Enantioselective Synthesis of α-Amidoboronates Catalyzed by Planar-Chiral NHC-Cu(I) Complexes

C. Benjamin Schwamb†, Keegan P. Fitzpatrick†, Alexander C. Brueckner,‡ H. Camille Richardson, ‡ Paul H.–Y. Cheong,‡ and Karl A. Scheidt*†

†Department of Chemistry, Center for Molecular Innovation and Drug Discovery, Chemistry of Life Processes Institute, Northwestern University, Evanston, IL 60208 (USA)

‡Department of Chemistry, Oregon State University, 153 Gilbert Hall, Corvallis, OR 97331 (USA)

Supporting Information

Table of Contents

General Information

All reactions were carried out under a nitrogen atmosphere in oven-dried glassware with magnetic stirring. THF, toluene, and DMF were purified by passage through a bed of activated alumina.[1] Reagents were purified prior to use unless otherwise stated following the guidelines of Perrin and Armarego.[2] Bis(pinacolato)diboron was recrystallized from hexanes. Silicycle SiliaFlash P60 silica gel 60 (230-400 mesh) was used for column chromatography. Analytical thin layer chromatography was performed on EM Reagent 0.25 mm silica gel 60-F plates. Visualization was accomplished with UV light. Infrared spectra were recorded on a Bruker Tensor 37 FT-IR spectrometer. ^{1}H NMR spectra were recorded on AVANCE III 500 MHz w/ direct cryoprobe (500 MHz) spectrometer and are reported in ppm using solvent as an internal standard ($CDCl_3$ at 7.26 ppm, $(CD_3)_2SO$ at 2.50 ppm). Data are reported as (ap = apparent, s = singlet, d = doublet, t = apparent triplet, q = quartet, m = multiplet, b = broad; coupling constant(s) in Hz; integration.) Proton-decoupled ^{13}C NMR spectra were recorded on an AVANCE III 500 MHz w/ direct cryoprobe (125 MHz) spectrometer and are reported in ppm using solvent as an internal standard ($CDCl_3$ at 77.16 ppm, $(CD_3)_2SO$ at 39.52 ppm). ^{19}F and ^{11}B NMR spectra were acquired at 26 °C on a 400 MHz Agilent 400MR-DD2 spectrometer equipped with a OneNMR probe and a 7600AS autosampler; this system was funded by NSF CRIF grant CHE-104873. Optical rotations were measured on a Perkin Elmer Model 341 Polarimeter with a sodium lamp. Mass spectra were obtained on a WATERS Acquity-H UPLC-MS with a single quad detector (ESI) or an Agilent 7890 gas chromatograph equipped with a 5975C single quadrupole EI-MS. Accurate masses were obtained using an Agilent 6120A LC-TOF MS.

Standardization of ^{11}B and ^{19}F NMR Spectra

Standardization of all heteronuclear spectra was conducted using the unified scale according to eqn. (1).

$$\Xi_X = 100\times(\nu_X/\nu_o) \quad (1)$$

where ν_o = the absolute ^{1}H frequency of 0.00 ppm (δ_{TMS}) for experiments conducted in $CDCl_3$, δ_{TMS} + 0.062 ppm for DMSO, and δ_{TMS} – 0.160 for acetone-d_6, taken consecutively with heteronucelar experiments.

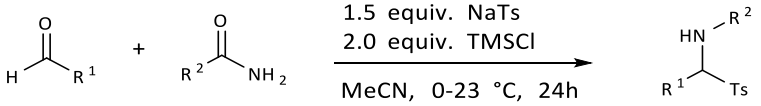
and Ξ_{19F} = 94.094011 and Ξ_{11B} = 32.083974.

and ν_x = abosolute frequency of the 0 ppm position for isotope x.

General Synthetic Procedures and Spectral Data for new Compounds

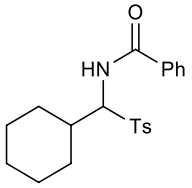
Synthesis & characterization of α-tosyl Benzamide starting materials

α-tosyl benzamides **1a** and **1c** were prepared according to a published procedure.[3]

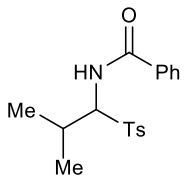


Method A: To a mixture of aldehyde (16.5 mmol 1.0 equiv.), sodium p-toluenesulfinate (4.41 g, 27.8 mmol, 1.5 equiv.), and amide (24.8 mmol, 1.5 equiv.) in MeCN (500 mL, 0.03 M) at 0 °C was added TMSCl (4.22 mL, 33.0 mmol, 2 equiv.) dropwise. Upon completion of addition the reaction was allowed to warm to room temperature and stirred for 24 hours. 500 mL water was then added and the reaction was stirred for 30 minutes. The resulting precipitate was isolated by filtration, washed with water (3 x 50 mL), and dried under vacuum at 50 °C for 16 hours to yield the product as a white solid.

Method B: Procedure followed that of **Method A** except that the reaction was immediately concentrated *in vacuo* after the reaction was deemed complete. 50 mL of diethyl ether was then added to the concentrate and the resulting suspention was stirred for 15 minutes. The solid impurities were removed by filtration, the filtrate was concentrated *in vacuo*, and the product was then purified via flash column chromotography on silica gel.

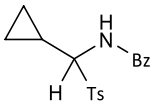


***N*-(cyclohexyl(tosyl)methyl)benzamide (1a)**: Prepared according to **Method A** using cyclohexane carboxaldehyde (1.85 g, 16.46 mmol, 1 equiv.) and benzamide (3.0 g, 24.8 mmol, 1.5 equiv.) to afford *N*-(cyclohexyl(tosyl)methyl)benzamide (5.29 g, 14.24 mmol, 87%). Analytical data matches that of previously reported spectra.[3] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.1 Hz, 2H), 7.62 (d, *J* = 7.2 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 2H), 6.61 (d, *J* = 10.8 Hz, 1H), 5.30 (dd, *J* = 10.8, 3.8 Hz, 1H), 2.57 (tq, *J* = 11.6, 3.5 Hz, 1H), 2.37 (s, 3H), 2.21 (dt, *J* = 12.4, 3.4 Hz, 1H), 1.89 (dt, *J* = 12.7, 3.4 Hz, 1H), 1.79 (tt, *J* = 12.7, 3.9 Hz, 2H), 1.73 – 1.58 (m, 2H), 1.39 (dtt, *J* = 17.0, 12.8, 3.6 Hz, 2H), 1.32 – 1.05 (m, 3H).

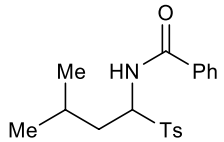


***N*-(2-methyl-1-tosylpropyl)benzamide (1b):** Prepared according to **Method B** using isobutyraldehyde (1.0 mL, 10.96 mmol, 1 equiv.) and benzamide (2.0 g, 16.4 mmol, 1.5 equiv.)

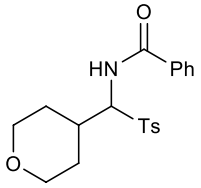
and purified by flash column chromatography (10-40% EtOAc/hex; TLC 40% EtOAc/hex, UV, CAM or KMnO4, R_f 0.57) to afford *N*-(2-methyl-1-tosylpropyl)benzamide (3.21 g, 9.7 mmol, 88%) as a white solid. Analytical data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 6.9 Hz, 1H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.25 (d, *J* = 7.7 Hz, 2H), 6.57 (d, *J* = 10.8 Hz, 1H), 5.32 (dd, *J* = 10.8, 3.7 Hz, 1H), 2.89 (dhept, *J* = 6.7, 3.7 Hz, 1H), 2.38 (s, 3H), 1.22 (d, *J* = 6.7 Hz, 3H), 1.12 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.77, 145.18, 134.97, 133.20, 132.40, 129.96, 128.94, 128.80, 127.03, 72.71, 27.48, 21.82, 20.87, 17.31. LRMS (ESI): Mass calcd. for $C_{18}H_{22}NO_3S$ $[M+H]^+$: 332; found 332.



***N*-(cyclopropyl(tosyl)methyl)benzamide (1c):** Prepared according to **Method B** using cyclopropane carbaldehyde (2.0 mL, 26.8 mmol, 1 equiv.) and benzamide (4.86 g, 40.1 mmol, 1.5 equiv.) and purified via flash column chromatography (30-70% EtOAc/hex; TLC 40% EtOAc/hex, UV, R_f 0.48) to afford *N*-(cyclopropyl(tosyl)methyl)benzamide (6.78 g, 20.58 mmol, 77%) as a white solid. Analytical data: Analytical data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 7.7 Hz, 2H), 7.52 (t, *J* = 7.7 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.27 (d, *J* = 7.6 Hz, 2H), 6.99 – 6.64 (m, 1H), 4.90 (t, *J* = 9.7 Hz, 1H), 2.39 (s, 3H), 1.47 (ddq, *J* = 13.0, 8.6, 4.8 Hz, 1H), 0.91 – 0.76 (m, 1H), 0.76 – 0.55 (m, 2H), 0.47 (dp, *J* = 6.0, 4.8 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.45, 145.28, 134.37, 133.07, 132.39, 129.91, 129.23, 128.86, 127.19, 73.24, 21.84, 9.65, 5.31, 2.60. LRMS (ESI): Mass calcd. for $C_{18}H_{20}NO_3S$ $[M+H]^+$: 330; found 330.

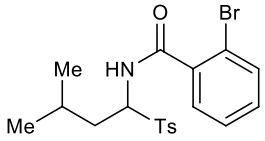


***N*-(3-methyl-1-tosylbutyl)benzamide (1d):** Prepared according to **Method A** using isovaleraldehyde (2.0 mL, 18.23 mmol, 1 equiv.) and benzamide (3.31 g, 27.3 mmol, 1.5 equiv.) to afford *N*-(3-methyl-1-tosylbutyl)benzamide (5.32 g, 15.4 mmol, 84%) as a white solid. Analytical data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.9 Hz, 2H), 7.61 (t, *J* = 8.0 Hz, 2H), 7.56 – 7.45 (m, 1H), 7.45 – 7.32 (m, 2H), 7.25 (d, *J* = 7.9 Hz, 2H), 6.95 – 6.43 (m, 1H), 5.71 – 5.33 (m, 1H), 2.38 (s, 3H), 2.21 – 2.03 (m, 1H), 2.03 – 1.84 (m, 1H), 1.82 – 1.65 (m, 1H), 0.97 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.56, 145.25, 133.77, 133.02, 132.25, 129.89, 129.22, 128.74, 127.18, 68.35, 34.98, 25.05, 23.43, 21.84, 21.41.

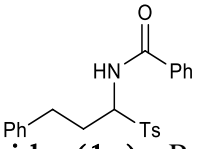


***N*-((tetrahydropyran-4-yl)(tosyl)methyl)benzamide (1e)**: Prepared according to **Method B** using tetrahydropyran-4-carbaldehyde (1.0 g, 8.76 mmol, 1 equiv.) and benzamide (1.59 g, 13.14 mmol, 2 equiv.) and purified by flash column chromatography (40-80% EtOAc/hex; TLC 40% EtOAc/hex, UV, R_f 0.25) to afford *N*-((tetrahydropyran-4-yl)(tosyl)methyl)benzamide (2.15 g, 5.76 mmol, 66%) as a white solid. Analytical data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 7.5 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 6.60 (d, *J* = 10.4 Hz, 1H), 5.33 (dd, *J* = 10.8, 4.3 Hz, 1H), 4.01 (ddd, *J* = 15.7, 11.8, 4.2 Hz, 2H), 3.50 (ddd, *J* = 11.9, 11.8, 6.2 Hz, 2H), 2.97 –

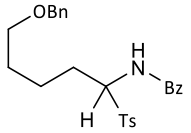
2.66 (m, 1H), 2.38 (s, 3H), 2.05 (d, J = 13.0 Hz, 1H), 1.79 (d, J = 13.2 Hz, 1H), 1.73 – 1.48 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.72, 145.46, 134.58, 132.91, 132.57, 130.04, 128.99, 128.81, 127.01, 71.71, 67.63, 67.32, 34.46, 30.20, 27.83, 21.85. LRMS (ESI): Mass calcd. for $C_{20}H_{24}NO_4S$ $[M+H]^+$: 374; found 374.



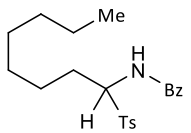
2-bromo-*N*-(3-methyl-1-tosylbutyl)benzamide (1f): Prepared according to **Method A** using isovaleraldehyde (0.730 mL, 6.7 mmol, 1 equiv.) and 2-bromobenzamide (2.0 g, 10.0 mmol, 1.5 equiv.) to afford 2-bromo-*N*-(3-methyl-1-tosylbutyl)benzamide (2.31 g, 5.4 mmol, 82%) as a white solid. Analytical data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, J = 7.9 Hz, 2H), 7.55 (d, J = 7.6 Hz, 1H), 7.34 (d, J = 8.0 Hz, 2H), 7.34 – 7.23 (m, 2H), 7.12 (dd, J = 7.3, 2.0 Hz, 1H), 6.35 (d, J = 10.4 Hz, 1H), 5.51 (ddd, J = 11.0, 10.4, 3.1 Hz, 1H), 2.44 (s, 3H), 2.09 (ddd, J = 14.2, 11.0, 2.8 Hz, 1H), 1.98 – 1.77 (m, 2H), 1.03 (d, J = 6.4 Hz, 3H), 0.99 (d, J = 6.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.40, 145.39, 136.21, 133.92, 133.77, 132.01, 129.98, 129.61, 129.35, 127.62, 119.16, 67.88, 35.13, 24.97, 23.58, 21.90, 21.28.



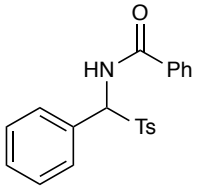
***N*-(3-phenyl-1-tosylpropyl)benzamide (1g):** Prepared according to **Method A** using hydrocinnamaldehyde (tech. grade 90% w/w, 2.42 mL, 16.5 mmol, 1 equiv.) and benzamide (3.0 g, 24.8 mmol, 1.5 equiv.) to afford *N*-(3-phenyl-1-tosylpropyl)benzamide (5.12 g, 14.0 mmol, 85%) as a white solid. Analytical data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, J = 8.0 Hz, 2H), 7.57 – 7.48 (m, 3H), 7.40 (t, J = 7.6 Hz, 2H), 7.35 – 7.21 (m, 4H), 7.21 – 7.11 (m, 3H), 6.46 (d, J = 10.4 Hz, 1H), 5.47 (ddd, J = 10.7, 10.4, 3.3 Hz, 1H), 2.83 (dd, J = 8.9, 7.2 Hz, 2H), 2.69 (dddd, J = 14.2, 8.9, 7.2, 3.3 Hz, 1H), 2.38 (s, 3H), 2.26 (ddt, J = 14.2, 10.7, 7.2 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.50, 145.39, 140.03, 133.71, 132.96, 132.40, 129.97, 129.18, 128.83, 128.54, 127.05, 126.59, 69.05, 31.81, 28.63, 21.85. LRMS (ESI): Mass calcd. for $C_{23}H_{24}NO_3S$ $[M+H]^+$: 394; found 394.



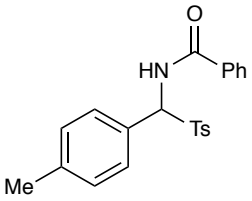
***N*-(5-(benzyloxy)-1-tosylpentyl)benzamide (1h):** Prepared according to **Method B** using 5-(benzyloxy)pentanal (400 mg, 2.08 mmol, 1 equiv.) and benzamide (378 mg, 3.12 mmol, 1.5 equiv.) and purified via flash column chromatography to afford *N*-(5-(benzyloxy)-1-tosylpentyl)benzamide (640 mg, 1.42 mmol, 68%) as a white solid. Analytical data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, J = 8.3 Hz, 2H), 7.57 (d, J = 7.4 Hz, 2H), 7.51 (t, J = 7.5 Hz, 1H), 7.40 (t, J = 7.7 Hz, 2H), 7.34 – 7.28 (m, 4H), 7.30 – 7.20 (m, 3H), 6.78 – 6.28 (m, 1H), 5.44 (td, J = 10.7, 3.2 Hz, 1H), 4.46 (d, J = 2.9 Hz, 2H), 3.56 – 3.32 (m, 2H), 2.38 (m, 4H), 2.03 – 1.88 (m, 1H), 1.78 – 1.46 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.65, 145.32, 138.48, 133.81, 133.04, 132.34, 129.94, 129.18, 128.84, 128.52, 127.84, 127.72, 127.09, 73.09, 69.84, 69.34, 29.14, 26.49, 22.62, 21.85. LRMS (ESI): Mass calcd. for $C_{26}H_{30}NO_4S$ $[M+H]^+$: 452; found 452.



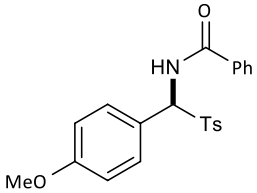
***N*-(1-tosyloctyl)benzamide (1i):** Prepared according to **Method B** using *n*-octanal (1.0 mL, 6.43 mmol, 1 equiv.) and benzamide (1.20 g, 9.65 mmol, 1.5 equiv.) and purified via flash column chromatography to afford *N*-(1-tosyloctyl)benzamide (1.88 g, 4.85 mmol, 75%) as a clear vicous oil that gradually solidified to a white solid under high vacuum. Analytical data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.9 Hz, 2H), 7.64 (d, *J* = 7.5 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.24 (d, *J* = 7.9 Hz, 2H), 7.02 (d, *J* = 10.3 Hz, 1H), 5.46 (td, *J* = 10.8, 3.3 Hz, 1H), 2.37 (s, 3H), 2.31 (dddd, *J* = 13.4, 9.8, 6.4, 3.3 Hz, 1H), 2.09 – 1.77 (m, 1H), 1.67 – 1.01 (m, 10H), 0.84 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.80, 145.17, 133.85, 132.98, 132.17, 129.83, 129.10, 128.65, 127.19, 69.55, 31.71, 29.08, 28.99, 26.60, 25.50, 22.61, 21.76, 14.11. LRMS (ESI): Mass calcd. for $C_{22}H_{30}NO_3S$ $[M+H]^+$: 388; found 388.



***N*-(phenyl(tosyl)methyl)benzamide (1j):** Prepared according to **Method A** using benzaldehyde (1.67 mL, 16.5 mmol, 1 equiv.) and benzamide (3.0 g, 24.6 mmol, 1.5 equiv.) to afford *N*-(phenyl(tosyl)methyl)benzamide: (4.41 g, 73%) as a white solid. Analytical data matches that of previously reported spectra[4]



***N*-(*p*-tolyl(tosyl)methyl)benzamide (1k):** Prepared according to **Method A** using *p*-tolualdehyde (1.9 mL, 16.5 mmol, 1 equiv.) and benzamide (3.0 g, 24.6 mmol, 1.5 equiv.) to afford *N*-(p-tolyl(tosyl)methyl)benzamide: (3.26 g, 53%) as a white solid. Analytical data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 – 7.74 (m, 2H), 7.68 – 7.64 (m, 2H), 7.55 – 7.50 (m, 1H), 7.46 – 7.40 (m, 4H), 7.28 – 7.21 (m, 4H), 7.19 – 7.07 (m, 1H), 6.42 (dt, *J* = 10.5, 3.1 Hz, 1H), 2.41 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.16, 145.42, 140.25, 133.95, 133.22, 132.43, 129.94, 129.77, 129.39, 128.93, 127.18, 72.32, 21.88, 21.47. HRMS (ESI/TOF) m/z: Calcd. for $C_{22}H_{21}NO_3S$: 379.1242; found 379.1249.

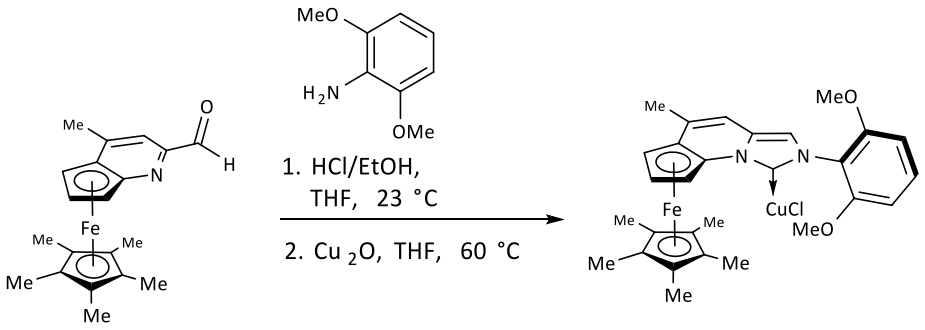


***N*-((4-methoxyphenyl)(tosyl)methyl)benzamide (1l):** Prepared according to **Method A** using 4-methoxybenzaldehyde (2.00 mL, 16.4 mmol, 1 equiv.) and benzamide (3.00 g, 24.6 mmol, 1.5 equiv.) to afford *N*-((4-methoxyphenyl)(tosyl)methyl)benzamide**:** (5.42 g, 16.4 mmol, 83%) as a white solid. Analytical data matches that of previously reported structure[4]: ^{1}H NMR (500 MHz, $CDCl_3$) δ δ 7.76 (d, *J* = 8.3 Hz, 2H), 7.66 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.53 (tt, *J* = 7.5, 1.9 Hz, 1H), 7.49 – 7.34 (m, 4H), 7.27 (d, *J* = 7.3 Hz, 2H), 7.08 (d, *J* = 10.3 Hz, 1H), 6.94 (d, *J* = 8.7 Hz, 2H), 6.40 (d, *J* = 10.3 Hz, 1H), 3.83 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.27, 161.13, 145.51, 134.01, 133.32, 132.56, 130.47, 130.05, 129.47, 129.03, 127.29, 122.26,

114.64, 72.15, 55.63, 21.98.

Synthesis & characterization of Catalysts C, G and H

Aldehyde **(-)-SI-1** was prepared according to our previously published procedure.[5]

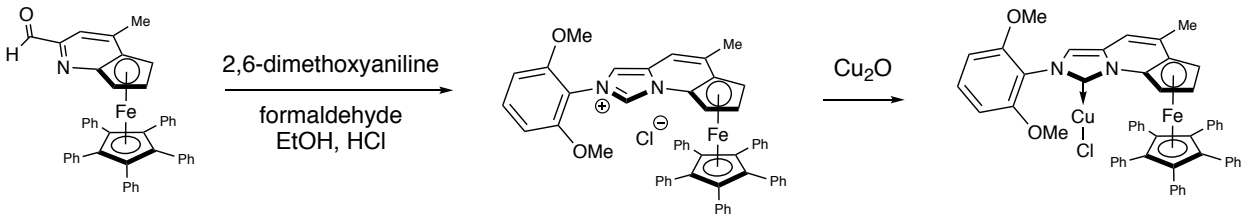


(-)-SI-1 **Catalyst C**

(–)-Ferrocenyl 2,6-dimethoxyphenyl imidazolium Copper Chloride Complex (Catalyst C):

A 2 dram vial equipped with a stir bar was charged with formaldehyde (37%, 69.7 mg, 0.859 mmol), THF (4.5 mL), and 2,6-dimethoxyaniline (79.0 mg, 0.515 mmol). The mixture was stirred at ambient temperature for 30 min. and then HCl (3.0 M in EtOH, 0.329 mL, 0.988 mmol) was added and the mixture was stirred for 30 min. (-)-Pentamethyl-η^5-cyclopentadienyl (1-methyl-η^5-cyclopenta[b]pyridinyl-3-carbaldehyde)iron (**SI-1**) (150 mg, 0.429 mmol) was then added, and the reaction was allowed to stir at ambient temperature for ~3 h while monitoring by TLC analysis (90:10:1, CH_2Cl_2:MeOH:AcOH, Rf~0.25). The solvent was then removed *in vacuo* and the residue was redissolved in 1.0 mL dichloromethane. The resulting homogeneous solution was directly loaded on a plug of neutral alumina and impurities were eluted using additional dichloromethane. The azolium salt was then eluted as a bright-orange band using CH_2Cl_2:EtOH (5:1), concentrated *in vacuo*, and redissolved in 5.0 mL THF (0.1 M) in a 1 dram vial under dry nitrogen atmosphere. To this solution was added Cu_2O (63 mg, 0.429 mmol) and the mixture was heated at 60 °C for 16 hours. The solution was then concentrated and the residue was purified by column chromatography on silica gel (CH_2Cl_2, Rf~0.4) to provide the complex as an orange solid (184 mg, 0.309 mmol, 72% yield). X-ray quality crystals were obtained by vapor diffusion (DCM/pentane, -30 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (t, J = 8.5 Hz, 1H), 7.03 (s, 1H), 6.75 – 6.62 (m, 3H), 5.53 (dd, J = 2.6, 1.2 Hz, 1H), 3.99 (dd, J = 2.6, 1.2 Hz, 1H), 3.88 – 3.71 (m, 7H), 2.25 (d, J = 1.4 Hz, 3H), 1.67 (s, 15H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.05, 156.00, 155.87, 135.08, 130.67, 130.05, 118.17, 115.88, 107.81, 104.72, 104.70, 93.18, 81.01, 71.25, 65.03, 62.85, 56.31, 56.10, 19.21, 9.99. IR (ATR, neat): 3107, 2921, 2852, 1596, 1481, 1100, 723 cm^{-1}. LCMS (ESI$^+$) mass calcd. for $C_{29}H_{32}CuFeN_2O_2$ [M-Cl]$^+$, 559.1; found 559.3.

Aldehyde (+)-**SI-2** was prepared analogously to (-)-**SI-1**, using pentaphenylcyclopentadiene, according to our previously published procedure.[5]



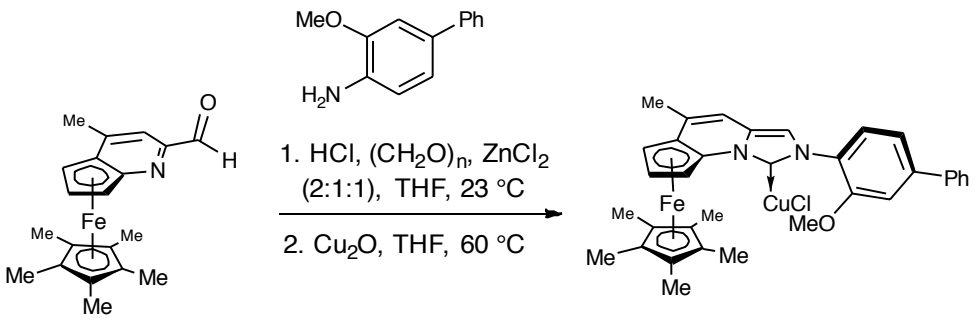
(+)-SI-2 **(+)-NHC G** **(+)-G**

(+)-Ferrocenyl 2,6-dimethoxyphenyl pentaphenyl imidazolium chloride (NHC G)

Prepared analogously to catalyst **C**, using aldehyde **SI-2** (390 mg, 1.1 mmol) and 2,6-dimethyoxy aniline. The unpurified residue was purified by flash chromatography on neutral alumina using CH_2Cl_2:EtOH(5:1) to afford the product as an orange solid (398 mg, 69%). Analytical data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.91 (s, 1H), 7.60 (s, 1H), 7.43 (t, J = 8.6 Hz, 1H), 7.17 -7.10 (m, 5H), 7.10 - 7.00 (m, 10H), 6.94 - 6.85 (m, 10H), 6.68 (d, J = 8.6 Hz, 2H), 6.17 (dd, J = 2.7, 1.2 Hz, 1H), 4.73 (dd, J = 2.8, 1.2 Hz, 1H), 4.46 (t, J = 2.7 Hz, 1H), 3.64 (s, 6H), 2.32 (d, J = 1.4 Hz, 3H); 13C NMR (126 MHz, CDCl3) δ 154.2, 137.4, 133.8, 132.1, 132.0, 130.0, 127.4, 126.8, 116.7, 112.4, 110.6, 104.4, 91.7, 87.7, 87.7, 81.0, 75.6, 68.0, 64.5, 56.6, 20.3. IR (neat): 3052, 2937, 2839, 1600, 1485, 1111, 741, 699 cm^{-1}. LCMS (ESI): Mass calcd for $C_{54}H_{43}FeN_2O_2$ $[M]^+$, 807.3; found 807.5.

(+)-Ferrocenyl 2,6-dimethoxyphenyl imidazolium Copper Chloride Complex ((+)-G)

Prepared analogously to catalyst **C,** using pentaphenyl imidazolium chloride (**NHC G**) (40 mg, 0.047 mmol) and copper(I) oxide (7.5 mg 0.052 mmol). Obtained as a bight orange solid (37 mg, 0.041 mmol, 86% yield) ^{1}H NMR (500 MHz, $CDCl_3$-*d*) δ 7.37 (t, *J* = 8.5 Hz, 1H), 7.18 – 7.08 (m, 5H), 7.05 (dd, *J* = 8.4, 6.8 Hz, 10H), 7.01 – 6.92 (m, 11H), 6.77 (d, *J* = 1.5 Hz, 1H), 6.65 (d, *J* = 8.5 Hz, 2H), 6.04 (dd, *J* = 2.7, 1.2 Hz, 1H), 4.64 (dd, *J* = 2.7, 1.2 Hz, 1H), 4.38 (t, *J* = 2.7 Hz, 1H), 3.74 (s, 3H), 3.44 (s, 3H), 2.20 (d, *J* = 1.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.81, 155.74, 155.49, 147.70, 134.79, 133.86, 132.41, 132.07, 130.73, 130.62, 127.63, 127.42, 126.52, 117.90, 117.07, 116.29, 111.98, 104.66, 104.59, 104.23, 97.13, 87.61, 80.34, 73.90, 67.02, 63.38, 56.25, 55.98, 20.31. IR (ATR, neat): 3084, 3056, 2935, 2836, 1599, 1481, 1259, 1109, 740, 698. cm^{-1}. LCMS (ESI$^+$) mass calcd. for $C_{54}H_{42}CuFeN_2O_2$ $[M\text{-}Cl]^+$, 869.2; found 869.1.



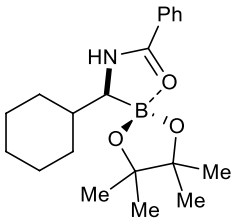
(-)-SI-1 Catalyst H

Catalyst H: To a solution of 3-methoxy-[1,1'-biphenyl]-2-amine (28 mg, 0.143 mmol, 1.0 equiv.) and (–)-pentamethyl-η^5-cyclopentadienyl (1-methyl-η^5-cyclopenta[b]pyridinyl-3-carbaldehyde)iron (**SI-1**) (50 mg, 0.143 mmol, 1.0 equiv.) in THF (1.4 mL, 0.1 M) was added dropwise a solution of paraformaldehyde (5.2 mg, 0.172 mmol, 1.2 equiv.) and $ZnCl_2$ (23.4 mg, 0.172 mmol, 1.2 equiv.) in concentrated HCl (27.4 µL, 38% w/w, 2.4 equiv.). The dark-green solution was stirred at room temperature for 30 minutes, whereupon the reaction changed to a red-orange color and a small amount of precipitate was observed. The solvent was then removed *in vacuo* and the residue was redissolved in 1.0 mL dichloromethane. The resulting homogeneous solution was directly loaded on a plug of neutral alumina and impurities were eluted using additional dichloromethane. The azolium salt was then eluted as a bright-orange band using CH_2Cl_2:EtOH (5:1), concentrated *in vacuo*, and redissolved in 1.4 mL THF (0.1 M) in a 1 dram vial under dry nitrogen atmosphere. To this solution was added Cu_2O (19 mg, 0.13 mmol) and the mixture was heated at 60 °C for 16 hours. The solution was then concentrated and the residue was purified by column chromatography on silica gel (CH_2Cl_2, Rf~0.4) to provide the complex as an orange solid (60 mg, 0.094 mmol, 72% yield). X-ray quality crystals were obtained by vapor diffusion (DCM/pentane, -30 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 – 7.61 (m, 2H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.53 – 7.46 (m, 2H), 7.42 (tt, *J* = 7.4, 1.8 Hz, 1H), 7.30 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.29 (s, 1H), 7.25 (s, 1H), 6.74 (q, *J* = 1.3 Hz, 1H), 5.59 (dd, *J* = 2.7, 1.1 Hz, 1H), 4.02 (dd, *J* = 2.7, 1.2 Hz, 1H), 3.92 (s, 3H), 3.85 (t, *J* = 2.6 Hz, 1H), 2.27 (d, *J* = 1.4 Hz, 3H), 1.67 (s, 15H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 180.37, 153.71, 144.01, 136.01, 130.53, 129.09, 128.68, 128.42, 128.17, 128.11, 127.49, 120.17, 115.45, 111.58, 107.52, 81.08, 71.51, 65.24, 62.99, 56.13, 19.26, 10.00. LCMS (ESI$^+$) mass calcd. for $C_{34}H_{34}CuFeN_2O$ [M-Cl]$^+$, 605.1; found 605.3.

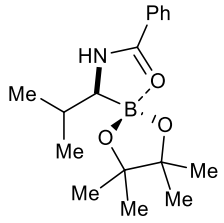
Synthesis & characterization of enantioenriched α-amidoboronic esters

All α-amidoboronic esters were prepared according to the following general procedure unless otherwise noted:

Inside a glovebox, to a 2-dram vial was added catalyst **C** (5 mol%), sodium *tert*-butoxide (6 mol%) and THF (0.17 M). The vial was capped with a teflon septum, and the resulting orange solution was stirred for 15 minutes at room temperature. To a separate 2-dram vial was added tosyl benzamide (1 equiv.), cesium carbonate (2.0 equiv.), B_2Pin_2 (1.2 equiv.) and a teflon stirbar. The orange solution in the first vial was then transferred to the other vial via syringe and stirred vigorously at room temperature for 12 hours, or until the reaction was deemed complete via GCMS. The crude mixture was then eluted through a short plug of deactivated silica gel (35% w/w H_2O), washing with 5-10 mL EtOAc. The crude material was then dry loaded on celite and purified via flash column chromatography on deactivated silica gel (35% w/w H_2O).

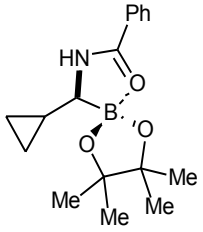


(*S*)-*N*-(cyclohexyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)benzamide (2a): Prepared according to the general procedure using 200 mg **1a** (0.538 mmol) to afford (*S*)-*N*-(cyclohexyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)benzamide (120 mg, 65% yield. Analytical data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.8 Hz, 2H), 7.52 (tt, *J* = 8.2, 7.4, 1.0 Hz, 1H), 7.43 (dd, *J* = 8.4, 7.0 Hz, 2H), 6.92 (s, 1H), 3.01 (dd, *J* = 6.2, 4.1 Hz, 1H), 1.95 – 1.79 (m, 2H), 1.79 – 1.49 (m, 4H), 1.28 (d, *J* = 3.0 Hz, 13H), 1.26 – 1.18 (m, 2H), 1.18 – 1.01 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.63, 132.45, 131.16, 128.76, 127.62, 82.32, 39.79, 31.39, 30.44, 26.63, 26.46, 25.40, 25.37. LRMS (EI) m/z: $[M-H]^+$ Calcd. for $C_{20}H_{29}BNO_3$ 342.2; Found 342.3. HRMS (ESI/TOF): $[M+H]^+$ Calcd. For $C_{20}H_{31}BNO_3$ 344.2392; Found 344.2390. Enantiomeric ratio was measured by chiral phase HPLC (Regis Whelk-O, 5% *i*-PrOH/Hexanes, 1.0 mL/min, 210 nm) Rt (major) = 5.5 min, Rt (minor) = 4.9 min; er = 98:2.

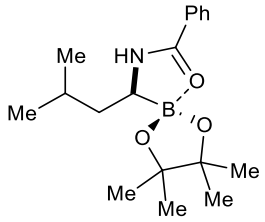


(*S*)-*N*-(2-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)benzamide (2b): Prepared according to the general procedure using 200 mg **1b** (0.603 mmol) to afford (*S*)-*N*-(2-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)benzamide (100 mg, 55% yield). Analytical data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.6 Hz, 1H), 7.54 (td, *J* = 7.3, 1.3 Hz, 1H), 7.48 – 7.42 (m, 2H), 6.65 (d, *J* = 14.1 Hz, 1H), 3.02 (dd, *J* = 6.2, 4.1 Hz, 1H), 2.13 – 1.96 (m, 1H), 1.36 – 1.13 (m, 18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.82, 132.52, 131.01, 128.77, 127.62, 82.21, 30.02, 25.44, 20.90, 20.07. LRMS (EI) m/z: $[M-H]^+$ Calcd. for $C_{17}H_{25}BNO_3$ 302.2; Found 302.2. HRMS (ESI/TOF) m/z: $[M+H]^+$ Calcd. for $C_{17}H_{27}BNO_3$ 304.2082; Found 304.2093. Enantiomeric ratio was measured by chiral phase

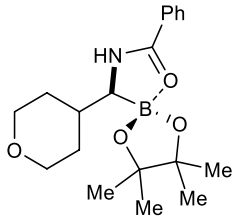
SFC (Chiracel ID-3, 5% *i*-MeOH/CO_2, 3.0 mL/min, 250 nm) Rt (major) = 1.9 min, Rt (minor) = 2.9 min; er = 97:3.



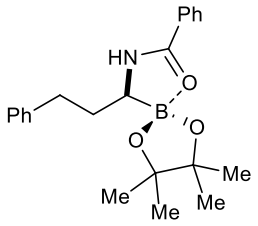
(*S*)-*N*-(cyclopropyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)benzamide (2c): Prepared according to the general procedure using 100 mg **1c** (0.304 mmol) to afford (*S*)-*N*-(2-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)benzamide (44 mg, 48% yield). Analytical data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 – 7.78 (m, 2H), 7.58 (td, *J* = 7.3, 1.3 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.04 (d, *J* = 9.9 Hz, 1H), 2.08 (d, *J* = 10.4 Hz, 1H), 1.29 (m, 12H), 1.15 – 1.03 (m, 1H), 0.61 (tdd, *J* = 8.6, 5.5, 4.4 Hz, 1H), 0.51 (dddd, *J* = 9.2, 7.4, 5.5, 3.9 Hz, 1H), 0.32 (dq, *J* = 9.7, 4.8 Hz, 1H), 0.19 (dtd, *J* = 10.3, 5.2, 4.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.93, 133.46, 132.19, 128.91, 128.04, 81.06, 25.07, 12.19, 4.19, 3.89. LRMS (EI) m/z: $[M-H]^+$ Calcd. for $C_{17}H_{23}BNO_3$ 300.2; Found 300.2. HRMS (ESI/TOF) m/z: $[M+Na]^+$ Calcd. for $C_{17}H_{24}BNO_3Na$ 324.1745; Found 324.1742. Enantiomeric ratio was measured by chiral phase SFC (Chiracel IG-3, 15% *i*-PrOH/CO_2, 3.0 mL/min, 250 nm) Rt (major) = 2.0 min, Rt (minor) = 2.9 min; er = 96:4.



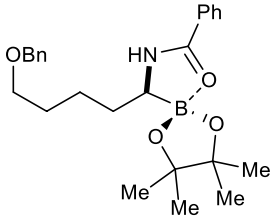
(*S*)-*N*-(3-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)benzamide (2d): Prepared according to the general procedure with the following modification: catalyst **H** was used in place of catalyst **C**. 100 mg **1d** (0.289 mmol) afforded (*S*)-*N*-(3-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)benzamide (56 mg, 61% yield). Analytical data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 7.9, 1.5 Hz, 2H), 7.62 – 7.52 (m, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 6.99 (s, 1H), 3.04 – 2.95 (m, 1H), 1.75 – 1.65 (m, 1H), 1.52 (t, *J* = 7.3 Hz, 2H), 1.31 – 1.23 (m, 12H), 0.97 (d, *J* = 6.5 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.79, 133.16, 128.82, 128.76, 127.93, 81.19, 40.47, 26.32, 25.39, 25.24, 23.60, 22.09. LRMS (EI) m/z: $[M-H]^+$ Calcd. for $C_{18}H_{27}BNO_3$ 316.2; Found 316.2. HRMS (ESI/TOF) m/z: $[M+H]^+$ Calcd. for $C_{18}H_{29}BNO_3$ 318.2238; Found 318.2251. Enantiomeric ratio was measured by chiral phase SFC (Chiracel IA-3, 5% *i*-PrOH/CO_2, 3.0 mL/min, 250 nm) Rt (major) = 7.4 min, Rt (minor) = 10.0 min; er = >99:1.



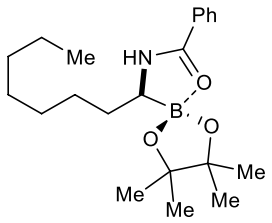
(*S*)-*N*-((tetrahydro-2H-pyran-4-yl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)benzamide (2e): Prepared according to the general procedure using 115 mg **1e** (0.308 mmol) to (*S*)-*N*-((tetrahydro-2H-pyran-4-yl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)benzamide (66 mg, 62% yield). Analytical data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 – 7.72 (m, 2H), 7.57 – 7.49 (m, 1H), 7.43 (dd, *J* = 8.3, 7.1 Hz, 2H), 6.97 (s, 1H), 3.95 (ddd, *J* = 11.2, 5.0, 1.8 Hz, 2H), 3.47 – 3.28 (m, 2H), 2.93 (dd, *J* = 6.2, 3.7 Hz, 1H), 1.94 (tdd, *J* = 10.7, 8.0, 5.4 Hz, 1H), 1.74 (dddd, *J* = 28.8, 12.9, 4.0, 2.1 Hz, 2H), 1.53 – 1.38 (m, 1H), 1.26 (s, 8H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.30, 132.91, 128.91, 127.67, 82.19, 68.21, 68.18, 37.01, 31.32, 30.17, 25.49, 25.36. LRMS (EI) m/z: $[M-H]^+$ Calcd. for $C_{19}H_{27}BNO_4$ 344.2; Found 344.2. HRMS (ESI/TOF) m/z: $[M+Na]^+$ Calcd. for $C_{19}H_{28}BNO_4Na$ 368.2007; Found 368.2013. Enantiomeric ratio was measured by chiral phase HPLC (Chiracel OD-H, 2% *i*-PrOH/Hexanes, 1.0 mL/min, 250 nm) Rt (major) = 7.8 min, Rt (minor) = 8.9 min; er = >99:1.



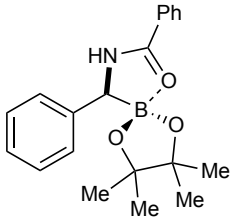
(*S*)-*N*-(3-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)benzamide (2g): Prepared according to the general procedure using 200 mg **1g** (0.508 mmol) to afford (*S*)-*N*-(3-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)benzamide (85 mg, 46% yield. Analytical data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 – 7.47 (m, 4H), 7.43 – 7.36 (m, 2H), 7.36 – 7.30 (m, 2H), 7.30 – 7.22 (m, 2H), 6.50 (s, 1H), 2.96 (ddd, *J* = 12.9, 7.3, 5.0 Hz, 1H), 2.91 (ddd, *J* = 9.8, 4.2, 2.3 Hz, 1H), 2.70 (ddd, *J* = 13.6, 8.8, 7.3 Hz, 1H), 2.19 – 2.09 (m, 1H), 1.96 – 1.83 (m, 1H), 1.27 (d, *J* = 4.7 Hz, 12H). LRMS (EI) m/z: $[M-H]^+$ Calcd. for $C_{22}H_{27}BNO_3$ 364.2; found 364.2. HRMS (ESI/TOF) m/z: $[M+Na]^+$ Calcd. for $C_{22}H_{29}BNO_3Na$ 388.2058; Found 388.2069. Enantiomeric ratio was measured by chiral phase SFC (Chiracel IA-3, 15% MeOH/CO_2, 3.0 mL/min, 250 nm) Rt (major) = 1.3 min, Rt (minor) = 1.1 min; er = 97:3.



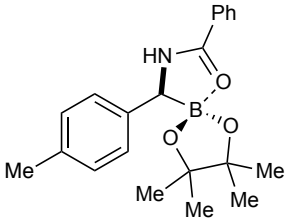
(*S*)-*N*-(5-(benzyloxy)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)benzamide (2h): Prepared according to the general procedure using 95 mg **1h** (0.211 mmol) to afford (*S*)-*N*-(5-(benzyloxy)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)benzamide (31 mg, 37% yield). Analytical data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.2 Hz, 2H), 7.62 – 7.49 (m, 2H), 7.42 – 7.36 (m, 2H), 7.32 (d, *J* = 4.4 Hz, 4H), 7.31 – 7.23 (m, 1H), 4.50 (s, 2H), 3.52 (t, *J* = 6.2 Hz, 2H), 2.93 – 2.82 (m, 1H), 1.77 – 1.49 (m, 5H), 1.26 (d, *J* = 2.7 Hz, 13H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.88, 138.56, 133.15, 128.79, 128.54, 127.96, 127.84, 127.75, 81.09, 73.13, 70.56, 30.89, 29.56, 25.45, 25.23, 24.67. LRMS (EI) m/z: $[M-H]^+$ Calcd. for $C_{25}H_{33}BNO_4$, 422.3; Found 422.2. HRMS (ESI/TOF) m/z: $[M+Na]^+$ Calcd. for $C_{25}H_{33}BNO_4Na$ 446.2478; Found 446.2481. Enantiomeric ratio was measured by chiral phase SFC (Chiracel ID-3, 10% *i*-PrOH/CO_2, 3.0 mL/min, 250 nm) Rt (major) = 5.3 min, Rt (minor) = 6.2 min; er = 88:12.



(*S*)-*N*-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octyl)benzamide (2i): Prepared according to the general procedure using 100 mg **1j** (0.258 mmol) to afford (*S*)- (*S*)-*N*-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octyl)benzamide (41 mg, 44% yield). Analytical data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.79 (d, *J* = 7.6 Hz, 2H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.35 (t, *J* = 7.7 Hz, 2H), 2.93 – 2.67 (m, 1H), 1.70 (ddt, *J* = 13.3, 9.5, 6.2 Hz, 1H), 1.56 (tdd, *J* = 13.5, 8.7, 5.6 Hz, 1H), 1.51 – 1.35 (m, 2H), 1.35 – 1.07 (m, 20H), 0.87 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.78, 133.05, 128.63, 128.14, 81.13, 32.02, 31.39, 29.90, 29.40, 28.04, 25.45, 25.28, 22.82, 14.25. LRMS (EI) m/z: $[M-H]^+$ Calcd. for $C_{21}H_{33}BNO_3$ 358.3; Found 358.3. HRMS (ESI/TOF) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{35}BNO_3$ 360.2708; Found 360.2718. Enantiomeric ratio was measured by chiral phase SFC (Chiracel IG-3, gradient: 5-10% *i*-PrOH/CO_2 0-7 mins, hold: 10% *i*-PrOH/CO_2 7-10 mins, 3.0 mL/min, 250 nm) Rt (major) = 6.4 min, Rt (minor) = 8.5 min; er = 95:5.

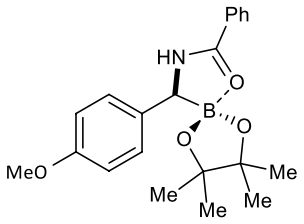


***(S)*-*N*-(phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)benzamide (2j):** Prepared according to the general procedure with the following modifications: MTBE was used as solvent in place of THF and reaction concentration was 0.1M instead of 0.17M. 20 mg **1j** (0.054 mmol) afforded *(S)*-*N*-(phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)benzamide (4.5 mg, 25 %). Data matches previously reported spectra.[6] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 – 7.85 (m, 2H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 2H), 7.43 (s, 1H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.24 (d, *J* = 7.3 Hz, 2H), 7.21 – 7.17 (m, 1H), 4.06 (s, 1H), 1.16 (s, 6H), 1.06 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.12, 141.00, 133.87, 128.89, 128.54, 128.20, 127.11, 126.92, 125.99, 81.01, 24.93, 24.60. The resonance pertaining to the carbon bound to boron was not observed due to quadrupolar relaxation of the ^{11}B nucleus. Enantiomeric ratio was measured by chiral phase HPLC (Regis Whelk-O, 2% *i*-PrOH/Hexanes, 1.0 mL/min, 250 nm) Rt (major) = 12.9 min, Rt (minor) = 10.3 min; er = 91:9.



***(S)*-*N*-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)(*p*-tolyl)methyl)benzamide (2k):** Prepared according to the general procedure with the following modifications: MTBE was used in place of THF and reaction concentration was 0.1M instead of 0.17M using 20.7 mg **1k** (0.054 mmol) afforded *(S)*-*N*-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)(*p*-tolyl)methyl)benzamide (8.5 mg, 45%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 – 7.85 (m, 2H), 7.60

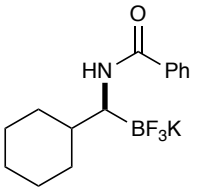
(t, J = 7.5 Hz, 1H), 7.47 (t, J = 7.7 Hz, 2H), 7.15 – 7.05 (m, 4H), 4.00 (s, 1H), 2.31 (s, 3H), 1.14 (s, 6H), 1.05 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.70, 137.68, 135.61, 133.76, 129.00, 128.22, 127. 64, 127.21, 81.20, 25.09, 24.75, 21.22. The resonance pertaining to the carbon bound to boron was not observed due to quadrupolar relaxation of the ^{11}B nucleus. HRMS (ESI/TOF) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{27}BNO_3$ 352.2082; Found 352.2088. Enantiomeric ratio was measured by chiral phase HPLC (Regis Whelk-O, 2% *i*-PrOH/Hexanes, 1.0 mL/min, 250 nm) Rt (major) = 15.2 min, Rt (minor) = 11.0 min; er = 93:7.



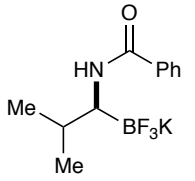
(*S*)-*N*-((4-methoxyphenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)benzamide (2l): Prepared according to the general procedure with the following modification: dichloromethane was used as solvent in place of THF. 100 mg **1i** (0.253 mmol) afforded (*S*)-*N*-((4-methoxyphenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)benzamide (62 mg, 67% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (br, 1H), 7.89 (d, J = 7.2 Hz, 2H), 7.63 – 7.51 (m, 1H), 7.50 – 7.35 (m, 2H), 7.21 – 7.05 (m, 2H), 6.82 (d, J = 8.8 Hz, 2H), 3.93 (s, 1H), 3.78 (s, 2H), 1.09 (s, 6H), 1.00 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.71, 158.14, 133.73, 132.92, 128.89, 128.58, 128.41, 128.39, 113.69, 81.10, 77.38, 55.41, 24.99, 24.63. The resonance pertaining to the carbon bound to boron was not observed due to quadrupolar relaxation of the ^{11}B nucleus. HRMS (ESI/TOF) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{27}BNO_4$ 368.2031; Found 368.2044. Enantiomeric ratio was measured by chiral phase HPLC (Regis Whelk-O, 5% *i*-PrOH/Hexanes, 1.0 mL/min, 250 nm) Rt (major) = 8.8 min, Rt (minor) = 11.7 min; er = 92:8.

Synthesis & characterization of enantioenriched potassium α-amidotrifluoroborates

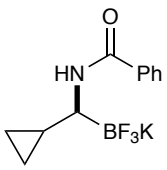
Following BPin adduct synthesis (see general procedure page S10), the crude mixture was eluted through a short plug of deactivated silica gel (35% w/w H_2O), then the filtered solution was concentrated *in vacuo*, and redissolved in a 1:1 mixture of MeCN:MeOH (0.25 M). Aqeous KF was then added to the mixture dropwise (4.0 eq, 10 M), and the reaction was stirred for a further 5 minutes or until complete dissolution is observed. L-(+)-tartaric acid in THF (2.05 equiv., 1.33 M) was then added dropwise over a period of 5 minutes, whereupon the reaction was diluted 1x with MeCN and any precipitate was broken up with a spatula. After stiring for a further 3-5 minutes, the reaction was again diluted 1x with MeCN, and filtered over a fritted funnel. The filter cake is washed thoroughly with MeCN, and the filtrate was concentrated *in vacuo*. The residue was titurated with Et_2O, and the resulting white precipitate was collected via filtration and washed with hot acetone to yield the pure trifluoroborate salt.



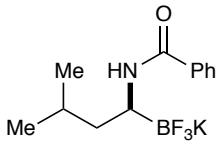
Potassium (*S*)-(benzamido(cyclohexyl)methyl)trifluoroborate (3a): Prepared according to the general trifluoroborate synthesis using 200 mg **1a** (0.539 mmol) to afford Potassium (*S*)-(benzamido(cyclohexyl)methyl)trifluoroborate (152 mg, 87% yield). Analytical data for N: ^{1}H NMR (500 MHz, DMSO-d_6) δ ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.69 (d, J = 6.6 Hz, 2H), 7.57 – 7.24 (m, 3H), 6.44 (d, J = 9.2 Hz, 1H), 2.82 (dt, J = 9.3, 4.7 Hz, 1H), 1.78 – 1.49 (m, 6H), 1.42 (tt, J = 11.8, 4.3 Hz, 1H), 1.18 – 0.96 (m, 5H). ^{13}C NMR (126 MHz, DMSO) δ 198.16, 165.54, 136.55, 130.15, 128.22, 126.49, 40.66, 31.42, 29.57, 26.64, 26.55. ^{11}B NMR (128 MHz, DMSO-d_6) δ 2.50. ^{19}F NMR (376 MHz, DMSO-d_6) δ -142.07. HRMS (ESI/TOF) m/z: [M-KHF]$^-$ Calcd. for $C_{14}H_{17}BF_2NO^-$ 264.1377; Found 264.1384.



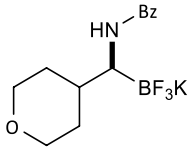
Potassium (*S*)-(1-benzamido-2-methylpropyl)trifluoroborate (3b): Prepared according to the general trifluoroborate synthesis using 100 mg **1b** (0.289 mmol) to afford Potassium (*S*)-(1-benzamido-2-methylpropyl)trifluoroborate (63 mg, 74% yield). Analytical data: ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.73 – 7.68 (m, 2H), 7.48 – 7.38 (m, 3H), 6.46 (d, J = 9.1 Hz, 1H), 2.83 (dt, J = 9.2, 4.6 Hz, 1H), 1.78 (dq, J = 13.2, 6.8 Hz, 1H), 0.83 (dd, J = 6.8, 3.0 Hz, 6H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 165.74, 136.59, 130.16, 128.23, 126.48, 30.12, 21.42, 20.01. ^{11}B NMR (128 MHz, DMSO-d_6) δ 2.66. ^{19}F NMR (376 MHz, DMSO-d_6) δ -149.57. HRMS (ESI/TOF) m/z: [M-KHF]$^-$ Calcd. for $C_{11}H_{13}BF_2NO^-$ 224.1064; Found 224.1060.



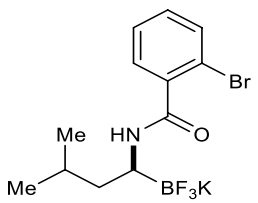
Potassium (*S*)-(benzamido(cyclopropyl)methyl)trifluoroborate (3c): Prepared according to the general trifluoroborate synthesis using 100 mg **1c** (0.303 mmol) to afford Potassium (*S*)-(benzamido(cyclopropyl)methyl)trifluoroborate (53 mg, 62% yield). Analytical data: ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.75 – 7.69 (m, 2H), 7.49 – 7.37 (m, 3H), 6.61 (d, J = 9.0 Hz, 1H), 2.66 – 2.55 (m, 1H), 0.90 – 0.73 (m, 1H), 0.34 – 0.14 (m, 2H), 0.16 – 0.03 (m, 2H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 165.64, 136.28, 130.21, 128.16, 126.62, 13.91, 3.34, 2.64. ^{11}B NMR (128 MHz, DMSO-d_6) δ 2.78. ^{19}F NMR (376 MHz, DMSO-d_6) δ -144.81. HRMS (ESI/TOF) m/z: [M-KHF]$^-$ Calcd. for $C_{11}H_{11}BF_2NO^-$ 222.0907; Found 222.0920.



Potassium (*S*)-(1-benzamido-3-methylbutyl)trifluoroborate (3d): Prepared according to the general trifluoroborate synthesis using 100 mg **1d** (0.289 mmol) to afford Potassium (*S*)-(1-benzamido-3-methylbutyl)trifluoroborate (73 mg, 85% yield). Analytical data: ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.76 – 7.68 (m, 2H), 7.46 – 7.35 (m, 3H), 6.54 (d, J = 9.3 Hz, 1H), 3.06 (tt, J = 9.4, 4.3 Hz, 1H), 1.55 (ddd, J = 11.3, 9.0, 5.7 Hz, 1H), 1.28 (ddd, J = 13.7, 10.4, 4.7 Hz, 1H), 1.17 (ddd, J = 13.6, 9.0, 4.4 Hz, 1H), 0.83 (dd, J = 13.1, 6.6 Hz, 6H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 165.10, 136.43, 130.02, 128.06, 126.64, 41.89, 24.98, 24.00, 22.48. ^{11}B NMR (128 MHz, DMSO-d_6) δ 2.84. ^{19}F NMR (376 MHz, DMSO-d_6) δ -146.05. HRMS (ESI/TOF) m/z: [M-KHF]$^-$ Calcd. for $C_{12}H_{15}BF_2NO^-$ 238.1220; Found 238.1220.



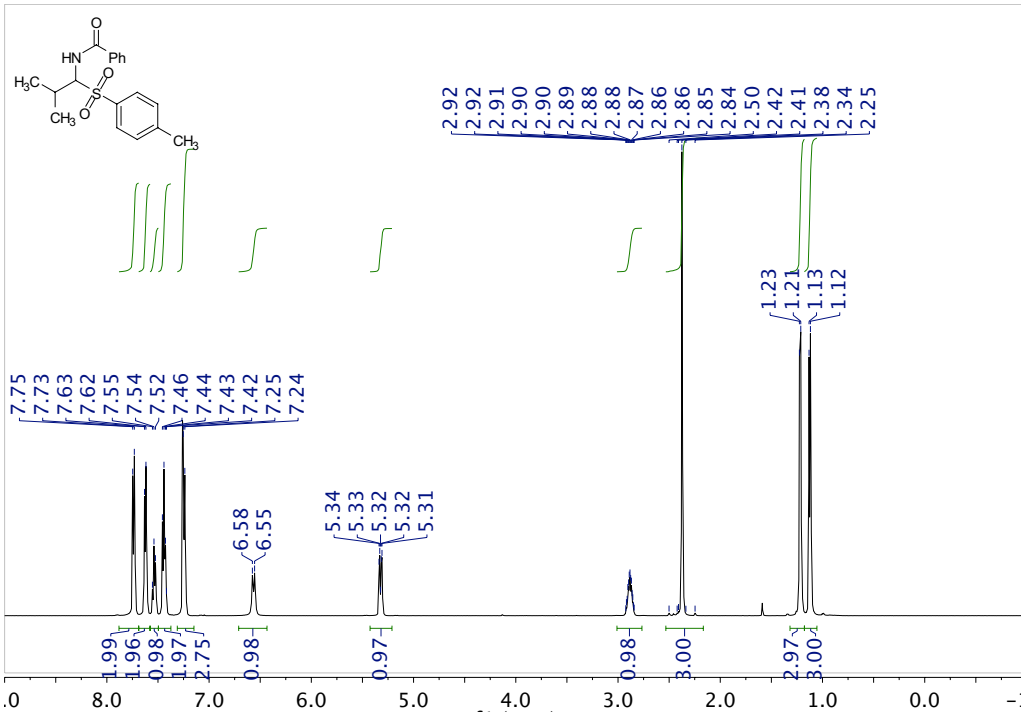
Potassium (*S*)-(benzamido(tetrahydro-2*H*-pyran-4-yl)methyl)trifluoroborate (3e): Prepared according to the general trifluoroborate synthesis using 115 mg **1e** (0.308 mmol) to afford Potassium (*S*)-(benzamido(tetrahydro-2*H*-pyran-4-yl)methyl)trifluoroborate (74 mg, 74% yield). Analytical data: ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.72 (d, J = 6.8, 1.5 Hz, 2H), 7.51 – 7.35 (m, 3H), 6.52 (d, J = 9.3 Hz, 1H), 3.77 (td, J = 11.2, 3.8 Hz, 2H), 3.18 (ddt, J = 13.0, 11.1, 2.2 Hz, 2H), 2.86 (dt, J = 9.7, 4.8 Hz, 1H), 1.58 – 1.47 (m, 2H), 1.31 (dtt, J = 17.8, 12.2, 5.2 Hz, 2H). ^{13}C NMR (126 MHz, DMSO) δ 165.78, 136.37, 130.21, 128.19, 126.58, 67.87, 67.71, 37.90, 31.54, 29.99. The resonance pertaning to the carbon bound to boron was not observed due to quadrupolar relaxation of the ^{11}B nucleus. ^{11}B NMR (128 MHz, DMSO-d_6) δ 2.78. ^{19}F NMR (376 MHz, DMSO-d_6) δ -142.30. HRMS (ESI/TOF) m/z: [M-KHF]$^-$ Calcd. for $C_{13}H_{15}BF_2NO_2^-$ 266.1169; Found 266.1171.

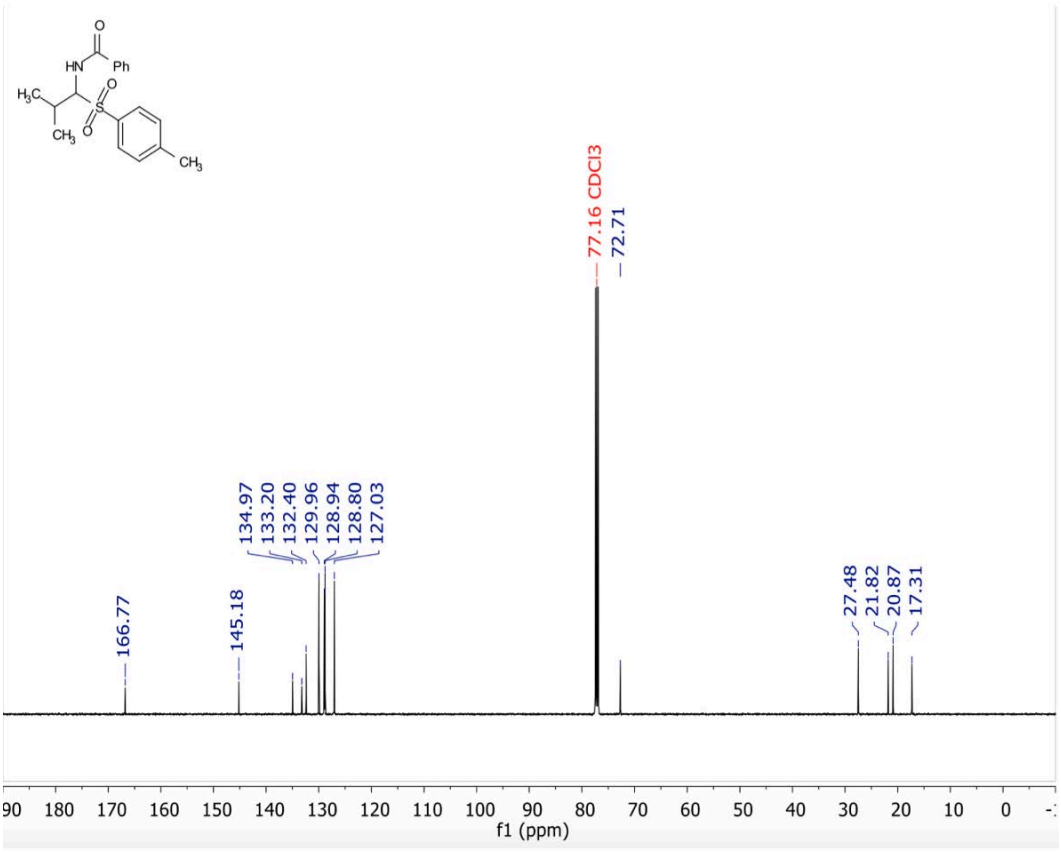


Potassium (*S*)-(1-(2-bromobenzamido)-3-methylbutyl)trifluoroborate (3f): Prepared according to the general trifluoroborate synthesis using 100 mg **1f** (0.236 mmol) to afford Potassium (*S*)-(1-(2-bromobenzamido)-3-methylbutyl)trifluoroborate (58 mg, 83% yield). Note: Intermediate BPin adduct **2f** was formed in 72% yield (NMR) and 99:1 er according to SFC analysis of the crude reaction mixure, however all attempts at conventional chromatographic purification led to complete degradation of the product precluding additional spectral charactertization of **2f**. Direct conversion of crude **2f** to **3f** according to the general trifluoroborate synthesis procedure afforded **3f** as a bench and air-stable salt. Analytical data for **3f**: ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.12 (d, J = 7.9 Hz, 1H), 6.92 (t, J = 7.6 Hz, 1H), 6.83 (dd, J = 14.3, 7.3 Hz, 2H), 5.89 (d, J = 9.4 Hz, 1H), 2.54 (tt, J = 9.9, 4.6 Hz, 1H), 1.27 (p, J = 6.8 Hz, 1H), 0.80 (ddd, J = 14.8, 10.4, 4.7 Hz, 1H), 0.69 (ddd, J = 13.6, 9.2, 4.4 Hz, 1H), 0.42 (d, J = 6.5 Hz, 3H), 0.38 (d, J = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, DMSO) δ 165.97, 140.52, 132.63, 130.10, 128.98, 127.36, 118.76, 41.80, 24.85, 24.03, 22.47. The resonance pertaining to the carbon bound to boron was not observed due to quadrupolar relaxation of the ^{11}B nucleus. ^{11}B NMR (128 MHz, DMSO-d_6) δ 2.85 (bs, J = 162.0 Hz). ^{19}F NMR (376 MHz, DMSO-d_6) δ -146.18. HRMS (ESI/TOF) m/z: [M-KHF]$^-$ Calcd. for $C_{12}H_{14}BBrF_2NO^-$ 316.0325; Found 316.0360.

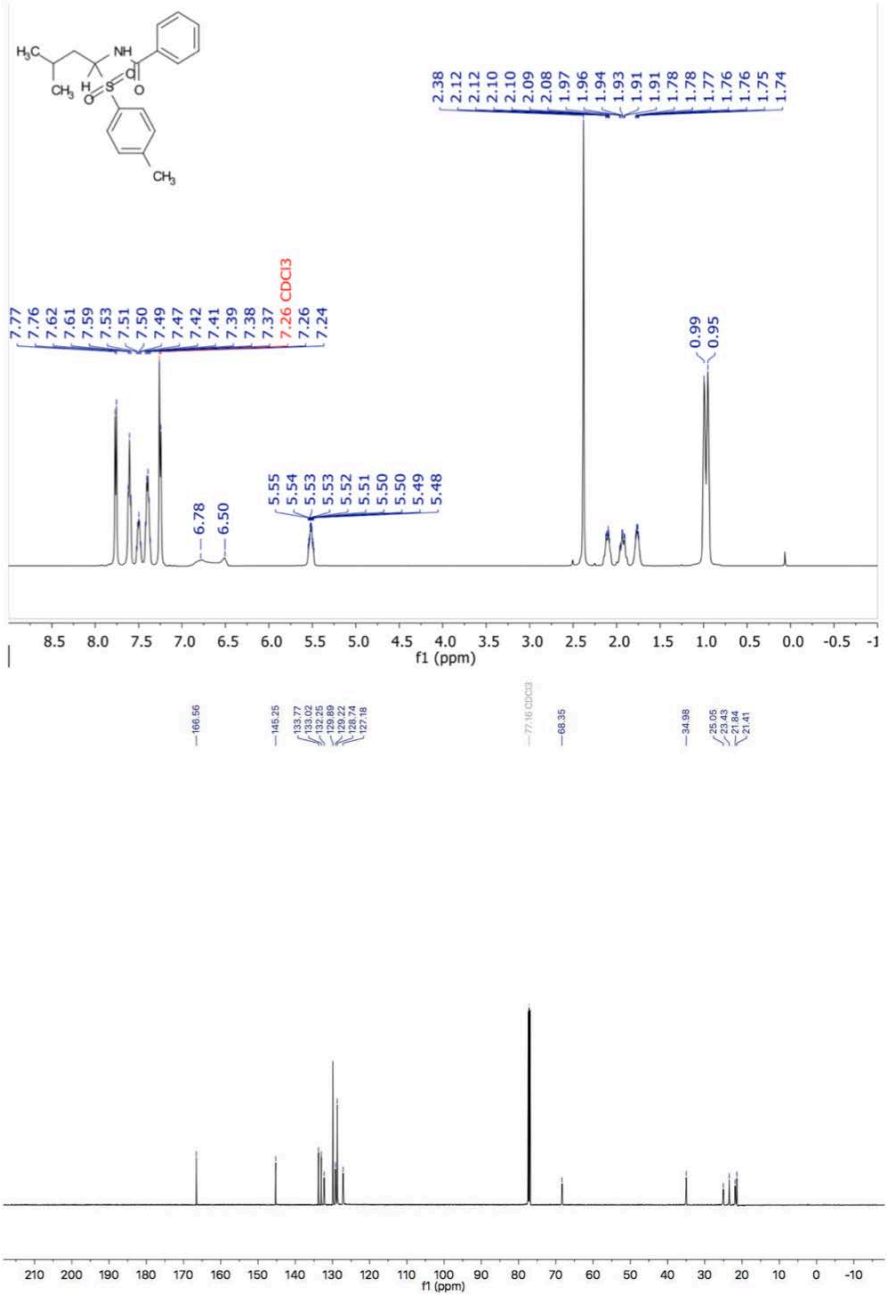
Selected NMR Spectra

1b

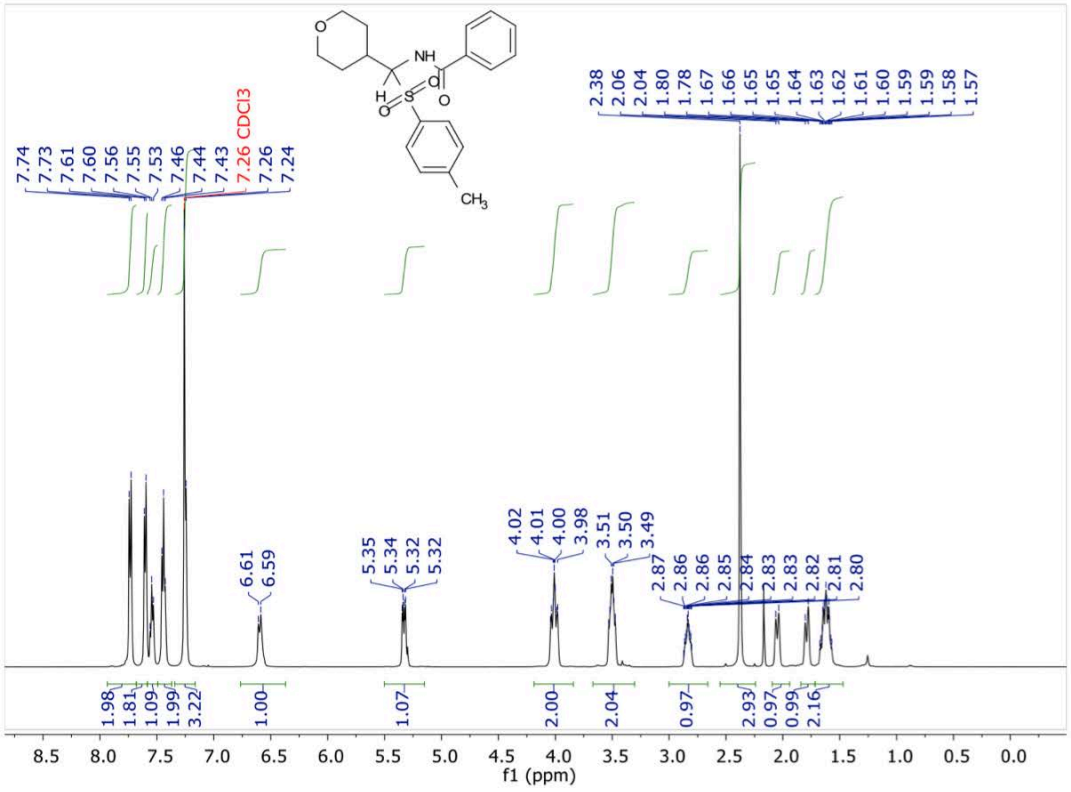


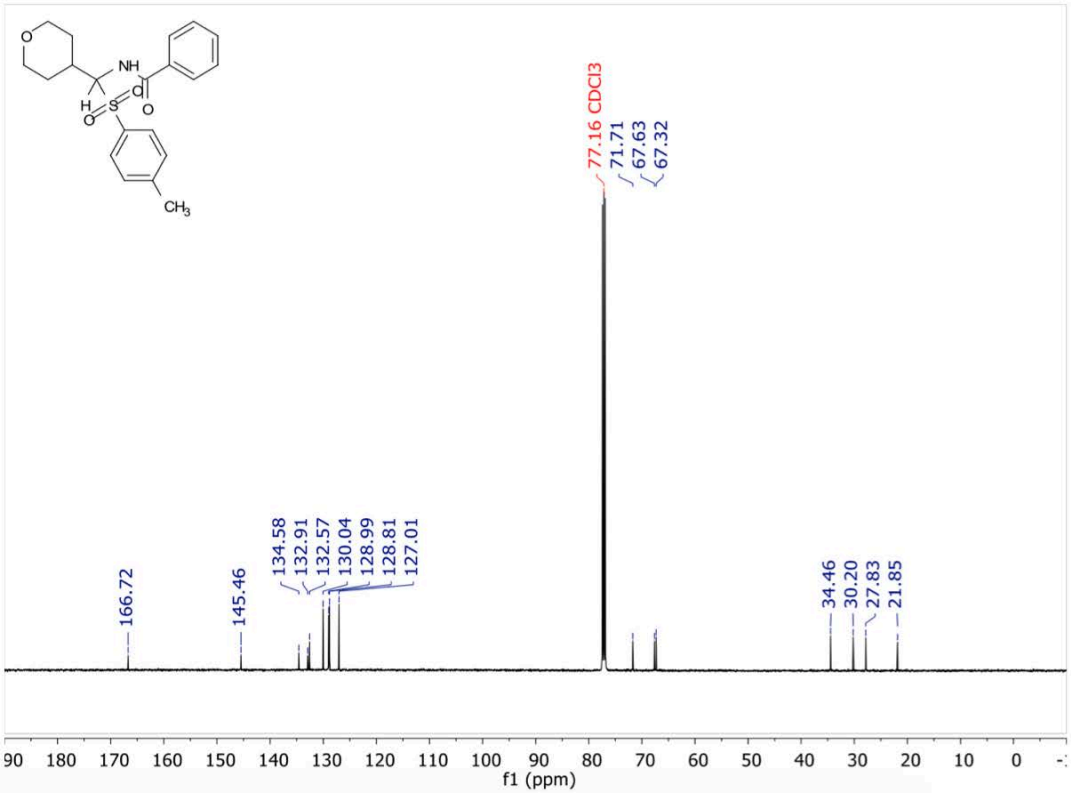


1d

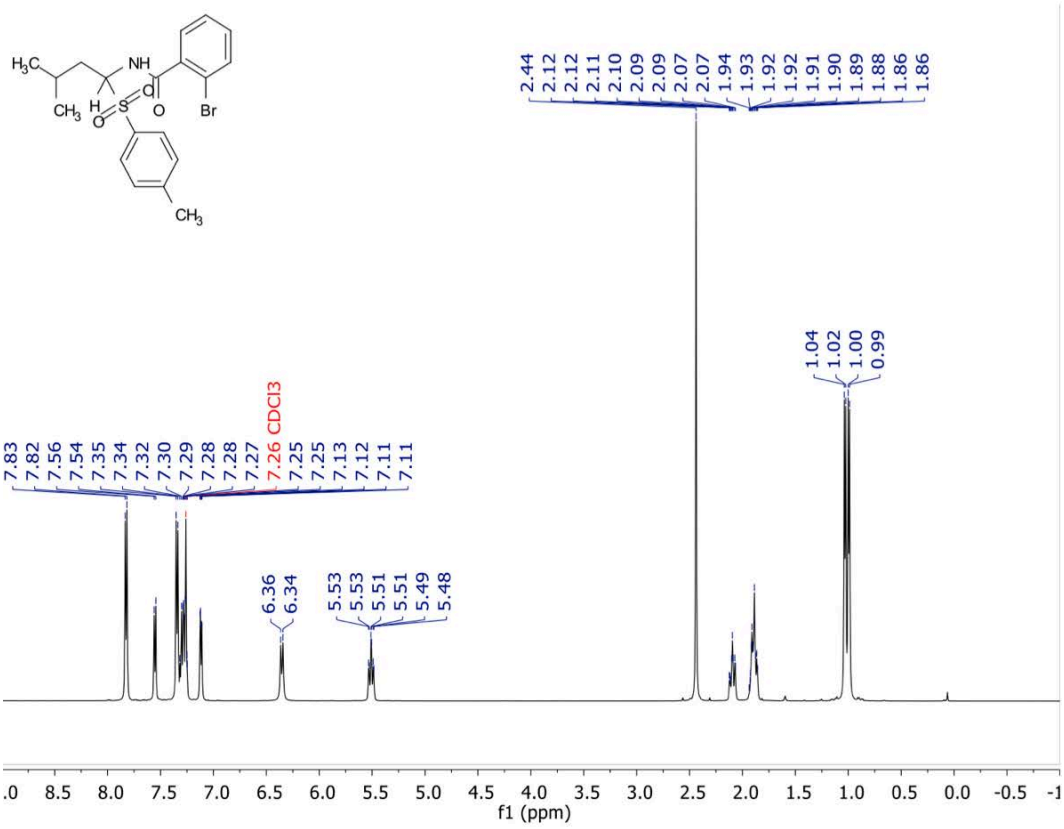

2.38
2.12
2.12
2.10
2.10
2.09
2.08
1.97
1.96
1.94
1.93
1.91
1.91
1.78
1.78
1.77
1.76
1.76
1.75
1.74
7.77
7.76
7.62
7.61
7.59
7.53
7.51
7.50
7.49
7.47
7.42
7.41
7.39
7.38
7.37
7.26 CDCl3
7.26
7.24
0.99
0.95
6.78
6.50
5.55
5.54
5.53
5.53
5.52
5.51
5.50
5.50
5.49
5.48
f1 (ppm)
166.56
145.25
133.77
133.02
132.25
129.89
129.22
128.74
127.18
77.16 CDCl3
68.35
34.98
25.05
23.43
21.84
21.41
f1 (ppm)

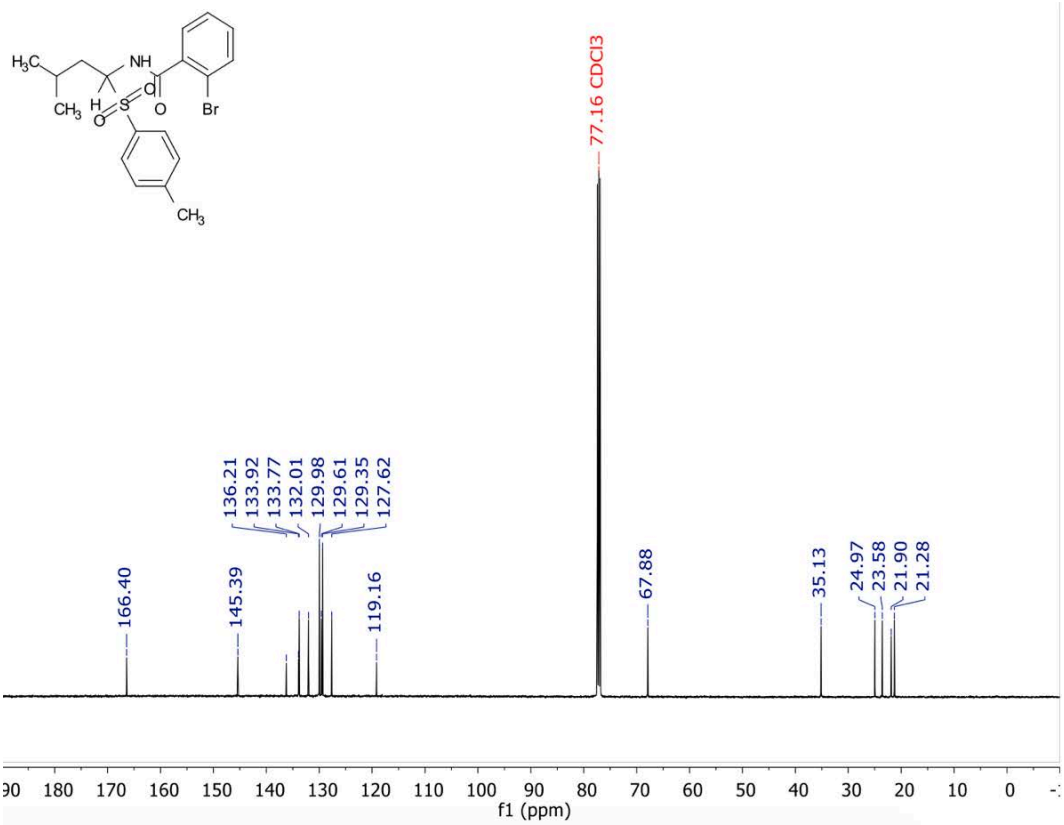
1e


7.74
7.73
7.61
7.60
7.56
7.55
7.53
7.46
7.44
7.43
7.26 CDCl3
7.26
7.24
2.38
2.06
2.04
1.80
1.78
1.67
1.66
1.65
1.65
1.64
1.63
1.62
1.61
1.60
1.59
1.59
1.58
1.57
6.61
6.59
5.35
5.34
5.32
5.32
4.02
4.01
4.00
3.98
3.51
3.50
3.49
2.87
2.86
2.86
2.85
2.84
2.83
2.83
2.82
2.81
2.80
1.98
1.81
1.09
1.99
3.22
1.00
1.07
2.00
2.04
0.97
2.93
0.97
0.99
2.16
f1 (ppm)

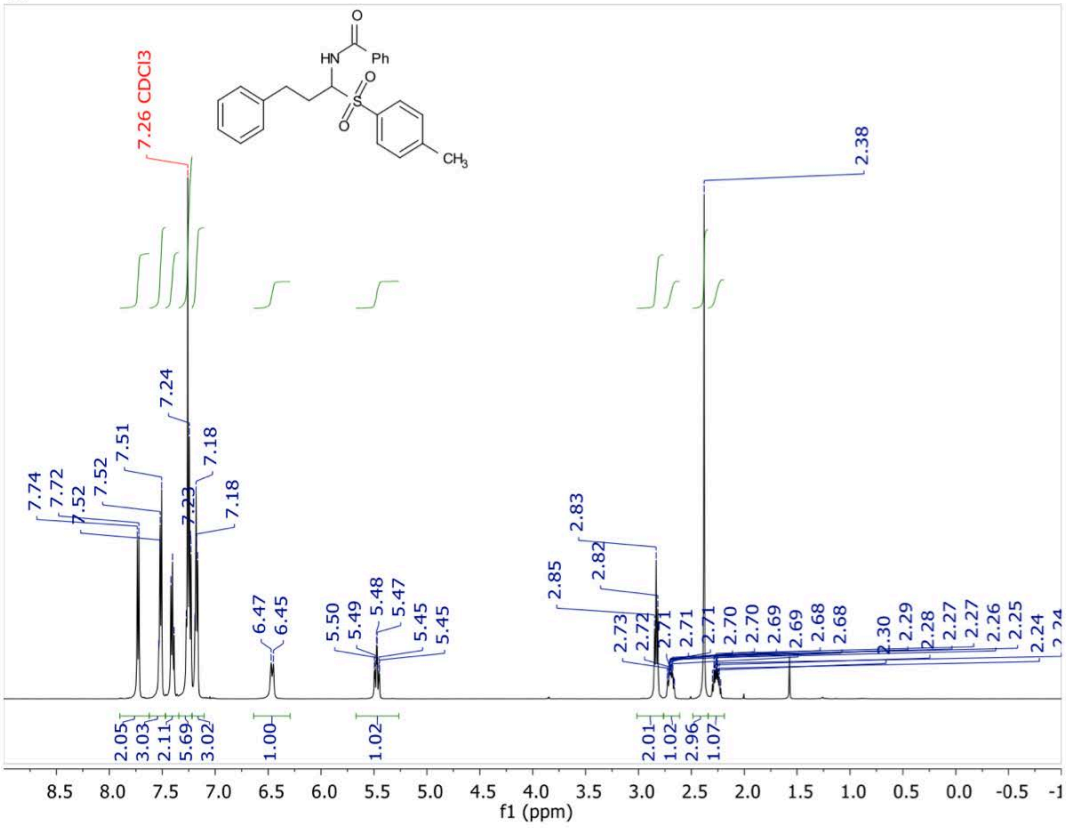

77.16 CDCl3
71.71
67.63
67.32
166.72
145.46
134.58
132.91
132.57
130.04
128.99
128.81
127.01
34.46
30.20
27.83
21.85
f1 (ppm)

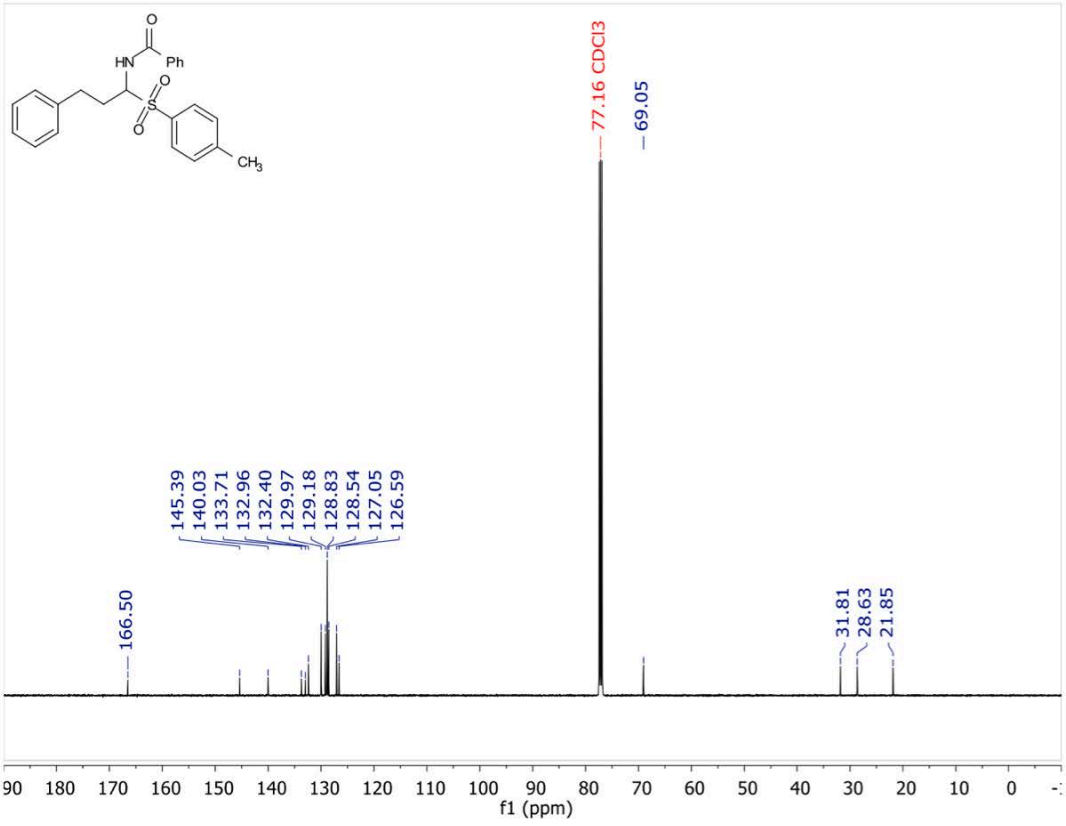
1f


2.44
2.12
2.12
2.11
2.10
2.09
2.09
2.07
2.07
1.94
1.93
1.92
1.92
1.91
1.90
1.89
1.88
1.86
1.86
1.04
1.02
1.00
0.99
7.83
7.82
7.56
7.54
7.35
7.34
7.32
7.30
7.29
7.28
7.28
7.27
7.26 CDCl3
7.25
7.13
7.12
7.11
7.11
6.36
6.34
5.53
5.53
5.51
5.51
5.49
5.48
f1 (ppm)

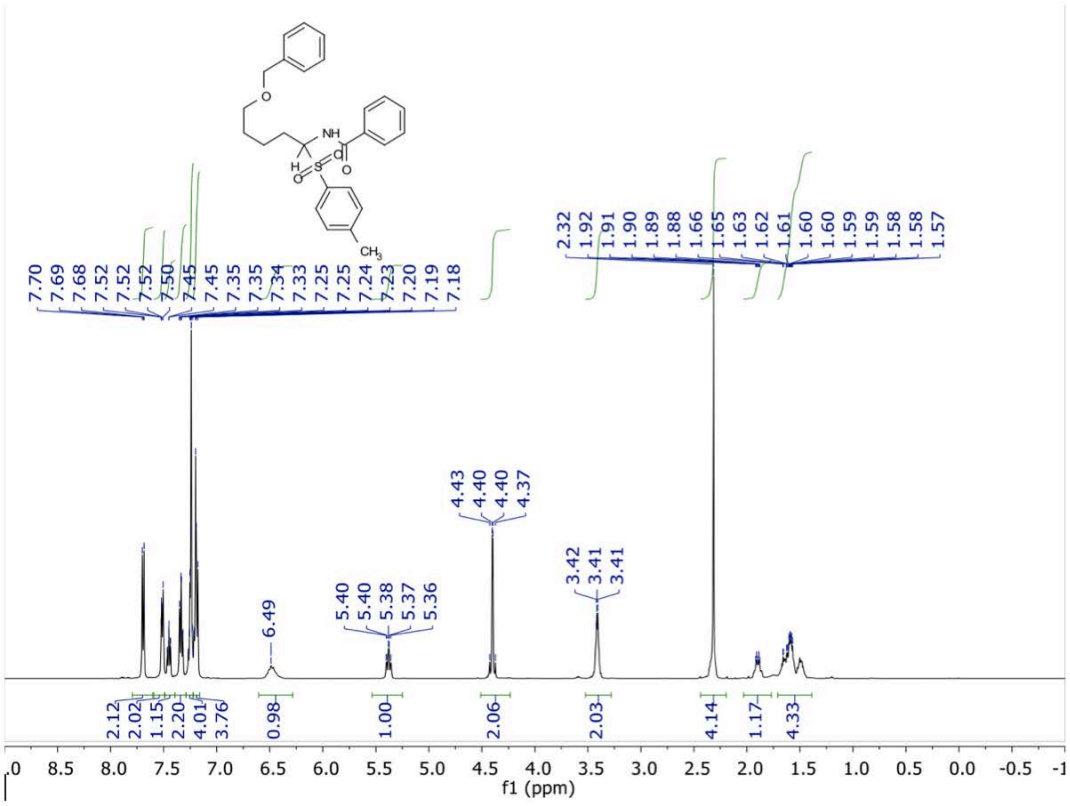

77.16 CDCl3
136.21
133.92
133.77
132.01
129.98
129.61
129.35
127.62
166.40
145.39
119.16
67.88
35.13
24.97
23.58
21.90
21.28
f1 (ppm)

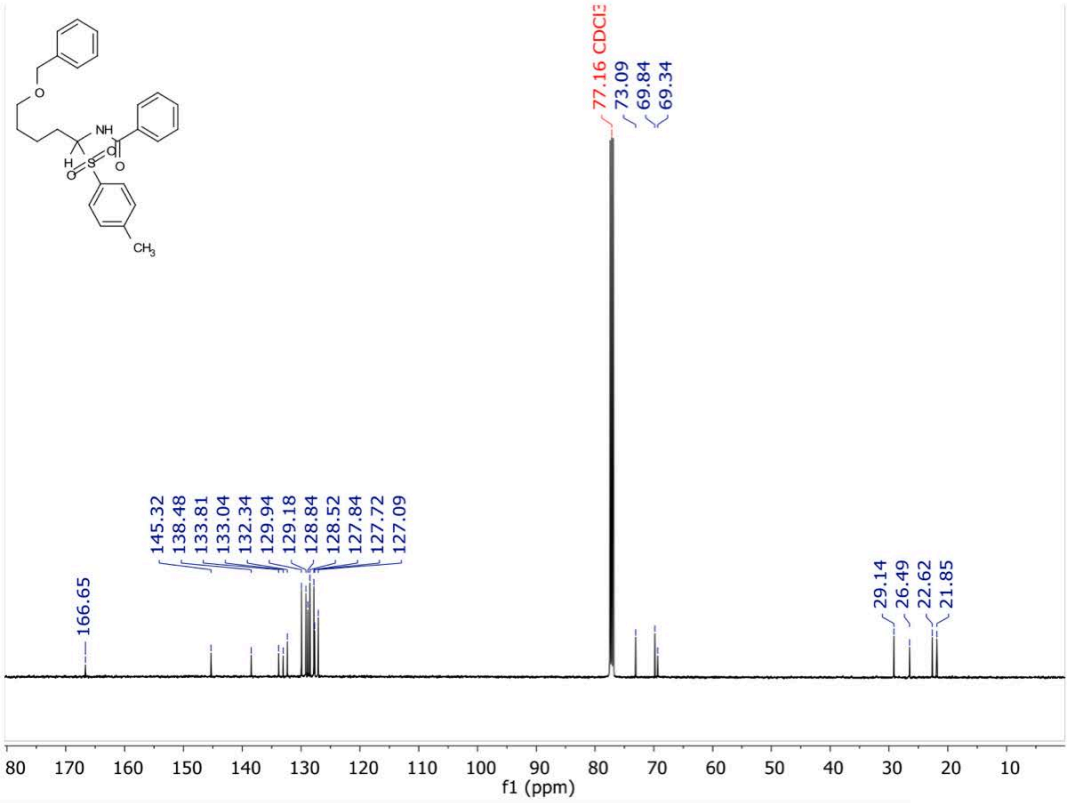
1g


7.26 CDCl3
2.38
7.74
7.72
7.52
7.52
7.51
7.24
7.23
7.18
7.18
6.47
6.45
5.50
5.49
5.48
5.47
5.45
5.45
2.85
2.83
2.82
2.73
2.72
2.71
2.71
2.71
2.70
2.70
2.69
2.69
2.68
2.68
2.30
2.29
2.28
2.27
2.27
2.26
2.25
2.24
2.05
3.03
2.11
5.69
3.02
1.00
1.02
2.01
1.02
2.96
1.07
f1 (ppm)

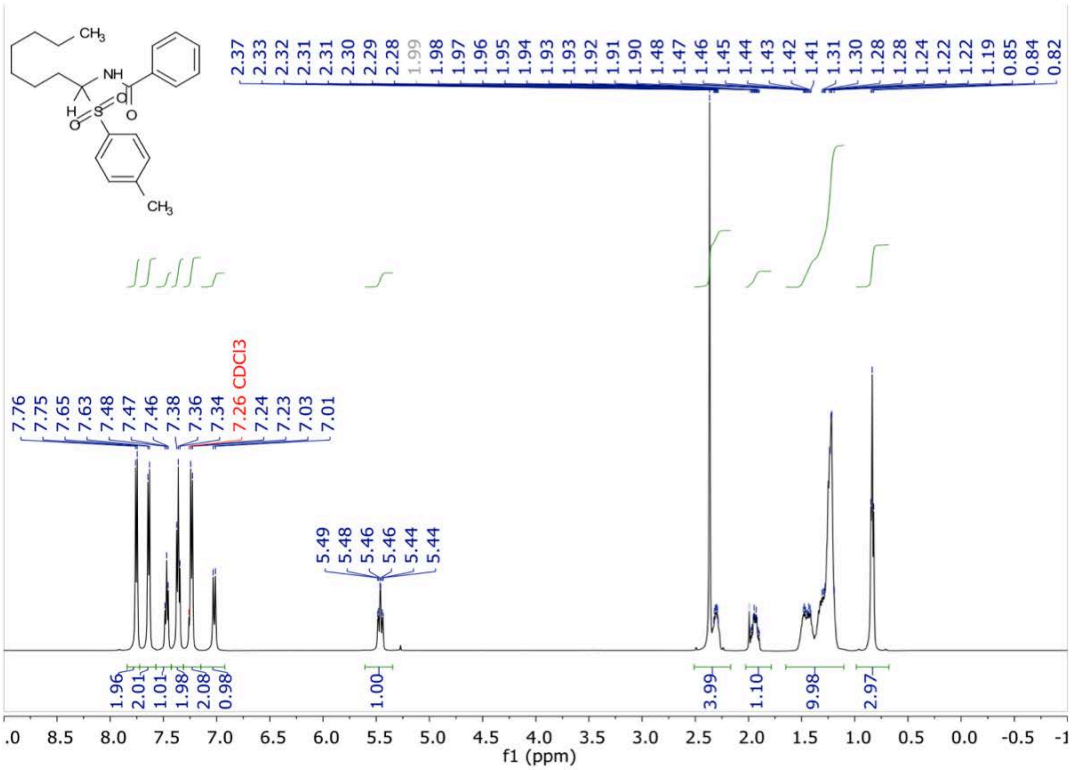

77.16 CDCl3
69.05
145.39
140.03
133.71
132.96
132.40
129.97
129.18
128.83
128.54
127.05
126.59
166.50
31.81
28.63
21.85
f1 (ppm)

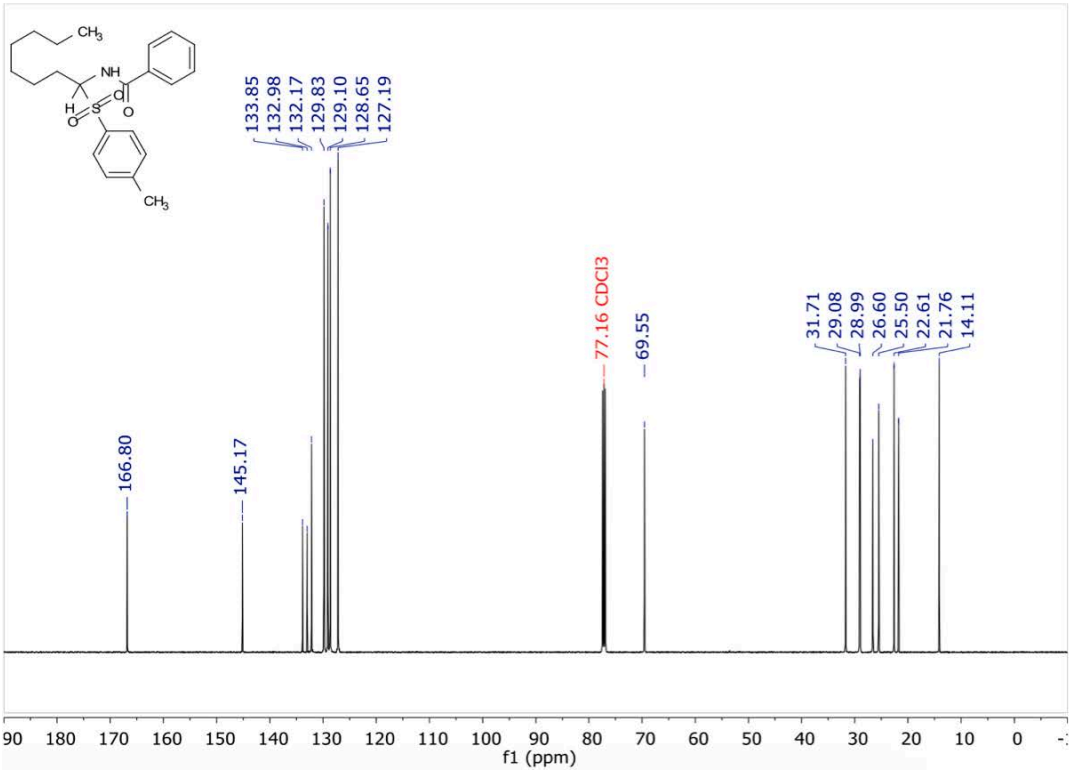
1h


7.70
7.69
7.68
7.52
7.52
7.52
7.50
7.45
7.45
7.35
7.35
7.34
7.33
7.25
7.25
7.24
7.23
7.20
7.19
7.18
2.32
1.92
1.91
1.90
1.89
1.88
1.66
1.65
1.63
1.62
1.61
1.60
1.60
1.59
1.59
1.58
1.58
1.57
4.43
4.40
4.40
4.37
3.42
3.41
3.41
6.49
5.40
5.40
5.38
5.37
5.36
2.12
2.02
1.15
2.20
4.01
3.76
0.98
1.00
2.06
2.03
4.14
1.17
4.33
f1 (ppm)

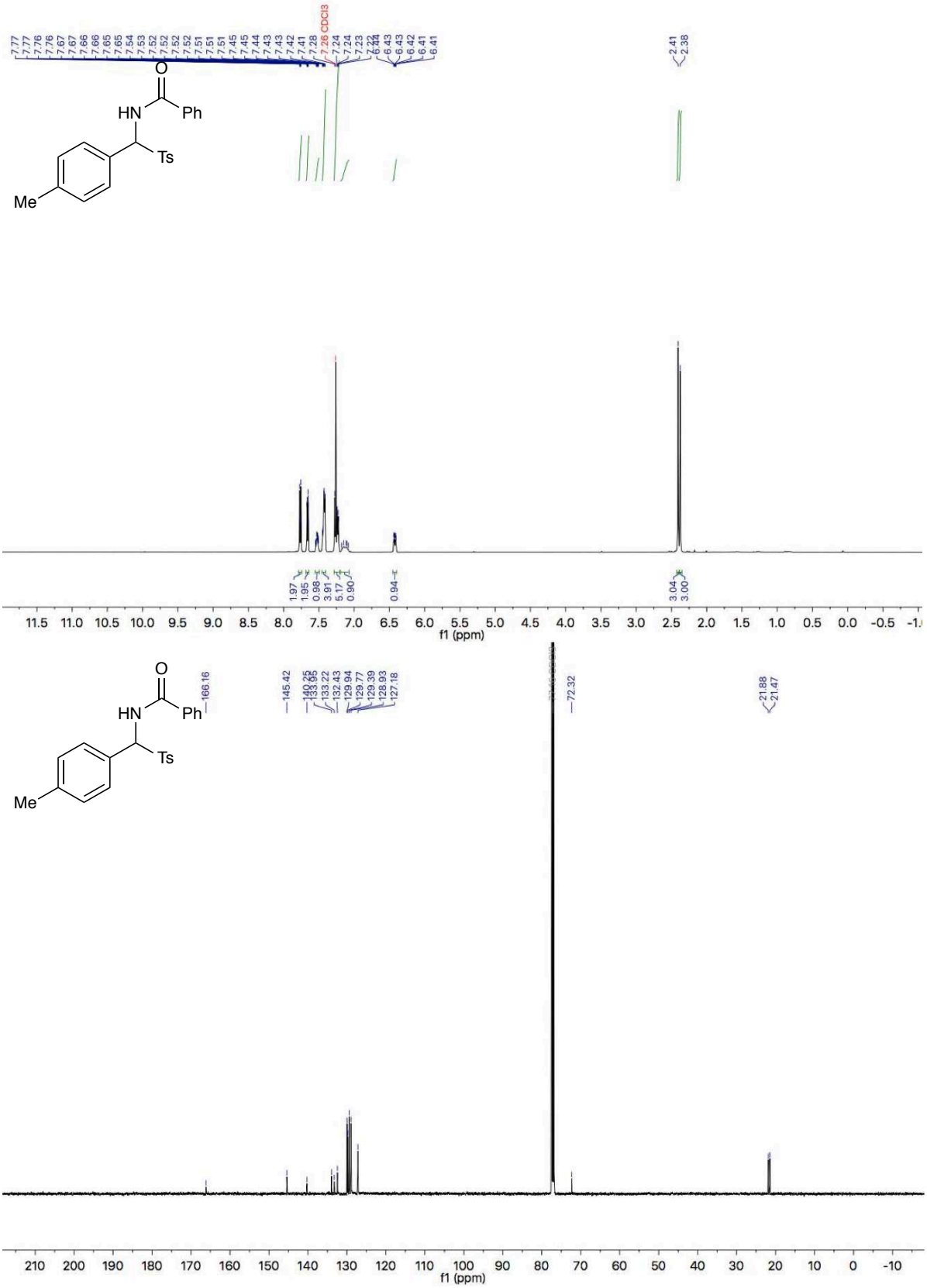

77.16 CDCl3
73.09
69.84
69.34
145.32
138.48
133.81
133.04
132.34
129.94
129.18
128.84
128.52
127.84
127.72
127.09
166.65
29.14
26.49
22.62
21.85
f1 (ppm)

1i

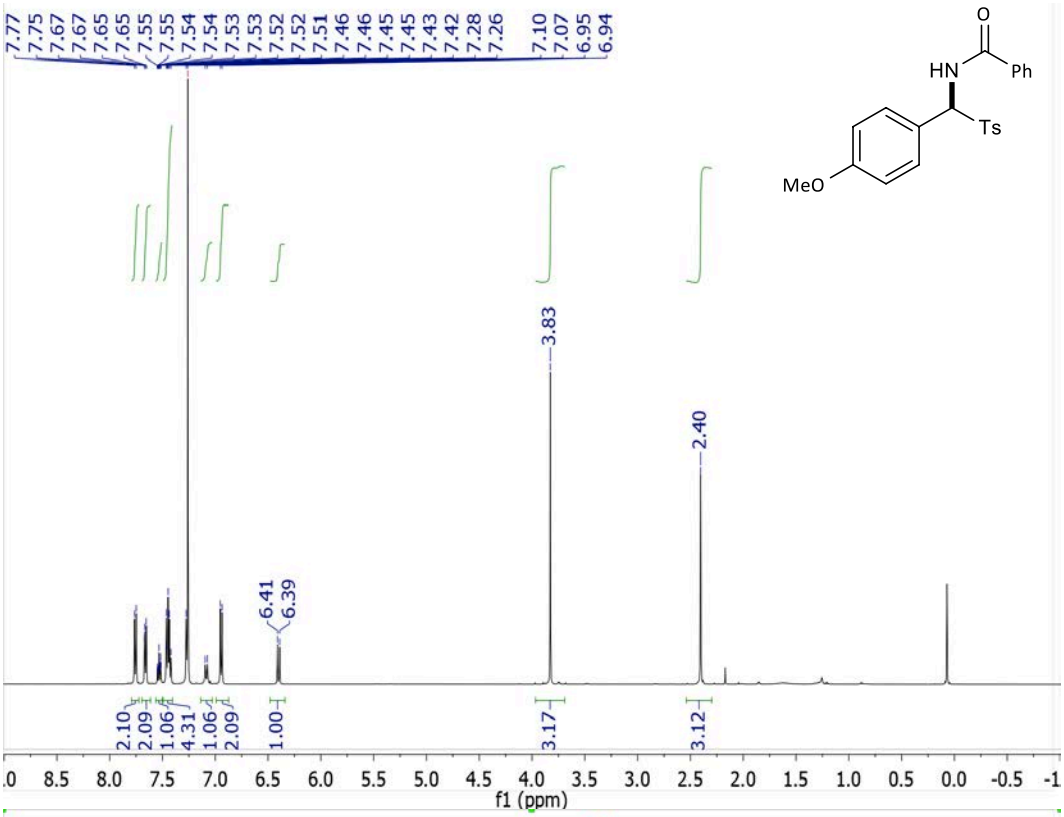

CH3
NH
Cl
H
S
O
O
CH3
2.37 2.33 2.32 2.31 2.31 2.30 2.29 2.28 1.99 1.98 1.97 1.96 1.95 1.94 1.93 1.93 1.92 1.91 1.90 1.48 1.47 1.46 1.45 1.44 1.43 1.42 1.41 1.31 1.30 1.28 1.28 1.24 1.22 1.22 1.19 0.85 0.84 0.82
7.76 7.75 7.65 7.63 7.48 7.47 7.46 7.38 7.36 7.34 7.26 CDCl3 7.24 7.23 7.03 7.01
5.49 5.48 5.46 5.46 5.44 5.44
1.96 2.01 1.01 1.98 2.08 0.98 1.00 3.99 1.10 9.98 2.97
f1 (ppm)

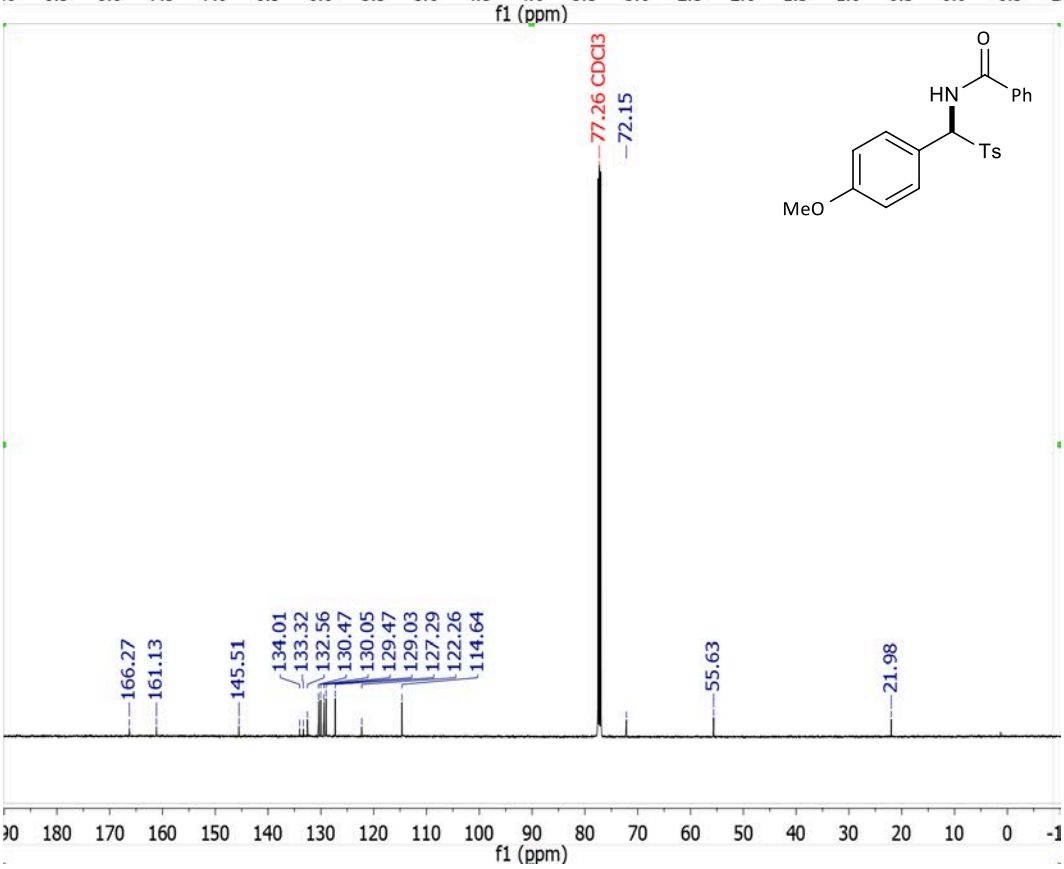

CH3
NH
Cl
H
S
O
O
CH3
133.85 132.98 132.17 129.83 129.10 128.65 127.19
77.16 CDCl3
69.55
31.71 29.08 28.99 26.60 25.50 22.61 21.76 14.11
166.80
145.17
f1 (ppm)

1k

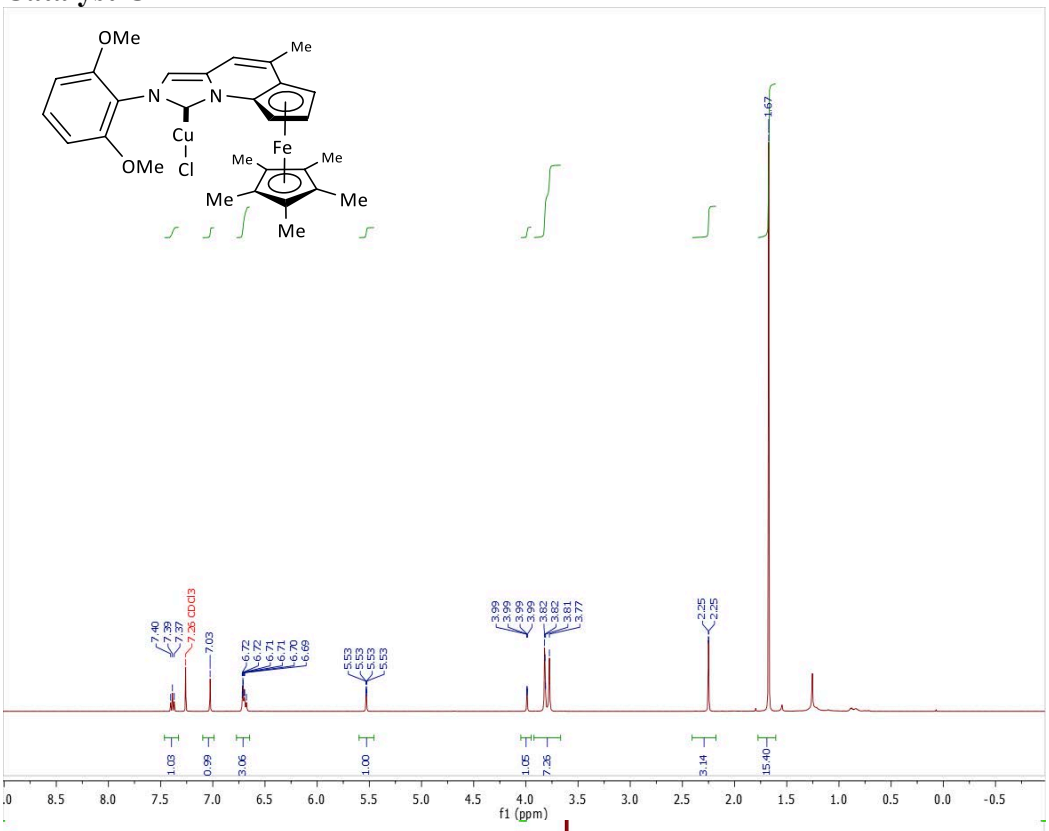

O
HN
Ph
Ts
Me
7.77
7.77
7.76
7.76
7.67
7.67
7.66
7.66
7.65
7.65
7.54
7.53
7.52
7.52
7.52
7.52
7.51
7.51
7.51
7.45
7.45
7.44
7.43
7.43
7.42
7.41
7.28
7.26 CDCl3
7.24
7.24
7.23
6.44
6.43
6.43
6.42
6.41
6.41
2.41
2.38
1.97
1.95
0.98
3.91
5.17
0.90
0.94
3.04
3.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
166.16
145.42
140.25
133.95
133.22
132.43
129.94
129.77
129.39
128.93
127.18
72.32
21.88
21.47
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)

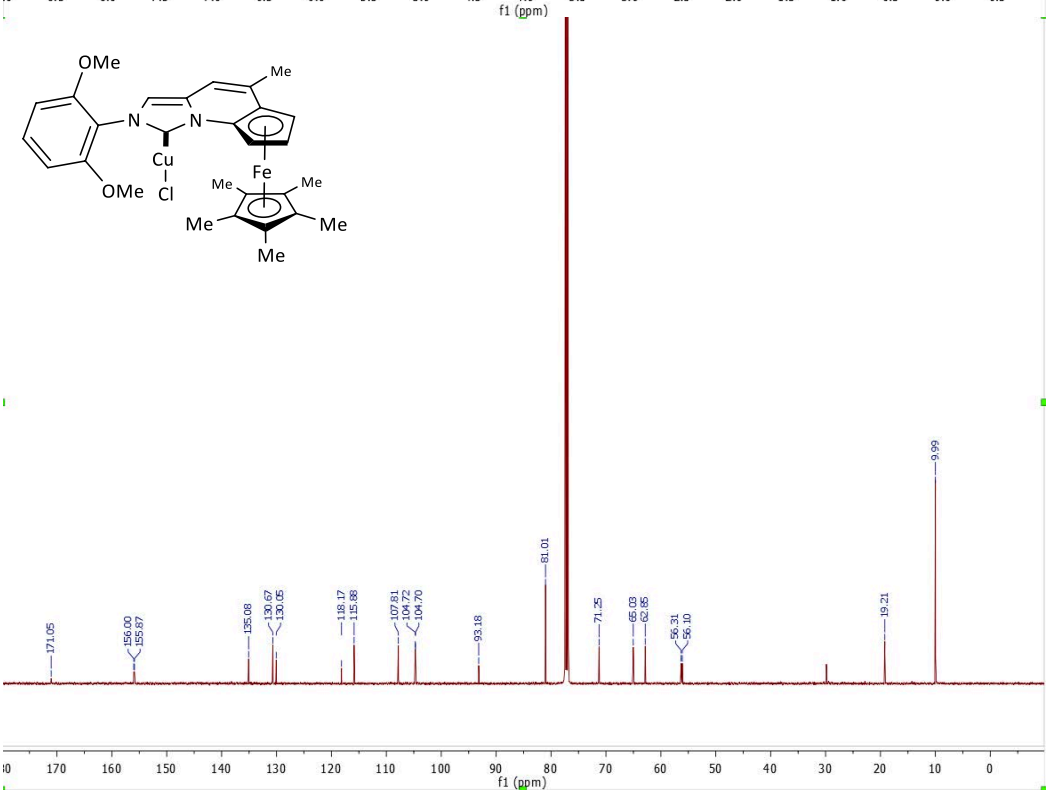
1l


7.77
7.75
7.67
7.67
7.65
7.65
7.55
7.55
7.54
7.54
7.53
7.53
7.52
7.52
7.51
7.46
7.46
7.45
7.45
7.43
7.42
7.28
7.26
7.10
7.07
6.95
6.94
3.83
2.40
6.41
6.39
2.10
2.09
1.06
4.31
1.06
2.09
1.00
3.17
3.12
f1 (ppm)
O
HN
Ph
Ts
MeO

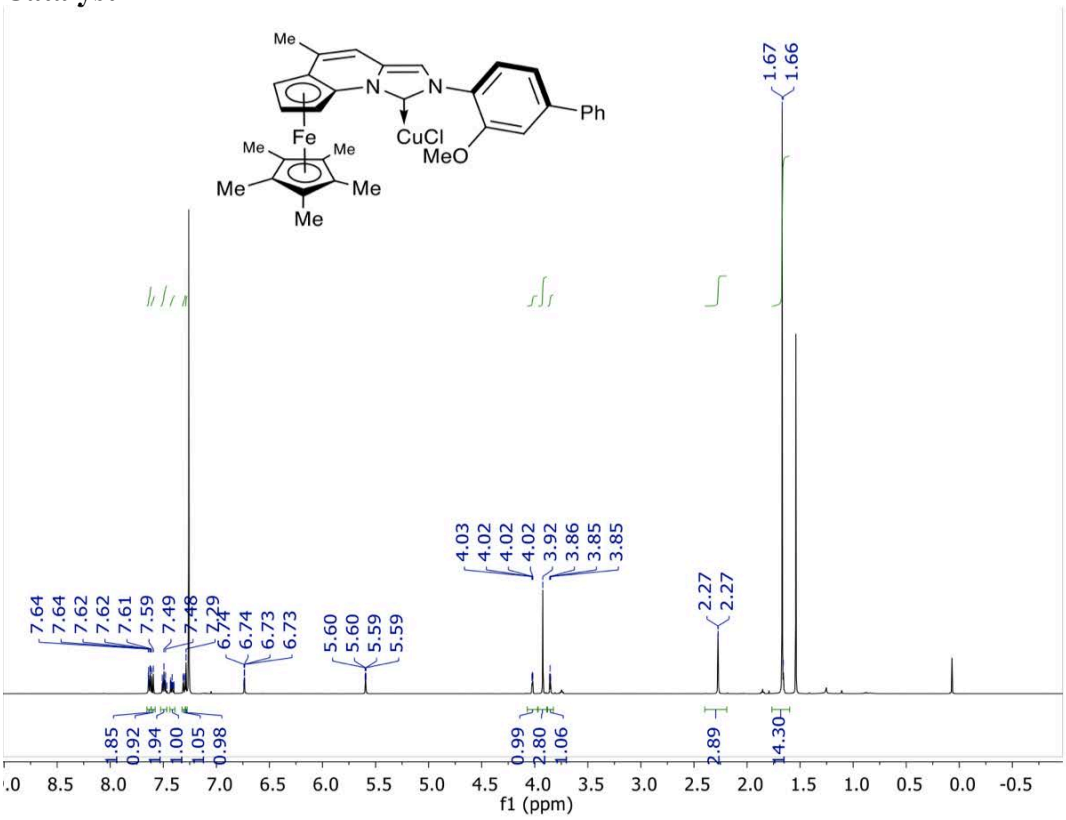

77.26 CDCl3
72.15
166.27
161.13
145.51
134.01
133.32
132.56
130.47
130.05
129.47
129.03
127.29
122.26
114.64
55.63
21.98
f1 (ppm)
O
HN
Ph
Ts
MeO

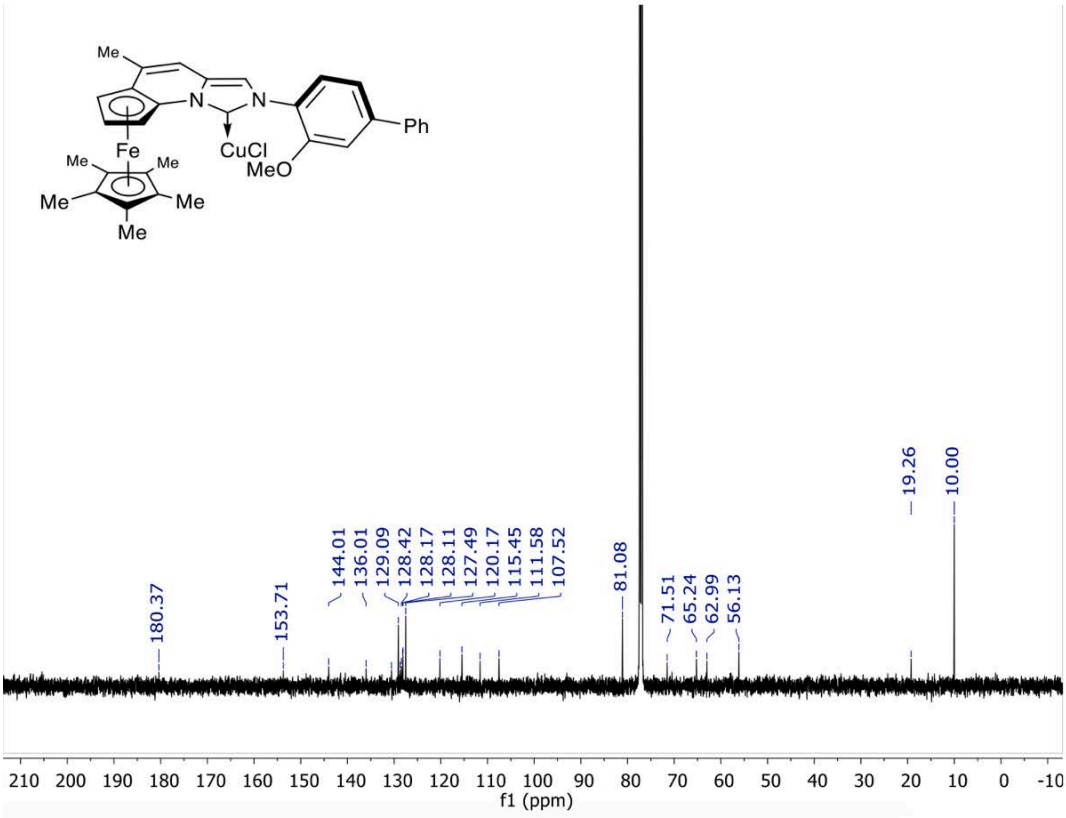
Catalyst C


OMe
Me
N
N
Cu
Cl
OMe
Fe
Me
Me
Me
Me
Me
7.40
7.39
7.37
7.26 CDCl3
7.03
6.72
6.72
6.71
6.71
6.70
6.69
5.53
5.53
5.53
5.53
5.53
3.99
3.99
3.99
3.99
3.99
3.82
3.82
3.81
3.77
2.25
2.25
1.67
1.03
0.99
3.06
1.00
1.05
7.26
3.14
15.40
f1 (ppm)

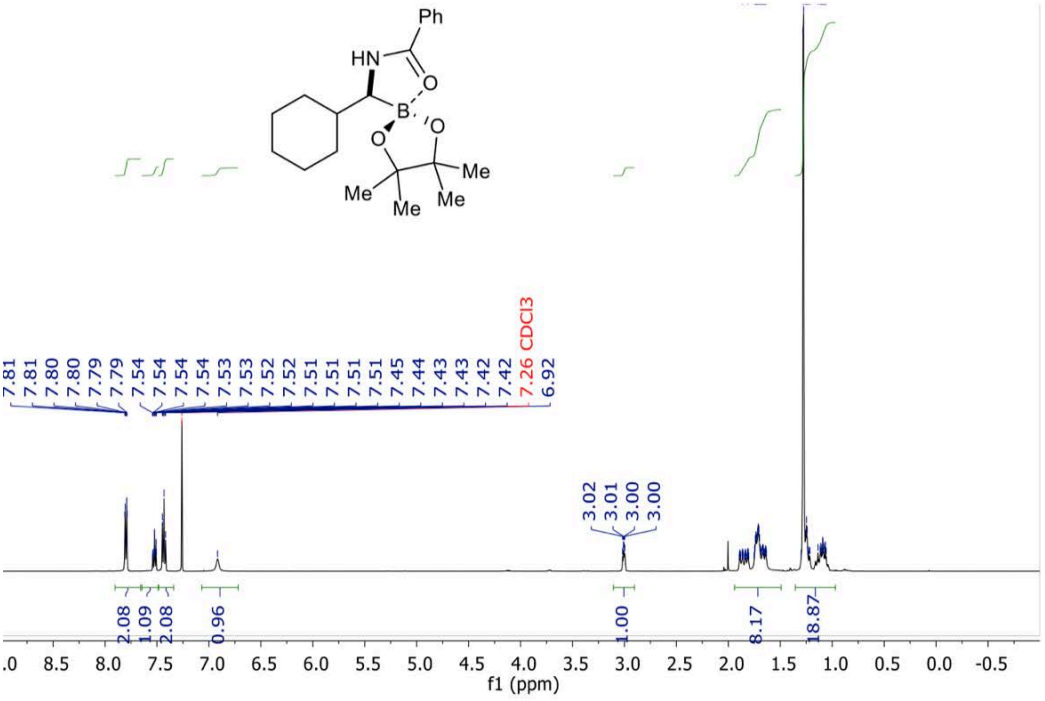

OMe
Me
N
N
Cu
Cl
OMe
Fe
Me
Me
Me
Me
Me
171.05
156.00
155.87
135.08
130.67
130.05
118.17
115.88
107.81
104.72
104.70
93.18
81.01
71.25
65.03
62.85
56.31
56.10
19.21
9.99
f1 (ppm)

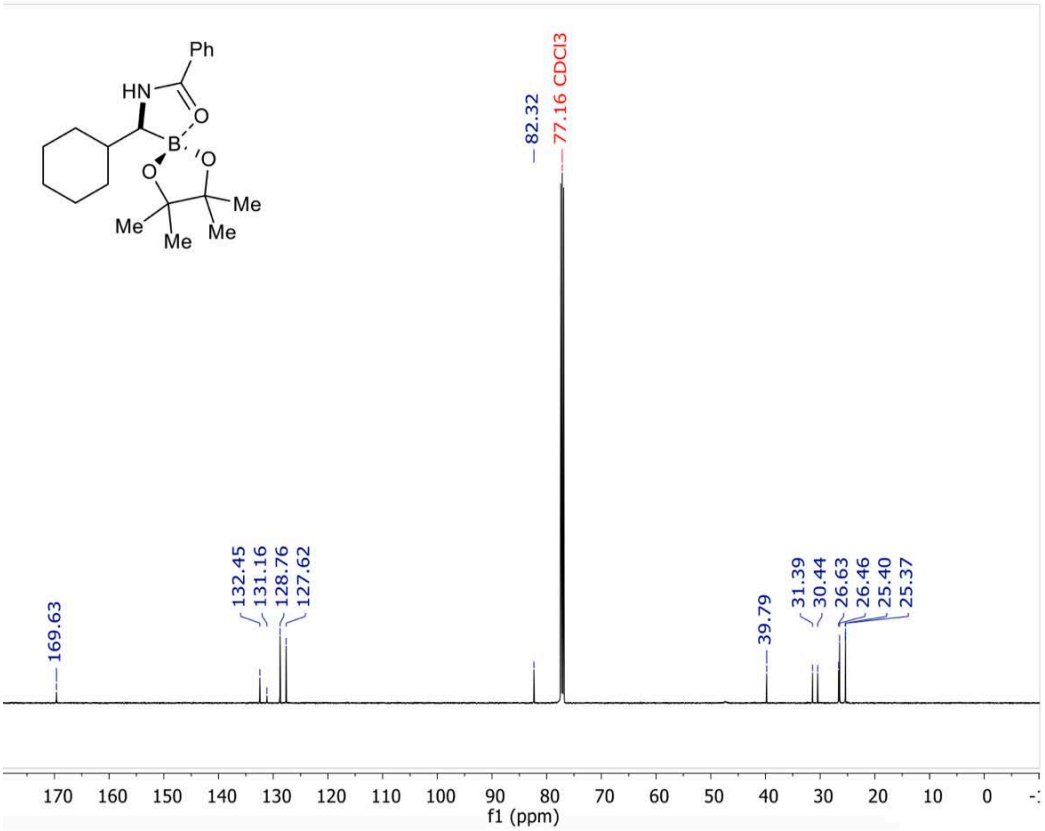
Catalyst H


Me
N
N
Ph
Fe
CuCl
MeO
Me
Me
Me
Me
1.67
1.66
4.03
4.02
4.02
4.02
3.92
3.86
3.85
3.85
2.27
2.27
7.64
7.64
7.62
7.62
7.61
7.59
7.49
7.48
7.29
6.74
6.74
6.73
6.73
5.60
5.60
5.59
5.59
1.85
0.92
1.94
1.00
1.05
0.98
0.99
2.80
1.06
2.89
14.30
f1 (ppm)

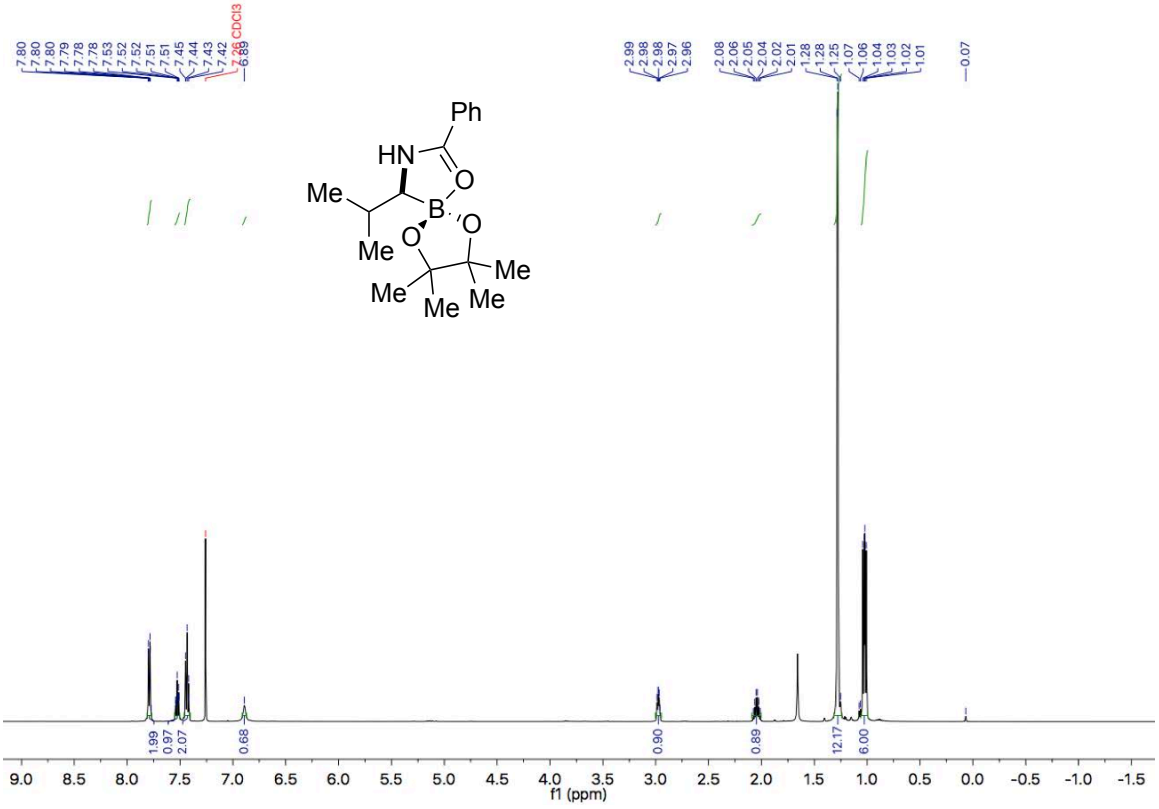

Me
N
N
Ph
Fe
CuCl
MeO
Me
Me
Me
Me
19.26
10.00
144.01
136.01
129.09
128.42
128.17
128.11
127.49
120.17
115.45
111.58
107.52
81.08
180.37
153.71
71.51
65.24
62.99
56.13
f1 (ppm)

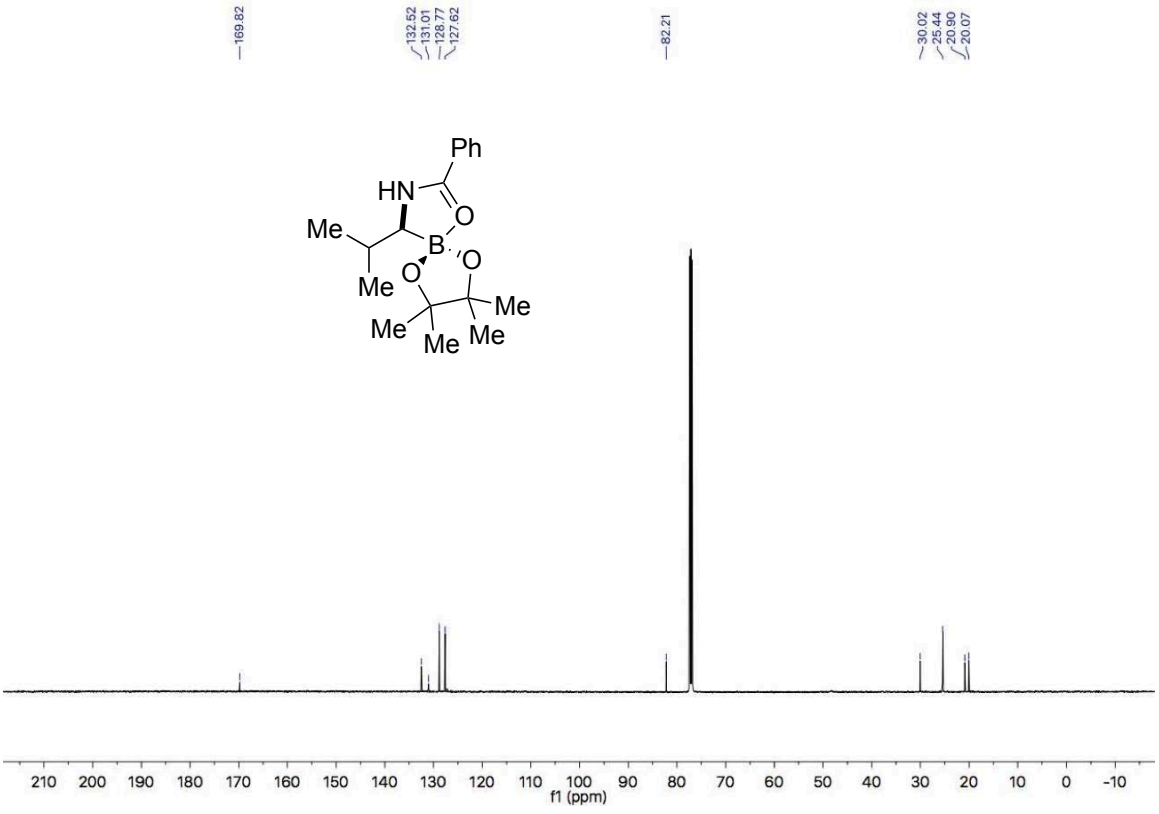
2a


Ph
HN
O
B
O
O
Me
Me
Me
Me
7.81
7.81
7.80
7.80
7.79
7.79
7.54
7.54
7.54
7.54
7.53
7.53
7.52
7.52
7.51
7.51
7.51
7.51
7.45
7.44
7.43
7.43
7.42
7.42
7.26 CDCl3
6.92
3.02
3.01
3.00
3.00
2.08
1.09
2.08
0.96
1.00
8.17
18.87
f1 (ppm)

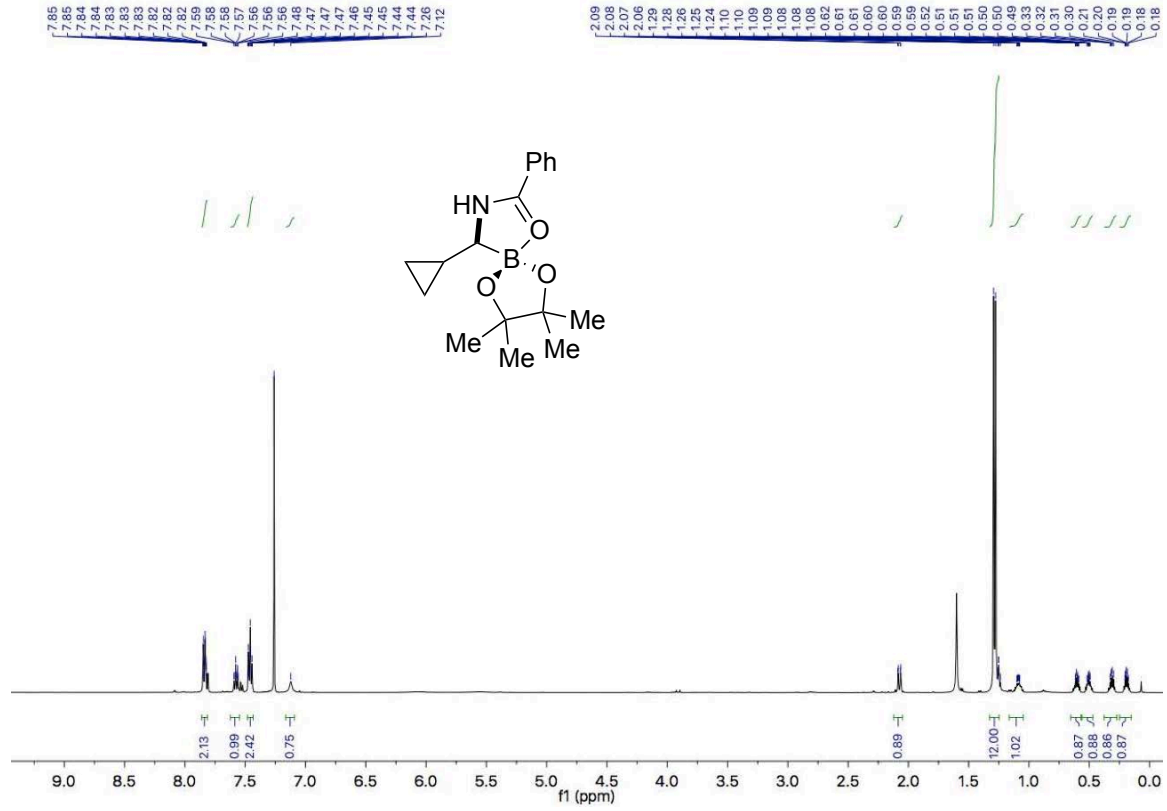

Ph
HN
O
B
O
O
Me
Me
Me
Me
82.32
77.16 CDCl3
169.63
132.45
131.16
128.76
127.62
39.79
31.39
30.44
26.63
26.46
25.40
25.37
f1 (ppm)

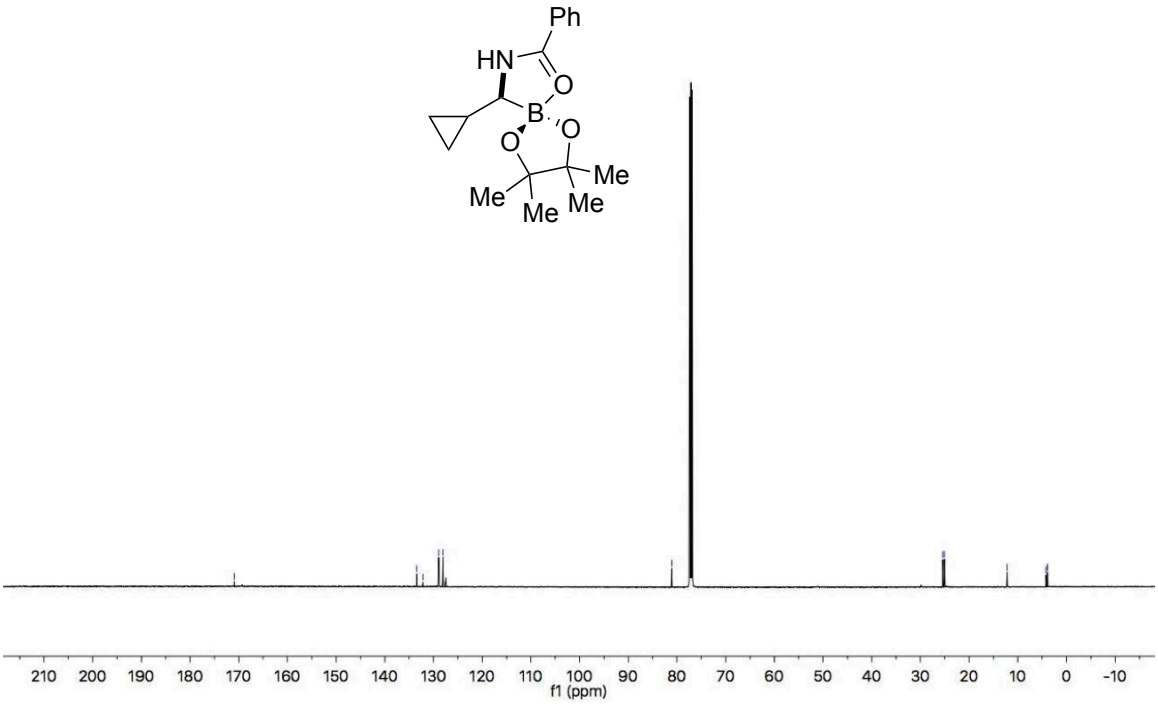
2b


7.80
7.80
7.80
7.79
7.78
7.78
7.53
7.52
7.52
7.51
7.51
7.45
7.44
7.43
7.42
7.26 CDCl3
0.89
2.99
2.98
2.98
2.97
2.96
2.08
2.06
2.05
2.04
2.02
2.01
1.28
1.28
1.25
1.07
1.06
1.04
1.03
1.02
1.01
0.07
Ph
HN
O
Me
B
O
O
Me
Me
Me
Me
Me
1.99
0.97
2.07
0.68
0.90
0.89
12.17
6.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

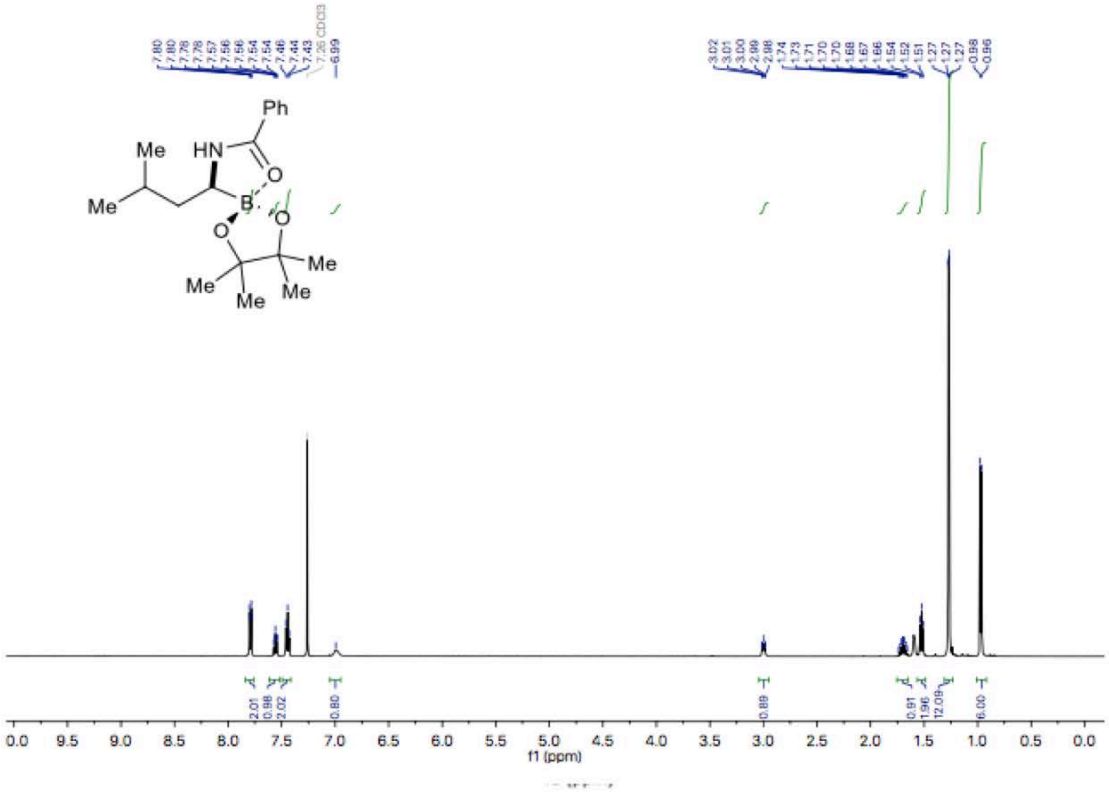

169.82
132.52
131.01
128.77
127.62
82.21
30.02
25.44
20.90
20.07
Ph
HN
O
Me
B
O
O
Me
Me
Me
Me
Me
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

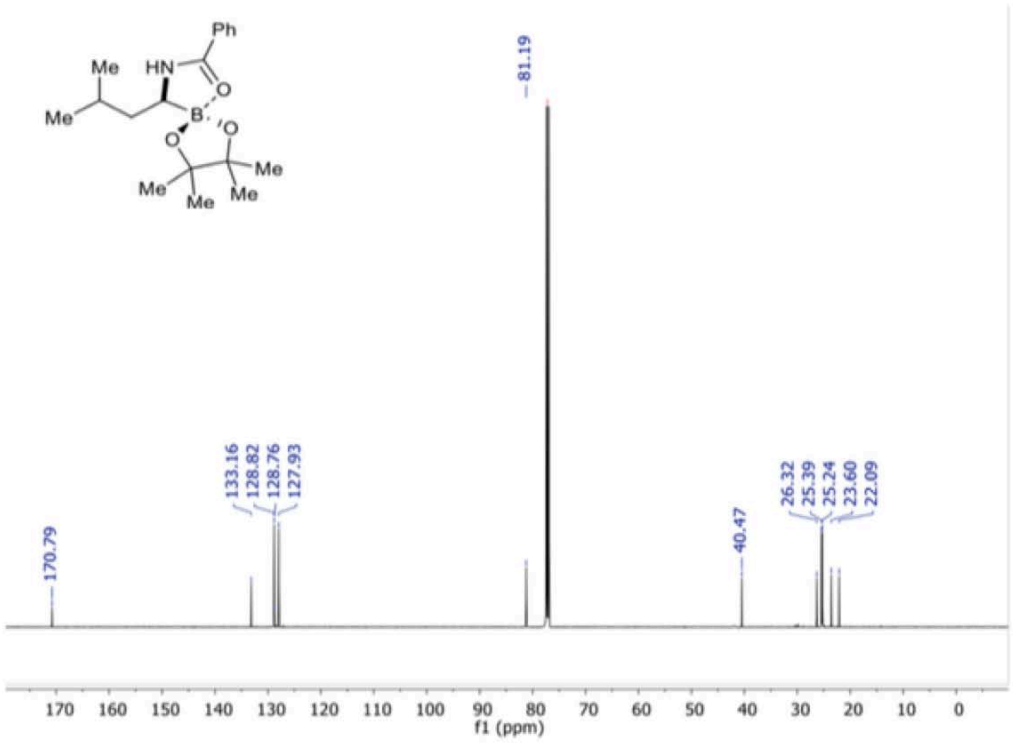
2c



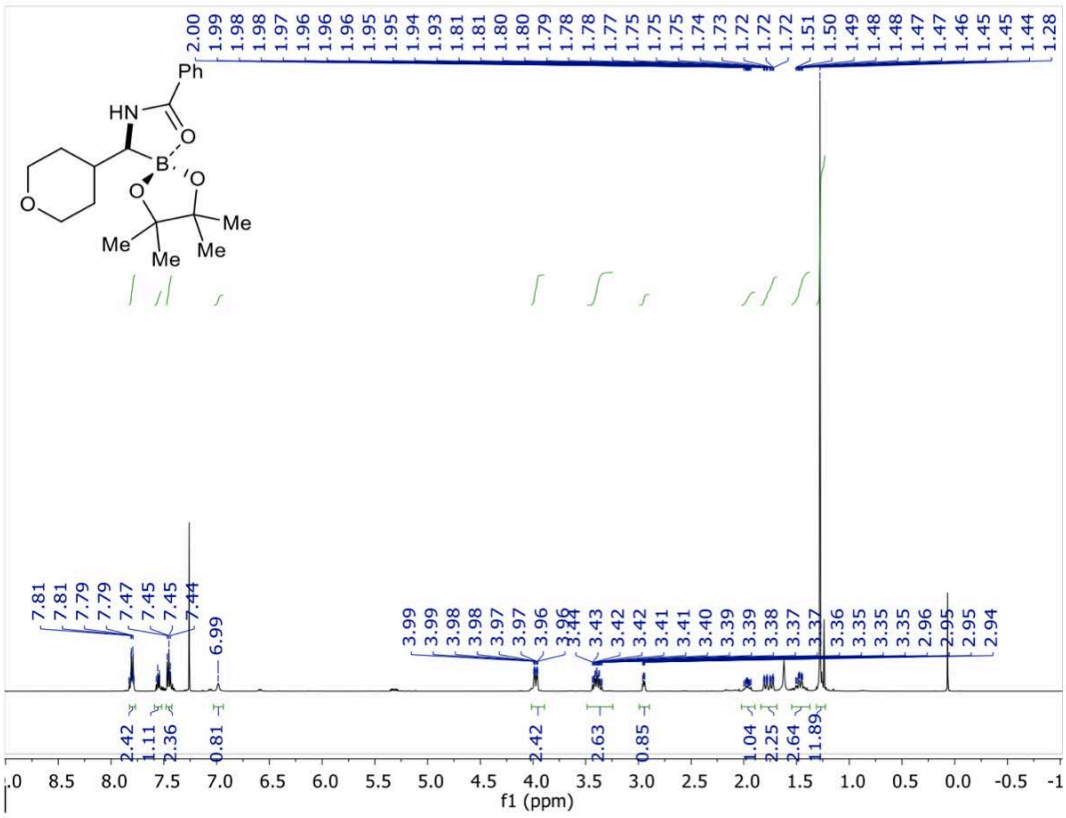


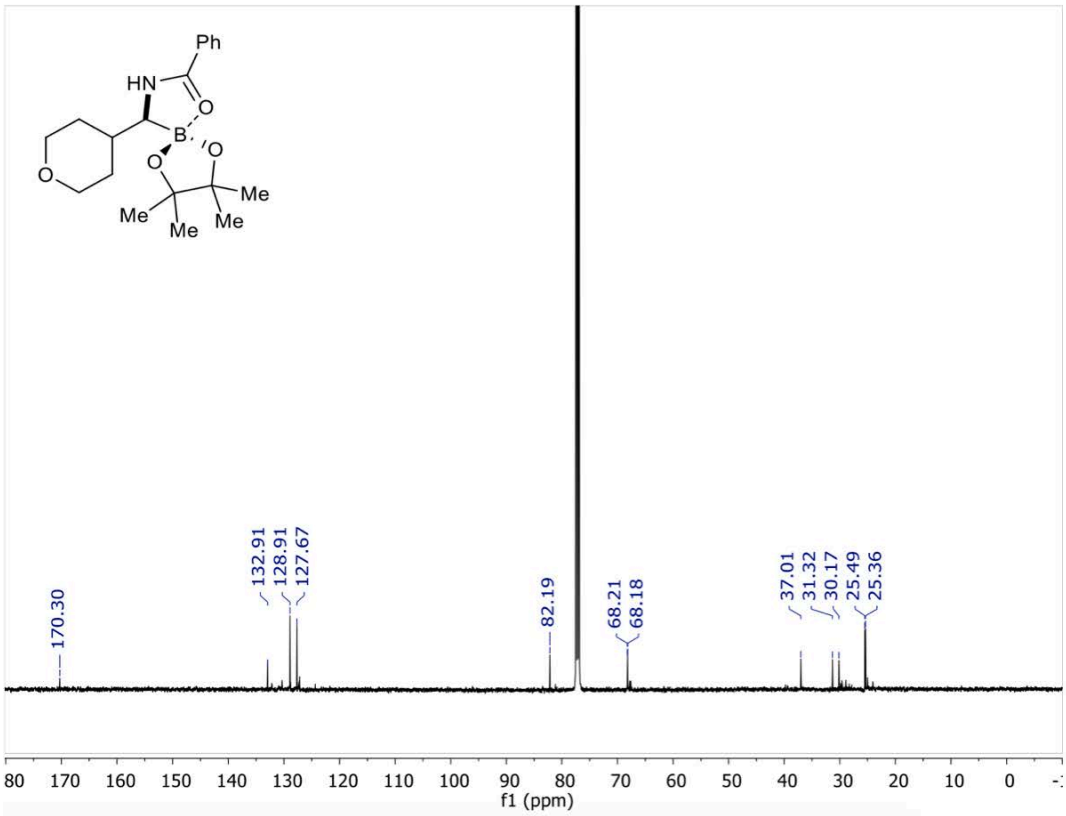
2d


Ph
Me
HN
O
Me
B
O
O
Me
Me
Me
Me
7.80
7.80
7.78
7.78
7.57
7.56
7.56
7.54
7.54
7.46
7.44
7.43
7.26 CDCl3
6.99
3.02
3.01
3.00
2.99
2.98
1.74
1.73
1.71
1.70
1.70
1.68
1.67
1.66
1.54
1.52
1.51
1.27
1.27
1.27
0.98
0.96
2.01
0.98
2.02
0.80
0.89
0.91
1.96
12.09
6.00
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

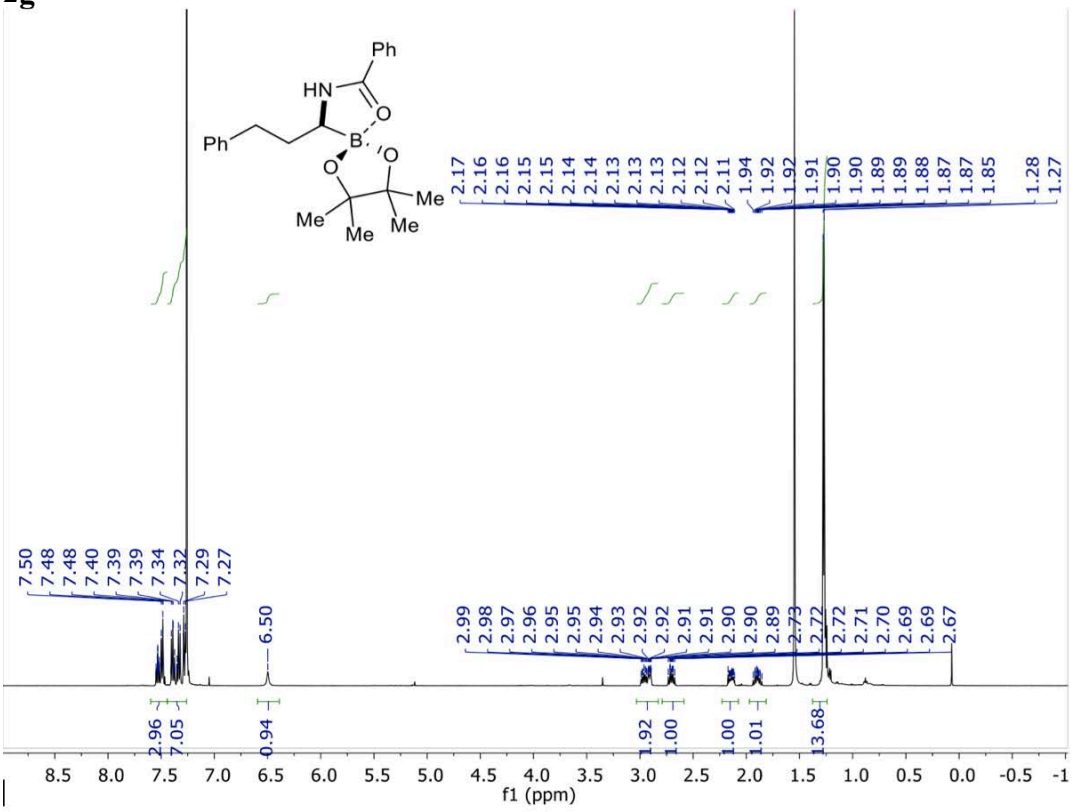

Ph
Me
HN
O
Me
B
O
O
Me
Me
Me
Me
81.19
133.16
128.82
128.76
127.93
170.79
40.47
26.32
25.39
25.24
23.60
22.09
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

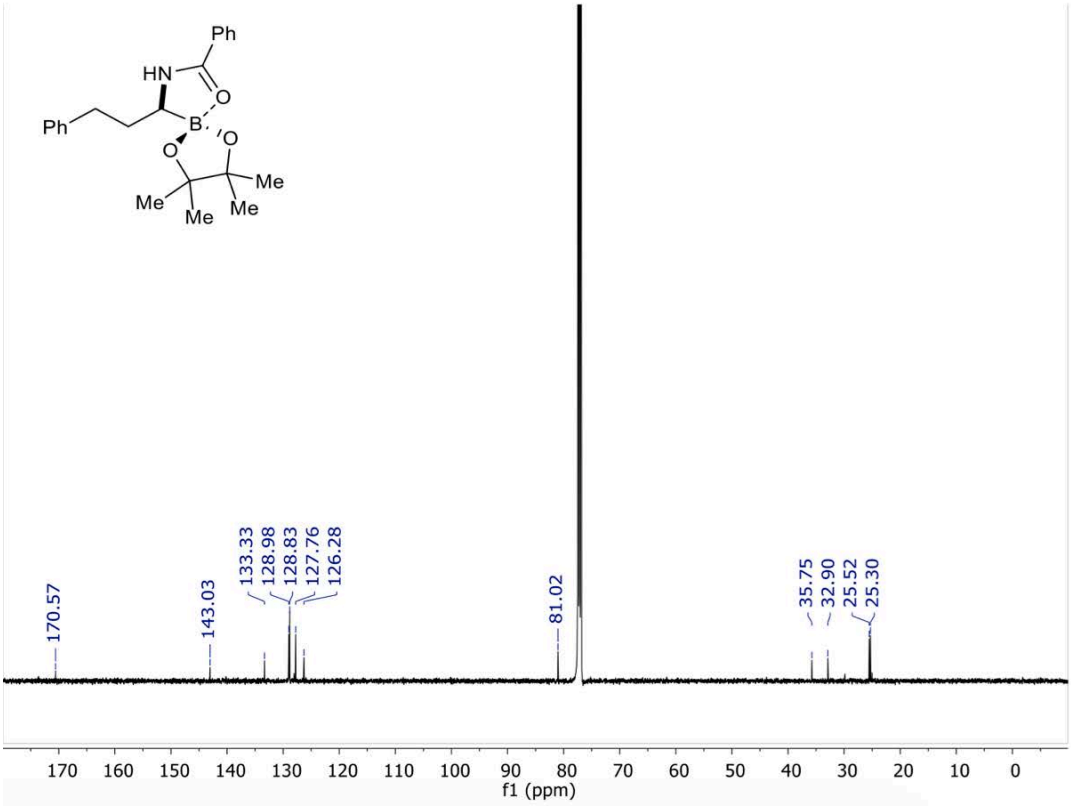
2e


Ph
HN
O
B
O
O
Me
Me
Me
Me
2.00 1.99 1.98 1.98 1.97 1.96 1.96 1.96 1.95 1.95 1.94 1.93 1.81 1.81 1.80 1.80 1.79 1.78 1.78 1.77 1.75 1.75 1.75 1.74 1.73 1.72 1.72 1.72 1.51 1.50 1.49 1.48 1.48 1.47 1.47 1.46 1.45 1.45 1.44 1.28
7.81 7.81 7.79 7.79 7.47 7.45 7.45 7.44 6.99
3.99 3.99 3.98 3.98 3.97 3.97 3.96 3.96 3.43 3.42 3.42 3.41 3.41 3.40 3.39 3.39 3.38 3.37 3.37 3.36 3.35 3.35 3.35 2.96 2.95 2.95 2.94
2.42 1.11 2.36 0.81 2.42 2.63 0.85 1.04 2.25 2.64 11.89
f1 (ppm)

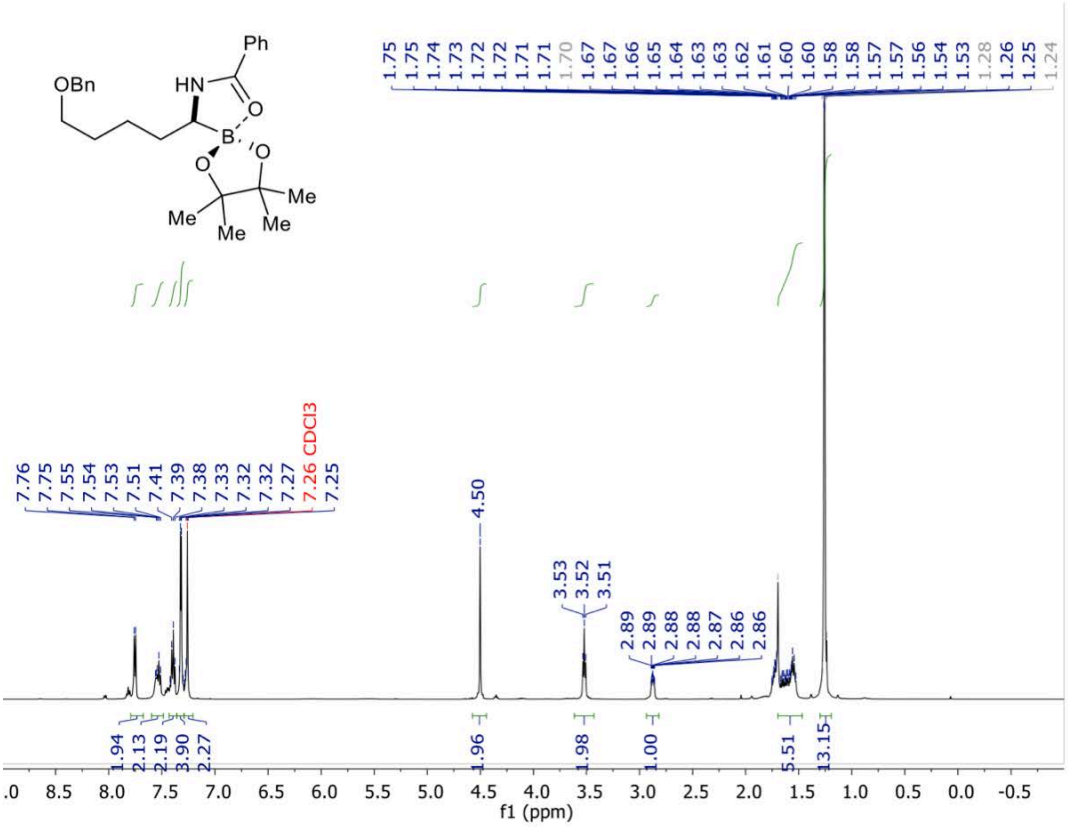

Ph
HN
O
B
O
O
Me
Me
Me
Me
170.30
132.91 128.91 127.67
82.19
68.21 68.18
37.01 31.32 30.17 25.49 25.36
f1 (ppm)

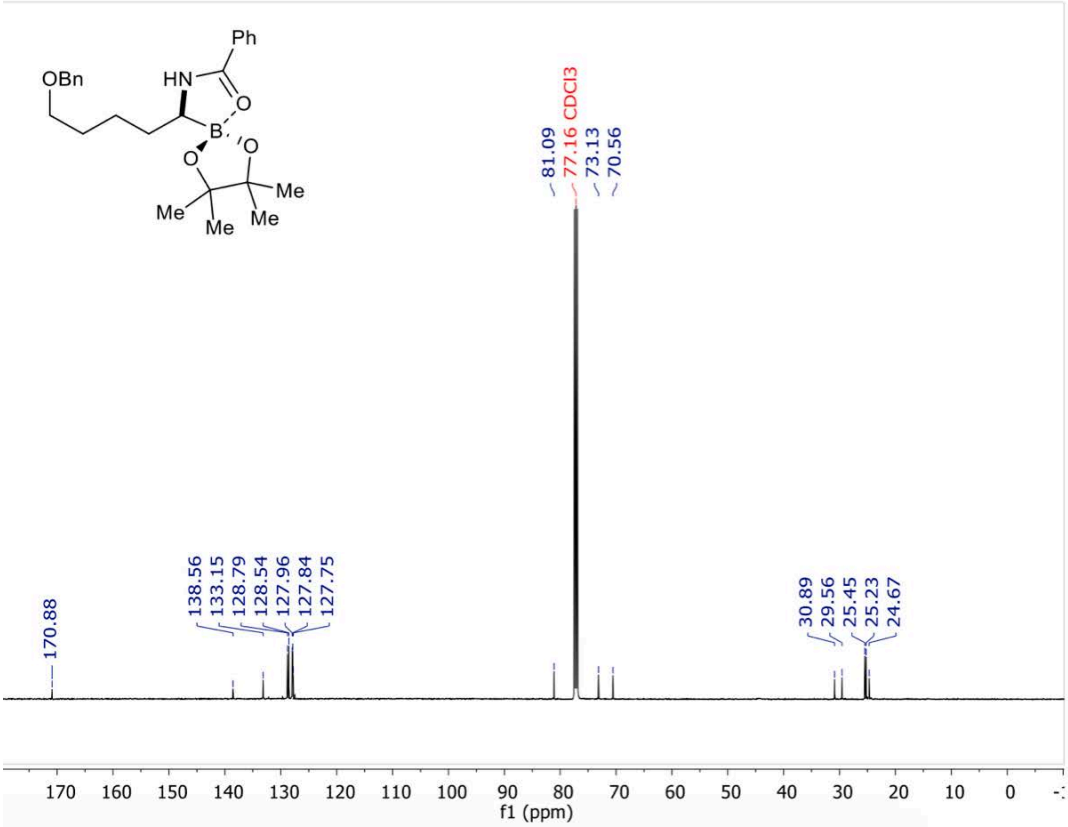
2g


Ph
HN
O
B
O
O
Ph
Me
Me
Me
Me
2.17 2.16 2.16 2.15 2.15 2.14 2.14 2.13 2.13 2.13 2.12 2.12 2.11 1.94 1.92 1.92 1.91 1.90 1.90 1.89 1.89 1.88 1.87 1.87 1.85 1.28 1.27
7.50 7.48 7.48 7.40 7.39 7.39 7.34 7.32 7.29 7.27
6.50
2.99 2.98 2.97 2.96 2.95 2.95 2.94 2.93 2.92 2.92 2.91 2.91 2.90 2.90 2.89 2.73 2.72 2.72 2.71 2.70 2.69 2.69 2.67
2.96 7.05 0.94 1.92 1.00 1.00 1.01 13.68
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

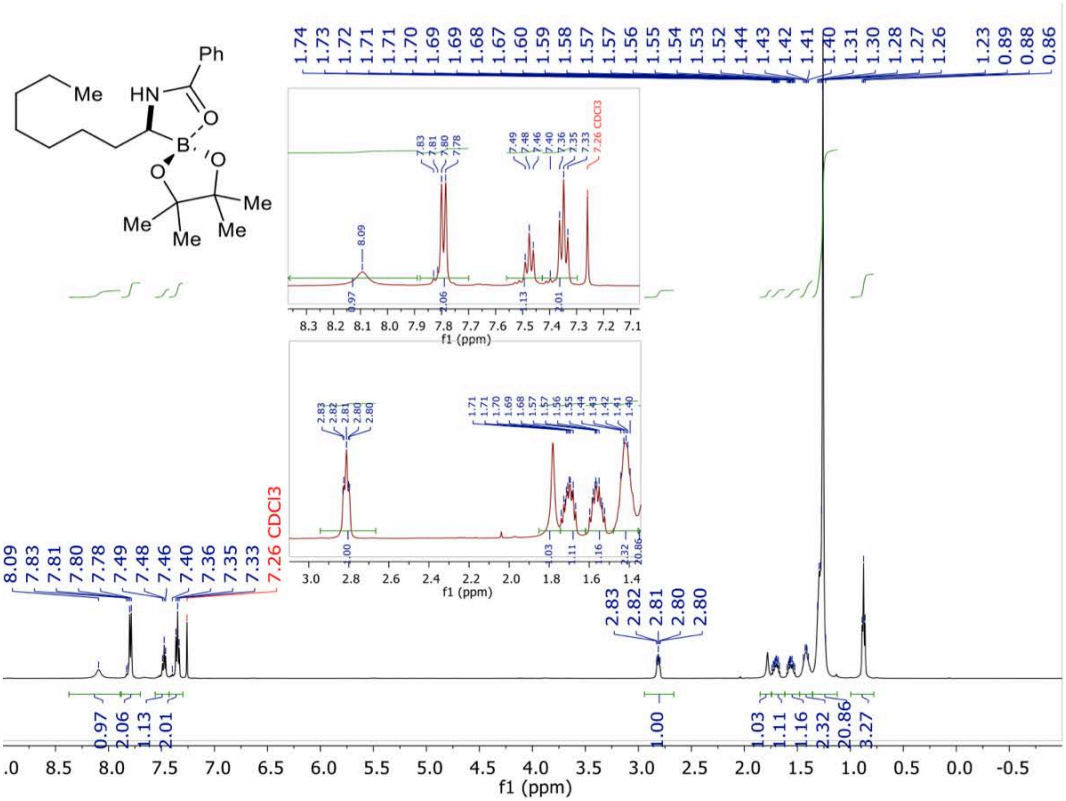

Ph
HN
O
B
O
O
Ph
Me
Me
Me
Me
170.57
143.03
133.33
128.98
128.83
127.76
126.28
81.02
35.75
32.90
25.52
25.30
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

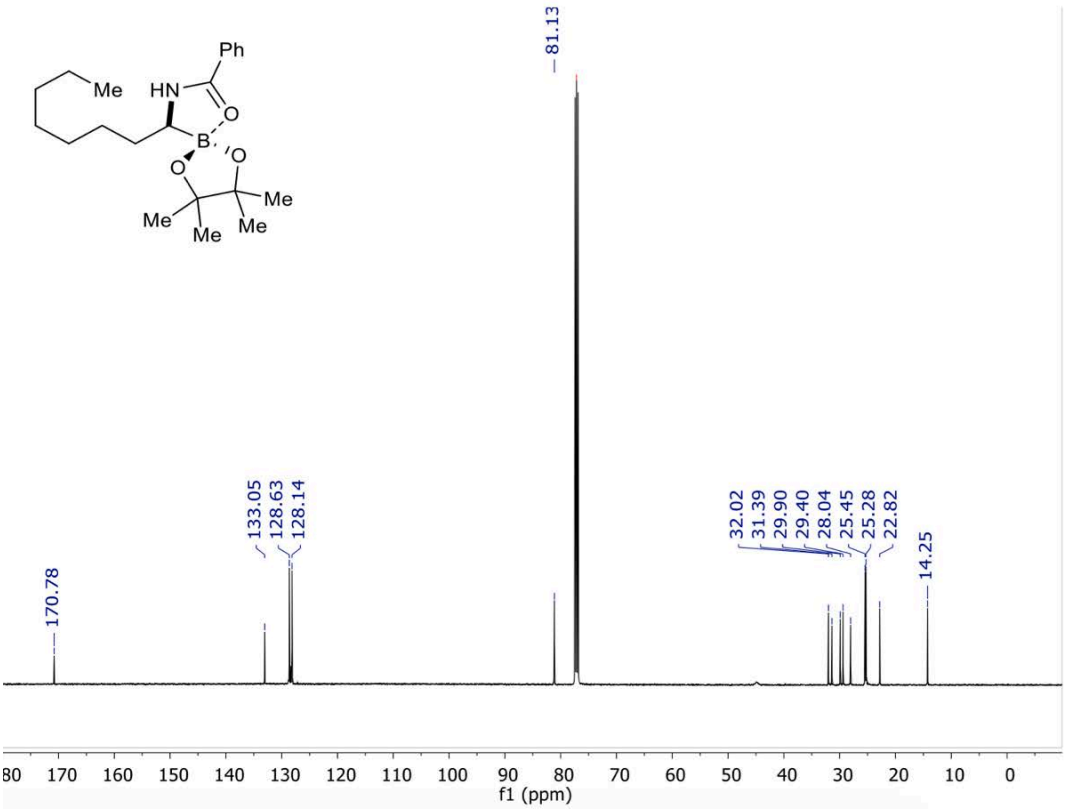
2h


Ph
OBn
HN
O
B
O
O
Me
Me
Me
Me
1.75
1.74
1.73
1.72
1.71
1.67
1.66
1.65
1.64
1.63
1.62
1.61
1.60
1.58
1.57
1.56
1.54
1.53
1.28
1.26
1.25
1.24
7.76
7.75
7.55
7.54
7.53
7.51
7.41
7.39
7.38
7.33
7.32
7.27
7.26 CDCl3
7.25
4.50
3.53
3.52
3.51
2.89
2.88
2.87
2.86
1.94
2.13
2.19
3.90
2.27
1.96
1.98
1.00
5.51
13.15
f1 (ppm)

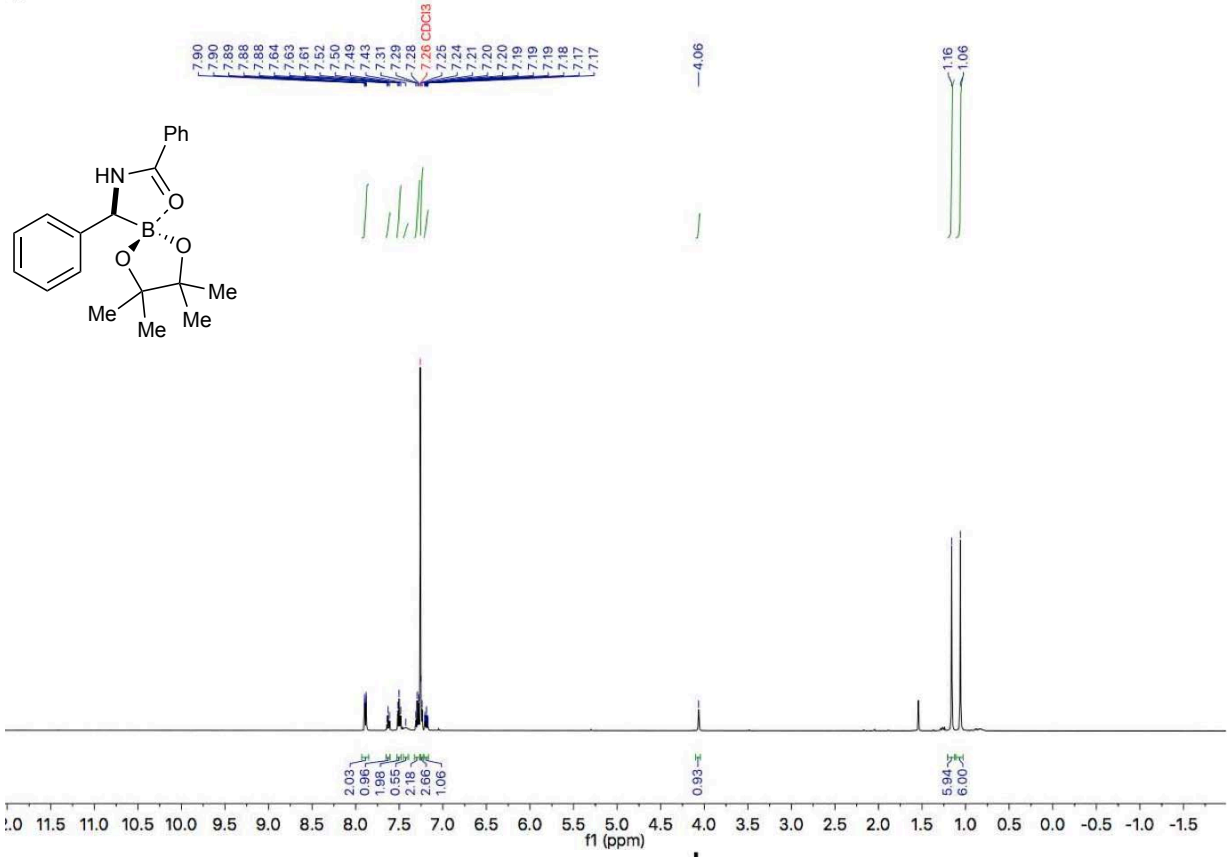

Ph
OBn
HN
O
B
O
O
Me
Me
Me
Me
81.09
77.16 CDCl3
73.13
70.56
170.88
138.56
133.15
128.79
128.54
127.96
127.84
127.75
30.89
29.56
25.45
25.23
24.67
f1 (ppm)

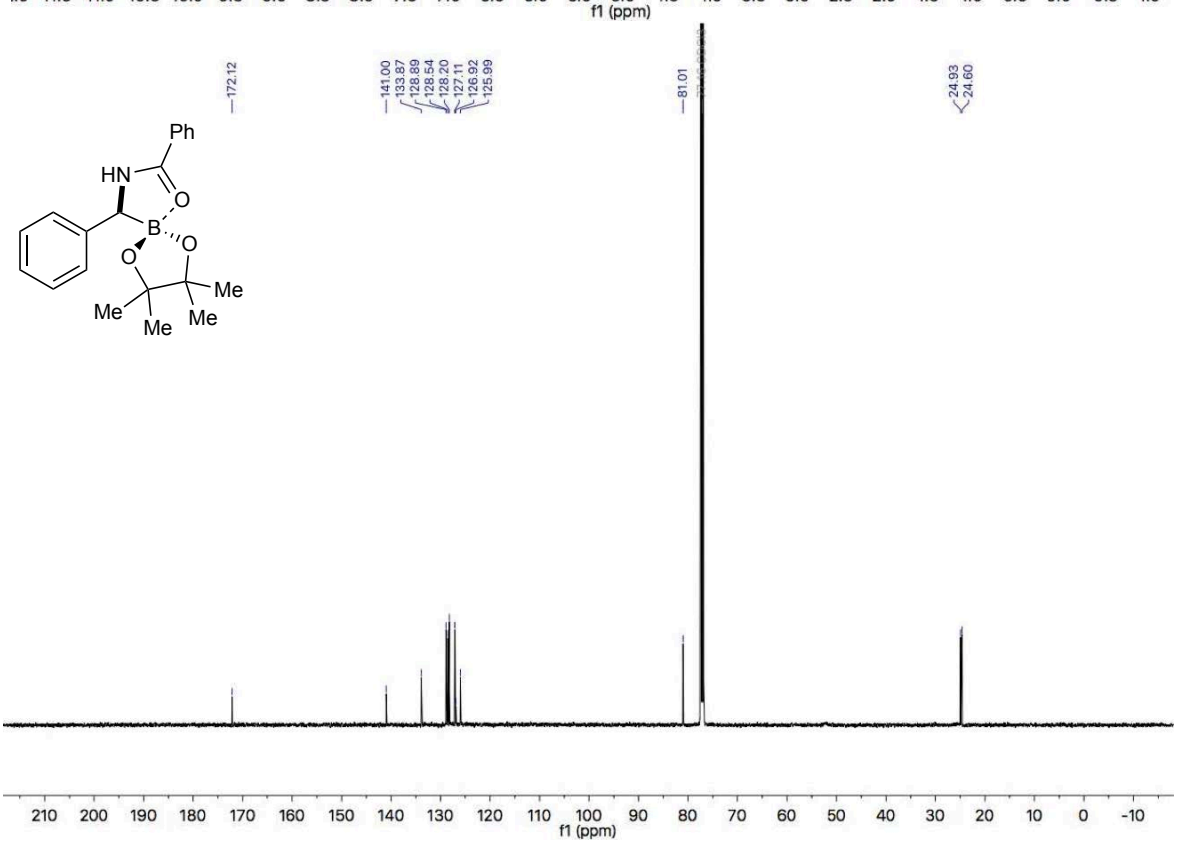
2i


Ph
Me
HN
O
B
O
O
Me
Me
Me
Me
1.74 1.73 1.72 1.71 1.71 1.70 1.69 1.69 1.68 1.67 1.60 1.59 1.58 1.57 1.57 1.56 1.55 1.54 1.53 1.52 1.44 1.43 1.42 1.41 1.40 1.31 1.30 1.28 1.27 1.26 1.23 0.89 0.88 0.86
8.09 7.83 7.81 7.80 7.78 7.49 7.48 7.46 7.40 7.36 7.35 7.33 7.26 CDCl3
2.83 2.82 2.81 2.80 2.80
0.97 2.06 1.13 2.01 1.00 1.03 1.11 1.16 2.32 20.86 3.27
f1 (ppm)

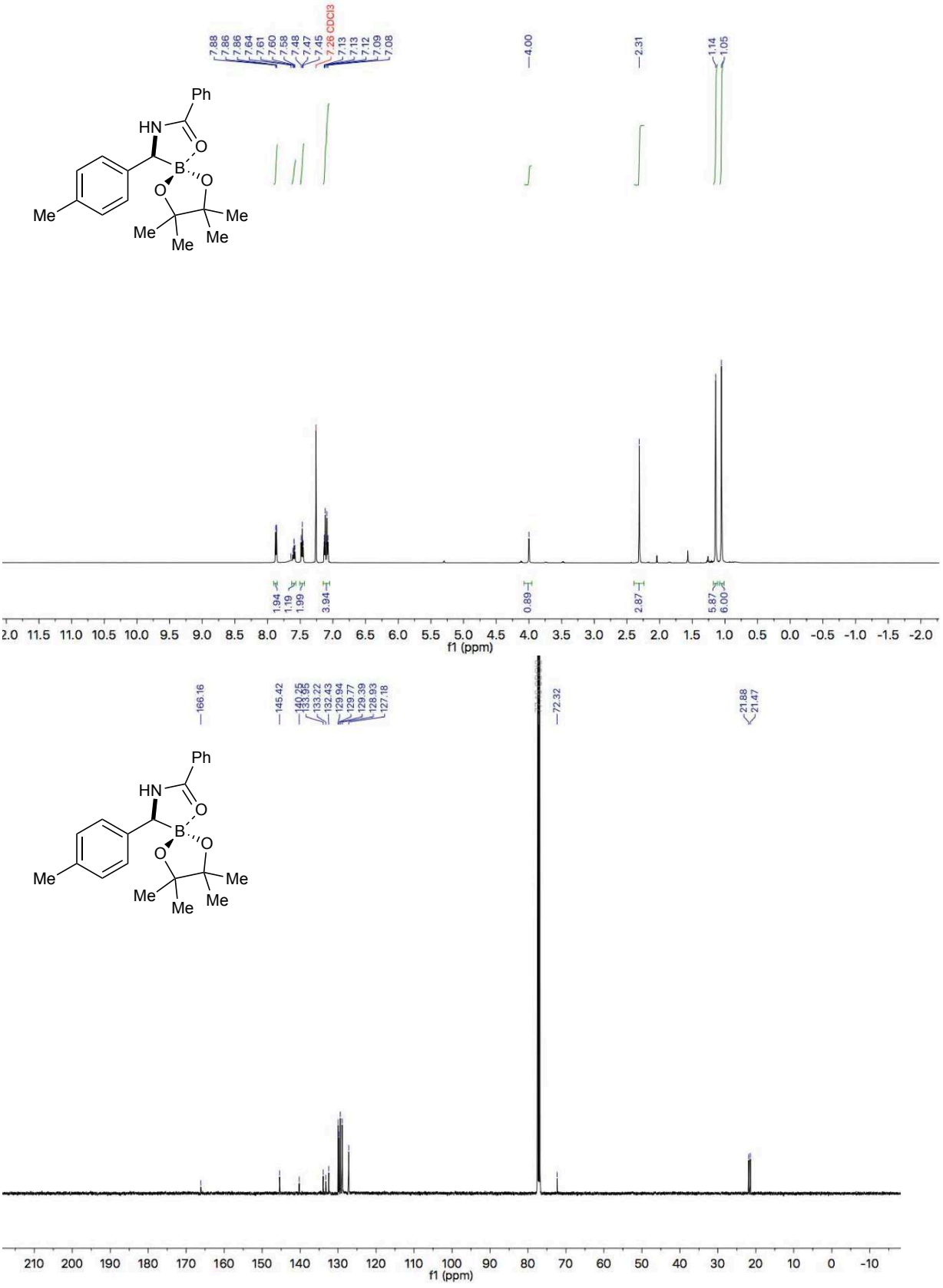

Ph
Me
HN
O
B
O
O
Me
Me
Me
Me
81.13
133.05 128.63 128.14
32.02 31.39 29.90 29.40 28.04 25.45 25.28 22.82 14.25
170.78
f1 (ppm)

2j

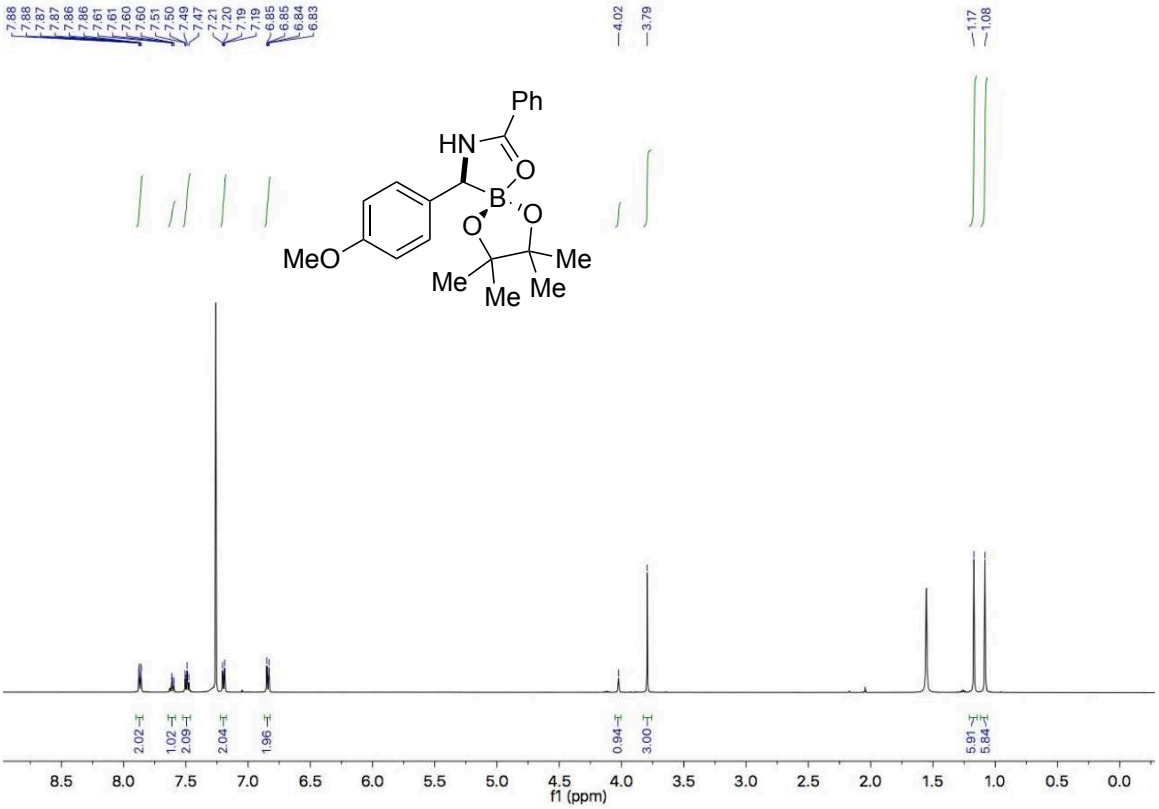

7.90
7.90
7.89
7.88
7.88
7.64
7.63
7.61
7.52
7.50
7.49
7.43
7.31
7.29
7.28
7.26 CDCl3
7.25
7.24
7.21
7.20
7.20
7.19
7.19
7.19
7.18
7.17
7.17
4.06
1.16
1.06
Ph
HN
O
B
O
O
Me
Me
Me
Me
2.03
0.96
1.98
0.55
2.18
2.66
1.06
0.93
5.94
6.00
f1 (ppm)

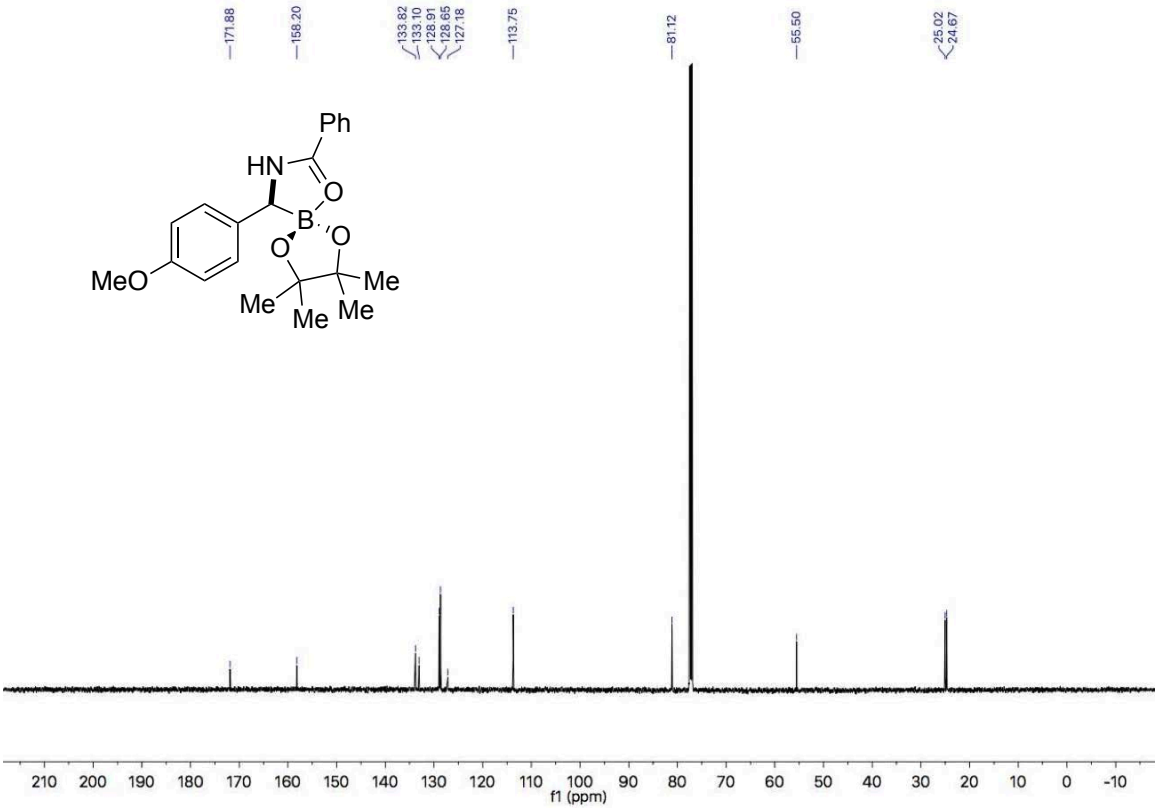

172.12
141.00
133.87
128.89
128.54
128.20
127.11
126.92
125.99
81.01
24.93
24.60
Ph
HN
O
B
O
O
Me
Me
Me
Me
f1 (ppm)

2k

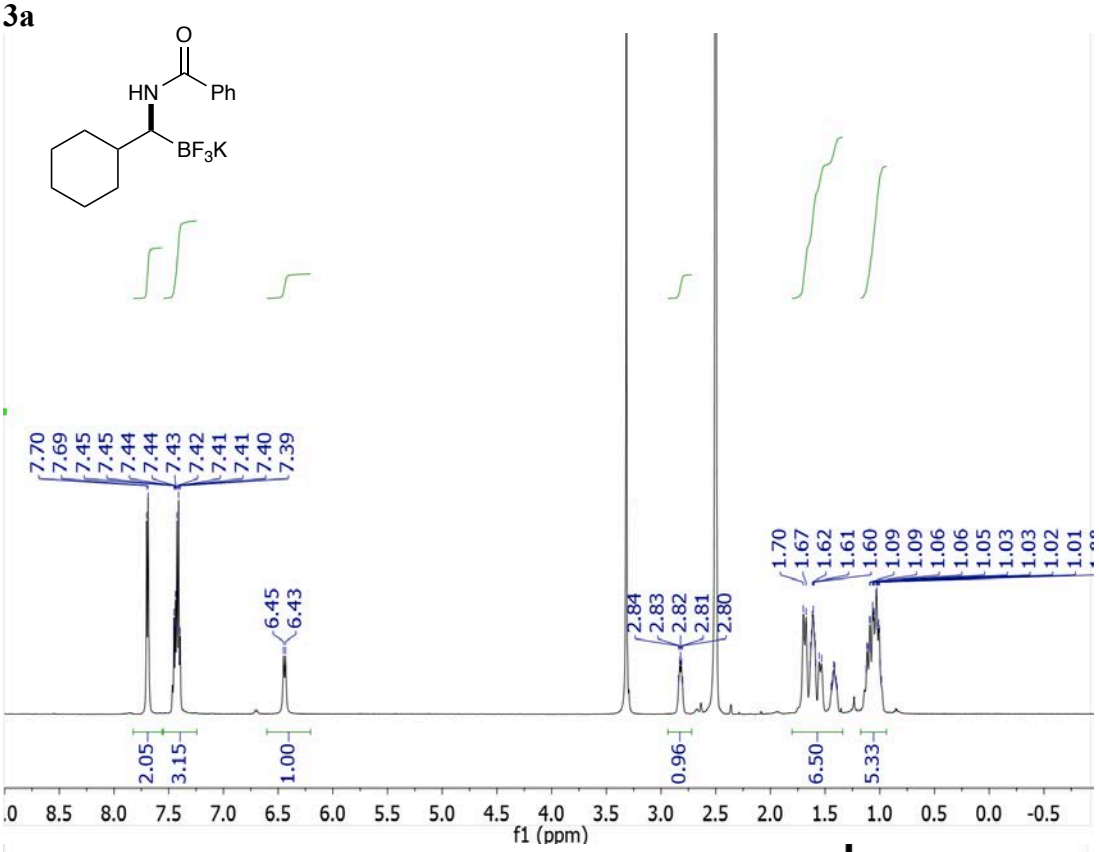

7.88
7.86
7.86
7.64
7.61
7.60
7.58
7.48
7.47
7.45
7.26 CDCl3
7.13
7.13
7.12
7.09
7.08
4.00
2.31
1.14
1.05
Ph
HN
O
B
O
O
Me
Me
Me
Me
1.94
1.19
1.99
3.94
0.89
2.87
5.87
6.00
f1 (ppm)
166.16
145.42
140.35
139.65
133.22
132.43
129.94
129.77
129.39
128.93
127.18
72.32
21.88
21.47
f1 (ppm)

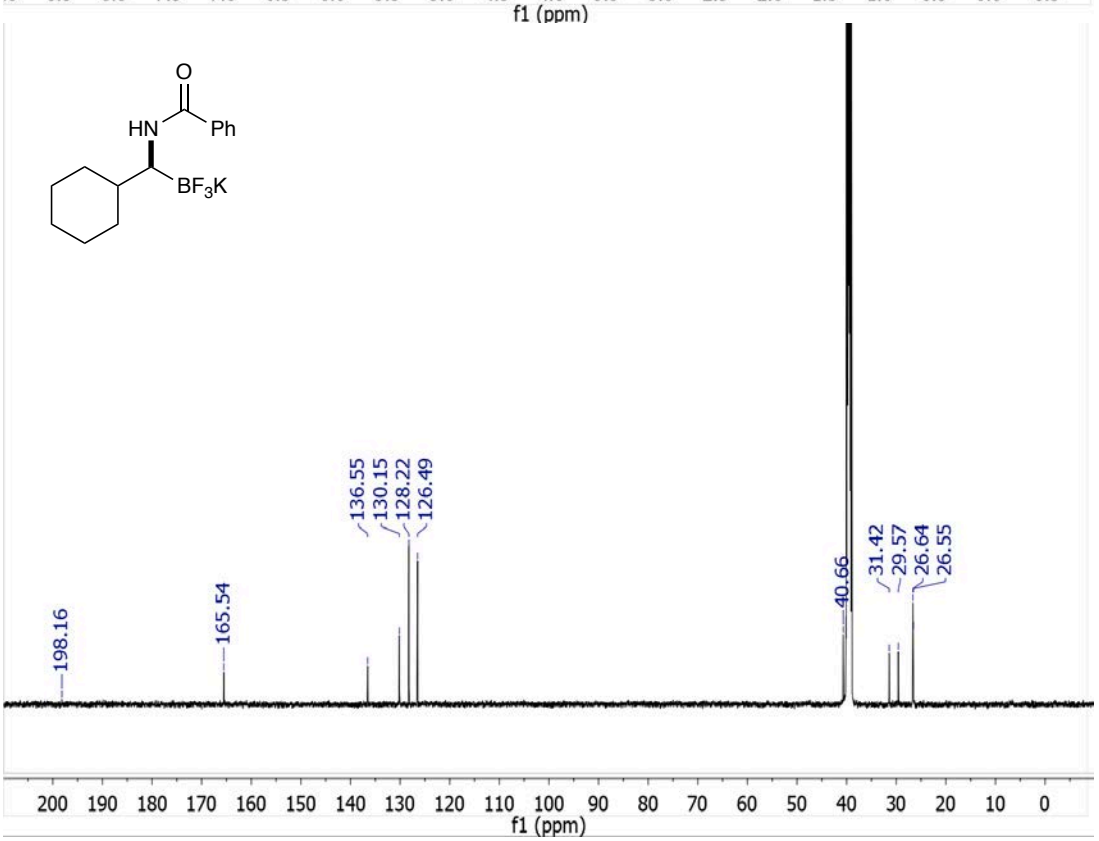
2l


7.88
7.88
7.87
7.87
7.86
7.86
7.61
7.61
7.60
7.60
7.51
7.50
7.49
7.47
7.21
7.20
7.19
7.19
6.85
6.85
6.84
6.83
4.02
3.79
1.17
1.08
Ph
HN
O
B
O
O
MeO
Me
Me
Me
Me
2.02
1.02
2.09
2.04
1.96
0.94
3.00
5.91
5.84
f1 (ppm)

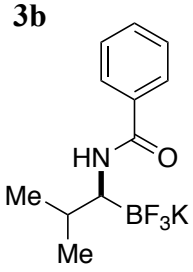

171.88
158.20
133.82
133.10
128.91
128.65
127.18
113.75
81.12
55.50
25.02
24.67
Ph
HN
O
B
O
O
MeO
Me
Me
Me
Me
f1 (ppm)

3a

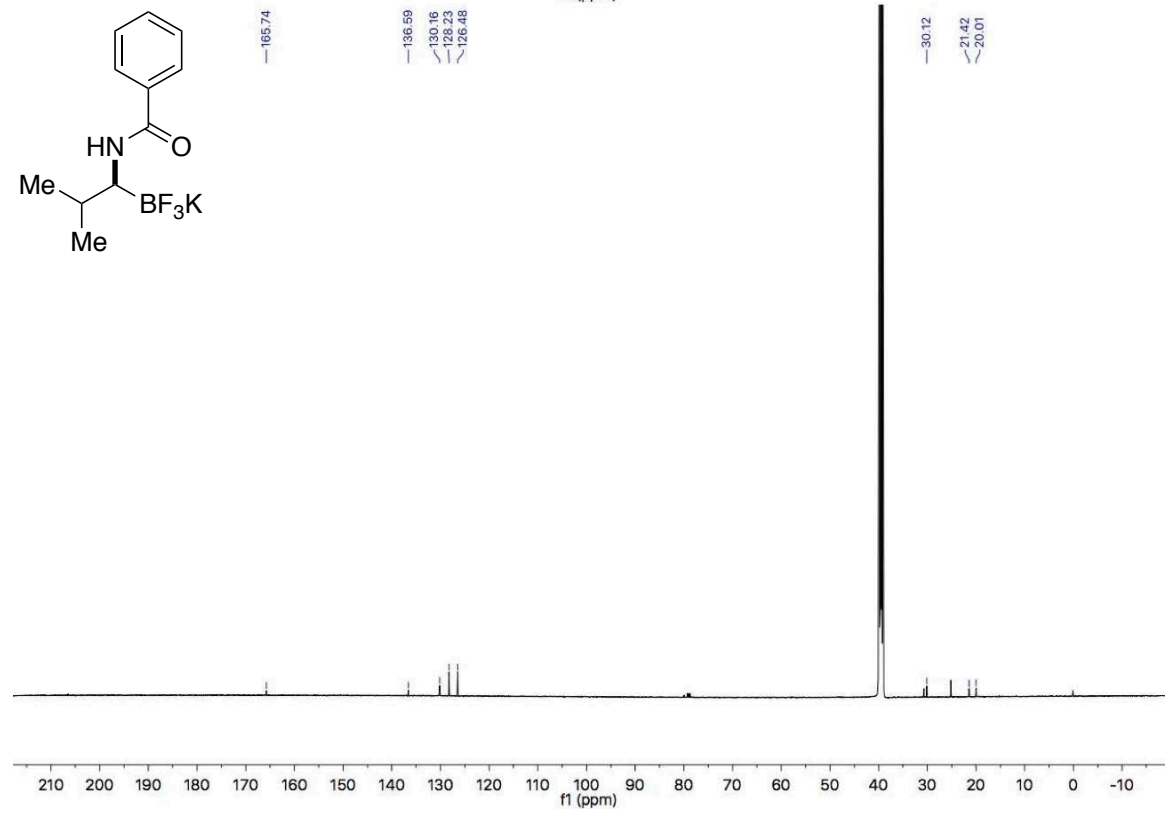

O
HN
Ph
BF3K
7.70
7.69
7.45
7.45
7.44
7.44
7.44
7.43
7.42
7.41
7.41
7.40
7.39
6.45
6.43
2.84
2.83
2.82
2.81
2.80
1.70
1.67
1.62
1.61
1.60
1.09
1.09
1.06
1.06
1.05
1.03
1.03
1.02
1.01
2.05
3.15
1.00
0.96
6.50
5.33
f1 (ppm)


O
HN
Ph
BF3K
198.16
165.54
136.55
130.15
128.22
126.49
40.66
31.42
29.57
26.64
26.55
f1 (ppm)

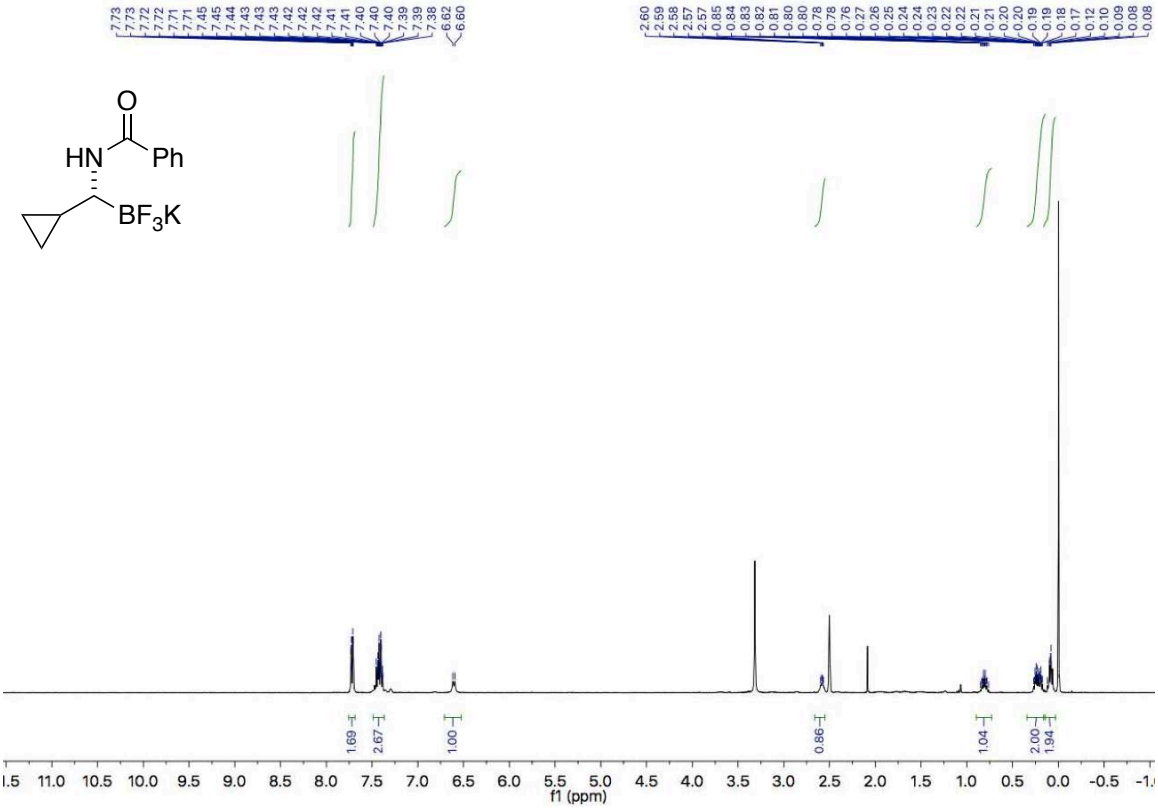
3b

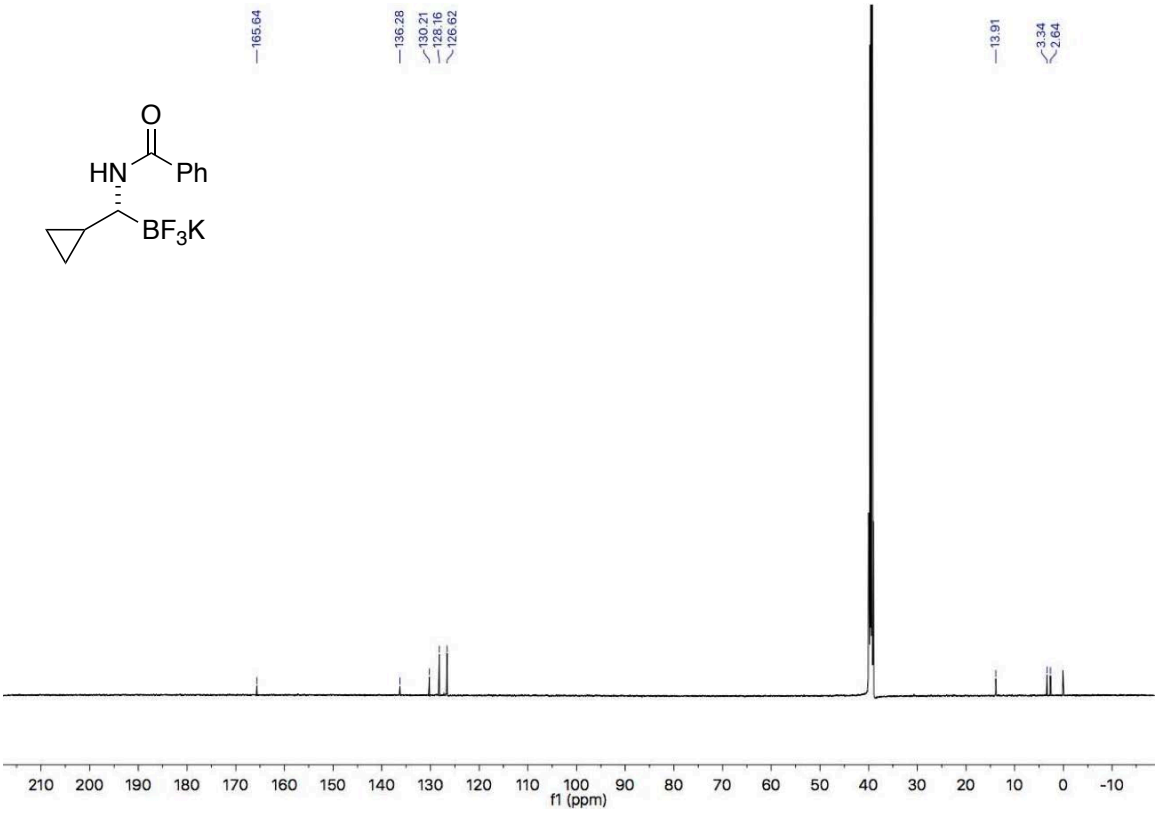

HN
O
Me
BF3K
Me

1.92
2.95
1.00
1.14
1.25
6.00
4
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

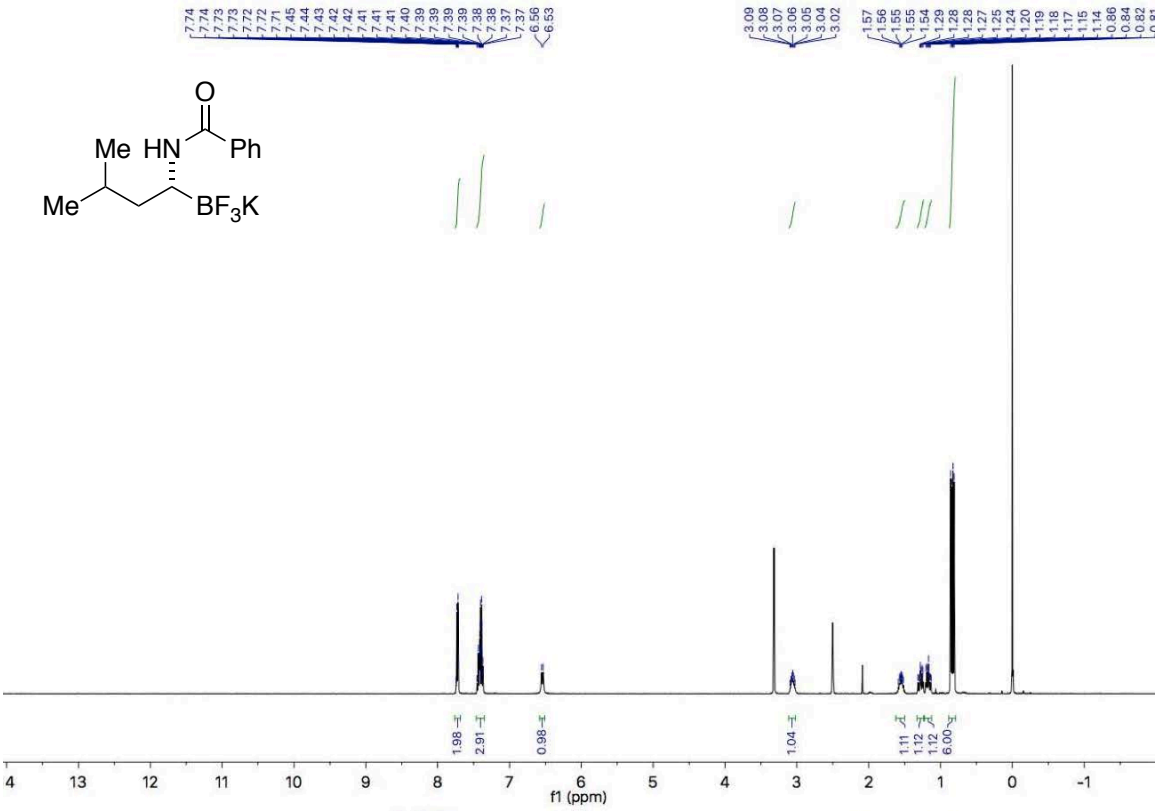

165.74
136.59
130.16
128.23
126.48
30.12
21.42
20.01
HN
O
Me
BF3K
Me
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

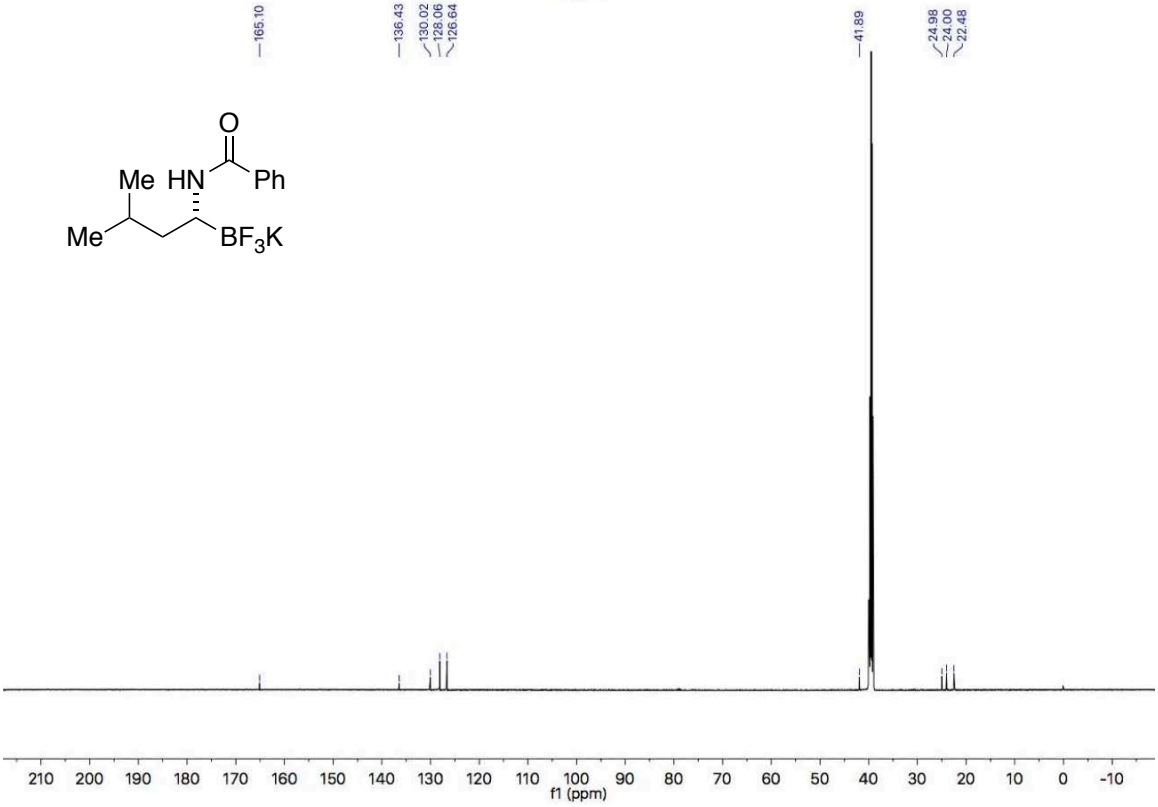
3c



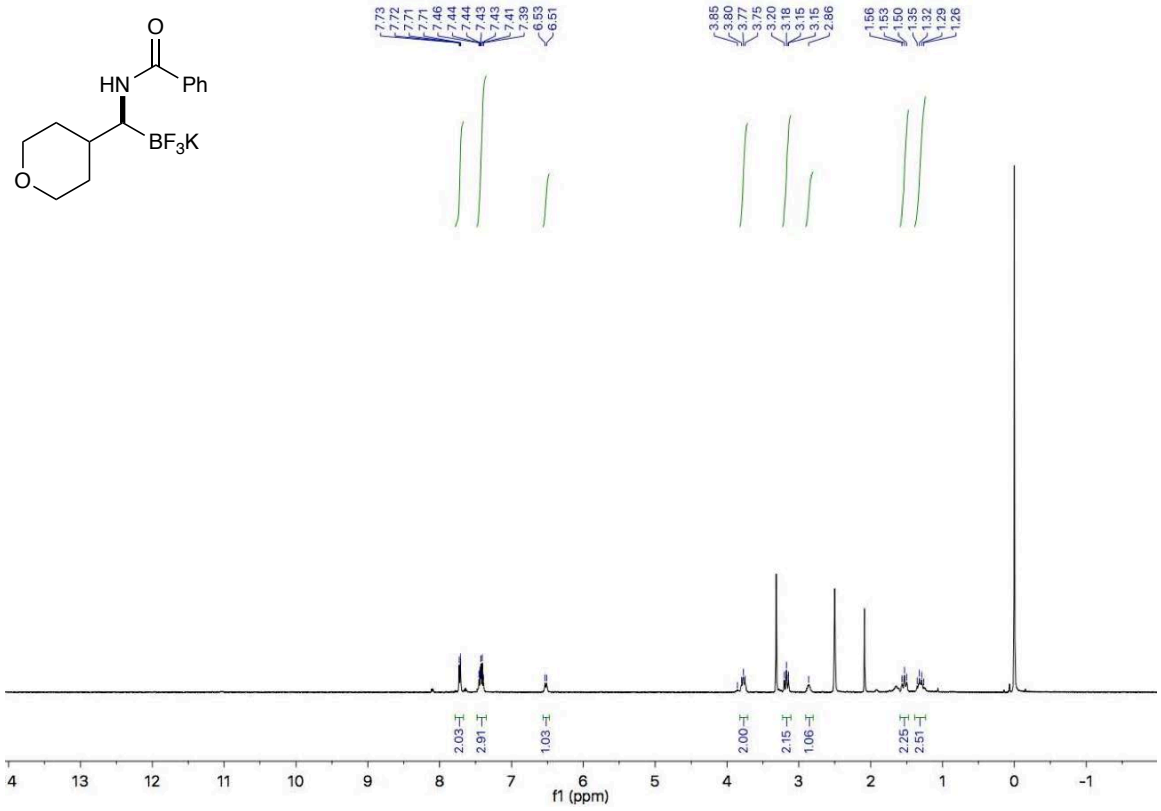


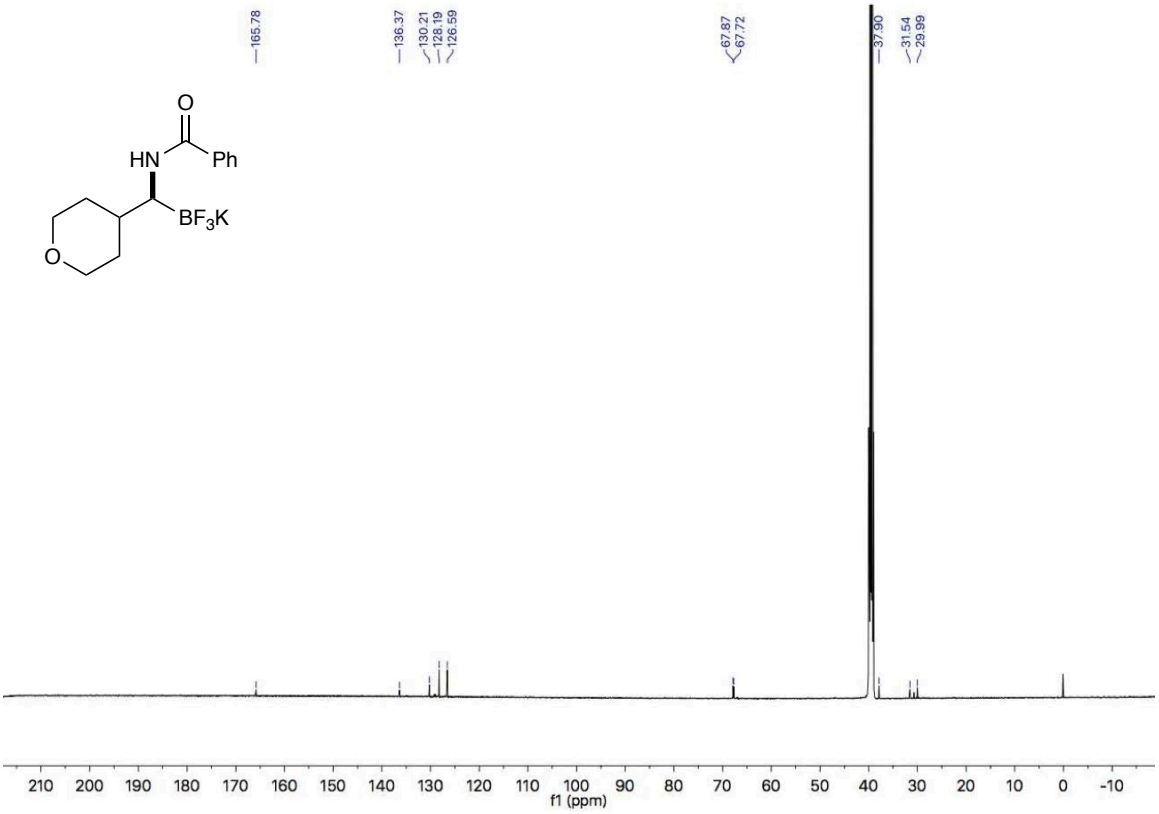
3d



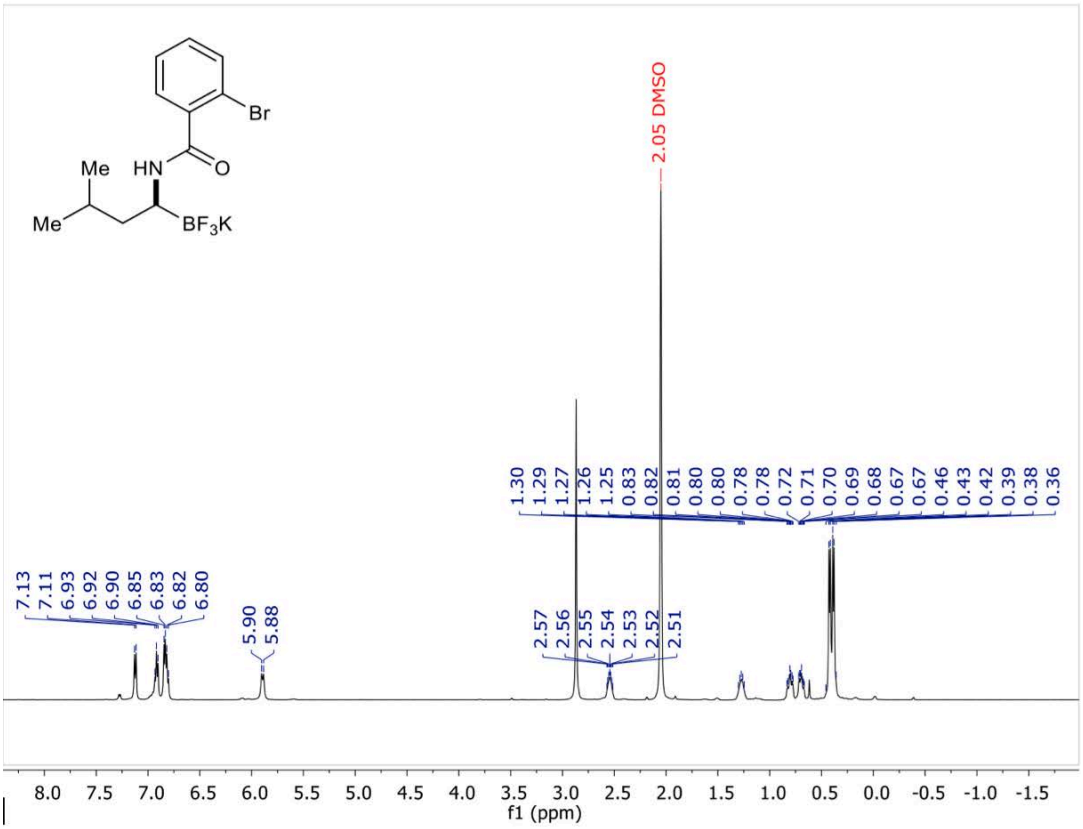


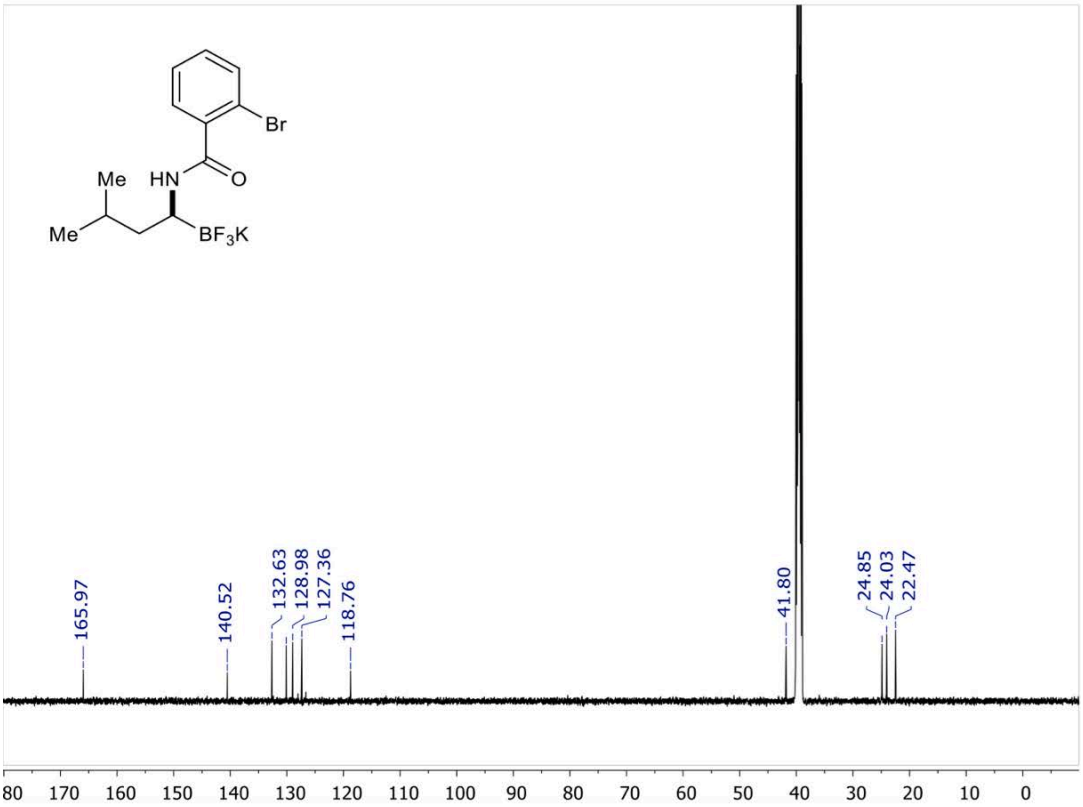
3e


7.73
7.72
7.71
7.71
7.46
7.44
7.44
7.43
7.43
7.41
7.39
6.53
6.51
3.85
3.80
3.77
3.75
3.20
3.18
3.15
3.15
2.86
1.56
1.53
1.50
1.35
1.32
1.29
1.26
2.03
2.91
1.03
2.00
2.15
1.06
2.25
2.51
f1 (ppm)


165.78
136.37
130.21
128.19
126.59
67.87
67.72
37.90
31.54
29.99
f1 (ppm)

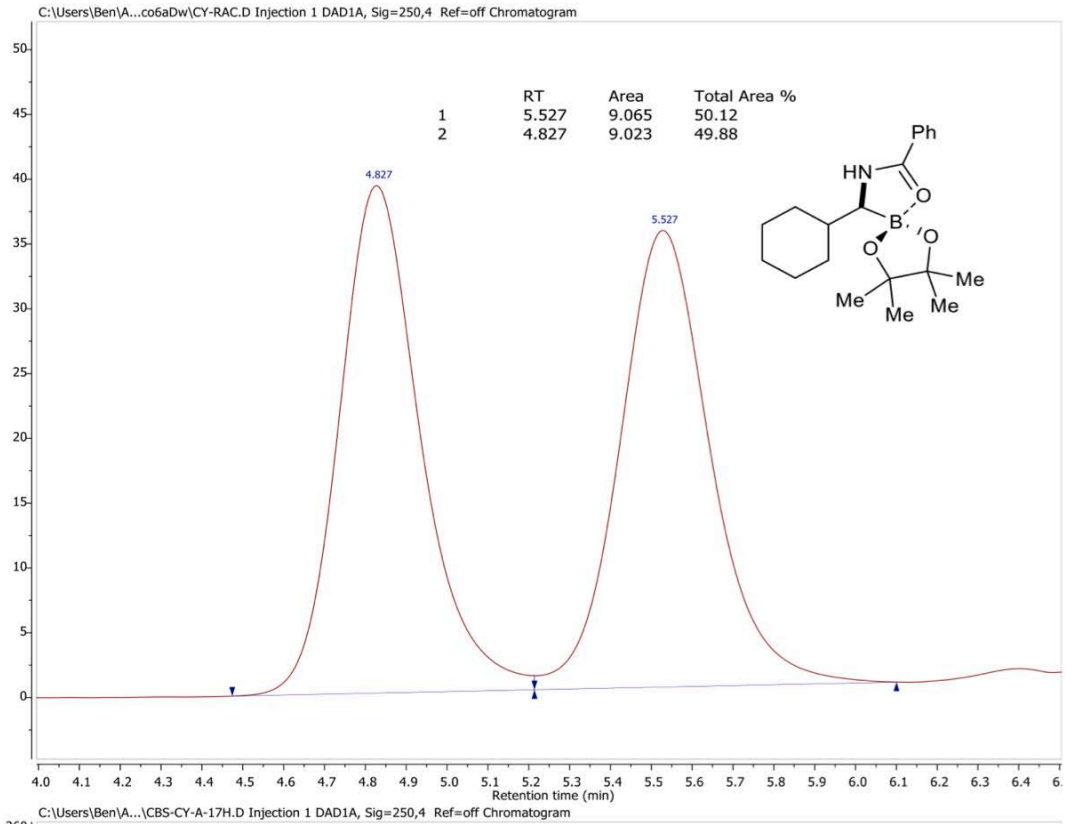
3f

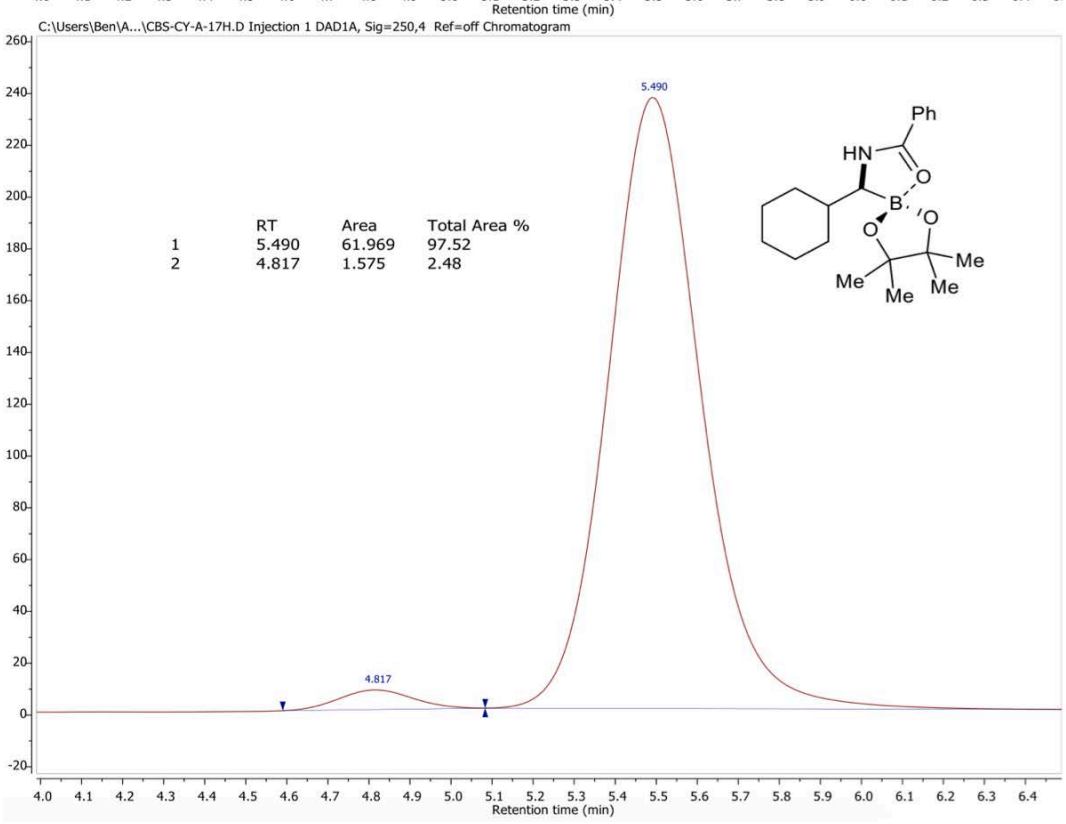

Br
Me
HN
O
Me
BF3K
2.05 DMSO
1.30
1.29
1.27
1.26
1.25
0.83
0.82
0.81
0.80
0.80
0.78
0.78
0.72
0.71
0.70
0.69
0.68
0.67
0.67
0.46
0.43
0.42
0.39
0.38
0.36
7.13
7.11
6.93
6.92
6.90
6.85
6.83
6.82
6.80
5.90
5.88
2.57
2.56
2.55
2.54
2.53
2.52
2.51
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)


Br
Me
HN
O
Me
BF3K
165.97
140.52
132.63
128.98
127.36
118.76
41.80
24.85
24.03
22.47
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

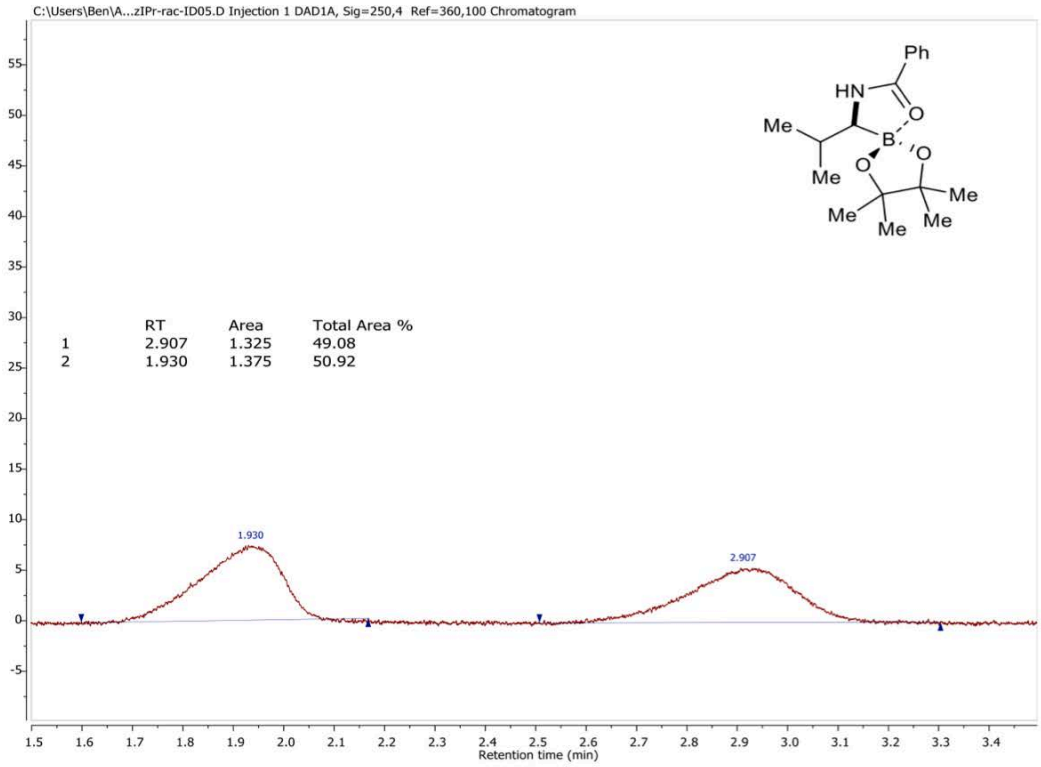
HPLC and SFC Traces of Racemic and Enantioenriched Compounds

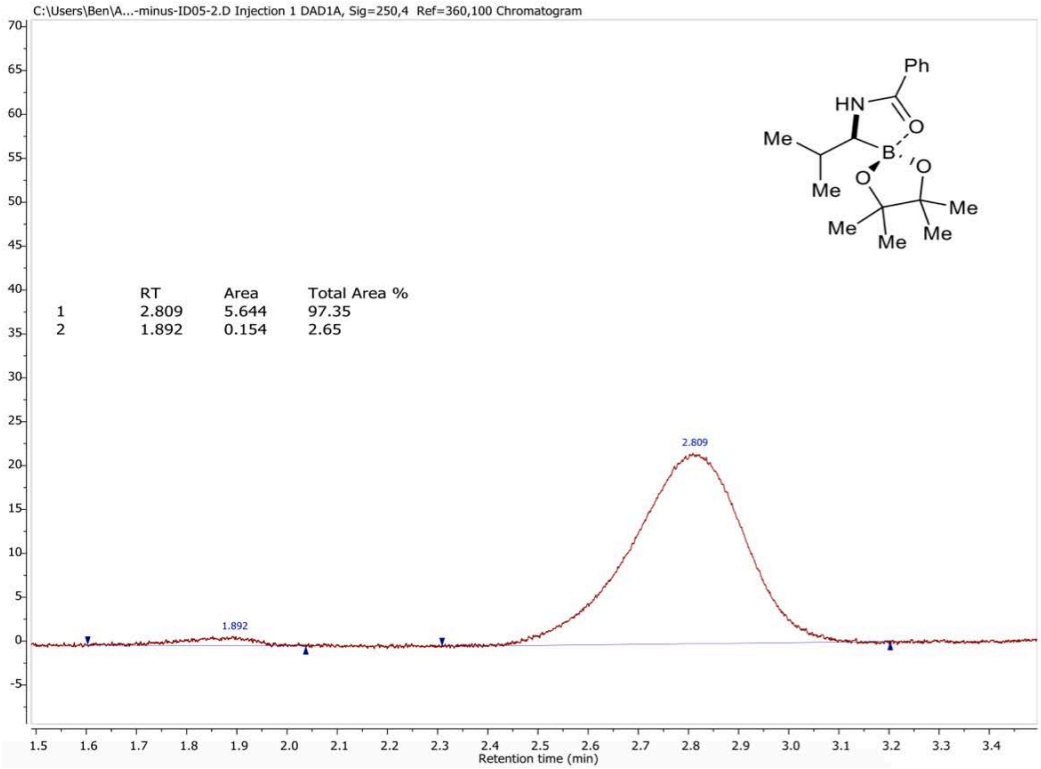
2a



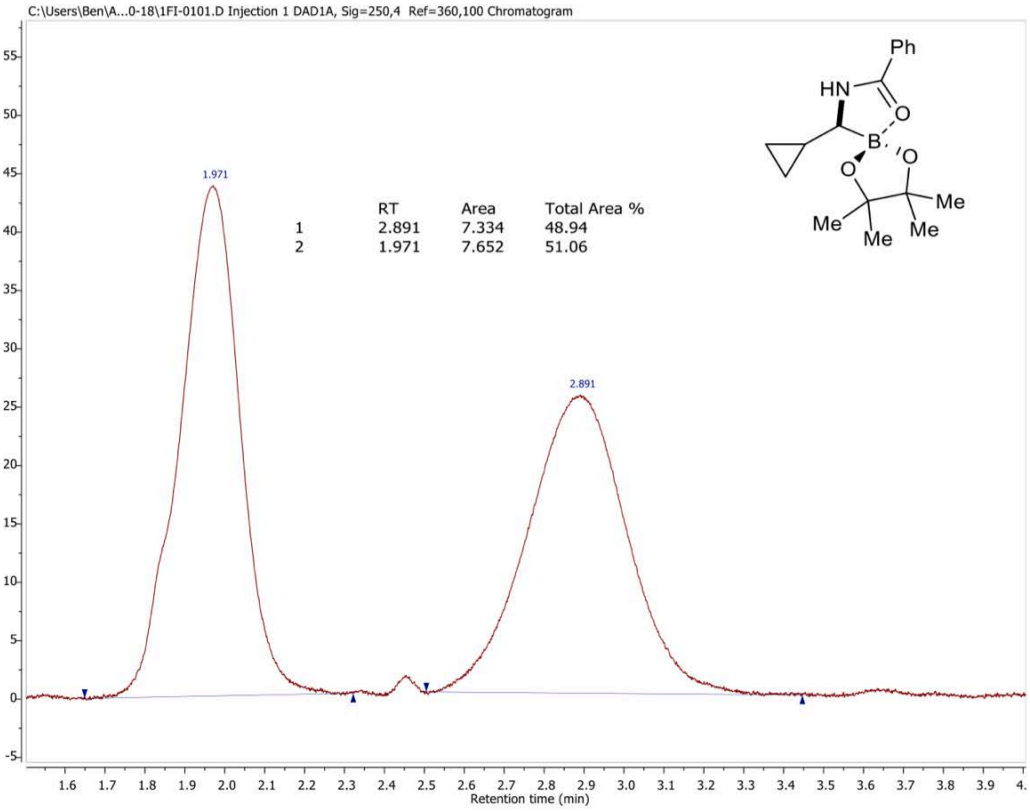


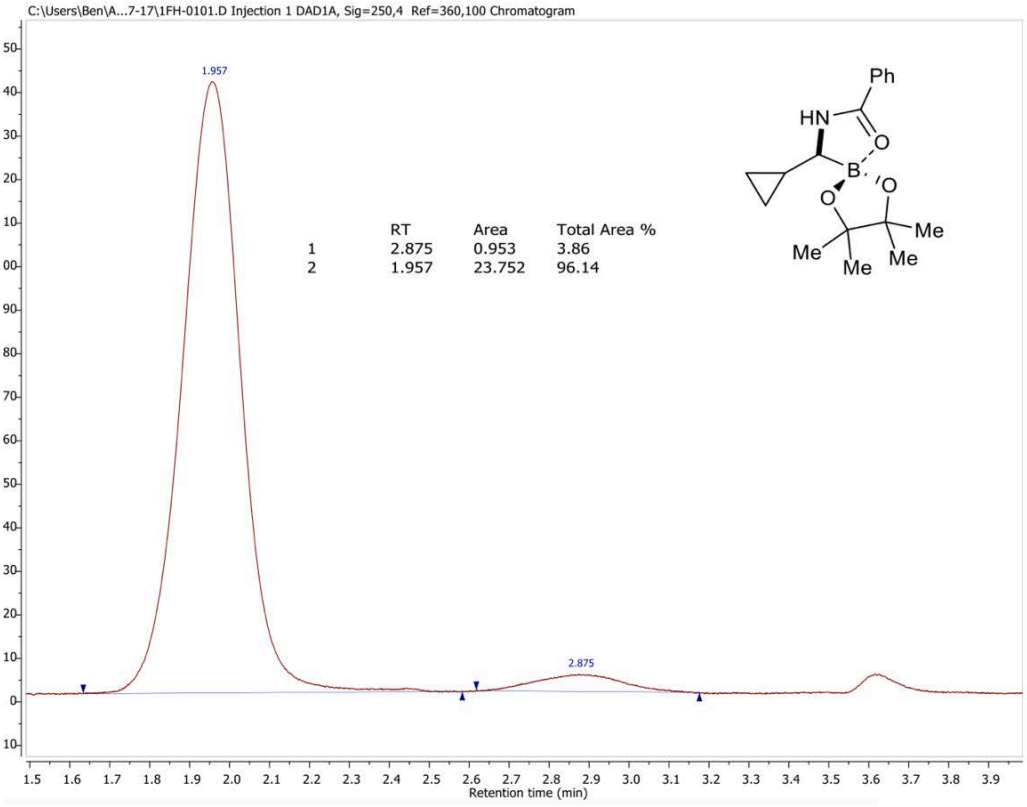
2b


C:\Users\Ben\A...zIPr-rac-ID05.D Injection 1 DAD1A, Sig=250,4 Ref=360,100 Chromatogram
Ph
HN
O
Me
B
O
O
Me
Me
Me
Me
Me
RT Area Total Area %
1 2.907 1.325 49.08
2 1.930 1.375 50.92
1.930
2.907
Retention time (min)

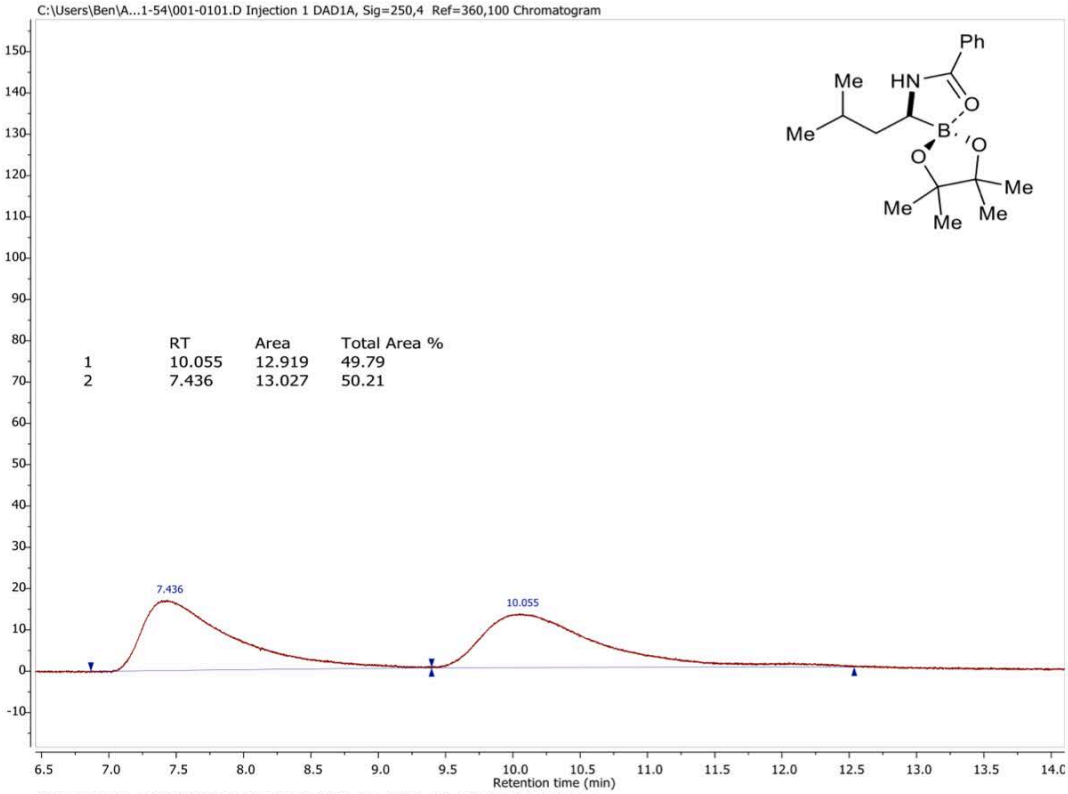

C:\Users\Ben\A...-minus-ID05-2.D Injection 1 DAD1A, Sig=250,4 Ref=360,100 Chromatogram
Ph
HN
O
Me
B
O
O
Me
Me
Me
Me
Me
RT Area Total Area %
1 2.809 5.644 97.35
2 1.892 0.154 2.65
2.809
1.892
Retention time (min)

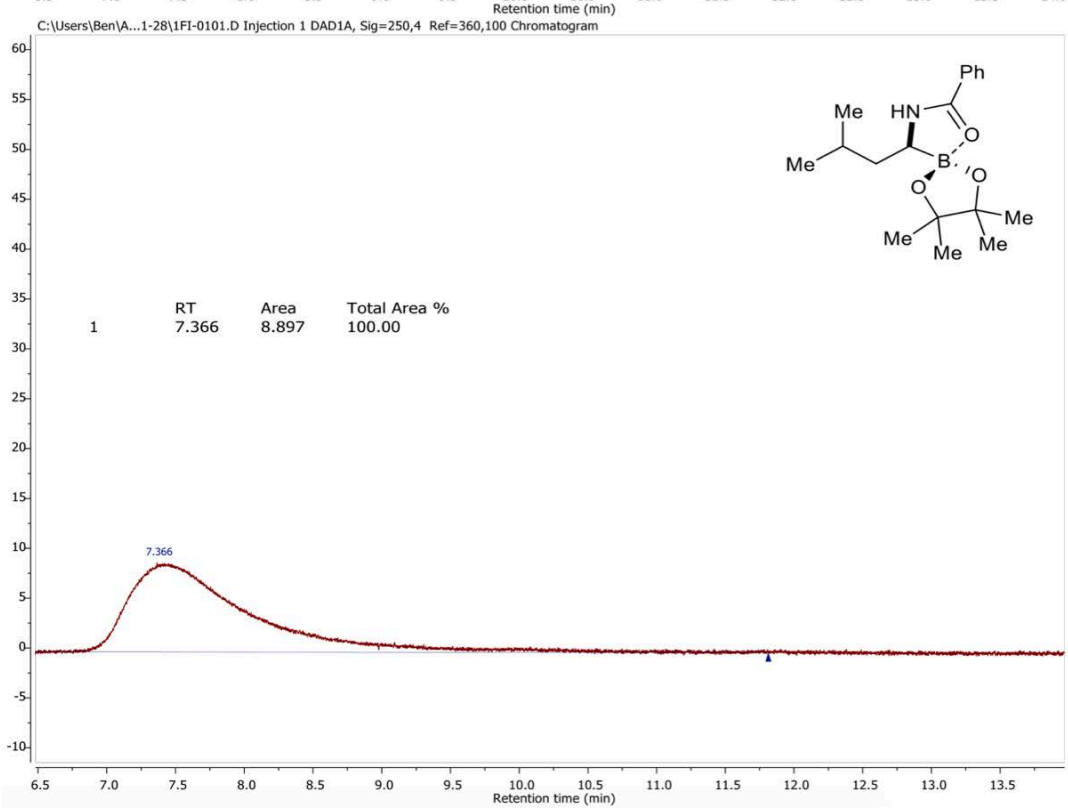
2c


C:\Users\Ben\A...0-18\1FI-0101.D Injection 1 DAD1A, Sig=250,4 Ref=360,100 Chromatogram
1.971
2.891
RT Area Total Area %
1 2.891 7.334 48.94
2 1.971 7.652 51.06
Ph
HN
O
B
O
O
Me
Me
Me
Me
Retention time (min)


C:\Users\Ben\A...7-17\1FH-0101.D Injection 1 DAD1A, Sig=250,4 Ref=360,100 Chromatogram
1.957
2.875
RT Area Total Area %
1 2.875 0.953 3.86
2 1.957 23.752 96.14
Ph
HN
O
B
O
O
Me
Me
Me
Me
Retention time (min)

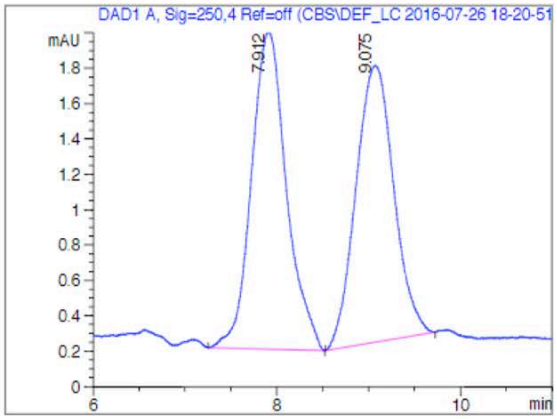
2d

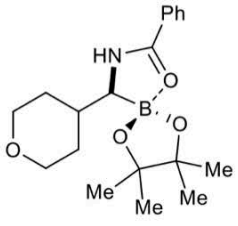

C:\Users\Ben\A...1-54\001-0101.D Injection 1 DAD1A, Sig=250,4 Ref=360,100 Chromatogram
Ph
Me
HN
O
Me
B
O
O
Me
Me
Me
Me
RT Area Total Area %
1 10.055 12.919 49.79
2 7.436 13.027 50.21
7.436
10.055
Retention time (min)


C:\Users\Ben\A...1-28\1FI-0101.D Injection 1 DAD1A, Sig=250,4 Ref=360,100 Chromatogram
Ph
Me
HN
O
Me
B
O
O
Me
Me
Me
Me
RT Area Total Area %
1 7.366 8.897 100.00
7.366
Retention time (min)

2e

```
Sample Name: CBS-THP-rac-iso-adh                                              1
================================================================================
Injection Date  : Tue, 26. Jul. 2016
Sample Name     : CBS-THP-rac-iso-adh          Inj. Vol.  :      10 µl
Acq Operator    : CBS
ODH, 2% IPA, 1 ml/min
```

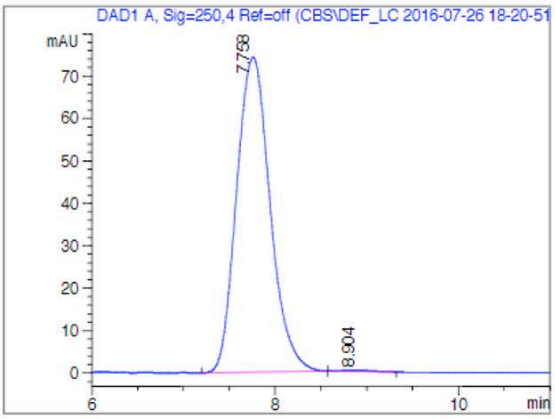


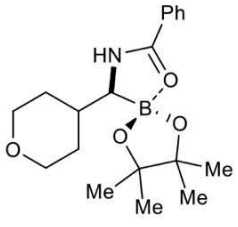



```
Signal  1: DAD1 A, Sig=250,4 Ref=off
```

Peak #	RT [min]	Type	Width [min]	Area	Area %	Name
1	7.912	BB	0.395	47.523	51.399	
2	9.075	BB	0.435	44.936	48.601	

```
Sample Name: THP-v91                                                          1
================================================================================
Injection Date  : Tue, 26. Jul. 2016
Sample Name     : THP-v91                      Inj. Vol.  :      10 µl
Acq Operator    : CBS
ODH, 2% IPA, 1 ml/min
```



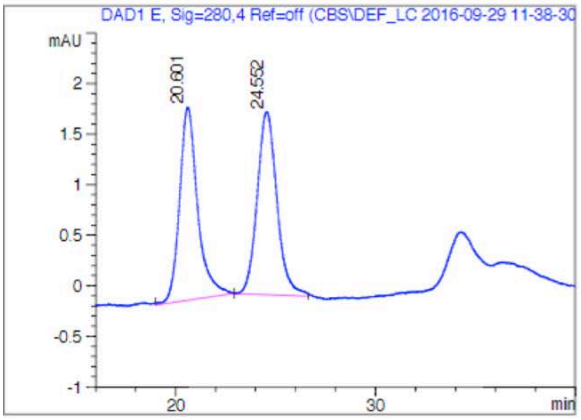


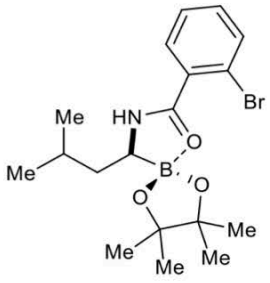

```
Signal  1: DAD1 A, Sig=250,4 Ref=off
```

Peak #	RT [min]	Type	Width [min]	Area	Area %	Name
1	7.758	BB	0.401	1890.386	99.675	
2	8.904	MM	0.409	6.169	0.325	

2f

```
Sample Name: CBS-valbr-5h-whk3-rac                                          1
================================================================================
Injection Date  : Thu, 29. Sep. 2016
Sample Name     : CBS-valbr-5h-whk3-rac          Inj. Vol.  :      10 µl
Acq Operator    : CBS
ODH, 2% IPA, 1 ml/min
```

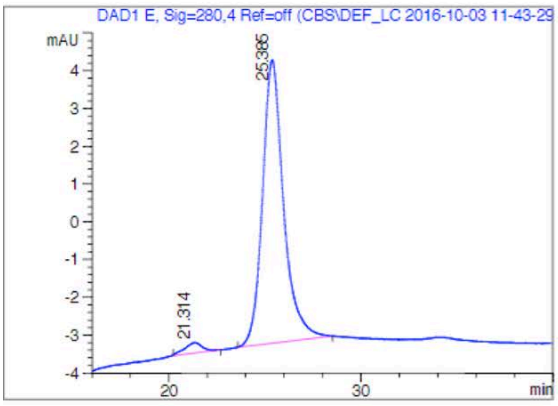


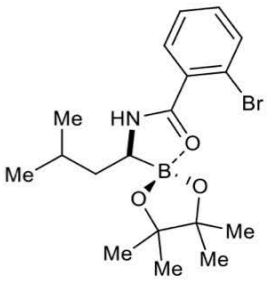



```
Signal  1: DAD1 E, Sig=280,4 Ref=off
```

Peak #	RT [min]	Type	Width [min]	Area	Area %	Name
1	20.601	MM	1.048	120.252	49.256	
2	24.552	MM	1.140	123.883	50.744	

```
Sample Name: valbr-e23-4d                                                   1
================================================================================
Injection Date  : Mon, 3. Oct. 2016
Sample Name     : valbr-e23-4d                Inj. Vol.  :      10 µl
Acq Operator    : CBS
ODH, 2% IPA, 1 ml/min
```

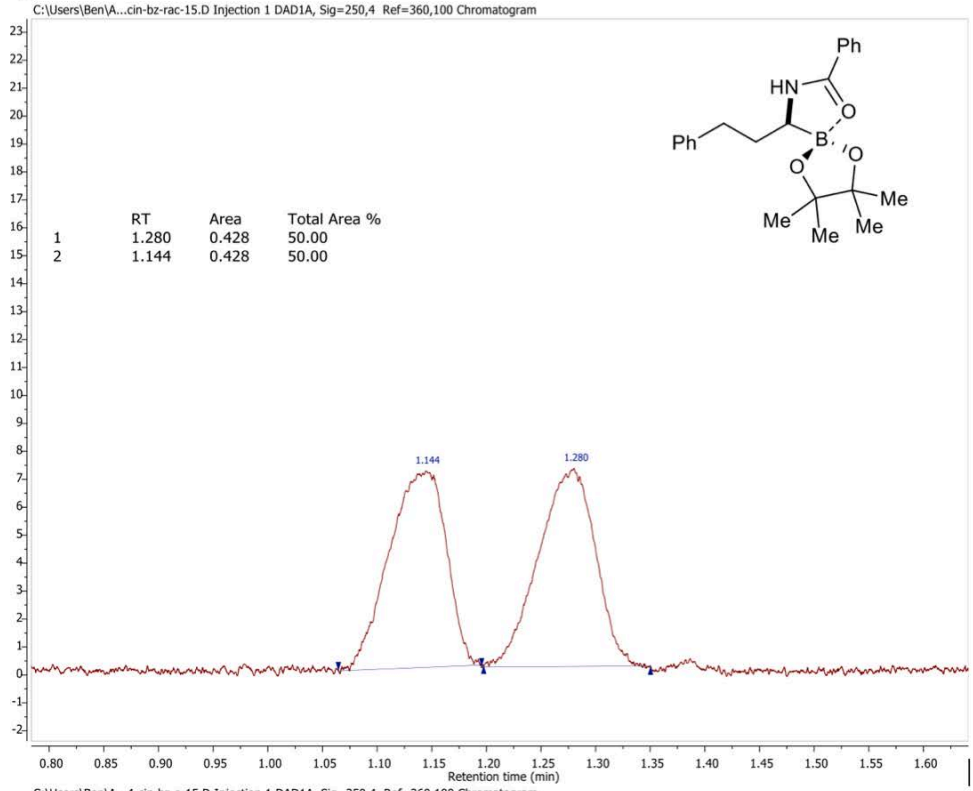


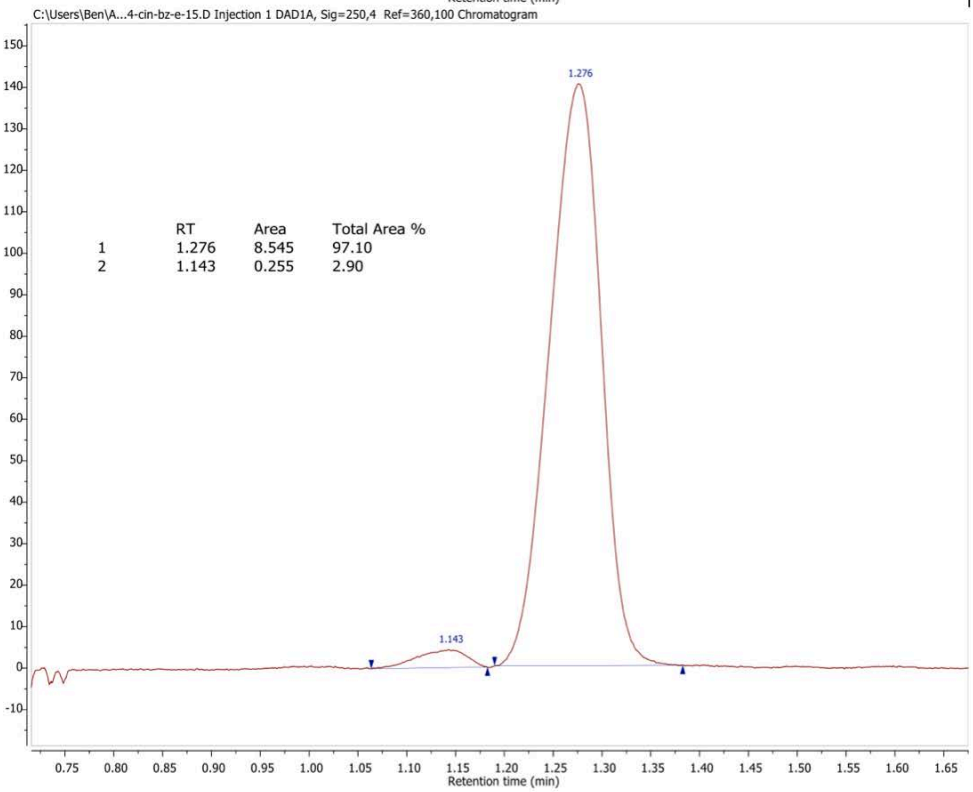



```
Signal  1: DAD1 E, Sig=280,4 Ref=off
```

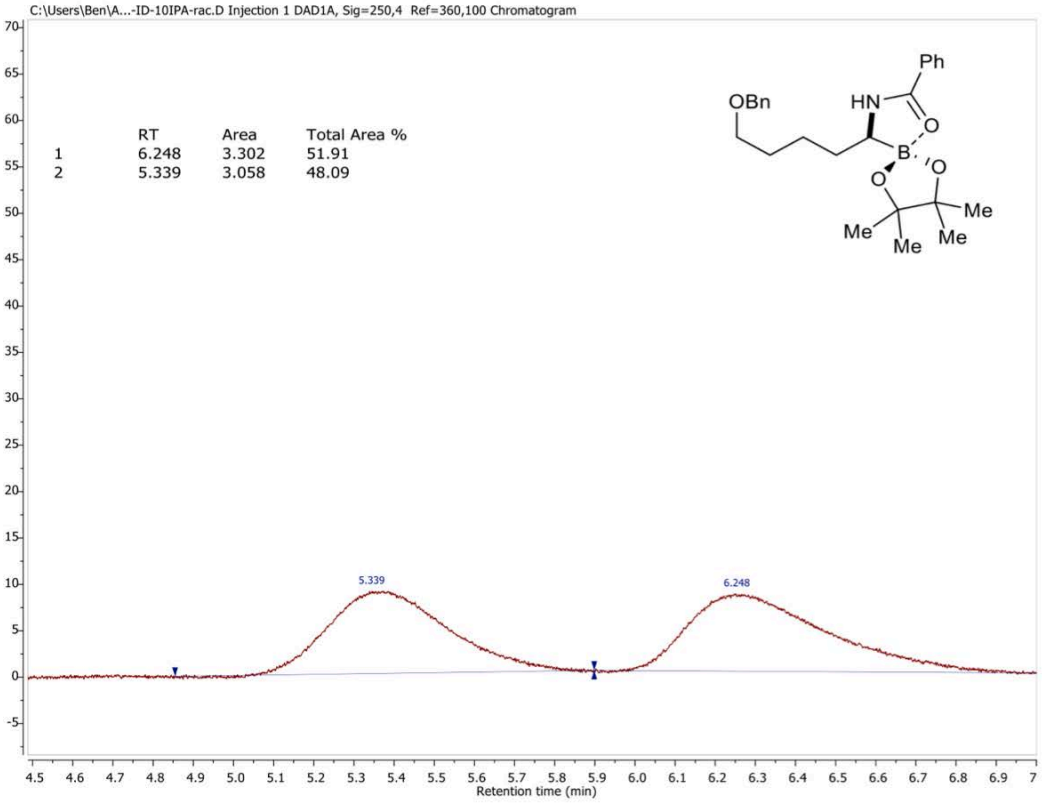
Peak #	RT [min]	Type	Width [min]	Area	Area %	Name
1	21.314	MM	1.054	17.373	2.953	
2	25.385	BB	1.015	571.006	97.047	

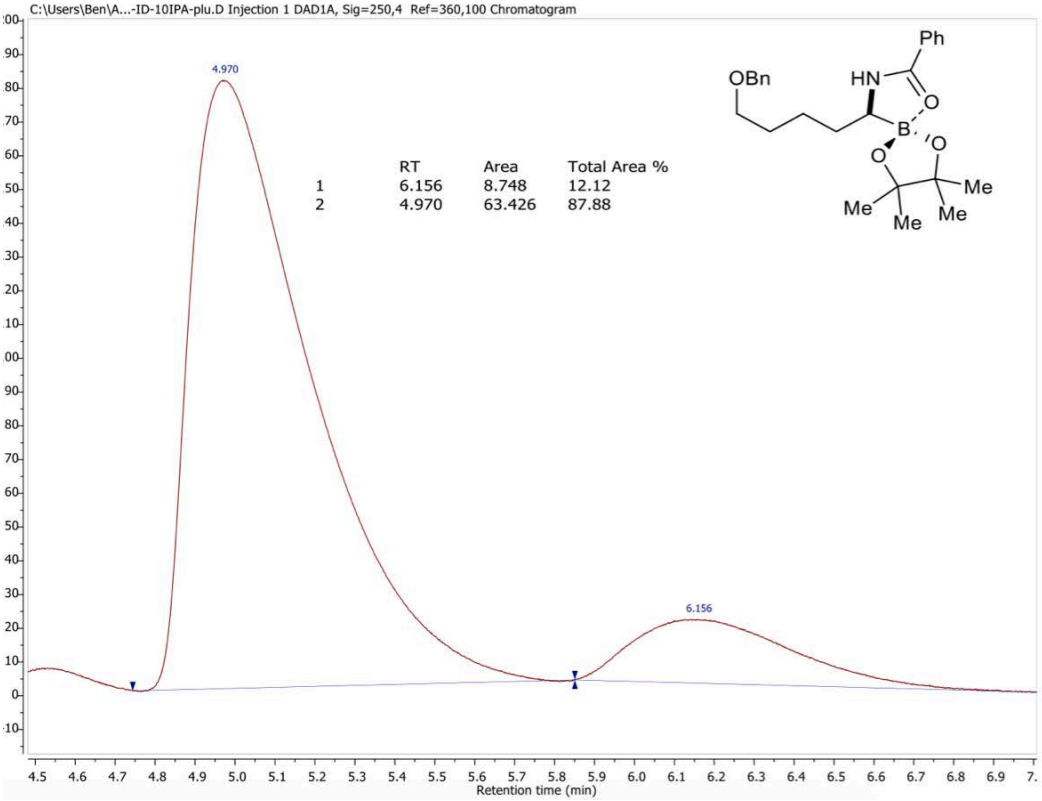
2g


C:\Users\Ben\A...cin-bz-rac-15.D Injection 1 DAD1A, Sig=250,4 Ref=360,100 Chromatogram
RT Area Total Area %
1 1.280 0.428 50.00
2 1.144 0.428 50.00
1.144
1.280
Retention time (min)

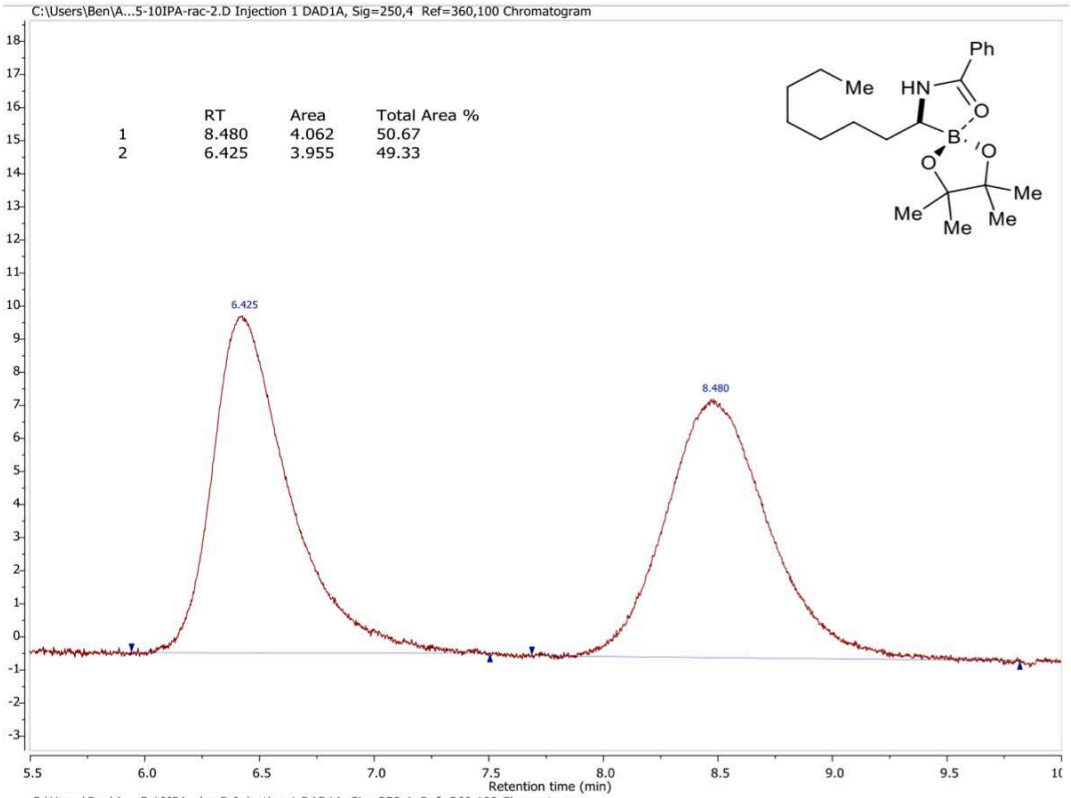

C:\Users\Ben\A...4-cin-bz-e-15.D Injection 1 DAD1A, Sig=250,4 Ref=360,100 Chromatogram
RT Area Total Area %
1 1.276 8.545 97.10
2 1.143 0.255 2.90
1.276
1.143
Retention time (min)

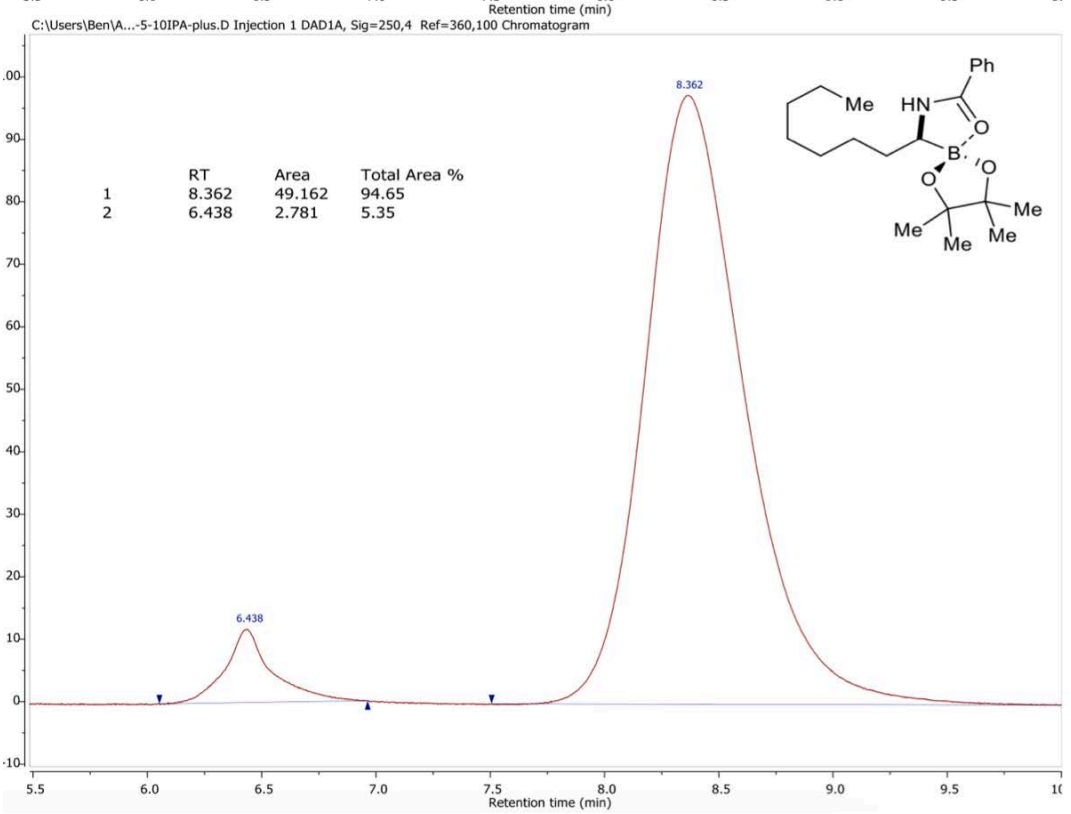
2h


C:\Users\Ben\A...-ID-10IPA-rac.D Injection 1 DAD1A, Sig=250,4 Ref=360,100 Chromatogram
RT Area Total Area %
1 6.248 3.302 51.91
2 5.339 3.058 48.09
5.339
6.248
Retention time (min)
Ph
OBn
HN
O
B
O
O
Me
Me
Me
Me

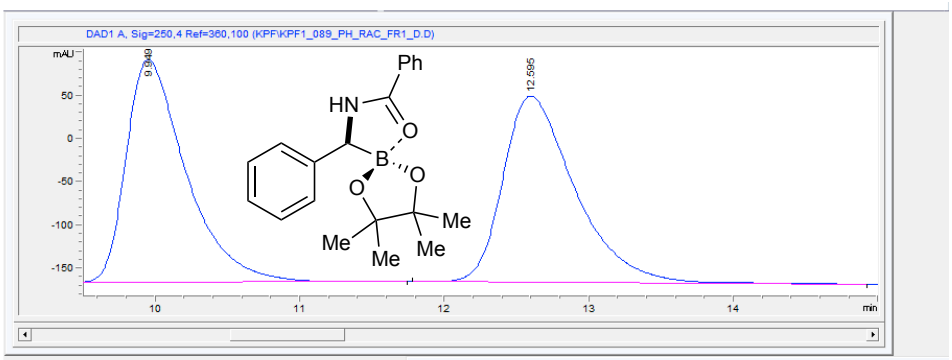

C:\Users\Ben\A...-ID-10IPA-plu.D Injection 1 DAD1A, Sig=250,4 Ref=360,100 Chromatogram
RT Area Total Area %
1 6.156 8.748 12.12
2 4.970 63.426 87.88
4.970
6.156
Retention time (min)
Ph
OBn
HN
O
B
O
O
Me
Me
Me
Me

2i


C:\Users\Ben\A...5-10IPA-rac-2.D Injection 1 DAD1A, Sig=250,4 Ref=360,100 Chromatogram
RT Area Total Area %
1 8.480 4.062 50.67
2 6.425 3.955 49.33
6.425
8.480
Retention time (min)

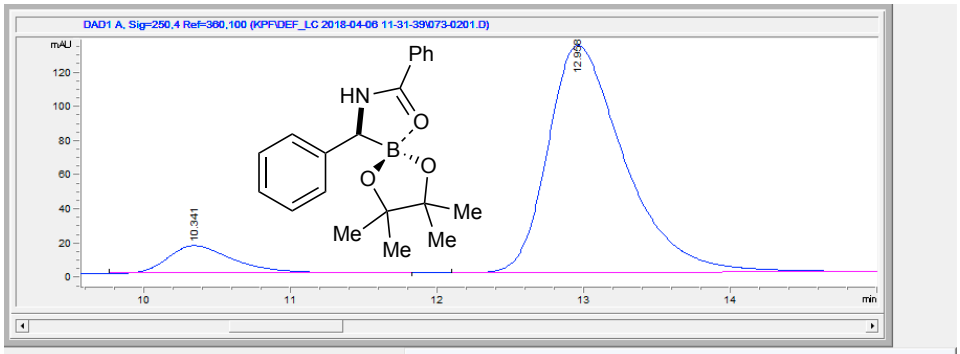

C:\Users\Ben\A...-5-10IPA-plus.D Injection 1 DAD1A, Sig=250,4 Ref=360,100 Chromatogram
RT Area Total Area %
1 8.362 49.162 94.65
2 6.438 2.781 5.35
8.362
6.438
Retention time (min)

2h



File Information	
LC-File	KPF1_089_PH_RAC_FR1_D.D
File Path	C:\CHEM32\1\DATA\KPF\
Date	28-Mar-18, 16:23:47
Sample	KPF1_089_PH_RAC_FR1_d
Sample Info	2%IPA WHELKO 1mL/min
Barcode	
Operator	KPF
Method	KPF 02IPA WHELKO 1MLMIN 40MIN.M

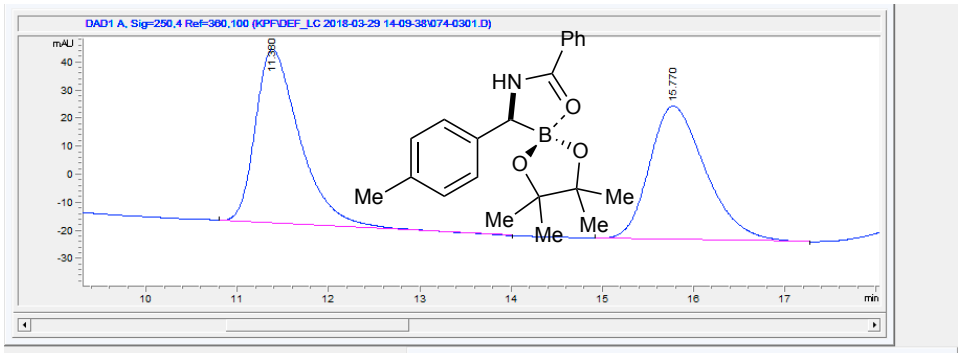
#	Time	Area	Height	Width	Area%	Symmetry
1	9.949	7452.8	257.6	0.4335	49.714	0.542
2	12.595	7538.5	215.9	0.5274	50.286	0.582



File Information	
LC-File	073-0201.D
File Path	C:\CHEM32\1\DATA\KPF\DEF_LC 2018-04-06 11-31-
Date	06-Apr-18, 12:25:12
Sample	kpf1_098_ph_e_mtbe
Sample Info	
Barcode	
Operator	KPF
Method	KPF 02IPA WHELKO 1MLMIN 40MIN.M

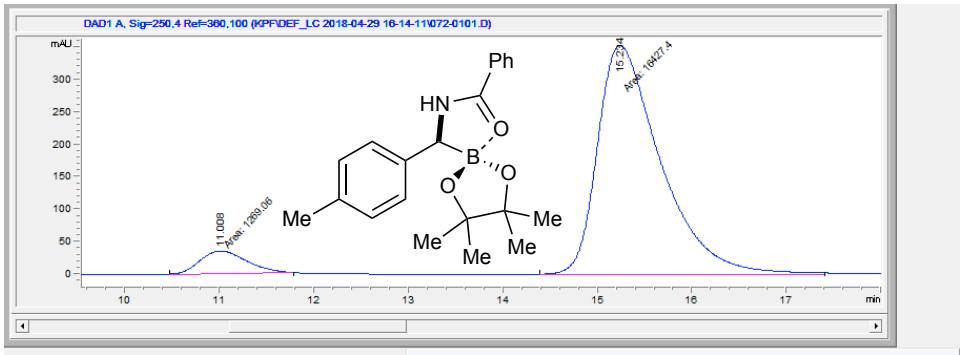
#	Time	Area	Height	Width	Area%	Symmetry
1	10.341	509.6	16.2	0.4673	9.495	0.629
2	12.958	4857.2	133.1	0.5517	90.505	0.603

2k



File Information	
LC-File	074-0301.D
File Path	C:\CHEM32\1\DATA\KPF\DEF_LC 2018-03-29 14-09-
Date	29-Mar-18, 15:35:55
Sample	kpf1_089_ptol_rac
Sample Info	
Barcode	
Operator	KPF
Method	KPF 02IPA WHELKO 1MLMIN 40MIN.M

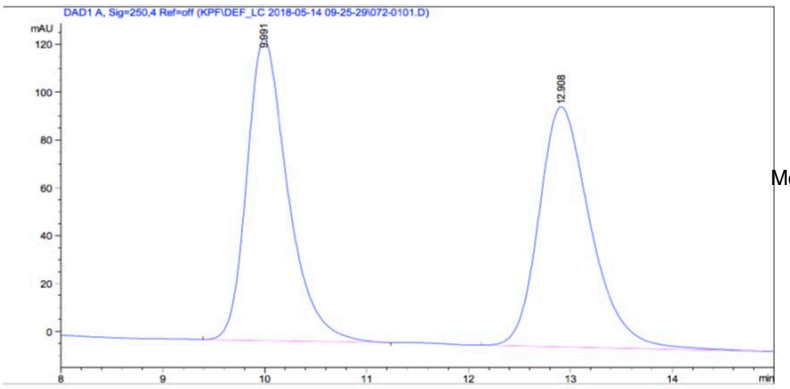
#	Time	Area	Height	Width	Area%	Symmetry
1	11.38	2119.5	62	0.5129	51.074	0.567
2	15.77	2030.4	47.6	0.6515	48.926	0.694

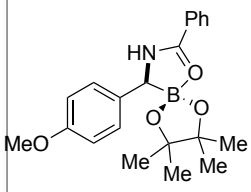


File Information	
LC-File	072-0101.D
File Path	C:\CHEM32\1\DATA\KPF\DEF_LC 2018-04-29 16-14-
Date	29-Apr-18, 16:25:13
Sample	kpf1_113_ptol_mtbe_1M
Sample Info	
Barcode	
Operator	KPF
Method	KPF 02IPA WHELKO 1MLMIN 40MIN.M

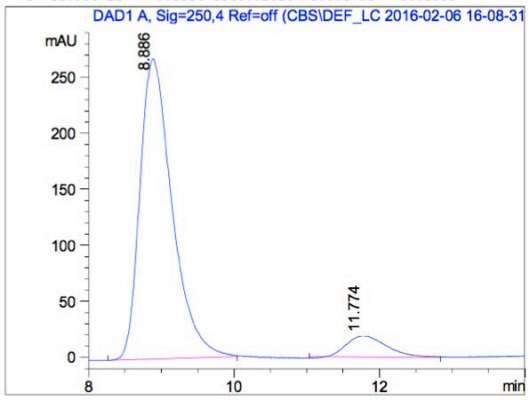
#	Time	Area	Height	Width	Area%	Symmetry
1	11.008	1269.1	35.7	0.5916	7.171	0.736
2	15.234	16427.4	352.9	0.7759	92.829	0.531

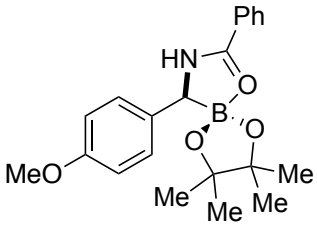
21






```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=250,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.991 BB    0.4231 3512.40039  126.04163  49.8042
   2  12.908 BB    0.5354 3540.02026  100.37937  50.1958
```





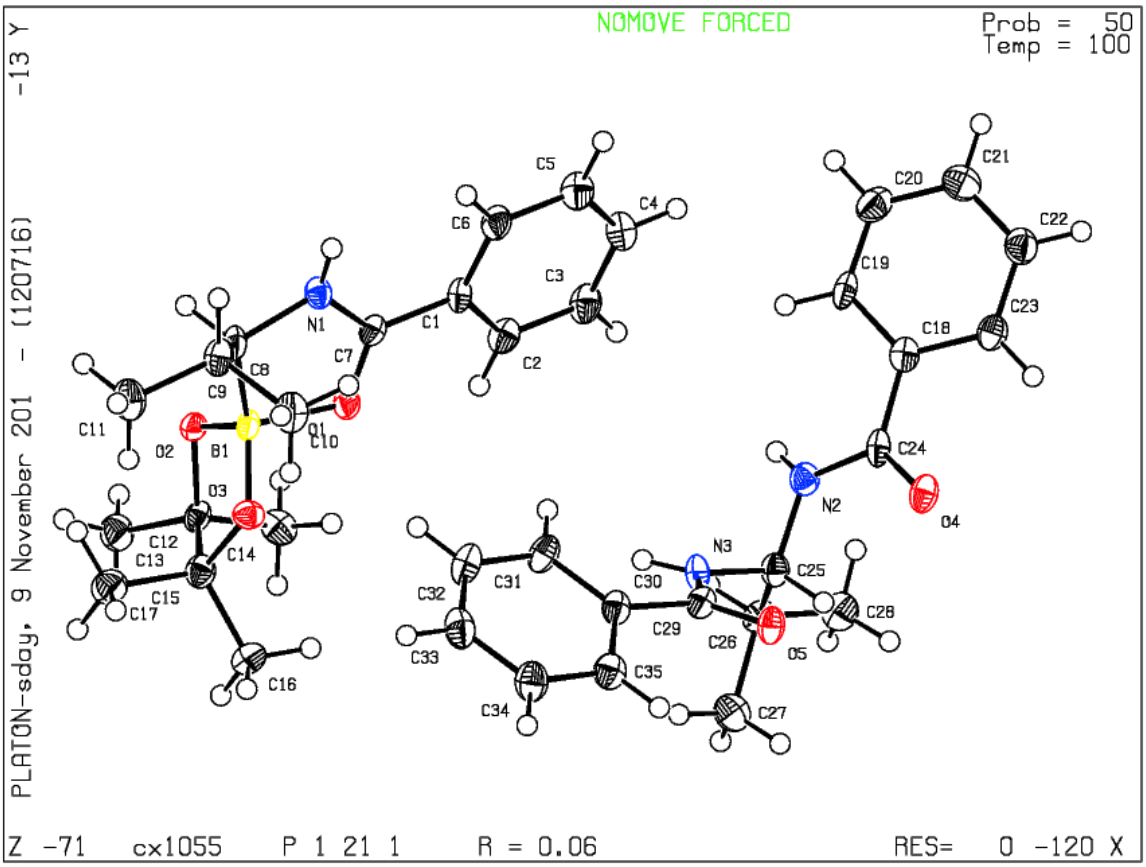

```
Signal  1: DAD1 A, Sig=250,4 Ref=off

|Peak|   RT    | Type  | Width |   Area    | Area % |     Name      |
| #  |  [min]  |       | [min] |           |        |               |
|----|---------|-------|-------|-----------|--------|---------------|
|   1|    8.886|BV     |  0.374| 8280.945| 91.822|               |
|   2|   11.774|MM     |  0.643|  737.493|  8.178|               |
---------------------------------------------------------------------
```

X-ray Crystallographic Data

Determination of Absolute Configuration of 2b

A suitable crystal was selected and the crystal was mounted on a MITIGEN holder in Paratone oil on a Kappa Apex 2 diffractometer. The crystal was kept at 100.01 K during data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program using Intrinsic Phasing and refined with the ShelXL [3] refinement package using Least Squares minimisation. The absolute structure parameter y (Hooft, Straver & Spek, 2008) was calculated using PLATON (Spek, 2010). The resulting value was y= –0.1(3) indicating that the absolute structure has probably been determined correctly. Structure contained cocrystal of impurity.

Crystal Data: monoclinic, space group $P2_1$ (no. 4), a = 10.9592(17) Å, b = 9.3307(12) Å, c = 16.2386(19) Å, β = 91.805(11)°, V = 1659.7(4) Å^3, Z = 2, T = 100.01 K, μ(CuKα) = 0.634 mm^{-1}, *Dcalc* = 1.200 g/mm^3, 12226 reflections measured (5.444 ≤ 2Θ ≤ 130.16), 5335 unique (R_{int} = 0.0970, R_{sigma} = 0.1119) which were used in all calculations. The final R_1 was 0.0574 (I > 2σ(I)) and wR_2 was 0.1361 (all data).
Refinement Details. No special refinement necessary.

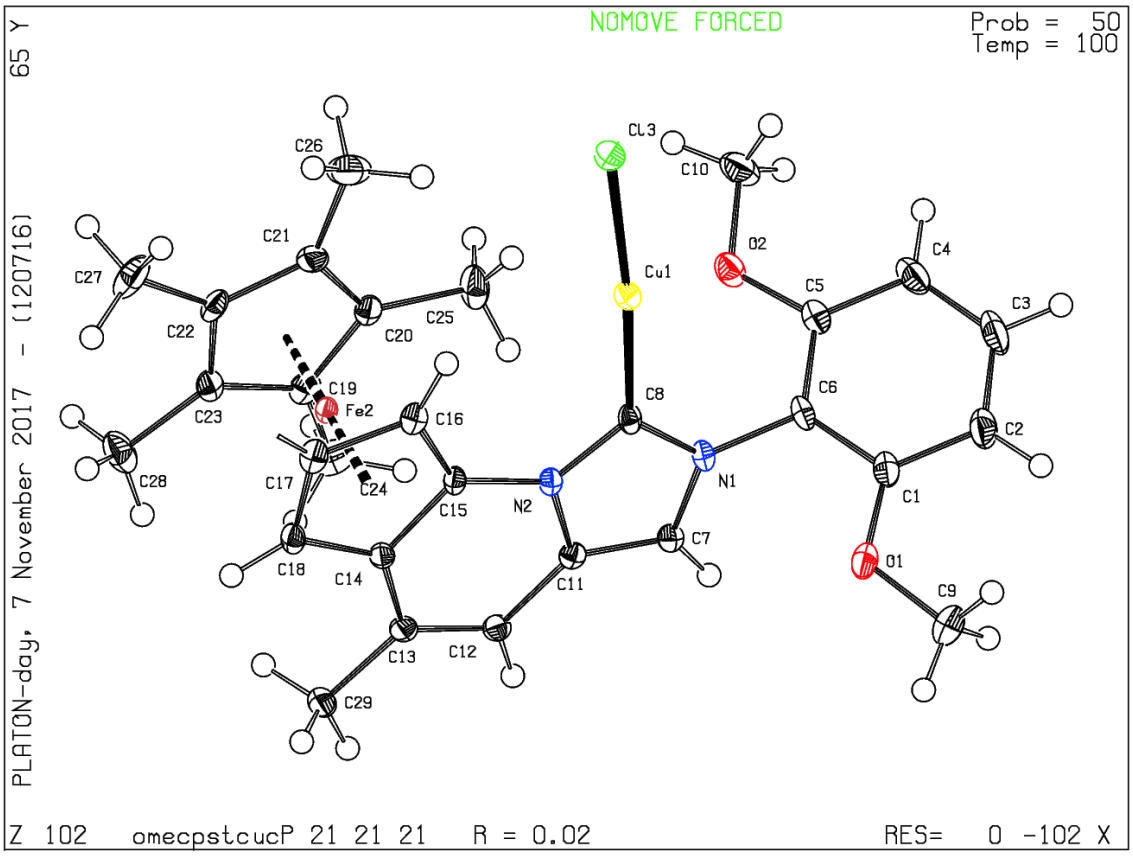


Structure of Catalyst C

Single crystals of (+)-Ferrocenyl 2,6-dimethoxyphenyl Imidazo[1,5-a]pyridine Copper Chloride (**(+)-C**) were recrystallized from slow evaporation of CH_2Cl_2/pentane at -30 °C. A suitable crystal was selected and mounted in inert oil and transferred to the cold gas stream of a 'Bruker APEX-II CCD' diffractometer. The crystal was kept at 99.98 K during data collection. Using Olex2 [1], the structure was solved with the ShelXS [4] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimisation. A multi-scan absorption correction was performed and the Flack parameter was -0.005(1)

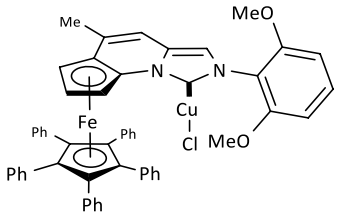
Crystal Data for Catalyst **C**: $C_{29}H_{32}ClCuFeN_2O_2$ (M =595.40): orthorhombic, space group $P2_12_12_1$ (no. 19), a = 11.4799(10) Å, b = 15.0428(13) Å, c = 15.3127(13) Å, V = 2644.3(4) Å^3, Z = 4, T = 99.98 K, μ(CuKα) = 6.549 mm^{-1}, *Dcalc* = 1.496 g/mm^3, 45535 reflections measured ($8.24 \leq 2\Theta \leq 136.396$), 4798 unique ($R_{int}$ = 0.0305, R_{sigma} = 0.0179) which were used in all calculations. The final R_1 was 0.0211 ($I > 2\sigma(I)$) and wR_2 was 0.0558 (all data).

Refinement Details. No special refinement necessary.



Structure of Catalyst G

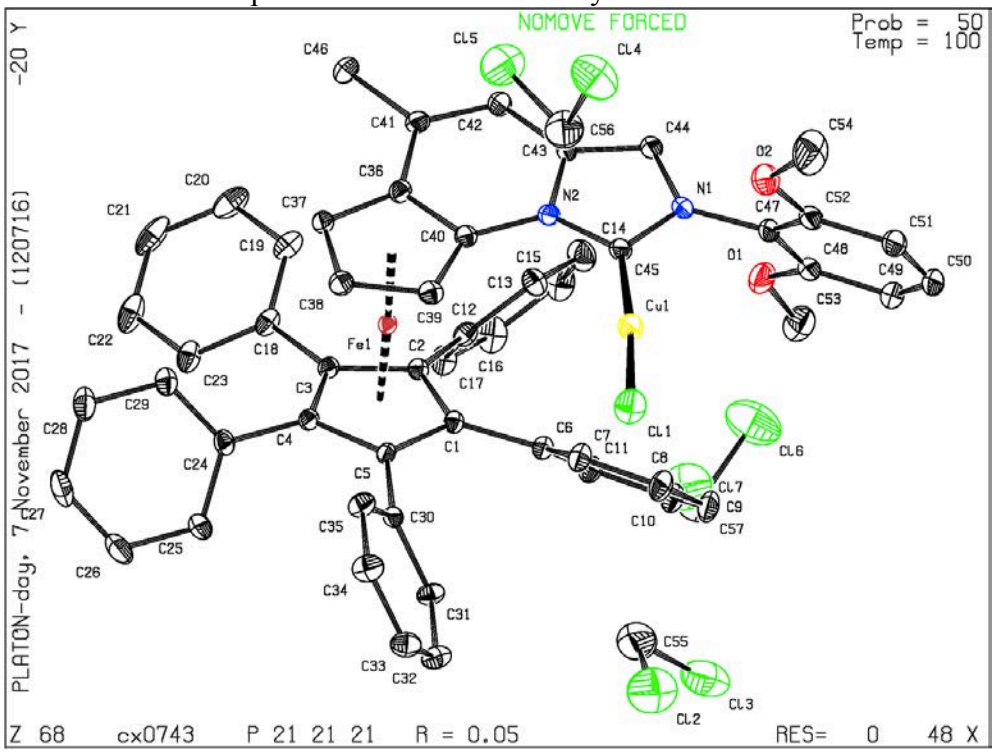
Determination of Structure of (–)-pentaphenyl ferrocenyl 2,6-dimethoxyphenyl Imidazo[1,5-a]pyridine Copper Chloride Complex G



Single crystals of $C_{57}H_{48}Cl_7CuFeN_2O_2$ **(–)-G** were submitted. A suitable crystal was selected and The crystal was mounted on a glass fibre in Paratone oil on a Kappa Apex 2 diffractometer. The crystal was kept at 100.04 K during data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimisation. The absolute structure parameter y (Hooft, Straver & Spek, 2008) was calculated using PLATON (Spek, 2010). The resulting value was y=0.001(3) indicating that the absolute structure has probably been determined correctly.

Crystal Data for $C_{57}H_{48}Cl_7CuFeN_2O_2$ (M =1160.51): orthorhombic, space group $P2_12_12_1$ (no. 19), a = 15.6465(4) Å, b = 16.9240(4) Å, c = 19.6011(5) Å, V = 5190.4(2) Å^3, Z = 4, T = 100.04 K, μ(MoKα) = 1.095 mm^{-1}, *Dcalc* = 1.485 g/mm^3, 198690 reflections measured ($3.18 \leq 2\Theta \leq 66.432$), 19753 unique ($R_{int}$ = 0.0438, R_{sigma} = 0.0358) which were used in all calculations. The final R_1 was 0.0479 ($I > 2\sigma(I)$) and wR_2 was 0.1371 (all data).

Refinement Details. No special refinement necessary.

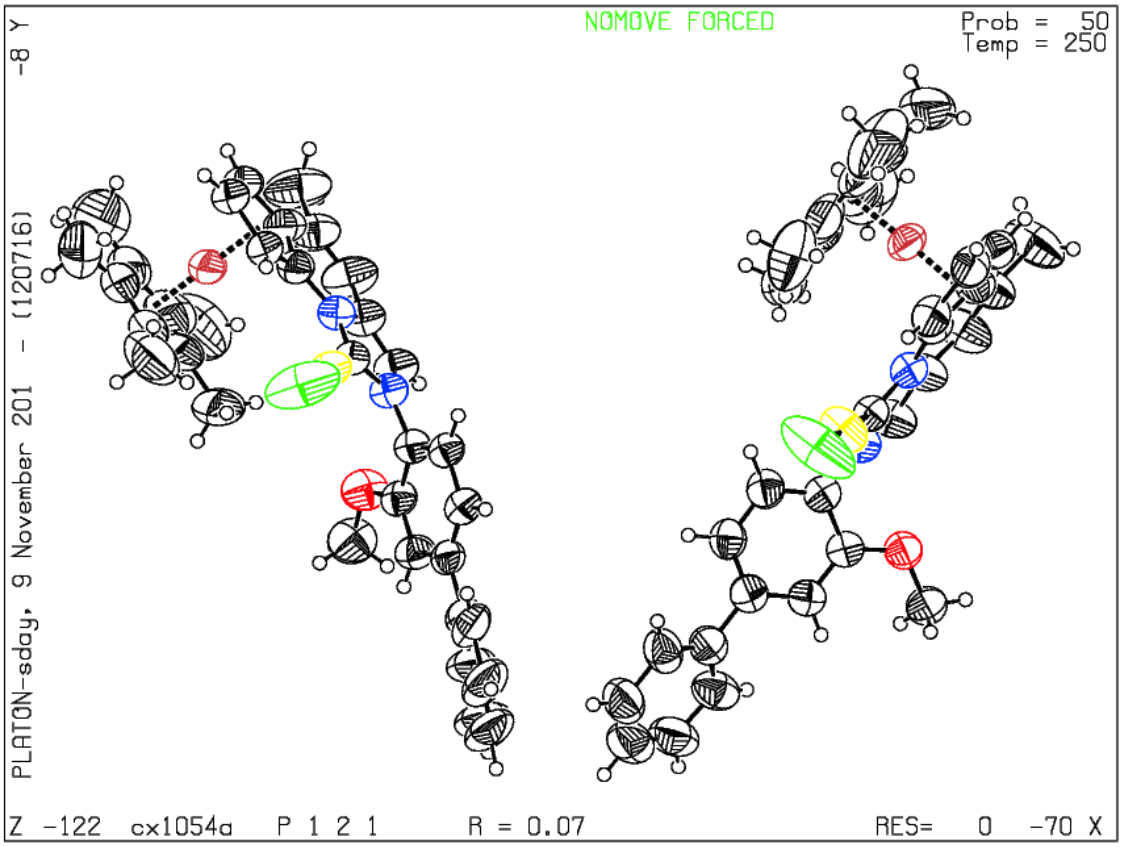


Structure of Catalyst H

Single crystals of (–)-Ferrocenyl Methoxy Biphenyl Imidazo[1,5-a]pyridine Copper Chloride Complex (Catalyst **H**) were supplied. A suitable crystal was selected and the crystal was mounted on a MITIGEN holder in Paratone oil on a Kappa Apex 2 diffractometer. The crystal was kept at 249.99 K during data collection. Using Olex2, the structure was solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package using Least Squares minimisation.

Crystal Data for Catalyst **H:** $C_{34}H_{34}N_3OClFeCu$ (M =641.47): monoclinic, space group P2 (no. 3), a = 18.3929(16) Å, b = 9.5949(8) Å, c = 18.9878(17) Å, β = 96.359(5)°, V = 3330.3(5) Å^3, Z = 4, T = 249.99 K, μ(CuKα) = 5.217 mm^{-1}, *Dcalc* = 1.279 g/mm^3, 22492 reflections measured (4.682 ≤ 2Θ ≤ 130.154), 11142 unique (R_{int} = 0.0685, R_{sigma} = 0.0974) which were used in all calculations. The final R_1 was 0.0691 (I > 2σ(I)) and wR_2 was 0.2034 (all data).
Refinement Details. The enhanced rigid-bond restraint (SHELX keyword RIGU) was applied globally. (Acta Cryst. A68 (2012) 448-451)

Solvent Treatment Details. The solvent masking procedure as implemented in Olex2 was used to remove the electronic contribution of solvent molecules from the refinement. As the exact solvent content is not known, only the atoms used in the refinement model are reported in the formula here. Total solvent accessible volume / cell = 440.2 Å^3 [13.2%] Total electron count / cell = 67.4



Buried Volume Calculations

Buried volume calculations were performed using the SambVca 2 web application available online at https://www.molnac.unisa.it/OMtools/sambvca2.0/index.html. The crystal structures of CuCl complexes **(+)-G**, **(+)-C** were uploaded in .xyz format. The xz plane was defined by the imidazopyridine ring system, the z-axis was oriented along the xz projection of NHC-metal bond, and the center of the sphere was set at a 2.0 Å distrance from the carbene carbon along the z-axis. All Cu, Cl, hydrogen atoms were excluded from the analysis. All calculations used atomic radii as described by Bondi scaled by a factor of 1.17. For the sake of clarity and comparison of to the TS model depicted in Fig. 3B using (-)-**C**, these coordinates were inverted in Figure 2B (%BV is not dependent on handedness as it measures the interaction of a hypothetical ligand with an isotropic sphere).

Calculation Parameters

Mesh spacing: 0.10 Å
M-L: 2.0 Å

Extended parameters for $\%V_{Bur}$ using a 3.5 Å radius sphere:

(+)-G

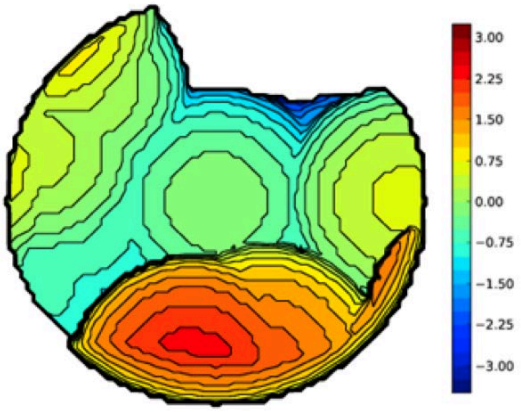
V Free	V Buried	V Total	V Exact		
87.4	92.1	179.5	179.6		
%V_Free	**%V_Bur**	% Tot/Ex			
48.7	**51.3**	100			
Quadrant	V_f	V_b	V_t	%V_f	**%V_b**
SW	18.8	26.1	44.9	41.8	**58.2**
NW	24.1	20.8	44.8	53.7	**46.3**
NE	30.6	14.3	44.9	68.1	**31.9**
SE	14	30.9	44.9	31.2	**68.8**

(+)-C

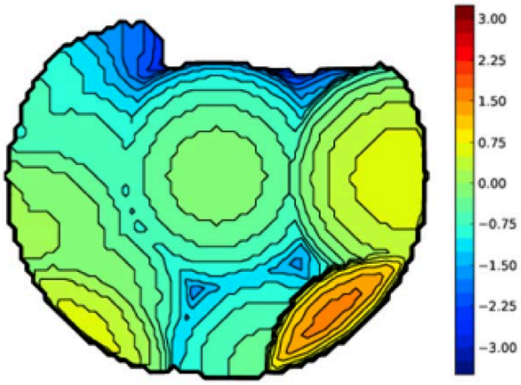
V Free	V Buried	V Total	V Exact		
108.6	70.9	179.5	179.6		
%V_Free	**%V_Bur**	% Tot/Ex			
60.5	**39.5**	100			
Quadrant	V_f	V_b	V_t	%V_f	**%V_b**
SW	24.6	20.3	44.9	54.7	**45.3**
NW	32.3	12.6	44.9	72	**28**
NE	30	14.9	44.8	66.8	**33.2**
SE	21.8	23.1	44.9	48.5	**51.5**

Steric contour maps using 3.5 Å radius spheres.

(+)-G


3.00
2.25
1.50
0.75
0.00
−0.75
−1.50
−2.25
−3.00

(+)-C


3.00
2.25
1.50
0.75
0.00
−0.75
−1.50
−2.25
−3.00

Computational Supporting Information: General Information & Computational Procedures

Part I: Complete Authorship of Gaussian 09:

Gaussian 09, Revision **D.01**, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E.

Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

Structures were optimized using B3LYP[7]-D3BJ[8]/6-31G(d)[9]//SMD[10](THF) level of theory. Final energy refinements were computed using M06[11]/6-31G(d)//SMD(THF).

Part II: General Computational Procedure

Manual, exhaustive conformation searches were performed to locate all relevant structures. All conformers were optimized using the Gaussian 09 computational package (see above reference) using B3LYP-D3BJ/6-31G(d) with implicit solvent modelled using SMD (Solvation Model based on Density) for tetrahydrofuran. Minima were confirmed with vibrational frequency computations, with transition states having one imaginary vibrational frequency. All 3D structure images were rendered in CYLview visualization software.[12]

All results discussed in the manuscript are at the following level of theory. Single point electronic energies were obtained at the M06/6-31G(d) level of theory. Final free energies were calculated by adding the single point energies and the thermal correction to Gibbs free energy obtained from vibration frequency calculations. If dispersion corrections were not included in the optimization or frequency calculation (EmpericalDispersion=GD3BJ keyword), D3BJ corrections were calculated using DFT-D3 software[13] and added to the final free energy.

Part III: Regioselectivity

To investigate the regioselectivity of the insertion of the imine substrate to the copper-Bpin species, we carried out DFT calculations on a simplified system – the planar chiral NHC was truncated to a simple achiral NHC in which phenyl rings were used on either side of the central carbene ring (**Figure S1**). Our results show that the disfavored pathway in which the nitrogen adds to the boron ($RegioTS_{disfavored}$) had an activation barrier 28.7 kcal/mol higher than the favored pathway in which the carbon adds to the boron ($RegioTS_{favored}$). These results are consistent with DFT studies on analogous borylation reactions of aldehydes.[14]

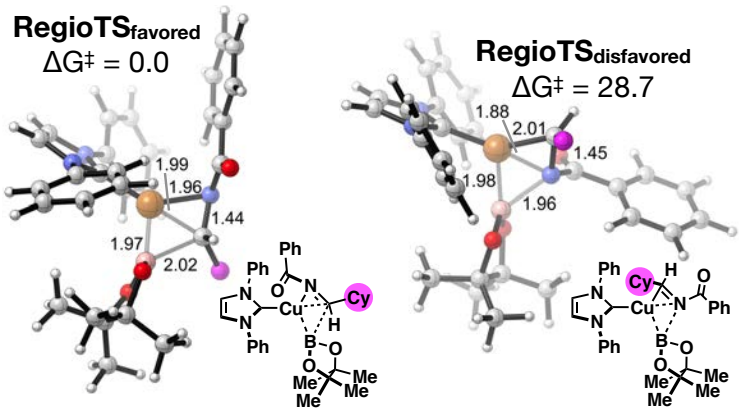
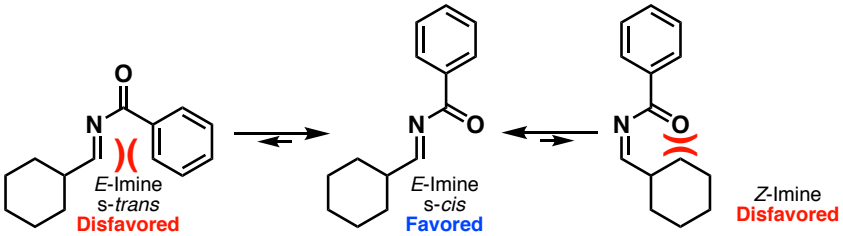


Figure S1. Regioselectivity for the imine addition to the copper-Bpin species. The addition of nitrogen to boron is disfavored by 28.7 kcal/mol.

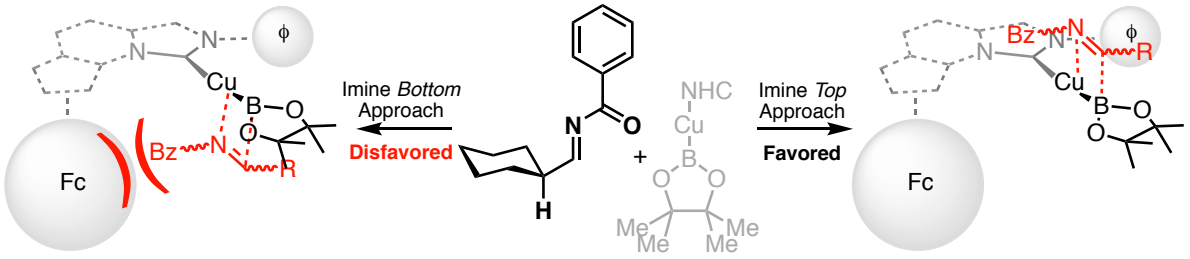
Part IV: Conformational Analyses

We examined the conformational space thorough a manual construction of available conformers. Given the restrictions imposed by the breaking and forming bonds in the transition state, we have discovered in this process that the critical transition state is quite rigid and can only accommodate few conformations that avoid severe steric interactions between the bulky catalyst substituents (ferrocenyl group, o,o-dimethoxyphenyl ring, etc.) and substrates (imine phenyl, imine cyclohexyl, and boronate).

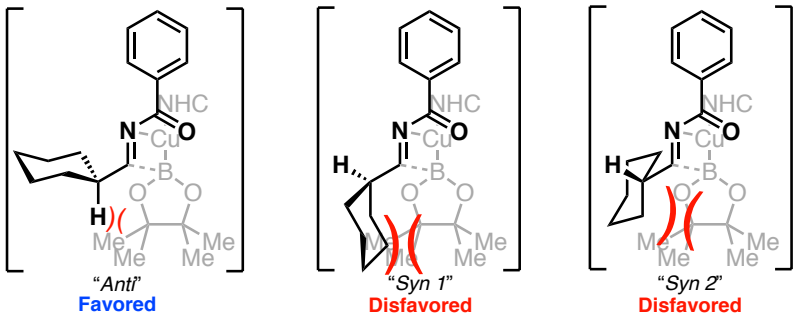
Analysis 1: Imine prefers E-configuration and the s-*cis* conformation.



Analysis 2: Imine prefers the top approach to the NHC-Cu-BPin species due to due to steric occlusion of the bottom face by the Ferrocene.



Analysis 3: Cyclohexyl group of the imine prefers the *anti* conformation with respect to the BPin functional group.



Elucidating Origins of Selectivity

Distortion Interaction Analysis

For a review on distortion interaction analyses[15], see *Angew. Chem. Int. Ed.*, **2017**, 10070. The **Minor-TS** imine was inverted and overlaid with the **Major-TS** imine for visual comparison (Figure S2, left; red and blue, respectively). Absolute distortion from the resting state imine to the **Major-TS** imine was 40.2 kcal/mol and 40.83 kcal/mol for the **Minor-TS** imine (ΔG = 0.7 kcal/mol). Additionally, the **Major-TS** and **Minor-TS** copper-Bpin species were overlaid (Figure S2, right; blue and red, respectively). Distortion from the resting state copper-Bpin species to the **Major-TS** copper-Bpin species was 15.7 kcal/mol and 18.30 kcal/mol for the **Minor-TS** copper-Bpin species (ΔG = 2.6 kcal/mol) indicating that the bulk of the selectivity comes from the difference in the major and minor copper-Bpin species rather than the imines. Upon visual inspection of the two overlaid species, the main differences come from the NHC-ferrocenyl unit and the Bpin ligands.

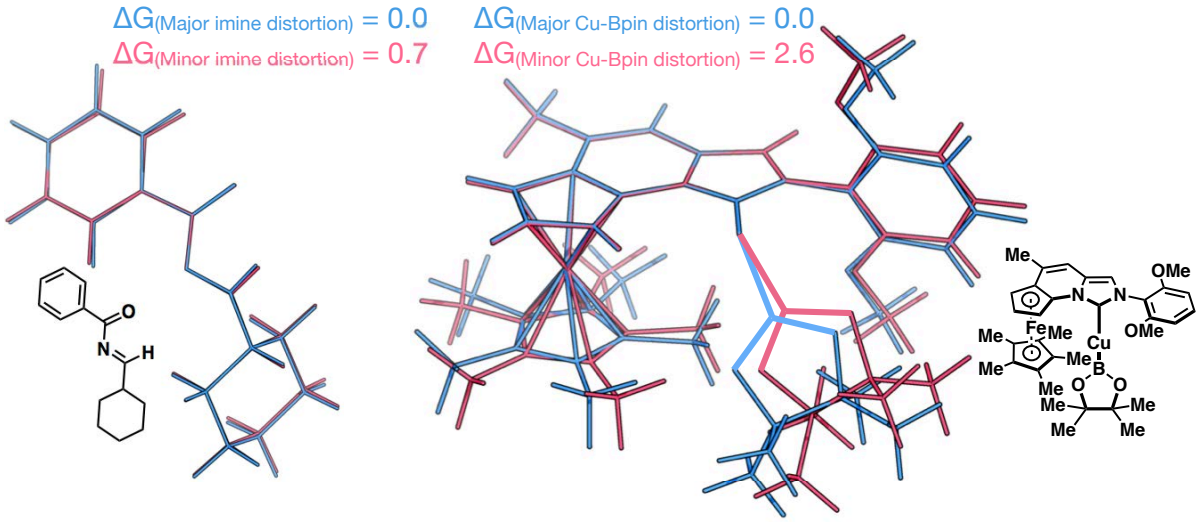


Figure S2. Overlay of **Major-** and **Minor-TS** (Left) imines (Right) copper-Bpin species and relative distortion energies. Energies are reported in kcal/mol.

Ferrocenyl Conformation

To test the eclipsed vs staggered conformations of the NHC-ferrocenyl unit, we computed the NHC-ferrocenyl-Cu(I) complexes in **Figure S3**. The major (staggered) complex was favored by 0.5 kcal/mol over the minor (eclipsed) complex. This indicates that there are additional stabilizing interactions in the full transition state to account for the observed selectivity in the full system.

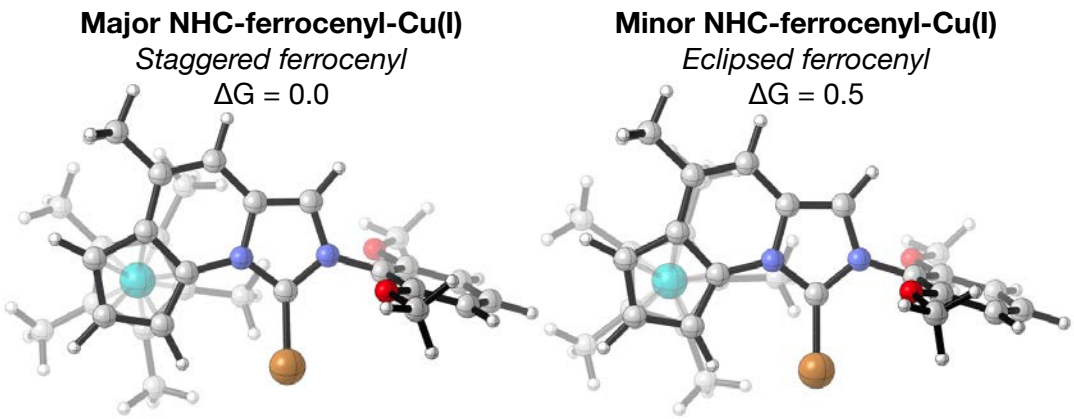


Figure S3. NHC-ferrocenyl-Cu(I) model systems for **Major-** and **Minor-TS**. The major ferrocenyl is in the staggered conformation and is favored by 0.5 kcal/mol.

Ferrocenyl-Bpin Interactions

The Bpin pivots to accommodate the prochiral face of the incoming imine, resulting in a gauche-(+) conformation in the **Major-TS**, and gauche-(–) in the **Minor-TS** (**Figure S4**). All atoms were hidden in CYLview except for the copper-Bpin atoms.

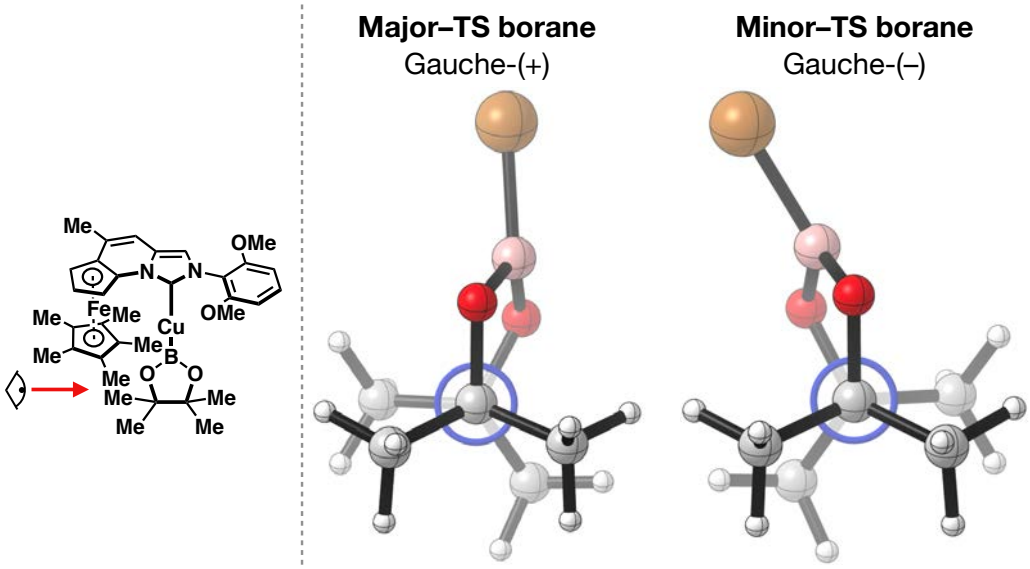


Figure S4. (Left) Orientation for the Newman projection assigning conformers of the borane ligand. (Right) Newman projection of the borane ligand for the **Major-** and **Minor-TS** structures.

In the **Major-TS**, the ferrocenyl group adopts a staggered conformation as opposed to an eclipsed conformation in the minor to avoid steric contact with the Bpin conformation (**Figure S5**, top). As a result, one of the Bpin oxygens is closer to the ferrocenyl iron in the **Major-TS** (Fe•••O = 5.09 Å vs 5.44 Å for the minor). The combination of ferrocenyl and Bpin conformations facilitates two C-H•••O interactions between the ferrocenyl group and the closest Bpin oxygen in the major but only one CH•••O interaction in the **Minor-TS** (**Figure S5**, bottom). To probe this interaction, we modeled the full copper-Bpin species as found in the

Major- and **Minor-TS** (see **Figure S1**). Note that the major is favored by 2.6 kcal/mol over the minor. This suggests that the C-H•••O interactions account for the majority of the stabilization in the **Major-TS**.

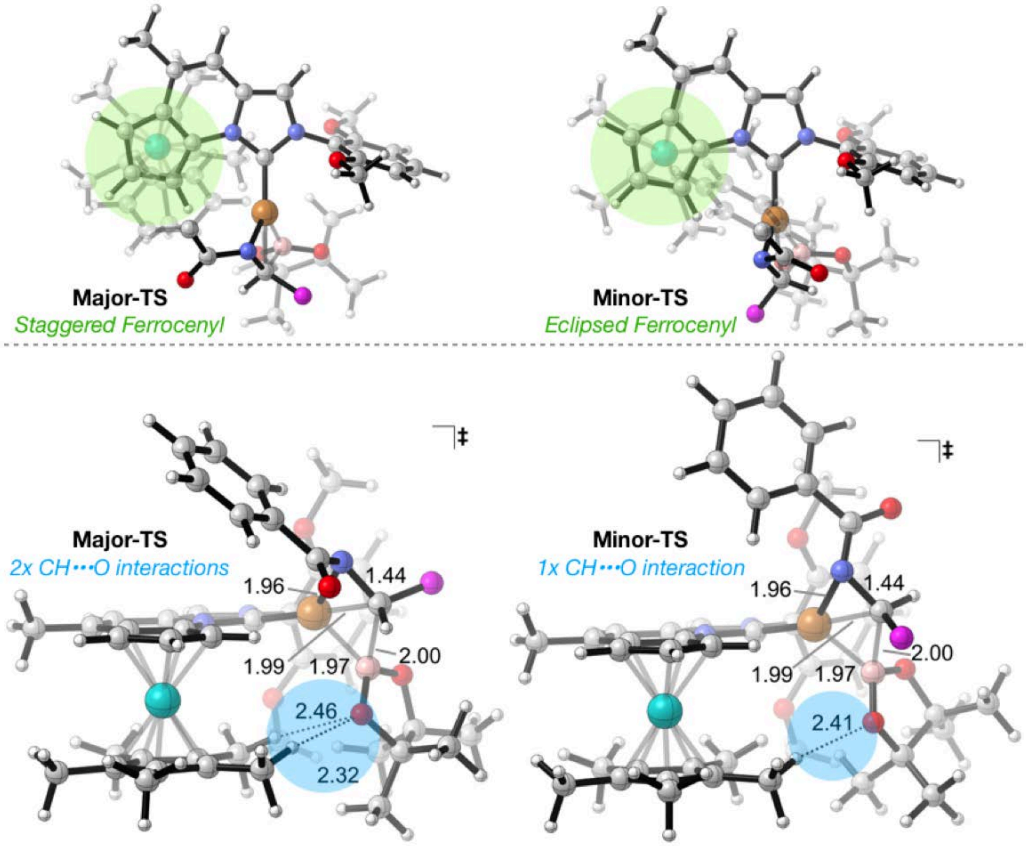
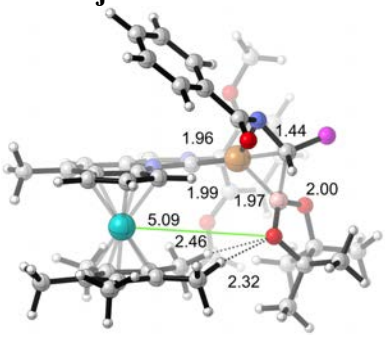


Figure S5. (Top) Top view of **Major-** and **Minor-TS**. Ferrocenyl groups are highlighted in green. The major features a staggered conformation while the minor features an eclipsed conformation. (Bottom) The **Major-TS** has two C-H•••O interactions while the **Minor-TS** only has one. C-H•••O interactions are highlighted in blue. Note that the second C-H•••O in the minor is >3.0 Å.

Computed Geometries and Energies

TS-Major



Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013
==========
#b3lyp/6-31G(d) EmpiricalDispersion=GD3BJ scf=(maxcycle=300,direct,tight)
density=current opt=(maxcycle=250,modredundant) iop(1/8=18)
Temperature=298.15 SCRF=(SMD,SOLVENT=THF)
Modredundant Input: B 45 89 F
Modredundant Input: B 46 92 F
Modredundant Input:
--link 1--
#b3lyp/6-31G(d) EmpiricalDispersion=GD3BJ
scf=(direct,tight,maxcycle=300,xqc)
opt=(nofreeze,maxcycle=250,ts,calcfc,noeigentest) iop(1/8=18) freq=noraman
Temperature=298.15 geom=check guess=read SCRF=(SMD,SOLVENT=THF)
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RB3LYP/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C49H61BCuFeN3O5 C1[X(C49H61BCuFeN3O5)] #Atoms= 121
Charge = 0 Multiplicity = 1

SCF Energy= -5373.63263027Predicted Change= -5.054331D-10
==========
Optimization completed. {Found 3 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00079	0.00180	[YES]	0.00079	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	4.529492	0.962970	2.174652
C	5.246227	0.259665	3.287273
H	5.710350	0.980835	3.974786
H	6.043223	-0.388463	2.908119
H	4.565546	-0.361796	3.877441
C	3.149863	1.359089	2.174084
C	2.170604	1.120167	3.284000
H	2.230094	1.918824	4.037309
H	2.372447	0.174470	3.798175
H	1.141360	1.085520	2.920406
C	2.884305	2.032377	0.933311
C	1.580303	2.628811	0.498054
H	1.437904	2.549939	-0.583614

H	1.533654	3.697340	0.752757
H	0.733564	2.135798	0.978891
C	4.100542	2.054180	0.173356
C	4.268708	2.690925	-1.171622
H	5.114326	2.264898	-1.718845
H	4.447461	3.770730	-1.073376
H	3.376231	2.559465	-1.790524
C	5.116703	1.389959	0.937135
C	6.556330	1.229201	0.550786
H	7.165446	2.048430	0.958275
H	6.689035	1.235982	-0.535448
H	6.976354	0.292489	0.930914
Fe	3.541993	0.130748	0.601164
C	2.068563	-1.289563	0.613227
H	1.164685	-1.267069	1.202047
C	2.242819	-0.766923	-0.694368
C	3.590969	-0.986096	-1.132432
C	4.265150	-1.659103	-0.059298
H	5.302323	-1.965305	-0.055884
C	3.323872	-1.856454	0.996228
H	3.526377	-2.333449	1.945671
N	1.339323	-0.137696	-1.554930
C	1.785644	0.327836	-2.808853
C	3.142887	0.110442	-3.229607
H	3.428558	0.478598	-4.209708
C	4.041766	-0.529042	-2.433639
C	5.464541	-0.768187	-2.841683
H	5.693610	-1.841459	-2.860245
H	6.158611	-0.309369	-2.126156
H	5.669062	-0.354672	-3.833536
C	0.018417	0.111374	-1.349321
Cu	-1.057642	-0.531540	0.049606
B	-1.858083	0.732101	1.328436
O	-2.948565	1.524817	1.041974
C	-2.826357	2.760975	1.806366
C	-2.220541	3.803114	0.866697
H	-2.875660	3.909872	-0.001801
H	-1.236196	3.490496	0.509637
H	-2.128392	4.779491	1.353515
C	-4.221066	3.190017	2.243254
H	-4.731495	2.401204	2.800664
H	-4.824806	3.426482	1.360653
H	-4.173145	4.087296	2.870261
O	-1.101550	1.255324	2.364335
C	-1.867439	2.340842	2.972938
C	-2.598762	1.731322	4.171047
H	-1.863009	1.276316	4.841582
H	-3.299153	0.950559	3.858146
H	-3.152693	2.490686	4.732657
C	-0.906914	3.426831	3.437505
H	-0.283383	3.047879	4.253500
H	-1.462595	4.293323	3.813172
H	-0.248015	3.757873	2.632388
N	-0.359356	0.767176	-2.482727
C	-1.659096	1.311579	-2.691096
C	0.688700	0.911236	-3.381478

H	0.559614	1.400949	-4.332871
C	-2.731418	0.476591	-3.043864
O	-2.440463	-0.838933	-3.182566
C	-3.495855	-1.721469	-3.564435
H	-3.882778	-1.463851	-4.557468
H	-4.311294	-1.708450	-2.835092
H	-3.051316	-2.717067	-3.592360
C	-4.000511	1.037523	-3.243239
H	-4.846072	0.415588	-3.506901
C	-4.162870	2.415024	-3.107262
H	-5.147256	2.846005	-3.265350
C	-3.101572	3.257987	-2.780584
H	-3.261232	4.324583	-2.687052
C	-1.836855	2.698551	-2.563153
O	-0.726424	3.401940	-2.225862
C	-0.797992	4.827116	-2.241201
H	-1.059460	5.195541	-3.240093
H	0.201578	5.172778	-1.973047
H	-1.518964	5.204971	-1.509471
N	-1.604169	-2.278417	0.736583
C	-0.668214	-3.037669	1.354976
C	0.065980	-3.990438	0.439770
C	-2.215516	-1.227991	1.513580
H	-1.853367	-1.221584	2.545059
C	-3.745908	-1.270039	1.441786
H	-4.140371	-0.416216	2.006496
O	-0.368195	-3.010231	2.566697
C	-4.264424	-2.553178	2.114892
H	-3.901611	-2.604273	3.149998
H	-3.843143	-3.420457	1.589855
C	-5.796213	-2.624429	2.083058
H	-6.210086	-1.804255	2.688572
H	-6.140986	-3.559166	2.544132
C	-6.332225	-2.510114	0.650021
H	-7.430142	-2.522151	0.650938
H	-6.006236	-3.388938	0.074235
C	-5.811148	-1.240883	-0.036182
H	-6.227445	-0.357681	0.471103
H	-6.163708	-1.198141	-1.075636
C	-4.280670	-1.167983	0.006556
H	-3.938864	-0.232192	-0.447670
H	-3.855453	-1.989839	-0.582222
C	-0.235642	-4.110043	-0.924083
H	-1.048771	-3.522027	-1.333926
C	0.506191	-4.961868	-1.741451
H	0.265254	-5.040883	-2.798610
C	1.559108	-5.709884	-1.206155
H	2.140564	-6.369638	-1.844924
C	1.858467	-5.605267	0.154236
H	2.674234	-6.185143	0.578644
C	1.114278	-4.752182	0.968937
H	1.337523	-4.649130	2.025404

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -5373.63263027 Predicted Change= -5.054331D-10
Zero-point correction (ZPE)= -5372.6129 1.01968
Internal Energy (U)= -5372.5533 1.07924
Enthalpy (H)= -5372.5524 1.08019
Gibbs Free Energy (G)= -5372.7058 0.92679

Frequencies -- -158.9577 12.4172 16.0067

M06/6-31G(d) = -5371.46639757

1st Higher Energy TS that leads to Major Product

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013
==========
#b3lyp/6-31G(d) EmpiricalDispersion=GD3BJ scf=(maxcycle=300,direct,tight)
density=current opt=(maxcycle=250,modredundant) iop(1/8=18)
Temperature=298.15 SCRF=(SMD,SOLVENT=THF)
Modredundant Input: B 45 89 F
Modredundant Input: B 46 92 F
Modredundant Input:
#b3lyp/6-31G(d) EmpiricalDispersion=GD3BJ
scf=(direct,tight,maxcycle=300,xqc)
opt=(nofreeze,maxcycle=250,ts,calcfc,noeigentest) iop(1/8=18) freq=noraman
Temperature=298.15 geom=check guess=read SCRF=(SMD,SOLVENT=THF)
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RB3LYP/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C49H61BCuFeN3O5 C1[X(C49H61BCuFeN3O5)] #Atoms= 121
Charge = 0 Multiplicity = 1

SCF Energy= -5373.62564844Predicted Change= -9.230249D-09
==========
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.03910	0.00180	[NO]	0.03910	0.00180	[NO]

Atomic Coordinates (Angstroms)

Type	X	Y	Z
C	4.517427	0.891122	2.306709
C	5.186263	0.136447	3.415571
H	5.619688	0.823690	4.155792
H	5.999074	-0.494233	3.040778
H	4.480518	-0.511072	3.944905
C	3.139779	1.292410	2.268592
C	2.116508	1.012573	3.327800
H	2.139376	1.787646	4.106996
H	2.302050	0.051784	3.819469
H	1.103759	0.984201	2.919628
C	2.923758	2.016110	1.046892
C	1.631888	2.618620	0.585105
H	1.567369	2.645299	-0.506667
H	1.528875	3.652830	0.942142
H	0.773009	2.053734	0.953115
C	4.169413	2.066019	0.336559

C	4.399749	2.763445	-0.968311
H	5.251861	2.341043	-1.508527
H	4.604706	3.831045	-0.808100
H	3.526806	2.690297	-1.623355
C	5.153045	1.366489	1.111479
C	6.604630	1.214117	0.770227
H	7.197646	2.033985	1.199588
H	6.769786	1.225794	-0.311544
H	7.015962	0.277291	1.159159
Fe	3.587834	0.130578	0.662473
C	2.117948	-1.286481	0.593003
H	1.215856	-1.283308	1.186083
C	2.303236	-0.701202	-0.688067
C	3.656328	-0.901847	-1.122928
C	4.319674	-1.626920	-0.078027
H	5.356699	-1.933736	-0.080414
C	3.369369	-1.873559	0.958327
H	3.563577	-2.394645	1.886045
N	1.411990	-0.025569	-1.528418
C	1.881770	0.519229	-2.742680
C	3.244742	0.324257	-3.154897
H	3.545702	0.749185	-4.107054
C	4.126983	-0.372740	-2.389493
C	5.551110	-0.604644	-2.796678
H	5.773770	-0.127069	-3.755339
H	5.764126	-1.677499	-2.888217
H	6.244309	-0.208309	-2.044002
C	0.083989	0.196052	-1.345275
Cu	-1.080559	-0.567853	-0.093912
B	-1.953062	0.603811	1.218378
O	-3.002893	1.446730	0.931384
C	-2.849149	2.655619	1.736264
C	-2.197960	3.702560	0.830834
H	-2.843483	3.855909	-0.037536
H	-1.220988	3.370588	0.469814
H	-2.078234	4.661350	1.345602
C	-4.233190	3.125530	2.166269
H	-4.775975	2.352032	2.714074
H	-4.821321	3.391345	1.281586
H	-4.157708	4.014563	2.802167
O	-1.212150	1.048957	2.301360
C	-1.922442	2.174386	2.908615
C	-2.679696	1.612759	4.114150
H	-1.961031	1.141534	4.792166
H	-3.409110	0.854379	3.819904
H	-3.200411	2.404069	4.663532
C	-0.912323	3.212547	3.381305
H	-0.310447	2.801113	4.197134
H	-1.432219	4.099068	3.761427
H	-0.237156	3.522037	2.582569
N	-0.273773	0.918921	-2.444601
C	-1.598400	1.393196	-2.661000
C	0.793068	1.125912	-3.307391
H	0.683434	1.666652	-4.232977
C	-2.638030	0.476450	-2.888270
O	-2.271435	-0.825985	-2.957463

C	-3.297563	-1.812533	-3.069438
H	-4.025438	-1.722611	-2.258574
H	-2.789251	-2.774304	-2.998111
H	-3.809725	-1.737232	-4.036157
C	-3.948878	0.944035	-3.042419
H	-4.765690	0.254024	-3.210353
C	-4.188525	2.316159	-2.990533
H	-5.204988	2.677776	-3.116125
C	-3.163167	3.239040	-2.788551
H	-3.382548	4.298622	-2.755159
C	-1.855282	2.771793	-2.608588
O	-0.777771	3.560763	-2.368546
C	-0.969815	4.974708	-2.348028
H	-1.666626	5.274324	-1.558710
H	-1.330566	5.338752	-3.317194
H	0.013668	5.400544	-2.143167
N	-1.621465	-2.354360	0.433609
C	-0.749816	-3.100536	1.152868
C	0.151550	-3.982958	0.320176
C	-2.402759	-1.376528	1.156998
H	-2.239727	-1.449440	2.236229
C	-3.901330	-1.414181	0.776051
H	-4.064292	-0.771097	-0.100256
O	-0.633923	-3.119850	2.396049
C	-4.798142	-0.891694	1.909760
H	-4.498759	0.119614	2.186130
H	-4.651380	-1.530613	2.793667
C	-6.280370	-0.898600	1.516295
H	-6.429416	-0.194502	0.684119
H	-6.893725	-0.532686	2.350175
C	-6.742786	-2.295347	1.087108
H	-7.787331	-2.268393	0.749649
H	-6.708865	-2.968425	1.956288
C	-5.836552	-2.856585	-0.014929
H	-5.963579	-2.251190	-0.925830
H	-6.140062	-3.879320	-0.274792
C	-4.359218	-2.834730	0.396643
H	-3.730661	-3.224387	-0.407402
H	-4.206575	-3.501108	1.258586
C	0.069946	-4.045655	-1.078042
H	-0.691237	-3.465380	-1.586991
C	0.960680	-4.833994	-1.805262
H	0.890155	-4.867884	-2.889579
C	1.943314	-5.577658	-1.144753
H	2.640048	-6.188645	-1.712767
C	2.023146	-5.531176	0.248981
H	2.783127	-6.107772	0.770320
C	1.131901	-4.739468	0.972972
H	1.184578	-4.680754	2.054963

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -5373.62564844 Predicted Change= -9.230249D-09
Zero-point correction (ZPE)= -5372.6056 1.02000
Internal Energy (U)= -5372.5464 1.07920

Enthalpy (H)= -5372.5454 1.08015
Gibbs Free Energy (G)= -5372.6981 0.92752

Frequencies -- -128.1592 4.3661 16.6230

M06/6-31G(d) = -5371.458482

2nd Higher Energy TS that leads to Major Product

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

#b3lyp/6-31G(d) EmpiricalDispersion=GD3BJ
scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250,ts,calcfc,noeigentest) iop(1/8=18) freq=noraman
Temperature=298.15 SCRF=(SMD,SOLVENT=THF)
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RB3LYP/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C49H61BCuFeN3O5 C1[X(C49H61BCuFeN3O5)] #Atoms= 121
Charge = 0 Multiplicity = 1

SCF Energy= -5373.62547978Predicted Change= -3.025979D-09

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00093	0.00180	[YES]	0.00093	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-4.248378	-0.427414	2.662871
C	-4.820883	0.526229	3.667733
H	-5.263476	-0.013378	4.516725
H	-5.608995	1.146947	3.228800
H	-4.055129	1.196600	4.069693
C	-2.883897	-0.868361	2.590534
C	-1.773146	-0.437529	3.500562
H	-1.740471	-1.061888	4.404645
H	-1.905771	0.599135	3.827940
H	-0.797356	-0.507769	3.014748
C	-2.777336	-1.793801	1.496646
C	-1.540899	-2.514915	1.054176
H	-1.555911	-2.721859	-0.020213
H	-1.447844	-3.481531	1.569126
H	-0.640424	-1.935709	1.268457
C	-4.075931	-1.928191	0.902089
C	-4.412962	-2.829288	-0.245596
H	-5.320127	-2.505196	-0.763352
H	-4.579660	-3.858054	0.102532
H	-3.605433	-2.857957	-0.983084
C	-4.984041	-1.079409	1.617478
C	-6.455389	-0.941290	1.366117
H	-7.030733	-1.623810	2.007489
H	-6.711549	-1.177920	0.328927

H	-6.808946	0.073605	1.573606
Fe	-3.437596	0.017938	0.851158
C	-1.942868	1.347140	0.432666
H	-0.990857	1.397094	0.937887
C	-2.253534	0.574193	-0.714561
C	-3.631843	0.751163	-1.068347
C	-4.185604	1.659446	-0.105063
H	-5.210066	2.004579	-0.075630
C	-3.143595	2.032686	0.797929
H	-3.244317	2.704002	1.639911
N	-1.447494	-0.252203	-1.499319
C	-2.017281	-0.961640	-2.576759
C	-3.406296	-0.790205	-2.907455
H	-3.791779	-1.348158	-3.754718
C	-4.212257	0.043429	-2.194670
C	-5.660619	0.252105	-2.521813
H	-5.862126	1.305521	-2.755485
H	-6.298015	-0.008742	-1.667272
H	-5.967231	-0.354669	-3.378799
C	-0.115238	-0.479515	-1.375943
Cu	1.135601	0.443512	-0.325994
B	2.087821	-0.529092	1.081515
O	1.440618	-0.786366	2.278134
C	2.174188	-1.837706	2.982320
C	3.025022	-1.141817	4.046353
H	3.743321	-0.448100	3.604886
H	3.570665	-1.868046	4.657561
H	2.365174	-0.567163	4.704185
C	1.182181	-2.773340	3.662076
H	0.460258	-3.190309	2.959275
H	0.630488	-2.230579	4.435826
H	1.713752	-3.599672	4.147281
O	3.105272	-1.423027	0.840226
C	3.004982	-2.500265	1.822639
C	2.276125	-3.652739	1.130255
H	2.176127	-4.520414	1.790325
H	2.856264	-3.950875	0.253310
H	1.282025	-3.351777	0.789454
C	4.413245	-2.932531	2.210743
H	5.002339	-2.103377	2.608453
H	4.931168	-3.325833	1.329773
H	4.377770	-3.726387	2.965304
N	0.148352	-1.372299	-2.372348
C	1.446235	-1.911062	-2.599820
C	-0.983842	-1.679482	-3.115638
H	-0.952655	-2.358810	-3.951543
C	2.487776	-1.065016	-3.016021
O	2.145118	0.225771	-3.246915
C	3.186766	1.160918	-3.530329
H	3.934220	1.173339	-2.732112
H	2.699663	2.134256	-3.589983
H	3.668982	0.932402	-4.488202
C	3.777068	-1.587396	-3.176663
H	4.596525	-0.952394	-3.487917
C	3.992245	-2.944236	-2.941268
H	4.991608	-3.348857	-3.072479

C	2.964382	-3.798856	-2.545921
H	3.165384	-4.847556	-2.368650
C	1.680241	-3.273280	-2.356711
O	0.608092	-3.986522	-1.928064
C	0.775940	-5.385651	-1.702926
H	1.513958	-5.580791	-0.917830
H	1.072048	-5.901428	-2.623932
H	-0.200654	-5.749348	-1.379473
N	1.726037	2.282316	-0.163666
C	0.909276	3.186508	0.423813
C	-0.007571	3.914032	-0.531356
C	2.516312	1.440954	0.704544
H	2.355369	1.686930	1.755159
C	4.011938	1.423900	0.295918
H	4.141697	0.687779	-0.506737
O	0.857127	3.461133	1.642122
C	4.951888	1.033411	1.452992
H	5.962677	0.905011	1.038915
H	4.662907	0.063132	1.856965
C	5.008005	2.091295	2.563839
H	5.719878	1.776156	3.338269
H	4.029345	2.167010	3.056398
C	5.398310	3.467259	2.008490
H	6.437085	3.427125	1.646724
H	5.370619	4.222301	2.805178
C	4.477400	3.873761	0.850963
H	4.802676	4.833370	0.427802
H	3.459362	4.024287	1.231929
C	4.455827	2.800023	-0.244712
H	5.468442	2.691155	-0.661995
H	3.795384	3.105992	-1.059270
C	0.039782	3.719436	-1.918943
H	0.783791	3.045943	-2.328843
C	-0.863701	4.371451	-2.756893
H	-0.819714	4.207134	-3.830603
C	-1.826015	5.231761	-2.219598
H	-2.533748	5.735633	-2.872767
C	-1.870994	5.441663	-0.839347
H	-2.614330	6.111581	-0.414533
C	-0.965464	4.787948	-0.004022
H	-0.989066	4.930303	1.071208

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

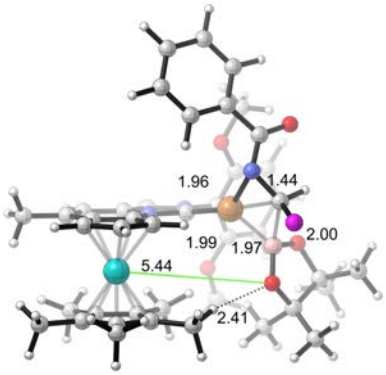
==========

SCF Energy= -5373.62547978 Predicted Change= -3.025979D-09
Zero-point correction (ZPE)= -5372.6037 1.02168
Internal Energy (U)= -5372.5452 1.08019
Enthalpy (H)= -5372.5443 1.08113
Gibbs Free Energy (G)= -5372.6927 0.93273

Frequencies -- -88.4623 15.4629 23.2509

M06/6-31G(d) = -5371.457844

TS-Minor



Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013
==========
#b3lyp/6-31G(d) EmpiricalDispersion=GD3BJ scf=(maxcycle=300,direct,tight)
density=current opt=(maxcycle=250,modredundant) iop(1/8=18)
Temperature=298.15 SCRF=(SMD,SOLVENT=THF)
Modredundant Input: B 45 89 F
Modredundant Input: B 46 92 F
Modredundant Input:
--link1--
#b3lyp/6-31G(d) EmpiricalDispersion=GD3BJ
scf=(direct,tight,maxcycle=300,xqc)
opt=(nofreeze,maxcycle=250,ts,calcfc,noeigentest) iop(1/8=18) freq=noraman
Temperature=298.15 geom=check guess=read SCRF=(SMD,SOLVENT=THF)
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RB3LYP/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C49H61BCuFeN3O5 C1[X(C49H61BCuFeN3O5)] #Atoms= 121
Charge = 0 Multiplicity = 1

SCF Energy= -5373.63311782Predicted Change= -1.317997D-08
==========
Optimization completed. {Found 3 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00157	0.00180	[YES]	0.00157	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-4.395570	-1.686257	1.491865
C	-4.825309	-1.718869	2.927474
H	-5.304896	-2.675958	3.176214
H	-5.544878	-0.924958	3.152129
H	-3.973326	-1.595581	3.603334
C	-3.112927	-2.087808	0.989387
C	-1.988487	-2.652290	1.802416
H	-2.115120	-3.737389	1.930118
H	-1.953335	-2.213719	2.804502
H	-1.014821	-2.493051	1.333405
C	-3.123974	-1.925934	-0.436078
C	-1.986110	-2.221719	-1.365098

H	-2.036512	-1.612923	-2.272070
H	-1.991079	-3.275318	-1.676383
H	-1.021802	-2.023738	-0.892620
C	-4.420876	-1.443857	-0.815625
C	-4.886564	-1.205414	-2.218912
H	-5.697317	-0.472512	-2.259769
H	-5.261863	-2.137078	-2.664420
H	-4.078100	-0.838327	-2.857566
C	-5.204673	-1.287347	0.375342
C	-6.635106	-0.842288	0.435843
H	-7.318554	-1.692756	0.303980
H	-6.866952	-0.114714	-0.348780
H	-6.873016	-0.379588	1.398699
Fe	-3.515862	-0.147741	0.487318
C	-1.945637	0.980743	1.182330
H	-1.044632	0.608250	1.644850
C	-2.150823	1.201962	-0.204633
C	-3.476114	1.699036	-0.431674
C	-4.109747	1.771354	0.854092
H	-5.124365	2.094921	1.042939
C	-3.164592	1.345889	1.836791
H	-3.343497	1.286495	2.902258
N	-1.290300	1.029263	-1.289903
C	-1.755221	1.292556	-2.594130
C	-3.086161	1.793375	-2.806910
H	-3.386345	1.998397	-3.829461
C	-3.943994	2.002211	-1.771804
C	-5.338837	2.518231	-1.959450
H	-5.568455	2.670822	-3.018036
H	-5.479620	3.472334	-1.435344
H	-6.073776	1.817036	-1.543699
C	-0.000715	0.601479	-1.273102
Cu	1.091449	0.335950	0.234563
B	2.016584	-1.384821	0.475132
O	3.114376	-1.735019	-0.279404
C	3.371069	-3.155274	-0.070412
C	3.884667	-3.754033	-1.372138
H	4.043786	-4.833016	-1.266316
H	4.843003	-3.293781	-1.633705
H	3.193136	-3.577506	-2.197061
C	4.450226	-3.250180	1.011305
H	4.747243	-4.288374	1.192434
H	4.112446	-2.816460	1.957183
H	5.332875	-2.693113	0.681464
O	1.371299	-2.492206	0.993684
C	1.968750	-3.684026	0.396831
C	2.010478	-4.775495	1.457883
H	0.989516	-5.058190	1.735686
H	2.526561	-4.441651	2.360722
H	2.516101	-5.669251	1.075643
C	1.064417	-4.103893	-0.761915
H	0.991876	-3.310798	-1.509399
H	0.060088	-4.302047	-0.376544
H	1.430742	-5.016732	-1.242706
N	0.339191	0.575991	-2.591935
C	1.624152	0.188142	-3.068606

C	-0.700489	0.990148	-3.412162
H	-0.594402	1.043459	-4.483429
C	2.697314	1.088413	-2.968949
O	2.400393	2.300876	-2.449066
C	3.471003	3.225376	-2.234994
H	3.995043	3.444210	-3.172706
H	4.164287	2.846024	-1.479200
H	2.997839	4.133802	-1.864040
C	3.964182	0.697191	-3.423666
H	4.813426	1.362624	-3.337451
C	4.116192	-0.561442	-4.002316
H	5.096315	-0.858180	-4.364786
C	3.051767	-1.453158	-4.130905
H	3.205468	-2.422332	-4.587369
C	1.795116	-1.081182	-3.639585
O	0.688437	-1.870188	-3.667027
C	0.784974	-3.135272	-4.319579
H	-0.198274	-3.596316	-4.215067
H	1.536583	-3.776913	-3.847829
H	1.022421	-3.012593	-5.382954
N	1.859515	1.464307	1.635887
C	2.676367	2.468310	1.236295
C	1.982027	3.804578	1.094519
C	2.424255	0.138094	1.700875
C	2.205875	-0.519127	3.068130
H	2.573131	-1.552024	3.017434
H	3.480302	0.131201	1.418584
C	2.751289	4.931426	0.778863
H	3.821042	4.800140	0.654442
C	2.155472	6.183788	0.625949
H	2.766712	7.048774	0.380742
C	0.775337	6.325915	0.788825
H	0.307274	7.299247	0.666572
C	-0.000016	5.208907	1.113690
H	-1.074210	5.310925	1.246491
C	0.599094	3.959741	1.270794
H	-0.000852	3.094803	1.528678
O	3.904409	2.394598	1.018364
C	3.035228	0.211940	4.138451
H	2.703025	1.257489	4.187189
H	4.092946	0.229412	3.844460
C	2.877206	-0.449325	5.514182
H	3.452464	0.103553	6.268278
H	3.301811	-1.463738	5.476217
C	1.403211	-0.538503	5.931152
H	1.010514	0.477965	6.080302
H	1.310571	-1.057785	6.894025
C	0.563982	-1.244927	4.858466
H	-0.495041	-1.252436	5.149167
H	0.877022	-2.297223	4.785531
C	0.733203	-0.574066	3.490707
H	0.338573	0.448885	3.533683
H	0.158729	-1.114004	2.733459

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

```
=====================================================================
 SCF Energy=     -5373.63311782   Predicted Change= -1.317997D-08
 Zero-point correction (ZPE)=       -5372.6126       1.02046
 Internal Energy (U)=             -5372.5536       1.07948
 Enthalpy (H)=                    -5372.5526       1.08042
 Gibbs Free Energy (G)=           -5372.7029 0.93021
---------------------------------------------------------------------
 Frequencies --   -157.3615              21.5710              21.8907

M06/6-31G(d) = -5371.46623084
```

1st Higher Energy TS that leads to Minor Product

```
---------------------------------------------------------------------
 Using  Gaussian 09:  AM64L-G09RevD.01 24-Apr-2013
=====================================================================
 #b3lyp/6-31G(d) EmpiricalDispersion=GD3BJ scf=(maxcycle=300,direct,tight)
 density=current opt=(maxcycle=250,modredundant) iop(1/8=18)
 Temperature=298.15 SCRF=(SMD,SOLVENT=THF)
 Modredundant Input:  B      45      89 F
 Modredundant Input:  B      46      92 F
 Modredundant Input:
 #b3lyp/6-31G(d) EmpiricalDispersion=GD3BJ
 scf=(direct,tight,maxcycle=300,xqc)
 opt=(nofreeze,maxcycle=250,ts,calcfc,noeigentest) iop(1/8=18) freq=noraman
 Temperature=298.15 geom=check guess=read SCRF=(SMD,SOLVENT=THF)
 #N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RB3LYP/6-31G(d) Freq
---------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C49H61BCuFeN3O5   C1[X(C49H61BCuFeN3O5)]  #Atoms= 121
 Charge = 0   Multiplicity = 1
---------------------------------------------------------------------
 SCF Energy= -5373.62867287Predicted Change= -1.562253D-08
=====================================================================
 Optimization completed.           {Found       2       times}
 Item      Max Val.    Criteria    Pass?      RMS Val.    Criteria    Pass?
 Force      0.00000 ||  0.00045   [ YES ]      0.00000 ||  0.00030   [ YES ]
 Displ      0.00719 ||  0.00180   [ NO ]       0.00719 ||  0.00180   [ NO ]
---------------------------------------------------------------------
     Atomic        Coordinates (Angstroms)
      Type       X         Y          Z
---------------------------------------------------------------------
      C        4.471744      0.976952      1.955817
      C        4.934637      0.447093      3.279239
      H        5.413105      1.236731      3.875413
      H        5.665978     -0.358629      3.158835
      H        4.100761      0.053757      3.868951
      C        3.187738      1.557561      1.684934
      C        2.083103      1.744613      2.679622
      H        2.207375      2.691873      3.224402
      H        2.074928      0.942991      3.424924
      H        1.097807      1.769965      2.208202
      C        3.166657      1.965563      0.309558
      C        2.019559      2.617071     -0.400899
      H        2.029305      2.396496     -1.472170
      H        2.053576      3.709750     -0.291579
```

H	1.059231	2.278883	-0.006896
C	4.444786	1.653316	-0.263218
C	4.872722	1.970611	-1.662672
H	5.670214	1.304450	-2.004081
H	5.253039	2.999448	-1.727066
H	4.043445	1.881248	-2.370352
C	5.248689	1.033828	0.750022
C	6.668913	0.579436	0.594836
H	7.370600	1.394811	0.819876
H	6.877526	0.242773	-0.425964
H	6.902707	-0.248336	1.271634
Fe	3.536028	-0.035713	0.456284
C	1.953436	-1.312912	0.718226
H	1.076346	-1.134553	1.320435
C	2.113833	-0.984890	-0.653749
C	3.414994	-1.383026	-1.104068
C	4.080058	-1.959041	0.029877
H	5.087771	-2.351634	0.040366
C	3.176087	-1.927827	1.135470
H	3.383694	-2.286965	2.134568
N	1.227336	-0.397769	-1.557241
C	1.637914	-0.165785	-2.885519
C	2.949657	-0.562234	-3.321224
H	3.213130	-0.368907	-4.356178
C	3.833965	-1.157273	-2.475348
C	5.209123	-1.579492	-2.897430
H	5.409646	-1.304639	-3.936979
H	5.336559	-2.665198	-2.797588
H	5.972561	-1.112216	-2.262644
C	-0.048002	0.011644	-1.328193
Cu	-1.085357	-0.289961	0.202636
B	-1.989184	1.211509	1.116687
O	-3.083474	1.845053	0.565797
C	-3.296940	3.088392	1.298200
C	-3.808917	4.147939	0.333208
H	-3.131241	4.286096	-0.509429
H	-3.934375	5.107644	0.847095
H	-4.783249	3.845181	-0.063486
C	-4.360262	2.792780	2.358939
H	-4.631172	3.693671	2.919175
H	-4.023604	2.031176	3.068267
H	-5.259571	2.415467	1.861811
O	-1.306278	2.030225	1.997460
C	-1.873862	3.372347	1.896556
C	-1.871272	3.994298	3.286510
H	-2.390377	3.364572	4.012646
H	-2.351273	4.979148	3.271145
H	-0.839466	4.126353	3.629187
C	-0.971989	4.171784	0.955112
H	-0.941751	3.721708	-0.040202
H	0.045456	4.179710	1.356392
H	-1.309843	5.209495	0.866250
N	-0.438056	0.516888	-2.531659
C	-1.742690	1.035292	-2.773851
C	0.560246	0.423242	-3.490659
H	0.412882	0.765819	-4.502015

C	-2.812650	0.145752	-2.968393
O	-2.491318	-1.168031	-2.971558
C	-3.548138	-2.128353	-3.060739
H	-4.148531	-1.970853	-3.964224
H	-4.176544	-2.098049	-2.165621
H	-3.052705	-3.096812	-3.119774
C	-4.101393	0.658228	-3.169815
H	-4.947892	-0.004642	-3.294533
C	-4.279474	2.039781	-3.218955
H	-5.277430	2.434800	-3.386545
C	-3.219221	2.931687	-3.062148
H	-3.394593	3.998838	-3.106420
C	-1.938967	2.422578	-2.816496
O	-0.830125	3.179929	-2.604997
C	-0.938837	4.591893	-2.775922
H	0.058114	4.988614	-2.577990
H	-1.649013	5.032764	-2.069141
H	-1.236951	4.842082	-3.800930
N	-1.855936	-1.839898	1.061332
C	-2.704106	-2.655061	0.396257
C	-2.019462	-3.787732	-0.334508
C	-2.406767	-0.648613	1.664837
C	-2.199756	-0.555169	3.185847
H	-2.558054	0.435070	3.485481
H	-3.465444	-0.527084	1.417126
C	-2.801227	-4.828717	-0.849527
H	-3.874902	-4.786093	-0.698657
C	-2.212919	-5.886519	-1.543643
H	-2.832797	-6.689236	-1.935307
C	-0.829382	-5.913383	-1.737028
H	-0.369523	-6.732990	-2.283113
C	-0.040177	-4.879360	-1.224593
H	1.036872	-4.889032	-1.372582
C	-0.630514	-3.828997	-0.523873
H	-0.024416	-3.021297	-0.132497
O	-3.951680	-2.580004	0.375333
C	-3.085788	-1.582686	3.931184
H	-4.084798	-1.600241	3.477967
H	-3.215629	-1.223032	4.963023
C	-2.506412	-3.002161	3.987674
H	-2.497744	-3.438818	2.984353
H	-3.155587	-3.634769	4.608148
C	-1.079338	-2.997258	4.548893
H	-0.673822	-4.017328	4.567410
H	-1.100665	-2.646618	5.592601
C	-0.172517	-2.079880	3.720589
H	-0.087026	-2.489046	2.709909
H	0.838176	-2.052510	4.152021
C	-0.733281	-0.652369	3.649717
H	-0.110217	-0.026535	3.004133
H	-0.668061	-0.207015	4.653724

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -5373.62867287 Predicted Change= -1.562253D-08

Zero-point correction (ZPE)= -5372.6082 1.02039
Internal Energy (U)= -5372.5489 1.07974
Enthalpy (H)= -5372.5479 1.08068
Gibbs Free Energy (G)= -5372.7013 0.92728

Frequencies -- -177.5810 6.9078 13.1117

M06/6-31G(d) = -5371.460729

2nd Higher Energy TS that leads to Minor Product

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013
==========
#b3lyp/6-31G(d) EmpiricalDispersion=GD3BJ scf=(maxcycle=300,direct,tight)
density=current opt=(maxcycle=250,modredundant) iop(1/8=18)
Temperature=298.15 SCRF=(SMD,SOLVENT=THF)
Modredundant Input: B 45 89 F
Modredundant Input: B 46 92 F
Modredundant Input:
#b3lyp/6-31G(d) EmpiricalDispersion=GD3BJ
scf=(direct,tight,maxcycle=300,xqc)
opt=(nofreeze,maxcycle=250,ts,calcfc,noeigentest) iop(1/8=18) freq=noraman
Temperature=298.15 geom=check guess=read SCRF=(SMD,SOLVENT=THF)
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RB3LYP/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C49H61BCuFeN3O5 C1[X(C49H61BCuFeN3O5)] #Atoms= 121
Charge = 0 Multiplicity = 1

SCF Energy= -5373.62775528Predicted Change= -1.160446D-08
==========
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00445	0.00180	[NO]	0.00445	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	4.669096	0.391897	1.770344
C	5.290421	-0.282071	2.955867
H	5.971964	0.398792	3.484862
H	5.872005	-1.161741	2.660980
H	4.532773	-0.609257	3.674427
C	3.403594	1.067752	1.748717
C	2.487949	1.238496	2.922471
H	2.821016	2.075698	3.552922
H	2.474108	0.345093	3.555591
H	1.461786	1.447467	2.614342
C	3.205901	1.593947	0.427509
C	2.038888	2.401536	-0.055279
H	1.779123	2.162767	-1.091034
H	2.268422	3.476070	-0.019322
H	1.150003	2.231702	0.554748
C	4.354075	1.249826	-0.360059
C	4.574041	1.648287	-1.786921

H	5.272916	0.976917	-2.293336
H	4.988749	2.664184	-1.846284
H	3.639114	1.641995	-2.355163
C	5.257374	0.504546	0.467215
C	6.609214	-0.006907	0.070361
H	7.392346	0.722306	0.321588
H	6.673818	-0.193010	-1.005966
H	6.857734	-0.939860	0.586372
Fe	3.445695	-0.434810	0.367717
C	1.747397	-1.558278	0.638551
H	0.894990	-1.318544	1.255148
C	1.919105	-1.223658	-0.730360
C	3.168191	-1.742241	-1.206687
C	3.792698	-2.392826	-0.090432
H	4.759003	-2.878161	-0.100857
C	2.912290	-2.290386	1.029580
H	3.100166	-2.679472	2.021378
N	1.082749	-0.534573	-1.611448
C	1.489844	-0.348697	-2.948479
C	2.740635	-0.882193	-3.414469
H	2.997367	-0.718395	-4.456171
C	3.579767	-1.560810	-2.586725
C	4.891334	-2.126726	-3.042149
H	4.910379	-3.218171	-2.926072
H	5.719906	-1.731160	-2.441531
H	5.083435	-1.890052	-4.092746
C	-0.130098	0.024716	-1.352518
Cu	-1.126746	-0.148639	0.236773
B	-1.658500	1.407276	1.334365
O	-2.665056	2.276112	0.965862
C	-2.262706	3.620645	1.369872
C	-1.599770	4.270658	0.156126
H	-0.722125	3.705760	-0.168735
H	-1.299853	5.301767	0.368960
H	-2.317475	4.281611	-0.667215
C	-3.511701	4.396775	1.766035
H	-4.082210	3.880649	2.541298
H	-4.159671	4.518371	0.891838
H	-3.246963	5.394988	2.132502
O	-0.752028	2.006929	2.190270
C	-1.258683	3.335383	2.540470
C	-1.933493	3.219615	3.907784
H	-2.243387	4.202426	4.278196
H	-1.223046	2.793139	4.622886
H	-2.814415	2.573354	3.873560
C	-0.081307	4.297660	2.624811
H	0.517459	4.290597	1.712430
H	0.568224	4.017098	3.460525
H	-0.435369	5.319449	2.801645
N	-0.484915	0.570540	-2.551662
C	-1.690930	1.293256	-2.780049
C	0.476723	0.360828	-3.530882
H	0.353469	0.725274	-4.537555
C	-2.915807	0.609678	-2.873167
O	-2.851976	-0.737737	-2.789411
C	-4.071810	-1.481275	-2.868231

H	-4.690414	-1.307051	-1.983480
H	-3.771053	-2.527316	-2.893872
H	-4.622909	-1.236786	-3.783608
C	-4.093886	1.342049	-3.076654
H	-5.053306	0.843473	-3.119886
C	-4.015668	2.723150	-3.242460
H	-4.929855	3.284548	-3.413069
C	-2.800853	3.406508	-3.202669
H	-2.773355	4.479562	-3.343414
C	-1.627678	2.684521	-2.952889
O	-0.388963	3.232441	-2.854275
C	-0.243221	4.622594	-3.139953
H	0.820819	4.834586	-3.023390
H	-0.814269	5.241582	-2.440212
H	-0.551430	4.847679	-4.167725
N	-2.099679	-1.626563	1.028991
C	-3.103640	-2.277005	0.403870
C	-2.647859	-3.467630	-0.407872
C	-2.416226	-0.419679	1.744581
C	-2.143829	-0.479715	3.255483
H	-2.327192	0.526911	3.640358
H	-3.443283	-0.090876	1.556257
C	-3.608823	-4.376482	-0.866468
H	-4.649148	-4.187149	-0.622704
C	-3.235446	-5.489046	-1.621047
H	-3.992320	-6.188108	-1.967964
C	-1.890150	-5.703775	-1.931781
H	-1.597317	-6.566404	-2.524694
C	-0.923258	-4.802198	-1.476732
H	0.125406	-4.959353	-1.716725
C	-1.298968	-3.696581	-0.715459
H	-0.555624	-2.990707	-0.365149
O	-4.324394	-2.023322	0.487922
C	-3.163398	-1.403137	3.967514
H	-4.166580	-1.222151	3.562422
H	-3.193824	-1.106294	5.026764
C	-2.829917	-2.899467	3.898946
H	-2.939934	-3.257195	2.871174
H	-3.550863	-3.458812	4.510512
C	-1.401221	-3.175125	4.381961
H	-1.172238	-4.246019	4.303472
H	-1.322038	-2.912378	5.448450
C	-0.385645	-2.353216	3.580157
H	-0.407262	-2.682307	2.537188
H	0.630242	-2.528981	3.961148
C	-0.701801	-0.852878	3.649561
H	-0.001314	-0.281894	3.032976
H	-0.538848	-0.514119	4.683571

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

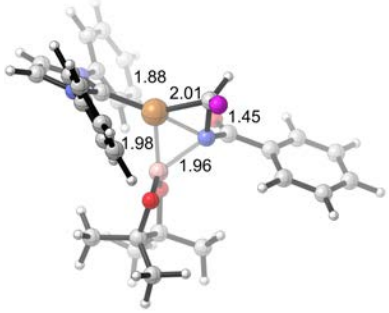
SCF Energy= -5373.62775528 Predicted Change= -1.160446D-08
Zero-point correction (ZPE)= -5372.6064 1.02133
Internal Energy (U)= -5372.5475 1.08018
Enthalpy (H)= -5372.5466 1.08112

Gibbs Free Energy (G)= -5372.6974 0.93026

Frequencies -- -136.3326 11.9855 14.7132

M06/6-31G(d) = -5371.45944264

RegioTS$_{Disfavored}$



Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

#b3lyp/6-31G(d) EmpiricalDispersion=GD3BJ
scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250,ts,calcfc,noeigentest) iop(1/8=18) freq=noraman
Temperature=298.15 SCRF=(SMD,SOLVENT=THF)
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RB3LYP/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C35H41BCuN3O3 C1[X(C35H41BCuN3O3)] #Atoms= 84
Charge = 0 Multiplicity = 1

SCF Energy= -3413.84161613Predicted Change= -5.180800D-09

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00481	0.00180	[NO]	0.00481	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	-3.407716	0.406143	0.120334
C	-3.148338	1.733237	0.571829
C	-4.686852	-0.144307	0.028812
H	-5.558381	0.374117	0.395023
C	-4.544144	-1.369844	-0.522129
H	-5.265737	-2.141709	-0.734996
N	-3.180385	-1.550374	-0.757220
C	-2.633158	-2.721065	-1.365302
C	-2.460230	-0.450628	-0.374162
Cu	-0.616848	-0.210535	-0.463970
B	0.348808	-0.775594	1.166408
C	-3.980667	2.772345	0.146096
H	-4.803549	2.565191	-0.530666
C	-3.727614	4.074268	0.577184
H	-4.371308	4.882388	0.242404

C	-2.644804	4.340073	1.418497
H	-2.446290	5.356275	1.746017
C	-1.817424	3.294097	1.831630
H	-0.972869	3.488911	2.486277
C	-2.066610	1.986178	1.416765
H	-1.433543	1.177116	1.760394
C	-1.455850	-3.286368	-0.871478
H	-0.945970	-2.846242	-0.023979
C	-0.946389	-4.433248	-1.478476
H	-0.025540	-4.864485	-1.098163
C	-1.607561	-5.020745	-2.558067
H	-1.204409	-5.915244	-3.024056
C	-2.787961	-4.450703	-3.039983
H	-3.306059	-4.895674	-3.884554
C	-3.301247	-3.295693	-2.451184
H	-4.203648	-2.833651	-2.838909
O	0.819105	-2.037774	1.468396
C	1.357863	-1.998010	2.825818
C	2.863834	-1.762142	2.703083
H	3.358470	-1.801668	3.679481
H	3.079963	-0.795054	2.242177
H	3.296272	-2.541866	2.068362
C	1.082756	-3.339469	3.490785
H	0.023115	-3.602005	3.444822
H	1.393731	-3.322510	4.541468
H	1.649729	-4.127206	2.983287
C	0.588217	-0.781155	3.447184
C	1.375071	0.023167	4.472548
H	0.768457	0.863184	4.827859
H	2.296648	0.427346	4.047423
H	1.631941	-0.597879	5.338084
C	-0.785926	-1.158742	4.006818
H	-1.364988	-1.734815	3.277985
H	-1.342276	-0.243408	4.233709
H	-0.701024	-1.743948	4.928076
O	0.354659	0.059050	2.279773
C	0.731283	0.974594	-1.358585
H	1.015810	0.707738	-2.378483
C	0.790853	2.456443	-1.050793
H	0.668730	2.580377	0.035310
N	1.244419	0.050552	-0.368089
C	2.034045	-0.950934	-0.975392
C	3.492211	-0.639723	-1.030837
C	4.078662	0.318310	-0.190832
H	3.450470	0.864552	0.502599
C	5.452428	0.549777	-0.239645
H	5.898858	1.290256	0.418169
C	6.253133	-0.172569	-1.128015
H	7.323567	0.009951	-1.167095
C	5.676345	-1.135291	-1.961706
H	6.296992	-1.700503	-2.651505
C	4.305169	-1.372346	-1.907926
H	3.844091	-2.121733	-2.542693
O	1.587786	-2.001670	-1.422761
C	-0.351394	3.222758	-1.743009
H	-1.313946	2.825027	-1.403416

H	-0.297651	3.033884	-2.826436
C	-0.286987	4.733954	-1.486728
H	-0.455191	4.919674	-0.417064
H	-1.100558	5.241090	-2.022115
C	1.069930	5.323530	-1.888086
H	1.104865	6.396175	-1.655980
H	1.199391	5.231224	-2.976722
C	2.212365	4.584254	-1.182499
H	2.141783	4.761802	-0.098805
H	3.183676	4.984060	-1.503074
C	2.148313	3.075435	-1.451229
H	2.960336	2.562702	-0.926609
H	2.308029	2.892324	-2.524877

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

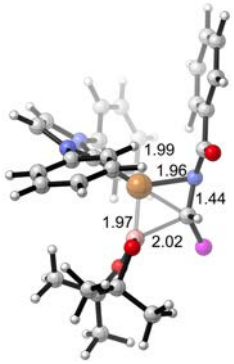
==========

SCF Energy= -3413.84161613 Predicted Change= -5.180800D-09
Zero-point correction (ZPE)= -3413.1396 0.70195
Internal Energy (U)= -3413.0999 0.74162
Enthalpy (H)= -3413.0990 0.74256
Gibbs Free Energy (G)= -3413.2144 0.62715

Frequencies -- -313.0024 7.1660 19.7239

M06/6-31G(d) = -3412.309096

RegioTS$_{favored}$



Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

#b3lyp/6-31G(d) EmpiricalDispersion=GD3BJ scf=(maxcycle=300,direct,tight)
density=current opt=(maxcycle=250,modredundant) iop(1/8=18)
Temperature=298.15 SCRF=(SMD,SOLVENT=THF)
Modredundant Input: B 10 52 F
Modredundant Input: B 11 55 F
Modredundant Input:
#b3lyp/6-31G(d) EmpiricalDispersion=GD3BJ
scf=(direct,tight,maxcycle=300,xqc)

opt=(nofreeze,maxcycle=250,ts,calcfc,noeigentest) iop(1/8=18) freq=noraman
Temperature=298.15 geom=check guess=read SCRF=(SMD,SOLVENT=THF)
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RB3LYP/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C35H41BCuN3O3 C1[X(C35H41BCuN3O3)] #Atoms= 84
Charge = 0 Multiplicity = 1

SCF Energy= -3413.89205183Predicted Change= -9.147902D-09

==========

Optimization completed. {Found 3 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00124	0.00180	[YES]	0.00124	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	-0.214018	-2.876046	0.935640
C	-1.239202	-3.174083	-0.012526
C	0.317259	-3.789548	1.845298
H	-0.028592	-4.809225	1.901247
C	1.284370	-3.134758	2.531510
H	1.936209	-3.458876	3.326965
N	1.317159	-1.835211	2.030033
C	2.274720	-0.840766	2.392368
C	0.390844	-1.661206	1.042904
Cu	0.086559	-0.106904	0.040629
B	-1.754023	0.586097	0.020101
C	-2.350855	-3.915614	0.393853
H	-2.433688	-4.246923	1.424183
C	-3.355031	-4.203212	-0.530343
H	-4.221856	-4.777740	-0.217257
C	-3.252981	-3.742927	-1.845490
H	-4.040419	-3.962510	-2.560408
C	-2.138863	-2.999592	-2.236970
H	-2.052485	-2.634326	-3.255628
C	-1.122660	-2.716558	-1.326648
H	-0.253774	-2.147289	-1.638345
C	1.877019	0.491728	2.517643
H	0.832387	0.757140	2.397658
C	2.830795	1.468262	2.799981
H	2.520722	2.504950	2.888705
C	4.170761	1.115269	2.972739
H	4.911216	1.878462	3.192516
C	4.555537	-0.222715	2.860708
H	5.596768	-0.504404	2.986538
C	3.611848	-1.205199	2.561410
H	3.914864	-2.238767	2.430073
O	-2.760752	0.053725	-0.750928
C	-4.036889	0.497107	-0.201053
C	-5.042380	-0.638398	-0.333135
H	-5.998354	-0.363146	0.126499
H	-4.678928	-1.556418	0.132047
H	-5.224502	-0.846621	-1.392541
C	-4.480203	1.698268	-1.038971
H	-3.767728	2.525157	-0.960478

H	-5.467907	2.059207	-0.734244
H	-4.533911	1.397517	-2.090075
C	-3.651097	0.872750	1.273217
C	-3.717207	-0.315617	2.235268
H	-3.190322	-1.185623	1.831780
H	-4.752121	-0.603371	2.447153
H	-3.240135	-0.035581	3.180097
C	-4.396265	2.067294	1.852325
H	-4.236110	2.968638	1.256361
H	-4.043025	2.265131	2.869899
H	-5.472321	1.866725	1.901114
O	-2.239918	1.230931	1.141386
N	1.046201	1.027234	-1.236407
C	1.391936	0.211783	-2.267765
C	2.807953	-0.315468	-2.181390
C	-0.335507	1.430343	-1.150817
H	-0.895131	1.198667	-2.060193
C	-0.489085	2.896273	-0.736568
H	-1.560172	3.109592	-0.616910
C	3.667288	0.001150	-1.117654
H	3.315659	0.663082	-0.334733
C	4.953556	-0.533455	-1.064216
H	5.603416	-0.285095	-0.229241
C	5.403509	-1.387299	-2.075986
H	6.406439	-1.804239	-2.033448
C	4.556856	-1.702100	-3.141527
H	4.900140	-2.364662	-3.932115
C	3.268306	-1.169457	-3.190884
H	2.593261	-1.406420	-4.006708
O	0.675515	-0.124160	-3.233854
C	0.038907	3.806829	-1.860535
H	-0.488019	3.582211	-2.797415
H	1.098227	3.573176	-2.030011
C	-0.113841	5.291545	-1.507192
H	-1.183494	5.539847	-1.436851
H	0.300344	5.914738	-2.310485
C	0.567235	5.620982	-0.172964
H	0.412507	6.676972	0.084457
H	1.652363	5.476022	-0.278798
C	0.048728	4.715037	0.950803
H	-1.014223	4.935004	1.131537
H	0.576613	4.933166	1.888774
C	0.201342	3.231887	0.592840
H	-0.223576	2.609934	1.387818
H	1.265212	2.978603	0.512625

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

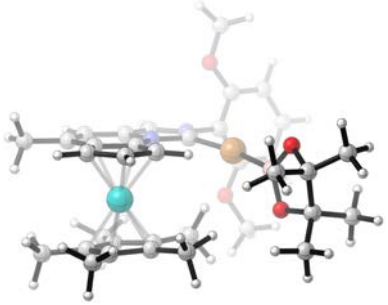
==========

SCF Energy= -3413.89205183 Predicted Change= -9.147902D-09
Zero-point correction (ZPE)= -3413.1881 0.70389
Internal Energy (U)= -3413.1489 0.74312
Enthalpy (H)= -3413.1479 0.74407
Gibbs Free Energy (G)= -3413.2608 0.63117

Frequencies -- -133.0836 15.3453 22.4670

M06/6-31G(d) = -3412.358796

Copper-Bpin Ground State



Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013
==========
# b3lyp/6-31G(d) EmpiricalDispersion=GD3BJ gfprint gfinput
scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250) freq=noraman
SCRF=(SMD,SOLVENT=TetraHydroFuran) iop(1/8=14) Temperature=298.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RB3LYP/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C35H44BCuFeN2O4 C1[X(C35H44BCuFeN2O4)] #Atoms= 88
Charge = 0 Multiplicity = 1

SCF Energy= -4699.76688735Predicted Change= -2.689340D-05
==========
Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00019	0.00045	[YES]	0.00002	0.00030	[YES]
Displ	0.55677	0.00180	[NO]	0.55677	0.00180	[NO]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-4.175931	0.903073	0.900548
C	-5.337635	1.691688	0.377167
H	-5.932622	2.113096	1.199347
H	-6.008176	1.072266	-0.227830
H	-5.003865	2.527314	-0.246087
C	-2.848714	1.402116	1.120063
C	-2.350356	2.790562	0.852394
H	-2.580363	3.460942	1.692671
H	-2.811410	3.221850	-0.042624
H	-1.265359	2.800526	0.714277
C	-2.054912	0.334623	1.654647
C	-0.595469	0.426433	1.973663
H	-0.216105	-0.512239	2.382640
H	-0.390135	1.224675	2.697008
H	0.005215	0.641186	1.078821
C	-2.888025	-0.827655	1.760406
C	-2.468046	-2.168948	2.279451
H	-3.023696	-2.978700	1.798030
H	-2.644276	-2.245543	3.361287
H	-1.404724	-2.354180	2.103773
C	-4.200654	-0.476913	1.293835

C	-5.402175	-1.373894	1.279683
H	-5.982269	-1.268017	2.207414
H	-5.118738	-2.427393	1.193061
H	-6.073613	-1.138219	0.447528
Fe	-2.812252	-0.163092	-0.171265
C	-1.450264	0.325203	-1.600528
H	-0.670419	1.058277	-1.445852
C	-1.331550	-1.048600	-1.267652
C	-2.568856	-1.725278	-1.513698
C	-3.479723	-0.735222	-2.016983
H	-4.509396	-0.906420	-2.300452
C	-2.783542	0.512584	-2.086729
H	-3.202557	1.452713	-2.420215
N	-0.235238	-1.767182	-0.789009
C	-0.365054	-3.146031	-0.530476
C	-1.613387	-3.816076	-0.781485
H	-1.661780	-4.880524	-0.574550
C	-2.702154	-3.148870	-1.255048
C	-4.013528	-3.823420	-1.529055
H	-4.825816	-3.345926	-0.967512
H	-3.982147	-4.882278	-1.255960
H	-4.277977	-3.750618	-2.592124
C	1.008255	-1.289464	-0.508228
Cu	1.509275	0.539102	-0.484363
B	1.659569	2.490956	-0.445989
O	1.273458	3.299835	0.632605
C	1.543413	4.690855	0.308012
C	0.465916	5.566595	0.936899
H	-0.536425	5.272426	0.617732
H	0.618137	6.620447	0.675380
H	0.510415	5.482412	2.028409
C	2.910898	5.033139	0.910141
H	3.701063	4.421313	0.463727
H	2.889669	4.826605	1.985394
H	3.165582	6.089460	0.769934
O	1.981609	3.309462	-1.536275
C	1.550969	4.667388	-1.253229
C	2.519723	5.643266	-1.911256
H	2.460730	5.546886	-3.001112
H	3.552680	5.448732	-1.612805
H	2.270378	6.679029	-1.652038
C	0.153646	4.826861	-1.864346
H	-0.561163	4.143561	-1.395368
H	0.202698	4.584177	-2.931148
H	-0.223674	5.850530	-1.763991
N	1.662255	-2.396664	-0.056144
C	3.021364	-2.360430	0.368867
C	0.861307	-3.531631	-0.057403
H	1.228387	-4.493114	0.263667
C	4.026266	-2.828636	-0.492879
O	3.596434	-3.316032	-1.682548
C	4.576257	-3.798950	-2.600697
H	4.019428	-4.129619	-3.478927
H	5.131372	-4.646244	-2.181047
H	5.276082	-3.006470	-2.889782
C	5.367563	-2.758146	-0.095610

H	6.159194	-3.108929	-0.745327
C	5.674348	-2.211646	1.149694
H	6.715037	-2.149597	1.454845
C	4.688129	-1.742892	2.015709
H	4.961855	-1.325475	2.976267
C	3.344589	-1.824368	1.625937
O	2.298697	-1.419151	2.386814
C	2.583888	-0.700637	3.586563
H	1.614927	-0.419380	3.999872
H	3.165839	0.203413	3.375098
H	3.119739	-1.327385	4.308986

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

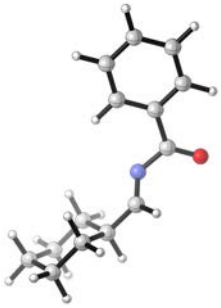
==========

SCF Energy= -4699.76688735 Predicted Change= -2.689340D-05
Zero-point correction (ZPE)= -4699.0336 0.73328
Internal Energy (U)= -4698.9883 0.77857
Enthalpy (H)= -4698.9873 0.77952
Gibbs Free Energy (G)= -4699.1134 0.65340

Frequencies -- 3.0068 8.2444 16.2160

M06/6-31G(d) = -4698.16308430

Imine Ground State



Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

#b3lyp/6-31G(d) EmpiricalDispersion=GD3BJ scf=(maxcycle=300,direct,tight)
density=current SCRF=(SOLVENT=THF,SMD) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C14H17NO C1[X(C14H17NO)] #Atoms= 33
Charge = 0 Multiplicity = 1

SCF Energy= -673.793527163Predicted Change= -1.625431D-08

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00876	0.00180	[NO]	0.00876	0.00180	[NO]

Atomic Coordinates (Angstroms)

Type	X	Y	Z
C	-2.274256	-0.758035	0.152048
C	-0.853699	-1.183508	0.349546
H	-0.654104	-1.800445	1.236973
N	0.094971	-0.832216	-0.427616
C	1.393753	-1.319099	-0.197072
C	2.448403	-0.270596	-0.103663
O	1.641381	-2.517384	-0.137761
H	-2.878568	-1.680022	0.170789
C	-2.526938	-0.020806	-1.167812
H	-2.228852	-0.654650	-2.010907
H	-1.885528	0.869494	-1.205403
C	-3.996432	0.398807	-1.297302
H	-4.627168	-0.499807	-1.360727
H	-4.143362	0.952551	-2.232827
C	-4.445180	1.247262	-0.100694
H	-5.507387	1.505573	-0.193930
H	-3.886999	2.194849	-0.101529
C	-4.193105	0.516941	1.224320
H	-4.829662	-0.378172	1.272399
H	-4.476409	1.153165	2.071927
C	-2.725341	0.095175	1.363423
H	-2.573020	-0.464214	2.294670
H	-2.088053	0.988872	1.418580
C	3.771648	-0.668126	0.136873
H	3.990734	-1.726535	0.231027
C	4.778523	0.285505	0.254139
H	5.802286	-0.026316	0.440305
C	4.471241	1.644289	0.132302
H	5.257718	2.388524	0.222610
C	3.155062	2.046254	-0.107534
H	2.916726	3.101548	-0.204905
C	2.145194	1.093096	-0.227200
H	1.122567	1.397215	-0.421899

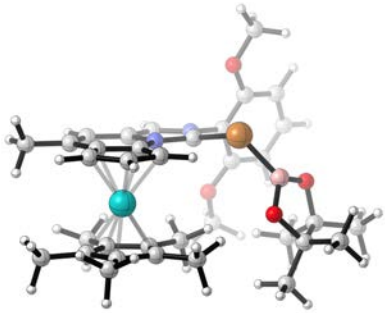
Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -673.793527163 Predicted Change= -1.625431D-08
Zero-point correction (ZPE)= -673.5096 0.28392
Internal Energy (U)= -673.4953 0.29815
Enthalpy (H)= -673.4944 0.29909
Gibbs Free Energy (G)= -673.5530 0.24046

Frequencies -- 20.3168 29.2165 53.5803

M06/6-31G(d) = -673.237783391

Major-TS Copper-Bpin Species



Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013
==========
#b3lyp/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(SOLVENT=THF,SMD) freq=noraman

Pointgroup= C1 Stoichiometry= C35H44BCuFeN2O4 C1[X(C35H44BCuFeN2O4)] #Atoms= 88
Charge = 0 Multiplicity = 1

SCF Energy= -4699.51175406Predicted Change= -6.235098D-03
==========
Optimization incomplete.

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.03169 ‖	0.00045	[NO]	0.00301 ‖	0.00030	[NO]
Displ	0.13408 ‖	0.00180	[NO]	0.13408 ‖	0.00180	[NO]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-4.123689	1.899628	0.234694
C	-5.134312	2.672652	-0.557367
H	-5.546852	3.502569	0.033599
H	-5.975007	2.041830	-0.864451
H	-4.694848	3.103700	-1.462302
C	-2.710292	2.146797	0.273482
C	-1.987625	3.214861	-0.491336
H	-2.003870	4.167901	0.056668
H	-2.454443	3.393743	-1.465787
H	-0.942051	2.953988	-0.668691
C	-2.121538	1.201844	1.181108
C	-0.672073	1.091616	1.545113
H	-0.378874	0.055641	1.738182
H	-0.452421	1.664668	2.457348
H	-0.028925	1.473644	0.750349
C	-3.172414	0.377133	1.703362
C	-2.993765	-0.717466	2.709662
H	-3.810164	-1.443924	2.667531
H	-2.964935	-0.309849	3.729755
H	-2.059407	-1.262430	2.545860
C	-4.409330	0.804205	1.116186
C	-5.772073	0.257072	1.418216
H	-6.260680	0.838429	2.212880
H	-5.726849	-0.782184	1.758031
H	-6.426734	0.291715	0.541545
Fe	-3.087153	0.244170	-0.338604
C	-1.950438	-0.044739	-2.015754

H	-1.165480	0.602804	-2.374562
C	-1.806551	-1.139448	-1.124549
C	-3.084419	-1.745102	-0.884383
C	-4.041546	-0.996308	-1.647450
H	-5.106269	-1.181869	-1.685272
C	-3.338612	0.029484	-2.349399
H	-3.780770	0.764336	-3.008539
N	-0.670241	-1.679258	-0.516108
C	-0.809335	-2.765514	0.372117
C	-2.098384	-3.355065	0.611309
H	-2.145163	-4.197017	1.294444
C	-3.222056	-2.879174	0.010162
C	-4.580830	-3.469337	0.241252
H	-5.015196	-3.836798	-0.697377
H	-5.272862	-2.714345	0.635329
H	-4.538177	-4.301101	0.950451
C	0.624134	-1.287179	-0.657370
Cu	1.313317	-0.060225	-1.901498
B	2.138580	1.611962	-1.272508
O	3.397545	1.683312	-0.716152
C	3.406923	2.775192	0.250824
C	3.179822	2.148770	1.626343
H	3.972204	1.418589	1.810292
H	2.222005	1.624540	1.670080
H	3.209984	2.900792	2.421551
C	4.772197	3.448302	0.195103
H	5.018606	3.781434	-0.815726
H	5.543234	2.739804	0.515929
H	4.806980	4.312960	0.867196
O	1.348353	2.684522	-0.892583
C	2.210602	3.663936	-0.234852
C	2.605078	4.679286	-1.309684
H	1.696082	5.107796	-1.743353
H	3.174662	4.207686	-2.116658
H	3.204280	5.494822	-0.891659
C	1.426911	4.348948	0.876181
H	0.618637	4.948867	0.446018
H	2.078825	5.021299	1.445106
H	0.984158	3.627247	1.565414
N	1.300837	-2.125493	0.177330
C	2.699763	-2.037083	0.430911
C	0.459120	-3.028848	0.811677
H	0.833172	-3.768374	1.500742
C	3.624286	-2.529014	-0.504385
O	3.100408	-3.090218	-1.620223
C	4.003623	-3.625850	-2.587626
H	4.586825	-4.452346	-2.164585
H	4.678906	-2.856160	-2.973135
H	3.378077	-3.998106	-3.399865
C	4.995484	-2.429827	-0.230593
H	5.729541	-2.792808	-0.938187
C	5.407949	-1.863990	0.974421
H	6.471258	-1.791572	1.183920
C	4.499817	-1.393315	1.921753
H	4.853863	-0.963224	2.849937
C	3.130282	-1.474543	1.643287

O	2.144902	-1.041088	2.469555
C	2.503174	-0.612324	3.782681
H	2.988323	-1.421904	4.340437
H	1.563961	-0.343853	4.268817
H	3.160150	0.262774	3.758535

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

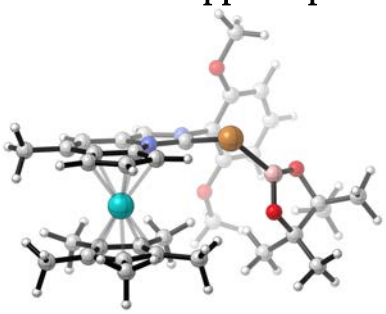
==========

SCF Energy= -4699.51175406 Predicted Change= -6.235098D-03
Zero-point correction (ZPE)= -4698.7795 0.73216
Internal Energy (U)= -4698.7354 0.77631
Enthalpy (H)= -4698.7344 0.77726
Gibbs Free Energy (G)= -4698.8541 0.65762

Frequencies -- -30.6323 -22.7179 8.3661

D3BJ(B3LYP) = -0.23550691
M06/6-31G(d) = -4698.14231452

Minor-TS Copper-Bpin Species



Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

#b3lyp/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(SOLVENT=THF,SMD) freq=noraman

Pointgroup= C1 Stoichiometry= C35H44BCuFeN2O4 C1[X(C35H44BCuFeN2O4)] #Atoms= 88
Charge = 0 Multiplicity = 1

SCF Energy= -4699.51027477Predicted Change= -5.915893D-03

==========

Optimization incomplete.

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.03253	0.00045	[NO]	0.00303	0.00030	[NO]
Displ	0.14589	0.00180	[NO]	0.14589	0.00180	[NO]

Atomic Coordinates (Angstroms)

Type	X	Y	Z
C	-3.986983	2.203387	0.039744
C	-4.740062	3.111003	-0.885362
H	-5.087427	4.012228	-0.360928
H	-5.622164	2.617696	-1.306183
H	-4.114020	3.440474	-1.720453
C	-2.570296	2.222549	0.266715
C	-1.595363	3.180537	-0.346298
H	-1.553953	4.111448	0.238061
H	-1.883636	3.454811	-1.365815
H	-0.581264	2.776024	-0.382934
C	-2.262982	1.214837	1.240556
C	-0.899439	0.885871	1.767651
H	-0.835326	-0.153555	2.101198
H	-0.640879	1.522216	2.625092
H	-0.130129	1.032201	1.006680
C	-3.493110	0.587517	1.630015
C	-3.638323	-0.471549	2.678921
H	-4.531938	-1.081813	2.520259
H	-3.721937	-0.017931	3.676206
H	-2.777502	-1.146040	2.696021
C	-4.557954	1.191554	0.882700
C	-6.015830	0.863667	1.005111
H	-6.483989	1.443835	1.812581
H	-6.175623	-0.195551	1.231546
H	-6.559223	1.091838	0.082910
Fe	-3.177826	0.382408	-0.383736
C	-2.050581	-0.059204	-2.043975
H	-1.237630	0.528959	-2.441049
C	-1.948309	-1.091869	-1.075555
C	-3.245260	-1.637116	-0.800502
C	-4.174996	-0.906724	-1.614151
H	-5.245972	-1.055377	-1.641150
C	-3.437021	0.044799	-2.382292
H	-3.856150	0.747578	-3.090244
N	-0.833127	-1.617083	-0.420841
C	-1.006128	-2.634518	0.539049
C	-2.312598	-3.173953	0.802931
H	-2.386647	-3.969859	1.536964
C	-3.419452	-2.708109	0.163554
C	-4.795679	-3.244667	0.418895
H	-4.784348	-4.020836	1.189644
H	-5.227254	-3.672878	-0.494996
H	-5.472699	-2.444282	0.743980
C	0.468564	-1.256550	-0.568862
Cu	1.190570	-0.105061	-1.868540
B	2.320563	1.406678	-1.309478
O	3.613161	1.227832	-0.868657
C	4.059971	2.476606	-0.262357
C	4.972870	2.149112	0.910743
H	5.290974	3.064746	1.421781
H	5.868293	1.635814	0.545527
H	4.482684	1.493507	1.631690
C	4.842780	3.230730	-1.340410
H	5.266782	4.162250	-0.951368

H	4.213451	3.470143	-2.202688
H	5.665399	2.598315	-1.689013
O	1.776359	2.590965	-0.848066
C	2.703383	3.166076	0.123265
C	2.679474	4.680166	-0.037468
H	1.688766	5.063186	0.229447
H	2.892546	4.980631	-1.065688
H	3.413674	5.152406	0.624715
C	2.197667	2.771089	1.510721
H	2.169069	1.684979	1.622648
H	1.181604	3.154235	1.642173
H	2.826412	3.196002	2.299869
N	1.117936	-2.047312	0.330311
C	2.528123	-2.022974	0.529190
C	0.252337	-2.890622	1.012079
H	0.604527	-3.592969	1.749905
C	3.366843	-2.658045	-0.401037
O	2.741414	-3.293731	-1.417533
C	3.545562	-3.877227	-2.446909
H	4.234315	-4.622831	-2.032762
H	4.090354	-3.104767	-2.996717
H	2.842445	-4.367632	-3.119100
C	4.755041	-2.617688	-0.211142
H	5.425346	-3.078748	-0.924985
C	5.264810	-1.983534	0.920262
H	6.340337	-1.963565	1.071653
C	4.439938	-1.372959	1.864441
H	4.870063	-0.890981	2.732749
C	3.056007	-1.375467	1.655461
O	2.147955	-0.783663	2.475973
C	2.623944	-0.190662	3.683181
H	1.743105	0.226016	4.173846
H	3.340122	0.613290	3.483382
H	3.087113	-0.941290	4.334504

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

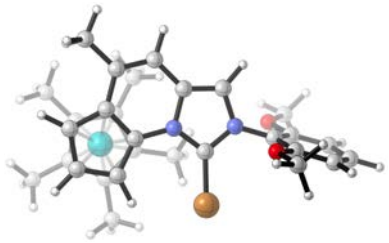
==========

SCF Energy= -4699.51027477 Predicted Change= -5.915893D-03
Zero-point correction (ZPE)= -4698.7782 0.73198
Internal Energy (U)= -4698.7350 0.77518
Enthalpy (H)= -4698.7341 0.77612
Gibbs Free Energy (G)= -4698.8499 0.66031

Frequencies -- -44.6121 -22.9218 -7.3740

D3BJ(B3LYP) = -0.23584926
M06/6-31G(d) = -4698.14083567

Major-TS NHC-ferrocenyl-Cu(I) Model Species



Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013
==========
#b3lyp/6-31G(d) EmpiricalDispersion=GD3BJ scf=(maxcycle=300,direct,tight)
density=current SCRF=(SOLVENT=THF,SMD) freq=noraman

Pointgroup= C1 Stoichiometry= C29H32CuFeN2O2(1+) C1[X(C29H32CuFeN2O2)] #Atoms= 67
Charge = 1 Multiplicity = 1

SCF Energy= -4288.29509210Predicted Change= -5.122350D-03
==========
Optimization incomplete.

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.02331 ||	0.00045	[NO]	0.00292 ||	0.00030	[NO]
Displ	0.21775 ||	0.00180	[NO]	0.21775 ||	0.00180	[NO]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-4.117888	0.900502	-1.122232
C	-5.318704	0.426736	-1.883725
H	-5.970048	1.269218	-2.156063
H	-5.920346	-0.273053	-1.294379
H	-5.035050	-0.079314	-2.811783
C	-2.852230	1.275344	-1.686051
C	-2.498400	1.239839	-3.142588
H	-2.811628	2.166671	-3.644313
H	-2.997030	0.410048	-3.654728
H	-1.423505	1.126827	-3.299312
C	-1.998646	1.700083	-0.611648
C	-0.587427	2.190515	-0.727974
H	0.014276	1.907833	0.140664
H	-0.558220	3.287366	-0.797801
H	-0.095041	1.788319	-1.615120
C	-2.740062	1.590714	0.611291
C	-2.229477	1.964356	1.968641
H	-2.778382	1.451501	2.763440
H	-2.330016	3.045093	2.140311
H	-1.171601	1.709557	2.081857
C	-4.048062	1.092668	0.297896
C	-5.172233	0.876677	1.266004
H	-5.818425	1.764167	1.320788
H	-4.805203	0.680047	2.278031
H	-5.804386	0.032681	0.972086
Fe	-2.616107	-0.223269	-0.331404
C	-1.444799	-1.630810	-1.245347
H	-0.900853	-1.507003	-2.168931
C	-0.967124	-1.362124	0.063458

C	-1.992353	-1.646159	1.025578
C	-3.134804	-2.098033	0.284180
H	-4.088425	-2.387532	0.704054
C	-2.786576	-2.102574	-1.100672
H	-3.435498	-2.390075	-1.916895
N	0.280458	-0.915534	0.507182
C	0.486648	-0.690038	1.883729
C	-0.554227	-0.968973	2.835151
H	-0.336422	-0.789159	3.882993
C	-1.769861	-1.437854	2.444161
C	-2.876784	-1.735085	3.410774
H	-3.174119	-2.790243	3.356364
H	-3.770140	-1.142634	3.175967
H	-2.577211	-1.513768	4.439311
C	1.387946	-0.645660	-0.234252
Cu	1.660725	-1.024438	-2.053692
N	2.291862	-0.219004	0.692206
C	3.593160	0.263121	0.370812
C	1.773622	-0.236171	1.979865
H	2.359276	0.064193	2.833337
C	4.625694	-0.634257	0.054419
O	4.303902	-1.949319	0.093835
C	5.329854	-2.898704	-0.197131
H	6.141544	-2.836734	0.537378
H	5.731504	-2.756821	-1.204898
H	4.852291	-3.877155	-0.132454
C	5.897271	-0.133893	-0.258171
H	6.708449	-0.802941	-0.514395
C	6.111704	1.242831	-0.226462
H	7.099166	1.626258	-0.466591
C	5.101366	2.143020	0.109028
H	5.302856	3.206449	0.128394
C	3.825769	1.647476	0.404076
O	2.753742	2.413090	0.729911
C	2.959385	3.809056	0.943187
H	3.672543	3.980011	1.758086
H	1.982947	4.209211	1.220625
H	3.310490	4.310628	0.035911

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

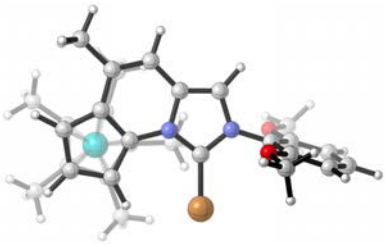
==========

SCF Energy= -4288.29509210 Predicted Change= -5.122350D-03
Zero-point correction (ZPE)= -4287.7459 0.54917
Internal Energy (U)= -4287.7138 0.58122
Enthalpy (H)= -4287.7129 0.58217
Gibbs Free Energy (G)= -4287.8066 0.48840

Frequencies -- -118.4029 -36.3333 -28.5562

M06/6-31G(d) = -4287.00066992

Minor-TS NHC-ferrocenyl-Cu(I) Model Species



Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013
==========
#b3lyp/6-31G(d) EmpiricalDispersion=GD3BJ scf=(maxcycle=300,direct,tight)
density=current SCRF=(SOLVENT=THF,SMD) freq=noraman

Pointgroup= C1 Stoichiometry= C29H32CuFeN2O2(1+) C1[X(C29H32CuFeN2O2)] #Atoms= 67
Charge = 1 Multiplicity = 1

SCF Energy= -4288.29542521Predicted Change= -5.157502D-03
==========
Optimization incomplete.

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.02438 ||	0.00045	[NO]	0.00299 ||	0.00030	[NO]
Displ	0.22335 ||	0.00180	[NO]	0.22335 ||	0.00180	[NO]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-3.976104	1.269774	-0.975858
C	-5.006708	1.145568	-2.057127
H	-5.629461	2.049163	-2.117079
H	-5.677057	0.298092	-1.881164
H	-4.542669	1.003560	-3.038126
C	-2.645676	1.782172	-1.138009
C	-2.062023	2.325178	-2.406282
H	-2.327965	3.385572	-2.527211
H	-2.442782	1.797056	-3.285971
H	-0.971637	2.260949	-2.423698
C	-1.999930	1.754192	0.142819
C	-0.596936	2.193938	0.431829
H	-0.179893	1.670997	1.296919
H	-0.554498	3.270404	0.647263
H	0.065027	2.002507	-0.415216
C	-2.939147	1.243630	1.099701
C	-2.700659	1.114018	2.572534
H	-3.338002	0.347379	3.022202
H	-2.916174	2.062751	3.083218
H	-1.662406	0.850522	2.793538
C	-4.157627	0.936067	0.408367
C	-5.416742	0.414199	1.033012
H	-6.040019	1.236939	1.410371
H	-5.205482	-0.247650	1.879225
H	-6.020397	-0.148308	0.314000
Fe	-2.606347	-0.120501	-0.391962
C	-1.423718	-1.226731	-1.656770
H	-0.863978	-0.853288	-2.500408
C	-0.962584	-1.327320	-0.318140

C	-1.994301	-1.868555	0.517117
C	-3.129427	-2.093546	-0.331868
H	-4.087476	-2.485223	-0.017948
C	-2.769135	-1.713895	-1.660814
H	-3.412685	-1.763867	-2.529209
N	0.275107	-1.009608	0.243387
C	0.471911	-1.173168	1.629392
C	-0.570912	-1.719739	2.454781
H	-0.359566	-1.843263	3.512055
C	-1.780452	-2.068545	1.938751
C	-2.890033	-2.635886	2.771848
H	-2.604404	-2.700260	3.825838
H	-3.166541	-3.640870	2.427802
H	-3.792218	-2.015525	2.695262
C	1.375792	-0.519420	-0.384707
Cu	1.644726	-0.340387	-2.237273
N	2.268891	-0.353014	0.630272
C	3.590991	0.143466	0.444981
C	1.750512	-0.741520	1.857296
H	2.331417	-0.688701	2.763649
C	4.579509	-0.705695	-0.078325
O	4.188988	-1.975216	-0.331961
C	5.125910	-2.859318	-0.954275
H	6.032815	-2.962050	-0.346991
H	5.368512	-2.517221	-1.964174
H	4.618869	-3.821659	-1.013616
C	5.875356	-0.208854	-0.275082
H	6.650159	-0.834797	-0.698558
C	6.159449	1.104602	0.093993
H	7.167312	1.484090	-0.048393
C	5.192468	1.948423	0.639526
H	5.448694	2.962718	0.916696
C	3.887534	1.467808	0.797955
O	2.846583	2.197855	1.279080
C	3.114043	3.521789	1.738679
H	2.152435	3.919753	2.066071
H	3.513055	4.154277	0.938731
H	3.814270	3.511663	2.582342

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

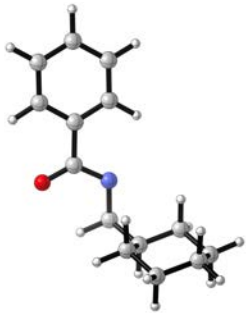
==========

SCF Energy= -4288.29542521 Predicted Change= -5.157502D-03
Zero-point correction (ZPE)= -4287.7456 0.54974
Internal Energy (U)= -4287.7130 0.58235
Enthalpy (H)= -4287.7121 0.58329
Gibbs Free Energy (G)= -4287.8067 0.48868

Frequencies -- -31.2483 -23.9407 -20.9541

M06/6-31G(d) = -4287.00017185

Major-TS Imine Model Species



Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013
==========
#b3lyp/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(SOLVENT=THF,SMD) freq=noraman

Pointgroup= C1 Stoichiometry= C14H17NO C1[X(C14H17NO)] #Atoms= 33
Charge = 0 Multiplicity = 1

SCF Energy= -673.666690519Predicted Change= -4.425231D-02
==========
Optimization incomplete.

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.14596	0.00045	[NO]	0.02131	0.00030	[NO]
Displ	0.24416	0.00180	[NO]	0.24416	0.00180	[NO]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	-0.033987	-0.396588	-0.828932
C	-1.082381	-1.066557	-0.293291
C	-2.306046	-0.214584	-0.045905
C	1.099453	-1.181804	-1.252761
H	0.963520	-2.244021	-1.032850
C	2.419925	-0.642871	-0.691581
H	3.239004	-1.250434	-1.095911
O	-1.122659	-2.281283	-0.007196
C	2.437442	-0.797231	0.839507
H	2.276535	-1.849121	1.110306
H	1.595787	-0.231120	1.259558
C	3.753455	-0.287680	1.440288
H	4.582202	-0.918879	1.086170
H	3.731988	-0.383094	2.533738
C	4.024979	1.168268	1.039689
H	4.989385	1.502184	1.444627
H	3.253530	1.812779	1.486475
C	3.996839	1.337289	-0.484771
H	4.837910	0.782199	-0.926536
H	4.144296	2.392106	-0.753507
C	2.684616	0.817674	-1.082753
H	2.710363	0.907425	-2.173690
H	1.848061	1.430423	-0.725484
C	-2.331173	1.163155	-0.303919
H	-1.429165	1.644998	-0.663256
C	-3.500474	1.898236	-0.113108
H	-3.507680	2.965016	-0.322416

C	-4.661844	1.266844	0.342149
H	-5.574573	1.839345	0.485502
C	-4.641852	-0.103413	0.612788
H	-5.540084	-0.601433	0.969134
C	-3.470386	-0.835623	0.420810
H	-3.437211	-1.902208	0.615381

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

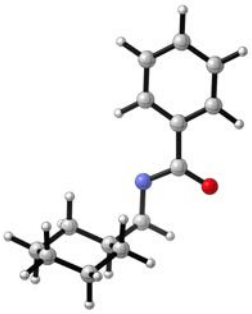
==========

SCF Energy= -673.666690519 Predicted Change= -4.425231D-02
Zero-point correction (ZPE)= -673.3846 0.28205
Internal Energy (U)= -673.3714 0.29525
Enthalpy (H)= -673.3704 0.29620
Gibbs Free Energy (G)= -673.4266 0.24000

Frequencies -- -44.3537 7.8067 45.6669

D3BJ(B3LYP) = -0.06388735
M06/6-31G(d) = -673.173335874

Minor-TS Imine Model Species



Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

#b3lyp/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(SOLVENT=THF,SMD) freq=noraman

Pointgroup= C1 Stoichiometry= C14H17NO C1[X(C14H17NO)] #Atoms= 33
Charge = 0 Multiplicity = 1

SCF Energy= -673.665080659Predicted Change= -4.431780D-02

==========

Optimization incomplete.

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.13594	0.00045	[NO]	0.02133	0.00030	[NO]
Displ	0.21135	0.00180	[NO]	0.21135	0.00180	[NO]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	0.038838	-0.411789	-0.929780
C	1.074799	-1.090787	-0.381432
C	2.292427	-0.236152	-0.107929
C	-1.124882	-1.175097	-1.310740
C	-2.413515	-0.610777	-0.702462
H	-3.262663	-1.176726	-1.106148
H	-1.007341	-2.237604	-1.082230
C	3.387117	-0.815645	0.545550
H	3.314067	-1.858350	0.836261
C	4.537615	-0.071829	0.809899
H	5.378896	-0.536530	1.318064
C	4.607727	1.268617	0.422888
H	5.503888	1.849987	0.623661
C	3.516454	1.859068	-0.221258
H	3.560526	2.902804	-0.522260
C	2.366258	1.114473	-0.479454
H	1.517790	1.573602	-0.973275
O	1.096370	-2.299412	-0.065568
C	-2.406362	-0.817245	0.822400
H	-1.546535	-0.281160	1.245750
H	-2.262076	-1.880522	1.055060
C	-3.704719	-0.305373	1.460465
H	-3.667727	-0.434766	2.550021
H	-4.546948	-0.914781	1.099846
C	-3.964121	1.165589	1.109075
H	-3.181575	1.787391	1.568026
H	-4.920710	1.495851	1.534792
C	-3.949044	1.385250	-0.409317
H	-4.083150	2.450563	-0.639990
H	-4.800811	0.856245	-0.862389
C	-2.647292	0.868149	-1.031817
H	-1.801493	1.454003	-0.650498
H	-2.671741	0.998363	-2.116904

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -673.665080659 Predicted Change= -4.431780D-02
Zero-point correction (ZPE)= -673.3830 0.28202
Internal Energy (U)= -673.3698 0.29522
Enthalpy (H)= -673.3689 0.29617
Gibbs Free Energy (G)= -673.4254 0.23960

Frequencies -- -45.2210 5.4790 44.4050

D3BJ(B3LYP) = -0.06396186
M06/6-31G(d) = -673.171853697

References

(1) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518–1520.
(2) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*; 3rd ed.; Pergamon Press: Oxford, 1988.
(3) Murry, J. A.; Frantz, D. E.; Soheili, A.; Tillyer, R.; Grabowski, E. J.; Reider, P. J. *J. Am. Chem. Soc.* **2001**, *123*, 9696-9697.
(4) Cowen, B. J.; Saunders, L. B.; Miller, S. J. *J. Am. Chem. Soc.* **2009**, *131*, 6105-6107.
(5) Check, C. T.; Jang, K. P.; Schwamb, C. B.; Wong, A. S.; Wang, M. H.; Scheidt, K. A. *Angew. Chem. Int. Ed.* **2015**, *54*, 4264–4268.
(6) Ohmura, T.; Awano, T.; Suginome, M. *J. Am. Chem. Soc.* **2010**, *132*, 13191-13193.
(7) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648-5652.
(8) Grimme, S.; Ehrlich, S.; Goerigk, L. *J. Comput. Chem.* **2011**, *32*, 1456-1465.
(9) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257-2261.
(10) Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. B* **2009**, *113*, 6378-6396.
(11) Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215-241.
(12) CYLview, 1.0b; Legault, C. Y., Université de Sherbrooke, 2009 (http://www.cylview.org)
(13) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, *132*, 154104.
(14) Kubota, K.; Jin, M.; Ito, H. *Organometallics* **2016**, *35*, 1376–1383.
(15) Matthias, B. F.; N., H. K. *Angew. Chem. Int. Ed.* **2017**, *56*, 10070-10086.