Regio- and Chemoselective Intermolecular Hydroamination of Allyl Imines for the Synthesis of 1,2-Diamines

Andrew R. Ickes, Seth C. Ensign, Anil K. Gupta and Kami L. Hull

Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61820

Supporting Information

Table of Contents

A. General Information

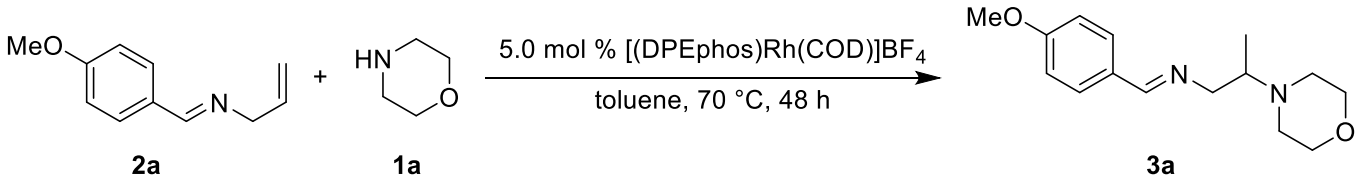
General Experimental Procedures: All reactions were carried out in flame-dried (or oven-dried at 140 °C for at least 2 h) glassware under an atmosphere of nitrogen unless otherwise indicated. Nitrogen was dried using a drying tube equipped with Drierite™ unless otherwise noted. Air- and moisture-sensitive reagents were handled in a nitrogen-filled glovebox (working oxygen level ~ 0.1 ppm). Column chromatography was performed with silica gel from Grace Davison Discovery Sciences (35-75 μm) with a column mixed as a slurry with the eluent and was packed, rinsed, and run under air pressure. Alternatively, automated columns were performed using a Teledyne ISCO system, employing either Biotage® SNAP Dry Load cartridges (loaded under suction with Davisil Chromatographic Silica Media 35-70 micron mesh), ValueBrand Silica Flash Chromatography Columns purchased from Practichem, or end capped cyano RediSep®Rf Gold columns (20-40 micron mesh) purchased from Teledyne Isco. Samples were eluted using a flow rate of 18–40 mL/min, with detection by UV (254 nm or 280 nm). Analytical thin-layer chromatography (TLC) was performed on precoated glass silica gel plates (by EMD Chemicals Inc.) with F-254 indicator. Visualization was either by short wave (254 nm) ultraviolet light, or by staining with potassium permanganate followed by brief heating on a hot plate or by a heat gun. Distillations were performed using a 3 cm short-path column under reduced pressure or by using a Hickman still at ambient pressure.

Instrumentation: ^{1}H NMR and ^{13}C NMR were recorded on a Varian Unity 400/500 MHz (100/125 MHz respectively for ^{13}C) or a VXR-500 MHz spectrometer. Spectra were referenced using either $CDCl_3$ or C_6D_6 as solvents (unless otherwise noted) with the residual solvent peak as the internal standard (^{1}H NMR: δ 7.26 ppm, ^{13}C NMR: δ 77.00 ppm for $CDCl_3$ and ^{1}H NMR: δ 7.15 ppm, ^{13}C NMR: δ 128.60 ppm for C_6D_6). Chemical shifts were reported in parts per million and multiplicities are as indicated: s (singlet,) d (doublet,) t (triplet,) q (quartet,) p (pentet,) m (multiplet,) and br (broad). Coupling constants, *J*, are reported in Hertz and integration is provided, along with assignments, as indicated. Analysis by Gas Chromatography-Mass Spectrometry (GC-MS) was performed using a Shimadzu GC-2010 Plus Gas chromatograph fitted with a Shimadzu GCMS-QP2010 SE mass spectrometer using electron impact (EI) ionization after analytes traveled through a SHRXI–5MS- 30m x 0.25 mm x 0.25 μm column using a helium carrier gas. Data are reported in the form of m/z (intensity relative to base peak = 100). Gas Chromatography (GC) was performed on a Shimadzu GC-2010 Plus gas chromatograph with SHRXI–MS- 15m x 0.25 mm x 0.25 μm column with nitrogen carrier gas and a flame ionization detector (FID). Low-resolution Mass Spectrometry and High Resolution Mass Spectrometry were performed in the Department of Chemistry at University of Illinois at Urbana-Champaign. The glove box, MBraun LABmaster sp, was maintained under nitrogen atmosphere. Melting points were recorded on a Thomas Hoover capillary melting point apparatus and are uncorrected.

Materials: Solvents used for extraction and column chromatography were reagent grade and used as received. Reaction solvents tetrahydrofuran (Fisher, unstabilized HPLC ACS grade), diethyl ether (Fisher, BHT stabilized ACS grade), methylene chloride (Fisher, unstabilized HPLC grade), dimethoxyethane (Fisher, certified ACS), toluene (Fisher, optima ACS grade), 1,4-dioxane (Fisher, certified ACS), acetonitrile (Fisher, HPLC grade), and hexanes (Fisher, ACS HPLC grade) were dried on a Pure Process Technology Glass Contour Solvent Purification System using activated Stainless Steel columns while following manufacture's recommendations for solvent preparation and dispensation unless otherwise noted. All amines (excluding allyl amine) were distilled and degassed by the freeze-pump-thaw method, and were stored over 4 Å molecular sieves under an atmosphere of nitrogen in glove box before use. Allylamine **10** was obtained from Aldrich Chemical Co., Inc. and used as received. All liquid aldehydes were distilled prior to use, and ketones, benzophenone and cyclohexanone, were used as received.

B. Select Optimization Reactions

Experimental Procedure for Scheme 1:



2a **1a** **3a**

N-(4-methoxybenzyl)-2-morpholinopropan-1-amine, 6a: These procedures were adapted from those previously published in the literature.[1] [(DPEphos)Rh(COD)]BF4 (42 mg, 0.050 mmol, 5.0 mol %) and dry toluene (1.0 mL) were mixed in an oven-dried 4 mL vial equipped with a stir bar in the glove box. To the reaction mixture was added imine **2a** (690 μL, 4.0 mmol, 4.0 equiv.) and morpholine, **1a** (85 μL, 1.0 mmol, 1.0 equiv). The resulting solution was sealed with Teflon cap, removed from glove box, and allowed to stir for 48 h at 70 °C. After 48 h, the reaction vial was cooled to room temperature followed by the addition of 1-methylnapthlene as an internal standard and diluted with methylene chloride. The crude yield (57%) was determined GC relative to a calibration curve.

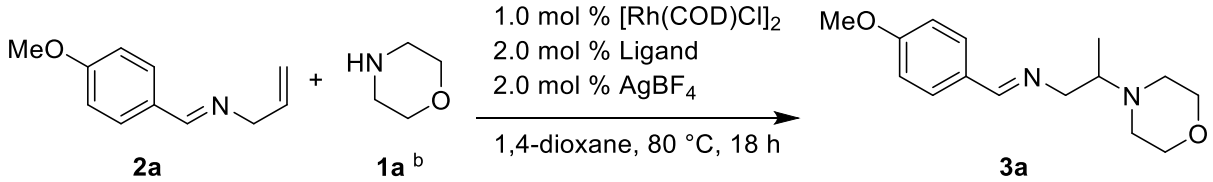
Representative Procedure for Table 1 (entry 5):

[Rh(COD)Cl]2 (1.0 mg, 0.0020 mmol, 0.50 mol %), AgBF4 (0.8 mg, 0.0041 mmol, 1.0 mol %), and DPEphos (2.2 mg, 0.0041 mmol, 1.0 mol %) were weighed in a 4 mL vial equipped with a stir bar. To this mixture was added MeCN (98 μL), imine **2a** (65 mg, 0.37 mmol, 1.0 equiv.), morpholine, **1a** (160 μL, 1.9 mmol, 5.0 equiv.), and 1-methylnaphthalene (10 μL, 0.071 mmol, 0.19 equiv.) as an internal standard. The resulting solution was sealed with Teflon cap, removed from glove box, and allowed to stir for 24 h at 60 °C. After 24 h, the reaction vial was cooled to room temperature and diluted with CH2Cl2. The crude yield (99%) was determined by GC relative to a calibration curve.

Alternative Procedure for Setup Outside of Glovebox:

[(DPEphos)Rh(COD)]BF_4 (7.3 mg, 0.0085 mmol, 1.0 mol %) was weighed into an oven-dried 0.5-2 mL microwave vial equipped with a stir bar. This was sealed under an atmosphere on N_2. Imine **2a** (147 μL, 0.85 mmol, 1.00 equiv.), dry CH_3CN (198 μL), morpholine, **1a** (370 μL, 4.3 mmol, 5.0 equiv.), and 1-methylnaphthalene (10 μL, 0.071 mmol, 0.083 equiv.) as an internal standard were added via syringe through the septum. The resulting solution was allowed to stir for 24 h at 60 °C. After 24 h, the reaction vial was cooled to room temperature and diluted with CH2Cl2. The crude yield (91%) was determined by GC relative to a calibration curve.

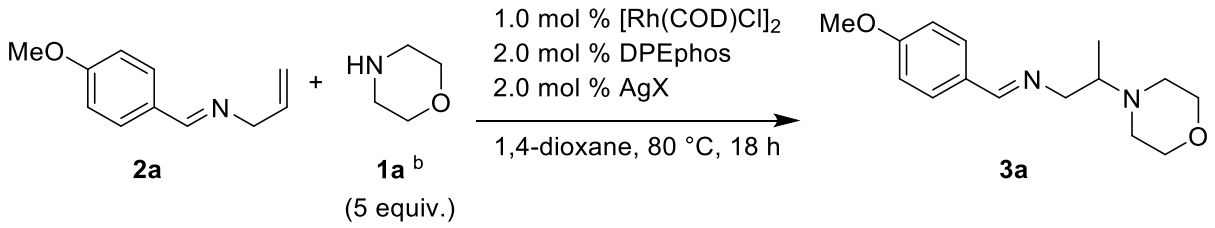
Table S1. Varying the ligand in optimizing the Rh-catalyzed hydroamination reaction.[a]



entry	Ligand	% yield **3a** [c]
1	Triphenylphosphine	<1
2	Tri(4-MeOC$_6$H$_5$)	14
3	Tri(2-furyl)phosphine	46
4	dppm	2
5	dppe	2
6	dppp	36
7	dpph	52
8	dppb	63
9	dppf	66
10	DPEphos	66

[a] Unless otherwise specified, all reactions were set up in glove box using oven dried 4mL vials and performed with 1.0 mol % catalyst at 1.1 M in **2a** (0.85 mmol) with 5.0 equiv. of **1a** for 18 h at 80 °C. [b] **1a** was distilled and transferred to glove box prior to use. [c] GC yield determined using 1-methylnaphthalene (24 μL, 0.17 mmol, 0.20 equiv.) as an internal standard.

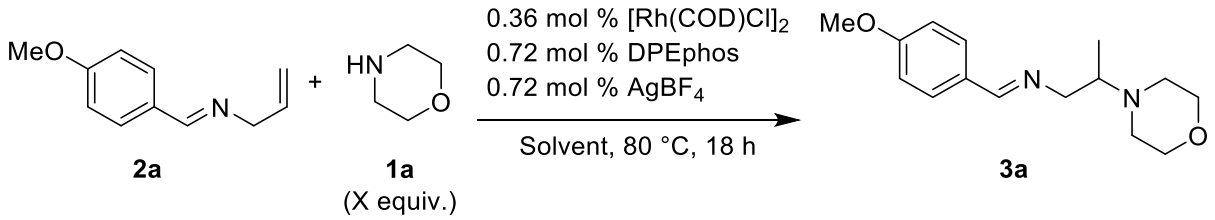
Table S2. Varying the silver salt in optimizing the Rh-catalyzed hydroamination reaction.[a]



entry	Silver Salt	% yield **3a** [c]
1	$AgBF_4$	54
2	$AgSbF_6$	41
3	$AgSO_3CF_3$	36
4	$AgSO_3CH_3$	19
5	$AgPF_6$	24
6	$Ag(O_2CCF_3)$	18
7	$Ag(O_2CCH_3)$	22

[a] Unless otherwise specified, all reactions were set up in glove box using oven dried 4mL vials and performed with 1.0 mol % catalyst at 1.1 M in **2a** (0.85 mmol) with 5.0 equiv. of **1a** for 18 h at 80 °C. [b] **1a** was distilled and transferred to glove box prior to use. [c] GC yield determined using 1-methylnaphthalene (24 μL, 0.17 mmol, 0.20 equiv.) as an internal standard.

Table S3. Varying the solvent in optimizing the Rh-catalyzed hydroamination reaction.[a]



entry	Solvent [b]	equiv. **1a** [c]	% yield **3a** [d]
1	1,4-dioxane	1.0	24
2	1,4-dioxane	3.0	42
3	1,4-dioxane	5.0	54
4	DME	1.0	18
5	DME	3.0	39
6	DME	5.0	44
7	THF	1.0	17
8	THF	3.0	34
9	THF	5.0	44
10	MeCN	1.0	29
11	MeCN	3.0	50
12	MeCN	5.0	70

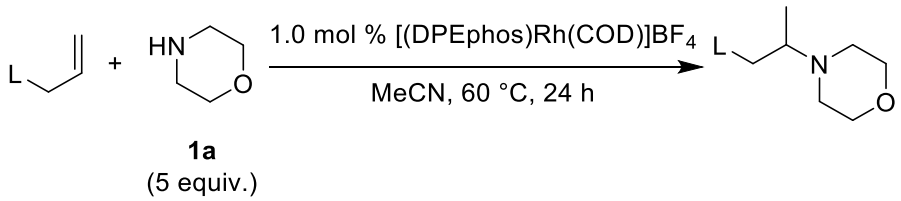
[a] Unless otherwise specified, all reactions were set up in glove box using oven dried 4mL vials and performed with 0.72 mol % catalyst at 1.1 M in **2a** (0.85 mmol) with x equiv. of **1a** for 18 h at 80 °C. [b] All solvents were freshly distilled and stored over 4 Å MS. [c] **1a** was distilled and transferred to glove box prior to use. [d] GC yield determined using 1-methylnaphthalene (24 μL, 0.17 mmol, 0.20 equiv.) as an internal standard.

Table S4. Varying the concentration, ratio of **1a**:**2a**, and temperature in optimizing the Rh-catalyzed hydroamination reaction.[a]

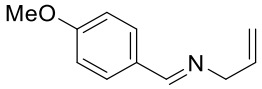
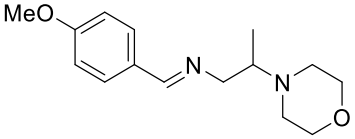
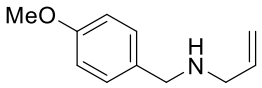
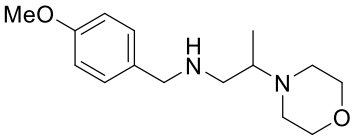
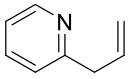
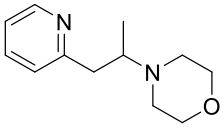
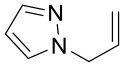
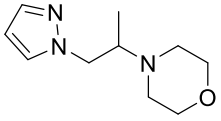
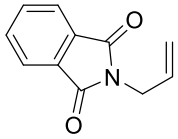
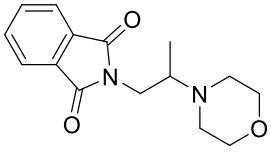
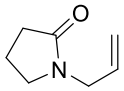
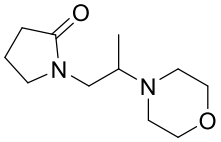
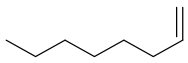
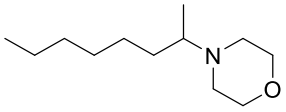
entry	Concentration (M)	Temp (°C)	equiv **1a** [b]	% yield **3a** [c]
1	0.63	80	60	59
2	0.76	80	6.0	64
3	0.95	80	6.0	67
4	1.3	80	6.0	72
5	1.9	80	6.0	78
6	3.8	80	6.0	84
7	3.8	80	5.0	85
8	3.8	80	3.0	78
9	3.8	80	1.0	29
10	3.8	70	5.0	90
11	3.8	70	3.0	79
12	3.8	70	1.0	39
13	3.8	60	5.0	90
14	3.8	60	3.0	85
15	3.8	60	1.0	47
16	3.8	50	5.0	87
17	3.8	50	3.0	83
18	3.8	50	1.0	47
19	3.8	40	5.0	68
20	3.8	40	3.0	55
21	3.8	40	1.0	19
22	3.8	30	5.0	56
23	3.8	30	3.0	55
24	3.8	30	1.0	33
25	3.8	25	5.0	40
26	3.8	25	3.0	46
27	3.8	25	1.0	28

[a] Unless otherwise specified, all reactions were set up in glove box using oven dried 4mL vials and performed with 1.0 mol % catalyst at C M in **2a** (0.85 mmol) with x equiv. of **1a** for 24 h at T °C. [b] **1a** was distilled and transferred to glove box prior to use. [c] GC yield determined using 1-methylnaphthalene (24 μL, 0.17 mmol, 0.2 equiv) as an internal standard.

Table S5. Screen of directing groups in the Rh-catalyzed hydroamination reaction.[a]

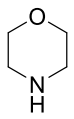
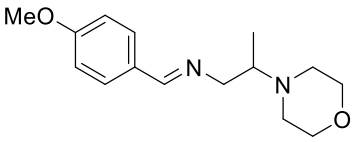
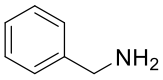
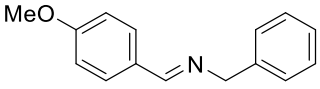
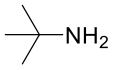
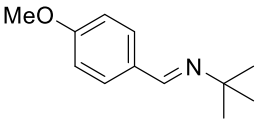
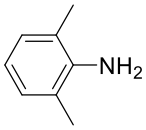
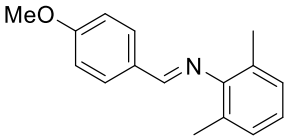
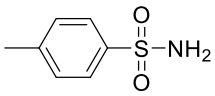
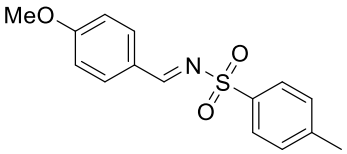
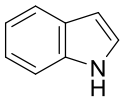
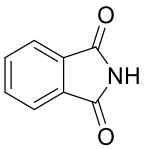


1a
(5 equiv.)

entry	alkene	product	% yield
1			94%
2			Not observed
3			Not observed
4			Not observed
5			Not observed
6			Not observed
7			Not observed

[a] Unless otherwise specified, all reactions were set up in glove box using oven dried 4mL vials and performed with 1.0 mol % catalyst at 4.3 M in **2a** (0.85 mmol) with 5.0 equiv. of **1a** for 24 h at 60 °C. Morpholine was distilled and transferred to glove box prior to use. [b] All alkenes were freshly prepared and used in its crude form. [c] GC yield determined using 1-methylnaphthalene (24 mL, 0.17 mmol, 0.20 equiv.) as an internal standard.

Table S6. Screen of amines, amides, and imides in Rh-catalyzed hydroamination reaction.[a]

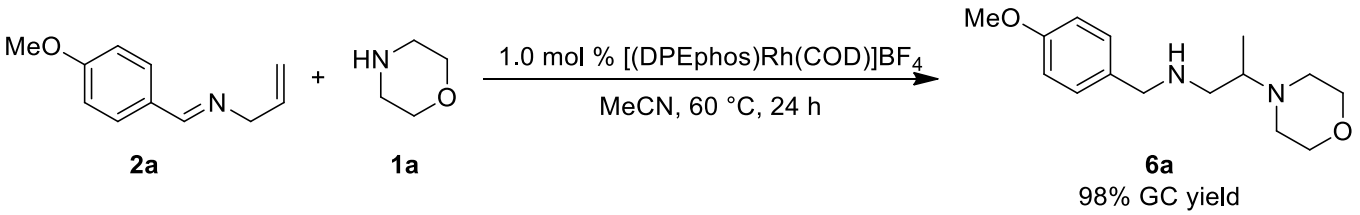
entry	amine	product	% yield
1			94%
2			Not Determined[d]
3			Not Determined[d]
4			Not Determined[d]
5			Not Determined[d]
6		No reaction observed	--
7		No reaction observed	--

8		No reaction observed	--

[a] Unless otherwise specified, all reactions were set up in glove box using oven dried 4mL vials and performed with 1.0 mol % catalyst at 4.3 M in 2a (0.85 mmol) with 3.0 equiv. of amine for 24 h at 60 °C. Liquid amines were distilled, transferred to glove box, and dried overnight over 4 Å MS prior to use. Solid amines were used as received. [b] Imine **2a** were freshly prepared and used in its crude form. [c] GC yield determined using 1-methylnaphthalene (24 mL, 0.17 mmol, 0.20 equiv.) as an internal standard. [d] Structure of product suggested by GCMS comparison to library structures.

C. Control Experiments

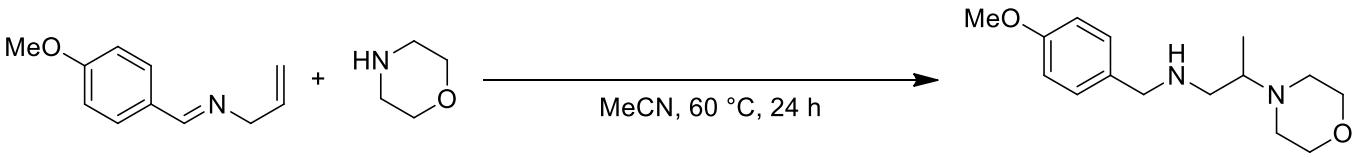
Under the optimized reaction conditions, in the presence of $[(DPEphos)Rh(COD)]BF_4$ **3a** is afforded in 98% GC yield.



2a **1a** **6a**

98% GC yield

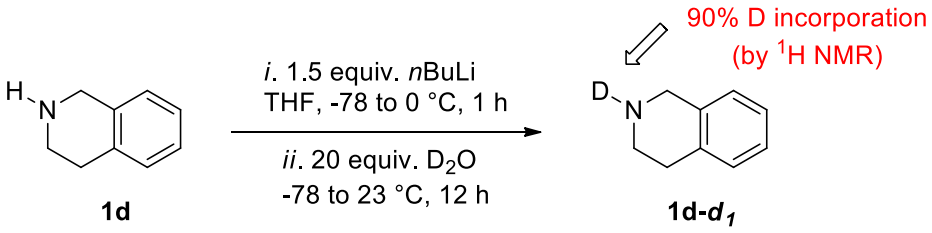
Under the optimized reaction conditions, in the absence of $[(DPEphos)Rh(COD)]BF_4$ **3a** is afforded in 0% GC yield; no reaction is observed by GC.



2a **1a** **6a**

0% GC yield

D. Deuterium Incorporation Study



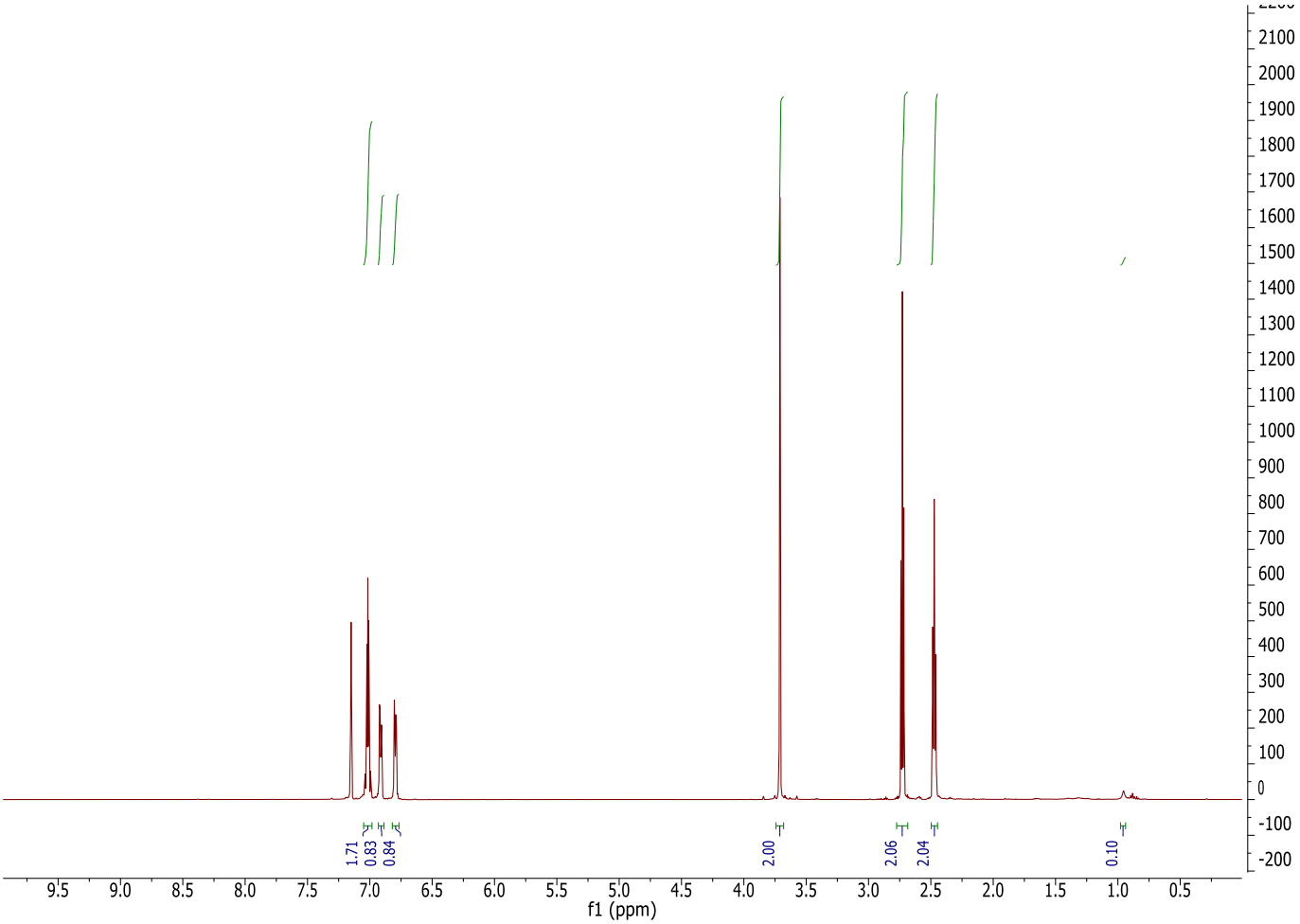
1,2,3,4-tetrahydroisoquinoline-2-*d* 16: To a flame dried 100 mL round bottom flask, equipped with a stir bar, was added tetrahydroisoquinoline **1d** (5 mL, 40 mmol, 1.0 equiv, freshly distilled) and dry THF (30 mL). The solution was cooled to –78 °C. To this solution was added BuLi (37.5 mL, 60 mmol, 1.5 equiv, 1.6 M in hexanes) in a dropwise manner. The reaction flask was stirred at –78 °C for 0.5 h followed by further stirring at 23 °C for another 0.5 h. Subsequently, the flask was cooled again to –78 °C followed by the dropwise addition of D_2O (14.5 mL, 800 mmol, 20 equiv). The resulting reaction mixture was warmed to room temperature and stirred overnight at ambient temperature. The organic layer was separated and the aqueous layer was extracted with dry Et_2O (30 mL × 2). All organic layers were combined, dried over anyhydrous $MgSO_4$, filtered, and concentrated *in vacuo* followed by drying under high vacuum (0.05 mm Hg) for 1 h to afford the crude amine **16** as yellow oil. Purification of the crude amine by distillation (43 °C, 0.2 mm Hg) afforded the pure deuterated amine **16** as a colorless liquid in 90% yield (4.8 g, 36 mmol). With the help of ^{1}H NMR analysis, it found that the deuterium incorporation was 90% only.

Data for **16**:

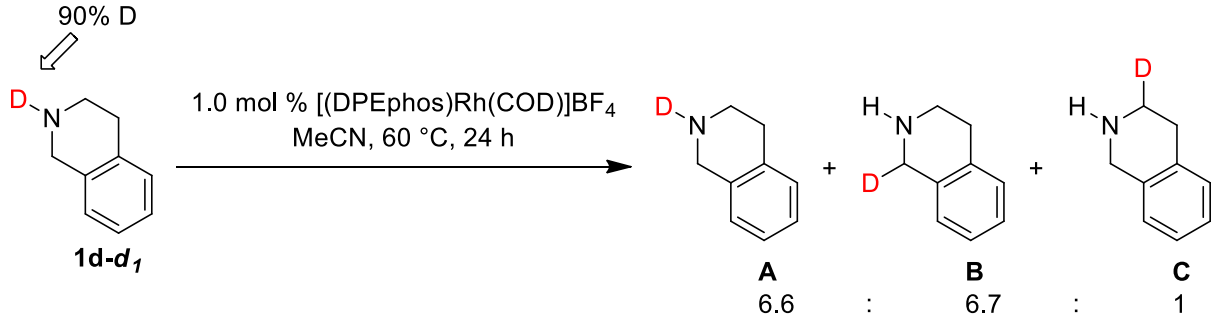
^{1}H NMR (C_6D_6, 500 MHz): δ 7.05 – 6.98 (m, 2H), 6.94 – 6.89 (m, 1H), 6.82 – 6.77 (m, 1H), 3.71 (s, 2H), 2.73 (t, J = 5.9 Hz, 2H), 2.47 (t, J = 6.1 Hz, 2H) ppm.

^{13}C NMR (C_6D_6, 125 MHz): δ 137.41, 136.00, 130.11, 127.06, 126.62, 126.41, 49.24, 44.74, 30.22 ppm.

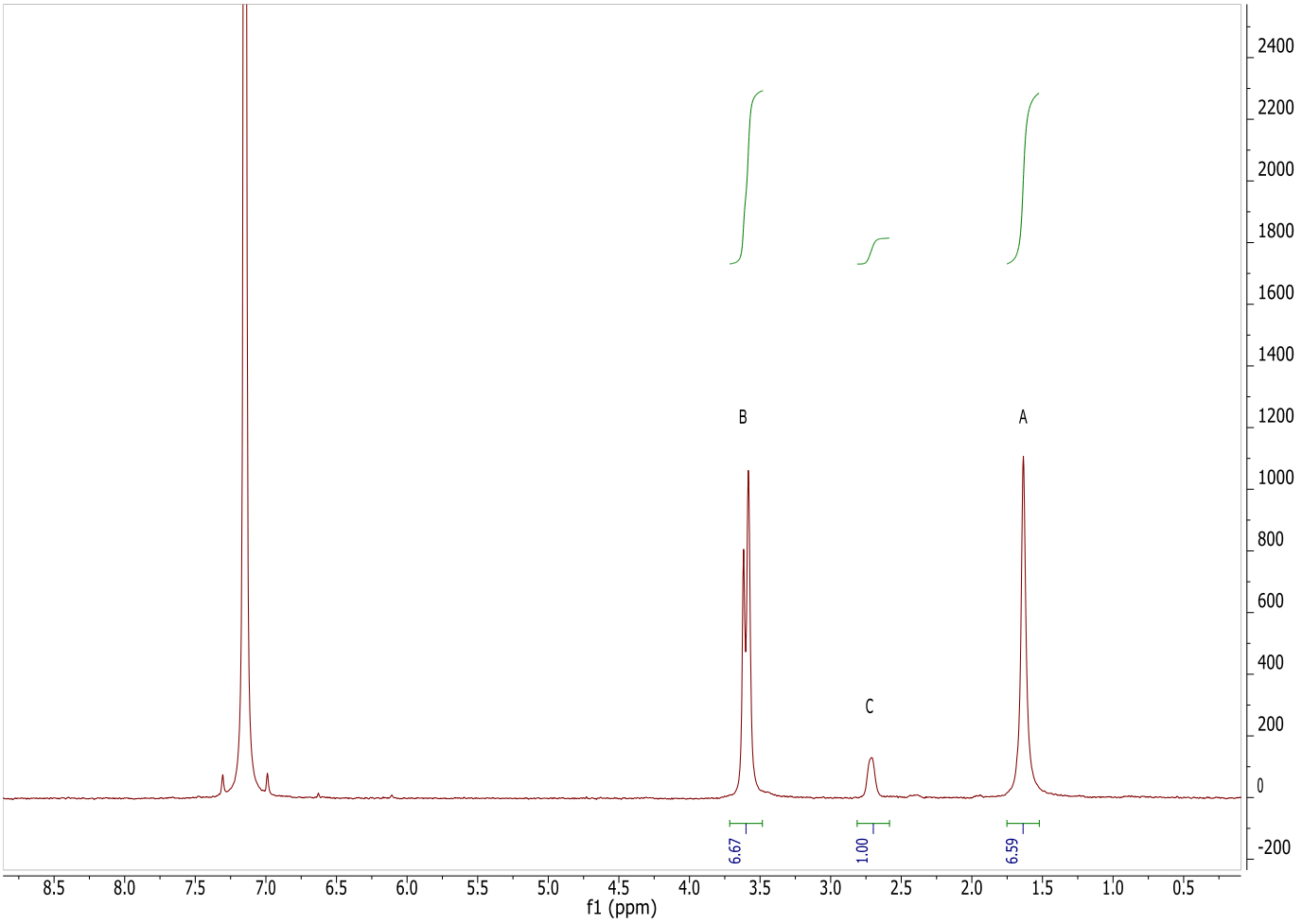
^{1}H NMR of **1d-d_1** (90% D)



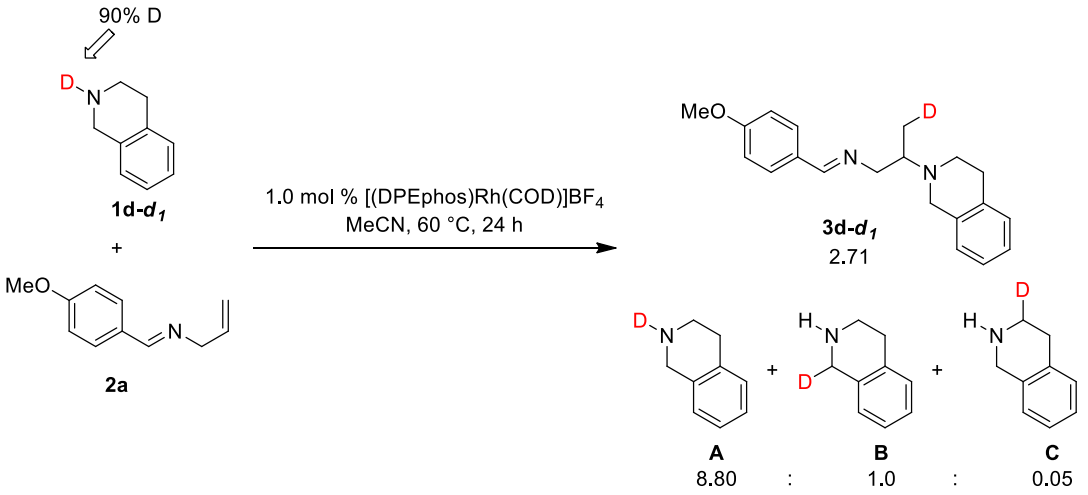
In the absence of *N*-allylimine, the deuterium atom is exchanged with the adjacent hydrogen atoms in the ring, as has been seen in related studies. The ^{2}H NMR was taken in MeCN (with C_6D_6 added for reference). Resonances are observed for three isomers, where the deuterium has been incorporated at the two adjacent carbon atoms with preference for the benzylic position. This is consistent with a Rh-catalyzed β-hydride elimination-reinsertion mechanism.



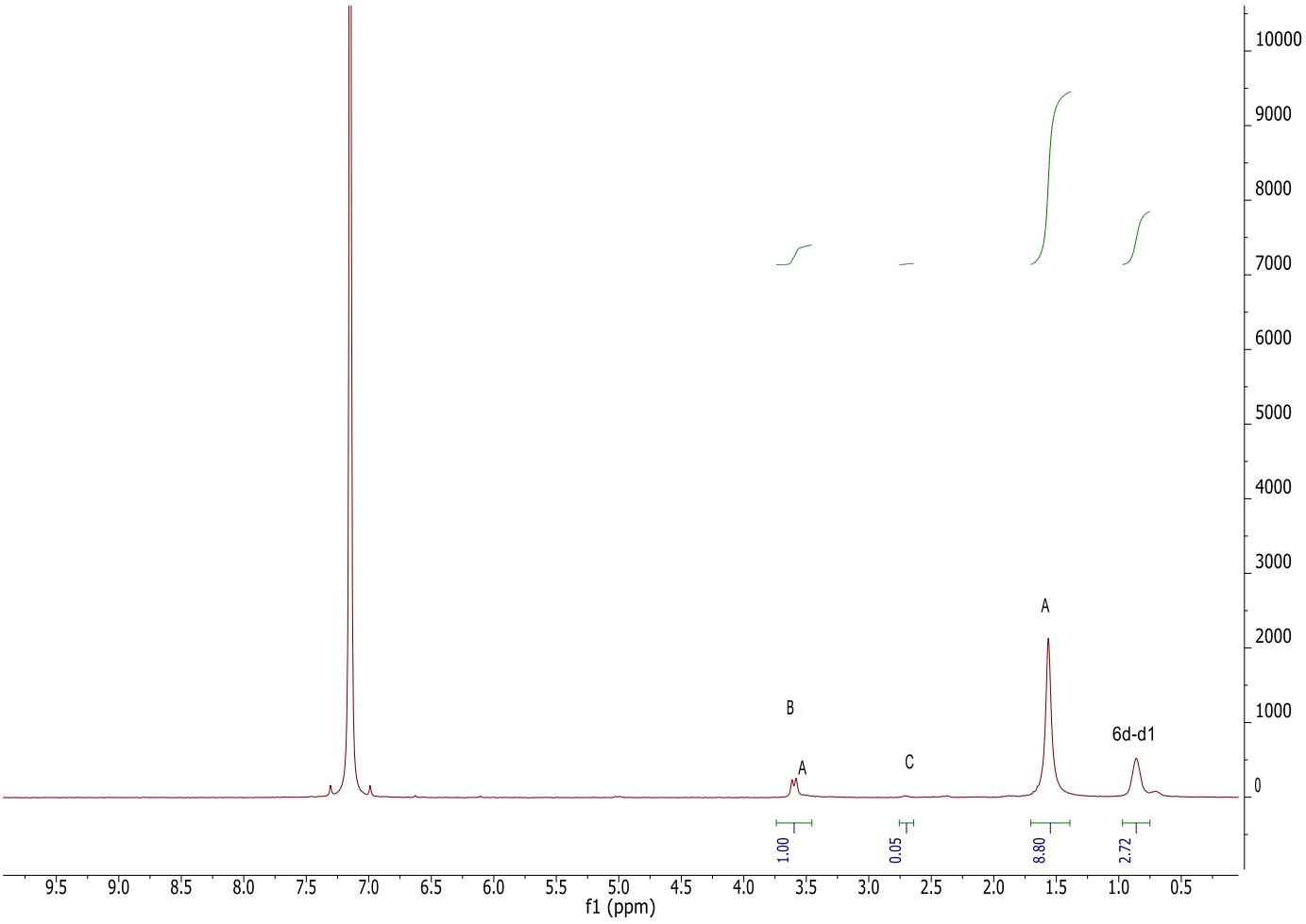
^{2}H NMR of crude reaction between **1d-*d*$_1$** and [Rh]-catalyst



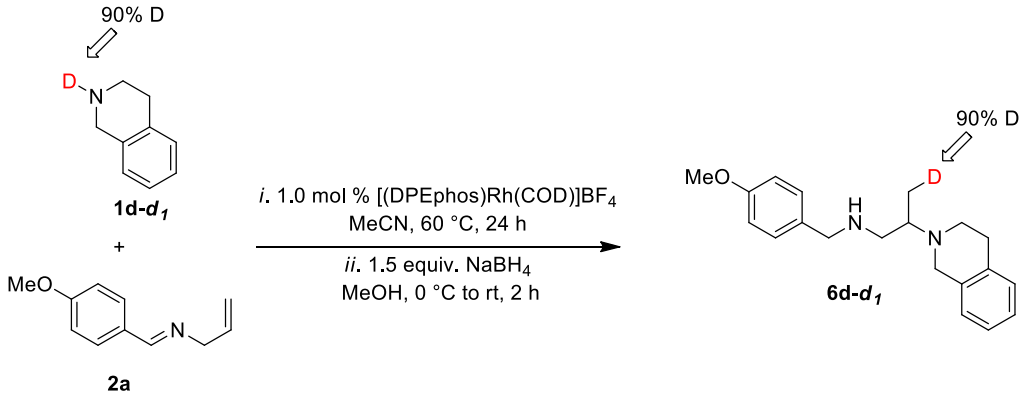
In the presence of *N*-allylimine the crude NMR shows deuterium incorporation at the terminal position as well as exchange into the nucleophile. The ^{2}H NMR was taken in MeCN (with C_6D_6 added for reference).



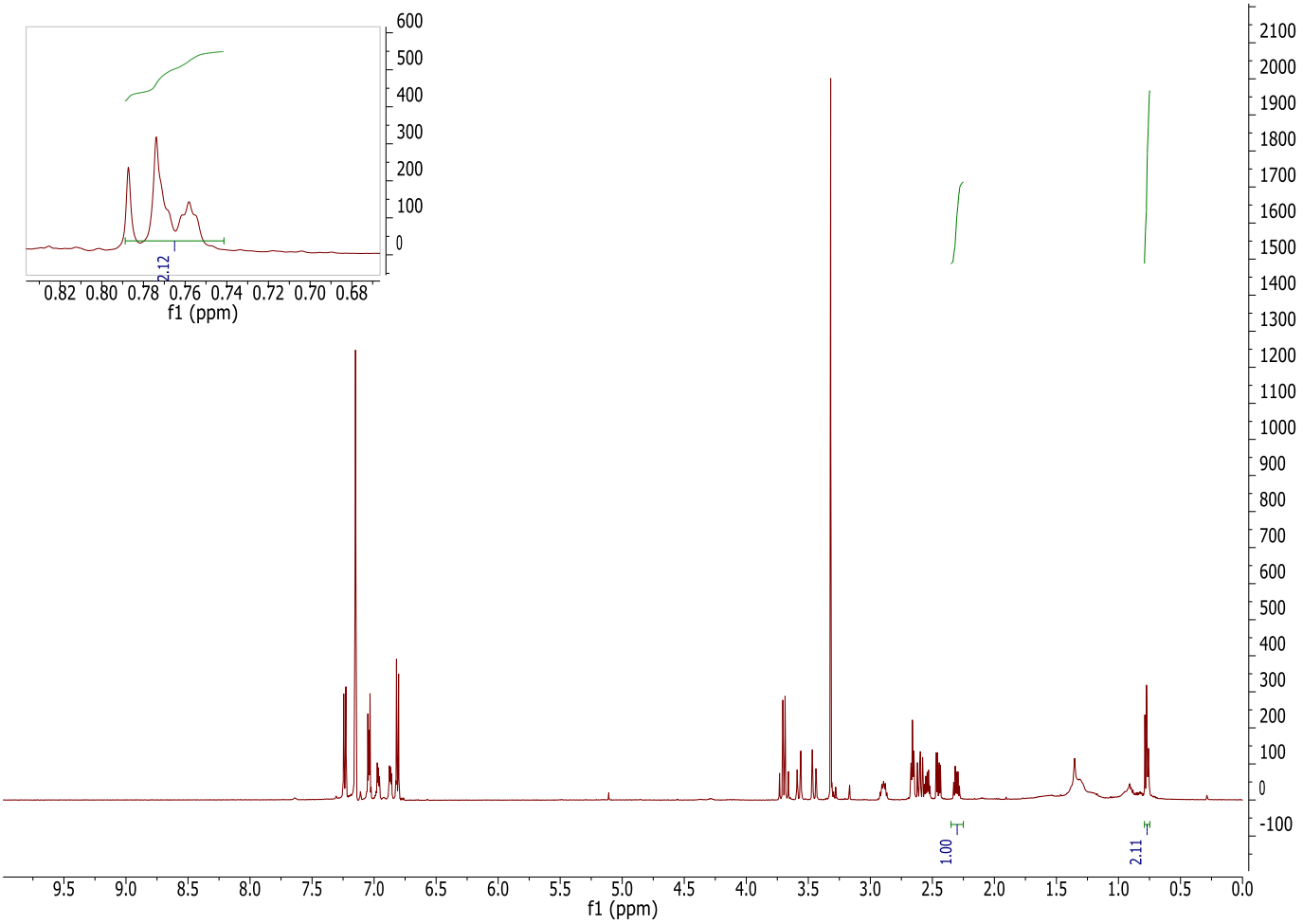
^{2}H NMR of crude reaction between **1d-*d*$_1$** and **2a**



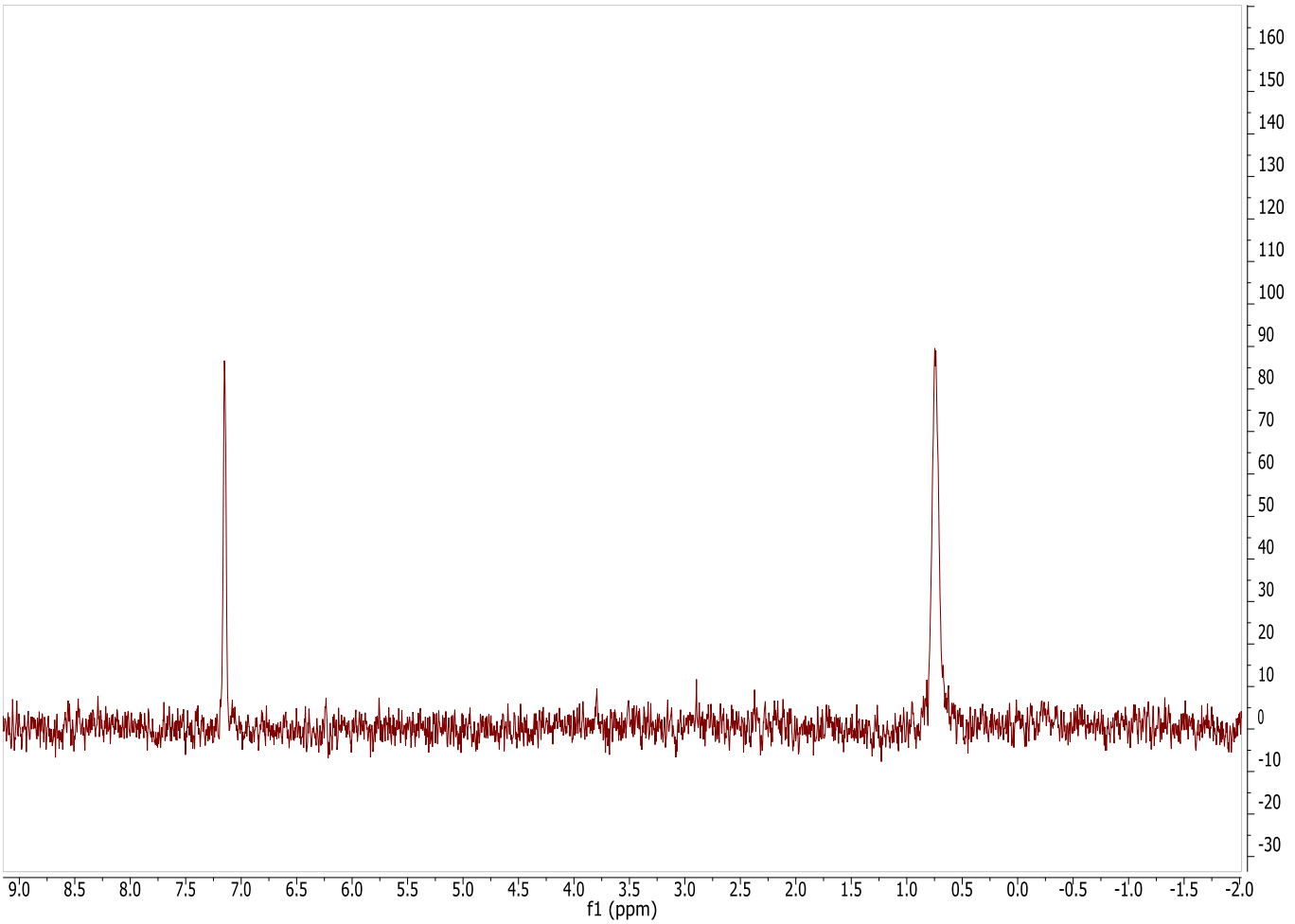
However, upon reduction and purification of **6d-*d1***, it is clear that the deuterium has been incorporated exclusively on the terminal methyl group. This suggests that the Rh-catalyzed hydroamination of *N*-allylimine **2a** is faster than H/D-exchange of the nucleophile. However, once the reaction is complete, then H/D exchange does occur.



^{1}H NMR of pure **6d-*d1***



^{2}H NMR of pure **6d-*d*$_1$**



2-(3,4-dihydroisoquinolin-2(1*H*)-yl)-*N*-(4-methoxybenzyl)propan-3-*d*-1-amine 6d-*d*$_1$: [Rh(COD)DPEPhos]BF_4 (4.2 mg, 0.005 mmol), imine **2a** (88 mg, 0.5 mmol) and dry CD_3CN (131 µL) were added to an oven-dried 4 mL vial equipped with a stir bar in the glove box. To the reaction mixture was then added amine **1d-*d*$_1$** (201 mg, 1.5 mmoL, 3.00 equiv). The resulting solution was allowed to stir for 24 h at 60 °C. After 24 h, the reaction vial was cooled to room temperature and the reaction mixture was further dissolved in 0.65 mL CD_3CN. After the ^{1}H NMR analysis of the crude reaction mixture in CD_3CN, the NMR sample was poured into the reaction vial and rinsed with MeOH (1 mL). Meanwhile, to an oven-dried 25 mL round bottom flask was added $NaBH_4$ (37.83 mg, 1.00 mmoL, 2.0 equiv) and MeOH (1 mL) and cooled to 0 °C. The imine solution is then added dropwise to the $NaBH_4$ solution. The vial was washed with MeOH (1 mL) and thereby transferred to the flask for reduction. The reaction was brought to room temperature and stirred for 2 h. The resulting mixture was concentrated *in vacuo*. The residue was then dissolved with $CHCl_3$ (20 mL) and then washed with saturated $NaHCO_3$ (15 mL). The organic layer was separated and the aqueous layer was extracted with $CHCl_3$ (15 mL × 3). All organic layers were combined, dried over anyhydrous

$MgSO_4$, filtered, and concentrated *in vacuo* followed by drying under high vacuum (0.05 mm Hg) for 1 h to afford the crude diamine **6d-*d*$_1$** as yellow viscous oil. The crude diamine was further subjected to ^{1}H NMR analysis in C_6D_6. Purification of the crude diamine by silica gel chromatography (13 mm × 4 mm column, 1:19 MeOH/CH_2Cl_2 as eluent) afforded the salt of the amine as yellow solid. Thereafter, The salt was dissolved in 10 mL $CHCl_3$. The amine salt was then basified using 2 M NaOH until pH~12. The organic layer was separated. The aqueous layer was extracted with $CHCl_3$ (50 mL x 3). All organic layers were then combined, dried over anhydrous $MgSO_4$ and filtered. The solution was concentrated *in vacuo* followed by drying under high vacuum (10 mm Hg) for 0.5 h to afford the a mixture of diamines **6d-*d*$_1$** and **6d** (as a 9:1 mixture) as yellow viscous oil.

With aid of ^{1}H NMR analysis, the deuterium incorporation was found to be 90%. As the nucleophile **16** itself was 90% D, hence in the case of diamine, the deuterium was incorporated exclusively at the terminal position of the diamine **6d-*d*$_1$**.

The aforementioned hydroamination reaction was also performed in CH_3CN for the ^{2}H NMR analysis. From ^{2}H NMR analysis, a single peak was found at δ = 0.71 ppm using C_6D_6 (δ = 7.15 ppm) as an internal standard for reference. This peak corresponds to deuterium incorporation at the terminal position of the diamine **6d-*d*$_1$**.

Data for the mixture of **6d-*d*$_1$** and **6d**:

R$_f$ = 0.6 (1:9 MeOH/CH_2Cl_2)

^{1}H NMR (C_6D_6, 500 MHz): δ 7.24 (d, *J* = 8.5 Hz, 2H), 7.07 – 7.01 (m, 2H), 6.97 (dd, *J* = 5.3, 3.6 Hz, 1H), 6.87 (dt, *J* = 5.3, 3.5 Hz, 1H), 6.81 (d, *J* = 8.6 Hz, 1H), 3.72 (d, *J* = 13.3 Hz, 1H), 3.67 (d, *J* = 13.3 Hz, 1H), 3.58 (d, *J* = 14.7 Hz, 1H), 3.45 (d, *J* = 14.7 Hz, 1H), 3.32 (s, 3H), 2.89 (dtd, *J* = 13.3, 6.7, 4.8 Hz, 1H), 2.66 (t, *J* = 5.8 Hz, 2H), 2.60 (dd, *J* = 11.6, 9.0 Hz, 1H), 2.54 (dt, *J* = 11.0, 5.3 Hz, 1H), 2.45 (dd, *J* = 11.6, 4.7 Hz, 1H), 2.30 (dt, *J* = 11.7, 6.0 Hz, 1H), 0.80 – 0.74 (m, 2.1H) ppm.

For Reference, **Pure 6d**; **^{1}H NMR** (C_6D_6, 500 MHz): δ 7.20 (d, *J* = 8.7 Hz, 2H), 7.01 (dd, *J* = 5.5, 3.5 Hz, 2H), 6.94 (dd, *J* = 5.3, 3.6 Hz, 1H), 6.84 (dd, *J* = 5.2, 3.7 Hz, 1H), 6.78 (d, *J* = 8.7 Hz, 2H), 3.69 (d, *J* = 13.3 Hz, 1H), 3.65 (d, *J* = 13.3 Hz, 1H), 3.55 (d, *J* = 14.7 Hz, 1H), 3.43 (d, *J* = 14.6 Hz, 1H), 3.31 (s, 3H), 2.91-2.84 (m, 1H), 2.64 (t, *J* = 5.7 Hz, 2H), 2.58 (dd, *J* = 11.6, 9.0 Hz, 1H), 2.53 (dt, *J* = 11.1, 5.5 Hz, 1H), 2.43 (dd, *J* = 11.6, 4.8 Hz, 1H), 2.29 (dt, *J* = 11.4, 5.8 Hz, 1H), 1.86-1.85 (br s, 1H), 0.77 (d, *J*=6.6 Hz, 3H) ppm.

^{2}H NMR (C_6D_6, 500 MHz): δ 0.75 (s, 1^{2}H)

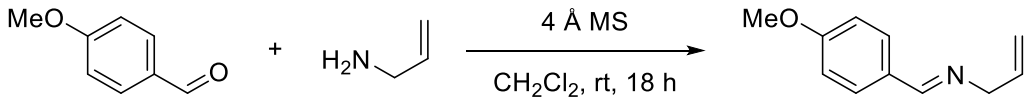
^{13}C NMR ($CDCl_3$, 125 MHz): δ 159.78, 136.78, 135.83, 134.21, 130.11, 129.60, 127.53, 126.68, 126.30, 114.65, 59.18, 59.12, 55.38, 54.21, 52.67, 52.64, 51.96, 46.28, 31.03, 11.90, 11.79, 11.64 (t, J^{CD} = 11.67 Hz) ppm.

For Reference, **Pure 6d**; **^{13}C-NMR** (C_6D_6, 125 MHz) δ 159.00, 136.06, 135.09, 133.62, 129.36, 127.71, 126.81, 125.96, 125.58, 113.89, 58.48, 54.65, 53.53, 52.00, 51.21, 45.51, 30.31, 11.15 ppm.

HRMS (ESI-TOF) *m/z*: [M+H$^+$] calcd for $C_{20}H_{26}{}^2HN_2O$, 312.2186; found, 312.2178.

HRMS (ESI-TOF) *m/z*: [M+H$^+$] calcd for $C_{20}H_{27}N_2O$, 311.2123; found, 312.2122.

E. Experimental Procedure, Isolation, and Characterization



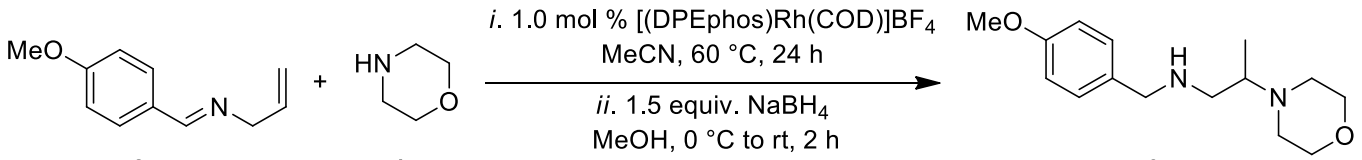
2a

(E)-*N*-allyl-1-(4-methoxyphenyl)methanimine, 2a: *p*-Anisaldehyde (30 mL, 250 mmol, 1.0 equiv.), 4 Å MS (10.0 g, beads) and dry CH_2Cl_2 (100 mL) were added to a 500 mL round bottom flask with a stir bar followed by allylamine (27 mL, 370 mmol, 1.5 equiv.). The reaction mixture was placed under N_2 and stirred at room temperature for 24 h. It was filtered through Celite, washing with CH_2Cl_2 (120 mL). The filtrate was washed with water (200 mL × 2) and brine (200 mL × 1). The organic layer was dried with $MgSO_4$, filtered, and concentrated under reduced pressure to give imine **2a** as a pale yellow oil in 84% yield (36 g, 210 mmol). The imine was used without further purification.

^{1}H NMR (C_6D_6, 500 MHz): δ 7.92 (s, 1H), 7.68 (d, J = 8.7 Hz, 2H), 6.70 (d, J = 8.7 Hz, 2H), 6.04 (ddt, J = 17.1, 10.2, 5.5 Hz, 1H), 5.23 (dd, J = 17.1, 1.9 Hz, 1H), 5.04 (dd, J = 10.3, 1.8 Hz, 1H), 4.17 – 3.93 (m, 2H), 3.22 (s, 3H) ppm.

^{13}C NMR (C_6D_6, 125 MHz): δ 161.87, 160.47, 136.96, 129.95, 129.90, 115.17, 114.10, 63.57, 54.70 ppm.

HRMS (ESI-TOF) *m/z*: [M+H$^+$] calculated for $C_{11}H_{14}NO$, 176.1075; found: 176.1074.



2a **1a** **6a**

N-(4-methoxybenzyl)-2-morpholinopropan-1-amine, 6a: [(DPEphos)Rh(COD)]BF_4 (13 mg, 0.015 mmol, 1.0 mol %), imine **2a** (259 μL, 1.50 mmol, 1.00 equiv.) and dry CH_3CN (350 μL) were added to an oven-dried 4 mL vial equipped with a stir bar in the glove box. To the reaction mixture was added morpholine, **1a** (390 μL, 4.5 mmol, 3.0 equiv.). The resulting solution was allowed to stir for 24 h at 60 °C. After 24 h, the reaction vial was cooled to room temperature followed by the addition of diphenylmethane as an internal standard. To the vial was added *p*-anisaldehyde (91 μL, 0.75 mmol, 0.50 equiv.) and the mixture was stirred for 2 hours. The reaction mixture was further dissolved in C_6D_6 (0.5 mL). The crude yield (92%) was determined by the analysis of the ^{1}H NMR. The NMR sample was poured into the reaction vial and was rinsed with MeOH (2 mL). Meanwhile, to an oven-dried 25 mL round bottom flask was added $NaBH_4$ (57 mg, 2.3 mmol, 1.5 equiv.) and MeOH (3 mL) and cooled to 0 °C. The solution of the aminoimine in MeOH was added dropwise, washing the vial with MeOH (2.5 mL). The reaction was brought to room temperature, stirred for 2 h, and then concentrated *in vacuo*. The residue was dissolved with $CHCl_3$ (20 mL) and washed with saturated $NaHCO_3$ (15 mL). The organic layer was separated and the aqueous layer was extracted with $CHCl_3$ (15 mL × 3). All organic layers were combined, dried over anhydrous $MgSO_4$, and filtered. The solution was concentrated *in vacuo* followed by drying under high vacuum (0.05 mm Hg) for 1 h to afford crude **6a** as a yellow oil. Purification of the crude diamine by silica gel

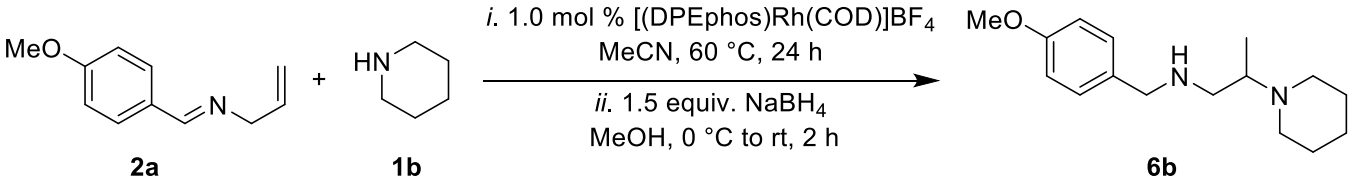
chromatography (125 mL silica, 3% NH_4OH : 3% MeOH : 94% $CHCl_3$ v/v prepared by extracting saturated NH_4OH with $CHCl_3$, removing aqueous layer, and adding methanol) afforded pure diamine **6a** as a pale yellow oil in 82% yield (323 mg, 1.22 mmol).

R_f = 0.55 (1:9 $NH_4OH/CHCl_3$).

^1H NMR (C_6D_6, 500 MHz): δ 7.25 (d, *J* = 8.7 Hz, 2H), 6.81 (d, *J* = 8.6 Hz, 2H), 3.66 (d, *J* = 12.9 Hz, 1H), 3.64 (d, *J* = 13.1 Hz, 1H), 3.49 (qdd, *J* = 11.3, 6.4, 3.3 Hz, 4H), 3.29 (s, 3H), 2.54 (dqd, *J* = 8.3, 6.6, 4.9 Hz, 1H), 2.43 (dd, *J* = 11.6, 8.4 Hz, 1H), 2.33 (dd, *J* = 11.6, 4.9 Hz, 1H), 2.21 (ddd, *J* = 10.5, 6.5, 3.5 Hz, 2H), 2.07 (ddd, *J* = 10.6, 6.6, 3.6 Hz, 2H) 1.55 (br s, 1H), 0.70 (d, *J* = 6.4 Hz, 3H) ppm.

^{13}C NMR (C_6D_6, 125 MHz): δ 159.0, 133.5, 129.3, 113.9, 67.4, 58.9, 54.7, 53.6, 51.6, 48.8, 11.7 ppm.

HRMS (ESI-TOF) *m/z*: [M+H$^+$] calculated for $C_{15}H_{25}N_2O_2$, 265.1916; found, 265.1906.



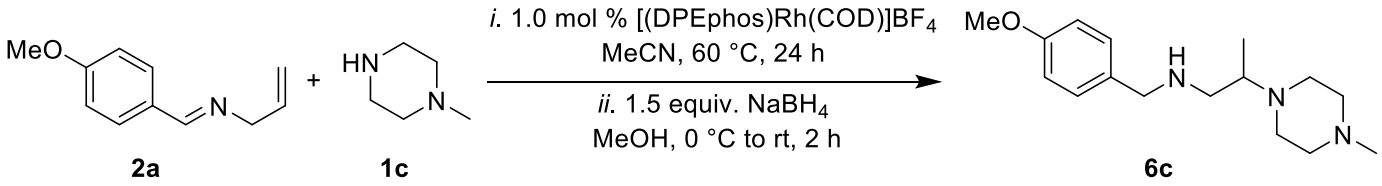
***N*-(4-methoxybenzyl)-2-(piperidin-1-yl)propan-1-amine, 6b:** [(DPEphos)Rh(COD)]BF_4 (13 mg, 0.015 mmol, 1.0 mol %), imine **2a** (259 μL, 1.50 mmol, 1.00 equiv.) and dry CH_3CN (350 μL) were added to an oven-dried 4 mL vial equipped with a stir bar in the glove box. To the reaction mixture was added piperidine, **1b** (185 μL, 2.25 mmol, 1.50 equiv.). The resulting solution was allowed to stir for 24 h at 60 °C. After 24 h, the reaction vial was cooled to room temperature followed by the addition of diphenylmethane as an internal standard. To the vial was added *p*-anisaldehyde (91.2 μL, 0.75 mmol, 0.50 equiv.) and the mixture was stirred for 2 hours. The reaction mixture was further dissolved in C_6D_6 (0.5 mL). The crude yield (91%) was determined by the analysis of the ^1H NMR. The NMR sample was poured into the reaction vial and was rinsed with MeOH (2 mL). Meanwhile, to an oven-dried 25 mL round bottom flask was added $NaBH_4$ (57 mg, 2.3 mmol, 1.5 equiv.) and MeOH (3 mL) and cooled to 0 °C. The solution of the aminoimine in MeOH was added dropwise, washing the vial with MeOH (2.5 mL). The reaction was brought to room temperature, stirred for 2 h, and then concentrated *in vacuo*. The residue was dissolved with $CHCl_3$ (20 mL) and washed with saturated $NaHCO_3$ (15 mL). The organic layer was separated and the aqueous layer was extracted with $CHCl_3$ (15 mL × 3). All organic layers were combined, dried over anhydrous $MgSO_4$ and filtered. The solution was concentrated *in vacuo* followed by drying under high vacuum (0.05 mm Hg) for 1 h to afford crude **6b** as a yellow oil. Purification of the crude diamine by silica gel chromatography (125 mL silica, 3% NH_4OH : 3% MeOH : 94% $CHCl_3$ v/v prepared by extracting saturated NH_4OH with $CHCl_3$, removing aqueous layer, and adding methanol) afforded pure diamine **6b** as a pale yellow oil in 87% yield (340 mg, 1.3 mmol).

R_f = 0.63 (1:9 $NH_4OH/CHCl_3$).

^1H NMR (C_6D_6, 500 MHz): δ 7.28 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 8.4 Hz, 2H), 3.72 (d, *J* = 13.2 Hz, 1H), 3.68 (d, *J* = 13.0 Hz, 1H), 3.28 (s, 3H), 2.77-2.70 (dqd, *J* = 9.2, 6.6, 4.7, 1H), 2.52 (dd, *J* = 11.3, 9.4 Hz, 1H), 2.39 (dd, *J* = 11.4, 4.8 Hz, 1H), 2.33 (ddd, *J* = 10.8, 7.3, 3.4 Hz, 2H), 2.14 (t, *J* = 7.1 Hz, 2H), 1.86 (s, 1H), 1.44-1.37 (m, 4H), 1.29-1.22 (m, 2H), 0.74 (d, *J* = 6.6 Hz, 3H) ppm.

^{13}C NMR (C_6D_6, 125 MHz): δ 159.0, 133.7, 129.4, 113.9, 59.2, 54.7, 53.6, 52.2, 49.3, 26.9, 25.3, 11.3 ppm.

HRMS (ESI-TOF) *m/z*: [M+H$^+$] calculated for $C_{16}H_{27}N_2O$, 263.2123; found, 263.2130.



2a **1c** **6c**

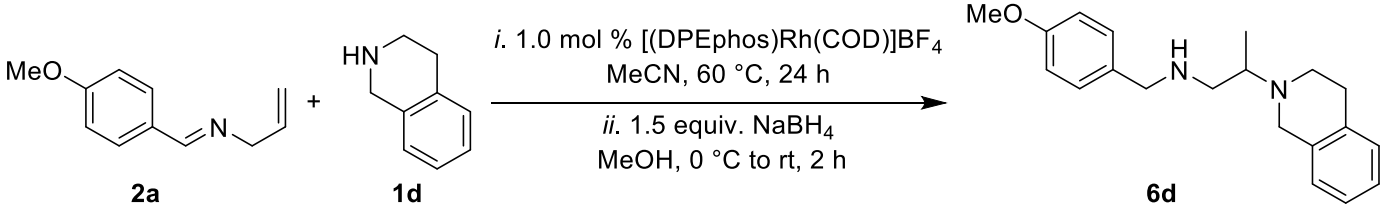
N-(4-methoxybenzyl)-2-(4-methylpiperazin-1-yl)propan-1-amine, 6c: [(DPEphos)Rh(COD)]BF_4 (13 mg, 0.015 mmol, 1.0 mol %), imine **2a** (259 μL, 1.50 mmol, 1.00 equiv.) and dry CH_3CN (350 μL) were added to an oven-dried 4 mL vial equipped with a stir bar in the glove box. To the reaction mixture was added 1-methylpiperazine, **1c** (749 μL, 6.75 mmol, 4.00 equiv.). The resulting solution was allowed to stir for 24 h at 60 °C. To the vial was added *p*-anisaldehyde (91 μL, 0.75 mmol, 0.50 equiv.) and the mixture was stirred for 2 hours. After 24 h, the reaction vial was cooled to room temperature followed by the addition of diphenylmethane as an internal standard. The reaction mixture was further dissolved in C_6D_6 (0.5 mL). The crude yield (88%) was determined by the analysis of the ^{1}H NMR. The NMR sample was poured into the reaction vial and was rinsed with MeOH (2 mL). Meanwhile, to an oven-dried 25 mL round bottom flask was added $NaBH_4$ (57 mg, 2.3 mmol, 1.5 equiv.) and MeOH (3 mL) and cooled to 0 °C. The solution of the aminoimine in MeOH was added dropwise, washing the vial with MeOH (2.5 mL). The reaction was brought to room temperature, stirred for 2 h, and then concentrated *in vacuo*. The residue was dissolved with $CHCl_3$ (20 mL) and washed with saturated $NaHCO_3$ (15 mL). The organic layer was separated and the aqueous layer was extracted with $CHCl_3$ (15 mL × 3). All organic layers were combined, dried over anhydrous $MgSO_4$ and filtered. The solution was concentrated *in vacuo* followed by drying under high vacuum (0.05 mm Hg) for 1 h to afford crude **6c** as a yellow oil. Purification of the crude diamine by silica gel chromatography (125 mL silica, 3% NH_4OH : 3% MeOH : 94% $CHCl_3$ v/v prepared by extracting saturated NH_4OH with $CHCl_3$, removing aqueous layer, and adding methanol) afforded pure diamine **6c** as a pale yellow oil in 66% yield (274 mg, 0.988 mmol).

R_f = 0.42 (1:9 $NH_4OH/CHCl_3$).

^{1}H NMR (C_6D_6, 500 MHz): δ 7.27 (d, *J* = 8.7 Hz, 2H), 6.80 (d, *J* = 8.7 Hz, 2H), 3.70 (d, *J* = 13.1 Hz, 1H), 3.67 (d, *J* = 13.2 Hz, 1H), 3.29 (s, 3H), 2.70 (dqd, *J* = 8.7, 6.7, 4.8 Hz, 1H), 2.49 (dd, *J* = 11.6, 8.8 Hz, 1H), 2.46-2.42 (m, 2H), 2.39 (dd, *J* = 11.6, 4.9 Hz, 1H), 2.30-2.15 (m, 6H), 2.08 (s, 3H), 1.76 (s, 1H), 0.76 (d, *J* = 6.6 Hz, 3H) ppm.

^{13}C NMR (C_6D_6, 125 MHz): δ 159.0, 133.7, 129.3, 113.9, 58.5, 55.9, 54.7, 54.7, 53.6, 52.1, 46.2, 11.7 ppm.

HRMS (ESI-TOF) *m/z*: [M+H$^+$] calculated for $C_{16}H_{28}N_3O$, 278.2232; found, 278.2228.



2a **1d** **6d**

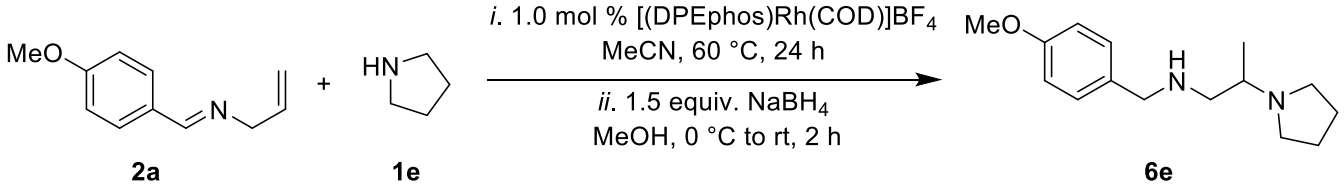
2-(3,4-dihydroisoquinolin-2(1H)-yl)-N-(4-methoxybenzyl)propan-1-amine, 6d: [(DPEphos)Rh(COD)]BF_4 (13 mg, 0.015 mmol, 1.0 mol %), imine **2a** (259 μL, 1.50 mmol, 1.00 equiv.) and dry CH_3CN (350 μL) were added to an oven-dried 4 mL vial equipped with a stir bar in the glove box. To the reaction mixture was added tetrahydroisoquinoline, **1d** (951 μL, 7.50 mmol, 5.00 equiv.). The resulting solution was allowed to stir for 24 h at 60 °C. After 24 h, the reaction vial was cooled to room temperature followed by the addition of diphenylmethane as an internal standard. To the vial was added *p*-anisaldehyde (91 μL, 0.75 mmol, 0.50 equiv.) and the mixture was stirred for 2 hours. The reaction mixture was further dissolved in C_6D_6 (0.5 mL). The crude yield (91%) was determined by the analysis of the ^{1}H NMR. The NMR sample was poured into the reaction vial and was rinsed with MeOH (2 mL). Meanwhile, to an oven-dried 25 mL round bottom flask was added $NaBH_4$ (57 mg, 2.3 mmol, 1.5 equiv.) and MeOH (3 mL) and cooled to 0 °C. The solution of the aminoimine in MeOH was added dropwise, washing the vial with MeOH (2.5 mL). The reaction was brought to room temperature, stirred for 2 h, and then concentrated *in vacuo*. The residue was dissolved with $CHCl_3$ (20 mL) and washed with saturated $NaHCO_3$ (15 mL). The organic layer was separated and the aqueous layer was extracted with $CHCl_3$ (15 mL × 3). All organic layers were combined, dried over anhydrous $MgSO_4$ and filtered. The solution was concentrated *in vacuo* followed by drying under high vacuum (0.05 mm Hg) for 1 h to afford crude **6d** as a yellow oil. Purification of the crude diamine by silica gel chromatography (125 mL silica, 2% NH_4OH : 2% MeOH : 96% $CHCl_3$ v/v prepared by extracting saturated NH_4OH with $CHCl_3$, removing aqueous layer, and adding methanol) afforded pure diamine **6d** as a pale yellow oil in 87% yield (404 mg, 1.30 mmol).

R_f = 0.60 (1:9 MeOH/CH_2Cl_2).

^{1}H NMR (C_6D_6, 500 MHz): δ 7.20 (d, *J* = 8.7 Hz, 2H), 7.01 (dd, *J* = 5.5, 3.5 Hz, 2H), 6.94 (dd, *J* = 5.3, 3.6 Hz, 1H), 6.84 (dd, *J* = 5.2, 3.7 Hz, 1H), 6.78 (d, *J* = 8.7 Hz, 2H), 3.69 (d, *J* = 13.3 Hz, 1H), 3.65 (d, *J* = 13.3 Hz, 1H), 3.55 (d, *J* = 14.7 Hz, 1H), 3.43 (d, *J* = 14.6 Hz, 1H), 3.31 (s, 3H), 2.91-2.84 (m, 1H), 2.64 (t, *J* = 5.7 Hz, 2H), 2.58 (dd, *J* = 11.6, 9.0 Hz, 1H), 2.53 (dt, *J* = 11.1, 5.5 Hz, 1H), 2.43 (dd, *J* = 11.6, 4.8 Hz, 1H), 2.29 (dt, *J* = 11.4, 5.8 Hz, 1H), 1.86-1.85 (br s, 1H), 0.77 (d, *J*=6.6 Hz, 3H) ppm.

^{13}C NMR (C_6D_6, 125 MHz): δ 159.00, 136.06, 135.09, 133.62, 129.36, 127.71, 126.81, 125.96, 125.58, 113.89, 58.48, 54.65, 53.53, 52.00, 51.21, 45.51, 30.31, 11.15 ppm.

HRMS (ESI-TOF) *m/z*: [M+H$^+$] calculated for $C_{20}H_{27}N_2O$, 311.2123; found, 311.2125.



2a **1e** **6e**

***N*-(4-methoxybenzyl)-2-(pyrrolidin-1-yl)propan-1-amine, 6e:** [(DPEphos)Rh(COD)]BF_4 (13 mg, 0.015 mmol, 1.0 mol %), imine **2a** (259 μL, 1.50 mmol, 1.00 equiv.) and dry CH_3CN (350 μL) were added to an oven-dried 4 mL vial equipped with a stir bar in the glove box. To the reaction mixture was added pyrrolidine, **1e** (185 μL, 2.25 mmol, 1.50 equiv.). The resulting solution was allowed to stir for 24 h at 60 °C. After 24 h, the reaction vial was cooled to room temperature followed by the addition of diphenylmethane as an internal standard. To the vial was added *p*-anisaldehyde (91 μL, 0.75 mmol, 0.50 equiv.) and the mixture was

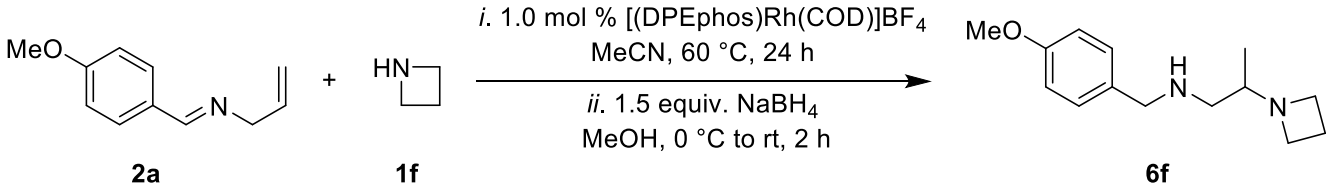
stirred for 2 hours. The reaction mixture was further dissolved in C_6D_6 (0.5 mL). The crude yield (97%) was determined by the analysis of the ^{1}H NMR. The NMR sample was poured into the reaction vial and was rinsed with MeOH (2 mL). Meanwhile, to an oven-dried 25 mL round bottom flask was added $NaBH_4$ (57 mg, 2.3 mmol, 1.5 equiv.) and MeOH (3 mL) and cooled to 0 °C. The solution of the aminoimine in MeOH was added dropwise, washing the vial with MeOH (2.5 mL). The reaction was brought to room temperature, stirred for 2 h, and then concentrated *in vacuo*. The residue was dissolved with $CHCl_3$ (20 mL) and washed with saturated $NaHCO_3$ (15 mL). The organic layer was separated and the aqueous layer was extracted with $CHCl_3$ (15 mL × 3). All organic layers were combined, dried over anhydrous $MgSO_4$ and filtered. The solution was concentrated *in vacuo* followed by drying under high vacuum (0.05 mm Hg) for 1 h to afford crude **6e** as a yellow oil. Purification of the crude diamine by silica gel chromatography (125 mL silica, 3% NH_4OH : 3% MeOH : 94% $CHCl_3$ v/v prepared by extracting saturated NH_4OH with $CHCl_3$, removing aqueous layer, and adding methanol) afforded pure diamine **6e** as a pale yellow oil in 76% yield (282 mg, 1.14 mmol).

R_f = 0.61 (1:9 $NH_4OH/CHCl_3$).

^{1}H NMR (C_6D_6, 500 MHz): δ 7.23 (d, J = 8.5 Hz, 2H), 6.78 (d, J = 8.5 Hz, 2H), 3.66 (s, 2H), 3.32 (s, 3H), 2.60-2.54 (m, 2H), 2.49 (dq, J = 11.6, 5.8 Hz, 1H), 2.38-2.35 (m, 4H), 1.72 (br s, 1H), 1.53 (m, 4H), 1.04 (d, J = 6.4 Hz, 3H) ppm.

^{13}C NMR (C_6D_6, 125 MHz): δ 158.99, 133.62, 129.30, 113.85, 57.74, 54.64, 54.01, 53.92, 50.15, 23.80, 15.53 ppm.

HRMS (ESI-TOF) *m/z*: [M+H$^+$] calculated for $C_{15}H_{25}N_2O$, 249.1967; found, 249.1960.



2a **1f** **6f**

2-(azetidin-1-yl)-N-(4-methoxybenzyl)propan-1-amine, 6f: [(DPEphos)Rh(COD)]BF_4 (13 mg, 0.015 mmol, 1.0 mol %), imine **2a** (259 μL, 1.50 mmol, 1.00 equiv.) and dry CH_3CN (350 μL) were added to an oven-dried 4 mL vial equipped with a stir bar in the glove box. To the reaction mixture was added azetidine, **1f** (152 μL, 2.25 mmol, 1.50 equiv.). The resulting solution was allowed to stir for 24 h at 60 °C. After 24 h, the reaction vial was cooled to room temperature followed by the addition of diphenylmethane as an internal standard. To the vial was added *p*-anisaldehyde (91 μL, 0.75 mmol, 0.50 equiv.) and the mixture was stirred for 2 hours. The reaction mixture was further dissolved in C_6D_6 (0.5 mL). The crude yield (78%) was determined by the analysis of the ^{1}H NMR. The NMR sample was poured into the reaction vial and was rinsed with MeOH (2 mL). Meanwhile, to an oven-dried 25 mL round bottom flask was added $NaBH_4$ (57 mg, 2.3 mmol, 1.5 equiv) and MeOH (3 mL) and cooled to 0 °C. The solution of the aminoimine in MeOH was added dropwise, washing the vial with MeOH (2.5 mL). The reaction was brought to room temperature, stirred for 2 h, and then concentrated *in vacuo*. The residue was dissolved with $CHCl_3$ (20 mL) and washed with saturated $NaHCO_3$ (15 mL). The organic layer was separated and the aqueous layer was extracted with $CHCl_3$ (15 mL × 3). All organic layers were combined, dried over anhydrous $MgSO_4$ and filtered. The solution was concentrated *in vacuo* followed by drying under high vacuum (0.05 mm Hg) for 1 h to afford crude **6f** as a yellow oil. Purification of the crude diamine by silica gel

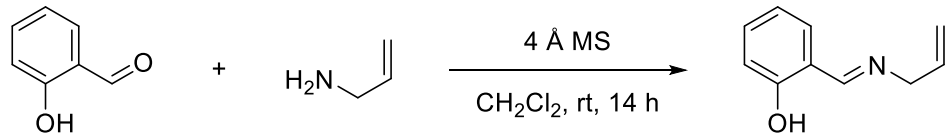
chromatography (125 mL silica, 4% NH_4OH : 4% MeOH : 92% $CHCl_3$ v/v prepared by extracting saturated NH_4OH with $CHCl_3$, removing aqueous layer, and adding methanol) afforded pure diamine **6f** as a pale yellow oil in 72% yield (253 mg, 1.08 mmol).

R_f = 0.53 (1:9 MeOH/CH_2Cl_2).

^{1}H NMR (C_6D_6, 500 MHz): δ 7.26 – 7.18 (m, 2H), 6.85 – 6.75 (m, 2H), 3.62 (s, 2H), 3.31 (s, 3H), 3.15 – 2.75 (m, 4H), 2.44 (qd, *J* = 11.4, 4.7 Hz, 2H), 2.26 – 2.05 (m, 1H), 1.71 (p, *J* = 6.8 Hz, 2H), 1.30 (s, 1H), 0.98 (d, *J* = 6.3 Hz, 3H) ppm.

^{13}C NMR (C_6D_6, 125 MHz): δ 159.01, 133.55, 129.28, 113.87, 62.83, 54.62, 54.00, 53.51, 52.19, 17.23, 15.21 ppm.

HRMS (ESI-TOF) *m/z*: [M+H$^+$] calculated for $C_{14}H_{23}N_2O$, 235.1810; found, 235.1811.



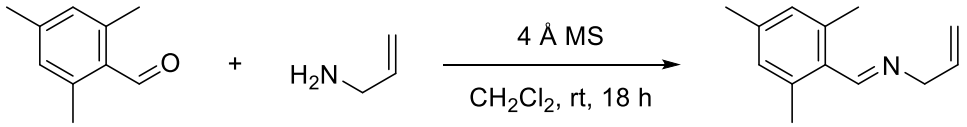
7a

(E)-2-((allylimino)methyl)phenol, 7a: Salicylaldehyde (1.62 g, 13.3 mmol, 1.00 equiv.), 4 Å MS (2.50 g, beads) and dry CH_2Cl_2 (10 mL) were added to a 25 mL oven-dried round bottom flask, equipped with a stir bar under an N_2 atmosphere. After stirring for 10 min, allylamine (1.5 mL, 20 mmol, 1.5 equiv.) was added. The reaction mixture was stirred at room temperature for 14 h and was filtered through Celite while rinsing with diethylether (100 mL). The filtrate was washed with water (50 mL × 3) and brine (50 mL × 1). The organic layer was dried with anhydrous $MgSO_4$, filtered, and concentrated by rotary evaporation to give imine **7a** as a pale orange, viscous oil in 88% isolated yield (1.89 g, 11.7 mmol). The resulting imine was used without any further purification.

^{1}H NMR (C_6D_6, 500 MHz): δ 7.71 (s, 1H), 7.06 (d, *J* = 4.2, 2H), 6.89 (d, *J* = 7.5, 1H), 6.68 (td, *J* = 6.2, 3.3, 1H), 5.68 (ddt, *J* = 16.8, 10.8, 5.6, 1H), 5.03 (dd, *J* = 17.2, 1.6, 1H), 4.95 (dd, *J* = 10.3, 1.4, 1H), 3.69 (d, *J* = 5.3, 2H), -2.47 (s, 1H) ppm.

^{13}C NMR (C_6D_6, 125 MHz): δ 166.0, 161.9, 135.2, 132.5, 131.7, 119.3, 118.6, 117.4, 116.2, 61.4 ppm.

HRMS (ESI-TOF) *m/z*: [M+H$^+$] calculated for $C_{10}H_{12}NO$, 162.0919; found, 162.0912.



7b

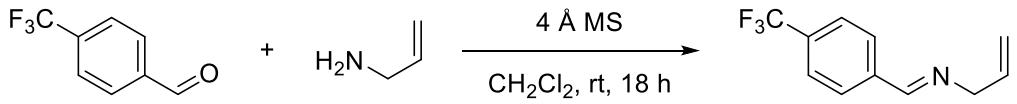
(E)-N-allyl-1-mesitylmethanimine, 7b: 2,4,6-trimethylbenzaldehyde (1.56 g, 10.5 mmol, 1.00 equiv.), 4 Å MS (2.0 g, beads) and dry CH_2Cl_2 (10 mL) were added to a 25 mL oven-dried round bottom flask equipped with a stir bar under an N_2 atmosphere. After stirring for 10 min, allylamine (2.0 mL, 27 mmol, 1.5 equiv.) was added. The reaction mixture was stirred at room temperature for 18 h and was filtered through Celite while rinsing with diethylether (100 mL). The filtrate was washed with water (100 mL × 2) and brine (100 mL × 1). The organic layer was dried with anhydrous $MgSO_4$, filtered, and concentrated by rotary evaporation to give

imine **7b** as a pale orange, viscous oil in 62% isolated yield (1.22 g, 6.51 mmol). The resulting imine was used without any further purification.

^{1}H NMR (C_6D_6, 500 MHz): δ 8.41 (s, 1H), 6.70 (s, 2H), 6.10-6.02 (m, 1H), 5.27 (dq, J = 17.2, 1.9, 1H), 5.08 (dd, J = 10.3, 1.6, 1H), 4.11 (dd, J = 5.4, 1.4, 2H), 2.39 (s, 6H), 2.09 (s, 3H) ppm.

^{13}C NMR (C_6D_6, 125 MHz): δ 161.4, 138.7, 138.1, 137.2, 131.2, 129.9, 115.2, 65.2, 21.24, 21.18 ppm.

HRMS (ESI-TOF) *m/z*: [M+H$^+$] calculated for $C_{13}H_{18}N$, 188.1439; found, 188.1438.



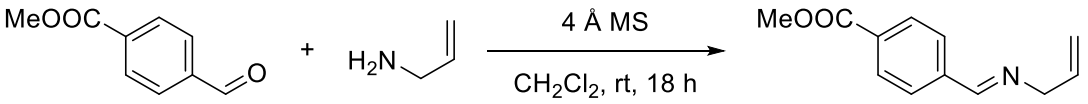
7c

(E)-N-allyl-1-(4-(trifluoromethyl)phenyl)methanimine, 7c: 4-(trifluoromethyl)benzaldehyde (2.16 g, 12.4 mmol, 1.00 equiv.), 4 Å MS (4.50 g, beads) and dry CH_2Cl_2 (10 mL) were added to a 25 mL oven-dried round bottom flask equipped with a stir bar under an N_2 atmosphere. After stirring for 10 min, allylamine (1.4 mL, 19 mmol, 1.5 equiv.) was added. The reaction mixture was stirred at room temperature for 18 h and was filtered through Celite while rinsing with diethylether (100 mL). The filtrate was washed with water (100 mL × 2) and brine (100 mL × 1). The organic layer was dried with anhydrous $MgSO_4$, filtered, and concentrated by rotary evaporation to give imine **7c** as a pale orange, viscous oil in 83% isolated yield (2.19 g, 10.3 mmol). The resulting imine was used without any further purification.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.32 (s, 1H), 7.85 (d, *J* = 8.1, 2H), 7.66 (d, *J* = 8.2, 2H), 6.07 (ddt, *J* = 17.2, 10.3, 5.7, 1H), 5.24 (dq, *J* = 17.2, 1.7, 1H), 5.18 (dq, *J* = 10.3, 1.5, 1H), 4.29 (dq, *J* = 5.7, 1.5, 2H) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz): δ 160.47, 139.42, 135.53, 132.36 (q, J^{CF} = 32.5), 128.43, 125.64 (q, J^{CF} = 3.8), 124.06 (q, J^{CF} = 272.1), 116.48, 63.81 ppm.

HRMS (ESI-TOF) *m/z*: [M+H$^+$] calculated for $C_{11}H_{11}NF_3$, 214.0844; found, 214.0841.



7d

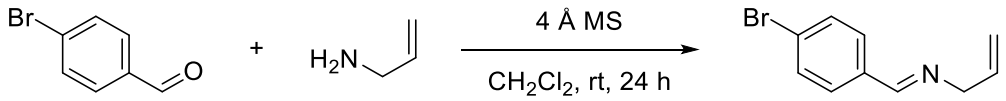
methyl (E)-4-((allylimino)methyl)benzoate, 7d: Methyl 4-formylbenzoate (2.22 g, 13.5 mmol, 1.00 equiv.), 4 Å MS (3.00 g, beads) and dry CH_2Cl_2 (10 mL) were added to a 25 mL oven-dried round bottom flask, equipped with a stir bar under an N_2 atmosphere. After stirring for 10 min, allylamine (1.23 mL, 20.3 mmol, 1.50 equiv.) was added. The reaction mixture was stirred at room temperature for 18 h and was filtered through Celite while rinsing with diethylether (100 mL). The filtrate was washed with water (50 mL × 3) and brine (50 mL × 1). The organic layer was dried with anhydrous $MgSO_4$, filtered, and concentrated by rotary

evaporation to give imine **7d** as a pale orange, viscous oil in 91% isolated yield (2.49 g, 12.3 mmol). The resulting imine was used without any further purification.

^{1}H NMR (C_6D_6, 500 MHz): δ 8.08 (d, *J* = 8.5, 2H), 7.79 (s, 1H), 7.65 (d, *J* = 8.4, 2H), 6.00 (ddt, *J* = 17.2, 10.4, 5.5, 1H), 5.20 (dq, *J* = 17.2, 1.7, 1H), 5.06 (dq, *J* = 10.3, 1.6, 1H), 4.02 (dq, *J* = 5.5, 1.6, 2H), 3.48 (s, 3H) ppm.

^{13}C NMR (C_6D_6, 125 MHz): δ 166.3, 160.4, 140.6, 136.3, 132.4, 130.1, 128.4, 115.8, 63.8, 51.7 ppm.

HRMS (ESI-TOF) *m/z*: [M+H$^+$] calculated for $C_{12}H_{14}NO_2$, 204.1025; found, 214.1015.



7e

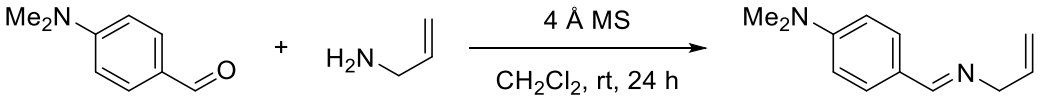
(*E*)-*N*-allyl-1-(4-bromophenyl)methanimine, 7e: 4-bromobenzaldehyde (925 mg, 5.00 mmol, 1.00 equiv.), 4 Å MS (1.50 g, beads) and dry CH_2Cl_2 (5.0 mL) were added to a 25 mL flame-dried round bottom flask, equipped with a stir bar under N_2 atmosphere. After stirring for 10 min, allylamine (0.50 mL, 6.5 mmol, 1.3 equiv.) was added. The reaction mixture was stirred at room temperature for 24 h. It was filtered through Celite, rinsing the round bottom flask with CH_2Cl_2 (10 mL × 4) and the Celite bed was washed with additional CH_2Cl_2 (10 mL). The filtrate was washed with water (15 mL × 2) and brine (15 mL × 1). The organic layer was dried with anhydrous $MgSO_4$, filtered, and concentrated by rotary evaporation to give imine **7e** as a pale yellow, viscous oil in 92% isolated yield (1.03 g, 4.60 mmol). The resulting imine was used without any further purification.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.23 (s, 1H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 6.05 (ddt, *J* = 17.3, 10.5, 5.7 Hz, 1H), 5.23 (dq, *J* = 17.2, 1.6 Hz, 1H), 5.16 (dq, *J* = 10.4, 1.5 Hz, 1H), 4.24 (dq, *J* = 5.8, 1.5 Hz, 2H) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz): δ 160.57, 135.55, 134.99, 131.75, 129.47, 125.02, 116.19, 63.40 ppm.

HRMS (ESI-TOF) *m/z*: [M+H$^+$] calculated for $C_{10}H_{11}BrN$, 224.0075; found, 224.0083 ppm.

These spectral data match those previously reported for this compound.[2]



7f

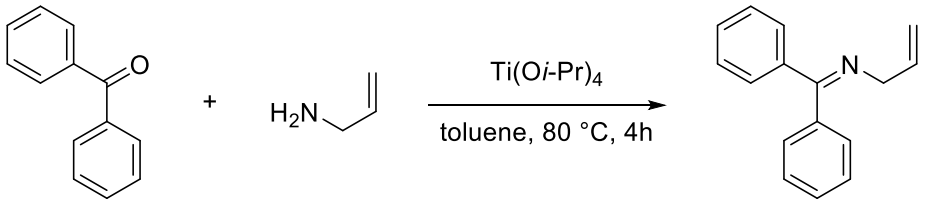
(*E*)-4-((allylimino)methyl)-*N*,*N*-dimethylaniline, 7f: 4-(dimethylamino)benzaldehyde (746 mg, 5.00 mmol, 1.00 equiv.), 4 Å MS (1.50 g, beads) and dry CH_2Cl_2 (5 mL) were added to a 25 mL flame-dried round bottom flask, equipped with a stir bar under N_2 atmosphere. After stirring for 10 min, allylamine (0.50 mL, 6.5 mmol, 1.3 equiv.) was added. The reaction mixture was stirred at room temperature for 24 h. It was filtered through Celite; the round bottom flask was rinsed with CH_2Cl_2 (10 mL × 4), the Celite bed was washed with additional CH_2Cl_2 (10 mL). The filtrate was washed with water (15 mL × 2) and brine (15 mL × 1). The organic

layer was dried with anhydrous $MgSO_4$, filtered, and concentrated by rotary evaporation to give imine **7f** as a pale yellow, viscous oil in 92% isolated yield (866 mg, 4.60 mmol). The resulting imine was used without any further purification.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.16 (s, 1H), 7.63 (d, *J* = 8.9 Hz, 2H), 6.69 (d, *J* = 8.8 Hz, 2H), 6.07 (ddt, *J* = 17.0, 10.2, 5.7 Hz, 1H), 5.23 (dq, *J* = 17.2, 1.6 Hz, 1H), 5.13 (dq, *J* = 10.3, 1.5 Hz, 1H), 4.23 – 4.17 (m, 2H), 3.00 (s, 6H) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz): δ 161.83, 151.98, 136.57, 129.44, 124.36, 115.47, 111.50, 63.42, 40.11 ppm.

HRMS (ESI-TOF) *m/z*: [M+H$^+$] calculated for $C_{12}H_{17}N_2$, 189.1392; found, 189.1383.



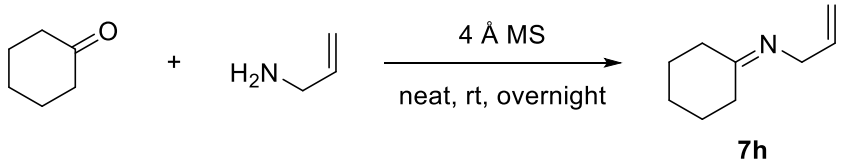
7g

N-allyl-1,1-diphenylmethanimine, 7g: Benzophenone (10.0 g, 54.9 mmol, 1.00 equiv.) and toluene (50 mL) were combined in a 250 mL round bottom flask with stir bar. Allylamine (6.16 mL, 82.3 mmol, 1.50 equiv.) and titanium isopropoxide (16 mL, 35 mmol, 0.64 equiv.) were added. The round bottom was fitted with a condenser, and the flask contents were heated for three hours, monitoring by GC-MS. The reaction mixture was cooled to room temperature, additional toluene (100 mL) was added, the reaction was quenched with water (5 mL), and the round bottom was stirred for 30 minutes. TiO_2 formed as a precipitate and was removed by filtration. The solid byproduct was washed with toluene (20 mL × 2). The organic layers were combined and washed with water (100 mL × 3) and brine (100 mL × 1). Toluene was removed under reduced pressure to obtain pure **7g** in 73% yield (8.90 g, 40.2 mmol).

^{1}H NMR (C_6D_6, 500 MHz): δ 7.88 – 7.82 (m, 2H), 7.12 – 7.03 (m, 6H), 6.89 (d, *J* = 7.6 Hz, 2H), 6.07 (ddd, *J* = 22.3, 10.3, 5.1 Hz, 1H), 5.25 (dd, *J* = 17.1, 1.9 Hz, 1H), 5.05 (dd, *J* = 10.3, 1.9 Hz, 1H), 4.00 (d, *J* = 5.2 Hz, 2H) ppm.

^{13}C NMR (C_6D_6, 125 MHz): δ 168.03, 140.19, 137.23, 137.12, 129.99, 128.79, 128.54, 128.23, 128.14, 127.73, 114.68, 56.44 ppm.

HRMS (ESI-TOF) *m/z*: [M+H$^+$] calculated for $C_{16}H_{16}N$, 222.1283; found, 222.1284.



7h

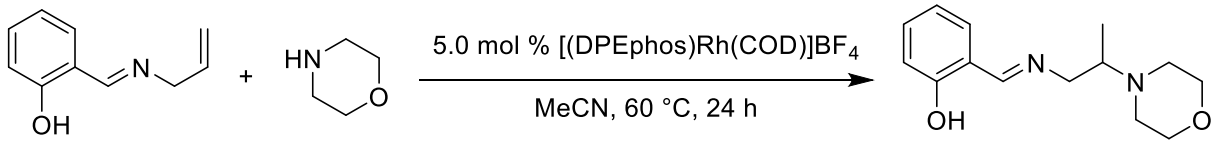
N-allylcyclohexanimine, 7h: Cyclohexanone (3.1 mL, 30 mmol, 1.0 equiv.) and allylamine (3.6 mL, 45 mmol, 1.5 equiv.) were added to a 20 mL scintillation vial equipped with stir bar and 4 Å mol sieves (200 mg). The vial was sealed with a Teflon cap and stirred overnight at room temperature. The solvent was decanted away from the mol. sieves, and the solid residue rinsed with CH_2Cl_2

(5 mL). The organic layers were filtered, and solvent was removed under reduced pressure. The crude mixture was purified by vacuum distillation (approximately 80 °C at 18 torr) with a Vigreux column to obtain pure **7h** in 63% yield (2.60 g, 18.9 mmol).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.94 (ddt, *J* = 17.1, 10.3, 5.7 Hz, 1H), 5.12 – 5.01 (m, 2H), 3.93 (d, *J* = 5.7 Hz, 2H), 2.34 – 2.16 (m, 4H), 1.74 – 1.53 (m, 6H) ppm.

^{13}C NMR (C_6D_6, 125 MHz): δ 171.66, 137.48, 114.00, 52.78, 39.94, 28.54, 27.82, 26.95, 26.14 ppm.

HRMS (ESI-TOF) *m/z*: [M+H$^+$] calculated for $C_9H_{16}N$, 138.1283; found, 138.1280.



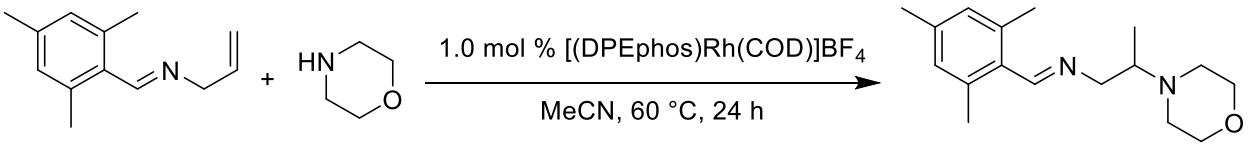
7a **1a** **8a**

(E)-2-(((2-morpholinopropyl)imino)methyl)phenol, 8a: [(DPEphos)Rh(COD)]BF_4 (9.5 mg, 0.011 mmol, 5.0 mol %), imine **7a** (36 mg, 0.22 mmol, 1.0 equiv.) and dry CH_3CN (60 μL) were added to an oven-dried 4 mL vial equipped with a stir bar in the glove box. To the reaction mixture was added morpholine, **1a** (98 μL, 1.1 mmol, 5.0 equiv.). The resulting solution was allowed to stir for 24 h at 60 °C. After 24 h, the reaction vial was cooled to room temperature followed by the addition of tetramethylsilane as an internal standard. The reaction mixture was further dissolved in $CDCl_3$ (0.5 mL). The NMR yield (98%) was determined by the analysis of the ^{1}H NMR of the crude reaction mixture. After the analysis, the NMR sample was poured into the original reaction vial and was rinsed with $CHCl_3$ (2 mL). This mixture was concentrated *in vacuo* to afford a crude oil. This was run through a short column of basic alumina (eluent 90% hexane : 10% ethyl acetate followed by 100% ethyl acetate). The resulting solution was concentrated *in vacuo* followed by drying under high vacuum (0.05 mm Hg) for 2 h at 40 °C to afford pure imine **8a** as a clear yellow oil in 90% yield (50 mg, 0.20 mmol). In one case where the imine was not pure, automated column chromatography was performed to using a 5.5 g cyano column received from Teledyne ISCO using hexane as the eluent.

^{1}H NMR (C_6D_6, 500 MHz): δ 7.78 (s, 1H), 7.13-7.06 (m, 2H), 6.97 (dd, *J* = 7.6, 1.6, 1H), 6.72 (td, *J* = 7.3, 1.3, 1H), 3.57-3.51 (m, 4H), 3.24 (ddd, *J* = 12.0, 5.8, 1.1, 1H), 3.01 (ddd, *J* = 11.9, 7.1, 1.1, 1H), 2.43 (sextet, *J* = 6.5, 1H), 2.24-2.17 (m, 4H), 0.78 (d, *J* = 6.7, 3H), -0.34 (s, 1H) ppm.

^{13}C NMR (C_6D_6, 125 MHz): δ 165.7, 162.1, 132.5, 131.4, 119.4, 118.6, 117.6, 67.5, 62.1, 60.0, 49.6, 13.3 ppm.

HRMS (EI-TOF) *m/z*: [M$^+$] calculated for $C_{14}H_{20}N_2O_2$, 248.1525; found, 248.1521.



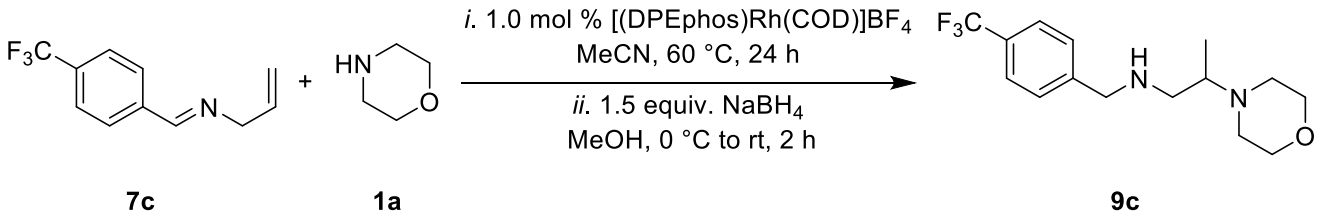
7b **1a** **8b**

(E)-1-mesityl-N-(2-morpholinopropyl)methanimine, 8b: [(DPEphos)Rh(COD)]BF_4 (8.4 mg, 0.010 mmol, 1.0 mol %), imine **7b** (180 mg, 0.96 mmol, 1.0 equiv.) and dry CH_3CN (260 μL) were added to an oven-dried 4 mL vial equipped with a stir bar in the glove box. To the reaction mixture was added morpholine, **1a** (430 μL, 5.0 mmol, 5.0 equiv.). The resulting solution was allowed to stir for 24 h at 60 °C. After 24 h, the reaction vial was cooled to room temperature followed by the addition of tetramethylsilane as an internal standard. The reaction mixture was further dissolved in $CDCl_3$ (0.5 mL). The NMR yield (98%) was determined by the analysis of the ^{1}H NMR of the crude reaction mixture. After the analysis, the NMR sample was poured into the original reaction vial and was rinsed with ethyl acetate (2 mL). This mixture was concentrated *in vacuo* to afford a crude oil. This was run through a short column of basic alumina (eluent 90% hexane : 10% ethyl acetate followed by 100% ethyl acetate). The resulting solution was concentrated *in vacuo* followed by drying under high vacuum (0.05 mm Hg) for 2 h at 60 °C to afford pure imine **8b** as a clear yellow oil in 90% yield (237 mg, 0.862 mmol).

^{1}H NMR (C_6D_6, 500 MHz): δ 8.43 (s, 1H), 6.74 (s, 2H), 2.79 (sextet, J = 6.2, 1H), 2.43 (s, 6H), 2.38 (t, J = 4.6, 4H), 2.11 (s, 3H), 1.02 (d, J = 6.7, 3H) ppm.

^{13}C NMR (C_6D_6, 125 MHz): δ 161.0, 138.6, 137.9, 131.6, 129.9, 67.7, 66.0, 60.5, 49.9, 21.21, 21.17, 13.8 ppm.

HRMS (ESI-TOF) *m/z*: [M+H$^+$] calculated for $C_{17}H_{27}N_2O$, 275.2123; found, 275.2120.



7c **1a** **9c**

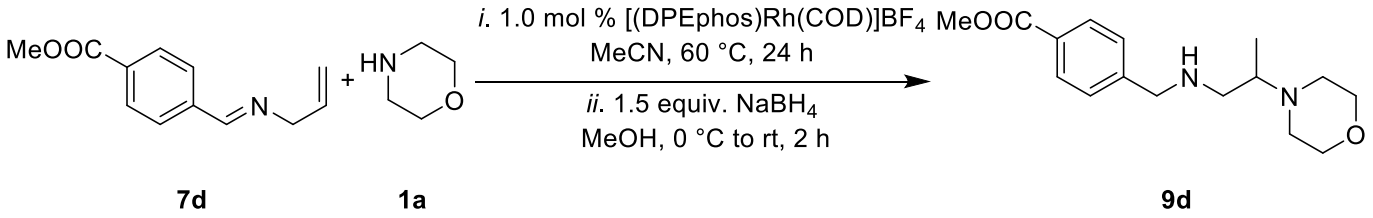
2-morpholino-N-(4-(trifluoromethyl)benzyl)propan-1-amine, 9c: [(DPEphos)Rh(COD)]BF_4 (5.7 mg, 0.0068 mmol, 1.0 mol %), imine **7c** (146 mg, 0.683 mmol, 1.00 equiv.) and dry CH_3CN (180 μL) were added to an oven-dried 4 mL vial equipped with a stir bar in the glove box. To the reaction mixture was added morpholine, **1a** (296 μL, 3.42 mmol, 5.00 equiv.). The resulting solution was allowed to stir for 24 h at 60 °C. After 24 h, the reaction vial was cooled to room temperature followed by the addition of tetrachlorobenzene as an internal standard. The reaction mixture was further dissolved in C_6D_6 (0.5 mL). The crude yield (86%) was determined by the analysis of the ^{1}H NMR. The NMR sample was poured into the reaction vial and was rinsed with MeOH (2 mL). Meanwhile, to an oven-dried 25 mL round bottom flask was added $NaBH_4$ (39 mg, 1.0 mmol, 1.5 equiv.) and MeOH (3 mL) and cooled to 0 °C. The solution of the aminoimine in MeOH was added dropwise, washing the vial with MeOH (2.5 mL). The reaction was brought to room temperature, stirred for 2 h, and then concentrated *in vacuo*. The residue was dissolved with $CHCl_3$ (20 mL) and washed with saturated $NaHCO_3$ (15 mL). The organic layer was separated and the aqueous layer was extracted with $CHCl_3$ (15 mL × 3). All organic layers were combined, dried over anhydrous $MgSO_4$ and filtered. The solution was concentrated *in vacuo* followed by drying under high vacuum (0.05 mm Hg) for 1 h to afford crude **9c** as a yellow oil. Purification of the crude diamine by silica gel chromatography (33 mm × 6 mm column, 1% NH_4OH : 99% $CHCl_3$ to 1% NH_4OH : 1% MeOH : 98% $CHCl_3$ v/v prepared by extracting saturated NH_4OH with $CHCl_3$, removing aqueous layer, and adding methanol) afforded pure diamine **9c** as a pale yellow oil in a 62% yield (127 mg, 0.420 mmol).

R_f = 0.50 (1:9 $NH_4OH/CHCl_3$).

^1H NMR (C_6D_6, 500 MHz): δ 7.40 (d, J = 8.0, 2H), 7.20 (d, J = 7.9, 2H), 3.56-3.47 (m, 6H), 2.52 (dq, J = 13.2, 6.6, 1H), 2.33 (dd, J = 11.6, 8.6, 1H), 2.24 (dd, J = 11.3, 4.4, 3H), 2.11 (ddd, J = 10.5, 6.5, 3.5, 2H), 1.85 (s, 1H), 0.72 (d, J = 6.6, 3H) ppm.

^{13}C NMR (C_6D_6, 125 MHz): δ 145.99, 129.18 (q, J^{CF} = 32.1), 128.46, 125.40 (q, J^{CF} = 3.8), 125.17 (q, J^{CF} = 271.5), 67.55, 59.09, 53.50, 51.92, 48.99, 11.74 ppm.

HRMS (ESI-TOF) *m/z*: [M+H$^+$] calculated for $C_{15}H_{22}N_2OF_3$, 303.1684; found, 303.1670.



7d **1a** **9d**

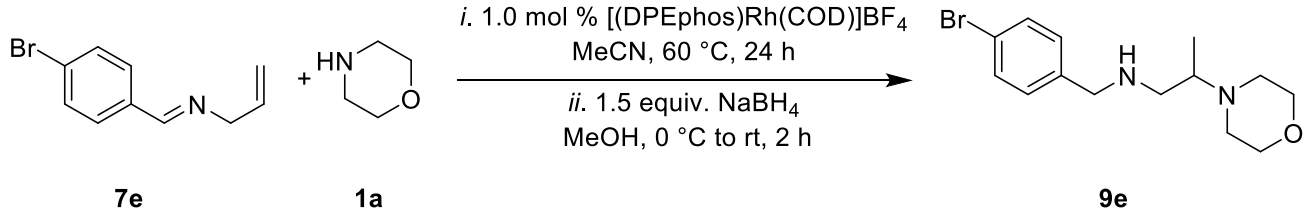
4-(((2-morpholinopropyl)amino)methyl)benzoate, 9d: [(DPEphos)Rh(COD)]BF_4 (8.1 mg, 0.0097 mmol, 1.0 mol %), imine **7d** (178 mg, 0.967 mmol, 1.00 equiv.) and dry CH_3CN (254 μL) were added to an oven-dried 4 mL vial equipped with a stir bar in the glove box. To the reaction mixture was added morpholine, **1a** (418 μL, 4.84 mmol, 5.00 equiv.). The resulting solution was allowed to stir for 24 h at 60 °C. After 24 h, the reaction vial was cooled to room temperature followed by the addition of tetramethylsilane as an internal standard. The reaction mixture was further dissolved in $CDCl_3$ (0.5 mL). The NMR yield (88%) was determined by the analysis of the ^1H NMR of the crude reaction mixture. After the analysis, the NMR sample was poured into the reaction vial and was rinsed with MeOH (2 mL). Meanwhile, to an oven-dried 25 mL round bottom flask was added $NaBH_4$ (55 mg, 1.5 mmol, 1.5 equiv) and MeOH (3 mL). The flask containing the reducing agent was brought to 0 °C and the solution of the aminoimine in MeOH was added dropwise, washing the vial with MeOH (2.5 mL). The reaction was brought to room temperature, stirred for 2 h, and then concentrated *in vacuo*. The residue was dissolved with $CHCl_3$ (20 mL) and was washed with saturated $NaHCO_3$ (15 mL). The organic layer was separated and the aqueous layer was extracted with $CHCl_3$ (15 mL × 3). All organic layers were combined, dried over anhydrous $MgSO_4$ and filtered. The solution was then concentrated *in vacuo* followed by drying under high vacuum (0.05 mm Hg) for 1 h to afford crude **9d** as a yellow oil. Purification of the crude diamine by silica gel chromatography (33 mm × 6 mm column, 2% NH_4OH : 98% $CHCl_3$ to 2% NH_4OH : 2% MeOH : 96% $CHCl_3$ v/v prepared by extracting saturated NH_4OH with $CHCl_3$, removing aqueous layer, and adding methanol) afforded pure diamine **9d** as a pale yellow oil in 52% yield (132 mg, 0.451 mmol).

R_f = 0.67 (1:9 $NH_4OH/CHCl_3$).

^1H NMR (C_6D_6, 500 MHz): δ 8.14 (d, J = 8.2, 2H), 7.29 (d, J = 8.1, 2H), 3.59 (s, 2H), 3.56-3.47 (m, 7H), 2.55-2.49 (m, 1H), 2.35 (dd, J = 11.6, 8.5, 1H), 2.23 (ddd, J = 18.7, 8.9, 4.1, 3H), 2.09 (ddd, J = 10.6, 6.5, 3.5, 2H), 1.92 (s, 1H), 0.71 (d, J = 6.6, 3H) ppm.

^{13}C NMR (C_6D_6, 125 MHz): δ 166.7, 147.0, 130.0, 129.5, 128.2, 67.5, 59.1, 53.7, 51.8, 51.6, 48.9, 11.8 ppm.

HRMS (ESI-TOF) *m/z*: [M+H$^+$] calculated for $C_{16}H_{25}N_2O_3$, 293.1865; found, 293.1858.



7e **1a** **9e**

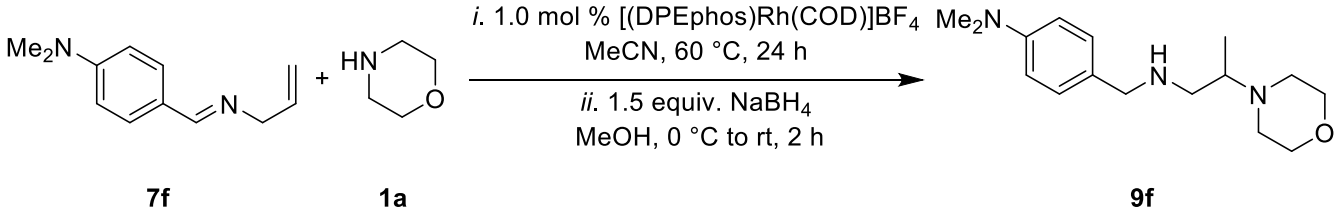
***N*-(4-bromobenzyl)-2-morpholinopropan-1-amine, 9e:** [(DPEphos)Rh(COD)]BF_4 (7.1 mg, 0.0085 mmol, 1.0 mol %), imine **7e** (191 mg, 0.850 mmol, 1.00 equiv.) and dry CH_3CN (223 μL) were added to an oven-dried 4 mL vial equipped with a stir bar in the glove box. To the reaction mixture was added morpholine, **1a** (370 μL, 4.25 mmol, 5.00 equiv.). The resulting solution was allowed to stir for 24 h at 60 °C. After 24 h, the reaction vial was cooled to room temperature followed by the addition of tetramethylsilane as an internal standard. The reaction mixture was further dissolved in $CDCl_3$ (0.5 mL). The NMR yield (78%) was determined by the analysis of the ^{1}H NMR of the crude reaction mixture. The NMR sample was poured into the reaction vial and was rinsed with MeOH (2 mL). Meanwhile, to an oven-dried 25 mL round bottom flask was added $NaBH_4$ (48 mg, 1.3 mmol, 1.5 equiv) and MeOH (3 mL). The flask containing the reducing agent was brought to 0 °C and the solution of the aminoimine in MeOH was added dropwise, washing the vial with MeOH (2.5 mL). The reaction was brought to room temperature and stirred for 2 h and then concentrated *in vacuo*. The residue was dissolved with $CHCl_3$ (20 mL) and washed with saturated $NaHCO_3$ (15 mL). The organic layer was separated and the aqueous layer was extracted with $CHCl_3$ (15 mL × 3). All organic layers were combined, dried over anhydrous $MgSO_4$ and filtered. The solution was concentrated *in vacuo* followed by drying under high vacuum (0.05 mm Hg) for 1 h to afford crude **9e** as a yellow oil. Purification of the crude diamine by silica gel chromatography (33 mm × 6 mm column, 3% NH_4OH : 97% $CHCl_3$ to 6% NH_4OH : 94% $CHCl_3$ v/v prepared by extracting saturated NH_4OH with $CHCl_3$, and removing aqueous layer) afforded pure diamine **9e** as a clear oil in 76% yield (202 mg, 0.646 mmol).

R_f = 0.50 (1:9 $NH_4OH/CHCl_3$).

^{1}H NMR (C_6D_6, 500 MHz): δ 7.30 (d, *J* = 8.3 Hz, 2H), 6.98 (d, *J* = 8.2 Hz, 2H), 3.52 (ddd, *J* = 14.9, 6.3, 3.1 Hz, 4H), 3.46 (s, 2H), 2.50 (ddd, *J* = 8.6, 6.6, 4.8 Hz, 1H), 2.31 (dd, *J* = 11.6, 8.5 Hz, 1H), 2.26-2.17 (m, 3H), 2.07 (ddd, *J* = 11.2, 6.2, 3.1 Hz, 2H), 1.63 (s, 1H), 0.70 (d, *J* = 6.6 Hz, 3H) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz): δ 139.65, 131.36, 129.72, 120.53, 67.41, 58.66, 53.17, 51.21, 48.39, 11.44 ppm.

HRMS (ESI-TOF) *m/z*: [M+H$^+$] calculated for $C_{14}H_{22}BrN_2$, 313.0916; found, 313.0908.



7f **1a** **9f**

***N*,*N*-dimethyl-4-(((2-morpholinopropyl)amino)methyl)aniline, 9f:** [(DPEphos)Rh(COD)]BF_4 (7.2 mg, 0.0086 mmol, 1.0 mol %), imine **7f** (160 mg, 0.850 mmol, 1.00 equiv.) and dry CH_3CN (223 μL) were added to an oven-dried 4 mL vial equipped with a stir bar in the glove box. To the reaction mixture was then added morpholine, **1a** (370 μL, 4.25 mmol, 5.00 equiv.).

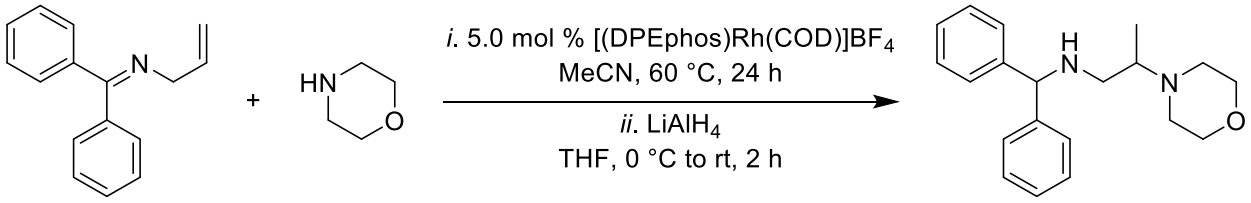
The resulting solution was allowed to stir for 24 h at 60 °C. After 24 h, the reaction vial was cooled to room temperature followed by the addition of tetramethylsilane as an internal standard. The reaction mixture was further dissolved in $CDCl_3$ (0.5 mL). The NMR yield (82%) was determined by the analysis of the ^1H NMR of the crude reaction mixture. The NMR sample was poured into the reaction vial and was rinsed with MeOH (2 mL). Meanwhile, to an oven-dried 25 mL round bottom flask was added $NaBH_4$ (48 mg, 1.3 mmol, 1.5 equiv.) and MeOH (3 mL) and cooled to 0 °C. The aminoimine solution was added dropwise to the $NaBH_4$ solution. The vial was washed with MeOH (2.5 mL) and transferred to the flask. The reaction was brought to room temperature and stirred for 2 h. The resulting mixture was concentrated *in vacuo*. The residue was dissolved with $CHCl_3$ (20 mL) and washed with saturated $NaHCO_3$ (15 mL). The organic layer was separated and the aqueous layer was extracted with $CHCl_3$ (15 mL × 3). All organic layers were combined, dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo* followed by drying under high vacuum (0.05 mm Hg) for 1 h to afford the crude diamine **9f** as a yellow oil. Purification of the crude diamine by silica gel chromatography (33 mm × 6 mm column, 3% NH_4OH : 97% $CHCl_3$ to 6% NH_4OH : 94% $CHCl_3$ v/v prepared by extracting saturated NH_4OH with $CHCl_3$ and removing aqueous layer) afforded pure diamine **9f** as a clear oil in 74% yield (174 mg, 0.629 mmol).

R_f = 0.33 (1:9 $NH_4OH/CHCl_3$).

^1H NMR (C_6D_6, 500 MHz): δ 7.34 (d, *J* = 8.6 Hz, 2H), 6.66 (d, *J* = 8.6 Hz, 2H), 3.79 (d, *J* = 12.9 Hz, 1H), 3.74 (d, *J* = 13.0 Hz, 1H), 3.53 (dtd, *J* = 13.9, 10.8, 5.4 Hz, 4H), 2.66-2.55 (m, 1H), 2.54-2.50 (m, 1H), 2.53 (s, 6H), 2.42 (dd, *J* = 11.5, 4.8 Hz, 1H), 2.29-2.21 (m, 2H), 2.15-2.07 (m, 2H), 1.80 (s, 1H), 0.75 (d, *J* = 6.6 Hz, 3H) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz): δ 149.70, 128.96, 128.61, 112.61, 67.45, 58.62, 53.27, 51.03, 48.32, 40.75, 11.41 ppm.

HRMS (ESI-TOF) *m/z*: [M+H$^+$] calculated for $C_{16}H_{28}N_3O$, 278.2232; found, 278.2234.



7g **1a** **9g**

***N*-benzhydryl-2-morpholinopropan-1-amine, 9g:** [(DPEphos)Rh(COD)]BF_4 (42 mg, 0.050 mmol, 5.0 mol %), imine **7g** (221 mg, 1.00 mmol, 1.00 equiv.) and dry CH_3CN (350 µL) were added to an oven-dried 4 mL vial equipped with a stir bar in the glove box. To the reaction mixture was added morpholine, **1a** (216 µL, 2.50 mmol, 2.50 equiv.). The resulting solution was allowed to stir for 24 h at 60 °C. After 24 h, the reaction vial was cooled to room temperature followed by the addition of diphenylmethane as an internal standard. The reaction mixture was further dissolved in C_6D_6 (0.5 mL). The crude yield (60%) was determined by the analysis of the ^1H NMR. Solvent was then removed under reduced pressure. The residual oil sample was rinsed into the reaction vial with THF (5 mL). Meanwhile, to an oven-dried 25 mL Schlenk flask under N_2 was added $LiAlH_4$ (76 mg, 2.0 mmol, 2.0 equiv) and THF (5 mL) and cooled to 0 °C. The solution of the aminoimine in THF was added dropwise, *via* syringe through septa. The reaction was brought to room temperature, stirred for 2 h, and then quenched with 1 M NaOH (5 mL). The residue was dissolved with $CHCl_3$ (20 mL) and washed with 1 M NaOH (15 mL). The organic layer was separated and the aqueous layer was extracted with $CHCl_3$ (15

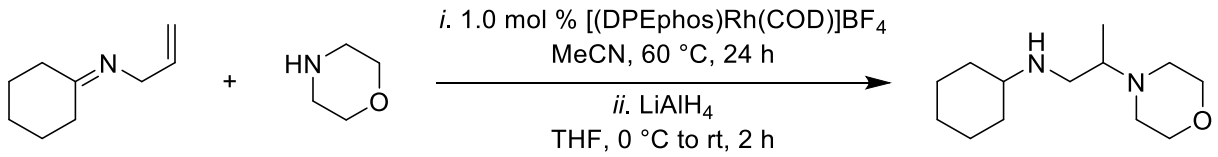
mL × 3). All organic layers were combined, dried over anhydrous $MgSO_4$ and filtered. The solution was concentrated *in vacuo* followed by drying under high vacuum (0.05 mm Hg) for 1 h to afford crude **9g** as a yellow oil. Purification of the crude diamine by silica gel chromatography (125 mL silica, 1% NH_4OH : 99% $CHCl_3$ v/v prepared by extracting saturated NH_4OH with $CHCl_3$ and removing aqueous layer) afforded pure diamine **9g** as a pale yellow oil in 40% yield (137 mg, 0.600 mmol).

R_f = 0.70 (1:9 $MeOH/CH_2Cl_2$).

^1H NMR (C_6D_6, 500 MHz): δ 7.51 (d, *J* = 7.0 Hz, 2H), 7.39 (d, *J* = 7.2 Hz, 2H), 7.16 (t, *J* = 7.7 Hz, 2H), 7.13 – 7.10 (m, 2H), 7.03 (dt, *J* = 14.8, 7.3 Hz, 2H), 4.72 (s, 1H), 3.44 (dddd, *J* = 19.9, 10.5, 6.9, 3.1 Hz, 4H), 2.56 (h, *J* = 6.7 Hz, 1H), 2.41 (d, *J* = 6.7 Hz, 2H), 2.17 (ddd, *J* = 10.3, 4.8, 2.0 Hz, 2H), 2.03 (ddd, *J* = 11.3, 6.1, 3.2 Hz, 2H), 1.33 (br s, 1H), 0.65 (d, *J* = 6.6 Hz, 3H) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz): δ 144.64, 144.33, 128.71, 128.64, 127.59 (2C, coincident peaks), 127.22, 127.12, 67.71, 67.69, 59.00, 50.87, 48.66, 11.85 ppm.

HRMS (ESI-TOF) *m/z*: [M+H$^+$] calculated for $C_{20}H_{27}N_2O$, 311.2123; found, 311.2123.



7h **1a** **9h**

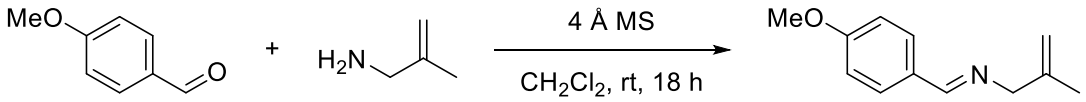
***N*-(2-morpholinopropyl)cyclohexanamine, 9h:** [(DPEphos)Rh(COD)]BF_4 (13 mg, 0.015 mmol, 1.0 mol %), imine **7h** (259 μL, 1.50 mmol, 1.00 equiv.) and dry CH_3CN (350 μL) were added to an oven-dried 4 mL vial equipped with a stir bar in the glove box. To the reaction mixture was added morpholine, **1a** (194 μL, 2.25 mmol, 1.50 equiv.). The resulting solution was allowed to stir for 24 h at 60 °C. After 24 h, the reaction vial was cooled to room temperature followed by the addition of diphenylmethane as an internal standard. The reaction mixture was further dissolved in C_6D_6 (0.5 mL). The crude yield (53%) was determined by the analysis of the ^1H NMR. Solvent was then removed under reduced pressure. The residual oil sample was rinsed into the reaction vial with THF (5 mL). Meanwhile, to an oven-dried 25 mL Schlenk flask was added $LiAlH_4$ (114 mg, 3.00 mmol, 2.00 equiv.) and THF (5 mL) and cooled to 0 °C. The solution of the aminoimine in THF was added dropwise, *via* syringe through septa. The reaction was brought to room temperature, stirred for 2 h, and then quenched with 5 mL 1 M NaOH. The residue was dissolved with $CHCl_3$ (20 mL) and washed with 1 M NaOH (15 mL). The organic layer was separated and the aqueous layer was extracted with $CHCl_3$ (15 mL × 3). All organic layers were combined, dried over anhydrous $MgSO_4$ and filtered. The solution was concentrated *in vacuo* followed by drying under high vacuum (0.05 mm Hg) for 1 h to afford crude **9h** as a yellow oil. Purification of the crude diamine by silica gel chromatography (125 mL silica, 1% saturated NH_4OH : 98% $CHCl_3$ v/v prepared by extracting saturated NH_4OH with $CHCl_3$ and then removing aqueous layer) afforded pure diamine **9h** as a pale yellow oil in 44% yield (137 mg, 0.600 mmol).

R_f = 0.37 (1:9 $MeOH/CH_2Cl_2$).

^{1}H NMR (C_6D_6, 400 MHz): δ 3.51 (dddd, *J* = 13.9, 10.8, 7.0, 3.9 Hz, 4H), 2.52 (h, *J* = 6.6 Hz, 1H), 2.39 (d, *J* = 6.6 Hz, 2H), 2.33 – 2.20 (m, 2H), 2.08 (dddd, *J* = 9.6, 6.1, 3.6, 1.0 Hz, 2H), 1.86 – 1.69 (m, 3H), 1.63 (dq, *J* = 11.3, 4.2 Hz, 2H), 1.48 (dd, *J* = 11.9, 4.5 Hz, 1H), 1.31 – 0.95 (m, 5H), 0.73 (d, *J* = 6.5 Hz, 3H) ppm.

^{13}C NMR (C_6D_6, 125 MHz): δ 171.66, 137.48, 114.00, 52.78, 39.94, 28.54, 27.82, 26.95, 26.14 ppm.

HRMS (ESI-TOF) *m/z*: [M+H$^+$] calculated for $C_{13}H_{27}N_2O$, 227.2123; found 227.2122.



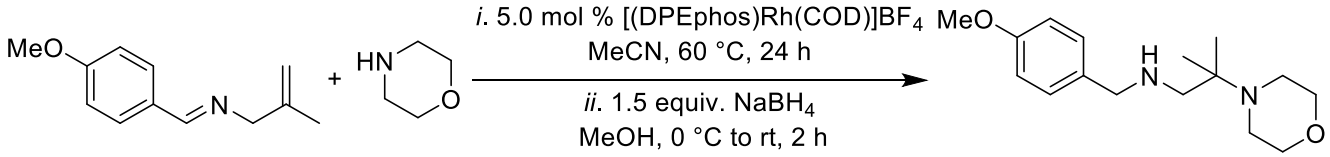
10a

(E)-1-(4-methoxyphenyl)-N-(2-methylallyl)methanimine, 10a: *p*-anisaldehyde (1.88 g, 13.8 mmol, 1.00 equiv.), 4 Å MS (4.00 g, beads) and dry CH_2Cl_2 (8 mL) were added to a 25 mL oven-dried round bottom flask, equipped with a stir bar under an N_2 atmosphere. After stirring for 10 min, 2-methylallylamine (1.08 mL, 15.2 mmol, 1.10 equiv.) was added. The reaction mixture was stirred at room temperature for 18 h and was filtered through Celite while rinsing with diethylether (100 mL). The filtrate was washed with water (50 mL × 3) and brine (50 mL × 1). The organic layer was dried with anhydrous $MgSO_4$, filtered, and concentrated by rotary evaporation to give imine **10a** as a pale orange, viscous oil in 80% yield (2.09 g, 11.0 mmol). The resulting imine was used without any further purification.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.13 (s, 1H), 7.67 (d, *J* = 8.8, 2H), 6.87 (d, *J* = 8.8, 2H), 4.89 (d, *J* = 0.7, 1H), 4.84 (d, *J* = 0.7, 1H), 4.07 (s, 2H), 3.73 (s, 3H), 1.78 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz): δ 161.4, 160.9, 143.6, 129.5, 129.0, 113.7, 111.0, 66.8, 55.0, 21.0 ppm.

HRMS (ESI-TOF) *m/z*: [M+H$^+$] calculated for $C_{12}H_{16}NO$, 190.1232; found, 190.1231.



10a **1a** **11a**

(E)-1-(4-methoxyphenyl)-N-(2-methyl-2-morpholinopropyl)methanimine, 11a: [(DPEphos)Rh(COD)]BF_4 (12 mg, 0.015 mmol, 5.0 mol %), imine **10a** (54.5 mg, 0.288 mmol, 1.00 equiv.) and dry CH_3CN (77 μL) were added to an oven-dried 4 mL vial equipped with a stir bar in the glove box. To the reaction mixture was added morpholine, **1a** (126 μL, 1.46 mmol, 5.00 equiv.). The resulting solution was allowed to stir for 24 h at 60 °C. After 24 h, the reaction vial was cooled to room temperature followed by the addition of tetramethylsilane as an internal standard. The reaction mixture was further dissolved in $CDCl_3$ (0.5 mL). The NMR yield (78%) was determined by the analysis of the ^{1}H NMR of the crude reaction mixture. After the analysis, the NMR sample was poured into the reaction vial and was rinsed with MeOH (0.5 mL). Meanwhile, to an oven-dried 10 mL round bottom

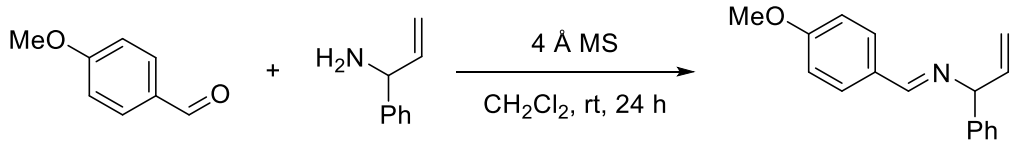
flask was added $NaBH_4$ (17 mg, 0.44 mmol, 1.5 equiv.) and MeOH (0.5 mL). The flask containing the reducing agent was brought to 0 °C and the solution of the aminoimine in MeOH was added dropwise, washing the vial with MeOH (0.5 mL). The reaction was brought to room temperature, stirred for 2 h, and then concentrated *in vacuo*. The residue was dissolved with $CHCl_3$ (10 mL) and was washed with saturated $NaHCO_3$ (10 mL). The organic layer was separated and the aqueous layer was extracted with $CHCl_3$ (15 mL × 3). All organic layers were combined, dried over anhydrous $MgSO_4$ and filtered. The solution was then concentrated *in vacuo* followed by drying under high vacuum (0.05 mm Hg) for 1 h to afford crude **11a** as a yellow oil. Purification of the crude diamine by silica gel chromatography (33 mm × 6 mm column, 2% NH_4OH : 98% $CHCl_3$ to 2% NH_4OH : 2% MeOH : 96% $CHCl_3$ v/v prepared by extracting saturated NH_4OH with $CHCl_3$, removing aqueous layer, and adding methanol) afforded pure diamine **11a** as a clear oil in 58% yield (46 mg, 0.17 mmol).

R_f = 0.53 (1:9 $NH_4OH/CHCl_3$).

^{1}H NMR (C_6D_6, 500 MHz): δ 7.25 (d, *J* = 8.6, 2H), 6.82 (d, *J* = 8.6, 2H), 3.67 (s, 2H), 3.54 (t, *J* = 4.6, 4H), 3.33 (s, 3H), 2.35 (s, 2H), 2.19 (t, *J* = 4.6, 4H), 0.90 (s, 6H) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz): δ 159.1, 133.4, 129.4, 113.9, 67.8, 56.7, 56.0, 54.6, 53.7, 45.9, 21.7 ppm.

HRMS (ESI-TOF) *m/z*: [M+H$^+$] calculated for $C_{16}H_{27}N_2O_2$, 279.2073; found, 279.2075.



12a

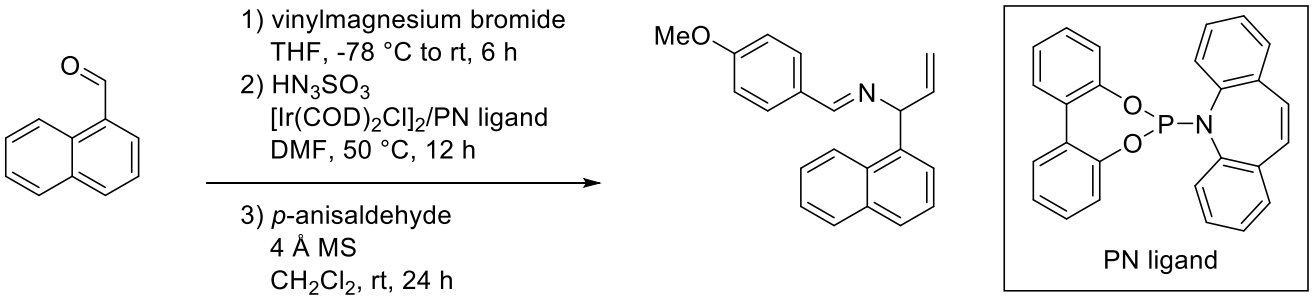
(E)-1-(4-methoxyphenyl)-N-(1-phenylallyl)methanimine, 12a: 1-phenylprop-2-en-1-amine[3] (0.87 g, 6.5 mmol, 1.0 equiv.), 4 Å MS (3.3 g, beads) and dry CH_2Cl_2 (6.5 mL) were added to a 25 mL oven-dried round bottom flask, equipped with a stir bar under an N_2 atmosphere. After stirring for 10 min, *p*-anisaldehyde (0.84 g, 6.2 mmol, 0.94 equiv.) was added. The reaction mixture was stirred at room temperature for 24 h and was filtered through Celite while rinsing with diethylether (100 mL). The filtrate was washed with water (50 mL × 3) and brine (50 mL × 1). The organic layer was dried with anhydrous $MgSO_4$, filtered, and concentrated by rotary evaporation to give imine **12a** as a pale orange solid in 48% yield (0.74 g, 2.9 mmol). The resulting imine was used without any further purification.

m.p. 55–57 °C.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.33 (s, 1H), 7.78 (d, *J* = 8.7, 2H), 7.44 (d, *J* = 7.8, 2H), 7.37 (t, *J* = 7.6, 2H), 7.27 (dd, *J* = 9.5, 5.1, 1H), 6.94 (d, *J* = 8.7, 2H), 6.21 (ddd, *J* = 17.0, 10.3, 6.6, 1H), 5.28 (dt, *J* = 17.1, 1.3, 1H), 5.20 (dd, *J* = 10.2, 1.1, 1H), 4.97 (d, *J* = 6.6, 1H), 3.85 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz): δ 161.8, 160.4, 142.8, 140.7, 130.1, 129.4, 128.6, 127.4, 127.1, 115.2, 114.0, 76.8, 55.5 ppm.

HRMS (ESI-TOF) *m/z*: [M+H$^+$] calculated for $C_{17}H_{18}NO$, 252.1388; found, 252.1381.



12b

1-(naphthalen-1-yl)prop-2-en-1-ol: To an 250 mL flame dried round bottom flask, charged with stir bar, was added 1-naphthaldehyde (1.6 g, 10 mmol, 1.0 equiv.) and THF (50 mL). The flask was placed under nitrogen and cooled to -78 °C. Vinylmagnesium bromide (20 mL, 20 mmol, 2.0 equiv., 1 M in THF) was added dropwise to the flask. The flask was warmed to room temperature and stirred for 6 h. The reaction mixture was quenched with the addition of saturated NH_4Cl (50 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (50 mL × 3). All organic layers were combined, dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo* followed by drying under high vacuum (10 mm Hg) for 1 h to afford the crude alcohol as yellow viscous oil. Purification by silica-gel flash chromatography (33 mm × 6 mm column, 10% ethyl acetate : 90% hexanes to 20% ethyl acetate: 80% hexanes as eluent) afforded the pure alcohol as a yellow viscous oil in 67% yield (1.2 g, 6.7 mmol).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.19 (d, J = 8.4, 1H), 7.91 – 7.84 (m, 1H), 7.82 (d, J = 8.3, 1H), 7.66 – 7.61 (m, 1H), 7.57 – 7.44 (m, 3H), 6.26 (ddd, J = 17.3, 10.4, 5.4 Hz, 1H), 5.99 – 5.91 (m, 1H), 5.46 (dt, J = 17.1, 1.5 Hz, 1H), 5.29 (dt, J = 10.4, 1.4 Hz, 1H), 2.07 (d, J = 4.1 Hz, 1H) ppm.

1-(naphthalen-1-yl)prop-2-en-1-amine: [4] To a flame dried 25 mL Schlenk flask, charged with stir bar, was added $[Ir(COD)_2Cl]_2$ (54 mg, 0.080 mmol, 1.5 mol %) and PN ligand (66 mg, 0.016 mmol, 3.0 mol %) in a glove box. The Schlenk flask was capped with a rubber septum, removed from glove box, and placed under nitrogen. Dry DMF (10 mL) was added via syringe through the rubber septum. The reaction was then allowed to stir for 15 min. The allylic alcohol (1.0 g, 5.4 mmol, 1.0 equiv.) was added via syringe through the rubber septum. Subsequently, under positive flow of nitrogen, sulfamic acid (520 mg, 5.4 mmol, 1.0 equiv.) was added and a new rubber septum was replaced on the flask. The reaction mixture was stirred at 50 °C for 12 h. DMF was removed under reduced pressure and the viscous residue was dissolved in CH_2Cl_2 (50 mL) and saturated $NaHCO_3$ (50 mL) and stirred for 15 min. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (50 mL × 3). The organic layers were combined, dried with $MgSO_4$, filtered, and concentrated *in vacuo* to afford the crude amine as dark red oil. The reaction mixture was further dissolved in $CHCl_3$ (10 mL). To the reaction mixture was then added 6M HCl dropwise until a pH ~1 was obtained. The organic layer was separated. The aqueous layer was washed with $CHCl_3$ (20 mL x 3) and was then basified using NaOH (2 M) until a pH ~12 was obtained. The aqueous layer was extracted with $CHCl_3$ (60 mL × 3). All organic layers were then combined, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo* followed by drying under high vacuum (10 mm Hg) for 1 h to afford the crude amine as a yellow viscous oil in 13% yield (130 mg, 0.70 mmol).

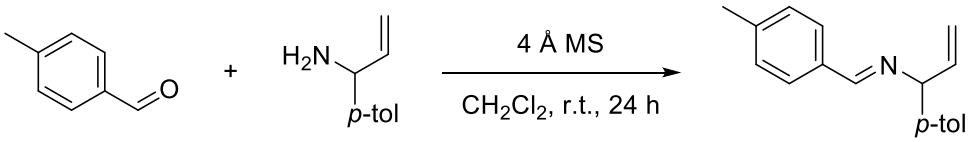
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.20 (d, J = 8.4 Hz, 1H), 7.90 – 7.85 (m, 1H), 7.78 (d, J = 8.3 Hz, 1H), 7.60 – 7.44 (m, 4H), 6.29 – 6.16 (m, 1H), 5.39 – 5.32 (m, 2H), 5.24 – 5.20 (m, 1H), 1.66 (s, 2H) ppm.

(*E*)-1-(4-methoxyphenyl)-*N*-(1-(naphthalen-1-yl)allyl)methanimine, 12b: 1-(naphthalen-1-yl)prop-2-en-1-amine (110 mg, 0.60 mmol, 1.0 equiv), 4 Å MS (0.5 g, beads) and dry CH_2Cl_2 (1 mL) were added to an oven-dried 20 mL scintillation vial equipped with a stir bar. After stirring for 10 min, *p*-anisaldehyde (77 μL, 0.63 mmol, 1.1 equiv.) was added. The reaction mixture was sealed with a Teflon cap and stirred at room temperature for 24 h. It was filtered through Celite, rinsing with CH_2Cl_2 (10 mL × 3). The organic layer was dried over $MgSO_4$, filtered, and concentrated *in vacuo* to afford imine **12b** as a pale yellow, viscous oil in 80% yield (150 mg, 0.48 mmol). The resulting imine was used without any further purification.

^{1}H NMR (C_6D_6, 500 MHz): δ 8.44 (d, *J* = 7.3 Hz, 1H), 8.14 (s, 1H), 7.91 (d, *J* = 7.2 Hz, 1H), 7.72 (d, *J* = 8.7 Hz, 2H), 7.69 (d, *J* = 8.3 Hz, 1H), 7.61 (d, *J* = 8.2 Hz, 1H), 7.38 (ddd, *J* = 8.3, 6.8, 1.4 Hz, 1H), 7.34 (dd, *J* = 8.2, 7.1 Hz, 1H), 7.28 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 6.72 (d, *J* = 8.7 Hz, 2H), 6.33 (ddd, *J* = 17.2, 10.3, 5.5 Hz, 1H), 5.61 (d, *J* = 5.5 Hz, 1H), 5.33 (dt, *J* = 17.2, 1.6 Hz, 1H), 5.10 (dt, *J* = 10.2, 1.6 Hz, 1H), 3.20 (s, 3H) ppm.

^{13}C NMR (C_6D_6, 125 MHz): δ 162.77, 160.91, 141.68, 139.92, 135.35, 132.32, 130.93, 130.64, 129.77, 128.75, 126.65, 126.56, 126.55, 126.26, 125.66, 115.82, 114.81, 74.14, 55.39 ppm.

HRMS (ESI-TOF) *m/z*: [M+H$^+$] calculated for $C_{21}H_{20}NO$, 302.1545; found, 302.1541.



12c

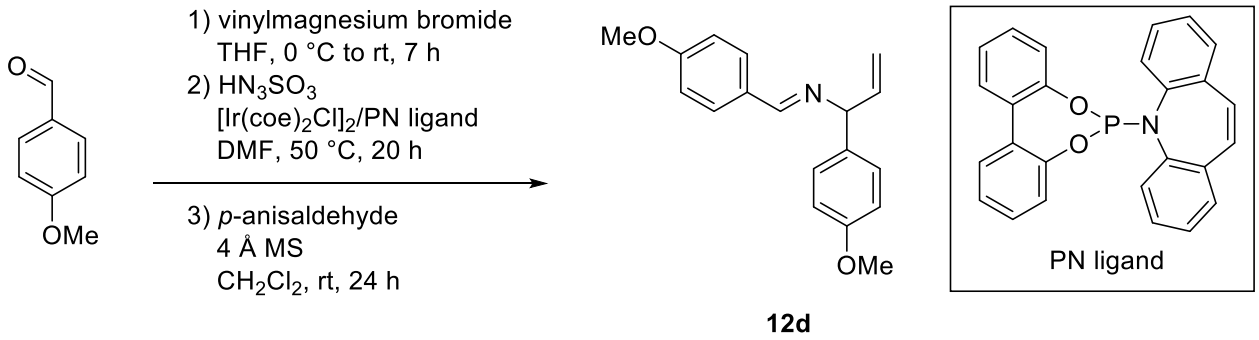
(E)-1-p-tolyl-N-(1-(p-tolyl)allyl)methanimine, 12c: 1-(*p*-tolyl)prop-2-en-1-amine[3] (0.38 g, 2.6 mmol, 1.1 equiv.), 4 Å MS (0.75 g, beads) and dry CH_2Cl_2 (10 mL) were added to a 25 mL oven-dried round bottom flask, equipped with a stir bar under an N_2 atmosphere. After stirring for 10 min, *p*-tolylbenzaldehyde (0.30 g, 2.5 mmol, 1.0 equiv.) was added. The reaction mixture was stirred at room temperature for 24 h and was filtered through Celite while rinsing with diethylether (100 mL). The filtrate was washed with water (50 mL × 3) and brine (50 mL × 1). The organic layer was dried with anhydrous $MgSO_4$, filtered, and concentrated by rotary evaporation to give imine **12c** as a pale orange solid in 60% yield (0.37 g, 1.5 mmol). The resulting imine was used without any further purification.

m.p. 57–59 °C.

^{1}H NMR (C_6D_6, 500 MHz): δ 8.12 (s, 1H), 7.71 (d, *J* = 7.9, 2H), 7.44 (d, *J* = 7.9, 2H), 7.05 (d, *J* = 7.8, 2H), 6.94 (d, *J* = 7.8, 2H), 6.26 (ddd, *J* = 17.0, 10.4, 6.5, 1H), 5.27 (dd, *J* = 17.1, 1.3, 1H), 5.05 (dd, *J* = 10.2, 1.1, 1H), 4.86 (d, *J* = 6.3, 1H), 2.12 (s, 3H), 2.02 (s, 3H) ppm.

^{13}C NMR (C_6D_6, 125 MHz): δ 160.5, 145.7, 141.6, 140.9, 140.5, 136.6, 134.7, 129.49, 129.46, 128.8, 114.5, 77.2, 21.4, 21.1 ppm.

HRMS (ESI-TOF) *m/z*: [M+H$^+$] calculated for $C_{18}H_{20}N$, 250.1596; found, 250.1595.



12d

1-(4-methoxyphenyl)prop-2-en-1-ol: To a flame dried 500 mL roundbottom flask charged with stir bar was added *p*-anisaldehyde (4.45 mL, 36.7 mmol, 1.00 equiv.) in dry THF (150 mL). The flask was placed under nitrogen and cooled to 0 °C. Vinylmagnesium bromide (55 mL, 55 mmol, 1.5 equiv., 1M solution) was added dropwise to the flask. The round bottom was warmed to room temperature and stirred for 7 hours. The reaction contents were quenched with the addition of saturated NH_4OH (100 mL). The organic layer was removed and the aqueous layer was extracted with Et_2O (100 mL × 3 mL). The organic layers were then combined and washed with water (100 mL × 3) and brine (100 mL × 1), dried with $MgSO_4$, filtered, and concentrated under reduced pressure. Purification by silica gel column chromatography (30% ethyl acetate: 70% hexanes) gave the product as a clear liquid in 41% yield (2.5 g, 15 mmol).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.29 (d, J = 8.4, 2H), 6.89 (d, J = 8.8, 2H), 6.05 (ddd, J = 17.1, 10.3, 5.9, 1H), 5.33 (dd, J = 17.1, 1.5, 1H), 5.20-5.15 (m, 2H), 3.80 (s, 3H), 1.97 (s, 1H) ppm.

1-(4-methoxyphenyl)prop-2-en-1-amine: [4] To an oven dried 50 mL Schlenk flask charged with stir bar was added $[Ir(coe)_2Cl]_2$ (100 mg, 0.11 mmol, 1.5 mol %), PN ligand (91 mg, 0.22 mmol, 3.0 mol %) in a glove box. The Schlenk flask was capped with a rubber septum, removed from glove box, and placed under nitrogen. Dry DMF (15 mL) was added via syringe through the septum. The Schlenk flask contents were stirred for 15 minutes. The alcohol (1.20 g, 6.81 mmol, 1.00 equiv.) was then added via syringe through the septum. The septum was removed, sulfamic acid (714 mg, 7.35 mmol, 1.10 equiv.) was added under positive flow of nitrogen, and the septum was replaced on the flask. The contents were stirred 20 h at 50 °C. DMF was removed under reduced pressure and the viscous residue was quenched with $NaHCO_3$ (30 mL) and CH_2Cl_2 (20 mL) was added. This was stirred for 30 minutes at 50 °C. The organic layer was removed and the aqueous layer extracted with CH_2Cl_2 (20 mL × 3). The organic layers were combined, dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was isolated via automated column chromatography (24 g, MeOH : 1% NH_4OH / $CHCl_3$ = 0 : 100 to 5 : 95 as gradient) to obtain the product in 25% yield (0.281 g, 1.72 mmol).

^{1}H NMR (C_6D_6, 500 MHz): δ 7.22 (d, J = 8.7, 2H), 6.80 (d, J = 8.7, 2H), 5.92 (ddd, J = 16.9, 10.4, 6.3, 1H), 5.14 (dt, J = 17.1, 1.6, 1H), 4.95 (dt, J = 10.2, 1.5, 1H), 4.27 (d, J = 6.1, 1H), 3.34 (d, J = 0.9, 3H), 1.15 (s, 2H) ppm.

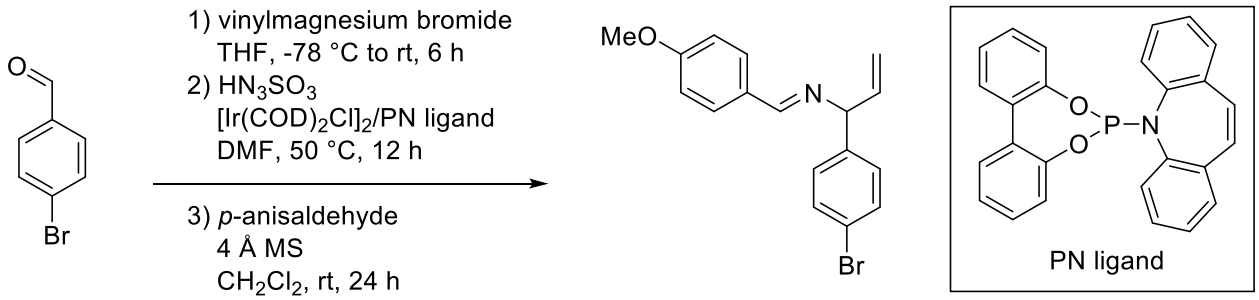
(E)-1-(4-methoxyphenyl)-N-(1-(4-methoxyphenyl)allyl)methanimine, 12d: *p*-Anisaldehyde (0.14 g, 1.0 mmol, 1.0 equiv.), 4 Å MS (1.0 g, beads) and dry CH_2Cl_2 (1 mL) were added to a 4 mL oven-dried screw-capped scintillation vial, equipped with a stir bar under an N_2 atmosphere. After stirring for 10 min, 1-(4-methoxyphenyl)prop-2-en-1-amine (0.20 mL, 1.2 mmol, 1.2 equiv.) was added. The reaction mixture was stirred at room temperature for 24 h and was filtered through Celite while rinsing with diethylether (100 mL). The filtrate was washed with water (50 mL × 3) and brine (50 mL × 1). The organic layer was dried with

anhydrous $MgSO_4$, filtered, and concentrated by rotary evaporation to give imine **12d** as a pale orange, viscous oil in 36% yield (0.10 g, 0.36 mmol). The resulting imine was used without any further purification.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.31 (s, 1H), 7.78 (d, *J* = 8.8 Hz, 2H), 7.36 (d, *J* = 8.8 Hz, 2H), 6.93 (dd, *J* = 13.8, 8.7 Hz, 4H), 6.21 (ddd, *J* = 17.0, 10.3, 6.6 Hz, 1H), 5.27 (dt, *J* = 17.1, 1.3 Hz, 2H), 5.19 (dt, *J* = 10.2, 1.2 Hz, 1H), 4.94 (d, *J* = 6.4 Hz, 1H), 3.84 (s, 3H), 3.81 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz): 161.6, 159.9, 158.5, 140.6, 134.7, 129.8, 129.2, 128.3, 114.8, 113.81, 113.75, 75.9, 55.24, 55.17 ppm.

HRMS (ESI-TOF) *m/z*: [M+H$^+$] calculated for $C_{18}H_{20}NO_2$, 282.1494; found, 282.1492.



12e

1-(4-bromophenyl)prop-2-en-1-ol:[4] To an 500 mL flame dried round bottom flask, charged with stir bar, was added 4-bromobenzaldehyde (3.7 g, 20 mmol, 1.0 equiv.) and THF (100 mL). The flask was placed under nitrogen and cooled to –78 °C. Vinylmagnesium bromide (40 mL, 40 mmol, 2.0 equiv., 1 M in THF) was added dropwise to the flask. Thereafter, the flask was warmed to room temperature and stirred for 6 h. The reaction mixture was quenched with the addition of saturated NH_4Cl (75 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (75 mL × 3). All organic layers were combined, dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo* followed by drying under high vacuum (10 mm Hg) for 1 h to afford the crude alcohol as yellow oil. Purification by silica-gel flash chromatography (33 mm × 6 mm column, 10% ethyl acetate : 90% hexanes to 20% ethyl acetate : 80% hexanes as eluent) afforded pure alcohol as a yellow oil in 90% yield (3.8 g, 18 mmol).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.48 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 6.00 (ddd, *J* = 17.1, 10.3, 6.1 Hz, 1H), 5.34 (dt, *J* = 17.1, 1.3 Hz, 1H), 5.21 (dt, *J* = 10.3, 1.3 Hz, 1H), 5.19 – 5.15 (m, 1H), 1.96 (d, *J* = 3.6 Hz, 1H) ppm.

1-(4-bromophenyl)prop-2-en-1-amine:[4] To a flame dried 50 mL Schlenk flask, charged with stir bar, was added $[Ir(COD)_2Cl]_2$ (100 mg, 0.15 mmol, 1.5 mol %) and PN ligand (120 mg, 0.30 mmol, 3.0 mol %) in a glove box. The Schlenk flask was capped with a rubber septum, removed from glove box, and placed under nitrogen. Dry DMF (20 mL) was added via syringe through the rubber septum. The reaction was then allowed to stir for 15 min. The allylic alcohol (2.13 g, 10.0 mmol, 1.00 equiv.) was then added via syringe through the rubber septum. Subsequently, under positive flow of nitrogen, sulfamic acid (971 mg, 10.0 mmol, 1.00 equiv.) was added and a new rubber septum was replaced on the flask. The reaction mixture was stirred at 50 °C for 12 h. DMF was removed under reduced pressure and the viscous residue was dissolved in CH_2Cl_2 (75 mL) and saturated $NaHCO_3$ (75 mL) and stirred for 15 min. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (80 mL × 3). The organic layers were combined, dried with $MgSO_4$, filtered, and concentrated *in vacuo* to afford the crude amine as dark red oil. The reaction mixture

was further dissolved in $CHCl_3$ (10 mL). To the reaction mixture was then added 6M HCl dropwise until a pH ~1 was obtained. The organic layer was separated. The aqueous layer was washed with $CHCl_3$ (20 mL × 3) and was then basified using NaOH (2 M) until a pH ~12 was obtained. The aqueous layer was extracted with $CHCl_3$ (60 mL × 3). All organic layers were then combined, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo* followed by drying under high vacuum (10 mm Hg) for 1 h to afford the crude amine as a yellow viscous oil in 40% yield (850 mg, 4.0 mmol).

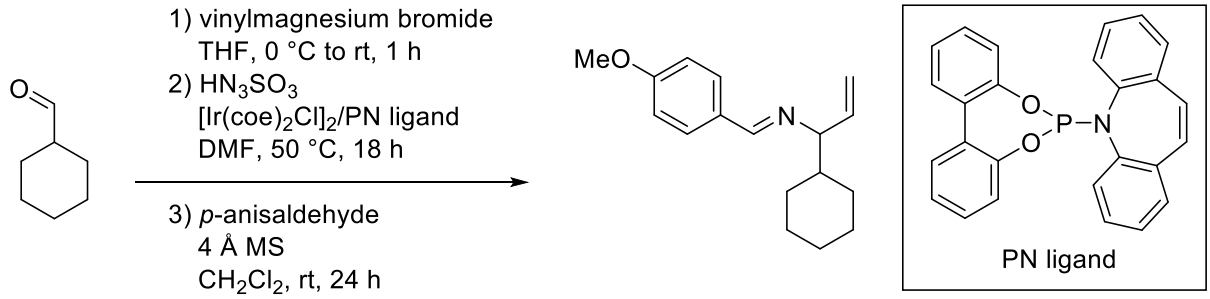
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 5.96 (ddd, *J* = 17.2, 10.2, 6.2 Hz, 1H), 5.23 (dt, *J* = 17.1, 1.4 Hz, 1H), 5.12 (dt, *J* = 10.3, 1.3 Hz, 1H), 4.49 (d, *J* = 6.2 Hz, 1H), 1.63 (s, 2H) ppm.

(*E*)-*N*-(1-(4-bromophenyl)allyl)-1-(4-methoxyphenyl)methanimine, 12e: Amine (768 mg, 3.62 mmol, 1.00 equiv), 4 Å MS (1.0 g, beads) and dry CH_2Cl_2 (3 mL) were added to an oven-dried 20 mL scintillation vial equipped with a stir bar. After stirring for 10 min, *p*-anisaldehyde (463 μL, 3.80 mmol, 1.05 equiv) was added. The reaction mixture was sealed with a Teflon cap and stirred at room temperature for 24 h. It was filtered through Celite rinsing with CH_2Cl_2 (10 mL × 3). The organic layer was then dried over $MgSO_4$, filtered, and concentrated *in vacuo* to afford imine **12e** as a pale yellow viscous oil in 85% yield (1.06 g, 3.08 mmol). The resulting imine was used without any further purification.

^{1}H NMR (C_6D_6, 500 MHz): δ 8.00 (s, 1H), 7.70 (d, *J* = 8.7 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 6.74 (d, *J* = 8.7 Hz, 2H), 6.07 (ddd, *J* = 16.9, 10.2, 6.4 Hz, 1H), 5.16 (dt, *J* = 17.1, 1.5 Hz, 1H), 5.01 (dt, *J* = 10.2, 1.3 Hz, 1H), 4.64 (d, *J* = 6.4 Hz, 1H), 3.22 (s, 3H) ppm.

^{13}C NMR (C_6D_6, 125 MHz): δ 162.89, 160.98, 143.04, 141.48, 132.36, 130.90, 130.35, 130.16, 121.78, 115.53, 114.87, 76.94, 55.44 ppm.

HRMS (ESI-TOF) *m/z*: [M+H$^+$] calculated for $C_{17}H_{17}OBrN$, 330.0494; found, 330.0487.



12f

1-cyclohexylprop-2-en-1-ol: To an oven dried 100 mL 2-neck flask charged with stir bar was added cyclohexanecarboxaldehyde (3.0 g, 27 mmol, 1.0 equiv.). The flask was placed under nitrogen and cooled to 0 °C. THF (36 mL) and vinylmagnesium bromide (32 mL, 32 mmol, 1.2 equiv., 1M solution) were added, the round bottom was warmed to room temperature and, after 1 hour, reaction contents were quenched with the addition of 60 mL saturated NH_4OH. The organic layer was removed and the aqueous layer was extracted with Et_2O (45 mL x 4). The organic layers were then combined, dried with $MgSO_4$, filtered, and concentrated under reduced pressure. Purification by automated silica gel chromatography (hexanes : ethyl acetate gradient) gave the product as a clear liquid in 57% yield (2.1 g, 15 mmol).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.83 (ddd, *J* = 17.1, 10.4, 6.6 Hz, 1H), 5.23 – 5.08 (m, 2H), 3.82 (s, 1H), 1.88 – 1.57 (m, 5H), 1.48 (s, 1H), 1.38 (dddt, *J* = 15.0, 9.5, 6.4, 3.3 Hz, 1H), 1.28 – 1.04 (m, 3H), 0.97 (qdd, *J* = 12.2, 6.4, 3.3 Hz, 2H) ppm.

1-cyclohexylprop-2-en-1-amine:[4] To an oven dried 50 mL Schlenk flask charged with stir bar was added $[Ir(coe)_2Cl]_2$ (87 mg, 0.097 mmol, 1.5 mol %), PN ligand (79 mg, 0.19 mmol, 3.0 mol %) in a glove box. The Schlenk flask was capped with a rubber septum, removed from glove box, and placed under nitrogen. Dry DMF (12 mL) was added via syringe through the septum. The Schlenk flask contents were stirred for 15 minutes. The alcohol (976 μL, 6.47 mmol, 1.00 equiv.) was then added via syringe through the septum. The septum was removed, sulfamic acid (628 mg, 6.47 mmol, 1.00 equiv.) was added under positive flow of nitrogen, and the septum was replaced on the flask. The contents were stirred for 18 h at 50 °C. DMF was removed under reduced pressure and the viscous residue was dissolved in $NaHCO_3$ (50 mL) and CH_2Cl_2 (50 mL). The organic layer was removed and the aqueous layer extracted with CH_2Cl_2 (75 mL x 3). The organic layers were combined, dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The crude amine was purified via column chromatography (300 mL silica, 2% NH_4OH : 98% $CHCl_3$ to 4% NH_4OH : 96% $CHCl_3$ v/v prepared by extracting saturated NH_4OH with $CHCl_3$ and removing aqueous layer) to obtain the amine in 64% yield (0.533 g, 3.83 mmol).

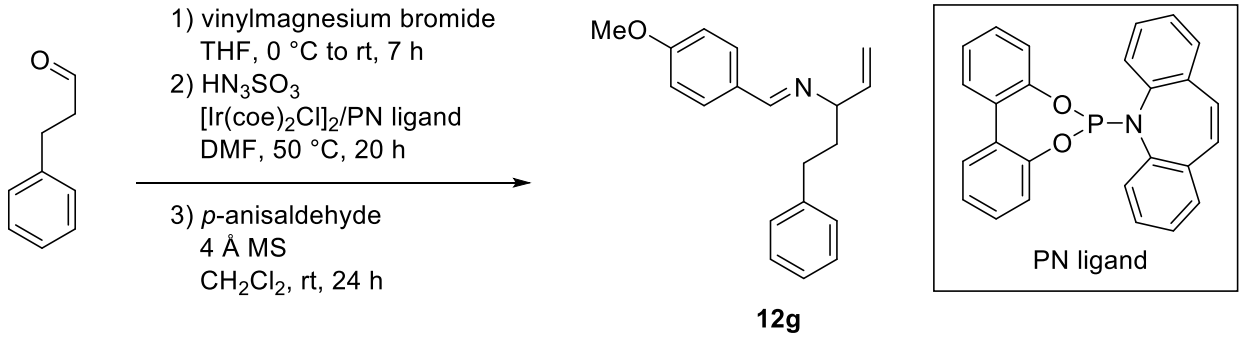
^{1}H NMR (C_6D_6, 500 MHz): δ 5.67 (ddd, *J* = 17.2, 10.3, 6.9 Hz, 1H), 5.04 – 4.91 (m, 2H), 2.87 (t, *J* = 6.4 Hz, 1H), 1.77 – 1.50 (m, 5H), 1.19 – 0.99 (m, 4H), 0.89 (dt, *J* = 20.9, 9.8 Hz, 2H), 0.64 (s, 2H) ppm.

***(E)-N*-(1-cyclohexylallyl)-1-(4-methoxyphenyl)methanimine, 12f**: *p*-Anisaldehyde (310 μL, 2.55 mmol, 1.00 equiv.), 4 Å MS (1.0 g, beads) and dry CH_2Cl_2 (10 mL) were added to a 20 mL scintillation vial with a stir bar and 1-cyclohexylprop-2-en-1-amine (533 mg, 3.83 mmol, 1.50 equiv.). The reaction mixture was sealed with Teflon cap and stirred at room temperature for 24 h. It was then filtered through Celite, rinsing with CH_2Cl_2 (30 mL). The filtrate was washed with water (15 mL × 2) and brine (15 mL × 1). The organic layer was dried with $MgSO_4$, filtered, and concentrated under reduced pressure to give imine **12f** as a beige solid in quantitative yield. The imine was used without further purification.

^{1}H NMR (C_6D_6, 500 MHz): δ 8.03 (s, 1H), 7.72 (d, *J* = 8.7 Hz, 2H), 6.72 (d, *J* = 8.7 Hz, 2H), 6.12 (ddd, *J* = 17.4, 10.3, 7.2 Hz, 1H), 5.32 – 4.96 (m, 2H), 3.38 (t, *J* = 7.0 Hz, 1H), 3.18 (s, 3H), 2.04 – 1.76 (m, 2H), 1.80 – 1.46 (m, 4H), 1.33 – 0.89 (m, 5H) ppm.

^{13}C NMR (C_6D_6, 125 MHz): δ 161.82, 158.79, 140.43, 130.10, 129.96, 114.69, 114.07, 80.14, 54.67, 43.31, 30.21, 29.92, 26.88, 26.64, 26.60 ppm.

HRMS (ESI-TOF) *m/z*: [M+H$^+$] calculated for $C_{17}H_{24}NO$ 258.1858, found: 258.1855.



12g

5-phenylpent-1-en-3-ol: To an oven dried 100 mL 2-neck flask charged with stir bar was added 3-phenylpropanal (8.0 mL, 61 mmol, 1.0 equiv.). The flask was placed under nitrogen and cooled to 0 °C. THF (60 mL) and vinylmagnesium bromide (67 mL, 67 mmol, 1.2 equiv., 1M solution) were added, the round bottom was warmed to room temperature and, after 1 hour, reaction contents were quenched with the addition of saturated NH_4OH (75 mL). The organic layer was removed and the aqueous layer was extracted with CH_2Cl_2 (75 mL x 3). The organic layers were then combined, dried with $MgSO_4$, filtered, and concentrated under reduced pressure. Purification by flash chromatography (11% ethyl acetate : 89% hexane to 20% ethyl acetate : 80% hexane as eluent) gave the product as a clear liquid in 70% yield (6.90 g, 42.5 mmol).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.39 (dd, *J* = 8.0, 6.9 Hz, 2H), 7.33 – 7.26 (m, 3H), 6.00 (ddd, *J* = 17.2, 10.4, 6.2 Hz, 1H), 5.34 (dt, *J* = 17.2, 1.4 Hz, 1H), 5.23 (dt, *J* = 10.4, 1.4 Hz, 1H), 4.21 (d, *J* = 6.4 Hz, 1H), 2.91 – 2.75 (m, 3H), 2.05 – 1.88 (m, 2H) ppm.

5-phenylpent-1-en-3-amine: [4] To an oven dried 50 mL Schlenk flask charged with stir bar was added $[Ir(coe)_2Cl]_2$ (190 mg, 0.21 mmol, 1.5 mol %), PN ligand (170 mg, 0.42 mmol, 3.0 mol %) in a glove box. The Schlenk flask was capped with a rubber septum and removed from glove box, placed under nitrogen. Dry DMF (24 mL) was added via syringe through the septum. The Schlenk flask contents were stirred for 15 minutes. The alcohol (2.31 mL, 14.0 mmol, 1.00 equiv.) was then added via syringe through the septum. The septum was removed, sulfamic acid (1.36 g, 14.0 mmol, 1.00 equiv.) was added under positive flow of nitrogen, and the septum was replaced on the flask. The contents were stirred 18 h at 50 °C. DMF was removed under reduced pressure and the viscous residue was dissolved in saturated $NaHCO_3$ (50 mL) and CH_2Cl_2 (50 mL). The organic layer was removed and the aqueous layer extracted with CH_2Cl_2 (125 mL x 3). The organic layers were combined, dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The crude amine was purified via column chromatography (300 mL silica, 2% NH_4OH : 98% $CHCl_3$ to 4% NH_4OH : 96% $CHCl_3$ v/v prepared by extracting saturated NH_4OH with $CHCl_3$ and removing aqueous layer) to obtain the product in 64% yield (1.44 g, 8.93 mmol).

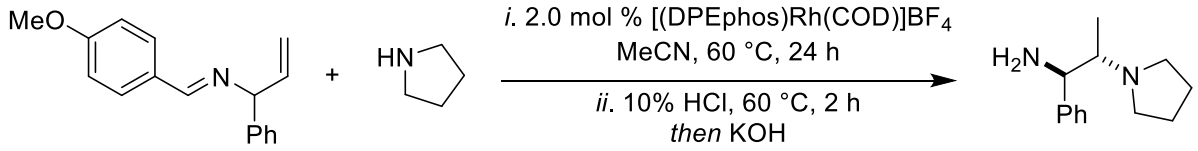
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.30 (t, *J* = 7.5 Hz, 2H), 7.23 – 7.15 (m, 3H), 5.84 (ddd, *J* = 17.2, 10.4, 6.9 Hz, 1H), 5.15 (d, *J* = 17.2 Hz, 1H), 5.07 (d, *J* = 10.3 Hz, 1H), 3.33 (q, *J* = 6.7 Hz, 1H), 2.68 (t, *J* = 8.5 Hz, 2H), 1.81 – 1.72 (m, 2H), 1.21 (s, 2H) ppm.

***(E)*-1-(4-methoxyphenyl)-*N*-(5-phenylpent-1-en-3-yl)methanimine, 12g**: *p*-Anisaldehyde (834 μL, 6.86 mmol, 1.0 equiv.), 4 Å MS (1.0 g, beads) and dry CH_2Cl_2 (5 mL) were added to a 20 mL scintillation vial with a stir bar and 5-phenylpent-1-en-3-amine (1.44 g, 8.92 mmol, 1.3 equiv.). The reaction mixture was sealed with Teflon cap and stirred at room temperature for 24 h. It was then filtered through Celite, rinsing with CH_2Cl_2 (30 mL). The filtrate was washed with water (15 mL × 2) and brine (15 mL × 1). The organic layer was dried with $MgSO_4$, filtered, and concentrated under reduced pressure to give imine **12g** as a beige solid in quantitative yield. The imine was used without further purification.

^{1}H NMR (C_6D_6, 500 MHz): δ 7.99 (s, 1H), 7.71 (d, *J* = 8.7 Hz, 2H), 7.13 (t, *J* = 7.4 Hz, 2H), 7.05 (d, *J* = 7.6 Hz, 3H), 6.72 (d, *J* = 8.7 Hz, 2H), 6.05 (ddd, *J* = 17.1, 10.3, 6.6 Hz, 1H), 5.14 (d, *J* = 17.2 Hz, 1H), 5.01 (d, *J* = 10.4 Hz, 1H), 3.66 (q, *J* = 6.3 Hz, 1H), 3.21 (s, 3H), 2.69 – 2.51 (m, 2H), 2.15 – 1.93 (m, 2H) ppm.

^{13}C NMR (C_6D_6, 125 MHz): δ 161.94, 159.36, 142.32, 141.38, 131.69, 130.01, 128.72, 128.53, 125.92, 114.28, 114.13, 73.17, 54.73, 38.41, 32.69 ppm.

HRMS (ESI-TOF) *m/z*: [M+H$^+$] calculated for $C_{19}H_{21}NO$, 280.1701; found: 280.1696.



12a **1e** **13a**

1-phenyl-2-(pyrrolidin-1-yl)propan-1-amine, 13a: [(DPEphos)Rh(COD)]BF_4 (3.4 mg, 0.0040 mmol, 2.0 mol %), imine **12a** (50 mg, 0.20 mmol, 1.0 equiv.) and dry CH_3CN (53 μL) were added to an oven-dried 4 mL vial equipped with a stir bar in the glove box. To the reaction mixture was then added pyrrolidine, **1e** (17 μL, 0.20 mmol, 1.0 equiv.). The resulting solution was allowed to stir for 24 h at 60 °C. After 24 h, the reaction vial was cooled to room temperature followed by the addition of diphenylmethane as an internal standard. The reaction mixture was further dissolved in C_6D_6 (0.5 mL). The NMR yield (60%) was determined by the analysis of the ^{1}H NMR of the crude reaction mixture. After the analysis, the NMR sample was poured into the reaction vial and was rinsed with $CHCl_3$ (2 mL). The solution was concentrated *in vacuo* followed by the addition of 10% aqueous HCl (2 mL). The vial was capped and stirred at 60 °C for 2 h. The solution was transferred to a separatory funnel. The reaction vial was rinsed with 10% aqueous HCl (1 mL) followed by $CHCl_3$ (4 mL). The aqueous layer was washed with $CHCl_3$ (10 mL × 3) and was then basified using KOH pellets until a pH ~12 was obtained. The aqueous layer was extracted with $CHCl_3$ (50 mL × 3). All organic layers were then combined, dried over anhydrous $MgSO_4$ and filtered. The solution was concentrated *in vacuo* followed by drying under high vacuum (10 mm Hg) for 0.5 h to afford the crude diamine **13a** as yellow oil. Purification of the crude diamine by automated silica gel chromatography (4 g, MeOH : 1% NH_4OH / $CHCl_3$ = 0 : 100 to 5 : 95 as gradient afforded pure diamine **13a** as a yellow oil in 50% yield (20 mg, 0.10 mmol).

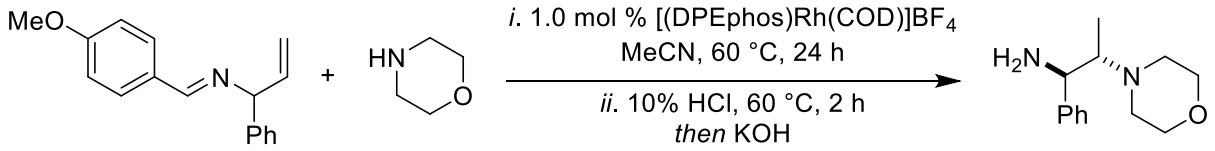
R_f = 0.17 (1:9 MeOH/CH_2Cl_2).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.37 (d, J = 7.2 Hz, 2H), 7.32 (t, J = 7.6 Hz, 2H), 7.22 (t, J = 7.2 Hz, 1H), 4.39 (d, J = 3.1 Hz, 1H), 2.72 – 2.61 (m, 4H), 2.38 (qd, J = 6.5, 3.1 Hz, 1H), 1.85 – 1.78 (m, 4H), 1.69 (s, 2H), 0.85 (d, J = 6.5 Hz, 3H) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz): δ 143.79, 128.00, 126.80, 126.44, 66.22, 56.44, 52.32, 23.47, 11.78 ppm.

HRMS (ESI-TOF) *m/z*: [M+H$^+$] calculated for $C_{13}H_{21}N_2$, 205.1705; found, 205.1702.

These spectral data match those previously reported for this compound.[5]



12a **1a** **14a**

2-morpholino-1-phenylpropan-1-amine, 14a: [(DPEphos)Rh(COD)]BF_4 (3.0 mg, 0.0036 mmol, 1.0 mol %), imine **12a** (100 mg, 0.36 mmol, 1.0 equiv.) and dry CH_3CN (95 μL) were added to an oven-dried 4 mL vial equipped with a stir bar in the glove

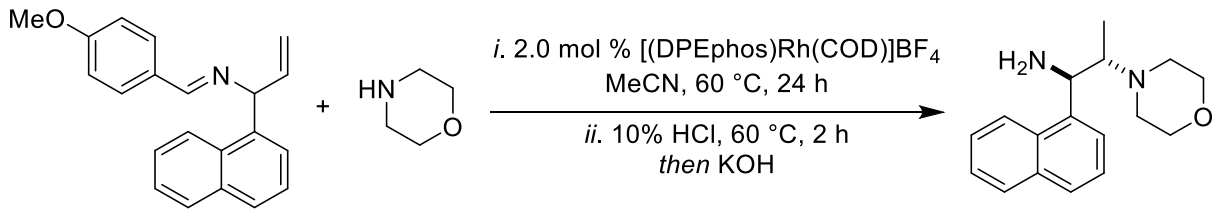
box. To the reaction mixture was added morpholine, **1a** (155 μL, 1.79 mmol, 5.0 equiv.). The resulting solution was allowed to stir for 24 h at 60 °C. After 24 h, the reaction vial was cooled to room temperature followed by the addition of tetramethylsilane as an internal standard. The reaction mixture was further dissolved in $CDCl_3$ (0.5 mL). The NMR yield (93%) was determined by the analysis of the ^1H NMR of the crude reaction mixture. After the analysis, the NMR sample was poured into the reaction vial and was rinsed with $CHCl_3$ (2 mL). The solution was then concentrated *in vacuo* followed by the addition of 10% aqueous HCl (2 mL) while stirring at room temperature. This was capped and heated to 60 °C for 2 h. The solution was then transferred to a separatory funnel. The reaction vial was washed with 10% aqueous HCl (1 mL) followed by $CHCl_3$ (4 mL). The aqueous layer was washed with $CHCl_3$ (10 mL × 3) and was then basified using KOH pellets until a pH ~12 was obtained. The aqueous layer was washed with $CHCl_3$ (50 mL × 3). All organic layers were then combined, dried over anhydrous $MgSO_4$ and filtered. The solution was concentrated *in vacuo* followed by drying under high vacuum (0.05 mm Hg) for 1 h to afford the crude diamine **14a** as yellow oil. Purification of the crude diamine by automated silica gel chromatography (4 g, MeOH : 1% NH_4OH / $CHCl_3$ = 0 : 100 to 10 : 90 as gradient) afforded pure diamine **14a** as a clear oil in 79% yield (61 mg, 0.28 mmol).

R_f = 0.48 (1:9 $NH_4OH/CHCl_3$).

^1H NMR (C_6D_6, 500 MHz): δ 7.32 (d, *J* = 7.4, 2H), 7.23 (t, *J* = 7.6, 2H), 7.13 (t, *J* = 7.3, 1H), 3.94 (d, *J* = 4.4, 1H), 3.52 (t, *J* = 4.4, 4H), 2.30-2.26 (m, 1H), 2.23 (t, *J* = 4.5, 4H), 1.34 (s, 2H), 0.78 (d, *J* = 6.7, 3H) ppm.

^{13}C NMR (C_6D_6, 125 MHz): δ 165.7, 162.1, 132.5, 131.4, 119.4, 118.6, 117.6, 67.5, 62.1, 60.0, 49.6, 13.3 ppm.

HRMS (ESI-TOF) *m/z*: [M+H$^+$] calculated for $C_{13}H_{21}N_2O$, 221.1654; found, 221.1651.



12b **1a** **14b**

2-morpholino-1-(naphthalen-1-yl)propan-1-amine, 14b: [(DPEphos)Rh(COD)]BF_4 (3.4 mg, 0.0040 mmol, 2.0 mol %), imine **12b** (60 mg, 0.20 mmol, 1.0 equiv.) and dry CH_3CN (53 μL) were added to an oven-dried 4 mL vial equipped with a stir bar in the glove box. To the reaction mixture was then added morpholine, **1a** (88 μL, 1.0 mmol, 5.0 equiv.). The resulting solution was allowed to stir for 24 h at 60 °C. After 24 h, the reaction vial was cooled to room temperature followed by the addition of diphenylmethane as an internal standard. The reaction mixture was further dissolved in C_6D_6 (0.5 mL). The NMR yield (78%) was determined by the analysis of the ^1H NMR of the crude reaction mixture. After the analysis, the NMR sample was poured into the reaction vial and was rinsed with $CHCl_3$ (2 mL). The solution was then concentrated *in vacuo* followed by the addition of 10% aqueous HCl (2 mL). The vial was capped and stirred at 60 °C for 2 h. The solution was then transferred to a separatory funnel. The reaction vial was rinsed with 10% aqueous HCl (1 mL) followed by $CHCl_3$ (4 mL). The aqueous layer was washed with $CHCl_3$ (10 mL × 3) and was then basified using KOH pellets until a pH ~12 was obtained. The aqueous layer was extracted with $CHCl_3$ (50 mL × 3). All organic layers were then combined, dried over anhydrous $MgSO_4$ and filtered. The solution was concentrated *in vacuo*

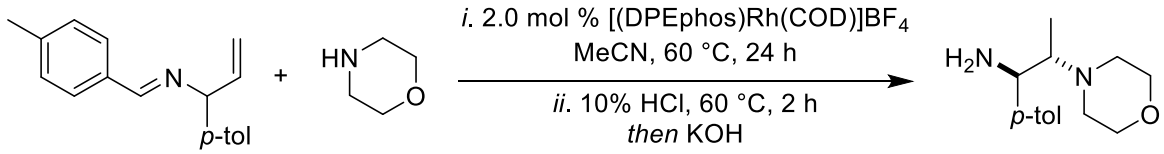
followed by drying under high vacuum (10 mm Hg) for 0.5 h to afford the pure diamine **14b** as an off white solid in 78% yield (42 mg, 0.16 mmol).

m.p. 103–105 °C.

^{1}H NMR (C_6D_6, 500 MHz): δ 8.06 (d, *J* = 8.5 Hz, 1H), 7.99 (d, *J* = 7.2 Hz, 1H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.62 (d, *J* = 8.1 Hz, 1H), 7.39 (ddd, *J* = 8.7, 7.0, 1.7 Hz, 2H), 7.30 (ddd, *J* = 8.0, 6.8, 1.1 Hz, 1H), 4.93 (d, *J* = 3.5 Hz, 1H), 3.54 (q, *J* = 4.2 Hz, 4H), 2.60 (qd, *J* = 6.6, 3.5 Hz, 1H), 2.34 (t, *J* = 4.5 Hz, 4H), 1.17 (s, 2H), 0.77 (d, *J* = 6.6 Hz, 3H) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz) δ 141.21, 135.12, 132.33, 130.07, 128.11, 126.40, 126.35, 126.03, 125.73, 124.01, 68.17, 64.20, 51.95, 51.87, 10.84 ppm.

HRMS (ESI-TOF) *m/z*: [M+H$^+$] calculated for $C_{17}H_{23}N_2O$, 271.1810; found, 270.1803.



12c **1a** **14c**

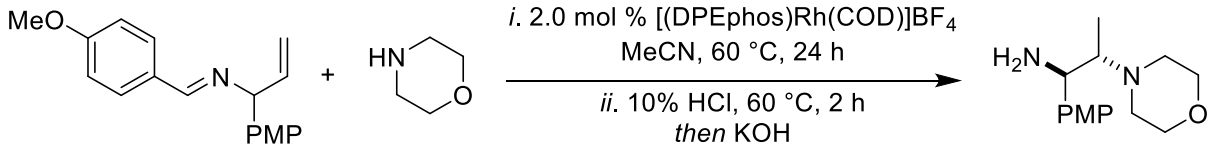
2-morpholino-1-(p-tolyl)propan-1-amine, 14c: [(DPEphos)Rh(COD)]BF_4 (5.5 mg, 0.0066 mmol, 2.0 mol %), imine **12c** (82 mg, 0.33 mmol, 1.0 equiv.) and dry CH_3CN (87 μL) were added to an oven-dried 4 mL vial equipped with a stir bar in the glove box. To the reaction mixture was added morpholine, **1a** (140 μL, 1.6 mmol, 5.0 equiv.). The resulting solution was allowed to stir for 24 h at 60 °C. After 24 h, the reaction vial was cooled to room temperature followed by the addition of tetramethylsilane as an internal standard. The reaction mixture was further dissolved in $CDCl_3$ (0.5 mL). The NMR yield (90%) was then determined by the analysis of the ^{1}H NMR of the crude reaction mixture. After the analysis, the NMR sample was poured into the reaction vial and was rinsed with $CHCl_3$ (2 mL). The solution was then concentrated *in vacuo* followed by the addition of 10% aqueous HCl (2 mL) while stirring at room temperature. This was capped and heated to 60 °C for 2 h. The solution was then transferred to a separatory funnel. The reaction vial was washed with 10% aqueous HCl (1 mL) followed by $CHCl_3$ (4 mL). The aqueous layer was washed with $CHCl_3$ (10 mL × 3) and was then basified using KOH pellets until a pH ~12 was obtained. The aqueous layer was washed with $CHCl_3$ (50 mL × 3). All organic layers were then combined, dried over anhydrous $MgSO_4$ and filtered. The solution was then concentrated *in vacuo* followed by drying under high vacuum (0.05 mm Hg) for 1 h to afford the crude diamine **14c** as yellow oil. Purification of the crude diamine by automated silica gel chromatography (4 g, MeOH : 1% NH_4OH / $CHCl_3$ = 0 : 100 to 18 : 82 as gradient) afforded pure diamine **14c** as a clear oil in 67% yield (52 mg, 0.22 mmol).

R_f = 0.40 (1:9 $NH_4OH/CHCl_3$).

^{1}H NMR (C_6D_6, 500MHz): δ 7.27 (d, *J* = 8.0, 2H), 7.08 (d, *J* = 7.8, 2H), 3.96 (d, *J* = 4.3, 1H), 3.54 (dd, *J* = 5.0, 2.9, 4H), 2.30 (qd, *J* = 6.7, 4.4, 1H), 2.25 (t, *J* = 4.6, 4H), 2.19 (s, 3H), 1.22 (s, 2H), 0.82 (d, *J* = 6.7, 3H) ppm.

^{13}C NMR (C_6D_6, 125 MHz): δ 142.3, 136.0, 129.0, 127.4, 67.6, 66.0, 55.6, 51.3, 21.1, 10.1 ppm.

HRMS (ESI-TOF) *m/z*: [M+H$^+$] calculated for $C_{14}H_{23}N_2O$, 235.1810; found, 235.1812.



12d **1a** **14d**

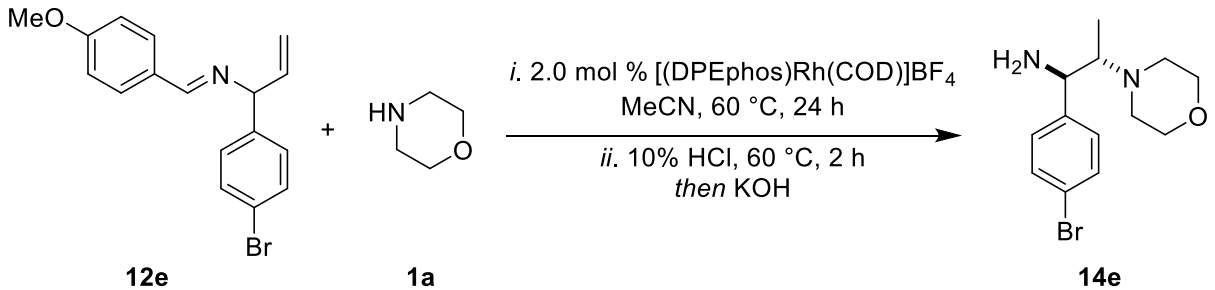
1-(4-methoxyphenyl)-2-morpholinopropan-1-amine, 14d: [(DPEphos)Rh(COD)]BF_4 (4.5 mg, 0.0054 mmol, 2.0 mol %), imine **12d** (77 mg, 0.27 mmol, 1.0 equiv.) and dry CH_3CN (72 μL) were added to an oven-dried 4 mL vial equipped with a stir bar in the glove box. To the reaction mixture was added morpholine, **1a** (120 μL, 1.4 mmol, 5.0 equiv.). The resulting solution was allowed to stir for 24 h at 60 °C. After 24 h, the reaction vial was cooled to room temperature followed by the addition of tetramethylsilane as an internal standard. The reaction mixture was further dissolved in $CDCl_3$ (0.5 mL). The NMR yield (92%) was determined by the analysis of the ^{1}H NMR of the crude reaction mixture. After the analysis, the NMR sample was poured into the reaction vial and was rinsed with $CHCl_3$ (2 mL). The solution was then concentrated *in vacuo* followed by the addition of 10% aqueous HCl (2 mL) while stirring at room temperature. This was capped and heated to 60 °C for 2 h. The solution was then transferred to a separatory funnel. The reaction vial was washed with 10% aqueous HCl (1 mL) followed by $CHCl_3$ (4 mL). The aqueous layer was washed with $CHCl_3$ (10 mL × 3) and was basified using KOH pellets until a pH ~12 was obtained. The aqueous layer was washed with $CHCl_3$ (50 mL × 3). All organic layers were combined, dried over anhydrous $MgSO_4$ and filtered. The solution was then concentrated *in vacuo* followed by drying under high vacuum (0.05 mm Hg) for 1 h to afford the crude diamine **14d** as yellow oil. Purification of the crude diamine by automated silica gel chromatography (24 g, MeOH : 1% NH_4OH / $CHCl_3$ = 0 : 100 to 10 : 90 as gradient) afforded pure diamine **14d** as a clear oil in 80% yield (54 mg, 0.22 mmol).

R_f = 0.48 (1:9 $NH_4OH/CHCl_3$).

^{1}H NMR (C_6D_6, 500 MHz): δ 7.26 (d, *J* = 8.3, 2H), 6.88 (d, *J* = 8.7, 2H), 3.94 (d, *J* = 4.4, 1H), 3.54 (t, *J* = 4.5, 4H), 3.37 (s, 3H), 2.30-2.25 (m, 5H), 1.19 (s, 2H), 0.83 (d, *J* = 6.7, 3H) ppm.

^{13}C NMR (C_6D_6, 125 MHz): δ 128.34, 159.03, 137.3, 113.8, 67.6, 66.0, 55.4, 54.8, 51.3, 10.1 ppm.

HRMS (ESI-TOF) *m/z*: [M+H$^+$] calculated for $C_{14}H_{23}N_2O_2$, 251.1760; found, 251.1759.



12e **1a** **14e**

1-(4-bromophenyl)-2-morpholinopropan-1-amine, 14e: [(DPEphos)Rh(COD)]BF_4 (2.5 mg, 0.0030 mmol, 1.0 mol %), imine **12e** (100 mg, 0.30 mmol, 1.0 equiv.) and dry CH_3CN (80 μL) were added to an oven-dried 4 mL vial equipped with a stir bar

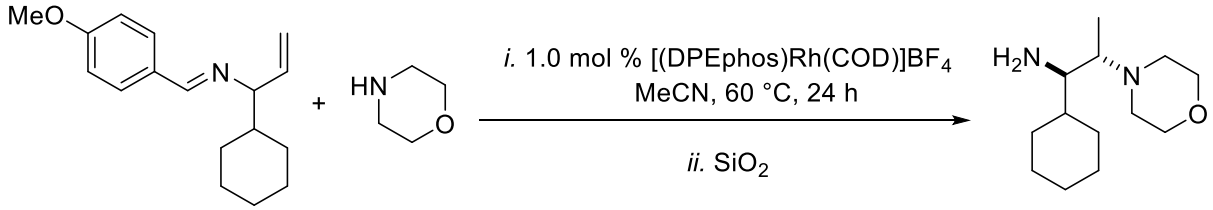
in the glove box. To the reaction mixture was then added morpholine, **1a** (79 μL, 0.90 mmol, 3.0 equiv.). The resulting solution was allowed to stir for 24 h at 60 °C. After 24 h, the reaction vial was cooled to room temperature followed by the addition of diphenylmethane as an internal standard. The reaction mixture was further dissolved in C_6D_6 (0.5 mL). The NMR yield (74%) was determined by the analysis of the ^{1}H NMR of the crude reaction mixture. After the analysis, the NMR sample was poured into the reaction vial and was rinsed with $CHCl_3$ (2 mL). The solution was then concentrated *in vacuo* followed by the addition of 10% aqueous HCl (3 mL). The vial was then capped and stirred at 60 °C for 2 h. The solution was then transferred to a separatory funnel. The reaction vial was rinsed with 10% aqueous HCl (1 mL) followed by $CHCl_3$ (4 mL). The aqueous layer was washed with $CHCl_3$ (10 mL × 3) and was then basified using KOH pellets until a pH ~12 was obtained. The aqueous layer was extracted with $CHCl_3$ (50 mL × 3). All organic layers were then combined, dried over anhydrous $MgSO_4$ and filtered. The solution was concentrated *in vacuo* followed by drying under high vacuum (10 mm Hg) for 0.5 h to afford the pure diamine **14e** as an off white solid in 69% yield (62 mg, 0.21 mmol).

m.p. 63–65 °C.

^{1}H NMR (C_6D_6, 500 MHz): δ 7.33 (d, J = 8.4 Hz, 2H), 6.95 (d, J = 8.3 Hz, 2H), 3.69 (d, J = 4.6 Hz, 1H), 3.48 (t, J = 5.0 Hz, 4H), 2.15 (td, J = 4.2, 1.9 Hz, 4H), 2.09 (qd, J = 6.7, 4.6 Hz, 1H), 0.95 (s, 2H), 0.67 (d, J = 6.7 Hz, 3H) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz): δ 144.96, 131.86, 129.75, 121.09, 68.03, 66.20, 56.00, 51.64, 10.53 ppm.

HRMS (ESI-TOF) *m/z*: [M+H$^+$] calcd for $C_{13}H_{20}N_2OBr$, 299.0759; found, 299.0761.



12f **1a** **14f**

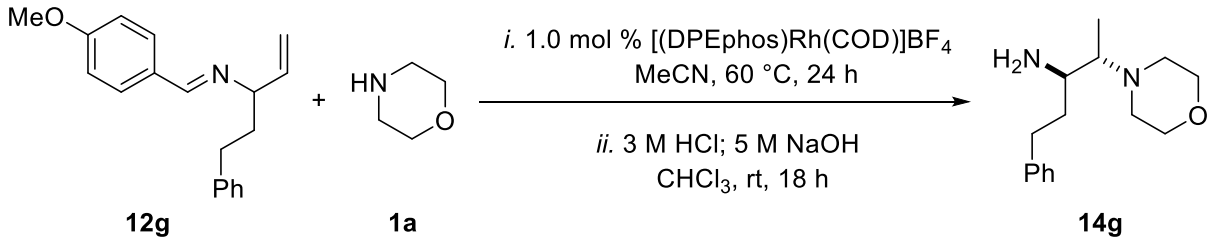
1-cyclohexyl-2-morpholinopropan-1-amine, 14f: [(DPEphos)Rh(COD)]BF_4 (8 mg, 0.01 mmol, 1 mol %), imine **12f** (257 mg, 1.00 mmol, 1.00 equiv.) and dry CH_3CN (300 μL) were added to an oven-dried 4 mL vial equipped with a stir bar in the glove box. To the reaction mixture was added morpholine, **1a** (604 μL, 7.00 mmol, 7.00 equiv.). The resulting solution was allowed to stir for 24 h at 60 °C. After 24 h, the reaction vial was cooled to room temperature followed by the addition of diphenylmethane as an internal standard. The reaction mixture was further dissolved in C_6D_6 (0.5 mL). The crude yield (78%) was determined by the analysis of the ^{1}H NMR. Subjection of the crude aminoimine to silica gel chromatography (125 mL silica, 1% MeOH : 1% NH_4OH : 98% $CHCl_3$ to 2% MeOH : 2% NH_4OH : 96% $CHCl_3$ gradient v/v prepared by extracting saturated NH_4OH with $CHCl_3$, removing aqueous layer, and adding methanol) afforded 1,2-diamine **14f** as a pale yellow oil in 58% yield (141 mg, 1.08 mmol).

R_f = 0.53 (1:9 MeOH/CH_2Cl_2).

^{1}H NMR (C_6D_6, 500 MHz): δ 3.67 – 3.43 (m, 4H), 2.35 (t, *J* = 5.8 Hz, 1H), 2.20 (tq, *J* = 11.4, 6.4, 5.4 Hz, 4H), 2.07 (p, *J* = 6.5 Hz, 1H), 1.69 (td, *J* = 25.1, 23.3, 13.1 Hz, 4H), 1.42 (d, *J* = 9.0 Hz, 2H), 1.29 – 1.05 (m, 3H), 1.01 – 0.84 (m, 2H), 0.82 (d, *J* = 6.6 Hz, 5H) ppm.

^{13}C NMR (C_6D_6, 125 MHz): δ 67.49, 61.10, 56.73, 50.30, 40.43, 30.27, 28.24, 27.03, 26.86, 26.70, 9.60 ppm.

HRMS (ESI-TOF) *m/z*: [M+H$^+$] calculated for $C_{13}H_{27}N_2O$, 227.2123; found, 227.2121.



4-morpholino-1-phenylpentan-3-amine, 14g: [(DPEphos)Rh(COD)]BF_4 (8 mg, 0.01 mmol, 1 mol %), imine **12g** (267 μL, 1.00 mmol, 1.00 equiv.) and dry CH_3CN (300 μL) were added to an oven-dried 4 mL vial equipped with a stir bar in the glove box. To the reaction mixture was added morpholine, **1a** (431 μL, 5.00 mmol, 5.00 equiv.). The resulting solution was allowed to stir for 24 h at 60 °C. After 24 h, the reaction vial was cooled to room temperature followed by the addition of diphenylmethane as an internal standard. The reaction mixture was further dissolved in C_6D_6 (0.5 mL). The crude yield (76%) was determined by the analysis of the ^{1}H NMR. The NMR sample and remaining reaction mixture were rinsed into a separate 20 mL scintillation vial with $CHCl_3$ (3 mL) and the solvent was reduced under reduced pressure. 3 M HCl (5 mL) was then added to the scintillation and the diphasic solution was vigorously stirred for 18 hours. The organic layer was discarded and the aqueous layer was basified with 5 M NaOH until a pH ~12 was obtained. The aqueous layer was extracted with $CHCl_3$ (75 mL × 3). The organic extracts were combined, dried over anhydrous $MgSO_4$, and filtered. The solution was concentrated *in vacuo* followed by drying under high vacuum (0.05 mm Hg) for 1 h to afford crude diamine **14g** as yellow oil. Purification of the crude diamine by silica gel chromatography (125 mL silica, 2% MeOH : 2% NH_4OH: 96% $CHCl_3$ v/v prepared by extracting saturated NH_4OH with $CHCl_3$, removing aqueous layer, and adding methanol) afforded pure diamine **14g** as a pale yellow oil in 73% yield (119 mg, 0.731 mmol).

R_f = 0.40 (1:9 MeOH/CH_2Cl_2).

^{1}H NMR (C_6D_6, 500 MHz): δ 7.19 – 7.14 (m, 3H), 7.09 – 7.03 (m, 2H), 3.57 – 3.46 (m, 4H), 2.72 (ddd, *J* = 13.6, 9.8, 5.2 Hz, 1H), 2.57 – 2.47 (m, 2H), 2.14 (tq, *J* = 10.8, 6.1, 4.9 Hz, 4H), 1.86 (p, *J* = 6.5 Hz, 1H), 1.79 (dddd, *J* = 13.3, 10.1, 7.0, 3.3 Hz, 1H), 1.40 (dddd, *J* = 13.8, 9.7, 8.7, 5.2 Hz, 1H), 0.72 (d, *J* = 6.6 Hz, 5H) ppm.

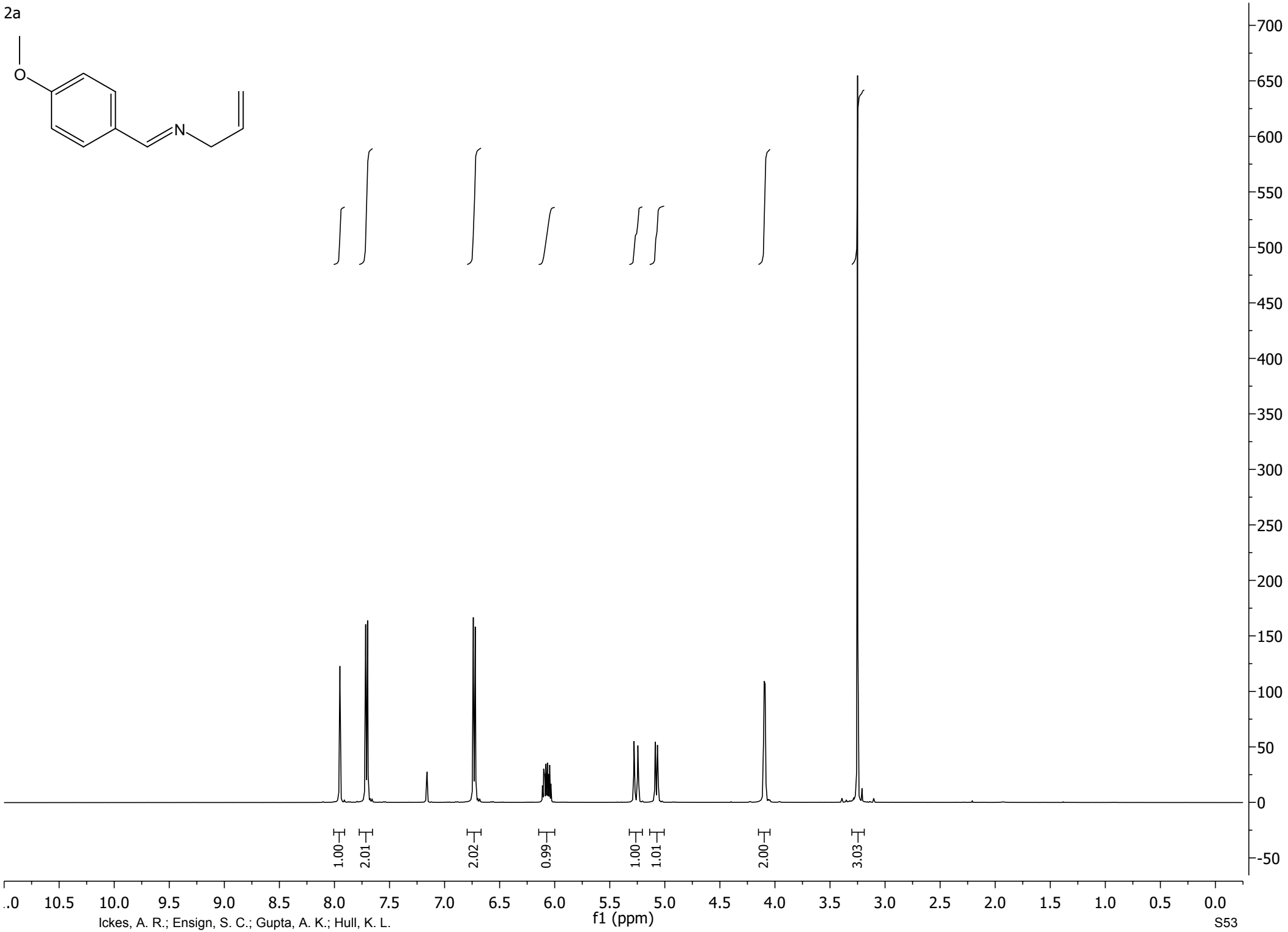
^{13}C NMR (C_6D_6, 125 MHz): δ 142.65, 128.60, 128.59, 126.00, 67.70, 64.20, 51.77, 50.60, 37.04, 33.17, 9.73 ppm.

HRMS (ESI-TOF) *m/z*: [M+H$^+$] calculated for $C_{15}H_{25}N_2O$, 249.1967; found, 249.1963.

[1] Utsunomiya, M.; Kuwano, R.; Kawatsura, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2003**, *125*, 5608

[2] Tehrani, K. A.; NguyenVan, T.; Karikomi, M.; Rottiers, M.; De Kimpe, N. *Tetrahedron* **2002**, *58*, 7145–7152.

[3] Knežević, A.; Landek, G.; Dokli, I.; Vinković, V. *Tetrahedron: Asymmetry* **2011**, *22*, 936–941.
[4] Defieber, C.; Ariger, M. A.; Moriel, P.; Carreira, E. M. Angew. Chem. Int. Ed. 2007, 46, 3139-3143.
[5] Xie, J.-H.; Liu, S.; Kong, W.-L.; Bai, W.-J.; Wang, X.-C.; Wang, L.-X.; Zhou, Q.-L. *J. Am. Chem. Soc.* **2009**, *131*, 4222-4223.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N
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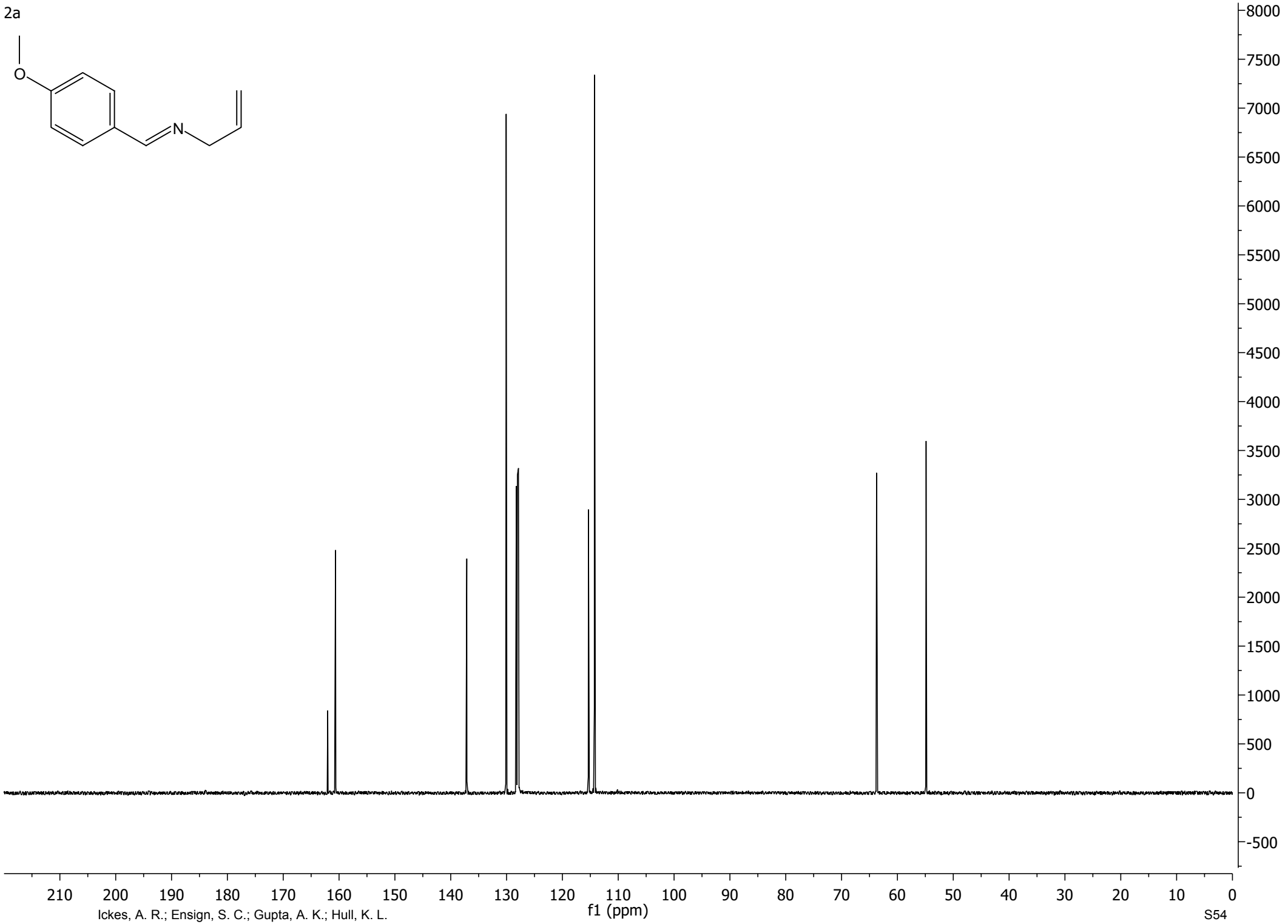
2.01
2.02
0.99
1.00
1.01
2.00
3.03
f1 (ppm)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7000
6500
6000
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4500
4000
3500
3000
2500
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1000
500
0
-500
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200
190
180
170
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140
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40
30
20
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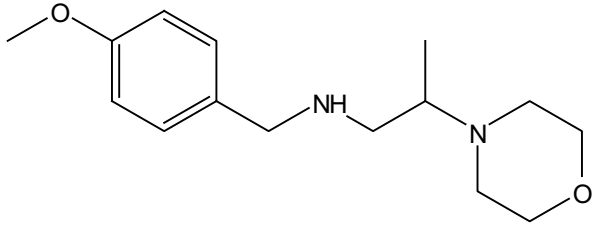
0
f1 (ppm)

6a



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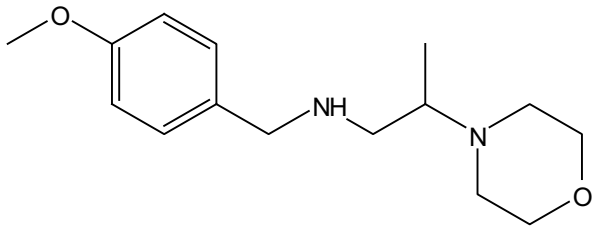
6a



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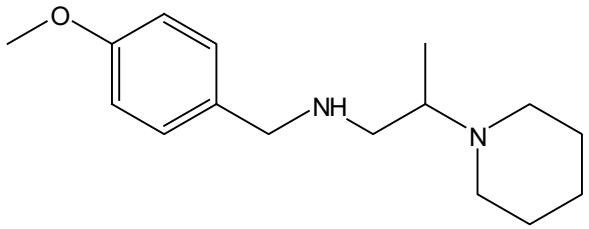
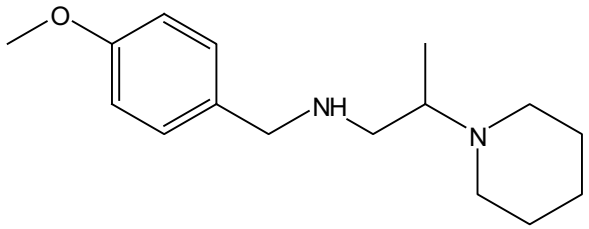


6b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NH
N

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3500
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0
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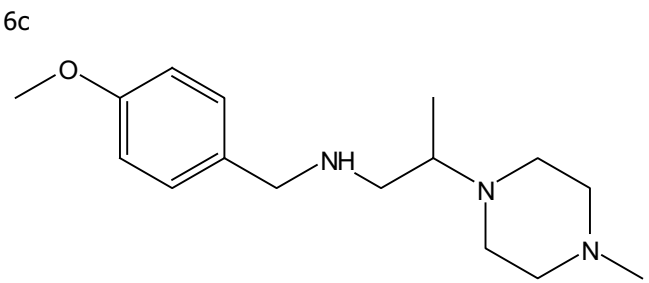
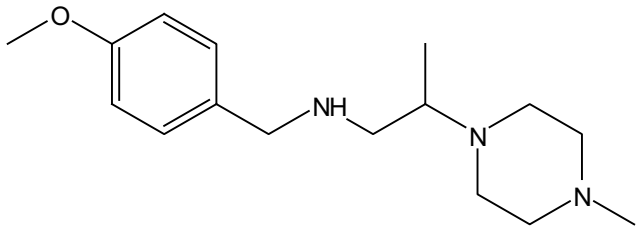
f1 (ppm)

6c



6c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4500
4000
3500
3000
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1000
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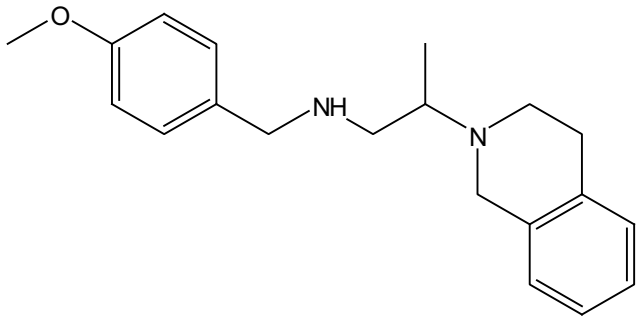
f1 (ppm)

6d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NH
N

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1.03
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1.07
1.19
1.06
1.01
2.93
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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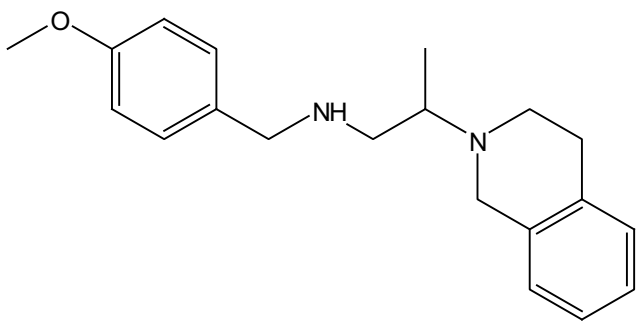
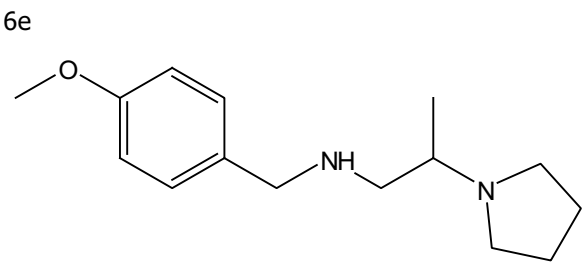
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

6d



6e



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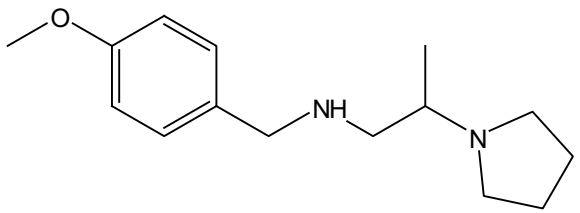
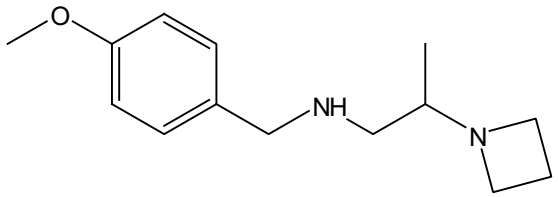
6e

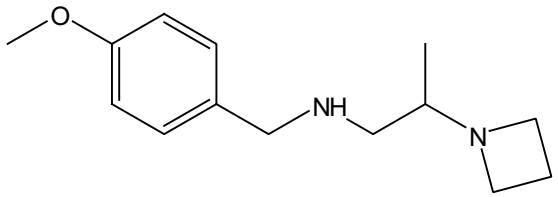


6f



Ickes, A. R.; Ensign, S. C.; Gupta, A. K.; Hull, K. L.

6f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NH
N

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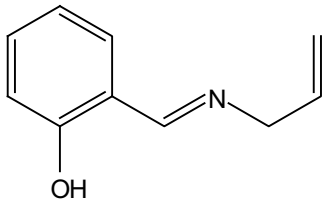
1000
500
0
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

7a



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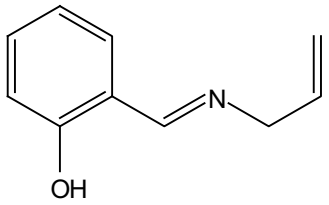
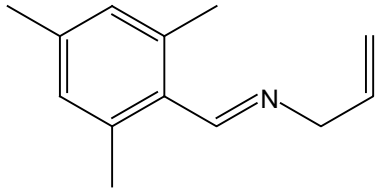


7b



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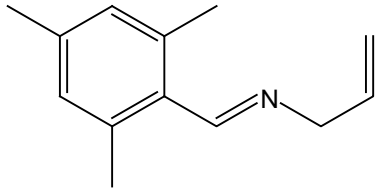
7b


N

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110
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90
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70
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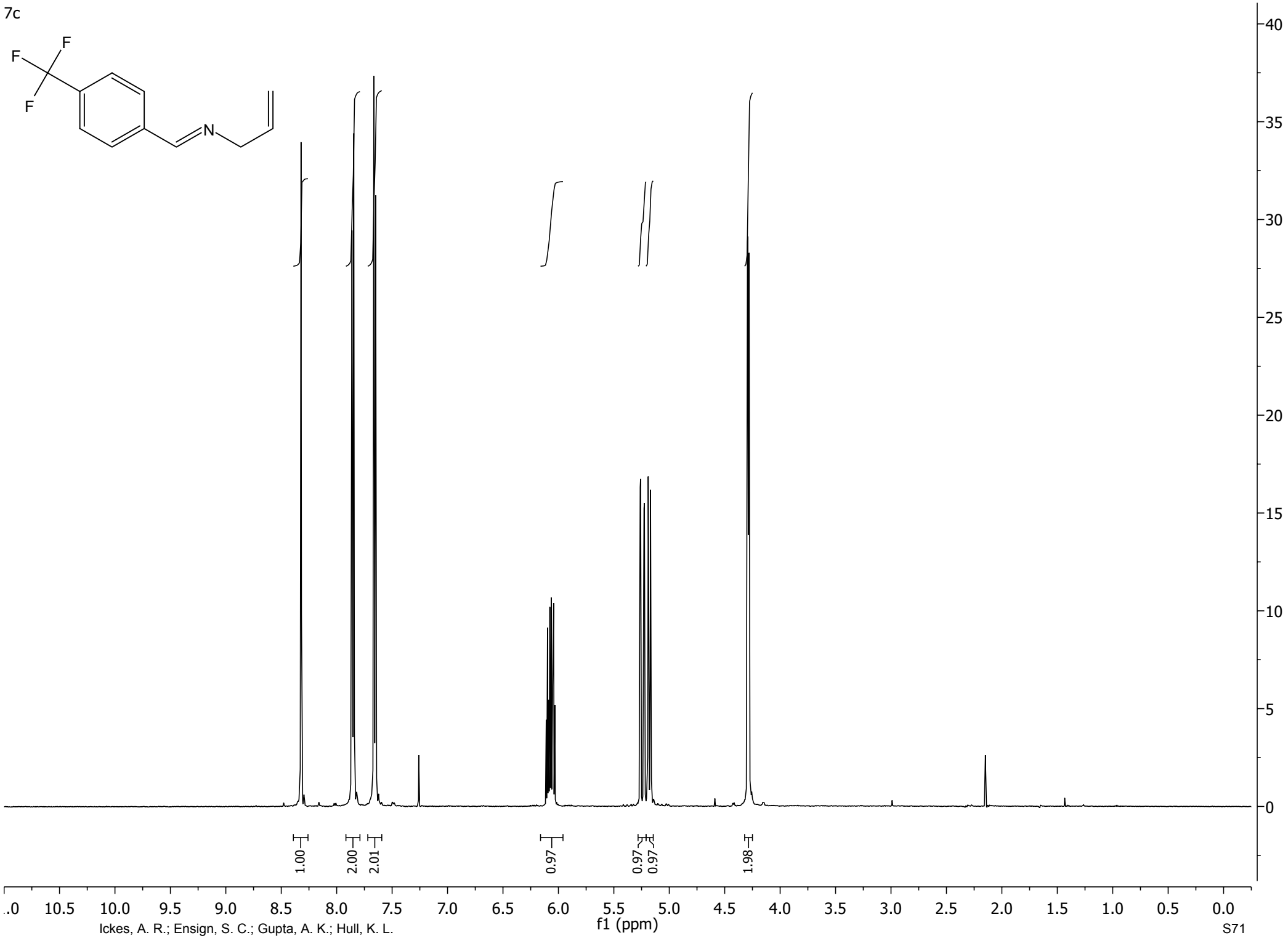
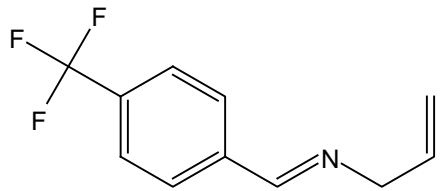
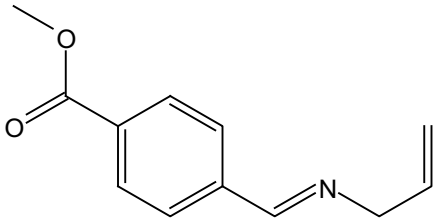
50
40
30
20
10
0
f1 (ppm)


7c
F
F
F
N
1.00
2.00
2.01
0.97
0.97
0.97
1.98
40
35
30
25
20
15
10
5
0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

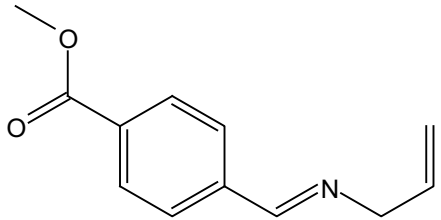
7c



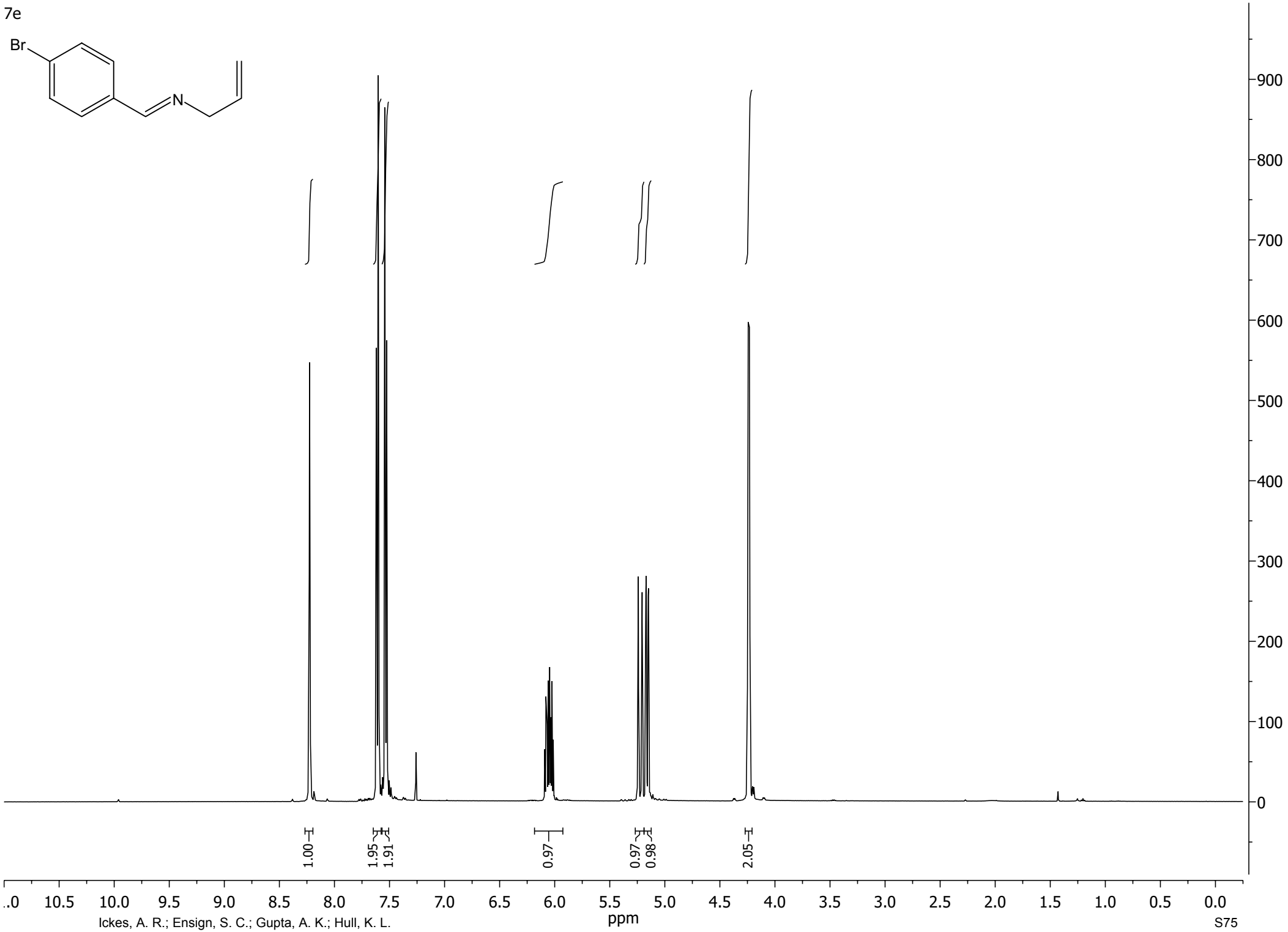
7d



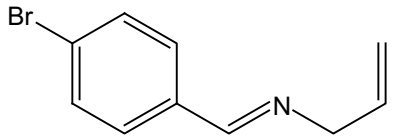
7d


O
O
N

800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

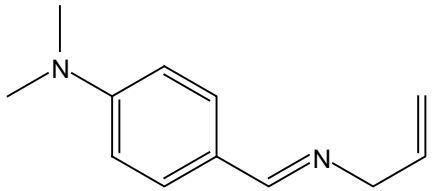

7e
Br
N
1.00
1.95
1.91
0.97
0.97
0.98
2.05
900
800
700
600
500
400
300
200
100
0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

7e


Br
N

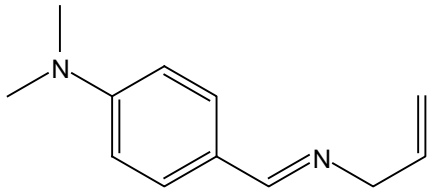
1000
900
800
700
600
500
400
300
200
100
0
-100
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

7f

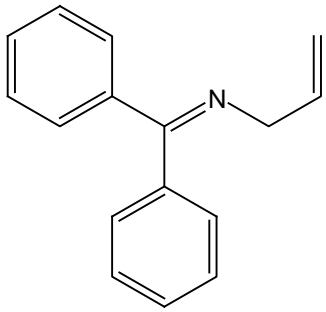

N
N

4500
4000
3500
3000
2500
2000
1500
1000
500
0
1.00
1.89
2.02
0.90
0.96
0.95
2.04
6.02
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
ppm

7f

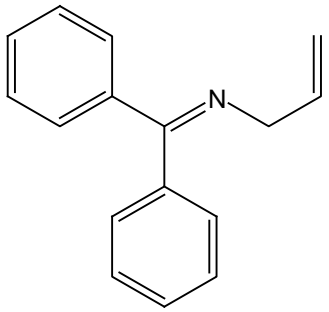


7g


N

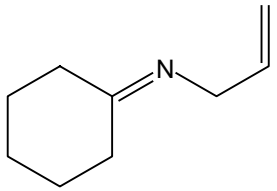
2.04
6.03
2.06
1.00
1.01
1.01
2.02
450
400
350
300
250
200
150
100
50
0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

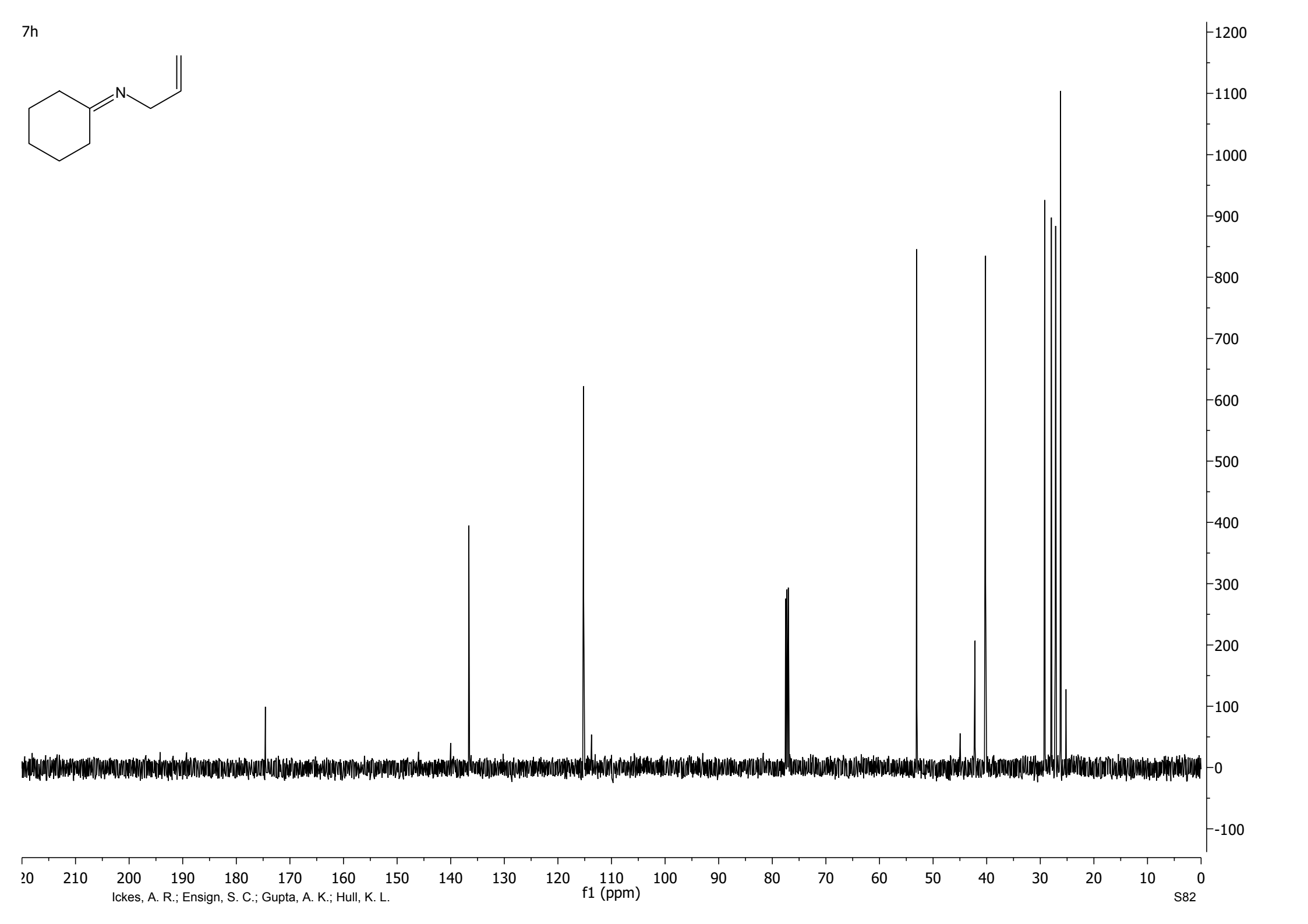
7g


N

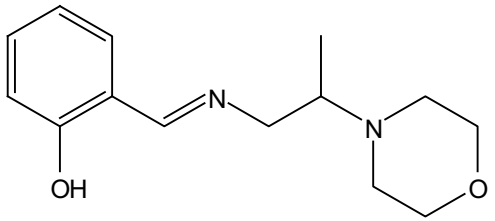
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

7h



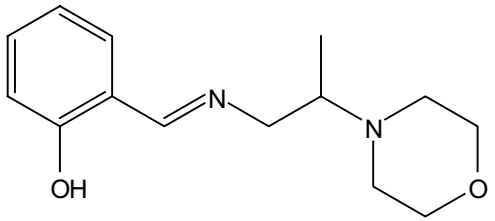

7h
N
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

8a


N
N
OH
O

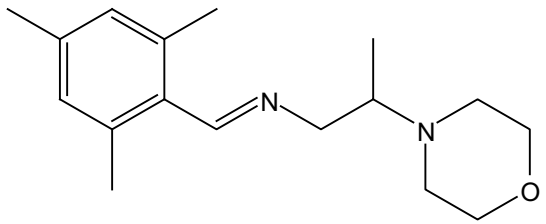
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
1.00
1.94
1.01
0.97
4.19
1.05
1.03
1.01
4.22
3.08
0.49
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

8a


N
N
OH
O

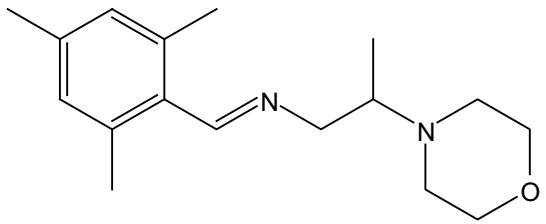
380
360
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

8b


N
N
O

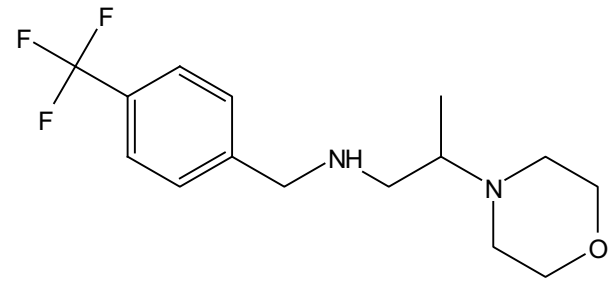
1.00
1.99
5.00
1.02
0.97
5.89
4.14
3.00
2.98
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

8b


N
N
O

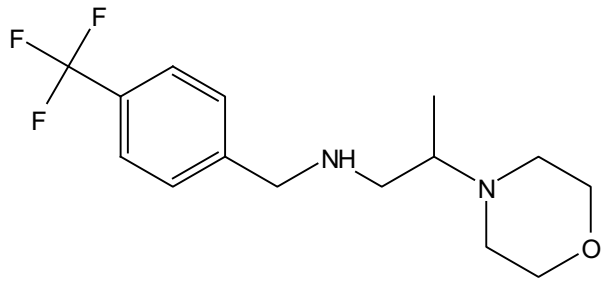
3500
3000
2500
2000
1500
1000
500
0
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

9c

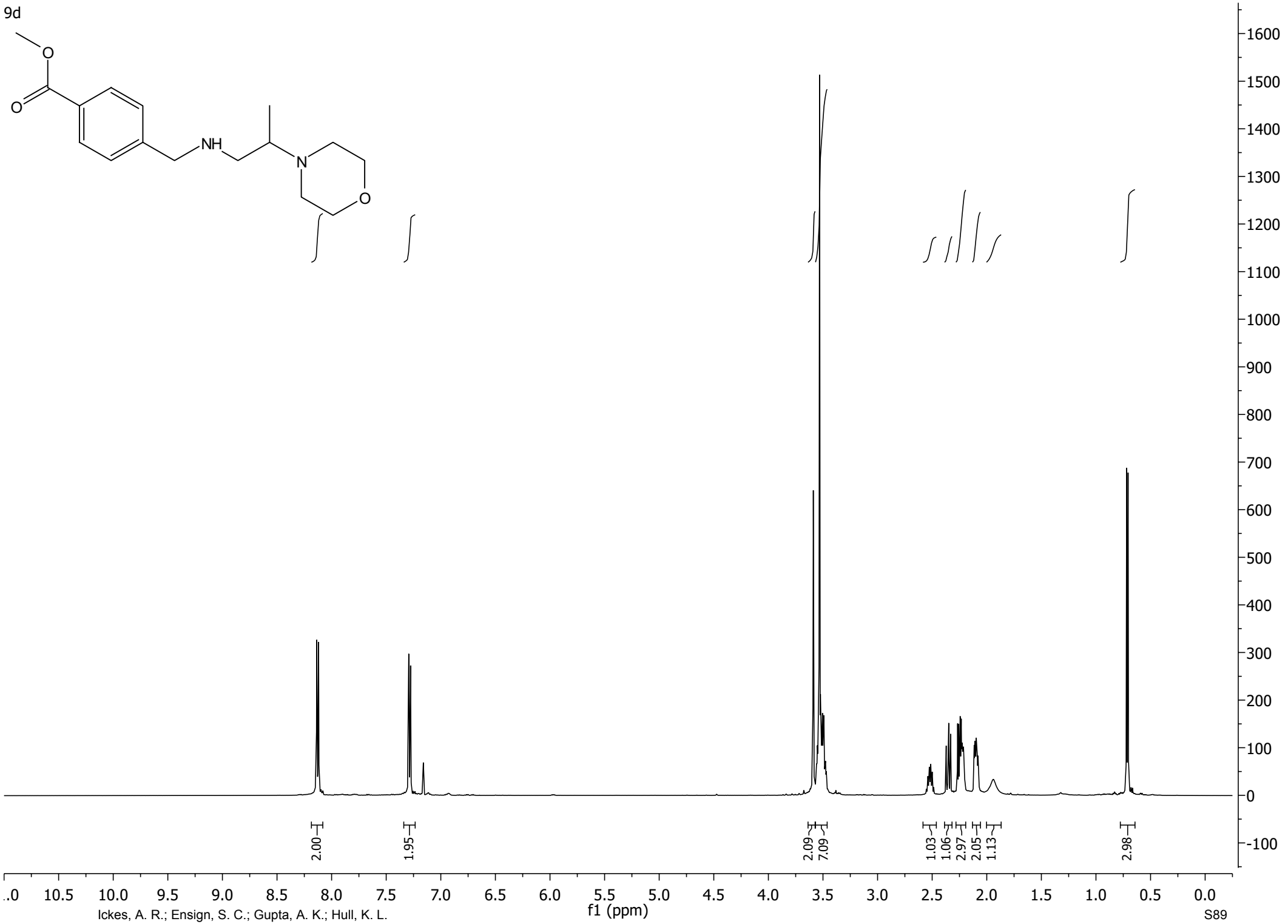


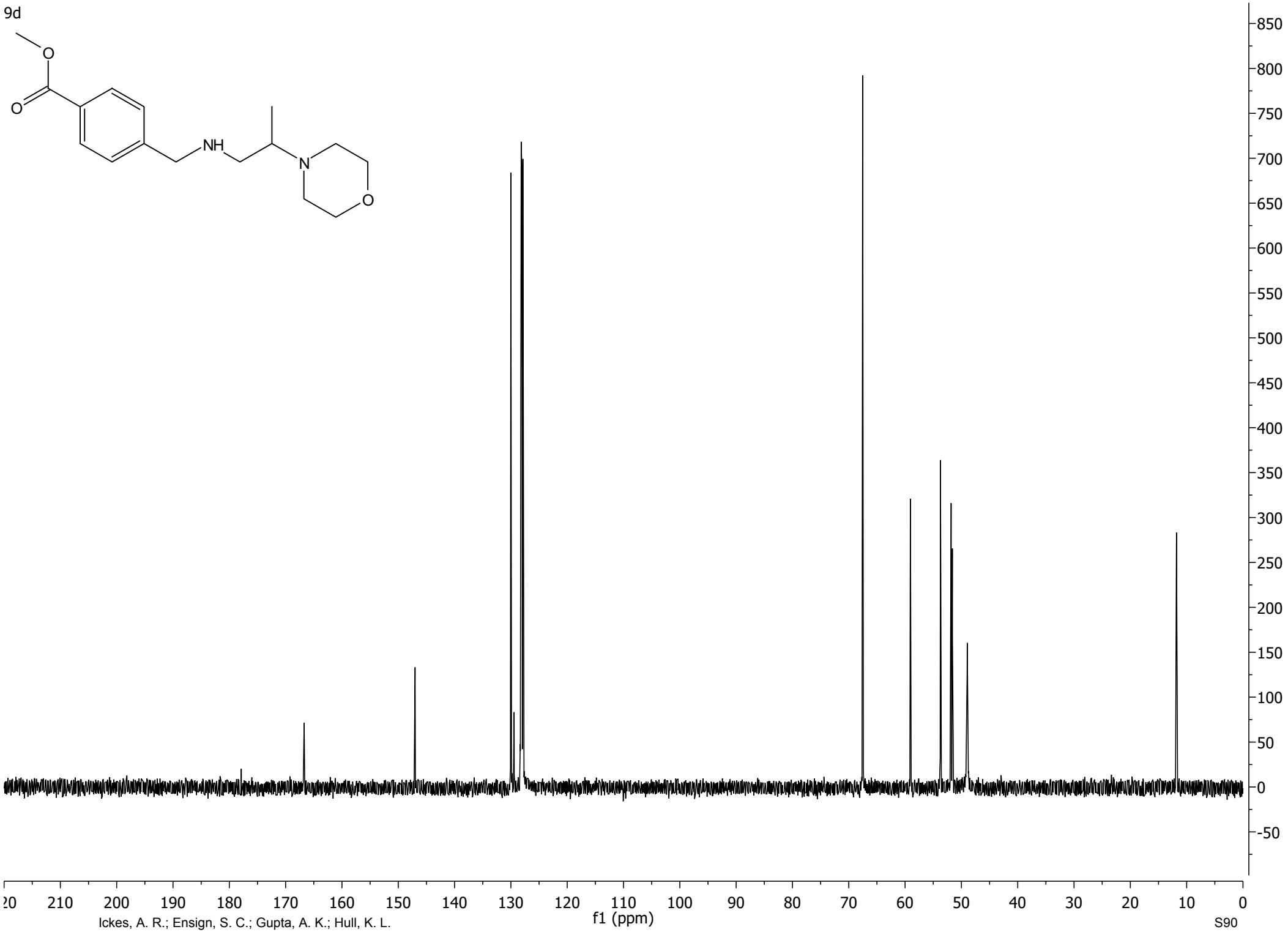
Ickes, A. R.; Ensign, S. C.; Gupta, A. K.; Hull, K. L.

9c

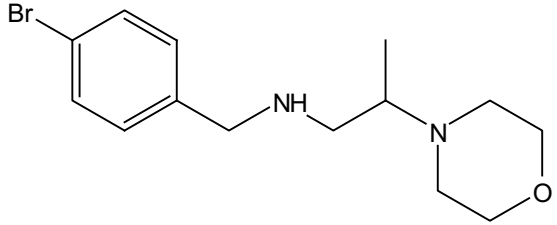

F
F
F
NH
N
O

10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

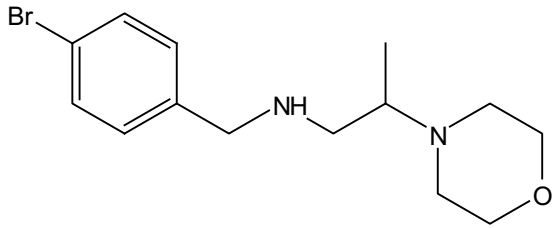

9d
O
O
NH
N
O
2.00
1.95
2.09
7.09
1.03
1.06
2.97
2.05
1.13
2.98
f1 (ppm)


9d
O
O
NH
N
O
850
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

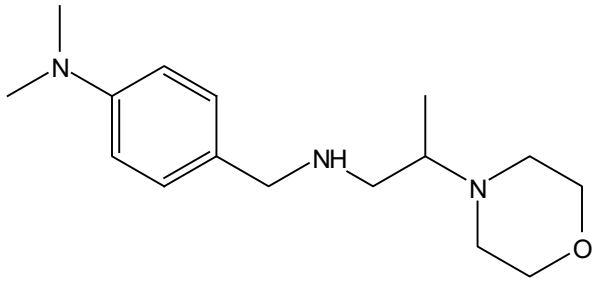
9e



9e

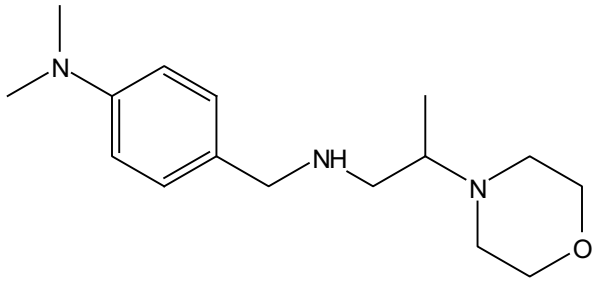


9f


N
NH
N
O

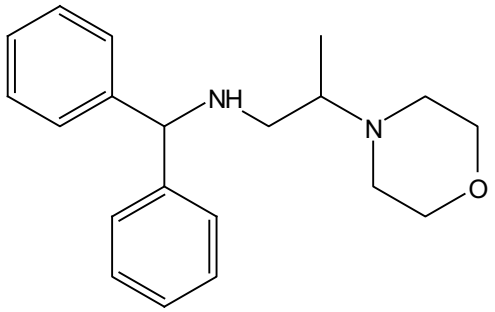
4500
4000
3500
3000
2500
2000
1500
1000
500
0
2.00
2.05
2.11
4.17
1.22
6.43
1.20
2.14
2.11
1.08
3.03
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

9f

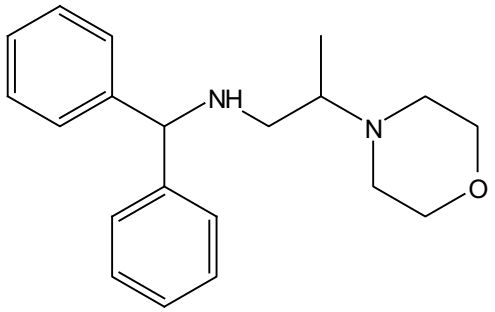

N
NH
N
O

700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

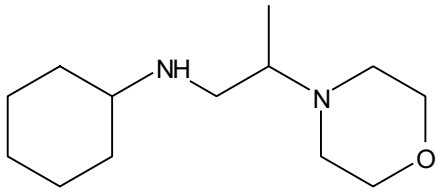
9g



9g

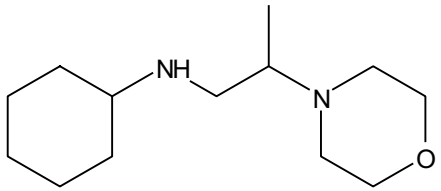


9h


NH
N
O

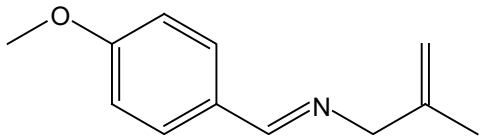
100
90
80
70
60
50
40
30
20
10
0
1.96
2.00
1.07
1.92
3.21
2.07
3.16
2.29
1.24
5.38
3.00
..0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

9h


NH
N
O

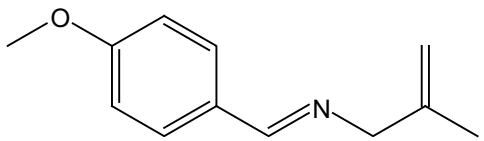
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

10a


O
N

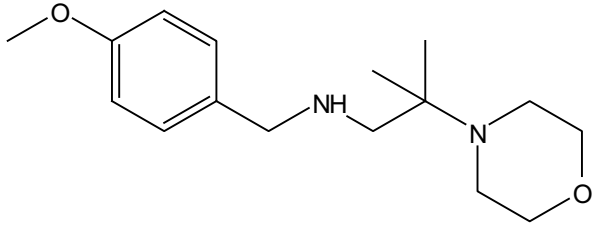
2500
2000
1500
1000
500
0
1.00
1.98
1.98
1.00
1.01
2.05
3.11
3.03
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

10a

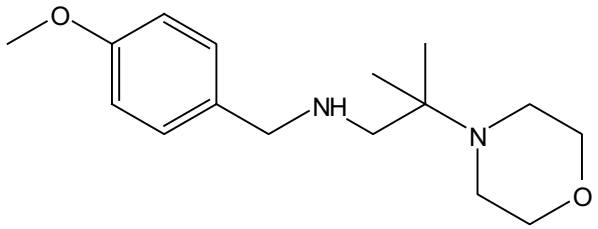

O
N

2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

11a

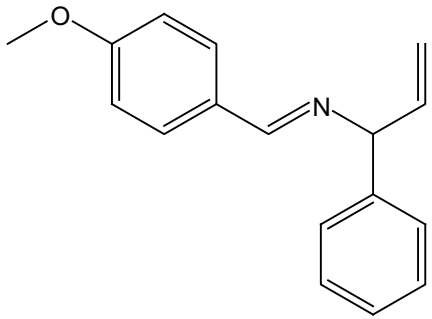


11a


O
NH
N
O

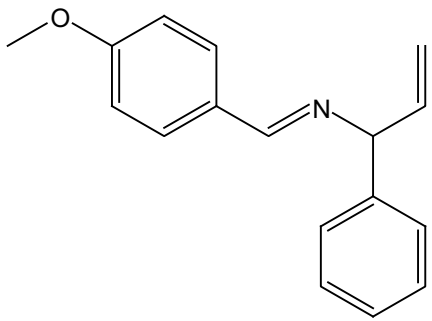
850
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

12a

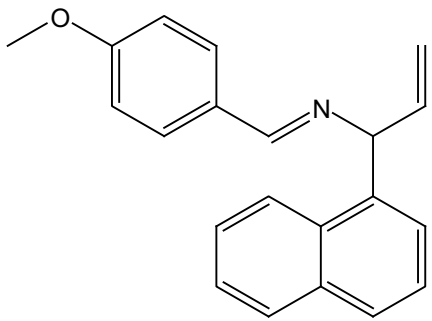

O
N

1.00
2.00
2.06
2.09
1.23
2.00
0.91
1.02
1.08
1.04
2.98
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
f1 (ppm)
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20

12a

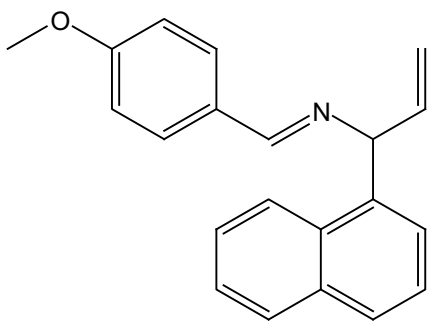


12b


O
N

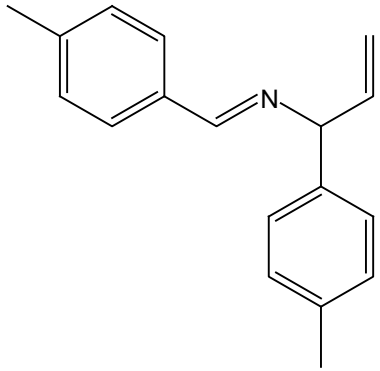
1.00
1.05
0.96
1.89
1.09
0.99
1.01
1.03
1.11
2.12
1.04
1.04
1.08
1.07
3.08
ppm

12b


O
N

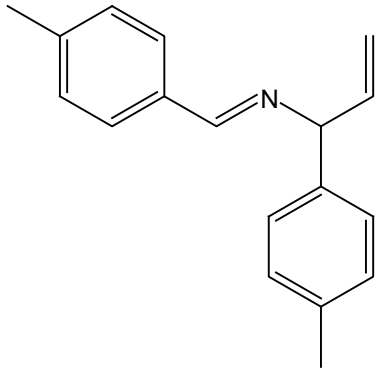
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

12c



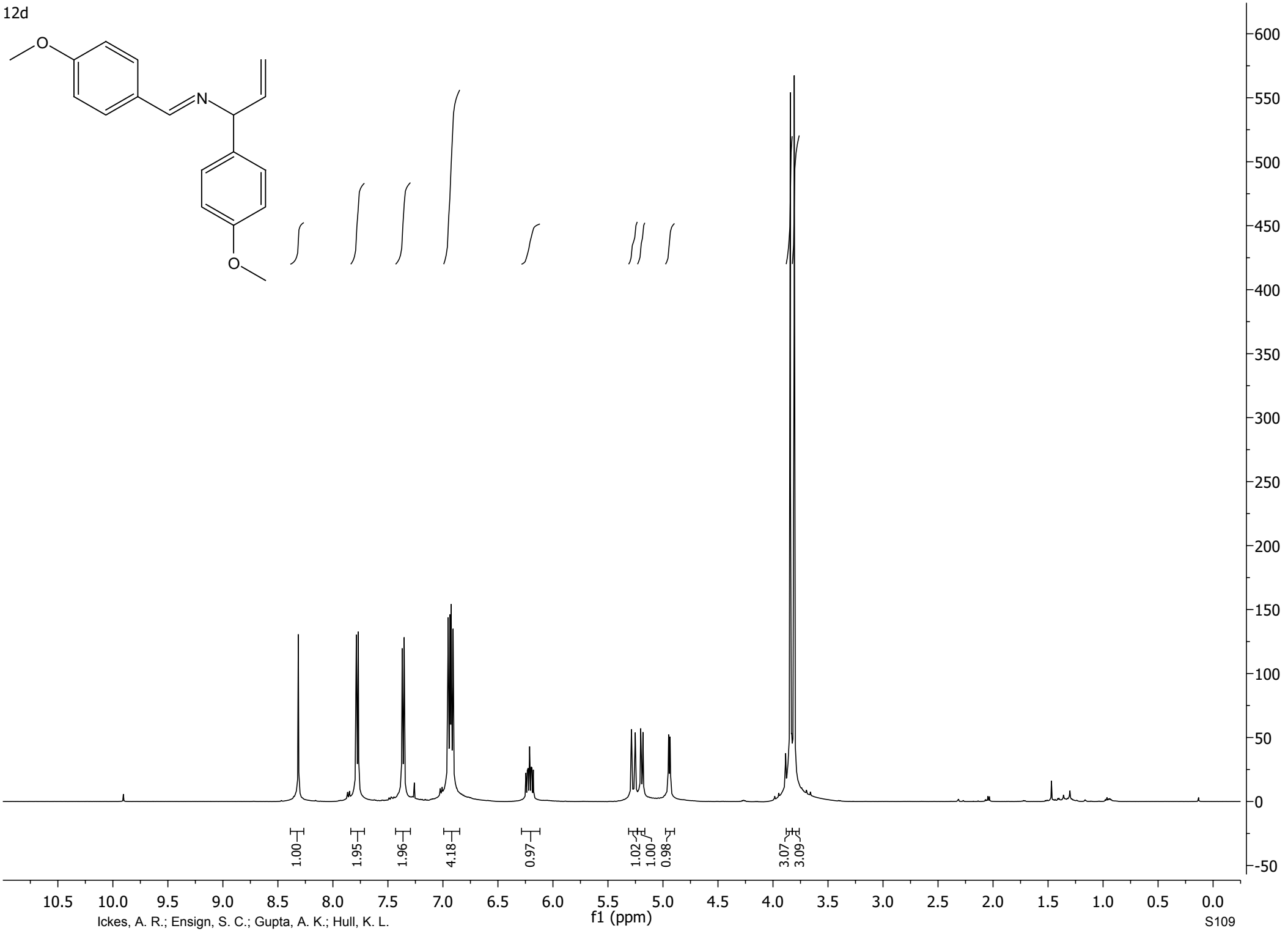
Ickes, A. R.; Ensign, S. C.; Gupta, A. K.; Hull, K. L.

12c

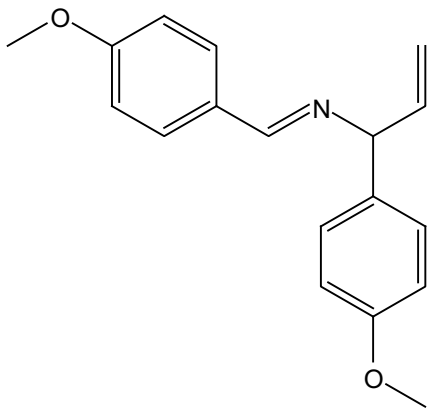

N

1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

12d

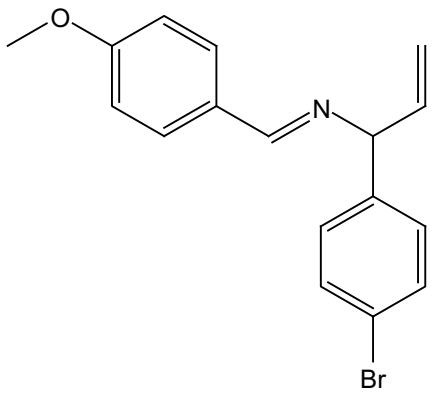

O
N
O
1.00
1.95
1.96
4.18
0.97
1.02
1.00
0.98
3.07
3.09
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

12d



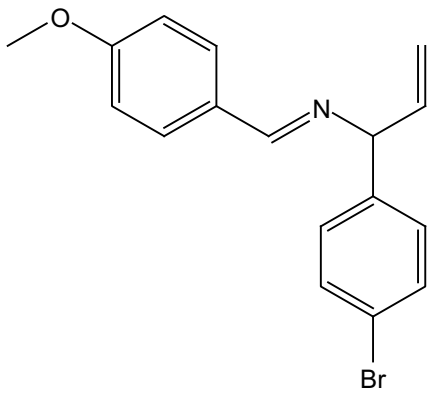
Ickes, A. R.; Ensign, S. C.; Gupta, A. K.; Hull, K. L.

12e

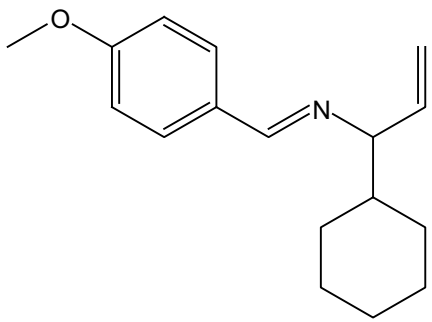

O
N
Br

1.00
1.92
1.87
1.92
1.96
0.98
1.04
1.04
1.01
3.01
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
ppm
2400 2300 2200 2100 2000 1900 1800 1700 1600 1500 1400 1300 1200 1100 1000 900 800 700 600 500 400 300 200 100 0 -100 -200

12e

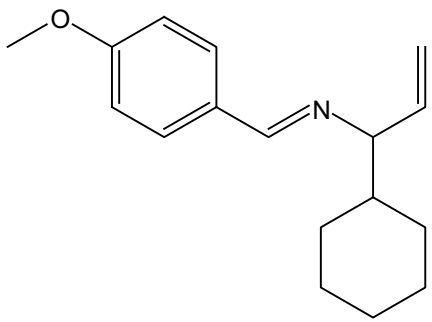


12f

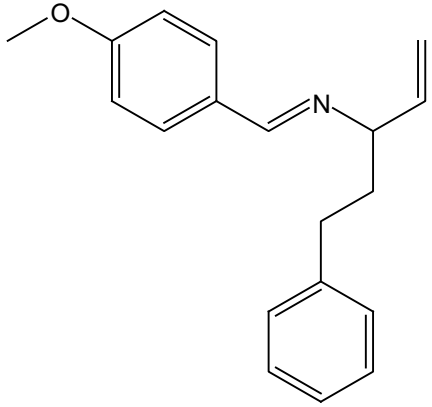

O
N

650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
1.00
2.01
2.00
1.14
1.08
1.07
1.01
2.87
2.14
3.18
1.18
5.52
..0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

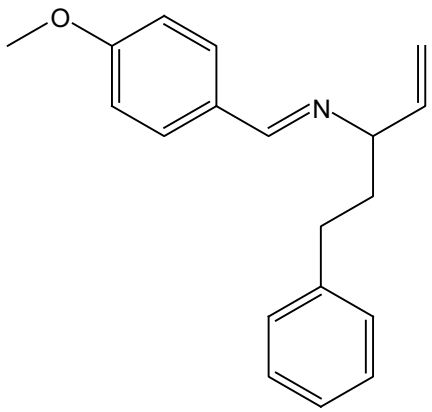
12f



12g

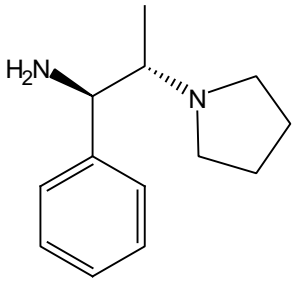


12g


O
N

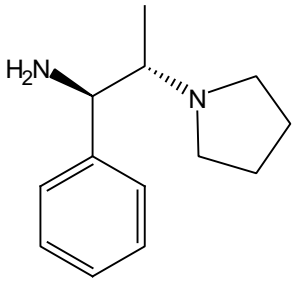
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

13a


H2N
N

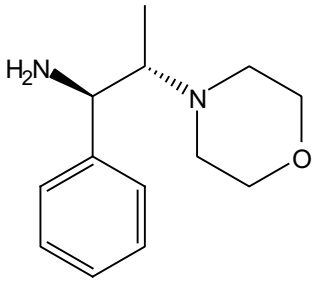
1.94
1.94
1.00
1.00
2.01
2.10
1.00
4.09
3.10
3.06
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

13a


H2N
N

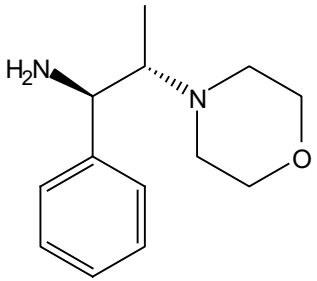
1000
900
800
700
600
500
400
300
200
100
0
-100
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

14a


H2N
N
O

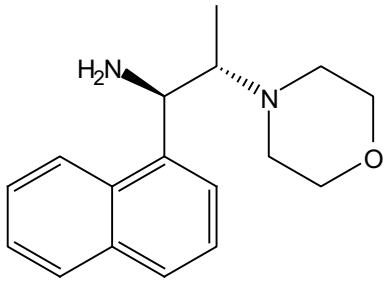
900
800
700
600
500
400
300
200
100
0
0.09
1.96
2.02
1.00
0.97
4.07
1.14
3.95
2.19
3.01
0.11
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

14a


H2N
N
O

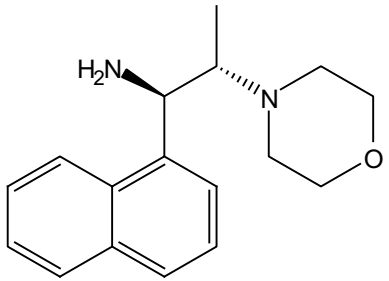
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

14b

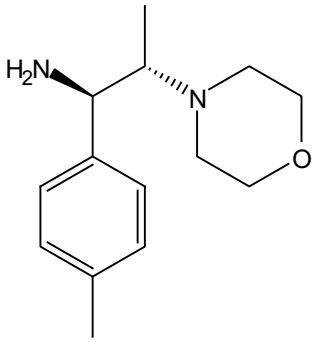


Ickes, A. R.; Ensign, S. C.; Gupta, A. K.; Hull, K. L.

14b

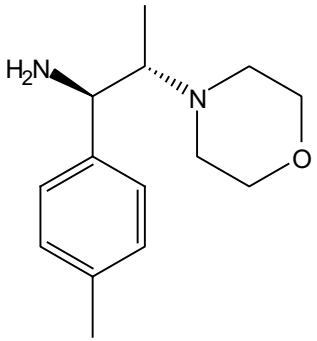


14c



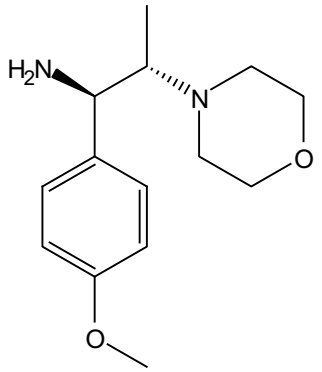
Ickes, A. R.; Ensign, S. C.; Gupta, A. K.; Hull, K. L.

14c


H2N
N
O

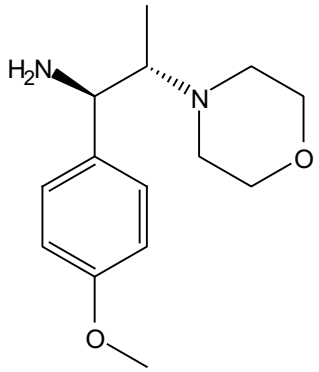
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

14d

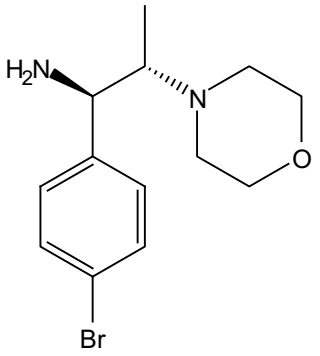

H2N
N
O
O

400
350
300
250
200
150
100
50
0
0.17
2.01
2.00
0.95
4.03
3.01
5.25
2.10
2.96
0.09
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
f1 (ppm)

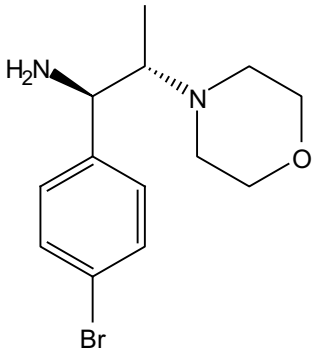
14d



14e

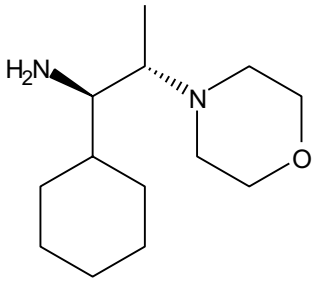


14e


H2N
N
O
Br

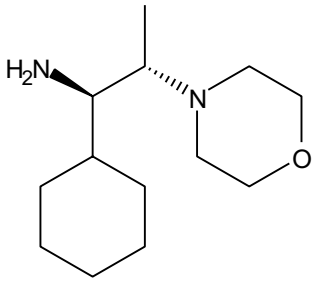
4500
4000
3500
3000
2500
2000
1500
1000
500
0
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

14f



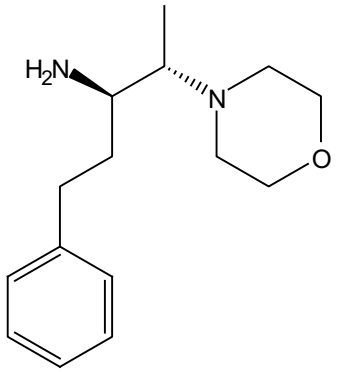
Ickes, A. R.; Ensign, S. C.; Gupta, A. K.; Hull, K. L.

14f


H2N
N
O

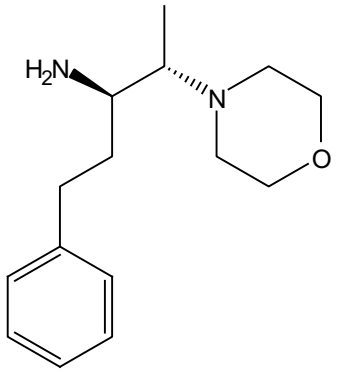
4500
4000
3500
3000
2500
2000
1500
1000
500
0
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

14g



Ickes, A. R.; Ensign, S. C.; Gupta, A. K.; Hull, K. L.

14g


H2N
N
O

2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)