15, 31.51, 28.28, 18.43, 17.62, 14.23; ^{19}F NMR (282 MHz, $CDCl_3$) δ -58.48; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{14}H_{16}F_3NO_2$) requires *m/z* 287.11331, found *m/z* 287.11276 difference 1.93 ppm.



3-(3-Bromophenyl)-4-isopropyloxazolidin-2-one (32)

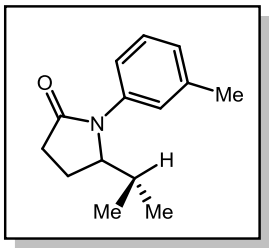
Followed general procedure with 3-methylbut-2-en-1-yl (3-bromophenyl)carbamate (284 mg, 1 mmol) for 36 hours and purified using silica column chromatography (gradient 100% hexanes to 33% EtOAc/hexanes) to give 261 mg (92% yield) of the title compound. IR (neat): 2963, 2931, 2875, 1744, 1590, 1568, 1479, 1434, 1402, 1391, 1350, 1321, 1270, 1204, 1147, 1117, 1092, 1073, 1055, 994, 968, 871, 837, 776, 755, 738, 705, 682 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.41 (dd, *J* = 8.1, 2.1 Hz, 1H), 7.30 (d, *J* = 7.9 Hz, 1H), 7.28 – 7.22 (m, 1H), 4.44 – 4.37 (m, 2H), 4.27 – 4.20 (m, 1H), 2.14 (pd, *J* = 7.0, 2.8 Hz, 1H), 0.92 (d, *J* = 7.0 Hz, 3H), 0.84 (d, *J* = 6.8 Hz, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.69, 138.27, 130.53, 128.26, 124.82, 122.89, 120.45, 62.57, 60.38, 27.59, 17.82, 14.29.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{12}H_{14}BrNO_2$) requires *m/z* 283.02079, found *m/z* 283.02075, difference 0.15 ppm.



5-Isopropyl-1-(*p*-tolyl)pyrrolidin-2-one (33)

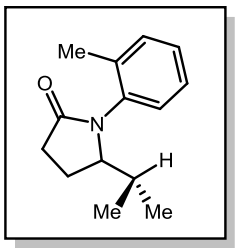
Synthesized using the general procedure, stirring with irradiation for 12 hours. The product is purified by silica gel column chromatography

(gradient from 0% EtOAc in Hexanes to 25% EtOAc in Hexanes) to yield 202 mg (93% yield) of the title compound as a white solid. IR (neat) 2962, 1692, 1514, 1468, 1392, 1326, 1292, 1225, 1162, 1102, 819 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.5 Hz, 2H), 4.18 (ddd, *J* = 8.6, 5.0, 3.5 Hz, 1H), 2.64 – 2.47 (m, 2H), 2.34 (s, 3H), 2.10 (dddd, *J* = 13.2, 10.0, 8.6, 7.2 Hz, 1H), 1.98 (pd, *J* = 6.9, 3.5 Hz, 1H), 1.89 (dddd, *J* = 13.2, 9.8, 6.5, 5.0 Hz, 1H), 0.88 (d, *J* = 7.0 Hz, 3H), 0.75 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.73, 135.90, 135.11, 129.76, 124.67, 64.59, 31.70, 28.49, 21.18, 18.61, 17.84, 14.39; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{14}H_{19}NO$) requires *m/z* 217.14666, found *m/z* 217.14645 difference 1.00 pm.



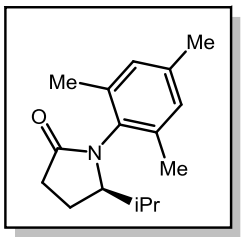
5-Isopropyl-1-(*m*-tolyl)pyrrolidin-2-one (34)

Synthesized using the general procedure, stirring with irradiation for 12 hours. The product is purified by silica gel column chromatography (gradient from 0% EtOAc in Hexanes to 25% EtOAc in Hexanes) to yield 191 mg (88%) of the title compound as a white solid. IR (neat) 2962, 1694, 1606, 1588, 1492, 1466, 1391, 1327, 1237, 1185, 1106, 785, 696 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.26 (m, 1H), 7.18 (s, 1H), 7.13 – 7.10 (m, 1H), 7.02 (m, 1H), 4.20 (ddd, *J* = 8.6, 4.9, 3.5 Hz, 1H), 2.64 – 2.46 (m, 2H), 2.36 (s, 3H), 2.11 (dddd, *J* = 13.2, 10.1, 8.6, 7.2 Hz, 1H), 1.99 (pd, *J* = 6.9, 3.5 Hz, 1H), 1.89 (dddd, *J* = 13.3, 9.9, 6.5, 5.0 Hz, 1H), 0.89 (d, *J* = 6.9 Hz, 3H), 0.76 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.72, 139.02, 137.66, 128.92, 127.02, 125.56, 121.76, 64.62, 31.78, 28.50, 21.65, 18.64, 17.82, 14.42; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{14}H_{19}NO$) requires *m/z* 217.14666, found *m/z* 217.14648 difference 0.83 ppm.



5-Isopropyl-1-(*o*-tolyl)pyrrolidin-2-one (35)

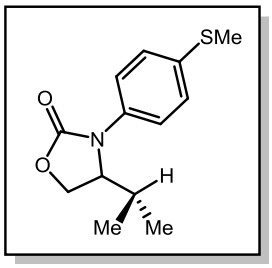
Synthesized using the general procedure, stirring with irradiation for 12 hours. The product is purified by silica gel column chromatography (gradient from 0% EtOAc in Hexanes to 25% EtOAc in Hexanes) to yield 188 mg (87% yield) of the title compound as a white solid. IR (neat) 2962, 1693, 1604, 1581, 1495, 1462, 1393, 1325, 1277, 1225, 1199, 1165, 764, 725, 666; N.B. product is a 1:1 mixture of rotamers at RT in $CDCl_3$ and was characterized at high temperature in DMSO, ^1H NMR (500 MHz, DMSO-d_6 at 120 °C) δ 7.31 – 7.10 (m, 4H), 4.02 (m, 1H), 2.41 (m, 2H), 2.20 (obscured, s, 3H), 2.28 – 2.07 (m, 1H), 1.99 – 1.70 (m, 2H), 0.83 (dd, *J* = 6.8, 2.6 Hz, 6H); ^{13}C NMR (75 MHz, DMSO-d_6 at 120 °C) δ 172.86, 136.81, 134.98, 130.03, 126.35, 126.11, 125.31, 64.23, 29.64, 28.51, 18.56, 17.73, 17.06, 14.64; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{14}H_{19}NO$) requires *m/z* 217.14666, found *m/z* 217.14635 difference 1.44 ppm.



5-Isopropyl-1-mesitylpyrrolidin-2-one (36)

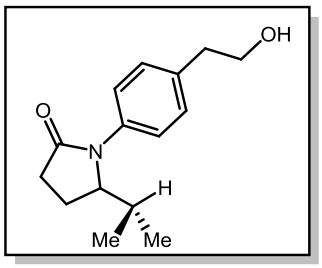
Synthesized using the general procedure, stirring with irradiation for 12 hours. The product is purified by silica gel column chromatography (gradient from 0% EtOAc in Hexanes to 30% EtOAc in Hexanes) to afford 201 mg (82% yield) of the title compound as a colorless oil. IR (neat) 2960,

1693, 1609, 1485, 1325, 1280, 1248, 1223, 1165, 1096, 1034, 851, 668; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.91 (s, 1H), 6.89 (s, 1H), 3.76 (dt, *J* = 8.3, 4.3 Hz, 1H), 2.67 – 2.44 (m, 2H), 2.26 (s, 3H), 2.22 (s, 3H), 2.16 (s, 3H), 2.02 – 1.93 (m, 1H), 1.77 (heptet of d, *J* = 6.8, 3.8 Hz, 1H), 0.95 (d, *J* = 6.7 Hz, 3H), 0.78 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.99, 137.64, 137.24, 134.93, 133.25, 129.76, 129.68, 66.22, 31.17, 30.48, 21.05, 21.01, 20.22, 19.07, 18.50, 16.78; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{16}H_{23}NO$) requires *m/z* 245.17796, found *m/z* 245.17779 difference 0.71 ppm.



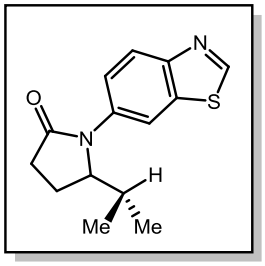
4-Isopropyl-3-(4-(methylthio)phenyl)oxazolidin-2-one (37)

Synthesized using the general procedure, stirring with irradiation for 12 hours. The product is purified by silica gel column chromatography (gradient from 0% EtOAc in Hexanes to 20% EtOAc in Hexanes) to yield 225 mg (90% yield) of the title compound as a white solid. IR (neat) 2962, 2922, 2875, 1740, 1596, 1496, 1414, 1400, 1392, 1320, 1308, 1288, 1266, 1210, 1148, 1120, 1094, 1054, 996, 960, 819, 756, 722, 706; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.5 Hz, 2H), 4.48 – 4.32 (m, 2H), 4.22 (dd, *J* = 6.9, 3.0 Hz, 1H), 2.47 (s, 3H), 2.10 (m, 1H), 0.89 (d, *J* = 7.0 Hz, 3H), 0.83 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.12, 135.33, 134.17, 127.77, 122.94, 62.63, 60.66, 27.71, 17.81, 16.39, 14.35; HRMS (ESI) exact mass calculated for $[M+Na]^+$ ($C_{13}H_{17}NO_2S$) requires *m/z* 251.09800, found *m/z* 251.09783 difference 0.67 ppm.



1-(4-(2-Hydroxyethyl)phenyl)-5-isopropylpyrrolidin-2-one (38)

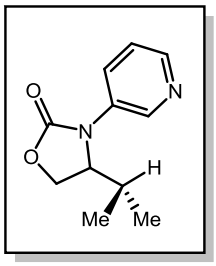
Synthesized using the general procedure, stirring with irradiation for 12 hours. The product is purified by silica gel column chromatography (gradient from 10% EtOAc in Hexanes to 80% EtOAc in Hexanes) to yield 222 mg (90% yield) of the title compound as a yellow oil. IR (neat) 3390, 2961, 2874, 1672, 1610, 1514, 1468, 1399, 1330, 1293, 1228, 1164, 1103, 1049, 963, 827, 668; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.9 Hz, 2H), 4.20 (m, 1H), 3.85 (q, *J* = 6.3 Hz, 2H), 2.85 (t, *J* = 6.5 Hz, 2H), 2.67 – 2.44 (m, 2H), 2.12 (m, 1H), 1.99 (pd, *J* = 6.9, 3.5 Hz, 1H), 1.90 (m, 1H), 1.47 (m, 1H) 0.89 (d, *J* = 7.0 Hz, 3H), 0.75 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.78, 136.39, 136.12, 129.78, 124.85, 64.51, 63.69, 38.89, 31.72, 28.46, 18.60, 17.78, 14.37; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{15}H_{22}NO_2$) requires *m/z* 247.15723, found *m/z* 247.15722 difference 0.02 ppm.



1-(Benzo[*d*]thiazol-6-yl)-5-isopropylpyrrolidin-2-one (39)

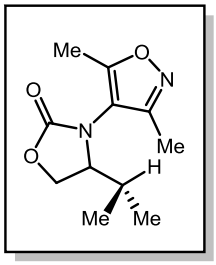
Followed general procedure with N-(Benzo[*d*]thiazol-6-yl)-5-methylhex-4-enamide (260 mg, 1 mmol) for 18 hours and purified using alumina column chromatography (gradient 100% hexanes to 33% EtOAc/hexanes) to give 234 mg (90% yield) of the title compound. IR (neat): 3059, 2961, 2873, 1682, 1599, 1555, 1469, 1447, 1414, 1385, 1357, 1322, 1311, 1288, 1252, 1223, 1198, 1162, 1105, 960, 915, 877, 836, 808, 731, 700, 670 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.97 (s, 1H), 8.13 (d, *J* = 8.8 Hz, 1H), 8.07 (d, *J* = 1.8 Hz, 1H), 7.46 (dd, *J* = 8.6 Hz, 1H), 4.34 – 4.29 (m, 1H), 2.68 – 2.53 (m, 2H), 2.22 – 2.11 (m, 1H), 2.07 – 1.98 (m, 1H), 1.98 –

1.89 (m, 1H), 0.91 (d, *J* = 7.0 Hz, 3H), 0.76 (d, *J* = 6.8 Hz, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.91, 154.34, 151.19, 135.41, 134.54, 123.84, 122.76, 118.20, 64.72, 31.72, 28.56, 18.58, 17.80, 14.42.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{11}H_{14}N_2O_2$) requires *m/z* 260.09833, found *m/z* 260.09784, difference 1.89 ppm.



4-Isopropyl-3-(pyridin-3-yl)oxazolidin-2-one (40)

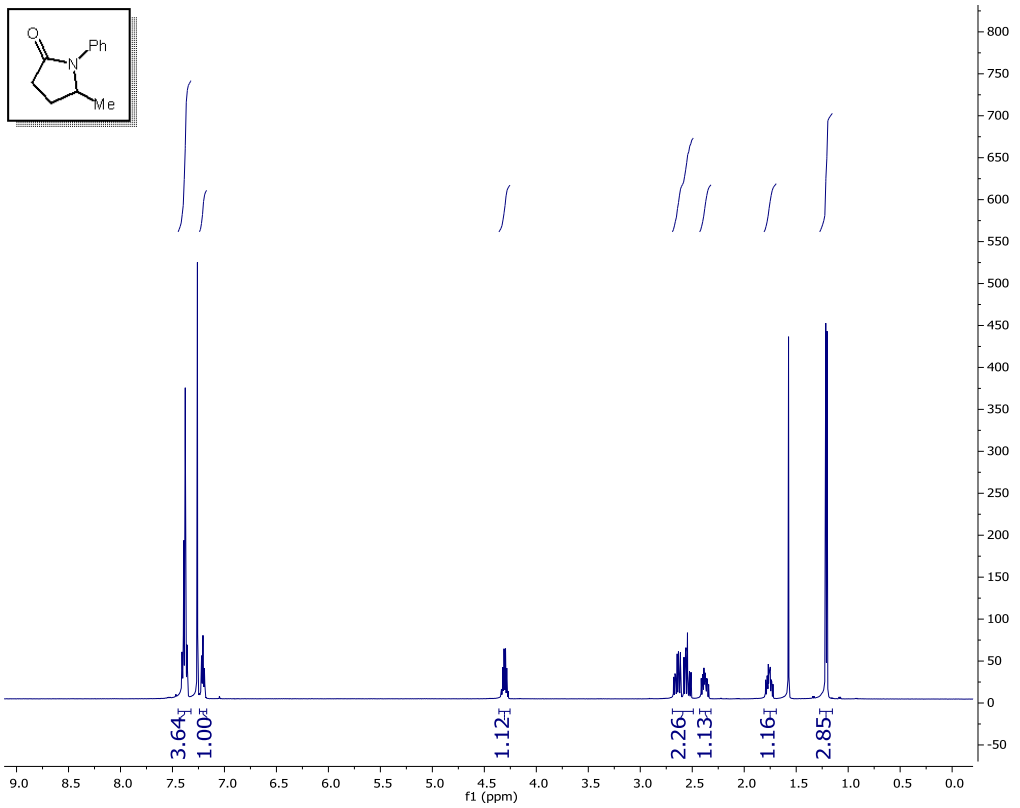
Followed general procedure with 3-methylbut-2-en-1-yl pyridin-3-ylcarbamate (206 mg, 1 mmol) for 36 hours and purified using alumina column chromatography (gradient 100% hexanes to 50% EtOAc/hexanes) to give 182 mg (88% yield) of the title compound. IR (neat): 2957, 2889, 1729, 1584, 1484, 1466, 1415, 1392, 1368, 1320, 1312, 1296, 1223, 1193, 1157, 1119, 1105, 1053, 1043, 1011, 996, 955, 924, 912, 835, 809, 763, 752, 732, 707, 698 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.62 (d, *J* = 2.7 Hz, 1H), 8.39 (d, *J* = 4.7 Hz, 1H), 7.97 (dd, *J* = 8.3, 3.3 Hz, 1H), 7.31 (dd, *J* = 8.4, 4.7 Hz, 1H), 4.52 – 4.38 (m, 2H), 4.26 (dd, *J* = 7.2, 2.9 Hz, 1H), 2.13 (pd, *J* = 7.0, 3.1 Hz, 1H), 0.90 (d, *J* = 7.0 Hz, 3H), 0.82 (d, *J* = 6.8 Hz, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.81, 146.04, 142.75, 133.76, 129.23, 123.84, 62.86, 59.89, 27.56, 17.71, 14.19.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{11}H_{14}N_2O_2$) requires *m/z* 206.10553, found *m/z* 206.10593, difference 1.95 ppm.



3-(3,5-Dimethylisoxazol-4-yl)-4-isopropyloxazolidin-2-one (41)

Synthesized using the general procedure, stirring with irradiation for 12 hours. The product is purified by silica gel column chromatography (gradient from 0% EtOAc in Hexanes to 35% EtOAc in Hexanes) to yield 193 mg (86% yield) of the title compound as a yellow oil. IR (neat) 2968, 1756, 1648, 1508, 1467, 1406, 1323, 1257, 1217, 1125, 1051, 990, 956, 756; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.45 (t, *J* = 9.0 Hz, 1H), 4.23 (dd, *J* = 9.1, 5.9 Hz, 1H), 4.01 (ddd, *J* = 9.2, 5.9, 3.7 Hz, 1H), 2.37 (s, 3H), 2.24 (s, 3H), 1.84 (m, 1H), 0.92 (d, *J* = 6.8 Hz, 3H), 0.88 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.39, 157.64, 156.52, 113.48, 64.13, 61.60, 28.94, 18.09, 15.05, 11.69, 10.42; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{11}H_{14}N_2O_2$) requires *m/z* 206.10553, found *m/z* 206.10593, difference 1.95 ppm.

^{1}H and ^{13}C NMR Spectra of Products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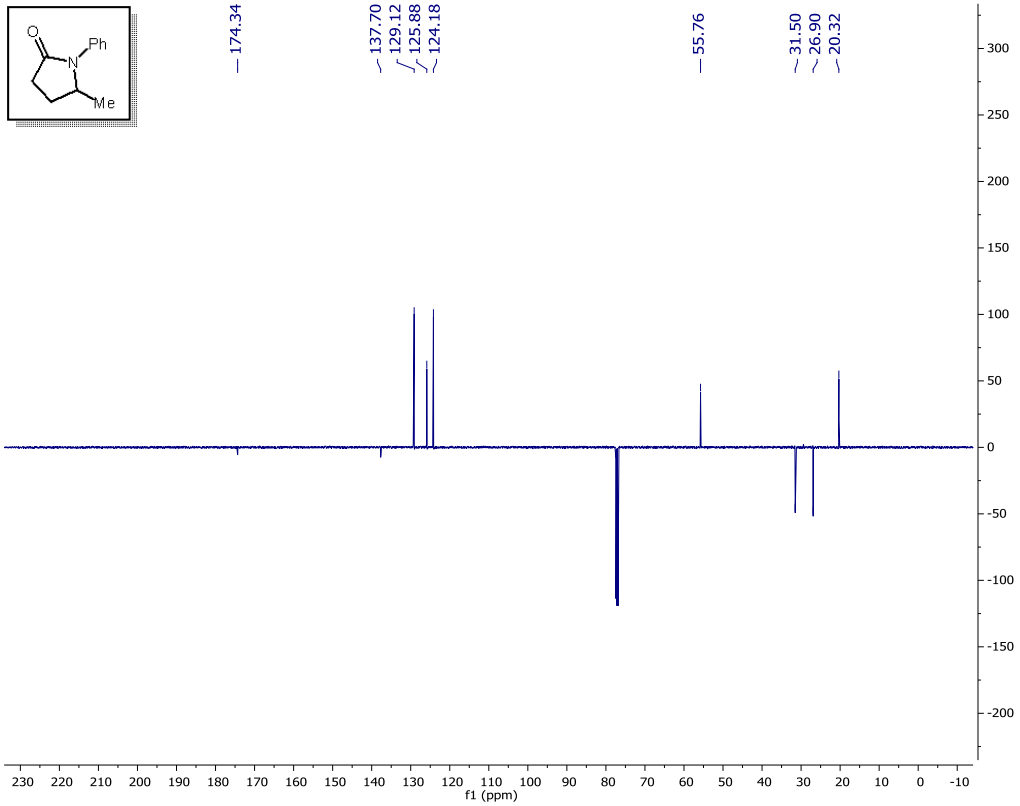
f1 (ppm)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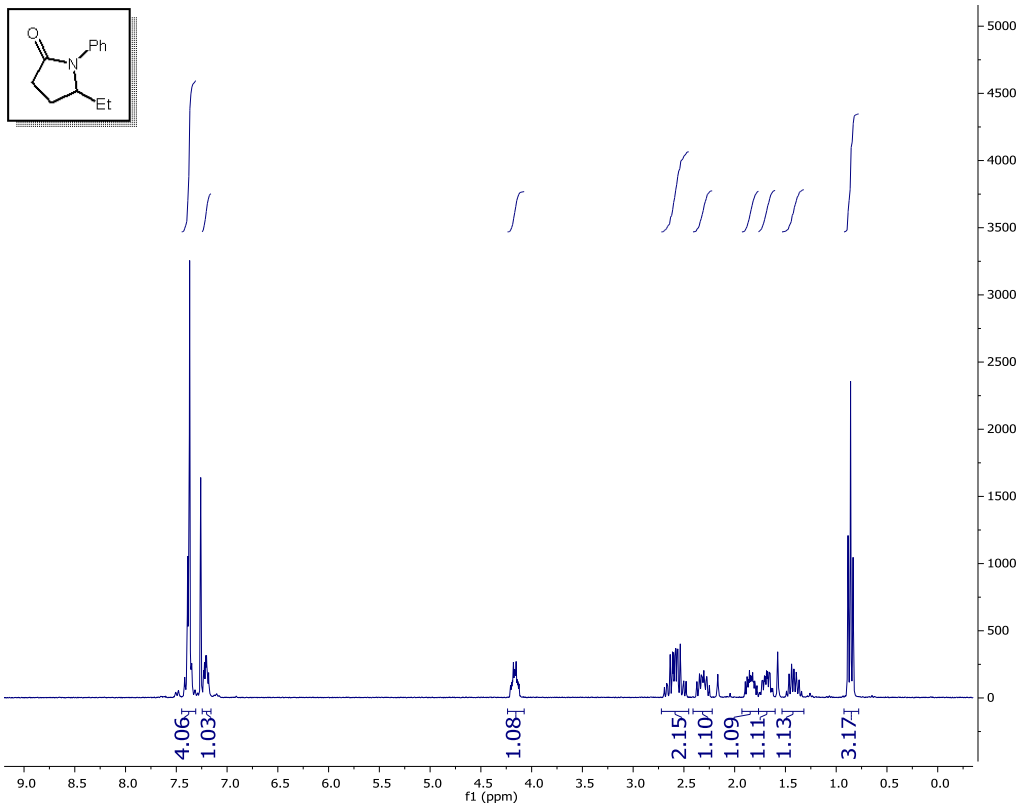
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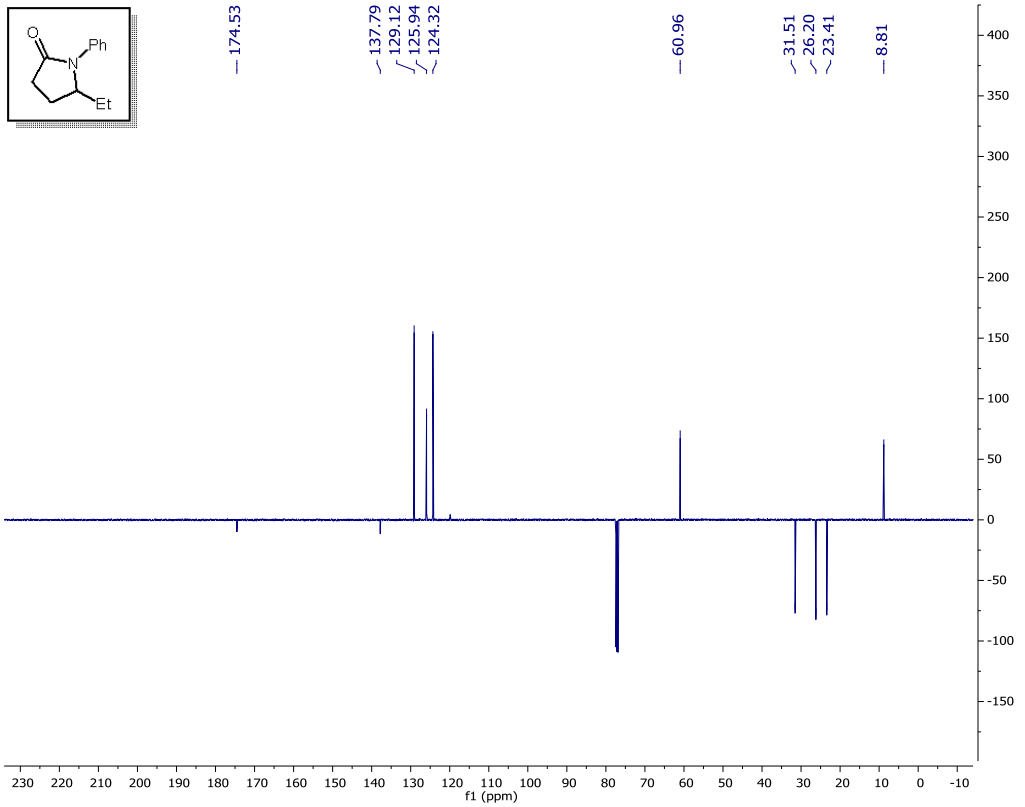
f1 (ppm)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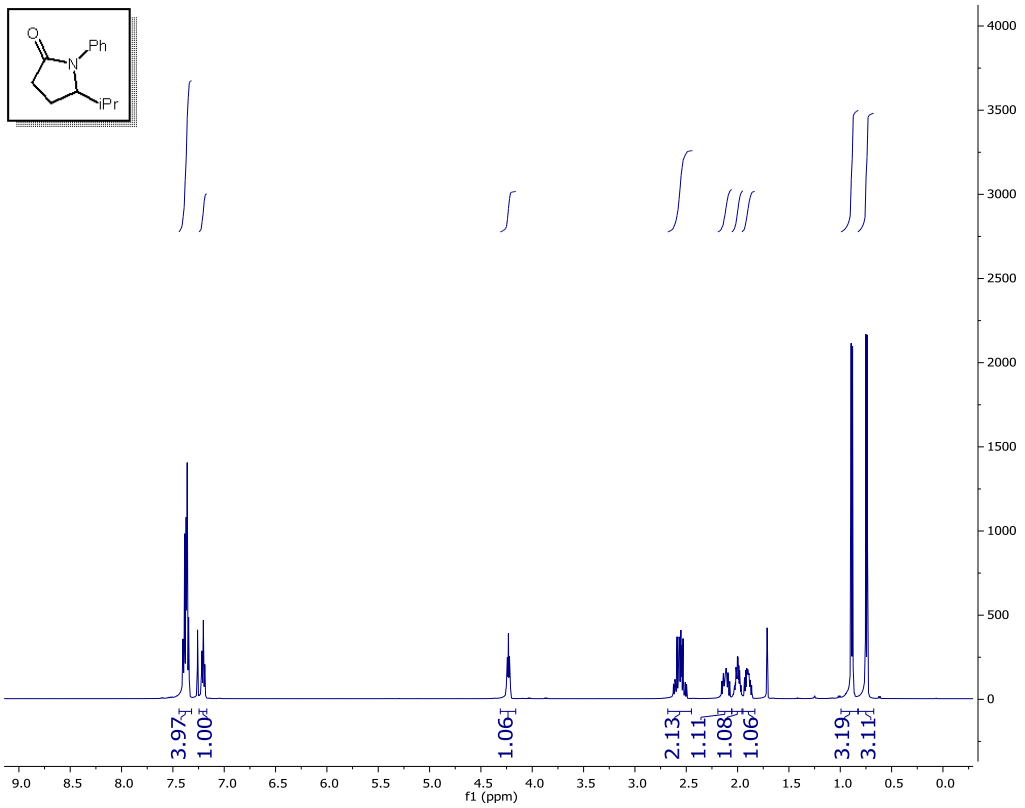
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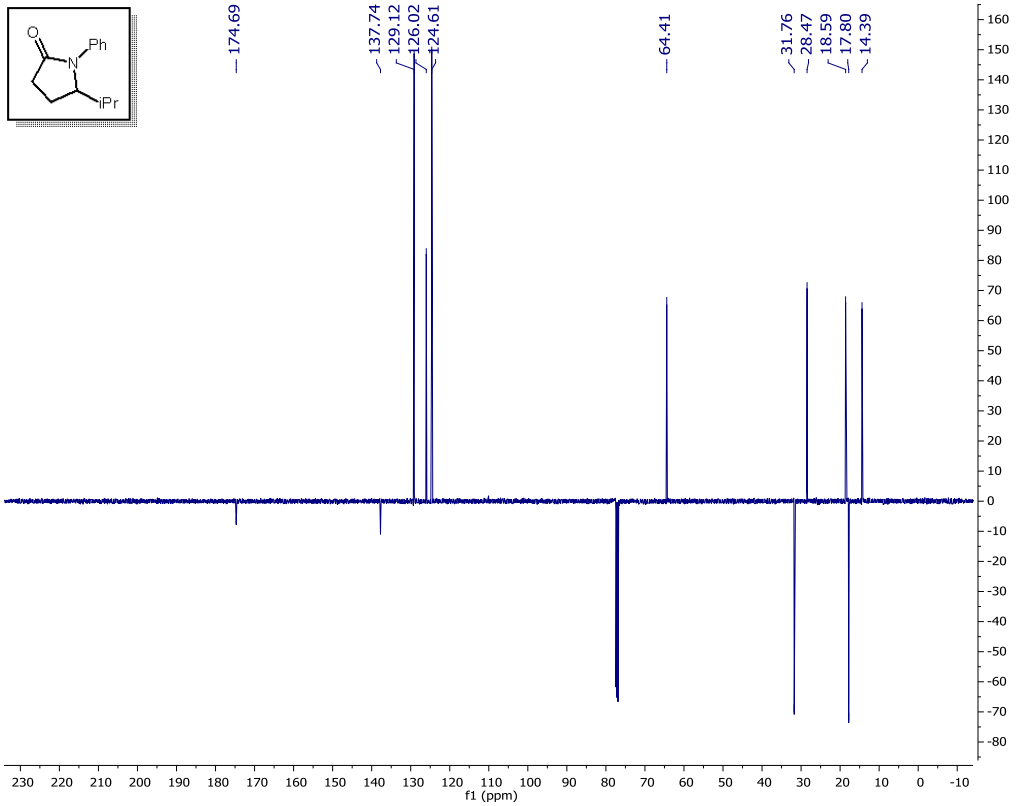
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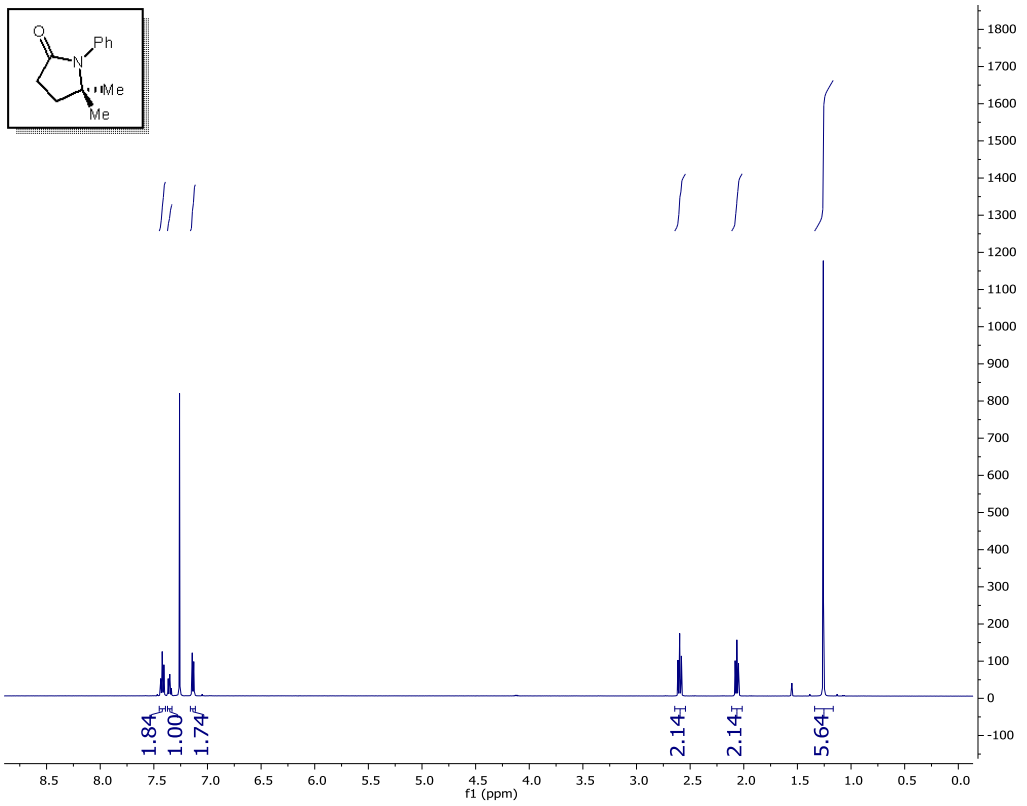
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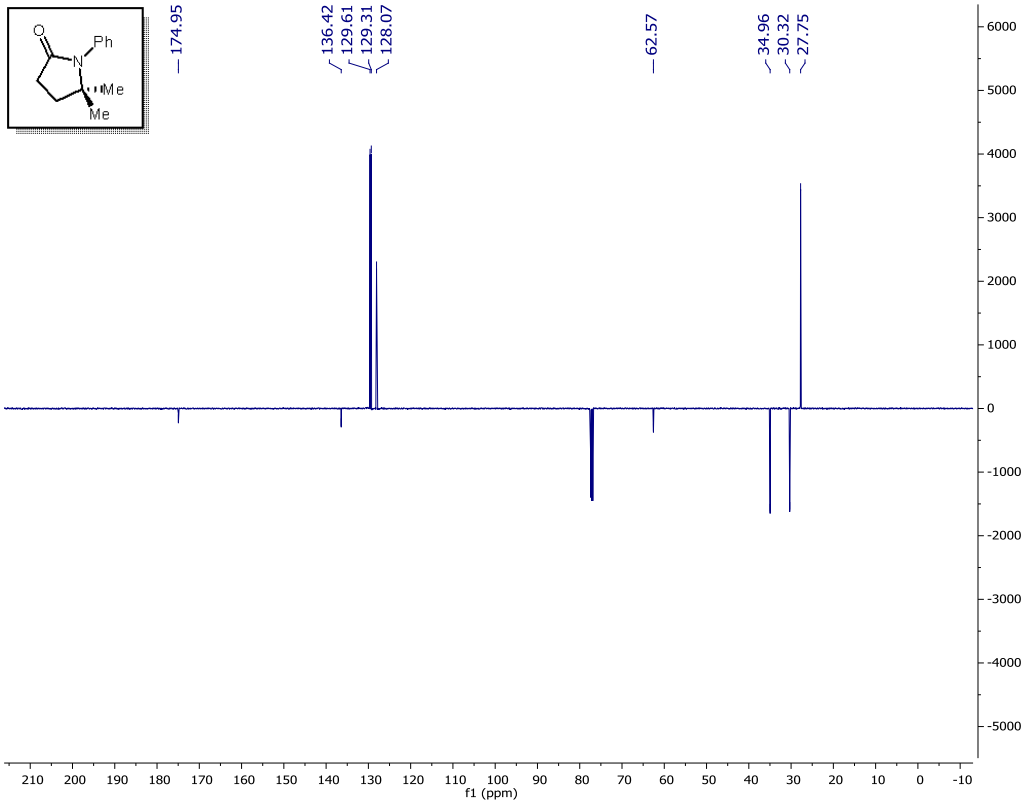
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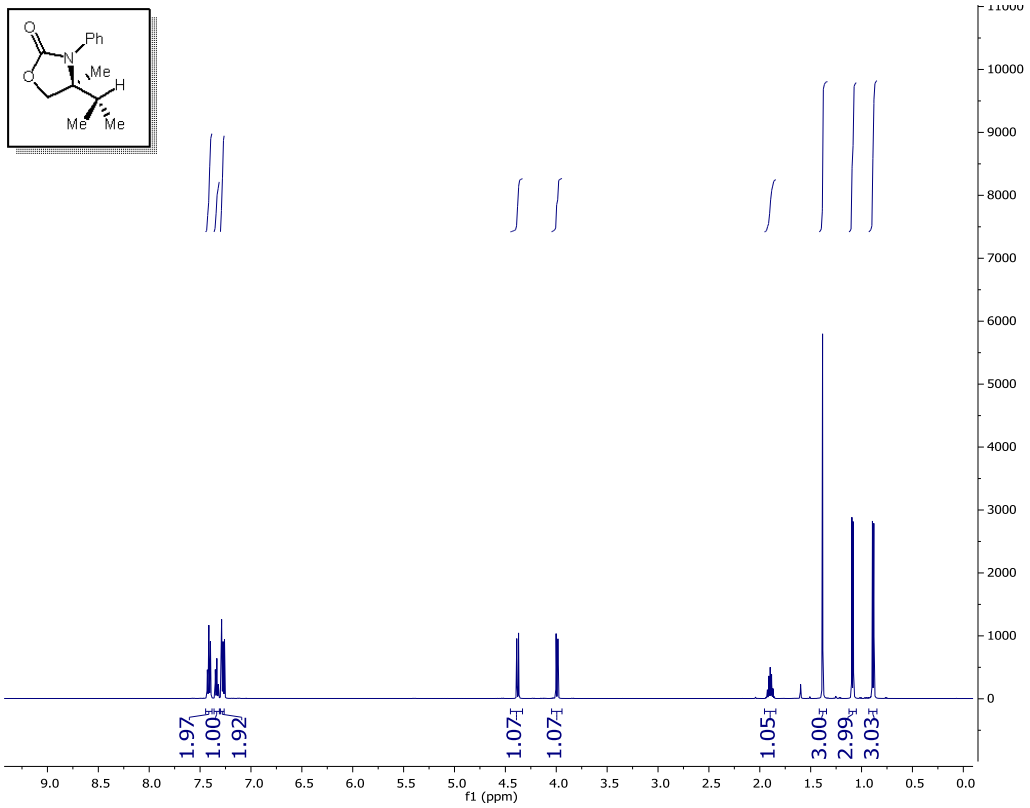
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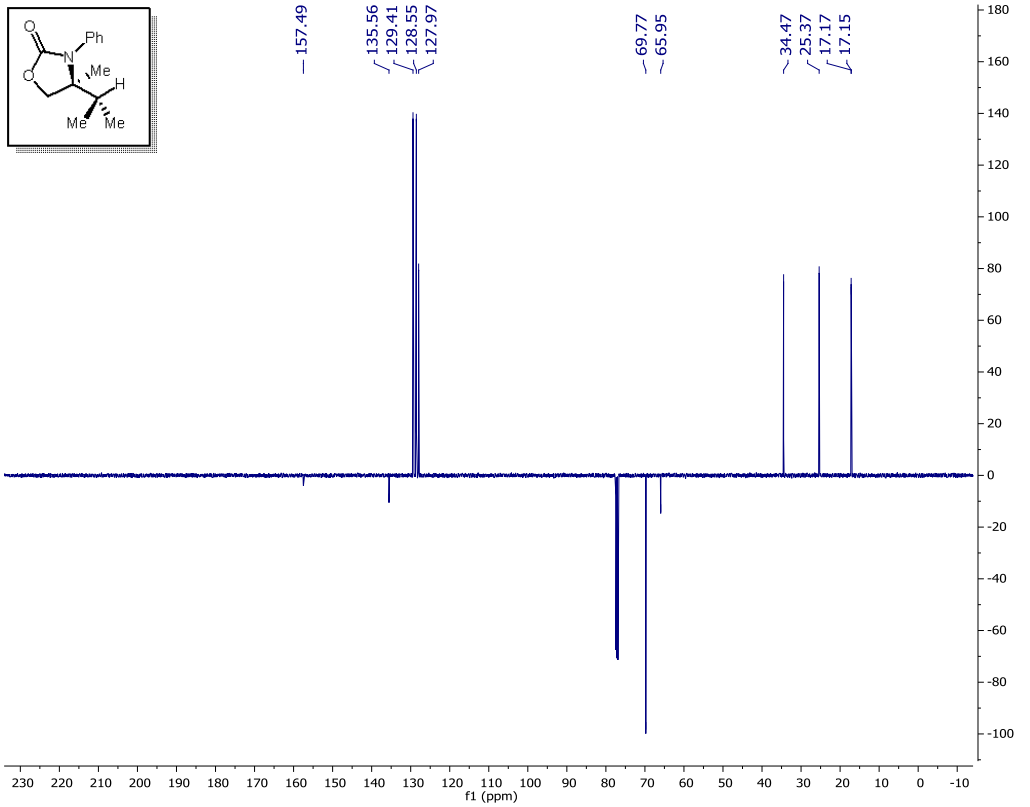
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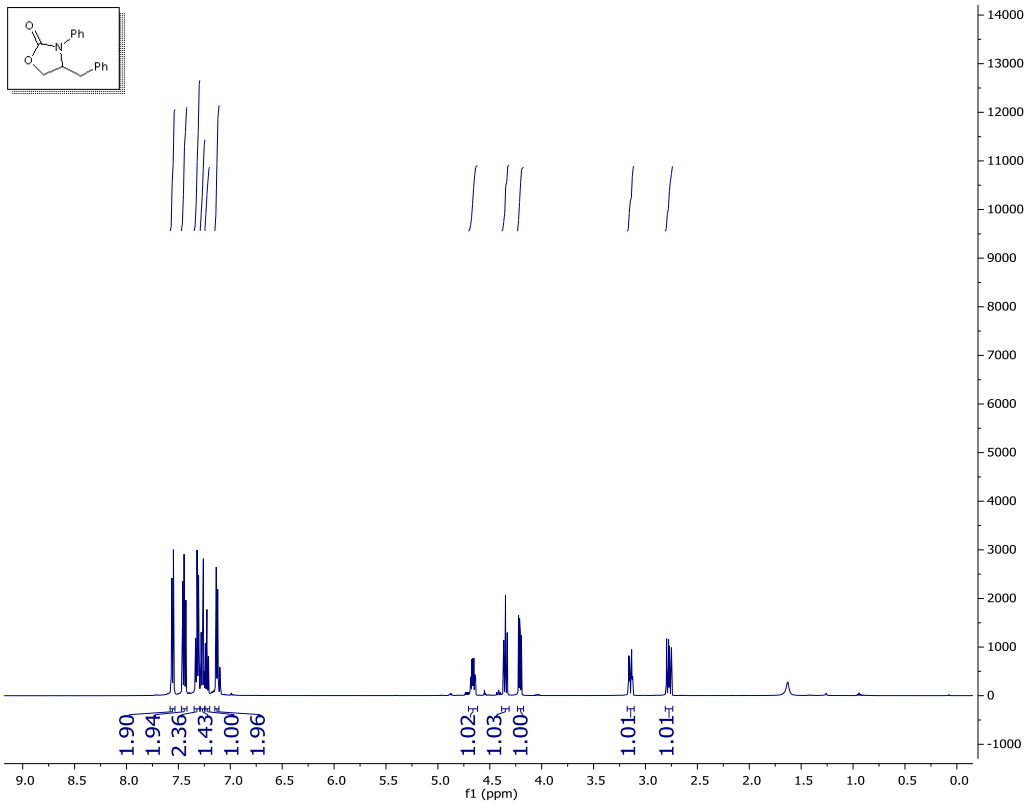
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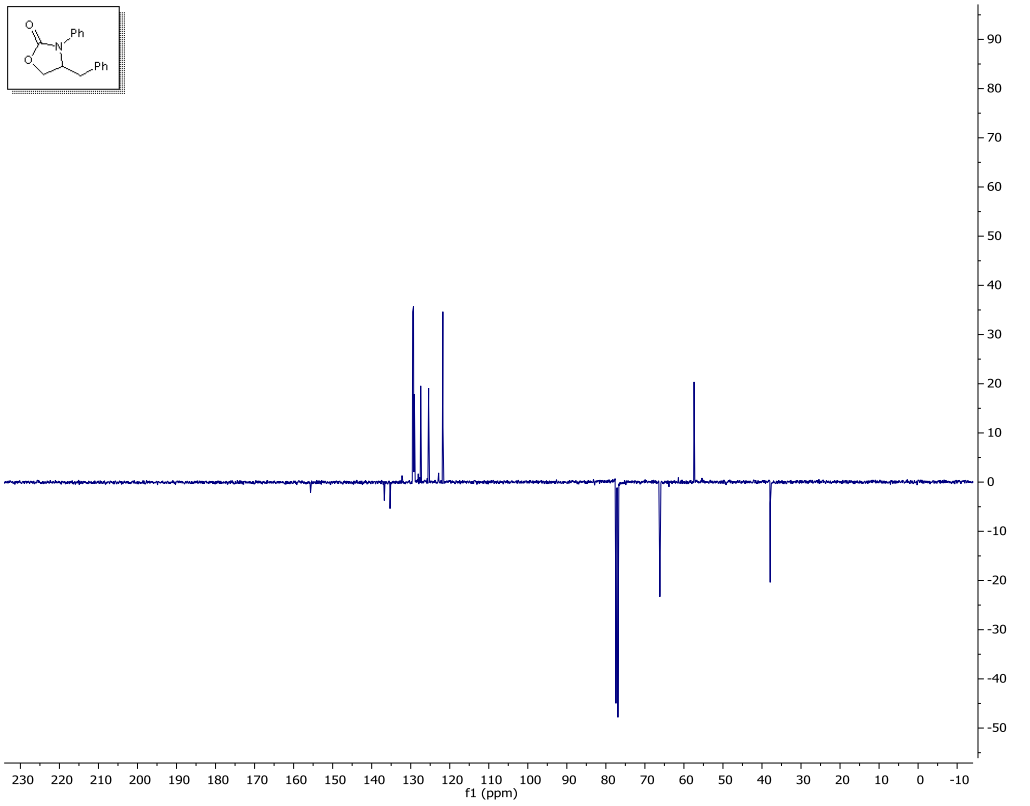
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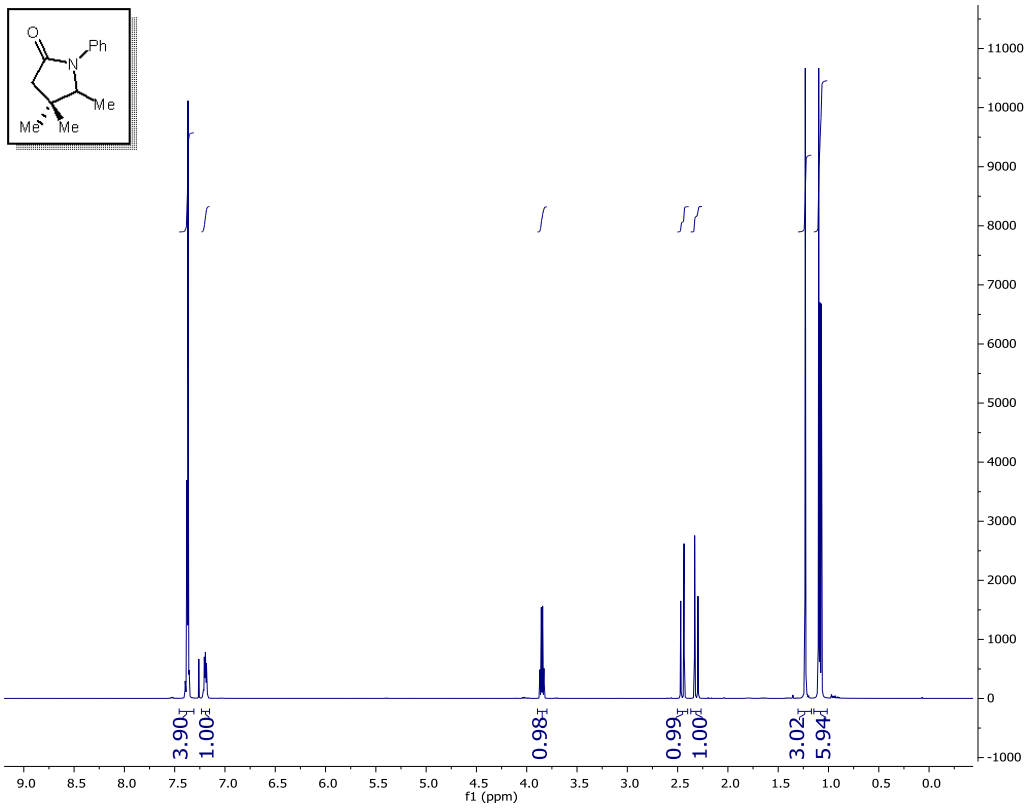
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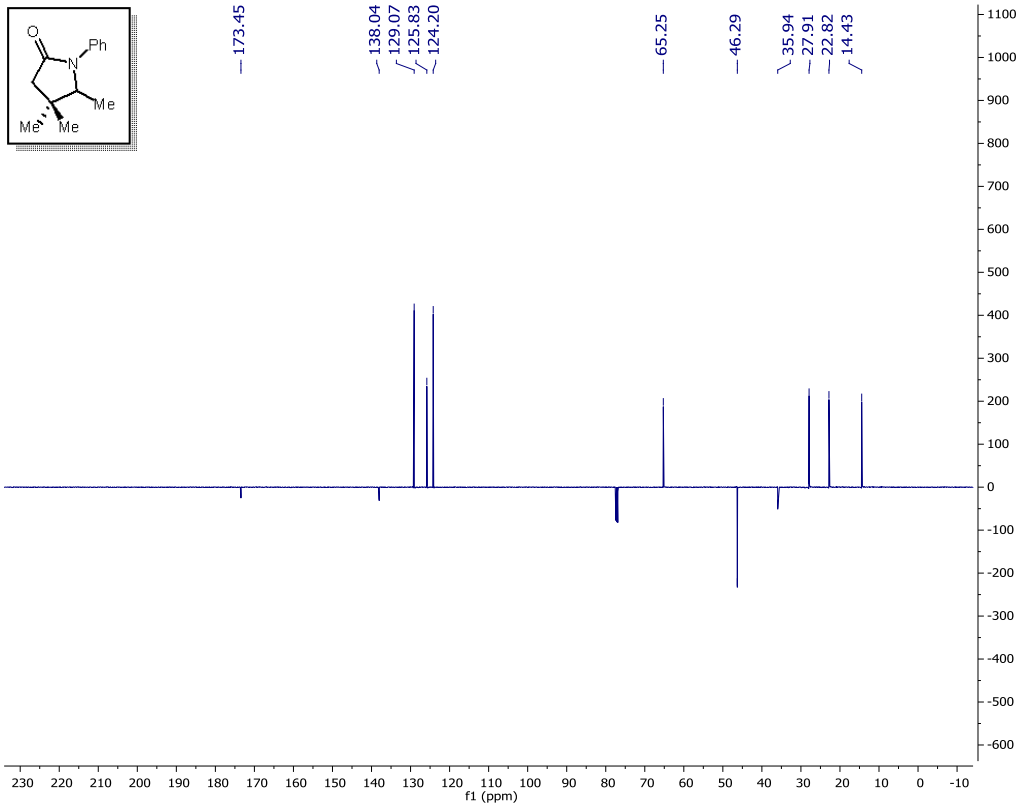
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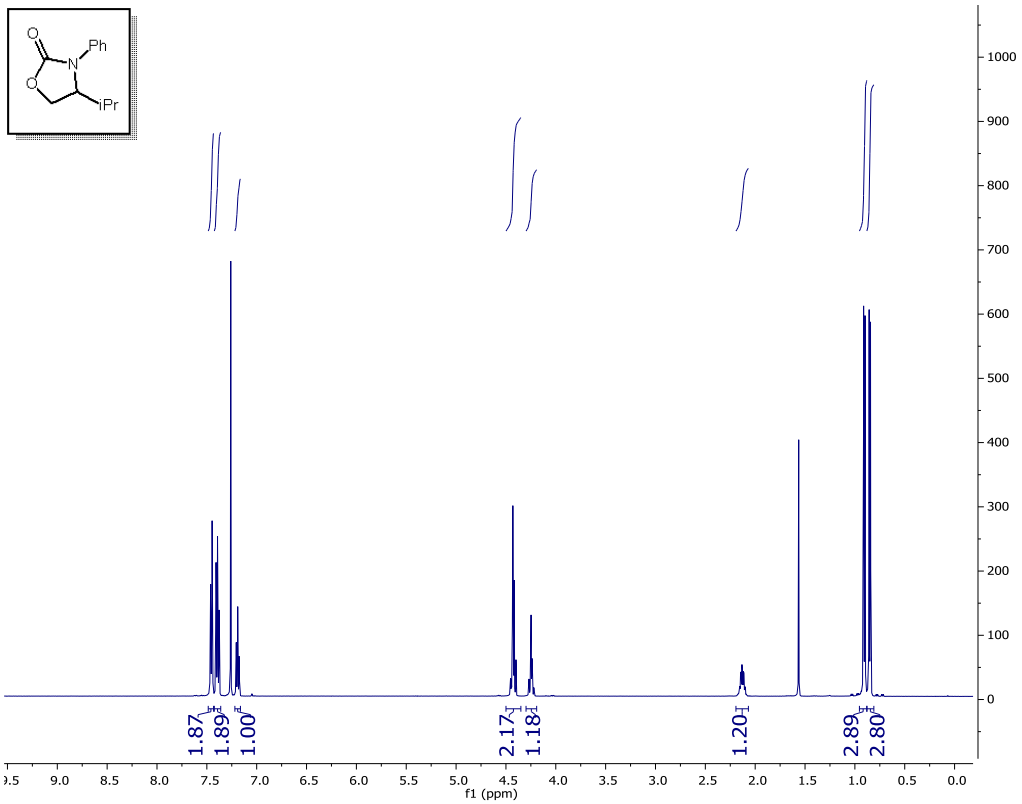
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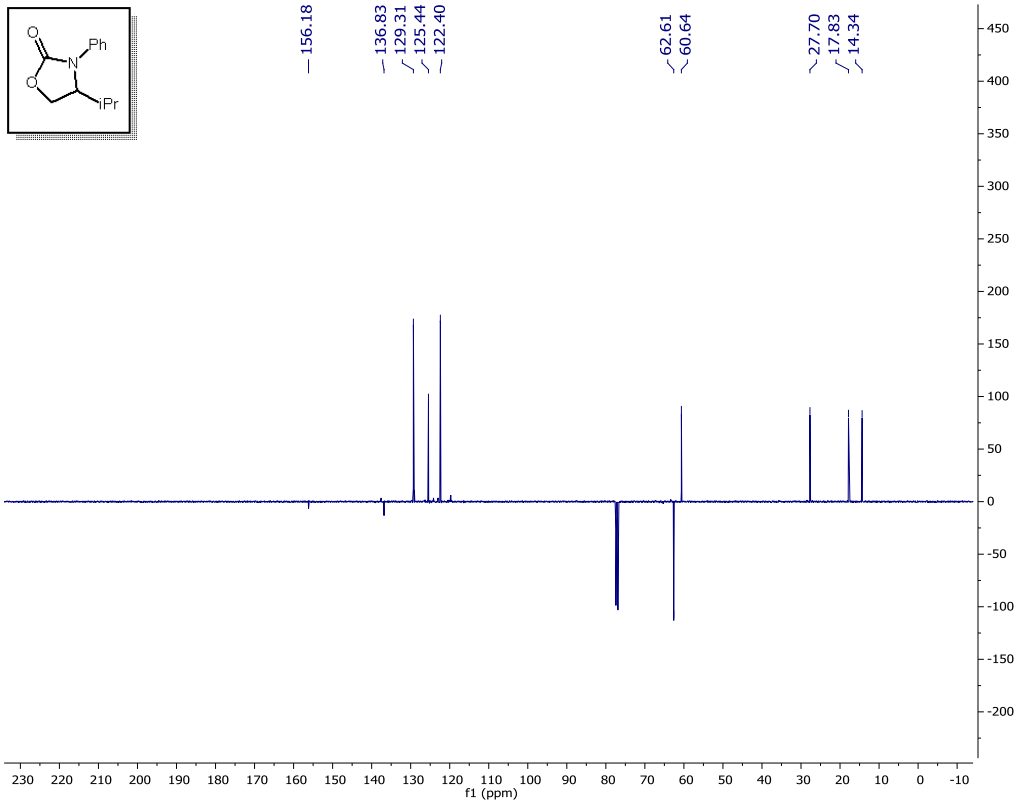
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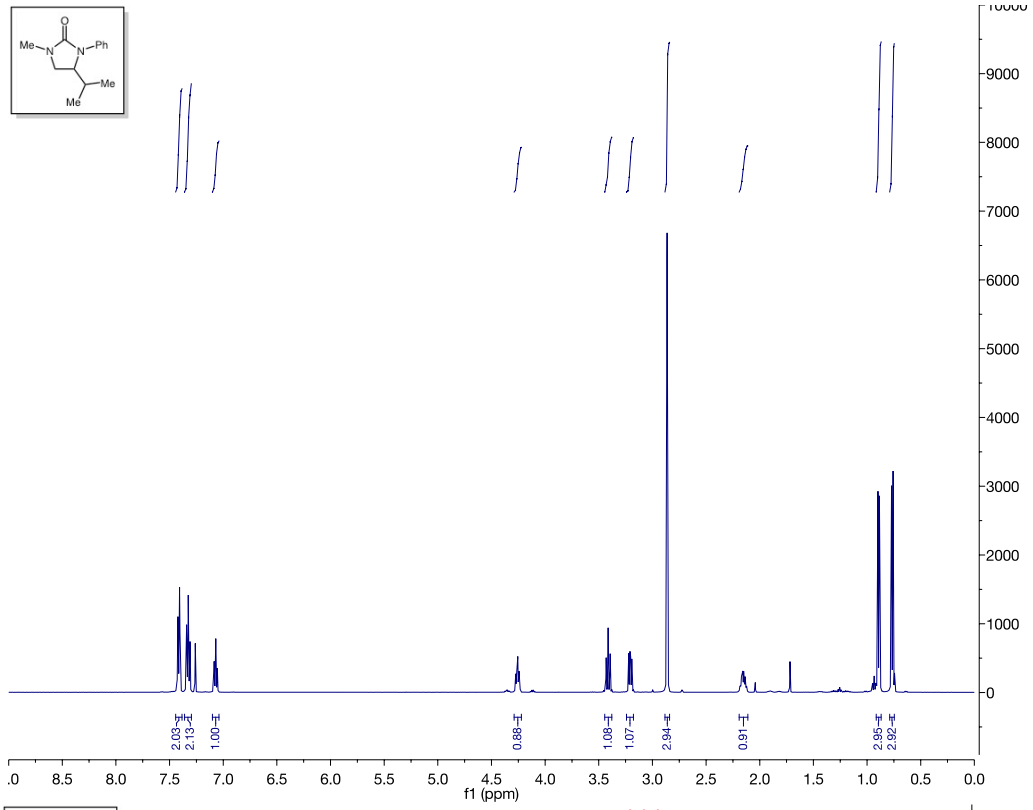
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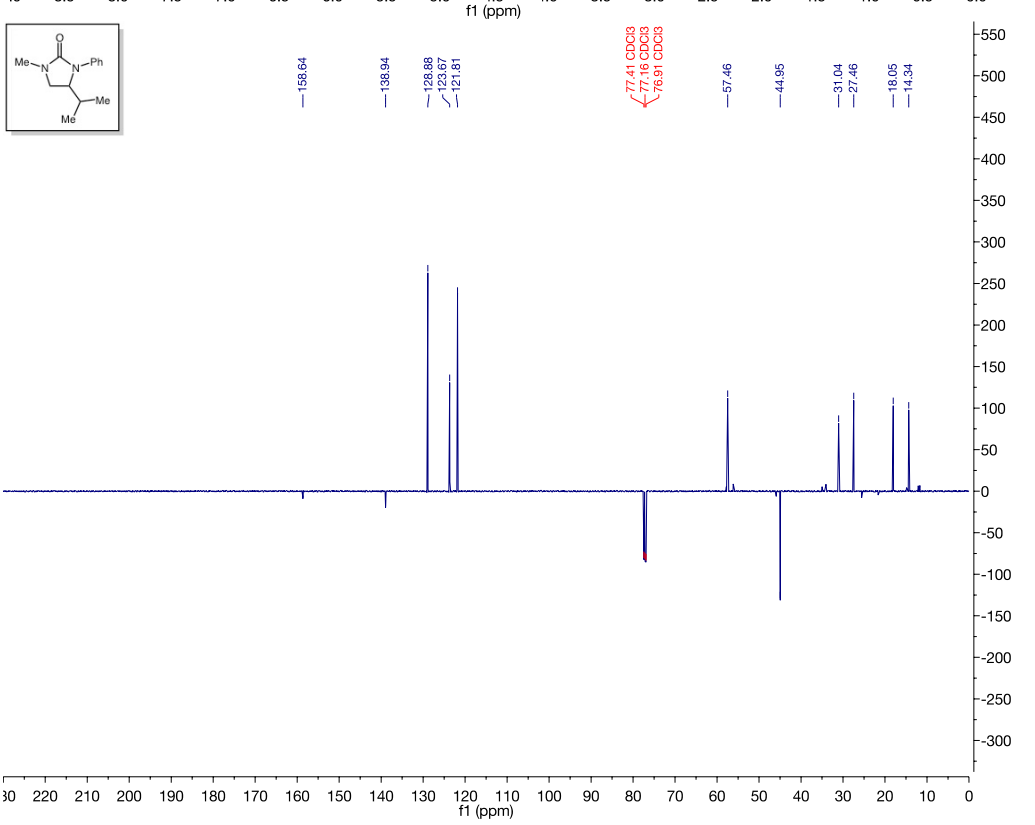
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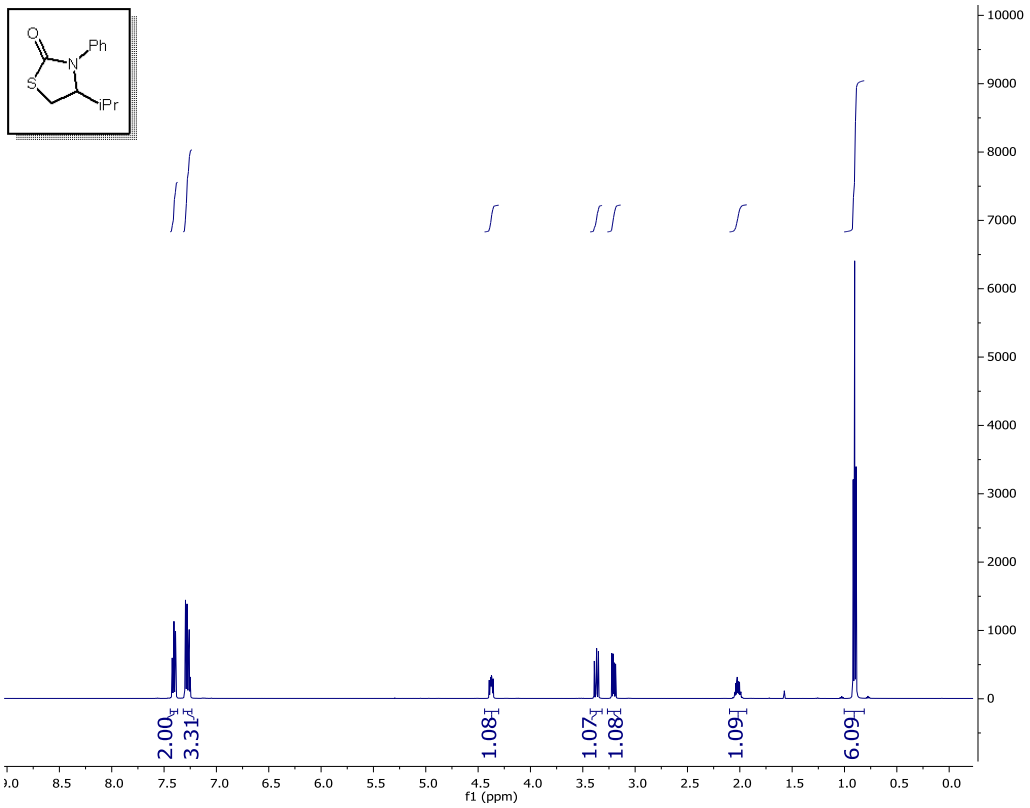
p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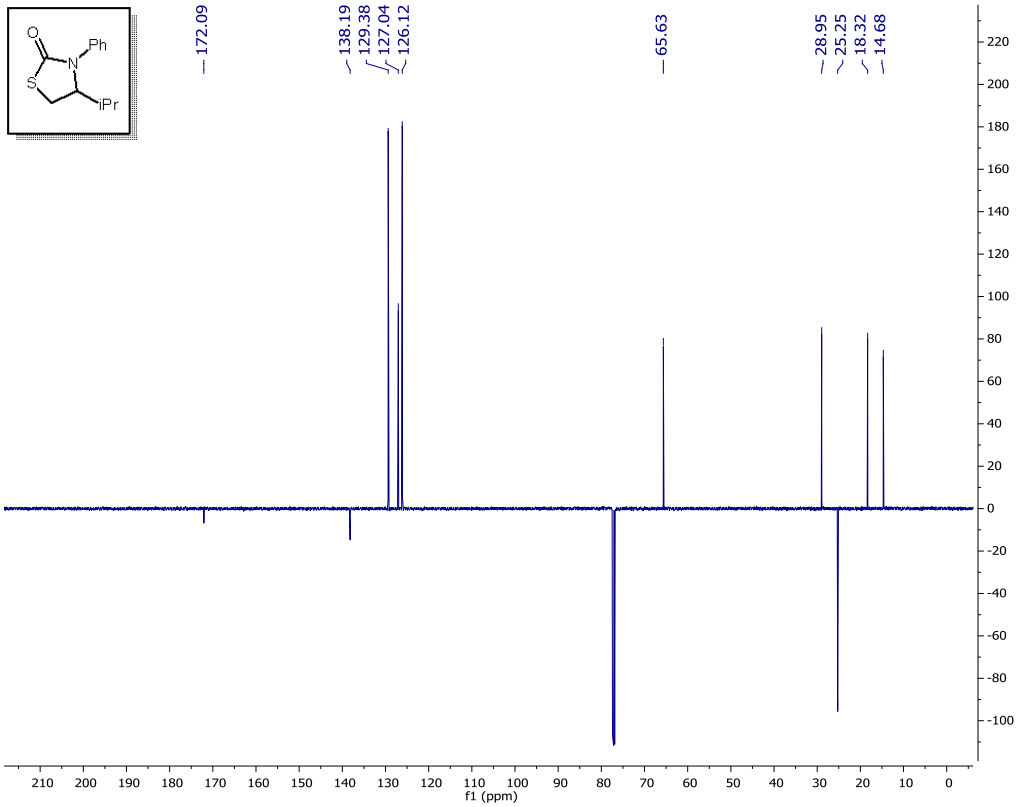
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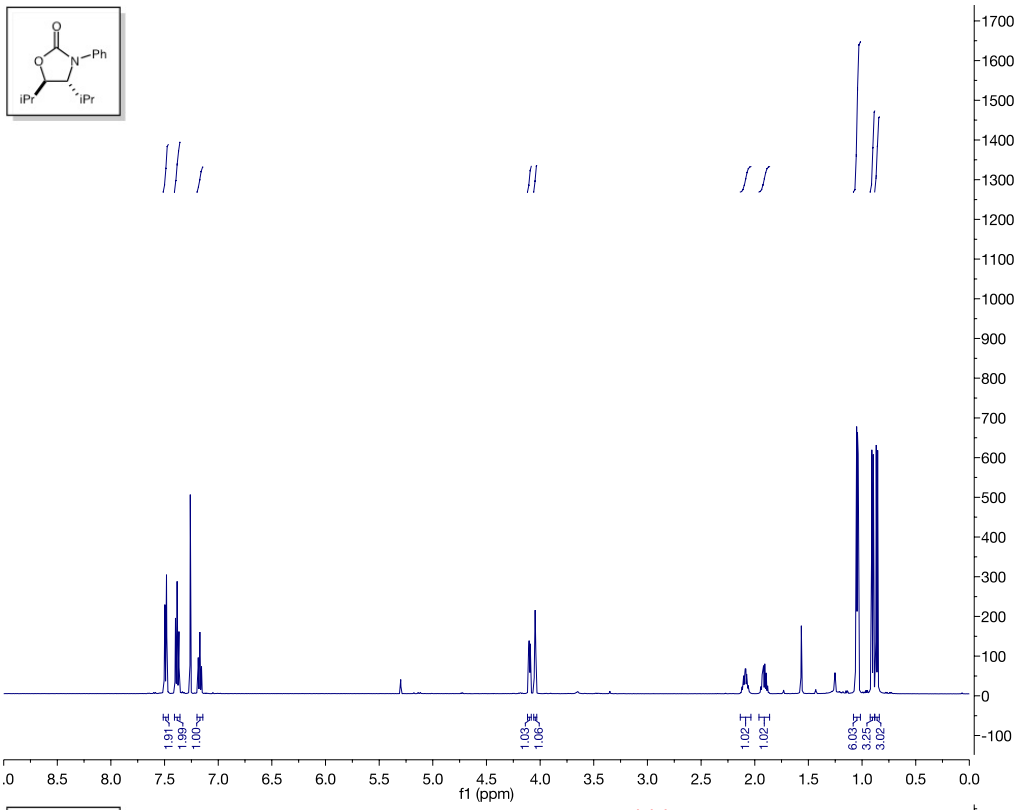
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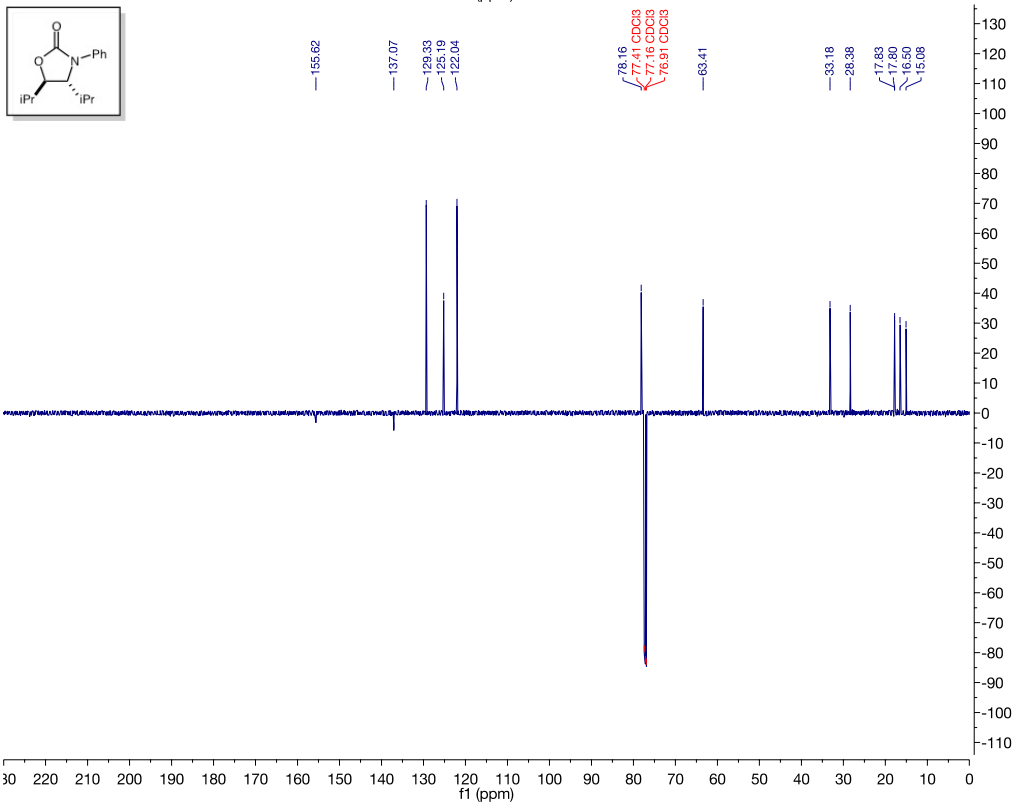
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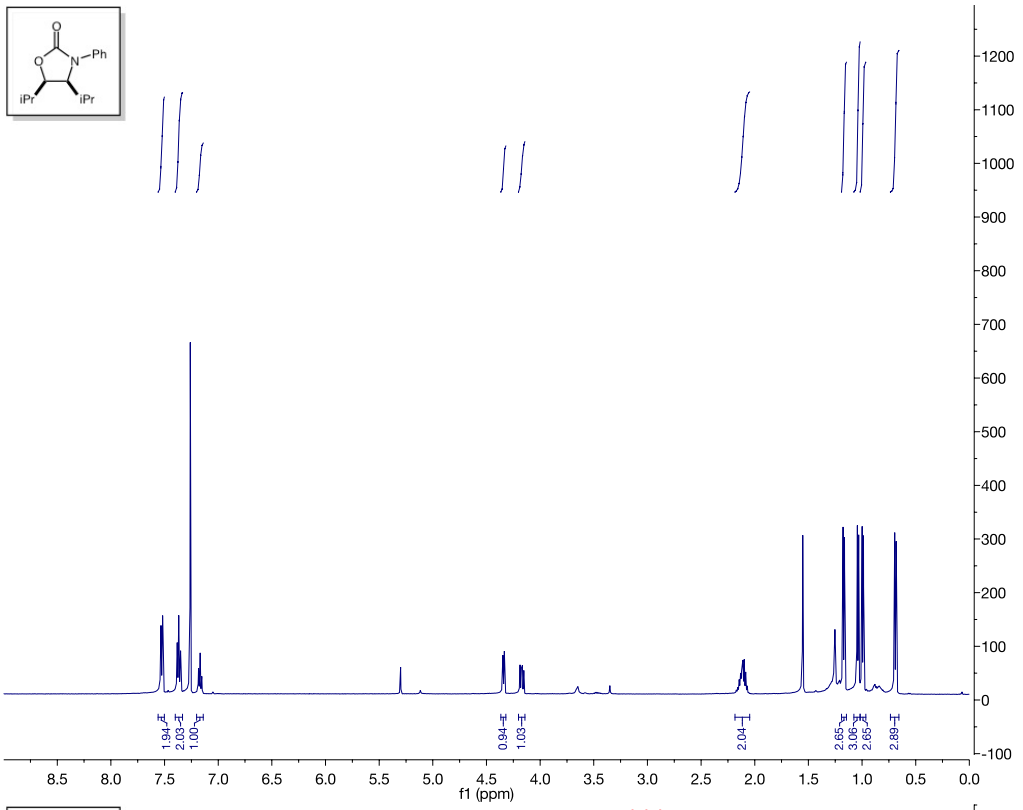
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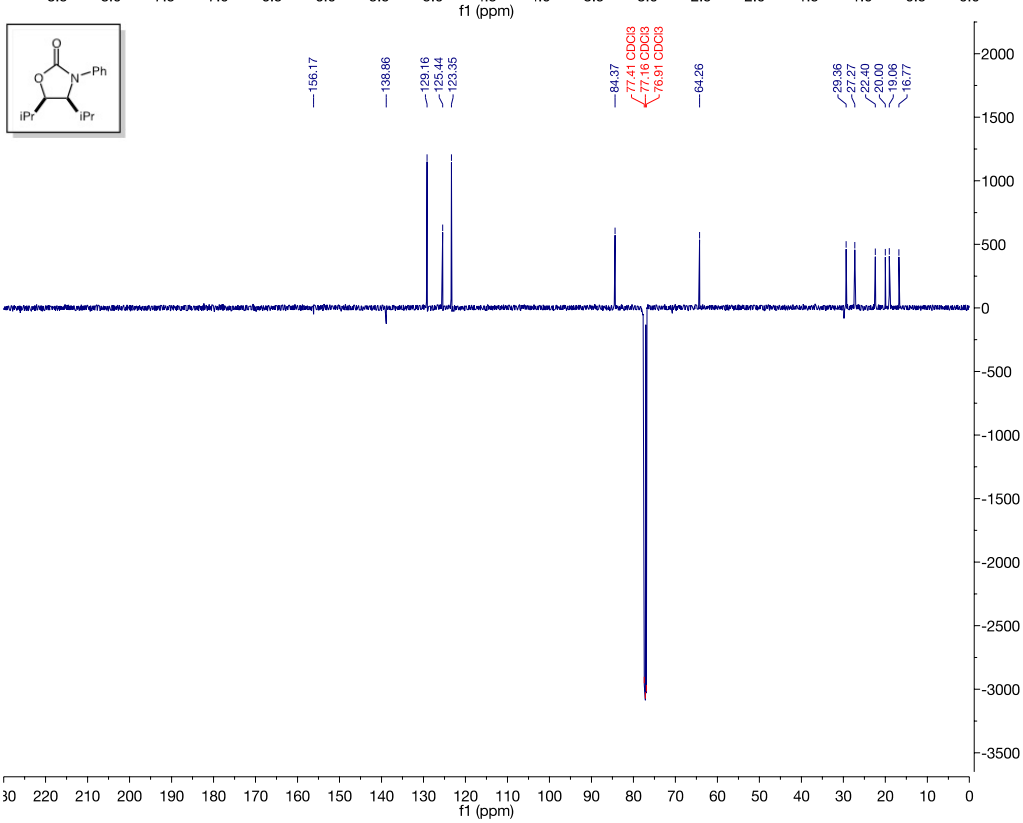
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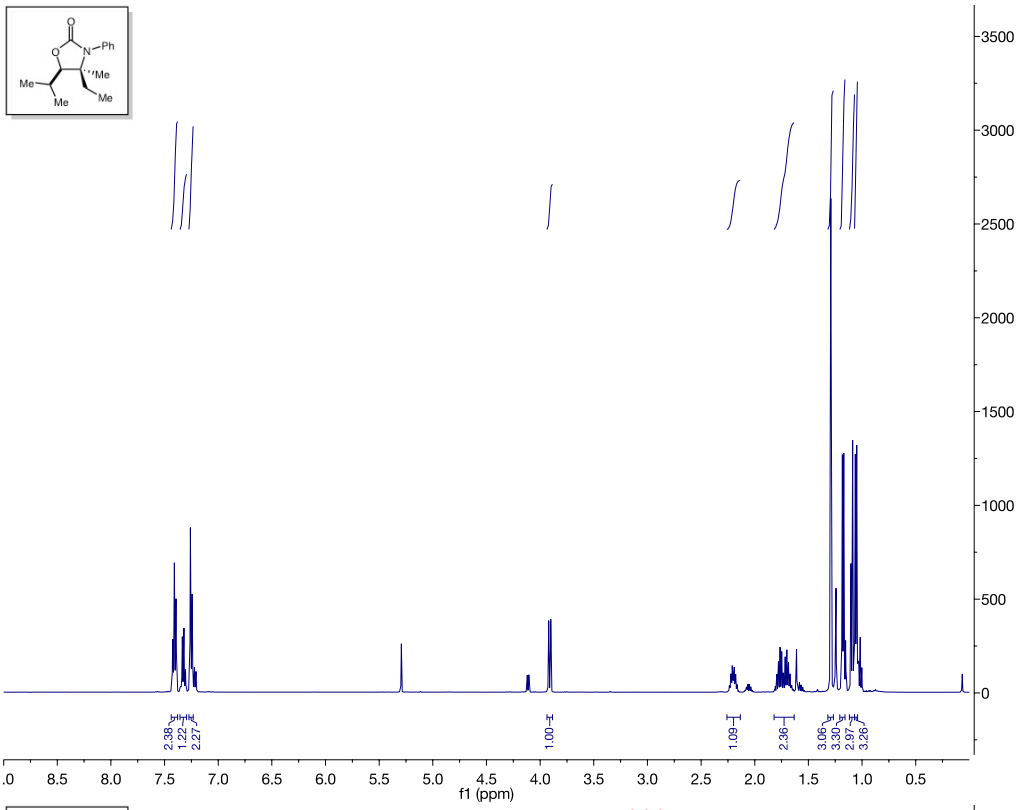
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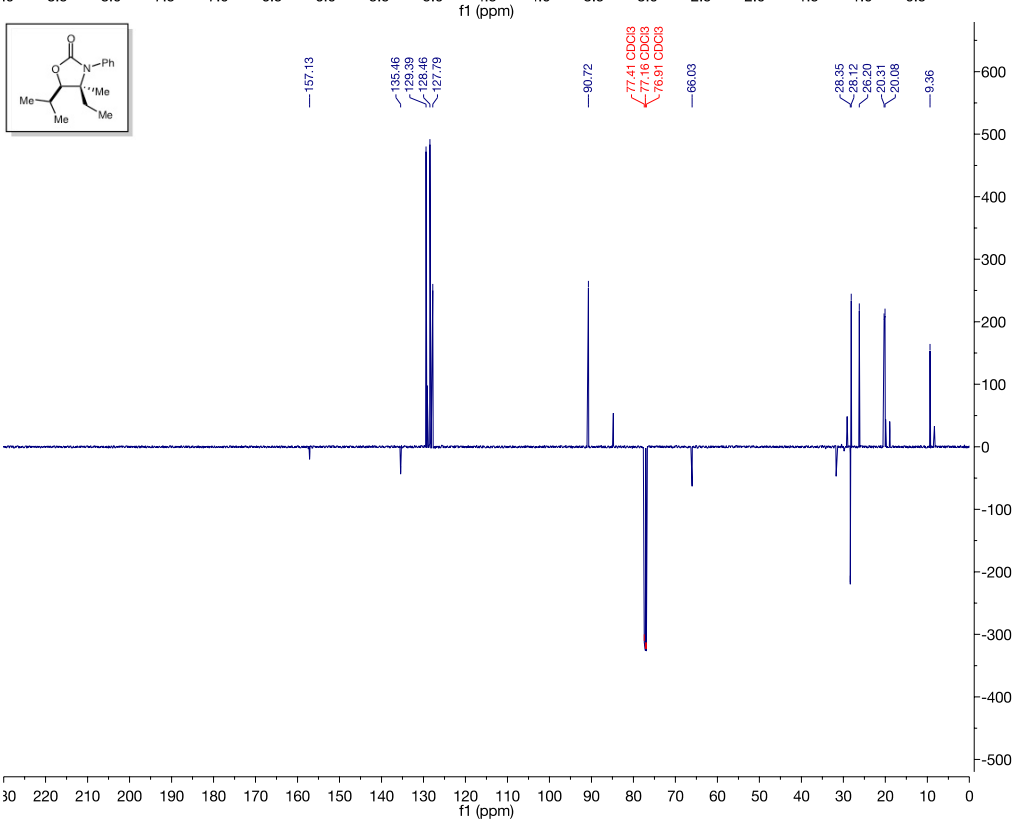
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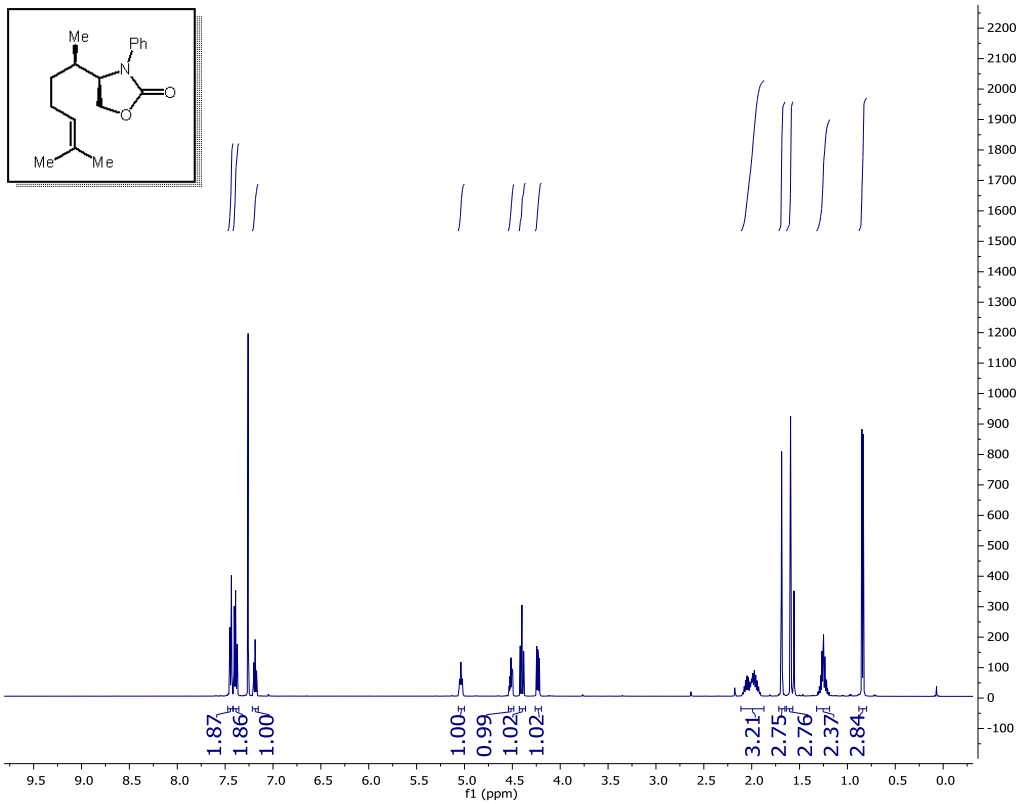
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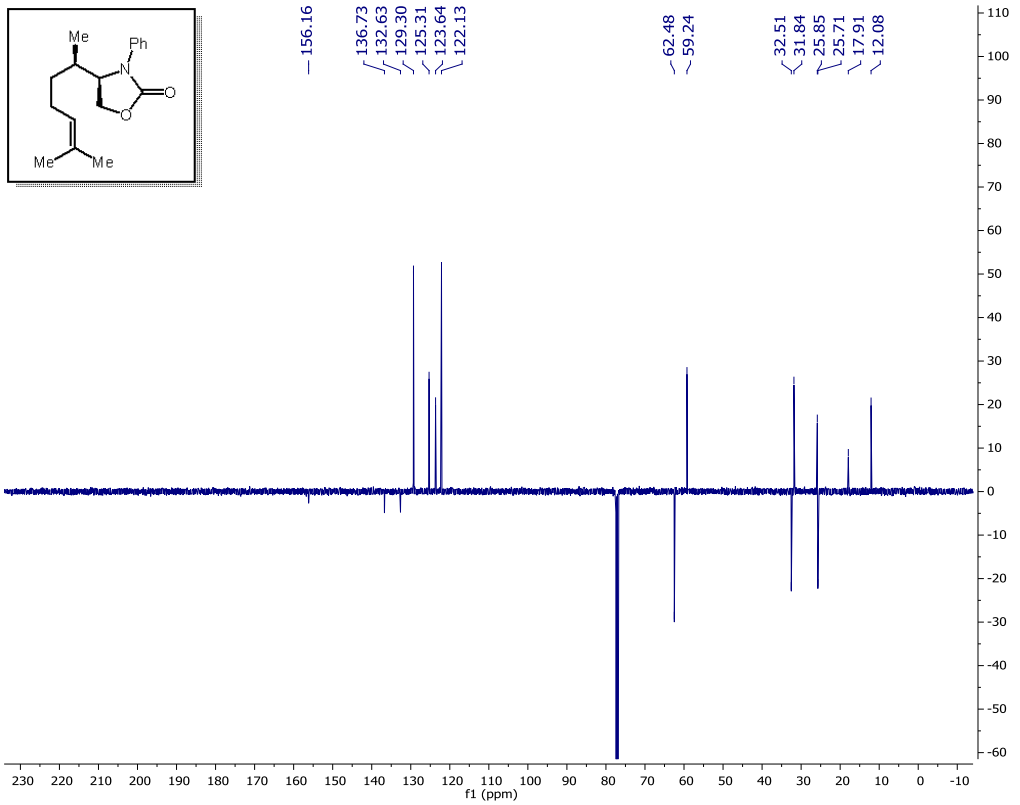
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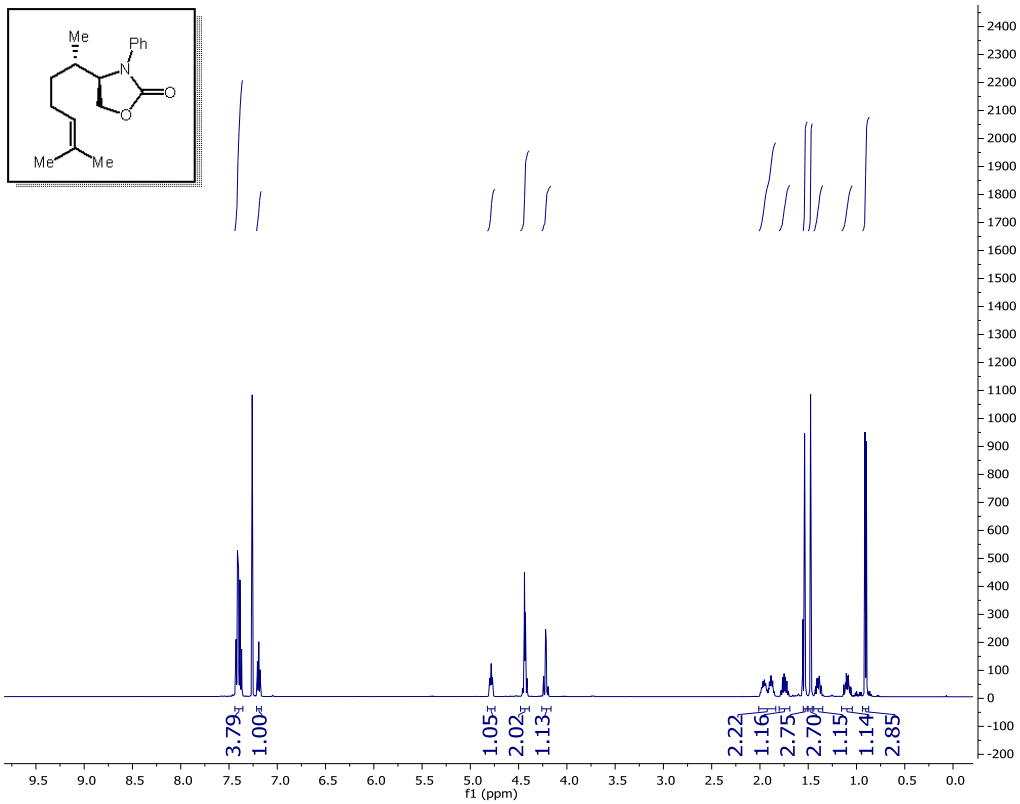
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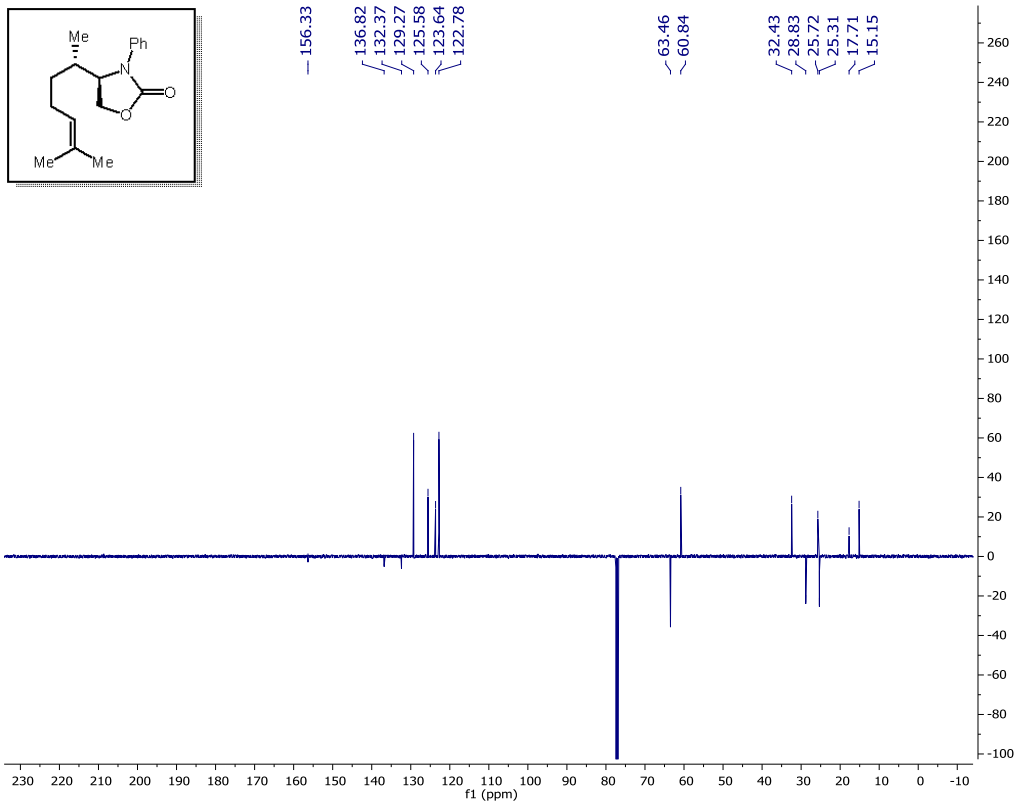
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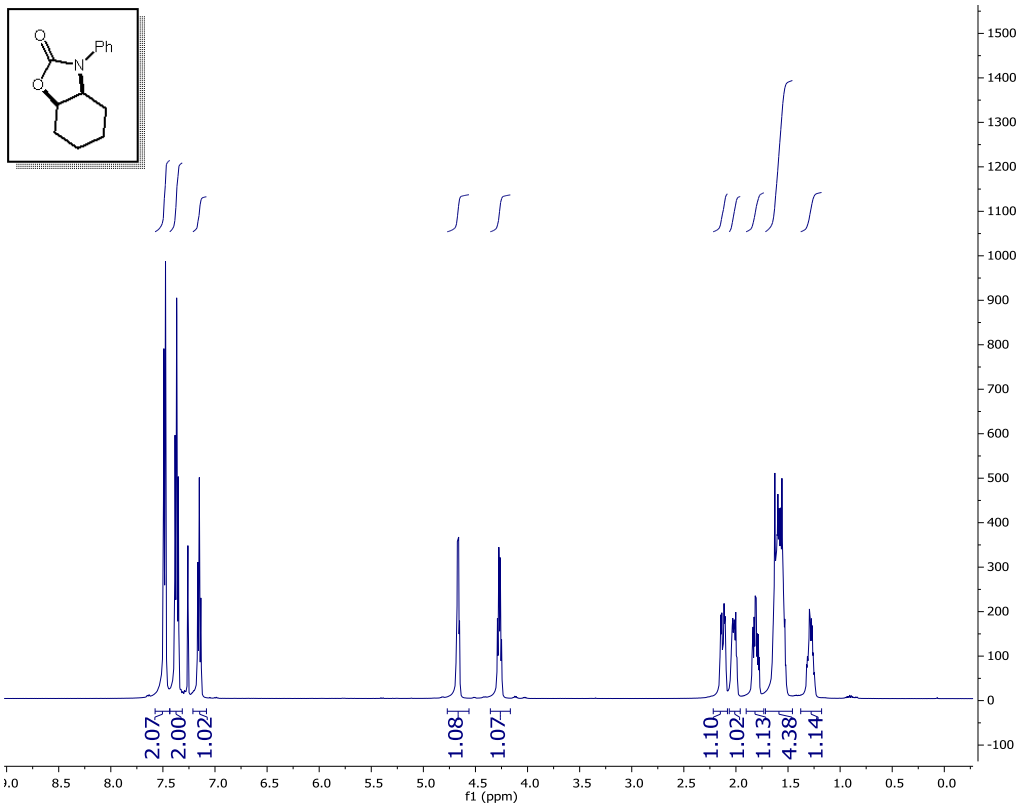
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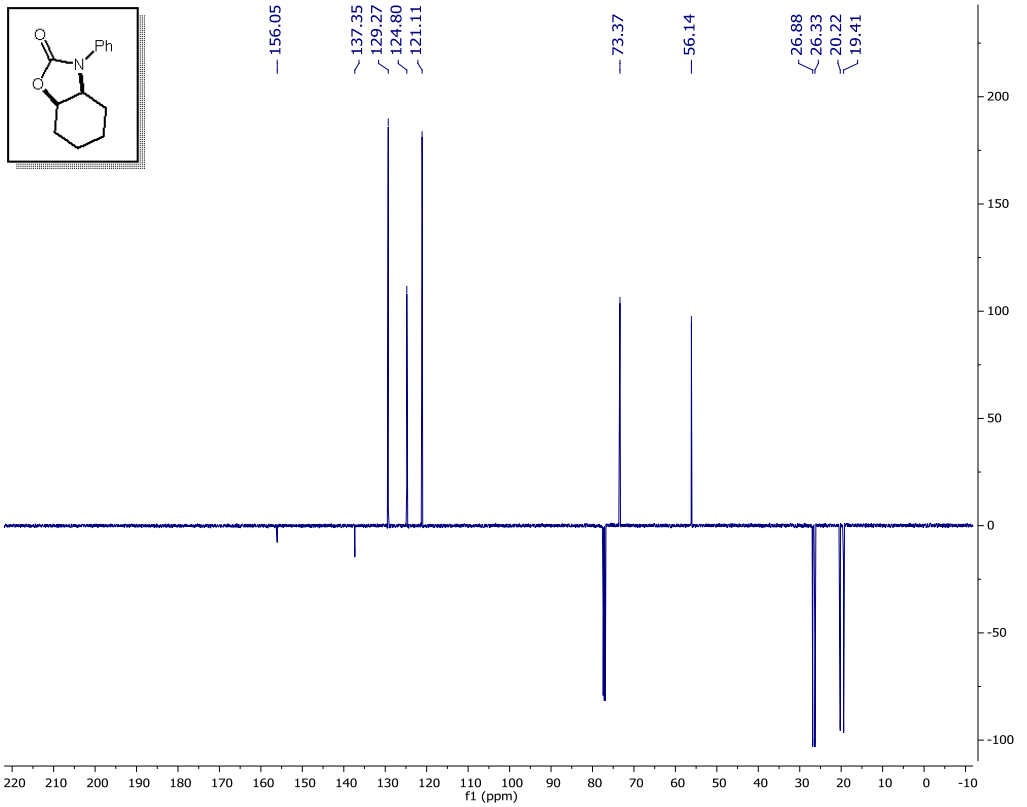
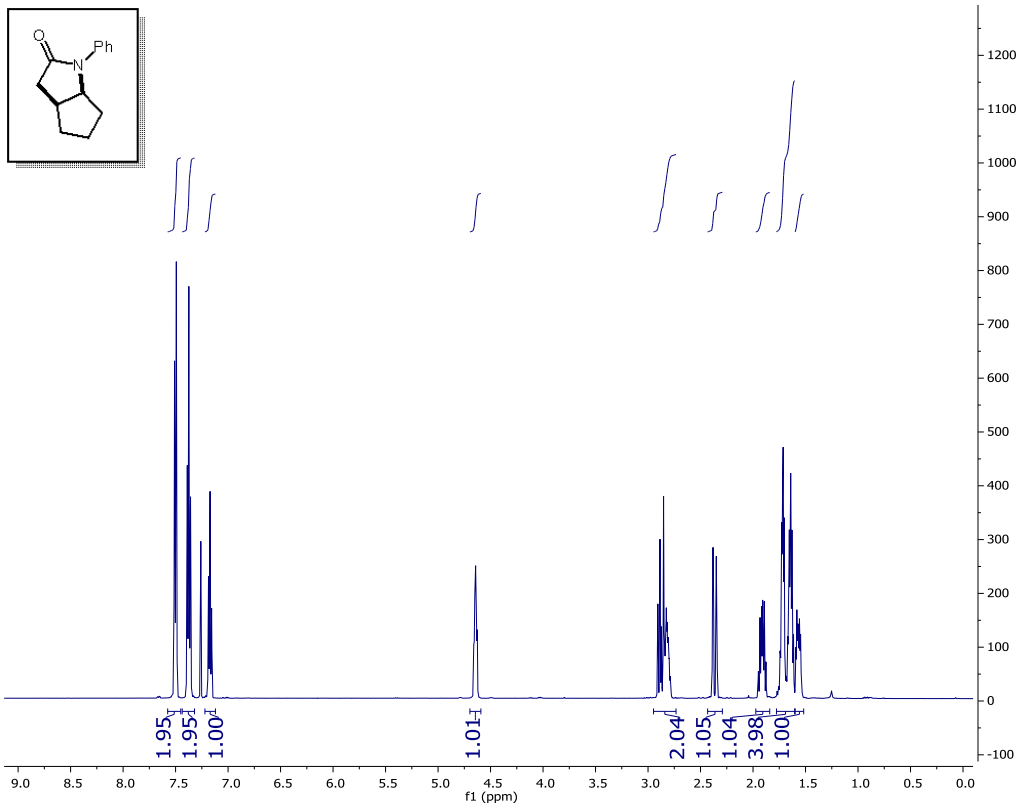
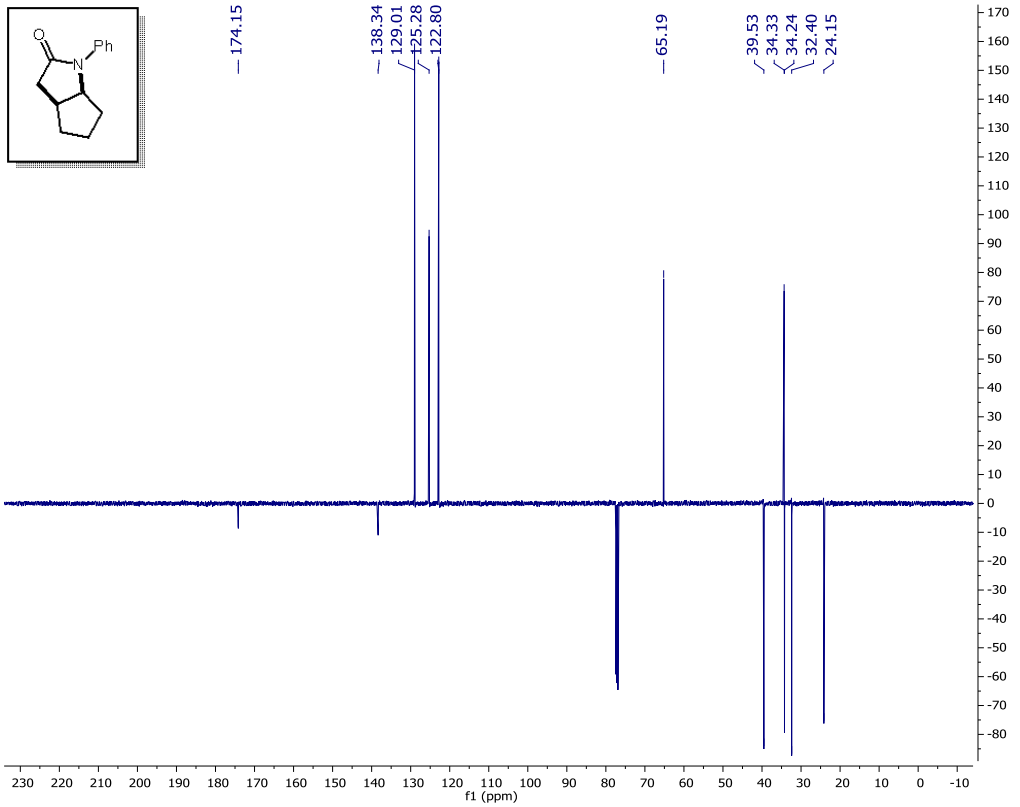
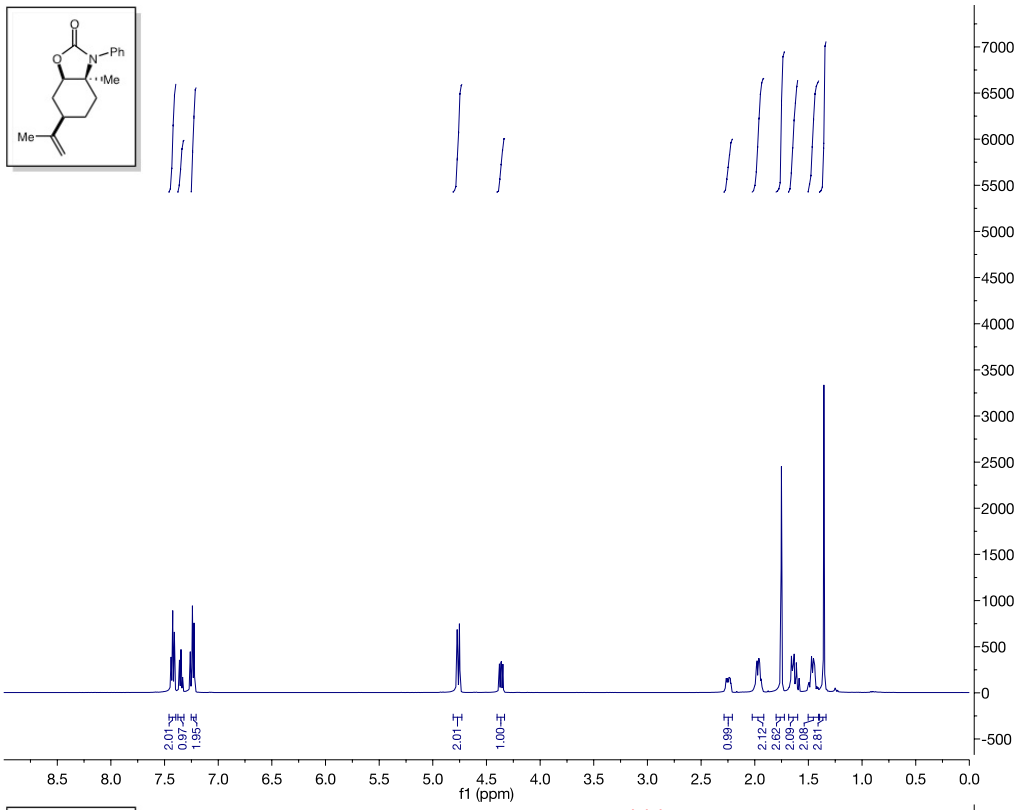
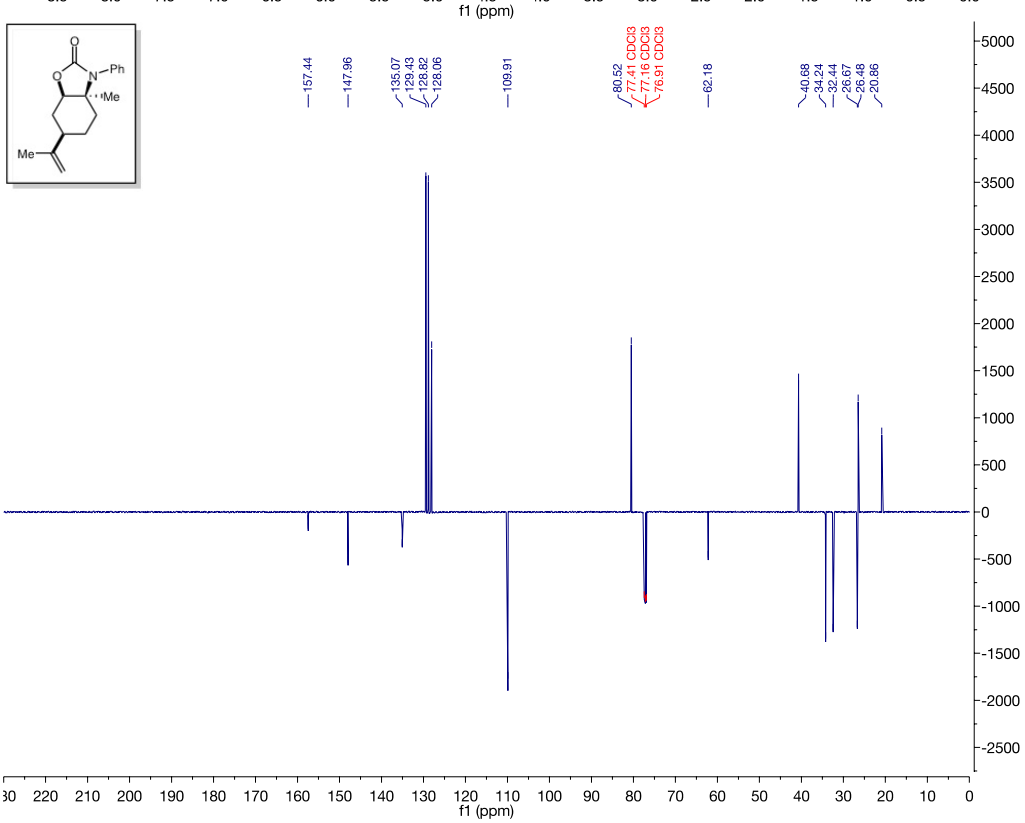
1.14
f1 (ppm)

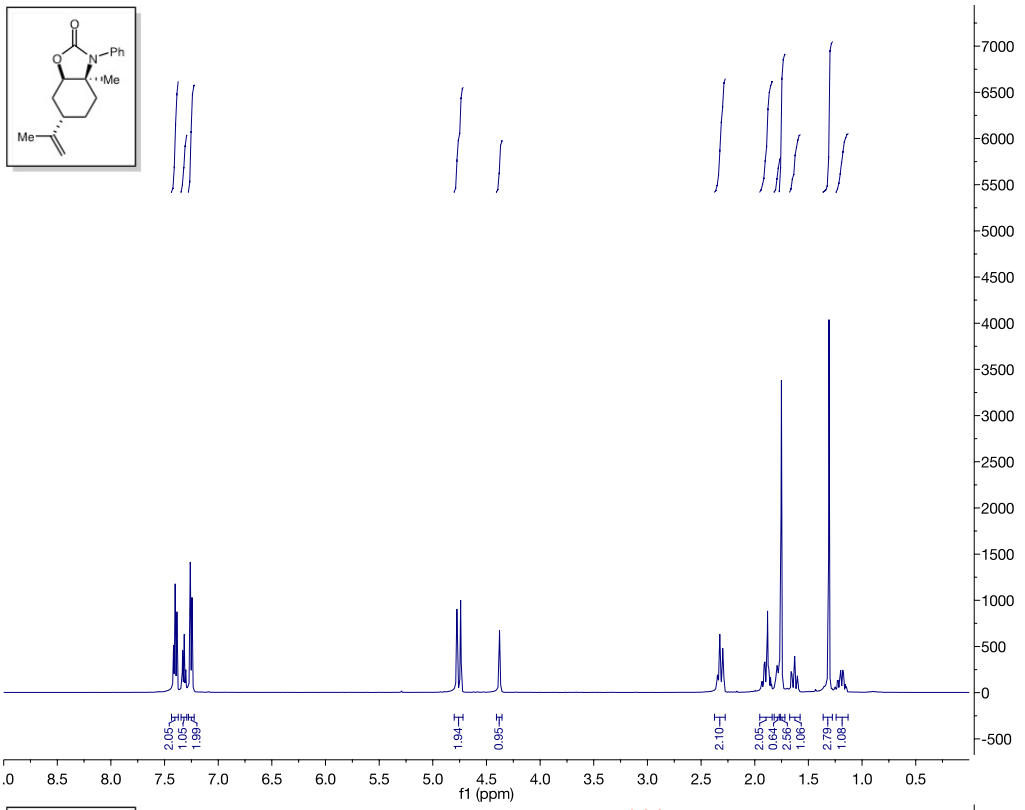

Ph
N
O
O
156.05
137.35
129.27
124.80
121.11
73.37
56.14
26.88
26.33
20.22
19.41
f1 (ppm)

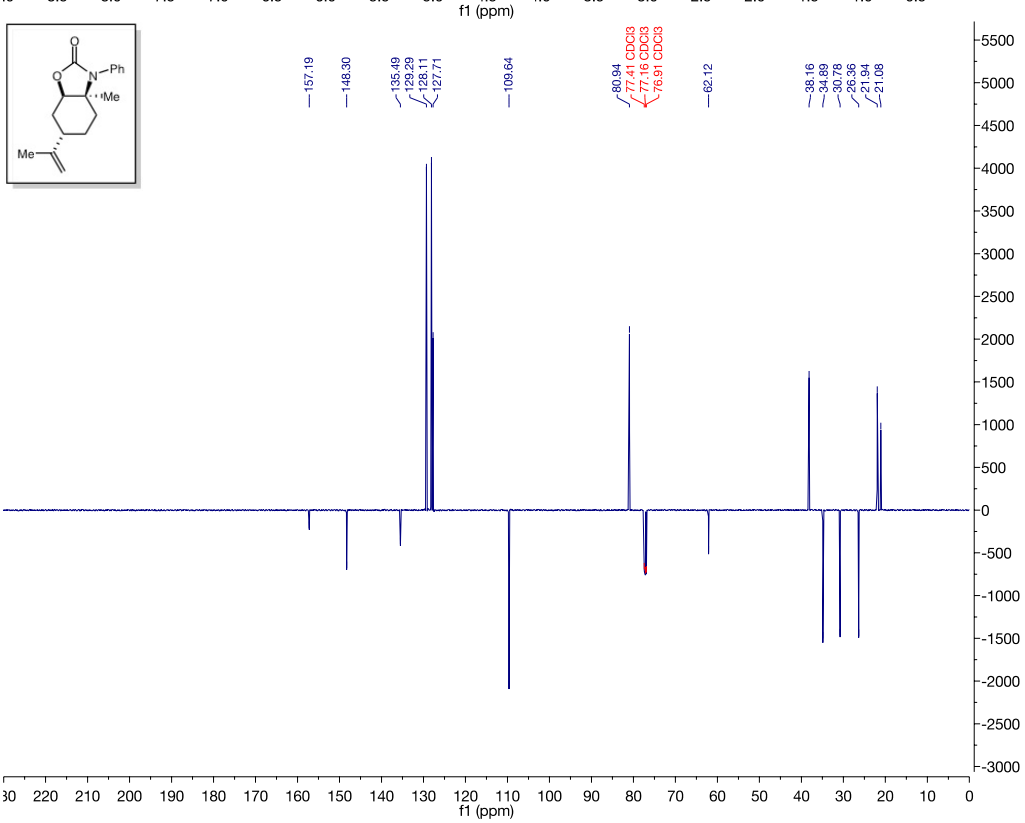

Ph
1.95
1.95
1.00
1.01
2.04
1.05
1.04
3.98
1.00
f1 (ppm)

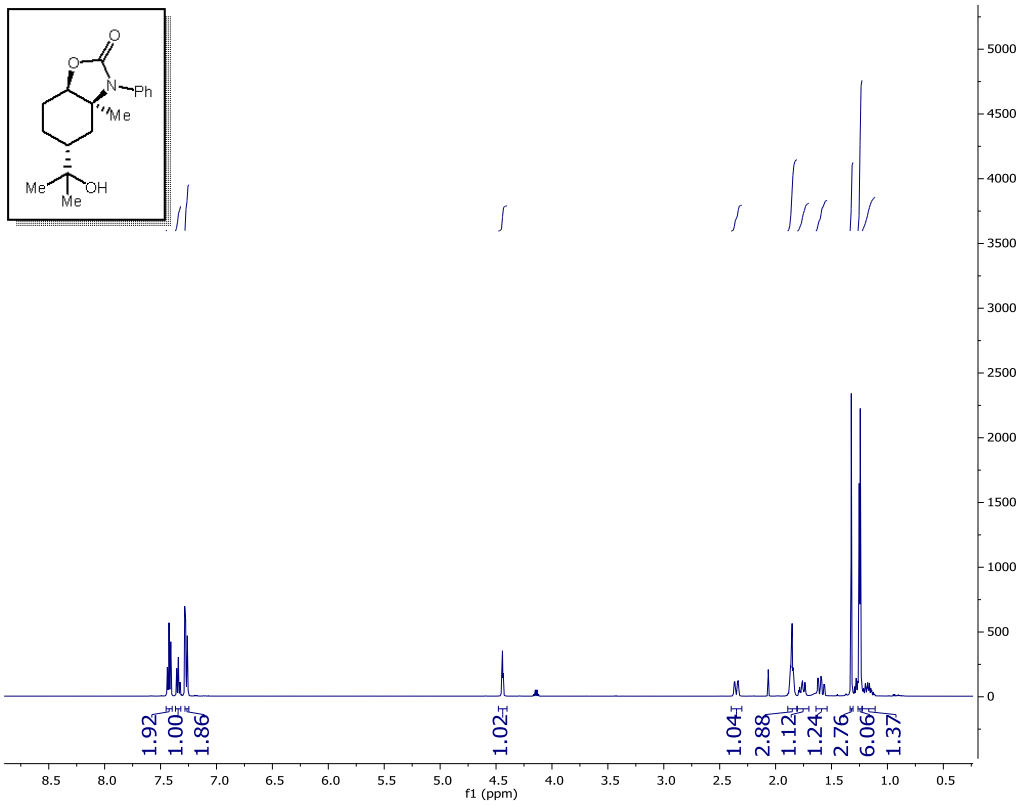

Ph
174.15
138.34
129.01
125.28
122.80
65.19
39.53
34.33
34.24
32.40
24.15
f1 (ppm)

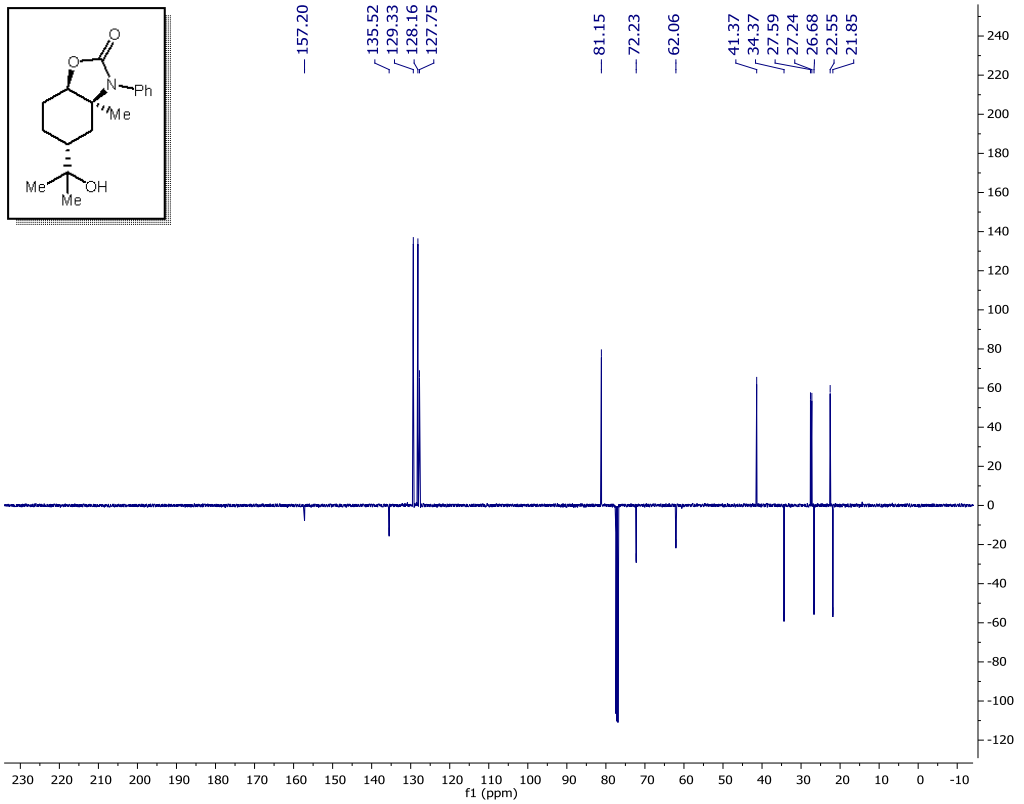

Ph
Me
Me
2.01
0.97
1.95
2.01
1.00
0.99
2.12
2.62
2.09
2.08
2.81
f1 (ppm)

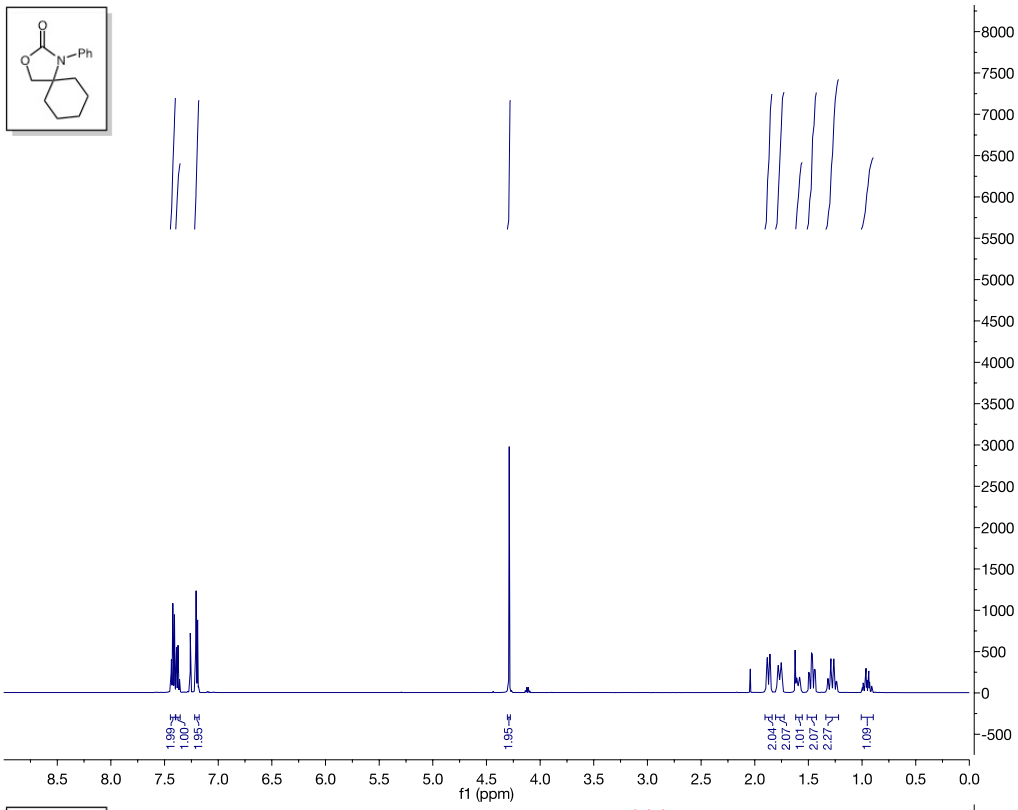

Ph
Me
Me
157.44
147.96
135.07
129.43
128.82
128.06
109.91
80.52
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
62.18
40.68
34.24
32.44
26.67
26.48
20.86
f1 (ppm)

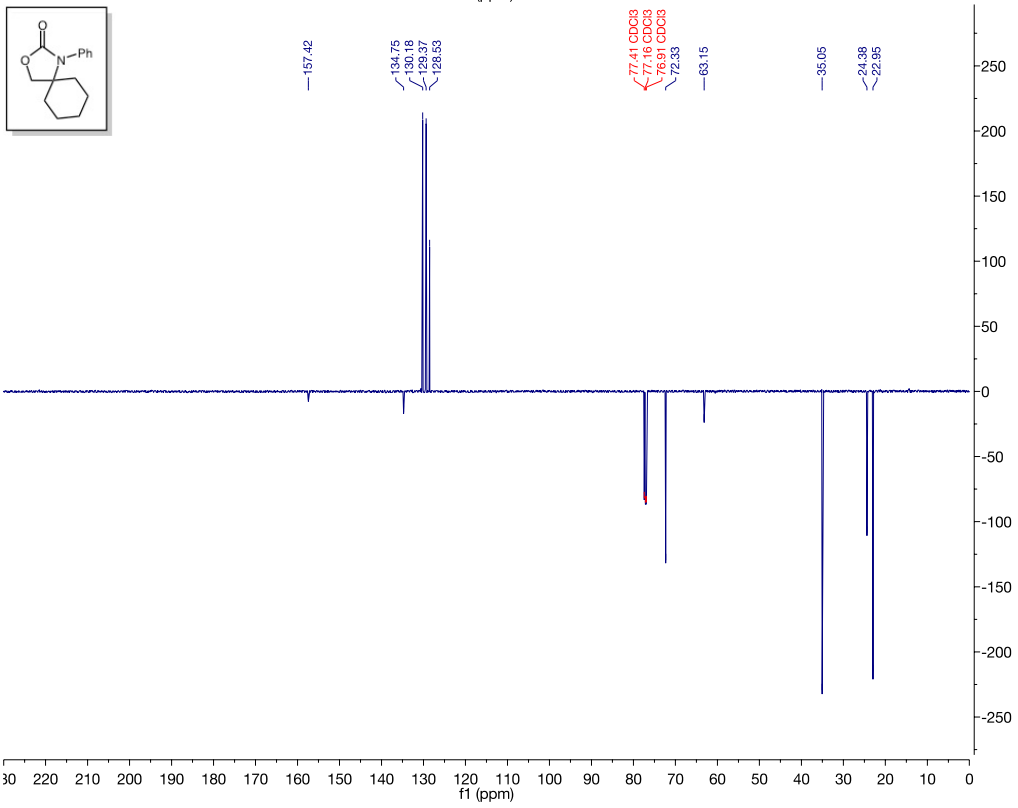

Ph
Me
Me
2.05
1.05
1.99
1.94
0.95
2.10
2.05
0.64
2.56
1.06
2.79
1.08
f1 (ppm)

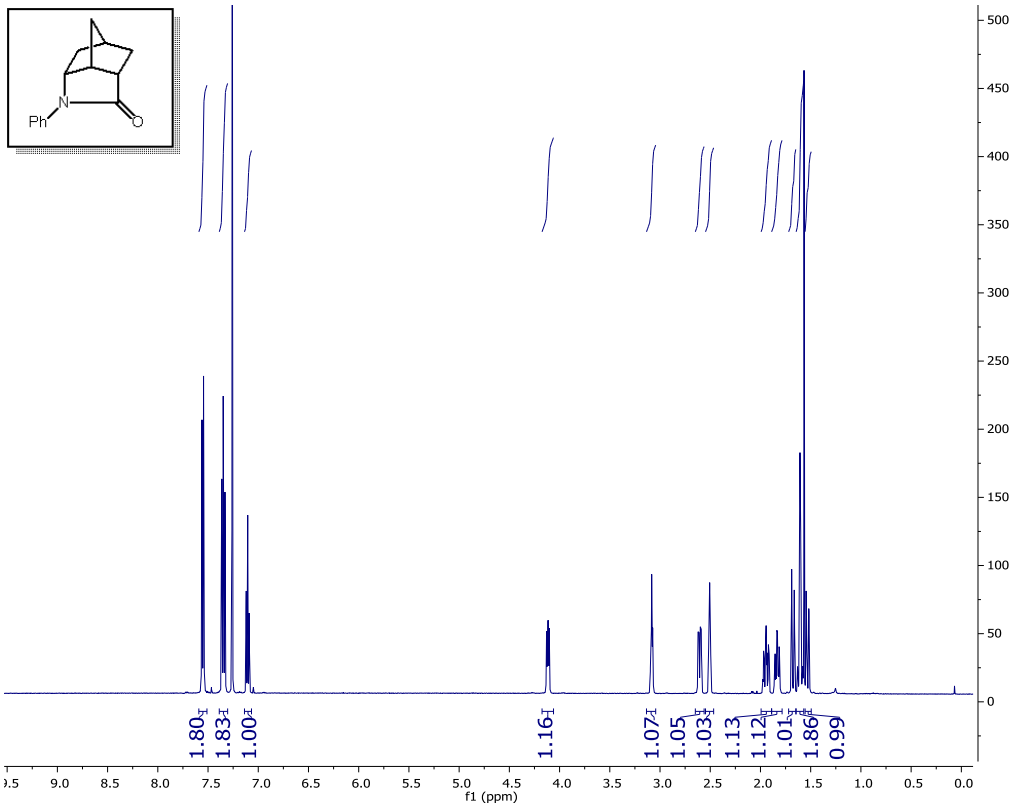

Ph
Me
Me
157.19
148.30
135.49
129.29
128.11
127.71
109.64
80.94
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
62.12
38.16
34.89
30.78
26.36
21.94
21.08
f1 (ppm)

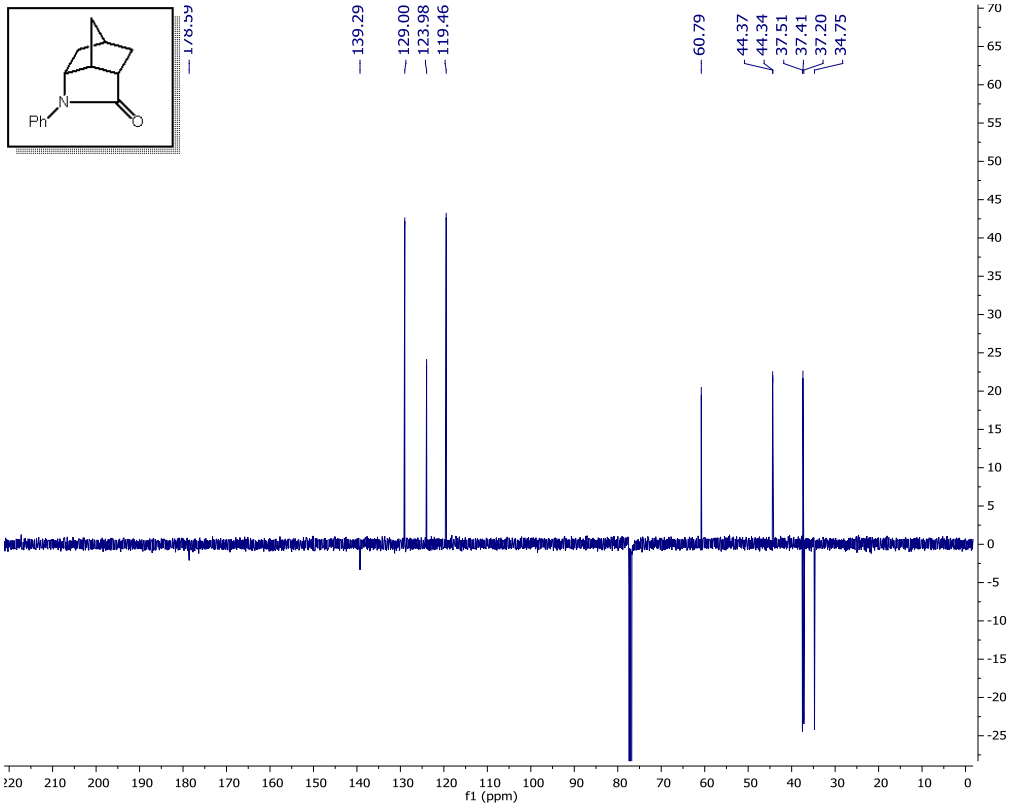

O
O
N
Ph
Me
Me
OH
Me
1.92
1.00
1.86
1.02
1.04
2.88
1.12
1.24
2.76
6.06
1.37
f1 (ppm)

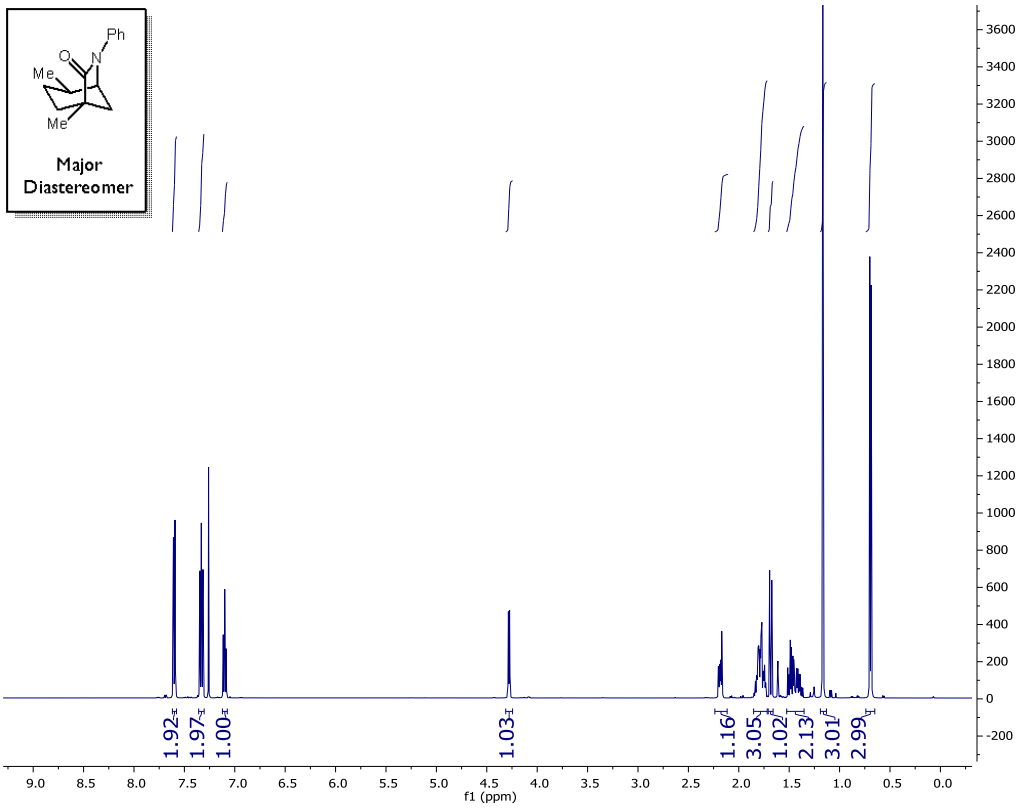

O
O
N
Ph
Me
Me
OH
Me
157.20
135.52
129.33
128.16
127.75
81.15
72.23
62.06
41.37
34.37
27.59
27.24
26.68
22.55
21.85
f1 (ppm)

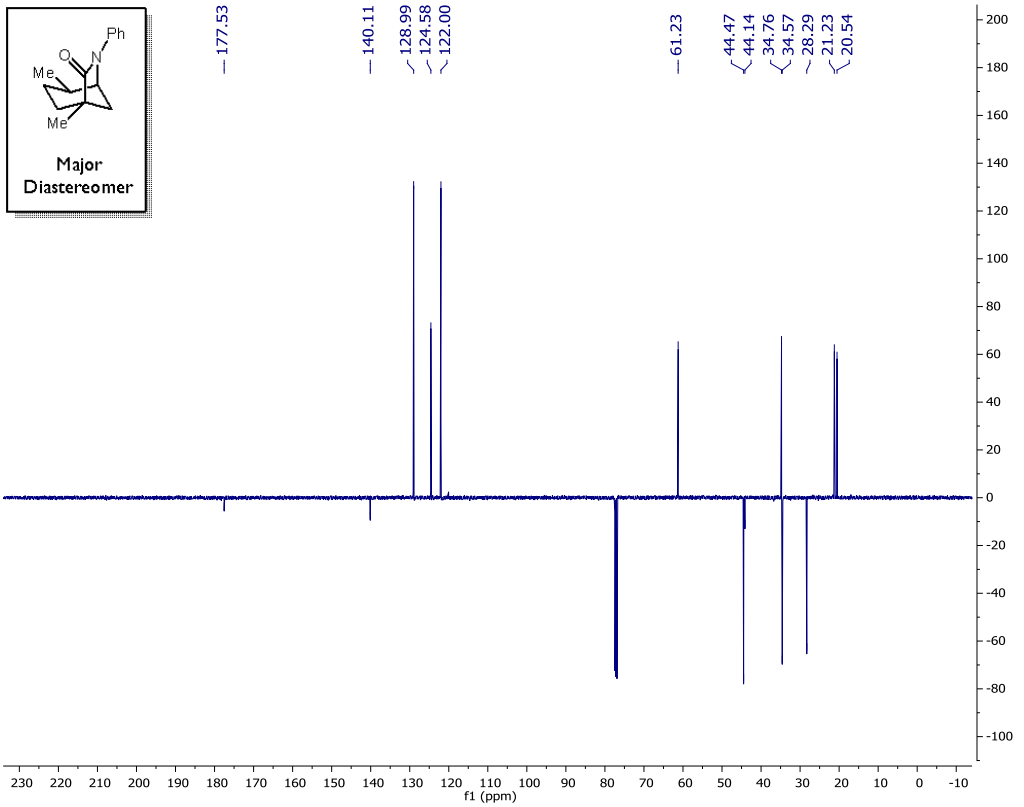

Ph
1.99
1.00
1.95
1.95
2.04
2.07
2.07
2.27
1.09
f1 (ppm)

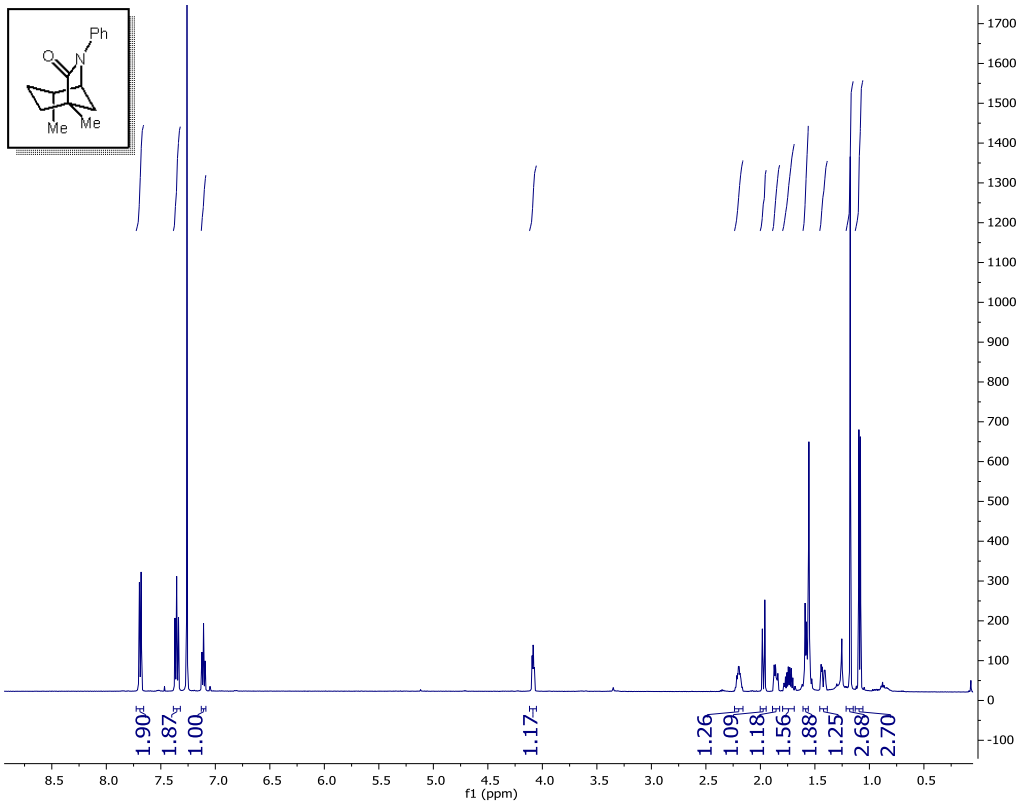

Ph
157.42
134.75
130.18
129.37
128.53
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
72.33
63.15
35.05
24.38
22.95
f1 (ppm)

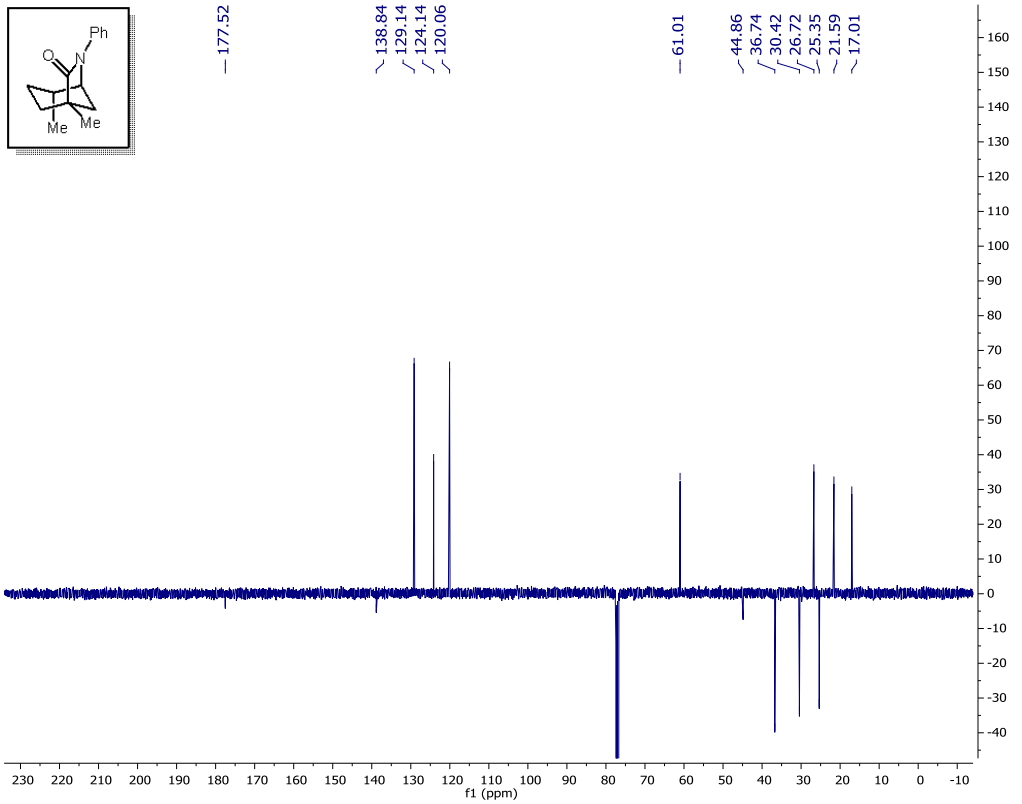

Ph
N
O
1.80
1.83
1.00
1.16
1.07
1.05
1.03
1.13
1.12
1.01
1.86
0.99
f1 (ppm)

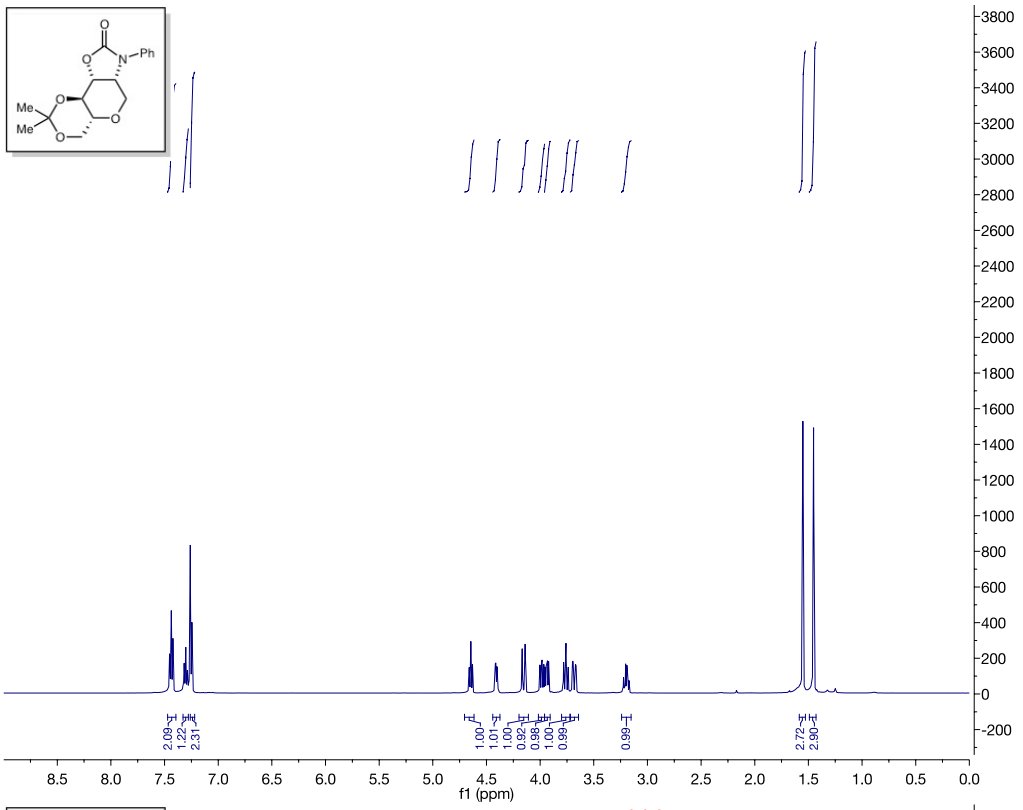

178.59
139.29
129.00
123.98
119.46
60.79
44.37
44.34
37.51
37.41
37.20
34.75
Ph
N
O
f1 (ppm)

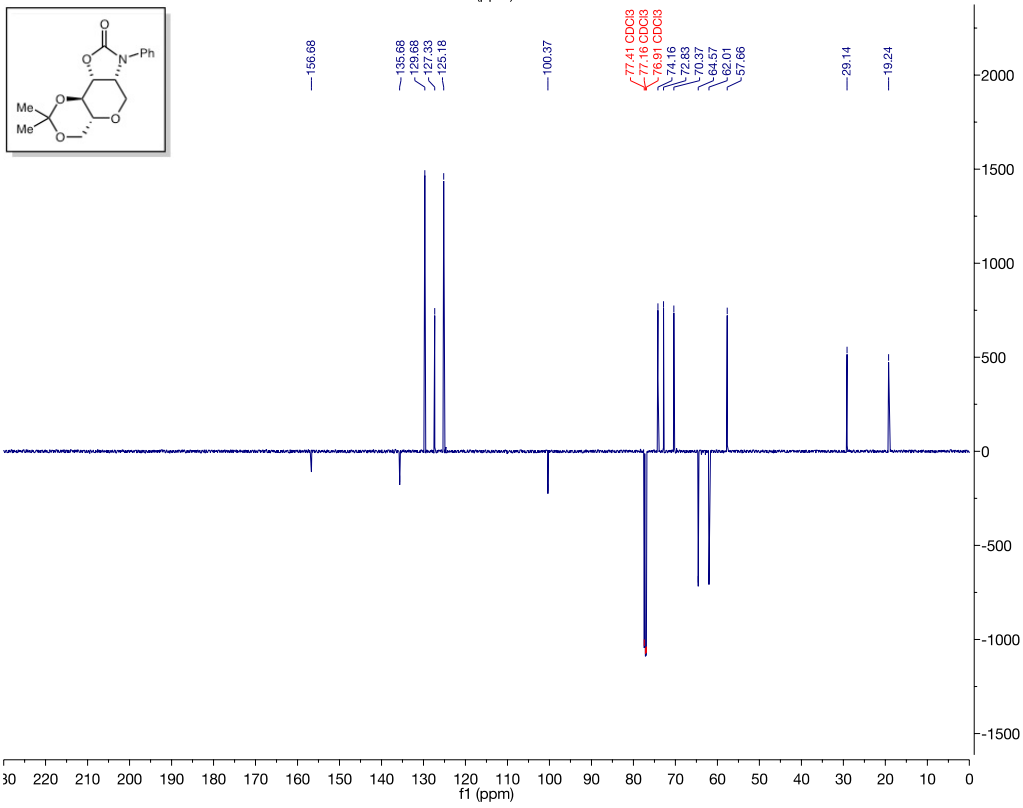

Ph
N
O
Me
Me
Major
Diastereomer
1.92
1.97
1.00
1.03
1.16
3.05
1.02
2.13
3.01
2.99
f1 (ppm)

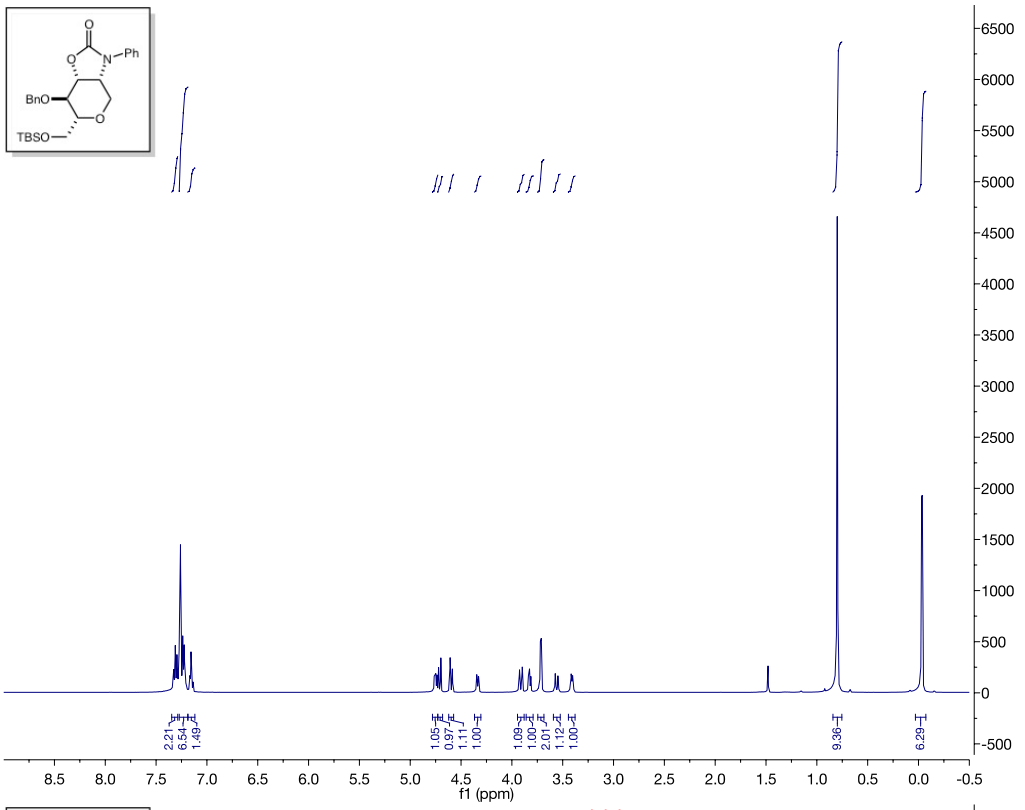

Ph
N
O
Me
Me
Major
Diastereomer
177.53
140.11
128.99
124.58
122.00
61.23
44.47
44.14
34.76
34.57
28.29
21.23
20.54
f1 (ppm)

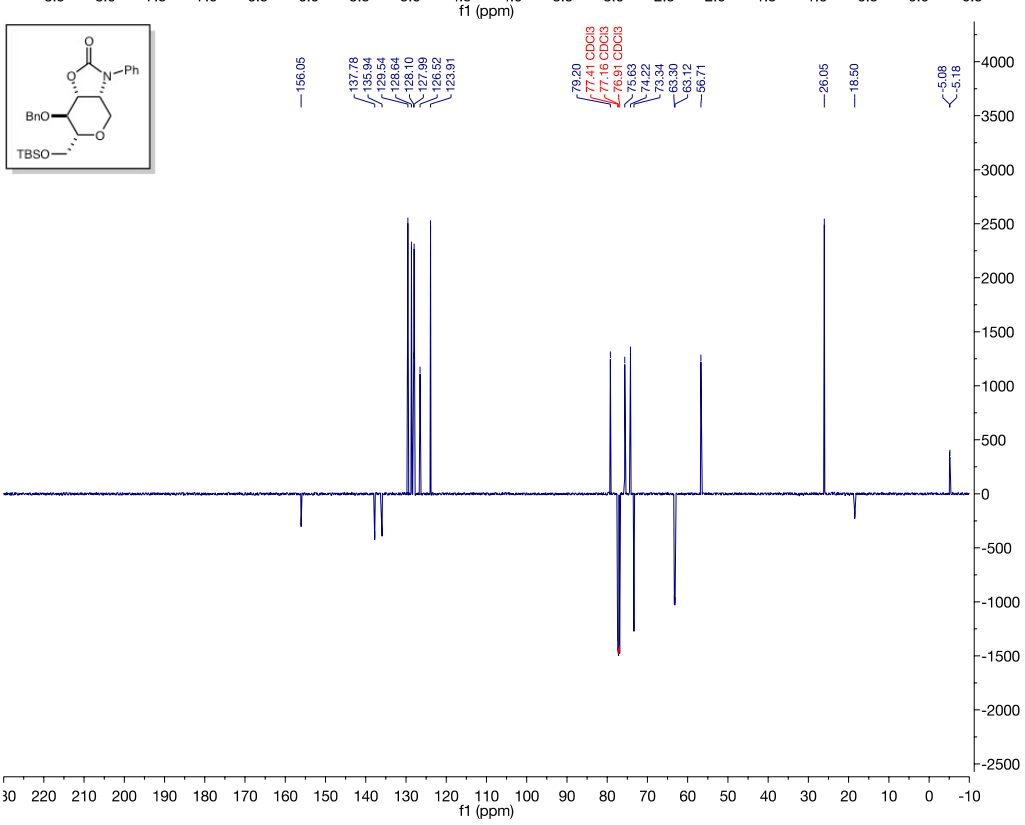

Ph
O
N
Me
Me
1.90
1.87
1.00
1.17
1.26
1.09
1.18
1.56
1.88
1.25
2.68
2.70
f1 (ppm)

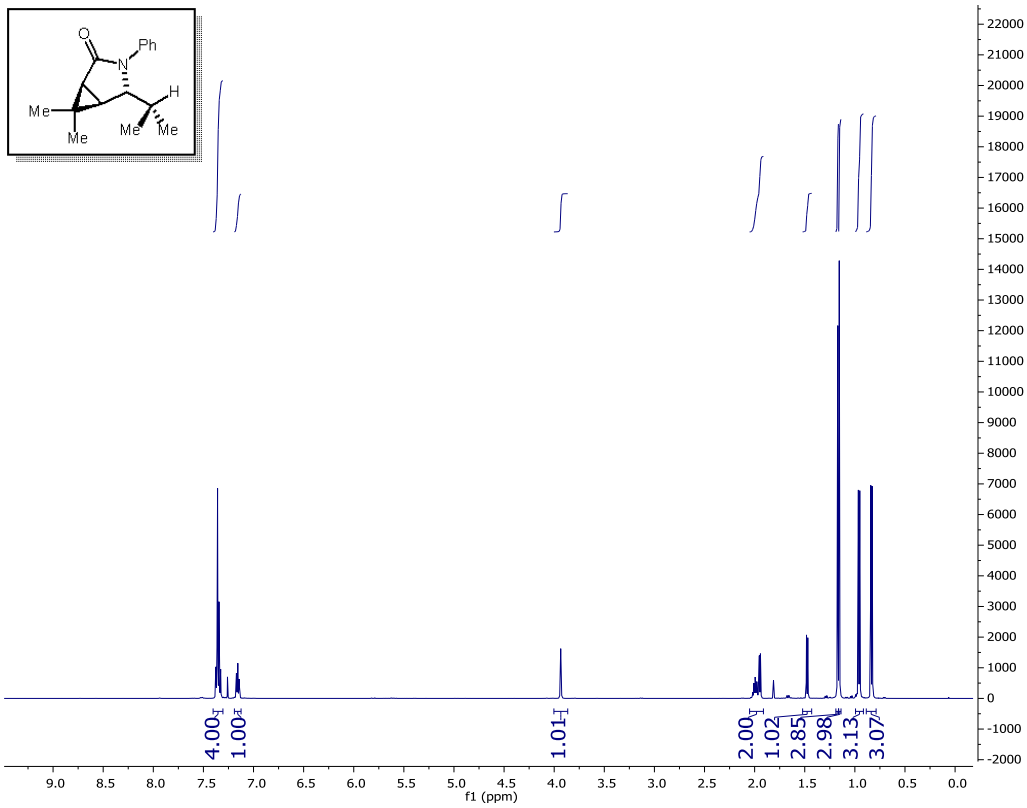

Ph
O
N
Me
Me
177.52
138.84
129.14
124.14
120.06
61.01
44.86
36.74
30.42
26.72
25.35
21.59
17.01
f1 (ppm)

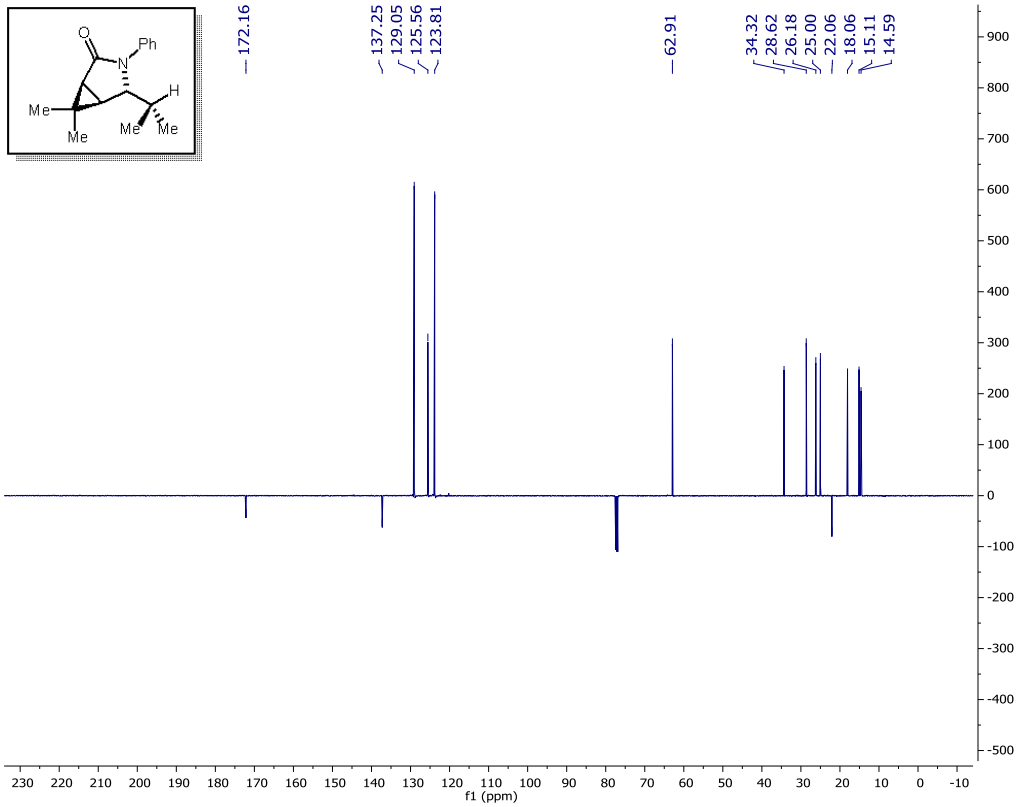

Ph
Me
Me
2.09
1.22
2.31
1.00
1.01
1.00
0.92
0.98
1.00
0.99
0.99
2.72
2.90
f1 (ppm)

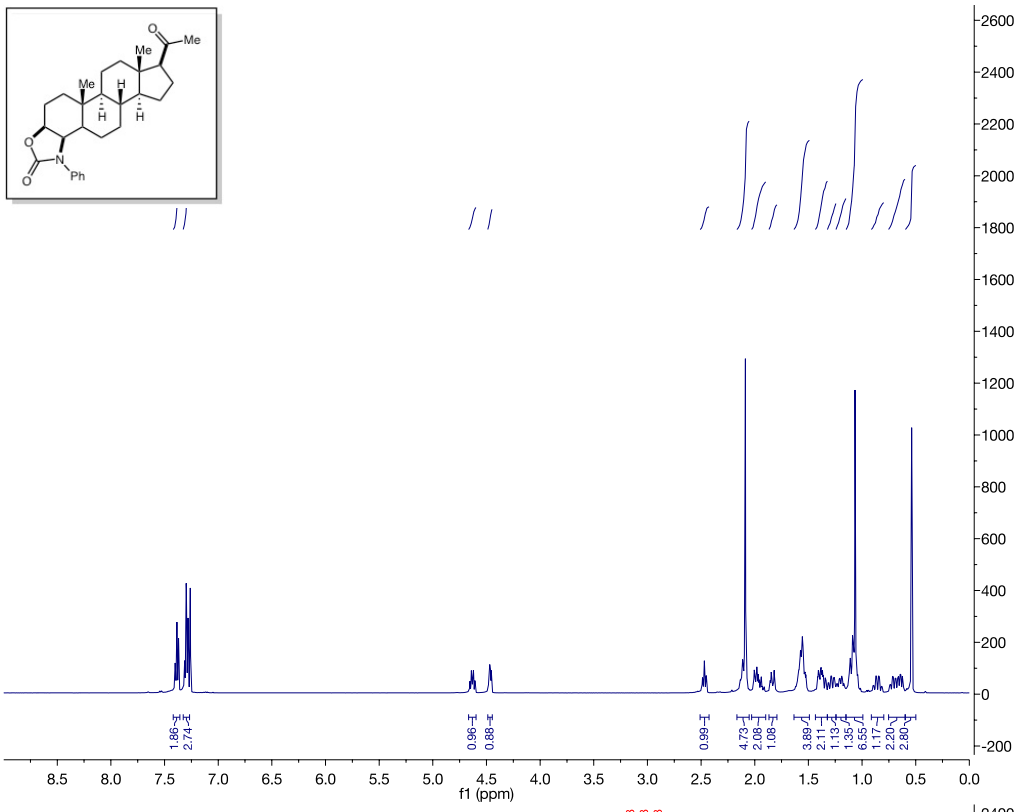

Ph
Me
Me
156.68
135.68
129.68
127.33
125.18
100.37
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
74.16
72.83
70.37
64.57
62.01
57.66
29.14
19.24
f1 (ppm)

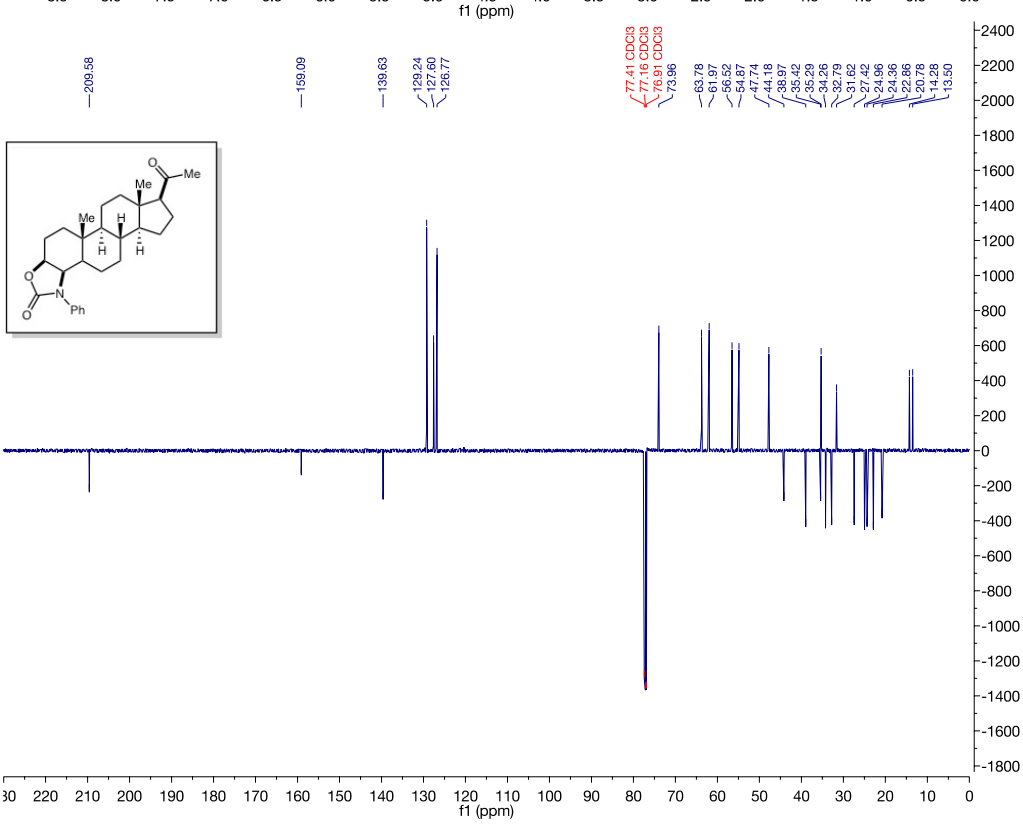

Ph
BnO
TBSO
2.21
6.54
1.49
1.05
0.97
1.11
1.00
1.09
1.00
2.01
1.12
1.00
9.36
6.29
f1 (ppm)

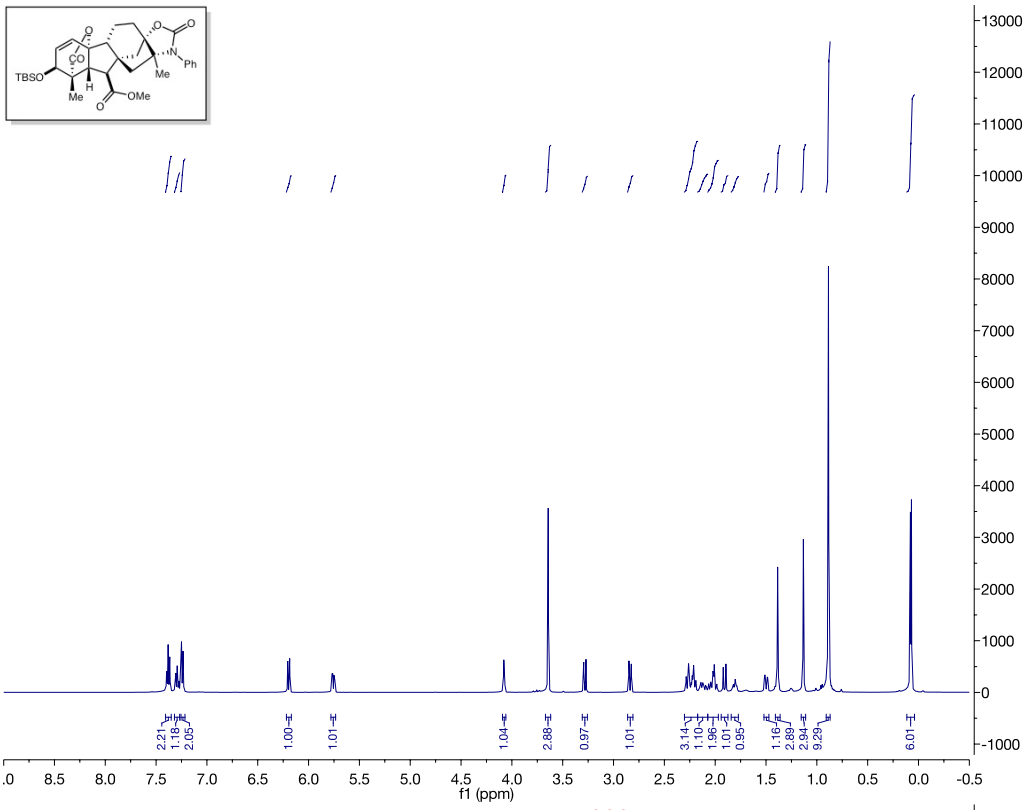

Ph
BnO
TBSO
156.05
137.78
135.94
129.54
128.64
128.10
127.99
126.52
123.91
79.20
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
75.83
74.22
73.34
63.30
63.12
56.71
26.05
18.50
-5.08
-5.18
f1 (ppm)

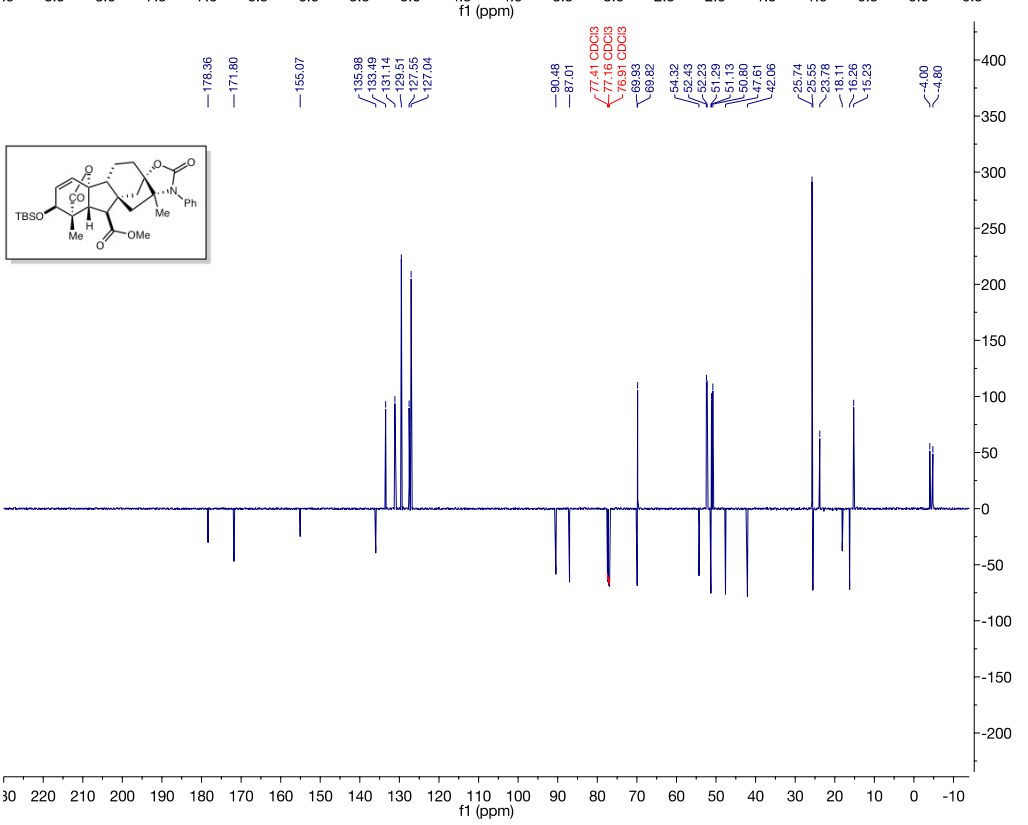

Ph
N
O
H
Me
Me
Me
Me
4.00
1.00
1.01
2.00
1.02
2.85
2.98
3.13
3.07
f1 (ppm)

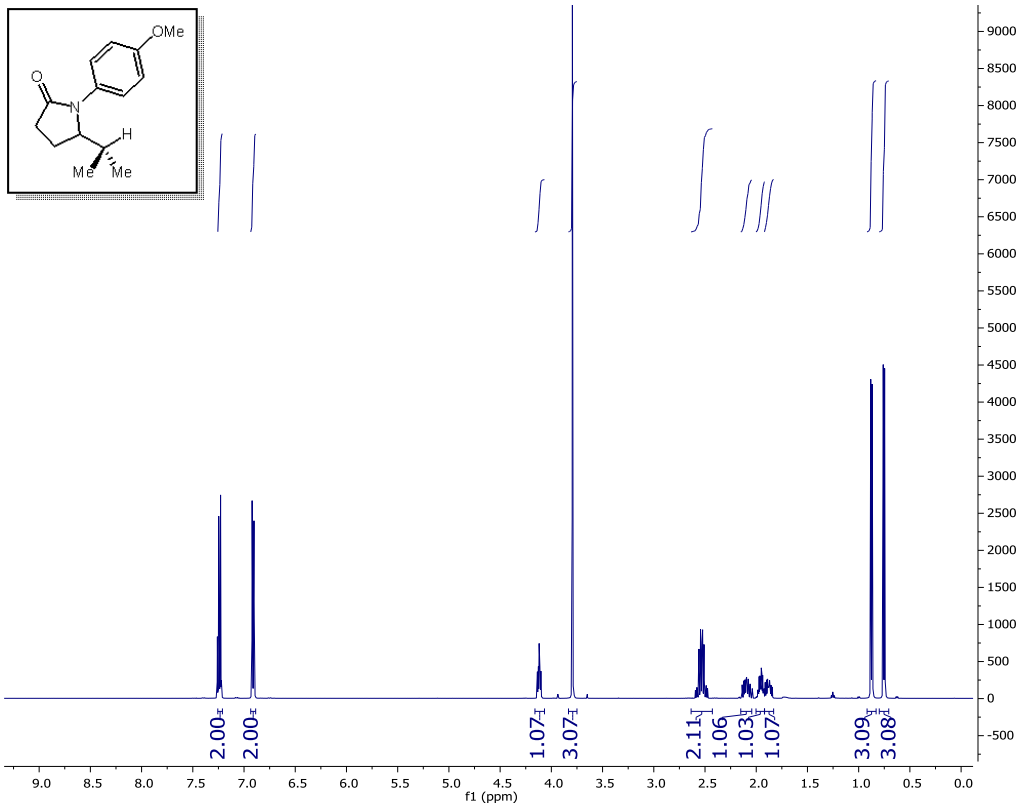

Ph
N
O
H
Me
Me
Me
Me
172.16
137.25
129.05
125.56
123.81
62.91
34.32
28.62
26.18
25.00
22.06
18.06
15.11
14.59
f1 (ppm)

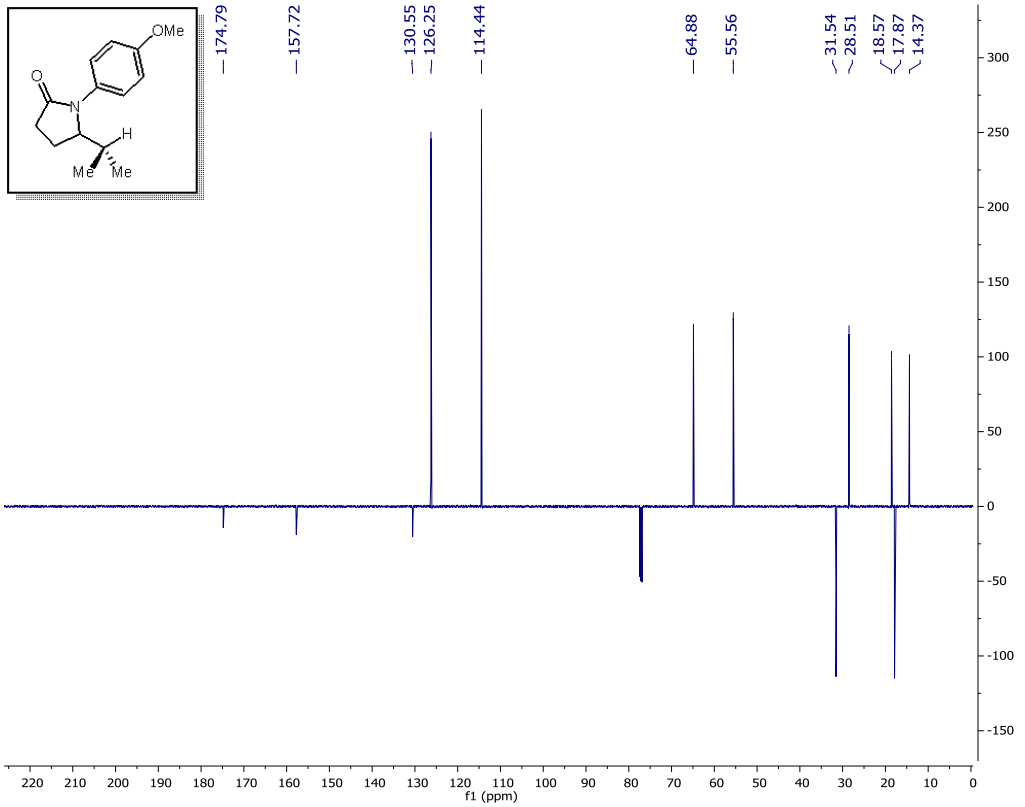

Me
Me
H
H
H
O
O
N
Ph
O
Me
1.86
2.74
0.96
0.88
0.99
4.73
2.08
1.08
3.89
2.11
1.13
1.35
6.55
1.17
2.20
2.80
f1 (ppm)

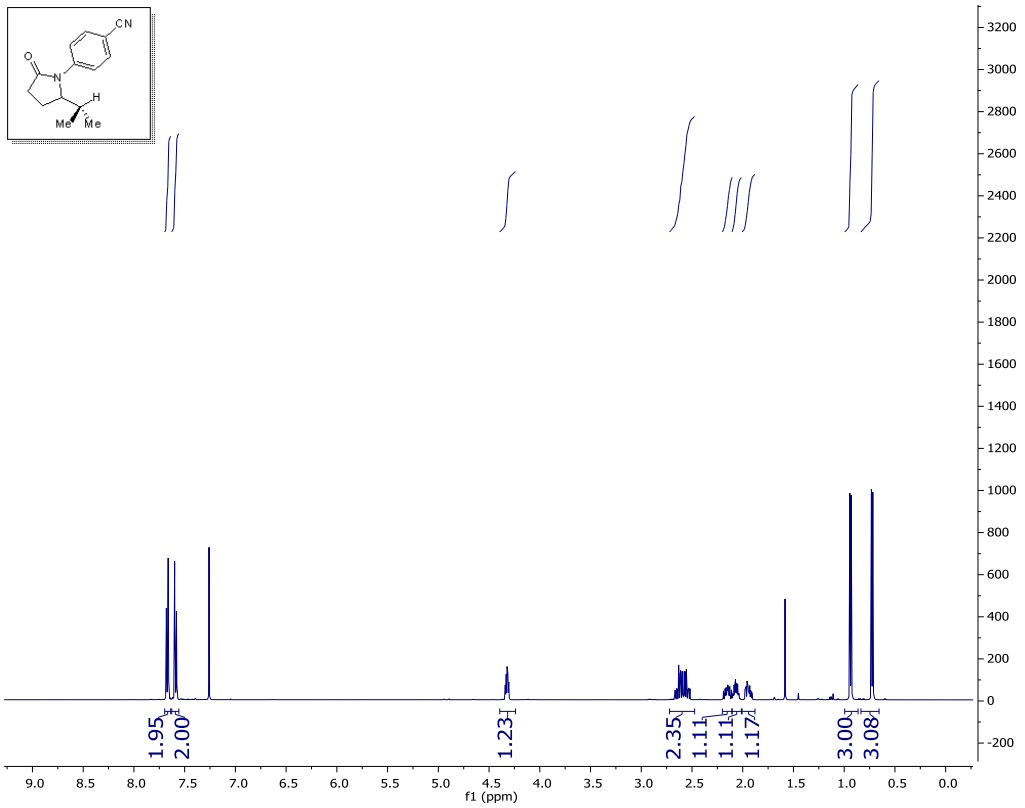

209.58
159.09
139.63
129.24
127.60
126.77
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
73.96
63.78
61.97
56.52
54.87
47.74
44.18
38.97
35.42
35.29
34.26
32.79
31.62
27.42
24.96
24.36
22.86
20.78
14.28
13.50
Me
Me
H
H
H
O
O
N
Ph
O
f1 (ppm)

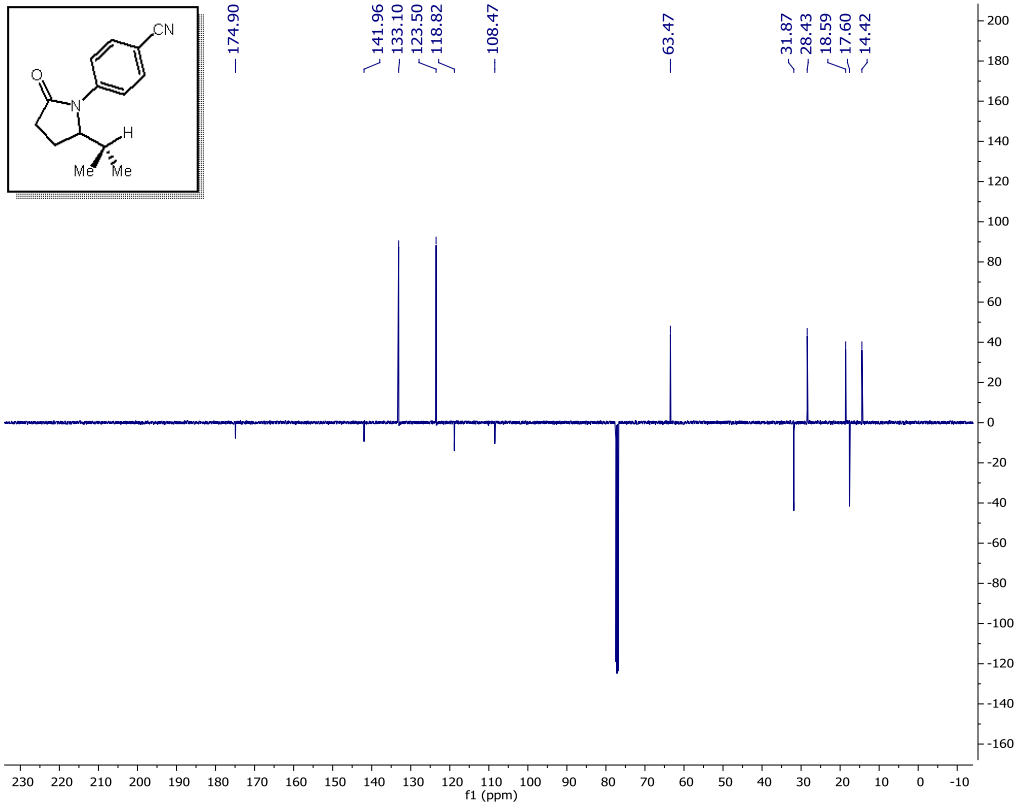

TBSO
Me
H
O
OMe
Me
N
Ph
O
O
O
2.21
1.18
2.05
1.00
1.01
1.04
2.88
0.97
1.01
3.14
1.10
1.96
1.01
0.95
1.16
2.89
2.94
9.29
6.01
f1 (ppm)

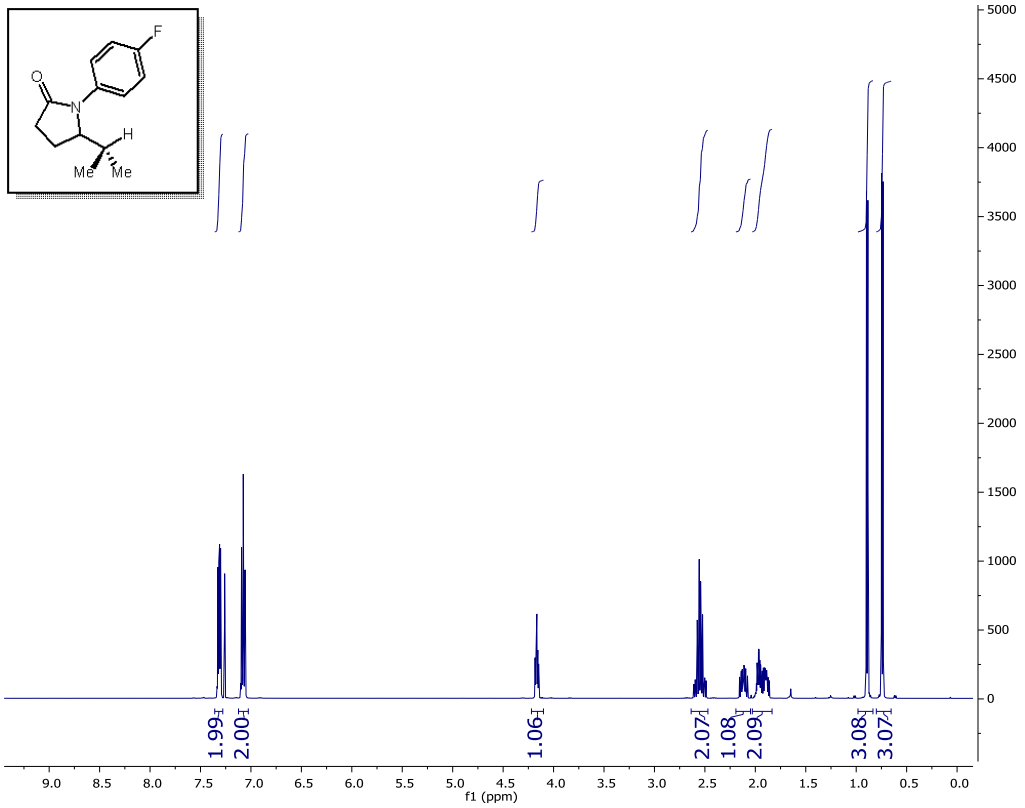

178.36
171.80
155.07
135.98
133.49
131.14
129.51
127.55
127.04
90.48
87.01
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
69.93
69.82
54.32
52.43
52.23
51.29
51.13
50.80
47.61
42.06
25.74
25.55
23.78
18.11
16.26
15.23
-4.00
-4.80
TBSO
Me
H
O
OMe
Me
N
Ph
O
O
O
f1 (ppm)

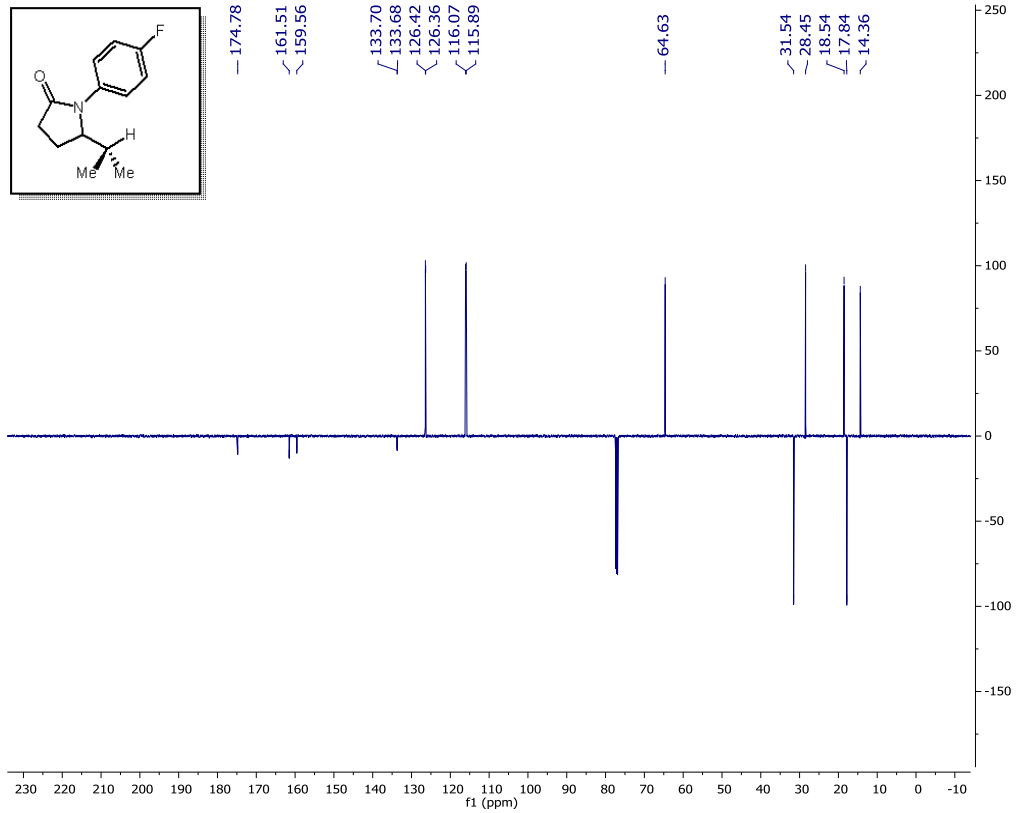

OMe
O
N
H
Me
Me
2.00
2.00
1.07
3.07
2.11
1.06
1.03
1.07
3.09
3.08
f1 (ppm)

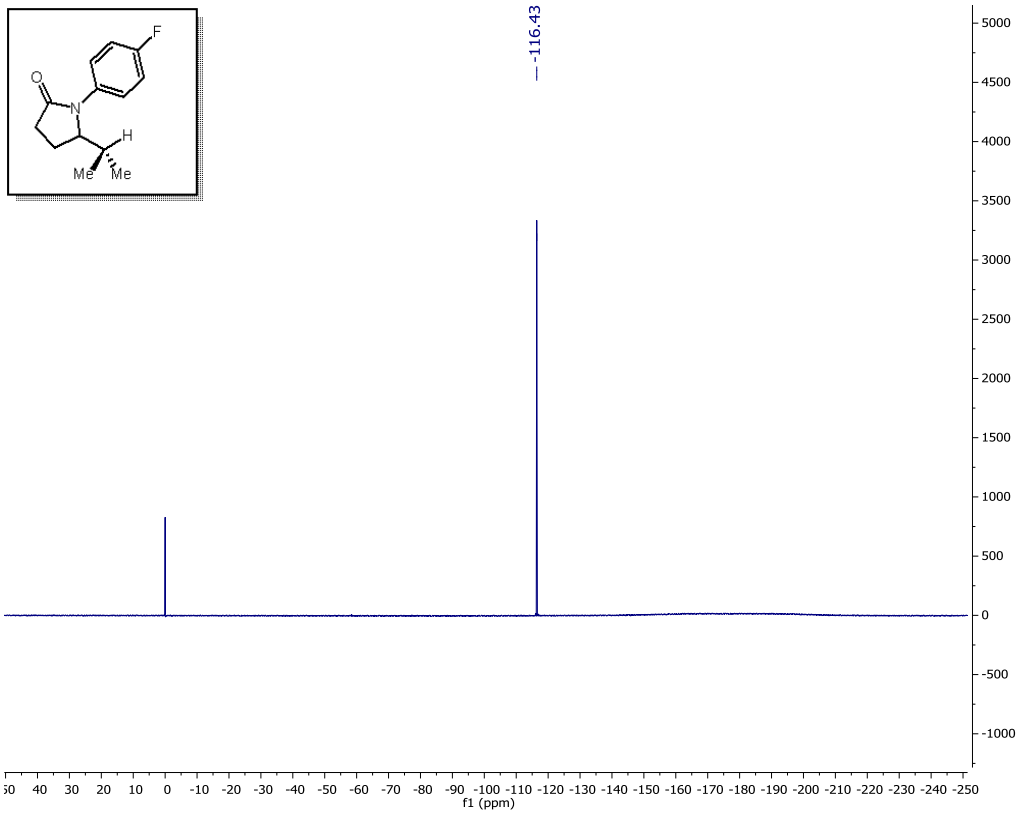

OMe
O
N
H
Me
Me
174.79
157.72
130.55
126.25
114.44
64.88
55.56
31.54
28.51
18.57
17.87
14.37
f1 (ppm)

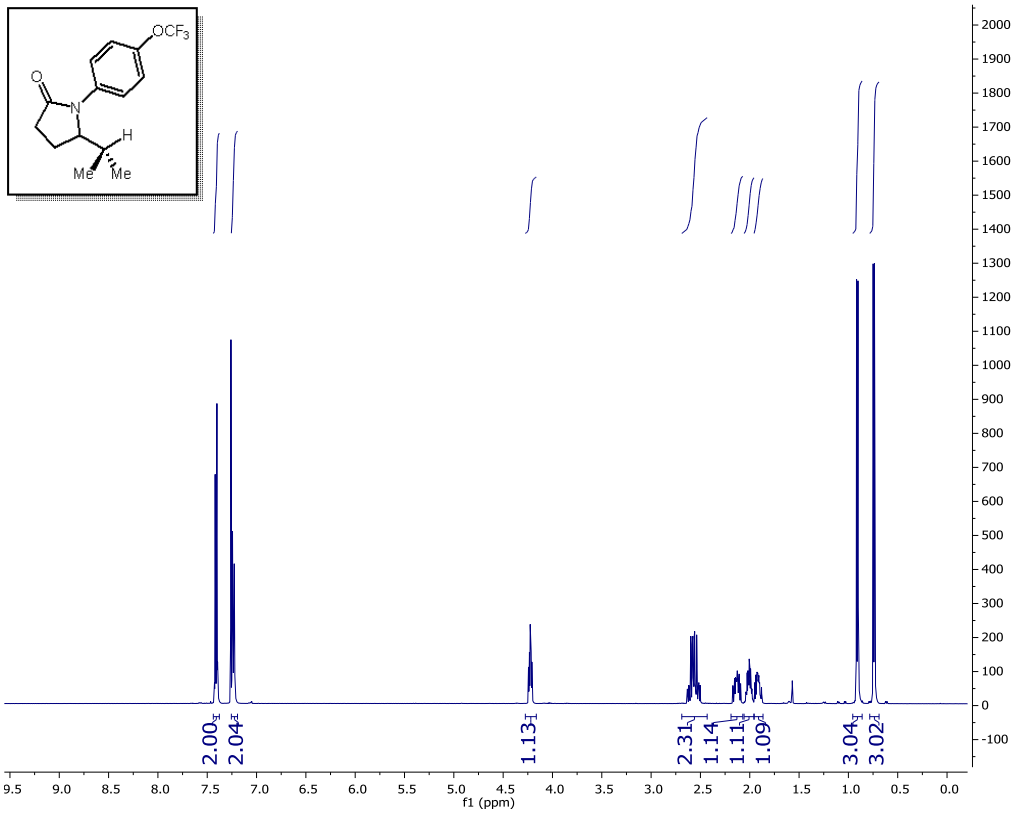

CN
O
N
H
Me
Me
1.95
2.00
1.23
2.35
1.11
1.11
1.17
3.00
3.08
f1 (ppm)

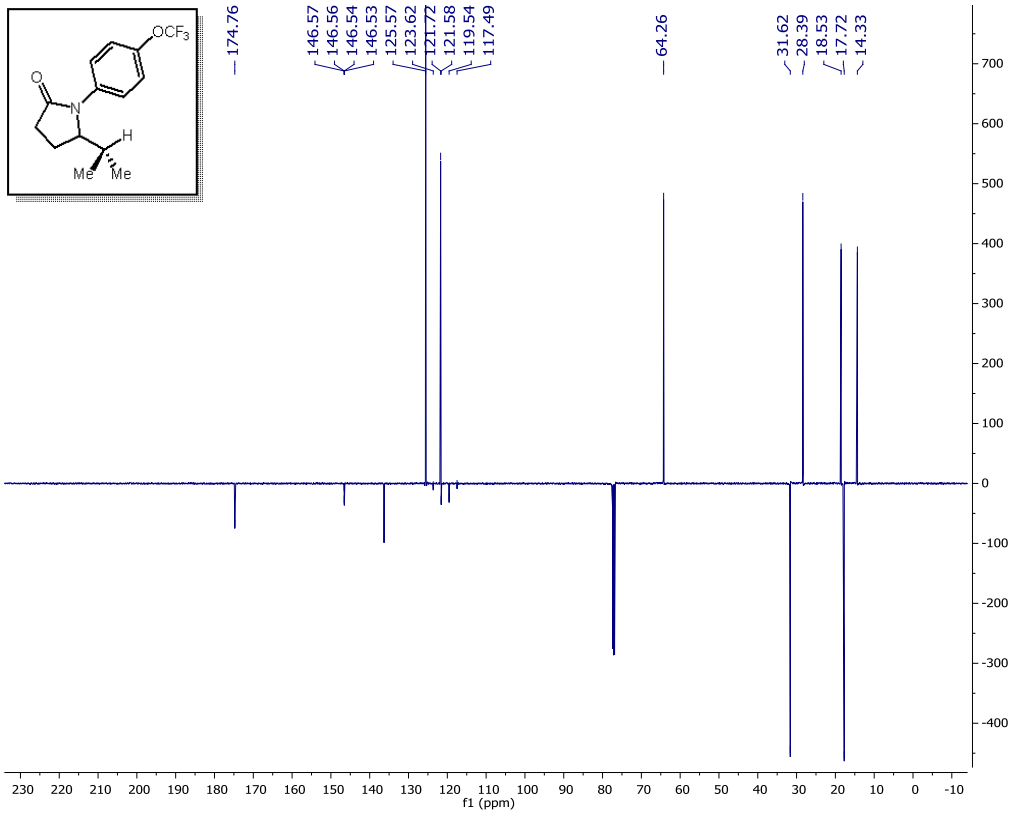

CN
O
N
H
Me
Me
174.90
141.96
133.10
123.50
118.82
108.47
63.47
31.87
28.43
18.59
17.60
14.42
f1 (ppm)

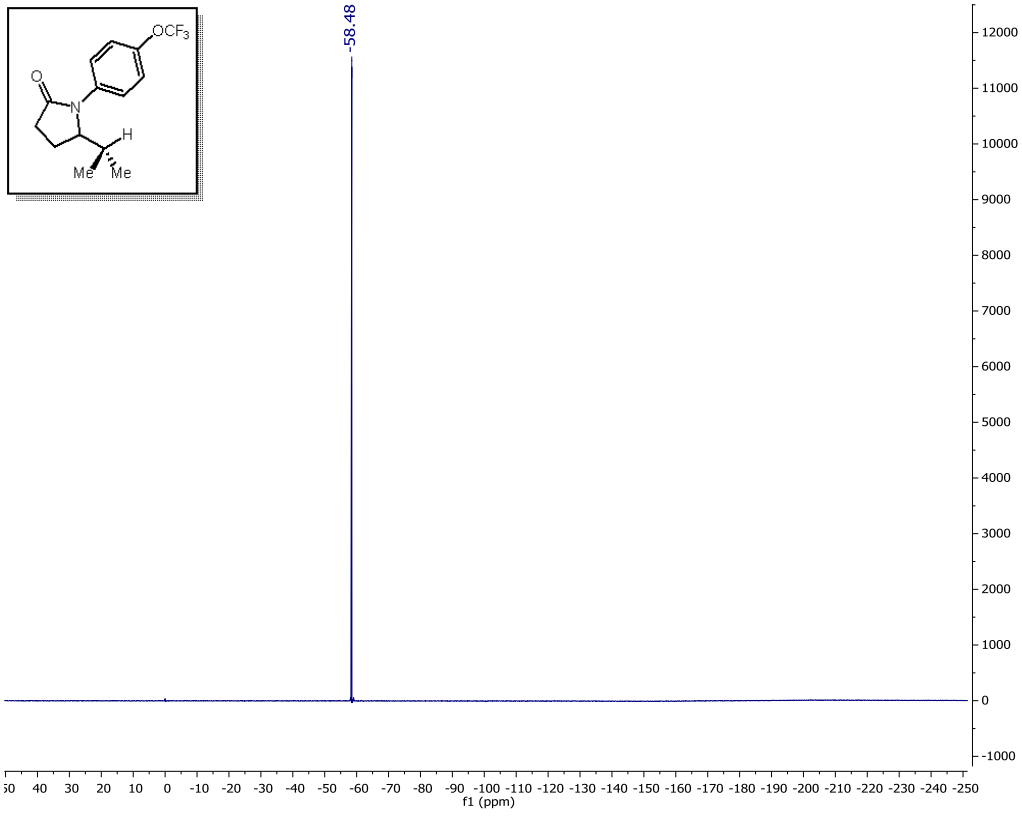

F
O
N
H
Me
Me
1.99
2.00
1.06
2.07
1.08
2.09
3.08
3.07
f1 (ppm)

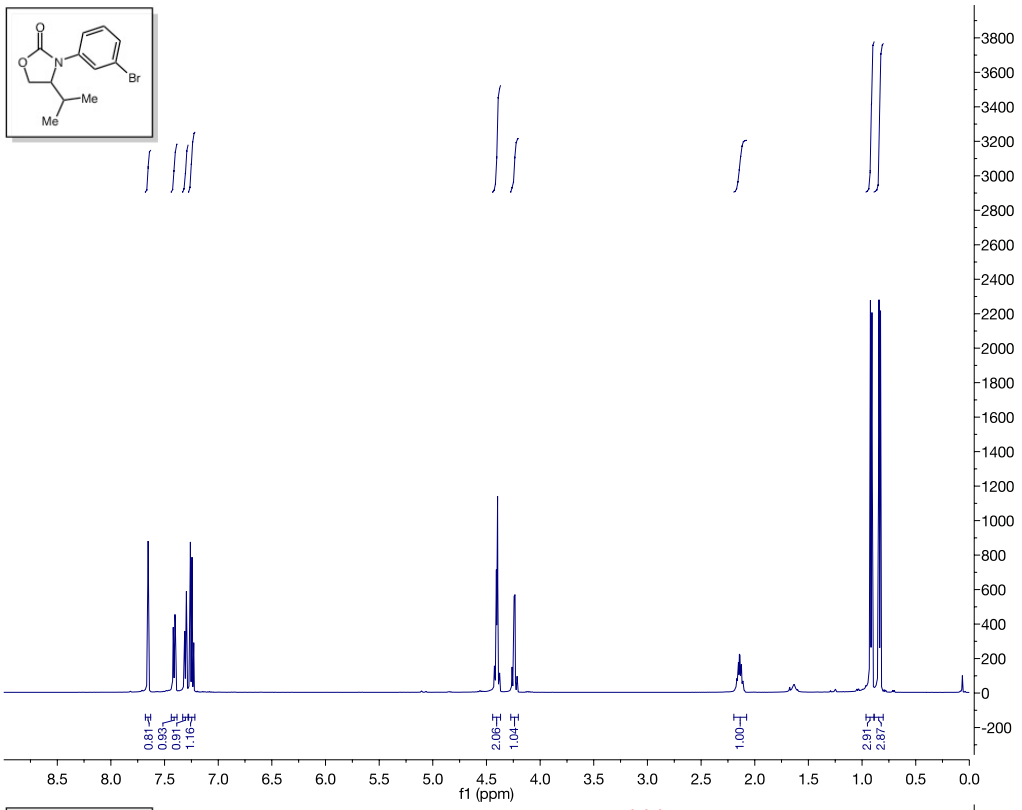

F
O
N
H
Me
Me
174.78
161.51
159.56
133.70
133.68
126.42
126.36
116.07
115.89
64.63
31.54
28.45
18.54
17.84
14.36
f1 (ppm)

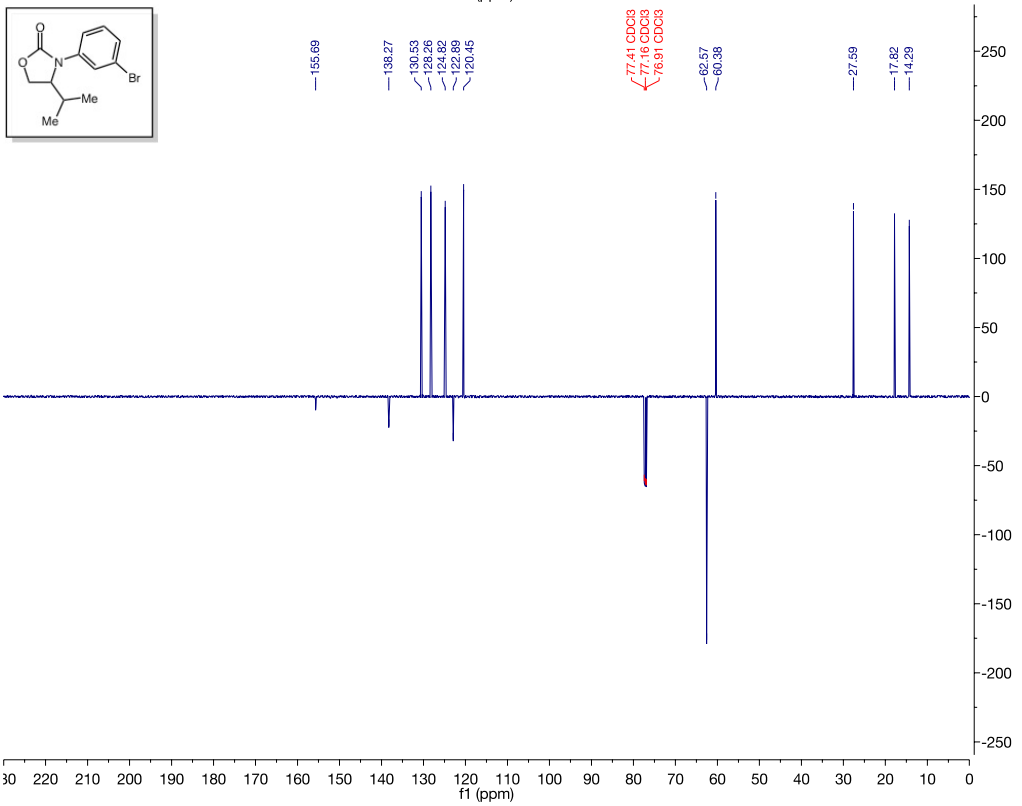

F
O
N
H
Me
Me
-116.43
f1 (ppm)

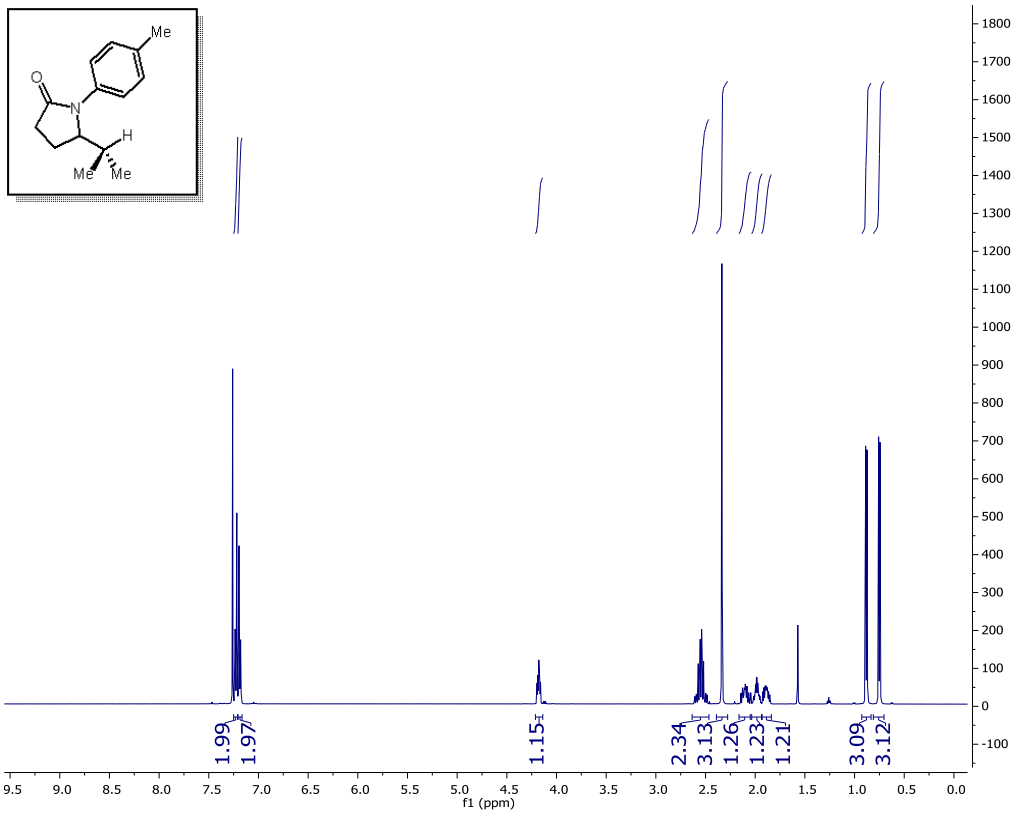

OCF3
O
N
H
Me
Me
2.00
2.04
1.13
2.31
1.14
1.11
1.09
3.04
3.02
f1 (ppm)

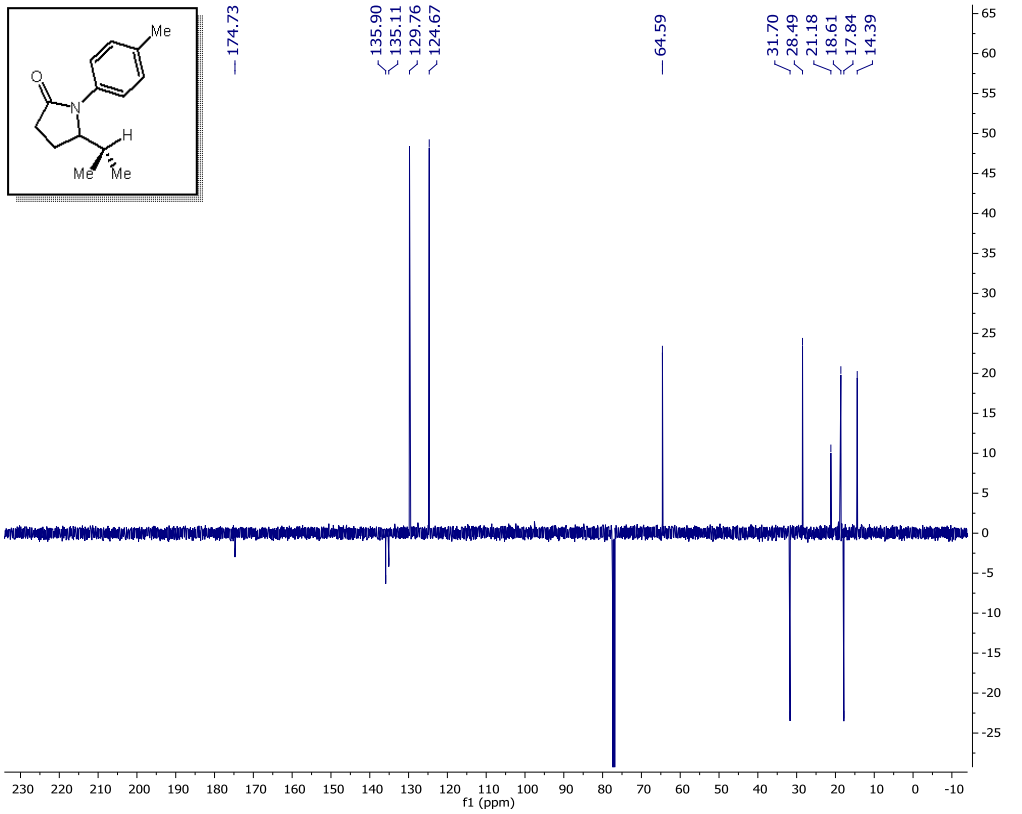

OCF3
O
N
H
Me
Me
174.76
146.57
146.56
146.54
146.53
125.57
123.62
121.72
121.58
119.54
117.49
64.26
31.62
28.39
18.53
17.72
14.33
f1 (ppm)

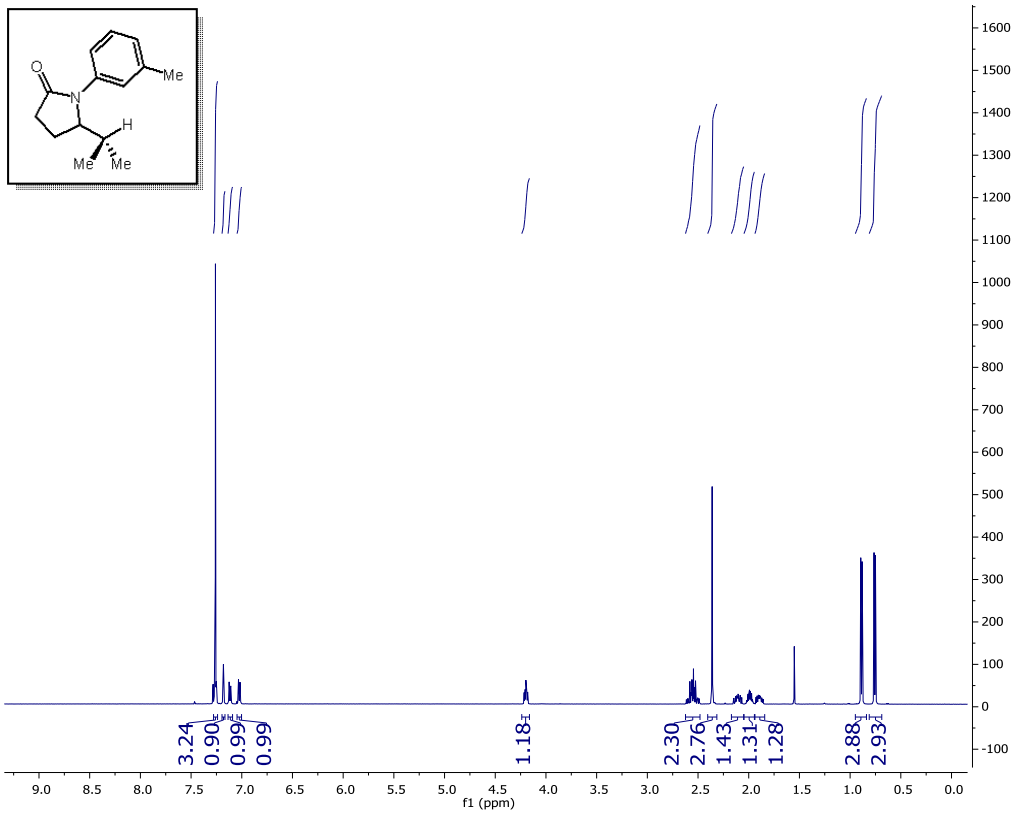

OCF3
O
N
H
Me
Me
-58.48
f1 (ppm)

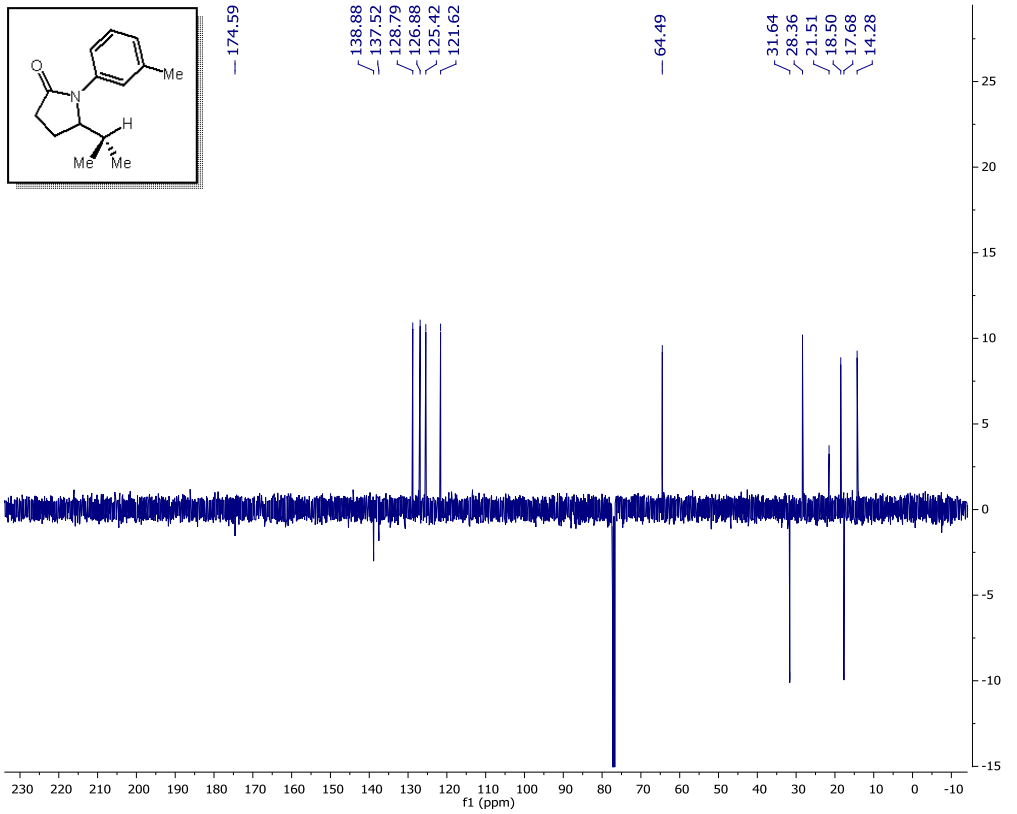

Br
Me
Me
0.81
0.93
0.91
1.16
2.06
1.04
1.00
2.91
2.87
f1 (ppm)


Br
Me
Me
155.69
138.27
130.53
128.26
124.82
122.89
120.45
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
62.57
60.38
27.59
17.82
14.29
f1 (ppm)

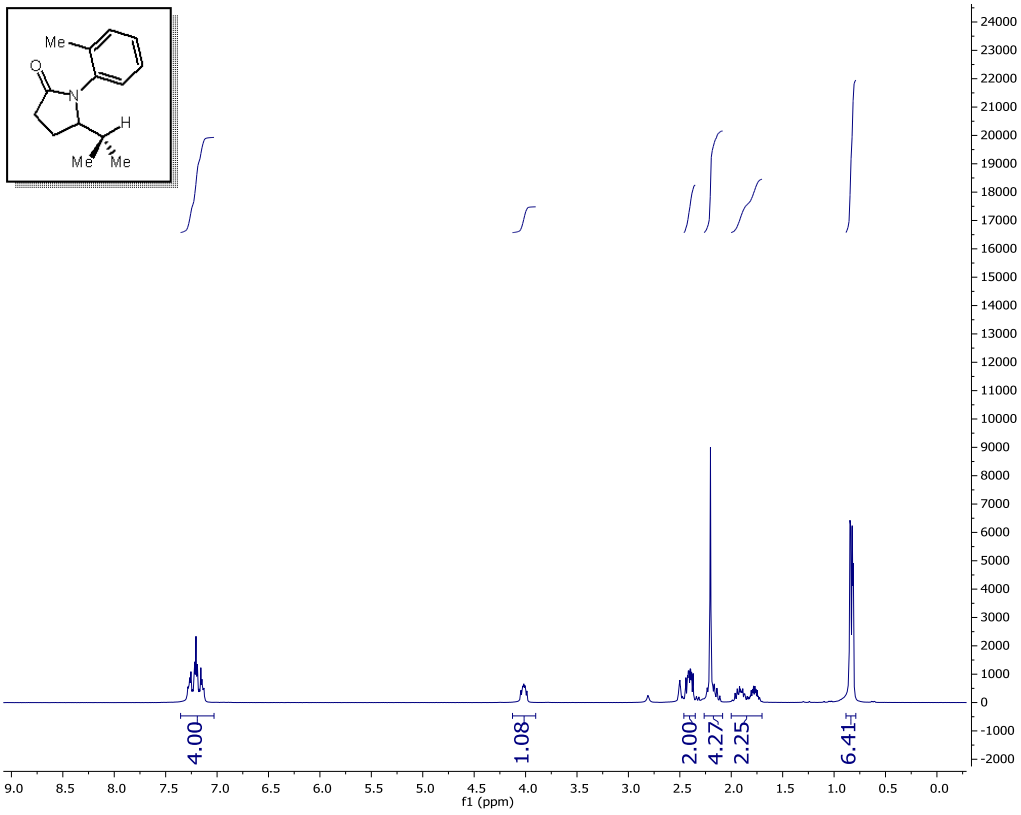

Me
O
N
H
Me
Me
1.99
1.97
1.15
2.34
3.13
1.26
1.23
1.21
3.09
3.12
f1 (ppm)

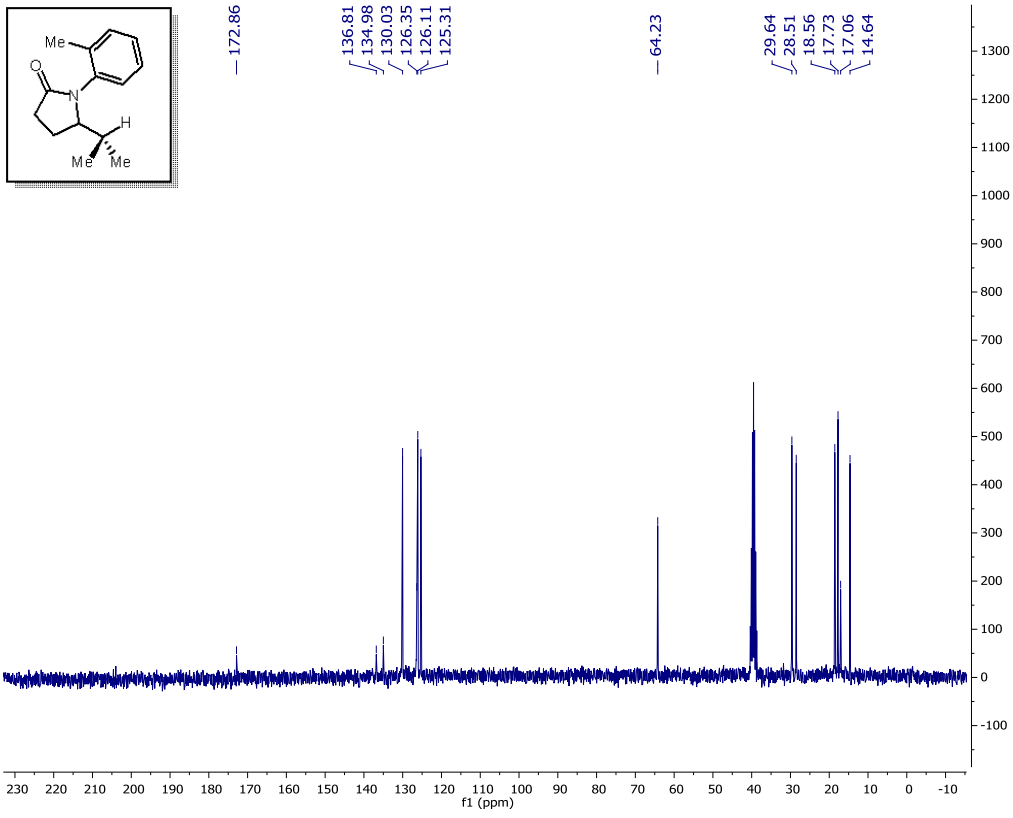

Me
O
N
H
Me
Me
174.73
135.90
135.11
129.76
124.67
64.59
31.70
28.49
21.18
18.61
17.84
14.39
f1 (ppm)

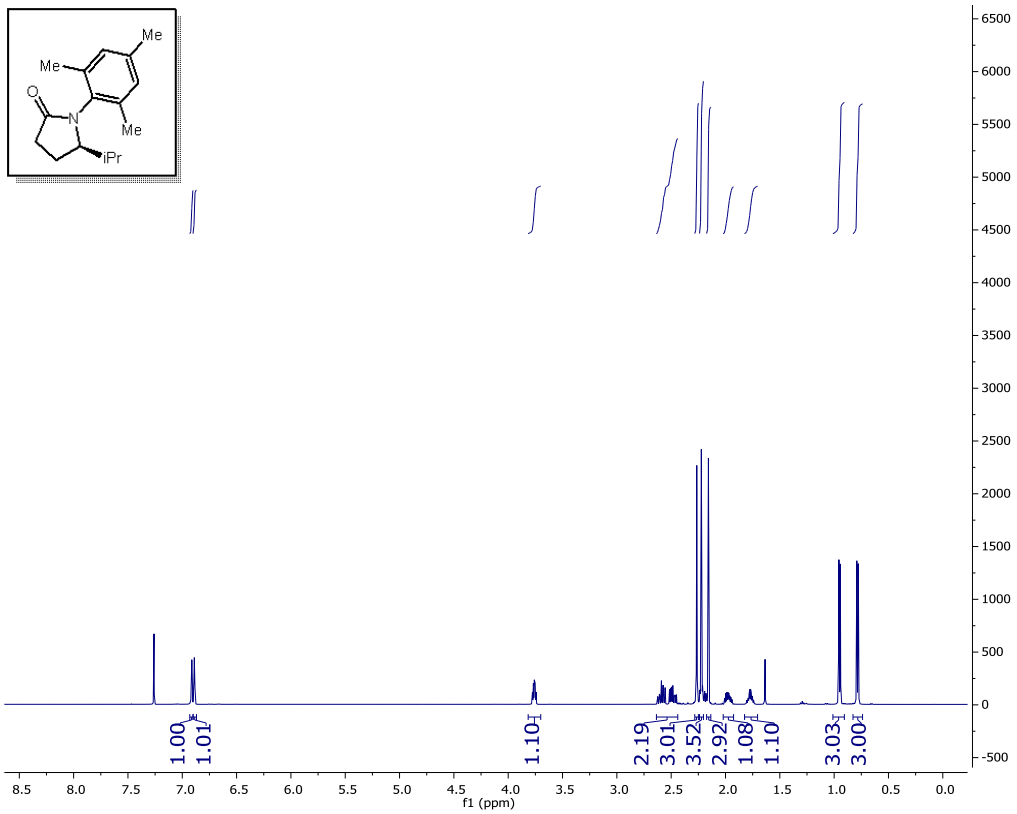

Me
O
N
H
Me
Me
3.24
0.90
0.99
0.99
1.18
2.30
2.76
1.43
1.31
1.28
2.88
2.93
f1 (ppm)

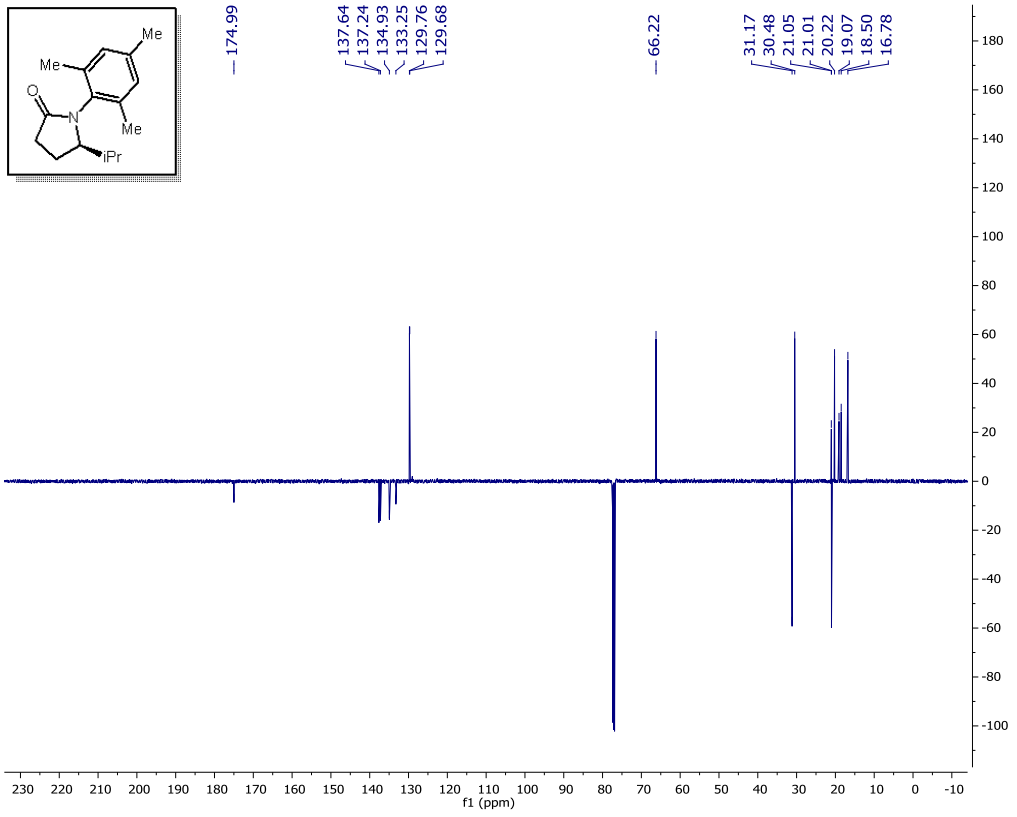

Me
O
N
H
Me
Me
174.59
138.88
137.52
128.79
126.88
125.42
121.62
64.49
31.64
28.36
21.51
18.50
17.68
14.28
f1 (ppm)

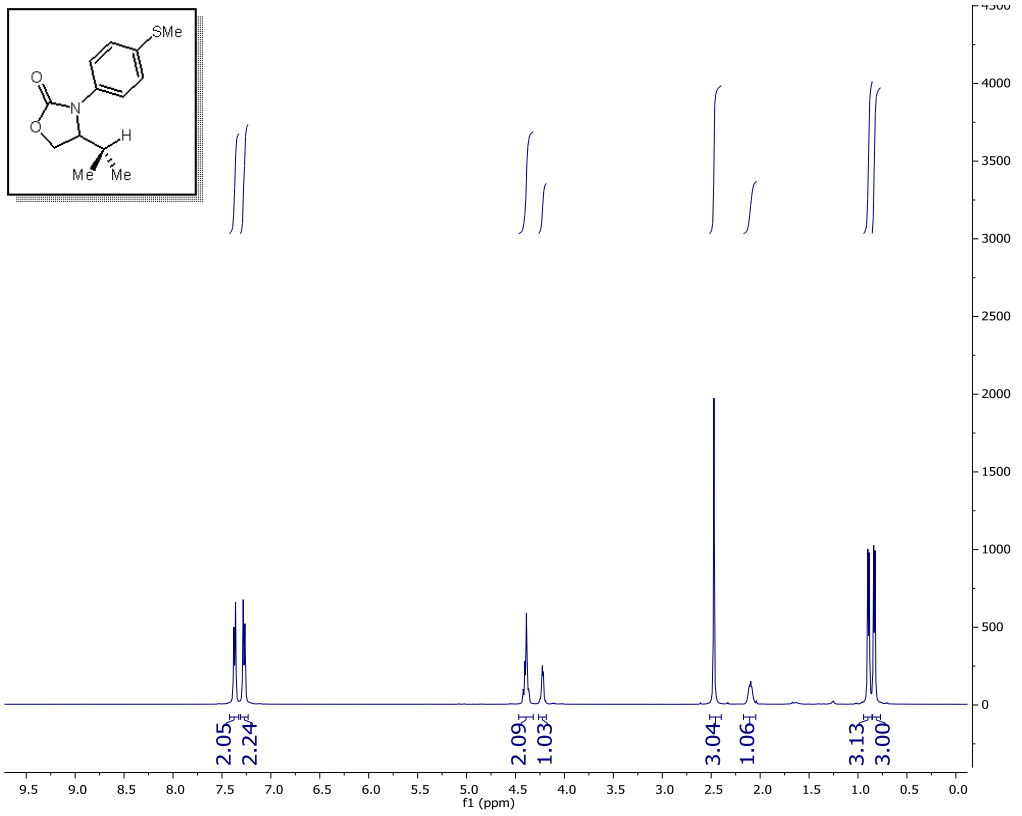
Note: Taken at 120 C in DMSO solvent on a Bruker 300

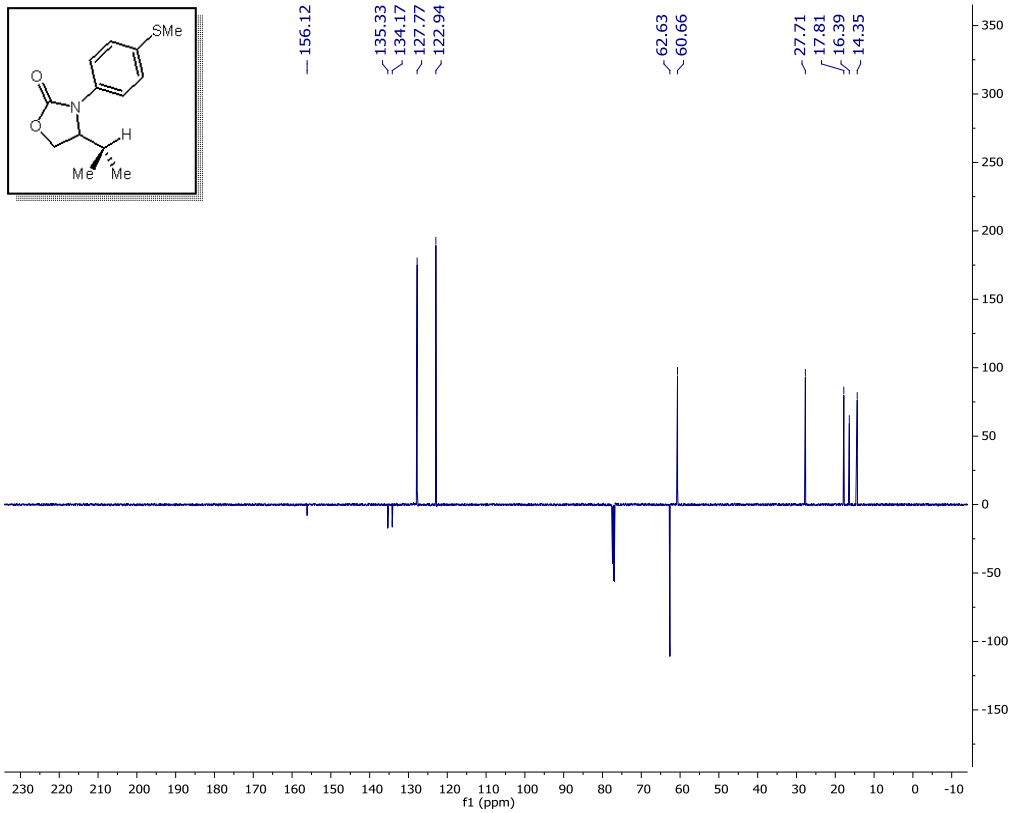


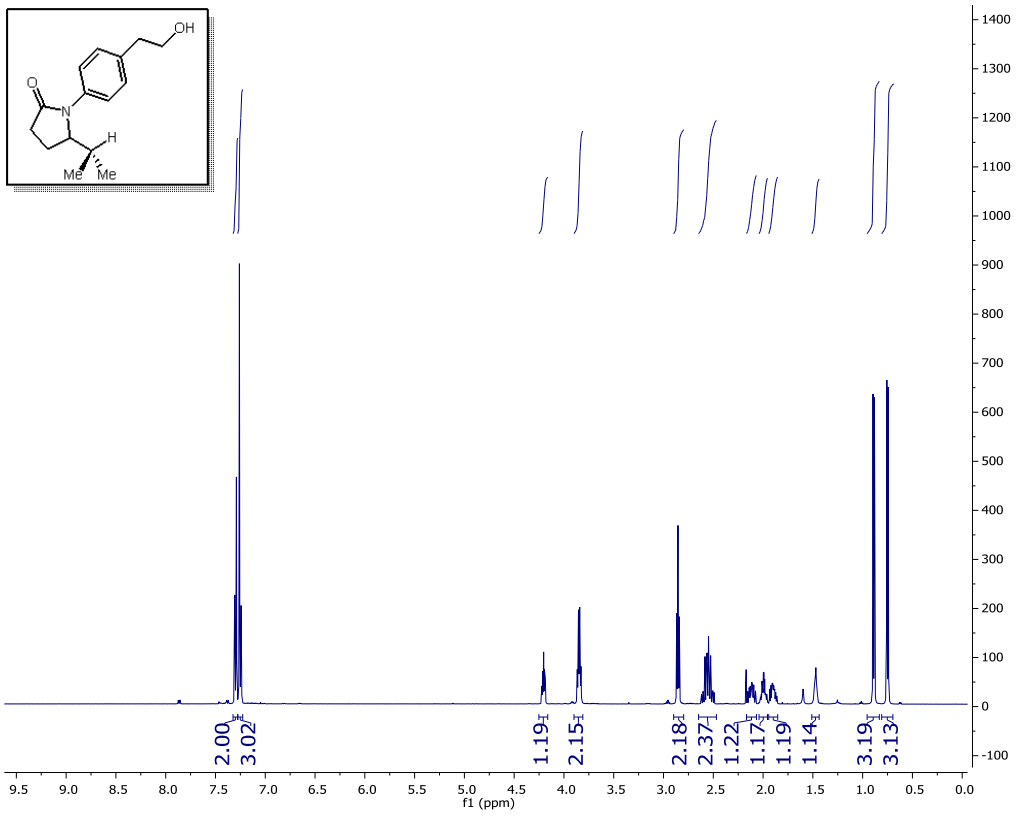


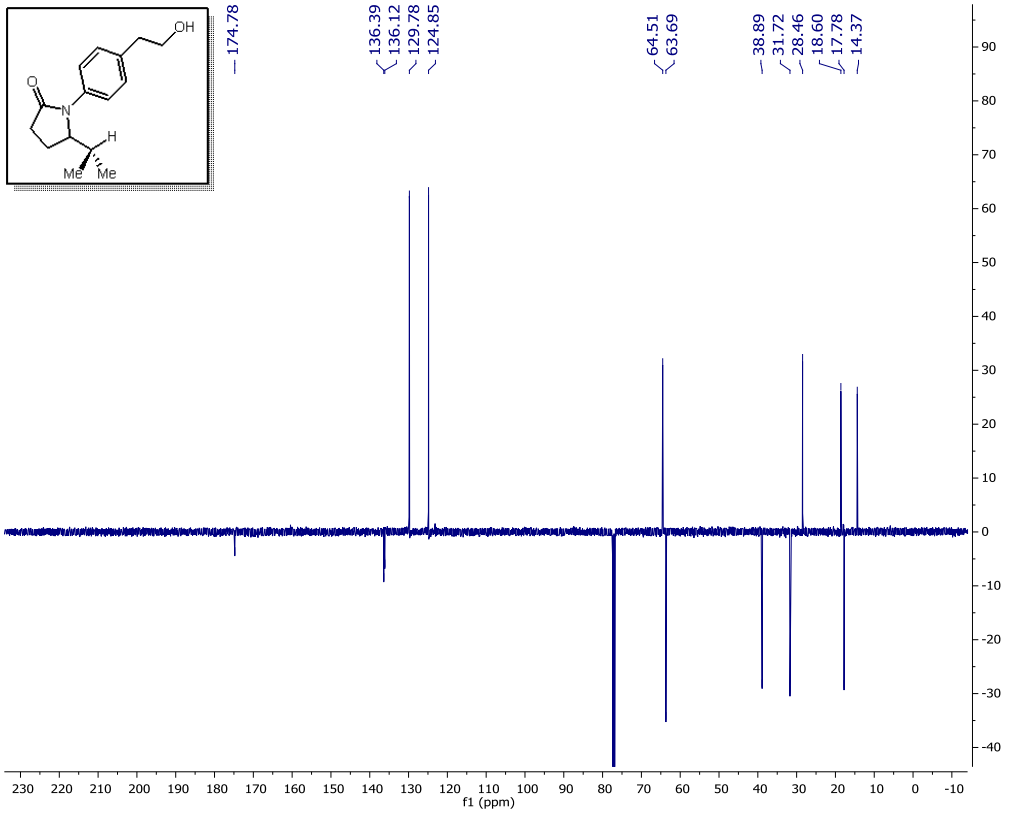

Me
Me
Me
iPr
1.00
1.01
1.10
2.19
3.01
3.52
2.92
1.08
1.10
3.03
3.00
f1 (ppm)

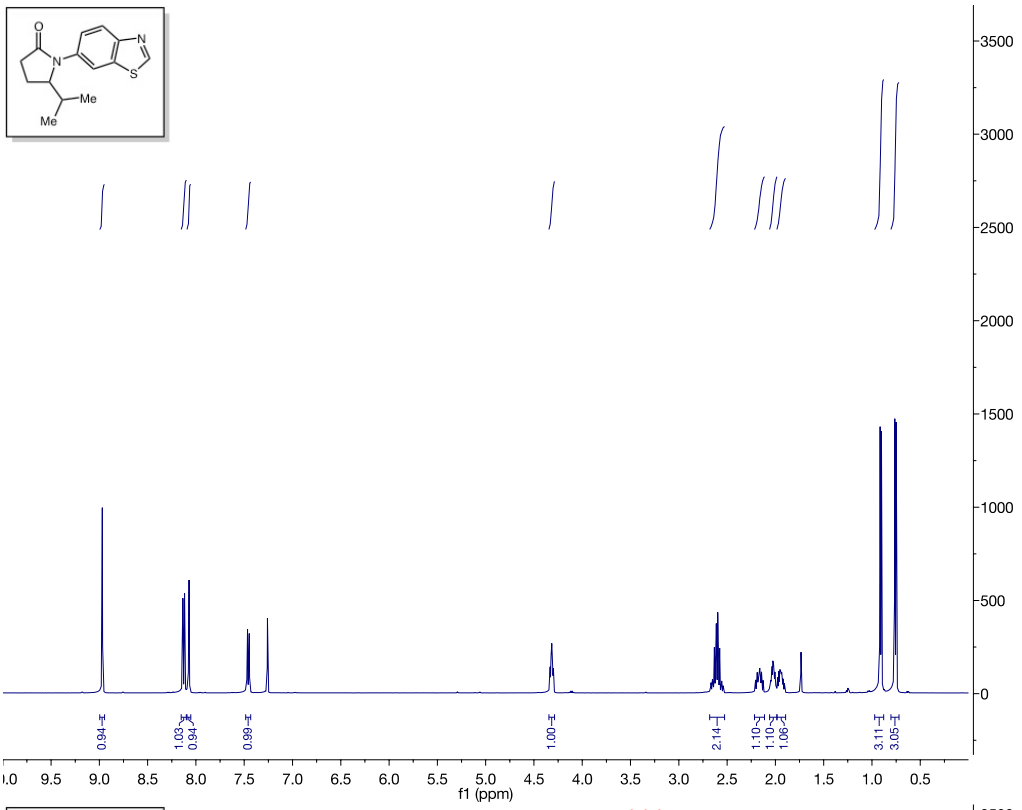

Me
Me
Me
iPr
174.99
137.64
137.24
134.93
133.25
129.76
129.68
66.22
31.17
30.48
21.05
21.01
20.22
19.07
18.50
16.78
f1 (ppm)

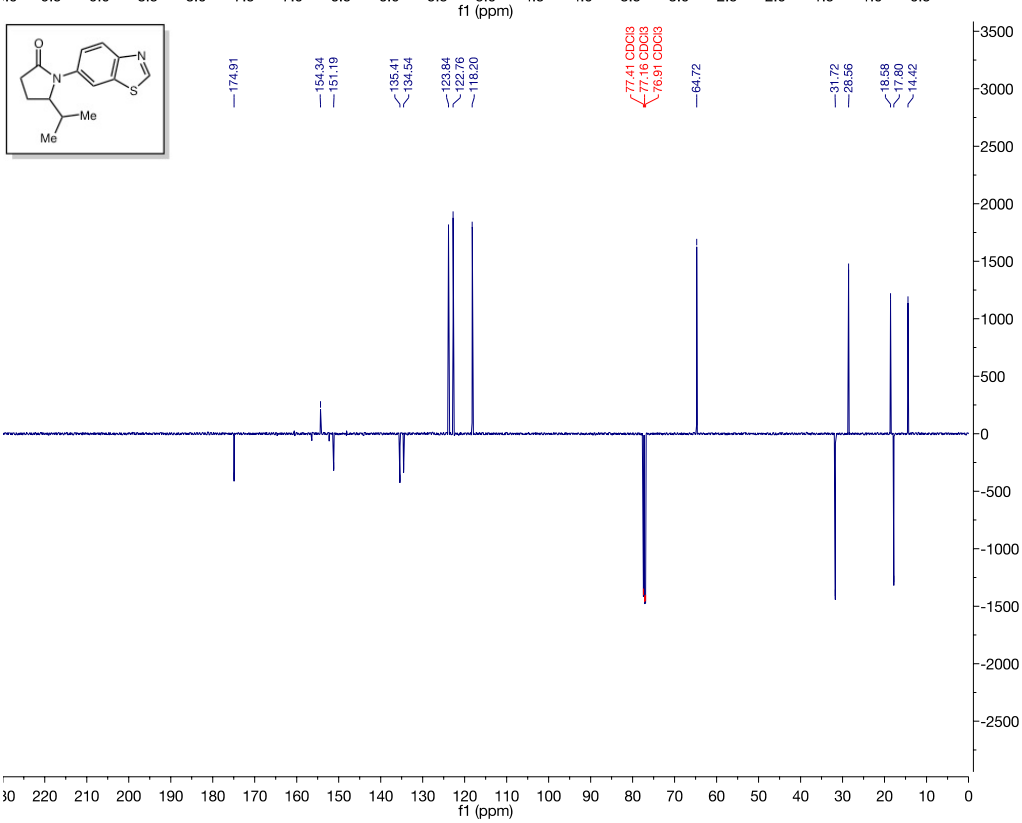

SMe
O
N
O
H
Me
Me
2.05
2.24
2.09
1.03
3.04
1.06
3.13
3.00
f1 (ppm)

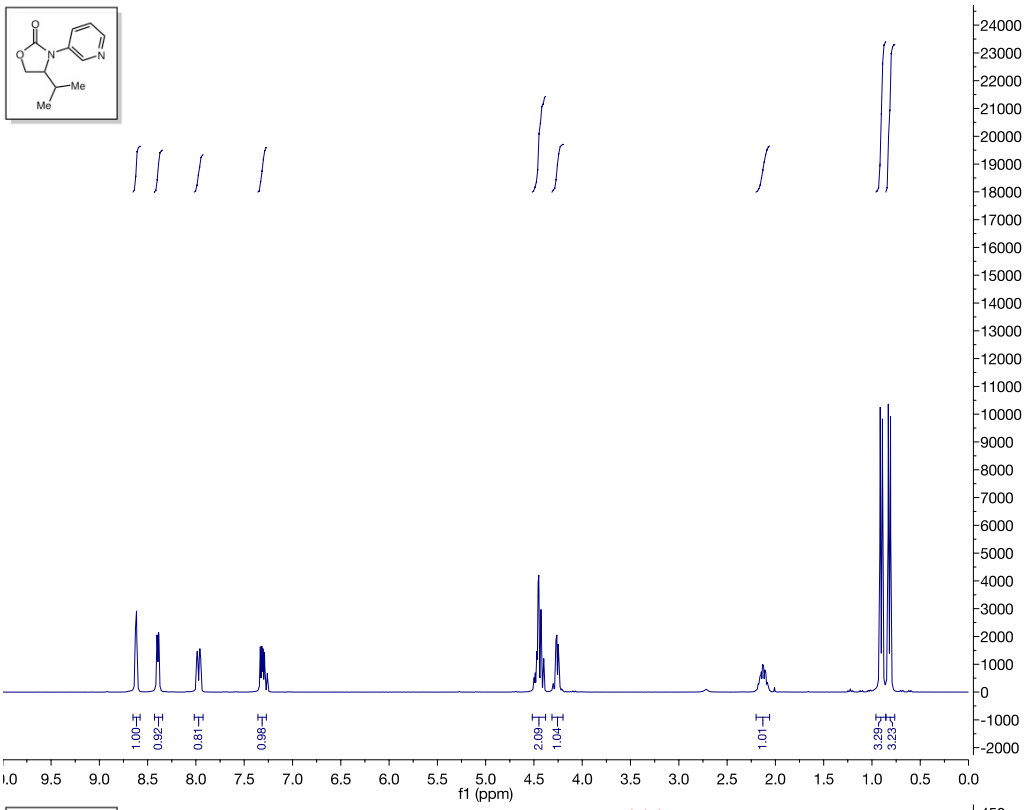

SMe
O
N
O
H
Me
Me
156.12
135.33
134.17
127.77
122.94
62.63
60.66
27.71
17.81
16.39
14.35
f1 (ppm)

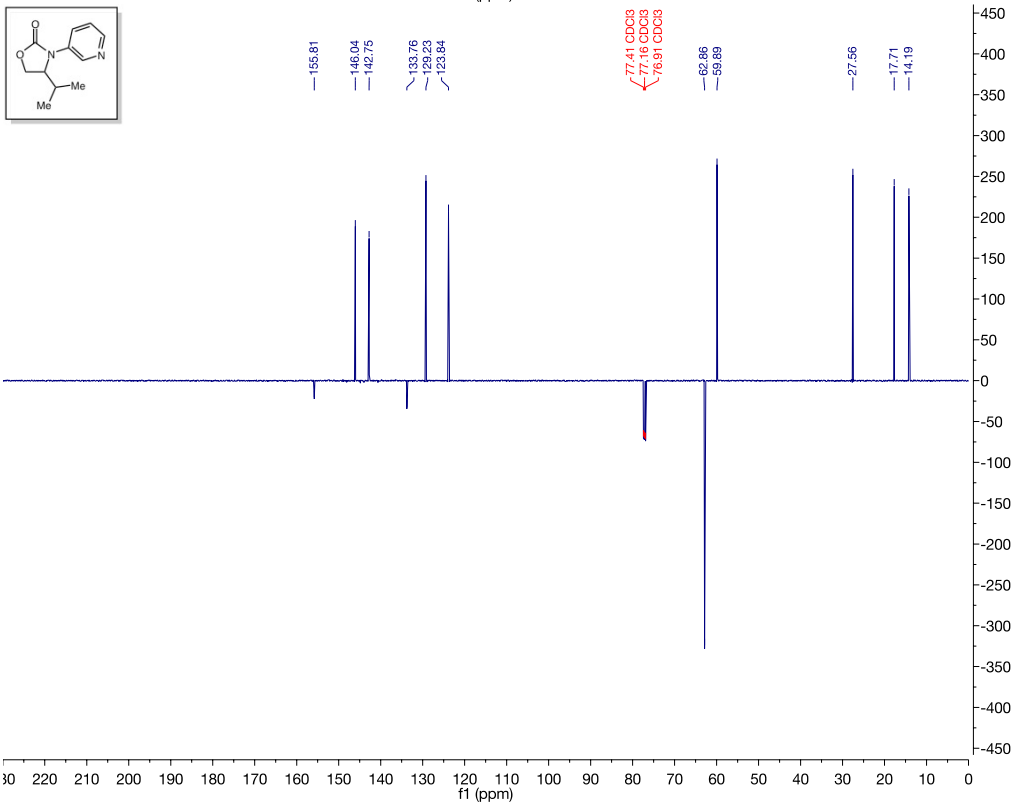

OH
O
N
H
Me
Me
2.00
3.02
1.19
2.15
2.18
2.37
1.22
1.17
1.19
1.14
3.19
3.13
f1 (ppm)

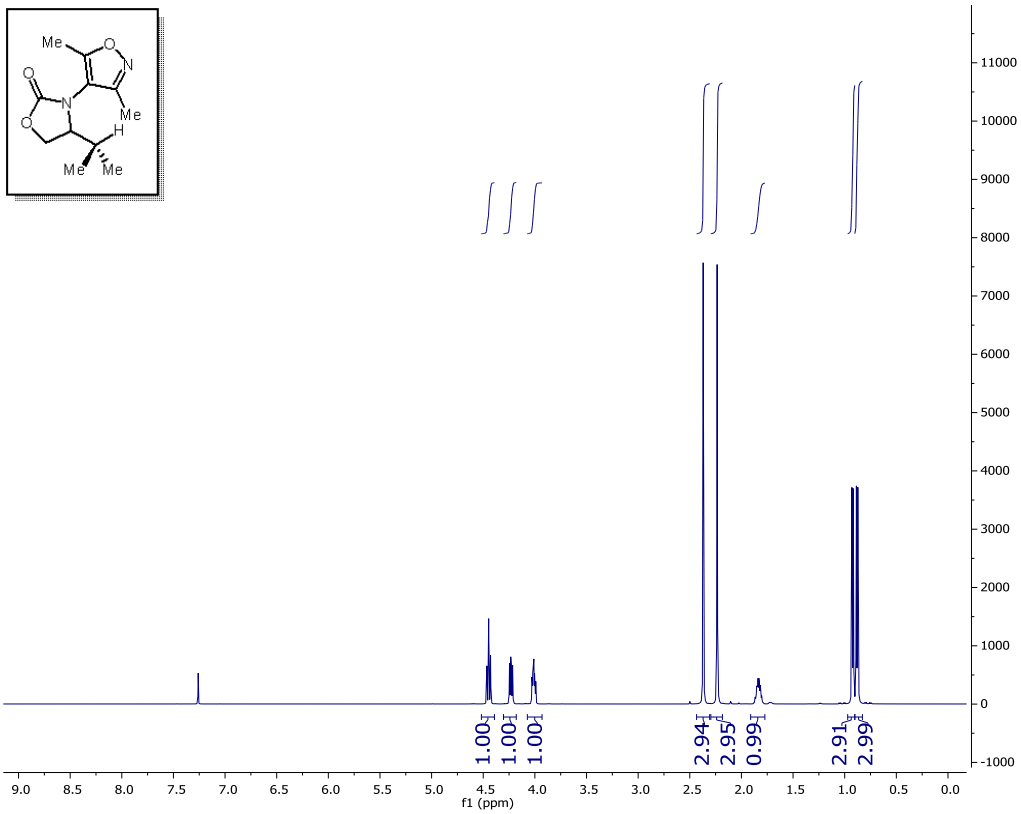

OH
O
N
H
Me
Me
174.78
136.39
136.12
129.78
124.85
64.51
63.69
38.89
31.72
28.46
18.60
17.78
14.37
f1 (ppm)

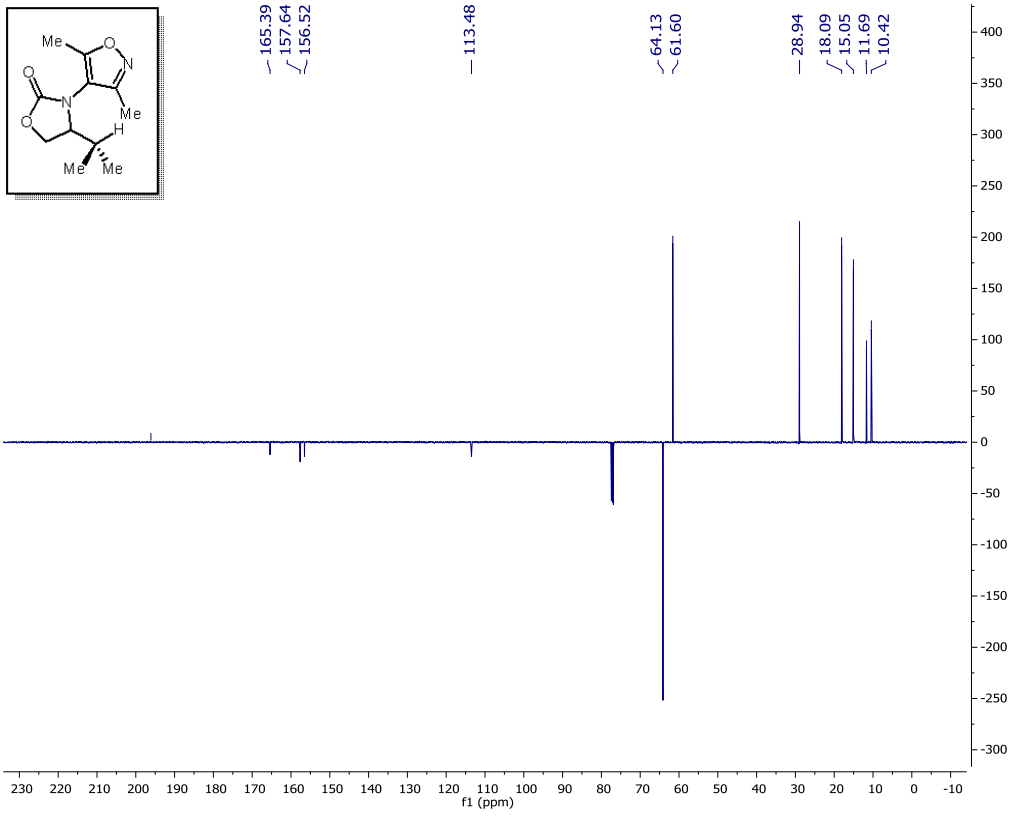

O
N
S
Me
Me
0.84
1.03
0.94
0.99
1.00
2.14
1.10
1.10
1.06
3.11
3.05
f1 (ppm)


O
N
S
Me
Me
174.91
154.34
151.19
135.41
134.54
123.84
122.76
118.20
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
64.72
31.72
28.56
18.58
17.80
14.42
f1 (ppm)


1.00
0.92
0.81
0.98
2.09
1.04
1.01
3.29
3.23
f1 (ppm)

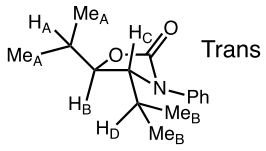

155.81
146.04
142.75
133.76
129.23
123.84
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
62.86
59.89
27.56
17.71
14.19
f1 (ppm)

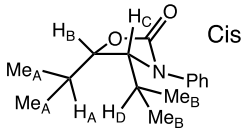

Me
O
N
O
N
Me
H
Me
Me
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
1.00
1.00
1.00
2.94
2.95
0.99
2.91
2.99
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


Me
O
N
O
N
Me
H
Me
Me
165.39
157.64
156.52
113.48
64.13
61.60
28.94
18.09
15.05
11.69
10.42
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

Diastereomer Identification

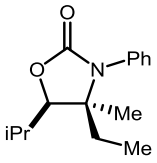
4,5-Diisopropyl-3-phenyloxazolidin-2-one:

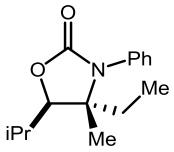




NOE?		NOE?	
H_A-H_B	medium	H_A-H_B	medium
H_B-H_C	none	H_B-H_C	strong
H_C-H_D	medium	H_C-H_D	weak

4-Ethyl-5-isopropyl-4-methyl-3-phenyloxazolidin-2-one:

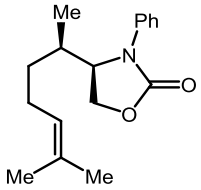




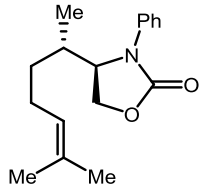
Major Minor

Diastereomeric assignment made based on allylic strain considerations

4-(6-methylhept-5-en-2-yl)-3-phenyloxazolidin-2-one:



Assigned by analogy given crystallographic data of other diastereomer



Assigned based on crystal structure

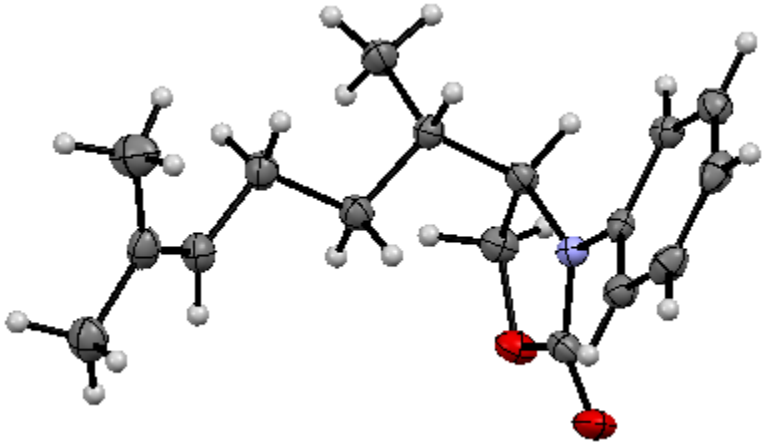
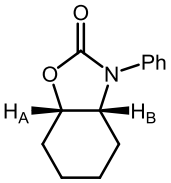


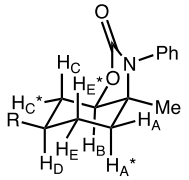
Figure S.2: Crystal structure of one diastereomer of 4-(6-methylhept-5-en-2-yl)-3-phenyloxazolidin-2-one. The CheckCIF has Alert Level C and G; the crystal is an inversion twin modeled with a twin fraction of 0.40 (i.e., a 60/40 twin with the supplied structure the majority fraction). For full information, consult the .cif file provided separately in the associated content.

3-phenylhexahydrobenzo[d]oxazol-2(3H)-one:



	NOE?
H_A-H_B	Medium

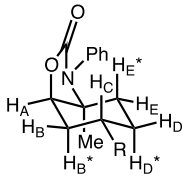
(3a*S*,6*R*,7a*R*)-3a-Methyl-3-phenyl-6-(prop-1-en-2-yl)hexahydrobenzo[*d*]oxazol-2(3*H*)-one:



NOE?

H_A-Me	weak
H_A*-H_B	medium
H_A*-H_D	medium
H_B-H_C*	weak
H_B-H_D	medium
H_C-H_D	none
H_C-H_E*	medium
H_D-H_E*	none

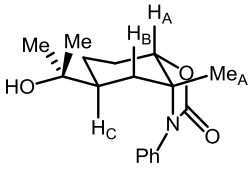
(3a*S*,6*S*,7a*R*)-3a-Methyl-3-phenyl-6-(prop-1-en-2-yl)hexahydrobenzo[*d*]oxazol-2(3*H*)-one:



NOE?

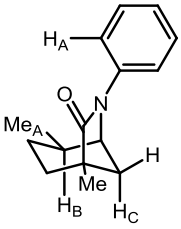
H_A-H_B	strong
H_B-H_C	medium
H_B*-Me	weak
H_B*-H_C	none
H_C-H_D	medium
H_C-H_D*	none
H_C-H_E*	medium
H_D*-Me	weak

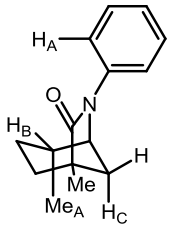
5-(2-hydroxypropan-2-yl)-3a-methyl-3-phenylhexahydrobenzo[d]oxazol-2(3H)-one



	NOE?
Me_A-H_A	Weak
Me_A-H_C	None
H_A-H_B	Weak

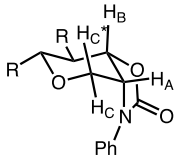
1,4-dimethyl-6-phenyl-6-azabicyclo[3.2.1]octan-7-one





	NOE?	NOE?
Me_A - H_A	Weak	None
Me_A - H_C	None	Medium
H_A - H_B	None	Weak
H_B - H_C	Medium	None

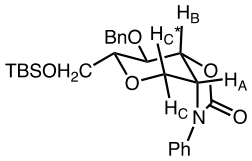
2,2-Dimethyl-7-phenylhexahydro-[1,3]dioxino[4',5':5,6]pyrano[3,4-*d*]oxazol-8(6*H*)-one:



NOE?

H_A-H_B	strong
H_A-H_C	medium
H_A-H_C*	none
H_A-Ph	strong
H_B-H_C	none
H_B-H_C*	strong
H_C-Ph	strong
H_C*-Ph	none

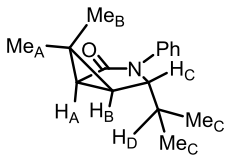
7-(Benzyloxy)-6-(((*tert*-butyldimethylsilyl)oxy)methyl)-3-phenylhexahydro-2*H*-pyrano[3,4-*d*]oxazol-2-one:



NOE?

H_A-H_B	strong
H_A-H_C	strong
H_A-H_C*	weak
H_A-Ph	strong
H_B-H_C	none
H_B-H_C*	strong
H_C-Ph	medium
H_C*-Ph	none

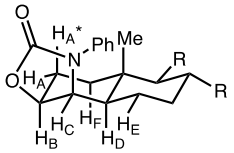
4-isopropyl-6,6-dimethyl-3-phenyl-3-azabicyclo[3.1.0]hexan-2-one



Me$_C$ protons are not equivalent but exact assignment is not necessary for analysis

	NOE?
Me$_A$-H$_A$	Strong
Me$_A$-H$_B$	Medium
Me$_B$-H$_C$	Strong
Me$_C$-H$_A$	Medium
Me$_B$-H$_D$	None
Me$_B$-Me$_C$	None

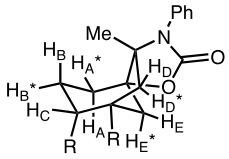
8-Acetyl-5a,7a-dimethyl-1-phenylhexadecahydro-1*H*-cyclopenta[7,8]phenanthro[1,2-*d*]oxazol-2(12b*H*)-one:



NOE?

H$_A$-H$_B$	medium
H$_A$*-H$_B$	none
H$_B$-H$_C$	strong
H$_B$-H$_D$	medium
H$_B$-H$_F$	weak
H$_B$-H$_D$	weak
H$_C$-H$_D$	strong
H$_C$-H$_E$	medium

Methyl 7-((*tert*-butyldimethylsilyl)oxy)-3a,6-dimethyl-2,14-dioxo-3-phenyl-3,3a,4,5,5a,6,7,9b,10,11-decahydro-2*H*-9a,6-(epoxymethano)-4a,11a-methanobenzo[1,2]azuleno[5,6-*d*]oxazole-5-carboxylate



NOE?

H_A*-Me	weak
H_B-Me	medium
H_D*-H_E	medium
H_D*-Me	none
H_E-Me	none

Stern Volmer Quenching Studies

Stern-Volmer experiments were conducted on an Agilent Technologies Cary Eclipse Fluorescence Spectrophotometer using the Cary Eclipse Scan Application. Solutions of each component were prepared prior to each set of experiments in dichloromethane solvent. The solutions were irradiated at 370 nm and luminescence was measured at 498 nm. In cases where quenching is observed, each experiment is run in triplicate; if no quenching is observed, the experiment is run in duplicate to validate the first result. I_o/I values per run are generated from the average of all three scans per data point. For determination of K_{sv}, the value for I_o/I from each run is averaged to yield an I_o/I value for the experiment and compromises nine total measurements of I_o/I. Linear regression of I_o/I against concentration to yield K_{sv} is done in Microsoft Excel.

Experiment 1: Constant Iridium; Varied Thiophenol

Species	Concentration (mM)
$[Ir(dF(CF3)ppy)_2(bpy)](PF_6)$	0.005
Bu_4N^+ $(BuO)_2PO_2^-$	0
Thiophenol	Varied
Acetanilide	0

Run	[PhSH] mM	Scan 1	Scan 2	Scan 3	Average	I_o/I
#1	0	433.089	437.541	431.302	433.977	1.00
	0.25	439.160	441.732	446.166	442.353	0.98
	0.50	442.932	441.732	446.166	433.610	0.98
	0.75	450.662	454.251	453.451	452.788	0.96
	1.00	441.382	450.429	445.279	445.697	0.97
#2	0	434.578	434.778	436.549	435.302	1.00
	0.25	433.787	434.280	431.796	433.288	1.00
	0.50	444.450	446.640	444.089	445.060	0.98
	0.75	457.736	453.576	458.349	456.554	0.95
	1.00	441.382	443.612	443.165	450	0.98

Table S.1: Relevant concentrations and tabulated quenching data for Experiment 1.

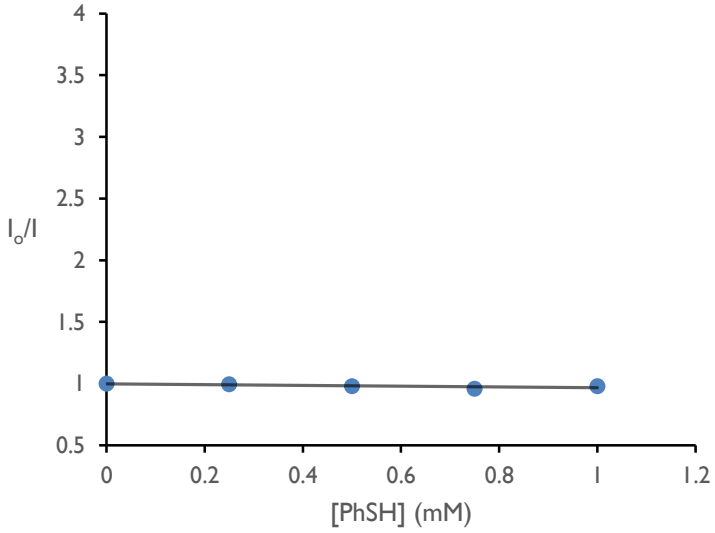


Figure S.3: Graphical representation of I_o/I data collected in Experiment 1.

Experiment 2: Constant Iridium; Varied Amide

Species	Concentration (mM)
$[Ir(dF(CF3)ppy)_2(bpy)](PF_6)$	0.01
Bu_4N^+ $(BuO)_2PO_2^-$	0
Thiophenol	0
Acetanilide	Varied

Run	[Acetanilide] mM	Scan 1	Scan 2	Scan 3	Average	I_o/I
#1	0	932.493	939.937	931.375	934.602	1.00
	0.2	889.777	883.373	886.327	886.492	1.05
	0.4	938.378	935.504	937.100	936.994	1.00
	0.6	935.183	930.535	939.139	934.952	1.00
	0.8	939.441	942.469	945.518	942.476	0.99
#2	0	885.978	886.403	888.521	886.967	1.00
	0.2	875.347	876.249	875.080	875.559	1.01
	0.4	872.750	870.688	871.210	871.549	1.02
	0.6	882.858	881.669	883.245	882.591	1.00
	0.8	845.201	845.971	843.890	845.021	1.05

Table S.2: Relevant concentrations and tabulated quenching data for Experiment 2.

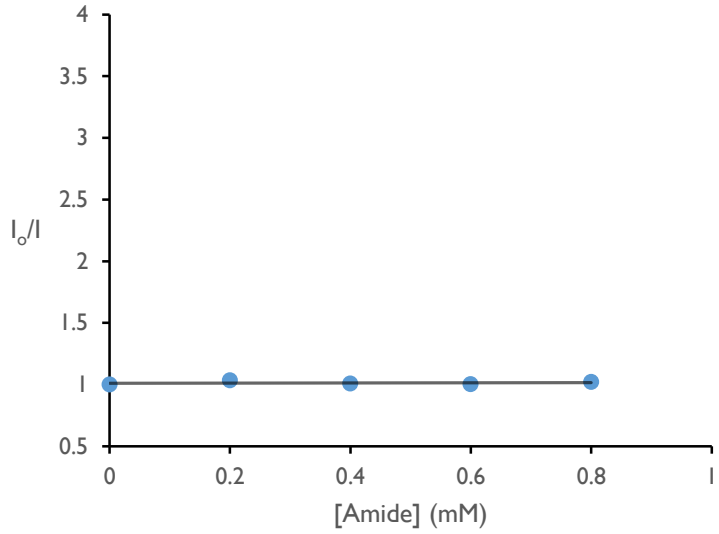


Figure S.4: Graphical representation of I_o/I data collected in Experiment 2

Experiment 3: Constant Iridium; Varied Base

Species	Concentration (mM)
$[Ir(dF(CF3)ppy)_2(bpy)](PF_6)$	0.01
Bu_4N^+ $(BuO)_2PO_2^-$	Varied
Thiophenol	0
Acetanilide	0

Run	[Phosphate] mM	Scan 1	Scan 2	Scan 3	Average	I_o/I
#1	0	789.752	790.186	783.810	787.916	1.00
	0.1	645.014	650.034	648.595	647.881	1.22
	0.2	635.267	634.266	638.530	636.021	1.24
	0.3	625.919	619.749	616.262	620.643	1.27
	0.4	591.196	591.397	591.752	591.448	1.33
#2	0	791.325	790.895	799.238	793.8193	1.00
	0.1	646.638	647.842	650.479	648.320	1.22
	0.2	657.171	657.934	659.459	658.188	1.21
	0.3	639.828	641.645	637.997	639.823	1.24
	0.4	653.018	650.684	652.056	651.919	1.22
#3	0	846.489	862.392	848.55	852.477	1.00
	0.1	694.675	694.147	692.492	693.771	1.23
	0.2	662.177	660.041	665.352	662.523	1.29
	0.3	635.686	632.086	637.833	635.202	1.34
	0.4	645.087	644.287	641.960	643.778	1.32

Table S.3: Relevant concentrations and tabulated quenching data for Experiment 3.

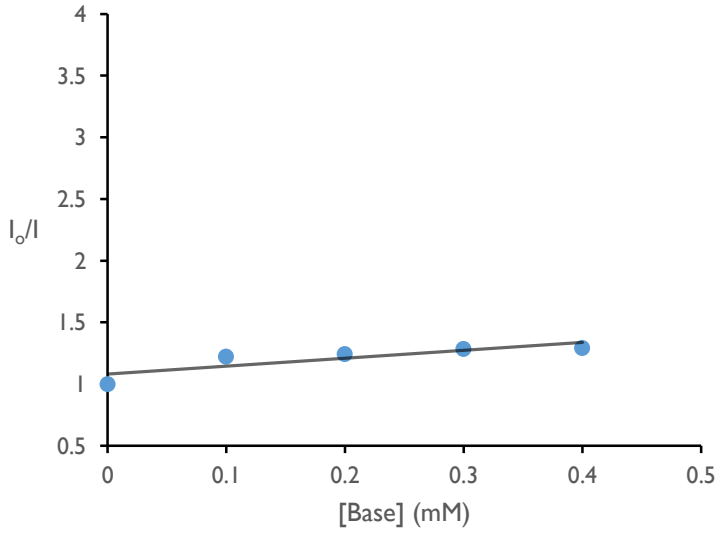


Figure S.5: Graphical representation of I_o/I data collected in Experiment 3; quenching is non-linear, suggesting that the base is not oxidized by the catalyst.

Experiment 4: Constant Iridium and Base; Varied Thiophenol

Species	Concentration (mM)
$[Ir(dF(CF3)ppy)_2(bpy)](PF_6)$	0.01
Bu_4N^+ $(BuO)_2PO_2^-$	0.20
Thiophenol	Varied
Acetanilide	0

Run	[PhSH] mM	Scan 1	Scan 2	Scan 3	Average	I_0/I
#1A	0	750.846	746.135	749.731	748.904	1.00
	0.1	632.271	627.895	627.44	629.202	1.19
	0.2	583.432	584.378	580.102	582.637	1.29
	0.3	539.585	541.144	536.424	539.051	1.39
	0.4	520.453	515.72	518.014	518.062	1.45
#1B	0	721.309	717.858	721.456	720.208	1.00
	0.5	477.430	484.373	473.379	478.394	1.51
	1.0	421.605	419.471	422.494	421.190	1.71
	1.5	373.433	369.575	372.084	371.697	1.94
	0.2	344.975	344.53	342.757	344.087	2.09
#2A	0	717.034	719.376	713.981	716.797	1.00
	0.1	568.158	569.11	567.99	568.419	1.26
	0.2	562.802	562.734	559.065	561.534	1.28
	0.3	548.664	550.08	549.071	549.272	1.30
	0.4	529.005	529.171	531.934	530.037	1.35
#2B	0	729.003	732.202	736.484	732.563	1.00
	0.5	481.695	476.457	477.42	478.524	1.53
	1.0	426.193	427.499	422.245	425.3123	1.72
	1.5	369.74	366.521	364.87	367.0437	2.00
	0.2	350.858	352.591	348.931	350.7933	2.09
#3A	0	725.107	722.44	728.595	725.381	1.00
	0.1	634.786	629.184	627.921	630.630	1.15
	0.2	568.433	569.086	536.744	558.088	1.30
	0.3	542.675	536.744	537.692	539.037	1.35
	0.4	526.683	530.667	526.388	527.913	1.37
#3B	0	769.101	771.692	765.438	768.744	1.00
	0.5	501.615	495.85	497.561	498.342	1.54
	1.0	420.417	418.756	415.23	418.134	1.84
	1.5	406.11	403.146	402.783	404.013	1.90
	0.2	372.305	368.086	366.569	368.987	2.08

Table S.4: Relevant concentrations and tabulated quenching data for Experiment 4.

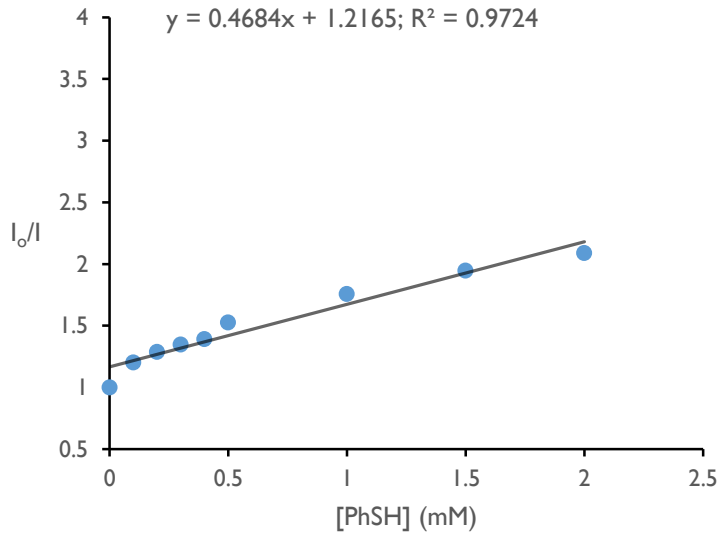


Figure S.6: Graphical representation of I_o/I data collected in Experiment 4. The initial data point where [PhSH] = 0 is thought to be low due to a) the small magnitude of the slope of quenching and b) background quenching by the phosphate. Because quenching looks to be otherwise linear over an order of magnitude, the trendline generated where the dataset is not forced to have an intercept of 1 (depicted) better reflects the value of K_{sv} than the trendline forced to have an intercept of 1 (K_{sv} = 635, R^2 = 0.8263).

Experiment 5: Constant Iridium and Base; Varied Amide

Species	Concentration (mM)
$[Ir(dF(CF3)ppy)_2(bpy)](PF_6)$	0.01
Bu_4N^+ $(BuO)_2PO_2^-$	0.20
Thiophenol	0
Acetanilide	Varied

Run	[Phosphate] mM	Scan 1	Scan 2	Scan 3	Average	I_o/I
#1	0	760.612	757.777	761.875	760.088	1.00
	0.2	463.507	456.618	464.257	461.461	1.65
	0.4	345.558	343.636	346.273	345.156	2.20
	0.6	289.813	290.840	287.861	289.505	2.63
	0.8	237.952	238.957	238.777	238.562	3.19
#2	0	757.608	758.384	754.294	756.762	1.00
	0.2	459.608	465.354	461.501	462.154	1.64
	0.4	337.150	339.800	339.305	338.752	2.23
	0.6	267.125	266.743	266.897	266.922	2.84
	0.8	240.492	238.997	238.813	239.434	3.16
#3	0	750.909	750.022	750.661	750.531	1.00
	0.2	461.413	463.009	461.957	462.126	1.62
	0.4	333.101	333.275	332.121	332.832	2.25
	0.6	282.849	280.871	280.252	281.324	2.67
	0.8	225.228	222.267	221.827	223.107	3.36

Table S.5: Relevant concentrations and tabulated quenching data for Experiment 5.

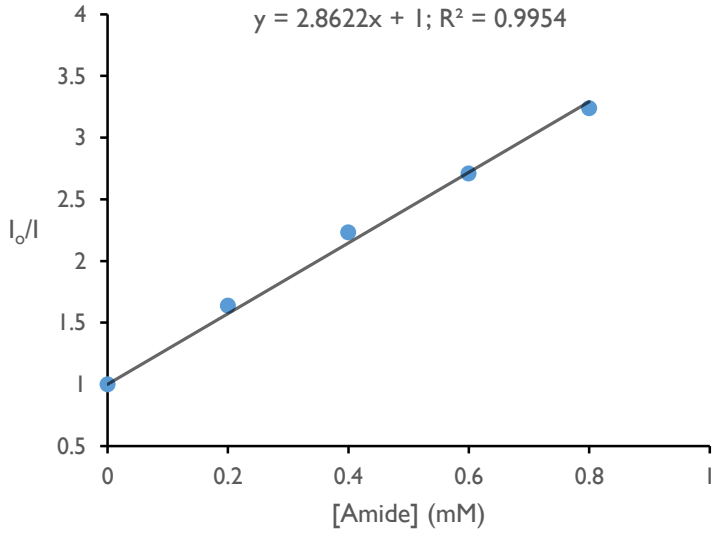


Figure S.7: Graphical representation of I_o/I data collected in Experiment 5.

Experiment 6: Constant Iridium, Base, and Thiophenol; Varied Amide

Species	Concentration (mM)
$[Ir(dF(CF3)ppy)_2(bpy)](PF_6)$	0.01
Bu_4N^+ $(BuO)_2PO_2^-$	0.20
Thiophenol	1.00
Acetanilide	Varied

Run	[Phosphate] mM	Scan 1	Scan 2	Scan 3	Average	I_o/I
#1	0	388.283	391.908	385.355	388.515	1.00
	0.1	326.134	328.565	326.391	327.030	1.19
	0.2	297.225	300.405	296.061	297.897	1.30
	0.3	279.350	277.059	280.083	278.831	1.39
	0.4	249.284	247.949	249.566	248.933	1.56
#2	0	383.622	385.36	379.809	382.930	1.00
	0.1	338.610	333.328	336.473	336.137	1.14
	0.2	302.227	302.875	300.110	301.737	1.27
	0.3	273.760	271.328	271.721	272.270	1.41
	0.4	250.741	249.216	249.63	249.862	1.53
#3	0	348.581	350.308	353.135	350.675	1.00
	0.1	314.83	315.003	313.107	314.313	1.12
	0.2	291.569	293.663	293.979	293.070	1.20
	0.3	274.320	274.791	275.559	274.890	1.28
	0.4	246.621	247.317	247.632	247.190	1.42

Table S.6: Relevant concentrations and tabulated quenching data for Experiment 6.

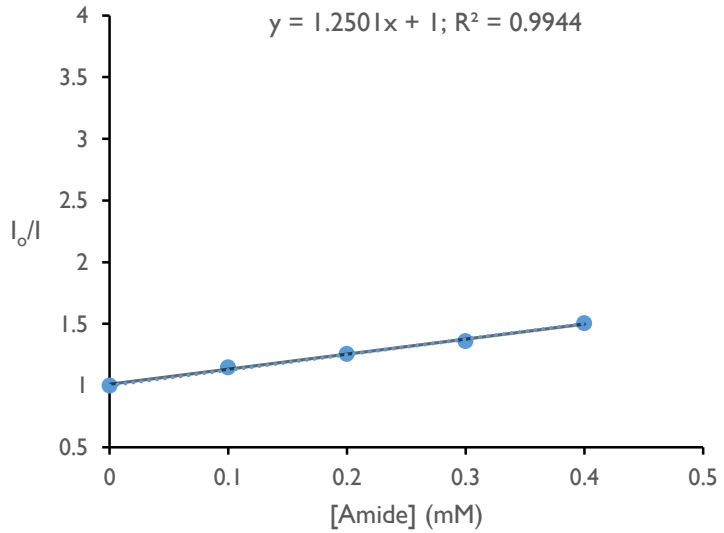


Figure S.8: Graphical representation of I_o/I data collected in Experiment 6.

Experiment 7: Constant Iridium, Base, and Amide; Varied Thiophenol

Species	Concentration (mM)
$[Ir(dF(CF3)ppy)_2(bpy)](PF_6)$	0.01
Bu_4N^+ $(BuO)_2PO_2^-$	0.20
Thiophenol	Varied
Acetanilide	1.00

Run	[Phosphate] mM	Scan 1	Scan 2	Scan 3	Average	I_o/I
#1	0	191.923	192.143	191.378	191.815	1.00
	0.1	199.127	198.669	197.794	198.530	0.97
	0.2	194.679	196.167	198.002	196.283	0.98
	0.3	200.583	199.419	197.359	199.120	0.96
	0.4	198.783	196.313	197.523	197.540	0.97
#2	0	194.939	197.248	192.456	194.881	1.00
	0.1	188.002	186.639	186.622	187.088	1.04
	0.2	206.518	204.309	205.296	205.374	0.95
	0.3	200.213	199.957	199.070	199.747	0.98
	0.4	197.970	196.815	199.029	197.938	0.98
#3	0	174.566	176.449	172.310	174.442	1.00
	0.1	176.818	177.043	175.878	176.580	0.99
	0.2	186.852	185.928	187.492	186.757	0.93
	0.3	181.780	181.235	180.267	181.094	0.96
	0.4	185.598	185.467	184.282	185.116	0.94

Table S.7: Relevant concentrations and tabulated quenching data for Experiment 7.

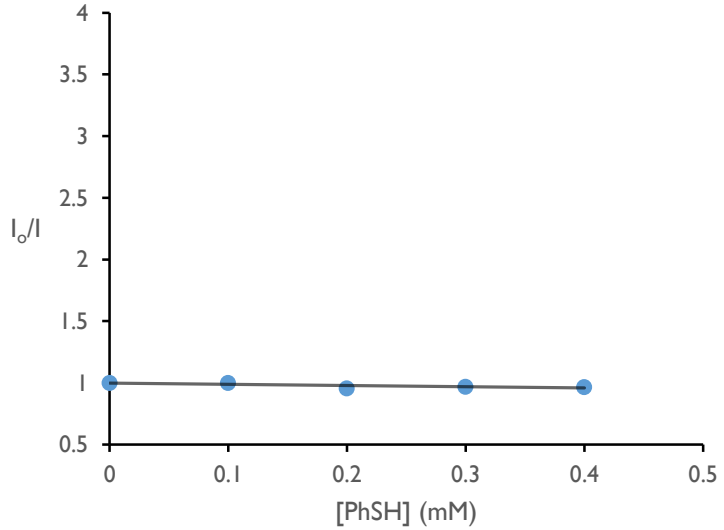


Figure S.9: Graphical representation of I_o/I data collected in Experiment 7.

Mechanistic Explanation for Luminescence Quenching Experiments 6 and 7

Both acetanilide and thiophenol are competent to quench the excited state of the photocatalyst in the presence of phosphate base. In competition-quenching experiments in which luminescence is observed as a function of a "varied quencher" in the presence of constant concentrations of phosphate and a "background quencher", the luminescence measured at I_o reflects some quenching pertinent to the interaction between the base and the background quencher. The luminescence observed does not indicate *absolute* quenching, but rather *relative* quenching of the varied quencher against the background quencher.

When luminescence is observed as a function of the thiophenol concentration in the presence of base *and* acetanilide, the observed quenching I does not vary relative to the background quenching incorporated into the I_o luminescence. These results indicate thiophenol-related quenching is inefficient relative to acetanilide-related quenching. When the opposite experiment is run, *i.e.* when acetanilide is varied and thiophenol is held constant in excess, the observed quenching I demonstrates a clean first-order dependence on the concentration of acetanilide relative to the background quenching I_o. Taken together, these experiments demonstrate that PCET to the amide is kinetically preferred over PCET to the thiophenol component based on *relative* quenching of the two components.

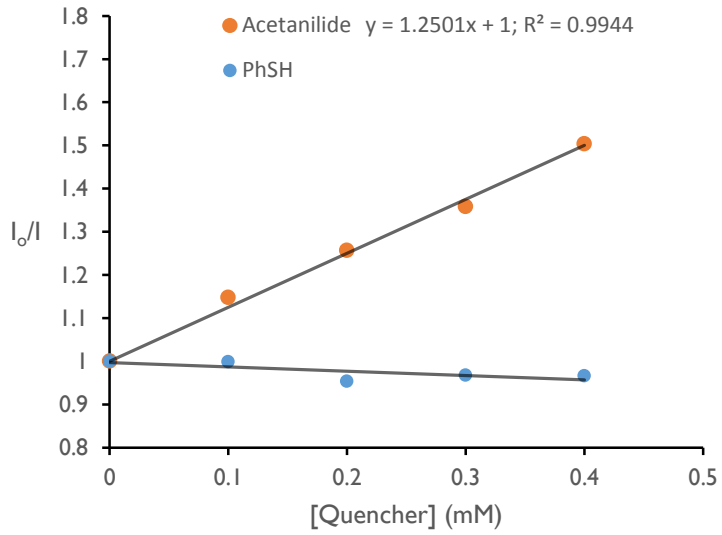


Figure S.10: Overlayed graphical representation of I_o/I data collected in Experiments 6 (red) and 7 (blue).

Computational Evaluation of Hydrogen Bonding

Computational Details

All calculations used DFT methodology[30] as implemented in the Gaussian 09 series of computer programs.[31] We employed the restricted ωB97XD functional.[32] All-electron, split-valence double-ζ plus polarization and diffuse functions 6-31G++(2d,2p) basis sets were used.[33] Solvation was modeled using the CPCM polarizable conductor calculation model with the solvent as dichloromethane.[34] All complexes underwent geometry optimization, and stationary points were subjected to normal mode analysis.

Figure S.11: Chemical equations for themodynamic analysis.

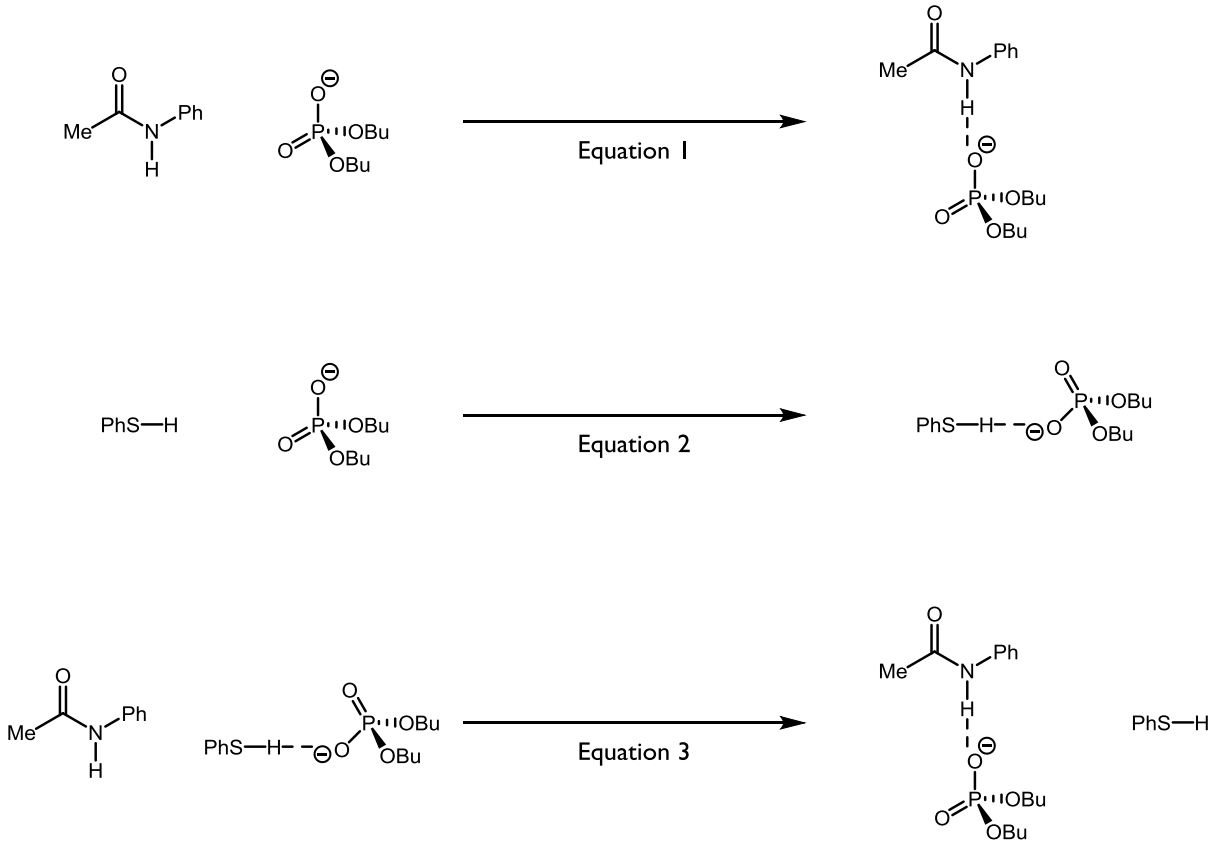


Table S.8: Thermodynamic stationary points for hydrogen bonding analysis. Energies are given in hartree and entropy is provided in entropy units.

Entry	Job Name	E+ZPE	G	H	S
1	acetanilide	-440.015090	-440.050801	-440.005061	96.269
2	thiophenol	-630.264668	-630.295093	-630.257530	79.059
3	dibutylphosphate [$(BuO)_2PO_2^-$]	-957.804105	-957.851320	-957.786766	135.865
4	acetanilide-dibutylphosphate	-1397.842297	-1397.901542	-1397.815008	182.126
5	thiophenol-dibutylphosphate	-1588.081965	-1588.137504	-1588.057556	168.264

Table S.9: Energetic analysis of hydrogen bonding presented in the chemical equations in Figure S.11 using the energy values provided in Table S.8. Energies are given in units of kcal mol^{-1}; using the conversion factor 627.51 kcal mol^{-1} per hartree and are rounded off after the third decimal place. Entropies are provided in entropy units and are rounded off after the third decimal place.

Equation	Entries for Δ	ΔE+ZPE	ΔG	ΔH	ΔS
1	=(4)-(1+3)	-8.278	5.590	-8.321	-46.660
2	=(5)-(2+3)	-14.497	0.363	-14.546	-50.008
3	=(4+2)-(5+1)	-6.219	-5.227	-6.226	-3.348

Optimized Geometries

Optimized geometries in Cartesian coordinates (Å) and energies (hartree) for stationary points.

Acetanilide (Entry 1)

```
 E(rwB97XD)                                -440.171509
 Zero-point correction=                   0.156418
 Thermal correction to Energy=            0.165503
 Thermal correction to Enthalpy=          0.166448
 Thermal correction to Gibbs Free Energy= 0.120707
 Sum of electronic and zero-point Energies=     -440.015090
 Sum of electronic and thermal Energies=        -440.006005
 Sum of electronic and thermal Enthalpies=      -440.005061
 Sum of electronic and thermal Free Energies=   -440.050801

Charge = 0; Multiplicity = 1
 C                  2.17075300    0.16136900   -0.01847000
 O                  2.12627000    1.38269300   -0.03179100
 N                  1.06359800   -0.63679800   -0.02033000
 H                  1.24156400   -1.62901500   -0.01365900
 C                  3.48268500   -0.58933600    0.03652100
 H                  3.74659000   -0.75356400    1.08448800
 H                  3.43684400   -1.55896700   -0.46140500
 H                  4.25705200    0.02268100   -0.42227900
 C                 -0.29847100   -0.28054200   -0.00982100
 C                 -0.75465800    1.04043400    0.00551600
 C                 -1.22756400   -1.32813900   -0.01373100
 C                 -2.12491800    1.29184700    0.01747000
 H                 -0.04589600    1.85336700    0.00768900
 C                 -2.58919600   -1.06204700   -0.00174000
 H                 -0.87894200   -2.35556200   -0.02615100
 C                 -3.04885400    0.25328600    0.01405500
 H                 -2.46707100    2.32026500    0.02991300
 H                 -3.29253000   -1.88625700   -0.00464300
 H                 -4.11162000    0.46186600    0.02389500
```

Thiophenol (Entry 2)

```
 E(rwB97XD)                                -630.365038
 Zero-point correction=                   0.100370
 Thermal correction to Energy=            0.106564
 Thermal correction to Enthalpy=          0.107509
 Thermal correction to Gibbs Free Energy= 0.069945
```

```
 Sum of electronic and zero-point Energies=           -630.264668
 Sum of electronic and thermal Energies=              -630.258474
 Sum of electronic and thermal Enthalpies=            -630.257530
 Sum of electronic and thermal Free Energies=         -630.295093

Charge = 0; Multiplicity = 1
 C                 -0.19130600    1.20831100   -0.00001000
 C                  0.50570500   -0.00075200    0.00004800
 C                 -0.19914200   -1.20654000    0.00003900
 C                 -1.59023100   -1.19844500   -0.00005900
 C                 -2.28922600    0.00581400   -0.00009700
 C                 -1.58329100    1.20557900   -0.00005000
 H                  0.34289400    2.15124200   -0.00002000
 H                  0.33433000   -2.15045600    0.00011200
 H                 -2.12618000   -2.14015200   -0.00008200
 H                 -3.37234300    0.00907900   -0.00015300
 H                 -2.11404600    2.15029000   -0.00007200
 S                  2.28152400   -0.08369800    0.00002000
 H                  2.51590300    1.23536300    0.00067700
```

Dibutyl Phosphate [$(BuO)_2PO_2^-$] (Entry 3)

```
 E(rwB97XD)                                            -958.069916
 Zero-point correction=                           0.265811
 Thermal correction to Energy=                    0.282206
 Thermal correction to Enthalpy=                  0.283151
 Thermal correction to Gibbs Free Energy=         0.218597
 Sum of electronic and zero-point Energies=           -957.804105
 Sum of electronic and thermal Energies=              -957.787710
 Sum of electronic and thermal Enthalpies=            -957.786766
 Sum of electronic and thermal Free Energies=         -957.851320

Charge = -1; Multiplicity = 1
 P                  0.00137900   -1.62201100    0.01175300
 O                  0.01350100   -1.86107900    1.48731800
 O                  0.29826500   -2.73168200   -0.93880500
 O                 -1.41155700   -0.98212600   -0.45896500
 O                  0.94174000   -0.32643000   -0.32631400
 C                 -1.98646300    0.07369600    0.30265400
 C                 -3.31081500    0.46906000   -0.32433700
 H                 -1.30162400    0.93006300    0.31466200
 H                 -2.13247600   -0.25707600    1.33659300
 C                 -3.97698800    1.62695100    0.41729000
 H                 -3.14022400    0.74871900   -1.37015200
 H                 -3.97821000   -0.40030000   -0.33118100
 C                 -5.30870900    2.03651200   -0.20892600
 H                 -4.13583200    1.34672900    1.46490600
 H                 -3.29801100    2.48743600    0.42756200
 H                 -5.76072000    2.87518700    0.32672100
 H                 -5.17222500    2.33855800   -1.25185200
 H                 -6.02093100    1.20589100   -0.19438600
 C                  2.29974800   -0.35278800    0.08596000
 C                  2.93505200    0.99325500   -0.21336400
 H                  2.83393000   -1.15000200   -0.44731400
 H                  2.35726600   -0.56823900    1.15947800
 C                  4.40809600    1.04147300    0.18947500
 H                  2.83618500    1.20367600   -1.28439500
 H                  2.37934200    1.77415800    0.31854800
 C                  5.05252100    2.39523600   -0.10334600
 H                  4.50087700    0.81713600    1.25831300
 H                  4.95534800    0.25332100   -0.34041800
 H                  6.10579200    2.40744200    0.18866800
 H                  4.99711200    2.63048700   -1.17065600
 H                  4.54346900    3.19713800    0.44031600
```

Acetanilide-Dibutylphosphate (Entry 4)

```
 E(rwB97XD)                                        -1398.267406
 Zero-point correction=                           0.425109
 Thermal correction to Energy=                    0.451453
 Thermal correction to Enthalpy=                  0.452398
 Thermal correction to Gibbs Free Energy=         0.365864
 Sum of electronic and zero-point Energies=          -1397.842297
 Sum of electronic and thermal Energies=             -1397.815952
 Sum of electronic and thermal Enthalpies=           -1397.815008
 Sum of electronic and thermal Free Energies=        -1397.901542


Charge = -1; Multiplicity = 1
 P                 -2.42172800    1.06403400    0.91305900
 O                 -3.34156200    2.10472800    1.44252200
 O                 -3.36650300   -0.16620200    0.44373500
 O                 -1.63289100    0.33522500    2.13360000
 C                 -2.77527100   -1.34614800   -0.09115000
 C                 -2.63674200   -1.29294800   -1.60456500
 H                 -3.42926000   -2.17327900    0.19976500
 H                 -1.80065500   -1.52286500    0.38014100
 C                 -2.03468000   -2.57938000   -2.16771400
 H                 -3.62390300   -1.12061300   -2.04777700
 H                 -2.01136700   -0.43514000   -1.87192200
 C                 -1.83449000   -2.51840900   -3.68037000
 H                 -1.07018200   -2.77199300   -1.68341100
 H                 -2.68054000   -3.42797300   -1.91395100
 H                 -1.40898700   -3.44864900   -4.06537900
 H                 -2.78527700   -2.34540500   -4.19354600
 H                 -1.15658500   -1.70269100   -3.94967700
 C                 -0.23431600    0.47780900    2.34938100
 C                  0.37585200   -0.87317800    2.67869700
 H                 -0.07923400    1.18002600    3.17632300
 H                  0.23949900    0.89775300    1.45893200
 C                  1.89318400   -0.79685500    2.83579300
 H                 -0.07874200   -1.26483000    3.59598300
 H                  0.12922800   -1.57498900    1.87407000
 C                  2.51678500   -2.15193000    3.16118500
 H                  2.33053000   -0.41141000    1.90754300
 H                  2.14457400   -0.07710500    3.62361600
 H                  3.60246000   -2.07486100    3.26263600
 H                  2.11850200   -2.55514800    4.09773900
 H                  2.30481500   -2.87491400    2.36765500
 O                 -1.44008100    1.40609800   -0.16986000
 H                  0.21122300    1.51956800   -0.71953700
 N                  1.20665800    1.56082500   -0.97840100
 C                  1.69078400    2.77167300   -1.35239000
 C                  1.89464900    0.33966900   -0.88899800
 O                  2.85313200    2.97855600   -1.69048400
 C                  0.66688600    3.88550600   -1.34951000
 C                  3.28799000    0.22335700   -0.86632100
 C                  1.11049400   -0.81493400   -0.76980100
 H                  0.45401200    4.15682600   -2.38641300
 H                 -0.26442400    3.60418800   -0.85714300
 H                  1.10109900    4.75762300   -0.85940600
 C                  3.87134000   -1.03340600   -0.72053200
 H                  3.90106800    1.10689000   -0.95525700
 C                  1.70442300   -2.05911000   -0.62105000
 H                  0.03104700   -0.71304300   -0.77330800
 C                  3.09207400   -2.17871700   -0.59630000
 H                  4.95246500   -1.11096900   -0.69826800
 H                  1.07999100   -2.93920600   -0.51543200
 H                  3.55742100   -3.14931700   -0.47528800
```

Thiophenol-Dibutylphosphate (Entry 5)

```
 E(rwB97XD)                                        -1588.450856
 Zero-point correction=                           0.368891
 Thermal correction to Energy=                    0.392355
 Thermal correction to Enthalpy=                  0.393299
 Thermal correction to Gibbs Free Energy=         0.313352
 Sum of electronic and zero-point Energies=          -1588.081965
 Sum of electronic and thermal Energies=             -1588.058500
 Sum of electronic and thermal Enthalpies=           -1588.057556
 Sum of electronic and thermal Free Energies=        -1588.137504
```

```
Charge = -1; Multiplicity = 1
 P                  1.19687100   -0.62066100    0.23174400
 O                  1.08077400   -0.44443600    1.70951200
 O                  0.14227300    0.30484700   -0.56294800
 O                  2.56643100    0.08847500   -0.29677000
 C                 -0.32123900    1.52977000   -0.00602600
 C                 -1.55627700    1.97293900   -0.76755700
 H                  0.47018800    2.28664100   -0.07282300
 H                 -0.56013300    1.37874700    1.05098700
 C                 -2.19698600    3.21468600   -0.15187700
 H                 -1.29265000    2.16743100   -1.81355800
 H                 -2.27895400    1.15072900   -0.76423900
 C                 -3.47428000    3.63038500   -0.87838400
 H                 -2.42697200    3.01270500    0.90088400
 H                 -1.47962200    4.04364200   -0.16061300
 H                 -3.91784300    4.52305200   -0.42970700
 H                 -3.27380600    3.84764300   -1.93214300
 H                 -4.21765300    2.82804700   -0.83954000
 C                  3.80715100   -0.42687000    0.16949700
 C                  4.92367900    0.51549900   -0.24180700
 H                  3.97242600   -1.42274800   -0.25989200
 H                  3.78072800   -0.52840200    1.26108100
 C                  6.29689800    0.00430600    0.19183700
 H                  4.90096700    0.64342300   -1.33002300
 H                  4.73821200    1.50070000    0.20092500
 C                  7.42839800    0.95547900   -0.19338500
 H                  6.30160000   -0.14765000    1.27733300
 H                  6.47590700   -0.97850300   -0.25896600
 H                  8.39911000    0.56649600    0.12459000
 H                  7.46467100    1.10389600   -1.27695600
 H                  7.29035500    1.93594500    0.27253900
 O                  1.07450500   -1.98957700   -0.36708800
 H                 -0.73051800   -2.47128200   -0.70057000
 S                 -2.00510200   -2.82725900   -1.04754400
 C                 -2.86844700   -1.58145400   -0.11691800
 C                 -4.09464400   -1.11406600   -0.59488900
 C                 -2.35846700   -1.07198800    1.07915000
 C                 -4.79737400   -0.14176400    0.11203700
 H                 -4.49306100   -1.49805300   -1.52723200
 C                 -3.05891500   -0.09011500    1.77126900
 H                 -1.40263800   -1.41633700    1.45609600
 C                 -4.27989500    0.38021000    1.29387000
 H                 -5.74321800    0.21929100   -0.27528900
 H                 -2.63989600    0.31352200    2.68590300
 H                 -4.81810300    1.15053100    1.83320500
```

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