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SUPPLEMENTARY INFORMATION

Development and mechanistic investigation of the dehydrogenation of alcohols with an iron(III) salen catalyst

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General experimental methods

NMR spectra were recorded at 400 MHz for ^{1}H-NMR and 101 MHz for ^{13}C-NMR on a Bruker Ascend 400 MHz spectrometer. Chemical shift (δ)-values are reported in ppm relative to the residual solvent signal in $CDCl_3$ (δ_H 7.26 ppm, δ_C 77.16 ppm) while coupling constants (J) are given in Hz. Reactions were monitored by thin-layer chromatography (TLC) on Merck Silica 60 F254 aluminium sheets. GC-MS was carried out on a Shimadzu GCMS-QP2010S instrument fitted with an Equity 5, 30 m × 0.25 mm × 0.25 µm column. Ionisation was performed by electronic impact (EI, 70 eV) and helium as the carrier gas. TLC plates were visualized under UV light (254 nm) or by using adequate stains. LC-MS was carried out on a Waters ACQUITY UPLC system equipped with PDA and SQD2 electrospray MS detector. Column: Thermo accucore C18 (2.6 µm, 2.1 × 50 mm). Column temp: 50 °C. Flow rate: 0.6 mL/min. Solvent A: 5 mM NH_4OAc in water, Solvent B: 5 mM NH_4OAc in acetonitrile/water 95/5. All commercial solvents and reagents were purchased from Sigma Aldrich or Strem Chemicals and used as supplied. Toluene was obtained by using a Pure Solv™ Micro solvent purification system and degassed before being used. The water content of the solvents and liquid reagents was measured on a Karl-Fischer apparatus. All experiments were carried out under a nitrogen flow using Schlenk flask techniques.

General procedure for imine synthesis

Iron complex **A** (20.5 mg, 0.05 mmol) and KO*t*Bu (22.5 mg, 0.2 mmol) were placed in an oven-dried tube, whereafter it was placed in a Radley carousel. Vacuum was applied and the flask was then filled with nitrogen gas (repeated three times). Anhydrous toluene (2 mL) was added and the reaction mixture was heated to reflux. Alcohol (1 mmol), amine (1 mmol), and tetradecane (0.1 mL as an internal standard in optimization and mechanistic studies) were added by a syringe, and the reaction was refluxed with stirring under a flow of nitrogen for 48 h. The mixture was cooled to room temperature and the catalyst and the inorganic base were removed by filtration using a nylon syringe filter (pore size: 0.22 µm) or by filtration on a short Celite® pad (in both cases the filter was washed with Et_3N (3 × 5 mL) afterwards). The filtrate was concentrated *in vacuo* to afford the desired imine.

Gas evolution

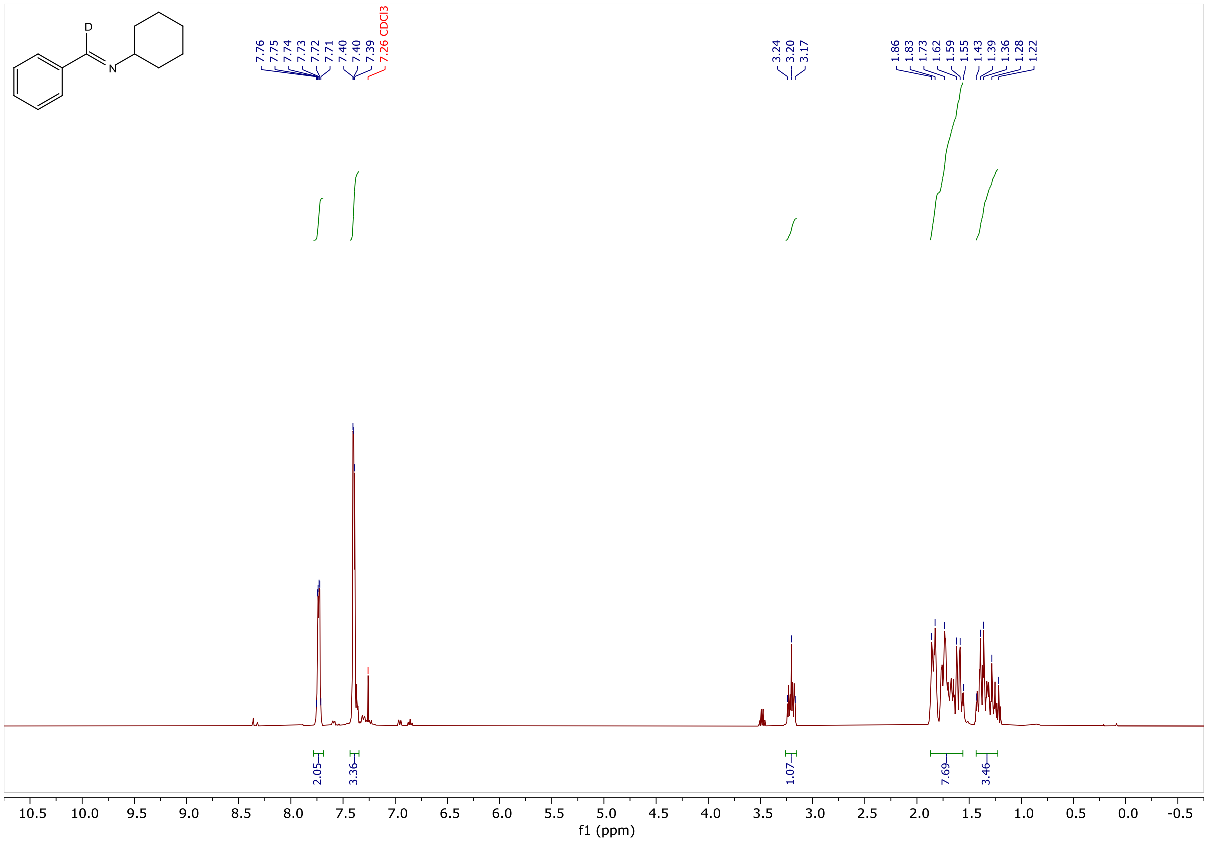
Catalyst **A** (20.55 mg, 0.05 mmol) and KO*t*Bu (22.44 mg, 0.2 mmol) were placed in an oven-dried Schlenk tube. The tube was subjected to vacuum and then filled with nitrogen gas (repeated three times). Anhydrous and freshly degassed toluene (2 mL) was added and the reaction mixture was heated to reflux. Benzyl alcohol (108 mg, 1 mmol), cyclohexylamine (99 mg, 1 mmol), and tetradecane (0.1 mL as internal standard) were added by a syringe. The Schlenk tube was connected by a tube ending with a needle at the bottom of a burette filled with water. The bottom of the burette was further connected to a water reservoir with a large surface area. At the end of the reaction, 17 mL of gas was collected, corresponding to 0.7 mmol of molecular hydrogen according to the ideal gas law (70% H_2 yield at a laboratory temperature of 25 °C). A GC sample of the reaction mixture showed 86% yield of the imine.

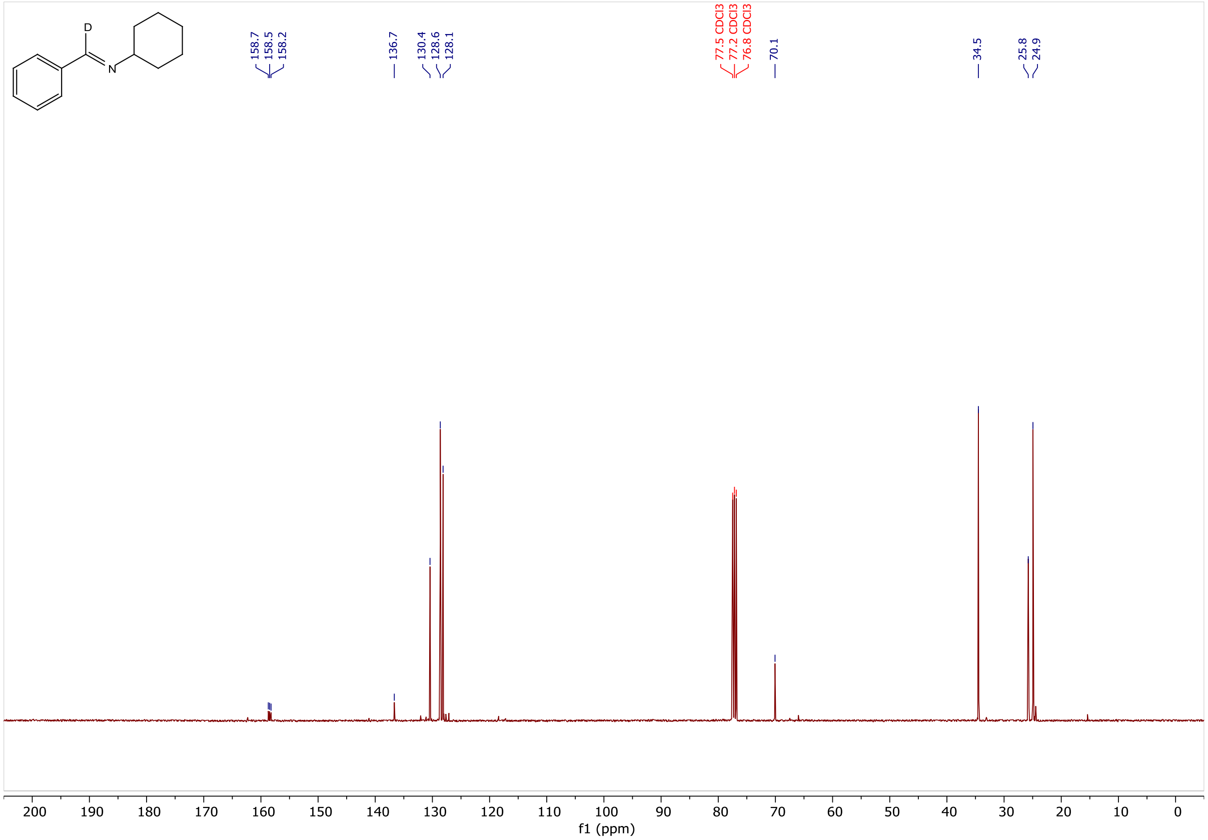
Identification of the liberated gas

Catalyst **A** (41.1 mg, 0.1 mmol) and KO*t*Bu (44.88 mg, 0.4 mmol) were placed in an oven-dried Schlenk tube. The tube was subjected to vacuum and then filled with nitrogen gas (repeated three times). Anhydrous and freshly degassed toluene (4 mL) was added and the reaction mixture was heated to reflux. Benzyl alcohol (216 mg, 2 mmol), cyclohexylamine (198 mg, 2 mmol), and tetradecane (0.2 mL as internal standard) were added by a syringe. The Schlenk tube was connected by a tube ending with a needle at the bottom of a burette filled with water. The bottom of the burette was further connected to a water reservoir with a large surface area. At the end of the reaction, 25 mL of gas was collected. The top of the burette was connected to a three cock valve. The ground glass joint of the valve was connected with a 25 mL round-bottom flask containing palladium on activated carbon (5 wt%) (20 mg), diphenylacetylene (45 mg, 0.25 mmol), and 3 mL of methanol. The system was subjected to a gentle vacuum that was applied through the third way of the valve and subsequently filled with the collected gas in the burette. The procedure was repeated three times with an interval of 3 h each and after the last one, the reaction was left to stir overnight. After 20 h, a GC sample was taken from the round bottom flask, which showed that diphenylacetylene had been completely reduced to 1,2-diphenylethane.

Deuterium/hydrogen scrambling experiment

Benzyl alcohol-*α,α*-d_2 (110 mg, 1.0 mmol) and cyclohexylamine (99.0 mg, 1.0 mmol) were placed in an oven-dried tube and subjected to the imination reaction following the general procedure for imine synthesis. Examination of the ^{1}H-NMR spectrum revealed that the product imine was obtained as a pure deuterium-labelled imine and no hydrogen/deuterium scrambling had occurred. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.18 – 1.45 (m, 3H), 1.53 – 1.89 (m, 7H), 3.15 – 3.26 (m, 1H), 7.35 – 7.43 (m, 3H), 7.69 – 7.78 (m, 2H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ 24.9, 25.8, 34.5, 70.1, 128.1, 128.6, 130.4, 136.7, 158.5 (t, $^1J_{CD}$ = 24.0 Hz). MS (EI) *m/z*: 188 $[M]^{\bullet+}$.





Catalyst deuterium labelling

Catalyst **A** (20.5 mg, 0.05 mmol) and KO*t*Bu (22.5 mg, 0.2 mmol) were placed in an oven-dried tube, whereafter it was placed in a Radley carousel. Vacuum was applied and the flask was then filled with nitrogen gas (repeated three times). Anhydrous toluene (2 mL) was added and the reaction mixture was heated to reflux. Benzyl alcohol (108 mg, 1.0 mmol) and cyclohexylamine (99.0 mg, 1.0 mmol) were added by a syringe. Just after the substrates have been added, an LC-MS sample was taken from the reaction mixture, which showed the peak corresponding to [M-Cl]$^+$of catalyst **A** (*m/z*: 376) with a retention time of 0.81 minutes (**Figure S1** a). After one hour, another LC-MS sample was taken from the reaction mixture, which showed the formation of a new species characterized by a peak with a retention time of 1.04 minutes and *m/z*: 380 (**Figure S1** b). The retention time and mass of this peak are consistent with the [M-Cl]$^+$ species obtained by a sample of catalyst **F** (*m/z*: 380) retention time of 1.05 minutes (**Figure S1** c).

A similar experiment was performed with benzyl alcohol-*α,α*-*d*$_2$ (110 mg, 1.0 mmol) and cyclohexylamine (99.0 mg, 1.0 mmol) following the general procedure for the imine synthesis. After one hour, an LC-MS sample was taken from the reaction mixture. The chromatogram showed the formation of a species characterized by a peak with a retention time of 1.10 min and *m/z*: 382.

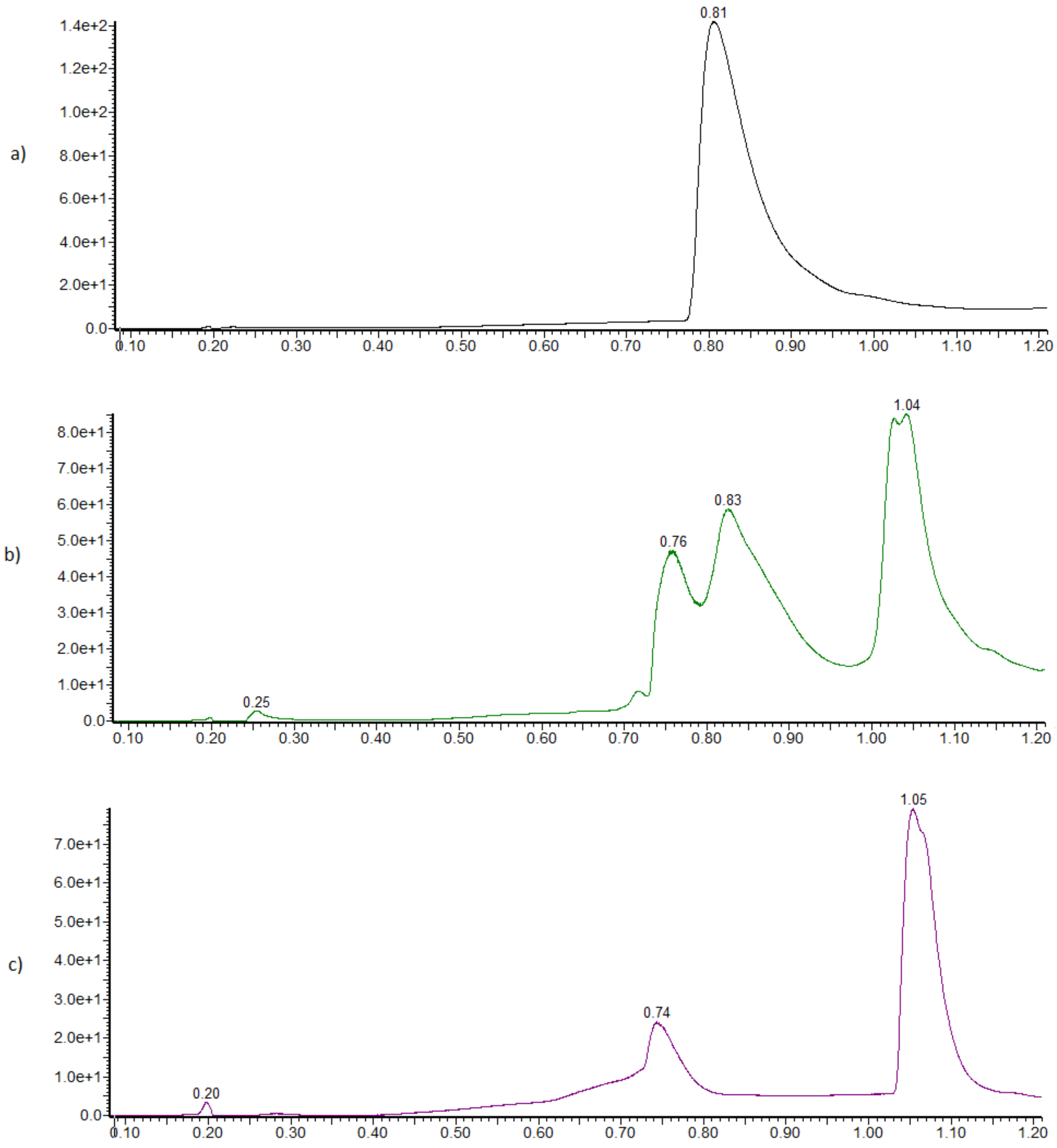


Figure S1. a) LC-MS chromatogram of the reaction mixture at t = 0. b) LC-MS chromatogram of the reaction mixture at t = 1 h. c) LC-MS chromatogram of the isolated catalyst **F**.

Determination of kinetic isotope effect

Benzyl alcohol (108 mg, 1.0 mmol), cyclohexylamine (99 mg, 1.0 mmol), and *n*-tetradecane (0.13 mL as internal standard) were placed in an oven-dried tube and subjected to the imination reaction following the general procedure for imine synthesis. Over 5 hours, a sample of 50 µL was taken out every 30 minutes, transferred to a GC vial, diluted to 1 mL with diethyl ether and then subjected to GC-MS analysis to follow the formation of *N*-benzylidenecyclohexylamine and determine the initial rate (r). The same procedure was repeated using benzyl alcohol-α,α- d_2 (110 mg, 1.0 mmol) instead of nondeuterated benzyl alcohol. The initial rate for the transformation of benzyl alcohol was $r_H = 1.51 \cdot 10^{-4}$. The initial rate for the reaction of benzyl alcohol-α,α-d_2 was $r_D = 1.13 \cdot 10^{-4}$. The isotope effect was $k_H/k_D = 1.34$ (Figure S2). The determination of the KIE was repeated three months later with new batches of substrates and complex **A**. In this case, the initial rate for the transformation of benzyl alcohol was $r_H = 5.22 \cdot 10^{-4}$ and the initial rate for the reaction of benzyl alcohol-α,α-d_2 $r_D = 3.85 \cdot 10^{-4}$. Thus, the isotope effect was $k_H/k_D = 1.36$ (Figure S3).

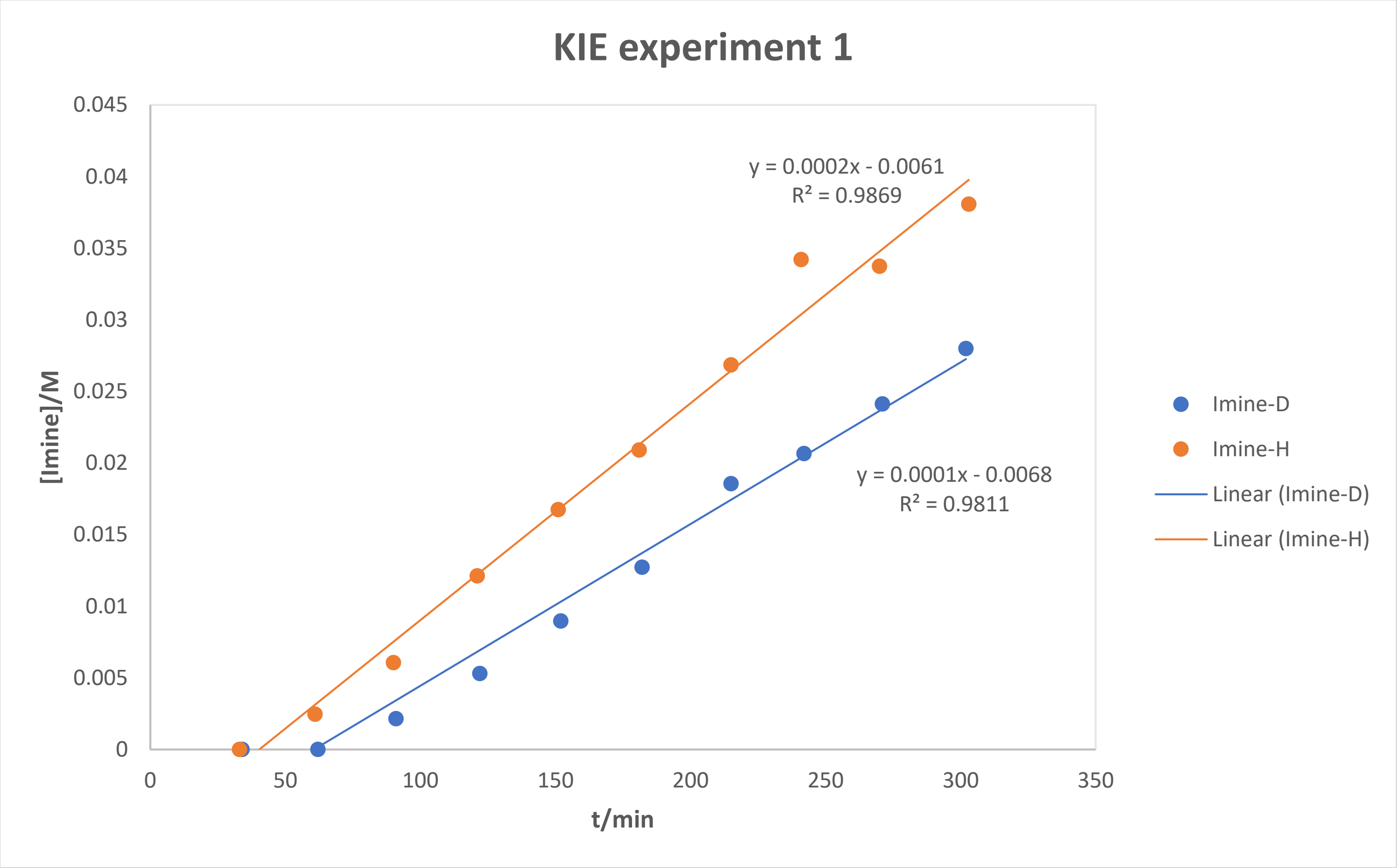


Figure S2. First initial rate plots for iminations with complex **A**.

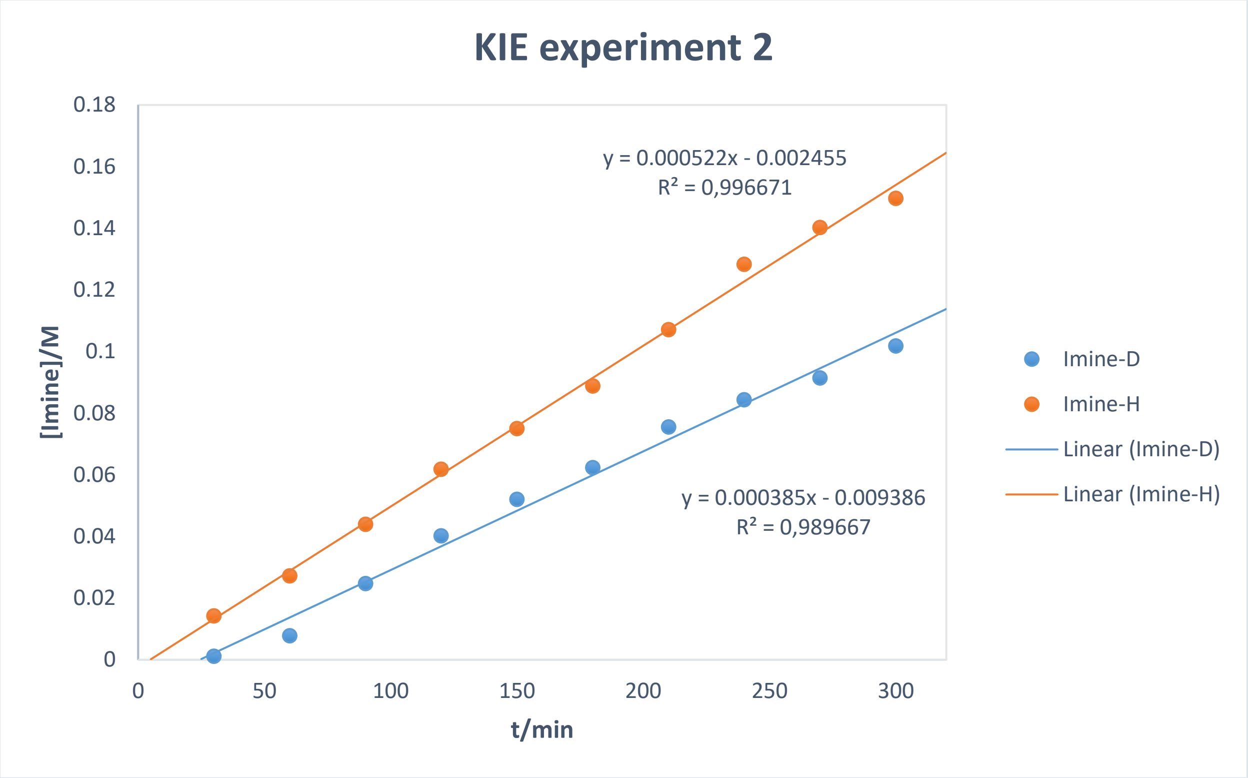
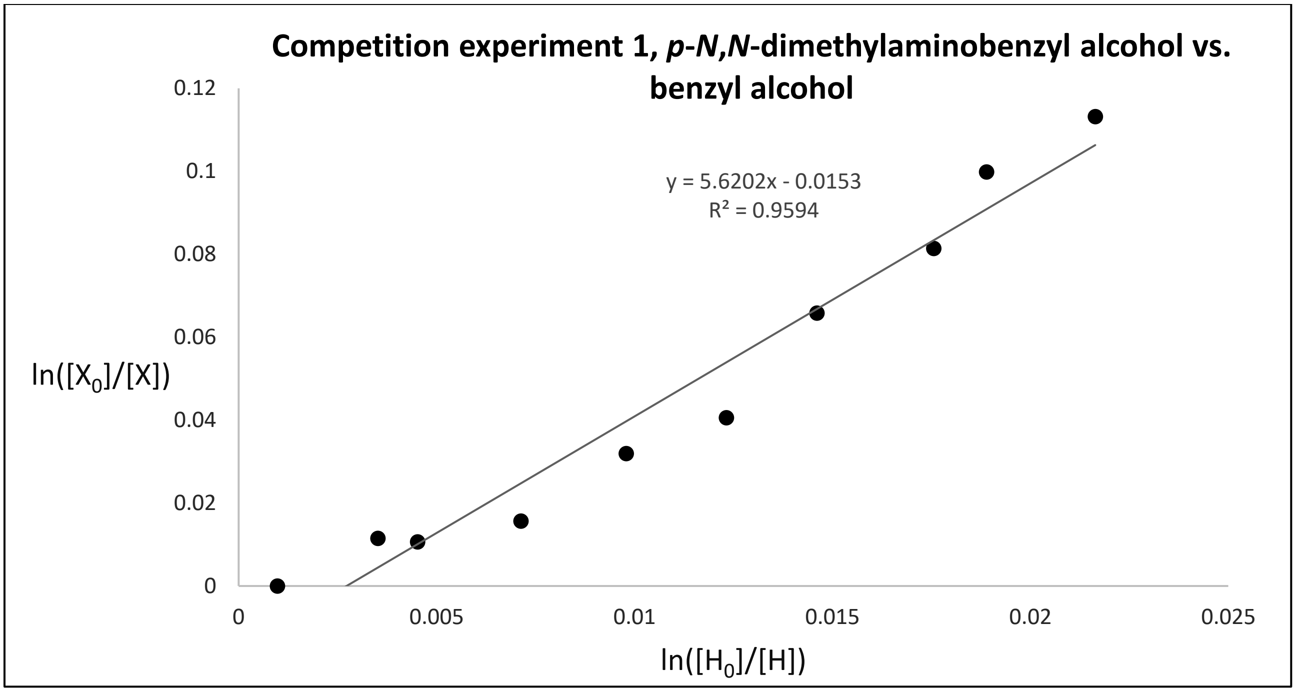


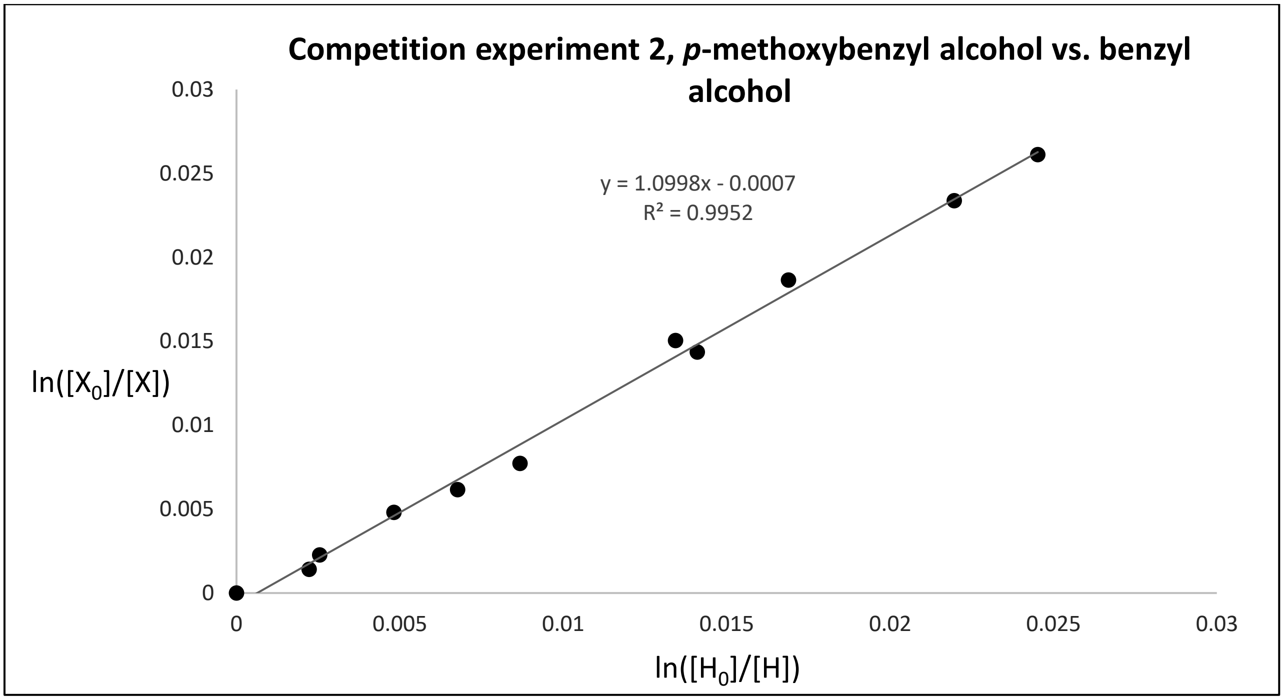
Figure S3. Second initial rate plots for iminations with complex **A**.

Hammett study

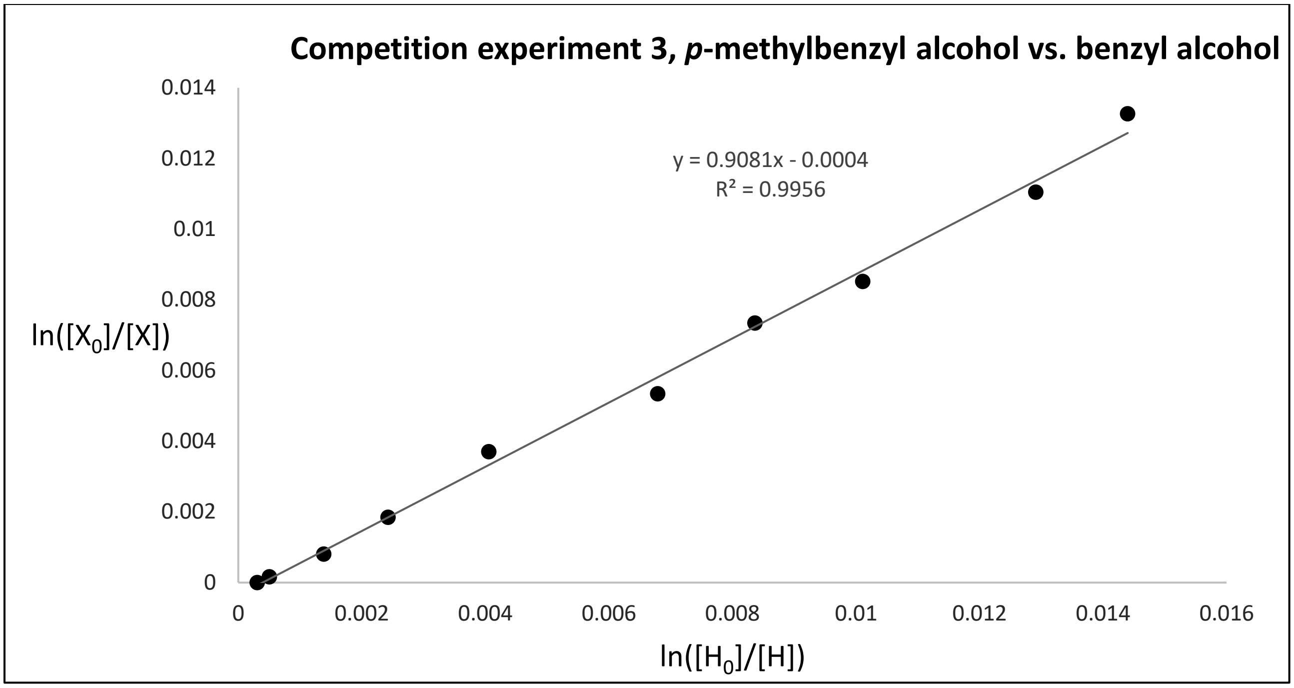
Benzyl alcohol (54 mg, 0.5 mmol), 4-substituted benzyl alcohol (0.5 mmol) and cyclohexylamine (99 mg, 1.0 mmol) were placed in an oven-dried tube and subjected to the imination reaction following the general procedure for imine synthesis. For 5 h, a sample of 50 μL was taken out every 30 minutes, transferred to a GC vial, diluted to 1 mL with diethyl ether and then subjected to GC-MS analysis to follow the formation of *N*-benzylidenecyclohexylamine and the 4-substituted *N*-benzylidenecyclohexylamine to determine k_{rel}.

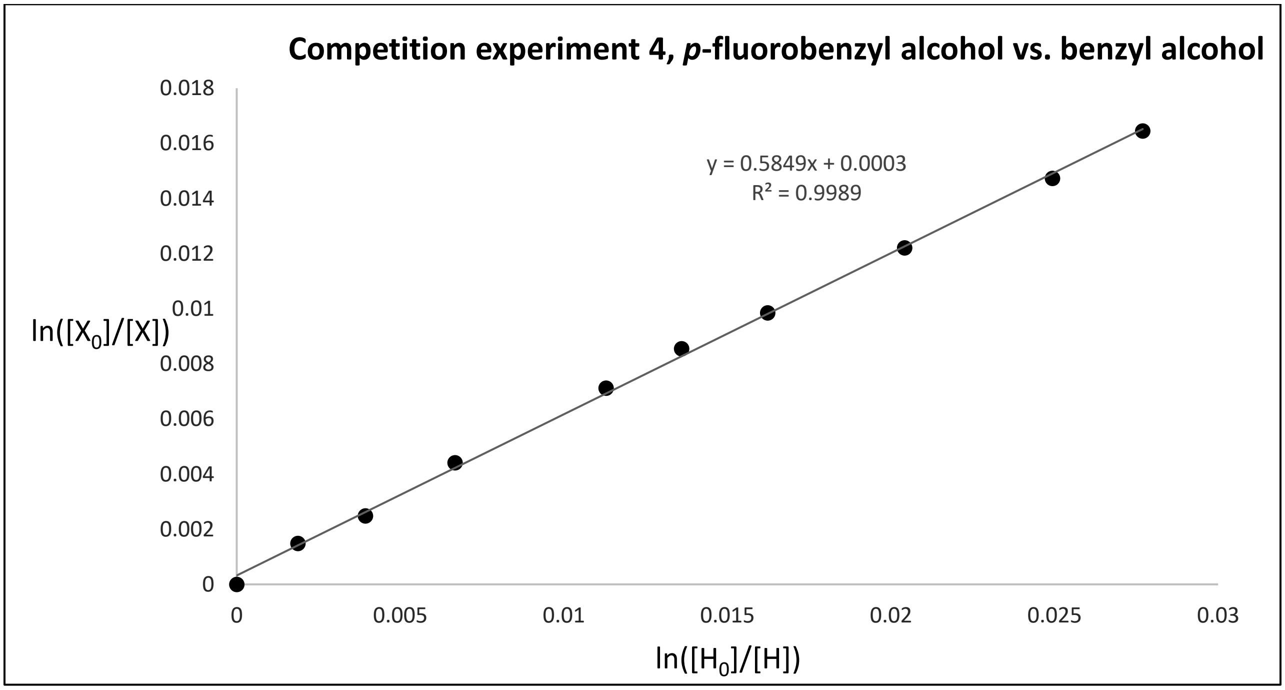


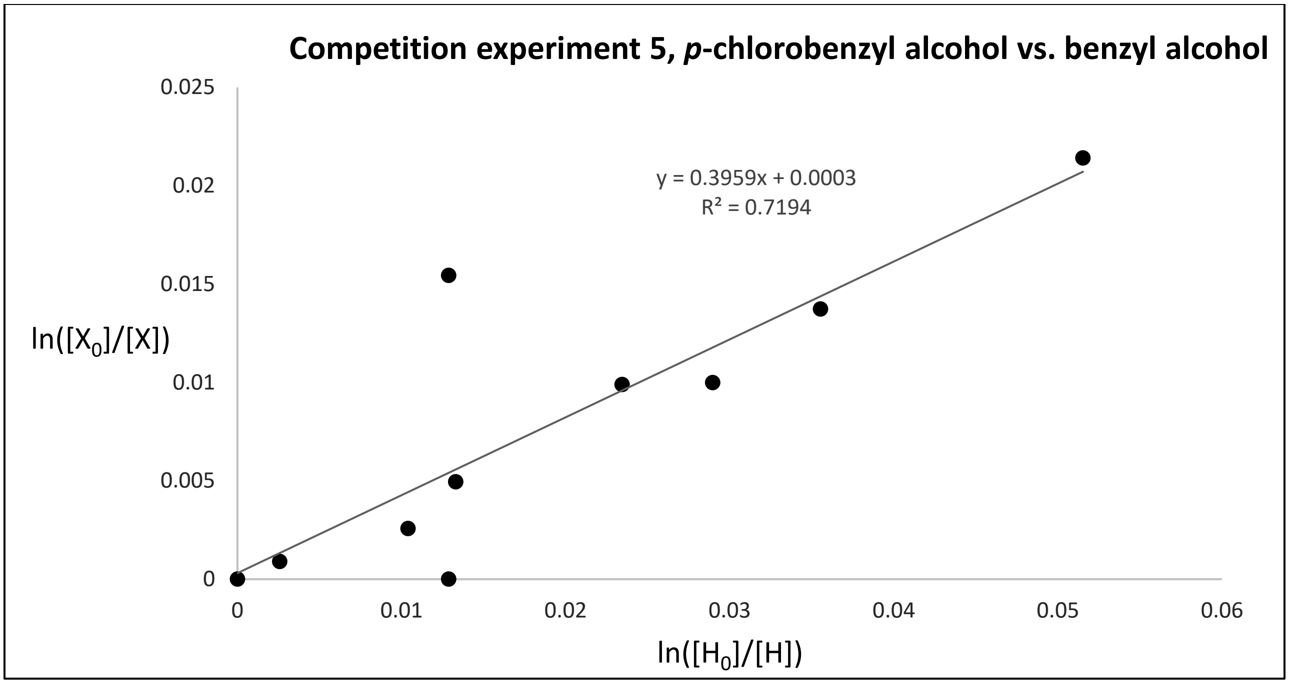
Competition experiment 1, *p*-*N*,*N*-dimethylaminobenzyl alcohol vs. benzyl alcohol

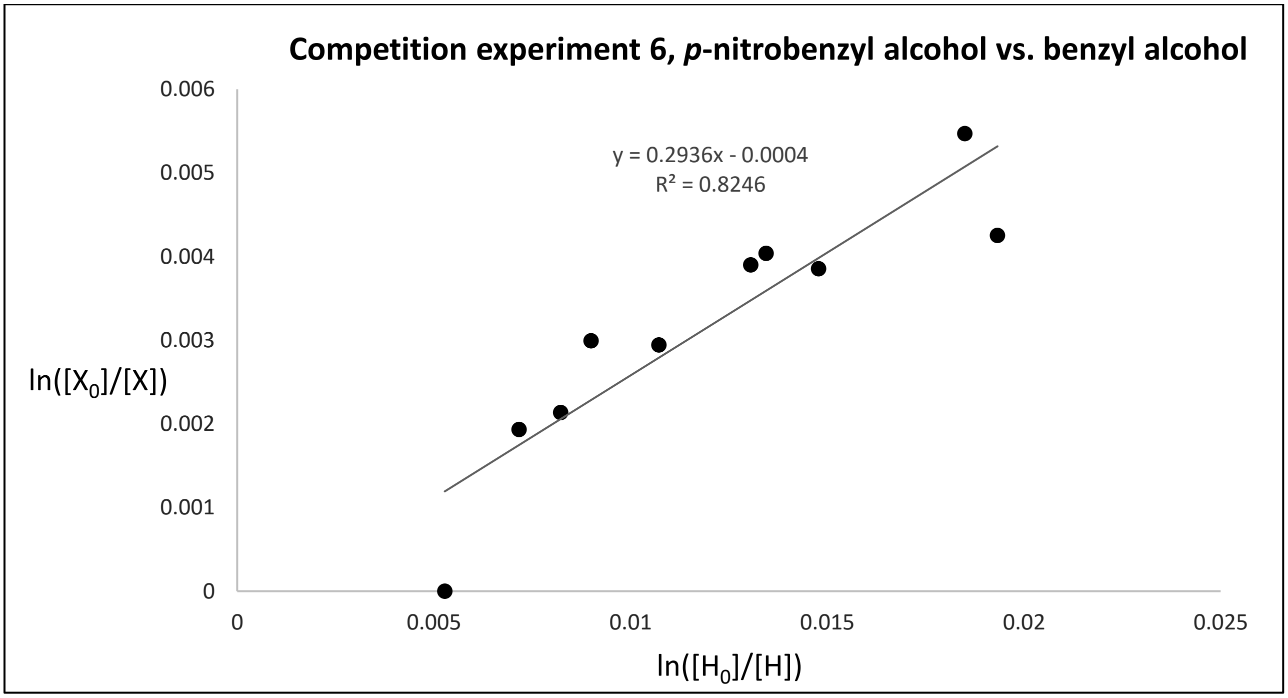


Competition experiment 2, *p*-methoxybenzyl alcohol vs. benzyl alcohol

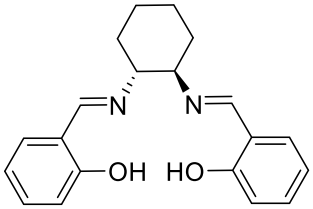

Competition experiment 3, *p*-methylbenzyl alcohol vs. benzyl alcohol
y = 0.9081x - 0.0004
R² = 0.9956
$\ln([X_0]/[X])$
0.014
0.012
0.01
0.008
0.006
0.004
0.002
0
0
0.002
0.004
0.006
0.008
0.01
0.012
0.014
0.016
$\ln([H_0]/[H])$


Competition experiment 4, *p*-fluorobenzyl alcohol vs. benzyl alcohol
y = 0.5849x + 0.0003
R² = 0.9989
$\ln([X_0]/[X])$
0.018
0.016
0.014
0.012
0.01
0.008
0.006
0.004
0.002
0
0
0.005
0.01
0.015
0.02
0.025
0.03
$\ln([H_0]/[H])$


Competition experiment 5, *p*-chlorobenzyl alcohol vs. benzyl alcohol
y = 0.3959x + 0.0003
R² = 0.7194
0.025
0.02
0.015
0.01
0.005
0
ln([X0]/[X])
0
0.01
0.02
0.03
0.04
0.05
0.06
ln([H0]/[H])


Competition experiment 6, *p*-nitrobenzyl alcohol vs. benzyl alcohol
y = 0.2936x - 0.0004
R² = 0.8246
0.006
0.005
0.004
0.003
0.002
0.001
0
ln([X0]/[X])
0
0.005
0.01
0.015
0.02
0.025
ln([H0]/[H])

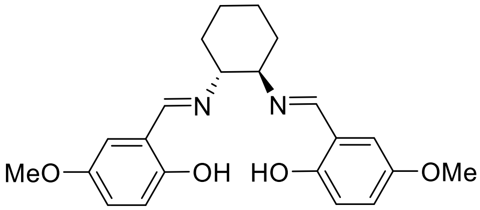
Procedure for ligand syntheses



(1*R*,2*R*)-*N*,*N'*-Bis(salicylidene)-1,2-cyclohexanediamine

A mixture of (1*R*,2*R*)-(+)-1,2-diaminocyclohexane L-tartrate (2.0 g, 7.6 mmol), K_2CO_3 (1.02 g, 7.4 mmol) and water (5 mL) was stirred until complete dissolution followed by addition of methanol (40 mL). The reaction mixture was heated to reflux. A solution of salicylaldehyde (1.6 mL, 15.2 mmol) in methanol (16 mL) was added over 30 min. The reaction mixture was refluxed for an additional 2 h, and then cooled to room temperature. The mixture was concentrated *in vacuo* and the residue dissolved in water (20 mL). The aqueous layer was extracted with ethyl acetate (3 × 15 mL). The combined organic layers were dried over anhydrous sodium sulfate and concentrated *in vacuo* to give the desired ligand as a yellow oil.

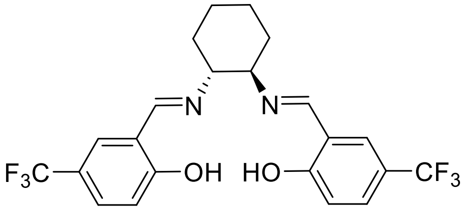
Yield: 99% (2.42 g). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.38 – 1.54 (m, 2H), 1.66 – 1.78 (m, 2H), 1.79 – 1.99 (m, 4H), 3.25 – 3.37 (m, 2H), 6.78 (td, *J* = 7.5, 1.1 Hz, 2H), 6.88 (dd, *J* = 8.3, 1.0 Hz, 2H), 7.14 (dd, *J* = 7.7, 1.7 Hz, 2H), 7.19 – 7.22 (m, 2H), 8.25 (s, 2H), 13.24 (s, 2H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ 24.3, 33.2, 72.8, 116.9, 118.7, 118.8, 131.6, 132.3, 161.1, 164.9. NMR data are in accordance with literature values.[1]



(1*R*,2*R*)-*N*,*N'*-Bis(2'-hydroxy-5'-methoxybenzylidene)-1,2-cyclohexanediamine

A mixture of (1*R*,2*R*)-(+)-1,2-diaminocyclohexane L-tartrate (695 mg, 2.63 mmol), K_2CO_3 (363 mg, 2.63 mmol) and water (2 mL) was stirred until complete dissolution followed by addition of methanol (15 mL). The reaction mixture was heated to reflux. A solution of 2-hydroxy-5-methoxybenzaldehyde (0.66 mL, 5.26 mmol) in methanol (10 mL) was added over 30 min. The reaction mixture was refluxed for an additional 3 h, and then cooled to room temperature. The mixture was concentrated *in vacuo* and the residue dissolved in water (20 mL). The aqueous layer was extracted with ethyl acetate (3 × 15 mL). The combined organic layers were dried over anhydrous sodium sulfate and concentrated *in vacuo* to give the desired ligand as a yellow oil.

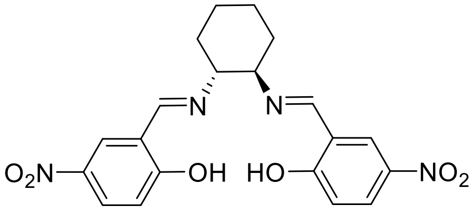
Yield: 99% (1.02 g). ^{1}H-NMR (400 MHz, $CDCl_3$): *δ* 1.46 – 1.58 (m, 2H), 1.67 – 1.82 (m, 2H), 1.85 – 2.01 (m, 4H), 3.26 – 3.38 (m, 2H), 3.37 (s, 6H), 6.66 (d, *J* = 2.8 Hz 2H), 6.85 (s, 2H), 6.86 (d, *J* = 2.8 Hz, 2H), 8.21 (s, 2H), 12.81 (s, 2H). ^{13}C-NMR (101 MHz, $CDCl_3$): *δ* 24.2, 33.0, 55.85, 55.87, 72.7, 114.8, 117.5, 119.4, 151.2, 155.1, 164.5. NMR data are in accordance with literature values.[2]



(1*R*,2*R*)-*N*,*N'*-Bis(2'-hydroxy-5'-trifluoromethylbenzylidene)-1,2-cyclohexanediamine

A mixture of (1*R*,2*R*)-(+)-1,2-diaminocyclohexane L-tartrate (674 mg, 2.55 mmol), K_2CO_3 (352 mg, 2.55 mmol) and water (2 mL) was stirred until complete dissolution followed by addition of methanol (15 mL). The reaction mixture was heated to reflux. A solution of 2-hydroxy-5-trifluoromethylbenzaldehyde (970 mg, 5.1 mmol) in methanol (10 mL) was added over 30 min. The reaction mixture was refluxed for an additional 3 h, and then cooled to room temperature. The mixture was concentrated *in vacuo* and the residue dissolved in water (20 mL). The aqueous layer was extracted with ethyl acetate (3 × 15 mL). The combined organic layers were dried over anhydrous sodium sulfate and concentrated *in vacuo* to give the desired ligand as a yellow amorphous solid.

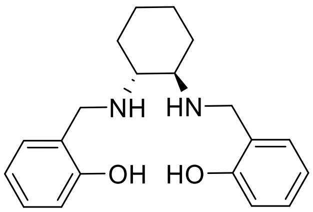
Yield: 98% (1.14 g). ^{1}H-NMR (400 MHz, $CDCl_3$): *δ* 1.45 – 1.62 (m, 2H), 1.73 – 1.91 (m, 2H), 1.93 – 2.00 (m, 4H), 3.22 – 3.63 (m, 2H), 7.00 (d, *J* = 8.7 Hz, 2H), 7.44 (d, *J* = 2.2 Hz, 2H), 7.52 (dd, *J* = 8.7, 2.3 Hz, 2H), 8.32 (s, 2H), 13.71 (s, 2H). ^{13}C-NMR (101 MHz, $CDCl_3$): *δ* 24.0, 32.9, 72.7, 117.6, 117.9, 121.0 (q, ${}^{2}J_{CF}$ = 33.4 Hz), 124.0 (q, ${}^{1}J_{CF}$ = 272 Hz), 128.7 (q, ${}^{3}J_{CF}$ = 3.9 Hz), 129.2 (q, ${}^{3}J_{CF}$ = 3.9 Hz), 163.7, 163.9. NMR data are in accordance with literature values.[2]



(1*R*,2*R*)-*N*,*N'*-Bis(2'-hydroxy-5'-nitrobenzylidene)-1,2-cyclohexanediamine

A mixture of (1*R*,2*R*)-(+)-1,2-diaminocyclohexane L-tartrate (1 g, 3.8 mmol), K_2CO_3 (525 mg, 3.8 mmol) and water (3 mL) was stirred until complete dissolution followed by addition of methanol (15 mL). The reaction mixture was heated to reflux. A solution of 2-hydroxy-5-nitrobenzaldehyde (1.27 g, 7.6 mmol) in methanol (10 mL) was added over 30 min. The reaction mixture was refluxed for an additional 3 h, and then cooled to room temperature. The mixture was concentrated *in vacuo* and the residue dissolved in water (20 mL). The aqueous layer was extracted with ethyl acetate (3 × 15 mL). The combined organic layers were dried over anhydrous sodium sulfate and concentrated *in vacuo* to give the desired ligand as a yellow amorphous solid.

Yield: 96% (1.505 g). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.39 – 1.63 (m, 2H), 1.69 – 1.82 (m, 2H), 1.88 – 2.10 (m, 4H), 3.19 – 3.65 (m, 2H), 6.98 (d, J = 9.2 Hz, 2H), 8.05 – 8.25 (m, 4H), 8.36 (s, 2H), 14.22 (s, 2H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ 23.9, 32.7, 71.9, 117.0, 118.3, 127.9, 128.1, 139.5, 163.7, 167.4. NMR data are in accordance with literature values.[2]



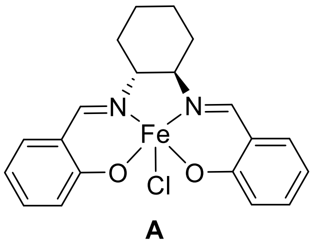
(1*R*,2*R*)-*N*,*N'*-Bis(2'-hydroxybenzyl)-1,2-cyclohexanediamine

Sodium borohydride (582 mg, 15.4 mmol) was added over 30 min to a solution of (1*R*,2*R*)-*N*,*N'*-bis(salicylidene)-1,2-cyclohexanediamine (2.49 g, 7.7 mmol) in methanol (30 mL) at room temperature and the reaction mixture was stirred under reflux for 1 h. After cooling to room temperature, water (35 mL) was added and the mixture was extracted with dichloromethane (3 × 15 mL). The combined organic layers were evaporated to dryness and the residue purified by silica gel flash column chromatography (0-10% EtOAc/hexane) to afford the desired ligand as a yellow oil.

Yield: 49% (1.25 g). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.16 – 1.42 (m, 4H), 1.65 – 1.80 (m, 2H), 2.10 – 2.31 (m, 2H), 2.40 – 2.62 (m, 2H), 3.87 – 4.22 (m, 4H), 6.75 – 6.89 (m, 4H), 6.98 (dd, *J* = 7.5, 1.6 Hz, 2H), 7.16 (td, *J* = 7.8, 1.7 Hz, 2H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ 24.2, 30.4, 49.6, 59.7, 116.5, 119.2, 122.8, 128.4, 128.9, 157.9. NMR data are in accordance with literature values.[3]

General procedure for the synthesis of iron(III) catalysts

The complexes were prepared by reacting $FeCl_3{\cdot}6H_2O$ or $FeBr_3$ with the respective ligand in ethanol at reflux for 1 h in an open system. The dark brown precipitate was isolated by suction filtration and washed with Et_2O (3 × 5 mL). Further purification was performed for catalyst **A**, which was recrystallized from EtOH and dried under high vacuum to give the desired product. The other complexes were used without performing additional purifications.



A

(1*R*,2*R*)-*N*,*N'*-Bis(salicylidene)-1,2-cyclohexanediaminoiron(III) chloride (A)

Following the general procedure for synthesis of iron(III) catalysts, $FeCl_3{\cdot}6H_2O$ (2.2 g, 8.3 mmol) and (1*R*,2*R*)-*N*,*N'*-bis(salicylidene)-1,2-cyclohexanediamine (2.5 g, 7.5 mmol) were reacted in ethanol (150 mL). The complex was obtained as black crystals. Yield: 39% (1.2 g). FTIR, v/cm^{-1}: 2934 m, 2847 m, 1613 s, 1543 s, 1442 m, 1307 s, 1284 s, 982 m, 754 w. λ_{max} (CH_2Cl_2)/nm: 263 (ε/dm^3 mol^{-1} cm^{-1} 28.435), 300 (12.192), 311 (12.192), 445shoulder (4.1386), 476 (4.5045). MS (ESI+) *m/z*: 376 $[M-Cl]^+$.

Anal. calc.: C, 58.35; H, 4.90; Cl, 8.61; Fe, 13.56; N, 6.80. Found: C, 58.15; H, 4.85; Cl, 8.55; Fe, 13.43; N, 7.08. Characterization data are in accordance with literature values.[4]

The UV-Vis measurements were conducted on an Agilent Cary 5000 UV-Vis-NIR Spectrophotometer with the following concentrations of Complex **A** in CH_2Cl_2 (mmol/L): 0.127, 0.210, 0.288, 0.408, 0.527.

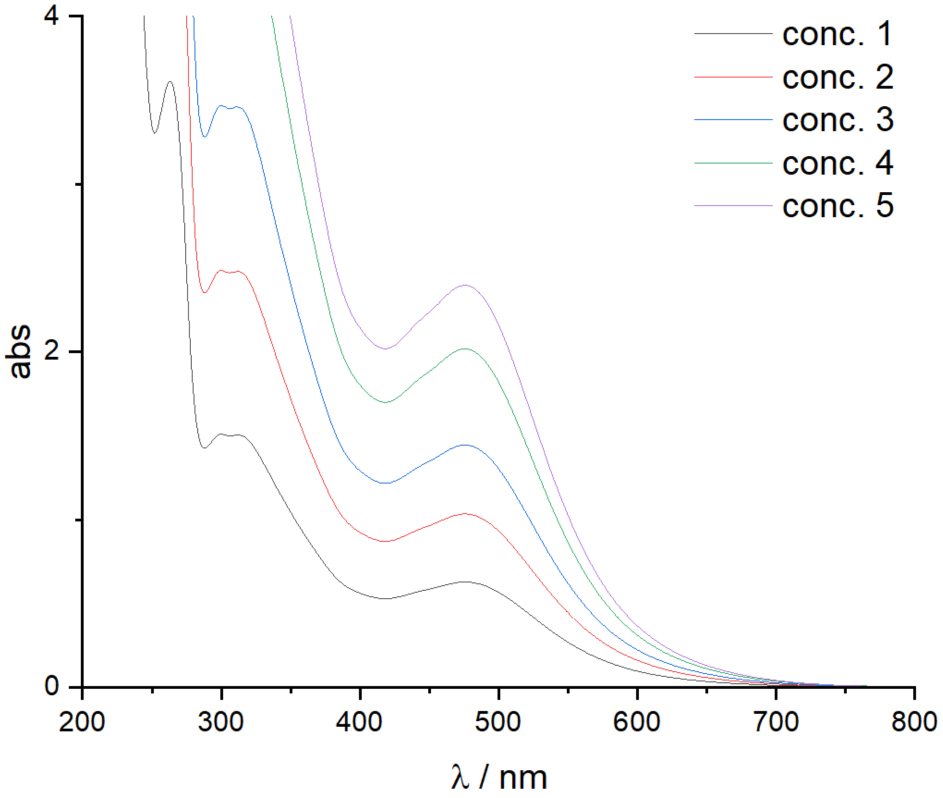
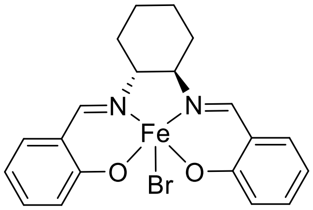


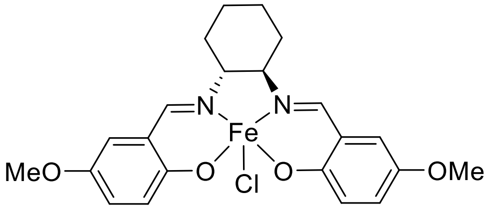
Figure S4. UV-Vis measurement of Complex **A** in CH_2Cl_2 (absorption values above 4 are unreliable due to instrument sensitivity).



B

(1*R*,2*R*)-*N*,*N′*-Bis(salicylidene)-1,2-cyclohexanediaminoiron(III) bromide (B)

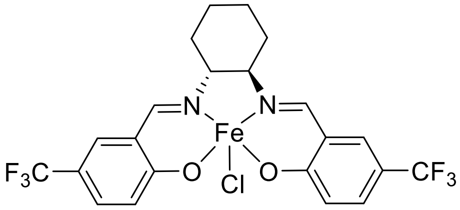
Following the general procedure for synthesis of iron(III) catalysts, $FeBr_3$ (393 mg, 1.33 mmol) and (1*R*,2*R*)-*N*,*N′*-bis(salicylidene)-1,2-cyclohexanediamine (357 mg, 1.1 mmol) were reacted in ethanol (80 mL). The complex was obtained as a black powder. Yield: 48% (250 mg). FTIR, *v*/cm^{-1}: 2937 m, 2850 m, 1618 s, 1543 s, 1445 m, 1302 s, 1252 s, 906 m, 751 s. MS (ESI+) *m/z*: 376 $[M-Br]^+$.



C

(1*R*,2*R*)-*N*,*N'*-Bis(2'-hydroxy-5'-methoxybenzylidene)-1,2-cyclohexanediaminoiron(III) chloride (C)

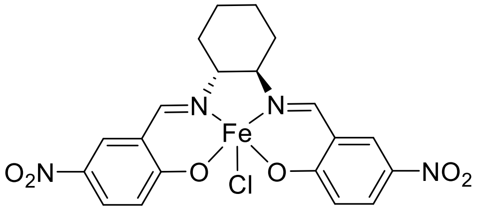
Following the general procedure for synthesis of iron(III) catalysts, $FeCl_3 \cdot 6H_2O$ (458 mg, 1.69 mmol) and (1*R*,2*R*)-*N*,*N'*-bis(2'-hydroxy-5'-methoxybenzylidene)-1,2-cyclohexanediamine (539 mg, 1.41 mmol) were reacted in ethanol (80 mL). The complex was obtained as a black powder. Yield: 48% (320 mg). FTIR, *v*/cm^{-1}: 2931 m, 2845 m, 1634 s, 1538 s, 1468 m, 1325 s, 1288 s, 952 m, 749 w. MS (ESI+) *m/z*: 436 [M-Cl]$^+$.



D

(1*R*,2*R*)-*N*,*N'*-Bis(2'-hydroxy-5'-trifluoromethylbenzylidene)-1,2-cyclohexanediaminoiron(III) chloride (D)

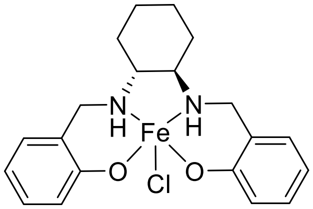
Following the general procedure for synthesis of iron(III) catalysts, $FeCl_3 \cdot 6H_2O$ (297 mg, 1.1 mmol) and (1*R*,2*R*)-*N*,*N'*-bis(2'-hydroxy-5'-trifluoromethylbenzylidene)-1,2-cyclohexanediamine (458 mg, 1 mmol) were reacted in ethanol (80 mL). The complex was obtained as a black powder. Yield: 44% (289 mg). FTIR, *v*/cm^{-1}: 2929 m, 2848 m, 1625 s, 1531 s, 1465 m, 1328 s, 1286 s, 959 m, 757 w. MS (ESI+) *m/z*: 512 [M-Cl]$^+$.



E

(1*R*,2*R*)-*N*,*N'*-Bis(2'-hydroxy-5'-nitrobenzylidene)-1,2-cyclohexanediaminoiron(III) chloride (E)

Following the general procedure for synthesis of iron(III) catalysts, $FeCl_3 \cdot 6H_2O$ (297 mg, 1.1 mmol) and (1*R*,2*R*)-*N*,*N'*-bis(2'-hydroxy-5'-nitrobenzylidene)-1,2-cyclohexanediamine (412 mg, 1 mmol) were reacted in ethanol (80 mL). The complex was obtained as a black powder. Yield: 40% (203 mg). FTIR, *v*/cm^{-1}: 3065 m, 2940 m, 1633 s, 1601 s, 1494 m, 1332 s, 1286 s, 969 m, 778 w. MS (ESI+) *m/z*: 466 $[M\text{-}Cl]^+$.



F

(1*R*,2*R*)-*N*,*N'*-Bis(2'-hydroxybenzyl)-1,2-cyclohexanediaminoiron(III) chloride (F)

Following the general procedure for the synthesis of iron(III) catalysts, $FeCl_3 \cdot 6H_2O$ (795 mg, 2.94 mmol) and (1*R*,2*R*)-*N*,*N'*-bis(2'-hydroxybenzyl)-1,2-cyclohexanediamine (871 mg, 2.67 mmol) were reacted in ethanol (100 mL) The complex was obtained as a black powder. Yield: 50% (554 mg). FTIR, *v*/cm^{-1}: 2946 m, 2011 m, 1595 m, 1480 s, 1449 s, 866 m, 754 w. MS (ESI+) *m/z*: 380 $[M\text{-}Cl]^+$.

X-ray crystallography

Powder X-ray diffraction:

The powder X-ray diffraction experiment was conducted on a Malvern Panalytical Empyrean diffractometer, equipped with a 1Der detector, using Cu Kα (λ = 1.5406 Å) radiation in reflection mode at V = 45 kV and I = 40 mA on a reflection/transmission spinner. The sample was measured at room temperature between 2θ = 3.5–90° with a step size of 0.008° and a scan rate of 0.025° s^{-1}.

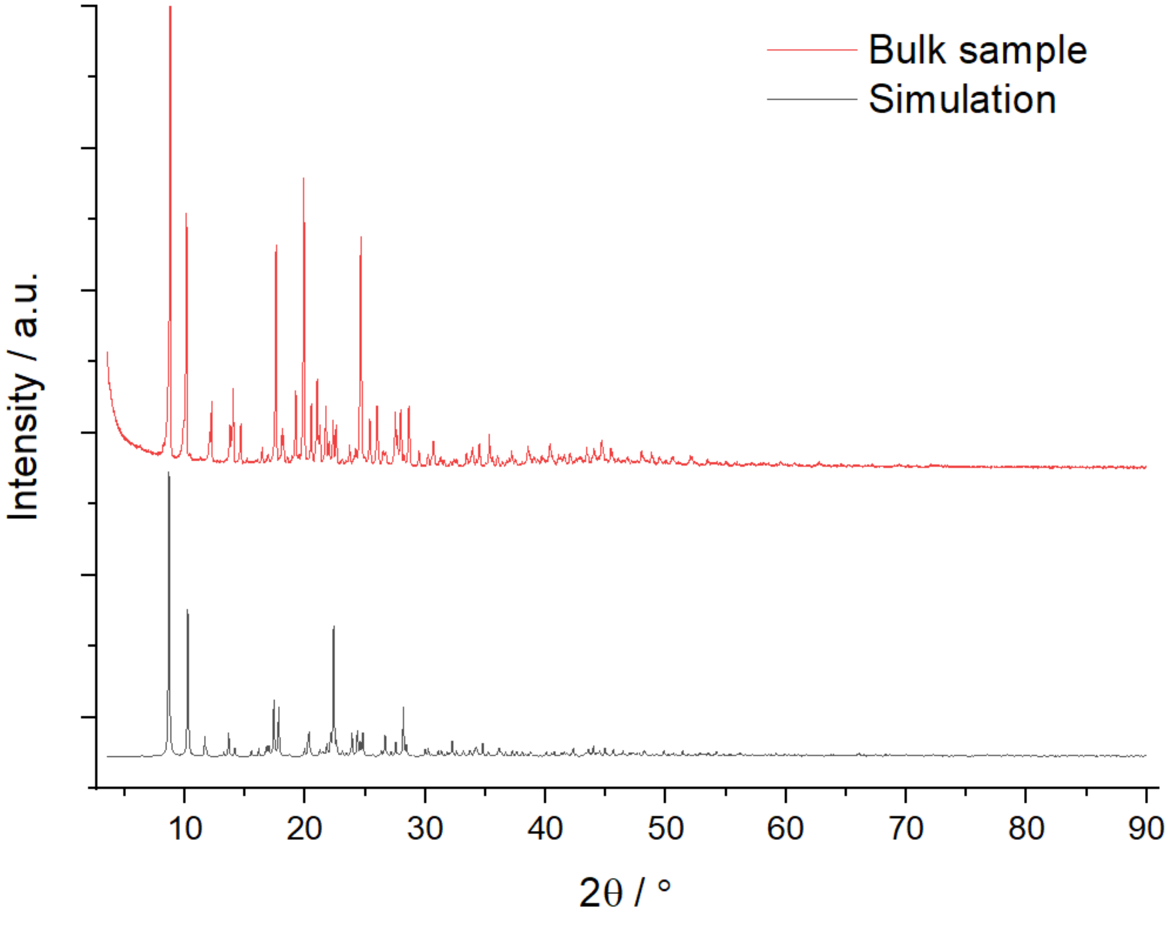


Figure S5. Powder XRD pattern of a bulk sample of Complex **A**.

A comparison is made between the bulk sample and the simulated powder pattern from the single crystal x-ray diffraction measurement. There are impurities in this specific bulk sample, but the peaks at 2θ = 8.7° and 2θ = 10.2° are recognizable.

Single crystal X-ray diffraction:

Dark reddish-black, single crystals of complex A were grown in CH_2Cl_2 with slow diffusion of Et_2O. They were suspended in polybutene oil (Aldrich, >90%) and mounted on a nylon loop, which was attached to a SuperNova, Dual, Cu at home/near, Atlas diffractometer. Data was collected using Cu Kα (λ = 1.54184 Å) radiation at temperature 120 K.

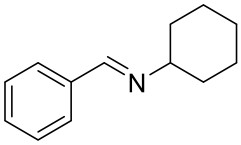
The structure was solved in Olex2[5] using the structure solution program SHELXT 2018/2[6] and subsequently refined with the SHELXL[7] refinement package using the least squares minimization. All non-hydrogen atoms were refined anisotropically. The dataset was measured with Friedel Pairs assumed though the molecule is chiral. The correct chirality is known from the synthesis, thus the structure obtained is the correct enantiomer. One bad reflection was omitted due to it lying in a zero plane, where the reflection was influenced by the beamstop.

Table S1. Crystallographic data and refinement parameters.

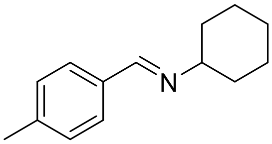
Compound	Complex **A**
CCDC Number	2261609
Temperature / K	120
Crystal system	Monoclinic
Space group	$P2_1$
a / Å	8.6369(1)
b / Å	15.1727(2)
c / Å	13.7486(2)
α / °	90
β / °	92.342(1)
γ / °	90
Volume / Å^3	1800.18(4)
Z	4
ρ_{calc} / g cm^{-3}	1.519

μ / mm^{-1}	8.223
Radiation	Cu Kα (λ = 1.54184)
2 ϑ range for data collection / °	8.684 to 152.828
Index ranges	$-10 \leq h \leq 10$
	$-17 \leq k \leq 19$
	$-16 \leq l \leq 17$
Reflections collected	11090
Independent reflections	5912 [R_{int} = 0.0257, R_{sigma} = 0.0370]
Data/restraints/parameters	5912/1/469
Goodness-of-fit on F^2	1.037
Final R index [$I \geq 2\sigma(I)$]	R_1 = 0.0266, wR_2 = 0.0682
Final R index [all data]	R_1 = 0.0279, wR_2 = 0.0691
Largest diff. peak/hole / e Å^{-3}	0.26/-0.32
Flack parameter	-0.005(3)

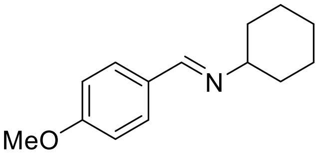
Characterization data for imines



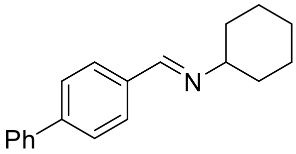
***N*-Benzylidenecyclohexylamine (1):** Isolated as a yellow liquid. Yield: 88% (175 mg). ^{1}H-NMR (400 MHz, CDCl$_3$): δ 1.14 – 1.47 (m, 3H), 1.52 – 1.91 (m, 7H), 3.11 – 3.28 (m, 1H), 7.34 – 7.46 (m, 3H), 7.66 – 7.80 (m, 2H), 8.32 (s, 1H). ^{13}C-NMR (101 MHz, CDCl$_3$): δ 24.9, 25.8, 34.5, 70.1, 128.1, 128.6, 130.4, 136.7, 158.7. MS (EI) *m/z*: 187 [M]$^{\bullet+}$. NMR data are in accordance with literature values.[1]



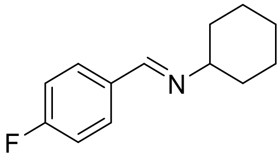
***N*-(4-Methylbenzylidene)-cyclohexylamine (2):** Isolated as a yellow liquid. Yield: 89% (178 mg). ^{1}H-NMR (400 MHz, CDCl$_3$): δ 1.18 – 1.51 (m, 3H), 1.51 – 1.79 (m, 5H), 1.80 – 1.92 (m, 2H), 2.37 (s, 3H), 3.12 – 3.21 (m, 1H), 7.20 (d, *J* = 7.8 Hz, 2H), 7.62 (d, *J* = 7.8 Hz, 2H), 8.28 (s, 1H). ^{13}C-NMR (101 MHz, CDCl$_3$): δ 21.6, 25.0, 25.8, 34.5, 70.1, 128.1, 129.3, 134.1, 140.6, 158.6. MS (EI) *m/z*: 201 [M]$^{\bullet+}$. NMR data are in accordance with literature values.[1]



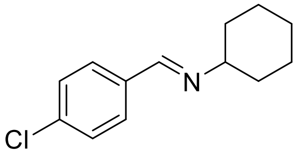
***N*-(4-Methoxybenzylidene)-cyclohexylamine (3):** Isolated as a yellow liquid. Yield: 94% (196 mg). ^{1}H-NMR (400 MHz, CDCl$_3$): δ 1.18 – 1.49 (m, 3H), 1.50 – 1.81 (m, 5H), 1.81 – 1.90 (m, 2H), 3.14 (tt, *J* = 10.6, 4.1 Hz, 1H), 3.80 (s, 3H), 6.90 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 8.6 Hz, 2H), 8.24 (s, 1H). ^{13}C-NMR (101 MHz, CDCl$_3$): δ 25.1, 25.8, 34.6, 55.5, 70.1, 114.0, 129.7, 132.1, 158.1, 161.5. MS (EI) *m/z*: 217 [M]$^{\bullet+}$. NMR data are in accordance with literature values.[1]



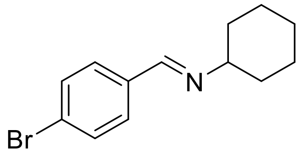
N-(4-Phenylbenzylidene)-cyclohexylamine (4): Isolated as a yellow solid. Yield: 94% (248 mg). ^{1}H-NMR (400 MHz, CDCl$_3$): δ 1.19 – 1.51 (m, 3H), 1.52 – 1.91 (m, 7H), 3.18 – 3.27 (m, 1H), 7.37 (t, J = 7.2 Hz, 1H), 7.46 (t, J = 7.5 Hz, 2H), 7.57 – 7.67 (m, 4H), 7.81 (d, J = 7.9 Hz, 2H), 8.36 (s, 1H). ^{13}C-NMR (101 MHz, CDCl$_3$): δ 25.0, 25.8, 34.5, 70.2, 127.2, 127.3, 127.8, 128.6, 128.9, 135.7, 140.6, 143.2, 158.3. MS (EI) *m/z*: 263 [M]$^{\bullet+}$. NMR data are in accordance with literature values.[1]



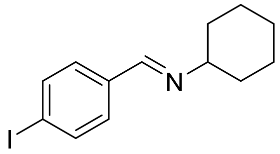
N-(4-Fluorobenzylidene)-cyclohexylamine (5): Isolated as a yellow liquid. Yield: 70% (146 mg). ^{1}H-NMR (400 MHz, CDCl$_3$) δ 1.20 – 1.42 (m, 3H), 1.52 – 1.77 (m, 5H), 1.78 – 1.88 (m, 2H), 3.13 – 3.24 (m, 1H), 7.07 (t, J = 8.6 Hz, 2H), 7.72 (dd, J = 8.7, 5.5 Hz, 2H), 8.27 (s, 1H). ^{13}C-NMR (101 MHz, CDCl$_3$): δ 24.9, 25.7, 34.5, 70.0, 115.7 (d, $^{2}J_{CF}$ = 22.0 Hz), 130.0 (d, $^{3}J_{CF}$ = 8.4 Hz), 133.0 (d, $^{4}J_{CF}$ = 3.3 Hz), 157.3, 164.2 (d, $^{1}J_{CF}$ = 250.2 Hz). MS (EI) *m/z*: 205 [M]$^{\bullet+}$. NMR data are in accordance with literature values.[1]



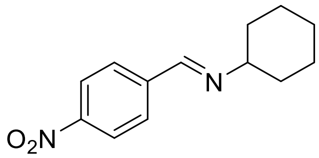
N-(4-Chlorobenzylidene)-cyclohexylamine (6): Isolated as a yellow liquid. Yield: 91% (201 mg). ^{1}H-NMR (400 MHz, CDCl$_3$): δ 1.19 – 1.43 (m, 3H), 1.51 – 1.82 (m, 5H), 1.82 – 1.93 (m, 2H), 3.17 (tt, J = 10.5, 4.1 Hz, 1H), 7.36 (d, J = 8.2 Hz, 2H), 7.66 (d, J = 8.2 Hz, 2H), 8.27 (s, 1H). ^{13}C-NMR (101 MHz, CDCl$_3$): δ 24.9, 25.7, 34.4, 70.1, 128.8, 129.4, 135.2, 136.3, 157.3. MS (EI) *m/z*: 221 [M]$^{\bullet+}$. NMR data are in accordance with literature values.[1]



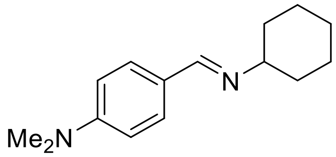
N-(4-Bromobenzylidene)-cyclohexylamine (7): Isolated as a yellow solid. Yield: 94% (250 mg). ^{1}H-NMR (400 MHz, CDCl$_3$): δ 1.18 – 1.45 (m, 3H), 1.47 – 1.91 (m, 7H), 3.15 – 3.23 (m, 1H), 7.50 – 7.62 (m, 4H), 8.25 (s, 1H). ^{13}C-NMR (101 MHz, CDCl$_3$): δ 24.9, 25.6, 34.4, 70.1, 124.7, 129.6, 131.8, 135.6, 157.4. MS (EI) *m/z*: 265 [M]$^{\bullet+}$. NMR data are in accordance with literature values.[1]



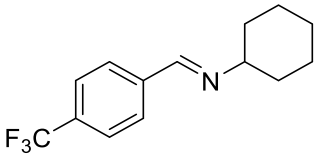
N-(4-Iodobenzylidene)-cyclohexylamine (8): Isolated as a brown solid. Yield: 88% (275 mg). ^{1}H-NMR (400 MHz, CDCl$_3$): δ 1.19 – 1.44 (m, 3H), 1.48 – 1.77 (m, 5H), 1.78 – 1.90 (m, 2H), 3.14 – 3.23 (m, 1H), 7.45 (d, J = 8.4 Hz, 2H), 7.73 (d, J = 8.4 Hz, 2H), 8.23 (s, 1H). ^{13}C-NMR (101 MHz, CDCl$_3$): δ 24.9, 25.7, 34.4, 70.1, 96.9, 129.7, 136.2, 137.8, 157.6. MS (EI) *m/z*: 313 [M]$^{\bullet+}$. NMR data are in accordance with literature values.[8]



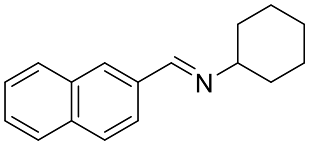
N-(4-Nitrobenzylidene)-cyclohexylamine (9): Isolated as a yellow solid. Yield: 87% (202 mg). ^{1}H-NMR (400 MHz, CDCl$_3$): δ 1.18 – 1.47 (m, 3H), 1.52 – 1.90 (m, 7H), 3.17 – 3.34 (m, 1H), 7.89 (d, J = 8.5 Hz, 2H), 8.25 (d, J = 8.4 Hz, 2H), 8.38 (s, 1H). ^{13}C-NMR (101 MHz, CDCl$_3$): δ 24.7, 25.7, 34.3, 70.3, 123.9, 128.8, 142.3, 148.9, 156.4. MS (EI) *m/z*: 232 [M]$^{\bullet+}$. NMR data are in accordance with literature values.[1]



N-(4-Dimethylaminobenzylidene)-cyclohexylamine (10): Following the general procedure for imine synthesis, the crude product was purified by silica gel flash column chromatography (98:2 hexane/Et_3N) to afford the desired imine as a white solid. Yield: 52 % (120 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.21 – 1.41 (m, 3H), 1.51 – 1.77 (m, 5H), 1.78 – 1.86 (m, 2H), 3.00 (s, 6H), 3.10 (tt, J = 8.3, 4.1 Hz, 1H), 6.69 (d, J = 8.9 Hz, 2H), 7.60 (d, J = 8.8 Hz, 2H), 8.19 (s, 1H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ 25.2, 25.8, 34.8, 40.4, 70.1, 111.8, 125.0, 129.5, 152.0, 158.7. MS (EI) m/z: 230 $[M]^{•+}$. NMR data are in accordance with literature values.[9]

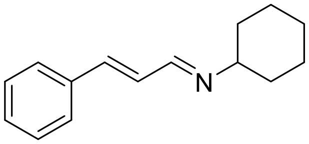


N-(4-Trifluoromethylbenzylidene)-cyclohexylamine (11): Following the general procedure for imine synthesis, the crude product was purified by silica gel flash column chromatography (98:2 hexane/Et_3N) to afford the desired imine as a yellow solid. Yield: 71 % (185 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.25 – 1.43 (m, 3H), 1.54 – 1.77 (m, 5H), 1.80 – 1.88 (m, 2H), 3.20 – 3.29 (m, 1H), 7.65 (d, J = 8.3 Hz, 2H), 7.84 (d, J = 8.3 Hz, 2H), 8.35 (s, 1H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ 24.8, 25.7, 34.4, 70.2, 124.1 (q, $^1J_{CF}$ = 272.5 Hz), 125.6 (q, $^3J_{CF}$ = 3.7 Hz), 128.4, 132.1 (q, $^2J_{CF}$ = 32.3 Hz), 139.9, 157.2. MS (EI) m/z: 255 $[M]^{•+}$. NMR data are in accordance with literature values.[8]

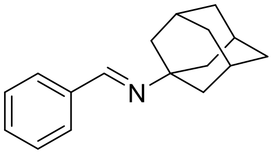


N-(1-Naphthalenylmethylene)-cyclohexylamine (12): Isolated as a yellow solid. Yield: 92% (219 mg). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.29 – 1.48 (m, 3H), 1.59 – 1.90 (m, 7H), 3.26 (tt, J = 10.5, 4.1 Hz, 1H), 7.46 – 7.55 (m, 2H), 7.80 – 7.93 (m, 3H), 7.97 – 8.06 (m, 2H), 8.49 (s, 1H). ^{13}C-NMR (101

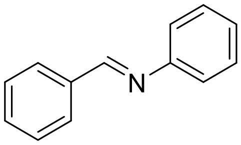
MHz, $CDCl_3$): δ 25.0, 25.8, 34.6, 70.3, 124.2, 126.5, 127.0, 127.9, 128.4, 128.7, 129.6, 133.3, 134.4, 134.7, 158.8. MS (EI) *m/z*: 237 $[M]^{\bullet+}$. NMR data are in accordance with literature values.[1]



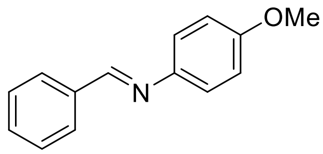
***N*-(Cinnamylidene)-cyclohexylamine (13):** Isolated as a yellow liquid. Yield: 88% (188 mg). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.17 – 1.41 (m, 3H), 1.42 – 1.86 (m, 7H), 3.06 (tt, *J* = 10.6, 4.1 Hz, 1H), 6.89 – 6.94 (m, 2H), 7.24 – 7.40 (m, 3H), 7.44 – 7.50 (m, 2H), 8.03 – 8.09 (m, 1H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ 24.9, 25.7, 34.6, 69.8, 127.3, 128.8, 128.9, 129.1, 136.0, 141.2, 160.5. MS (EI) *m/z*: 213 $[M]^{\bullet+}$. NMR data are in accordance with literature values.[10]



***N*-Benzylidene-1-adamantanylamine (14):** Isolated as a yellow solid. Yield: 81% (206 mg). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.65 – 1.87 (m, 12H), 2.12 – 2.21 (m, 3H), 7.36 – 7.43 (m, 3H), 7.72 – 7.78 (m, 2H), 8.29 (s, 1H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ 29.8, 36.8, 43.3, 57.6, 128.0, 128.6, 130.2, 137.4, 155.0. MS (EI) *m/z*: 239 $[M]^{\bullet+}$. NMR data are in accordance with literature values.[1]



***N*-Benzylideneaniline (15):** Isolated as a yellow solid. Yield: 85% (164 mg). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.23 – 7.32 (m, 3H), 7.38 – 7.47 (m, 5H), 7.92 – 8.02 (m, 2H), 8.50 (s, 1H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ 121.0, 126.0, 128.9, 128.9, 129.3, 131.5, 136.3, 152.2, 160.5. MS (EI) *m/z*: 181 $[M]^{\bullet+}$. NMR data are in accordance with literature values.[1]



***N*-Benzylidene-*p*-anisidine (16):** Isolated as a yellow solid. Yield: 88% (198 mg). ^{1}H-NMR (400 MHz, CDCl$_3$): δ 3.83 (s, 3H), 6.94 (d, J = 8.8 Hz, 2H), 7.25 (d, J = 8.9 Hz, 2H), 7.45 – 7.50 (m, 3H), 7.87– 7.93 (m, 2H), 8.51 (s, 1H). ^{13}C-NMR (101 MHz, CDCl$_3$): δ 55.6, 114.5, 122.3, 128.7, 128.8, 131.1, 136.6, 145.0, 158.4, 158.5. MS (EI) *m/z*: 211 $[M]^{\bullet+}$. NMR data are in accordance with literature values.[1]

Computational details

The DFT calculations used to determine the ground state multiplicity of different Fe(III) intermediates were performed with ORCA version 4.2.0. For each intermediate, geometry optimizations in the gas phase were performed for each multiplicity (doublet, quartet, sextet) with three different functionals (PBE0, OPBE, B3LYP). In all cases, the D3BJ dispersion correction, the def2-TZVP basis set and an unrestricted SCF spin treatment was employed. The electronic energy was used directly to determine the ground state multiplicity of the intermediates.

The DFT calculations used to investigate the coordination of a second axial ligand were performed with ORCA version 4.2.0. All structures were optimized in the gas phase using the B3LYP-D3BJ \\ def2-TZVP method and unrestricted SCF spin treatment. For iron containing structures, a high-spin sextet was assumed. Vibrational frequencies and thermochemistry were calculated at T = 383 K and standard state (1 atm), which provided ΔG_{gas} directly. The free energy of solvation for each structure was calculated at the B3LYP-D3BJ \\ def2-TZVP level using the SMD model with the standard parameters for toluene. Finally, the solvated Gibbs free energy of each structure was calculated as $\Delta G_{tot} = \Delta G_{gas} + \Delta G_{solv}$ and the binding energy of the additional axial ligand was calculated as $\Delta G_{bind} = \Delta G_{tot,\,6coord} - (\Delta G_{tot,\,5coord} + \Delta G_{tot,\,ligand})$.

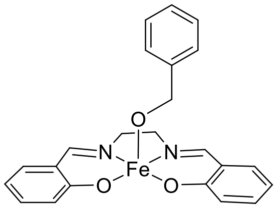
The DFT calculations used to construct the final model of the reaction were performed with Jaguar (version 10.7, release 13) by Schrodinger LLC. All geometry optimizations were performed in the gas phase using the B3LYP-D3 functional and the LACVP** basis set. Unrestricted SCF spin treatment were used in all calculations and the multiplicity of all iron complexes were assumed to be high-spin (HS) sextet (based on the initial multiplicity calculations). Frequency calculations were performed on all optimized structures to ensure that intermediates had no imaginary frequencies and that transitions states had one imaginary frequency. To match the experimental conditions, the frequency calculations were performed at the boiling point of toluene (383 K) and at standard state (1 atm). The solvation free energy G_{solv} of structures containing iron were calculated with the PBF solver in Jaguar using the standard parameters for toluene and the B3LYP-D3 \\ LACVP** method. Solvation free energies of benzyl alcohol and cyclohexylamine were calculated using the SM8 model and the B3LYP-D3 \\ 6-31G* method. To obtain more accurate electronic energies, the electronic energy of all complexes were recalculated with the larger basis set LACV3P**++. The final free energies were calculated as the sum $\Delta G_{tot} = E(\text{LACVP3**++}) + \Delta G_{solv} + ZPE + \Delta H - T\Delta S$. In all cases, T was set to the boiling point of toluene (383 K).

The computional Hammett study was conducted by calculating the free energy difference ($\Delta G^{\ddagger}$) between the appropriate reactant and transition state using the methodology described above. This calculation was repeated with different para-substituted benzyl alkoxide ligands. The ratio of the rate constants was subsequently calculated by $k_x / k_H = \text{EXP}[(\Delta G^{\ddagger}(H) - \Delta G^{\ddagger}(x)) / RT]$ with $T = 383$ K and $R = 0.001987204$ kcal K^{-1} mol^{-1} .

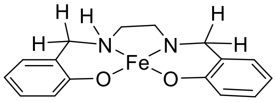
The theoretical kinetic isotope effects were calculated by performing frequency calculations on the relevant structures where the weights of the benzylic hydrogen atoms were set to 2. The thermochemistry from the deuterated frequency calculation was then employed in the calculation of the free energies using $\Delta G_{tot} = E(\text{LACVP3**++}) + \Delta G_{solv} + ZPE + \Delta H – T\Delta S$. From the calculated $\Delta G^{\ddagger}$(prot) and $\Delta G^{\ddagger}$(deut), the ratio k_H / k_D was calculated using $k_H / k_D = \text{EXP}[(\Delta G^{\ddagger}(\text{deut}) - \Delta G^{\ddagger}(\text{prot})) / RT]$ with $T = 383$ K and $R = 0.001987204$ kcal K^{-1} mol^{-1}.

Study of iron(III) multiplicity

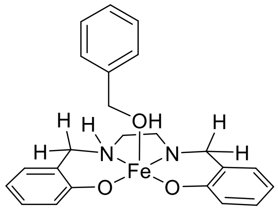
The starting point of the computational investigation was calculating the ground state multiplicity of selected iron(III) intermediates to determine which spin state to employ in the further DFT calculations. Thus, selected geometries (**17**, **22**, **23**, **24** and **25**) were optimized at three different multiplicities. It is clear that the doublet state is energetically unfeasible across the board. For **17**, **24** and **25**, the high-spin state is predicted to be the ground state by all three functionals. For **22**, the quartet state is slightly favored by the three functionals and for **23**, the OPBE and B3LYP functionals favor the quartet slightly, whereas the PBE0 functional predicts the sextet to be the ground state. Ultimately, the possibility of a quartet ground state for intermediates containing an amido ligand (**22** and **23**) cannot be excluded, but for the sake of simplicity, the multiplicity of all iron(III) complexes was assumed to be the high-spin sextet in all further DFT calculations.



17



22



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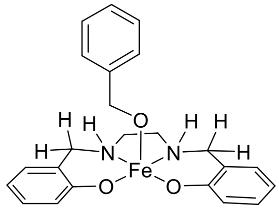
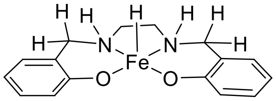


24



25

PBE0	doublet	quartet	sextet
17	-2486.932813	-2486.944803	-2486.966835
22	-2142.775369	-2142.799966	-2142.797128
23	-2489.309272	-2489.341799	-2489.344838
24	-2489.334815	-2489.352441	-2489.375256
25	-2143.971064	-2143.974498	-2143.989597

OPBE	doublet	quartet	sextet
17	-2488.537016	-2488.540501	-2488.550164
22	-2144.072622	-2144.09801	-2144.091862

23	-2490.931055	-2490.95634	-2490.95314
24	-2490.949391	-2490.9648	-2490.979965
25	-2145.280724	-2145.281007	-2145.283573

B3LYP	doublet	quartet	sextet
17	-2487.860058	-2487.867892	-2487.883384
22	-2143.477229	-2143.496788	-2143.489168
23	-2490.22427	-2490.255247	-2490.254131
24	-2490.254191	-2490.266412	-2490.284692
25	-2144.673932	-2144.673031	-2144.682624

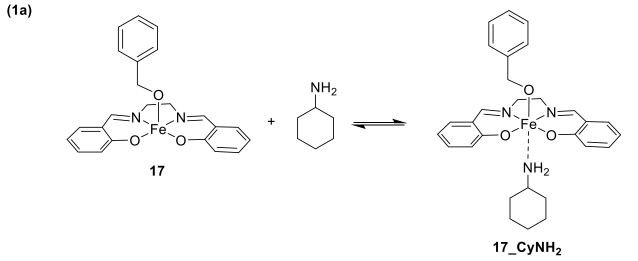
PBE0	doublet	quartet	sextet
17	21.34886816	13.82514776	0
22	13.65350987	-1.78127606	0
23	22.31782971	1.907175572	0
24	25.37718174	14.31665808	0
25	11.62954876	9.475025455	0

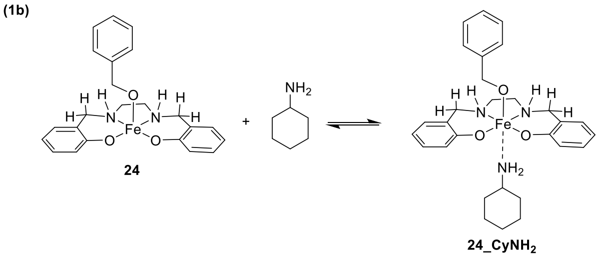
OPBE	doublet	quartet	sextet
17	8.250414119	6.064077434	0
22	12.07311753	-3.8576971	0
23	13.8581066	-2.00790114	0
24	19.18497577	9.515531327	0
25	1.787391457	1.610048931	0

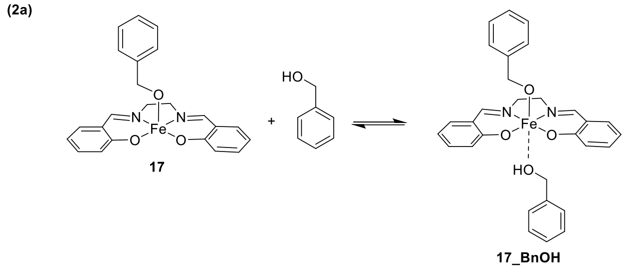
B3LYP	doublet	quartet	sextet
17	14.63658742	9.720783666	0
22	7.491760809	-4.78139644	0
23	18.73776921	-0.70029092	0
24	19.13914698	11.47090212	0
25	5.454474512	6.019869061	0

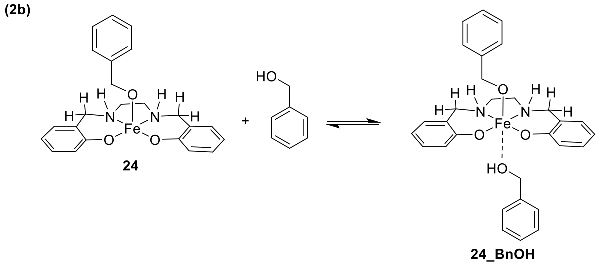
Coordination of cyclohexylamine and benzyl alcohol to 17 and 24

The possibility of coordinating cyclohexylamine and benzyl alcohol to form octahedral iron(III) intermediates was investigated computationally for **17** and **24**. In all cases, ΔG_{bind} was highly positive, so the coordination of an additional axial ligand was deemed unlikely. Therefore, no additional axial ligand was included in the further DFT calculations.









Scheme	ΔG(**17**) + ΔG(CycNH$_2$) / kcal mol^{-1}	ΔG(**17_CyNH$_2$**) / kcal mol^{-1}	ΔG_{bind} (kcal mol^{-1})
1a	-1743588.409	-1743580.078	+8.331

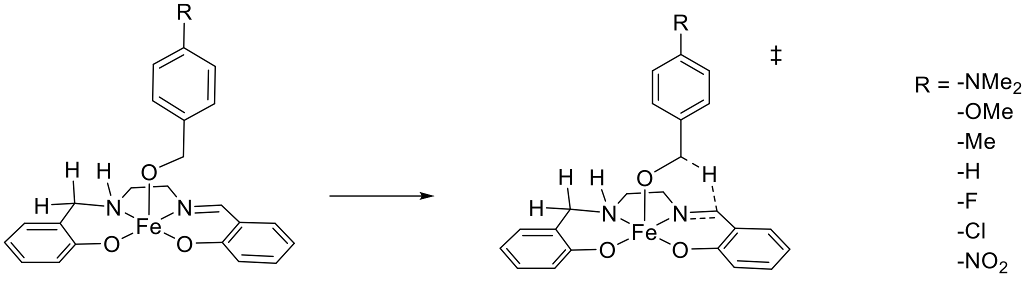
Scheme	ΔG(**24**) + ΔG(CycNH$_2$) / kcal mol^{-1}	ΔG(**24_CyNH$_2$**) / kcal mol^{-1}	ΔG_{bind} (kcal mol^{-1})
1b	-1745068.803	-1745056.752	+12.05

Scheme	ΔG(**17**) + ΔG(BnOH) / kcal mol^{-1}	ΔG(**17_BnOH**) / kcal mol^{-1}	ΔG_{bind} (kcal mol^{-1})
2a	-1778487.295	-1778476.104	+11.19

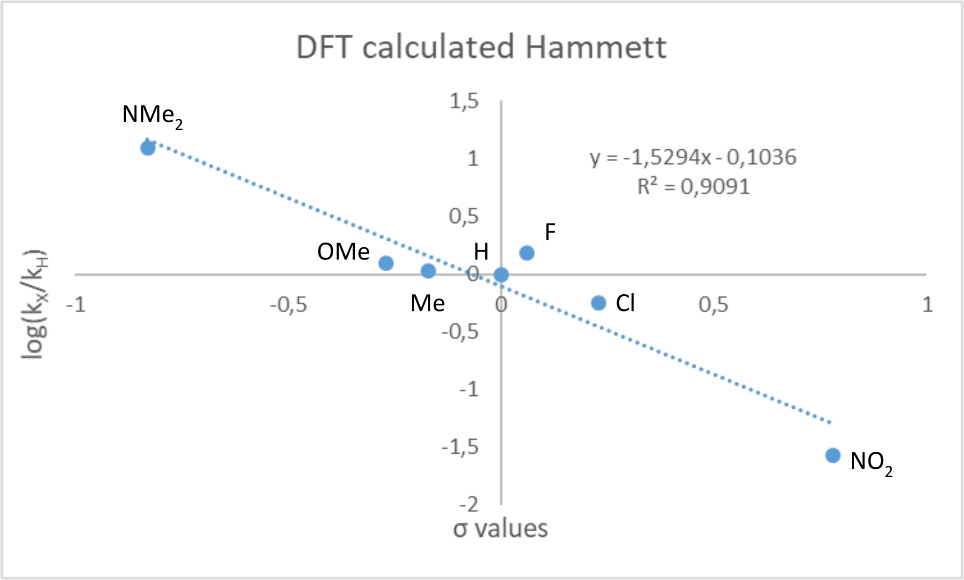
Scheme	ΔG(**24**) + ΔG(BnOH) / kcal mol^{-1}	ΔG(**24_BnOH**) / kcal mol^{-1}	ΔG_{bind} (kcal mol^{-1})
2b	-1779967.688	-1779959.141	+8.547

Calculated Hammett plots and KIEs

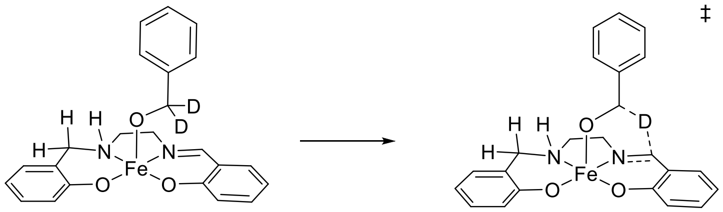
Hammett plot of **20** to **20ts**:



20 **20ts**



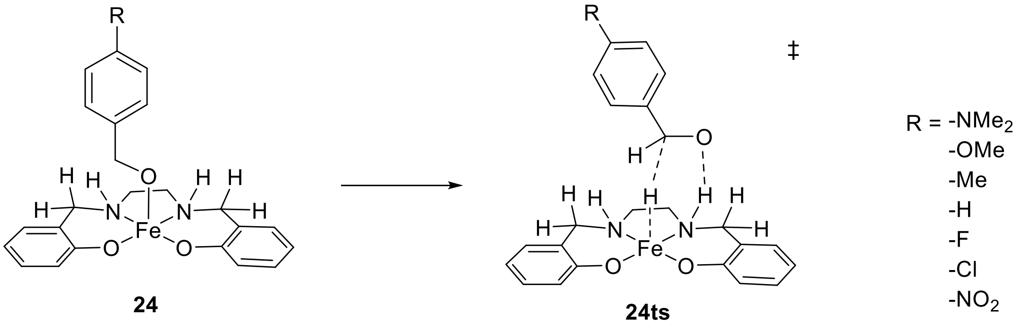
Calculated KIE from **20** to **20ts**:

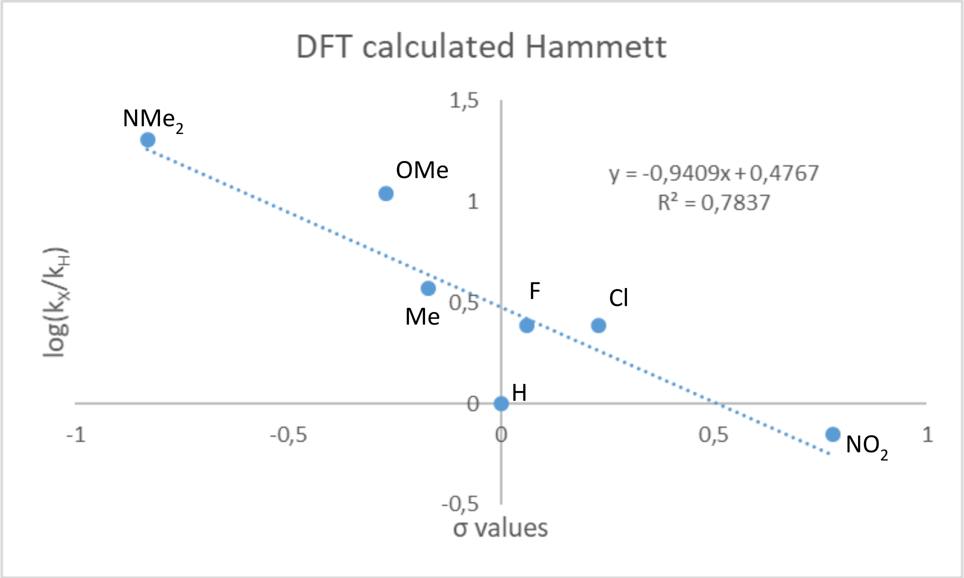


20 **20ts**

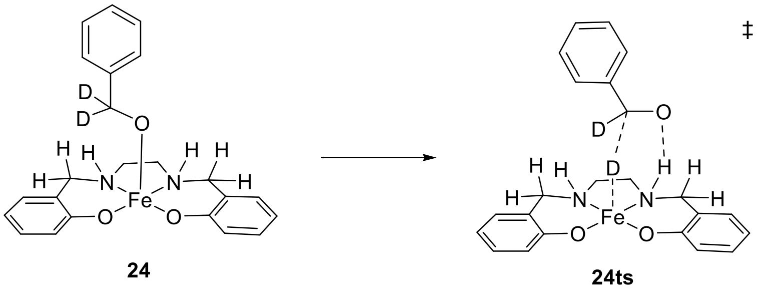
The kinetic isotope effect based on the transition from **20** to **20ts** was calculated to 2.9.

Hammett plot of **24** to **24ts**:





Calculated KIE of **24** to **24ts**:



The kinetic isotope effect based on the transition from **24** to **24ts** was calculated to 4.1**.**

Catalyst poisoning with trimethylphosphine and mercury

Preparation of stock solution of trimethylphosphine in toluene: An ampoule containing pure trimethylphosphine (5 mL) was cracked and rapidly transferred into a flame-dried and purged Schlenk flask where it was kept under a flow of nitrogen. From this flask, trimethylphosphine (0.2 mL, 2 mmol) was transferred to a second flame-dried and purged Schlenk flask and diluted to 10 mL with freshly degassed, anhydrous toluene.

Iron complex **A** (20.5 mg, 0.05 mmol) and KO*t*Bu (22.5 mg, 0.2 mmol) were placed in an oven-dried Schlenk flask equipped with a cold finger. Vacuum was applied and the flask was filled with nitrogen gas (repeated three times). Freshly degassed, anhydrous toluene (2 mL) was added and the reaction mixture was heated to reflux using an oil bath. Benzyl alcohol (108 mg, 1 mmol), cyclohexylamine (99 mg, 1 mmol), tetradecane (0.1 mL as an internal standard) and catalyst poison (either 1 drop of metallic mercury or 0.1 mL of a freshly prepared 0.2 mol/L stock solution of trimethylphosphine in toluene) were added, and the reaction was refluxed while stirring under a flow of nitrogen for 48 h. The experiment was repeated with addition of catalyst poison after 24 hours of refluxing. In all cases, the reaction progress was monitored by GC-MS using the following sampling procedure:

After 48 hours, a 0.1 mL aliquot was taken, diluted to 1 mL with diethyl ether, filtered through a nylon syringe filter (pore size: 0.22 µm) and subjected to GC-MS analysis where the yield of *N*-benzylidenecyclohexylamine was quantified using a calibration curve. The calculated GC yields are reported in the table below.

Entry	Poison	Yield (%)
1	None (for reference)	85
2	0.02 mmol PMe3 (added at 0 h)	15
3	1 drop Hg (added at 0 h)	24
4	0.02 mmol PMe3 (added after 24 h)	39
5	1 drop Hg (added after 24 h)	41

Energies of complexes

	E LACV3P**++	ZPE	H	S	Solv
BnOH	-346.8833855	83.641	5.096	84.812	-4.494
PhCHO	-345.6767939	69.174	4.519	79.302	-4.014
17	-1348.208136	248.038	25.414	192.371	-5.8911
17ts	-1348.157015	245.048	24.668	187.004	-6.4551
18	-1348.173252	246.846	25.699	194.245	-7.2337
19	-1349.391399	262.100	26.133	195.998	-5.7491
19ts	-1349.377856	259.808	25.500	192.465	-5.1515
20	-1349.424427	263.785	25.686	193.494	-6.4317
20ts	-1349.368705	260.532	25.026	188.743	-6.6923
21	-1349.385938	262.477	26.03	195.881	-7.6794
22	-1003.673843	191.767	18.574	155.351	-7.2627
23	-1350.603648	277.872	26.366	196.622	-6.6365
23ts	-1350.590454	275.517	25.766	193.493	-5.5745
24	-1350.63268	279.251	26.001	194.772	-6.9269
24ts	-1350.570639	274.900	25.925	194.036	-7.4501
25	-1004.878202	204.613	19.278	158.36	-8.6738
25ts	-1004.832248	200.756	19.026	157.25	-7.3066

Cartesian coordinates of complexes

17

C	-1.8952	1.2407	-2.9598
C	-1.6527	-0.2659	-3.1142
H	-1.1373	1.798	-3.5196
H	-2.5215	-0.8087	-2.7166
N	-0.4683	-0.6237	-2.3268
N	-1.7086	1.5475	-1.5536
Fe	0.2235	0.8634	-0.9123
C	0.0817	-1.7793	-2.528
H	-0.318	-2.4119	-3.3329
C	-2.6458	2.0628	-0.8363
H	-3.5995	2.322	-1.3152
C	-2.4716	2.9382	3.3062
C	-1.3409	2.4305	2.6892
C	-1.3397	2.1078	1.3102
C	-2.5475	2.3351	0.574
C	-3.6808	2.8582	1.2333
C	-3.6583	3.1576	2.583

H	-4.5865	3.0266	0.6536
C	3.1816	-3.6344	-0.3235
C	2.7302	-2.3965	0.0924
C	1.712	-1.7088	-0.6188
C	1.1613	-2.3515	-1.7785
C	1.6462	-3.6227	-2.1704
C	2.6438	-4.2637	-1.4649
H	1.2103	-4.0961	-3.0483
O	1.3051	-0.5511	-0.1865
O	-0.2443	1.6362	0.7707
H	-0.4224	2.2568	3.2404
H	3.1351	-1.9086	0.973
O	1.2893	1.905	-1.9714
C	1.6102	3.2742	-1.876
H	2.2247	3.5459	-2.7479
H	2.2192	3.4526	-0.9765
C	-2.0568	5.5546	-1.7408
C	-1.5329	5.1397	-2.9686
C	-0.3259	4.4417	-3.0111
C	0.3681	4.1426	-1.8322
C	-0.1595	4.5722	-0.6105
C	-1.3644	5.2741	-0.5617
H	-2.9987	6.096	-1.7048
H	-2.0642	5.3635	-3.8904
H	0.0814	4.114	-3.9655
H	0.3594	4.3199	0.3097
H	-1.7724	5.5802	0.3974
H	-1.537	-0.5384	-4.1719
H	-2.8912	1.5218	-3.3289
H	-2.4399	3.1684	4.3683
H	3.9639	-4.1331	0.2436
H	-4.5397	3.5543	3.0766
H	3.0057	-5.2376	-1.7785

17ts

C	-2.7957	0.8158	-2.0056
C	-2.6987	-0.6911	-2.2778
H	-2.2336	1.3612	-2.7826
H	-3.3902	-1.2149	-1.6062
N	-1.3389	-1.1064	-1.9474
N	-2.2196	1.0398	-0.6939
Fe	-0.4461	0.0971	-0.405

C	-0.6863	-1.9146	-2.7156
H	-1.185	-2.3044	-3.6139
C	-2.2496	2.3161	-0.1946
H	-3.0579	2.9604	-0.5704
C	-1.496	2.945	3.9876
C	-0.8779	1.8843	3.3385
C	-1.0973	1.6467	1.9673
C	-1.9878	2.5047	1.2615
C	-2.5907	3.5715	1.938
C	-2.3577	3.7998	3.2905
H	-3.2611	4.2284	1.387
C	3.2867	-3.3159	-2.2281
C	2.7666	-2.4624	-1.2713
C	1.4504	-1.9521	-1.3836
C	0.6669	-2.3626	-2.5121
C	1.2299	-3.2386	-3.4677
C	2.5217	-3.713	-3.3409
H	0.6228	-3.537	-4.3203
O	1.0012	-1.1366	-0.4652
O	-0.4431	0.6502	1.3812
H	-0.1974	1.218	3.8589
H	3.3492	-2.1488	-0.4111
H	2.9406	-4.3808	-4.0868
H	-2.8419	4.6291	3.7972
O	0.2479	1.5722	-1.5646
C	0.1373	2.8294	-1.2894
H	-1.2455	2.9148	-0.7346
H	-0.0515	3.5046	-2.1391
C	2.1608	4.5786	2.0543
C	1.2518	5.3373	1.3116
C	0.6089	4.7708	0.2158
C	0.8624	3.4393	-0.1429
C	1.7808	2.6852	0.5986
C	2.4273	3.2569	1.6916
H	2.6585	5.0178	2.9144
H	1.0396	6.3644	1.5943
H	-0.1134	5.3513	-0.3546
H	1.9708	1.6549	0.317
H	3.1356	2.6669	2.2659
H	-2.966	-0.9346	-3.3154
H	-3.8452	1.144	-2.0563
H	-1.3046	3.1107	5.0447
H	4.304	-3.6831	-2.1176

18

C	-3.1535	0.4893	-1.8788
C	-2.8122	-0.977	-2.1846
H	-2.7476	1.1313	-2.6821
H	-3.412	-1.6234	-1.5314
N	-1.4072	-1.1777	-1.8588
N	-2.5468	0.8466	-0.6163
Fe	-0.7689	0.089	-0.2434
C	-0.6217	-1.8244	-2.656
H	-1.0371	-2.241	-3.5849
C	-2.9227	2.1523	-0.1206
H	-4.0078	2.3104	-0.2379
C	-1.8777	3.2306	3.9466
C	-1.0881	2.3108	3.2674
C	-1.3991	1.9072	1.9524
C	-2.5443	2.458	1.3181
C	-3.3259	3.3753	2.0284
C	-3.009	3.7701	3.3276
H	-4.2085	3.7925	1.5455
C	3.5241	-2.5797	-2.157
C	2.8545	-1.8933	-1.1608
C	1.4702	-1.5977	-1.2673
C	0.7843	-2.0538	-2.4443
C	1.5017	-2.7572	-3.4399
C	2.8526	-3.0207	-3.3141
H	0.9647	-3.0924	-4.3256
O	0.8826	-0.9348	-0.309
O	-0.5897	1.0324	1.3571
H	-0.2043	1.8745	3.7231
H	3.3658	-1.5525	-0.2657
H	3.3871	-3.5579	-4.0908
H	-3.6401	4.4828	3.8506
O	-0.0082	1.6795	-1.6412
C	0.5516	2.7585	-1.4364
H	-2.449	2.9111	-0.7792
H	0.3422	3.5925	-2.1345
C	3.1906	3.7789	1.7275
C	2.6367	4.7786	0.9223
C	1.791	4.4243	-0.1229
C	1.4779	3.0725	-0.3519
C	2.0472	2.069	0.4538

C	2.9043	2.4313	1.4865
H	3.8536	4.0521	2.5441
H	2.8655	5.823	1.1114
H	1.3545	5.1925	-0.7576
H	1.8236	1.0254	0.2622
H	3.346	1.6616	2.112
H	-3.0429	-1.2317	-3.229
H	-4.2467	0.6318	-1.8716
H	-1.615	3.5242	4.9597
H	4.5868	-2.7808	-2.0435

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C	-2.9153	0.4071	-1.7072
C	-2.8394	-1.1187	-1.8955
H	-2.3753	0.9091	-2.5297
H	-3.5623	-1.5897	-1.217
N	-1.5057	-1.5293	-1.4866
N	-2.3223	0.7113	-0.4234
Fe	-0.8663	-0.4241	0.2566
C	-0.8194	-2.377	-2.1768
H	-1.2776	-2.8362	-3.0649
C	-2.5663	2.0372	0.1237
H	-3.5412	2.4227	-0.2126
C	-2.4325	2.1185	4.4482
C	-1.4149	1.4886	3.7368
C	-1.4422	1.4264	2.3285
C	-2.5261	2.0411	1.6401
C	-3.5367	2.6613	2.3788
C	-3.5054	2.7057	3.7741
H	-4.3668	3.1222	1.846
C	3.2084	-3.5301	-1.5291
C	2.6659	-2.5437	-0.7259
C	1.3152	-2.1356	-0.8699
C	0.5375	-2.7674	-1.8969
C	1.1282	-3.7639	-2.7065
C	2.4415	-4.1561	-2.5301
H	0.5236	-4.2257	-3.4851
O	0.8437	-1.209	-0.0808
O	-0.4765	0.7744	1.6824
H	-0.5715	1.0279	4.2437
H	3.2509	-2.0526	0.0446
H	2.8781	-4.9262	-3.1582

H	-4.3062	3.1904	4.3246
H	-1.8062	2.7368	-0.2699
H	-3.0789	-1.4155	-2.9267
H	-3.9633	0.7442	-1.7616
H	-2.3893	2.1464	5.5342
H	4.2459	-3.8231	-1.3862
C	-2.0234	-2.0272	2.8085
H	-2.8921	-2.5786	3.1876
O	-2.372	-1.4756	1.5047
H	-3.0062	-0.7501	1.6285
H	-1.7964	-1.2	3.4884
C	1.3847	-4.5702	2.1831
C	1.5626	-3.2236	2.5015
C	0.456	-2.4048	2.7222
C	-0.8382	-2.9318	2.6363
C	-1.0105	-4.2837	2.3159
C	0.0961	-5.101	2.0889
H	2.2478	-5.2031	1.9961
H	2.5624	-2.8039	2.5556
H	0.5852	-1.3431	2.914
H	-2.0152	-4.6936	2.2399
H	-0.0443	-6.1485	1.8363

19ts

C	-3.1725	0.1826	-1.5472
C	-2.8277	-1.2464	-1.9765
H	-2.6843	0.8961	-2.2332
H	-3.4094	-1.9522	-1.3697
N	-1.4168	-1.4738	-1.6748
N	-2.7072	0.3733	-0.1811
Fe	-0.8415	-0.6058	0.192
C	-0.6764	-2.1866	-2.4577
H	-1.1222	-2.5966	-3.3744
C	-2.8436	1.7454	0.3025
H	-3.8762	2.0989	0.1475
C	-1.8025	2.2355	4.4735
C	-0.936	1.5642	3.6163
C	-1.2742	1.3684	2.2651
C	-2.4963	1.8863	1.7674
C	-3.3476	2.5541	2.6504
C	-3.0172	2.7317	3.9954
H	-4.2913	2.9433	2.2736

C	3.3823	-3.2657	-1.8754
C	2.7786	-2.4378	-0.9453
C	1.429	-2.0375	-1.0922
C	0.7059	-2.5174	-2.2318
C	1.3569	-3.3549	-3.1658
C	2.676	-3.7324	-2.9998
H	0.7941	-3.7094	-4.0272
O	0.8988	-1.2485	-0.1927
O	-0.4373	0.6695	1.4892
H	0.0109	1.1641	3.966
H	3.3141	-2.0715	-0.0757
H	3.16	-4.3802	-3.7237
H	-3.7009	3.2493	4.6616
H	-2.198	2.4144	-0.2955
H	-3.0597	-1.419	-3.0361
H	-4.26	0.3451	-1.6344
H	-1.5305	2.3662	5.5176
H	4.4197	-3.5585	-1.7341
C	-2.3745	-1.9427	2.5243
H	-3.3204	-2.431	2.7913
O	-2.3979	-1.6397	1.1211
H	-2.9026	-0.6979	0.72
H	-2.2861	-1.016	3.1051
C	1.0259	-4.5384	3.0643
C	1.1917	-3.1527	3.0522
C	0.0824	-2.3169	2.9232
C	-1.2043	-2.8576	2.7938
C	-1.3614	-4.2478	2.8065
C	-0.2538	-5.0852	2.9448
H	1.8893	-5.1909	3.1645
H	2.1847	-2.7204	3.1387
H	0.213	-1.2387	2.8924
H	-2.3558	-4.6752	2.6993
H	-0.3873	-6.1638	2.9534

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C	-2.5165	1.8862	-2.196
C	-2.0895	0.5532	-2.8125
H	-1.8582	2.6818	-2.5658
H	-2.7539	-0.237	-2.4454
N	-0.7228	0.2426	-2.3571
N	-2.331	1.7688	-0.7565

Fe	-0.3623	1.112	-0.2248
C	-0.3883	-1.2035	-2.4229
H	-0.6537	-1.6186	-3.4058
C	-3.3073	2.0309	0.0521
H	-4.2631	2.3627	-0.3767
C	-3.3315	1.7416	4.2758
C	-2.1656	1.431	3.6019
C	-2.0929	1.5065	2.1867
C	-3.2715	1.9237	1.482
C	-4.4471	2.234	2.2066
C	-4.4904	2.1471	3.5834
H	-5.331	2.5463	1.6532
C	3.7885	-1.7375	-1.5552
C	2.9527	-1.1224	-0.626
C	1.5827	-0.954	-0.9007
C	1.0699	-1.4238	-2.1352
C	1.9243	-2.0354	-3.0523
C	3.2824	-2.1991	-2.7745
H	1.5196	-2.3795	-4.0021
O	0.7883	-0.3615	-0.0131
O	-0.9788	1.1908	1.5911
H	-1.2703	1.1153	4.1277
H	3.3295	-0.757	0.3244
O	0.5891	2.6116	-0.6739
C	1.872	2.645	-1.2566
H	2.5207	1.8681	-0.8259
H	2.3305	3.6214	-1.0344
C	1.3823	1.9951	-5.5039
C	0.6967	3.031	-4.8585
C	0.8934	3.2543	-3.4969
C	1.774	2.4477	-2.7588
C	2.4569	1.4173	-3.4112
C	2.2631	1.1935	-4.7785
H	1.2246	1.8148	-6.564
H	0.0091	3.66	-5.4185
H	0.3483	4.0409	-2.9819
H	3.1093	0.7584	-2.8453
H	2.7871	0.3753	-5.2643
H	-2.1617	0.5764	-3.9086
H	-3.5526	2.1319	-2.469
H	-0.0507	0.7594	-2.9255
H	-1.011	-1.6979	-1.6662
H	-5.3997	2.3865	4.1252

H	3.9366	-2.6759	-3.4981
H	-3.3534	1.6697	5.3604
H	4.845	-1.855	-1.3272

20ts

C	-2.8307	0.8394	-2.0029
C	-2.6838	-0.6254	-2.4056
H	-2.3283	1.4779	-2.7531
H	-3.2393	-1.2499	-1.6971
N	-1.2628	-0.9844	-2.288
N	-2.2255	0.9995	-0.693
Fe	-0.4748	0.0129	-0.388
C	-0.9578	-2.4301	-2.3677
H	-1.4183	-2.8837	-3.2577
C	-2.2016	2.2833	-0.202
H	-2.983	2.9532	-0.5896
C	-1.3977	2.9959	3.9552
C	-0.8058	1.9094	3.3245
C	-1.0511	1.6431	1.9627
C	-1.9351	2.4985	1.2482
C	-2.5118	3.5914	1.9051
C	-2.256	3.8471	3.249
H	-3.1777	4.2473	1.3474
C	3.3031	-3.0618	-2.3286
C	2.697	-2.3307	-1.3117
C	1.3084	-2.1098	-1.3208
C	0.5311	-2.6565	-2.3733
C	1.1617	-3.3828	-3.3855
C	2.5413	-3.5919	-3.3738
H	0.5593	-3.7912	-4.1948
O	0.7485	-1.3934	-0.3456
O	-0.4292	0.6245	1.3847
H	-0.128	1.2452	3.8512
H	3.2724	-1.907	-0.4943
O	0.2707	1.4413	-1.5927
C	0.2042	2.7026	-1.3158
H	-1.1758	2.8341	-0.7485
H	0.0287	3.3833	-2.1637
C	2.3088	4.3943	2.007
C	1.4086	5.1761	1.2775
C	0.7392	4.6276	0.1884
C	0.9566	3.2913	-0.1765

C	1.8656	2.514	0.5525
C	2.5395	3.0674	1.6381
H	2.8272	4.8195	2.8619
H	1.2238	6.207	1.5653
H	0.0234	5.2265	-0.371
H	2.0262	1.4796	0.2684
H	3.2406	2.4595	2.2026
H	-3.0816	-0.813	-3.4136
H	-3.8942	1.1234	-1.999
H	-0.719	-0.4841	-2.9936
H	-1.4172	-2.8907	-1.483
H	-2.7195	4.696	3.7425
H	3.0161	-4.1571	-4.1701
H	-1.1883	3.1856	5.0048
H	4.3791	-3.2153	-2.3083

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C	-3.3402	0.3994	-1.8291
C	-2.8643	-0.985	-2.2661
H	-3.1172	1.1359	-2.6263
H	-3.2221	-1.7328	-1.5492
N	-1.3974	-0.9983	-2.2127
N	-2.6628	0.7697	-0.6059
Fe	-0.8861	0.0471	-0.2332
C	-0.7588	-2.3241	-2.3608
H	-1.0701	-2.8165	-3.2944
C	-3.1226	2.0361	-0.0712
H	-4.2254	2.0752	-0.0879
C	-1.8634	3.3738	3.8542
C	-1.0948	2.4274	3.19
C	-1.4734	1.9349	1.9231
C	-2.6624	2.4233	1.3223
C	-3.4218	3.37	2.0191
C	-3.0403	3.8519	3.2698
H	-4.3383	3.7415	1.563
C	3.5215	-1.9433	-2.1273
C	2.7231	-1.5228	-1.0672
C	1.3195	-1.6258	-1.1355
C	0.7398	-2.1938	-2.3012
C	1.5591	-2.6056	-3.3534
C	2.948	-2.485	-3.2807
H	1.0989	-3.0313	-4.2437

O	0.5643	-1.1898	-0.1295
O	-0.6879	1.03	1.3456
H	-0.1775	2.0358	3.6197
H	3.1623	-1.1018	-0.1679
O	0.0661	1.5027	-1.6279
C	0.824	2.4683	-1.506
H	-2.8004	2.8349	-0.772
H	0.7843	3.2535	-2.2856
C	3.6236	3.3012	1.5726
C	3.3031	4.2775	0.6243
C	2.3936	3.9784	-0.3832
C	1.7862	2.71	-0.4369
C	2.1191	1.7276	0.5147
C	3.0394	2.0317	1.5116
H	4.3371	3.53	2.3598
H	3.7626	5.2601	0.6733
H	2.1386	4.7285	-1.1286
H	1.6703	0.7434	0.4649
H	3.3006	1.2772	2.2475
H	-3.2583	-1.2503	-3.259
H	-4.4369	0.3969	-1.7118
H	-1.0126	-0.3591	-2.909
H	-1.1214	-2.9331	-1.5225
H	-3.6548	4.5856	3.7833
H	3.5718	-2.8088	-4.1086
H	-1.5495	3.7371	4.8296
H	4.6022	-1.8449	-2.0535

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Fe	0.7815	-0.1876	2.9918
N	2.1896	-1.0507	1.9842
H	4.1545	-0.9606	2.6775
C	3.5137	-0.4633	1.9216
H	-1.2573	-3.4284	4.443
C	-1.1074	-2.4786	3.9149
C	0.7674	-2.9856	2.3362
C	2.1616	-2.4969	1.9306
H	0.0487	-2.7028	1.5594
H	2.9156	-2.9163	2.6231
N	0.337	-2.2866	3.5727
H	3.9833	-0.6894	0.9491
H	-1.6328	-2.5377	2.9559

C	-2.7098	0.9057	6.0246
C	-2.1673	1.0623	4.7516
C	-1.629	-0.0428	4.0695
C	-1.6543	-1.3172	4.699
C	-2.1964	-1.4497	5.9777
C	-2.7261	-0.3459	6.6481
H	-3.1175	1.7715	6.5405
H	-2.2074	-2.4301	6.4508
C	3.9111	3.7863	2.6703
C	2.9887	3.0509	3.404
C	2.8	1.6757	3.1618
C	3.5792	1.0328	2.1599
C	4.4914	1.8019	1.4298
C	4.667	3.1637	1.6718
H	4.037	4.8469	2.8703
H	5.0807	1.3167	0.6541
O	1.8736	1.0227	3.8813
O	-1.0817	0.0831	2.8468
H	-2.1385	2.0299	4.2604
H	2.3802	3.5098	4.177
H	5.3828	3.7329	1.0861
H	-3.1435	-0.4587	7.6441
H	0.9177	-2.5731	4.3604
H	2.4126	-2.8905	0.931
H	0.7412	-4.0784	2.4421

23

C	-2.5494	0.9558	-1.6229
C	-3.1562	-0.3993	-2.012
H	-1.7816	1.2504	-2.3637
H	-4.0178	-0.6034	-1.3681
N	-2.1535	-1.4297	-1.7204
N	-1.9862	0.8207	-0.2984
Fe	-1.436	-0.9144	0.3939
C	-2.609	-2.8352	-1.7315
H	-3.1808	-3.0626	-2.6438
C	-1.7476	2.0412	0.4659
H	-2.3073	2.8868	0.0409
C	-2.8082	1.5604	4.6336
C	-1.9819	0.6261	4.0146
C	-1.6339	0.7537	2.6542
C	-2.1335	1.8696	1.9244

C	-2.965	2.7895	2.568
C	-3.3097	2.6477	3.9141
H	-3.3484	3.6361	2.0013
C	0.7054	-5.5724	-1.3514
C	0.6221	-4.4694	-0.5075
C	-0.4399	-3.5499	-0.6159
C	-1.4292	-3.7698	-1.6138
C	-1.3166	-4.8783	-2.456
C	-0.2647	-5.7864	-2.3344
H	-2.0788	-5.0367	-3.2169
O	-0.4984	-2.5322	0.2373
O	-0.8902	-0.1856	2.07
H	-1.5833	-0.2253	4.5589
H	1.3646	-4.2884	0.264
H	-0.6782	2.3056	0.4
H	-3.4906	-0.4129	-3.0603
H	-3.3268	1.7358	-1.6601
H	-1.3586	-1.3357	-2.3525
H	-3.2875	-2.9542	-0.8776
H	-3.9615	3.3733	4.3915
H	-0.201	-6.6436	-2.998
H	-3.0666	1.4354	5.6823
H	1.5338	-6.2683	-1.2431
C	-2.5452	-4.3007	1.7251
C	-2.6034	-5.5612	1.1286
C	-3.8163	-6.0462	0.6398
C	-4.9737	-5.2695	0.7475
C	-4.9121	-4.0074	1.3357
C	-3.6959	-3.5125	1.8259
H	-1.5943	-3.9022	2.0632
H	-1.6952	-6.1455	1.0184
H	-3.8598	-7.0236	0.167
H	-5.9198	-5.6462	0.3679
H	-5.8083	-3.395	1.4074
C	-3.6104	-2.1114	2.3583
H	-2.7337	-1.9697	2.9976
H	-4.5129	-1.8376	2.9157
O	-3.4938	-1.2083	1.214
H	-3.6389	-0.2973	1.5242

23ts

C	-2.9296	0.8237	-1.5815

C	-3.1706	-0.5447	-2.2195
H	-2.0996	1.3353	-2.1044
H	-4.0261	-1.0257	-1.7364
N	-1.9942	-1.3935	-1.9474
N	-2.6227	0.6218	-0.1746
Fe	-1.4658	-1.1013	0.2371
C	-2.2105	-2.8511	-2.1355
H	-2.7281	-3.0494	-3.0848
C	-2.2726	1.8517	0.5351
H	-3.0205	2.6348	0.3294
C	-1.9488	1.3347	4.8199
C	-1.2921	0.4556	3.9638
C	-1.407	0.5935	2.5685
C	-2.1818	1.6524	2.0319
C	-2.8318	2.5181	2.9144
C	-2.7263	2.3711	4.2989
H	-3.4349	3.326	2.5052
C	1.5407	-4.9699	-1.9727
C	1.1973	-4.0873	-0.954
C	-0.0216	-3.3852	-0.996
C	-0.8994	-3.5921	-2.0922
C	-0.5289	-4.4766	-3.1064
C	0.6809	-5.1708	-3.0565
H	-1.2028	-4.626	-3.9479
O	-0.3254	-2.5479	-0.0086
O	-0.7956	-0.3037	1.7838
H	-0.6854	-0.3604	4.3449
H	1.8515	-3.914	-0.1053
H	-1.3097	2.2411	0.1553
H	-3.3794	-0.4654	-3.2954
H	-3.822	1.4568	-1.7236
H	-1.2134	-1.0999	-2.5351
H	-2.872	-3.1651	-1.3175
H	-3.2471	3.0558	4.9617
H	0.951	-5.8558	-3.8545
H	-1.8567	1.2064	5.8953
H	2.4872	-5.5022	-1.9244
C	-1.9537	-3.3692	2.7284
C	-1.3506	-4.6198	2.8574
C	-2.067	-5.7772	2.5485
C	-3.389	-5.6796	2.1087
C	-3.989	-4.427	1.9748
C	-3.2774	-3.2621	2.283

H	-1.387	-2.4652	2.9355
H	-0.3186	-4.6889	3.1896
H	-1.5965	-6.7519	2.6462
H	-3.9497	-6.5786	1.8662
H	-5.0153	-4.35	1.6222
C	-3.8708	-1.8998	2.0271
H	-3.5214	-1.1749	2.773
H	-4.967	-1.9363	2.0641
O	-3.4757	-1.4681	0.7128
H	-3.4439	-0.3658	0.4713

24

C	-1.6188	1.63	-1.9356
C	-1.3763	0.1628	-2.2798
H	-0.801	2.2507	-2.3163
H	-2.1983	-0.4441	-1.8793
N	-0.1332	-0.2898	-1.6372
N	-1.613	1.7746	-0.4668
Fe	0.3982	1.0367	0.2009
C	-0.0853	-1.7466	-1.3613
H	-0.2764	-2.3278	-2.2755
C	-1.8208	3.1776	-0.0103
H	-2.7326	3.5897	-0.4651
C	-1.9827	3.4526	4.2819
C	-0.8876	2.8557	3.6646
C	-0.8287	2.7444	2.2632
C	-1.9005	3.2593	1.4889
C	-2.9935	3.8446	2.131
C	-3.045	3.9497	3.5214
H	-2.0113	3.5246	5.3663
H	-3.813	4.2321	1.5284
C	3.6257	-2.8947	0.4853
C	2.826	-1.9177	1.0713
C	1.62	-1.5256	0.4646
C	1.2273	-2.1475	-0.7469
C	2.0466	-3.1215	-1.3205
C	3.2443	-3.5025	-0.7145
H	4.5572	-3.1824	0.9663
H	1.7373	-3.591	-2.2526
O	0.8544	-0.5893	1.0337
O	0.223	2.1672	1.6894
H	-0.0586	2.4549	4.2397

H	3.1084	-1.4322	2.0005
H	3.8721	-4.2615	-1.1718
H	-3.9019	4.4095	4.0046
H	-0.9701	3.7508	-0.3871
H	-1.3704	0.0137	-3.3684
H	-2.5608	1.984	-2.379
O	1.6205	1.7885	-0.9569
C	2.4564	2.8918	-0.6615
H	3.2529	2.9318	-1.4203
H	2.9404	2.7545	0.3166
C	0.0411	6.4788	-0.6818
C	0.5136	5.9616	0.5261
C	1.3251	4.825	0.5324
C	1.675	4.1909	-0.6645
C	1.2025	4.7211	-1.8728
C	0.3908	5.8561	-1.8842
H	-0.5966	7.3586	-0.6876
H	0.2352	6.4292	1.4664
H	1.6533	4.3962	1.474
H	1.4688	4.2307	-2.8068
H	0.0302	6.2561	-2.8285
H	0.6768	-0.0156	-2.1944
H	-0.9047	-1.9474	-0.6585
H	-2.3482	1.1932	-0.0606

24ts

Fe	-0.1628	-0.1642	2.955
H	1.0092	0.0524	0.5873
N	1.5222	-0.1485	1.4608
H	2.95	0.6912	2.7192
C	2.5191	0.9139	1.7328
H	-0.9525	-4.0685	2.3274
C	-1.0357	-3.0481	2.7263
C	0.9925	-2.5217	1.3788
C	2.1148	-1.4905	1.3248
H	0.2849	-2.3082	0.5719
H	2.8119	-1.6433	2.1596
N	0.28	-2.3561	2.6613
H	3.3366	0.8694	0.9988
H	-1.7075	-2.4851	2.0648
C	-2.5715	-3.1148	6.7514
C	-2.1466	-1.9142	6.1928

C	-1.6357	-1.8744	4.8815
C	-1.5616	-3.0806	4.1364
C	-1.9879	-4.2751	4.7216
C	-2.4958	-4.3042	6.0204
H	-2.962	-3.1246	7.7657
H	-1.9241	-5.1962	4.1456
C	0.8238	4.8683	1.8794
C	0.2877	3.8542	2.6652
C	0.8117	2.5523	2.6012
C	1.9044	2.288	1.7384
C	2.4204	3.3199	0.9519
C	1.8906	4.609	1.014
H	0.3986	5.8671	1.9331
H	3.255	3.109	0.2861
O	0.2819	1.5915	3.3615
O	-1.233	-0.712	4.3761
H	-2.1949	-0.9804	6.7443
H	-0.5535	4.0312	3.3274
H	2.3041	5.4004	0.3958
H	-2.8247	-5.242	6.4577
H	0.8585	-2.7054	3.4267
C	-1.4511	0.0088	0.0272
H	-1.2454	-0.107	1.6314
O	-0.4237	-0.4359	-0.5445
H	-2.331	-0.6515	0.1643
C	-2.4016	4.1915	0.0363
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C	-0.934	2.3791	-0.5963
C	-1.7767	1.4701	0.0503
C	-2.9315	1.9295	0.6958
C	-3.2431	3.2858	0.6905
H	-2.6429	5.2512	0.0344
H	-0.5868	4.4408	-1.1
H	-0.0443	2.0041	-1.0913
H	-3.5704	1.2192	1.2171
H	-4.137	3.6401	1.1966
H	2.6876	-1.5911	0.3926
H	1.3799	-3.5421	1.2538

25

H	-0.0048	0.1856	1.2732
Fe	0.5786	0.1921	2.8494

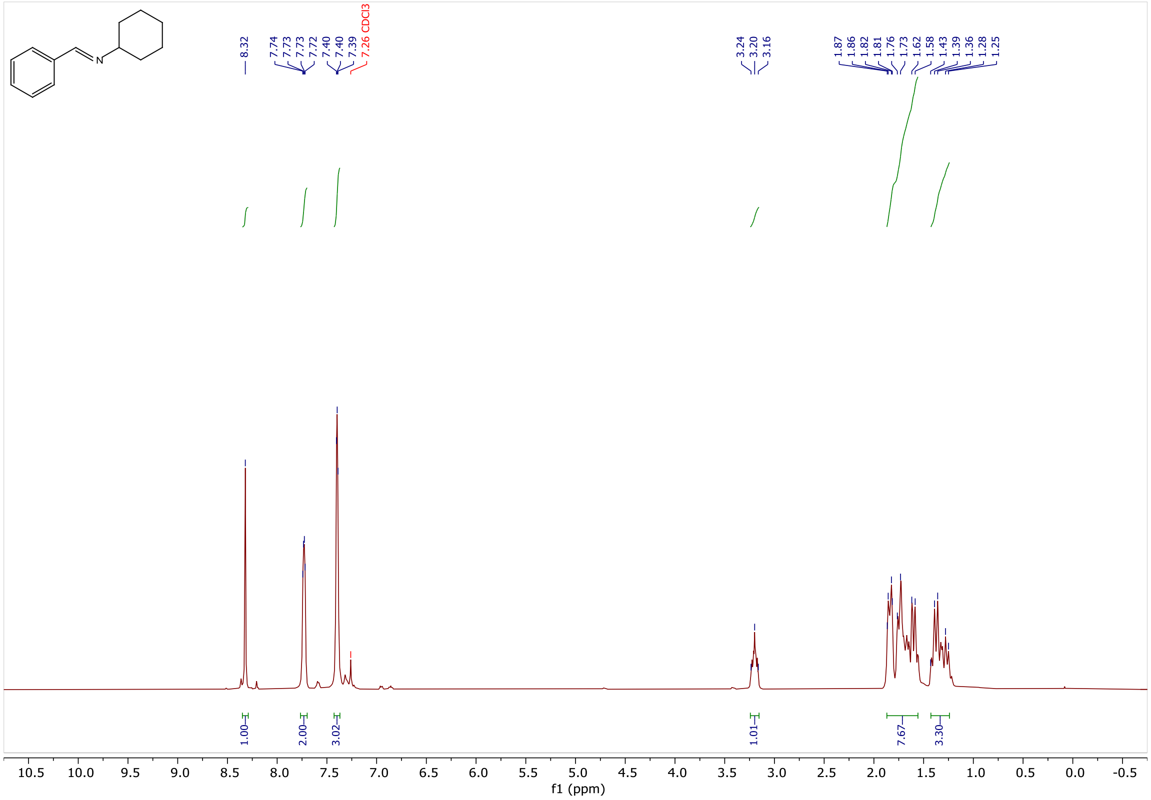
H	2.3737	-0.816	1.0957
N	2.4346	-1.0189	2.0933
H	3.6519	-0.5488	3.71
C	3.7143	-0.4719	2.6165
H	-1.6675	-3.1343	3.3734
C	-1.3658	-2.078	3.4046
C	0.7672	-2.7919	2.3371
C	2.2576	-2.4624	2.3246
H	0.3155	-2.5251	1.3753
H	2.6896	-2.6973	3.3054
N	0.1194	-1.9612	3.3654
H	4.5657	-1.0822	2.2825
H	-1.7312	-1.5896	2.4918
C	-2.899	-0.1048	6.9065
C	-2.1041	0.5949	6.0047
C	-1.5935	-0.0433	4.858
C	-1.9111	-1.4086	4.6352
C	-2.7039	-2.0933	5.5585
C	-3.2043	-1.4529	6.6923
H	-3.2806	0.4034	7.7883
H	-2.9354	-3.1421	5.3819
C	4.1972	3.6506	1.4974
C	3.0733	3.248	2.2127
C	2.9045	1.8995	2.5729
C	3.8985	0.9606	2.2015
C	5.0155	1.3847	1.4787
C	5.1755	2.7242	1.1235
H	4.3099	4.6969	1.2248
H	5.7714	0.6543	1.1957
O	1.8309	1.5196	3.2687
O	-0.8241	0.6303	4.0121
H	-1.852	1.6395	6.1575
H	2.3022	3.9531	2.5068
H	6.0489	3.0413	0.5618
H	-3.8208	-1.9974	7.401
H	0.4803	-2.2092	4.2877
H	2.7896	-3.0759	1.5847
H	0.6024	-3.8657	2.507

25ts

N	0.5181	0.0318	-0.4247
H	0.4034	0.2626	0.9472

H	0.8056	0.3531	1.8605
Fe	2.3057	0.2298	0.6062
H	0.4244	0.9878	-2.2763
C	-0.0328	1.0867	-1.2763
H	2.3684	-3.7224	1.7197
C	2.6684	-2.6681	1.6375
C	0.5781	-2.276	0.3186
C	0.0257	-1.3043	-0.728
H	0.1129	-2.0772	1.2894
H	0.3545	-1.6065	-1.7377
N	2.0204	-2.0228	0.4686
H	-1.1129	0.9285	-1.4201
H	2.292	-2.1427	2.5257
C	6.9559	-2.3198	1.3471
C	6.157	-1.1875	1.2236
C	4.7558	-1.2845	1.3133
C	4.1676	-2.557	1.5339
C	4.9894	-3.6811	1.6473
C	6.3777	-3.5752	1.5597
H	8.0359	-2.2242	1.2736
H	4.5312	-4.6547	1.8102
C	0.54	5.1887	-0.0126
C	1.5223	4.2477	0.2721
C	1.3584	2.8976	-0.0915
C	0.1767	2.4983	-0.7645
C	-0.7986	3.4639	-1.0308
C	-0.6318	4.8	-0.6663
H	0.6856	6.225	0.2805
H	-1.71	3.1603	-1.5424
O	2.328	2.0381	0.2306
O	4.0162	-0.183	1.1929
H	6.5853	-0.2042	1.0559
H	2.4381	4.5188	0.7882
H	-1.4082	5.5264	-0.887
H	6.9996	-4.4604	1.6521
H	2.5088	-2.3246	-0.3757
H	-1.0751	-1.3509	-0.73
H	0.3626	-3.3196	0.0497

NMR Spectra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7.40
7.39
7.26 CDCl3
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1.87
1.86
1.82
1.81
1.76
1.73
1.62
1.58
1.43
1.39
1.36
1.28
1.25
1.00
2.00
3.02
1.01
7.67
3.30
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
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2.0
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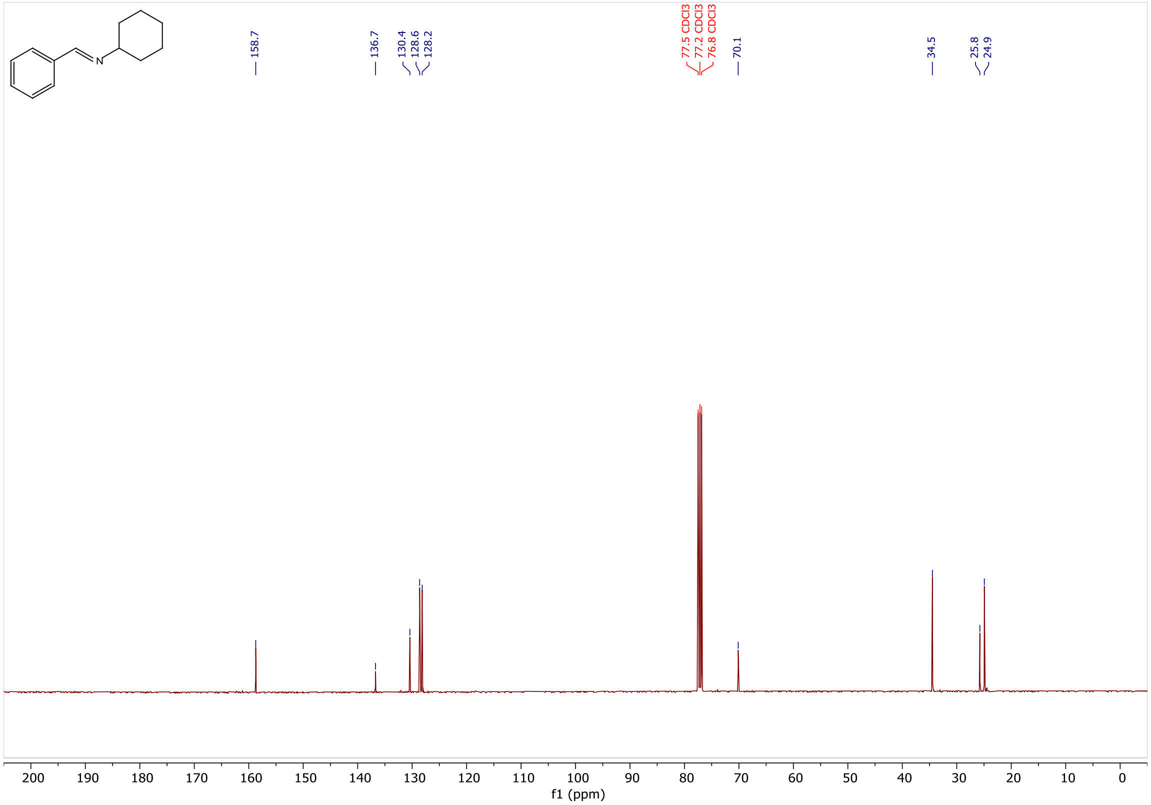
f1 (ppm)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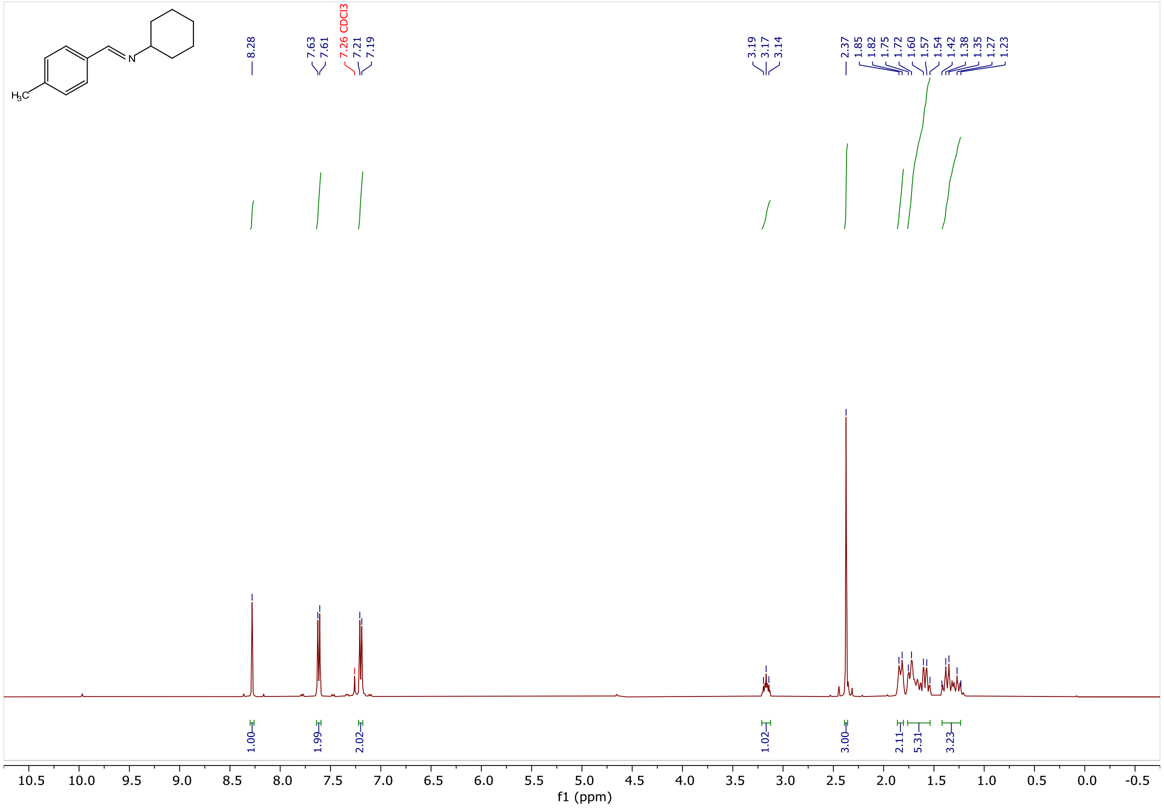
130.4
128.6
128.2
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
70.1
34.5
25.8
24.9
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.26 CDCl3
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7.19
3.19
3.17
3.14
2.37
1.85
1.82
1.75
1.72
1.60
1.57
1.54
1.42
1.38
1.35
1.27
1.23
1.00
1.99
2.02
1.02
3.00
2.11
5.31
3.23
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
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3.0
2.5
2.0
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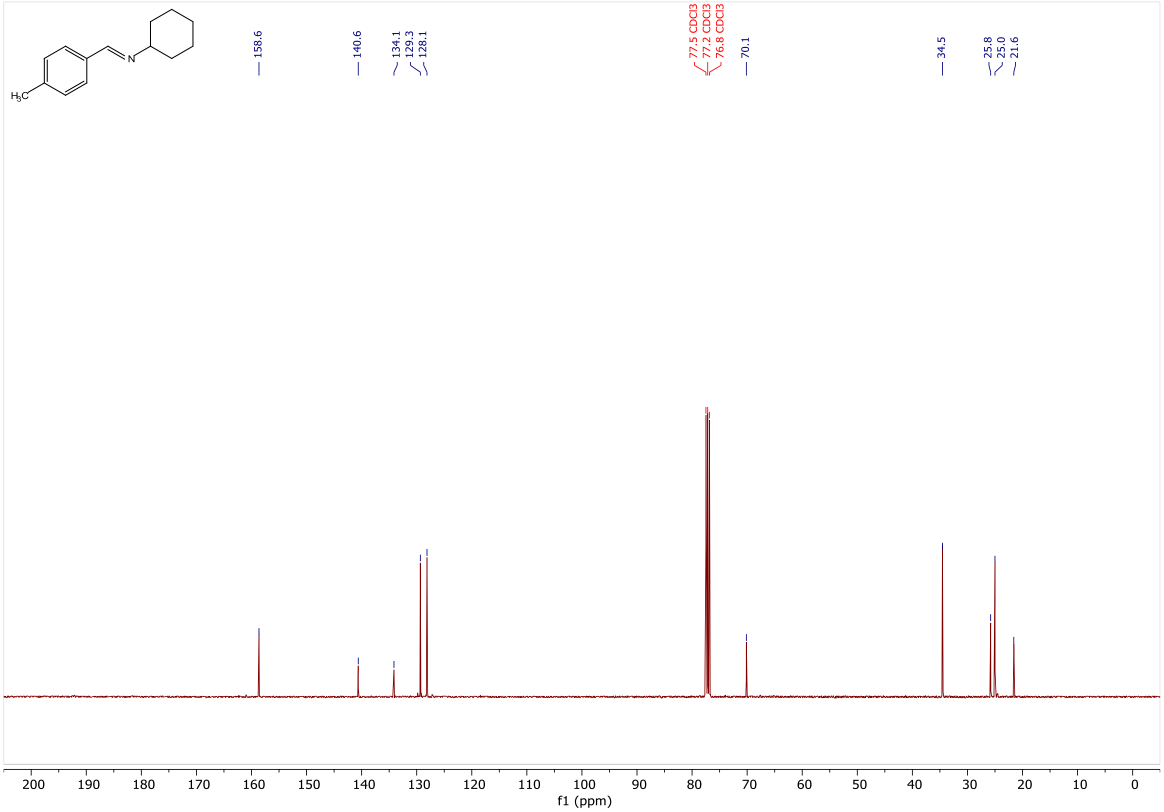
-0.5
f1 (ppm)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140.6
134.1
129.3
128.1
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
70.1
34.5
25.8
25.0
21.6
200
190
180
170
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150
140
130
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110
100
90
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70
60
50
40
30
20
10
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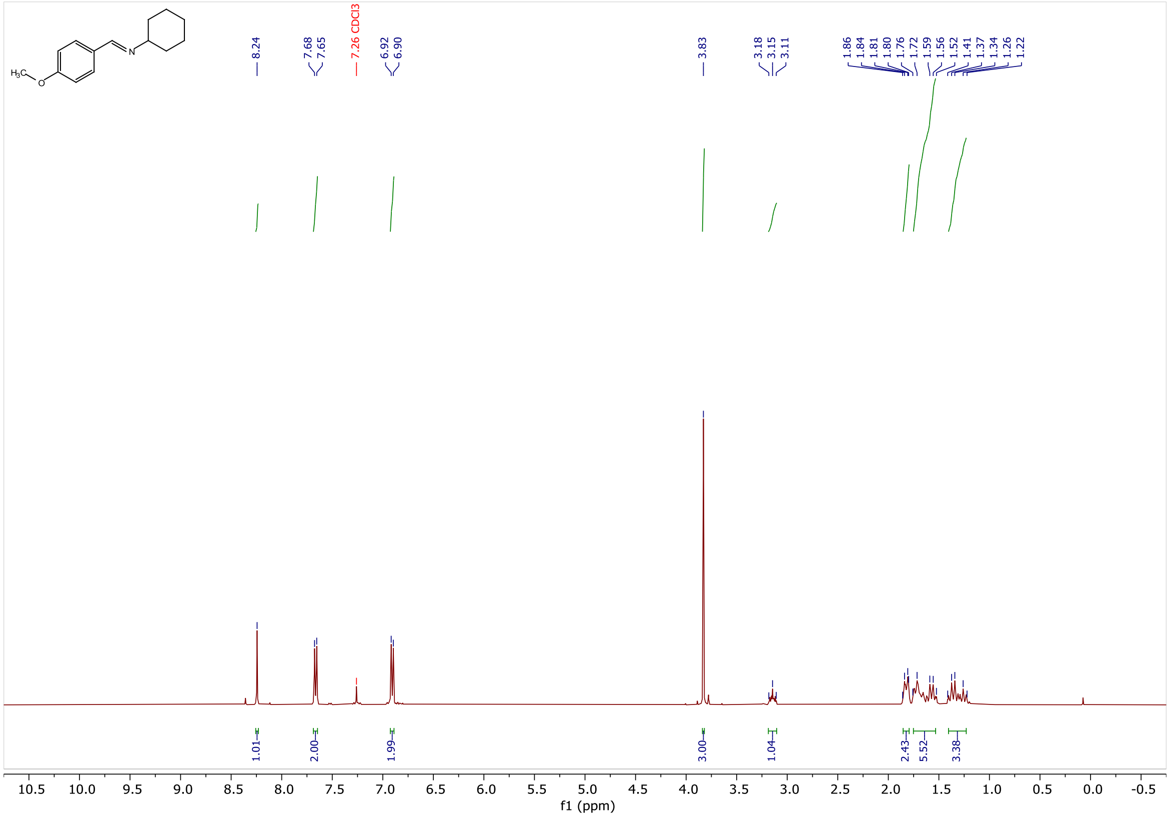
f1 (ppm)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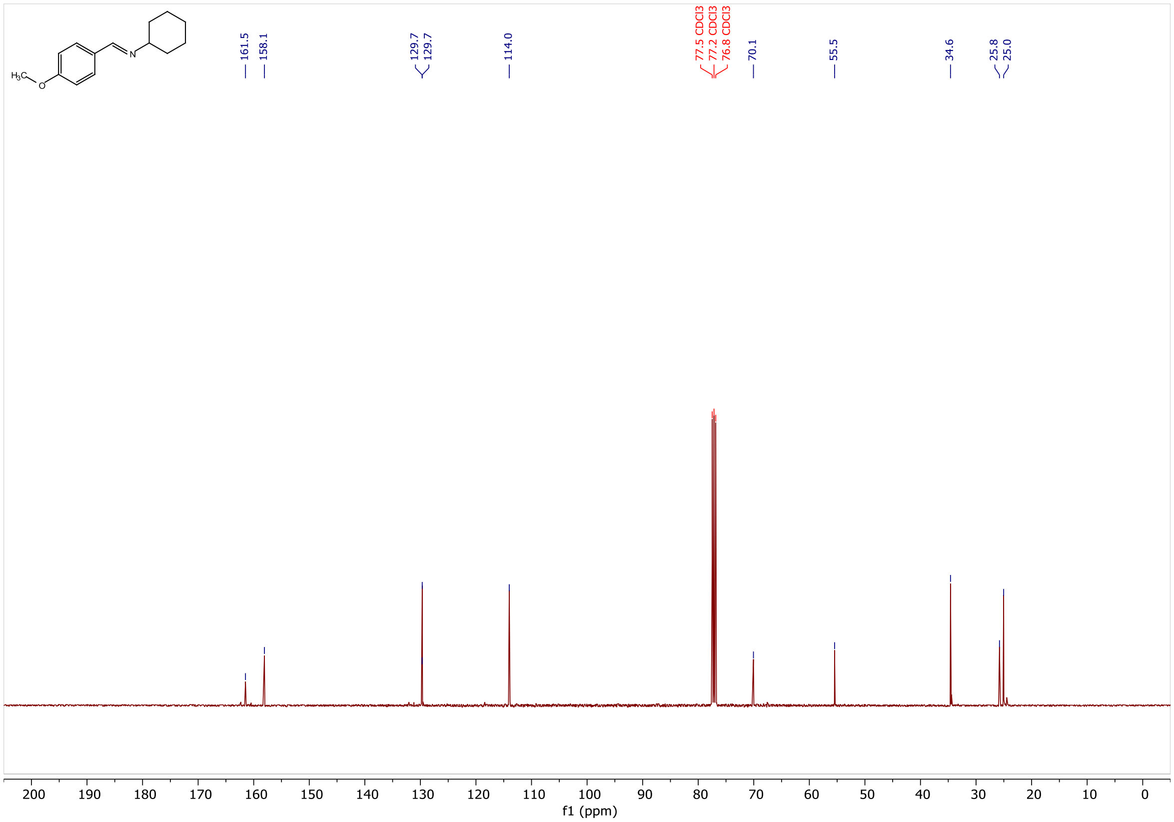
3.11
1.86
1.84
1.81
1.80
1.76
1.72
1.59
1.56
1.52
1.41
1.37
1.34
1.26
1.22
1.01
2.00
1.99
3.00
1.04
2.43
5.52
3.38
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


H3C
O
N
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77.2 CDCl3
76.8 CDCl3
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55.5
34.6
25.8
25.0
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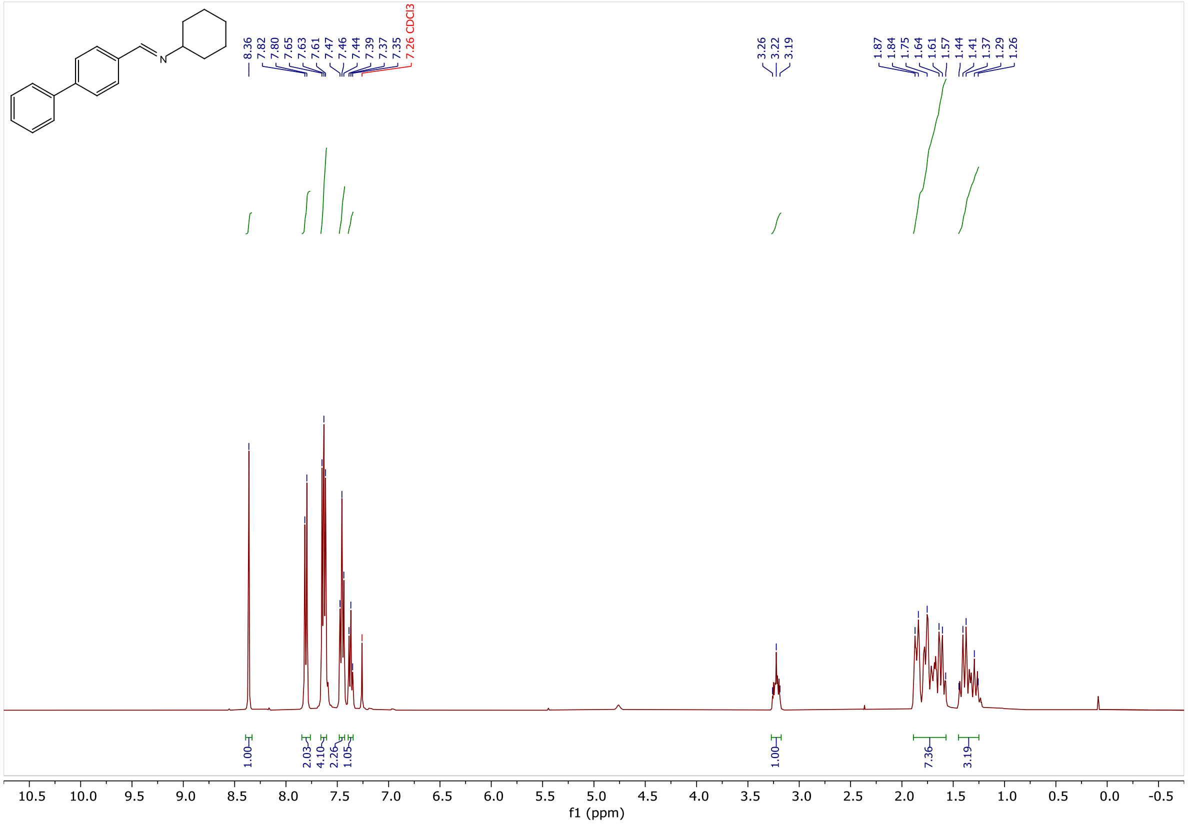
f1 (ppm)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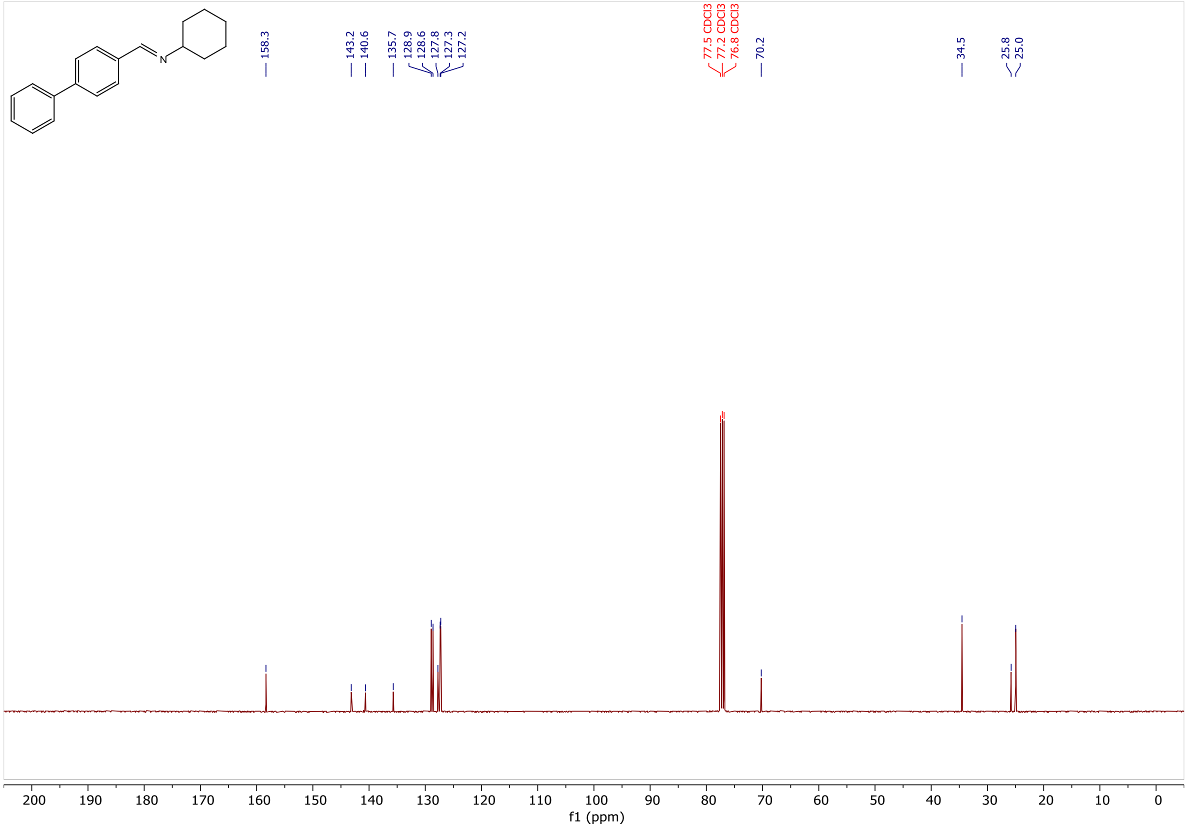
7.39
7.37
7.35
7.26 CDCl3
3.26
3.22
3.19
1.87
1.84
1.75
1.64
1.61
1.57
1.44
1.41
1.37
1.29
1.26
1.00
2.03
4.10
2.26
1.05
1.00
7.36
3.19
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


N
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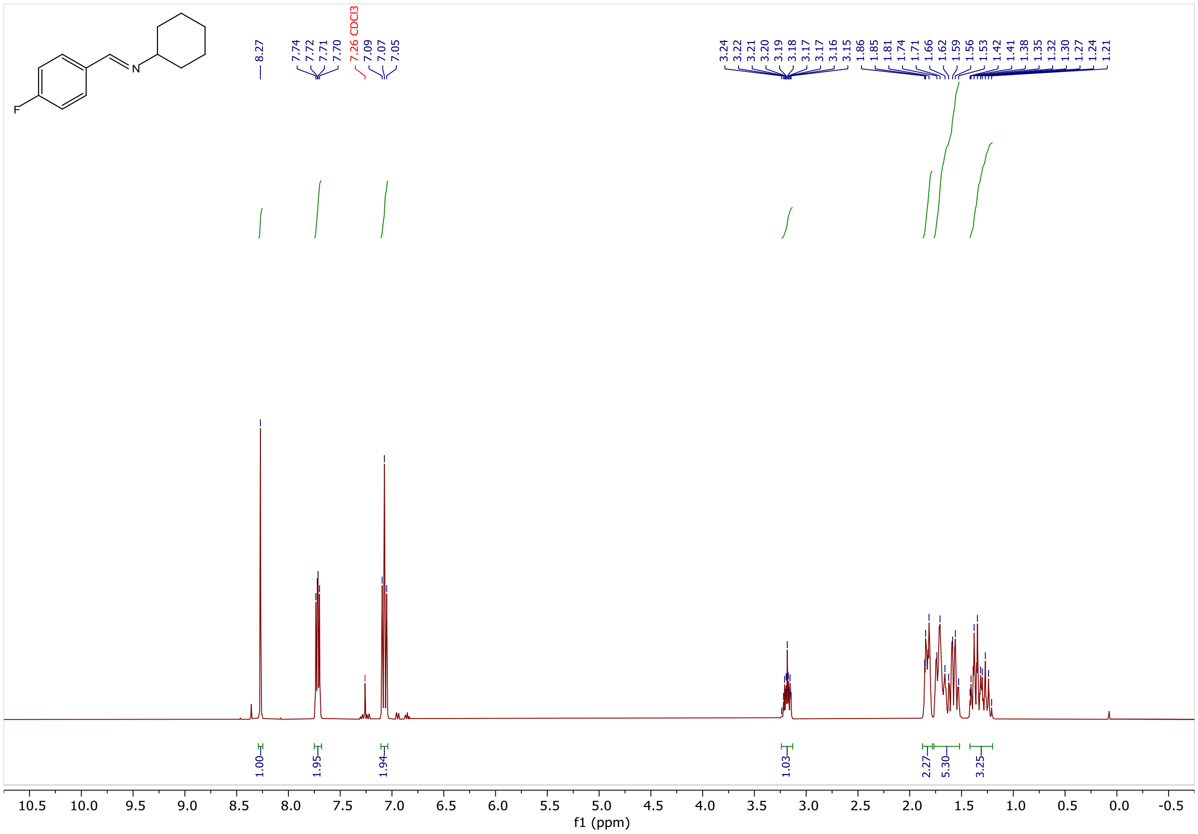
140.6
135.7
128.9
128.6
127.8
127.3
127.2
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
70.2
34.5
25.8
25.0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.70
7.26 CDCl3
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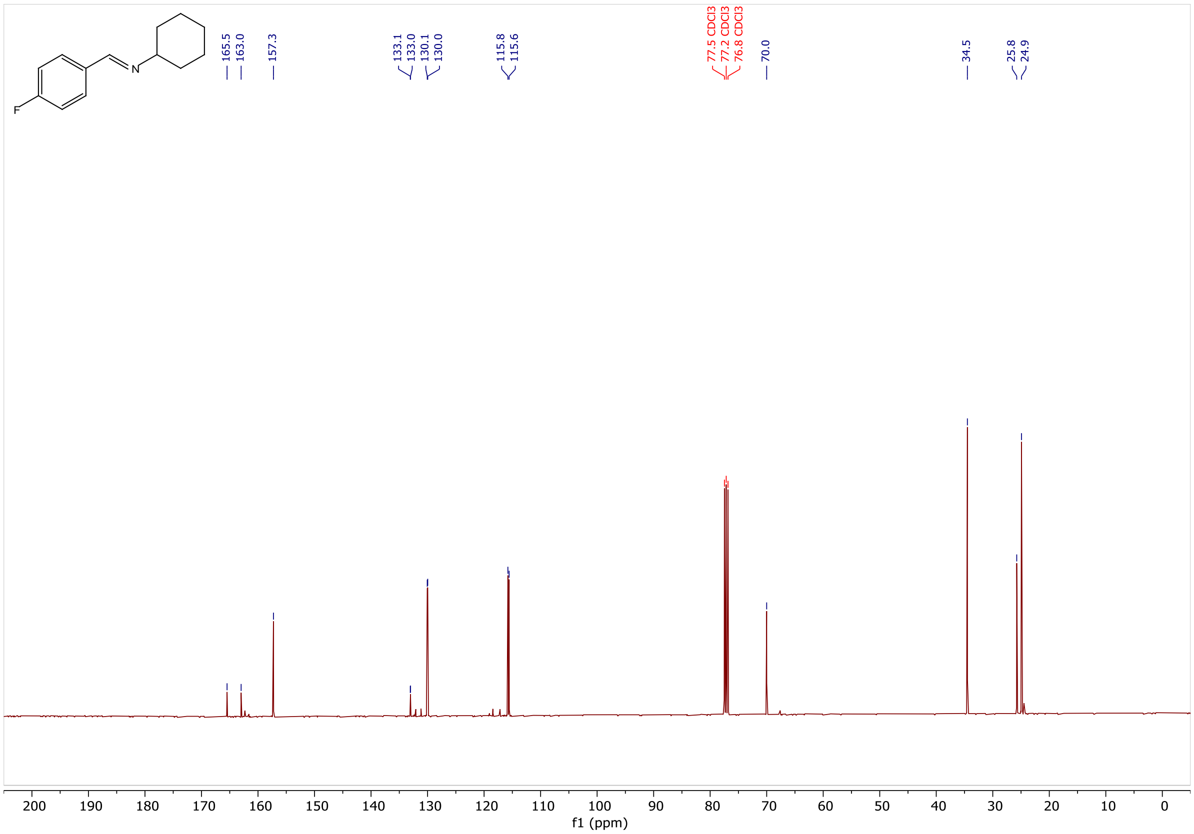
7.07
7.05
3.24
3.22
3.21
3.20
3.19
3.18
3.17
3.17
3.16
3.15
1.86
1.85
1.81
1.74
1.71
1.66
1.62
1.59
1.56
1.53
1.42
1.41
1.38
1.35
1.32
1.30
1.27
1.24
1.21
1.00
1.95
1.94
1.03
2.27
5.30
3.25
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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133.0
130.1
130.0
115.8
115.6
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
70.0
34.5
25.8
24.9
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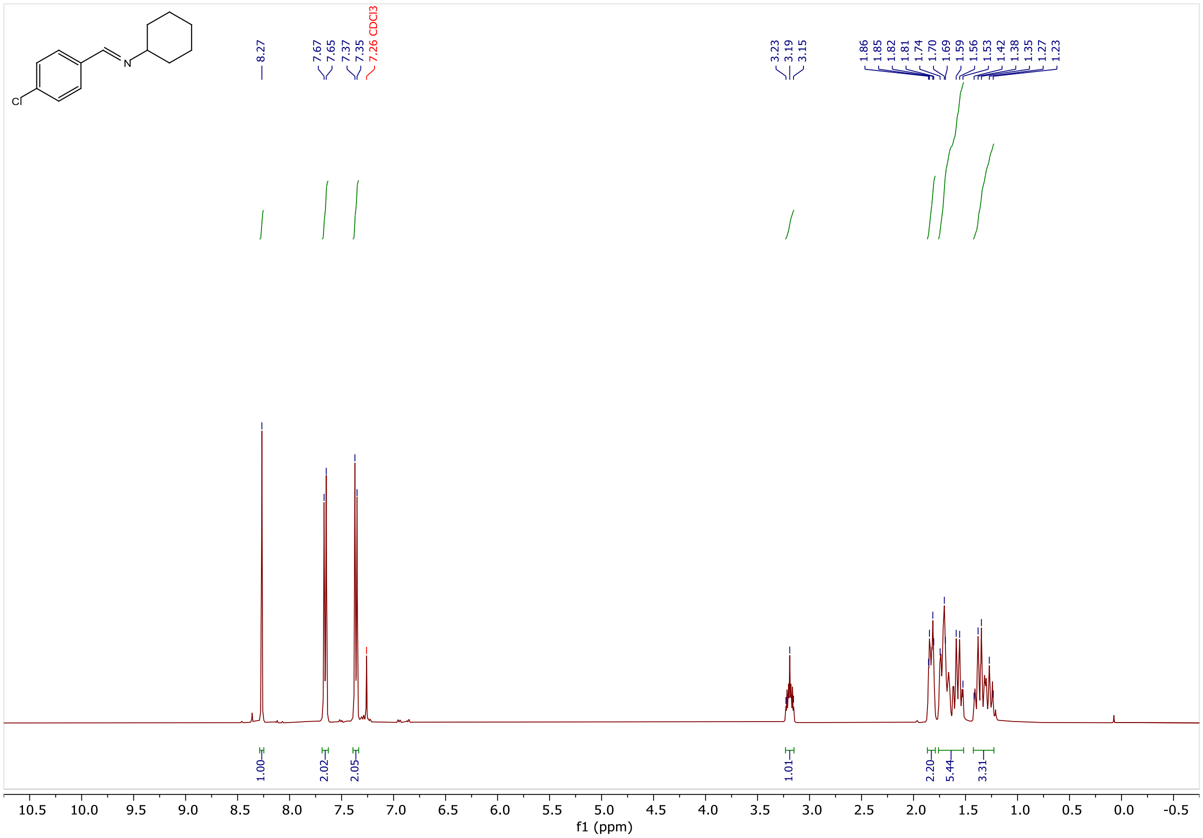
f1 (ppm)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3.19
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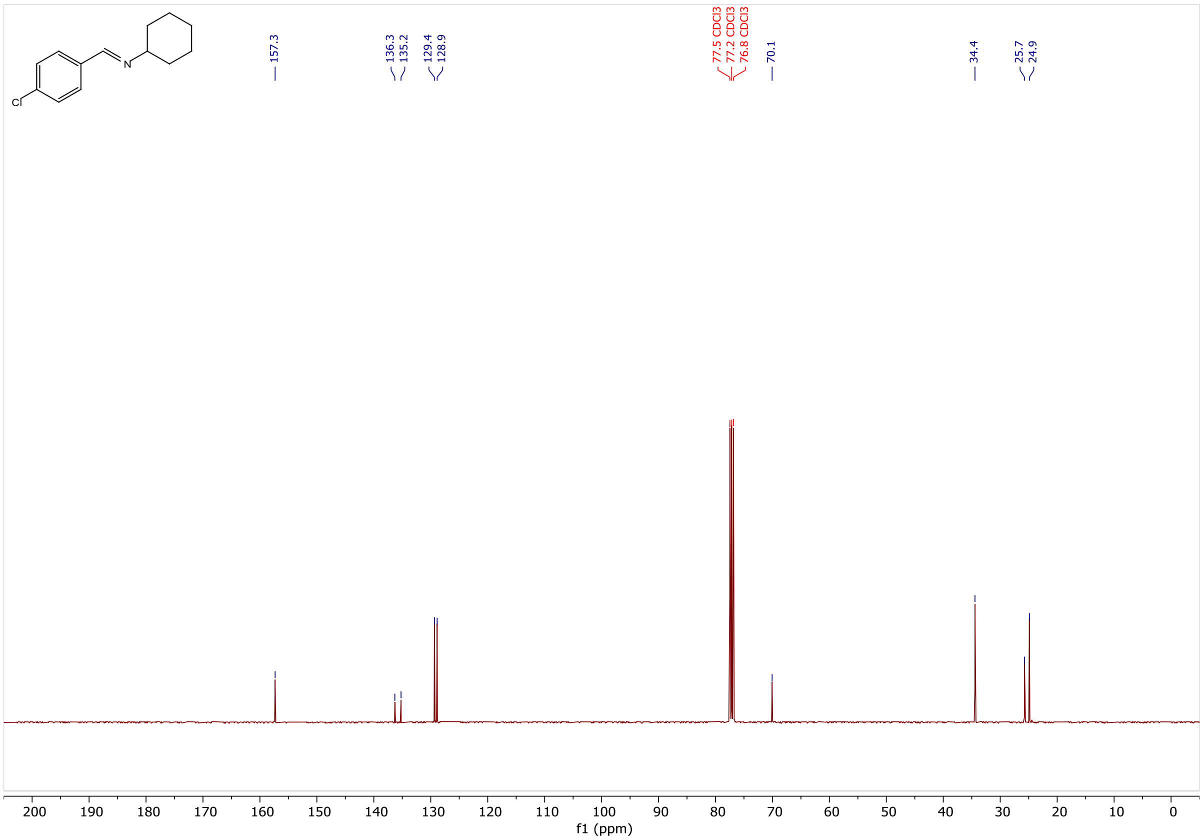
1.85
1.82
1.81
1.74
1.70
1.69
1.59
1.56
1.53
1.42
1.38
1.35
1.27
1.23
1.00
2.02
2.05
1.01
2.20
5.44
3.31
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


Cl
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77.2 CDCl3
76.8 CDCl3
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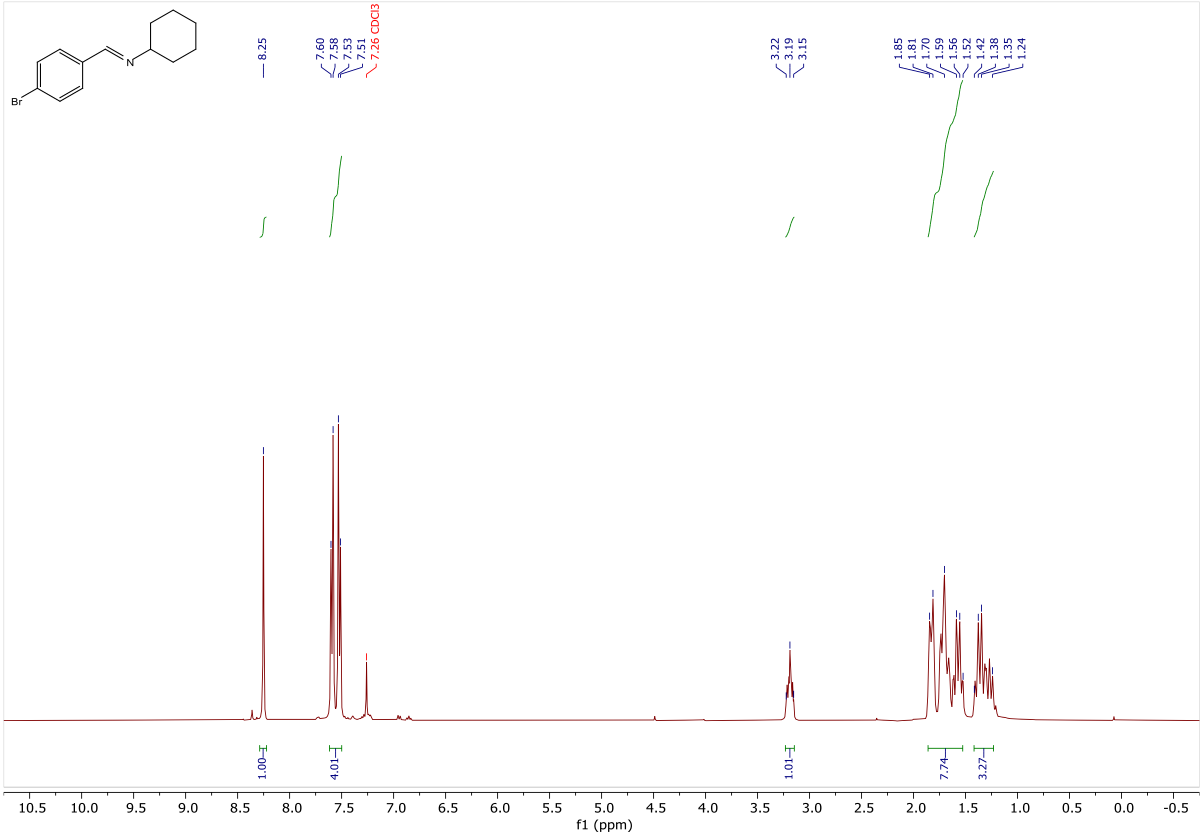
34.4
25.7
24.9
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Br
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7.51
7.26 CDCl3
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3.19
3.15
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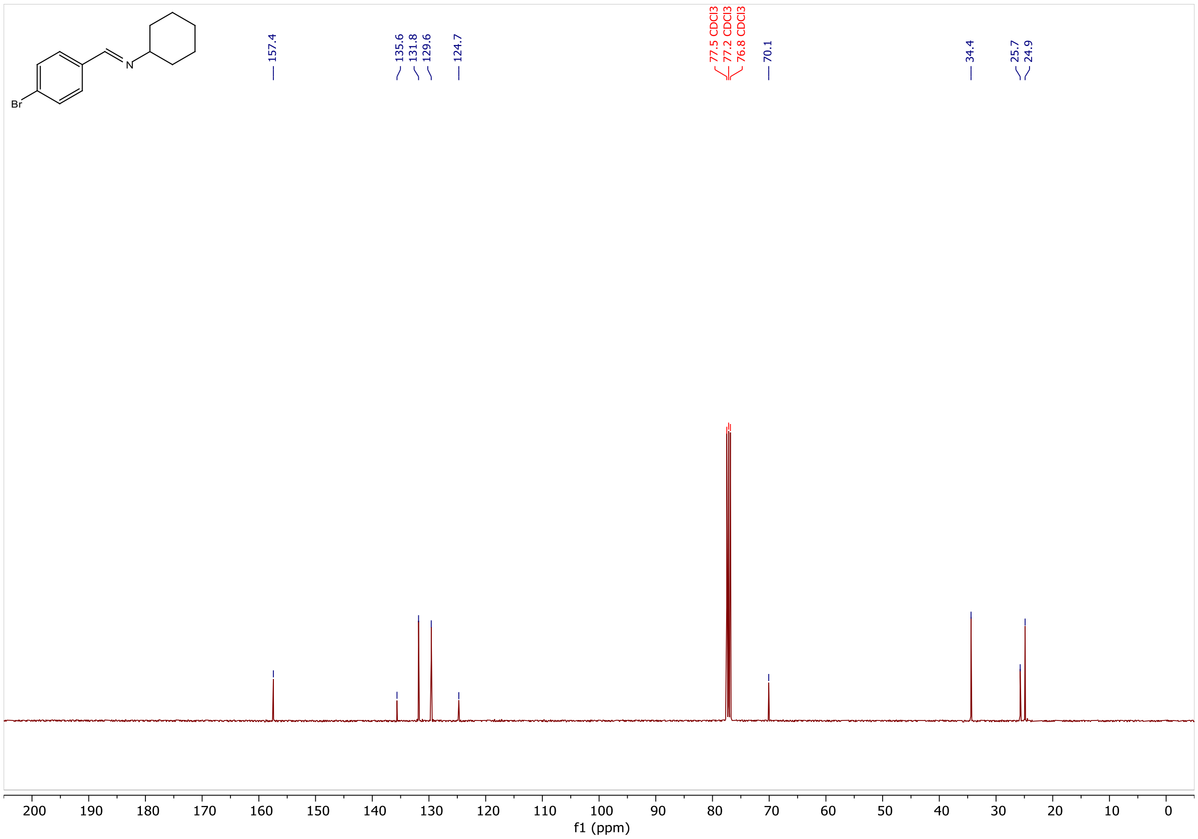
1.81
1.70
1.59
1.56
1.52
1.42
1.38
1.35
1.24
1.00
4.01
1.01
7.74
3.27
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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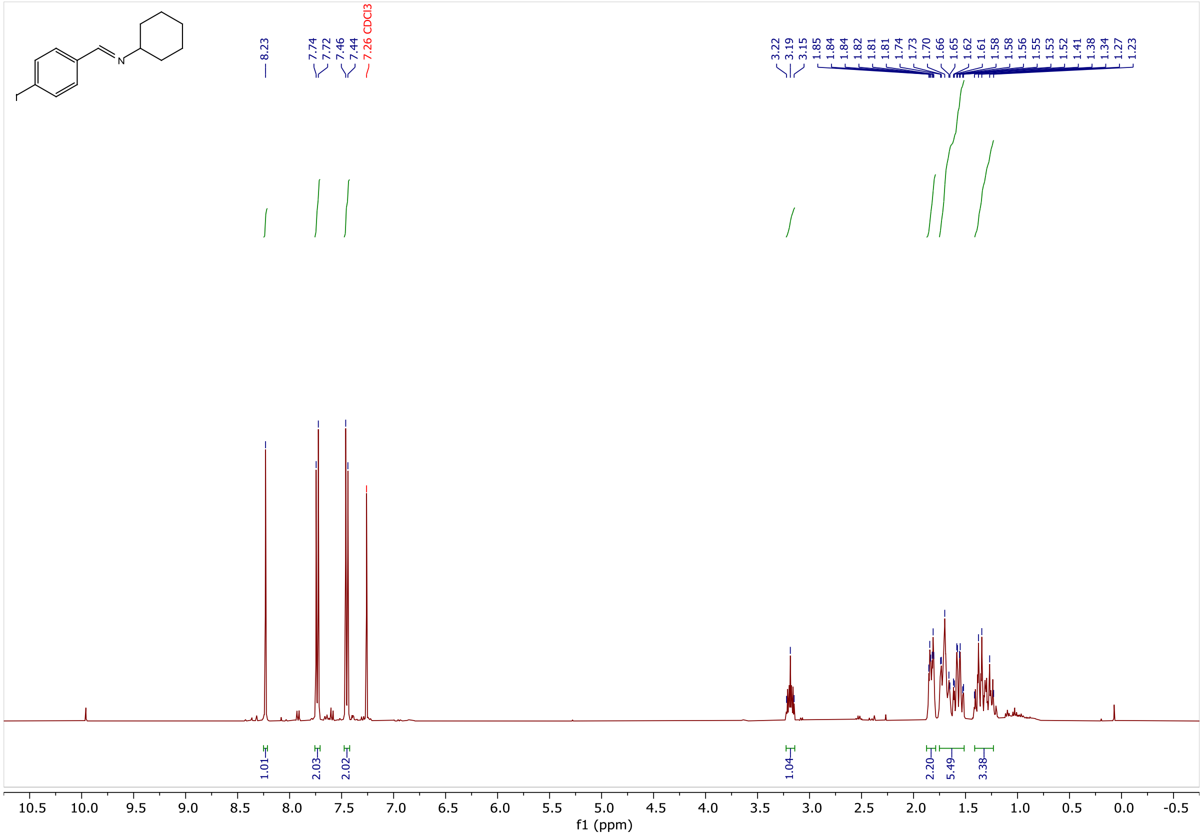
f1 (ppm)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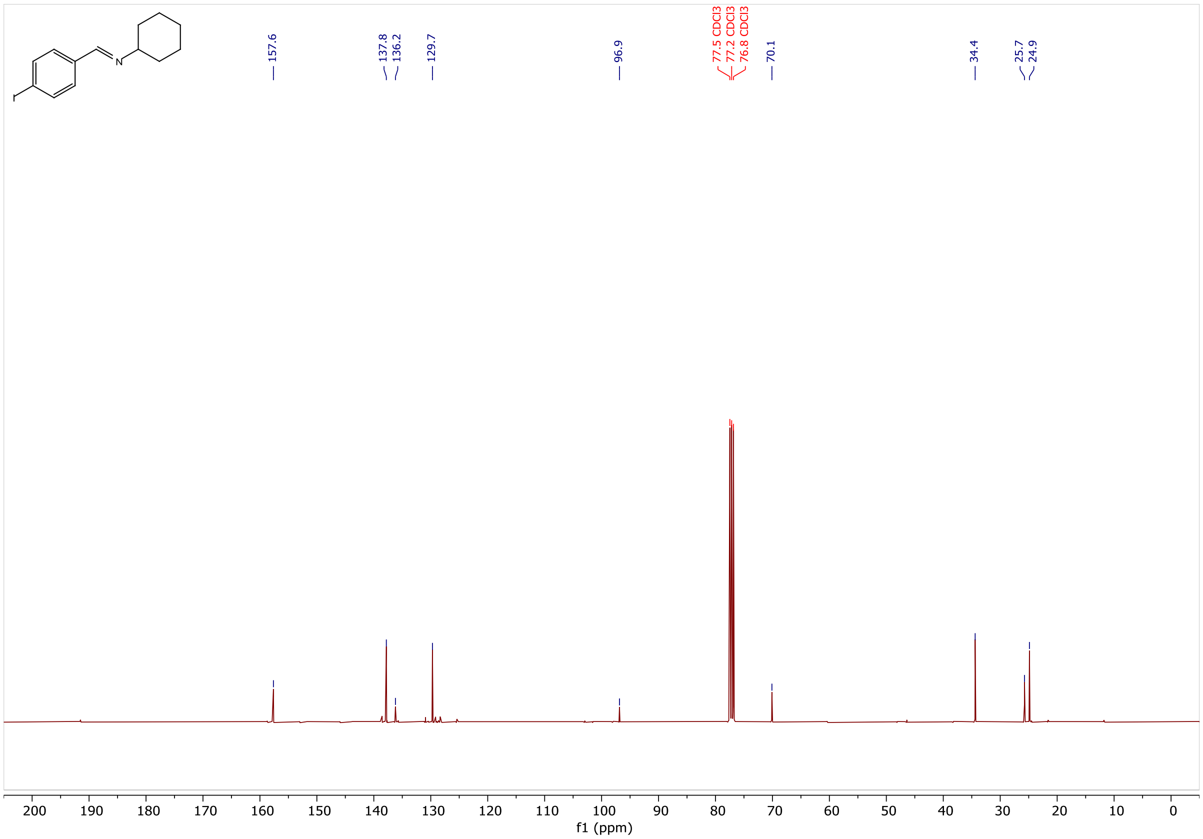
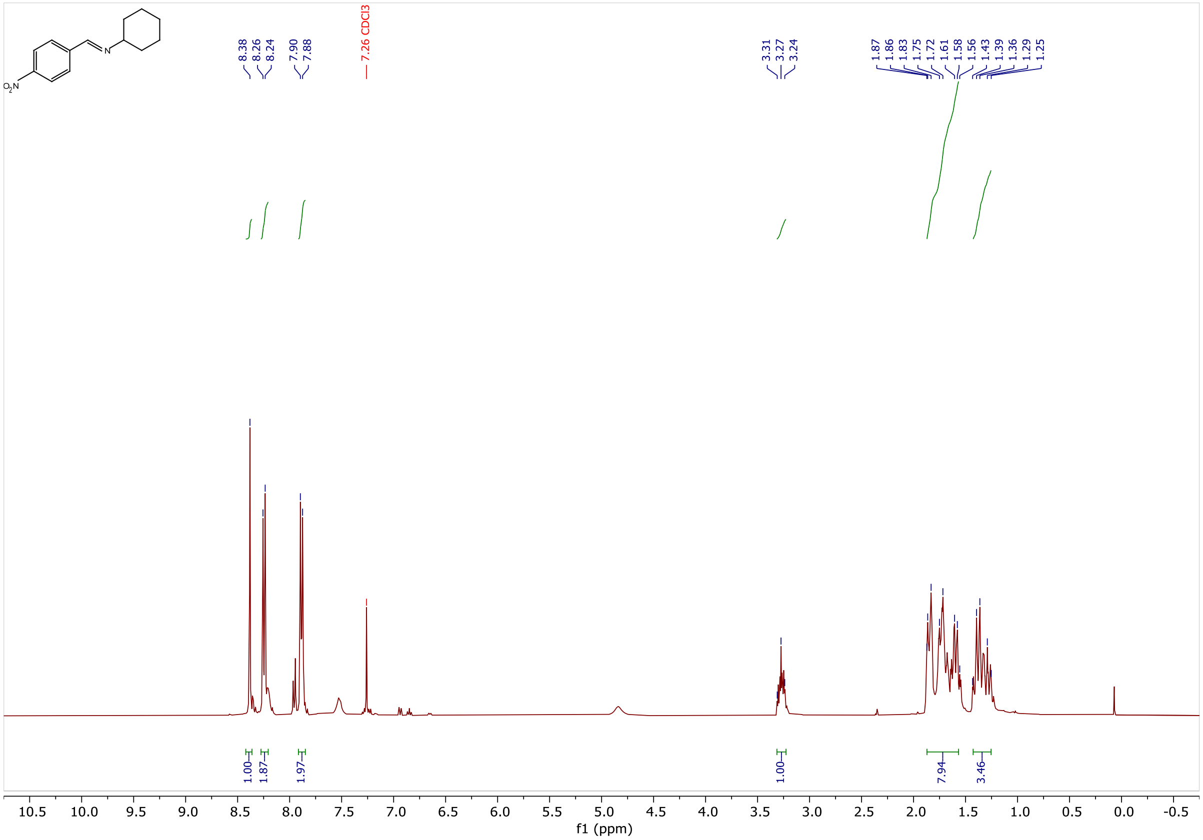
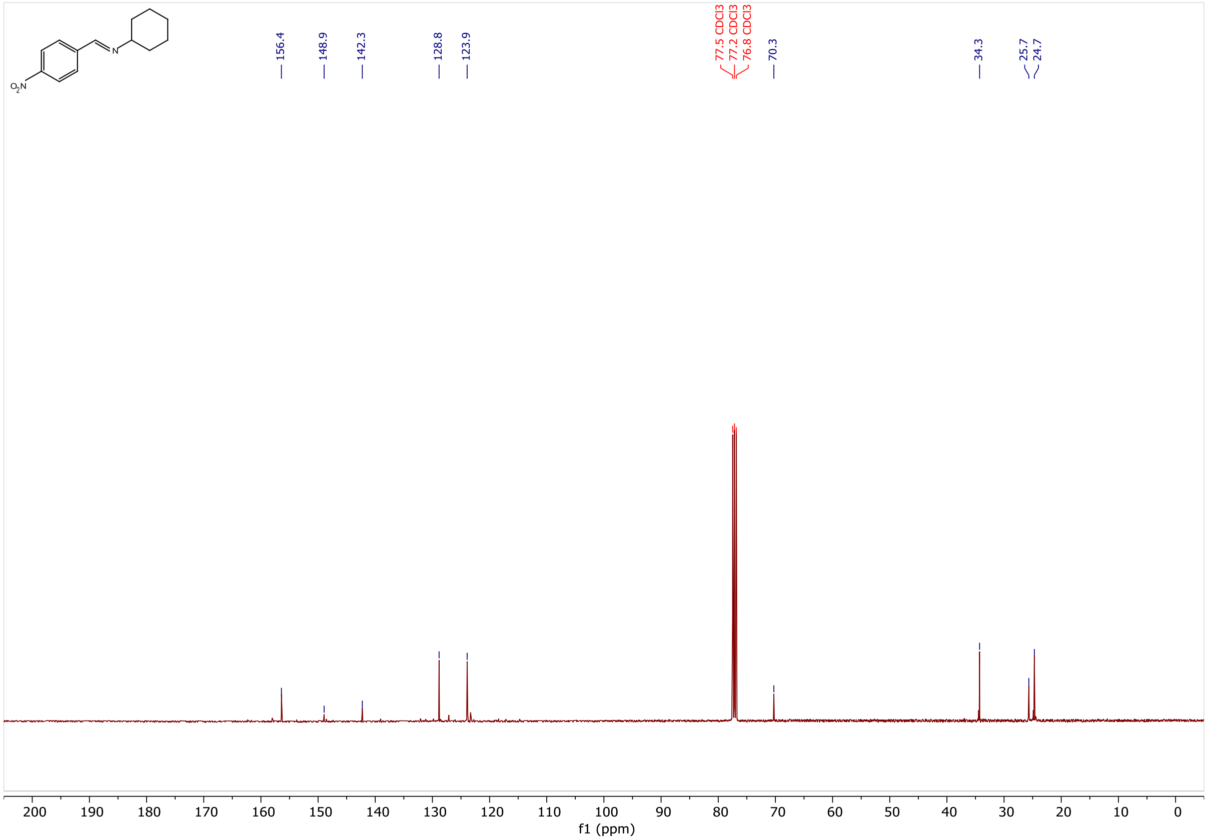
8.23
7.74
7.72
7.46
7.44
7.26 CDCl3
3.22
3.19
3.15
1.85
1.84
1.84
1.82
1.81
1.81
1.74
1.73
1.70
1.66
1.65
1.62
1.61
1.58
1.58
1.56
1.55
1.53
1.52
1.41
1.38
1.34
1.27
1.23
1.01
2.03
2.02
1.04
2.20
5.49
3.38
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


I
N
157.6
137.8
136.2
129.7
96.9
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
70.1
34.4
25.7
24.9
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O2N
N
8.38
8.26
8.24
7.90
7.88
7.26 CDCl3
3.31
3.27
3.24
1.87
1.86
1.83
1.75
1.72
1.61
1.58
1.56
1.43
1.39
1.36
1.29
1.25
1.00
1.87
1.97
1.00
7.94
3.46
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)


O2N
N
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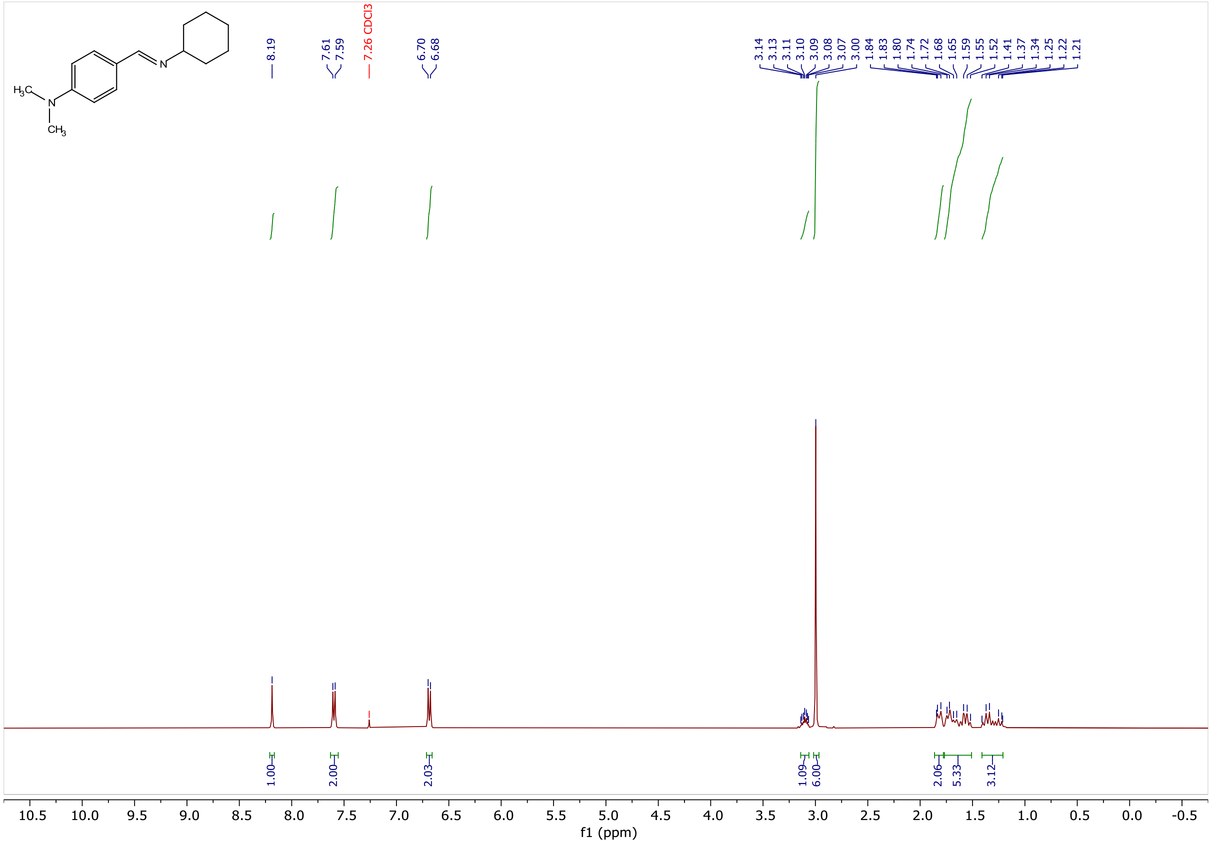
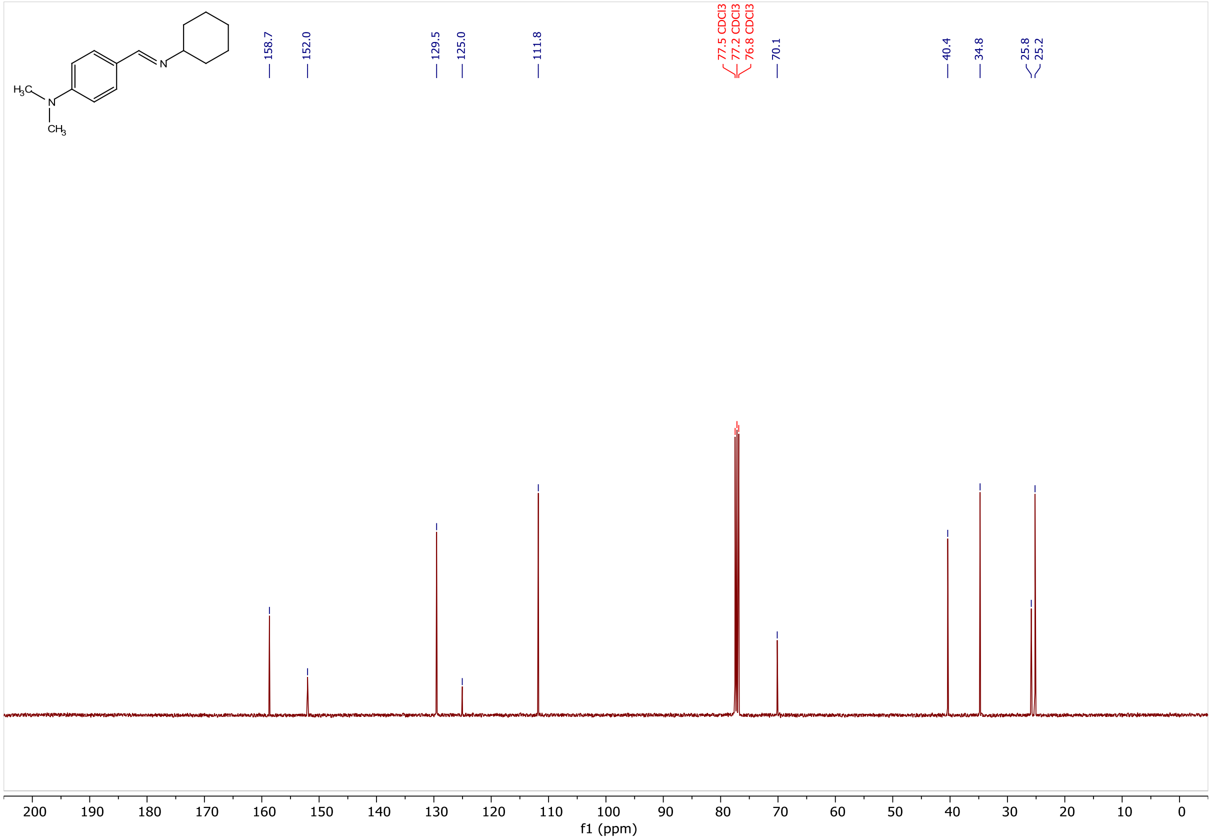
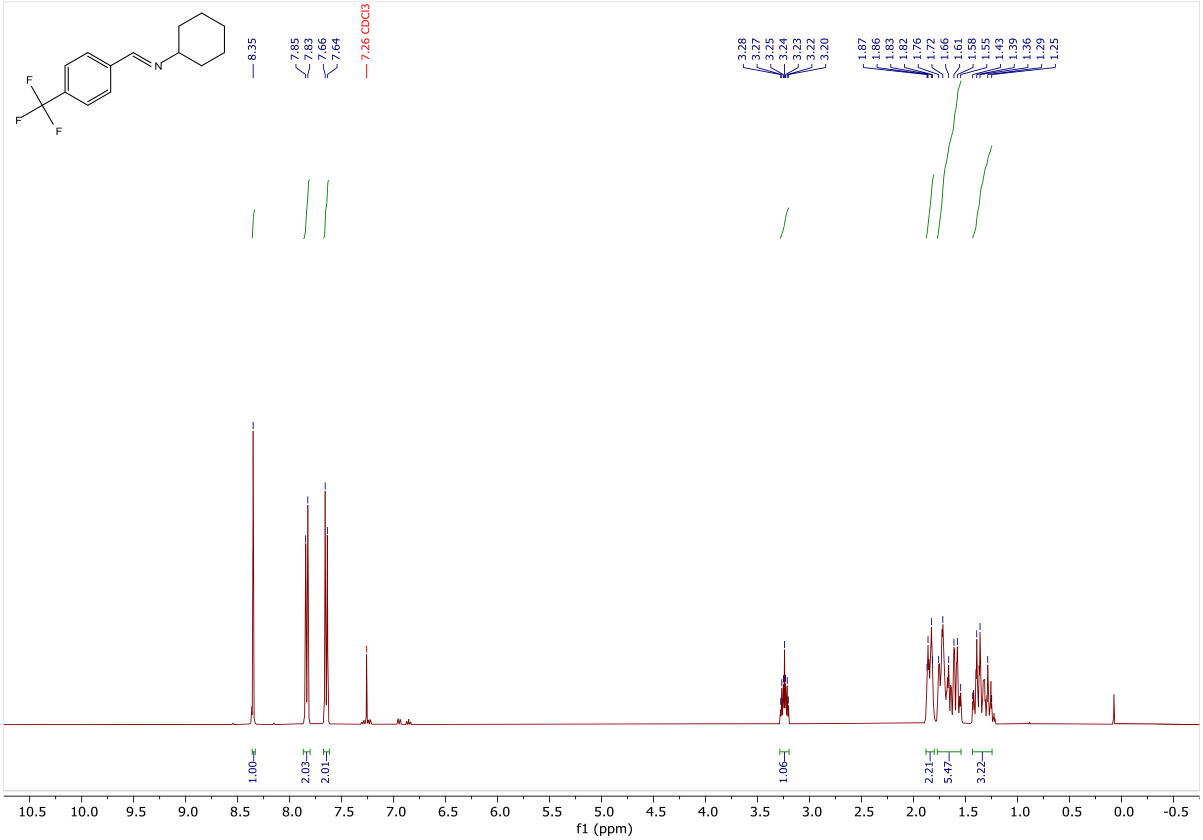
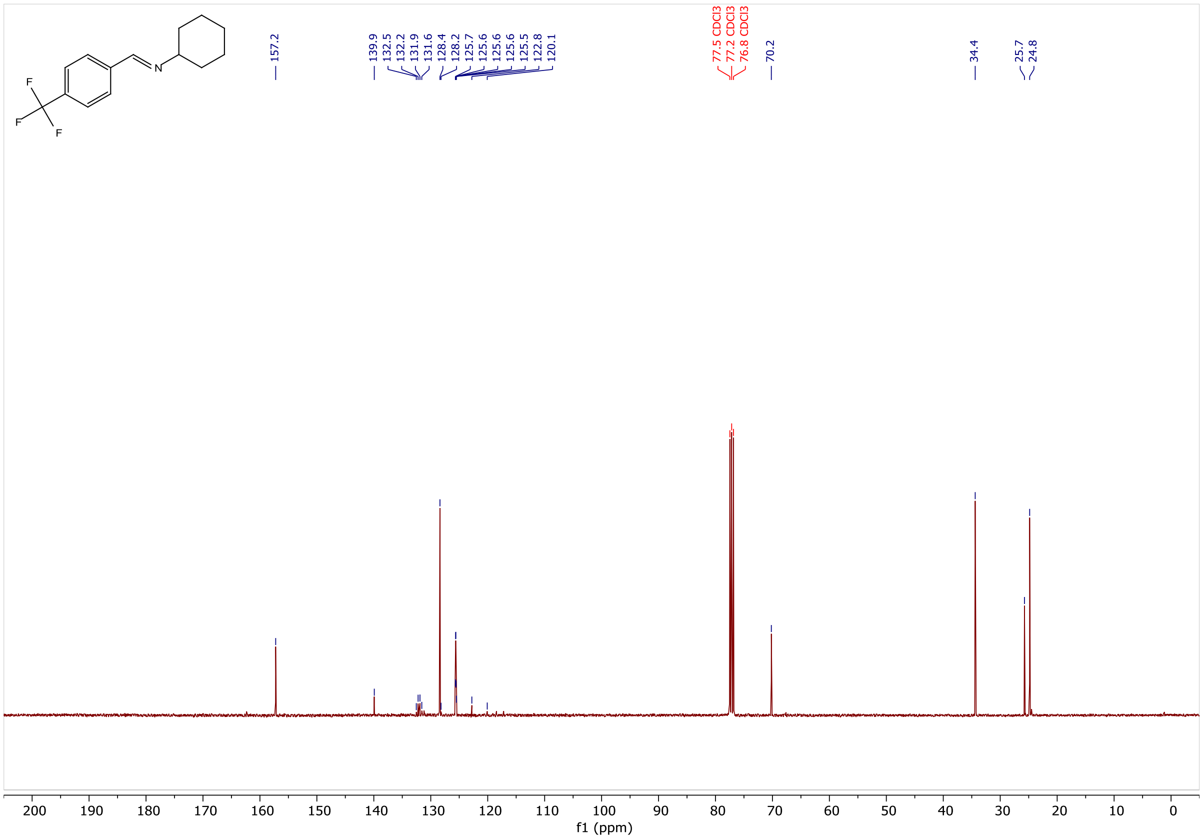
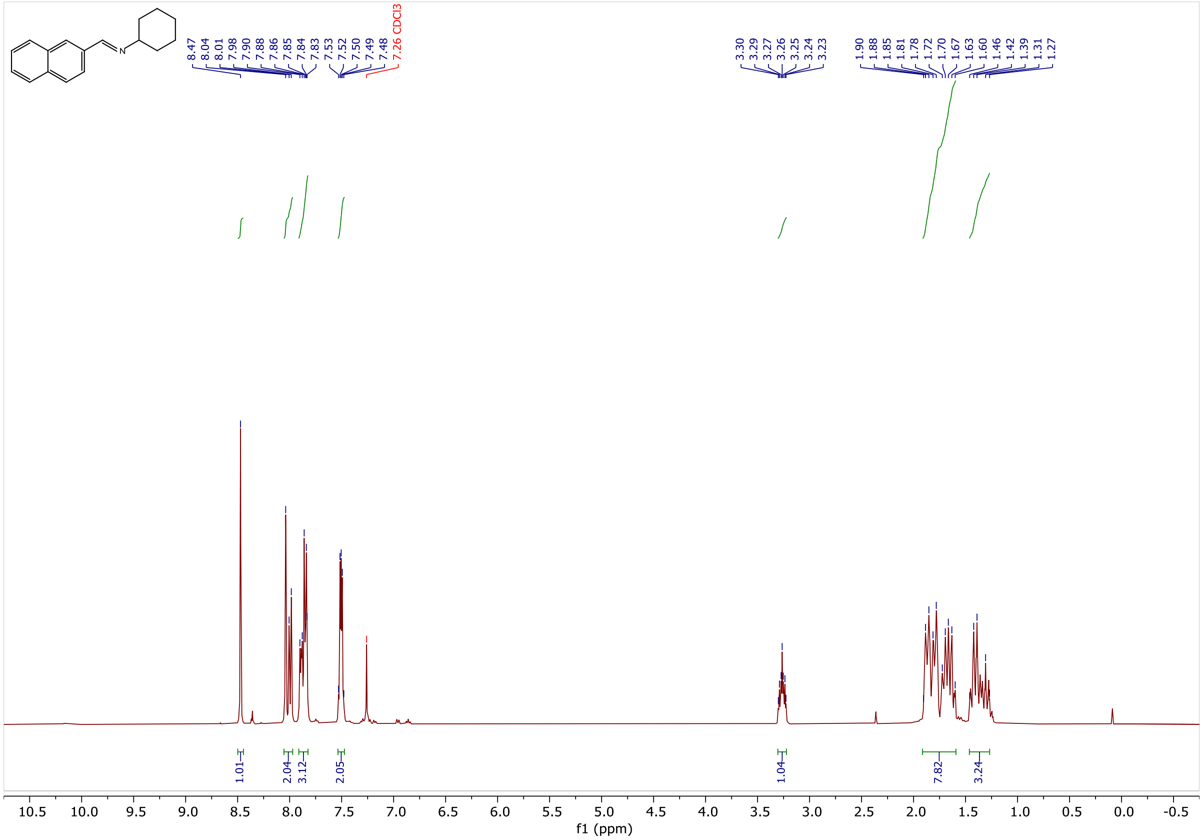
148.9
142.3
128.8
123.9
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
70.3
34.3
25.7
24.7
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

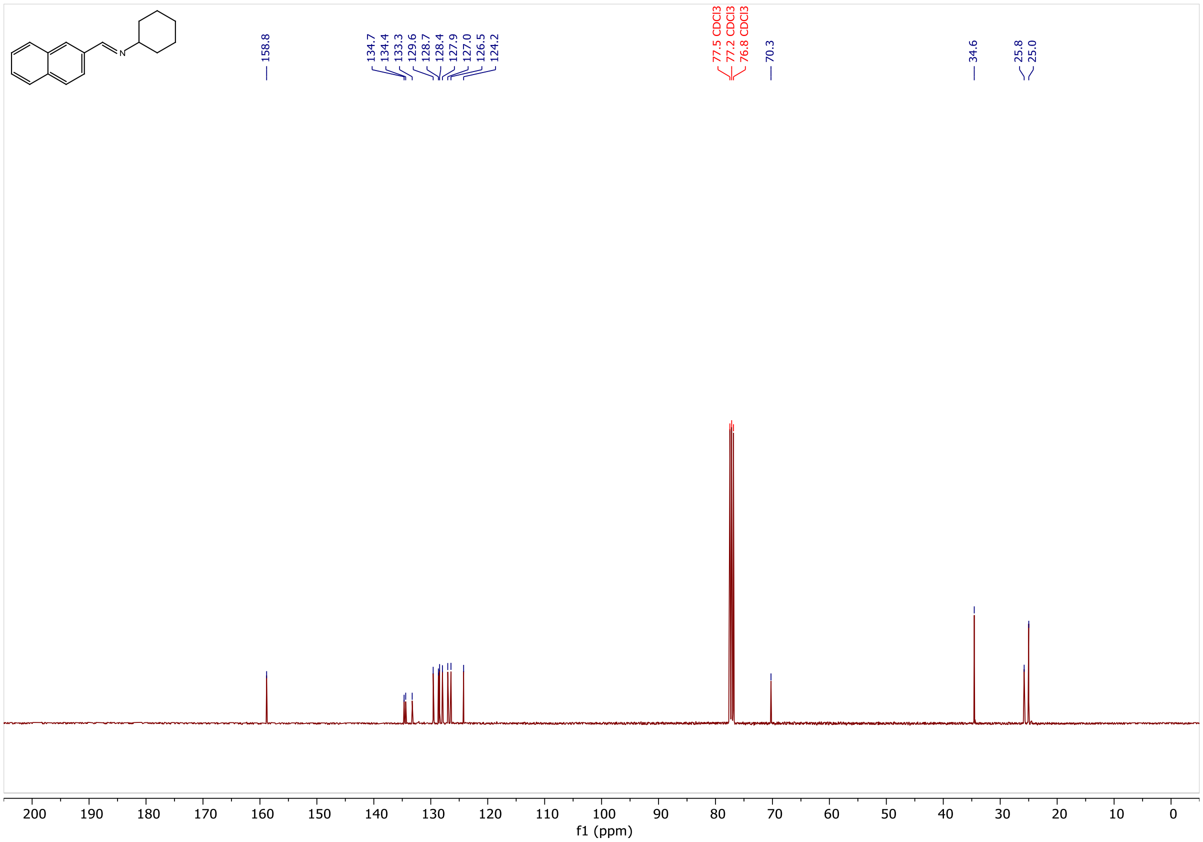

H$_3$C
N
CH$_3$
N
8.19
7.61
7.59
7.26 CDCl3
6.70
6.68
3.14
3.13
3.11
3.10
3.09
3.08
3.07
3.00
1.84
1.83
1.80
1.74
1.72
1.68
1.65
1.59
1.55
1.52
1.41
1.37
1.34
1.25
1.22
1.21
1.00
2.00
2.03
1.09
6.00
2.06
5.33
3.12
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

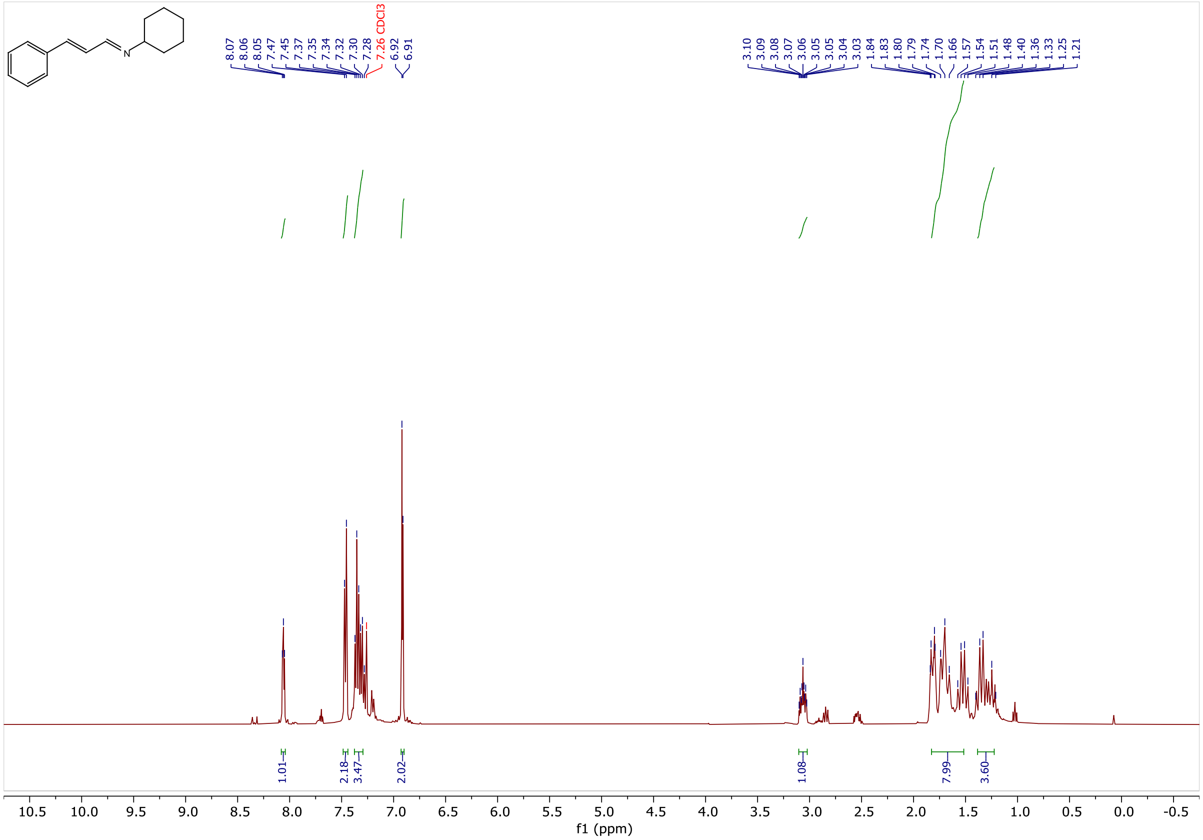

H$_3$C
N
CH$_3$
N
158.7
152.0
129.5
125.0
111.8
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
70.1
40.4
34.8
25.8
25.2
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

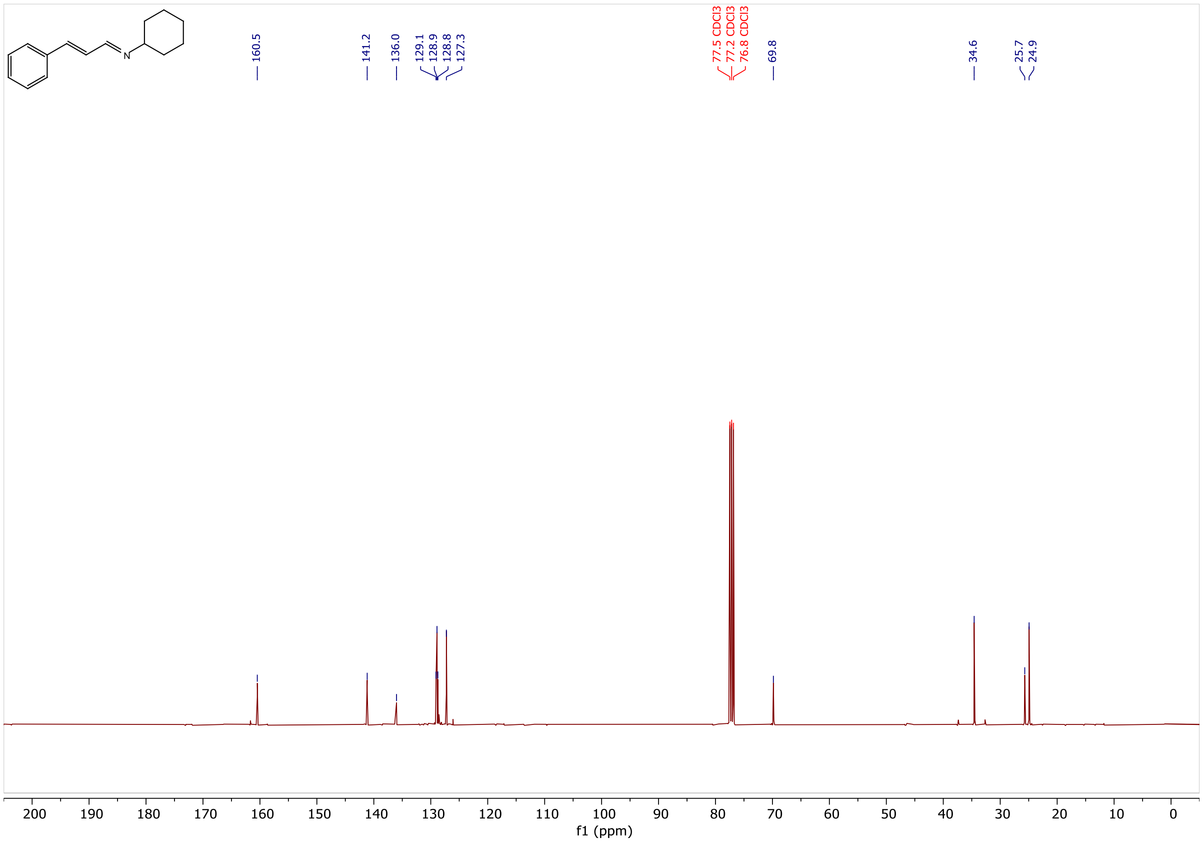

F
F
F
N
8.35
7.85
7.83
7.66
7.64
7.26 CDCl3
3.28
3.27
3.25
3.24
3.23
3.22
3.20
1.87
1.86
1.83
1.82
1.76
1.72
1.66
1.61
1.58
1.55
1.43
1.39
1.36
1.29
1.25
1.00
2.03
2.01
1.06
2.21
5.47
3.22
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

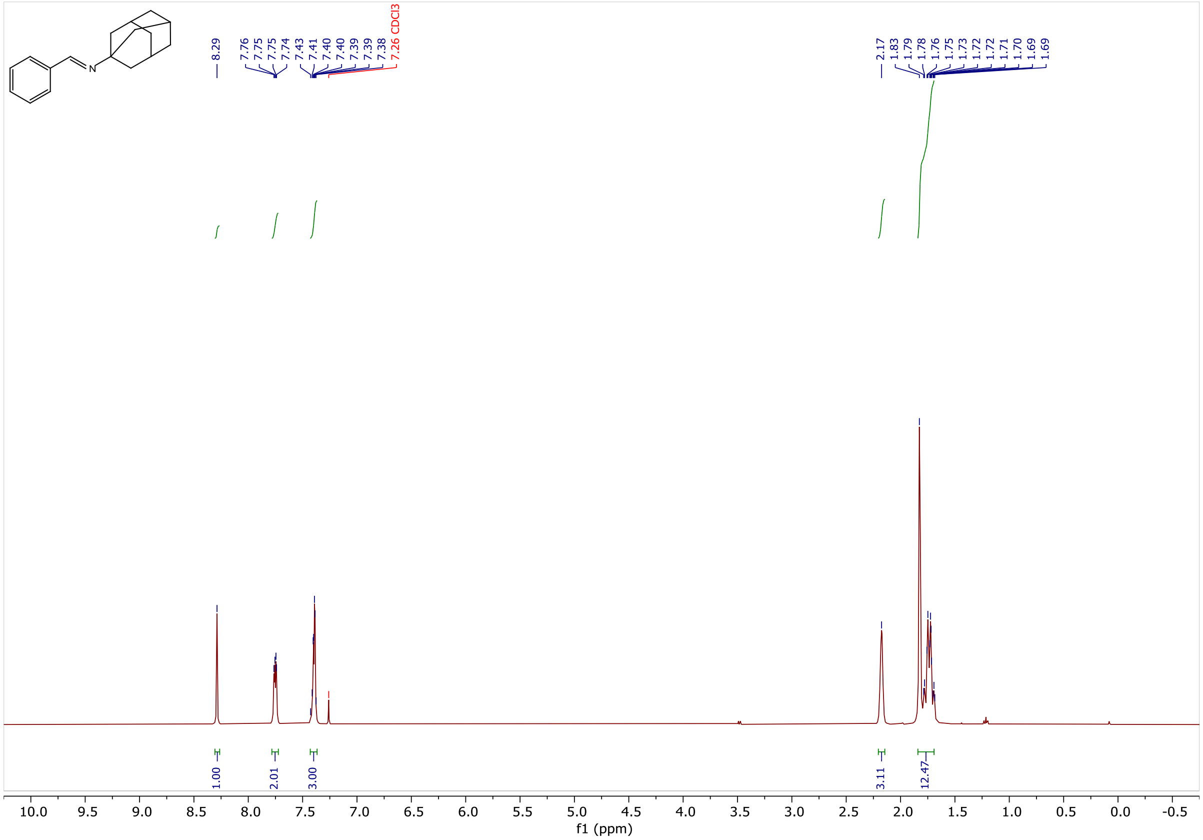

F
F
F
N
157.2
139.9
132.5
132.2
131.9
131.6
128.4
128.2
125.7
125.6
125.6
125.5
122.8
120.1
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
70.2
34.4
25.7
24.8
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


N
8.47
8.04
8.01
7.98
7.90
7.88
7.86
7.85
7.84
7.83
7.53
7.52
7.50
7.49
7.48
7.26 CDCl3
3.30
3.29
3.27
3.26
3.25
3.24
3.23
1.90
1.88
1.85
1.81
1.78
1.72
1.70
1.67
1.63
1.60
1.46
1.42
1.39
1.31
1.27
1.01
2.04
3.12
2.05
1.04
7.82
3.24
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)


N
158.8
134.7
134.4
133.3
129.6
128.7
128.4
127.9
127.0
126.5
124.2
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
70.3
34.6
25.8
25.0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.07
8.06
8.05
7.47
7.45
7.37
7.35
7.34
7.32
7.30
7.28
7.26 CDCl3
6.92
6.91
3.10
3.09
3.08
3.07
3.06
3.05
3.05
3.04
3.03
1.84
1.83
1.80
1.79
1.74
1.70
1.66
1.57
1.54
1.51
1.48
1.40
1.36
1.33
1.25
1.21
N
1.01
2.18
3.47
2.02
1.08
7.99
3.60
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)


160.5
141.2
136.0
129.1
128.9
128.8
127.3
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
69.8
34.6
25.7
24.9
N
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


N
8.29
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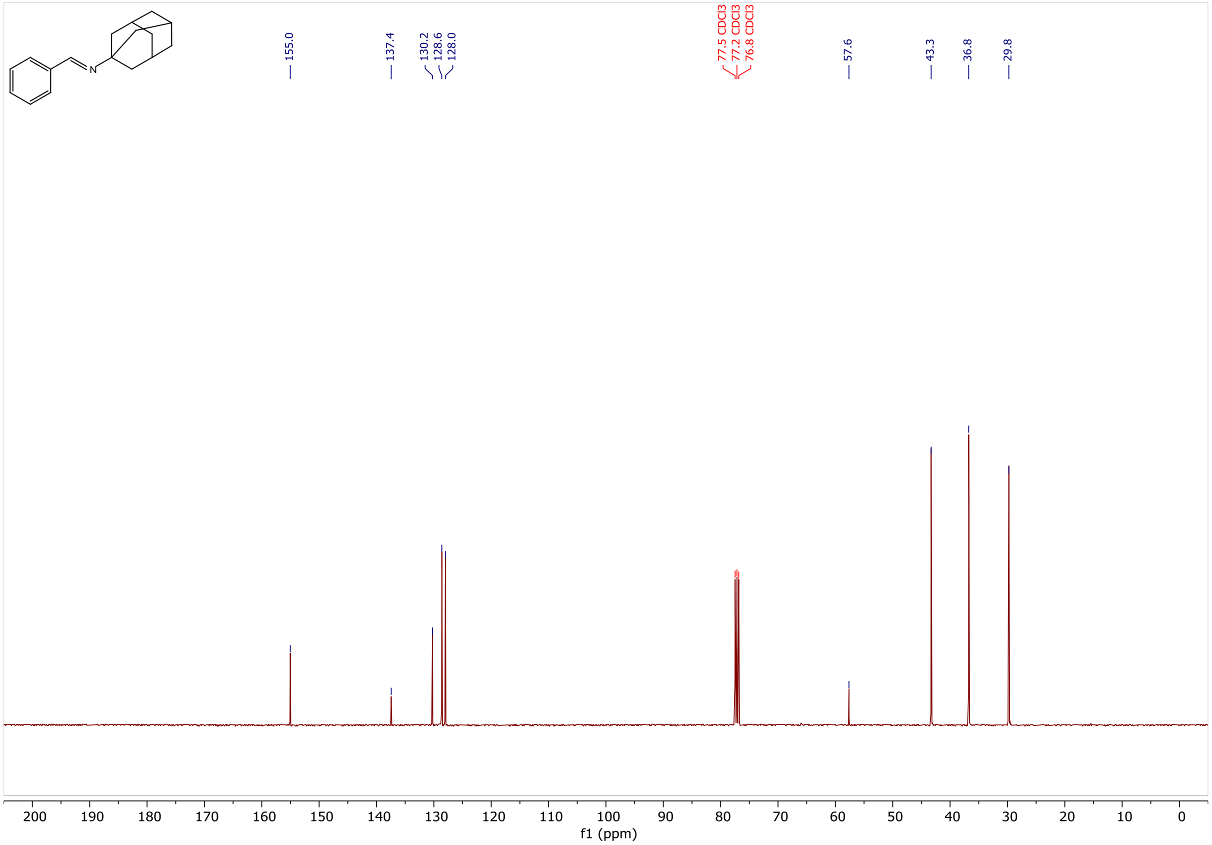
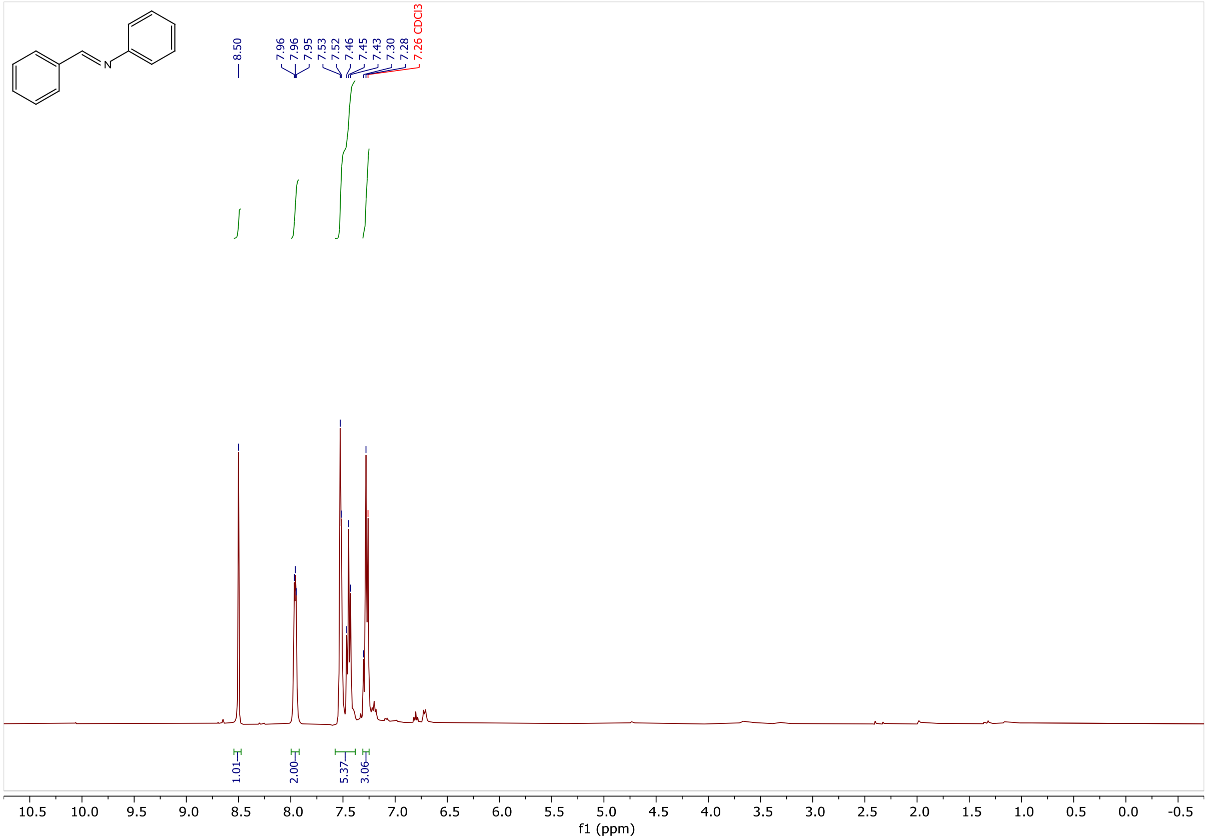
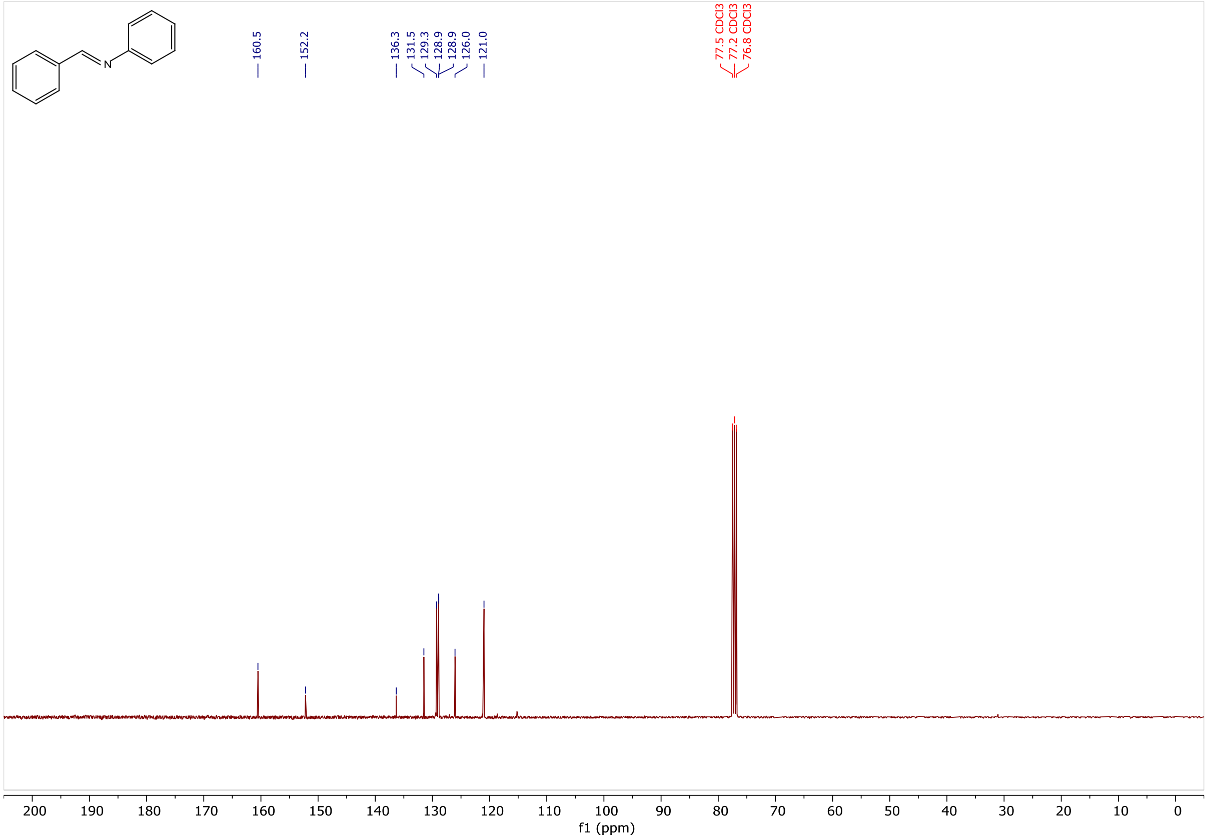
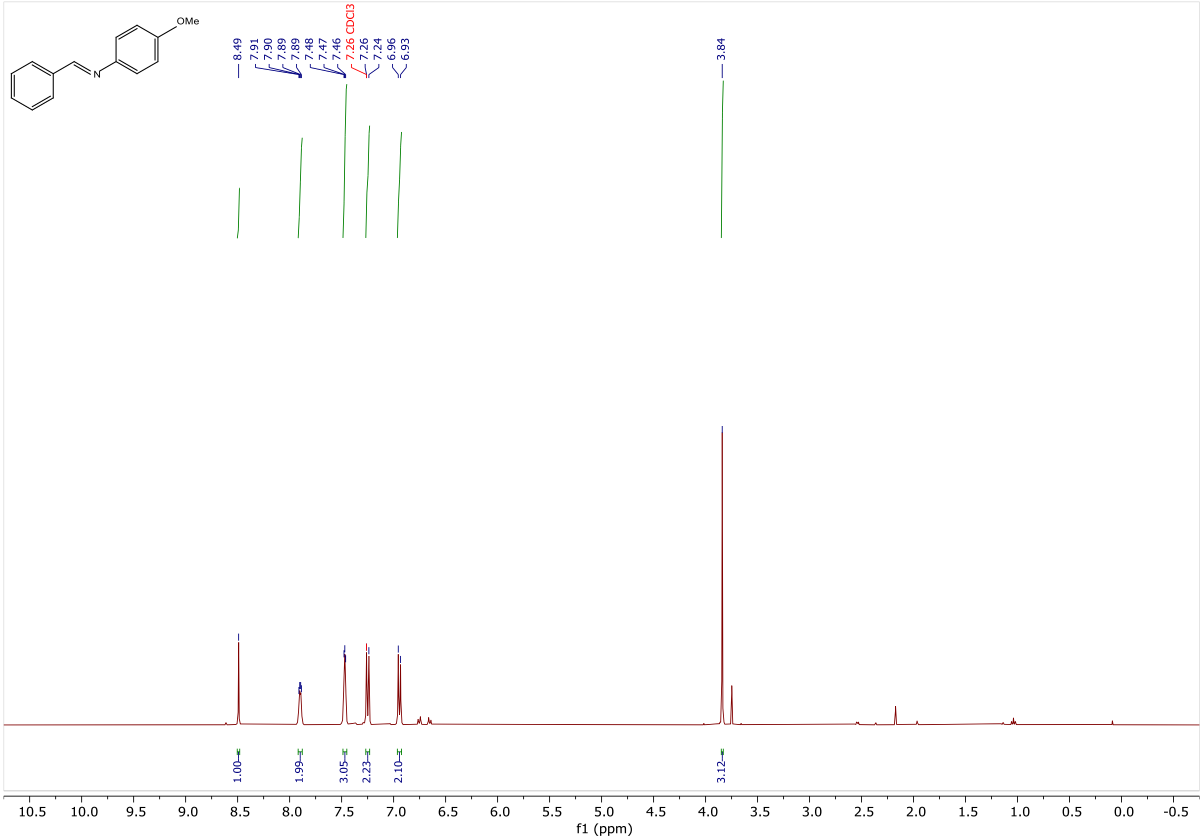
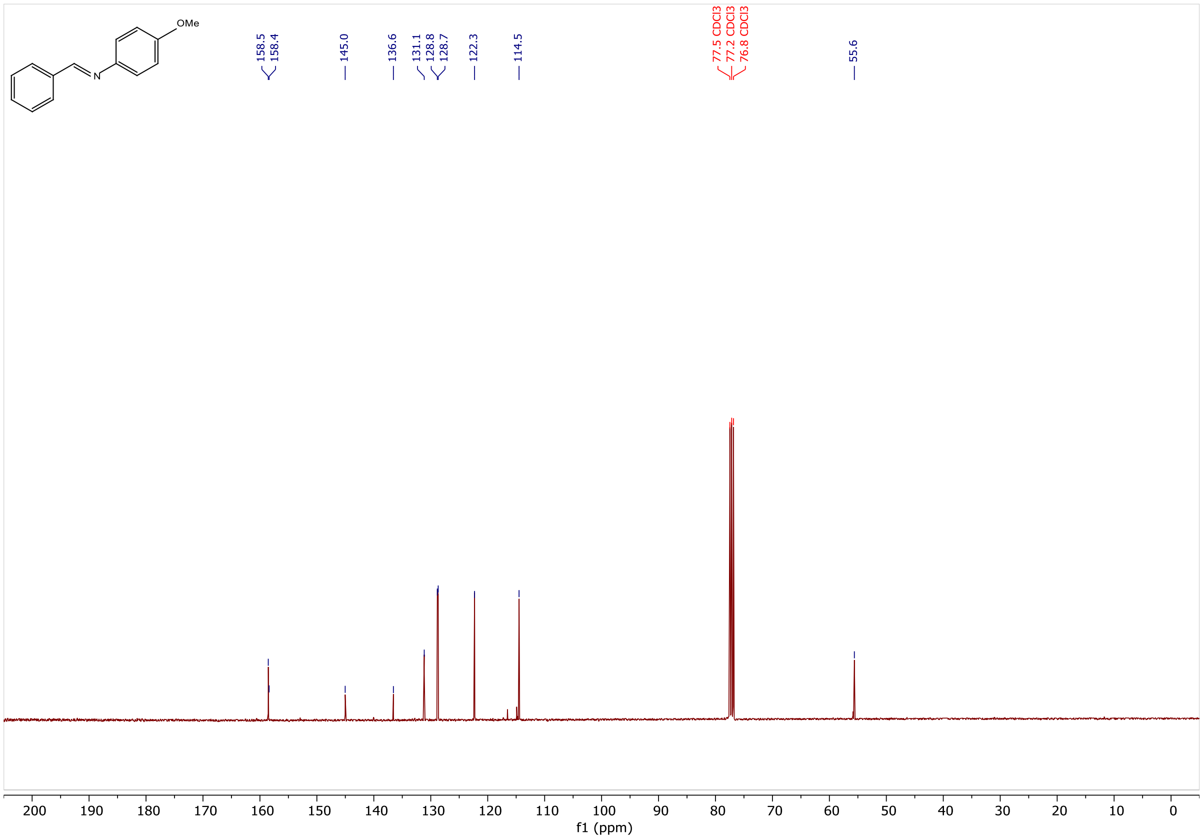
7.75
7.75
7.74
7.43
7.41
7.40
7.40
7.39
7.39
7.38
7.26 CDCl3
2.17
1.83
1.79
1.78
1.76
1.75
1.73
1.72
1.72
1.71
1.70
1.69
1.69
1.00
2.01
3.00
3.11
12.47
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


N
155.0
137.4
130.2
128.6
128.0
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
57.6
43.3
36.8
29.8
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


N
8.50
7.96
7.96
7.95
7.53
7.52
7.46
7.45
7.43
7.30
7.28
7.26 CDCl3
1.01
2.00
5.37
3.06
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)


N
160.5
152.2
136.3
131.5
129.3
128.9
128.9
126.0
121.0
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OMe
N
8.49
7.91
7.90
7.89
7.89
7.48
7.47
7.46
7.26 CDCl3
7.26
7.24
6.96
6.93
3.84
1.00
1.99
3.05
2.23
2.10
3.12
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)


OMe
N
158.5
158.4
145.0
136.6
131.1
128.8
128.7
122.3
114.5
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
55.6
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

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