SUPPORTING INFORMATION

Pd(0)-Catalyzed Directed *syn*-1,2-Carboboration and -Silylation: Alkene Scope, Applications in Dearmoatization, and Stereocontrol via a Chiral Auxiliary

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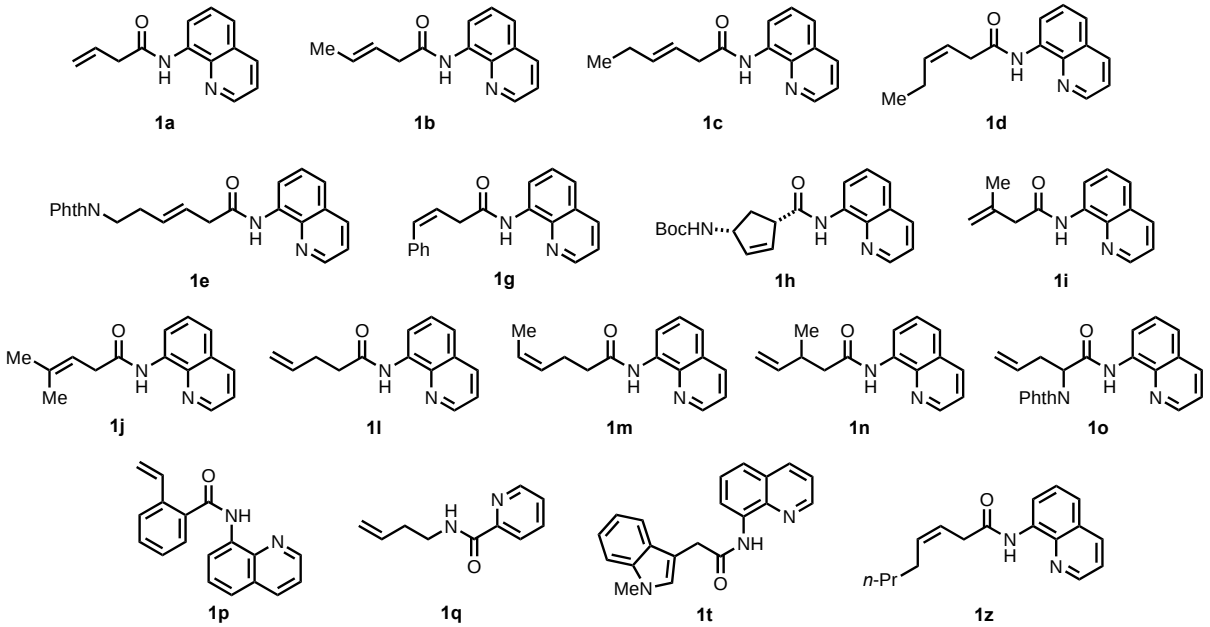
GENERAL INFORMATION

Unless otherwise noted, all materials were used as received from commercial sources without further purification. All carbon electrophiles, B_2pin_2, $PhMe_2Si–Bpin$, Pd_2dba_3, ligands, and solvents were purchased from Aldrich, Alfa Aesar, Oakwood, Strem, and Combi-Blocks. 4 Å molecular sieves was purchased form Aldrich and stored in a desiccator. Before using, an appropriate amount of molecular sieves was placed in a flask and activated in a microwave for 45 seconds (×3). NMR spectra were recorded on Bruker AV-400, DRX-500 and AV-600 instruments. Spectra were internally referenced to $SiMe_4$ or solvent signals. The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet. High-resolution mass spectra (HRMS) for new compounds were recorded on a Waters LC-TOF mass spectrometer, and the reported masses were automatically calibrated to be the neutral adduct of [M+H] by adding the mass of an electron. Enantiomeric excess (*ee*) was determined on a Waters UPC^2 system using commercially available chiral columns.

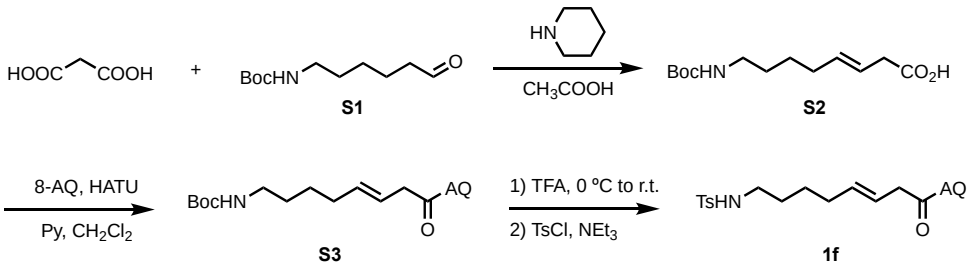
EXPERIMENTAL PROCEDURES

Alkene Substrate Synthesis

Table S1. Alkene substrates **1a–e**, **1g–j**, **1l–q**, **1t** and **1z**.



Alkene substrates **1a**–**e**, **1g**–**j**, **1l**–**q**, **1t** and **1z** were prepared according to literature procedures.[1–7]



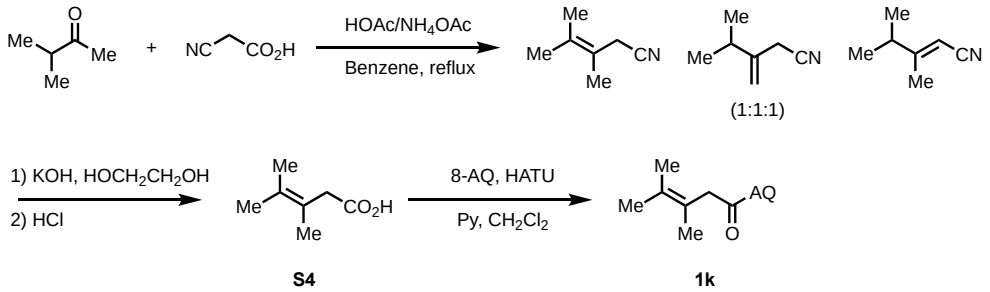
Scheme S1: Synthesis of (*E*)-8-((4-methylphenyl)sulfonamido)-*N*-(quinolin-8-yl)oct-3-enamide (**1f**).[1,8,9]

(*E*)-8-((4-methylphenyl)sulfonamido)-*N*-(quinolin-8-yl)oct-3-enamide (1f): The title compound was prepared by adapting several literature procedures.

Knoevenagel condensation:[8] Malonic acid (1.8 g, 17.3 mmol), *tert*-butyl (6-oxohexyl)carbamate[10] (**S1**) (3.4 g, 15.7 mmol), acetic acid (6 μL) and piperidine (10 μL) were charged into a 25-mL round-bottom flask equipped with a Teflon-coated magnetic stir bar containing DMSO (8 mL). The reaction mixture was stirred at 100 ºC for 8 h. Upon completion, the reaction was quenched with brine (10 mL), and extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over Na_2SO_4, concentrated under vacuum, and purified by column chromatography (1:2 to 1:3 hexanes:EtOAc) to afford compound **S2** as a colorless oil (3.1 g, 76%).

Amide coupling:[1] Acid **S2** (3.0 g, 12 mmol) was charged into a 100-mL round-bottom flask equipped with a Teflon-coated magnetic stir bar containing CH_2Cl_2 (18 mL). 8-Aminoquinoline (1.7 g, 12 mmol), pyridine (2.0 mL, 24 mmol), and HATU (6.84 g, 18 mmol) were added sequentially, and the reaction was stirred at ambient temperature for 36 h. The dark brown solution was diluted with EtOAc (100 mL), washed with sat. $NaHCO_3$ (2 × 50 mL) and brine (50 mL), and purified by column chromatography (5:1 to 3:1 hexanes:EtOAc) to afford amide **S3** (3.4 g, 73%) as a light-yellow oil.

Boc deprotection/Tosyl protection:[9] To a stirred solution of **S3** (383 mg, 1 mmol) in CH_2Cl_2 (20 mL) was added TFA (1 mL) dropwise at 0 ºC. After being allowed to stir at room temperature for 1 h, the reaction mixture was diluted with EtOAc and quenched by slow addition of saturated $NaHCO_3$ (10 mL). The organic phase was separated and washed with brine (20 mL), dried over Na_2SO_4, and concentrated under vacuum to afford free amine, which was carried forward to the next step without further purification. The crude product was dissolved in THF (4 mL), followed by addition of TsCl (196 mg, 1 mmol) and NEt_3 (277 μL, 2 mmol). The reaction mixture was stirred at room temperature for 1 h. Upon completion, the reaction was diluted with EtOAc and washed with saturated $NaHCO_3$ (10 mL). After being dried over Na_2SO_4 and concentrated under vacuum, the resulting residue was purified by column chromatography (1:1 hexanes:EtOAc) to afford compound **1f** as a yellow solid (289 mg, 66%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.99 (s, 1H), 8.88–8.65 (m, 2H), 8.16 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.84–7.66 (m, 2H), 7.61–7.37 (m, 3H), 7.28 (d, *J* = 8.0 Hz, 2H), 5.86–5.56 (m, 2H), 4.43 (t, *J* = 6.2 Hz, 1H), 3.25 (d, *J* = 5.7 Hz, 2H), 2.96 (q, *J* = 6.7 Hz, 2H), 2.41 (s, 3H), 2.23–2.06 (m, 2H), 1.59–1.43 (m, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.8, 148.2, 143.3, 138.5, 136.9, 136.3, 135.9, 134.4, 129.7, 127.9, 127.4, 127.1, 123.0, 121.6, 121.6, 116.3, 43.1, 42.0, 32.0, 29.0, 26.0, 21.5; **HRMS** (ESI-TOF) Calcd for $C_{24}H_{28}N_3O_3S$ [M+H] 438.1851, found 438.1848.



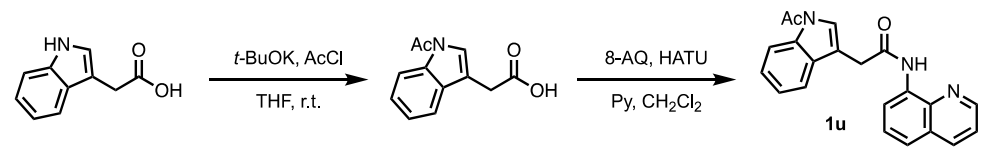
Scheme S2: Synthesis of 3,4-dimethyl-*N*-(quinolin-8-yl)pent-3-enamide (**1k**).[1,11,12]

3,4-dimethyl-*N*-(quinolin-8-yl)pent-3-enamide (1k): The title compound was prepared by adapting several literature procedures.

Knoevenagel condensation:[11,12] In a 100-mL round-bottom flask, a mixture of cyanoacetic acid (8.51g, 100 mmol), isopropyl methyl ketone (8.61 g, 100 mmol), acetic acid (3.0 g, 50 mmol), ammonium acetate (1.5 g, 20 mmol) and 20 mL of benzene were heated with a Dean-Stark trap until completion (around 2 days). The reaction mixture was diluted with diethyl ether (60 mL), washed with sat. $NaHCO_3$ (3 × 20 mL) and brine (3 × 20 mL), and dried over Na_2SO_4. A mixture of nitrile isomers was isolated by silica gel column chromatography (30:1 hexanes:EtOAc).

Hydrolysis of nitriles:[11,12] A mixture of nitriles (180 mg, 1.65 mmol) and KOH (194 mg, 3.46 mmol) was heated in ethylene glycol (15 mL) at reflux for 2 days. The solution was cooled, diluted with water (50 mL) and washed with diethyl ether (2 × 20 mL). The aqueous layer was then acidified with 3 N HCl solution and extracted with 3:1 EtOAc/toluene mixture (×3). The organic layer was further washed with brine (2 × 20 mL) and dried over Na_2SO_4. After removal of the volatiles, the acid **S4** (115 mg, 54%) was carried on to the next step without further purification.

Amide coupling:[1] 3,4-Dimethylpent-3-enoic acid (**S4**) (64 mg, 0.5 mmol) and 8-aminoquinoline (63 mg, 0.44 mmol) were used to prepare amide **1k** following the above amide coupling procedure. The final product was isolated as a white solid (66 mg, 60%) by column chromatography (30:1 to 15:1 hexanes:EtOAc). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.24 (s, 1H), 9.09–8.56 (m, 2H), 8.14 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.64–7.34 (m, 3H), 3.32 (s, 2H), 1.90–1.82 (m, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 169.9, 148.3, 138.7, 136.2, 134.6, 130.7, 127.9, 127.4, 122.2, 121.5, 121.3, 116.2, 44.2, 20.9, 20.8, 19.5; **HRMS** (ESI-TOF) Calcd for $C_{16}H_{19}N_2O$ [M+H] 255.1497, found 255.1499.



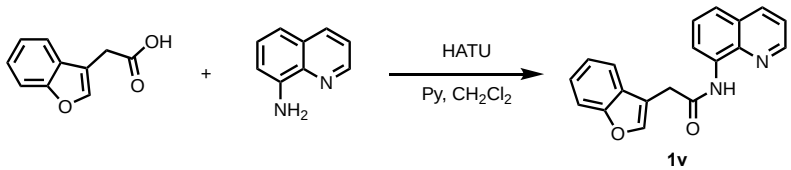
Scheme S3: Synthesis of 2-(1-acetyl-1*H*-indol-3-yl)-*N*-(quinolin-8-yl)acetamide (**1u**).[1,13]

2-(1-acetyl-1*H*-indol-3-yl)-*N*-(quinolin-8-yl)acetamide (1u): The title compound was prepared by adapting several literature procedures.

Acetyl protection:[13] To a stirring solution of 2-(1*H*-indol-3-yl)acetic acid (1.75 g, 10 mmol) in THF (80 mL) was added a solution of *t*-BuOK (2.24 g, 20 mmol) in THF (80 mL) dropwise at –78 ºC. After being stirred at this temperature for 1 h, a solution of acetyl chloride (1.18 g, 15 mmol) in THF (2 mL) was added dropwise, and the resulting solution was stirred at room temperature for 16 h. Upon completion, the reaction was quenched by dropwise addition of 12 N HCl solution. The organic layer was separated, and the aqueous layer was extracted by EtOAc (2 × 20 mL). The combined organic layers were further

washed with water (20 mL) brine (20 mL) and then dried over Na_2SO_4. The crude acid was purified by silica gel column chromatography (2:1 hexanes:EtOAc to pure EtOAc).

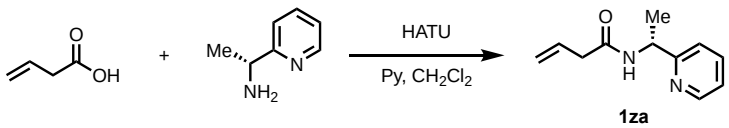
Amide coupling:[1] 2-(1-acetyl-1*H*-indol-3-yl)acetic acid (542 mg, 2.5 mmol) and 8-aminoquinoline (300 mg, 2.1 mmol) were used to prepare amide **1u** following the above amide coupling procedure. The final product was isolated as a yellow solid (286 mg, 40% in 2 steps) by column chromatography (2:1 hexanes:EtOAc). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.11 (s, 1H), 8.76 (dd, *J* = 7.4, 1.5 Hz, 1H), 8.64 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.48 (d, *J* = 8.3 Hz, 1H), 8.12 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.74–7.28 (m, 7H), 4.00 (d, *J* = 1.1 Hz, 2H), 2.67 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 168.1, 167.8, 147.7, 138.0, 135.8, 135.5, 133.7, 129.6, 127.4, 126.9, 125.2, 123.7, 123.4, 121.3, 121.2, 118.5, 116.3, 116.0, 115.3, 34.2, 23.6; **HRMS** (ESI-TOF) Calcd for $C_{21}H_{18}N_3O_2$ [M+H] 344.1399, found 344.1397.



1v

Scheme S4: Synthesis of 2-(benzofuran-3-yl)-*N*-(quinolin-8-yl)acetamide (**1v**).[1]

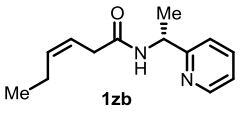
2-(benzofuran-3-yl)-*N*-(quinolin-8-yl)acetamide (1v): 2-(Benzofuran-3-yl)acetic acid (506 mg, 2.9 mmol) and 8-aminoquinoline (360 mg, 2.5 mmol) were used to prepare amide **1u** following the above amide coupling procedure.[1] The final product was isolated as a light-yellow solid (656 mg, 87%) by column chromatography (15:1 hexanes:EtOAc). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.08 (s, 1H), 8.76 (dd, *J* = 7.4, 1.5 Hz, 1H), 8.63 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.10 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.78 (s, 1H), 7.73–7.62 (m, 1H), 7.58–7.44 (m, 3H), 7.42–7.22 (m, 3H), 3.97 (d, *J* = 1.0 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 168.2, 155.5, 148.2, 143.2, 138.4, 136.2, 134.2, 127.8, 127.5, 127.3, 124.7, 122.8, 121.7, 121.5, 119.8, 116.4, 113.9, 111.5, 33.4; **HRMS** (ESI-TOF) Calcd for $C_{19}H_{15}N_2O_2$ [M+H] 303.1134, found 303.1134.



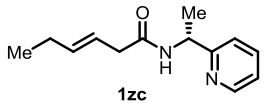
1za

Scheme S5: Synthesis of (*R*)-*N*-(1-(pyridine-2-yl)ethyl)but-3-enamide (**1za**).[1]

(*R*)-*N*-(1-(pyridine-2-yl)ethyl)but-3-enamide (1y): But-3-enoic acid (405 mg, 4.7 mmol) and (*R*)-1-(pyridine-2-yl)ethan-1-amine (500 mg, 4.1 mmol) were used to prepare amide **1y** following the above amide coupling procedure.[1] The final product was isolated as a white solid (389 mg, 50%, 98% *ee*) by column chromatography (1:1 to 1:2 hexanes:EtOAc). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.54 (dt, *J* = 4.8, 1.3 Hz, 1H), 7.66 (td, *J* = 7.7, 1.8 Hz, 1H), 7.26–7.15 (m, 2H), 7.03 (s, 1H), 6.15–5.79 (m, 1H), 5.34–5.19 (m, 2H), 5.14 (p, *J* = 6.9 Hz, 1H), 3.05 (dq, *J* = 7.2, 1.2 Hz, 2H), 1.46 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.8, 160.8, 149.0, 136.8, 131.3, 122.3, 121.5, 119.5, 49.7, 41.7, 22.7; **HRMS** (ESI-TOF) Calcd for $C_{11}H_{15}N_2O$ [M+H] 191.1184, found 191.1186; **HPLC** (chiral column) The enantiomeric excess was determined by chiral HPLC on a Daicel AD-H column (5 μm, 4.6×250 mm), 20% *i*-PrOH/Hexanes, 1.0 mL/min, λ = 246 nm, t (major) = 4.293 min, t (minor) = 5.773 min.



(*R*,*Z*)-*N*-(1-(pyridine-2-yl)ethyl)hex-3-enamide (1zb): (*Z*)-Hex-3-enoic acid[14] (700 mg, 6 mmol) and (*R*)-1-(pyridine-2-yl)ethan-1-amine (700 mg, 5 mmol) were used to prepare amide **1zb** following the above amide coupling procedure.[1] The final product was isolated as a yellow oil (796 mg, 73%) by column chromatography (1:1 to 1:2 hexanes:EtOAc). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.53 (ddd, *J* = 4.9, 1.8, 0.9 Hz, 1H), 7.65 (td, *J* = 7.7, 1.8 Hz, 1H), 7.24–7.15 (m, 2H), 7.08 (s, 1H), 5.70 (dtt, *J* = 10.1, 7.3, 1.4 Hz, 1H), 5.56 (dtt, *J* = 10.8, 7.6, 1.6 Hz, 1H), 5.13 (p, *J* = 6.9 Hz, 1H), 3.05 (dd, *J* = 7.6, 1.3 Hz, 2H), 2.08 (pd, *J* = 7.5, 1.5 Hz, 2H), 1.45 (d, *J* = 6.8 Hz, 3H), 0.99 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 160.9, 149.0, 136.7, 136.5, 122.2, 121.4, 121.0, 49.6, 35.2, 22.6, 20.6, 13.8; **HRMS** (ESI-TOF) Calcd for $C_{13}H_{19}N_2O$ [M+H] 219.1497, found 219.1494.



(*R*,*E*)-*N*-(1-(pyridin-2-yl)ethyl)hex-3-enamide (1zc): (*E*)-Hex-3-enoic acid (600 mg, 5 mmol) and (*R*)-1-(pyridine-2-yl)ethan-1-amine (500 mg, 4 mmol) were used to prepare amide **1zb** following the above amide coupling procedure.[1] The final product was isolated as a white solid (654 mg, 75% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.53 (dt, *J* = 4.8, 1.5 Hz, 1H), 7.65 (td, *J* = 7.7, 1.8 Hz, 1H), 7.25–7.16 (m, 2H), 7.06 (s, 1H), 5.80–5.62 (m, 1H), 5.62–5.48 (m, 1H), 5.12 (p, *J* = 6.9 Hz, 1H), 2.98 (ddt, *J* = 7.1, 2.6, 1.2 Hz, 2H), 2.19–2.00 (m, 2H), 1.46 (d, *J* = 6.8 Hz, 3H), 1.03 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.7, 161.0, 149.0, 137.7, 136.8, 122.3, 121.7, 121.5, 49.7, 40.6, 25.6, 22.8, 13.6; **HRMS** (ESI-TOF) Calcd for $C_{13}H_{19}N_2O$ [M+H] 219.1497, found 219.1495.

Reaction Optimization Details

Table S2. Optimization of 1,2-arylboration reaction.[a]

R = H, **1a**
R = Et, **1c**

2a

3a

4a or **4c**

entry	Substrate	Solvent	Base	Ligand	Yield[b] (%)
1	**1a**	DMPU	K_2CO_3	Cy-JohnPhos	61
2	**1a**	DMPU	KF	Cy-JohnPhos	70
3	**1a**	DMPU	K_2HPO_4	Cy-JohnPhos	89
4	**1a**	DMPU	*i*-Pr_2NEt	Cy-JohnPhos	90
5	**1a**	*t*-AmylOH	KF	Cy-JohnPhos	95
6	**1a**	DMSO	KF	Cy-JohnPhos	15
7	**1a**	toluene	KF	Cy-JohnPhos	89
8[c]	**1a**	*t*-AmylOH	*i*-Pr_2NEt	Cy-JohnPhos	(98)
9[c]	**1c**	*t*-AmylOH	*i*-Pr_2NEt	PPh_3	trace
10[c]	**1c**	*t*-AmylOH	*i*-Pr_2NEt	$CyPPh_2$	12
11[c]	**1c**	*t*-AmylOH	*i*-Pr_2NEt	RuPhos	>99
12[c]	**1c**	*t*-AmylOH	*i*-Pr_2NEt	XPhos	98

[a] Reaction conditions: **1a** or **1c** (0.1 mmol), **2a** (1.5 equiv), **3a** (2 equiv), Pd_2dba_3 (10 mol%), Ligand (20 mol%), base (2 equiv), 4Å MS (15–30 mg), 100 °C, N_2, 16–20 h. [b] Yields were determined by ^1H NMR analysis of the crude reaction mixture using CH_2Br_2 as internal standard. Values in parentheses represent isolated yields. [c] Pd_2dba_3 (3 mol%), Ligand (6 mol%), 90 °C.

General Procedure for Aryl- and Alkenylboration of Alkenes

General Procedure: To a 4-mL scintillation vial equipped with a Teflon-coated magnetic stir bar were added the alkene substrate (0.1 mmol), bis(pinacolato)diboron (50.8 mg, 0.2 mmol), $Pd_2(dba)_3$ (2.8 mg, 3 mol%), Cy-JohnPhos (2.2 mg, 6 mol%), and 4Å molecular sieves (~28 mg). The vial was sealed with a screw-top septum cap and was then evacuated and backfilled with N_2 (×3). Under positive N_2 pressure, aryl or alkenyl triflate (0.15 mmol), *i*-Pr_2Net (34.8 µL, 0.2 mmol), and *t*-AmylOH (0.2 mL) were added. All needle inlets/outlets were removed, and the reaction was placed in a heating block that was pre-heated to 90 °C. (*Note: To prevent solvent evaporation through the punctures in the septum, at this stage we typically switch the old cap for new cap under a flow of N_2 gas.*) After 40–44 h, the black reaction mixture was allowed to cool to room temperature and filtered through a short plug of celite (CH_2Cl_2 or EtOAc as eluent). The solvent was removed in *vacuo* to afford a dark brown residue. Upon purification by column chromatography with 5:1 to 3:1 hexanes:EtOAc as the eluent, the pure product was obtained.

Note:[1] *Column chromatography should be performed quickly to prevent product decomposition on silica. (We typically aim to complete the column in 10–15 min for a reaction on this scale.) If pinacol is still present after column purification, it can be removed by heating under vacuum at 80 ºC for 1 h.*

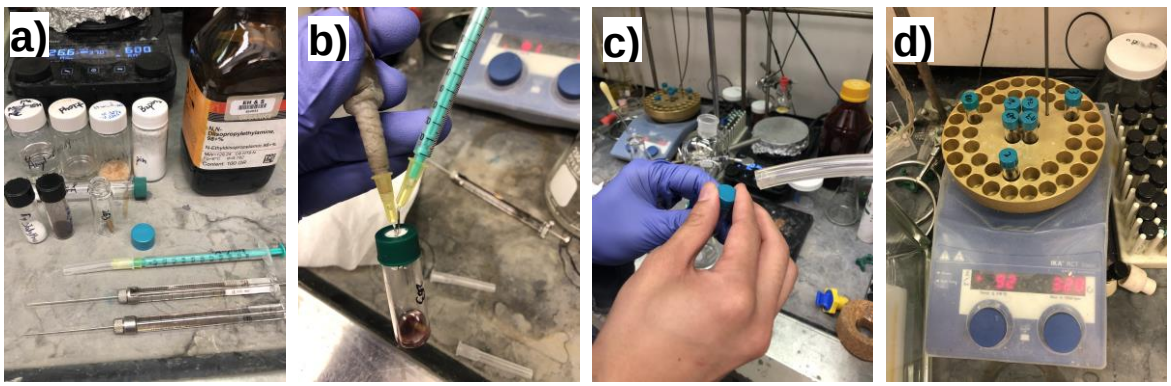
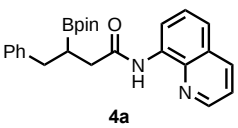


Figure S1: Photographic depiction of reaction setup.

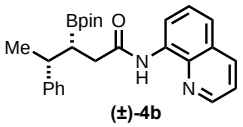
S) Reactants. B) Adding solvent. C) Switching cap under N_2. D) Heating on stir plate.



4a

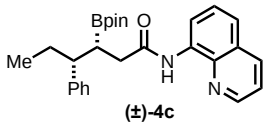
4-phenyl-*N*-(quinolin-8-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanamide (4a): The title compound was prepared from **1a** (21.2 mg, 0.1 mmol), phenyl triflate (24.4 µL, 0.15 mmol), and bis(pinacolato)diboron (50.8 mg, 0.2 mmol) with *t*-AmylOH (0.4 mL) according to the general carboboration procedure. Purification using silica gel chromatography with 5:1 hexanes:EtOAc as the eluent gave the product as a colorless oil (40.8 mg, 98% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.72 (s, 1H), 8.99–8.64 (m, 2H), 8.16 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.67–7.40 (m, 3H), 7.31–7.25 (m, 4H), 7.23–7.17 (m, 1H), 2.98 (dd, *J* = 13.9, 6.3 Hz, 1H), 2.75 (dd, *J* = 13.9, 9.4 Hz, 1H), 2.71–2.57 (m, 2H), 1.87 (ddt, *J* = 9.5, 8.0, 6.4 Hz, 1H), 1.27 (s, 6H), 1.24 (s, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 171.6, 148.0,

141.5, 138.3, 136.2, 134.7, 129.0, 128.2, 127.9, 127.4, 125.8, 121.5, 121.2, 116.4, 83.3, 38.4, 36.0, 24.8, 24.7; **HRMS** (ESI-TOF) Calcd for $C_{25}H_{30}BN_2O_3$ [M+H] 416.2386, found 416.2382.



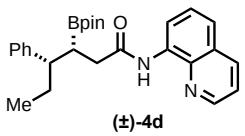
(±)-4b

4-phenyl-*N*-(quinolin-8-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide ((±)-4b): The title compound was prepared from **1b** (22.6 mg, 0.1 mmol), phenyl triflate (24.4 μL, 0.15 mmol), and bis(pinacolato)diboron (50.8 mg, 0.2 mmol) with *t*-AmylOH (0.4 mL) according to the general carboboration procedure. Purification using silica gel chromatography with 10:1 to 5:1 hexanes:EtOAc as the eluent gave the product as a colorless oil (42.6 mg, 99% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.74 (s, 1H), 9.02–8.53 (m, 2H), 8.14 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.62–7.40 (m, 3H), 7.34–7.22 (m, 4H), 7.20–7.10 (m, 1H), 2.99 (p, *J* = 7.1 Hz, 1H), 2.76–2.52 (m, 2H), 1.92 (ddd, *J* = 10.2, 7.7, 5.8 Hz, 1H), 1.38 (d, *J* = 7.1 Hz, 3H), 1.10 (s, 6H), 1.02 (s, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 171.9, 148.0, 146.5, 138.3, 136.3, 134.7, 128.1, 127.9, 127.7, 127.5, 126.0, 121.5, 121.0, 116.4, 83.1, 40.7, 37.7, 24.8, 24.6, 20.7; **HRMS** (ESI-TOF) Calcd for $C_{26}H_{32}BN_2O_3$ [M+H] 430.2542, found 430.2535.



(±)-4c

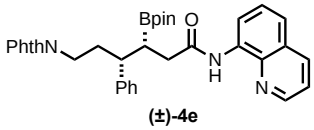
4-phenyl-*N*-(quinolin-8-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanamide ((±)-4c): The title compound was prepared from **1c** (24.0 mg, 0.1 mmol), phenyl triflate (24.4 μL, 0.15 mmol), and bis(pinacolato)diboron (50.8 mg, 0.2 mmol) with *t*-AmylOH (0.4 mL) according to the general carboboration procedure. Purification using silica gel chromatography with 10:1 to 5:1 hexanes:EtOAc as the eluent gave the product as a yellow solid (44.0 mg, 99% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.74 (s, 1H), 8.94–8.61 (m, 2H), 8.14 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.63–7.36 (m, 3H), 7.30–7.21 (m, 4H), 7.21–7.11 (m, 1H), 2.80–2.47 (m, 3H), 2.04–1.86 (m, 2H), 1.77–1.64 (m, 1H), 1.08 (s, 6H), 1.00 (s, 6H), 0.76 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 171.9, 148.0, 144.4, 138.3, 136.2, 134.7, 128.7, 128.0, 127.9, 127.4, 126.1, 121.5, 121.0, 116.4, 83.0, 49.0, 38.4, 27.8, 24.8, 24.6, 12.2; **HRMS** (ESI-TOF) Calcd for $C_{27}H_{34}BN_2O_3$ [M+H] 444.2699, found 444.2702.



(±)-4d

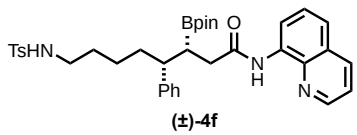
4-phenyl-*N*-(quinolin-8-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanamide ((±)-4d): The title compound was prepared from **1d** (24.0 mg, 0.1 mmol), phenyl triflate (24.4 μL, 0.15 mmol), and bis(pinacolato)diboron (50.8 mg, 0.2 mmol) with *t*-AmylOH (4 mL) according to the general carboboration procedure. Purification using silica gel chromatography with 10:1 to 5:1 hexanes:EtOAc as the eluent gave the product as a white solid (43.1 mg, 97% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.49 (s, 1H), 8.95–8.56 (m, 2H), 8.11 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.66–7.36 (m, 3H), 7.29 (dd, *J* = 17.2, 9.7 Hz, 2H), 7.24–7.08 (m, 3H), 2.59 (td, *J* = 11.0, 3.5 Hz, 1H), 2.49 (dd, *J* = 15.8, 11.2 Hz, 1H), 2.35 (dd, *J* = 15.8, 4.9 Hz, 1H), 1.96–1.84 (m, 1H), 1.80 (td, *J* = 11.1, 4.9 Hz, 1H), 1.69–1.61 (m, 1H), 1.30 (s, 6H), 1.27 (s, 6H), 0.70 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 171.9, 147.9, 144.7, 138.2, 136.2, 134.7, 128.3, 128.1, 127.8, 127.4, 126.1, 121.4, 120.9, 116.3, 83.2, 48.8,

38.9, 29.4, 25.0, 24.9, 12.2; **HRMS** (ESI-TOF) Calcd for $C_{27}H_{34}BN_2O_3$ [M+H] 444.2699, found 444.2699.



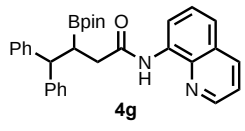
(±)-4e

6-(1,3-dioxoisoindolin-2-yl)-4-phenyl-*N*-(quinolin-8-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanamide ((±)-4e): The title compound was prepared from **1e** (38.5 mg, 0.1 mmol), phenyl triflate (24.4 μL, 0.15 mmol), and bis(pinacolato)diboron (50.8 mg, 0.2 mmol) according to the general carboboration procedure. Purification using silica gel chromatography with 3:1 to 2:1 hexanes:EtOAc as the eluent gave the product as a white solid (51.3 mg, 87% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.70 (s, 1H), 9.07–8.63 (m, 2H), 8.12 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.89–7.70 (m, 2H), 7.70–7.60 (m, 2H), 7.54–7.37 (m, 3H), 7.35–7.28 (m, 2H), 7.28–7.20 (m, 2H), 7.16–7.05 (m, 1H), 3.68–3.40 (m, 2H), 2.88 (q, *J* = 7.4 Hz, 1H), 2.72–2.50 (m, 2H), 2.38–2.15 (m, 2H), 1.95 (q, *J* = 7.8 Hz, 1H), 1.11 (s, 6H), 1.03 (s, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 171.5, 168.2, 147.9, 142.8, 138.2, 136.2, 134.6, 133.6, 132.1, 128.4, 128.2, 127.8, 127.4, 126.4, 122.9, 121.4, 121.0, 116.3, 83.2, 44.9, 37.8, 36.9, 32.8, 24.8, 24.6; **HRMS** (ESI-TOF) Calcd for $C_{35}H_{37}BN_3O_5$ [M+H] 589.2863, found 589.2872.



(±)-4f

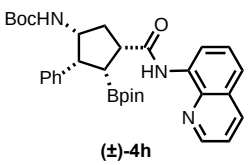
8-((4-methylphenyl) yridine ne)-4-phenyl-*N*-(quinolin-8-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octanamide ((±)-4f): The title compound was prepared from **1f** (43.8 mg, 0.1 mmol), phenyl triflate (24.4 μL, 0.15 mmol), and bis(pinacolato)diboron (50.8 mg, 0.2 mmol) according to the general carboboration procedure. Purification using silica gel chromatography with 1:1 hexanes:EtOAc as the eluent gave the product as a gray solid (62.8 mg, 98% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.73 (s, 1H), 9.22–8.52 (m, 2H), 8.29–7.97 (m, 1H), 7.70 (d, *J* = 8.1 Hz, 2H), 7.60–7.36 (m, 3H), 7.26 (dd, *J* = 11.3, 7.7 Hz, 4H), 7.18 (d, *J* = 7.3 Hz, 3H), 4.42 (t, *J* = 6.1 Hz, 1H), 2.85 (q, *J* = 6.8 Hz, 2H), 2.71–2.55 (m, 3H), 2.40 (s, 3H), 1.93 (q, *J* = 7.9 Hz, 1H), 1.86–1.72 (m, 1H), 1.70–1.53 (m, 1H), 1.40 (dddd, *J* = 22.2, 14.6, 10.7, 4.5 Hz, 2H), 1.08 (s, 6H), 1.01 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.7, 148.0, 144.2, 143.2, 138.3, 137.0, 136.3, 134.6, 129.6, 128.4, 128.1, 127.9, 127.4, 127.0, 126.3, 121.5, 121.1, 116.4, 83.1, 46.9, 43.0, 38.3, 34.3, 29.4, 24.8, 24.6, 24.5, 21.5; **HRMS** (ESI-TOF) Calcd for $C_{36}H_{45}BN_3O_5S$ [M+H] 641.3209, found 641.3212.



4g

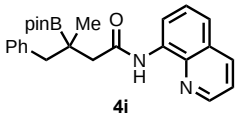
4,4-diphenyl-*N*-(quinolin-8-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanamide (4g): The title compound was prepared from **1g** (28.8 mg, 0.1 mmol), phenyl triflate (24.4 μL, 0.15 mmol), and bis(pinacolato)diboron (50.8 mg, 0.2 mmol) according to the general carboboration procedure. Purification using silica gel chromatography with 5:1 hexanes:EtOAc as the eluent gave the product as a white solid (47.3 mg, 96% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.58 (s, 1H), 9.10–8.47 (m, 2H), 8.12 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.60–7.33 (m, 7H), 7.31–7.20 (m, 4H), 7.20–7.07 (m, 2H), 3.98 (d, *J* = 12.1 Hz, 1H), 2.85–2.36 (m, 3H), 1.00 (s, 6H), 0.92 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.4, 147.9, 144.7,

144.4, 138.2, 136.2, 134.6, 128.7, 128.2, 128.2, 127.8, 127.6, 127.4, 126.3, 121.4, 121.1, 116.4, 83.1, 53.6, 39.6, 24.5, 24.5; **HRMS** (ESI-TOF) Calcd for $C_{31}H_{34}BN_2O_3$ [M+H] 492.2699, found 492.2698.



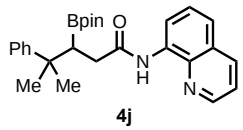
(±)-4h
dr = 16:1

***tert*-butyl (2-phenyl-4-(quinolin-8-ylcarbamoyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentyl)carbamate ((±)-4h):** The title compound was prepared from **1h** (17.7 mg, 0.05 mmol), phenyl triflate (24.4 μL, 0.15 mmol), and bis(pinacolato)diboron (38.1 mg, 0.15 mmol) according to the general carboboration procedure. $Pd_2(dba)_3$ (2.3 mg, 5 mol%), Cy-JohnPhos (1.8 mg, 10 mol%), and *i*-Pr_2Net (26.1 μL, 0.15 mmol) were used in this experiment. The reaction mixture was heated at 100 ºC. Purification using silica gel chromatography with 3:1 hexanes:EtOAc as the eluent gave the product as a white solid (25.6 mg, 92% yield). This product was isolated as an inseparable 16:1 mixture of diastereomers. The reported *dr* was determined by ^{1}H NMR analysis of purified **4h** and is consistent with that of the crude reaction mixture. The following analytical data correspond to the major diastereomer. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.86 (s, 1H), 9.02–8.55 (m, 2H), 8.16 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.58–7.44 (m, 3H), 7.43–7.37 (m, 2H), 7.30–7.23 (m, 1H), 7.16 (t, *J* = 7.3 Hz, 1H), 6.74 (d, *J* = 10.5 Hz, 1H), 4.80 (dtd, *J* = 11.0, 7.8, 3.7 Hz, 1H), 3.62 (t, *J* = 7.4 Hz, 1H), 3.35 (td, *J* = 9.9, 7.9 Hz, 1H), 2.90 (ddd, *J* = 14.0, 10.1, 8.3 Hz, 1H), 2.50 (t, *J* = 7.7 Hz, 1H), 2.21 (ddd, *J* = 13.9, 9.9, 3.8 Hz, 1H), 1.31 (s, 9H), 1.19 (s, 6H), 1.11 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 173.2, 155.8, 148.2, 139.6, 138.3, 136.3, 134.5, 128.7, 127.9, 127.7, 127.3, 125.8, 121.6, 121.3, 116.4, 83.7, 78.0, 51.5, 51.4, 49.7, 38.0, 28.4, 25.0, 24.9; **HRMS** (ESI-TOF) Calcd for $C_{32}H_{41}BN_3O_5$ [M+H] 557.3176, found 557.3167.



4i

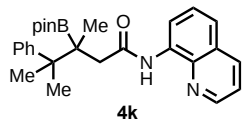
3-methyl-4-phenyl-*N*-(quinolin-8-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanamide (4i): The title compound was prepared from **1i** (11.3 mg, 0.05 mmol), phenyl triflate (12.2 μL, 0.075 mmol), and bis(pinacolato)diboron (25.4 mg, 0.1 mmol) with $Pd_2(dba)_3$ (1.4 mg, 3 mol%), Cy-JohnPhos (1.1 mg, 6 mol%), *i*-Pr_2Net (17.4 μL, 0.1 mmol), and *t*-AmylOH (0.1 mL) according to the general carboboration procedure. Purification using silica gel chromatography with 5:1 hexanes:EtOAc as the eluent gave the product as a white solid (21.3 mg, 99% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.68 (s, 1H), 9.09–8.51 (m, 2H), 8.14 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.63–7.35 (m, 3H), 7.31–7.16 (m, 5H), 2.99–2.76 (m, 2H), 2.73–2.35 (m, 2H), 1.31 (s, 6H), 1.29 (s, 6H), 1.06 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 171.2, 148.0, 138.8, 138.3, 136.3, 134.6, 130.7, 127.9, 127.7, 127.4, 125.8, 121.5, 121.1, 116.5, 83.3, 45.9, 42.8, 24.9, 24.9, 21.1; **HRMS** (ESI-TOF) Calcd for $C_{26}H_{32}BN_2O_3$ [M+H] 430.2542, found 430.2547.



4j

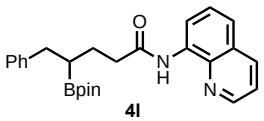
4-methyl-4-phenyl-*N*-(quinolin-8-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (4j): The title compound was prepared from **1j** (12.0 mg, 0.05 mmol), phenyl triflate (16.3 μL, 0.1 mmol), and bis(pinacolato)diboron (38.1 mg, 0.15 mmol) with $Pd_2(dba)_3$ (2.1 mg, 4.5 mol%), Cy-JohnPhos (1.7 mg, 9 mol%), *i*-Pr_2Net (26.1 μL, 0.15 mmol), and *t*-AmylOH

(0.15 mL) according to the general carboboration procedure. Purification using preparative TLC (10:1 hexanes:EtOAc) gave the product as a white solid (20.4 mg, 92% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.54 (s, 1H), 8.99–8.26 (m, 2H), 8.11 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.54–7.37 (m, 5H), 7.32 (t, *J* = 7.7 Hz, 2H), 7.17 (t, *J* = 7.3 Hz, 1H), 2.66 (dd, *J* = 15.4, 12.5 Hz, 1H), 2.18 (dd, *J* = 15.4, 3.9 Hz, 1H), 2.07 (dd, *J* = 12.5, 3.9 Hz, 1H), 1.44 (d, *J* = 3.2 Hz, 6H), 1.26 (s, 6H), 1.19 (s, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 172.2, 149.8, 147.9, 138.2, 136.2, 134.8, 128.1, 127.8, 127.4, 125.9, 125.6, 121.4, 120.8, 116.1, 83.2, 38.7, 36.4, 31.4, 25.0, 24.7; **HRMS** (ESI-TOF) Calcd for $C_{27}H_{34}BN_2O_3$ [M+H] 444.2699, found 444.2694.



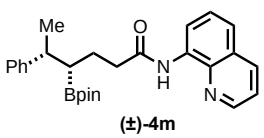
4k

3,4-dimethyl-4-phenyl-*N*-(quinolin-8-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (4k): The title compound was prepared from **1k** (12.7 mg, 0.05 mmol), phenyl triflate (16.3 μL, 0.1 mmol), and bis(pinacolato)diboron (38.1 mg, 0.15 mmol) with $Pd_2(dba)_3$ (2.1 mg, 4.5 mol%), Cy-JohnPhos (1.7 mg, 9 mol%), *i*-Pr_2Net (26.1 μL, 0.15 mmol), *t*-AmylOH (0.15 mL) according to the general carboboration procedure. Purification using preparative TLC (10:1 hexanes:EtOAc) gave the product as a white solid (14.0 mg, 61% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.55 (s, 1H), 8.82–8.66 (m, 2H), 8.12 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.53–7.37 (m, 5H), 7.34 (t, *J* = 7.8 Hz, 2H), 7.25–7.16 (m, 1H), 3.17 (d, *J* = 15.1 Hz, 1H), 2.05 (d, *J* = 15.1 Hz, 1H), 1.54 (s, 3H), 1.49 (s, 3H), 1.36 (s, 6H), 1.30 (s, 6H), 0.99 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 171.8, 147.9, 146.6, 138.2, 136.3, 134.8, 128.3, 127.9, 127.4, 127.2, 125.6, 121.4, 120.9, 116.3, 83.3, 43.8, 41.9, 26.6, 26.0, 25.4, 25.3, 18.4; **HRMS** (ESI-TOF) Calcd for $C_{28}H_{36}BN_2O_3$ [M+H] 458.2855, found 458.2853.



4l

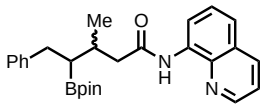
5-phenyl-*N*-(quinolin-8-yl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (4l): The title compound was prepared from **1l** (22.6 mg, 0.1 mmol), phenyl triflate (24.4 μL, 0.15 mmol), and bis(pinacolato)diboron (50.8 mg, 0.2 mmol) with *t*-AmylOH (0.4 mL) according to the general carboboration procedure. Purification using silica gel chromatography with 10:1 to 5:1 hexanes:EtOAc as the eluent gave the product as a colorless oil (42.2 mg, 98% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.00–9.46 (m, 1H), 9.03–8.57 (m, 2H), 8.18 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.67–7.39 (m, 3H), 7.28–7.22 (m, 4H), 7.16 (ddd, *J* = 8.7, 5.0, 3.9 Hz, 1H), 2.92–2.73 (m, 2H), 2.72–2.48 (m, 2H), 1.98 (dtd, *J* = 8.9, 6.8, 2.1 Hz, 2H), 1.52 (p, *J* = 7.9 Hz, 1H), 1.23 (s, 6H), 1.21 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.7, 148.0, 141.8, 138.4, 136.3, 134.6, 128.9, 128.1, 127.9, 127.4, 125.7, 121.5, 121.2, 116.4, 83.2, 37.8, 37.1, 27.0, 24.8, 24.8; **HRMS** (ESI-TOF) Calcd for $C_{26}H_{32}BN_2O_3$ [M+H] 430.2542, found 430.2542.



(±)-4m

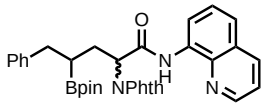
5-phenyl-*N*-(quinolin-8-yl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanamide ((±)-4m): The title compound was prepared from **1m** (24.0 mg, 0.1 mmol), phenyl triflate (24.4 μL, 0.15 mmol), and bis(pinacolato)diboron (50.8 mg, 0.2 mmol) with *t*-AmylOH (0.4 mL) according to the general carboboration procedure. Purification using silica gel chromatography with 10:1 to 5:1 hexanes:EtOAc as the eluent gave the product as a

colorless oil (37.8 mg, 85% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.71 (s, 1H), 9.06–8.61 (m, 2H), 8.14 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.74–7.36 (m, 3H), 7.29–7.23 (m, 2H), 7.22–7.19 (m, 2H), 7.17–7.12 (m, 1H), 2.85 (dq, *J* = 10.5, 6.9 Hz, 1H), 2.50 (ddd, *J* = 14.6, 10.1, 5.7 Hz, 1H), 2.38 (ddd, *J* = 14.6, 9.9, 6.9 Hz, 1H), 1.80–1.65 (m, 2H), 1.42–1.35 (m, 1H), 1.34–1.31 (m, 12H), 1.29 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 171.6, 147.9, 147.0, 138.4, 136.3, 134.6, 128.4, 127.9, 127.4, 127.3, 125.9, 121.5, 121.2, 116.3, 83.4, 41.4, 37.8, 26.0, 25.0, 25.0, 22.7; **HRMS** (ESI-TOF) Calcd for $C_{27}H_{34}BN_2O_3$ [M+H] 444.2699, found 444.2701.



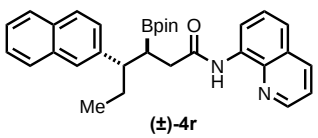
4n
dr = 1.2:1

3-methyl-5-phenyl-*N*-(quinolin-8-yl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (4n): The title compound was prepared from **1n** (24.0 mg, 0.1 mmol), phenyl triflate (24.4 μL, 0.15 mmol), and bis(pinacolato)diboron (50.8 mg, 0.2 mmol) according to the general carboboration procedure. Purification using silica gel chromatography with 10:1 to 5:1 hexanes:EtOAc as the eluent gave the product as a yellow oil (44.0 mg, 99% yield). This product was isolated as an inseparable 1.2:1 mixture of diastereomers. The reported *dr* was determined by ^{1}H NMR analysis of purified **4n** and is consistent with that of the crude reaction mixture. The following analytical data correspond to the mixture. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.16–9.61 (m, 1H), 9.10–8.51 (m, 2H), 8.16 (ddd, *J* = 8.3, 4.8, 1.7 Hz, 1H), 7.68–7.35 (m, 3H), 7.26–7.17 (m, 4H), 7.17–7.08 (m, 1H), 2.96–2.68 (m, 3H), 2.57–2.30 (m, 2H), 1.60–1.47 (m, 1H), 1.24–1.03 (m, 15H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 171.5, 171.5, 148.0, 148.0, 142.1, 142.0, 138.5, 138.4, 136.3, 136.3, 134.7, 134.7, 129.0, 128.9, 128.1, 128.0, 128.0, 127.9, 127.4, 125.6, 125.6, 121.5, 121.5, 121.3, 116.5, 116.4, 83.2, 45.6, 44.2, 35.4, 34.6, 32.8, 32.6, 24.9, 24.9, 24.8, 24.8, 19.8, 18.5; **HRMS** (ESI-TOF) Calcd for $C_{27}H_{34}BN_2O_3$ [M+H] 444.2699, found 444.2697.



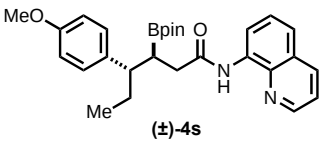
4o
dr = 2:1

2-(1,3-dioxoisoindolin-2-yl)-5-phenyl-*N*-(quinolin-8-yl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (4o): The title compound was prepared from **1o** (37.1 mg, 0.1 mmol), phenyl triflate (24.4 μL, 0.15 mmol), and bis(pinacolato)diboron (50.8 mg, 0.2 mmol) according to the general carboboration procedure. Purification using silica gel chromatography with 3:1 to 1:1 hexanes:EtOAc as the eluent gave the product as a brown solid (57.0 mg, 99% yield). This product was isolated as an inseparable 2:1 mixture of diastereomers. The reported *dr* was determined by ^{1}H NMR analysis of purified **4o** and is consistent with that of the crude reaction mixture. The following analytical data correspond to the mixture. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.53–10.06 (m, 1H), 8.93–8.45 (m, 2H), 8.21–8.03 (m, 1H), 7.93–7.81 (m, 2H), 7.77–7.67 (m, 2H), 7.54–7.38 (m, 3H), 7.30–7.07 (m, 5H), 5.39–5.16 (m, 1H), 3.22–2.36 (m, 4H), 1.63–1.38 (m, 1H), 1.28–0.90 (m, 12H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 168.1, 168.0, 167.3, 167.1, 148.2, 148.2, 141.1, 140.9, 138.5, 136.2, 134.1, 134.0, 134.0, 132.0, 132.0, 129.0, 128.9, 128.2, 128.1, 127.8, 127.2, 125.9, 125.8, 123.5, 123.4, 121.8, 121.7, 121.5, 116.7, 116.6, 83.6, 83.4, 55.1, 54.5, 37.4, 36.4, 30.2, 29.7, 25.1, 24.7, 24.6; **HRMS** (ESI-TOF) Calcd for $C_{34}H_{35}BN_3O_5$ [M+H] 575.2706, found 575.2708.



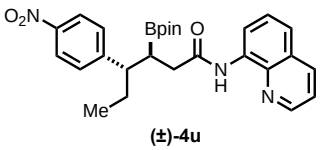
(±)-4r

4-(yridine ne-2-yl)-*N*-(quinolin-8-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanamide ((±)-4r): The title compound was prepared from **1c** (24.0 mg, 0.1 mmol), yridine ne-2-yl trifluoromethanesulfonate (41.4 mg, 0.15 mmol), and bis(pinacolato)diboron (50.8 mg, 0.2 mmol) according to the general carboboration procedure. Purification using silica gel chromatography with 10:1 to 5:1 hexanes:EtOAc as the eluent gave the product as a white solid (48.4 mg, 98% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.74 (s, 1H), 8.97–8.63 (m, 2H), 8.11 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.84–7.64 (m, 4H), 7.55–7.36 (m, 6H), 2.84 (ddd, *J* = 10.3, 7.7, 4.2 Hz, 1H), 2.76–2.62 (m, 2H), 2.09 (q, *J* = 7.9 Hz, 1H), 2.05–1.94 (m, 1H), 1.91–1.79 (m, 1H), 1.05 (s, 6H), 0.96 (s, 6H), 0.79 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 171.9, 147.9, 141.9, 138.3, 136.2, 134.7, 133.4, 132.3, 127.8, 127.6, 127.6, 127.4, 127.4, 127.2, 127.0, 125.6, 125.0, 121.4, 121.0, 116.3, 83.0, 49.1, 38.4, 27.6, 24.7, 24.6, 12.3; **HRMS** (ESI-TOF) Calcd for $C_{31}H_{36}BN_2O_3$ [M+H] 494.2855, found 494.2859.



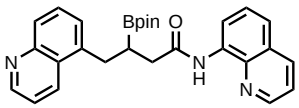
(±)-4s

4-(4-methoxyphenyl)-*N*-(quinolin-8-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanamide ((±)-4s): The title compound was prepared from **1c** (24.0 mg, 0.1 mmol), 4-methoxyphenyl trifluoromethanesulfonate (27 μL, 0.15 mmol), and bis(pinacolato)diboron (50.8 mg, 0.2 mmol) according to the general carboboration procedure. Purification using silica gel chromatography with 5:1 hexanes:EtOAc as the eluent gave the product as a white solid (46.9 mg, 99% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.74 (s, 1H), 9.14–8.57 (m, 2H), 8.14 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.61–7.32 (m, 3H), 7.21–7.03 (m, 2H), 6.92–6.54 (m, 2H), 3.78 (s, 3H), 2.98–2.44 (m, 3H), 2.08–1.83 (m, 2H), 1.67 (tdd, *J* = 14.3, 11.2, 8.1 Hz, 1H), 1.09 (s, 6H), 1.03 (s, 6H), 0.75 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 172.0, 158.0, 147.9, 138.3, 136.5, 136.2, 134.7, 129.5, 127.9, 127.4, 121.4, 121.0, 116.3, 113.4, 83.0, 55.2, 48.1, 38.4, 27.9, 24.8, 24.6, 12.2; **HRMS** (ESI-TOF) Calcd for $C_{28}H_{36}BN_2O_4$ [M+H] 474.2804, found 474.2799.



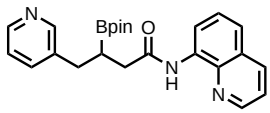
(±)-4u

4-(4-nitrophenyl)-*N*-(quinolin-8-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanamide ((±)-4u): The title compound was prepared from **1c** (24.0 mg, 0.1 mmol), 4-nitrophenyl trifluoromethanesulfonate (40.7 mg, 0.15 mmol), and bis(pinacolato)diboron (50.8 mg, 0.2 mmol) with *t*-AmylOH (0.4 mL) according to the general carboboration procedurePurification using silica gel chromatography with 3:1 to 2:1 hexanes:EtOAc as the eluent gave the product as a white solid (47.9 mg, 98% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.73 (s, 1H), 8.99–8.53 (m, 2H), 8.33–7.94 (m, 3H), 7.56–7.35 (m, 5H), 2.82 (ddd, *J* = 10.2, 8.1, 4.3 Hz, 1H), 2.76–2.62 (m, 2H), 2.11–1.91 (m, 2H), 1.73 (ddq, *J* = 14.4, 10.3, 7.3 Hz, 1H), 1.10 (s, 6H), 1.03 (s, 6H), 0.75 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 171.3, 152.8, 148.1, 146.5, 138.2, 136.3, 134.5, 129.5, 127.9, 127.4, 123.3, 121.6, 121.3, 116.4, 83.3, 48.7, 38.0, 27.6, 24.8, 24.6, 12.0; **HRMS** (ESI-TOF) Calcd for $C_{27}H_{33}BN_3O_5$ [M+H] 489.2550, found 489.2546; **X-ray** (single-crystal) Colorless block crystals of X-ray diffraction quality were obtained by vapor diffusion of pentane into a saturated solution of **(±)-4u** in CH_2Cl_2 (CCDC 1939487).[15]



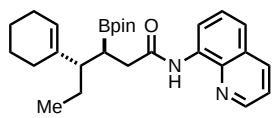
4v

4-(quinolin-5-yl)-*N*-(quinolin-8-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanamide (4v): The title compound was prepared from **1a** (21.2 mg, 0.1 mmol), quinolin-5-yl trifluoromethanesulfonate (27.3 μL, 0.15 mmol), and bis(pinacolato)diboron (50.8 mg, 0.2 mmol) according to the general carboboration procedure. Purification using silica gel chromatography with 2:1 hexanes:EtOAc as the eluent gave the product as a yellow solid (32.7 mg, 70% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.67 (s, 1H), 8.88–8.70 (m, 3H), 8.51 (d, *J* = 8.5 Hz, 1H), 8.14 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 1H), 7.59 (dd, *J* = 8.5, 7.0 Hz, 1H), 7.56–7.39 (m, 4H), 7.33 (dd, *J* = 8.5, 4.2 Hz, 1H), 3.51–3.06 (m, 2H), 2.74–2.58 (m, 2H), 1.94 (dq, *J* = 9.1, 6.9 Hz, 1H), 1.24 (s, 6H), 1.21 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.2, 149.8, 148.8, 148.0, 138.3, 138.2, 136.3, 134.5, 132.7, 128.8, 128.0, 127.9, 127.4, 127.2, 127.2, 121.5, 121.2, 120.7, 116.4, 83.4, 38.6, 32.3, 24.8; **HRMS** (ESI-TOF) Calcd for $C_{28}H_{30}BN_3O_3$ [M+H] 467.2495, found 467.2487.



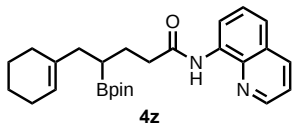
4w

4-(yridine-3-yl)-*N*-(quinolin-8-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanamide (4w): The title compound was prepared from **1a** (21.2 mg, 0.1 mmol), yridine-3-yl trifluoromethanesulfonate (24.1 μL, 0.15 mmol), and bis(pinacolato)diboron (50.8 mg, 0.2 mmol) according to the general carboboration procedure. Purification using silica gel chromatography with 1:1 hexanes:EtOAc as the eluent gave the product as a yellow oil (25.9 mg, 62% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.73 (s, 1H), 8.82–8.66 (m, 2H), 8.51 (d, *J* = 2.2 Hz, 1H), 8.43 (dd, *J* = 4.8, 1.6 Hz, 1H), 8.15 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.59 (dt, *J* = 7.8, 2.0 Hz, 1H), 7.56–7.46 (m, 2H), 7.44 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.19 (dd, *J* = 7.8, 4.8 Hz, 1H), 3.06–2.72 (m, 2H), 2.72–2.56 (m, 2H), 1.83 (p, *J* = 7.4 Hz, 1H), 1.22 (s, 6H), 1.20 (s, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 171.1, 150.4, 148.1, 147.4, 138.3, 136.9, 136.4, 136.3, 134.5, 127.9, 127.4, 123.2, 121.5, 121.3, 116.4, 83.4, 38.4, 33.2, 24.7; **HRMS** (ESI-TOF) Calcd for $C_{24}H_{29}BN_3O_3$ [M+H] 417.2338, found 417.2338.



(±)-4y

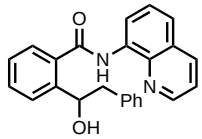
4-(cyclohex-1-en-1-yl)-*N*-(quinolin-8-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanamide ((±)-4y): The title compound was prepared from **1c** (24.0 mg, 0.1 mmol), cyclohex-1-en-1-yl trifluoromethanesulfonate (26.3 μL, 0.15 mmol), and bis(pinacolato)diboron (50.8 mg, 0.2 mmol) according to the general carboboration procedure. Purification using silica gel chromatography with 10:1 to 5:1 hexanes:EtOAc as the eluent gave the product as a yellow oil (38.6 mg, 86% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.76 (s, 1H), 8.93–8.54 (m, 2H), 8.14 (dt, *J* = 8.3, 1.5 Hz, 1H), 7.71–7.38 (m, 3H), 5.43 (td, *J* = 3.6, 1.8 Hz, 1H), 2.78–2.50 (m, 2H), 2.13–1.93 (m, 4H), 1.87 (s, 1H), 1.73–1.50 (m, 6H), 1.37 (ddq, *J* = 14.3, 10.8, 7.2 Hz, 1H), 1.21 (s, 6H), 1.17 (s, 6H), 0.79 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 172.4, 147.9, 139.0, 138.3, 136.2, 134.8, 127.9, 127.5, 123.1, 121.4, 120.9, 116.3, 82.9, 50.7, 38.4, 25.3, 25.0, 25.0, 24.7, 24.1, 22.9, 22.8, 12.1; **HRMS** (ESI-TOF) Calcd for $C_{27}H_{38}BN_2O_3$ [M+H] 448.3012, found 448.3007.



4z

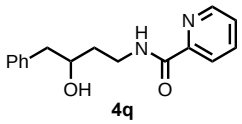
5-(cyclohex-1-en-1-yl)-*N*-(quinolin-8-yl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (4z): The title compound was prepared from **1l** (22.6 mg, 0.1 mmol), cyclohex-1-en-1-yl trifluoromethanesulfonate (26.3 μL, 0.15 mmol), and bis(pinacolato)diboron (50.8 mg, 0.2 mmol) according to the general carboboration procedure. Purification using silica gel chromatography with 10:1 to 5:1 hexanes:EtOAc as the eluent gave the product as a yellow oil (40.0 mg, 92% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.83 (s, 1H), 9.06–8.63 (m, 2H), 8.15 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.69–7.36 (m, 3H), 5.45 (dt, *J* = 3.9, 2.2 Hz, 1H), 2.69–2.46 (m, 2H), 2.21–2.02 (m, 2H), 2.02–1.76 (m, 6H), 1.62–1.47 (m, 4H), 1.40–1.28 (m, 1H), 1.26 (s, 12H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 172.0, 148.0, 138.4, 137.1, 136.3, 134.7, 127.9, 127.5, 121.8, 121.5, 121.2, 116.4, 83.1, 39.6, 37.9, 28.2, 27.1, 25.2, 24.9, 24.9, 23.0, 22.6; **HRMS** (ESI-TOF) Calcd for $C_{26}H_{36}BN_2O_3$ [M+H] 434.2855, found 434.2852.

General Procedure for Boronate Oxidation:[1] The alkene substrate was carboborylated according to the general procedure and was filtered and concentrated to obtain the crude boronate ester product. The crude boronate ester, $NaBO_3$•$4H_2O$ (77 mg, 0.5 mmol), THF (0.5 mL), and H_2O (0.5 mL) were added to a 10-mL round-bottom flask containing a Teflon-coated magnetic stir bar. The reaction mixture was stirred at room temperature for at least 3 h until the boronate ester was completely consumed. The aqueous layer was then washed with Et_2O (2 × 5 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified by preparative TLC to afford the pure product.



4p

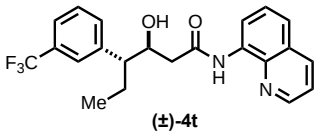
2-(1-hydroxy-2-phenylethyl)-*N*-(quinolin-8-yl)benzamide (4p): The title compound was prepared from **1p** (27.4 mg, 0.1 mmol), phenyl triflate (32.5 μL, 0.2 mmol), and bis(pinacolato)diboron (76.2 mg, 0.3 mmol) with $Pd_2(dba)_3$ (4.2 mg, 4.5 mol%), Cy-JohnPhos (3.3 mg, 9 mol%), *i*-Pr_2Net (52.2 μL, 0.15 mmol), and *t*-AmylOH (0.3 mL) according to the general carboboration/oxidation procedure. Purification by preparative TLC (3:1 hexanes:EtOAc) gave the product as a colorless oil (25.8 mg, 70% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.42 (s, 1H), 8.94 (dd, *J* = 7.4, 1.6 Hz, 1H), 8.77 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.23 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.80 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.72–7.59 (m, 3H), 7.56 (td, *J* = 7.6, 1.4 Hz, 1H), 7.52–7.43 (m, 2H), 7.28–7.22 (m, 4H), 7.18–7.13 (m, 1H), 5.31 (dt, *J* = 8.7, 4.0 Hz, 1H), 4.33–4.01 (m, 1H), 3.24 (qd, *J* = 13.6, 6.9 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 168.6, 148.4, 143.1, 138.7, 138.7, 136.5, 135.4, 134.4, 131.1, 129.5, 128.3, 128.0, 127.9, 127.8, 127.6, 127.4, 126.3, 122.3, 121.7, 117.1, 73.3, 43.8; **HRMS** (ESI-TOF) Calcd for $C_{24}H_{21}N_2O_2$ [M+H] 369.1603, found 369.1597.



4q

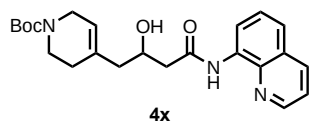
***N*-(3-hydroxy-4-phenylbutyl)picolinamide (4q):** The title compound was prepared from **1q** (17.6 mg, 0.1 mmol), phenyl triflate (24.4 μL, 0.15 mmol), and bis(pinacolato)diboron (50.8 mg, 0.2 mmol) with *t*-AmylOH (0.4 mL) according to the general carboboration/oxidation procedure. Purification by preparative TLC (1:1 hexanes:EtOAc) gave the product as a yellow solid (14.6 mg, 54% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.56 (ddd, *J* = 4.8, 1.7, 0.9

Hz, 1H), 8.36 (s, 1H), 8.20 (dt, *J* = 7.8, 1.1 Hz, 1H), 7.87 (td, *J* = 7.7, 1.7 Hz, 1H), 7.44 (ddd, *J* = 7.6, 4.8, 1.3 Hz, 1H), 7.35–7.27 (m, 2H), 7.26–7.16 (m, 3H), 4.06–3.81 (m, 2H), 3.44 (dq, *J* = 14.0, 5.3 Hz, 1H), 3.33 (d, *J* = 3.5 Hz, 1H), 2.93–2.65 (m, 2H), 1.93–1.79 (m, 1H), 1.78–1.66 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.2, 149.6, 148.1, 138.5, 137.4, 129.5, 128.4, 126.4, 126.2, 122.3, 69.8, 43.8, 36.8, 36.4; **HRMS** (ESI-TOF) Calcd for $C_{16}H_{19}N_2O_2$ [M+H] 271.1447, found 271.1447.



(±)-4t

3-hydroxy-*N*-(quinolin-8-yl)-4-(3-(trifluoromethyl)phenyl)hexanamide ((±)-4t): The title compound was prepared from **1c** (24.0 mg, 0.1 mmol), 3-(trifluoromethyl)phenyl trifluoromethanesulfonate (40 μL, 0.2 mmol), and bis(pinacolato)diboron (76.2 mg, 0.3 mmol) with *t*-AmylOH (0.6 mL) according to the general carboboration/oxidation procedure. Purification by preparative TLC (3:1 hexanes:EtOAc) gave the product as a white solid (33.4 mg, 83% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.90 (s, 1H), 8.78 (dd, *J* = 4.3, 1.7 Hz, 1H), 8.70 (dd, *J* = 5.9, 3.1 Hz, 1H), 8.15 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.68–7.39 (m, 7H), 4.48 (ddd, *J* = 9.8, 5.1, 2.4 Hz, 1H), 3.57 (s, 1H), 2.74–2.60 (m, 2H), 2.49 (dd, *J* = 15.5, 9.7 Hz, 1H), 2.06–1.90 (m, 1H), 1.89–1.75 (m, 1H), 0.84 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.9, 148.2, 142.3, 138.3, 136.4, 134.0, 132.7, 130.5 (q, *J* = 32.1 Hz), 128.7, 127.9, 127.3, 125.9 (q, *J* = 4.0 Hz), 124.3 (q, *J* = 273.4 Hz), 123.6 (q, *J* = 3.7 Hz), 121.9, 121.6, 116.9, 70.9, 53.2, 42.4, 25.2, 12.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ –62.6; **HRMS** (ESI-TOF) Calcd for $C_{22}H_{22}F_3N_2O_2$ [M+H] 403.1633, found 403.1637.

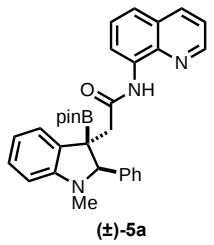


4x

***tert*-butyl 4-(2-hydroxy-4-oxo-4-(quinolin-8-ylamino)butyl)-3,6-dihydropyridine-1(2*H*)-carboxylate (4x):** The title compound was prepared from **1a** (21.2 mg, 0.1 mmol), *tert*-butyl 4-(((trifluoromethyl)sulfonyl)oxy)-3,6-dihydropyridine-1(2*H*)-carboxylate (49.7 mg, 0.15 mmol), and bis(pinacolato)diboron (50.8 mg, 0.2 mmol) according to the general carboboration/oxidation procedure. Purification by preparative TLC (1:1 hexanes:EtOAc) gave the product as a yellow solid (25.1 mg, 61% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.02 (s, 1H), 8.81 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.74 (dd, *J* = 6.4, 2.6 Hz, 1H), 8.16 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.63–7.38 (m, 3H), 5.53 (s, 1H), 4.33 (d, *J* = 8.1 Hz, 1H), 3.90 (s, 2H), 3.65–3.33 (m, 3H), 2.94–2.52 (m, 2H), 2.47–2.04 (m, 4H), 1.47 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.8, 148.3, 138.4, 136.4, 134.1, 128.0, 127.3, 121.9, 121.7, 116.8, 79.5, 66.5, 44.8, 43.6, 28.6, 28.5; **HRMS** (ESI-TOF) Calcd for $C_{23}H_{30}N_3O_4$ [M+H] 412.2236, found 412.2237.

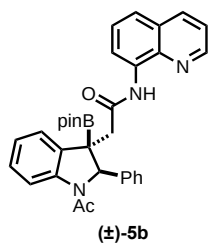
General Procedure for Dearomative Aryl- and Alkenylboration of Heterocycles

General Procedure: To a 4-mL scintillation vial equipped with a Teflon-coated magnetic stir bar were added the heterocycle substrate (0.05 mmol), bis(pinacolato)diboron (38.1 mg, 0.15 mmol), $Pd_2(dba)_3$ (2.3 mg, 5 mol%), Cy-JohnPhos (1.8 mg, 10 mol%), and 4 Å molecular sieves (~30 mg). The vial was sealed with a screw-top septum cap and was then evacuated and backfilled with N_2 (×3). Under positive N_2 pressure, aryl or alkenyl triflate (0.15 mmol), *i*-Pr_2Net (26.1 μL, 0.15 mmol) and *t*-AmylOH (0.2 mL) were added. All needle inlets/outlets were removed, and the reaction was placed in a heating block that was pre-heated to 100 °C. (*To prevent solvent evaporation through the punctures in the septum, at this stage we typically switch the old cap for new cap under a flow of N_2 gas.*) After 40–44 hours, the black reaction mixture was allowed to cool to room temperature and filtered through a short plug of celite (CH_2Cl_2 or EtOAc as eluent). The solvent was removed in *vacuo* to afford a dark brown residue. Upon purification by preparative TLC with 5:1 hexanes:EtOAc as the eluent, afforded the pure product.



(±)-5a

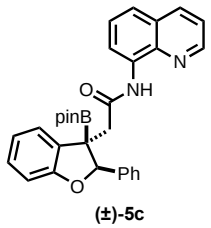
2-(1-methyl-2-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)indolin-3-yl)-*N*-(quinolin-8-yl)acetamide ((±)-5a): The title compound was prepared from **1t** (15.7 mg, 0.05 mmol), phenyl triflate (24.4 μL, 0.15 mmol), and bis(pinacolato)diboron (38.1 mg, 0.15 mmol) according to the general dearomative carboboration procedure. Purification by preparative TLC (5:1 hexanes:EtOAc) gave the product as a yellow oil (16.4 mg, 63% yield). (*Note: In this case, it was necessary to pre-treat the PTLC plate with Net_3 prior to loading on the crude product in order to prevent decomposition on silica gel.*) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.59 (s, 1H), 8.77 (dd, *J* = 7.6, 1.3 Hz, 1H), 8.70 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.11 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.56–7.48 (m, 1H), 7.45 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.39 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.36 (dd, *J* = 7.3, 1.2 Hz, 1H), 7.25–7.17 (m, 5H), 7.05 (td, *J* = 7.6, 1.3 Hz, 1H), 6.63 (td, *J* = 7.4, 1.0 Hz, 1H), 6.39 (d, *J* = 7.7 Hz, 1H), 4.50 (s, 1H), 3.31 (d, *J* = 15.1 Hz, 1H), 3.13 (d, *J* = 15.1 Hz, 1H), 2.59 (s, 3H), 0.94 (s, 6H), 0.92 (s, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 170.1, 151.8, 147.9, 139.3, 138.3, 136.1, 134.7, 133.9, 128.0, 127.8, 127.7, 127.5, 127.3, 126.0, 121.4, 121.0, 117.4, 116.4, 105.3, 83.4, 78.2, 47.4, 32.7, 24.8, 24.7; **HRMS** (ESI-TOF) Calcd for $C_{32}H_{35}BN_3O_3$ [M+H] 519.2808, found 519.2826.



(±)-5b

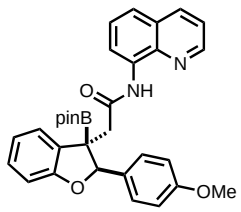
2-(1-acetyl-2-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)indolin-3-yl)-*N*-(quinolin-8-yl)acetamide ((±)-5b): The title compound was prepared from **1u** (34.3 mg, 0.1 mmol), phenyl triflate (48.8 μL, 0.3 mmol), and bis(pinacolato)diboron (76.2 mg, 0.3 mmol) according to the general dearomative carboboration procedure. Purification by preparative TLC (3:1 hexanes:EtOAc) gave the product as a light-yellow solid (36.1 mg, 66% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.50 (s, 1H), 8.81–8.69 (m, 2H), 8.24 (d, *J* = 8.1 Hz, 1H), 8.13 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.57–7.40 (m, 4H), 7.27–7.15 (m, 6H), 7.02 (t, *J* = 7.5 Hz, 1H), 5.21 (s, 1H), 3.36 (d, *J* = 14.7 Hz, 1H), 2.95 (d, *J* = 14.8 Hz, 1H), 2.09 (s, 3H), 1.07 (s, 6H), 0.89 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 169.4, 169.0, 148.0, 142.8, 139.7, 138.2, 136.2, 135.7, 134.3, 128.6, 128.3, 127.8,

127.3, 127.3, 124.2, 121.6, 121.4, 116.6, 116.3, 83.8, 49.4, 25.0, 24.8, 24.3; **HRMS** (ESI-TOF) Calcd for $C_{33}H_{35}BN_3O_4$ [M+H] 547.2753, found 547.2753.



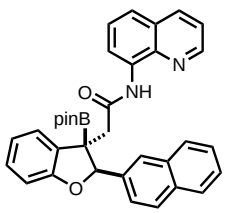
(±)-5c

2-(2-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3-dihydrobenzofuran-3-yl)-*N*-(quinolin-8-yl)acetamide ((±)-5c): The title compound was prepared from **1v** (15.1 mg, 0.05 mmol), phenyl triflate (24.4 μL, 0.15 mmol), and bis(pinacolato)diboron (38.1 mg, 0.15 mmol) according to the general dearomative carboboration procedure. Purification by preparative TLC (5:1 hexanes:EtOAc) gave the product as a white solid (21.8 mg, 86% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.58 (s, 1H), 8.82–8.64 (m, 2H), 8.12 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.61–7.36 (m, 4H), 7.31–7.28 (m, 2H), 7.25–7.21 (m, 3H), 7.11 (td, *J* = 7.7, 1.4 Hz, 1H), 6.97–6.74 (m, 2H), 5.56 (s, 1H), 3.43 (d, *J* = 15.1 Hz, 1H), 3.03 (d, *J* = 15.1 Hz, 1H), 0.98 (s, 6H), 0.90 (s, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.2, 159.7, 148.0, 140.1, 138.2, 136.2, 134.5, 132.6, 128.3, 128.1, 128.1, 127.9, 127.4, 127.3, 126.9, 121.5, 121.2, 120.9, 116.3, 108.8, 92.2, 83.7, 49.1, 24.8, 24.8; **HRMS** (ESI-TOF) Calcd for $C_{31}H_{32}BN_2O_4$ [M+H] 506.2491, found 506.2484.



(±)-5d

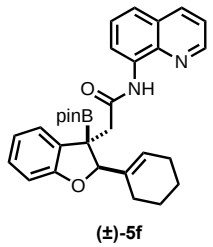
2-(2-(4-methoxyphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3-dihydrobenzofuran-3-yl)-*N*-(quinolin-8-yl)acetamide ((±)-5d): The title compound was prepared from **1v** (30.2 mg, 0.1 mmol), 4-methoxyphenyl trifluoromethanesulfonate (36 μL, 0.2 mmol), and bis(pinacolato)diboron (76.2 mg, 0.3 mmol) with $Pd_2(dba)_3$ (4.2 mg, 4.5 mol%), Cy-JohnPhos (3.3 mg, 9 mol%), *i*-Pr_2Net (52.2 μL, 0.15 mmol), and *t*-AmylOH (0.3 mL) according to the general dearomative carboboration procedure. Purification by preparative TLC (5:1 hexanes:EtOAc) gave the product as a white solid (39.1 mg, 73% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.56 (s, 1H), 8.82–8.65 (m, 2H), 8.12 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.57–7.38 (m, 4H), 7.24–7.18 (m, 2H), 7.10 (td, *J* = 7.7, 1.5 Hz, 1H), 6.89–6.62 (m, 4H), 5.51 (s, 1H), 3.75 (s, 3H), 3.41 (d, *J* = 15.1 Hz, 1H), 3.00 (d, *J* = 15.2 Hz, 1H), 1.00 (s, 6H), 0.95 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 169.3, 159.8, 159.6, 148.0, 138.2, 136.2, 134.5, 132.7, 132.6, 128.2, 128.0, 127.9, 127.4, 127.3, 121.5, 121.2, 120.8, 116.3, 113.5, 108.9, 92.0, 83.7, 55.4, 49.0, 24.9, 24.8; **HRMS** (ESI-TOF) Calcd for $C_{32}H_{34}BN_2O_5$ [M+H] 536.2597, found 536.2599.



(±)-5e

2-(2-(naphthalen-2-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3-dihydrobenzofuran-3-yl)-*N*-(quinolin-8-yl)acetamide ((±)-5e): The title compound was prepared from **1v** (30.2 mg, 0.1 mmol), yridine ne-2-yl trifluoromethanesulfonate (82.8 mg, 0.3 mmol), and bis(pinacolato)diboron (76.2 mg, 0.3 mmol) according to the general dearomative carboboration procedure. Purification by preparative TLC (5:1 hexanes:EtOAc) gave the product as a white solid (48.3 mg, 87% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.63 (s, 1H), 8.89–8.66 (m, 2H), 8.12 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.87–7.65 (m, 4H), 7.59–7.34 (m, 7H), 7.17 (td, *J* = 7.7, 1.4 Hz, 1H), 7.01–6.81 (m, 2H), 5.78 (s, 1H), 3.49 (d, *J* = 15.1 Hz, 1H), 3.11 (d, *J* = 15.1 Hz, 1H), 0.83 (s, 6H), 0.75 (s,

6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.2, 159.7, 148.0, 138.2, 137.6, 136.2, 134.5, 133.4, 133.0, 132.6, 128.1, 128.1, 127.9, 127.5, 127.3, 127.3, 125.9, 125.9, 125.8, 124.7, 121.5, 121.3, 121.0, 116.3, 108.9, 92.3, 83.6, 49.1, 24.7, 24.6; **HRMS** (ESI-TOF) Calcd for $C_{35}H_{34}BN_2O_4$ [M+H] 556.2648, found 556.2656.



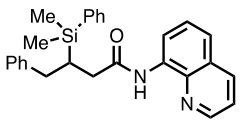
(±)-5f

2-(2-(cyclohex-1-en-1-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3-dihydrobenzofuran-3-yl)-*N*-(quinolin-8-yl)acetamide ((±)-5f): The title compound was prepared from **1v** (15.1 mg, 0.05 mmol), cyclohex-1-en-1-yl trifluoromethanesulfonate (26.3 μL, 0.15 mmol), and bis(pinacolato)diboron (38.1 mg, 0.15 mmol) according to the general dearomative carboboration procedure. Purification by preparative TLC (5:1 hexanes:EtOAc) gave the product as a colorless oil (18.4 mg, 72% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.55 (s, 1H), 8.90–8.58 (m, 2H), 8.13 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.64–7.36 (m, 4H), 7.07 (td, *J* = 7.7, 1.4 Hz, 1H), 6.86–6.67 (m, 2H), 5.79 (dq, *J* = 3.7, 1.8 Hz, 1H), 4.98 (s, 1H), 3.28 (d, *J* = 15.4 Hz, 1H), 2.93 (d, *J* = 15.4 Hz, 1H), 2.18–1.76 (m, 5H), 1.64–1.49 (m, 4H), 1.36 (s, 6H), 1.33 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 169.5, 159.5, 148.0, 138.2, 137.5, 136.2, 134.5, 133.5, 127.8, 127.3, 126.2, 125.5, 121.5, 121.1, 120.3, 116.3, 108.5, 95.6, 83.8, 48.9, 25.6, 25.0, 24.9, 23.5, 22.2, 22.0; **HRMS** (ESI-TOF) Calcd for $C_{31}H_{36}BN_2O_4$ [M+H] 510.2804, found 510.2795.

General Procedure for Aryl- and Alkenylsilylation of Alkenes

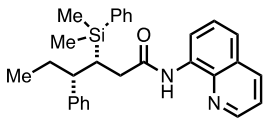
General Procedure: To a 4-mL scintillation vial equipped with a Teflon-coated magnetic stir bar were added the alkene substrate (0.1 mmol), dimethylphenylsilylpinacolatoboron (55.2 mg, 0.2 mmol), $Pd_2(dba)_3$ (4.6 mg, 5 mol%), Cy-JohnPhos (3.5 mg, 10 mol%), and 4 Å molecular sieves (~30 mg). The vial was sealed with a screw-top septum cap and was then evacuated and backfilled with N_2 (×3). Under positive N_2 pressure, aryl or alkenyl triflate (0.15 mmol), *i*-Pr_2Net (34.8 μL, 0.2 mmol) and DMF (0.4 mL) were added. All needle inlets/outlets were removed, and the reaction was placed in a heating block that was pre-heated to 100 °C. After 40–44 h, the black reaction mixture was allowed to cool to room temperature and filtered through a short plug of celite (CH_2Cl_2 or EtOAc as eluent). The solvent was removed in *vacuo* to afford a dark brown residue, which upon purification by preparative TLC with 5:1 hexanes:EtOAc as the eluent, afforded the pure product.

Note: Dimethylphenylsilylpinacolatoboron was used from a fresh bottle. It is suggested that this chemical be stored in a glovebox to prevent decomposition.



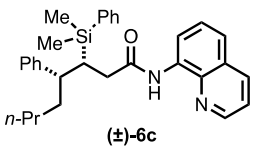
6a

3-(dimethyl(phenyl)silyl)-4-phenyl-*N*-(quinolin-8-yl)butanamide (6a): The title compound was prepared from **1a** (21.2 mg, 0.1 mmol), phenyl triflate (24.4 μL, 0.15 mmol), and dimethylphenylsilylpinacolatoboron (55.2 mg, 0.2 mmol) according to the general carbosilylation procedure. Purification by preparative TLC (10:1 to 5:1 hexanes:EtOAc) gave the product as a yellow oil (33.5 mg, 79% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.61 (s, 1H), 8.80 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.65 (dd, *J* = 7.1, 1.9 Hz, 1H), 8.15 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.58 (tt, *J* = 5.3, 2.6 Hz, 2H), 7.53–7.39 (m, 3H), 7.33 (dd, *J* = 4.8, 1.9 Hz, 3H), 7.24–7.13 (m, 4H), 7.08–7.01 (m, 1H), 2.88 (dd, *J* = 14.1, 5.7 Hz, 1H), 2.65 (dd, *J* = 14.1, 9.8 Hz, 1H), 2.60–2.38 (m, 2H), 2.04 (ddt, *J* = 9.8, 7.4, 6.0 Hz, 1H), 0.34 (s, 3H), 0.30 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 171.5, 147.9, 141.3, 138.3, 137.7, 136.3, 134.4, 134.0, 129.0, 129.0, 128.2, 127.8, 127.8, 127.4, 125.8, 121.5, 121.2, 116.3, 38.1, 36.1, 24.6, –4.0, –4.2; **HRMS** (ESI-TOF) Calcd for $C_{27}H_{29}N_2Osi$ [M+H] 425.2049, found 425.2049.



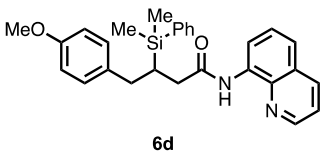
(±)-6b

3-(dimethyl(phenyl)silyl)-4-phenyl-*N*-(quinolin-8-yl)hexanamide ((±)-6b): The title compound was prepared from **1c** (24.0 mg, 0.1 mmol), phenyl triflate (24.4 μL, 0.15 mmol), and dimethylphenylsilylpinacolatoboron (55.2 mg, 0.2 mmol) according to the general carbosilylation procedure. Purification by preparative TLC (50:1 benzene:acetone) gave the product as a yellow oil (32.1 mg, 71% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.66 (s, 1H), 8.81 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.70 (dd, *J* = 7.4, 1.6 Hz, 1H), 8.16 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.75–7.35 (m, 5H), 7.31–7.18 (m, 7H), 7.16–7.11 (m, 1H), 2.89–2.51 (m, 3H), 2.14 (td, *J* = 7.4, 5.2 Hz, 1H), 1.78 (dtt, *J* = 14.6, 7.3, 3.8 Hz, 1H), 1.72–1.62 (m, 1H), 0.64 (t, *J* = 7.3 Hz, 3H), 0.18 (s, 3H), 0.11 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.8, 148.0, 144.4, 138.8, 138.3, 136.3, 134.6, 133.9, 128.7, 128.7, 128.1, 127.9, 127.7, 127.4, 126.1, 121.5, 121.1, 116.3, 48.6, 36.7, 29.5, 26.5, 12.5, –2.2, –3.7; **HRMS** (ESI-TOF) Calcd for $C_{29}H_{33}N_2Osi$ [M+H] 453.2362, found 453.2359.



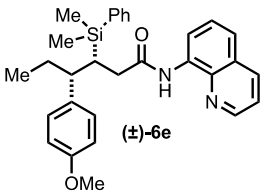
(±)-6c

3-(dimethyl(phenyl)silyl)-4-phenyl-*N*-(quinolin-8-yl)octanamide ((±)-6c): The title compound was prepared from **1z** (26.8 mg, 0.1 mmol), phenyl triflate (24.4 μL, 0.15 mmol), and dimethylphenylsilylpinacolatoboron (55.2 mg, 0.2 mmol) according to the general carbosilylation procedure. Purification by preparative TLC (10:1 hexanes:EtOAc) gave the product as a colorless oil (34.1 mg, 71% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.31 (s, 1H), 8.75 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.65 (dd, *J* = 7.6, 1.4 Hz, 1H), 8.12 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.66–7.56 (m, 2H), 7.49 (t, *J* = 7.9 Hz, 1H), 7.46–7.40 (m, 2H), 7.29–7.22 (m, 3H), 7.18–7.13 (m, 4H), 7.01 (td, *J* = 6.3, 3.2 Hz, 1H), 2.82 (ddd, *J* = 10.8, 9.1, 3.7 Hz, 1H), 2.47 (dd, *J* = 15.8, 5.5 Hz, 1H), 2.39 (dd, *J* = 15.9, 6.6 Hz, 1H), 2.08 (dt, *J* = 9.2, 6.0 Hz, 1H), 1.75 (dddd, *J* = 13.5, 10.0, 6.6, 3.8 Hz, 1H), 1.57–1.47 (m, 1H), 1.18–1.01 (m, 2H), 0.95 (tdd, *J* = 11.2, 9.4, 6.3 Hz, 2H), 0.70 (t, *J* = 7.3 Hz, 3H), 0.40 (s, 3H), 0.34 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 171.8, 147.8, 144.7, 139.5, 138.2, 136.2, 134.6, 133.9, 128.6, 128.6, 128.1, 127.8, 127.7, 127.4, 126.0, 121.4, 121.0, 116.1, 47.0, 37.5, 36.0, 30.1, 28.6, 22.5, 13.9, –2.4, –3.0; **HRMS** (ESI-TOF) Calcd for $C_{31}H_{37}N_2Osi$ [M+H] 481.2675, found 481.2667.



6d

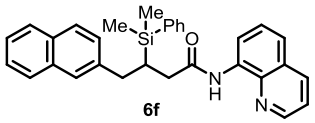
3-(dimethyl(phenyl)silyl)-4-(4-methoxyphenyl)-*N*-(quinolin-8-yl)butanamide (6d): The title compound was prepared from **1a** (21.2 mg, 0.1 mmol), 4-methoxyphenyl trifluoromethanesulfonate (36 μL, 0.2 mmol), and dimethylphenylsilylpinacolatoboron (55.2 mg, 0.2 mmol) according to the general carbosilylation procedure. Purification by preparative TLC (30:1 toluene:EtOAc) gave the product as a colorless oil (36.8 mg, 81% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.56 (s, 1H), 8.80 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.64 (dd, *J* = 7.1, 1.9 Hz, 1H), 8.14 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.67–7.37 (m, 5H), 7.37–7.28 (m, 3H), 7.15–7.01 (m, 2H), 6.73–6.61 (m, 2H), 3.61 (s, 3H), 2.84 (dd, *J* = 14.1, 5.7 Hz, 1H), 2.65–2.38 (m, 3H), 2.00 (ddt, *J* = 9.9, 7.7, 5.8 Hz, 1H), 0.34 (s, 3H), 0.31 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.6, 157.7, 147.9, 138.2, 137.8, 136.2, 134.5, 134.0, 133.3, 129.9, 129.0, 127.8, 127.8, 127.4, 121.5, 121.1, 116.3, 113.6, 55.0, 38.2, 35.3, 24.8, –4.0, –4.2; **HRMS** (ESI-TOF) Calcd for $C_{28}H_{31}N_2O_2Si$ [M+H] 455.2155, found 455.2157.



(±)-6e

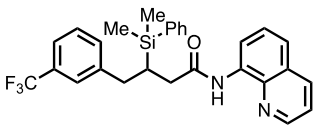
3-(dimethyl(phenyl)silyl)-4-(4-methoxyphenyl)-*N*-(quinolin-8-yl)hexanamide ((±)-6e): The title compound was prepared from **1c** (24.0 mg, 0.1 mmol), 4-methoxyphenyl trifluoromethanesulfonate (27 μL, 0.15 mmol), and dimethylphenylsilylpinacolatoboron (55.2 mg, 0.2 mmol) according to the general carbosilylation procedure. Purification by preparative TLC (40:1 benzene:acetone) gave the product as a colorless oil (34.7 mg, 72% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.68 (s, 1H), 8.83 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.73 (dd, *J* = 7.5, 1.5 Hz, 1H), 8.18 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.60–7.45 (m, 5H), 7.36–7.28 (m, 3H), 7.20–7.09 (m, 2H), 6.86–6.73 (m, 2H), 3.76 (s, 3H), 2.77–2.65 (m, 2H), 2.60 (dd, *J* = 15.8, 7.7 Hz, 1H), 2.13 (td, *J* = 7.4, 5.0 Hz, 1H), 1.79 (dqd, *J* = 14.6, 7.3, 3.7 Hz, 1H), 1.67–1.59 (m, 1H), 0.66 (t, *J* = 7.2 Hz, 3H), 0.22 (s, 3H), 0.17 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 171.5, 157.4, 147.5, 138.5, 137.9, 135.9, 135.9, 134.2, 133.4, 129.1, 128.2, 127.5, 127.2, 127.0, 121.1, 120.7, 115.9, 113.0, 54.7, 47.3, 36.3, 29.3,

26.1, 12.1, –2.7, –3.9; **HRMS** (ESI-TOF) Calcd for $C_{30}H_{35}N_2O_2Si$ [M+H] 483.2468, found 483.2466.



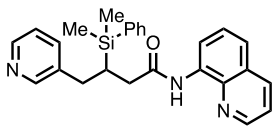
6f

3-(dimethyl(phenyl)silyl)-4-(naphthalen-2-yl)-*N*-(quinolin-8-yl)butanamide (6f): The title compound was prepared from **1a** (21.2 mg, 0.1 mmol), yridine ne-2-yl trifluoromethanesulfonate (41.4 mg, 0.15 mmol), and dimethylphenylsilylpinacolatoboron (55.2 mg, 0.2 mmol) according to the general carbosilylation procedure. Purification by preparative TLC (10:1 hexanes:EtOAc) gave the product as a colorless solid (41.2 mg, 87% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.54 (s, 1H), 8.73 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.57 (dd, *J* = 6.2, 2.8 Hz, 1H), 8.10 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.72–7.54 (m, 6H), 7.46–7.40 (m, 3H), 7.35 (ddt, *J* = 9.6, 4.9, 2.3 Hz, 4H), 7.32–7.26 (m, 2H), 3.06 (dd, *J* = 14.0, 5.5 Hz, 1H), 2.80 (dd, *J* = 14.1, 10.1 Hz, 1H), 2.57 (dd, *J* = 15.1, 5.8 Hz, 1H), 2.47 (dd, *J* = 15.1, 7.6 Hz, 1H), 2.16 (ddt, *J* = 10.0, 7.7, 5.7 Hz, 1H), 0.38 (s, 3H), 0.35 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 171.5, 147.9, 138.8, 138.1, 137.7, 136.2, 134.3, 134.0, 133.3, 132.0, 129.0, 127.9, 127.8, 127.8, 127.5, 127.3, 127.3, 127.3, 127.2, 125.5, 124.9, 121.4, 121.1, 116.2, 38.2, 36.4, 24.5, –4.0, –4.1; **HRMS** (ESI-TOF) Calcd for $C_{31}H_{31}N_2Osi$ [M+H] 475.2206, found 475.2203.



6g

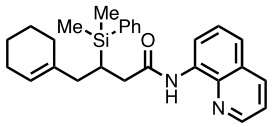
3-(dimethyl(phenyl)silyl)-*N*-(quinolin-8-yl)-4-(3-(trifluoromethyl)phenyl)butanamide (6g): The title compound was prepared from **1a** (21.2 mg, 0.1 mmol), 3-(trifluoromethyl)phenyl trifluoromethanesulfonate (30 μL, 0.15 mmol), and dimethylphenylsilylpinacolatoboron (55.2 mg, 0.2 mmol) according to the general carbosilylation procedure. Purification by preparative TLC (10:1 hexanes:EtOAc) gave the product as a yellow oil (33.5 mg, 68% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.61 (s, 1H), 8.78 (dd, *J* = 4.3, 1.7 Hz, 1H), 8.62 (dd, *J* = 6.4, 2.5 Hz, 1H), 8.14 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.61–7.51 (m, 2H), 7.49–7.42 (m, 3H), 7.41–7.30 (m, 5H), 7.28–7.20 (m, 2H), 2.90 (dd, *J* = 14.2, 6.0 Hz, 1H), 2.72 (dd, *J* = 14.2, 9.5 Hz, 1H), 2.58 (dd, *J* = 15.2, 5.5 Hz, 1H), 2.41 (dd, *J* = 15.2, 8.2 Hz, 1H), 2.06 (ddt, *J* = 9.5, 8.1, 5.7 Hz, 1H), 0.33 (s, 3H), 0.32 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.1, 148.0, 142.3, 138.2, 137.2, 136.3, 134.3, 134.0, 132.4, 130.3 (q, *J* = 32.0 Hz), 129.2, 128.5, 127.9, 127.8, 127.3, 125.7 (q, *J* = 4.6, 3.8 Hz), 124.1 (q, *J* = 273.4 Hz), 122.7 (q, *J* = 3.6 Hz), 121.5, 121.3, 116.3, 38.2, 36.1, 24.5, –4.1, –4.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ –62.8;**HRMS** (ESI-TOF) Calcd for $C_{28}H_{28}F_3N_2Osi$ [M+H] 493.1923, found 493.1928.



6h

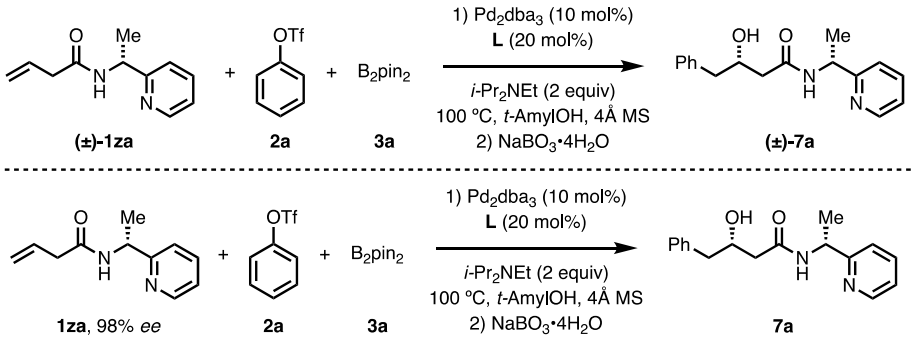
3-(dimethyl(phenyl)silyl)-4-(yridine-3-yl)-*N*-(quinolin-8-yl)butanamide (6h): The title compound was prepared from **1a** (21.2 mg, 0.1 mmol), yridine-3-yl trifluoromethanesulfonate (24.1 μL, 0.15 mmol), and dimethylphenylsilylpinacolatoboron (55.2 mg, 0.2 mmol) according to the general carbosilylation procedure. Purification by preparative TLC (1:1 hexanes:EtOAc) gave the product as a yellow oil (20.0 mg, 47% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.64 (s, 1H), 8.80 (dt, *J* = 4.0, 1.7 Hz, 1H), 8.63 (dt, *J* = 6.5, 2.1 Hz, 1H), 8.41 (d, *J* = 2.3 Hz, 1H), 8.30 (dd, *J* = 4.1, 2.3 Hz, 1H), 8.15 (dt, *J* = 8.3, 1.8 Hz, 1H), 7.69–

7.40 (m, 6H), 7.34 (dp, *J* = 5.6, 2.0 Hz, 3H), 7.06 (dd, *J* = 8.0, 4.8 Hz, 1H), 2.99–2.37 (m, 4H), 2.11–1.94 (m, 1H), 1.68 (s, 1H), 0.34 (s, 3H), 0.32 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.0, 150.3, 148.1, 147.4, 138.2, 137.2, 136.7, 136.4, 136.3, 134.3, 133.9, 129.2, 127.9, 127.9, 127.3, 123.1, 121.6, 121.4, 116.4, 38.0, 33.4, 24.3, –4.1, –4.1; **HRMS** (ESI-TOF) Calcd for $C_{26}H_{28}N_3Osi$ [M+H] 426.2002, found 426.1995.

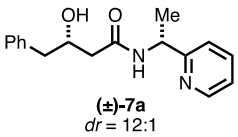


6i

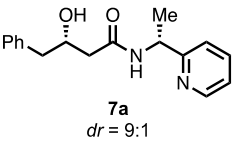
4-(cyclohex-1-en-1-yl)-3-(dimethyl(phenyl)silyl)-*N*-(quinolin-8-yl)butanamide (6i): The title compound was prepared from **1a** (21.2 mg, 0.1 mmol), cyclohex-1-en-1-yl trifluoromethanesulfonate (52.6 μL, 0.3 mmol), and dimethylphenylsilylpinacolatoboron (55.2 mg, 0.2 mmol) according to the general carbosilylation procedure. Purification by preparative TLC (10:1 hexanes:EtOAc) gave the product as a yellow oil (36.4 mg, 85% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.68 (s, 1H), 8.89–8.44 (m, 2H), 8.15 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.66–7.39 (m, 5H), 7.36–7.29 (m, 3H), 5.46–5.37 (m, 1H), 2.60–2.34 (m, 2H), 2.24–2.01 (m, 2H), 2.00–1.86 (m, 2H), 1.84–1.63 (m, 3H), 1.56–1.40 (m, 2H), 1.39–1.23 (m, 2H), 0.36 (s, 3H), 0.36 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 172.0, 147.9, 138.3, 137.9, 136.5, 136.3, 134.7, 134.0, 128.9, 127.9, 127.7, 127.4, 123.4, 121.5, 121.0, 116.2, 39.4, 38.6, 27.4, 25.2, 22.8, 22.2, 19.5, –4.2, –4.3; **HRMS** (ESI-TOF) Calcd for $C_{27}H_{33}N_2Osi$ [M+H] 429.2362, found 429.2363.



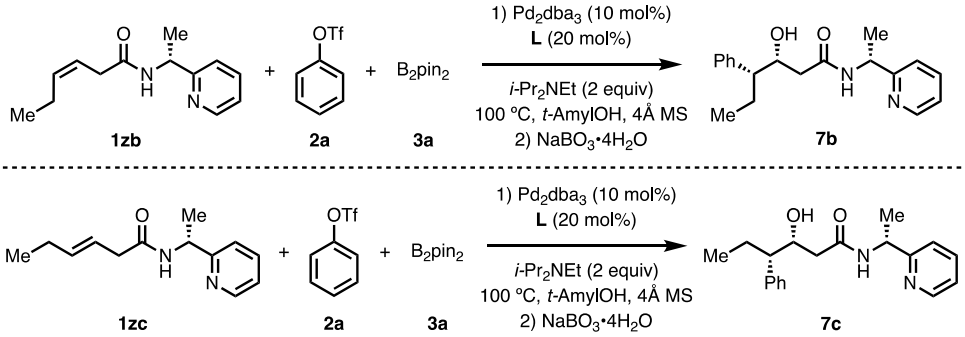
Scheme S6: Arylboration/oxidation of terminal alkene using a chiral auxiliary.



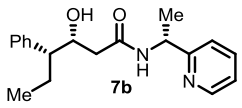
3-hydroxy-4-phenyl-*N*-(I-1-(yridine-2-yl)ethyl)butanamide ((±)-7a): The title compound was prepared from **(±)-1za** (9.5 mg, 0.05 mmol), phenyl triflate (12.2 μL, 0.075 mmol), and bis(pinacolato)diboron (25.4 mg, 0.1 mmol) with $Pd_2(dba)_3$ (4.6 mg, 10 mol%), Cy-JohnPhos (3.5 mg, 20 mol%), and *i*-Pr_2Net (17.4 μL, 0.1 mmol) according to the general carboboration/oxidation procedure. Purification by preparative TLC (1:1 to 1:2 hexanes:EtOAc) gave the product as a white solid (7.8 mg, 55% yield). This product was isolated as an inseparable 12:1 mixture of diastereomers. The following analytical data correspond to the mixture. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.77–8.40 (m, 1H), 7.68 (td, *J* = 7.7, 1.8 Hz, 1H), 7.39–7.15 (m, 7H), 7.10–6.76 (m, 1H), 5.17 (p, *J* = 6.9 Hz, 1H), 4.40–3.99 (m, 1H), 3.03–2.67 (m, 2H), 2.55–2.14 (m, 2H), 1.59–1.37 (m, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 171.8, 171.4, 160.8, 160.6, 148.9, 148.8, 138.0, 138.0, 137.0, 137.0, 129.5, 129.4, 128.5, 128.5, 126.5, 126.5, 122.4, 122.4, 121.6, 121.5, 69.7, 49.8, 49.7, 43.3, 43.1, 42.4, 41.4, 22.6, 22.5; **HRMS** (ESI-TOF) Calcd for $C_{17}H_{21}N_2O_2$ [M+H] 285.1603, found 285.1607; **X-ray** (single-crystal) Colorless needle crystals of X-ray diffraction quality were obtained by vapor diffusion of pentane into a saturated solution of **(±)-7a** in CH_2Cl_2 (CCDC 1939488).[15]



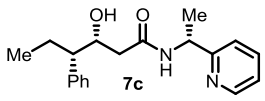
(*S*)-3-hydroxy-4-phenyl-*N*-(I-1-(yridine-2-yl)ethyl)butanamide (7a): The title compound was prepared from **1za** (9.5 mg, 0.05 mmol), phenyl triflate (12.2 μL, 0.075 mmol), and bis(pinacolato)diboron (25.4 mg, 0.1 mmol) with $Pd_2(dba)_3$ (4.6 mg, 10 mol%), Cy-JohnPhos (3.5 mg, 20 mol%), and *i*-Pr_2Net (17.4 μL, 0.1 mmol) according to the general carboboration/oxidation procedure. Purification by preparative TLC (1:1 to 1:2 hexanes:EtOAc) gave the product as a white solid (9.7 mg, 68% yield, >99% *ee*). This product was isolated as an inseparable 9:1 mixture of diastereomers. The analytical data is identical to the racemic compound. **SFC** (chiral column) The enantiomeric excess was determined by chiral SFC on a Daicel IH column (3 μm, 4.6×250 mm), 7% MeOH/CO_2, 4.0 mL/min, λ = 214 nm, t (major) = 5.131 min, t (minor) = 6.481 min.



Scheme S7: Diastereoselective arylboration/oxidation of internal alkenes.

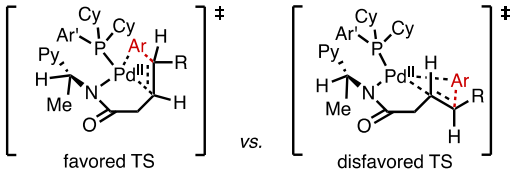


(3*R*,4*R*)-3-hydroxy-4-phenyl-*N*-(I-1-(pyridin-2-yl)ethyl)hexanamide (7b): The title compound was prepared from **1zb** (10.9 mg, 0.05 mmol), phenyl triflate (12.2 μL, 0.075 mmol), and bis(pinacolato)diboron (25.4 mg, 0.1 mmol) with $Pd_2(dba)_3$ (4.6 mg, 10 mol%), Cy-JohnPhos (3.5 mg, 20 mol%), and *i*-Pr_2Net (17.4 μL, 0.1 mmol) according to the general carboboration/oxidation procedure. Purification by preparative TLC (1:1 hexanes:EtOAc) gave the product as a white solid (8.0 mg, 51% yield). This product was isolated as an inseparable 8:1 mixture of diastereomers. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.48 (d, *J* = 4.9 Hz, 1H), 7.64 (t, *J* = 7.7 Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.24–7.10 (m, 5H), 6.77 (d, *J* = 7.5 Hz, 1H), 5.10 (p, *J* = 7.1 Hz, 1H), 4.51 (s, 1H), 4.07 (td, *J* = 8.8, 2.8 Hz, 1H), 2.67–2.42 (m, 1H), 2.28–2.05 (m, 3H), 1.44 (d, *J* = 6.9 Hz, 3H), 0.72 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 172.0, 160.5, 148.9, 142.1, 136.9, 128.5, 128.5, 126.5, 122.4, 121.5, 72.5, 54.1, 49.6, 40.1, 24.9, 22.6, 12.0; **HRMS** (ESI-TOF) Calcd for $C_{19}H_{25}N_2O_2$ [M+H] 313.1916, found 313.1916.



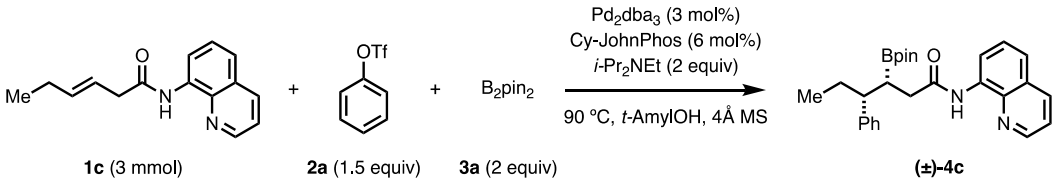
(3*R*,4*S*)-3-hydroxy-4-phenyl-*N*-(I-1-(pyridin-2-yl)ethyl)hexanamide (7c): The title compound was prepared from **1zc** (10.9 mg, 0.05 mmol), phenyl triflate (12.2 μL, 0.075 mmol), and bis(pinacolato)diboron (25.4 mg, 0.1 mmol) with $Pd_2(dba)_3$ (4.6 mg, 10 mol%), Cy-JohnPhos (3.5 mg, 20 mol%), and *i*-Pr_2Net (17.4 μL, 0.1 mmol) according to the general carboboration/oxidation procedure. Purification by preparative TLC (1:1 hexanes:EtOAc) gave the product as a white solid (5.0 mg, 32% yield). This product was isolated as an inseparable 7:1 mixture of diastereomers. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.50 (dd, *J* = 17.0, 4.6 Hz, 1H), 7.78–7.59 (m, 1H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.26–7.16 (m, 5H), 7.13–6.98 (m, 1H), 5.13 (p, *J* = 7.1 Hz, 1H), 4.38–4.15 (m, 1H), 2.50 (dt, *J* = 10.4, 5.3 Hz, 1H), 2.39 (dd, *J* = 15.3, 2.5 Hz, 1H), 2.22 (dd, *J* = 15.3, 9.7 Hz, 1H), 1.94–1.69 (m, 2H), 1.42 (d, *J* = 7.0 Hz, 3H), 0.80 (dt, *J* = 14.9, 7.3 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 171.6, 160.8, 149.0, 141.0, 136.9, 129.1, 128.3, 126.6, 122.4, 121.5, 71.4, 53.3, 49.7, 40.8, 24.6, 22.6, 12.2; **HRMS** (ESI-TOF) Calcd for $C_{19}H_{25}N_2O_2$ [M+H] 313.1916, found 313.1910.

Alternative Stereoinduction Model for Diastereoselective Arylboration



Scheme S8: Plausible transition states for migratory insertion with the phosphine ligand coordinated to the palladium center and the chiral directing group bound in a monodentate fashion. This model is related to earlier work by He, Peng, and Chen, who proposed dissociation of the quinoline moiety of the 8-aminoquinoline directing group during enantioselective Pd(0)/PR_3-catalyzed C(sp^3)–H arylation.[16]

Large-Scale Synthesis of (±)-4c



Scheme S9: Large-scale synthesis of boronate **(±)-4c**.

Procedure for Large-Scale Synthesis of (±)-4c: Alkene substrate **1c** (720 mg, 3 mmol), *N*-bis(pinacolato)diboron (1.52 g, 6 mmol), $Pd_2(dba)_3$ (84 mg, 0.09 mmol), Cy-JohnPhos (66 mg, 0.18 mmol), and 4Å molecular sieves (800 mg) were added to a 50-mL round-bottom flask. The reaction flask was sealed with a rubber septum and was then evacuated and backfilled with N_2 (×3). Under positive N_2 pressure, phenyl triflate (0.73 mL, 4.5 mmol), *i*-Pr_2NEt (1.04 mL, 6 mmol) and *t*-AmylOH (6 mL) were added. The flask was submerged into a silicon oil bath that was pre-heated to 90 °C. After 40 h, the dark brown reaction mixture was cooled to room temperature, diluted with EtOAc (10 mL), and filtered through a short plug of celite. The organic solution was concentrated to afford a brown residue that upon purification by rapid silica gel column chromatography (with 30:1 to 15:1 hexanes:EtOAc as the eluent) afforded **(±)-4c** (1.21 g, 91%) as a white solid. Analytical data was consistent with the information reported above.

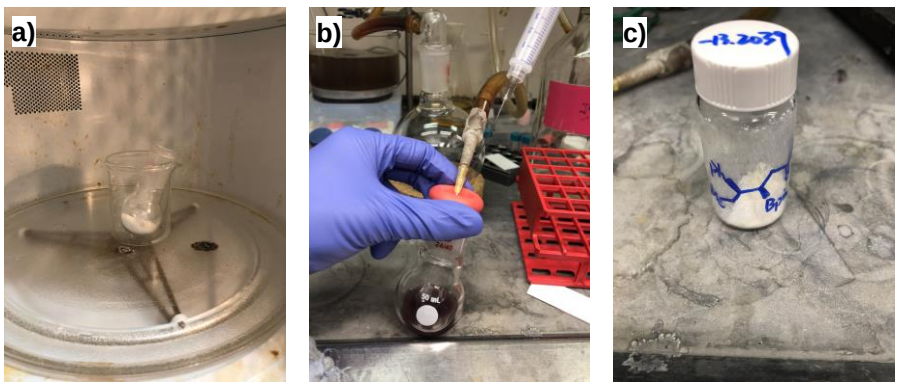
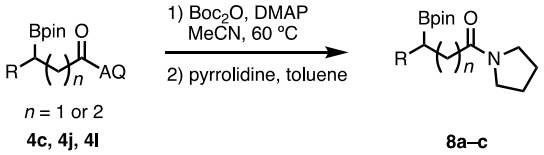


Figure S2: Photographic depiction of the procedure for gram-scale synthesis of **(±)-4c**.

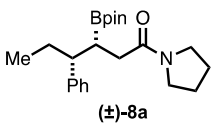
a) Activating 4 Å molecular sieves. b) Adding solvent. c) Isolated pure **(±)-4c**.

Procedures for the Transformations of Borylated Products



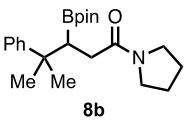
Scheme S10: Transamination deprotection of 8-aminoquinoline amides.

General Procedure for Transamination:[17] To a 25-mL round-bottom flask containing a Teflon-coated magnetic stir bar, were added AQ amide, 4-(dimethylamino)pyridine (10 mol%), and Boc anhydride (2 equiv). The reaction flask was evacuated and backfilled with N_2 (×1), followed by addition of anhydrous MeCN (0.1 M). The reaction mixture was heated at 60 ºC for 2 h. After cooling to room temperature, the reaction was concentrated under vacuum and purified by column chromatography (2:1 hexanes:EtOAc) to afford the Boc-protected amide. The Boc amide was then dissolved in toluene (0.5 M), followed by addition of pyrrolidine (1.5 equiv). The reaction mixture was heated under N_2 atmosphere at 60 ºC overnight. Upon completion, the organic mixture was concentrated under vacuum and purified by column chromatography (1:2 hexanes:EtOAc) to afford pure product.



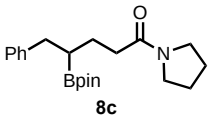
(±)-8a

4-phenyl-1-(pyrrolidin-1-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-1-one ((±)-8a): The title compound was prepared from **(±)-4c** (444 mg, 1 mmol) following the general transamination procedure. Compound **(±)-8a** was isolated as a white solid (345 mg, 93% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28–7.08 (m, 5H), 3.53–3.22 (m, 4H), 2.58 (ddd, *J* = 10.5, 8.2, 3.9 Hz, 1H), 2.51–2.27 (m, 2H), 1.99–1.71 (m, 6H), 1.66–1.54 (m, 1H), 1.11 (s, 6H), 1.02 (s, 6H), 0.74 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 172.0, 144.8, 128.7, 127.8, 125.8, 82.4, 48.9, 46.5, 45.7, 35.3, 27.6, 26.0, 24.9, 24.7, 24.4, 12.1; **HRMS** (ESI-TOF) Calcd for $C_{16}H_{23}BNO_2$ [M–$C_6H_{11}O$] 271.1858, found 271.1865 (*Note: Based on the observed molecular weight, during ionization, compound **8a** apparently underwent hydrolysis to the boronic acid, followed by dehydration.*)



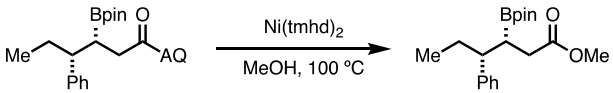
8b

4-methyl-4-phenyl-1-(pyrrolidin-1-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentan-1-one (8b): The title compound was prepared from **4j** (40.0 mg, 0.09 mmol) following the general transamination procedure. Compound **8b** was isolated as a white solid (26.4 mg, 79% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.42–7.32 (m, 2H), 7.32–7.23 (m, 2H), 7.20–7.03 (m, 1H), 3.34 (t, *J* = 6.8 Hz, 2H), 3.22 (dt, *J* = 10.2, 6.5 Hz, 1H), 3.00 (dt, *J* = 10.2, 6.7 Hz, 1H), 2.27 (dd, *J* = 17.0, 13.1 Hz, 1H), 1.90–1.63 (m, 6H), 1.40 (s, 3H), 1.37 (s, 3H), 1.29 (s, 6H), 1.23 (s, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 172.1, 150.3, 127.9, 125.8, 125.3, 82.7, 46.2, 45.5, 38.6, 33.6, 31.4, 25.9, 25.1, 24.9, 24.4, 24.3; **HRMS** (ESI-TOF) Calcd for $C_{22}H_{35}BNO_3$ [M+H] 371.2746, found 371.2740.



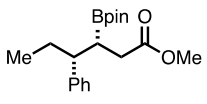
8c

5-phenyl-1-(pyrrolidin-1-yl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentan-1-one (8c): The title compound was prepared from **4l** (215 mg, 0.5 mmol) following the general transamination procedure. Compound **8c** was isolated as a yellow oil (150 mg, 84% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24–7.05 (m, 5H), 3.51–3.26 (m, 4H), 2.81–2.61 (m, 2H), 2.37–2.17 (m, 2H), 1.83 (dtdd, *J* = 41.1, 14.0, 7.5, 3.4 Hz, 6H), 1.37 (p, *J* = 7.8 Hz, 1H), 1.15 (s, 6H), 1.12 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.6, 141.8, 128.8, 128.0, 125.6, 83.0, 46.5, 45.5, 37.2, 34.4, 26.3, 26.0, 24.7, 24.7, 24.3; **HRMS** (ESI-TOF) Calcd for $C_{15}H_{21}BNO_2$ [M–$C_6H_{11}O$] 257.1702, found 257.1705 (Note: Compound **8c** was hydrolyzed to boronic acid, followed by dehydration to the corresponding molecular weight.)



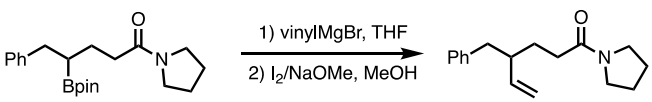
(±)-4c (±)-9

Scheme S11: Methanolysis of AQ amide **(±)-4c**.



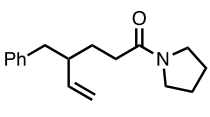
(±)-9

methyl 4-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanoate ((±)-9): The title compound was prepared by adapting a literature procedure.[18] To a 15-mL reaction tube containing a Teflon-coated magnetic stir bar, were added compound **(±)-4c** (44.4 mg, 0.1 mmol), and $Ni(tmhd)_2$ (64 mg, 0.15 mmol). The reaction vessel was evacuated and backfilled with N_2 (×3), followed by addition of anhydrous MeOH (1 mL). The reaction mixture was heated at 100 ºC for 6 days. After cooling to room temperature, the reaction was diluted with EtOAc (10 mL) and filtered through a plug of celite with EtOAc as the eluent. The resulting solution was concentrated under vacuum and purified by preparative TLC (5:1 hexanes:EtOAc) to afford the product as a yellow oil (25.9 mg, 78% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.28–7.24 (m, 2H), 7.22–7.15 (m, 3H), 3.65 (s, 3H), 2.63–2.35 (m, 3H), 1.96–1.71 (m, 2H), 1.70–1.48 (m, 1H), 1.10 (s, 6H), 1.02 (s, 6H), 0.74 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 174.4, 144.1, 128.5, 128.0, 126.1, 83.0, 51.4, 48.6, 34.3, 27.2, 24.8, 24.5, 12.1; **HRMS** (ESI-TOF) Calcd for $C_{13}H_{18}BO_3$ [M–$C_6H_{11}O$] 232.1385, found 232.1384 (Note: Compound **(±)-9** was hydrolyzed to boronic acid, followed by dehydration to the corresponding molecular weight.)



8c 10

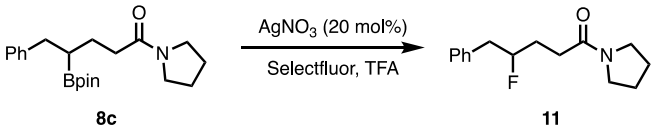
Scheme S12: Synthesis of compound **10** from arylborylated product **8c**.



10

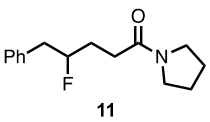
4-benzyl-1-(pyrrolidin-1-yl)hex-5-en-1-one (10): The title compound was prepared by adapting a literature procedure.[19] To a solution of **8c** (18

mg, 0.05 mmol) in THF (0.5 mL) was added vinylmagnesium bromide (0.2 mL, 1 M, 0.2 mmol) dropwise at room temperature. The reaction mixture was then stirred for 30 minutes. Next, a solution of iodine (51 mg, 0.2 mmol in 0.67 mL MeOH) was slowly added to the reaction flask at –78 ºC. After further stirring at this temperature for 30 minutes, a solution of NaOMe (22 mg, 0.4 mmol in 0.83 mL MeOH) was added dropwise to the reaction mixture. After warming to room temperature, the resultant mixture was stirred for another 1.5 h. Upon completion, the reaction was diluted with pentane (10 mL) and wash with saturated $Na_2S_2O_3$ (5 mL) and brine (5 mL). The organic phase was dried over Na_2SO_4, concentrated under vacuum and purified by preparative TLC (2:1 hexanes:EtOAc) to afford the product as a colorless oil (11.2 mg, 87% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.35–7.21 (m, 2H), 7.17–7.05 (m, 3H), 5.59 (ddd, *J* = 17.1, 10.2, 8.7 Hz, 1H), 5.01–4.77 (m, 2H), 3.43 (t, *J* = 6.9 Hz, 2H), 3.33 (t, *J* = 6.8 Hz, 2H), 2.67 (qd, *J* = 13.6, 7.1 Hz, 2H), 2.41–2.20 (m, 2H), 2.16 (ddd, *J* = 15.6, 9.8, 6.3 Hz, 1H), 1.99–1.73 (m, 5H), 1.58 (dtd, *J* = 13.6, 9.9, 5.3 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.5, 141.8, 140.2, 129.3, 128.1, 125.8, 115.3, 46.5, 45.6, 42.0, 32.5, 29.1, 26.1, 24.4; **HRMS** (ESI-TOF) Calcd for $C_{17}H_{24}NO$ [M+H] 258.1858, found 258.1858.



8c **11**

Scheme S13: Fluorination of arylborylated product **8c**.



11

4-fluoro-5-phenyl-1-(pyrrolidin-1-yl)pentan-1-one (11): The title compound was prepared by adapting a literature procedure.[20] To a 15-mL reaction tube containing a Teflon-coated magnetic stir bar were added compound **8c** (17.9 mg, 0.05 mmol), $AgNO_3$ (1.7 mg, 0.01 mmol), and Selectfluor (53 mg, 0.15 mmol). The reaction vessel was evacuated and backfilled with N_2 (×3). CH_2Cl_2 (0.25 mL), H_2O (0.25 mL), and TFA (14.5 μL, 0.2 mmol) were then added. The reaction mixture was stirred at 50 ºC for 24 h. After cooling to room temperature, the reaction was quenched by slow addition of saturated $NaHCO_3$ (4 mL), and the resulting mixture was extracted with EtOAc (3 × 5 mL). The combined organic layers were concentrated under vacuum and purified by silica gel chromatography (2:1 hexanes:EtOAc) to afford the product as a colorless oil (4.6 mg, 37% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.40–7.09 (m, 5H), 4.76 (ddddd, *J* = 49.3, 9.8, 7.5, 4.9, 2.7 Hz, 1H), 3.55–3.36 (m, 4H), 3.08–2.76 (m, 2H), 2.57–2.32 (m, 2H), 2.18–2.00 (m, 1H), 1.98–1.77 (m, 5H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 170.5, 137.1 (d, *J* = 4.4 Hz), 129.4, 128.4, 126.5, 94.0 (d, *J* = 170.6 Hz), 46.5, 45.6, 41.8 (d, *J* = 21.0 Hz), 30.0 (d, *J* = 9.0 Hz), 29.9 (d, *J* = 8.2 Hz), 26.1, 24.4; **^{19}F NMR** (376 MHz, $CDCl_3$) δ –181.8; **HRMS** (ESI-TOF) Calcd for $C_{15}H_{21}FNO$ [M+H] 250.1607, found 250.1610.

X-RAY CRYSTALLOGRAPHY

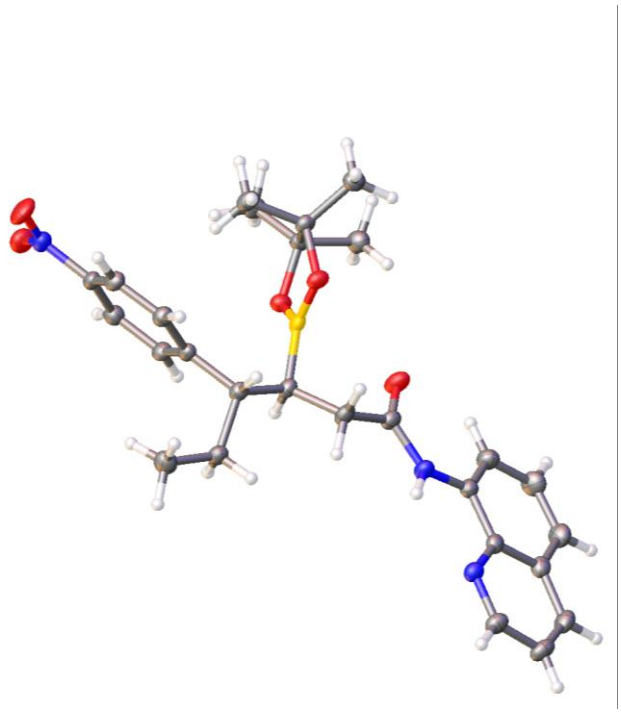


Table S3. Crystal data and structure refinement for **(±)-4u**.

Report date	2019-04-01	
Identification code	engle177	
Empirical formula	C27 H32 B N3 O5	
Molecular formula	C27 H32 B N3 O5	
Formula weight	489.36	
Temperature	100.0 K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 14.9780(2) Å	α= 90°.
	b = 16.2305(2) Å	β= 95.8100(10)°.
	c = 20.9234(2) Å	γ = 90°.
Volume	5060.36(10) $Å^3$	
Z	8	

Density (calculated)	1.285 Mg/m^3
Absorption coefficient	0.716 mm^{-1}
F(000)	2080
Crystal size	0.15 x 0.15 x 0.1 mm^3
Crystal color, habit	clear colourless block
Theta range for data collection	2.965 to 70.125°.
Index ranges	-18<=h<=18, -19<=k<=19, -25<=l<=25
Reflections collected	85700
Independent reflections	9620 [R(int) = 0.0308]
Completeness to theta = 67.679°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.5220 and 0.4402
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9620 / 100 / 718
Goodness-of-fit on F^2	1.019
Final R indices [I>2sigma(I)]	R1 = 0.0367, wR2 = 0.0905
R indices (all data)	R1 = 0.0411, wR2 = 0.0939
Extinction coefficient	n/a
Largest diff. peak and hole	0.349 and -0.232 $e.Å^{-3}$

Table S4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **(±)-4u**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	4474(1)	-429(1)	8279(1)	33(1)
O(2)	5314(1)	764(1)	7136(1)	23(1)
O(3)	4233(1)	-152(1)	6743(1)	23(1)
O(4)	3552(1)	2517(1)	4265(1)	41(1)
O(5)	2733(1)	1420(1)	4217(1)	36(1)
N(1)	3417(1)	383(1)	10330(1)	23(1)
N(2)	3970(1)	120(1)	9180(1)	24(1)
N(3)	3172(1)	1957(1)	4520(1)	28(1)
C(1)	3117(1)	522(1)	10891(1)	27(1)
C(2)	3056(1)	-84(1)	11366(1)	31(1)
C(3)	3314(1)	-868(1)	11246(1)	30(1)
C(4)	3618(1)	-1058(1)	10647(1)	25(1)
C(5)	3871(1)	-1862(1)	10474(1)	31(1)
C(6)	4137(1)	-2000(1)	9881(1)	33(1)
C(7)	4184(1)	-1358(1)	9428(1)	29(1)
C(8)	3959(1)	-566(1)	9584(1)	22(1)
C(9)	3661(1)	-404(1)	10202(1)	21(1)
C(10)	4206(1)	163(1)	8568(1)	24(1)
C(11)	4110(1)	1009(1)	8268(1)	26(1)
C(12)	3758(1)	950(1)	7551(1)	22(1)
C(13)	5670(1)	357(1)	6592(1)	22(1)
C(14)	6659(1)	189(1)	6763(1)	29(1)

C(15)	5547(1)	956(1)	6029(1)	28(1)
C(16)	5062(1)	-422(1)	6496(1)	23(1)
C(17)	4843(1)	-683(1)	5800(1)	29(1)
C(18)	5415(1)	-1153(1)	6903(1)	30(1)
C(19)	3544(1)	1830(1)	7283(1)	22(1)
C(20)	2698(1)	2186(1)	7546(1)	26(1)
C(21)	2370(1)	3004(1)	7256(1)	33(1)
C(22)	3438(1)	1849(1)	6554(1)	22(1)
C(23)	3852(1)	2470(1)	6231(1)	24(1)
C(24)	3756(1)	2517(1)	5565(1)	25(1)
C(25)	3253(1)	1920(1)	5224(1)	23(1)
C(26)	2828(1)	1293(1)	5525(1)	25(1)
C(27)	2916(1)	1268(1)	6192(1)	24(1)
B(1)	4452(1)	492(1)	7154(1)	21(1)
O(6)	1652(1)	4494(1)	3114(1)	32(1)
O(9)	2256(1)	6557(1)	-737(1)	49(1)
O(10)	1322(1)	7565(1)	-740(1)	48(1)
N(4)	1094(1)	5154(1)	5293(1)	26(1)
N(5)	1652(1)	4967(1)	4135(1)	24(1)
N(6)	1808(1)	7045(1)	-460(1)	32(1)
C(28)	809(1)	5256(1)	5863(1)	31(1)
C(29)	535(1)	4612(1)	6250(1)	34(1)
C(30)	565(1)	3827(1)	6029(1)	32(1)
C(31)	865(1)	3674(1)	5421(1)	28(1)
C(32)	905(1)	2879(1)	5151(1)	33(1)
C(33)	1182(1)	2784(1)	4557(1)	34(1)
C(34)	1444(1)	3464(1)	4197(1)	29(1)

C(35)	1416(1)	4247(1)	4446(1)	23(1)
C(36)	1121(1)	4367(1)	5068(1)	23(1)
C(37)	1721(1)	5065(1)	3499(1)	23(1)
C(38)	1875(1)	5936(1)	3282(1)	25(1)
C(39)	1943(1)	5954(1)	2554(1)	23(1)
C(46)	1840(1)	6845(1)	2292(1)	25(1)
C(47)	2525(1)	7465(1)	2623(1)	30(1)
C(48)	3503(1)	7276(1)	2549(1)	33(1)
C(49)	1858(1)	6882(1)	1566(1)	25(1)
C(50)	2390(1)	6361(1)	1232(1)	26(1)
C(51)	2377(1)	6408(1)	566(1)	27(1)
C(52)	1839(1)	6996(1)	242(1)	26(1)
C(53)	1321(1)	7537(1)	558(1)	32(1)
C(54)	1332(1)	7466(1)	1219(1)	31(1)
B(2B)	1180(1)	5392(1)	2201(1)	23(1)
O(7A)	1294(1)	4881(1)	1692(1)	22(1)
O(8A)	296(1)	5480(3)	2319(3)	26(1)
C(40A)	436(1)	4488(1)	1495(1)	24(1)
C(41A)	324(1)	4435(1)	768(1)	33(1)
C(42A)	473(1)	3625(1)	1782(1)	33(1)
C(43A)	-247(1)	5068(1)	1792(1)	29(1)
C(44A)	-603(1)	5755(1)	1334(1)	51(1)
C(45A)	-1016(1)	4629(1)	2063(1)	50(1)
O(7B)	1159(9)	5112(10)	1590(4)	22(1)
O(8B)	278(11)	5400(40)	2270(30)	26(1)
C(40B)	246(9)	4865(8)	1360(6)	24(1)
C(41B)	78(15)	5540(11)	857(8)	41(4)

C(42B)	365(16)	4023(11)	1060(11)	41(4)
C(43B)	-373(12)	4844(12)	1918(9)	29(1)
C(44B)	-1207(13)	5362(17)	1743(13)	59(6)
C(45B)	-211(17)	4069(10)	2325(9)	46(4)

Table S5. Bond lengths [Å] and angles [°] for **(±)-4u**.

O(1)-C(10)	1.2231(16)	C(4)-C(5)	1.4148(19)
O(2)-C(13)	1.4623(14)	C(4)-C(9)	1.4180(17)
O(2)-B(1)	1.3680(17)	C(5)-H(5A)	0.9500
O(3)-C(16)	1.4599(14)	C(5)-C(6)	1.359(2)
O(3)-B(1)	1.3715(16)	C(6)-H(6)	0.9500
O(4)-N(3)	1.2239(16)	C(6)-C(7)	1.4151(19)
O(5)-N(3)	1.2276(16)	C(7)-H(7)	0.9500
N(1)-C(1)	1.3182(16)	C(7)-C(8)	1.3768(18)
N(1)-C(9)	1.3638(16)	C(8)-C(9)	1.4335(17)
N(2)-H(2)	0.858(13)	C(10)-C(11)	1.5096(18)
N(2)-C(8)	1.3998(16)	C(11)-H(11A)	0.9900
N(2)-C(10)	1.3645(16)	C(11)-H(11B)	0.9900
N(3)-C(25)	1.4670(15)	C(11)-C(12)	1.5430(16)
C(1)-H(1)	0.9500	C(12)-H(12)	1.0000
C(1)-C(2)	1.4066(19)	C(12)-C(19)	1.5564(17)
C(2)-H(2A)	0.9500	C(12)-B(1)	1.5807(18)
C(2)-C(3)	1.361(2)	C(13)-C(14)	1.5128(17)
C(3)-H(3)	0.9500	C(13)-C(15)	1.5246(17)
C(3)-C(4)	1.4106(19)	C(13)-C(16)	1.5590(17)

C(14)-H(14A)	0.9800	C(24)-H(24)	0.9500
C(14)-H(14B)	0.9800	C(24)-C(25)	1.3814(19)
C(14)-H(14C)	0.9800	C(25)-C(26)	1.3842(18)
C(15)-H(15A)	0.9800	C(26)-H(26)	0.9500
C(15)-H(15B)	0.9800	C(26)-C(27)	1.3905(18)
C(15)-H(15C)	0.9800	C(27)-H(27)	0.9500
C(16)-C(17)	1.5190(17)	O(6)-C(37)	1.2243(16)
C(16)-C(18)	1.5236(18)	O(9)-N(6)	1.2213(17)
C(17)-H(17A)	0.9800	O(10)-N(6)	1.2242(17)
C(17)-H(17B)	0.9800	N(4)-C(28)	1.3156(17)
C(17)-H(17C)	0.9800	N(4)-C(36)	1.3630(17)
C(18)-H(18A)	0.9800	N(5)-H(5)	0.868(13)
C(18)-H(18B)	0.9800	N(5)-C(35)	1.4010(16)
C(18)-H(18C)	0.9800	N(5)-C(37)	1.3550(16)
C(19)-H(19)	1.0000	N(6)-C(52)	1.4681(16)
C(19)-C(20)	1.5441(17)	C(28)-H(28)	0.9500
C(19)-C(22)	1.5187(16)	C(28)-C(29)	1.408(2)
C(20)-H(20A)	0.9900	C(29)-H(29)	0.9500
C(20)-H(20B)	0.9900	C(29)-C(30)	1.358(2)
C(20)-C(21)	1.5203(19)	C(30)-H(30)	0.9500
C(21)-H(21A)	0.9800	C(30)-C(31)	1.413(2)
C(21)-H(21B)	0.9800	C(31)-C(32)	1.413(2)
C(21)-H(21C)	0.9800	C(31)-C(36)	1.4184(18)
C(22)-C(23)	1.3929(18)	C(32)-H(32)	0.9500
C(22)-C(27)	1.3975(18)	C(32)-C(33)	1.359(2)
C(23)-H(23)	0.9500	C(33)-H(33)	0.9500
C(23)-C(24)	1.3872(17)	C(33)-C(34)	1.413(2)

C(34)-H(34)	0.9500	C(53)-C(54)	1.3875(19)
C(34)-C(35)	1.3761(19)	C(54)-H(54)	0.9500
C(35)-C(36)	1.4291(17)	B(2B)-O(7A)	1.3753(17)
C(37)-C(38)	1.5093(17)	B(2B)-O(8A)	1.3782(19)
C(38)-H(38A)	0.9900	B(2B)-O(7B)	1.355(8)
C(38)-H(38B)	0.9900	B(2B)-O(8B)	1.372(9)
C(38)-C(39)	1.5376(16)	O(7A)-C(40A)	1.4568(16)
C(39)-H(39)	1.0000	O(8A)-C(43A)	1.464(3)
C(39)-C(46)	1.5496(17)	C(40A)-C(41A)	1.5175(19)
C(39)-B(2B)	1.5848(19)	C(40A)-C(42A)	1.523(2)
C(46)-H(46)	1.0000	C(40A)-C(43A)	1.563(2)
C(46)-C(47)	1.5489(18)	C(41A)-H(41A)	0.9800
C(46)-C(49)	1.5226(17)	C(41A)-H(41B)	0.9800
C(47)-H(47A)	0.9900	C(41A)-H(41C)	0.9800
C(47)-H(47B)	0.9900	C(42A)-H(42A)	0.9800
C(47)-C(48)	1.519(2)	C(42A)-H(42B)	0.9800
C(48)-H(48A)	0.9800	C(42A)-H(42C)	0.9800
C(48)-H(48B)	0.9800	C(43A)-C(44A)	1.531(2)
C(48)-H(48C)	0.9800	C(43A)-C(45A)	1.512(2)
C(49)-C(50)	1.3975(19)	C(44A)-H(44A)	0.9800
C(49)-C(54)	1.3894(19)	C(44A)-H(44B)	0.9800
C(50)-H(50)	0.9500	C(44A)-H(44C)	0.9800
C(50)-C(51)	1.3927(18)	C(45A)-H(45A)	0.9800
C(51)-H(51)	0.9500	C(45A)-H(45B)	0.9800
C(51)-C(52)	1.3807(19)	C(45A)-H(45C)	0.9800
C(52)-C(53)	1.383(2)	O(7B)-C(40B)	1.459(8)
C(53)-H(53)	0.9500	O(8B)-C(43B)	1.461(9)

C(40B)-C(41B)	1.521(8)	N(1)-C(1)-C(2)	124.09(13)
C(40B)-C(42B)	1.522(8)	C(2)-C(1)-H(1)	118.0
C(40B)-C(43B)	1.564(10)	C(1)-C(2)-H(2A)	120.5
C(41B)-H(41D)	0.9800	C(3)-C(2)-C(1)	119.01(12)
C(41B)-H(41E)	0.9800	C(3)-C(2)-H(2A)	120.5
C(41B)-H(41F)	0.9800	C(2)-C(3)-H(3)	120.3
C(42B)-H(42D)	0.9800	C(2)-C(3)-C(4)	119.41(12)
C(42B)-H(42E)	0.9800	C(4)-C(3)-H(3)	120.3
C(42B)-H(42F)	0.9800	C(3)-C(4)-C(5)	123.28(12)
C(43B)-C(44B)	1.519(8)	C(3)-C(4)-C(9)	117.38(12)
C(43B)-C(45B)	1.525(8)	C(5)-C(4)-C(9)	119.34(12)
C(44B)-H(44D)	0.9800	C(4)-C(5)-H(5A)	120.1
C(44B)-H(44E)	0.9800	C(6)-C(5)-C(4)	119.85(12)
C(44B)-H(44F)	0.9800	C(6)-C(5)-H(5A)	120.1
C(45B)-H(45D)	0.9800	C(5)-C(6)-H(6)	119.1
C(45B)-H(45E)	0.9800	C(5)-C(6)-C(7)	121.82(13)
C(45B)-H(45F)	0.9800	C(7)-C(6)-H(6)	119.1
B(1)-O(2)-C(13)	107.19(9)	C(6)-C(7)-H(7)	120.0
B(1)-O(3)-C(16)	107.02(9)	C(8)-C(7)-C(6)	119.98(12)
C(1)-N(1)-C(9)	117.28(11)	C(8)-C(7)-H(7)	120.0
C(8)-N(2)-H(2)	114.1(11)	N(2)-C(8)-C(9)	115.08(11)
C(10)-N(2)-H(2)	117.0(11)	C(7)-C(8)-N(2)	125.55(11)
C(10)-N(2)-C(8)	128.93(11)	C(7)-C(8)-C(9)	119.35(11)
O(4)-N(3)-O(5)	123.34(11)	N(1)-C(9)-C(4)	122.78(11)
O(4)-N(3)-C(25)	118.29(11)	N(1)-C(9)-C(8)	117.57(11)
O(5)-N(3)-C(25)	118.37(11)	C(4)-C(9)-C(8)	119.64(11)
N(1)-C(1)-H(1)	118.0	O(1)-C(10)-N(2)	123.49(12)

O(1)-C(10)-C(11)	122.11(11)	C(13)-C(15)-H(15B)	109.5
N(2)-C(10)-C(11)	114.40(11)	C(13)-C(15)-H(15C)	109.5
C(10)-C(11)-H(11A)	109.5	H(15A)-C(15)-H(15B)	109.5
C(10)-C(11)-H(11B)	109.5	H(15A)-C(15)-H(15C)	109.5
C(10)-C(11)-C(12)	110.85(10)	H(15B)-C(15)-H(15C)	109.5
H(11A)-C(11)-H(11B)	108.1	O(3)-C(16)-C(13)	102.56(9)
C(12)-C(11)-H(11A)	109.5	O(3)-C(16)-C(17)	108.31(10)
C(12)-C(11)-H(11B)	109.5	O(3)-C(16)-C(18)	107.15(10)
C(11)-C(12)-H(12)	108.3	C(17)-C(16)-C(13)	114.60(10)
C(11)-C(12)-C(19)	109.31(10)	C(17)-C(16)-C(18)	110.30(11)
C(11)-C(12)-B(1)	111.22(10)	C(18)-C(16)-C(13)	113.26(10)
C(19)-C(12)-H(12)	108.3	C(16)-C(17)-H(17A)	109.5
C(19)-C(12)-B(1)	111.37(10)	C(16)-C(17)-H(17B)	109.5
B(1)-C(12)-H(12)	108.3	C(16)-C(17)-H(17C)	109.5
O(2)-C(13)-C(14)	108.79(10)	H(17A)-C(17)-H(17B)	109.5
O(2)-C(13)-C(15)	106.79(10)	H(17A)-C(17)-H(17C)	109.5
O(2)-C(13)-C(16)	102.22(9)	H(17B)-C(17)-H(17C)	109.5
C(14)-C(13)-C(15)	109.71(11)	C(16)-C(18)-H(18A)	109.5
C(14)-C(13)-C(16)	115.42(11)	C(16)-C(18)-H(18B)	109.5
C(15)-C(13)-C(16)	113.23(10)	C(16)-C(18)-H(18C)	109.5
C(13)-C(14)-H(14A)	109.5	H(18A)-C(18)-H(18B)	109.5
C(13)-C(14)-H(14B)	109.5	H(18A)-C(18)-H(18C)	109.5
C(13)-C(14)-H(14C)	109.5	H(18B)-C(18)-H(18C)	109.5
H(14A)-C(14)-H(14B)	109.5	C(12)-C(19)-H(19)	107.7
H(14A)-C(14)-H(14C)	109.5	C(20)-C(19)-C(12)	111.21(10)
H(14B)-C(14)-H(14C)	109.5	C(20)-C(19)-H(19)	107.7
C(13)-C(15)-H(15A)	109.5	C(22)-C(19)-C(12)	112.14(10)

C(22)-C(19)-H(19)	107.7	C(25)-C(26)-C(27)	118.45(12)
C(22)-C(19)-C(20)	110.16(10)	C(27)-C(26)-H(26)	120.8
C(19)-C(20)-H(20A)	108.4	C(22)-C(27)-H(27)	119.5
C(19)-C(20)-H(20B)	108.4	C(26)-C(27)-C(22)	120.97(11)
H(20A)-C(20)-H(20B)	107.5	C(26)-C(27)-H(27)	119.5
C(21)-C(20)-C(19)	115.31(11)	O(2)-B(1)-O(3)	113.25(11)
C(21)-C(20)-H(20A)	108.4	O(2)-B(1)-C(12)	122.41(11)
C(21)-C(20)-H(20B)	108.4	O(3)-B(1)-C(12)	123.99(11)
C(20)-C(21)-H(21A)	109.5	C(28)-N(4)-C(36)	117.03(11)
C(20)-C(21)-H(21B)	109.5	C(35)-N(5)-H(5)	114.0(11)
C(20)-C(21)-H(21C)	109.5	C(37)-N(5)-H(5)	117.1(11)
H(21A)-C(21)-H(21B)	109.5	C(37)-N(5)-C(35)	127.11(11)
H(21A)-C(21)-H(21C)	109.5	O(9)-N(6)-O(10)	123.26(12)
H(21B)-C(21)-H(21C)	109.5	O(9)-N(6)-C(52)	118.44(12)
C(23)-C(22)-C(19)	119.72(11)	O(10)-N(6)-C(52)	118.28(12)
C(23)-C(22)-C(27)	118.57(11)	N(4)-C(28)-H(28)	117.7
C(27)-C(22)-C(19)	121.69(11)	N(4)-C(28)-C(29)	124.58(14)
C(22)-C(23)-H(23)	119.3	C(29)-C(28)-H(28)	117.7
C(24)-C(23)-C(22)	121.37(12)	C(28)-C(29)-H(29)	120.7
C(24)-C(23)-H(23)	119.3	C(30)-C(29)-C(28)	118.55(13)
C(23)-C(24)-H(24)	120.8	C(30)-C(29)-H(29)	120.7
C(25)-C(24)-C(23)	118.39(12)	C(29)-C(30)-H(30)	120.1
C(25)-C(24)-H(24)	120.8	C(29)-C(30)-C(31)	119.79(12)
C(24)-C(25)-N(3)	118.38(11)	C(31)-C(30)-H(30)	120.1
C(24)-C(25)-C(26)	122.22(11)	C(30)-C(31)-C(36)	117.10(13)
C(26)-C(25)-N(3)	119.39(12)	C(32)-C(31)-C(30)	123.43(12)
C(25)-C(26)-H(26)	120.8	C(32)-C(31)-C(36)	119.46(12)

C(31)-C(32)-H(32)	120.1	C(46)-C(39)-H(39)	109.1
C(33)-C(32)-C(31)	119.87(13)	C(46)-C(39)-B(2B)	109.32(10)
C(33)-C(32)-H(32)	120.1	B(2B)-C(39)-H(39)	109.1
C(32)-C(33)-H(33)	119.1	C(39)-C(46)-H(46)	106.6
C(32)-C(33)-C(34)	121.75(13)	C(47)-C(46)-C(39)	114.22(11)
C(34)-C(33)-H(33)	119.1	C(47)-C(46)-H(46)	106.6
C(33)-C(34)-H(34)	120.1	C(49)-C(46)-C(39)	112.25(10)
C(35)-C(34)-C(33)	119.86(12)	C(49)-C(46)-H(46)	106.6
C(35)-C(34)-H(34)	120.1	C(49)-C(46)-C(47)	110.02(10)
N(5)-C(35)-C(36)	115.22(11)	C(46)-C(47)-H(47A)	108.5
C(34)-C(35)-N(5)	125.08(12)	C(46)-C(47)-H(47B)	108.5
C(34)-C(35)-C(36)	119.71(12)	H(47A)-C(47)-H(47B)	107.5
N(4)-C(36)-C(31)	122.96(12)	C(48)-C(47)-C(46)	115.16(11)
N(4)-C(36)-C(35)	117.69(11)	C(48)-C(47)-H(47A)	108.5
C(31)-C(36)-C(35)	119.35(12)	C(48)-C(47)-H(47B)	108.5
O(6)-C(37)-N(5)	123.15(12)	C(47)-C(48)-H(48A)	109.5
O(6)-C(37)-C(38)	121.12(11)	C(47)-C(48)-H(48B)	109.5
N(5)-C(37)-C(38)	115.72(11)	C(47)-C(48)-H(48C)	109.5
C(37)-C(38)-H(38A)	109.7	H(48A)-C(48)-H(48B)	109.5
C(37)-C(38)-H(38B)	109.7	H(48A)-C(48)-H(48C)	109.5
C(37)-C(38)-C(39)	110.02(10)	H(48B)-C(48)-H(48C)	109.5
H(38A)-C(38)-H(38B)	108.2	C(50)-C(49)-C(46)	123.00(11)
C(39)-C(38)-H(38A)	109.7	C(54)-C(49)-C(46)	118.75(11)
C(39)-C(38)-H(38B)	109.7	C(54)-C(49)-C(50)	118.25(12)
C(38)-C(39)-H(39)	109.1	C(49)-C(50)-H(50)	119.5
C(38)-C(39)-C(46)	110.78(10)	C(51)-C(50)-C(49)	121.05(12)
C(38)-C(39)-B(2B)	109.50(10)	C(51)-C(50)-H(50)	119.5

C(50)-C(51)-H(51)	120.7	C(40A)-C(41A)-H(41B)	109.5
C(52)-C(51)-C(50)	118.54(12)	C(40A)-C(41A)-H(41C)	109.5
C(52)-C(51)-H(51)	120.7	H(41A)-C(41A)-H(41B)	109.5
C(51)-C(52)-N(6)	119.13(12)	H(41A)-C(41A)-H(41C)	109.5
C(51)-C(52)-C(53)	122.14(12)	H(41B)-C(41A)-H(41C)	109.5
C(53)-C(52)-N(6)	118.72(12)	C(40A)-C(42A)-H(42A)	109.5
C(52)-C(53)-H(53)	120.9	C(40A)-C(42A)-H(42B)	109.5
C(52)-C(53)-C(54)	118.17(13)	C(40A)-C(42A)-H(42C)	109.5
C(54)-C(53)-H(53)	120.9	H(42A)-C(42A)-H(42B)	109.5
C(49)-C(54)-H(54)	119.1	H(42A)-C(42A)-H(42C)	109.5
C(53)-C(54)-C(49)	121.81(13)	H(42B)-C(42A)-H(42C)	109.5
C(53)-C(54)-H(54)	119.1	O(8A)-C(43A)-C(40A)	103.77(14)
O(7A)-B(2B)-C(39)	124.61(11)	O(8A)-C(43A)-C(44A)	105.7(3)
O(7A)-B(2B)-O(8A)	113.46(14)	O(8A)-C(43A)-C(45A)	108.6(2)
O(8A)-B(2B)-C(39)	121.17(13)	C(44A)-C(43A)-C(40A)	112.95(14)
O(7B)-B(2B)-C(39)	125.5(6)	C(45A)-C(43A)-C(40A)	114.78(14)
O(7B)-B(2B)-O(8B)	99(2)	C(45A)-C(43A)-C(44A)	110.33(16)
O(8B)-B(2B)-C(39)	128.5(12)	C(43A)-C(44A)-H(44A)	109.5
B(2B)-O(7A)-C(40A)	107.89(10)	C(43A)-C(44A)-H(44B)	109.5
B(2B)-O(8A)-C(43A)	106.78(18)	C(43A)-C(44A)-H(44C)	109.5
O(7A)-C(40A)-C(41A)	108.20(11)	H(44A)-C(44A)-H(44B)	109.5
O(7A)-C(40A)-C(42A)	107.16(11)	H(44A)-C(44A)-H(44C)	109.5
O(7A)-C(40A)-C(43A)	102.65(11)	H(44B)-C(44A)-H(44C)	109.5
C(41A)-C(40A)-C(42A)	109.76(12)	C(43A)-C(45A)-H(45A)	109.5
C(41A)-C(40A)-C(43A)	115.00(13)	C(43A)-C(45A)-H(45B)	109.5
C(42A)-C(40A)-C(43A)	113.42(12)	C(43A)-C(45A)-H(45C)	109.5
C(40A)-C(41A)-H(41A)	109.5	H(45A)-C(45A)-H(45B)	109.5

H(45A)-C(45A)-H(45C)	109.5	C(45B)-C(43B)-C(40B)	111.2(14)
H(45B)-C(45A)-H(45C)	109.5	C(43B)-C(44B)-H(44D)	109.5
B(2B)-O(7B)-C(40B)	109.6(10)	C(43B)-C(44B)-H(44E)	109.5
B(2B)-O(8B)-C(43B)	124.2(19)	C(43B)-C(44B)-H(44F)	109.5
O(7B)-C(40B)-C(41B)	96.6(12)	H(44D)-C(44B)-H(44E)	109.5
O(7B)-C(40B)-C(42B)	103.7(13)	H(44D)-C(44B)-H(44F)	109.5
O(7B)-C(40B)-C(43B)	111.4(12)	H(44E)-C(44B)-H(44F)	109.5
C(41B)-C(40B)-C(42B)	112.3(15)	C(43B)-C(45B)-H(45D)	109.5
C(41B)-C(40B)-C(43B)	117.6(13)	C(43B)-C(45B)-H(45E)	109.5
C(42B)-C(40B)-C(43B)	113.0(14)	C(43B)-C(45B)-H(45F)	109.5
C(40B)-C(41B)-H(41D)	109.5	H(45D)-C(45B)-H(45E)	109.5
C(40B)-C(41B)-H(41E)	109.5	H(45D)-C(45B)-H(45F)	109.5
C(40B)-C(41B)-H(41F)	109.5	H(45E)-C(45B)-H(45F)	109.5
H(41D)-C(41B)-H(41E)	109.5		
H(41D)-C(41B)-H(41F)	109.5		
H(41E)-C(41B)-H(41F)	109.5		
C(40B)-C(42B)-H(42D)	109.5		
C(40B)-C(42B)-H(42E)	109.5		
C(40B)-C(42B)-H(42F)	109.5		
H(42D)-C(42B)-H(42E)	109.5		
H(42D)-C(42B)-H(42F)	109.5		
H(42E)-C(42B)-H(42F)	109.5		
O(8B)-C(43B)-C(40B)	87(2)		
O(8B)-C(43B)-C(44B)	106(3)		
O(8B)-C(43B)-C(45B)	100(4)		
C(44B)-C(43B)-C(40B)	110.0(15)		
C(44B)-C(43B)-C(45B)	132.2(19)		

Symmetry transformations used to generate equivalent atoms:

Table S6. Anisotropic displacement parameters ($Å^2$ x 10^3) for **(±)-4u**. 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}
O(1)	49(1)	29(1)	24(1)	-1(1)	13(1)	6(1)
O(2)	27(1)	24(1)	18(1)	-4(1)	6(1)	-2(1)
O(3)	22(1)	26(1)	22(1)	-3(1)	4(1)	1(1)
O(4)	56(1)	44(1)	23(1)	12(1)	9(1)	-2(1)
O(5)	41(1)	44(1)	24(1)	-7(1)	1(1)	3(1)
N(1)	26(1)	24(1)	19(1)	-1(1)	2(1)	-1(1)
N(2)	29(1)	24(1)	19(1)	-1(1)	6(1)	4(1)
N(3)	31(1)	34(1)	20(1)	2(1)	4(1)	9(1)
C(1)	32(1)	28(1)	21(1)	-4(1)	5(1)	-3(1)
C(2)	38(1)	38(1)	19(1)	-2(1)	7(1)	-7(1)
C(3)	33(1)	34(1)	23(1)	8(1)	3(1)	-5(1)
C(4)	22(1)	27(1)	25(1)	5(1)	0(1)	-3(1)
C(5)	34(1)	26(1)	34(1)	8(1)	5(1)	0(1)
C(6)	40(1)	22(1)	38(1)	2(1)	7(1)	4(1)
C(7)	32(1)	29(1)	26(1)	-1(1)	7(1)	4(1)
C(8)	20(1)	25(1)	21(1)	2(1)	1(1)	1(1)
C(9)	19(1)	24(1)	20(1)	1(1)	-1(1)	-1(1)
C(10)	26(1)	28(1)	18(1)	-1(1)	4(1)	0(1)
C(11)	35(1)	28(1)	16(1)	-1(1)	4(1)	2(1)

C(12)	26(1)	22(1)	17(1)	1(1)	4(1)	-1(1)
C(13)	25(1)	25(1)	17(1)	-2(1)	4(1)	0(1)
C(14)	24(1)	36(1)	26(1)	-4(1)	3(1)	0(1)
C(15)	35(1)	29(1)	22(1)	3(1)	8(1)	0(1)
C(16)	23(1)	25(1)	20(1)	-2(1)	4(1)	2(1)
C(17)	31(1)	32(1)	25(1)	-8(1)	3(1)	1(1)
C(18)	34(1)	25(1)	31(1)	3(1)	7(1)	4(1)
C(19)	26(1)	21(1)	19(1)	0(1)	4(1)	0(1)
C(20)	30(1)	30(1)	21(1)	0(1)	6(1)	5(1)
C(21)	36(1)	31(1)	33(1)	-2(1)	3(1)	8(1)
C(22)	24(1)	22(1)	20(1)	2(1)	5(1)	6(1)
C(23)	28(1)	23(1)	22(1)	1(1)	4(1)	1(1)
C(24)	29(1)	23(1)	23(1)	5(1)	7(1)	3(1)
C(25)	26(1)	27(1)	17(1)	3(1)	4(1)	7(1)
C(26)	25(1)	26(1)	24(1)	0(1)	2(1)	2(1)
C(27)	25(1)	24(1)	24(1)	5(1)	6(1)	2(1)
B(1)	27(1)	22(1)	14(1)	4(1)	1(1)	2(1)
O(6)	48(1)	28(1)	22(1)	-4(1)	8(1)	-3(1)
O(9)	64(1)	60(1)	24(1)	-2(1)	11(1)	12(1)
O(10)	59(1)	58(1)	27(1)	17(1)	2(1)	11(1)
N(4)	30(1)	28(1)	20(1)	2(1)	3(1)	-2(1)
N(5)	32(1)	23(1)	19(1)	-1(1)	4(1)	-2(1)
N(6)	35(1)	39(1)	22(1)	5(1)	3(1)	-5(1)
C(28)	37(1)	36(1)	22(1)	-1(1)	5(1)	-3(1)
C(29)	32(1)	49(1)	21(1)	5(1)	5(1)	-4(1)
C(30)	27(1)	41(1)	29(1)	16(1)	2(1)	-3(1)
C(31)	22(1)	30(1)	30(1)	10(1)	-1(1)	-1(1)

C(32)	30(1)	26(1)	44(1)	12(1)	4(1)	0(1)
C(33)	31(1)	21(1)	49(1)	2(1)	3(1)	2(1)
C(34)	26(1)	28(1)	32(1)	-1(1)	4(1)	3(1)
C(35)	21(1)	24(1)	23(1)	3(1)	1(1)	0(1)
C(36)	21(1)	26(1)	22(1)	4(1)	-1(1)	0(1)
C(37)	22(1)	27(1)	19(1)	-1(1)	3(1)	0(1)
C(38)	31(1)	25(1)	18(1)	-1(1)	4(1)	-3(1)
C(39)	26(1)	23(1)	19(1)	1(1)	5(1)	1(1)
C(46)	29(1)	23(1)	23(1)	1(1)	7(1)	2(1)
C(47)	45(1)	24(1)	22(1)	-1(1)	6(1)	-6(1)
C(48)	43(1)	27(1)	29(1)	-2(1)	-2(1)	-6(1)
C(49)	29(1)	23(1)	23(1)	2(1)	4(1)	-5(1)
C(50)	28(1)	26(1)	24(1)	6(1)	1(1)	-2(1)
C(51)	28(1)	28(1)	24(1)	1(1)	5(1)	-2(1)
C(52)	29(1)	31(1)	19(1)	4(1)	3(1)	-6(1)
C(53)	36(1)	32(1)	28(1)	8(1)	4(1)	3(1)
C(54)	38(1)	28(1)	27(1)	3(1)	10(1)	4(1)
B(2B)	27(1)	24(1)	18(1)	3(1)	5(1)	0(1)
O(7A)	22(1)	24(1)	19(1)	-2(1)	3(1)	0(1)
O(8A)	28(1)	28(1)	22(1)	-6(1)	4(1)	0(1)
C(40A)	22(1)	28(1)	22(1)	-3(1)	0(1)	-1(1)
C(41A)	39(1)	37(1)	23(1)	-7(1)	0(1)	-1(1)
C(42A)	35(1)	29(1)	34(1)	1(1)	-3(1)	-4(1)
C(43A)	23(1)	36(1)	28(1)	-7(1)	1(1)	0(1)
C(44A)	55(1)	54(1)	42(1)	-8(1)	-12(1)	28(1)
C(45A)	26(1)	74(1)	50(1)	-28(1)	12(1)	-13(1)
O(7B)	22(1)	24(1)	19(1)	-2(1)	3(1)	0(1)

O(8B)	28(1)	28(1)	22(1)	-6(1)	4(1)	0(1)
C(40B)	22(1)	28(1)	22(1)	-3(1)	0(1)	-1(1)
C(41B)	54(9)	47(7)	18(6)	2(5)	-9(5)	-1(7)
C(42B)	60(11)	38(5)	30(10)	-16(5)	16(8)	-13(6)
C(43B)	23(1)	36(1)	28(1)	-7(1)	1(1)	0(1)
C(44B)	29(6)	87(15)	61(13)	-5(10)	-2(6)	18(7)
C(45B)	73(13)	31(5)	37(8)	-5(5)	13(8)	-12(5)

Table S7. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **(±)-4u**.

	x	y	z	U(eq)
H(2)	3789(10)	568(9)	9343(7)	28
H(1)	2931	1066	10981	32
H(2A)	2838	53	11763	38
H(3)	3290	-1284	11564	36
H(5A)	3854	-2303	10771	38
H(6)	4296	-2544	9767	40
H(7)	4371	-1473	9017	35
H(11A)	4700	1289	8312	31
H(11B)	3689	1341	8497	31
H(12)	3187	625	7514	26
H(14A)	6979	712	6838	43
H(14B)	6898	-106	6410	43
H(14C)	6739	-148	7154	43

H(15A)	4905	1044	5906	43
H(15B)	5824	727	5663	43
H(15C)	5832	1483	6155	43
H(17A)	5402	-783	5606	44
H(17B)	4503	-245	5563	44
H(17C)	4484	-1189	5783	44
H(18A)	5543	-979	7351	45
H(18B)	5966	-1360	6744	45
H(18C)	4962	-1591	6875	45
H(19)	4061	2194	7434	27
H(20A)	2207	1778	7471	32
H(20B)	2824	2258	8016	32
H(21A)	2176	2929	6798	50
H(21B)	2859	3408	7306	50
H(21C)	1865	3203	7476	50
H(23)	4208	2869	6471	29
H(24)	4029	2950	5350	30
H(26)	2483	890	5280	30
H(27)	2618	849	6406	29
H(5)	1622(11)	5411(9)	4363(7)	29
H(28)	787	5802	6024	38
H(29)	333	4725	6657	40
H(30)	385	3383	6282	39
H(32)	739	2411	5385	40
H(33)	1199	2247	4378	40
H(34)	1639	3381	3784	34
H(38A)	2436	6153	3512	30

H(38B)	1373	6291	3387	30
H(39)	2542	5734	2466	27
H(46)	1232	7039	2383	30
H(47A)	2384	8021	2445	36
H(47B)	2446	7482	3086	36
H(48A)	3590	7250	2091	50
H(48B)	3666	6746	2752	50
H(48C)	3883	7711	2756	50
H(50)	2767	5968	1462	31
H(51)	2730	6045	340	32
H(53)	966	7946	327	38
H(54)	971	7827	1441	37
H(41A)	383	4987	585	50
H(41B)	-270	4211	624	50
H(41C)	788	4074	624	50
H(42A)	971	3319	1624	50
H(42B)	-92	3338	1654	50
H(42C)	566	3662	2251	50
H(44A)	-924	6162	1570	77
H(44B)	-1014	5520	987	77
H(44C)	-100	6022	1151	77
H(45A)	-777	4235	2392	74
H(45B)	-1374	4335	1717	74
H(45C)	-1394	5033	2256	74
H(41D)	169	6080	1063	61
H(41E)	-540	5499	655	61
H(41F)	496	5475	529	61

H(42D)	746	4075	708	62
H(42E)	-223	3805	893	62
H(42F)	648	3647	1387	62
H(44D)	-1652	5244	2043	89
H(44E)	-1459	5228	1304	89
H(44F)	-1048	5947	1767	89
H(45D)	424	4039	2491	70
H(45E)	-371	3583	2061	70
H(45F)	-581	4088	2685	70

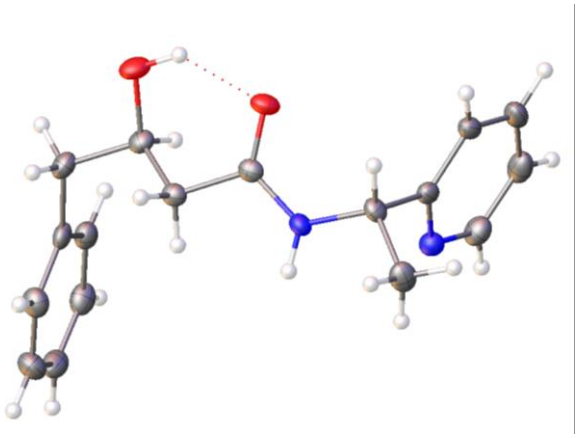


Table S8. Crystal data and structure refinement for **(±)-7a**.

Report date	2019-05-21	
Identification code	engle187	
Empirical formula	C17 H20 N2 O2	
Molecular formula	C17 H20 N2 O2	
Formula weight	284.35b	
Temperature	100.0 K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 17.9183(4) Å	α= 90°.
	b = 8.8857(2) Å	β= 105.785(2)°.
	c = 19.8929(4) Å	γ = 90°.
Volume	3047.84(12) $Å^3$	
Z	8	
Density (calculated)	1.239 Mg/m^3	
Absorption coefficient	0.655 mm^{-1}	
F(000)	1216	
Crystal size	0.2 x 0.025 x 0.01 mm^3	

Crystal color, habit	clear colourless needle
Theta range for data collection	2.946 to 68.294°.
Index ranges	-21<=h<=21, -10<=k<=10, -23<=l<=23
Reflections collected	31057
Independent reflections	5568 [R(int) = 0.0642]
Completeness to theta = 67.679°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7531 and 0.6540
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5568 / 2 / 391
Goodness-of-fit on F^2	1.017
Final R indices [I>2sigma(I)]	R1 = 0.0518, wR2 = 0.1234
R indices (all data)	R1 = 0.0851, wR2 = 0.1418
Extinction coefficient	n/a
Largest diff. peak and hole	0.444 and -0.250 e.$Å^{-3}$

Table S9. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **(±)-7a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	6192(1)	4113(2)	1319(1)	25(1)
O(2)	6941(1)	1596(2)	1898(1)	36(1)
N(1)	4101(1)	5992(2)	1560(1)	21(1)
N(2)	5767(1)	5745(2)	1999(1)	20(1)
C(1)	3368(1)	5524(3)	1310(1)	24(1)
C(2)	3038(1)	5184(3)	618(1)	27(1)
C(3)	3481(1)	5356(2)	156(1)	24(1)
C(4)	4238(1)	5862(2)	400(1)	22(1)
C(5)	4533(1)	6155(2)	1110(1)	19(1)
C(6)	5357(1)	6703(2)	1420(1)	21(1)
C(7)	5367(1)	8317(2)	1677(1)	28(1)
C(8)	6153(1)	4515(2)	1904(1)	20(1)
C(9)	6556(1)	3639(2)	2554(1)	21(1)
C(10)	6553(1)	1940(3)	2412(1)	24(1)
C(11)	6959(1)	1079(3)	3075(1)	29(1)
C(12)	6543(1)	1180(3)	3636(1)	24(1)
C(13)	5864(1)	367(2)	3572(1)	26(1)
C(14)	5479(1)	419(3)	4084(1)	28(1)
C(15)	5762(1)	1288(3)	4671(1)	26(1)
C(16)	6425(1)	2137(3)	4740(1)	28(1)
C(17)	6813(1)	2087(3)	4225(1)	26(1)
O(3)	3723(1)	8410(2)	3651(1)	25(1)

O(4)	3151(1)	11048(2)	3055(1)	28(1)
N(3)	5802(1)	6317(2)	3508(1)	23(1)
N(4)	4142(1)	6713(2)	2992(1)	20(1)
C(18)	6537(1)	6728(3)	3799(1)	28(1)
C(19)	6823(1)	7064(3)	4499(1)	31(1)
C(20)	6334(1)	6950(3)	4927(1)	30(1)
C(21)	5576(1)	6502(2)	4636(1)	24(1)
C(22)	5331(1)	6209(2)	3924(1)	20(1)
C(23)	4502(1)	5724(2)	3578(1)	20(1)
C(24)	4477(1)	4107(2)	3318(1)	28(1)
C(25)	3777(1)	7980(2)	3075(1)	19(1)
C(26)	3406(1)	8860(2)	2415(1)	20(1)
C(27)	3497(1)	10560(2)	2528(1)	21(1)
C(28)	3113(1)	11442(2)	1865(1)	24(1)
C(29)	3506(1)	11279(2)	1289(1)	21(1)
C(30)	3185(1)	10444(3)	692(1)	28(1)
C(31)	3539(1)	10352(3)	158(1)	31(1)
C(32)	4230(1)	11099(3)	213(1)	29(1)
C(33)	4567(1)	11921(3)	802(1)	28(1)
C(34)	4208(1)	12013(2)	1336(1)	24(1)

Table S10. Bond lengths [Å] and angles [°] for **(±)-7a**.

O(1)-C(8)	1.238(3)	N(1)-C(5)	1.341(3)
O(2)-C(10)	1.418(3)	N(2)-C(6)	1.459(3)
N(1)-C(1)	1.338(3)	N(2)-C(8)	1.335(3)

C(1)-C(2)	1.376(3)	C(23)-C(24)	1.524(3)
C(2)-C(3)	1.376(3)	C(25)-C(26)	1.517(3)
C(3)-C(4)	1.386(3)	C(26)-C(27)	1.530(3)
C(4)-C(5)	1.391(3)	C(27)-C(28)	1.528(3)
C(5)-C(6)	1.517(3)	C(28)-C(29)	1.506(3)
C(6)-C(7)	1.521(3)	C(29)-C(30)	1.386(3)
C(8)-C(9)	1.513(3)	C(29)-C(34)	1.398(3)
C(9)-C(10)	1.535(3)	C(30)-C(31)	1.380(3)
C(10)-C(11)	1.527(3)	C(31)-C(32)	1.383(3)
C(11)-C(12)	1.504(3)	C(32)-C(33)	1.375(3)
C(12)-C(13)	1.391(3)	C(33)-C(34)	1.386(3)
C(12)-C(17)	1.396(3)	C(1)-N(1)-C(5)	118.19(18)
C(13)-C(14)	1.379(3)	C(8)-N(2)-C(6)	122.36(17)
C(14)-C(15)	1.377(3)	N(1)-C(1)-C(2)	123.4(2)
C(15)-C(16)	1.382(3)	C(3)-C(2)-C(1)	118.3(2)
C(16)-C(17)	1.388(3)	C(2)-C(3)-C(4)	119.3(2)
O(3)-C(25)	1.236(2)	C(3)-C(4)-C(5)	118.82(19)
O(4)-C(27)	1.423(2)	N(1)-C(5)-C(4)	121.88(19)
N(3)-C(18)	1.337(3)	N(1)-C(5)-C(6)	115.90(18)
N(3)-C(22)	1.338(3)	C(4)-C(5)-C(6)	122.22(18)
N(4)-C(23)	1.461(3)	N(2)-C(6)-C(5)	111.08(17)
N(4)-C(25)	1.334(3)	N(2)-C(6)-C(7)	109.14(17)
C(18)-C(19)	1.380(3)	C(5)-C(6)-C(7)	111.15(17)
C(19)-C(20)	1.380(3)	O(1)-C(8)-N(2)	122.24(19)
C(20)-C(21)	1.382(3)	O(1)-C(8)-C(9)	121.28(19)
C(21)-C(22)	1.388(3)	N(2)-C(8)-C(9)	116.48(18)
C(22)-C(23)	1.520(3)	C(8)-C(9)-C(10)	111.85(17)

O(2)-C(10)-C(9)	111.48(18)	C(25)-C(26)-C(27)	112.15(17)
O(2)-C(10)-C(11)	107.55(17)	O(4)-C(27)-C(26)	111.01(17)
C(11)-C(10)-C(9)	110.96(18)	O(4)-C(27)-C(28)	107.17(16)
C(12)-C(11)-C(10)	113.22(17)	C(28)-C(27)-C(26)	111.98(17)
C(13)-C(12)-C(11)	119.9(2)	C(29)-C(28)-C(27)	114.43(16)
C(13)-C(12)-C(17)	118.1(2)	C(30)-C(29)-C(28)	122.22(19)
C(17)-C(12)-C(11)	121.9(2)	C(30)-C(29)-C(34)	117.6(2)
C(14)-C(13)-C(12)	121.1(2)	C(34)-C(29)-C(28)	120.2(2)
C(15)-C(14)-C(13)	120.2(2)	C(31)-C(30)-C(29)	121.4(2)
C(14)-C(15)-C(16)	119.9(2)	C(30)-C(31)-C(32)	120.0(2)
C(15)-C(16)-C(17)	120.0(2)	C(33)-C(32)-C(31)	119.9(2)
C(16)-C(17)-C(12)	120.6(2)	C(32)-C(33)-C(34)	119.8(2)
C(18)-N(3)-C(22)	117.64(19)	C(33)-C(34)-C(29)	121.3(2)
C(25)-N(4)-C(23)	122.33(17)		
N(3)-C(18)-C(19)	123.2(2)		
C(20)-C(19)-C(18)	118.8(2)		
C(19)-C(20)-C(21)	118.6(2)		
C(20)-C(21)-C(22)	118.9(2)		
N(3)-C(22)-C(21)	122.73(19)		
N(3)-C(22)-C(23)	116.26(18)		
C(21)-C(22)-C(23)	121.01(19)		
N(4)-C(23)-C(22)	110.91(16)		
N(4)-C(23)-C(24)	109.32(17)		
C(22)-C(23)-C(24)	110.89(17)		
O(3)-C(25)-N(4)	122.64(19)		
O(3)-C(25)-C(26)	121.11(18)		
N(4)-C(25)-C(26)	116.23(18)		

Symmetry transformations used to generate equivalent atoms:

Table S11. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **(±)-7a**. 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}
O(1)	32(1)	27(1)	19(1)	0(1)	11(1)	2(1)
O(2)	44(1)	41(1)	31(1)	6(1)	22(1)	19(1)
N(1)	24(1)	21(1)	17(1)	0(1)	6(1)	4(1)
N(2)	22(1)	26(1)	14(1)	0(1)	6(1)	1(1)
C(1)	22(1)	28(1)	23(1)	0(1)	9(1)	3(1)
C(2)	24(1)	30(1)	26(1)	1(1)	4(1)	4(1)
C(3)	30(1)	27(1)	14(1)	0(1)	1(1)	7(1)
C(4)	28(1)	23(1)	16(1)	1(1)	8(1)	7(1)
C(5)	25(1)	15(1)	19(1)	3(1)	7(1)	5(1)
C(6)	26(1)	21(1)	18(1)	4(1)	9(1)	1(1)
C(7)	33(1)	24(1)	26(1)	1(1)	6(1)	-2(1)
C(8)	18(1)	22(1)	20(1)	2(1)	7(1)	-4(1)
C(9)	19(1)	25(1)	19(1)	2(1)	6(1)	-1(1)
C(10)	23(1)	30(1)	23(1)	4(1)	11(1)	4(1)
C(11)	29(1)	30(1)	31(1)	5(1)	12(1)	11(1)
C(12)	25(1)	26(1)	20(1)	7(1)	6(1)	10(1)
C(13)	35(1)	19(1)	22(1)	0(1)	5(1)	2(1)
C(14)	28(1)	26(1)	30(1)	9(1)	6(1)	-1(1)
C(15)	29(1)	28(1)	22(1)	6(1)	11(1)	8(1)

C(16)	34(1)	28(1)	18(1)	-3(1)	3(1)	3(1)
C(17)	22(1)	31(1)	24(1)	6(1)	2(1)	0(1)
O(3)	32(1)	28(1)	17(1)	-4(1)	10(1)	-2(1)
O(4)	34(1)	28(1)	28(1)	-2(1)	19(1)	5(1)
N(3)	23(1)	23(1)	22(1)	-2(1)	6(1)	1(1)
N(4)	21(1)	24(1)	14(1)	1(1)	4(1)	2(1)
C(18)	22(1)	28(1)	35(1)	-1(1)	9(1)	2(1)
C(19)	23(1)	26(1)	39(1)	-5(1)	-2(1)	1(1)
C(20)	34(1)	28(1)	22(1)	-5(1)	-4(1)	7(1)
C(21)	30(1)	21(1)	18(1)	-1(1)	5(1)	6(1)
C(22)	24(1)	16(1)	19(1)	0(1)	5(1)	3(1)
C(23)	23(1)	22(1)	16(1)	4(1)	5(1)	0(1)
C(24)	32(1)	20(1)	30(1)	2(1)	3(1)	-3(1)
C(25)	17(1)	22(1)	19(1)	-2(1)	6(1)	-4(1)
C(26)	18(1)	22(1)	20(1)	-2(1)	5(1)	-2(1)
C(27)	19(1)	24(1)	24(1)	-1(1)	9(1)	2(1)
C(28)	21(1)	21(1)	30(1)	1(1)	8(1)	4(1)
C(29)	20(1)	20(1)	24(1)	7(1)	6(1)	8(1)
C(30)	23(1)	31(1)	28(1)	1(1)	3(1)	-2(1)
C(31)	34(1)	36(1)	22(1)	-2(1)	3(1)	1(1)
C(32)	36(1)	30(1)	26(1)	9(1)	15(1)	9(1)
C(33)	26(1)	25(1)	34(1)	10(1)	11(1)	2(1)
C(34)	24(1)	21(1)	26(1)	2(1)	4(1)	2(1)

Table S12. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for **(±)-7a**.

	x	y	z	U(eq)
H(2)	6756(14)	2190(30)	1519(14)	55
H(2A)	5705(13)	5920(30)	2421(9)	24
H(1)	3059	5421	1627	29
H(2B)	2517	4840	462	32
H(3)	3269	5129	-325	29
H(4)	4550	6006	88	27
H(6)	5637	6665	1049	25
H(7A)	5133	8359	2068	42
H(7B)	5070	8957	1296	42
H(7C)	5903	8677	1831	42
H(9A)	6292	3835	2923	25
H(9B)	7099	3992	2727	25
H(10)	6003	1587	2245	29
H(11A)	7003	7	2954	35
H(11B)	7491	1481	3259	35
H(13)	5663	-234	3168	31
H(14)	5017	-147	4032	34
H(15)	5502	1305	5029	31
H(16)	6615	2754	5140	33
H(17)	7267	2676	4274	32
H(4A)	3310(13)	10420(30)	3444(13)	42
H(4B)	4187(13)	6470(30)	2575(9)	24

H(18)	6879	6792	3509	34
H(19)	7347	7369	4684	37
H(20)	6516	7174	5411	36
H(21)	5229	6398	4919	28
H(23)	4198	5786	3930	24
H(24A)	3936	3790	3133	42
H(24B)	4737	3447	3705	42
H(24C)	4741	4043	2947	42
H(26A)	2847	8608	2255	24
H(26B)	3647	8556	2043	24
H(27)	4062	10812	2677	26
H(28A)	2568	11103	1689	28
H(28B)	3105	12521	1987	28
H(30)	2711	9924	649	34
H(31)	3308	9775	-247	38
H(32)	4471	11043	-157	35
H(33)	5045	12426	844	34
H(34)	4444	12585	1742	29

Table S13. Hydrogen bonds for **(±)-7a** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(4)-H(4A)...O(3)	0.93	1.94	2.699(2)	137.7
N(4)-H(4B)...N(1)	0.883(16)	2.028(17)	2.903(2)	170(2)

Symmetry transformations used to generate equivalent atoms:

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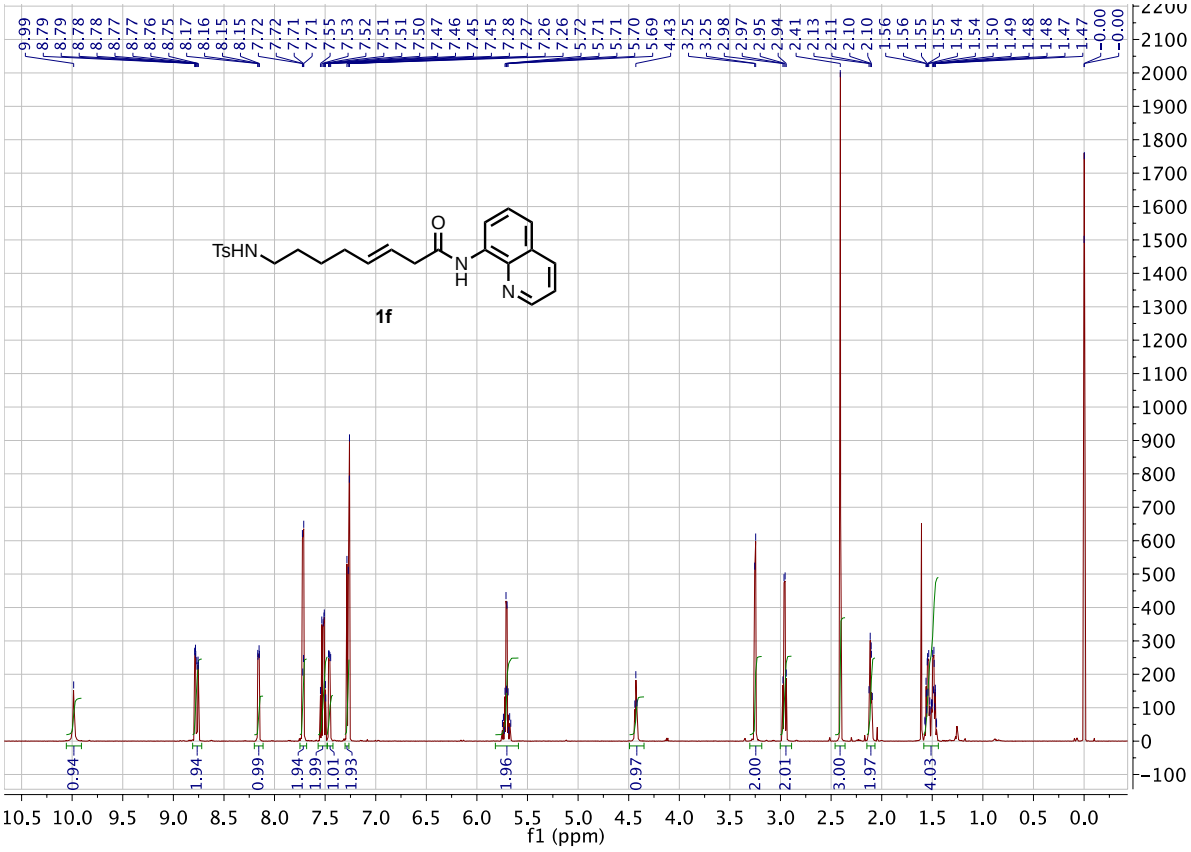
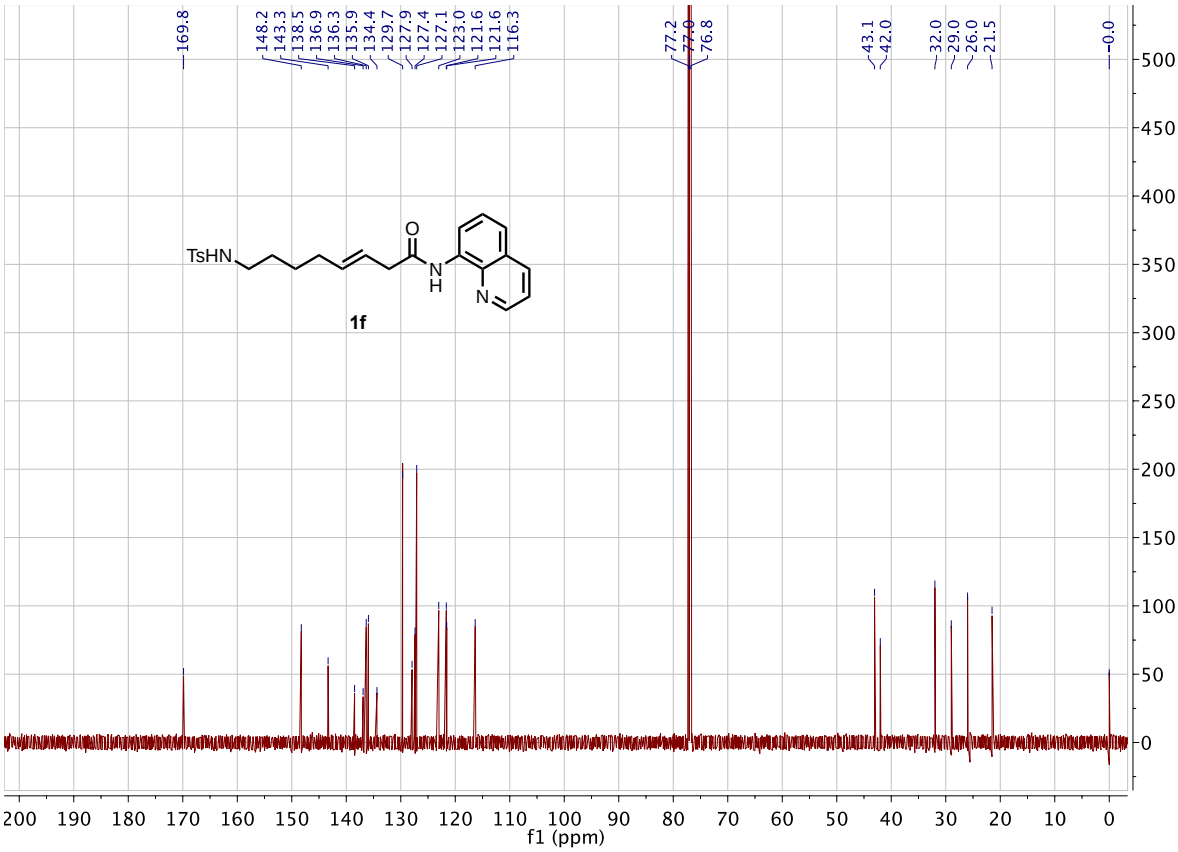
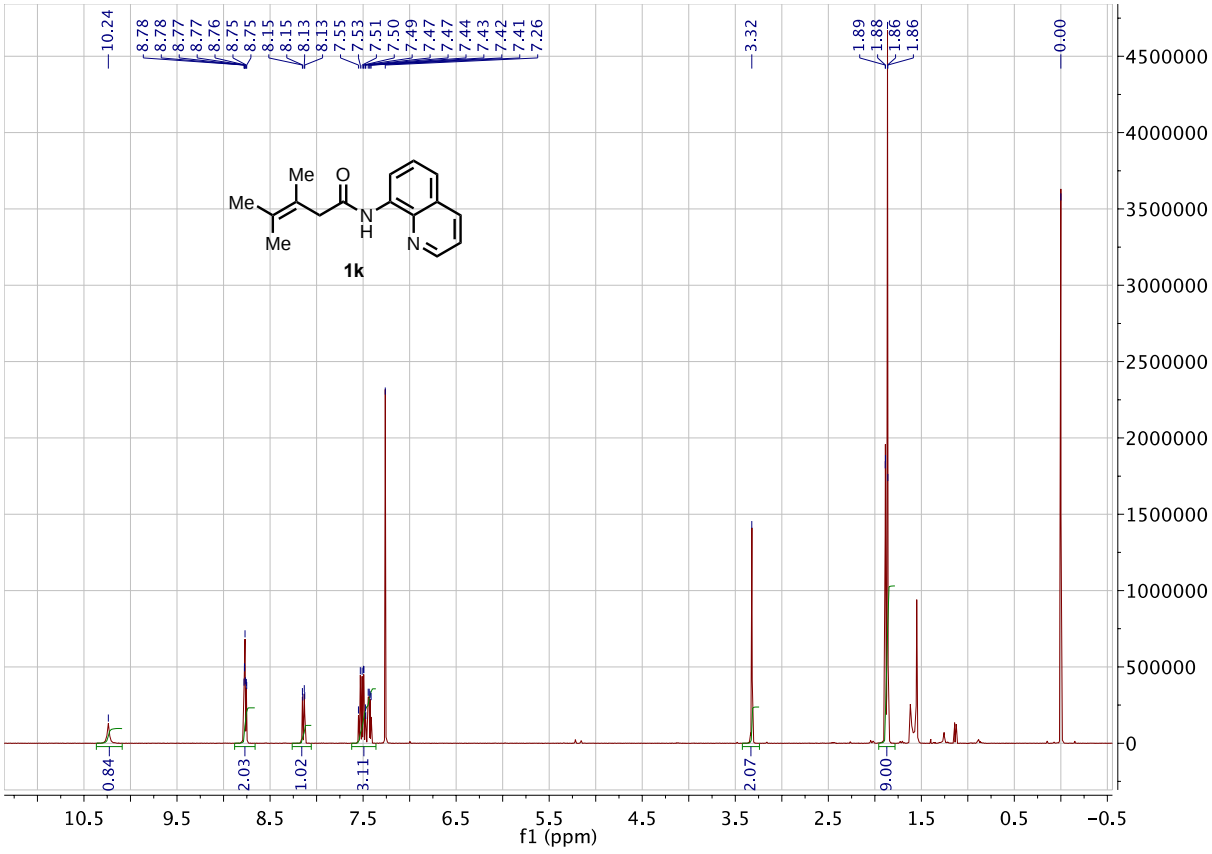
NMR Spectra and SFC Chromatograms



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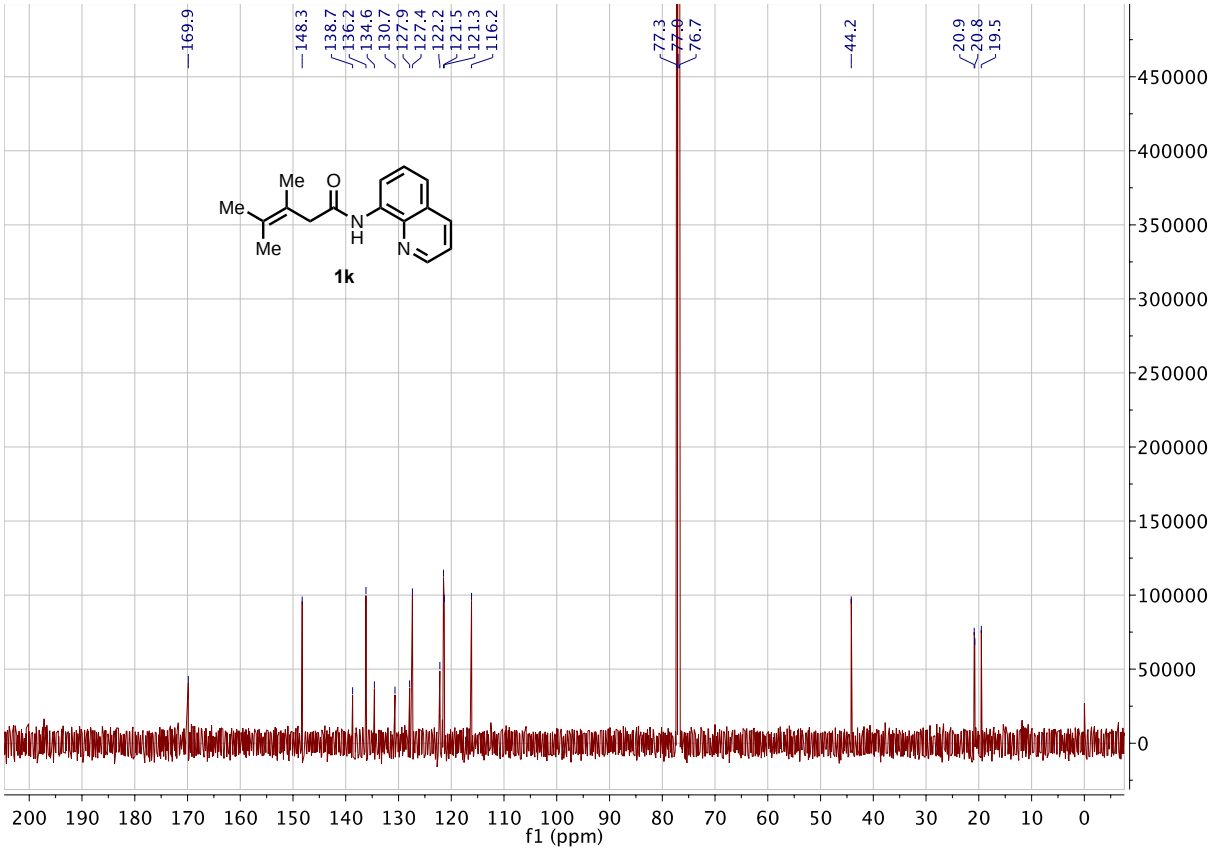
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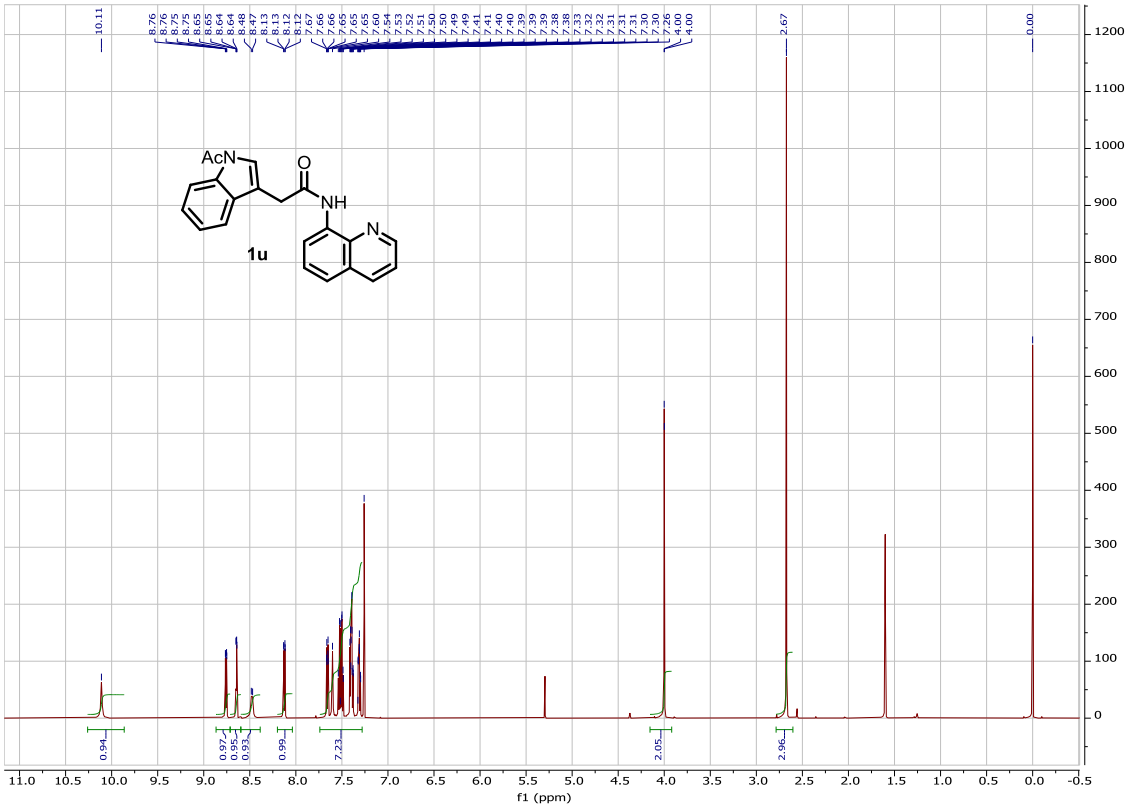
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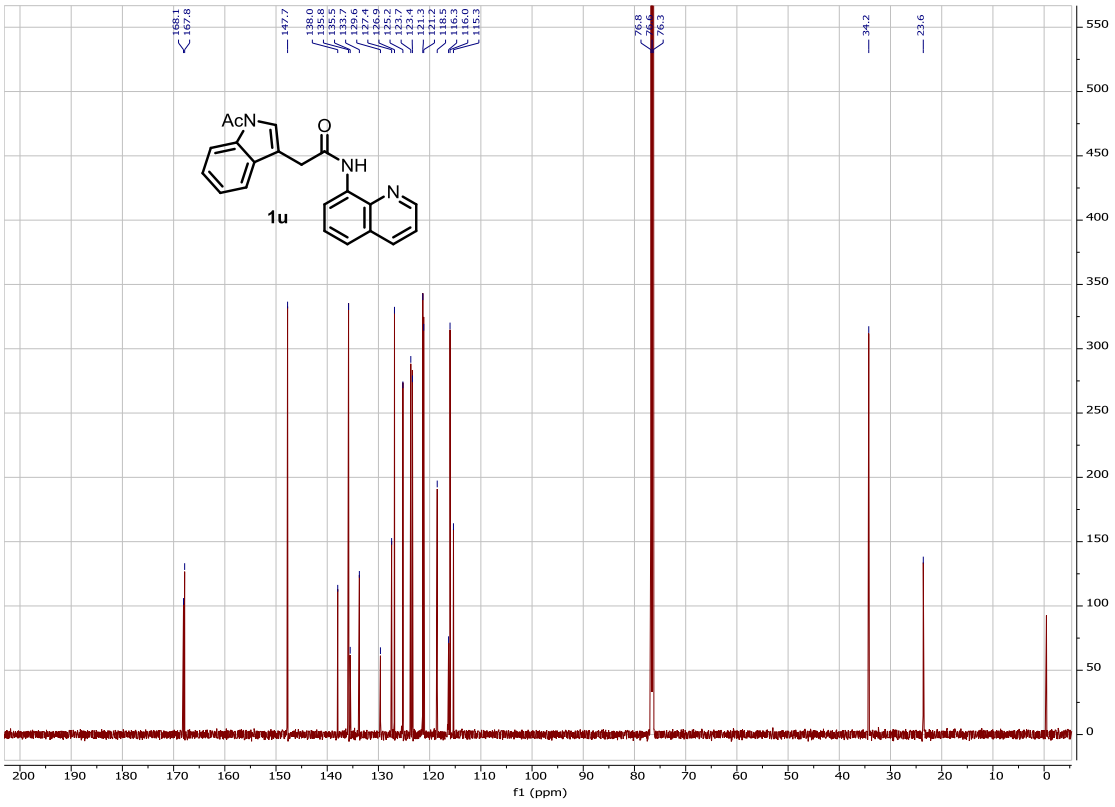
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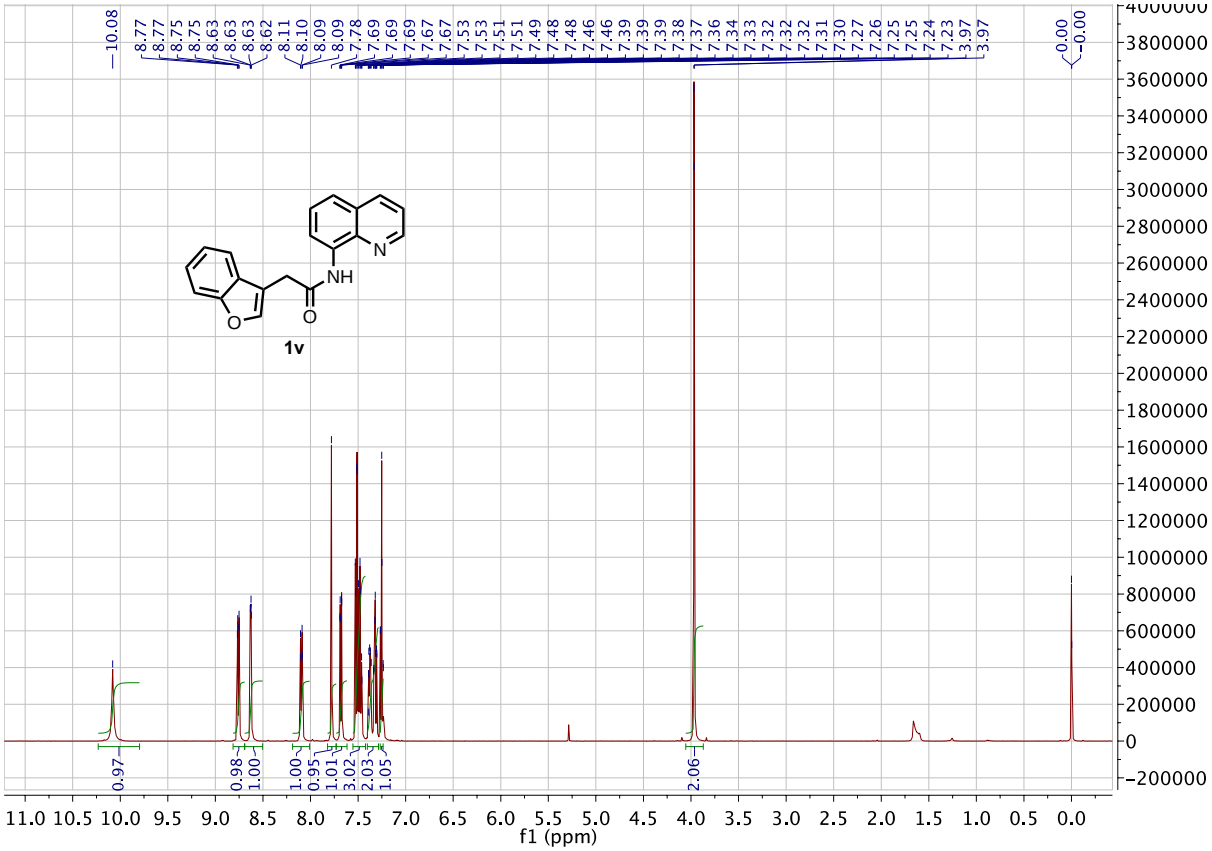
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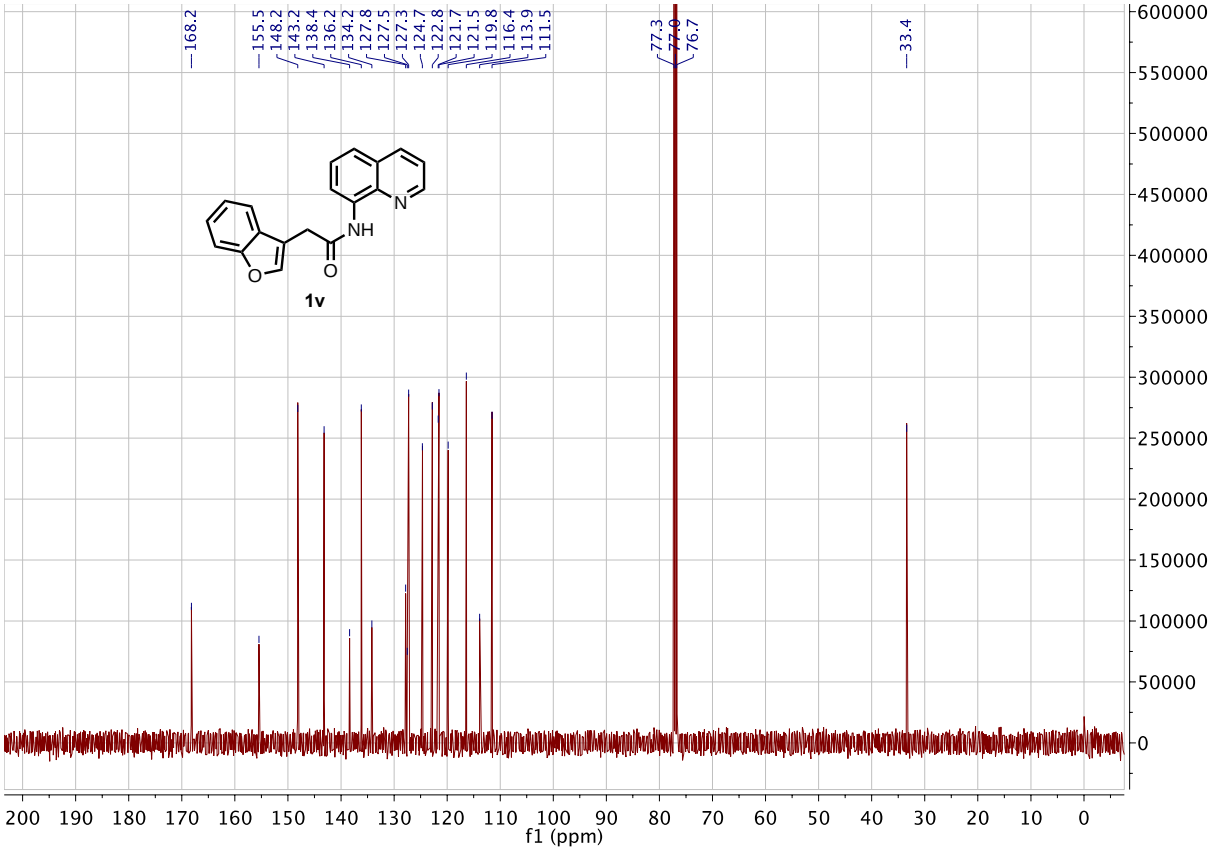
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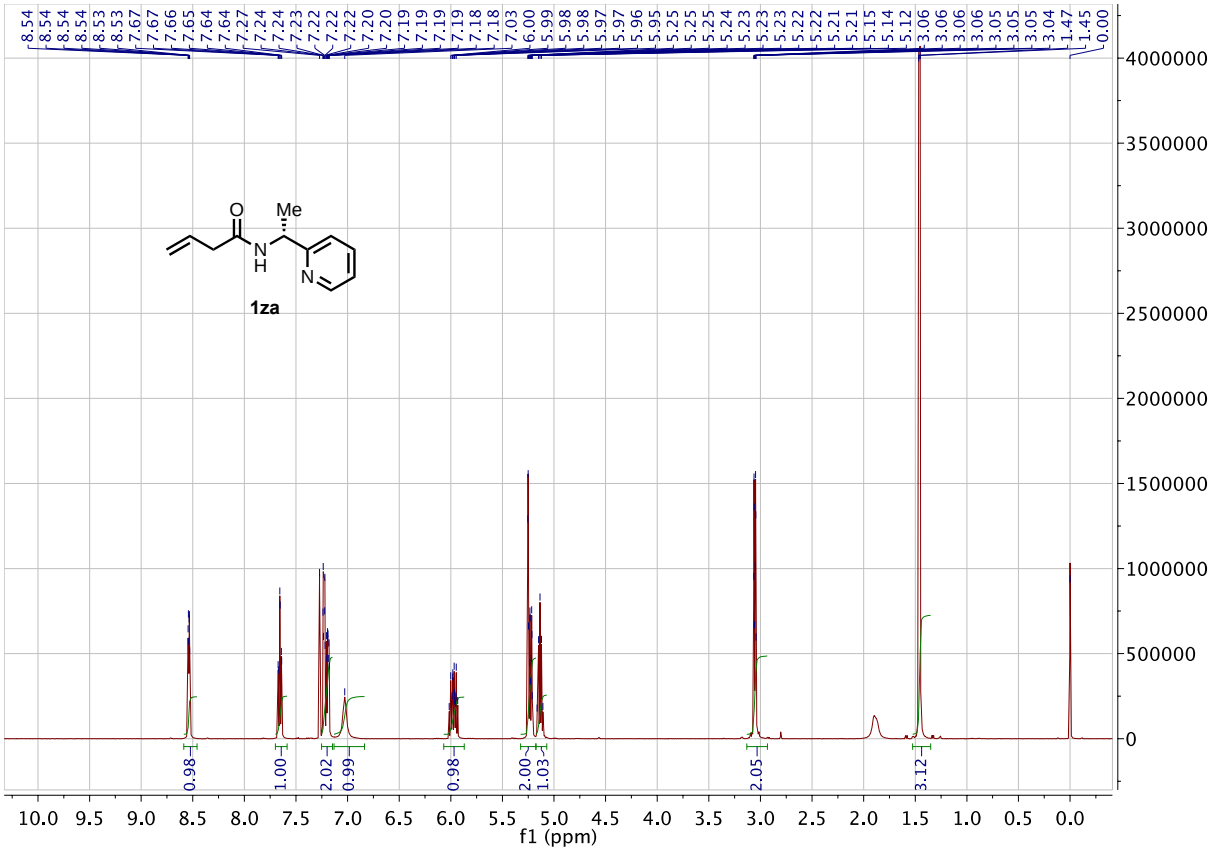
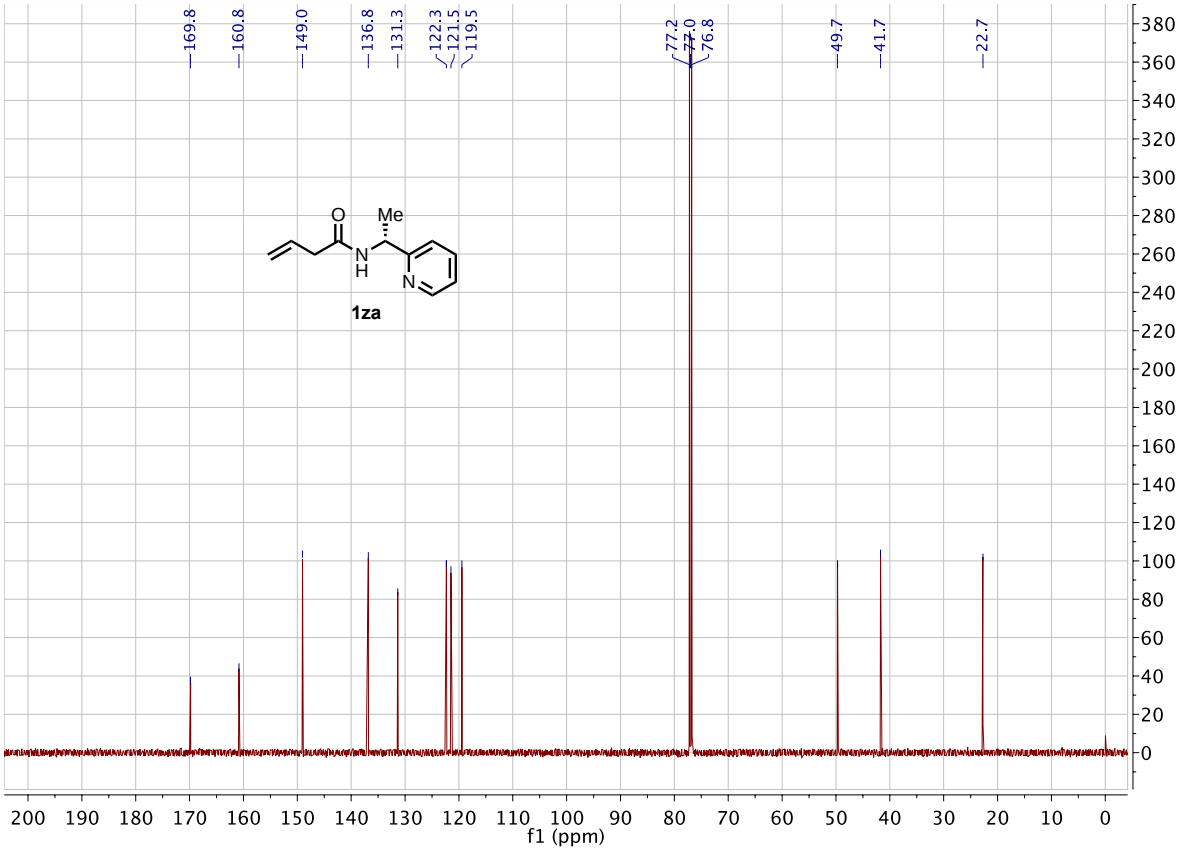
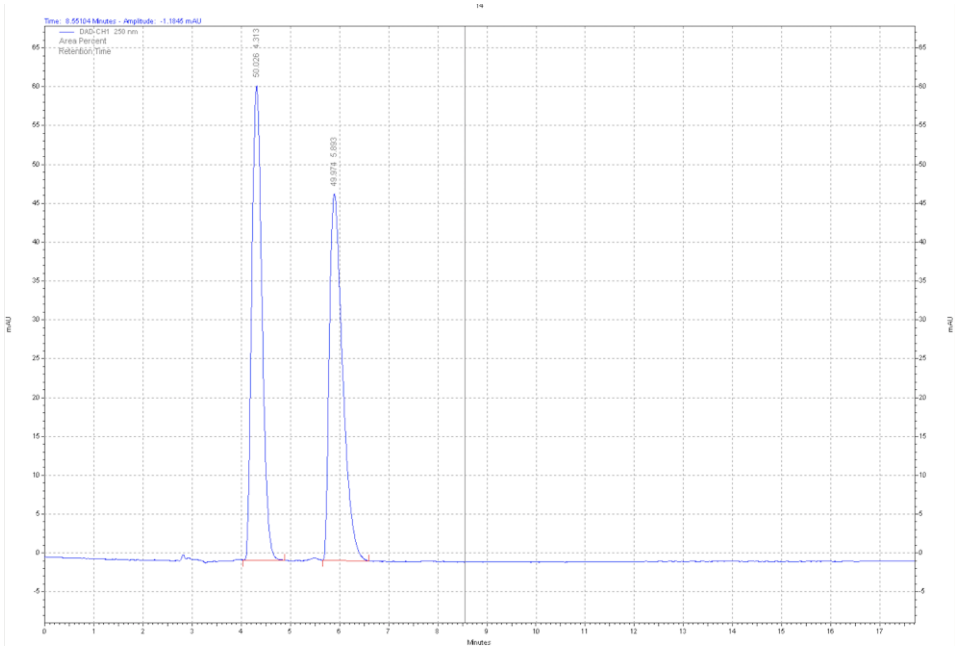
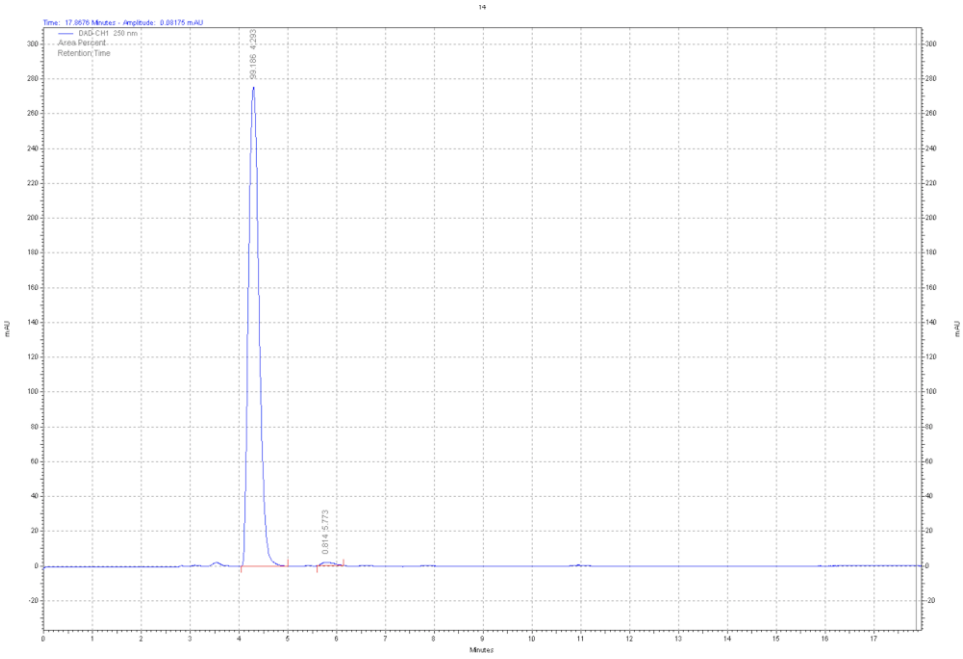
O
1v
f1 (ppm)


1za
f1 (ppm)


1za
f1 (ppm)

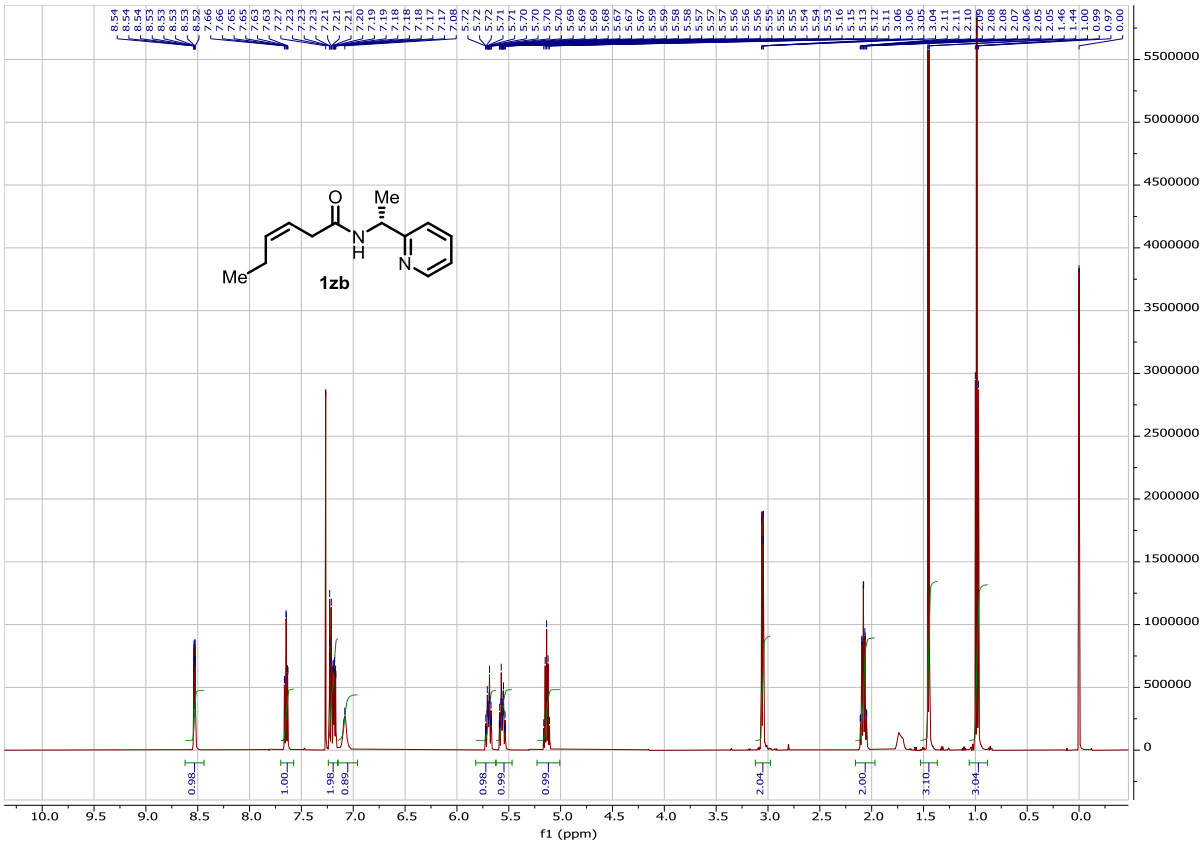
HPLC Chromatograms of **1za**

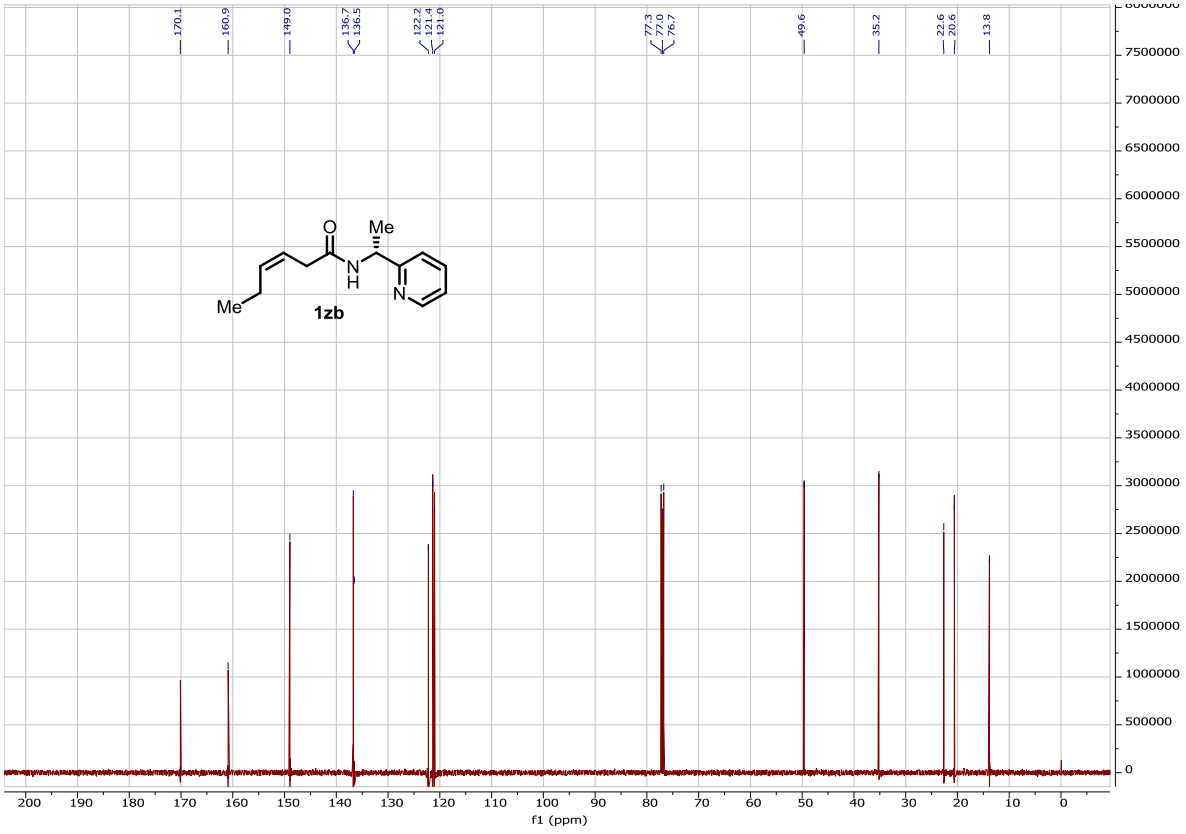


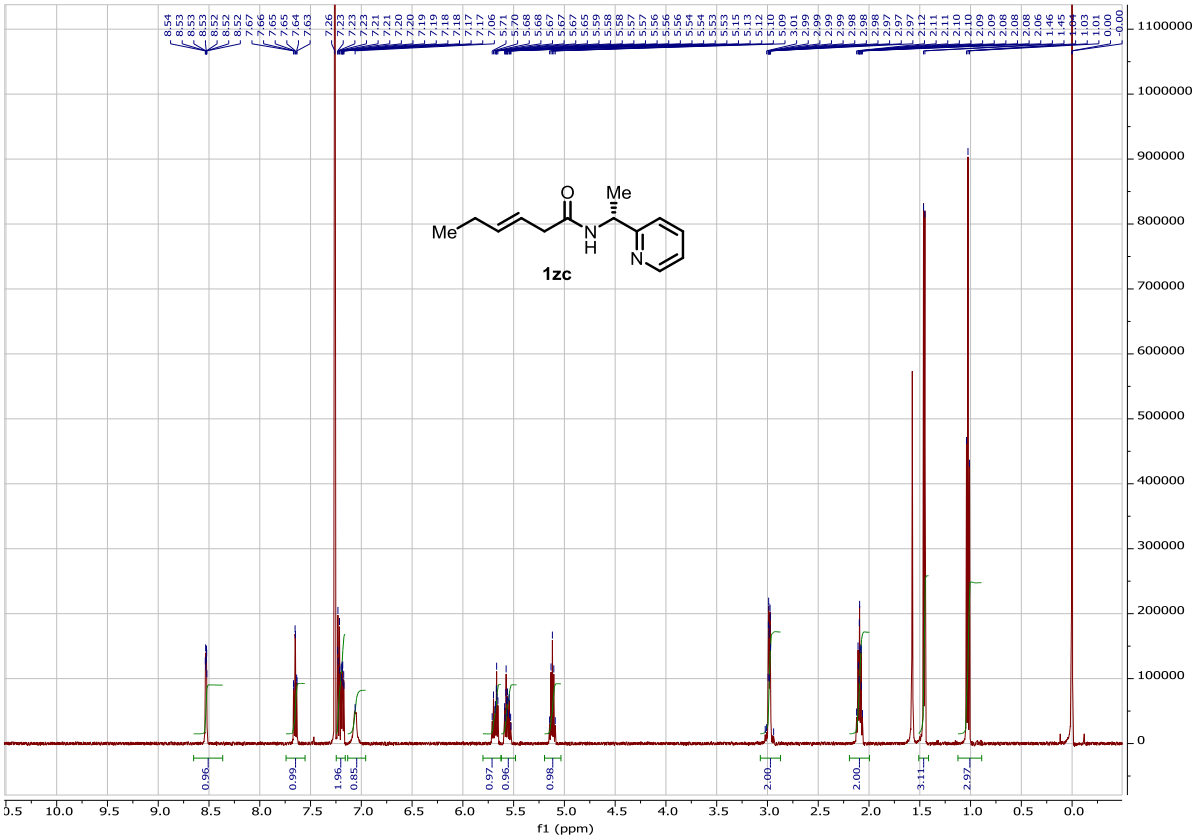


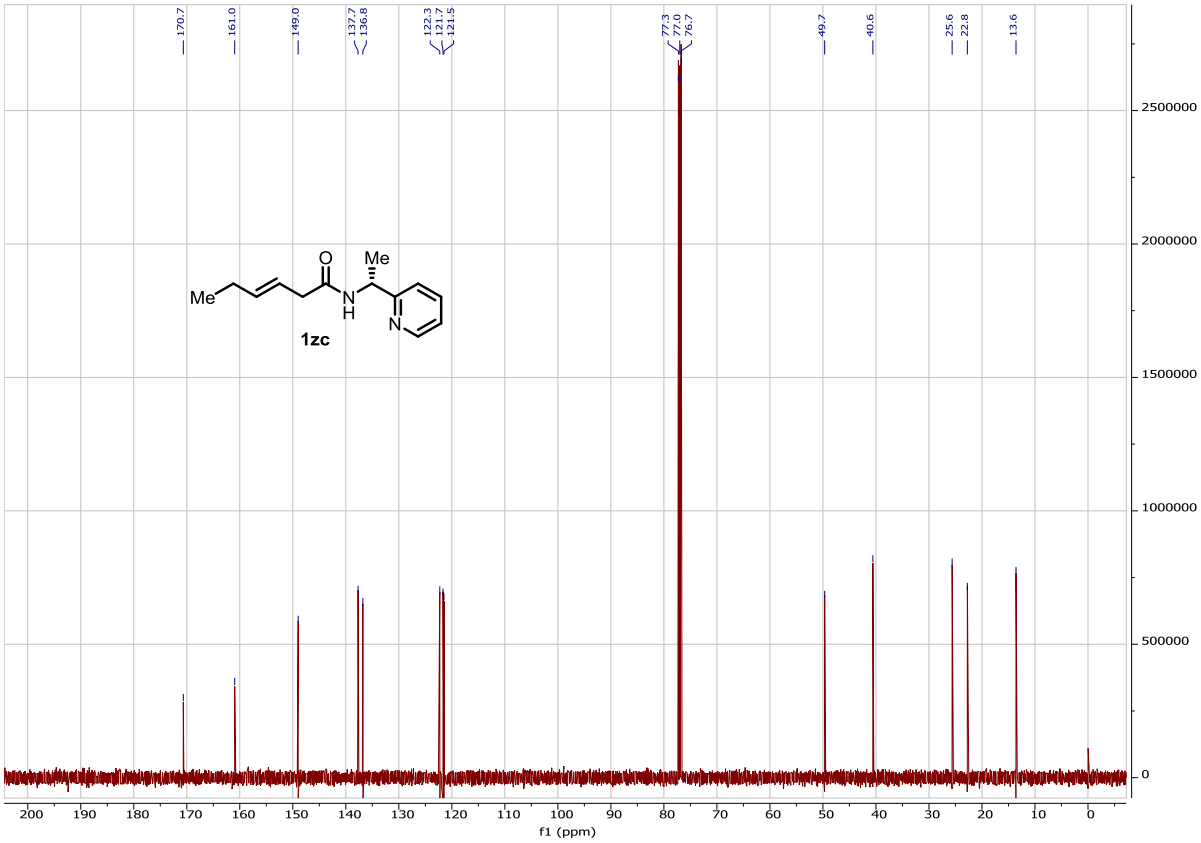
Area Summarized by Name

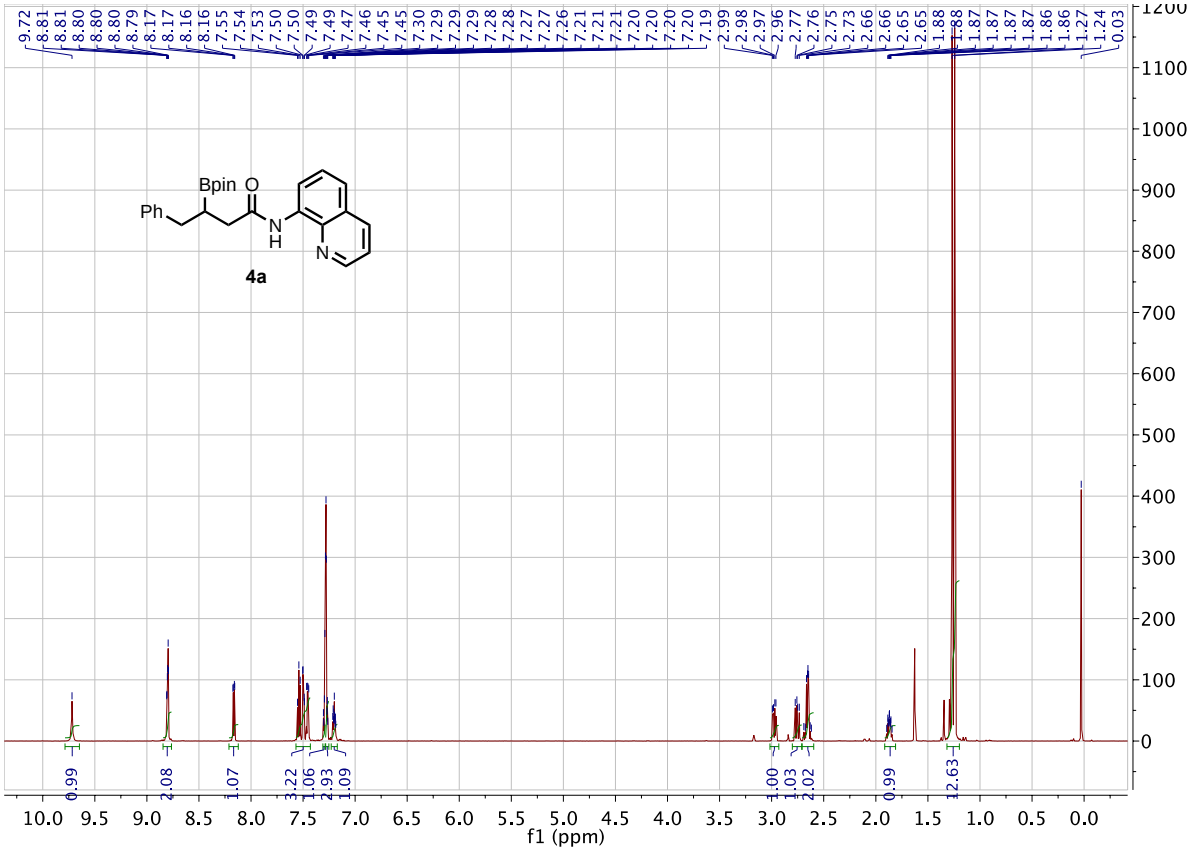
	SampleName	ent	ent	ee	Area1	Area2
1	**1za**-Rac	50.03	49.97	0.06	3527704	3524038
2	**1za**-Enant	99.19	0.81	98.34	16498107	135394

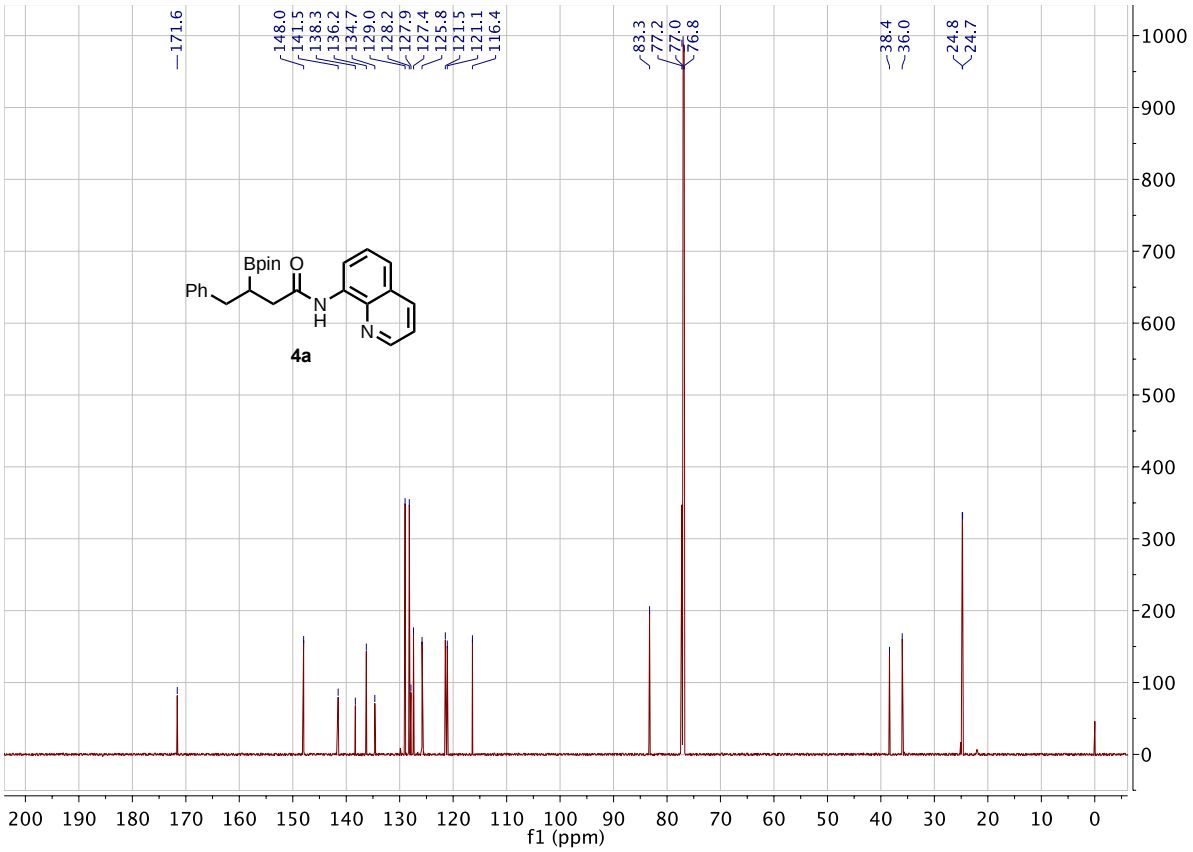

1zb
f1 (ppm)

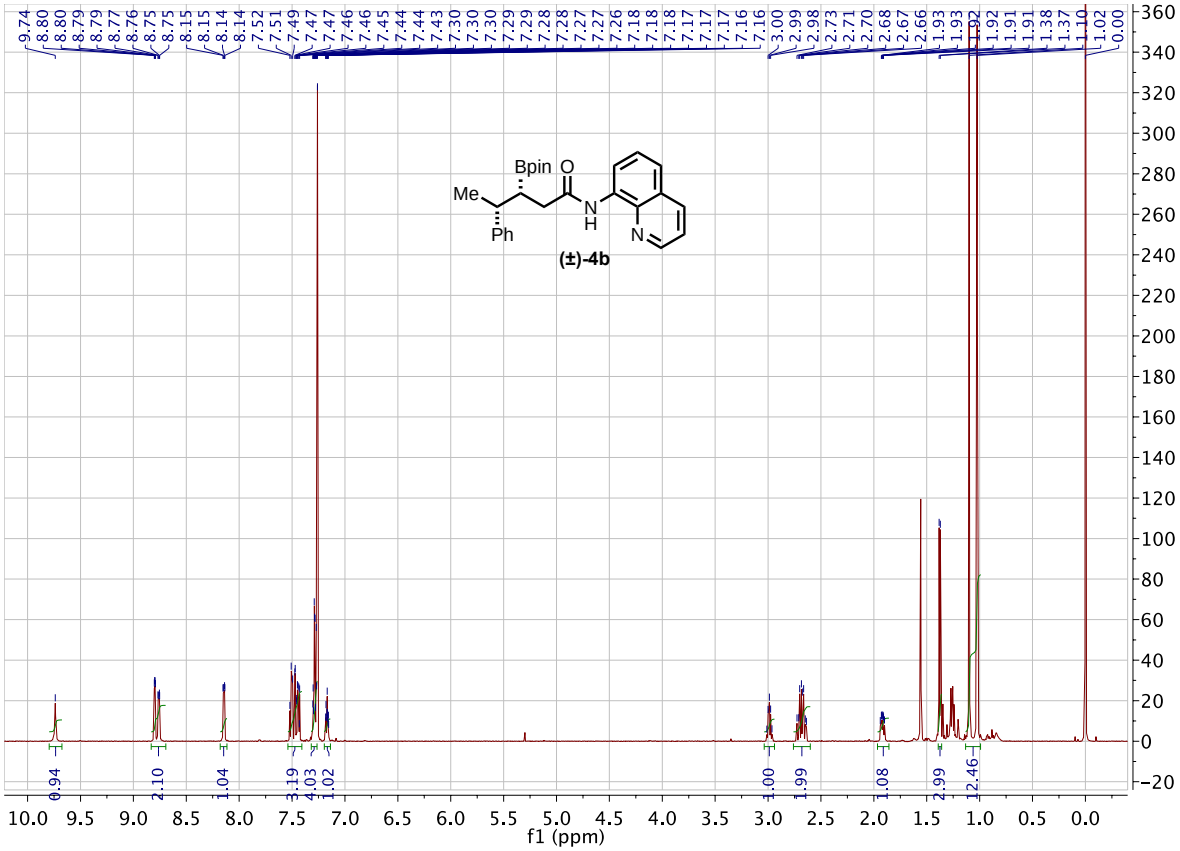

1zb
f1 (ppm)

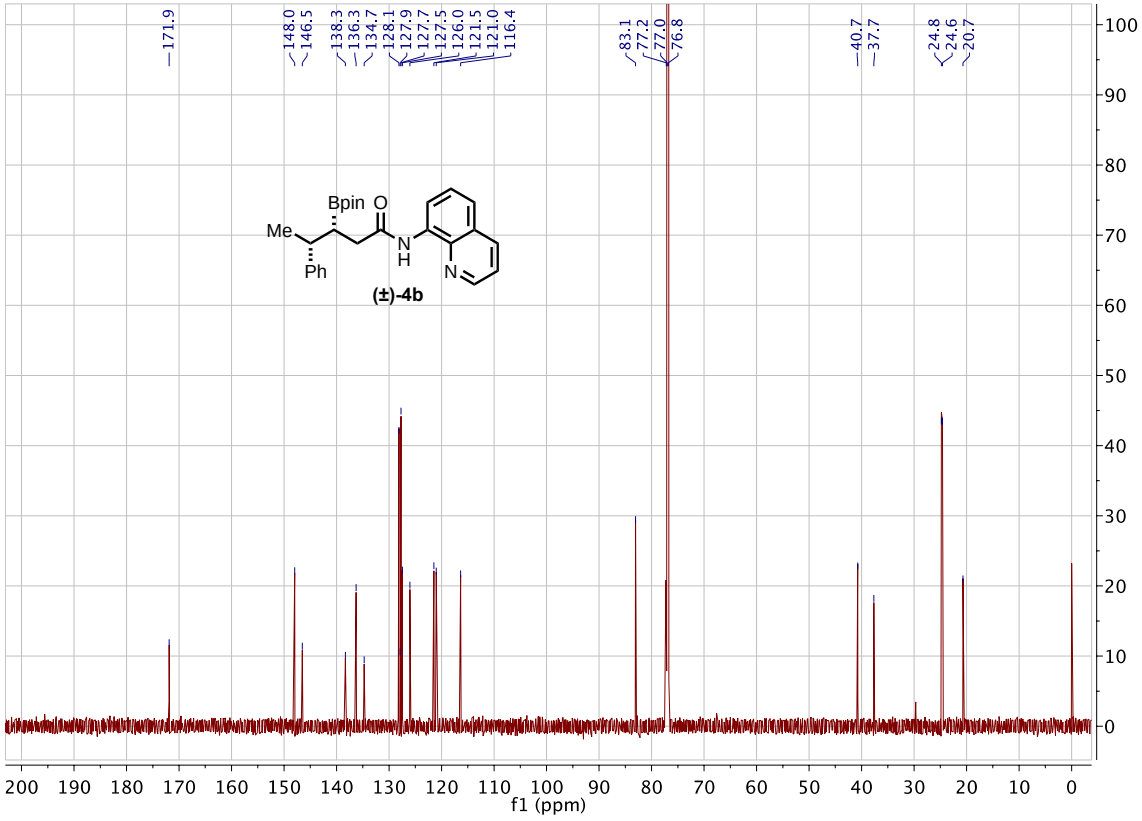

1zc
f1 (ppm)

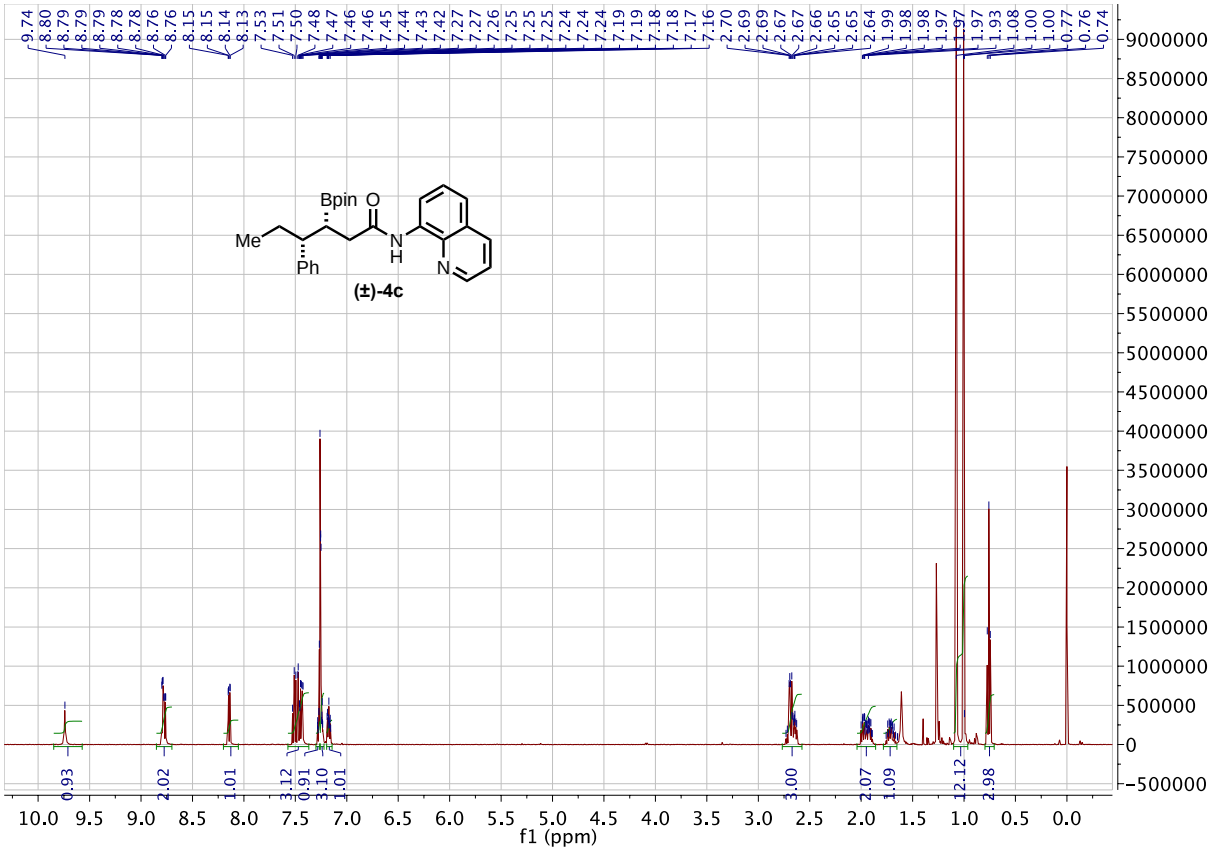

1zc
f1 (ppm)

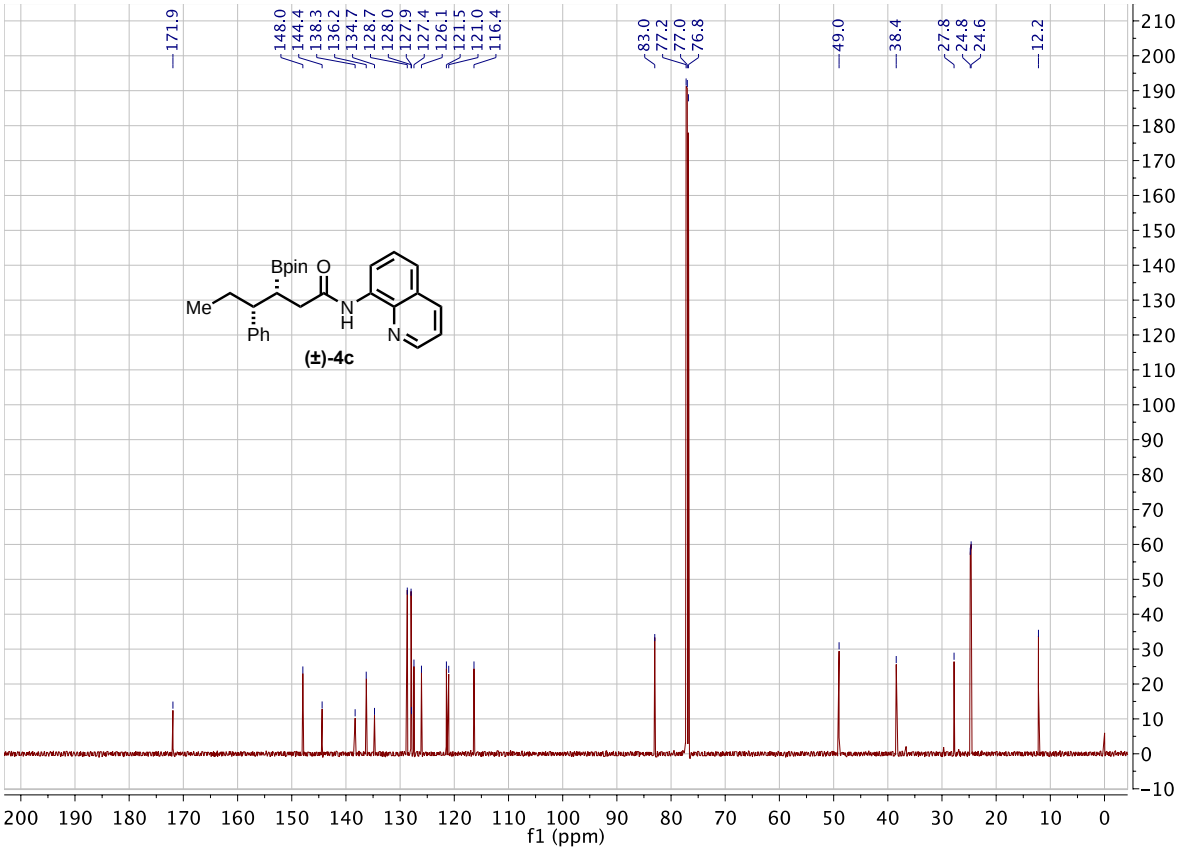

Bpin
O
Ph
N
H
N
4a
f1 (ppm)

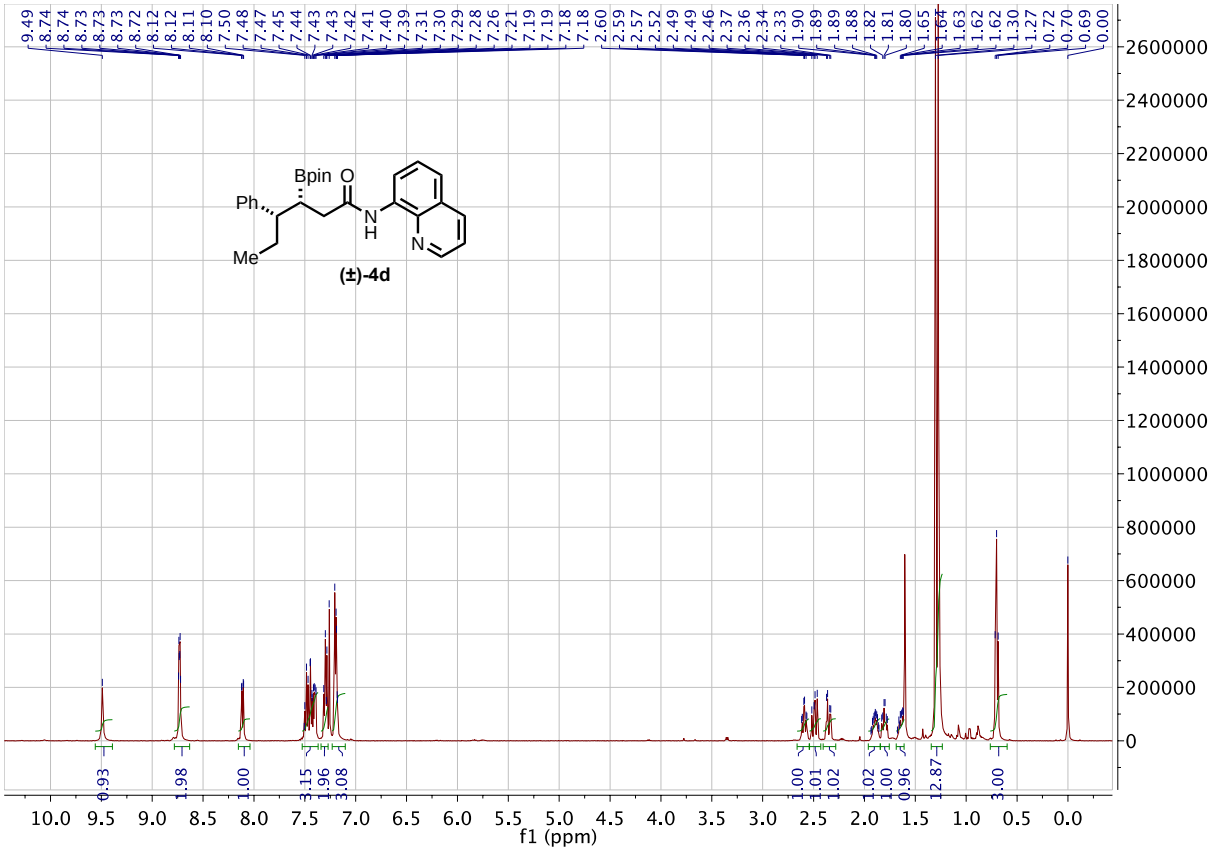

Bpin
O
Ph
N
H
N
4a
f1 (ppm)

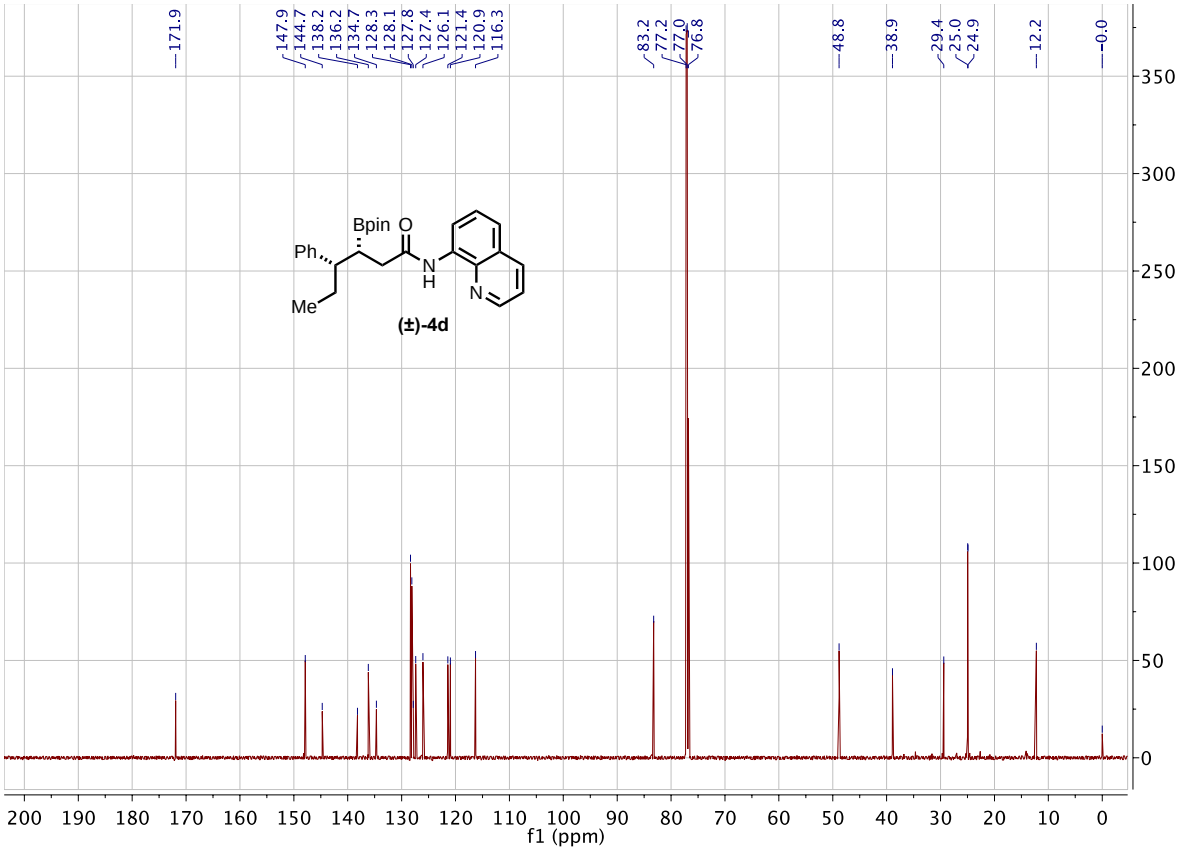

Bpin
O
Me
Ph
N
H
N
(±)-4b
f1 (ppm)

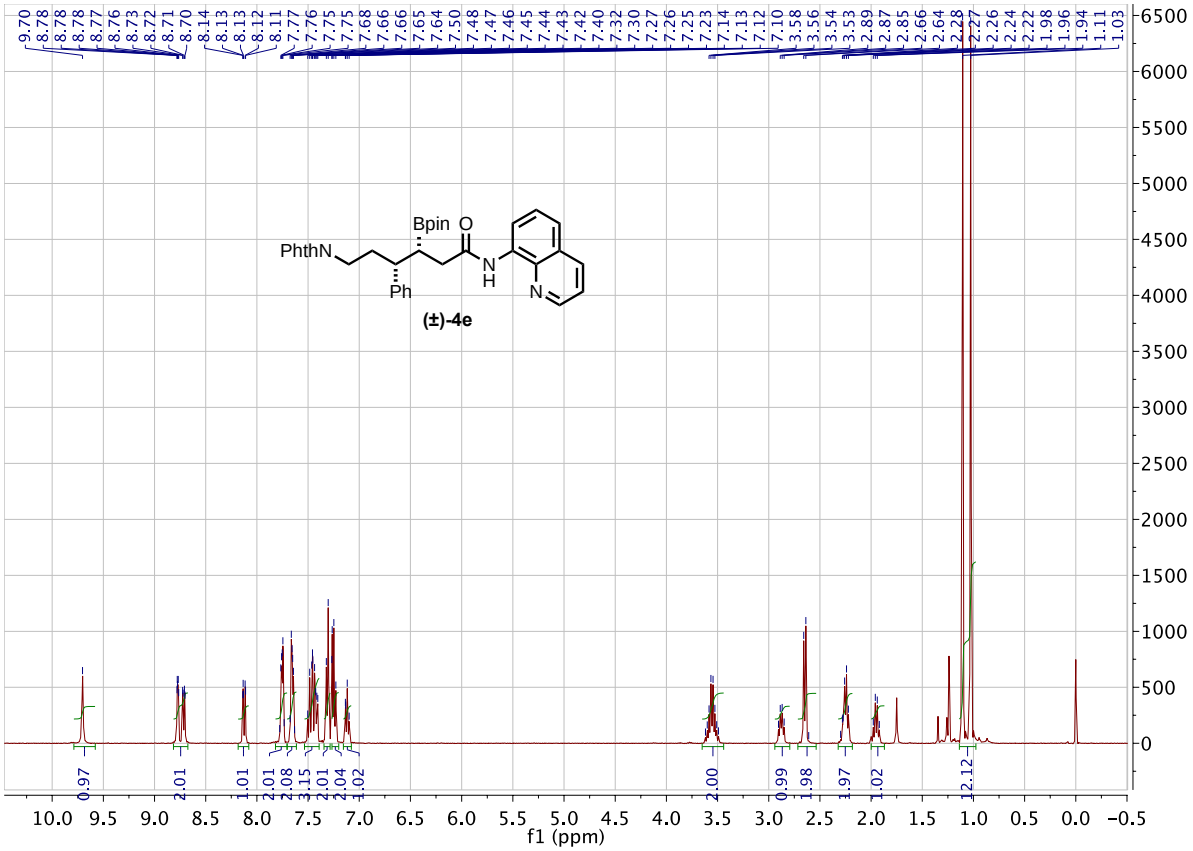

Bpin
O
Me
Ph
N
H
N
(±)-4b
f1 (ppm)

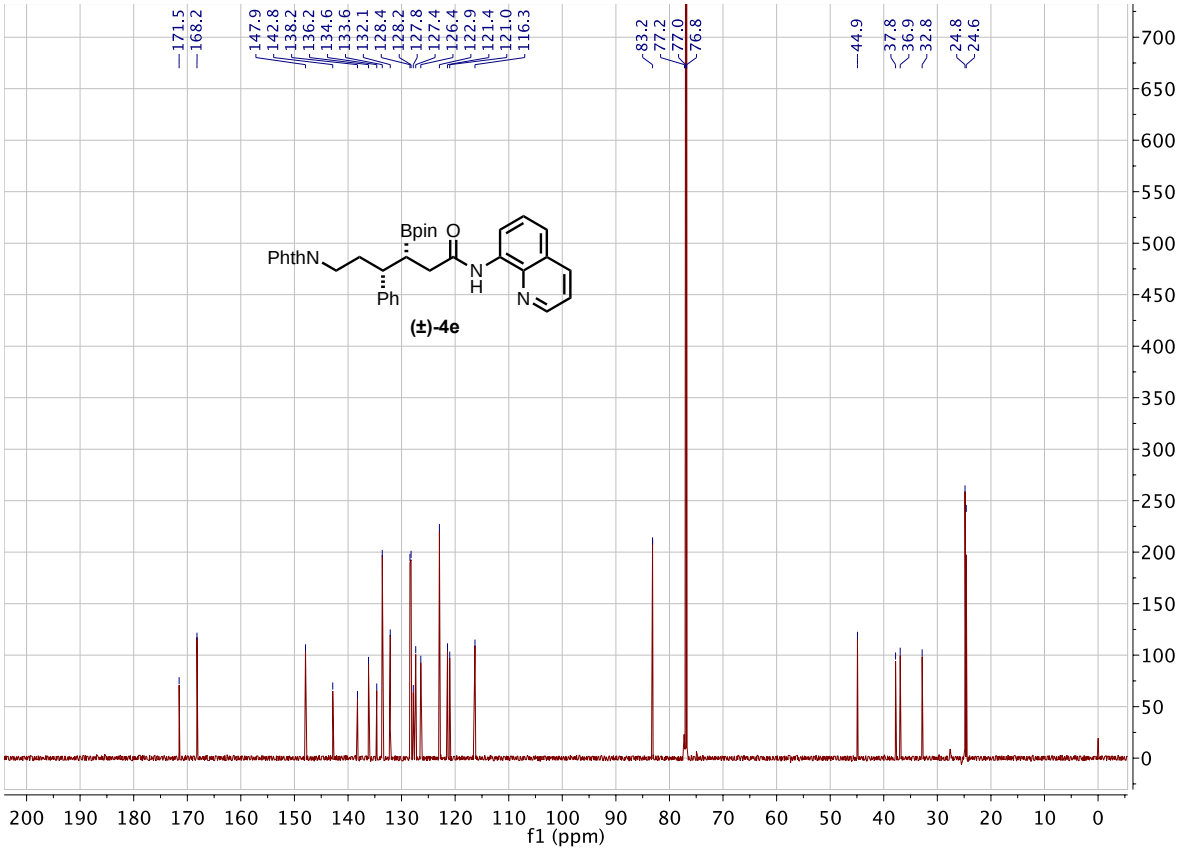

Bpin
O
Me
Ph
N
H
N
(±)-4c
f1 (ppm)

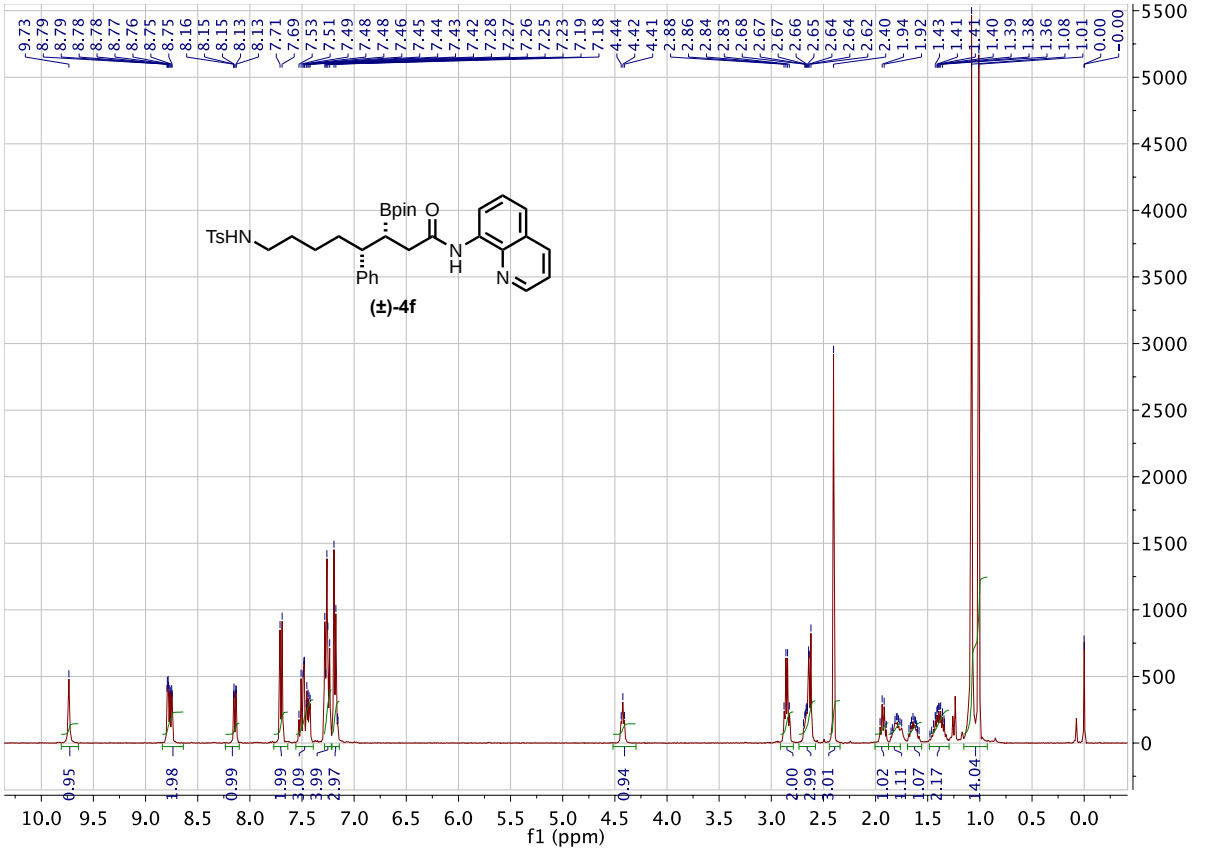

Bpin
O
Me
Ph
N
H
N
(±)-4c
f1 (ppm)

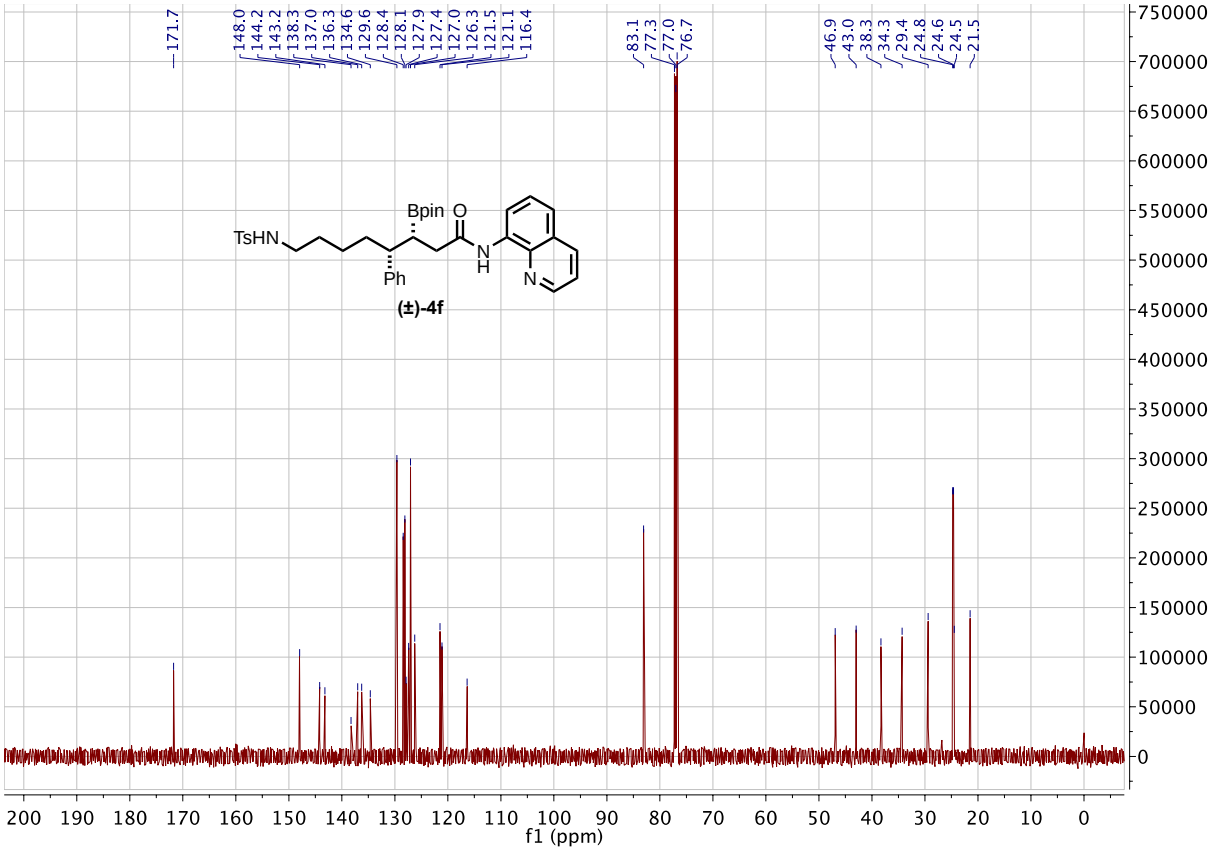

Bpin
O
Ph
N
H
N
Me
(±)-4d
f1 (ppm)

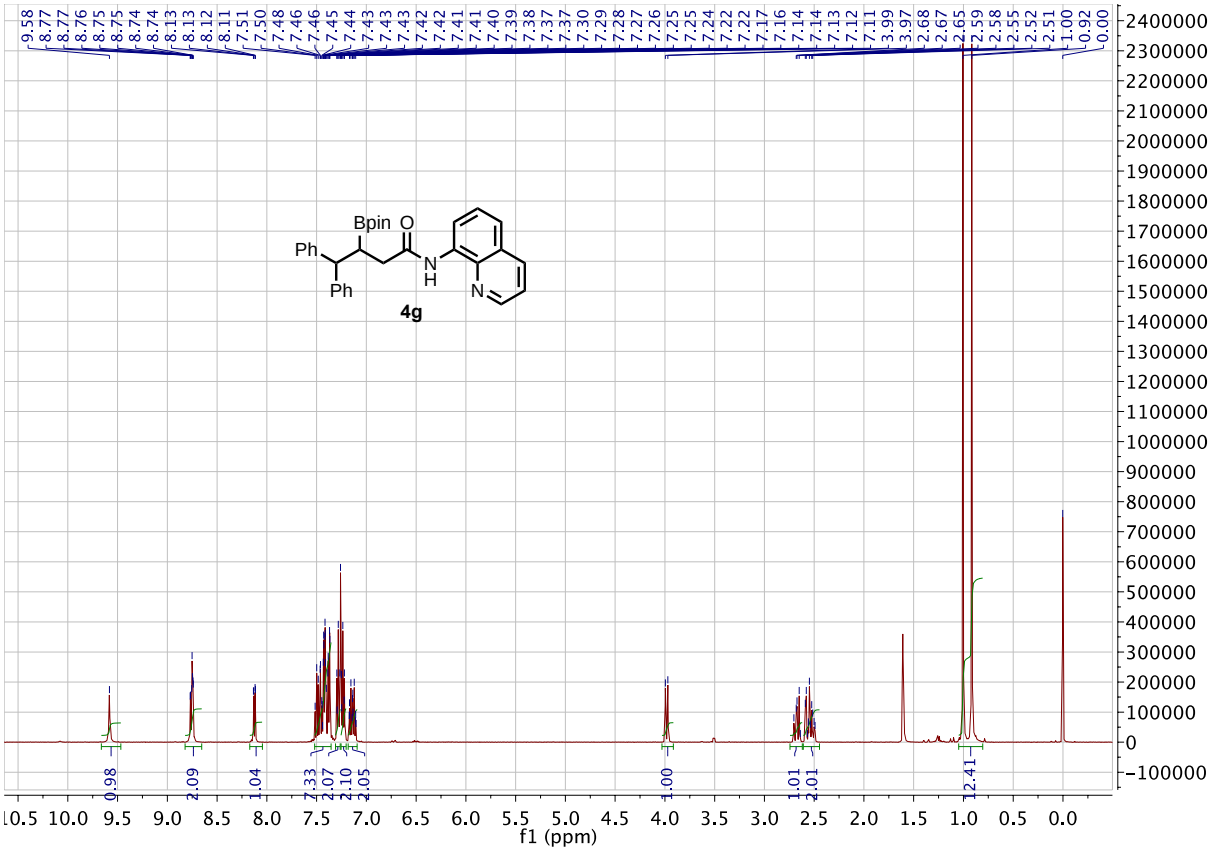

Bpin
O
Ph
N
H
N
Me
(±)-4d
f1 (ppm)

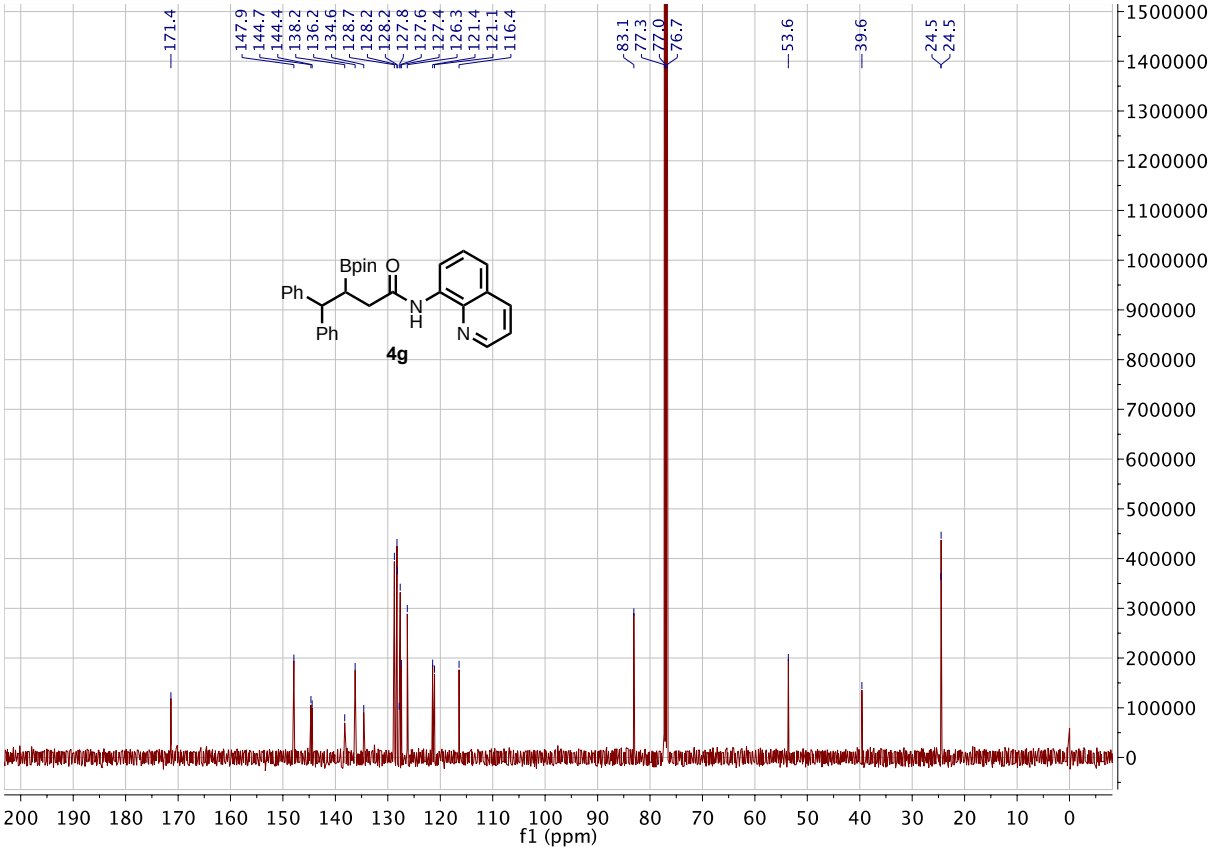

Bpin
O
PhthN
N
H
Ph
N
(±)-4e
f1 (ppm)

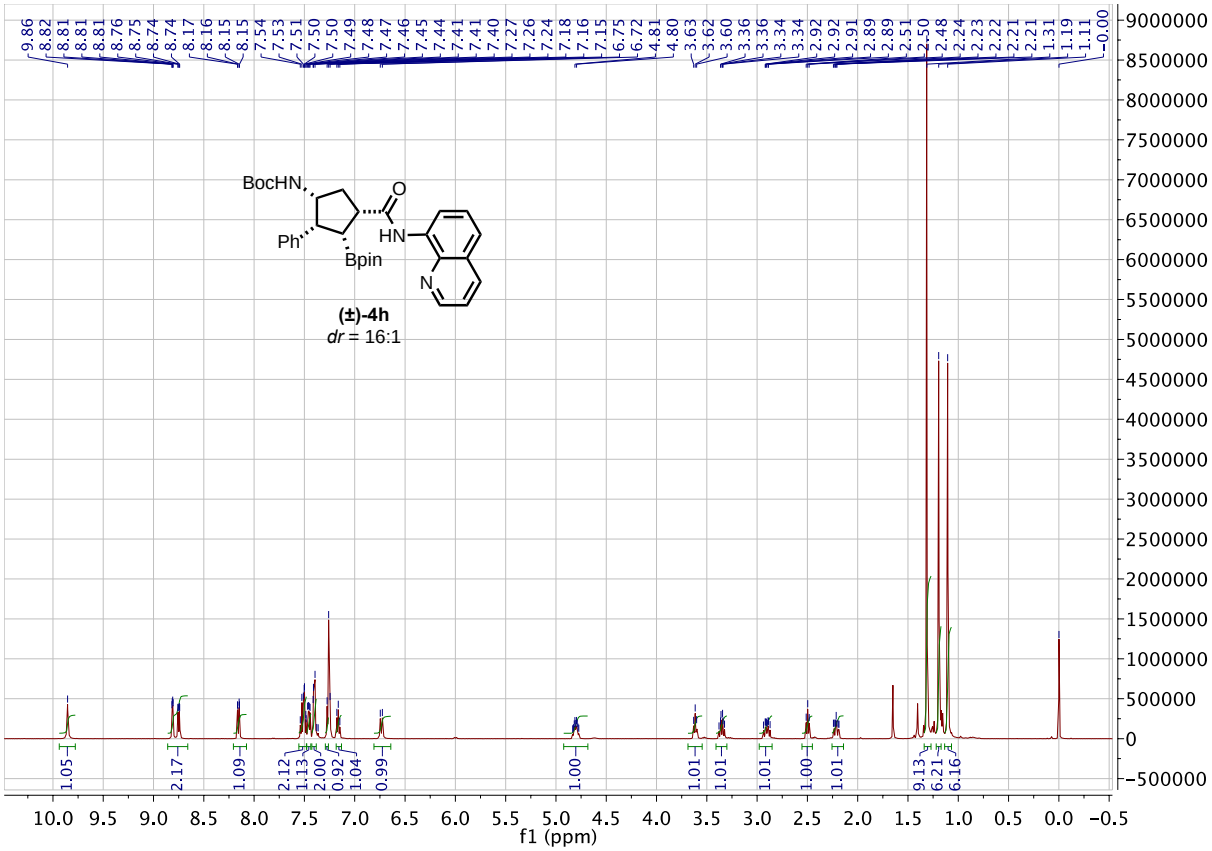

Bpin
O
PhthN
N
H
Ph
N
(±)-4e
f1 (ppm)

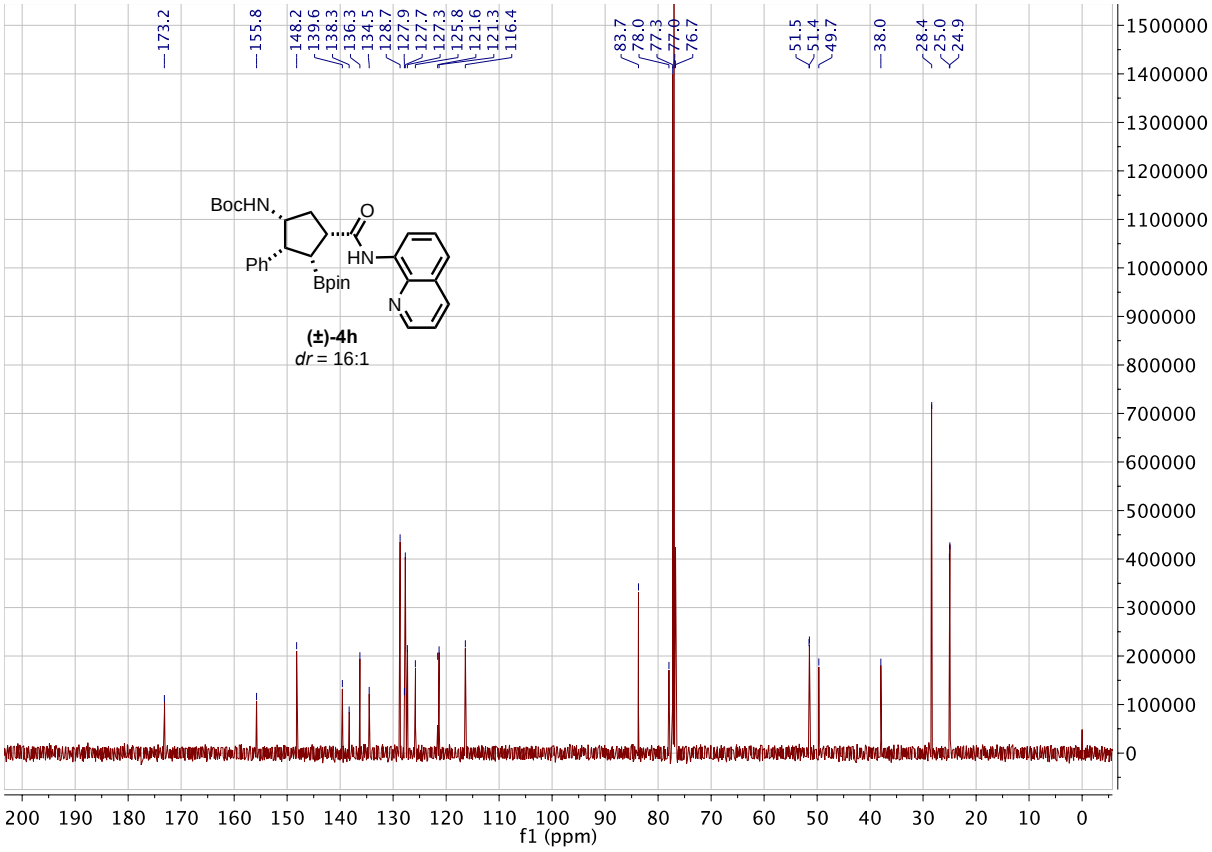

Bpin
O
TsHN
N
H
Ph
N
(±)-4f
f1 (ppm)

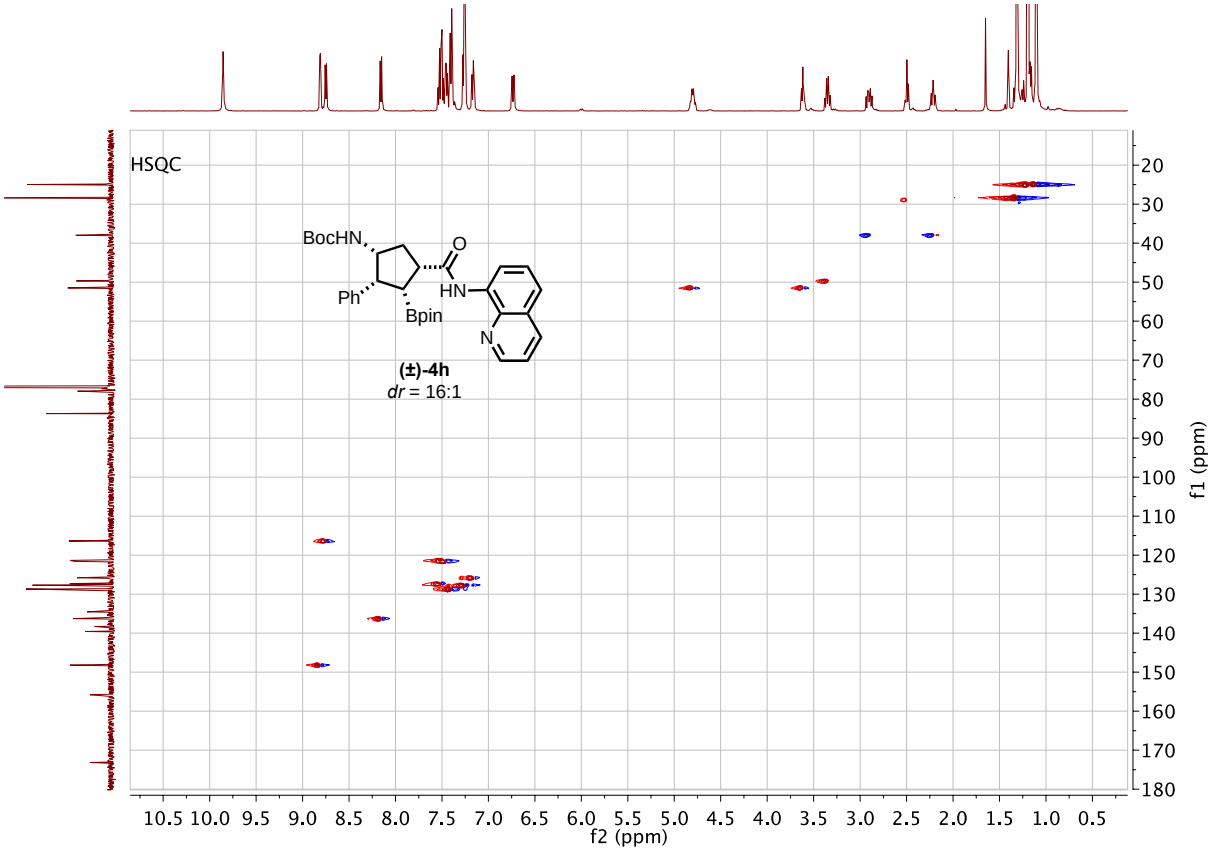

Bpin
O
TsHN
N
H
Ph
N
(±)-4f
f1 (ppm)

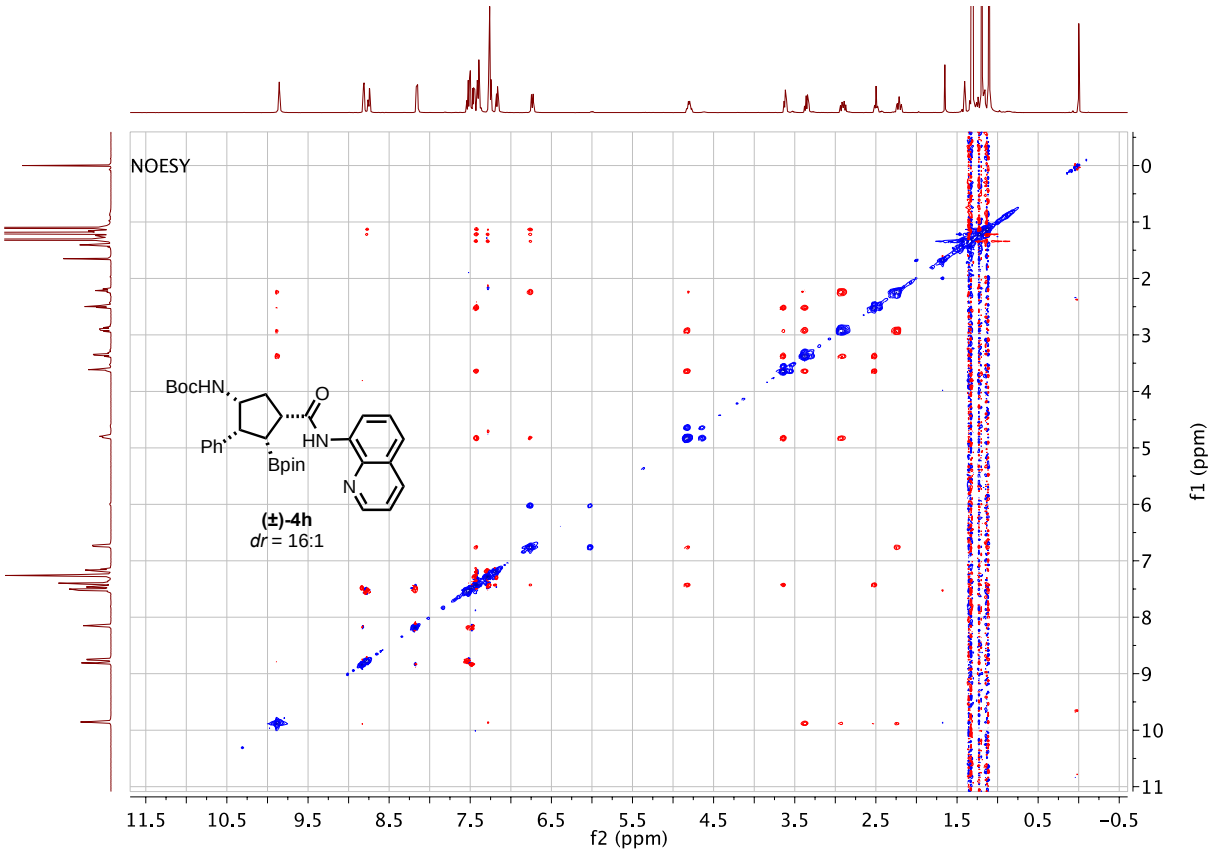

Bpin
O
Ph
Ph
N
H
N
4g
f1 (ppm)

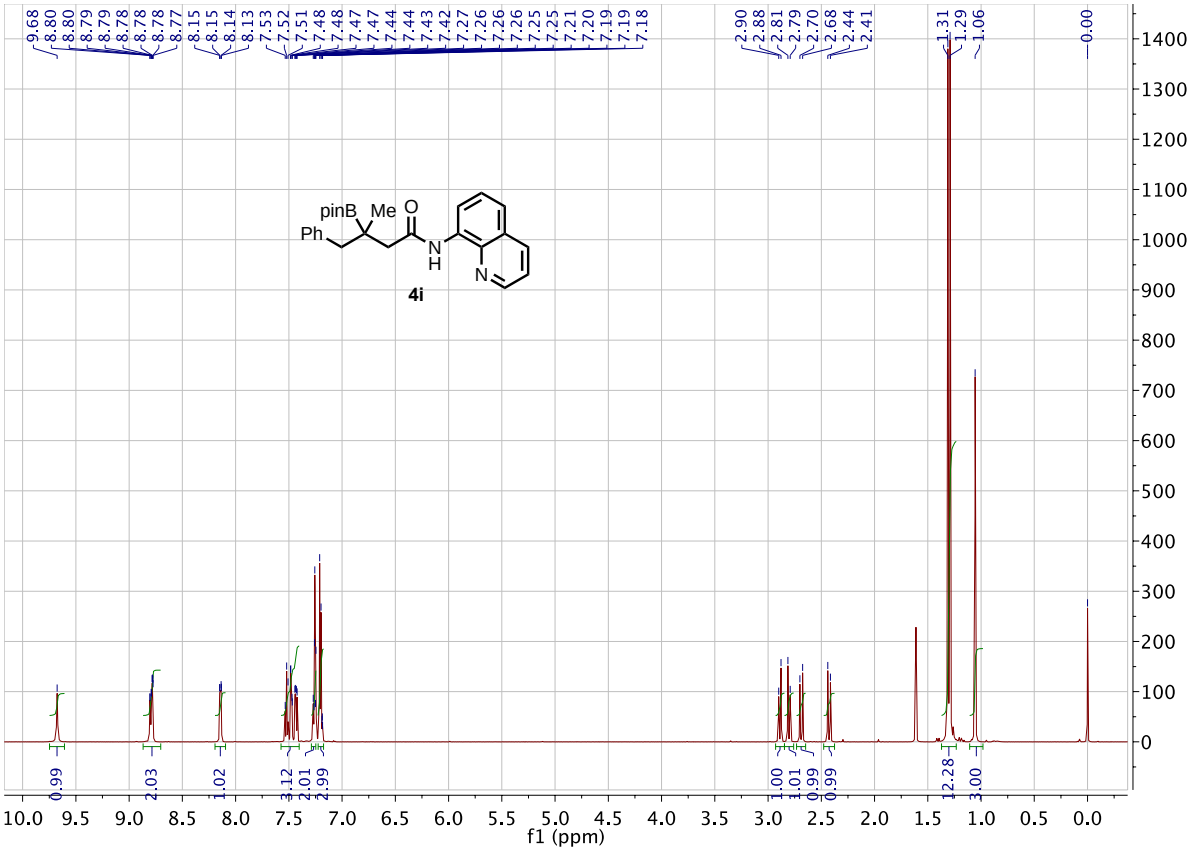

Bpin
O
Ph
Ph
N
H
N
4g
f1 (ppm)

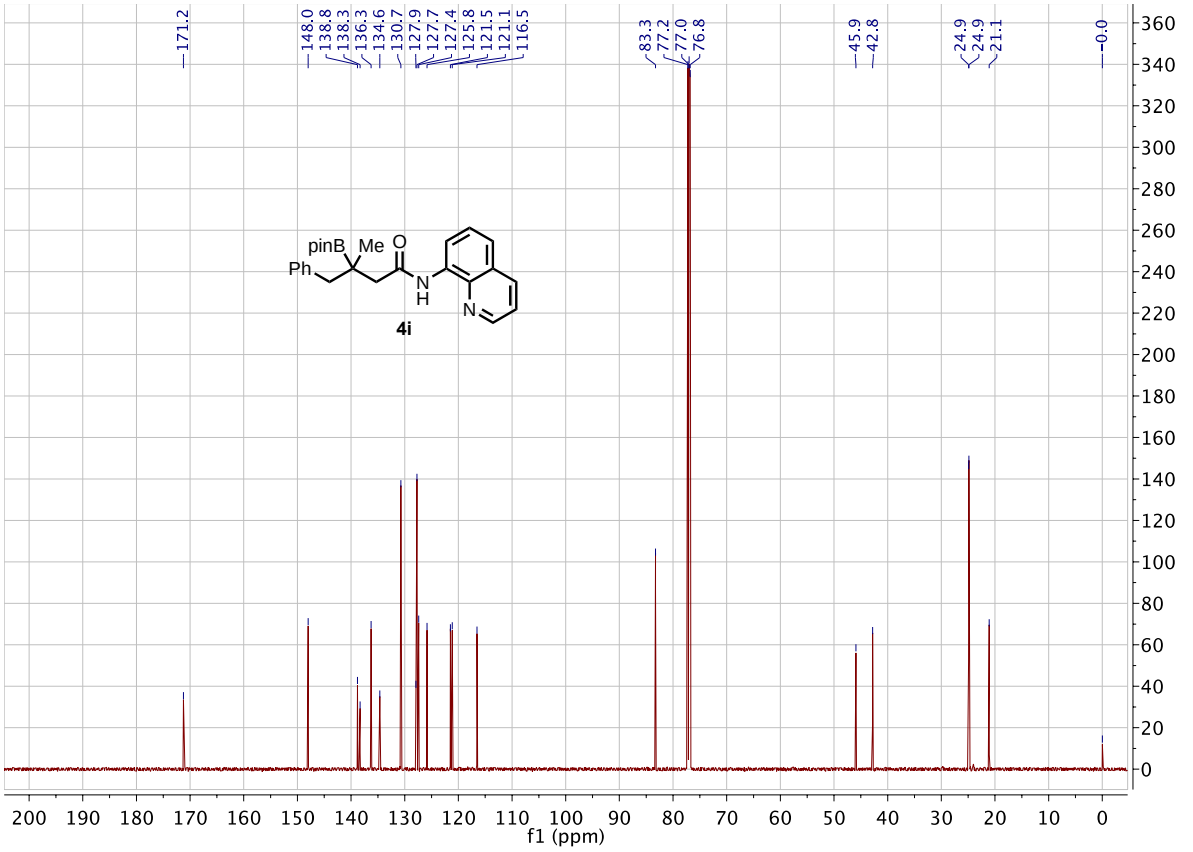

BocHN
O
HN
Ph
Bpin
N
(±)-4h
dr = 16:1
f1 (ppm)

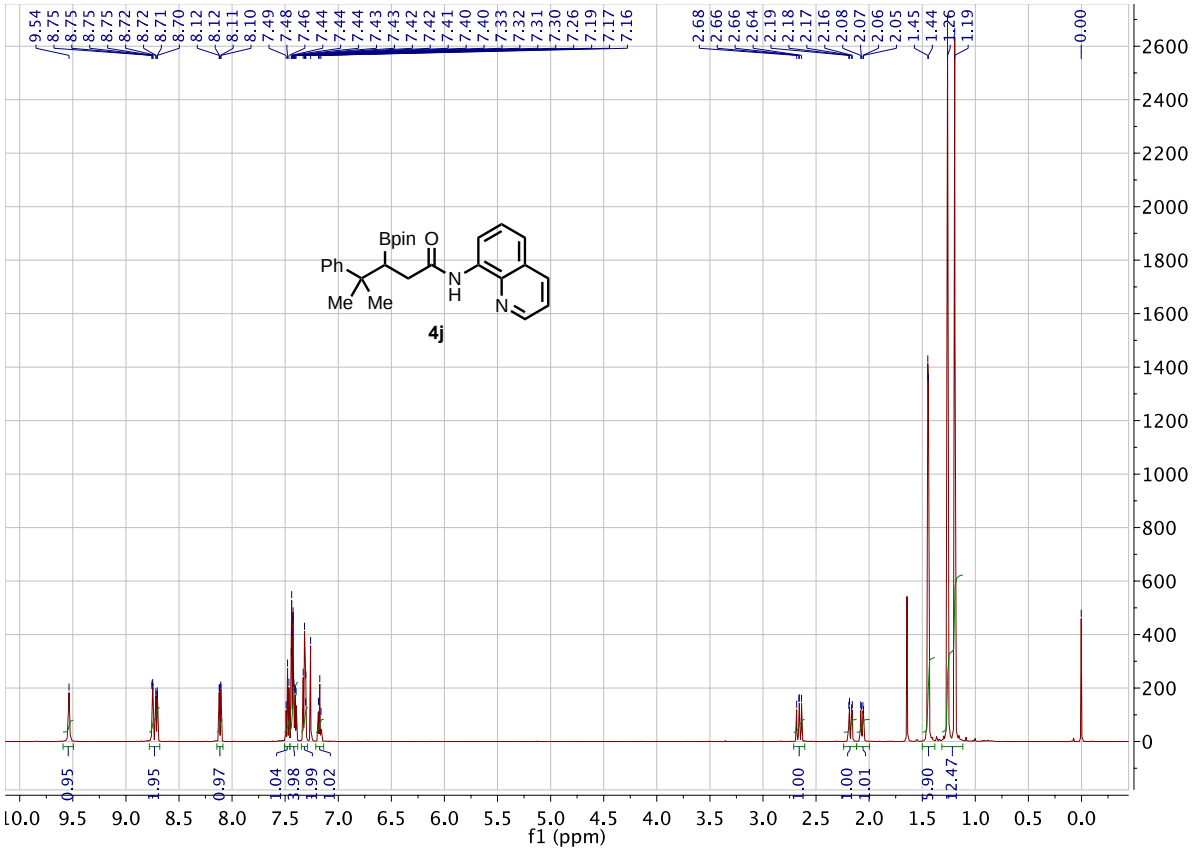

BocHN
O
HN
Ph
Bpin
N
(±)-4h
dr = 16:1
f1 (ppm)

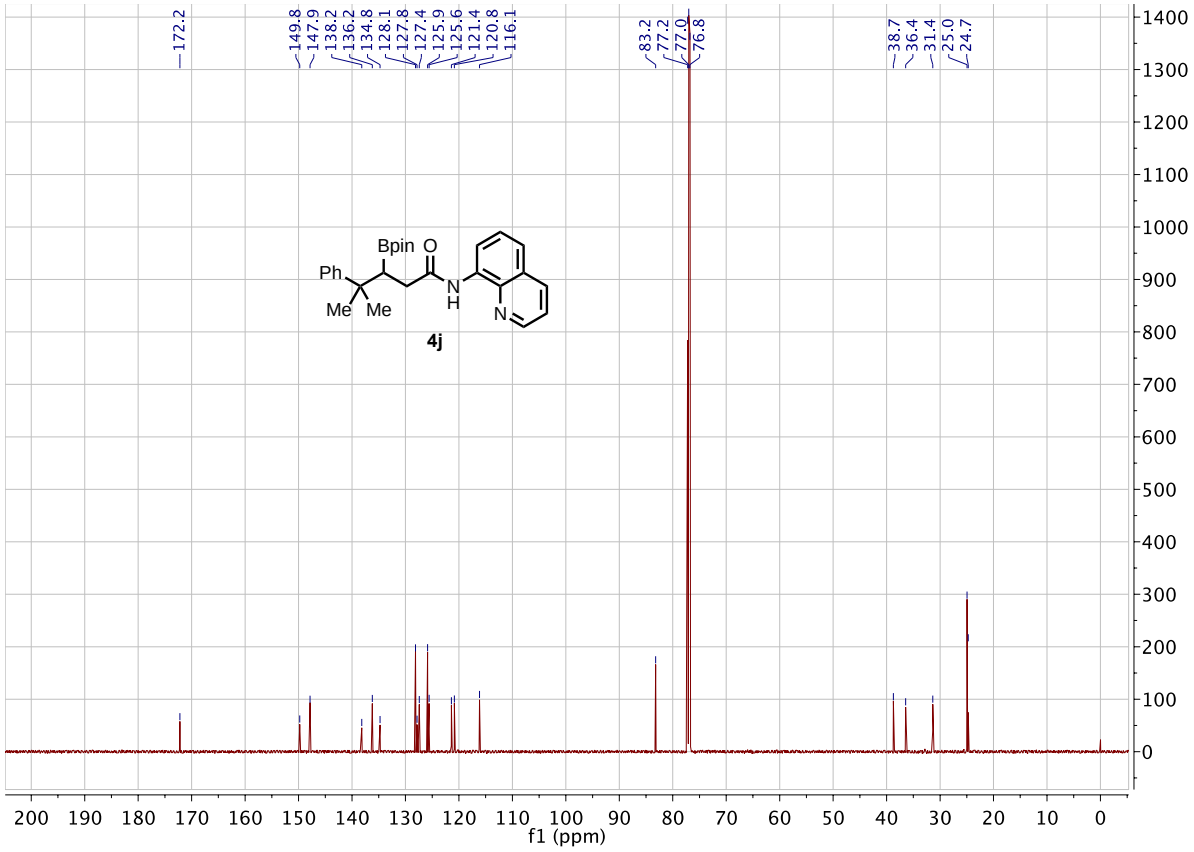

HSQC
BocHN
O
HN
Ph
Bpin
N
(±)-4h
dr = 16:1
f1 (ppm)
f2 (ppm)

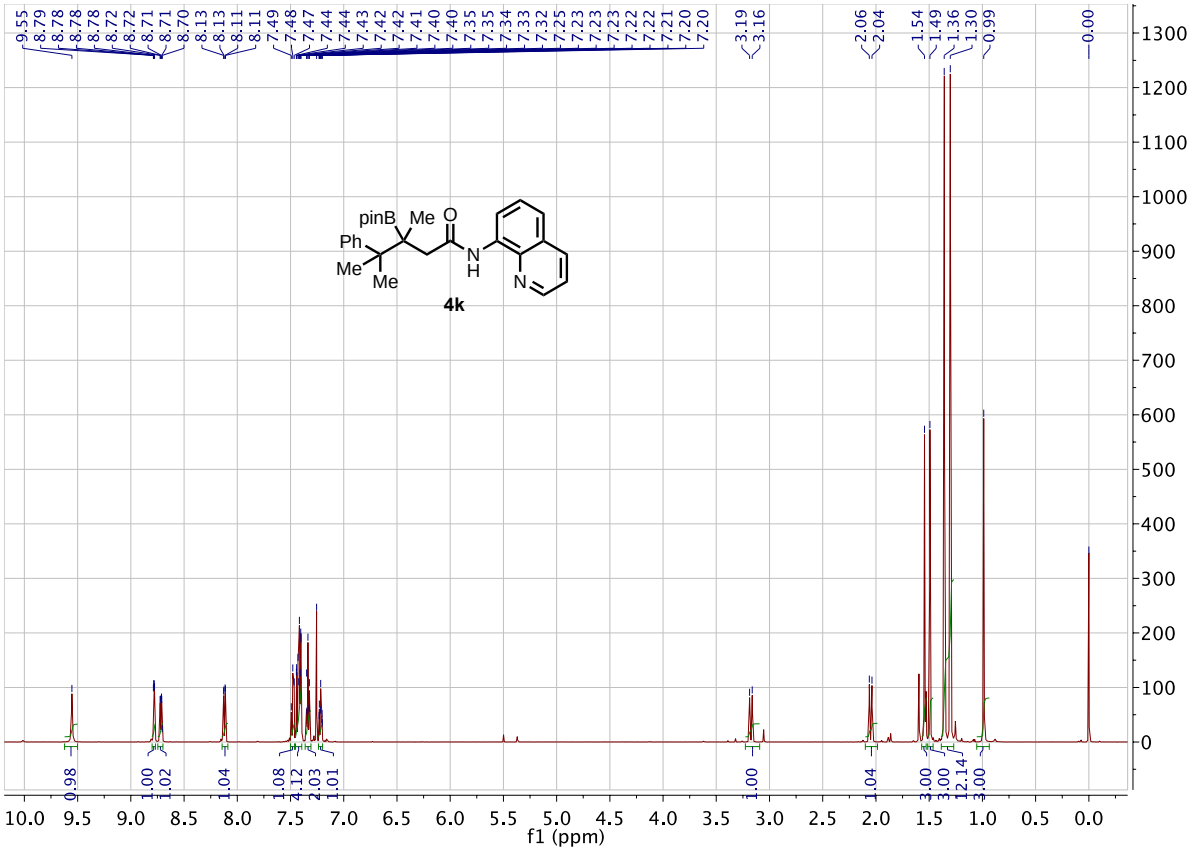

NOESY
BocHN
O
HN
Ph
Bpin
N
(±)-4h
dr = 16:1
f1 (ppm)
f2 (ppm)

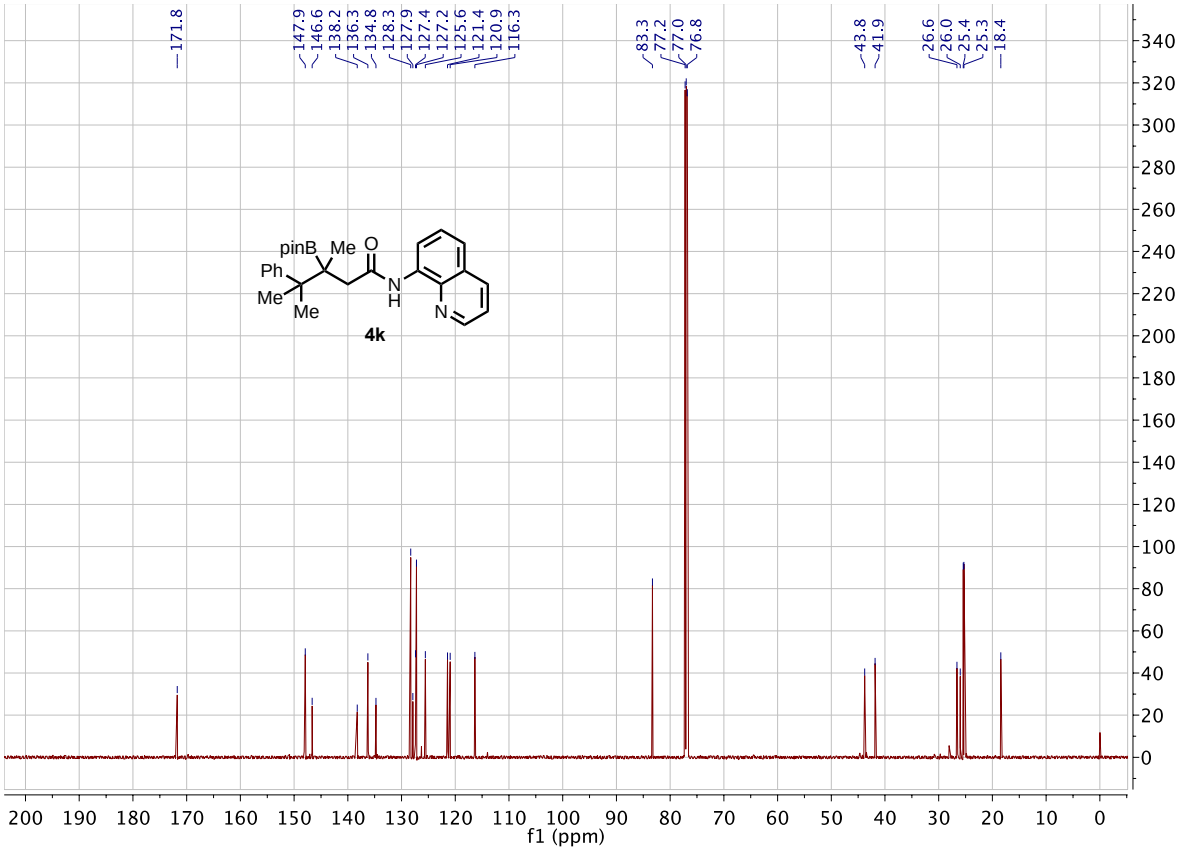

9.68
8.80
8.80
8.79
8.79
8.78
8.78
8.78
8.77
8.15
8.15
8.14
8.13
7.53
7.52
7.51
7.48
7.48
7.47
7.47
7.44
7.44
7.43
7.42
7.27
7.26
7.26
7.26
7.25
7.25
7.21
7.20
7.19
7.19
7.18
2.90
2.88
2.81
2.79
2.70
2.68
2.44
2.41
1.31
1.29
1.06
0.00
pinB
Me
O
Ph
N
H
N
4i
0.99
2.03
1.02
3.12
2.01
2.99
1.00
1.01
0.99
0.99
12.28
3.00
f1 (ppm)

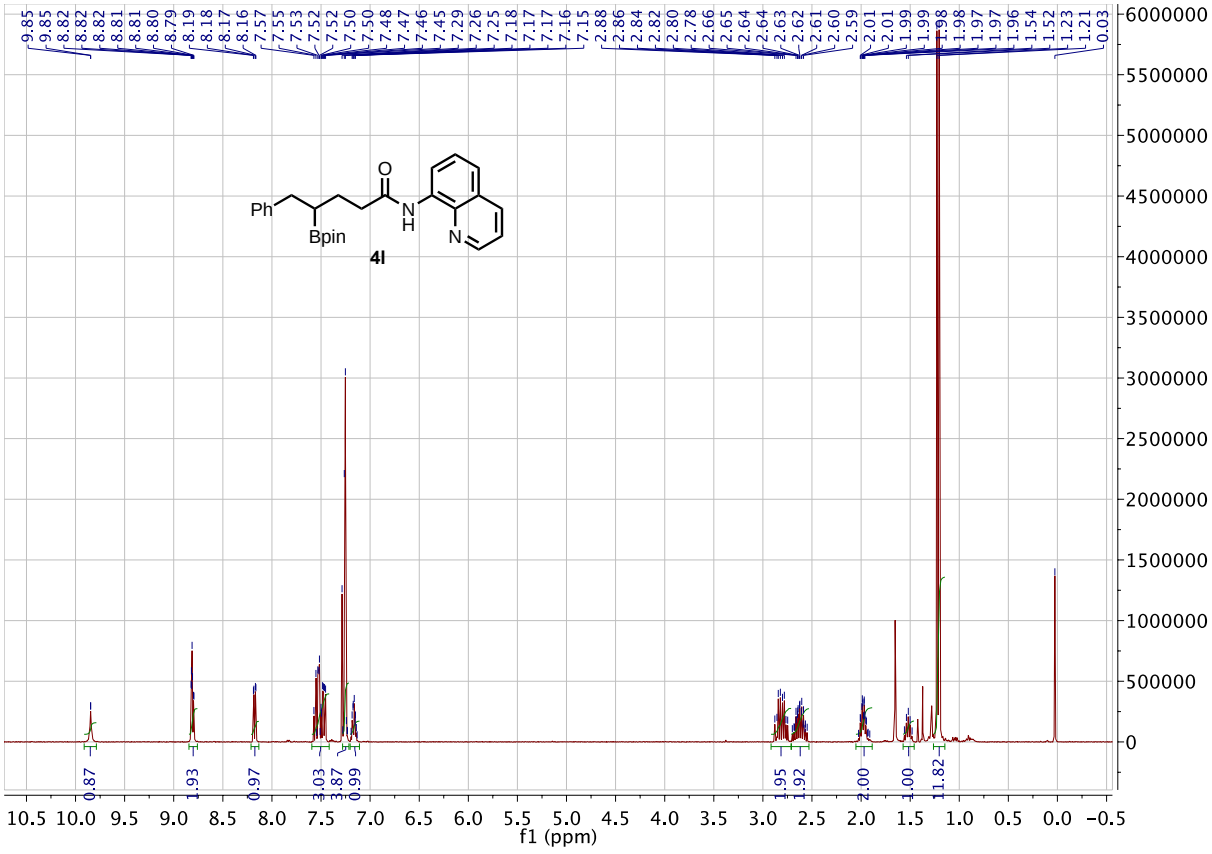

171.2
148.0
138.8
138.3
136.3
134.6
130.7
127.9
127.7
127.4
125.8
121.5
121.1
116.5
83.3
77.2
77.0
76.8
45.9
42.8
24.9
24.9
21.1
0.0
pinB
Me
O
Ph
N
H
N
4i
f1 (ppm)

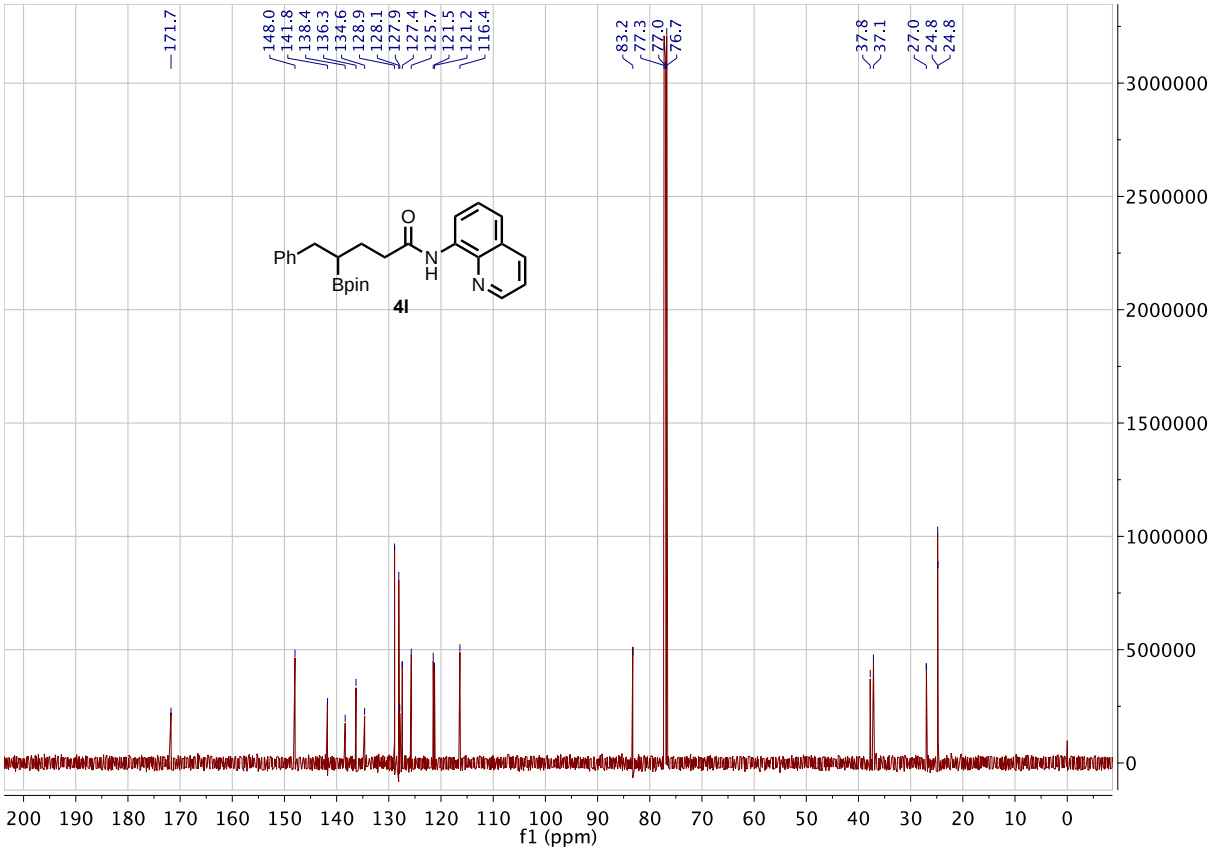

Bpin
O
Ph
N
H
Me
Me
N
4j
f1 (ppm)

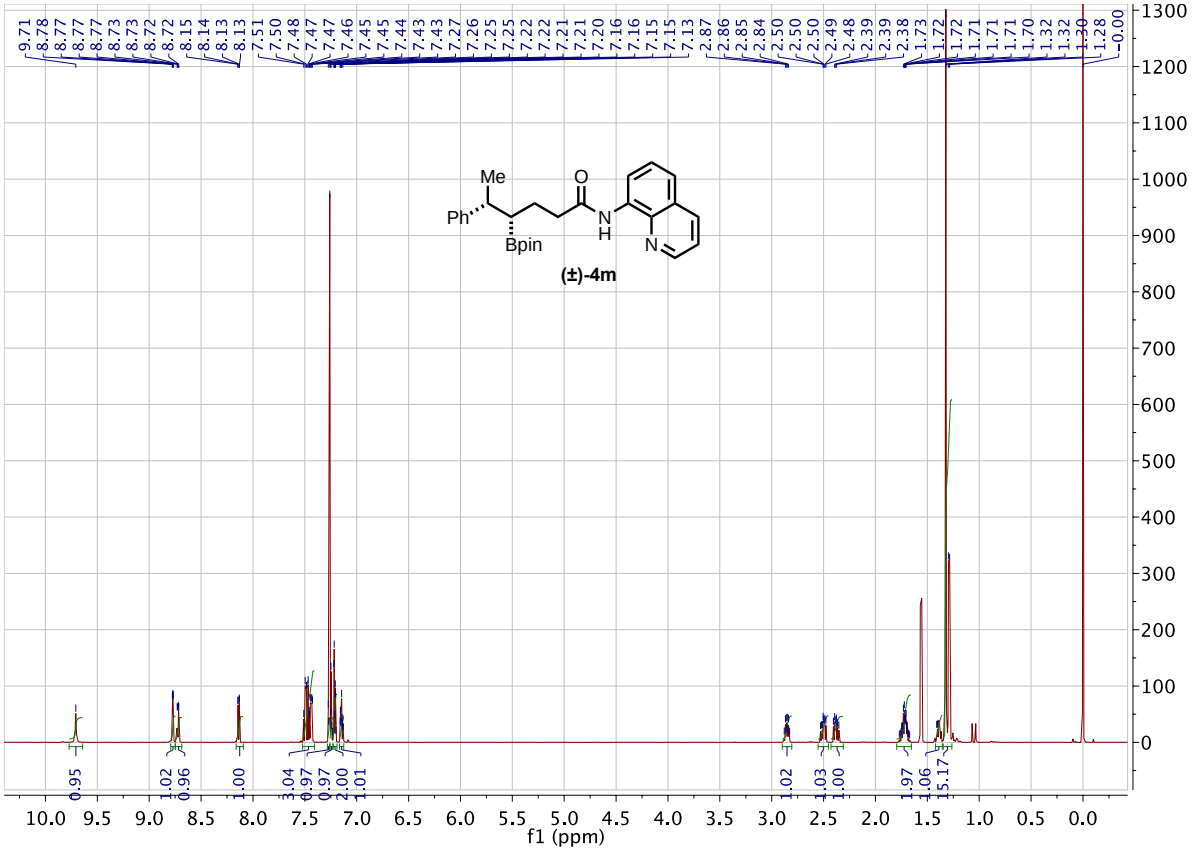

Bpin
O
Ph
N
H
Me
Me
N
4j
f1 (ppm)

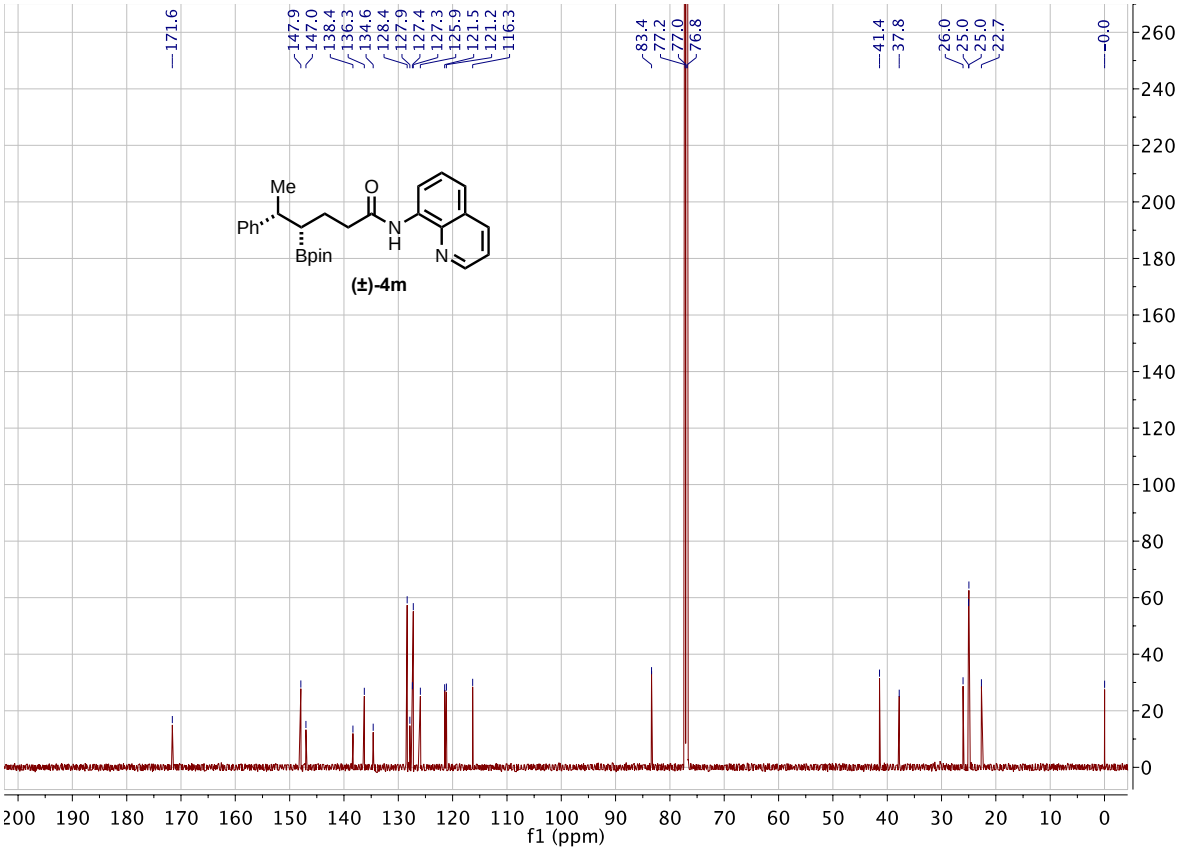

9.55
8.79
8.78
8.78
8.78
8.72
8.72
8.71
8.71
8.70
8.13
8.13
8.11
8.11
7.49
7.48
7.47
7.44
7.44
7.43
7.42
7.42
7.41
7.40
7.40
7.35
7.35
7.34
7.33
7.32
7.25
7.23
7.23
7.23
7.22
7.22
7.21
7.20
7.20
3.19
3.16
2.06
2.04
1.54
1.49
1.36
1.30
0.99
0.00
pinB
Me
O
Ph
Me
Me
N
H
N
4k
0.98
1.00
1.02
1.04
1.08
4.12
2.03
1.01
1.00
1.04
3.00
3.00
12.14
3.00
f1 (ppm)

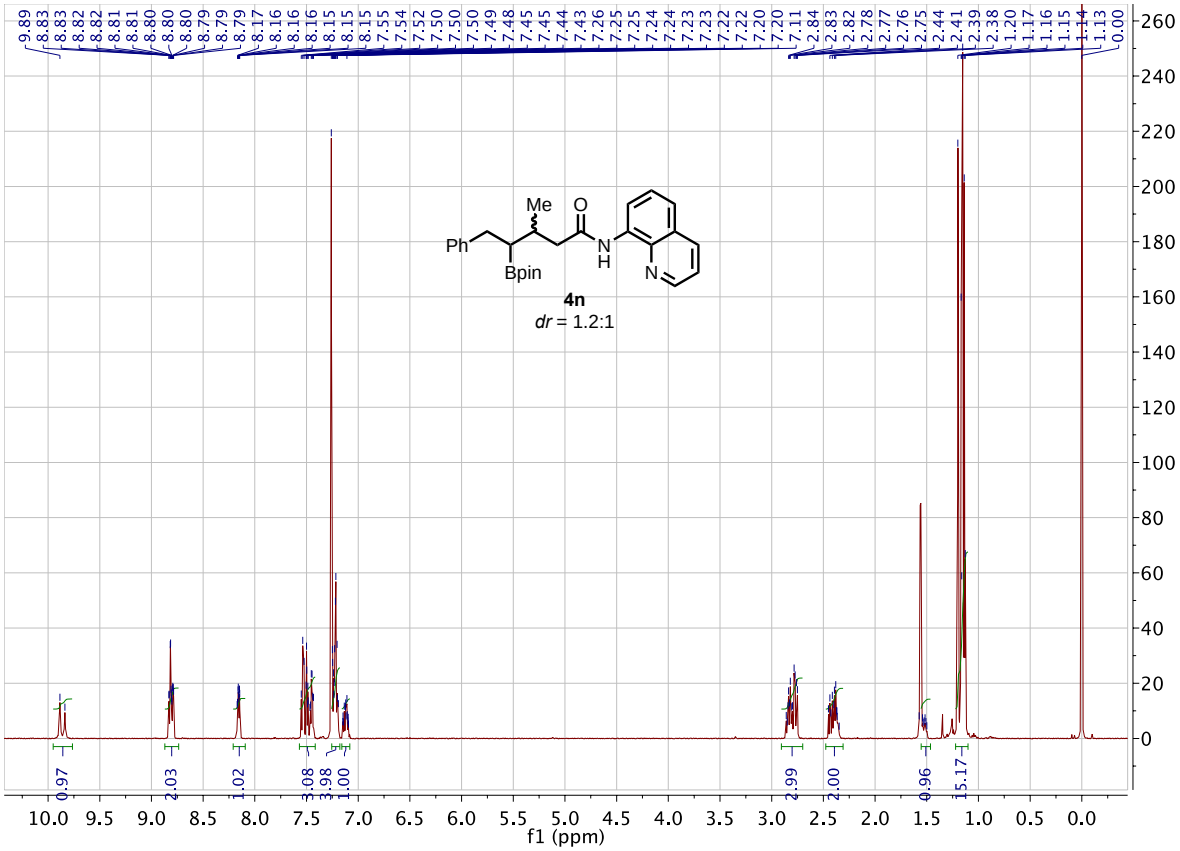

171.8
147.9
146.6
138.2
136.3
134.8
128.3
127.9
127.4
127.2
125.6
121.4
120.9
116.3
83.3
77.2
77.0
76.8
43.8
41.9
26.6
26.0
25.4
25.3
18.4
pinB
Me
O
Ph
Me
Me
N
H
N
4k
f1 (ppm)

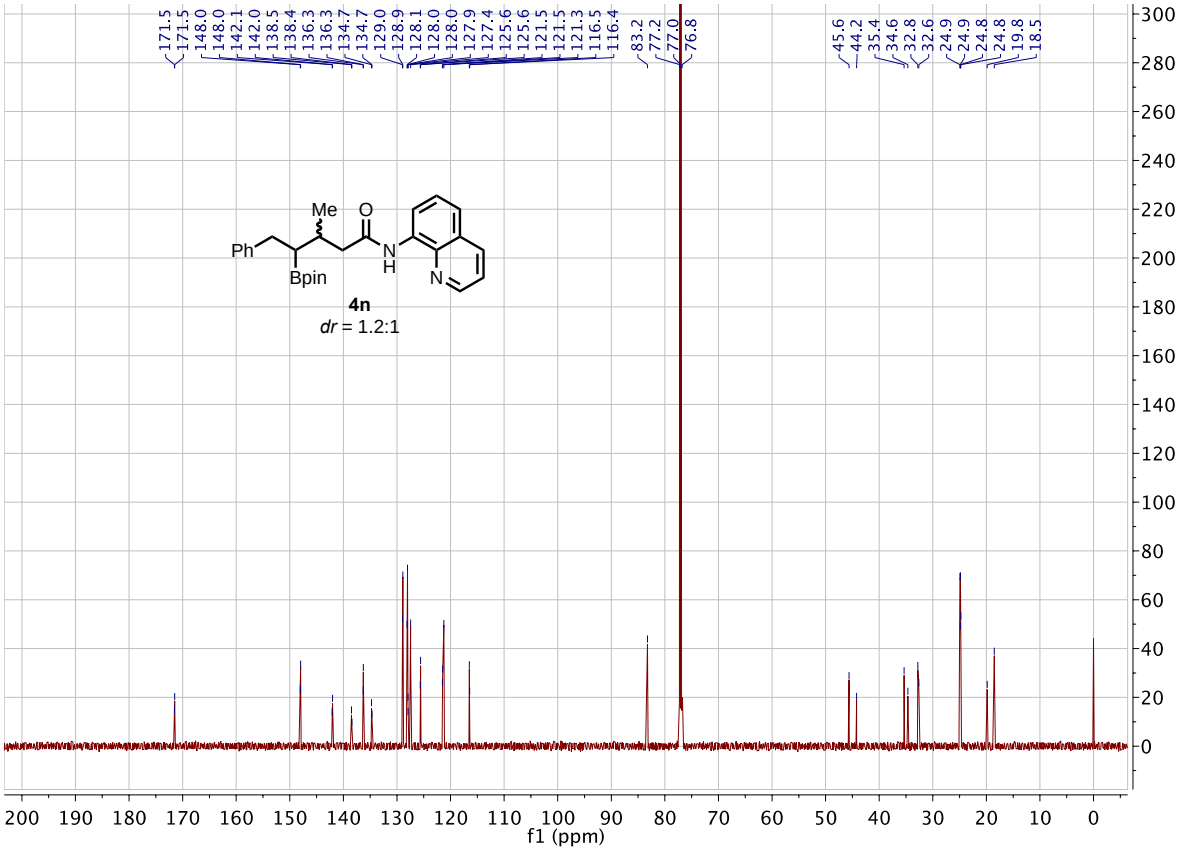

9.85 9.85 8.82 8.82 8.82 8.81 8.81 8.80 8.79 8.19 8.18 8.17 8.16 7.57 7.55 7.53 7.52 7.52 7.50 7.50 7.48 7.47 7.46 7.45 7.29 7.26 7.25 7.18 7.17 7.17 7.16 7.15 2.88 2.86 2.84 2.82 2.80 2.78 2.66 2.65 2.64 2.64 2.63 2.62 2.61 2.60 2.59 2.01 2.01 1.99 1.99 1.98 1.98 1.97 1.97 1.96 1.54 1.52 1.23 1.21 0.03
Ph
Bpin
O
N
H
N
4l
0.87 1.93 0.97 3.03 3.87 0.99 1.95 1.92 2.00 1.00 11.82
f1 (ppm)

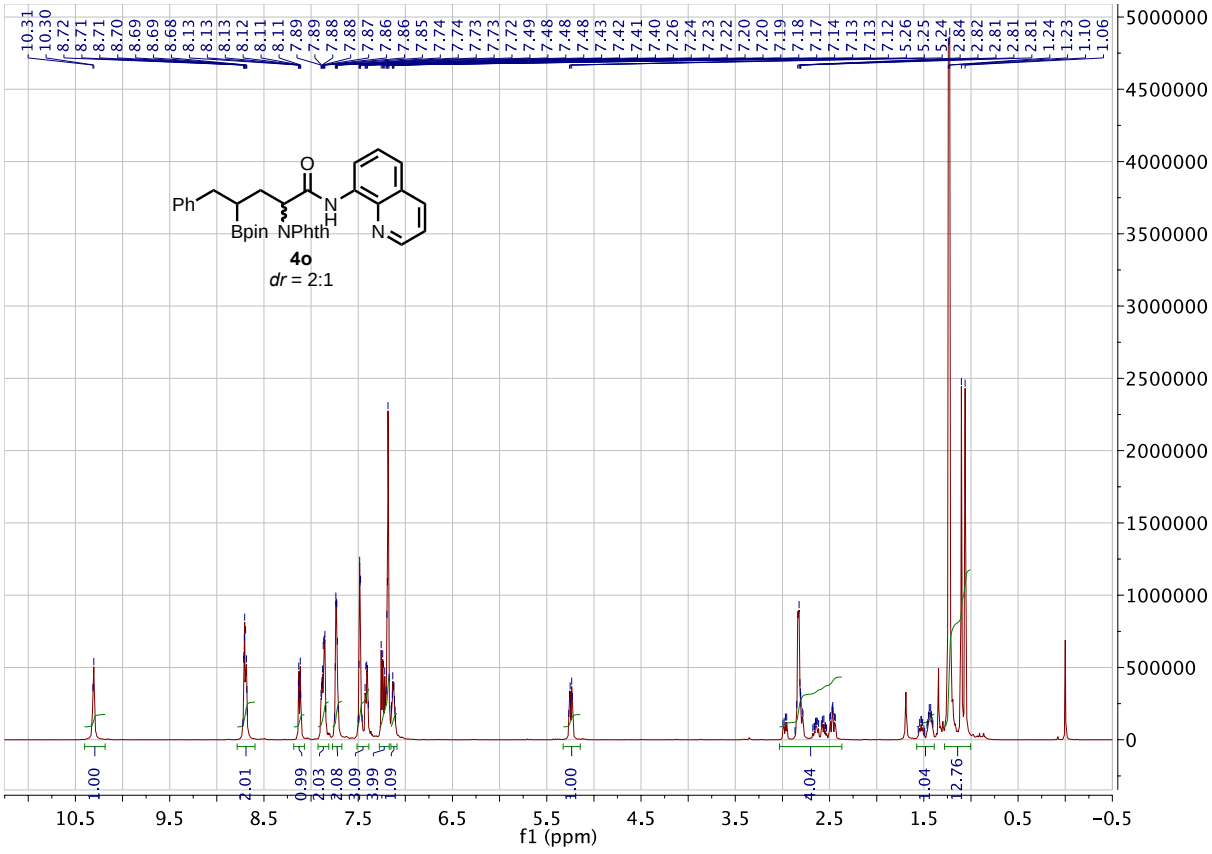

171.7
148.0 141.8 138.4 136.3 134.6 128.9 128.1 127.9 127.4 125.7 121.5 121.2 116.4
83.2 77.3 77.0 76.7
37.8 37.1 27.0 24.8 24.8
Ph
Bpin
O
N
H
N
4l
f1 (ppm)

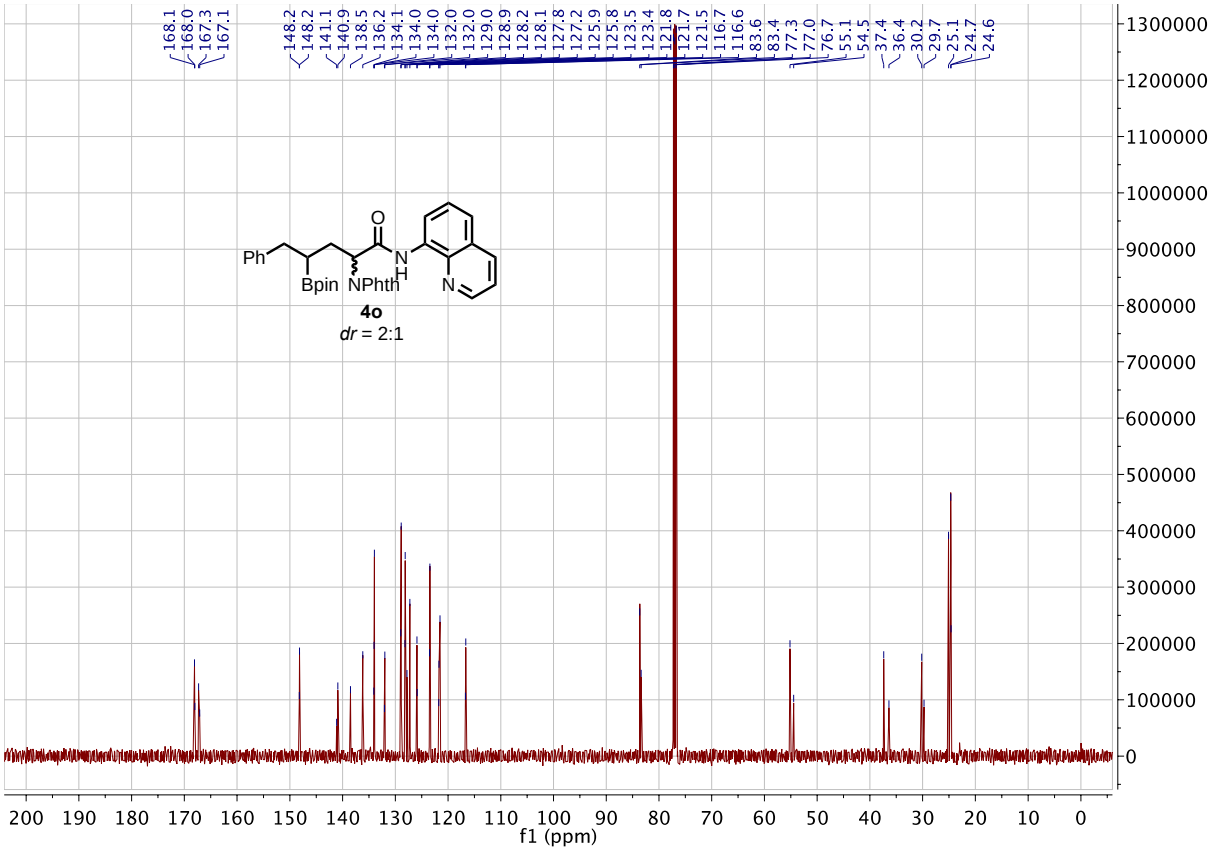

Me
O
Ph
N
H
Bpin
N
(±)-4m
f1 (ppm)

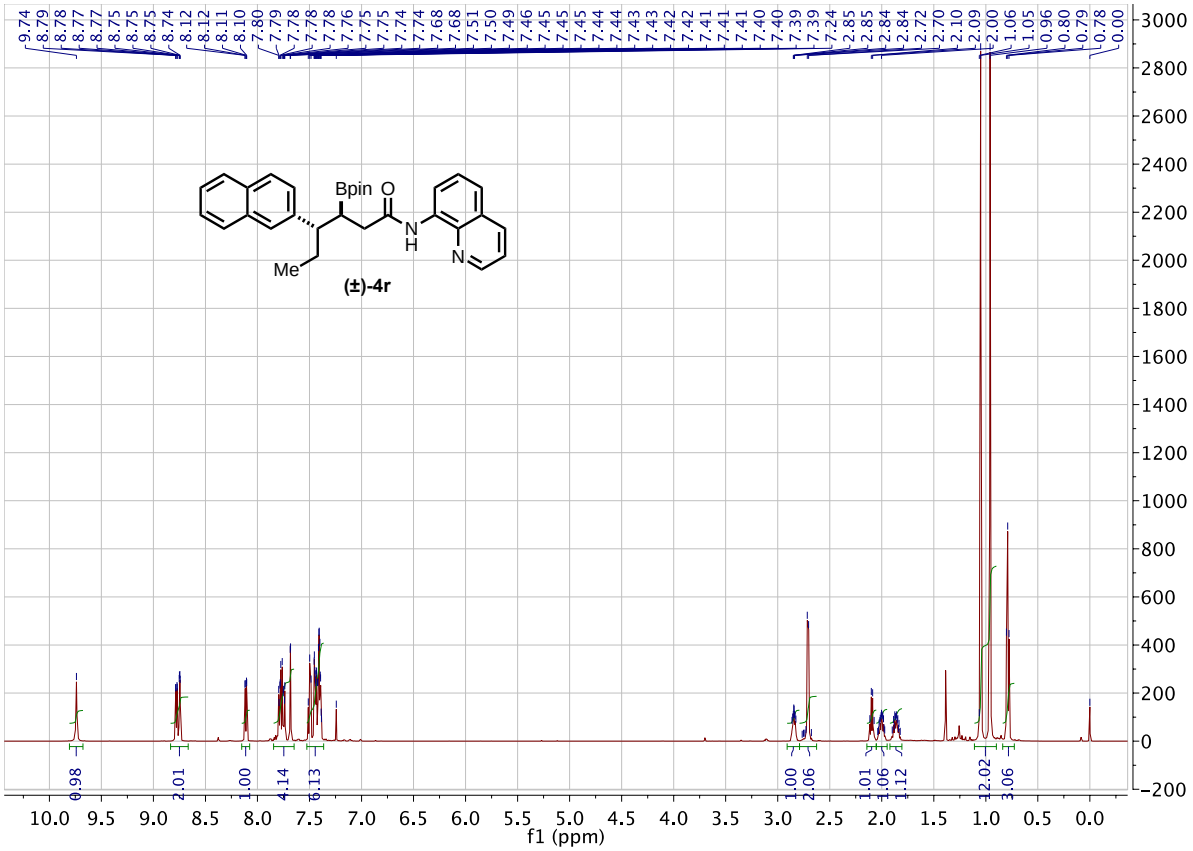

Me
O
Ph
N
H
Bpin
N
(±)-4m
f1 (ppm)

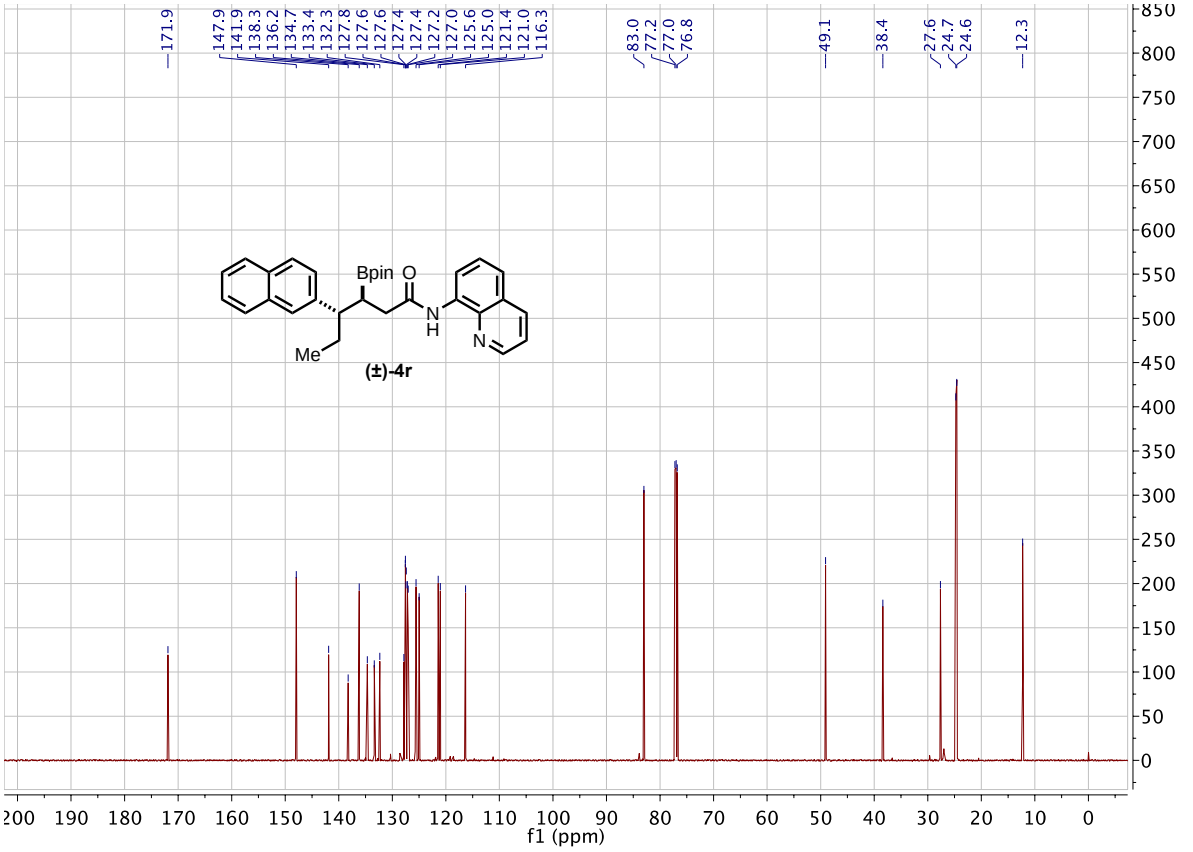

Me
O
Ph
N
H
Bpin
N
4n
dr = 1.2:1
f1 (ppm)

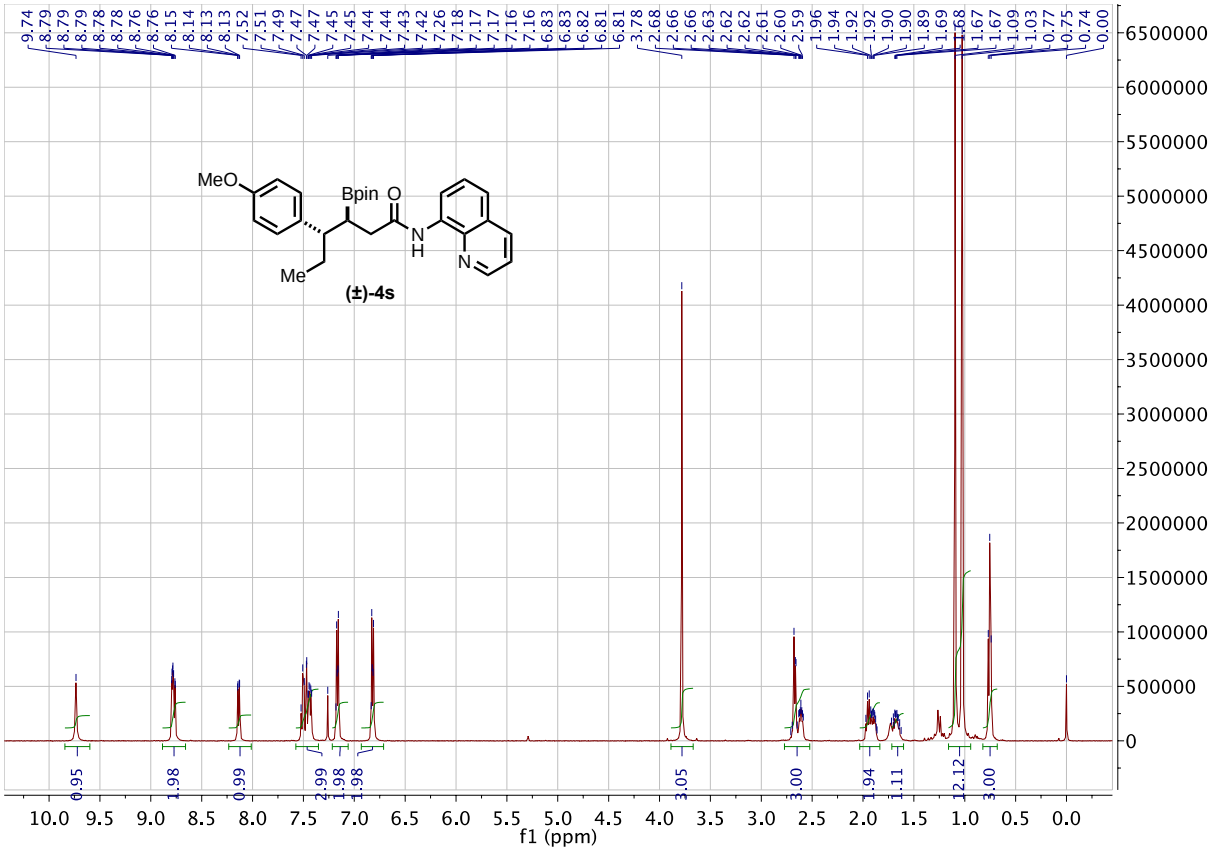

Me
O
Ph
N
H
Bpin
N
4n
dr = 1.2:1
f1 (ppm)

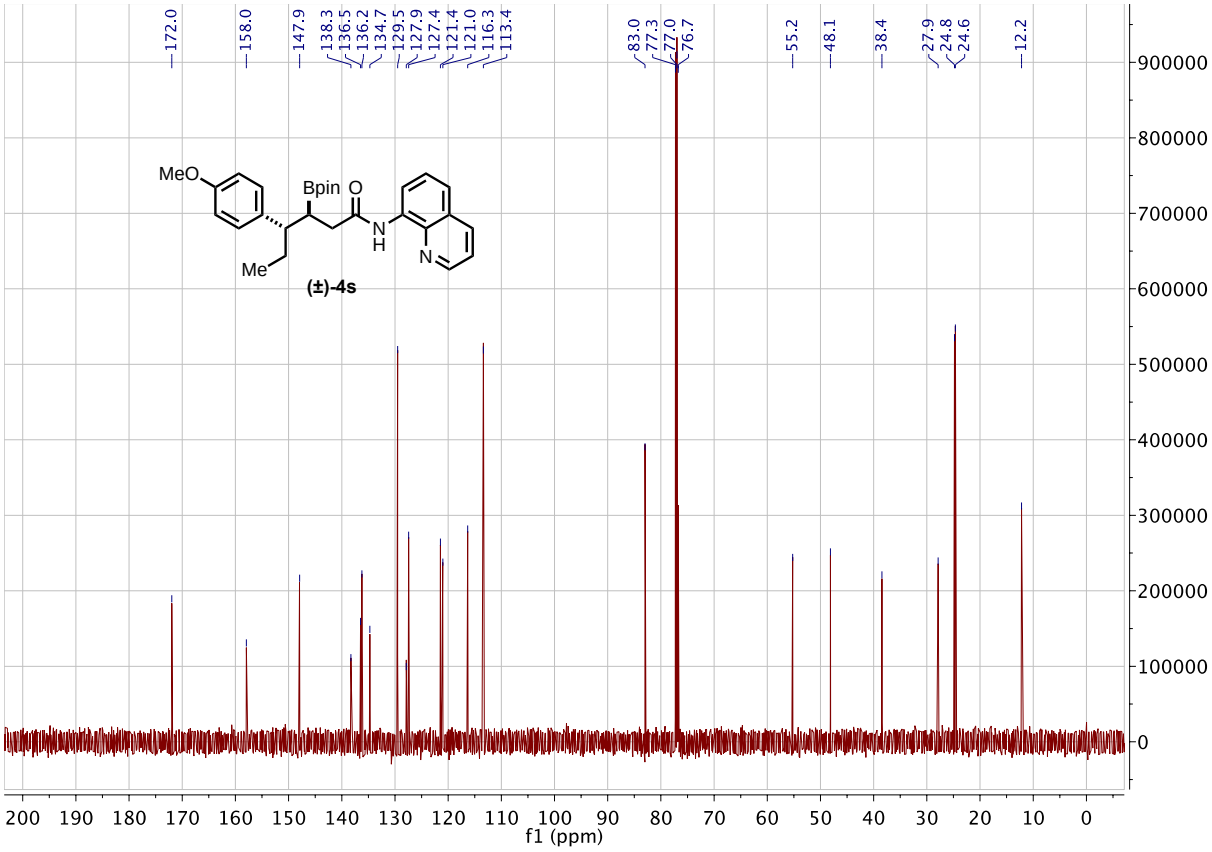

Ph
Bpin
NPhth
O
N
H
N
4o
dr = 2:1
f1 (ppm)


Ph
Bpin
NPhth
O
N
H
N
4o
dr = 2:1
f1 (ppm)


Bpin
O
N
H
N
Me
(±)-4r
f1 (ppm)


Bpin
O
N
H
N
Me
(±)-4r
f1 (ppm)


MeO
Bpin
O
N
H
N
Me
(±)-4s
f1 (ppm)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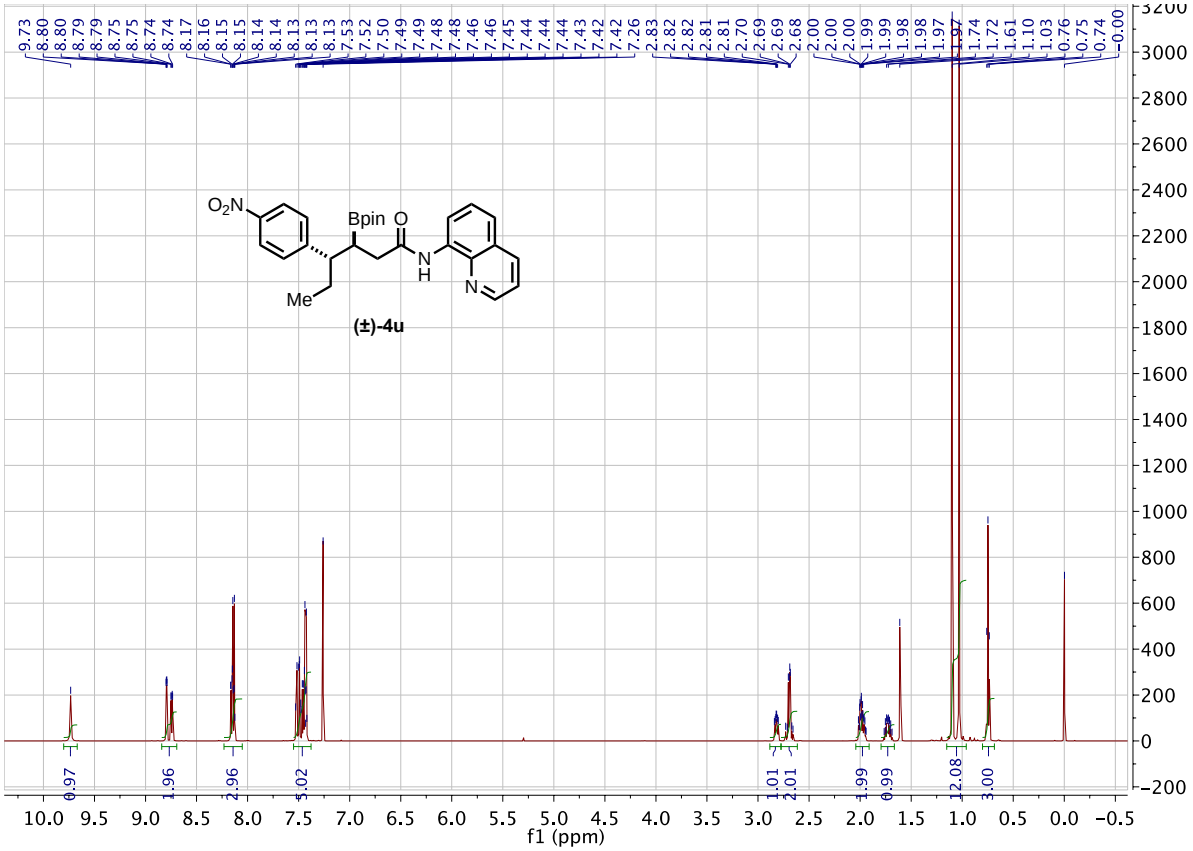
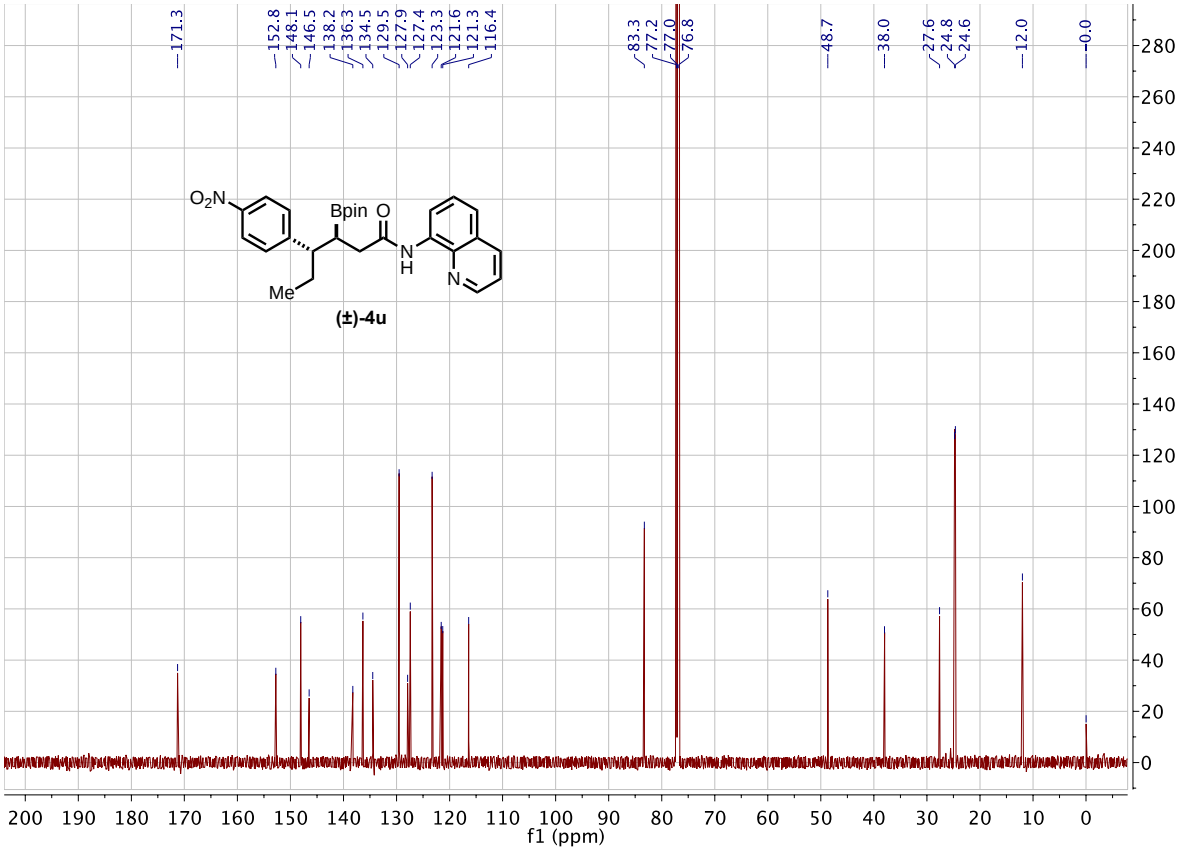
Bpin
O
N
H
N
Me
(±)-4s
f1 (ppm)


O2N
Bpin
O
N
H
N
Me
(±)-4u
f1 (ppm)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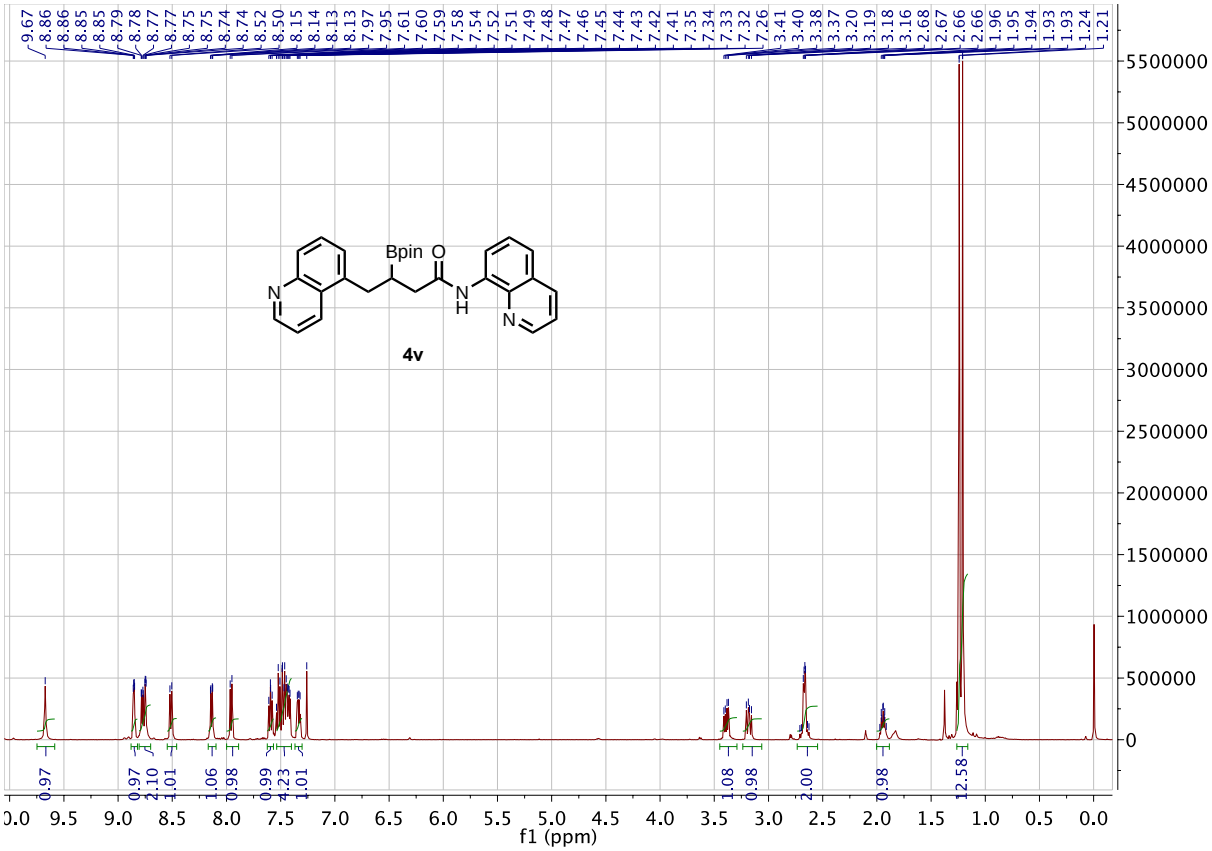
Bpin
O
N
H
N
Me
(±)-4u
f1 (ppm)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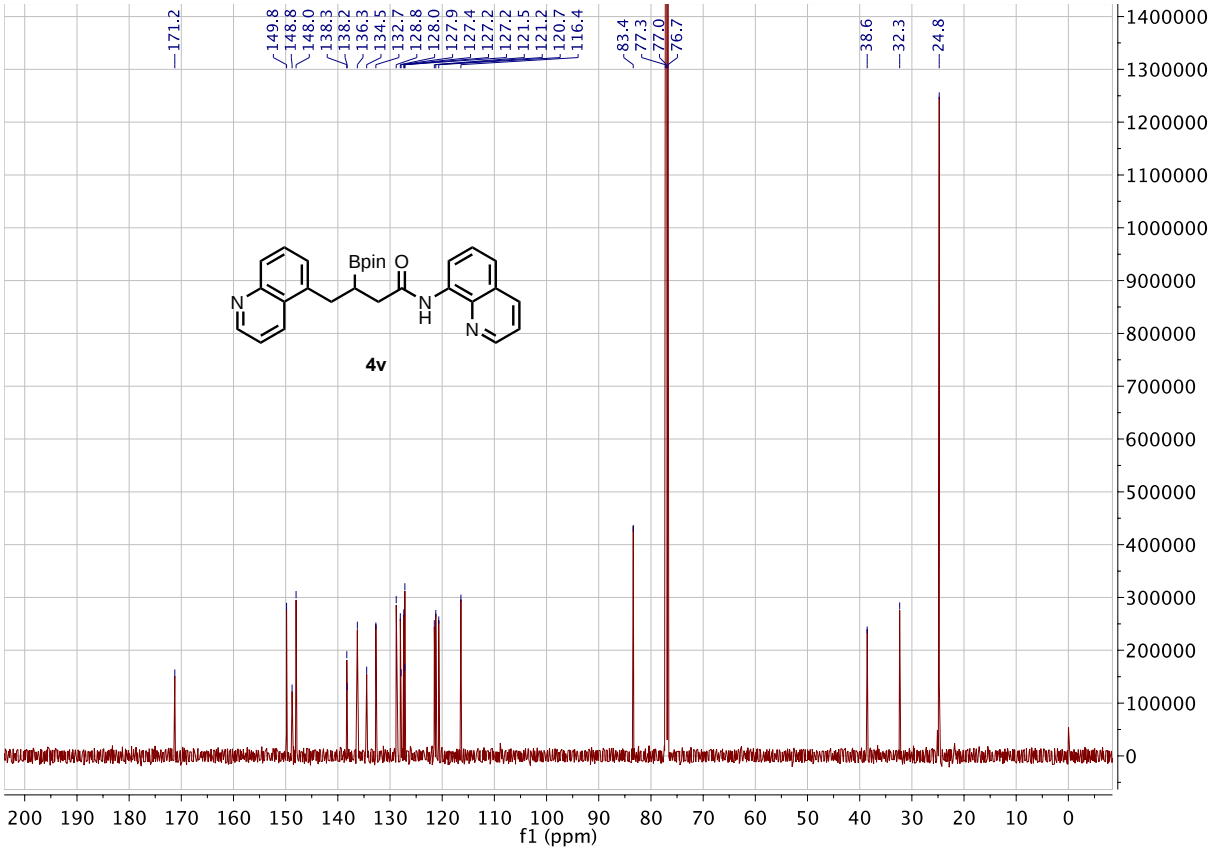
O
N
H
N
4v
f1 (ppm)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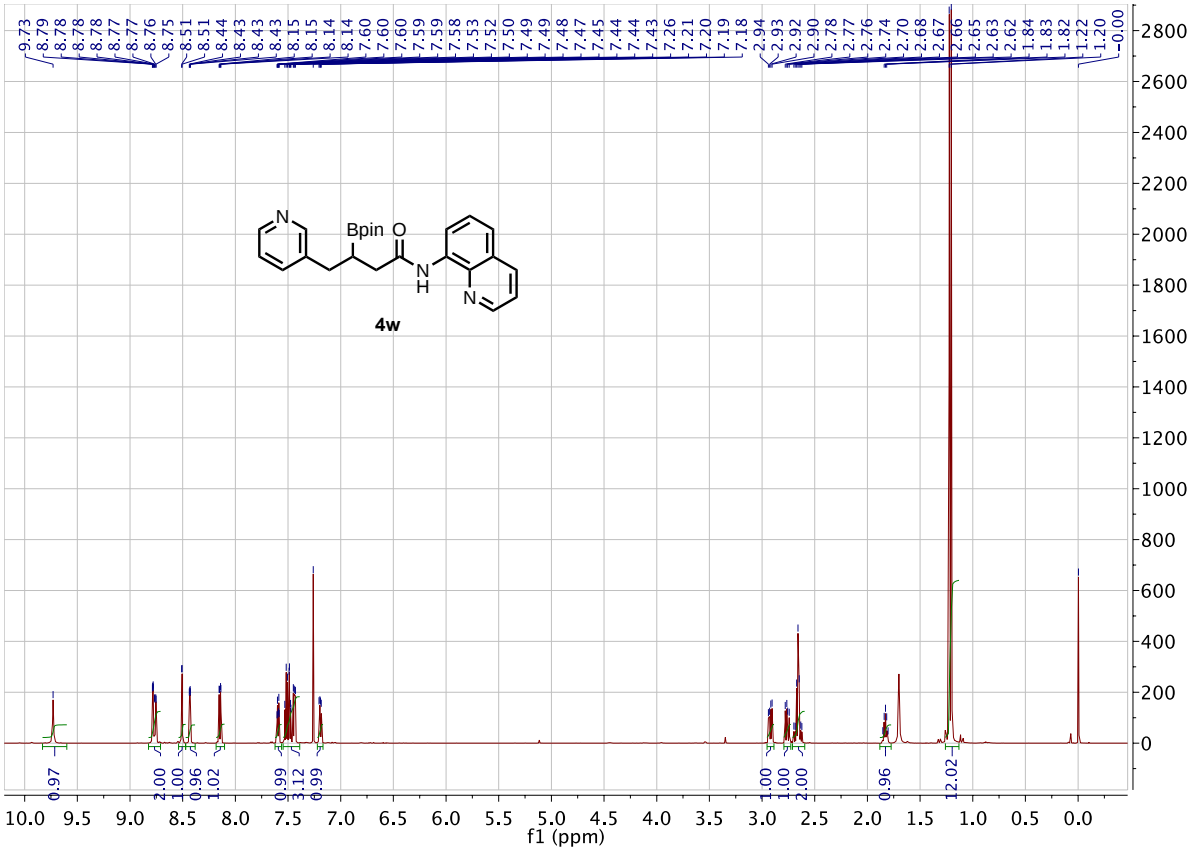
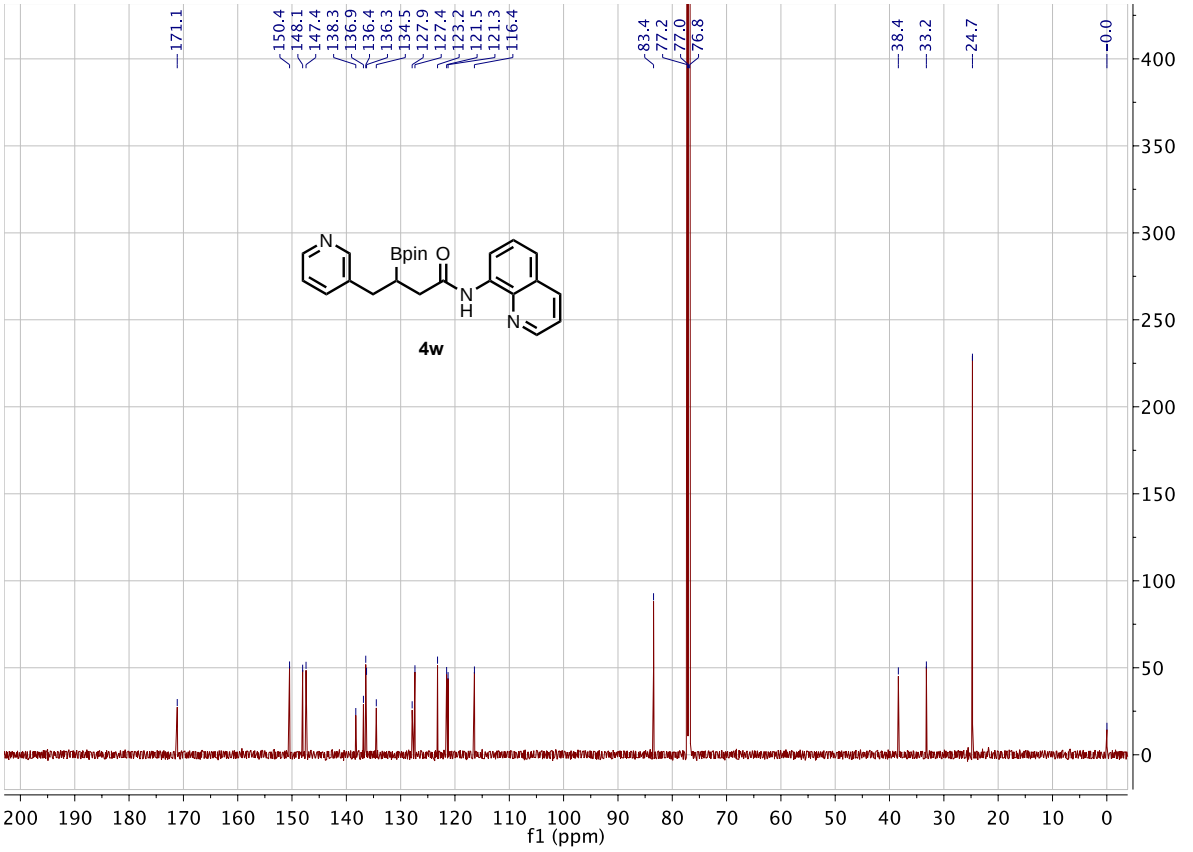
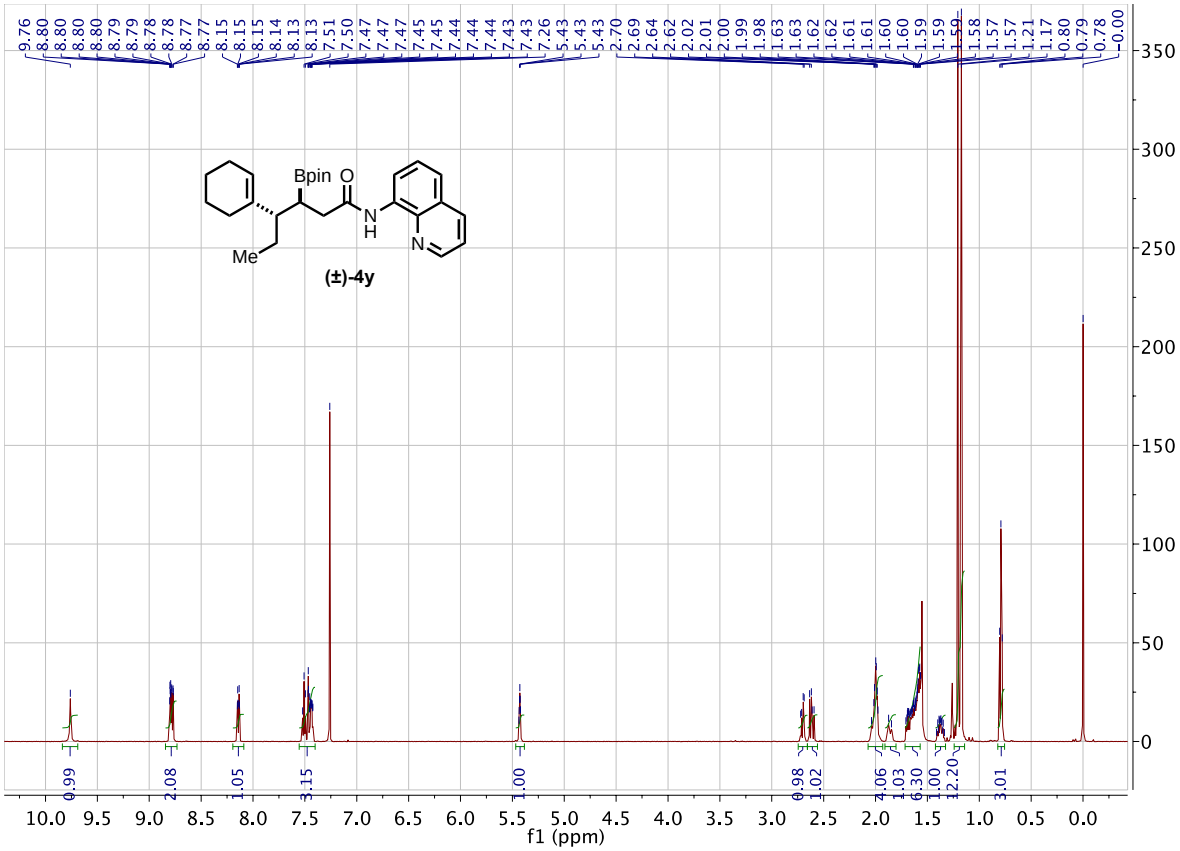
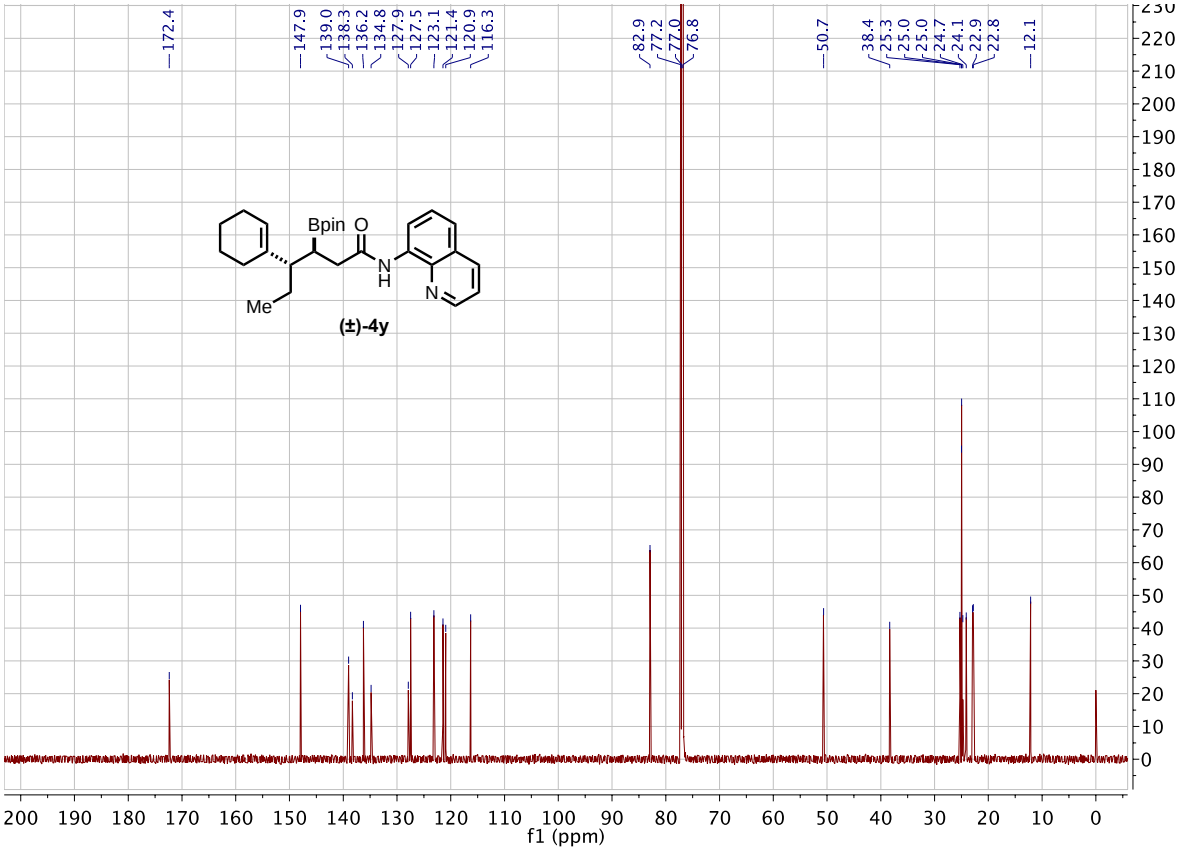
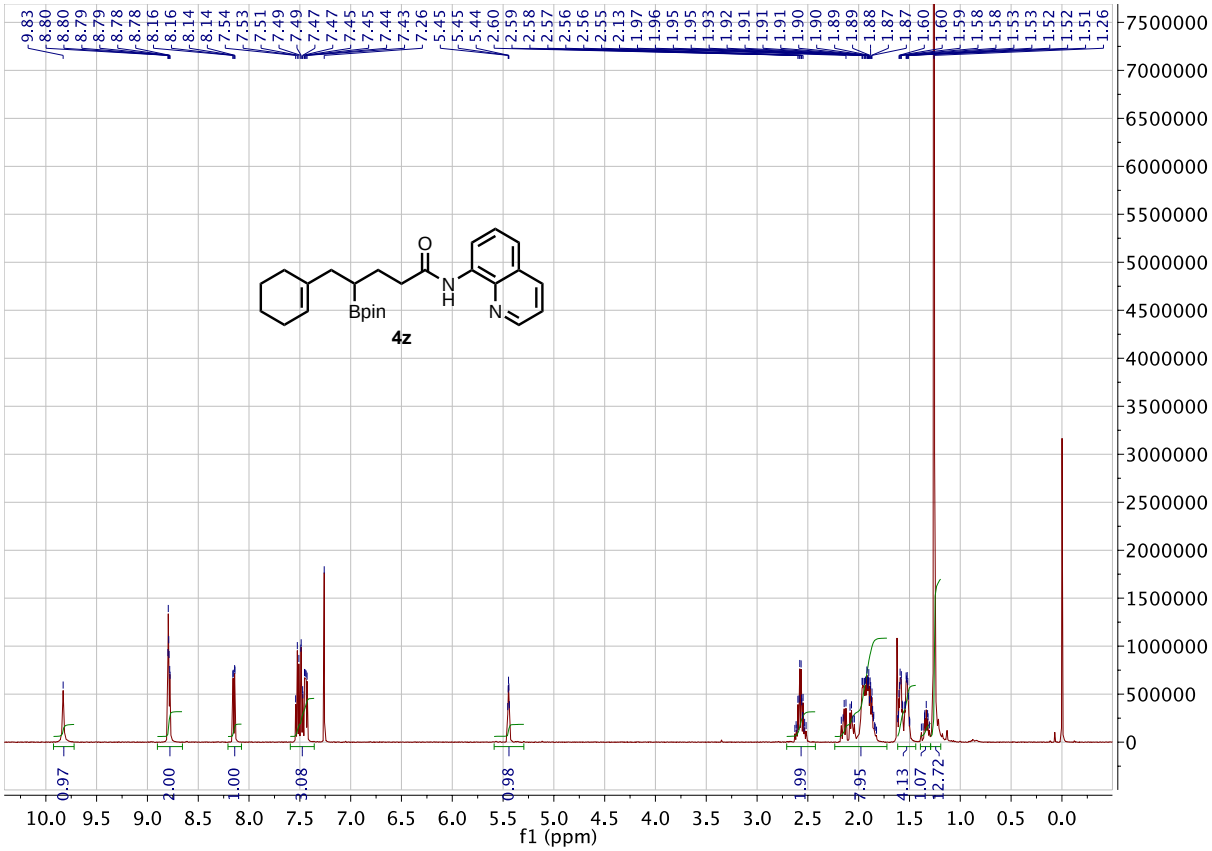
O
N
H
N
4v
f1 (ppm)

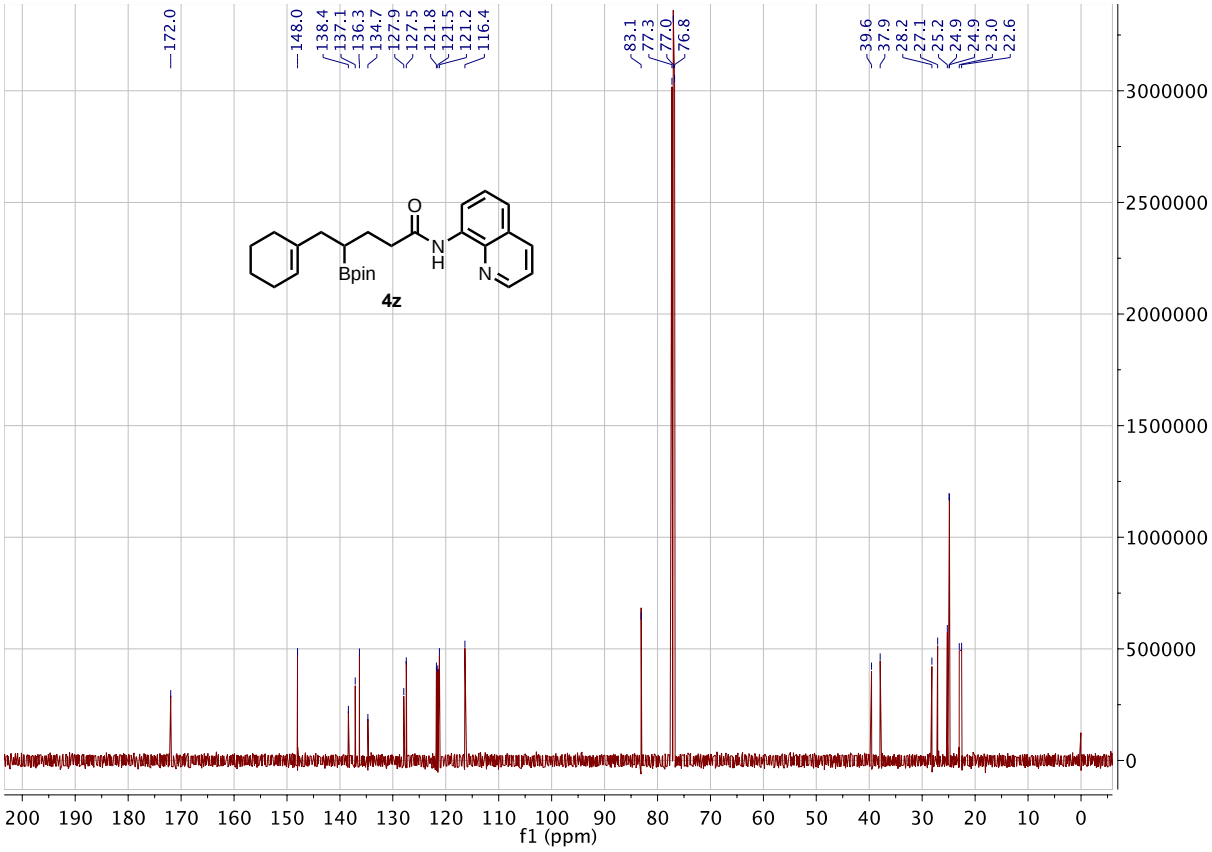

Bpin
O
N
H
N
4w
f1 (ppm)

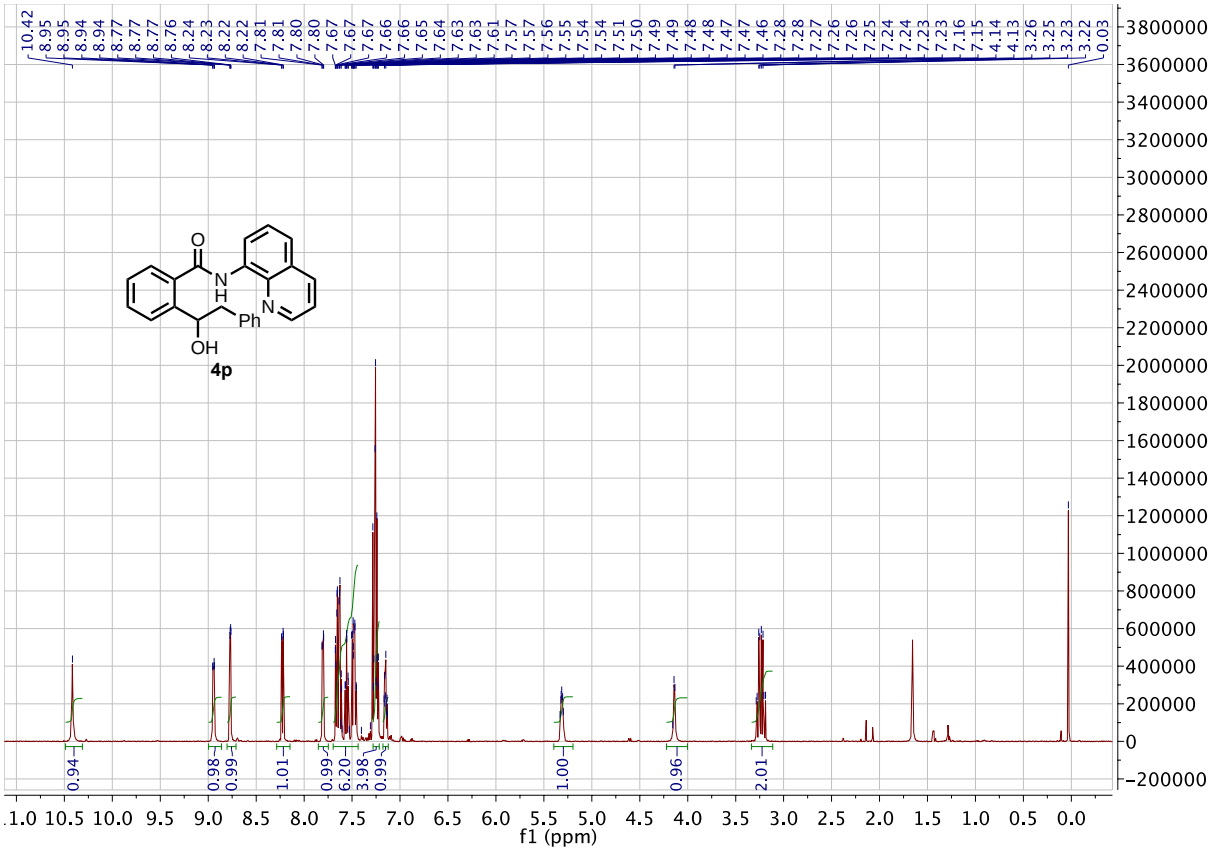

Bpin
O
N
H
N
4w
f1 (ppm)

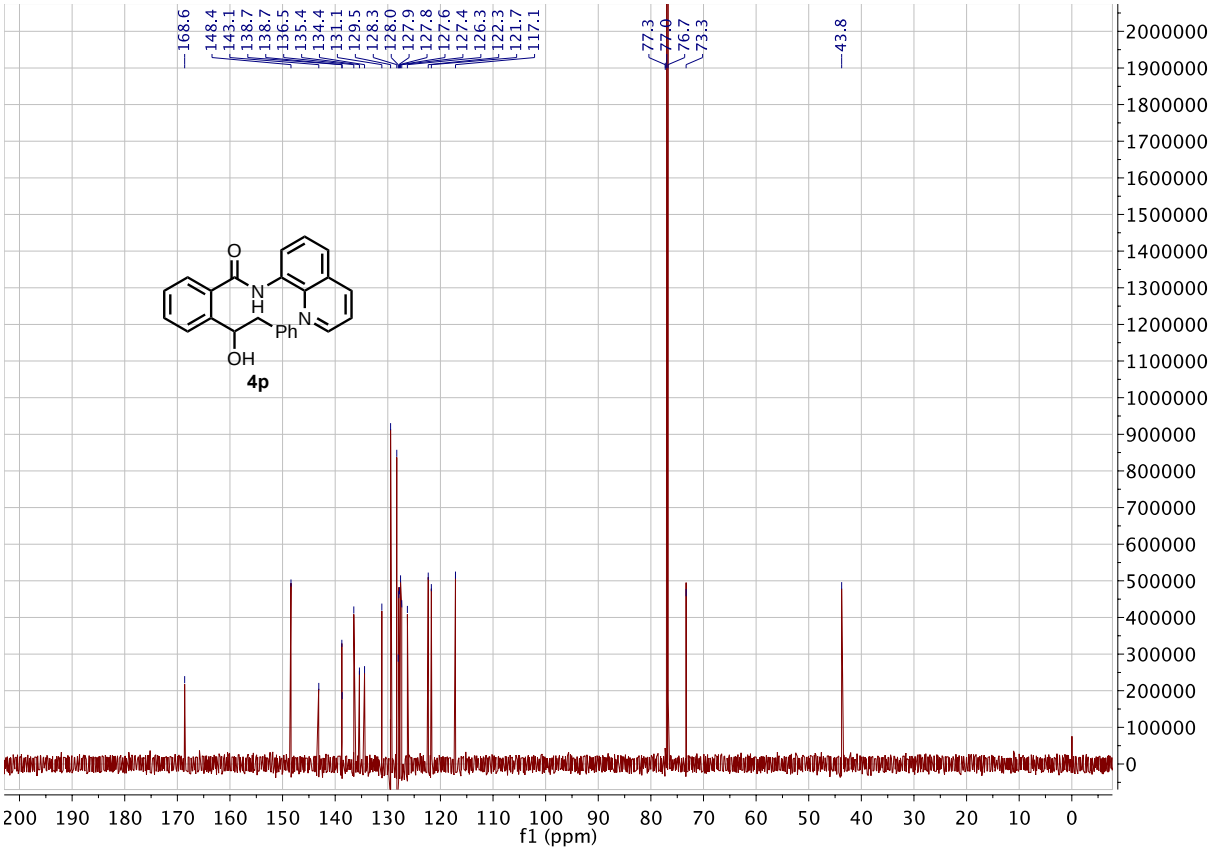

Bpin
O
N
H
N
Me
(±)-4y
f1 (ppm)

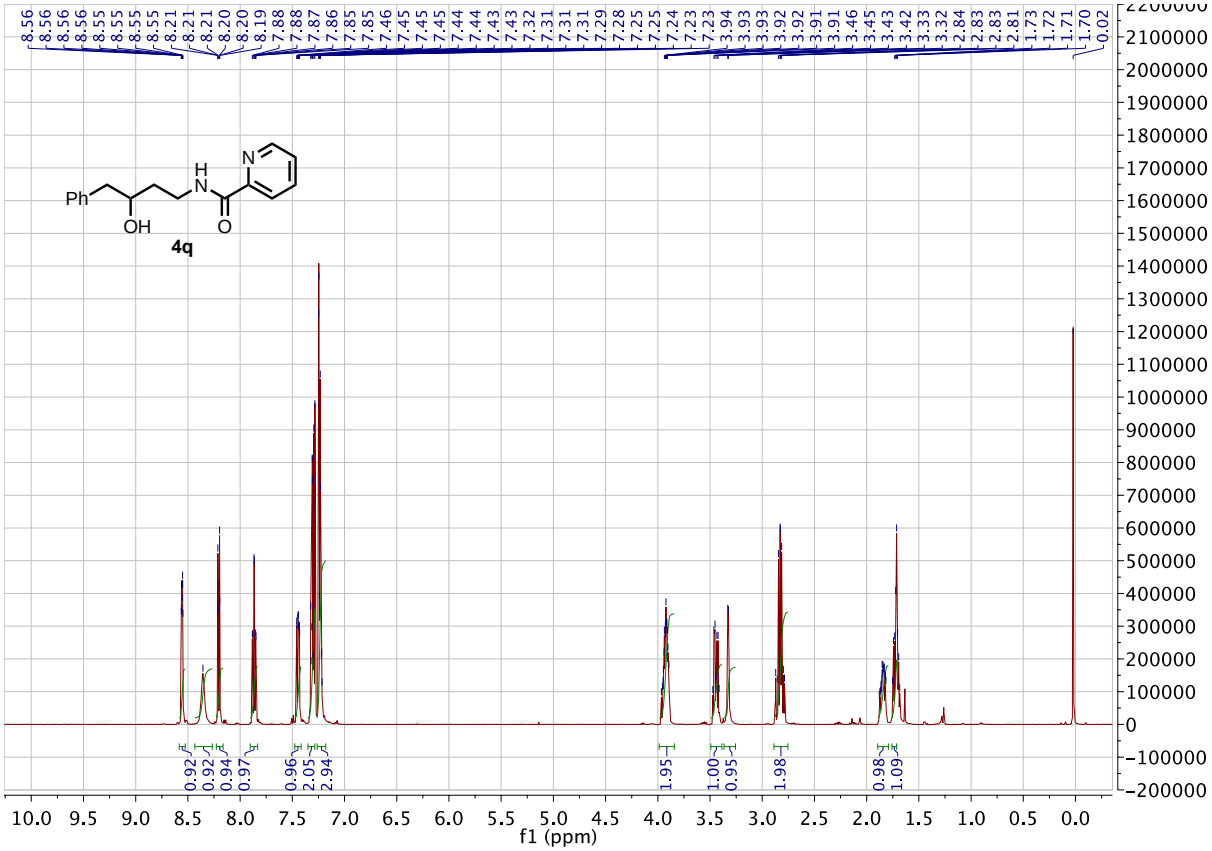

Bpin
O
N
H
N
Me
(±)-4y
f1 (ppm)

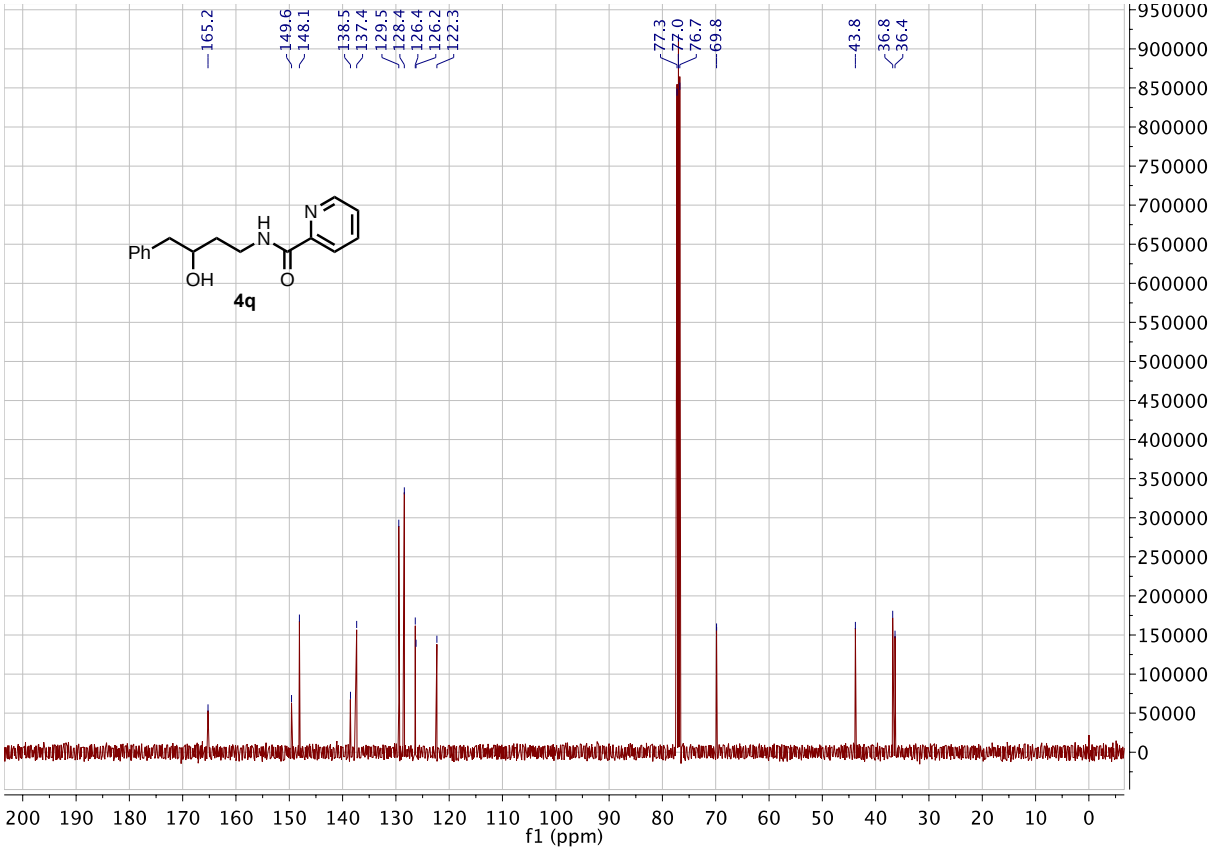

9.83 8.80 8.80 8.79 8.79 8.78 8.78 8.78 8.16 8.16 8.14 8.14 7.54 7.53 7.51 7.49 7.49 7.47 7.47 7.45 7.45 7.44 7.43 7.26 5.45 5.45 5.44 2.60 2.59 2.58 2.57 2.56 2.56 2.55 2.13 1.97 1.96 1.95 1.95 1.93 1.92 1.91 1.91 1.91 1.90 1.90 1.89 1.89 1.88 1.87 1.87 1.60 1.60 1.59 1.58 1.58 1.53 1.53 1.52 1.52 1.51 1.26
O
N
H
N
Bpin
4z
0.97 2.00 1.00 3.08 0.98 1.99 7.95 4.13 1.07 12.72
f1 (ppm)

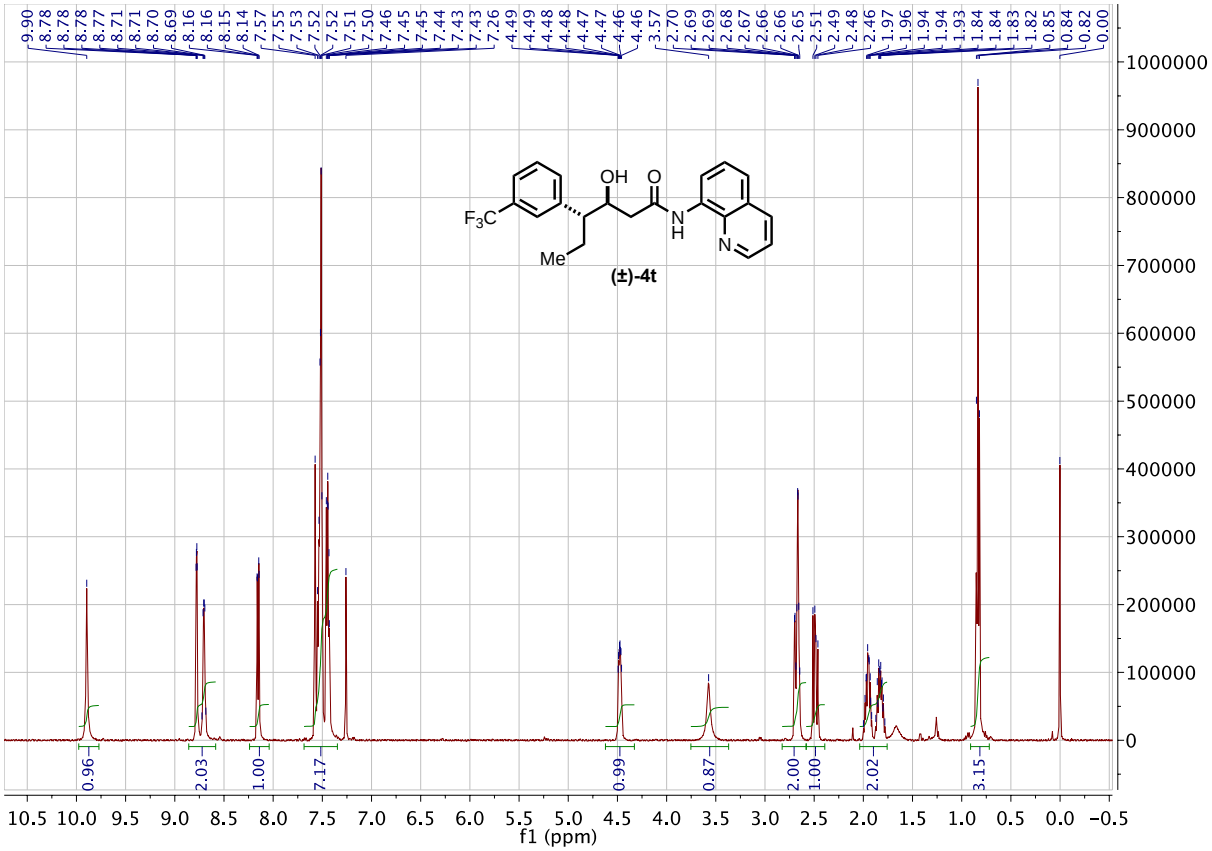

172.0
148.0 138.4 137.1 136.3 134.7 127.9 127.5 121.8 121.5 121.2 116.4
83.1 77.3 77.0 76.8
39.6 37.9 28.2 27.1 25.2 24.9 24.9 23.0 22.6
O
N
H
N
Bpin
4z
f1 (ppm)

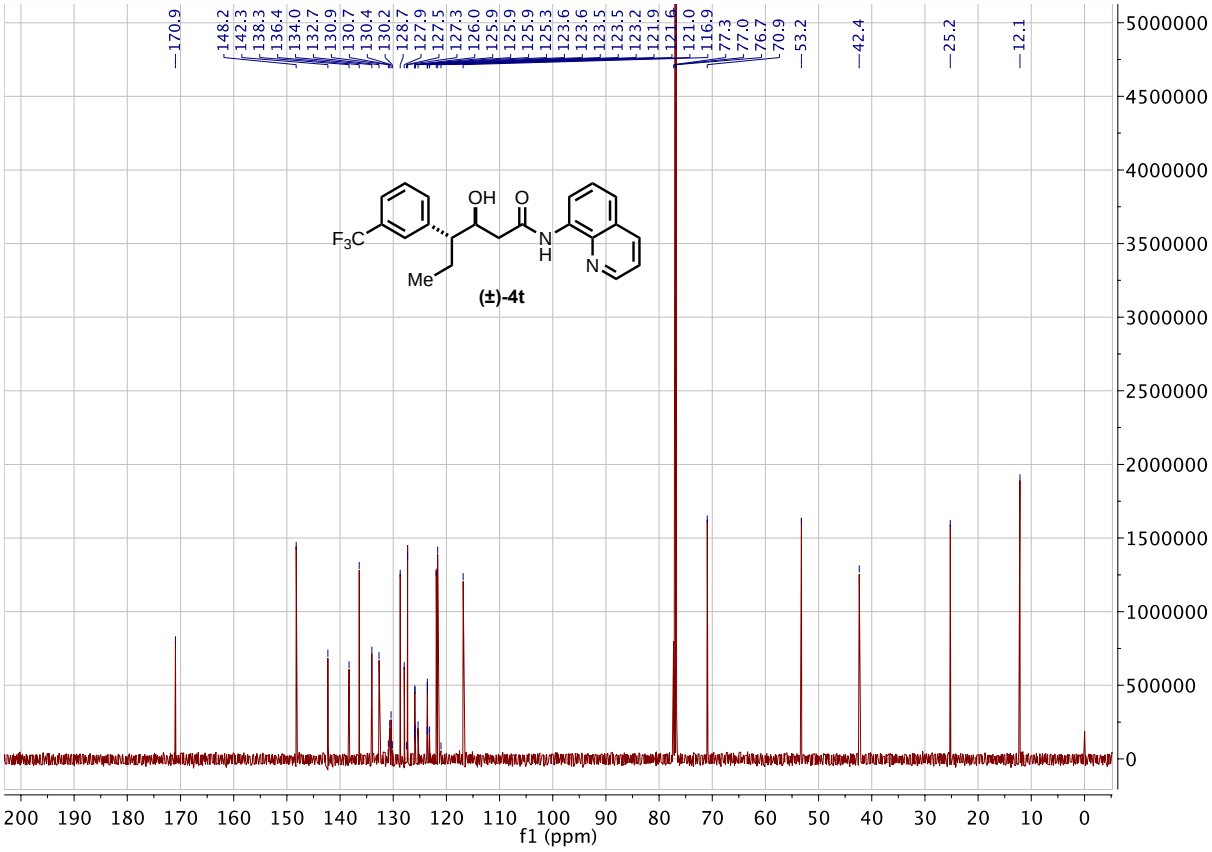

4p
f1 (ppm)

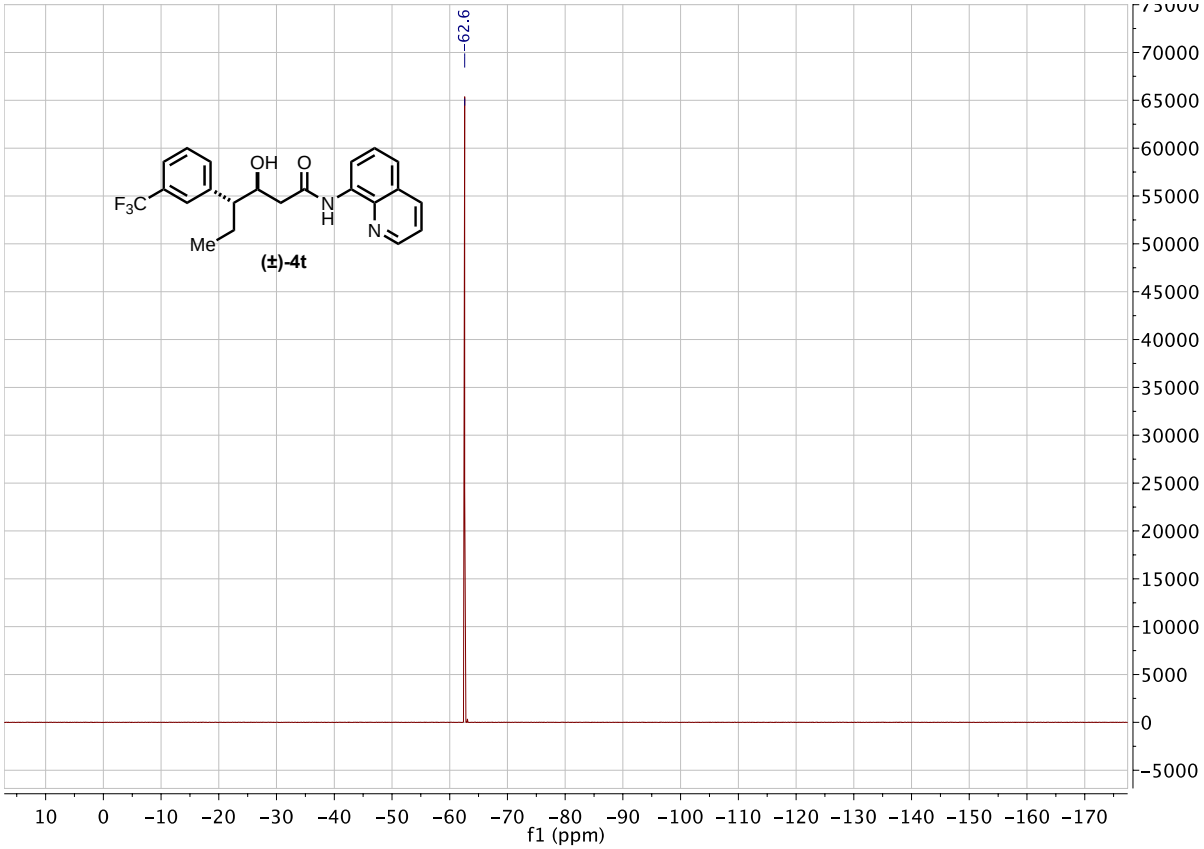

4p
f1 (ppm)

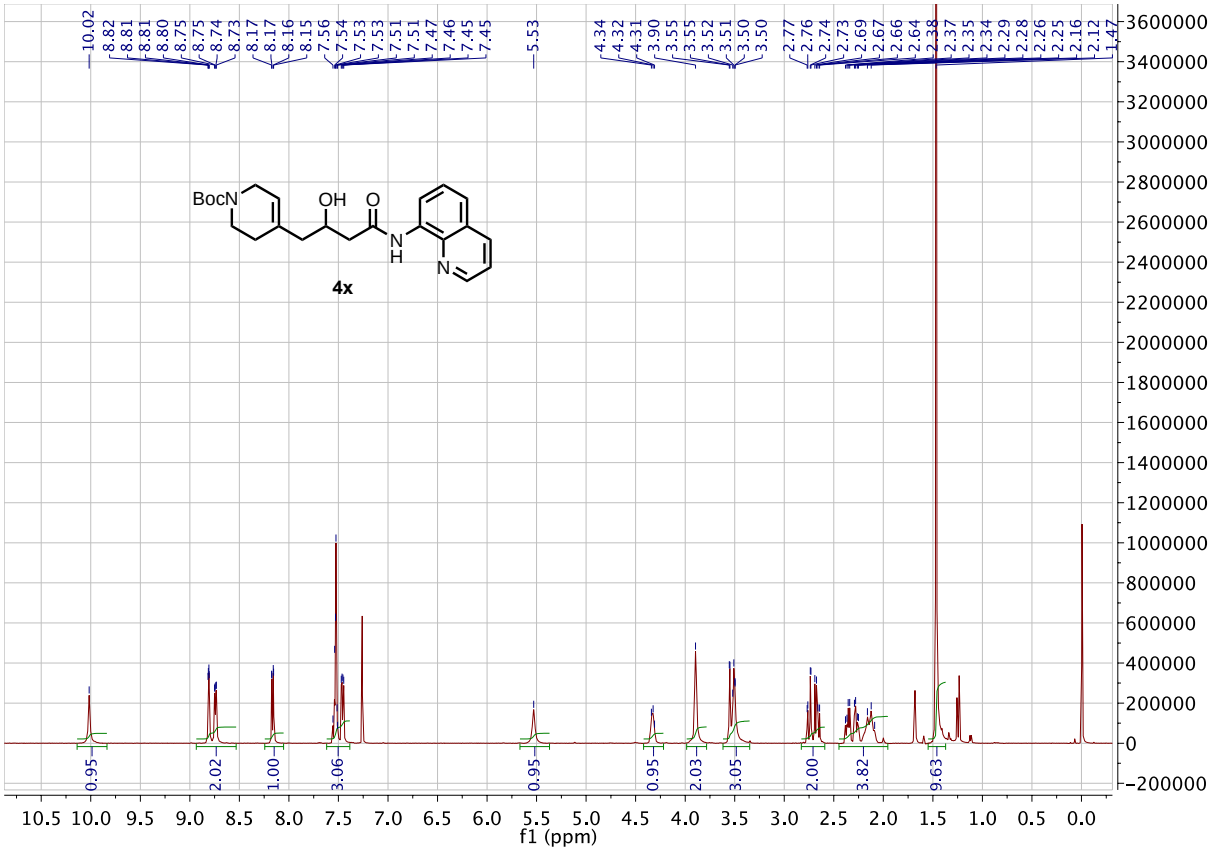

8.56 8.56 8.56 8.56 8.55 8.55 8.55 8.55 8.21 8.21 8.20 8.20 8.19 7.88 7.88 7.87 7.86 7.85 7.85 7.46 7.45 7.45 7.45 7.44 7.44 7.43 7.43 7.32 7.31 7.31 7.31 7.29 7.28 7.25 7.25 7.24 7.23 7.23 3.94 3.93 3.93 3.92 3.92 3.91 3.91 3.46 3.45 3.43 3.42 3.33 3.32 2.84 2.83 2.83 2.81 1.73 1.72 1.71 1.70 0.02
Ph
OH
H
N
N
O
4q
0.92 0.92 0.94 0.97 0.96 2.05 2.94 1.95 1.00 0.95 1.98 0.98 1.09
f1 (ppm)

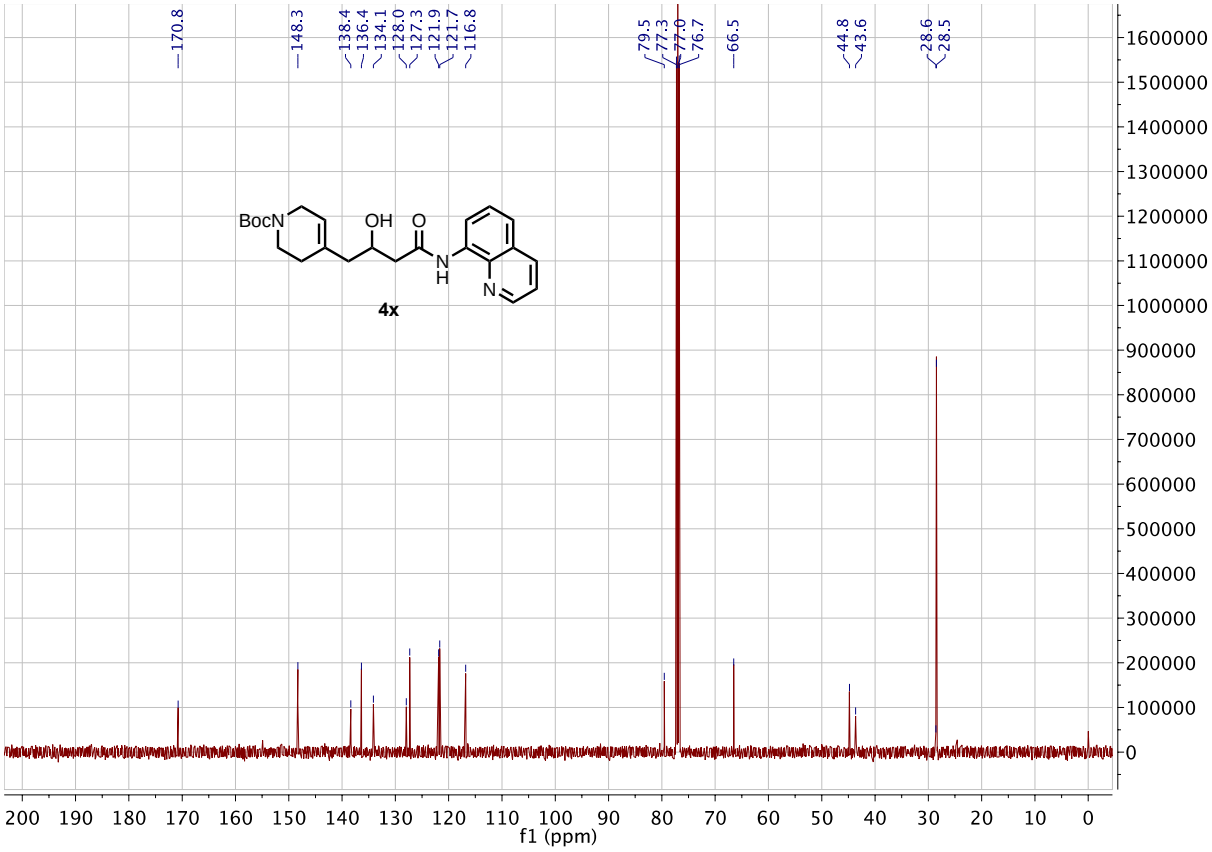

165.2
149.6
148.1
138.5
137.4
129.5
128.4
126.4
126.2
122.3
77.3
77.0
76.7
69.8
43.8
36.8
36.4
Ph
OH
H
N
N
O
4q
f1 (ppm)

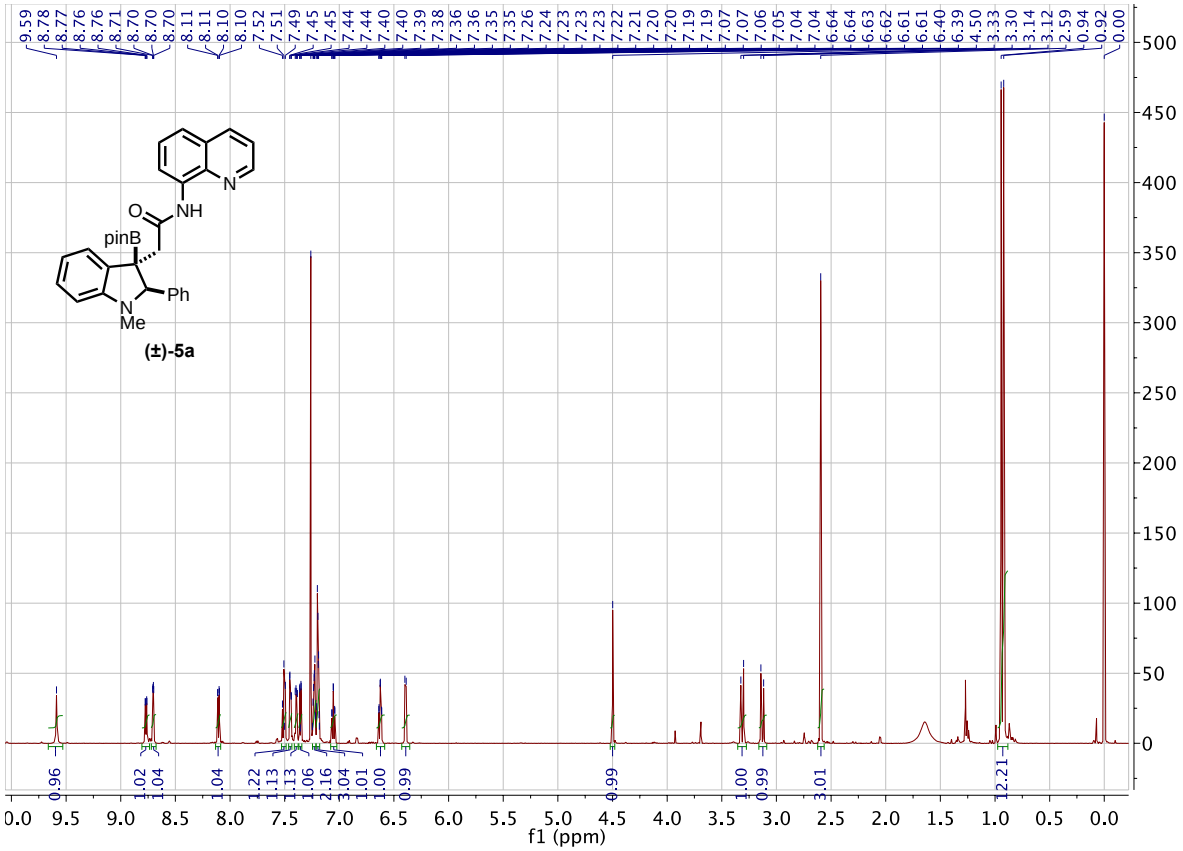

OH
O
F3C
N
H
N
Me
(±)-4t
f1 (ppm)

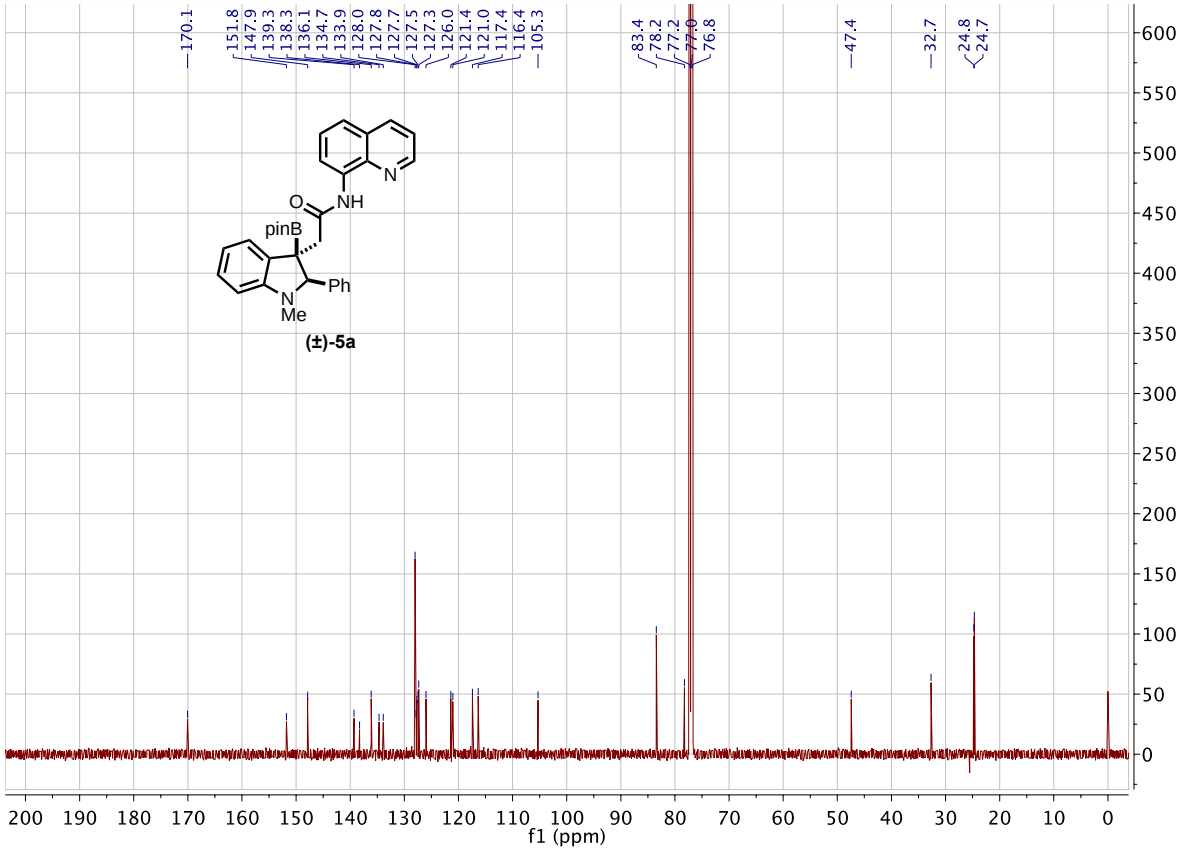

OH
O
F3C
N
H
N
Me
(±)-4t
f1 (ppm)

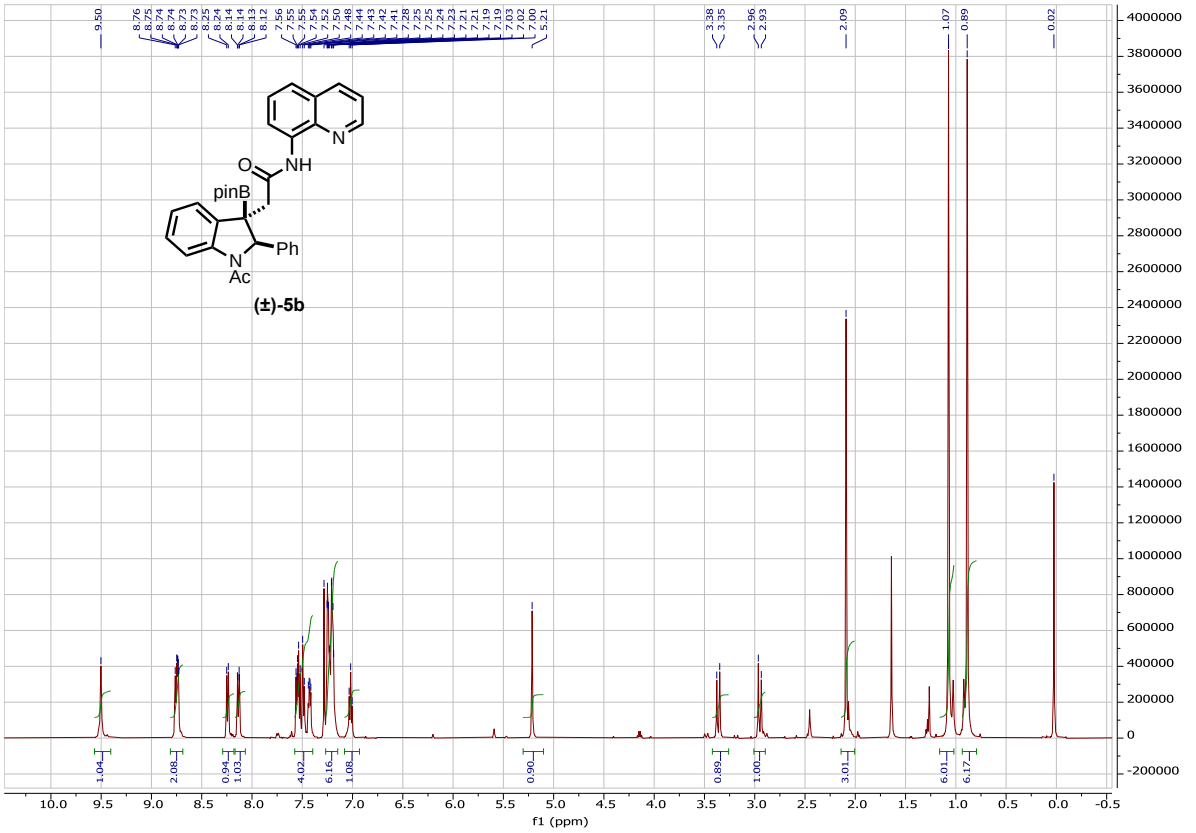

-62.6
OH
O
N
H
N
F3C
Me
(±)-4t
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)

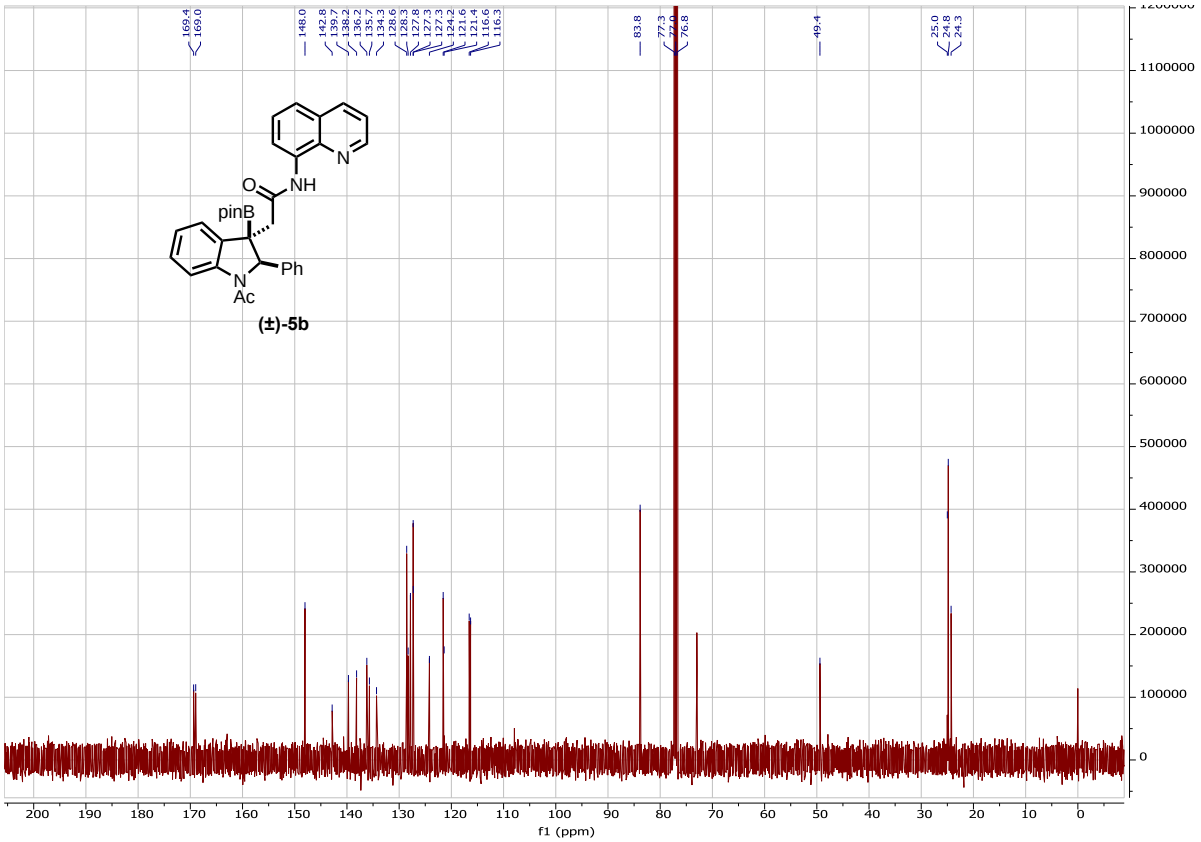

BocN
OH
O
N
H
N
4x
f1 (ppm)

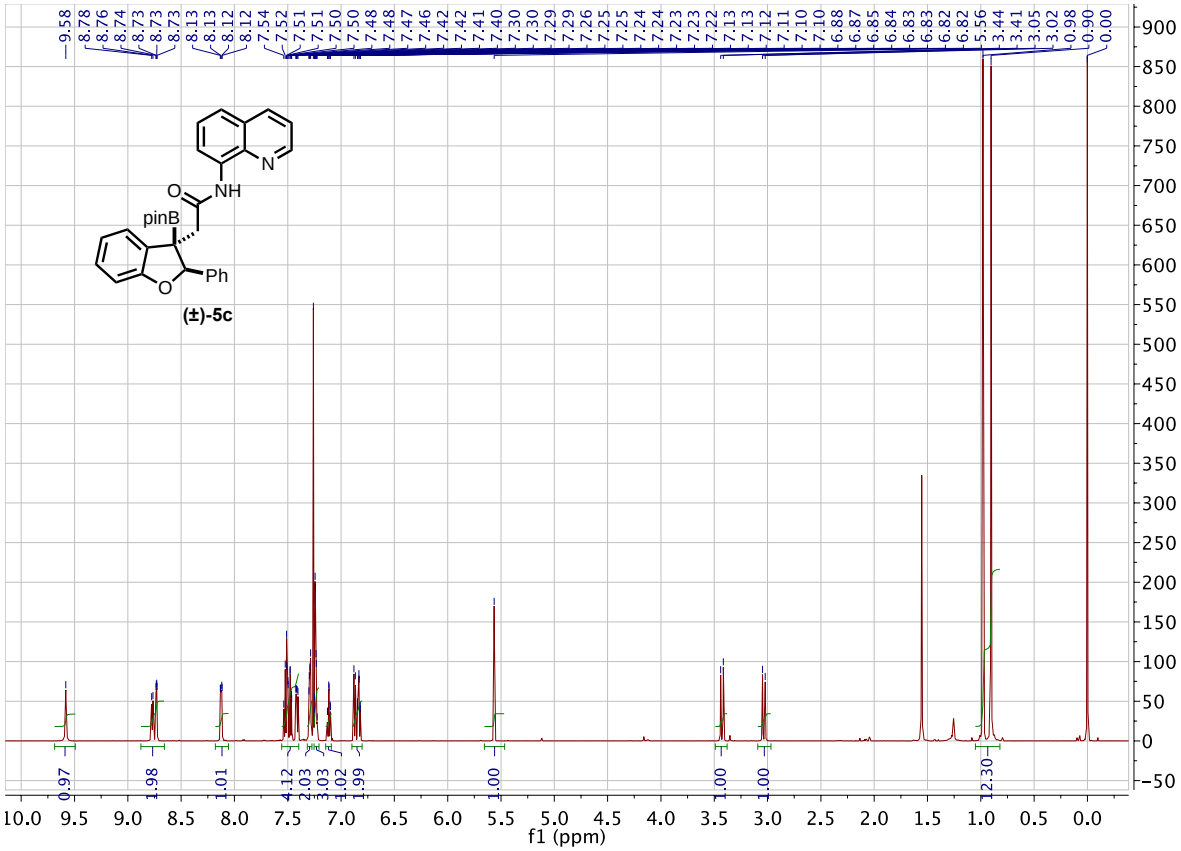

BocN
OH
O
N
H
N
4x
f1 (ppm)

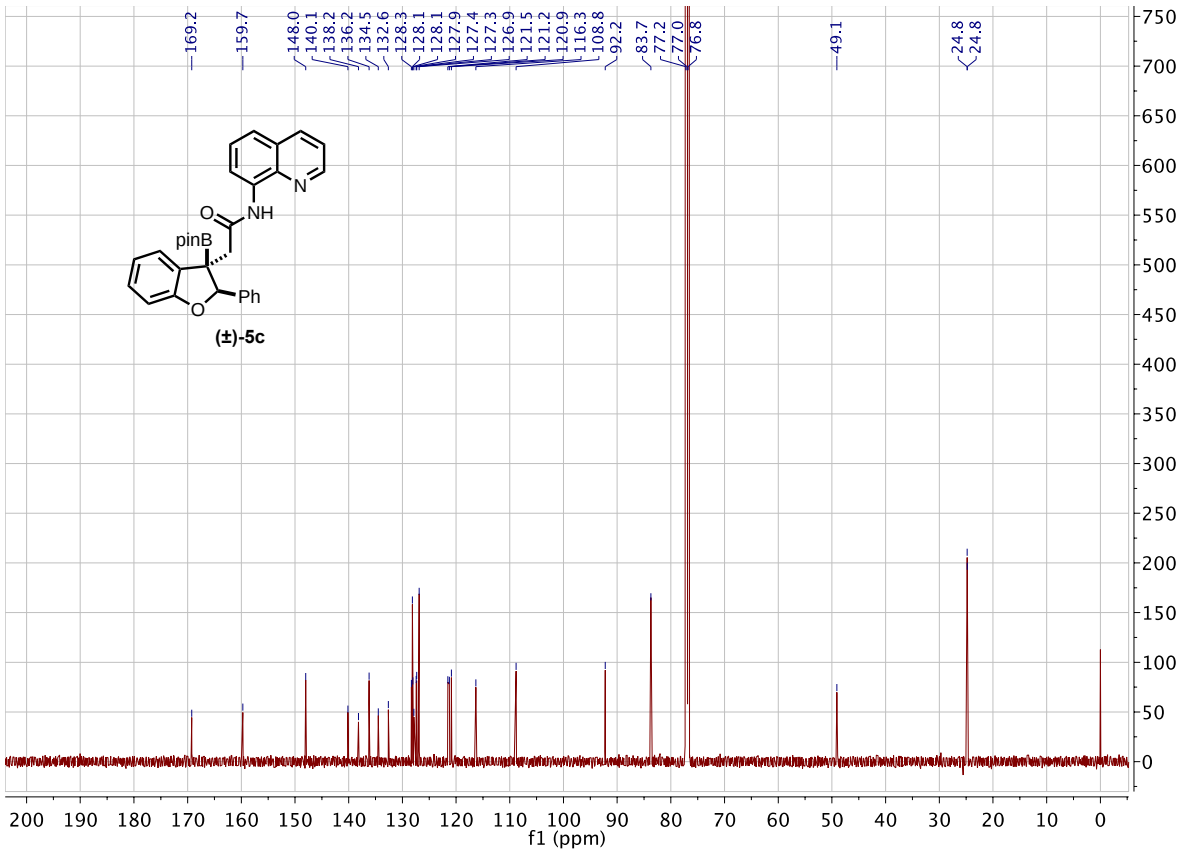

pinB
Ph
Me
NH
O
N
(±)-5a
f1 (ppm)

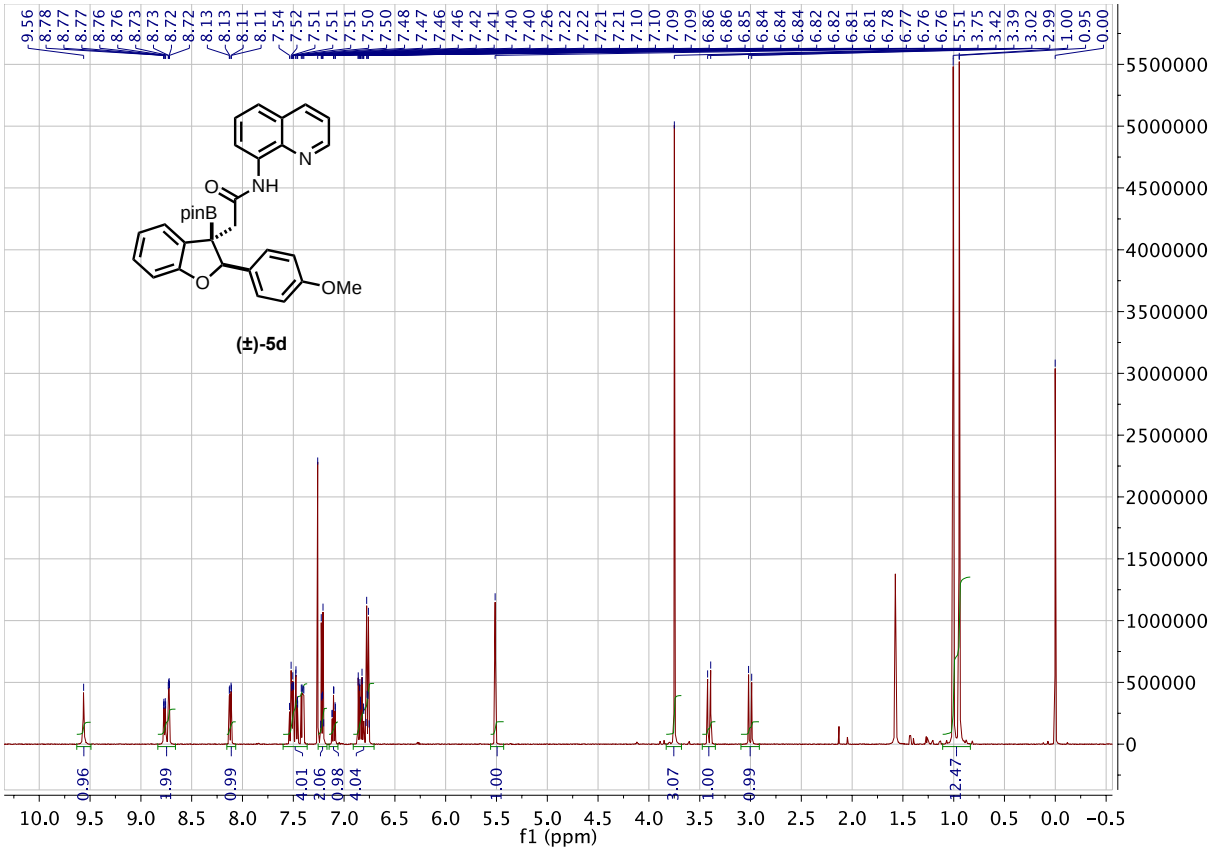

pinB
Ph
Me
NH
O
N
(±)-5a
f1 (ppm)

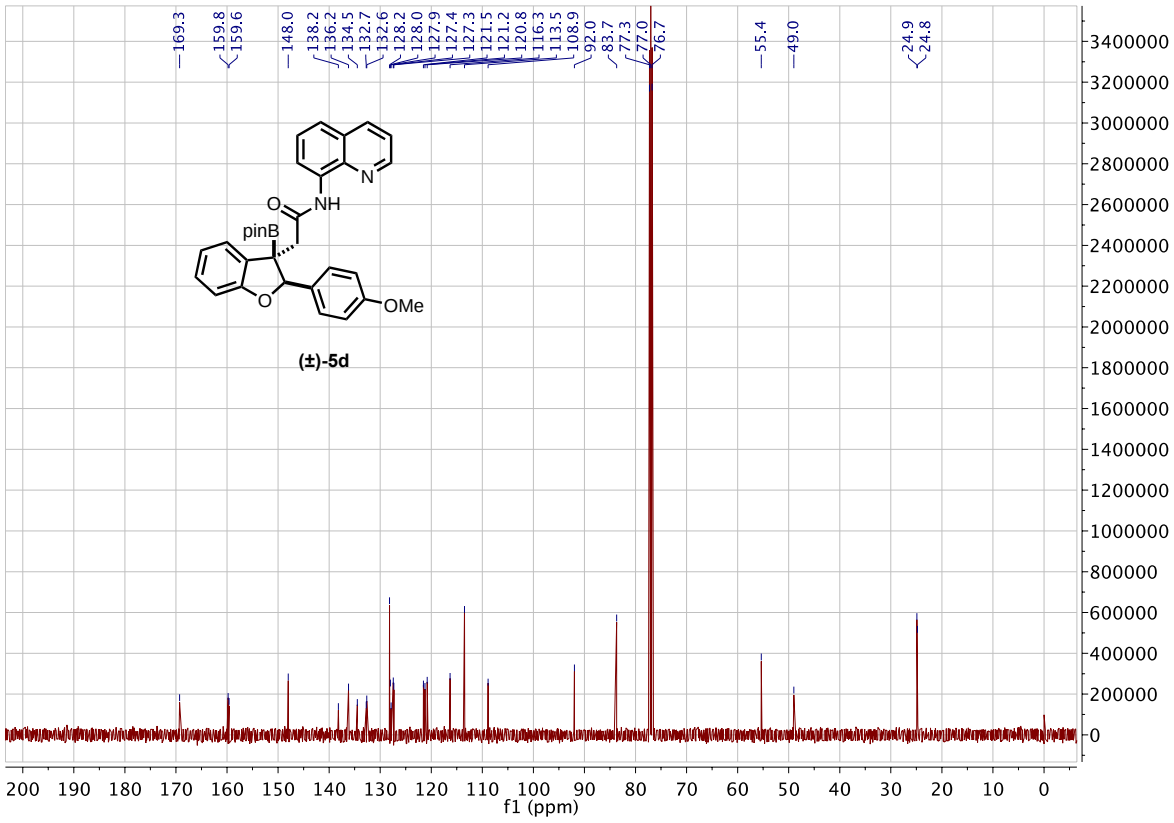

(±)-5b

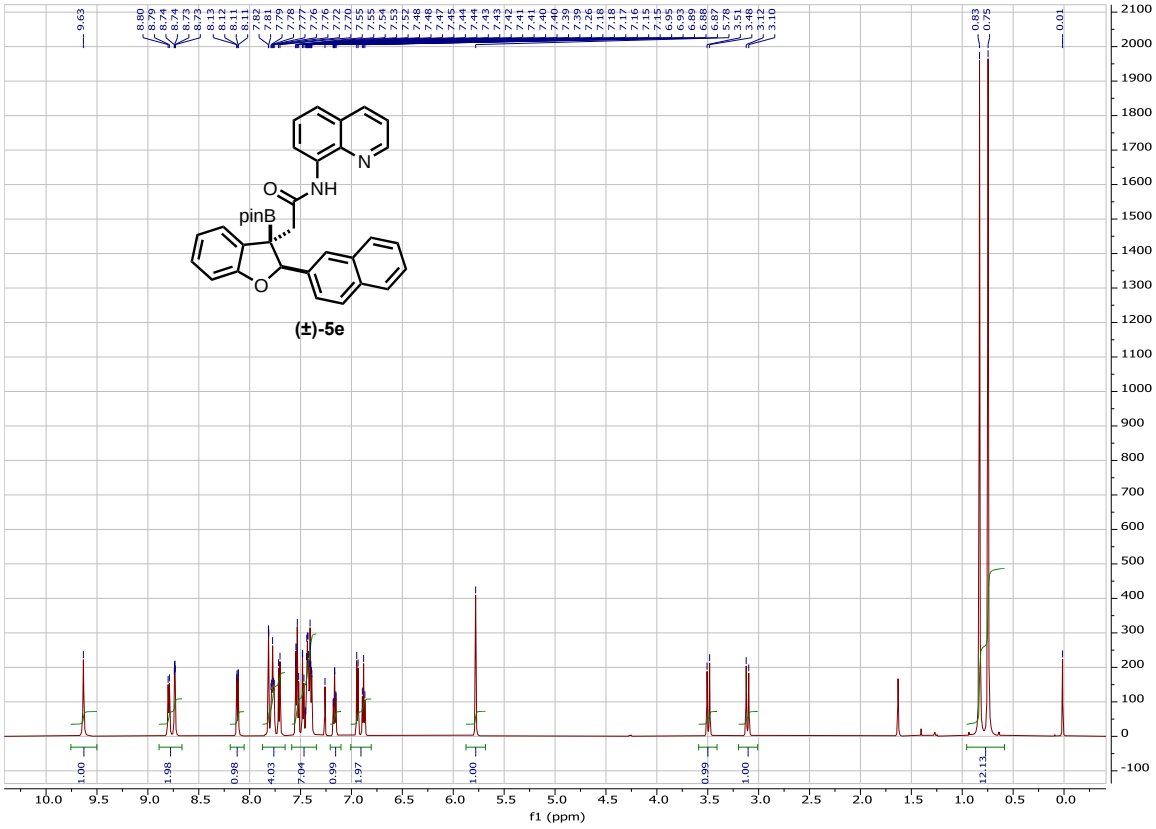

(±)-5b

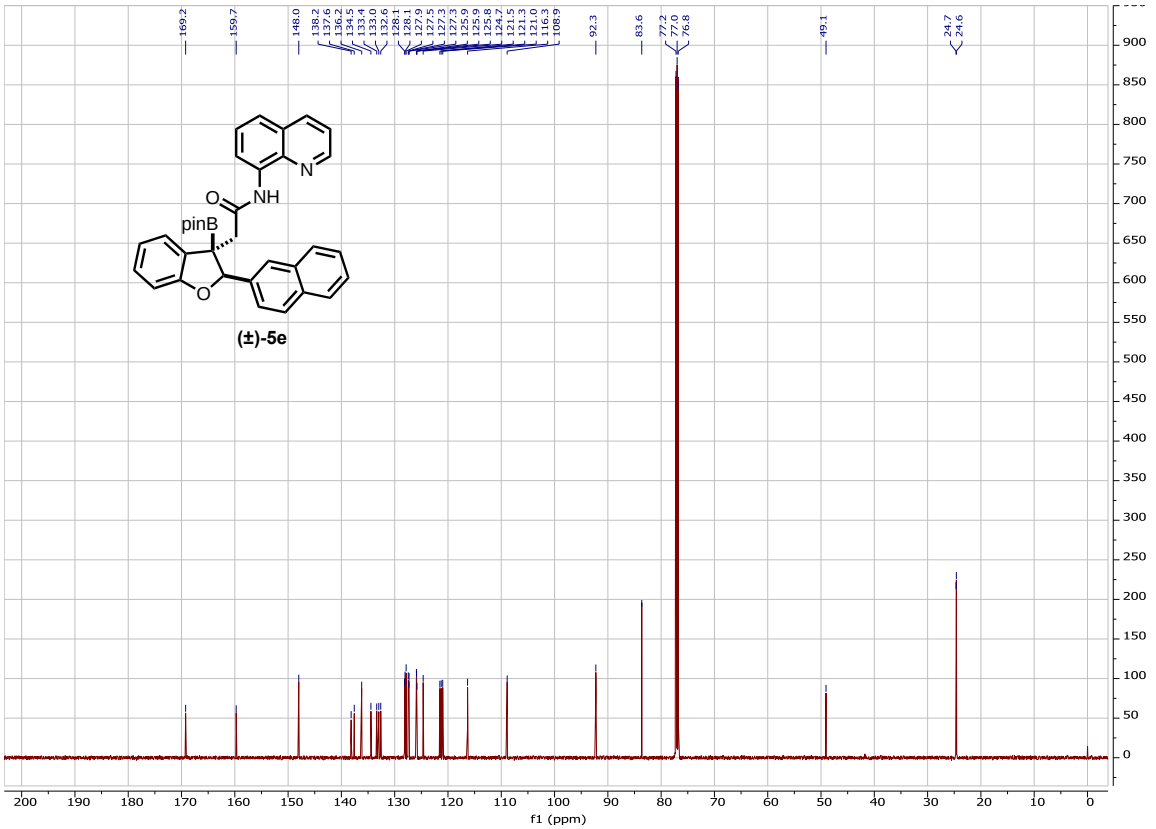

9.58
8.78
8.76
8.74
8.73
8.73
8.13
8.13
8.12
8.12
7.54
7.52
7.51
7.51
7.50
7.50
7.48
7.48
7.47
7.46
7.42
7.42
7.41
7.40
7.30
7.30
7.29
7.29
7.26
7.25
7.25
7.24
7.24
7.23
7.23
7.22
7.13
7.13
7.12
7.11
7.10
7.10
6.88
6.87
6.85
6.84
6.83
6.83
6.82
6.82
5.56
3.44
3.41
3.05
3.02
0.98
0.90
0.00
N
O
NH
pinB
Ph
O
(±)-5c
0.97
1.98
1.01
4.12
2.03
3.03
1.02
1.99
1.00
1.00
1.00
12.30
f1 (ppm)

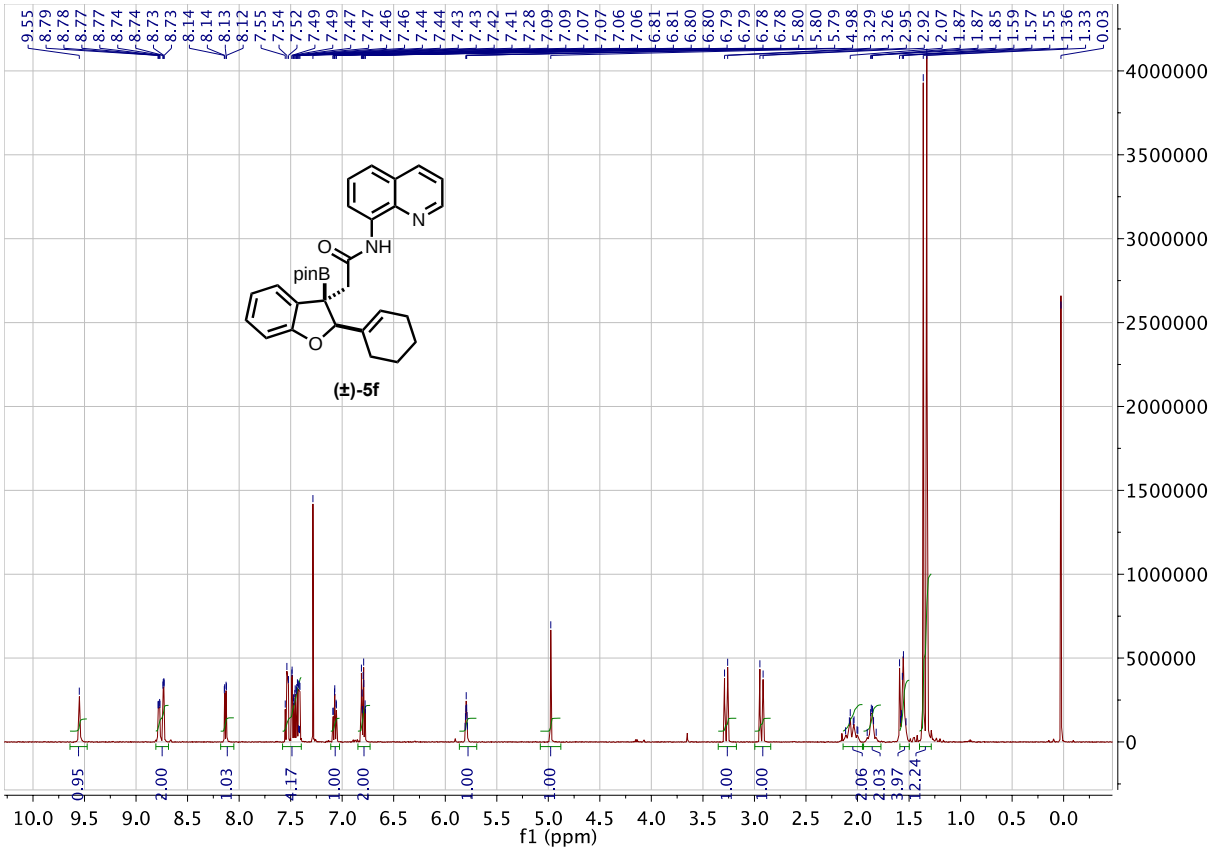

169.2
159.7
148.0
140.1
138.2
136.2
134.5
132.6
128.3
128.1
128.1
127.9
127.4
127.3
126.9
121.5
121.2
120.9
116.3
108.8
92.2
83.7
77.2
77.0
76.8
49.1
24.8
24.8
N
O
NH
pinB
Ph
O
(±)-5c
f1 (ppm)

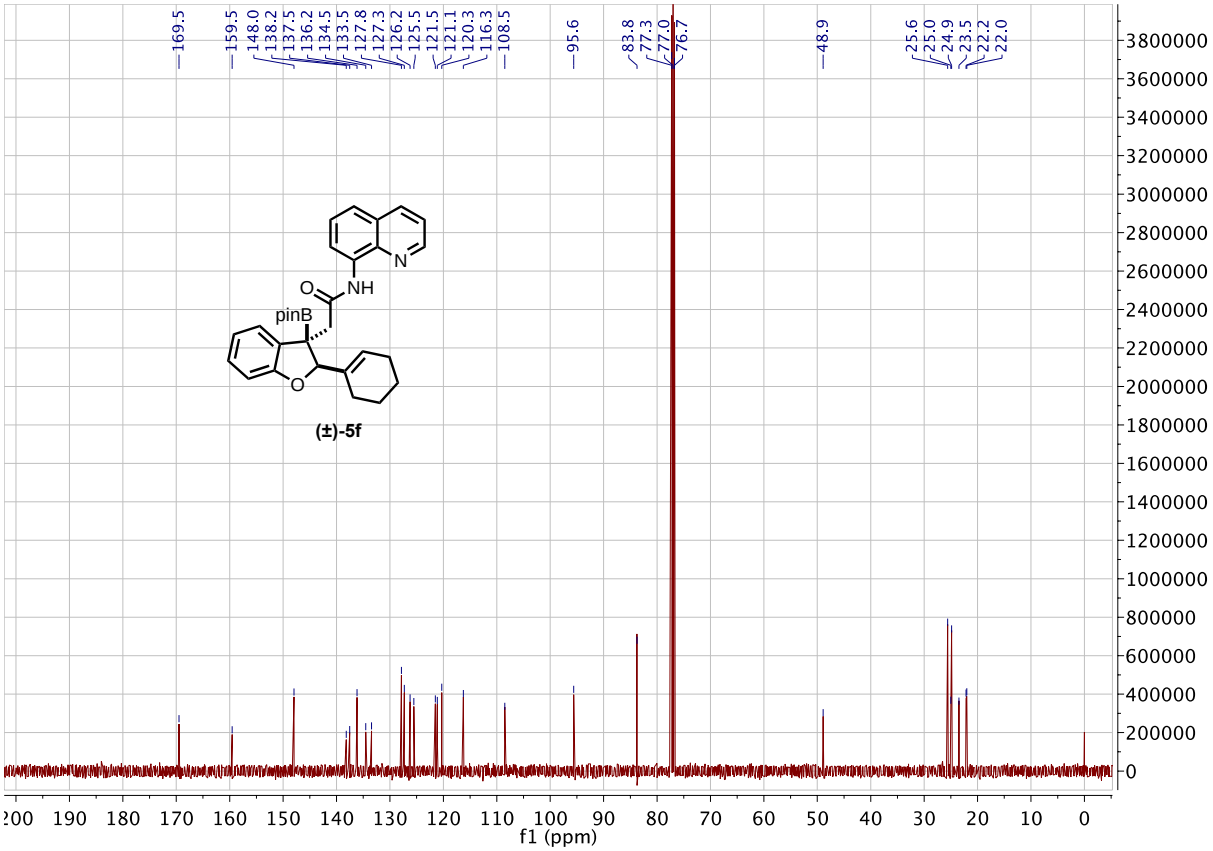

9.56 8.78 8.77 8.77 8.76 8.76 8.73 8.73 8.72 8.72 8.13 8.13 8.11 8.11 7.54 7.52 7.51 7.51 7.51 7.50 7.50 7.48 7.47 7.46 7.46 7.42 7.41 7.40 7.40 7.26 7.22 7.22 7.21 7.21 7.10 7.10 7.09 7.09 6.86 6.86 6.85 6.84 6.84 6.84 6.82 6.82 6.81 6.81 6.78 6.77 6.76 6.76 5.51 3.75 3.42 3.39 3.02 2.99 1.00 0.95 0.00
N
O
NH
pinB
O
OMe
(±)-5d
0.96 1.99 0.99 4.01 2.06 0.98 4.04 1.00 3.07 1.00 0.99 12.47
5500000 5000000 4500000 4000000 3500000 3000000 2500000 2000000 1500000 1000000 500000 0
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)

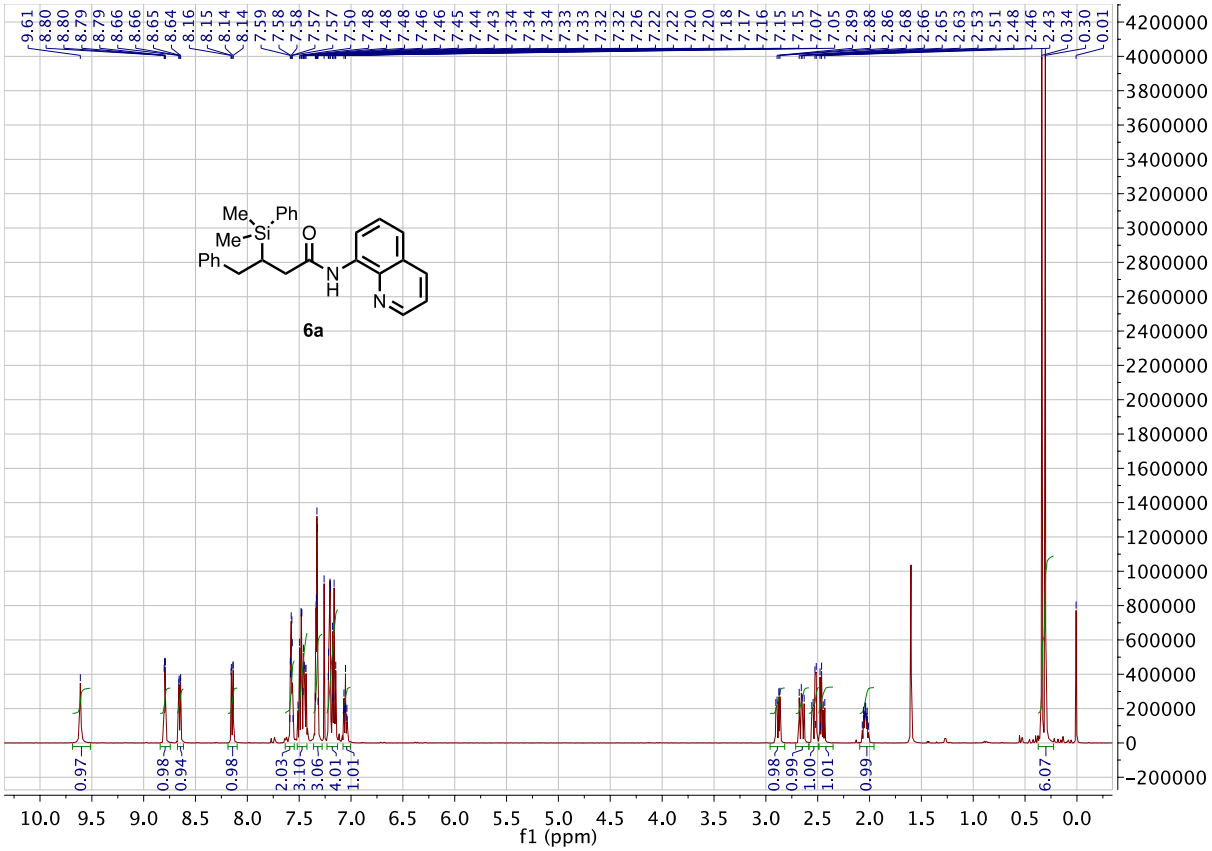

169.3 159.8 159.6 148.0 138.2 136.2 134.5 132.7 132.6 128.2 128.0 127.9 127.4 127.3 121.5 121.2 120.8 116.3 113.5 108.9 92.0 83.7 77.3 77.0 76.7 55.4 49.0 24.9 24.8
N
O
NH
pinB
O
OMe
(±)-5d
3400000 3200000 3000000 2800000 2600000 2400000 2200000 2000000 1800000 1600000 1400000 1200000 1000000 800000 600000 400000 200000 0
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

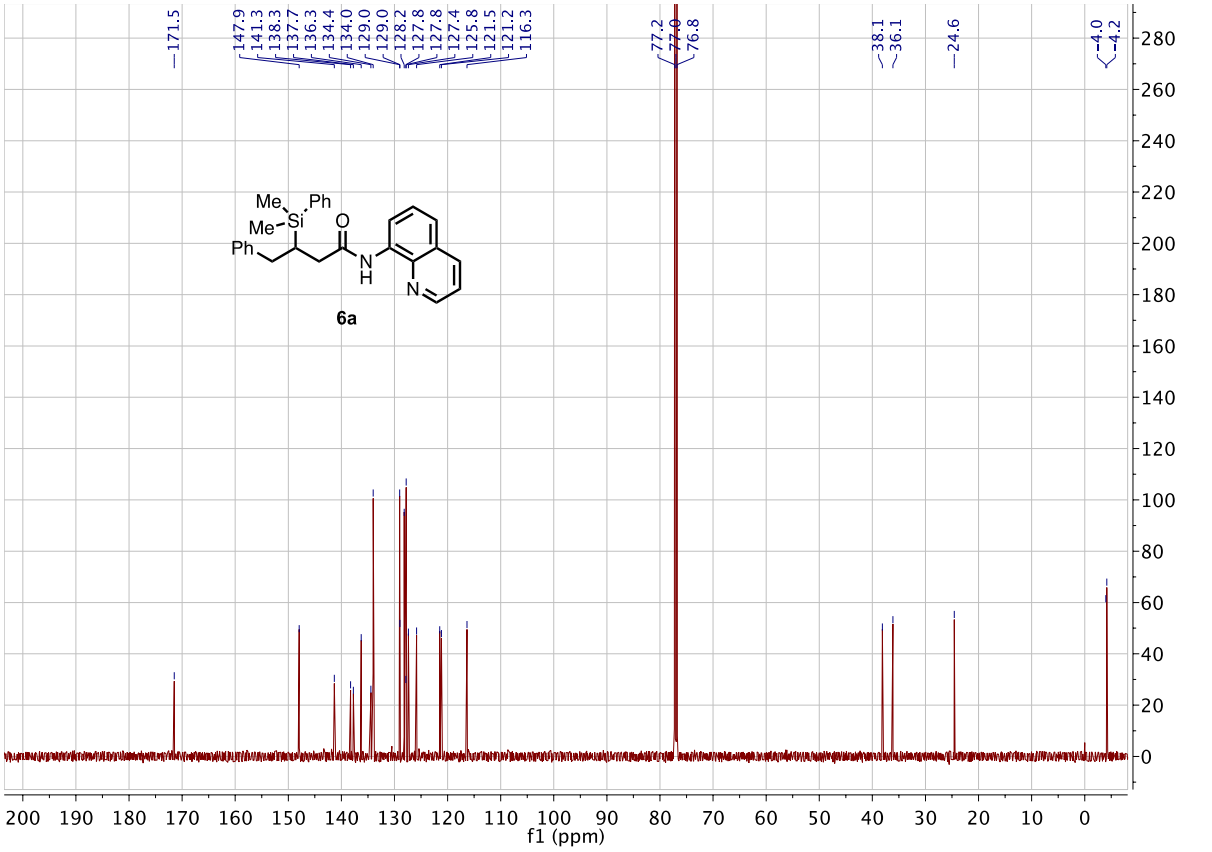

N
O
NH
pinB
O
(±)-5e
f1 (ppm)

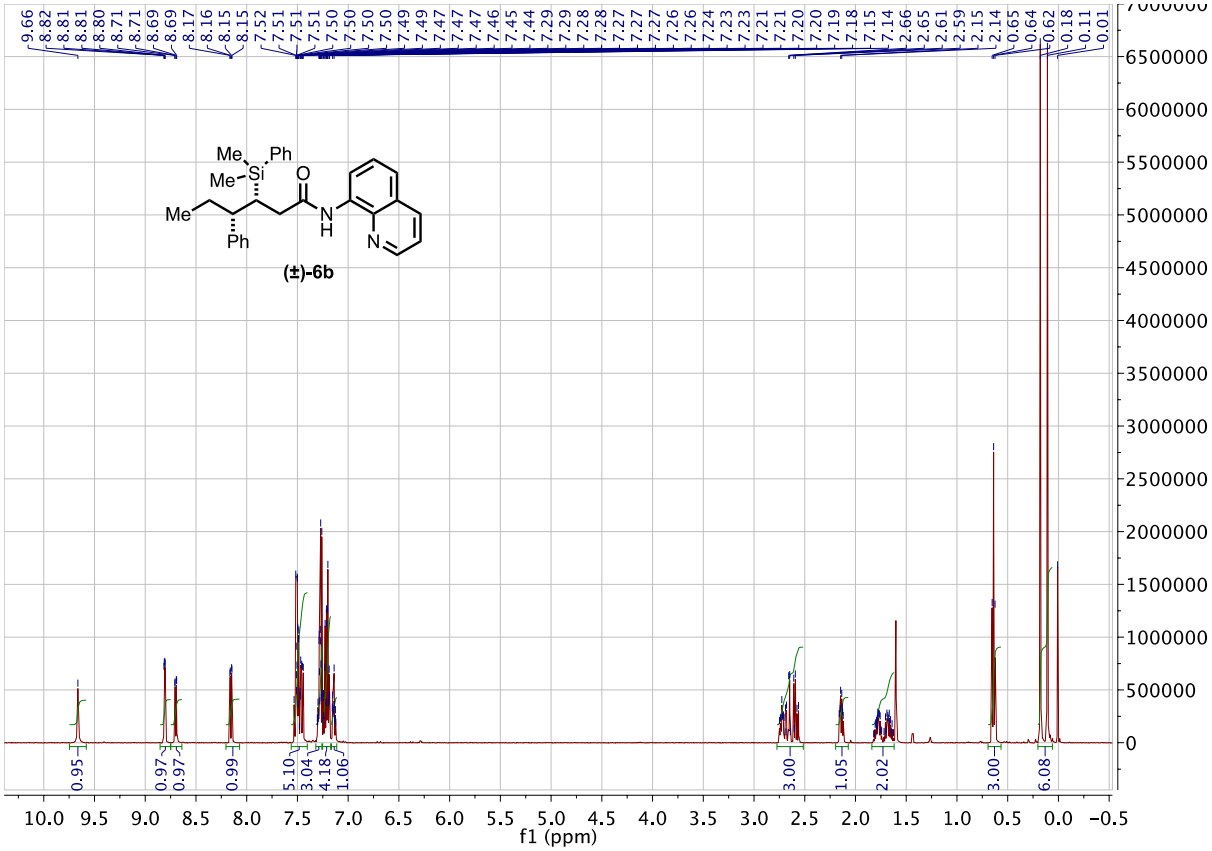

N
O
NH
pinB
O
(±)-5e
f1 (ppm)

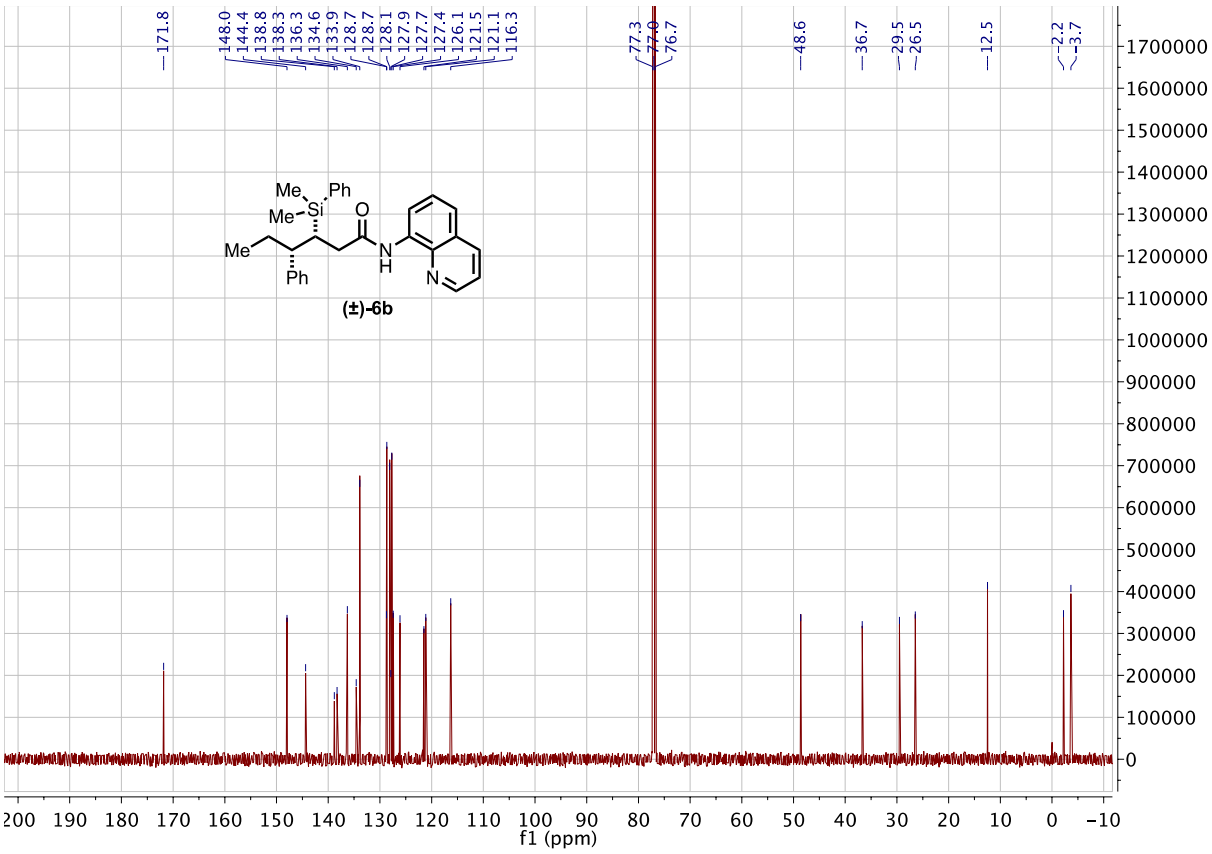

9.55 8.79 8.78 8.77 8.77 8.74 8.74 8.73 8.73 8.14 8.14 8.13 8.12 7.55 7.54 7.52 7.49 7.49 7.47 7.47 7.46 7.46 7.44 7.44 7.43 7.43 7.42 7.41 7.28 7.09 7.09 7.07 7.07 7.06 7.06 6.81 6.81 6.80 6.80 6.79 6.79 6.78 6.78 5.80 5.80 5.79 4.98 3.29 3.26 2.95 2.92 2.07 1.87 1.87 1.85 1.59 1.57 1.55 1.36 1.33 0.03
N
O
NH
pinB
O
(±)-5f
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
0.95 2.00 1.03 4.17 1.00 2.00 1.00 1.00 1.00 1.00 2.06 2.03 3.97 12.24
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

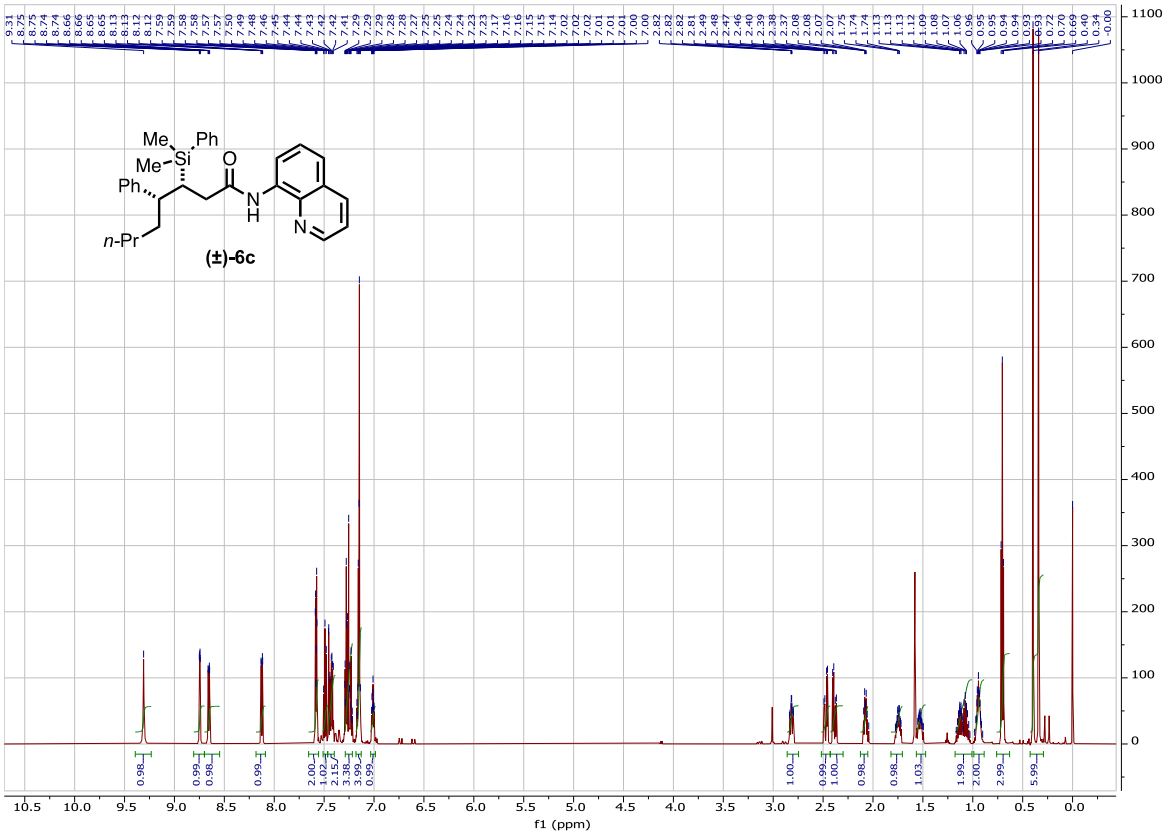

169.5 159.5 148.0 138.2 137.5 136.2 134.5 133.5 127.8 127.3 126.2 125.5 121.5 121.1 120.3 116.3 108.5 95.6 83.8 77.3 77.0 76.7 48.9 25.6 25.0 24.9 23.5 22.2 22.0
N
O
NH
pinB
O
(±)-5f
3800000
3600000
3400000
3200000
3000000
2800000
2600000
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

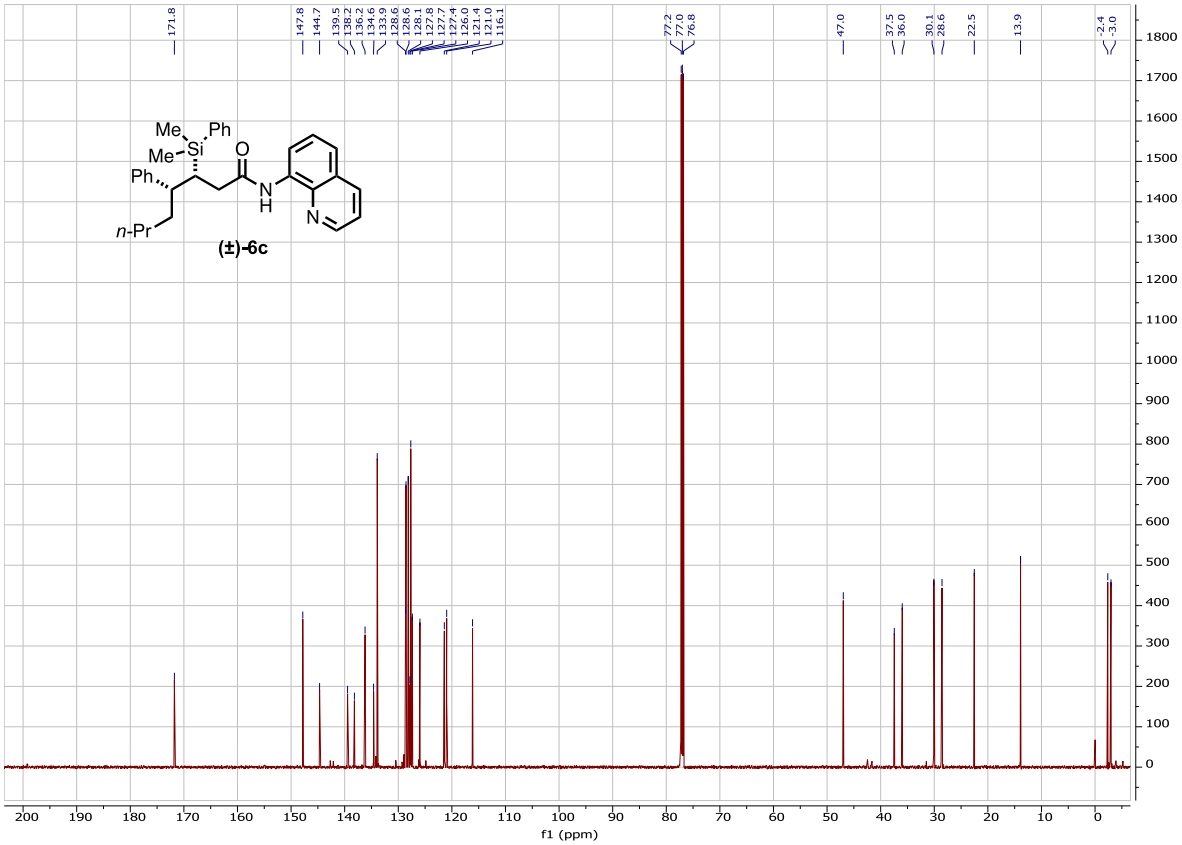

9.61 8.80 8.80 8.79 8.79 8.66 8.66 8.65 8.64 8.16 8.15 8.14 8.14 7.59 7.58 7.58 7.57 7.57 7.50 7.48 7.48 7.48 7.46 7.46 7.45 7.44 7.43 7.34 7.34 7.33 7.33 7.32 7.32 7.26 7.22 7.22 7.20 7.20 7.18 7.17 7.16 7.15 7.15 7.07 7.05 2.89 2.88 2.86 2.68 2.66 2.65 2.63 2.53 2.51 2.48 2.46 2.43 0.34 0.30 0.01
Me Ph Me Si Ph O N H N
6a
0.97 0.98 0.94 0.98 2.03 3.10 3.06 4.01 1.01 0.98 0.99 1.00 1.01 0.99 6.07
f1 (ppm)

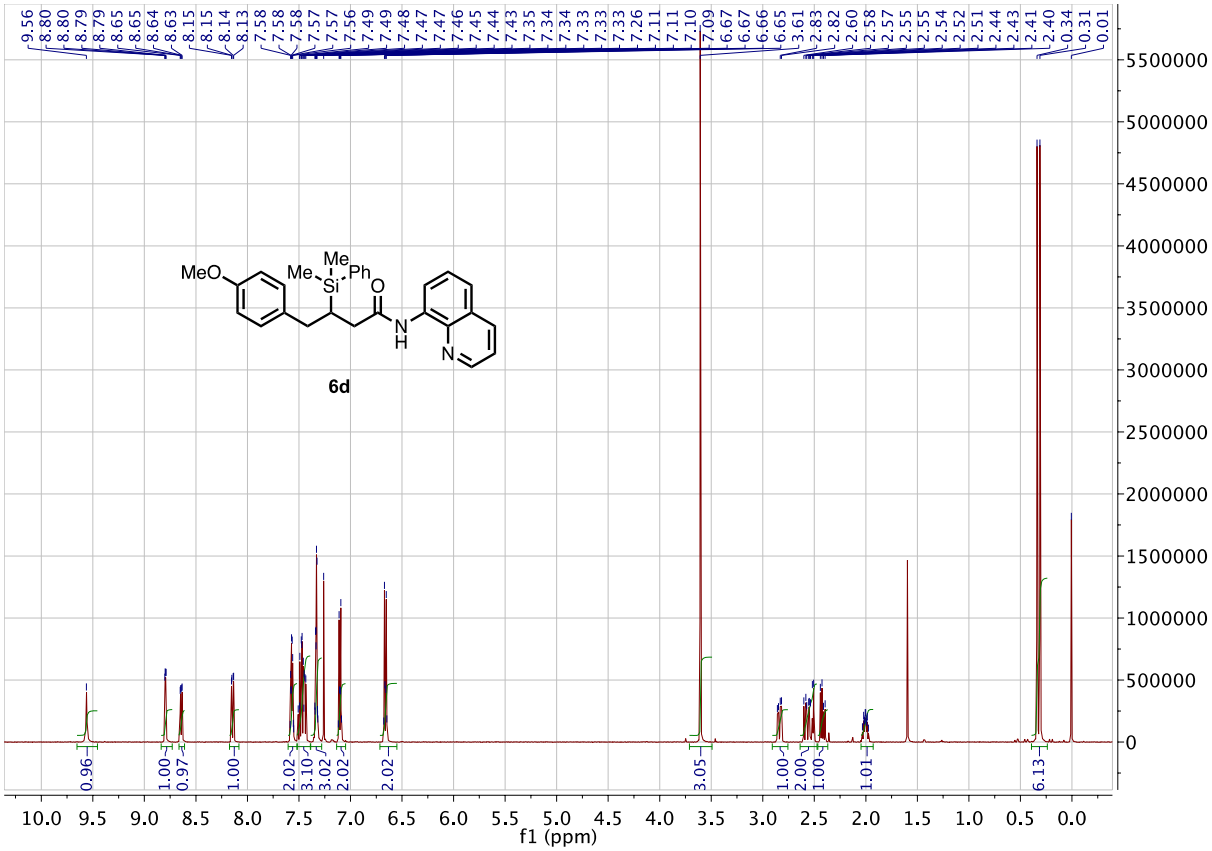

171.5 147.9 141.3 138.3 137.7 136.3 134.4 134.0 129.0 129.0 128.2 127.8 127.8 127.4 125.8 121.5 121.2 116.3 77.2 77.0 76.8 38.1 36.1 24.6 -4.0 -4.2
Me Ph Me Si Ph O N H N
6a
f1 (ppm)

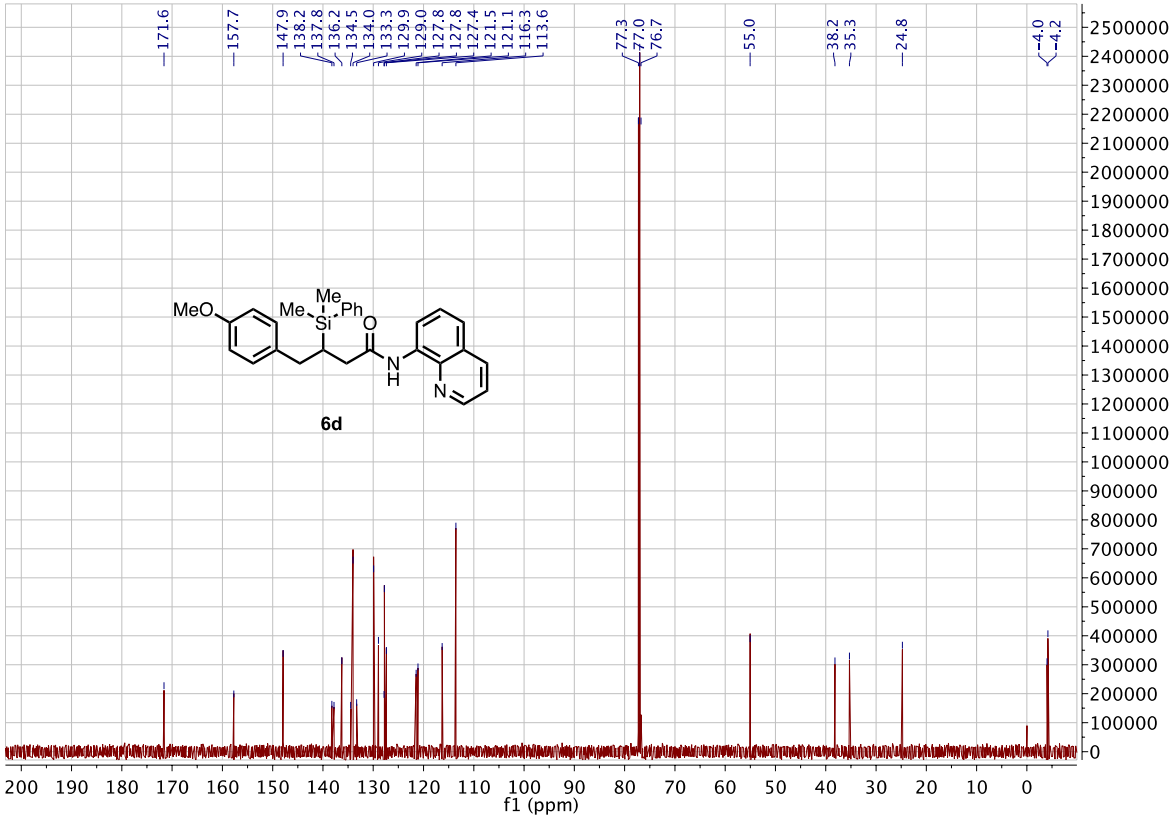

Me
Ph
Me
Si
O
N
H
Me
Ph
N
(±)-6b
f1 (ppm)

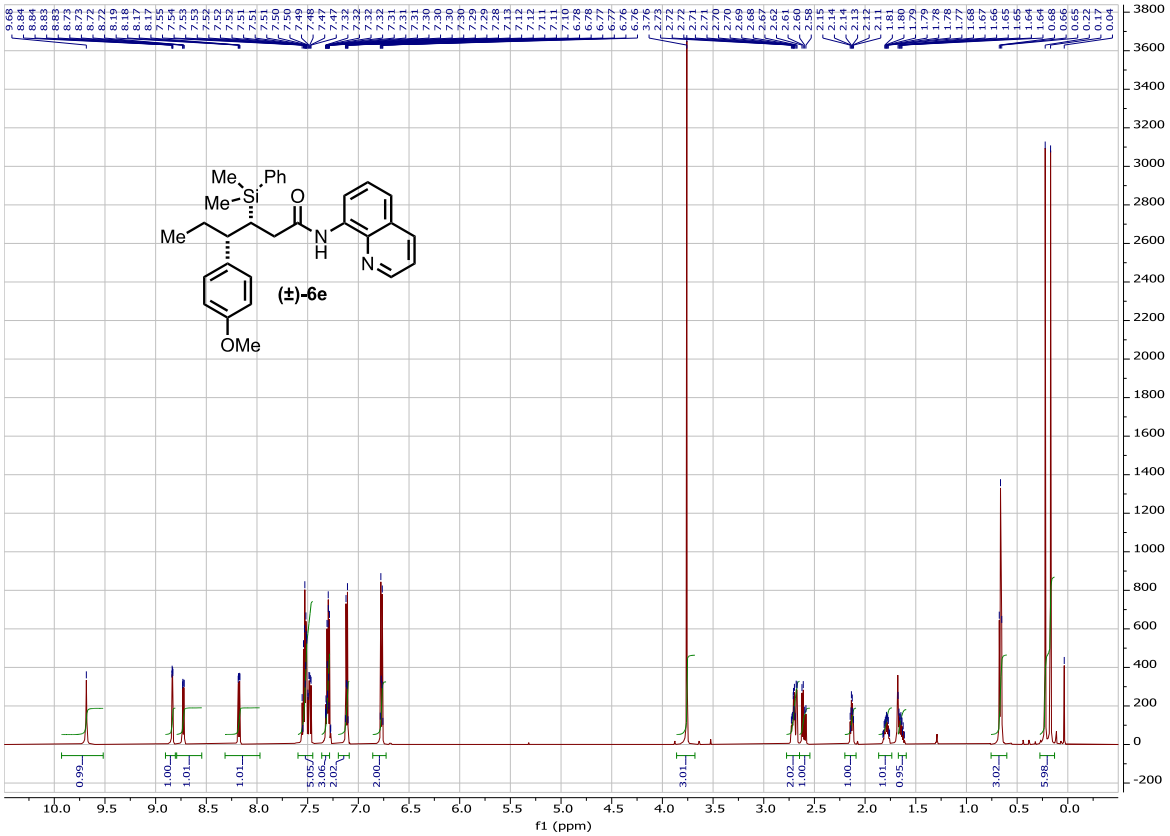

Me
Ph
Me
Si
O
N
H
Me
Ph
N
(±)-6b
f1 (ppm)

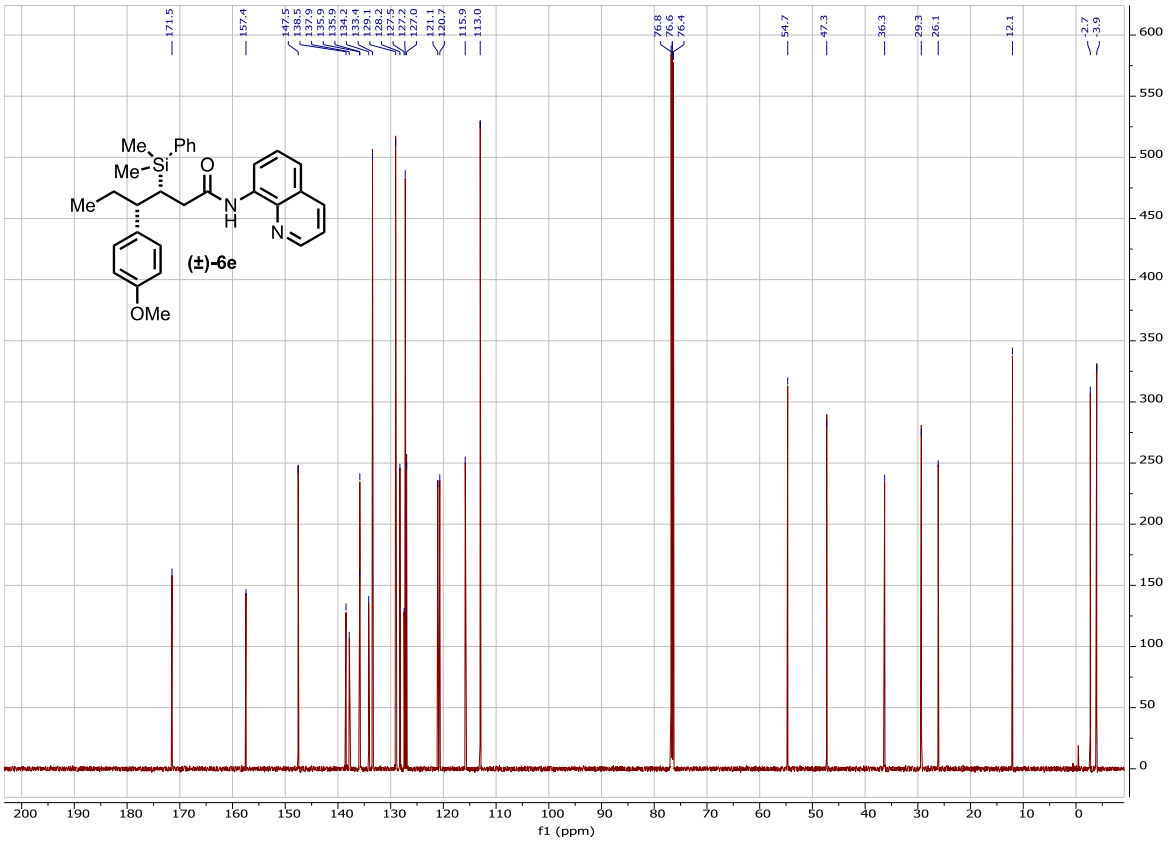

Me
Ph
Me
Si
O
Ph
N
H
N
n-Pr
(±)-6c
f1 (ppm)

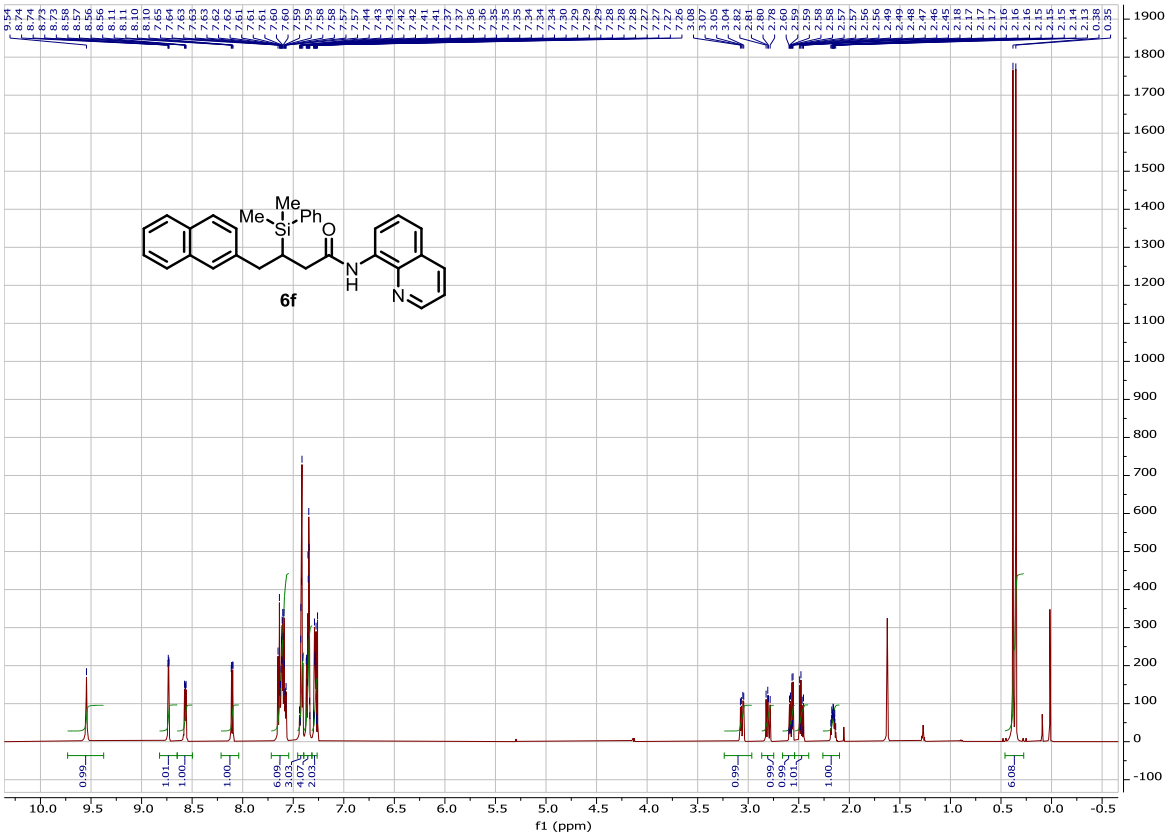

Me
Ph
Me
Si
O
Ph
N
H
N
n-Pr
(±)-6c
f1 (ppm)

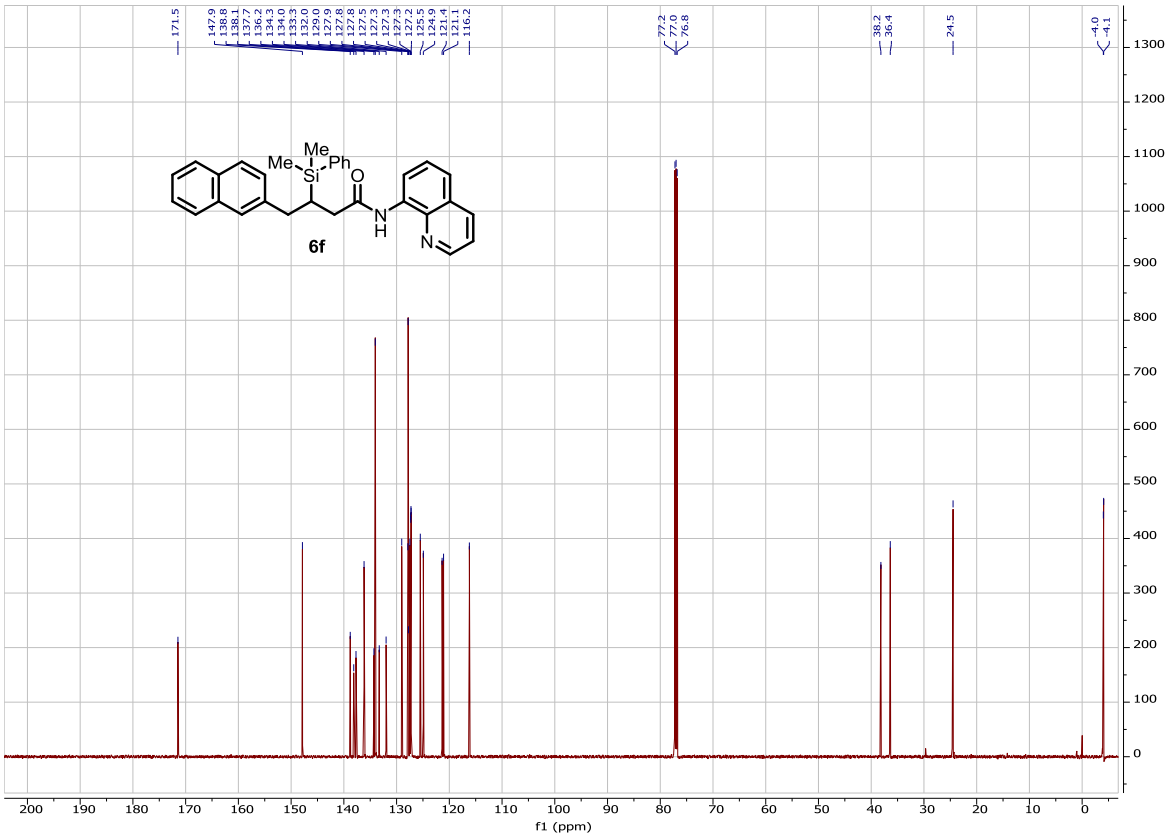

MeO
Me
Si
Me
Ph
O
N
H
N
6d
f1 (ppm)

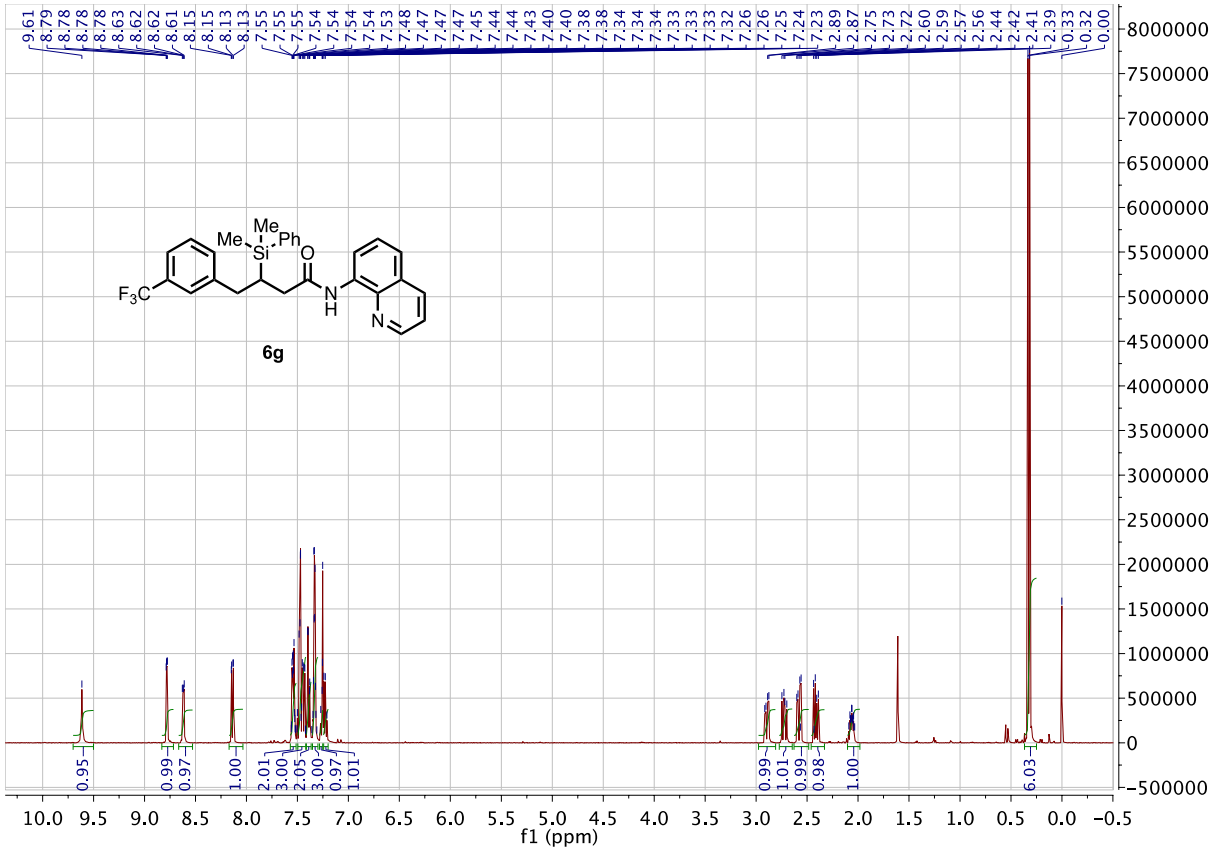

MeO
Me
Si
Me
Ph
O
N
H
N
6d
f1 (ppm)

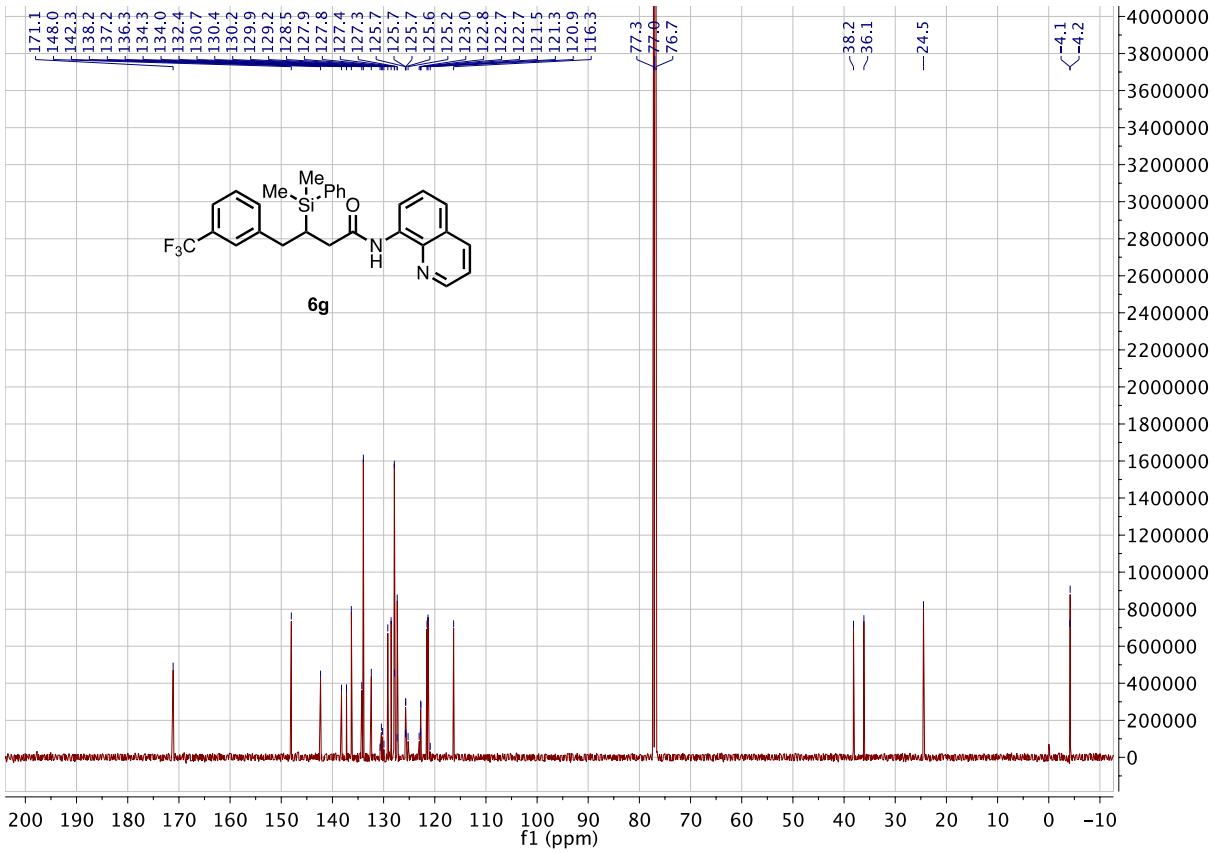

Me
Ph
Me
Si
O
Me
N
H
N
(±)-6e
OMe
f1 (ppm)

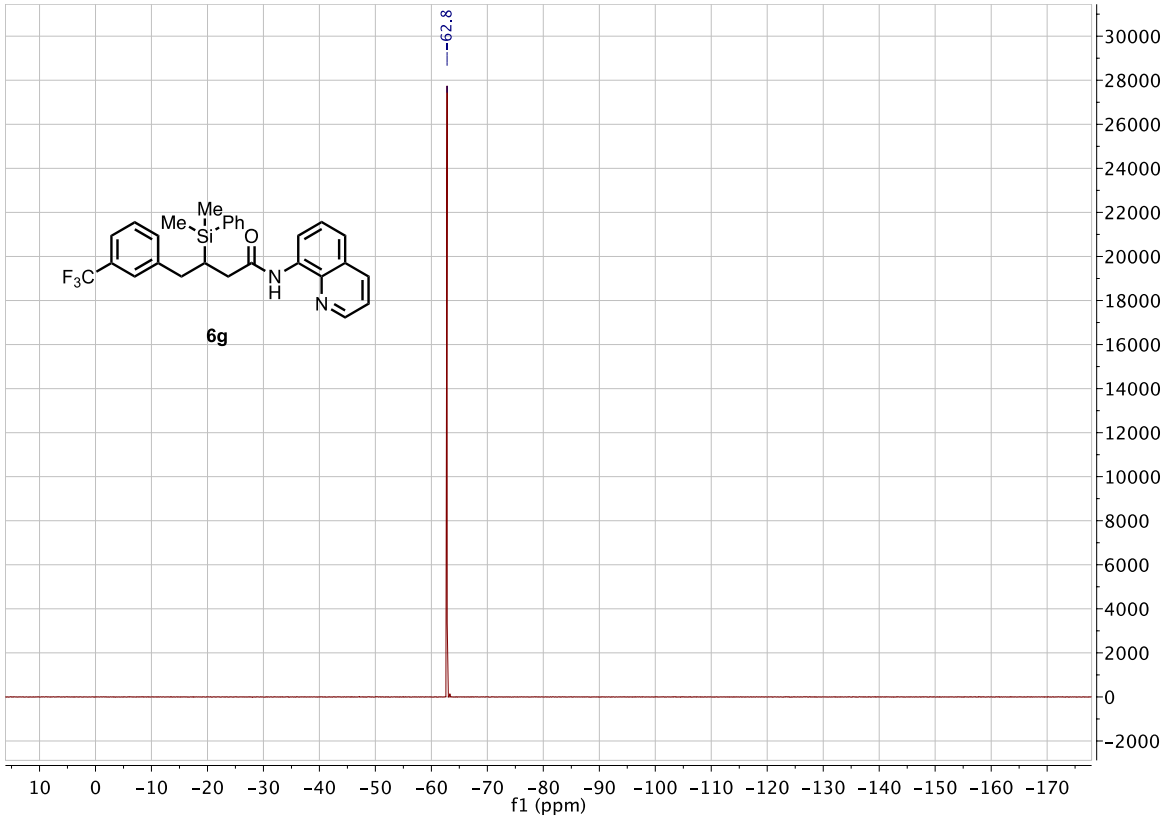

Me
Ph
Me
Si
O
Me
N
H
N
(±)-6e
OMe
f1 (ppm)

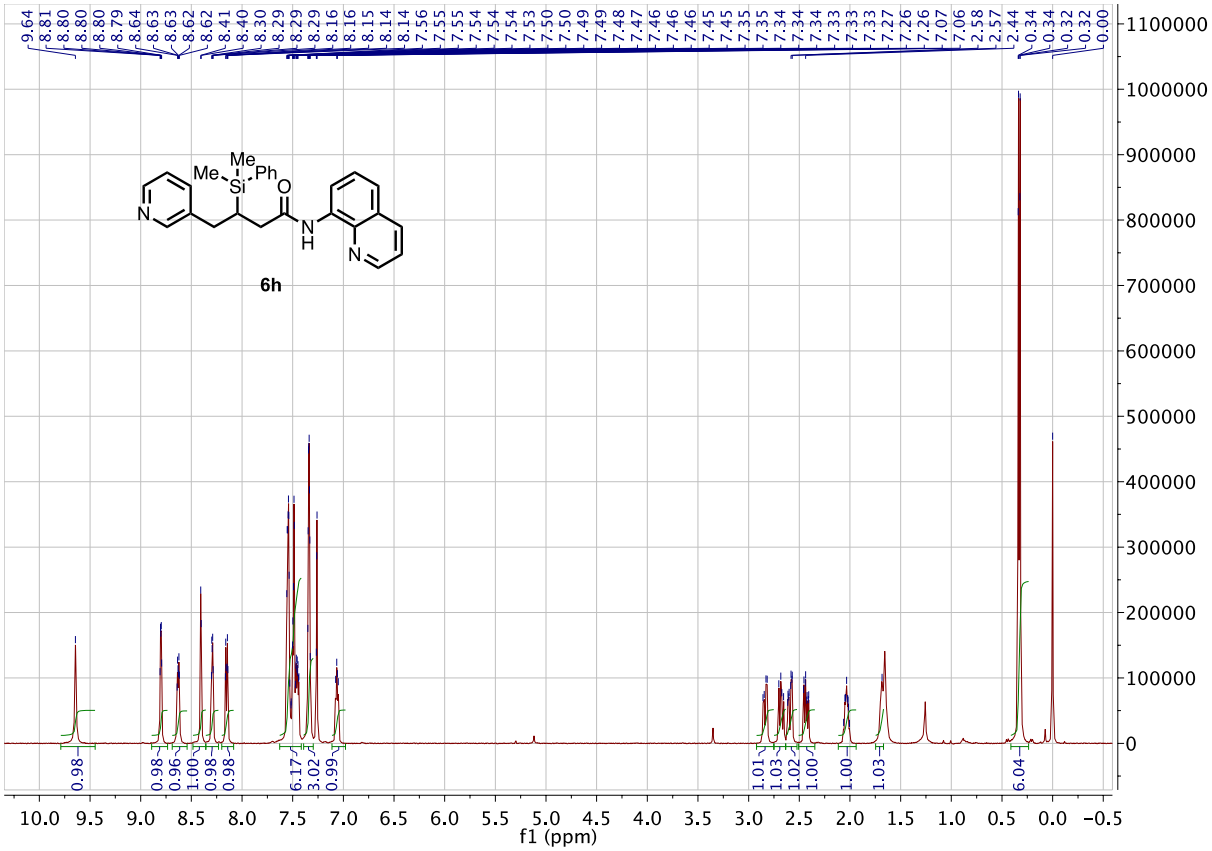

Me
Me
Si
Ph
O
N
H
N
6f
f1 (ppm)

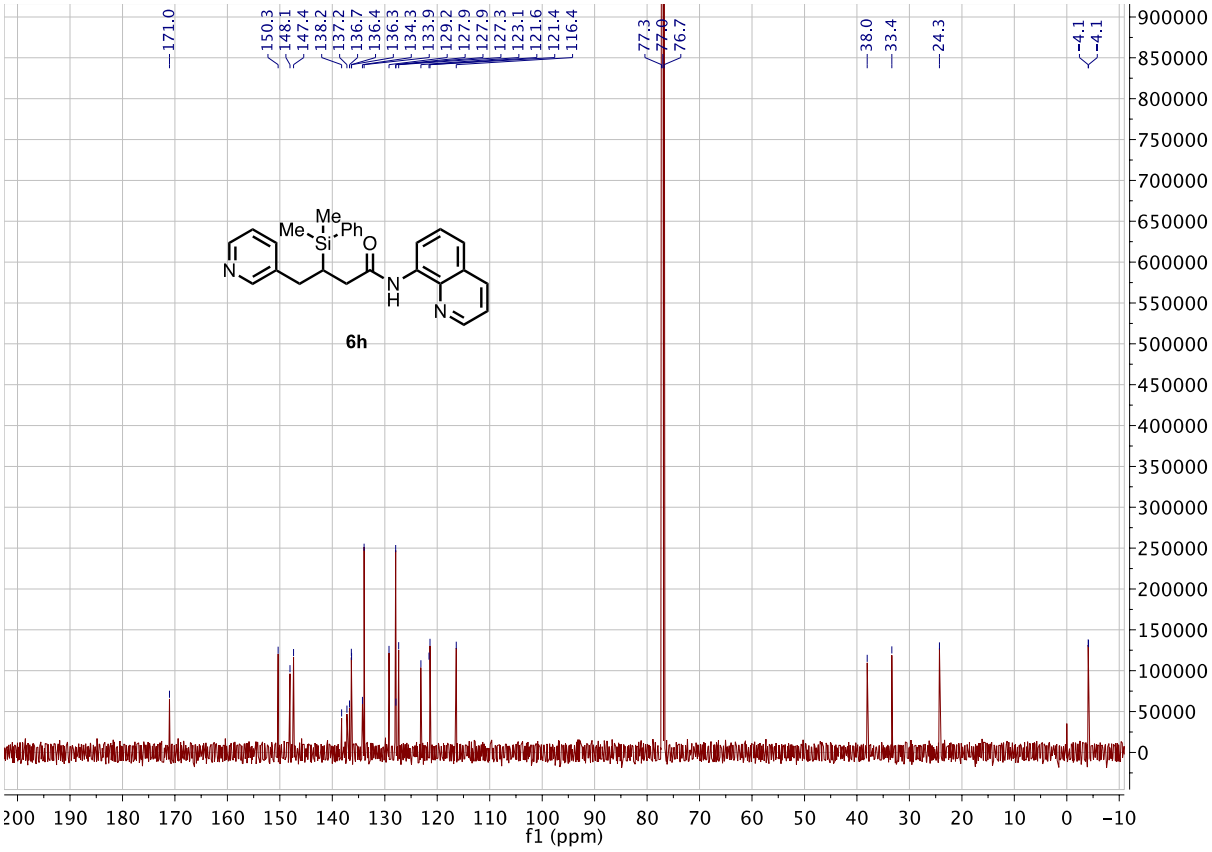

Me
Me
Si
Ph
O
N
H
N
6f
f1 (ppm)

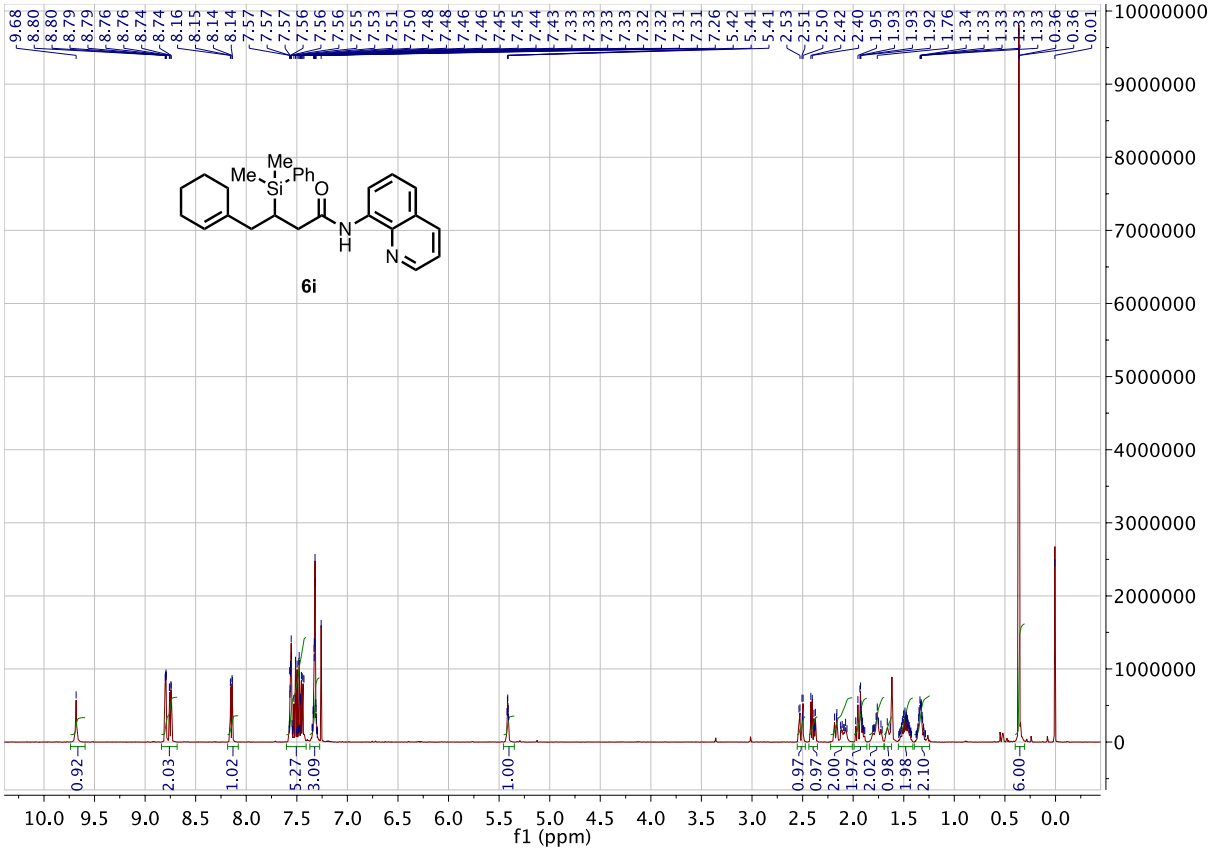

9.61 8.79 8.78 8.78 8.78 8.63 8.62 8.62 8.61 8.15 8.13 8.13 7.55 7.55 7.55 7.54 7.54 7.54 7.54 7.53 7.48 7.47 7.47 7.47 7.45 7.44 7.44 7.43 7.40 7.40 7.38 7.38 7.34 7.34 7.34 7.33 7.33 7.33 7.32 7.26 7.26 7.25 7.24 7.23 2.89 2.87 2.75 2.73 2.72 2.60 2.59 2.57 2.56 2.44 2.42 2.41 2.39 0.33 0.32 0.00
Me
Si
Ph
O
N
H
F3C
6g
0.95 0.99 0.97 1.00 2.01 3.00 2.05 3.00 0.97 1.01 0.99 1.01 0.99 0.98 1.00 6.03
f1 (ppm)

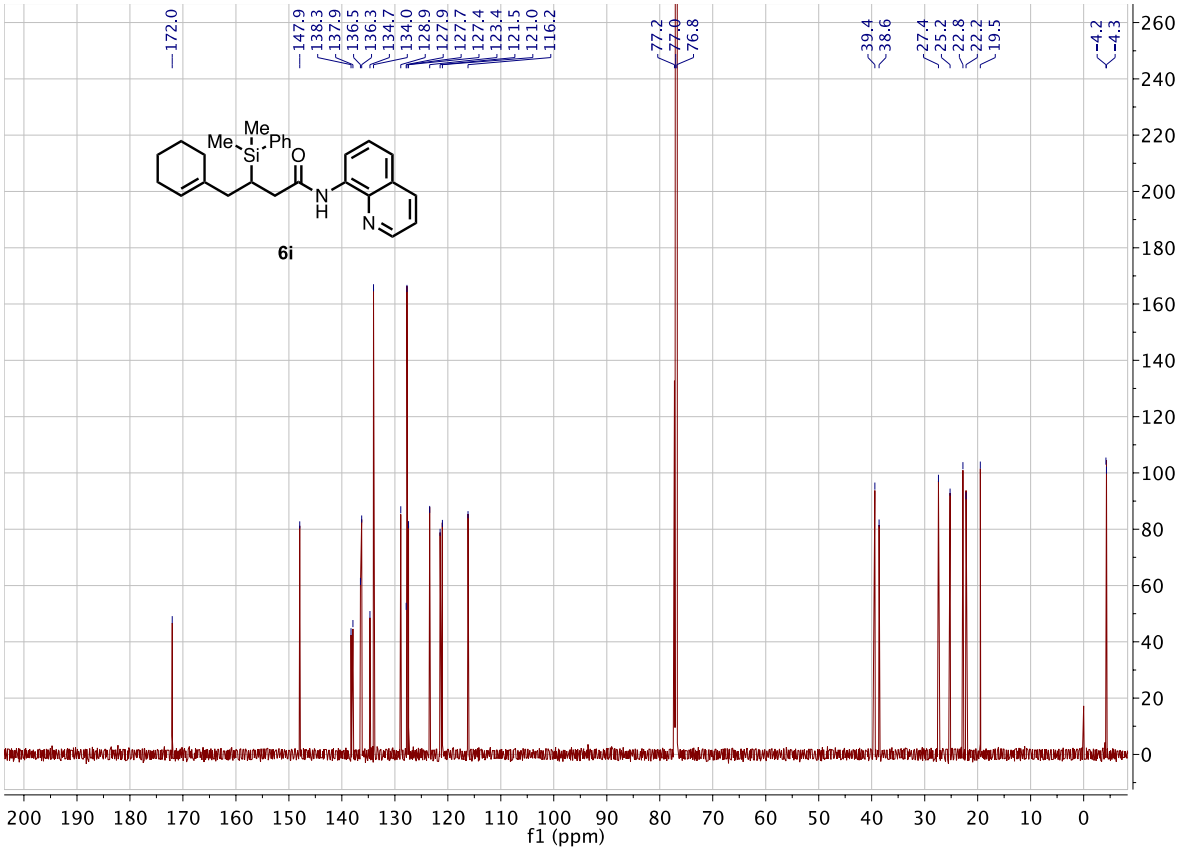

171.1 148.0 142.3 138.2 137.2 136.3 134.3 134.0 132.4 130.7 130.4 130.2 129.9 129.2 128.5 127.9 127.8 127.4 127.3 125.7 125.7 125.7 125.6 125.2 123.0 122.8 122.7 122.7 121.5 121.3 120.9 116.3 77.3 77.0 76.7 38.2 36.1 24.5 14.1 14.2
Me
Si
Ph
O
N
H
F3C
6g
f1 (ppm)

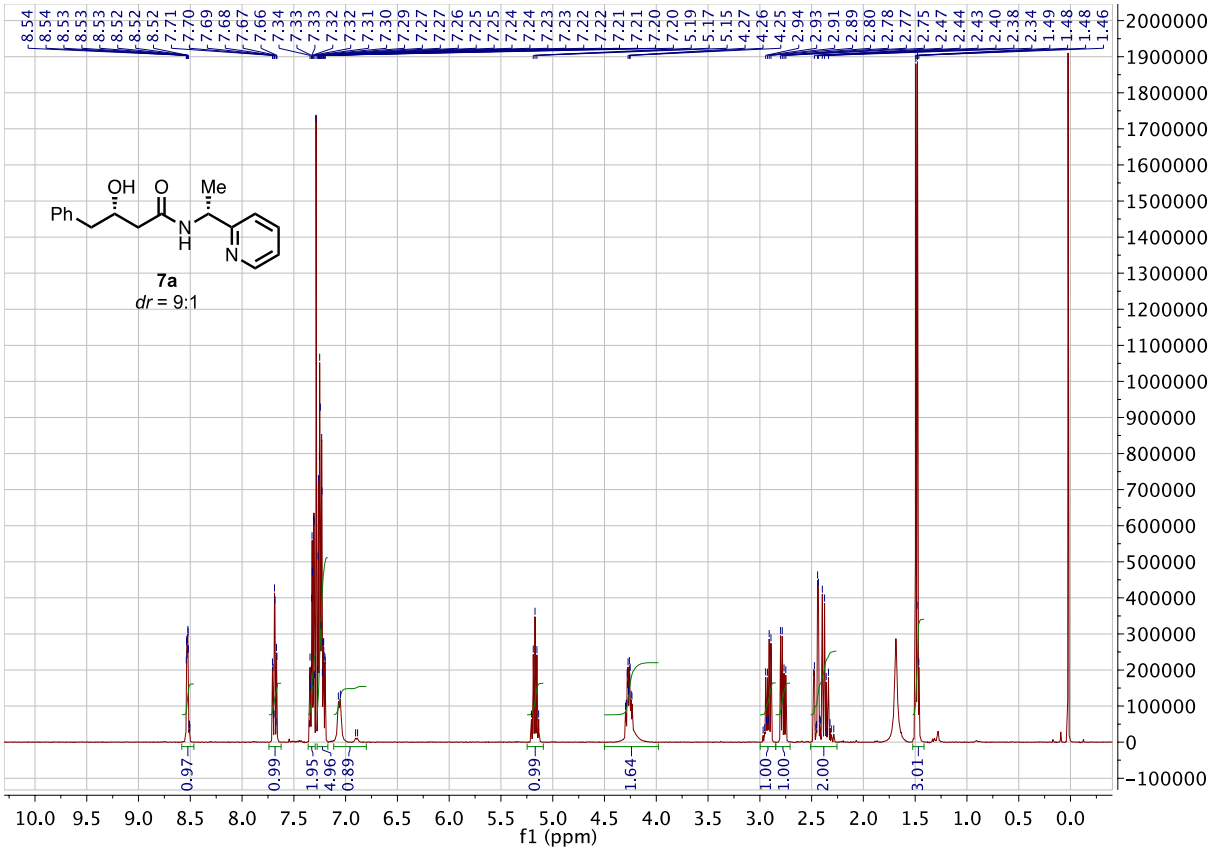

-62.8
Me
Si
Ph
Me
O
N
H
N
F3C
6g
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170
f1 (ppm)

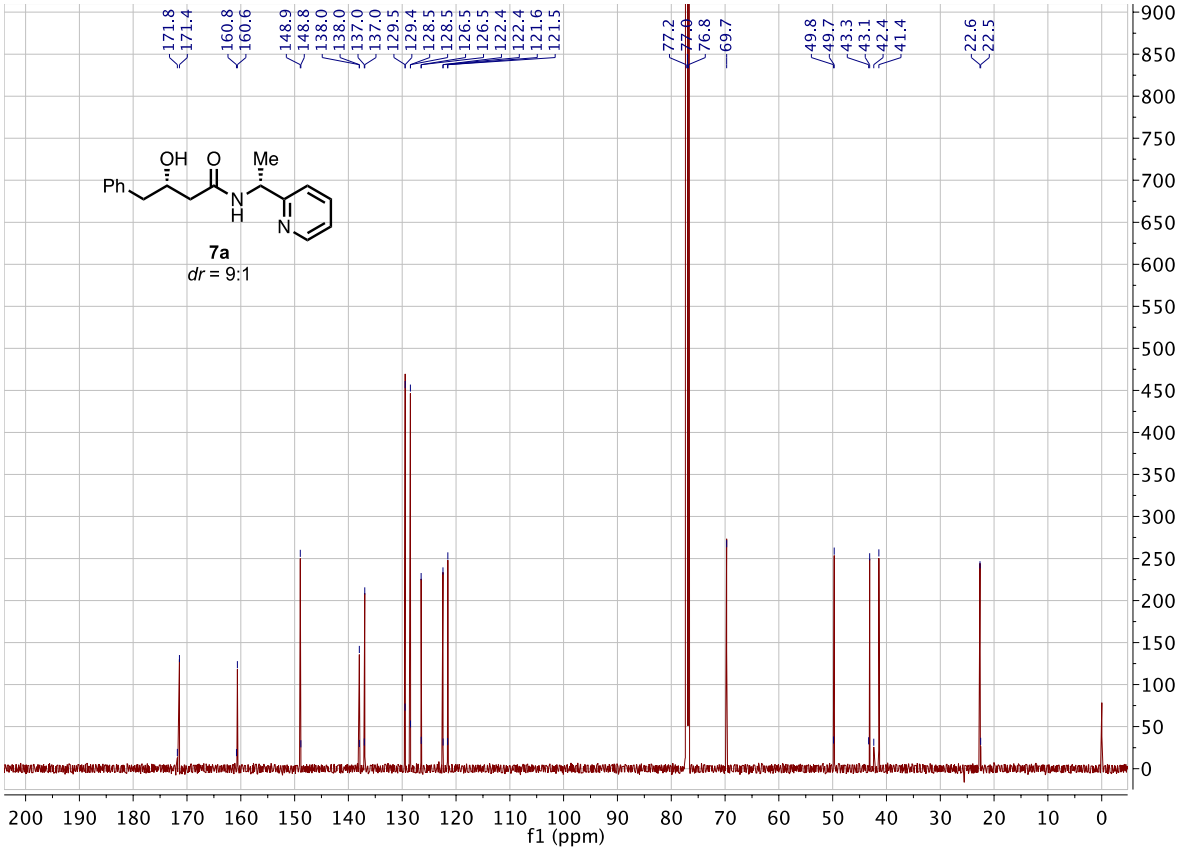

Me
Ph
Si
Me
O
N
H
N
6h
f1 (ppm)


Me
Ph
Si
Me
O
N
H
N
6h
f1 (ppm)

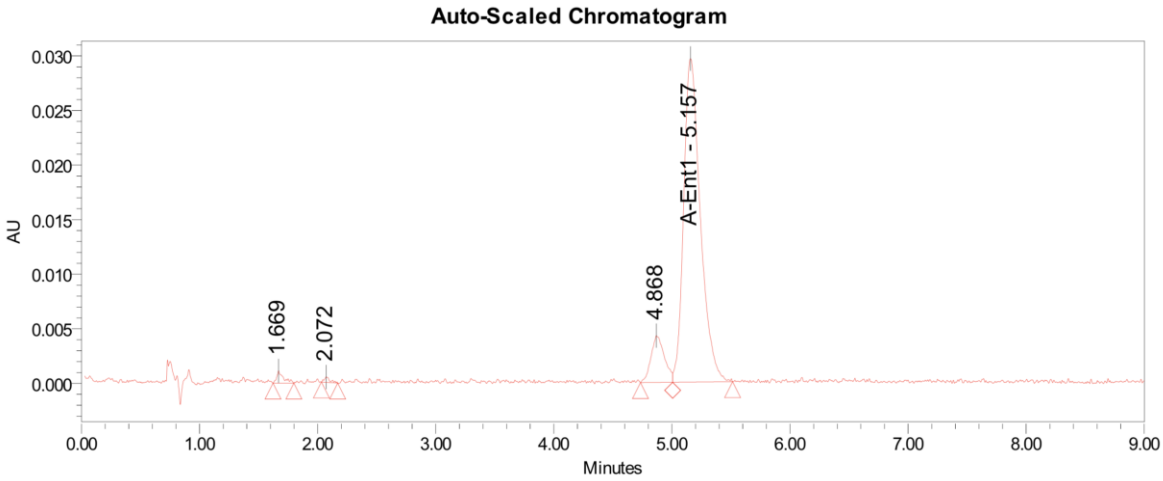

Me
Ph
Si
Me
O
N
H
N
6i
f1 (ppm)

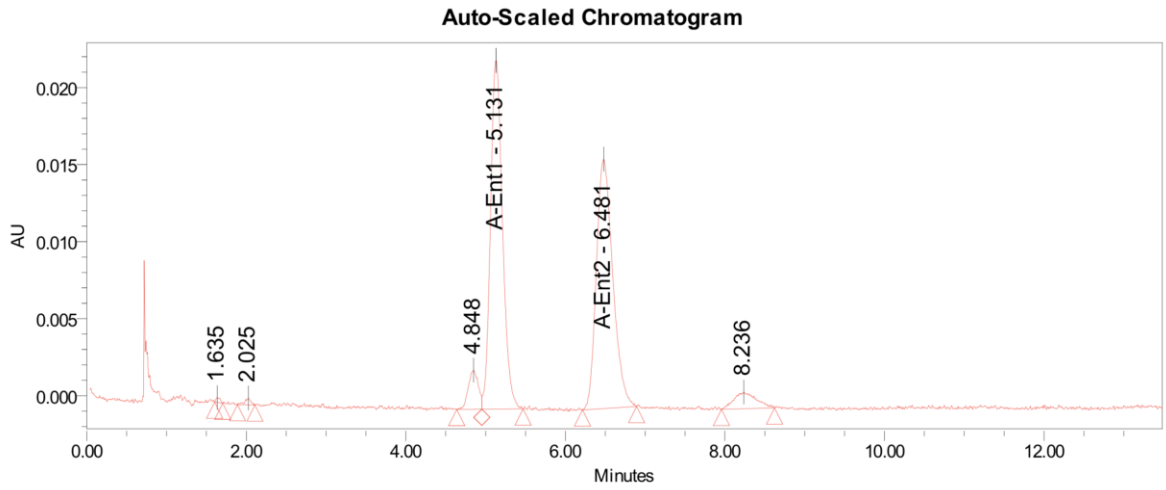

Me
Ph
Si
Me
O
N
H
N
6i
f1 (ppm)


OH
O
Me
Ph
N
H
N
7a
dr = 9:1
f1 (ppm)


OH
O
Me
Ph
N
H
N
7a
dr = 9:1
f1 (ppm)

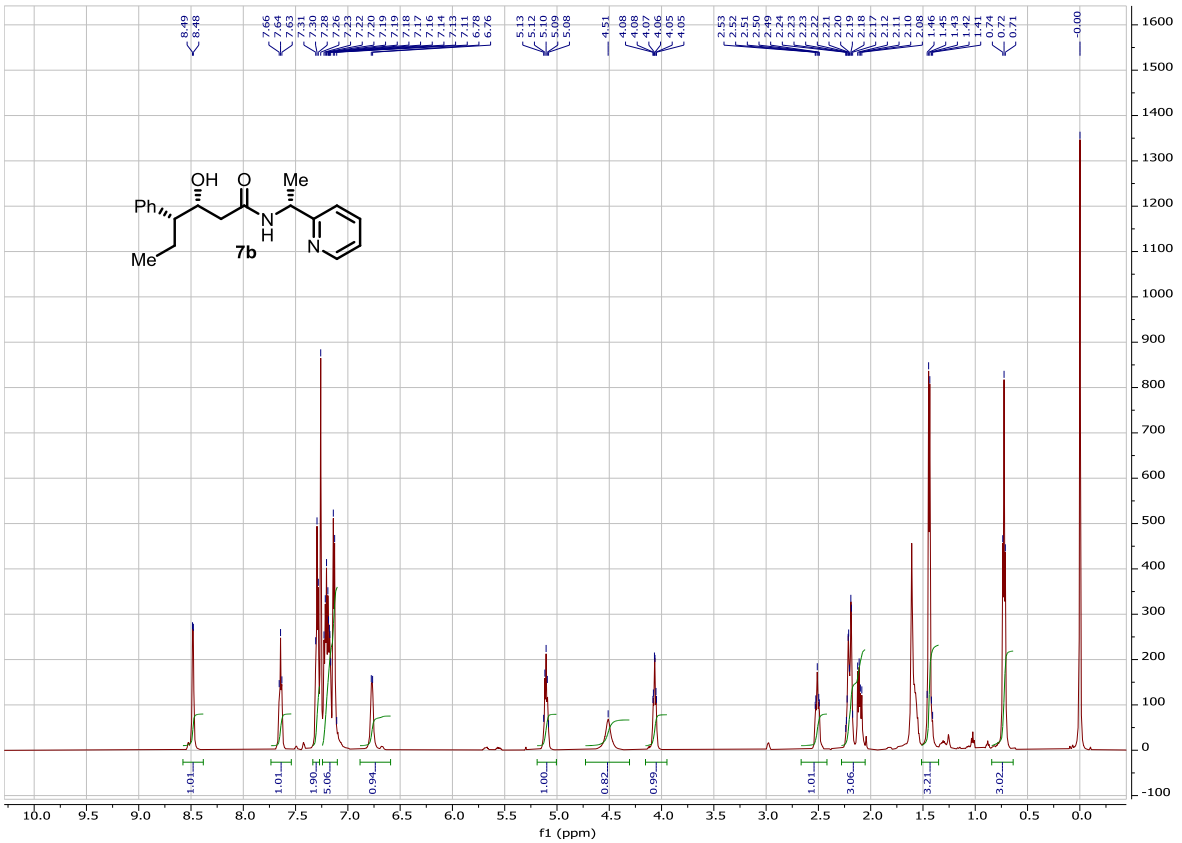
SFC Chromatograms of **7a**

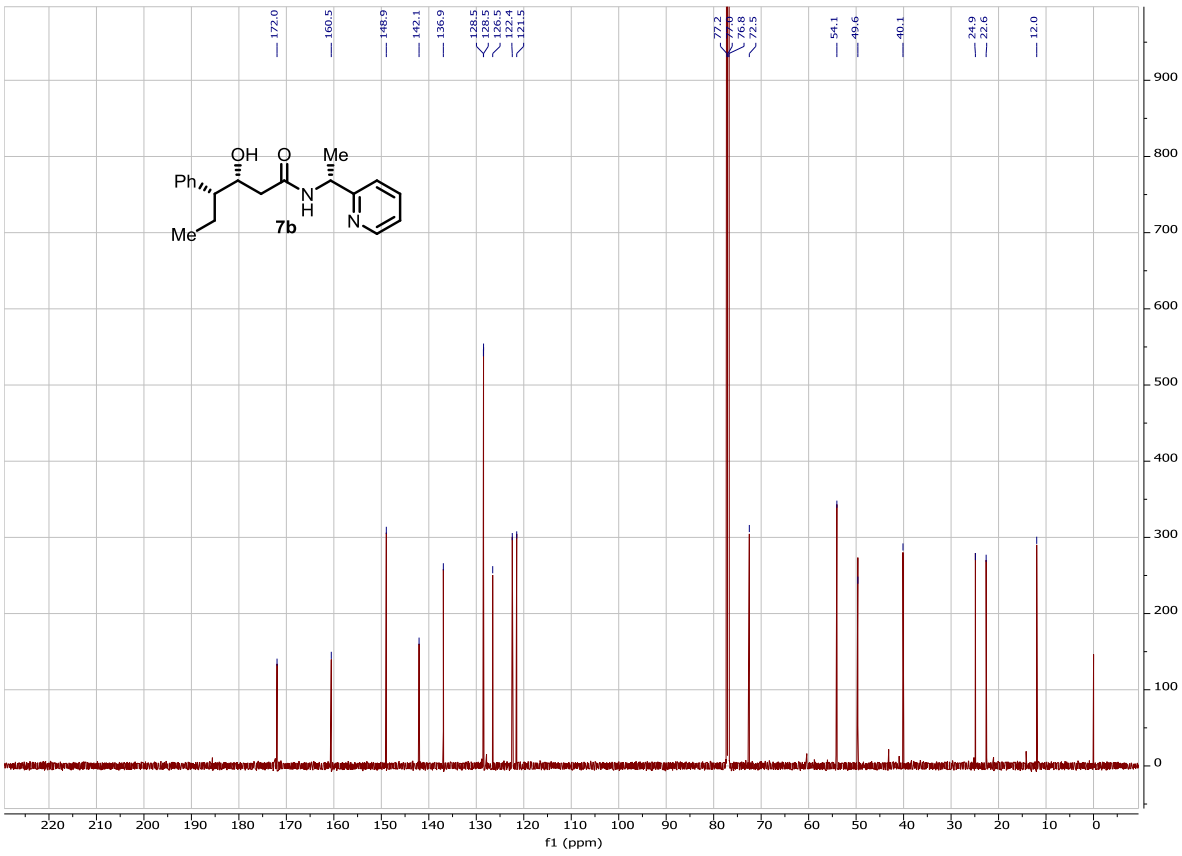


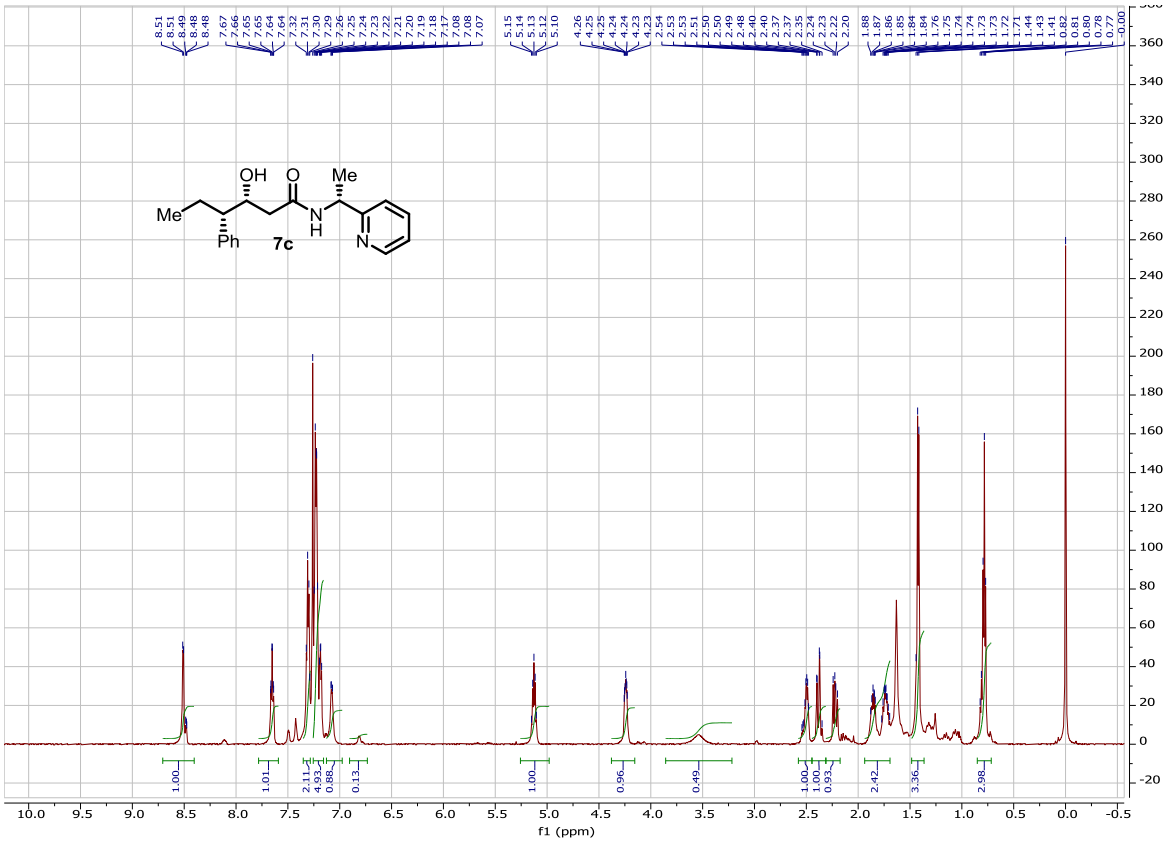


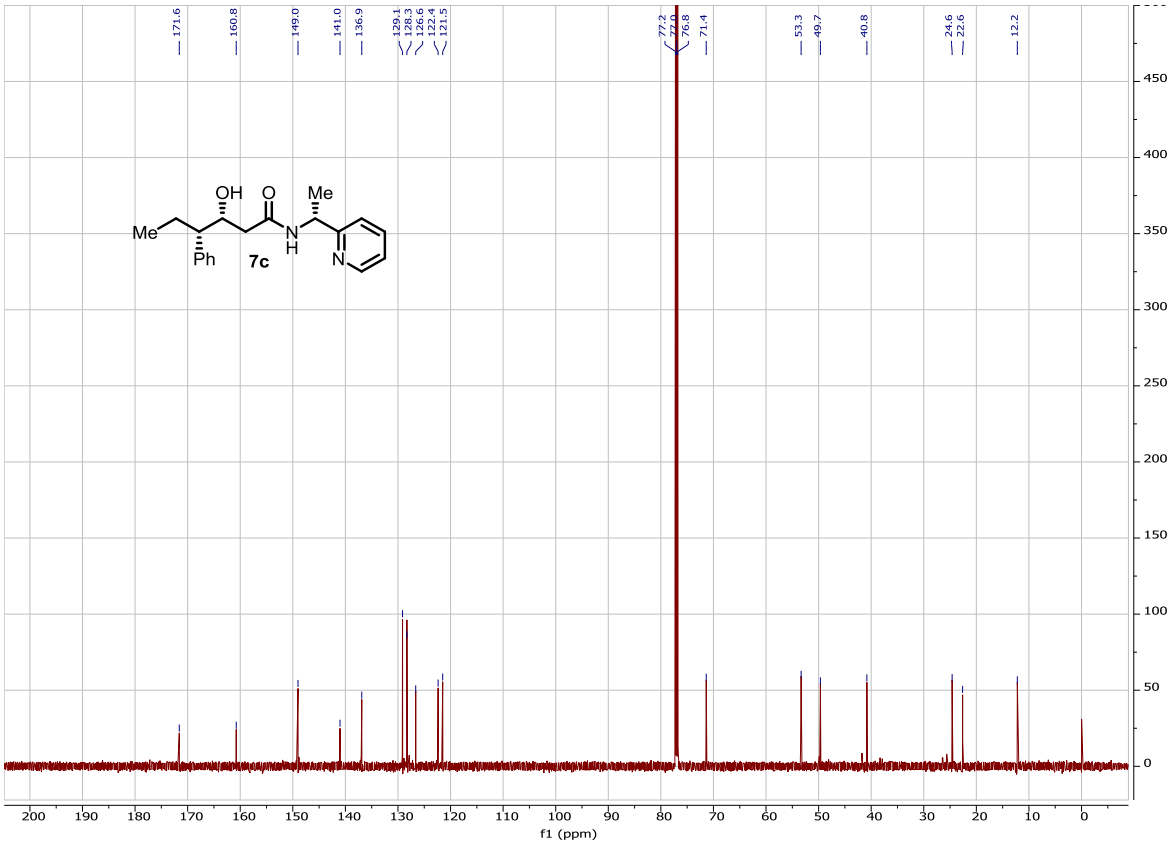
Area Summarized by Name

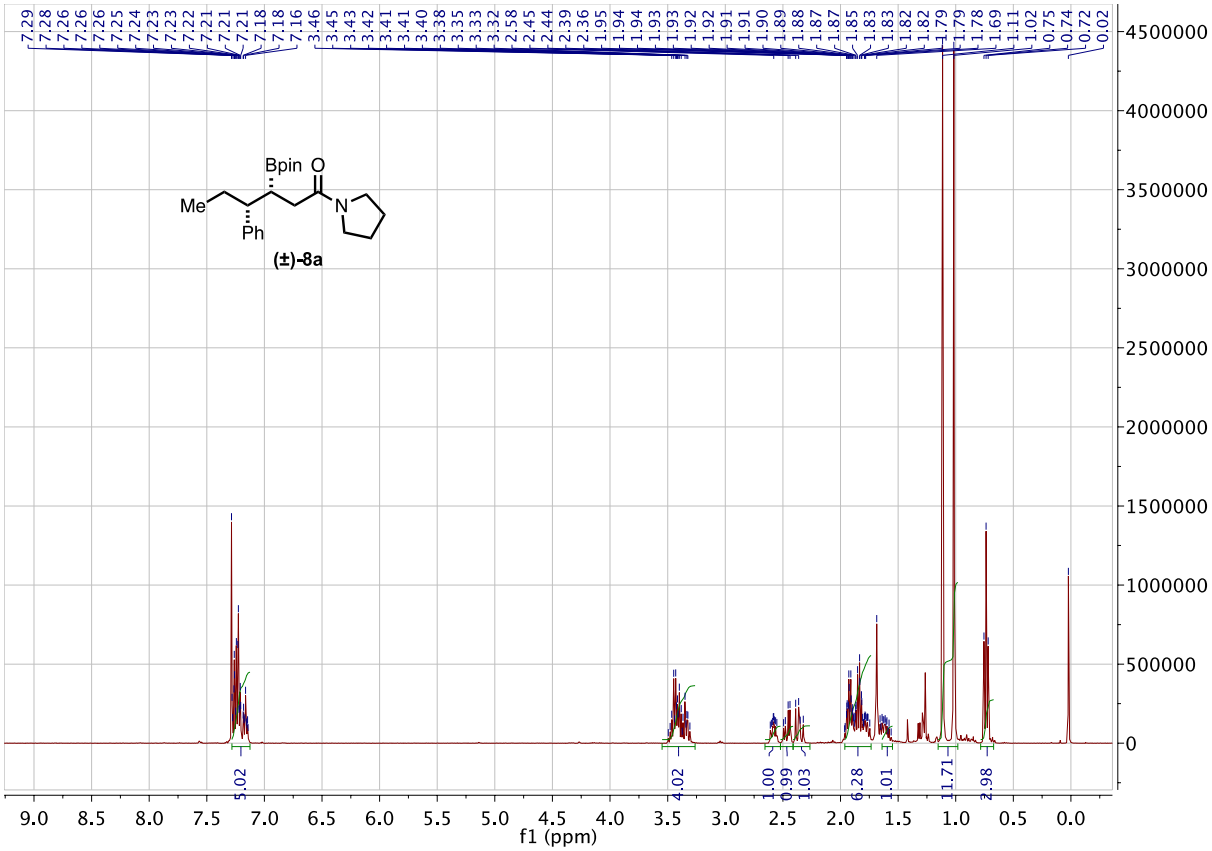
	SampleName	ent1	ent2	ee	Area1	Area2
1	**7a**-major diastereomer-Rac	50.51	49.49	1.03	236387	231589
2	**7a**-major diastereomer-Enant	100.00	--	100.00	291730	--
3	**7a**-minor diastereomer-Enant	51.45	48.55	2.91	22198	20943
4	**7a**-minor diastereomer-Chiral	100.00	--	100.00	33917	--

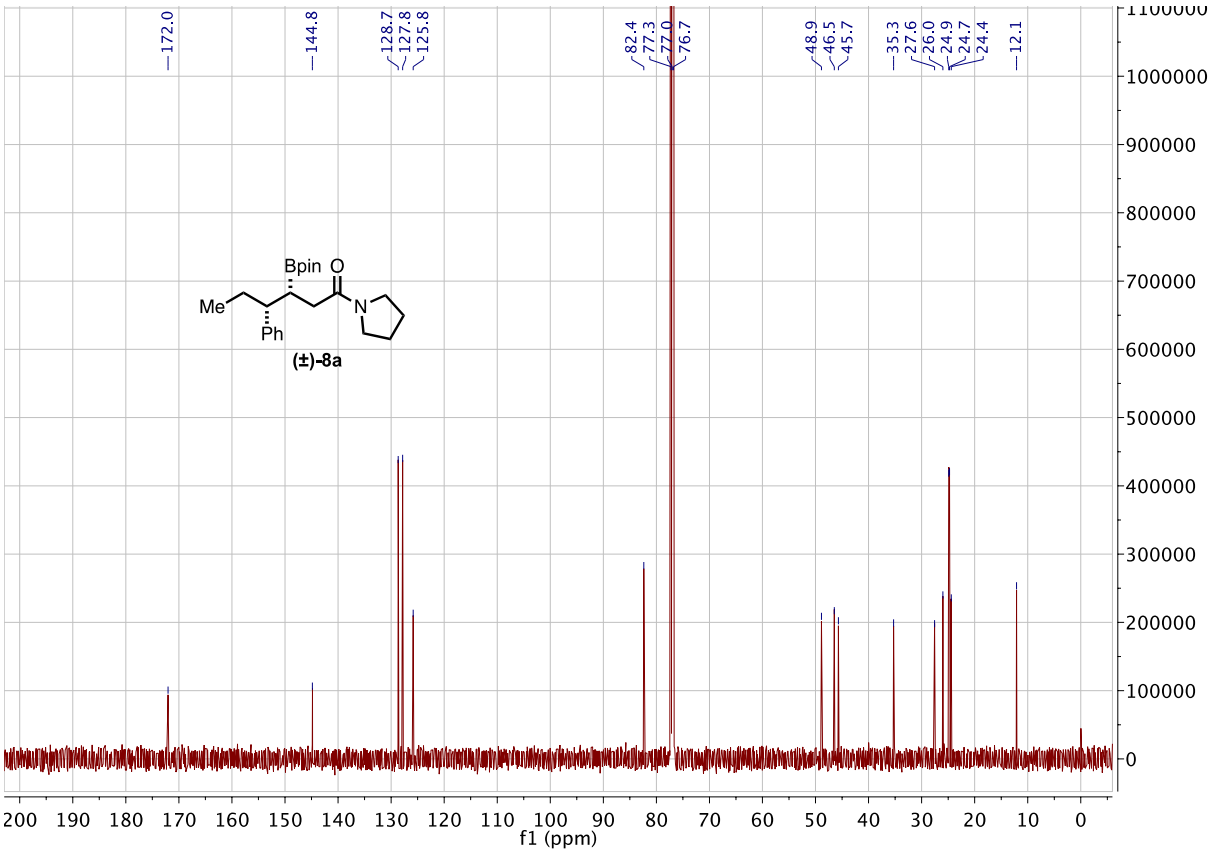

OH
O
Me
Ph
N
H
N
Me
7b
f1 (ppm)

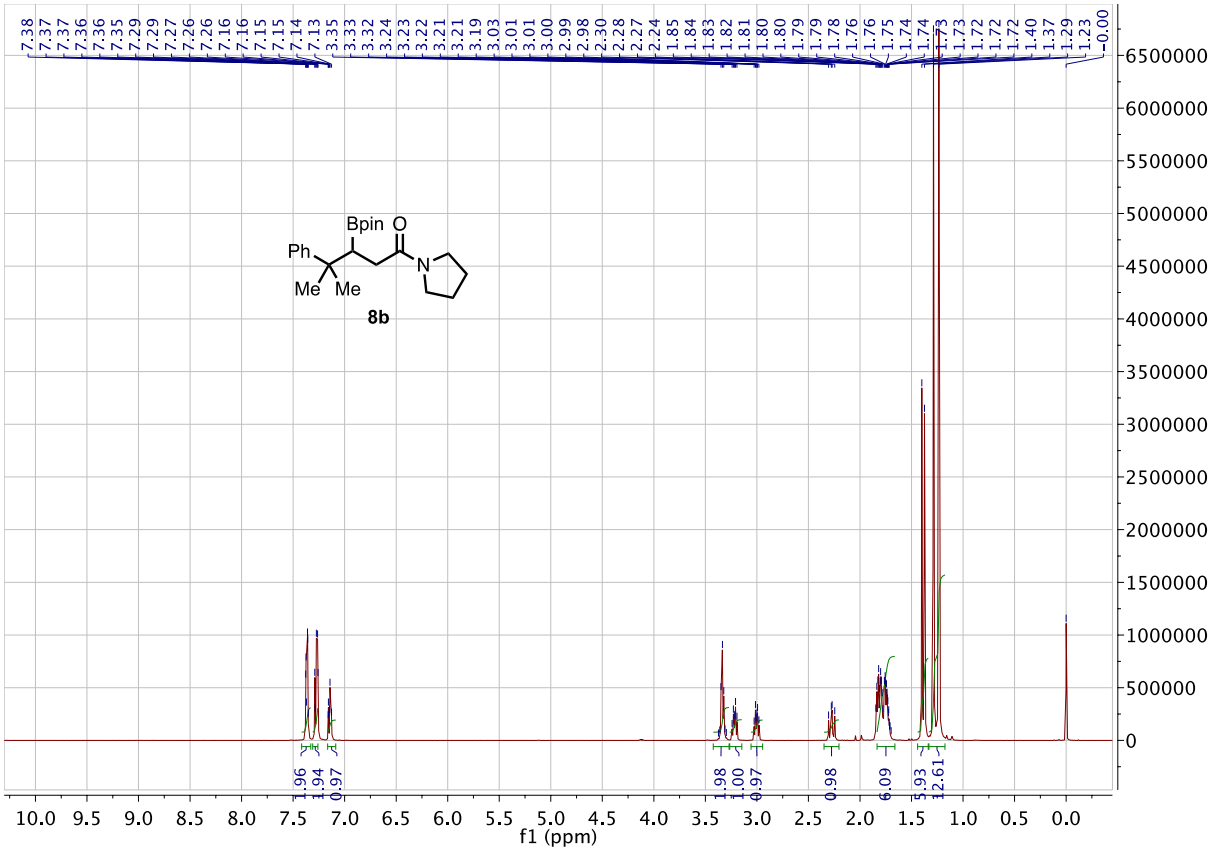

OH
O
Me
Ph
N
H
N
Me
7b
f1 (ppm)

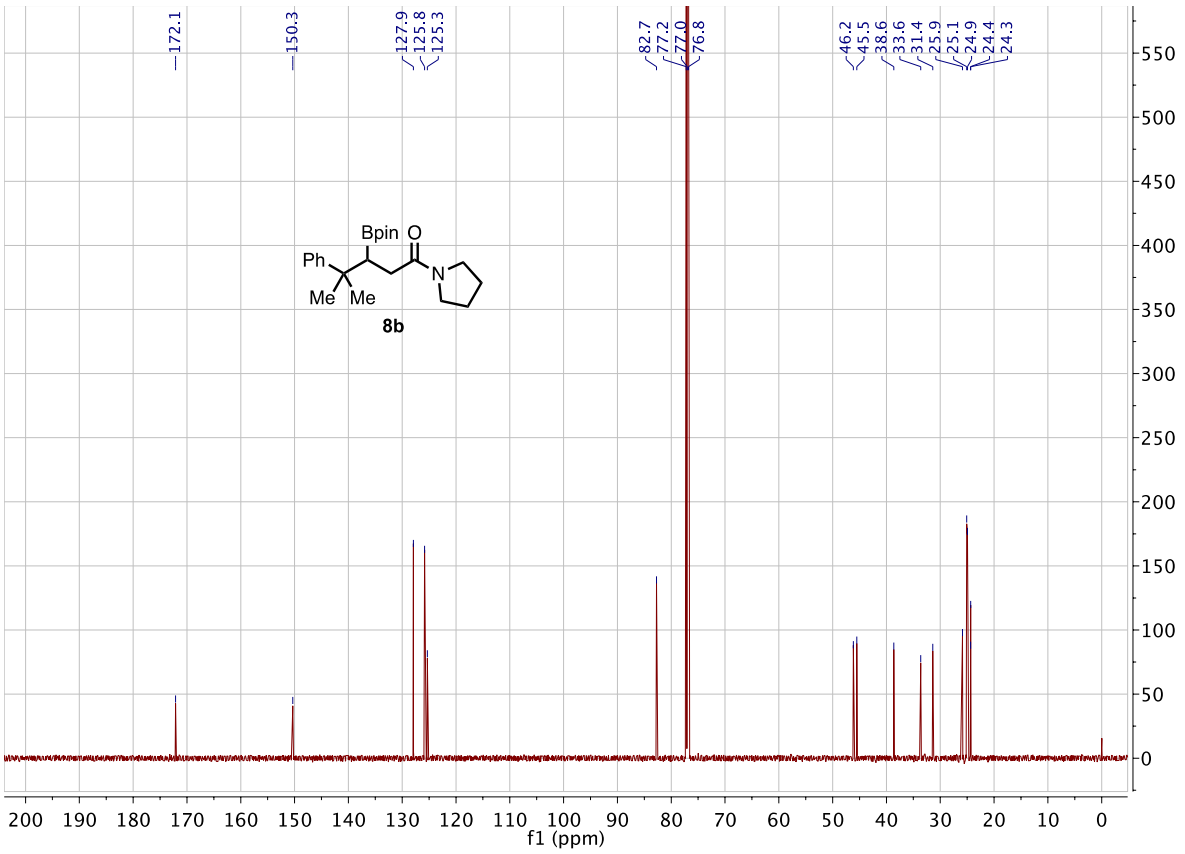

OH
O
Me
Me
N
H
Ph
7c
N
f1 (ppm)

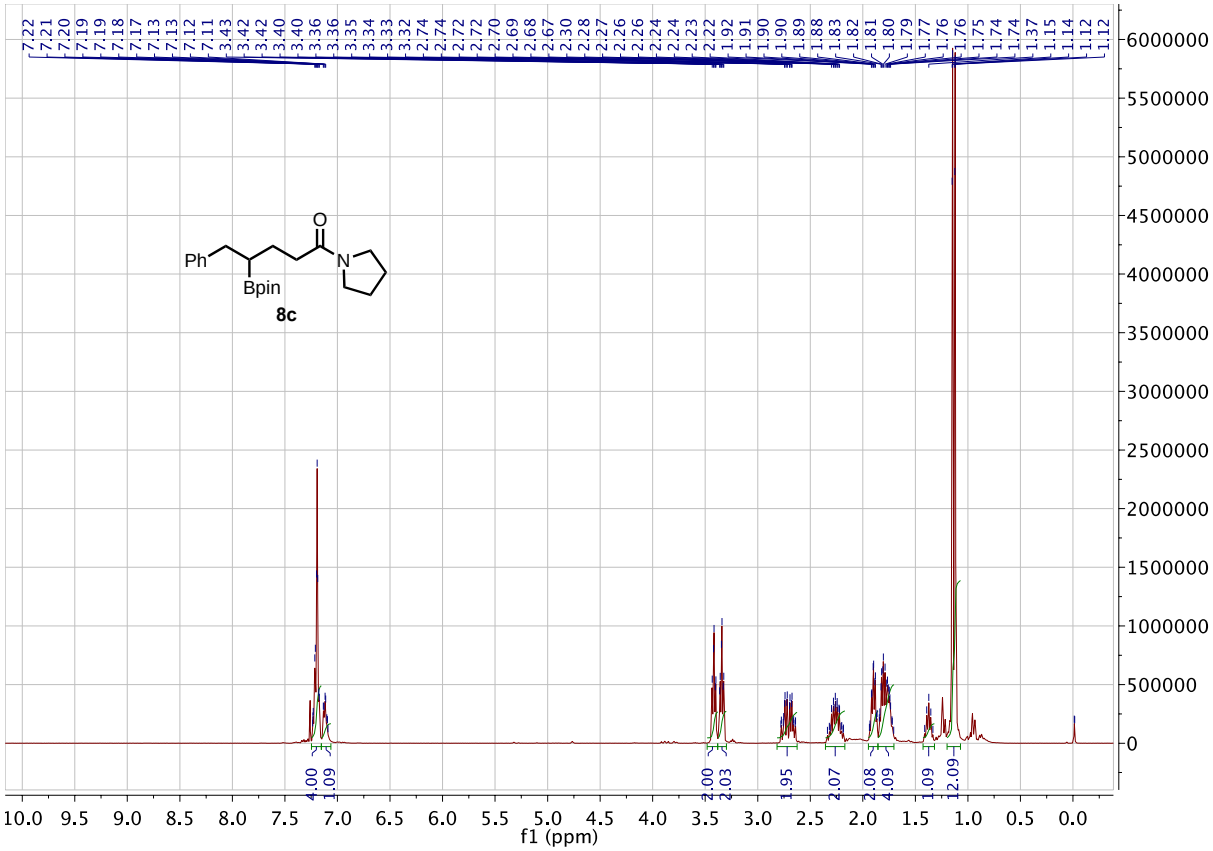

OH
O
Me
Me
N
H
Ph
7c
N
f1 (ppm)

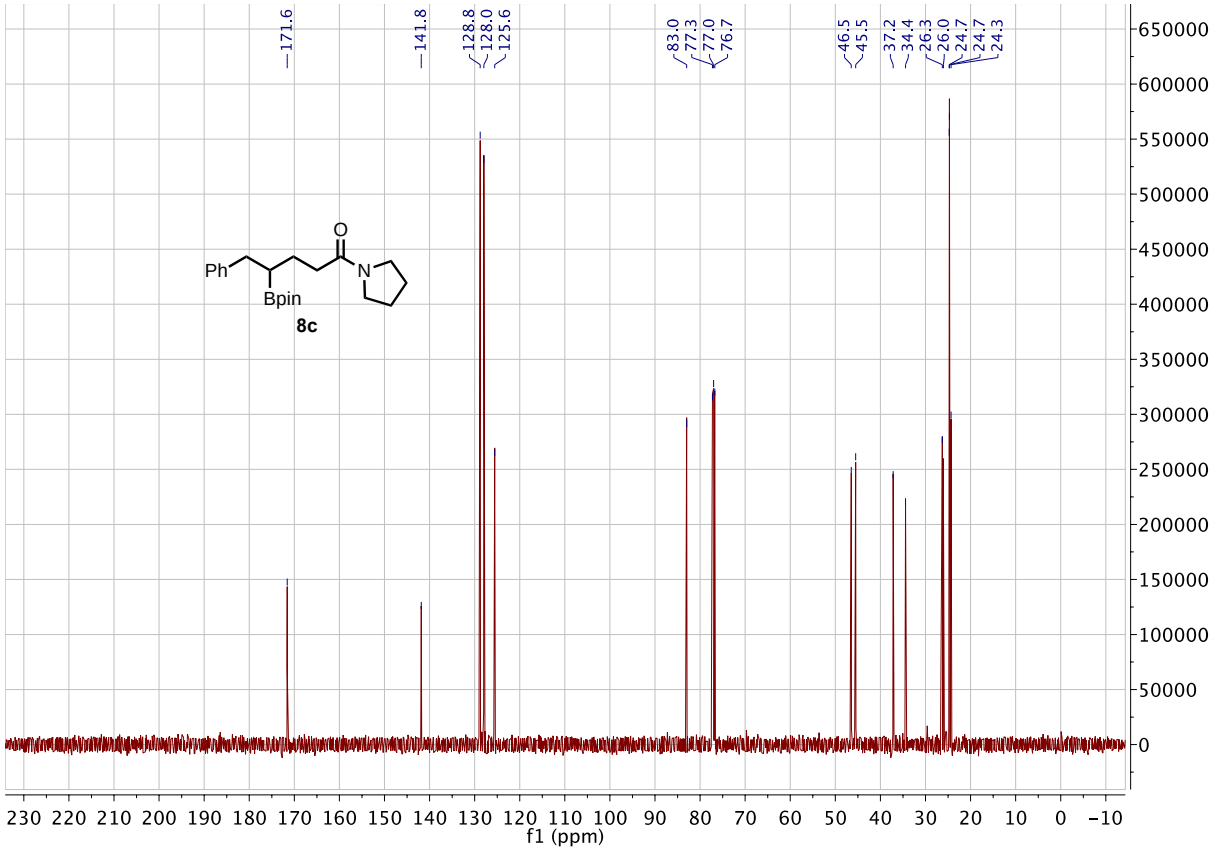

Bpin O
Me
N
Ph
(±)-8a
f1 (ppm)

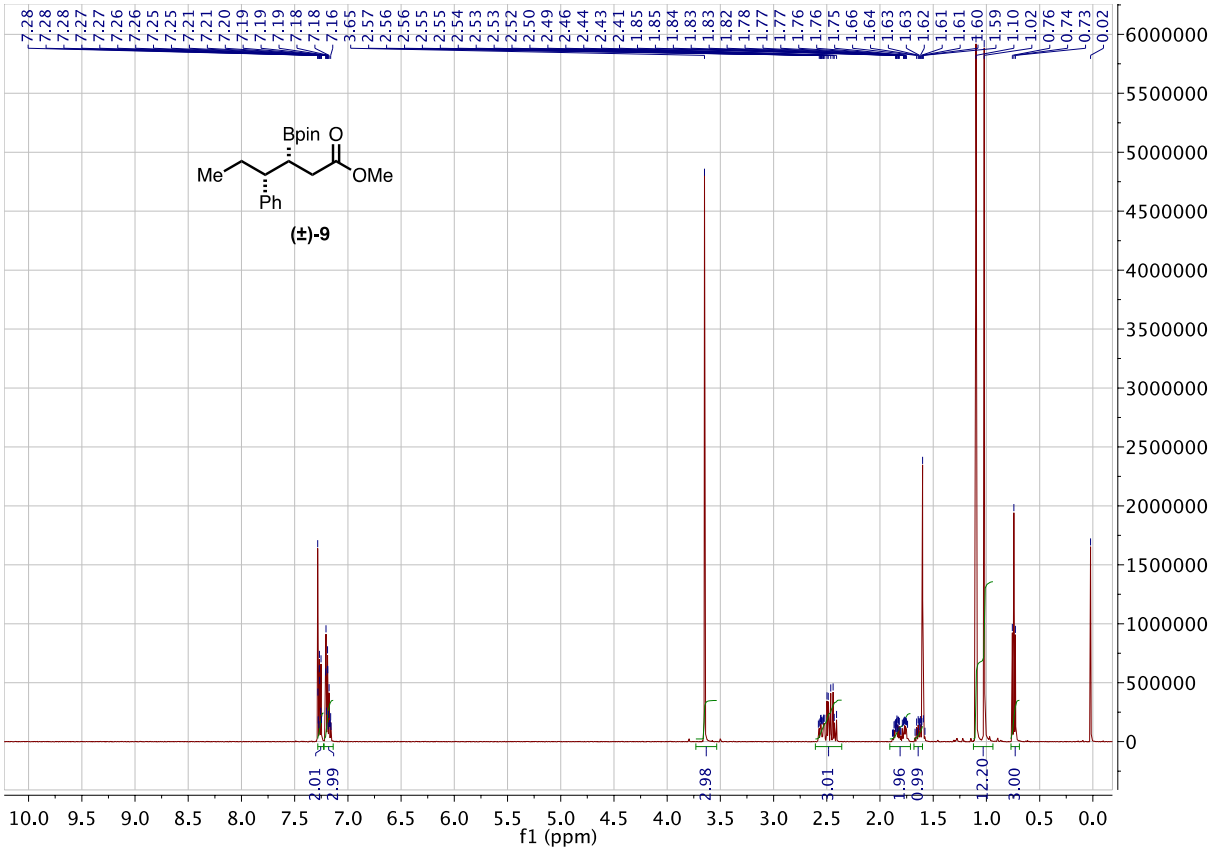

Bpin O
Me
N
Ph
(±)-8a
f1 (ppm)

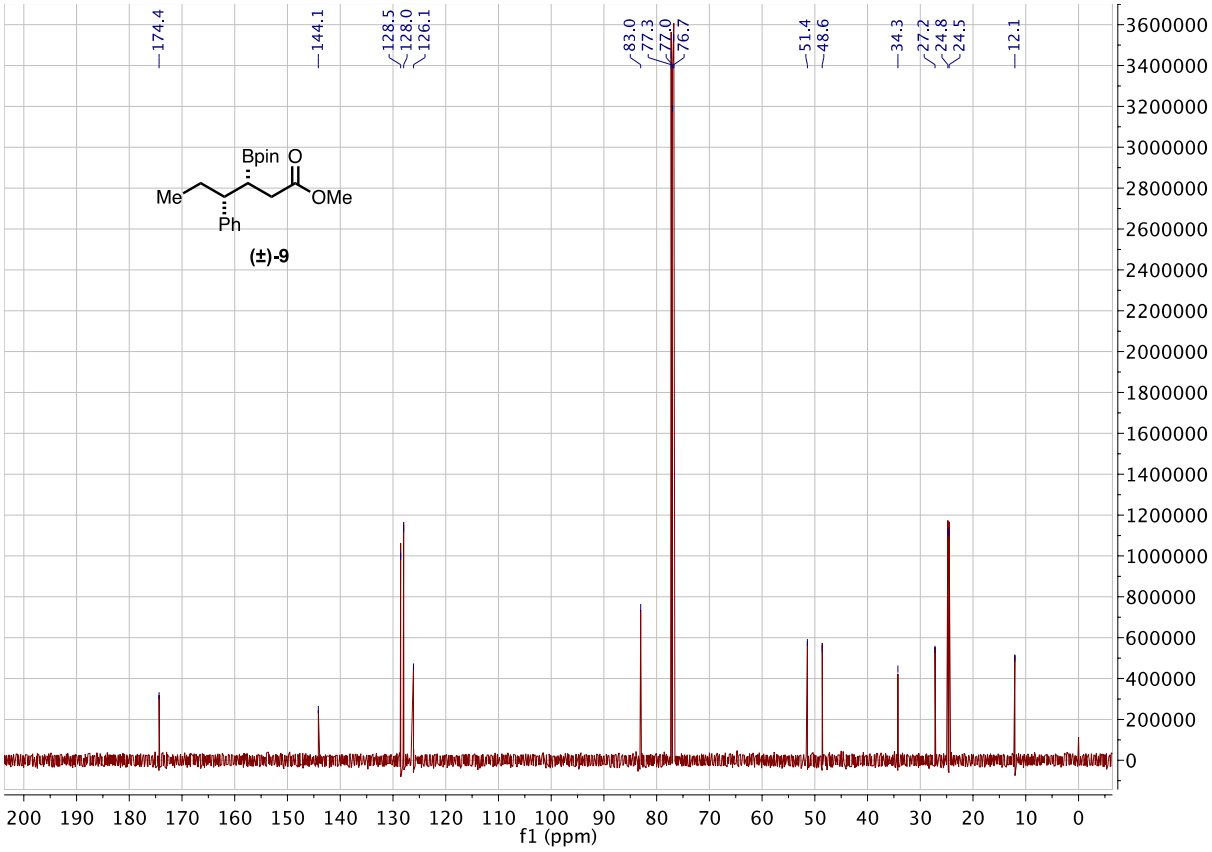

Bpin O
Ph
Me Me
N
8b
f1 (ppm)

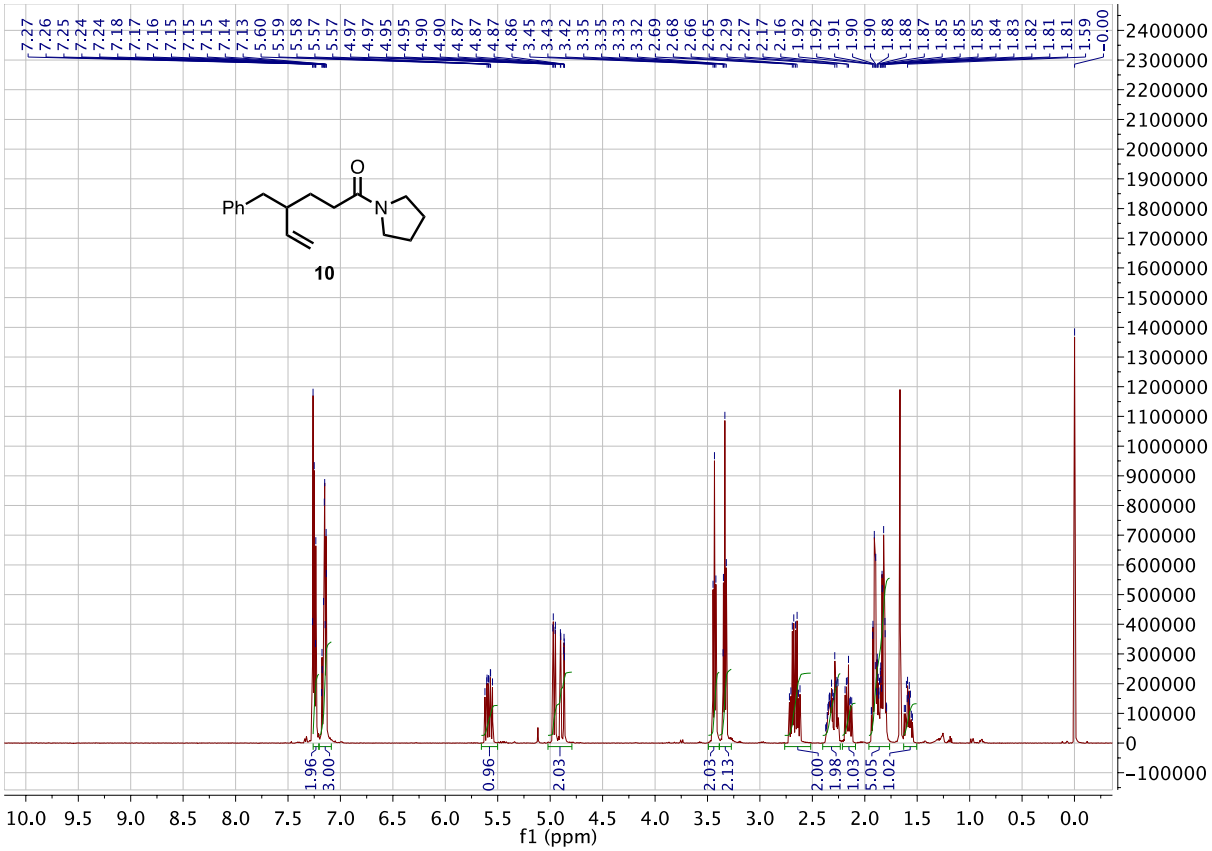

Bpin O
Ph
Me Me
N
8b
f1 (ppm)

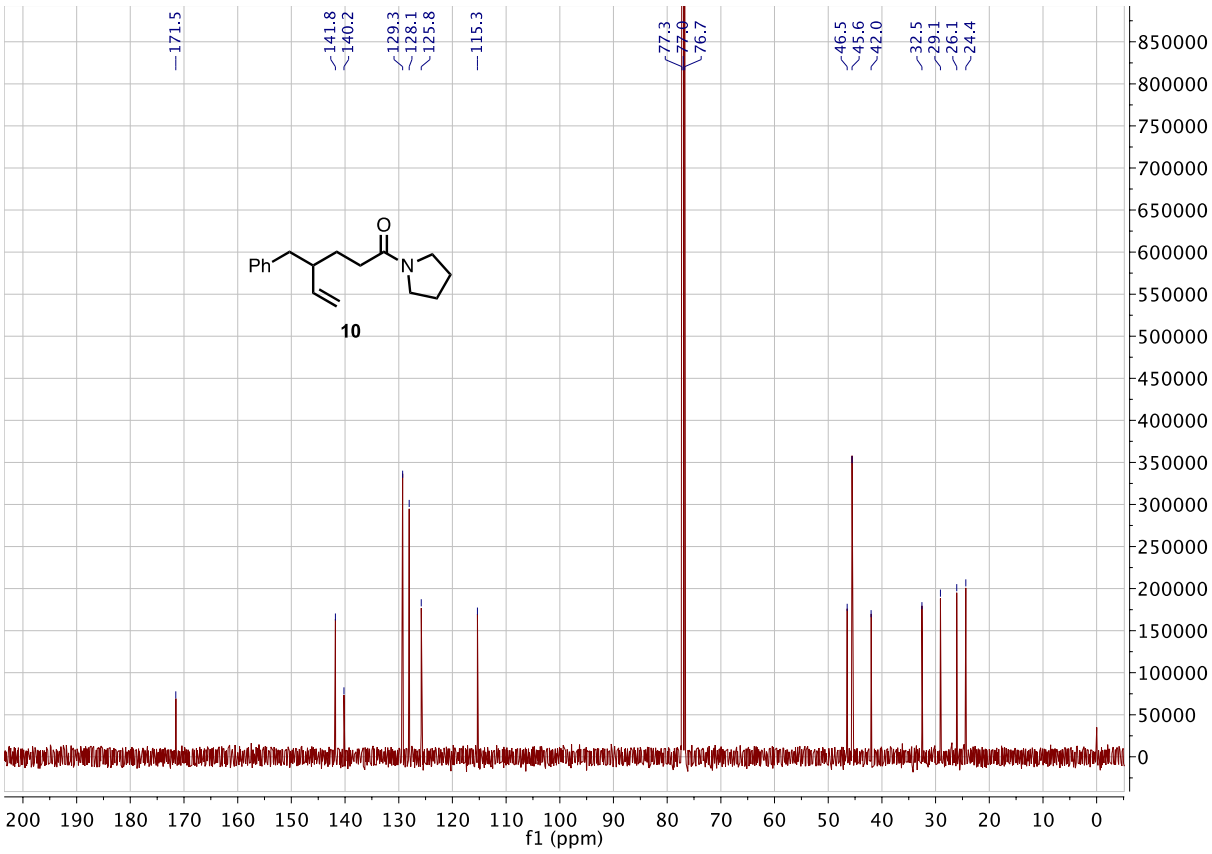

Ph
Bpin
O
N
8c
f1 (ppm)

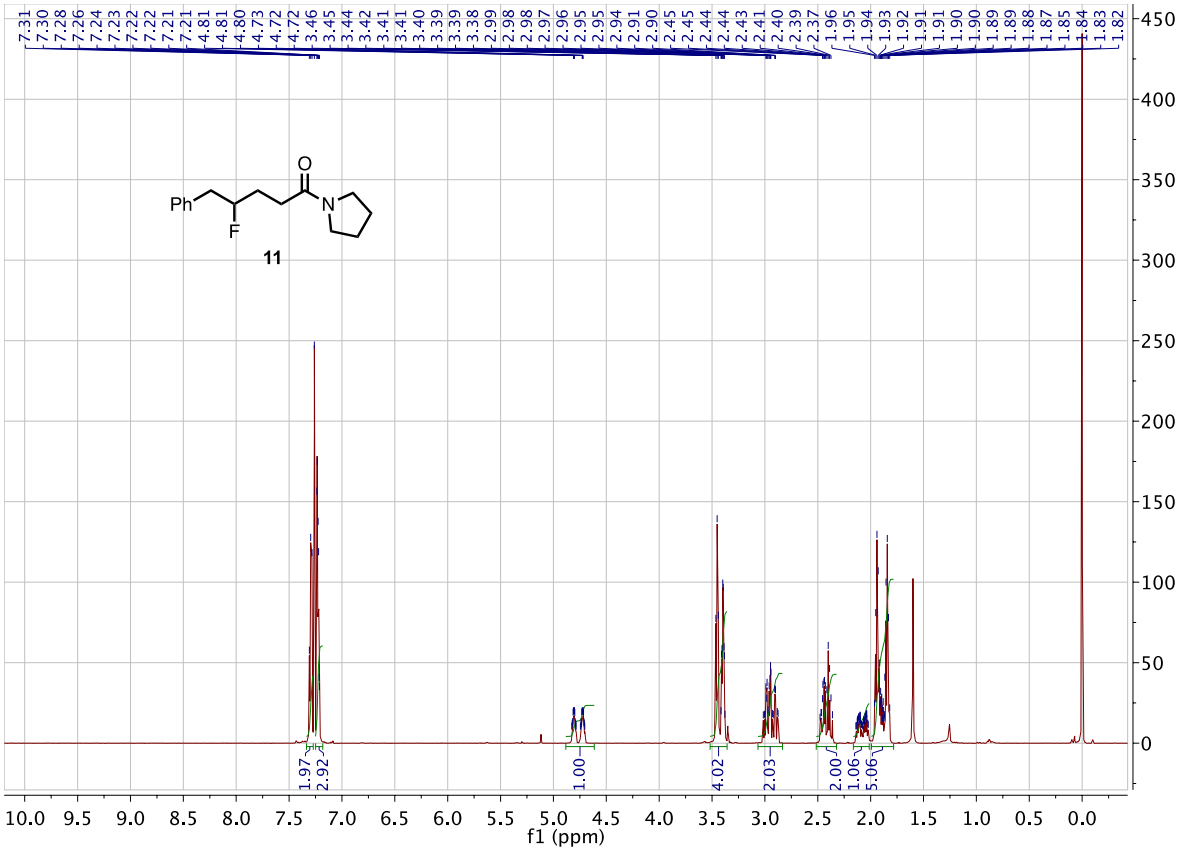

Ph
Bpin
O
N
8c
f1 (ppm)

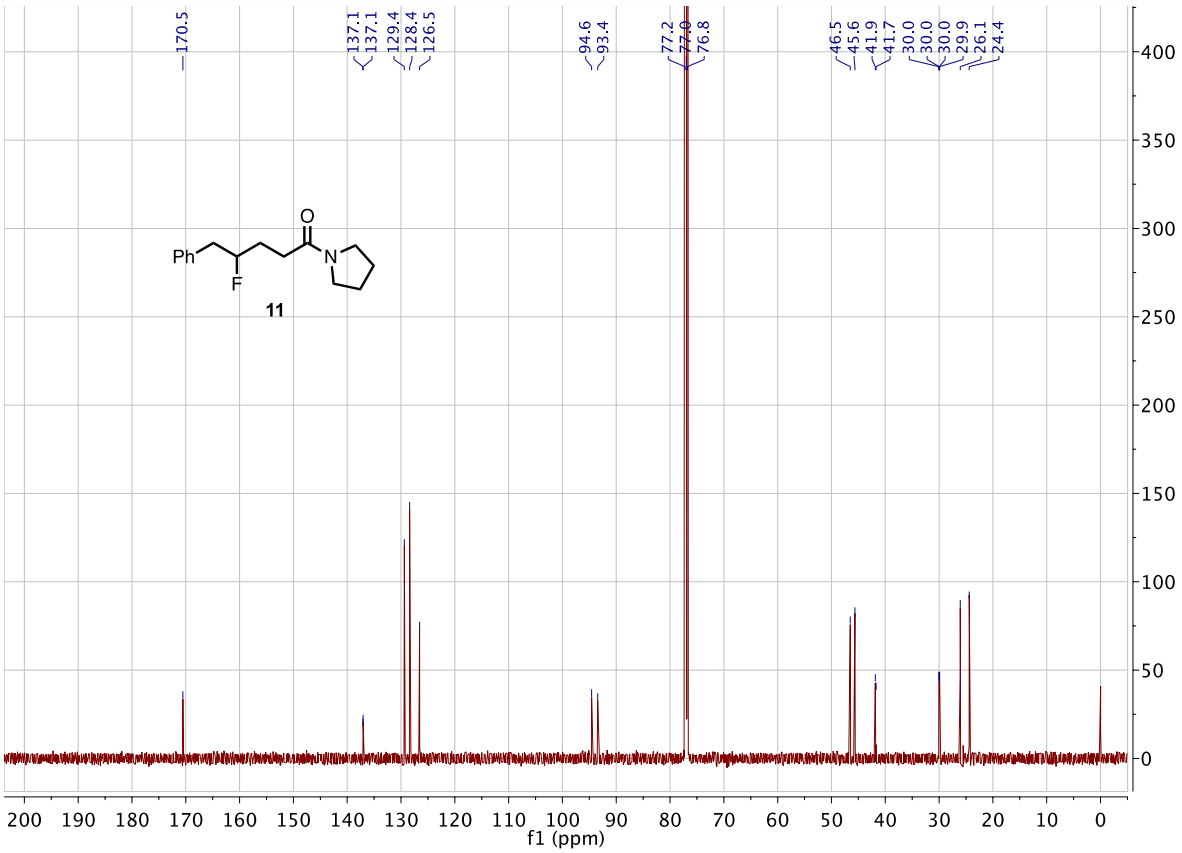

Bpin O
Me
OMe
Ph
(±)-9
f1 (ppm)

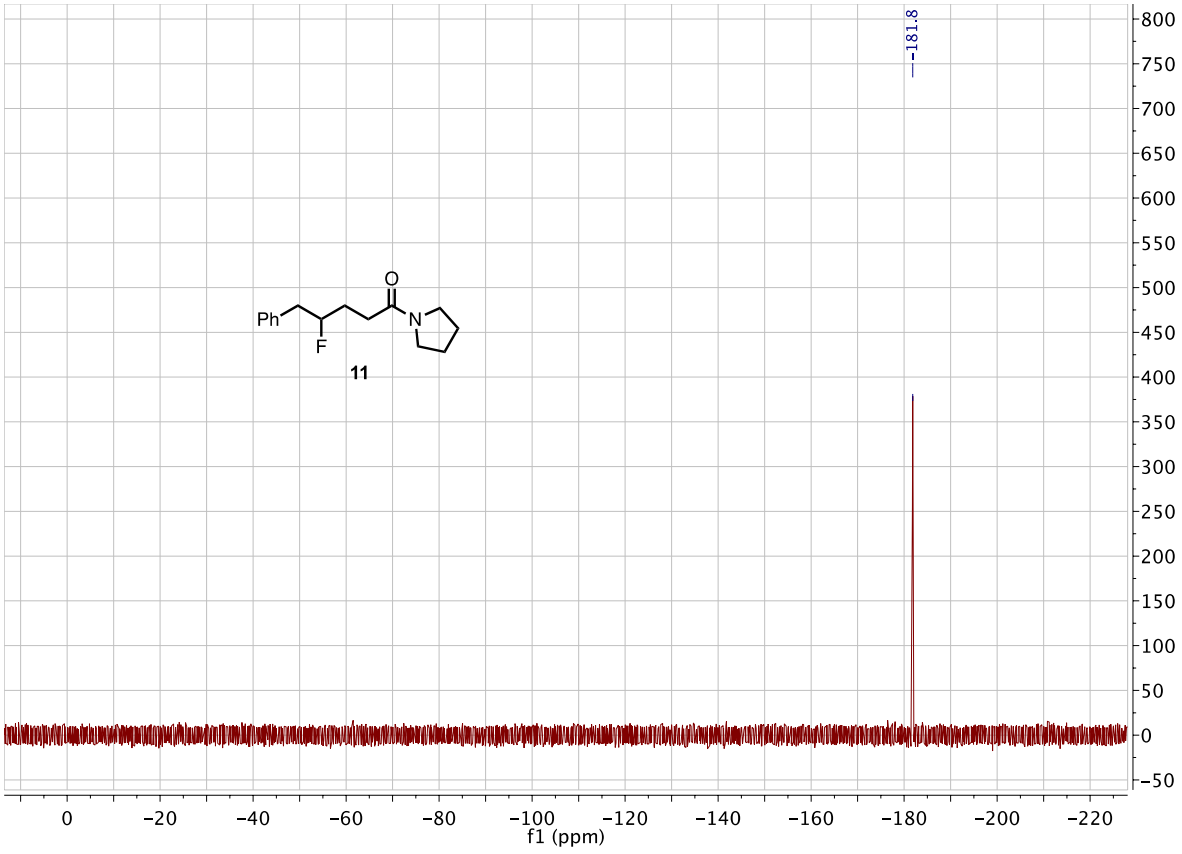

Bpin O
Me
OMe
Ph
(±)-9
f1 (ppm)


Ph
O
N
10
f1 (ppm)


Ph
O
N
10
f1 (ppm)


7.31 7.30 7.28 7.26 7.24 7.23 7.22 7.22 7.21 7.21 4.81 4.81 4.80 4.73 4.72 4.72 3.46 3.45 3.44 3.42 3.41 3.41 3.40 3.39 3.39 3.38 2.99 2.98 2.98 2.97 2.96 2.95 2.95 2.94 2.91 2.90 2.45 2.45 2.44 2.44 2.43 2.41 2.40 2.39 2.37 1.96 1.95 1.94 1.93 1.92 1.91 1.91 1.90 1.90 1.89 1.89 1.88 1.87 1.85 1.84 1.83 1.82
Ph
F
O
N
11
1.97
2.92
1.00
4.02
2.03
2.00
1.06
5.06
f1 (ppm)


170.5
137.1
137.1
129.4
128.4
126.5
94.6
93.4
77.2
77.0
76.8
46.5
45.6
41.9
41.7
30.0
30.0
30.0
29.9
26.1
24.4
Ph
F
O
N
11
f1 (ppm)


181.8
O
Ph
F
N
11
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
−50
0
−20
−40
−60
−80
−100
−120
−140
−160
−180
−200
−220
f1 (ppm)