Supporting Information for:

Three-Component 1,2-Carboamidation of Bridged Bicyclic Alkenes *via* Rh^{III}-Catalyzed Addition of C–H Bonds and Amidating Reagents

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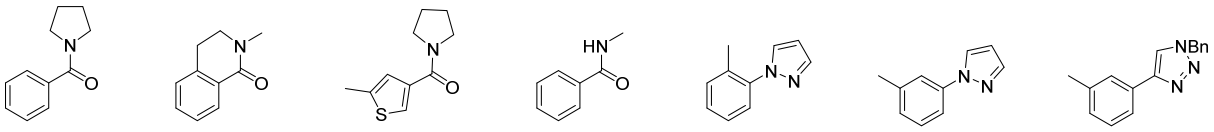
Table of Contents

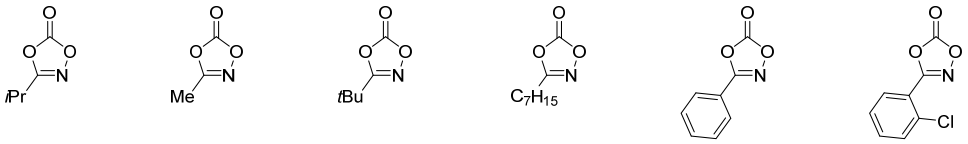
I. Structures of Starting Materials

C-H Bond Substrates

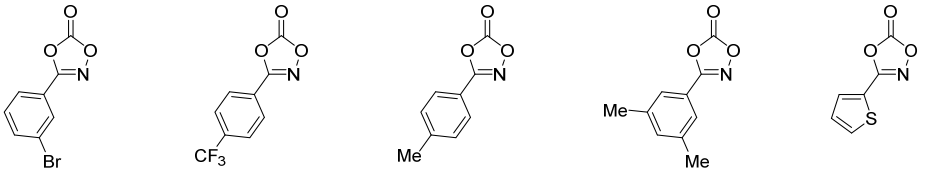


1a **1b** **1c** **1d** **1e** **1f** **1g**

Dioxazolones

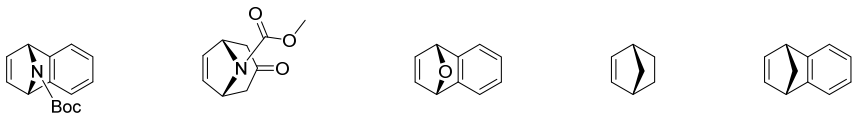


2a **2b** **2c** **2d** **2e** **2f**



2g **2h** **2i** **2j** **2k**

Bridged Bicyclic Alkenes



3a **3b** **3c** **3d** **3e**

II. General Methods

Unless otherwise noted, all Rh^{III}-catalyzed reactions were set up in a N_2-filled glovebox, using glassware that was oven-dried (130 °C) and evacuated while hot prior to use. Unless otherwise indicated, all reactions for substrate preparation were carried out on the benchtop under a N_2 atmosphere. Solvents were sparged with argon and purified by elution through a column of activated alumina under argon before use, and were stored in a N_2 filled glovebox in the presence of activated 3Å molecular sieves (molecular sieves were dried at 200 °C overnight under vacuum). Unless otherwise noted, all reagents were purchased from commercial sources and used without further purification. Microwave vials and caps were purchased from Biotage with part numbers 351521 and 352298, respectively. Product purification was performed by either flash column chromatography with SiliaFlash®P60 (230-400 mesh) silica gel, reverse phase chromatography with a Teledyne Isco automated chromatography system using C-18 gold columns, or preparative thin-layer chromatography with plates from Analtech (1 mm SiO_2, 20 x 20 cm). ^{1}H, ^{13}C, and ^{19}F-NMR spectra were recorded on either a 400, 500, or 600 MHz instrument. Data are reported in the following format: chemical shift in ppm, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, bs = broad singlet, m = multiplet, dd = doublet of doublets, etc.), coupling constant J in

Hz, and integration. NMR solvents were used as received. NMR chemical shifts are reported in ppm relative to $CDCl_3$ (7.26 ppm for ^1H and 77.16 ppm for ^{13}C), CD_3CN (1.94 ppm for ^1H and 1.32 ppm for ^{13}C), or DMSO-*d*$_6$ (2.50 ppm for ^1H and 39.52 ppm for ^{13}C). Partial IR spectra are reported. High-resolution mass spectra (HRMS) were obtained using electrospray ionization (ESI) on a time of flight (TOF) mass spectrometer. Compounds that did not ionize using this method were sent to UIUC for analysis using an electron ionization mass spectrometer. Enantiomeric ratios were determined using an Agilent 1100 series HPLC equipped with Chiralpak AD-H, OD-H, and IB analytical columns (4.6 mm x 25 cm) and a multiwavelength detector.

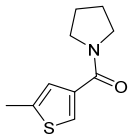
III. Preparation of Catalysts and Substrates

Catalysts/Additives: $[Cp^*RhCl_2]_2$,[1] $Cp^*Rh(OAc)_2$,[2] chiral Rh precatalyst **6**,[3,4,5] and $[Cp^*Rh(MeCN)_3](SbF_6)_2$[6] were synthesized according to published literature procedures.

C–H Bond Substrates: The previously reported compounds 1-benzyl-4-(*m*-tolyl)-1*H*-1,2,3-triazole,[7] phenyl(pyrrolidin-1-yl)methanone,[8] 2-methyl-3,4-dihydroisoquinolin-1(*2H*)-one,[9] 1-(o-tolyl)-1H-pyrazole,[10] and 1-(m-tolyl)-1H-pyrazole[10] were synthesized according to published literature procedures. *N*-Methylbenzamide was purchased commercially and used without further purification.

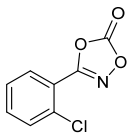
Dioxazolones: The previously reported compounds 3-phenyl-1,4,2-dioxazol-5-one, 3-(p-tolyl)-1,4,2-dioxazol-5-one, 3-methyl-1,4,2-dioxazol-5-one, and 3-heptyl-1,4,2-dioxazol-5-one were synthesized according to a published literature procedure.[11] 3-isopropyl-1,4,2-dioxazol-5-one, 3-(*tert*-butyl)-1,4,2-dioxazol-5-one and 3-(thiophen-2-yl)-1,4,2-dioxazol-5-one were synthesized according to the literature procedure[11] and the characterization data matched those reported in the literature.[12]

Alkene Substrates: The previously reported compounds *tert*-butyl 1,4-dihydro-1,4-epiminonaphthalene-9-carboxylate,[13] 1,4-dihydro-1,4-epoxynaphthalene,[14, 15] 1,4-dihydro-1,4-methanonaphthalene,[16] and methyl 3-oxo-8-azabicyclo[3.2.1]oct-6-ene-8-carboxylate,[17] were synthesized according to published literature procedures. Bicyclo[2.2.1]hept-2-ene was purchased from laboratory chemical supply companies and used without further purification.

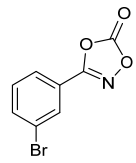


(5-Methylthiophen-3-yl)(pyrrolidin-1-yl)methanone (1c): A flame-dried, 50 mL round-bottom flask was charged with 5-methylthiophene-3-carboxylic acid (569 mg, 4.00 mmol, 1 equiv) along with a stir bar. The flask was flushed with nitrogen, followed by the addition of thionyl chloride neat (4.00 mL, 54.8 mmol, 13.7 equiv). The mixture was refluxed at 85 °C in a preheated oil bath for 30 min and was then cooled to room temperature. The mixture was then concentrated down in the same flask to a brown oil. The flask was flushed with nitrogen, followed by the addition of dry CH_2Cl_2 (10 mL). The solution was cooled to 0 °C in an ice-bath with stirring, followed by the dropwise addition of pyrrolidine (0.394 mL, 4.80 mmol, 1.2 equiv). After 1 min, triethylamine (0.669 mL, 4.80 mmol, 1.2 equiv) was added dropwise, and stirring was continued for 5 min. After 5 min, the mixture was warmed to rt, stirring for an additional 2 h. The mixture was washed with water (1x), sat. $NaHCO_3$ solution (1x), and brine (1x) successively. The organic layer was then dried over $MgSO_4$ and was concentrated

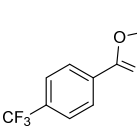
in vacuo. Purification by silica gel chromatography (100% ethyl acetate) afforded the product **1c** (606 mg, 78% yield) as an orange solid. IR (neat): 3112, 2956, 2871, 1598, 1456, 1424, 854, 739 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 1.5 Hz, 1H), 7.00 – 6.97 (m, 1H), 3.63 – 3.48 (m, 4H), 2.44 (d, *J* = 1.1 Hz, 3H), 2.03 – 1.76 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.6, 139.7, 137.8, 125.8, 125.2, 49.2, 46.5, 26.5, 24.3, 15.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{10}H_{14}NOS^+$: 196.0796. Found 196.0788.



3-(2-Chlorophenyl)-1,4,2-dioxazol-5-one (2f): A 100 mL round-bottom flask was charged with hydroxylamine chloride (1.57 g, 22.6 mmol, 1.5 equiv), sodium carbonate (4.78 g, 45.1 mmol, 3 equiv), and 45 mL of a 1:1 solution of EtOAc/water. The solution was stirred at 0 °C and 2-chlorobenzoyl chloride (1.68 mL, 15.0 mmol, 1 equiv) was added dropwise. The solution was warmed to rt and stirred for 2 h. The reaction was quenched with 75 mL of 1M HCl, and the resulting mixture was extracted with EtOAc (3x) and dried over $MgSO_4$. The crude hydroxamic acid was concentrated and dried in vacuo. The hydroxamic acid was taken up in 75 mL dry CH_2Cl_2 under N_2, and 1,1'-carbonyldiimidazole (2.44 g, 15.0 mmol, 1 equiv) was added to the flask. Reaction progress was monitored by TLC, and the reaction was quenched after 20 min with 75 mL of 1M HCl. The crude product was then extracted with CH_2Cl_2 (2x), dried over $MgSO_4$, and concentrated in vacuo. Purification by silica gel chromatography (50% CH_2Cl_2 in hexanes) afforded the product **2f** (1.21 g, 41% yield) as a white solid. IR (neat): 1862, 1834, 1590, 1335, 1173, 1040, 974, 754 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.8 Hz, 1H), 7.57 (d, *J* = 4.2 Hz, 2H), 7.45 (dt, *J* = 8.4, 4.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5, 153.5, 134.3, 133.8, 131.7, 130.7, 127.5, 119.6. HRMS (EI) m/z: [M/Z] Calcd. for $C_8H_4ClNO_3$: 196.9880. Found 196.9875.

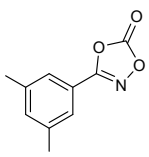


3-(3-Bromophenyl)-1,4,2-dioxazol-5-one (2g): A 100 mL round-bottom flask was charged with hydroxylamine chloride (1.25 g, 18.0 mmol, 1.5 equiv), sodium carbonate (3.82 g, 36.0 mmol, 3 equiv), and 36 mL of a 1:1 solution of EtOAc/water. The solution was stirred at 0 °C and 3-bromobenzoyl chloride (1.58 mL, 12.0 mmol, 1 equiv) was added dropwise. The solution was warmed to rt and stirred for 2 h. The reaction was quenched with 60 mL of 1M HCl, and the resulting mixture was extracted with EtOAc (3x) and dried over $MgSO_4$. The crude hydroxamic acid was concentrated and dried in vacuo. The hydroxamic acid was taken up in 60 mL of dry CH_2Cl_2 under N_2, and 1,1'-carbonyldiimidazole (1.96 g, 12.0 mmol, 1 equiv) was added to the flask. Reaction progress was monitored by TLC, and the reaction was quenched after 20 min with 60 mL of 1M HCl. The crude product was then extracted with CH_2Cl_2 (2x), dried over $MgSO_4$, and concentrated in vacuo. Purification by silica gel chromatography (50% CH_2Cl_2 in hexanes) afforded the product **2g** (1.02 g, 35% yield) as a white solid. IR (neat): 3066, 1838, 1622, 1561, 1367, 1172, 984, 755 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.97 (m, 1H), 7.82 – 7.75 (m, 2H), 7.44 (t, *J* = 8.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5, 153.5, 137.0, 131.1, 129.6, 125.3, 123.6, 122.1. HRMS (EI) m/z: [M/Z] Calcd. for $C_8H_4BrNO_3$: 240.9375. Found 240.9370.



3-[4-(Trifluoromethyl)phenyl]-1,4,2-dioxazol-5-one (2h): A flame dried 500 mL round-bottom flask was charged with 4-(trifluoromethyl)benzoic acid (3.80 g, 20 mmol, 1 equiv) in 100 mL of dry CH_2Cl_2 and cooled to 0 °C. Oxalyl chloride (12.0 mL, 24 mmol, 1.2 equiv) was added along with 8 drops of DMF. The solution was brought to stirring reflux at 40 °C in a preheated oil bath for 2 h, and concentrated in

vacuo. The crude acid chloride was then dissolved in minimal EtOAc, and added dropwise to a 250 mL round-bottom flask containing hydroxylamine chloride (2.08 g, 30.0 mmol, 1.5 equiv), sodium carbonate (6.36 g, 6.00 mmol, 3 equiv), and 60 mL of a 1:1 solution of EtOAc/water at 0 °C. The solution was warmed to rt and stirred for 2 h. The reaction was quenched with 100 mL of 1M HCl, and the resulting mixture was extracted with EtOAc (3x) and dried over $MgSO_4$. The crude hydroxamic acid was concentrated and dried in vacuo. The hydroxamic acid was taken up in 100 mL of dry CH_2Cl_2 under N_2, and 1,1'-carbonyldiimidazole (3.24 g, 20.0 mmol, 1 equiv) was added to the flask. Reaction progress was monitored by TLC, and the reaction was quenched after 20 min with 100 mL of 1M HCl. The crude product was then extracted with CH_2Cl_2 (2x), dried over $MgSO_4$, and concentrated in vacuo. Purification by silica gel chromatography (50% CH_2Cl_2 in hexanes) afforded the product **2h** (2.11 g, 46% yield) as a white solid. IR (neat): 1863, 1825, 1320, 1069, 1016, 971, 762 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.2 Hz, 2H), 7.83 (d, J = 8.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6, 153.4, 135.5 (q, $2J_{C–F}$ = 33.3 Hz), 127.3, 126.6 (q, $3J_{C–F}$ = 3.8 Hz), 123.6, 123.2 (q, $1J_{C–F}$ = 272.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.46. HRMS (EI) m/z: [M/Z] Calcd. for $C_9H_4F_3NO_3$: 231.0143. Found 231.0148.

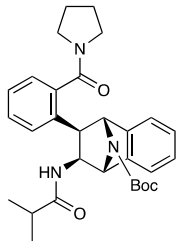


3-(3,5-Dimethylphenyl)-1,4,2-dioxazol-5-one (2j): A flame dried 500 mL round-bottom flask was charged with 3,5-dimethylbenzoic acid (5.00 g, 33.0 mmol, 1 equiv) in 170 mL of dry CH_2Cl_2 and cooled to 0 °C. Oxalyl chloride (20.0 mL, 40.0 mmol, 1.2 equiv) was added along with 13 drops of DMF. The solution was brought to stirring reflux at 40 °C in a preheated oil bath for 2 h, and after allowing to cool to rt, then concentrated in vacuo. The crude acid chloride was then dissolved in minimal EtOAc and added dropwise to a 500 mL round-bottom flask containing hydroxylamine chloride (3.47 g, 50.0 mmol, 1.5 equiv), sodium carbonate (10.6 g, 100 mmol, 3 equiv), and 100 mL of a 1:1 solution of EtOAc/water at 0 °C. The solution was warmed to rt and stirred for 2 h. The reaction was quenched with 170 mL of 1M HCl, extracted with EtOAc (3x), and dried over $MgSO_4$. The crude hydroxamic acid was concentrated and dried in vacuo. The hydroxamic acid was taken up in 170 mL dry CH_2Cl_2 under N_2, and 1,1'-carbonyldiimidazole (5.40 g, 33 mmol, 1 equiv) was added to the flask. Reaction progress was monitored by TLC, and the reaction was quenched after 20 min with 170 mL of 1M HCl. The crude product was then extracted with CH_2Cl_2 (2x), dried over $MgSO_4$, and concentrated in vacuo. Purification by silica gel chromatography (33% CH_2Cl_2 in hexanes) afforded the product **2j** (3.70 g, 58% yield) as a white solid. IR (neat): 1831, 1354, 1247, 1156, 968, 755, 699 cm^{-1}; ^1H NMR (600 MHz, DMSO) δ 7.45 (s, 2H), 7.36 (s, 1H), 2.36 (s, 6H). ^{13}C NMR (151 MHz, DMSO) δ 163.2, 154.0, 139.1, 135.1, 123.9, 120.1, 20.6. HRMS (EI) m/z: [M/Z] Calcd. for $C_{10}H_9NO_3$: 191.0583. Found 191.0586.

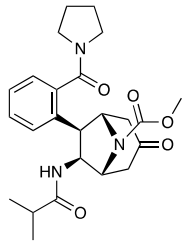
IV. Rh^{III}-Catalyzed Coupling Reactions

General procedure:
In a N_2-filled glovebox, a 2–5 mL microwave vial was charged with the indicated C–H bond substrate (0.200 mmol, 1.0 equiv), alkene (0.400 mmol, 2.0 equiv), and dioxazolone (0.600 mmol, 3.0 equiv), followed by sodium acetate (16.4 mg, 0.200 mmol, 1.0 equiv) and $[Cp^*Rh(MeCN)_3](SbF_6)_2$ (16.7 mg, 0.020 mmol, 0.1 equiv). Finally, 1,4-dioxane (1.0 mL, 0.2 M) was added to the vial. The reaction vial was then equipped with a magnetic stir bar, sealed with a microwave cap, and taken outside the glovebox. The reaction mixture was stirred at either 50 or 70 °C in a preheated oil bath for 2-15 h. The reaction mixture was then allowed to cool to room temperature, and filtered through a small celite plug (1 cm long in a pipette), which was washed with CH_2Cl_2. The resulting mixture was then concentrated and purified by the corresponding chromatographic method to afford the desired product.

Characterization Data:

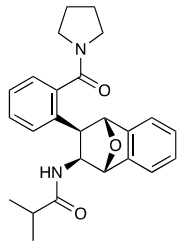


(±) *tert*-Butyl 2-isobutyramido-3-(2-(pyrrolidine-1-carbonyl)phenyl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-9-carboxylate (4a): Derived from phenyl(pyrrolidin-1-yl)methanone (35.0 mg, 0.200 mmol, 1.0 equiv), *tert*-butyl 1,4-dihydro-1,4-epiminonaphthalene-9-carboxylate (97.3 mg, 0.400 mmol, 2.0 equiv), and 3-isopropyl-1,4,2-dioxazol-5-one (77.5 mg, 0.600 mmol, 3.0 equiv). The reaction was conducted at 70 °C for 15 h. Purification by silica gel chromatography (60-80% ethyl acetate in hexanes) followed by preparative TLC (90/10/1 CH_2Cl_2/MeOH/NH_4OH) afforded the product **4a** (86.7 mg, 86% yield) as an off-white foam. IR (neat): 2972, 2874, 1698, 1615, 1338, 1153, 752, 572 cm^{-1}; ^1H NMR (500 MHz, CD_3CN, 50 °C) δ 7.75 (d, *J* = 7.9 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 1H), 7.45 – 7.41 (m, 1H), 7.40 – 7.30 (m, 2H), 7.29 – 7.18 (m, 3H), 5.92 (s, 1H), 5.12 (s, 1H), 4.89 (s, 1H), 4.14 (t, *J* = 8.5 Hz, 1H), 3.43 – 3.31 (m, 3H), 3.17 – 3.03 (m, 2H), 2.12 – 2.06 (m, 1H), 1.87 – 1.69 (m, 4H), 1.34 (s, 9H), 0.88 (d, *J* = 6.8 Hz, 3H), 0.66 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, CD_3CN, 50 °C) δ 176.7, 169.4, 157.2, 148.4, 144.9, 140.4, 137.0, 130.2, 129.2, 128.4, 128.1, 128.0, 127.6, 122.6, 120.9, 81.3, 68.8, 68.2, 54.1, 49.5, 47.5, 46.2, 35.9, 28.6, 26.8, 25.1, 19.6, 19.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{30}H_{38}N_3O_4^+$: 504.2862. Found 504.2888.

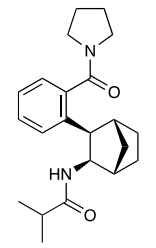


(±) Methyl 6-isobutyramido-3-oxo-7-(2-(pyrrolidine-1-carbonyl)phenyl)-8-azabicyclo[3.2.1]octane-8-carboxylate (4b): Derived from phenyl(pyrrolidin-1-yl)methanone (35.0 mg, 0.200 mmol, 1.0 equiv), methyl 3-oxo-8-azabicyclo[3.2.1]oct-6-ene-8-carboxylate (72.5 mg, 0.400 mmol, 2.0 equiv), and 3-isopropyl-1,4,2-dioxazol-5-one (77.5 mg, 0.600 mmol, 3.0 equiv). The reaction was conducted at 70 °C for 15 h. Purification by silica gel chromatography (90-100% ethyl acetate in hexanes) afforded the product **4b** (57.0 mg, 65% yield) as an off-white foam. IR (neat): 2966, 2874, 1700, 1612, 1445, 1200, 1101, 1013, 750 cm^{-1}; ^1H NMR (500 MHz, CD_3CN, 50 °C) δ 7.21 (t, *J* = 7.5 Hz, 1H), 7.14 (t, *J* = 6.8 Hz, 2H), 7.08 (d, *J* = 8.2 Hz, 1H), 4.33 (t, *J* = 8.8 Hz, 1H), 4.28 (s, 1H), 4.12 (d, *J* = 5.6 Hz, 1H), 3.61 (s, 3H), 3.50 – 3.38 (m, 2H), 3.36 – 3.27 (m, 1H), 3.07 (dt, *J* = 10.3, 7.1 Hz, 1H), 2.99 (dt, *J* = 11.0, 6.0 Hz, 1H), 2.64 – 2.48 (m, 2H), 2.38 – 2.26 (m, 2H), 1.89 – 1.82 (m, 1H), 1.82 – 1.76 (m, 2H), 1.76 – 1.67 (m, 2H), 0.66 (d, *J* = 6.8 Hz, 3H), 0.39 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, CD_3CN, 65 °C) δ 206.8,

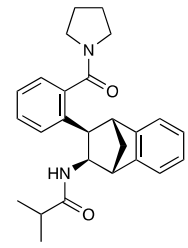
176.8, 170.3, 155.4, 138.8, 136.5, 131.4, 130.3, 128.4, 128.2, 62.2, 59.8, 57.7, 53.4, 52.6, 50.0, 49.8, 46.7, 46.5, 36.0, 26.9, 25.3, 19.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{24}H_{32}N_3O_5^+$: 442.2342. Found 442.2350.



(±) *N*-(3-(2-(Pyrrolidine-1-carbonyl)phenyl)-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl)isobutyramide (4c): Derived from phenyl(pyrrolidin-1-yl)methanone (35.0 mg, 0.200 mmol, 1.0 equiv), 1,4-dihydro-1,4-epoxynaphthalene (57.7 mg, 0.400 mmol, 2.0 equiv), and 3-isopropyl-1,4,2-dioxazol-5-one (77.5 mg, 0.600 mmol, 3.0 equiv). The reaction was conducted at 70 °C for 15 h. Purification by silica gel chromatography (60% ethyl acetate in hexanes) followed by preparative TLC (90/10/1 CH_2Cl_2/MeOH/NH_4OH) afforded the product **4c** (66.5 mg, 82% yield) as a white foam. IR (neat): 3334, 2965, 2872, 1621, 1526, 1429, 1252, 727 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.9 Hz, 1H), 7.42 (td, *J* = 7.5, 1.0 Hz, 1H), 7.38 – 7.35 (m, 1H), 7.30 (td, *J* = 7.6, 1.2 Hz, 1H), 7.25 – 7.23 (m, 1H), 7.22 – 7.20 (m, 1H), 7.19 – 7.17 (m, 2H), 5.93 (s, 1H), 5.39 (s, 1H), 5.19 (s, 1H), 4.37 (t, *J* = 8.5 Hz, 1H), 3.54 – 3.41 (m, 3H), 3.14 – 3.07 (m, 1H), 3.07 – 3.00 (m, 1H), 2.06 (septet, *J* = 6.9 Hz, 1H), 1.90 – 1.74 (m, 4H), 0.85 (d, *J* = 7.0 Hz, 3H), 0.70 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.2, 169.0, 146.2, 143.1, 138.8, 135.5, 129.5, 128.8, 127.6, 127.4, 127.1, 126.7, 120.8, 119.2, 84.9, 84.8, 53.4, 48.8, 46.9, 45.5, 35.5, 26.0, 24.4, 19.1, 19.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{25}H_{29}N_2O_3^+$: 405.2178. Found 405.2155.



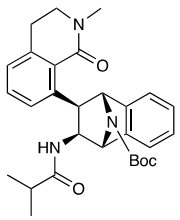
(±) *N*-(3-(2-(Pyrrolidine-1-carbonyl)phenyl)bicyclo[2.2.1]heptan-2-yl)isobutyramide (4d): Derived from phenyl(pyrrolidin-1-yl)methanone (35.0 mg, 0.200 mmol, 1.0 equiv), bicyclo[2.2.1]hept-2-ene (37.7 mg, 0.400 mmol, 2.0 equiv), and 3-isopropyl-1,4,2-dioxazol-5-one (77.5 mg, 0.600 mmol, 3.0 equiv). The reaction was conducted at 70 °C for 15 h. Purification by silica gel chromatography (60% ethyl acetate in hexanes) followed by preparative TLC (75% ethyl acetate in hexanes) afforded the product **4d** (52.6 mg, 74% yield) as a white solid. IR (neat): 3312, 2956, 2872, 1668, 1590, 1435, 1225, 753, 651 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 2H), 7.25 – 7.20 (m, 1H), 7.17 (d, *J* = 7.0 Hz, 1H), 5.34 (s, 1H), 3.91 (t, *J* = 8.0 Hz, 1H), 3.66 – 3.54 (m, 2H), 3.24 (bs, 1H), 3.16 – 3.05 (m, 1H), 3.05 – 2.96 (m, 1H), 2.40 (bs, 1H), 2.33 (bs, 1H), 2.03 – 1.85 (m, 3H), 1.84 – 1.72 (m, 3H), 1.63 – 1.54 (m, 1H), 1.54 – 1.45 (m, 1H), 1.38 – 1.28 (m, 3H), 0.80 (d, *J* = 6.9 Hz, 3H), 0.73 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.6, 169.4, 138.8, 137.1, 129.2, 127.6, 126.8, 126.6, 56.6, 48.8, 48.3, 45.5, 42.4, 41.5, 36.0, 35.6, 31.2, 26.0, 25.3, 24.5, 19.2, 19.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{22}H_{31}N_2O_2^+$: 355.2386. Found 355.2375.



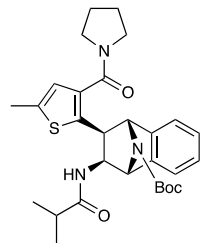
(±) *N*-(3-(2-(Pyrrolidine-1-carbonyl)phenyl)-1,2,3,4-tetrahydro-1,4-methanonaphthalen-2-yl)isobutyramide (4e): Derived from phenyl(pyrrolidin-1-yl)methanone (35.0 mg, 0.200 mmol, 1.0 equiv), 1,4-dihydro-1,4-methanonaphthalene (56.9 mg, 0.400 mmol, 2.0 equiv), and 3-isopropyl-1,4,2-dioxazol-5-one (77.5 mg, 0.600 mmol, 3.0 equiv). The reaction was conducted at 70 °C for 15 h. Purification by silica gel chromatography (60-80% ethyl acetate in hexanes) afforded the product **4e** (70.0 mg, 87% yield) as a tan solid. IR (neat): 2968, 2874, 1611, 1534, 1432, 1227, 728, 658 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.49 – 7.40 (m, 2H), 7.33 – 7.27 (m, 2H), 7.21 (d, *J* = 7.5 Hz, 1H), 7.16 – 7.10 (m, 1H),

7.09 – 7.04 (m, 2H), 5.49 (s, 1H), 4.03 (t, J = 7.7 Hz, 1H), 3.51 (s, 1H), 3.45 (s, 1H), 3.48 – 3.36 (m, 2H), 3.24 (d, J = 5.2 Hz, 1H), 3.12 – 3.03 (m, 2H), 2.28 (d, J = 9.8 Hz, 1H), 2.09 – 1.99 (m, 2H), 1.90 – 1.71 (m, 4H), 0.85 (d, J = 6.9 Hz, 3H), 0.78 (d, J = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.1, 169.0, 150.1, 145.7, 139.2, 136.7, 129.5, 127.4, 127.2, 126.7, 126.5, 126.0, 122.8, 120.2, 54.2, 49.8, 48.7, 48.5, 47.0, 46.7, 45.4, 35.6, 26.0, 24.4, 19.2, 19.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{26}H_{31}N_2O_2^+$: 403.2386. Found 403.2395.

Large Scale Reaction: For the reaction performed at 1.00 mmol scale, a 5 mol % catalyst loading was used. In a N_2-filled glovebox, a 10–20 mL microwave vial was charged with phenyl(pyrrolidin-1-yl)methanone (175 mg, 1.00 mmol, 1.0 equiv), 1,4-dihydro-1,4-methanonaphthalene (284 mg, 2.00 mmol, 2.0 equiv), 3-isopropyl-1,4,2-dioxazol-5-one (387 mg, 3.00 mmol, 3.0 equiv), followed by sodium acetate (82.0 mg, 1.00 mmol, 1.0 equiv) and $[Cp^*Rh(MeCN)_3](SbF_6)_2$ (41.6 mg, 0.050 mmol, 0.05 equiv). Finally, 1,4-dioxane (5.0 mL, 0.2 M) was added to the vial. The reaction vial was then equipped with a magnetic stir bar, sealed with a microwave cap, and taken outside the glovebox. The reaction mixture was stirred at 70 °C in a pre-heated oil bath for 15 h. Then, the reaction mixture was cooled to room temperature and vacuum filtered through a celite plug, eluting with CH_2Cl_2. The mixture was concentrated and purified by silica gel chromatography (60-80% ethyl acetate in hexanes) to afford the product **4e** (284 mg, 71% yield) as a tan solid. The spectroscopic data match with those from the standard conditions.

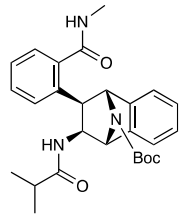


(±) *tert*-Butyl 2-isobutyramido-3-(2-methyl-1-oxo-1,2,3,4-tetrahydroisoquinolin-8-yl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-9-carboxylate (4f): Derived from 2-methyl-3,4-dihydroisoquinolin-1-one (32.2 mg, 0.200 mmol, 1.0 equiv), *tert*-butyl 1,4-dihydro-1,4-epiminonaphthalene-9-carboxylate (97.3 mg, 0.400 mmol, 2.0 equiv), and 3-isopropyl-1,4,2-dioxazol-5-one (77.5 mg, 0.600 mmol, 3.0 equiv). The reaction was conducted at 70 °C for 15 h. Purification by silica gel chromatography (80% ethyl acetate in hexanes) followed by preparative TLC (90/10/1 CH_2Cl_2/MeOH/NH_4OH) afforded the product **4f** (69.5 mg, 71% yield) as an off-white foam. IR (neat): 2972, 1703, 1641, 1493, 1331, 1153, 753, 576 cm^{-1}; ^{1}H NMR (500 MHz, CD_3CN, 50 °C) δ 7.68 (d, J = 7.9 Hz, 1H), 7.49 (t, J = 7.8 Hz, 1H), 7.47 – 7.42 (m, 1H), 7.36 – 7.30 (m, 1H), 7.28 – 7.21 (m, 2H), 7.19 (d, J = 7.5 Hz, 1H), 5.29 (d, J = 8.9 Hz, 1H), 5.26 (s, 1H), 4.84 (s, 1H), 4.53 (d, J = 8.2 Hz, 1H), 4.34 (t, J = 8.4 Hz, 1H), 3.48 – 3.36 (m, 2H), 2.94 (s, 3H), 2.91 (t, J = 6.5 Hz, 2H), 1.99 (septet, J = 6.9 Hz, 1H), 1.36 (s, 9H), 0.82 (d, J = 6.9 Hz, 3H), 0.65 (d, J = 6.6 Hz, 3H). ^{13}C NMR (126 MHz, CD_3CN, 50 °C) δ 176.3, 165.2, 157.2, 148.7, 145.3, 141.6, 141.3, 132.0, 130.1, 128.3, 127.9, 127.4, 122.5, 120.9, 81.2, 68.8, 67.0, 54.6, 48.5, 47.8, 35.9, 35.3, 30.2, 28.6, 19.9, 19.5 (2 aromatic peaks overlap). HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{29}H_{36}N_3O_4^+$: 490.2706. Found 490.2701.

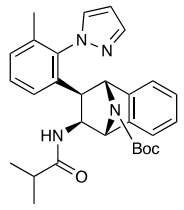


(±) *tert*-Butyl 2-isobutyramido-3-(5-methyl-3-(pyrrolidine-1-carbonyl)thiophen-2-yl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-9-carboxylate (4g): Derived from (5-methyl-3-thienyl)-pyrrolidin-1-yl-methanone (39.1 mg, 0.200 mmol, 1.0 equiv), *tert*-butyl 1,4-dihydro-1,4-epiminonaphthalene-9-carboxylate (97.3 mg, 0.400 mmol, 2.0 equiv), and 3-isopropyl-1,4,2-dioxazol-5-one (77.5 mg, 0.600 mmol, 3.0 equiv). The reaction was conducted at 70 °C for 15 h. Purification by reverse phase chromatography

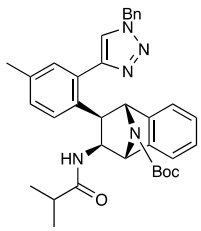
(40-100% acetonitrile in water with 0.1% triethylamine) followed by silica gel chromatography (50-75% ethyl acetate in hexanes) afforded the product **4g** (78.4 mg, 75% yield) as a white foam. IR (neat): 2972, 2874, 1706, 1611, 1331, 1154, 754, 563 cm^{-1}; ^1H NMR (500 MHz, CD_3CN, 50 °C) δ 7.42 – 7.37 (m, 1H), 7.37 – 7.32 (m, 1H), 7.24 – 7.18 (m, 2H), 6.68 (s, 1H), 5.02 (s, 1H), 4.87 (s, 1H), 4.13 (t, *J* = 8.4 Hz, 1H), 3.65 (d, *J* = 7.9 Hz, 1H), 3.45 – 3.20 (m, 4H), 2.43 (s, 3H), 2.23 (septet, *J* = 6.9 Hz, 1H), 1.83 (bs, 4H), 1.31 (s, 9H), 0.95 (d, *J* = 6.8 Hz, 3H), 0.79 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, CD_3CN, 50 °C) δ 177.0, 166.6, 157.5, 147.1, 145.0, 139.8, 138.8, 138.0, 128.4, 128.2, 125.5, 122.2, 121.4, 81.5, 69.3, 69.0, 54.6, 49.3, 46.4, 45.8, 36.1, 28.6, 26.8, 25.1, 19.7, 19.6, 15.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{29}H_{38}N_3O_4S^+$: 524.2583. Found 524.2578.



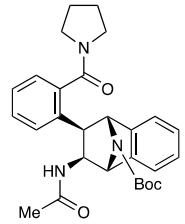
(±) *tert*-Butyl 2-isobutyramido-3-(2-(methylcarbamoyl)phenyl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-9-carboxylate (4h): Derived from *N*-methylbenzamide (27.0 mg, 0.200 mmol, 1.0 equiv), *tert*-butyl 1,4-dihydro-1,4-epiminonaphthalene-9-carboxylate (97.3 mg, 0.400 mmol, 2.0 equiv), and 3-isopropyl-1,4,2-dioxazol-5-one (77.5 mg, 0.600 mmol, 3.0 equiv). The reaction was conducted at 70 °C for 2 h. Purification by reverse phase chromatography (40-100% acetonitrile in water with 0.1% triethylamine) afforded the product **4h** (52.1 mg, 56% yield) as an off-white solid. IR (neat): 3241 (br), 2972, 1710, 1633, 1552, 1329, 1154, 753, 577 cm^{-1}; ^1H NMR (500 MHz, CD_3CN, 50 °C) δ 7.89 (s, 1H), 7.69 (d, *J* = 7.9 Hz, 1H), 7.53 – 7.40 (m, 2H), 7.38 – 7.30 (m, 1H), 7.30 – 7.20 (m, 4H), 6.56 (s, 1H), 5.05 (s, 1H), 5.00 (s, 1H), 4.24 (t, *J* = 7.8 Hz, 1H), 3.23 (d, *J* = 7.1 Hz, 1H), 2.68 (d, *J* = 2.8 Hz, 3H), 2.13 (septet, *J* = 6.6 Hz, 1H), 1.34 (s, 9H), 0.85 (d, *J* = 6.9 Hz, 3H), 0.40 (d, *J* = 4.4 Hz, 3H). ^{13}C NMR (126 MHz, CD_3CN, 50 °C) δ 179.0, 171.1, 157.4, 148.7, 144.6, 140.7, 136.7, 130.2, 129.1, 128.6, 128.3, 127.9, 127.9, 123.0, 120.9, 81.5, 69.2, 67.6, 55.4, 49.5, 35.5, 28.6, 26.5, 19.5, 19.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{27}H_{34}N_3O_4^+$: 464.2549. Found 464.2560.



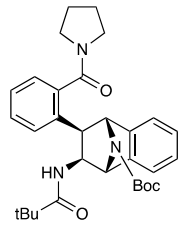
(±) *tert*-Butyl 2-isobutyramido-3-(3-methyl-2-(1*H*-pyrazol-1-yl)phenyl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-9-carboxylate (4i): Derived from 1-(o-tolyl)pyrazole (31.6 mg, 0.200 mmol, 1.0 equiv), *tert*-butyl 1,4-dihydro-1,4-epiminonaphthalene-9-carboxylate (97.3 mg, 0.400 mmol, 2.0 equiv), and 3-isopropyl-1,4,2-dioxazol-5-one (77.5 mg, 0.600 mmol, 3.0 equiv). The reaction was conducted at 70 °C for 15 h. Purification by silica gel chromatography (25% ethyl acetate in hexanes) afforded the product **4i** (83.1 mg, 85% yield) as an off-white foam. IR (neat): 2973, 2872, 1701, 1675, 1509, 1342, 1161, 751 cm^{-1}; ^1H NMR (500 MHz, CD_3CN, 50 °C) δ 7.74 – 7.58 (m, 2H), 7.53 (s, 1H), 7.48 (t, *J* = 7.7 Hz, 1H), 7.41 – 7.35 (m, 1H), 7.28 (d, *J* = 7.6 Hz, 1H), 7.25 – 7.20 (m, 1H), 7.19 – 7.13 (m, 2H), 6.29 (s, 1H), 5.97 (s, 1H), 5.12 (s, 1H), 4.86 (s, 1H), 4.00 (t, *J* = 8.8 Hz, 1H), 2.52 (d, *J* = 7.9 Hz, 1H), 2.13 (septet, *J* = 6.8 Hz, 1H), 1.88 (s, 3H), 1.34 (s, 9H), 0.90 (d, *J* = 7.0 Hz, 3H), 0.61 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, CD_3CN, 50 °C) δ 177.1, 157.3, 148.3, 144.7, 141.2, 141.0, 138.3, 137.9, 133.7, 130.5, 130.3, 128.5, 128.0, 126.6, 122.7, 120.8, 106.6, 81.5, 68.4, 68.1, 54.2, 46.4, 35.8, 28.6, 19.6, 19.4, 17.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{29}H_{35}N_4O_3^+$: 487.2709. Found 487.2703.



(±) *tert*-Butyl 2-isobutyramido-3-(4-methyl-2-(1*H*-1,2,3-triazol-4-yl)phenyl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-9-carboxylate (4j): Derived from 1-benzyl-4-(m-tolyl)triazole (49.9 mg, 0.200 mmol, 1.0 equiv), *tert*-butyl 1,4-dihydro-1,4-epiminonaphthalene-9-carboxylate (97.3 mg, 0.400 mmol, 2.0 equiv), and 3-isopropyl-1,4,2-dioxazol-5-one (77.5 mg, 0.600 mmol, 3.0 equiv). The reaction was conducted at 70 °C for 15 h. Purification by reverse phase chromatography (40-100% acetonitrile in water with 0.1% triethylamine) afforded the product **4j** (60.7 mg, 52% yield) as a white foam. IR (neat): 2972, 2929, 1700, 1665, 1498, 1367, 1156, 718, 564 cm^{-1}; ^1H NMR (500 MHz, CD_3CN, 50 °C) δ 7.92 (s, 1H), 7.68 (d, *J* = 7.9 Hz, 1H), 7.42 (d, *J* = 7.1 Hz, 1H), 7.34 – 7.15 (m, 10H), 5.74 (d, *J* = 9.2 Hz, 1H), 5.52 – 5.43 (m, 2H), 5.17 (s, 1H), 4.87 (s, 1H), 4.17 (t, *J* = 8.7 Hz, 1H), 3.37 (d, *J* = 8.0 Hz, 1H), 2.36 (s, 3H), 2.04 – 1.96 (m, 1H), 1.35 (s, 9H), 0.81 (d, *J* = 7.0 Hz, 3H), 0.50 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, CD_3CN, 50 °C) δ 176.8, 157.3, 148.3, 148.3, 147.6, 137.9, 137.1, 135.1, 133.0, 131.3, 130.4, 130.0, 129.3, 128.8, 128.5, 128.3, 127.9, 124.7, 122.5, 121.0, 81.3, 68.4, 68.3, 54.5, 48.1, 35.8, 30.5, 28.6, 21.0, 19.6, 19.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{35}H_{40}N_5O_3^+$: 578.3131. Found 578.3124.

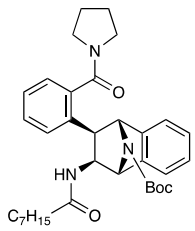


(±) *tert*-Butyl 2-acetamido-3-(2-(pyrrolidine-1-carbonyl)phenyl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-9-carboxylate (4k): Derived from phenyl(pyrrolidin-1-yl)methanone (35.0 mg, 0.200 mmol, 1.0 equiv), *tert*-butyl 1,4-dihydro-1,4-epiminonaphthalene-9-carboxylate (97.3 mg, 0.400 mmol, 2.0 equiv), and 3-methyl-1,4,2-dioxazol-5-one (60.6 mg, 0.600 mmol, 3.0 equiv). The reaction was conducted at 70 °C for 15 h. Purification by silica gel chromatography (90-100% ethyl acetate in hexanes) followed by preparative TLC (90/10/1 CH_2Cl_2/MeOH/NH_4OH) afforded the product **4k** (81.5 mg, 86% yield) as a white foam. IR (neat): 2974, 2874, 1704, 1672, 1615, 1366, 1336, 1153 cm^{-1}; ^1H NMR (500 MHz, CD_3CN, 50 °C) δ 7.74 (d, *J* = 7.9 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.45 – 7.40 (m, 1H), 7.38 – 7.30 (m, 2H), 7.28 – 7.19 (m, 3H), 5.99 (s, 1H), 5.12 (s, 1H), 4.88 (s, 1H), 4.15 (t, *J* = 8.6 Hz, 1H), 3.44 (d, *J* = 8.3 Hz, 1H), 3.40 – 3.33 (m, 2H), 3.19 – 3.11 (m, 1H), 3.10 – 3.04 (m, 1H), 1.88 – 1.71 (m, 4H), 1.59 (s, 3H), 1.34 (s, 9H). ^{13}C NMR (126 MHz, CD_3CN, 50 °C) δ 170.0, 169.4, 157.4, 148.4, 144.9, 140.1, 137.0, 130.2, 129.2, 128.4, 128.0, 127.5, 122.6, 120.9, 81.4, 68.9, 68.3, 54.4, 49.5, 47.1, 46.2, 28.6, 26.8, 25.1, 23.2 (2 aromatic peaks overlap). HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{28}H_{34}N_3O_4^+$: 476.2549. Found 476.2538.

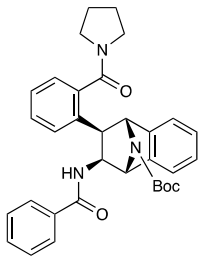


(±) *tert*-Butyl 2-pivalamido-3-(2-(pyrrolidine-1-carbonyl)phenyl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-9-carboxylate (4l): Derived from phenyl(pyrrolidin-1-yl)methanone (35.0 mg, 0.200 mmol, 1.0 equiv), *tert*-butyl 1,4-dihydro-1,4-epiminonaphthalene-9-carboxylate (97.3 mg, 0.400 mmol, 2.0 equiv), and 3-tert-butyl-1,4,2-dioxazol-5-one (85.9 mg, 0.600 mmol, 3.0 equiv). The reaction was conducted at 70 °C for 15 h. Purification by silica gel chromatography (60% ethyl acetate in hexanes) followed by preparative TLC (90/10/1 CH_2Cl_2/MeOH/NH_4OH) afforded the product **4l** (65.6 mg, 63% yield) as an off-white foam. IR (neat): 2972, 2873, 1705, 1624, 1338, 1154, 752 cm^{-1}; ^1H NMR (500 MHz, CD_3CN, 50 °C) δ 7.77 (d, *J* = 7.9 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.46 – 7.41 (m, 1H), 7.40 – 7.32 (m, 2H), 7.28 (d, *J* = 7.6 Hz, 1H), 7.25 – 7.21 (m, 2H), 5.64 (d, *J* = 7.9 Hz, 1H), 5.20 (s, 1H), 4.90 (s, 1H), 4.03 (t, *J* = 8.1 Hz, 1H), 3.40 – 3.31 (m, 3H), 3.15 – 3.02 (m, 2H), 1.86 – 1.70 (m, 4H), 1.35 (s,

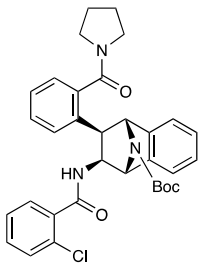
9H), 0.84 (s, 9H). ^{13}C NMR (126 MHz, CD_3CN, 50 °C) δ 178.2, 169.2, 156.9, 148.2, 144.8, 140.7, 136.9, 130.5, 128.4, 128.4, 128.0, 127.8, 122.6, 120.9, 81.4, 68.6, 67.6, 54.4, 49.5, 47.3, 46.2, 39.3, 28.6, 27.5, 26.8, 25.1 (2 aromatic peaks overlap). HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{31}H_{40}N_3O_4^+$: 518.3019. Found 518.3030.



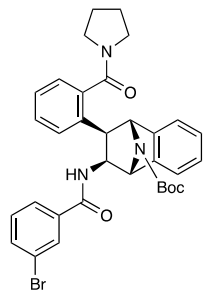
(±) *tert*-Butyl 2-octanamido-3-(2-(pyrrolidine-1-carbonyl)phenyl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-9-carboxylate (4m): Derived from phenyl(pyrrolidin-1-yl)methanone (35.0 mg, 0.200 mmol, 1.0 equiv), *tert*-butyl 1,4-dihydro-1,4-epiminonaphthalene-9-carboxylate (97.3 mg, 0.400 mmol, 2.0 equiv), and 3-heptyl-1,4,2-dioxazol-5-one (111 mg, 0.600 mmol, 3.0 equiv). The reaction was conducted at 70 °C for 15 h. Purification by silica gel chromatography (60% ethyl acetate in hexanes) afforded the product **4m** (102 mg, 91% yield) as an orange foam. IR (neat): 2927, 2857, 1698, 1668, 1618, 1530, 1427, 1339, 1154, 752 cm^{-1}; ^{1}H NMR (500 MHz, CD_3CN, 50 °C) δ 7.73 (d, J = 7.7 Hz, 1H), 7.47 (t, J = 7.8 Hz, 1H), 7.44 – 7.41 (m, 1H), 7.38 – 7.29 (m, 2H), 7.28 – 7.16 (m, 3H), 5.97 (d, J = 8.8 Hz, 1H), 5.10 (s, 1H), 4.89 (s, 1H), 4.16 (t, J = 8.4 Hz, 1H), 3.41 – 3.30 (m, 3H), 3.18 – 3.03 (m, 2H), 1.92 – 1.84 (m, 1H), 1.84 – 1.72 (m, 5H), 1.34 (s, 9H), 1.32 – 1.25 (m, 3H), 1.23 – 1.13 (m, 5H), 1.07 (q, J = 7.9, 7.4 Hz, 2H), 0.89 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, CD_3CN, 50 °C) δ 173.1, 169.5, 157.3, 148.4, 144.9, 140.3, 137.0, 130.2, 129.2, 128.4, 128.1, 128.0, 127.5, 122.6, 120.9, 81.4, 68.9, 68.4, 54.4, 49.6, 47.5, 46.3, 37.1, 32.5, 29.8, 28.6, 26.8, 26.3, 25.2, 23.4, 14.5 (2 aliphatic peaks overlap). HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{34}H_{46}N_3O_4^+$: 560.3488. Found 560.3465.



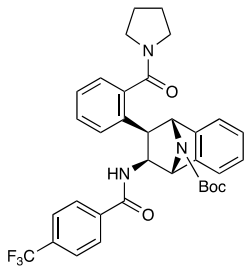
(±) *tert*-Butyl 2-benzamido-3-(2-(pyrrolidine-1-carbonyl)phenyl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-9-carboxylate (4n): Derived from phenyl(pyrrolidin-1-yl)methanone (35.0 mg, 0.200 mmol, 1.0 equiv), *tert*-butyl 1,4-dihydro-1,4-epiminonaphthalene-9-carboxylate (97.3 mg, 0.400 mmol, 2.0 equiv), and 3-phenyl-1,4,2-dioxazol-5-one (97.9 mg, 0.600 mmol, 3.0 equiv). The reaction was conducted at 70 °C for 15 h. Purification by reverse phase chromatography (40-100% acetonitrile in water with 0.1% triethylamine) afforded the product **4n** (75.0 mg, 69% yield) as a brown solid. IR (neat): 2974, 2874, 1703, 1619, 1338, 1153, 570 cm^{-1}; ^{1}H NMR (500 MHz, CD_3CN, 50 °C) δ 7.86 (d, J = 7.9 Hz, 1H), 7.55 (t, J = 7.7 Hz, 1H), 7.51 – 7.47 (m, 1H), 7.46 – 7.42 (m, 1H), 7.41 – 7.36 (m, 2H), 7.35 – 7.29 (m, 4H), 7.29 – 7.24 (m, 3H), 6.45 (s, 1H), 5.26 (s, 1H), 5.04 (s, 1H), 4.35 (t, J = 8.3 Hz, 1H), 3.53 (d, J = 8.3 Hz, 1H), 3.42 – 3.32 (m, 2H), 3.12 – 2.98 (m, 2H), 1.87 – 1.64 (m, 4H), 1.33 (s, 9H). ^{13}C NMR (126 MHz, CD_3CN, 50 °C) δ 169.3, 167.1, 157.3, 148.3, 144.9, 140.2, 137.0, 135.6, 132.5, 130.6, 129.5, 129.1, 128.5, 128.3, 128.1, 127.9, 127.7, 122.7, 121.1, 81.4, 68.8, 67.9, 54.9, 49.5, 47.7, 46.3, 28.6, 26.7, 25.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{33}H_{36}N_3O_4^+$: 538.2706. Found 538.2690.



(±) *tert*-Butyl 2-(2-chlorobenzamido)-3-(2-(pyrrolidine-1-carbonyl)phenyl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-9-carboxylate (4o): Derived from phenyl(pyrrolidin-1-yl)methanone (35.0 mg, 0.200 mmol, 1.0 equiv), *tert*-butyl 1,4-dihydro-1,4-epiminonaphthalene-9-carboxylate (97.3 mg, 0.400 mmol, 2.0 equiv), and 3-(2-chlorophenyl)-1,4,2-dioxazol-5-one (119 mg, 0.600 mmol, 3.0 equiv). The reaction was conducted at 50 °C for 2 h. Purification by silica gel chromatography (60% ethyl acetate in hexanes) afforded the product **4o** (98.1 mg, 86% yield) as an orange foam. IR (neat): 2973, 2876, 1700, 1620, 1152, 750, 657 cm^{-1}; ^1H NMR (500 MHz, CD_3CN, 50 °C) δ 7.75 (d, J = 7.8 Hz, 1H), 7.51 – 7.48 (m, 1H), 7.45 (t, J = 8.0 Hz, 1H), 7.42 – 7.30 (m, 4H), 7.28 – 7.22 (m, 3H), 7.22 – 7.15 (m, 1H), 6.99 – 6.88 (m, 1H), 6.65 (d, J = 8.7 Hz, 1H), 5.20 (s, 1H), 5.07 (s, 1H), 4.39 (t, J = 8.6 Hz, 1H), 3.38 (d, J = 8.2 Hz, 1H), 3.37 – 3.30 (m, 2H), 3.13 (m, 2H), 1.86 – 1.69 (m, 4H), 1.33 (s, 9H). ^{13}C NMR (126 MHz, CD_3CN, 50 °C) δ 169.5, 166.8, 157.0, 148.4, 144.7, 140.2, 136.8, 136.4, 132.4, 131.5, 131.0, 130.5, 130.5, 129.2, 128.6, 128.3, 128.1, 128.0, 127.6, 122.8, 121.0, 81.5, 68.6, 68.1, 55.5, 49.6, 47.9, 46.3, 28.6, 26.8, 25.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{33}H_{35}ClN_3O_4^+$: 572.2316. Found 572.2318.

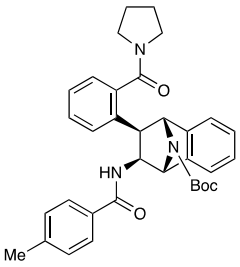


(±) *tert*-Butyl 2-(3-bromobenzamido)-3-(2-(pyrrolidine-1-carbonyl)phenyl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-9-carboxylate (4p): Derived from phenyl(pyrrolidin-1-yl)methanone (35.0 mg, 0.200 mmol, 1.0 equiv), *tert*-butyl 1,4-dihydro-1,4-epiminonaphthalene-9-carboxylate (97.3 mg, 0.400 mmol, 2.0 equiv), and 3-(3-bromophenyl)-1,4,2-dioxazol-5-one (145 mg, 0.600 mmol, 3.0 equiv). The reaction was conducted at 50 °C for 2 h. Purification by reverse phase chromatography (40-100% acetonitrile in water with 0.1% triethylamine) afforded the product **4p** (82.1 mg, 66% yield) as an off-white solid. IR (neat): 2974, 2875, 1703, 1620, 1337, 1152, 745, 572 cm^{-1}; ^1H NMR (500 MHz, CD_3CN, 50 °C) δ 7.84 (d, J = 7.8 Hz, 1H), 7.58 (d, J = 8.4 Hz, 1H), 7.54 (t, J = 7.8 Hz, 1H), 7.49 – 7.46 (m, 1H), 7.43 – 7.34 (m, 3H), 7.30 – 7.20 (m, 5H), 6.60 (s, 1H), 5.25 (s, 1H), 5.03 (s, 1H), 4.35 (t, J = 8.4 Hz, 1H), 3.51 (d, J = 8.2 Hz, 1H), 3.42 – 3.30 (m, 2H), 3.17 – 2.96 (m, 2H), 1.88 – 1.64 (m, 4H), 1.33 (s, 9H). ^{13}C NMR (126 MHz, CD_3CN, 50 °C) δ 169.3, 165.8, 157.3, 148.4, 144.8, 140.0, 137.9, 136.9, 135.2, 131.4, 130.9, 130.5, 129.4, 128.5, 128.4, 128.1, 127.9, 126.7, 123.0, 122.7, 121.1, 81.4, 68.7, 67.9, 55.0, 49.5, 48.1, 46.3, 28.6, 26.7, 25.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{33}H_{35}BrN_3O_4^+$: 616.1811. Found 616.1823.

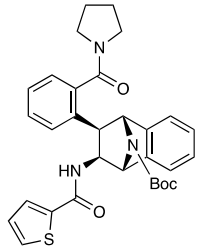


(±) *tert*-Butyl 2-(2-(pyrrolidine-1-carbonyl)phenyl)-3-(4-(trifluoromethyl)benzamido)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-9-carboxylate (4q): Derived from phenyl(pyrrolidin-1-yl)methanone (35.0 mg, 0.200 mmol, 1.0 equiv), *tert*-butyl 1,4-dihydro-1,4-epiminonaphthalene-9-carboxylate (97.3 mg, 0.400 mmol, 2.0 equiv), and 3-[4-(trifluoromethyl)phenyl]-1,4,2-dioxazol-5-one (139 mg, 0.600 mmol, 3.0 equiv). The reaction was conducted at 50 °C for 2 h. Purification by silica gel chromatography (40% ethyl acetate in hexanes) followed by preparative TLC (90/10/1 CH_2Cl_2/MeOH/NH_4OH) afforded the product **4q** (99.6 mg, 82% yield) as a white solid. IR (neat): 2974, 2875, 1697, 1620, 1324, 1161, 1126, 753 cm^{-1}; ^1H NMR (500 MHz, CD_3CN, 50 °C) δ 7.82 (d, J = 7.9 Hz, 1H), 7.61 (d, J = 8.0 Hz, 2H), 7.52 (t, J = 7.7 Hz, 1H),

7.49 – 7.46 (m, 1H), 7.44 (d, J = 8.1 Hz, 2H), 7.38 (d, J = 7.5 Hz, 2H), 7.29 – 7.20 (m, 3H), 6.75 (s, 1H), 5.23 (s, 1H), 5.05 (s, 1H), 4.38 (t, J = 8.5 Hz, 1H), 3.51 (d, J = 8.3 Hz, 1H), 3.43 – 3.31 (m, 2H), 3.14 – 3.00 (m, 2H), 1.87 – 1.66 (m, 4H), 1.31 (s, 9H). ^{13}C NMR (126 MHz, CD_3CN, 50 °C) δ 169.4, 166.1, 157.4, 148.4, 144.9, 140.1, 139.4, 136.9, 133.3 (q, $2J_{C-F}$ = 32.4 Hz), 130.5, 129.4, 128.6, 128.5, 128.4, 128.1, 127.9, 126.4 (q, $3J_{C-F}$ = 3.8 Hz), 125.2 (q, $1J_{C-F}$ = 271.7 Hz), 122.7, 121.1, 81.5, 68.7, 68.0, 55.2, 49.6, 48.2, 46.3, 28.6, 26.7, 25.1. ^{19}F NMR (470 MHz, CD_3CN, 50 °C) δ -63.01. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{34}H_{35}F_3N_3O_4^+$: 606.2580. Found 606.2560.



(±) *tert*-Butyl 2-(4-methylbenzamido)-3-(2-(pyrrolidine-1-carbonyl)phenyl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-9-carboxylate (4r): Derived from phenyl(pyrrolidin-1-yl)methanone (35.0 mg, 0.200 mmol, 1.0 equiv), *tert*-butyl 1,4-dihydro-1,4-epiminonaphthalene-9-carboxylate (97.3 mg, 0.400 mmol, 2.0 equiv), and 3-(*p*-tolyl)-1,4,2-dioxazol-5-one (106 mg, 0.600 mmol, 3.0 equiv). The reaction was conducted at 50 °C for 2 h. Purification by silica gel chromatography (40-80% ethyl acetate in hexanes) afforded the product **4r** (67.1 mg, 61% yield) as an off-white foam. IR (neat): 2973, 2879, 1702, 1613, 1339, 1154, 749, 658 cm^{-1}; ^{1}H NMR (500 MHz, CD_3CN, 50 °C) δ 7.85 (d, J = 7.8 Hz, 1H), 7.54 (t, J = 7.7 Hz, 1H), 7.50 – 7.45 (m, 1H), 7.41 – 7.32 (m, 2H), 7.29 – 7.22 (m, 3H), 7.19 (d, J = 7.6 Hz, 2H), 7.12 (d, J = 7.9 Hz, 2H), 6.40 (s, 1H), 5.24 (s, 1H), 5.02 (s, 1H), 4.34 (t, J = 8.5 Hz, 1H), 3.48 (d, J = 8.2 Hz, 1H), 3.37 – 3.31 (m, 2H), 3.10 – 2.97 (m, 2H), 2.32 (s, 3H), 1.87 – 1.62 (m, 4H), 1.33 (s, 9H). ^{13}C NMR (126 MHz, CD_3CN, 50 °C) δ 169.3, 167.2, 157.3, 148.3, 144.9, 143.1, 140.2, 137.0, 132.8, 130.5, 130.1, 129.0, 128.5, 128.3, 128.1, 127.8, 127.8, 122.7, 121.0, 81.5, 68.8, 67.9, 54.9, 49.5, 47.8, 46.3, 28.6, 26.7, 25.1, 21.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{34}H_{38}N_3O_4^+$: 552.2863. Found 552.2849.



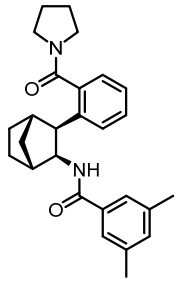
(±) *tert*-Butyl 2-(2-(pyrrolidine-1-carbonyl)phenyl)-3-(thiophene-2-carboxamido)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-9-carboxylate (4s): Derived from phenyl(pyrrolidin-1-yl)methanone (35.0 mg, 0.200 mmol, 1.0 equiv), *tert*-butyl 1,4-dihydro-1,4-epiminonaphthalene-9-carboxylate (97.3 mg, 0.400 mmol, 2.0 equiv), and 3-(2-thienyl)-1,4,2-dioxazol-5-one (101 mg, 0.600 mmol, 3.0 equiv). The reaction was conducted at 70 °C for 15 h. Purification by reverse phase chromatography (40-100% acetonitrile in water with 0.1% triethylamine) afforded the product **4s** (49.3 mg, 45% yield) as a brown foam. IR (neat): 2973, 2875, 1704, 1620, 1421, 1337, 1257, 1154, 732, 567 cm^{-1}; ^{1}H NMR (500 MHz, CD_3CN, 50 °C) δ 7.81 (d, J = 7.8 Hz, 1H), 7.53 (t, J = 7.7 Hz, 1H), 7.50 – 7.46 (m, 2H), 7.39 – 7.34 (m, 2H), 7.29 – 7.23 (m, 3H), 7.03 (d, J = 3.7 Hz, 1H), 6.97 (dd, J = 5.0, 3.7 Hz, 1H), 6.46 (s, 1H), 5.24 (s, 1H), 5.04 (s, 1H), 4.30 (t, J = 8.4 Hz, 1H), 3.53 (d, J = 8.3 Hz, 1H), 3.43 – 3.33 (m, 2H), 3.13 – 3.00 (m, 2H), 1.87 – 1.66 (m, 4H), 1.33 (s, 9H). ^{13}C NMR (126 MHz, CD_3CN, 50 °C) δ 169.3, 161.8, 157.4, 148.4, 144.9, 140.3, 140.0, 136.8, 131.5, 130.5, 129.3, 128.8, 128.8, 128.5, 128.4, 128.1, 128.0, 122.7, 121.1, 81.5, 68.8, 67.8, 54.9, 49.6, 47.9, 46.3, 28.6, 26.8, 25.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{31}H_{34}N_3O_4S^+$: 544.2270. Found 544.2291.

V. Asymmetric Rh^{III}-Catalyzed Coupling Reactions

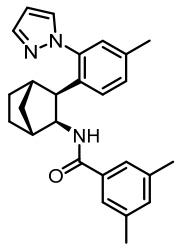
General Procedure:

In a N_2-filled glove box, a 2–5 mL microwave vial was charged with the indicated C–H bond substrate (0.050 mmol, 1.0 equiv), alkene (0.100 mmol, 2.0 equiv or 0.200 mmol, 4.0 equiv), and dioxazolone (0.150 mmol, 3.0 equiv), followed by sodium acetate (4.1 mg, 0.050 mmol, 1.0 equiv), precatalyst **6** (3.6 mg, 0.0025 mmol, 0.050 equiv), $AgSbF_6$ (6.9 mg, 0.020 mmol, 0.40 equiv) and either 1,2-dichloroethane or 1,4-dioxane (0.25 mL, 0.2 M). The reaction vial was then equipped with a magnetic stir bar, sealed with a microwave cap, and taken outside the glove box. The reaction mixture was then stirred at 70 °C in a preheated oil bath. After 48 h, the reaction mixture was allowed to cool to room temperature and filtered through a small celite plug (1 cm long in a pipette), which was washed with CH_2Cl_2. The resulting mixture was then concentrated and purified by the corresponding chromatographic method to afford the desired product.

Authentic racemic products were synthesized by the same method for 15 h using $[Cp^*Rh(MeCN)_3](SbF_6)_2$ as the catalyst system.

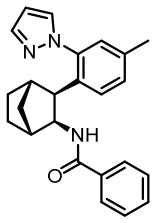


3,5-Dimethyl-*N*-((1*R*,2*S*,3*S*,4*S*)-3-(2-(pyrrolidine-1-carbonyl)phenyl)bicyclo[2.2.1]heptan-2-yl)benzamide (5a): Derived from phenyl(pyrrolidin-1-yl)methanone (8.8 mg, 0.050 mmol, 1.0 equiv), bicyclo[2.2.1]hept-2-ene (18.8 mg, 0.200 mmol, 4.0 equiv), and 3-(3,5-dimethylphenyl)-1,4,2-dioxazol-5-one (28.7 mg, 0.150 mmol, 3.0 equiv). The reaction was conducted in DCE at 70 °C for 48 h. Purification by silica gel chromatography (70% ethyl acetate in hexanes), followed by preparative TLC (1% methanol in CH_2Cl_2) afforded the product **5a** (12.2 mg, 59% yield) as a white solid. $[\alpha]_D^{20}$ +40.55° (*c* = 0.1, $CHCl_3$). 90:10 er (Chiralpak AD-H, 80:20 hexanes:isopropanol, 1 mL/min, 254 nm, t_r (minor) = 11.30 min, t_r (major) = 12.88 min). IR (neat): 2958, 1622, 1596, 1510, 1423, 1092, 1028, 729 cm^{-1}; ^1H NMR (500 MHz, CD_3CN, 50 °C) δ 7.54 (d, *J* = 7.8 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.06 (s, 1H), 6.83 (s, 2H), 6.06 (s, 1H), 4.09 (t, *J* = 7.9 Hz, 1H), 3.56 (t, *J* = 7.1 Hz, 2H), 3.25 (d, *J* = 8.4 Hz, 1H), 3.09 – 2.99 (m, 2H), 2.47 (d, *J* = 1.5 Hz, 1H), 2.38 (d, *J* = 4.8 Hz, 1H), 2.22 (s, 6H), 2.02 (d, *J* = 9.6 Hz, 1H), 1.93 – 1.87 (m, 2H), 1.81 – 1.73 (m, 2H), 1.72 – 1.66 (m, 1H), 1.65 – 1.58 (m, 1H), 1.46 – 1.35 (m, 3H). ^{13}C NMR (151 MHz, $CDCl_3$, 3 mm tube) δ 169.2, 166.6, 138.7, 138.2, 137.6, 134.4, 133.0, 129.5, 127.2, 127.1, 126.8, 124.5, 57.2, 48.9, 48.0, 45.9, 42.5, 41.6, 36.3, 31.0, 26.1, 25.4, 24.5, 21.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{27}H_{33}N_2O_2^+$: 417.2542. Found 417.2541.

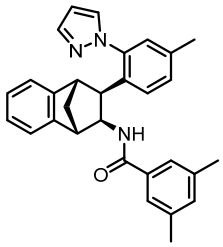


3,5-Dimethyl-*N*-((1*R*,2*S*,3*S*,4*S*)-3-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)bicyclo[2.2.1]heptan-2-yl)benzamide (5b): Derived from 1-(m-tolyl)pyrazole (7.9 mg, 0.050 mmol, 1.0 equiv), bicyclo[2.2.1]hept-2-ene (18.8 mg, 0.200 mmol, 4.0 equiv), and 3-(3,5-dimethylphenyl)-1,4,2-dioxazol-5-one (28.7 mg, 0.150 mmol, 3.0 equiv). The reaction was conducted in DCE at 70 °C for 48 h. Purification by silica gel chromatography (20% ethyl acetate in hexanes) afforded the product **5b** (11.6 mg, 58% yield) as a white solid. $[\alpha]_D^{20}$ +3.81° (*c* = 0.77, $CHCl_3$). 92:8 er (Chiralpak IB, 97:3 hexanes:isopropanol, 1 mL/min, 230 nm, t_r (minor) = 27.08 min, t_r (major) = 22.18 min). IR (neat): 2960, 1648, 1604, 1510, 1313, 1239, 1042

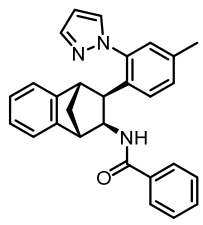
cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 (d, *J* = 1.8 Hz, 1H), 7.46 (d, *J* = 7.9 Hz, 1H), 7.42 (d, *J* = 2.4 Hz, 1H), 7.35 (d, *J* = 8.8 Hz, 1H), 7.18 (s, 1H), 7.02 (s, 1H), 6.71 (s, 2H), 6.38 (t, *J* = 2.0 Hz, 1H), 5.55 (d, *J* = 8.1 Hz, 1H), 3.86 (t, *J* = 8.3 Hz, 1H), 3.15 (d, *J* = 8.4 Hz, 1H), 2.55 (d, *J* = 2.4 Hz, 1H), 2.42 (s, 3H), 2.37 (d, *J* = 4.3 Hz, 1H), 2.22 (s, 6H), 1.74 (d, *J* = 10.5 Hz, 1H), 1.64 – 1.58 (m, 1H), 1.57 – 1.50 (m, 1H), 1.41 (d, *J* = 10.5 Hz, 1H), 1.36 – 1.24 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.4, 141.1, 140.8, 138.3, 137.6, 134.9, 134.0, 132.9, 131.4, 129.9, 128.7, 127.1, 124.5, 106.6, 57.0, 46.2, 42.7, 40.9, 36.0, 30.5, 25.7, 21.3, 20.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{26}H_{30}N_3O^+$: 400.2389. Found 400.2387.



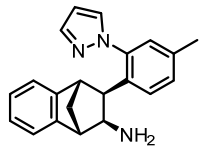
***N*-((1*R*,2*S*,3*S*,4*S*)-3-(4-Methyl-2-(1*H*-pyrazol-1-yl)phenyl)bicyclo[2.2.1]heptan-2-yl)benzamide (5c):** Derived from 1-(m-tolyl)pyrazole (7.9 mg, 0.050 mmol, 1.0 equiv), bicyclo[2.2.1]hept-2-ene (18.8 mg, 0.200 mmol, 4.0 equiv), and 3-phenyl-1,4,2-dioxazol-5-one (24.5 mg, 0.150 mmol, 3.0 equiv). The reaction was conducted in dioxane at 70 °C for 48 h. Purification by silica gel chromatography (20% ethyl acetate in hexanes), followed by an additional flash column (5-10% ethyl acetate in CH_2Cl_2) afforded the product **5c** (9.5 mg, 51% yield) as a white solid. $[\alpha]_D^{20}$ +86.88° (*c* = 0.1, $CHCl_3$). 92:8 er (Chiralpak OD-H, 90:10 hexanes:isopropanol, 1 mL/min, 230 nm, t_r (minor) = 8.50 min, t_r (major) = 9.87 min). IR (neat): 2953, 2810, 1648, 1515, 1483, 1284, 1099, 1041, 948, 756, 709, 691 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 (d, *J* = 1.9 Hz, 1H), 7.47 – 7.43 (m, 2H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.35 – 7.30 (m, 1H), 7.28 (t, *J* = 7.8 Hz, 2H), 7.22 – 7.18 (m, 2H), 7.16 (s, 1H), 6.39 (t, *J* = 2.0 Hz, 1H), 5.63 (d, *J* = 7.9 Hz, 1H), 3.91 (t, *J* = 8.2 Hz, 1H), 3.12 (d, *J* = 8.4 Hz, 1H), 2.53 (d, *J* = 2.2 Hz, 1H), 2.41 (d, *J* = 5.4 Hz, 1H), 2.40 (s, 3H), 1.76 (d, *J* = 10.5 Hz, 1H), 1.67 – 1.58 (m, 1H), 1.58 – 1.49 (m, 1H), 1.42 (d, *J* = 10.6 Hz, 1H), 1.37 – 1.30 (m, 1H), 1.30 – 1.23 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.2, 141.0, 140.8, 137.7, 134.9, 133.7, 131.4, 131.4, 129.9, 128.6, 128.6, 127.1, 126.6, 106.6, 57.4, 46.2, 42.7, 41.2, 36.1, 30.5, 25.7, 20.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{24}H_{26}N_3O^+$: 372.2076. Found 372.2064.



3,5-Dimethyl-*N*-((1*S*,2*S*,3*S*,4*S*)-3-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)-1,2,3,4-tetrahydro-1,4-methanonaphthalen-2-yl)benzamide (5d): Derived from 1-(m-tolyl)pyrazole (7.9 mg, 0.050 mmol, 1.0 equiv), tricyclo[6.2.1.02,7]undeca-2(7),3,5,9-tetraene (14.2 mg, 0.100 mmol, 2.0 equiv), and 3-(3,5-dimethylphenyl)-1,4,2-dioxazol-5-one (28.7 mg, 0.150 mmol, 3.0 equiv). The reaction was conducted in dioxane at 70 °C for 48 h. Purification by silica gel chromatography (20% ethyl acetate in hexanes), followed by trituration with hexanes afforded the product **5d** (11.2 mg, 50% yield) as a white solid. $[\alpha]_D^{20}$ +30.91° (*c* = 0.58, $CHCl_3$). 90:10 er (Chiralpak AD-H, 90:10 hexanes:isopropanol, 1 mL/min, 230 nm, t_r (minor) = 23.86 min, t_r (major) = 19.23 min). IR (neat): 2998, 1651, 1516, 1460, 1210, 1041, 751, 527 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.9 Hz, 1H), 7.55 – 7.52 (m, 1H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 7.1 Hz, 1H), 7.30 (d, *J* = 2.4 Hz, 1H), 7.21 (s, 1H), 7.16 (d, *J* = 6.2 Hz, 1H), 7.13 – 7.06 (m, 2H), 7.05 (s, 1H), 6.78 (s, 2H), 6.25 (t, *J* = 2.0 Hz, 1H), 5.68 (d, *J* = 8.1 Hz, 1H), 3.97 (t, *J* = 8.2 Hz, 1H), 3.59 (s, 1H), 3.48 (s, 1H), 3.34 (d, *J* = 8.3 Hz, 1H), 2.46 (s, 3H), 2.24 (s, 6H), 2.20 (d, *J* = 9.8 Hz, 1H), 2.07 (d, *J* = 9.8 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.5, 149.3, 145.7, 141.5, 141.0, 138.4, 138.1, 134.7, 133.6, 133.1, 130.9, 130.1, 128.8, 127.2, 126.5, 126.2, 124.5, 122.8, 120.8, 106.8, 54.2, 50.4, 47.6, 46.4, 44.5, 21.3, 20.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{30}H_{30}N_3O^+$: 448.2389. Found 448.2380.



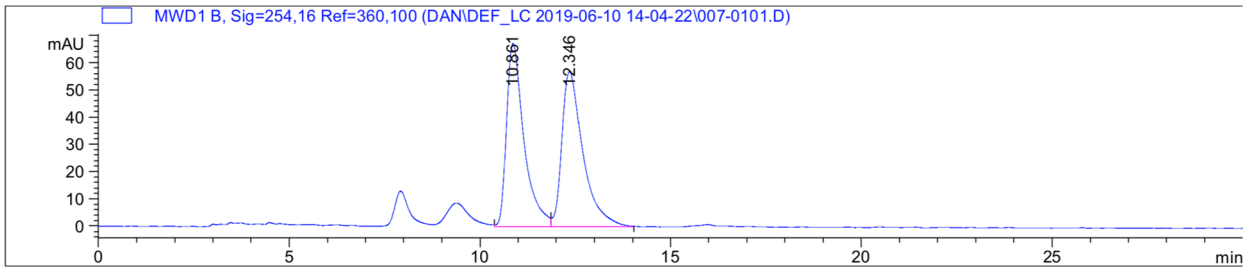
***N*-((1*S*,2*S*,3*S*,4*S*)-3-(4-Methyl-2-(1*H*-pyrazol-1-yl)phenyl)-1,2,3,4-tetrahydro-1,4-methanonaphthalen-2-yl)benzamide (5e):** Derived from 1-(m-tolyl)pyrazole (7.9 mg, 0.050 mmol, 1.0 equiv), tricyclo[6.2.1.02,7]undeca-2(7),3,5,9-tetraene (14.2 mg, 0.100 mmol, 2.0 equiv), and 3-phenyl-1,4,2-dioxazol-5-one (24.5 mg, 0.150 mmol, 3.0 equiv). The reaction was conducted in dioxane at 70 °C for 48 h. Purification by silica gel chromatography (30% ethyl acetate in hexanes), followed by an additional flash column (20% acetone in hexanes) afforded the product **5e** (12.0 mg, 57% yield) as a white solid. $[\alpha]_D^{20}$ +71.08° (*c* = 0.58, $CHCl_3$). 90:10 er (Chiralpak IB, 90:10 hexanes:isopropanol, 1 mL/min, 254 nm, t_r (minor) = 11.07 min, t_r (major) = 13.59 min). IR (neat): 1649, 1516, 1483, 1458, 1285, 1042, 951, 754, 707 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.0 Hz, 1H), 7.50 (d, *J* = 1.8 Hz, 1H), 7.43 – 7.35 (m, 2H), 7.33 – 7.26 (m, 3H), 7.25 – 7.21 (m, 3H), 7.16 (s, 1H), 7.14 – 7.08 (m, 1H), 7.08 – 7.04 (m, 2H), 6.23 (t, *J* = 2.1 Hz, 1H), 5.74 (d, *J* = 7.7 Hz, 1H), 3.98 (t, *J* = 8.0 Hz, 1H), 3.55 (s, 1H), 3.50 (s, 1H), 3.28 (d, *J* = 8.4 Hz, 1H), 2.42 (s, 3H), 2.19 (d, *J* = 9.9 Hz, 1H), 2.05 (d, *J* = 9.8 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.3, 149.4, 145.6, 141.4, 141.0, 138.2, 134.7, 133.1, 131.6, 130.8, 130.1, 128.7, 128.7, 127.2, 126.7, 126.5, 126.2, 122.8, 120.8, 106.8, 54.6, 50.3, 47.8, 46.5, 44.5, 20.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{28}H_{26}N_3O^+$: 420.2076. Found 420.2083.



(1S,2S,3S,4S)-3-(4-Methyl-2-(1H-pyrazol-1-yl)phenyl)-1,2,3,4-tetrahydro-1,4-methanonaphthalen-2-amine (7): Adapted from the published literature procedure.[18] A 2–5 mL microwave vial was charged with amide **5d** (9.0 mg, 0.020 mmol, 1 equiv), which was purified to 100% enantiopurity for the major enantiomer by semi-prep HPLC purification using a 10 mm x 25 cm Chiralpak AD-H column (93:7 hexanes:isopropanol, 3 mL/min, 300 µL injection of 50 mg/mL in isopropanol, 254 nm, t_r (major) = 31.7 min). Next, 1.0 mL of a 6N HCl solution was added. The mixture was stirred and refluxed at 110 °C for 48 h. The crude reaction mixture was then treated with 1M NaOH at 0 °C until the pH was ~8. The crude product was then extracted with CH_2Cl_2 (2x), dried over $MgSO_4$, and concentrated in vacuo. Purification by silica gel chromatography (95/5/1 CH_2Cl_2/MeOH/NH_4OH), followed by trituration with hexanes afforded the product **7** (6.0 mg, 95% yield) as a white solid. 100:0 er (Chiralpak AD-H, 90:10 hexanes:isopropanol + 0.1% diethylamine, 1 mL/min, 254 nm, t_r (major) = 13.36 min). IR (neat): 3103, 2943, 2857, 1512, 1458, 1391, 1038, 833, 752, 519 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.58 – 7.51 (m, 2H), 7.46 (d, *J* = 7.9 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.19 (d, *J* = 6.7 Hz, 1H), 7.09 (d, *J* = 6.3 Hz, 2H), 7.07 – 6.99 (m, 2H), 6.33 – 6.27 (m, 1H), 3.47 (s, 1H), 3.18 (s, 1H), 3.00 (d, *J* = 7.5 Hz, 1H), 2.69 (d, *J* = 7.4 Hz, 1H), 2.44 – 2.32 (m, 4H), 1.98 (d, *J* = 9.4 Hz, 1H), 1.44 (bs, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.8, 147.7, 140.7, 140.4, 137.0, 135.0, 130.7, 129.9, 128.0, 127.9, 125.9, 125.8, 121.9, 120.6, 106.5, 57.4, 52.3, 48.5, 46.7, 45.7, 20.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{21}N_3^+$: 316.1808. Found 316.1808.

HPLC Traces:

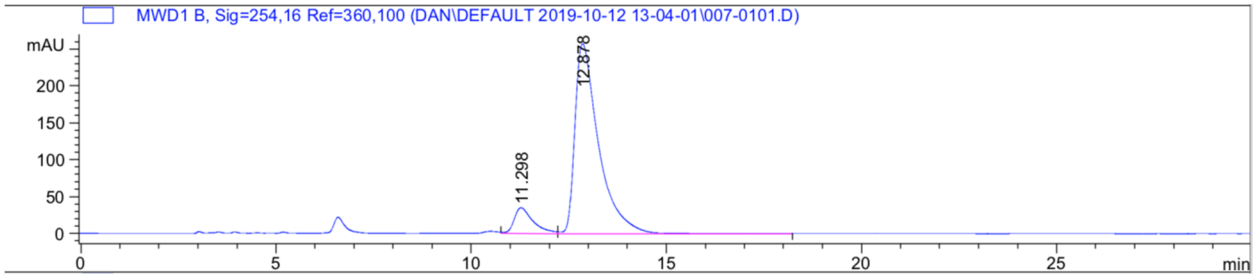
Racemic **5a** (Chiralpak AD-H, 80:20 hexanes:isopropanol, 1 mL/min, 254 nm):



Signal 2: MWD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.861	VV	0.4728	2136.03003	67.20137	49.4702
2	12.346	VB	0.5698	2181.77759	56.83976	50.5298
Totals :				4317.80762	124.04113	

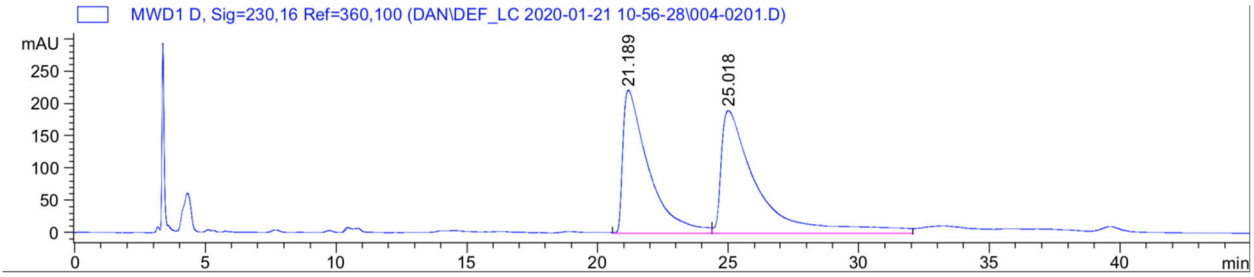
Enantiomerically enriched **5a** (90:10 er):



Signal 2: MWD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.298	VV	0.5349	1201.02539	34.43762	9.9070
2	12.878	VV	0.6405	1.09220e4	256.65607	90.0930
Totals :				1.21230e4	291.09369	

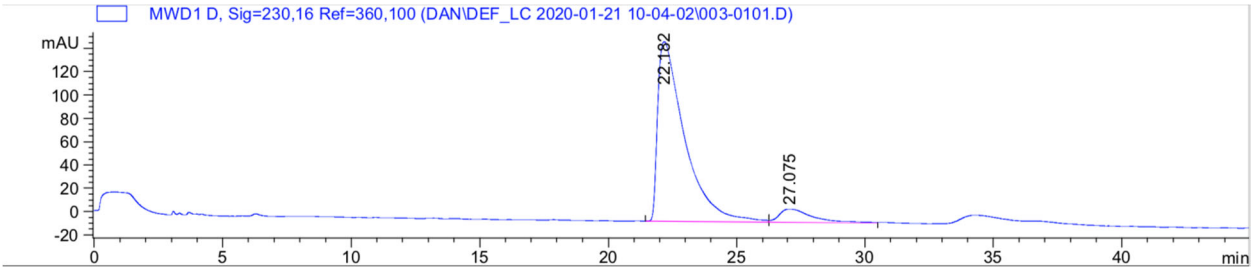
Racemic **5b** (Chiralpak IB, 97:3 hexanes:isopropanol, 1 mL/min, 230 nm):



Signal 4: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.189	VV	0.9849	1.50548e4	221.51482	45.2452
2	25.018	VV	1.3357	1.82190e4	189.83542	54.7548
Totals :				3.32738e4	411.35023	

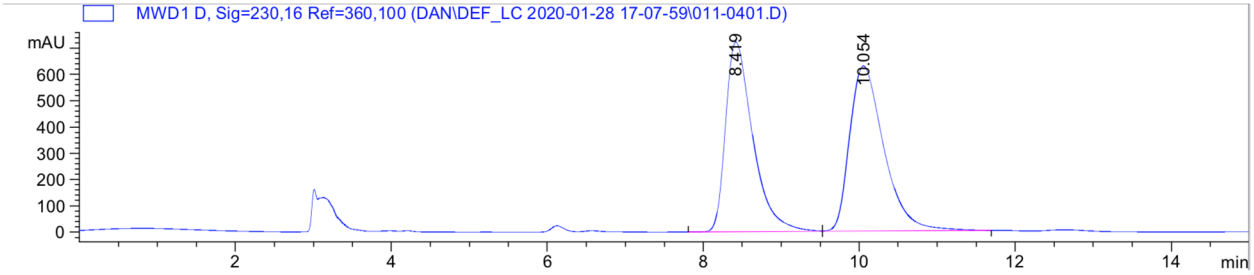
Enantiomerically enriched **5b** (92:8 er):



Signal 4: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.182	VV	1.0818	1.12352e4	154.24986	91.7409
2	27.075	VB	1.3194	1011.46753	11.35285	8.2591
Totals :				1.22467e4	165.60271	

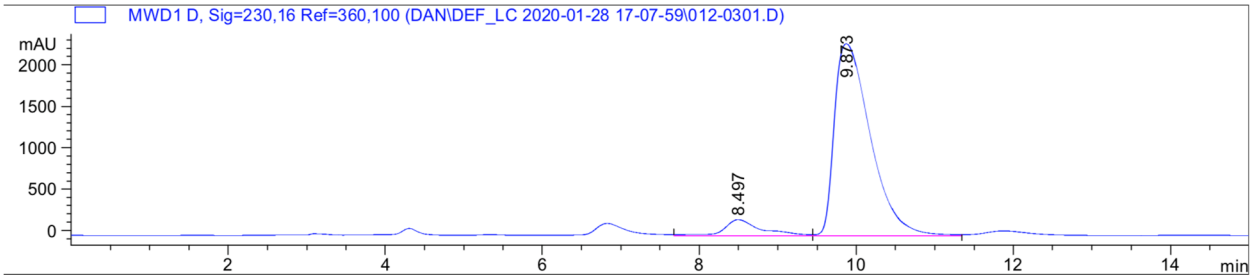
Racemic **5c** (Chiralpak OD-H, 90:10 hexanes:isopropanol, 1 mL/min, 230 nm):



Signal 4: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.419	VV	0.3698	1.75860e4	722.84894	47.9240
2	10.054	VB	0.4765	1.91097e4	628.83636	52.0760
Totals :				3.66957e4	1351.68530	

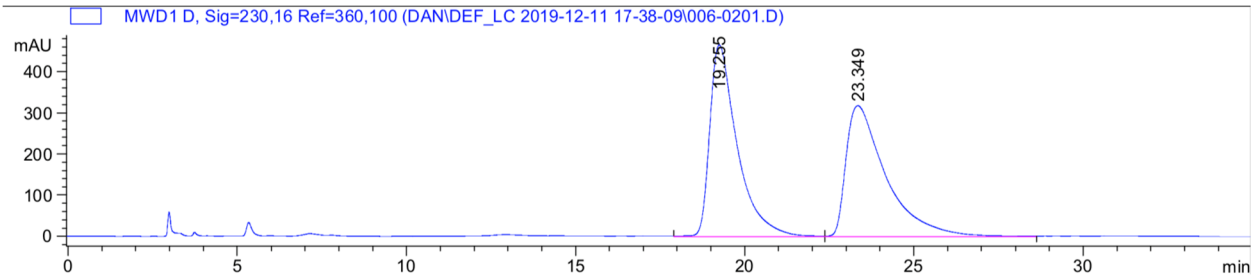
Enantiomerically enriched **5c** (92:8 er):



Signal 4: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.497	VV	0.4604	6083.48389	190.56099	7.6424
2	9.873	VV	0.4903	7.35184e4	2316.55347	92.3576
Totals :				7.96019e4	2507.11446	

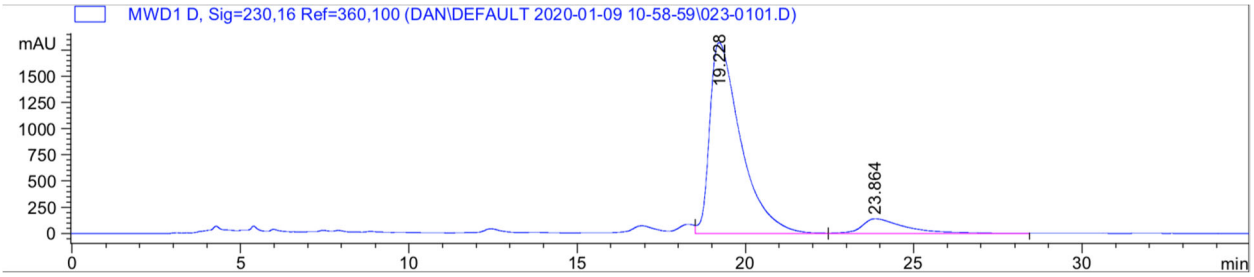
Racemic **5d** (Chiralpak AD-H, 90:10 hexanes:isopropanol, 1 mL/min, 230 nm):



Signal 4: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.255	VV	0.8259	2.61915e4	464.44534	50.2289
2	23.349	VV	1.1866	2.59528e4	317.18253	49.7711
Totals :				5.21443e4	781.62787	

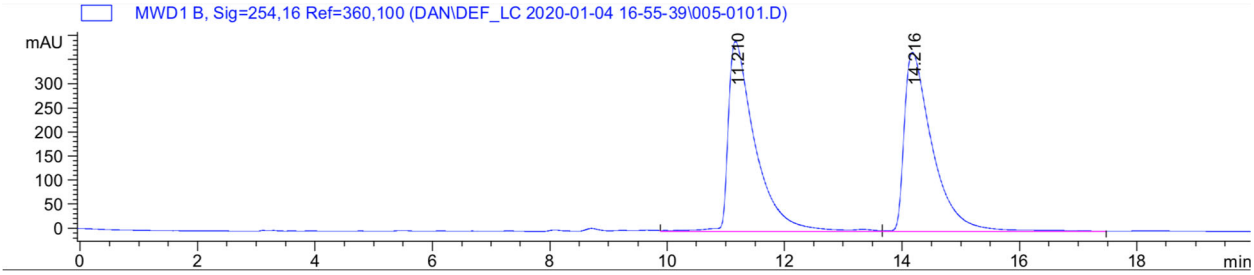
Enantiomerically enriched **5d** (90:10 er):



Signal 4: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.228	VV	0.9656	1.17157e5	1823.50867	90.0852
2	23.864	VV	1.2957	1.28944e4	141.42340	9.9148
Totals :				1.30052e5	1964.93207	

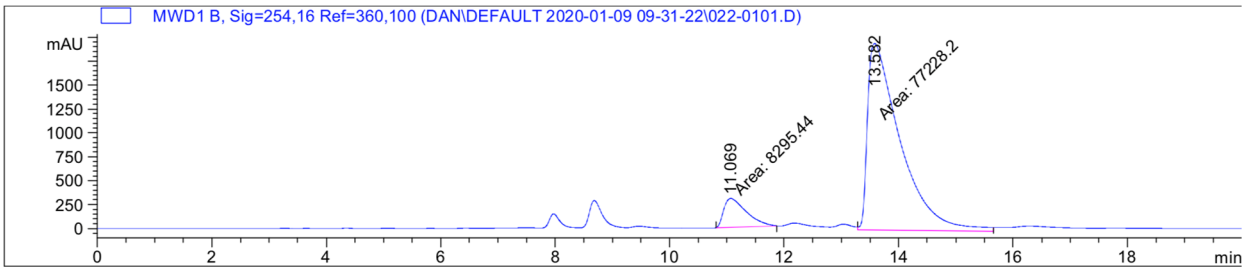
Racemic **5e** (Chiralpak IB, 90:10 hexanes:isopropanol, 1 mL/min, 254 nm):



Signal 2: MWD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.210	VV	0.4851	1.26030e4	377.86429	50.4537
2	14.216	VV	0.5050	1.23764e4	367.40448	49.5463
Totals :				2.49794e4	745.26877	

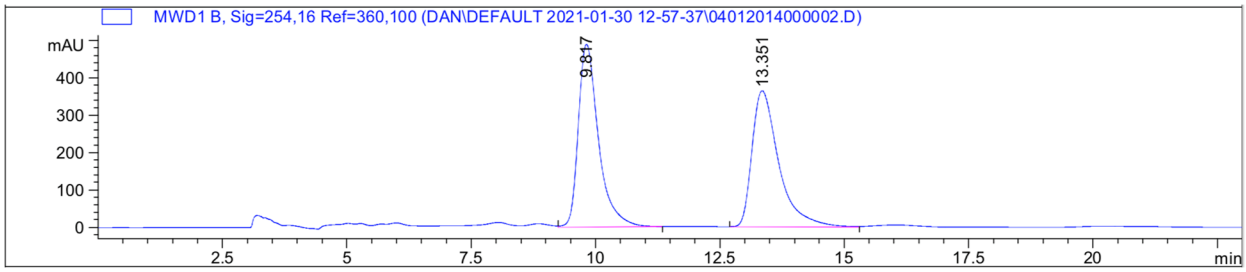
Enantiomerically enriched **5e** (90:10 er):



Signal 2: MWD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.069	MM	0.4564	8295.44043	302.94525	9.6996
2	13.582	MM	0.6604	7.72282e4	1948.89355	90.3004
Totals :				8.55236e4	2251.83881	

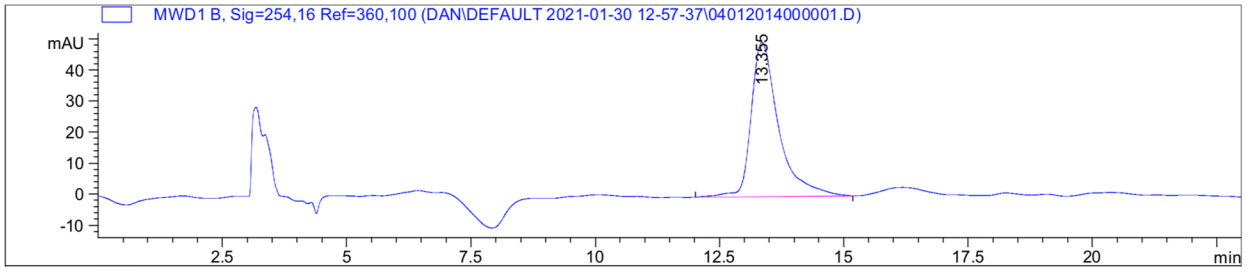
Racemic amine **7-rac** (Chiralpak AD-H, 90:10 hexanes:isopropanol+0.1% diethylamine, 1 mL/min, 254 nm):



Signal 2: MWD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.817	VB	0.4236	1.38156e4	489.00223	50.4008
2	13.351	BB	0.5657	1.35958e4	364.08530	49.5992
Totals :				2.74114e4	853.08752	

Enantiopure **7** (100:0 er):



VI. X-Ray Crystallographic Data

Product 7

Crystal Growth

Product **7** (6.0 mg, 0.019 mmol) was combined with 0.9 equiv of picrylsulfonic acid dihydrate (5.6 mg, 0.017 mmol) in a 1-dram vial. The mixture was dissolved in 10 drops of toluene combined with 5 drops of methanol. About 1 mL of hexanes was added dropwise until the cloud point was reached. Single crystals suitable for X-ray diffraction grew at room temperature overnight.

Experimental

Low-temperature diffraction data (ω-scans) were collected on a Rigaku MicroMax-007HF diffractometer coupled to a Dectris Pilatus3R detector with Mo Kα (λ = 0.71073 Å) for the structure of 007c-21017. The diffraction images were processed and scaled using Rigaku Oxford Diffraction software (CrysAlisPro; Rigaku OD: The Woodlands, TX, 2015). The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL (Sheldrick, G. M. Acta Cryst. 2008, A64, 112–122). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). The only H1A, H1B, H1C, and H10A, which were found in the difference map and freely refined. The full numbering scheme of compound 007c-21017 can be found in the full details of the X-ray structure determination (CIF), which is included as Supporting Information. CCDC number 2061171 (007c-21017) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

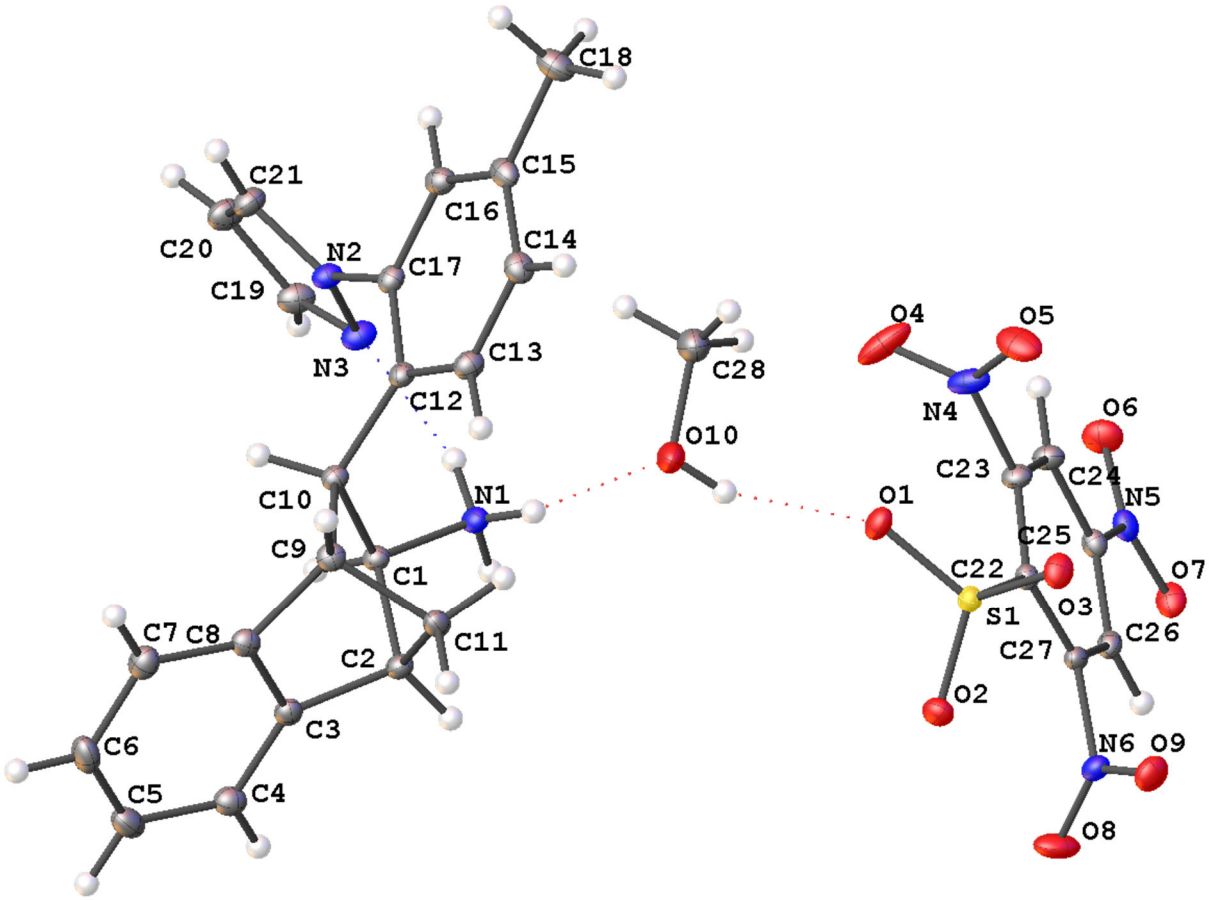


Figure 1. The complete numbering scheme of 007c-21017 with 50% thermal ellipsoid probability levels. The hydrogen atoms are shown as circles for clarity.

Table 1. Crystal data and structure refinement for 007c-21017.

Identification code	007c-21017	
Empirical formula	C28 H28 N6 O10 S	
Formula weight	640.62	
Temperature	93(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 7.6746(2) Å	α= 90°.
	b = 13.9618(4) Å	β= 90°.
	c = 26.7763(8) Å	γ = 90°.
Volume	2869.11(14) $Å^3$	
Z	4	
Density (calculated)	1.483 Mg/m^3	
Absorption coefficient	0.183 mm^{-1}	
F(000)	1336	
Crystal size	0.200 x 0.200 x 0.200 mm^3	
Crystal color and habit	Colorless Block	
Diffractometer	Dectris Pilatus 3R	
Theta range for data collection	3.016 to 30.506°.	
Index ranges	-10<=h<=10, -18<=k<=16, -38<=l<=35	
Reflections collected	25001	
Independent reflections	7751 [R(int) = 0.0188]	
Observed reflections (I > 2sigma(I))	7373	
Completeness to theta = 25.242°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.48881	
Solution method	SHELXT-2014/5 (Sheldrick, 2014)	
Refinement method	SHELXL-2014/7 (Sheldrick, 2014)	
Data / restraints / parameters	7751 / 0 / 424	
Goodness-of-fit on F^2	1.028	
Final R indices [I>2sigma(I)]	R1 = 0.0267, wR2 = 0.0691	
R indices (all data)	R1 = 0.0289, wR2 = 0.0699	
Absolute structure parameter	0.014(14)	
Largest diff. peak and hole	0.315 and -0.258 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 007c-21017. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	-300(1)	6658(1)	5914(1)	11(1)
O(1)	700(2)	5777(1)	5875(1)	16(1)
O(2)	633(2)	7436(1)	6144(1)	16(1)
O(3)	-2073(2)	6517(1)	6086(1)	16(1)
O(4)	723(2)	4867(1)	4839(1)	31(1)
O(5)	-1817(2)	4976(1)	5199(1)	26(1)
O(6)	-426(2)	7168(1)	3423(1)	20(1)
O(7)	-707(2)	8672(1)	3620(1)	17(1)
O(8)	430(2)	9374(1)	5457(1)	25(1)
O(9)	-1895(2)	8755(1)	5788(1)	19(1)
N(4)	-541(2)	5317(1)	4989(1)	18(1)
N(5)	-589(2)	7820(1)	3725(1)	13(1)
N(6)	-702(2)	8760(1)	5489(1)	13(1)
C(22)	-563(2)	7024(1)	5268(1)	10(1)
C(23)	-571(2)	6355(1)	4881(1)	13(1)
C(24)	-587(2)	6594(1)	4380(1)	14(1)
C(25)	-626(2)	7555(1)	4258(1)	12(1)
C(26)	-655(2)	8266(1)	4618(1)	12(1)
C(27)	-636(2)	7979(1)	5114(1)	11(1)
O(10)	3050(2)	4395(1)	6289(1)	26(1)
C(28)	2371(2)	3660(1)	5972(1)	24(1)
N(1)	6623(2)	4520(1)	6191(1)	13(1)
N(2)	7698(2)	2130(1)	5951(1)	12(1)
N(3)	7919(2)	2928(1)	5661(1)	15(1)
C(1)	7932(2)	4348(1)	6593(1)	11(1)
C(2)	7741(2)	5103(1)	7018(1)	12(1)
C(3)	9411(2)	5032(1)	7315(1)	13(1)
C(4)	10820(2)	5642(1)	7367(1)	16(1)
C(5)	12172(2)	5364(1)	7687(1)	19(1)
C(6)	12107(2)	4493(1)	7938(1)	20(1)
C(7)	10697(2)	3862(1)	7876(1)	17(1)

C(8)	9349(2)	4147(1)	7565(1)	13(1)
C(9)	7633(2)	3681(1)	7427(1)	13(1)
C(10)	7744(2)	3348(1)	6868(1)	11(1)
C(11)	6465(2)	4583(1)	7372(1)	13(1)
C(12)	6226(2)	2695(1)	6722(1)	11(1)
C(13)	4751(2)	2581(1)	7027(1)	14(1)
C(14)	3470(2)	1902(1)	6931(1)	15(1)
C(15)	3594(2)	1287(1)	6522(1)	14(1)
C(16)	5024(2)	1402(1)	6209(1)	14(1)
C(17)	6295(2)	2089(1)	6304(1)	12(1)
C(18)	2252(2)	529(1)	6411(1)	19(1)
C(19)	9080(2)	2664(1)	5317(1)	18(1)
C(20)	9591(2)	1702(1)	5377(1)	19(1)
C(21)	8658(2)	1385(1)	5782(1)	17(1)

Table 3. Bond lengths [Å] and angles [°] for 007c-21017.

S(1)-O(2)	1.4399(12)
S(1)-O(3)	1.4507(12)
S(1)-O(1)	1.4547(11)
S(1)-C(22)	1.8143(15)
O(4)-N(4)	1.224(2)
O(5)-N(4)	1.225(2)
O(6)-N(5)	1.2234(18)
O(7)-N(5)	1.2250(17)
O(8)-N(6)	1.2237(18)
O(9)-N(6)	1.2161(18)
N(4)-C(23)	1.4775(19)
N(5)-C(25)	1.4752(19)
N(6)-C(27)	1.4823(19)
C(22)-C(23)	1.396(2)
C(22)-C(27)	1.396(2)
C(23)-C(24)	1.382(2)
C(24)-C(25)	1.381(2)
C(24)-H(24)	0.9500
C(25)-C(26)	1.384(2)
C(26)-C(27)	1.388(2)
C(26)-H(26)	0.9500
O(10)-C(28)	1.430(2)
O(10)-H(10A)	0.82(3)
C(28)-H(28A)	0.9800
C(28)-H(28B)	0.9800
C(28)-H(28C)	0.9800
N(1)-C(1)	1.493(2)
N(1)-H(1A)	0.92(3)
N(1)-H(1B)	0.87(2)
N(1)-H(1C)	0.89(2)
N(2)-C(21)	1.353(2)
N(2)-N(3)	1.3694(18)
N(2)-C(17)	1.433(2)
N(3)-C(19)	1.333(2)

C(1)-C(2)	1.559(2)
C(1)-C(10)	1.585(2)
C(1)-H(1)	1.0000
C(2)-C(3)	1.511(2)
C(2)-C(11)	1.543(2)
C(2)-H(2)	1.0000
C(3)-C(4)	1.383(2)
C(3)-C(8)	1.406(2)
C(4)-C(5)	1.400(2)
C(4)-H(4)	0.9500
C(5)-C(6)	1.390(3)
C(5)-H(5)	0.9500
C(6)-C(7)	1.405(2)
C(6)-H(6)	0.9500
C(7)-C(8)	1.387(2)
C(7)-H(7)	0.9500
C(8)-C(9)	1.514(2)
C(9)-C(11)	1.553(2)
C(9)-C(10)	1.569(2)
C(9)-H(9)	1.0000
C(10)-C(12)	1.530(2)
C(10)-H(10)	1.0000
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(12)-C(13)	1.405(2)
C(12)-C(17)	1.405(2)
C(13)-C(14)	1.391(2)
C(13)-H(13)	0.9500
C(14)-C(15)	1.394(2)
C(14)-H(14)	0.9500
C(15)-C(16)	1.392(2)
C(15)-C(18)	1.507(2)
C(16)-C(17)	1.391(2)
C(16)-H(16)	0.9500
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800

C(18)-H(18C)	0.9800
C(19)-C(20)	1.408(2)
C(19)-H(19)	0.9500
C(20)-C(21)	1.374(2)
C(20)-H(20)	0.9500
C(21)-H(21)	0.9500

O(2)-S(1)-O(3)	115.62(7)
O(2)-S(1)-O(1)	114.00(7)
O(3)-S(1)-O(1)	113.72(7)
O(2)-S(1)-C(22)	104.62(7)
O(3)-S(1)-C(22)	103.74(7)
O(1)-S(1)-C(22)	103.23(7)
O(4)-N(4)-O(5)	125.73(14)
O(4)-N(4)-C(23)	116.84(15)
O(5)-N(4)-C(23)	117.32(15)
O(6)-N(5)-O(7)	125.31(13)
O(6)-N(5)-C(25)	117.08(12)
O(7)-N(5)-C(25)	117.61(13)
O(9)-N(6)-O(8)	125.75(13)
O(9)-N(6)-C(27)	117.84(13)
O(8)-N(6)-C(27)	116.36(13)
C(23)-C(22)-C(27)	114.89(13)
C(23)-C(22)-S(1)	121.33(11)
C(27)-C(22)-S(1)	123.60(11)
C(24)-C(23)-C(22)	123.96(14)
C(24)-C(23)-N(4)	115.36(13)
C(22)-C(23)-N(4)	120.67(13)
C(25)-C(24)-C(23)	117.64(14)
C(25)-C(24)-H(24)	121.2
C(23)-C(24)-H(24)	121.2
C(24)-C(25)-C(26)	122.23(14)
C(24)-C(25)-N(5)	118.10(13)
C(26)-C(25)-N(5)	119.66(13)
C(25)-C(26)-C(27)	117.34(13)
C(25)-C(26)-H(26)	121.3

C(27)-C(26)-H(26)	121.3
C(26)-C(27)-C(22)	123.91(13)
C(26)-C(27)-N(6)	115.73(13)
C(22)-C(27)-N(6)	120.36(13)
C(28)-O(10)-H(10A)	106.1(19)
O(10)-C(28)-H(28A)	109.5
O(10)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28B)	109.5
O(10)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5
C(1)-N(1)-H(1A)	106.3(15)
C(1)-N(1)-H(1B)	106.1(16)
H(1A)-N(1)-H(1B)	107(2)
C(1)-N(1)-H(1C)	113.8(14)
H(1A)-N(1)-H(1C)	116(2)
H(1B)-N(1)-H(1C)	107(2)
C(21)-N(2)-N(3)	111.59(13)
C(21)-N(2)-C(17)	126.73(13)
N(3)-N(2)-C(17)	120.03(12)
C(19)-N(3)-N(2)	104.49(13)
N(1)-C(1)-C(2)	110.77(12)
N(1)-C(1)-C(10)	114.61(12)
C(2)-C(1)-C(10)	104.33(11)
N(1)-C(1)-H(1)	109.0
C(2)-C(1)-H(1)	109.0
C(10)-C(1)-H(1)	109.0
C(3)-C(2)-C(11)	100.66(12)
C(3)-C(2)-C(1)	105.08(12)
C(11)-C(2)-C(1)	100.96(12)
C(3)-C(2)-H(2)	116.0
C(11)-C(2)-H(2)	116.0
C(1)-C(2)-H(2)	116.0
C(4)-C(3)-C(8)	121.32(15)
C(4)-C(3)-C(2)	132.51(14)
C(8)-C(3)-C(2)	106.17(13)

C(3)-C(4)-C(5)	118.04(15)
C(3)-C(4)-H(4)	121.0
C(5)-C(4)-H(4)	121.0
C(6)-C(5)-C(4)	120.76(16)
C(6)-C(5)-H(5)	119.6
C(4)-C(5)-H(5)	119.6
C(5)-C(6)-C(7)	121.29(16)
C(5)-C(6)-H(6)	119.4
C(7)-C(6)-H(6)	119.4
C(8)-C(7)-C(6)	117.74(15)
C(8)-C(7)-H(7)	121.1
C(6)-C(7)-H(7)	121.1
C(7)-C(8)-C(3)	120.83(15)
C(7)-C(8)-C(9)	132.23(14)
C(3)-C(8)-C(9)	106.92(14)
C(8)-C(9)-C(11)	100.18(12)
C(8)-C(9)-C(10)	108.19(12)
C(11)-C(9)-C(10)	100.45(12)
C(8)-C(9)-H(9)	115.3
C(11)-C(9)-H(9)	115.3
C(10)-C(9)-H(9)	115.3
C(12)-C(10)-C(9)	112.30(12)
C(12)-C(10)-C(1)	118.36(12)
C(9)-C(10)-C(1)	100.78(11)
C(12)-C(10)-H(10)	108.3
C(9)-C(10)-H(10)	108.3
C(1)-C(10)-H(10)	108.3
C(2)-C(11)-C(9)	94.21(12)
C(2)-C(11)-H(11A)	112.9
C(9)-C(11)-H(11A)	112.9
C(2)-C(11)-H(11B)	112.9
C(9)-C(11)-H(11B)	112.9
H(11A)-C(11)-H(11B)	110.3
C(13)-C(12)-C(17)	115.17(14)
C(13)-C(12)-C(10)	122.15(13)
C(17)-C(12)-C(10)	122.31(13)

C(14)-C(13)-C(12)	122.69(14)
C(14)-C(13)-H(13)	118.7
C(12)-C(13)-H(13)	118.7
C(13)-C(14)-C(15)	121.10(15)
C(13)-C(14)-H(14)	119.4
C(15)-C(14)-H(14)	119.4
C(16)-C(15)-C(14)	117.19(15)
C(16)-C(15)-C(18)	120.06(15)
C(14)-C(15)-C(18)	122.75(15)
C(17)-C(16)-C(15)	121.47(14)
C(17)-C(16)-H(16)	119.3
C(15)-C(16)-H(16)	119.3
C(16)-C(17)-C(12)	122.34(14)
C(16)-C(17)-N(2)	115.75(14)
C(12)-C(17)-N(2)	121.91(14)
C(15)-C(18)-H(18A)	109.5
C(15)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(15)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
N(3)-C(19)-C(20)	111.81(14)
N(3)-C(19)-H(19)	124.1
C(20)-C(19)-H(19)	124.1
C(21)-C(20)-C(19)	104.62(14)
C(21)-C(20)-H(20)	127.7
C(19)-C(20)-H(20)	127.7
N(2)-C(21)-C(20)	107.45(14)
N(2)-C(21)-H(21)	126.3
C(20)-C(21)-H(21)	126.3

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 007c-21017. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	11(1)	11(1)	10(1)	1(1)	0(1)	1(1)
O(1)	17(1)	14(1)	15(1)	0(1)	-2(1)	6(1)
O(2)	17(1)	16(1)	16(1)	-2(1)	-4(1)	-1(1)
O(3)	13(1)	17(1)	18(1)	4(1)	4(1)	1(1)
O(4)	56(1)	16(1)	21(1)	1(1)	12(1)	14(1)
O(5)	33(1)	18(1)	25(1)	8(1)	-7(1)	-11(1)
O(6)	28(1)	21(1)	12(1)	-1(1)	-1(1)	-2(1)
O(7)	16(1)	16(1)	18(1)	7(1)	0(1)	0(1)
O(8)	27(1)	17(1)	31(1)	-8(1)	5(1)	-10(1)
O(9)	18(1)	19(1)	21(1)	-2(1)	5(1)	4(1)
N(4)	34(1)	10(1)	11(1)	0(1)	-3(1)	-2(1)
N(5)	11(1)	16(1)	13(1)	3(1)	-1(1)	-1(1)
N(6)	16(1)	10(1)	14(1)	-1(1)	-2(1)	2(1)
C(22)	9(1)	11(1)	11(1)	1(1)	0(1)	0(1)
C(23)	16(1)	9(1)	14(1)	1(1)	0(1)	-2(1)
C(24)	17(1)	11(1)	12(1)	-1(1)	0(1)	-1(1)
C(25)	11(1)	13(1)	11(1)	2(1)	-1(1)	-1(1)
C(26)	11(1)	11(1)	16(1)	2(1)	0(1)	0(1)
C(27)	9(1)	10(1)	13(1)	-2(1)	0(1)	0(1)
O(10)	17(1)	15(1)	46(1)	-5(1)	-10(1)	4(1)
C(28)	20(1)	19(1)	32(1)	-3(1)	-6(1)	1(1)
N(1)	15(1)	10(1)	14(1)	1(1)	-2(1)	1(1)
N(2)	15(1)	9(1)	13(1)	0(1)	1(1)	-1(1)
N(3)	20(1)	11(1)	14(1)	2(1)	3(1)	-1(1)
C(1)	13(1)	10(1)	11(1)	1(1)	0(1)	0(1)
C(2)	14(1)	10(1)	13(1)	-1(1)	-1(1)	1(1)
C(3)	13(1)	13(1)	12(1)	-2(1)	0(1)	1(1)
C(4)	16(1)	15(1)	17(1)	-1(1)	2(1)	-2(1)
C(5)	14(1)	22(1)	21(1)	-6(1)	0(1)	-3(1)
C(6)	14(1)	27(1)	17(1)	-3(1)	-4(1)	2(1)
C(7)	19(1)	18(1)	15(1)	0(1)	-1(1)	3(1)

C(8)	14(1)	14(1)	12(1)	-1(1)	2(1)	0(1)
C(9)	14(1)	13(1)	11(1)	1(1)	2(1)	-1(1)
C(10)	12(1)	10(1)	11(1)	1(1)	1(1)	0(1)
C(11)	12(1)	14(1)	14(1)	-3(1)	1(1)	0(1)
C(12)	12(1)	9(1)	13(1)	1(1)	0(1)	0(1)
C(13)	15(1)	13(1)	14(1)	0(1)	2(1)	0(1)
C(14)	14(1)	16(1)	16(1)	3(1)	1(1)	-2(1)
C(15)	15(1)	13(1)	15(1)	4(1)	-4(1)	-2(1)
C(16)	18(1)	12(1)	14(1)	1(1)	-2(1)	0(1)
C(17)	13(1)	10(1)	12(1)	2(1)	1(1)	1(1)
C(18)	20(1)	20(1)	17(1)	1(1)	-3(1)	-7(1)
C(19)	22(1)	16(1)	15(1)	-1(1)	4(1)	-2(1)
C(20)	20(1)	17(1)	18(1)	-3(1)	5(1)	1(1)
C(21)	18(1)	12(1)	19(1)	-1(1)	2(1)	2(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 007c-21017.

	x	y	z	U(eq)
H(24)	-573	6115	4128	16
H(26)	-688	8925	4530	15
H(28A)	1954	3945	5660	35
H(28B)	1404	3336	6141	35
H(28C)	3292	3194	5898	35
H(1)	9129	4396	6447	13
H(2)	7392	5761	6911	15
H(4)	10869	6232	7191	20
H(5)	13144	5776	7733	23
H(6)	13034	4321	8155	23
H(7)	10669	3261	8042	20
H(9)	7200	3188	7668	15
H(10)	8854	2983	6823	13
H(11A)	5328	4443	7213	16
H(11B)	6290	4927	7692	16
H(13)	4624	2985	7310	17
H(14)	2493	1856	7148	18
H(16)	5135	1003	5923	17
H(18A)	1993	528	6053	29
H(18B)	1184	665	6599	29
H(18C)	2705	-100	6509	29
H(19)	9510	3075	5062	21
H(20)	10402	1352	5181	22
H(21)	8682	757	5919	20
H(1A)	6880(30)	4095(17)	5940(9)	27(6)
H(1B)	6840(30)	5093(18)	6073(8)	24(6)
H(1C)	5530(30)	4523(14)	6298(8)	15(5)
H(10A)	2500(40)	4879(19)	6222(10)	34(7)

Table 6. Torsion angles [°] for 007c-21017.

O(2)-S(1)-C(22)-C(23)	147.19(12)
O(3)-S(1)-C(22)-C(23)	-91.22(13)
O(1)-S(1)-C(22)-C(23)	27.65(14)
O(2)-S(1)-C(22)-C(27)	-27.67(15)
O(3)-S(1)-C(22)-C(27)	93.92(14)
O(1)-S(1)-C(22)-C(27)	-147.21(13)
C(27)-C(22)-C(23)-C(24)	2.2(2)
S(1)-C(22)-C(23)-C(24)	-173.13(13)
C(27)-C(22)-C(23)-N(4)	-178.55(15)
S(1)-C(22)-C(23)-N(4)	6.2(2)
O(4)-N(4)-C(23)-C(24)	61.8(2)
O(5)-N(4)-C(23)-C(24)	-114.65(17)
O(4)-N(4)-C(23)-C(22)	-117.54(17)
O(5)-N(4)-C(23)-C(22)	66.0(2)
C(22)-C(23)-C(24)-C(25)	-1.0(3)
N(4)-C(23)-C(24)-C(25)	179.63(15)
C(23)-C(24)-C(25)-C(26)	-0.3(2)
C(23)-C(24)-C(25)-N(5)	178.15(14)
O(6)-N(5)-C(25)-C(24)	-4.1(2)
O(7)-N(5)-C(25)-C(24)	176.59(14)
O(6)-N(5)-C(25)-C(26)	174.42(14)
O(7)-N(5)-C(25)-C(26)	-4.9(2)
C(24)-C(25)-C(26)-C(27)	0.4(2)
N(5)-C(25)-C(26)-C(27)	-178.08(13)
C(25)-C(26)-C(27)-C(22)	0.9(2)
C(25)-C(26)-C(27)-N(6)	-178.88(13)
C(23)-C(22)-C(27)-C(26)	-2.1(2)
S(1)-C(22)-C(27)-C(26)	173.07(12)
C(23)-C(22)-C(27)-N(6)	177.71(14)
S(1)-C(22)-C(27)-N(6)	-7.1(2)
O(9)-N(6)-C(27)-C(26)	121.87(15)
O(8)-N(6)-C(27)-C(26)	-55.81(19)
O(9)-N(6)-C(27)-C(22)	-57.9(2)
O(8)-N(6)-C(27)-C(22)	124.38(16)

C(21)-N(2)-N(3)-C(19)	-1.82(18)
C(17)-N(2)-N(3)-C(19)	-168.17(14)
N(1)-C(1)-C(2)-C(3)	-164.15(12)
C(10)-C(1)-C(2)-C(3)	72.03(14)
N(1)-C(1)-C(2)-C(11)	91.53(14)
C(10)-C(1)-C(2)-C(11)	-32.30(14)
C(11)-C(2)-C(3)-C(4)	-145.74(17)
C(1)-C(2)-C(3)-C(4)	109.72(18)
C(11)-C(2)-C(3)-C(8)	34.53(15)
C(1)-C(2)-C(3)-C(8)	-70.02(14)
C(8)-C(3)-C(4)-C(5)	-1.7(2)
C(2)-C(3)-C(4)-C(5)	178.63(16)
C(3)-C(4)-C(5)-C(6)	1.1(2)
C(4)-C(5)-C(6)-C(7)	0.5(3)
C(5)-C(6)-C(7)-C(8)	-1.4(3)
C(6)-C(7)-C(8)-C(3)	0.8(2)
C(6)-C(7)-C(8)-C(9)	-177.49(16)
C(4)-C(3)-C(8)-C(7)	0.7(2)
C(2)-C(3)-C(8)-C(7)	-179.49(14)
C(4)-C(3)-C(8)-C(9)	179.44(14)
C(2)-C(3)-C(8)-C(9)	-0.79(16)
C(7)-C(8)-C(9)-C(11)	145.57(17)
C(3)-C(8)-C(9)-C(11)	-32.92(15)
C(7)-C(8)-C(9)-C(10)	-109.78(19)
C(3)-C(8)-C(9)-C(10)	71.73(15)
C(8)-C(9)-C(10)-C(12)	168.64(12)
C(11)-C(9)-C(10)-C(12)	-86.90(14)
C(8)-C(9)-C(10)-C(1)	-64.44(14)
C(11)-C(9)-C(10)-C(1)	40.03(14)
N(1)-C(1)-C(10)-C(12)	-3.28(19)
C(2)-C(1)-C(10)-C(12)	118.03(14)
N(1)-C(1)-C(10)-C(9)	-126.08(13)
C(2)-C(1)-C(10)-C(9)	-4.77(14)
C(3)-C(2)-C(11)-C(9)	-51.83(13)
C(1)-C(2)-C(11)-C(9)	56.00(13)
C(8)-C(9)-C(11)-C(2)	51.03(13)

C(10)-C(9)-C(11)-C(2)	-59.80(13)
C(9)-C(10)-C(12)-C(13)	12.0(2)
C(1)-C(10)-C(12)-C(13)	-104.84(16)
C(9)-C(10)-C(12)-C(17)	-160.69(14)
C(1)-C(10)-C(12)-C(17)	82.49(18)
C(17)-C(12)-C(13)-C(14)	1.6(2)
C(10)-C(12)-C(13)-C(14)	-171.55(14)
C(12)-C(13)-C(14)-C(15)	0.4(2)
C(13)-C(14)-C(15)-C(16)	-1.8(2)
C(13)-C(14)-C(15)-C(18)	178.79(15)
C(14)-C(15)-C(16)-C(17)	1.2(2)
C(18)-C(15)-C(16)-C(17)	-179.34(15)
C(15)-C(16)-C(17)-C(12)	0.8(2)
C(15)-C(16)-C(17)-N(2)	179.92(13)
C(13)-C(12)-C(17)-C(16)	-2.2(2)
C(10)-C(12)-C(17)-C(16)	170.97(14)
C(13)-C(12)-C(17)-N(2)	178.77(13)
C(10)-C(12)-C(17)-N(2)	-8.1(2)
C(21)-N(2)-C(17)-C(16)	-49.4(2)
N(3)-N(2)-C(17)-C(16)	114.70(15)
C(21)-N(2)-C(17)-C(12)	129.71(17)
N(3)-N(2)-C(17)-C(12)	-66.2(2)
N(2)-N(3)-C(19)-C(20)	0.92(19)
N(3)-C(19)-C(20)-C(21)	0.3(2)
N(3)-N(2)-C(21)-C(20)	2.04(19)
C(17)-N(2)-C(21)-C(20)	167.27(15)
C(19)-C(20)-C(21)-N(2)	-1.35(19)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for 007c-21017 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1A)...N(3)	0.92(3)	1.96(2)	2.8187(19)	155(2)
N(1)-H(1B)...O(3)#1	0.87(2)	2.16(3)	2.9746(18)	156(2)
N(1)-H(1B)...O(5)#1	0.87(2)	2.56(2)	2.981(2)	110.3(18)
N(1)-H(1C)...O(10)	0.89(2)	1.91(2)	2.761(2)	160(2)
O(10)-H(10A)...O(1)	0.82(3)	2.08(3)	2.8639(17)	160(3)
O(10)-H(10A)...O(7)#2	0.82(3)	2.48(3)	2.8740(18)	111(2)

Symmetry transformations used to generate equivalent atoms:

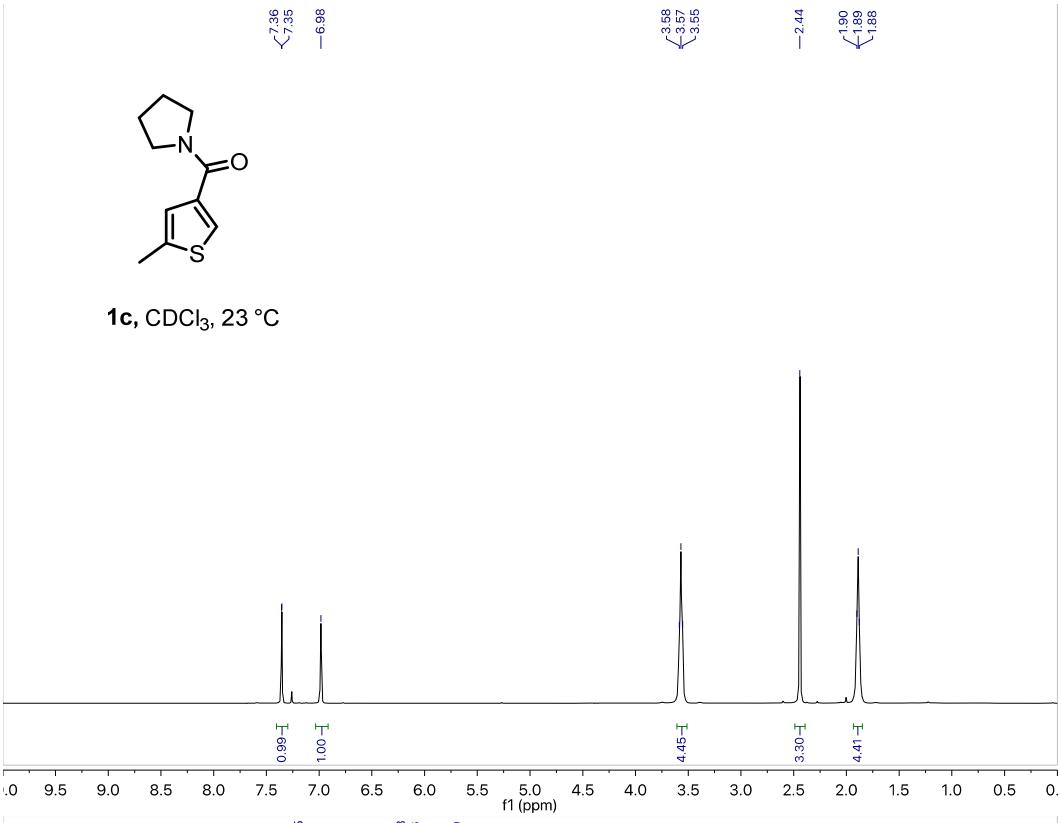
#1 x+1,y,z #2 x+1/2,-y+3/2,-z+1

VII. References

1. Fujita, K.; Takahashi, Y.; Owaki, M.; Yamamoto, K.; Yamaguchi, R. Synthesis of Five-, Six-, and Seven-Membered Ring Lactams by Cp*Rh Complex-Catalyzed Oxidative N-Heterocyclization of Amino Alcohols. *Org. Lett.* **2004***, 6*, 2785–2788.
2. Neely, J. M.; Rovis, T. Rh(III)-Catalyzed Decarboxylative Coupling of Acrylic Acids with Unsaturated Oxime Esters: Carboxylic Acids Serve as Traceless Activators. *J. Am. Chem. Soc.* **2014**, *136*, 2735–2738.
3. Potter, T. J.; Kamber, D. N.; Ellman, J. A. Rh(III)-Catalyzed Aryl and Alkenyl C–H Bond Addition to Diverse Nitroalkenes. *ACS. Catal.* **2017**, *7*, 150–153.
4. Ye, B.; Cramer, N. A Tunable Class of Chiral Cp Ligands for Enantioselective Rhodium(III)-Catalyzed C–H Allylations of Benzamides. *J. Am. Chem. Soc.* **2013**, *135*, 636–639.
5. Reddy Chidipudi, S.; Burns, D. J.; Khan, I.; Lam, H. W. Enantioselective Synthesis of Spiroindenes by Enol-Directed Rhodium(III)-Catalyzed C–H Functionalization and Spiroannulation. *Angew. Chem. Int. Ed.* **2015**, *54*, 13975–13979.
6. Shin, K.; Ryu, J.; Chang, S. Orthogonal Reactivity of Acyl Azides in C–H Activation: Dichotomy between C–C and C–N Amidations Based on Catalyst Systems. *Org. Lett.* **2014**, *16*, 2022–2025.
7. Gower, M.L.; Crowley, J.D. Self-assembly of silver(I) metallomacrocycles using unsupported 1,4-substituted-1,2,3-triazole “click” ligands. *Dalton Trans.* **2010**, *39*, 2371–2378.
8. Wangweerawong, A.; Bergman, R. G.; Ellman, J. A. Asymmetric Synthesis of α-Branched Amines via Rh(III)-Catalyzed C–H Bond Functionalization. *J. Am. Chem. Soc.* **2014**, *136*, 8520–8523.
9. Too, P.-C.; Chan, G.-H.; Tnay, Y.-L.; Hirao, H.; Chiba, S. Hydride Reduction by a Sodium Hydride–Iodide Composite. *Angew. Chem. Int. Ed.* **2016**, *55*, 3719–3723.
10. Liu, P. M.; Frost, C. G. Ruthenium-Catalyzed C–H Functionalization of Arylpyrazoles: Regioselective Acylation with Acid Chlorides. *Org. Lett.* **2013**, *15*, 5862–5865.
11. Park, Y.; Park, K. T.; Kim, J. G.; Chang, S. Mechanistic Studies on the Rh(III)-Mediated Amido Transfer Process Leading to Robust C–H Amination with a New Type of Amidating Reagent. *J. Am. Chem. Soc.* **2015**, *137*, 4534–4542.

12. Bizet, V.; Bolm, C. Sulfur Imidations by Light-Induced Ruthenium-Catalyzed Nitrene Transfer Reactions. *Eur. J. Org. Chem.* **2015**, 2854–2860.
13. Lautens, M.; Fagnou, K.; Zunic V. An Expedient Enantioselective Route to Diaminotetralins: Application in the Preparation of Analgesic Compounds. *Org. Lett.* **2002**, *4*, 3465–3468.
14. Gandeepan, P.; Rajamalli, P.; Cheng, C-H. Diastereoselective [3+2] Annulation of Aromatic/Vinylic Amides with Bicyclic Alkenes through Cobalt-Catalyzed C−H Activation and Intramolecular Nucleophilic Addition. *Angew. Chem. Int. Ed.* **2016**, *55*, 4308–4311.
15. Nishimura, T.; Kawamoto, T.; Sasaki, K.; Tsurumaki, E.; Hayashi, T. Rhodium-Catalyzed Asymmetric Cyclodimerization of Oxa- and Azabicyclic Alkenes. *J. Am. Chem. Soc.* **2007**, *129*, 1492–1493.
16. Coe, J.; Wirtz, M.; Bashore, C.; Candler, J. Formation of 3-Halobenzyne: Solvent Effects and Cycloaddition Adducts. *Org. Lett.* **2004**, *6*, 1589–1592.
17. Kulkarni, K.; Zhao, A.; Purcell, A.; Perlmutter, P. The Enantioselective Total Synthesis and Unambiguous Proof of the Absolute Stereochemistry of Pervilleine C. *Synlett*, **2008**, *14*, 2209–2212.
18. Ben-Ishai, D.; Altman, J.; Peled, N. The synthesis of p-substituted d,l-phenylglycines by the amidoalkylation of benzylchloride and N-benzylbenzamide. *Tetrahedron*, **1977**, *33*, 2715–2717.

VIII. NMR Data



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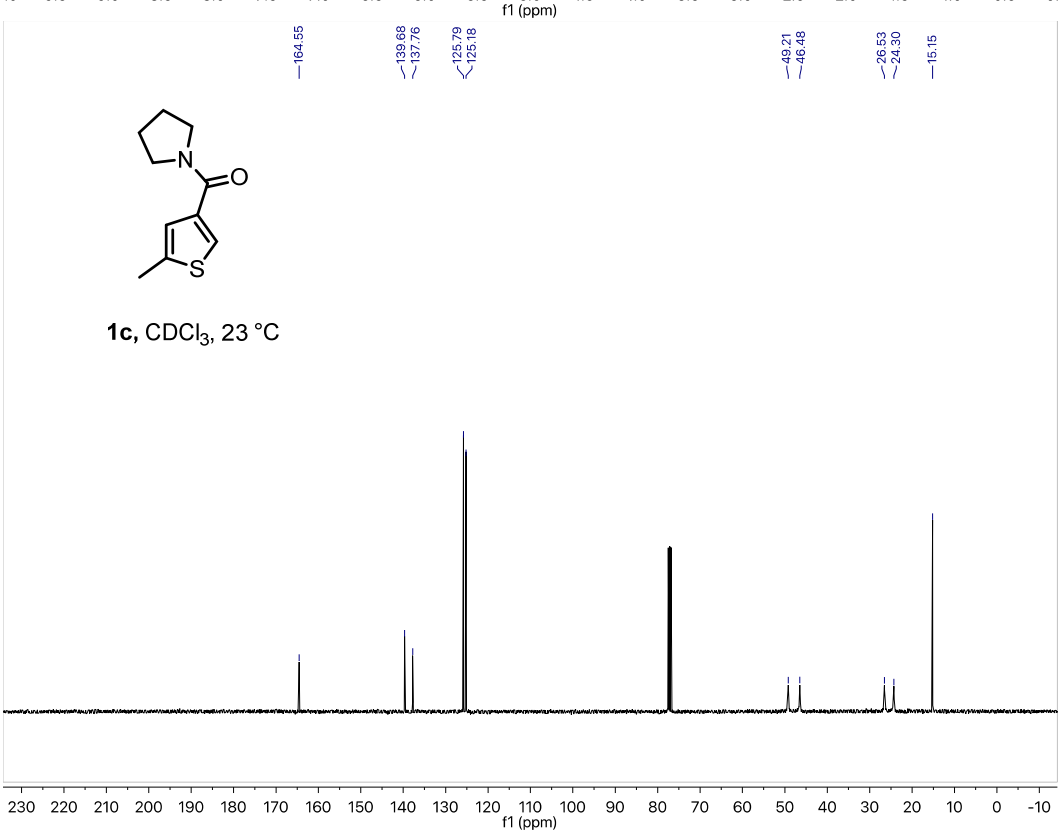

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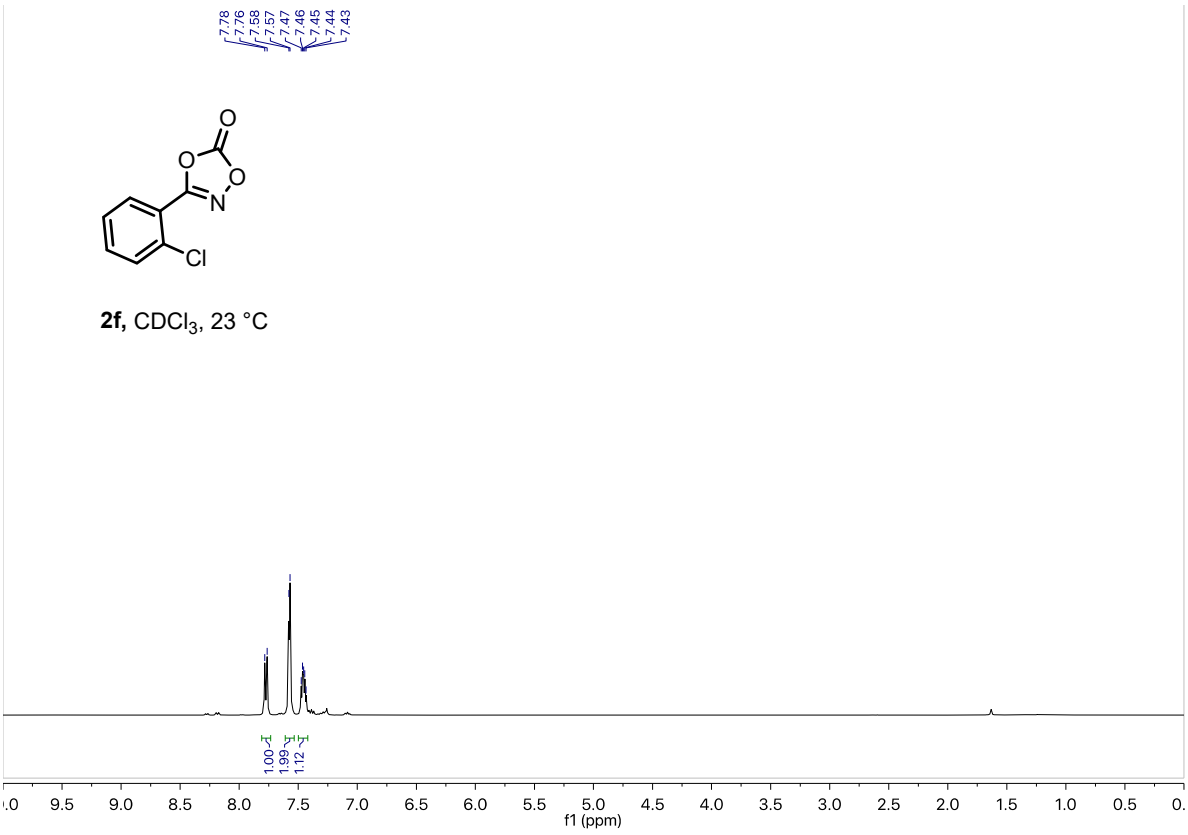

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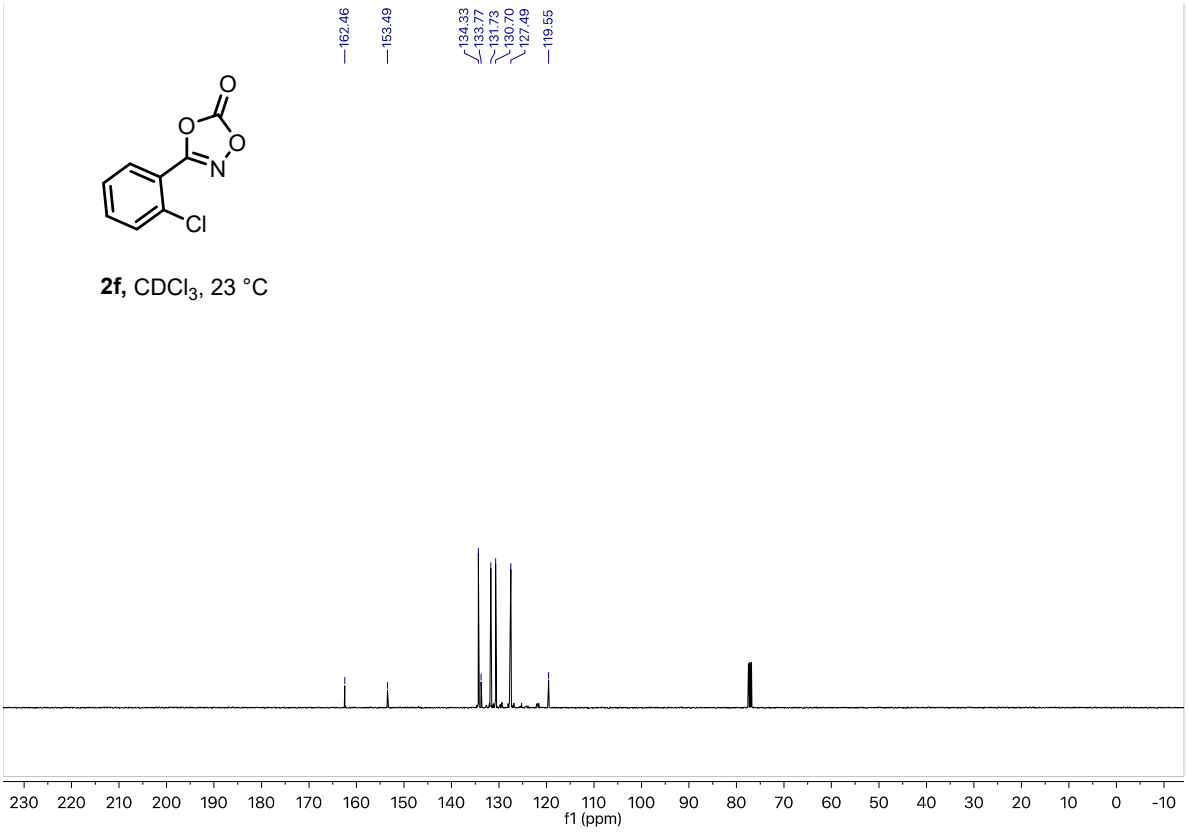

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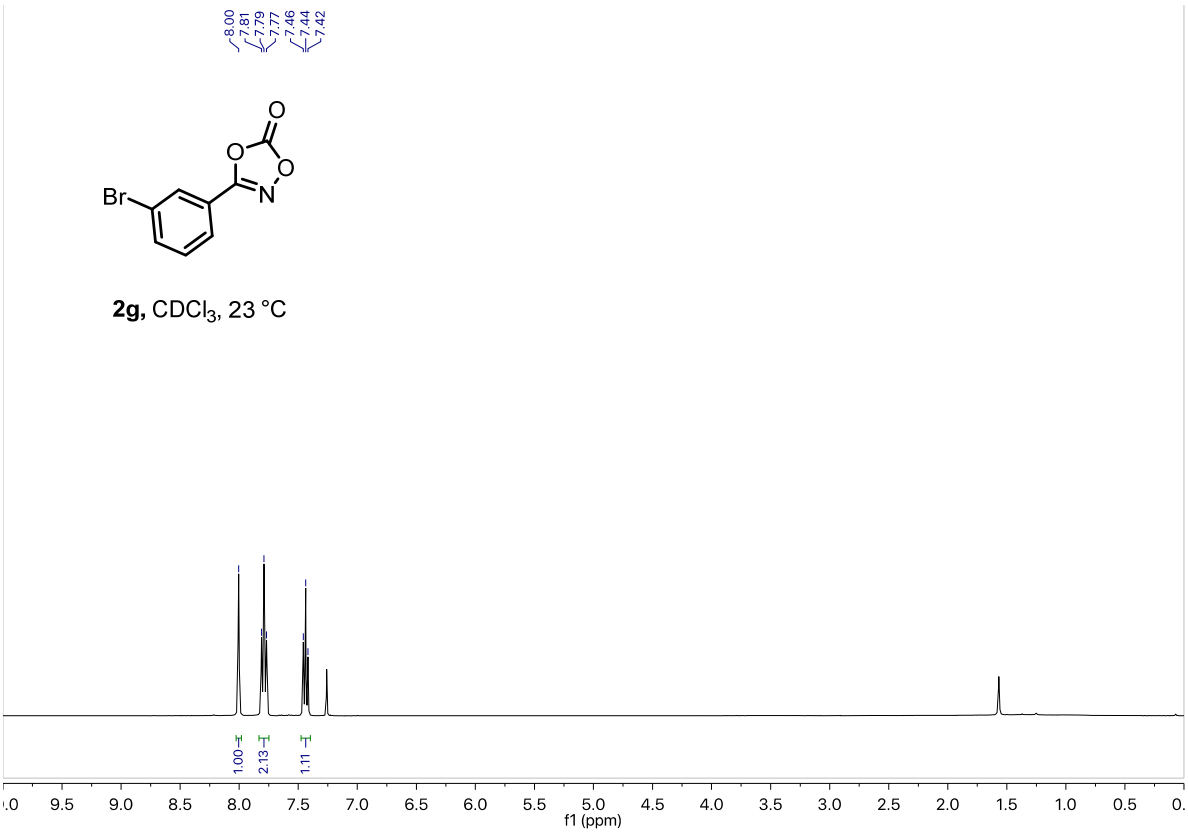
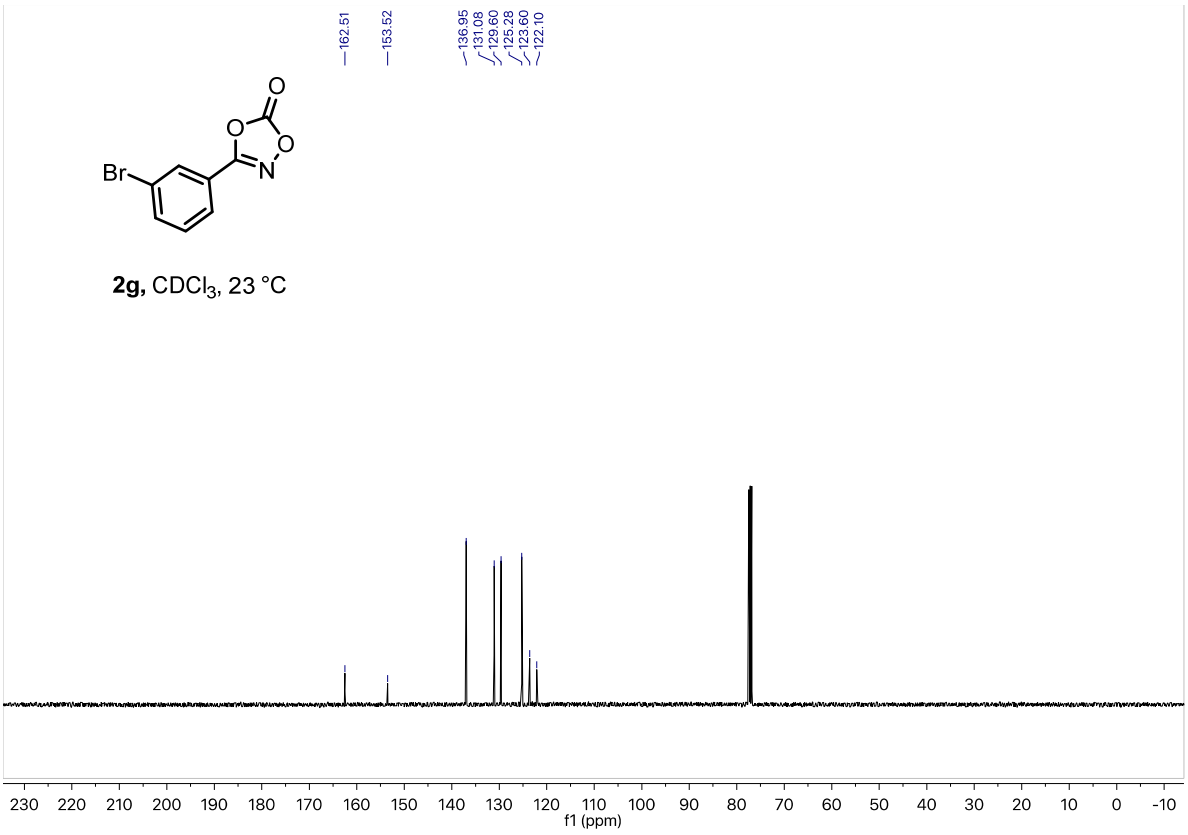

8.00
7.81
7.79
7.77
7.46
7.44
7.42
Br
O
O
O
N
2g, CDCl3, 23 °C
1.00
2.13
1.11
f1 (ppm)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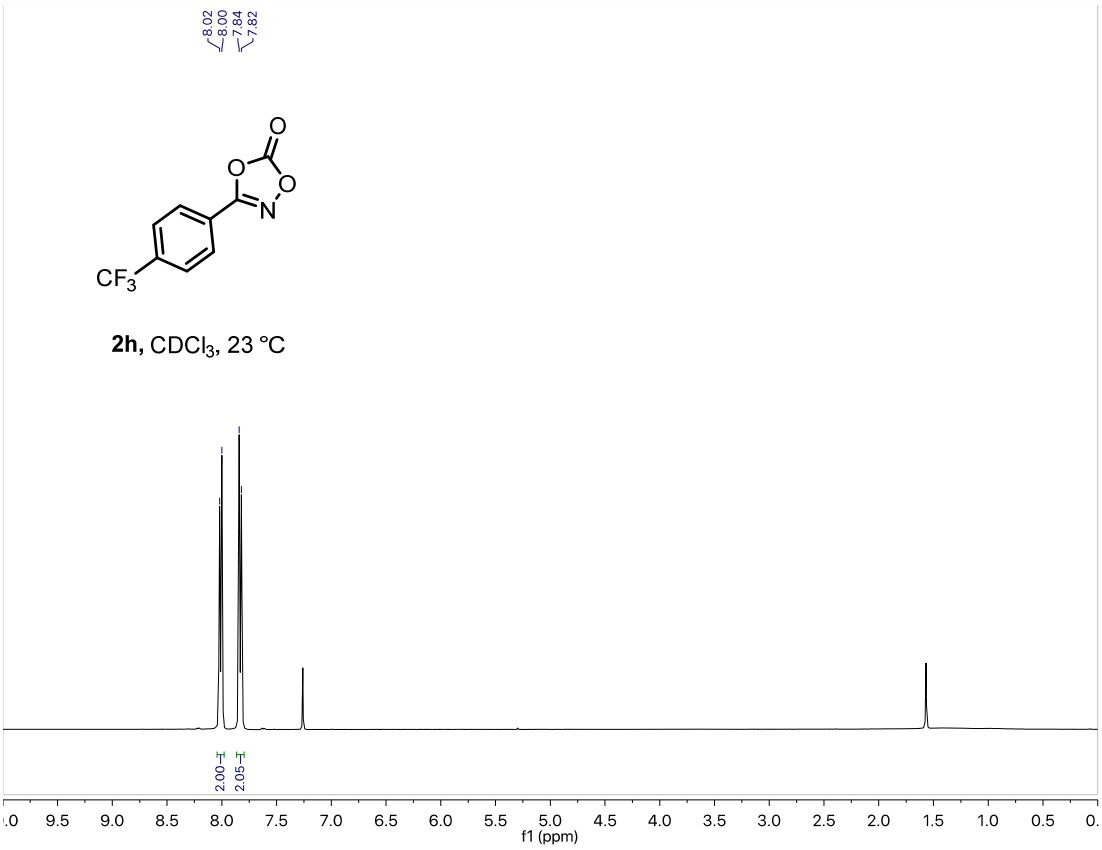
Br
O
O
O
N
2g, CDCl3, 23 °C
f1 (ppm)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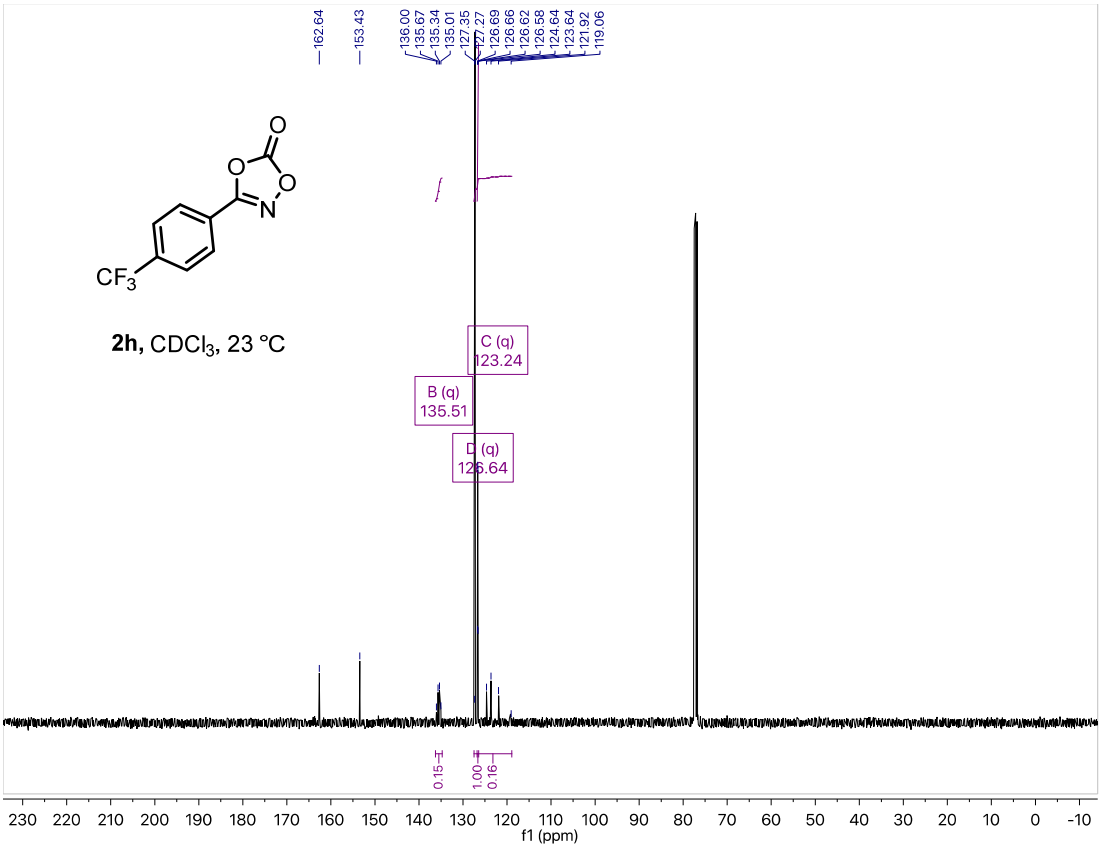
O
O
N
CF3
2h, CDCl3, 23 °C
2.00
2.05
f1 (ppm)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127.27
126.69
126.66
126.62
126.58
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123.64
121.92
119.06
O
O
O
N
CF3
2h, CDCl3, 23 °C
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B (q)
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D (q)
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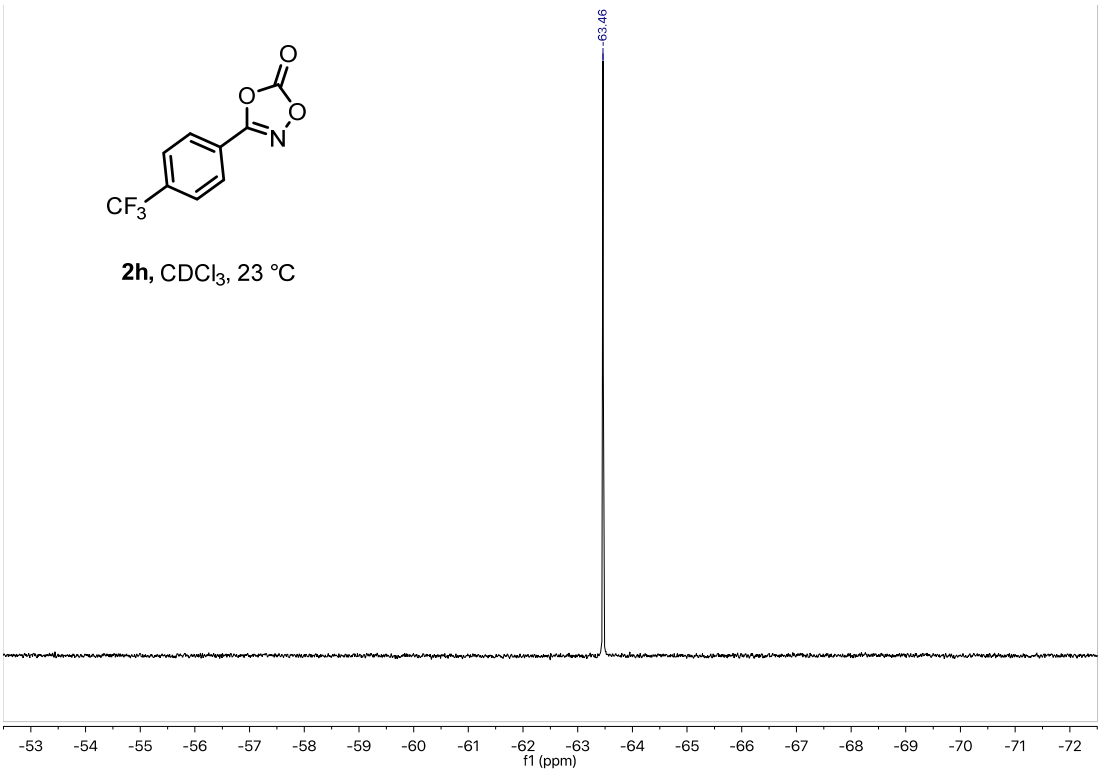
1.00
0.16
f1 (ppm)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O
O
N
CF3
2h, CDCl3, 23 °C
-53
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-55
-56
-57
-58
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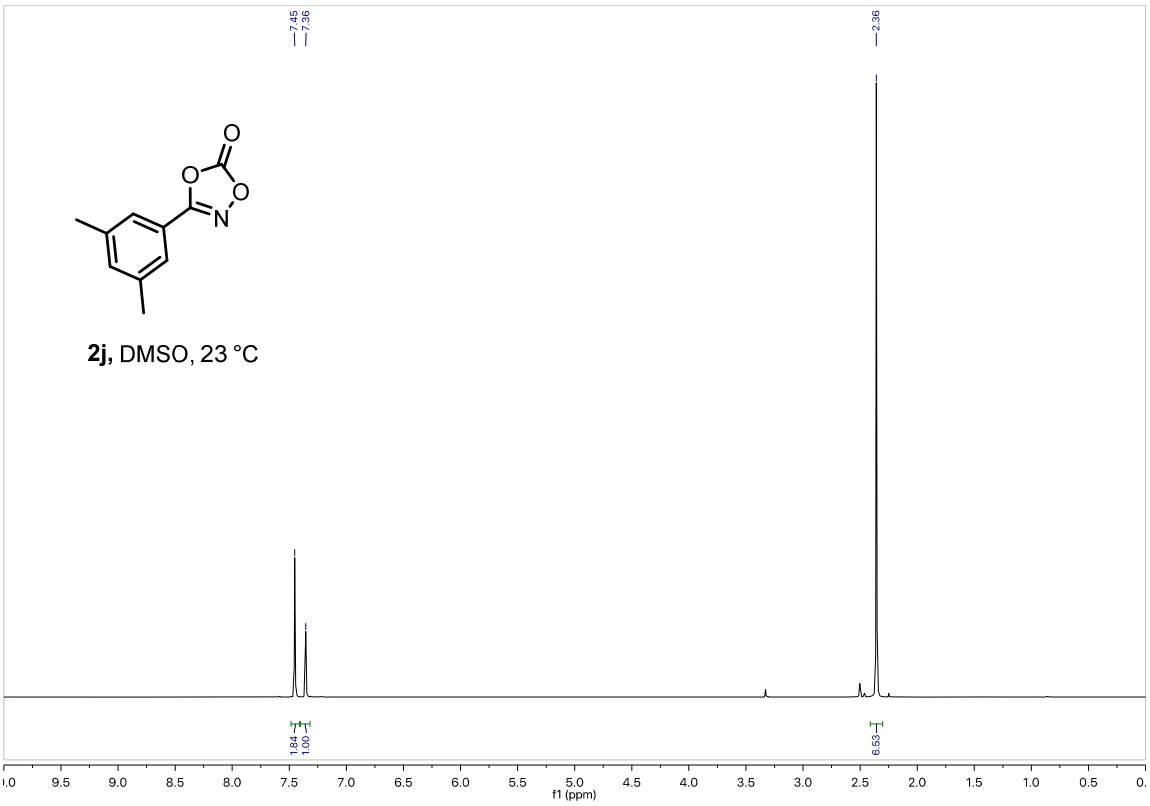
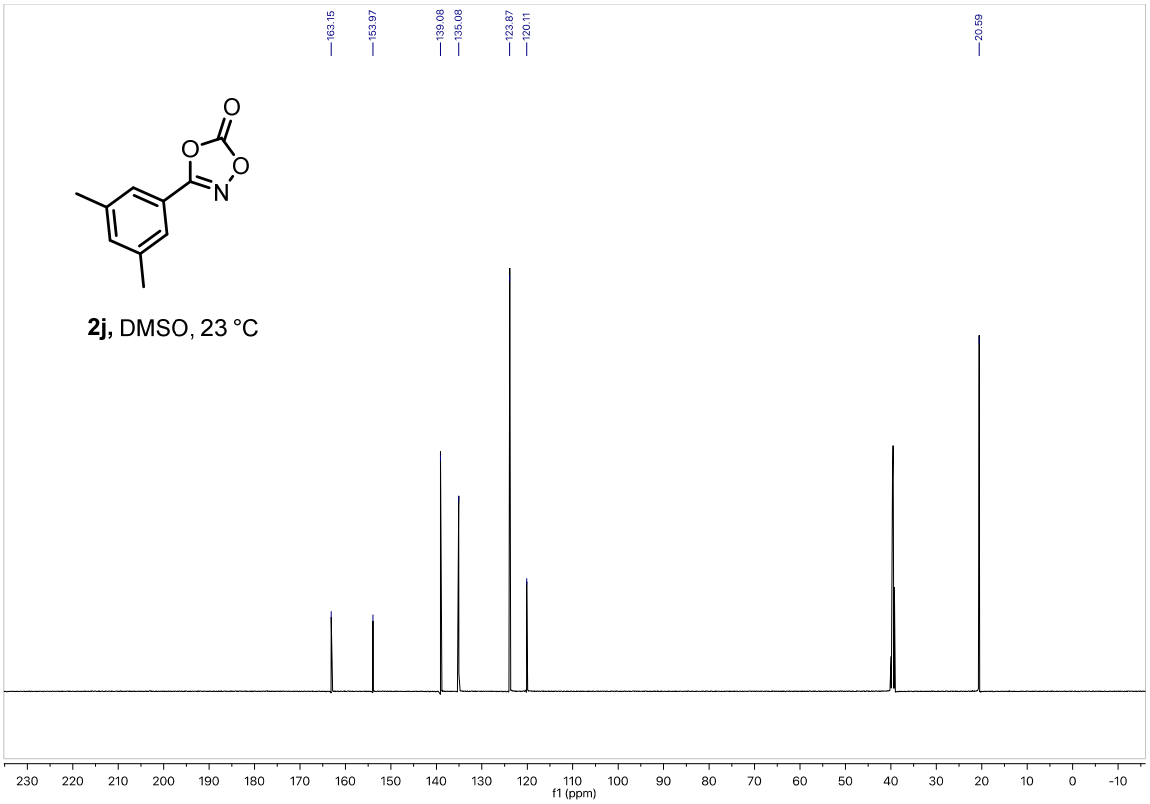
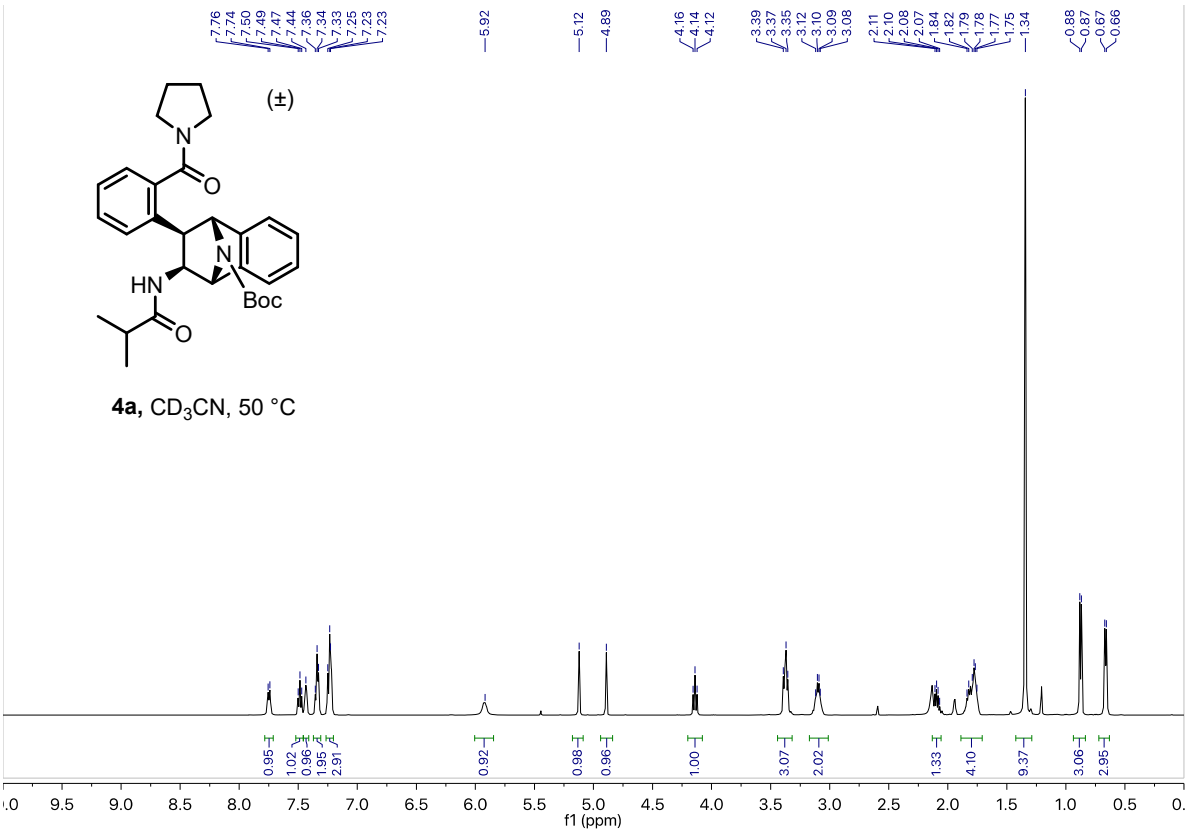
-68
-69
-70
-71
-72
f1 (ppm)

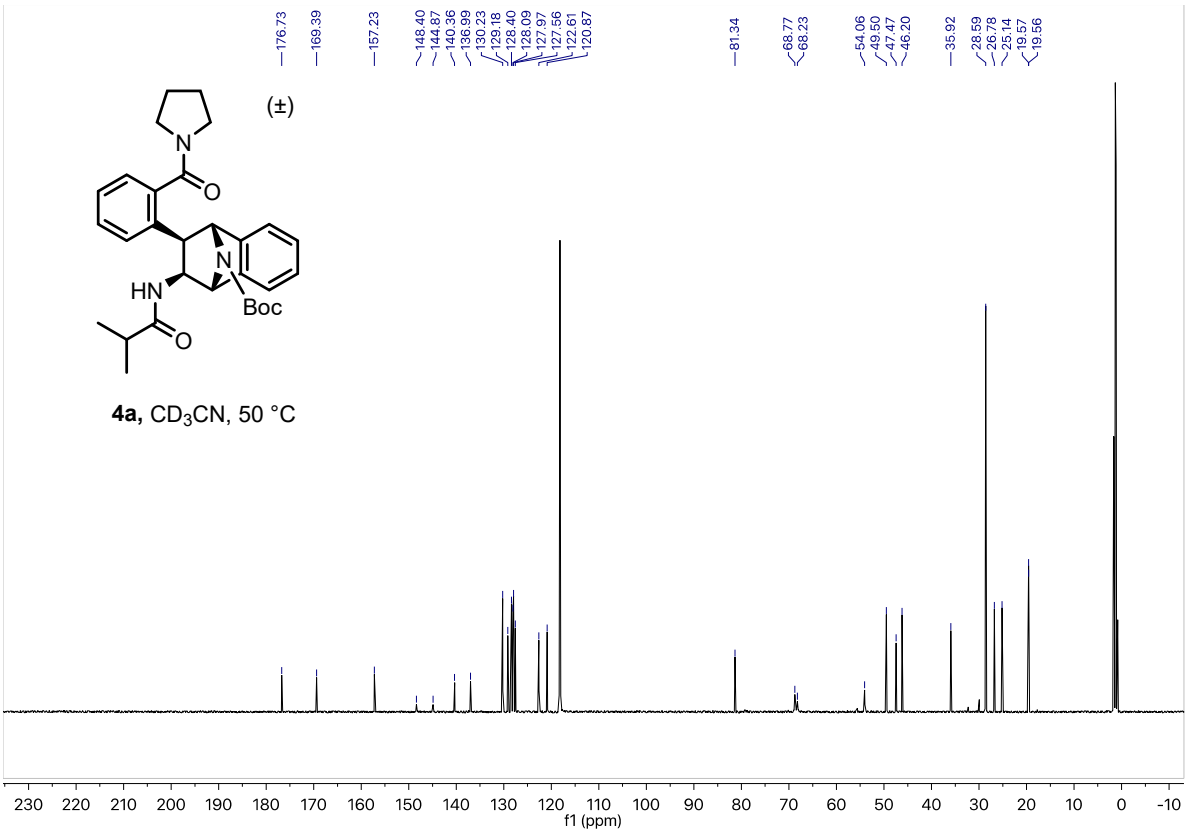


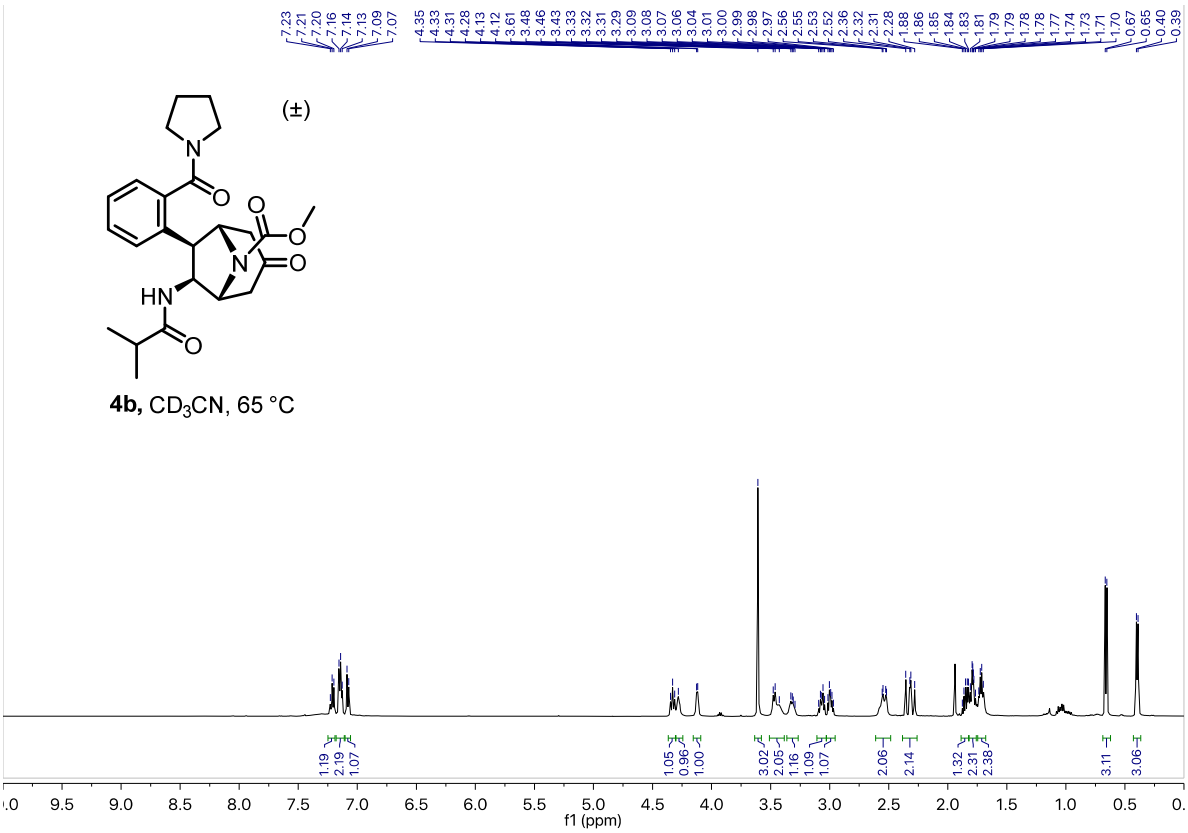
2j, DMSO, 23 °C

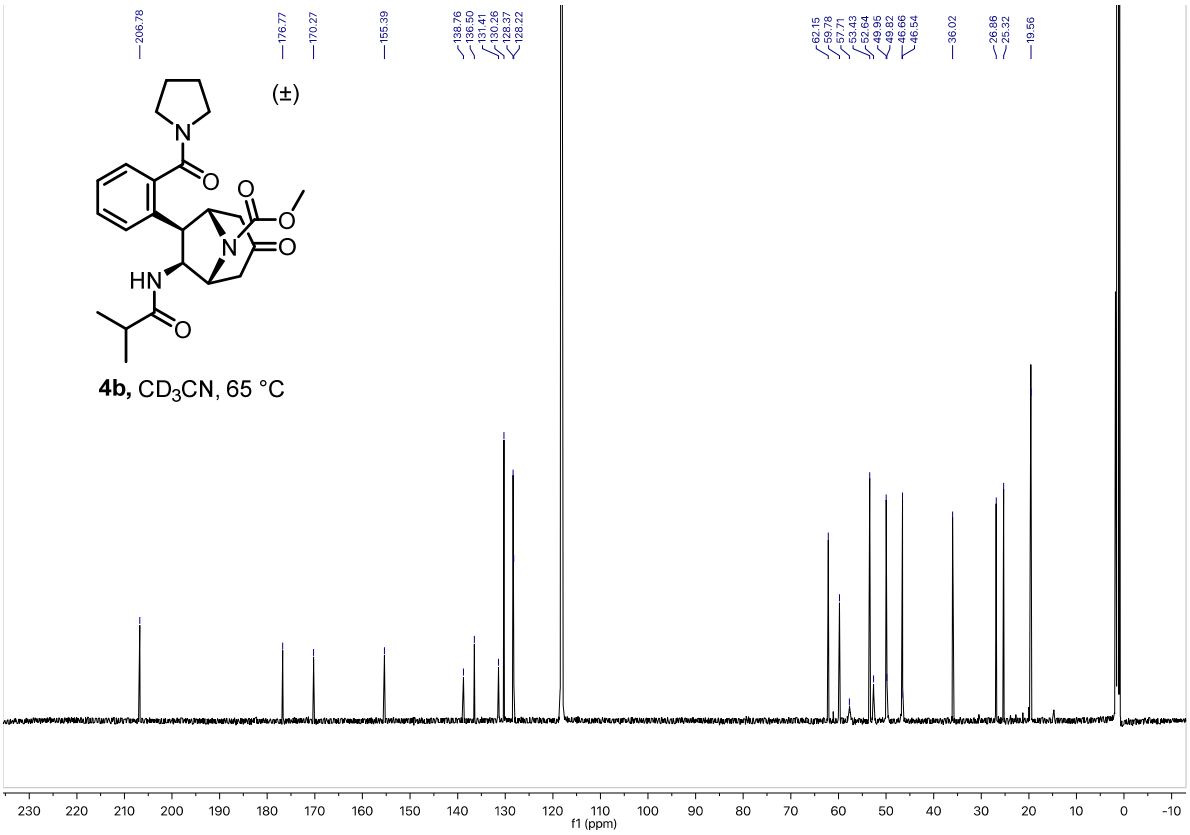


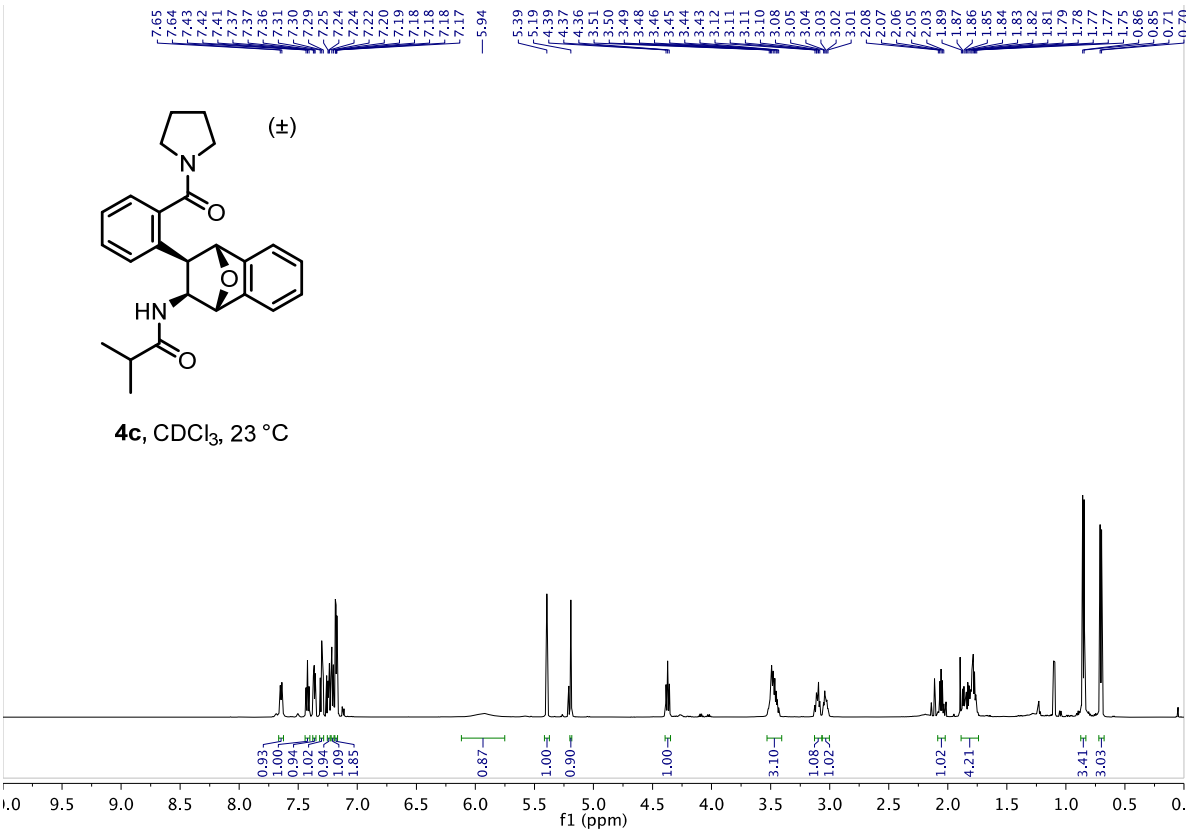
2j, DMSO, 23 °C

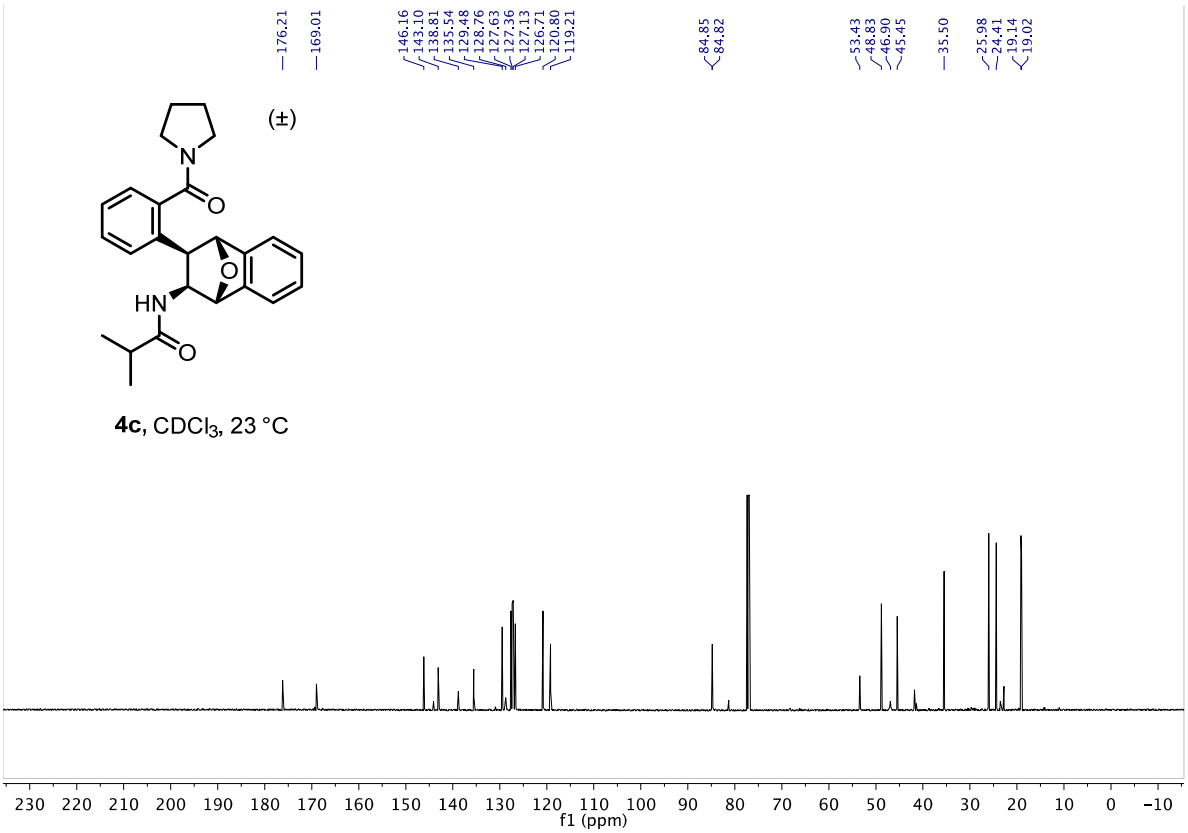

(±)
N
O
N
HN
Boc
O
4a, CD3CN, 50 °C
f1 (ppm)

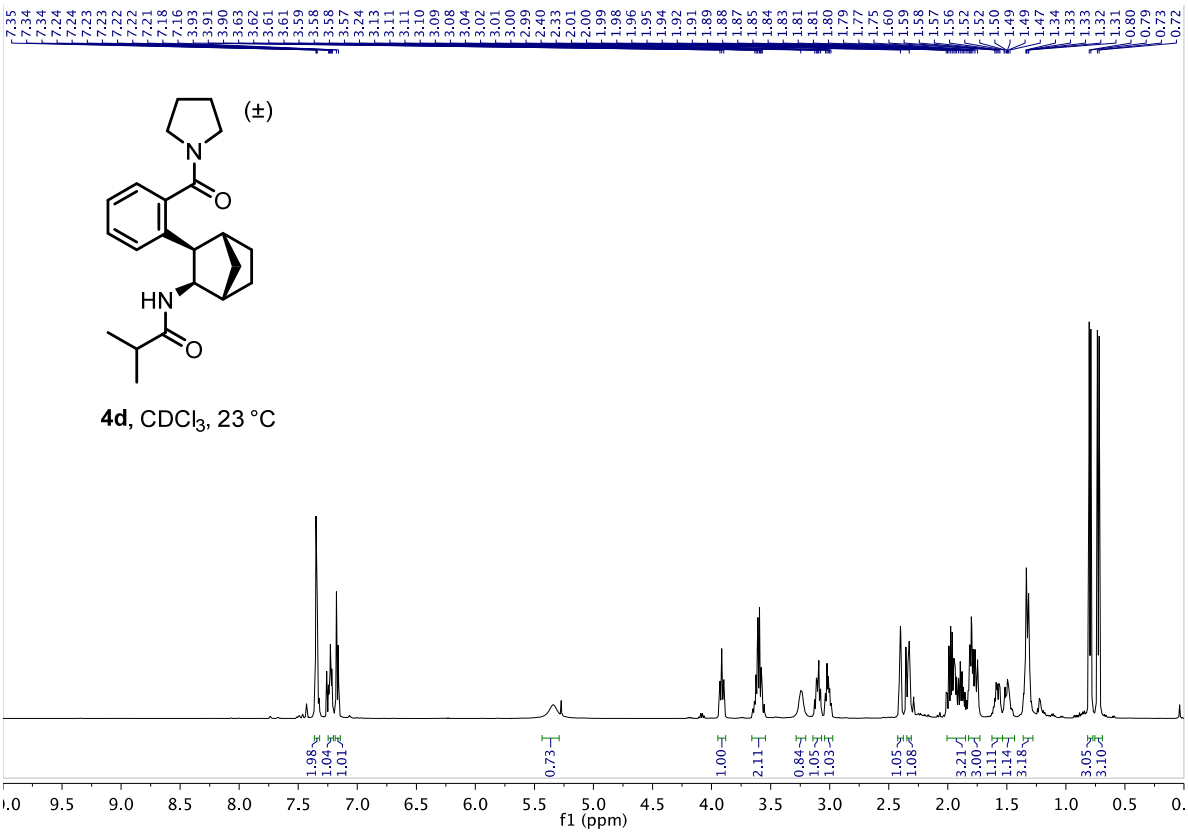

(±)
N
O
N
HN
Boc
O
4a, CD3CN, 50 °C
f1 (ppm)

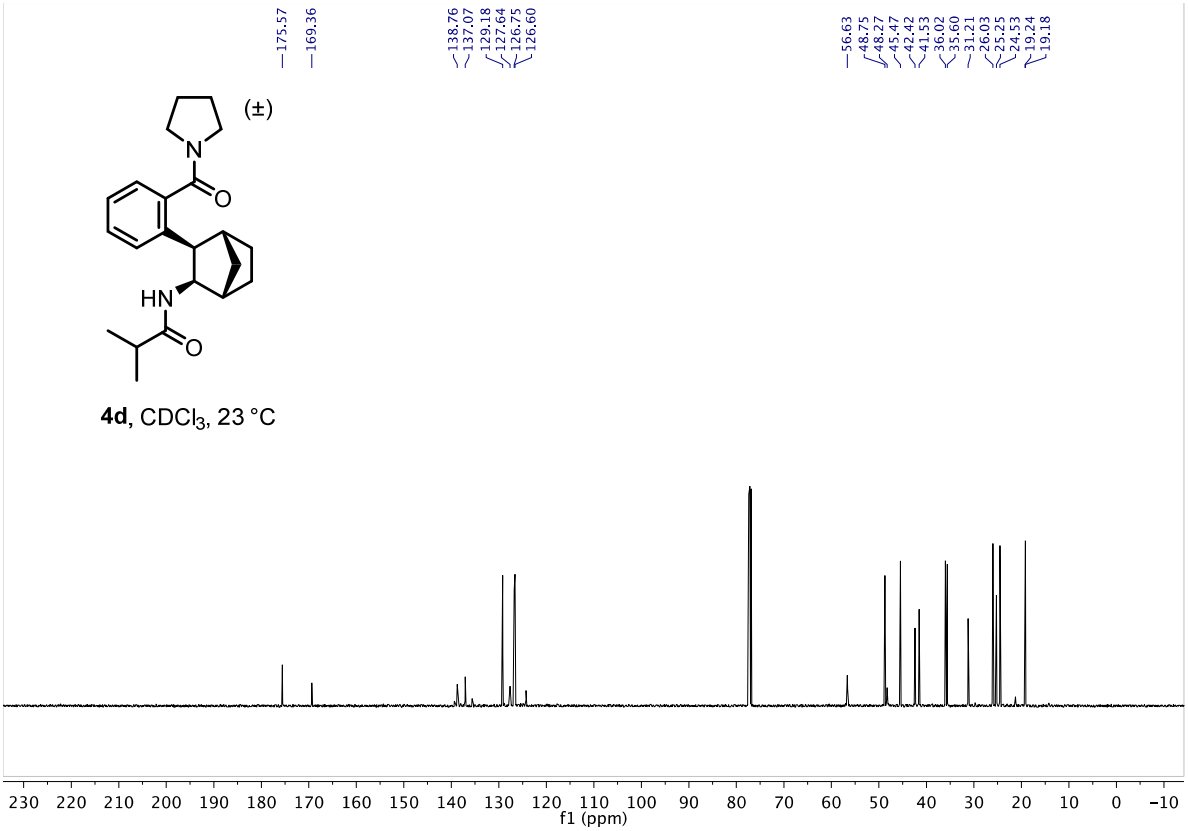

(±)
4b, CD3CN, 65 °C
f1 (ppm)

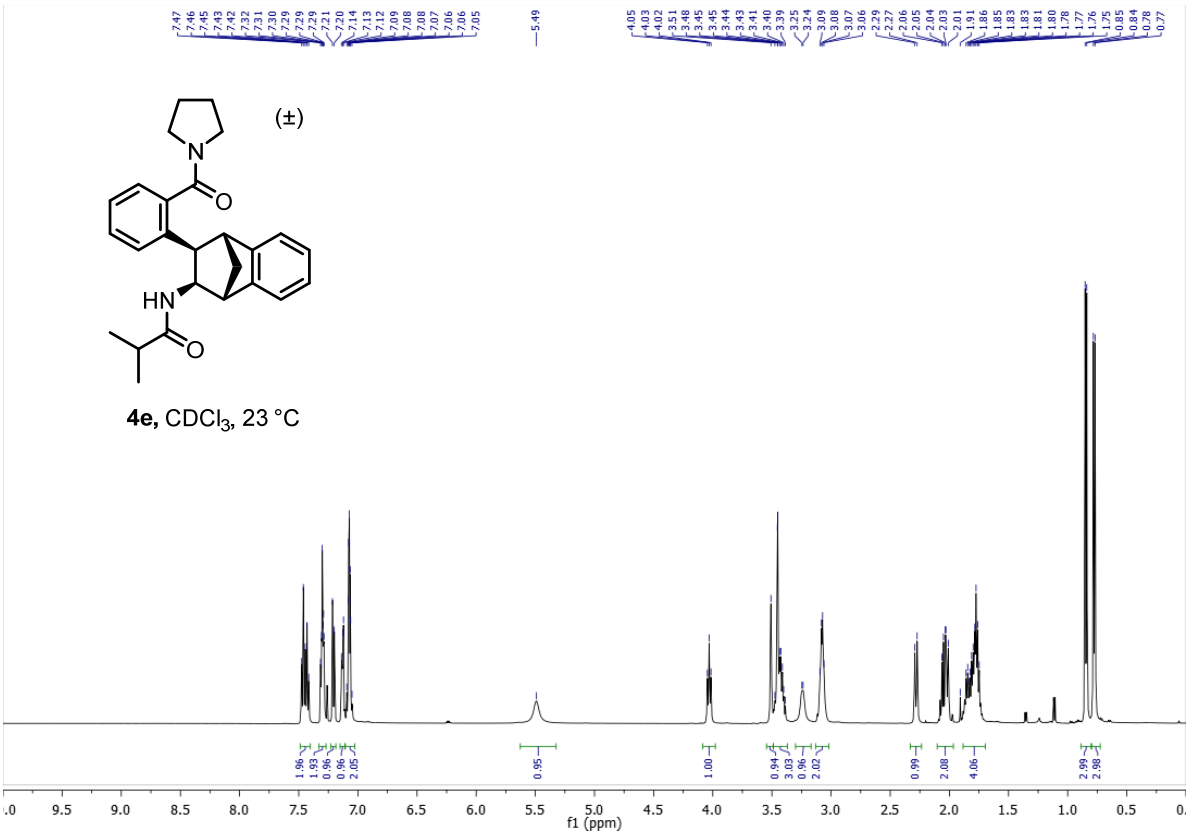

(±)
4b, CD3CN, 65 °C
f1 (ppm)

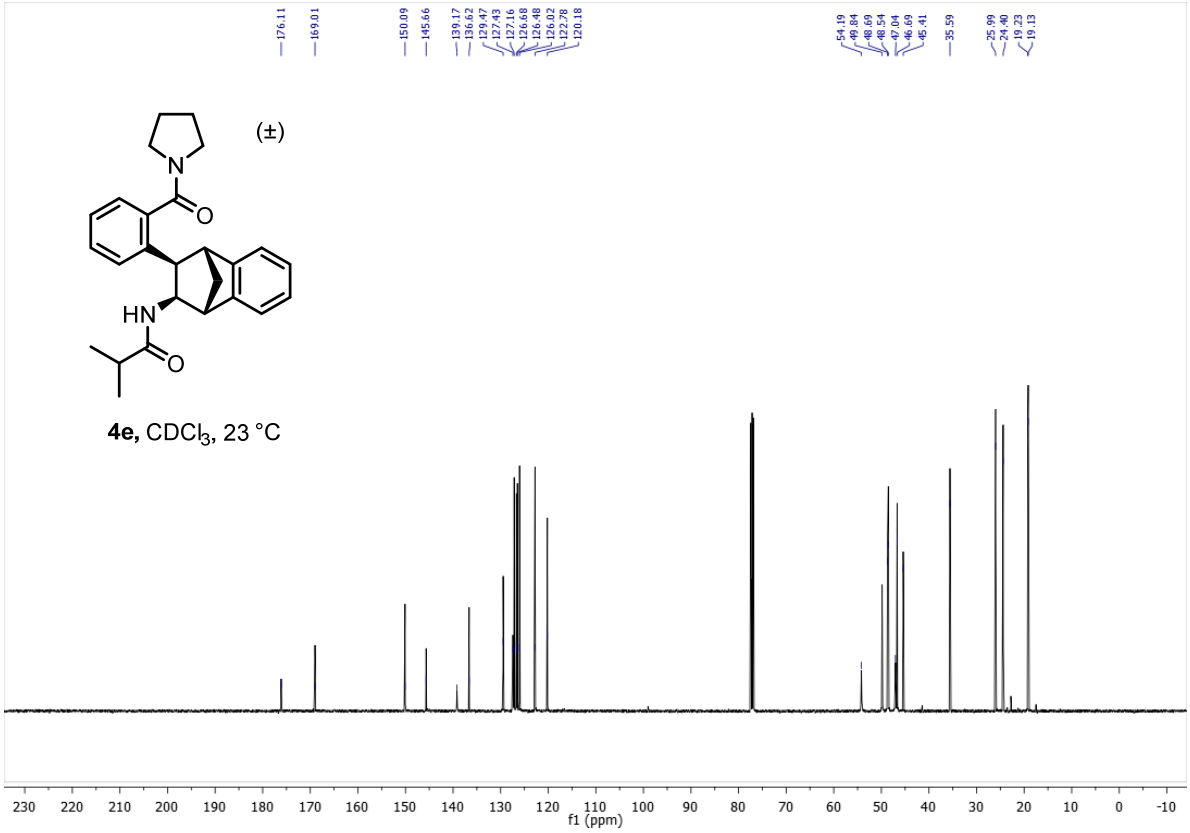

(±)
4c, CDCl3, 23 °C
f1 (ppm)


(±)
4c, CDCl3, 23 °C
f1 (ppm)

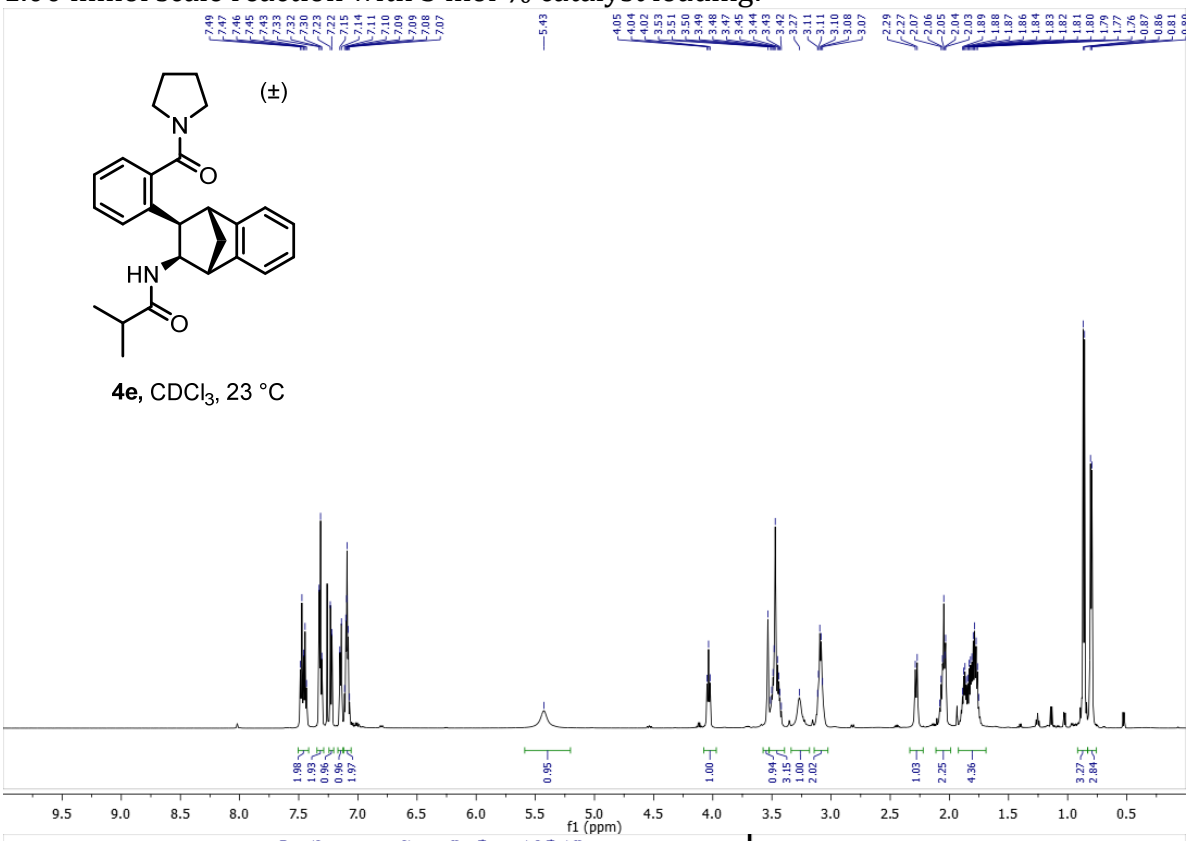

(±)
4d, CDCl3, 23 °C
f1 (ppm)

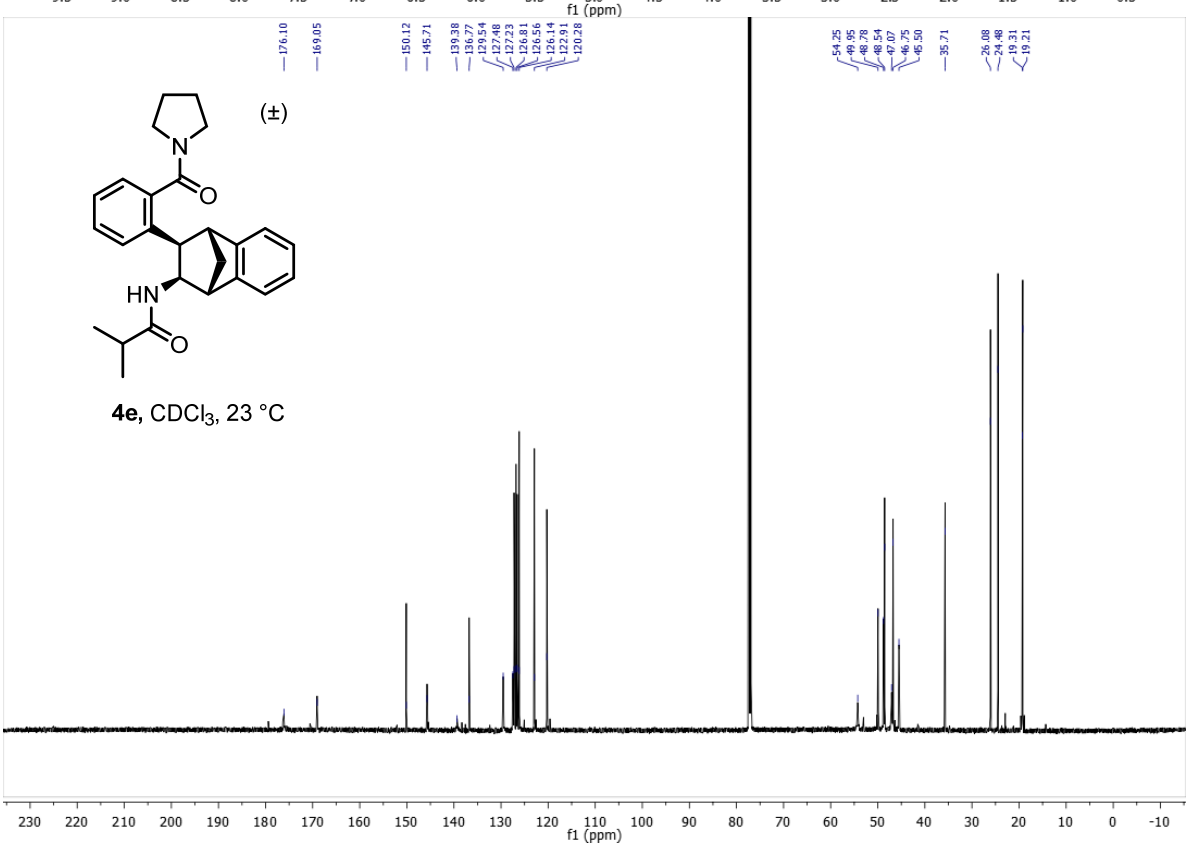

(±)
4d, CDCl3, 23 °C
f1 (ppm)

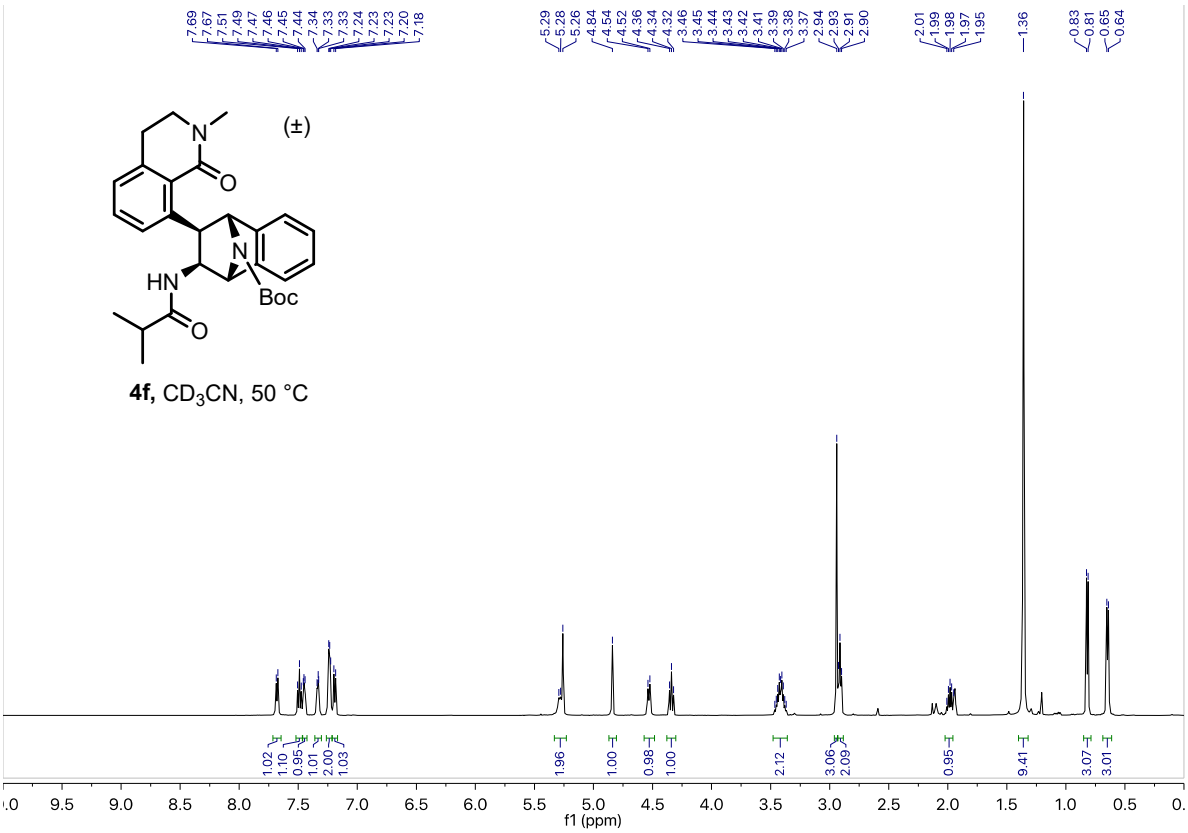

(±)
N
O
HN
O
4e, CDCl3, 23 °C
f1 (ppm)

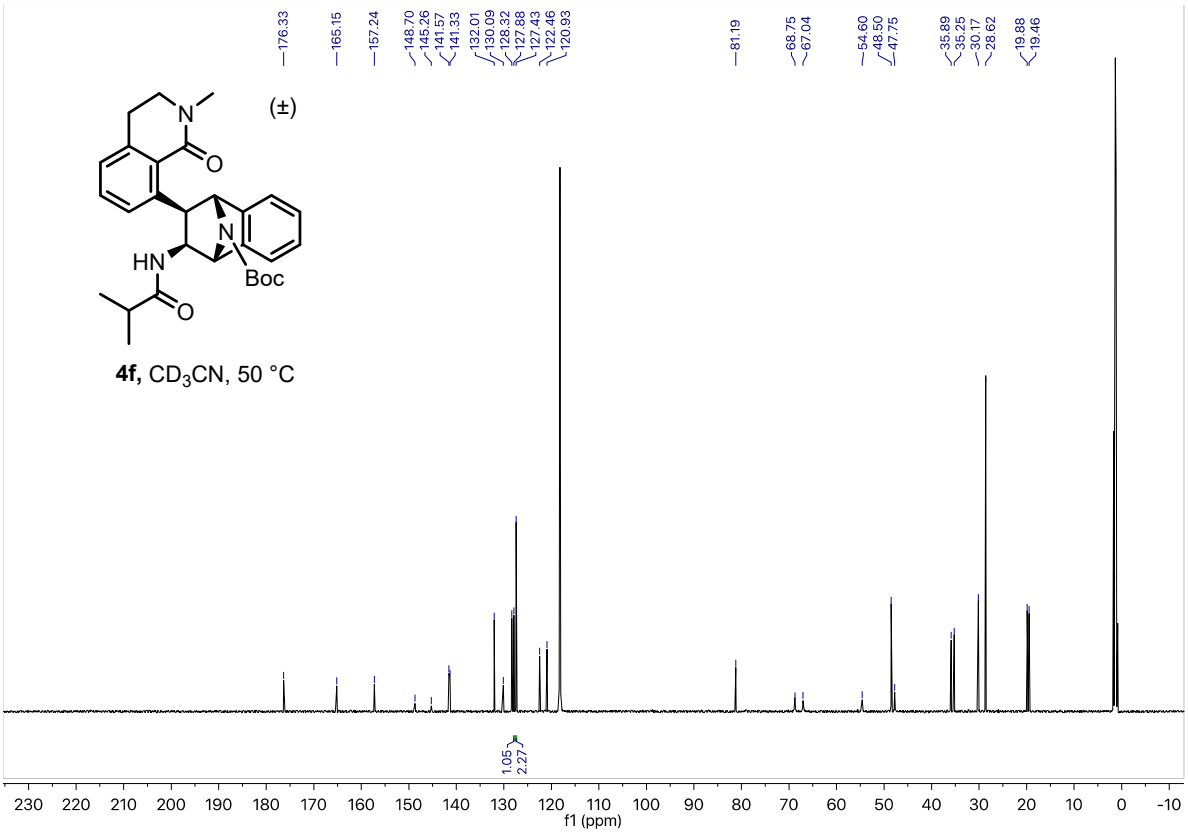

(±)
N
O
HN
O
4e, CDCl3, 23 °C
f1 (ppm)

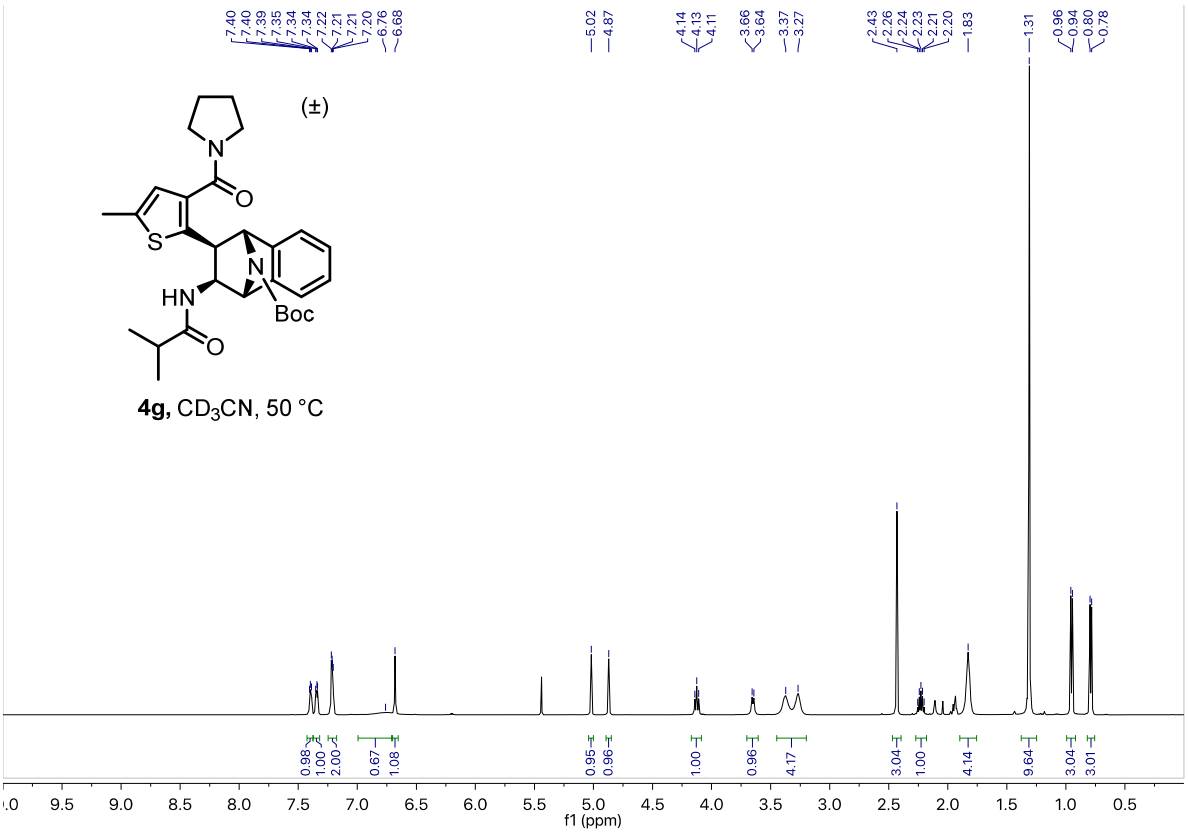
1.00 mmol scale reaction with 5 mol % catalyst loading:

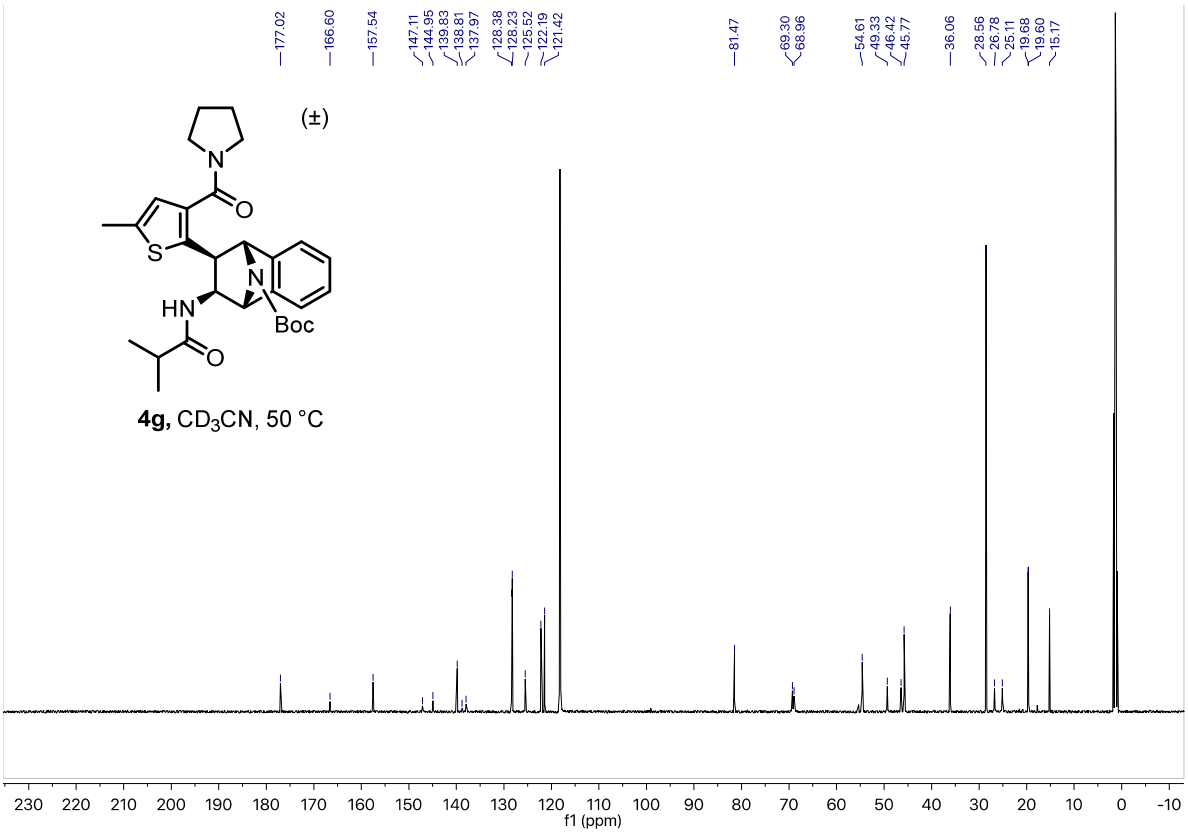


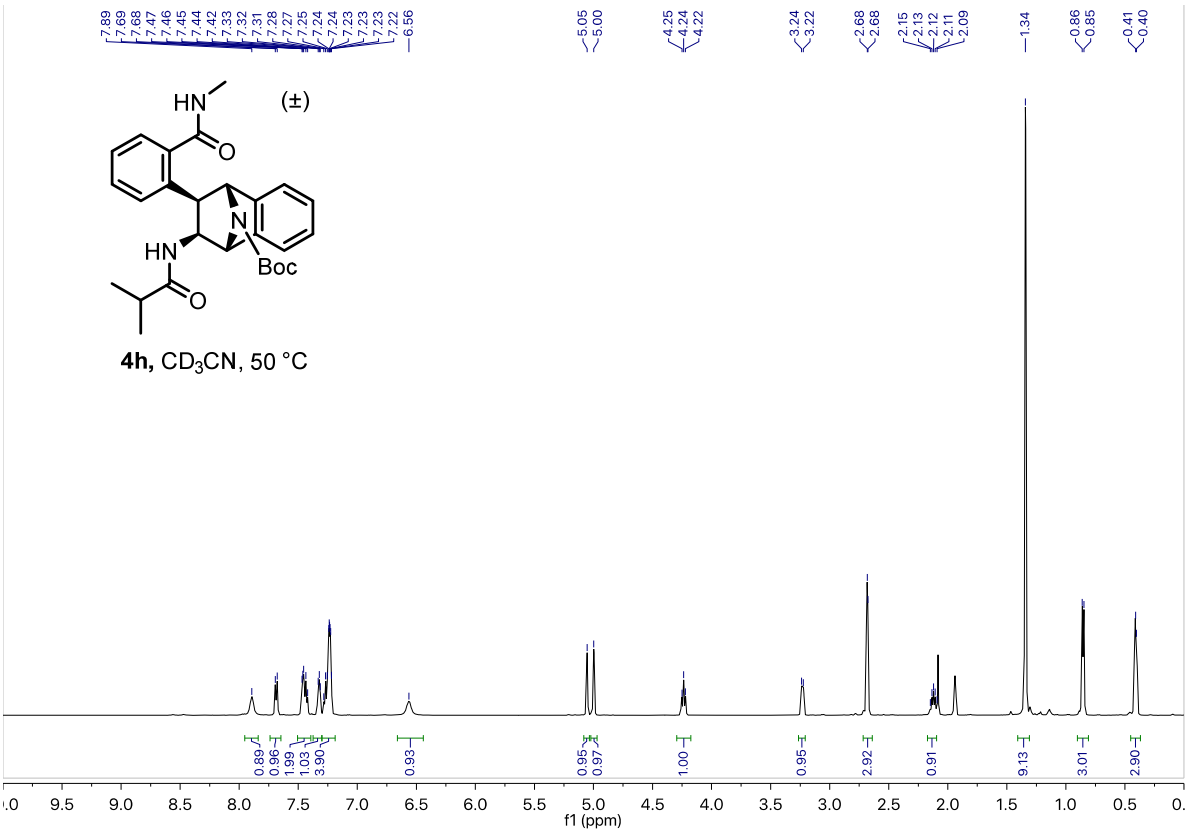


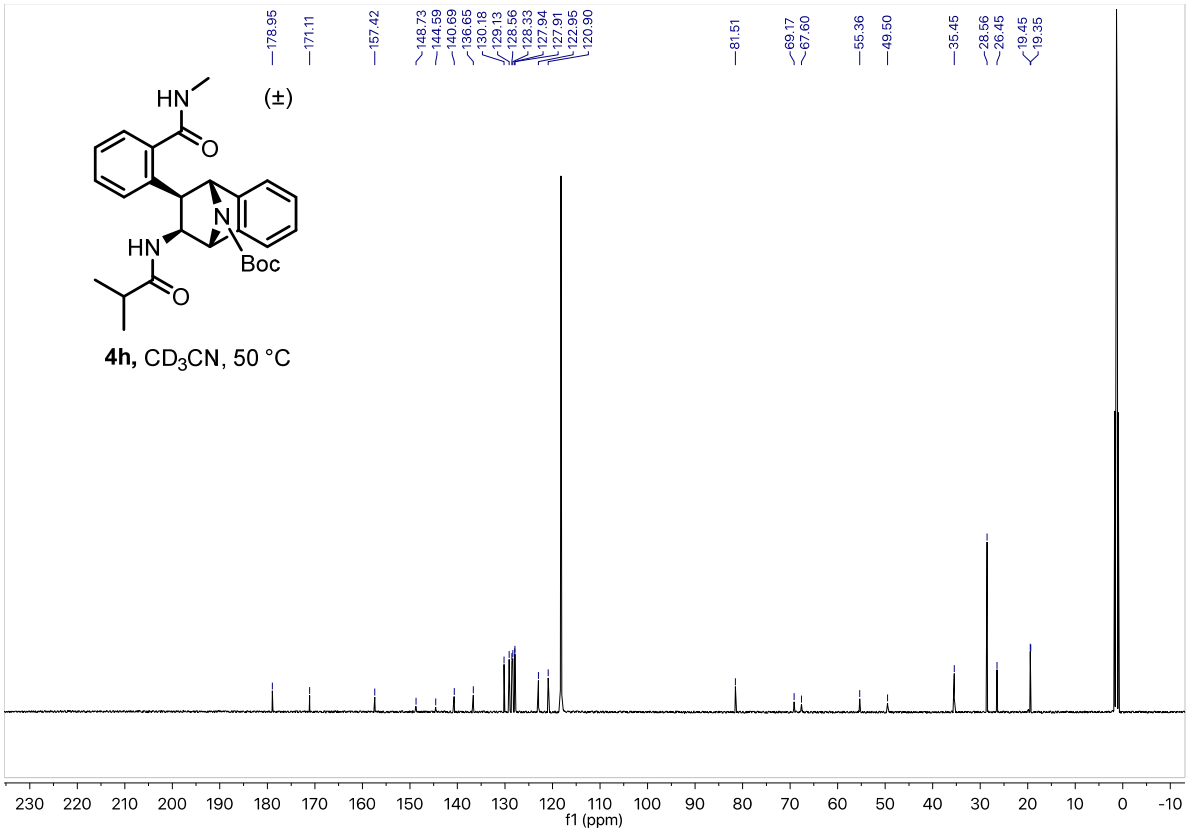

(±)
4f, CD3CN, 50 °C
f1 (ppm)

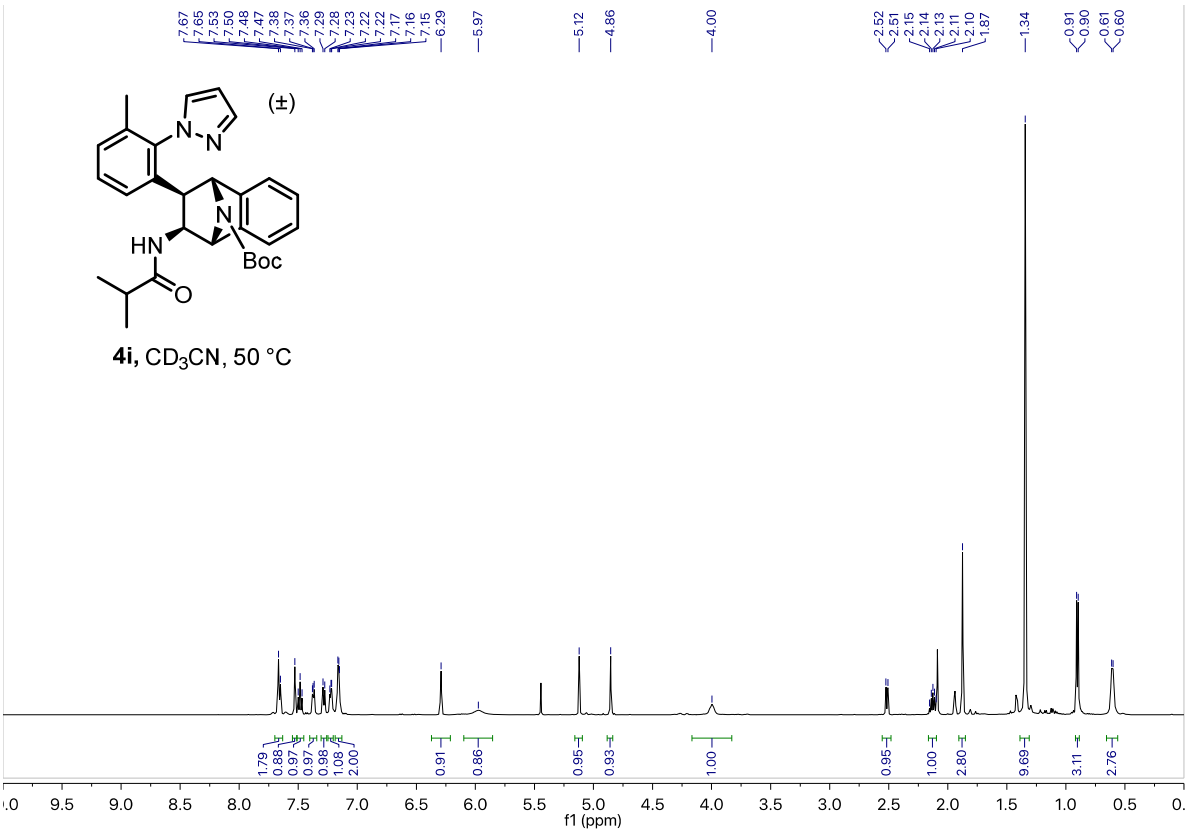

(±)
4f, CD3CN, 50 °C
f1 (ppm)

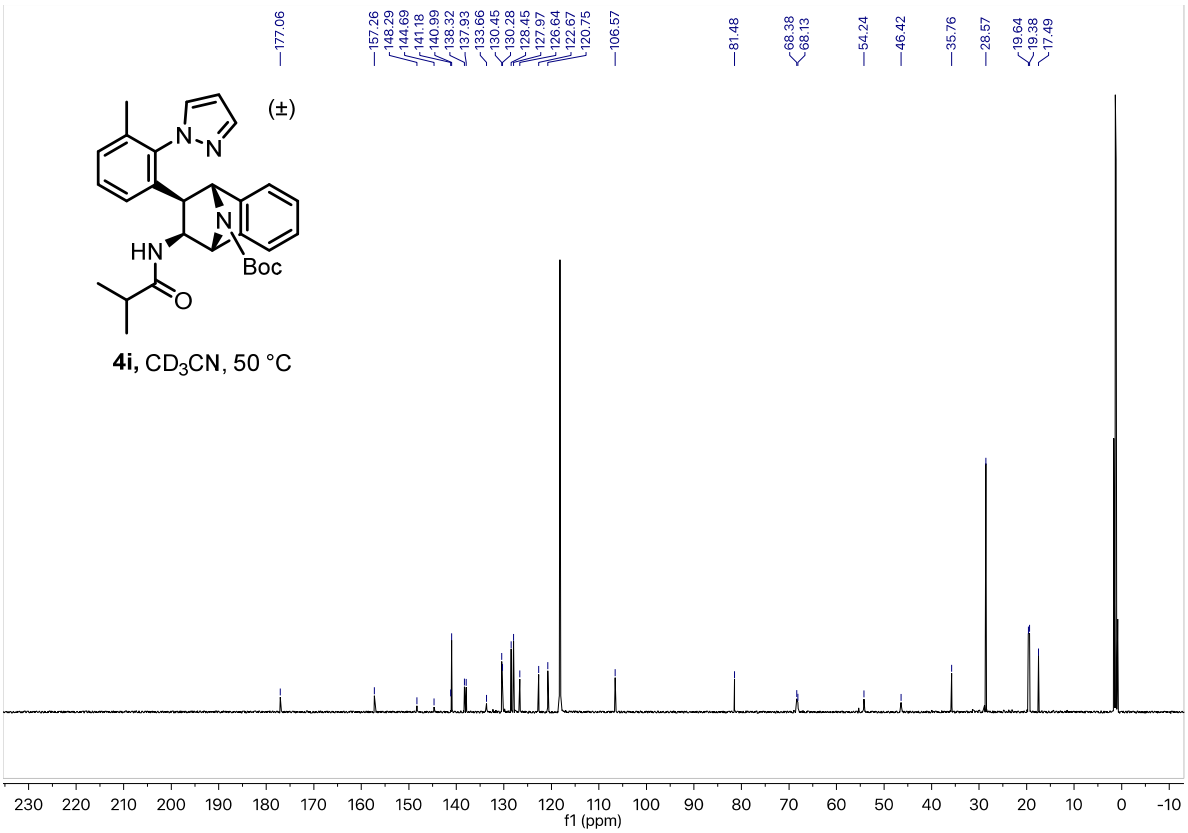

(±)
4g, CD3CN, 50 °C
f1 (ppm)

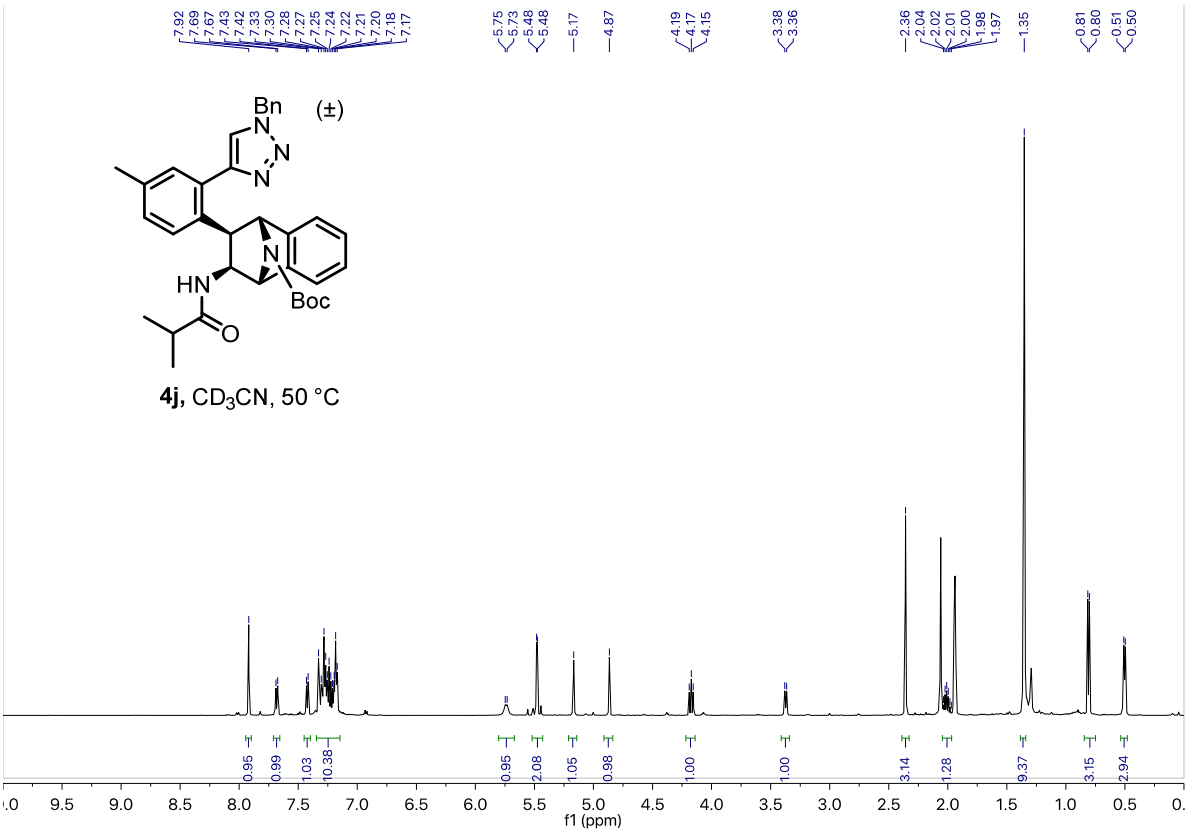

(±)
4g, CD3CN, 50 °C
f1 (ppm)

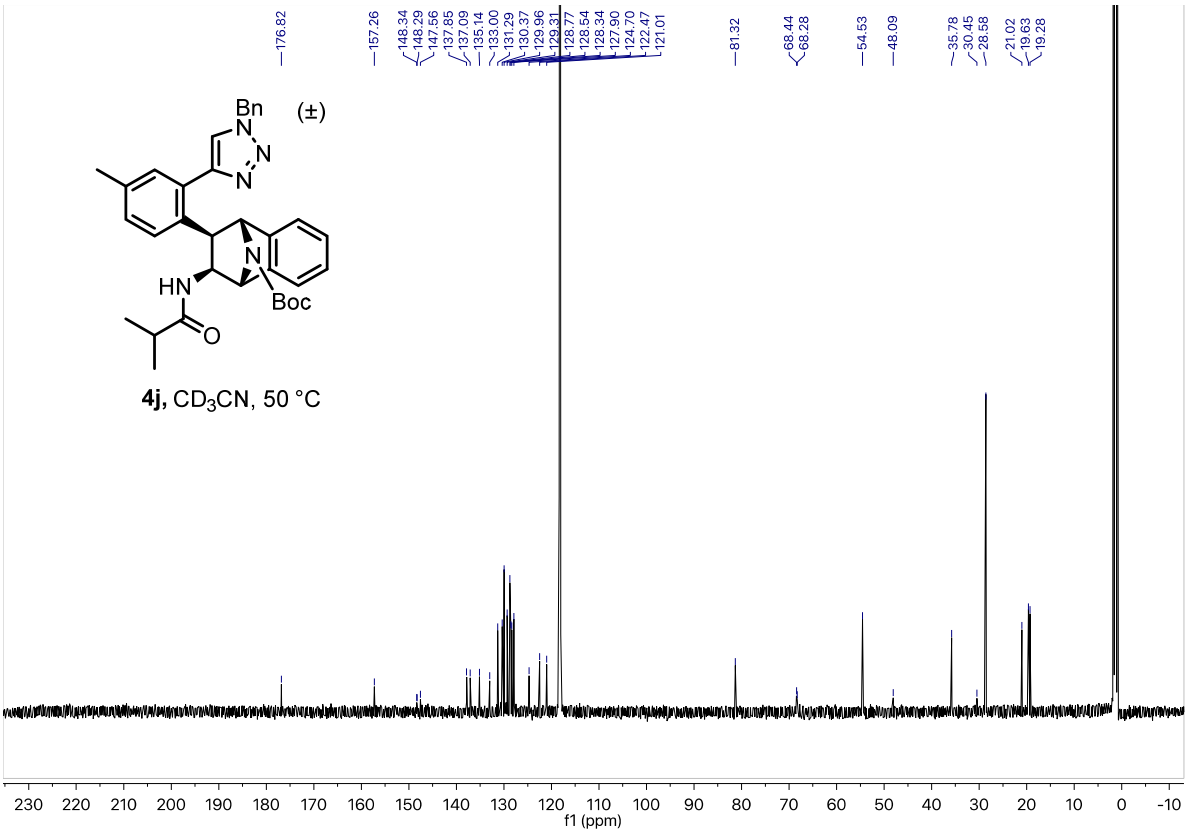

7.89
7.69
7.68
7.47
7.46
7.45
7.44
7.42
7.33
7.32
7.31
7.28
7.27
7.25
7.24
7.24
7.23
7.23
7.23
7.22
6.56
5.05
5.00
4.25
4.24
4.22
3.24
3.22
2.68
2.68
2.15
2.13
2.12
2.11
2.09
1.34
0.86
0.85
0.41
0.40
HN
(±)
O
N
HN
Boc
O
4h, CD3CN, 50 °C
0.89
0.96
1.99
1.03
3.90
0.93
0.95
0.97
1.00
0.95
2.92
0.91
9.13
3.01
2.90
f1 (ppm)

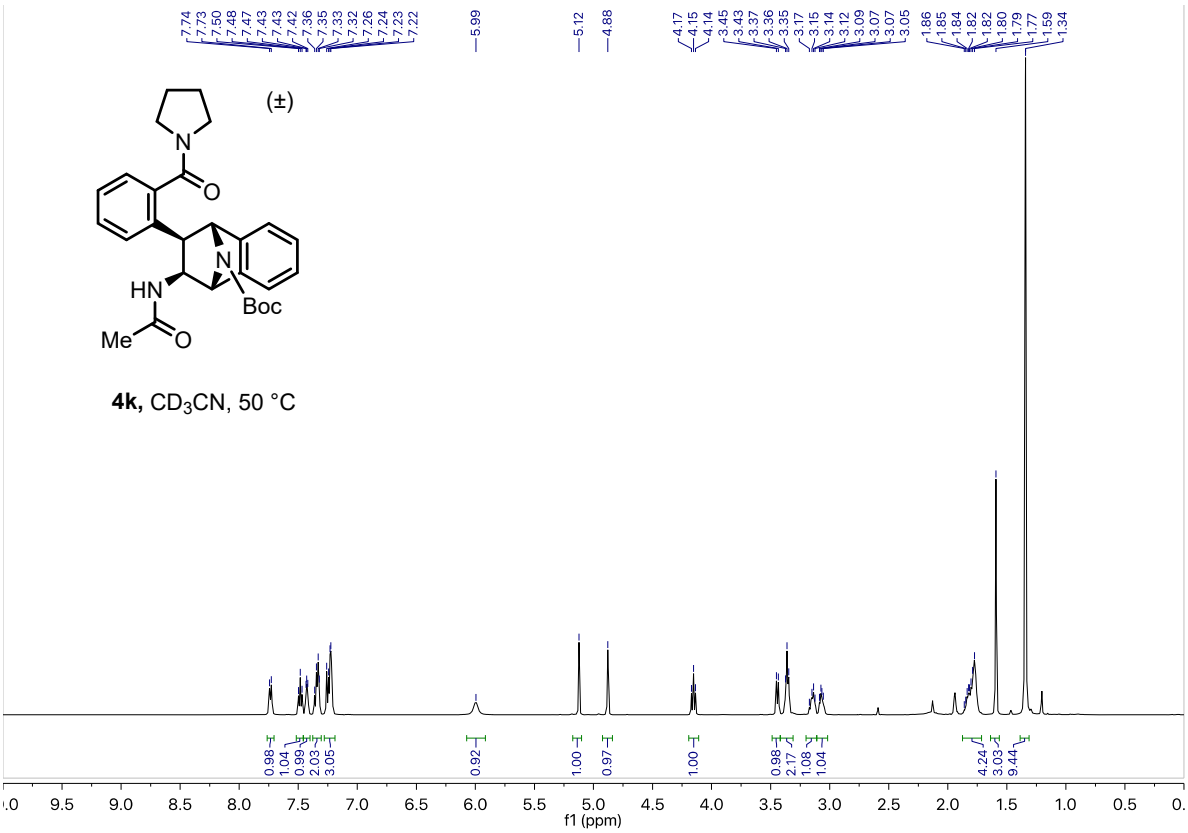

178.95
171.11
157.42
148.73
144.59
140.69
136.65
130.18
129.13
128.56
128.33
127.94
127.91
122.95
120.90
81.51
69.17
67.60
55.36
49.50
35.45
28.56
26.45
19.45
19.35
HN
(±)
O
N
HN
Boc
O
4h, CD3CN, 50 °C
f1 (ppm)

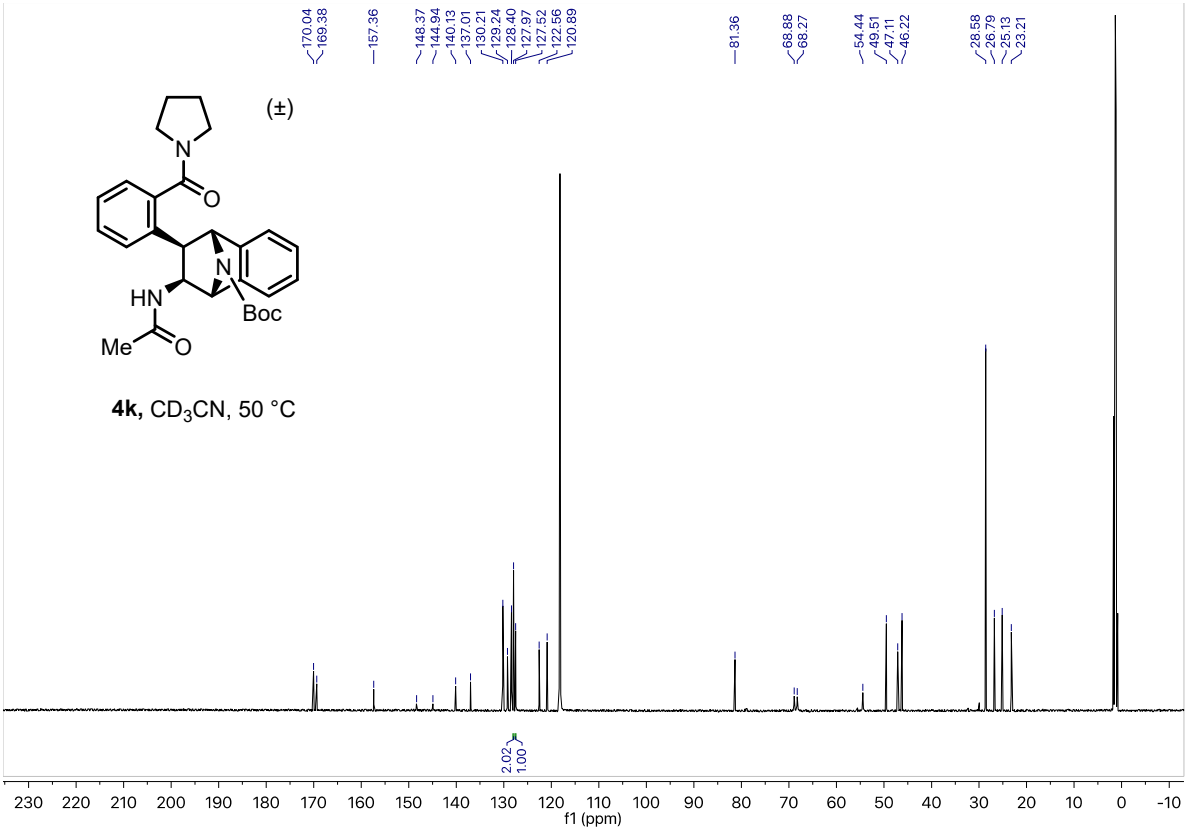

(±)
HN
Boc
O
4i, CD3CN, 50 °C
f1 (ppm)

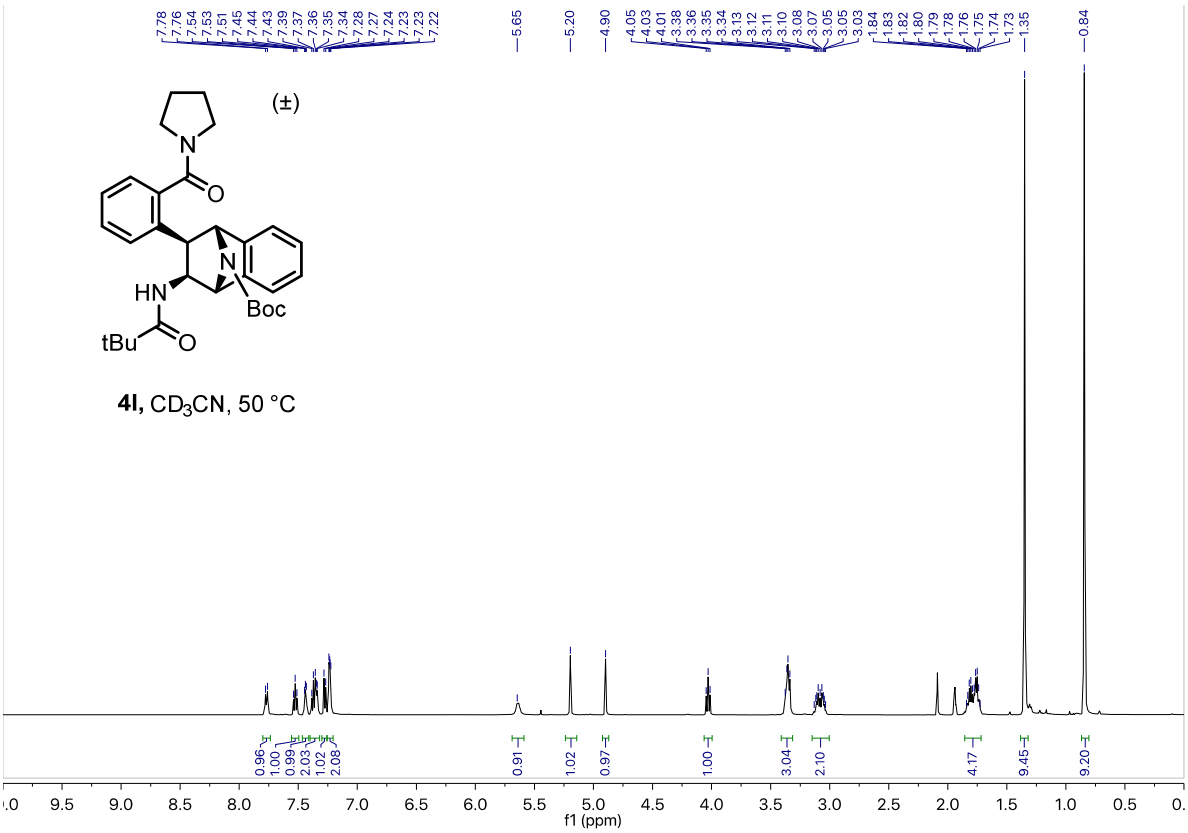

(±)
HN
Boc
O
4i, CD3CN, 50 °C
f1 (ppm)

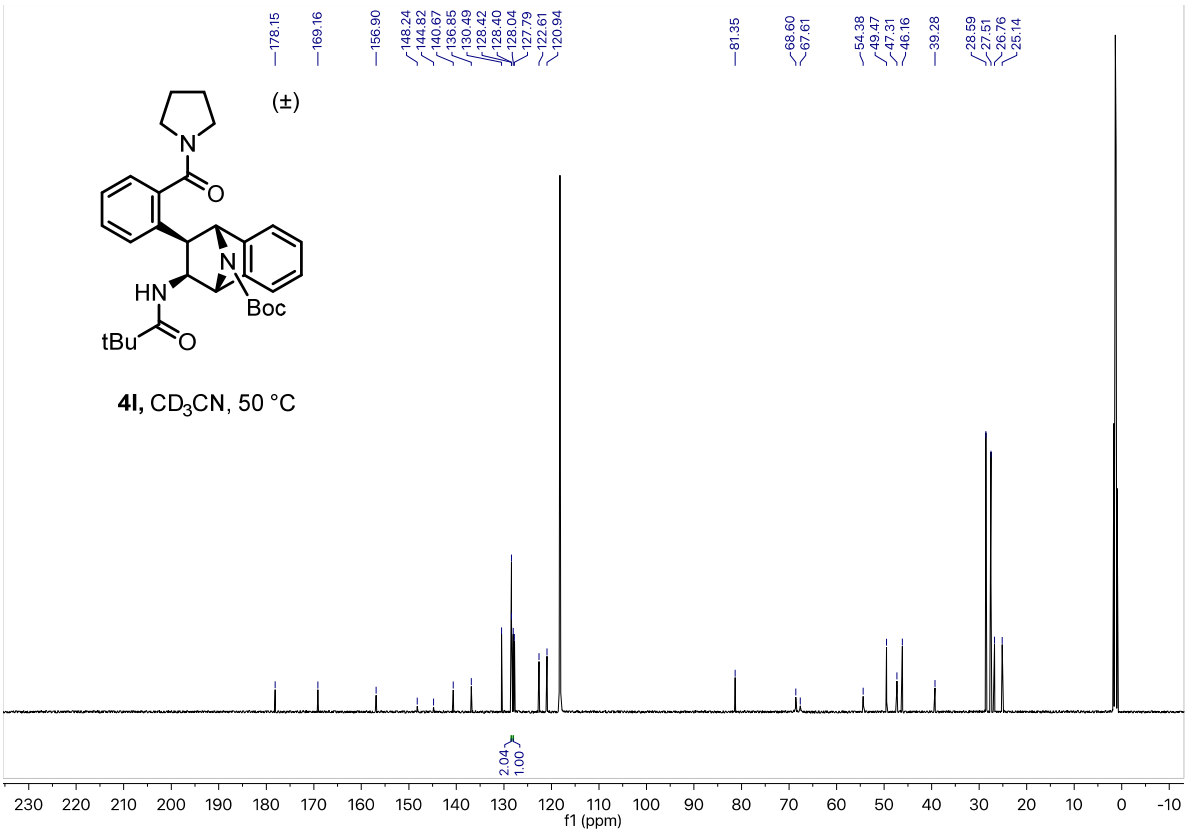

Bn
(±)
HN
Boc
O
4j, CD3CN, 50 °C
f1 (ppm)

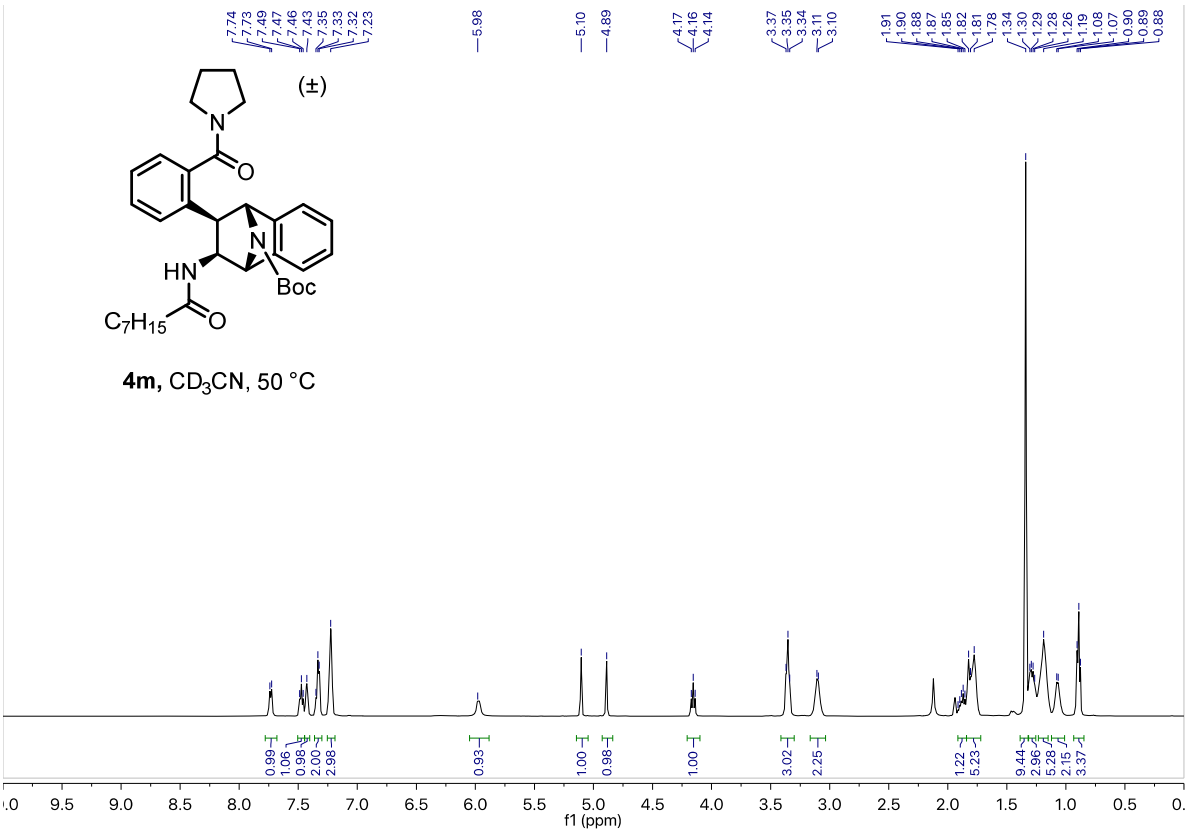

Bn
(±)
HN
Boc
O
4j, CD3CN, 50 °C
f1 (ppm)

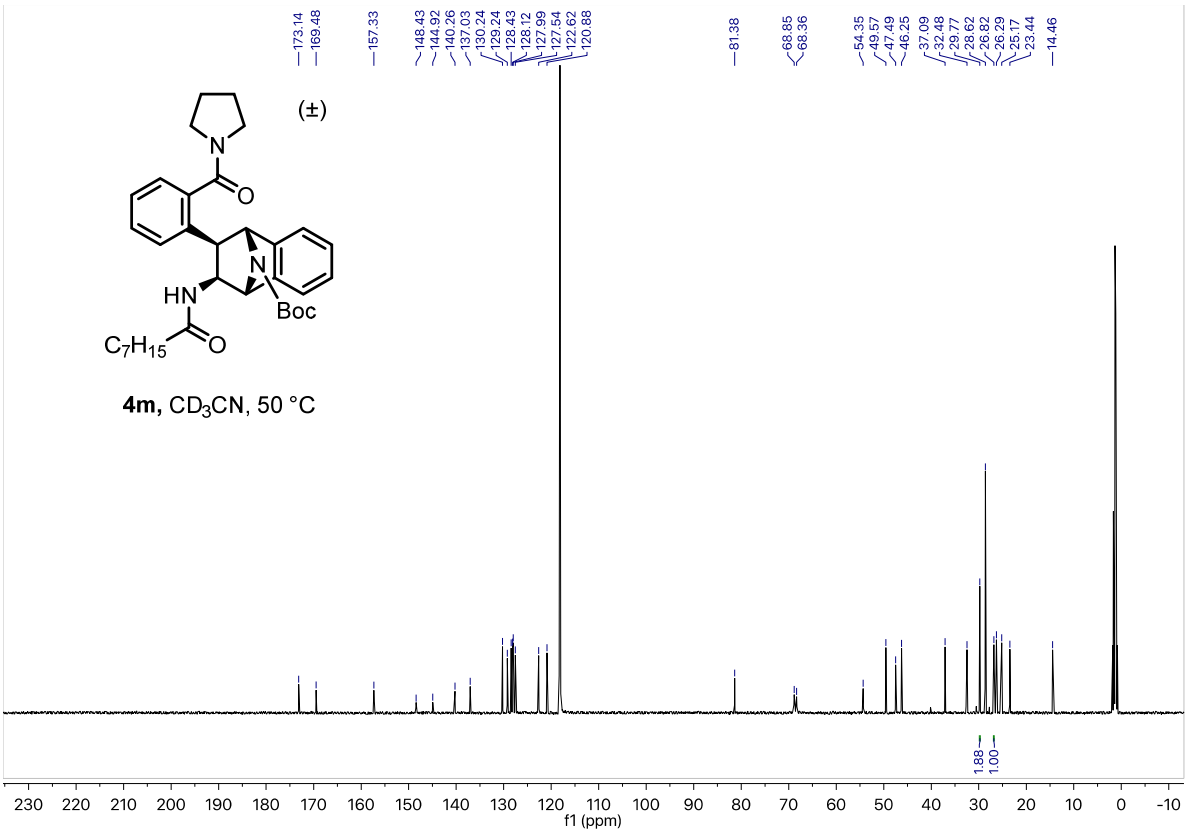

(±)
N
O
N
HN
Boc
Me
O
4k, CD3CN, 50 °C
f1 (ppm)

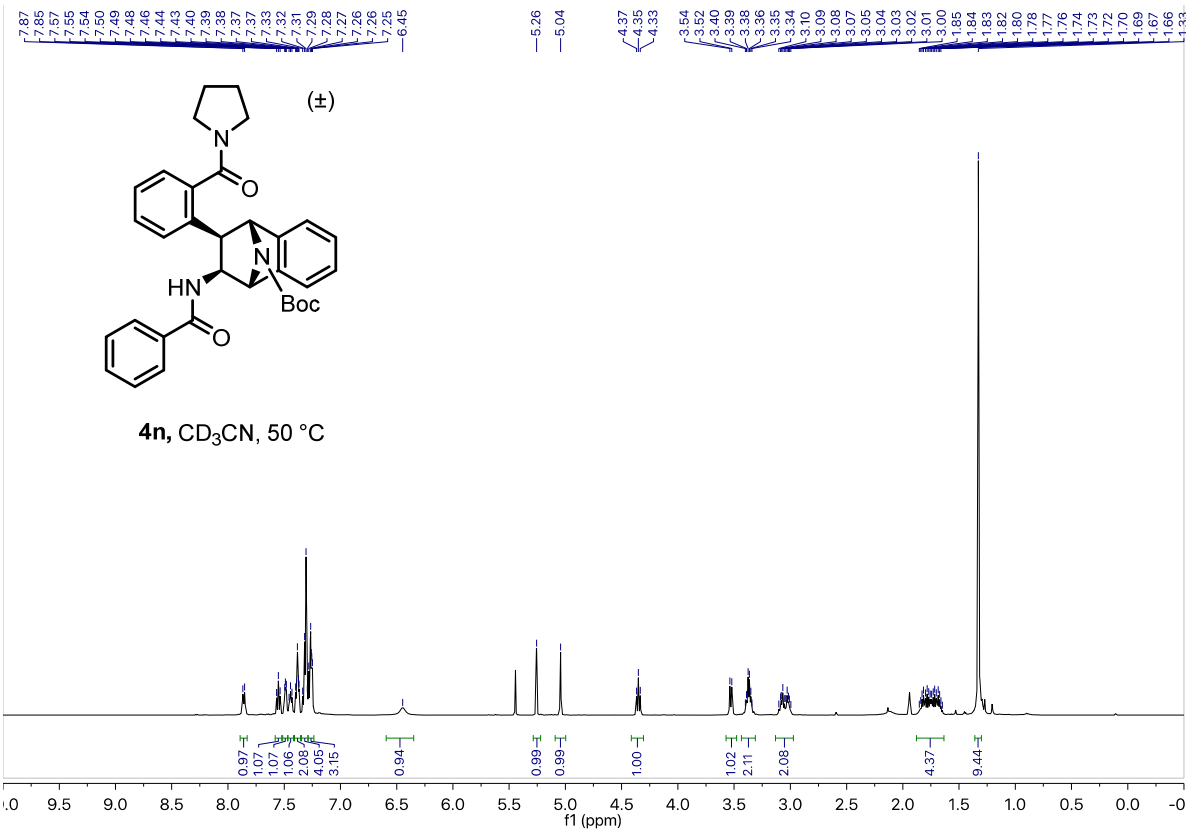

(±)
N
O
N
HN
Boc
Me
O
4k, CD3CN, 50 °C
f1 (ppm)

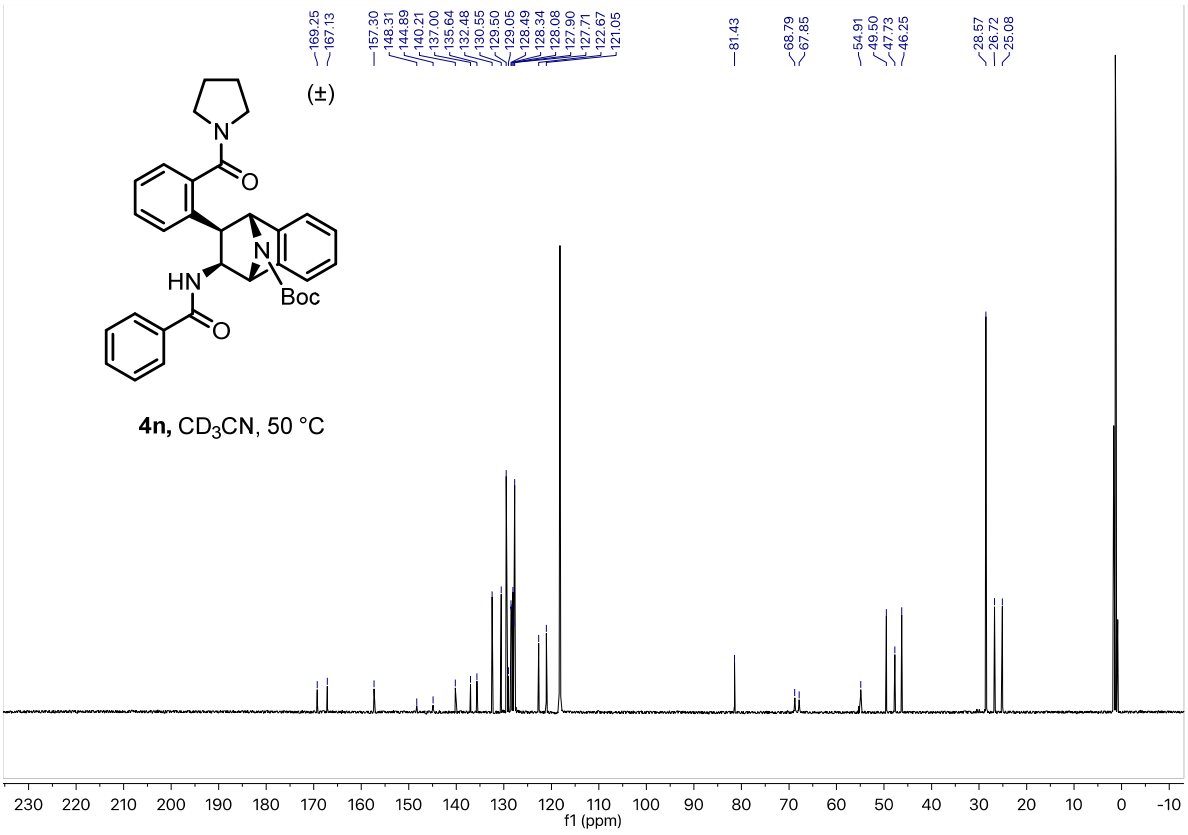

(±)
N
O
N
HN
Boc
tBu
O
4l, CD3CN, 50 °C
f1 (ppm)

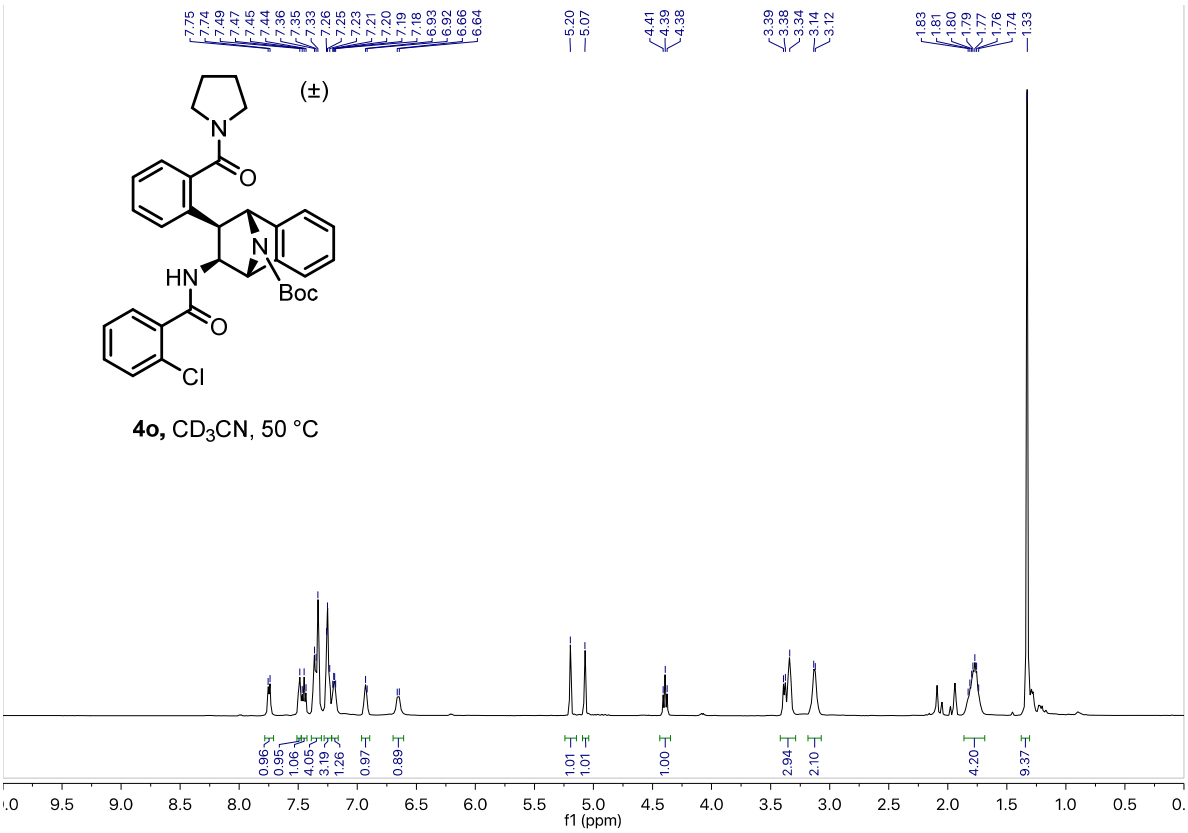

(±)
N
O
N
HN
Boc
tBu
O
4l, CD3CN, 50 °C
f1 (ppm)


(±)
N
O
N
HN
Boc
C7H15
O
4m, CD3CN, 50 °C
f1 (ppm)

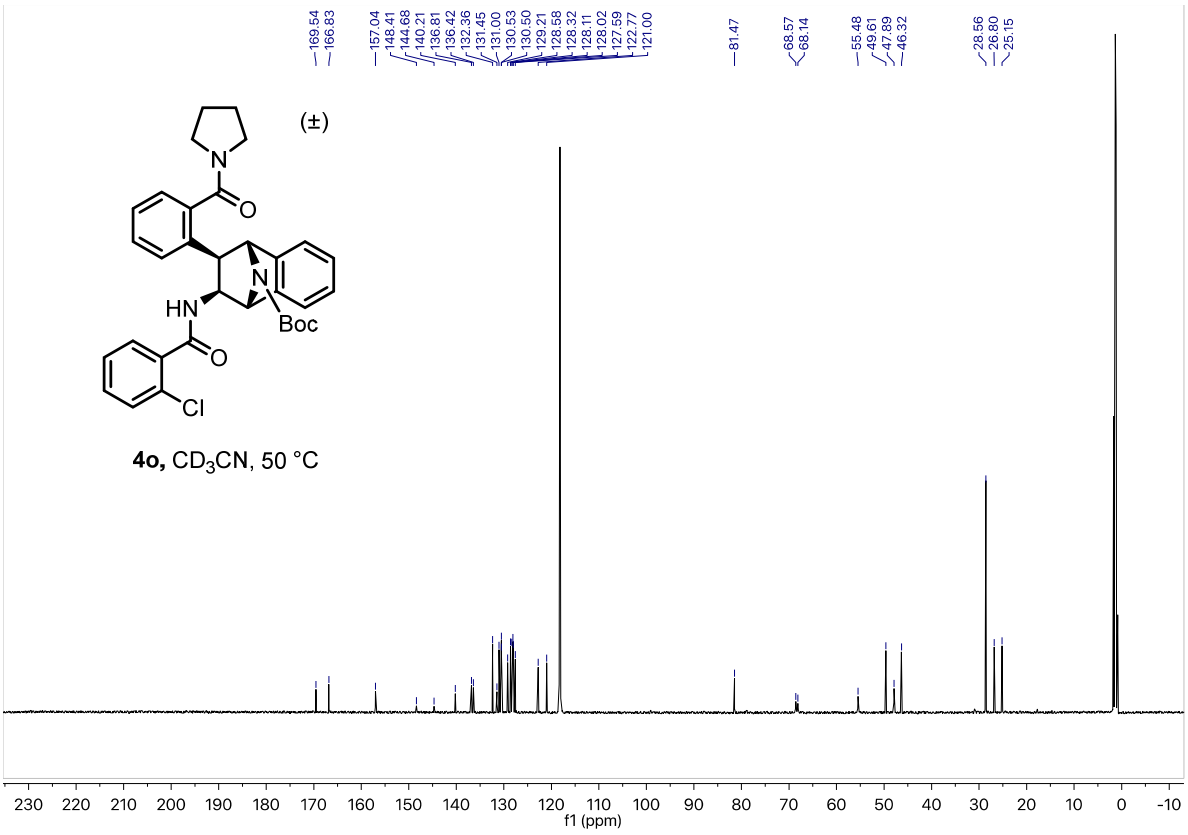

(±)
N
O
N
HN
Boc
C7H15
O
4m, CD3CN, 50 °C
f1 (ppm)


(±)
N
O
N
HN
Boc
O
4n, CD3CN, 50 °C
f1 (ppm)

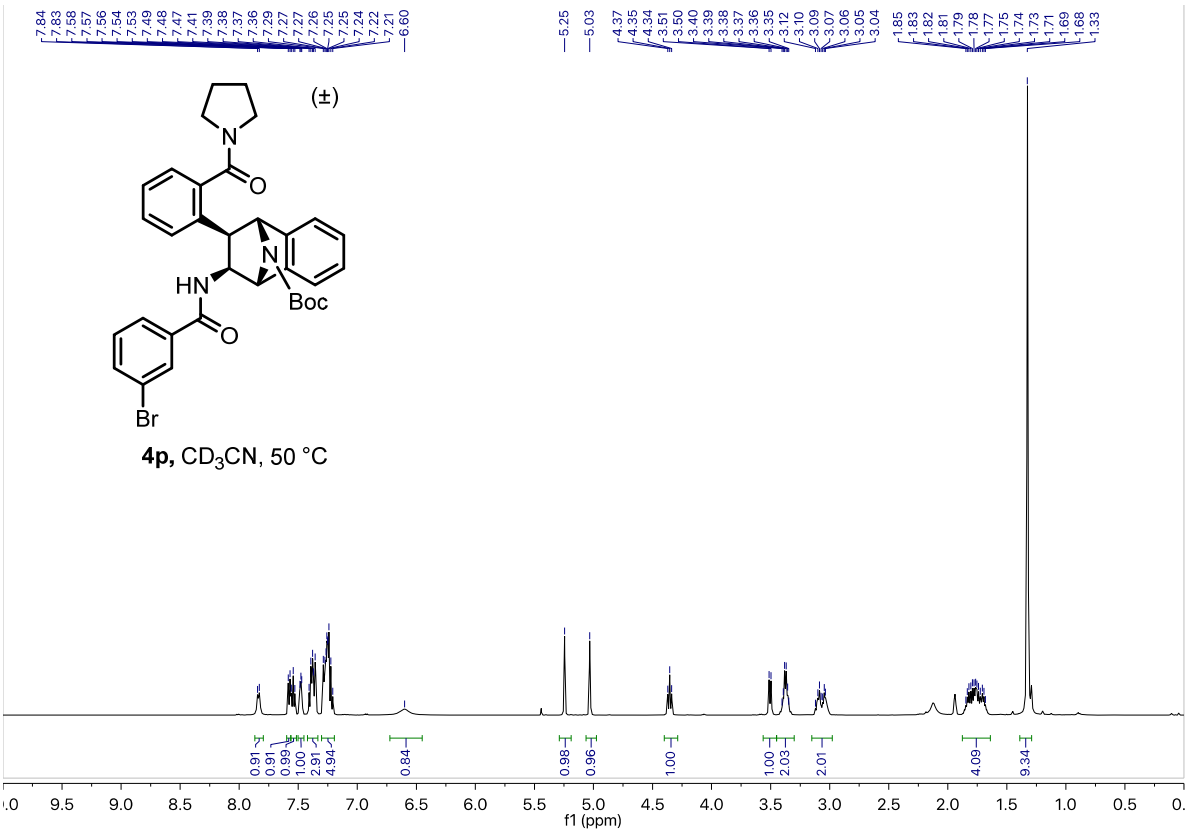

(±)
N
O
N
HN
Boc
O
4n, CD3CN, 50 °C
f1 (ppm)

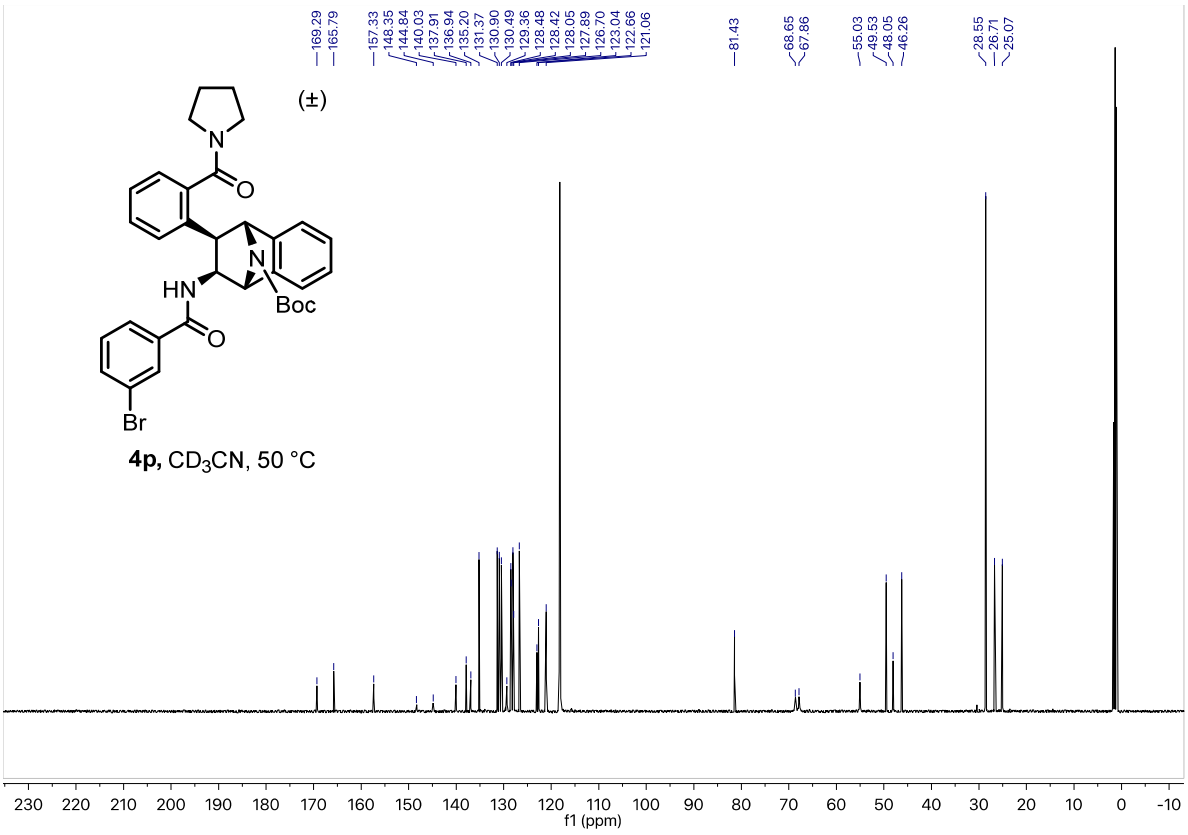


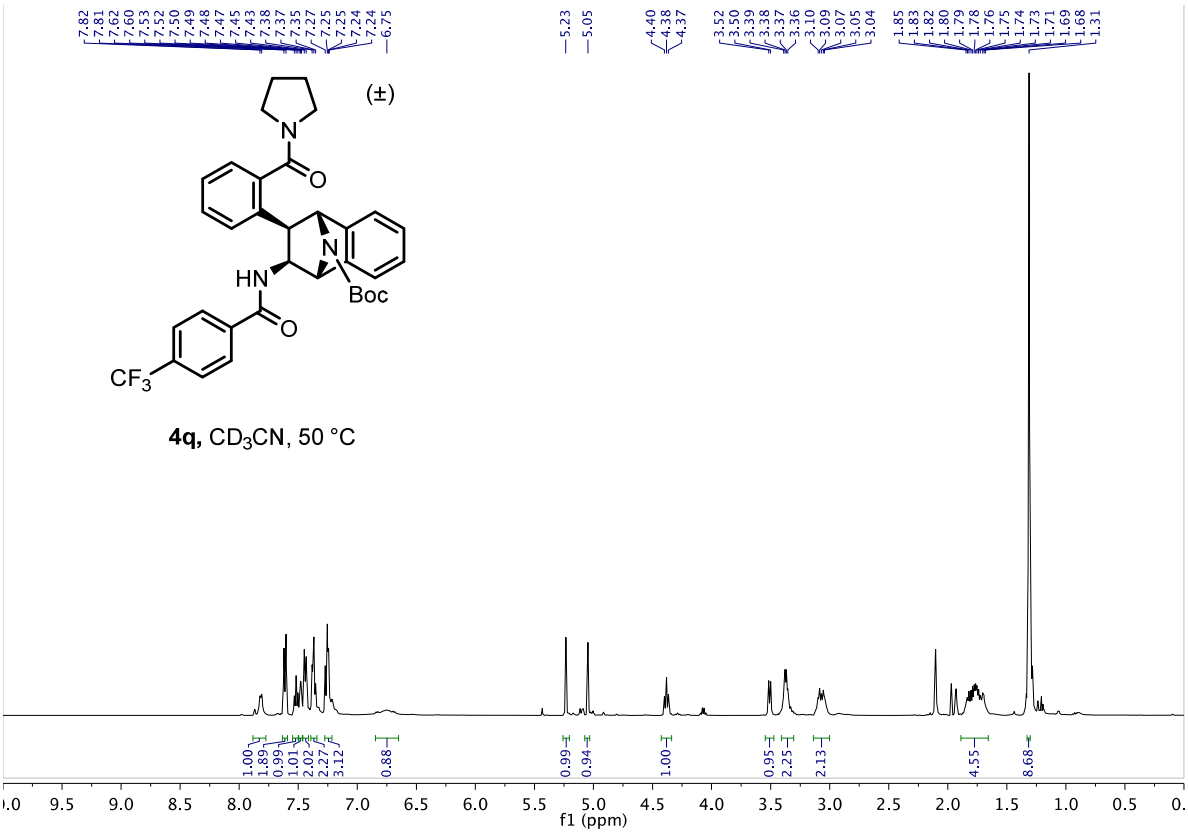
4o, CD_3CN, 50 °C

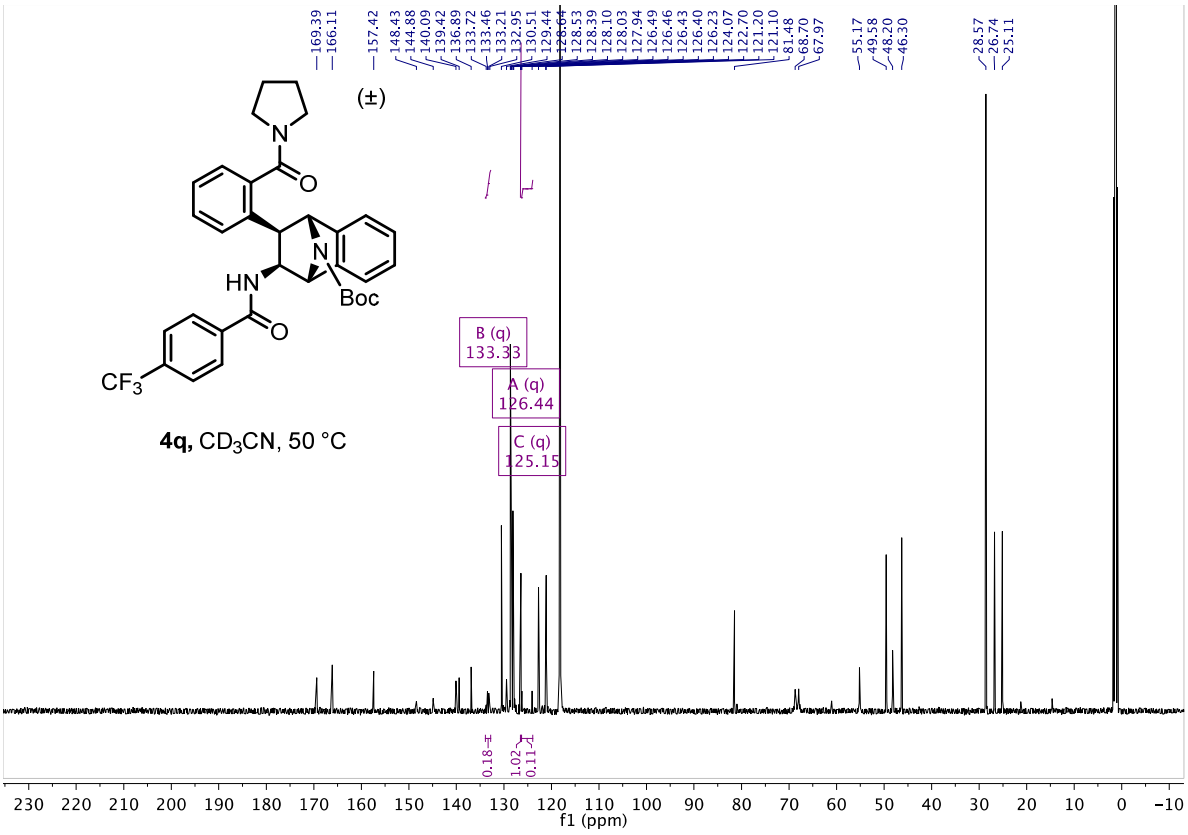


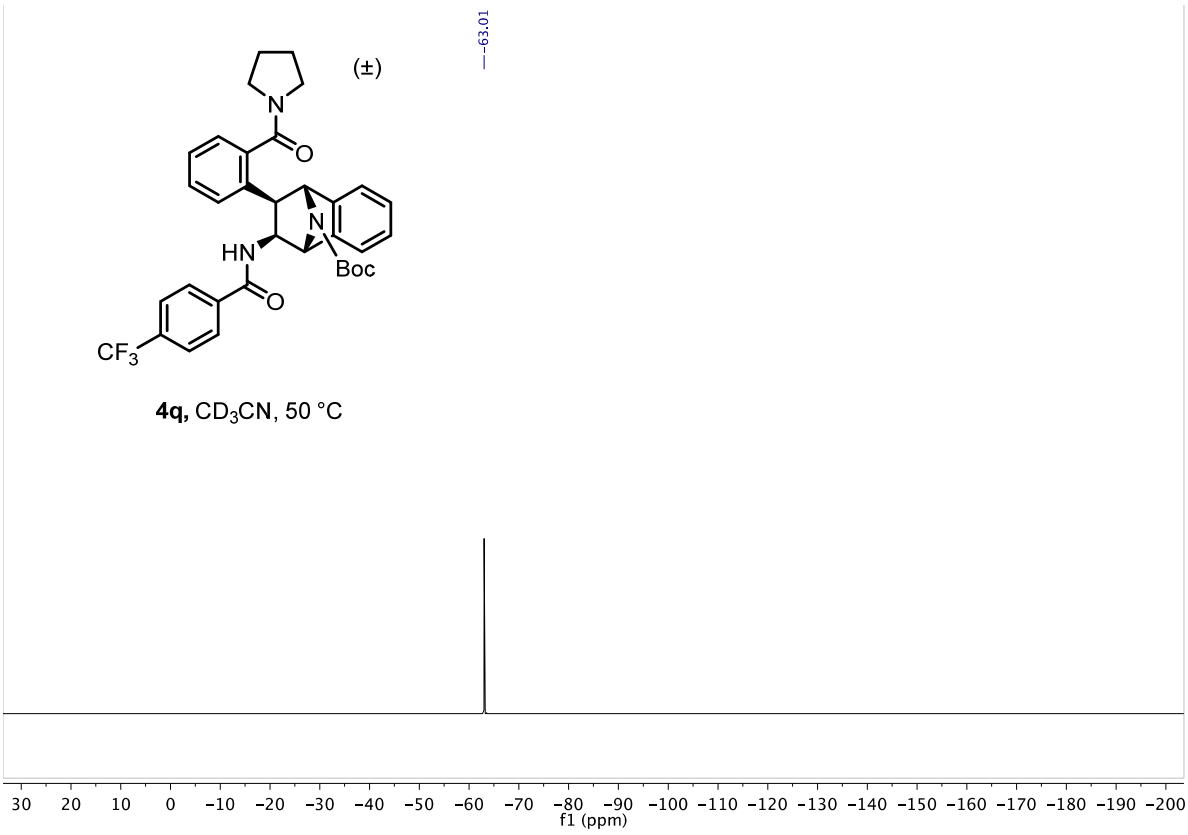
4o, CD_3CN, 50 °C

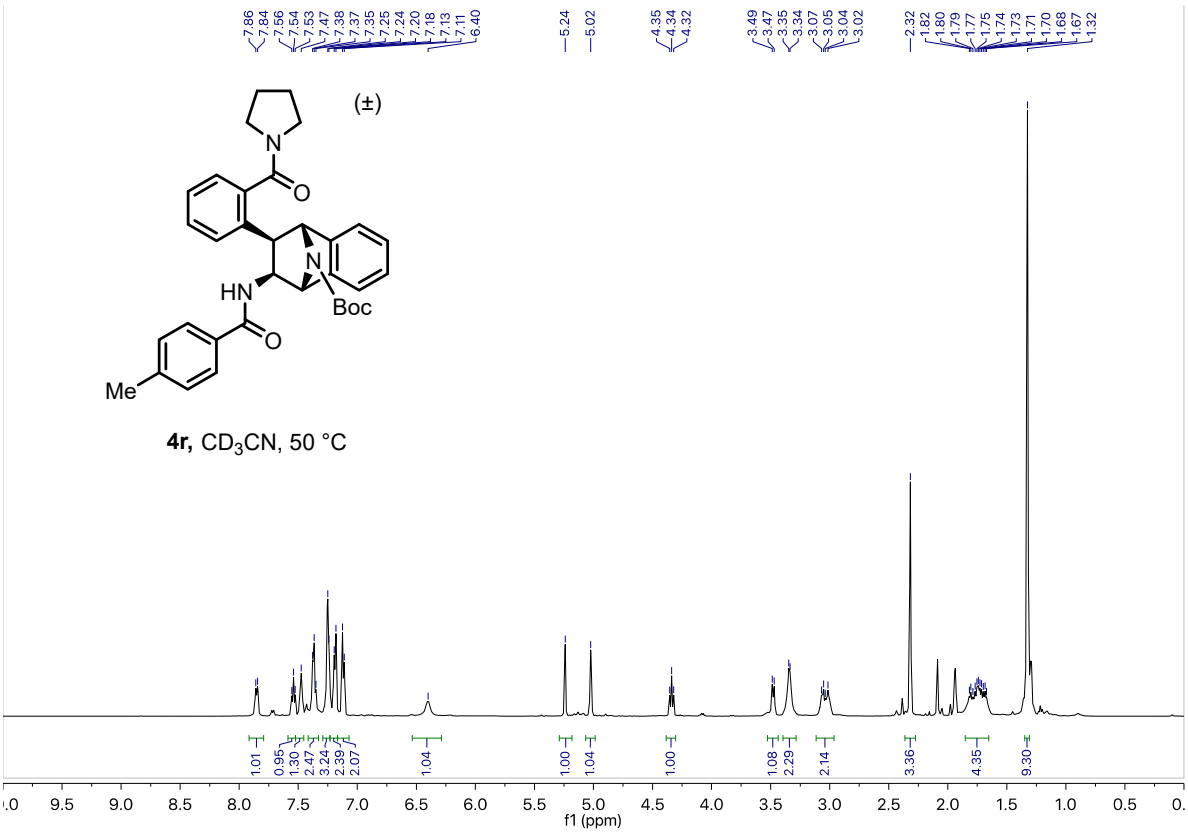

(±)
N
O
N
HN
Boc
O
Br
4p, CD3CN, 50 °C
f1 (ppm)

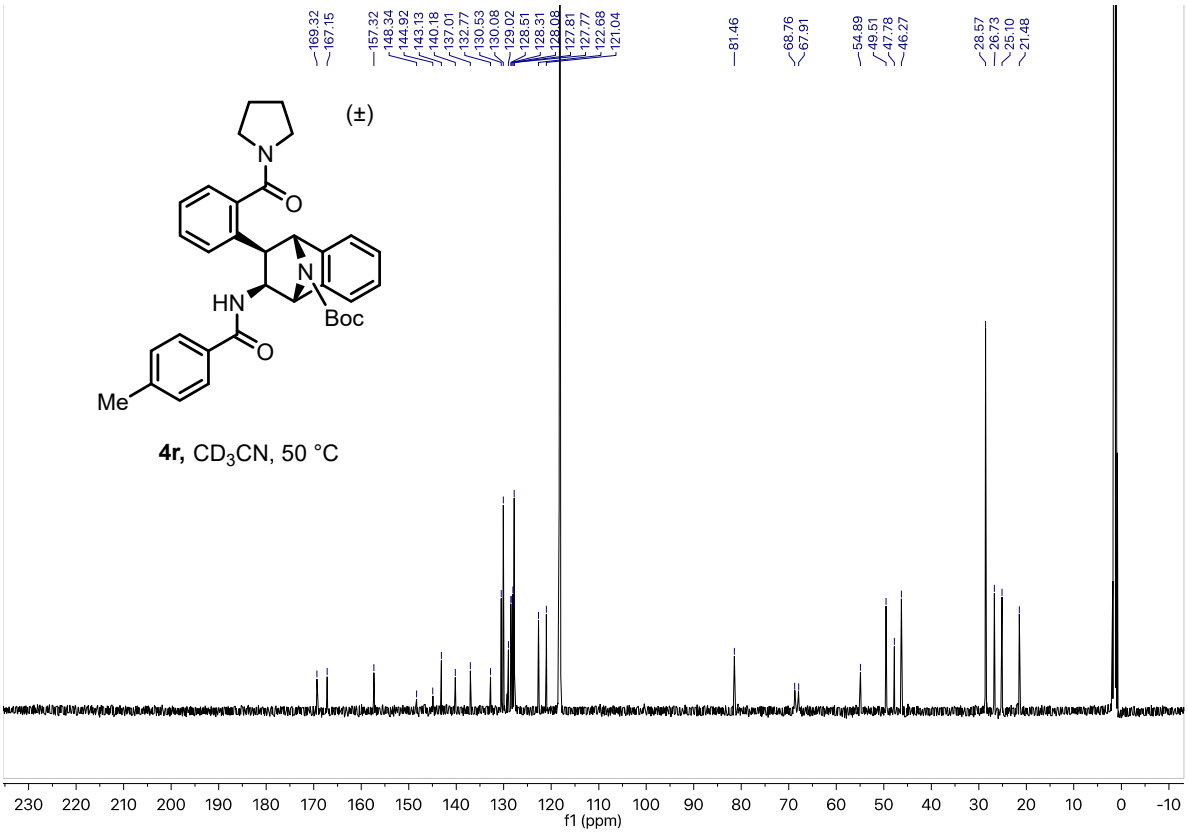

(±)
N
O
N
HN
Boc
O
Br
4p, CD3CN, 50 °C
f1 (ppm)

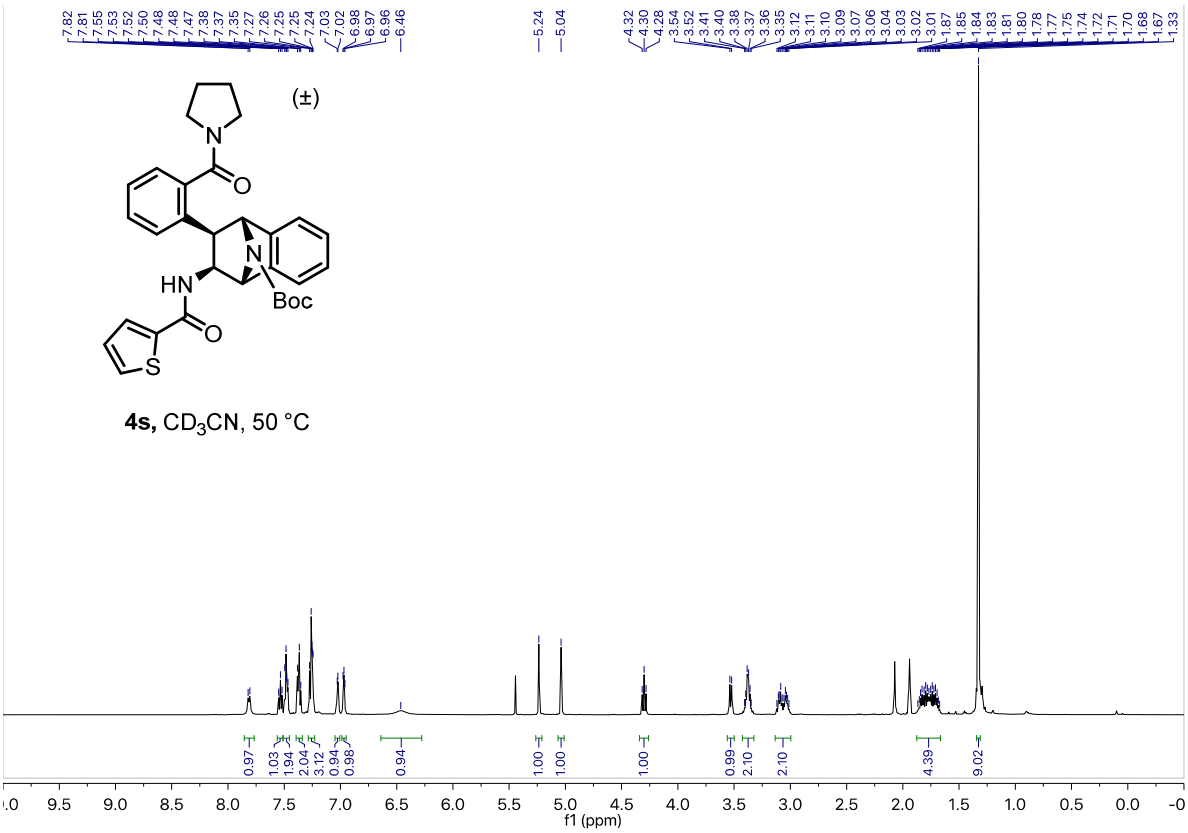

(±)
N
O
N
HN
Boc
O
CF3
4q, CD3CN, 50 °C
f1 (ppm)

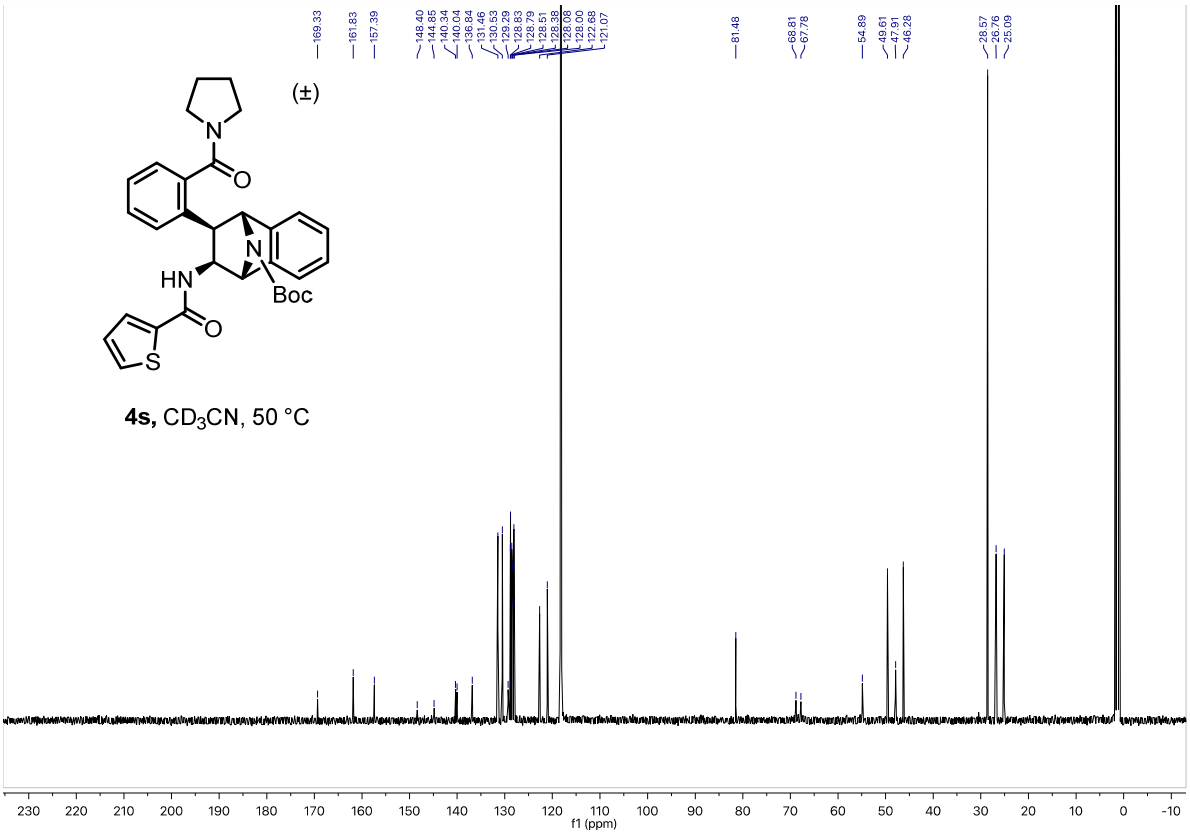

(±)
N
O
N
HN
Boc
O
CF3
4q, CD3CN, 50 °C
B (q)
133.33
A (q)
126.44
C (q)
125.15
f1 (ppm)

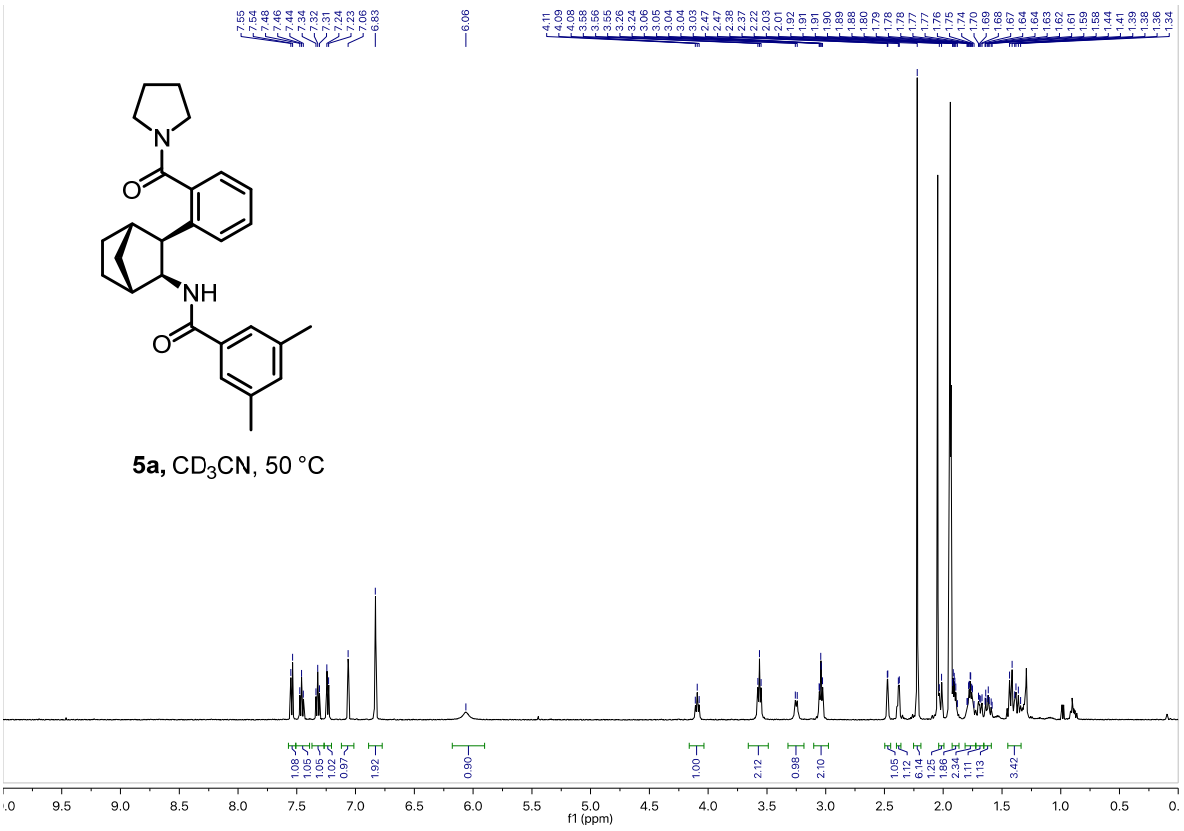

(±)
N
O
N
HN
Boc
O
CF3
4q, CD3CN, 50 °C
-63.01
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

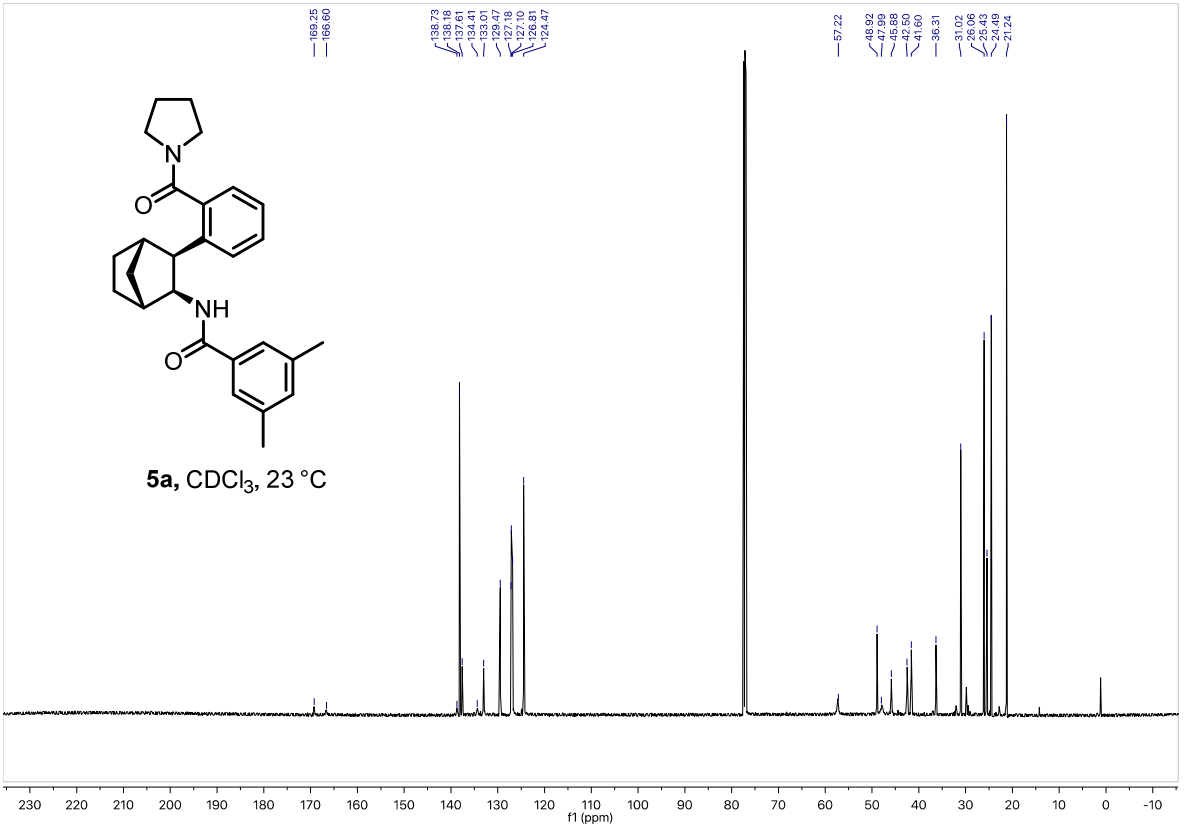

(±)
N
O
N
HN
Boc
O
Me
4r, CD3CN, 50 °C
f1 (ppm)

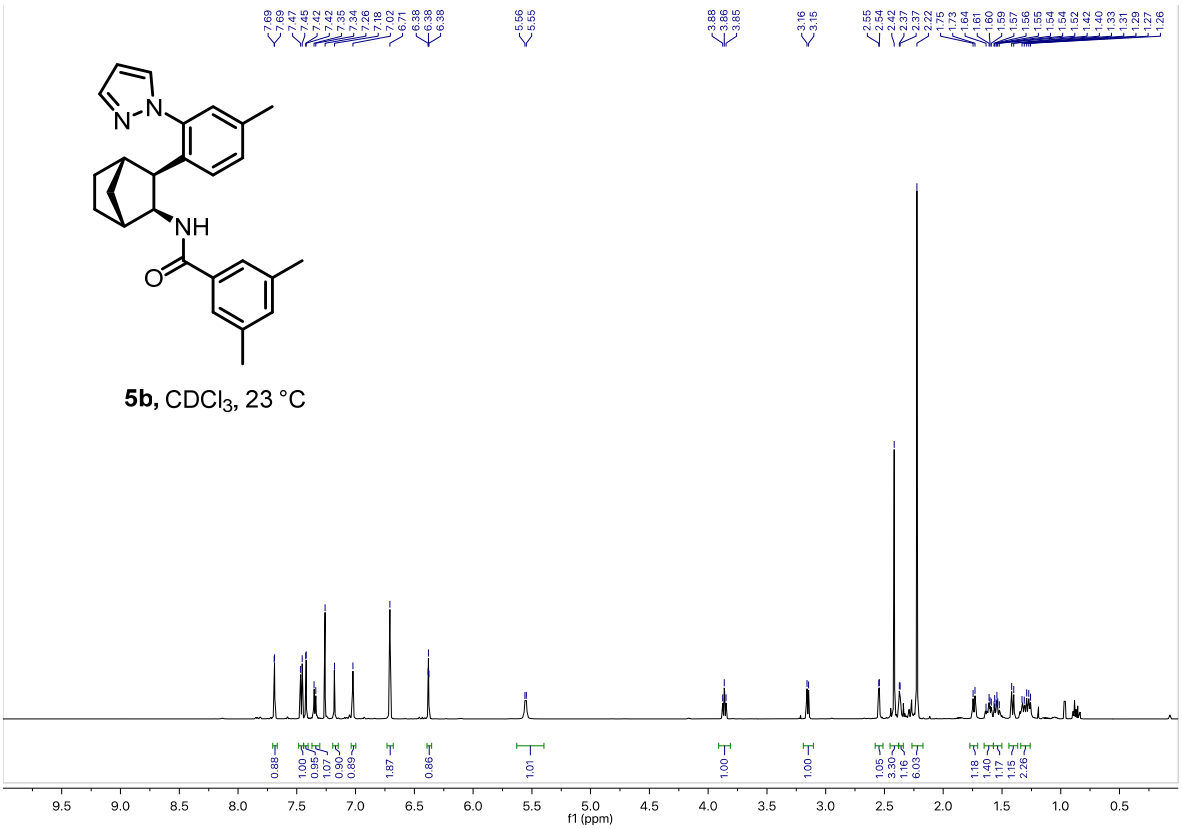

(±)
N
O
N
HN
Boc
O
Me
4r, CD3CN, 50 °C
f1 (ppm)


(±)
N
O
N
HN
Boc
O
S
4s, CD3CN, 50 °C
f1 (ppm)

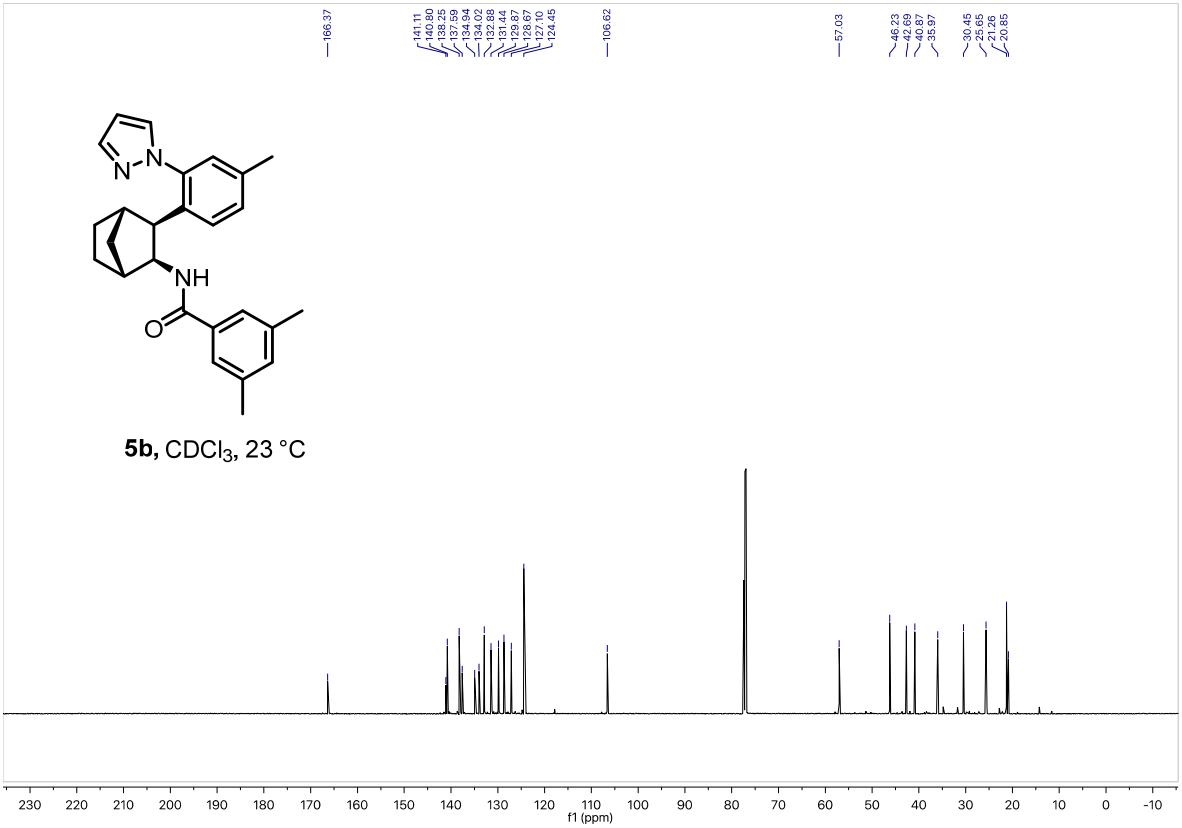

(±)
N
O
N
HN
Boc
O
S
4s, CD3CN, 50 °C
f1 (ppm)


N
O
NH
O
5a, CD3CN, 50 °C
f1 (ppm)

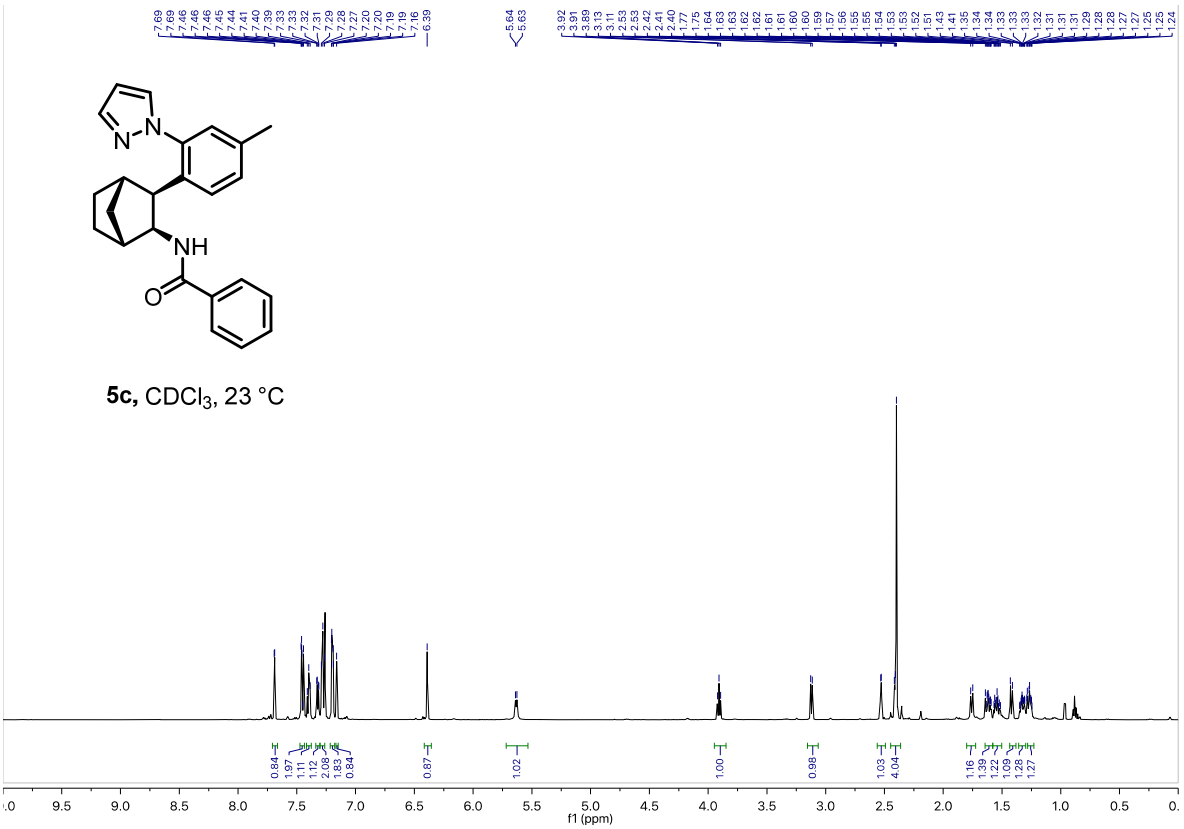

N
O
NH
O
5a, CDCl3, 23 °C
f1 (ppm)



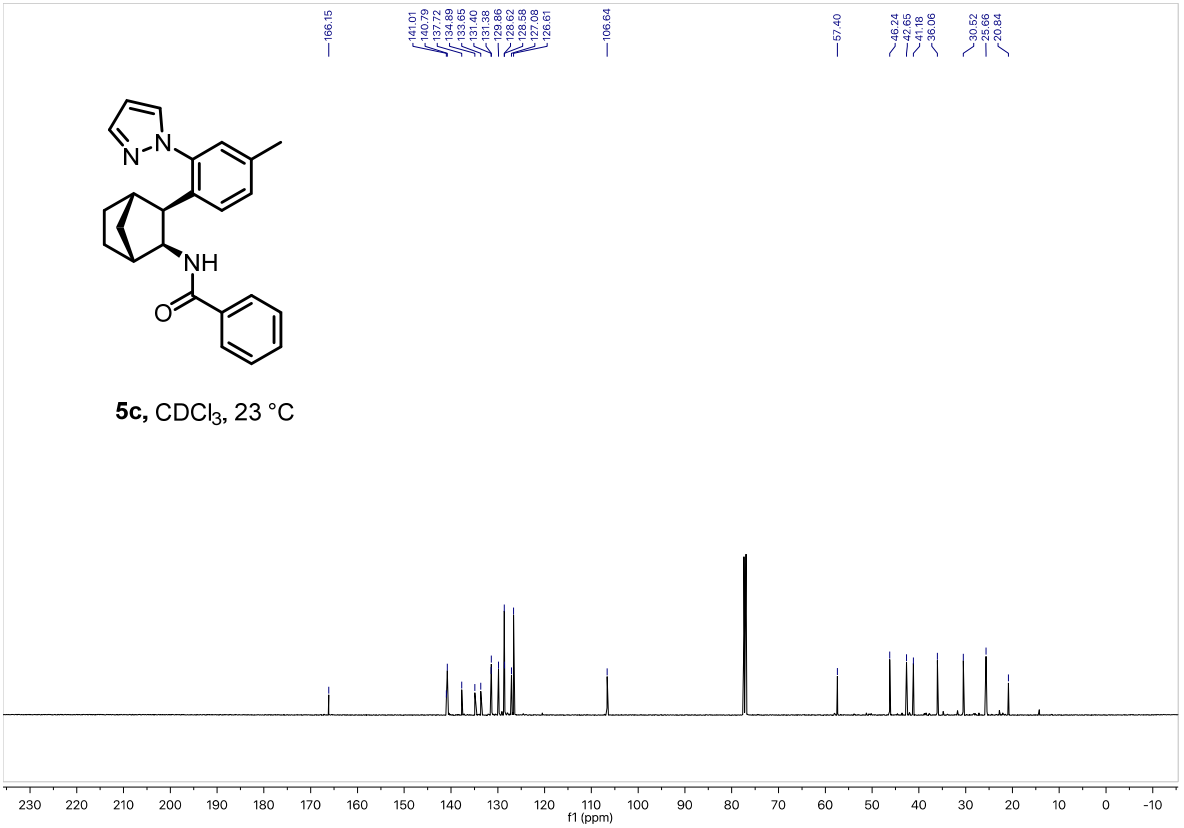
5b, $CDCl_3$, 23 °C



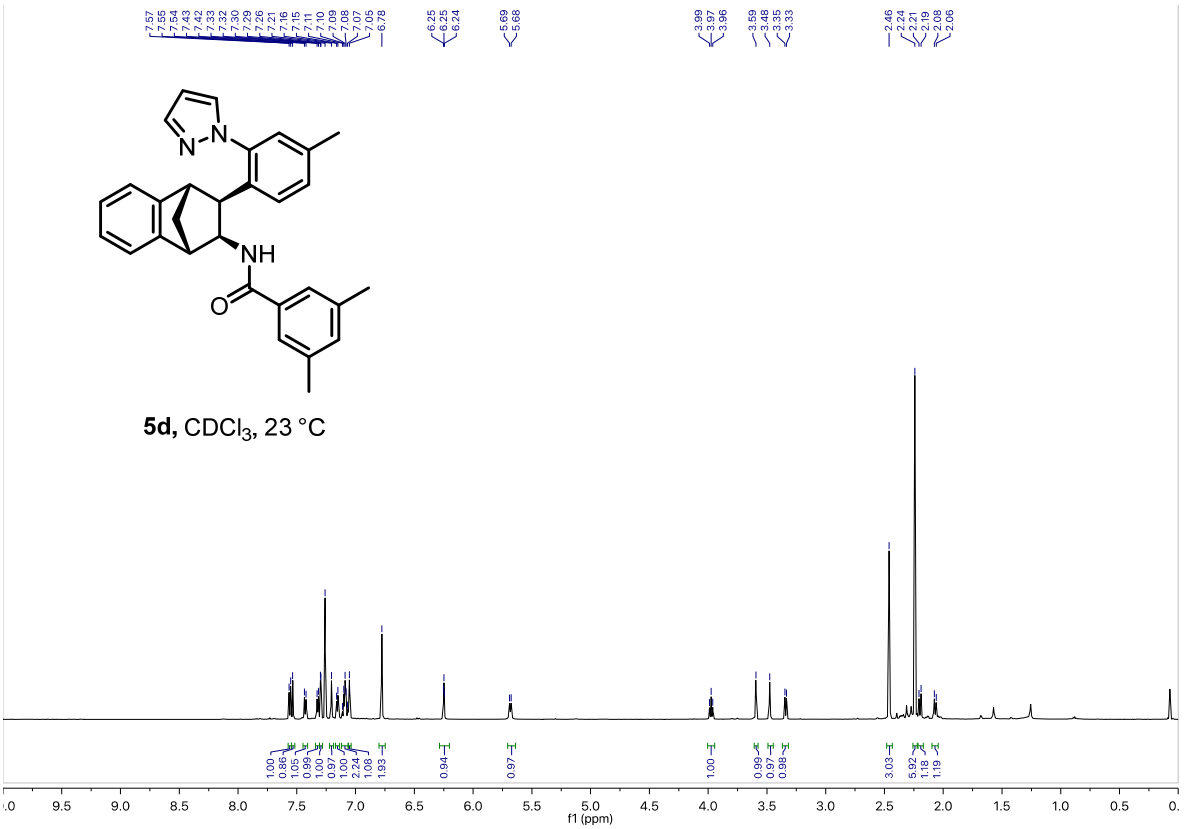
5b, $CDCl_3$, 23 °C



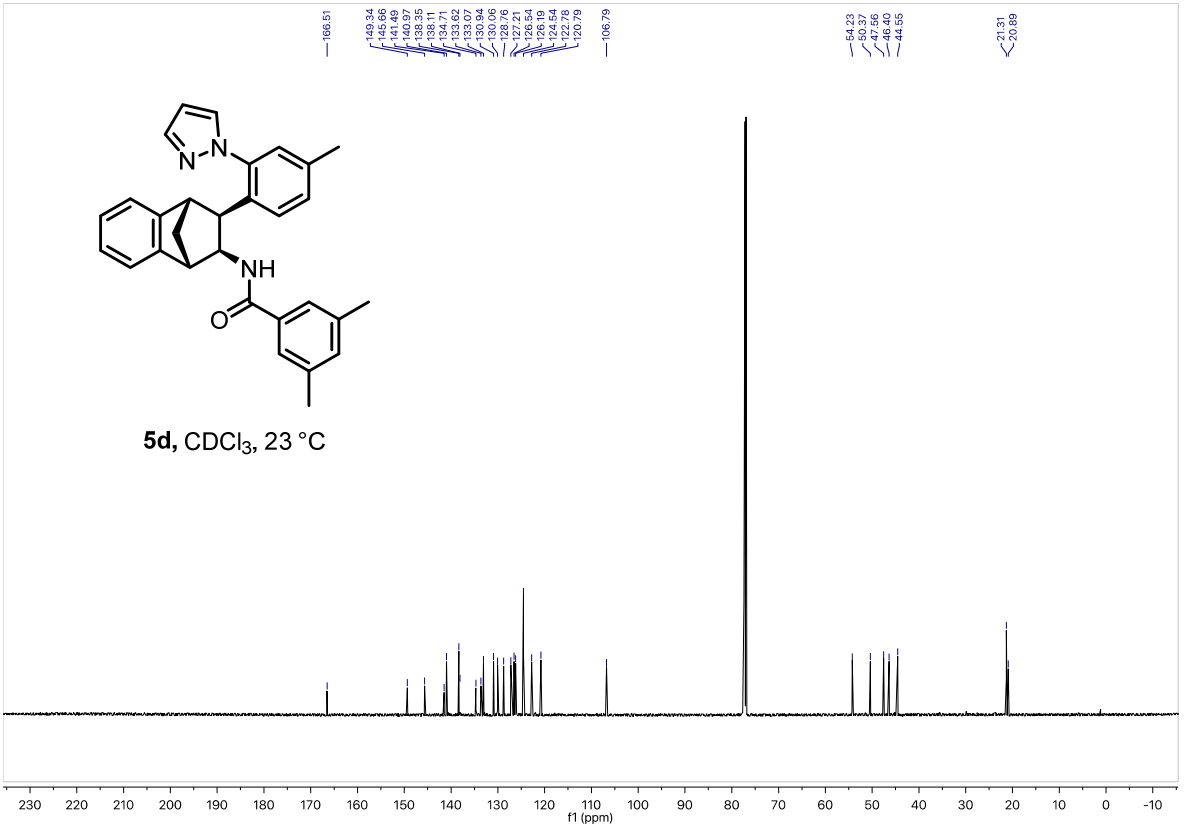
5c, $CDCl_3$, 23 °C



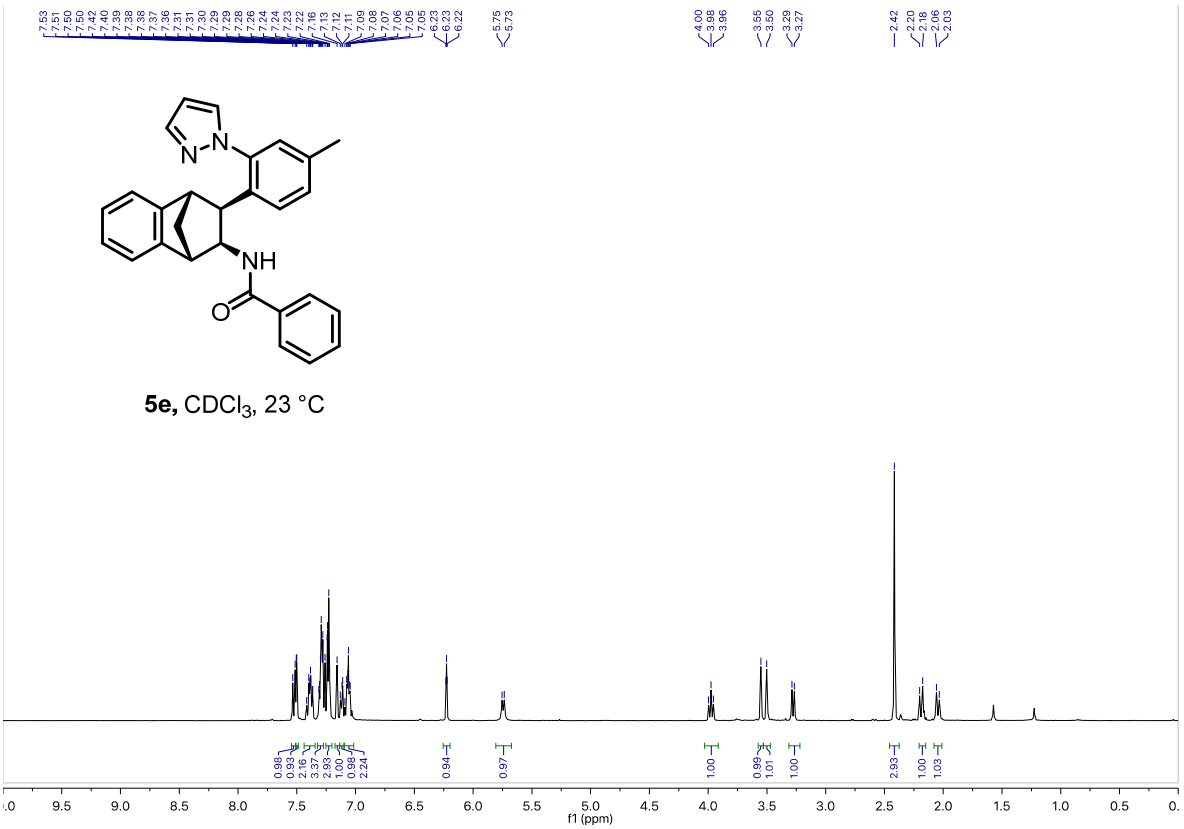
5c, $CDCl_3$, 23 °C



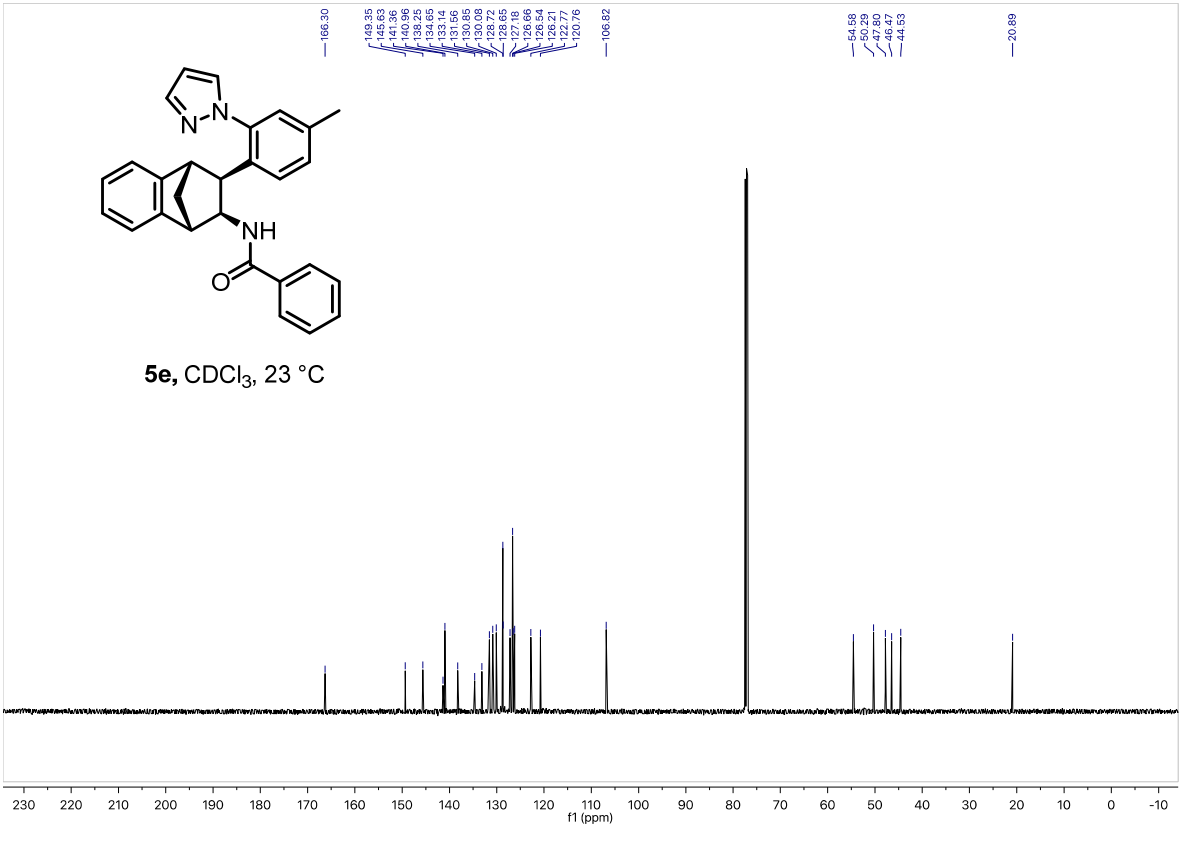
5d, $CDCl_3$, 23 °C



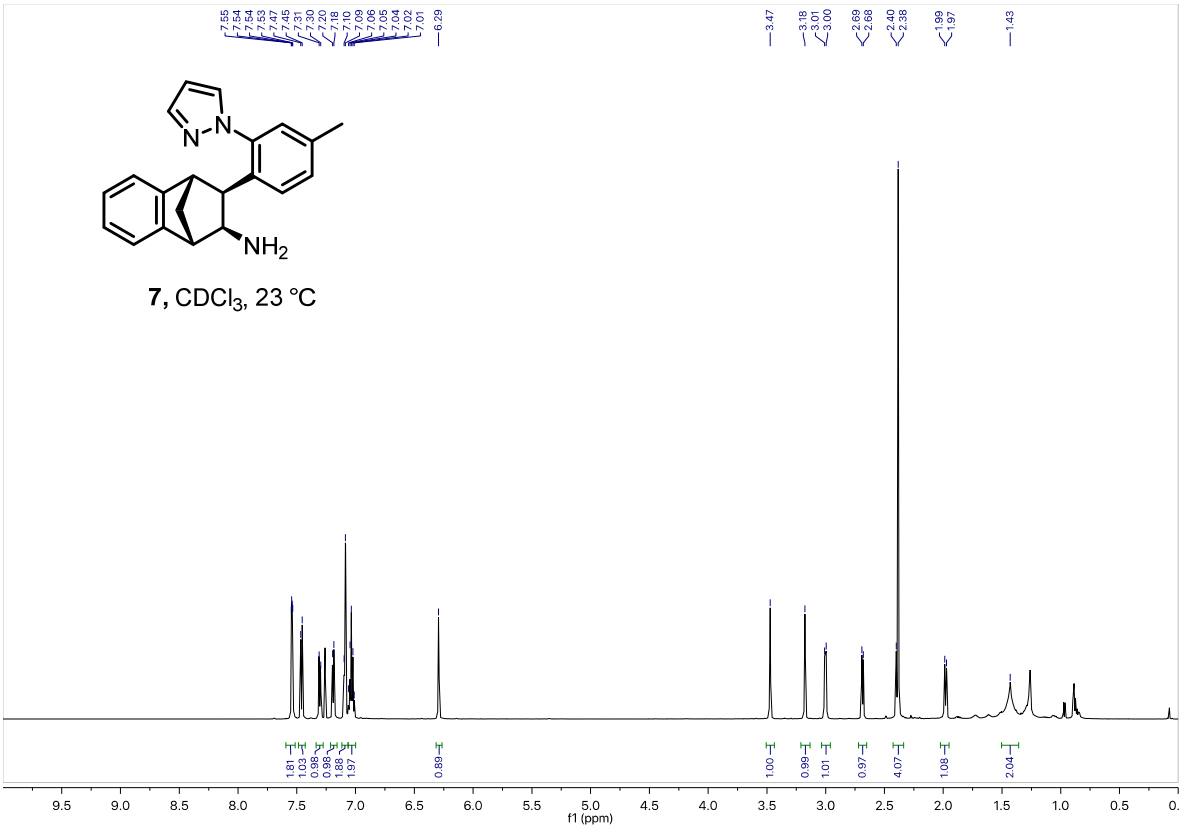
5d, $CDCl_3$, 23 °C

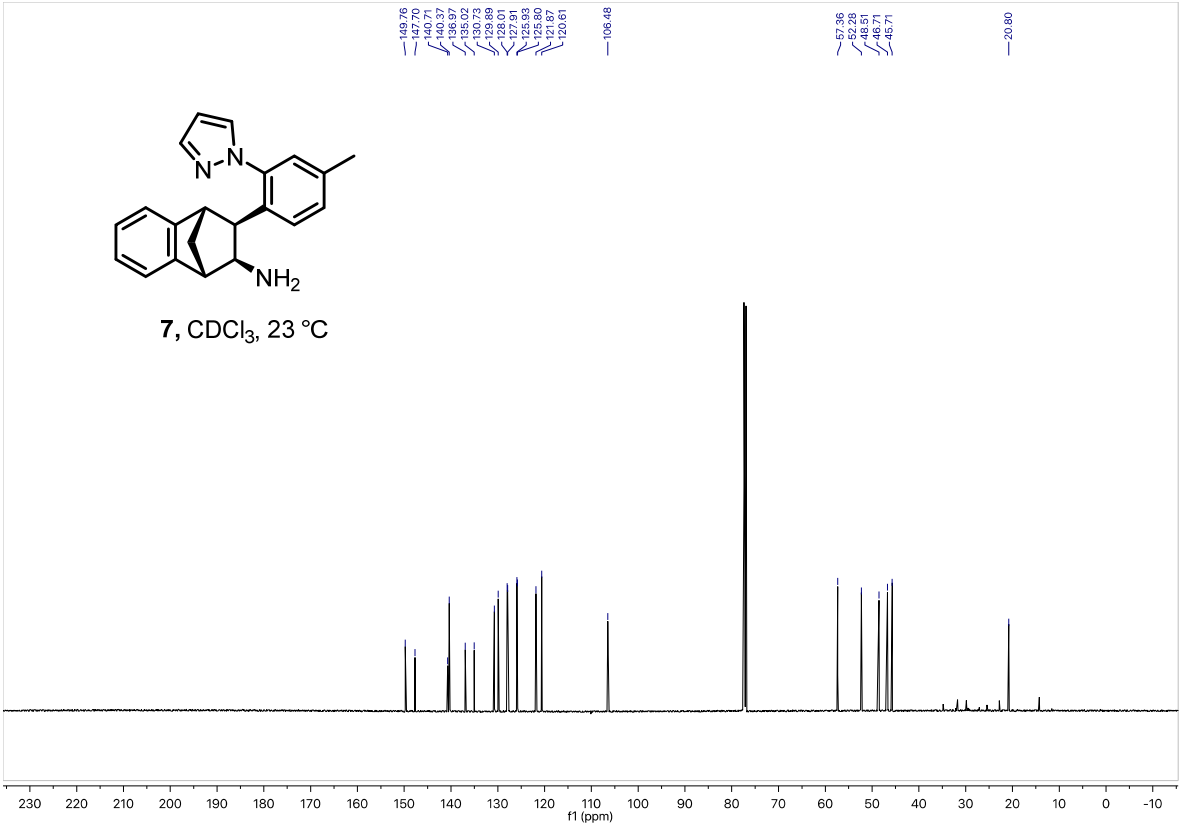


5e, $CDCl_3$, 23 °C



5e, $CDCl_3$, 23 °C


7.55
7.54
7.54
7.53
7.47
7.46
7.31
7.30
7.20
7.18
7.10
7.09
7.06
7.06
7.04
7.02
7.01
6.29
3.47
3.18
3.01
3.00
2.69
2.68
2.40
2.38
1.99
1.97
1.43
NH2
7, CDCl3, 23 °C
1.81
1.03
0.94
0.98
1.88
1.97
0.89
1.00
0.99
1.01
0.97
4.07
1.08
2.04
f1 (ppm)


149.76
147.70
140.71
140.37
136.97
135.02
130.73
129.89
128.01
127.91
125.93
125.89
121.87
120.61
106.48
57.36
52.28
48.51
46.71
45.71
20.80
NH2
7, CDCl3, 23 °C
f1 (ppm)