Supporting Information for:

Enantioselective Conjugate Additions of α-Amino Radicals via Cooperative Photoredox and Lewis Acid Catalysis.

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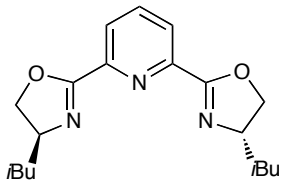
I. General Information

Acetonitrile, toluene and THF were purified by elution through alumina as described by Grubbs.[1] $Ru(bpy)_3Cl_2$ $6H_2O$ and $Sc(OTf)_3$ were purchased from Strem and used without further purification. Substrates **1**,[2] **2b**,[3] from Table 1 and 1-((trimethylsilyl)methyl)piperidine[4] from Table 2 were prepared as previously described. All other substrates were synthesized as described below. All other chemicals were purchased from commercial suppliers and used without further purification. Flash column chromatography[5] was performed using Purasil 60Å silica gel (230−400 mesh). All glassware was oven-dried at 130 °C for at least 1 h or flame-dried immediately prior to use.

All NMR spectra were obtained at ambient temperature on Varian Unity-500 and Varian Inova-500 spectrometers. Chemical shifts are reported in parts per million (δ) relative to TMS (0.0 ppm) for ^1H NMR data and $CDCl_3$ (77.23 ppm) for ^{13}C NMR data. IR spectral data were obtained using a Bruker Vector 22 spectrometer. Melting points were obtained using a Mel-Temp II (Laboratory Devices, Inc., USA) melting point apparatus. Mass spectrometry was performed with a Micromass LCT (electrospray ionization, time-of-flight analyzer or electron impact). These facilities are funded by the NSF (CHE-9974839, CHE-9304546), NIH (RR08389−01) and the University of Wisconsin. Enantiomeric excesses were determined by chiral SFC of isolated material using a Waters Investigator system with Daicel CHIRALPAK® columns and Chromasolv®-grade *i*-PrOH and MeOH. The enantiomeric excess of compound 5-55 was determined by chiral GC of isolated material using a β-DEX 225 column (30 m x 0.25 mm i.d.). Optical rotations were measured using a Rudolph Research Autopol III polarimeter at room temperature

II. Ligand Synthesis

2,6-Bis((*S*)-4-isobutyl-4,5-dihydrooxazol-2-yl)pyridine (**(*S*,*S*)-4c**). Prepared using a modification of the procedure described by García, Pires, and coworkers.[6] A 100 mL round bottom flask fitted with a reflux condenser was charged with pyridine-2,6-dicarbonitrile (555 mg, 4.3 mmol, 1 equiv) and flame-dried zinc triflate (153 mg, 0.42 mmol, 0.1 equiv). The system was purged with argon, and anhydrous toluene (28 mL) was added. The solution was stirred for 5 min and a solution of (*S*)-leucinol (1 g, 8.6 mmol, 2 equiv) in anhydrous toluene (12 mL) was added. The solution was heated under reflux for 48 h. The system was allowed to cool, and the reaction was diluted with 40 mL of EtOAc. The solution was then washed with brine (3 x 60 mL) and $NaHCO_3$ (3 x 50 mL), dried with $MgSO_4$, and the solvent evaporated to give crude product (1.25 g, 3.8 mmol, 89% yield). The crude product was further purified by recrystallization from hot hexanes before use. $[\alpha]_D^{22}$ –121.1 (*c*1.020, CH_2Cl_2). IR (thin film): 2951, 2900, 1633, 1568, 1461cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (d, *J* = 7.8 Hz, 2H), 7.85 (t, *J* = 7.8 Hz, 1H), 4.61 (dd, *J* = 9.5, 8.2 Hz, 2H), 4.39 (dtd, *J* = 9.4, 7.9, 6.7 Hz, 2H), 4.09 (t, *J* = 8.2 Hz, 2H), 1.85 (dp, *J* = 13.4, 6.7 Hz, 2H), 1.73 (dt, *J* = 13.6, 6.8 Hz, 2H), 1.40 (dt, *J* = 13.4, 7.3 Hz, 2H), 0.98 (dd, *J* = 9.1, 6.6 Hz, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.11, 146.94, 137.21, 125.61, 73.81, 65.38, 45.49, 25.45, 22.80, 22.71. HRMS (ESI$^+$) calc'd for $[C_{19}H_{27}N_3O_2+H]^+$ requires *m/z* 330.2177, found *m/z* 330.2184. (mp = 120–123 ºC).



2,6-Bis((*R*)-4-isobutyl-4,5-dihydrooxazol-2-yl)pyridine (**(*R*,*R*)-4c**). The enantiomeric ligand was produced using the same protocol beginning with (*R*)-leucinol. Obtained 1.09 g (3.3 mmol, 80% yield). The crude product was further purified by recrystallization from hot hexanes. $[\alpha]_D^{22}$ +119.5 (*c*0.960, CH_2Cl_2). (mp = 121–125 ºC).

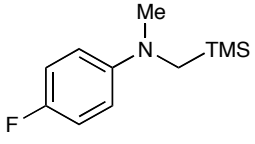
III. Synthesis of Substrates

A) Synthesis of aniline derivatives

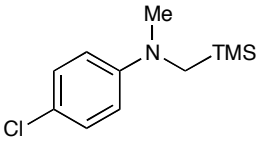
General Procedure A: This protocol is based upon a procedure described by Mariano and coworkers.[2] To a solution of aniline (9.3 mmol, 1 equiv) in THF (0.3 M) under N_2 at –78 °C was added dropwise a solution of *n*BuLi in hexanes (1.6 M, 8 mL, 10.2 mmol, 1.1 equiv). The solution was then allowed to warm to room temperature. After 24 h, (iodomethyl)trimethylsilane (10.2 mmol, 1.6 mL, 1.1 equiv) was added slowly, and the resulting solution was stirred for 12 h. The reaction was then quenched by slow addition of a saturated solution of NH_4Cl (10 mL) and extracted with Et_2O (3 x 20 mL). The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo to afford a residue that was purified on silica gel.

General Procedure B: To a solution of aniline (3 mmol, 1 equiv) in THF (0.3 M) and freshly distilled HMPA (17% in volume, 1.7 mL) under N_2 at 78 °C was added dropwise a solution of *n*BuLi in hexanes (1.6 M, 2.6 mL, 1.1 equiv). The solution was then allowed to warm to room temperature. After 24 h (iodomethyl)trimethylsilane (0.6 mL, 1.1 equiv) was added slowly, and the resulting solution was stirred for 12 h at room temperature. The reaction was then quenched by the slow addition of a saturated solution of NH_4Cl (6 mL) and extracted with Et_2O (3 x 15 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo to afford a residue that was purified on silica gel.

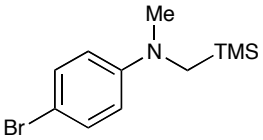
4-Fluoro-*N*-methyl-*N*-((trimethylsilyl)methyl)aniline. (Table 2, entry 2). Followed procedure A. The crude oil obtained was purified by chromatography on silica gel using 95:5 hexanes:Et_2O as the eluent to afford the product as a yellow oil (1.2 g, 63% yield). IR (thin film): 2955, 1515, 1227 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.90 (dd, *J* = 9.2, 8.4 Hz, 2H), 6.58 (dd, *J* = 9.2, 4.3 Hz, 2H), 2.88 (s, 3H), 2.79 (s, 2H), 0.07 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.9 (*J* = 232.5 Hz), 149.8 (*J* = 1.3 Hz), 117.4 (*J* = 21.3 Hz), 114.2 (*J* = 6.3 Hz), 45.1, 41.1, -0.9. HRMS (ESI$^+$) calc'd for $[C_{11}H_{18}FNSi+H]^+$ requires *m/z* 212.1268, found *m/z* 212.1266.



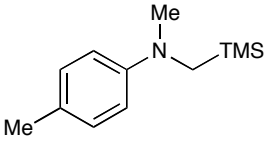
4-Chloro-*N*-methyl-*N*-((trimethylsilyl)methyl)aniline. (Table 2, entry 3). Followed procedure A. The crude oil obtained was purified by chromatography on silica gel using 95:5 hexanes:Et_2O as the eluent to afford the product as a yellow oil (920 mg, 45% yield). IR (thin film): 2954, 1596, 1503, 1369 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.12 (d, *J* = 9.1 Hz, 2H), 6.54 (d, *J* = 9.1 Hz, 2H), 2.90 (s, 3H), 2.83 (s, 2H), 0.07 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.3, 146.6, 114.8, 114.3, 56.1, 45.6, 41.6, -0.9. HRMS (ESI^+) calc'd for $[C_{11}H_{18}ClNSi+H]^+$ requires *m/z* 228.0970, found *m/z* 228.0970.



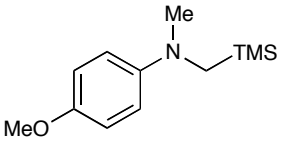
4-Bromo-*N*-methyl-*N*-((trimethylsilyl)methyl)aniline. (Table 2, entry 4). Followed procedure A. The crude oil obtained was purified by chromatography on silica gel using 20:1 hexanes:EtOAc as the eluent to afford the product as a yellow oil (1.4 g, 56% yield). IR (thin film): 2953, 2894, 1592, 1501 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, *J* = 9.0 Hz, 2H), 6.49 (d, *J* = 8.9 Hz, 2H), 2.90 (s, 3H), 2.82 (s, 2H), 0.07 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.4, 131.7, 113.4, 106.9, 44.2, 40.5, -0.9. HRMS (ESI^+) calc'd for $[C_{11}H_{18}BrNSi+H]^+$ requires *m/z* 272.0465, found *m/z* 272.0664.



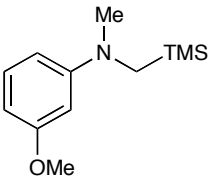
***N*,4-Dimethyl-*N*-((trimethylsilyl)methyl)aniline.** (Table 2, entry 5). Followed procedure A. The crude oil obtained was purified by chromatography on silica gel using 95:5 hexanes:Et_2O as the eluent to afford the product as a yellow oil (1.4 g, 74% yield). IR (thin film): 2553, 2801, 1618, 1520 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.01 (d, *J* = 8.4 Hz, 2H), 6.59 (d, *J* = 8.6 Hz, 2H), 2.88 (s, 3H), 2.80 (s, 2H), 2.23 (s, 3H), 0.08 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.0, 129.6, 124.6, 112.4, 44.5, 40.7, 20.4, -0.9. HRMS (ESI^+) calc'd for $[C_{12}H_{21}NSi+H]^+$ requires *m/z* 208.1519, found *m/z* 208.1517.



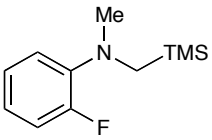
4-Methoxy-*N*-methyl-*N*-((trimethylsilyl)methyl)aniline. (Table 2, entry 6). Followed procedure A. The crude oil obtained was purified by chromatography on silica gel using 80:20 hexanes:EtOAc as the eluent to afford the product as a yellow oil (1.2 g, 60% yield). IR (thin film): 2952, 2831, 1512, 1465 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.81 (d, *J* = 9.1 Hz, 2H), 6.67 (d, *J* = 9.0 Hz, 2H), 3.75 (s, 3H), 2.85 (s, 3H), 2.75 (s, 2H), 0.07 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.3, 146.6, 114.8, 114.3, 56.0, 45.5, 41.6, -0.9. HRMS (ESI^+) calc'd for $[C_{11}H_{21}NOSi+H]^+$ requires *m/z* 224.1456, found *m/z* 224.1466.



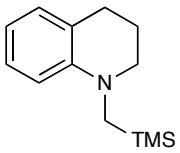
3-Methoxy-*N*-methyl-*N*-((trimethylsilyl)methyl)aniline. (Table 2, entry 7). Follow procedure A. The crude oil obtained was purified by chromatography on silica gel using 95:5 hexanes:Et_2O as the eluent to afford the product as a yellow oil (1.4 g, 69% yield). IR (thin film): 2952, 2833, 1610, 1500 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.10 (t, *J* = 8.1 Hz, 1H), 6.28 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.14 (m, 2H), 3.79 (s, 3H), 2.91 (s, 3H), 2.84 (s, 2H), 0.09 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.8, 152.1, 129.7, 105.3, 100.2, 98.4, 55.3, 44.3, 40.4, -0.9. HRMS (ESI^+) calc'd for $[C_{12}H_{21}NOSi+H]^+$ requires *m/z* 224.1467, found *m/z* 224.1466.



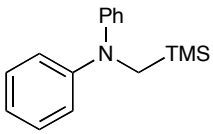
2-Fluoro-*N*-methyl-*N*-((trimethylsilyl)methyl)aniline. (Table 2, entry 8). Followed procedure B. The crude oil obtained was purified by chromatography on silica gel using 30:1 hexanes:EtOAc as the eluent to afford the product as a yellow oil (315 mg, 50% yield). IR (thin film): 2955, 2786, 1611, 1501 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.04−6.88 (m, 3H), 6.84−6.78 (m, 1H), 2.82 (s, 3H), 2.75 (s, 2H), 0.06 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.5 (*J* = 243.8 Hz), 142.4 (*J* = 8.8 Hz), 124.3 (*J* = 3.8 Hz), 120.8 (*J* = 7.5 Hz), 119.1 (*J* = 3.8 Hz), 116.3 (*J* = 21.3 Hz), 47.4 (*J* = 3.8 Hz), 43.6 (*J* = 2.5 Hz), -0.9. HRMS (ESI^+) calc'd for $[C_{11}H_{18}FNSi+H]^+$ requires *m/z* 212.1266, found *m/z* 212.1262.



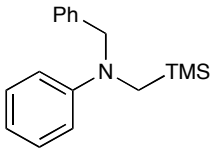
1-((Trimethylsilyl)methyl)-1,2,3,4-tetrahydroquinoline (Table 2, entry 9). Followed procedure B. The crude oil obtained was purified by chromatography on silica gel using 95:5 hexanes:Et_2O as the eluent to afford the product as a yellow oil (420 mg, 64% yield). IR (thin film): 3028, 2950, 2840, 1601, 1504 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.10 (t, *J* = 8.1 Hz, 1H), 7.02 (d, *J* = 7.3 Hz, 1H), 6.90 (d, *J* = 7.1 Hz, 1H), 6.53 – 6.44 (m, 2H), 3.26 – 3.20 (m, 3H), 2.79 – 2.68 (m, 4H), 1.99 – 1.89 (m, 2H), 0.10 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.8, 128.9, 122.1, 122.1, 114.8, 110.7, 51.7, 42.7, 28.4, 22.6, -0.8. HRMS (ESI^+) calc'd for $[C_{13}H_{21}NSi+H]^+$ requires *m/z* 220.1517, found *m/z* 220.1521.



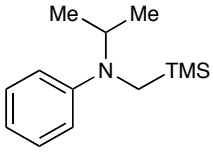
***N*-Phenyl-*N*-((trimethylsilyl)methyl)aniline** (Table 2, entry 11). Followed procedure B. The crude oil obtained was purified by chromatography on silica gel using 30:1 hexanes:EtOAc as the eluent to afford the product as a yellow oil (678 mg, 89% yield). IR (thin film): 2952, 2895, 1914, 1588, 1494 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.37 (m, 4H), 7.16 (dt, *J* = 7.9, 1.1 Hz, 4H), 7.11 – 7.05 (m, 2H), 3.47 (s, 2H), 0.12 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.7, 129.3, 121.3, 43.8, -1.1. HRMS (ESI^+) calc'd for $[C_{16}H_{21}NSi+H]^+$ requires *m/z* 256.1517, found *m/z* 256.1520.



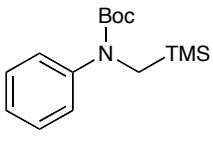
***N*-Benzyl-*N*-((trimethylsilyl)methyl)aniline** (Table 2, entry 12). Followed procedure B. The crude oil obtained was purified by chromatography on silica gel using 30:1 hexanes:EtOAc as the eluent to afford the product as a yellow oil (687 mg, 85% yield). IR (thin film): 2952, 2895, 1598, 1551, 1353 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.6 Hz, 2H), 7.44 – 7.32 (m, 5H), 6.88 – 6.76 (m, 3H), 4.73 (s, 2H), 3.17 (s, 2H), 0.27 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.8, 138.9, 129.2, 128.7, 126.9, 115.5, 112.2, 55.9, 42.5, -0.8. HRMS (ESI^+) calc'd for $[C_{17}H_{23}NSi+H]^+$ requires *m/z* 270.1673, found *m/z* 270.1675.



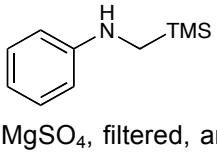
***N*-Isopropyl-*N*-((trimethylsilyl)methyl)aniline** (Table 2, entry 13). Followed procedure B. The crude oil obtained was purified by chromatography on silica gel using 30:1 hexanes:EtOAc as the eluent to afford the product as a yellow oil (571 mg, 86% yield). IR (thin film): 2966, 2806, 1549, 1502, 1196); ^1H NMR (500 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 8.8, 7.1 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 6.77 (t, *J* = 7.2 Hz, 1H), 4.12 (hept, *J* = 6.6 Hz, 1H), 2.68 (s, 1H), 1.22 (d, *J* = 6.6 Hz, 3H), 0.12 (s, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.4, 128.7, 116.3, 115.2, 52.0, 33.6, 19.5, -1.1. HRMS (ESI^+) calc'd for $[C_{13}H_{23}NSi+H]^+$ requires *m/z* 222.1672, found *m/z* 222.1673.



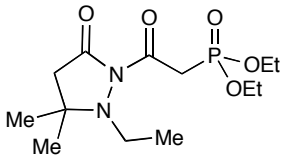
***tert*-Butyl phenyl((trimethylsilyl)methyl)carbamate** (Table 2, entry 14). Followed procedure B. The crude oil obtained was purified by chromatography on silica gel using 30:1 hexanes:EtOAc as the eluent to afford the product as a yellow oil (469 mg, 55% yield). IR (thin film): 2976, 2900, 1548, 1498, 1455 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.41 (m, 2H), 7.38 (m, 2H), 7.35 – 7.28 (m, 1H), 3.44 (s, 2H), 1.60 (s, 9H), 0.12 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.94, 144.25, 128.69, 126.91, 125.71, 80.05, 41.75, 28.57, -1.54. HRMS (ESI^+) calc'd for $[C_{15}H_{25}NO_2Si+H]^+$ requires *m/z* 280.1728, found *m/z* 280.1734.



***N*-((Trimethylsilyl)methyl)aniline** (Scheme 2, **7**)[7]. Aniline (23 mmol, 5 equiv) was added to a solution containing (iodomethyl)trimethylsilane (4.7 mmol, 1 equiv) in toluene (5 mL). The reaction mixture was stirred at 130 °C for 12 h and allowed to cool to room temperature. The reaction was then quenched with water and extracted with Et_2O (3 x 5 mL). The combined organic layers were washed with brine and dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude oil obtained was purified by chromatography on silica gel using 20:1 hexanes:EtOAc as the eluent to afford the product as a yellow oil (228 mg, 27% yield). IR (thin film): 3052, 2895, 2800, 1641, 1443 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.4 Hz, 2H), 6.71 – 6.63 (m, 3H), 3.45 (s, 1H), 2.49 (s, 2H), 0.13 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.7, 129.3, 117.2, 112.6, 33.7, -2.4. HRMS (ESI^+) calc'd for $[C_{10}H_{17}NSi+H]^+$ requires *m/z* 180.1204, found *m/z* 180.1207.



B) Synthesis of acceptors

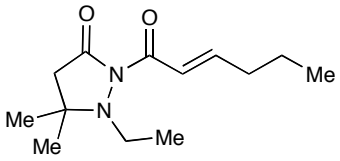


Diethyl (2-(2-ethyl-3,3-dimethyl-5-oxopyrazolidin-1-yl)-2-oxoethyl) phosphonate (**11**). A solution of 1-ethyl-5,5-dimethylpyrazolidin-3-one[3] (2 g, 14.1 mmol, 1 equiv) in THF (50 mL) was placed in a round bottomed flask and cooled to –78 °C. Butyllithium (1.6 M, 11.4 mL, 1.3 equiv) was added dropwise and the resulting dark orange solution was allowed to stir at –78 °C for 30 min. A solution of bromoacetyl bromide (1.8 mL, 21.1 mmol, 1.5 equiv) in THF (25 mL) was then added, and the mixture was allowed to warm to room temperature overnight. At that point, the reaction was quenched with saturated aqueous NH_4Cl (10 mL) and the organic layer was washed with saturated aqueous $NaHCO_3$ (10 mL). The aqueous layer was then extracted with Et_2O (3 x 20 mL). The combined organic extracts were washed with water and brine, dried over $MgSO_4$, and concentrated. The crude residue was then dissolved in $P(OEt)_3$ (12 mL) and heated at 50 °C overnight. The solution was allowed to cool, and excess triethylphosphite was distilled away under vacuum. The residue remaining in the pot was purified by flash chromatography on silica gel using 30:1 DCM:MeOH as the eluent to afford the product as an orange oil (3.1 g, 69% yield over two steps). IR (thin film): 2982, 2876, 1747, 1704, 1394 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.27 – 4.04 (m, 4H), 3.80 (s, 1H), 3.76 (s, 1H), 3.02 (q, *J* = 7.1 Hz, 2H), 2.63 (s, 2H), 1.38 – 1.24 (m, 12H), 1.12 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.42, 162.47, 62.72, 62.67, 60.30, 47.12, 43.93, 35.50, 34.47, 25.76, 16.37, 16.32, 12.60. HRMS (ESI^+) calc'd for $[C_{13}H_{25}N_2O_5P+H]^+$ requires *m/z* 321.1574, found *m/z* 3211577.

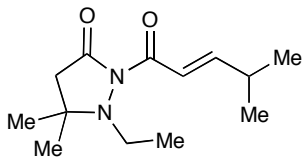
General Procedure A: A suspension of NaH (149.8 mg, 3.7 mmol, 1.2 equiv) in THF (3 mL) was cooled to 0 °C. A solution of phosphonate **11** (1 g, 3.1 mmol, 1 equiv) in THF (6 mL) was then added, and the resulting mixture was stirred for 30 min at 0 °C. The aldehyde (9.4 mmol, 3 equiv) was then added in THF (3.5 mL), and the reaction was followed by TLC. After completion, the reaction was quenched with water, and the aqueous layer was extracted with Et_2O (x3). The combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated. The crude residue was purified on silica gel by flash column chromatography.

General Procedure B: A solution of KO^tBu (633 mg, 5.6 mmol, 1.2 equiv) in THF (15 mL) was cooled to –78 °C. A solution of phosphonate **11** (1.5 g, 4.7 mmol, 1 equiv) in THF (2 mL) was then added, and the resulting mixture was stirred for 30 min at –78 °C. The aldehyde (14 mmol, 3 equiv) was then added, and the reaction was followed by TLC. After completion, the reaction was quenched with saturated aqueous NH_4Cl, and the aqueous layer was extracted with E_2O (x3). The combined organic extracts were washed with water and brine, dried over $MgSO_4$, and concentrated. The crude residue was purified on silica gel by flash column chromatography.

(*E*)-1-Ethyl-2-(hex-2-enoyl)-5,5-dimethylpyrazolidin-3-one (Table 3, entry 1) Followed procedure A. Reaction time was 2 h. The crude product was purified by chromatography on silica gel using 50:50 hexanes: Et_2O as the eluent to afford the product as a colorless oil (547 mg, 74% yield). IR (thin film): 2964, 1739, 1686, 1635 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.16 (dt, *J* = 15.3, 6.9 Hz, 1H), 7.02 (d, *J* = 15.4 Hz, 1H), 3.00 (q, *J* = 7.1 Hz, 2H), 2.58 (s, 2H), 2.29 – 2.20 (m, 2H), 1.52 (h, *J* = 7.4 Hz, 2H), 1.32 (s, 6H), 1.08 (t, *J* = 7.1 Hz, 3H), 0.95 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.1, 164.1, 151.1, 121.5, 60.5, 47.3, 44.0, 34.7, 25.8, 21.4, 13.7, 12.8. HRMS (ESI^+) calc'd for $[C_{13}H_{22}N_2O_2+H]^+$ requires *m/z* 239.1755, found *m/z* 239.1756.

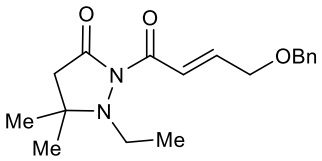


(*E*)-1-Ethyl-5,5-dimethyl-2-(4-methylpent-2-enoyl)pyrazolidin-3-one (Table 3, entry 2). Followed procedure A. Reaction time was 2 h. The crude product was purified by chromatography on silica gel using 50:50 hexanes: Et_2O as the eluent to afford the product as a colorless oil (473 mg, 64% yield). IR (thin film): 2968, 1740, 1684, 1633 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.13 (dd, *J* = 15.5, 6.7 Hz, 1H), 6.99 (dd, *J* = 15.5, 1.2 Hz, 1H), 3.00 (q, *J* = 7.1 Hz, 2H), 2.59 (s, 2H), 2.53 (dqd, *J* = 13.5, 6.8, 1.3 Hz, 2H), 1.32 (s, 6H), 1.09 (d, *J* = 6.8 Hz, 6H), 1.08 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.1, 164.4, 157.2, 118.9, 60.5, 47.3, 44.1, 31.5,

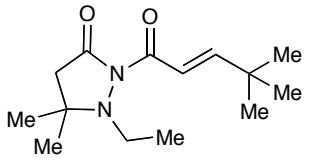


25.8, 21.4, 12.8. HRMS (ESI$^+$) calc'd for $[C_{13}H_{22}N_2O_2+H]^+$ requires *m/z* 239.1755, found *m/z* 239.1751.

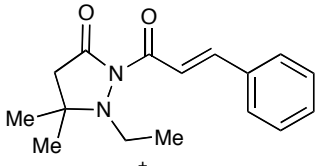
(*E*)-2-(4-(Benzyloxy)but-2-enoyl)-1-ethyl-5,5-dimethylpyrazolidin-3-one (Table, 3, entry 3). Followed procedure A. Reaction time was 2 h. The crude product was purified by chromatography on silica gel using 30:70 hexanes: Et_2O as the eluent to afford the product as a colorless oil (588 mg, 60% yield). IR (thin film): 2973, 1739, 1686, 1641 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.27 (m, 6H), 7.16 (dt, *J* = 15.5, 4.3 Hz, 1H), 4.60 (s, 2H), 4.24 (dd, *J* = 4.3, 1.9 Hz, 2H), 3.01 (q, *J* = 7.1 Hz, 2H), 2.59 (s, 2H), 1.32 (s, 6H), 1.08 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.1, 163.7, 145.7, 137.8, 128.5, 127.8, 127.7, 121.5, 72.8, 69.1, 60.6, 47.3, 43.9, 25.8, 12.8. HRMS (ESI$^+$) calc'd for $[C_{14}H_{24}N_2O_2+H]^+$ requires *m/z* 317.1860, found *m/z* 317.1862.



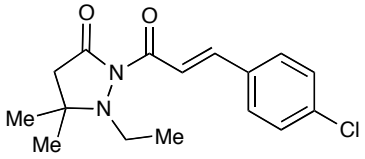
(*E*)-2-(4,4-Dimethylpent-2-enoyl)-1-ethyl-5,5-dimethylpyrazolidin-3-one (Table, 3, entry 4). Followed procedure A. Reaction time was 2 h. The crude product was purified by chromatography on silica gel using 50:50 hexanes: Et_2O as the eluent to afford the product as a colorless oil (464 mg, 59% yield). IR (thin film): 2963, 1740, 1688, 1631 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 (d, *J* = 15.6 Hz, 1H), 6.97 (d, *J* = 15.6 Hz, 1H), 3.01 (q, *J* = 7.1 Hz, 2H), 2.59 (s, 2H), 1.32 (s, 6H), 1.11 (s, 9H), 1.08 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.2, 164.6, 160.7, 117.0, 60.5, 47.3, 44.1, 34.3, 28.8, 25.8, 12.8. HRMS (ESI$^+$) calc'd for $[C_{14}H_{24}N_2O_2+H]^+$ requires *m/z* 253.1911, found *m/z* 239.1915.



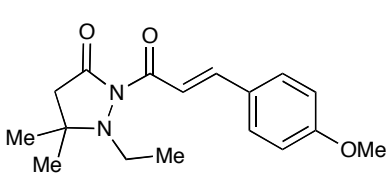
(*E*)-2-Cinnamoyl-1-ethyl-5,5-dimethylpyrazolidin-3-one. (Table 3, entry 5). Followed procedure B. Reaction time was 1 h. The crude was purified by chromatography on silica gel using 70:30 hexanes: EtOAc as the eluent to afford the product as a yellow solid (834 mg, 66% yield). IR (thin film): 3006, 1740, 1698, 1654 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 15.7 Hz, 1H), 7.70 (d, *J* = 15.8 Hz, 1H), 7.64 – 7.58 (m, 2H), 7.39 (dd, *J* = 4.9, 1.9 Hz, 3H), 3.05 (q, *J* = 7.1 Hz, 2H), 2.63 (s, 2H), 1.35 (s, 6H), 1.12 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.2, 164.2, 145.9, 134.9, 130.4, 128.9, 128.5, 118.3, 60.6, 47.4, 44.1, 25.8, 12.8. HRMS (ESI$^+$) calc'd for $[C_{16}H_{20}N_2O_2+H]^+$ requires *m/z* 273.1598, found *m/z* 273.1593. (mp = 55–56 ºC).



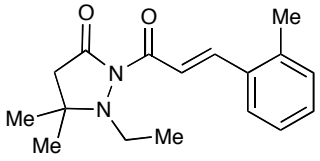
(*E*)-2-(3-(4-Chlorophenyl)acryloyl)-1-ethyl-5,5-dimethylpyrazolidin-3-one. (Table 3, entry 6). Followed procedure B. Reaction time was 1 h. The crude was purified by chromatography on silica gel using 60:40 hexanes: EtOAc as the eluent to afford the product as a yellow solid (820 mg, 59% yield). IR (thin film): 2978, 1724, 1685, 1592, 1326 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 15.7 Hz, 1H), 7.68 (d, *J* = 15.7 Hz, 1H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 2H), 3.05 (q, *J* = 7.1 Hz, 2H), 2.63 (s, 2H), 1.35 (s, 6H), 1.11 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.3, 163.9, 144.4, 136.3, 133.4, 129.6, 129.1, 118.9, 60.6, 47.4, 44.0, 25.8, 12.8. HRMS (ESI$^+$) calc'd for $[C_{16}H_{19}ClN_2O_2+H]^+$ requires *m/z* 307.1208, found *m/z* 307.1200. (mp = 82–85 ºC).



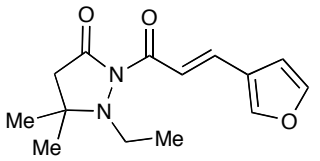
(*E*)-1-Ethyl-2-(3-(4-methoxyphenyl)acryloyl)-5,5-dimethylpyrazolidin-3-one. (Table 3, entry 7). Followed procedure B. Reaction time was 12 h. The crude was purified by chromatography on silica gel using 70:30 hexanes: EtOAc as the eluent to afford the product as a yellow oil (795 mg, 57% yield). IR (thin film): 2976, 1741, 1682, 1601, 1573, 1173 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 15.7 Hz, 1H), 7.63 – 7.52 (m, 3H), 6.96 – 6.87 (m, 2H), 3.84 (s, 3H), 3.04 (q, *J* = 7.1 Hz, 2H), 2.62 (s, 2H), 1.35 (s, 6H), 1.11 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.2, 164.5, 161.5, 145.8, 130.2, 127.7, 115.8, 114.3, 60.6, 55.4, 47.4, 44.1, 25.8, 12.8 5. HRMS (ESI$^+$) calc'd for $[C_{17}H_{22}N_2O_3+H]^+$ requires *m/z* 303.1704, found *m/z* 303.1713. (mp = 79–81 ºC).



(*E*)-1-Ethyl-5,5-dimethyl-2-(3-(*o*-tolyl)acryloyl)pyrazolidin-3-one. (Table 3, entry 8). Followed procedure B. Reaction time was 3 h. The crude was purified by chromatography on silica gel using 70:30 hexanes: EtOAc as the eluent to afford the product as a yellow oil (833 mg, 62% yield). IR (thin film): 2977, 1743, 1617, 1327, 1230 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, *J* = 15.7 Hz, 1H), 7.66 (d, *J* = 7.4 Hz, 1H), 7.61 (d, *J* = 15.6 Hz, 1H), 7.32 – 7.25 (m, 1H), 7.25 – 7.17 (m, 2H), 3.05 (q, *J* = 7.1 Hz, 2H), 2.62 (s, 2H), 2.47 (s, 3H), 1.35 (s, 6H), 1.12 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.2, 164.2, 143.5, 138.1, 133.8, 130.8, 130.1, 126.9, 126.3, 119.3, 60.6, 47.4, 44.0, 25.8, 19.9, 12.9. HRMS (ESI^+) calc'd for $[C_{17}H_{22}N_2O_2+H]^+$ requires *m/z* 287.1755, found *m/z* 287.1756.



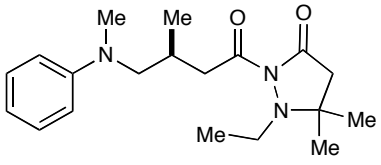
(*E*)-1-Ethyl-2-(3-(furan-3-yl)acryloyl)-5,5-dimethylpyrazolidin-3-one. (Table 3, entry 9). Followed procedure B. Reaction time was 30 min. The crude was purified by chromatography on silica gel using 70:30 hexanes: EtOAc as the eluent to afford the product as a yellow oil (570 mg, 47% yield). IR (thin film): 2972, 1742, 1685, 1324, 1232 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 15.6 Hz, 1H), 7.66 – 7.57 (m, 1H), 7.40 – 7.29 (m, 2H), 6.62 (d, *J* = 1.9 Hz, 1H), 2.97 (q, *J* = 7.2 Hz, 2H), 2.55 (s, 2H), 1.27 (s, 7H), 1.03 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.2, 163.1, 144.1, 143.3, 135.0, 122.2, 116.9, 106.7, 59.5, 46.3, 43.1, 24.8, 11.8. HRMS (ESI^+) calc'd for $[C_{14}H_{18}N_2O_3+H]^+$ requires *m/z* 263.1391, found *m/z* 263.1389.



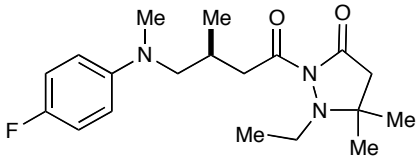
IV. Photochemical Reactions

General procedure for asymmetric α-amino radical addition: A dry 25 mL Schlenk tube was charged with $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.02 equiv.), $Sc(OTf)_3$ (0.15 equiv.), ligand (0.20 equiv.), and TBACl (0.30 equiv.). A solution containing the amine (1 equiv.) and the acceptor (1.5 equiv.) in acetonitrile (0.05 M) was then added. The reaction was degassed by 3 freeze/pump/thaw cycles under nitrogen in the dark. The reaction was then allowed to stir while being irradiated by a 23 W (1280 lumen) compact fluorescent lamp at a distance of 30 cm. Upon completion of the reaction, the solvent was removed by rotary evaporation, and the crude residue loaded directly onto silica for purification by flash column chromatography.

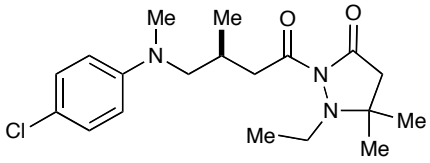
(*S*)-1-Ethyl-5,5-dimethyl-2-(3-methyl-4-(methyl(phenyl)amino)butanoyl)pyrazolidin-3-one (Table 2, entry 1, **3b**). Experiment 1: Prepared according to the general procedure using 98 mg (0.50 mmol) of *N*-methyl-*N*-((trimethylsilyl)methyl)aniline, 158 mg (0.75 mmol) of (*E*)-2-(but-2-enoyl)-1-ethyl-5,5-dimethylpyrazolidin-3-one, 7.5 mg (0.01 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 37 mg $Sc(OTf)_3$ (0.075 mmol), 33 mg (0.10 mmol) (*S*)-*i*BuPyBox, 42 mg (0.15 mmol) TBACl, 10 mL acetonitrile and irradiated for 6 h. Purified by chromatography using 70:30 hexanes:EtOAc to yield 140 mg (0.42 mmol, 84% yield) of product (93% ee) as a colorless oil. Experiment 2: 97 mg (0.50 mmol) of *N*-methyl-*N*-((trimethylsilyl)methyl)aniline, 158 mg (0.75 mmol) of (*E*)-2-(but-2-enoyl)-1-ethyl-5,5-dimethylpyrazolidin-3-one, 7.5 mg (0.01 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 37 mg $Sc(OTf)_3$ (0.075 mmol), 33 mg (0.1 mmol) (S)-*i*BuPyBox, 42 mg (0.15 mmol) TBACl, 10 mL acetonitrile. Isolated 148 mg (0.45 mmol, 89% yield), 92% ee. [Daicel Chiracel OD-H, 8% MeOH, 3 mL/min, 249 nm; t_1= 5.75 min, t_2= 6.49 min], $[\alpha]_D^{22}$ −4.7 (*c*0.885, CH_2Cl_2). IR (thin film): 2972, 2874, 1744, 1507 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.22 (td, *J* = 8.8, 7.2 Hz, 2H), 6.77 (d, J = 8.8 Hz, 2H), 6.67 (t, *J* = 7.2 Hz, 1H), 3.40 (dd, *J* = 14.5, 6.6 Hz, 1H), 3.04 (t, *J* = 3.8, 3.0 Hz, 1H), 3.01 − 2.93 (m, 6H), 2.73 (dd, *J* = 16.6, 7.2 Hz, 1H), 2.57 (s, 3H), 1.29 (d, *J* = 9.0 Hz, 6H), 1.06 (t, *J* = 7.2 Hz, 3H), 1.01 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.2, 170.2, 149.6, 129.1, 115.9, 112.1, 60.4, 59.1, 47.0, 44.0, 40.9, 39.4, 29.0, 18.0, 12.8. HRMS (ESI^+) calc'd for $[C_{19}H_{29}N_3O_2+H]^+$ requires *m/z* 332.2333, found *m/z* 332.2328.



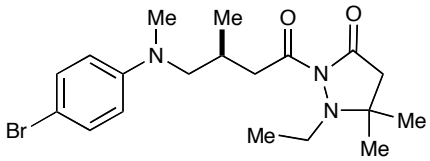
(*S*)-1-Ethyl-2-(4-((4-fluorophenyl)(methyl)amino)-3-methylbutanoyl)-5,5-dimethylpyrazolidin-3-one (Table 2, entry 2). Experiment 1: Prepared according to the general procedure using 106 mg (0.50 mmol) of 4-fluoro-*N*-methyl-*N*-((trimethylsilyl)methyl)aniline, 158 mg (0.75 mmol) of (*E*)-2-(but-2-enoyl)-1-ethyl-5,5-dimethylpyrazolidin-3-one, 7.5 mg (0.01 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 37 mg $Sc(OTf)_3$ (0.075 mmol), 33 mg (0.10 mmol) (*S*)-*i*BuPyBox, 42 mg (0.15 mmol) TBACl, 10 mL acetonitrile and irradiated for 6 h. Purified by chromatography using 70:30 hexanes:EtOAc to yield 164 mg (0.47 mmol, 94% yield) of product (93% ee) as a colorless oil. Experiment 2: 106 mg (0.50 mmol) of 4-fluoro-*N*-methyl-*N*-((trimethylsilyl)methyl)aniline, 158 mg (0.75 mmol) of (*E*)-2-(but-2-enoyl)-1-ethyl-5,5-dimethylpyrazolidin-3-one, 7.5 mg (0.01 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 37 mg $Sc(OTf)_3$ (0.075 mmol), 33 mg (0.1 mmol) (*S*)-*i*BuPyBox, 42 mg (0.15 mmol) TBACl, 10 mL acetonitrile. Isolated 162 mg (0.46 mmol, 93% yield), 94% ee. [Daicel Chiracel AD-H, 5 to 50% MeOH, 3 mL/min, 249 nm; t_1= 4.84 min, t_2= 5.15 min]. $[\alpha]_D^{22}$ −2.7 (*c*0.962, CH_2Cl_2). IR (thin film): 2972, 2874, 1744, 1707, 1514 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.96 − 6.87 (m, 2H), 6.73 − 6.65 (m, 2H), 3.35 (dd, *J* = 14.4, 6.6 Hz, 1H), 2.97 (m, 4H), 2.91 (s, 3H), 2.72 (dd, *J* = 16.7, 6.9 Hz, 1H), 2.62 − 2.50 (m, 3H), 1.29 (d, *J* = 10.7 Hz, 6H), 1.06 (t, *J* = 7.1 Hz, 3H), 1.01 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.3, 170.3, 155.2 (*J* = 233.7 Hz), 146.5 (*J* = 1.3 Hz), 115.4 (*J* = 21.3 Hz), 113.2 (*J* = 6.3 Hz), 60.4, 60.0, 47.0, 44.1, 40.9, 39.8, 28.9, 25.8, 25.7, 18.1, 12.8. HRMS (ESI^+) calc'd for $[C_{19}H_{28}FN_3O_2+H]^+$ requires *m/z* 350.2239, found *m/z* 350.2236.



(*S*)-2-(4-((4-Chlorophenyl)(methyl)amino)-3-methylbutanoyl)-1-ethyl-5,5-dimethylpyrazolidin-3-one (Table 2, entry 3). Experiment 1: Prepared according to the general procedure using 115 mg (0.50 mmol) of 4-chloro-*N*-methyl-*N*-((trimethylsilyl)methyl)aniline, 158 mg (0.75 mmol) of (*E*)-2-(but-2-enoyl)-1-ethyl-5,5-dimethylpyrazolidin-3-one, 7.5 mg (0.01 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 37 mg $Sc(OTf)_3$ (0.075 mmol), 33 mg (0.10 mmol) (*S*)-*i*BuPyBox, 42 mg (0.15 mmol) TBACl, 10 mL acetonitrile and irradiated for 6 h. Purified by chromatography using 70:30 hexanes:EtOAc to yield 181 mg (0.49 mmol, 98% yield) of product (93% ee) as a colorless oil. Experiment 2: 115 mg (0.50 mmol) of 4-chloro-*N*-methyl-*N*-((trimethylsilyl)methyl)aniline, 158 mg (0.75 mmol) of (*E*)-2-(but-2-enoyl)-1-ethyl-5,5-dimethylpyrazolidin-3-one, 7.5 mg (0.01 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 37 mg $Sc(OTf)_3$ (0.075 mmol), 33 mg (0.1 mmol) (*S*)-*i*BuPyBox, 42 mg (0.15 mmol) TBACl, 10 mL acetonitrile. Isolated 176 mg (0.48 mmol, 95% yield), 93% ee. [Daicel Chiracel AD-H, 5 to 50% MeOH, 3 mL/min, 249 nm; t_1= 4.41 min, t_2= 4.75 min]. $[\alpha]_D^{22}$ −2.4 (*c*0.967, CH_2Cl_2). IR (thin film): 2972, 2935, 2874, 1745, 1706 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.14 (d, 2H), 6.68 (d, 2H), 3.41 (dd, *J* = 14.5, 6.4 Hz, 1H), 3.02 − 2.95 (m, 4H), 2.94 (s, 3H), 2.72 (dd, *J* = 16.7, 6.8 Hz, 1H), 2.57 (s, 3H), 1.29 (d, *J* = 9.2 Hz, 6H), 1.06 (t, *J* = 7.1 Hz, 3H), 1.00 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.3, 170.2, 148.1, 128.8, 120.7, 113.2, 60.4, 59.1, 47.0, 44.1 40.9, 39.6, 28.9, 25.7, 18.0, 12.8. HRMS (ESI^+) calc'd for $[C_{19}H_{28}ClN_3O_2+H]^+$ requires *m/z* 366.1942, found *m/z* 366.1943.

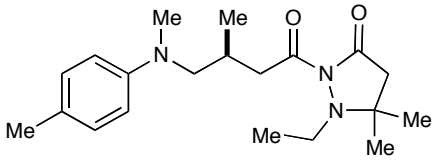


(*S*)-2-(4-((4-Bromophenyl)(methyl)amino)-3-methylbutanoyl)-1-ethyl-5,5-dimethylpyrazolidin-3-one (Table 2, entry 4). Experiment 1: Prepared according to the general procedure using 138.3 mg (0.51 mmol) of 4-bromo-*N*-methyl-*N*-((trimethylsilyl)methyl)aniline, 158 mg (0.75 mmol) of (*E*)-2-(but-2-enoyl)-1-ethyl-5,5-dimethylpyrazolidin-3-one, 7.5 mg (0.01 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 37 mg $Sc(OTf)_3$ (0.075 mmol), 33 mg (0.10 mmol) (*S*)-*i*BuPyBox, 42 mg (0.15 mmol) TBACl, 10 mL acetonitrile and irradiated for 6 h. Purified by chromatography using 70:30 hexanes:EtOAc to yield 181.9 mg (0.44 mmol, 87% yield) of product (92% ee) as a colorless oil. Experiment 2: 136.1 mg (0.50 mmol) of 4-bromo-*N*-methyl-*N*-((trimethylsilyl)methyl)aniline, 158 mg (0.75 mmol) of (*E*)-2-(but-2-enoyl)-1-ethyl-5,5-dimethylpyrazolidin-3-one, 7.5 mg (0.01 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 37 mg $Sc(OTf)_3$ (0.075 mmol), 33 mg (0.1 mmol) (*S*)-*i*BuPyBox, 42 mg (0.15 mmol) TBACl, 10 mL acetonitrile. Isolated 190.7 mg (0.46 mmol, 93% yield), 92% ee. [Daicel Chiracel AD-H, 12% MeOH, 3 mL/min, 249 nm; t_1= 4.45 min, t_2= 5.16 min]. $[\alpha]_D^{22}$ −2.9 (*c*1.155, CH_2Cl_2). IR (thin film): 2962, 1697, 1598, 1499 cm^{-1}; ^1H NMR (500 MHz,

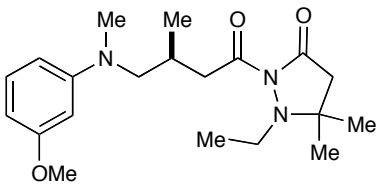


$CDCl_3$) δ 7.27 (d, *J* = 9.0 Hz, 2H), 6.63 (d, *J* = 9.1 Hz, 2H), 3.41 (dd, *J* = 14.5, 6.4 Hz, 1H), 3.02 − 2.95 (m, 6H), 2.94 (s, 3H), 2.71 (dd, *J* = 16.6, 6.9 Hz, 1H), 2.60 − 2.50 (m, 3H), 1.29 (d, *J* = 8.9 Hz, 8H), 1.06 (t, *J* = 7.1 Hz, 4H), 1.00 (d, *J* = 6.7 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ175.3, 170.1, 148.5, 131.7, 113.7, 107.8, 60.4, 59.0, 47.0, 44.0, 40.9, 39.6, 28.8, 25.8, 25.7, 18.0, 12.8. HRMS (ESI$^+$) calc'd for $[C_{19}H_{28}BrN_3O_2+H]^+$ requires *m/z* 410.1438, found *m/z* 410.1443.

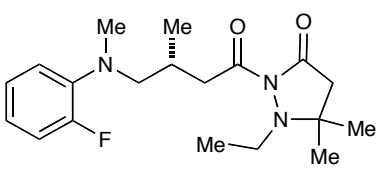
(*S*)-1-Ethyl-5,5-dimethyl-2-(3-methyl-4-(methyl(p-tolyl)amino)butanoyl)pyrazolidin-3-one (Table 2, entry 5). Experiment 1: Prepared according to the general procedure using 104 mg (0.50 mmol) of *N*-4-dimethyl-*N*-((trimethylsilyl)methyl)aniline, 158 mg (0.75 mmol) of (*E*)-2-(but-2-enoyl)-1-ethyl-5,5-dimethylpyrazolidin-3-one, 7.5 mg (0.01 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 37 mg $Sc(OTf)_3$ (0.075 mmol), 33 mg (0.10 mmol) (*S*)-*i*BuPyBox, 42 mg (0.15 mmol) TBACl, 10 mL acetonitrile and irradiated for 12 h. Purified by chromatography using 70:30 hexanes:EtOAc to yield 135 mg (0.39 mmol, 78% yield) of product (91% ee) as a colorless oil. Experiment 2: 104 mg (0.50 mmol) of *N*-4-dimethyl-*N*-((trimethylsilyl)methyl)aniline, 158 mg (0.75 mmol) of (*E*)-2-(but-2-enoyl)-1-ethyl-5,5-dimethylpyrazolidin-3-one, 7.5 mg (0.01 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 37 mg $Sc(OTf)_3$ (0.075 mmol), 33 mg (0.1 mmol) (*S*)-*i*BuPyBox, 42 mg (0.15 mmol) TBACl, 10 mL acetonitrile. Isolated 139 mg (0.40 mmol, 80% yield), 90% ee. [Daicel Chiracel AD-H, 5 to 50% *i*-PrOH, 3 mL/min, 249 nm; t_1= 4.65 min, t_2= 5.09 min]. $[\alpha]_D^{22}$ −3.0 (*c*0.905, CH_2Cl_2). IR (thin film): 2972, 2872, 1744, 1708, 1568 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.03 (d, *J* = 8.2 Hz, 2H), 6.69 (d, *J* = 8.6 Hz, 2H), 3.33 (dd, *J* = 14.4, 6.7 Hz, 1H), 3.03 − 2.94 (m, 4H), 2.92 (s, 3H), 2.72 (dd, *J* = 16.5, 7.3 Hz, 1H), 2.61 − 2.52 (m, 3H), 2.24 (s, 3H), 1.29 (d, *J* = 9.4 Hz, 6H), 1.06 (t, *J* = 7.1 Hz, 3H), 1.00 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.2, 170.3, 147.8, 129.6, 125.2, 112.5, 60.4, 59.5, 47.0, 44.1, 40.9, 39.4, 29.1, 20.2, 18.0, 12.8. HRMS (ESI$^+$) calc'd for $[C_{20}H_{31}N_3O_2+H]^+$ requires *m/z* 346.2490, found *m/z* 346.2488.



(*S*)-1-Ethyl-2-(4-((3-methoxyphenyl)(methyl)amino)-3-methylbutanoyl)-5,5-dimethylpyrazolidin-3-one (Table 2, entry 7). Experiment 1: Prepared according to the general procedure using 117.1 mg (0.50 mmol) of 3-methoxy-*N*-methyl-*N*-((trimethylsilyl)methyl)aniline, 158 mg (0.75 mmol) of (*E*)-2-(but-2-enoyl)-1-ethyl-5,5-dimethylpyrazolidin-3-one, 7.5 mg (0.01 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 37 mg $Sc(OTf)_3$ (0.075 mmol), 33 mg (0.10 mmol) (*S*)-*i*BuPyBox, 42 mg (0.15 mmol) TBACl, 10 mL acetonitrile and irradiated for 6 h. Purified by chromatography using 70:30 hexanes:EtOAc to yield 150.0 mg (0.41 mmol, 83% yield) of product (91% ee) as a colorless oil. Experiment 2: 117.8 mg (0.50 mmol) of 3-methoxy-*N*-methyl-*N*-((trimethylsilyl)methyl)aniline, 158 mg (0.75 mmol) of (*E*)-2-(but-2-enoyl)-1-ethyl-5,5-dimethylpyrazolidin-3-one, 7.5 mg (0.01 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 37 mg $Sc(OTf)_3$ (0.075 mmol), 33 mg (0.1 mmol) (*S*)-*i*BuPyBox, 42 mg (0.15 mmol) TBACl, 10 mL acetonitrile. Isolated 160.0 mg (0.44 mmol, 92% yield), 92% ee. [Daicel Chiracel OD-H, 5 to 50% MeOH, 3 mL/min, 249 nm; t_1= 5.33 min, t_2= 5.73 min]. $[\alpha]_D^{22}$ −2.0 (*c*0.687, CH_2Cl_2). IR (thin film): 2970, 2874, 1744, 1707, 1610 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 (t, *J* = 8.2 Hz, 1H), 6.40 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.32 − 6.22 (m, 2H), 3.80 (s, 3H), 3.39 (dd, *J* = 14.5, 6.6 Hz, 1H), 3.07 − 2.95 (m, 4H), 2.95 (s, 3H), 2.72 (dd, *J* = 16.4, 7.4 Hz, 1H), 2.57 (s, 3H), 1.29 (d, *J* = 7.5 Hz, 6H), 1.06 (t, *J* = 7.1 Hz, 3H), 1.00 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.2, 170.2, 160.7, 151.0, 129.8, 105.3, 101.0, 98.4, 60.4, 59.0, 55.1, 47.0, 44.1, 40.9, 39.4, 29.1, 25.8, 25.7, 17.9, 12.8. HRMS (ESI$^+$) calc'd for $[C_{20}H_{31}N_3O_3+H]^+$ requires *m/z* 362.2439, found *m/z* 362.2436.

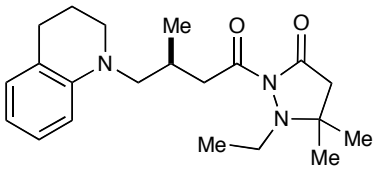


(*R*)-1-Ethyl-2-(4-((2-fluorophenyl)(methyl)amino)-3-methylbutanoyl)-5,5-dimethylpyrazolidin-3-one (Table 2, entry 8). Experiment 1: Prepared according to the general procedure using 107.1 mg (0.50 mmol) of 2-fluoro-*N*-methyl-*N*-((trimethylsilyl)methyl)aniline, 158 mg (0.75 mmol) of (*E*)-2-(but-2-enoyl)-1-ethyl-5,5-dimethylpyrazolidin-3-one, 7.5 mg (0.01 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 37 mg $Sc(OTf)_3$ (0.075 mmol), 33 mg (0.10 mmol) (*R*)-*i*BuPyBox, 42 mg (0.15 mmol) TBACl, 10 mL acetonitrile and irradiated for 6 h. Purified by chromatography using 70:30 hexanes:EtOAc to yield 144.2 mg (0.41 mmol, 81% yield)

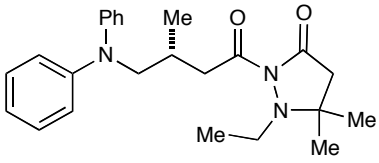


of product as a colorless oil. The enantiomeric excess of the product was determined to be −95% by conversion to the corresponding alcohol and analysis by SFC. Experiment 2: 107.0 mg (0.50 mmol) of 2-fluoro-*N*-methyl-*N*-((trimethylsilyl)methyl)aniline, 158 mg (0.75 mmol) of (*E*)-2-(but-2-enoyl)-1-ethyl-5,5-dimethylpyrazolidin-3-one, 7.5 mg (0.01 mmol) $Ru(bpy)_3Cl_2·6H_2O$, 37 mg $Sc(OTf)_3$ (0.075 mmol), 33 mg (0.1 mmol) (*R*)-*i*BuPyBox, 42 mg (0.15 mmol) TBACl, 10 mL acetonitrile. Isolated 138.0 mg (0.39 mmol, 78% yield), −96% ee. $[\alpha]_D^{22}$ −4.8 (*c*1.065, CH_2Cl_2). IR (thin film): 2972, 2933, 1745, 1706, 1503 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.05 − 6.91 (m, 3H), 6.87 − 6.76 (m, 1H), 3.13 − 3.03 (m, 2H), 2.99 (q, *J* = 7.1 Hz, 2H), 2.90 (dd, *J* = 13.2, 7.4 Hz, 1H), 2.82 (s, 3H), 2.72 (dd, *J* = 16.7, 7.9 Hz, 1H), 2.57 (s, 2H), 2.55 − 2.48 (m, 1H), 1.29 (d, *J* = 5.5 Hz, 6H), 1.07 (t, *J* = 7.1 Hz, 3H), 0.99 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.1, 170.7, 155.1 (*J* = 244.7 Hz), 140.7 (*J* = 8.2 Hz), 124.2 (*J* = 3.5 Hz), 120.9 (*J* = 7.7 Hz), 119.2 (*J* = 3.4 Hz), 116.2 (*J* = 21.1 Hz), 61.2 (*J* = 4.1 Hz), 60.4 , 47.1 , 44.1 , 40.9 , 40.0 (*J* = 2.3 Hz), 28.2 , 25.8 (*J* = 11.5 Hz), 12.8. HRMS (ESI^+) calc'd for $[C_{19}H_{28}FN_3O_2+H]^+$ requires *m/z* 350.2239, found *m/z* 350.2236.

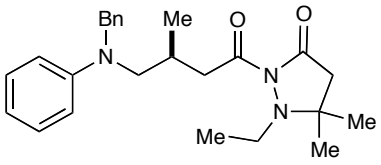
(*S*)-2-(4-(3,4-Dihydroquinolin-1(2H)-yl)-3-methylbutanoyl)-1-ethyl-5,5-dimethylpyrazolidin-3-one (Table 2, entry 9) Experiment 1: Prepared according to the general procedure using 112.9 mg (0.51 mmol) of 1-((trimethylsilyl)methyl)-1,2,3,4-tetrahydroquinoline, 158 mg (0.75 mmol) of (*E*)-2-(but-2-enoyl)-1-ethyl-5,5-dimethylpyrazolidin-3-one, 7.5 mg (0.01 mmol) $Ru(bpy)_3Cl_2·6H_2O$, 37 mg $Sc(OTf)_3$ (0.075 mmol), 33 mg (0.10 mmol) (*S*)-*i*BuPyBox, 42 mg (0.15 mmol) TBACl, 10 mL acetonitrile and irradiated for 12 h. Purified by chromatography using 70:30 hexanes:EtOAc to yield 147.5 mg (0.41 mmol, 80% yield) of product (90% ee) as a colorless oil. Experiment 2: 111.4 mg (0.50 mmol) of 1-((trimethylsilyl)methyl)-1,2,3,4-tetrahydroquinoline, 158 mg (0.75 mmol) of (*E*)-2-(but-2-enoyl)-1-ethyl-5,5-dimethylpyrazolidin-3-one, 7.5 mg (0.01 mmol) $Ru(bpy)_3Cl_2·6H_2O$, 37 mg $Sc(OTf)_3$ (0.075 mmol), 33 mg (0.1 mmol) (*S*)-*i*BuPyBox, 42 mg (0.15 mmol) TBACl, 10 mL acetonitrile. Isolated 141.2 mg (0.39 mmol, 79% yield), 89% ee. [Daicel Chiracel AD-H, 5 to 50% *i*-PrOH, 3 mL/min, 249 nm; t_1= 5.14 min, t_2= 5.38 min]. $[\alpha]_D^{22}$ −10.8 (*c*1.107, CH_2Cl_2). IR (thin film): 2968, 2873, 1744, 1706, 1601 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.04 (t, *J* = 7.7 Hz, 1H), 6.92 (d, *J* = 7.3 Hz, 1H), 6.71 (d, *J* = 8.3 Hz, 1H), 6.54 (t, *J* = 7.3 Hz, 1H), 3.38 − 3.24 (m, 3H), 3.05 − 2.89 (m, 4H), 2.79 − 2.68 (m, 3H), 2.64 − 2.52 (m, 3H), 1.98 − 1.87 (m, 2H), 1.29 (d, *J* = 6.5 Hz, 6H), 1.07 (t, *J* = 7.1 Hz, 3H), 1.03 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.2, 170.3, 145.8, 129.1, 127.2, 122.0, 115.4, 111.1, 60.4, 58.1, 50.9, 47.0, 44.1, 41.0, 28.8, 28.2, 25.9, 25.7, 22.1, 18.0, 12.9. HRMS (ESI^+) calc'd for $[C_{21}H_{31}N_3O_2+H]^+$ requires *m/z* 358.2490, found *m/z* 358.2484.



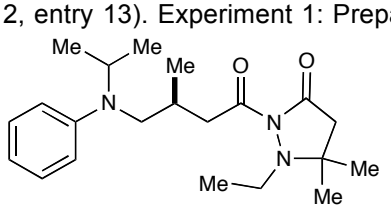
(*R*)-2-(4-(Diphenylamino)-3-methylbutanoyl)-1-ethyl-5,5-dimethylpyrazolidin-3-one (Table 2, entry 11). Experiment 1: Prepared according to the general procedure using 128.0 mg (0.50 mmol) of *N*-phenyl-*N*-((trimethylsilyl)methyl)aniline, 158 mg (0.75 mmol) of (*E*)-2-(but-2-enoyl)-1-ethyl-5,5-dimethylpyrazolidin-3-one, 7.5 mg (0.01 mmol) $Ru(bpy)_3Cl_2·6H_2O$, 37 mg $Sc(OTf)_3$ (0.075 mmol), 33 mg (0.10 mmol) (*R*)-*i*BuPyBox, 42 mg (0.15 mmol) TBACl, 10 mL acetonitrile and irradiated for 12 h. Purified by chromatography using 70:30 hexanes:EtOAc to yield 186.0 mg (0.47 mmol, 95% yield) of product as a colorless oil. The enantiomeric excess of the product was determined to be −91% by conversion to the corresponding alcohol and analysis by SFC Experiment 2: 130.8 mg (0.51 mmol) of *N*-phenyl-*N*-((trimethylsilyl)methyl)aniline, 158 mg (0.75 mmol) of (*E*)-2-(but-2-enoyl)-1-ethyl-5,5-dimethylpyrazolidin-3-one, 7.5 mg (0.01 mmol) $Ru(bpy)_3Cl_2·6H_2O$, 37 mg $Sc(OTf)_3$ (0.075 mmol), 33 mg (0.1 mmol) (*R*)-*i*BuPyBox, 42 mg (0.15 mmol) TBACl, 10 mL acetonitrile. Isolated 182.1 mg (0.46 mmol, 91% yield), −92% ee. $[\alpha]_D^{22}$ 24.7 (*c*0.970, CH_2Cl_2). IR (thin film): 2971, 2873, 1743, 1589, 1495 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.28 − 7.21 (m, 4H), 7.08 − 7.02 (m, 4H), 6.96 − 6.89 (m, 2H), 3.83 (dd, *J* = 14.5, 6.1 Hz, 1H), 3.48 (dd, *J* = 14.5, 8.8 Hz, 1H), 3.06 − 2.94 (m, 3H), 2.78 (dd, *J* = 16.8, 7.1 Hz, 1H), 2.57 (d, *J* = 4.1 Hz, 3H), 1.29 (d, *J* = 2.4 Hz, 6H), 1.09 − 1.02 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.2, 170.2, 148.7, 129.2, 121.3, 121.3, 60.4, 58.2, 47.1, 44.0, 40.9, 28.7, 25.9, 25.7, 18.1, 12.9. HRMS (ESI^+) calc'd for $[C_{24}H_{31}N_3O_2+H]^+$ requires *m/z* 394.2490, found *m/z* 394.2501.



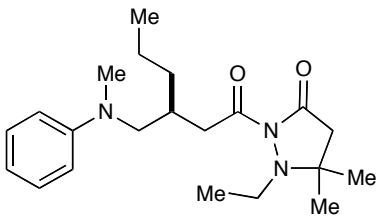
(*S*)-2-(4-(Benzyl(phenyl)amino)-3-methylbutanoyl)-1-ethyl-5,5-dimethylpyrazolidin-3-one (Table 2, entry 12). Experiment 1: Prepared according to the general procedure using 135.7 mg (0.50 mmol) of *N*-benzyl-*N*-((trimethylsilyl)methyl)aniline, 158 mg (0.75 mmol) of (*E*)-2-(but-2-enoyl)-1-ethyl-5,5-dimethylpyrazolidin-3-one, 7.5 mg (0.01 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 37 mg $Sc(OTf)_3$ (0.075 mmol), 33 mg (0.10 mmol) (*S*)-*i*BuPyBox, 42 mg (0.15 mmol) TBACl, 10 mL acetonitrile and irradiated for 6 h. Purified by chromatography using 70:30 hexanes:EtOAc to yield 121.0 mg (0.30 mmol, 58% yield) of product as a colorless oil. The enantiomeric excess of the product was determined to be 93% by conversion to the corresponding alcohol and analysis by SFC Experiment 2: 135.0 mg (0.50 mmol) of *N*-benzyl-*N*-((trimethylsilyl)methyl)aniline, 158 mg (0.75 mmol) of (*E*)-2-(but-2-enoyl)-1-ethyl-5,5-dimethylpyrazolidin-3-one, 7.5 mg (0.01 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 37 mg $Sc(OTf)_3$ (0.075 mmol), 33 mg (0.1 mmol) (*S*)-*i*BuPyBox, 42 mg (0.15 mmol) TBACl, 10 mL acetonitrile. Isolated 123.8 mg (0.31 mmol, 61% yield), 95% ee. $[\alpha]_D^{22}$ −5.5 (*c*1.050, CH_2Cl_2). IR (thin film): 3027, 2934, 2875, 1744,1706 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.30 − 7.23 (m, 2H), 7.23 − 7.12 (m, 5H), 6.78 (d, *J* = 7.2 Hz, 2H), 6.65 (t, *J* = 7.2 Hz, 1H), 4.73 − 4.51 (m, 2H), 3.55 (dd, *J* = 14.6, 6.2 Hz, 1H), 3.18 (dd, *J* = 14.7, 8.4 Hz, 1H), 3.04 − 2.91 (m, 3H), 2.75 (dd, *J* = 16.5, 7.2 Hz, 1H), 2.72 − 2.62 (m, 1H), 2.56 (d, *J* = 1.4 Hz, 2H), 1.29 (d, *J* = 5.8 Hz, 6H), 1.09 − 1.01 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.2, 170.2, 148.6, 138.6, 129.1, 128.5, 126.6, 126.6, 116.2, 112.6, 60.4, 57.4, 55.0, 47.0, 44.0, 41.0, 28.9, 25.9, 25.7, 18.1, 12.8. HRMS (ESI^+) calc'd for $[C_{25}H_{33}N_3O_2+H]^+$ requires *m/z* 408.2646, found *m/z* 408.2662.



(*S*)-1-Ethyl-2-(4-(isopropyl(phenyl)amino)-3-methylbutanoyl)-5,5-dimethylpyrazolidin-3-one (Table 2, entry 13). Experiment 1: Prepared according to the general procedure using 110.8 mg (0.50 mmol) of *N*-isopropyl-*N*-((trimethylsilyl)methyl)aniline, 158 mg (0.75 mmol) of (*E*)-2-(but-2-enoyl)-1-ethyl-5,5-dimethylpyrazolidin-3-one, 7.5 mg (0.01 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 37 mg $Sc(OTf)_3$ (0.075 mmol), 33 mg (0.10 mmol) (*S*)-*i*BuPyBox, 42 mg (0.15 mmol) TBACl, 10 mL acetonitrile and irradiated for 12 h. Purified by chromatography using 70:30 hexanes:EtOAc to yield 62.8 mg (0.17 mmol, 35% yield) of product (95% ee) as a colorless oil. Experiment 2: 111.4 mg (0.50 mmol) of *N*-isopropyl-*N*-((trimethylsilyl)methyl)aniline, 158 mg (0.75 mmol) of (*E*)-2-(but-2-enoyl)-1-ethyl-5,5-dimethylpyrazolidin-3-one, 7.5 mg (0.01 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 37 mg $Sc(OTf)_3$ (0.075 mmol), 33 mg (0.1 mmol) (*S*)-*i*BuPyBox, 42 mg (0.15 mmol) TBACl, 10 mL acetonitrile. Isolated 56.1 mg (0.16 mmol, 31% yield), 95% ee. [Daicel Chiracel AD-H, 10% MeOH, 3 mL/min, 236 nm; t_1= 5.10 min, t_2= 5.58 min]. $[\alpha]_D^{22}$ −31.5 (*c*1.200, CH_2Cl_2). IR (thin film): 2970, 2873, 1743, 1710, 1597 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.2 Hz, 2H), 6.92 (d, *J* = 8.2 Hz, 2H), 6.73 (t, *J* = 7.2 Hz, 1H), 3.99 (p, *J* = 6.7 Hz, 1H), 3.09 (dd, *J* = 14.2, 6.7 Hz, 1H), 3.04 − 2.94 (m, 3H), 2.85 (dd, *J* = 14.2, 8.2 Hz, 1H), 2.69 (dd, *J* = 16.7, 7.8 Hz, 1H), 2.57 (d, *J* = 2.8 Hz, 2H), 2.47 − 2.37 (m, 1H), 1.30 (s, 6H), 1.14 (dd, *J* = 10.8, 6.7 Hz, 6H), 1.07 (t, *J* = 7.1 Hz, 3H), 0.97 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.2, 170.5, 149.6, 128.8, 117.7, 116.8, 60.4, 52.2, 49.0, 47.0, 44.1, 41.3, 27.8, 25.9, 25.6, 20.2, 19.8, 18.0, 12.9. HRMS (ESI^+) calc'd for $[C_{21}H_{33}N_3O_2+H]^+$ requires *m/z* 360.2646, found *m/z* 360.2643.

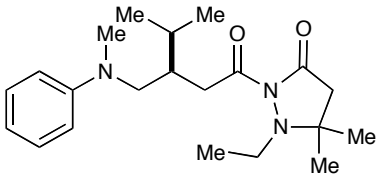


(*S*)-1-Ethyl-5,5-dimethyl-2-(3-((methyl(phenyl)amino)methyl)hexanoyl)pyrazolidin-3-one (Table 3, entry 1). Experiment 1: Prepared according to the general procedure using 97 mg (0.50 mmol) of *N*-methyl-*N*-((trimethylsilyl)methyl)aniline, 179 mg (0.75 mmol) of (*E*)-1-ethyl-2-(hex-2-enoyl)-5,5-dimethylpyrazolidin-3-one, 7.5 mg (0.01 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 37 mg $Sc(OTf)_3$ (0.075 mmol), 33 mg (0.10 mmol) (*S*)-*i*BuPyBox, 42 mg (0.15 mmol) TBACl, 10 mL acetonitrile and irradiated for 6 h. Purified by chromatography using 60:40 hexanes:Et_2O to yield 137 mg (0.38 mmol, 76% yield) of product (93% ee) as a colorless oil. Experiment 2: 97 mg (0.50 mmol) of *N*-methyl-*N*-((trimethylsilyl)methyl)aniline, 179 mg (0.75 mmol) of (*E*)-1-ethyl-2-(hex-2-enoyl)-5,5-dimethylpyrazolidin-3-one, 7.5 mg (0.01 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 37 mg $Sc(OTf)_3$ (0.075 mmol), 33 mg (0.1 mmol) (*S*)-*i*BuPyBox, 42 mg (0.15 mmol) TBACl, 10 mL acetonitrile. Isolated 136 mg (0.38 mmol, 76% yield), 92% ee. [Daicel Chiracel AD-H, 5 to 50% MeOH, 3 mL/min, 249 nm; t_1=

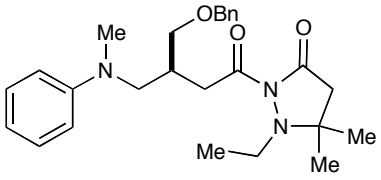


3.20 min, t_2= 3.52 min], $[\alpha]_D^{22}$ 0.8 (*c*0.968, CH_2Cl_2). IR (thin film): 2959, 2870, 1740, 1505 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.21 (dd, *J* = 8.8, 7.3 Hz, 2H), 6.77 (d, *J* = 8.3 Hz, 2H), 6.67 (t, *J* = 7.2 Hz, 1H), 3.35 (dd, *J* = 14.4, 7.2 Hz, 1H), 3.12 (dd, *J* = 14.4, 7.8 Hz, 1H), 2.97 (q, *J* = 7.3 Hz, 2H), 2.94 – 2.82 (m, 5H), 2.58 – 2.46 (m, 3H), 1.49 – 1.30 (m, 4H), 1.29 (s, 3H), 1.25 (s, 3H), 1.05 (t, *J* = 7.1 Hz, 3H), 0.89 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.2, 170.6, 149.9, 129.1, 116.1, 112.3, 60.3, 57.5, 47.0, 44.1, 39.1, 38.4, 34.3, 33.3, 25.8, 20.0, 14.4, 12.8; HRMS (ESI^+) calculated for $[C_{21}H_{33}N_3O_2+H]^+$ requires *m/z* 360.2646, found *m/z* 360.2651.

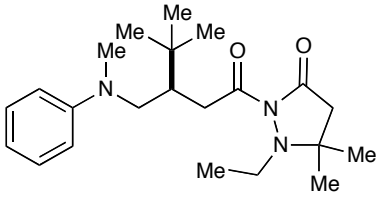
(*R*)-1-Ethyl-5,5-dimethyl-2-(4-methyl-3-((methyl(phenyl)amino)methyl)pentanoyl)pyrazolidin-3-one (Table 3, entry 2). Experiment 1: Prepared according to the general procedure using 97 mg (0.50 mmol) of *N*-methyl-*N*-((trimethylsilyl)methyl)aniline, 179 mg (0.75 mmol) of (*E*)-1-ethyl-5,5-dimethyl-2-(4-methylpent-2-enoyl)pyrazolidin-3-one, 7.5 mg (0.01 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 37 mg $Sc(OTf)_3$ (0.075 mmol), 33 mg (0.10 mmol) (*S*)-*i*BuPyBox, 42 mg (0.15 mmol) TBACl, 10 mL acetonitrile and irradiated for 6 h. Purified by chromatography using 60:40 hexanes:Et_2O to yield 129 mg (0.36 mmol, 71% yield) of product (93% ee) as a colorless oil. Experiment 2: 97 mg (0.50 mmol) of *N*-methyl-*N*-((trimethylsilyl)methyl)aniline, 179 mg (0.75 mmol) of (*E*)-1-ethyl-5,5-dimethyl-2-(4-methylpent-2-enoyl)pyrazolidin-3-one, 7.5 mg (0.01 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 37 mg $Sc(OTf)_3$ (0.075 mmol), 33 mg (0.1 mmol) (*S*)-*i*BuPyBox, 42 mg (0.15 mmol) TBACl, 10 mL acetonitrile. Isolated 127 mg (0.35 mmol, 70% yield), 93% ee. [Daicel Chiracel AD-H, 5 to 50% MeOH, 3 mL/min, 249 nm; t_1= 2.92 min, t_2= 3.32 min], $[\alpha]_D^{22}$ 8.6 (*c*0.996, CH_2Cl_2). IR (thin film): 2960, 2872, 1741, 1506 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.21 (dd, *J* = 8.8, 7.2 Hz, 2H), 6.79 (d, *J* = 8.0 Hz, 2H), 6.67 (t, *J* = 7.2 Hz, 1H), 3.34 (dd, *J* = 14.4, 7.4 Hz, 1H), 3.14 (dd, *J* = 14.4, 7.9 Hz, 1H), 2.96 (qd, *J* = 7.0, 3.5 Hz, 2H), 2.90 (s, 3H), 2.84 (dd, *J* = 6.5, 2.1 Hz, 2H), 2.60 – 2.48 (m, 3H), 1.90 (ddt, *J* = 10.3, 6.9, 3.4 Hz, 1H), 1.29 (s, 3H), 1.23 (s, 3H), 1.03 (t, *J* = 7.1 Hz, 3H), 0.95 (dd, *J* = 6.9, 5.4 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.2, 169.9, 149.2, 128.1, 115.1, 111.5, 59.3, 53.9, 46.0, 43.2, 37.8, 37.2, 33.7, 26.8, 24.7, 19.3, 17.1, 11.8. HRMS (ESI^+) calculated for $[C_{21}H_{33}N_3O_2+H]^+$ requires *m/z* 360.2646, found *m/z* 360.2650.



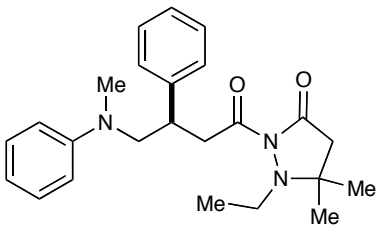
(*S*)-2-(4-(Benzyloxy)-3-((methyl(phenyl)amino)methyl)butanoyl)-1-ethyl-5,5-dimethylpyrazolidin-3-one (Table 3, entry 3). Experiment 1: Prepared according to the general procedure using 97 mg (0.50 mmol) of *N*-methyl-*N*-((trimethylsilyl)methyl)aniline, 237 mg (0.75 mmol) of (*E*)-2-(4-(benzyloxy)but-2-enoyl)-1-ethyl-5,5-dimethylpyrazolidin-3-one, 7.5 mg (0.01 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 37 mg $Sc(OTf)_3$ (0.075 mmol), 33 mg (0.10 mmol) (*S*)-*i*BuPyBox, 42 mg (0.15 mmol) TBACl, 10 mL acetonitrile and irradiated for 6 h. Purified by chromatography using 50:50 hexanes:Et_2O to yield 159 mg (0.36 mmol, 73% yield) of product (91% ee) as a colorless oil. Experiment 2: 97 mg (0.50 mmol) of *N*-methyl-*N*-((trimethylsilyl)methyl)aniline, 237 mg (0.75 mmol) of (*E*)-2-(4-(benzyloxy)but-2-enoyl)-1-ethyl-5,5-dimethylpyrazolidin-3-one, 7.5 mg (0.01 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 37 mg $Sc(OTf)_3$ (0.075 mmol), 33 mg (0.1 mmol) (*S*)-*i*BuPyBox, 42 mg (0.15 mmol) TBACl, 10 mL acetonitrile. Isolated 169 mg (0.39 mmol, 77% yield), 91% ee. [Daicel Chiracel AD-H, 5 to 50% *i*-PrOH, 3 mL/min, 249 nm; t_1= 6.42 min, t_2= 8.4 min], $[\alpha]_D^{22}$ 12.0 (*c*1.063, CH_2Cl_2). IR (thin film): 2973, 2860, 1741, 1506 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.24 (m, 5H), 7.23 – 7.18 (m, 2H), 6.80 (d, J = 8.2 Hz, 2H), 6.66 (t, J = 7.2 Hz, 1H), 4.46 (s, 2H), 3.57 – 3.47 (m, 2H), 3.44 – 3.33 (m, 2H), 3.07 (dd, J = 17.6, 6.3 Hz, 1H), 3.01 – 2.90 (m, 6H), 2.76 – 2.68 (m, 1H), 2.56 (s, 2H), 1.28 (s, 3H), 1.27 (s, 3H), 1.04 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.1, 170.4, 149.6, 138.5, 129.1, 128.3, 127.6, 127.5, 116.0, 111.9, 73.1, 70.2, 60.5, 54.0, 47.1, 43.9, 38.9, 36.3, 34.3, 25.7, 12.8. HRMS (ESI^+) calculated for $[C_{26}H_{35}N_3O_3+H]^+$ requires *m/z* 438.2752, found *m/z* 438.2748.



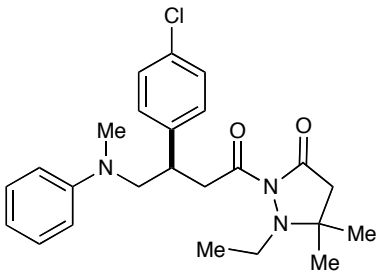
(*R*)-2-(4,4-Dimethyl-3-((methyl(phenyl)amino)methyl)pentanoyl)-1-ethyl-5,5-dimethylpyrazolidin-3-one (Table 3, entry 4). Experiment 1: Prepared according to the general procedure using 97 mg (0.50 mmol) of *N*-methyl-*N*-((trimethylsilyl)methyl)aniline, 189 mg (0.75 mmol) of (*E*)-2-(4,4-dimethylpent-2-enoyl)-1-ethyl-5,5-dimethylpyrazolidin-3-one, 7.5 mg (0.01 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 37 mg $Sc(OTf)_3$ (0.075 mmol), 33 mg (0.10 mmol) (*S*)-*i*BuPyBox, 42 mg (0.15 mmol) TBACl, 10 mL acetonitrile and irradiated for 6 h. Purified by chromatography using 60:45 hexanes:Et_2O to yield 59 mg (0.16 mmol, 32% yield) of product (96% ee) as a colorless oil. Experiment 2: 97 mg (0.50 mmol) of *N*-methyl-*N*-((trimethylsilyl)methyl)aniline, 189 mg (0.75 mmol) of (*E*)-2-(4,4-dimethylpent-2-enoyl)-1-ethyl-5,5-dimethylpyrazolidin-3-one, 7.5 mg (0.01 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 37 mg $Sc(OTf)_3$ (0.075 mmol), 33 mg (0.1 mmol) (*S*)-*i*BuPyBox, 42 mg (0.15 mmol) TBACl, 10 mL acetonitrile. Isolated 74 mg (0.20 mmol, 40% yield), 95% ee. [Daicel Chiracel AD-H, 3% MeOH, 3 mL/min, 249 nm; t_1= 4.25 min, t_2= 5.51 min], $[\alpha]_D^{22}$ 34.5 (*c*1.014, CH_2Cl_2). IR (thin film): 2963, 2870, 1739, 1505 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.18 (dd, *J* = 8.8, 7.3 Hz, 2H), 6.76 (d, *J* = 8.0 Hz, 2H), 6.67 (t, *J* = 7.2 Hz, 1H), 3.27 (dd, *J* = 13.9, 11.2 Hz, 1H), 3.18 (dd, *J* = 13.9, 4.8 Hz, 1H), 3.03 (dd, *J* = 18.0, 6.7 Hz, 1H), 2.95 – 2.79 (m, 3H), 2.77 (s, 3H), 2.64 (ddt, *J* = 9.4, 6.5, 4.7 Hz, 1H), 1.21 (s, 3H), 1.06 (s, 3H), 0.98 (s, 9H), 0.92 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.3, 170.7, 151.4, 129.0, 116.9, 113.6, 59.9, 55.1, 46.9, 44.5, 41.3, 37.7, 35.2, 32.6, 27.8, 25.8, 25.5, 12.6. HRMS (ESI^+) calculated for $[C_{22}H_{35}N_3O_2+H]^+$ requires *m/z* 374.2803, found *m/z* 374.2806.



(*R*)-1-Ethyl-5,5-dimethyl-2-(4-(methyl(phenyl)amino)-3-phenylbutanoyl)pyrazolidin-3-one (Table 3, entry 5) Experiment 1: Prepared according to the general procedure using 99.5 mg (0.51 mmol) of *N*-methyl-*N*-((trimethylsilyl)methyl)aniline, 204 mg (0.75 mmol) of (*E*)-2-cinnamoyl-1-ethyl-5,5-dimethylpyrazolidin-3-one, 7.5 mg (0.01 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 37 mg $Sc(OTf)_3$ (0.075 mmol), 33 mg (0.10 mmol) (*S*)-*i*BuPyBox, 42 mg (0.15 mmol) TBACl, 10 mL acetonitrile and irradiated for 12 h. Purified by chromatography using 70:30 hexanes: EtOAc to yield 149.2 mg (0.38 mmol, 74% yield) of product (93% ee) as a colorless oil. Experiment 2: 97.9 mg (0.51 mmol) of *N*-methyl-*N*-((trimethylsilyl)methyl)aniline, 204 mg (0.75 mmol) of (*E*)-2-cinnamoyl-1-ethyl-5,5-dimethylpyrazolidin-3-one, 7.5 mg (0.01 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 37 mg $Sc(OTf)_3$ (0.075 mmol), 33 mg (0.1 mmol) (*S*)-*i*BuPyBox, 42 mg (0.15 mmol) TBACl, 10 mL acetonitrile. Isolated 148.3 mg (0.38 mmol, 74% yield), 92% ee. [Daicel Chiracel AD-H, 5 to 50% MeOH, 3 mL/min, 249 nm; t_1= 4.25 min, t_2= 5.73 min]. $[\alpha]_D^{22}$ +72.7 (*c*1.094, CH_2Cl_2). IR (thin film): 2979, 2935, 2878, 1744, 1507 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.12 (m, 7H), 6.78 – 6.72 (m, 2H), 6.69 (d, *J* = 7.2 Hz, 1H), 3.84 – 3.72 (m, 2H), 3.41 (dd, *J* = 16.8, 7.0 Hz, 1H), 3.34 – 3.21 (m, 2H), 2.88 (q, *J* = 7.0 Hz, 2H), 2.63 (s, 3H), 2.58 – 2.44 (m, 2H), 1.23 (s, 3H), 1.14 (s, 3H), 0.89 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.3, 169.7, 149.1, 142.3, 129.2, 128.5, 128.1, 126.8, 116.1, 112.1, 60.3, 59.4, 47.0, 44.1, 40.0, 39.3, 39.3, 25.6, 12.6. HRMS (ESI^+) calc'd for $[C_{24}H_{31}N_3O_2+H]^+$ requires *m/z* 394.2490, found *m/z* 394.2488.

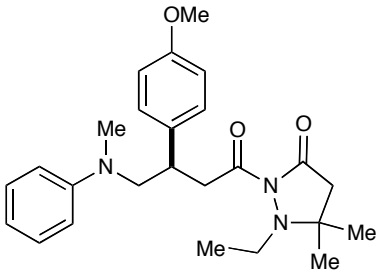


(*R*)-2-(3-(4-Chlorophenyl)-4-(methyl(phenyl)amino)butanoyl)-1-ethyl-5,5-dimethylpyrazolidin-3-one (Table 3, entry 6) Experiment 1: Prepared according to the general procedure using 101.6 mg (0.53 mmol) of *N*-methyl-*N*-((trimethylsilyl)methyl)aniline, 231 mg (0.75 mmol) of (*E*)-2-(3-(4-chlorophenyl)acryloyl)-1-ethyl-5,5-dimethylpyrazolidin-3-one, 7.5 mg (0.01 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 37 mg $Sc(OTf)_3$ (0.075 mmol), 33 mg (0.10 mmol) (*S*)-*i*BuPyBox, 42 mg (0.15 mmol) TBACl, 10 mL acetonitrile and irradiated for 12 h. Purified by chromatography using 70:30 hexanes: EtOAc to yield 134.9 mg (0.32 mmol, 60% yield) of product (90% ee) as a colorless oil. Experiment 2: 99.0 mg (0.51 mmol) of *N*-methyl-*N*-((trimethylsilyl)methyl)aniline, 231 mg (0.75 mmol) of (*E*)-2-(3-(4-chlorophenyl)acryloyl)-1-ethyl-5,5-dimethylpyrazolidin-3-one, 7.5 mg (0.01 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 37 mg $Sc(OTf)_3$ (0.075 mmol), 33 mg (0.1 mmol) (*S*)-*i*BuPyBox, 42 mg

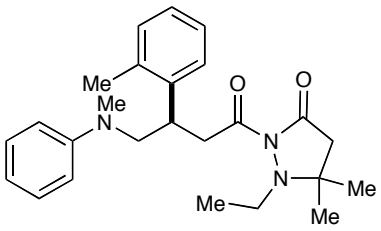


(0.15 mmol) TBACl, 10 mL acetonitrile. Isolated 142.0 mg (0.33 mmol, 65% yield), 91% ee. [Daicel Chiracel AD-H, 5 to 50% *i*-PrOH, 3 mL/min, 249 nm; t_1= 6.52 min, t_2= 7.94 min]. $[\alpha]_D^{22}$ +80.0 (*c*1.050, CH_2Cl_2). IR (thin film): 2978, 2878, 1744, 1599, 1233 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.28 – 7.19 (m, 4H), 7.19 – 7.12 (m, 2H), 6.74 (d, *J* = 8.1 Hz, 2H), 6.69 (t, *J* = 7.2 Hz, 1H), 3.82 – 3.70 (m, 2H), 3.37 (dd, *J* = 17.0, 6.9 Hz, 1H), 3.25 (tt, *J* = 11.8, 6.5 Hz, 2H), 2.90 (q, *J* = 7.1 Hz, 3H), 2.64 (s, 3H), 2.59 – 2.49 (m, 2H), 0.91 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.4, 169.4, 148.9, 140.9, 132.5, 129.5, 129.2, 128.6, 116.3, 112.1, 60.4, 59.3, 47.0, 44.0, 39.4, 39.2, 25.6, 12.6. HRMS (ESI^+) calc'd for $[C_{24}H_{30}ClN_3O_2+H]^+$ requires *m/z* 428.2100, found *m/z* 428.2108.

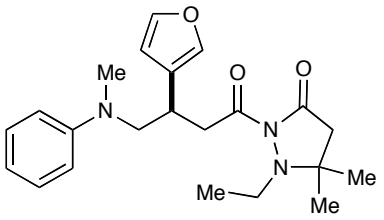
(*R*)-1-Ethyl-2-(3-(4-methoxyphenyl)-4-(methyl(phenyl)amino)butanoyl)-5,5-dimethylpyrazolidin-3-one (Table 3, entry 7) Experiment 1: Prepared according to the general procedure using 100.0 mg (0.52 mmol) of *N*-methyl-*N*-((trimethylsilyl)methyl)aniline, 227 mg (0.75 mmol) of (E)-1-ethyl-2-(3-(4-methoxyphenyl)acryloyl)-5,5-dimethylpyrazolidin-3-one, 7.5 mg (0.01 mmol) $Ru(bpy)_3Cl_2·6H_2O$, 37 mg $Sc(OTf)_3$ (0.075 mmol), 33 mg (0.10 mmol) (*S*)-*i*BuPyBox, 42 mg (0.15 mmol) TBACl, 10 mL acetonitrile and irradiated for 12 h. Purified by chromatography using 60:40 hexanes: EtOAc to yield 184.0 mg (0.43 mmol, 84% yield) of product (94% ee) as a white solid. Experiment 2: 100.7 mg (0.52 mmol) of *N*-methyl-*N*-((trimethylsilyl)methyl)aniline, 227 mg (0.75 mmol) of (*E*)-1-ethyl-2-(3-(4-methoxyphenyl)acryloyl)-5,5-dimethylpyrazolidin-3-one, 7.5 mg (0.01 mmol) $Ru(bpy)_3Cl_2·6H_2O$, 37 mg $Sc(OTf)_3$ (0.075 mmol), 33 mg (0.1 mmol) (*S*)-*i*BuPyBox, 42 mg (0.15 mmol) TBACl, 10 mL acetonitrile. Isolated 181.0 mg (0.43 mmol, 82% yield), 94% ee. [Daicel Chiracel AD-H, 5 to 50% MeOH, 3 mL/min, 249 nm; t_1= 5.30 min, t_2= 6.15 min]. $[\alpha]_D^{22}$ +81.2 (*c*1.039, CH_2Cl_2). IR (thin film): 2972, 2835, 1741, 1599, 1509 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.25 – 7.20 (m, 2fH), 7.14 (d, *J* = 8.6 Hz, 2H), 6.80 (d, *J* = 8.6 Hz, 2H), 6.75 (d, *J* = 8.1 Hz, 2H), 6.68 (t, *J* = 7.2 Hz, 1H), 3.81 – 3.67 (m, 2H), 3.76 (s, 3H), 3.37 (dd, *J* = 16.7, 7.2 Hz, 1H), 3.30 – 3.17 (m, 2H), 2.89 (q, *J* = 6.9 Hz, 2H), 2.63 (s, 3H), 2.58 – 2.47 (m, 2H), 1.23 (s, 3H), 1.15 (s, 3H), 0.91 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.3, 169.8, 158.4, 149.1, 134.3, 129.1, 129.0, 116.0, 113.8, 112.0, 60.3, 59.4, 55.2, 47.0, 44.1, 39.5, 39.3, 39.2, 25.6, 12.5. HRMS (ESI^+) calc'd for $[C_{25}H_{33}N_3O_3+H]^+$ requires *m/z* 424.2595, found *m/z* 424.2599. (mp = 153–158 ºC).



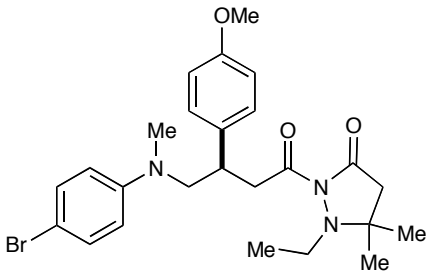
(*R*)-1-Ethyl-5,5-dimethyl-2-(4-(methyl(phenyl)amino)-3-(o-tolyl)butanoyl)pyrazolidin-3-one (Table 3, entry 8) Experiment 1: Prepared according to the general procedure using 98.5 mg (0.51 mmol) of *N*-methyl-*N*-((trimethylsilyl)methyl)aniline, 214 mg (0.75 mmol) of (*E*)-1-ethyl-5,5-dimethyl-2-(3-(*o*-tolyl)acryloyl)pyrazolidin-3-one, 7.5 mg (0.01 mmol) $Ru(bpy)_3Cl_2·6H_2O$, 37 mg $Sc(OTf)_3$ (0.075 mmol), 33 mg (0.10 mmol) (*S*)-*i*BuPyBox, 42 mg (0.15 mmol) TBACl, 10 mL acetonitrile and irradiated for 12 h. Purified by chromatography using 70:30 hexanes: EtOAc to yield 165.0 mg (0.41 mmol, 81% yield) of product (81% ee) as a colorless oil. Experiment 2: 100.4 mg (0.52 mmol) of *N*-methyl-*N*-((trimethylsilyl)methyl)aniline, 214 mg (0.75 mmol) of (*E*)-1-ethyl-5,5-dimethyl-2-(3-(*o*-tolyl)acryloyl)pyrazolidin-3-one, 7.5 mg (0.01 mmol) $Ru(bpy)_3Cl_2·6H_2O$, 37 mg $Sc(OTf)_3$ (0.075 mmol), 33 mg (0.1 mmol) (*S*)-*i*BuPyBox, 42 mg (0.15 mmol) TBACl, 10 mL acetonitrile. Isolated 163.0 mg (0.40 mmol, 80% yield), 83% ee. [Daicel Chiracel OD-H, 5 to 50% MeOH, 3 mL/min, 249 nm; t_1= 5.36 min, t_2= 5.84 min]. $[\alpha]_D^{22}$ +60.1 (*c*1.048, CH_2Cl_2). IR (thin film): 2976, 2877, 1744, 1705, 1599, 1507 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.29 (d, *J* = 7.7 Hz, 1H), 7.25 – 7.20 (m, 2H), 7.19 – 7.13 (m, 1H), 7.06 (d, *J* = 4.1 Hz, 2H), 6.74 (d, *J* = 8.1 Hz, 2H), 6.68 (d, *J* = 7.2 Hz, 1H), 4.15 – 4.04 (m, 1H), 3.76 (dd, *J* = 14.6, 6.9 Hz, 1H), 3.52 (dd, *J* = 16.8, 8.2 Hz, 1H), 3.29 (dd, *J* = 14.6, 8.1 Hz, 1H), 3.19 (dd, *J* = 16.9, 6.5 Hz, 1H), 2.85 (dd, *J* = 7.2, 3.9 Hz, 1H), 2.65 (s, 3H), 2.56 – 2.45 (m, 2H), 2.22 (s, 3H), 1.22 (s, 3H), 1.10 (s, 3H), 0.84 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.4, 169.9, 149.2, 140.9, 137.3, 130.5, 129.2, 126.3, 126.2, 126.0, 116.1, 111.9, 60.3, 59.3, 47.0, 44.0, 39.4, 39.2, 34.9, 25.6, 25.5, 19.8, 12.4. HRMS (ESI^+) calc'd for $[C_{25}H_{33}N_3O_2+H]^+$ requires *m/z* 408.2646, found *m/z* 408.2649.



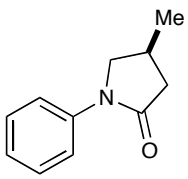
(*R*)-1-Ethyl-2-(3-(furan-3-yl)-4-(methyl(phenyl)amino)butanoyl)-5,5-dimethylpyrazolidin-3-one
(Table 3, entry 9) Experiment 1: Prepared according to the general procedure using 97.1 mg (0.50 mmol) of *N*-methyl-*N*-((trimethylsilyl)methyl)aniline, 197 mg (0.75 mmol) of (*E*)-1-ethyl-2-(3-(furan-3-yl)acryloyl)-5,5-dimethylpyrazolidin-3-one, 7.5 mg (0.01 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 37 mg $Sc(OTf)_3$ (0.075 mmol), 33 mg (0.10 mmol) (*S*)-*i*BuPyBox, 42 mg (0.15 mmol) TBACl, 10 mL acetonitrile and irradiated for 12 h. Purified by chromatography using 60:40 hexanes: EtOAc to yield 164.0 mg (0.43 mmol, 86% yield) of product (93% ee) as a colorless oil. Experiment 2: 97.0 mg (0.50 mmol) of *N*-methyl-*N*-((trimethylsilyl)methyl)aniline, 214 mg (0.75 mmol) of (*E*)-1-ethyl-2-(3-(furan-3-yl)acryloyl)-5,5-dimethylpyrazolidin-3-one, 7.5 mg (0.01 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 37 mg $Sc(OTf)_3$ (0.075 mmol), 33 mg (0.1 mmol) (*S*)-*i*BuPyBox, 42 mg (0.15 mmol) TBACl, 10 mL acetonitrile. Isolated 153.0 mg (0.40 mmol, 80% yield), 90% ee. [Daicel Chiracel AD-H, 5 to 50% MeOH, 3 mL/min, 249 nm; t_1= 4.11 min, t_2= 4.98 min]. $[\alpha]_D^{22}$ +19.2 (*c*1.018, CH_2Cl_2). IR (thin film): 2978, 2878, 1744, 1600, 1507, 1231 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.34 (t, *J* = 1.7 Hz, 1H), 7.27 – 7.18 (m, 3H), 6.80 – 6.72 (m, 2H), 6.72 – 6.63 (m, 1H), 6.36 (dd, *J* = 1.8, 0.9 Hz, 1H), 3.77 – 3.62 (m, 2H), 3.27 (ddd, *J* = 17.2, 7.4, 4.1 Hz, 2H), 3.17 (dd, *J* = 16.6, 6.2 Hz, 1H), 2.92 (q, *J* = 6.9 Hz, 2H), 2.80 (s, 3H), 2.54 (d, *J* = 2.7 Hz, 2H), 1.25 (s, 3H), 1.21 (s, 3H), 0.95 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.3, 169.6, 149.2, 142.9, 139.6, 129.2, 125.6, 116.2, 112.2, 109.8, 60.3, 58.5, 47.0, 44.0, 39.3, 39.2, 30.9, 25.6, 12.6. HRMS (ESI^+) calc'd for $[C_{22}H_{29}N_3O_3+H]^+$ requires *m/z* 384.2282, found *m/z* 384.2279.



(*R*)-2-(4-((4-bromophenyl)(methyl)amino)-3-(4-methoxyphenyl)butanoyl)-1-ethyl-5,5-dimethylpyrazolidin-3-one. Experiment 1: Prepared according to the general procedure using 136.0 mg (0.50 mmol) of 4-bromo-*N*-methyl-*N*-((trimethylsilyl)methyl)aniline, 227.1 mg (0.75 mmol) of (*E*)-1-ethyl-2-(3-(4-methoxyphenyl)acryloyl)-5,5-dimethylpyrazolidin-3-one, 7.5 mg (0.01 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 37 mg $Sc(OTf)_3$ (0.075 mmol), 33 mg (0.10 mmol) (*S*)-*i*BuPyBox, 42 mg (0.15 mmol) TBACl, 10 mL acetonitrile and irradiated for 12 h. Purified by chromatography using 60:40 hexanes: EtOAc to yield 205.6 mg (0.41 mmol, 82% yield) of product (94% ee) as a colorless oil. Experiment 2: 135.9 mg (0.50 mmol) of 4-bromo-*N*-methyl-*N*-((trimethylsilyl)methyl)aniline, 227.0 mg (0.75 mmol) of (*E*)-1-ethyl-2-(3-(4-methoxyphenyl)acryloyl)-5,5-dimethylpyrazolidin-3-one, 7.5 mg (0.01 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 37 mg $Sc(OTf)_3$ (0.075 mmol), 33 mg (0.1 mmol) (*S*)-*i*BuPyBox, 42 mg (0.15 mmol) TBACl, 10 mL acetonitrile. Isolated 214.0 mg (0.43 mmol, 85% yield), 94% ee. [Daicel Chiracel OJ-H, 5 to 50% MeOH, 3 mL/min, 249 nm; t_1= 6.39 min, t_2= 6.88 min]. $[\alpha]_D^{22}$ +101.5 (*c*1.012, CH_2Cl_2). IR (thin film): 2972, 2934, 1740, 1701, 1609 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.27 (d, *J* = 9.0 Hz, 2H), 7.10 (d, *J* = 8.6 Hz, 2H), 6.80 (d, *J* = 8.6 Hz, 2H), 6.61 (d, *J* = 9.1 Hz, 2H), 3.80 – 3.75 (m, 4H), 3.72 – 3.62 (m, 1H), 3.31 (dd, *J* = 16.9, 6.7 Hz, 1H), 2.91 (q, *J* = 7.1 Hz, 2H), 2.56 (s, 3H), 2.55 (d, *J* = 3.4 Hz, 2H), 1.25 (s, 3H), 1.18 (s, 3H), 0.93 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.3, 169.7, 158.5, 147.9, 134.1, 131.8, 129.0 113.9, 113.6, 107.8, 60.3, 59.3, 55.2, 47.0, 44.0, 39.5, 39.5, 38.7, 25.7, 25.6, 12.6. HRMS (ESI^+) calc'd for $[C_{25}H_{32}BrN_3O_3+H]^+$ requires *m/z* 502.1700, found *m/z* 502.1698.



(*S*)-4-Methyl-1-phenylpyrrolidin-2-one (Scheme 2, **8**) Experiment 1: Prepared according to the general procedure using 91.7 mg (0.51 mmol) of N-((trimethylsilyl)methyl)aniline, 158 mg (0.75 mmol) of (E)-2-(but-2-enoyl)-1-ethyl-5,5-dimethylpyrazolidin-3-one, 7.5 mg (0.01 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 37 mg $Sc(OTf)_3$ (0.075 mmol), 33 mg (0.10 mmol) (S)-*i*BuPyBox, 42 mg (0.15 mmol) TBACl, 10 mL acetonitrile and irradiated for 18 h. Purified by chromatography using 70:30 hexanes:EtOAc to yield 77.2 mg (0.44 mmol, 86% yield) of product (93% ee) as a colorless oil. Experiment 2: 93.9 mg (0.52 mmol) of *N*-((trimethylsilyl)methyl)aniline, 158 mg (0.75 mmol) of (E)-2-(but-2-enoyl)-1-ethyl-5,5-dimethylpyrazolidin-3-one, 7.5 mg (0.01 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 37 mg $Sc(OTf)_3$ (0.075 mmol), 33 mg (0.1 mmol) (S)-*i*BuPyBox, 42 mg (0.15 mmol) TBACl, 10 mL acetonitrile. Isolated

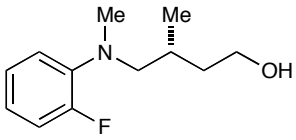


78.0 mg (0.44 mmol, 85% yield), 93% ee. [Supelco's Beta Dex 225, 140 °C for 45 min, then 5 °C/min to 180 °C; t_1= 49.95 min, t_2= 50.39 min]. $[\alpha]_D^{22}$ −3.1 (*c*1.152, CH_2Cl_2). IR (thin film): 2972, 1745, 1704, 1591, 1500 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.9 Hz, 2H), 7.36 (t, *J* = 8.0 Hz, 2H), 7.14 (t, *J* = 7.4 Hz, 1H), 3.95 (dd, *J* = 9.5, 7.6 Hz, 1H), 3.45 (dd, *J* = 9.4, 6.4 Hz, 1H), 2.76 (dd, *J* = 16.8, 8.4 Hz, 1H), 2.64 − 2.48 (m, 1H), 2.26 (dd, *J* = 16.8, 7.5 Hz, 1H), 1.21 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.8, 139.4, 128.8, 124.4, 119.9, 55.9, 41.0, 26.3, 19.5. HRMS (ESI^+) calc'd for $[C_{11}H_{13}FNO+H]^+$ requires *m/z* 176.1070, found *m/z* 176.1065.

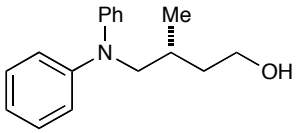
V. Removal of pyrazolidinone moiety

General procedure for the formation of alcohols: A solution of EtSH (3.4 equiv) in THF (0.1 M) was cooled to –78 °C and treated with *n*-BuLi (1.6 M in hexane, 2.5 equiv). The reaction was stirred at 0 °C for 30 min. A solution of the substrate (1 equiv) in THF (0.06 M) was then added. The reaction was stirred at 0 °C until the consumption of the starting material was complete as judged by TLC (0.5 – 1 h). The reaction was quenched with saturated NH_4Cl (aq) and the phases separated. The aqueous layer was extracted with Et_2O (x 3), the combined organic layers were dried over $MgSO_4$, and the solvent removed by rotary evaporation. The crude product was then dissolved in Et_2O (0.1 M) and added to a suspension of $LiAlH_4$ (3 equiv) in Et_2O at room temperature. The mixture was stirred until the consumption of the starting material was judged to be complete by TLC (0.5 – 2 h). The reaction was carefully quenched by the addition of water at 0 °C. The aqueous layer was then extracted with Et_2O (x 3) and the combined organic layers were dried over $MgSO_4$ and the solvents removed to yield the crude product, which was purified by column chromatography.

(*R*)-4-((2-Fluorophenyl)(methyl)amino)-3-methylbutan-1-ol. Experiment 1: Prepared according to the general procedure using 104 μL (1.4 mmol) of ethanethiol, 0.6 mL (1.0 mmol) of *n*-BuLi and 144.2 mg (0.41 mmol) of 1-ethyl-(*S*)-2-(4-((2-fluorophenyl)(methyl)amino)-3-methylbutanoyl)-5,5-dimethylpyrazolidin-3-one. Subsequent to aqueous workup, the crude thioester was used in the next step without further purification using 47 mg (1.2 mmol) of $LiAlH_4$. Column chromatography using 70:30 hexanes:EtOAc yields 64.4 mg (0.30 mmol, 74% yield) of product (−95% ee) as a colorless oil. Experiment 2: 104 μL (1.4 mmol) of ethanethiol, 0.6 mL (1.0 mmol) of *n*-BuLi and 138.0 mg (0.40 mmol) of 1-ethyl-2-(4-((2-fluorophenyl)(methyl)amino)-3-methylbutanoyl)-5,5-dimethylpyrazolidin-3-one. Subsequent to aqueous workup, the crude thioester was used in the next step without further purification using 47 mg (1.2 mmol) of $LiAlH_4$. Isolated 62.6 mg (0.30 mmol, 75% yield), −96% ee. [Daicel Chiracel OD-H, 3% *i*-PrOH, 5 mL/min, 249 nm; t_1= 6.28 min, t_2= 7.08 min]. $[\alpha]_D^{22}$ −8.5 (*c*1.175, CH_2Cl_2). IR (thin film): 3450, 2957, 2872, 16336, 1612 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.08 − 6.96 (m, 3H), 6.96 − 6.88 (m, 1H), 3.78 − 3.69 (m, 1H), 3.70 − 3.56 (m, 1H), 3.00 (s, 1H), 2.98 − 2.88 (m, 2H), 2.80 (s, 3H), 2.02 − 1.87 (m, 1H), 1.72 − 1.57 (m, 1H), 1.57 − 1.45 (m, 1H), 0.96 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.0 (*J* = 245.7 Hz), 140.1 (*J* = 8.9 Hz), 124.3 (*J* = 3.6 Hz), 122.4 (*J* = 7.8 Hz), 120.3 (*J* = 3.2 Hz), 116.4 (*J* = 20.9 Hz), 62.1 (*J* = 3.2 Hz), 61.5, 41.6 (*J* = 2.6 Hz), 39.0, 29.8, 19.2. HRMS (ESI^+) calc'd for $[C_{12}H_{18}FNO+H]^+$ requires *m/z* 212.1446, found *m/z* 212.1442.

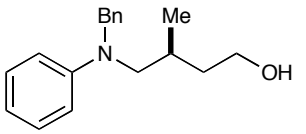


(*R*)-4-(Diphenylamino)-3-methylbutan-1-ol. Experiment 1: Prepared according to the general procedure using 104 μL (1.4 mmol) of ethanethiol, 0.6 mL (1.0 mmol) of *n*-BuLi and 162.7 mg (0.41 mmol) of (*S*)-2-(4-(diphenylamino)-3-methylbutanoyl)-1-ethyl-5,5-dimethylpyrazolidin-3-one. Subsequent to aqueous workup, the crude thioester was used in the next step without further purification using 47 mg (1.2 mmol) of $LiAlH_4$. Column chromatography using 70:30 hexanes:EtOAc yields 71.6 mg (0.28 mmol, 76% yield) of product (−91% ee) as a colorless oil. Experiment 2: 119 μL (1.6 mmol) of ethanethiol, 0.7 mL (1.0 mmol) of *n*-BuLi and 186.0 mg (0.47 mmol) of 2-(4-(diphenylamino)-3-methylbutanoyl)-1-ethyl-5,5-dimethylpyrazolidin-3-one. Subsequent to aqueous workup, the crude thioester was used in the next step without further purification using 54 mg (1.4 mmol) of $LiAlH_4$. Isolated 93.6 mg (0.37 mmol, 78% yield), −92% ee. [Daicel Chiracel OJ-H, 5% *i*-PrOH, 4 mL/min, 249 nm; t_1= 8.03 min, t_2= 8.83 min]. $[\alpha]_D^{22}$ 12.7 (*c*0.780, CH_2Cl_2). IR (thin film): 3440, 3059, 2927,

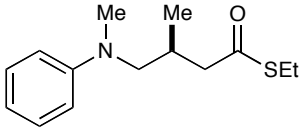


2870, 1589, 1496 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.29 − 7.21 (m, 4H), 7.00 (d, *J* = 8.6 Hz, 3H), 6.94 (t, *J* = 7.3 Hz, 3H), 3.76 − 3.68 (m, 1H), 3.68 − 3.60 (m, 2H), 3.53 (dd, *J* = 14.6, 7.7 Hz, 1H), 2.12 − 2.00 (m, 1H), 1.84 − 1.73 (m, 1H), 1.47 − 1.35 (m, 1H), 1.26 (s, 1H), 0.99 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.8, 129.2, 121.3, 121.3, 61.1, 59.1, 37.7, 28.9, 17.9. HRMS (ESI^+) calc'd for $[C_{17}H_{21}NO+H]^+$ requires *m/z* 256.1696, found *m/z* 256.1698.

(*S*)-4-(Benzyl(phenyl)amino)-3-methylbutan-1-ol. Experiment 1: Prepared according to the general procedure using 76 μL (1.0 mmol) of ethanethiol, 0.5 mL (0.75 mmol) of *n*-BuLi and 13.0 mg (0.30 mmol) of (*S*)-2-(4-(benzyl(phenyl)amino)-3-methylbutanoyl)-1-ethyl-5,5-dimethylpyrazolidin-3-one. Subsequent to aqueous workup, the crude thioester was used in the next step without further purification using 34 mg (0.9 mmol) of $LiAlH_4$. Column chromatography using 70:30 hexanes:EtOAc yields 51.6 mg (0.19 mmol, 64% yield) of product (93% ee) as a colorless oil. Experiment 2: 75 μL (1.0 mmol) of ethanethiol, 0.5 mL (0.70 mmol) of *n*-BuLi and 121.0 mg (0.29 mmol) of 2-(4-(benzyl(phenyl)amino)-3-methylbutanoyl)-1-ethyl-5,5-dimethylpyrazolidin-3-one. Subsequent to aqueous workup, the crude thioester was used in the next step without further purification using 33 mg (0.87 mmol) of $LiAlH_4$. Isolated 49.2 mg (0.18 mmol, 63% yield), 95% ee. [Daicel Chiracel OD-H, 5 to 50% *i*-PrOH, 3 mL/min, 249 nm; t_1= 7.22 min, t_2= 8.17 min]. $[\alpha]_D^{22}$ 2.9 (*c*0.805, CH_2Cl_2). IR (thin film): 3404, 2927, 2871, 1598, 1505, 1358 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.31 − 7.25 (m, 2H), 7.24 − 7.14 (m, 5H), 6.75 − 6.64 (m, 3H), 4.59 (s, 2H), 3.78 − 3.69 (m, 1H), 3.69 − 3.61 (m, 1H), 3.34 (dd, *J* = 14.7, 7.1 Hz, 1H), 3.21 (dd, *J* = 14.6, 7.5 Hz, 1H), 2.22 − 2.07 (m, 1H), 1.79 − 1.69 (m, 1H), 1.45 (s, 1H), 1.43 − 1.35 (m, 1H), 0.97 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.7, 138.5, 129.1, 128.5, 126.8, 126.7, 116.5, 113.0, 61.1, 58.4, 55.6, 37.8, 29.2, 18.0. HRMS (ESI^+) calc'd for $[C_{18}H_{23}NO+H]^+$ requires *m/z* 270.1853, found *m/z* 270.1850.

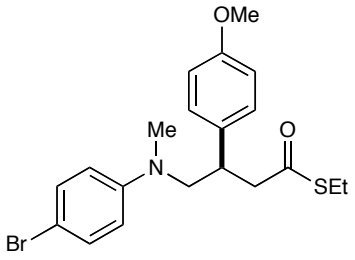


(*S*)-S-Ethyl 3-methyl-4-(methyl(phenyl)amino)butanethioate (Scheme 2, **5**)**.** *n*-BuLi (1.6 M in hexane, 0.34 mL, 1.5 equiv) was added at –78 °C to a solution of ethanethiol (53 μL, 0.72 mmol, 2.0 equiv) in THF (5 mL). The solution was stirred at 0 °C for 30 minutes. A solution of (*S*)-1-ethyl-5,5-dimethyl-2-(3-methyl-4-(methyl(phenyl)amino)butanoyl)pyrazolidin-3-one (120.7 mg, 0.36 mmol, 1 equiv) in THF (5 mL) was then added. The reaction was stirred at 0 °C for 10 minutes. The reaction was then quenched with saturated NH_4Cl (5 mL) and the phases separated. The aqueous layer was extracted with DCM (10 mL x 3) and the combined organic layers were dried over $MgSO_4$ and the solvents removed. The aqueous layer was then rotovaped, triturated with DCM and the organic solvent removed. The combined crude product was purified by column chromatography using 100:1 to 10:1 DCM: MeOH. Isolated 50.3 mg 1-ethyl-5,5-dimethylpyrazolidin-3-one (0.35 mmol, 95% recovery) and 88.9 mg of thioester (0.35 mmol, 98% yield), 93% ee. [Daicel Chiracel OJ-H, 3% MeOH, 3 mL/min, 249 nm; t_1= 5.36 min, t_2= 6.14 min]. $[\alpha]_D^{22}$ – 1.9 (*c*1.155, CH_2Cl_2). IR (thin film): 2963, 2872, 1685, 1599, 1506 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.22 (dd, *J* = 8.9, 7.1 Hz, 2H), 6.74 – 6.65 (m, 3H), 3.26 (dd, *J* = 14.5, 7.3 Hz, 1H), 3.08 (dd, *J* = 14.5, 7.6 Hz, 1H), 2.94 (s, 3H), 2.87 (q, *J* = 7.4 Hz, 2H), 2.62 (dd, *J* = 14.5, 5.5 Hz, 1H), 2.56 – 2.46 (m, 1H), 2.40 (dd, *J* = 14.5, 8.0 Hz, 1H), 1.24 (t, *J* = 7.4 Hz, 3H), 0.98 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.8, 149.6, 129.1, 116.2, 112.1, 58.8, 48.8, 39.2, 30.5, 23.4, 17.6, 14.8. HRMS (ESI^+) calc'd for $[C_{14}H_{21}NOS+H]^+$ requires *m/z* 252.1417, found *m/z* 252.1417.

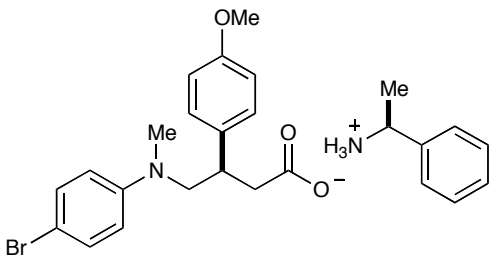


VI. Synthesis of Compounds for X-Ray Structures

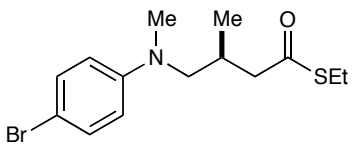
(*R*)-S-Ethyl-4-((4-bromophenyl)(methyl)amino)-3-(4-methoxyphenyl)butanethioate. A solution of ethanethiol (38 μL, 0.52 mmol, 2.0 equiv) in THF (4 mL) was cooled to –78 °C, and *n*-BuLi (1.6 M in hexane, 0.28 mL, 1.5 equiv) was added. The reaction was stirred at 0 °C for 30 min. A solution of (*R*)-2-(4-((4-bromophenyl)(methyl)amino)-3-(4-methoxyphenyl)butanoyl)-1-ethyl-5,5-dimethylpyrazolidin-3-one (131.0 mg, 0.26 mmol, 1 equiv) in THF (4 mL) was then added. The reaction was stirred at 0 °C for 10 min. The reaction was then quenched with saturated NH_4Cl (5 mL) and the phases separated. The aqueous layer was extracted with Et_2O (10 mL x 3) and the combined organic layers were dried over $MgSO_4$ and the solvents removed by rotary evaporation. The crude product was purified by column chromatography using 70:30 hexanes: EtOAc. Isolated 102.0 mg of thioester (0.24 mmol, 93% yield), 94% ee. [Daicel Chiracel AD-H, 5 to 50% *i*-PrOH, 3 mL/min, 249 nm; t_1= 6.96 min, t_2= 7.72 min]. $[\alpha]_D^{22}$ + 86.5 (*c*1.068, CH_2Cl_2). IR (thin film): 2930, 2832,m 1679, 1609, 1588 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, *J* = 9.0 Hz, 2H), 7.06 (d, *J* = 8.6 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 6.52 (d, *J* = 9.0 Hz, 2H), 3.78 (s, 4H), 3.66 (dd, *J* = 14.5, 6.6 Hz, 1H), 3.62 − 3.53 (m, 3H), 3.22 (dd, *J* = 14.5, 8.3 Hz, 1H), 2.96 − 2.85 (m, 2H), 2.82 (qd, *J* = 7.5, 3.1 Hz, 3H), 2.60 (s, 3H), 1.18 (t, *J* = 7.4 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.8, 158.6, 147.8, 133.5, 131.8, 128.6, 114.0, 113.6, 108.1, 59.0, 55.2, 47.6, 39.8, 39.5, 23.4, 14.7. HRMS (ESI^+) calc'd for $[C_{20}H_{24}BrNO_2S+H]^+$ requires *m/z* 422.0784, found *m/z* 422.0782.



(*S*)-1-Phenylethanaminium (*R*)-4-((4-bromophenyl)(methyl)amino)-3-(4-methoxyphenyl)butanoate. A solution of (*R*)-S-ethyl 4-((4-bromophenyl)(methyl)amino)-3-(4-methoxyphenyl)butanethioate (83.1 mg, 0.20 mmol, 1 equiv) in MeOH (3 mL) and 1 M NaOH (1.5 mL) was stirred at room temperature overnight. After that time, the solution was acidified to pH 4 with 10% citric acid. The resulting mixture was extracted with DCM (5 mL x 3) and the combined organic layers were dried over $MgSO_4$. The solvent was then removed by rotary evaporation. The crude product was dissolved in DCM (3 mL) and (*S*)-1-phenylethaneamine (21 μL, 0.17 mmol, 1 equiv) was added. The resulting mixture was stirred overnight. After that time, the solvent was removed by rotary evaporation to obtain 77.6 mg (0.16 mmol, 78% yield over two steps) of the desired salt. $[\alpha]_D^{22}$ + 121.7 (*c*1.035, $CHCl_3$). IR (thin film): 2924, 2890, 1606, 1590, 1555 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.29 − 7.19 (m, 7H), 6.98 (d, *J* = 8.5 Hz, 2H), 6.76 (d, *J* = 8.5 Hz, 2H), 6.53 (d, *J* = 9.0 Hz, 2H), 5.79 (*br* s, 3H), 4.06 − 3.93 (m, 1H), 3.73 (s, 3H), 3.58 (dd, *J* = 14.6, 6.2 Hz, 1H), 3.45 − 3.33 (m, 1H), 3.06 (dd, *J* = 14.6, 8.8 Hz, 1H), 2.52 (s, 3H), 2.47 − 2.32 (m, 2H), 1.35 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.23, 158.4, 147.9, 144.9, 134.2, 131.7, 128.7, 128.6, 127.4, 125.8, 113.9, 113.6, 107.9, 59.5, 6.2, 51.1, 39.6, 39.4, 38.7, 24.0. HRMS (ESI^-) calc'd for $[C_{12}H_{15}BrNO_2]^-$ requires *m/z* 284.0291, found *m/z* 284.0292. (mp = 160–163 ºC).



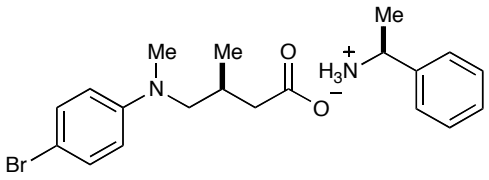
(*S*)-S-Ethyl 4-((4-bromophenyl)(methyl)amino)-3-methylbutanethioate. A solution of ethanethiol (53 μL, 0.72 mmol, 2.0 equiv) in THF (5 mL) was cooled to –78 °C, and *n*-BuLi (1.6 M in hexane, 0.39 mL, 1.5 equiv) was added. The reaction was stirred at 0 °C for 30 min. A solution of (*S*)-2-(4-((4-bromophenyl)(methyl)amino)-3-methylbutanoyl)-1-ethyl-5,5-dimethylpyrazolidin-3-one (149.4 mg, 0.36 mmol, 1 equiv) in THF (5 mL) was then added. The reaction was stirred at 0 °C for 10 min. The reaction was then quenched with saturated NH_4Cl (5 mL) and the phases separated. The aqueous layer was extracted with Et_2O (10 mL x 3) and the combined organic layers were dried over $MgSO_4$ and the solvents removed by rotary evaporation. The crude product was purified by column chromatography using 70:30 hexanes: EtOAc. Isolated 84.5 mg of thioester (0.26 mmol, 85% yield), $[\alpha]_D^{22}$ –5.9 (*c*1.003, CH_2Cl_2). IR (thin film): 2962, 2871, 1680, 1589, 1496 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, *J* = 9.1 Hz, 2H), 6.56 (d, *J* = 9.0 Hz, 2H), 3.25 (dd, *J* = 14.6, 7.1 Hz, 1H), 3.05 (dd, *J* = 14.6, 7.6 Hz, 1H), 2.91 (s, 3H), 2.87 (q, *J* = 7.4 Hz, 2H), 2.57 (dd, *J* =



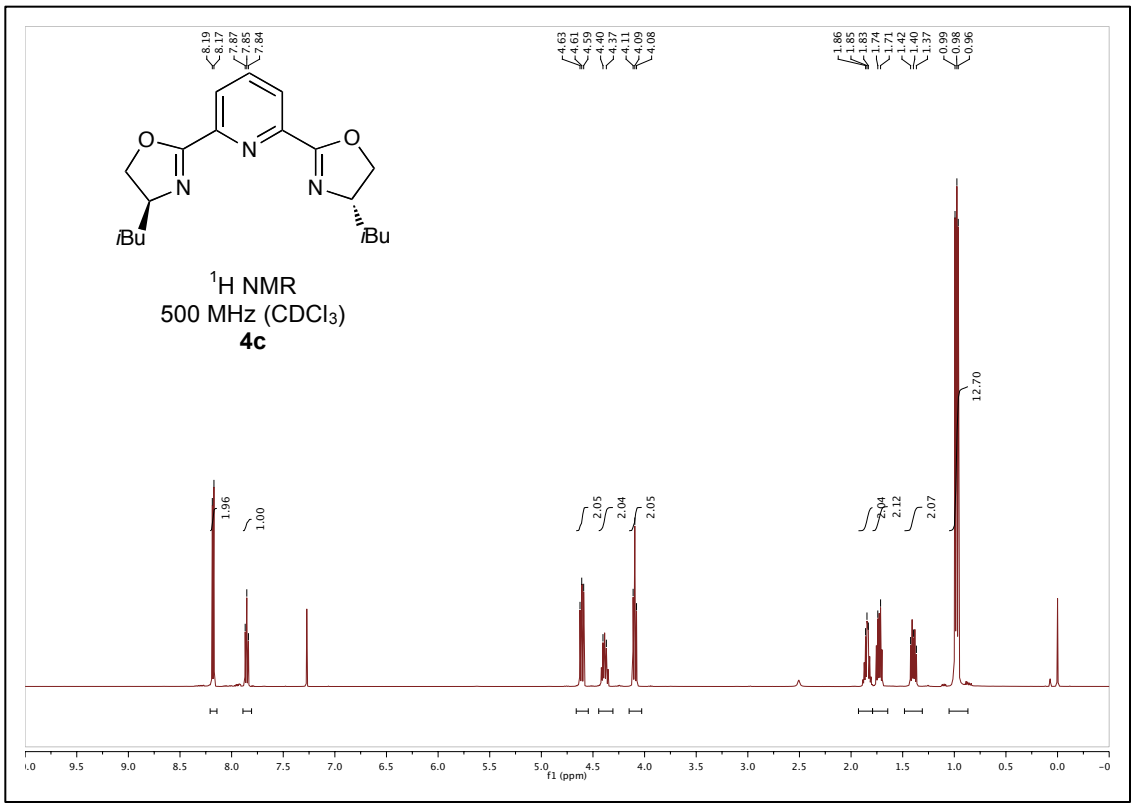
14.3, 5.7 Hz, 1H), 2.49 (dq, *J* = 13.5, 6.9 Hz, 1H), 2.40 (dd, *J* = 14.3, 7.4 Hz, 1H), 1.24 (t, *J* = 7.4 Hz, 3H), 0.96 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.6, 148.5, 131.7, 113.7, 108.1, 58.6, 48.7, 39.4, 30.3, 23.4, 17.7, 14.8. HRMS (ESI^+) calc'd for $[C_{14}H_{20}BrNOS+H]^+$ requires *m/z* 330.0522, found *m/z* 330.0525.

(*S*)-1-Phenylethanaminium (*S*)-4-((4-bromophenyl)(methyl)amino)-3-methylbutanoate.

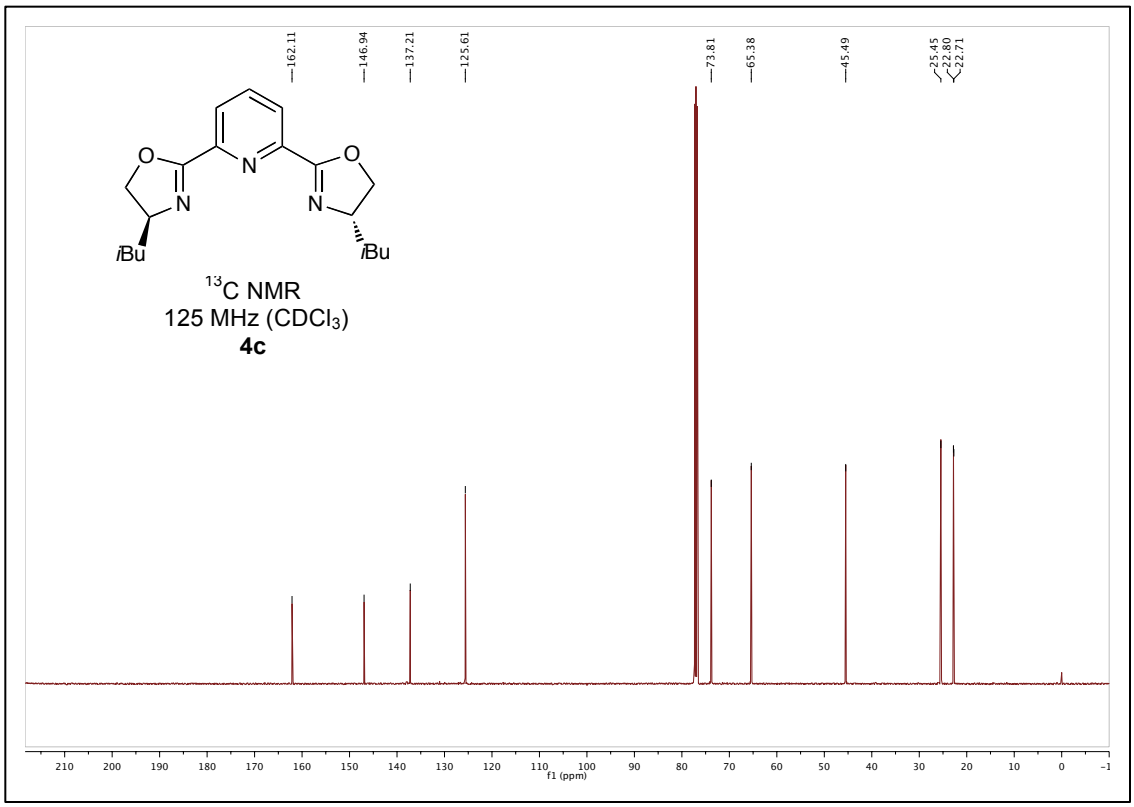
A solution of (*S*)-S-ethyl 4-((4-bromophenyl)(methyl)amino)-3-methylbutanethioate (84.5 mg, 0.26 mmol, 1 equiv) in MeOH (4 mL) and 1 M NaOH (2.0 mL) was stirred at room temperature overnight. After that time, the solution was acidified to pH 4 with 10% citric acid. The resulting mixture was extracted with DCM (5 mL x 3) and the combined organic layers were dried over $MgSO_4$. The solvent was then removed by rotary evaporation. The crude product was dissolved in DCM (3 mL) and (*S*)-1-phenylethaneamine (33 μL, 0.26 mmol, 1 equiv) was added. The resulting mixture was stirred overnight. After that time, the solvent was removed by rotary evaporation to obtain 98.7 mg (0.24 mmol, 93% yield over two steps) of the desired salt. $[\alpha]_D^{22}$ – 2.6 (*c*0.995, CH_2Cl_2). IR (thin film): 2927, 2870, 1588, 1556, 1497 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.23 (m, 3H), 7.19 (t, *J* = 4.4 Hz, 4H), 6.55 – 6.45 (m, 2H), 4.73 (s, 3H), 4.08 (q, *J* = 6.7 Hz, 1H), 3.16 (dd, *J* = 14.6, 7.2 Hz, 1H), 2.96 (dd, *J* = 14.6, 7.7 Hz, 1H), 2.84 (s, 3H), 2.31 (h, *J* = 7.0 Hz, 1H), 2.20 (dd, *J* = 15.3, 6.2 Hz, 1H), 2.03 (dd, *J* = 15.4, 7.5 Hz, 1H), 1.37 (d, *J* = 6.6 Hz, 3H), 0.88 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.1, 147.5, 144.0, 130.7, 127.7, 126.4, 124.8, 112.7, 106.9, 57.9, 50.1, 39.0, 38.5, 28.5, 23.1, 16.9. HRMS (ESI^-) calc'd for $[C_{18}H_{19}BrNO_3]^-$ requires *m/z* 376.0553, found *m/z* 376.0555. (mp = 166–168 ºC).



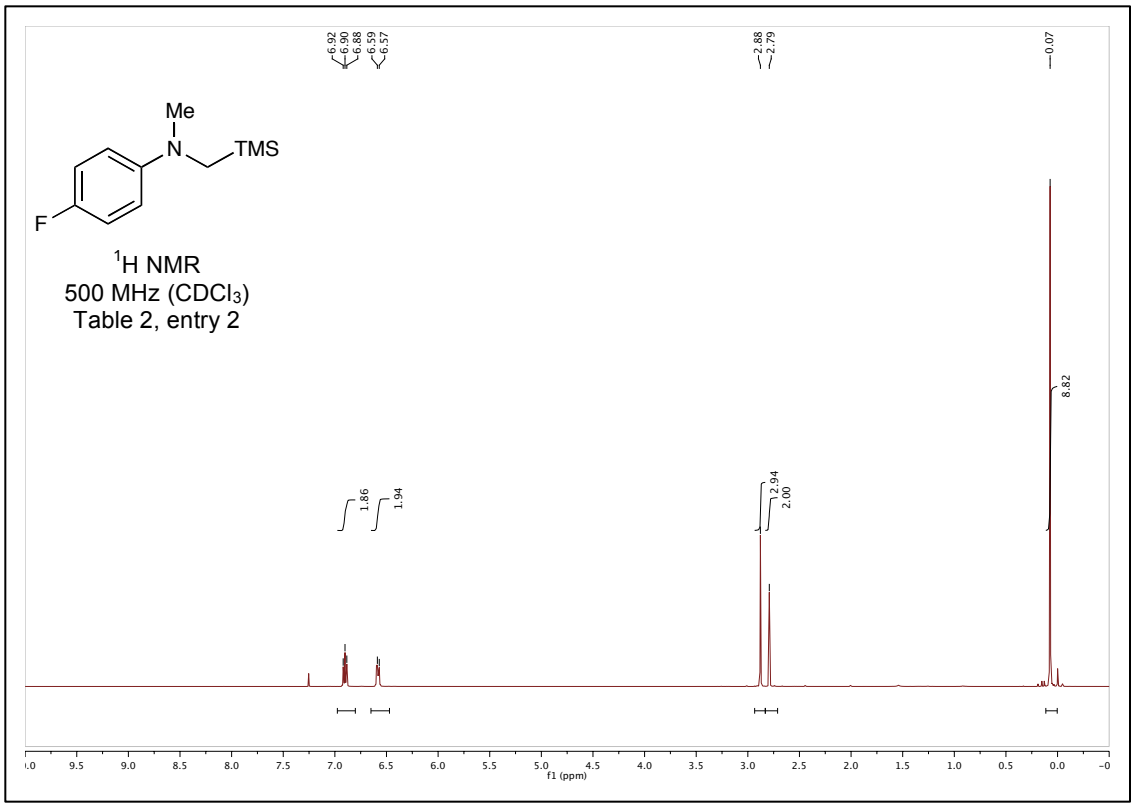
VII. Spectra



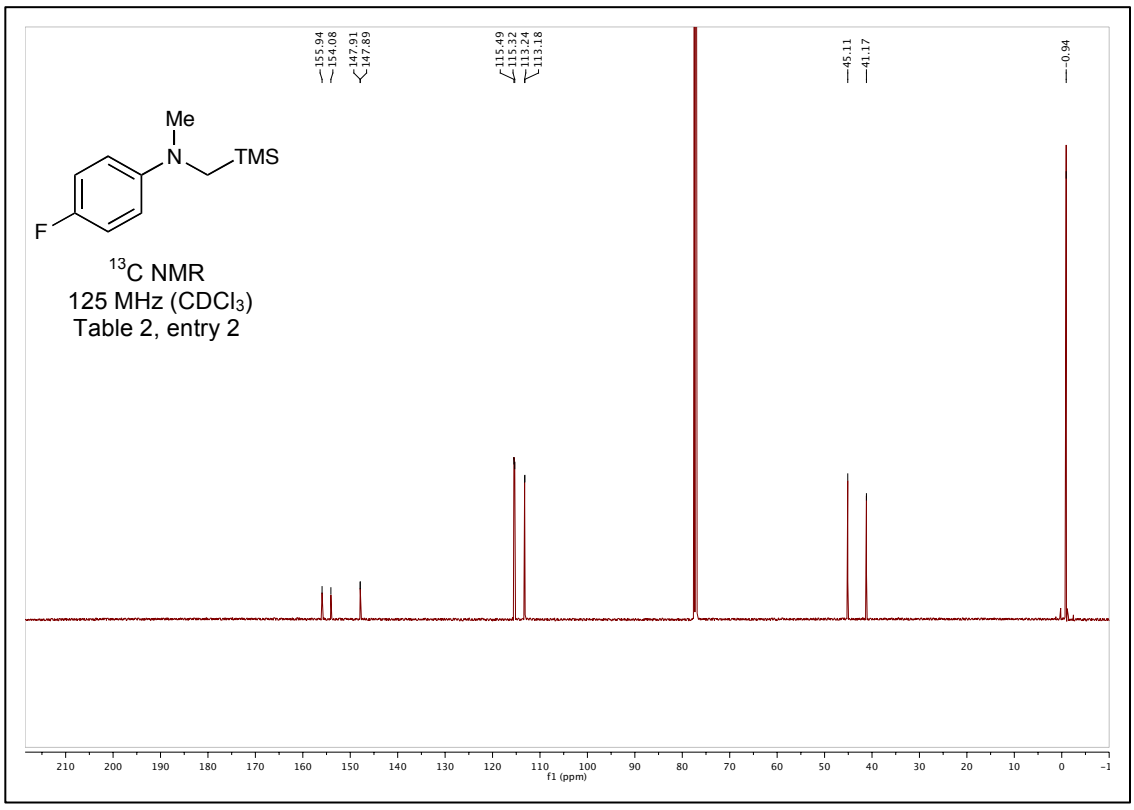
^{1}H NMR
500 MHz ($CDCl_3$)
4c



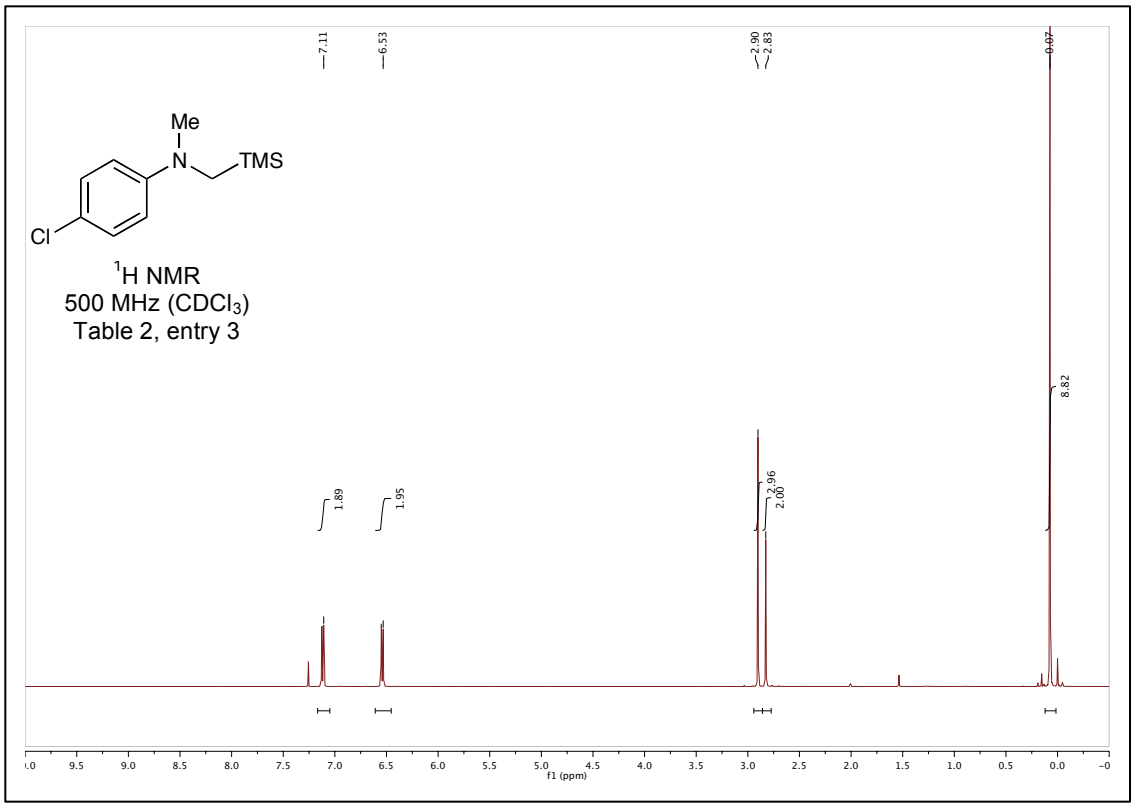
^{13}C NMR
125 MHz ($CDCl_3$)
4c



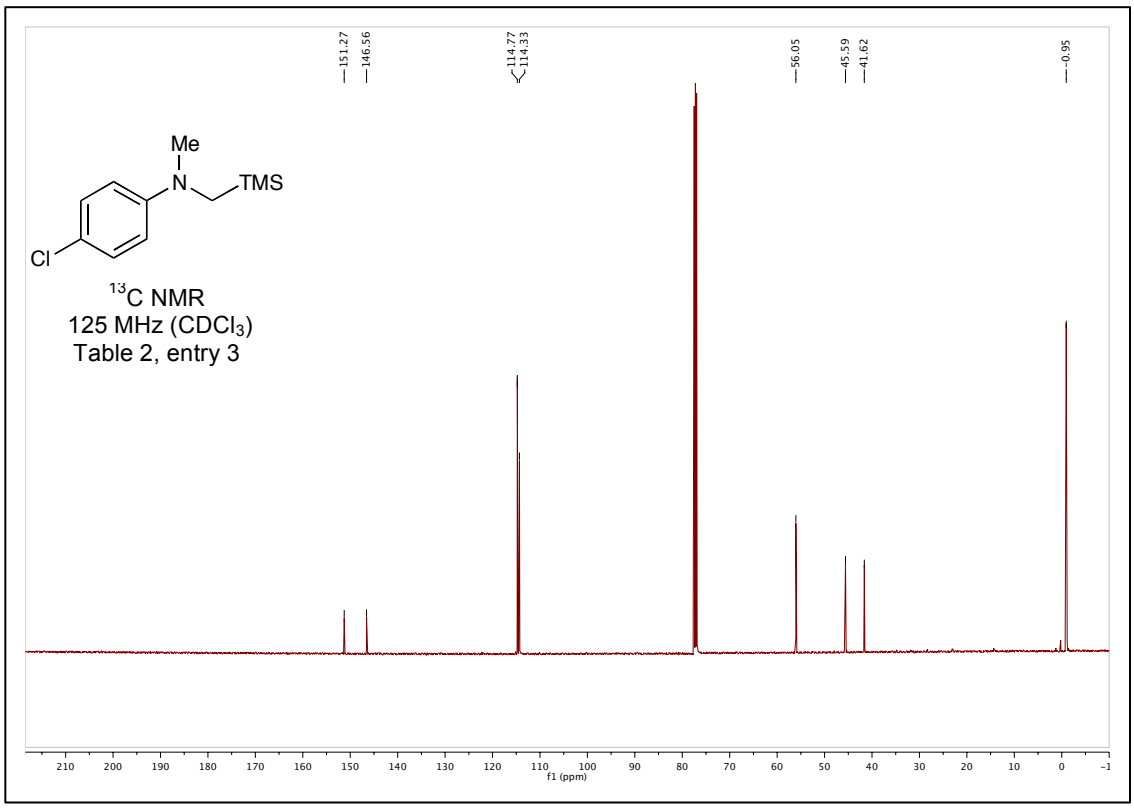
^{1}H NMR
500 MHz ($CDCl_3$)
Table 2, entry 2



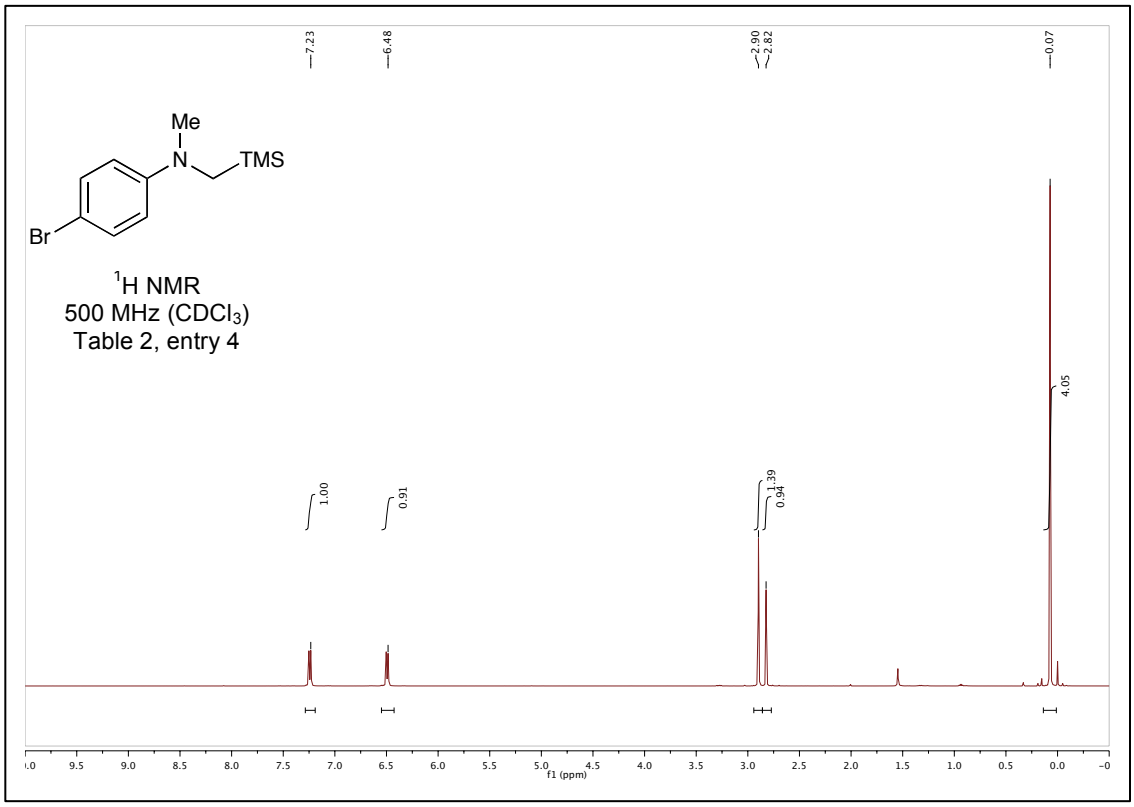
^{13}C NMR
125 MHz ($CDCl_3$)
Table 2, entry 2



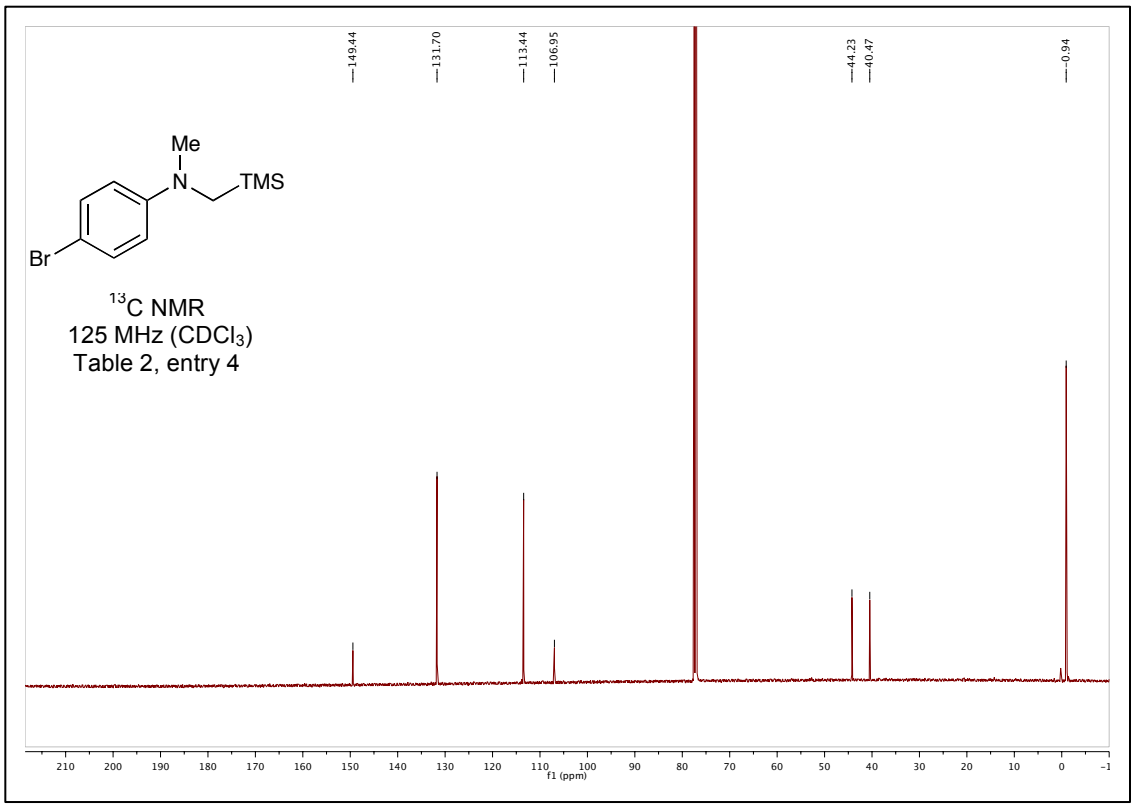
^{1}H NMR
500 MHz ($CDCl_3$)
Table 2, entry 3



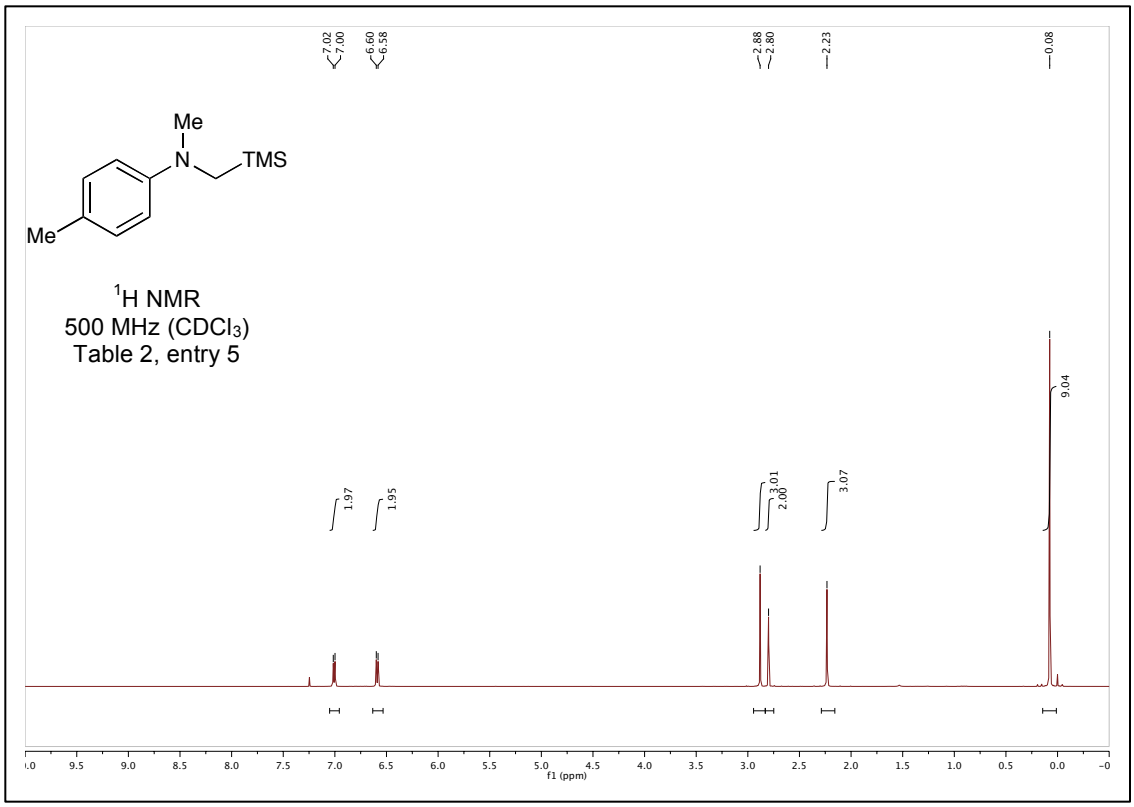
^{13}C NMR
125 MHz ($CDCl_3$)
Table 2, entry 3

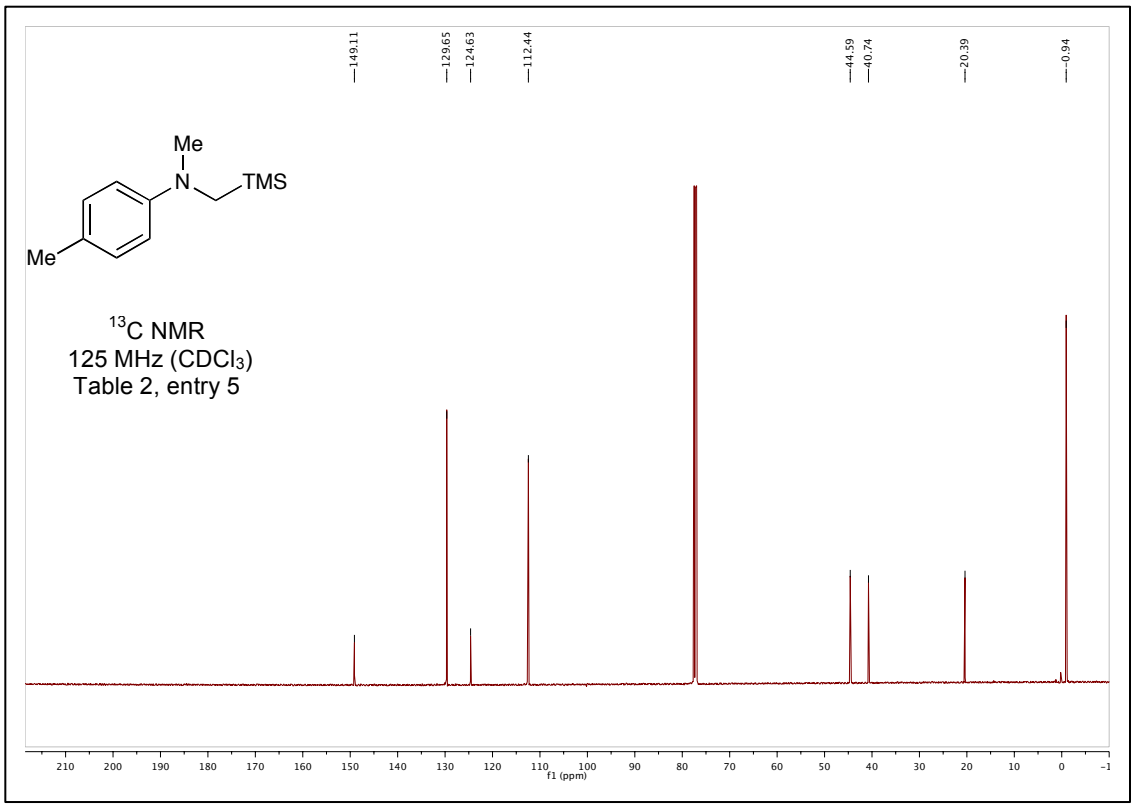


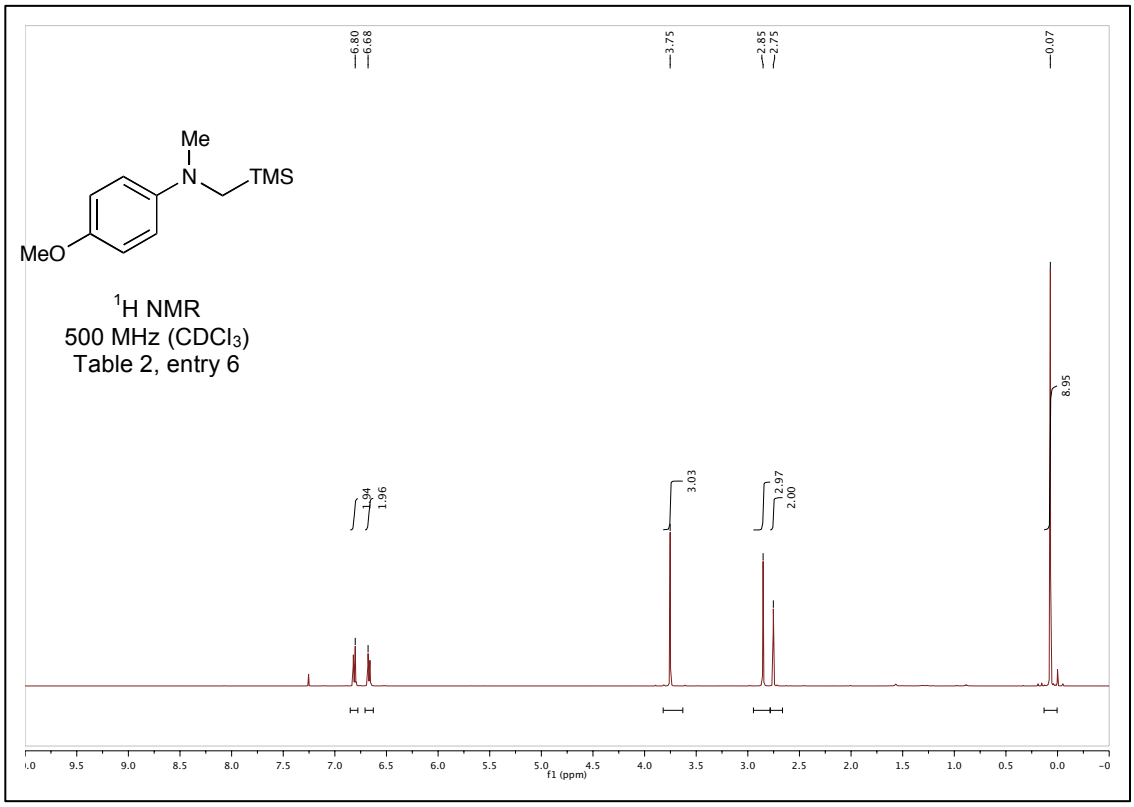
^{1}H NMR
500 MHz ($CDCl_3$)
Table 2, entry 4



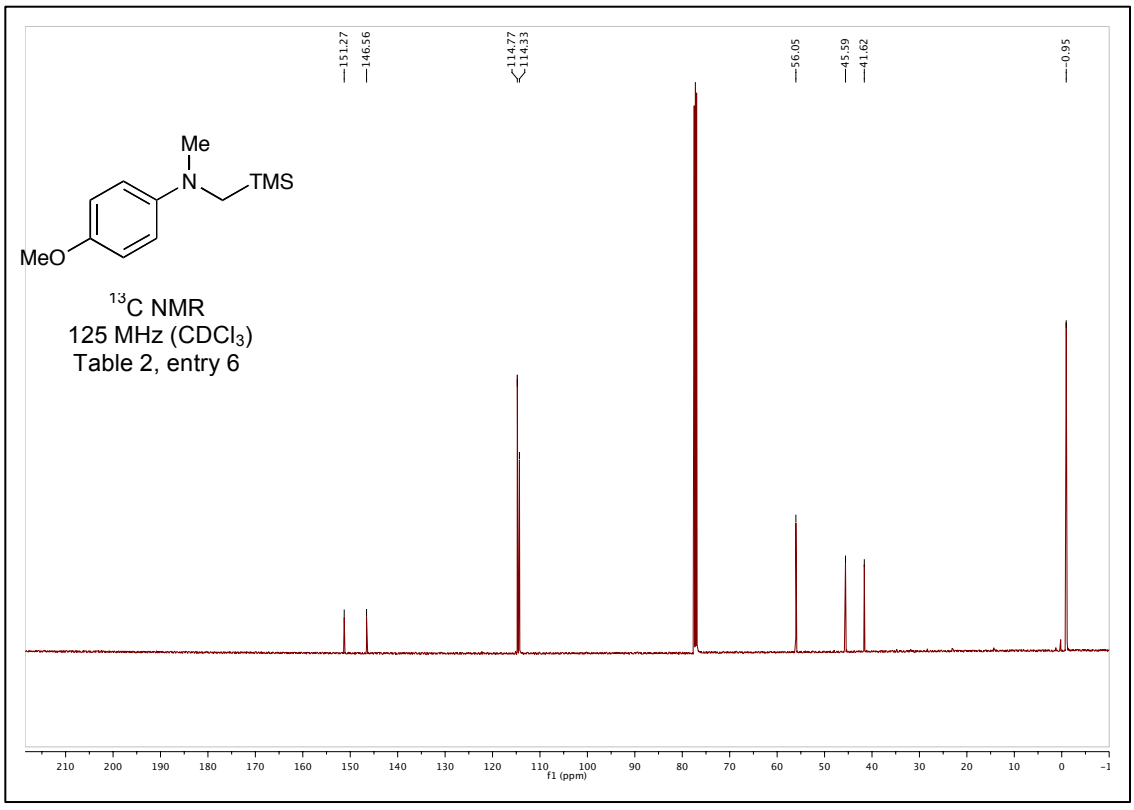
^{13}C NMR
125 MHz ($CDCl_3$)
Table 2, entry 4


Me
N
TMS
Me
^{1}H NMR
500 MHz ($CDCl_3$)
Table 2, entry 5
7.02
7.00
6.60
6.58
2.88
2.80
2.23
0.08
9.04
1.97
1.95
3.01
2.00
3.07
f1 (ppm)

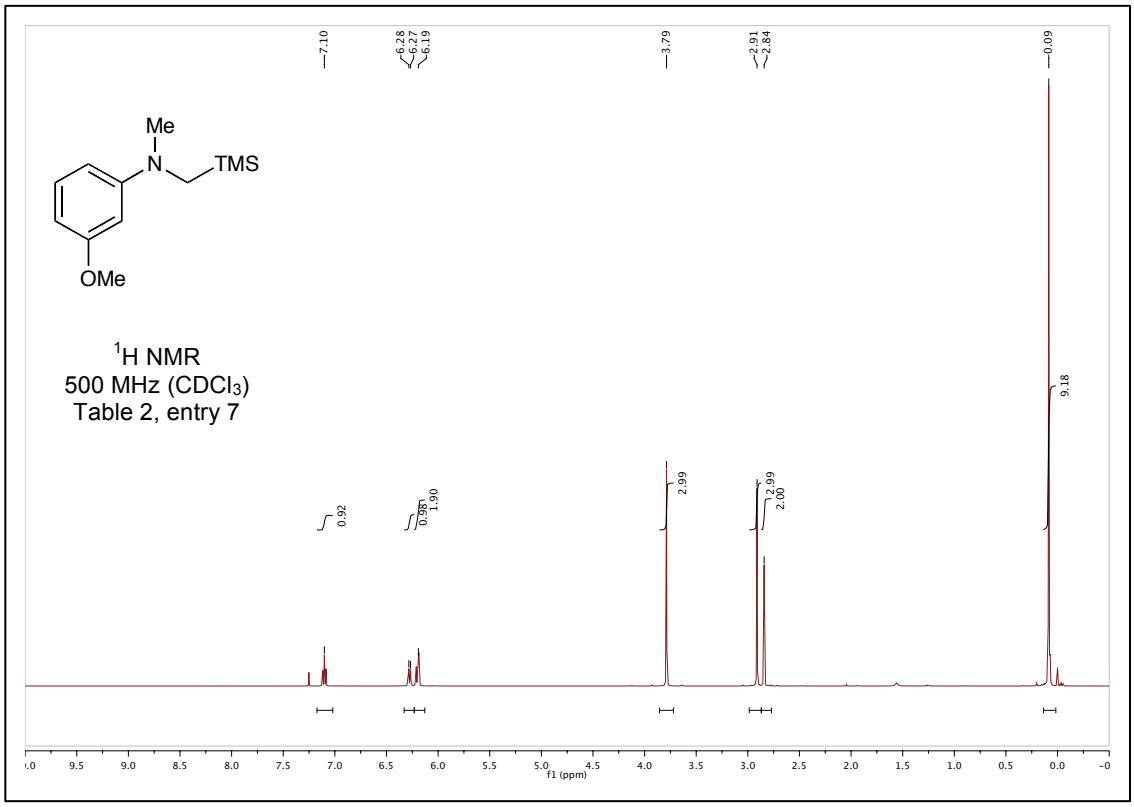

Me
N
TMS
Me
^{13}C NMR
125 MHz ($CDCl_3$)
Table 2, entry 5
149.11
129.65
124.63
112.44
44.59
40.74
20.39
0.94
f1 (ppm)

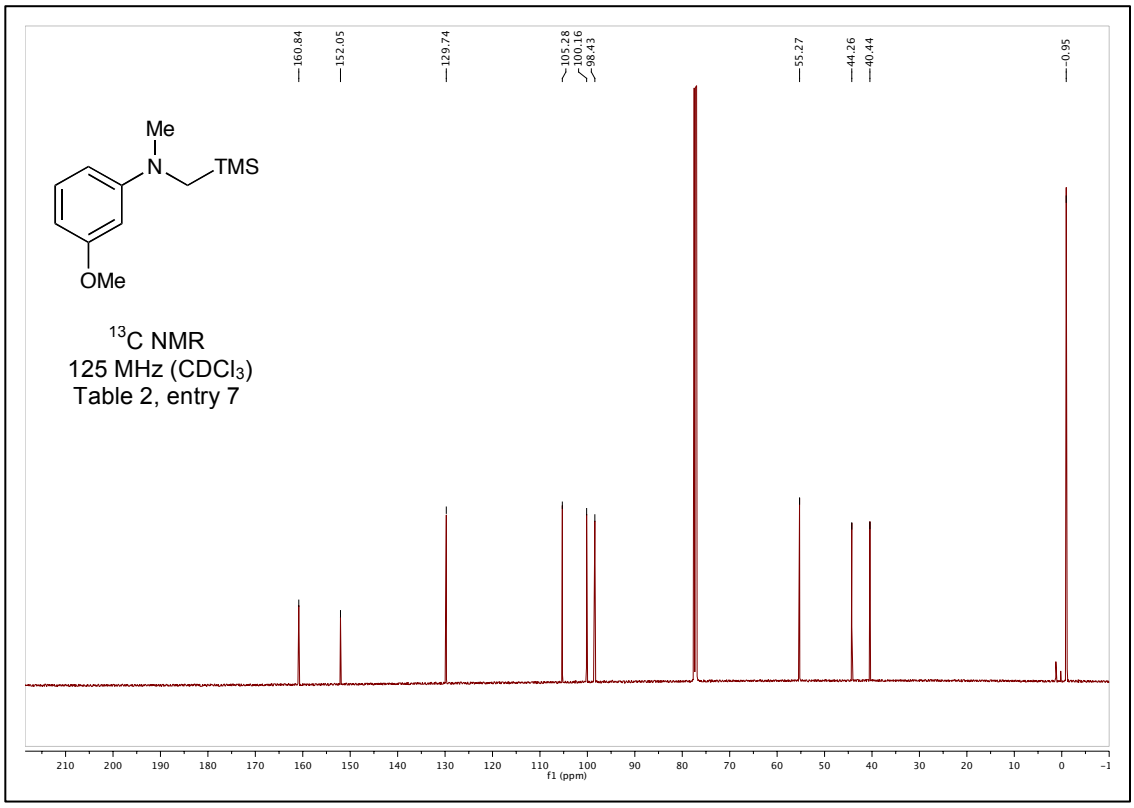


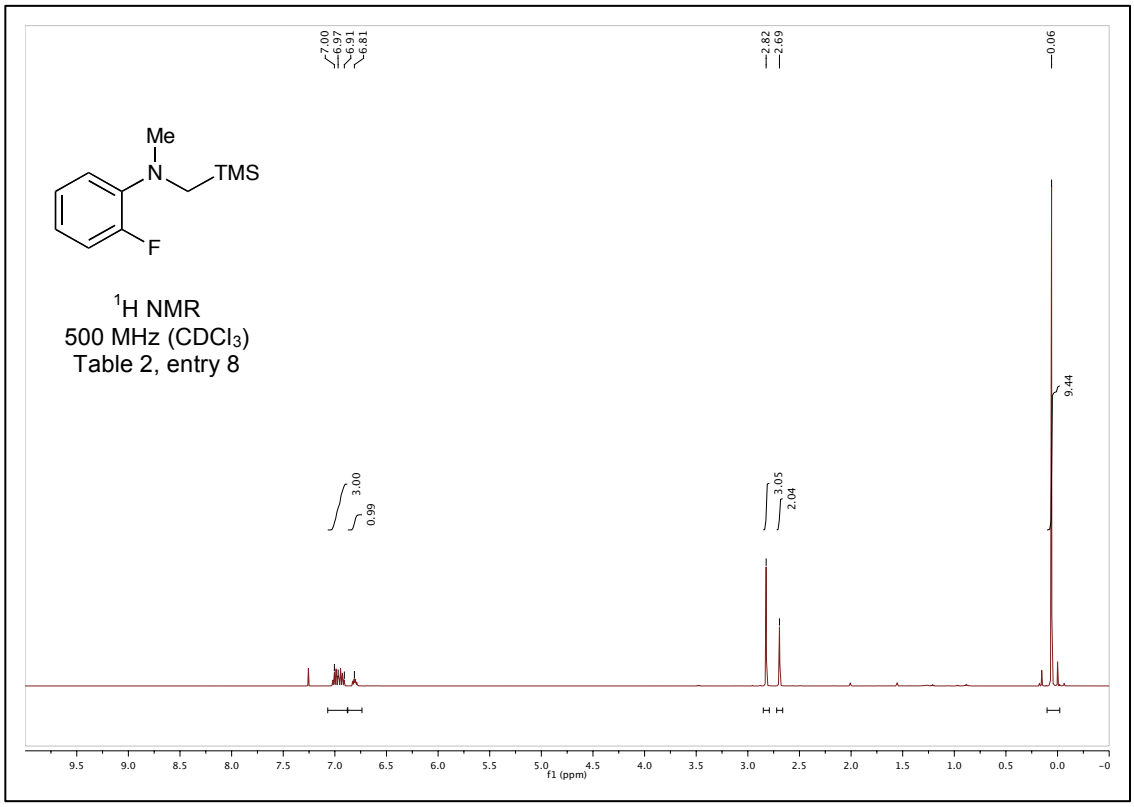
^{1}H NMR
500 MHz ($CDCl_3$)
Table 2, entry 6

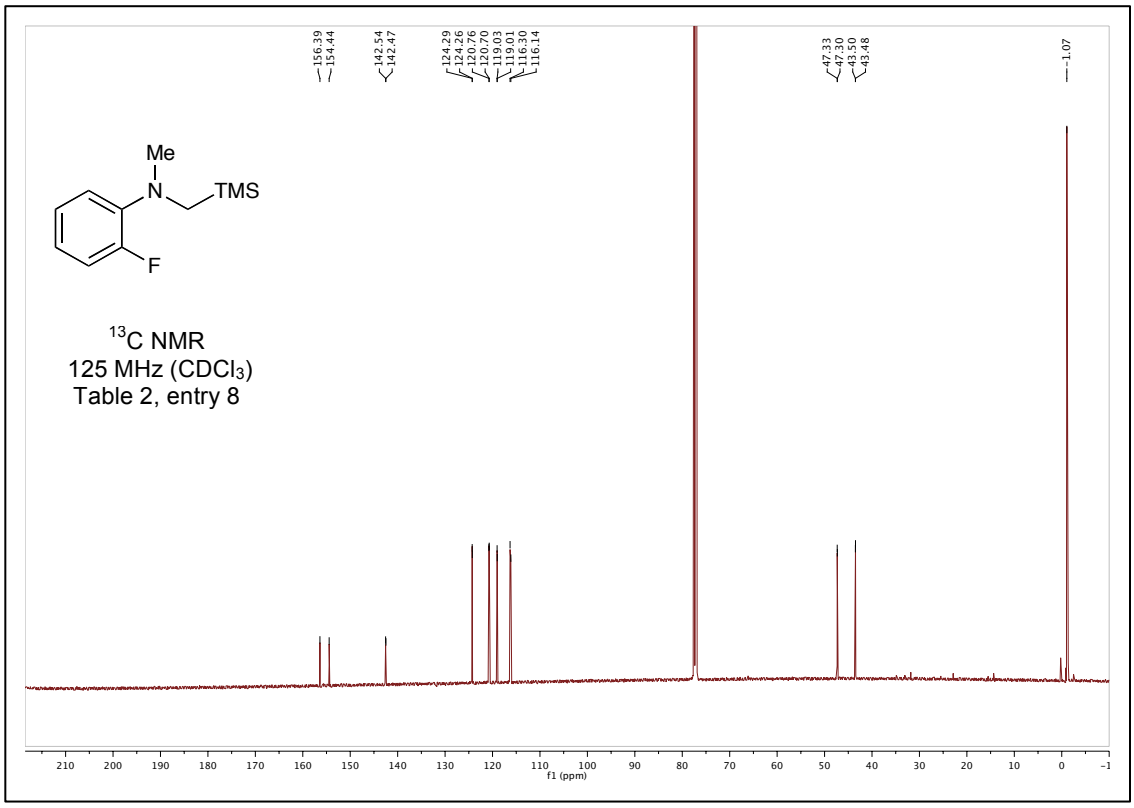


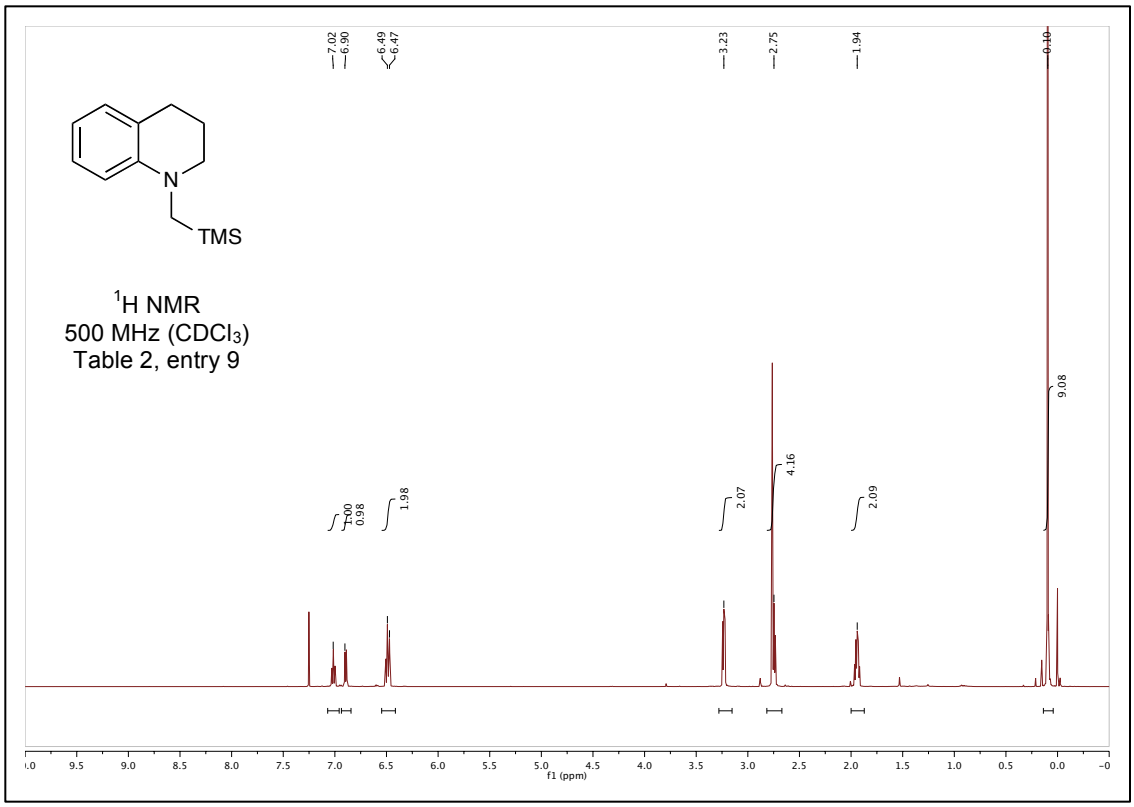
^{13}C NMR
125 MHz ($CDCl_3$)
Table 2, entry 6

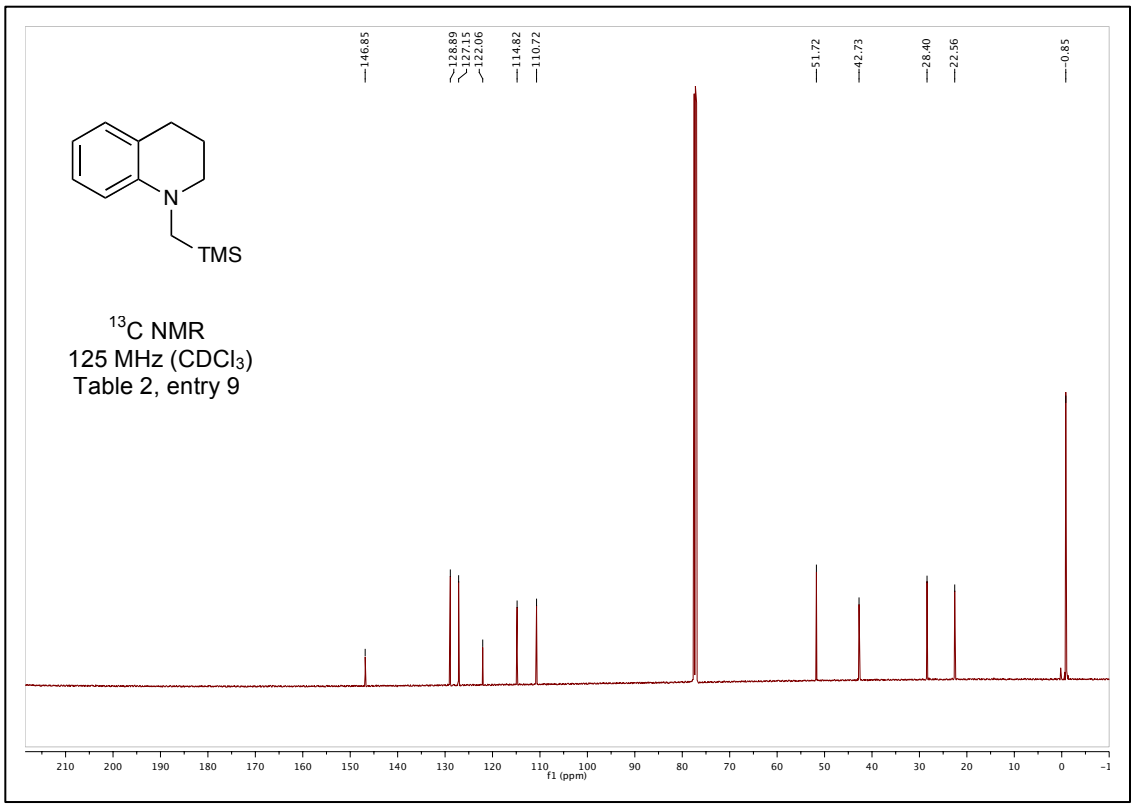

Me
N
TMS
OMe
^{1}H NMR
500 MHz ($CDCl_3$)
Table 2, entry 7
7.10
6.28
6.27
6.19
3.79
2.91
2.84
0.09
9.18
0.92
0.98
1.90
2.99
2.99
2.00
f1 (ppm)

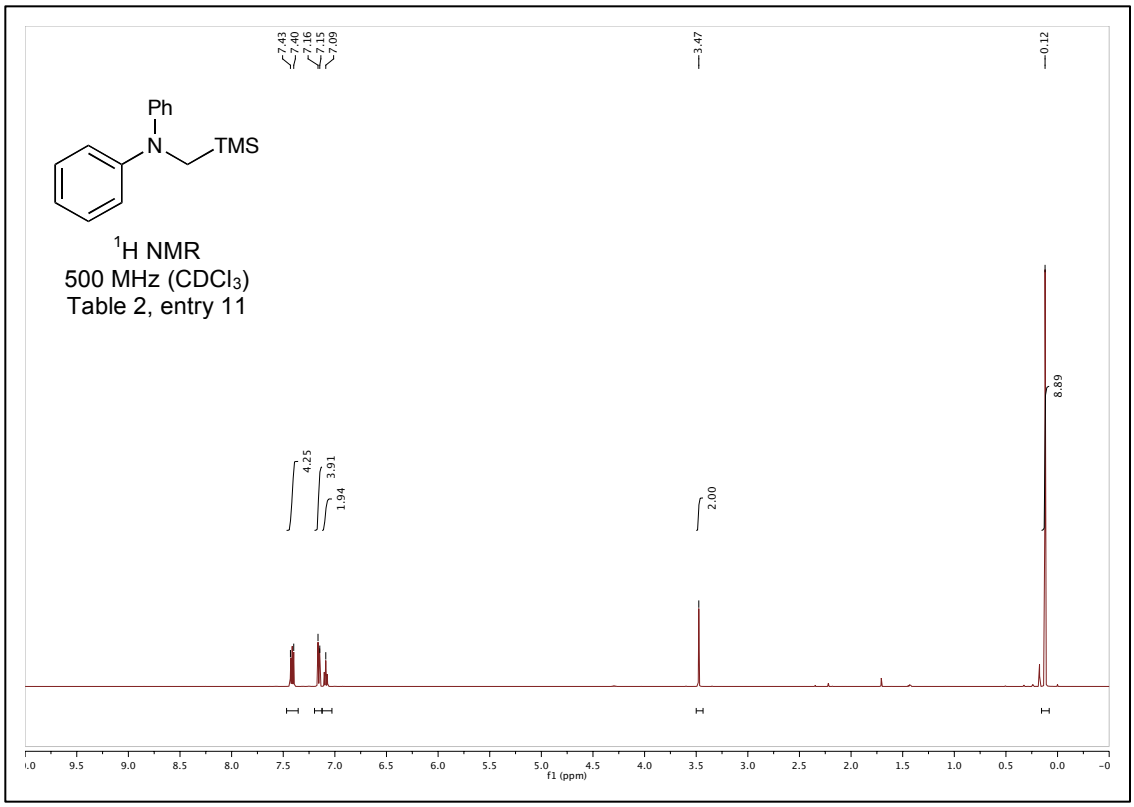

Me
N
TMS
OMe
^{13}C NMR
125 MHz ($CDCl_3$)
Table 2, entry 7
160.84
152.05
129.74
105.28
100.16
98.43
55.27
44.26
40.44
-0.95
f1 (ppm)

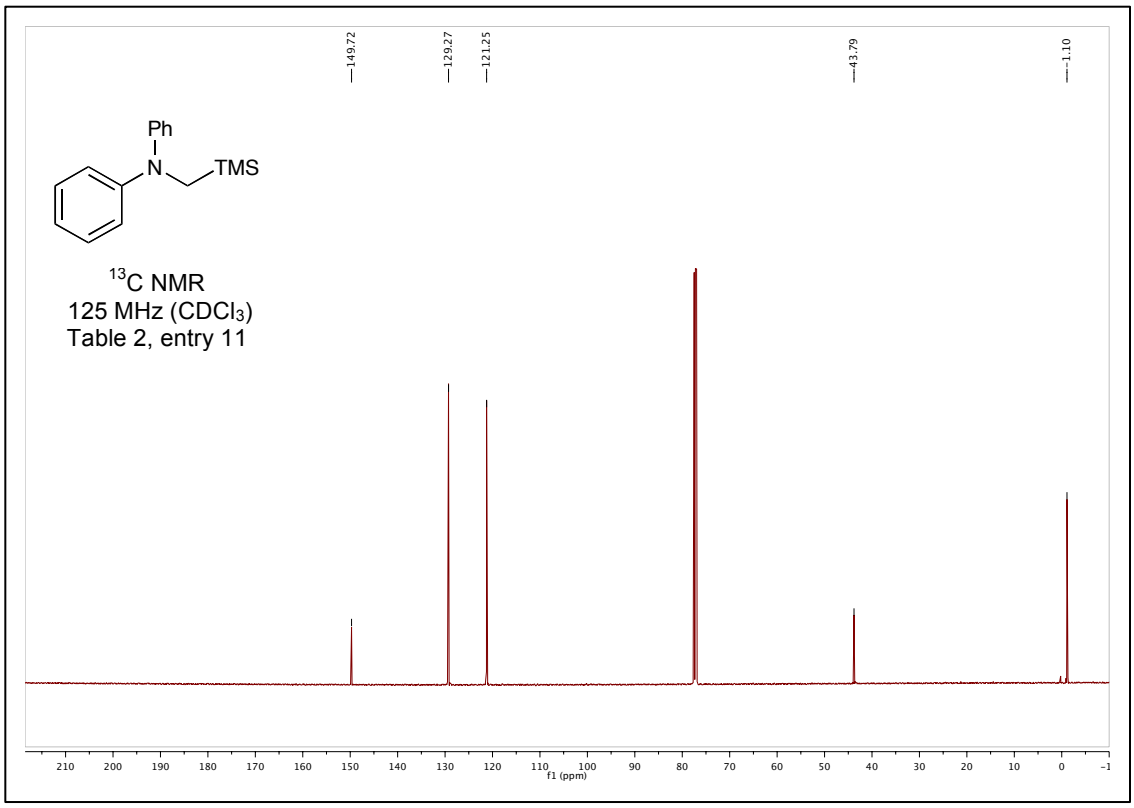

Me
N
TMS
F
1H NMR
500 MHz (CDCl3)
Table 2, entry 8
7.00
6.97
6.91
6.81
2.82
2.69
0.06
3.00
0.99
3.05
2.04
9.44
f1 (ppm)

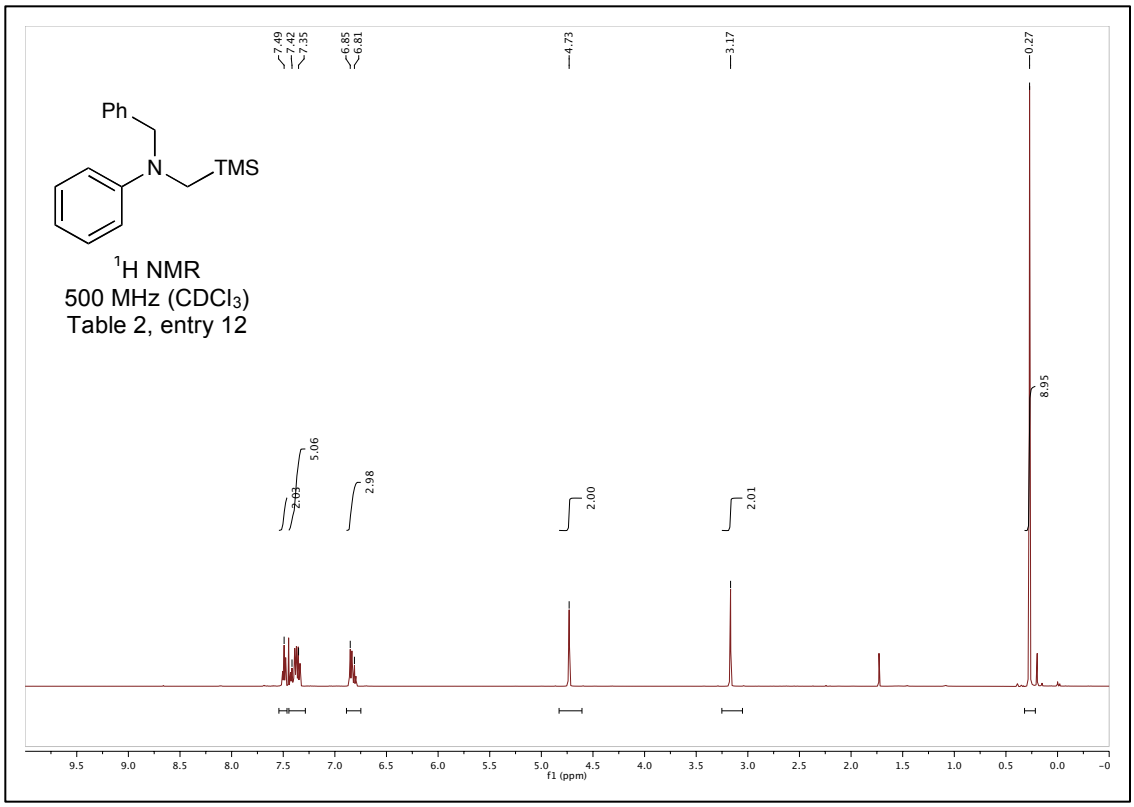

Me
N
TMS
F
13C NMR
125 MHz (CDCl3)
Table 2, entry 8
156.39
154.44
142.54
142.47
124.29
124.26
120.76
120.70
119.03
119.01
116.30
116.14
47.33
47.30
43.50
43.48
-1.07
f1 (ppm)


7.02
6.90
6.49
6.47
3.23
2.75
1.94
0.10
N
TMS
^{1}H NMR
500 MHz ($CDCl_3$)
Table 2, entry 9
1.00
0.98
1.98
2.07
4.16
2.09
9.08
f1 (ppm)

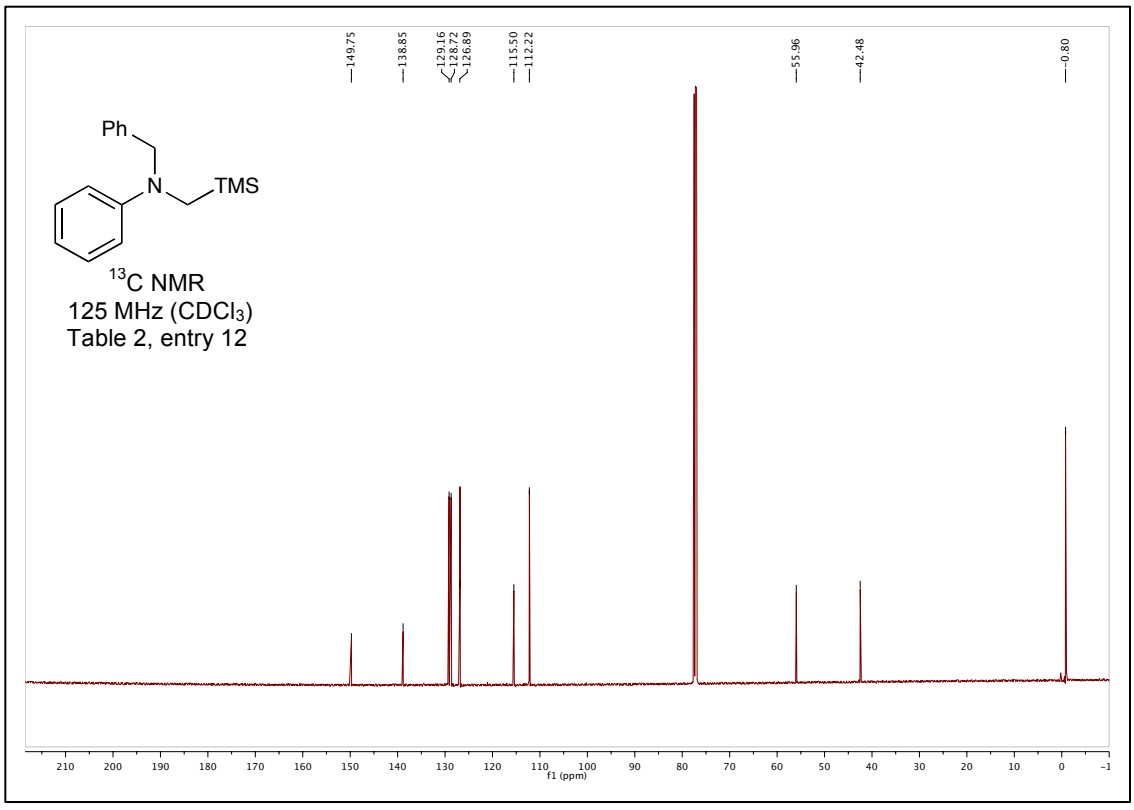

146.85
128.89
127.15
122.06
114.82
110.72
51.72
42.73
28.40
22.56
0.85
N
TMS
^{13}C NMR
125 MHz ($CDCl_3$)
Table 2, entry 9
f1 (ppm)


Ph
N
TMS
1H NMR
500 MHz (CDCl3)
Table 2, entry 11
7.43
7.40
7.16
7.15
7.09
3.47
0.12
4.25
3.91
1.94
2.00
8.89
f1 (ppm)

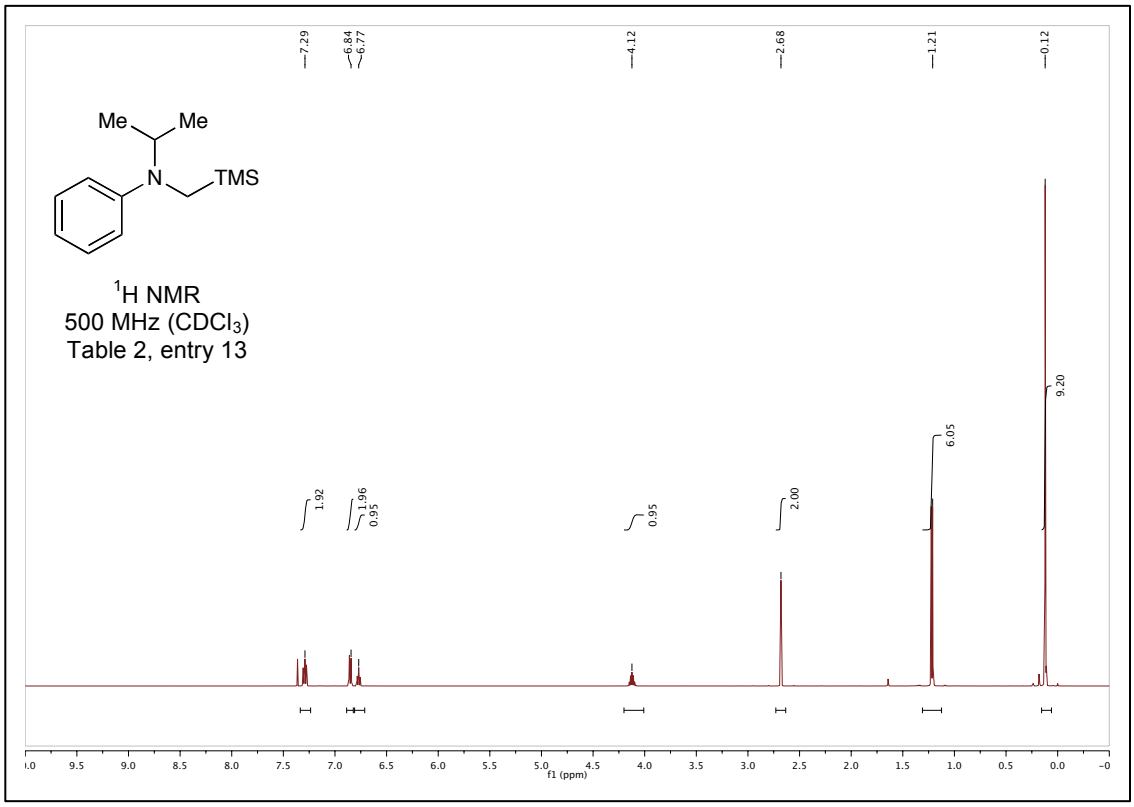

Ph
N
TMS
13C NMR
125 MHz (CDCl3)
Table 2, entry 11
149.72
129.27
121.25
43.79
1.10
f1 (ppm)



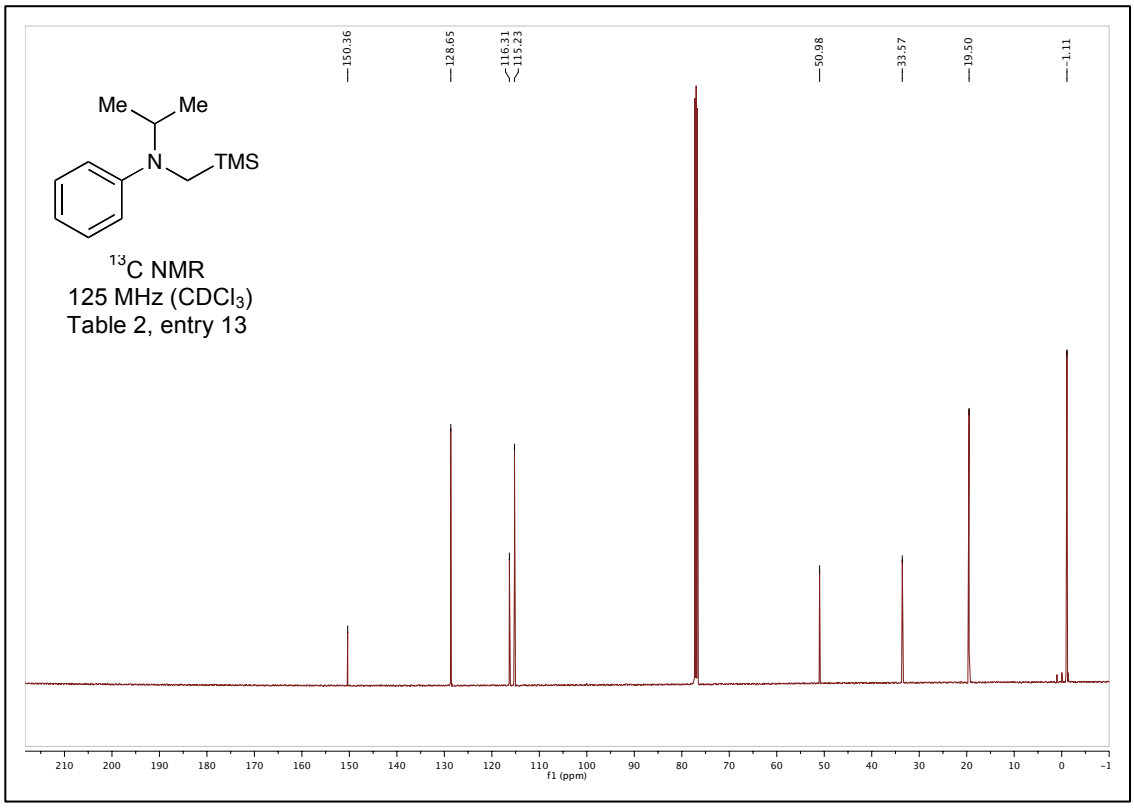
^{1}H NMR
500 MHz ($CDCl_3$)
Table 2, entry 12



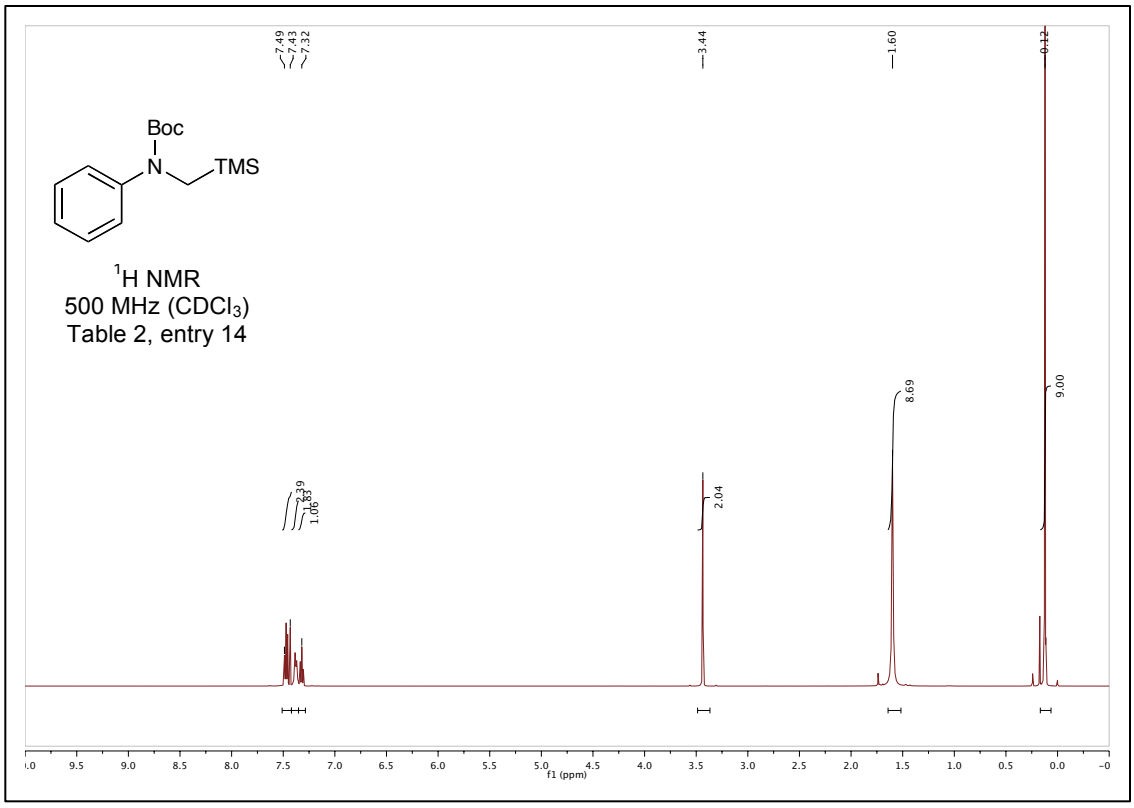
^{13}C NMR
125 MHz ($CDCl_3$)
Table 2, entry 12



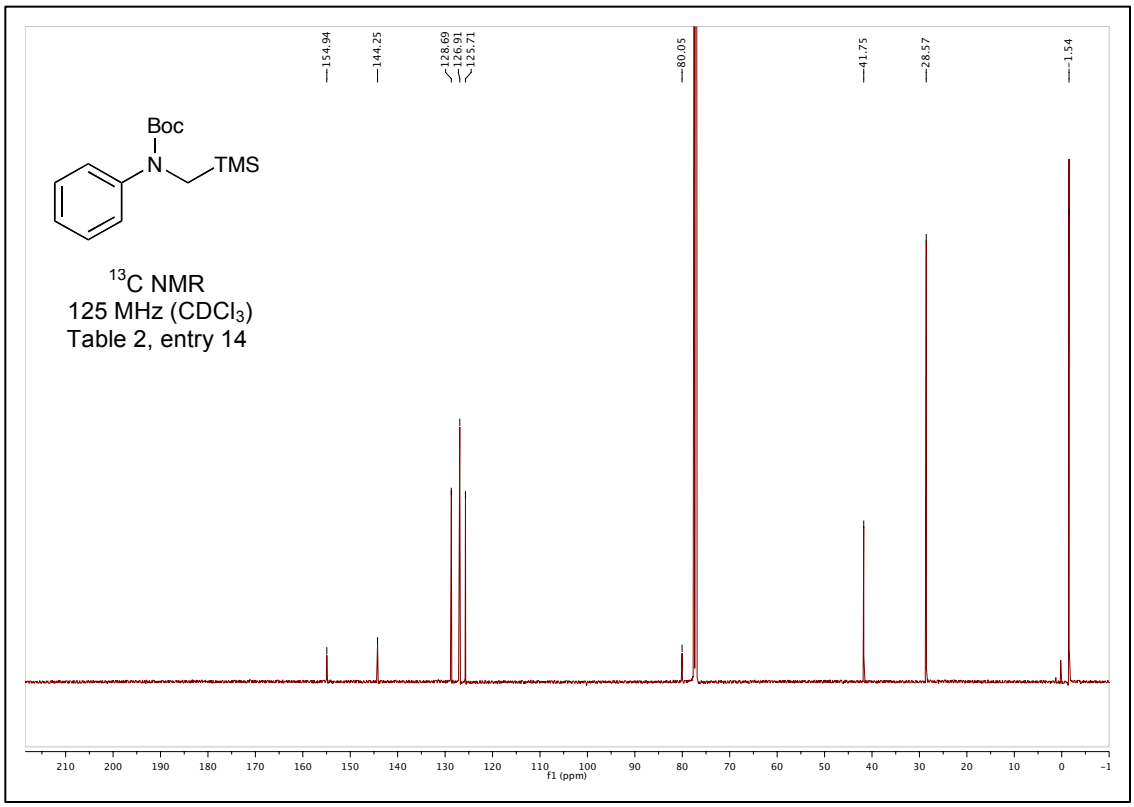
^{1}H NMR
500 MHz ($CDCl_3$)
Table 2, entry 13



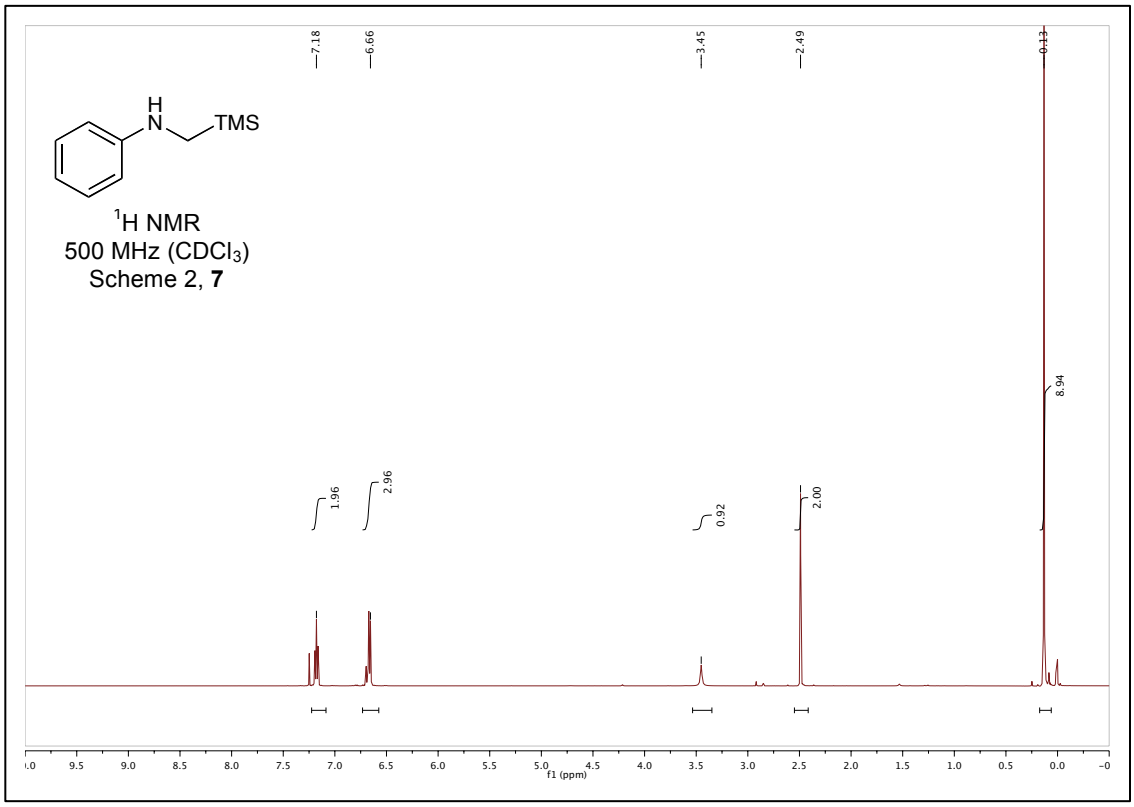
^{13}C NMR
125 MHz ($CDCl_3$)
Table 2, entry 13



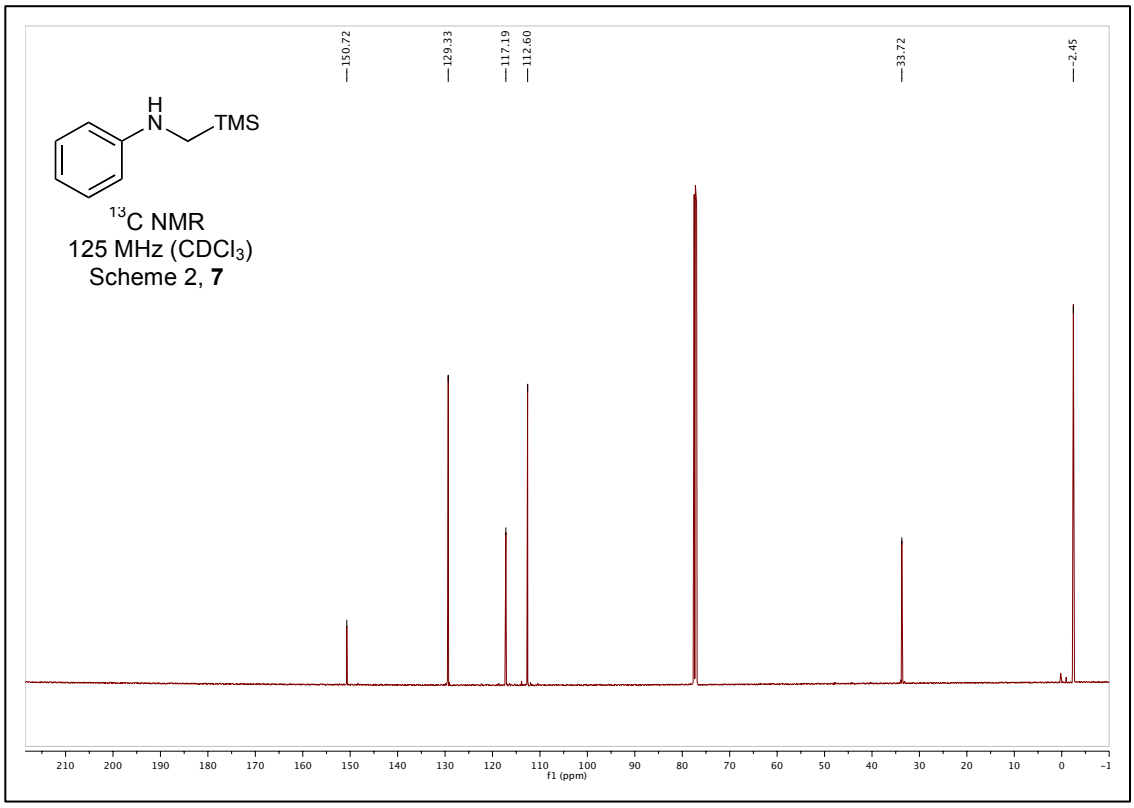
^{1}H NMR
500 MHz ($CDCl_3$)
Table 2, entry 14



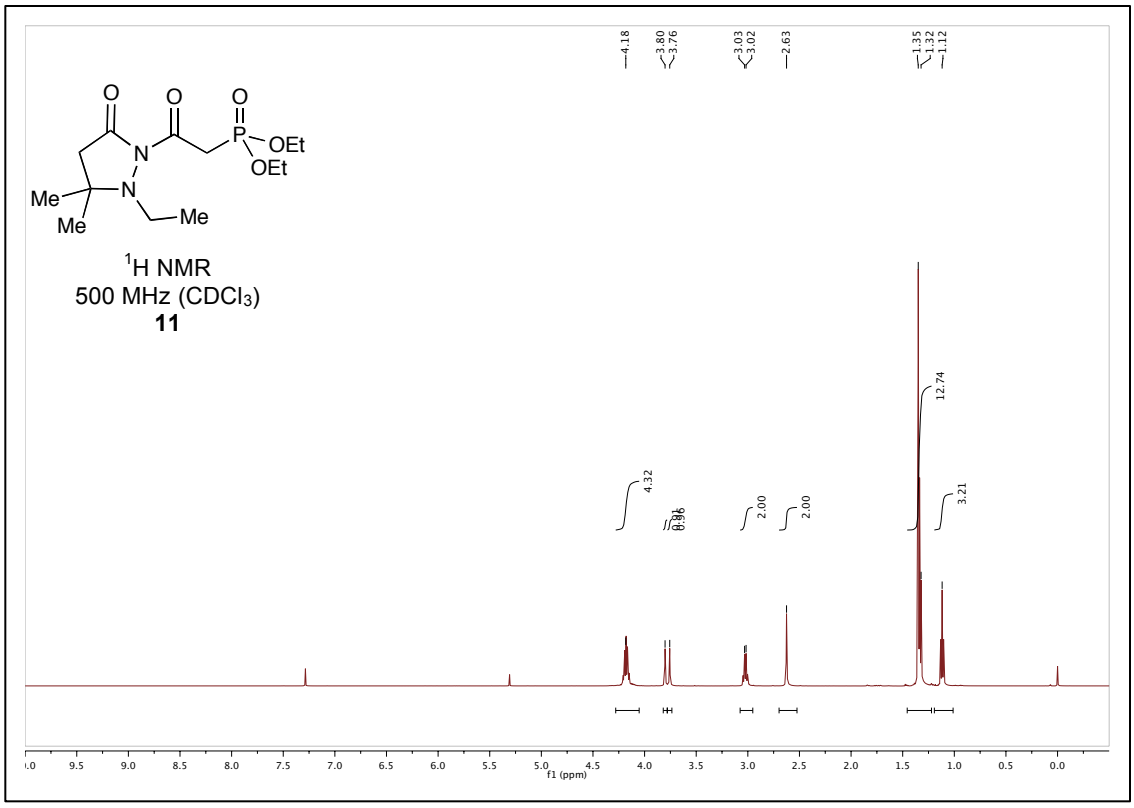
^{13}C NMR
125 MHz ($CDCl_3$)
Table 2, entry 14



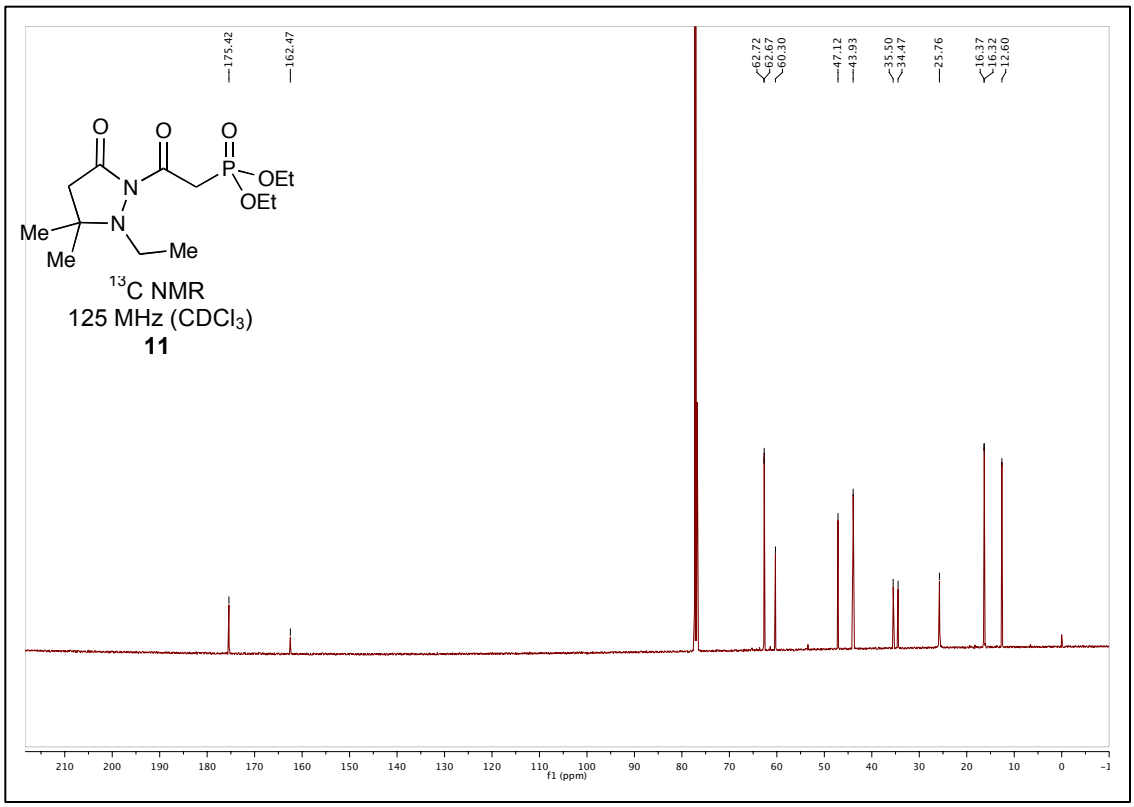
^{1}H NMR
500 MHz ($CDCl_3$)
Scheme 2, **7**



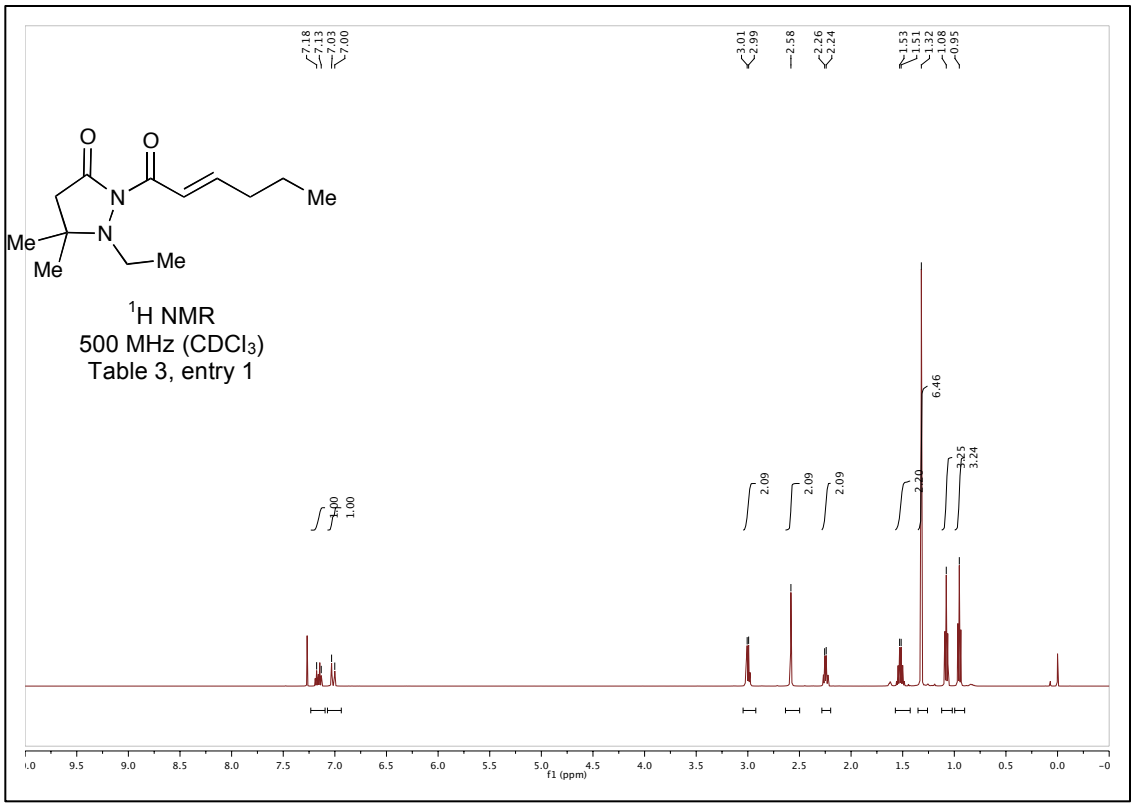
^{13}C NMR
125 MHz ($CDCl_3$)
Scheme 2, **7**

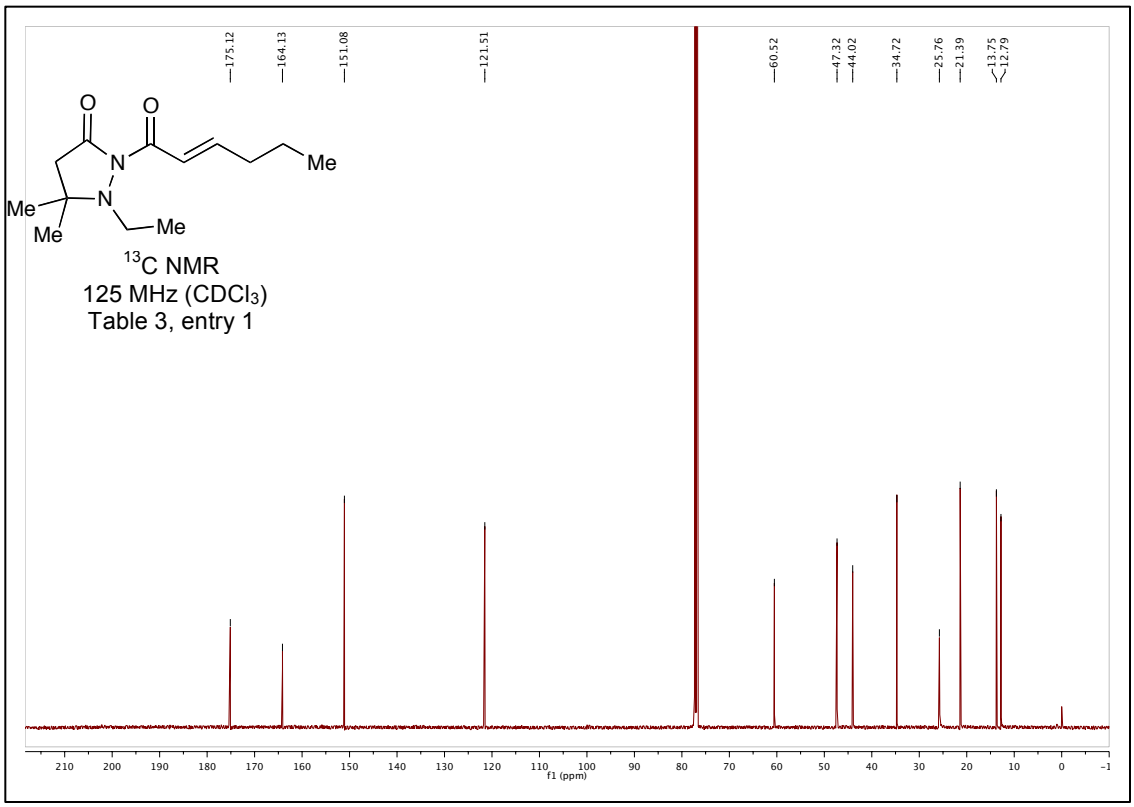


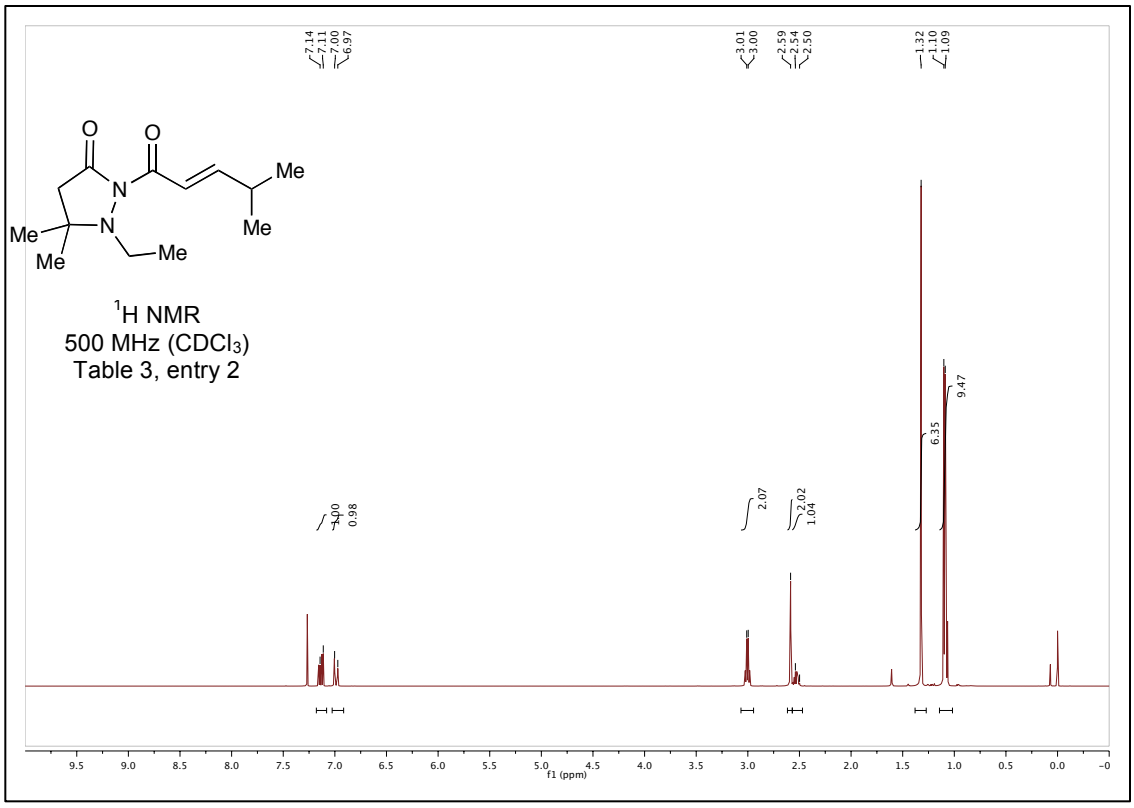
^{1}H NMR
500 MHz ($CDCl_3$)
11



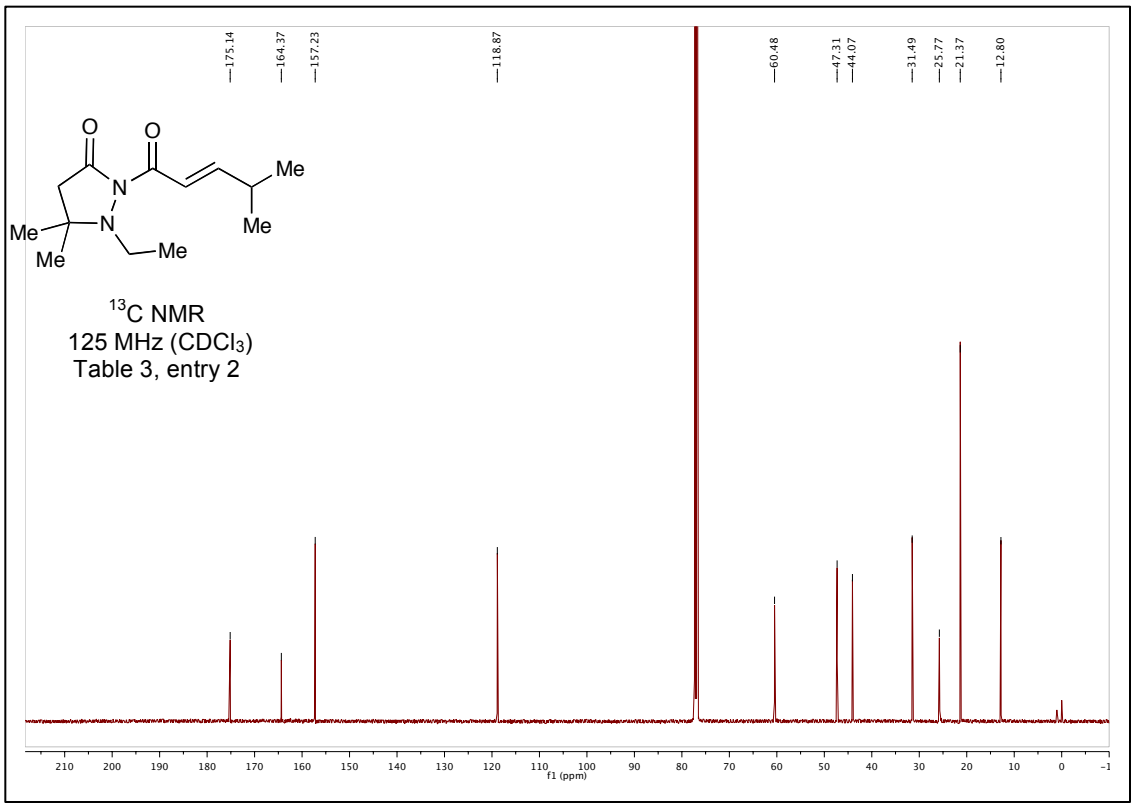
^{13}C NMR
125 MHz ($CDCl_3$)
11


O
O
N
N
Me
Me
Me
Me
^{1}H NMR
500 MHz ($CDCl_3$)
Table 3, entry 1
7.18
7.13
7.03
7.00
3.01
2.99
2.58
2.26
2.24
1.53
1.51
1.32
1.08
0.95
6.46
3.25
3.24
2.09
2.09
2.09
2.20
1.00
1.00
f1 (ppm)

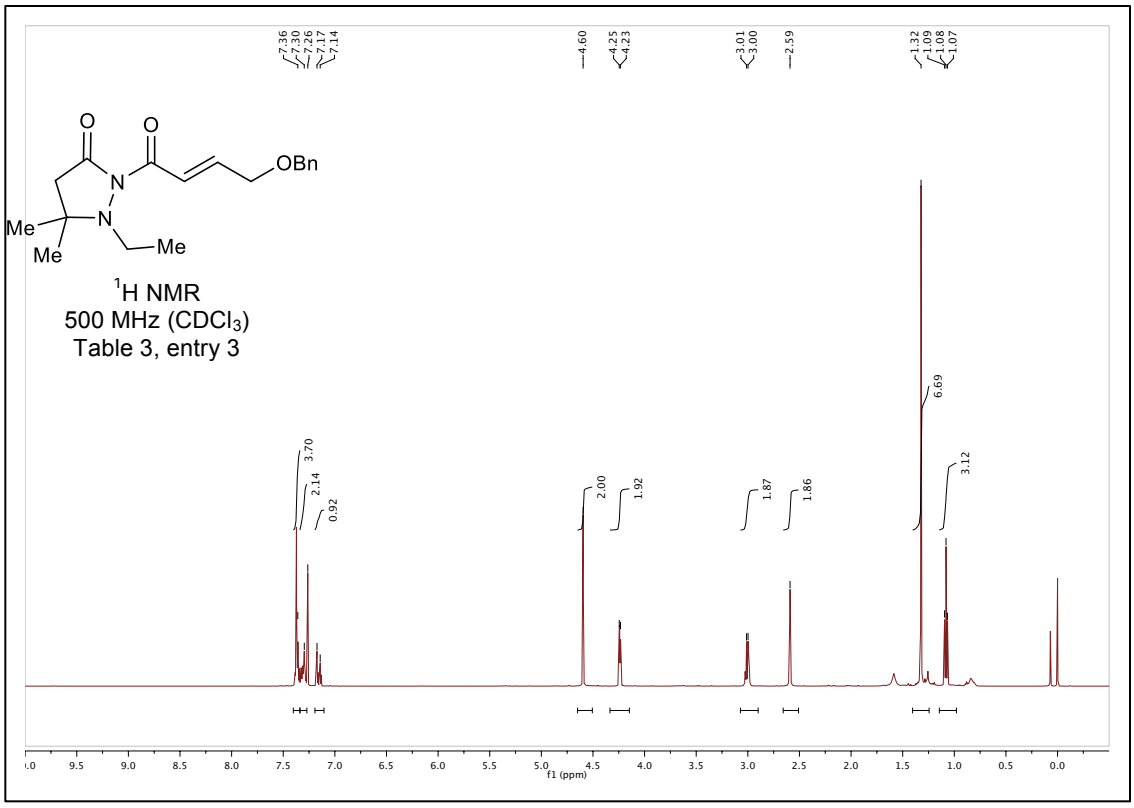

O
O
N
N
Me
Me
Me
Me
^{13}C NMR
125 MHz ($CDCl_3$)
Table 3, entry 1
175.12
164.13
151.08
121.51
60.52
47.32
44.02
34.72
25.76
21.39
13.75
12.79
f1 (ppm)

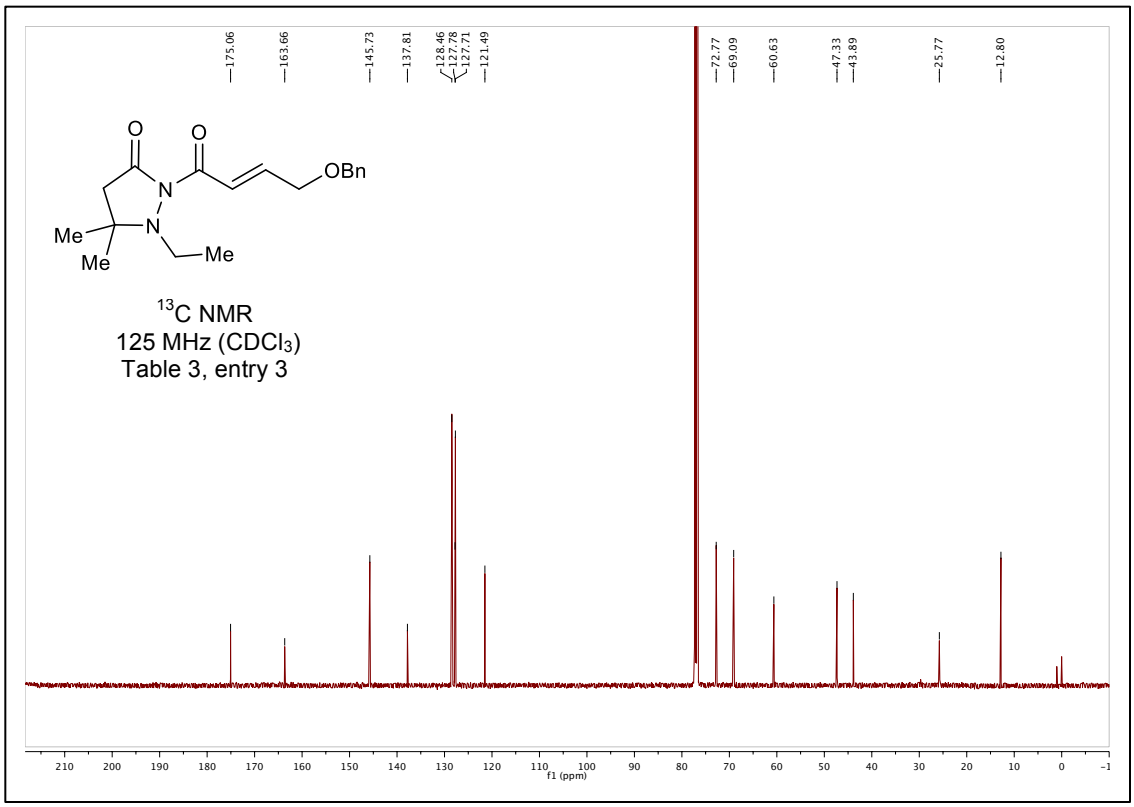


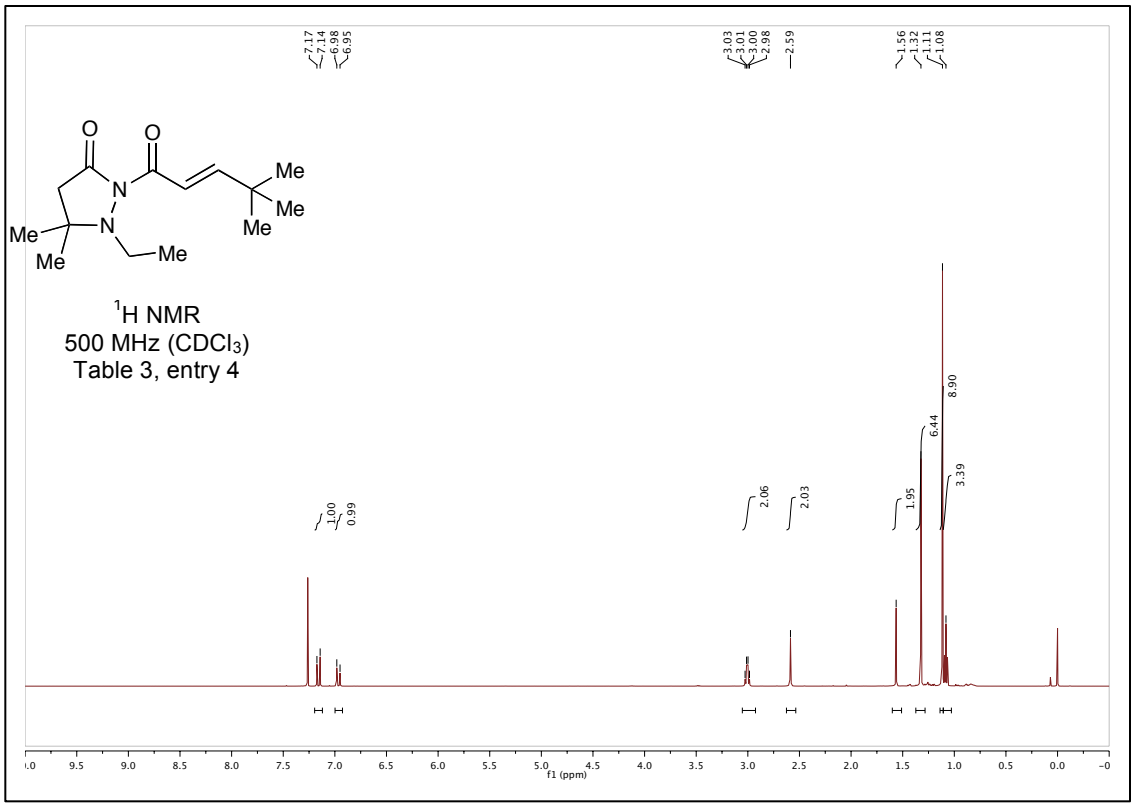
^{1}H NMR
500 MHz ($CDCl_3$)
Table 3, entry 2

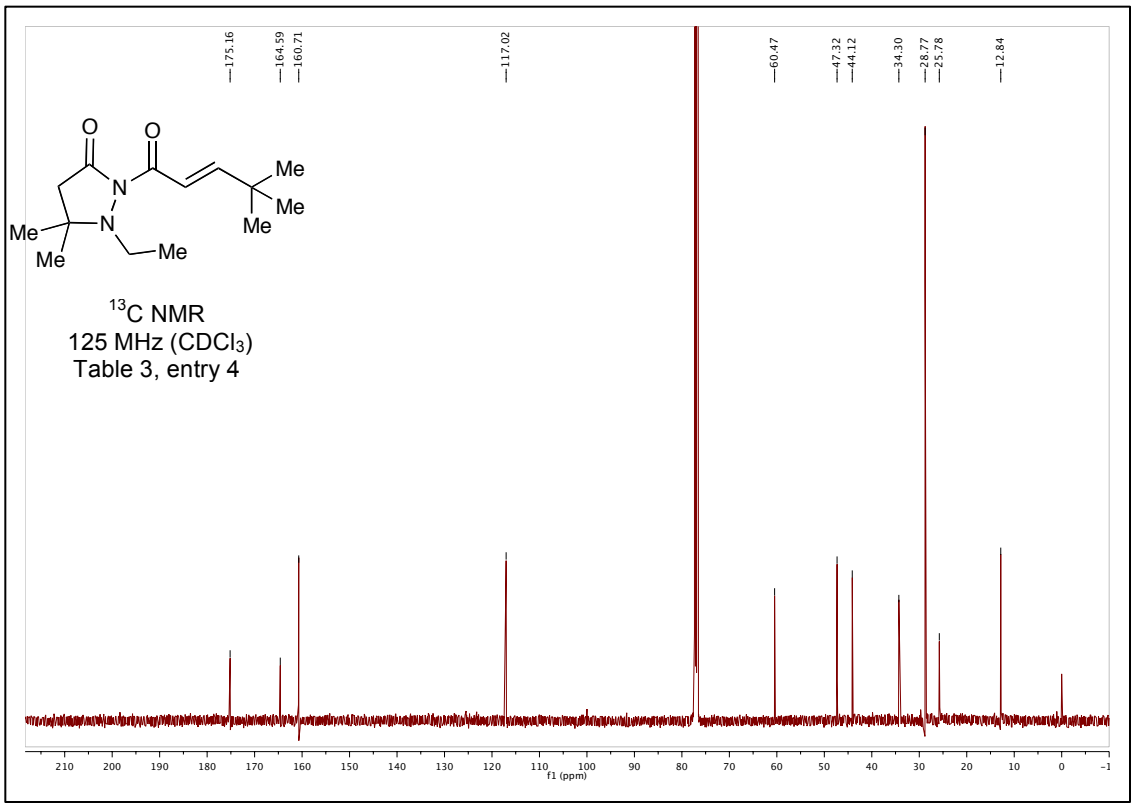


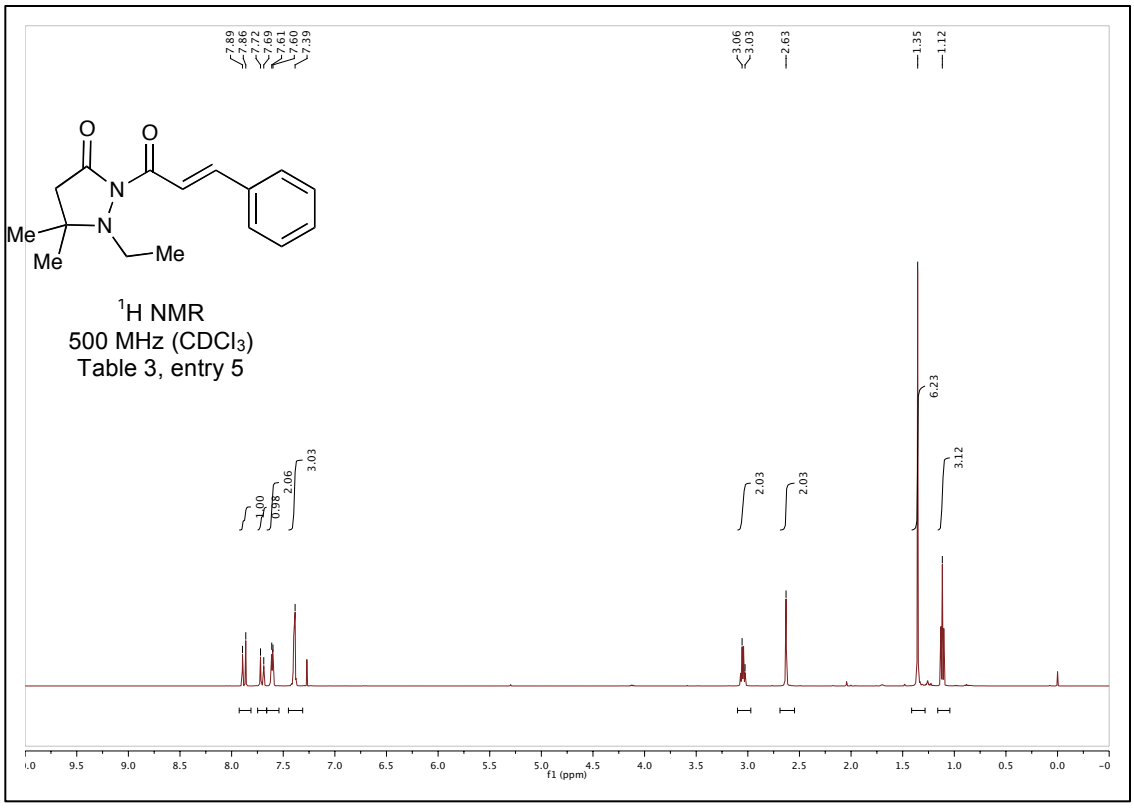
^{13}C NMR
125 MHz ($CDCl_3$)
Table 3, entry 2

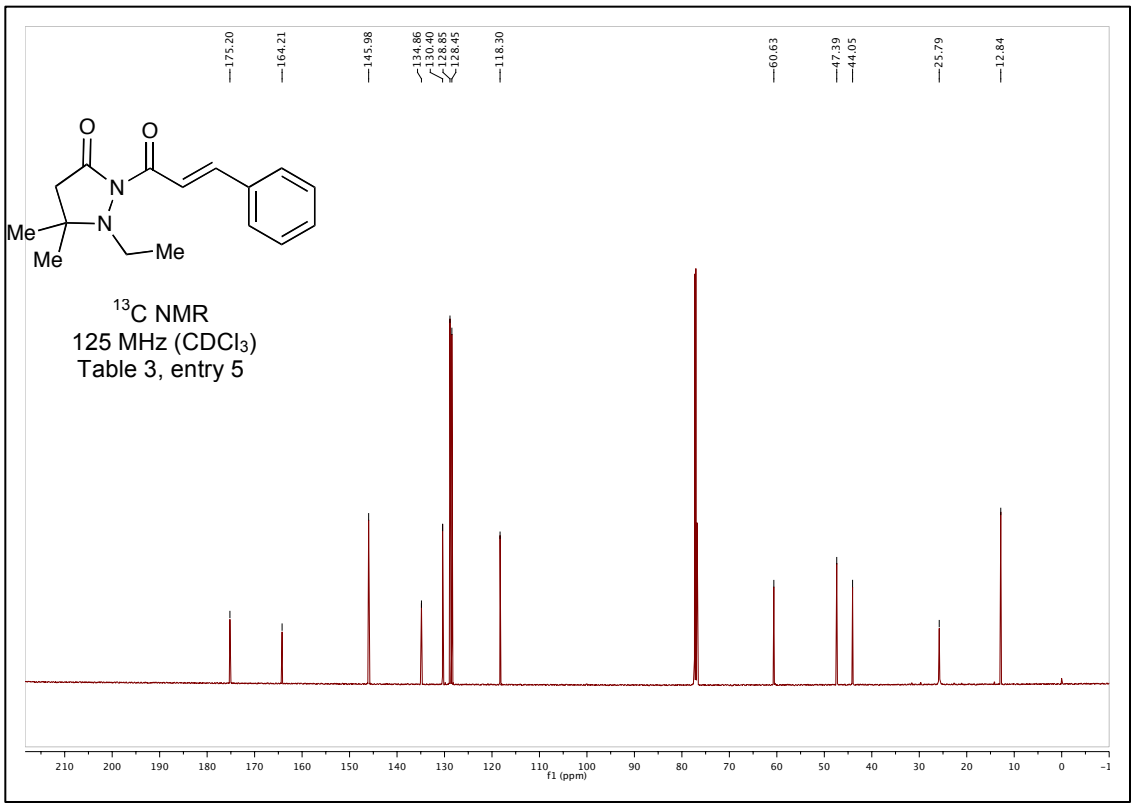

7.36
7.30
7.26
7.17
7.14
4.60
4.25
4.23
3.01
3.00
2.59
1.32
1.09
1.08
1.07
O
O
N
N
OBn
Me
Me
Me
^{1}H NMR
500 MHz ($CDCl_3$)
Table 3, entry 3
6.69
3.70
2.14
0.92
2.00
1.92
1.87
1.86
3.12
f1 (ppm)

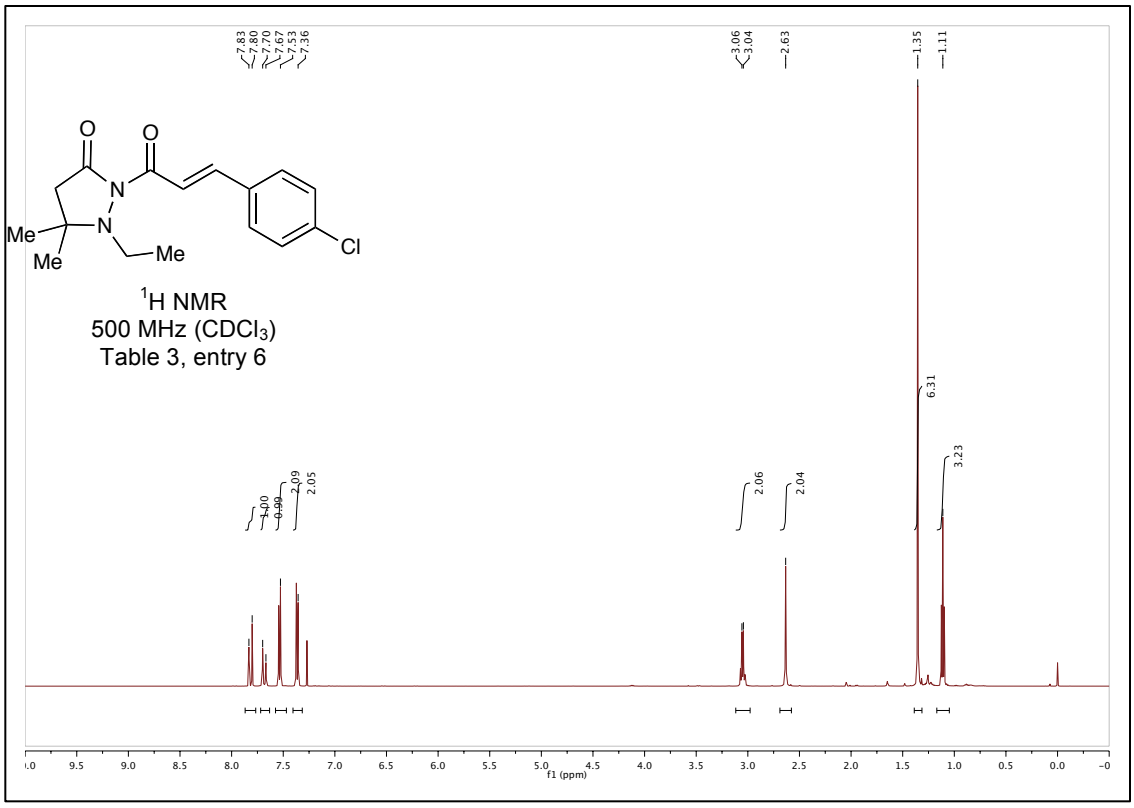

175.06
163.66
145.73
137.81
128.46
127.78
127.71
121.49
72.77
69.09
60.63
47.33
43.89
25.77
12.80
O
O
N
N
OBn
Me
Me
Me
^{13}C NMR
125 MHz ($CDCl_3$)
Table 3, entry 3
f1 (ppm)


7.17
7.14
6.98
6.95
3.03
3.01
3.00
2.98
2.59
1.56
1.32
1.11
1.08
O
O
N
N
Me
Me
Me
Me
Me
Me
^{1}H NMR
500 MHz ($CDCl_3$)
Table 3, entry 4
1.00
0.99
2.06
2.03
1.95
6.44
8.90
3.39
f1 (ppm)

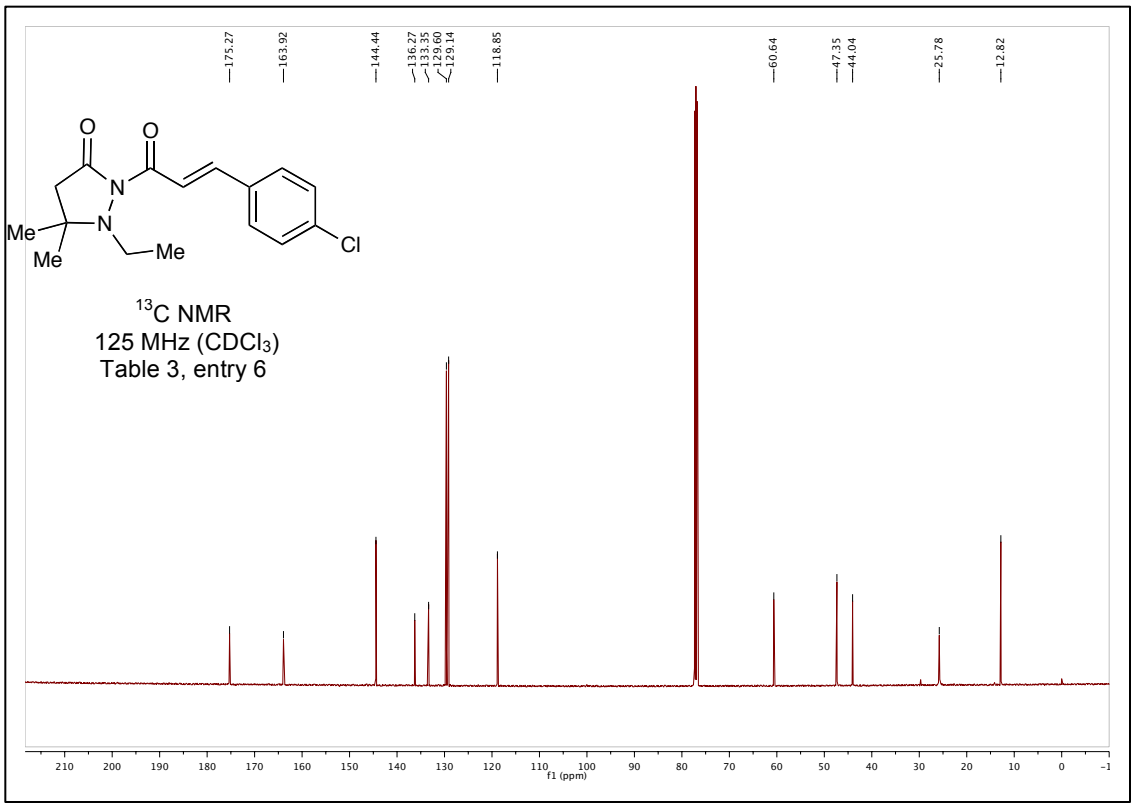

175.16
164.59
160.71
117.02
60.47
47.32
44.12
34.30
28.77
25.78
12.84
O
O
N
N
Me
Me
Me
Me
Me
Me
^{13}C NMR
125 MHz ($CDCl_3$)
Table 3, entry 4
f1 (ppm)


7.89
7.86
7.72
7.69
7.61
7.60
7.39
3.06
3.03
2.63
1.35
1.12
O
O
N
N
Me
Me
Me
1H NMR
500 MHz (CDCl3)
Table 3, entry 5
6.23
3.12
3.03
2.06
1.00
0.98
2.03
2.03
f1 (ppm)

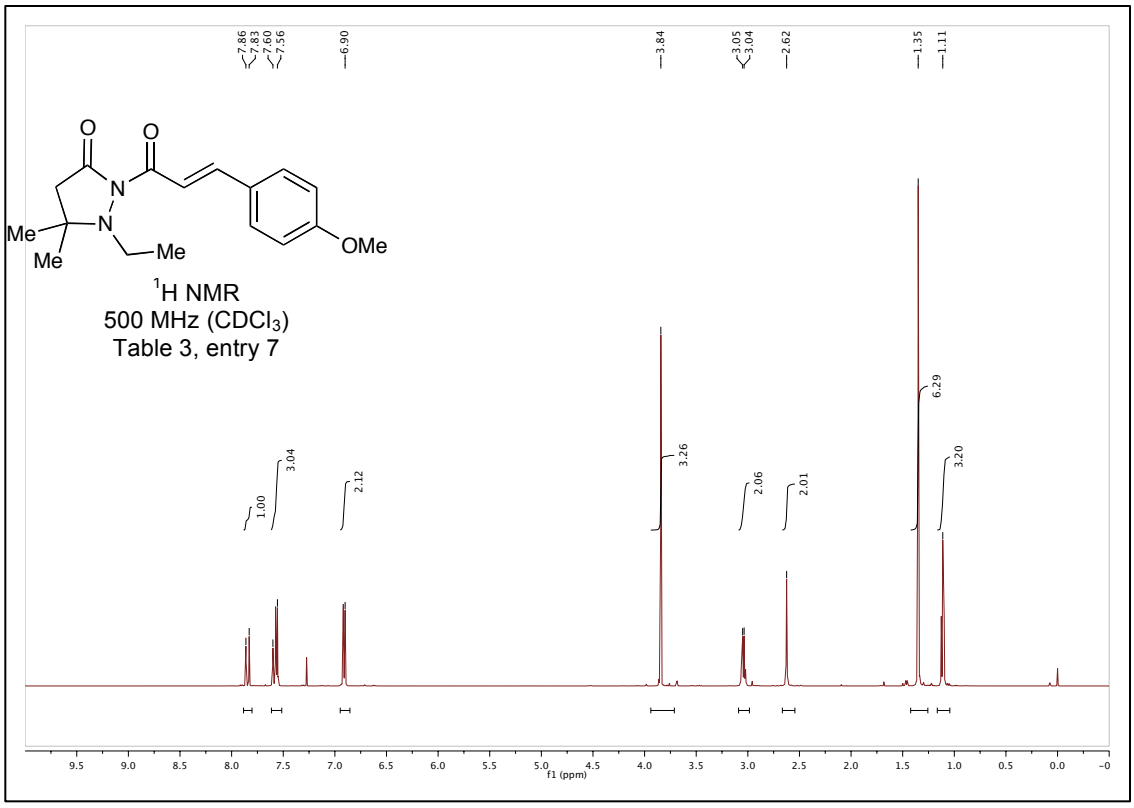

175.20
164.21
145.98
134.86
130.40
128.85
128.45
118.30
60.63
47.39
44.05
25.79
12.84
O
O
N
N
Me
Me
Me
13C NMR
125 MHz (CDCl3)
Table 3, entry 5
f1 (ppm)



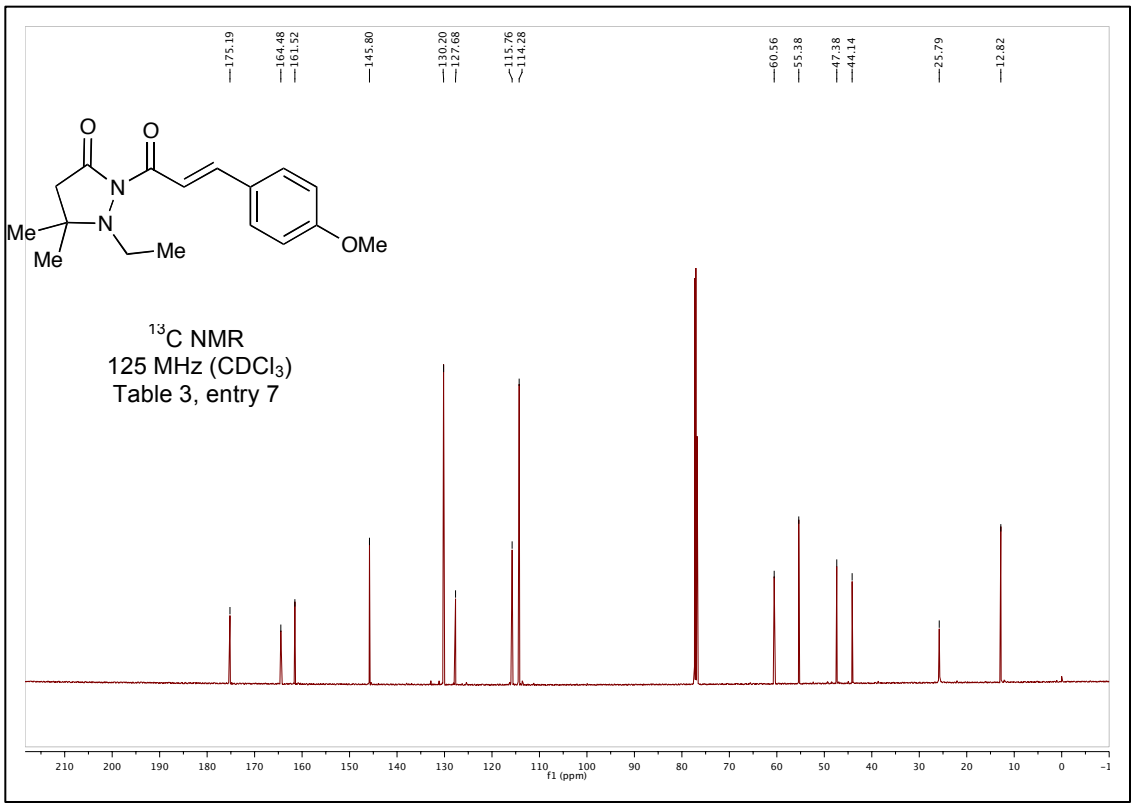
^{1}H NMR
500 MHz ($CDCl_3$)
Table 3, entry 6



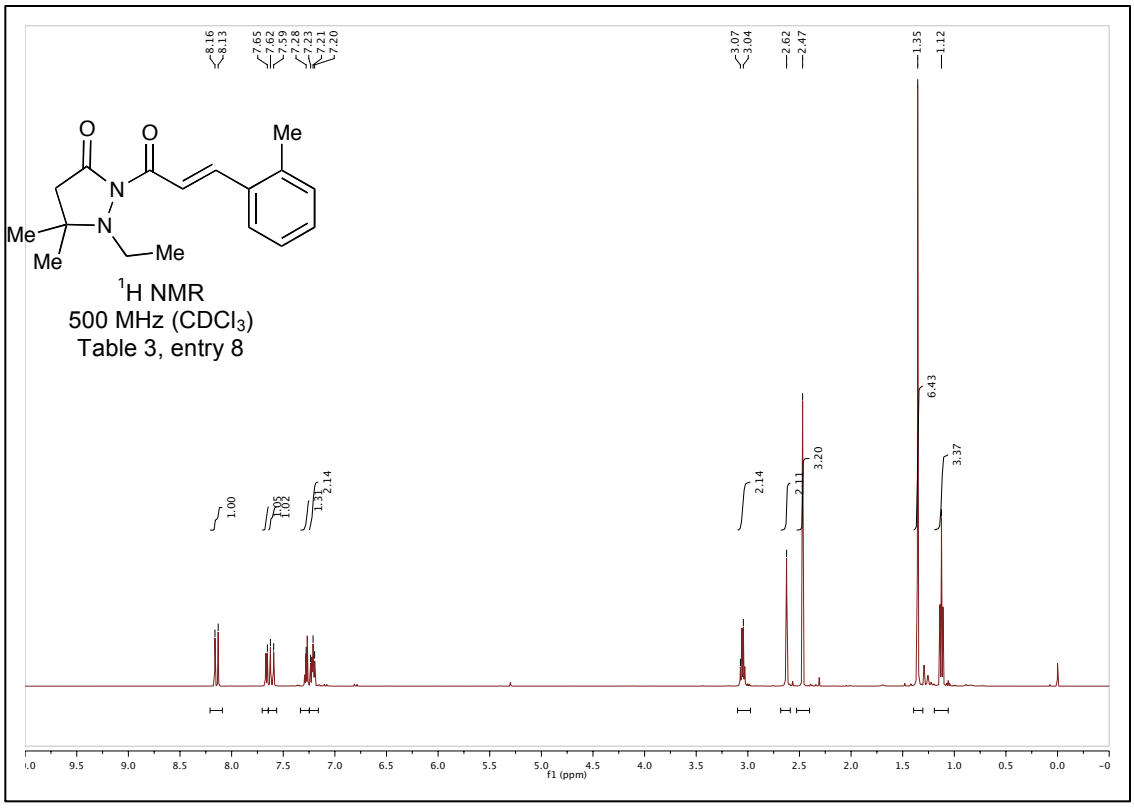
^{13}C NMR
125 MHz ($CDCl_3$)
Table 3, entry 6



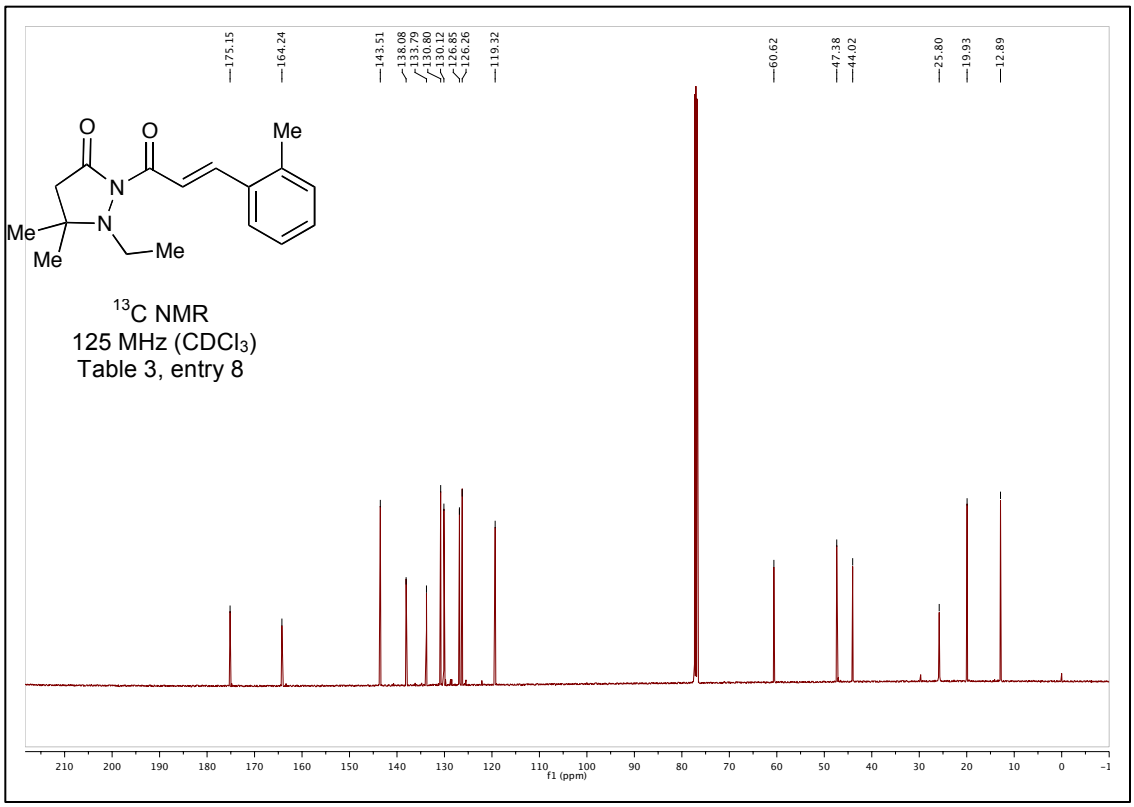
^{1}H NMR
500 MHz ($CDCl_3$)
Table 3, entry 7



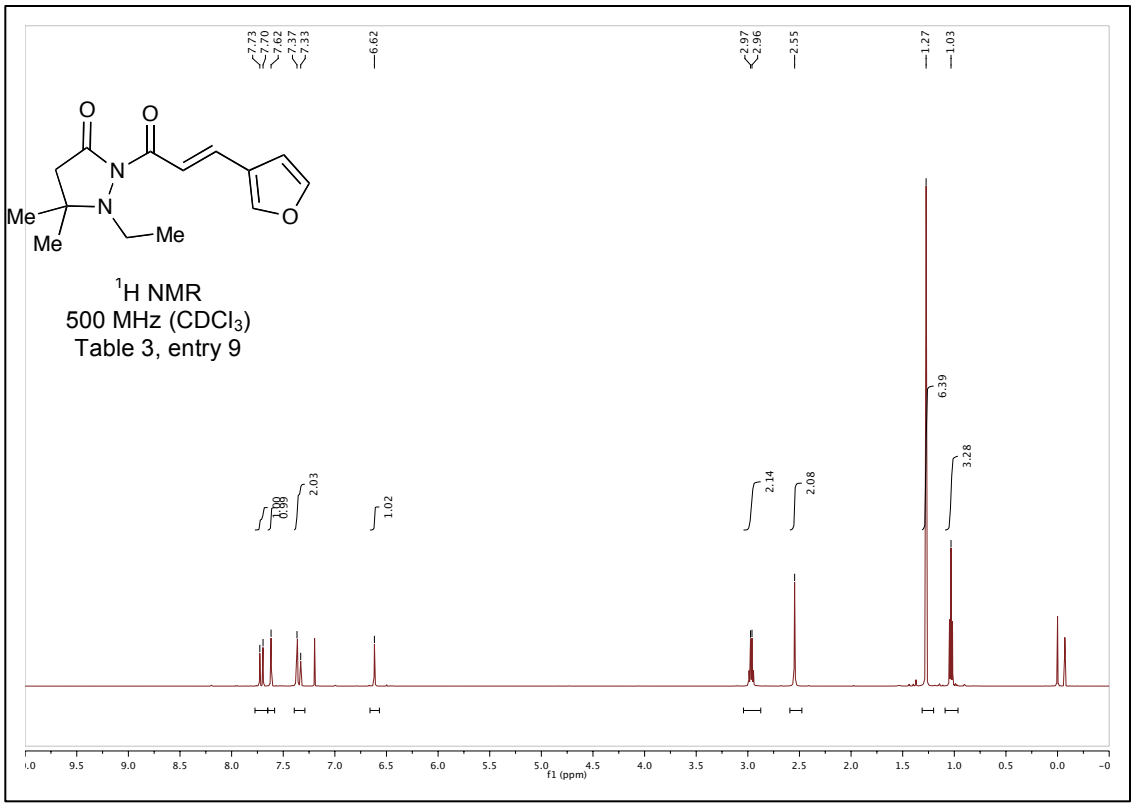
^{13}C NMR
125 MHz ($CDCl_3$)
Table 3, entry 7



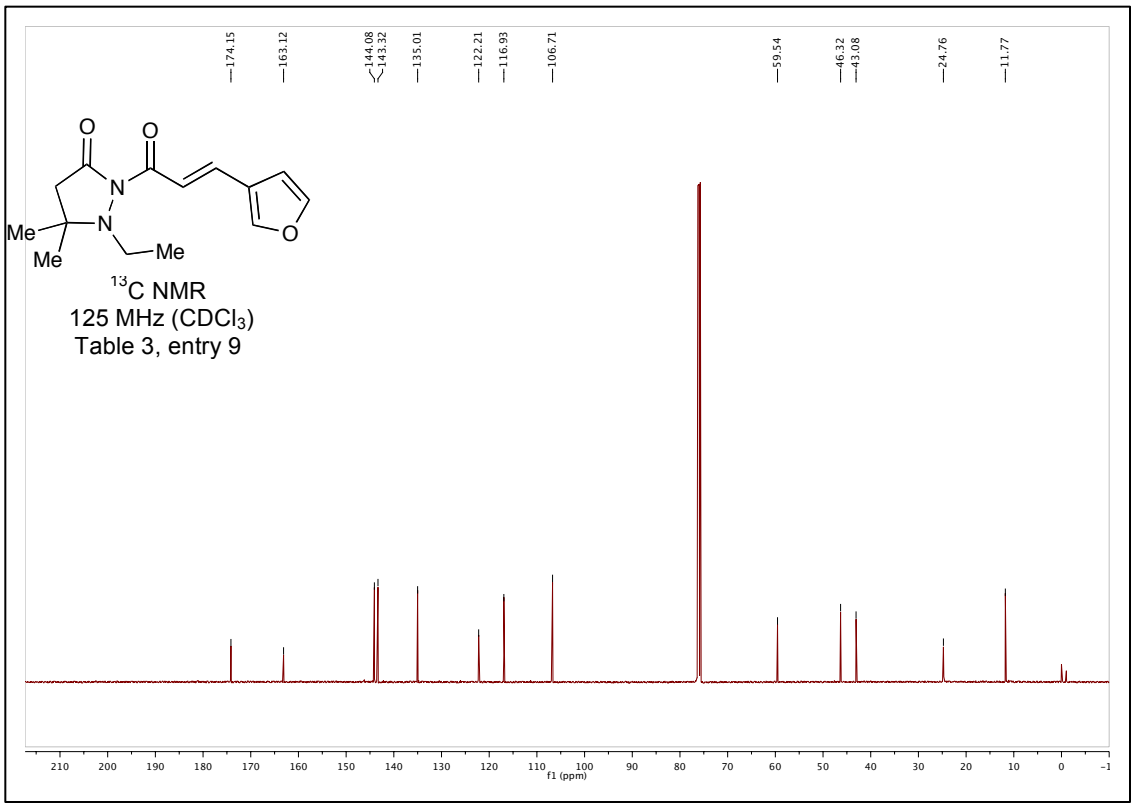
^{1}H NMR
500 MHz ($CDCl_3$)
Table 3, entry 8



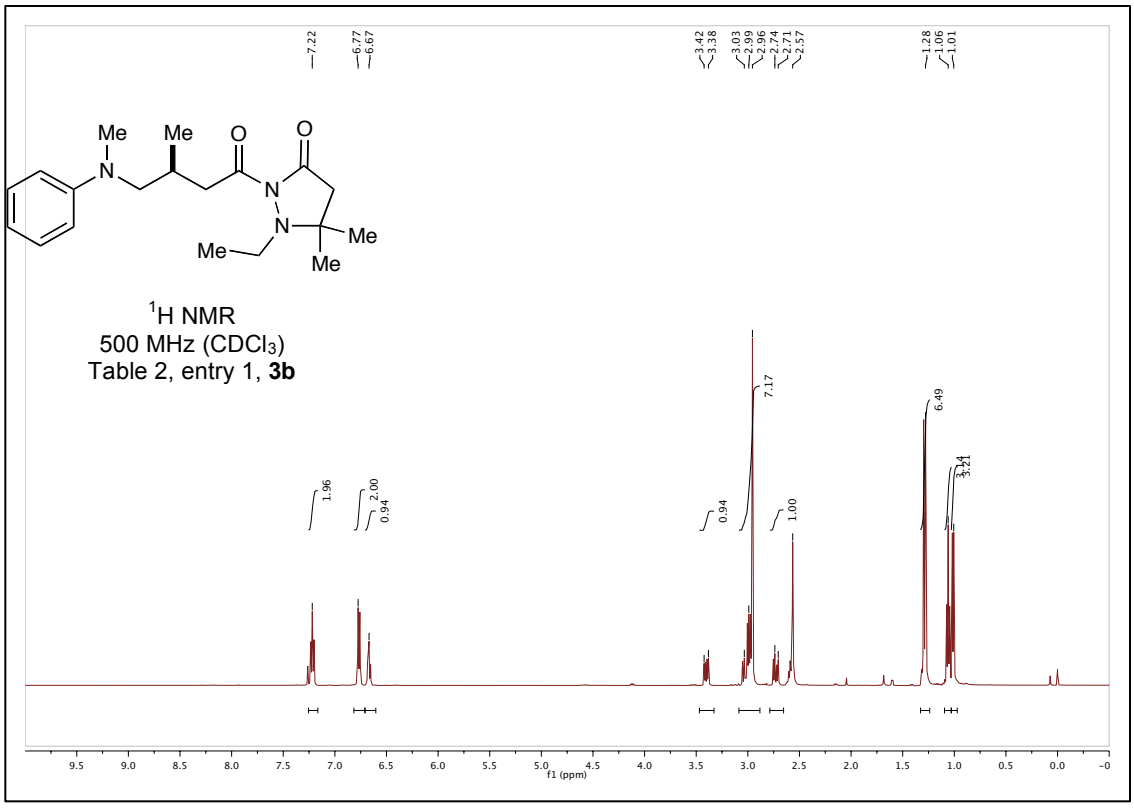
^{13}C NMR
125 MHz ($CDCl_3$)
Table 3, entry 8

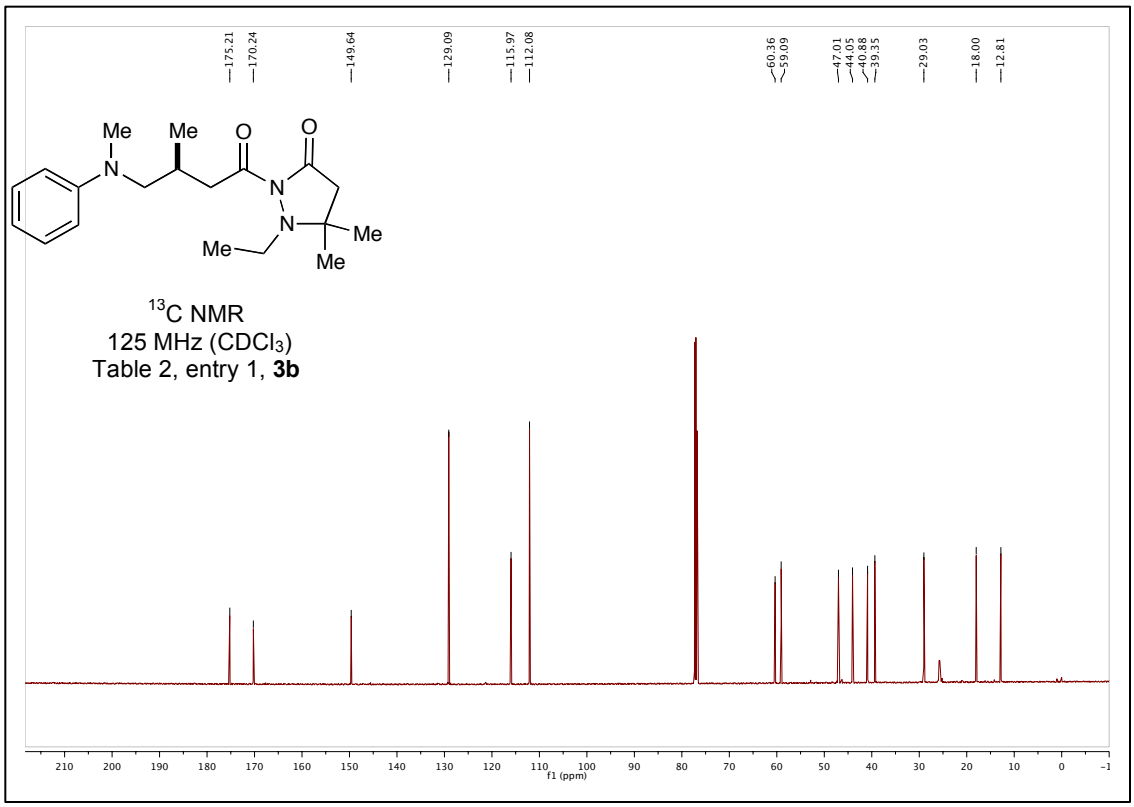


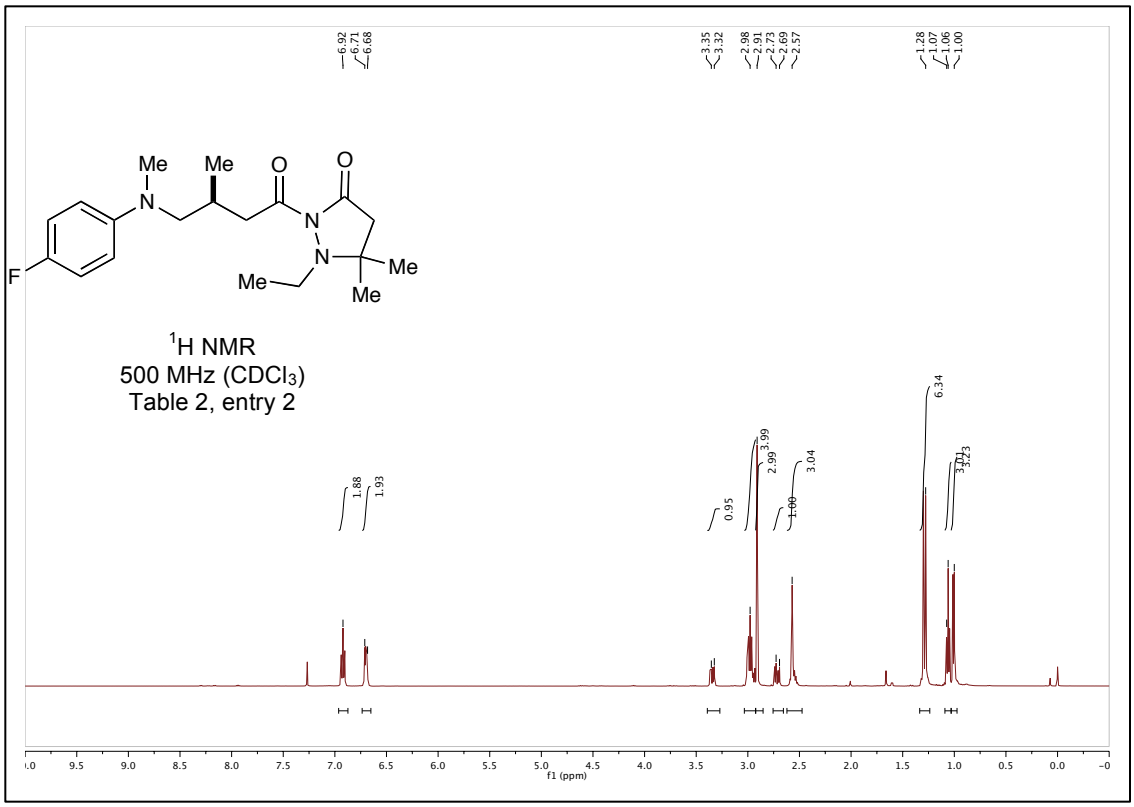
^{1}H NMR
500 MHz ($CDCl_3$)
Table 3, entry 9

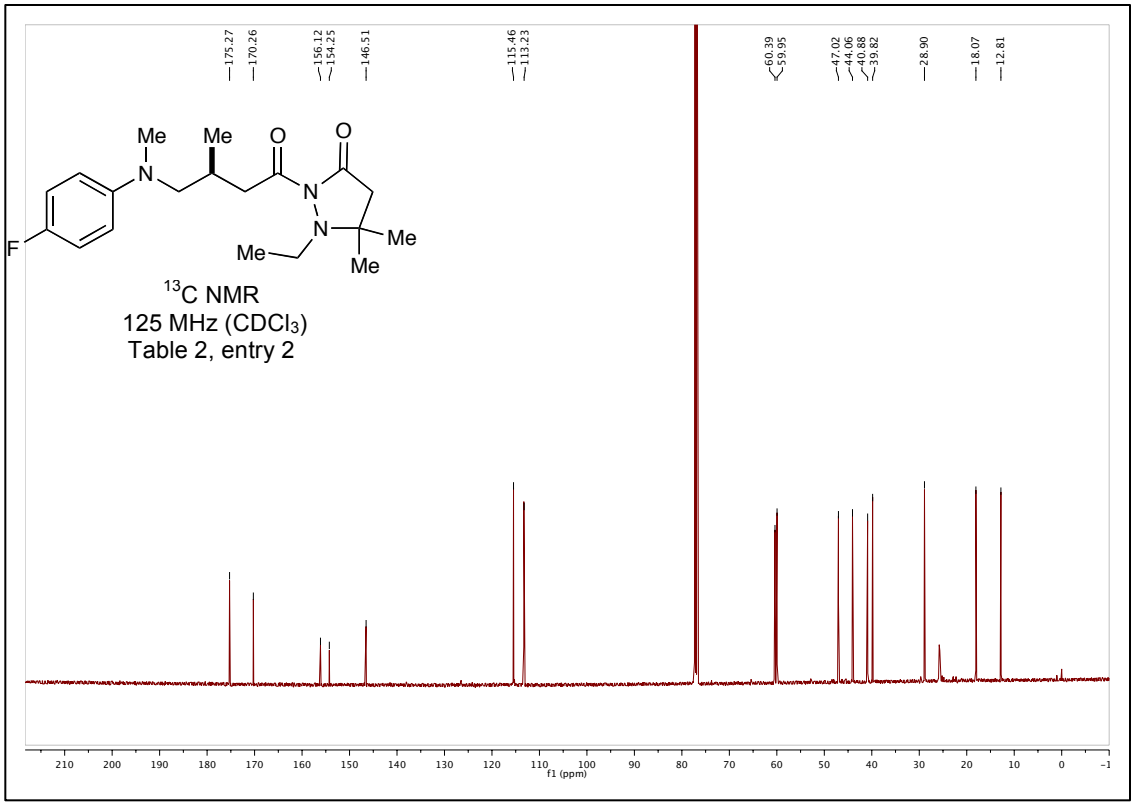


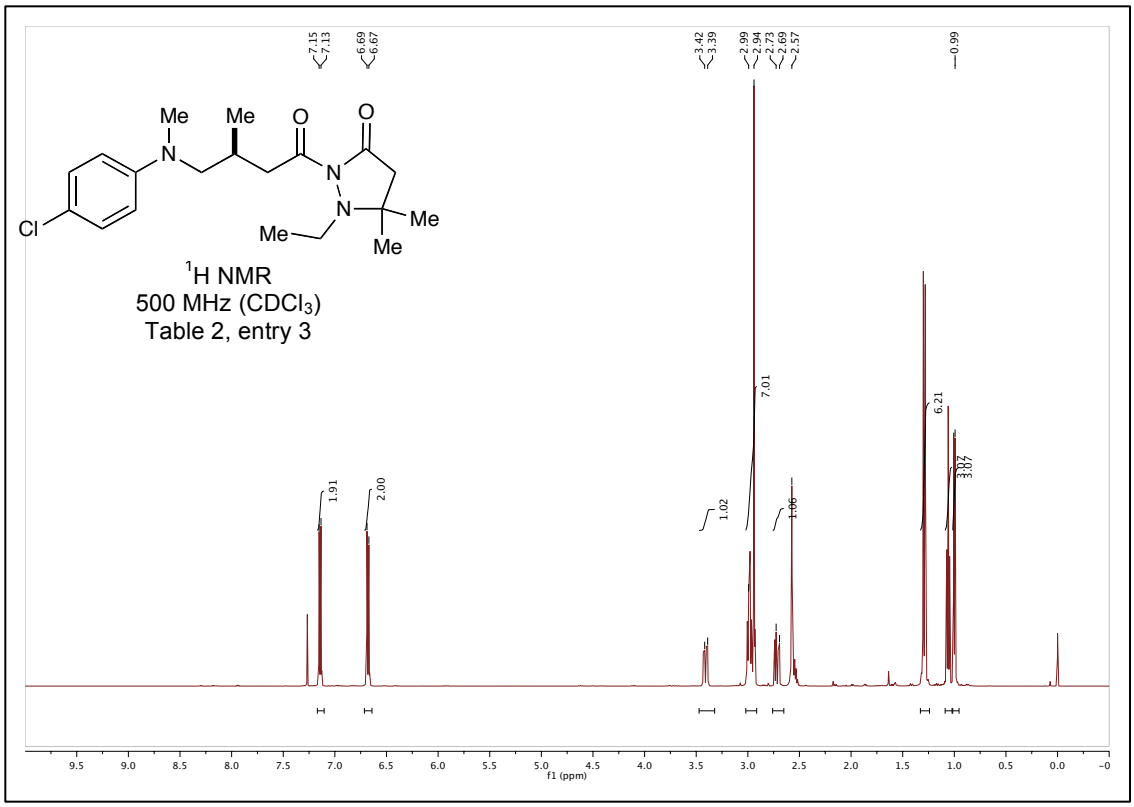
^{13}C NMR
125 MHz ($CDCl_3$)
Table 3, entry 9


7.22
6.77
6.67
3.42
3.38
3.03
2.99
2.96
2.74
2.71
2.57
1.28
1.06
1.01
Me
Me
O
O
N
N
N
Me
Me
Me
1H NMR
500 MHz (CDCl3)
Table 2, entry 1, 3b
1.96
2.00
0.94
0.94
7.17
1.00
6.49
3.24
3.21
f1 (ppm)

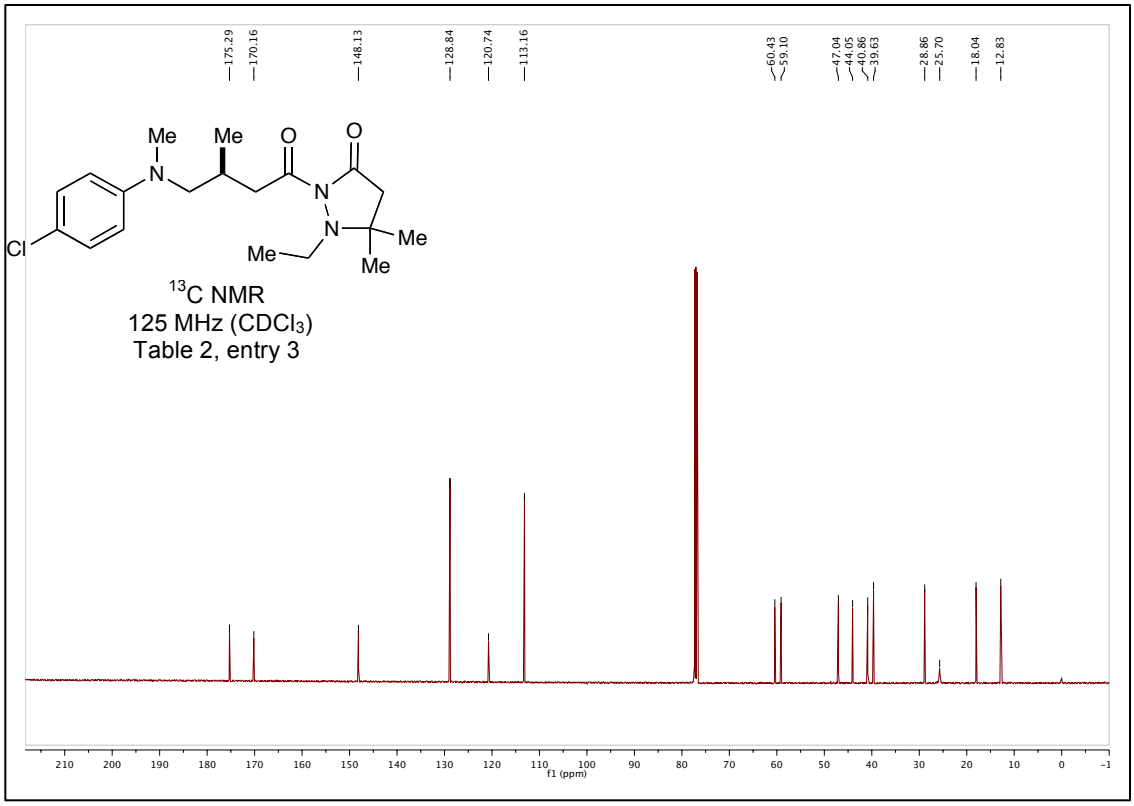

175.21
170.24
149.64
129.09
115.97
112.08
60.36
59.09
47.01
44.05
40.88
39.35
29.03
18.00
12.81
Me
Me
O
O
N
N
N
Me
Me
Me
13C NMR
125 MHz (CDCl3)
Table 2, entry 1, 3b
f1 (ppm)


Me
Me
O
O
N
N
N
F
Me
Me
Me
^{1}H NMR
500 MHz ($CDCl_3$)
Table 2, entry 2
6.92
6.71
6.68
3.35
3.32
2.98
2.91
2.73
2.69
2.57
1.28
1.07
1.06
1.00
1.88
1.93
0.95
3.99
2.99
3.04
1.00
6.34
3.71
3.23
f1 (ppm)

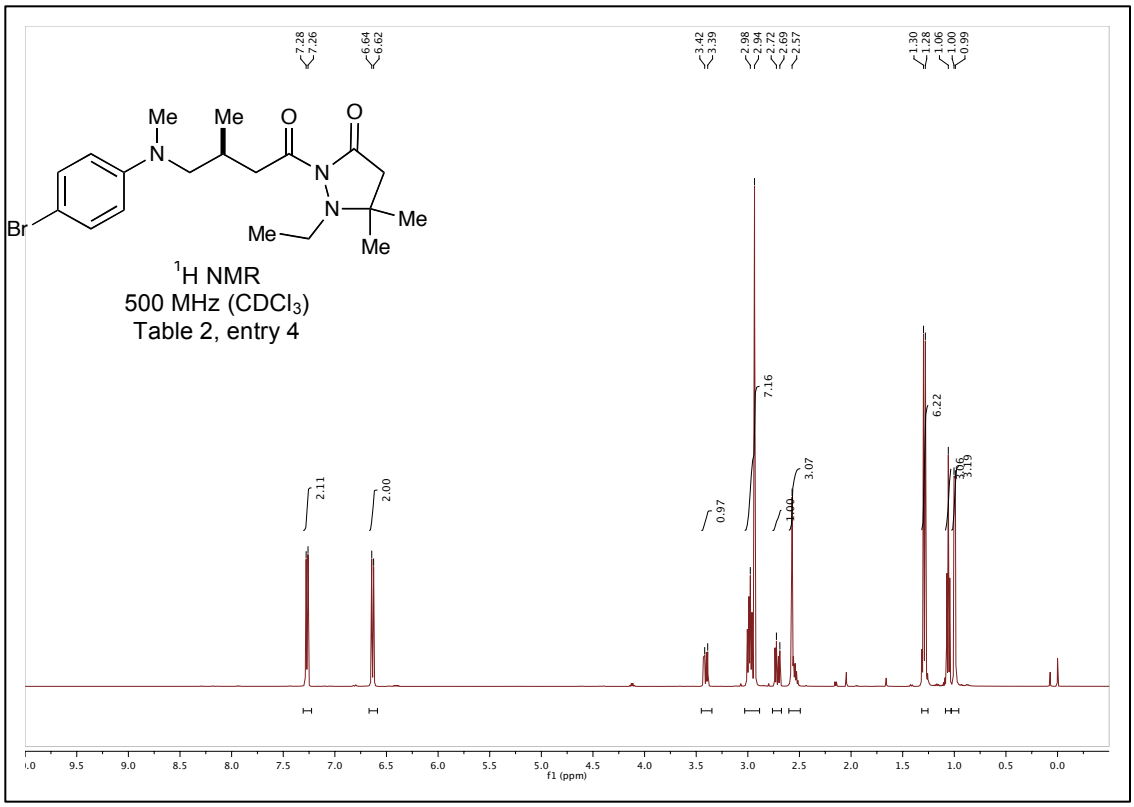

Me
Me
O
O
N
N
N
F
Me
Me
Me
^{13}C NMR
125 MHz ($CDCl_3$)
Table 2, entry 2
175.27
170.26
156.12
154.25
146.51
115.46
113.23
60.39
59.95
47.02
44.06
40.88
39.82
28.90
18.07
12.81
f1 (ppm)

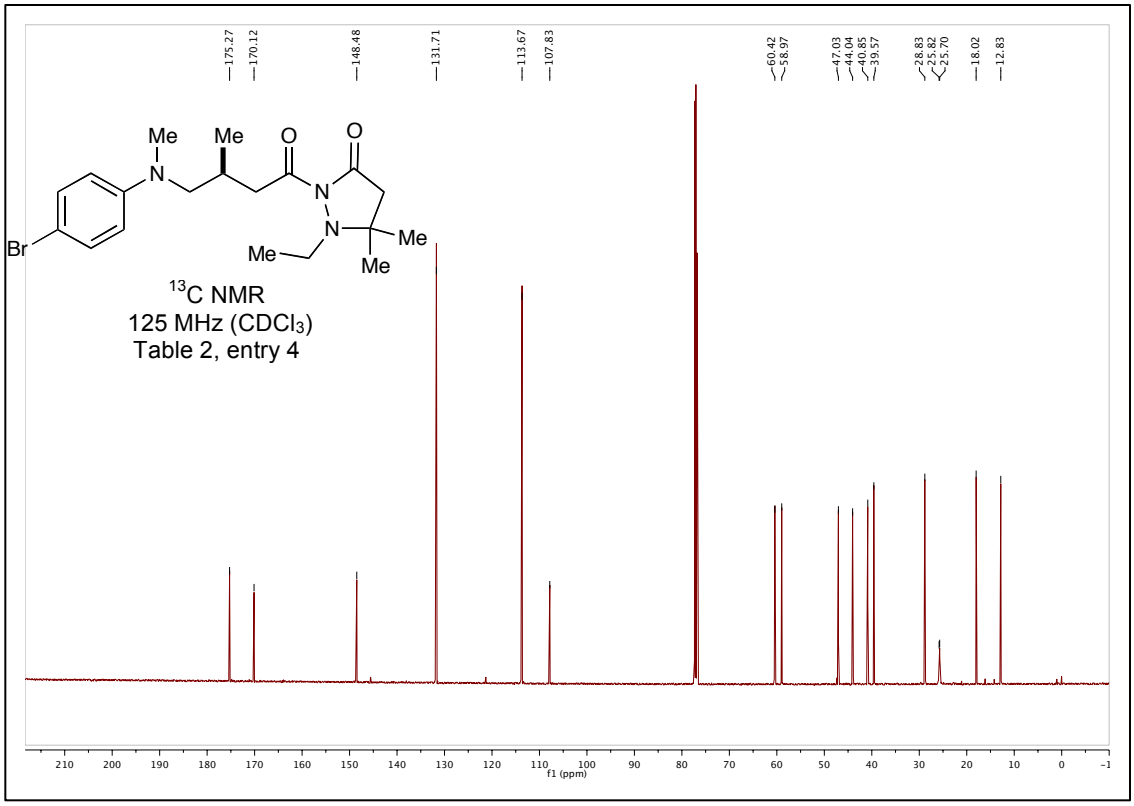


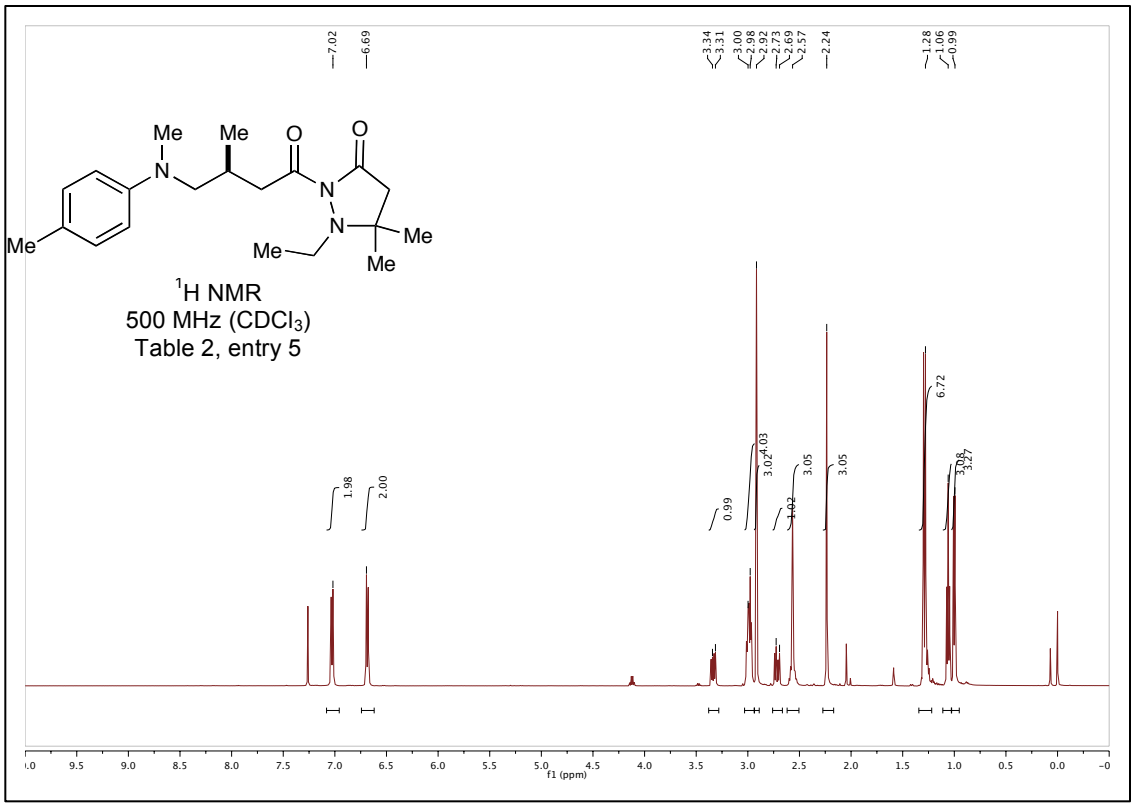
^{1}H NMR
500 MHz ($CDCl_3$)
Table 2, entry 3



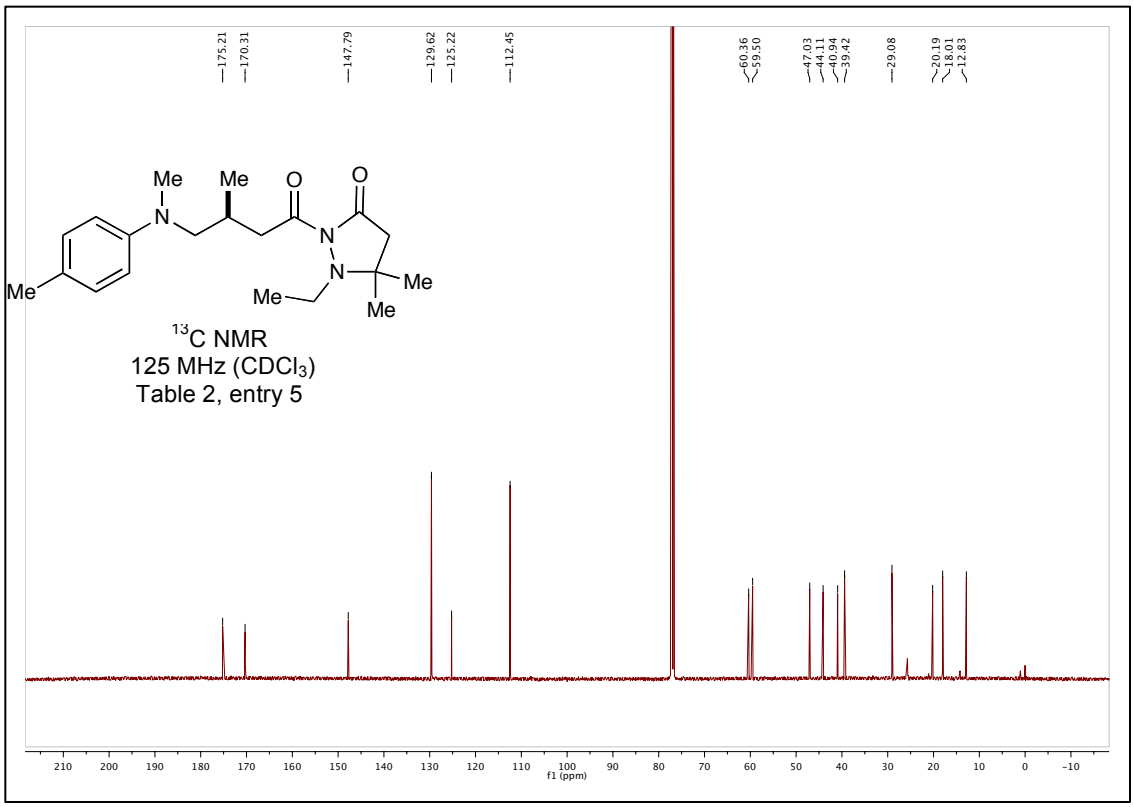
^{13}C NMR
125 MHz ($CDCl_3$)
Table 2, entry 3


Me
Me
O
O
N
N
N
Br
Me
Me
Me
^{1}H NMR
500 MHz ($CDCl_3$)
Table 2, entry 4
7.28
7.26
6.64
6.62
3.42
3.39
2.98
2.94
2.72
2.69
2.57
1.30
1.28
1.06
1.00
0.99
2.11
2.00
0.97
7.16
1.00
3.07
6.22
f1 (ppm)

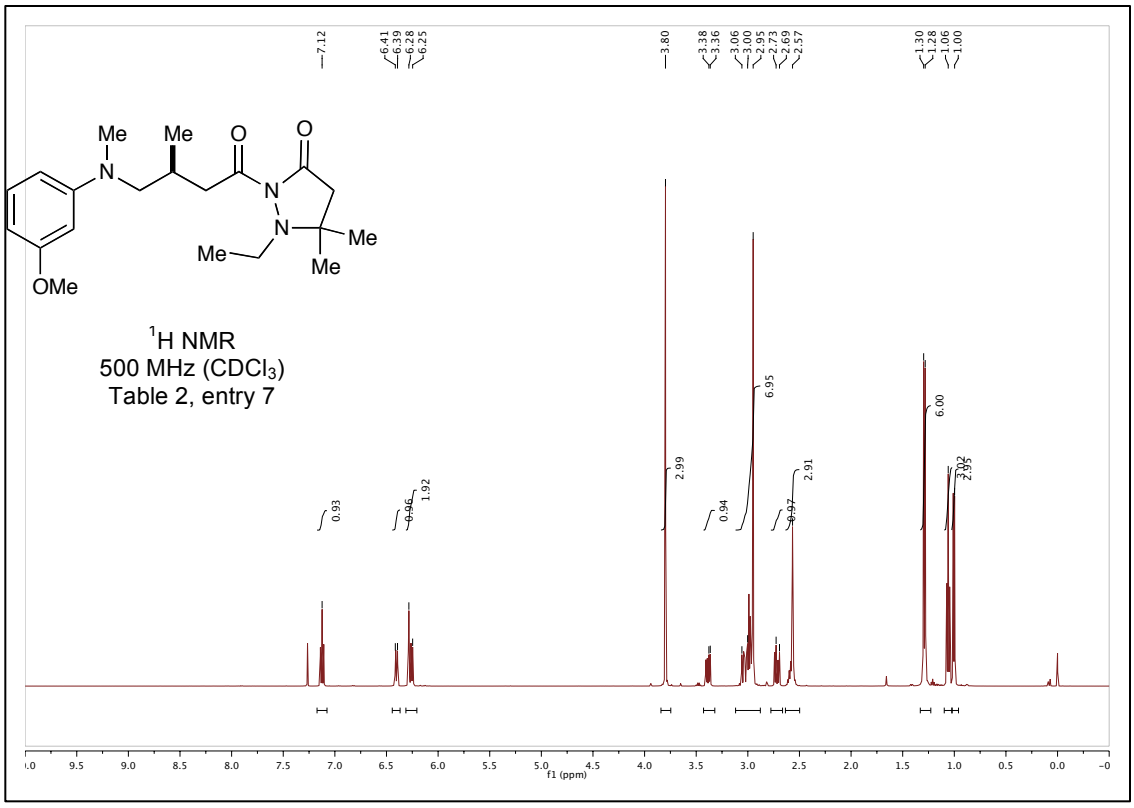

Me
Me
O
O
N
N
N
Br
Me
Me
Me
^{13}C NMR
125 MHz ($CDCl_3$)
Table 2, entry 4
175.27
170.12
148.48
131.71
113.67
107.83
60.42
58.97
47.03
44.04
40.85
39.57
28.83
25.82
25.70
18.02
12.83
f1 (ppm)

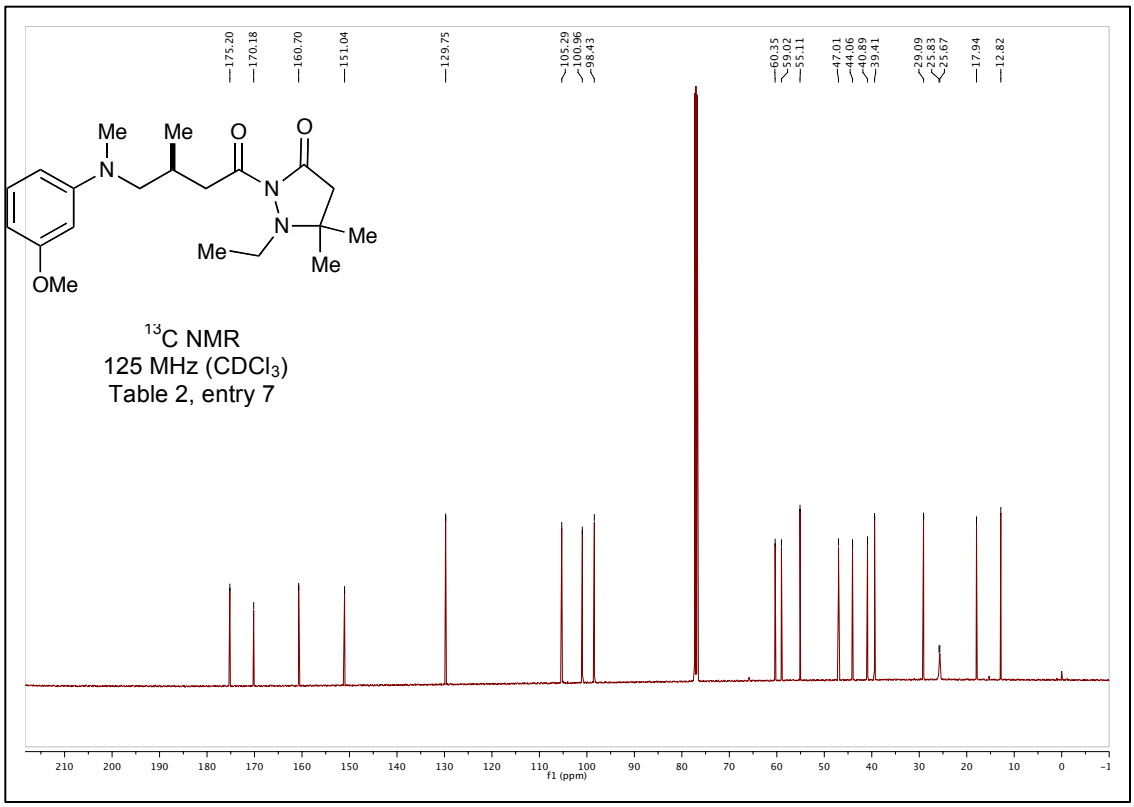


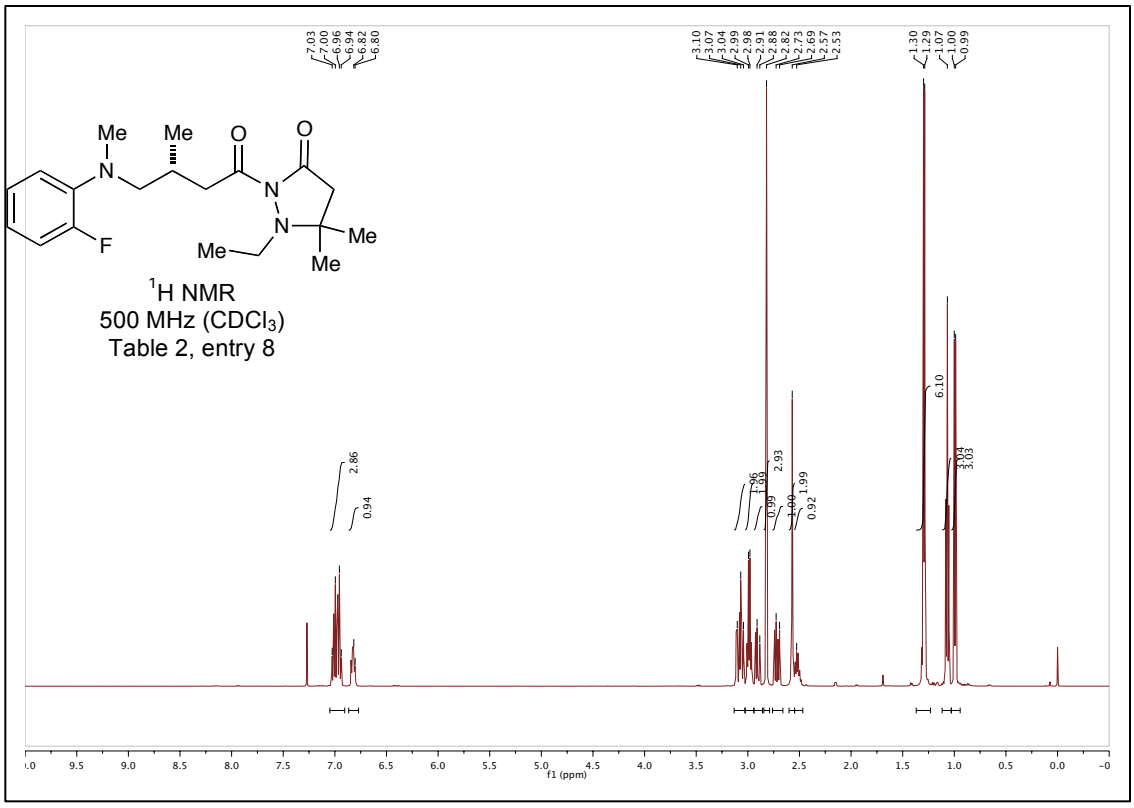
^{1}H NMR
500 MHz ($CDCl_3$)
Table 2, entry 5



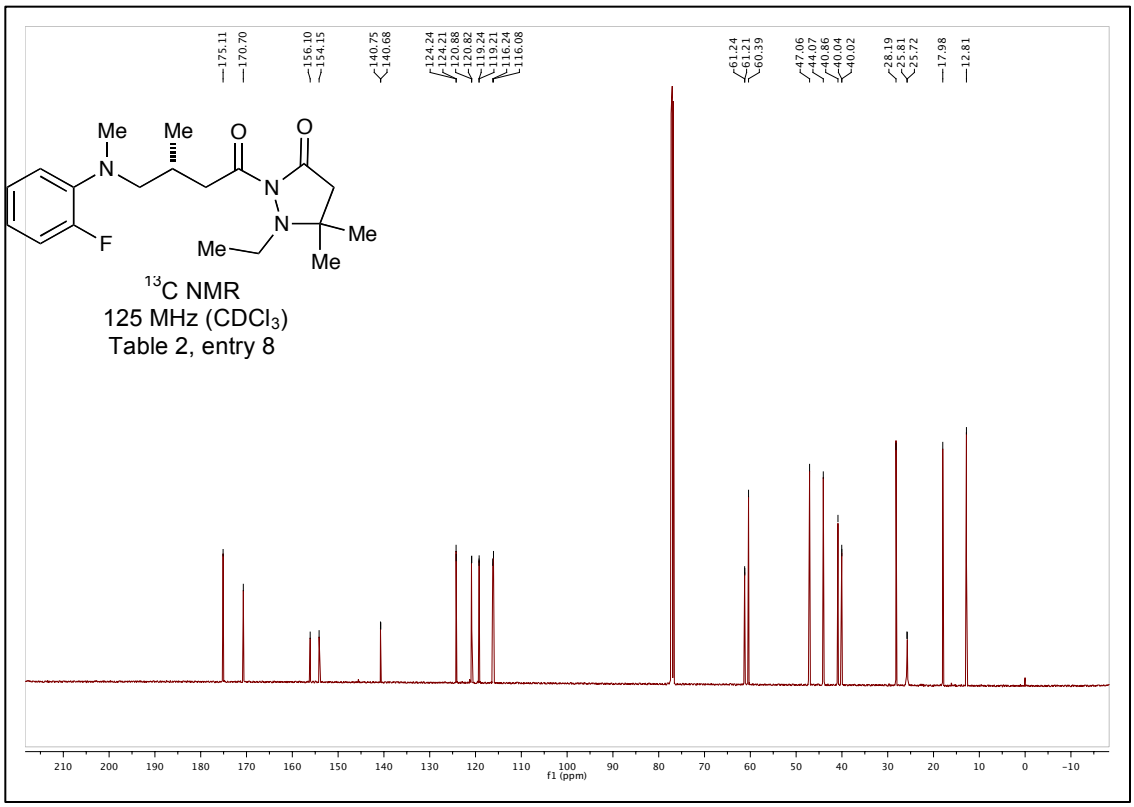
^{13}C NMR
125 MHz ($CDCl_3$)
Table 2, entry 5


Me
Me
O
O
N
N
N
Me
Me
Me
OMe
1H NMR
500 MHz (CDCl3)
Table 2, entry 7
f1 (ppm)

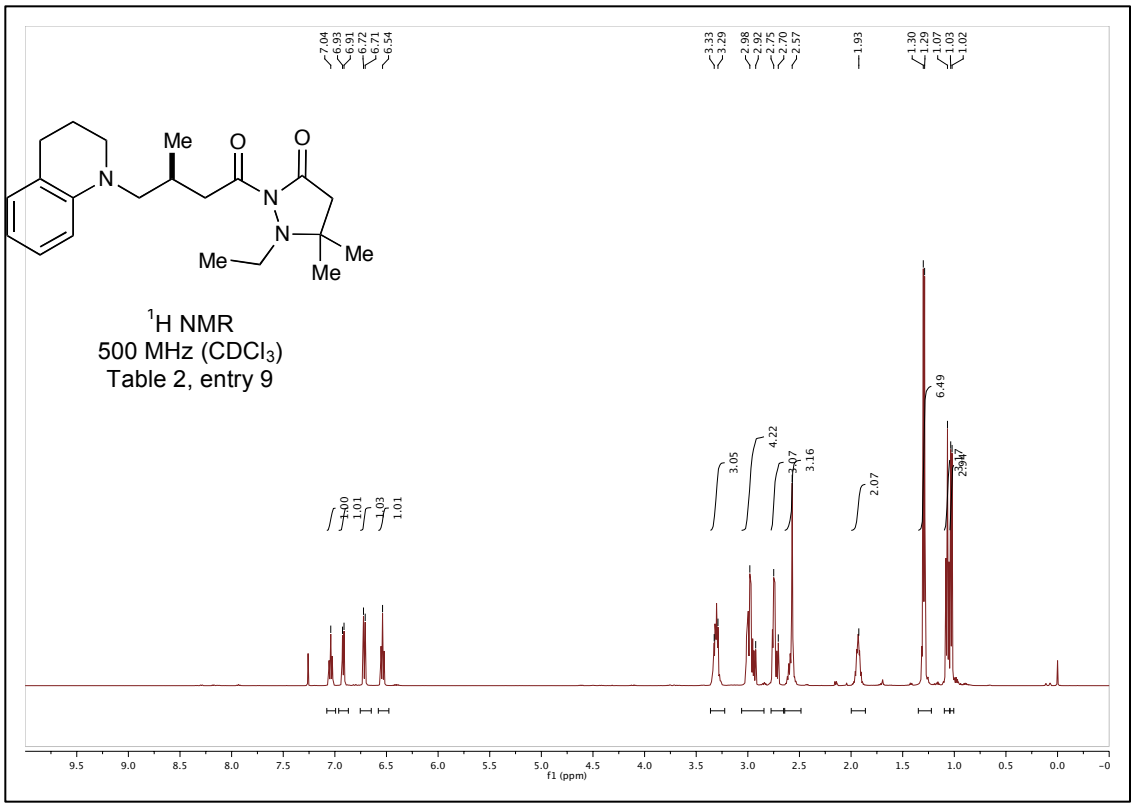

Me
Me
O
O
N
N
N
Me
Me
Me
OMe
13C NMR
125 MHz (CDCl3)
Table 2, entry 7
f1 (ppm)



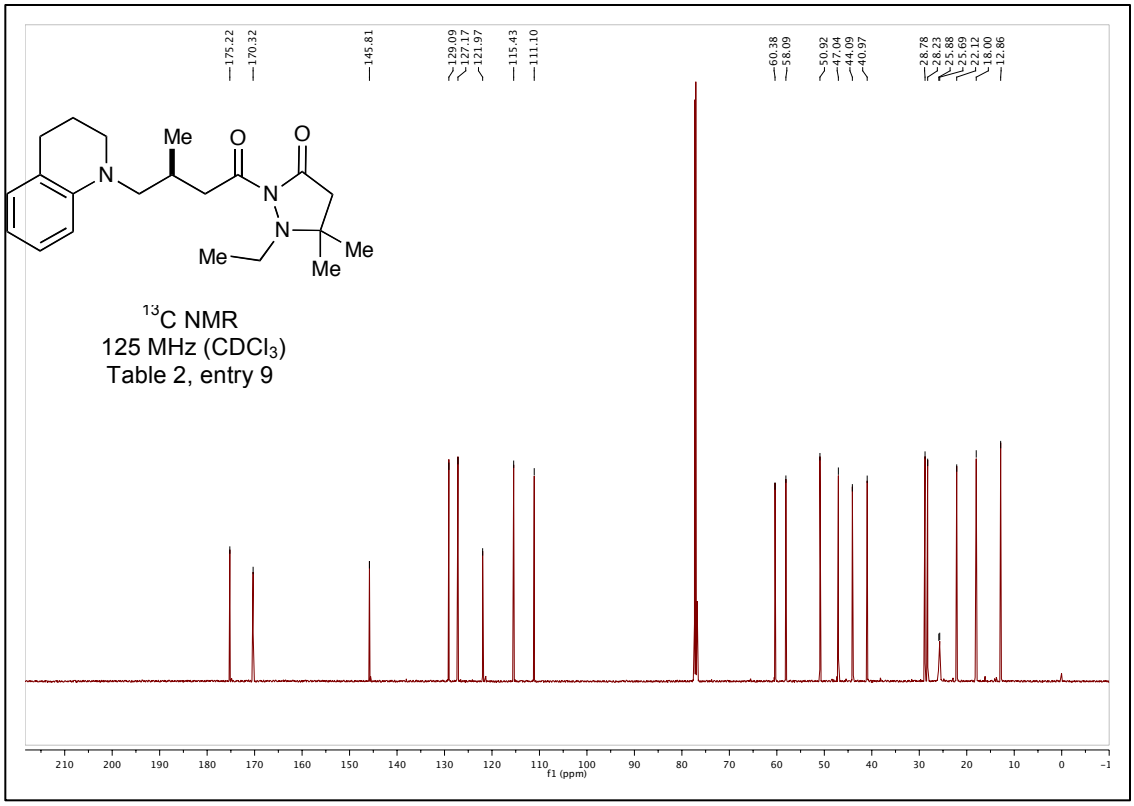
^{1}H NMR
500 MHz ($CDCl_3$)
Table 2, entry 8



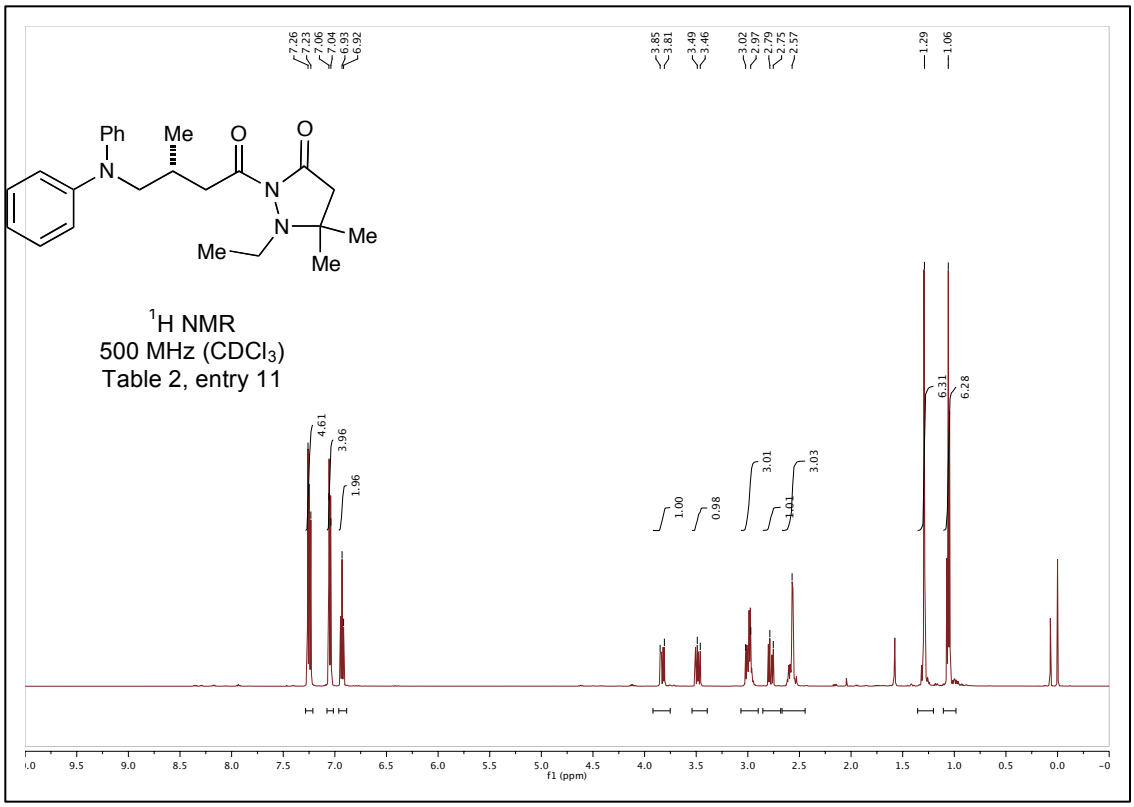
^{13}C NMR
125 MHz ($CDCl_3$)
Table 2, entry 8



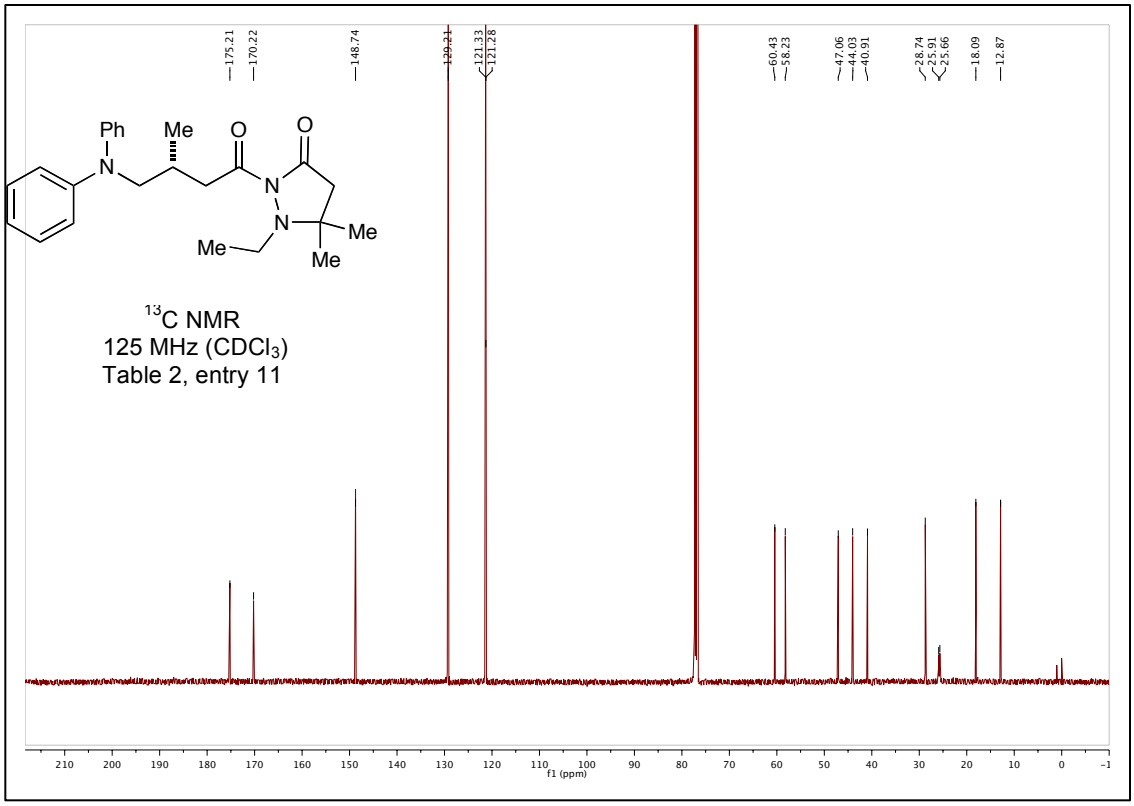
^{1}H NMR
500 MHz ($CDCl_3$)
Table 2, entry 9



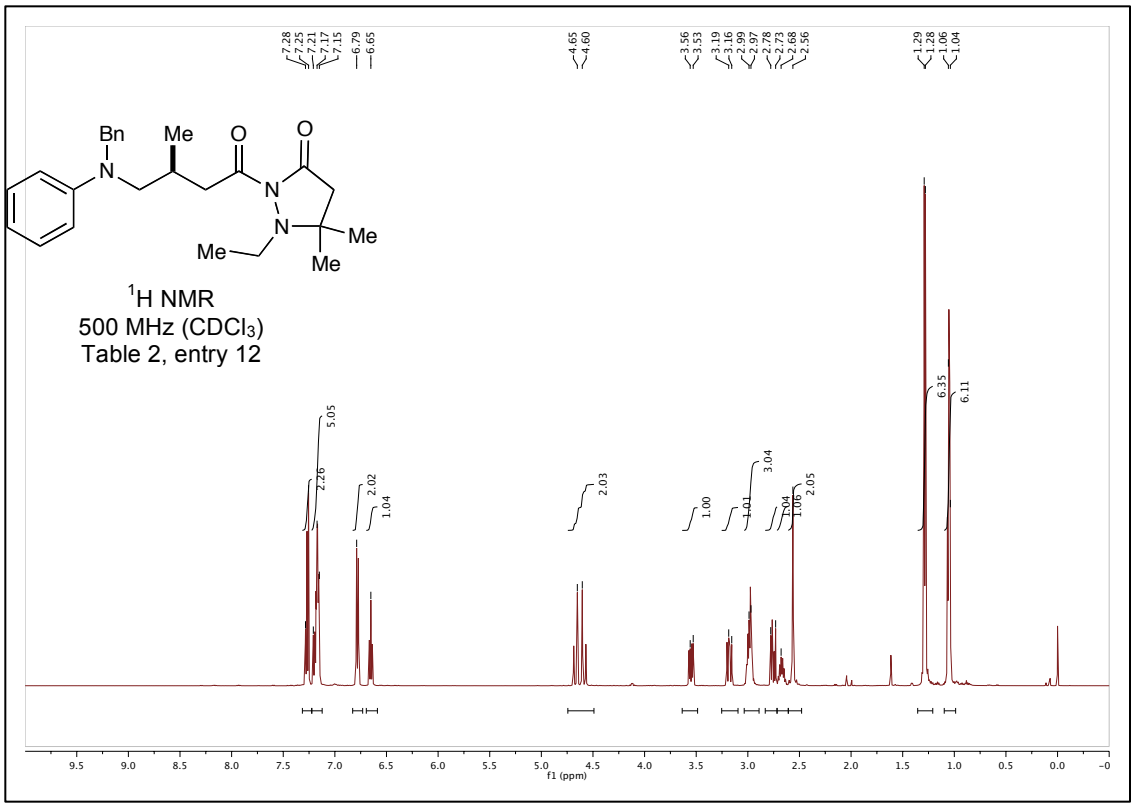
^{13}C NMR
125 MHz ($CDCl_3$)
Table 2, entry 9



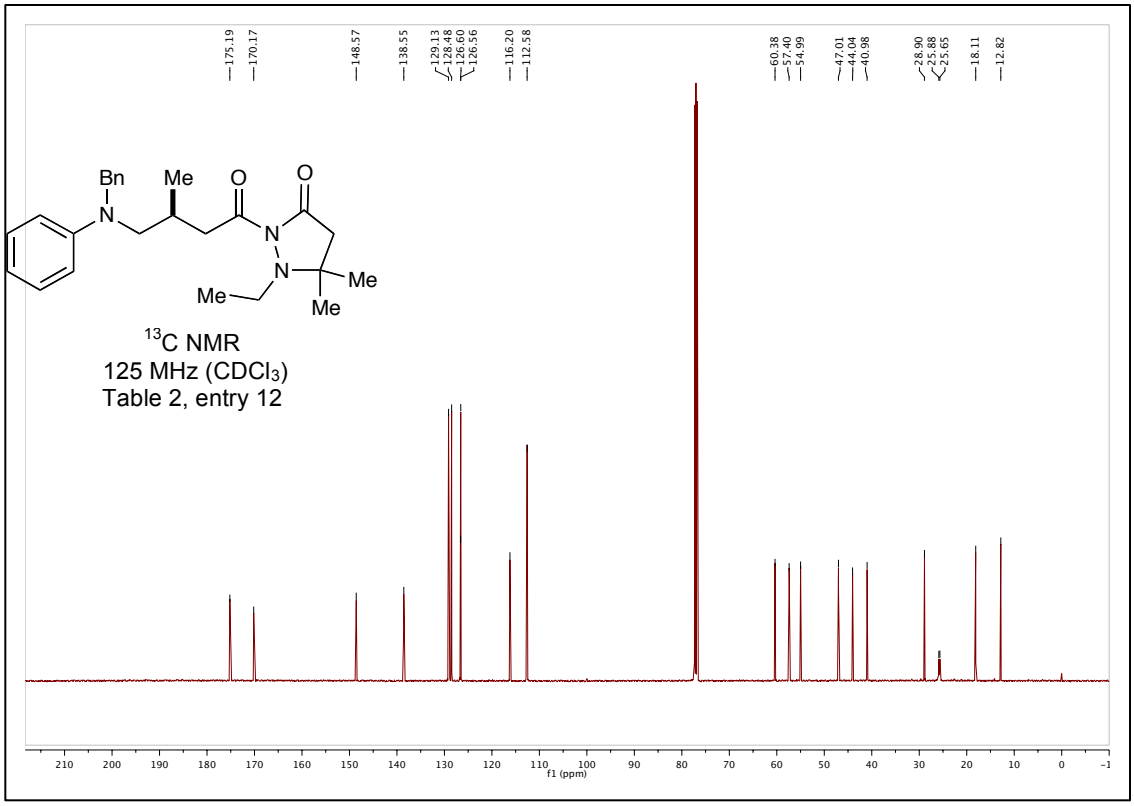
^{1}H NMR
500 MHz ($CDCl_3$)
Table 2, entry 11



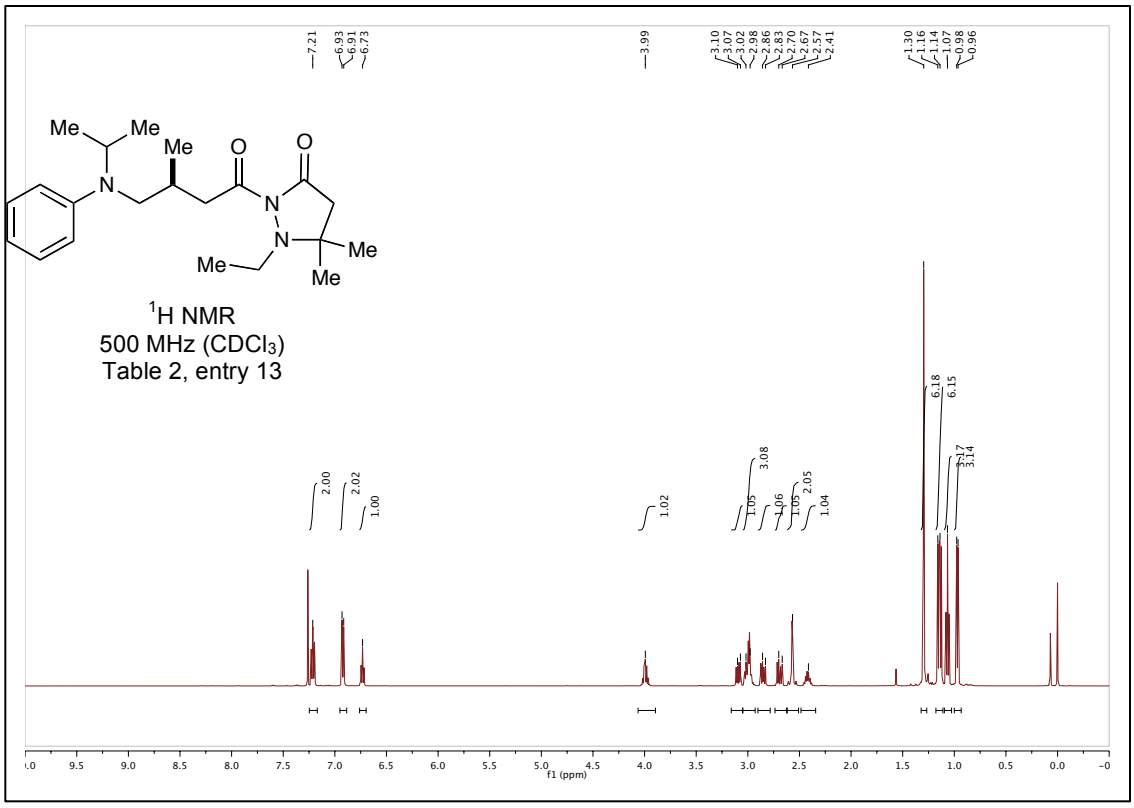
^{13}C NMR
125 MHz ($CDCl_3$)
Table 2, entry 11



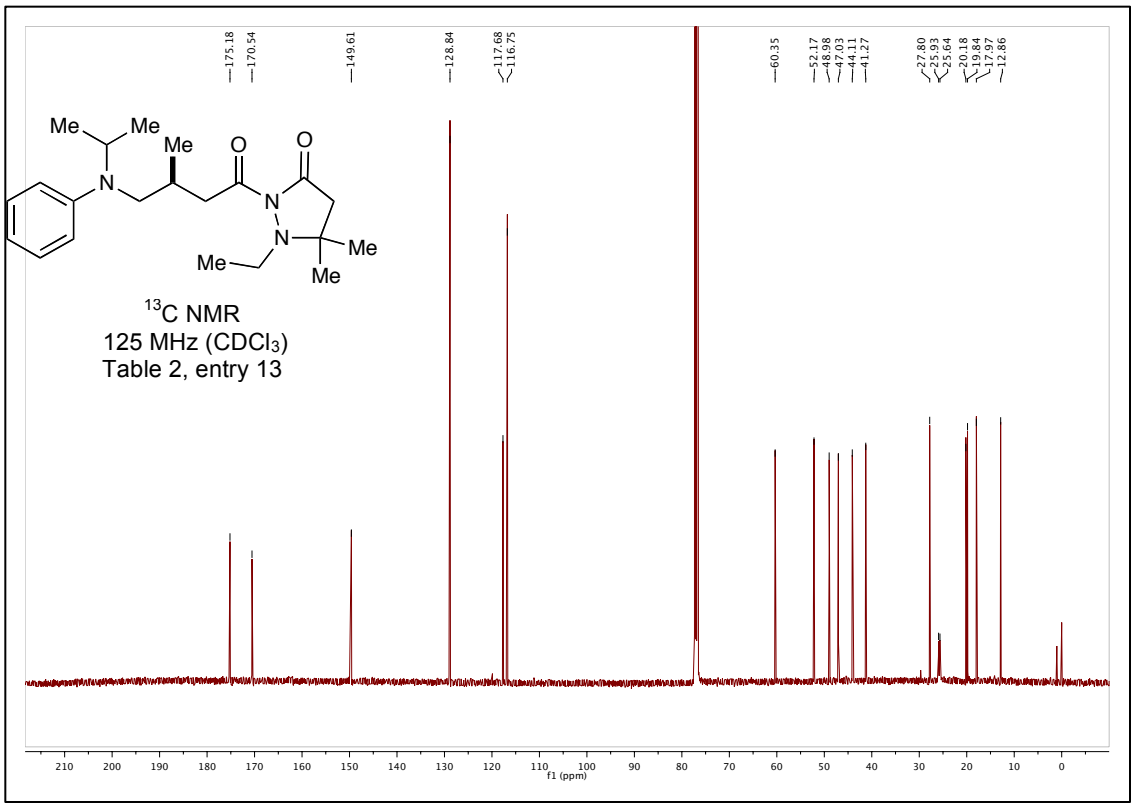
^{1}H NMR
500 MHz ($CDCl_3$)
Table 2, entry 12



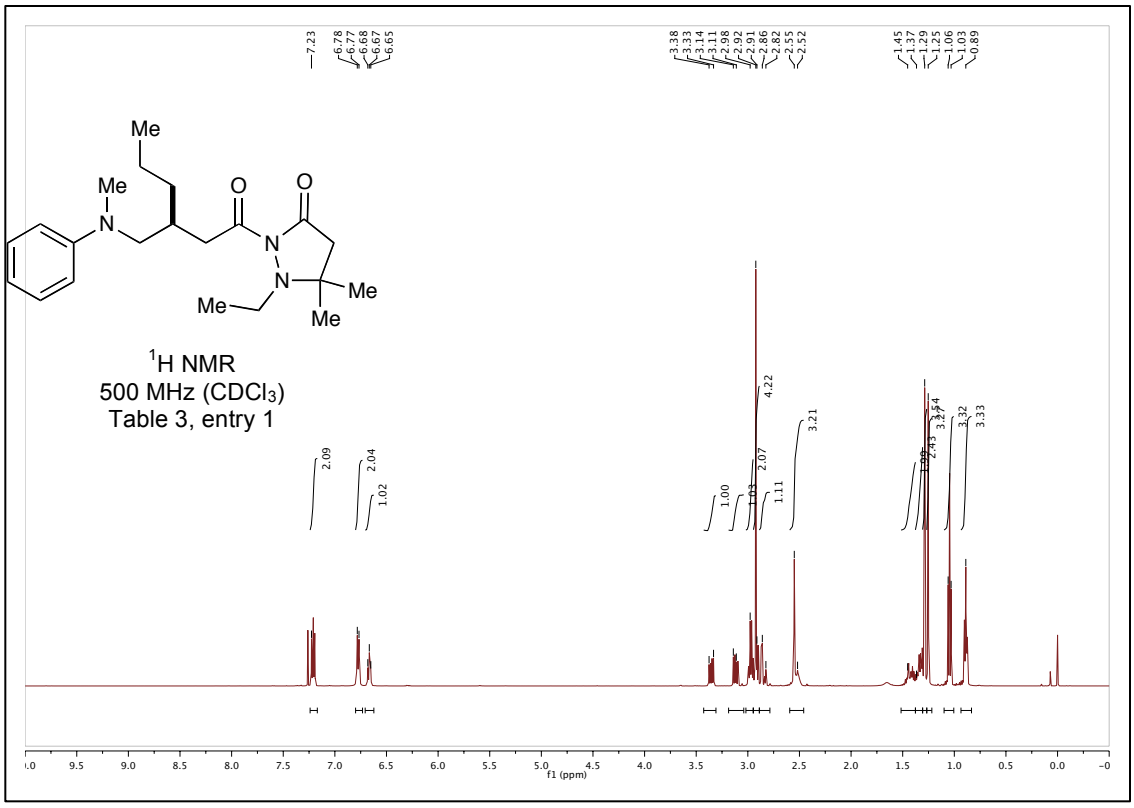
^{13}C NMR
125 MHz ($CDCl_3$)
Table 2, entry 12

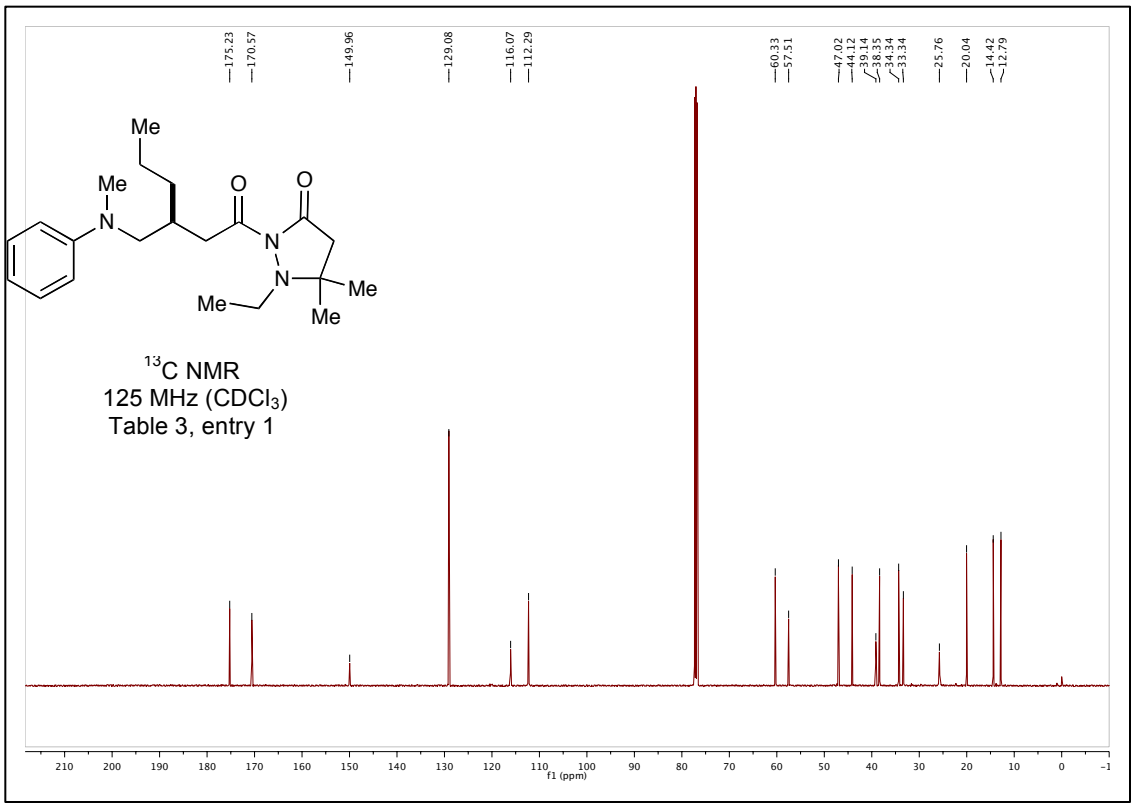


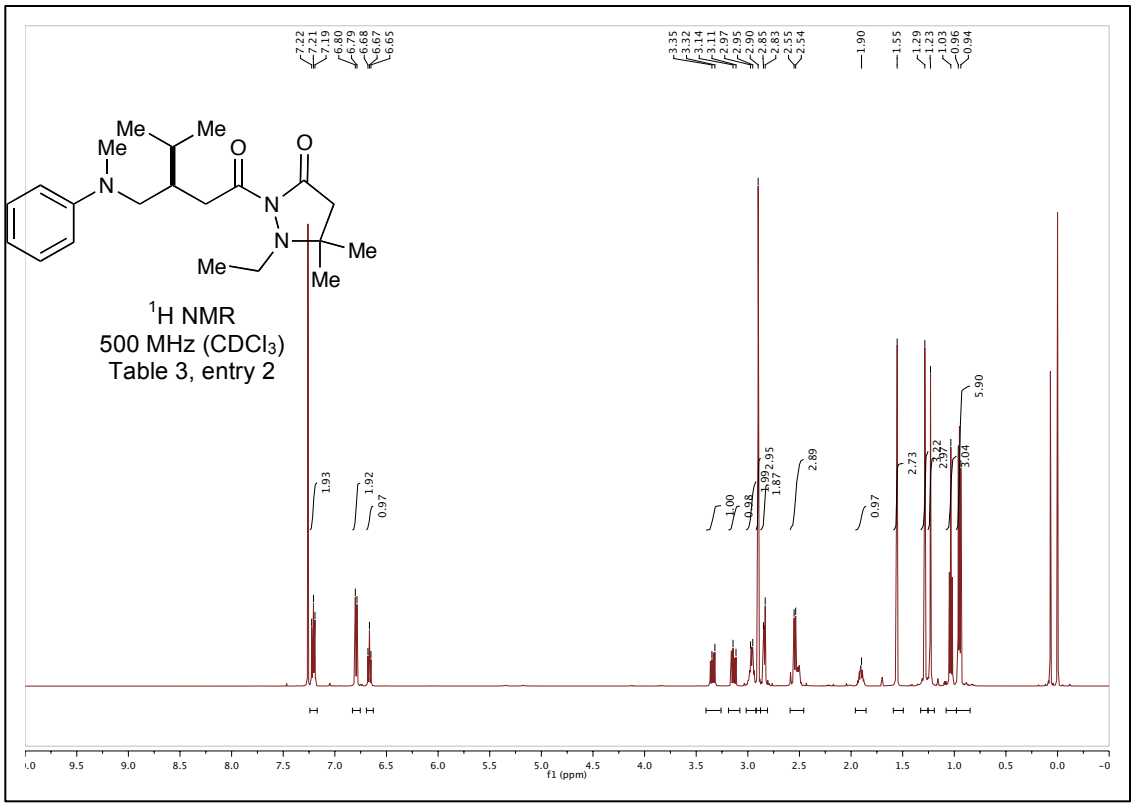
^{1}H NMR
500 MHz ($CDCl_3$)
Table 2, entry 13

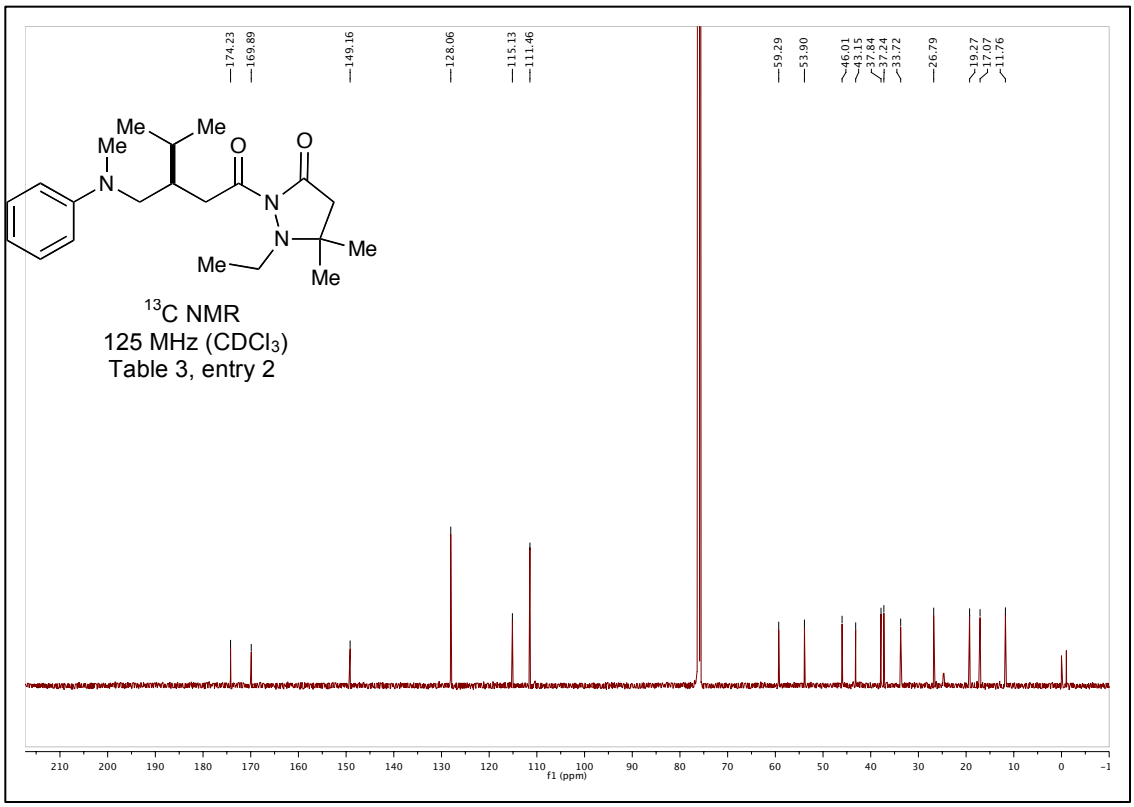


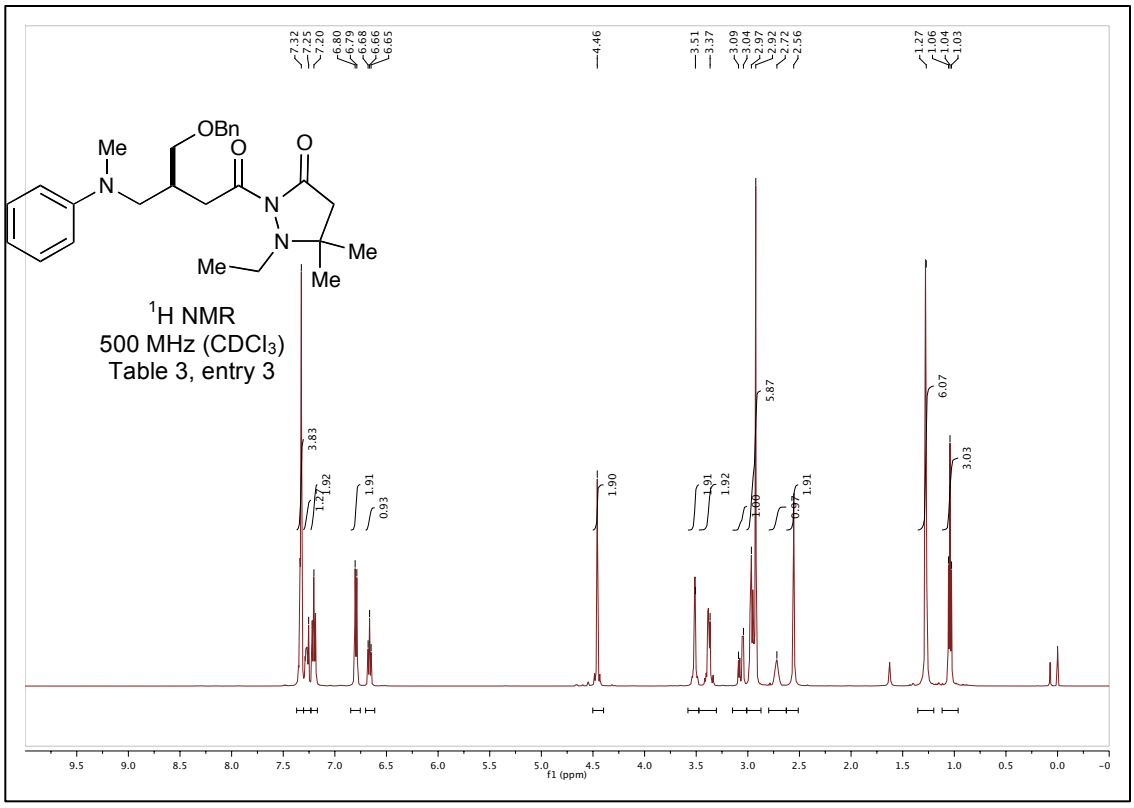
^{13}C NMR
125 MHz ($CDCl_3$)
Table 2, entry 13

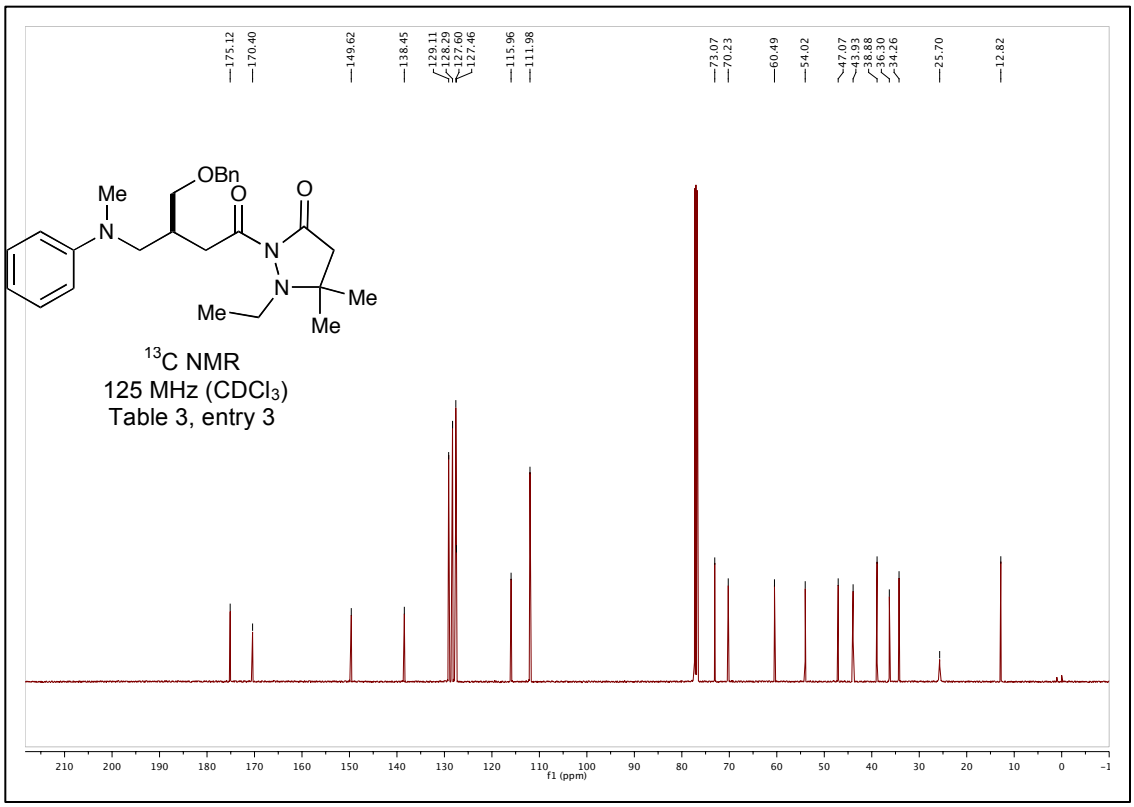

Me
Me
N
O
O
N
N
Me
Me
Me
Me
^{1}H NMR
500 MHz ($CDCl_3$)
Table 3, entry 1
f1 (ppm)

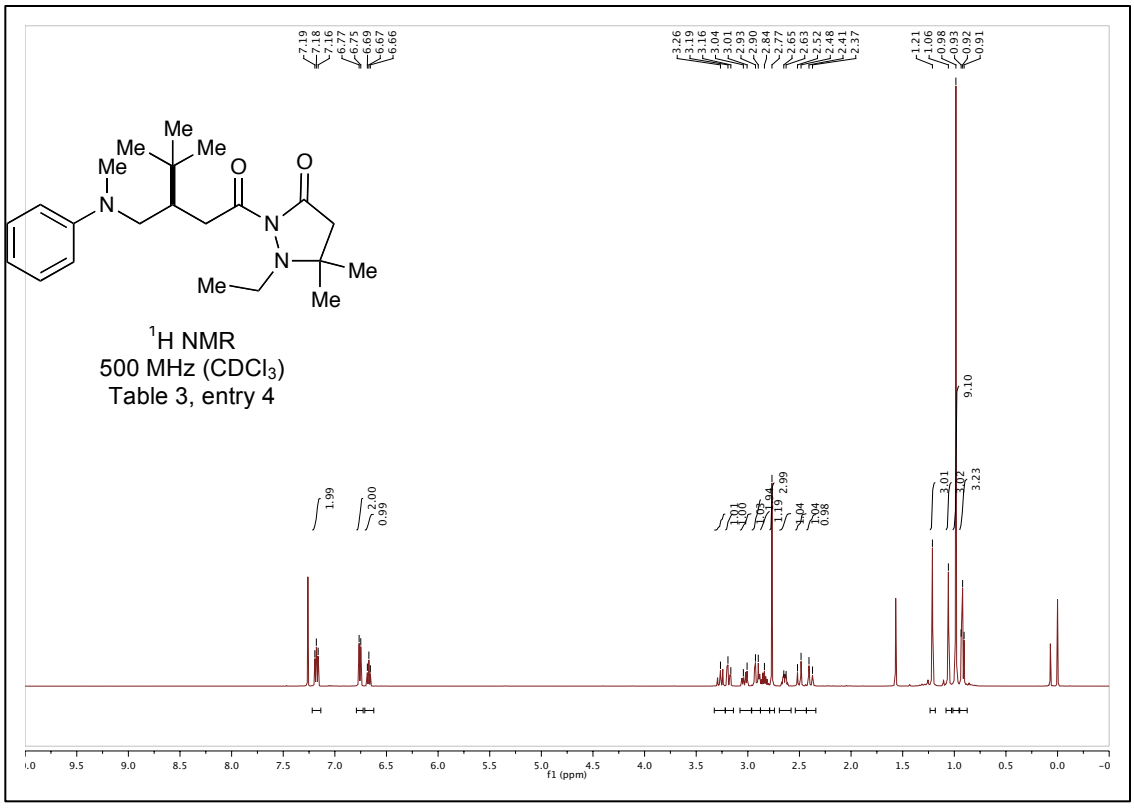

Me
Me
N
O
O
N
N
Me
Me
Me
Me
^{13}C NMR
125 MHz ($CDCl_3$)
Table 3, entry 1
f1 (ppm)


Me
Me
Me
N
O
O
N
N
Me
Me
Me
Me
^{1}H NMR
500 MHz ($CDCl_3$)
Table 3, entry 2
f1 (ppm)

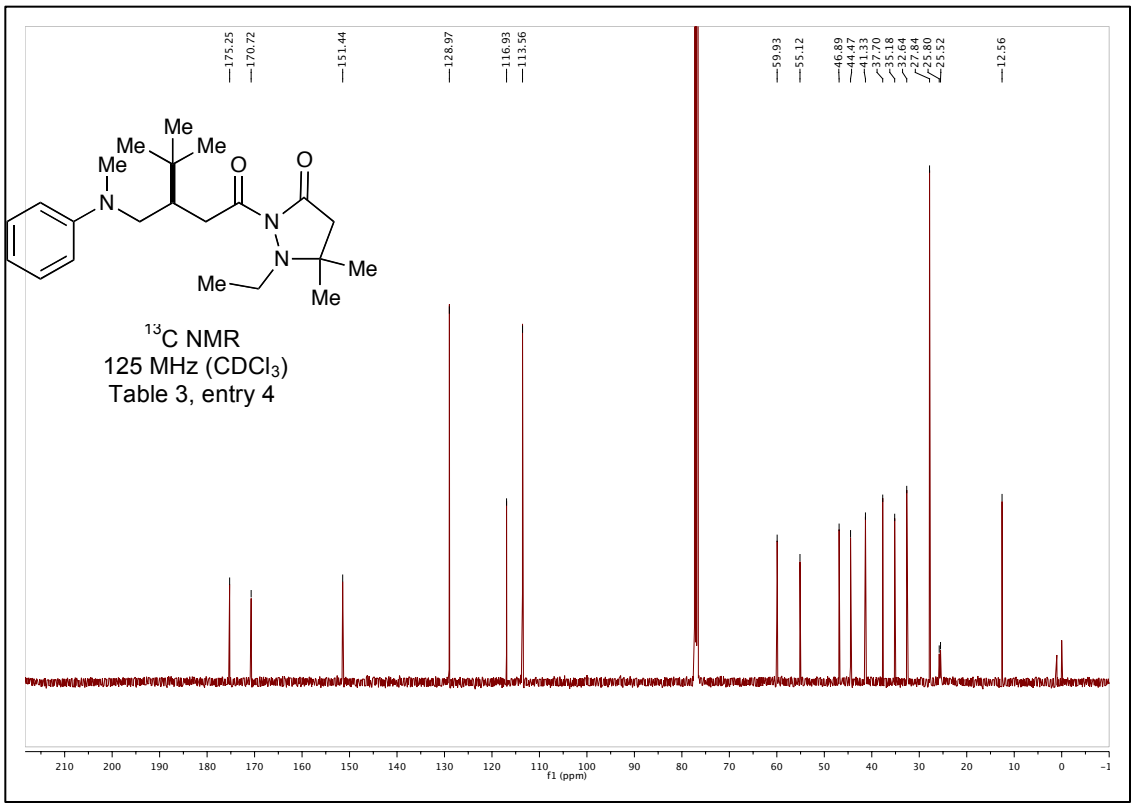

Me
Me
Me
N
O
O
N
N
Me
Me
Me
Me
^{13}C NMR
125 MHz ($CDCl_3$)
Table 3, entry 2
f1 (ppm)


OBn
Me
N
O
O
N
N
Me
Me
Me
^{1}H NMR
500 MHz ($CDCl_3$)
Table 3, entry 3
f1 (ppm)

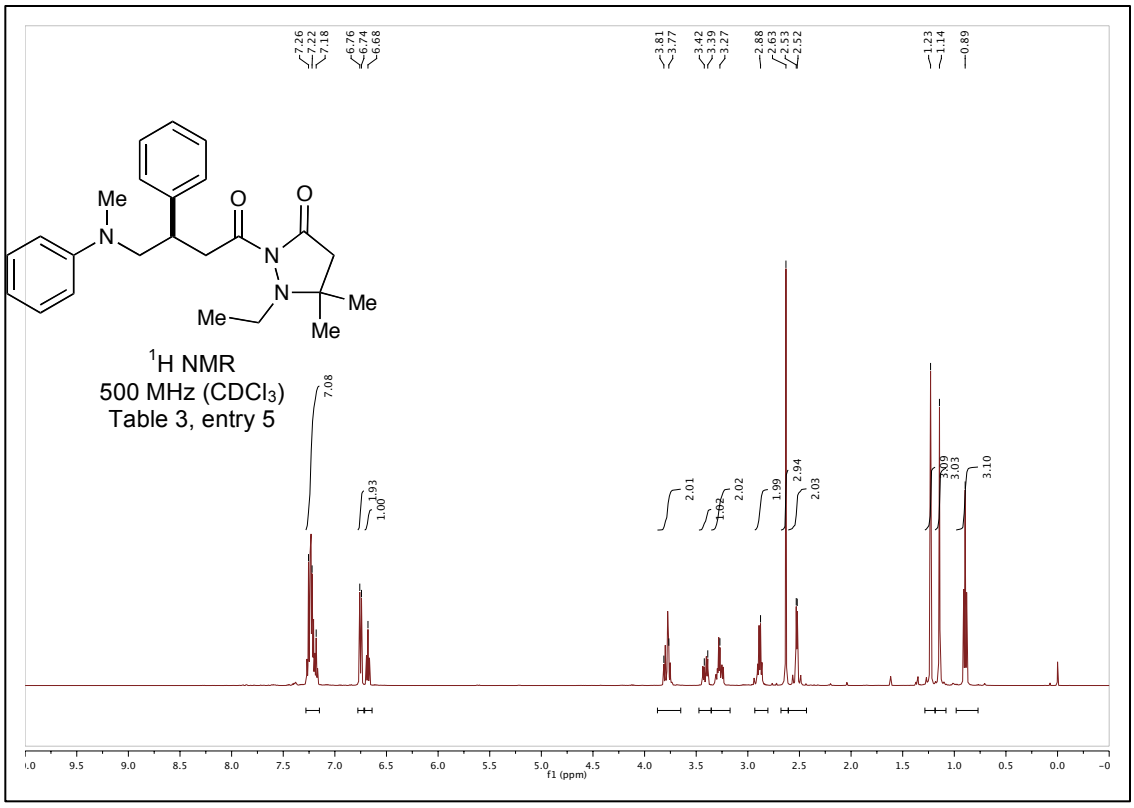

OBn
Me
N
O
O
N
N
Me
Me
Me
^{13}C NMR
125 MHz ($CDCl_3$)
Table 3, entry 3
f1 (ppm)

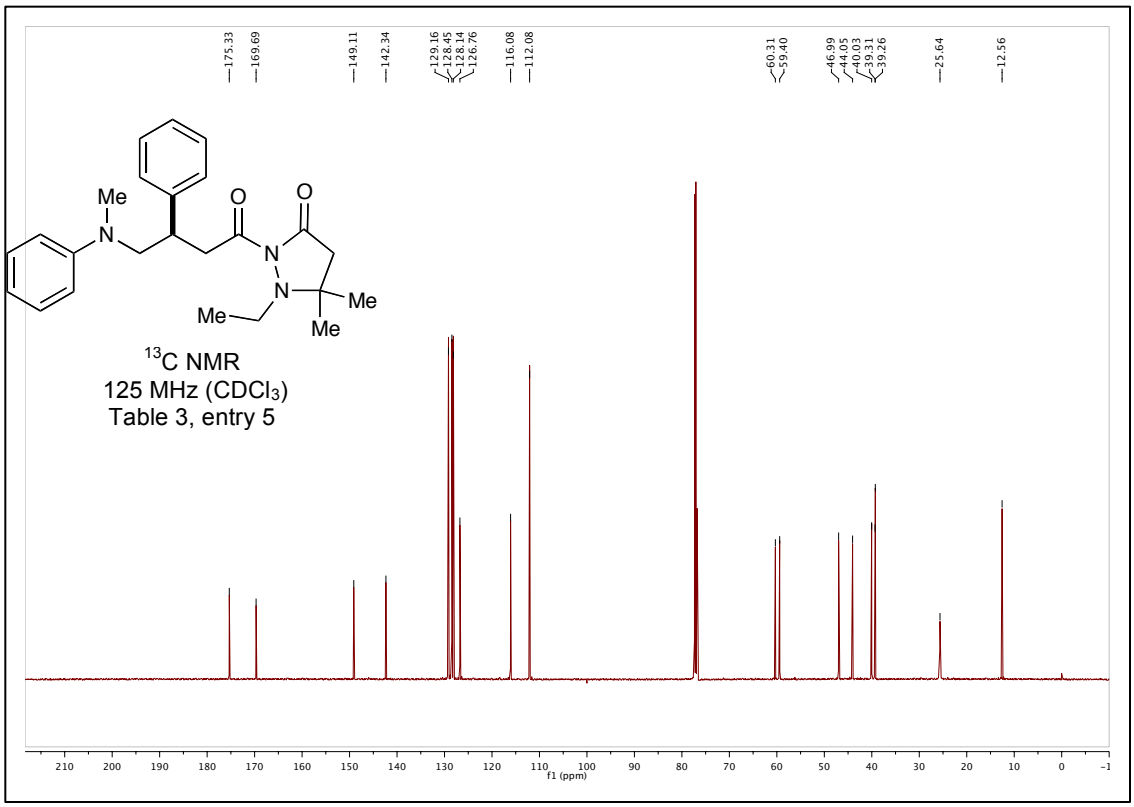


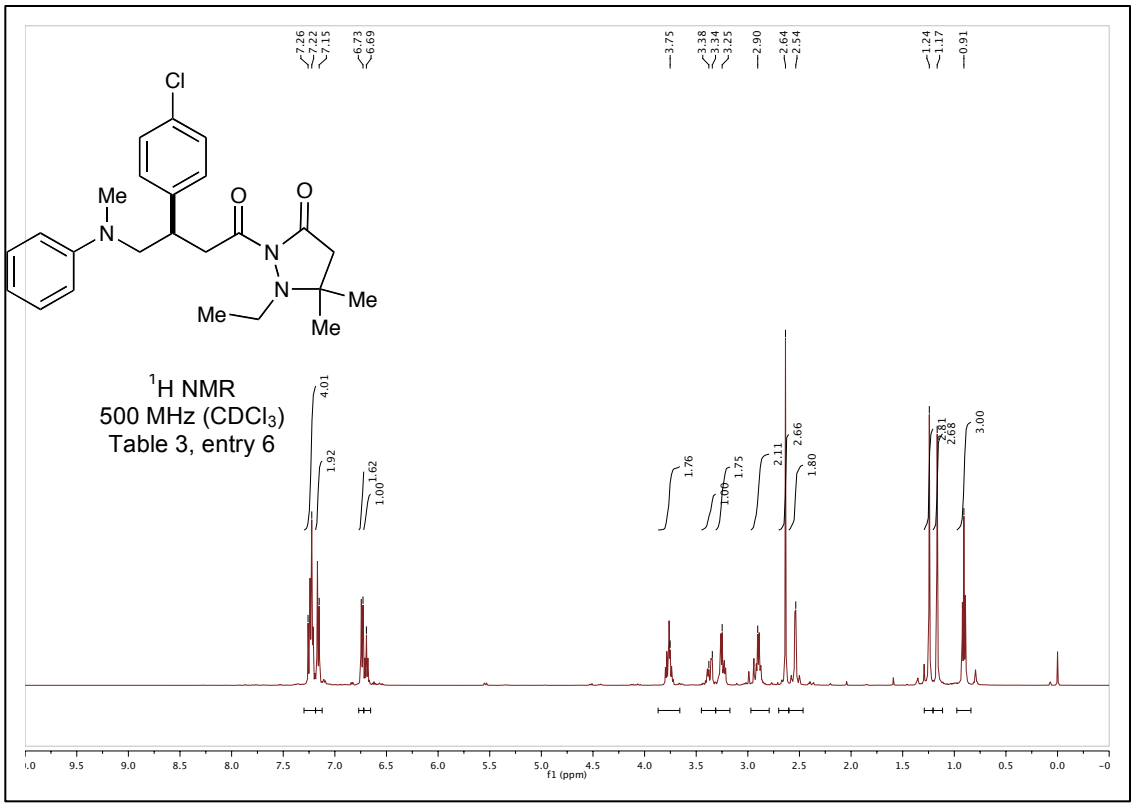
^{1}H NMR
500 MHz ($CDCl_3$)
Table 3, entry 4

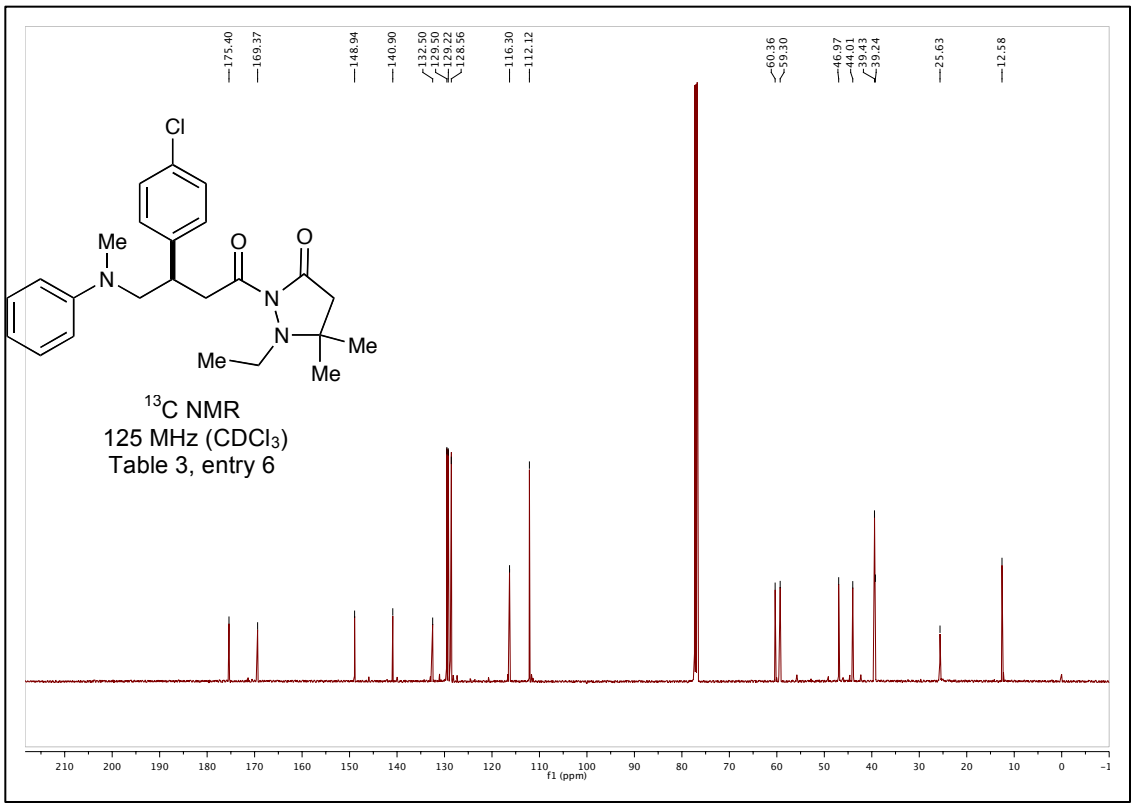


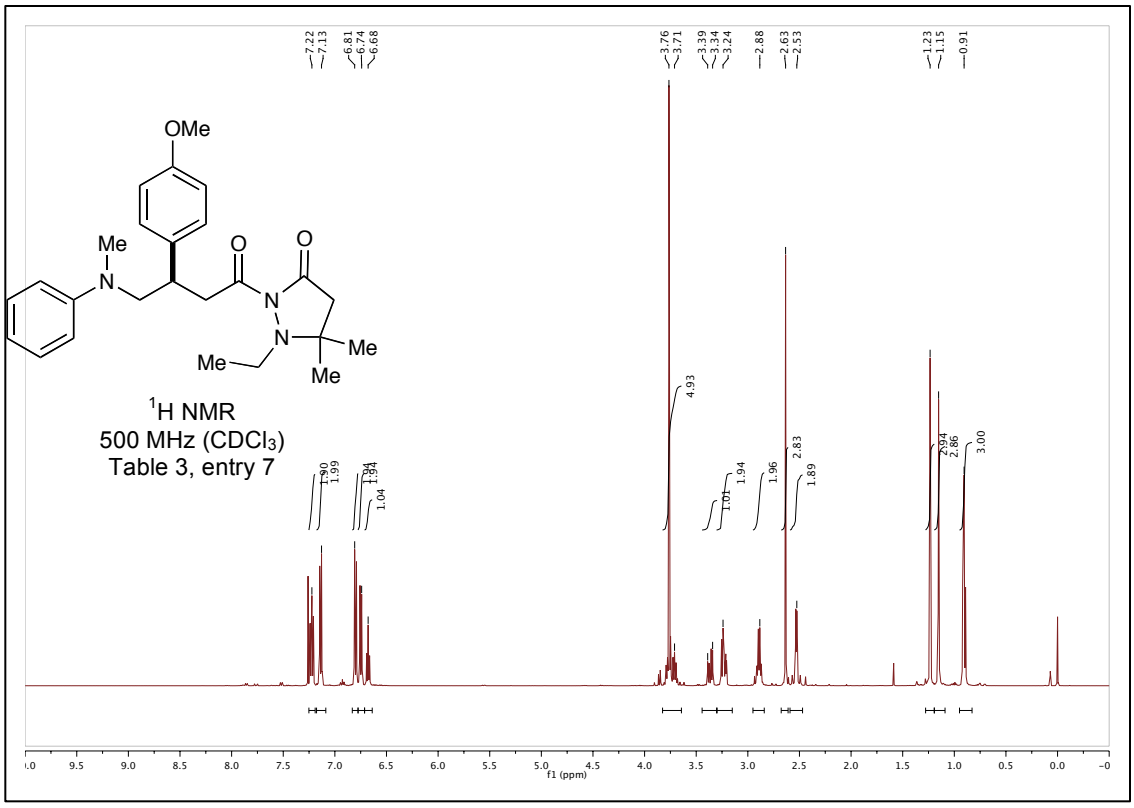
^{13}C NMR
125 MHz ($CDCl_3$)
Table 3, entry 4

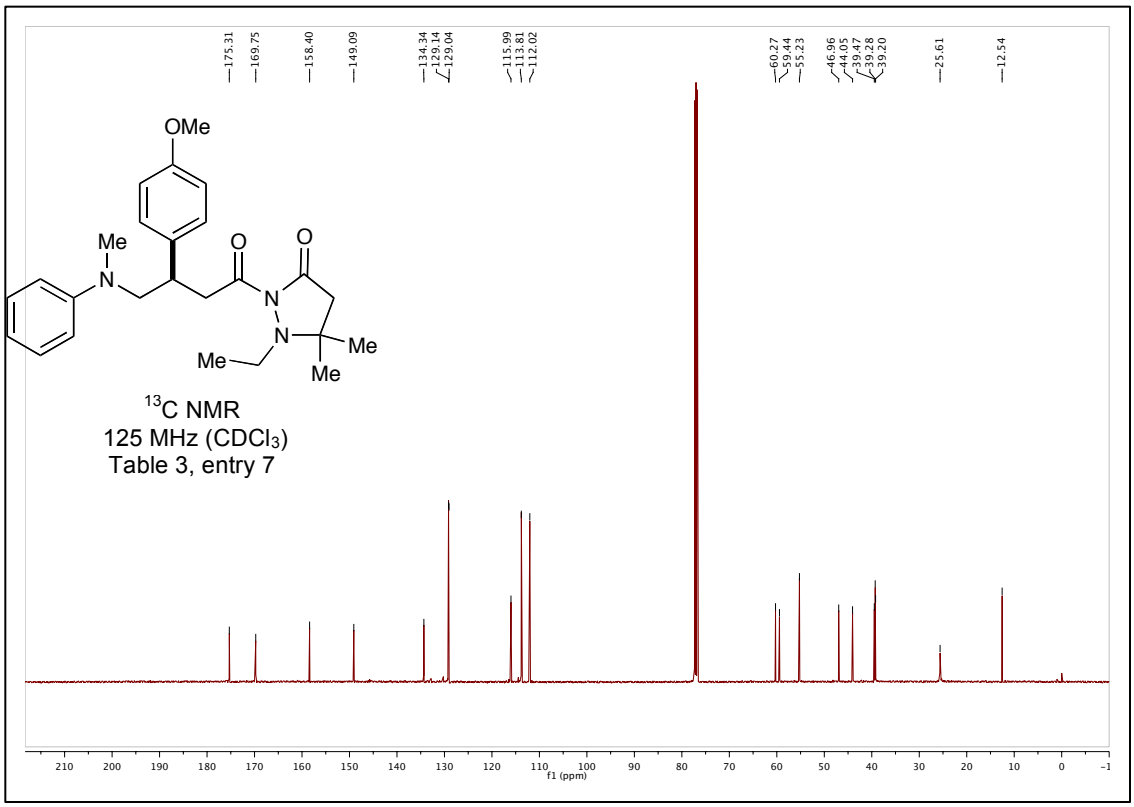

Me
N
O
O
N
N
Me
Me
Me
^{1}H NMR
500 MHz ($CDCl_3$)
Table 3, entry 5
7.26
7.22
7.18
6.76
6.74
6.68
3.81
3.77
3.42
3.39
3.27
2.88
2.63
2.53
2.52
1.23
1.14
0.89
7.08
1.93
1.00
2.01
2.02
1.99
2.94
2.03
3.09
3.03
3.10
f1 (ppm)

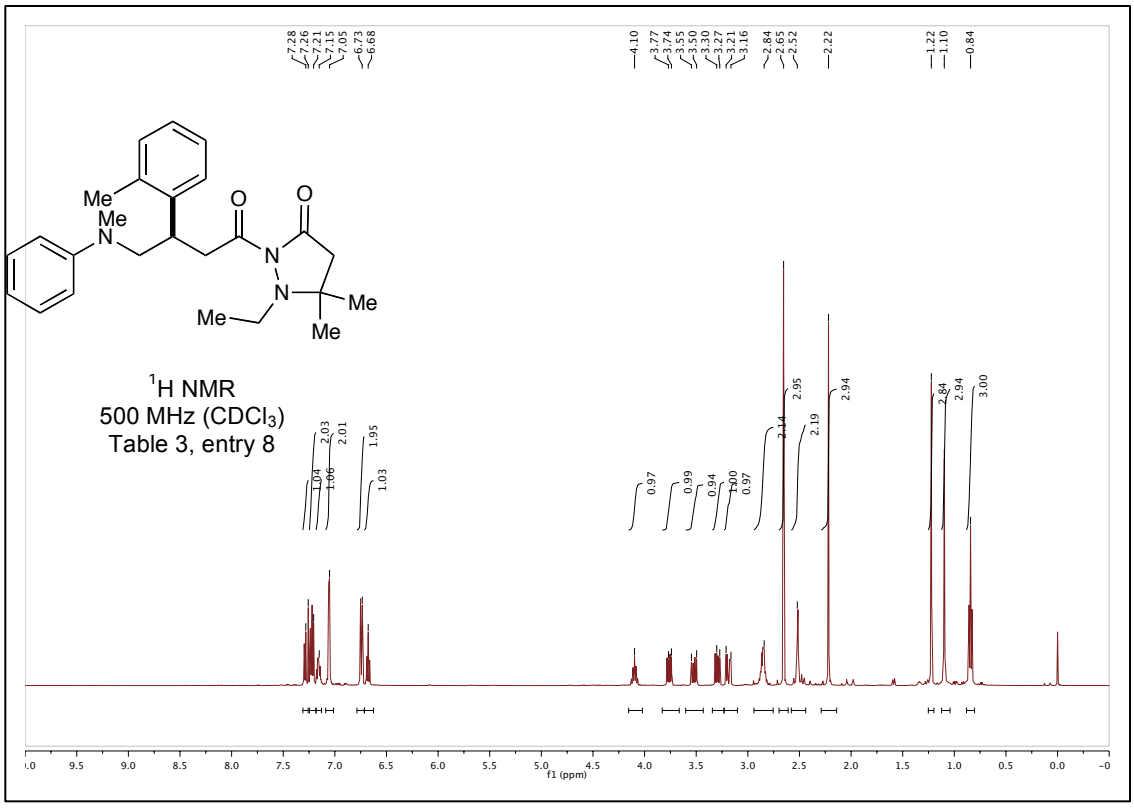

Me
N
O
O
N
N
Me
Me
Me
^{13}C NMR
125 MHz ($CDCl_3$)
Table 3, entry 5
175.33
169.69
149.11
142.34
129.16
128.45
128.14
126.76
116.08
112.08
60.31
59.40
46.99
44.05
40.03
39.31
39.26
25.64
12.56
f1 (ppm)

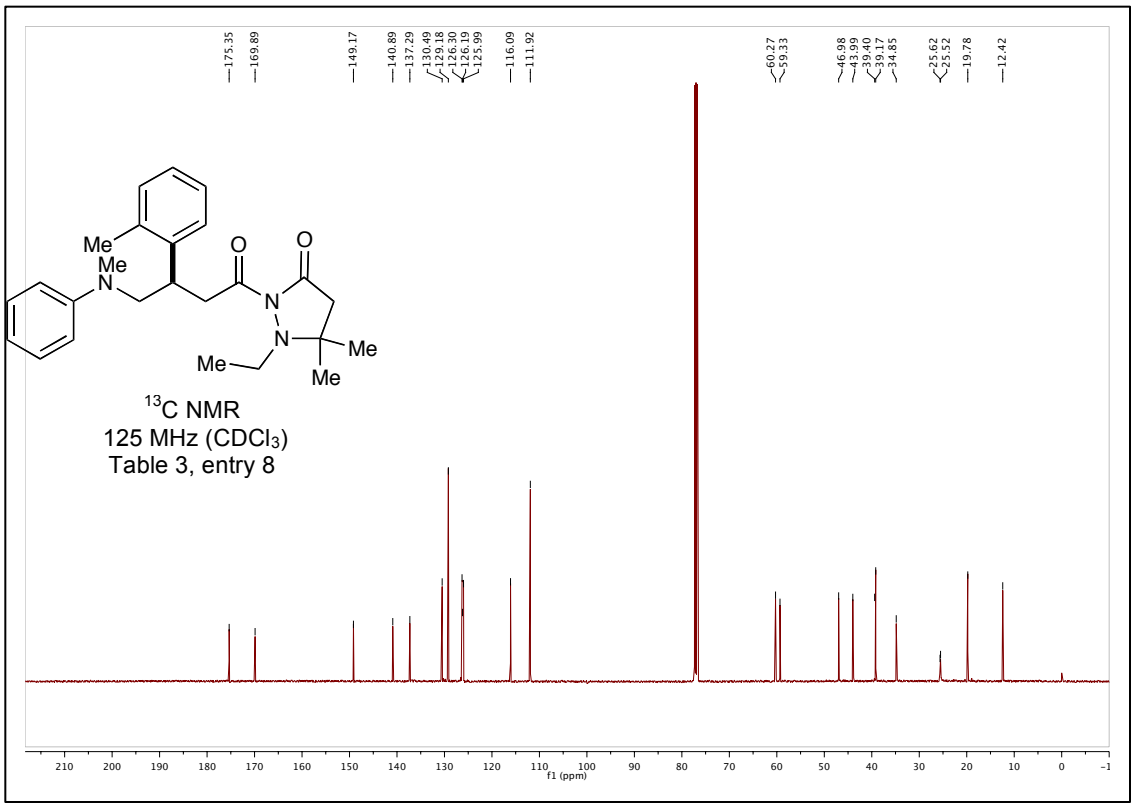

Cl
Me
N
O
O
N
N
Me
Me
Me
^{1}H NMR
500 MHz ($CDCl_3$)
Table 3, entry 6
7.26
7.22
7.15
6.73
6.69
3.75
3.38
3.34
3.25
2.90
2.64
2.54
1.24
1.17
0.91
4.01
1.92
1.62
1.00
1.76
1.00
1.75
2.11
2.66
1.80
2.81
2.68
3.00
f1 (ppm)

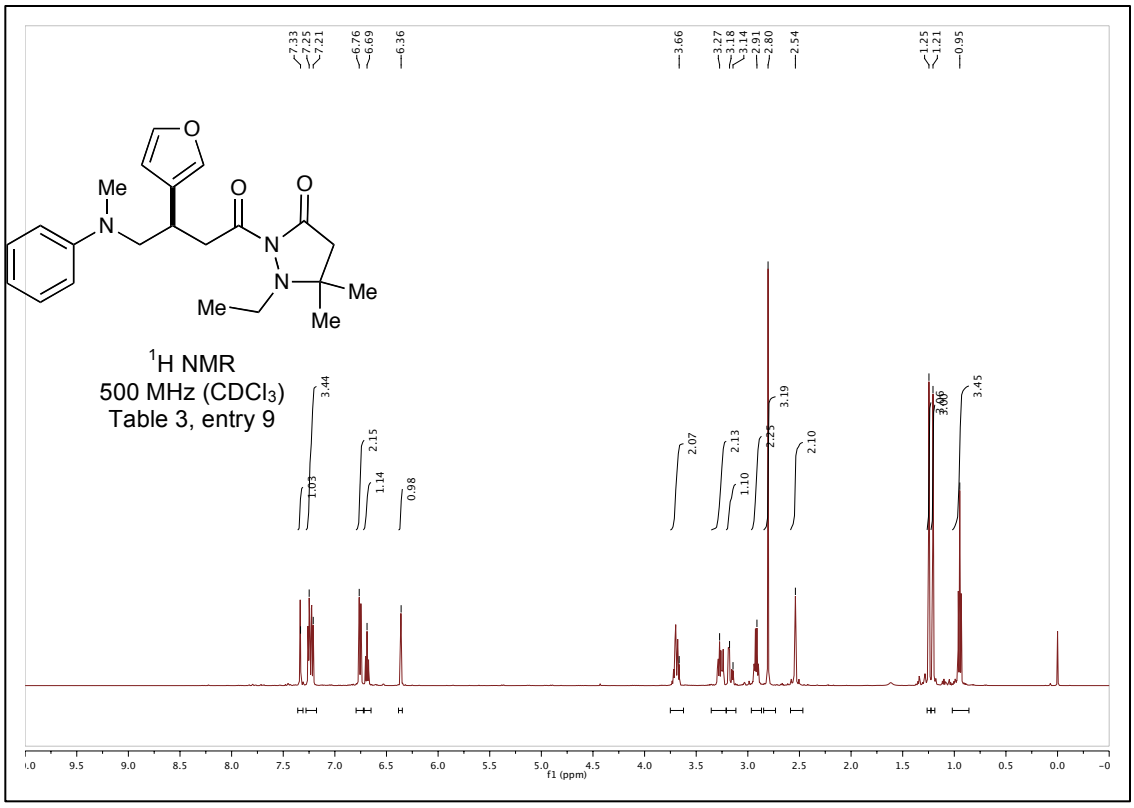

Cl
Me
N
O
O
N
N
Me
Me
Me
^{13}C NMR
125 MHz ($CDCl_3$)
Table 3, entry 6
175.40
169.37
148.94
140.90
132.50
129.50
129.22
128.56
116.30
112.12
60.36
59.30
46.97
44.01
39.43
39.24
25.63
12.58
f1 (ppm)

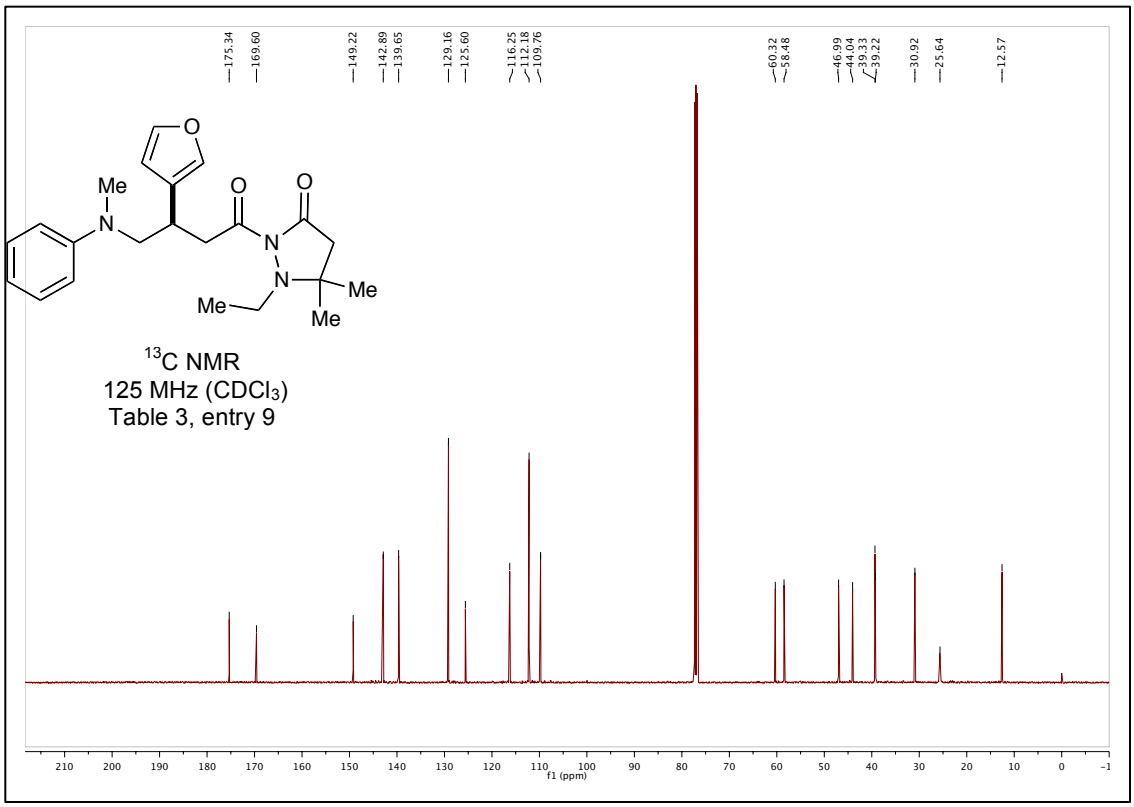

OMe
Me
N
O
O
N
N
Me
Me
Me
^{1}H NMR
500 MHz ($CDCl_3$)
Table 3, entry 7
7.22
7.13
6.81
6.74
6.68
3.76
3.71
3.39
3.34
3.24
2.88
2.63
2.53
1.23
1.15
0.91
4.93
1.94
1.96
2.83
1.89
2.94
2.86
3.00
1.90
1.99
1.94
1.04
f1 (ppm)

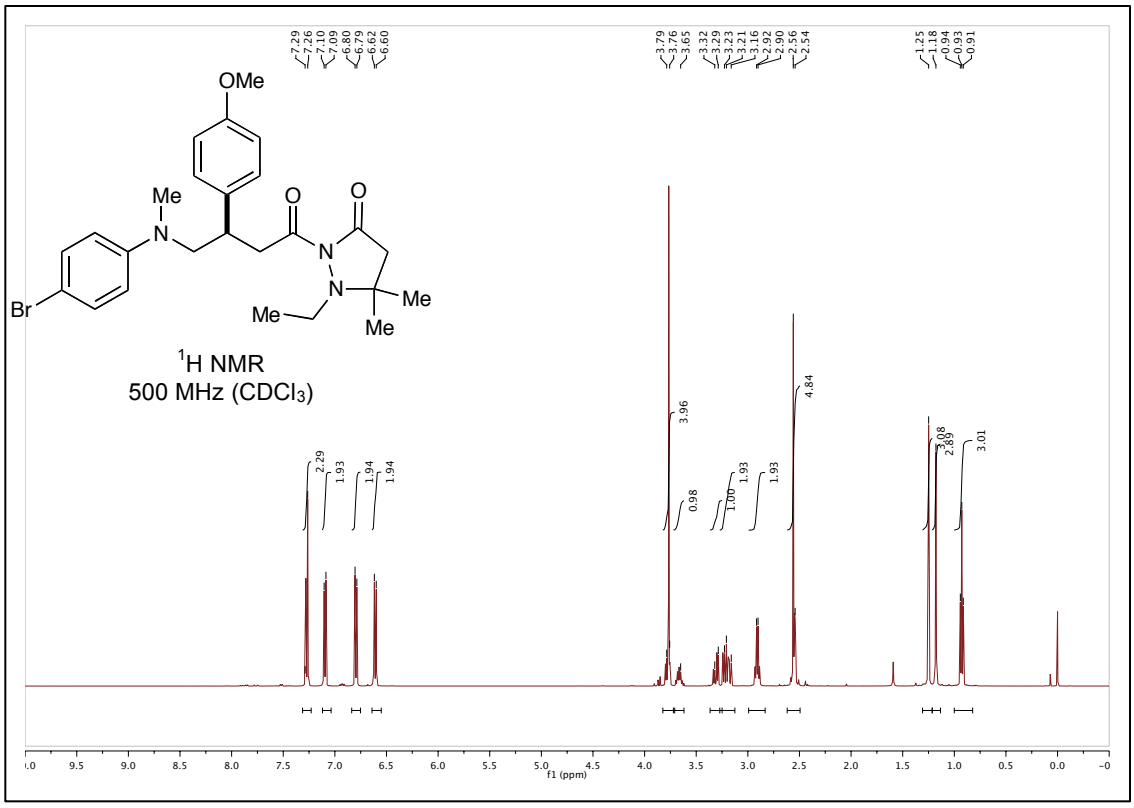

OMe
Me
N
O
O
N
N
Me
Me
Me
^{13}C NMR
125 MHz ($CDCl_3$)
Table 3, entry 7
175.31
169.75
158.40
149.09
134.34
129.14
129.04
115.99
113.81
112.02
60.27
59.44
55.23
46.96
44.05
39.47
39.28
39.20
25.61
12.54
f1 (ppm)

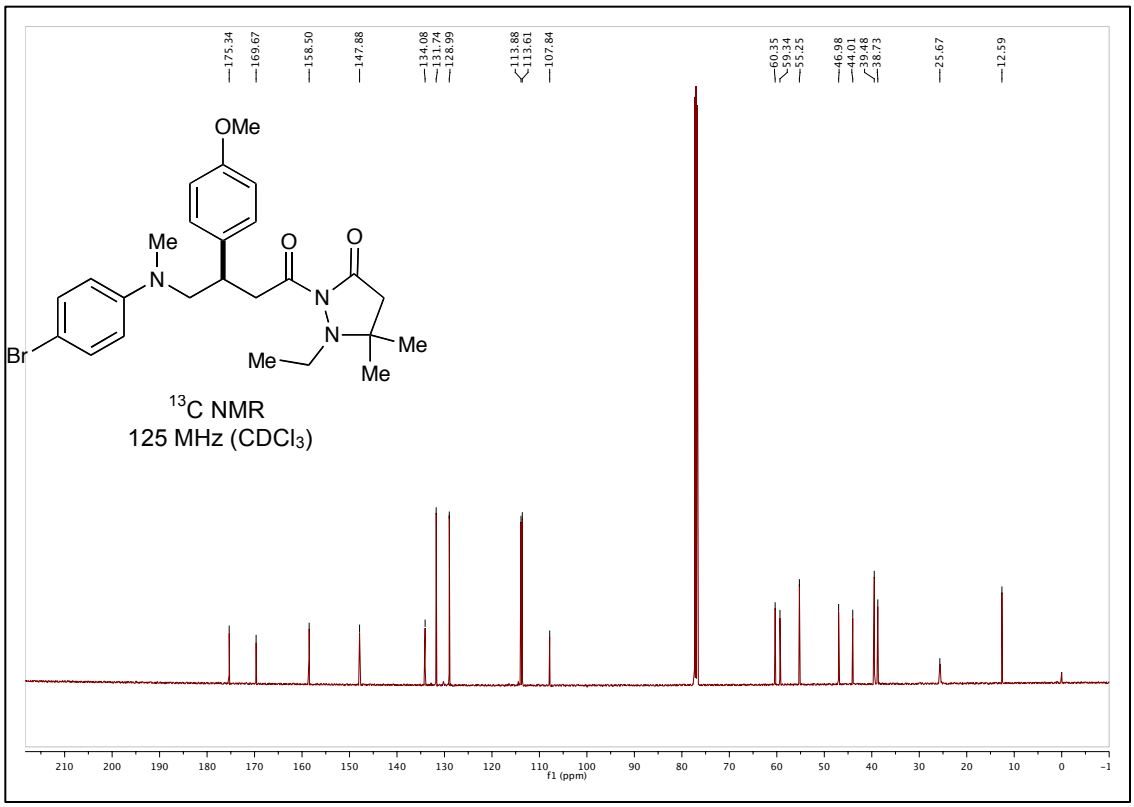

Me
Me
N
O
O
N
N
Me
Me
Me
Me
^{1}H NMR
500 MHz ($CDCl_3$)
Table 3, entry 8
f1 (ppm)

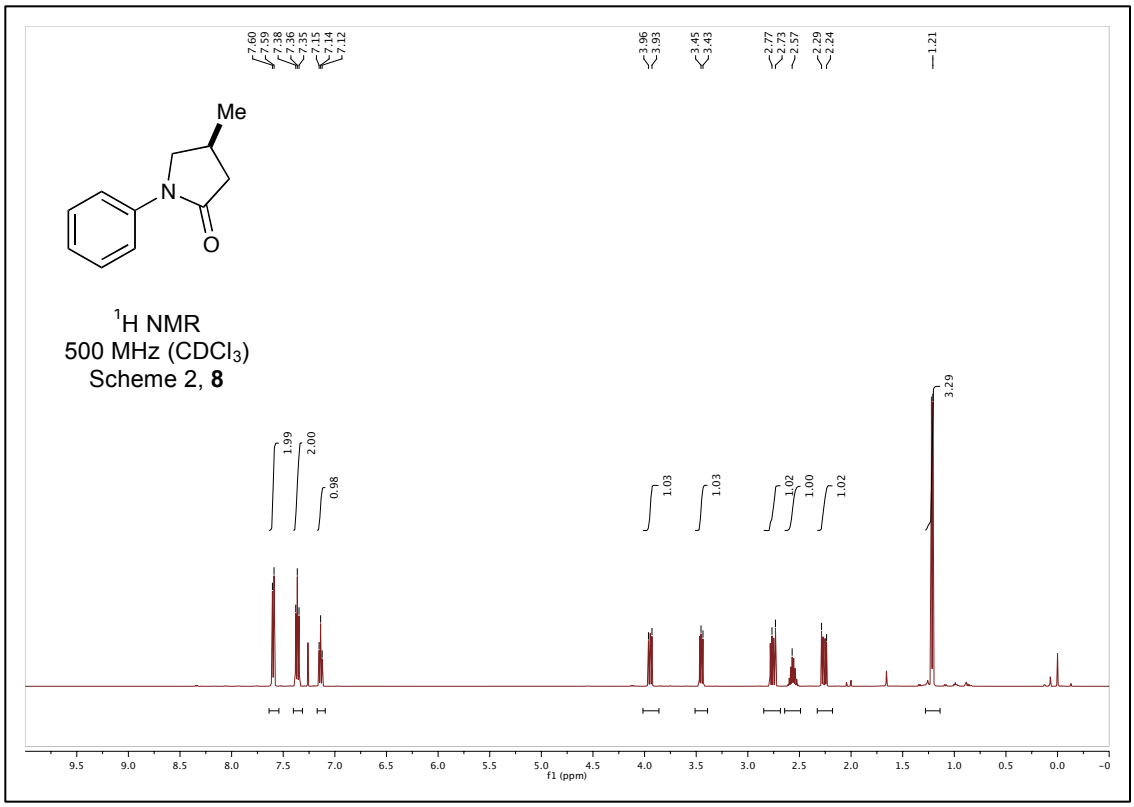

Me
Me
N
O
O
N
N
Me
Me
Me
Me
^{13}C NMR
125 MHz ($CDCl_3$)
Table 3, entry 8
f1 (ppm)

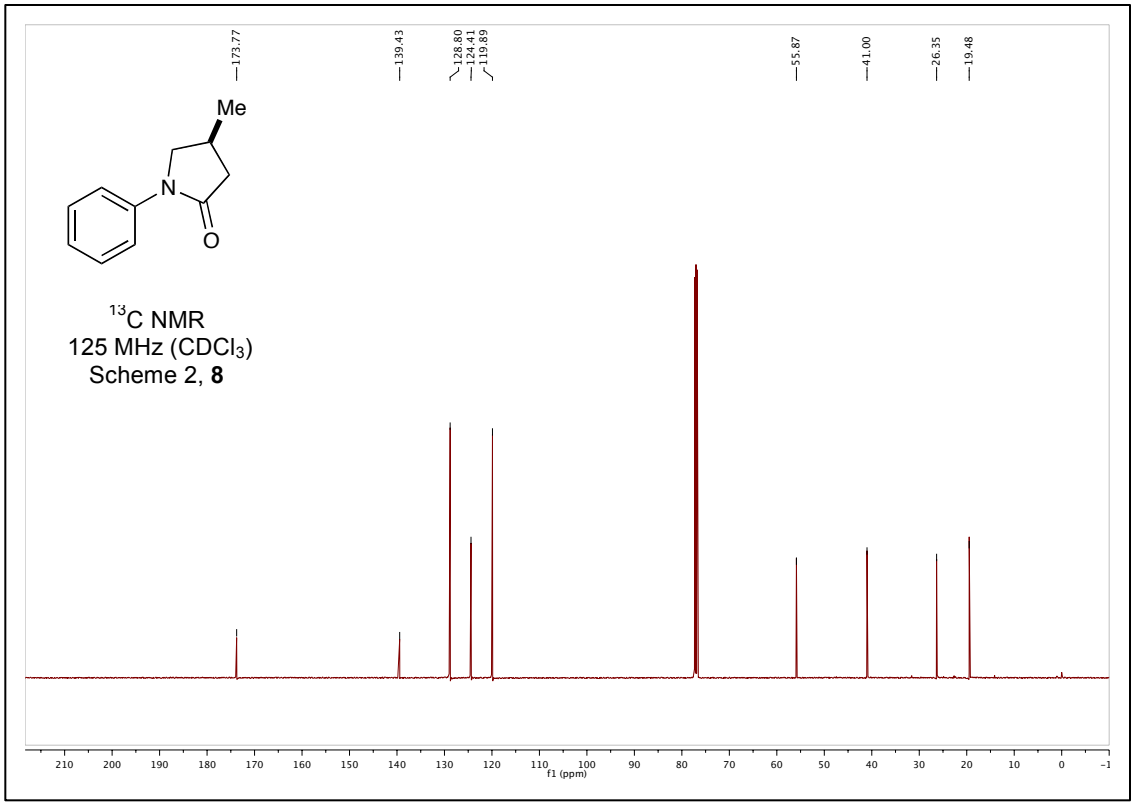

Me
N
O
O
N
N
Me
Me
Me
^{1}H NMR
500 MHz ($CDCl_3$)
Table 3, entry 9
f1 (ppm)

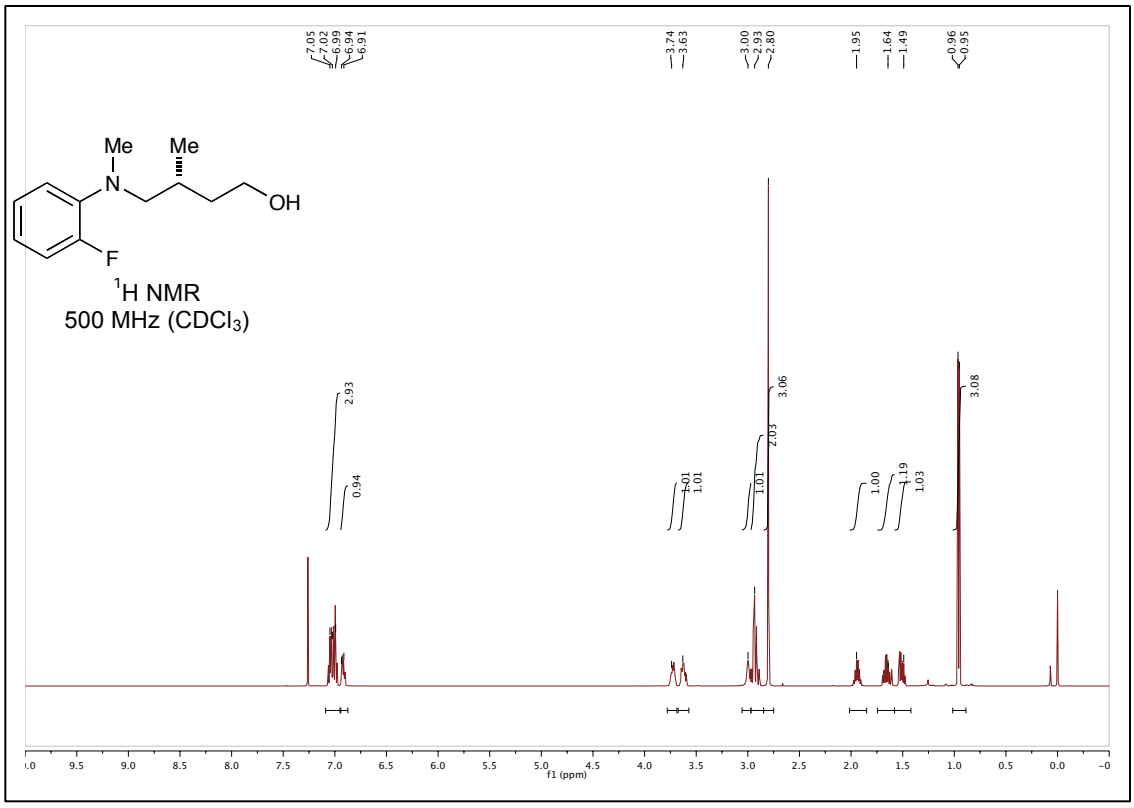

Me
N
O
O
N
N
Me
Me
Me
^{13}C NMR
125 MHz ($CDCl_3$)
Table 3, entry 9
f1 (ppm)

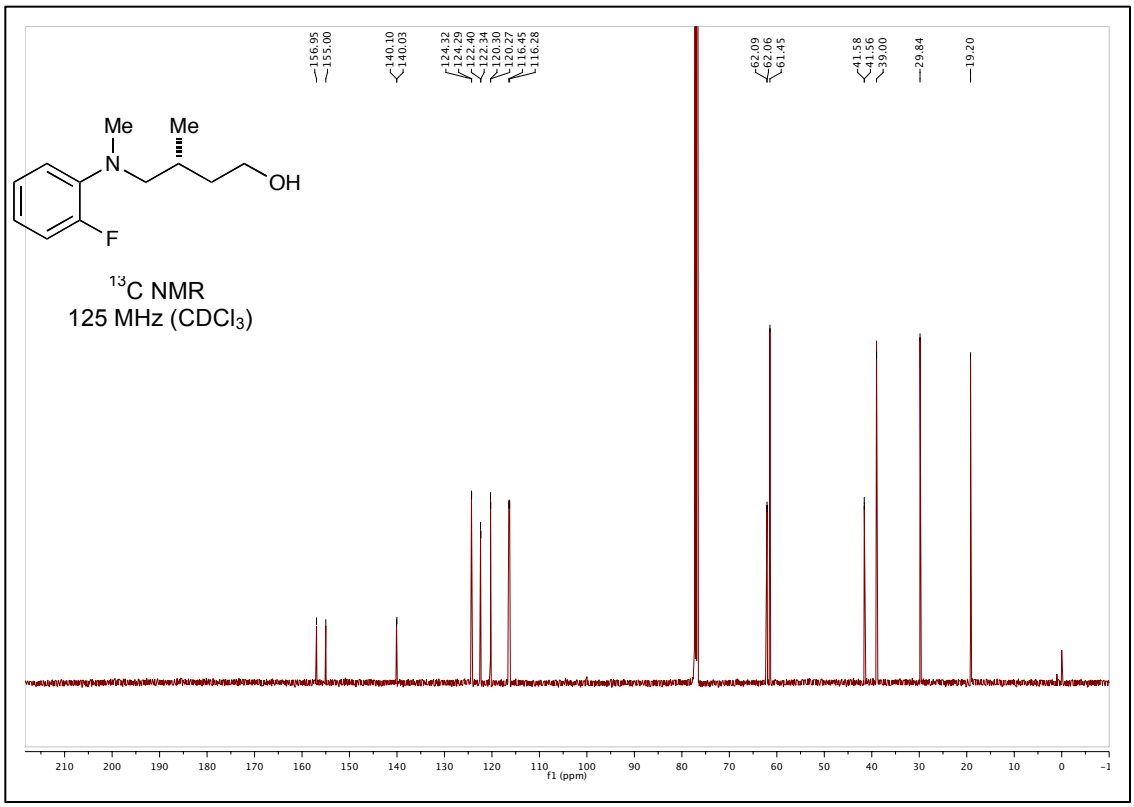

OMe
Me
N
O
O
N
N
Br
Me
Me
Me
^{1}H NMR
500 MHz ($CDCl_3$)
f1 (ppm)

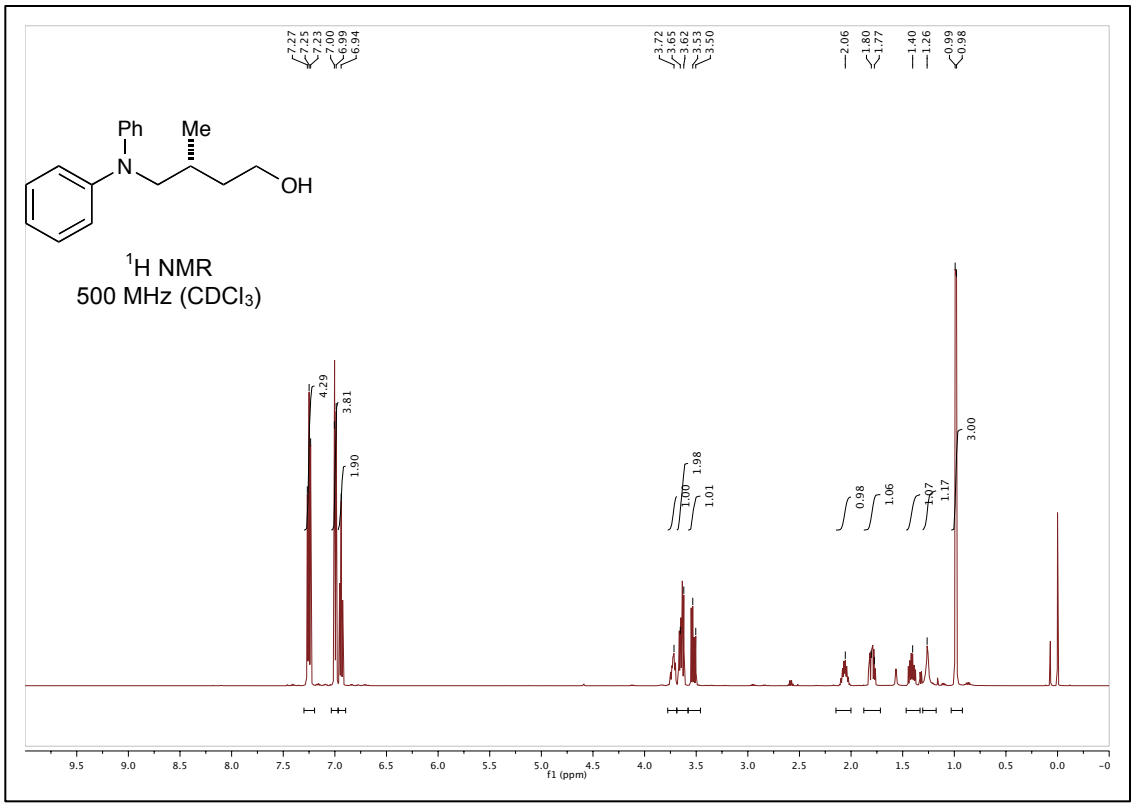

OMe
Me
N
O
O
N
N
Br
Me
Me
Me
^{13}C NMR
125 MHz ($CDCl_3$)
f1 (ppm)

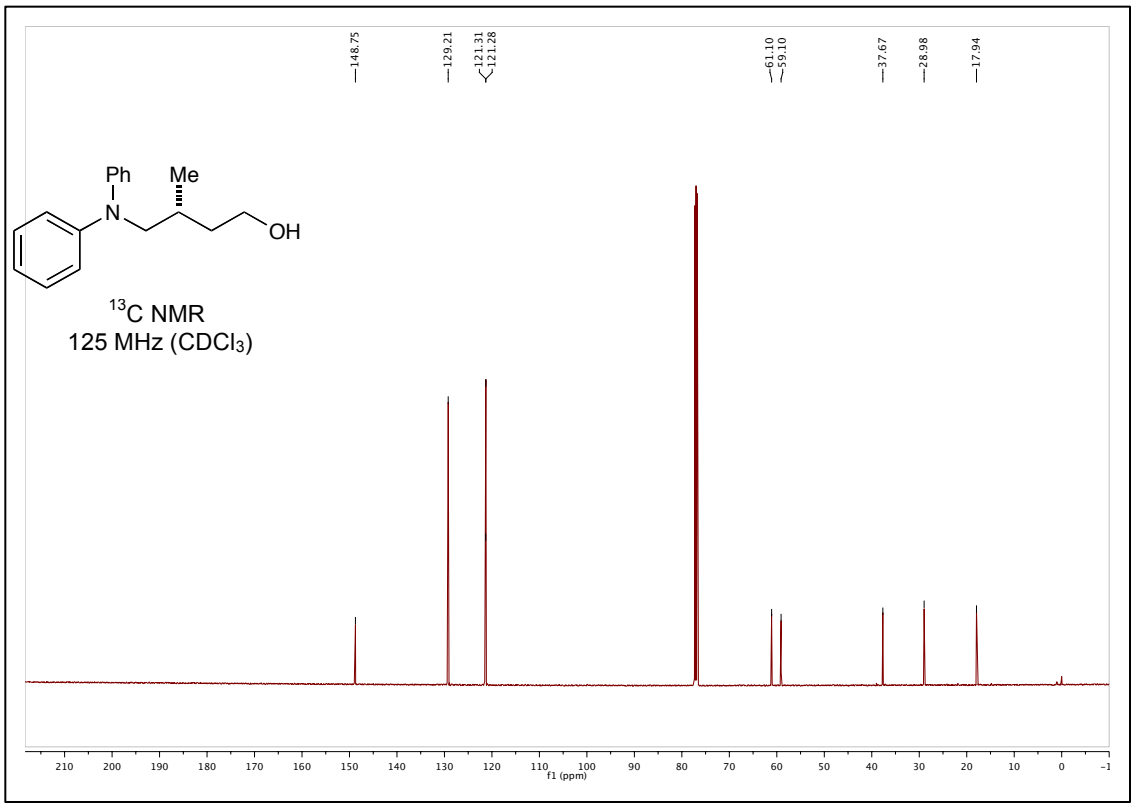

Me
N
O
1H NMR
500 MHz (CDCl3)
Scheme 2, 8
f1 (ppm)

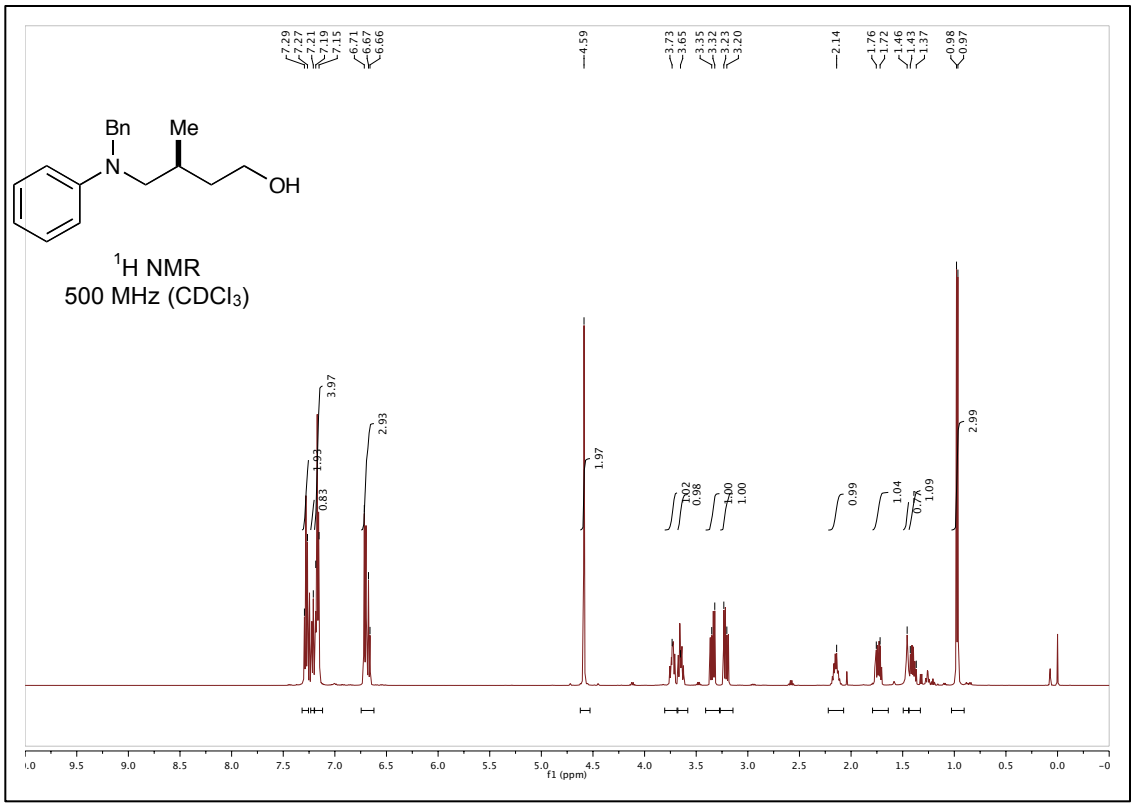

Me
N
O
13C NMR
125 MHz (CDCl3)
Scheme 2, 8
f1 (ppm)

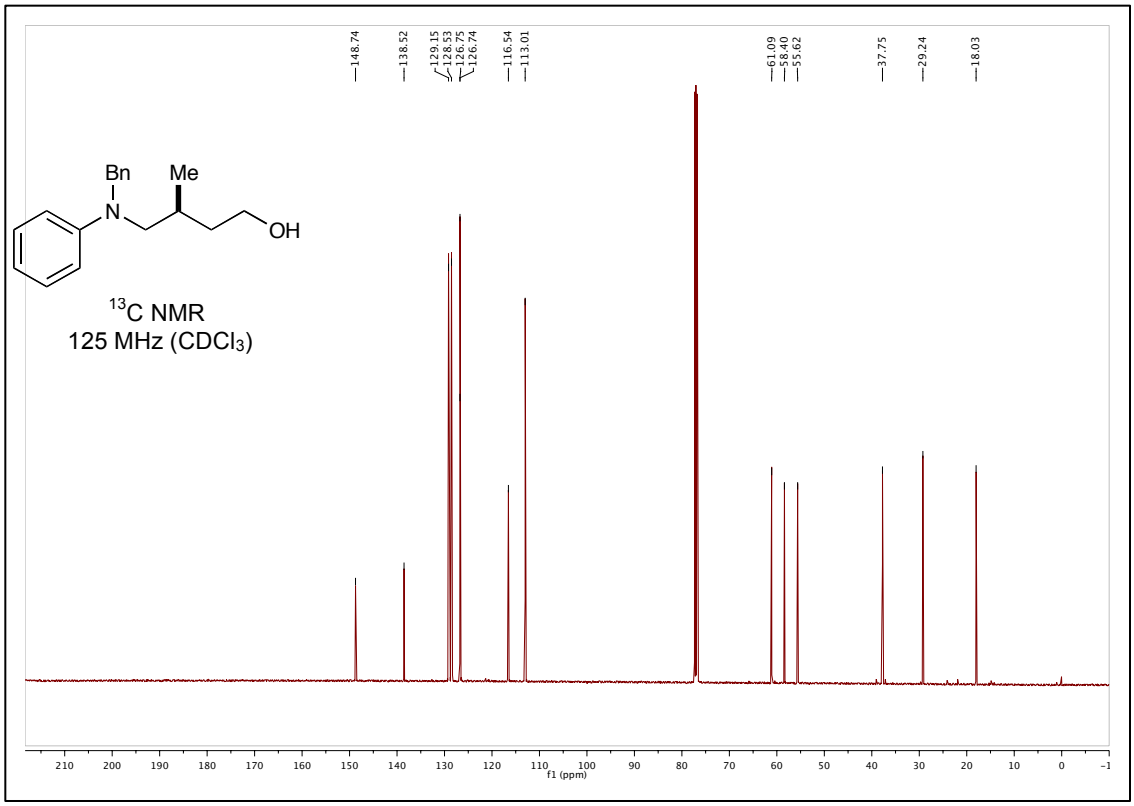

Me
Me
N
OH
F
^{1}H NMR
500 MHz ($CDCl_3$)
f1 (ppm)

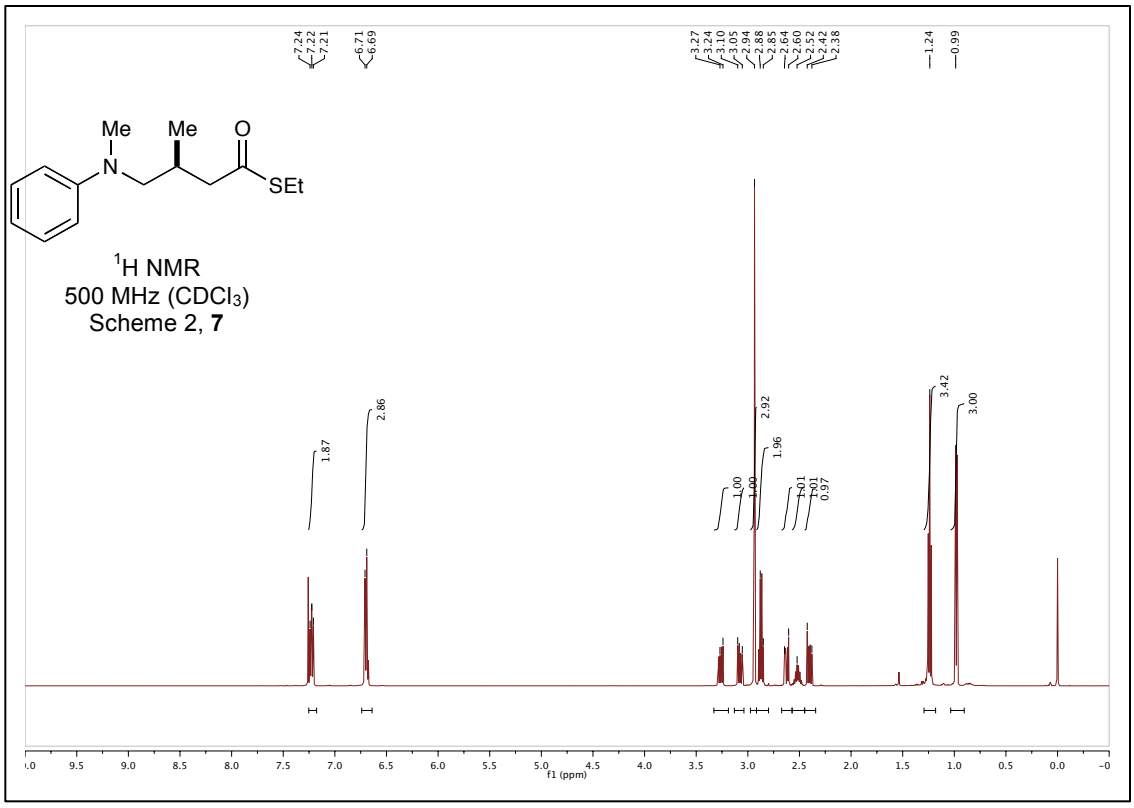

Me
Me
N
OH
F
^{13}C NMR
125 MHz ($CDCl_3$)
f1 (ppm)

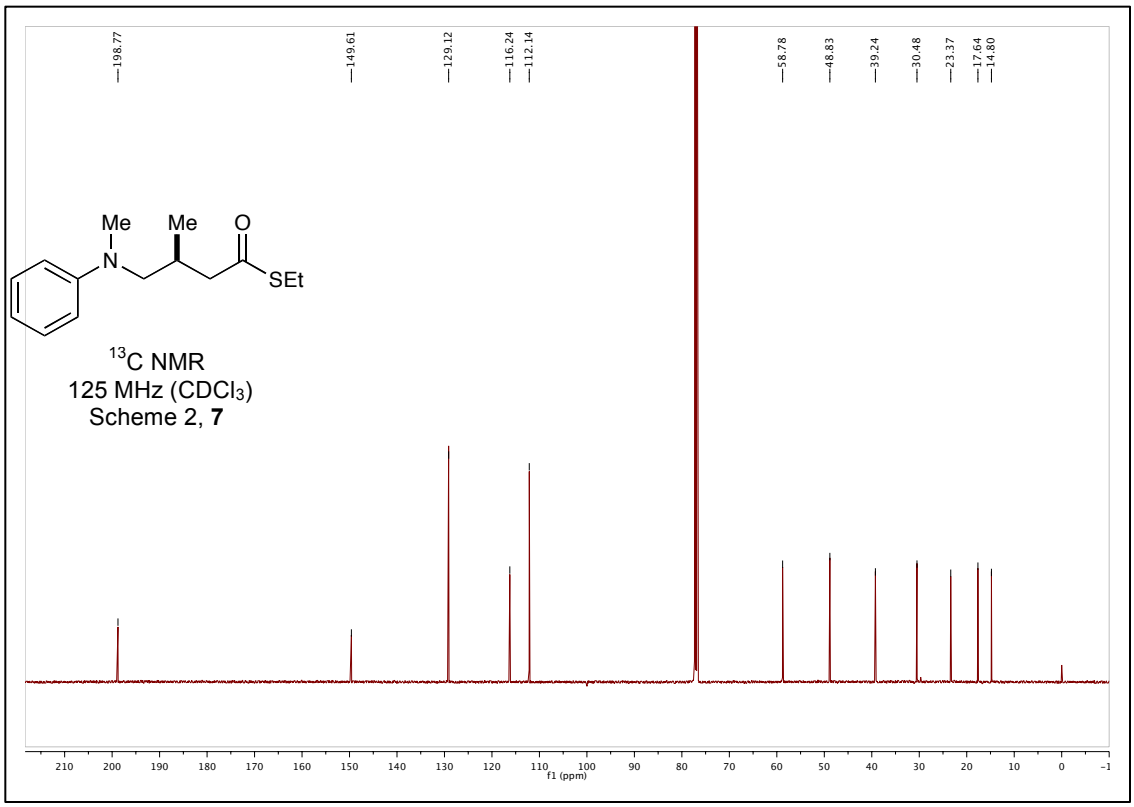

Ph
Me
N
OH
^{1}H NMR
500 MHz ($CDCl_3$)
7.27
7.25
7.23
7.00
6.99
6.94
3.72
3.65
3.62
3.53
3.50
2.06
1.80
1.77
1.40
1.26
0.99
0.98
4.29
3.81
1.90
1.98
1.00
1.01
0.98
1.06
1.07
1.17
3.00
f1 (ppm)

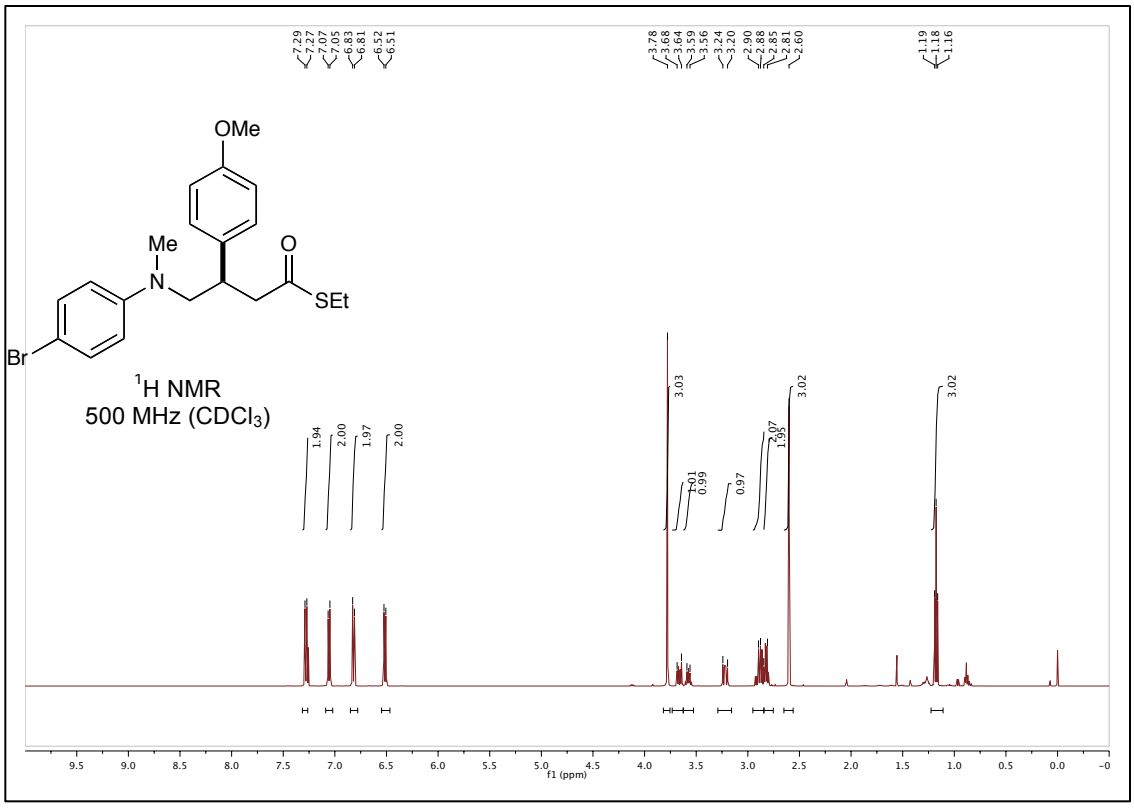

Ph
Me
N
OH
^{13}C NMR
125 MHz ($CDCl_3$)
148.75
129.21
121.31
121.28
61.10
59.10
37.67
28.98
17.94
f1 (ppm)

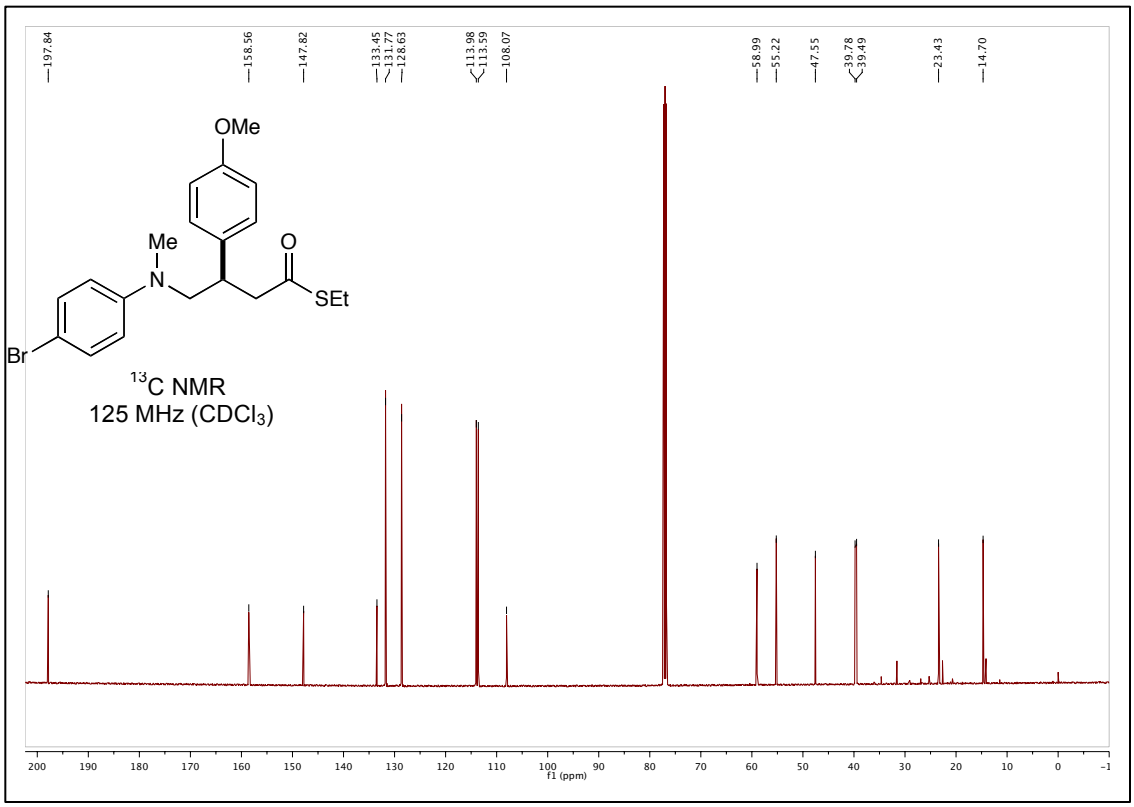

Bn
Me
N
OH
^{1}H NMR
500 MHz ($CDCl_3$)
f1 (ppm)

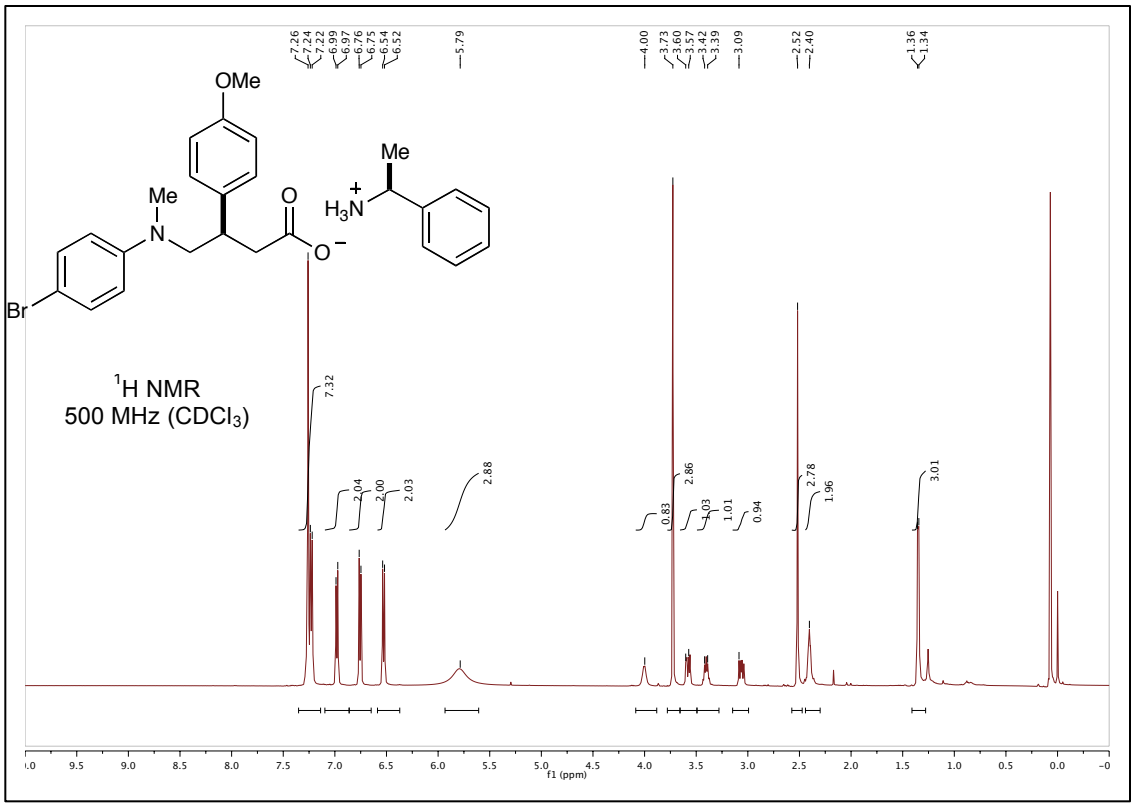

Bn
Me
N
OH
^{13}C NMR
125 MHz ($CDCl_3$)
f1 (ppm)

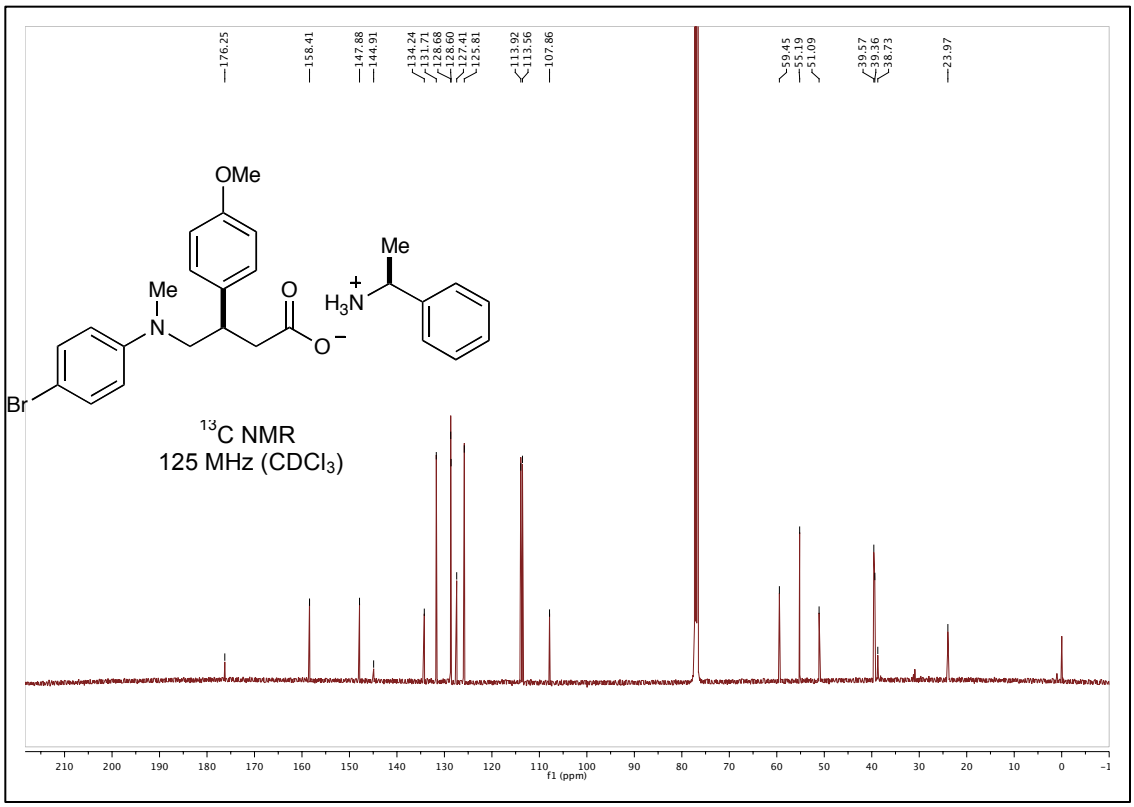

Me
Me
O
N
SEt
^{1}H NMR
500 MHz ($CDCl_3$)
Scheme 2, **7**
f1 (ppm)

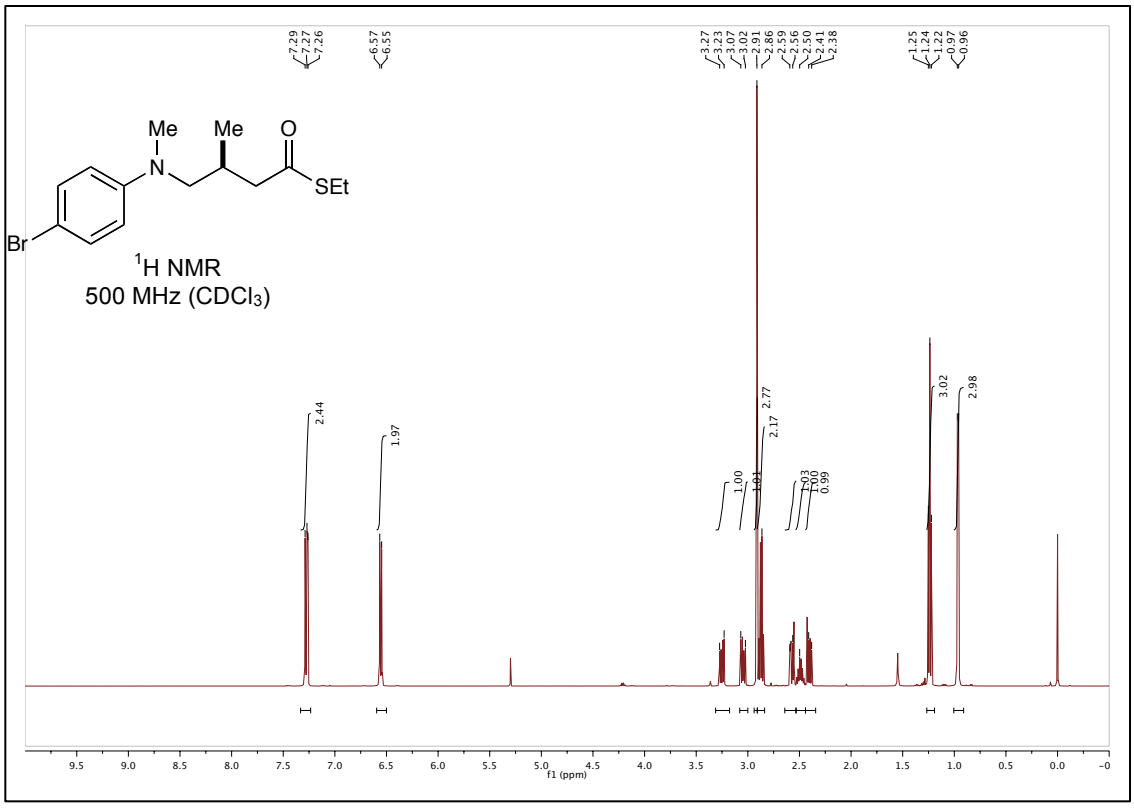

Me
Me
O
N
SEt
^{13}C NMR
125 MHz ($CDCl_3$)
Scheme 2, **7**
f1 (ppm)

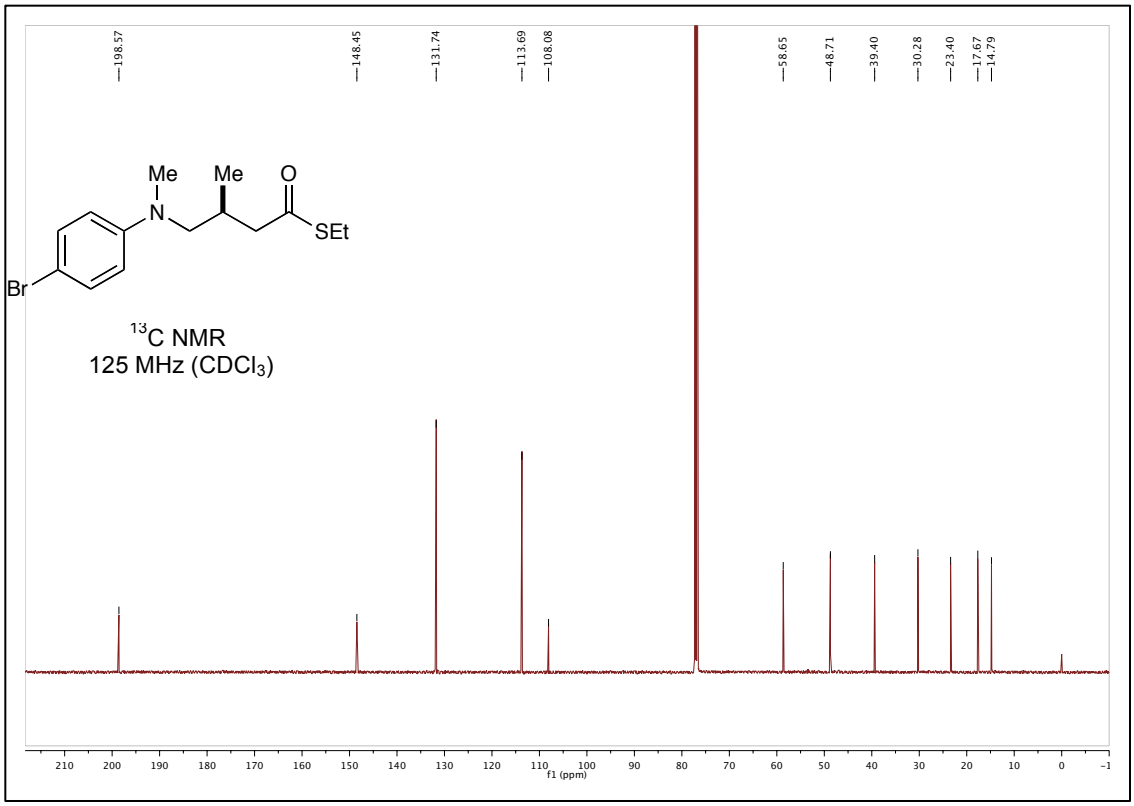

OMe
Me
N
O
SEt
Br
^{1}H NMR
500 MHz ($CDCl_3$)
f1 (ppm)

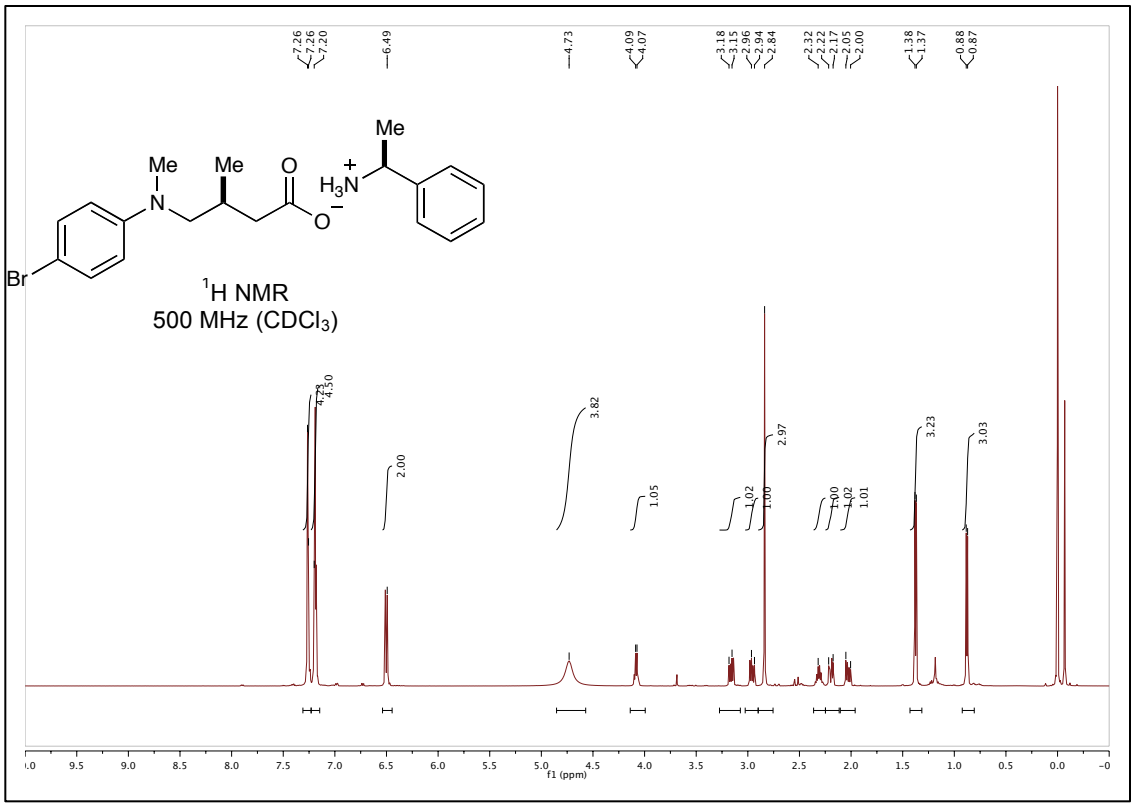

OMe
Me
N
O
SEt
Br
^{13}C NMR
125 MHz ($CDCl_3$)
f1 (ppm)

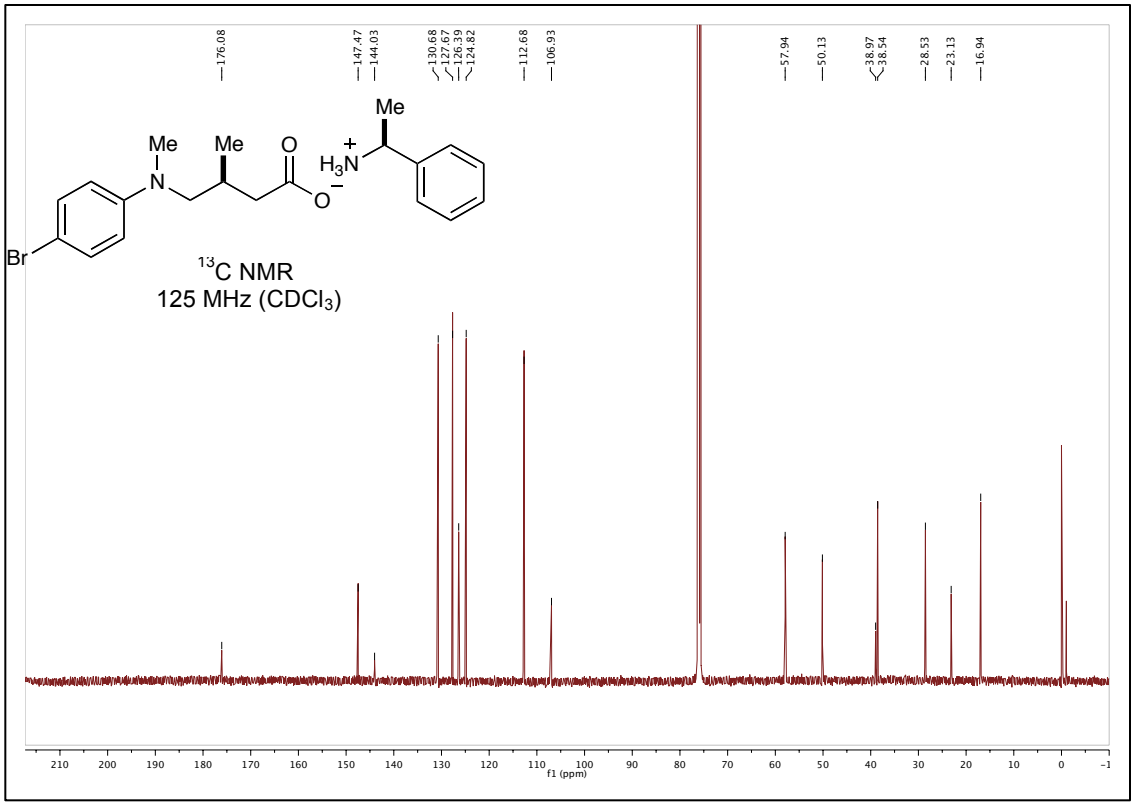

OMe
Me
N
O
O⁻
H₃N⁺
Me
Br
¹H NMR
500 MHz (CDCl₃)
f1 (ppm)


OMe
Me
N
O
O⁻
H₃N⁺
Me
Br
¹³C NMR
125 MHz (CDCl₃)
f1 (ppm)

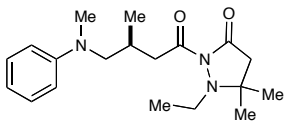

Me
Me
O
N
SEt
Br
^{1}H NMR
500 MHz ($CDCl_3$)
f1 (ppm)


Me
Me
O
N
SEt
Br
^{13}C NMR
125 MHz ($CDCl_3$)
f1 (ppm)


Me
Me
Me
O
H_3N^+
N
O^-
Br
^{1}H NMR
500 MHz ($CDCl_3$)
f1 (ppm)


Me
Me
Me
O
H_3N^+
N
O^-
Br
^{13}C NMR
125 MHz ($CDCl_3$)
f1 (ppm)

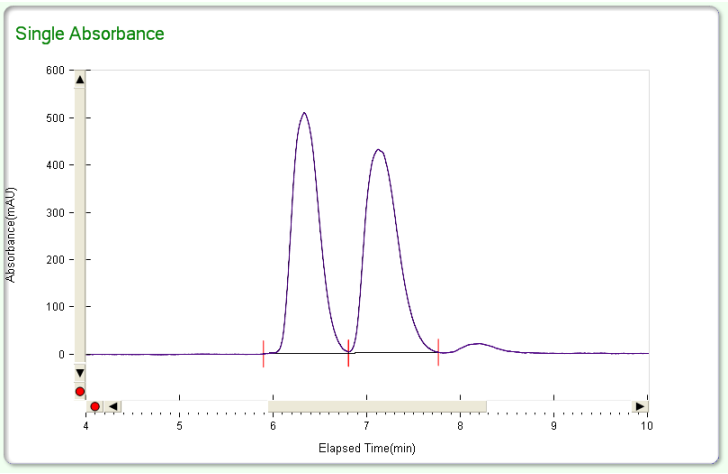
VIII. SFC Traces



(*S*)-1-ethyl-5,5-dimethyl-2-(3-methyl-4-(methyl(phenyl)amino)butanoyl)pyrazolidin-3-one
(Table 2, entry 1)

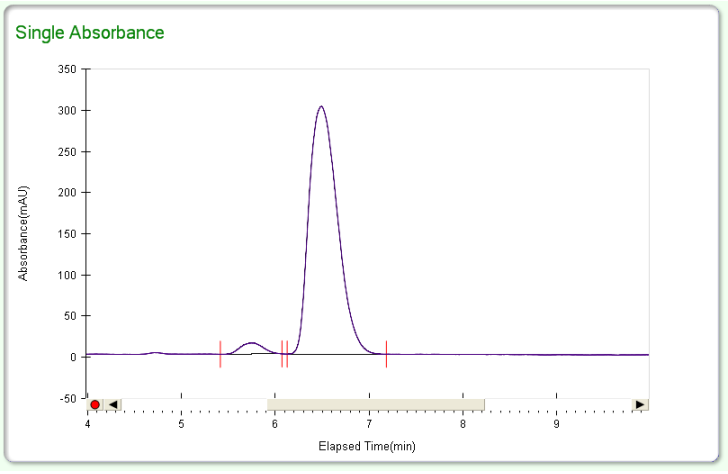
Racemic: SFC, Chiracel OD-H, 8% MeOH/CO_2, 3 mL/min, 249 nm

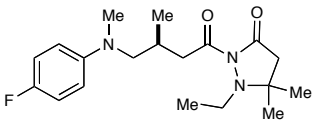
peak	% area	area	RT (min)	height (mV)
1	49.256	10143.0713	6.33	508.9341
2	50.744	10449.4973	7.12	430.4294
Total	100	20592.5686		



Scalemic: SFC, Chiracel OD-H, 8% MeOH/CO_2, 3 mL/min, 249 nm

peak	% area	area	RT (min)	height (mV)
1	3.4782	228.0808	5.75	13.4634
2	96.5218	6329.4161	6.49	301.138
Total	100	6557.4969		

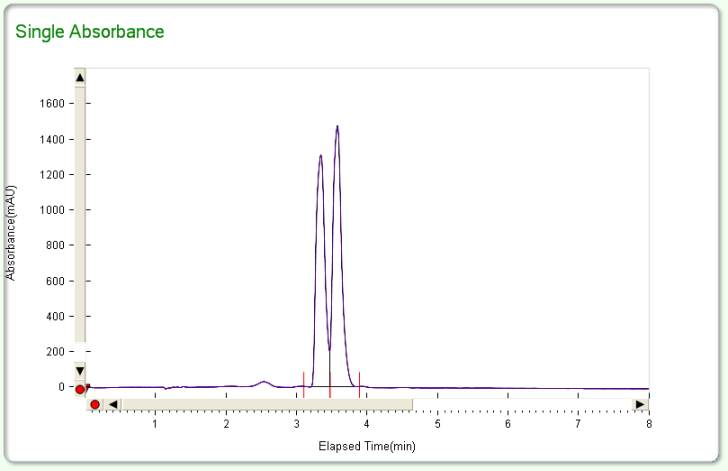




(*S*)-1-ethyl-2-(4-((4-fluorophenyl)(methyl)amino)-3-methylbutanoyl)-5,5-dimethylpyrazolidin-3-one
(Table 2, entry 2)

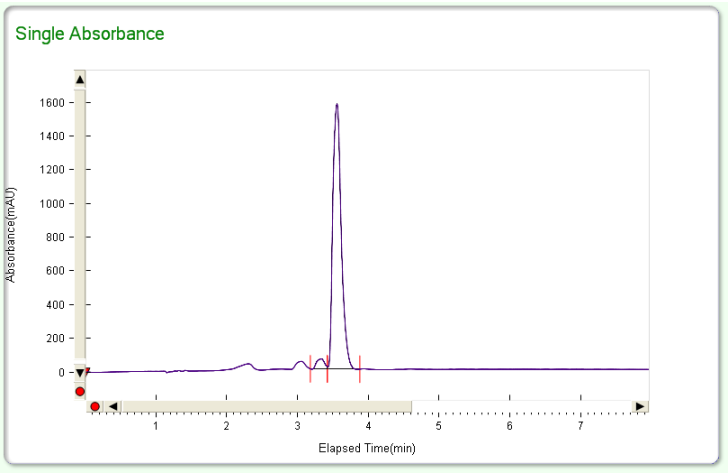
Racemic: SFC, Chiracel AD-H, 5 to 50% MeOH/CO_2, 3 mL/min, 249 nm

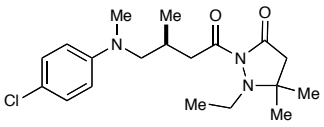
peak	% area	area	RT (min)	height (mV)
1	47.265	11099.7149	3.34	1304.5357
2	52.735	12384.2808	3.58	1467.2547
Total	100	23483.9956		



Scalemic: SFC, Chiracel AD-H, 5 to 50% MeOH/CO_2, 3 mL/min, 249 nm

peak	% area	area	RT (min)	height (mV)
1	3.3882	454.2170	3.34	59.2667
2	96.6118	12951.7187	3.56	1571.3618
Total	100	13405.9357		

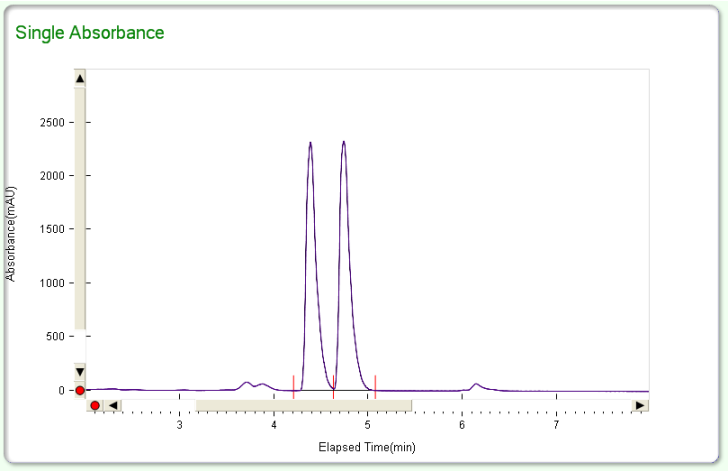




(*S*)-2-(4-((4-chlorophenyl)(methyl)amino)-3-methylbutanoyl)-1-ethyl-5,5-dimethylpyrazolidin-3-one
(Table 2, entry 3)

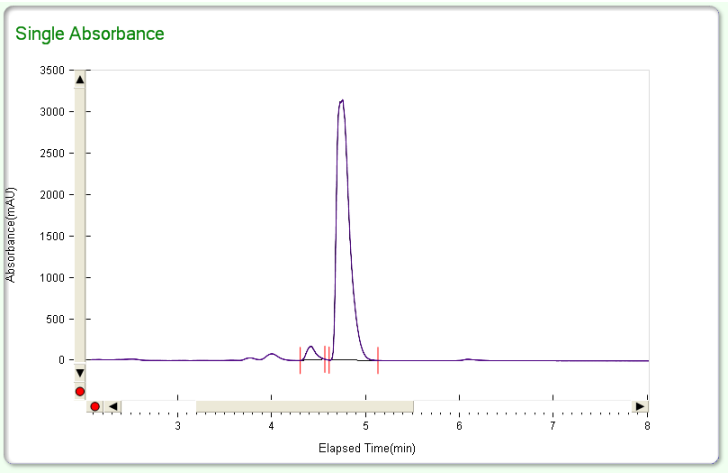
Racemic: SFC, Chiracel AD-H, 5 to 50% MeOH/CO_2, 3 mL/min, 249 nm

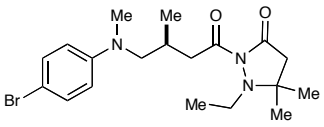
peak	% area	area	RT (min)	height (mV)
1	49.0277	17259.4213	4.39	2313.6117
2	50.9723	17943.9865	4.74	2324.8204
Total	100	35203.4078		



Scalemic: SFC, Chiracel AD-H, 5 to 50% MeOH/CO_2, 3 mL/min, 249 nm

peak	% area	area	RT (min)	height (mV)
1	3.4557	1071.6016	4.41	163.1213
2	96.5443	29937.9552	4.75	3148.0144
Total	100	31009.5568		

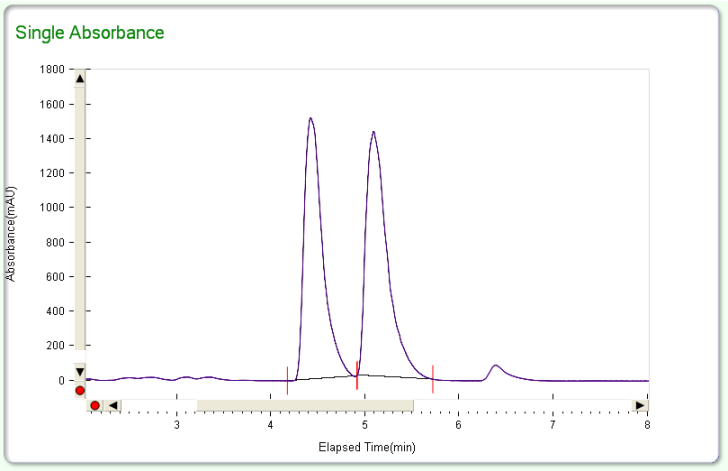




(*S*)-2-(4-((4-bromophenyl)(methyl)amino)-3-methylbutanoyl)-1-ethyl-5,5-dimethylpyrazolidin-3-one
(Table 2, entry 4)

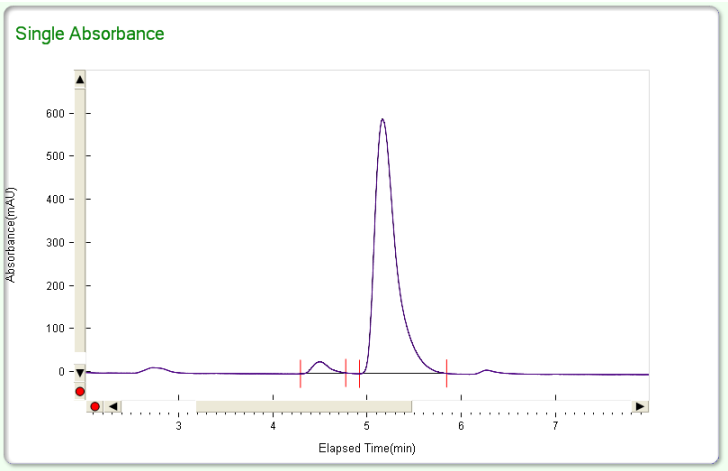
Racemic: SFC, Chiracel AD-H, 12% MeOH/CO_2, 3 mL/min, 249 nm

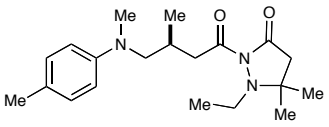
peak	% area	area	RT (min)	height (mV)
1	48.0217	20620.8468	4.42	1514.1716
2	51.9783	22319.8349	5.09	1415.8950
Total	100	42940.6817		



Scalemic: SFC, Chiracel AD-H, 12% MeOH/CO_2, 3 mL/min, 249 nm

peak	% area	area	RT (min)	height (mV)
1	3.3717	318.4937	4.5	26.9311
2	51.9783	9127.534	5.16	590.4464
Total	100	9446.0277		

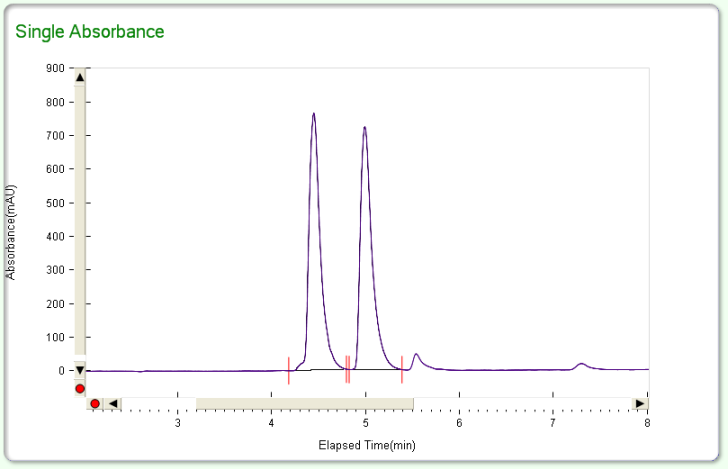




(*S*)-1-ethyl-5,5-dimethyl-2-(3-methyl-4-(methyl(p-tolyl)amino)butanoyl)pyrazolidin-3-one
(Table 2, entry 5)

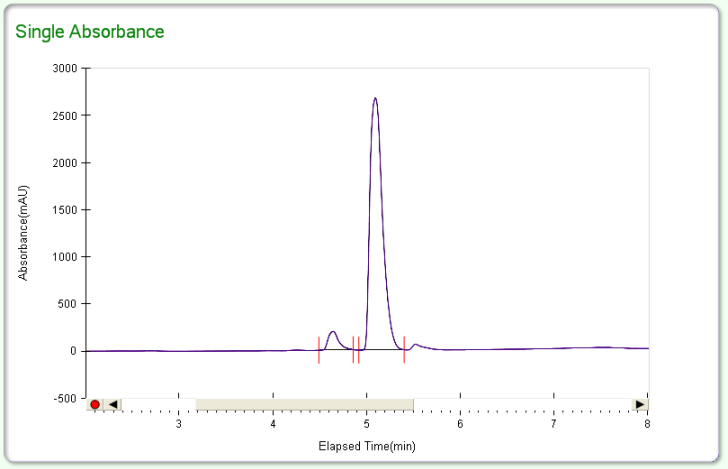
Racemic: SFC, Chiracel AD-H, 5 to 50% *i*-PrOH/CO_2, 3 mL/min, 249 nm

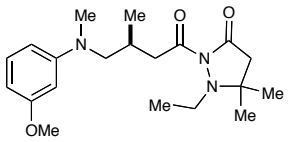
peak	% area	area	RT (min)	height (mV)
1	50.7422	6346.3218	4.45	763.857
2	49.2578	6209.2164	4.99	721.5931
Total	100	12605.5381		



Scalemic: SFC, Chiracel AD-H, 5 to 50% *i*-PrOH/CO_2, 3 mL/min, 249 nm

peak	% area	area	RT (min)	height (mV)
1	5.4095	1425.4502	4.65	193.5395
2	94.5905	24925.3698	5.09	2671.2094
Total	100	26350.82		

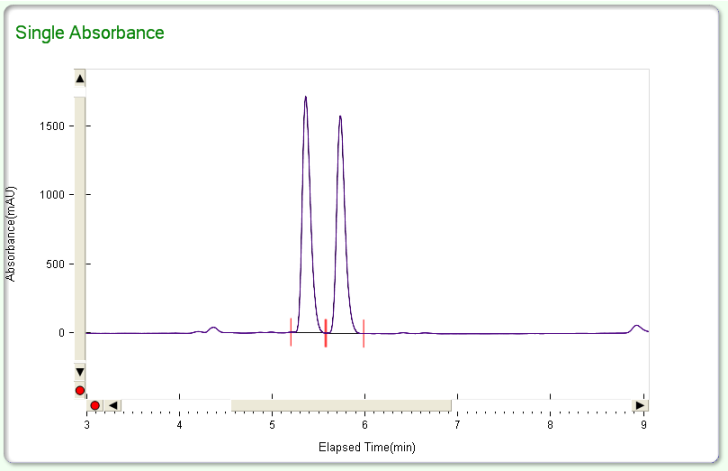




(*S*)-1-ethyl-2-(4-((3-methoxyphenyl)(methyl)amino)-3-methylbutanoyl)-5,5-dimethylpyrazolidin-3-one
(Table 2, entry 7)

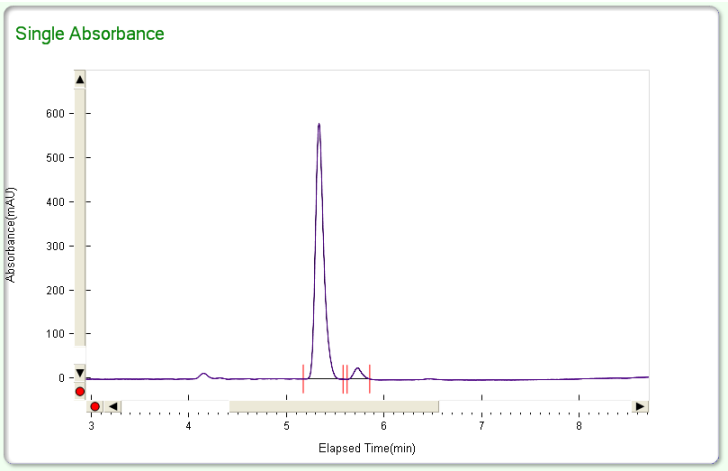
Racemic: SFC, Chiracel OD-H, 5 to 50% MeOH/CO_2, 3 mL/min, 249 nm

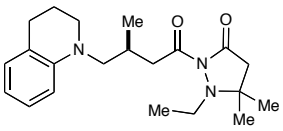
peak	% area	area	RT (min)	height (mV)
1	50.8908	10277.5731	5.36	1696.7083
2	49.1092	9917.7745	5.73	1578.3648
Total	100	20195.3476		



Scalemic: SFC, Chiracel OD-H, 5 to 50% MeOH/CO_2, 3 mL/min, 249 nm

peak	% area	area	RT (min)	height (mV)
1	95.986	3420.6893	5.33	578.7093
2	4.014	143.05	5.73	25.2032
Total	100	3563.7394		

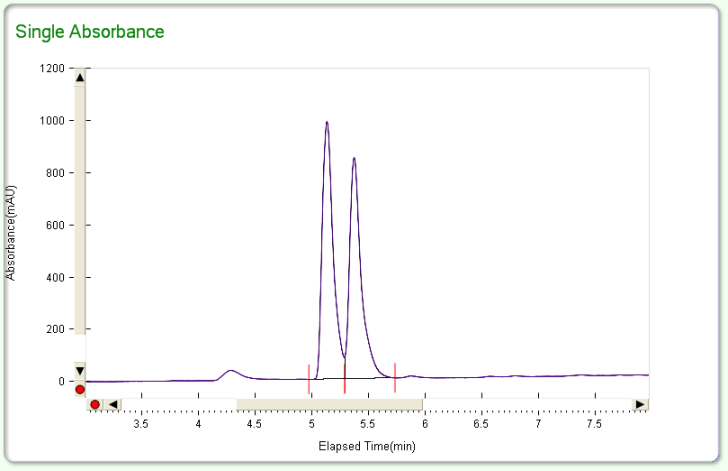




(*S*)-2-(4-(3,4-dihydroquinolin-1(2H)-yl)-3-methylbutanoyl)-1-ethyl-5,5-dimethylpyrazolidin-3-one
(Table 2, entry 9)

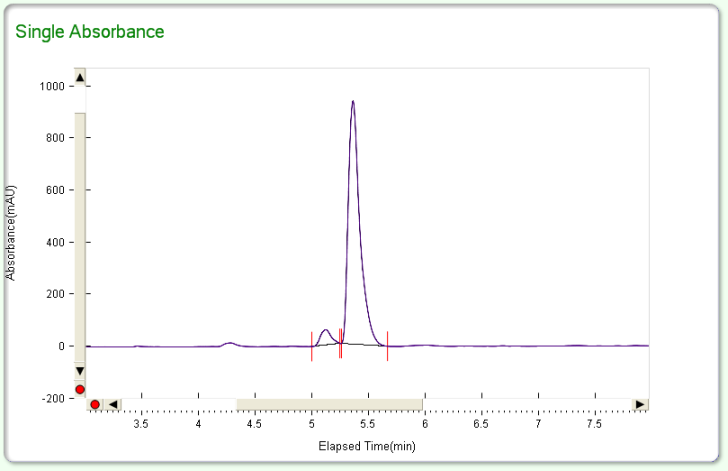
Racemic: SFC, Chiracel AD-H, 5 to 50% *i*-PrOH/CO_2, 3 mL/min, 249 nm

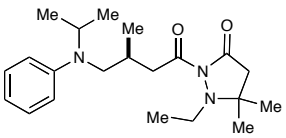
peak	% area	area	RT (min)	height (mV)
1	51.9556	6381.6846	5.14	942.0845
2	48.0444	5901.2782	5.38	807.5846
Total	100	12282.9628		



Scalemic: SFC, Chiracel AD-H, 5 to 50% *i*-PrOH/CO_2, 3 mL/min, 249 nm

peak	% area	area	RT (min)	height (mV)
1	4.8502	337.2443	5.12	55.7599
2	95.1498	6615.9126	5.37	934.2393
Total	100	6953.1569		

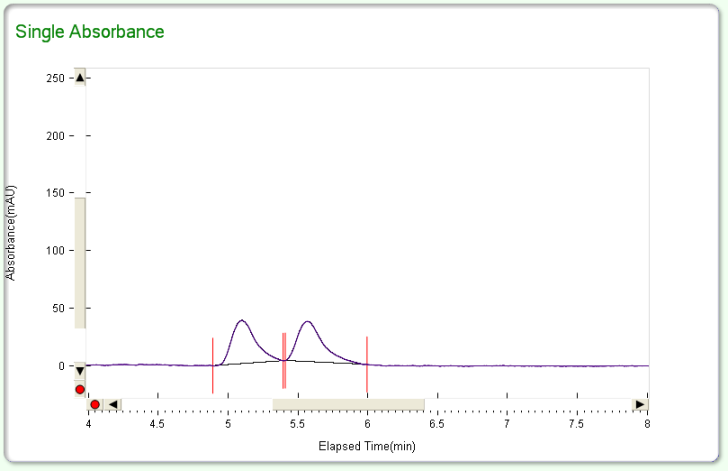




(*S*)-1-ethyl-2-(4-(isopropyl(phenyl)amino)-3-methylbutanoyl)-5,5-dimethylpyrazolidin-3-one
(Table 2, entry 13)

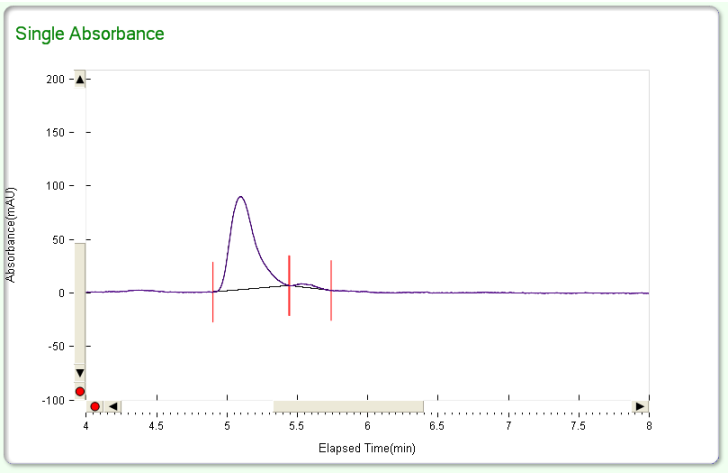
Racemic: SFC, Chiracel AD-H, 10% MeOH/CO_2, 3 mL/min, 236 nm

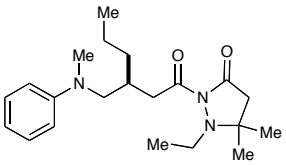
peak	% area	area	RT (min)	height (mV)
1	49.9858	440.9966	5.1	37.5691
2	50.0142	441.2472	5.57	34.8653
Total	100	882.24386		



Scalemic: SFC, Chiracel AD-H, 10% MeOH/CO_2, 3 mL/min, 236 nm

peak	% area	area	RT (min)	height (mV)
1	97.445	1072.8867	5.09	86.835
2	2.555	28.1307	5.53	3.1001
Total	100	1101.0174		

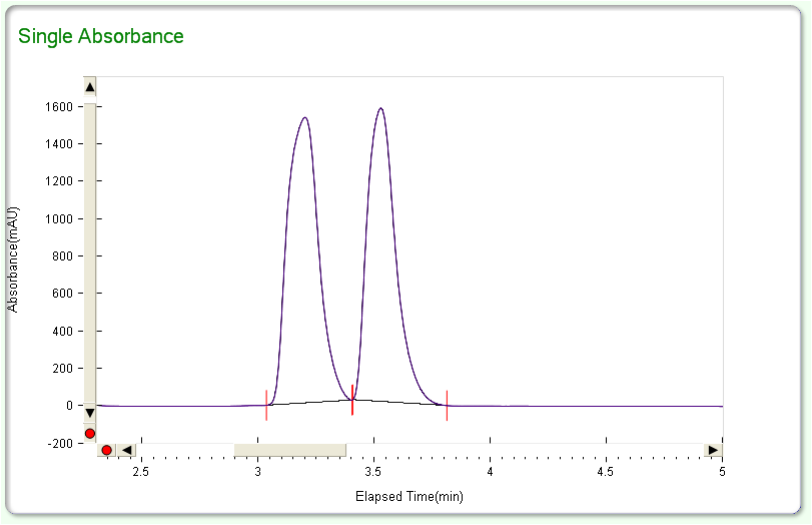




(*S*)-1-ethyl-5,5-dimethyl-2-(3-((methyl(phenyl)amino)methyl)hexanoyl)pyrazolidin-3-one
(Table 3, entry 1)

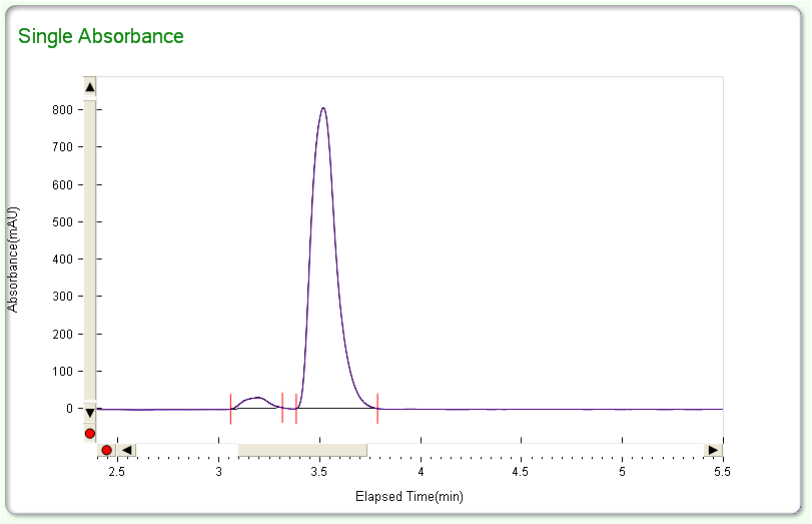
Racemic: SFC, Chiracel AD-H, 5 to 50% MeOH/CO_2, 3 mL/min, 249 nm

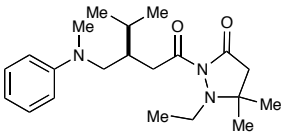
peak	% area	area	RT (min)	height (mV)
1	50.7163	4879.6126	3.20 min	527.0616
2	49.2837	4741.781	3.53 min	546.7968
Total	100	9621.3936		



Scalemic: SFC, Chiracel AD-H, 5 to 50% MeOH/CO_2, 3 mL/min, 249 nm

peak	% area	area	RT (min)	height (mV)
1	3.6500	89.8125	3.20 min	10.2960
2	96.3500	2370.8343	3.53 min	277.8255
Total	100	2460.6467		

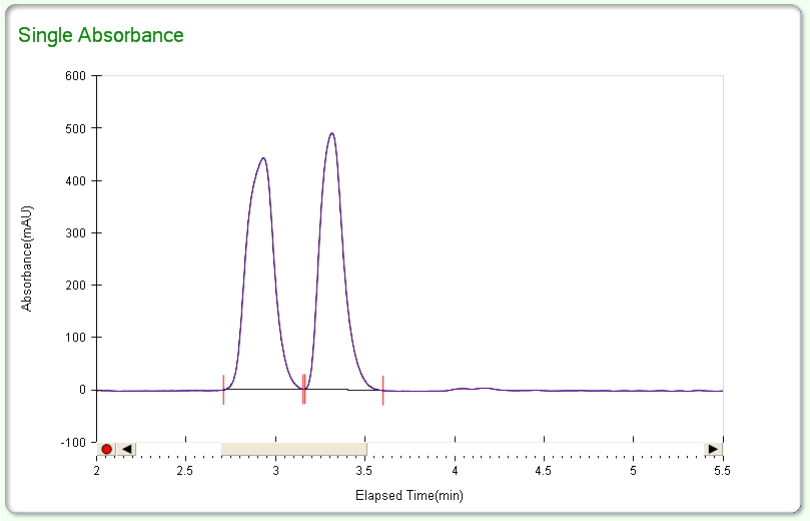




(*R*)-1-ethyl-5,5-dimethyl-2-(4-methyl-3-((methyl(phenyl)amino)methyl)pentanoyl)pyrazolidin-3-one
(Table 3, entry 2)

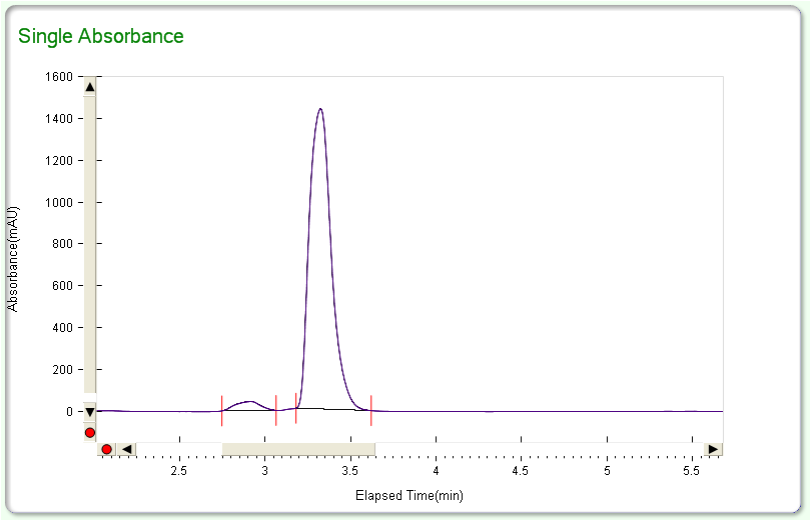
Racemic: SFC, Chiracel AD-H, 5 to 50% MeOH/CO_2, 3 mL/min, 249 nm

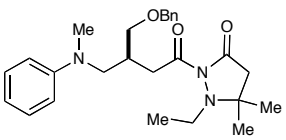
peak	% area	area	RT (min)	height (mV)
1	50.8580	1636.3725	2.93 min	155.7033
2	49.1420	1581.1571	3.31 min	172.9655
Total	100	3217.5295		



Scalemic: SFC, Chiracel AD-H, 5 to 50% MeOH/CO_2, 3 mL/min, 249 nm

peak	% area	area	RT (min)	height (mV)
1	3.6070	167.7042	2.91 min	16.2200
2	96.393	4481.7273	3.32 min	515.2296
Total	100	4649.4314		

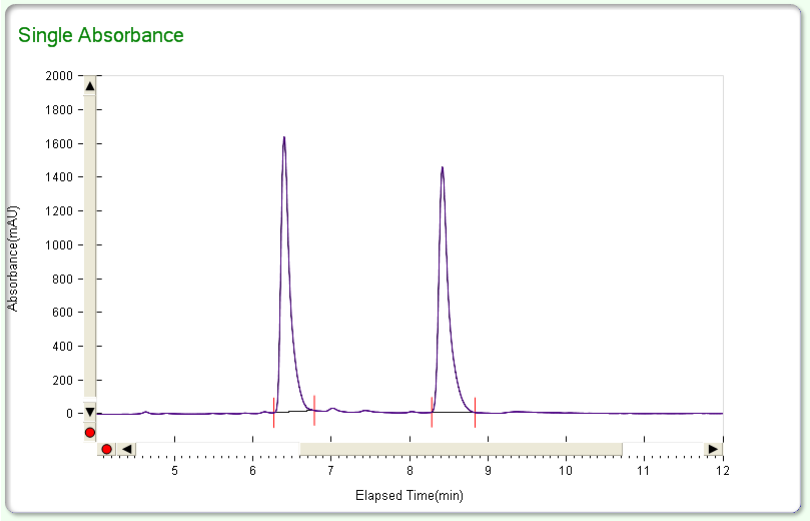




(*S*)-2-(4-(benzyloxy)-3-((methyl(phenyl)amino)methyl)butanoyl)-1-ethyl-5,5-dimethylpyrazolidin-3-one
(Table 3, entry 3)

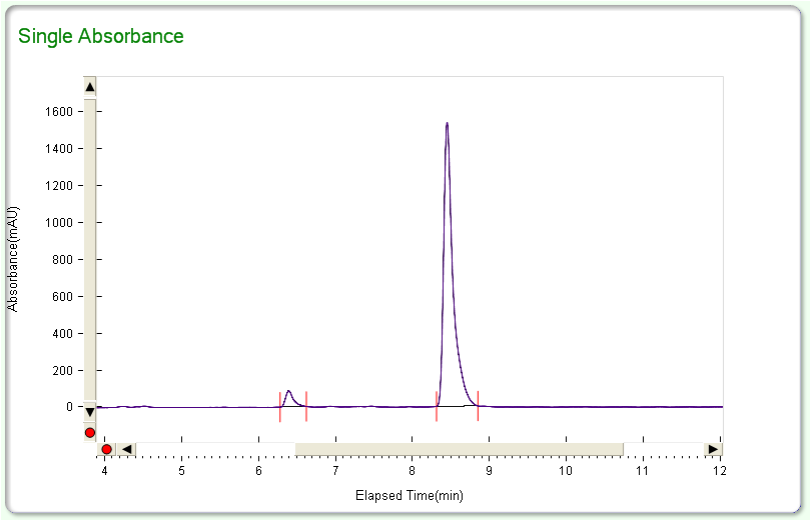
Racemic: SFC, Chiracel AD-H, 5 to 50% *i*-PrOH /CO_2, 3 mL/min, 249 nm

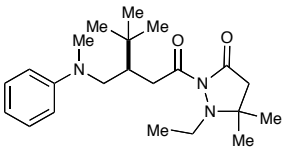
peak	% area	area	RT (min)	height (mV)
1	50.4594	4373.3147	6.40 min	545.9539
2	49.5406	4293.6861	8.42 min	489.6286
Total	100	8667.0008		



Scalemic: SFC, Chiracel AD-H, 5 to 50% *i*-PrOH /CO_2, 3 mL/min, 249 nm

peak	% area	area	RT (min)	height (mV)
1	4.7919	216.8380	6.39 min	28.3508
2	95.2081	4308.2817	8.45 min	514.9895
Total	100	4525.1197		

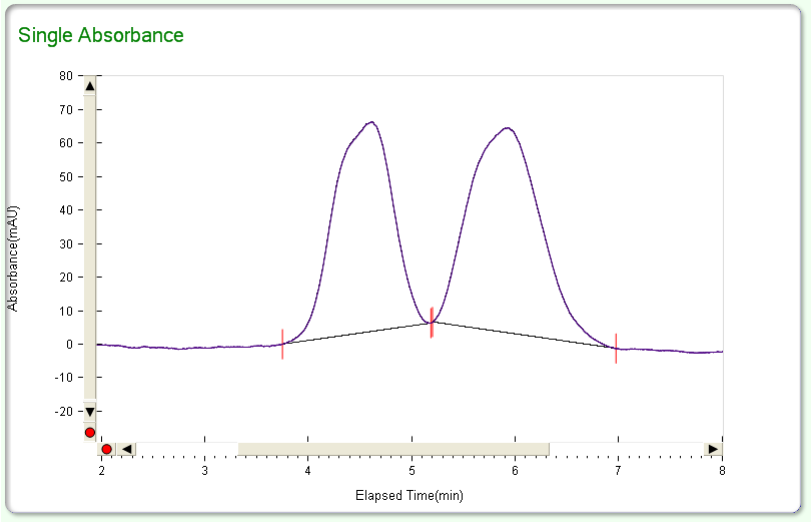




(*R*)-2-(4,4-dimethyl-3-((methyl(phenyl)amino)methyl)pentanoyl)-1-ethyl-5,5-dimethylpyrazolidin-3-one
(Table 3, entry 4)

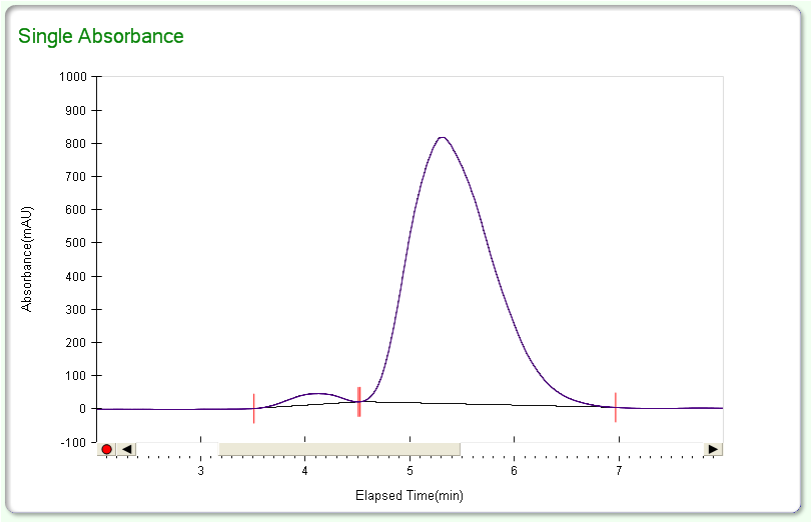
Racemic: SFC, Chiracel AD-H, 3% MeOH/CO_2, 3 mL/min, 249 nm

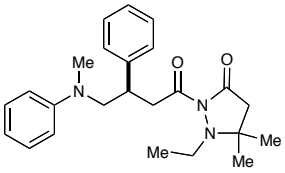
peak	% area	area	RT (min)	height (mV)
1	46.6334	930.2134	4.25 min	24.8752
2	53.3666	1064.523	5.54 min	23.0197
Total	100	1994.7364		



Scalemic: SFC, Chiracel AD-H, 5 to 50% MeOH/CO_2, 3 mL/min, 249 nm

peak	% area	area	RT (min)	height (mV)
1	2.2599	613.1346	4.33 min	18.4249
2	97.7401	26517.8668	5.61 min	439.063
Total	100	27131.0013		

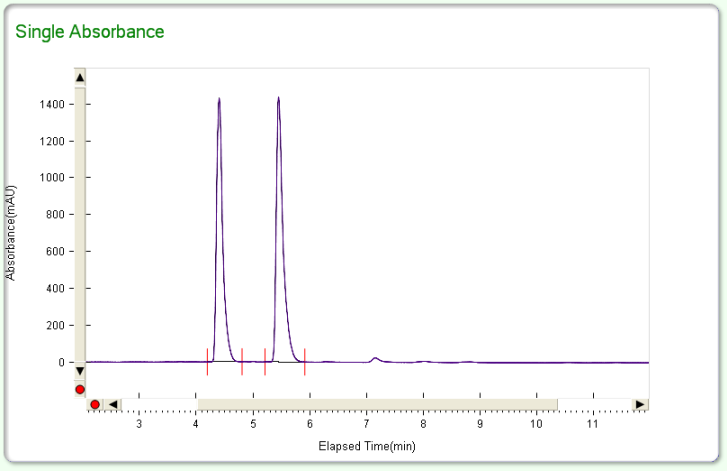




(*R*)-1-ethyl-5,5-dimethyl-2-(4-(methyl(phenyl)amino)-3-phenylbutanoyl)pyrazolidin-3-one
(Table 3, entry 5)

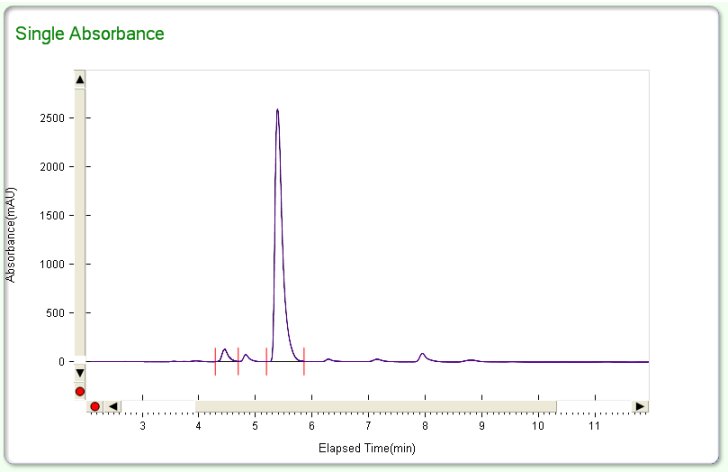
Racemic: SFC, Chiracel AD-H, 5 to 50% MeOH/CO_2, 3 mL/min, 249 nm

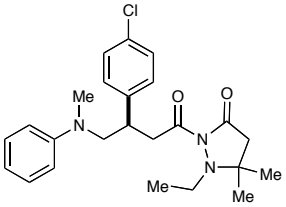
peak	% area	area	RT (min)	height (mV)
1	47.6477	10889.5762	4.40 min	1429.5604
2	52.3523	11964.7876	5.45 min	1437.086
Total	100	22854.3638		



Scalemic: SFC, Chiracel AD-H, 5 to 50% MeOH/CO_2, 3 mL/min, 249 nm

peak	% area	area	RT (min)	height (mV)
1	3.8739		4.46 min	125.5653
2	96.1261	23882.5624	5.39 min	2594.4194
Total	100	24845.0259		

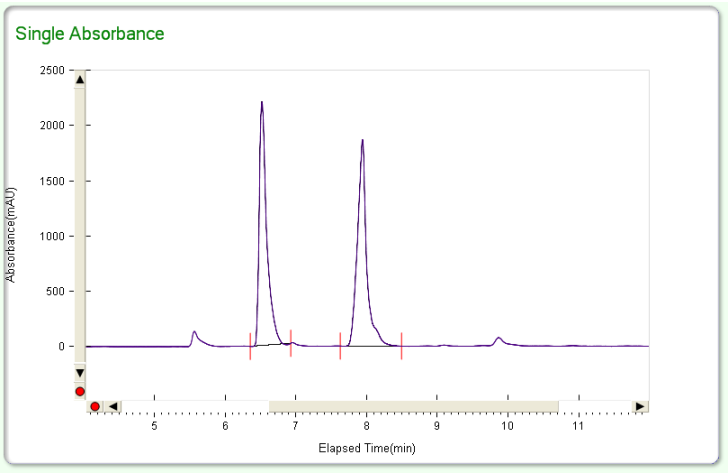




(*R*)-2-(3-(4-chlorophenyl)-4-(methyl(phenyl)amino)butanoyl)-1-ethyl-5,5-dimethylpyrazolidin-3-one
(Table 3, entry 6)

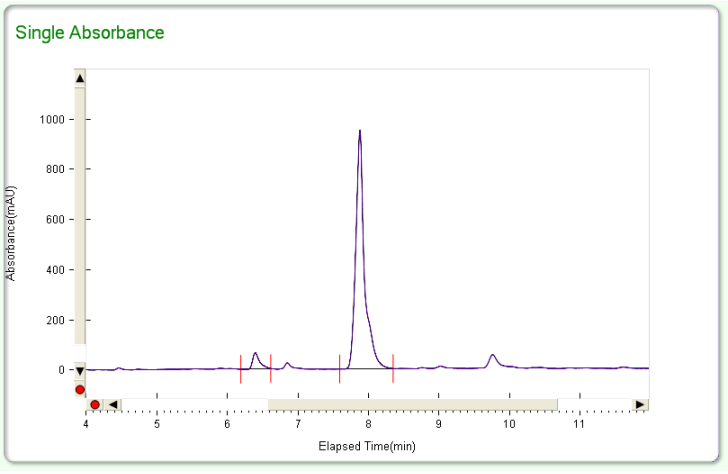
Racemic: SFC, Chiracel AD-H, 5 to 50% *i*-PrOH/CO_2, 3 mL/min, 249 nm

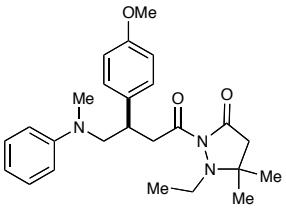
peak	% area	area	RT (min)	height (mV)
1	49.1522	16353.2013	6.52 min	2205.4375
2	50.8478	16917.3027	7.94 min	1870.9806
Total	100	33270.504		



Scalemic: SFC, Chiracel AD-H, 5 to 50% *i*-PrOH/CO_2, 3 mL/min, 249 nm

peak	% area	area	RT (min)	height (mV)
1	5.0012	428.3304	6.39 min	63.6496
2	94.9988	8136.2905	7.88 min	950.2956
Total	100	8564.6209		

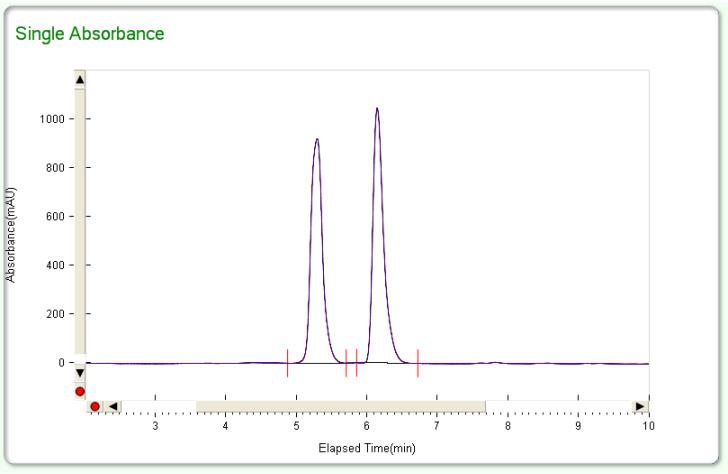




(*R*)-1-ethyl-2-(3-(4-methoxyphenyl)-4-(methyl(phenyl)amino)butanoyl)-5,5-dimethylpyrazolidin-3-one
(Table 3, entry 7)

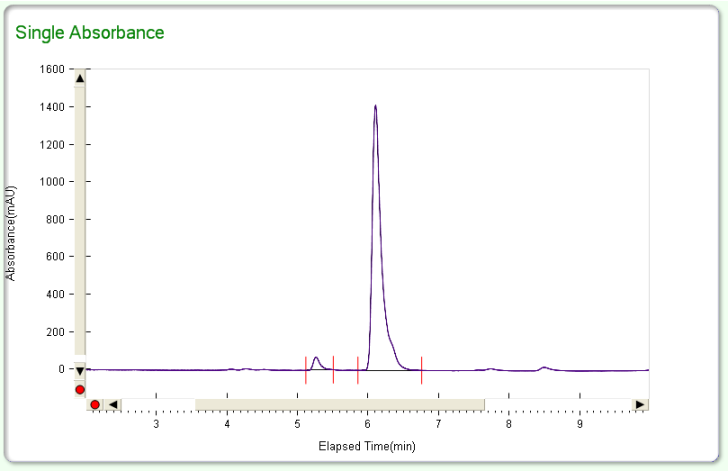
Racemic: SFC, Chiracel AD-H, 5 to 50% MeOH/CO_2, 3 mL/min, 249 nm

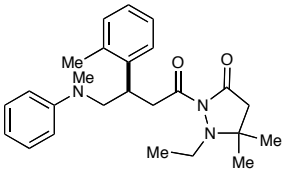
peak	% area	area	RT (min)	height (mV)
1	48.9206	10571.3389	5.3 min	919.6501
2	51.0794	11037.8302	6.15 min	1043.9818
Total	100	21609.1691		



Scalemic: SFC, Chiracel AD-H, 5 to 50% MeOH/CO_2, 3 mL/min, 249 nm

peak	% area	area	RT (min)	height (mV)
1	3.4078	459.5595	5.26 min	69.2989
2	96.5922	13026.0484	6.11 min	1414.0359
Total	100	13485.6079		

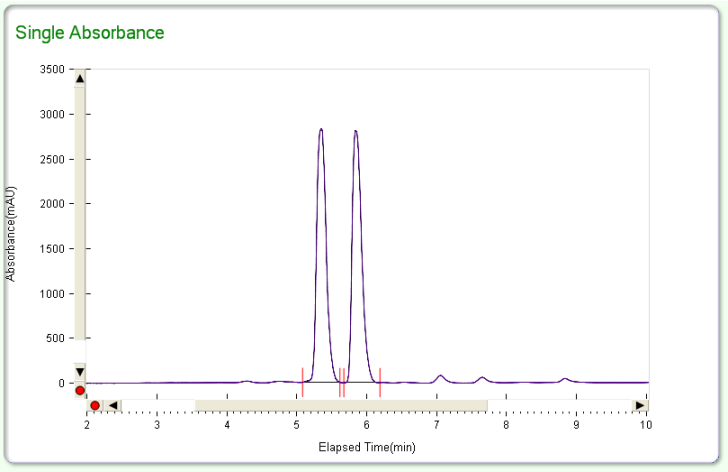




(*R*)-1-ethyl-5,5-dimethyl-2-(4-(methyl(phenyl)amino)-3-(o-tolyl)butanoyl)pyrazolidin-3-one
(Table 3, entry 8)

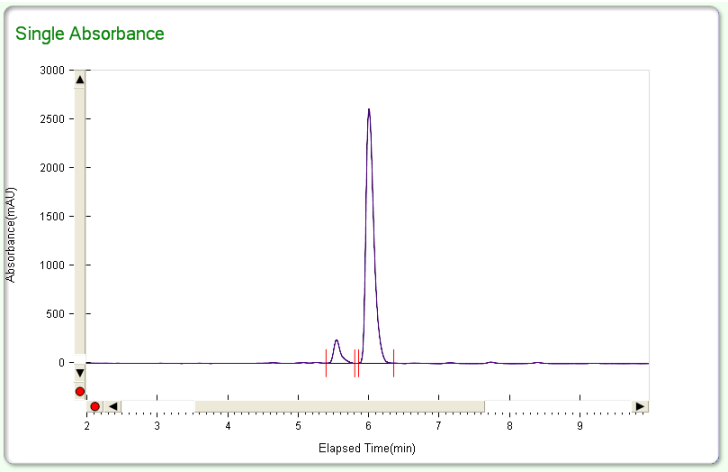
Racemic: SFC, Chiracel OD-H, 5 to 50% MeOH/CO_2, 3 mL/min, 249 nm

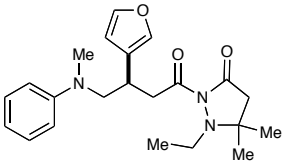
peak	% area	area	RT (min)	height (mV)
1	50.171	26671.4925	5.36 min	2828.0754
2	49.829	26489.6366	5.84 min	2814.1501
Total	100	53161.1292		



Scalemic: SFC, Chiracel OD-H, 5 to 50% MeOH/CO_2, 3 mL/min, 249 nm

peak	% area	area	RT (min)	height (mV)
1	7.448	1648.8362	5.54 min	240.5873
2	92.552	20488.9988	6.01 min	2606.2135
Total	100	22137.835		

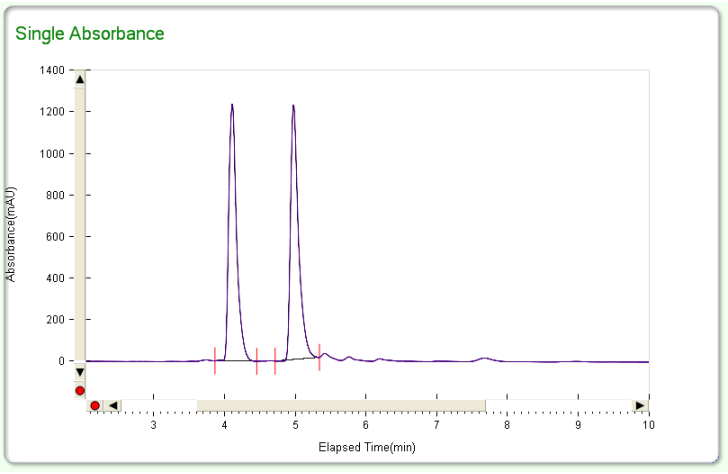




(*R*)-1-ethyl-2-(3-(furan-3-yl)-4-(methyl(phenyl)amino)butanoyl)-5,5-dimethylpyrazolidin-3-one
(Table 3, entry 9)

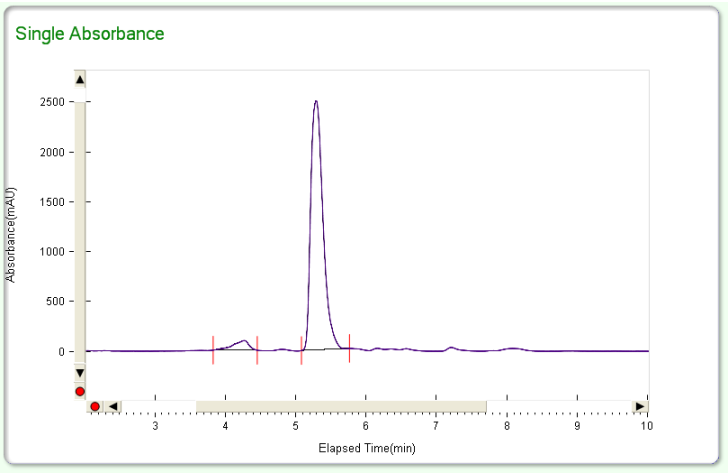
Racemic: SFC, Chiracel AD-H, 5 to 50% MeOH/CO_2, 3 mL/min, 249 nm

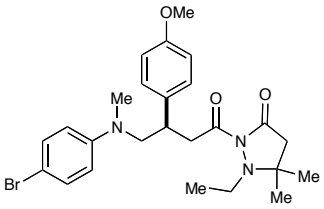
peak	% area	area	RT (min)	height (mV)
1	49.8914	9560.9141	4.11 min	1235.1085
2	50.1086	9602.5298	4.98 min	1225.88
Total	100	19163.4439		



Scalemic: SFC, Chiracel AD-H, 5 to 50% MeOH/CO_2, 3 mL/min, 249 nm

peak	% area	area	RT (min)	height (mV)
1	4.8025	1518.7972	4.27 min	96.6807
2	95.1975	30106.2993	5.29 min	2496.3385
Total	100	31625.0965		

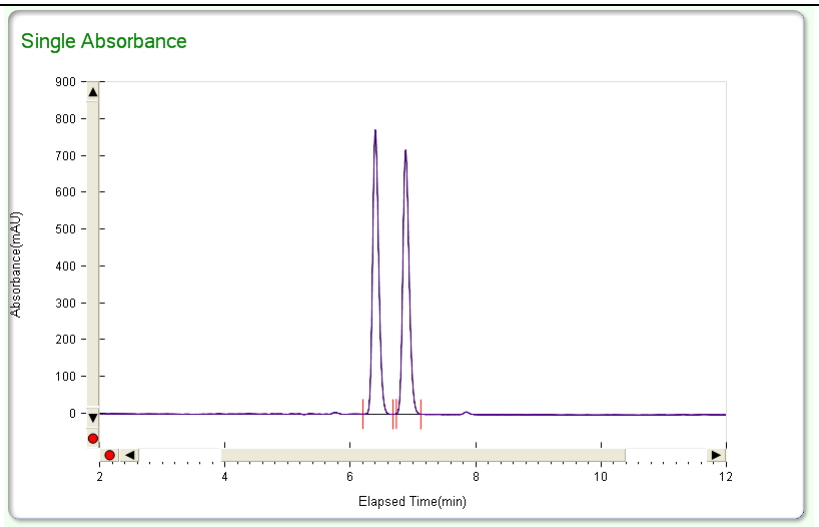




(*R*)-2-(4-((4-bromophenyl)(methyl)amino)-3-(4-methoxyphenyl)butanoyl)-1-ethyl-5,5-dimethylpyrazolidin-3-one

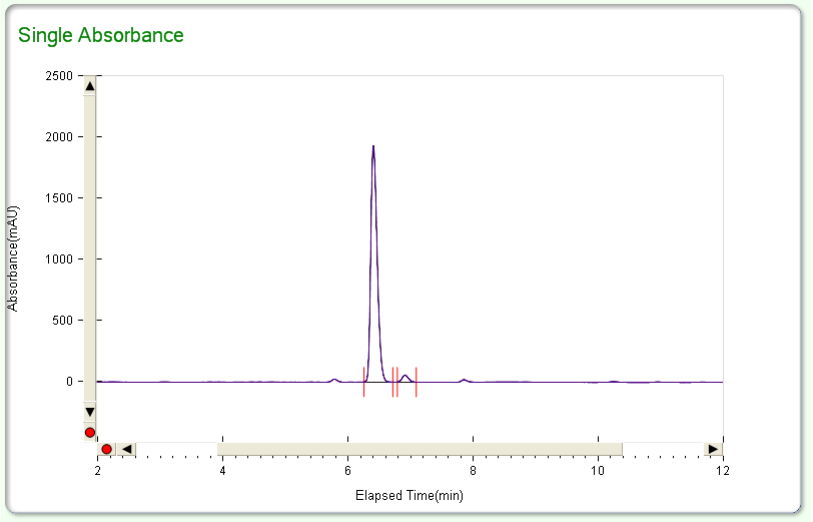
Racemic: SFC, Chiracel OJ-H, 5 to 50% MeOH/CO_2, 3 mL/min, 249 nm

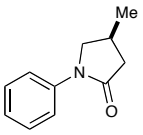
peak	% area	area	RT (min)	height (mV)
1	50.8407	5203.5567	6.40 min	772.8044
2	49.1593	5031.4597	6.88 min	717.1919
Total	100	10235.0164		



Scalemic: SFC, Chiracel OJ-H, 5 to 50% MeOH/CO_2, 3 mL/min, 249 nm

peak	% area	area	RT (min)	height (mV)
1	97.1597	13693.4821	6.40 min	1932.9375
2	2.8403	400.3000	6.91 min	57.935
Total	100	14093.7821		

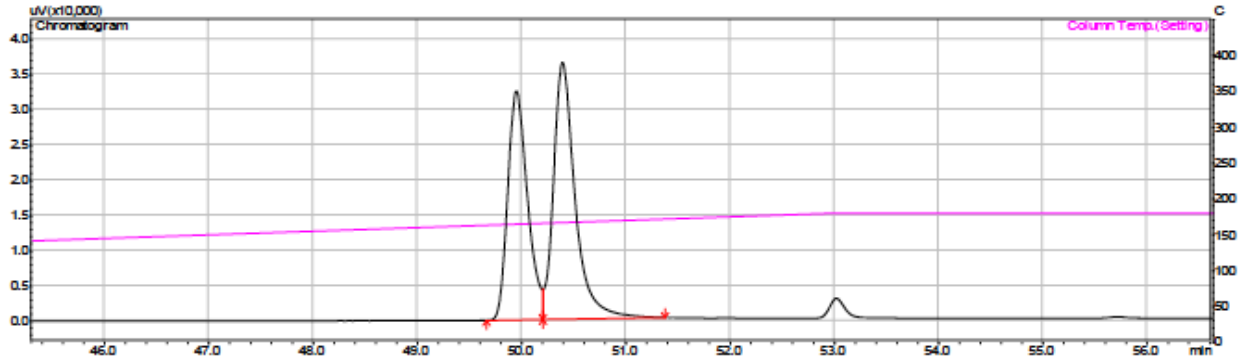




(*S*)-4-methyl-1-phenylpyrrolidin-2-one
(Scheme 2, **10**)

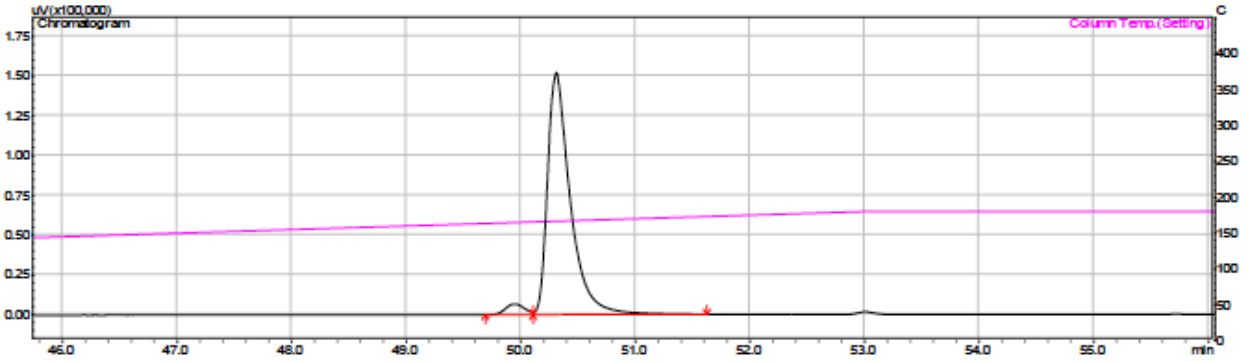
Racemic: GC, Supelco's Beta Dex 225, 140 °C for 45 min, then 5 °C/min to 180 °C

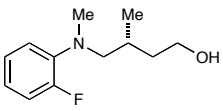
peak	% area	area	RT (min)	height (mV)
1	44.90048	429330.3	49.950	32515.1
2	55.09952	526851.8	50.391	36479.1
Total	100	956182.1		



Scalemic: GC, Supelco's Beta Dex 225, 140 °C for 45 min, then 5 °C/min to 180 °C

peak	% area	area	RT (min)	height (mV)
1	3.72478	81501.0	49.950	6892.2
2	96.27522	2106571.5	50.311	152274.9
Total	100	2188072.5		

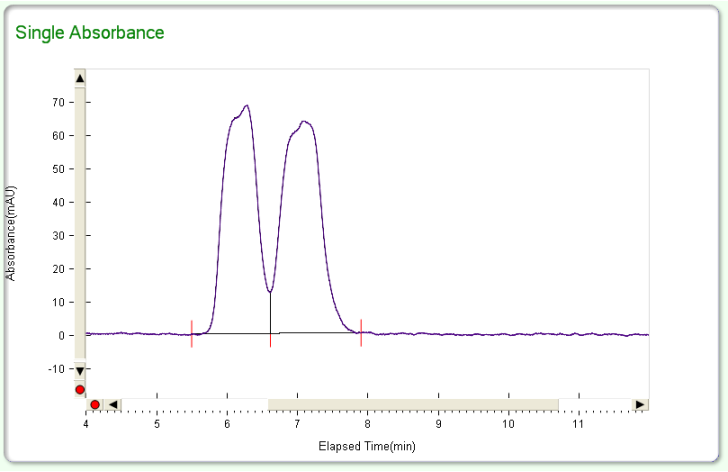




(*R*)-4-((2-fluorophenyl)(methyl)amino)-3-methylbutan-1-ol

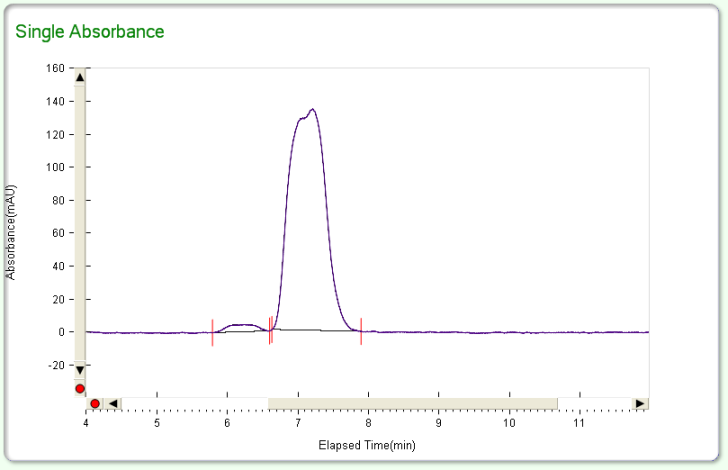
Racemic: SFC, Chiracel OD-H, 3% *i*-PrOH/CO_2, 5 mL/min, 249 nm

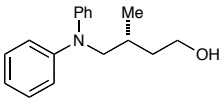
peak	% area	area	RT (min)	height (mV)
1	47.9386	2253.4702	6.28	68.5808
2	52.0614	2444.2724	7.08	63.7617
Total	100	4700.7425		



Scalemic: SFC, Chiracel AD-H, 5 to 50% *i*-PrOH/CO_2, 3 mL/min, 249 nm

peak	% area	area	RT (min)	height (mV)
1	2.5986	128.3118	6.28	4.3175
2	97.4014	4809.4984	7.21	134.326
Total	100	4937.8102		

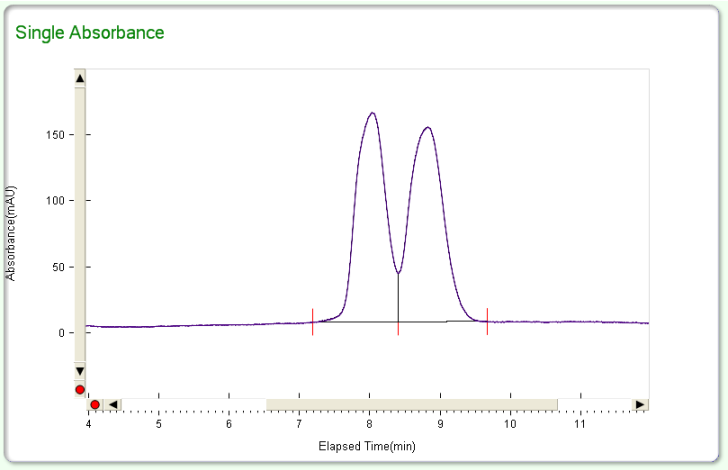




(*R*)-4-(diphenylamino)-3-methylbutan-1-ol

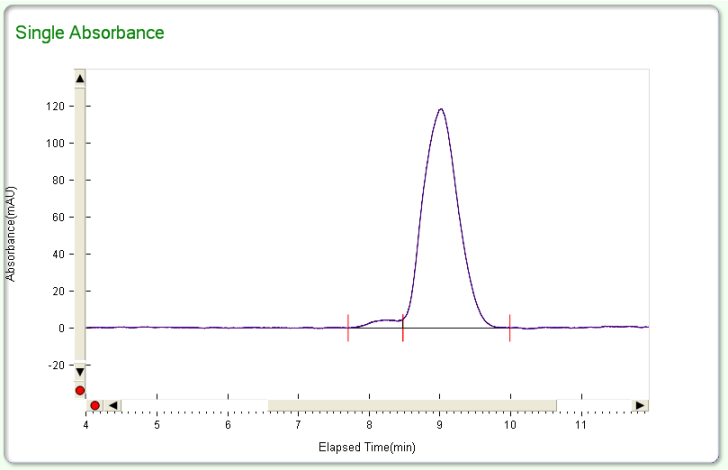
Racemic: SFC, Chiracel OJ-H, 5% *i*-PrOH/CO_2, 4 mL/min, 249 nm

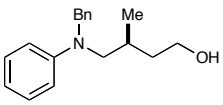
peak	% area	area	RT (min)	height (mV)
1	48.6215	4684.7542	8.03	158.5619
2	51.3785	4950.3929	8.83	147.5679
Total	100	9635.1471		



Scalemic: SFC, Chiracel OJ-H, 5% *i*-PrOH/CO_2, 4 mL/min, 249 nm

peak	% area	area	RT (min)	height (mV)
1	3.0044	126.4144	8.47	4.5919
2	96.2393	4081.2393	9.02	118.3445
Total	100	4207.6537		

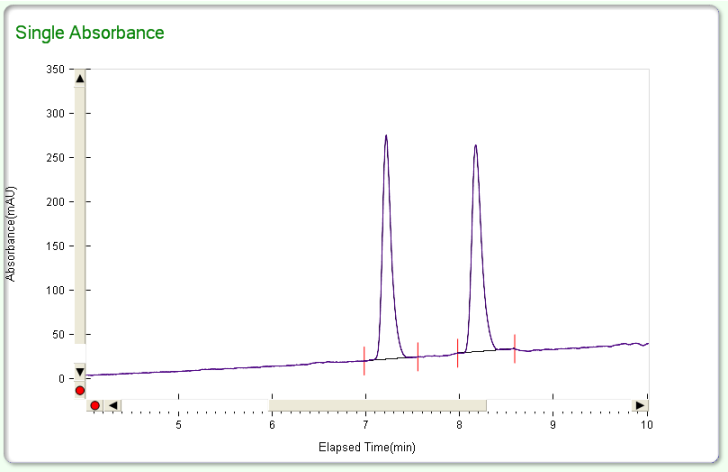




(*S*)-4-(benzyl(phenyl)amino)-3-methylbutan-1-ol

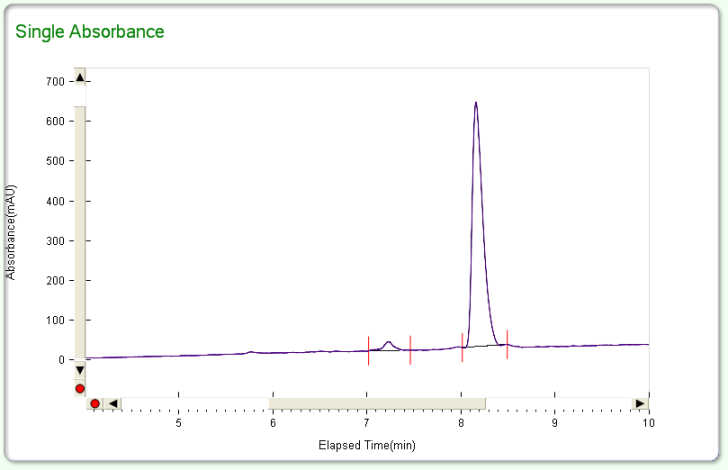
Racemic: SFC, Chiracel OD-H, 5% to 50% *i*-PrOH/CO_2, 3 mL/min, 249 nm

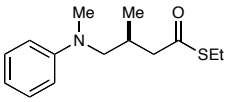
peak	% area	area	RT (min)	height (mV)
1	49.3552	1680.7896	7.22	253.4013
2	50.6448	1724.7091	8.17	234.1595
Total	100	3405.4988		



Scalemic: SFC, Chiracel OD-H, 5% to 50% *i*-PrOH/CO_2, 3 mL/min, 249 nm

peak	% area	area	RT (min)	height (mV)
1	3.4983	174.1503	7.23	21.9352
2	96.5017	4804.0269	8.16	614.7831
Total	100	4978.1772		

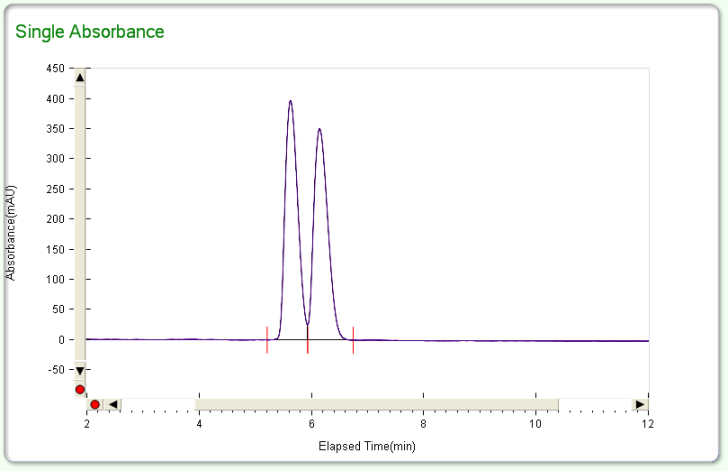




(*S*)-S-ethyl 3-methyl-4-(methyl(phenyl)amino)butanethioate
(Scheme 2, **7**)

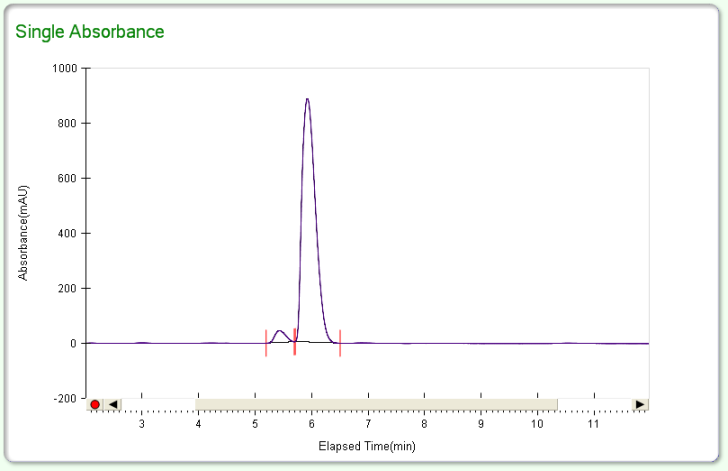
Racemic: SFC, Chiracel OJ-H, 3% MeOH/CO_2, 3 mL/min, 249 nm

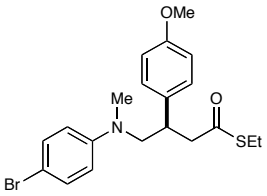
peak	% area	area	RT (min)	height (mV)
1	50.4536	6212.0804	5.63 min	397.5879
2	49.5464	6100.3929	6.14 min	350.7472
Total	100	12312.4732		



Scalemic: SFC, Chiracel OJ-H, 3% MeOH/CO_2, 3 mL/min, 249 nm

peak	% area	area	RT (min)	height (mV)
1	3.7355	568.4328	5.43 min	43.4693
2	96.2645	14648.6639	5.92 min	885.7859
Total	100	15217.0968		

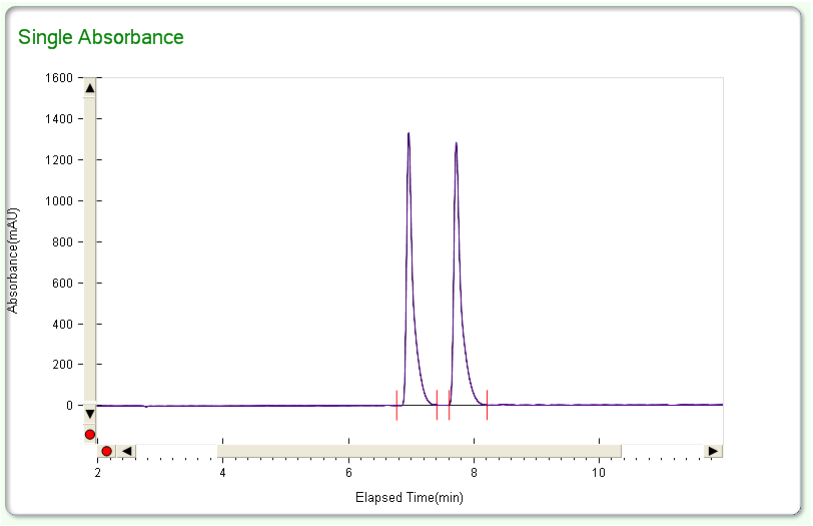




(*R*)-S-ethyl-4-((4-bromophenyl)(methyl)amino)-3-(4-methoxyphenyl)butanethioate

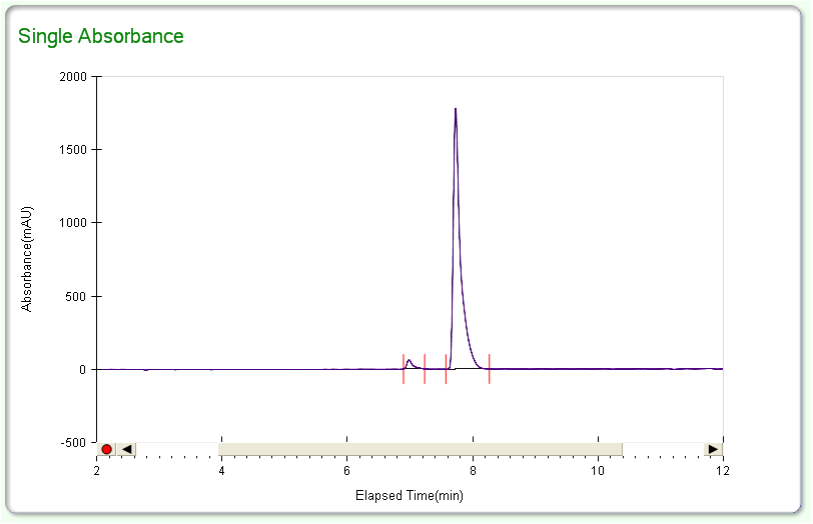
Racemic: SFC, Chiracel AD-H, 5 to 50% i-PrOH/CO_2, 3 mL/min, 249 nm

peak	% area	area	RT (min)	height (mV)
1	48.8607	9764.4937	6.96 min	1330.9417
2	51.1393	10219.8625	7.72 min	1282.8100
Total	100	19984.3562		



Scalemic: SFC, Chiracel AD-H, 5 to 50% i-PrOH/CO_2, 3 mL/min, 249 nm

peak	% area	area	RT (min)	height (mV)
1	2.7265	405.3188	6.98 min	62.9752
2	97.2735	14460.5767	7.73 min	1785.2633
Total	100	14865.8955		



IX. X-Ray Crystallographic Data

(*S*)-1-phenylethanaminium (*R*)-4-((4-bromophenyl)(methyl)amino)-3-(4-methoxyphenyl)butanoate

Data Collection

A colorless crystal with approximate dimensions 0.624 x 0.035 x 0.023 mm^3 was selected under oil under ambient conditions and attached to the tip of a MiTeGen MicroMount©. The crystal was mounted in a stream of cold nitrogen at 100(1) K and centered in the X-ray beam by using a video camera.

The crystal evaluation and data collection were performed on a Bruker Quazar SMART APEXII diffractometer with Mo K_α (λ = 0.71073 Å) radiation and the diffractometer to crystal distance of 4.96 cm.

The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 12 frames collected at intervals of 0.5º in a 60º range about ω with the exposure time of 60 seconds per frame. The reflections were successfully indexed by an automated indexing routine built in the APEXII program suite. The final cell constants were calculated from a set of 4577 strong reflections from the actual data collection.

The data were collected by using the full sphere data collection routine to survey the reciprocal space to the extent of a full sphere to a resolution of 0.70 Å. A total of 35907 data were harvested by collecting 4 sets of frames with 0.5º scans in ω and φ with exposure times of 120 sec per frame. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements. [8]

Structure Solution and Refinement

The systematic absences in the diffraction data were uniquely consistent for the space group $P2_12_12_1$ that yielded chemically reasonable and computationally stable results of refinement. [9,10,11]

A successful solution by the direct methods provided most non-hydrogen atoms from the *E*-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients.

The asymmetric unit consists of the carboxylate shown in Figure S1 and the *S*-methylbenzyl ammonium counter ion. The absolute configuration was established by anomalous dispersion and is consistent with the known stereochemistry of the *S*-methylbenzyl ammonium reference ion.

The carboxylate and ammonium ions pack to form an infinite chain of two independent rings. Each ring is formed by hydrogen bonds between N2, O2, and O3 of adjacent ions (Graph set notation: $R_4^3(10)R_4^3(10)$). The two independent rings share an edge formed by hydrogen bonds between N3 and O3 of adjacent ions through H3C.

The final least-squares refinement of 294 parameters against 5011 data resulted in residuals *R* (based on F^2 for $I \geq 2\sigma$) and *wR* (based on F^2 for all data) of 0.0362 and 0.0760, respectively. The final difference Fourier map was featureless.

Summary

Crystal Data for $C_{18}H_{19}BrNO_3$, $C_8H_{12}N$ (*M* =499.44): orthorhombic, space group $P2_12_12_1$ (no. 19), *a* = 6.426(2) Å, *b* = 18.229(7) Å, *c* = 20.879(7) Å, *V* = 2445.7(15) $Å^3$, *Z* = 4, *T* = 100.0 K, μ(MoKα) = 1.710 mm^{-1}, *Dcalc* = 1.356 g/mm^3, 35907 reflections measured (2.966 ≤ 2Θ ≤ 52.902), 5011 unique (R_{int} = 0.0816, R_{sigma} = 0.0497) which were used in all calculations. The final R_1 was 0.0362 (I > 2σ(I)) and wR_2 was 0.0760 (all data).

The molecular diagram is drawn with 50% probability ellipsoids. All H atoms except those on heteroatoms and chiral carbons are omitted for clarity.

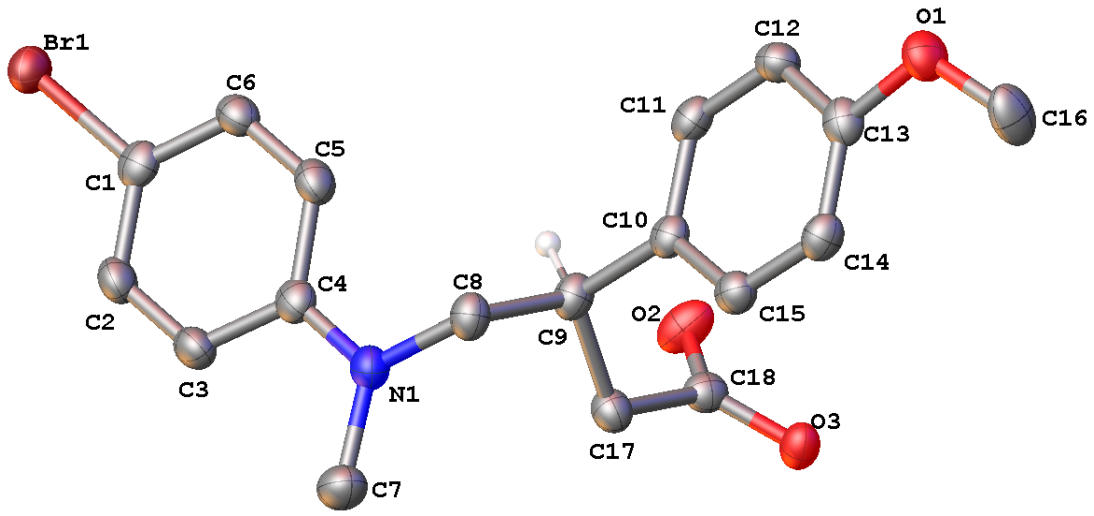


Figure S1. A molecular drawing of (*S*)-1-phenylethanaminium (*R*)-4-((4-bromophenyl)(methyl)amino)-3-(4-methoxyphenyl)butanoate.

Table S1. Crystal data and structure refinement for Yoon35.

Identification code	Yoon35
Empirical formula	$C_{18}H_{19}BrNO_3$, $C_8H_{12}N$
Formula weight	499.44
Temperature/K	100.0
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	6.426(2)
b/Å	18.229(7)
c/Å	20.879(7)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2445.7(15)
Z	4
ρ_{calc}mg/mm^3	1.356
μ/mm^{-1}	1.710
F(000)	1040.0
Crystal size/mm^3	0.624 × 0.035 × 0.023
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection	2.966 to 52.902°
Index ranges	-8 ≤ h ≤ 8, -21 ≤ k ≤ 22, -26 ≤ l ≤ 26
Reflections collected	35907
Independent reflections	5011 [R_{int} = 0.0816, R_{sigma} = 0.0497]
Data/restraints/parameters	5011/0/294
Goodness-of-fit on F^2	1.041

Final R indexes [I>=2σ (I)]	R_1 = 0.0362, wR_2 = 0.0721
Final R indexes [all data]	R_1 = 0.0484, wR_2 = 0.0760
Largest diff. peak/hole / e Å^{-3}	0.34/-0.40
Flack x parameter	-0.012(11)
Hooft y parameter	0.002(5)

Table S2. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Yoon35. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Br1	12248.7(6)	6159.3(2)	9668.4(2)	31.72(12)
O1	-128(5)	4424.0(17)	5768.5(15)	34.1(7)
O2	7123(5)	7166.7(17)	6198.0(14)	37.6(7)
O3	4264(4)	7600.3(16)	5744.2(14)	28.8(7)
N1	4397(6)	7150(2)	8294.4(16)	29.2(8)
C1	9859(7)	6486(2)	9215(2)	28.3(10)
C2	9021(7)	7165(3)	9340(2)	30.8(10)
C3	7241(7)	7391(2)	9028.6(18)	30.1(9)
C4	6230(7)	6937(2)	8582(2)	27.7(10)
C5	7158(6)	6247(2)	8460.8(18)	29.5(9)
C6	8937(6)	6030(2)	8771(2)	28.5(10)
C7	3457(7)	7843(3)	8466(2)	37.2(11)
C8	3288(6)	6655(2)	7864.7(19)	28.1(10)
C9	4194(7)	6620(2)	7180(2)	27.1(10)
C10	3009(6)	6056(2)	6791.2(18)	24.5(9)
C11	3901(7)	5378(2)	6650(2)	27.9(10)
C12	2822(7)	4849(2)	6310.3(19)	27.9(9)
C13	810(6)	4992(2)	6096(2)	27.6(10)
C14	-96(6)	5659(2)	6227(2)	28.2(10)
C15	987(6)	6176(3)	6577.0(18)	27.4(9)
C16	-1938(6)	4583(3)	5409(2)	41.1(11)
C17	4204(7)	7381(2)	6873.0(19)	27(1)
C18	5292(6)	7380(2)	6224(2)	25.9(9)
N2	192(5)	7830.3(18)	5472.2(15)	23.9(8)
C19	200(6)	8651(2)	5485.3(19)	27.3(10)
C20	-1795(7)	8939(2)	5188(2)	36.8(11)
C21	608(6)	8905(2)	6167(2)	30.1(9)
C22	2561(7)	9155(2)	6343.2(19)	30.0(9)
C23	2982(8)	9366(2)	6969(2)	35.1(11)
C24	1433(8)	9320(3)	7423(2)	39.8(12)
C25	-532(8)	9082(3)	7253(2)	48.0(14)
C26	-947(7)	8867(3)	6628(2)	39.8(11)

Table S3. Anisotropic Displacement Parameters ($Å^2×10^3$) for Yoon35. The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+…]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	32.4(2)	31.9(2)	30.8(2)	0.2(2)	-5.38(19)	-1.6(2)
O1	34.3(17)	33.7(18)	34.3(18)	-3.6(14)	-3.4(14)	-5.9(14)
O2	25.6(15)	46.4(18)	40.9(17)	15.8(15)	6.2(14)	4.3(16)
O3	27.6(15)	36.0(18)	22.8(16)	0.3(14)	-0.3(12)	4.3(14)
N1	35(2)	29(2)	23.5(19)	-0.7(16)	-2.6(15)	0.7(17)
C1	30(2)	32(2)	23(2)	6.6(19)	2.4(18)	-3(2)
C2	39(3)	28(2)	25(2)	-5(2)	-2.7(19)	-4(2)
C3	39(2)	27(2)	25(2)	-3.6(17)	2(2)	2(2)
C4	34(2)	27(2)	22(2)	3.2(18)	1.8(18)	-2.1(19)
C5	37(2)	27(2)	25(2)	-2.5(17)	-0.8(18)	-5(2)
C6	35(2)	23(3)	27(2)	-1.4(19)	1.8(18)	-1.6(19)
C7	41(3)	34(3)	36(3)	0(2)	0(2)	8(2)
C8	28(2)	33(2)	23(2)	1.5(18)	-0.1(17)	-2.9(19)
C9	25(2)	32(2)	24(2)	4.0(19)	-1.0(17)	-3.0(19)
C10	25.9(19)	27(2)	20.4(19)	4.9(17)	1.4(16)	-2(2)
C11	25(2)	34(3)	25(2)	7.5(19)	-0.8(18)	0(2)
C12	30(2)	25(2)	28(2)	0.2(17)	3.0(19)	3(2)
C13	28(2)	31(2)	23(2)	1.4(19)	3.5(17)	-7(2)
C14	23(2)	35(3)	27(2)	4(2)	-0.6(18)	-1.1(19)
C15	29(2)	29(2)	24(2)	1(2)	2.8(16)	2(2)
C16	29(2)	54(3)	41(3)	-15(2)	-5(2)	-5(2)
C17	30(2)	27(2)	24(2)	-1.5(18)	1.7(17)	-3.0(19)
C18	25(2)	23(2)	30(2)	0.5(18)	-0.1(18)	-2.6(18)
N2	23.6(17)	31(2)	17.1(19)	-2.1(15)	-0.4(14)	1.7(15)
C19	34(2)	24(2)	24(2)	-0.1(16)	1.0(17)	-5.3(17)
C20	45(2)	31(2)	34(3)	0(2)	-8.0(19)	4(2)
C21	39(2)	23(2)	28(2)	-1(2)	-2.3(18)	1(2)
C22	33(2)	26(2)	31(2)	-0.2(17)	0(2)	1(2)
C23	38(2)	29(2)	39(3)	-6(2)	-10(2)	7(2)
C24	52(3)	38(3)	29(3)	-11(2)	-6(2)	6(2)
C25	51(3)	60(4)	33(3)	-15(2)	8(2)	-9(3)
C26	39(2)	47(3)	34(3)	-14(3)	4.2(19)	-3(3)

Table S4. Bond Lengths for Yoon35.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	C1	1.899(4)	C10	C11	1.393(6)
O1	C13	1.380(5)	C10	C15	1.391(5)
O1	C16	1.414(5)	C11	C12	1.383(6)
O2	C18	1.240(5)	C12	C13	1.392(6)
O3	C18	1.265(5)	C13	C14	1.374(6)

N1	C4	1.378(5)	C14	C15	1.381(6)
N1	C7	1.447(6)	C17	C18	1.525(6)
N1	C8	1.458(5)	N2	C19	1.497(5)
C1	C2	1.374(6)	C19	C20	1.517(6)
C1	C6	1.380(6)	C19	C21	1.519(6)
C2	C3	1.379(6)	C21	C22	1.385(6)
C3	C4	1.405(6)	C21	C26	1.389(6)
C4	C5	1.414(6)	C22	C23	1.389(6)
C5	C6	1.372(6)	C23	C24	1.376(7)
C8	C9	1.544(6)	C24	C25	1.381(7)
C9	C10	1.516(6)	C25	C26	1.389(6)
C9	C17	1.529(6)			

Table S5. Bond Angles for Yoon35.

Atom	**Atom**	**Atom**	**Angle/˚**	**Atom**	**Atom**	**Atom**	**Angle/˚**
C13	O1	C16	117.9(3)	C11	C12	C13	119.9(4)
C4	N1	C7	119.6(4)	O1	C13	C12	115.1(4)
C4	N1	C8	120.8(4)	C14	C13	O1	125.2(4)
C7	N1	C8	119.3(4)	C14	C13	C12	119.7(4)
C2	C1	Br1	120.3(3)	C13	C14	C15	119.7(4)
C2	C1	C6	120.1(4)	C14	C15	C10	122.2(4)
C6	C1	Br1	119.6(3)	C18	C17	C9	112.0(4)
C1	C2	C3	120.3(4)	O2	C18	O3	124.1(4)
C2	C3	C4	121.4(4)	O2	C18	C17	118.3(4)
N1	C4	C3	121.3(4)	O3	C18	C17	117.6(4)
N1	C4	C5	122.1(4)	N2	C19	C20	109.6(3)
C3	C4	C5	116.6(4)	N2	C19	C21	108.8(3)
C6	C5	C4	121.5(4)	C20	C19	C21	115.1(3)
C5	C6	C1	120.1(4)	C22	C21	C19	120.4(4)
N1	C8	C9	114.3(3)	C22	C21	C26	119.0(4)
C10	C9	C8	109.6(3)	C26	C21	C19	120.6(4)
C10	C9	C17	113.1(3)	C21	C22	C23	121.2(4)
C17	C9	C8	110.6(4)	C24	C23	C22	119.3(4)
C11	C10	C9	120.5(4)	C23	C24	C25	120.3(4)
C15	C10	C9	122.3(4)	C24	C25	C26	120.3(5)
C15	C10	C11	117.1(4)	C25	C26	C21	119.9(4)
C12	C11	C10	121.4(4)				

Table S6. Hydrogen Bonds for Yoon35.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N2	H2A	O2[1]	0.91	1.86	2.765(4)	171.1
N2	H2B	O3	0.91	1.84	2.710(4)	158.5
N2	H2C	O3[2]	0.91	1.82	2.724(4)	172.1

[1]-1+X,+Y,+Z; [2]-1/2+X,3/2-Y,1-Z

Table S7. Torsion Angles for Yoon35.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Br1	C1	C2	C3	-177.6(3)	C9	C17	C18	O3	122.8(4)
Br1	C1	C6	C5	177.2(3)	C10	C9	C17	C18	-62.5(5)
O1	C13	C14	C15	178.0(4)	C10	C11	C12	C13	0.8(6)
N1	C4	C5	C6	-177.2(4)	C11	C10	C15	C14	-1.4(6)
N1	C8	C9	C10	176.4(3)	C11	C12	C13	O1	-179.4(4)
N1	C8	C9	C17	-58.2(5)	C11	C12	C13	C14	-0.3(6)
C1	C2	C3	C4	0.5(6)	C12	C13	C14	C15	-0.9(6)
C2	C1	C6	C5	-1.2(6)	C13	C14	C15	C10	1.8(6)
C2	C3	C4	N1	176.8(4)	C15	C10	C11	C12	0.1(6)
C2	C3	C4	C5	-1.3(6)	C16	O1	C13	C12	-165.2(4)
C3	C4	C5	C6	0.9(6)	C16	O1	C13	C14	15.8(6)
C4	N1	C8	C9	-79.6(5)	C17	C9	C10	C11	130.5(4)
C4	C5	C6	C1	0.3(6)	C17	C9	C10	C15	-51.5(5)
C6	C1	C2	C3	0.8(6)	N2	C19	C21	C22	102.3(4)
C7	N1	C4	C3	-1.7(6)	N2	C19	C21	C26	-75.5(5)
C7	N1	C4	C5	176.4(4)	C19	C21	C22	C23	-177.9(4)
C7	N1	C8	C9	106.2(4)	C19	C21	C26	C25	178.2(5)
C8	N1	C4	C3	-175.9(4)	C20	C19	C21	C22	-134.4(4)
C8	N1	C4	C5	2.2(6)	C20	C19	C21	C26	47.8(6)
C8	C9	C10	C11	-105.6(4)	C21	C22	C23	C24	0.7(6)
C8	C9	C10	C15	72.4(5)	C22	C21	C26	C25	0.3(7)
C8	C9	C17	C18	174.1(3)	C22	C23	C24	C25	-1.6(7)
C9	C10	C11	C12	178.2(4)	C23	C24	C25	C26	1.9(8)
C9	C10	C15	C14	-179.5(4)	C24	C25	C26	C21	-1.3(8)
C9	C17	C18	O2	-57.5(5)	C26	C21	C22	C23	0.0(7)

Table S8. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Yoon35.

Atom	*x*	*y*	*z*	U(eq)
H2	9671	7480	9643	37
H3	6686	7863	9117	36
H5	6535	5927	8157	35
H6	9534	5565	8679	34
H7A	3229	7860	8930	56
H7B	2122	7896	8244	56
H7C	4385	8245	8340	56
H8A	1817	6813	7838	34
H8B	3308	6156	8051	34
H9	5670	6450	7214	33
H11	5279	5278	6789	33
H12	3453	4389	6223	33
H14	-1460	5763	6077	34
H15	329	6629	6675	33
H16A	-3042	4751	5698	62
H16B	-2398	4140	5184	62
H16C	-1627	4969	5096	62
H17A	2752	7551	6818	32
H17B	4919	7730	7162	32
H2A	-862	7660	5722	29
H2B	1428	7659	5624	29
H2C	5	7673	5063	29
H19	1387	8823	5214	33
H20A	-2993	8741	5422	55
H20B	-1868	8785	4739	55
H20C	-1811	9476	5212	55
H22	3632	9182	6030	36
H23	4324	9542	7083	42
H24	1718	9452	7854	48
H25	-1605	9066	7566	58
H26	-2293	8695	6516	48

(*S*)-1-phenylethanaminium (*S*)-4-((4-bromophenyl)(methyl)amino)-3-methylbutanoate

Data Collection

A colorless crystal with approximate dimensions 0.788 x 0.121 x 0.084 mm^3 was selected under oil under ambient conditions and attached to the tip of a MiTeGen MicroMount©. The crystal was mounted in a stream of cold nitrogen at 100(1) K and centered in the X-ray beam by using a video camera.

The crystal evaluation and data collection were performed on a Bruker SMART APEXII diffractometer with Cu K_α (λ = 1.54178 Å) radiation and the diffractometer to crystal distance of 4.03 cm.

The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 41 frames collected at intervals of 0.6º in a 25º range about ω with the exposure time of 5 seconds per frame. The reflections were successfully indexed by an automated indexing routine built in the APEXII program. The final cell constants were calculated from a set of 9976 strong reflections from the actual data collection.

The data were collected by using the full sphere data collection routine to survey the reciprocal space to the extent of a full sphere to a resolution of 0.82 Å. A total of 29437 data were harvested by collecting 31 sets of frames with 0.6º scans in ω and φ with an exposure time 10-20 sec per frame. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements.[8]

Structure Solution and Refinement

The systematic absences in the diffraction data were consistent for the space groups $P2_1$ and $P2_1/m$. The *E*-statistics strongly suggested the non-centrosymmetric space group $P2_1$ that yielded chemically reasonable and computationally stable results of refinement.[9,10,11]

A successful solution by the direct methods provided most non-hydrogen atoms from the *E*-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients. The ammonium H atoms were located from the difference map and refined independently. All other hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients.

The asymmetric unit of the Yoon36 consists of the carboxylate shown in Figure S2 and the *S*-methylbenzyl ammonium counter ion. Bond distance restraints were used on the N-H bonds of the *S*-methylbenzyl ammonium cation to ensure a chemically reasonable and computationally stable refinement.

The absolute configuration of the carboxylate shown in Figure S2 is *S*. The absolute configuration was unequivocally established by anomalous dispersion, and it is consistent with the known configuration of the *S*-methylbenzyl ammonium reference ion.

The carboxylate and ammonium ions pack to form an infinite chain of two symmetry-independent hydrogen-bonded rings in the crystallographic *b* direction. Each ring is formed by hydrogen bonds between N2, O1, and O2 of adjacent ions (graph set notation: $R_4^3(10)R_4^3(10)$). The two independent rings share an edge formed by hydrogen bond N2-H2B…O1 between adjacent ions.

The final least-squares refinement of 230 parameters against 3904 data resulted in residuals *R* (based on F^2 for $I \geq 2\sigma$) and *wR* (based on F^2 for all data) of 0.0314 and 0.0854, respectively. The final difference Fourier map was featureless.

Summary

Crystal Data for $C_{20}H_{27}N_2O_2Br$ (*M* =407.34 g/mol): monoclinic, space group $P2_1$ (no. 4), *a* = 11.787(4) Å, *b* = 6.031(2) Å, *c* = 15.094(4) Å, β = 111.35(2)°, *V* = 999.5(6) $Å^3$, *Z* = 2, *T* = 100.0 K, μ(CuKα) = 2.915 mm^{-1}, *Dcalc* = 1.353 g/cm^3, 29437 reflections measured (6.286° ≤ 2Θ ≤ 144.632°), 3904 unique (R_{int} = 0.0316, R_{sigma} = 0.0142) which were used in all calculations. The final R_1 was 0.0314 (I > 2σ(I)) and wR_2 was 0.0855 (all data).

The molecular diagram is drawn with 50% probability ellipsoids. All H atoms except those on heteroatoms and chiral carbons are omitted for clarity.

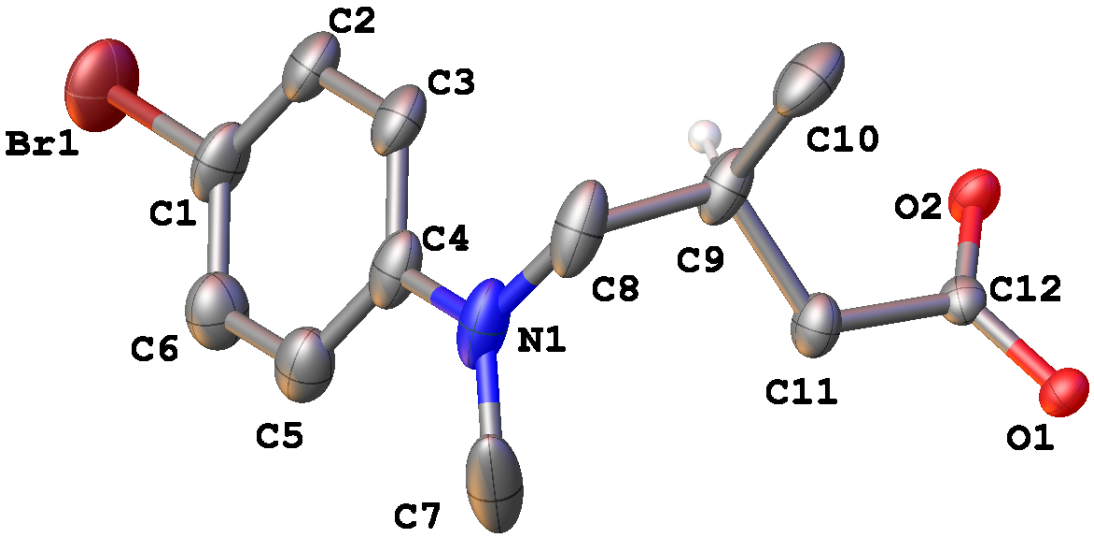


Figure S2. A molecular drawing of (*S*)-1-phenylethanaminium (*S*)-4-((4-bromophenyl)(methyl)amino)-3-methylbutanoate.

Table S9. Crystal data and structure refinement for Yoon36.

Identification code	Yoon36
Empirical formula	$[C_8H_{12}N]^+ [C_{12}H_{15}BrNO_2]^-$
Formula weight	407.34
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1$
a/Å	11.787(4)
b/Å	6.031(2)
c/Å	15.094(4)
α/°	90
β/°	111.35(2)
γ/°	90
Volume/Å^3	999.5(6)
Z	2
ρ_{calc} g/cm^3	1.353
μ/mm^{-1}	2.915
F(000)	424.0
Crystal size/mm^3	0.788 × 0.121 × 0.084
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	6.286 to 144.632
Index ranges	-14 ≤ h ≤ 14, -7 ≤ k ≤ 7, -18 ≤ l ≤ 18
Reflections collected	29437
Independent reflections	3904 [R_{int} = 0.0316, R_{sigma} = 0.0142]
Data/restraints/parameters	3904/4/230

Goodness-of-fit on F^2	1.085
Final R indexes [I>=2σ (I)]	R_1 = 0.0314, wR_2 = 0.0850
Final R indexes [all data]	R_1 = 0.0317, wR_2 = 0.0854
Largest diff. peak/hole / e $Å^{-3}$	0.76/-0.70
Flack parameter	-0.03(2)

Table S10. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for Yoon36. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Br1	8644.5(4)	3468.3(7)	2576.9(3)	57.23(17)
O1	8689.5(18)	1131(3)	9128.8(15)	21.6(4)
O2	8285.1(19)	3901(3)	8084.8(14)	25.8(5)
N1	7238(3)	-1584(7)	5505.7(19)	44.9(7)
C1	8221(2)	1868(4)	3493.4(15)	40.4(8)
C2	7332(2)	2723(3)	3799.8(15)	38.0(8)
C3	7003.4(18)	1576(4)	4468.4(15)	36.3(8)
C4	7564(2)	-427(4)	4830.7(14)	36.7(8)
C5	8454(2)	-1282(3)	4524.3(16)	42.5(8)
C6	8782(2)	-134(4)	3855.7(17)	43.0(8)
C7	7972(6)	-3503(7)	5977(3)	65.7(15)
C8	6313(4)	-768(8)	5843(2)	47.4(10)
C9	6713(3)	1074(6)	6601(2)	34.4(8)
C10	5626(3)	1842(8)	6833(3)	45.1(9)
C11	7740(3)	222(5)	7487(2)	28.6(6)
C12	8263(2)	1905(5)	8288(2)	20.5(5)
N2	8926(2)	6699(4)	9617.7(17)	19.1(5)
C13	6208(3)	7445(5)	9055(2)	24.8(6)
C14	4986(3)	7079(6)	8518(2)	28.1(6)
C15	4445(3)	5072(6)	8570(2)	30.3(7)
C16	5119(3)	3429(6)	9172(2)	30.9(6)
C17	6346(3)	3782(5)	9709(2)	26.7(6)
C18	6896(3)	5782(5)	9650(2)	23.0(6)
C19	8229(2)	6158(5)	10243(2)	21.7(5)
C20	8432(3)	7991(5)	10980(2)	27.4(6)

Table S11. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for Yoon36. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	79.7(3)	56.6(3)	44.7(2)	10.5(2)	33.7(2)	-14.9(2)
O1	20.3(9)	22.2(10)	19.3(9)	1.3(8)	3.8(7)	-1.4(7)
O2	31.9(10)	22.5(11)	20.7(9)	2.9(8)	6.7(8)	-3.3(8)
N1	63.4(18)	48.8(17)	22.5(12)	-3.1(16)	15.6(12)	-22.8(18)

C1	53(2)	44(2)	24.5(15)	6.5(15)	13.8(14)	-16.0(17)
C2	38.7(16)	48(2)	21.4(15)	3.4(13)	3.3(13)	-5.1(15)
C3	32.1(15)	51(2)	20.3(14)	0.9(15)	3.4(12)	-6.0(15)
C4	45.6(18)	39.3(18)	21.5(14)	-2.5(14)	7.8(14)	-18.2(16)
C5	60(2)	33.4(19)	33.1(16)	-1.9(16)	16.2(15)	-9.0(18)
C6	54(2)	42(2)	39.3(19)	-0.7(16)	24.2(17)	-7.4(17)
C7	144(5)	25.2(18)	43(2)	-3.1(16)	52(3)	-14(2)
C8	52(2)	64(3)	23.1(16)	-4.2(16)	11.2(15)	-32.0(19)
C9	32.4(15)	46.3(19)	20.3(14)	1.3(14)	4.6(12)	-17.9(15)
C10	29.2(16)	69(3)	30.2(17)	10.7(18)	2.4(13)	-3.6(17)
C11	31.1(15)	30.1(16)	22.9(14)	-4.3(12)	7.7(12)	-8.3(12)
C12	15.8(11)	23.9(13)	20.7(13)	-2.0(11)	5.4(9)	-1.1(10)
N2	16.4(10)	18.1(11)	20.5(12)	1.6(10)	4.0(9)	0.5(9)
C13	21.6(13)	24.8(14)	27.8(15)	4.2(12)	8.8(11)	-0.7(11)
C14	20.8(13)	32.6(16)	29.7(15)	6.0(13)	7.8(11)	2.2(12)
C15	21.2(13)	36.0(17)	34.0(17)	0.0(13)	10.5(12)	-2.8(12)
C16	29.7(14)	26.8(14)	41.5(16)	2.1(16)	19.1(12)	-4.2(14)
C17	26.1(13)	22.6(15)	35.4(14)	6.6(13)	16.2(11)	5.1(12)
C18	22.6(13)	24.2(14)	24.9(14)	2.1(12)	11.9(11)	1.9(11)
C19	19.9(12)	22.3(13)	22.9(13)	5.0(11)	7.6(10)	3.8(10)
C20	26.1(13)	30.9(17)	24.9(14)	-0.2(12)	8.7(11)	5.6(12)

Table S12. Bond Lengths for Yoon36.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	C1	1.8964(16)	C9	C10	1.518(5)
O1	C12	1.272(4)	C9	C11	1.529(4)
O2	C12	1.245(4)	C11	C12	1.526(4)
N1	C4	1.400(3)	N2	C19	1.496(4)
N1	C7	1.465(7)	C13	C14	1.389(4)
N1	C8	1.447(6)	C13	C18	1.393(4)
C1	C2	1.3900	C14	C15	1.384(5)
C1	C6	1.3900	C15	C16	1.384(5)
C2	C3	1.3900	C16	C17	1.393(4)
C3	C4	1.3900	C17	C18	1.388(4)
C4	C5	1.3900	C18	C19	1.516(4)
C5	C6	1.3900	C19	C20	1.523(4)
C8	C9	1.540(5)			

Table S13. Bond Angles for Yoon36.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C4	N1	C7	118.5(3)	C11	C9	C8	109.8(3)

C4	N1	C8	121.9(4)	C12	C11	C9	115.6(3)
C8	N1	C7	119.0(3)	O1	C12	C11	116.5(3)
C2	C1	Br1	118.98(13)	O2	C12	O1	124.4(3)
C2	C1	C6	120.0	O2	C12	C11	119.1(3)
C6	C1	Br1	121.02(13)	C14	C13	C18	119.9(3)
C3	C2	C1	120.0	C15	C14	C13	120.5(3)
C4	C3	C2	120.0	C14	C15	C16	119.8(3)
C3	C4	N1	120.1(2)	C15	C16	C17	119.9(3)
C3	C4	C5	120.0	C18	C17	C16	120.4(3)
C5	C4	N1	119.9(2)	C13	C18	C19	120.5(3)
C6	C5	C4	120.0	C17	C18	C13	119.5(3)
C5	C6	C1	120.0	C17	C18	C19	120.0(3)
N1	C8	C9	116.1(3)	N2	C19	C18	110.4(2)
C10	C9	C8	109.6(3)	N2	C19	C20	109.0(2)
C10	C9	C11	111.5(3)	C18	C19	C20	113.2(2)

Table S14. Hydrogen Bonds for Yoon36.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N2	H2A	O1[1]	0.80(2)	1.97(2)	2.760(3)	168(3)
N2	H2B	O1[2]	0.80(2)	2.00(2)	2.779(3)	163(3)
N2	H2C	O2	0.81(2)	1.93(2)	2.738(3)	178(4)

[1]+X,1+Y,+Z; [2]2-X,1/2+Y,2-Z

Table S15. Torsion Angles for Yoon36.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Br1	C1	C2	C3	179.76(18)	C8	N1	C4	C5	-179.7(2)
Br1	C1	C6	C5	-179.75(18)	C8	C9	C11	C12	177.8(3)
N1	C4	C5	C6	-179.8(2)	C9	C11	C12	O1	150.5(3)
N1	C8	C9	C10	176.5(3)	C9	C11	C12	O2	-31.8(4)
N1	C8	C9	C11	-60.7(4)	C10	C9	C11	C12	-60.5(4)
C1	C2	C3	C4	0.0	C13	C14	C15	C16	1.1(5)
C2	C1	C6	C5	0.0	C13	C18	C19	N2	-58.9(4)
C2	C3	C4	N1	179.8(2)	C13	C18	C19	C20	63.6(3)
C2	C3	C4	C5	0.0	C14	C13	C18	C17	-0.8(4)
C3	C4	C5	C6	0.0	C14	C13	C18	C19	-179.7(3)
C4	N1	C8	C9	-79.2(4)	C14	C15	C16	C17	-1.4(5)
C4	C5	C6	C1	0.0	C15	C16	C17	C18	0.5(5)
C6	C1	C2	C3	0.0	C16	C17	C18	C13	0.6(4)
C7	N1	C4	C3	-170.8(3)	C16	C17	C18	C19	179.5(3)
C7	N1	C4	C5	9.0(4)	C17	C18	C19	N2	122.2(3)

C7	N1	C8	C9	92.0(5)		C17	C18	C19	C20	-115.3(3)	
C8	N1	C4	C3	0.5(4)		C18	C13	C14	C15	0.0(5)	

Table S16. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Yoon36.

Atom	*x*	*y*	*z*	U(eq)
H2	6948	4092	3552	46
H3	6395	2160	4678	44
H5	8837	-2651	4772	51
H6	9390	-719	3646	52
H7A	7901	-4666	5507	99
H7B	7679	-4070	6464	99
H7C	8826	-3057	6277	99
H8A	6006	-2034	6109	57
H8B	5623	-202	5290	57
H9	7025	2357	6337	41
H10A	4968	2294	6247	68
H10B	5866	3102	7272	68
H10C	5344	625	7131	68
H11A	7432	-1065	7739	34
H11B	8410	-315	7294	34
H2A	8770(30)	7930(40)	9410(20)	16(8)
H2B	9640(20)	6790(60)	9940(20)	13(7)
H2C	8740(40)	5850(60)	9180(20)	24(10)
H13	6574	8827	9015	30
H14	4519	8216	8113	34
H15	3613	4823	8192	36
H16	4746	2061	9219	37
H17	6809	2648	10118	32
H19	8565	4749	10589	26
H20A	8110	9392	10657	41
H20B	9305	8148	11344	41
H20C	8009	7613	11411	41

X. Chloride Effect Control Experiments

Procedure. The experiments summarized in Table S17 below were conducted using the following procedure. A dry 25 mL Schlenk tube was charged with $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (0.02 equiv.). Sc(III) Lewis acid (0.15 equiv), ligand **1c** (0.20 equiv), and TBACl (0.30 equiv) were added as appropriate. A solution containing amine **1** (1 equiv) and acceptor **2b** (1.5 equiv) in acetonitrile (0.05 M) was then added. The reaction was degassed by 3 freeze/pump/thaw cycles under nitrogen in the dark. The reaction was then allowed to stir while being irradiated by a 23 W (1280 lumen) compact fluorescent lamp at a distance of 30 cm for the time indicated. The reaction mixture was loaded directly through silica, concentrated by rotary evaporation, and analyzed by ^{1}H NMR using phenanthrene as an internal standard.

Table S17. Control experiments probing chloride effect

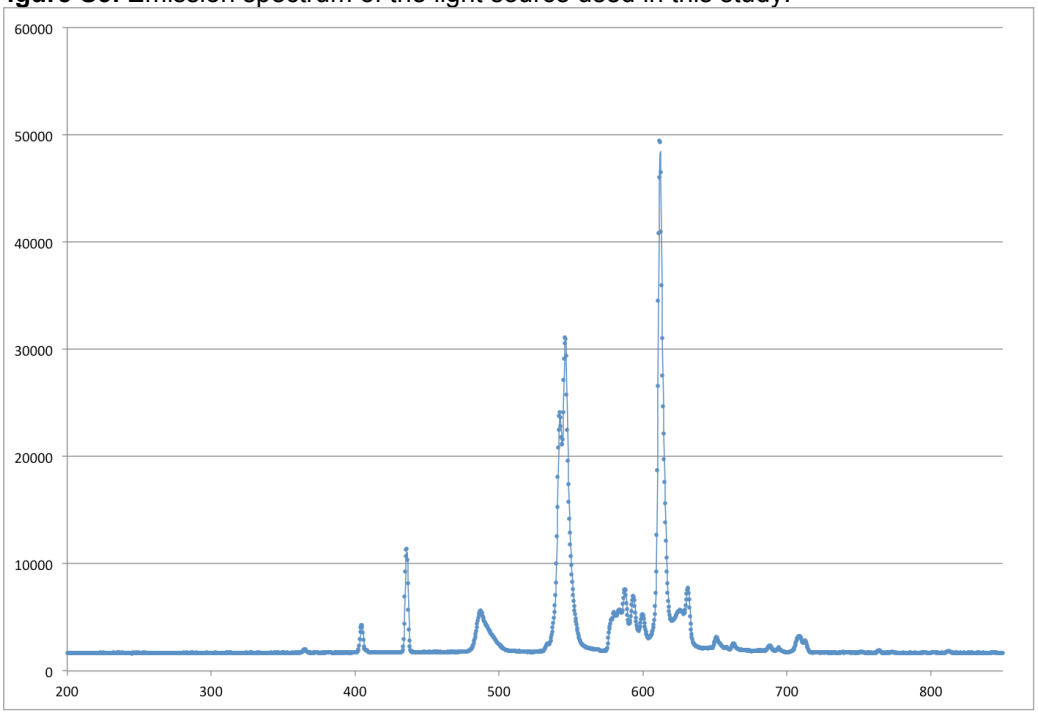
entry	Lewis acid	additive	time	yield[a]
1	none	none	3 h	25%
2	none	30 mol% $Bu_4N^+Cl^-$	3 h	28%
3	**1c**•$Sc(OTf)_3$	none	2 h	67%
4	**1c**•$Sc(OTf)_3$	30 mol% $Bu_4N^+Cl^-$	2 h	98%
5	**1c**•$Sc(Cl)_3$	none	6 h	61%

[a] Determined by ^{1}H NMR analysis against a calibrated internal standard.

XI. CFL Emission

The emission spectrum of the light source utilized in this study was analyzed using an Ocean Optics USB 2000+ UV-vis spectrometer and is shown in Figure S3.

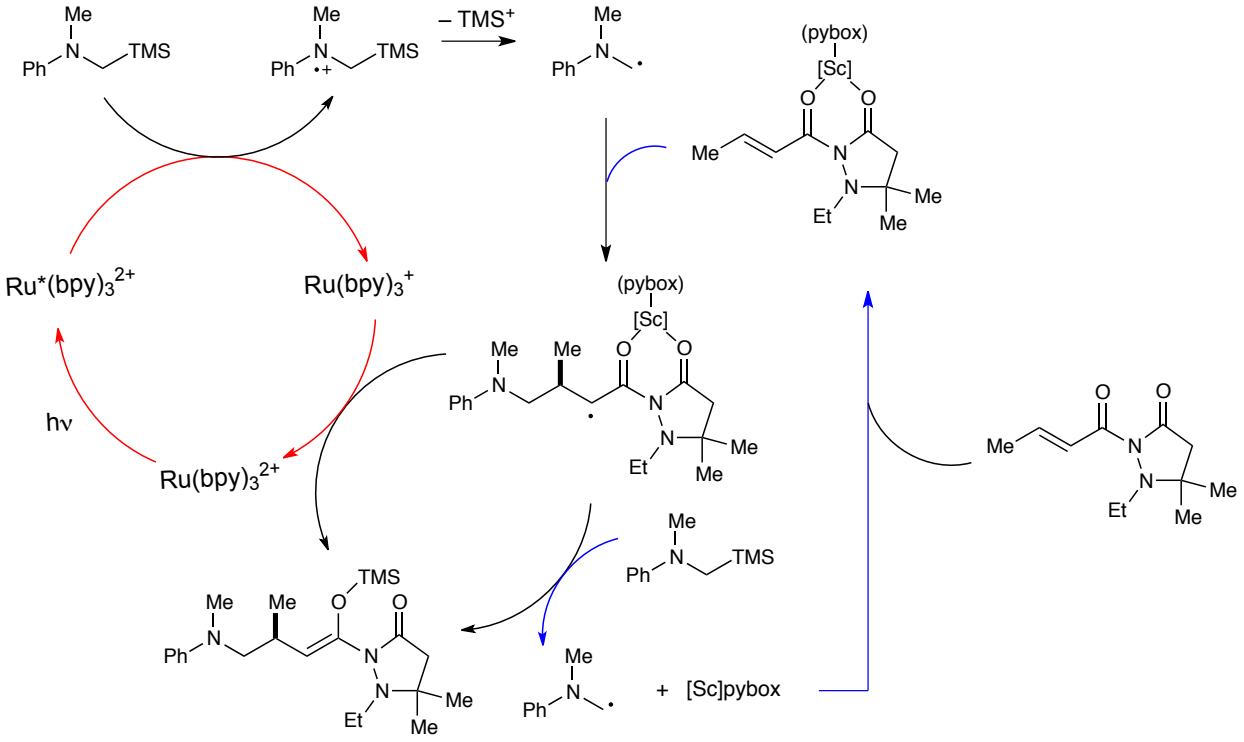
Figure S3. Emission spectrum of the light source used in this study.



The power density of the 435 nm emission band at the reaction distance of 30 cm was measured to be 28 mW/cm^2 using a Newport Multi-Function Optical Meter outfitted with a low-power UV enhanced silicon photodetector (model 818-UV).

XII. Proposed mechanism. Based upon prior investigations of Brønsted acid-catalyzed α-amino radical additions recently conducted in our laboratory,[12] we propose the mechanism depicted in Scheme S-1 to account for the reaction described in this manuscript. The reaction involves two independent catalytic functions — a photoredox process (red) and a Lewis acid catalyzed process (blue). The photocatalyst initates the reaction by photooxidation of the α-silylamine to afford an α-amino radical. The Lewis acid controls the stereoselectivity of a product-forming chain process by activating the *N*-acyl pyrazolidinone Michael acceptor towards nucleophilic attack.

Scheme S-1



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