Diastereoselective Hydrogenation of Imines Using $B(C_6F_5)_3$

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Supporting Information

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1) Synthetic and Experimental Procedures

All preparations and manipulations were performed on a double manifold N_2/vacuum line with Schlenk-type glassware or in a N_2-filled VAC glove box. Solvents (Aldrich) were dried using an Innovative Technologies solvent system, and degassed before use. NMR spectra were obtained on a Bruker Avance 400 MHz spectrometer and spectra were referenced to residual solvent (^{1}H, ^{13}C) or externally (^{11}B; $BF_3{\cdot}OEt_2$, ^{19}F; $CFCl_3$, ^{31}P; 85% H_3PO_4). Chemical shifts are reported in ppm. NMR solvents were purchased from Cambridge Isotopes, dried over CaH_2, vacuum distilled prior to use and stored over 4Å molecular sieves in the glovebox. $B(C_6F_5)_3$ was generously provided by Nova Chemicals (from Boulder Scientific Company).

N-(1-(*S*)-phenylethyl)-1-phenylethanimine (3). A 125 mL toluene solution of 10 ml (85 mmol) acetophenone and 11 ml (86 mmol) (*S*)-α-methylbenzylamine in the presence of 15 mL of 4Å molecular sieves was refluxed in a Dean-Stark apparatus. The water was removed and the toluene solution was reduced down to 50 mL by distillation. The reaction mixture was then filtered and the solvent was removed under reduced pressure. The resulting yellowish-brown colored liquid was distilled twice under vacuum resulting in a colorless liquid. The imine was found to be stable to the air (with no signs of degradation) over the course of a week, and was stored for extended periods of time under a nitrogen atmosphere in a glovebox. Yield 8.83 g (46.5 %). ^{1}H NMR (400 MHz, C_6D_6) δ 1.51 (d, 3H, $^3J_{HH}$ = 6.5 Hz, PhCH*Me*N=C(Me)Ph), 1.78 (s, 3H, PhCHMeN=C(*Me*)Ph), 4.64 (q, 1H, $^3J_{HH}$ = 6.5 Hz, PhC*H*MeN=C(Me)Ph), 7.07-7.92 (m, 10H, phenyl protons) . ^{13}C NMR (100 MHz, C_6D_6) δ 15.10, 26.06, 60.51, 127.18, 127.42, 127.58, 128.62, 129.05, 129.98, 141.88, 147.31, 162.77. Anal. Calc. $C_{16}H_{17}N$: C 86.05, H 7.67 , N 6.27; Found: C 85.99, H 8.40, N 6.30. Spectroscopic data was found to match with the data previously reported.[1]

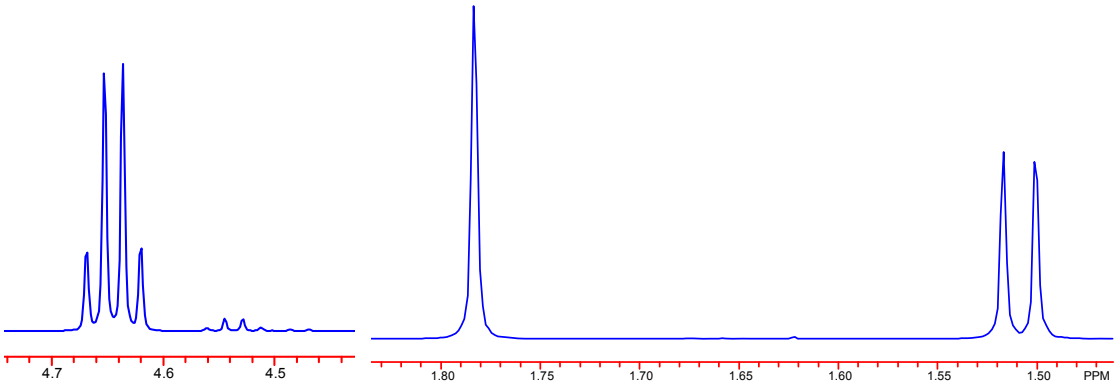


Figure S1. ^{1}H NMR spectrum (left) benzylic region and (right) aliphatic region of imine **3** in C_6D_6.

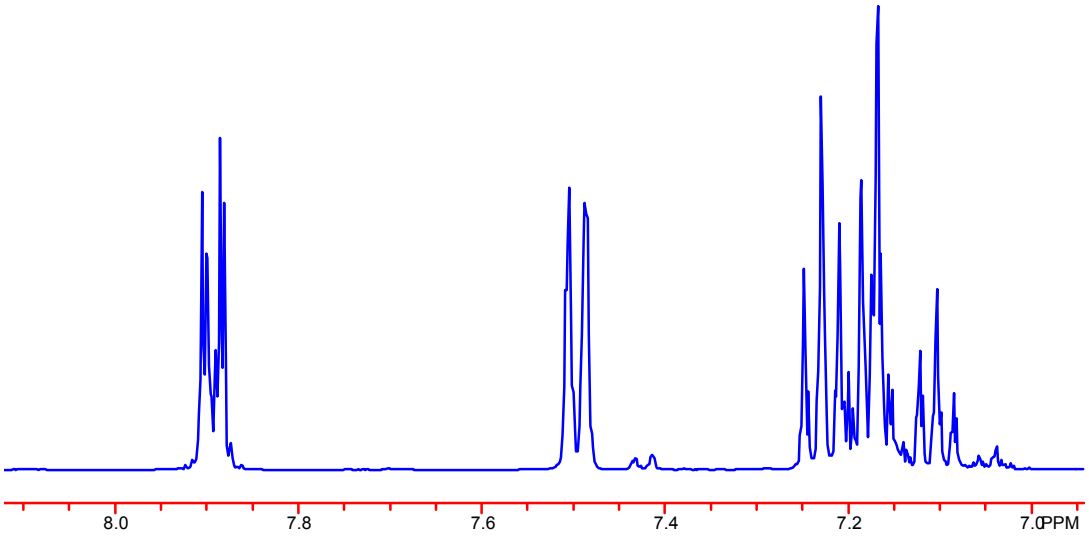


Figure S2. ^{1}H NMR spectrum of the phenyl region of imine **3** in C_6D_6.

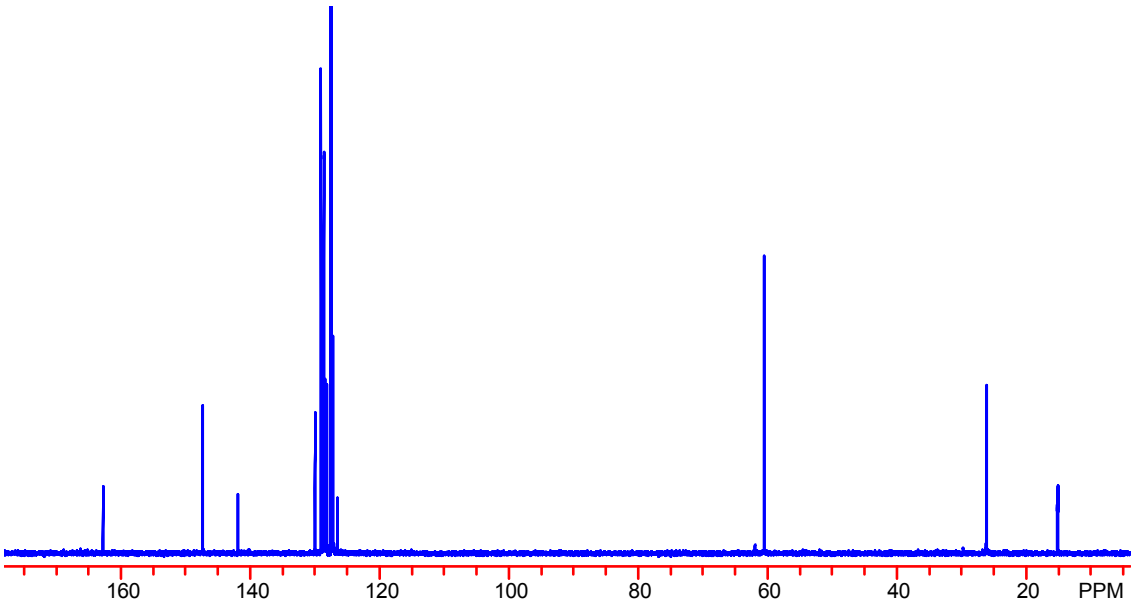


Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum of imine **3** in C_6D_6.

N-(1-(*S*)-cyclohexylethyl)-1-phenylethanimine (2). A similar procedure to the synthesis of N-(1-(*S*)-phenylethyl)-1-phenylethanimine was used where (*S*)-α-methylbenzylamine was replaced with 1-(*S*)-cyclohexylethyl amine. Yield 5.16 g (63 %). ^{1}H NMR (400 MHz, C_6D_6) δ 0.92-1.33 (m, 5H , cyclohexyl protons), 1.10 (d, 3H, J=6.7 Hz, $C_6H_{11}CH$*Me*N=C(Me)Ph), 1.48-1.91 (m, 6H , cyclohexyl protons), 1.85 (s, 3H, $C_6H_{11}CHMeN=C($*Me*$)Ph$), 3.31 (q, 1H, J=6.3 Hz, $C_6H_{11}C$*H*$MeN=C(Me)Ph$), 7.14-7.22 (m, 3H, phenyl protons), 7.84-7.90 (m, 2H, phenyl protons). ^{13}C NMR (100 MHz, C_6D_6) δ 14.53, 19.16, 27.32, 27.36, 27.56, 30.36, 30.63, 45.53, 61.30, 127.47, 128.53, 129.67, 142.20, 160.95. Anal. Calc. $C_{14}H_{13}N$: C 83.79, H 10.11 , N 6.11; Found: C 83.80, H 10.72, N 6.14. Spectroscopic data was found to match with the data previously reported.[1]

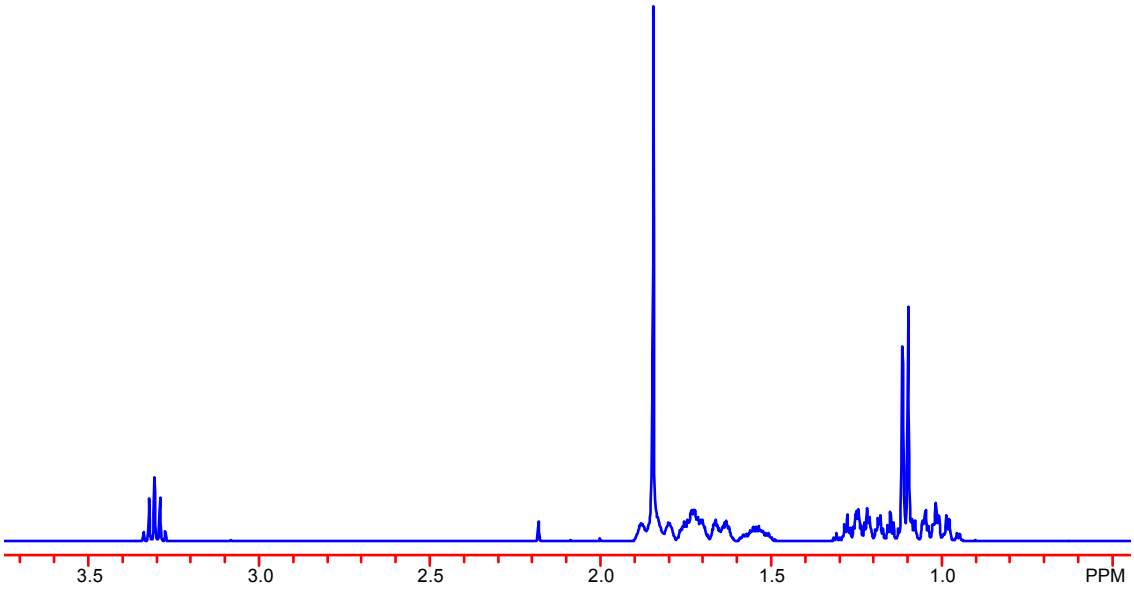


Figure S4. ^{1}H NMR spectrum of the aliphatic and benzylic region of imine **2** in C_6D_6.

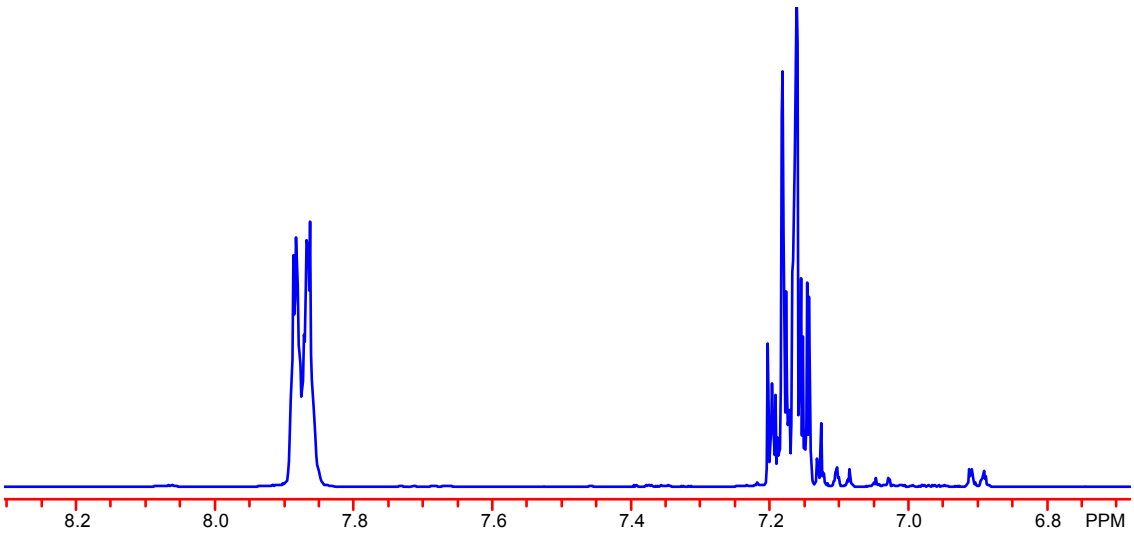


Figure S5. ^{1}H NMR spectrum of the phenyl region of imine **2** in C_6D_6.

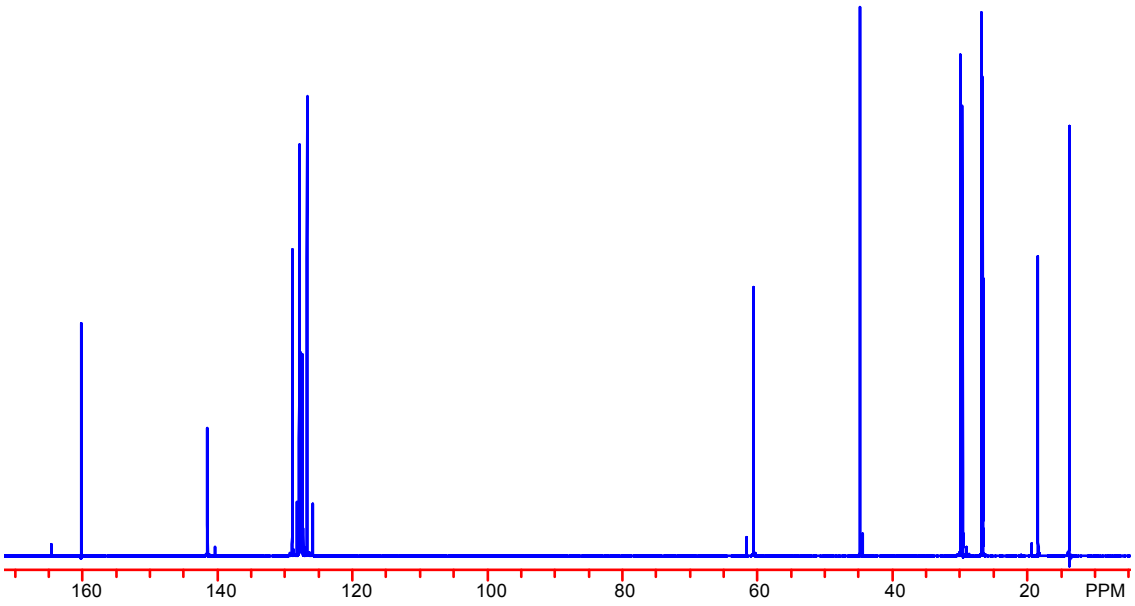


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of imine **2** in C_6D_6.

N-(2,2-(*S*)-dimethyl-1-butyl)-1-phenylethanimine (1). A similar procedure to the synthesis of N-(1-(*S*)-phenylethyl)-1-phenylethanimine was used where (*S*)-α-methylbenzylamine was replaced with 2,2-(*S*)-dimethyl-1-butylamine. Yield 5.18 g (60 %). ^{1}H NMR (400 MHz, C_6D_6) δ 0.95 (d, $^{3}J_{HH}$ = 6.6 Hz, 3H, $Me_3CCHMeN=C(Me)Ph$), 0.97 (s, $Me_3CCHMeN=C(Me)Ph$), 1.79 (s, 3H, $Me_3CCHMeN=C(Me)Ph$), 3.20 (q, $^{3}J_{HH}$ = 6.6 Hz, 1H, $Me_3CCHMeN=C(Me)Ph$), 7.05-7.85 (5H, phenyl protons) . ^{13}C NMR (100 MHz, C_6D_6) δ 14.24, 16.35, 27.15, 35.43, 64.83, 127.42, 128.56, 129.66, 142.21, 160.83. Spectroscopic data was found to match with the data previously reported.[2]

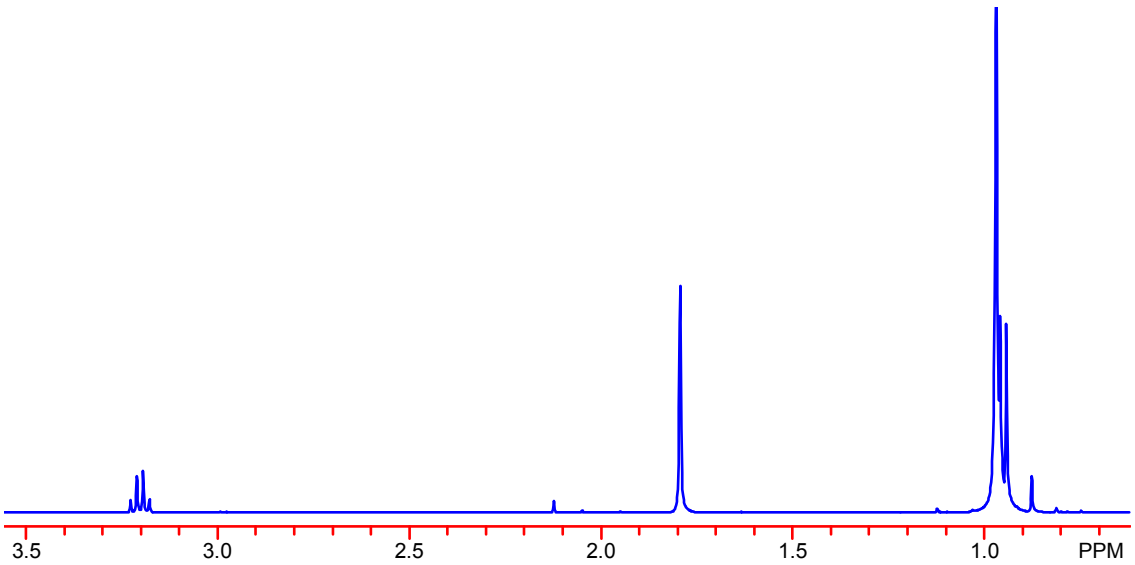


Figure S7. ^{1}H NMR spectrum of the aliphatic and benzylic region of imine **1** in C_6D_6.

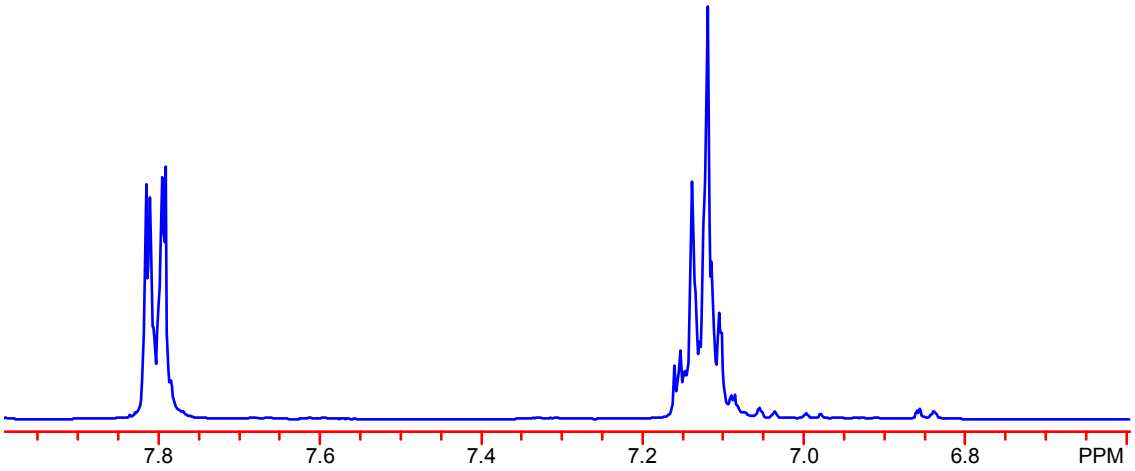


Figure S8. ^{1}H NMR spectrum of the phenyl region of imine **1** in C_6D_6.

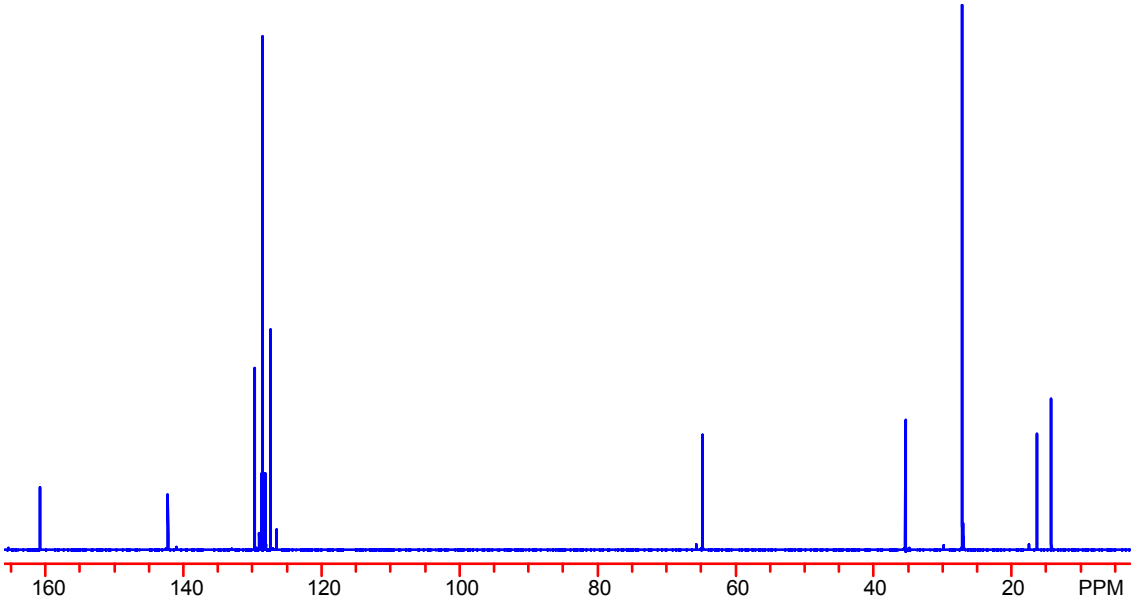


Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum of imine **1** in C_6D_6.

N-(1-(*S*)-phenylethyl)-propiophenonimine (4). A similar procedure to the synthesis of N-(1-(*S*)-phenylethyl)-1-phenylethanimine was used where acetophenone was replaced with propiophenone. A 3:2 E:Z isomer ratio was found to result from the described procedure. Yield 12.13 g (68 %). ^{1}H NMR (400 MHz, C_6D_6) δ 0.75 (t, $^{3}J_{HH}$ = 7.9 Hz, 3H, PhCHMeN=C(CH_2CH_3)Ph, E-isomer), 1.12 (t, $^{3}J_{HH}$ = 7.9 Hz, 3H, PhCHMeN=C(CH_2CH_3)Ph, Z-isomer), 1.38 (d, $^{3}J_{HH}$ = 6.6 Hz, 3H, PhCH*Me*N=C(CH_2CH_3)Ph, Z-isomer), 1.49 (d, $^{3}J_{HH}$ = 6.6 Hz, 3H, PhCH*Me*N=C(CH_2CH_3)Ph, E-isomer), 2.41 (m, 2H, PhCHMeN=C(CH_2CH_3)Ph, E and Z-isomer), 4.51 (q, $^{3}J_{HH}$ = 6.1 Hz, 1H, PhC*H*MeN=C(CH_2CH_3)Ph, Z-isomer), 4.72 (q, $^{3}J_{HH}$ = 6.4 Hz, 1H, PhC*H*MeN=C(CH_2CH_3)Ph, E-isomer), 6.70-7.95 (20H, phenyl protons) . ^{13}C NMR (100 MHz, C_6D_6) δ 11.11, 12.61, 21.83, 26.41, 26.54, 36.69, 60.08, 61.56, 61.60, 126.84, 127.15, 127.26, 127.35, 127.42, 127.95, 128.78, 128.97, 129.02, 129.09,

129.96, 140.14, 140.19, 140.50, 140.53, 147.52, 147.54, 147.57, 167.34, 170.34. Spectroscopic data was found to match with the data previously reported.[3,4]

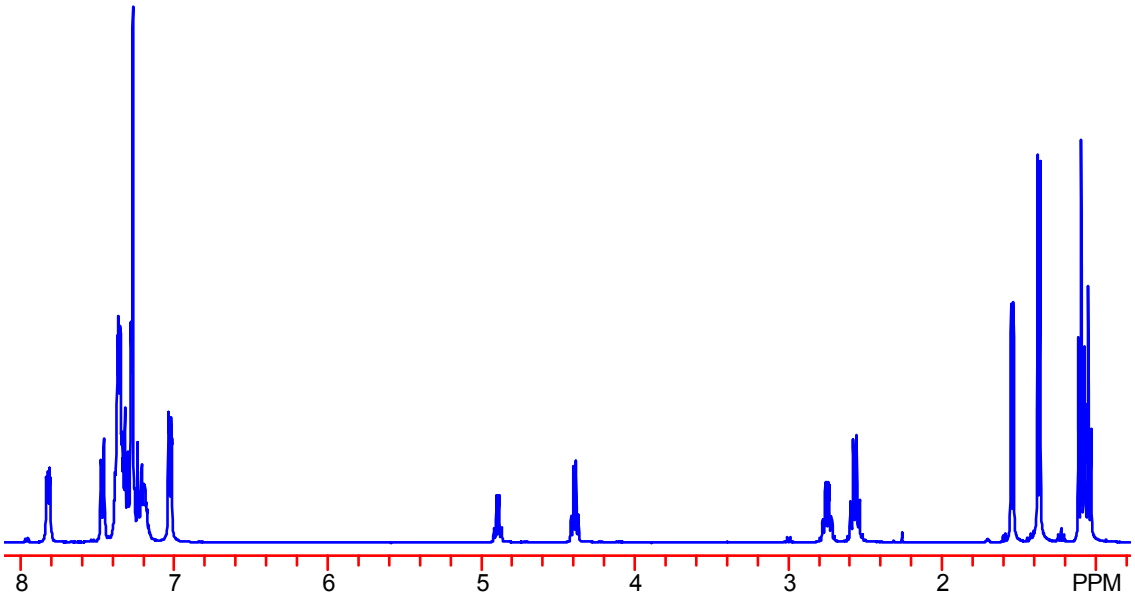


Figure S10. ^{1}H NMR spectrum of imine **4** in $CDCl_3$.

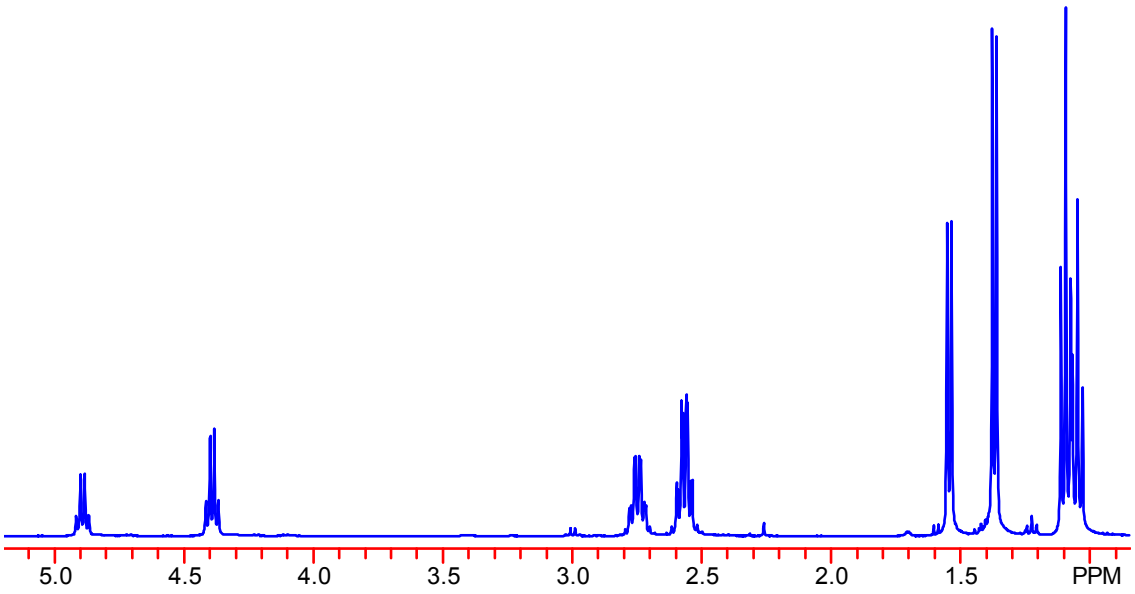


Figure S11. ^{1}H NMR spectrum of aliphatic and benzylic region of imine **4** in $CDCl_3$.

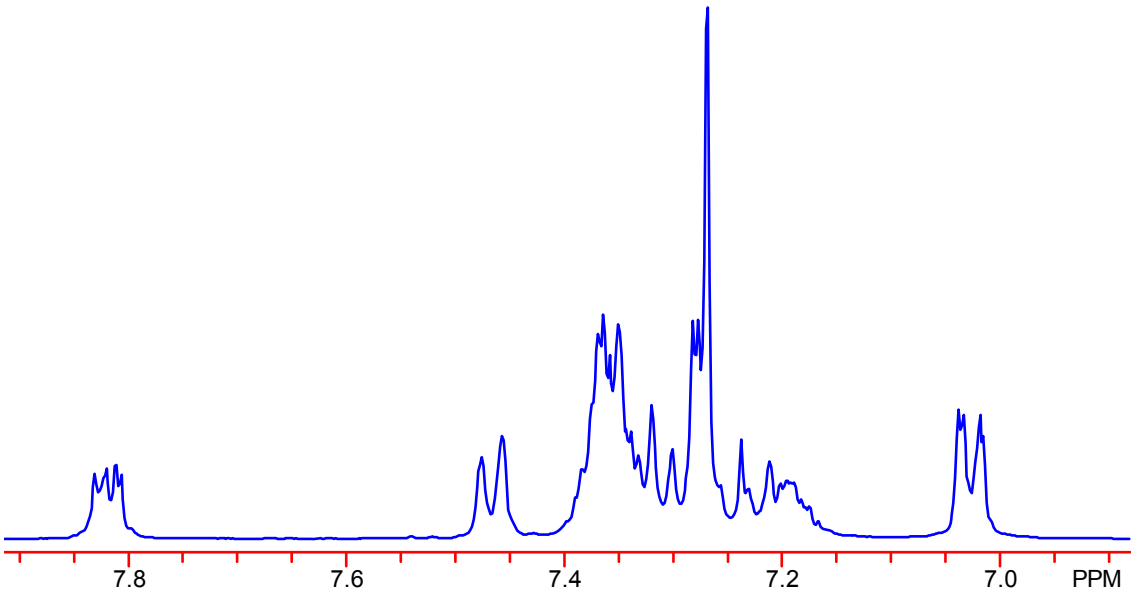


Figure S12. ^{1}H NMR spectrum of the phenyl region of imine **4** in $CDCl_3$.

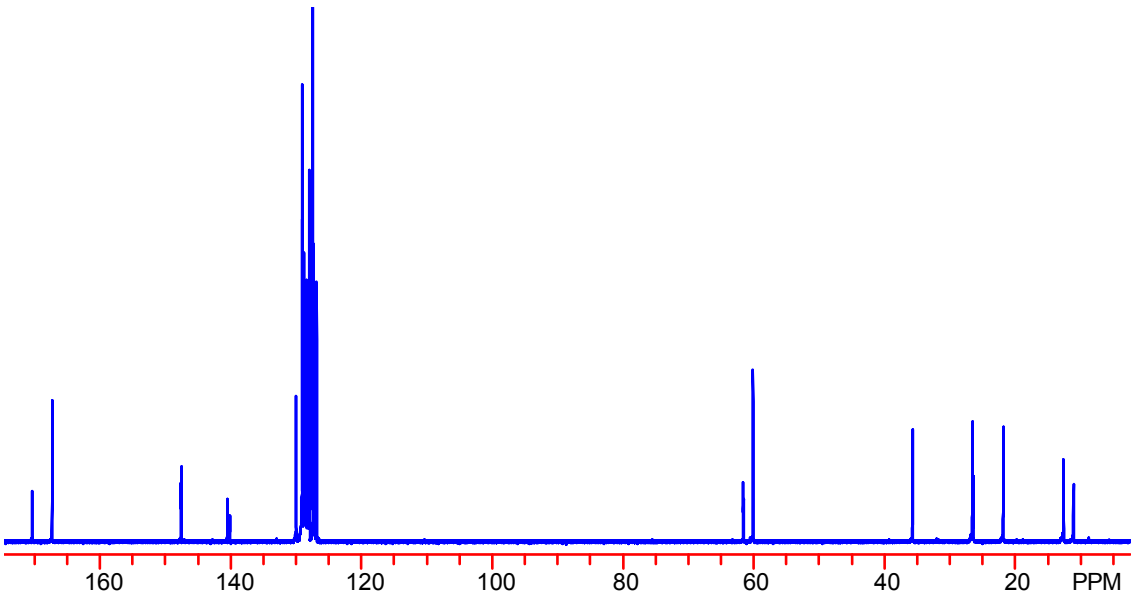


Figure S13. $^{13}C\{^{1}H\}$ NMR spectrum of imine **4** in C_6D_6.

N-(1-(*S*)-phenylethyl)-isobutyrophenonimine (5). A similar procedure to the synthesis of N-(1-(*S*)-phenylethyl)-1-phenylethanimine was used where acetophenone was replaced with isobutyrophenone. The imine was found to be moderately moisture sensitive and slowly hydrolyzed in air. Yield 4.50 g (34 %). ^{1}H NMR (400 MHz, C_6D_6) δ ^{1}H NMR (400 MHz, C_6D_6) δ 1.10 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, PhCHMeN=C(CHC*H*$_3$CH$_3$)Ph), 1.18 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, PhCHMeN=C(CHCH$_3$*CH*$_3$)Ph), 1.39 (d, $^{3}J_{HH}$ = 6.4 Hz, 3H, PhCH*Me*N=C(CHCH$_3$CH$_3$)Ph), 2.68 (septet, $^{3}J_{HH}$ = 6.8 Hz, 1H, PhCHMeN=C(C*H*CH$_3$CH$_3$)Ph), 4.47 (q, $^{3}J_{HH}$ = 6.4 Hz, 1H,

PhC*H*MeN=C(CHCH$_3$CH$_3$)Ph), 6.78-7.44 (10H, phenyl protons). ^{13}C NMR (100 MHz, C_6D_6) δ 20.59, 20.70, 26.33, 39.58, 61.37, 127.06, 127.25, 128.23, 128.79, 128.95, 139.55, 147.63, 173.82. Spectroscopic data was found to match with the data previously reported.[5]

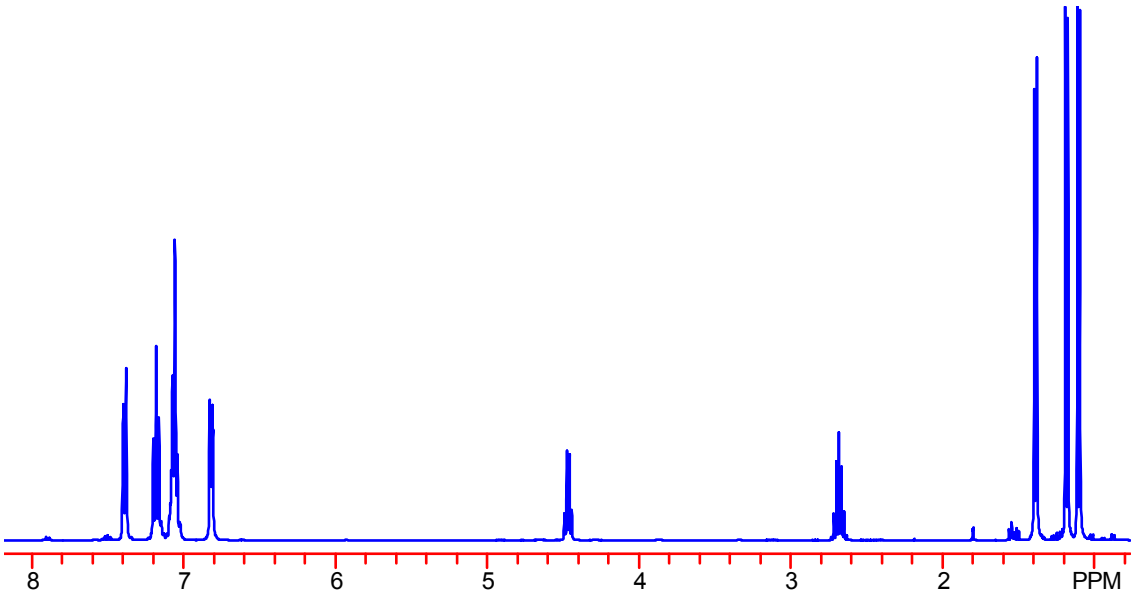


Figure S14. ^{1}H NMR spectrum of imine **5** in $CDCl_3$.

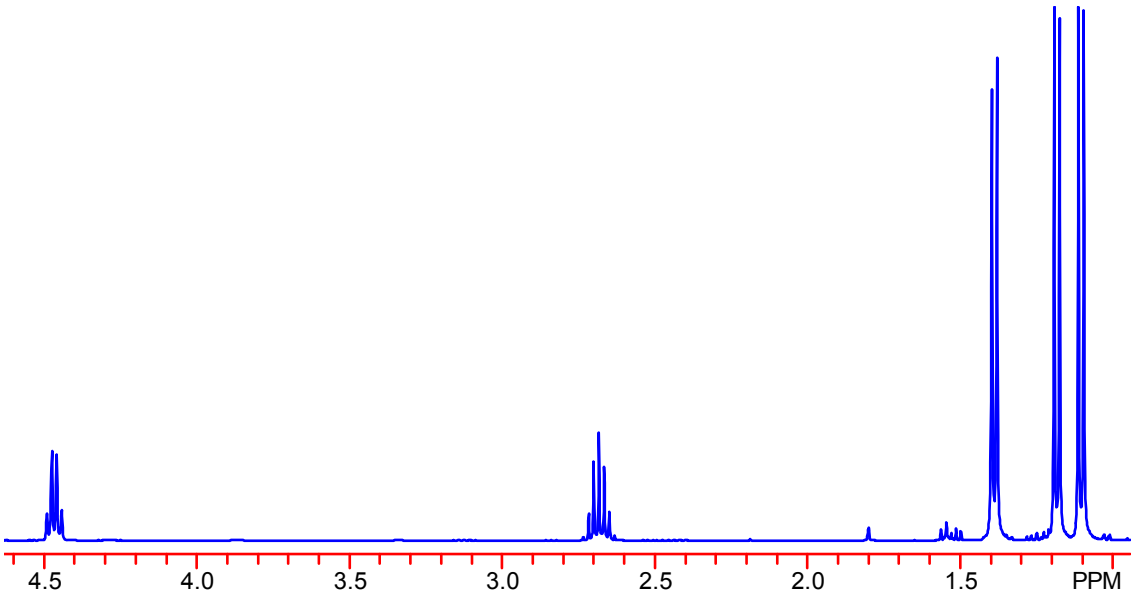


Figure S15. ^{1}H NMR spectrum of aliphatic and benzylic region of imine **5** in $CDCl_3$.

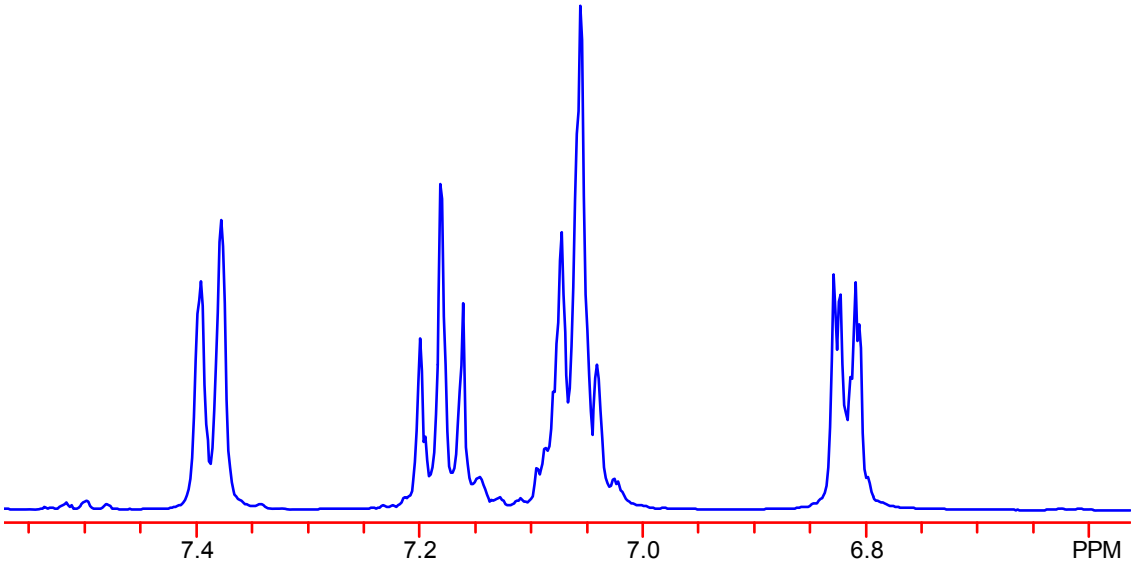


Figure S16. ^{1}H NMR spectrum of the phenyl region of imine **5** in $CDCl_3$.

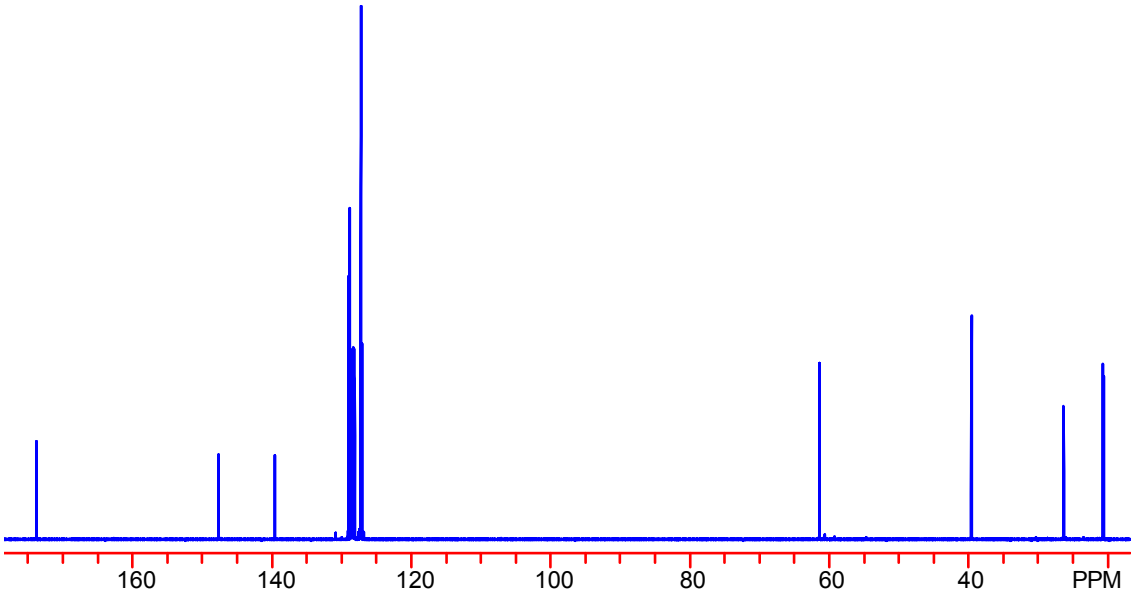


Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum of imine **5** in C_6D_6.

N-(1-(*S*)-phenylpropyl)-propiophenonimine (6). A similar procedure to the synthesis of N-(1-(*S*)-phenylethyl)-1-phenylethanimine was used where acetophenone was replaced with propiophenone and (S)-methylbenzylamine was replaced with (S)-ethylbenzylamine. A 8:7 E:Z isomer ratio was found to result from the described procedure. Yield 4.43 g (51 %). ^{1}H NMR (400 MHz, C_6D_6) δ 0.75 (t, $^{3}J_{HH}$ = 7.5 Hz, 6H, PhCH(CH_2CH_3)N=C(CH_2CH_3)Ph, E and Z-isomers), 0.87 (t, $^{3}J_{HH}$ = 7.2 Hz, 3H, PhCH(CH_2CH_3)N=C(CH_2CH_3)Ph, E-isomer), 1.68-2.05 (m, 4H, PhCH(CH_2CH_3)N=C(CH_2CH_3)Ph, E and Z-isomers), 2.33-2.55 (m, 4H, PhCH(CH_2CH_3)N=C(CH_2CH_3)Ph, E and Z-isomers), 4.24 (dd, $^{3}J_{HH}$ = 6.5, 6.8 Hz, 1H,

PhC*H*(CH_2CH_3)N=C(CH_2CH_3)Ph, Z-isomer), 4.49 (dd, $^3J_{HH}$ = 6.5, 6.8 Hz, 1H, PhC*H*(CH_2CH_3)N=C(CH_2CH_3)Ph, E-isomer), 6.74-7.92 (20H, phenyl protons). ^{13}C NMR (100 MHz, C_6D_6) δ 11.18, 11.56, 11.72, 12.41, 22.08, 33.53, 33.88, 35.69, 66.68, 68.12, 127.01, 127.18, 127.28, 127.86, 127.92, 128.32, 128.77, 128.88, 128.94, 128.98, 129.93, 140.42, 140.58, 146.30, 146.49, 168.06, 171.00. Spectroscopic data was found to match with the data previously reported.[6]

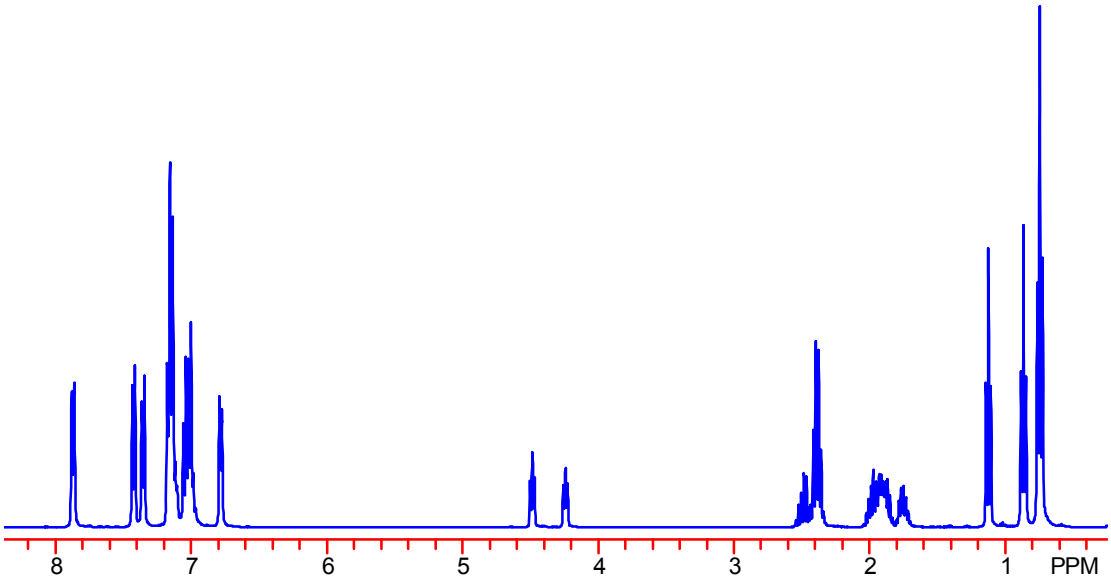


Figure S18. ^{1}H NMR spectrum of imine **6** in $CDCl_3$.

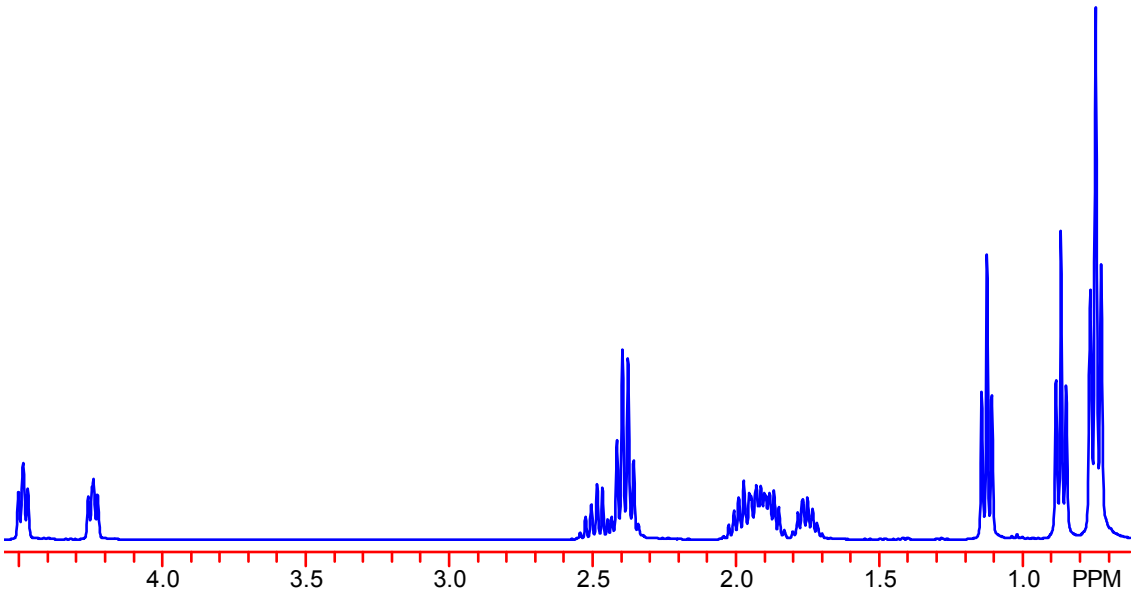


Figure S19. ^{1}H NMR spectrum of aliphatic and benzylic region of imine **6** in $CDCl_3$.

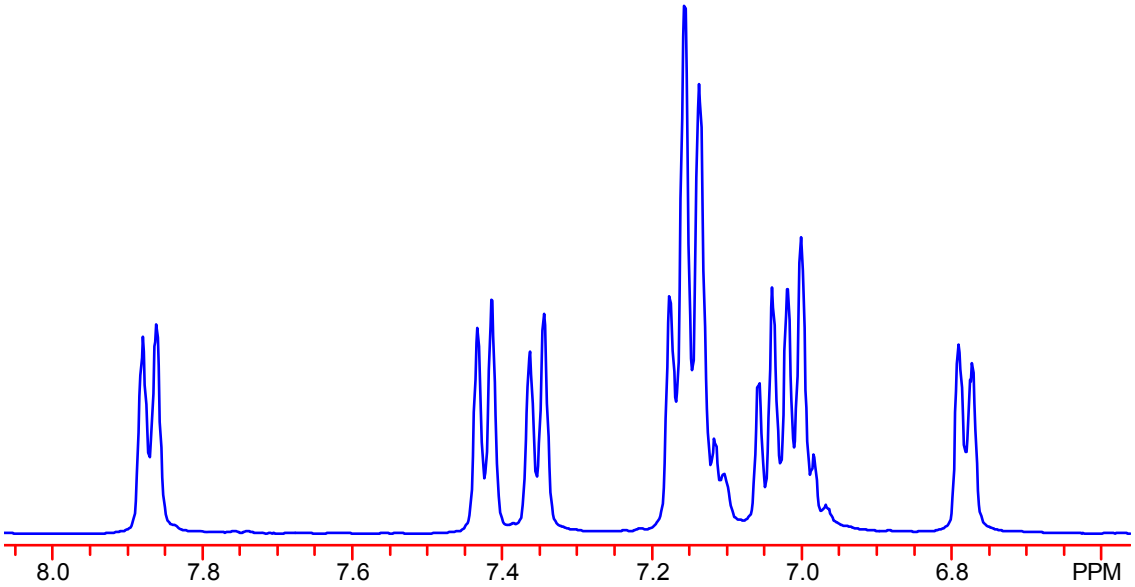


Figure S20. ^{1}H NMR spectrum of the phenyl region of imine **6** in $CDCl_3$.

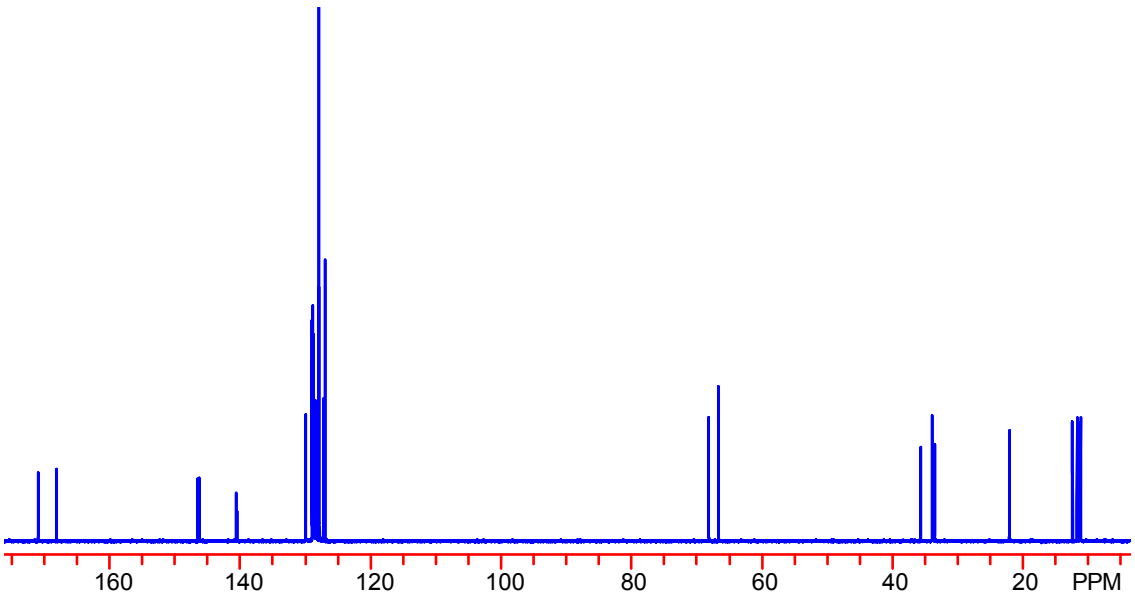


Figure S21. $^{13}C\{^{1}H\}$ NMR spectrum of imine **6** in C_6D_6.

N-(benzyl)-(D)-camphorimine (7). A similar procedure to the synthesis of N-(1-(*S*)-phenylethyl)-1-phenylethanimine was used where (*S*)-α-methylbenzylamine was replaced with benzylamine and acetophenone with (D)-(+)-camphor. Yield 7.54 g (56 %). ^{1}H NMR (400 MHz, C_6D_6) δ 0.66 (s, 3H), 0.78 (s, 3H), 0.99 (m, 1H), 1.14 (s, 3H), 1.36 (m, 1H), 1.60 (m, 4H), 2.09 (dt, 1H, J= 3.7, 16.7 Hz), 4.34 (m, 2H), 7.11 (t, 1H, J=7.4 Hz), 7.24 (t, 2H, J=8.4 Hz), 7.44 (d, 2H, J=7.4 Hz). ^{13}C NMR (100 MHz, C_6D_6) δ 12.21, 19.49, 20.13, 28.14, 32.91, 35.96, 44.66, 47.46, 54.40, 56.12, 126.86, 128.24, 128.81, 141.99, 181.53. Anal. Calc. $C_{25}H_{23}N$: C 84.59, H 9.60 , N 5.80; Found: C

84.42, H 10.02, N 5.87. Spectroscopic data was found to match with the data previously reported by Page and coworkers.[7]

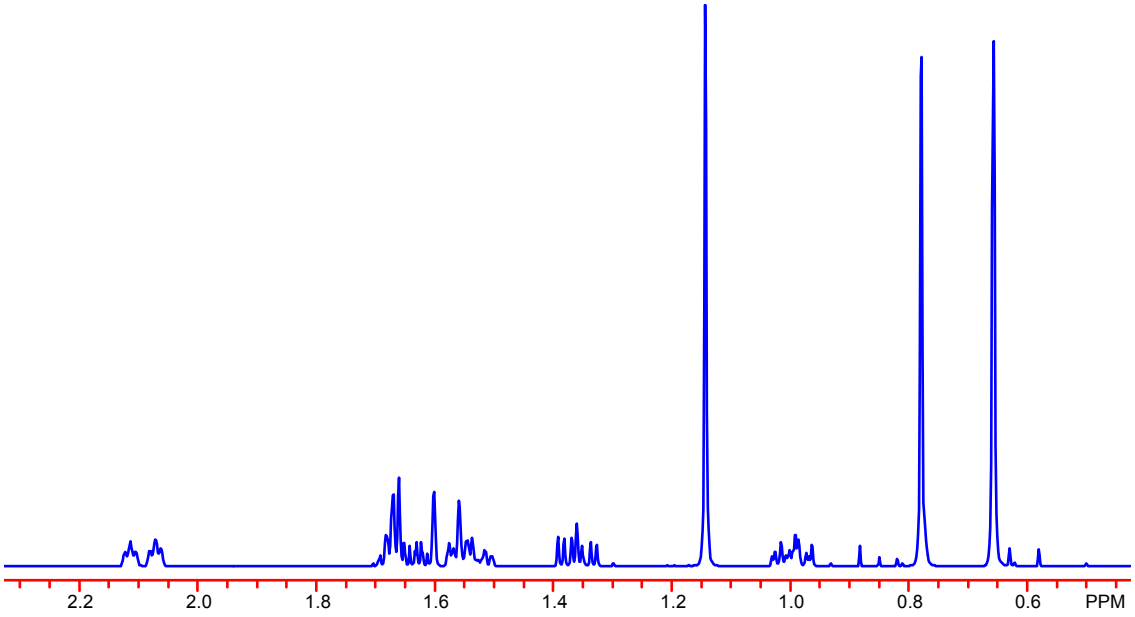


Figure S22. ^{1}H NMR spectrum of the aliphatic region of imine **7** in C_6D_6.

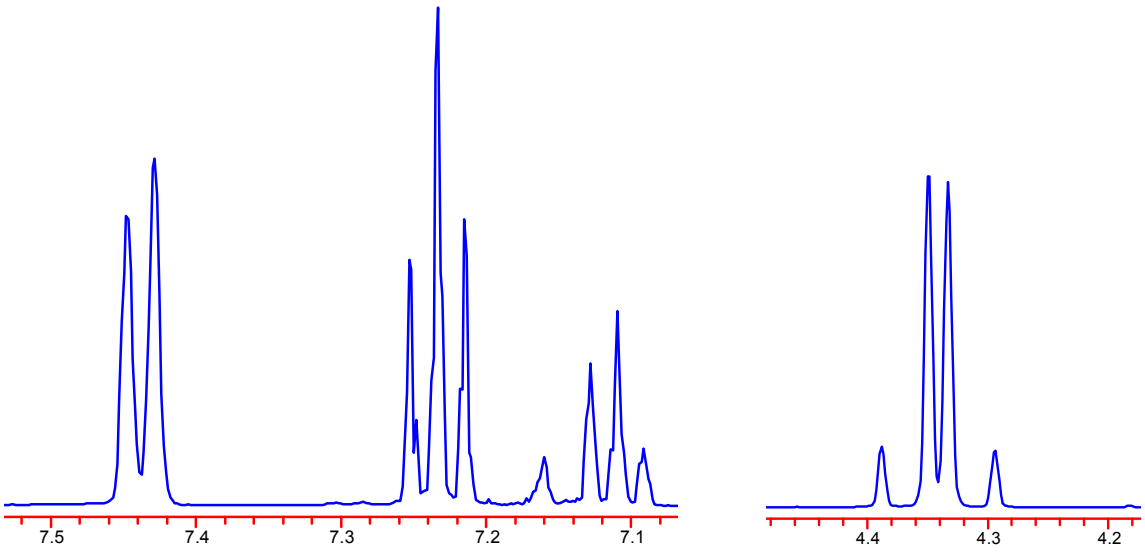


Figure S23. ^{1}H NMR spectrum of the (left) phenyl region and (right) benzylic region of imine **7** in C_6D_6.

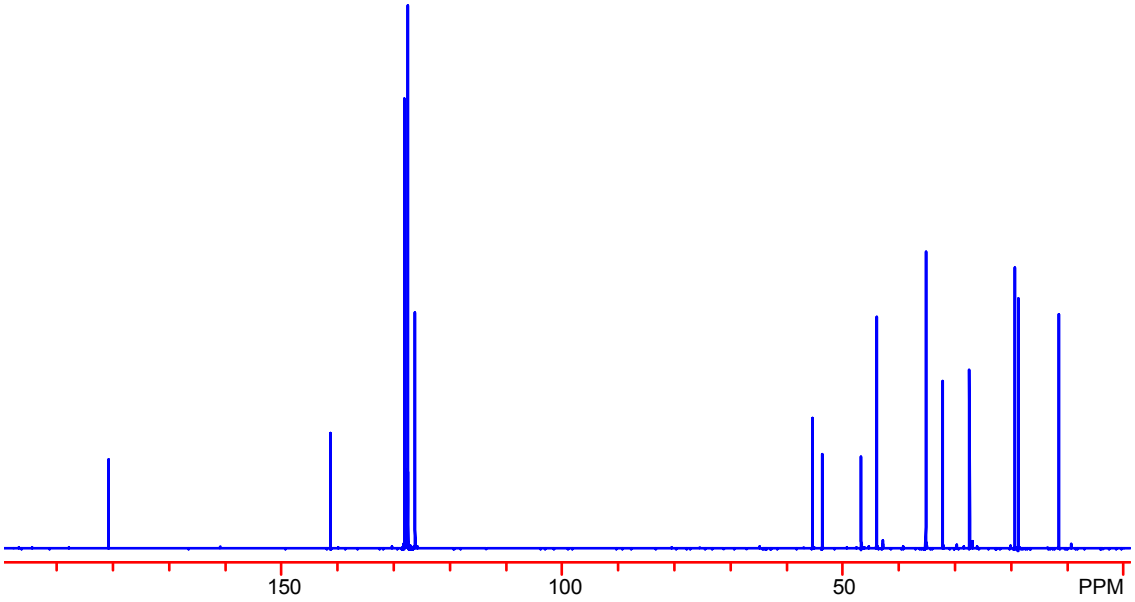


Figure S24. $^{13}C\{^{1}H\}$ NMR spectrum of imine **7** in C_6D_6.

N-(phenyl)-(D)-camphorimine (8). A similar procedure to the synthesis of N-(1-(*S*)-phenylethyl)-1-phenylethanimine was used where (*S*)-α-methylbenzylamine was replaced with aniline and acetophenone with (D)-(+)-camphor. Yield 7.23 g (48 %). ^{1}H NMR (400 MHz, C_6D_6) δ 0.72 (s, 3H,), 0.75 (s, 3H), 0.98 (m, 1H), 1.16 (s, 3H), 1.40-2.08 (m, 6H), 6.27-7.20 (m, 5H, phenyl protons). ^{13}C (100 MHz, C_6D_6) δ 12.00, 19.44, 20.04, 28.05, 32.77, 36.47, 44.49, 47.40, 54.47, 120.06, 123.46, 129.59, 153.48, 183.20. Anal. Calc. $C_{16}H_{21}N$: C 84.53, H 9.31 , N 6.16; Found: C 84.16, H 10.00, N 6.12. Spectroscopic data was found to match with the data previously reported.[8]

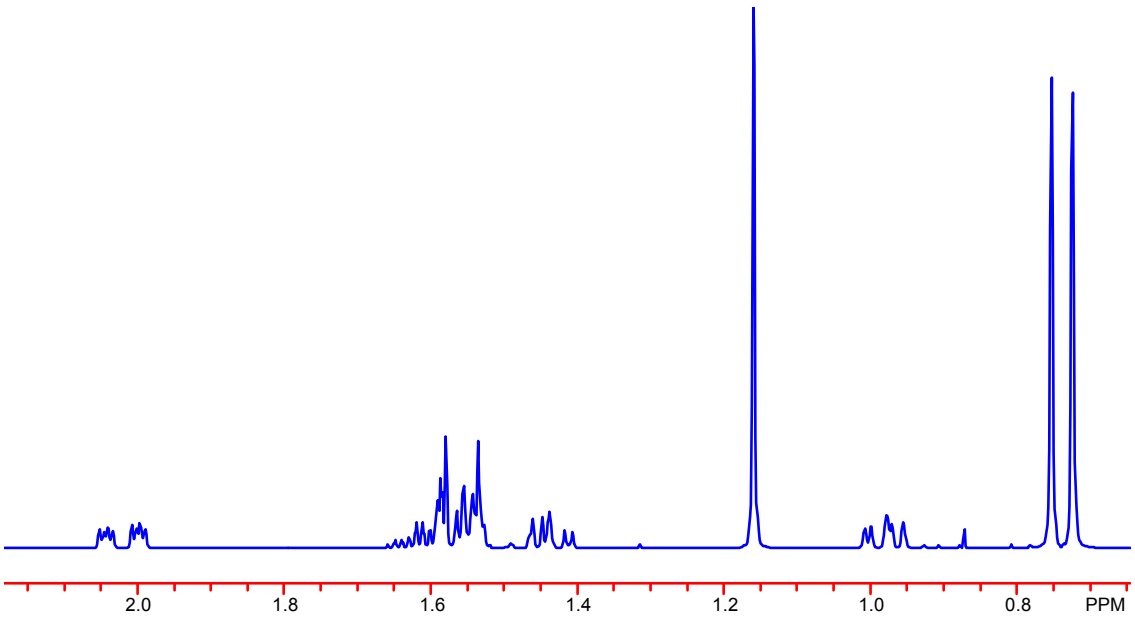


Figure S25. ^{1}H NMR spectrum of the aliphatic region of imine **8** in C_6D_6.

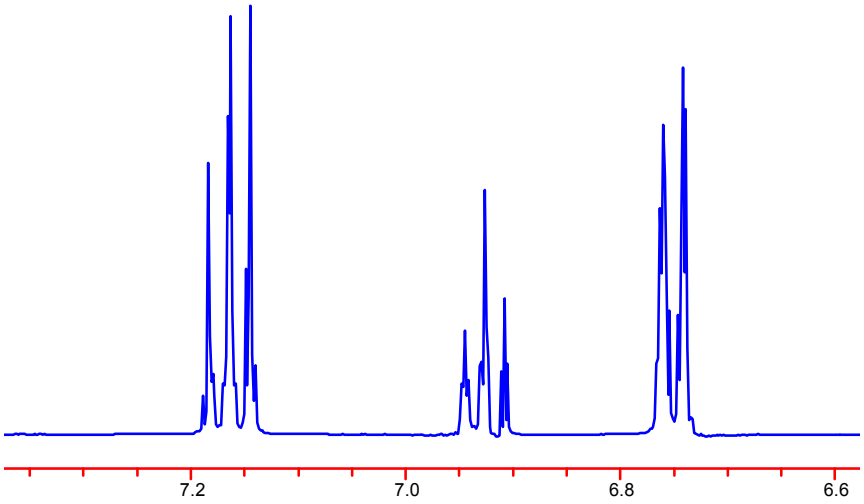


Figure S26. ^{1}H NMR spectrum of the phenyl region of imine **8** in C_6D_6.

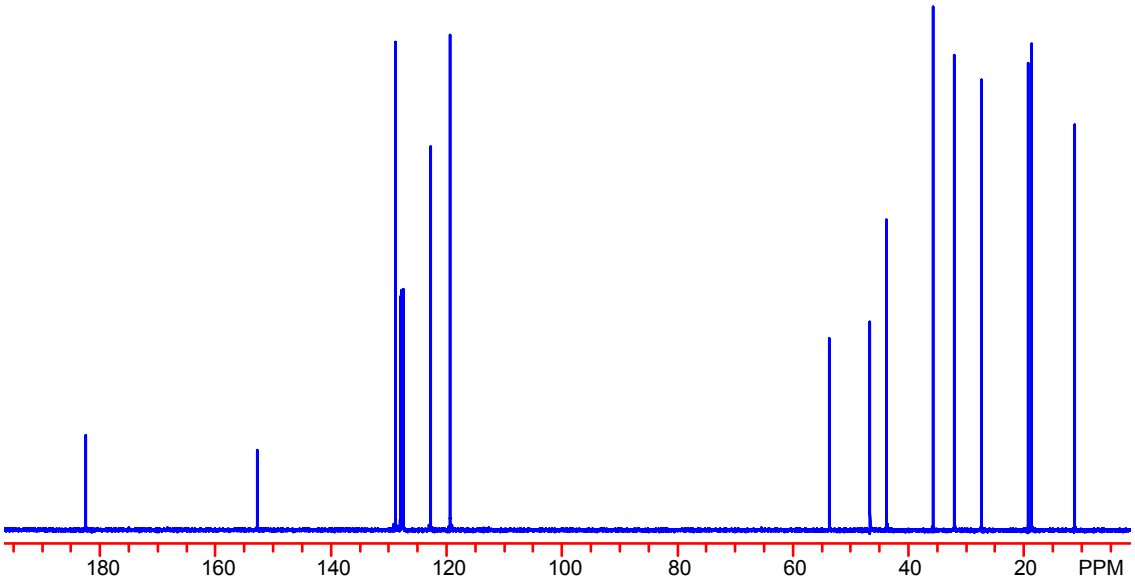


Figure S27. $^{13}C\{^{1}H\}$ NMR spectrum of imine **8** in C_6D_6.

N-(benzyl)- menthonimine (9). A similar procedure to the synthesis of N-(1-(*S*)-phenylethyl)-1-phenylethanimine was used where (*S*)-α-methylbenzylamine was replaced with benzylamine and acetophenone with (L)-(-)-menthone. Yield 7.32 g (52 %). Three isomers were found to be present. ^{1}H NMR (400 MHz, C_6D_6) δ 0.68 (d, J = 6.5 Hz), 0.77 (d, J = 6.5 Hz), 0.83 (d, J = 6.5 Hz), 0.87 (d, J = 6.5 Hz), 0.99 (d, J = 7.1 Hz), 1.03 (d, J = 6.7 Hz), 0.90-2.58 (cyclohexyl protons), 4.47 (m, benzylic protons), 7.05-7.50 (phenyl protons). ^{13}C NMR (100 MHz, C_6D_6) δ 19.74, 20.71, 21.03, 21.50, 21.96, 22.54, 22.64, 22.68, 23.11, 27.16, 27.52, 27.61, 28.50, 28.88, 29.87, 30.66, 34.33, 34.69, 34.74, 34.88, 35.99, 37.84, 44.28, 45.74, 53.88, 54.38, 54.67, 55.21, 126.85, 126.90, 128.25, 128.43, 128.49, 128.83, 128.86, 142.31, 142.40, 142.45,

173.24, 174.46, 175.09. Anal. Calc. $C_{17}H_{25}N$: C 83.89, H 10.35 , N 5.75; Found: C 83.52, H 10.70, N 5.77. Spectroscopic data was found to match with the data previously reported.[9]

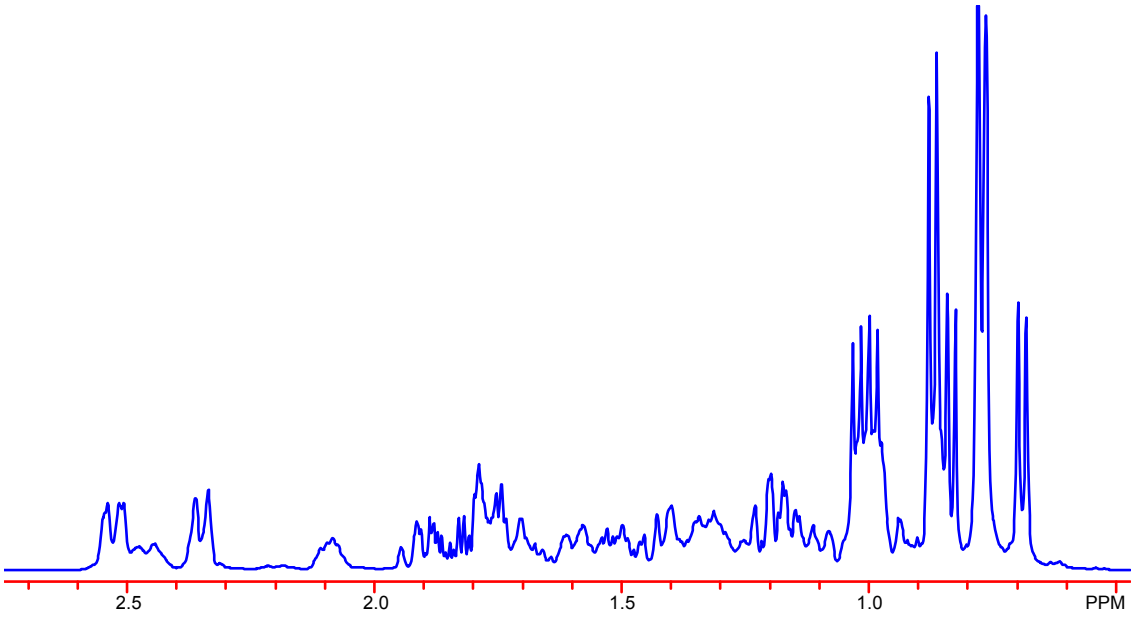


Figure S28. ^{1}H NMR spectrum of the aliphatic region of imine **9** in C_6D_6.

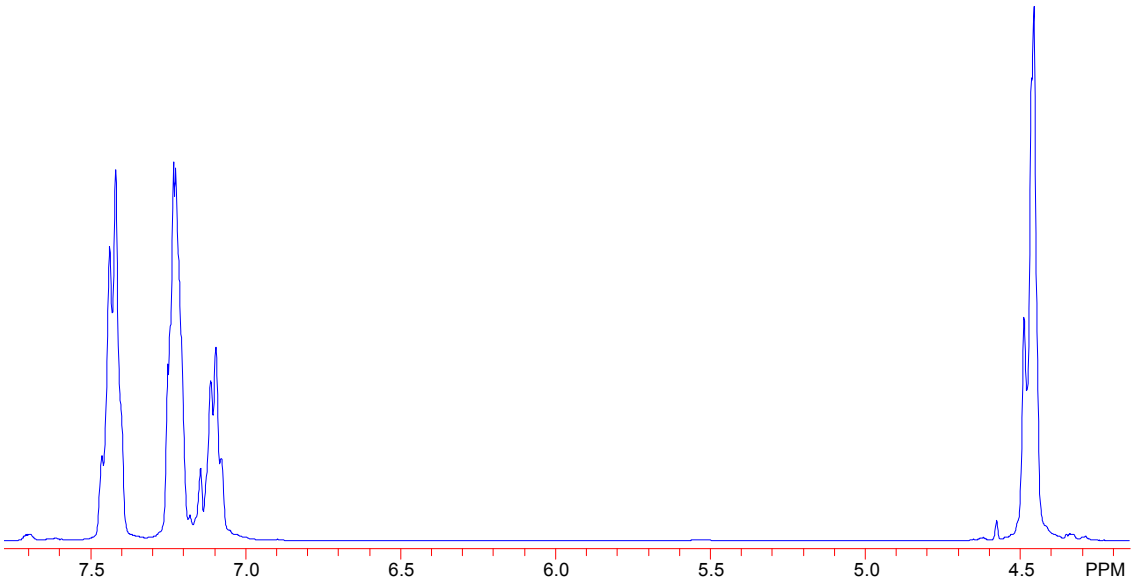


Figure S29. ^{1}H NMR spectrum of the phenyl and benzylic region of imine **9** in C_6D_6.

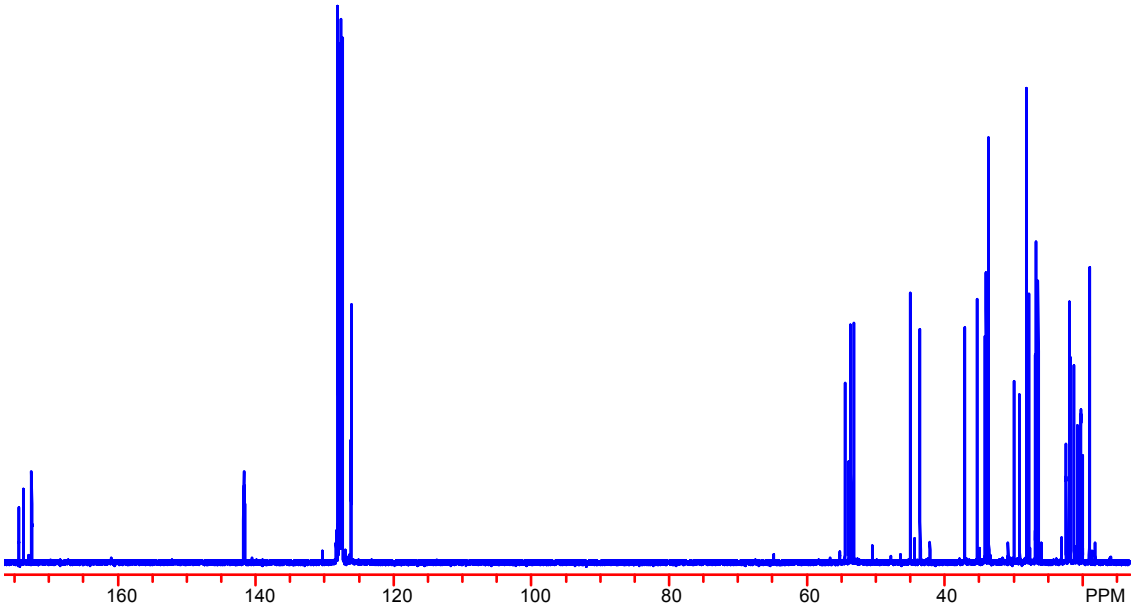


Figure S30. $^{13}C\{^{1}H\}$ NMR spectrum of imine **9** in C_6D_6.

N-(phenyl)- menthonimine (10). A similar procedure to the synthesis of N-(1-(*S*)-phenylethyl)-1-phenylethanimine was used where (*S*)-α-methylbenzylamine was replaced with aniline and acetophenone with (L)-(-)-menthone. Yield 6.82 g (51 %). Three isomers were found to be present. ^{1}H NMR (400 MHz, C_6D_6) δ 0.48 (d, J = 6.3 Hz), 0.57 (d, J = 6.3 Hz), 0.66 (d, J = 6.3 Hz), 0.82 (d, J = 7.2 Hz), 0.84 (d, J = 6.3 Hz), 0.92 (d, J = 6.3 Hz), 0.96 (d, J = 7.2 Hz), 1.01 (d, J = 6.3 Hz), 0.86-2.50 (cyclohexyl protons), 6.60-7.20 (phenyl protons). ^{13}C NMR (100 MHz, C_6D_6) δ 19.61, 20.26, 21.00, 21.80, 22.03, 22.31, 22.39, 22.47, 23.06, 27.23, 27.38, 27.79, 28.48, 28.69, 29.61, 30.01, 30.23, 34.41, 35.16, 35.46, 36.65, 36.92, 39.89, 44.65, 46.35, 53.19, 54.32, 120.00, 120.13, 120.25, 122.98, 123.03, 123.18, 129.41, 129.47, 129.47, 129.49, 152.44, 152.49, 152.75, 174.18, 175.62, 176.46. Spectroscopic data was found to match with the data previously reported.[10]

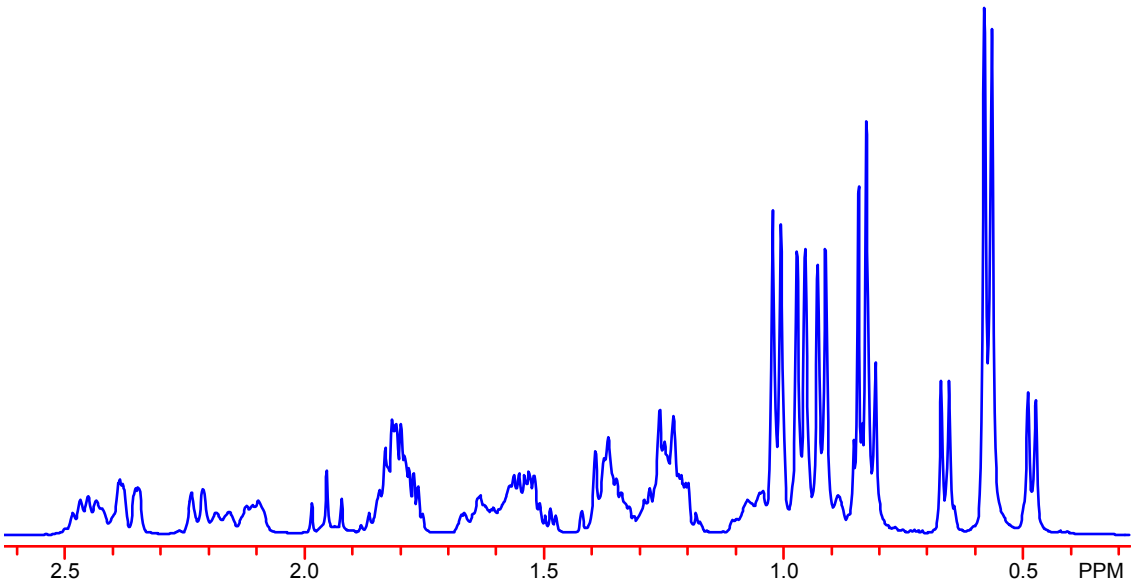


Figure S31. ^{1}H NMR spectrum of the aliphatic region of imine **10** in C_6D_6.

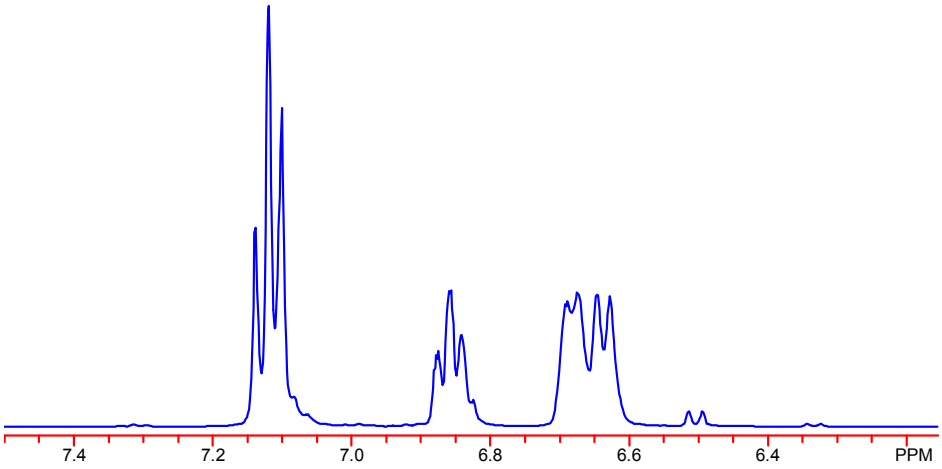


Figure S32. ^{1}H NMR spectrum of the phenyl region of imine **10** in C_6D_6.

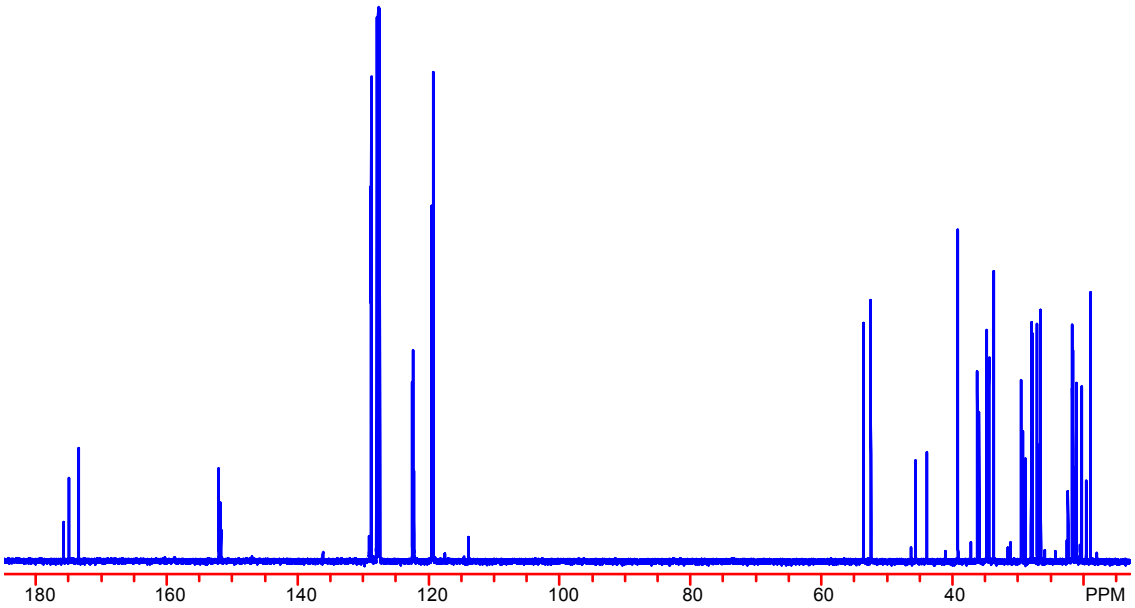


Figure S33. $^{13}C\{^{1}H\}$ NMR spectrum of imine **10** in C_6D_6.

Stoichimetric reduction of chiral imines with $NaBH_3CN$ or $NaHB(OAc)_3$. The amines were prepared by a similar procedure previously described by Abdel-Magid and coworkers.[11] One gram (~ 5 mmol) imine was dissolved in 30 mL acetonitrile and treated with the respective reducing agent (6 mmol) and acetic acid (6 mmol). The slurry was allowed to stir for 16 hours and was quenched with 50 mL of a 2 M NaOH solution. Further addition of NaOH was required if the aqueous layer was not basic. Extraction and distillation of the organic layer under reduced pressure resulted in the respective amines which matched the previously described literature values (see also Figures S44-S55).[3,10,12]

Stoichiometric hydrogenation of chiral imines with $B(C_6F_5)_3$. 10 mg (0.02 mmol) $B(C_6F_5)_3$, 8 mg (0.05 mmol) 1,3,5-trimethoxybenzene (internal standard), and the appropriate amount of imine was dissolved in 0.8 mL C_6D_5Br or toluene-d_8. The solution was transferred to J. Young NMR Tube and degassed by three freeze pump thaw cycles followed by a fill with H_2 and evacuation before pressurizing the reaction vessel at 1 atm H_2 at 77K (~ 4 atm H_2 at 298K). The reaction was monitored at room temperature for 48 hours followed by heating at 70°C for 48 hours. Reaction products and diastereomer excess was determined by ^{1}H NMR spectroscopy and integrated with respect to the resonances of 1,3,5-trimethoxybenzene.

Catalytic hydrogenation of chiral imines with $B(C_6F_5)_3$. 10 mg (0.02 mmol) $B(C_6F_5)_3$ and the appropriate amount of imine was dissolved in 8 mL toluene. The solution was transferred to a thick walled reaction vessel and degassed by three freeze pump thaw cycles followed by a fill with H_2 and evacuation before pressurizing the reaction vessel at 1 atm H_2 at 77K (~ 4 atm H_2 at 298K). The reaction was heated for the designated amount of time (Table 3) and the pressure was vented and the solvent was removed under reduced pressure. Reaction products and diastereomer excess was determined by NMR spectroscopy (Figures S44-S55).

N-benzyl bornylammonium $HB(C_6F_5)_3$. A colorless toluene solution (15 mL) containing 150 mg (0.62 mmol) imine **7** and 320 mg (0.63 mmol) $B(C_6F_5)_3$ was degassed by three freeze pump thaw cycles followed by a fill with H_2 and evacuation before pressurizing the reaction vessel at 1 atm H_2 at 77K (~ 4 atm H_2 at 298K). The reaction was heated at 115°C for 72 hours. The pressure was vented and the solvent was removed under reduced pressure, resulting in a colorless oil. Thirty mL of n-hexanes was added and the slurry was allowed to triturate for 24 hours, resulting in a colorless solid. The slurry was filtered resulting in a white solid which was recrystallized from 1,2-dichloroethane/hexanes and dried under vacuum for three hours. Yield: 0.174 g (37 %). ^{1}H NMR (400 MHz, CD_3CN) δ 0.86 (s, 3H, -C*H*$_3$), 0.93 (s, 3H, -C*H*$_3$), 0.96 (s, 3H, -C*H*$_3$), 1.05-2.00 (5H, cyclohexyl protons), 3.12 (dd, $^3J_{HH}$ = 5.3 Hz, $^3J_{HH}$ = 8.8 Hz, 1H, cyclohexyl proton), 3.62 (br q, $^1J_{BH}$ = 94.5 Hz, B-*H*), 4.20 (m, 2H, benzylic protons), 6.25 (br s, -N*H*$_2$), 7.43-7.56 (m, 5H, phenyl protons). ^{11}B NMR (128 MHz, CD_3CN) δ -25.57 (d, $^1J_{BH}$ = 94.5 Hz). ^{19}F NMR (377 MHz, CD_3CN) δ -134.66 (s, 2F), -164.98 (t, $^3J_{FF}$ = 19.4 Hz, 2F), -168.30 (m, 1F).

2) Multinuclear NMR of Imine 3 with $B(C_6F_5)_3$ and H_2

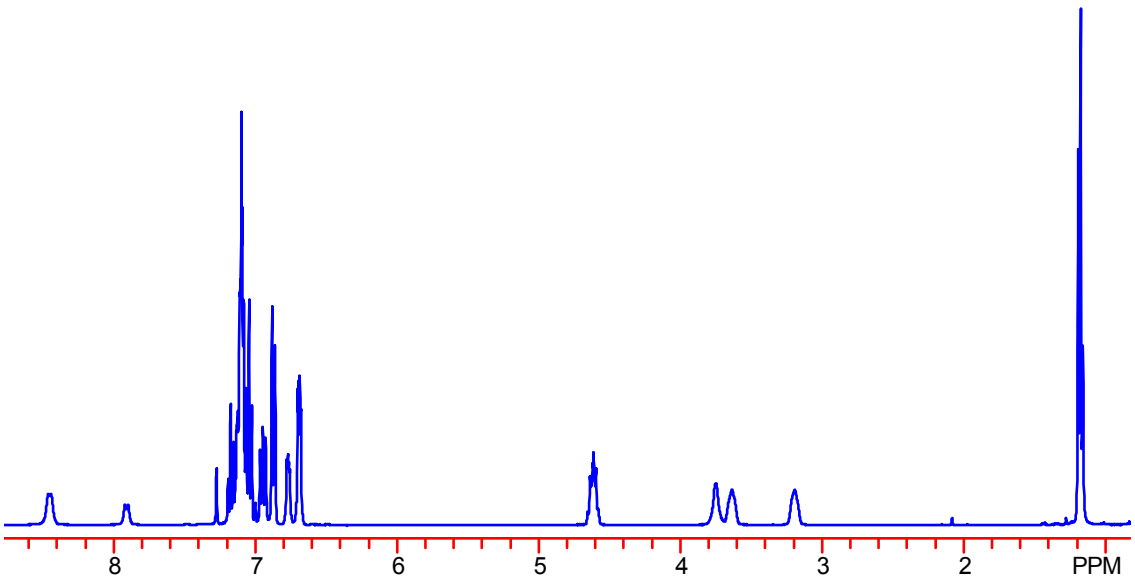


Figure S34. ^{1}H NMR (C_6D_5Br) of imine **3** with one equivalent of $B(C_6F_5)_3$ before H_2.

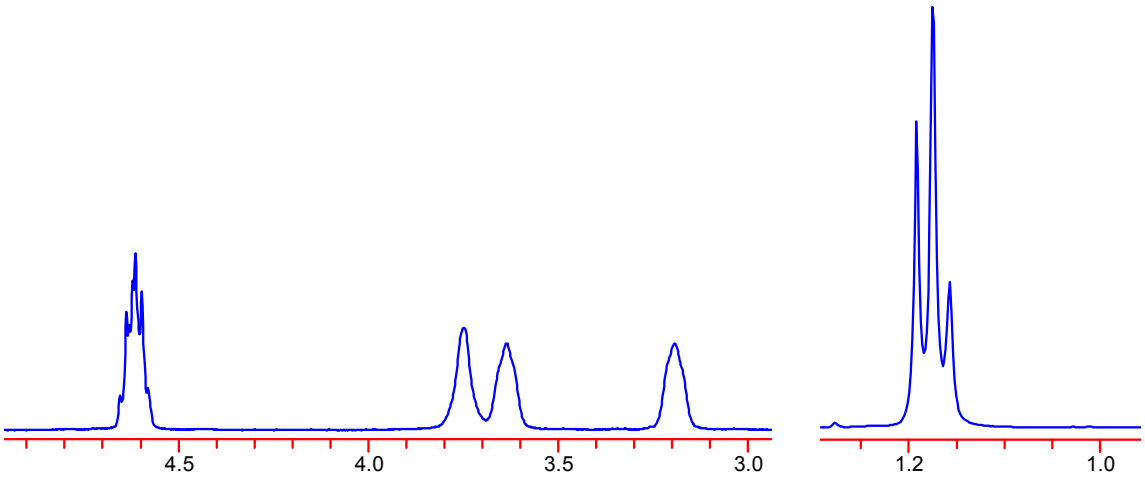


Figure S35. ^{1}H NMR (C_6D_5Br) of benzylic CHMe region of imine **3** with one equivalent of $B(C_6F_5)_3$ before H_2.

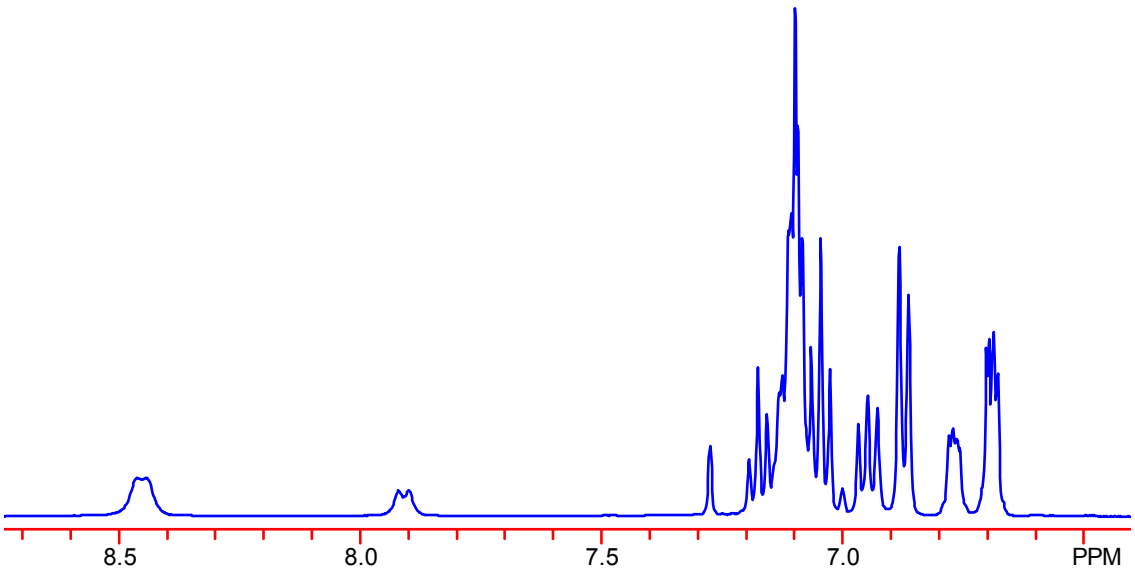


Figure S36. ^{1}H NMR (C_6D_5Br) of phenyl region of imine **3** with one equivalent of $B(C_6F_5)_3$ before H_2.

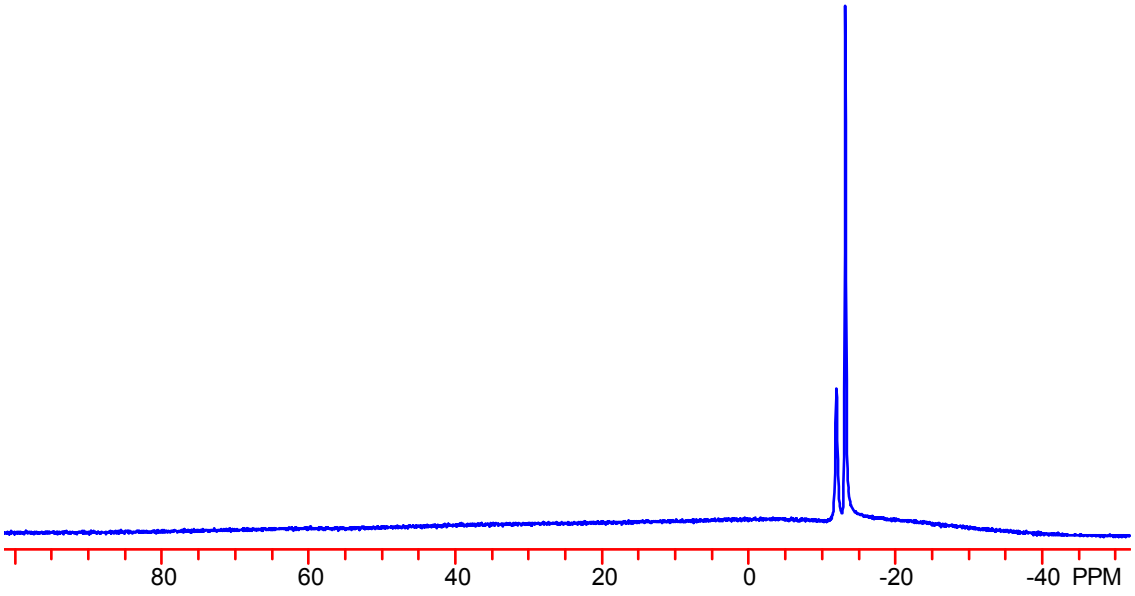


Figure S37. ^{11}B NMR (C_6D_5Br) of imine **3** with one equivalent of $B(C_6F_5)_3$ before H_2.

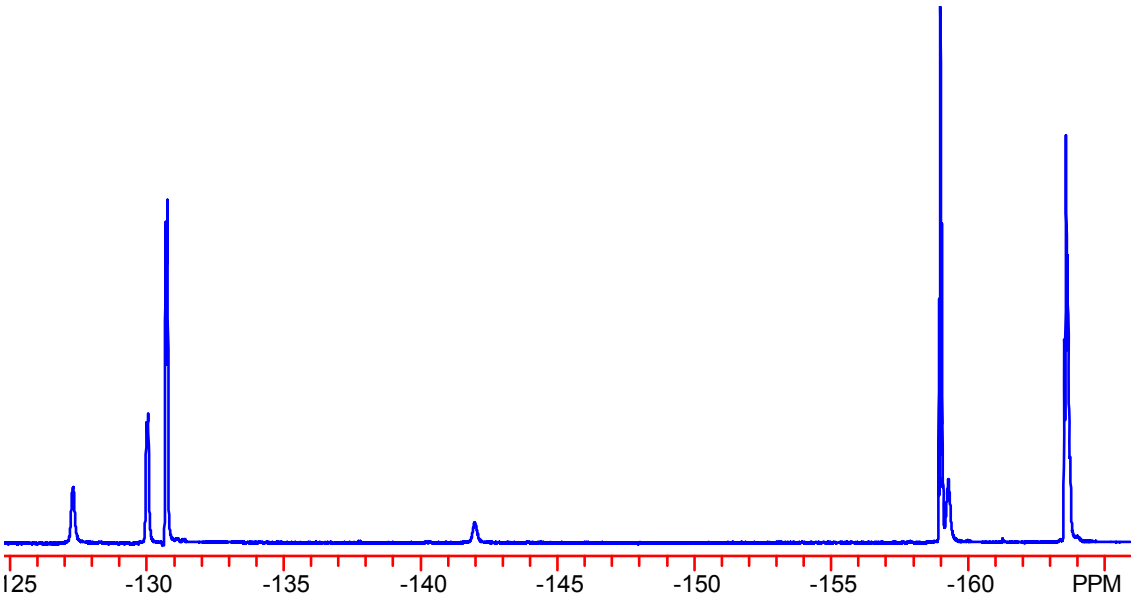


Figure S38. ^{19}F NMR (C_6D_5Br) of imine **3** with one equivalent of $B(C_6F_5)_3$ before H_2.

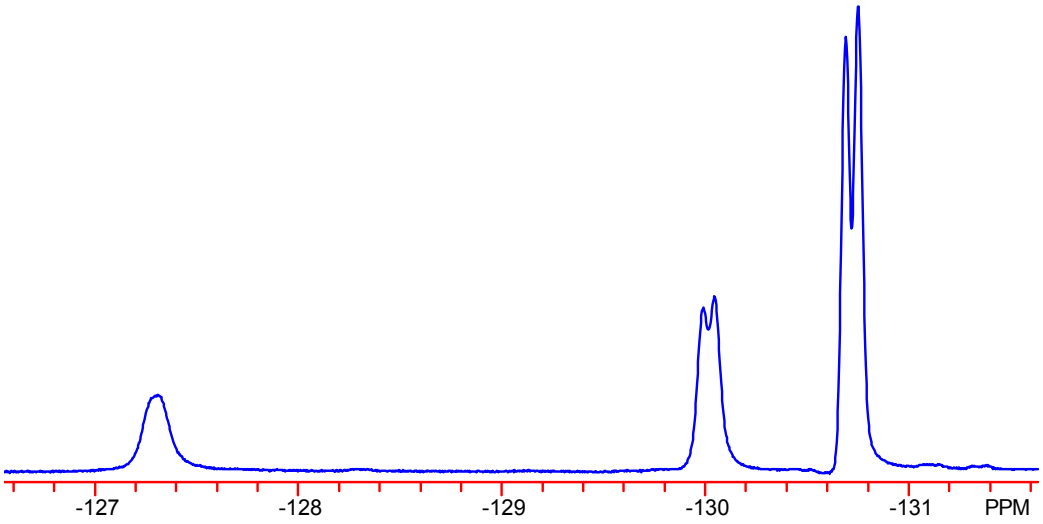


Figure S39. ^{19}F NMR (C_6D_5Br) of imine **3** with one equivalent of $B(C_6F_5)_3$ before H_2.

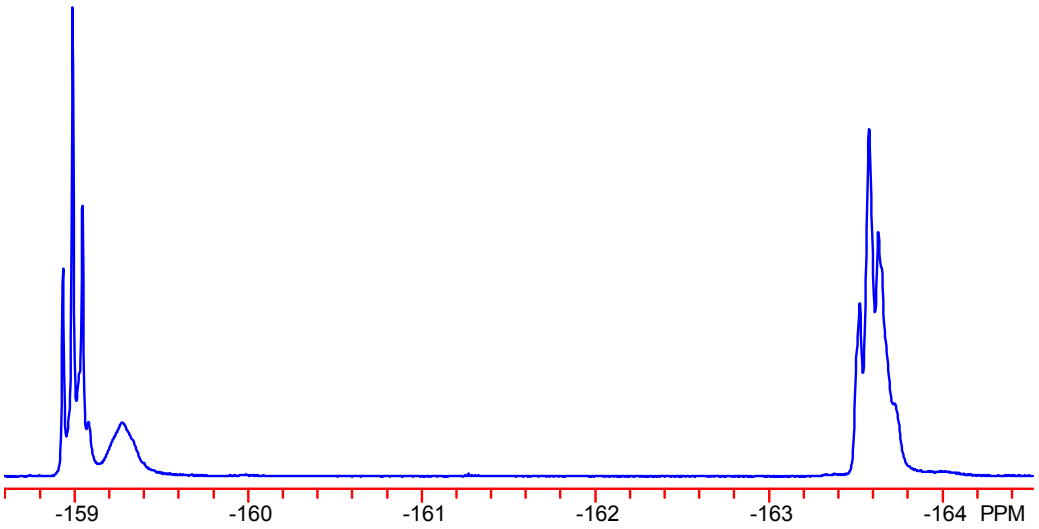


Figure S40. ^{19}F NMR (C_6D_5Br) of imine **3** with one equivalent of $B(C_6F_5)_3$ before H_2.

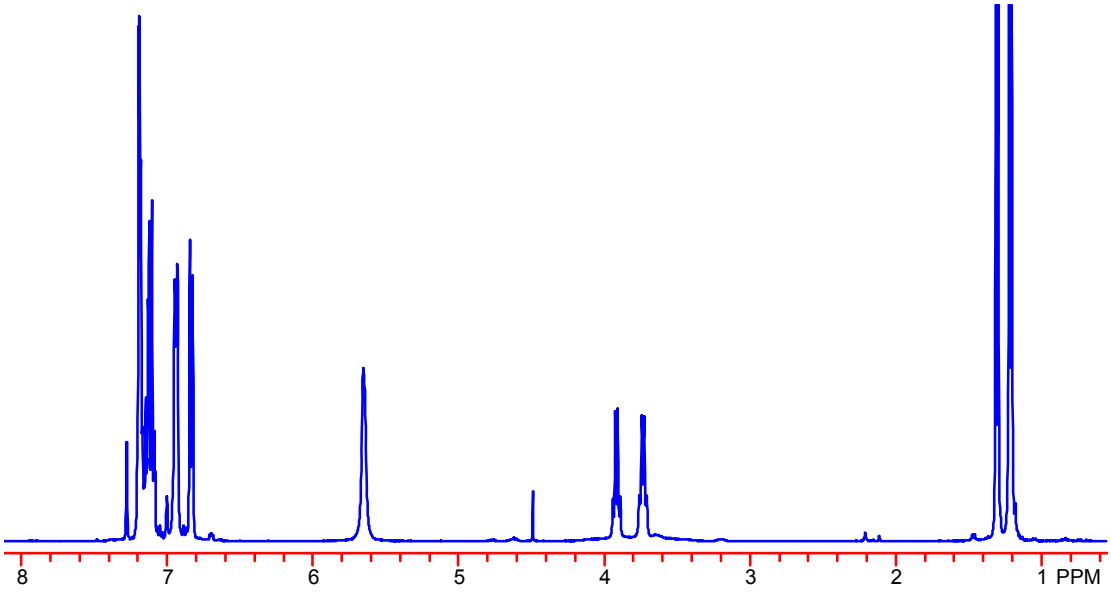


Figure S41. ^{1}H NMR (C_6D_5Br) of imine **3** with one equivalent of $B(C_6F_5)_3$ with H_2 after heating at 65°C for 48 hours.

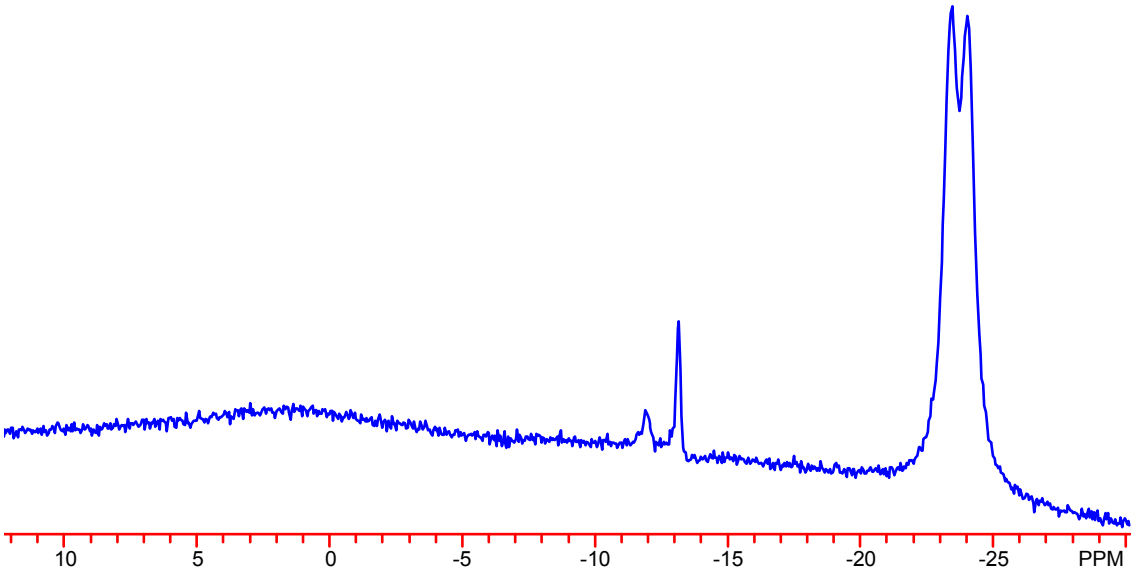


Figure S42. ^{11}B NMR (C_6D_5Br) of imine **3** with one equivalent of $B(C_6F_5)_3$ with H_2 after heating at 65°C for 48 hours.

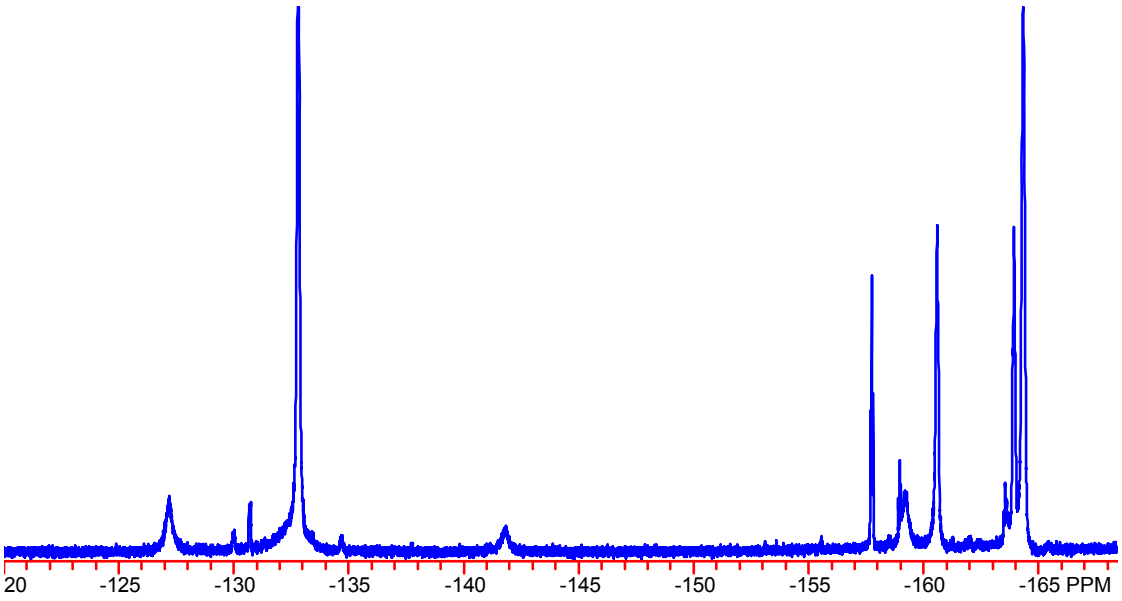


Figure S43. ^{19}F NMR (C_6D_5Br) of imine **3** with one equivalent of $B(C_6F_5)_3$ with H_2 after heating at 65°C for 48 hours.

3) ^{1}H NMR of Catalytic Reductions of Chiral Imines with $B(C_6F_5)_3$

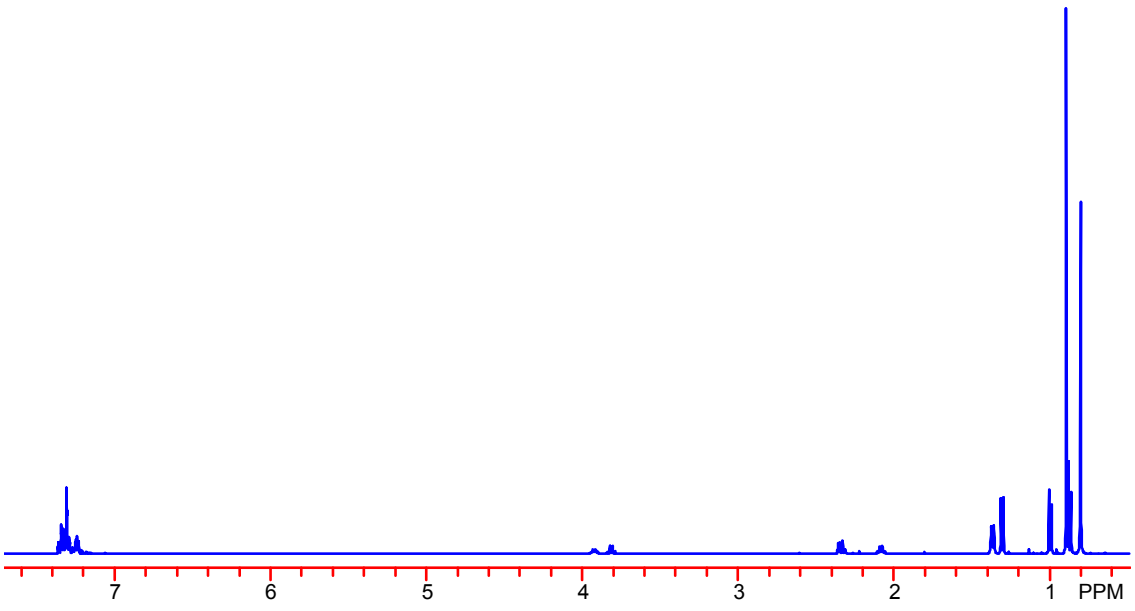


Figure S44. Crude ^{1}H NMR ($CDCl_3$) of catalytic hydrogenation of imine **1** with 10 mol % $B(C_6F_5)_3$.

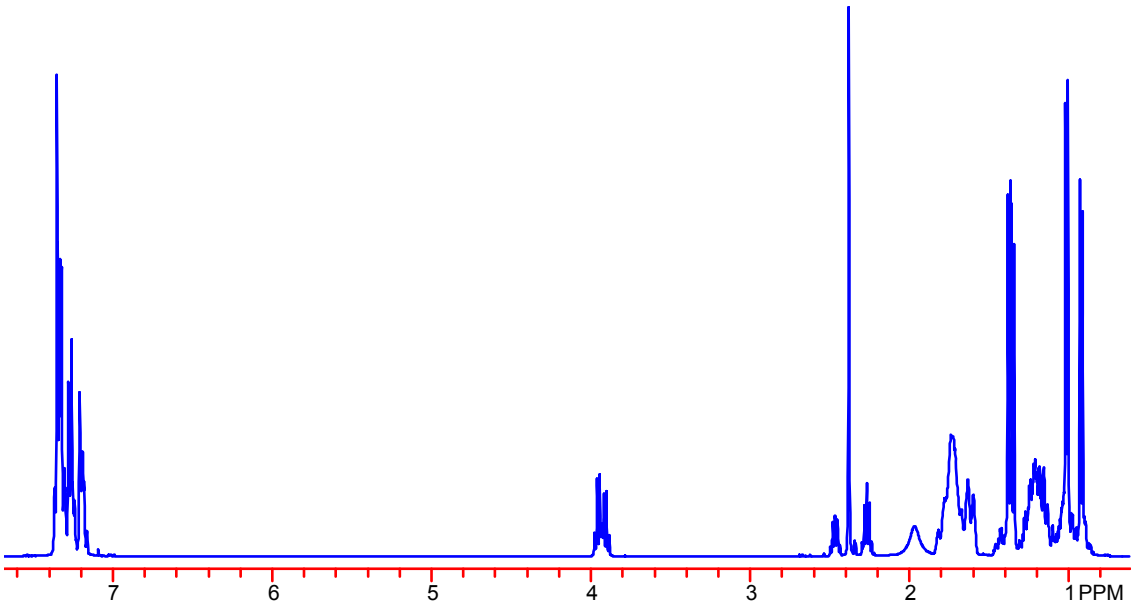


Figure S45. Crude ^{1}H NMR ($CDCl_3$) of catalytic hydrogenation of imine **2** with 10 mol % $B(C_6F_5)_3$.

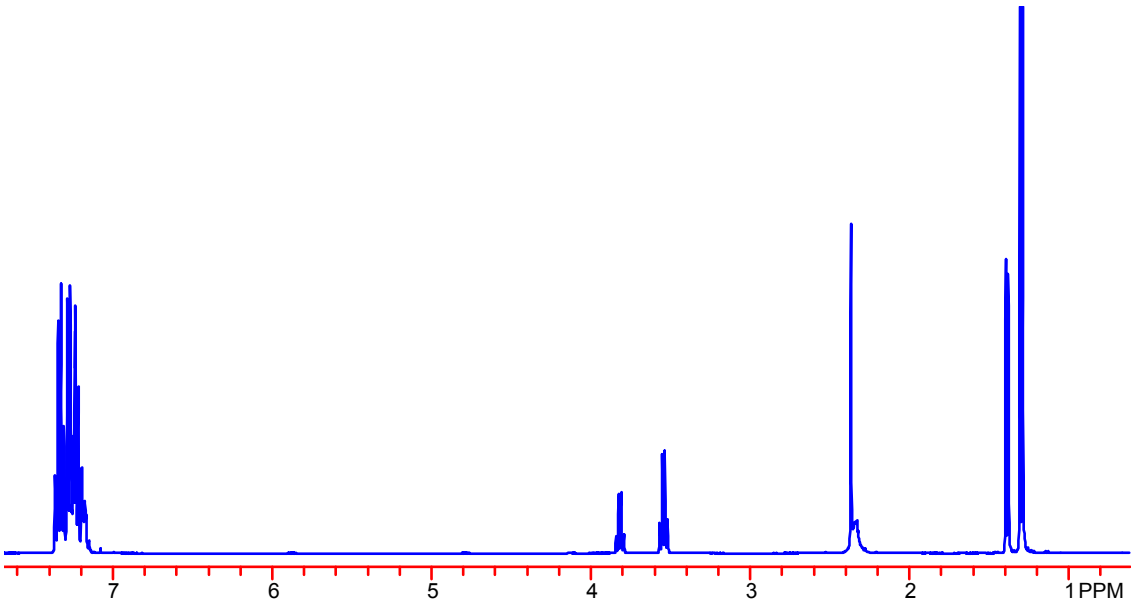


Figure S46. Crude ^{1}H NMR ($CDCl_3$) of catalytic hydrogenation of imine **3** with 10 mol % $B(C_6F_5)_3$.

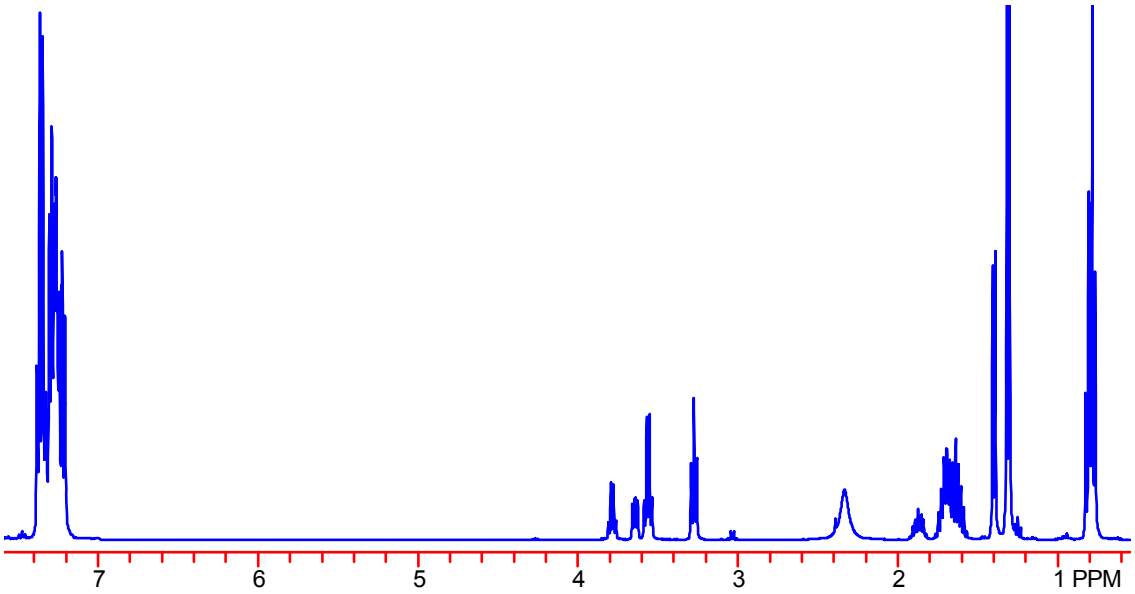


Figure S47. Crude ^{1}H NMR ($CDCl_3$) of catalytic hydrogenation of imine **4** with 10 mol % $B(C_6F_5)_3$.

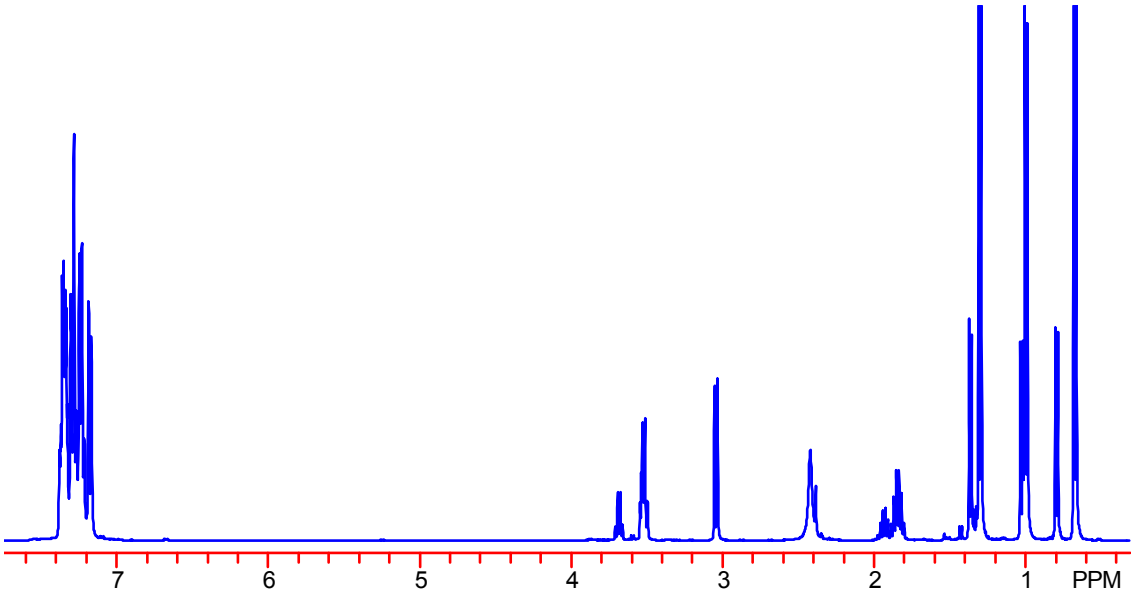


Figure S48. Crude ^{1}H NMR ($CDCl_3$) of catalytic hydrogenation of imine **5** with 10 mol % $B(C_6F_5)_3$.

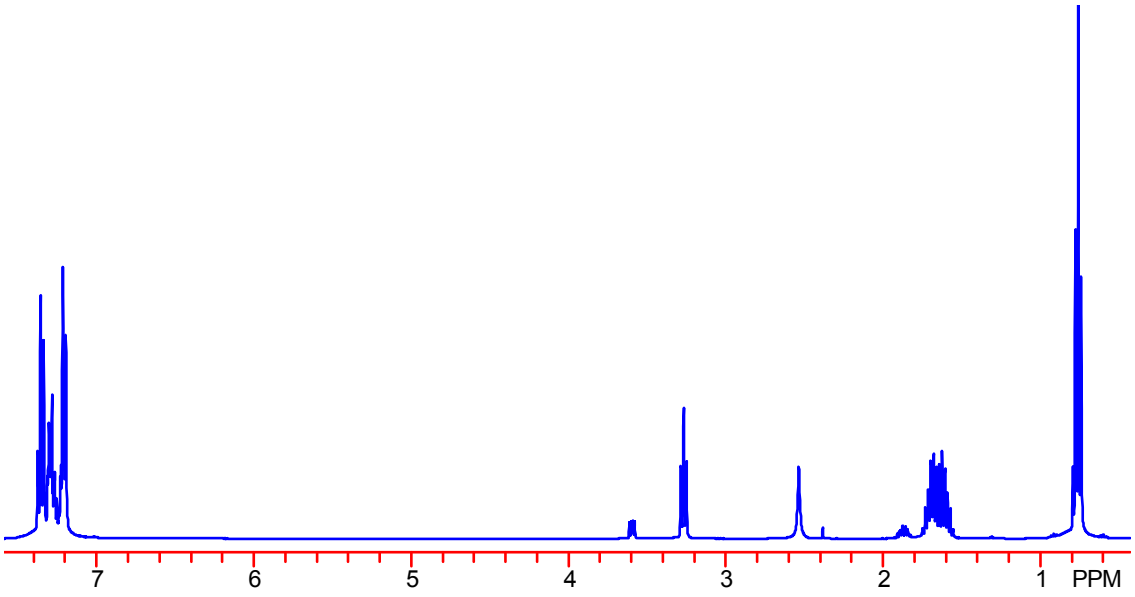


Figure S49. Crude ^{1}H NMR ($CDCl_3$) of catalytic hydrogenation of imine **6** with 10 mol % $B(C_6F_5)_3$.

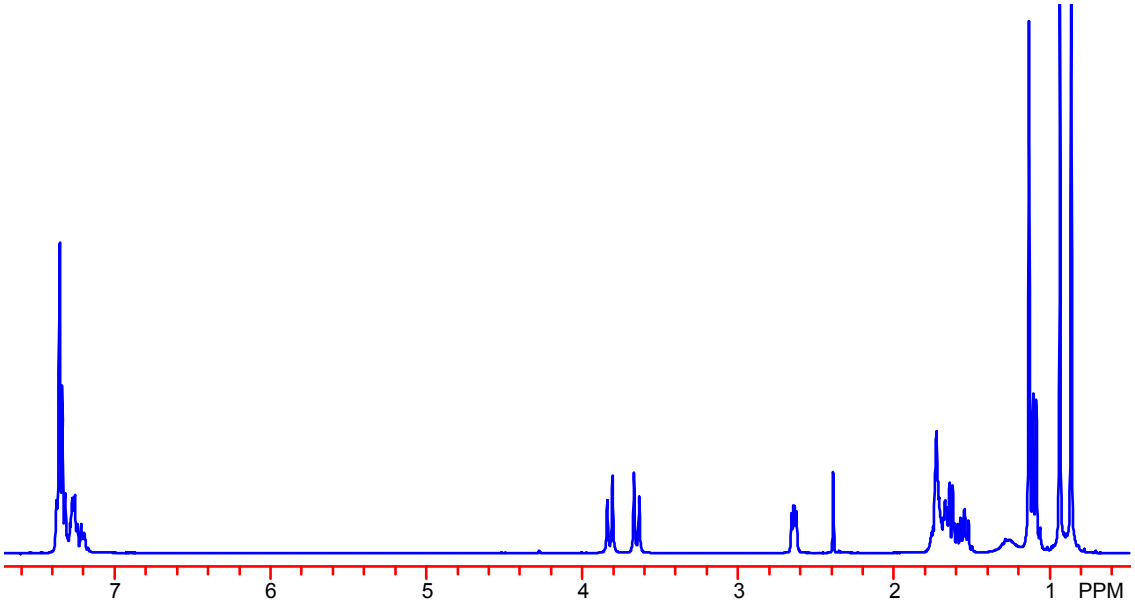


Figure S50. Crude ^{1}H NMR ($CDCl_3$) of catalytic hydrogenation of imine **7** with 10 mol % $B(C_6F_5)_3$.

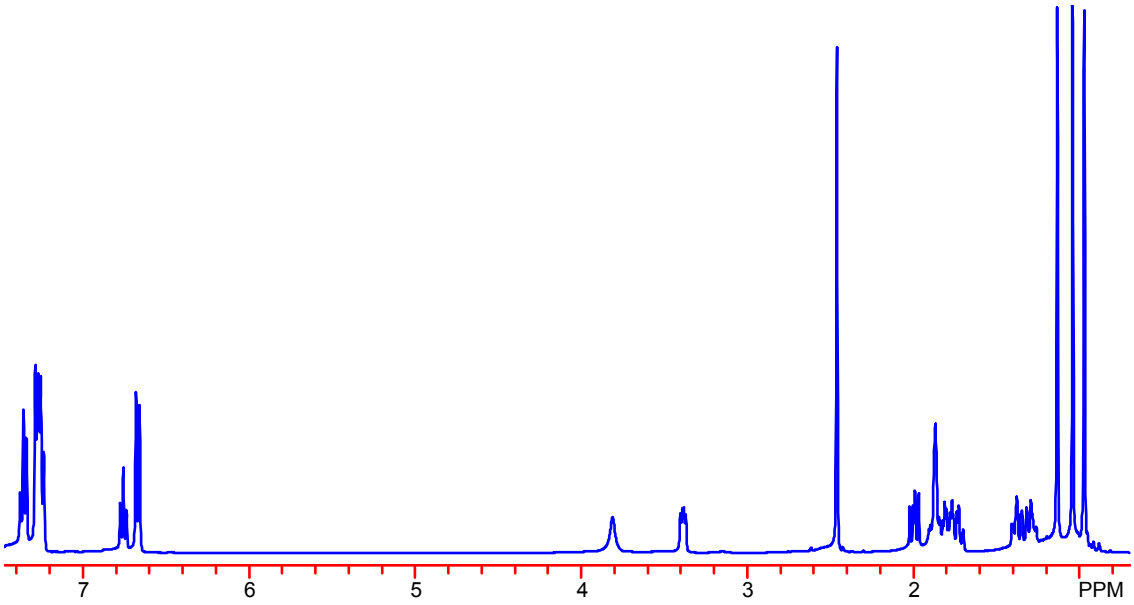


Figure S51. Crude ^{1}H NMR ($CDCl_3$) of catalytic hydrogenation of imine **8** with 10 mol % $B(C_6F_5)_3$.

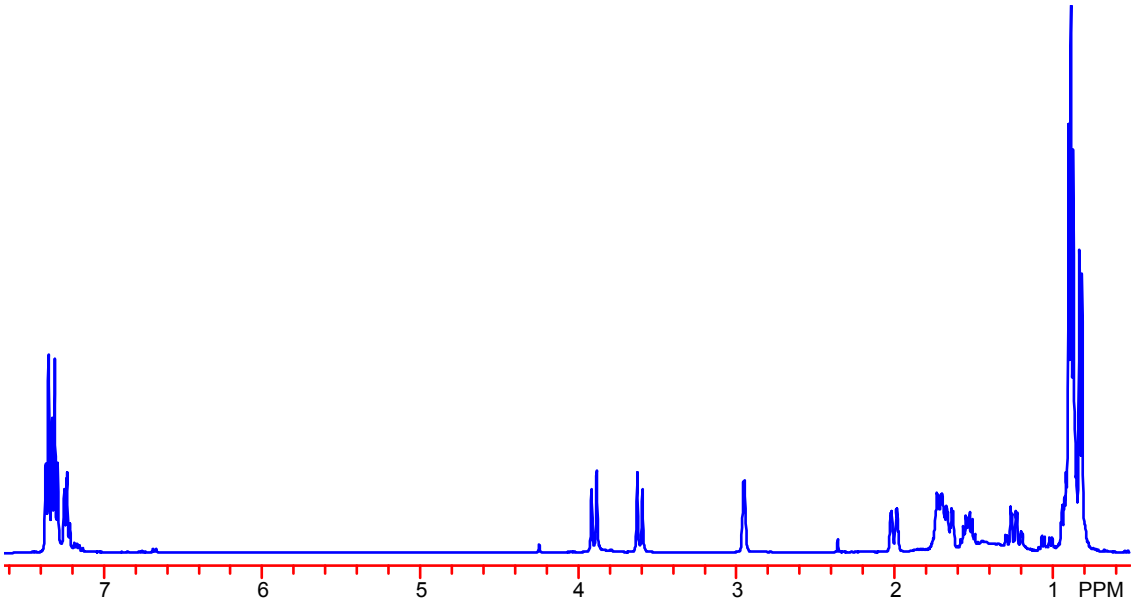


Figure S52. Crude ^{1}H NMR ($CDCl_3$) of catalytic hydrogenation of imine **9** with 20 mol % $B(C_6F_5)_3$.

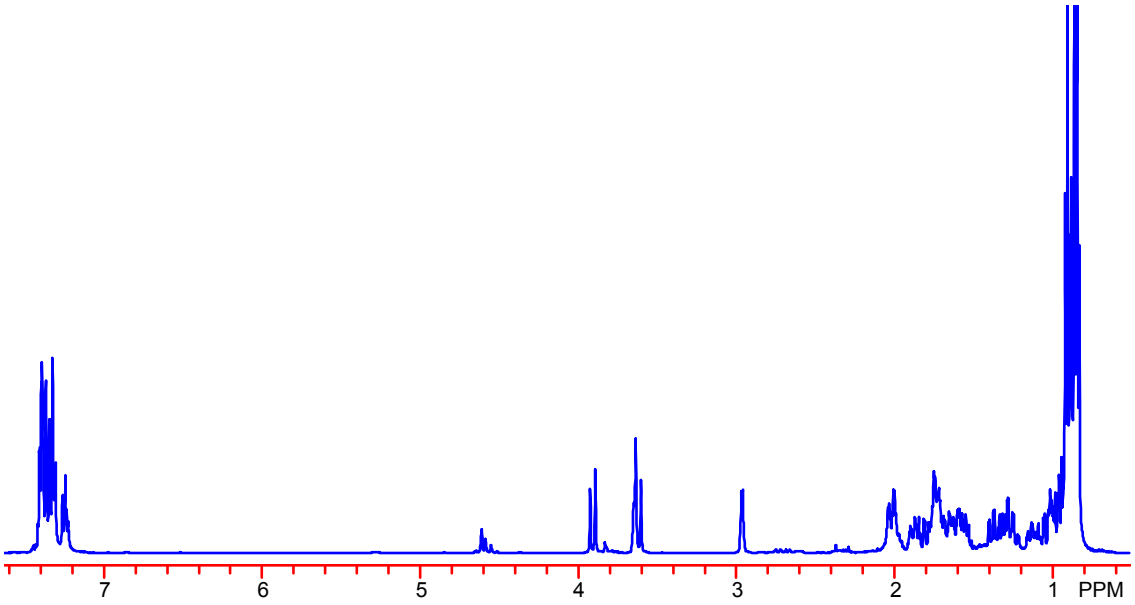


Figure S53. Crude ^{1}H NMR ($CDCl_3$) of catalytic hydrogenation of imine **9** with 10 mol % $B(C_6F_5)_3$.

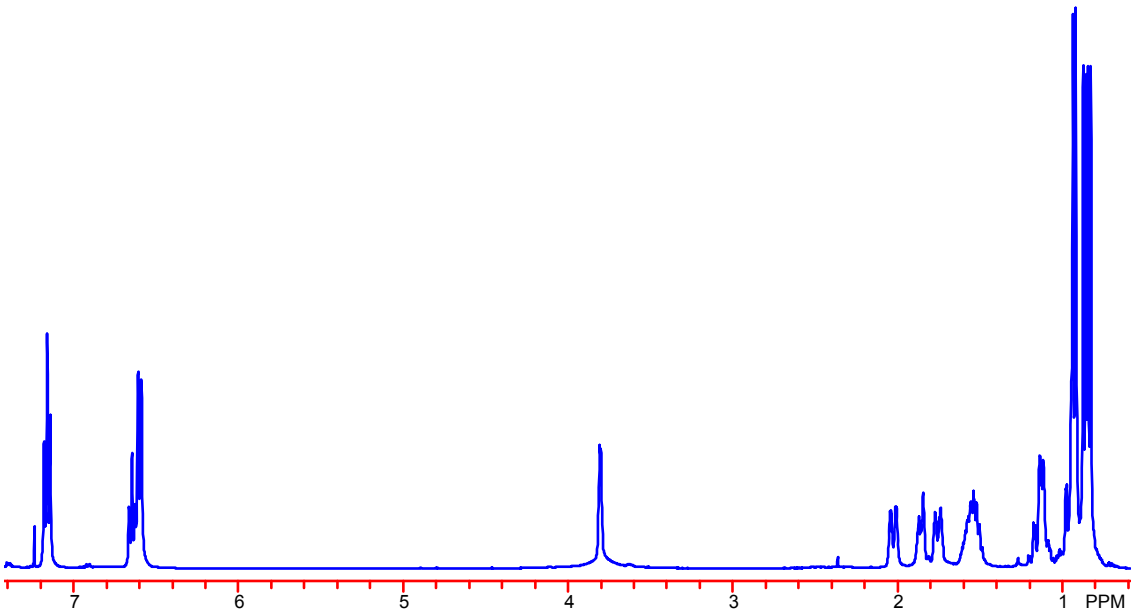


Figure S54. Crude ^{1}H NMR ($CDCl_3$) of catalytic hydrogenation of imine **10** with 20 mol % $B(C_6F_5)_3$.

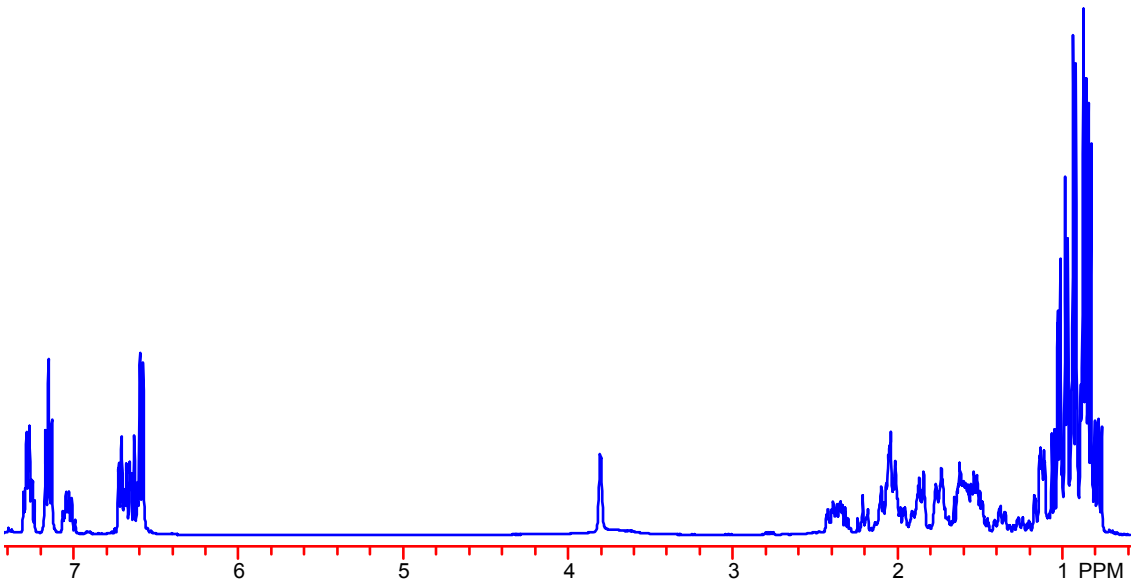
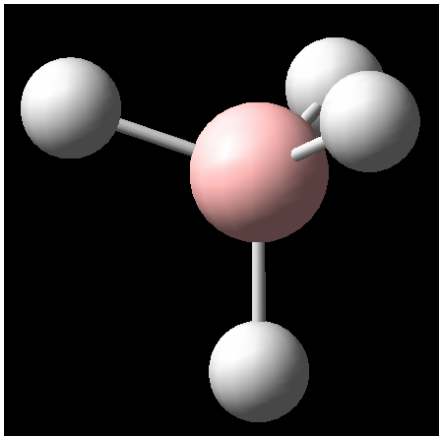
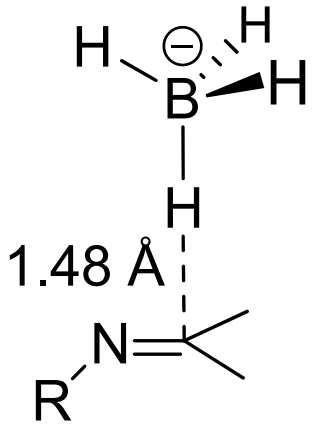
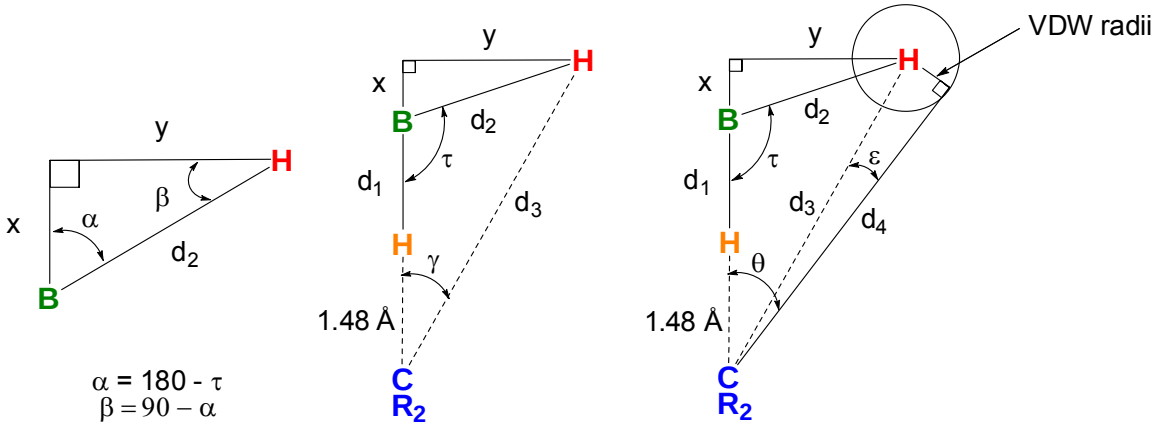


Figure S55. Crude ^{1}H NMR ($CDCl_3$) of catalytic hydrogenation of imine **10** with 10 mol % $B(C_6F_5)_3$.

4) Sample Calculation of Borohydride Cone Angle







$$d_3^2 = (x + d_1 + 1.48)^2 + y^2$$

$$\gamma = \tan^{-1}\left(y/(x + d_1 + 1.48)\right)$$

$$\varepsilon = \sin^{-1}\left((\text{VDW radius})/d_3\right)$$

$$\Theta = 2\,\theta = 2(\gamma + \varepsilon)$$

For BH_4^-: $d_1 = d_2 = 1.24118$ Å

$\tau = 109.47°$

Van der Waal's Radius[13] for H : 1.2 Å

$$\alpha = 180° - \tau = 180° - 109.47° = 70.53°$$

$$\beta = 90 - \alpha = 90° - 70.53° = 19.47°$$

$$x = d_2 \sin\beta = 1.24118\ \text{Å} \cdot \sin(19.47°) = 0.413727\ \text{Å}$$

$$y = d_2 \sin\alpha = 1.24118\ \text{Å} \cdot \sin(70.53°) = 1.170196\ \text{Å}$$

$$d_3 = \sqrt{\left(x + d_1 + 1.48\ \text{Å}\right)^2 + y^2} = \sqrt{\left(0.413727\ \text{Å} + 1.24118\ \text{Å} + 1.48\ \text{Å}\right)^2 + \left(1.170196\ \text{Å}\right)^2} = 3.346192\ \text{Å}$$

$$\gamma = \tan^{-1}\left(\frac{y}{x + d_1 + 1.48\ \text{Å}}\right) = \tan^{-1}\left(\frac{1.170196\ \text{Å}}{0.413727\ \text{Å} + 1.24118\ \text{Å} + 1.48\ \text{Å}}\right) = 20.47°$$

$$\varepsilon = \sin^{-1}\left(\frac{\text{Van der Waal's Radius}}{d_3}\right) = \sin^{-1}\left(\frac{1.2}{3.346192}\right) = 21.02°$$

$$\Theta = 2(\gamma + \varepsilon) = 2(20.47° + 21.02°) = 82.97°$$

For borohydrides containing different ligands or orientations of ligands, the reported cone angle is the average of the cone angle of each ligand of the low energy structure minimized at the B3LYP/6-31g(d) level of theory.

A value of 1.48 Å was taken as the average distance between a B-H and an imininium carbon in the hydride transfer transition state.[14]

Table S1. List of cone angles for main group hydrides of interest.

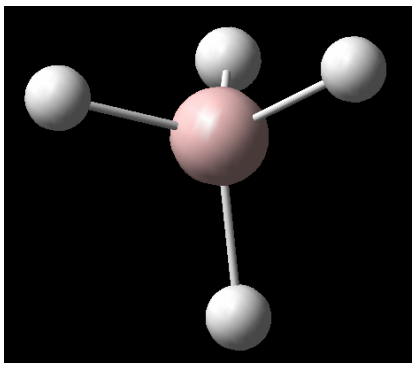
Borohydride	Cone Angle (°)
BH_4^-	83.0
AlH_4^-	85.3
BH_3CN^-	92.2
$HBEt_3^-$	155.7
$HBPh_3^-$	162.5
$HB(OAc)_3^-$	163.0
Selectride	168.0
$HB(C_6F_5)_3^-$	186.3

5) 3D Coordinates of Triel Hydrides for Cone Angle Calculations

Only the lowest energy configurations of the hydrides were used in the cone angle calculations. All coordinates are taken from the .xyz files with units of Ångstroms.[15] All structures were minimized using the Gaussian 03 program. All minimized structures were found to contain no imaginary frequencies. Transition states contained only one imaginary frequency and the transition states were connected to the minimized structures via IRC analysis.

Gray = Carbon
Pink = Boron
White = Hydrogen
Light Green = Fluorine
Red = Oxygen

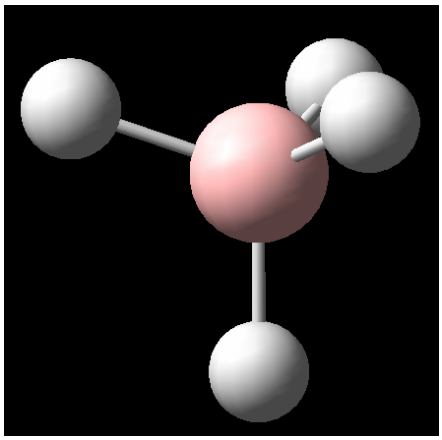
Complex: AlH_4^-, gas phase



3D Coordinates:

Al	0.00000	0.00000	0.00000
H	0.95155	0.95155	0.95155
H	-0.95155	0.95155	-0.95155
H	0.95155	-0.95155	-0.95155
H	-0.95155	-0.95155	0.95155

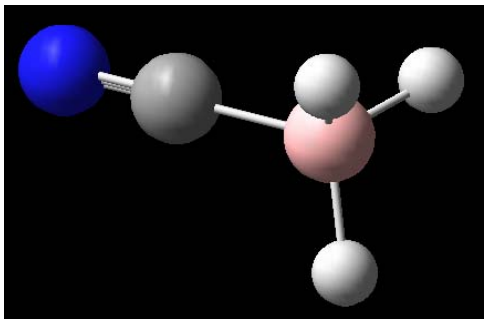
Complex: BH_4^-, gas phase



3D Coordinates:

B	0.00000	0.00000	0.00000
H	0.71660	0.71660	0.71660
H	-0.71660	0.71660	-0.71660
H	0.71660	-0.71660	-0.71660
H	-0.71660	-0.71660	0.71660

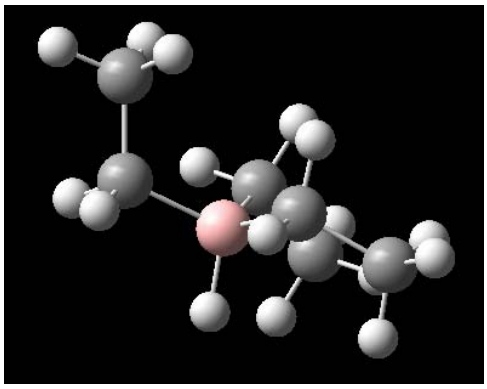
Complex: BH_3CN^-, gas phase



3D Coordinates:

B	0.00000	0.00000	-1.32000
H	0.00000	1.16138	-1.71751
H	1.00578	-0.58069	-1.71751
H	-1.00578	-0.58069	-1.71751
C	0.00000	0.00000	0.27403
N	0.00000	0.00000	1.44406

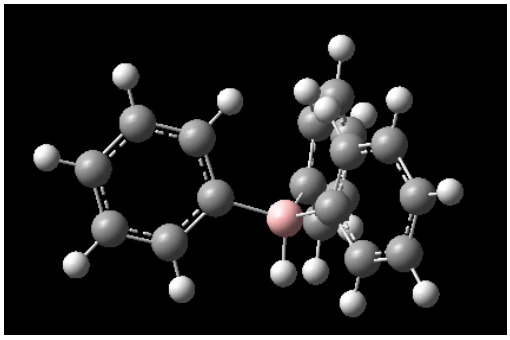
Complex: $HBEt_3^-$, gas phase



3D Coordinates:

B	-0.00084	-0.00128	0.17153
H	-0.00347	0.00002	1.42314
C	-1.57241	-0.07616	-0.35600
H	-2.09003	0.88146	-0.16214
H	-1.60752	-0.19662	-1.45725
C	0.85077	-1.32723	-0.34852
H	0.28530	-2.25367	-0.13882
H	0.96212	-1.31010	-1.45114
C	0.72221	1.39764	-0.35208
H	1.80895	1.36978	-0.15099
H	0.64281	1.48786	-1.45398
C	2.24930	-1.49942	0.26812
H	2.78279	-2.40608	-0.07133
H	2.89930	-0.64354	0.03612
H	2.18237	-1.55068	1.36442
C	0.17905	2.69518	0.26995
H	0.68720	3.61116	-0.08312
H	-0.89162	2.82429	0.05734
H	0.27788	2.66795	1.36471
C	-2.42813	-1.18995	0.27141
H	-3.47664	-1.20377	-0.07826
H	-2.01028	-2.18483	0.06042
H	-2.44967	-1.08722	1.36592

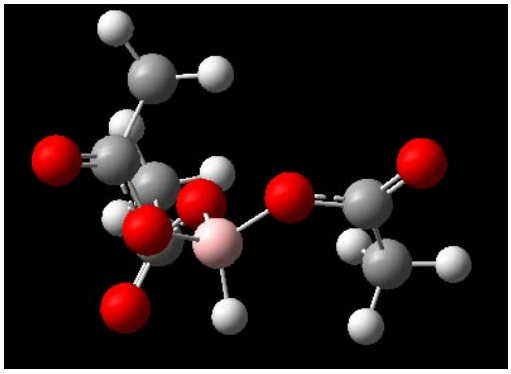
Complex: $HBPh_3^-$, gas phase



3D Coordinates:

B	0.00067	-0.00034	-0.78085
C	1.26272	-0.94702	-0.31170
C	1.60777	-1.23998	1.02435
C	2.09517	-1.53518	-1.28570
C	2.69179	-2.05247	1.36615
H	1.01269	-0.82258	1.83366
C	3.18413	-2.35102	-0.96532
H	1.87185	-1.34025	-2.33314
C	3.49190	-2.61716	0.36996
H	2.91351	-2.24651	2.41546
H	3.79409	-2.78010	-1.76039
H	4.33799	-3.25137	0.63050
C	-1.45138	-0.61973	-0.31461
C	-1.87045	-0.79439	1.02104
C	-2.38638	-1.02087	-1.29047
C	-3.11710	-1.32575	1.36105
H	-1.20413	-0.50741	1.83157
C	-3.63836	-1.55504	-0.97192
H	-2.11238	-0.90580	-2.33770
C	-4.01484	-1.71230	0.36311
H	-3.38971	-1.43897	2.41022
H	-4.32240	-1.84853	-1.76830
H	-4.98799	-2.12687	0.62209
C	0.18894	1.56562	-0.30999
C	0.24580	2.01122	1.02728
C	0.30788	2.57940	-1.28223
C	0.40811	3.35536	1.37232
H	0.16164	1.28738	1.83511
C	0.47099	3.92960	-0.95860
H	0.26987	2.28832	-2.33050
C	0.52267	4.32963	0.37790
H	0.44577	3.64419	2.42258
H	0.55777	4.67178	-1.75227
H	0.64937	5.37884	0.64070
H	0.00253	0.00005	-2.01107

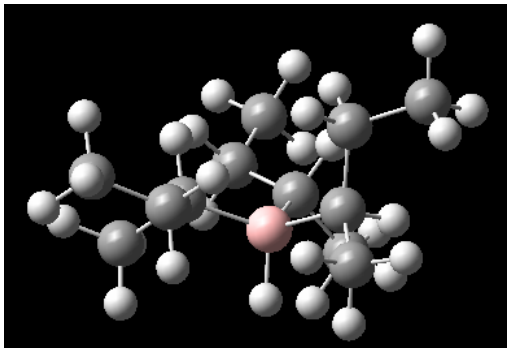
Complex: $HB(OAc)_3^-$, gas phase



3D Coordinates:

B	-0.02013	-0.05971	-0.79155
O	-1.09226	-1.07989	-0.93858
O	1.18768	-0.78323	-0.24160
O	-0.38067	0.96249	0.24498
C	2.37047	-0.20571	-0.14421
C	-0.93955	2.12988	-0.03131
C	-1.62932	-1.87384	-0.02385
O	2.64445	0.95442	-0.40691
O	-1.42165	2.48150	-1.09348
O	-2.50436	-2.67641	-0.31722
C	-0.91931	3.04154	1.19374
H	0.11875	3.24309	1.48159
H	-1.43136	3.98062	0.97205
H	-1.40167	2.54724	2.04486
C	-1.12366	-1.77068	1.41263
H	-0.06805	-2.05487	1.45357
H	-1.18417	-0.73912	1.76939
H	-1.71879	-2.43399	2.04463
C	3.42434	-1.19015	0.36225
H	3.16026	-1.53885	1.36771
H	3.45985	-2.07309	-0.28563
H	4.40391	-0.70769	0.38870
H	0.19856	0.41803	-1.87207

Complex: Selectride (tri-sec-butylborohydride), gas phase

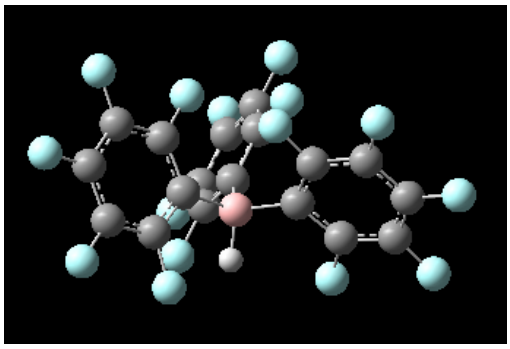


3D Coordinates:

B	0.09617	-0.03463	0.68568
H	0.10827	-0.27514	1.90668
C	-0.72769	1.42433	0.49799
H	0.00175	2.19055	0.82383
C	-0.57120	-1.38616	-0.05484
H	-0.29713	-1.40263	-1.12953
C	1.69069	0.30038	0.20633
H	1.62712	1.07401	-0.58503
C	-0.00965	-2.67974	0.57796
H	-0.28569	-3.60159	0.03859
H	1.08141	-2.66384	0.64309
H	-0.38169	-2.77920	1.60816
C	2.46514	0.94388	1.37513
H	3.44415	1.36980	1.09369
H	1.88339	1.75319	1.83350
H	2.64544	0.20157	2.16617
C	-1.94271	1.61627	1.42964
H	-2.34611	2.64417	1.42803
H	-2.77520	0.95085	1.16648
H	-1.66145	1.37739	2.46291
C	2.54435	-0.82494	-0.42151
H	2.84660	-1.54392	0.35631
H	1.93672	-1.39544	-1.13669
C	3.81345	-0.35454	-1.15592
H	4.50896	0.16503	-0.48498
H	4.36134	-1.19503	-1.60807
H	3.55848	0.34580	-1.96358
C	-2.11609	-1.46037	-0.01715
H	-2.44723	-1.48323	1.03322
H	-2.54057	-0.54404	-0.44138
C	-2.75778	-2.64795	-0.75925
H	-2.48333	-3.61339	-0.31745
H	-3.85630	-2.58552	-0.74962
H	-2.43905	-2.67013	-1.81125
C	-1.07524	1.79935	-0.96286
H	-1.93547	1.20836	-1.31148

H	-0.23818	1.51333	-1.61602
C	-1.38308	3.28610	-1.21519
H	-0.53154	3.91544	-0.92138
H	-1.59421	3.48964	-2.27599
H	-2.25245	3.62744	-0.63868

Complex: $HB(C_6F_5)_3^-$, gas phase



3D Coordinates:

F	-1.1921	2.1346	0.0479
F	-0.7702	4.6647	0.7598
F	1.7315	5.4985	1.5487
F	3.7913	3.7019	1.5859
F	3.4012	1.1622	0.8792
F	1.3593	-0.0417	2.8821
F	0.0816	-1.4728	4.7409
F	-1.9818	-3.1297	4.0464
F	-2.7400	-3.3161	1.4207
F	-1.4591	-1.9201	-0.4654
F	1.2452	-0.2085	-2.9988
F	3.2001	-1.5493	-4.1918
F	5.0545	-2.9369	-2.7220
F	4.8832	-2.9321	0.0077
F	2.9363	-1.5868	1.2441
C	1.0913	1.5038	0.4097
C	0.0901	2.4702	0.4300
C	0.2610	3.8009	0.7936
C	1.5244	4.2248	1.1897
C	2.5695	3.3054	1.2035
C	2.3370	1.9824	0.8261
C	0.0217	-0.9010	1.1091
C	0.3607	-0.8423	2.4639
C	-0.2885	-1.5765	3.4556
C	-1.3368	-2.4225	3.1073
C	-1.7120	-2.5217	1.7719
C	-1.0278	-1.7731	0.8176
C	1.9794	-0.8220	-0.7950
C	2.1279	-0.8625	-2.1805

C	3.1336	-1.5561	-2.8492
C	4.0741	-2.2611	-2.1079
C	3.9813	-2.2564	-0.7194
C	2.9537	-1.5471	-0.1012
B	0.7372	-0.0249	-0.0794
H	-0.1057	0.1079	-0.9466

6) References

(1) Funabiki, K.; Honma, N.; Hashimoto, W.; Matsui, M. *Org. Lett.* **2003**, *5*, 2059-2061.
(2) Jaeger, D. A.; Cram, D. J. *J. Am. Chem. Soc.* **1971**, *93*, 5153-61.
(3) Garcia Ruano, J. L.; Perez-Ossorio, R. *Anales de Quimica (1968-1979)* **1975**, *71*, 93-7.
(4) Perez-Ossorio, R.; Garcia Ruano, J. L.; Pascual Rigau, C. *Afinidad* **1978**, *35*, 200-2.
(5) Boyd, D. R.; Jennings, W. B.; Waring, L. C. *J. Org. Chem.* **1986**, *51*, 992-5; Perez-Ossorio, R.; del Olmo, V. S. *Tetrahedron Lett.* **1961**, 737-43; Arjona, O.; Perez-Ossorio, R.; Perez-Rubalcaba, A.; Plumet, J.; Santesmases, M. J. *J. Org. Chem.* **1984**, *49*, 2624-6.
(6) Yoshida, T.; Harada, K. *Bull. Chem. Soc. Jap.* **1972**, *45*, 3706-10.
(7) Page, P. C. B.; Limousin, C.; Murrell, V. L. *J. Org. Chem.* **2002**, *67*, 7787-7796.
(8) Love, B. E.; Ren, J. *J. Org. Chem.* **1993**, *58*, 5556-7.
(9) Ma, Y.; Lobkovsky, E.; Collum, D. B. *J. Org. Chem.* **2005**, *70*, 2335-2337.
(10) El Abed, R.; Touati, R.; M'Saddak, M.; Ben Hassine, B. *J. Soc. Chim. Tunis.* **2004**, *6*, 139-146.
(11) Abdel-Magid, A. F.; Carson, K. G.; Harris, B. D.; Maryanoff, C. A.; Shah, R. D. *J. Org. Chem.* **1996**, *61*, 3849-3862.
(12) Nugent, T. C.; Ghosh, A. K.; Wakchaure, V. N.; Mohanty, R. R. *Adv. Synth. Catal.* **2006**, *348*, 1289-1299; Alvaro, G.; Savoia, D.; Valentinetti, M. R. *Tetrahedron* **1996**, *52*, 12571-12586; Bolton, R.; Danks, T. N.; Paul, J. M. *Tetrahedron Lett.* **1994**, *35*, 3411-12; Vetter, A. H.; Berkessel, A. *Synthesis* **1995**, 419-22; Alexakis, A.; Gille, S.; Prian, F.; Rosset, S.; Ditrich, K. *Tetrahedron Lett.* **2004**, *45*, 1449-1451; Gracheva, R. A.; Budanova, L. I.; Vsemirnova, E. A.; Potapov, V. M. *Zhurnal Organicheskoi Khimii* **1973**, *9*, 1235-9.
(13) Pauling, L. C. *The Nature of the Chemical Bond and the Structure of Molecules and Crystals. An Introduction to Modern Structural Chemistry. 3rd ed*, 1960.
(14) Rokob, T. A.; Hamza, A.; Stirling, A.; Papai, I. *J. Am. Chem. Soc.* **2009**, *131*, 2029-2036; Heiden, Z. M.; Stephan, D. W. *unpublished results.*
(15) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; J. A. Montgomery, J.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; J. Tomasi; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.;

Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A.; Gaussian, Inc.: Wallingford CT, 2004.