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]

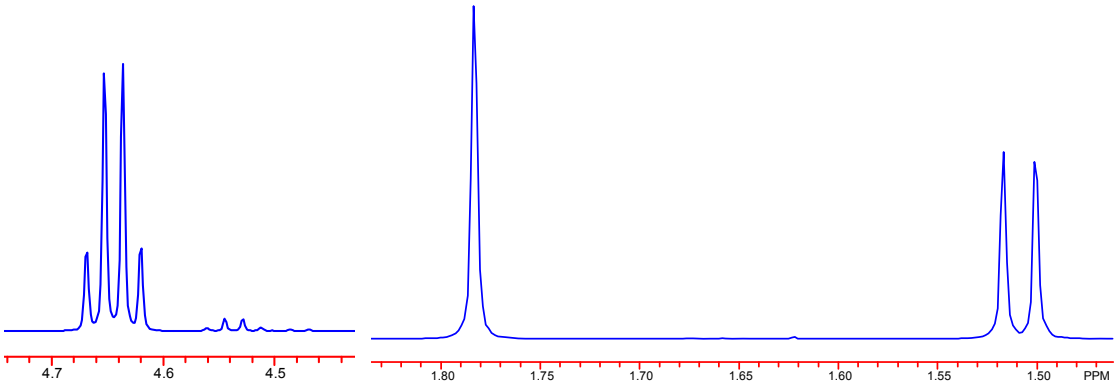

Figure S1. ^{1}H NMR spectrum (left) benzylic region and (right) aliphatic region of imine **3** in C_6D_6.

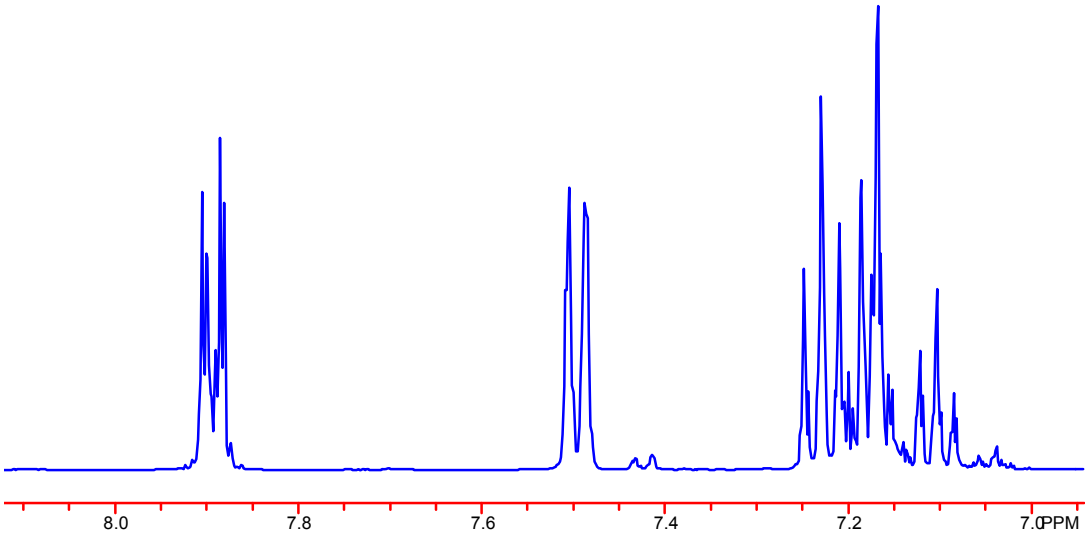

Figure S2. ^{1}H NMR spectrum of the phenyl region of imine **3** in C_6D_6.

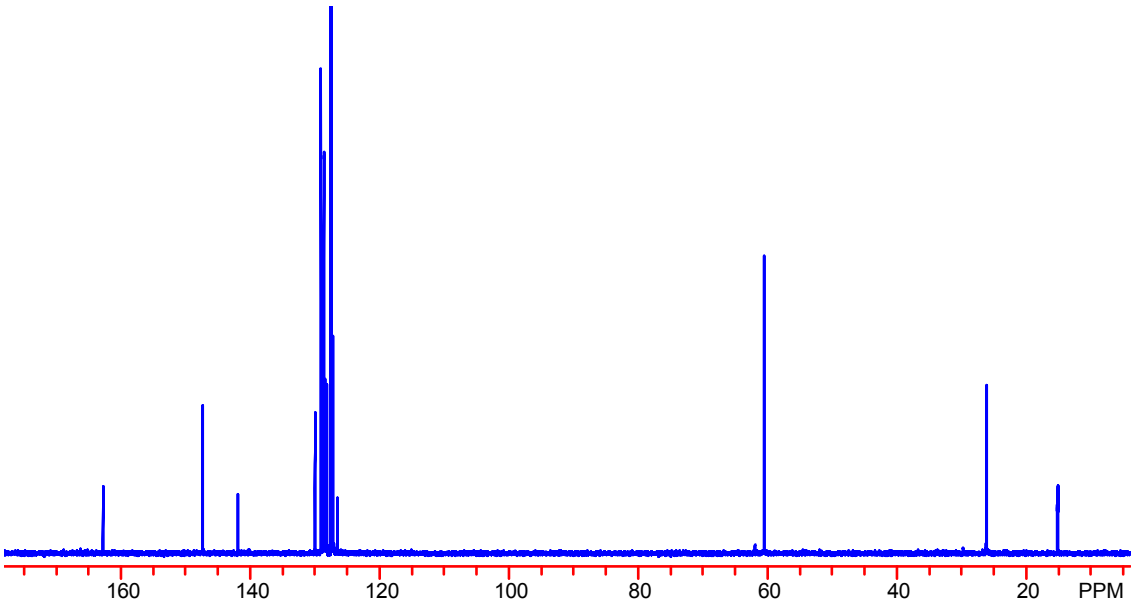

Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum of imine **3** in C_6D_6.

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]

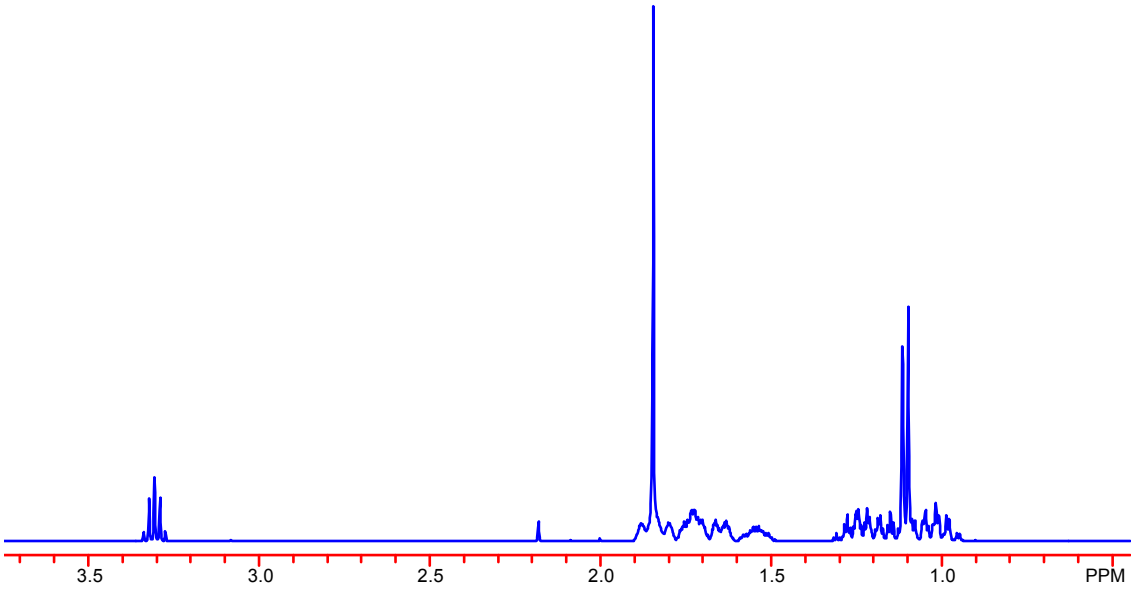

Figure S4. ^{1}H NMR spectrum of the aliphatic and benzylic region of imine **2** in C_6D_6.

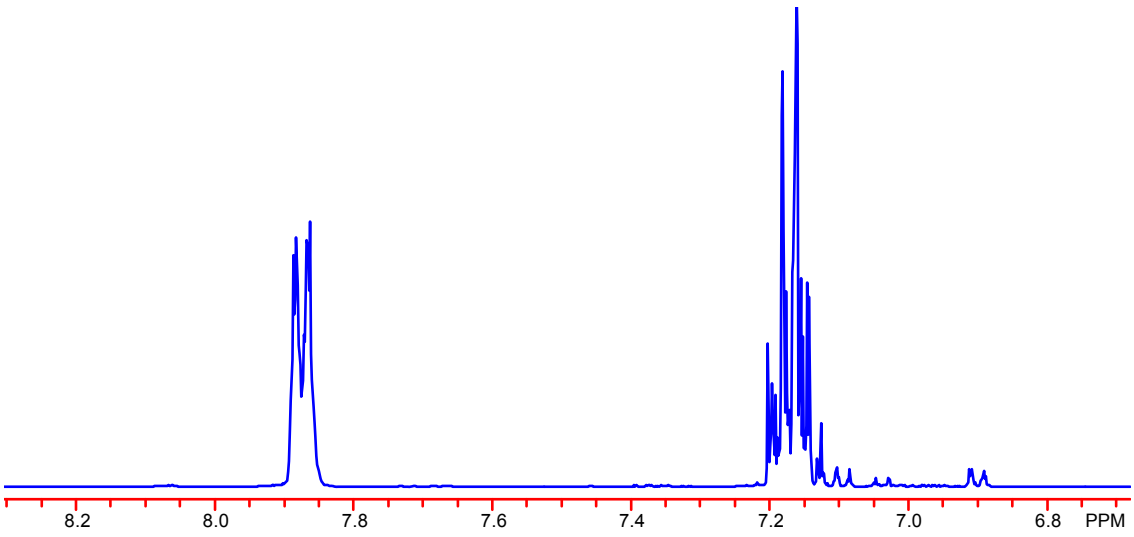

Figure S5. ^{1}H NMR spectrum of the phenyl region of imine **2** in C_6D_6.

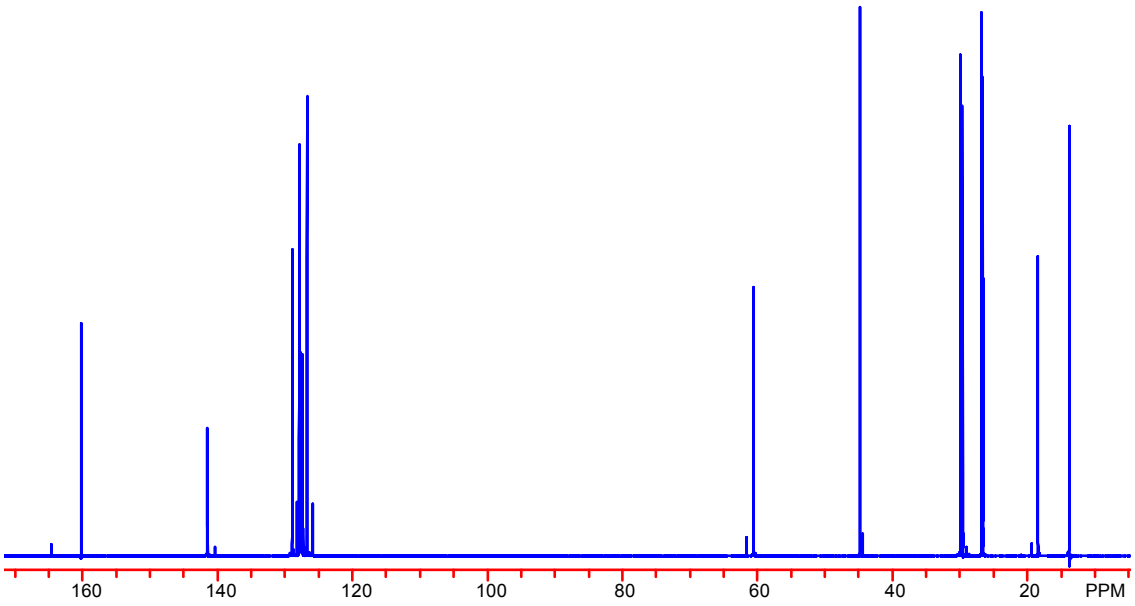

Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of imine **2** in C_6D_6.

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]

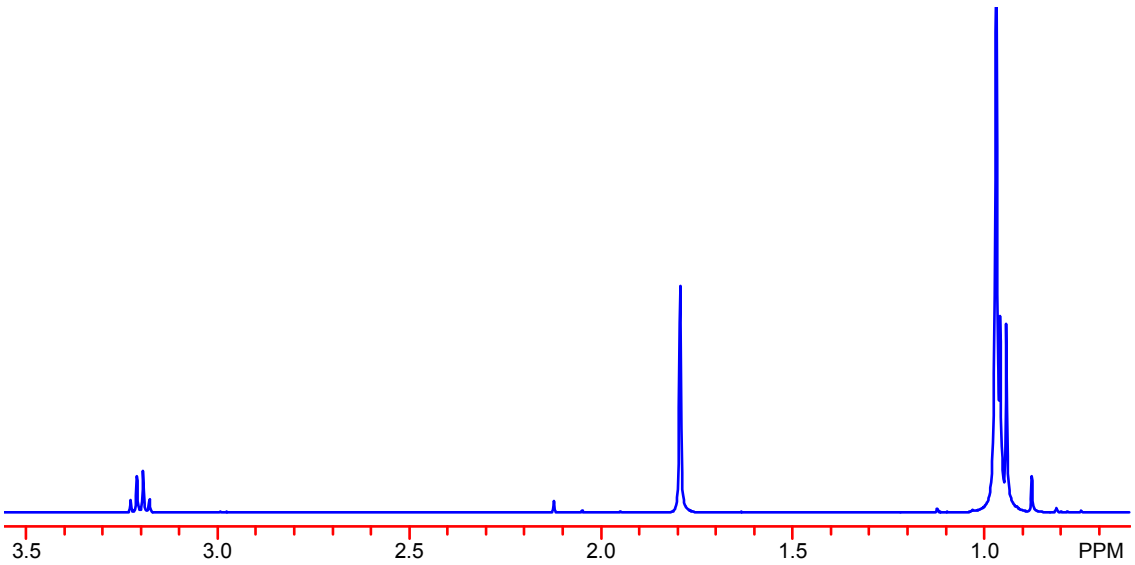

Figure S7. ^{1}H NMR spectrum of the aliphatic and benzylic region of imine **1** in C_6D_6.

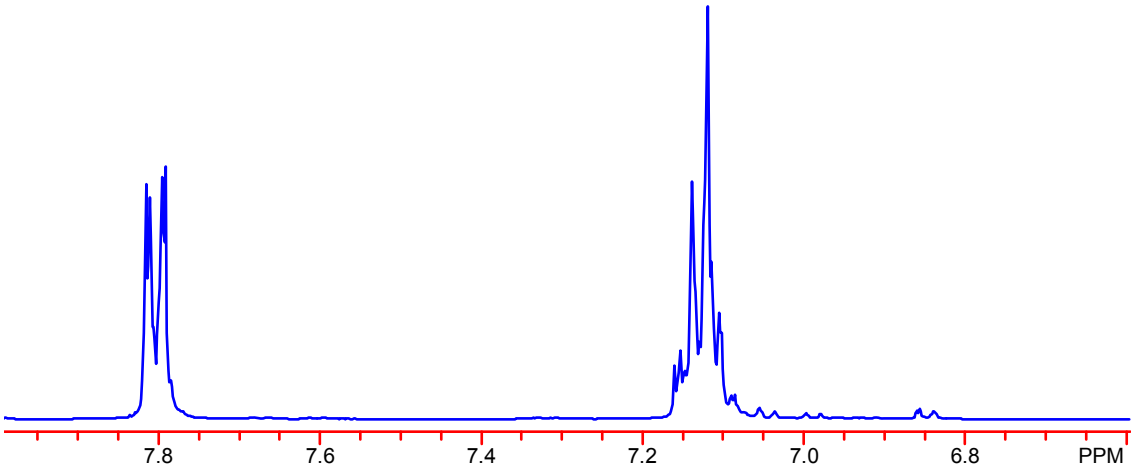

Figure S8. ^{1}H NMR spectrum of the phenyl region of imine **1** in C_6D_6.

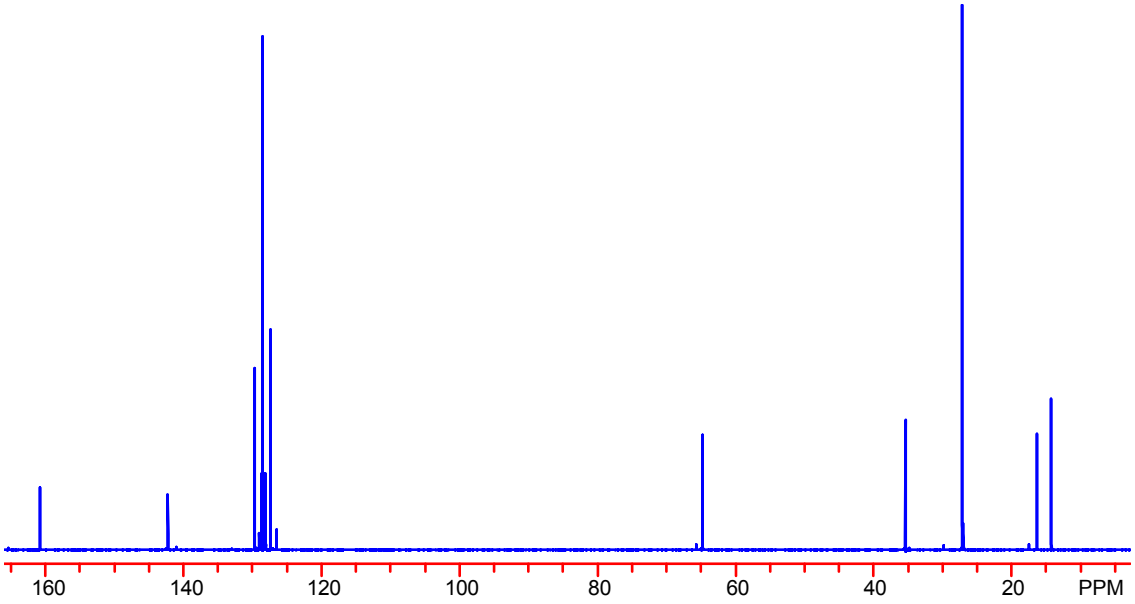

Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum of imine **1** in C_6D_6.

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]

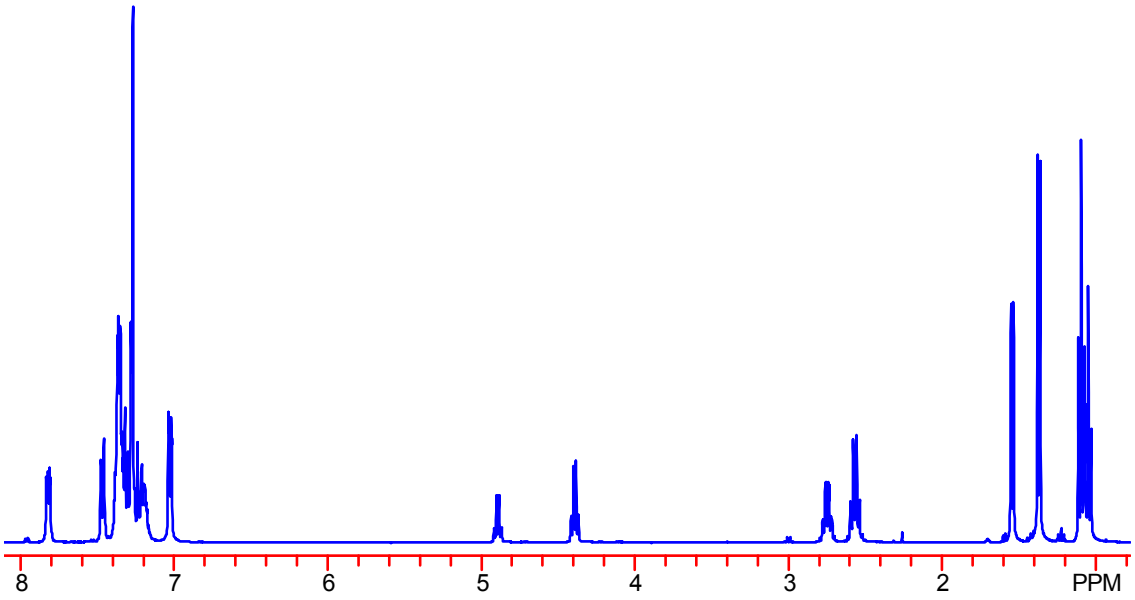

Figure S10. ^{1}H NMR spectrum of imine **4** in $CDCl_3$.

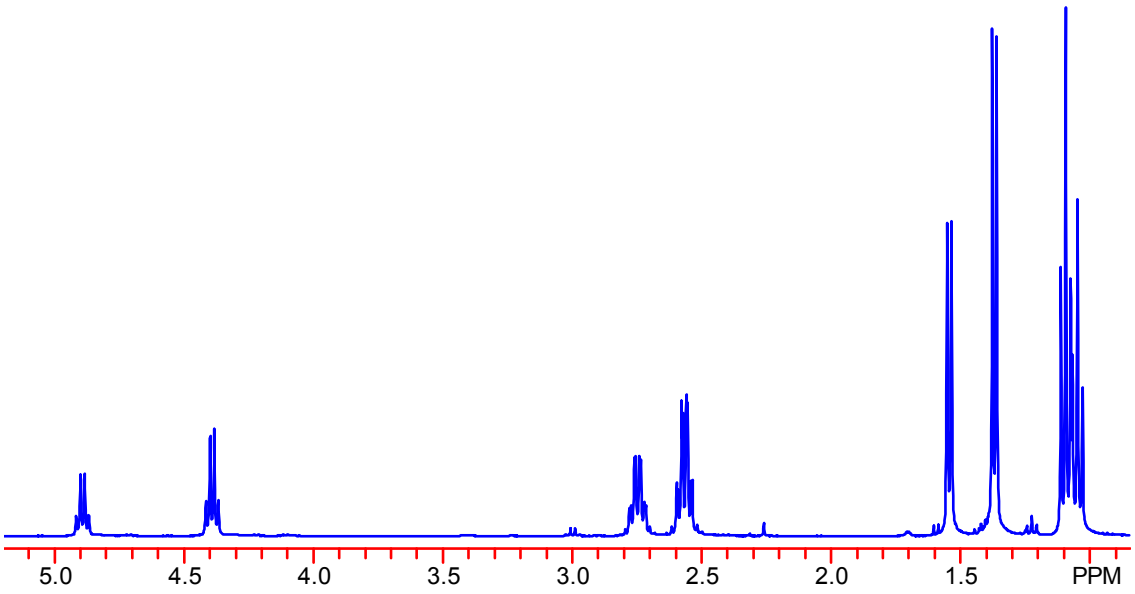

Figure S11. ^{1}H NMR spectrum of aliphatic and benzylic region of imine **4** in $CDCl_3$.

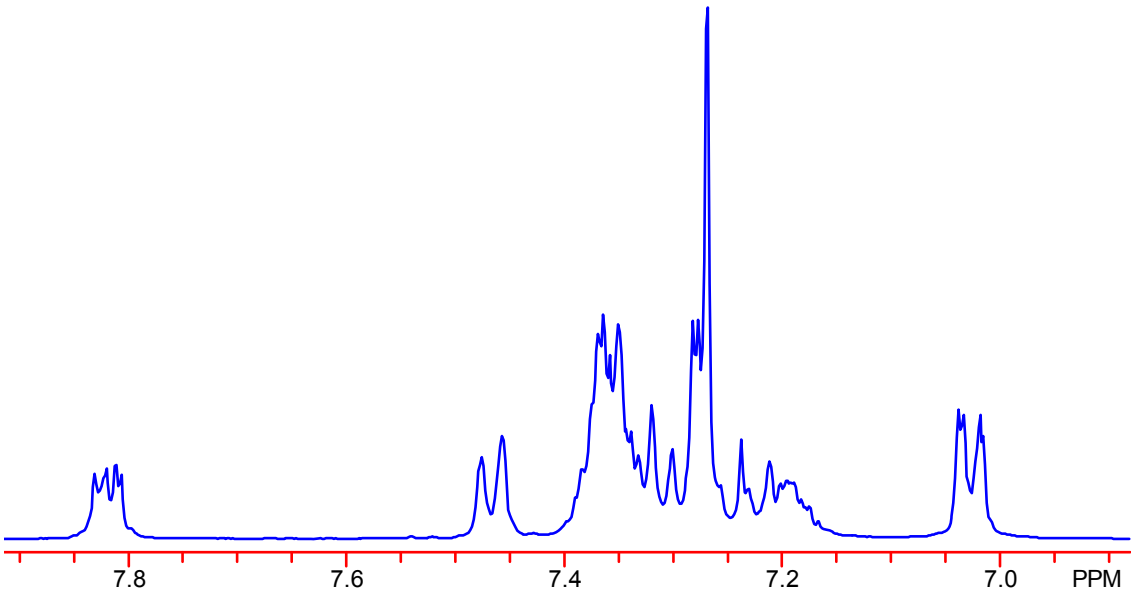

Figure S12. ^{1}H NMR spectrum of the phenyl region of imine **4** in $CDCl_3$.

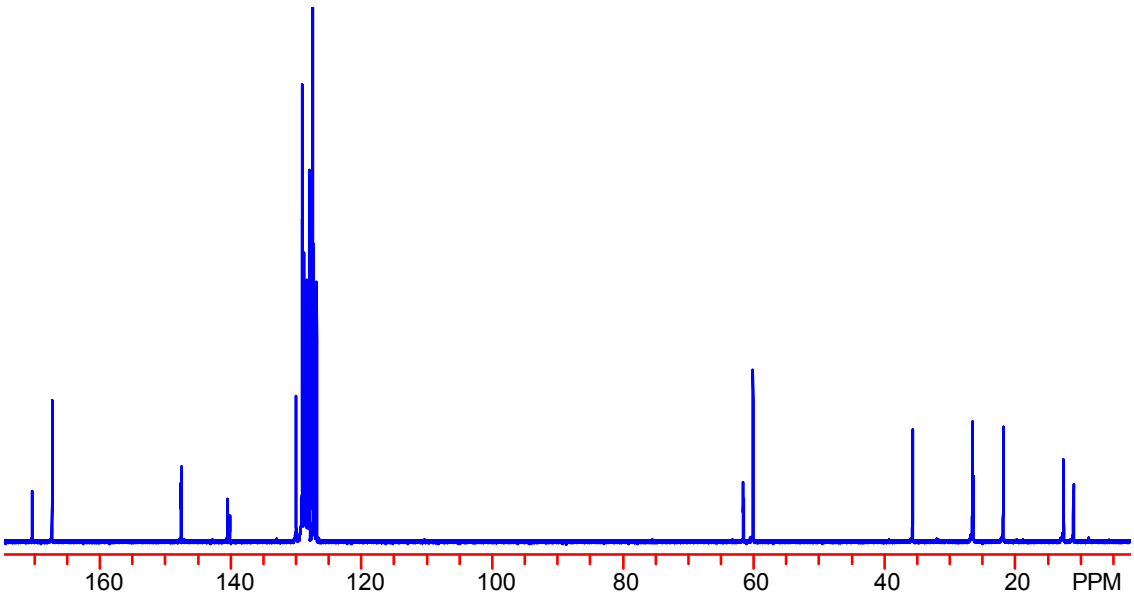

Figure S13. $^{13}C\{^{1}H\}$ NMR spectrum of imine **4** in C_6D_6.

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]

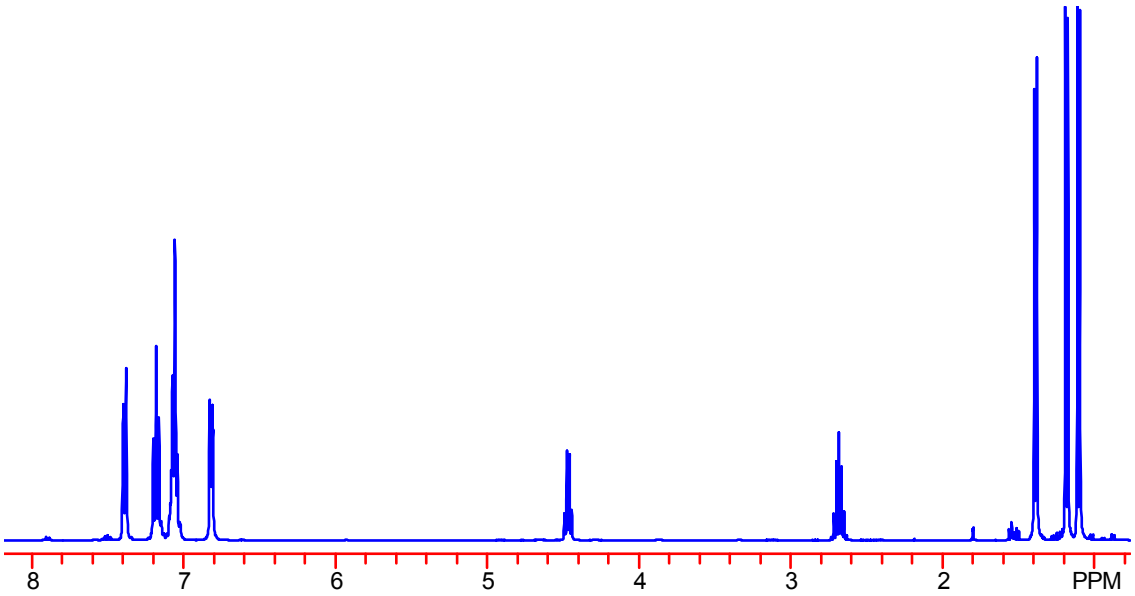

Figure S14. ^{1}H NMR spectrum of imine **5** in $CDCl_3$.

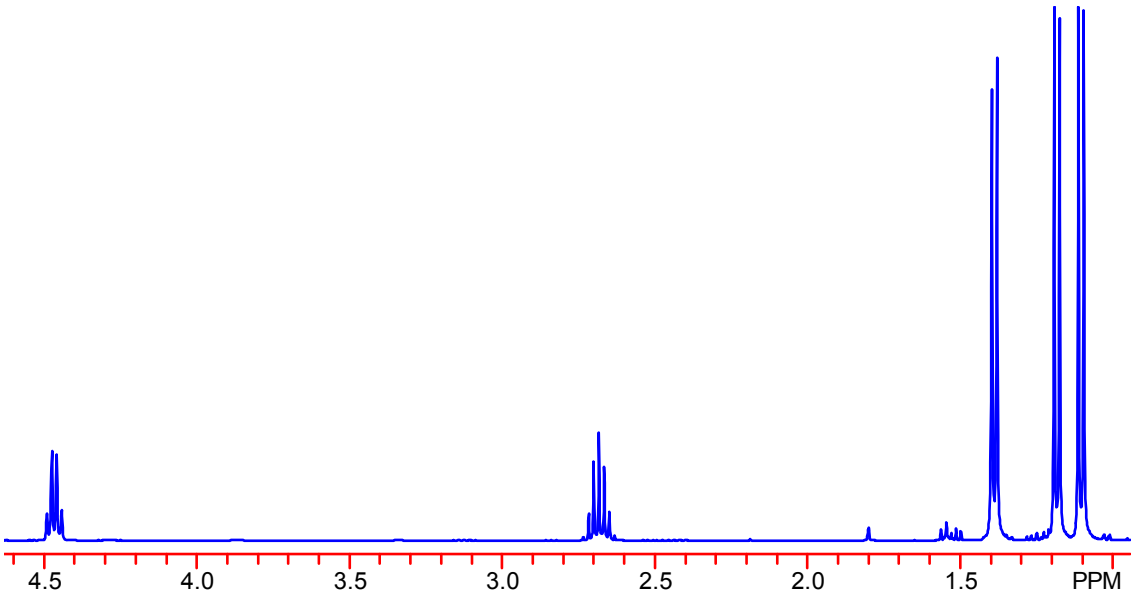

Figure S15. ^{1}H NMR spectrum of aliphatic and benzylic region of imine **5** in $CDCl_3$.

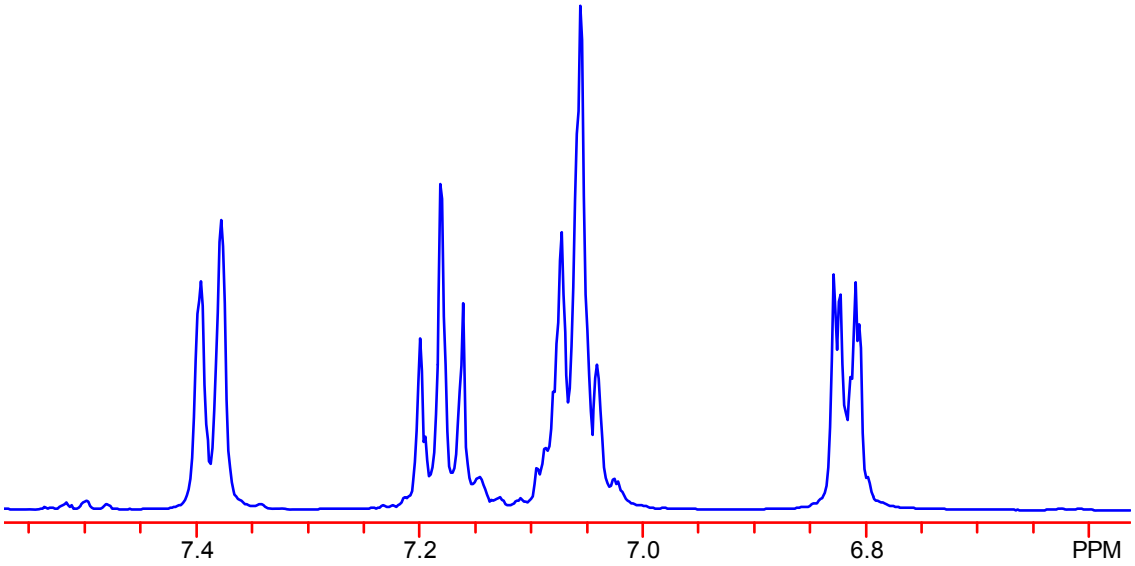

Figure S16. ^{1}H NMR spectrum of the phenyl region of imine **5** in $CDCl_3$.

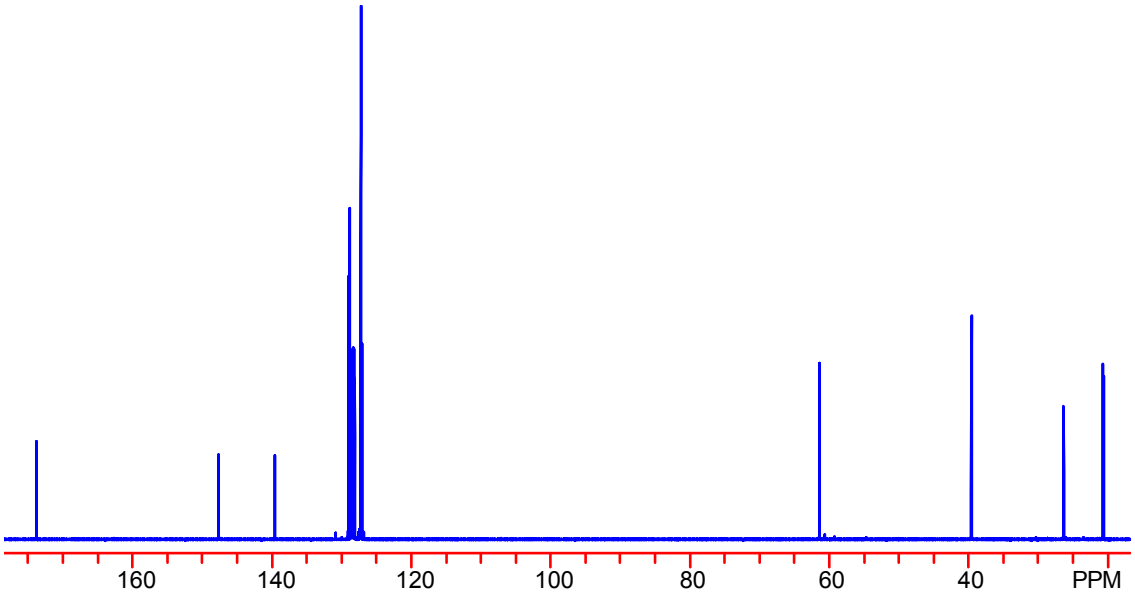

Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum of imine **5** in C_6D_6.

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,