Mechanism-Based Design of an Amide-Directed Ni-Catalyzed Arylboration of Cyclopentene Derivatives

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Supporting Information

Contents

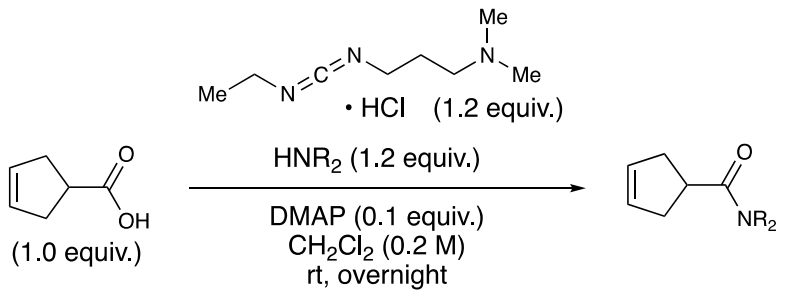
■ **General Considerations:** Infrared (IR) spectra were recorded on a Bruker Tensor II FT-IR Spectrometer, ν_{max} in cm^{-1}. Bands are characterized as broad (br), strong (s), medium (m), and weak (w). ^{1}H NMR spectra were recorded at room temperature unless otherwise noted on a Varian I400 (400 MHz), Varian VXR400 (400 MHz), Varian I500 (500 MHz), or a Varian I600 (600 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the residual solvent resonance as the internal standard ($CHCl_3$: δ 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz), and integration. ^{13}C NMR spectra were recorded on a Varian I400 (100 MHz), Varian VXR400 (100 MHz), Varian I500 (125 MHz), or a Varian I600 (150 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: δ 77.16 ppm). ^{19}F NMR spectra were recorded on Varian VXR400 (375 MHz) spectrometer. High Resolution Mass Spectrometry (HRMS) analysis was obtained using Electron Impact Ionization (EI), Chemical Ionization (CI), Atmospheric Pressure Chemical Ionization (APCI) or Electrospray Ionization (ESI) and reported as m/z (relative intensity). ESI was acquired using a Waters/Micromass LCT Classic (ESI-TOF). The diastereomeric and regioisomeric ratios were determined using NMR or GC analysis of unpurified reaction mixtures. GC analyses were performed by means of Agilent 6850 Gas Chromatograph equipped with Agilent 19091Z-413E, 30 m x 320 μm x 0.25 μm column. Helium was used as the GC carrier gas and maintained at a constant flow rate of 25.0 mL/min. The capillary column was held for 1.0 minutes at the initial temperature (60 °C) and subsequently ramped at a rate of 25 °C /min to a final temperature of 300 °C. Total run time was 9.60 min.
Unless otherwise noted, all reactions have been carried out with distilled and degassed solvents under an atmosphere of dry N_2 in oven- (150 °C) or flame-dried glassware with standard vacuum-line techniques. Dichloromethane (DCM), tetrahydrofuran (THF), diethyl ether (Et_2O), dioxane and dimethylformamide (DMF) were purified under a positive pressure of dry argon by passage through two columns of activated alumina. Toluene (PhMe) was purified under a positive pressure of dry argon by passage through columns of activated alumina and Q5 (Grubbs apparatus). All work-up and purification procedures were carried out with reagent grade solvents (purchased from Sigma-Aldrich) in air. Standard column chromatography techniques using ZEOprep 60/40-63 μm silica gel or a CombiFlash Rf 150 with pre-packed silica cartridges were used for purification.

■ Reagents and Catalysts

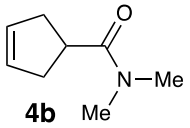
Allylbromide was purchased from Sigma Aldrich and used as received.
Benzylamine was purchased from Fluka and used as received.
Bis(pinacolato)diboron was purchased from Oakwood Chemical and recrystallized in pentane prior to use.
Bromobenzene was purchased from Sigma Aldrich and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use.
α-(Bromomethyl)styrene was synthesized in accordance with literature procedure.[1]
4-Bromoanisol was purchased from Combi-Blocks and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use.
4-(4-bromobenzyl)morpholine was synthesized in accordance with literature procedure.[2]
1-Bromo-4-chlorobenzene was purchased from Sigma Aldrich and recrystallized in pentane prior to use.
4-Bromofluorobenzene was purchased from TCI Chemicals and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use.
3-bromofuran was purchased from Combi-Blocks and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use.
5-Bromo-2-methoxypyridine was purchased from Combi-Blocks and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use.
5-Bromo-1-methyl-1H-indole was synthesized in accordance with literature procedure.[3]
1-Bromo-2-methylprop-1-ene was purchased from Combi-Blocks and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use.
1-Bromonaphthalene was purchased from Oakwood Chemical and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use.
2-Bromoprop-1-ene was purchased from Oakwood Chemical and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use.
2-Bromotoluene was purchased from Oakwood Chemical and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use.
3-Chloro-*N*-methylaniline was purchased from TCI Chemicals and was distilled on a Kugelröhr distillation apparatus before use.
Citric acid was purchased from Oakwood Chemical and used as received.
Cyclohex-3-ene-1-carboxylic acid was purchased from Oakwood Chemical and used as received.
Cyclopent-3-ene-1-carboxylic acid was purchased from Combi-Blocks and used as received.
Dibromomethane was purchased from Alfa Aesar and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use.
Diethyl allylmalonate was purchased from Alfa Aesar and used as received.
Diisobutylaluminium hydride (1.0 M in hexanes) was purchased from Sigma Aldrich and used as received.
Diisopropylamine was purchased from Sigma Aldrich and distilled over calcium hydride immediately prior to use.
Dimethylamine hydrochloride solution (2 M in THF) was purchased from Sigma Aldrich and used as received.
4-Dimethylaminopyridine was purchased from Oakwood Chemical and used as received.
1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide was purchased from AK Scientific and used as received.

Hydrogen peroxide solution (30% in water) was purchased from Macron Chemicals and used as received.
Indoline was purchased from Sigma Aldrich and used as received.
4-Methoxy-*N*-methylaniline was purchased from Combi-Blocks and was distilled on a Kugelröhr distillation apparatus before use.
1-Methylcyclopent-3-ene-1-carboxylic acid was synthesized in accordance with literature procedure.[4]
3-Methylcyclopent-3-ene-1-carboxylic acid was synthesized in accordance with literature procedure.[4]
***n*-Butyllithium solution (2.5 M in hexanes)** was purchased from Sigma Aldrich and titrated before use.
Nickel (II) chloride, dimethoxyethane adduct was purchased from Strem Chemicals and used as received.
***N*,2-Dimethylaniline** was purchased from Combi-Blocks and was distilled on a Kugelröhr distillation apparatus before use.
***N*-Ethylaniline** was purchased from Combi-Blocks and was distilled on a Kugelröhr distillation apparatus before use.
***N*-Methylaniline** was purchased from Combi-Blocks and was distilled on a Kugelröhr distillation apparatus before use.
N,N-Dimethylacetamide (DMA) was purchased from Sigma Aldrich in a Sure-Seal™ bottle and used as received.
***N,O*-Dimethylhydroxylamine hydrochloride** was purchased from Oakwood Chemical and used as received.
1-Phenylpyrrolidin-2-one was purchased from Combi-Blocks and used as received.
Potassium hydroxide was purchased from Macron Chemicals and used as received.
Potassium *tert*-butoxide was purchased from Strem Chemicals and used as received.
Sodium hydride (60 wt% in mineral oil) was purchased from Sigma Aldrich and used as received.
Sodium *tert*-butoxide was purchased from Strem Chemicals and used as received.
Sodium thiosulfate was purchased from Oakwood Chemical and used as received.
***tert*-Butyl (4-bromophenyl)(methyl)carbamate** was synthesized in accordance with literature procedure.[5]
***tert*-Butyllithium (2.5 M in pentane)** was purchased from Sigma Aldrich and titrated before use.
1,3,5-Trimethylbenzene was purchased from Sigma-Aldrich and purified via column chromatography (100% pentane) and stored over activated 4Å molecular sieves.
Zhan-1B catalyst was purchased from Strem Chemicals and used as received.

■ Substrate Synthesis

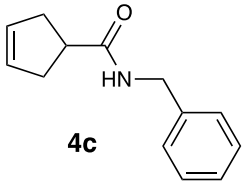


General Procedure A: Amidation
To a flame-dried round-bottom flask equipped with a stir bar was added 4-dimethylaminopyridine (0.1 equiv) and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (1.2 equiv). The flask was evacuated/backfilled with N_2 (3x) and CH_2Cl_2 (0.2 M), carboxylic acid (1.0 equiv), and amine (1.2 equiv) were added. After stirring at room temperature overnight, the reaction was quenched with citric acid (0.08M in H_2O). The organic layers were collected and washed with citric acid (2x, 0.08M in H_2O), saturated $NaHCO_3$, and brine, then dried over $MgSO_4$, gravity filtered, and concentrated under reduced pressure.



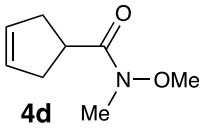
4b

***N,N*-dimethylcyclopent-3-ene-1-carboxamide (4b):** The title compound was synthesized via General Procedure A with cyclopent-3-ene-1-carboxylic acid and dimethylamine hydrochloride solution (2 M in THF). Purification via silica gel column chromatography (2:1 hexanes:diethyl ether) and Kugelröhr short path distillation yielded product as a colorless oil (0.95 g, 57%).
IR (neat): 3054 (w), 2925 (m), 2849 (m), 1632 (s), 1396 (m), 1140 (m), 728 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 5.62 (s, 2H), 3.30 (tt, *J* = 9.4, 6.8 Hz, 1H), 3.03 (s, 3H), 2.94 (s, 3H), 2.72 – 2.49 (m, 4H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 175.5, 128.8, 39.3, 37.2, 36.6, 35.7; **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd for $C_8H_{13}NONa$ 162.0889; Found 162.0889.



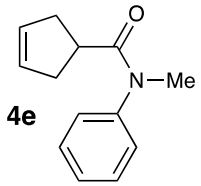
4c

***N*-benzylcyclopent-3-ene-1-carboxamide (4c):** The title compound was synthesized via General Procedure A with cyclopent-3-ene-1-carboxylic acid and benzylamine. Purification via silica gel column chromatography (4:1 hexanes:ethyl acetate) yielded product as a white solid (0.69 g, 68%). Spectral data was in accordance with that of the literature.[4]
IR (neat): 3271 (s), 3053 (m), 2898 (m), 1636 (s), 1544 (s), 693 (s) cm^{-1}; **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.56 – 6.90 (m, 5H), 5.74 (br s, 1H), 5.69 (s, 2H), 4.46 (d, *J* = 5.7 Hz, 2H), 2.98 (td, *J* = 8.9, 4.6 Hz, 1H), 2.75 – 2.46 (m, 4H); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 175.8, 138.6, 129.3, 128.7, 127.8, 127.5, 43.6, 43.5, 37.0.



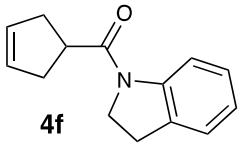
4d

***N*-methoxy-*N*-methylcyclopent-3-ene-1-carboxamide (4d):** The title compound was synthesized via General Procedure A with cyclopent-3-ene-1-carboxylic acid and *N*,*O*-dimethylhydroxylamine hydrochloride. Purification via silica gel column chromatography (1:1 hexanes:diethyl ether) yielded product as a colorless oil (1.3 g, 71%). Spectral data was in accordance with that of the literature.[6]
^{1}H NMR (600 MHz, $CDCl_3$): δ 5.65 (s, 2H), 3.70 (s, 3H), 3.48 (s, 1H), 3.20 (s, 3H), 2.70 – 2.55 (m, 4H).



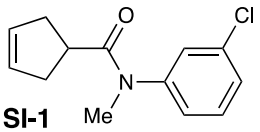
4e

***N*-methyl-*N*-phenylcyclopent-3-ene-1-carboxamide (4e):** The title compound was synthesized via General Procedure A with cyclopent-3-ene-1-carboxylic acid and *N*-methylaniline. Purification via silica gel column chromatography (3:1 hexanes:diethyl ether) and Kugelröhr short path distillation yielded product as a colorless oil (4.3 g, 71%).
IR (neat): 3054 (w), 2916 (w), 1737 (m), 1650 (s), 1593 (s), 729 (s) cm^{-1}; **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.40 (td, *J* = 7.8, 1.9 Hz, 2H), 7.34 – 7.29 (m, 1H), 7.20 – 7.15 (m, 2H), 5.55 – 5.52 (m, 2H), 3.26 (d, *J* = 2.2 Hz, 3H), 3.01 – 2.93 (m, 1H), 2.65 (dd, *J* = 14.9, 7.3 Hz, 2H), 2.28 (dd, *J* = 15.0, 9.5 Hz, 2H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 176.2, 144.3, 129.7, 128.8, 127.7, 127.5, 39.9, 37.7, 27.1; **LRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{13}H_{16}NO$ 202.1; Found 202.2.



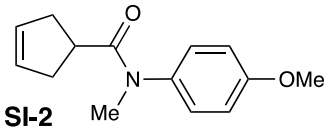
4f

cyclopent-3-en-1-yl(indolin-1-yl)methanone (4f): The title compound was synthesized via General Procedure A with cyclopent-3-ene-1-carboxylic acid and indoline. Purification via silica gel column chromatography (10:1 hexanes:diethyl ether) and recrystallization in hexanes:EtOAc yielded product as a purple solid (0.48 g, 45%).
IR (neat): 2938 (w), 2846 (w), 1646 (s), 1597 (m), 1459 (s), 765 (s) cm^{-1}; **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.27 (d, *J* = 8.1 Hz, 1H), 7.19 (t, *J* = 8.3 Hz, 2H), 7.01 (t, *J* = 7.4 Hz, 1H), 5.71 (s, 2H), 4.15 (t, *J* = 8.5 Hz, 2H), 3.35 (td, *J* = 9.3, 4.7 Hz, 1H), 3.21 (t, *J* = 8.6 Hz, 2H), 2.81 (dt, *J* = 10.9, 5.3 Hz, 2H), 2.69 (dd, *J* = 15.0, 9.3 Hz, 2H); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 174.1, 143.4, 131.2, 128.8, 127.6, 124.5, 123.5, 117.3, 48.1, 41.9, 36.5, 30.9, 28.1; **LRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{14}H_{16}NO$ 214.1; Found 214.2.



SI-1

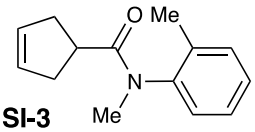
***N*-(3-chlorophenyl)-*N*-methylcyclopent-3-ene-1-carboxamide (SI-1):** The title compound was synthesized via General Procedure A with cyclopent-3-ene-1-carboxylic acid and 3-chloro-*N*-methylaniline. Purification via silica gel column chromatography (75:23:2 hexanes:diethyl ether:triethylamine) and Kugelröhr short path distillation yielded product as a colorless oil (1.9 g, 68%).
IR (neat): 3057 (w), 2919 (w), 2850 (w), 1651 (s), 1589 (s), 726 (s) cm^{-1}; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.41 – 7.32 (m, 2H), 7.24 (t, *J* = 2.0 Hz, 1H), 7.12 (dt, *J* = 7.4, 1.8 Hz, 1H), 5.59 (s, 2H), 3.29 (s, 3H), 2.99 (s, 1H), 2.69 (dd, *J* = 14.2, 7.2 Hz, 2H), 2.39 – 2.31 (m, 2H); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 176.0, 145.5, 135.1, 130.7, 128.8, 128.1, 127.9, 125.9, 77.2, 40.1, 37.7; **LRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{13}H_{15}ClNO$ 236.1; Found 236.0.



SI-2

***N*-(4-methoxyphenyl)-*N*-methylcyclopent-3-ene-1-carboxamide (SI-2):** The title compound was synthesized via General Procedure A with cyclopent-3-ene-1-carboxylic acid and 4-methoxy-*N*-methylaniline. Purification via silica gel column chromatography (75:23:2 hexanes:diethyl ether:triethylamine) and recrystallization (CH_2Cl_2/pentane) yielded product as a colorless oil (2.2 g, 79%).

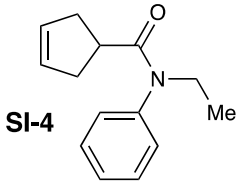
IR (neat): 3052 (w), 2914 (w), 2840 (w), 1645 (s), 1508 (s), 1244 (s), 727 (s) cm^{-1}; **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 7.16 – 7.09 (m, 2H), 6.97 – 6.90 (m, 2H), 5.57 (s, 2H), 3.85 (s, 3H), 3.26 (s, 3H), 3.01 (tt, *J* = 9.5, 7.4 Hz, 1H), 2.72 – 2.62 (m, 2H), 2.36 – 2.26 (m, 2H); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 176.5, 158.9, 137.1, 128.9, 128.6, 114.8, 55.5, 40.0, 37.8, 37.6; **LRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{14}H_{18}NO_2$ 232.1; Found 232.2.



SI-3

***N*-methyl-*N*-(*o*-tolyl)cyclopent-3-ene-1-carboxamide (SI-3):** The title compound was synthesized via General Procedure A with cyclopent-3-ene-1-carboxylic acid and *N*,2-dimethylaniline. Purification via silica gel column chromatography (3:1 hexanes:diethyl ether) and Kugelröhr short path distillation yielded product as a white solid (0.66 g, 61%).

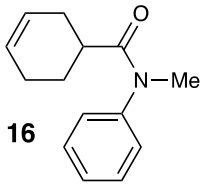
IR (neat): 3054 (w), 2918 (w), 2849 (w), 1737 (w), 1646 (s), 1384 (m), 1101 (m), 725 (s) cm^{-1}; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.34 – 7.22 (m, 3H), 7.13 (dd, *J* = 7.1, 1.9 Hz, 1H), 5.62 – 5.51 (m, 2H), 3.22 (s, 3H), 2.84 (tt, *J* = 9.2, 7.6 Hz, 1H), 2.75 (ddp, *J* = 15.7, 7.9, 2.8 Hz, 1H), 2.60 (ddp, *J* = 15.6, 7.8, 2.7 Hz, 1H), 2.36 – 2.26 (m, 2H), 2.25 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$, *mix of rotomers*):** δ 176.5, 142.8, 135.6, 131.4, 129.2, 128.5, 128.3, 128.3, 127.3, 40.1, 38.0, 37.0, 36.2, 17.4; **LRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{14}H_{18}NO$ 216.1; Found 216.2.



SI-4

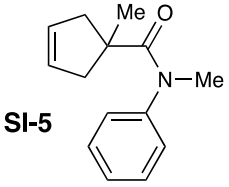
***N*-ethyl-*N*-phenylcyclopent-3-ene-1-carboxamide (SI-4):** The title compound was synthesized via General Procedure A with cyclopent-3-ene-1-carboxylic acid and *N*-ethylaniline. Purification via silica gel column chromatography (75:23:2 hexanes:diethyl ether:triethylamine) and Kugelröhr short path distillation yielded product as a colorless oil (2.2 g, 83%).

IR (neat): 3055 (w), 2970 (w), 2931 (w), 1649 (s), 1594 (m), 1246 (s), 698 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.40 (dd, *J* = 8.3, 6.7 Hz, 2H), 7.36 – 7.28 (m, 1H), 7.18 – 7.11 (m, 2H), 5.52 (s, 2H), 3.74 (q, *J* = 7.1 Hz, 2H), 2.88 (tt, *J* = 9.5, 7.4 Hz, 1H), 2.63 (dd, *J* = 14.4, 7.3 Hz, 2H), 2.26 (dt, *J* = 14.1, 6.6 Hz, 2H), 1.09 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 175.5, 142.5, 129.5, 128.8, 128.7, 127.8, 44.2, 40.3, 37.6, 13.0; **LRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{14}H_{18}NO$ 216.1; Found 216.2.



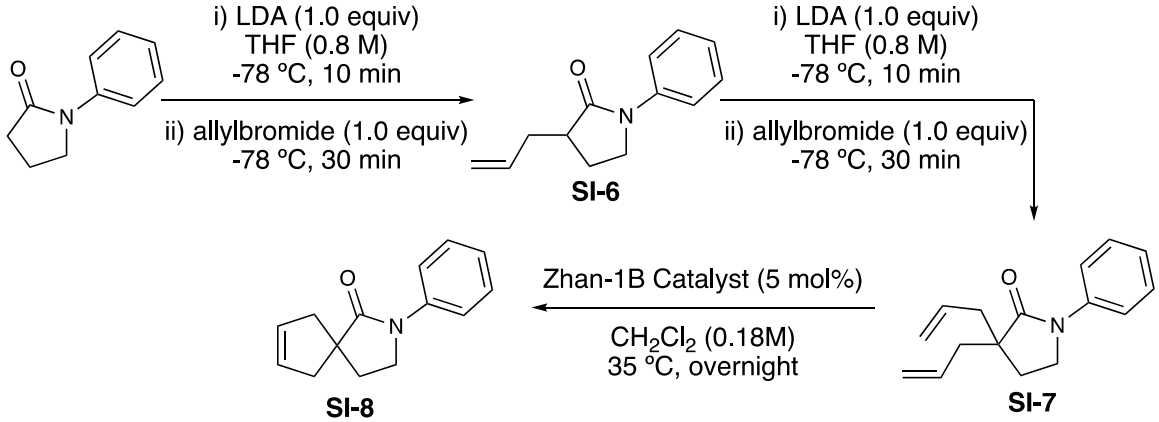
16

***N*-methyl-*N*-phenylcyclohex-3-ene-1-carboxamide (16):** The title compound was synthesized via General Procedure A with cyclohex-3-ene-1-carboxylic acid and *N*-methylaniline. Purification via silica gel column chromatography (3:1 hexanes:diethyl ether) and Kugelröhr short path distillation yielded product as a colorless oil (1.3 g, 60%).
IR (neat): 3023 (w), 2910 (w), 2838 (w), 1645 (s), 1594 (m), 1494 (m), 1386 (m), 1118 (m), 719 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.39 (dd, *J* = 8.3, 6.7 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 1H), 7.20 – 7.12 (m, 2H), 5.54 (h, *J* = 9.6 Hz, 2H), 3.24 (s, 3H), 2.42 (dq, *J* = 12.1, 5.8 Hz, 1H), 2.31 (ddq, *J* = 15.1, 11.1, 2.2 Hz, 1H), 2.01 – 1.87 (m, 2H), 1.72 (d, *J* = 6.1 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 176.2, 144.1, 129.8, 127.7, 127.2, 126.1, 125.7, 37.5, 37.2, 28.2, 25.8, 24.6; **LRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{14}H_{18}NO$ 216.1; Found 216.2.



SI-5

***N*,1-dimethyl-*N*-phenylcyclopent-3-ene-1-carboxamide (SI-5):** The title compound was synthesized via General Procedure A with 1-methylcyclopent-3-ene-1-carboxylic acid[4] and *N*-methylaniline. Purification via silica gel column chromatography (4:1 hexanes:diethyl ether) and recrystallization (hexanes) yielded product as a white solid (1.7 g, 57%).
IR (neat): 3052 (w), 2930 (w), 1635 (s), 1592 (s), 1493 (m), 1354 (m), 701 (s), 574 (s) cm^{-1}; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.45 – 7.38 (m, 2H), 7.38 – 7.31 (m, 1H), 7.30 – 7.23 (m, 2H), 5.50 (s, 2H), 3.27 (s, 3H), 2.82 (d, *J* = 15.1 Hz, 2H), 1.83 (d, *J* = 15.9 Hz, 2H), 1.21 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 177.6, 144.6, 129.1, 128.7, 128.0, 127.6, 50.3, 45.2, 40.4, 27.9; **LRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{14}H_{18}NO$ 216.1; Found 216.2.



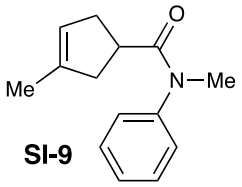
3-allyl-1-phenylpyrrolidin-2-one (SI-6): To a flame-dried round-bottom flask equipped with a stir bar was added diisopropylamine (2.8 mL, 20 mmol, 1.0 equiv.) and THF (10 mL) and the contents were cooled to -78 °C in a dry ice/acetone bath. *n*-Butyllithium solution (1.9 M in hexanes, 10.6 mL, 20 mmol, 1.0 equiv.) was added slowly and the reaction contents were stirred for 15 min

at -78 ºC. A second flame-dried round-bottom flask equipped with a stir bar was charged with 1-phenylpyrrolidin-2-one (3.2 g, 20 mmol, 1.0 equiv.) then evacuated/backfilled with N_2 (3x). THF (15 mL) was added, and this solution was transferred via syringe to the lithium diisopropylamide solution slowly. After stirring for 10 min at -78 ºC, allylbromide (1.7 mL, 20 mmol, 1.0 equiv.) was added and reaction stirs for an additional 30 min at -78 ºC. The reaction was quenched with sat. ammonium chloride (20 mL) and product was extracted with CH_2Cl_2 (3x 20 mL). Combined organics were dried over $MgSO_4$, gravity filtered, and concentrated under reduced pressure. Purification via silica gel column chromatography (10:1 hexanes:diethyl ether) and recrystallization (CH_2Cl_2/pentane) yielded product as a white solid (2.6 g, 64%). Spectral data was in accordance with that of the literature.[7]
IR (neat): 3057 (w), 2967 (w), 1686 (s), 1596 (m), 1401 (s), 1318 (s), 906 (s), 760 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.65 – 7.58 (m, 2H), 7.39 – 7.30 (m, 2H), 7.16 – 7.08 (m, 1H), 5.82 (ddt, *J* = 17.1, 10.2, 7.0 Hz, 1H), 5.12 (dq, *J* = 17.0, 1.5 Hz, 1H), 5.11 – 5.03 (m, 1H), 3.83 – 3.70 (m, 2H), 2.76 – 2.61 (m, 2H), 2.34 – 2.21 (m, 2H), 1.85 (dq, *J* = 12.8, 8.6 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 175.2, 139.5, 135.4, 128.8, 124.4, 119.7, 117.1, 46.7, 42.9, 35.4, 23.9.

3,3-diallyl-1-phenylpyrrolidin-2-one (SI-7): To a flame-dried round-bottom flask equipped with a stir bar was added diisopropylamine (0.85 mL, 6.1 mmol, 1.0 equiv.) and THF (5 mL) and the contents were cooled to -78 ºC in a dry ice/acetone bath. *n*-Butyllithium solution (1.9 M in hexanes, 3.2 mL, 6.1 mmol, 1.0 equiv.) was added slowly and the reaction contents are stirred for 15 min at -78 ºC. A second flame-dried round-bottom flask equipped with a stir bar was charged with 3-allyl-1-phenylpyrrolidin-2-one (1.2 g, 6.1 mmol, 1.0 equiv.) then evacuated/backfilled with N_2 (3x). THF (10 mL) was added, and this solution was transferred via syringe to the lithium diisopropylamide solution slowly. After stirring for 10 min at -78 ºC, allylbromide (0.53 mL, 6.1 mmol, 1.0 equiv.) was added and reaction was stirred for an additional 30 min at -78 ºC. The reaction was quenched with sat. ammonium chloride (10 mL) solution and product was extracted with CH_2Cl_2 (3x 10 mL). Combined organics were dried over $MgSO_4$, gravity filtered, and concentrated under reduced pressure. Purification via silica gel column chromatography (20:1 hexanes:diethyl ether) yielded product as a colorless oil (0.53 g, 22%). Spectral data was in accordance with that of the literature.[7]
IR (neat): 3051 (w), 2897 (w), 1686 (s), 1638 (m), 1488 (s), 1392 (s), 1223 (m), 914 (s), 757 (s), 689 (s) cm^{-1}; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.70 – 7.64 (m, 2H), 7.43 – 7.35 (m, 2H), 7.17 (td, *J* = 7.4, 1.2 Hz, 1H), 5.82 (dddd, *J* = 16.9, 10.1, 8.3, 6.5 Hz, 2H), 5.21 – 5.10 (m, 4H), 3.77 – 3.70 (m, 2H), 2.48 (ddt, *J* = 13.6, 6.4, 1.4 Hz, 2H), 2.30 (dd, *J* = 13.7, 8.3 Hz, 2H), 2.12 – 2.06 (m, 2H); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 176.8, 139.5, 133.7, 128.8, 124.5, 120.0, 118.8, 49.0, 45.7, 41.7, 26.4.

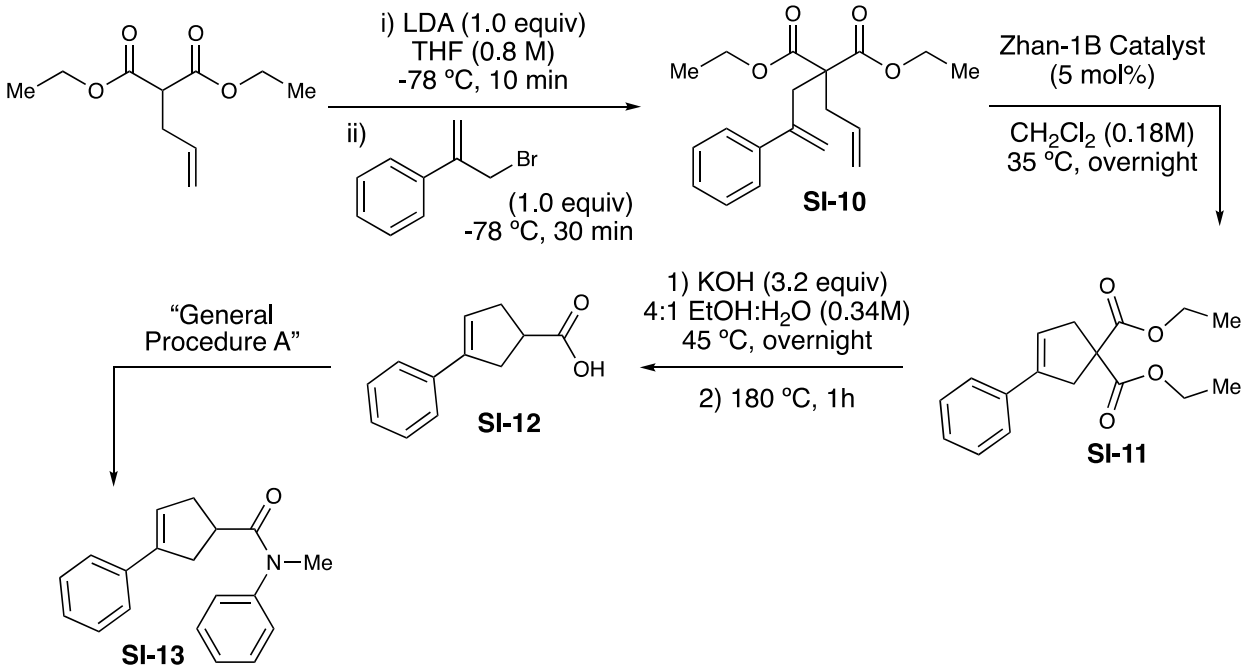
2-phenyl-2-azaspiro[4.4]non-7-en-1-one (SI-8): Procedure adapted from literature procedure.[8] To a flame-dried round-bottom flask equipped with a stir bar was added Zhan-1B catalyst (29 mg, 0.040 mmol, 0.050 equiv.) in a N_2 filled glovebox. The flask was capped with a septum and removed from the glovebox. CH_2Cl_2 (5 mL) was added to make a catalyst solution. A second flame-dried round-bottom flask equipped with a stir bar was charged with 3,3-diallyl-1-phenylpyrrolidin-2-one (1.9 g, 7.9 mmol, 1.0 equiv.) then evacuated/backfilled with N_2 (3x). CH_2Cl_2 (40 mL) was added, followed by transferring the catalyst solution via syringe. The reaction was heated in an oil bath to 35 ºC and stirred overnight. Solvent was concentrated under reduced

pressure. Purification via silica gel column chromatography (3:1 hexanes:diethyl ether) and recrystallization (hexanes/diethyl ether) yielded product as a white crystal (791 mg, 47%).
IR (neat): 3094 (w), 2966 (w), 2871 (w), 1674 (s), 1596 (m), 1486 (s), 1391 (s), 1224 (s), 756 (s), 688 (s), 672 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.70 – 7.63 (m, 2H), 7.40 – 7.31 (m, 2H), 7.12 (tt, *J* = 7.2, 1.2 Hz, 1H), 5.66 (s, 2H), 3.77 (t, *J* = 6.7 Hz, 2H), 2.92 (dd, *J* = 4.3, 1.6 Hz, 1H), 2.87 (s, 1H), 2.41 – 2.36 (m, 1H), 2.34 (s, 1H), 2.12 (t, *J* = 6.7 Hz, 2H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 178.4, 139.8, 128.8, 128.3, 124.2, 119.5, 51.4, 45.5, 43.6, 35.0; **LRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{14}H_{16}NO$ 214.1; Found 214.2.



SI-9

***N*,3-dimethyl-*N*-phenylcyclopent-3-ene-1-carboxamide (SI-9):** The title compound was synthesized via General Procedure A with 3-methylcyclopent-3-ene-1-carboxylic acid[4] and *N*-methylaniline. Purification via silica gel column chromatography (4:1 hexanes:diethyl ether) and Kugelröhr short path distillation yielded product as a colorless oil (1.2 g, 69%).
IR (neat): 3040 (w), 2912 (w), 1737 (s), 1594 (m), 1494 (m), 1422 (m), 1120 (m), 773 (s), 727 (s) cm^{-1}; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.43 (dd, *J* = 8.4, 7.0 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.23 – 7.17 (m, 2H), 5.14 (d, *J* = 3.4 Hz, 1H), 3.29 (s, 3H), 3.06 (ddd, *J* = 16.8, 9.5, 7.4 Hz, 1H), 2.69 – 2.59 (m, 2H), 2.17 (td, *J* = 12.3, 10.8, 4.7 Hz, 1H), 1.66 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 176.4, 144.4, 138.5, 129.7, 127.7, 127.5, 122.4, 41.7, 40.8, 37.9, 37.6, 16.2; **LRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{14}H_{18}NO$ 216.1; Found 216.2.



diethyl 2-allyl-2-(2-phenylallyl)malonate (SI-10): To a flame-dried round-bottom flask equipped with a stir bar was added sodium hydride (60 wt% in mineral oil, 0.40 g, 10 mmol, 1.2 equiv.) then evacuated/backfilled with N_2 (3x). THF (60 mL) was added and the solution was

cooled to 0 ºC in an ice bath. Diethyl allylmalonate (1.6 mL, 8.5 mmol, 1.0 equiv.) was added dropwise and after gas evolution ceased, α-(bromomethyl)styrene[9] (2.0 g, 10 mmol, 1.2 equiv.) was added dropwise. Reaction was allowed to slowly warm to rt over 1 h then was heated in an oil bath to 60 ºC overnight. After cooling to rt, the reaction is quenched with sat. ammonium chloride (60 mL). Product was extracted with diethyl ether (3x 50 mL) and combined organics were washed with brine, dried over $MgSO_4$, gravity filtered, and concentrated under reduced pressure. Purification via silica gel column chromatography (20:1 hexanes:diethyl ether) yielded product as a colorless oil (2.3 g, 84%). Spectral data was in accordance with that of the literature.[10]
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.32 – 7.25 (m, 4H), 7.25 – 7.19 (m, 1H), 5.60 (ddt, *J* = 17.4, 10.2, 7.3 Hz, 1H), 5.25 (d, *J* = 1.7 Hz, 1H), 5.14 (d, *J* = 1.6 Hz, 1H), 5.05 (ddt, *J* = 10.3, 2.1, 1.1 Hz, 1H), 4.98 (dq, *J* = 17.0, 1.6 Hz, 1H), 3.93 (dq, *J* = 10.7, 7.1 Hz, 2H), 3.79 (dq, *J* = 10.7, 7.1 Hz, 2H), 3.15 (d, *J* = 0.9 Hz, 2H), 2.57 (dt, *J* = 7.3, 1.3 Hz, 2H), 1.13 (t, *J* = 7.1 Hz, 6H), -1.95 (s, 1H).

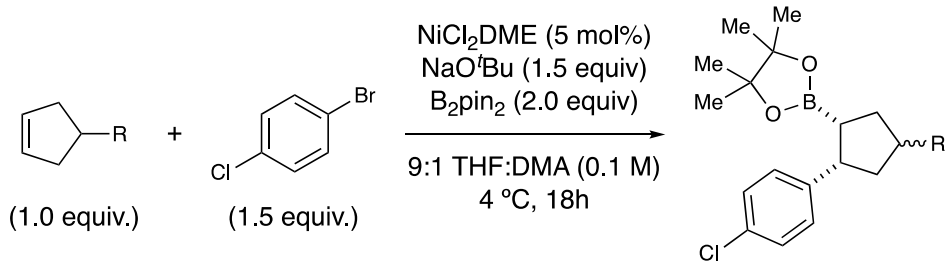
diethyl 3-phenylcyclopent-3-ene-1,1-dicarboxylate (SI-11): To a flame-dried round-bottom flask equipped with a stir bar was added Zhan-1B catalyst (26 mg, 0.36 mmol, 0.050 equiv.) in a N_2 filled glovebox. The flask was capped with a septum and removed from the glovebox. CH_2Cl_2 (5 mL) was added to make a catalyst solution. A second flame-dried round-bottom flask equipped with a stir bar was charged with diethyl 2-allyl-2-(2-phenylallyl)malonate (2.3 g, 7.2 mmol, 1.0 equiv.) then evacuated/backfilled with N_2 (3x). CH_2Cl_2 (30 mL) was added, followed by transferring the catalyst solution via syringe. The reaction was heated to 35 ºC in an oil bath and stirred overnight. Solvent was concentrated under reduced pressure. Purification via silica gel column chromatography (3:1 hexanes:diethyl ether) yielded product as a colorless oil (2.0 g, 95%). Spectral data was in accordance with that of the literature.[10]
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.43 – 7.38 (m, 2H), 7.31 (dd, *J* = 8.4, 7.0 Hz, 2H), 7.26 – 7.20 (m, 1H), 6.01 (p, *J* = 2.3 Hz, 1H), 4.21 (q, *J* = 7.2 Hz, 4H), 3.41 (q, *J* = 2.1 Hz, 2H), 3.20 (q, *J* = 2.3 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 6H).

3-phenylcyclopent-3-ene-1-carboxylic acid (SI-12): Procedure adapted from literature procedure.[Error! Bookmark not defined.] To a round-bottom flask equipped with a stir bar was added diethyl 3-phenylcyclopent-3-ene-1,1-dicarboxylate (2.0 g, 6.8 mmol, 1.0 equiv.), ethanol (16 mL), water (4 mL), and potassium hydroxide (1.3 g, 22 mmol, 3.2 equiv.). Reaction contents were heated to 45 ºC in an oil bath and stirred overnight then concentrated under reduced pressure. Diethyl ether (10 mL), hexanes (5 mL), and water (15 mL) were added to the resulting oil. The mixture was acidified with conc. sulfuric acid until pH is 1. The mixture was extracted with ethyl acetate (3 x 15 mL) and combined organics were dried over $MgSO_4$, gravity filtered, and concentrated under reduced pressure. The resulting solid was heated to 180 ºC for 1 h and then returned to rt. Purification via silica gel column chromatography (3:1 hexanes:acetone) yielded product as an orange oil (0.73 g, 57%). Spectral data was in accordance with that of the literature.[11]
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 – 7.37 (m, 2H), 7.30 (dd, *J* = 8.5, 6.8 Hz, 2H), 7.25 – 7.18 (m, 1H), 6.08 (p, *J* = 2.3 Hz, 1H), 3.34 (tt, *J* = 9.2, 7.1 Hz, 1H), 3.17 – 2.97 (m, 2H), 2.88 (dq, *J* = 9.2, 2.2 Hz, 2H).

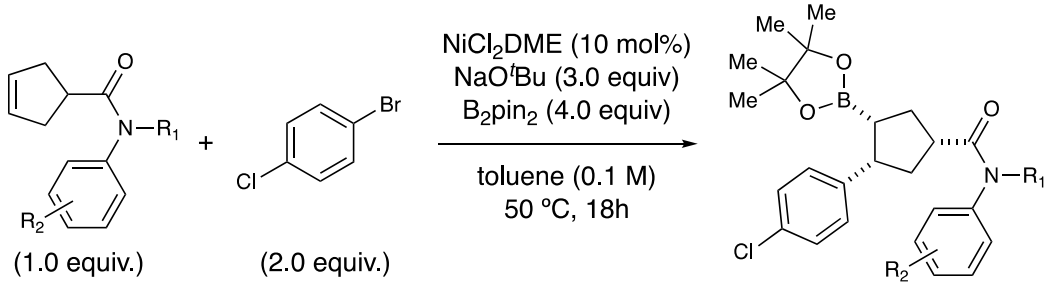
***N*-methyl-*N*,3-diphenylcyclopent-3-ene-1-carboxamide (SI-13):** The title compound was synthesized via General Procedure A with 3-phenylcyclopent-3-ene-1-carboxylic acid and *N*-

methylaniline. Purification via silica gel column chromatography (4:1 hexanes:diethyl ether) and recrystallization (ethyl acetate) yielded product as a white crystal (0.17 g, 16%).
IR (neat): 3020(m), 2970 (m), 1738 (s), 1652 (s),1594 (s), 1380 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.42 (t, *J* = 7.6 Hz, 2H), 7.37 – 7.30 (m, 3H), 7.26 (t, *J* = 6.7 Hz, 2H), 7.26 – 7.15 (m, 3H), 5.95 (s, 1H), 3.30 (s, 3H), 3.13 (ddd, *J* = 26.2, 13.9, 8.3 Hz, 2H), 2.91 – 2.80 (m, 1H), 2.64 (dd, *J* = 15.2, 9.2 Hz, 1H), 2.45 (dd, *J* = 17.2, 9.1 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 175.8, 144.2, 140.6, 136.1, 129.8, 128.2, 127.8, 127.5, 127.0, 125.5, 123.8, 40.6, 38.2, 37.7, 27.1; **LRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{19}H_{20}NO$ 278.2; Found 278.2.

■ Arylboration Reactions

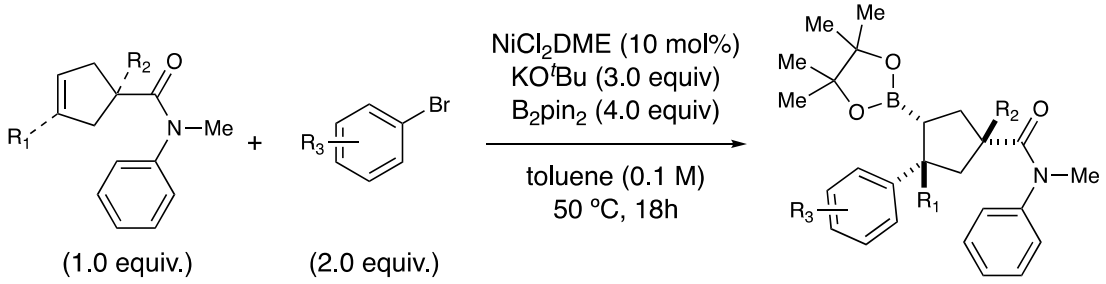


General Procedure B: Ni-Catalyzed Arylboration of Alkenes Optimization With Varied Directing Groups (Used in Scheme 2)
In an N_2-filled glovebox, to an oven-dried 16 x 100 mm screw-capped vial was added bis(pinacolato)diboron (254 mg, 1.00 mmol, 2.00 equiv.), 1-bromo-4-chlorobenzene (144 mg, 0.750 mmol, 1.50 equiv.), and NaO*t*-Bu (72 mg, 0.75 mmol, 1.5 equiv.). Note: if the alkene (0.5 mmol, 1.0 equiv) is a solid, it was added to the vial in the glovebox. A separate oven-dried 2-dram vial was charged with Ni(DME)Cl_2 (8.2 mg, 0.038 mmol, 0.075 equiv.) in an N_2-filled glovebox. Both vials were sealed with a septum and removed from the glovebox. THF (4.5 mL) was added to the reaction vial followed by alkene (0.5 mmol, 1.0 equiv) and the contents were cooled to 0 ºC in an ice bath. DMA (0.75 mL) was added to the vial containing Ni(DME)Cl_2 to prepare the catalyst solution. The catalyst solution (0.50 mL, 0.050 equiv of Ni(DME)Cl_2) was transferred to the reaction vial via syringe. The septum was then quickly replaced by a Teflon-lined screw cap and the reaction was stirred at 4 °C for 18 h in a temperature controlled refrigerator. The reaction was quenched upon the addition of 1 M HCl (5 mL), and the mixture was extracted with EtOAc (3 x 3 mL), dried over $MgSO_4$, gravity filtered, and concentrated. 1,3,5-Trimethylbenzene or 1,3,5-trimethoxybenzene was added as an internal standard and a small aliquot was analyzed via ^{1}H NMR.



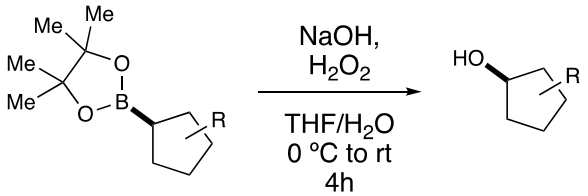
General Procedure C: Ni-Catalyzed Arylboration of Alkenes Optimization with Variation on Methylaniline Directing Group (Used in Scheme 3)

In an N_2-filled glovebox, to an oven-dried 16 x 100 mm screw-capped vial was added Ni(DME)Cl_2 (11 mg, 0.050 mmol, 0.10 equiv.), bis(pinacolato)diboron (508 mg, 2.00 mmol, 4.00 equiv.), 1-bromo-4-chlorobenzene (192 mg, 1.00 mmol, 2.00 equiv.), and NaO*t*-Bu (144 mg, 1.50 mmol, 3.00 equiv.). Note: if the alkene (0.5 mmol, 1 equiv.) is a solid, it was added to the vial in the glovebox. The vial was sealed with a septum and removed from the glovebox. Toluene (5.0 mL) was added to the reaction vial immediately followed by alkene (0.5 mmol, 1.0 equiv.). The septum was then quickly replaced by a Teflon-lined screw cap and the reaction was stirred at 50 °C for 18 h in a temperature-controlled aluminum block. The reaction was quenched upon the addition of 1 M HCl (5 mL), and the mixture was extracted with EtOAc (3 x 3 mL), washed with 1 M KOH (3 x 5 mL), dried over $MgSO_4$, gravity filtered, and concentrated. 1,3,5-Trimethylbenzene or 1,3,5-trimethoxybenzene was added as an internal standard and a small aliquot was analyzed via ^{1}H NMR.



General Procedure D: Ni-Catalyzed Arylboration of Alkenes

In an N_2-filled glovebox, to an oven-dried 16 x 100 mm screw-capped vial was added Ni(DME)Cl_2 (11 mg, 0.050 mmol, 0.10 equiv.), bis(pinacolato)diboron (508 mg, 2.00 mmol, 4.00 equiv.), and KO*t*-Bu (168 mg, 1.50 mmol, 3.00 equiv.). Note: if the alkene (0.5 mmol, 1 equiv.) or aryl bromide (1.0 mmol, 2.0 equiv.) is a solid, it was added to the vial in the glovebox. The vial was sealed with a septum and removed from the glovebox. Toluene (5.0 mL) was added to the reaction vial, followed by alkene (0.5 mmol, 1 equiv.) and arylbromide (1.0 mmol, 2.0 equiv.). The septum was then quickly replaced by a Teflon-lined screw cap and the reaction was stirred at 50 °C for 18 h in a temperature-controlled aluminum block. The reaction was quenched upon the addition of 1 M HCl (5 mL), and the mixture was extracted with EtOAc (3 x 3 mL), washed with 1 M KOH (3 x 5 mL), dried over $MgSO_4$, gravity filtered, and concentrated. 1,3,5-Trimethylbenzene or 1,3,5-trimethoxybenzene was added as an internal standard and a small aliquot was analyzed via ^{1}H NMR.



General Procedure E: Oxidation of Alkyl Boronic Esters

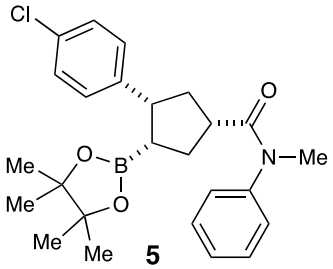
Alkyl boronic ester was dissolved in THF (3 mL) and cooled to 0 ºC before NaOH (2M aq., 3 mL) and hydrogen peroxide (30 % aq., 3 mL) were added. The reaction was allowed to stir at 0 ºC for 4 h. before being carefully quenched with saturated $Na_2S_2O_3$ (3 mL). The aqueous layer was extracted with ethyl acetate (3 x 5 mL) and the combined organic extracts were dried over $MgSO_4$,

gravity filtered, and the solvent removed under reduced pressure. The crude material was then purified via silica gel chromatography.

In cases where separation from pinacol is problematic: The crude mixture was dissolved in acetone/H_2O (1:1, 5 mL) before $NaIO_4$ (545 mg, 2.50 mmol, 5.00 equiv.) and NH_4OAc (197 mg, 2.60 mmol, 5.20 equiv.) were added. The mixture was stirred for 2 h. before being quenched with H_2O (5 mL). The aqueous layer was extracted with EtOAc (3 x 5 mL). The combined organic extracts were dried over $MgSO_4$ and gravity filtered. The solvent was then removed under reduced pressure, and the crude material was then purified via silica gel chromatography.

■ Characterization Data

In ^{13}C NMR spectra, signals of carbons directly bonded to boron were not detected because of quadrupolar relaxation.

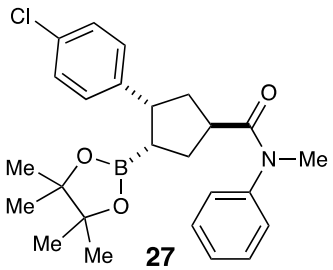


5

3-(4-chlorophenyl)-*N*-methyl-*N*-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentane-1-carboxamide (5): The title compound was prepared according to General Procedure D. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (Gradient: toluene to 20:1 toluene: acetone) yielded **5** as a white solid. Crystals suitable for X-ray analysis were prepared by slow diffusion of pentane into a concentrated solution of **5** in dichloromethane.

Average over 2 runs: 151 mg, 68% isolated yield

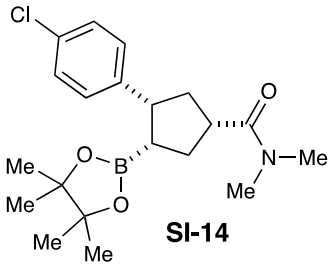
IR (neat): 3065 (w), 2976 (w), 2949 (w), 1647 (s), 1595 (m), 1493 (m), 1413 (s), 1323 (s), 1142 (s) cm^{-1}; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.45 (t, *J* = 7.6 Hz, 2H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.34 – 7.28 (m, 2H), 7.27 – 7.18 (m, 4H), 3.30 (s, 3H), 3.28 – 3.21 (m, 1H), 2.75 – 2.64 (m, 1H), 2.28 – 2.10 (m, 3H), 1.83 (dq, *J* = 13.0, 6.7, 6.2 Hz, 1H), 1.60 (td, *J* = 11.0, 7.4 Hz, 1H), 0.92 (d, *J* = 4.3 Hz, 12H); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 175.3, 145.0, 144.3, 131.4, 129.9, 129.8, 127.9, 127.8, 127.5, 82.9, 45.7, 44.2, 38.8, 37.7, 33.7, 24.6, 24.6; **HRMS (APCI)** m/z: $[M+H]^+$ Calcd for $C_{25}H_{32}BClNO_3$ 440.2158; Found 440.2157.



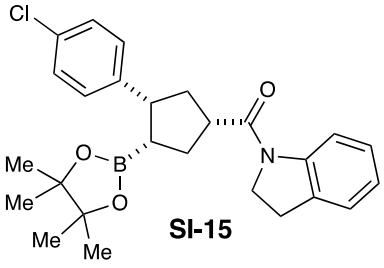
27

3-(4-chlorophenyl)-*N*-methyl-*N*-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentane-1-carboxamide (27): The title compound was prepared according to a modified

version of General Procedure D with DMA as the solvent. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (Gradient: toluene to 20:1 toluene: acetone) yielded **33** as a white solid (48 mg, 22%, low isolated yield because of difficult separation).
IR (neat): 2976 (m), 2931 (m), 2870 (m), 1650 (s), 1594 (s), 1494 (s), 1371 (s), 1141 (s) cm^{-1}; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.42 (t, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.21 (dd, *J* = 7.4, 1.7 Hz, 2H), 7.12 (d, *J* = 8.1 Hz, 2H), 7.02 (d, *J* = 8.1 Hz, 2H), 3.58 (q, *J* = 7.7 Hz, 1H), 3.28 (s, 3H), 3.06 (td, *J* = 9.1, 4.6 Hz, 1H), 2.35 (ddd, *J* = 13.5, 8.3, 5.7 Hz, 1H), 2.14 – 2.00 (m, 2H), 1.91 – 1.79 (m, 1H), 0.93 (s, 6H), 0.88 (s, 6H); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 176.9, 144.4, 143.8, 131.2, 129.6, 129.0, 127.8, 127.6, 127.6, 82.8, 46.8, 41.1, 37.6, 37.2, 33.4, 24.6, 24.5; **HRMS (+EI)** m/z: $[M]^+$ Calcd for $C_{25}H_{31}BClNO_3$ 439.2085; Found 439.2088.

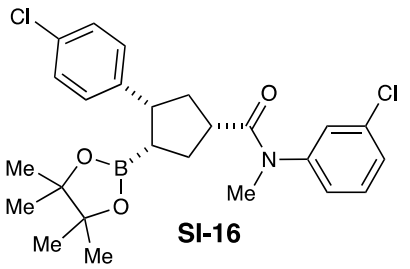


3-(4-chlorophenyl)-*N*,*N*-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentane-1-carboxamide (SI-14): The title compound was prepared according to General Procedure B. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (Gradient: hexane to 10:1 hexanes: acetone) yielded product as a white solid (81 mg, 43%).
IR (neat): 2929 (m), 1738 (m), 1646 (s), 1377 (s), 1322 (m), 1139 (s) cm^{-1}; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.30 – 7.25 (m, 2H), 7.21 – 7.15 (m, 2H), 3.43 (dt, *J* = 9.9, 8.0 Hz, 1H), 3.07 (s, 3H), 3.02 (ddd, *J* = 18.2, 10.5, 7.6 Hz, 1H), 2.96 (s, 3H), 2.32 (dt, *J* = 13.2, 8.0 Hz, 1H), 2.26 – 2.09 (m, 2H), 2.02 (dt, *J* = 13.3, 7.1 Hz, 1H), 1.82 (ddd, *J* = 11.7, 10.2, 7.3 Hz, 1H), 0.91 (d, *J* = 8.7 Hz, 12H); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 174.6, 144.8, 131.5, 129.8, 127.9, 82.9, 45.6, 43.5, 37.7, 37.1, 35.7, 32.6, 24.6, 24.6; **HRMS (APCI)** m/z: $[M+H]^+$ Calcd for $C_{20}H_{30}BClNO_3$ 378.2005; Found 378.2012.



(3-(4-chlorophenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentyl)(indolin-1-yl)methanone (SI-15): The title compound was prepared according to General Procedure B. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (Gradient: hexanes to 50:1 hexanes: acetone) yielded product as a white solid (79 mg, 35%).
IR (neat): 2971 (w), 1738 (m), 1650 (s), 1486 (m), 1408 (s), 1319 (s), 1141 (s), 752 (s) cm^{-1}; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.28 (d, *J* = 8.1 Hz, 1H), 7.22 (dt, *J* = 13.5, 6.8 Hz, 6H), 7.03 (td, *J*

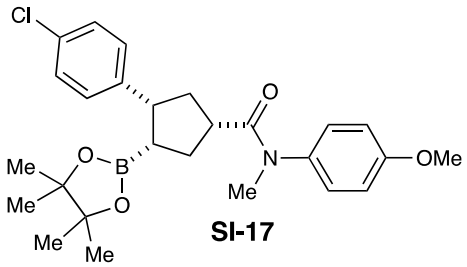
= 7.4, 1.1 Hz, 1H), 4.18 (td, *J* = 8.9, 5.6 Hz, 2H), 3.67 (q, *J* = 7.5 Hz, 1H), 3.36 (p, *J* = 7.7 Hz, 1H), 3.22 (t, *J* = 8.5 Hz, 2H), 2.53 (ddd, *J* = 13.0, 7.8, 5.3 Hz, 1H), 2.31 – 2.21 (m, 2H), 2.18 (ddd, *J* = 13.0, 8.9, 6.8 Hz, 1H), 2.11 (q, *J* = 8.0 Hz, 1H), 1.03 (d, *J* = 18.3 Hz, 12H); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 174.7, 143.7, 143.4, 131.5, 131.2, 129.2, 128.0, 127.6, 124.5, 123.5, 117.2, 83.0, 48.1, 46.7, 43.4, 36.6, 31.9, 28.1, 24.7, 24.6; **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd for $C_{26}H_{31}BClNO_3Na$ 474.1978; Found 474.1977.



SI-16

***N*-(3-chlorophenyl)-3-(4-chlorophenyl)-*N*-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentane-1-carboxamide (SI-16):** The title compound was prepared according to General Procedure C. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (Gradient: hexanes to 10:1 hexanes: acetone) yielded product as a white solid (104 mg, 44%).

IR (neat): 2971 (w), 1714 (m), 1654 (s), 1589 (m), 1371 (s), 1323 (m), 1141 (m) cm^{-1}; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.42 – 7.33 (m, 2H), 7.33 – 7.27 (m, 2H), 7.25 (d, *J* = 1.9 Hz, 1H), 7.23 – 7.17 (m, 2H), 7.13 (dt, *J* = 7.2, 1.9 Hz, 1H), 3.28 (s, 3H), 2.68 (s, 1H), 2.27 – 2.09 (m, 3H), 1.93 – 1.78 (m, 1H), 1.68 – 1.56 (m, 1H), 1.34 – 1.23 (m, 1H), 0.92 (d, *J* = 5.1 Hz, 12H); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 175.1, 145.5, 144.9, 135.1, 131.5, 130.7, 129.9, 128.1, 127.9, 127.8, 125.8, 82.9, 45.7, 44.2, 38.8, 37.7, 33.7, 24.6; **HRMS (APCI)** m/z: $[M+H]^+$ Calcd for $C_{25}H_{31}BCl_2NO_3$ 474.1773; Found 474.1778.

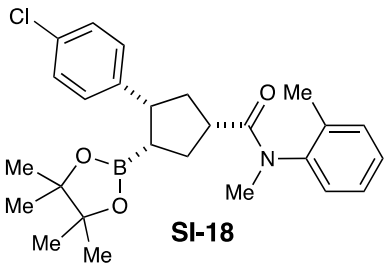


SI-17

3-(4-chlorophenyl)-*N*-(4-methoxyphenyl)-*N*-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentane-1-carboxamide (SI-17): The title compound was prepared according to General Procedure C. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (Gradient: hexanes to 10:1 hexanes: acetone) yielded product as a white solid (134 mg, 57%).

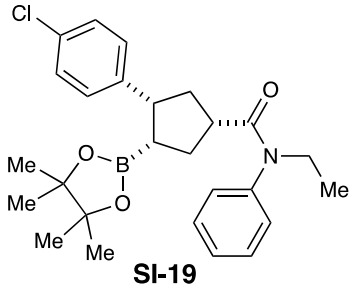
IR (neat): 2971 (m), 1738 (s), 1650 (s), 1509 (s), 1377 (s), 1247 (s), 837 (m) cm^{-1}; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.29 (d, *J* = 8.3 Hz, 2H), 7.23 – 7.16 (m, 2H), 7.15 – 7.08 (m, 2H), 6.96 – 6.89 (m, 2H), 3.84 (s, 3H), 3.29 – 3.20 (m, 4H), 2.74 – 2.63 (m, 1H), 2.24 – 2.08 (m, 3H), 1.81 (dt, *J* = 13.4, 7.1 Hz, 1H), 1.59 (ddd, *J* = 12.0, 10.2, 7.4 Hz, 1H), 0.90 (d, *J* = 4.2 Hz, 12H); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 175.5, 158.9, 145.1, 137.1, 131.4, 129.9, 128.5, 127.9, 114.8, 82.9, 55.5,

45.7, 44.0, 38.7, 37.8, 33.7, 24.6, 24.6; **HRMS (APCI)** m/z: $[M+H]^+$ Calcd for $C_{26}H_{34}BClNO_4$ 470.2269; Found 470.2274.



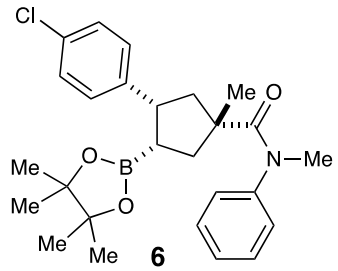
SI-18

3-(4-chlorophenyl)-*N*-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-*N*-(*o*-tolyl)cyclopentane-1-carboxamide (SI-18): The title compound was prepared according to General Procedure C. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (Gradient: hexanes to 10:1 hexanes: acetone) yielded product as a white solid (117 mg, 51%).
IR (neat): 2970 (w), 1738 (s), 1650 (s), 1372 (s), 1321 (m), 1216 (s), 1143 (m) cm^{-1}; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.33 – 7.20 (m, 5H), 7.18 (dd, *J* = 8.4, 1.6 Hz, 2H), 7.12 (ddd, *J* = 23.4, 7.4, 1.7 Hz, 1H), 3.28 – 3.16 (m, 1H), 3.20 (s, 3H), 2.55 – 2.45 (m, 1H), 2.32 – 2.21 (m, 4H), 2.12 (dqd, *J* = 17.0, 12.2, 8.0 Hz, 2H), 1.79 (ddt, *J* = 24.2, 13.4, 7.1 Hz, 1H), 1.57 (dtd, *J* = 11.9, 9.5, 7.2 Hz, 1H), 0.94 – 0.81 (m, 12H); **^{13}C NMR (126 MHz, $CDCl_3$, *mix of rotomers*):** δ 175.5, 175.5, 145.1, 145.0, 142.8, 142.8, 135.6, 135.6, 131.4, 131.4, 129.9, 129.9, 128.3, 128.2, 127.9, 127.4, 127.3, 82.9, 82.8, 45.8, 45.7, 44.2, 44.0, 39.2, 38.4, 36.2, 36.1, 34.0, 33.2, 24.6, 24.6, 17.5; **HRMS (APCI)** m/z: $[M+H]^+$ Calcd for $C_{26}H_{34}BClNO_3$ 454.2319; Found 454.2326.



SI-19

3-(4-chlorophenyl)-*N*-ethyl-*N*-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentane-1-carboxamide (SI-19): The title compound was prepared according to General Procedure C. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (Gradient: hexanes to 20:1 hexanes: acetone) yielded product as a white solid (97 mg, 43%).
IR (neat): 2975 (w), 1647 (s), 1594 (m), 1493 (s), 1372 (s), 1258 (s), 1142 (s), 728 (s), 700 (s) cm^{-1}; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.44 (t, *J* = 7.5 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.22 – 7.17 (m, 4H), 3.78 (qq, *J* = 13.9, 7.2 Hz, 2H), 3.24 (dt, *J* = 10.2, 7.9 Hz, 1H), 2.60 (tt, *J* = 10.2, 7.4 Hz, 1H), 2.27 – 2.09 (m, 3H), 1.82 (dt, *J* = 13.3, 7.1 Hz, 1H), 1.58 (ddd, *J* = 12.1, 10.2, 7.3 Hz, 1H), 1.13 (t, *J* = 7.1 Hz, 3H), 0.91 (d, *J* = 2.7 Hz, 12H); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 174.6, 145.1, 142.6, 131.4, 129.9, 129.6, 128.5, 127.9, 127.8, 82.9, 45.7, 44.5, 44.3, 38.8, 33.8, 24.6, 24.6, 13.1; **HRMS (APCI)** m/z: $[M+H]^+$ Calcd for $C_{26}H_{34}BClNO_3$ 454.2319; Found 454.2326.

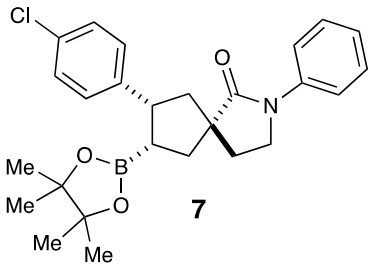


6

3-(4-chlorophenyl)-*N*,1-dimethyl-*N*-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentane-1-carboxamide (6): The title compound was prepared according to General Procedure D. Purification by silica gel column chromatography (Gradient: toluene to 20:1 toluene: acetone) yielded **6** as a white solid.

Average over 2 runs: 156 mg, 69% isolated yield

IR (neat): 2970 (w), 1738 (w), 1628 (s), 1594 (m), 1492 (s), 1356 (s), 1318 (s), 1141 (s) cm^{-1}; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.40 (dd, *J* = 8.2, 6.8 Hz, 2H), 7.37 – 7.30 (m, 1H), 7.28 – 7.22 (m, 2H), 7.22 – 7.16 (m, 2H), 7.15 – 7.08 (m, 2H), 3.29 (m, 4H), 2.38 (t, *J* = 12.1 Hz, 1H), 2.25 (dd, *J* = 13.1, 9.9 Hz, 1H), 1.86 (td, *J* = 11.1, 7.9 Hz, 1H), 1.63 – 1.58 (m, 1H), 1.49 (dd, *J* = 13.1, 7.9 Hz, 1H), 1.23 (s, 3H), 0.96 (s, 6H), 0.87 (s, 6H); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 177.8, 144.8, 144.3, 131.4, 129.6, 129.2, 128.9, 127.9, 127.7, 82.8, 52.3, 45.7, 44.0, 40.8, 40.6, 25.4, 24.8, 24.4; **HRMS (APCI)** m/z: $[M+H]^+$ Calcd for $C_{26}H_{34}BClNO_3$ 454.2315; Found 454.2317.

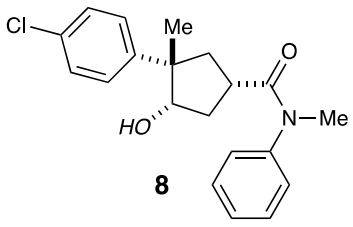


7

7-(4-chlorophenyl)-2-phenyl-8-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-azaspiro[4.4]nonan-1-one (7): The title compound was prepared according to General Procedure D. Purification by silica gel column chromatography (Gradient: toluene to 50:1 toluene: acetone) yielded **7** as a white solid.

Average over 2 runs: 53 mg, 58% isolated yield

IR (neat): 2972 (w), 2869 (w), 1688 (s), 1490 (m), 1370 (s), 1323 (s), 1141 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.65 – 7.58 (m, 2H), 7.35 – 7.25 (m, 4H), 7.17 – 7.12 (m, 2H), 7.07 (t, *J* = 7.4 Hz, 1H), 3.73 (td, *J* = 6.4, 5.7, 1.8 Hz, 2H), 3.54 – 3.43 (m, 1H), 2.40 (dd, *J* = 13.4, 7.9 Hz, 1H), 2.31 (t, *J* = 12.6 Hz, 1H), 2.13 – 1.95 (m, 3H), 1.92 (td, *J* = 11.2, 7.0 Hz, 1H), 1.76 (dd, *J* = 13.0, 6.8 Hz, 1H), 0.85 (d, *J* = 10.0 Hz, 12H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 177.6, 144.4, 139.8, 131.7, 129.9, 128.8, 128.0, 124.3, 119.6, 83.0, 54.1, 45.5, 45.2, 44.4, 38.3, 32.8, 24.6, 24.6; **HRMS (APCI)** m/z: $[M+H]^+$ Calcd for $C_{26}H_{32}BClNO_3$ 452.2158; Found 452.2159.

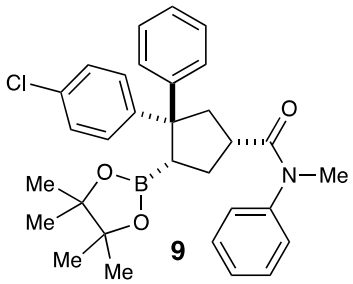


8

3-(4-chlorophenyl)-4-hydroxy-*N*,3-dimethyl-*N*-phenylcyclopentane-1-carboxamide (8): The title compound was prepared according to General Procedure D followed by General Procedure E. Purification by silica gel column chromatography (Gradient: toluene to 20:1 toluene: acetone) yielded **8** as a white solid.

Average over 2 runs: 91 mg, 53% isolated yield (two steps)

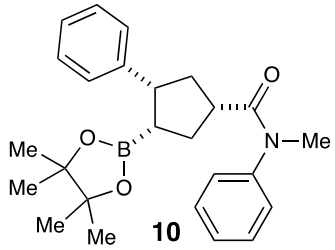
IR (neat): 3388 (br), 2969 (w), 1738 (s), 1620 (s), 1591 (s), 1493 (s), 1372 (s), 720 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.47 (dd, *J* = 8.3, 6.8 Hz, 2H), 7.43 – 7.32 (m, 1H), 7.28 – 7.17 (m, 6H), 4.46 (s, 1H, br), 4.15 (d, *J* = 4.1 Hz, 1H), 3.27 (s, 3H), 3.08 – 2.97 (m, 1H), 2.41 (dd, *J* = 12.7, 7.3 Hz, 1H), 2.21 (ddd, *J* = 14.6, 10.3, 4.2 Hz, 1H), 2.06 – 1.90 (m, 2H), 0.96 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 178.8, 145.3, 143.9, 131.4, 130.0, 128.5, 128.3, 128.2, 127.2, 79.4, 54.2, 40.3, 38.6, 38.0, 37.0, 28.8; **HRMS (APCI)** m/z: $[M+H]^+$ Calcd for $C_{20}H_{23}ClNO_2$ 344.1412; Found 344.1414.



3-(4-chlorophenyl)-*N*-methyl-*N*,3-diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentane-1-carboxamide (9): The title compound was prepared according to General Procedure D (0.10 mmol scale). Purification by silica gel column chromatography (Gradient: toluene to 50:1 toluene: acetone) yielded **9** as a white solid.

Average over 2 runs: 7.6 mg, 15% isolated yield

IR (neat): 2973 (w), 1738 (m), 1651 (s), 1594 (m), 1493 (s), 1363 (s), 1142 (s), 698 (s) cm^{-1}; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.24 – 7.12 (m, 3H), 7.12 – 7.03 (m, 4H), 6.97 (dt, *J* = 18.4, 6.6 Hz, 7H), 3.18 (s, 3H), 2.87 (t, *J* = 11.6 Hz, 1H), 2.50 (s, 1H), 2.22 (s, 1H), 2.17 – 2.02 (m, 1H), 1.47 (s, 2H), 0.91 (s, 6H), 0.84 (s, 6H); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 175.0, 149.1, 147.6, 143.9, 131.3, 129.6, 129.5, 127.8, 127.6, 127.5, 127.2, 126.7, 125.5, 83.0, 57.4, 43.8, 41.1, 37.5, 31.2, 24.5, 24.4; **HRMS (APCI)** m/z: $[M+H]^+$ Calcd for $C_{31}H_{36}BClNO_3$ 516.2477; Found 516.2482.

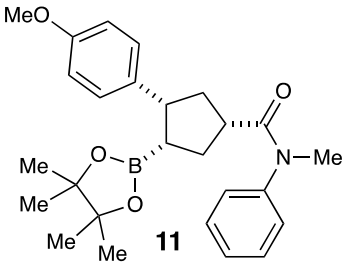


***N*-methyl-*N*,3-diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentane-1-carboxamide (10):** The title compound was prepared according to General Procedure D. Purification by silica gel column chromatography (Gradient: toluene to 20:1 toluene: acetone) yielded **10** as a white solid.

Average over 2 runs: 120 mg, 59% isolated yield

IR (neat): 2976 (w), 2872 (w), 1737 (m), 1650 (s), 1593 (m), 1492 (m), 1413 (s), 1379 (s), 1144 (s), 696 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.41 (dd, *J* = 8.3, 6.8 Hz, 2H), 7.37 – 7.28 (m,

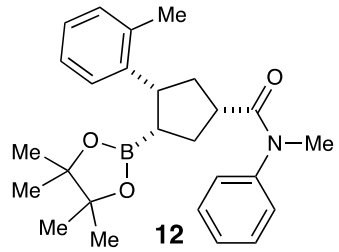
3H), 7.24 – 7.15 (m, 4H), 7.15 – 7.04 (m, 1H), 3.27 (m, 4H), 2.69 – 2.61 (m, 1H), 2.31 – 2.16 (m, 2H), 2.11 (dt, *J* = 13.9, 7.9 Hz, 1H), 1.80 (dt, *J* = 13.1, 7.1 Hz, 1H), 1.58 (dd, *J* = 19.4, 10.5 Hz, 1H), 0.84 (d, *J* = 9.4 Hz, 12H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 175.3, 146.3, 144.3, 129.7, 127.9, 127.7, 127.6, 127.5, 125.7, 82.7, 46.3, 44.3, 38.8, 37.6, 33.7, 24.6, 24.6; **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd for $C_{25}H_{32}BNO_3Na$ 428.2367; Found 428.2370.



3-(4-methoxyphenyl)-*N*-methyl-*N*-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentane-1-carboxamide (11): The title compound was prepared according to General Procedure D. Purification by silica gel column chromatography (Gradient: toluene to 20:1 toluene: acetone) yielded **11** as a white solid.

Average over 2 runs: 113 mg, 52% isolated yield

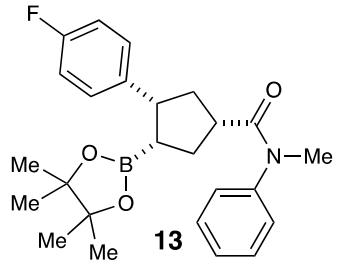
IR (neat): 2971 (m), 2951 (m), 1738 (m), 1649 (s), 1511 (m), 1378 (s), 1248 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.40 (dd, *J* = 8.3, 6.7 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.28 – 7.11 (m, 4H), 6.79 – 6.71 (m, 2H), 3.72 (s, 3H), 3.26 (s, 3H), 3.24 – 3.15 (m, 1H), 2.64 (dd, *J* = 12.8, 5.7 Hz, 1H), 2.31 – 2.14 (m, 2H), 2.09 (dt, *J* = 13.4, 8.1 Hz, 1H), 1.77 (dt, *J* = 13.2, 7.1 Hz, 1H), 1.54 (td, *J* = 10.8, 7.5 Hz, 1H), 0.86 (d, *J* = 6.0 Hz, 12H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 175.4, 157.8, 144.4, 138.7, 129.7, 129.4, 127.7, 127.5, 113.3, 82.7, 55.3, 45.5, 44.3, 38.9, 37.6, 33.6, 27.1, 24.6, 24.6; **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd for $C_{26}H_{34}BNO_4Na$ 458.2473; Found 458.2475.



***N*-methyl-*N*-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(*o*-tolyl)cyclopentane-1-carboxamide (12):** The title compound was prepared according to General Procedure D Purification by silica gel column chromatography (Gradient: toluene to 20:1 toluene: acetone) yielded **12** as a white solid.

Average over 2 runs: 83 mg, 40% isolated yield

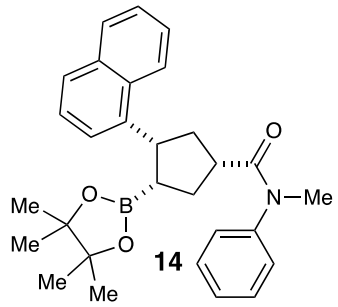
IR (neat): 2971 (w), 1738 (m), 1650 (s), 1591 (m), 1374 (s), 1140 (s), 669 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.45 (d, *J* = 7.8 Hz, 1H), 7.40 (dd, *J* = 8.3, 6.7 Hz, 2H), 7.37 – 7.29 (m, 1H), 7.27 – 7.04 (m, 3H), 7.02 – 6.93 (m, 2H), 3.36 (q, *J* = 9.5 Hz, 1H), 3.27 (s, 3H), 2.64 (s, 1H), 2.42 – 2.29 (m, 1H), 2.24 (s, 3H), 2.23 – 2.17 (m, 1H), 2.14 (s, 3H), 2.06 – 1.91 (m, 1H), 1.80 (dt, *J* = 12.9, 7.4 Hz, 1H), 1.67 (q, *J* = 10.5 Hz, 1H), 0.84 (s, 6H), 0.77 (s, 6H); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 175.2, 144.4, 143.6, 136.4, 129.7, 129.6, 127.7, 127.5, 127.4, 125.8, 125.6, 82.7, 44.3, 41.9, 38.1, 37.7, 33.6, 24.7, 24.4, 20.2; **HRMS (APCI)** m/z: $[M+H]^+$ Calcd for $C_{26}H_{35}BNO_3$ 420.2705; Found 420.2703.



3-(4-fluorophenyl)-*N*-methyl-*N*-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentane-1-carboxamide (13): The title compound was prepared according to General Procedure D. Purification by silica gel column chromatography (Gradient: toluene to 20:1 toluene: acetone) yielded **13** as a white solid.

Average over 2 runs: 124 mg, 59% isolated yield

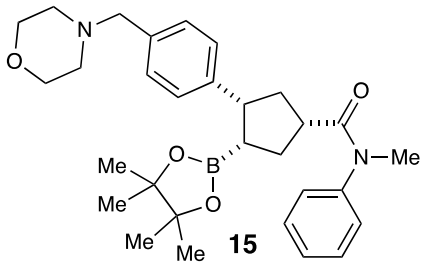
IR (neat): 2948 (w), 1646 (s), 1594 (m), 1508 (m), 1372 (s), 1221 (s), 841 (s), 776 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.40 (dd, *J* = 8.3, 6.8 Hz, 2H), 7.36 – 7.25 (m, 3H), 7.22 – 7.14 (m, 2H), 6.93 – 6.82 (m, 2H), 3.25 (s, 3H), 3.21 (t, *J* = 8.7 Hz, 1H), 2.64 (p, *J* = 9.3 Hz, 1H), 2.25 – 2.05 (m, 3H), 1.78 (dt, *J* = 13.2, 7.1 Hz, 1H), 1.54 (ddd, *J* = 12.2, 9.9, 7.2 Hz, 1H), 0.86 (d, *J* = 3.2 Hz, 12H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 175.3, 161.3 (C-F, $^{1}J_{C\text{-}F}$ = 242 Hz), 144.3, 142.2, 129.85 (C-F, $^{3}J_{C\text{-}F}$ = 7.7 Hz), 129.7, 127.7, 127.4, 114.4 (C-F, $^{2}J_{C\text{-}F}$ = 20.9 Hz), 82.8, 45.5, 44.1, 39.0, 37.6, 33.6, 24.6; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -118.23 (td, *J* = 8.9, 4.4 Hz); **HRMS (APCI)** m/z: $[M+H]^+$ Calcd for $C_{25}H_{32}BFNO_3$ 424.2458; Found 424.2464.



***N*-methyl-3-(naphthalen-1-yl)-*N*-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentane-1-carboxamide (14):** The title compound was prepared according to General Procedure D. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (10:1 hexanes: acetone) yielded **14** as a white solid.

Average over 2 runs: 116 mg, 51% isolated yield

IR (neat): 3050 (s), 2974 (s), 1647 (s), 1370 (s), 1140 (s), 779 (s), 669 (s) cm^{-1}; **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.00 (d, *J* = 8.5 Hz, 1H), 7.76 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.67 (d, *J* = 7.2 Hz, 1H), 7.63 (d, *J* = 8.1 Hz, 1H), 7.47 – 7.34 (m, 7H), 7.24 (t, *J* = 1.2 Hz, 1H), 3.98 (q, *J* = 9.2 Hz, 1H), 3.31 (s, 3H), 2.82 – 2.76 (m, 1H), 2.60 (q, *J* = 11.0 Hz, 1H), 2.30 – 2.21 (m, 1H), 2.13 (p, *J* = 6.7 Hz, 1H), 1.90 (h, *J* = 7.9 Hz, 2H), 0.67 (s, 6H), 0.52 (s, 6H); **^{13}C NMR (151 MHz, $CDCl_3$):** δ 175.2, 144.3, 140.9, 133.7, 132.3, 129.8, 128.4, 127.8, 127.5, 126.3, 125.4, 125.4, 125.0, 124.4, 124.3, 82.5, 44.0, 41.4, 37.8, 37.7, 33.7, 24.3, 24.2; **HRMS (APCI)** m/z: $[M+H]^+$ Calcd for $C_{29}H_{35}BNO_3$ 456.2705; Found 456.2704.

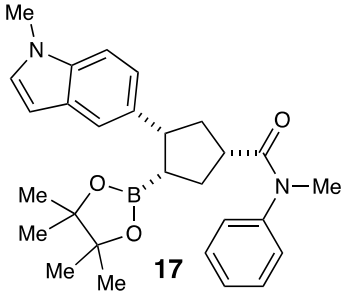


15

***N*-methyl-3-(4-(morpholinomethyl)phenyl)-*N*-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentane-1-carboxamide (15):** The title compound was prepared according to General Procedure D. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (Gradient: 2:1 to 1.5:1 DCM: acetone) yielded **15** as a white solid.

Average over 2 runs: 161 mg, 64% isolated yield

IR (neat): 2972 (m), 2762 (s), 1651 (s), 1372 (s), 1115 (s), 700 (s) cm^{-1}; **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.40 (t, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.27 (d, *J* = 7.8 Hz, 2H), 7.21 – 7.18 (m, 2H), 7.15 (d, *J* = 7.8 Hz, 2H), 3.65 (t, *J* = 4.6 Hz, 4H), 3.41 (s, 2H), 3.27 (s, 3H), 3.23 (q, *J* = 8.8 Hz, 1H), 2.64 (dq, *J* = 10.5, 7.3, 5.1 Hz, 1H), 2.39 (q, *J* = 8.2, 4.7 Hz, 4H), 2.27 – 2.17 (m, 2H), 2.10 (dt, *J* = 13.6, 7.9 Hz, 1H), 1.80 (dt, *J* = 13.2, 6.9 Hz, 1H), 1.58 (td, *J* = 11.1, 7.6 Hz, 1H), 0.85 (d, *J* = 14.7 Hz, 12H); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 175.3, 145.3, 144.4, 134.8, 129.7, 128.9, 128.4, 127.7, 127.5, 82.7, 66.9, 63.1, 53.4, 46.0, 44.3, 38.8, 37.7, 33.7, 24.6, 24.6; **HRMS (APCI)** m/z: $[M+H]^+$ Calcd for $C_{30}H_{42}BN_2O_4$ 505.3232; Found 505.3227.

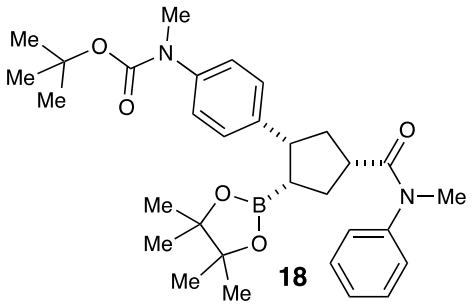


17

***N*-methyl-3-(1-methyl-1*H*-indol-5-yl)-*N*-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentane-1-carboxamide (17):** The title compound was prepared according to General Procedure D. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (6:1 hexanes: acetone) yielded **17** as a white solid.

Average over 2 runs: 167 mg, 73% isolated yield

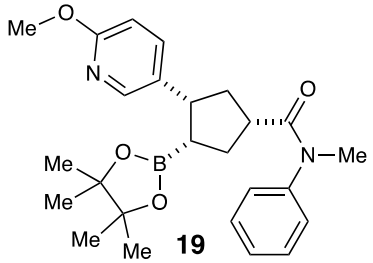
IR (neat): 2973 (s), 1650 (s), 1372 (s), 1142 (s), 701 (s) cm^{-1}; **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.53 (d, *J* = 1.6 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.21 (ddd, *J* = 10.4, 7.8, 1.6 Hz, 3H), 7.15 (d, *J* = 8.4 Hz, 1H), 6.95 (d, *J* = 2.9 Hz, 1H), 6.36 (d, *J* = 3.0 Hz, 1H), 3.72 (s, 3H), 3.40 – 3.32 (m, 1H), 3.29 (s, 3H), 2.66 (d, *J* = 7.3 Hz, 1H), 2.40 – 2.25 (m, 2H), 2.15 (dt, *J* = 14.0, 7.6 Hz, 1H), 1.82 (dt, *J* = 13.4, 7.4 Hz, 1H), 1.72 – 1.55 (m, 1H), 0.78 (s, 6H), 0.71 (s, 6H); **^{13}C NMR (151 MHz, $CDCl_3$):** δ 175.4, 144.4, 137.0, 135.6, 129.7, 128.5, 128.4, 127.6, 127.5, 122.6, 120.0, 108.4, 100.7, 82.5, 46.4, 44.5, 39.5, 37.7, 33.8, 32.8, 24.6, 24.5; **HRMS (APCI)** m/z: $[M+H]^+$ Calcd for $C_{28}H_{36}BN_2O_3$ 459.2813; Found 459.2821.



***tert*-butyl methyl(4-(4-(methyl(phenyl)carbamoyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentyl)phenyl)carbamate (18):** The title compound was prepared according to General Procedure D. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (6:1 hexanes: acetone) yielded **18** as a white solid.

Average over 2 runs: 171 mg, 64% isolated yield

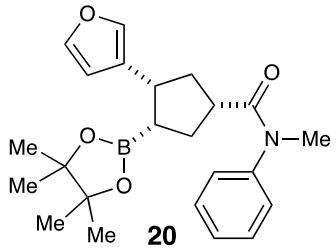
IR (neat): 2976 (s), 2872 (s), 1698 (s), 1652 (s), 1365 (s), 704 (s) cm^{-1}; **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.38 (t, *J* = 7.7 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.24 (d, *J* = 8.3 Hz, 2H), 7.19 – 7.11 (m, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 3.24 (s, 3H), 3.20 (d, *J* = 9.2 Hz, 1H), 3.13 (s, 3H), 2.62 (td, *J* = 10.5, 5.3 Hz, 1H), 2.19 (qd, *J* = 11.9, 10.3, 4.6 Hz, 2H), 2.08 (dt, *J* = 13.4, 8.1 Hz, 1H), 1.77 (dt, *J* = 13.6, 7.2 Hz, 1H), 1.55 (td, *J* = 11.2, 7.6 Hz, 1H), 1.38 (s, 9H), 0.85 (d, *J* = 7.6 Hz, 12H); **^{13}C NMR (151 MHz, $CDCl_3$):** δ 218.0, 175.3, 154.7, 144.3, 143.4, 141.6, 129.7, 128.5, 127.4, 124.8, 82.7, 79.9, 45.7, 44.2, 38.7, 37.6, 37.4, 33.6, 28.3, 28.3, 24.6; **HRMS (APCI)** m/z: $[M+H]^+$ Calcd for $C_{31}H_{44}BN_2O_5$ 535.3338; Found 535.3339.



3-(6-methoxypyridin-3-yl)-*N*-methyl-*N*-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentane-1-carboxamide (19): The title compound was prepared according to General Procedure D. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (6:1 hexanes: acetone) yielded **19** as a white solid.

Average over 2 runs: 188 mg, 68% isolated yield

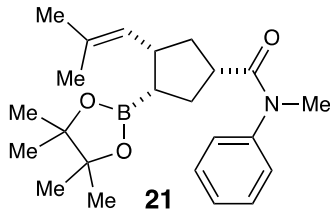
IR (neat): 2975 (s), 1650 (s), 1493 (s), 1142 (s), 699 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.95 (d, *J* = 2.5 Hz, 1H), 7.72 (dd, *J* = 8.6, 2.5 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.31 (d, *J* = 7.2 Hz, 1H), 7.16 (d, *J* = 7.6 Hz, 2H), 6.62 (d, *J* = 8.6 Hz, 1H), 3.81 (s, 3H), 3.23 (s, 3H), 3.18 (d, *J* = 8.7 Hz, 1H), 2.67 – 2.56 (m, 1H), 2.26 (s, 1H), 2.13 – 2.03 (m, 2H), 1.77 (dt, *J* = 13.3, 7.0 Hz, 1H), 1.52 (td, *J* = 10.9, 7.4 Hz, 1H), 0.86 (d, *J* = 2.9 Hz, 12H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 175.3, 162.6, 146.1, 144.2, 138.9, 134.5, 129.7, 127.7, 127.3, 110.0, 82.9, 53.3, 44.0, 42.8, 38.5, 37.6, 33.6, 24.6, 24.5; **HRMS (ESI+)** m/z: $[M+H]^+$ Calcd for $C_{25}H_{34}BN_2O_4$ 437.2606; Found 437.2612.



3-(furan-3-yl)-*N*-methyl-*N*-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentane-1-carboxamide (20): The title compound was prepared according to General Procedure D. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (6:1 hexanes: acetone) yielded **20** as a clear oil.

Average over 2 runs: 158 mg, 80% isolated yield

IR (neat): 2950 (s), 1649 (s), 1373 (s), 1142 (s), 708 (s) cm^{-1}; **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.38 (t, *J* = 7.7 Hz, 2H), 7.31 (dd, *J* = 7.2, 4.4 Hz, 2H), 7.22 (t, *J* = 1.7 Hz, 1H), 7.21 – 7.14 (m, 2H), 6.48 (d, *J* = 1.7 Hz, 1H), 3.24 (s, 3H), 3.15 (q, *J* = 8.0 Hz, 1H), 2.65 – 2.56 (m, 1H), 2.11 (q, *J* = 12.0 Hz, 1H), 2.03 (dq, *J* = 9.0, 4.2, 2.3 Hz, 2H), 1.75 (dt, *J* = 13.2, 7.0 Hz, 1H), 1.44 – 1.37 (m, 1H), 0.98 (d, *J* = 11.4 Hz, 12H); **^{13}C NMR (151 MHz, $CDCl_3$):** δ 175.5, 144.3, 141.8, 139.0, 129.7, 129.3, 127.7, 127.4, 111.5, 82.8, 77.3, 77.1, 76.9, 43.7, 38.4, 37.6, 36.6, 33.2, 24.7, 24.6; **HRMS (APCI)** m/z: $[M+H]^+$ Calcd for $C_{23}H_{31}BNO_4$ 396.2341; Found 396.2345.

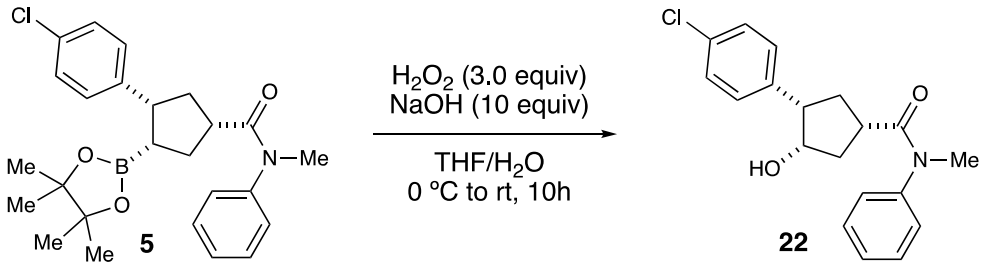


***N*-methyl-3-(2-methylprop-1-en-1-yl)-*N*-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentane-1-carboxamide (21):** The title compound was prepared according to General Procedure D. NMR yield of the unpurified reaction mixture was determined using 1,3,5-trimethylbenzene as an NMR standard. Purification by silica gel column chromatography (8:1 hexanes: acetone) yielded **21** as a clear oil.

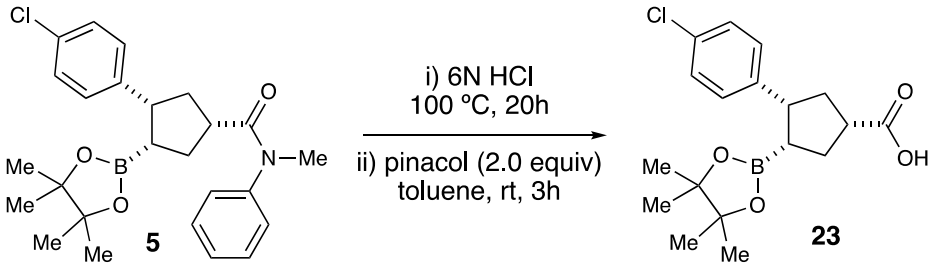
Average over 2 runs: 157 mg, 82% isolated yield

IR (neat): 2976 (s), 1647 (s), 1373 (s), 1142 (s), 750 (s) cm^{-1}; **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.39 (t, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.20 – 7.14 (m, 2H), 5.28 (dd, *J* = 10.4, 2.3 Hz, 1H), 3.23 (s, 3H), 2.86 (p, *J* = 7.9 Hz, 1H), 2.53 (p, *J* = 8.7 Hz, 1H), 2.00 (q, *J* = 11.8 Hz, 1H), 1.80 (dt, *J* = 15.7, 8.2 Hz, 1H), 1.69 (ddt, *J* = 20.6, 13.2, 7.2 Hz, 2H), 1.61 (s, 3H), 1.53 (s, 3H), 1.32 – 1.24 (m, 1H), 1.16 (d, *J* = 5.3 Hz, 12H); **^{13}C NMR (151 MHz, $CDCl_3$):** δ 175.8, 144.4, 129.6, 129.5, 129.2, 127.6, 127.5, 82.9, 44.0, 39.6, 38.6, 37.7, 33.2, 25.8, 24.9, 24.8, 18.0; **HRMS (APCI)** m/z: $[M+H]^+$ Calcd for $C_{23}H_{35}BNO_3$ 384.2705; Found 384.2705.

■ **Further Functionalization:**

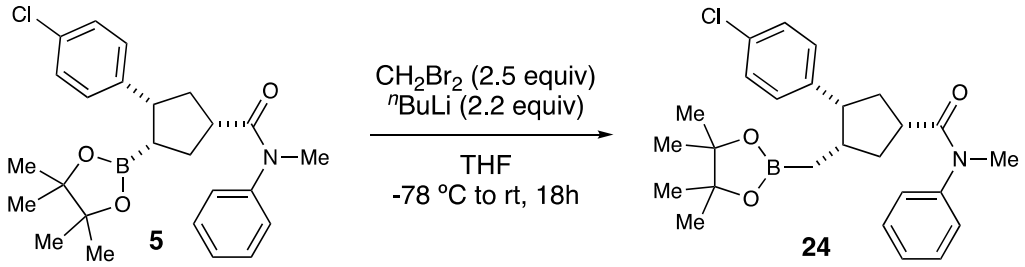


3-(4-chlorophenyl)-4-hydroxy-*N*-methyl-*N*-phenylcyclopentane-1-carboxamide (22): A 25mL round-bottom flask was charged with **5** (220 mg, 0.50 mmol, 1.0 equiv.), THF (5.0 mL) and NaOH (2.5 mL, 2.0 M aqueous solution, 5.0 mmol, 10 equiv.). The reaction flask was placed in an ice bath and cooled to 0 ºC, then, H_2O_2 (0.150 mL, 30% aqueous solution, 1.35 mmol, 3.00 equiv.) was added via syringe. The ice bath was removed and the solution was stirred at room temperature for 10 hours then quenched upon the addition of water (5 mL). The aqueous layer was extracted with EtOAc (3 x 10 mL) and the combined organic layers were dried over anhydrous $MgSO_4$, gravity filtered, and concentrated under reduced pressure. Purification by silica gel column chromatography (2:1 hexanes:EtOAc) yielded a clear oil. To remove the small amount of pinacol mixed in the product, the mixture was reacted with $NaIO_4$ (107mg, 0.5 mmol, 1.0 equiv.) and NH_4OAc (39 mg, 0.5 mmol, 1.0 equiv.) in acetone (2 mL) and water (2 mL) at room temperature for 15 min. The resulting mixture was washed with water (2 mL) and extracted with EtOAc (3 x 10 mL), the combined organic layers were dried over anhydrous $MgSO_4$, gravity filtered, concentrated under reduced pressure to yield **22** as a white solid (148 mg, 90% yield).
IR (neat): 3256 (br), 2931 (s), 1622 (s), 1493 (s), 670 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.48 – 7.40 (m, 2H), 7.40 – 7.32 (m, 1H), 7.29 – 7.15 (m, 6H), 4.67 – 4.19 (m, 1H), 4.16 (t, *J* = 3.7 Hz, 1H), 3.29 (s, 3H), 3.02 – 2.90 (m, 1H), 2.83 (ddd, *J* = 12.0, 8.3, 3.2 Hz, 1H), 2.24 – 2.02 (m, 3H), 1.92 (ddd, *J* = 14.2, 10.2, 4.1 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 178.9, 143.8, 138.4, 132.0, 130.0, 130.0, 128.2, 128.1, 127.2, 75.6, 52.1, 39.2, 39.0, 37.9, 34.9; **HRMS (APCI+)** m/z: $[M+H]^+$ Calcd for $C_{19}H_{21}O_2NCl$ 330.1255; Found 330.1254.

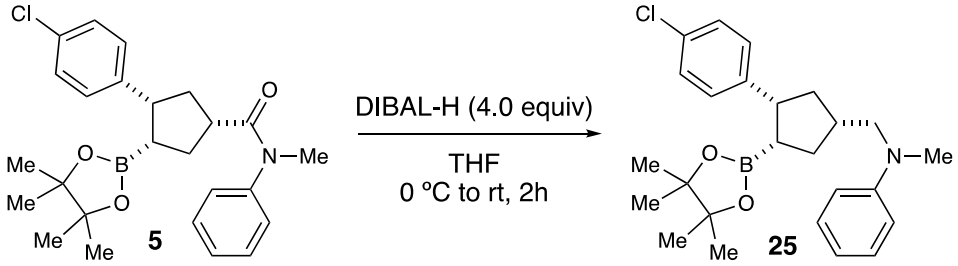


3-(4-chlorophenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentane-1-carboxylic acid (23): To a 16 x 100 mm screw-capped vial was added **5** (130 mg, 0.30 mmol, 1.0 equiv.) and HCl (2.0 mL, 6 M aqueous solution) The vial was capped and stirred vigorously in a preheated oil bath at 100 °C for 20 h. The reaction mixture was then allowed to cool to room temperature, diluted with H_2O (10 mL) and extracted with ethyl acetate (3 x 5 mL). The combined organic fractions were washed with brine (10 mL), dried over $MgSO_4$ and concentrated under reduced pressure. To the resulting oil was added pinacol (71 mg, 0.60 mmol, 2.00 equiv.) and toluene (3.0 mL). The mixture was stirred at room temperature for 3h. Volatile components were

removed under reduced pressure and purified via silica gel column chromatography (10:3 hexanes: acetone) to provide **23** as a white solid (73 mg, 69%). Crystals suitable for X-ray analysis were prepared by slow diffusion of pentane into a concentrated solution of **23** in dichloromethane.
IR (neat): 3052 (br), 2978 (s), 1702 (s), 1379 (s), 1142 (s), 737 (s) cm^{-1}; **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.23 – 7.20 (m, 4H), 3.41 (q, *J* = 8.9 Hz, 1H), 2.94 (p, *J* = 9.2 Hz, 1H), 2.46 (dt, *J* = 11.9, 8.0 Hz, 1H), 2.24 – 2.15 (m, 3H), 1.89 (q, *J* = 9.1 Hz, 1H), 0.96 (s, 6H), 0.91 (s, 6H); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 180.9, 143.6, 131.8, 129.5, 128.1, 83.2, 46.0, 45.0, 36.8, 32.2, 24.6, 24.5; **HRMS (APCI+)** m/z: $[M+H]^+$ Calcd for $C_{18}H_{25}O_4BCl$ 351.1529; Found 351.1534.

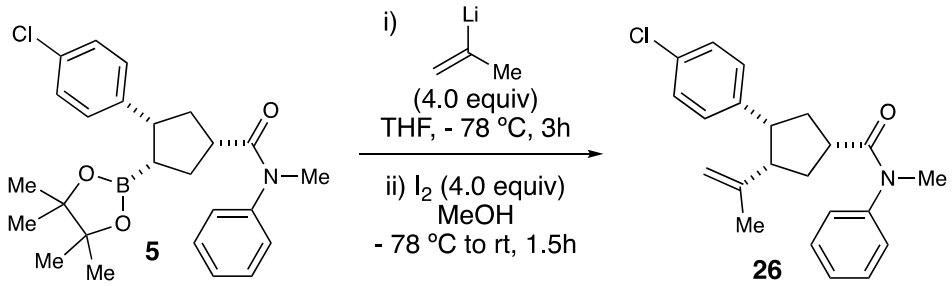


3-(4-chlorophenyl)-*N*-methyl-*N*-phenyl-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)cyclopentane-1-carboxamide (24): To an oven-dried 13 x 100 mm screw-cap vial was added boronic ester **5** (88 mg, 0.20 mmol, 1.0 equiv.). The vial was evacuated/backfilled with N_2 (3x) and sealed with a septum. THF (2 mL) and CH_2Br_2 (35 µL, 0.50 mmol, 2.5 equiv.) were then added via syringe. The solution was cooled to -78 ºC before the addition of ^{n}BuLi in hexane (1.91 M, 0.23 mL, 0.44 mmol, 2.2 equiv.) dropwise over 10 min. The reaction was stirred for 5 min. at -78 ºC before warming to room temperature. The reaction was allowed to stir for 18 h at room temperature before being quenched upon the addition of H_2O (3 mL). The aqueous layer was then extracted with EtOAc (3 x 2 mL), and the combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude mixture was purified via silica gel chromatography (6:1 hexanes: acetone) to yield **24** as a white solid (63 mg, 69%).
IR (neat): 2974 (s), 2925 (s), 1650 (s), 1371 (s), 1143 (s), 700 (s) cm^{-1}; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.45 – 7.39 (m, 2H), 7.35 (t, *J* = 7.3 Hz, 1H), 7.25 – 7.16 (m, 6H), 3.29 (s, 3H), 3.05 (q, *J* = 8.0 Hz, 1H), 2.72 (p, *J* = 9.1 Hz, 1H), 2.20 (tdd, *J* = 12.8, 10.8, 9.3, 4.8 Hz, 2H), 2.05 (dt, *J* = 13.2, 8.2 Hz, 1H), 1.88 – 1.71 (m, 2H), 1.16 (d, *J* = 11.5 Hz, 12H), 0.45 – 0.16 (m, 2H); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 175.7, 144.3, 142.4, 131.5, 130.4, 129.7, 127.9, 127.8, 127.5, 82.8, 48.1, 41.6, 40.1, 38.4, 37.7, 36.6, 25.0, 24.6; **HRMS (APCI+)** m/z: $[M+H]^+$ Calcd for $C_{26}H_{34}O_3NBCl$ 454.2315; Found 454.2322.



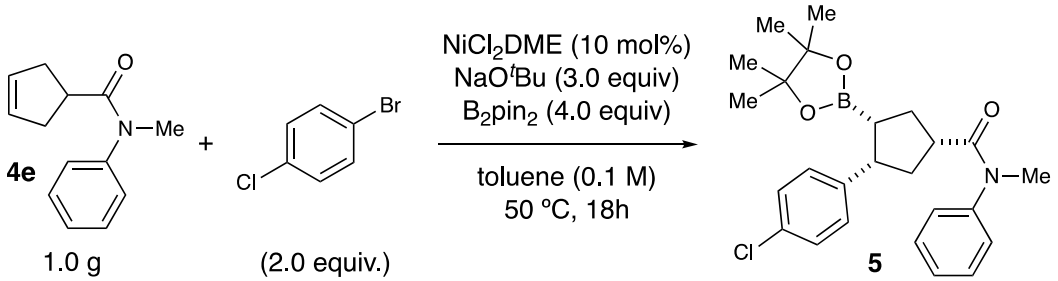
***N*-((3-(4-chlorophenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentyl)methyl)-*N*-methylaniline (25):** To an oven-dried 25 mL round bottom flask was added boronic ester **5** (220 mg, 0.50 mmol, 1.0 equiv.). The flask was evacuated/backfilled with N_2 (3x) and sealed with a septum. THF (5 mL) was added and the resulting solution was cooled to 0 ºC in an ice bath.

DIBAL-H (2.0 mL, 1.0 M in hexanes, 4.0 equiv.) was added dropwise over 5 min. The resulting solution was stirred at 0 ºC for 2 hours. The reaction was quenched upon adding Rochelle's salt solution (sat. solution in H_2O, 10 mL). The resulting mixture was stirred at room temperature for 1 hour and NaOH (5 mL, 2 M aqueous solution) was added. The aqueous layer was extracted with Et_2O (3 x 15 mL), and the combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude mixture was purified via silica gel column chromatography (20:1 hexanes: EtOAc) to yield **25** as a white solid (134 mg, 63%).
IR (neat): 2974 (s), 2976 (s), 2862 (s), 1598 (s), 1378 (s), 1141 (s), 746 (s) cm^{-1}; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.28 – 7.19 (m, 6H), 6.77 (d, *J* = 8.2 Hz, 2H), 6.71 (t, *J* = 7.3 Hz, 1H), 3.46 (d, *J* = 7.0 Hz, 2H), 3.37 (td, *J* = 10.3, 7.2 Hz, 1H), 3.02 (s, 3H), 2.55 – 2.42 (m, 1H), 2.25 (dt, *J* = 13.3, 6.9 Hz, 1H), 2.06 (dt, *J* = 12.6, 7.9 Hz, 1H), 1.90 (dt, *J* = 10.3, 8.5 Hz, 1H), 1.71 – 1.53 (m, 2H), 1.02 (s, 6H), 0.95 (s, 6H); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 149.5, 144.5, 131.4, 129.4, 129.1, 128.0, 115.8, 112.0, 82.9, 57.6, 46.0, 40.0, 39.0, 38.9, 33.5, 24.8, 24.5; **HRMS (ESI+)** m/z: $[M+H]^+$ Calcd for $C_{25}H_{34}O_2NBCl$ 426.2366; Found 426.2365.



3-(4-chlorophenyl)-*N*-methyl-*N*-phenyl-4-(prop-1-en-2-yl)cyclopentane-1-carboxamide (26): A flame-dried 25 mL round bottom flask under N_2 was charged with 2-bromoprop-1-ene (71 µL, 0.80 mmol, 4.0 equiv.). THF (4.0 mL) was added and the solution cooled to -78 °C in a dry ice/acetone bath. ^{t}BuLi (0.60 mL, 2.6 M in pentane, 1.6 mmol, 8.0 equiv.) was added dropwise and the solution stirred at -78 °C for 1 hour. A solution of **5** (88 mg, 0.20 mmol, 1.0 equiv.) in THF (0.8 mL) was added dropwise at -78 °C and the mixture was allowed to stir at -78 °C for 3 h. A solution of I_2 (200 mg, 0.80 mmol, 4.0 equiv.) in MeOH (0.8 mL) was added dropwise down the side of the flask and the reaction was stirred at -78 °C for 30 minutes then allowed to warm to room temperature and stirred for 1 h. The reaction was quenched upon the addition of $Na_2S_2O_3$ (sat. solution in H_2O, 10.0 mL) and stirred for another 1 h. The organic layer was separated and the aqueous phase extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with brine (1 x 10 mL), dried over $MgSO_4$, gravity filtered, and concentrated under reduced pressure. Crude material was purified by silica gel column chromatography (12:1 hexanes: acetone) to yield **26** as a colorless oil (53 mg, 75% yield).
IR (neat): 2939 (s), 1650 (s), 1493 (s), 1120 (s), 700 (s) cm^{-1}; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.45 (t, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.26 – 7.17 (m, 6H), 4.67 (s, 1H), 4.59 (s, 1H), 3.32 (s, 3H), 3.21 (q, *J* = 8.1 Hz, 1H), 2.82 – 2.71 (m, 1H), 2.65 (td, *J* = 10.3, 6.7 Hz, 1H), 2.35 – 2.12 (m, 3H), 1.81 (dt, *J* = 13.2, 6.8 Hz, 1H), 1.29 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 175.4, 145.1, 144.1, 142.3, 131.5, 130.1, 129.8, 127.9, 127.8, 127.4, 111.8, 51.6, 47.0, 41.3, 37.7, 37.6, 34.9, 22.6; **HRMS (ESI+)** m/z: $[M+H]^+$ Calcd for $C_{22}H_{25}ONCl$ 354.1619; Found 354.1620.

■ Gram Scale Reaction Procedure



In an N_2-filled glovebox, to a flame-dried 100-mL round-bottomed flask equipped with a stir bar was added Ni(DME)Cl_2 (110 mg, 0.50 mmol, 0.10 equiv.), bis(pinacolato)diboron (5.08 g, 20.0 mmol, 4.00 equiv.), 1-bromo-4-chlorobenzene (1.92 g, 10.0 mmol, 2.00 equiv.), and NaO*t*-Bu (1.44 g, 15.0 mmol, 3.00 equiv.). The flask was sealed with a septum and removed from the glovebox. Toluene (50 mL) was added to the reaction vial immediately followed by *N*-methyl-*N*-phenylcyclopent-3-ene-1-carboxamide (**4e**) (0.95 mL, 1.0 g, 5.0 mmol, 1.0 equiv.). The reaction was stirred at 50 °C for 18 h in an oil bath, then quenched upon the addition of 1 M HCl (50 mL), and the mixture was extracted with EtOAc (3 x 30 mL), washed with 1 M KOH (3 x 50 mL), dried over $MgSO_4$, gravity filtered, and concentrated. 1,3,5-Trimethylbenzene was added as an internal standard and a small aliquot was analyzed via ^{1}H NMR. Purification by silica gel column chromatography (Gradient: toluene to 20:1 toluene: acetone) yielded product **5** as a white solid (1.6 g, 71%).

■ Mechanism Studies:

Counterion Studies (Scheme 6A):

In an N_2-filled glovebox, to an oven-dried 16 x 100 mm screw-capped vial was added Ni(DME)Cl_2 (11 mg, 0.050 mmol, 0.10 equiv.), bis(pinacolato)diboron (508 mg, 2.00 mmol, 4.00 equiv.), 1-bromo-4-chlorobenzene (192 mg, 1.00 mmol, 2.00 equiv.), and base (1.50 mmol, 3.00 equiv.). The vial was sealed with a septum and removed from the glovebox. The toluene (5.0 mL, 0.1 M) was added to the reaction vial, followed by alkene **4e** (95 μL, 0.50 mmol, 1.0 equiv.). The septum was then quickly replaced by a Teflon-lined screw cap and the reaction was stirred at 50 °C for 18 h in a temperature-controlled aluminum block. The reaction was quenched upon the addition of 1 M HCl (5 mL), and the mixture was extracted with EtOAc (3 x 3 mL), washed with 1 M KOH (3 x 5 mL), dried over $MgSO_4$, gravity filtered, and concentrated. 1,3,5-Trimethylbenzene (28 μL, 0.2 mmol) was added as an internal standard and a small aliquot was analyzed via ^{1}H NMR.

Table S1: Counterion effect on diastereoselectivity

Entry	Base	% *syn* (*5*)	% *anti* (27)	dr (*syn:anti*)
1	KO*t*Bu	80	3	23:1
2	NaO*t*Bu	79	6	12:1
3	LiO*t*Bu	39	6	7:1

Counterion Studies with Corresponding Crown Ether (Scheme 6A):

In an N_2-filled glovebox, to an oven-dried 16 x 100 mm screw-capped vial was added Ni(DME)Cl_2 (11 mg, 0.050 mmol, 0.10 equiv.), bis(pinacolato)diboron (508 mg, 2.00 mmol, 4.00 equiv.), 1-bromo-4-chlorobenzene (192 mg, 1.00 mmol, 2.00 equiv.), base (1.50 mmol, 3.00 equiv.), and 18-crown-6 (396 mg, 1.50 mmol, 3.0 equiv.) when applicable. The vial was sealed with a septum and removed from the glovebox. The toluene (5.0 mL, 0.1 M) was added to the reaction vial, followed

by alkene **4e** (95 μL, 0.50 mmol, 1.0 equiv.) and 15-crown-5 (297 μL, 1.50 mmol, 3.00 equiv.) or 12-crown-4 (243 μL, 1.50 mmol, 3.00 equiv.) when applicable. The septum was then quickly replaced by a Teflon-lined screw cap and the reaction was stirred at 50 °C for 18 h in a temperature-controlled aluminum block. The reaction was quenched upon the addition of 1 M HCl (5 mL), and the mixture was extracted with EtOAc (3 x 3 mL), washed with 1 M KOH (3 x 5 mL), dried over $MgSO_4$, gravity filtered, and concentrated. 1,3,5-Trimethylbenzene (28 μL, 0.2 mmol) was added as an internal standard and a small aliquot was analyzed via ^{1}H NMR.

Table S2: Crown Ether effect on diastereoselectivity

Entry	Base	Crown Ether	% *syn* (*5*)	% *anti* (27)	dr (*syn:anti*)
1	KO^{t}Bu	18-crown-6	25	< 1	> 30:1
2	NaO^{t}Bu	15-crown-5	81	< 1	> 30:1
3	LiO^{t}Bu	12-crown-4	86	< 1	> 30:1

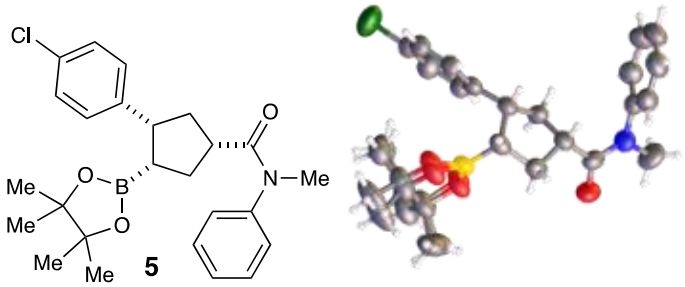
Solvent Ratios Studies (Scheme 6B):

In an N_2-filled glovebox, to an oven-dried 16 x 100 mm screw-capped vial was added Ni(DME)Cl_2 (11 mg, 0.050 mmol, 0.10 equiv.), bis(pinacolato)diboron (508 mg, 2.00 mmol, 4.00 equiv.), 1-bromo-4-chlorobenzene (192 mg, 1.00 mmol, 2.00 equiv.), and KO*t*-Bu (168 mg, 1.50 mmol, 3.00 equiv.). The vial was sealed with a septum and removed from the glovebox. The toluene:DMA solvent (5.0 mL, 0.1 M) was added to the reaction vial, followed by alkene **4e** (95 μL, 0.50 mmol, 1.0 equiv.). The septum was then quickly replaced by a Teflon-lined screw cap and the reaction was stirred at 50 °C for 18 h in a temperature-controlled aluminum block. The reaction was quenched upon the addition of 1 M HCl (5 mL), and the mixture was extracted with EtOAc (3 x 3 mL), washed with 1 M KOH (3 x 5 mL), dried over $MgSO_4$, gravity filtered, and concentrated. 1,3,5-Trimethylbenzene (28 μL, 0.2 mmol) was added as an internal standard and a small aliquot was analyzed via ^{1}H NMR.

Table S3: Relating solvent ratio to diastereoselectivity

Entry	toluene:DMA	% *syn* (*5*)	% *anti* (27)	dr (*syn:anti*)
1	1:0	75	3	23:1
2	9:1	77	3	26:1
3	4:1	78	5	16:1
4	2:1	70	11	6.1:1
5	1:1	54	24	2.2:1
6	1:2	39	49	1:1.3
7	1:4	35	56	1:1.6
8	1:9	25	61	1:2.4
9	0:1	23	66	1:3.0

■ **X-ray Crystal Structures:**



The ellipsoid contour percent probability level is 50% for the image of the structure.

Table S4. Crystal data and structure refinement for 5.

Empirical formula	C25 H31 B Cl N O3	
Formula weight	439.77	
Crystal color, shape, size	colourless plate, 0.25 × 0.1 × 0.02 mm^3	
Temperature	100.0 K	
Wavelength	0.71073 Å	
Crystal system, space group	Monoclinic, P 1 21/c 1	
Unit cell dimensions	a = 7.2807(4) Å	α = 90°.
	b = 37.463(3) Å	β = 112.541(2)°.
	c = 9.2992(6) Å	γ = 90°.
Volume	2342.7(3) $Å^3$	
Z	4	
Density (calculated)	1.247 g/cm^3	
Absorption coefficient	0.189 mm^{-1}	
F(000)	936	

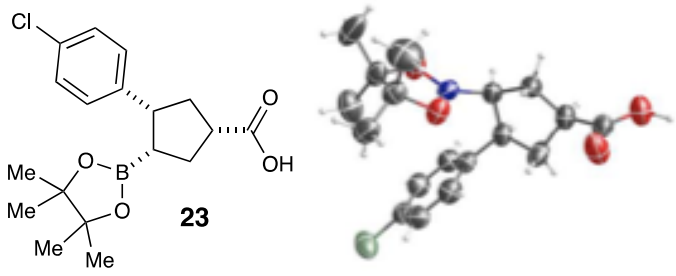
Data collection

Diffractometer	Bruker Venture D8, Photon III
Theta range for data collection	2.174 to 26.372°.
Index ranges	-9<=h<=9, -46<=k<=46, -11<=l<=11
Reflections collected	29834
Independent reflections	4786 [Rint = 0.1008]
Observed Reflections	2805
Completeness to theta = 25.242°	99.8 %

Solution and Refinement

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7454 and 0.5317
Solution	Intrinsic methods
Refinement method	Full-matrix least-squares on F^2

Weighting scheme	$w = [\sigma^2 Fo^2 + AP^2 + BP]^{-1}$, with $P = (Fo^2 + 2\,Fc^2)/3$, A = , B =
Data / restraints / parameters	4786 / 359 / 308
Goodness-of-fit on F^2	1.088
Final R indices [I>2σ(I)]	R1 = 0.0762, wR2 = 0.1916
R indices (all data)	R1 = 0.1182, wR2 = 0.2204
Extinction coefficient	n/a
Largest diff. peak and hole	0.273 and -0.412 e.Å^{-3}



The ellipsoid contour percent probability level is 50% for the image of the structure.

Table S5. Crystal data and structure refinement for 23.

Empirical formula	C18 H24 B Cl O4	
Formula weight	350.63	
Crystal color, shape, size	colorless needle, 0.21 × 0.05 × 0.05 mm^3	
Temperature	253(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	Triclinic, P-1	
Unit cell dimensions	a = 6.6223(5) Å	α = 108.954(3)°.
	b = 10.8658(10) Å	β = 101.208(3)°.
	c = 13.8513(13) Å	γ = 91.627(3)°.
Volume	920.16(14) Å^3	
Z	2	
Density (calculated)	1.266 Mg/m^3	
Absorption coefficient	0.225 mm^{-1}	
F(000)	372	

Data collection

Diffractometer	Venture D8, Bruker
Source	IμS 3.0, Incoatec
Detector	Photon III

Theta range for data collection	1.991 to 25.715°.
Index ranges	-8<=h<=8, -13<=k<=13, -16<=l<=16
Reflections collected	44351
Independent reflections	3479 [Rint = 0.1211]
Observed Reflections	2180
Completeness to theta = 25.242°	99.6 %

Solution and Refinement

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7453 and 0.6822
Solution	Intrinsic methods
Refinement method	Full-matrix least-squares on F^2
Weighting scheme	$w = [\sigma^2 Fo^2 + AP^2 + BP]^{-1}$, with $P = (Fo^2 + 2\,Fc^2)/3$, A = 0.0783, B = 0.7349
Data / restraints / parameters	3479 / 212 / 254
Goodness-of-fit on F^2	1.067
Final R indices [I>2σ(I)]	R1 = 0.0627, wR2 = 0.1508
R indices (all data)	R1 = 0.1055, wR2 = 0.2058
Largest diff. peak and hole	0.345 and -0.375 e.$Å^{-3}$

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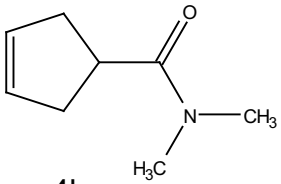
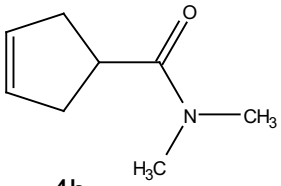
■ **^{1}H, ^{13}C, and ^{19}F NMR Spectra:**

CDCl3, 400 MHz



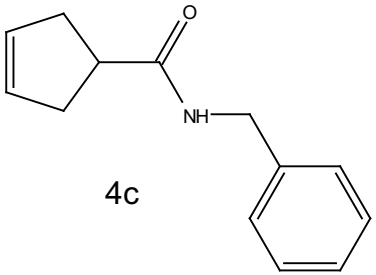
4b

CDCl3, 101 MHz



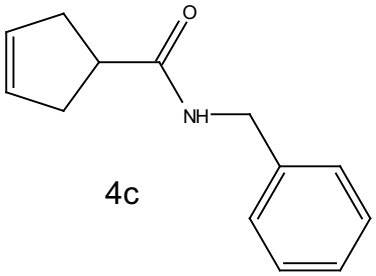
4b

CDCl3, 600 MHz



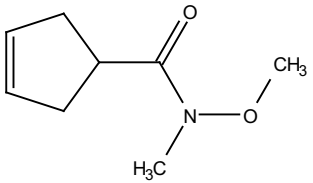
4c

CDCl3, 126 MHz

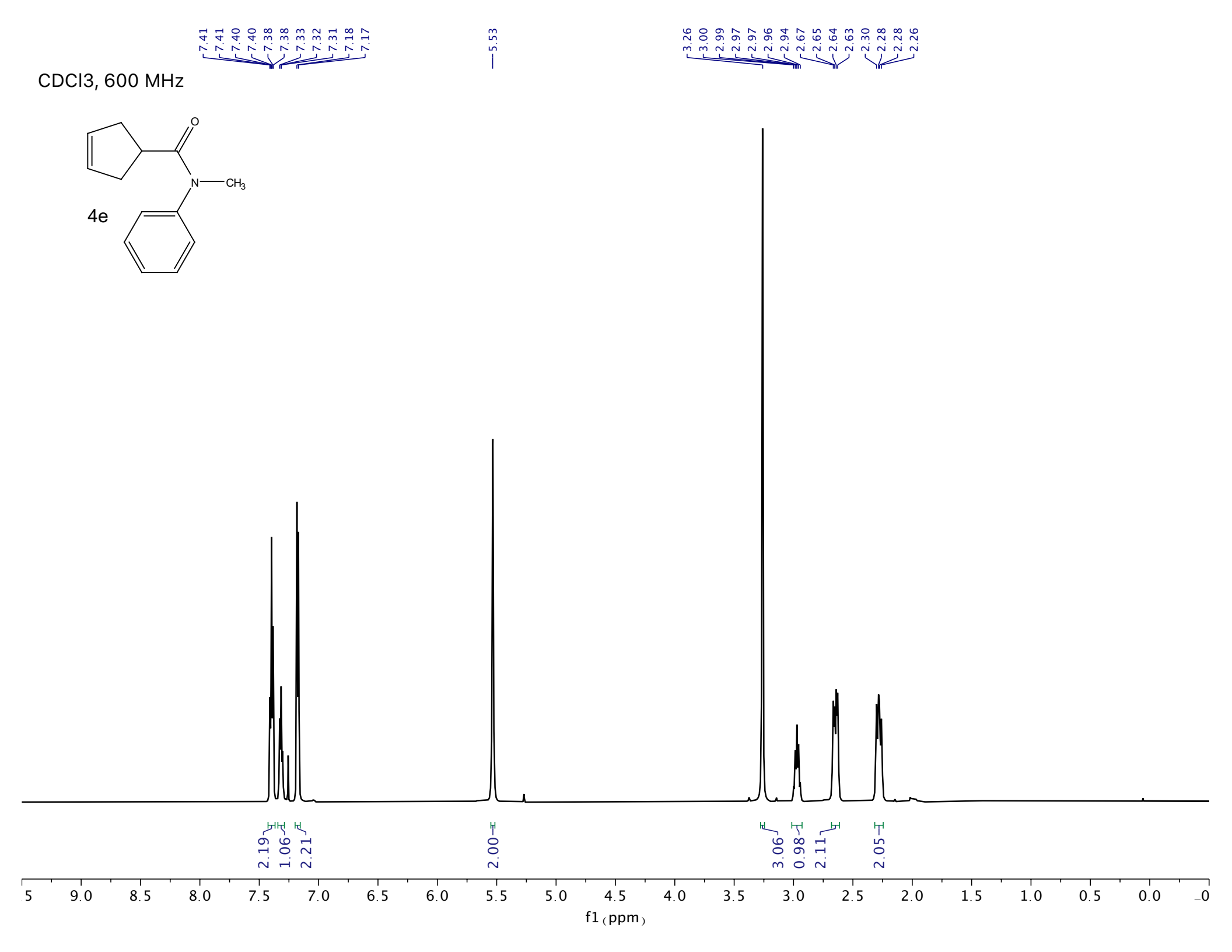


4c

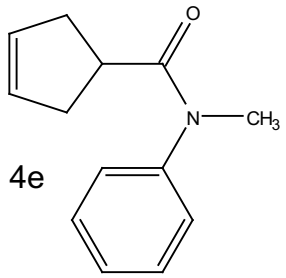
CDCl3, 600 MHz



4d


7.41
7.41
7.40
7.40
7.38
7.38
7.33
7.32
7.31
7.18
7.17
5.53
3.26
3.00
2.99
2.97
2.97
2.96
2.94
2.67
2.65
2.64
2.63
2.30
2.28
2.28
2.26
CDCl3, 600 MHz
O
N
CH3
4e
2.19
1.06
2.21
2.00
3.06
0.98
2.11
2.05
f1 (ppm)

CDCl3, 101 MHz



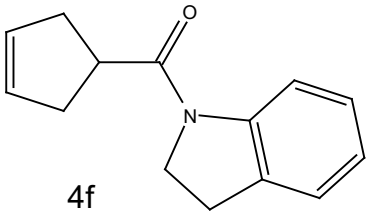
4e

176.20
144.27
129.67
128.80
127.70
127.49
77.38 cdcl3
77.06 cdcl3
76.74 cdcl3
39.96
37.67
37.61
27.06

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10

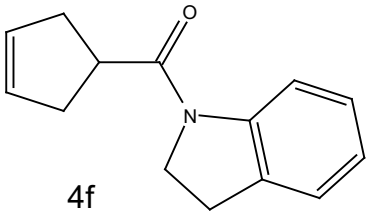
f1 (ppm)

CDCl3, 600 MHz



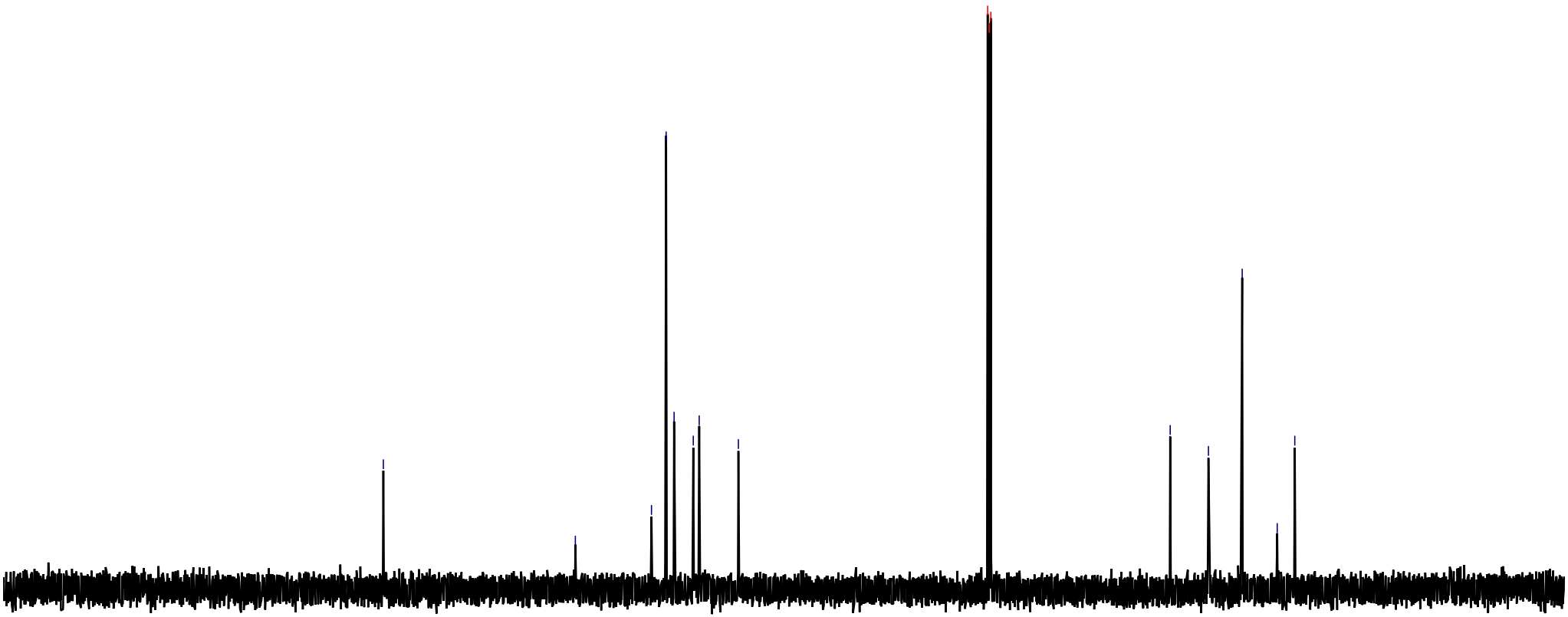
4f

CDCl3, 126 MHz



4f

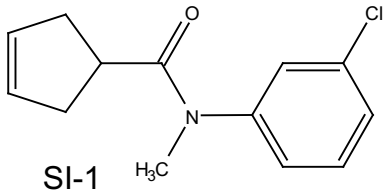
174.13
143.37
131.17
128.83
127.55
124.48
123.53
117.25
77.32 cdcl3
77.06 cdcl3
76.81 cdcl3
48.07
41.95
36.54
30.93
28.11



230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10

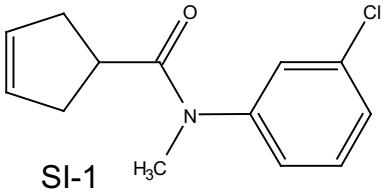
f1 (ppm)

CDCl3, 500 MHz



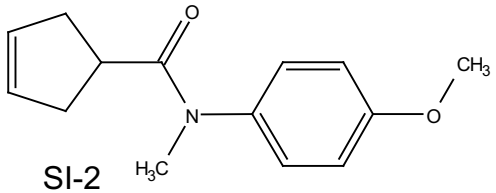
SI-1

CDCl3, 126 MHz



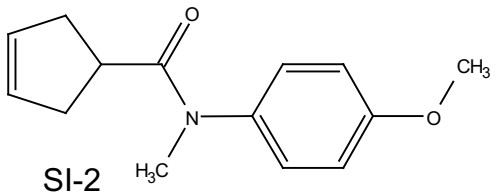
SI-1

CDCl3, 500 MHz



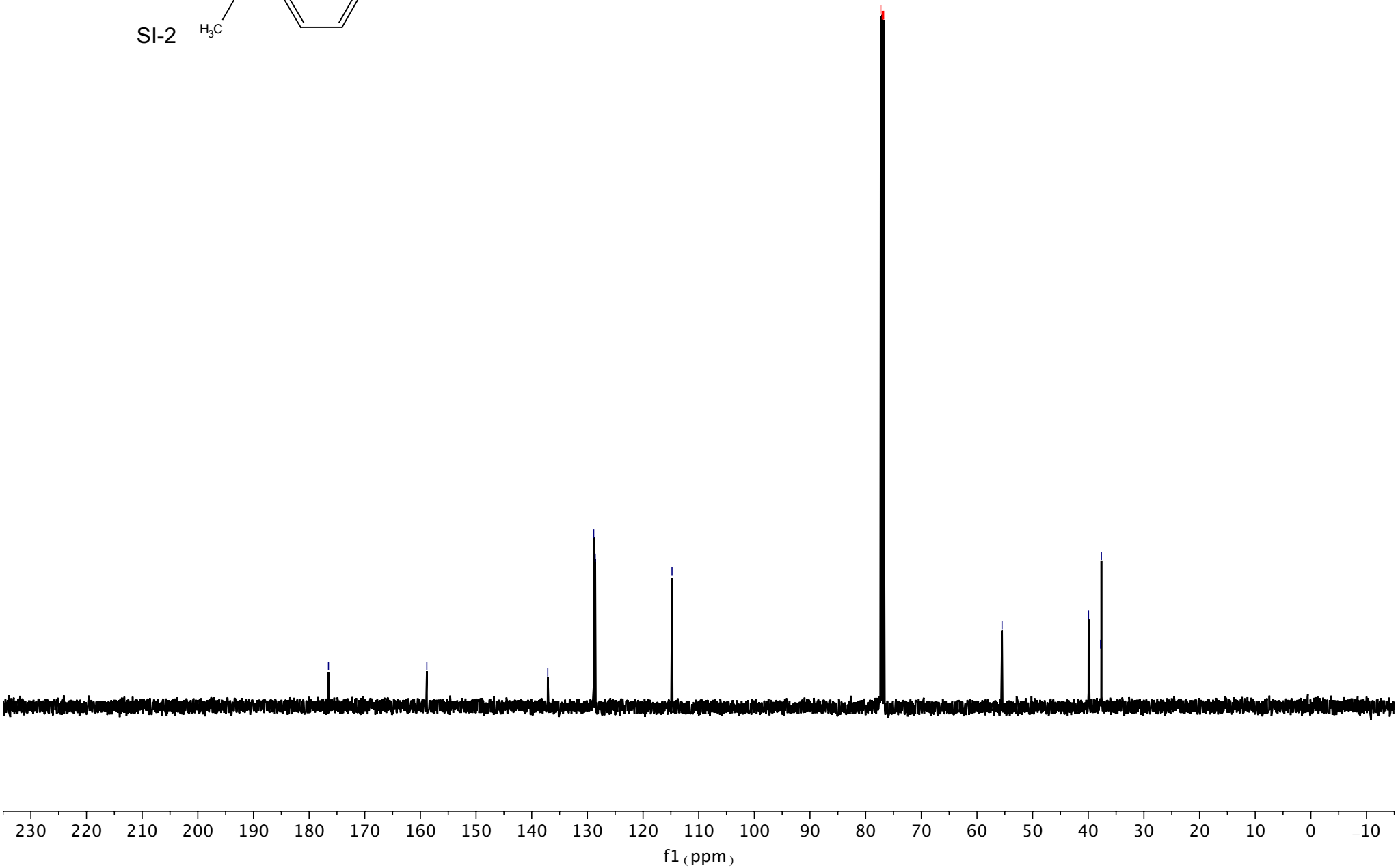
SI-2

CDCl3, 126 MHz

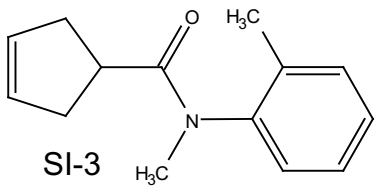


SI-2

176.52
158.85
137.12
128.86
128.60
114.79
77.27 cdcl3
77.02 cdcl3
76.77 cdcl3
55.50
39.95
37.79
37.64

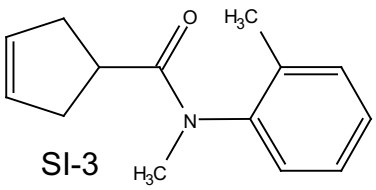


CDCl3, 500 MHz



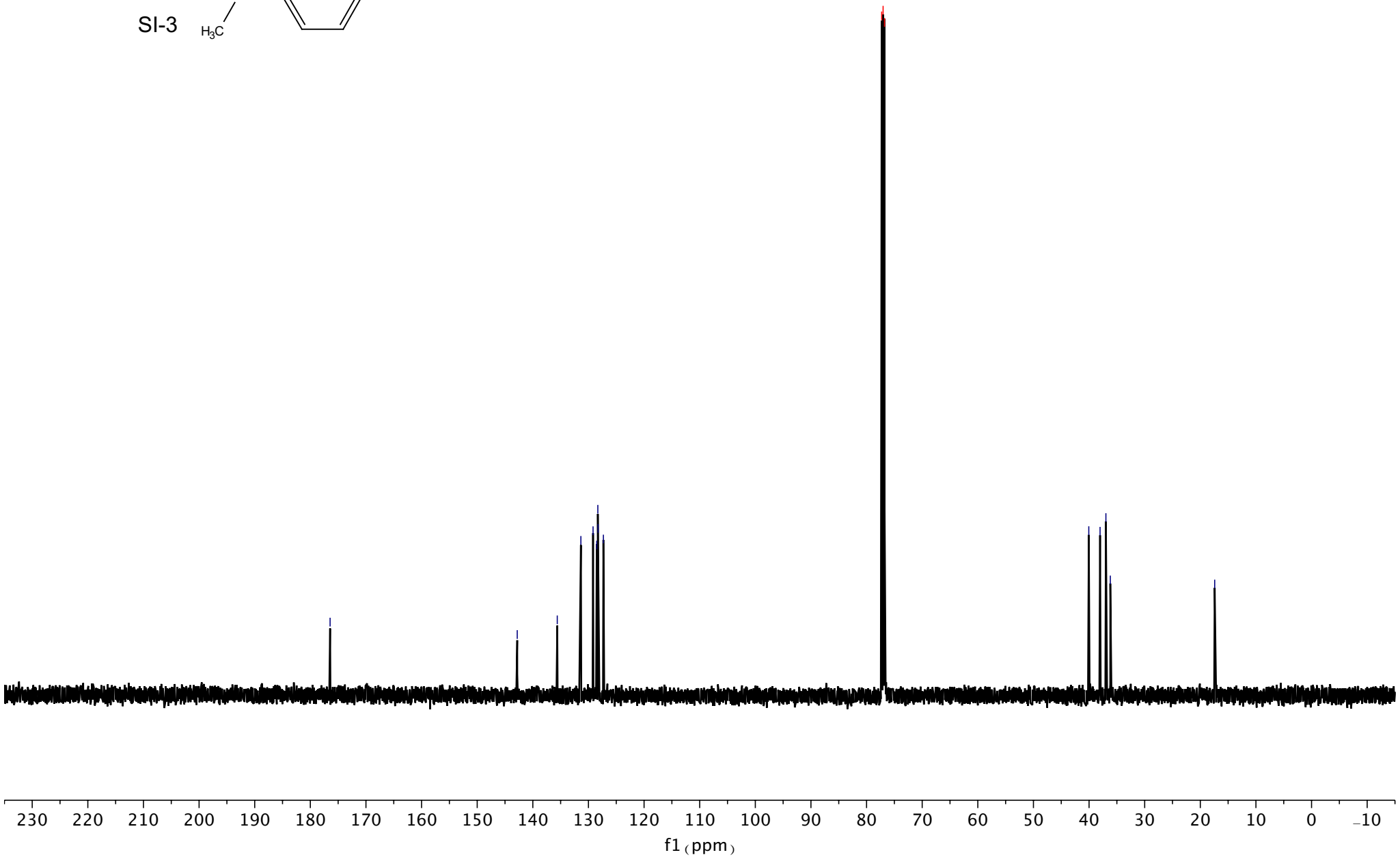
SI-3

CDCl3, 126 MHz

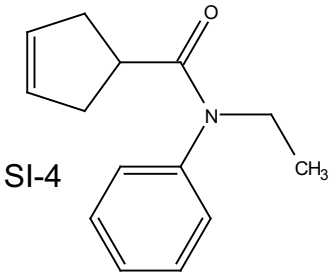


SI-3

176.45
142.80
135.61
131.36
129.17
128.51
128.31
128.27
127.31
77.28 cdcl3
77.03 cdcl3
76.77 cdcl3
40.05
38.02
36.97
36.18
17.41

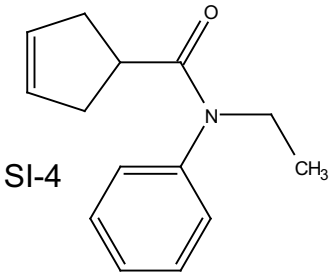


CDCl3, 400 MHz



SI-4

CDCl3, 101 MHz



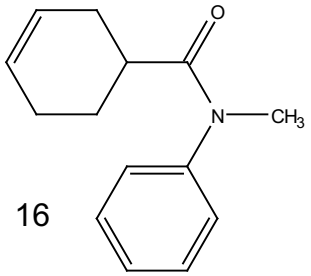
SI-4

175.52
142.54
129.53
128.81
128.67
127.77
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
44.17
40.32
37.61
13.03

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10

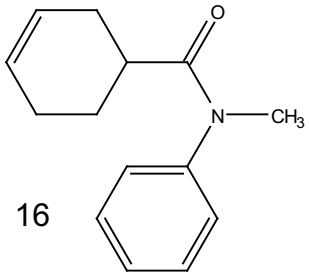
f1 (ppm)

CDCl3, 400 MHz



16

CDCl3, 101 MHz



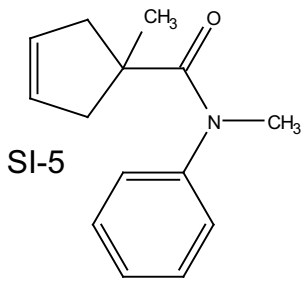
16

176.21
144.13
129.76
127.74
127.20
126.12
125.72
77.32 cdcl3
77.00 cdcl3
76.69 cdcl3
37.51
37.24
28.16
25.81
24.56

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10

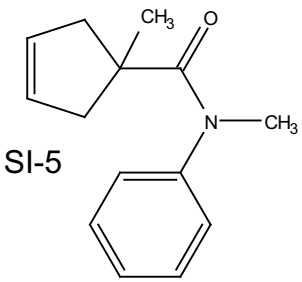
f1 (ppm)

CDCl3, 500 MHz



SI-5

CDCl3, 101 MHz



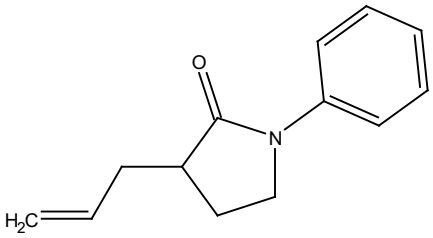
SI-5

177.59
144.59
129.10
128.65
128.03
127.61
77.35 cdcl3
77.03 cdcl3
76.71 cdcl3
50.29
45.17
40.40
27.93

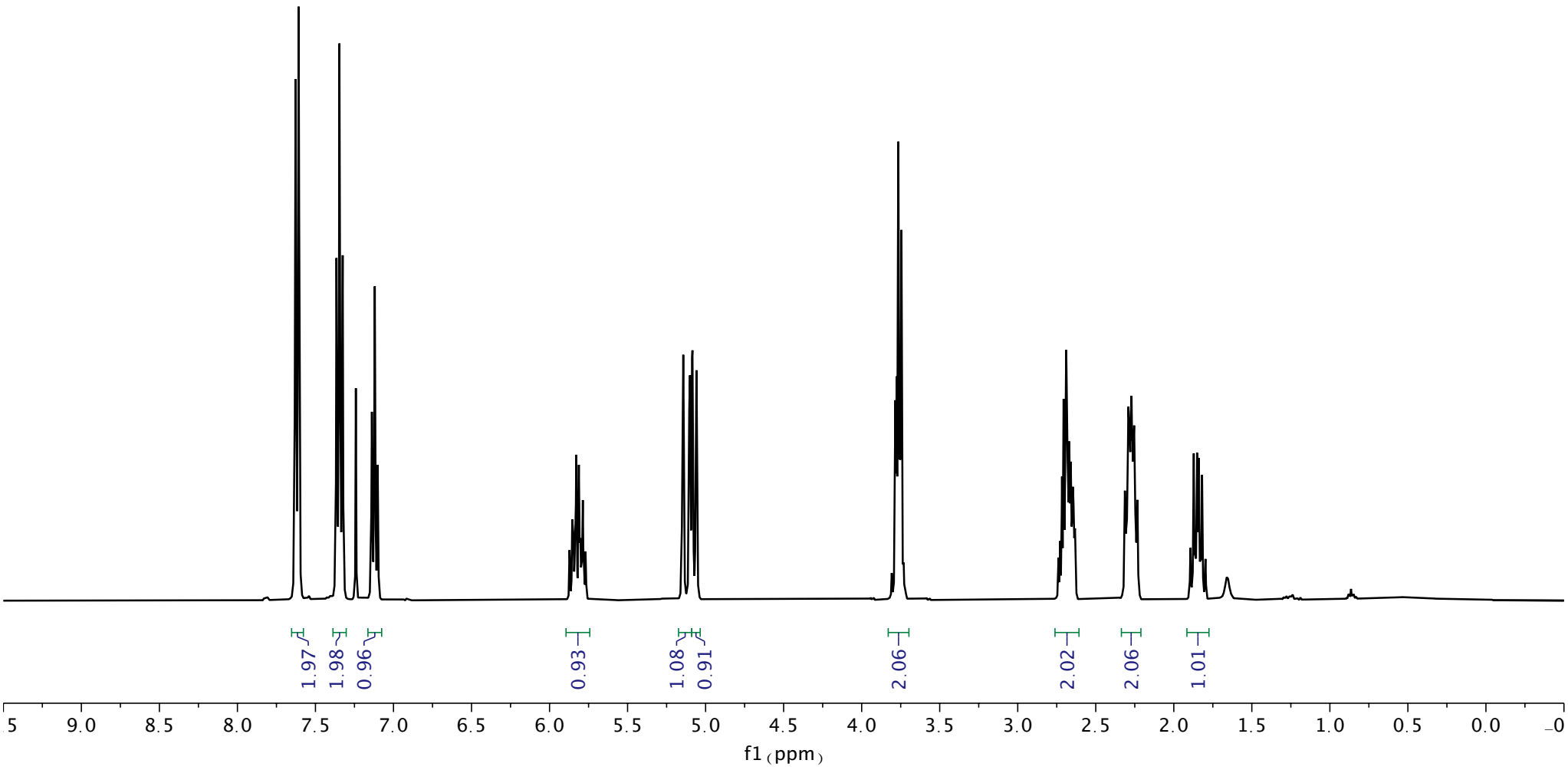
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10

f1 (ppm)

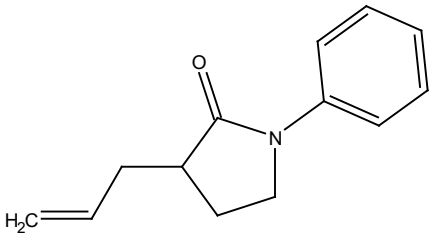
CDCl3, 400 MHz



SI-6



CDCl3, 101 MHz



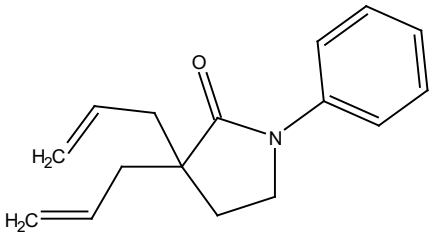
SI-6

175.24
139.51
135.37
128.78
124.39
119.72
117.09
77.33 cdcl3
77.01 cdcl3
76.69 cdcl3
46.71
42.93
35.38
23.91

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10

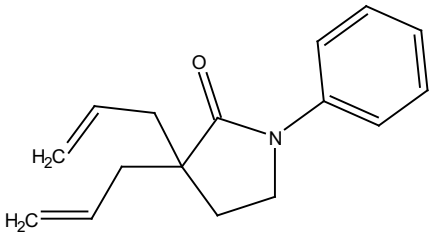
f1 (ppm)

CDCl3, 500 MHz



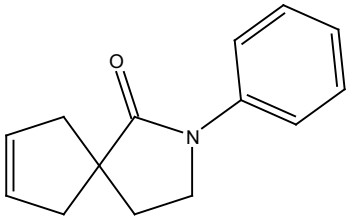
SI-7

CDCl3, 126 MHz



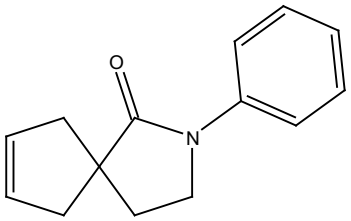
SI-7

CDCl3, 400 MHz



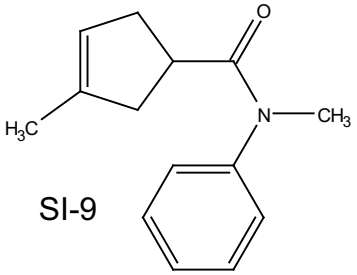
SI-8

CDCl3, 101 MHz



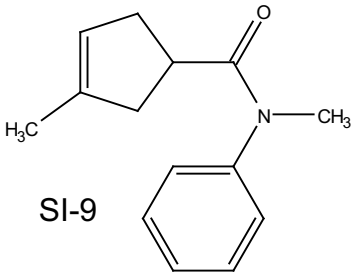
SI-8

CDCl3, 500 MHz



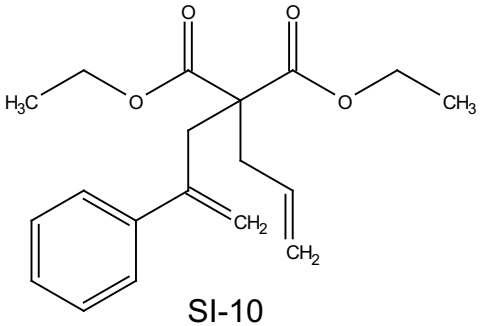
SI-9

CDCl3, 126 MHz

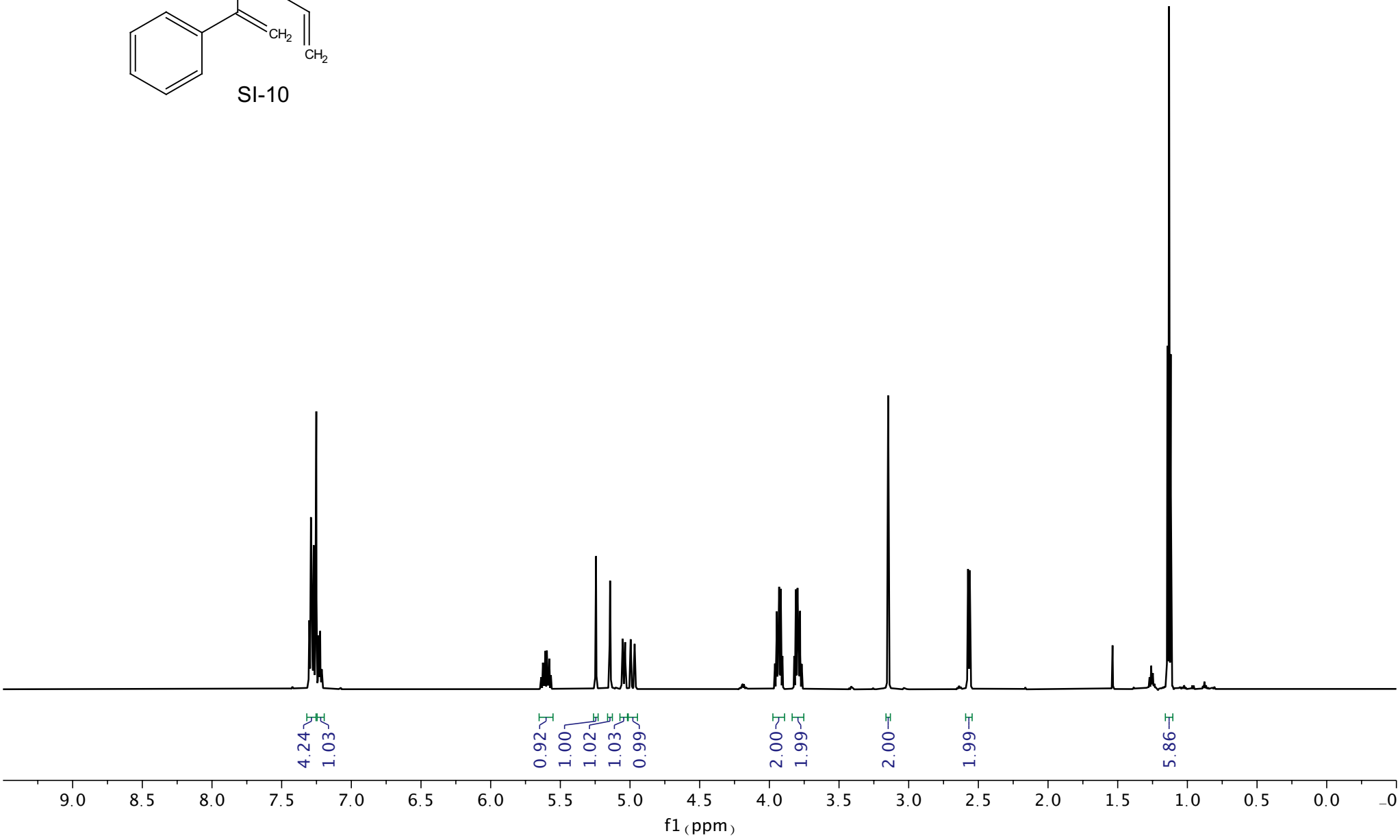


SI-9

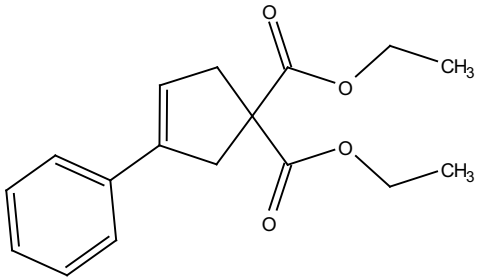
CDCl3, 600 MHz



SI-10

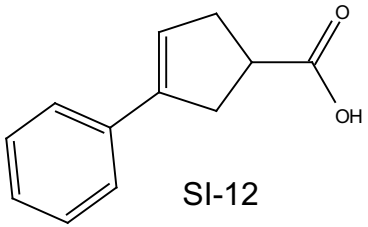


CDCl3, 600 MHz

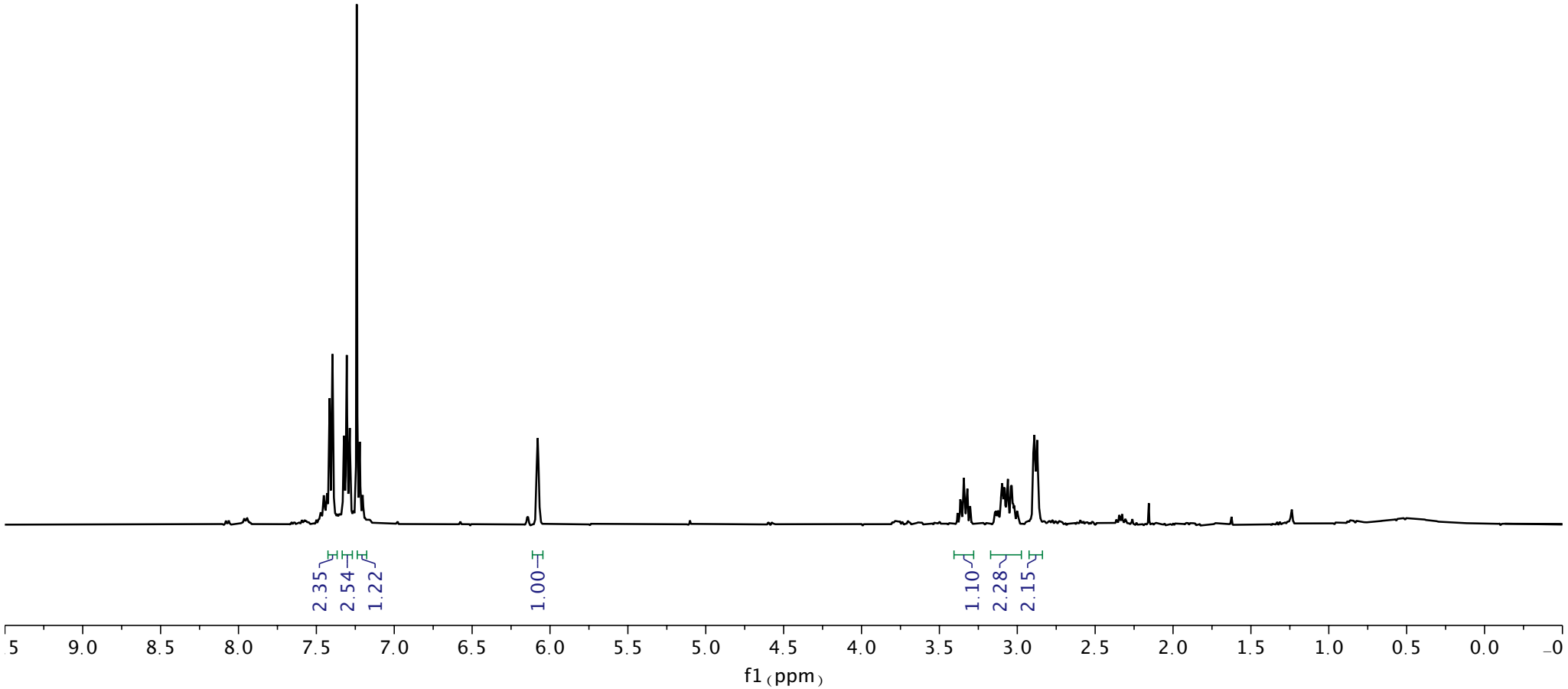


SI-11

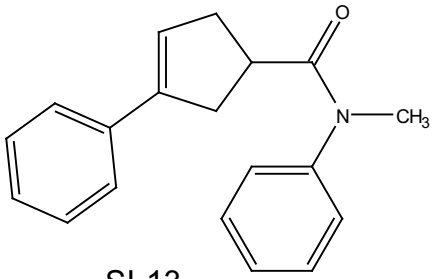
CDCl3, 400 MHz



SI-12

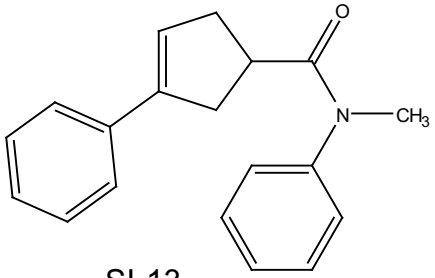


CDCl3, 400 MHz



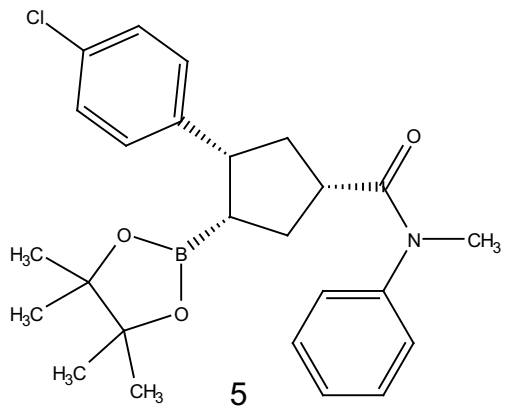
SI-13

CDCl3, 101 MHz



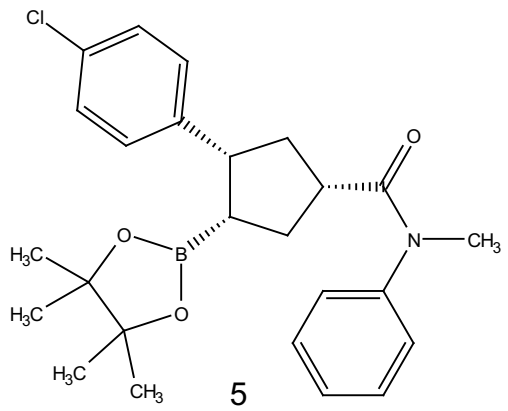
SI-13

CDCl3, 500 MHz



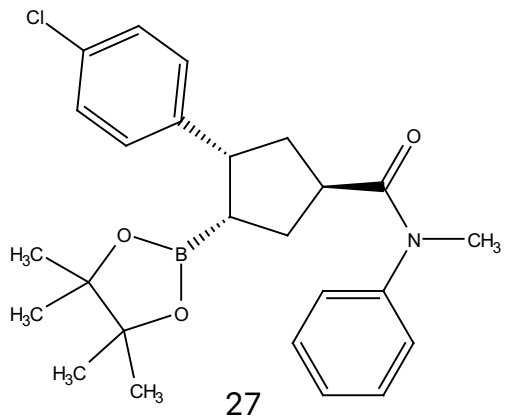
5

CDCl3, 126 MHz



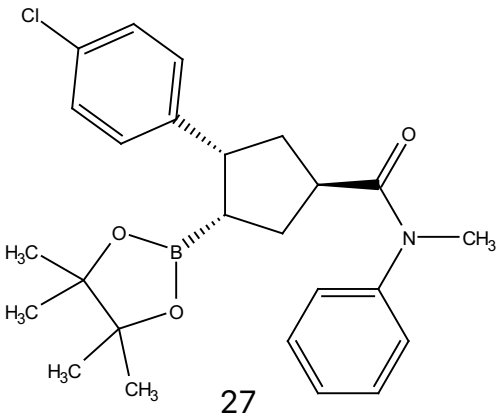
5

CDCl3, 500 MHz



27

CDCl3, 126 MHz



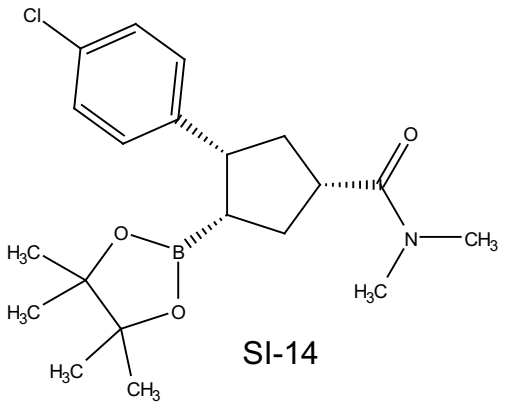
27

176.86
144.36
143.79
131.24
129.64
129.04
127.83
127.59
127.56
82.80
77.35 cdcl3
77.09 cdcl3
76.84 cdcl3
46.83
41.06
37.55
37.20
33.41
24.60
24.46

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10

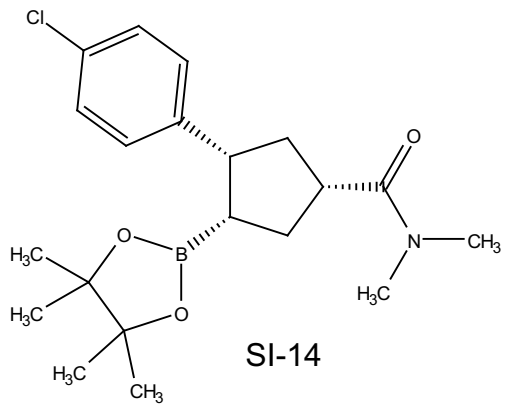
f1 (ppm)

CDCl3, 500 MHz



SI-14

CDCl3, 126 MHz



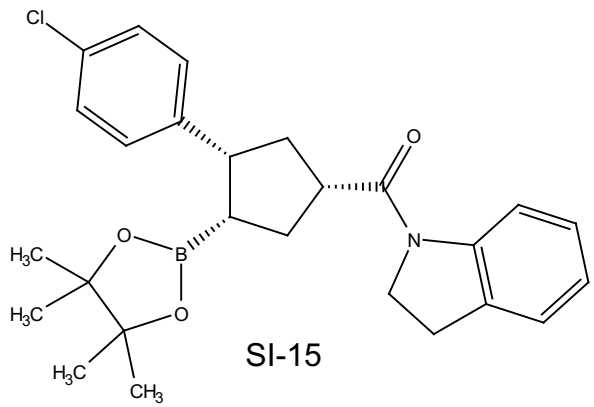
SI-14

174.63
144.82
131.45
129.87
127.89
82.92
77.34 cdcl3
77.09 cdcl3
76.84 cdcl3
45.59
43.46
37.69
37.12
35.66
32.61
24.62
24.60

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10

f1 (ppm)

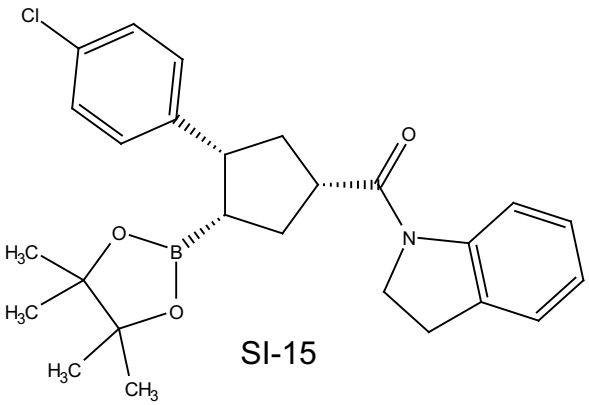
CDCl3, 500 MHz



SI-15

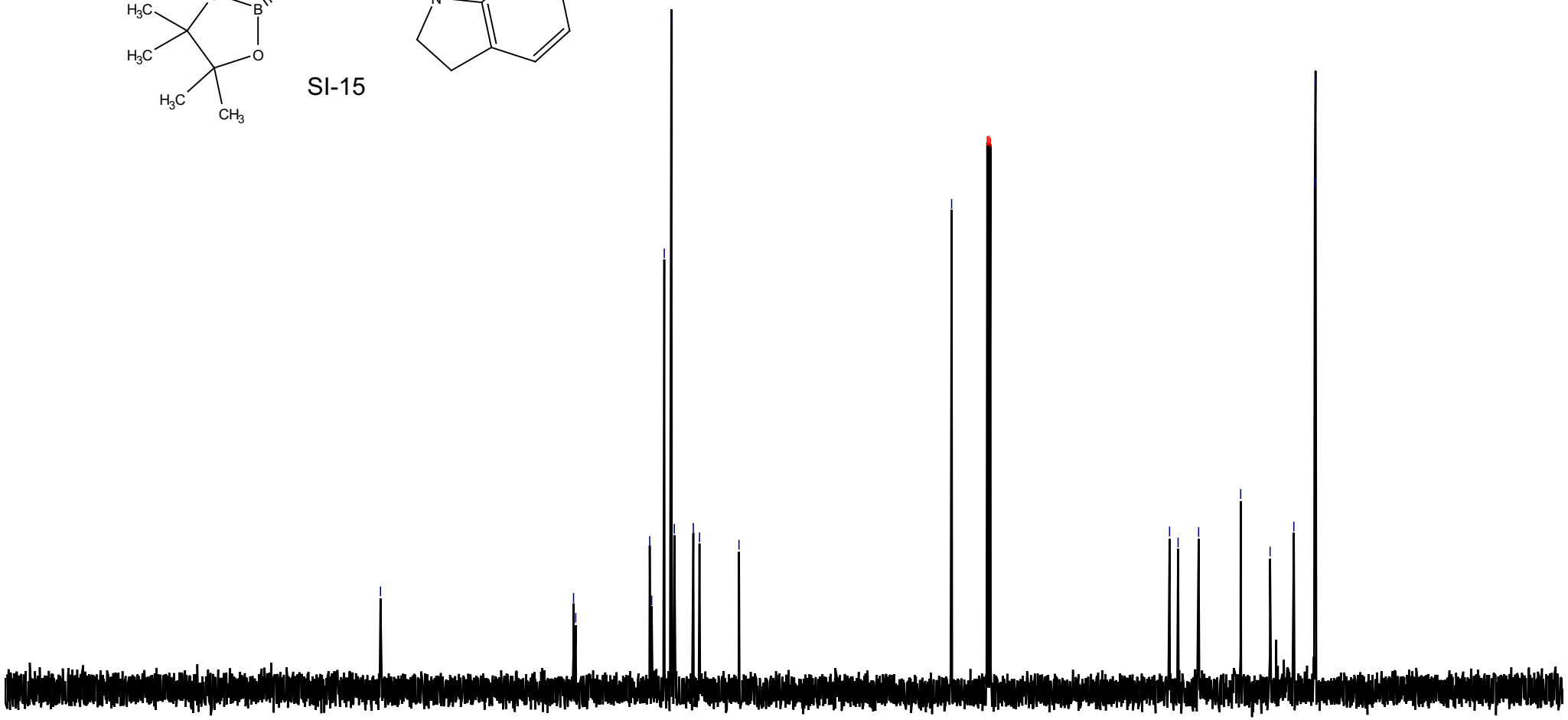
f1 (ppm)

CDCl3, 126 MHz



SI-15

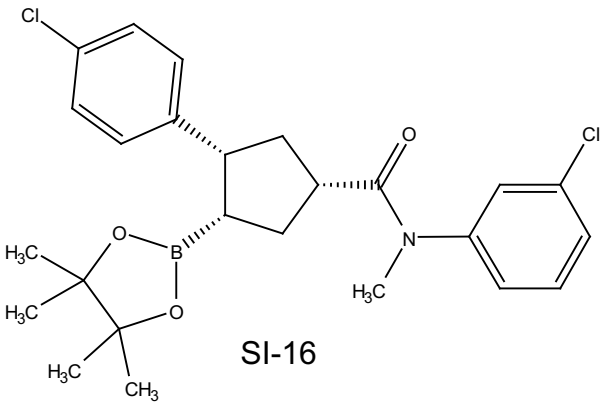
174.71
143.73
143.38
131.50
131.18
129.16
128.02
127.55
124.50
123.51
117.17
83.04
77.31 cdcl3
77.06 cdcl3
76.81 cdcl3
48.06
46.69
43.39
36.64
31.92
28.11
24.74
24.62



230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10

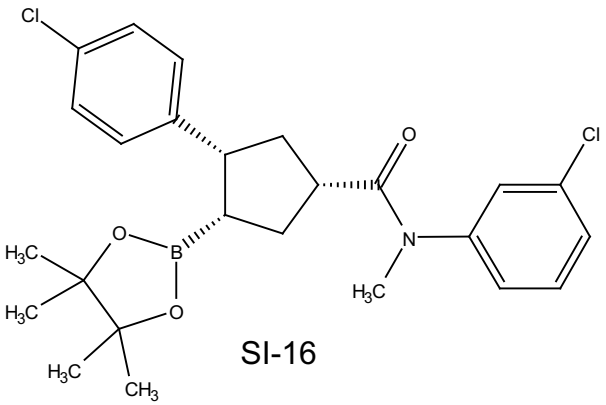
f1 (ppm)

CDCl3, 500 MHz



SI-16

CDCl3, 126 MHz



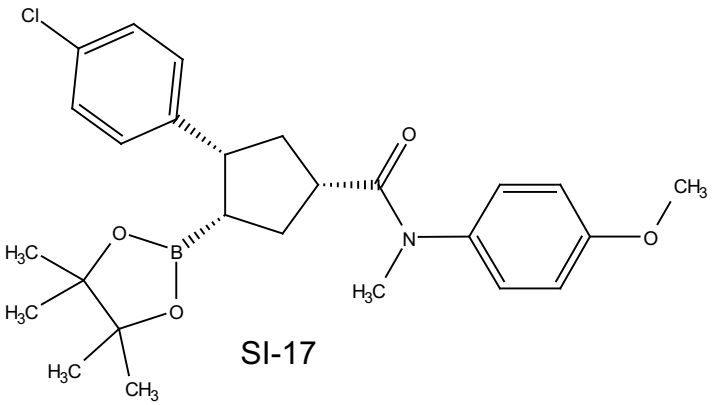
SI-16

175.09
145.46
144.85
135.13
131.51
130.72
129.88
128.11
127.93
127.80
125.80
82.94
77.30 cdcl3
77.04 cdcl3
76.79 cdcl3
45.70
44.19
38.78
37.66
33.73
24.60

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10

f1 (ppm)

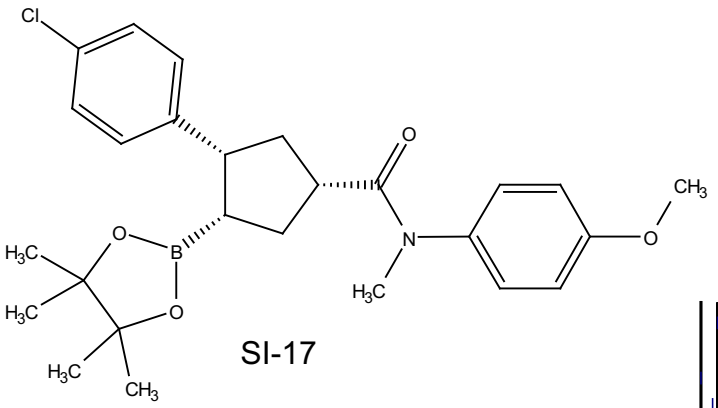
CDCl3, 500 MHz



SI-17

CDCl3, 126 MHz

175.53
158.85
145.06
137.05
131.40
129.91
128.48
127.86
114.83
82.85
77.34 cdcl3
77.08 cdcl3
76.83 cdcl3
55.47
45.71
44.04
38.74
37.77
33.65
24.60
24.59

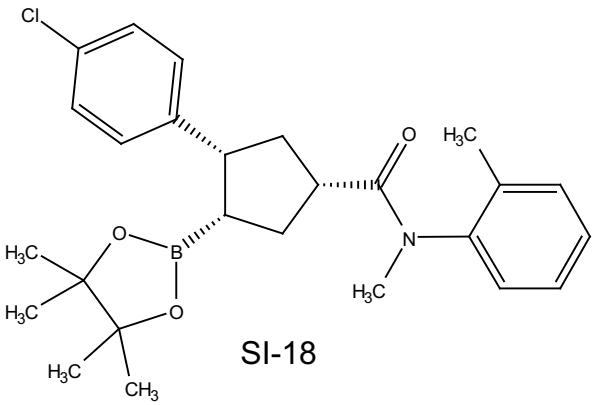


SI-17

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10

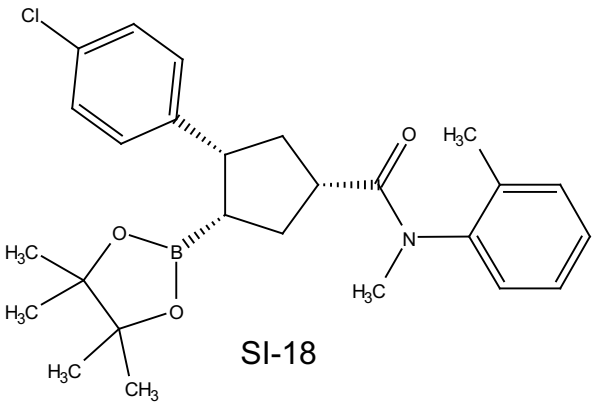
f1 (ppm)

CDCl3, 500 MHz



SI-18

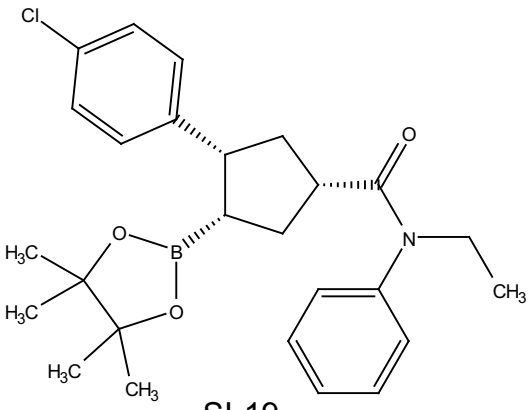
CDCl3, 126 MHz



SI-18

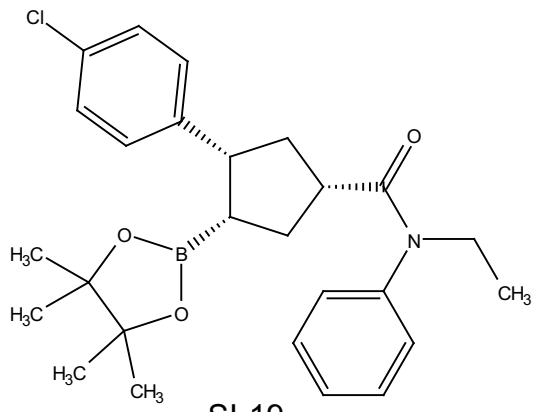
175.50
175.45
145.06
145.01
142.77
142.75
135.64
135.59
131.41
131.38
129.93
129.88
128.27
128.16
127.86
127.37
127.34
82.86
82.83
77.37 cdcl3
77.11 cdcl3
76.86 cdcl3
45.75
45.66
44.15
44.02
39.20
38.39
36.16
36.14
33.99
33.15
24.62
24.58
17.46

CDCl3, 500 MHz



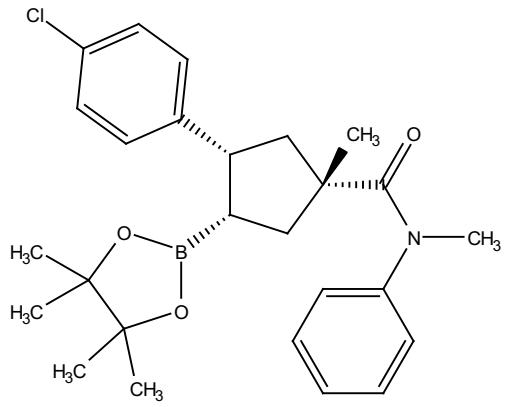
SI-19

CDCl3, 126 MHz

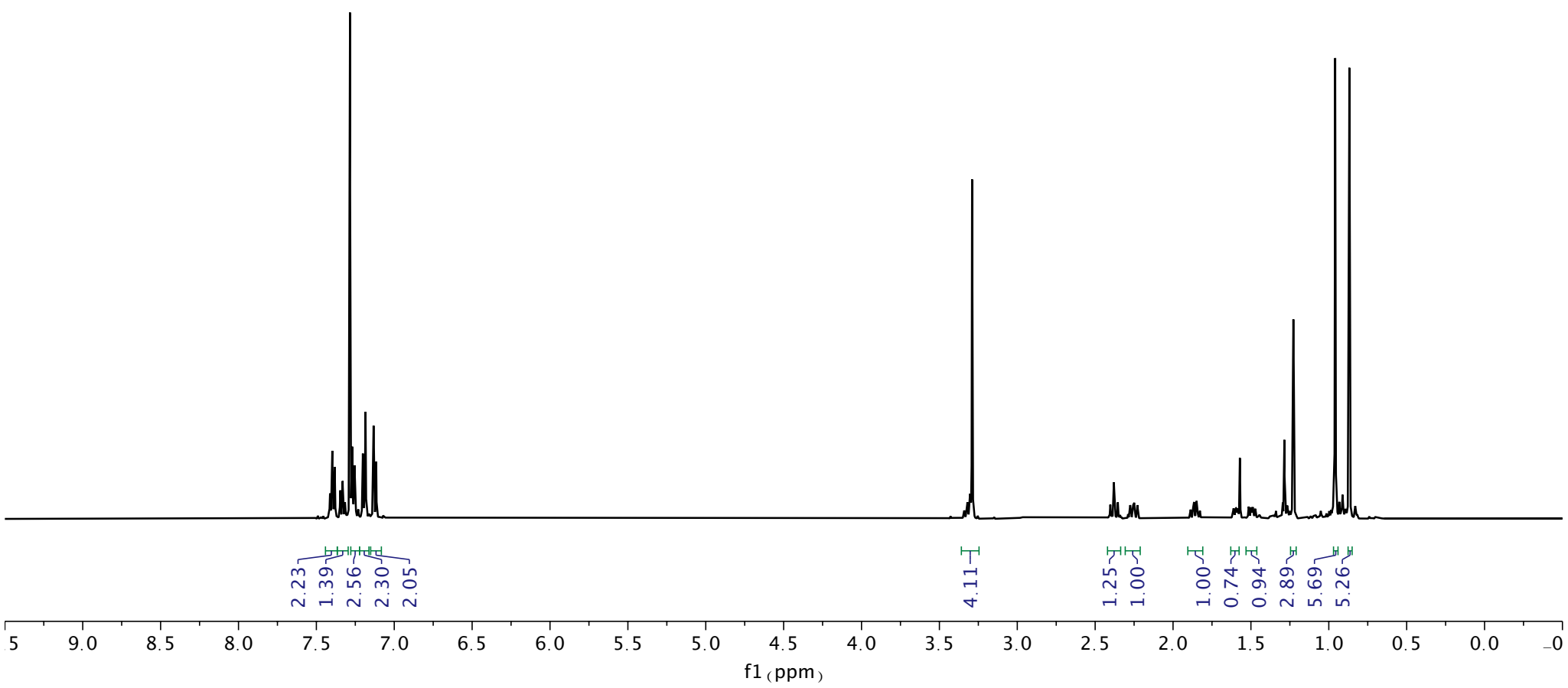


SI-19

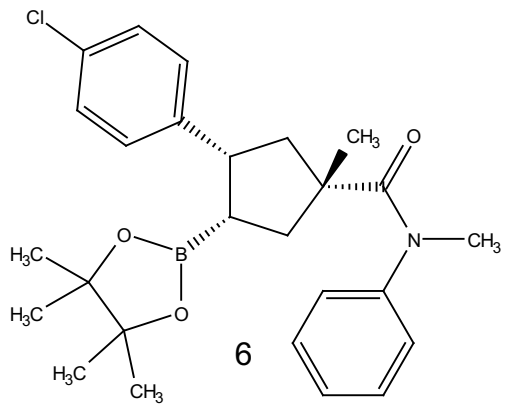
CDCl3, 500 MHz



6



CDCl3, 126 MHz



6

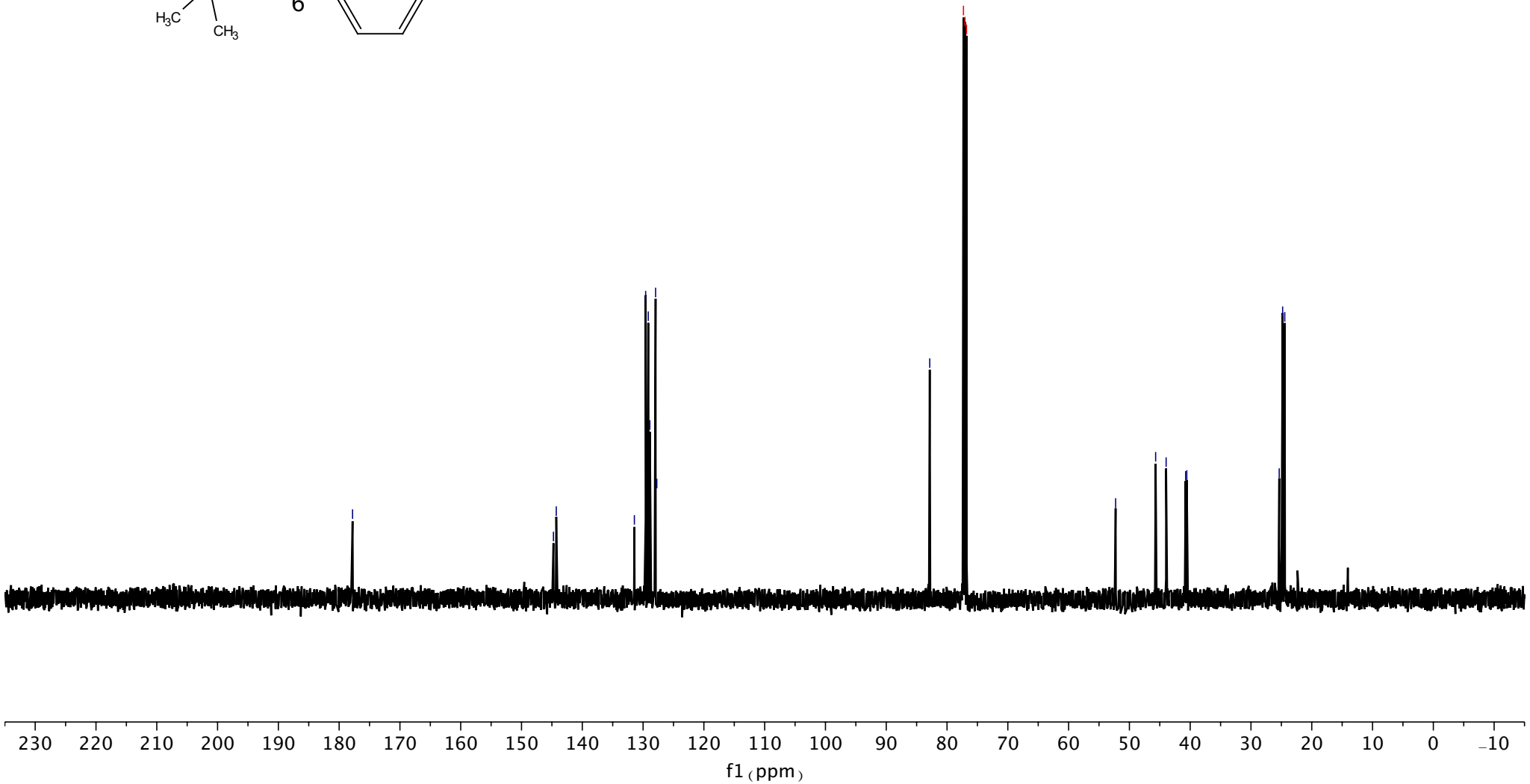
177.79

144.75
144.28
131.43
129.58
129.15
128.88
127.94
127.74

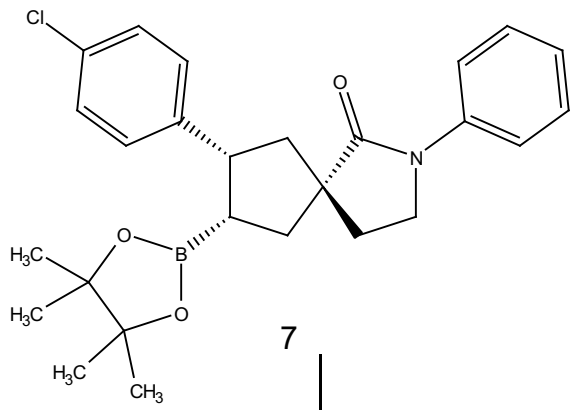
82.84
77.30 cdcl3
77.04 cdcl3
76.79 cdcl3

52.27
45.68
43.96
40.75
40.56

25.35
24.79
24.44

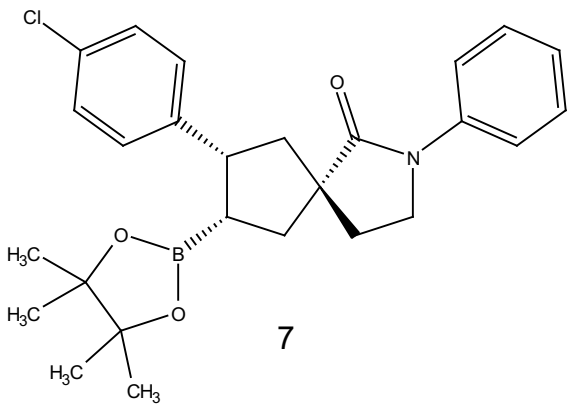


CDCl3, 400 MHz



7

CDCl3, 101 MHz



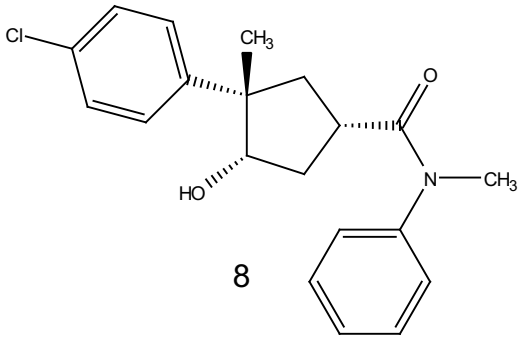
7

177.62
144.38
139.77
131.65
129.88
128.77
128.01
124.25
119.61
83.04
77.34 cdcl3
77.02 cdcl3
76.70 cdcl3
54.06
45.49
45.22
44.41
38.32
32.77
24.64
24.58

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10

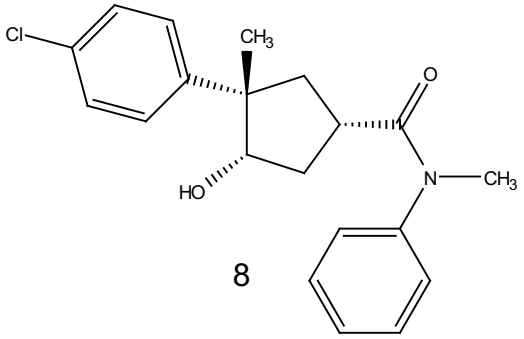
f1 (ppm)

CDCl3, 400 MHz



8

CDCl3, 126 MHz



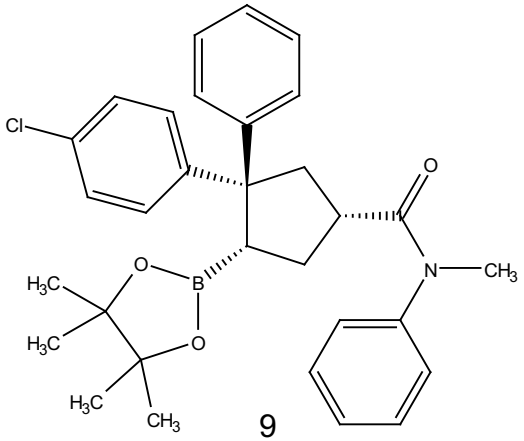
8

178.76
145.34
143.87
131.36
130.02
128.53
128.26
128.21
127.17
79.40
77.32 cdcl3
77.06 cdcl3
76.81 cdcl3
54.17
40.27
38.55
37.99
37.00
28.77

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10

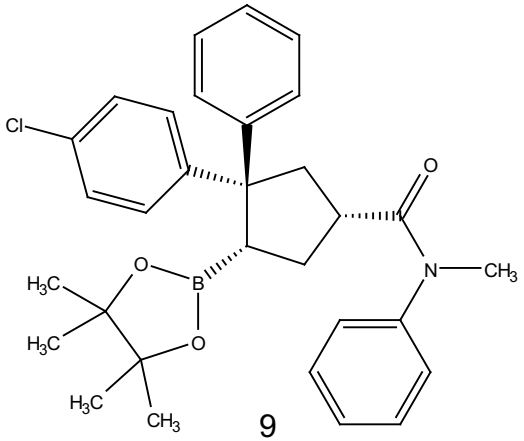
f1 (ppm)

CDCl3, 500 MHz



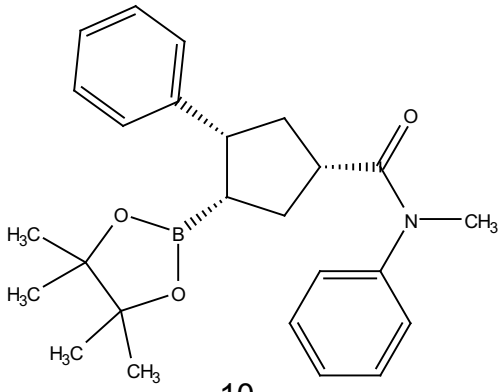
9

CDCl3, 126 MHz



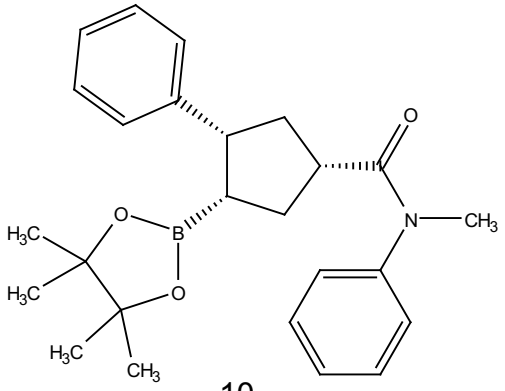
9

CDCl3, 400 MHz



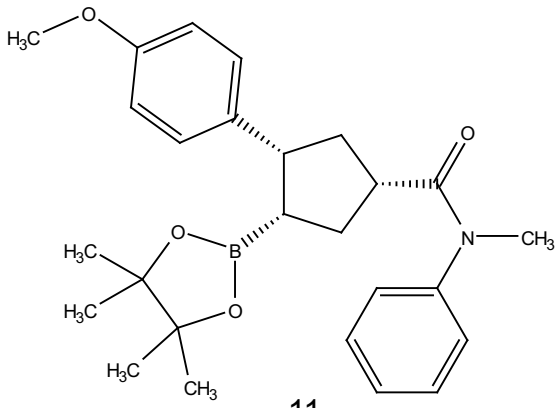
10

CDCl3, 101 MHz



10

CDCl3, 400 MHz

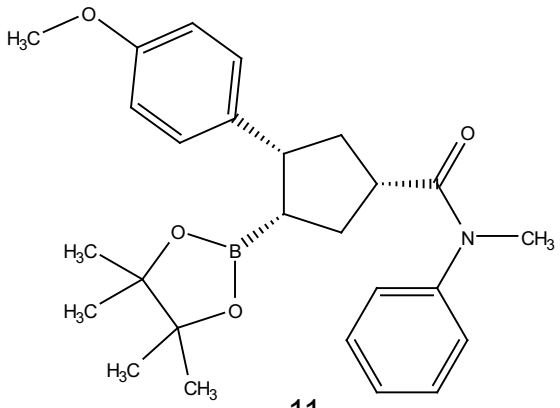


11

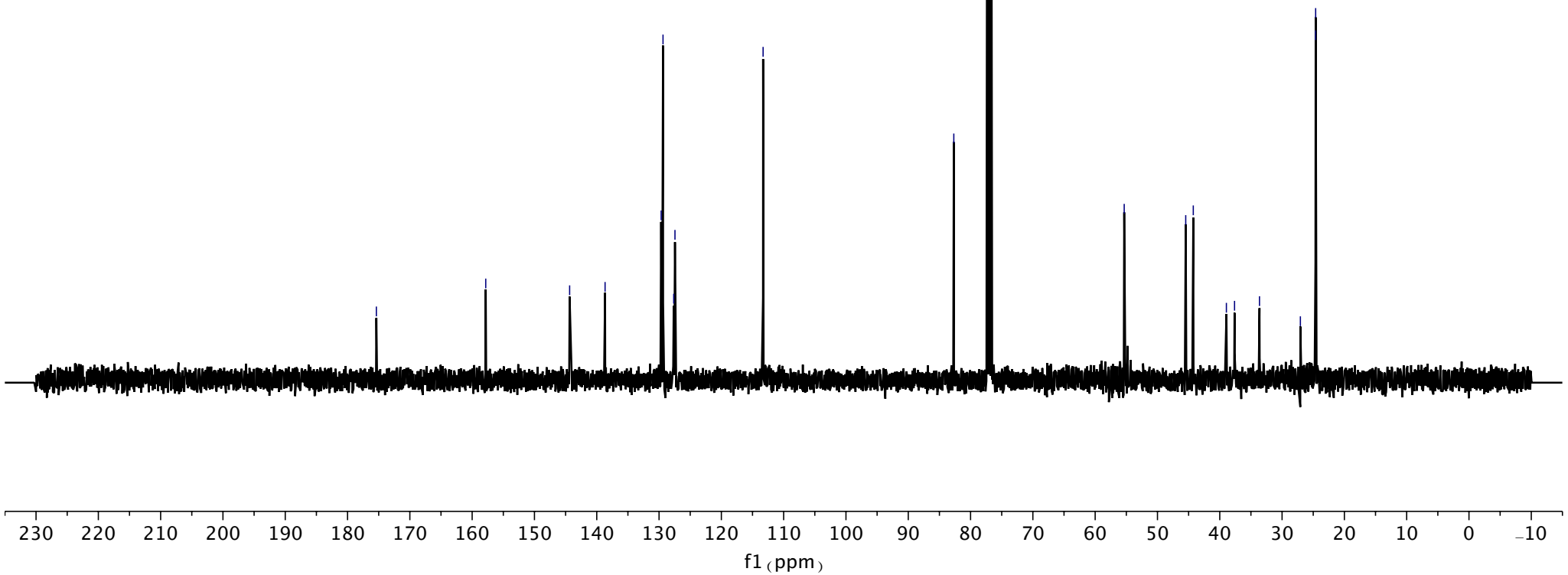
f1 (ppm)

CDCl3, 101 MHz

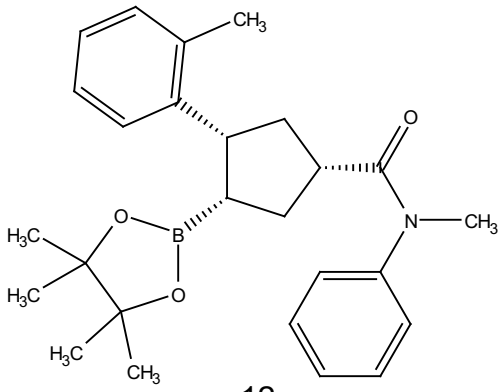
175.38
157.82
144.35
138.66
129.67
129.36
127.65
127.45
113.30
82.69
77.32 cdcl3
77.01 cdcl3
76.69 cdcl3
55.34
45.46
44.25
38.94
37.63
33.62
27.06
24.63
24.61



11



CDCl3, 400 MHz



12

CDCl3, 126 MHz

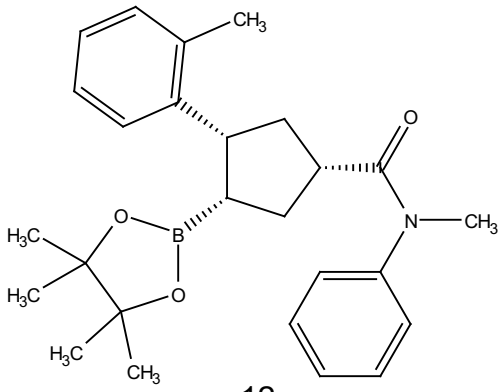
175.24

144.41
143.59
136.38
129.71
129.59
127.69
127.50
127.38
125.83
125.63

82.65
77.28 cdcl3
77.03 cdcl3
76.77 cdcl3

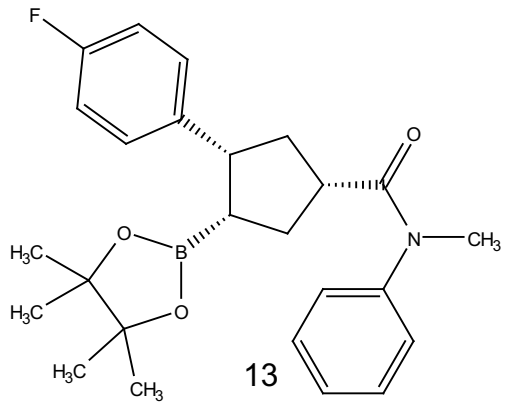
44.26
41.91
38.11
37.68
33.63

24.70
24.43
20.15



12

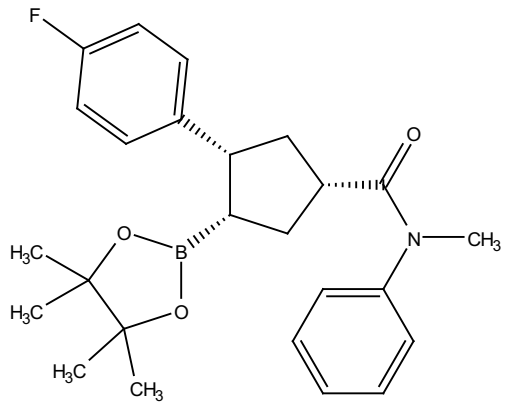
CDCl3, 400 MHz



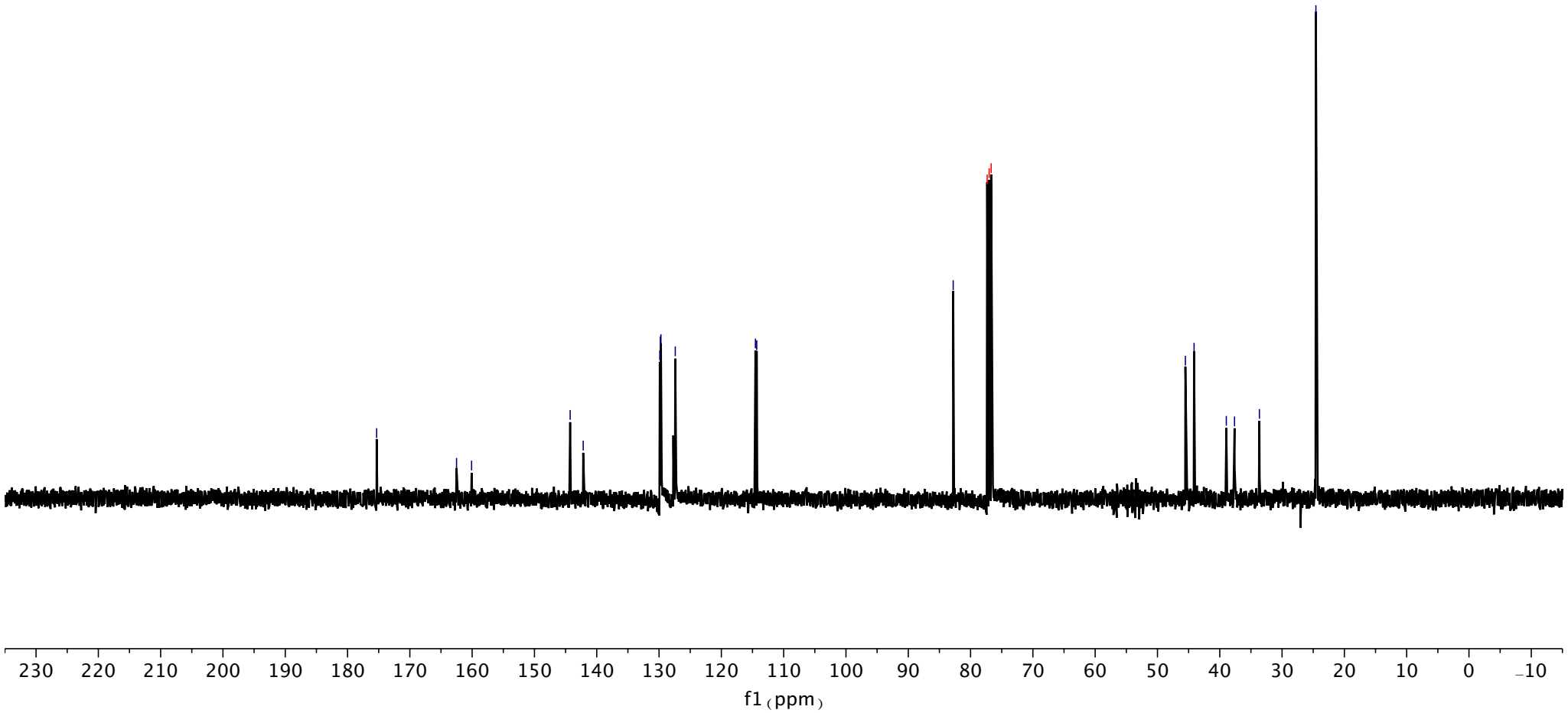
13

CDCl3, 101 MHz

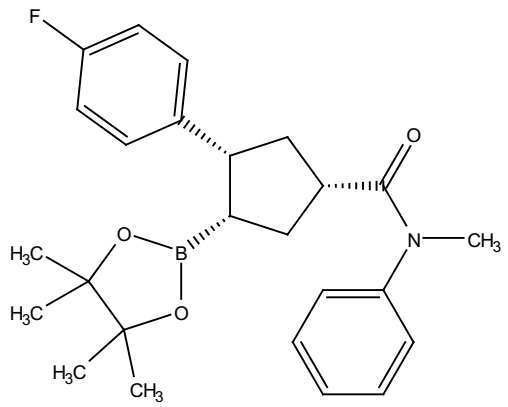
175.33
162.51
160.09
144.27
142.17
129.88
129.81
129.70
127.40
114.53
114.32
82.79
77.34 cdcl3
77.02 cdcl3
76.70 cdcl3
45.52
44.12
38.95
37.63
33.64
24.57



13

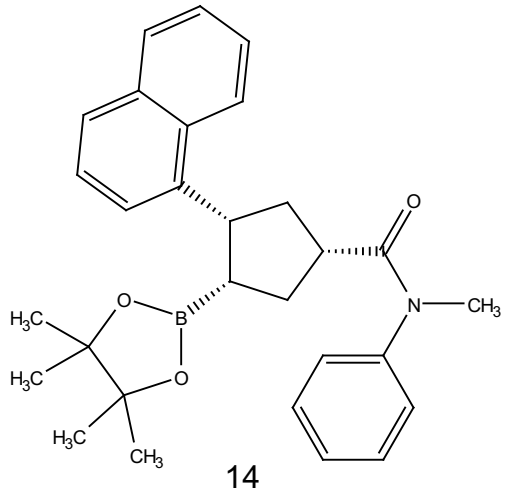


CDCl3, 376 MHz



13

CDCl3, 600 MHz

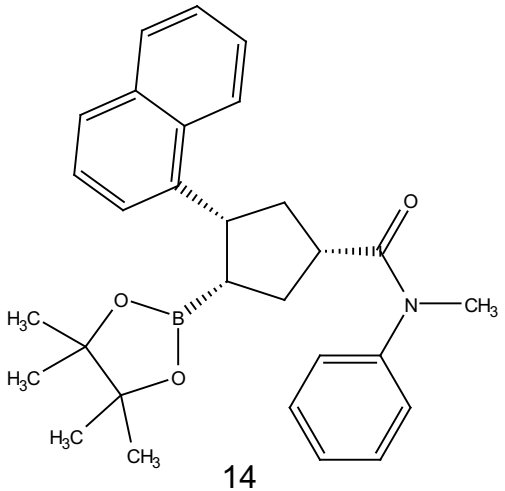


14

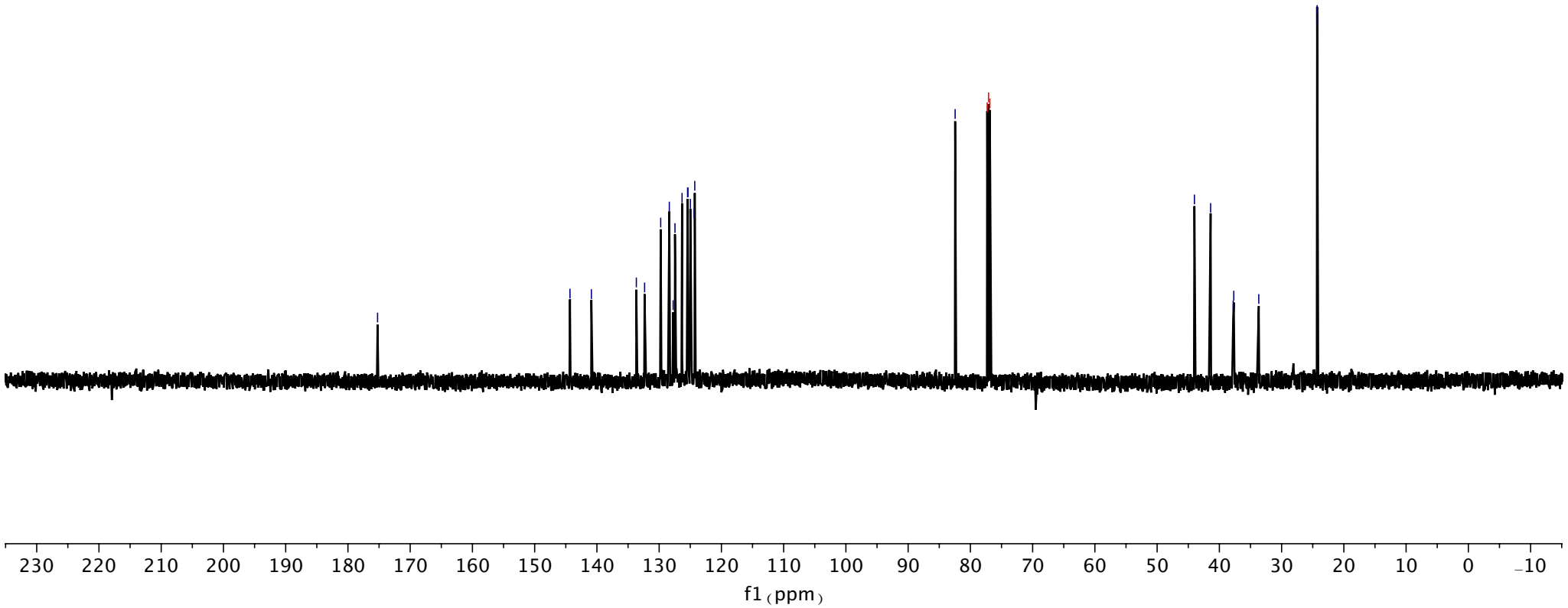
f1 (ppm)

CDCl3, 151 MHz

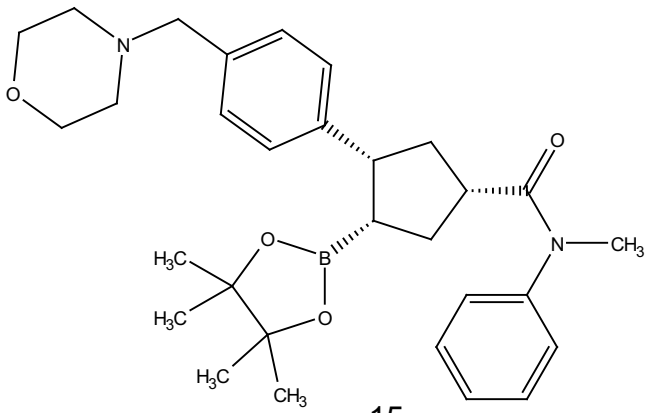
175.24
144.33
140.89
133.67
132.34
129.75
128.37
127.75
127.46
126.32
125.44
125.38
124.99
124.38
124.28
82.45
77.30 cdcl3
77.09 cdcl3
76.87 cdcl3
44.01
41.40
37.78
37.69
33.67
24.30
24.24



14



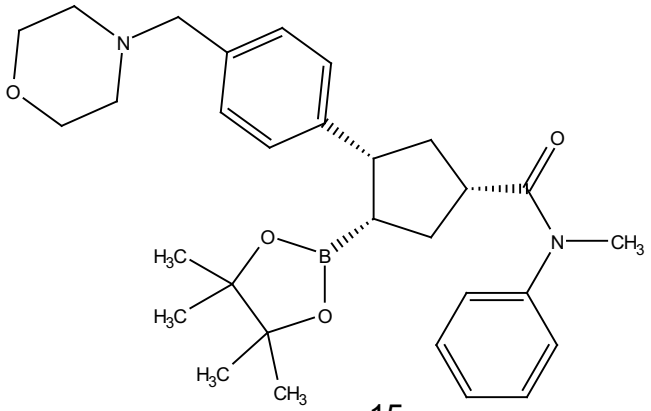
CDCl3, 600 MHz



15

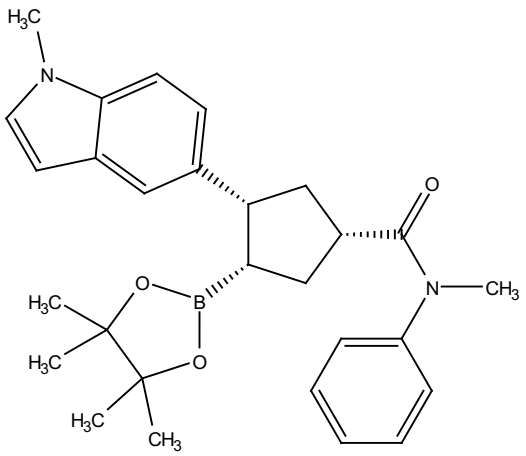
CDCl3, 126 MHz

175.32
145.31
144.36
134.79
129.71
128.92
128.36
127.71
127.47
82.73
77.32 cdcl3
77.06 cdcl3
76.81 cdcl3
66.93
63.07
53.41
46.01
44.26
38.82
37.67
33.67
24.63
24.59



15

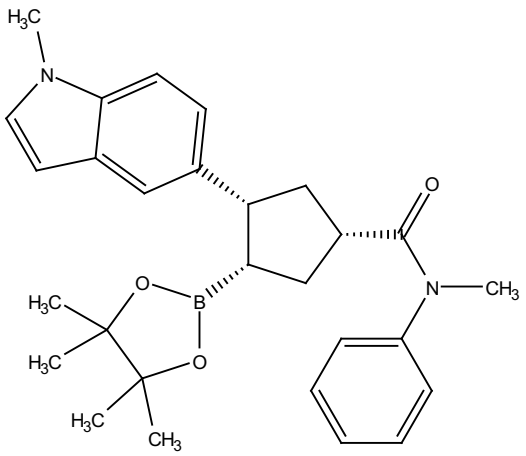
CDCl3, 600 MHz



17

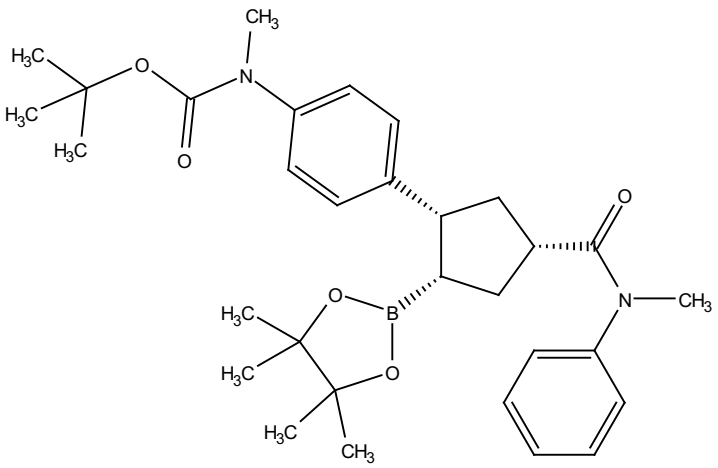
CDCl3, 151 MHz

175.42
144.44
136.99
135.59
129.66
128.50
128.42
127.62
127.49
122.64
120.00
108.37
100.70
82.50
77.31 cdcl3
77.10 cdcl3
76.88 cdcl3
46.39
44.54
39.48
37.65
33.80
32.75
24.61
24.52



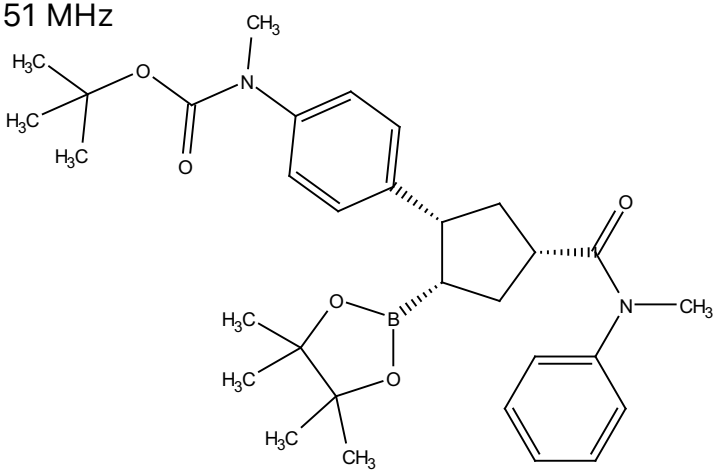
17

CDCl3, 600 MHz



18

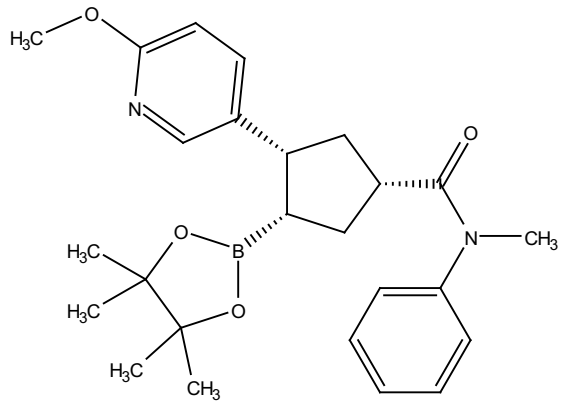
CDCl3, 151 MHz



18

217.96
175.27
154.73
144.28
143.42
141.63
129.67
128.53
127.39
124.84
82.69
79.93
77.30 cdcl3
77.09 cdcl3
76.88 cdcl3
45.74
44.16
38.74
37.59
37.43
33.60
28.33
28.30
24.58

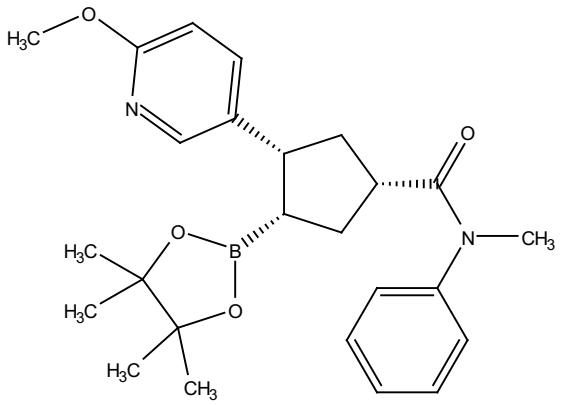
CDCl3, 400 MHz



19

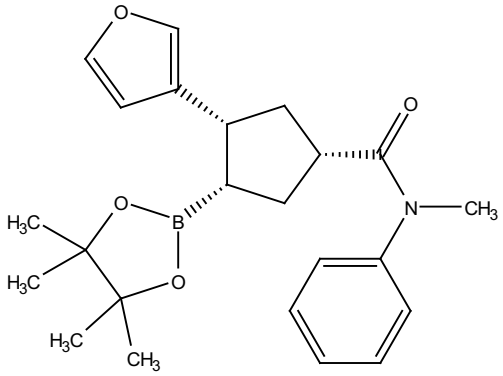
CDCl3, 101 MHz

175.33
162.58
146.11
144.19
138.87
134.45
129.71
127.74
127.34
110.04
82.87
77.36 cdcl3
77.04 cdcl3
76.72 cdcl3
53.25
44.00
42.79
38.50
37.62
33.57
24.59
24.49



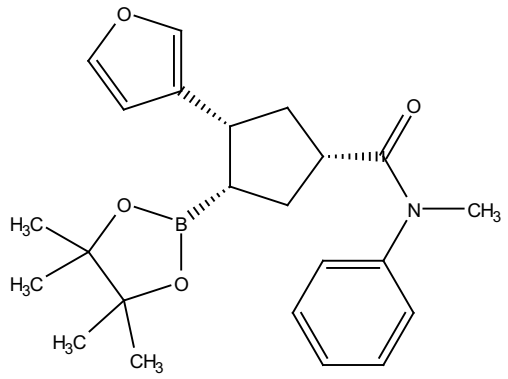
19

CDCl3, 600 MHz



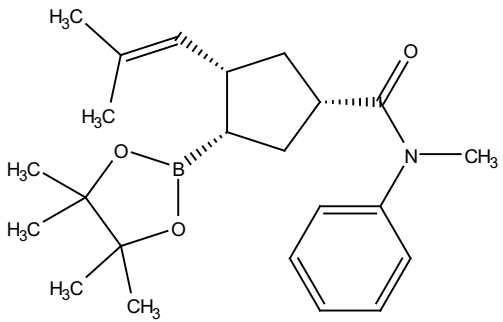
20

CDCl3, 151 MHz



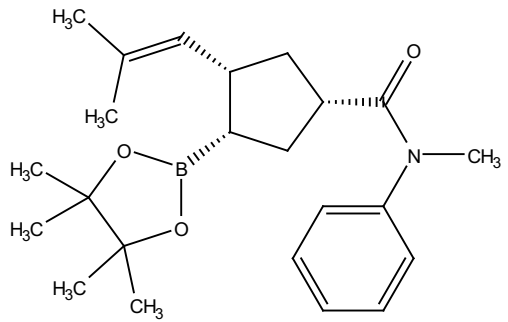
20

CDCl3, 600 MHz



21

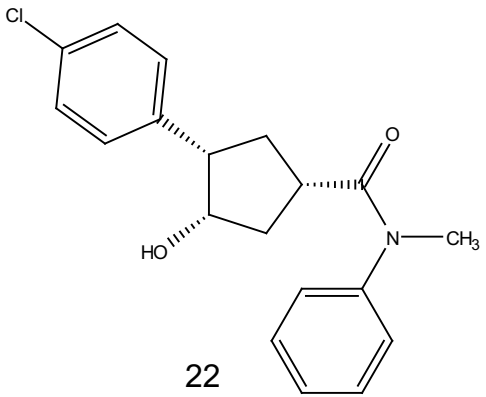
CDCl3, 126 MHz



2

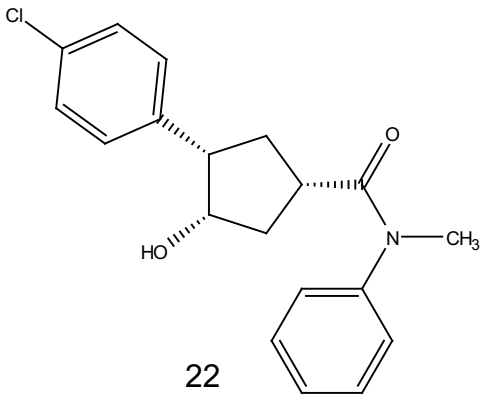
175.81
144.44
129.63
129.47
129.22
127.59
127.48
82.88
77.30 cdcl3
77.05 cdcl3
76.79 cdcl3
43.95
39.56
38.62
37.67
33.18
25.77
24.93
24.79
17.95

CDCl3, 400 MHz



22

CDCl3, 101 MHz



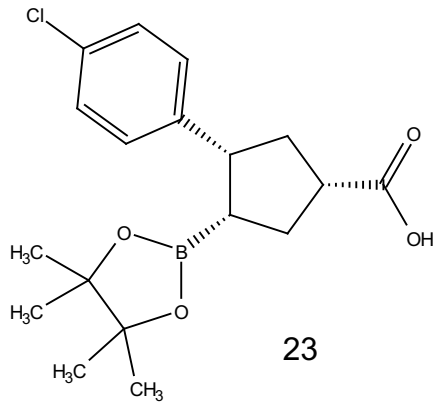
22

178.91
143.75
138.42
131.99
130.03
129.95
128.17
128.07
127.16
77.37 cdcl3
77.05 cdcl3
76.74 cdcl3
75.62
52.10
39.16
39.04
37.85
34.93

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10

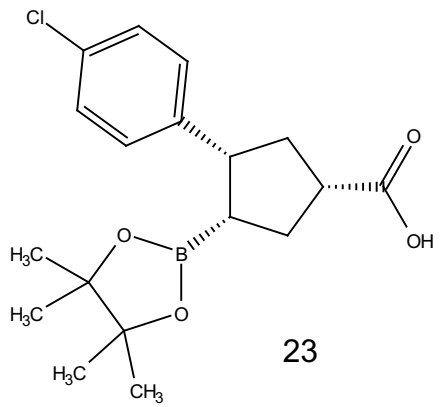
f1 (ppm)

CDCl3, 600 MHz



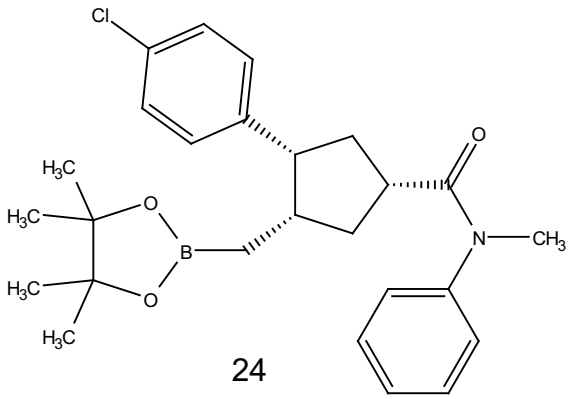
23

CDCl3, 126 MHz



23

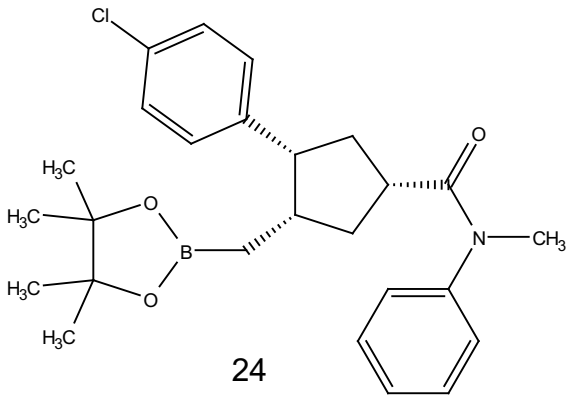
CDCl3, 500 MHz



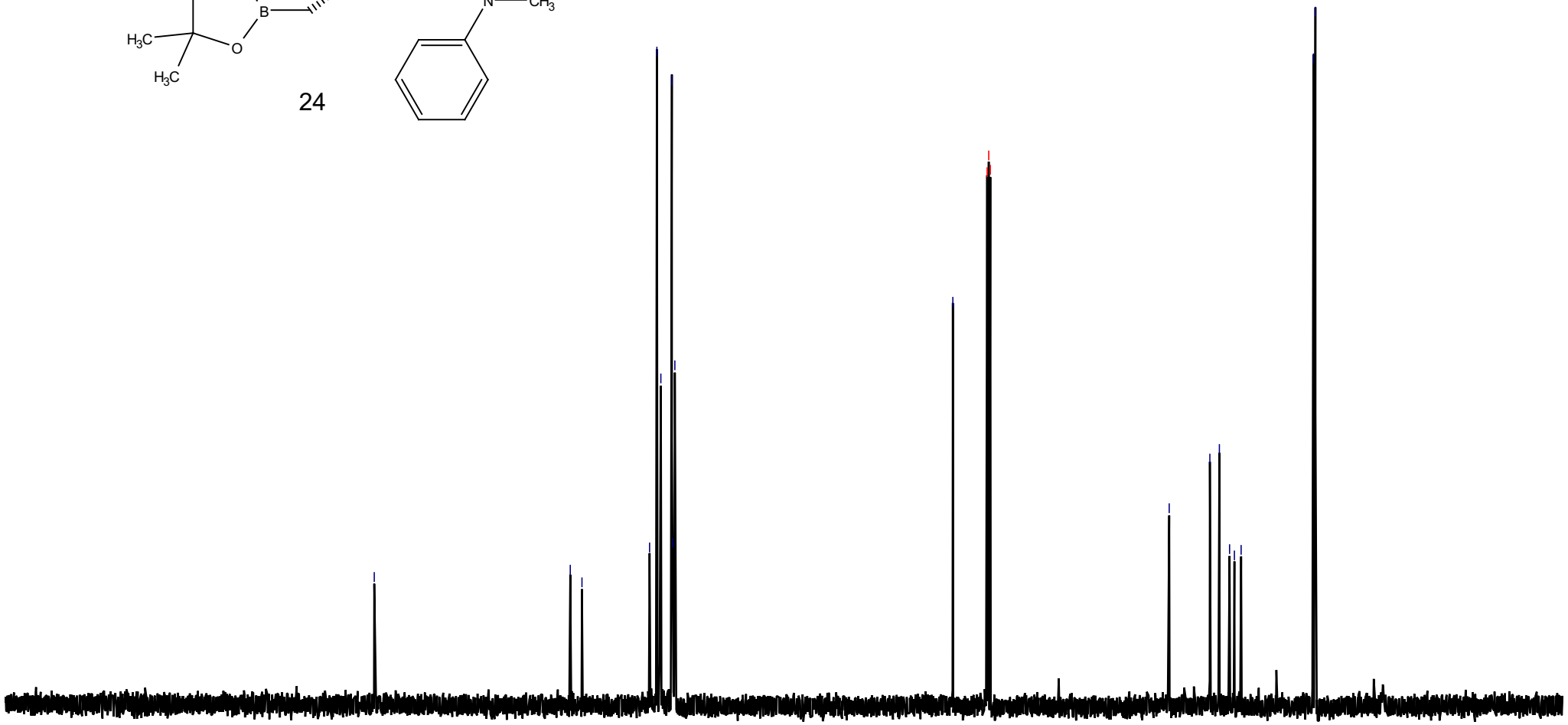
24

CDCl3, 126 MHz

175.71
144.25
142.37
131.52
130.35
129.71
127.94
127.78
127.47
82.84
77.33 cdcl3
77.08 cdcl3
76.82 cdcl3
48.11
41.59
40.06
38.42
37.65
36.57
24.95
24.64



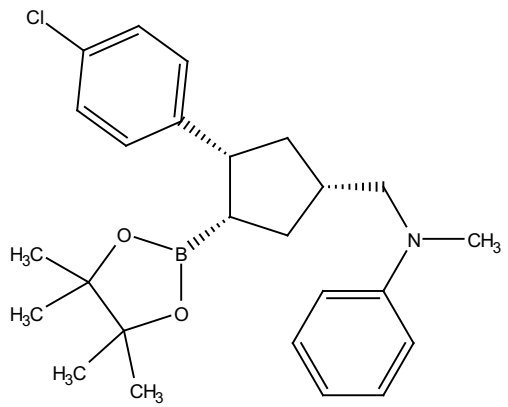
24



230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10

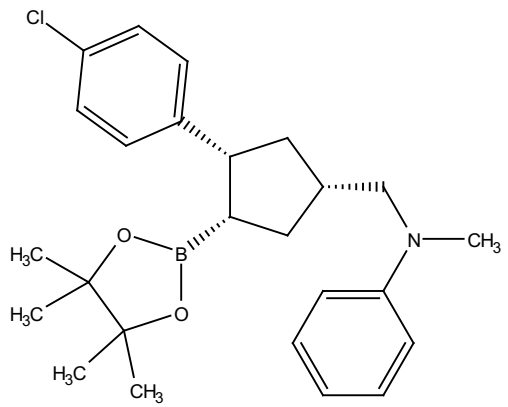
f1 (ppm)

CDCl3, 500 MHz



25

CDCl3, 126 MHz



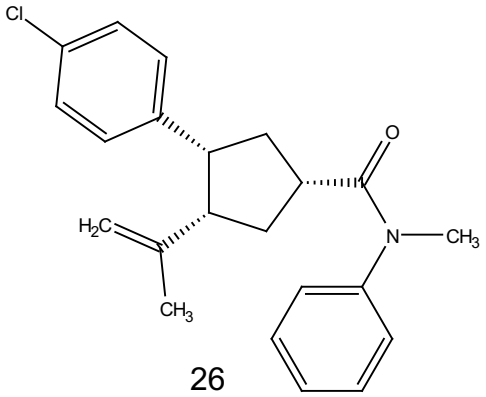
25

149.47
144.50
131.41
129.40
129.13
127.99
115.79
112.02
82.90
77.31 cdcl3
77.05 cdcl3
76.80 cdcl3
57.57
45.95
40.01
39.00
38.86
33.49
24.78
24.53

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10

f1 (ppm)

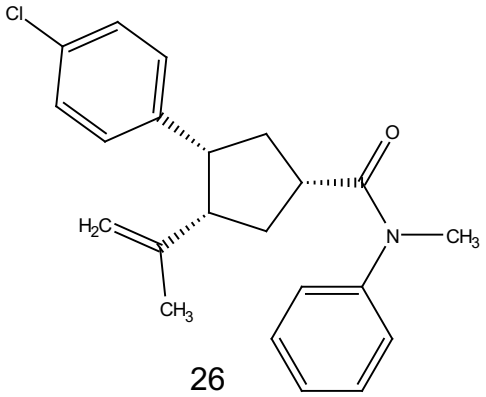
CDCl3, 500 MHz



26

f1 (ppm)

CDCl3, 126 MHz



26

175.42
145.14
144.14
142.33
131.53
130.07
129.82
127.91
127.76
127.42
111.80
77.32 cdcl3
77.07 cdcl3
76.81 cdcl3
51.59
46.96
41.30
37.67
37.55
34.89
22.64

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10

f1 (ppm)