Supporting Information

Synthesis of Oxazolines and Thiazolines via Photoredox Catalyzed Alkene Hydrofunctionalization

Peter D. Morse, David A. Nicewicz

Department of Chemistry, University of North Carolina at Chapel Hill, New Venable Laboratories, Chapel Hill, NC 27599-3290, USA

Email:Nicewicz@unc.edu

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I. General Information

General Methods. Infrared (IR) spectra were obtained using a Jasco 260 Plus Fourier transform infrared spectrometer. Proton, carbon, and fluorine magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded on a Bruker model DRX 400 or 600 (^{1}H NMR at 400 MHz or 600 MHz and ^{13}C NMR at 100 MHz or 150 MHz spectrometer. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in solvent (^{1}H NMR: $CHCl_3$ at 7.26 ppm). Chemical shifts for carbons are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the residual solvent peak (^{13}C NMR: $CDCl_3$ at 77.0 ppm). NMR data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublet, ddd = doublet of doublet of doublet, dddd = doublet of doublet of doublet of doublet, dtd = doublet of triplet of doublet, t = triplet, q = quartet, qd = quartet of doublet, sept = septuplet, m = multiplet), coupling constants (Hz), and integration. Mass spectra were obtained using either a Micromass Quattro II (triple quad) instrument with nanoelectrospray ionization or an Agilent 6850 series gas chromatograph instrument equipped with a split-mode capillary injection system and Agilent 5973 network mass spec detector (MSD). Thin layer chromatography (TLC) was performed on SiliaPlate 250 μm thick silica gel plates purchased from Silicycle. Visualization was accomplished using fluorescence quenching, $KMnO_4$ stain, or ceric ammonium molybdate (CAM) stain followed by heating. Organic solutions were concentrated under reduced pressure using a Büchi rotary evaporator. Purification of the reaction products was carried out by chromatography using Siliaflash-P60 (40-63 μm) or Siliaflash-T60 (5-20 μm) silica gel purchased from Silicycle. All reactions were carried out under an inert atmosphere of nitrogen in flame-dried glassware with magnetic stirring unless otherwise noted. Irradiation of photochemical reactions was carried out using a Par38 Royal Blue Aquarium LED lamp (Model # 6851) fabricated with high-power Cree LEDs as purchased from Ecoxotic (www.ecoxotic.com), with standard borosilicate glass vials purchased from Fisher Scientific. Yield refers to isolated yield of analytically pure material unless otherwise noted. NMR yields were determined using hexamethyldisiloxane as an internal standard. Cyclic voltammograms were obtained with a glassy carbon working electrode, Ag/AgCl reference electrode, platinum wire counter electrode, and Pine Instruments Wavenow potentiostat. All measurements were taken in N_2-sparged MeCN with 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as a supporting electrolyte where the analyte concentration was 5-10 mM. The potential was scanned from 1.0 V to a vertex potential of 2.5 V in the forward direction at a sweep rate of 100 mV/s, and the reverse sweep showed no indication of a reversible electrochemical event. The half-wave potential for irreversible oxidation is estimated at $E_{p/2}$ the potential where the current is equal to one-half the peak current of the oxidation event. The values for $E_{p/2}$ are referenced to SCE (Saturated Calomel Electrode) by adding +30 mV to the potential measured against Ag/AgCl (3 M NaCl) .

Materials. Commercially available reagents were purchased from Sigma Aldrich, Acros, Alfa Aesar, or TCI, and used as received unless otherwise noted. Diethyl ether (Et_2O),

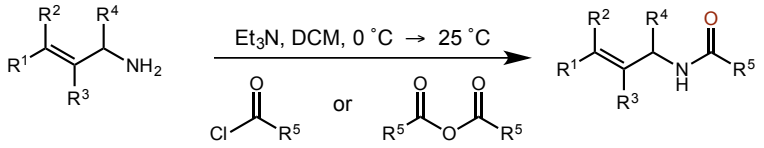
dichloroethane (DCE), dichloromethane (DCM), tetrahydrofuran (THF), toluene, and dimethylformamide (DMF) were dried by passing through activated alumina columns under nitrogen prior to use. Triethylamine (Et_3N) was distilled from calcium hydride. Other common solvents and chemical reagents were purified by standard published methods if noted.

II. Preparation of 9-Mesityl-10-methylacridinium Tetrafluoroborate (1)

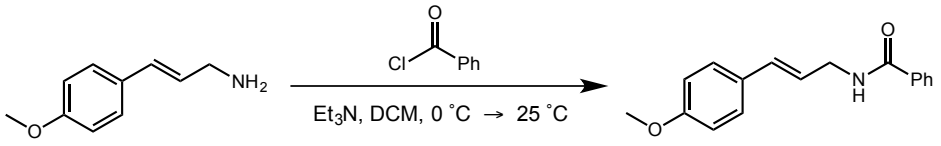
The photocatalyst used in this study, 9-mesityl-10-methylacridinium tetrafluoroborate, was synthesized by the method of Fukuzumi et al[1]. Tetrafluoroboric acid (diethyl ether complex) was substituted for perchloric acid during the hydrolysis. The spectral data matched the values reported in the literature for the perchlorate and hexafluorophosphate salts.

^{1}H NMR (600 MHz, CDCl3) δ 8.60 (d, *J* = 9.0 Hz, 2H), 8.37 (t, *J* = 9.0 Hz, 2H), 7.84 (s, 4H), 7.23 (s, 2H), 4.81 (s, 3H), 2.46 (s, 3H), 1.68 (s, 6H).

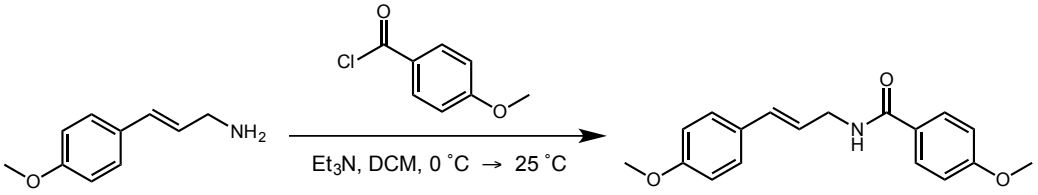
III. Preparation of Substrates



General Procedure A: The allylic amide substrates were synthesized according to a modified literature procedure[1]. The allylic amine (1.0 equiv.) was added to a flame-dried round bottom flask equipped with a stir bar, which was sealed with a septum and purged with nitrogen. Dry dichloromethane [0.2 M] was added and the reaction was cooled to 0 °C. Freshly distilled triethylamine (1.2 equiv.) was added dropwise by syringe, followed by dropwise addition of the appropriate acyl chloride or anhydride (1.5 equiv.). The reaction was allowed to warm to room temperature and stirred overnight. The reaction was then diluted with an equal volume of water and extracted with dichloromethane (3 times). The organic layer was washed with water followed by brine, and dried over Na_2SO_4. After concentration, the crude mixture was purified by either recrystallization or flash chromatography.



(*E*)-*N*-(3-(4-methoxyphenyl)allyl)benzamide (**3a)**: Substrate **3a** was prepared according to General Procedure **A** using 500 mg (*E*)-4-methoxycinnamylamine (3.06 mmol), 0.51 mL triethylamine (3.67 mmol), 0.53 mL benzoyl chloride (4.59 mmol), and 15 mL DCM. Product was purified by recrystallization from ethyl acetate and hexanes to furnish 458 mg pure product as colorless crystals in 56% yield. Spectral data was in agreement with reported literature values[2].



(*E*)-4-methoxy-*N*-(3-(4-methoxyphenyl)allyl)benzamide (3b): Substrate **3b** was prepared according to General Procedure **A** using 500 mg (*E*)-4-methoxycinnamylamine (3.06 mmol), 0.53 mL triethylamine (4.59 mmol), 0.83 mL 4-methoxybenzoyl chloride (6.12 mmol), and 15 mL DCM. Product was purified by flash chromatography on silica gel (50% EtOAc/Hexanes) and recrystallization from ethyl acetate and hexanes to furnish 340 mg pure product as pale yellow crystals in 34% yield.

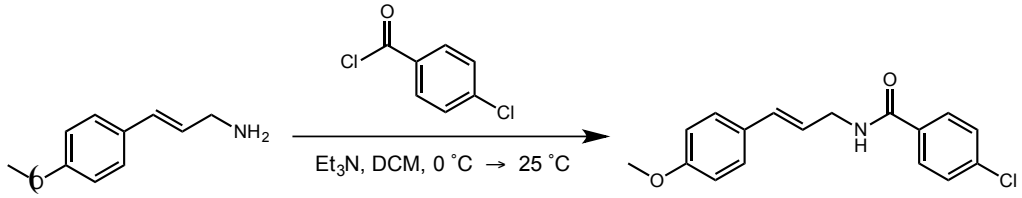
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.9 Hz, 1H), 7.31 (d, *J* = 8.6 Hz, 1H), 6.93 (d, *J* = 8.8 Hz, 1H), 6.85 (d, *J* = 8.7 Hz, 1H), 6.54 (d, *J* = 15.8 Hz, 0H), 6.20 – 6.12 (m, 1H), 4.21 (ddd, *J* = 6.7, 5.8, 1.5 Hz, 1H), 3.85 (s, 2H), 3.81 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.72, 162.16, 159.31, 132.01, 129.26, 128.69, 127.57, 126.74, 123.31, 114.00, 113.75, 55.40, 55.28, 42.17.

MS (ESI) Calculated *m/z* for $[M+H]^+$ = 298.14, Found *m/z* for $[M+H]^+$ = 298.22

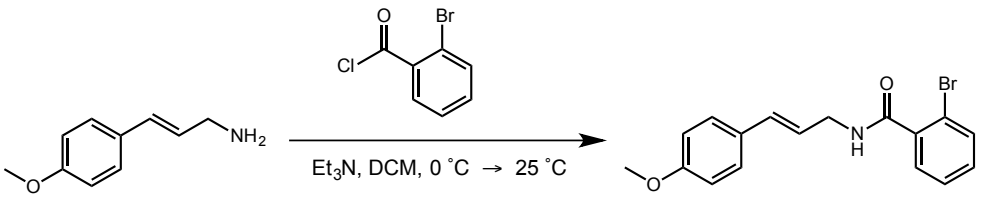
IR (thin film): 2906, 2836, 1603, 1548, 1506, 1456, 1297, 1251

CV $E_{p/2}$ = +1.30 V vs. SCE

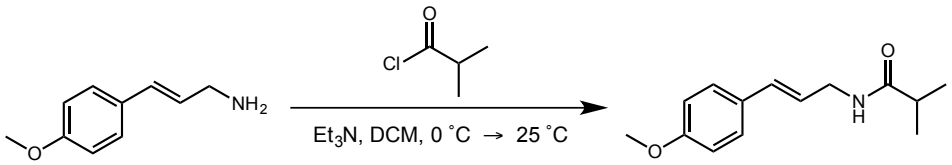


***E*)-4-chloro-*N*-(3-(4-methoxyphenyl)allyl)benzamide** (**3c)**: Substrate **3c** was prepared according to General Procedure **A** using 730 mg (*E*)-4-methoxycinnamylamine (4.47 mmol), 0.75 mL triethylamine (5.36 mmol), 0.49 mL 4-chlorobenzoyl chloride

(6.70 mmol), and 20 mL DCM. Product was purified by recrystallization from ethyl acetate and hexanes to furnish 603 mg pure product as colorless crystals in a 43% yield.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.5 Hz, 1H), 7.41 (d, *J* = 8.7 Hz, 1H), 7.31 (d, *J* = 8.7 Hz, 1H), 6.85 (d, *J* = 8.7 Hz, 1H), 6.55 (d, *J* = 15.8 Hz, 1H), 6.14 (dt, *J* = 15.8, 6.6 Hz, 1H), 4.22 (t, *J* = 6.1 Hz, 1H), 3.81 (s, 1H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 166.17, 159.43, 137.77, 132.84, 132.49, 129.10, 128.87, 128.36, 127.62, 122.73, 114.05, 55.31, 42.35.
MS (ESI) Calculated *m/z* for $[M+H]^+$ = 302.19, Found *m/z* for $[M+H]^+$ = 302.22
IR (thin film): 3299, 3079, 3029, 2911, 1785, 1632, 1547, 1508, 1422, 1315, 1248
CV $E_{p/2}$ = +1.40 V vs. SCE

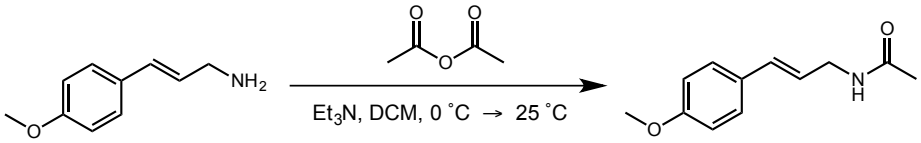


(*E*)-2-bromo-*N*-(3-(4-methoxyphenyl)allyl)benzamide (3d): Substrate **3d** was prepared according to General Procedure **A** using 1.00 g 4-methoxycinnamylamine (6.2 mmol), 1.0 mL triethylamine (7.32 mmol), 2.0 g 2-bromobenzoyl chloride (9.15 mmol) (prepared according to literature procedure), and 30 mL DCM. Product was purified by flash chromatography on silica (25% EtOAc/Hexanes) to furnish 930 mg pure product as colorless crystals in a 43% yield.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 (ddd, *J* = 25.2, 7.8, 1.4 Hz, 3H), 7.39 – 7.22 (m, 6H), 6.85 (d, *J* = 8.7 Hz, 2H), 6.57 (d, *J* = 15.8 Hz, 1H), 6.17 (s, 1H), 6.14 (dt, *J* = 15.8, 6.4 Hz, 1H), 4.21 (td, *J* = 6.0, 1.5 Hz, 3H), 3.80 (s, 4H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 167.37, 159.29, 137.73, 133.31, 132.19, 131.19, 129.51, 129.18, 127.57, 127.49, 122.51, 119.22, 113.96, 55.24, 42.18.
MS (ESI) Calculated *m/z* for $[M+H]^+$ = 346.04, Found *m/z* for $[M+H]^+$ = 346.02
IR (thin film): 3414, 3263, 1645, 1607, 1510, 1465, 1297, 1250, 1175

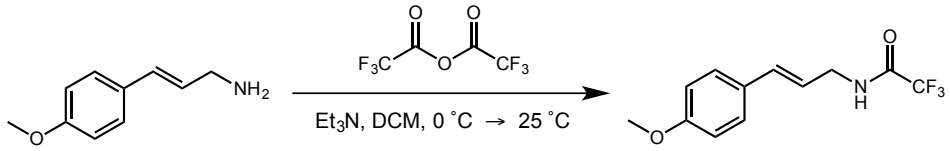


(*E*)-*N*-(3-(4-methoxyphenyl)allyl)isobutyramide (3e): Substrate **3e** was prepared according to General Procedure **A** using 1.00 g (*E*)-4-methoxycinnamylamine (6.2 mmol), 1.0 mL triethylamine (7.32 mmol), 0.96 mL isobutyrl chloride (9.15 mmol),

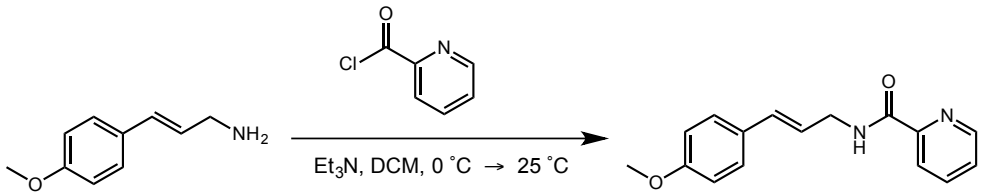
and 30 mL DCM. Product was purified by recrystallization from ethyl acetate and hexanes to furnish 374 mg pure product as colorless crystals in a 26% yield.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 6.45 (d, *J* = 15.8 Hz, 1H), 6.04 (dt, *J* = 15.8, 6.5 Hz, 1H), 5.62 (s, 1H), 4.00 (ddd, *J* = 6.7, 5.8, 1.5 Hz, 3H), 3.80 (s, 4H), 2.38 (hept, *J* = 6.9 Hz, 1H), 1.18 (d, *J* = 6.9 Hz, 8H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 176.65, 159.25, 131.70, 129.27, 127.50, 123.42, 113.95, 55.25, 41.55, 35.68, 19.64.
MS (ESI) Calculated *m/z* for $[M+H]^+$ = 234.24, Found *m/z* for $[M+H]^+$ = 234.10
IR (thin film): 3292, 2973, 2871, 1644, 1511, 1438, 1245, 1188



(*E*)-*N*-(3-(4-methoxyphenyl)allyl)acetamide (**3f**): Substrate **3f** was prepared according to General Procedure **A** using 1.00 g (*E*)-4-methoxycinnamylamine (6.2 mmol), 1.0 mL triethylamine (7.32 mmol), 0.48 mL acetic anhydride (12.32 mmol), and 30 mL DCM. Product was purified by recrystallization from ethyl acetate to furnish 516 mg pure product as colorless crystals in a 41% yield. Spectral data were in agreement with literature values[3].



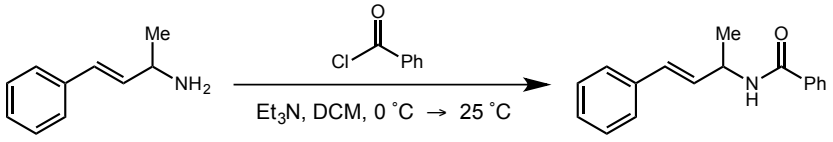
(*E*)-2,2,2-trifluoro-*N*-(3-(4-methoxyphenyl)allyl)acetamide (**3g**): Substrate **3g** was prepared according to General Procedure **A** using 500 mg (*E*)-4-methoxycinnamylamine (3.06 mmol), 0.51 mL triethylamine (3.67 mmol), 0.65 mL trifluoroacetic anhydride (4.59 mmol), and 15 mL DCM. Product was purified by flash chromatography on silica gel (15% EtOAc/Hexanes) to furnish 587 mg pure product as a white solid in 74% yield.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.7 Hz, 1H), 6.87 (d, *J* = 8.7 Hz, 1H), 6.70 – 6.47 (m, 1H), 6.38 (s, 1H), 6.03 (dt, *J* = 15.7, 6.7 Hz, 1H), 4.12 (td, *J* = 6.3, 1.4 Hz, 1H), 3.82 (s, 2H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 159.69, 157.08, 156.84, 133.91, 128.53, 127.76, 120.25, 116.76, 114.09, 55.29, 42.07.
MS (ESI) Calculated *m/z* for $[M+H]^+$ = 260.18, Found *m/z* for $[M+H]^+$ = 260.17
IR (thin film): 3287, 3112, 2955, 2837, 1702, 1555, 1513, 1435, 1307, 1258, 1178



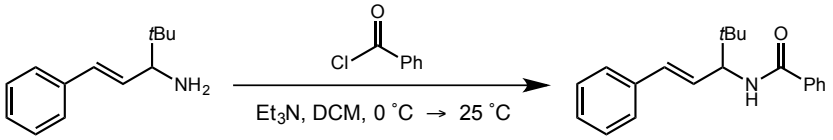
(*E*)-*N*-(3-(4-methoxyphenyl)allyl)picolinamide (3h): Substrate **3h** was prepared according to General Procedure **A** using 1.09 g (*E*)-4-methoxycinnamylamine (6.66 mmol), 1.11 mL triethylamine (7.99 mmol), 1.40 g 2-pyridinecarboxylic acid chloride (9.99 mmol) (prepared according to literature procedure[4] and used without purification). In a slight modification to the procedure, the amine substrate and triethylamine were stirred in 15 mL DCM at 0 °C, and the crude acid chloride was dissolved in an additional 15 mL DCM in a separate round bottom flask and added via cannula. The reaction was noted to immediately turn deep purple and was then allowed to warm to room temperature and was subjected to the same workup procedure. Product was purified by flash chromatography using silica gel (33% EtOAc/Hexanes + 2% triethylamine) giving 337 mg of the desired product as an off white solid in 18% yield.
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.55 (d, *J* = 4.7 Hz, 0H), 8.23 (d, *J* = 7.9 Hz, 1H), 8.18 (s, 1H), 7.86 (td, *J* = 7.7, 1.7 Hz, 1H), 7.43 (ddd, *J* = 7.6, 4.7, 1.2 Hz, 1H), 7.31 (d, *J* = 8.7 Hz, 1H), 6.84 (d, *J* = 8.8 Hz, 1H), 6.56 (d, *J* = 15.8 Hz, 1H), 6.16 (dt, *J* = 15.8, 6.4 Hz, 1H), 4.25 (td, *J* = 6.2, 1.5 Hz, 2H), 3.80 (s, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 164.09, 159.24, 149.91, 148.06, 137.35, 131.79, 129.38, 127.57, 126.16, 123.14, 122.29, 113.95, 55.27, 41.55.
MS (ESI) Calculated *m/z* for $[M+H]^+$ = 269.22, Found *m/z* for $[M+H]^+$ = 269.14
IR (thin film): 3390, 2934, 1666, 1590, 1510, 1464, 1288, 1248, 1175

***N*-cinnamylbenzamide (3i)**: Substrate **3i** was prepared according to published procedure; spectral data were in agreement with literature values[5].

***N*-(3-methylbut-2-en-1-yl)benzamide (3j)**: Substrate **3j** was prepared according to published procedure; spectral data were in agreement with literature values[6].

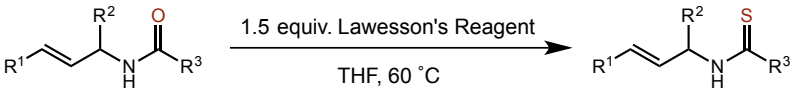


(*E*)-*N*-(4-phenylbut-3-en-2-yl)benzamide (3k): Substrate **3k** was prepared according to General Procedure **A** using 640 mg (*E*)-1-phenylbut-3-en-2-amine (4.3 mmol), 0.73 mL triethylamine (5.2 mmol), 0.75 mL benzoyl chloride (6.45 mmol), and 15 mL DCM. Product was purified by flash chromatography on silica gel (25% EtOAc/Hexanes) furnish 270 mg pure product as a colorless solid in a 25% yield. (*E*)-1-phenylbut-3-en-2-amine was prepared according to published procedure. Spectral data were in agreement with literature values[7].



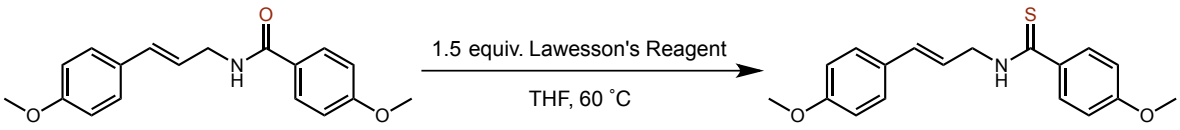
(*E*)-*N*-(4,4-dimethyl-1-phenylpent-1-en-3-yl)benzamide (3l): Substrate **3l** was prepared according to General Procedure **A** using 1.5 g (*E*)-4,4-dimethyl-1-phenylpent-1-en-3-amine (4.59 mmol), 0.77 mL triethylamine (5.63 mmol), 0.80 mL benzoyl chloride (6.88 mmol), and 25 mL DCM. Product was purified by flash chromatography on silica gel (10% EtOAc/Hexanes) to give 430 mg of product as a white solid in 32% yield. (*E*)-4,4-dimethyl-1-phenylpent-1-en-3-amine was prepared according to published procedure. Spectral data were in agreement with literature values[7].

***N*-(2-phenylallyl)benzamide (3m)**: Substrate **3m** was prepared according to published procedure; spectral data were in agreement with literature values[8].

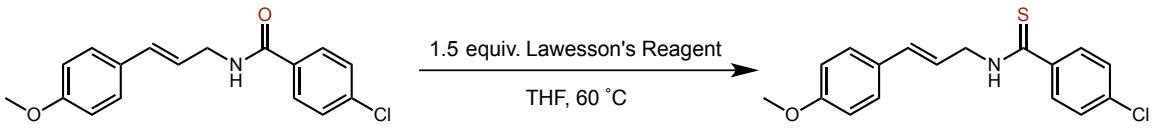


General Procedure B: The allylic thioamide substrates were synthesized according to a published procedure[9]. The allylic amide (1 equiv.) and Lawesson's Reagent (1.5 equiv.) were added to a dried round bottom flask with stir bar added, sealed with a septum, and purged with nitrogen. Dry THF was added via syringe ([0.1 M]) and

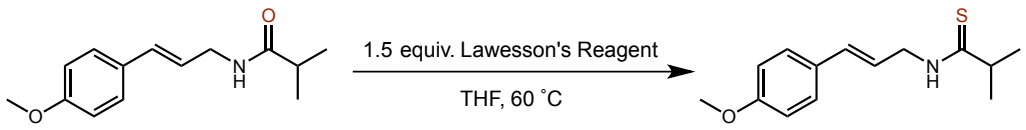
the reaction heated to 60 °C with stirring for 4 hours. The reaction was cooled to room temperature, and solvent was removed by rotary evaporation. Crude material was then purified using column chromatography (25% ethyl acetate/hexanes) to furnish the desired product.



(*E*)-4-methoxy-*N*-(3-(4-methoxyphenyl)allyl)benzothioamide (3n): Substrate **3n** was prepared according to General Procedure **B** using 490 mg **3b** (1.65 mmol), 1.00 g Lawesson's Reagent, and 15 mL THF. The pure product was obtained as a yellow solid in 48% yield after chromatography.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.9 Hz, 1H), 7.51 (s, 1H), 7.34 (d, *J* = 8.7 Hz, 1H), 6.88 (dd, *J* = 11.4, 8.8 Hz, 2H), 6.64 (d, *J* = 15.9 Hz, 1H), 6.23 (dt, *J* = 15.8, 6.8 Hz, 1H), 4.60 (ddd, *J* = 6.8, 5.3, 1.4 Hz, 2H), 3.84 (s, 2H), 3.82 (s, 2H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 197.83, 162.20, 159.58, 134.11, 133.97, 128.87, 128.49, 127.73, 120.71, 114.06, 113.65, 55.48, 55.30, 49.04.
MS (ESI) Calculated *m/z* for $[M+H]^+$ = 314.11, Found *m/z* for $[M+H]^+$ = 314.17
IR (thin film):3271, 2933, 1835, 1604, 1504, 1379, 1296, 1249, 1174, 1115
CV $E_{p/2}$ = +1.14 V vs. SCE



(*E*)-4-chloro-*N*-(3-(4-methoxyphenyl)allyl)benzothioamide (3o): Substrate **3o** was prepared according to General Procedure **B** using 350 mg **3c** (1.11 mmol), 677 mg Lawesson's Reagent, and 15 mL THF. The pure product was obtained as a yellow solid in 35% yield after chromatography.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.6 Hz, 1H), 7.55 (s, 1H), 7.35 (dd, *J* = 16.0, 8.6 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 1H), 6.64 (d, *J* = 15.8 Hz, 1H), 6.22 (dt, *J* = 15.8, 6.8 Hz, 1H), 4.57 (ddd, *J* = 6.8, 5.2, 1.3 Hz, 1H), 3.82 (s, 2H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 197.46, 159.67, 139.95, 137.38, 134.54, 128.72, 128.68, 128.00, 127.76, 120.17, 114.09, 55.31, 49.18.
MS (ESI) Calculated *m/z* for $[M+H]^+$ = 318.06, Found *m/z* for $[M+H]^+$ = 318.15
IR (thin film):3433, 1644, 1509, 1403, 1248, 1174, 1091
CV $E_{p/2}$ = +1.23 V vs. SCE



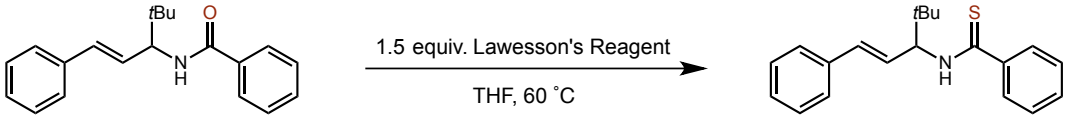
(*E*)-*N*-(3-(4-methoxyphenyl)allyl)-2-methylpropanethioamide (3p): Substrate **3p** was prepared according to General Procedure **B** using 290 mg **3c** (1.24 mmol), 754 mg Lawesson's Reagent, and 12 mL THF. The pure product was obtained as a yellow solid in 60% yield after chromatography.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.7 Hz, 1H), 7.54 (s, 1H), 7.35 (dd, *J* = 17.4, 8.6 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 1H), 6.65 (d, *J* = 15.8 Hz, 1H), 6.22 (dt, *J* = 15.8, 6.8 Hz, 1H), 4.58 (ddd, *J* = 6.7, 5.3, 1.4 Hz, 2H), 3.82 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.50, 159.70, 139.98, 137.41, 134.58, 128.71, 128.02, 127.78, 120.19, 114.12, 55.33, 49.20.

MS (ESI) Calculated *m/z* for $[M+H]^+$ = 250.12, Found *m/z* for $[M+H]^+$ = 250.14

IR (thin film): 3255, 2966, 2930, 1606, 1511, 1441, 1294, 1250, 1175



(*E*)-*N*-(4,4-dimethyl-1-phenylpent-1-en-3-yl)benzothioamide (3q): Substrate **3q** was prepared according to General Procedure **B** using 398 mg **3l** (1.36 mmol), 823 mg Lawesson's Reagent, and 14 mL THF. The pure product was obtained as a yellow oil in 61% yield after chromatography.

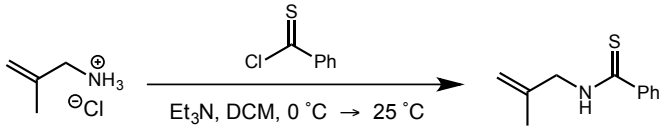
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.0 Hz, 1H), 7.60 (d, *J* = 9.7 Hz, 1H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.47 – 7.36 (m, 5H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.24 (t, *J* = 7.4 Hz, 1H), 6.67 (d, *J* = 15.8 Hz, 1H), 6.21 (dd, *J* = 15.8, 7.3 Hz, 1H), 5.42 (ddd, *J* = 9.6, 7.3, 1.2 Hz, 1H), 1.11 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 198.80, 142.72, 136.53, 133.43, 130.98, 128.62, 128.55, 127.80, 126.54, 126.49, 124.49, 65.59, 35.67, 26.65.

MS (ESI) Calculated *m/z* for $[M+H]^+$ = 310.26, Found *m/z* for $[M+H]^+$ = 310.18

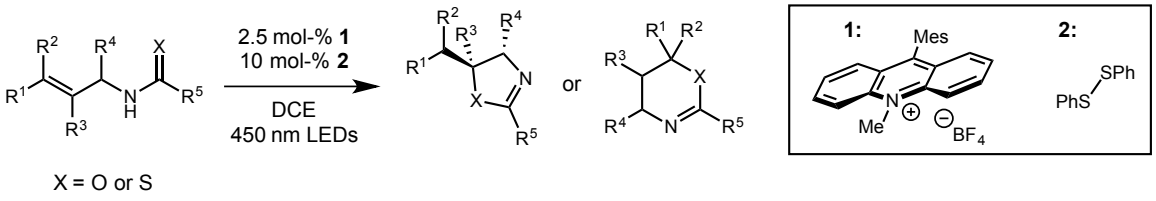
IR (thin film): 3393, 3058, 2962, 2867, 1508, 1474, 1371, 1317

***N*-allylbenzothioamide (3r)**: Substrate **3r** was prepared according to published procedure; spectral data were in agreement with literature values[9].

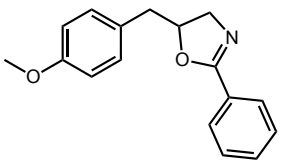


***N*-(2-methylallyl)benzothioamide (3s)**: Substrate **3s** was prepared according to General Procedure **A** using 1.07 g 2-methylprop-2-en-1-aminium chloride (10 mmol), 3.5 mL triethylamine (25 mmol, 2.5 equiv), 1.57 g thiobenzoyl chloride (10 mmol), and 5 mL DCM. Thiobenzoyl chloride was dissolved in an additional 5 mL DCM in a separate flask and added to the reaction via cannula. Product was purified by flash chromatography (25% ethyl acetate/hexanes) to furnish pure product as a yellow oil (56% yield). Thiobenzoyl chloride was prepared according to published procedure[10] and was used without purification.

III. General Procedure for Alkene Hydrofunctionalization

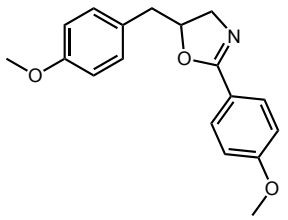


General Procedure C: Substrate (100 mg), 9-mesityl-10-methylacridinium tetrafluoroborate (2.5 mol %), and phenyl disulphide (10 mol %) were added to a flame-dried 2-dram vial equipped with a stir bar. Inside a glove-box, dichloroethane (0.1 [M] final concentration) was added to the vial, which was then sealed by a polypropylene cap equipped with a PTFE/silicone septum and removed from the glove box. The reaction was placed on a magnetic stir plate approximately 3cm from the light source (450 nm), and a hood of tin foil was placed over the entire setup. The reaction was then irradiated for the indicated amount of time. The test reactions appear bright yellow initially and gradually turn deep red over the course of the reaction. Upon completion, the stir bar was removed and the reaction concentrated. The crude mixture was purified by flash chromatography to furnish the final product. A small quantity of DCM is sometimes used to aid in solubilizing the material for flash chromatography.

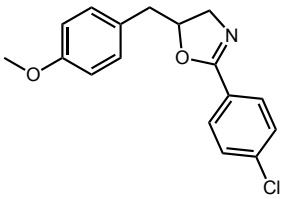


5-(4-methoxybenzyl)-2-phenyl-4,5-dihydrooxazole (4a): The average yield for the title compound was 82% (2 trials), using 100 mg (0.37 mmol) **3a**, 3.7 mg **1** (0.009

mmol), and 8.1 mg **2** (0.037 mmol). Irradiated for 14 hours. Eluent for purification: 25% ethyl acetate/hexanes.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.54 – 7.45 (m, 1H), 7.41 (dd, *J* = 8.2, 6.8 Hz, 2H), 7.18 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 1H), 4.90 (dtd, *J* = 9.5, 7.0, 6.2 Hz, 1H), 4.06 (dd, *J* = 14.6, 9.4 Hz, 1H), 3.80 (s, 3H), 3.79 – 3.61 (m, 1H), 3.05 (dd, *J* = 14.1, 7.0 Hz, 1H), 2.85 (dd, *J* = 14.1, 6.2 Hz, 1H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 163.81, 158.40, 131.21, 130.28, 128.75, 128.28, 128.07, 127.87, 113.96, 80.40, 59.40, 55.20, 40.48.
MS (GC-MS) Calculated *m/z* = 267.13, Found *m/z* = 267.1
IR (thin film): 2954, 1645, 1607, 1509, 1463, 1345, 1301, 1299, 1168

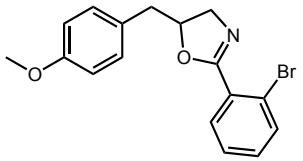


5-(4-methoxybenzyl)-2-(4-methoxyphenyl)-4,5-dihydrooxazole (4b): The average yield for the title compound was 77% (2 trials), using 100 mg (0.336 mmol) **3b**, 3.4 mg **1** (0.0084 mmol), and 7.3 mg **2** (0.0336 mmol). Irradiated for 14 hours. Eluent for purification: 50% ethyl acetate/hexanes.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.4 Hz, 1H), 7.17 (d, *J* = 7.7 Hz, 1H), 6.91 (d, *J* = 7.3 Hz, 1H), 6.86 (d, *J* = 7.1 Hz, 1H), 4.87 (p, *J* = 6.9 Hz, 1H), 4.03 (dd, *J* = 14.5, 9.1 Hz, 1H), 3.84 (s, 2H), 3.79 (s, 1H), 3.74 (dd, *J* = 14.4, 7.0 Hz, 1H), 3.04 (dd, *J* = 14.1, 7.0 Hz, 1H), 2.83 (dd, *J* = 14.1, 6.2 Hz, 1H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 163.58, 161.94, 158.37, 130.28, 129.77, 128.88, 120.43, 113.94, 113.62, 80.28, 59.37, 55.30, 55.20, 40.50.
MS (GC-MS) Calculated *m/z* for $[M+H]^+$ = 297.13, Found *m/z* for $[M+H]^+$ = 297.2
IR (thin film): 3420, 2935, 2836, 2359, 1646, 1609, 1512, 1461, 1346, 1302, 1252, 1170

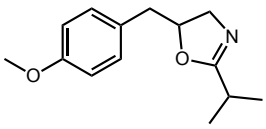


2-(4-chlorophenyl)-5-(4-methoxybenzyl)-4,5-dihydrooxazole (4c): The average yield for the title compound was 78% (2 trials), using 100 mg (0.319 mmol) **3c**, 3.2 mg **1** (0.0080 mmol), and 7.0 mg **2** (0.032 mmol). Irradiated for 14 hours. Eluent for purification: 25% ethyl acetate/hexanes.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.6 Hz, 1H), 7.38 (d, *J* = 8.6 Hz, 1H), 7.16 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 1H), 4.90 (dtd, *J* = 9.5, 7.0, 6.1 Hz, 1H), 4.05 (dd, *J*

= 14.7, 9.4 Hz, 1H), 3.80 (s, 3H), 3.76 (dd, *J* = 14.7, 7.1 Hz, 1H), 3.03 (dd, *J* = 14.1, 6.9 Hz, 1H), 2.85 (dd, *J* = 14.1, 6.2 Hz, 1H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 163.00, 158.49, 137.43, 130.31, 129.47, 128.64, 128.60, 126.43, 114.03, 80.67, 59.48, 55.26, 40.47.
MS (GC-MS) Calculated *m/z* = 309.09, found = 309.1
IR (thin film): 3362, 3033, 2934, 2870, 2834, 1718, 1650, 1598, 1512, 1490, 1403, 1344, 1248, 1178

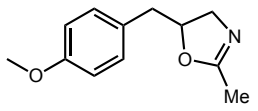


2-(2-bromophenyl)-5-(4-methoxybenzyl)-4,5-dihydrooxazole (4d): The average yield for the title compound was 77% (2 trials), using 100 mg (0.289 mmol) **3d**, 2.9 mg **1** (0.0072 mmol), and 7.1 μL 4-methoxythiophenol (0.058 mmol). Irradiated for 14 hours. Eluent for purification: 25% ethyl acetate/hexanes.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 – 7.61 (m, 2H), 7.33 (td, *J* = 7.6, 1.3 Hz, 1H), 7.30 – 7.25 (m, 1H), 7.19 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 4.93 (dq, *J* = 9.6, 6.7 Hz, 1H), 4.10 (dd, *J* = 14.7, 9.6 Hz, 1H), 3.82 (dd, *J* = 14.7, 7.2 Hz, 1H), 3.79 (s, 3H), 3.11 (dd, *J* = 14.1, 6.7 Hz, 1H), 2.88 (dd, *J* = 14.2, 6.4 Hz, 1H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 163.04, 158.39, 133.78, 131.49, 131.25, 130.26, 129.73, 128.54, 127.01, 121.71, 113.95, 80.63, 59.68, 55.17, 40.28.
MS (GC-MS) Calculated *m/z* = 345.04, found *m/z* = 345.1
IR (thin film): 3062, 3032, 3005, 2934, 2834, 1651, 1612, 1590, 1512, 1464, 1431, 1341, 1246, 1178

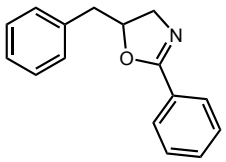


2-isopropyl-5-(4-methoxybenzyl)-4,5-dihydrooxazole (4e): The average yield for the title compound was 79% (2 trials), using 100 mg (0.428 mmol) **3e**, 4.3 mg **1** (0.011 mmol), and 9.3 mg **2** (0.0428 mmol). Irradiated for 14 hours. Eluent for purification: 50% ethyl acetate/hexanes.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 4.68 (dd, *J* = 9.5, 6.5 Hz, 1H), 3.85 – 3.78 (m, 1H), 3.78 (s, 4H), 3.52 (dd, *J* = 14.0, 6.7 Hz, 1H), 2.90 (dd, *J* = 14.0, 6.8 Hz, 1H), 2.73 (dd, *J* = 14.1, 6.2 Hz, 1H), 2.54 (hept, *J* = 7.0 Hz, 1H), 1.18 (d, *J* = 7.0 Hz, 5H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 171.92, 158.39, 130.32, 128.82, 113.93, 79.85, 58.79, 55.23, 40.47, 28.20, 19.72, 19.61.
MS (GC-MS) Calculated *m/z* = 233.14, found *m/z* = 233.2

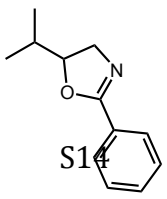
IR (thin film): 3378, 2970, 2935, 2875, 2835, 1732, 1662, 1612, 1513, 1466, 1388, 1309, 1247, 1199



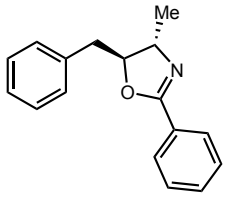
5-(4-methoxybenzyl)-2-methyl-4,5-dihydrooxazole (4f): The average yield for the title compound was 77% (2 trials), using 100 mg (0.487 mmol) **3f**, 4.9 mg **1** (0.0122 mmol), and 10.6 mg **2** (0.049 mmol). Irradiated for 14 hours. Eluent for purification: ethyl acetate.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8.3 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 4.70 (dq, *J* = 9.5, 6.7 Hz, 1H), 3.93 – 3.79 (m, 1H), 3.78 (s, 3H), 3.51 (dd, *J* = 14.0, 7.0 Hz, 1H), 2.91 (dd, *J* = 14.1, 6.8 Hz, 1H), 2.76 (dd, *J* = 14.1, 6.2 Hz, 1H), 1.95 (s, 2H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 164.75, 158.38, 130.17, 128.69, 113.92, 80.14, 59.09, 55.19, 40.42, 14.10.
MS (GC-MS) Calculated *m/z* = 205.11, found *m/z* = 205.1
IR (thin film): 3096, 2934, 2835, 1736, 1669, 1582, 1512, 1440, 1393, 1300, 1246, 1178, 1110



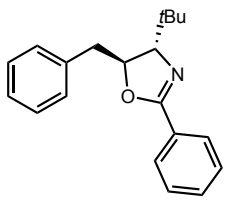
5-(4-methoxybenzyl)-2-phenyl-4,5-dihydrooxazole (4i): The average yield for the title compound was 76% (2 trials), using 100 mg (0.447 mmol) **3a**, 4.3 mg **1** (0.011 mmol), and 9.7 mg **2** (0.044 mmol). Eluent for purification: 25% ethyl acetate/hexanes.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 – 7.92 (m, 1H), 7.51 – 7.47 (m, 1H), 7.42 (dd, *J* = 8.2, 6.8 Hz, 1H), 7.34 (dd, *J* = 8.1, 6.8 Hz, 2H), 7.27 (d, *J* = 13.5 Hz, 2H), 4.95 (dtd, *J* = 9.5, 7.1, 6.1 Hz, 1H), 4.09 (dd, *J* = 14.6, 9.4 Hz, 1H), 3.80 (dd, *J* = 14.6, 7.1 Hz, 1H), 3.13 (dd, *J* = 14.0, 7.1 Hz, 1H), 2.91 (dd, *J* = 14.0, 6.2 Hz, 1H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 163.77, 136.77, 131.21, 129.29, 128.53, 128.27, 128.07, 127.84, 126.69, 80.19, 59.53, 41.42.
MS (GC-MS) Calculated *m/z* = 237.12, found = 237.2
IR (thin film): 3062, 3028, 2940, 2869, 1649, 1579, 1495, 1451, 1345, 1259, 1176



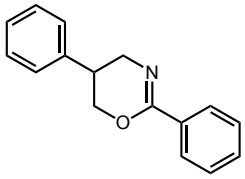
5-isopropyl-2-phenyl-4,5-dihydrooxazole (4j): The average yield for the title compound was 59% (2 trials), using 100 mg (0.57 mmol) **3a**, 5.7 mg **1** (0.014 mmol), and 12.5 mg **2** (0.057 mmol). Eluent for purification: 25% ethyl acetate/hexanes.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (d, *J* = 6.9 Hz, 1H), 7.47 (t, *J* = 7.3 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 2H), 4.45 (ddd, *J* = 9.7, 7.8, 6.6 Hz, 1H), 4.05 (dd, *J* = 14.7, 9.7 Hz, 1H), 3.74 (dd, *J* = 14.7, 7.8 Hz, 1H), 1.89 (h, *J* = 6.7 Hz, 1H), 0.99 (dd, *J* = 38.1, 6.8 Hz, 6H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 164.13, 131.13, 128.27, 128.05, 84.86, 57.68, 32.68, 17.71, 17.50.
MS (GC-MS) Calculated *m/z* = 189.12, found = 189.1
IR (thin film): 3330, 3062, 2962, 2875, 1717, 1648, 1579, 1536, 1494, 1450, 1346, 1287, 1259, 1176



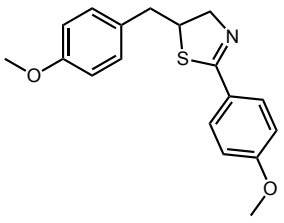
5-benzyl-4-methyl-2-phenyl-4,5-dihydrooxazole (4k): The average yield for the title compound was 64% (2 trials), using 100 mg (0.398 mmol) **3a**, 4.0 mg **1** (0.01 mmol), and 8.7 mg **2** (0.04 mmol). Eluent for purification: 25% ethyl acetate/hexanes.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.9 Hz, 2H), 7.68 (d, *J* = 7.7 Hz, 2H), 7.52 – 7.14 (m, 16H), 4.42 (q, *J* = 6.7 Hz, 1H), 4.29 (p, *J* = 6.9 Hz, 1H), 4.04 (p, *J* = 6.7 Hz, 1H), 3.13 (dd, *J* = 13.9, 7.2 Hz, 1H), 2.89 (dd, *J* = 13.9, 6.1 Hz, 1H), 2.74 (t, *J* = 7.9 Hz, 2H), 1.90 (q, *J* = 7.4 Hz, 2H), 1.29 (d, *J* = 6.5 Hz, 3H), 1.23 (d, *J* = 6.7 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.81, 162.67, 141.74, 136.78, 134.87, 133.17, 131.33, 131.29, 130.05, 129.35, 128.59, 128.52, 128.37, 128.36, 128.32, 128.22, 127.96, 126.78, 126.73, 125.96, 87.05, 66.81, 45.75, 41.01, 38.63, 32.53, 21.43, 21.12.
MS (GC-MS) Calculated *m/z* = 251.13, found *m/z* = 251.2
IR (thin film): 3062, 3029, 2931, 1644, 1579, 1495, 1450, 1351, 1298, 1269



5-benzyl-4-(*tert*-butyl)-2-phenyl-4,5-dihydrooxazole (4l): The average yield for the title compound was 81% (2 trials), using 100 mg (0.341 mmol) **3a**, 3.4 mg **1** (0.0085 mmol), and 7.4 mg **2** (0.0341 mmol). Eluent for purification: 15% ethyl acetate/hexanes.
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 – 7.96 (m, 2H), 7.96 – 7.91 (m, 0H), 7.56 – 7.44 (m, 1H), 7.47 – 7.39 (m, 2H), 7.39 – 7.22 (m, 7H), 4.89 (ddd, *J* = 11.3, 8.7, 2.3 Hz, 0H), 4.64 (dt, *J* = 7.6, 5.4 Hz, 1H), 4.01 (d, *J* = 8.7 Hz, 0H), 3.70 (d, *J* = 5.4 Hz, 1H), 3.16 (dd, *J* = 14.0, 2.3 Hz, 0H), 3.10 – 2.97 (m, 1H), 2.82 (dd, *J* = 13.9, 5.4 Hz, 1H), 1.21 (s, 2H), 0.86 (s, 9H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 163.00, 162.17, 139.21, 137.10, 131.14, 129.59, 129.26, 128.51, 128.48, 128.41, 128.33, 128.28, 128.28, 128.26, 128.20, 128.13, 126.70, 126.42, 84.75, 81.26, 80.71, 77.54, 42.72, 37.18, 34.21, 34.10, 28.03, 25.75.
MS (GC-MS) Calculated *m/z* for = 293.16, found *m/z* = 293.1
IR (thin film): 3063, 3028, 2956, 2868, 1650, 1603, 1580, 1495, 1465, 1394, 1340, 1299, 1252, 1176



2,5-diphenyl-5,6-dihydro-4*H*-1,3-oxazine (4m): The average yield for the title compound was 53% (2 trials), using 100 mg (0.429 mmol) **3a**, 4.3 mg **1** (0.011 mmol), and 52.7 μL 4-methoxythiophenol (0.429 mmol, 1.0 equiv.). Eluent for purification: 25% ethyl acetate/hexanes.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 7.1, 1.3 Hz, 2H), 7.50 – 7.42 (m, 1H), 7.42 – 7.36 (m, 4H), 7.34 – 7.28 (m, 1H), 7.28 – 7.23 (m, 2H), 4.52 (ddd, *J* = 10.5, 4.3, 2.8 Hz, 1H), 4.29 (t, *J* = 10.6 Hz, 1H), 3.89 (ddd, *J* = 16.6, 5.1, 2.8 Hz, 1H), 3.71 (dd, *J* = 16.5, 10.5 Hz, 1H), 3.21 (ddd, *J* = 10.6, 5.9, 4.7 Hz, 1H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 155.18, 139.43, 133.61, 130.44, 128.90, 128.07, 127.49, 127.34, 127.03, 69.21, 49.64, 37.94.
MS (GC-MS) Calculated *m/z* = 237.12, found *m/z* = 237.1
IR (thin film):2058, 2942, 2908, 1652, 1491, 1445, 1334, 1264, 1130



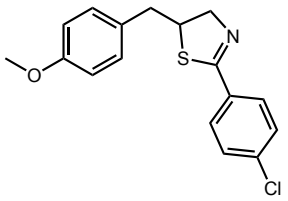
5-(4-methoxybenzyl)-2-(4-methoxyphenyl)-4,5-dihydrothiazole (4n): The average yield for the title compound was 80% (2 trials), using 100 mg (0.32 mmol) **3a**, 3.2 mg **1** (0.0080 mmol), and 7.0 mg **2** (0.032 mmol). Eluent for purification: 25% ethyl acetate/hexanes.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.8 Hz, 2H), 7.14 (d, *J* = 8.6 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 4.34 (dd, *J* = 15.6, 4.2 Hz, 1H), 4.25 (dd, *J* = 15.6, 7.8 Hz, 1H), 4.10 (qd, *J* = 7.7, 4.2 Hz, 1H), 3.85 (s, 3H), 3.80 (s, 3H), 2.88 (d, *J* = 7.7 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 167.03, 161.89, 158.37, 131.04, 130.01, 129.91, 126.24, 113.91, 113.73, 69.09, 55.39, 55.25, 53.07, 41.40.

MS (GC-MS) Calculated *m/z* = 313.11, found *m/z* = 313.1

IR (thin film): 3006, 2967, 2933, 2915, 2840, 1608, 1512, 1444, 1302, 1249, 1180, 1107



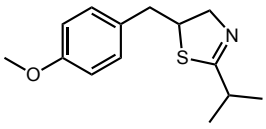
2-(4-chlorophenyl)-5-(4-methoxybenzyl)-4,5-dihydrothiazole (4o): The average yield for the title compound was 60% (2 trials), using 100 mg (0.303 mmol) **3a**, 3.0 mg **1** (0.010 mmol), and 6.6 mg **2** (0.040 mmol). Eluent for purification: 25% ethyl acetate/hexanes.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.6 Hz, 1H), 7.38 (d, *J* = 8.6 Hz, 1H), 7.14 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 1H), 4.36 (dd, *J* = 15.9, 4.3 Hz, 1H), 4.28 (dd, *J* = 15.9, 7.9 Hz, 1H), 4.15 (qd, *J* = 7.8, 4.2 Hz, 1H), 3.80 (s, 3H), 2.89 (d, *J* = 7.7 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.65, 158.46, 137.19, 131.93, 130.77, 130.02, 129.53, 128.71, 113.98, 69.28, 55.27, 53.48, 41.40.

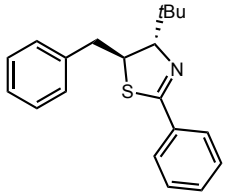
MS (GC-MS) Calculated *m/z* = 317.83, found *m/z* = 317.1

IR (thin film): 3031, 2933, 2835, 1608, 1511, 1439, 1399, 1301, 1247, 1176, 1092

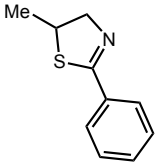


2-isopropyl-5-(4-methoxybenzyl)-4,5-dihydrothiazole (4p): The average yield for the title compound was 62% (2 trials), using 100 mg (0.303 mmol) **3a**, 4.0 mg **1**

(0.010 mmol), and 8.7 mg **2** (0.030 mmol). Eluent for purification: 25% ethyl acetate/hexanes.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.10 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 4.10 (dd, *J* = 15.2, 4.3 Hz, 1H), 4.03 (dd, *J* = 15.1, 7.8 Hz, 1H), 3.96 (qd, *J* = 7.6, 4.2 Hz, 1H), 3.79 (s, 3H), 2.85 – 2.73 (m, 3H), 1.21 (dd, *J* = 6.9, 2.1 Hz, 6H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 176.85, 158.32, 130.98, 129.97, 113.83, 68.41, 55.22, 52.59, 41.37, 34.09, 21.11, 20.98.
MS (GC-MS) Calculated *m/z* = 249.12, found *m/z* = 249.1
IR (thin film): 2965, 2933, 1835, 1654, 1613, 1512, 1464, 1440, 1300, 1247, 1178, 1109

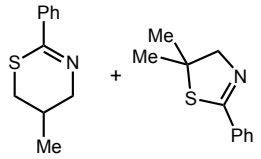


5-benzyl-4-(*tert*-butyl)-2-phenyl-4,5-dihydrothiazole (4q): The average yield for the title compound was 82% (2 trials), using 100 mg (0.32 mmol) **3a**, 3.2 mg **1** (0.0081 mmol), and 6.7 mg **2** (0.032 mmol). Eluent for purification: 10% ethyl acetate/hexanes.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 6.7 Hz, 1H), 7.42 (ddd, *J* = 14.5, 7.9, 6.2 Hz, 3H), 7.33 (dd, *J* = 7.9, 6.7 Hz, 2H), 7.26 (d, *J* = 7.2 Hz, 3H), 4.35 (d, *J* = 3.3 Hz, 1H), 4.03 (ddd, *J* = 8.3, 6.8, 3.3 Hz, 1H), 3.08 – 2.85 (m, 2H), 0.95 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 164.80, 138.86, 133.58, 130.90, 129.29, 128.47, 128.37, 126.68, 92.03, 52.98, 45.61, 36.65, 26.40.
MS (GC-MS) Calculated *m/z* = 309.16, found *m/z* = 309.1
IR (thin film): 3058, 2958, 2868, 1580, 1504, 1462, 1390, 1340, 1252, 1227, 1157, 1172

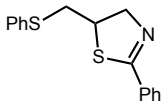


5-methyl-2-phenyl-4,5-dihydrothiazole (4r): The average yield for the title compound was 60% (2 trials), using 100 mg (0.56 mmol) **3a**, 5.6 mg **1** (0.014 mmol), and 13.9 μL **2** (0.11 mmol). Eluent for purification: 15% ethyl acetate/hexanes. Spectral data were in agreement with literature values[9].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.80 (m, 2H), 7.51 – 7.36 (m, 3H), 4.40 (dd, *J* = 15.7, 7.9 Hz, 1H), 4.20 (dd, *J* = 15.7, 4.4 Hz, 1H), 4.11 – 3.96 (m, 1H), 1.40 (d, *J* = 6.8 Hz, 3H).



The average yield for the title compound was 75% (2 trials), using 100 mg (0.52 mmol) **3a**, 5.2 mg **1** (0.013 mmol), and 12.8 μL **2** (0.10 mmol). Eluent for purification: 15% ethyl acetate/hexanes. Spectral data were in agreement with literature values[9].
5-methyl-2-phenyl-5,6-dihydro-4*H*-1,3-thiazine (4s): **^{1}H NMR** (400 MHz, CDCl3) δ 7.77 (dt, *J* = 6.7, 1.7 Hz, 1H), 7.57 – 7.32 (m, 2H), 4.26 – 3.91 (m, 1H), 3.41 (dd, *J* = 16.6, 9.5 Hz, 1H), 3.26 – 3.02 (m, 1H), 2.88 (dd, *J* = 12.0, 10.1 Hz, 1H), 1.96 (ddt, *J* = 9.9, 6.5, 3.2 Hz, 0H), 1.11 (d, *J* = 6.6 Hz, 2H).
5,5-dimethyl-2-phenyl-4,5-dihydrothiazole (5s): **^{1}H NMR** (400 MHz, CDCl3) δ 7.80 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.63 – 7.32 (m, 1H), 4.13 (s, 1H), 1.58 (s, 3H).



2-phenyl-5-((phenylthio)methyl)-4,5-dihydrothiazole (6a): The yield of the title compound was 11%, using 100 mg **3r** (0.56 mmol) and 12.2 mg **2** (0.056 mmol). Eluent for purification: 10% ethyl acetate/hexanes.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.0 Hz, 1H), 7.49 – 7.45 (m, 1H), 7.44 – 7.39 (m, 4H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.27 – 7.20 (m, 1H), 4.65 (dd, *J* = 16.2, 3.1 Hz, 1H), 4.31 (dd, *J* = 16.2, 8.0 Hz, 1H), 4.00 (dddd, *J* = 9.2, 8.1, 6.3, 3.0 Hz, 1H), 3.17 (dd, *J* = 13.6, 6.3 Hz, 1H), 3.05 (dd, *J* = 13.6, 8.8 Hz, 1H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 167.20, 134.66, 133.09, 131.23, 130.47, 130.46, 129.14, 128.47, 128.27, 126.89, 77.21, 77.00, 76.79, 68.75, 49.87, 39.92.
MS (GC-MS) Calculated *m/z* = 285.06, found *m/z* = 285.1
IR (thin film): 3366, 3266, 1622, 1449, 1397, 1325, 1279

V. References

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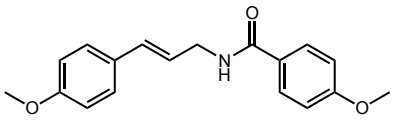
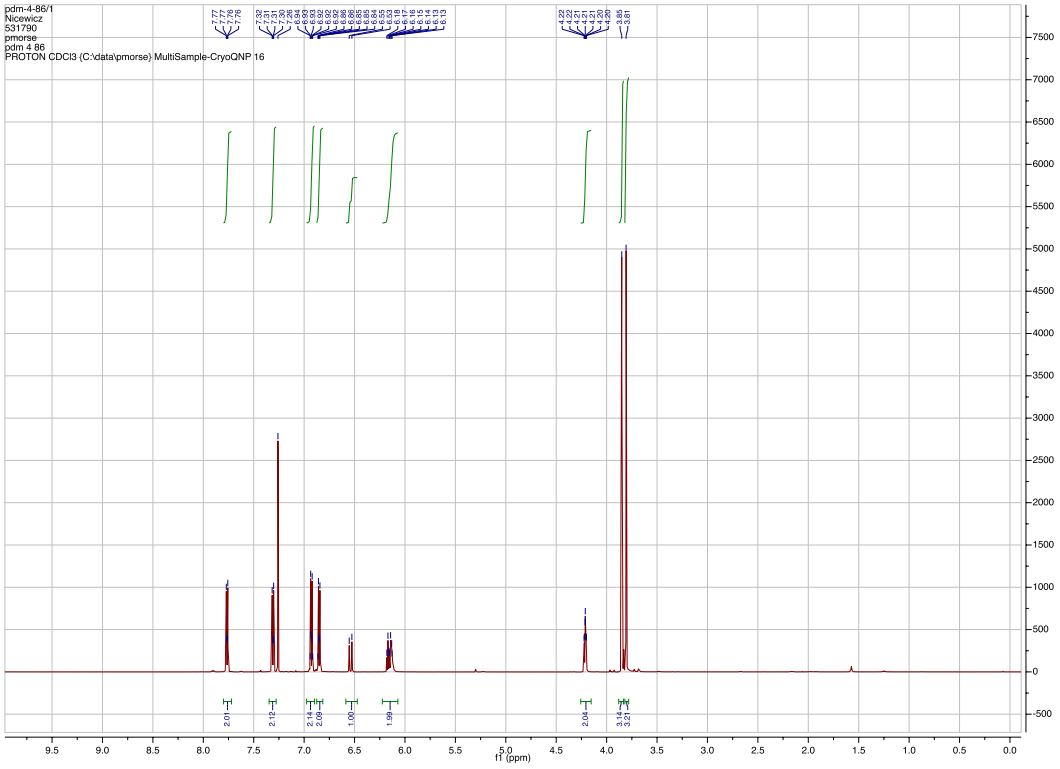
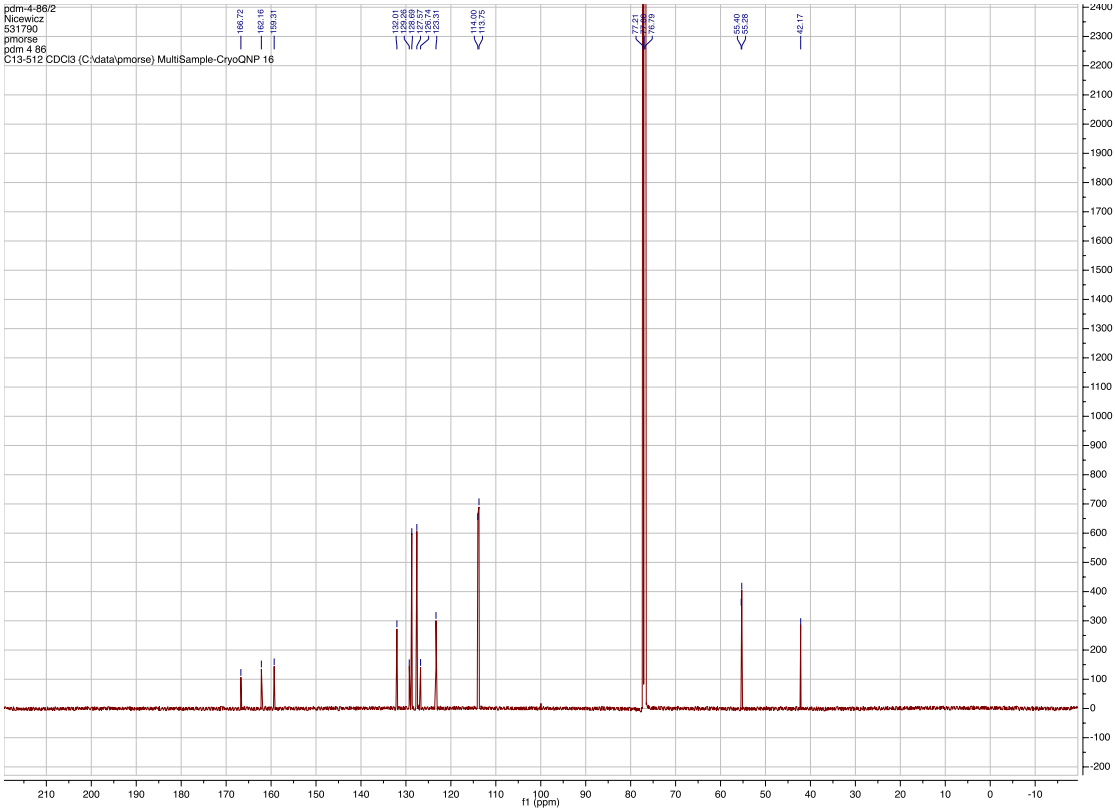
VI. ^{1}H and ^{13}C Spectra

(*E*)-4-methoxy-*N*-(3-(4-methoxyphenyl)allyl)benzamide (3b)

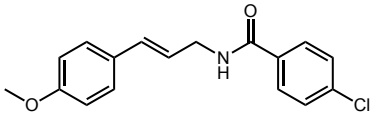


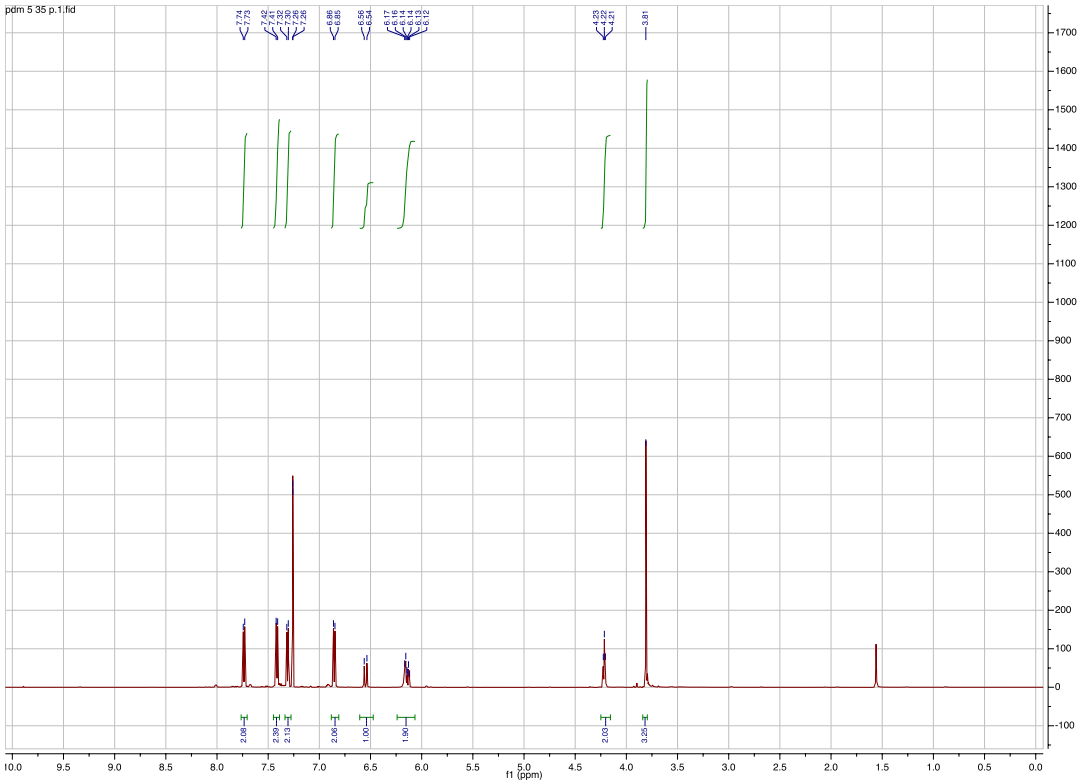


(*E*)-4-methoxy-*N*-(3-(4-methoxyphenyl)allyl)benzamide (3b)

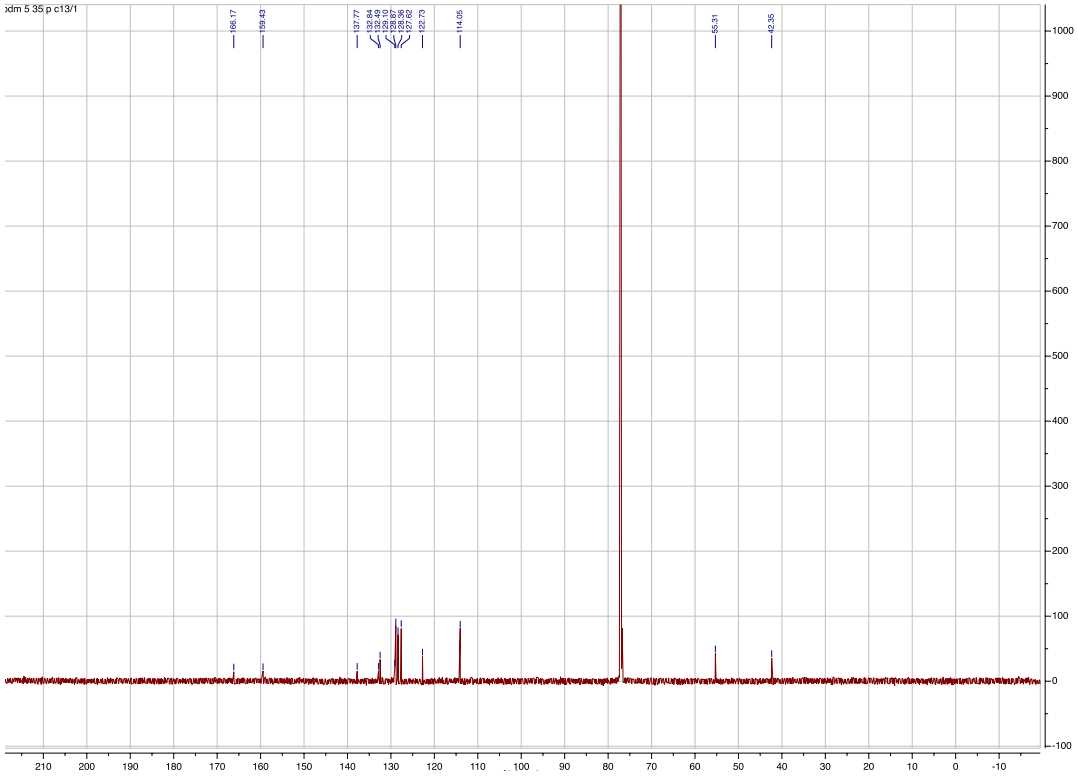


(*E*)-4-chloro-*N*-(3-(4-methoxyphenyl)allyl)benzamide (3c)

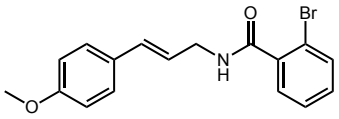


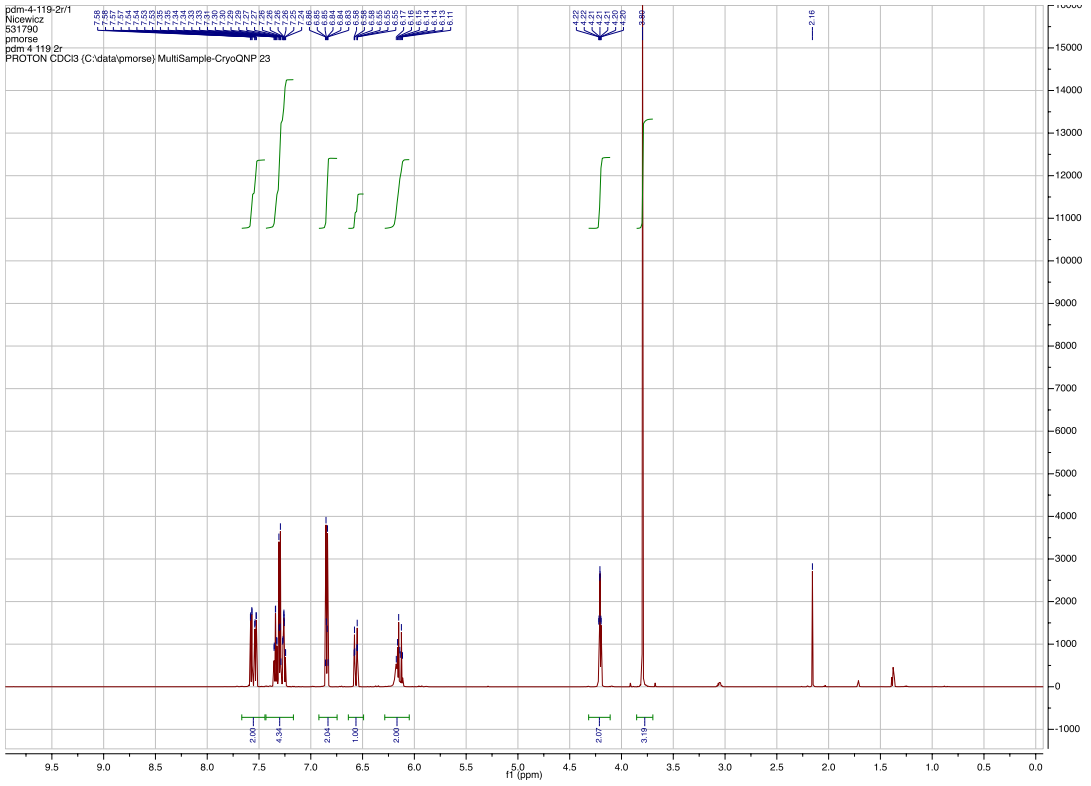


(*E*)-4-chloro-*N*-(3-(4-methoxyphenyl)allyl)benzamide (3c)

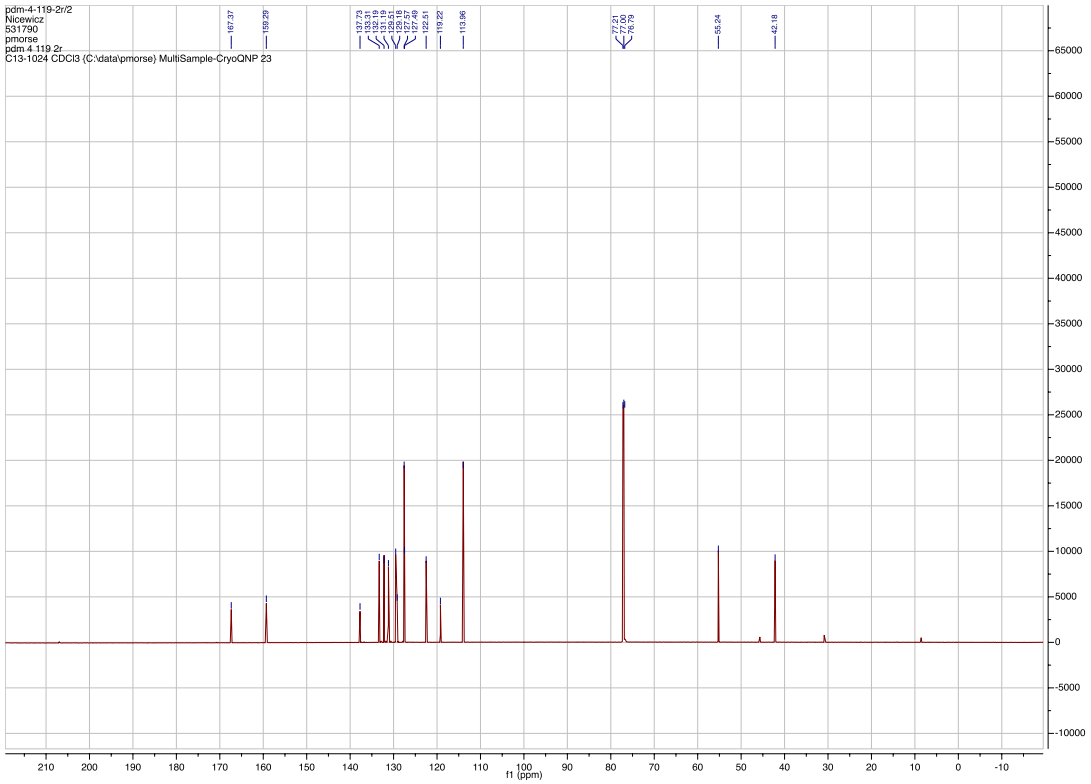


(*E*)-2-bromo-*N*-(3-(4-methoxyphenyl)allyl)benzamide (3d)

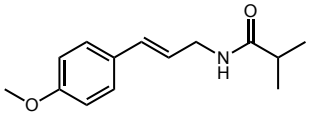


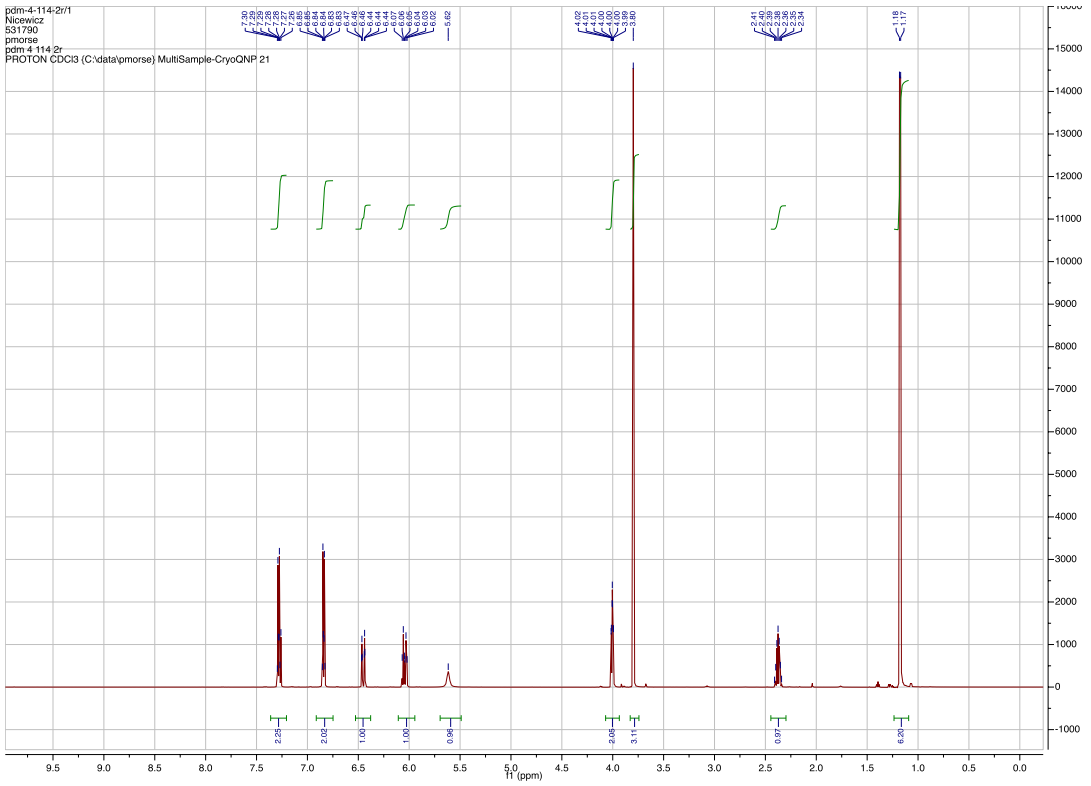


(*E*)-2-bromo-*N*-(3-(4-methoxyphenyl)allyl)benzamide (3d)

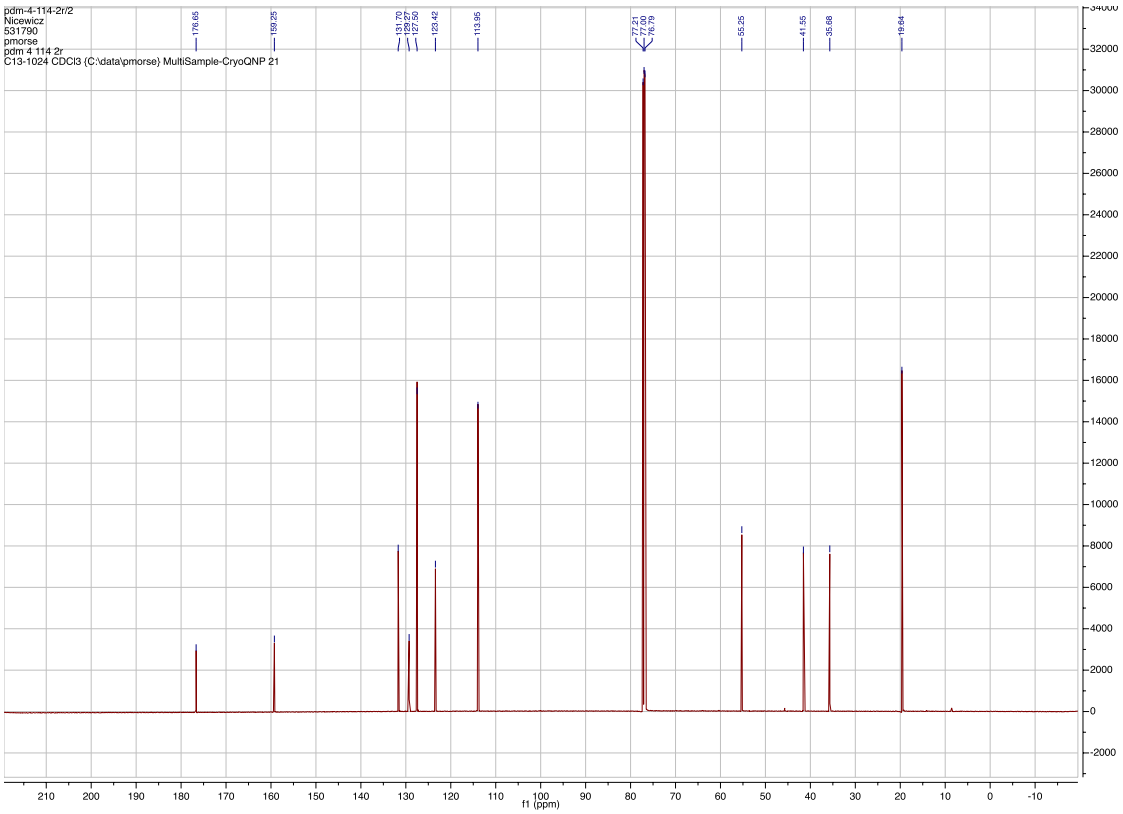


(*E*)-*N*-(3-(4-methoxyphenyl)allyl)isobutyramide (3e)

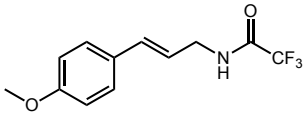


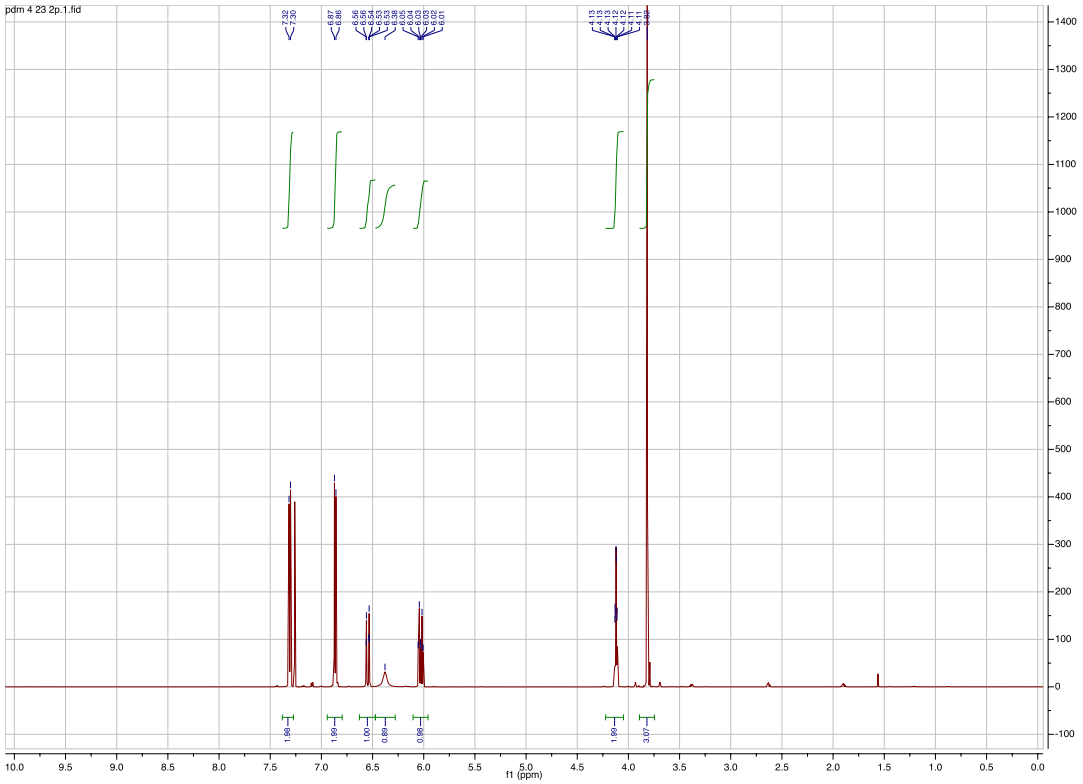


(*E*)-*N*-(3-(4-methoxyphenyl)allyl)isobutyramide (3e)

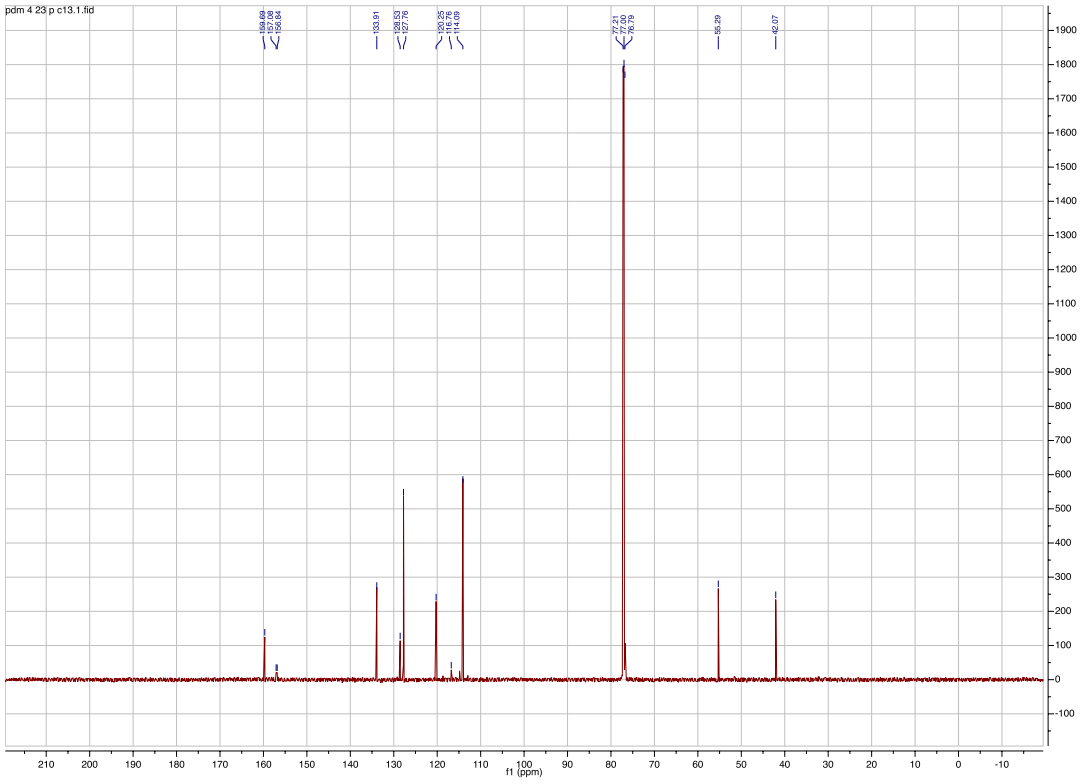


(*E*)-2,2,2-trifluoro-*N*-(3-(4-methoxyphenyl)allyl)acetamide (3g)

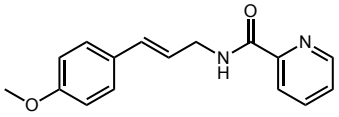


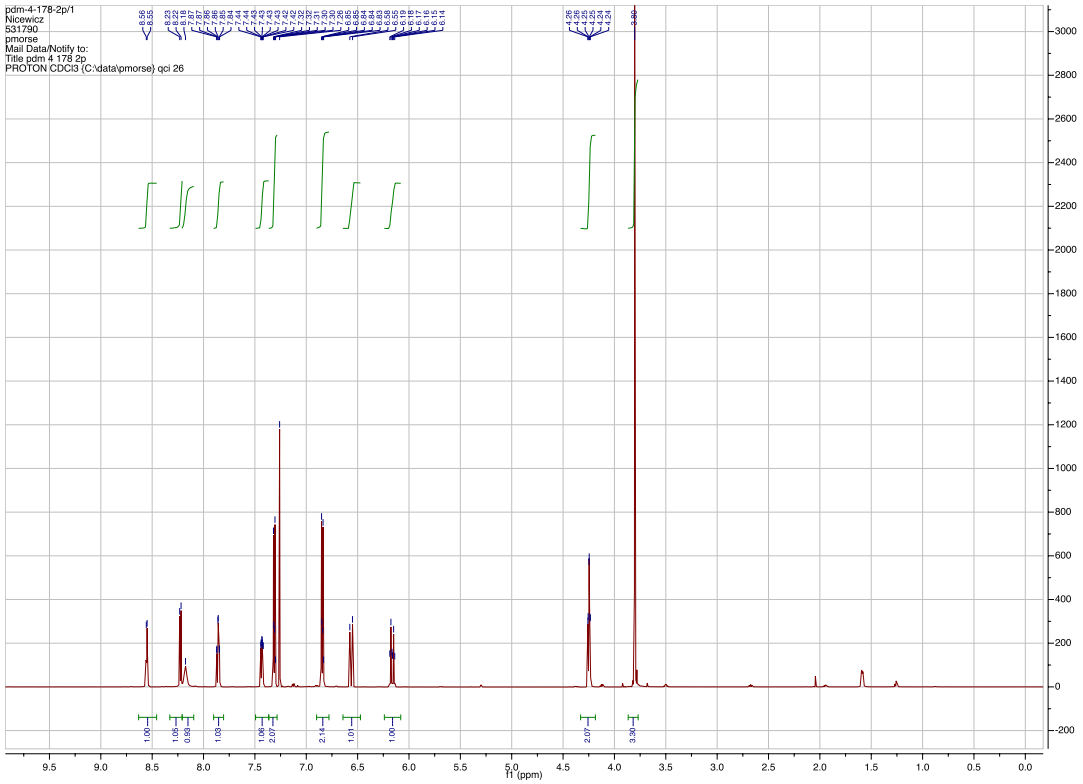


(*E*)-2,2,2-trifluoro-*N*-(3-(4-methoxyphenyl)allyl)acetamide (3g)

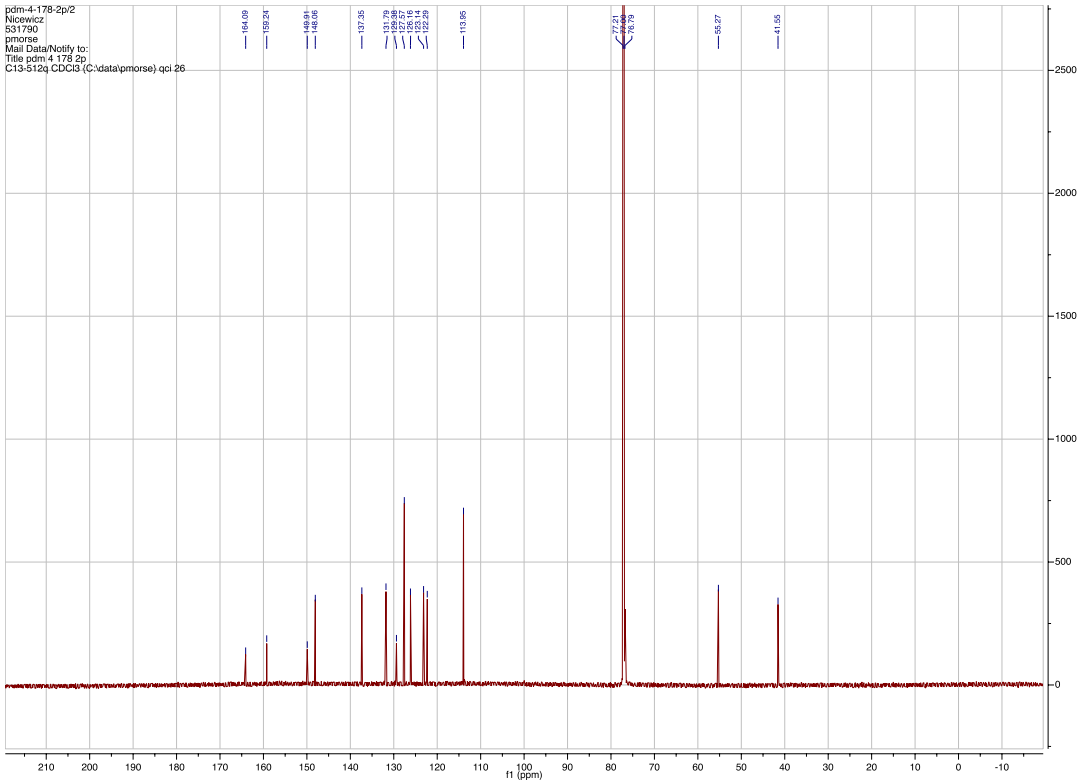


(*E*)-*N*-(3-(4-methoxyphenyl)allyl)picolinamide (3h)

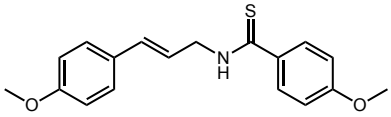


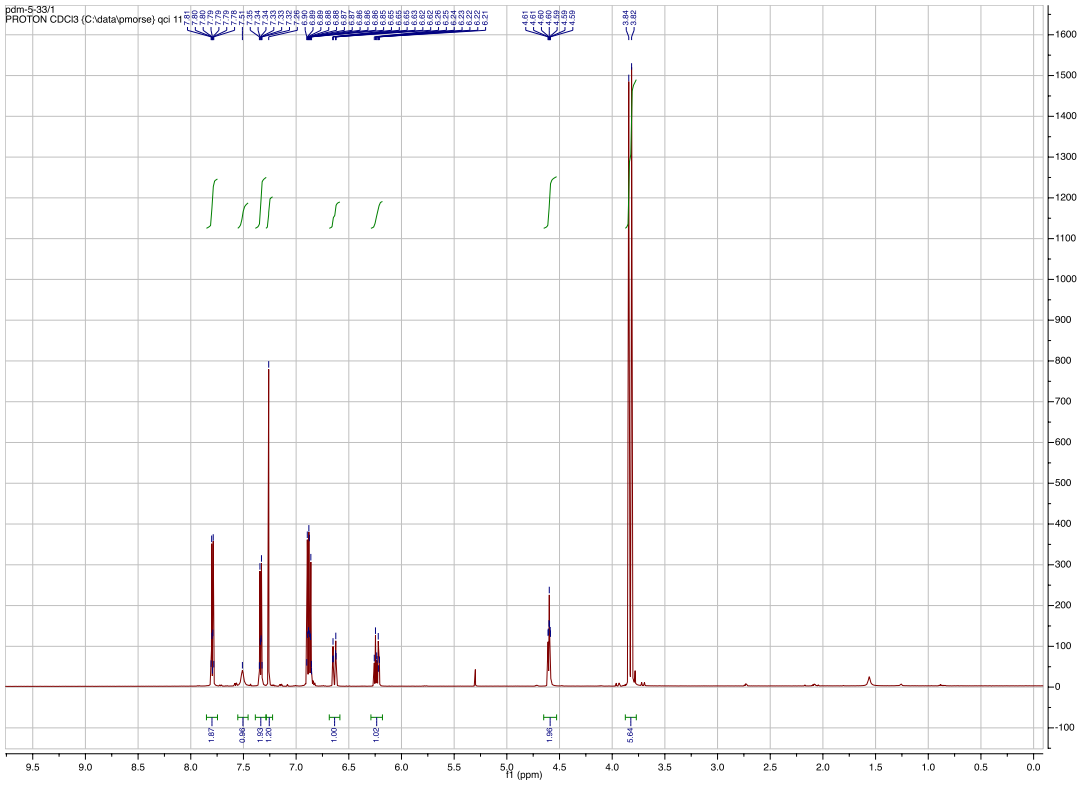


(*E*)-*N*-(3-(4-methoxyphenyl)allyl)picolinamide (3h)

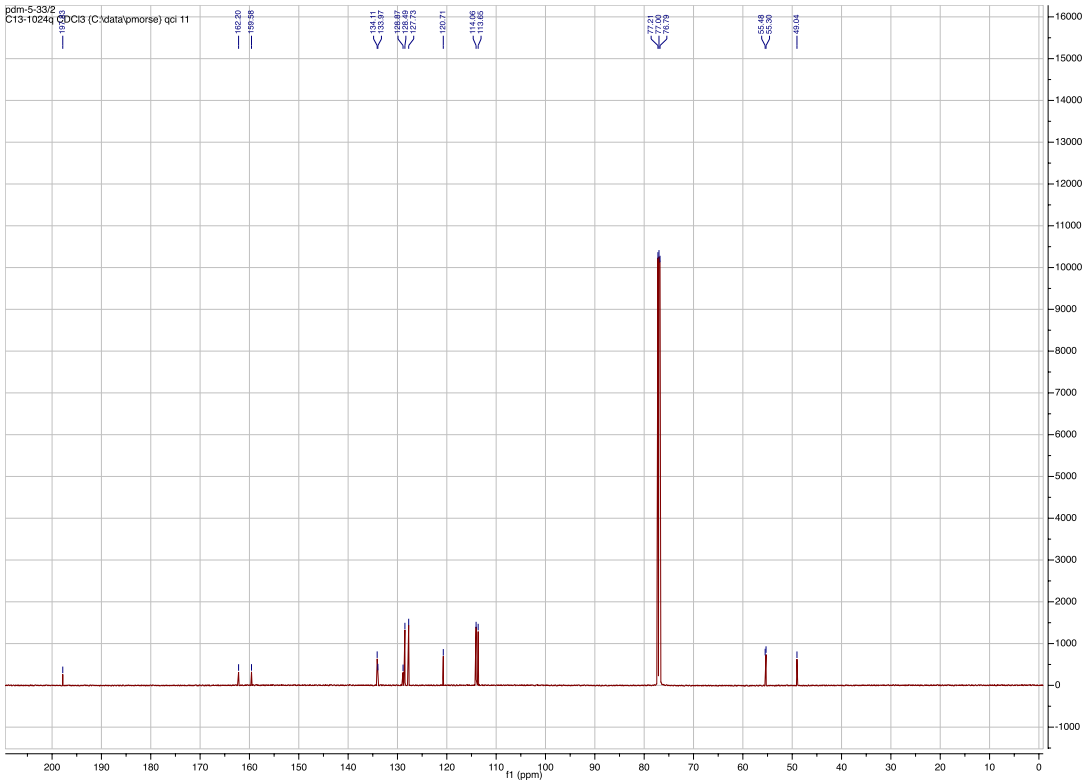


(*E*)-4-methoxy-*N*-(3-(4-methoxyphenyl)allyl)benzothioamide (3n)

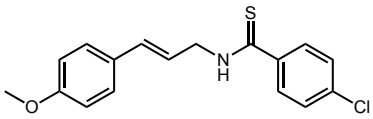


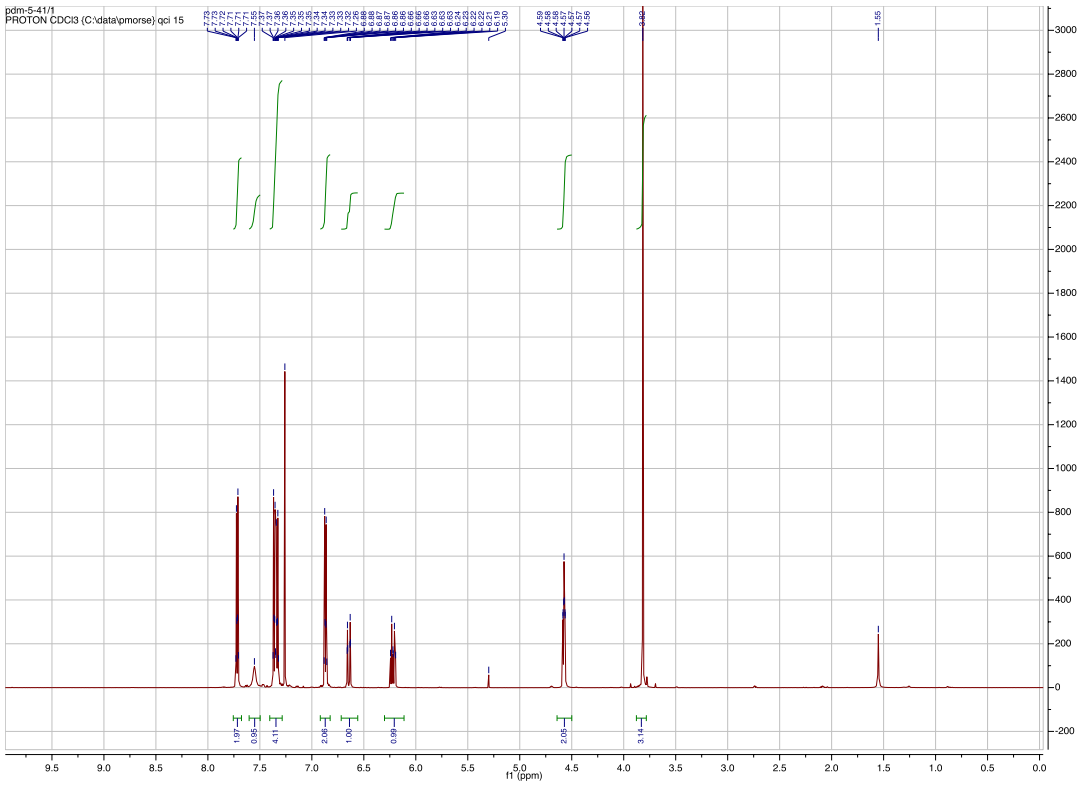


(*E*)-4-methoxy-*N*-(3-(4-methoxyphenyl)allyl)benzothioamide (3n)

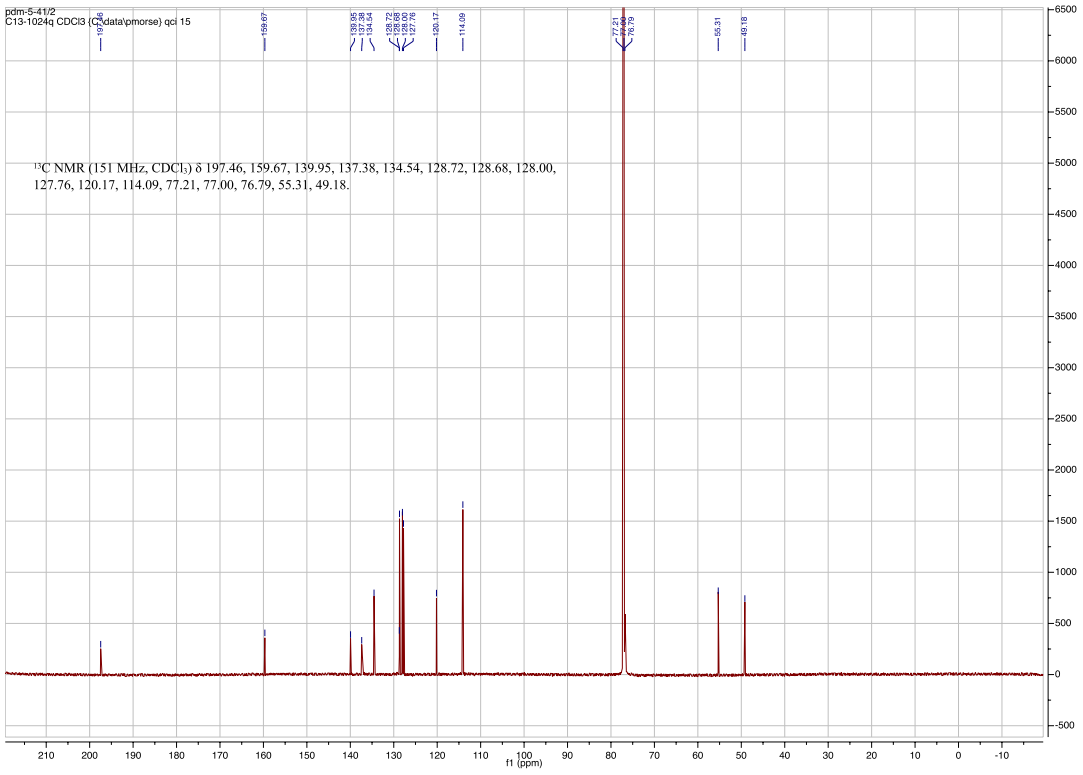


(*E*)-4-chloro-*N*-(3-(4-methoxyphenyl)allyl)benzothioamide (3o)

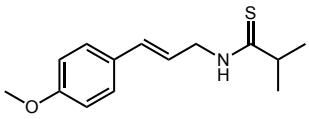


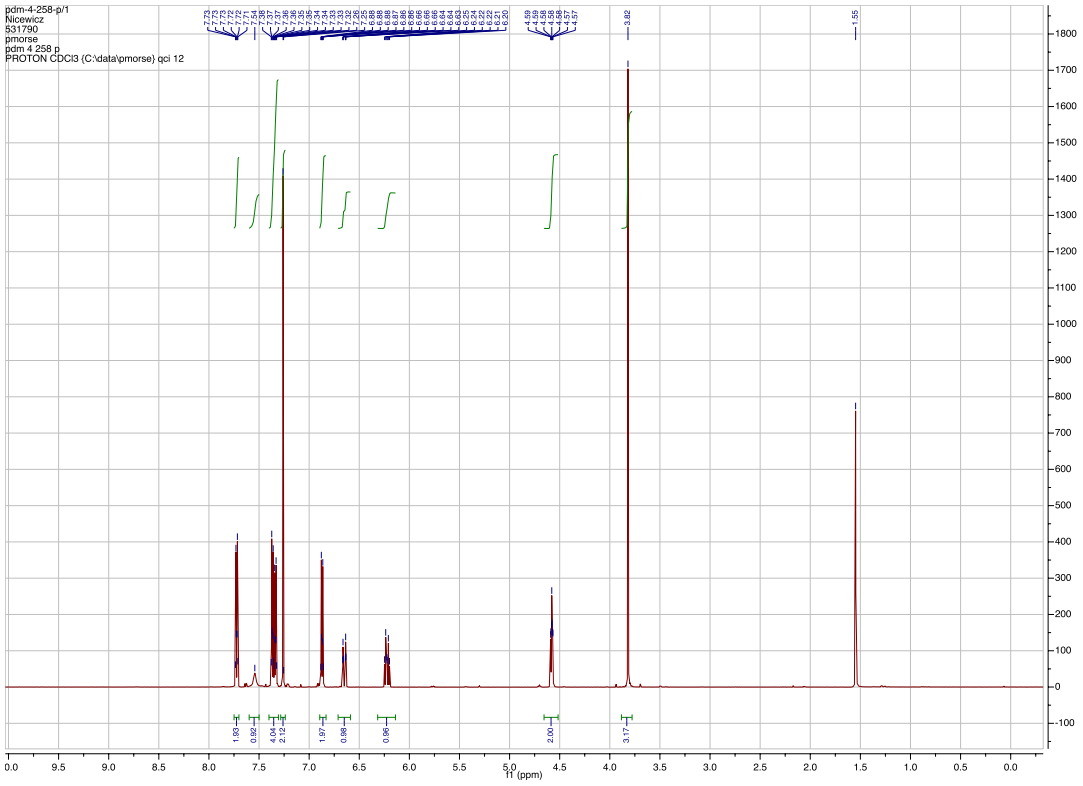


(*E*)-4-chloro-*N*-(3-(4-methoxyphenyl)allyl)benzothioamide (3o)

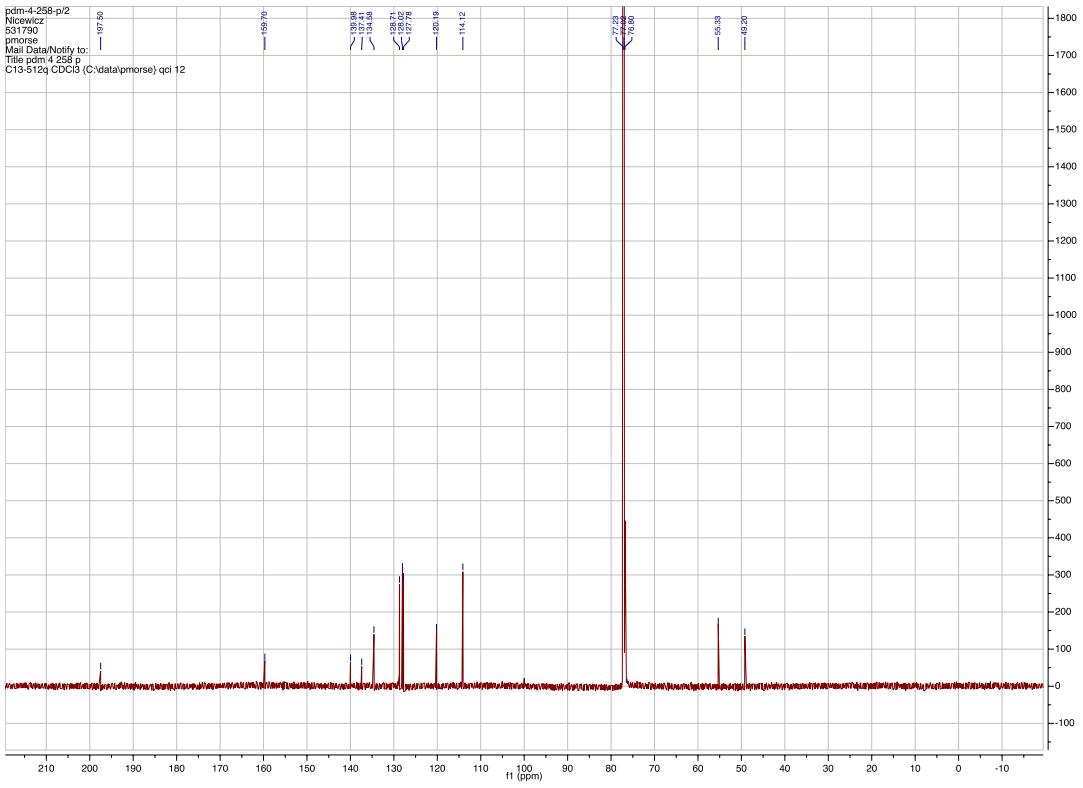


(*E*)-*N*-(3-(4-methoxyphenyl)allyl)-2-methylpropanethioamide (3p)

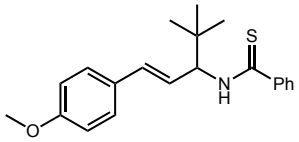


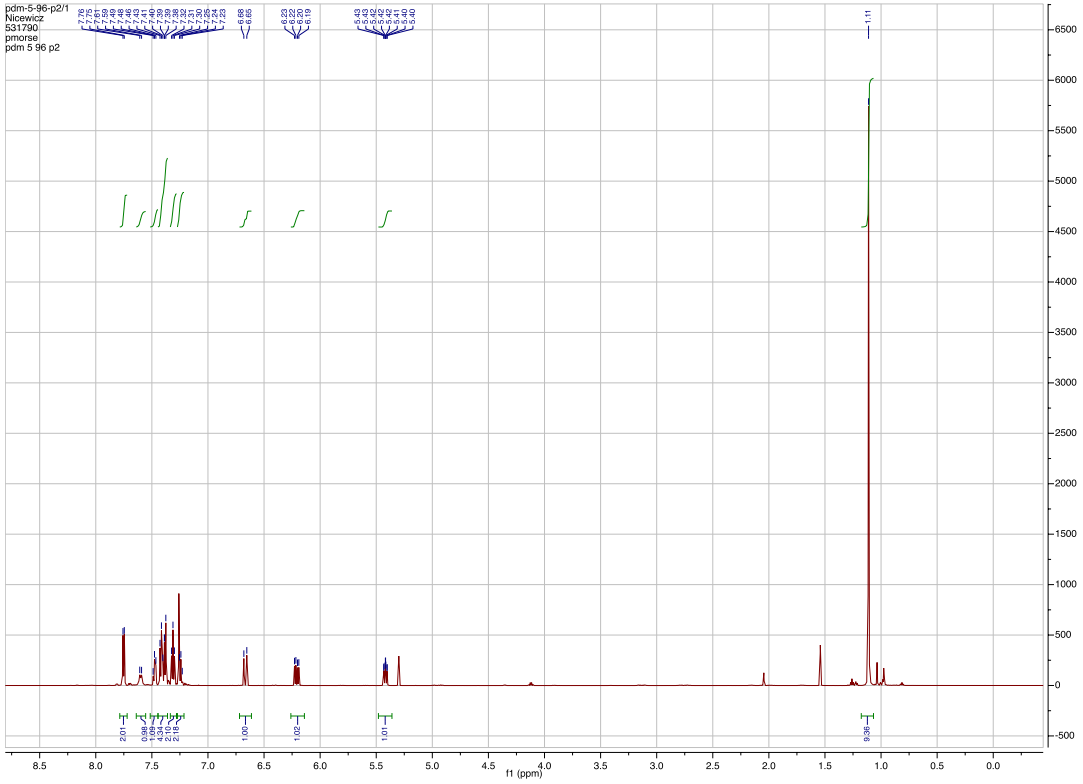


(*E*)-*N*-(3-(4-methoxyphenyl)allyl)-2-methylpropanethioamide (3p)

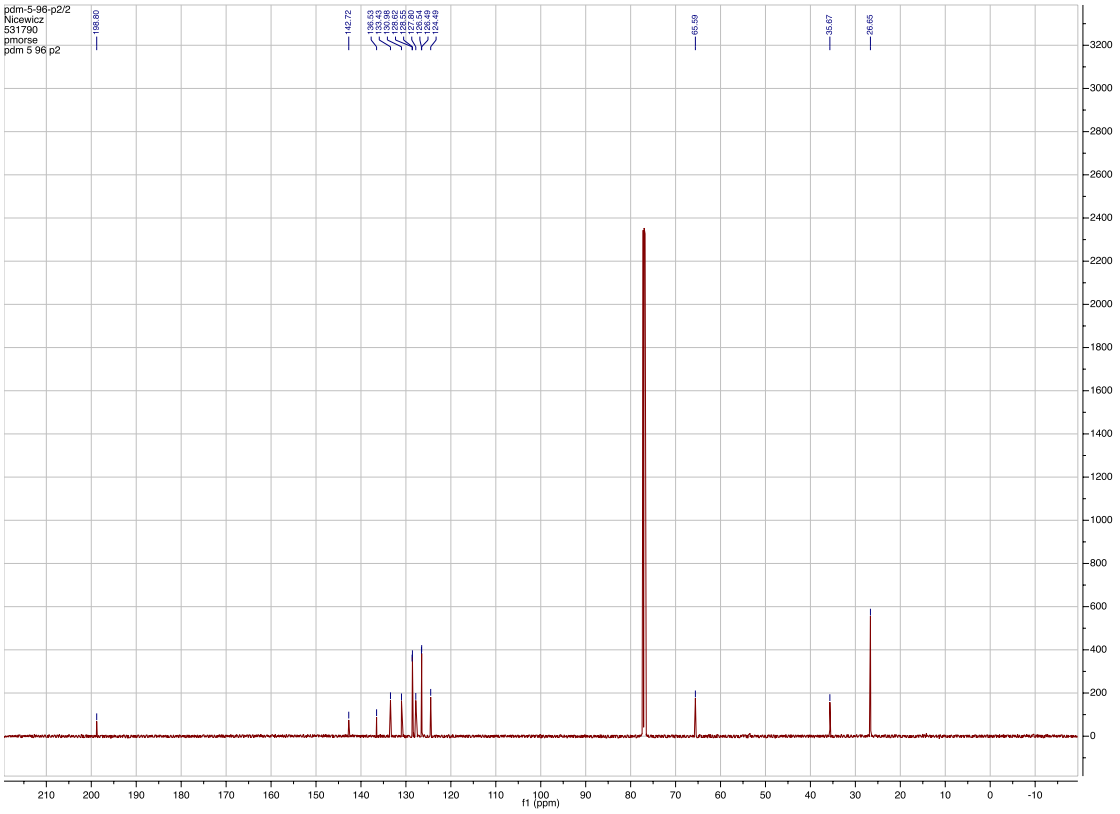


(*E*)-*N*-(4,4-dimethyl-1-phenylpent-1-en-3-yl)benzothioamide (3q)

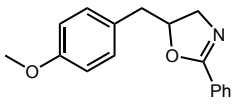


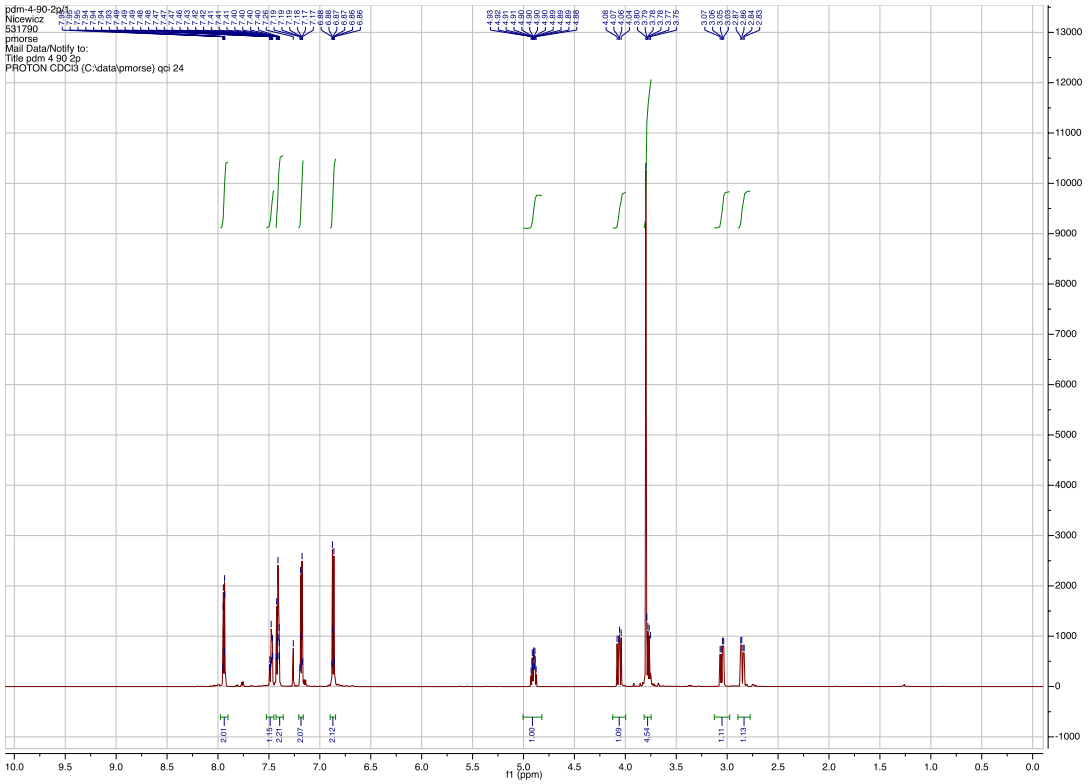


(*E*)-*N*-(4,4-dimethyl-1-phenylpent-1-en-3-yl)benzothioamide (3q)

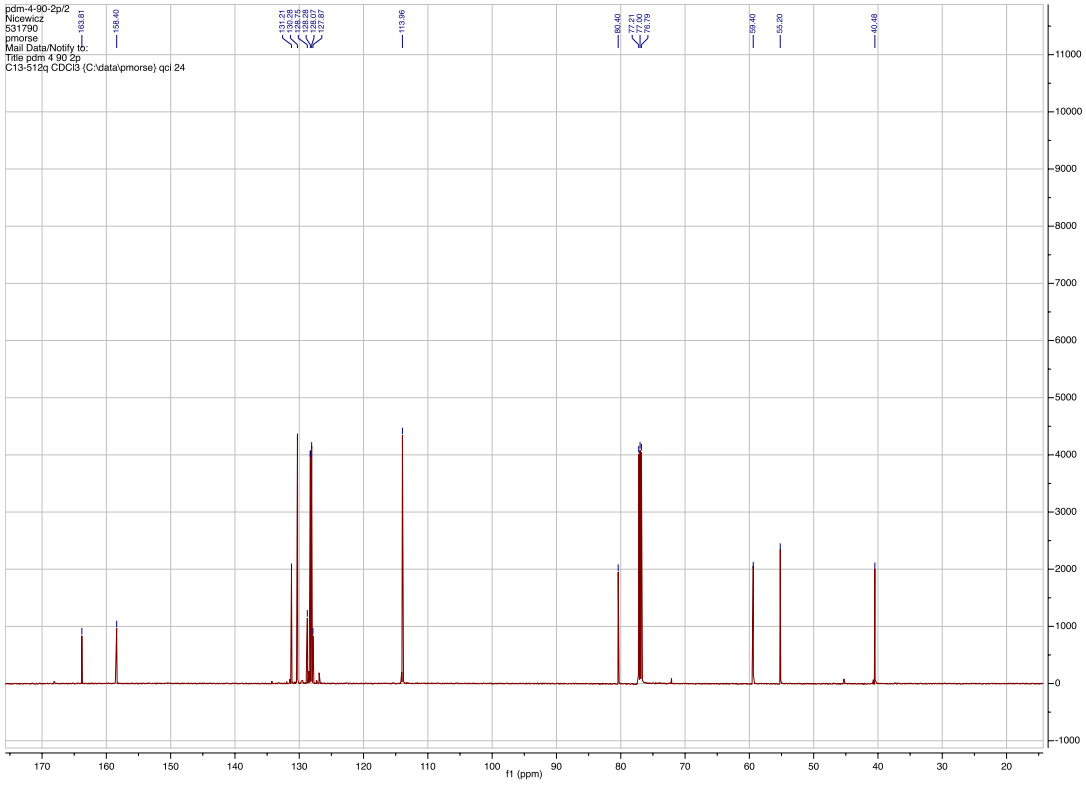


5-(4-methoxybenzyl)-2-phenyl-4,5-dihydrooxazole (4a)

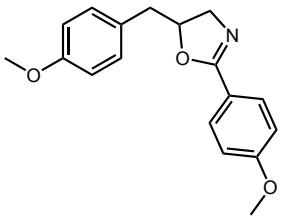


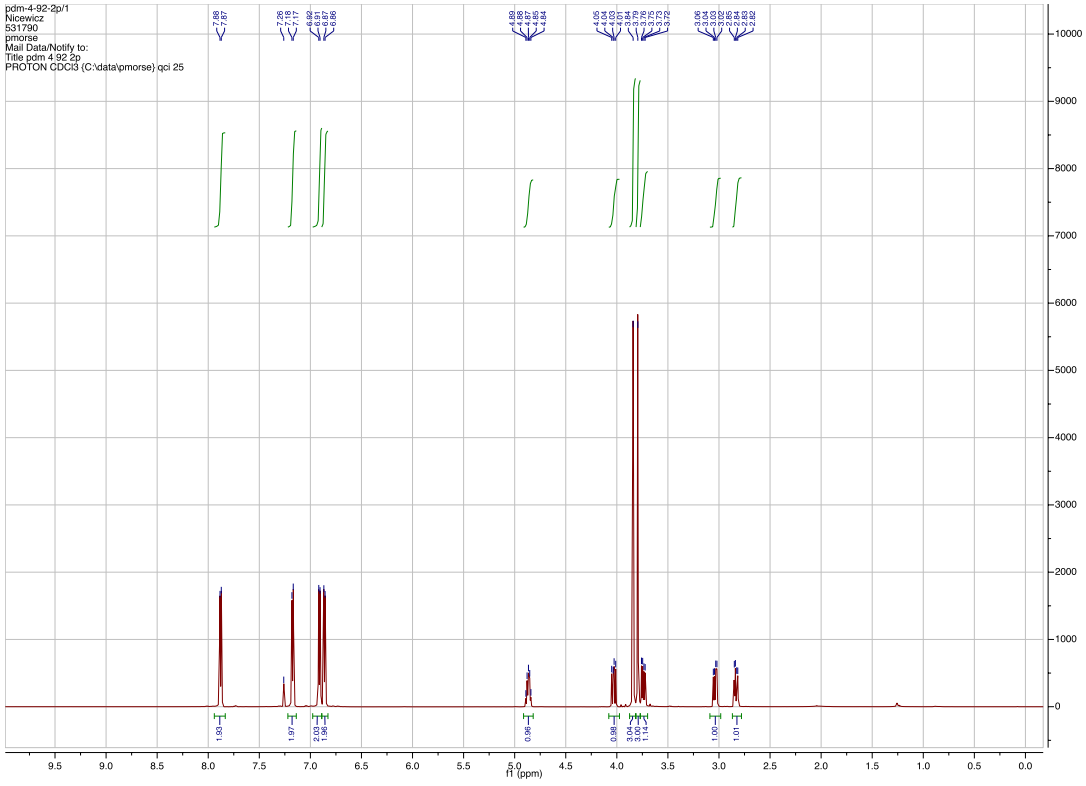


5-(4-methoxybenzyl)-2-phenyl-4,5-dihydrooxazole (4a)

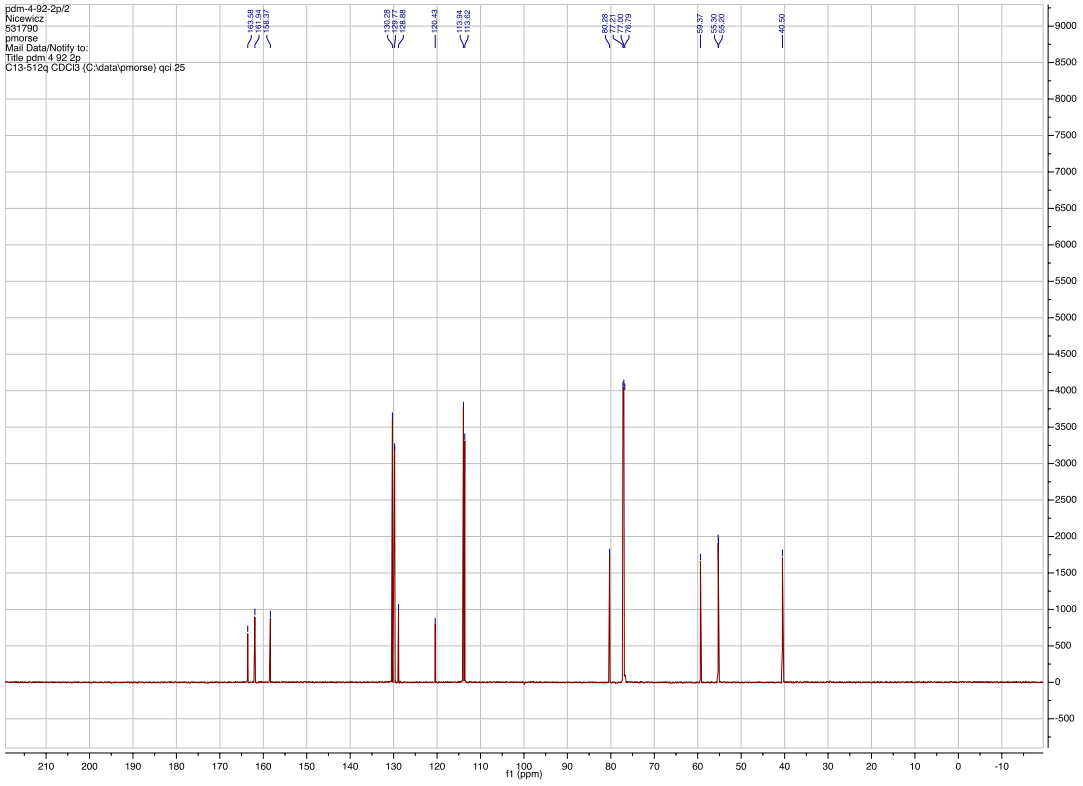


5-(4-methoxybenzyl)-2-(4-methoxyphenyl)-4,5-dihydrooxazole (4b)

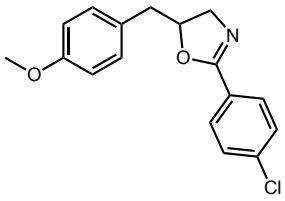


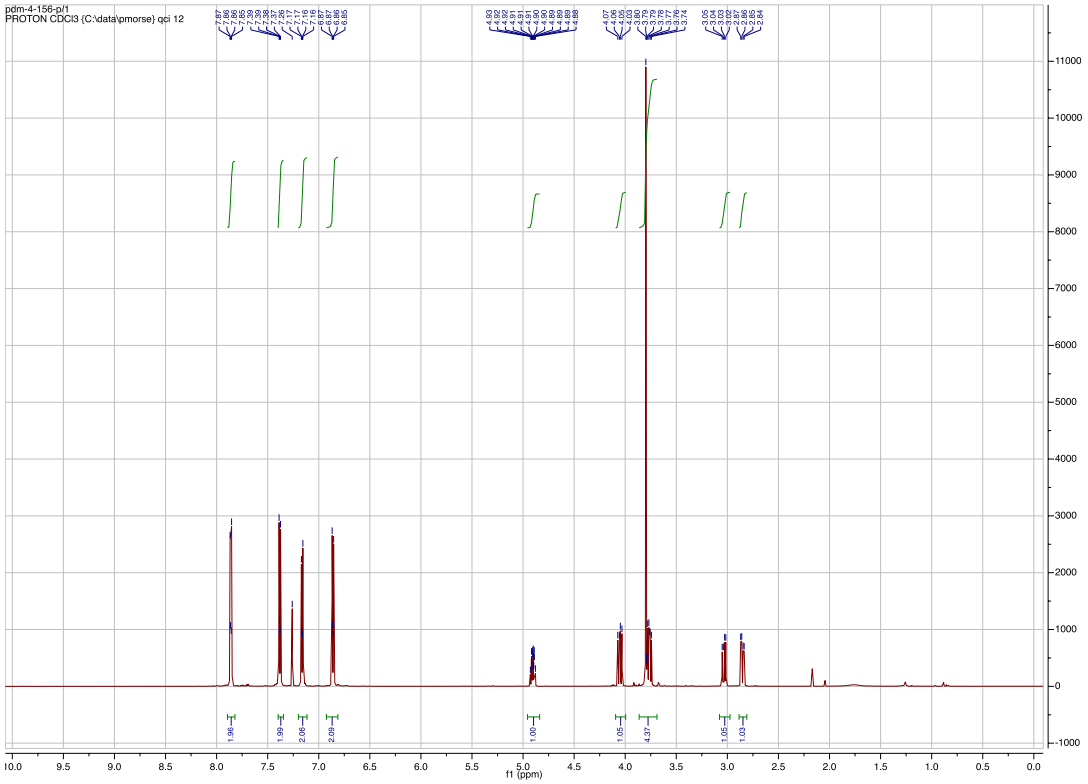


5-(4-methoxybenzyl)-2-(4-methoxyphenyl)-4,5-dihydrooxazole (4b)

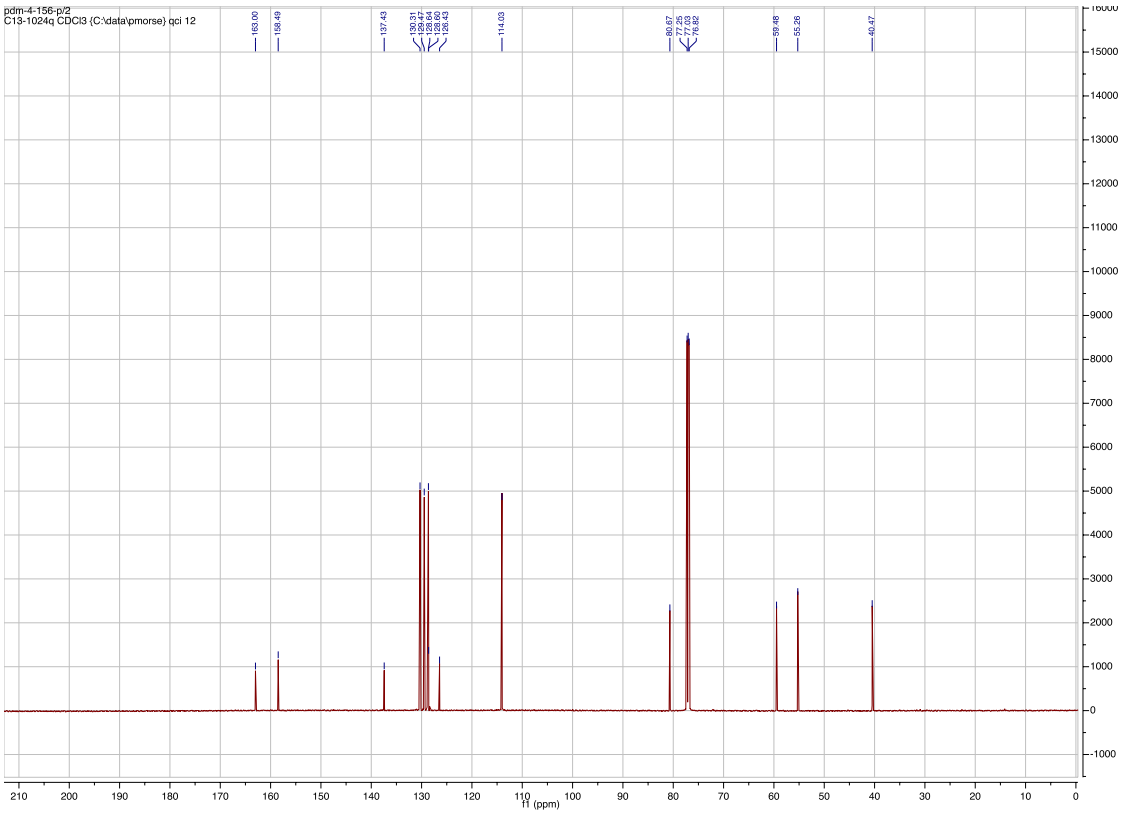


2-(4-chlorophenyl)-5-(4-methoxybenzyl)-4,5-dihydrooxazole (4c)

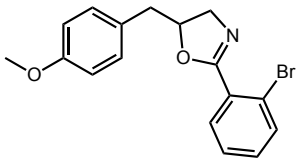


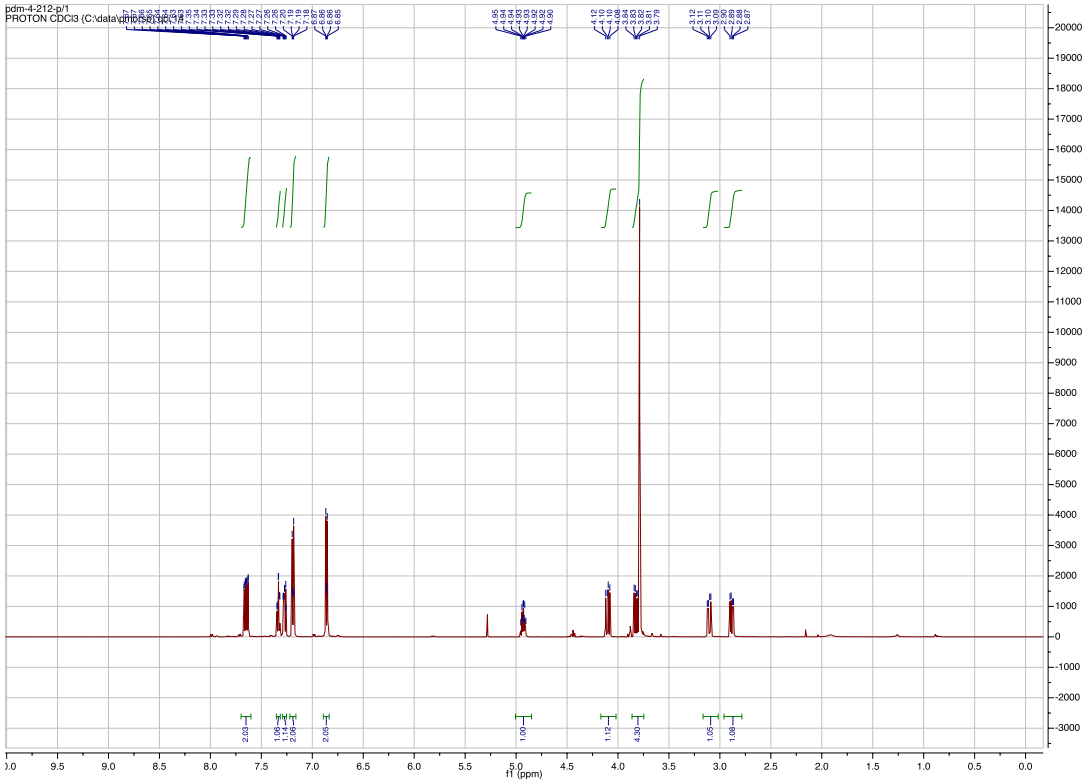


2-(4-chlorophenyl)-5-(4-methoxybenzyl)-4,5-dihydrooxazole (4c)

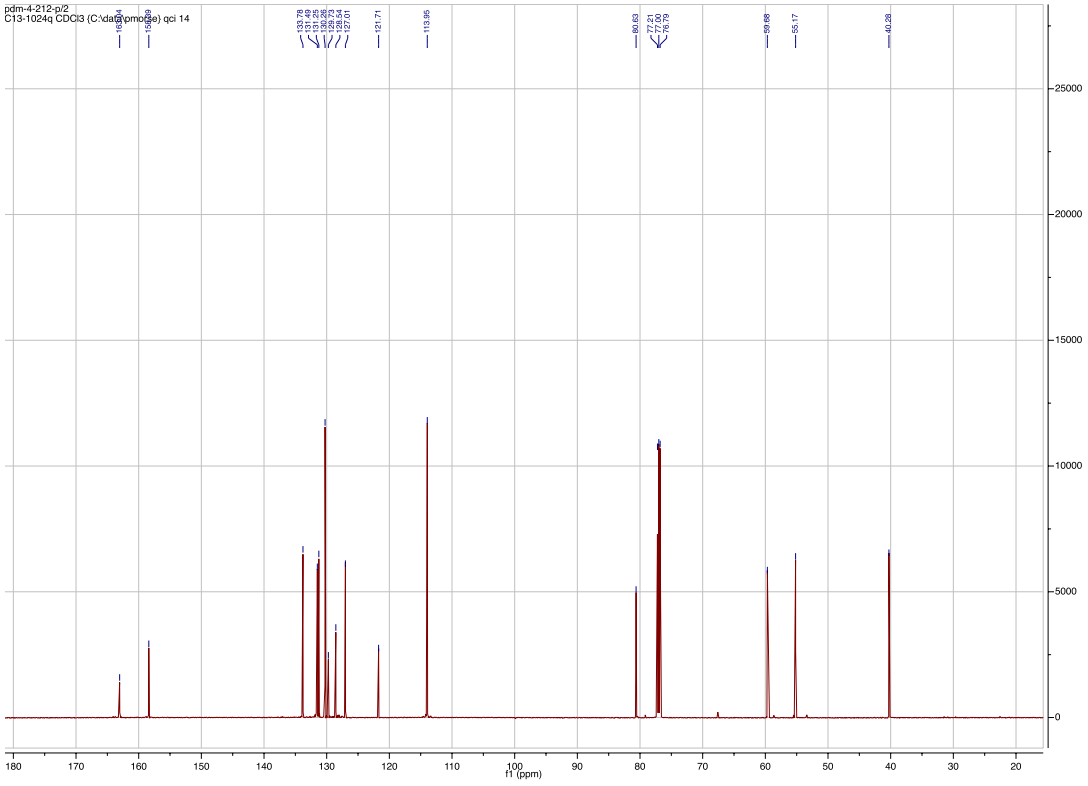


2-(2-bromophenyl)-5-(4-methoxybenzyl)-4,5-dihydrooxazole (4d)

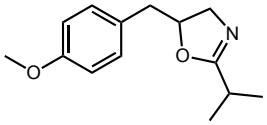


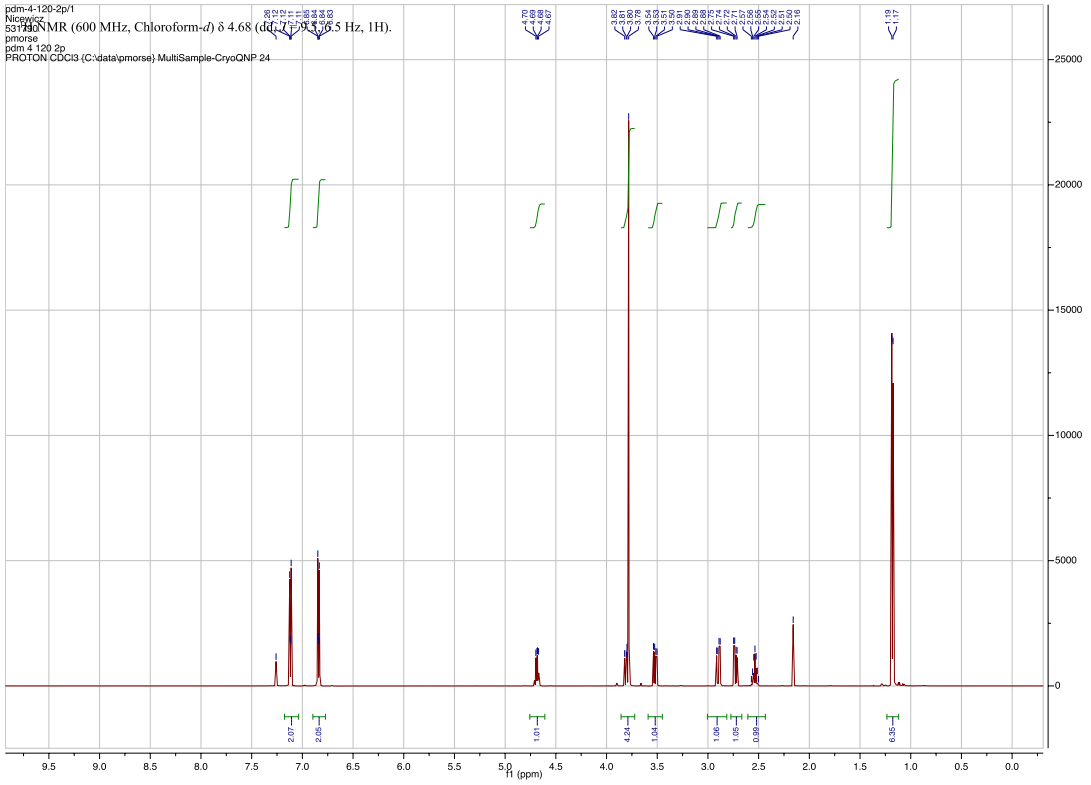


2-(2-bromophenyl)-5-(4-methoxybenzyl)-4,5-dihydrooxazole (4d)

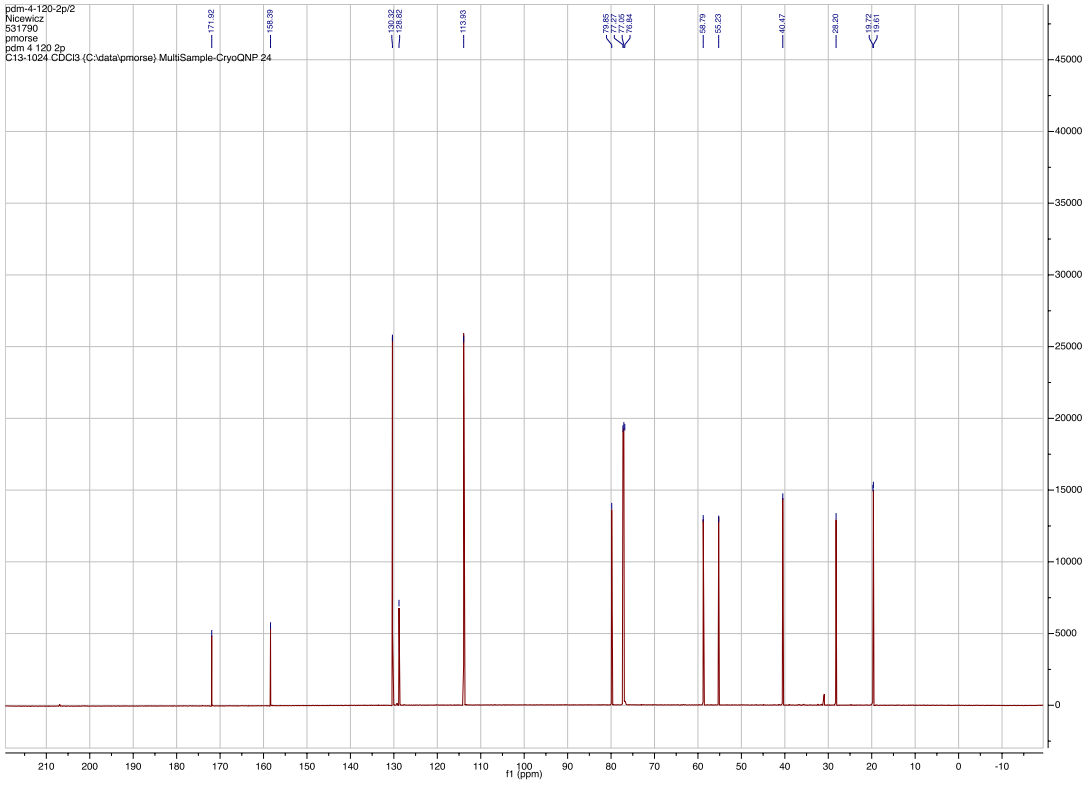


2-isopropyl-5-(4-methoxybenzyl)-4,5-dihydrooxazole (4e)

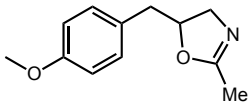




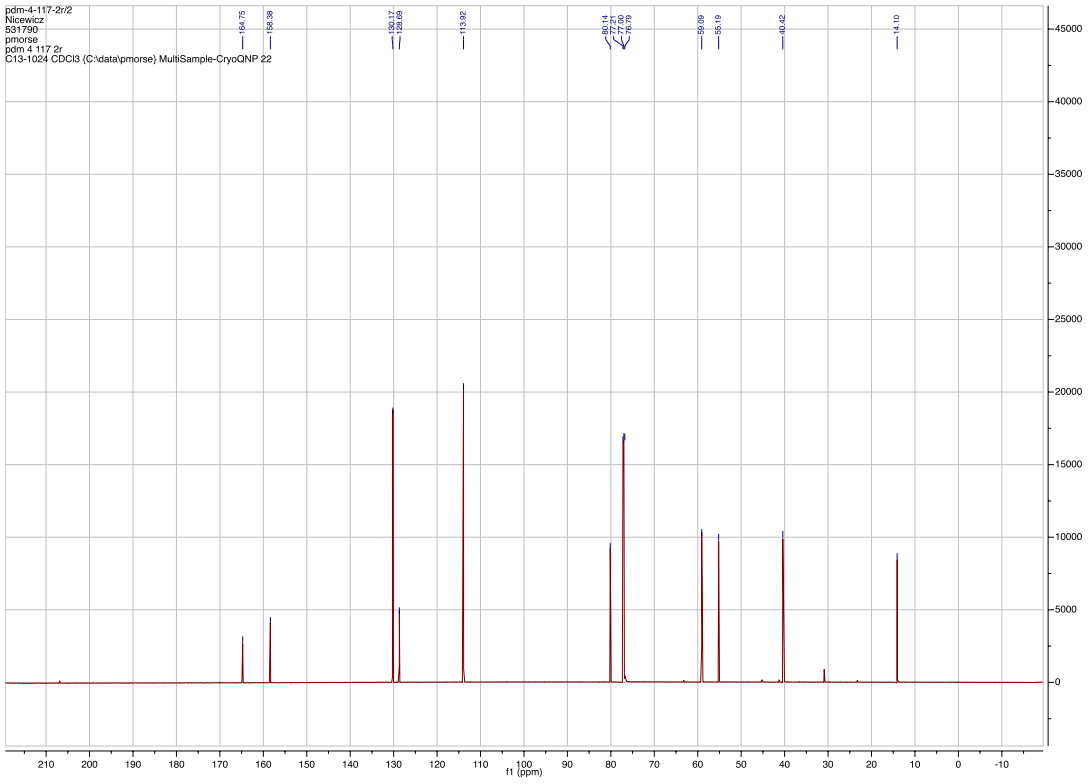
2-isopropyl-5-(4-methoxybenzyl)-4,5-dihydrooxazole (4e)



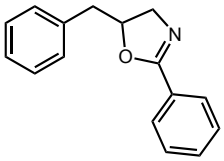
5-(4-methoxybenzyl)-2-methyl-4,5-dihydrooxazole (4f)



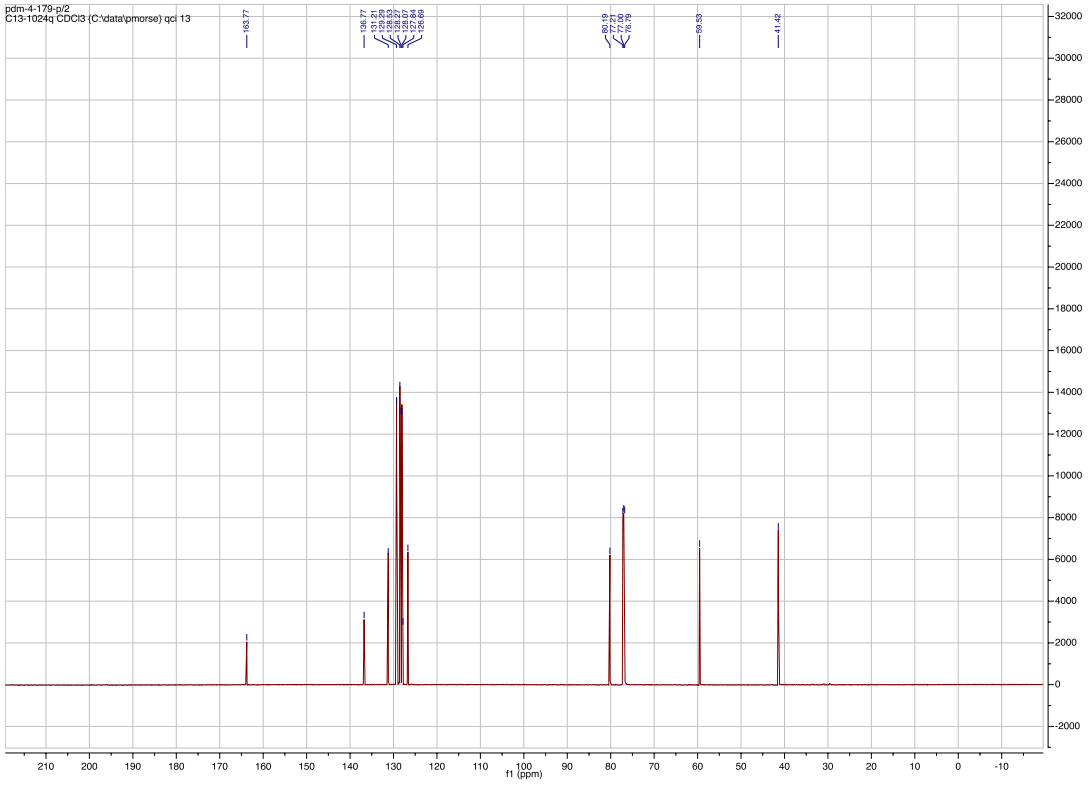
5-(4-methoxybenzyl)-2-methyl-4,5-dihydrooxazole (4f)



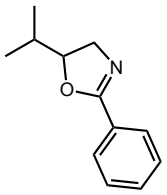
5-(4-methoxybenzyl)-2-phenyl-4,5-dihydrooxazole (4i)

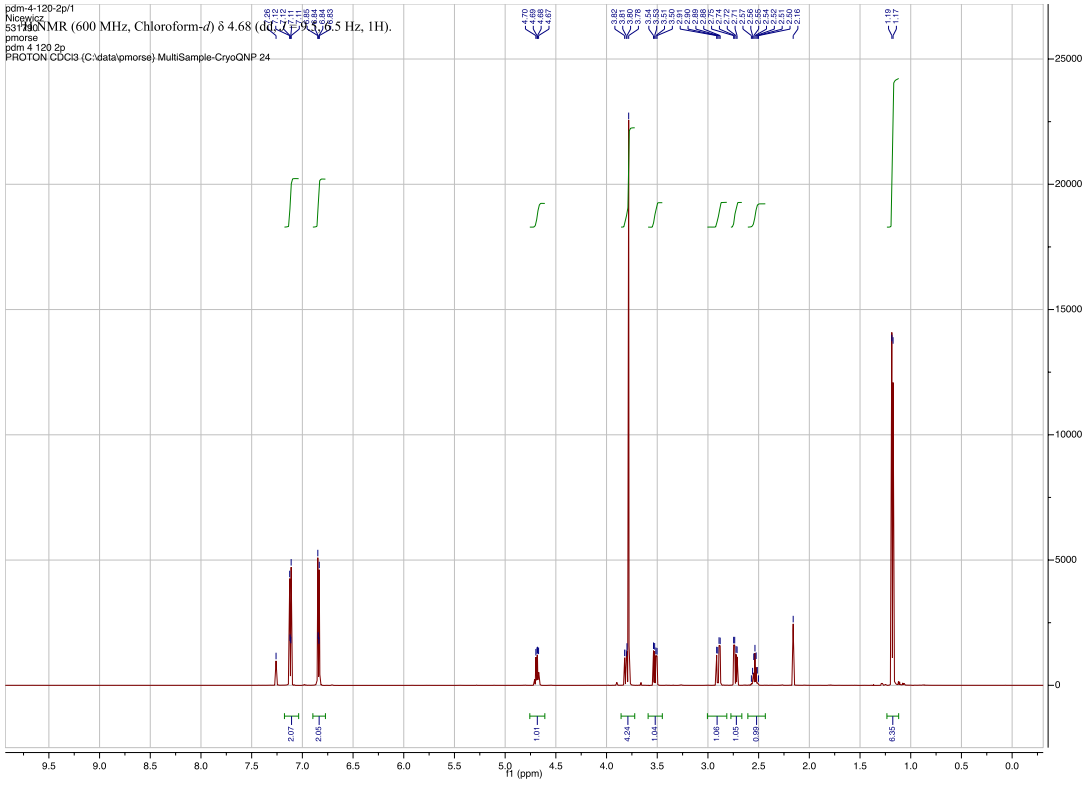


5-(4-methoxybenzyl)-2-phenyl-4,5-dihydrooxazole (4i)

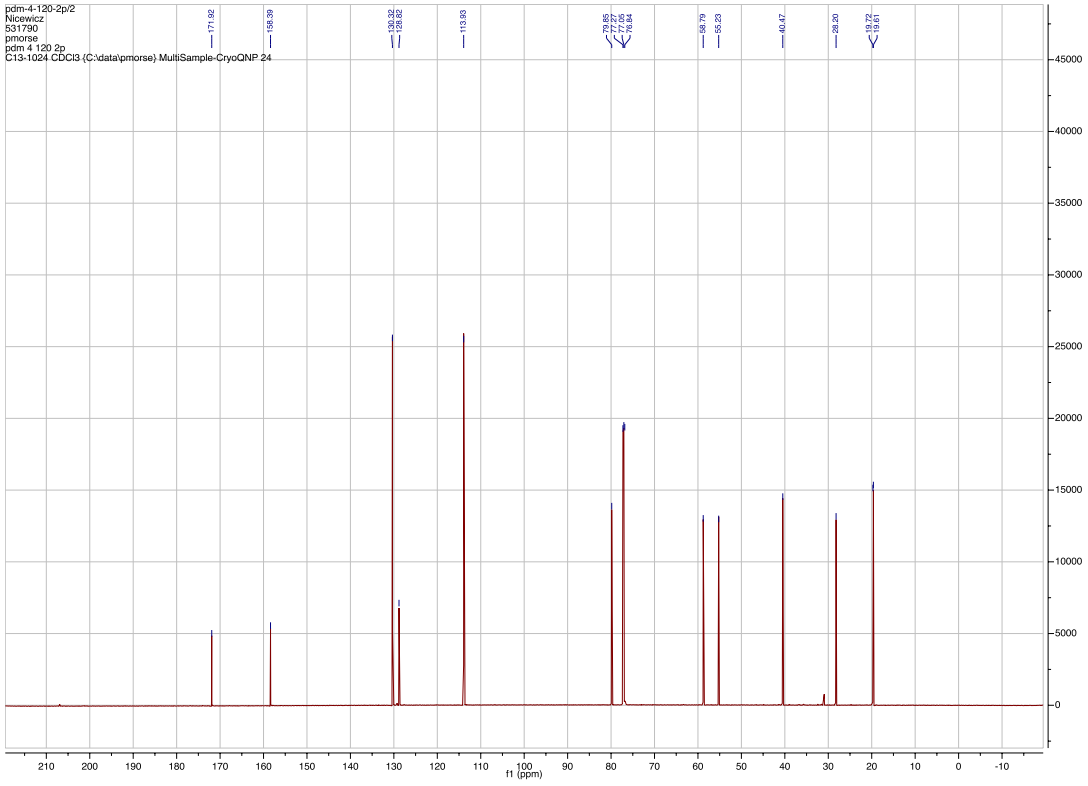


5-isopropyl-2-phenyl-4,5-dihydrooxazole (4j)

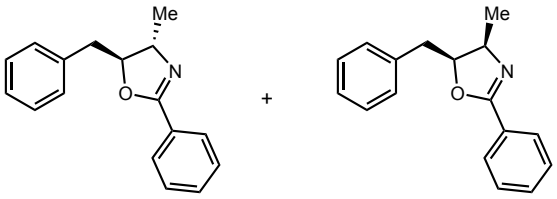


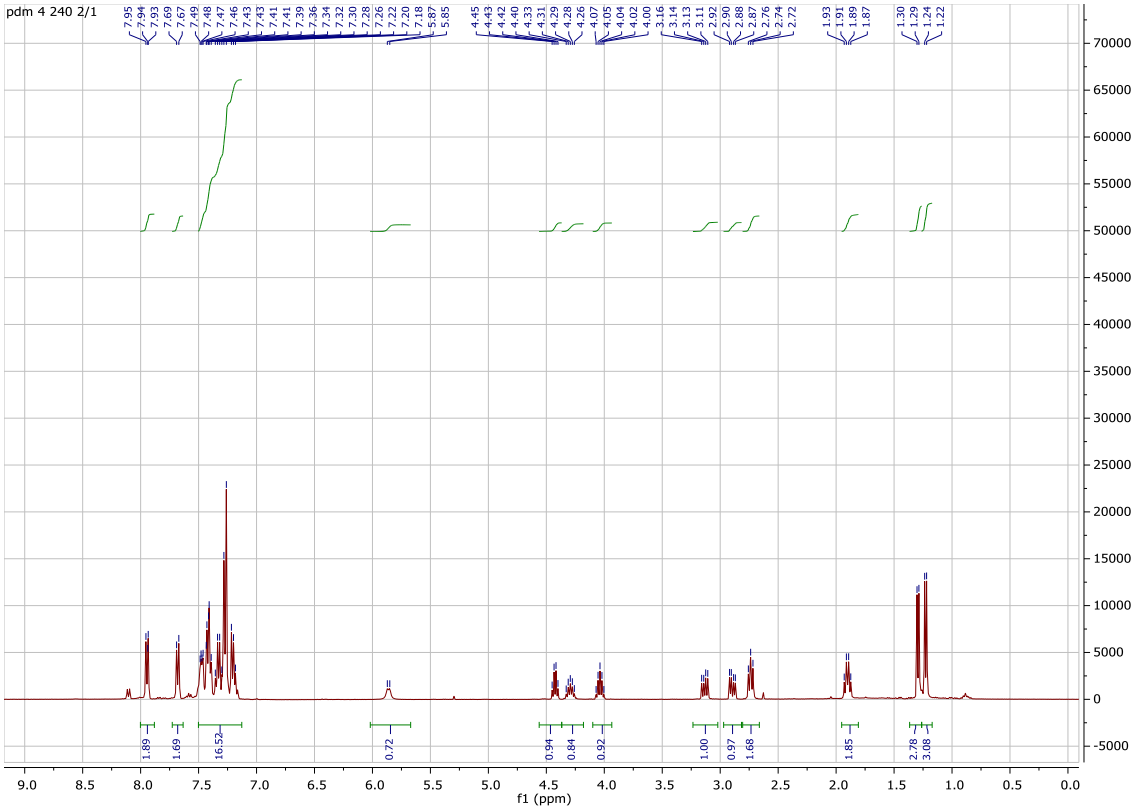


5-isopropyl-2-phenyl-4,5-dihydrooxazole (4j)

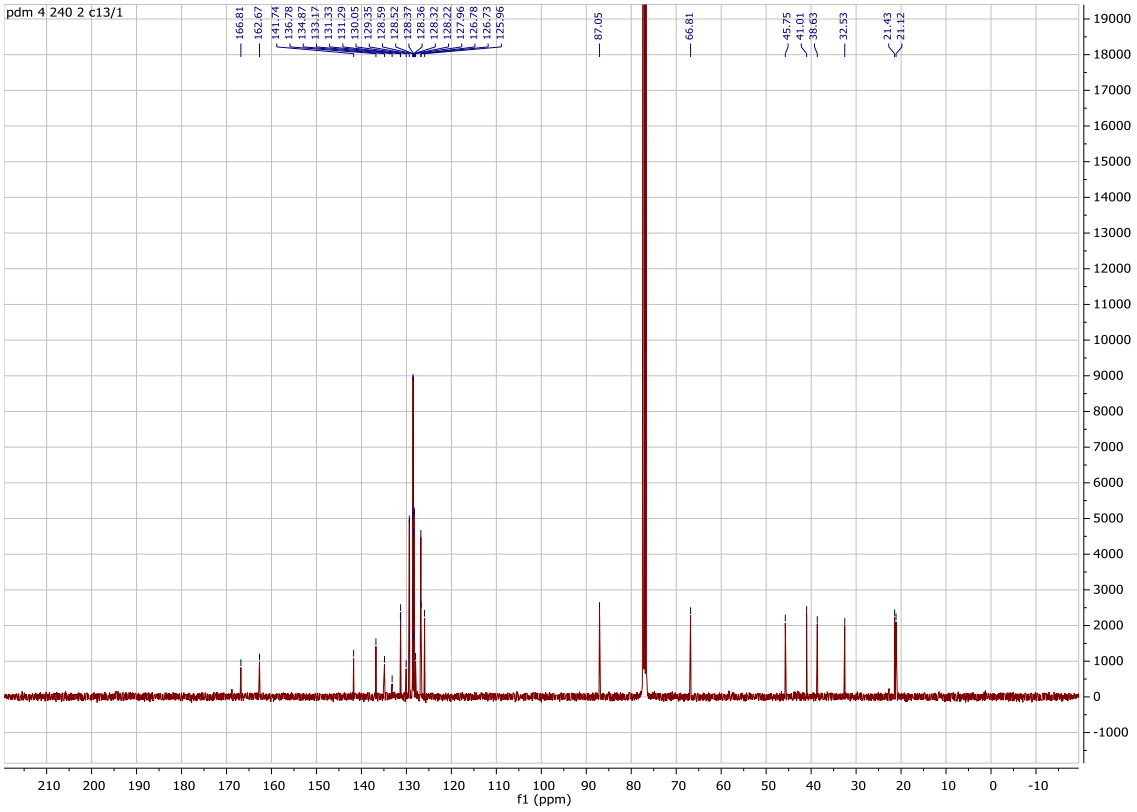


5-benzyl-4-methyl-2-phenyl-4,5-dihydrooxazole (4k):

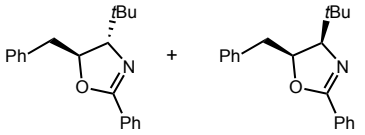


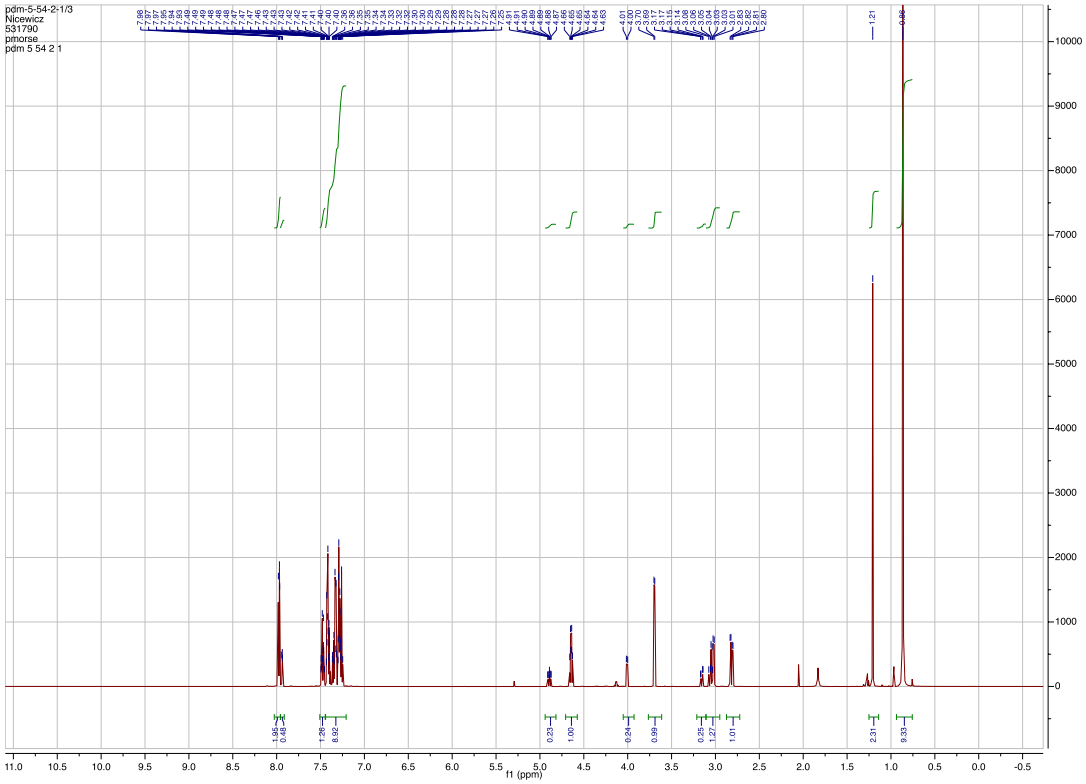


5-benzyl-4-methyl-2-phenyl-4,5-dihydrooxazole (4k):

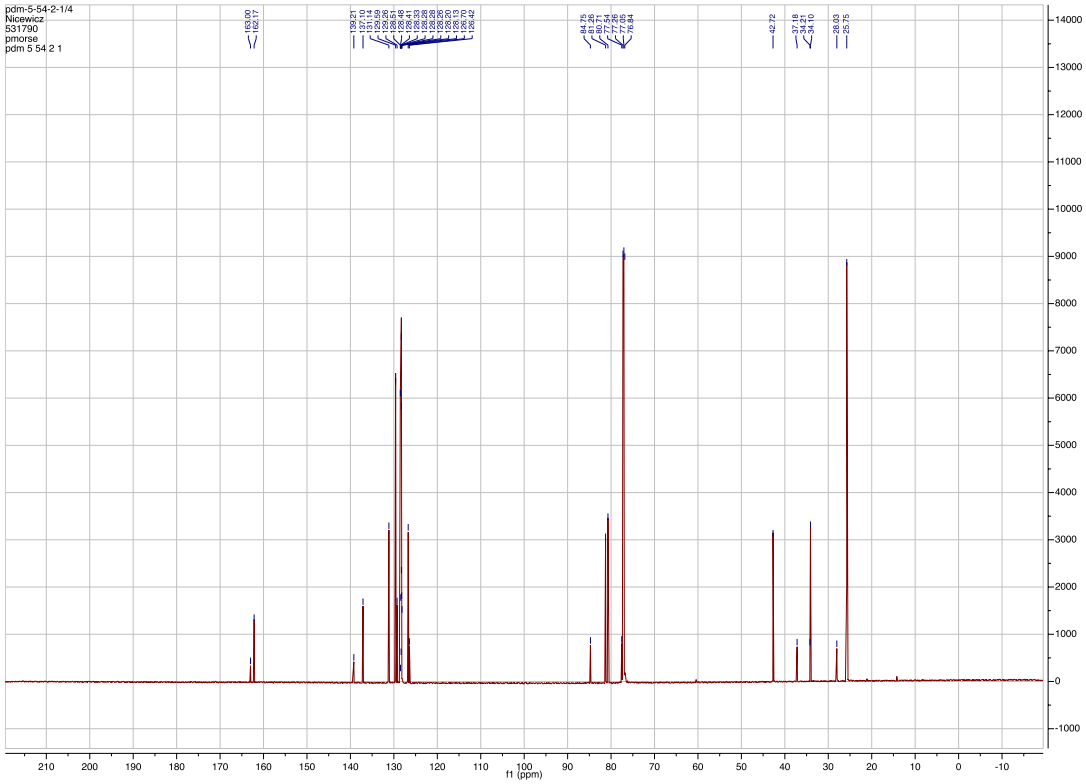


5-benzyl-4-(*tert*-butyl)-2-phenyl-4,5-dihydrooxazole (4l)

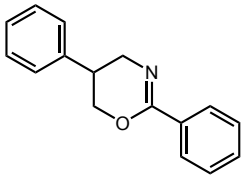


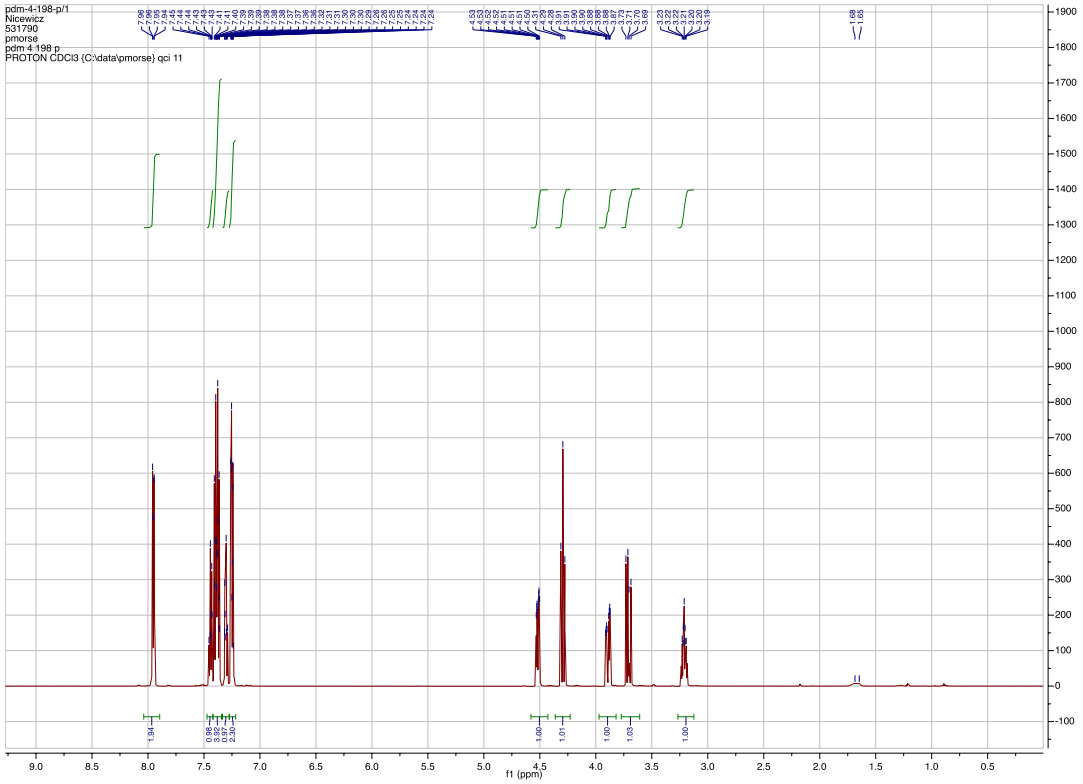


5-benzyl-4-(*tert*-butyl)-2-phenyl-4,5-dihydrooxazole (4l)

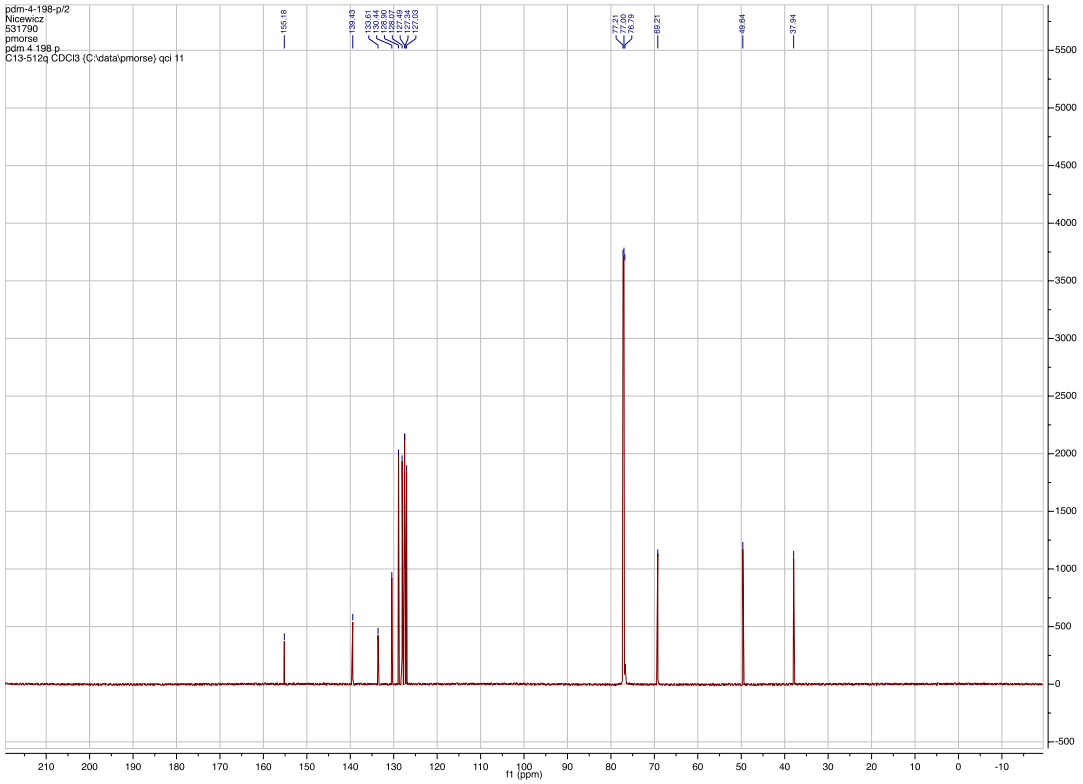


2,5-diphenyl-5,6-dihydro-4*H*-1,3-oxazine (4m)

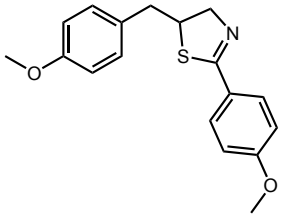


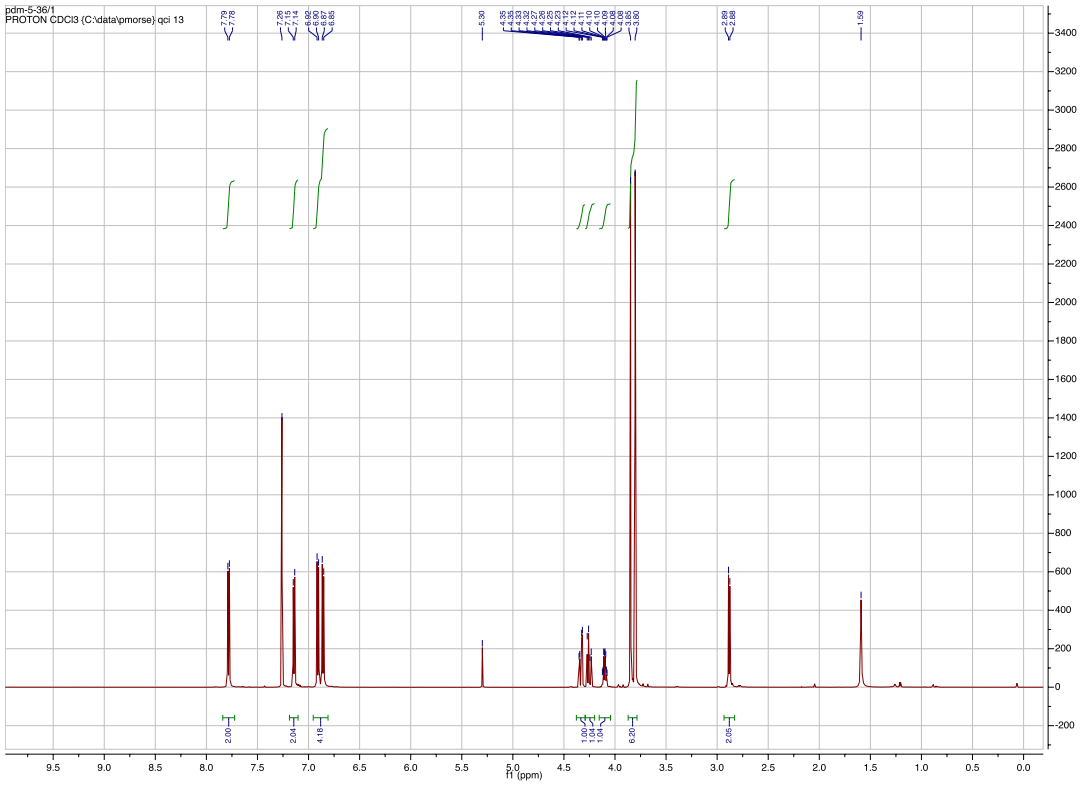


2,5-diphenyl-5,6-dihydro-4*H*-1,3-oxazine (4m)

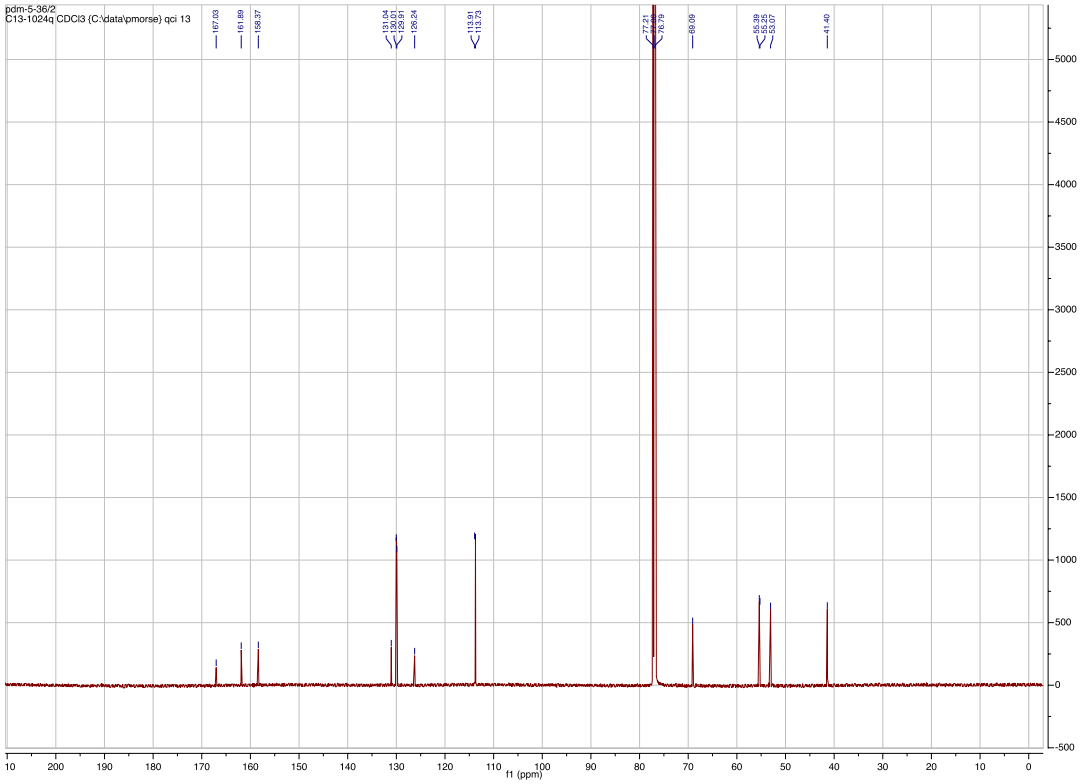


5-(4-methoxybenzyl)-2-(4-methoxyphenyl)-4,5-dihydrothiazole (4n)

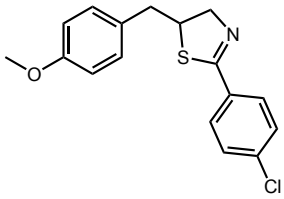


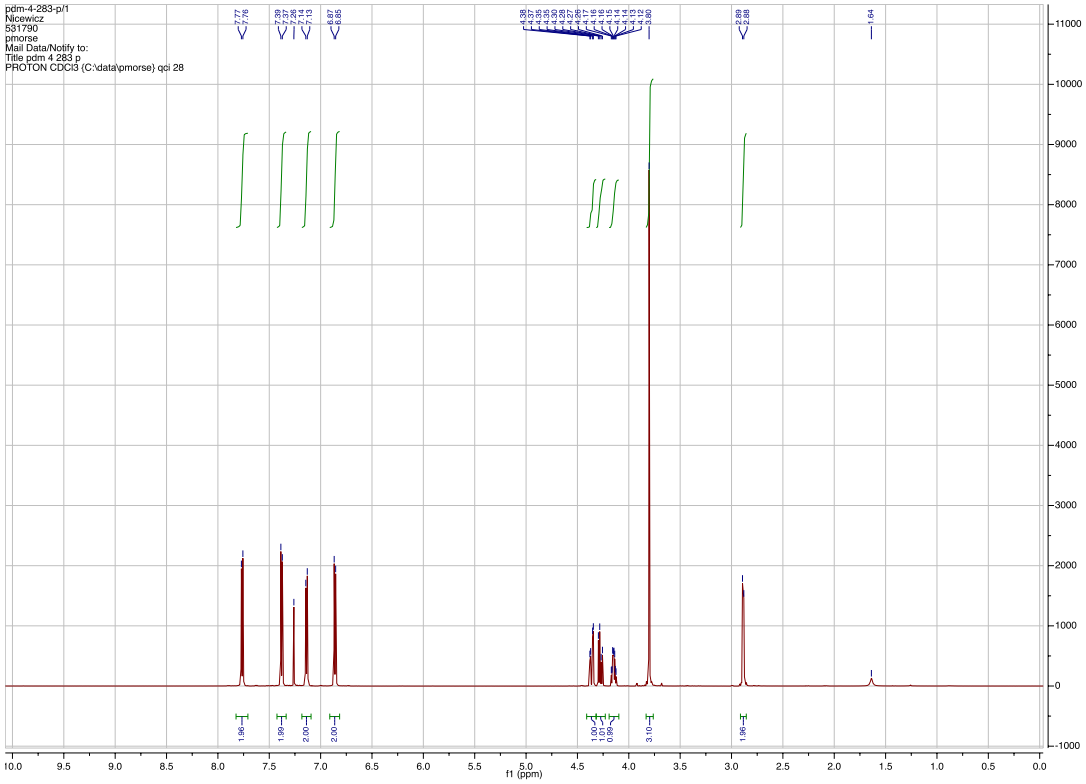


5-(4-methoxybenzyl)-2-(4-methoxyphenyl)-4,5-dihydrothiazole (4n)

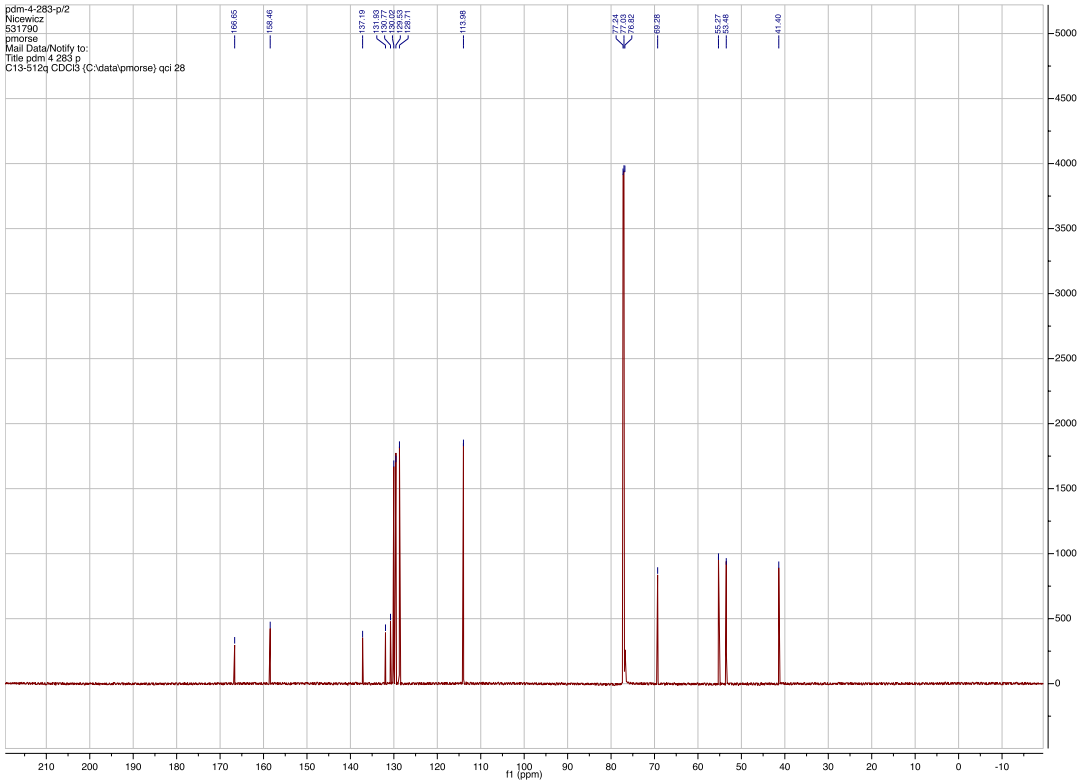


2-(4-chlorophenyl)-5-(4-methoxybenzyl)-4,5-dihydrothiazole (4o)

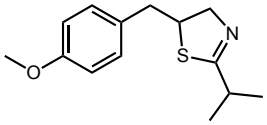


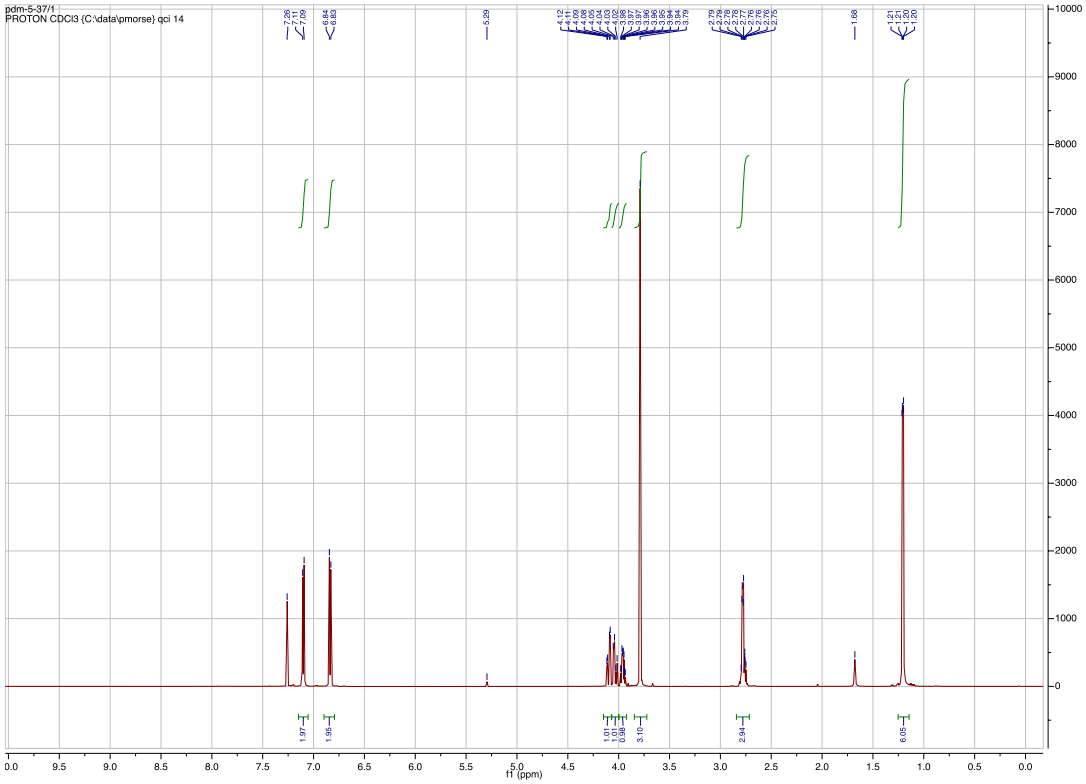


2-(4-chlorophenyl)-5-(4-methoxybenzyl)-4,5-dihydrothiazole (4o)

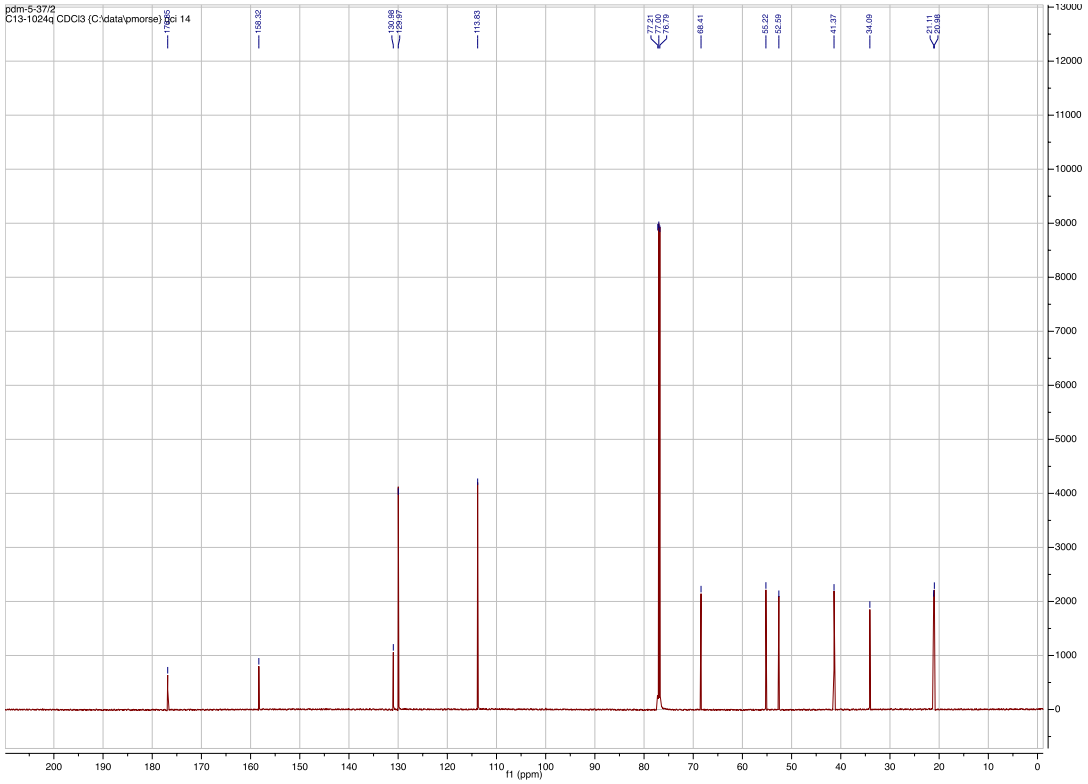


2-isopropyl-5-(4-methoxybenzyl)-4,5-dihydrothiazole (4p)

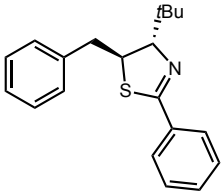


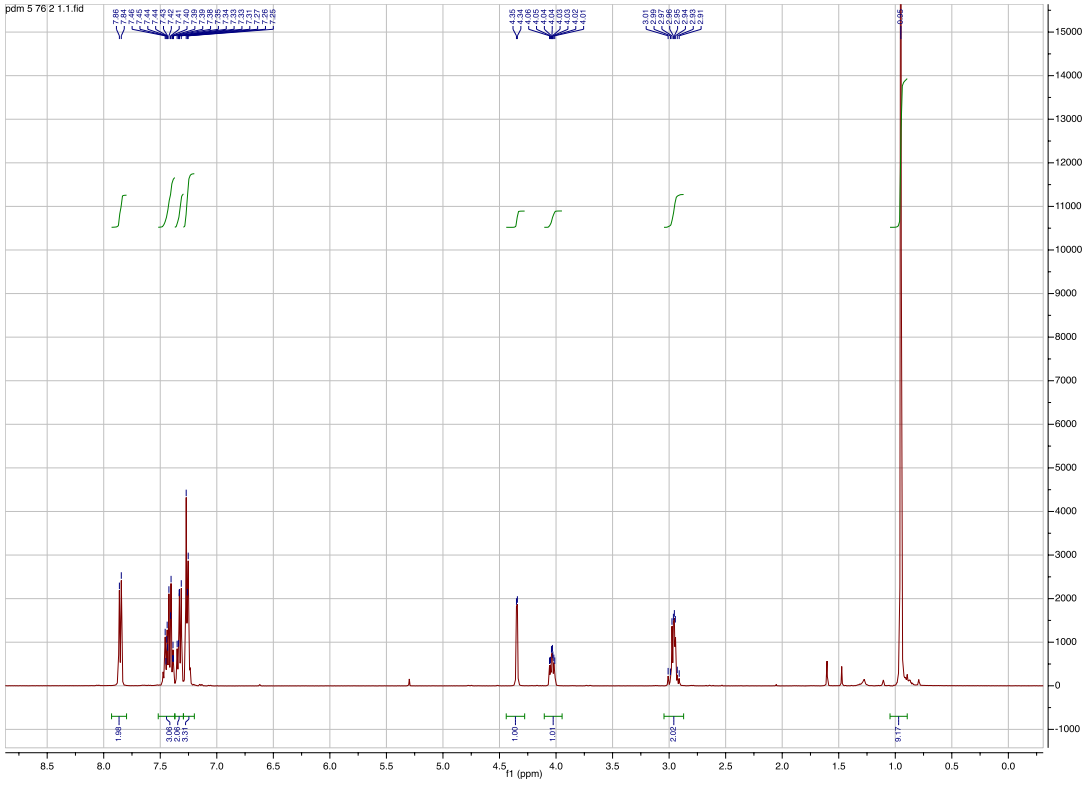


2-isopropyl-5-(4-methoxybenzyl)-4,5-dihydrothiazole (4p)

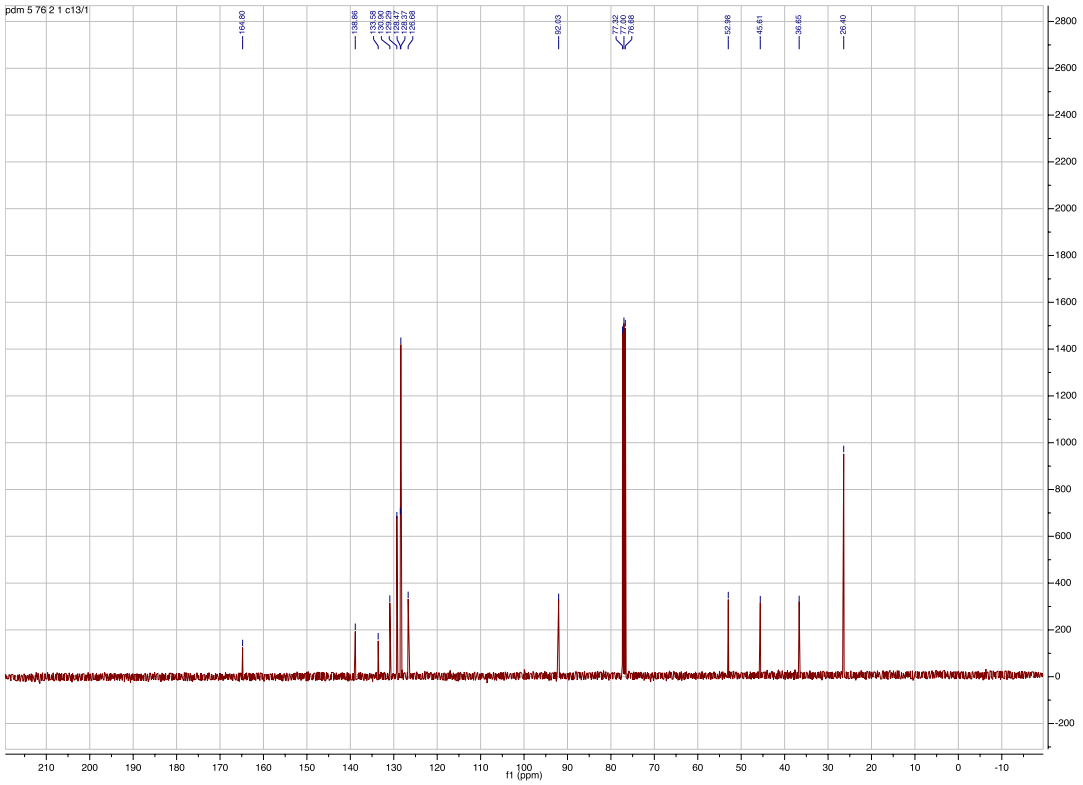


5-benzyl-4-(*tert*-butyl)-2-phenyl-4,5-dihydrothiazole (4q)

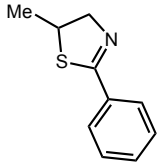


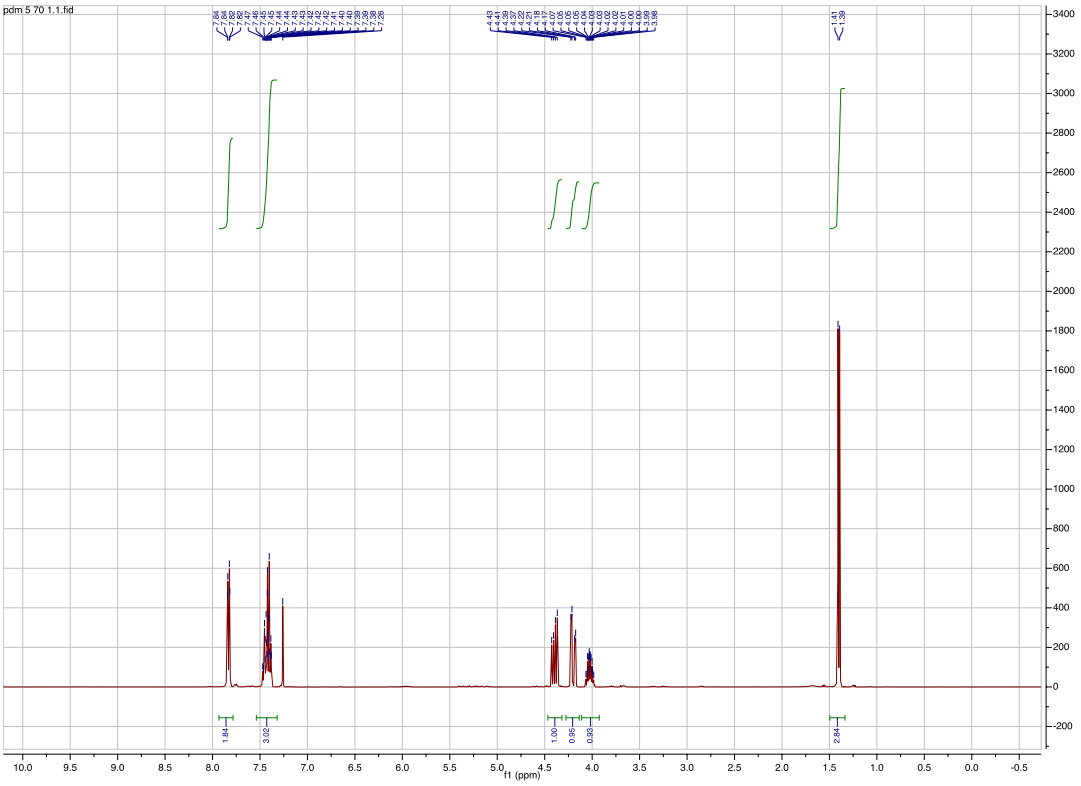


5-benzyl-4-(*tert*-butyl)-2-phenyl-4,5-dihydrothiazole (4q)

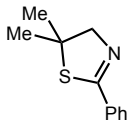


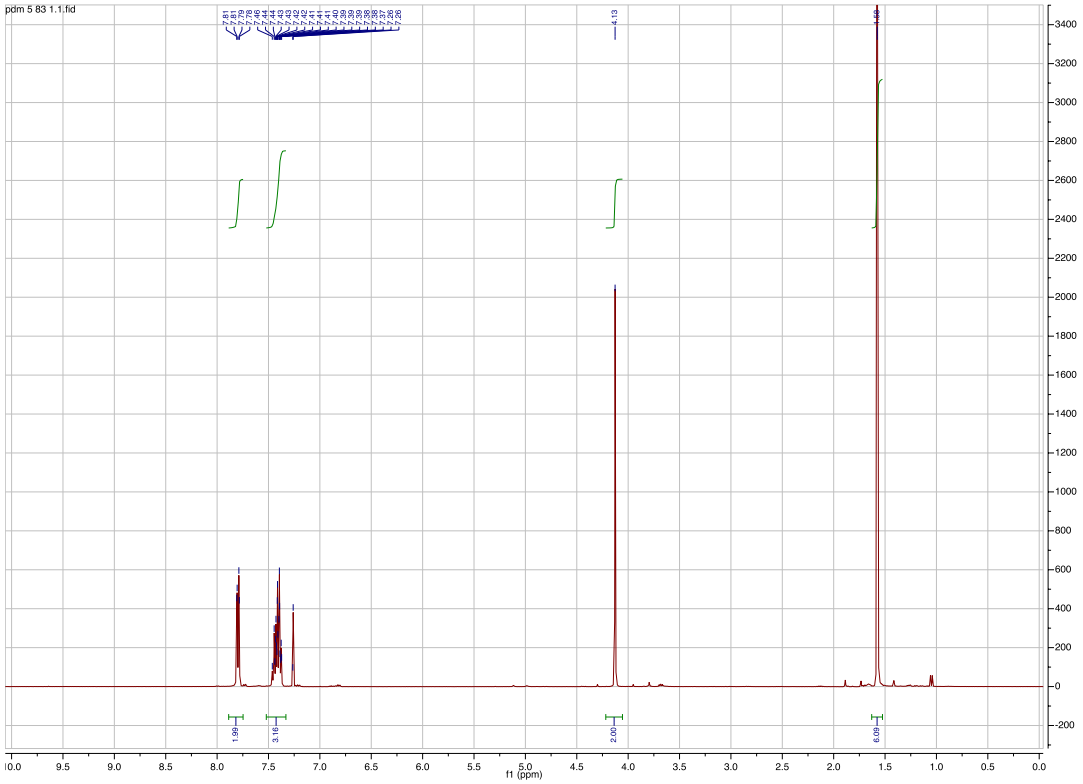
5-methyl-2-phenyl-4,5-dihydrothiazole (4r)



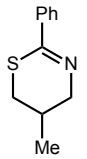


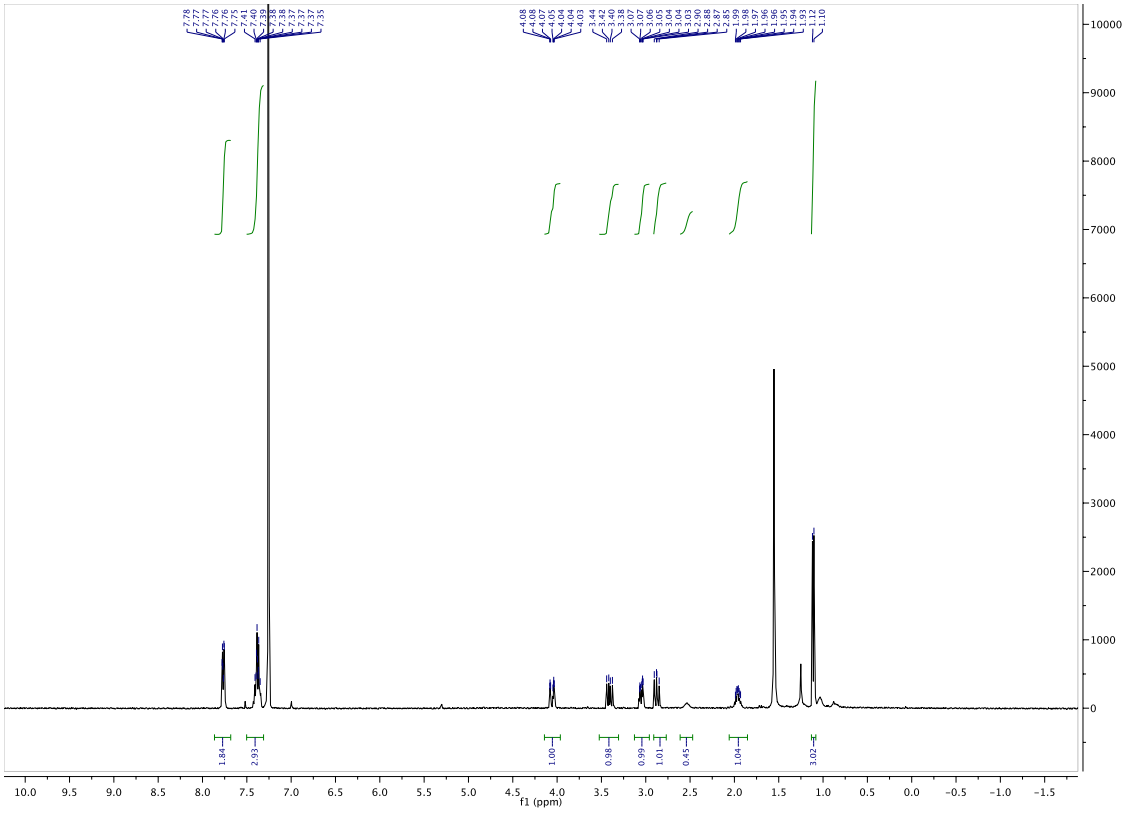
5,5-dimethyl-2-phenyl-4,5-dihydrothiazole (5s)



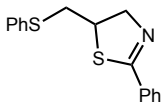


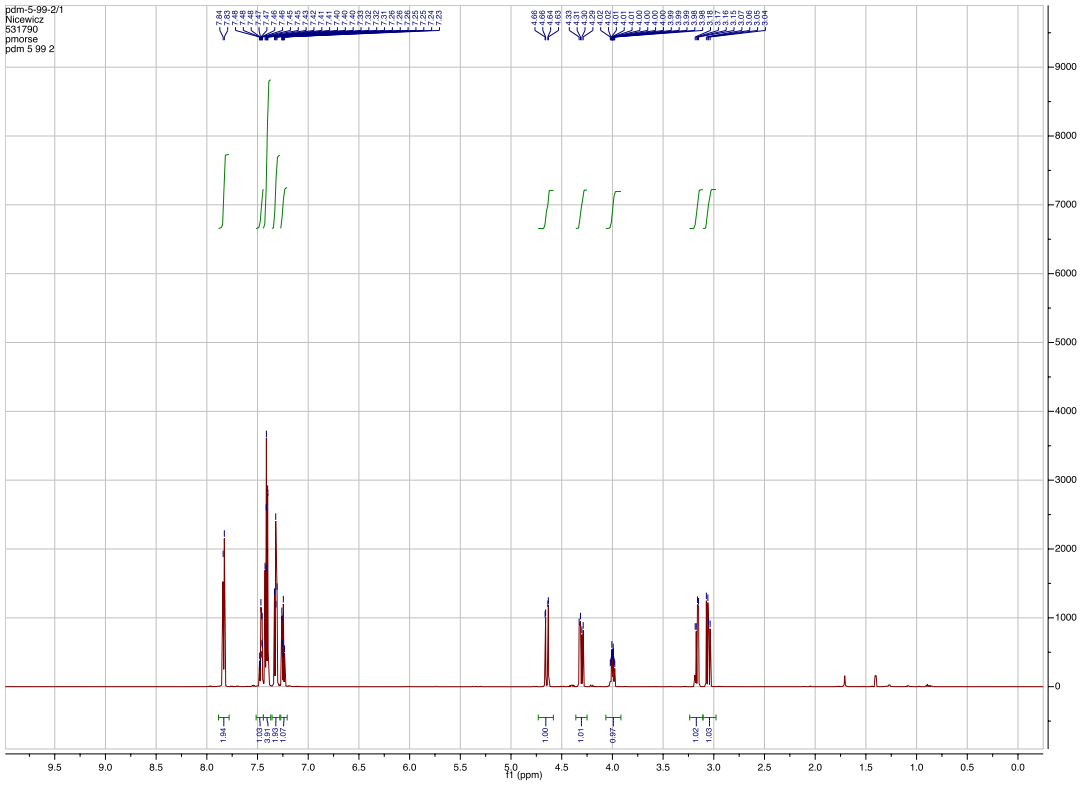
5-methyl-2-phenyl-5,6-dihydro-4*H*-1,3-thiazine (4s):





2-phenyl-5-((phenylthio)methyl)-4,5-dihydrothiazole (6a)





2-phenyl-5-((phenylthio)methyl)-4,5-dihydrothiazole (6a)