Supporting Information

Development and Mechanistic Investigations of Enantioselective Pd-Catalyzed Intermolecular Hydroaminations of Internal Dienes

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I. General Information

General Procedures. All reactions were carried out in oven- (120 °C) or flame-dried glassware under an inert atmosphere of dry N_2 unless otherwise noted. Oven-dried (60 °C or 120 °C) stainless steel cannulas and/or glass syringes (or N_2-flushed plastic syringes) were used for reagent transfer. Organic solutions were concentrated under reduced pressure using a rotary evaporator (Büchi). Flash column chromatography was performed using SiliCycle SiliaFlash® P60 Silica Gel.

Reagents.

(*R*)-(+)-[(*R*)-2-Diphenylphosphinoferrocenyl](*N*,*N*-dimethylamino)(2-diphenylphosphinophenyl)-methane (Strem), (*R*,*R*)-(-)-2,3-bis(*t*-butylmethylphosphino)quinoxaline (Strem), (*S*)-1-[(Rp)-2-di-*tert*-butylphosphino]ferrocenyl]ethyldiphenylphophine (Sigma-Aldrich), (*R*)-(+)-2,2'-bis(diphenylphosphino)-5,5',6,6',7,7',8,8'-octahydro-1.1'-binaphthyl (Strem), (*R*)-(+)-2.2'-bis[di(3,5-xylyl)phosphino]-1,1'-binaphthyl (Strem), (*R*)-(+)-5,5'-dichloro-6,6'-dimenthoxy-2.2'-bis(diphenylphosphino)-1,1'-biphenyl (Strem), (*R*)-(+)-5,5'-bis(diphenylphosphino)-4,4'-bi-1,3-benzodioxole (Strem), (*R*)-(+)-2,2',6,6'-tetramethoxy-4,4'-bis-(di(3,5-xylylphosphino)-3,3'-bipyridine (Strem), (*S*)-(+)-2,2'-bis[di(3,5-di-butyl-4-methoxyphenyl)phosphino]-6,6'-dimethoxy-1,1'-biphenyl (Strem), (*S*)-(+)-5,5'-bis[di(3,5-di-*t*-butyl-4-methoxyphenyl)phosphino]-4,4'-bi-1,3-benzodioxole (Sigma Aldrich), (*S*)-(6,6'-dimethoxybiphenyl-2,2'diyl)bis(diisopropylphosphine) (Strem), (-)-1,2-bis[(2R,5R)-2,5-dimethylphospholano]benzene (Strem), (*S*,*S*)-DIPAMP (Strem), (2*S*,4*S*)-2,4-bis(diphenylphosphino)pentane (Strem), *trans*-1-bromo-1-propene (Sigma-Aldrich), *β*-bromostyrene (Sigma-Aldrich), 1,3-bis(trifluoromethyl)-5-bromobenzene (Chem-Impex), *n*-BuLi in cyclohexane 2.0 M (Sigma-Aldrich), (*n*-butyl)triphenylphosphonium bromide (Acros), catecholborane (Sigma-Aldrich), chlorobis[3,5-bis(trifluoromethyl)phenyl]phosphine (Alfa Aesar), chlorobis[4-(trifluoromethyl)phenyl]phosphine (Alfa Aesar), cesium carbonate (Sigma-Aldrich), 4-chlorocinnamaldehyde (Sigma-Aldrich), 4-chlorocinnamic acid (Matrix), *trans*-cinnamaldehyde (Alfa Aesar), 4-(dimethylamino)cinnamaldehyde (Sigma-Aldrich), diisobutylaluminum hydride (Sigma-Aldrich), ethylenediamine (Sigma-Aldrich), isoamyltriphenylphosphonium bromide (Sigma-Aldrich), ethyltriphenylphosphonium bromide (Acros), 4-methylcinnamic acid (Sigma-Aldrich), *trans*-*p*-methoxycinnamaldehyde (Acros), nickel(II) acetate tetrahydrate (Alfa Aesar), 1-phenylpiperazine (Alfa), 5-phenyl-1-pentyne (BeanTown Chemical), 1-propynyl magnesium bromide in THF 0.5 M

(Sigma-Aldrich), sodium borohydride (VWR), *o*-tolualdehyde (TCI), tetrakis(triphenylphosphine)palladium (0) (Strem), thionyl chloride (Sigma-Aldrich), 4-(trifluoromethyl)cinnamaldehyde (Sigma-Aldrich) and 4-(trifluoromethyl)cinnamic acid (Matrix) were used as received. Sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($NaBAr^F_4$) was prepared according to a reported procedure.[1]

Aniline (Sigma-Aldrich), 1-Boc-piperazine (Matrix), indoline (Acros), 1-methylpiperazine (TCI), *N*-methylbenzylamine (Sigma-Aldrich), morpholine (Sigma-Aldrich), 4-propylaniline (Sigma-Aldrich), 1,2,3,4-tetrahydroisoquinoline (Sigma-Aldrich) and triethylamine (Alfa Aesar) were distilled over CaH_2 before use.

Solvents. Solvents were sparged with dry N_2 and purified under a positive pressure of dry N_2 by an Innovative Technologies PureSolve solvent purification system: tetrahydrofuran (Sigma-Aldrich), dichloromethane (Sigma-Aldrich) and diethyl ether (Sigma-Aldrich), and toluene (Sigma-Aldrich) were passed through two consecutive alumina columns. Acetonitrile (Fisher) and ethanol (200 proof, Koptec) used for reactions were distilled over CaH_2 prior to use. Benzene (*anhyd.*, EMD Millipore), methanol (Sigma-Aldrich), DMF (*anhyd.*, Alfa Aesar), and *tert*-butanol were used as received. Hexanes (Fisher) and ethyl acetate (Fisher) were used for flash column chromatography and used as received. HPLC-grade hexanes (Sigma-Aldrich), methanol (Sigma-Aldrich), acetonitrile (Sigma-Aldrich) and isopropanol (Sigma-Aldrich) were used as received.

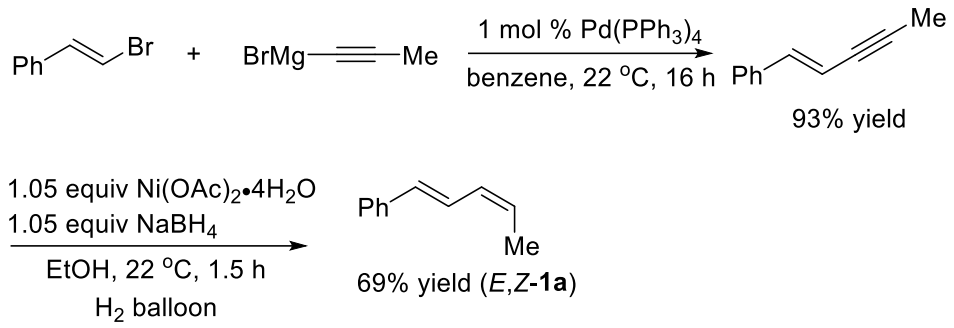
Instrumentation. ^{1}H-NMR spectra were recorded on a Varian INOVA (400 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance resulting from incomplete deuteration as the internal reference ($CDCl_3$: δ 7.24, CD_2Cl_2: δ 5.32). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet, app. = apparent), coupling constant(s) (Hz). ^{13}C-NMR spectra were recorded on a Varian/Agilent VNMRS (500 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the natural abundane of deuterium in the solvent resonance resulting from chloroform as the internal reference ($CDCl_3$: δ 77.08, CD_2Cl_2: δ 53.84). ^{19}F-NMR spectra were recorded on a Varian INOVA (400 MHz) spectrometer. ^{31}P-NMR spectra were recorded on a Varian INOVA (400 MHz) spectrometer. Enantiomer ratios (er) were determined by HPLC (Phenomenex™ Lux® Cellulose III or Chiralpak™ 1A-3 columns) in comparison with authentic

racemic materials on a Shimadzu Prominence Modular HPLC. High-resolution mass spectrometry was performed on an Agilent (1200 Series) LCMS-TOF-DART at the Duke University Mass Spectrometry Facility. MALDI-MS data were recorded on a Bruker Autoflex Speed LRF MALDI-TOF. Specific rotation values were recorded on a Rudolph Autopol IV Polarimeter.[i] Infrared (IR) spectra were collected on a Nicolet 6700 FT-IR spectrometer, υ_{max} in cm^{-1}. Bands are characterized as broad (br), strong (s), medium (m), or weak (w). Melting points were measured on an Electrothermal MelTemp® capillary melting point apparatus and are uncorrected.

HRMS data are an average of 3–4 runs. Polarimetry data are an average of 5–6 trials. Melting point data are an average of 3 runs.

II. Preparation of Substrates

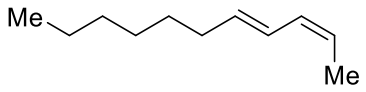
1. Preparation of pure *E,Z*- and *E,E*-internal diene isomers



General Method A: (1*E*,3*Z*)-1-Phenyl-1,3-pentadiene ((*E*,Z)-1a): [$Pd(PPh_3)_4$] (116 mg, 0.100 mmol, 1.00 mol %) was dissolved in benzene (24 mL) in a 100-mL round-bottom flask. *trans-β*-Bromostyrene (1.28 mL, 10.0 mmol) was added followed by dropwise addition of a solution of 1-propynyl magnesium bromide in THF (0.5 M, 24 mL, 12.0 mmol) at 0 °C. After complete addition of 1-propynyl magnesium bromide, the reaction mixture was allowed to stir for 16 h at room temperature. The reaction was quenched with aqueous HCl (1.0 M, 25 mL) and after addition of hexanes (5 mL) the layers were separated. The organic layer was washed with saturated aqueous $NaHCO_3$ solution (15 mL) and dried over $MgSO_4$. After filtration, solvent was evaporated under reduced pressure to give the residue, which was purified by silica gel chromatography (eluting with hexanes) to afford (*E*)-pent-1-en-3-yn-1-ylbenzene as a colorless oil (1.33 g, 9.34 mmol, 93.4 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 (2H, dd, J = 8.4, 1.6 Hz), 7.33–7.27 (2H, m), 7.27–7.21 (1H, m), 6.86 (1H, d, J = 16.2 Hz), 6.12 (1H, dq, J = 16.4, 2.6 Hz), 2.00 (3H, d, J = 2.4 Hz). Spectral data matched those previously reported.[2]

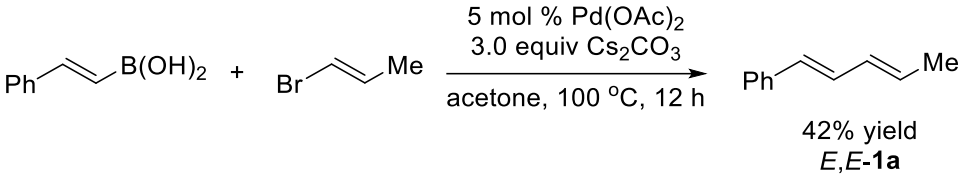
To a 250-mL round-bottom flask were added $Ni(OAc)_2•4H_2O$ (2.44 g, 9.81 mmol) and $NaBH_4$ (371 mg, 9.81 mmol) and a magnetic stirring bar. The flask was evacuated with nitrogen and then backfilled with H_2 (balloon), EtOH (90 mL) was added via syringe. The reaction mixture was allowed to stir for 30 min after which ethylenediamine (2.50 mL, 37.4 mmol) was added followed by the conjugated enyne (1.33 g, 9.34 mmol as a solution in 20 mL EtOH). Once all of the alkyne had been consumed (TLC analysis), the reaction mixture was diluted with Et_2O and filtered through celite. The celite was washed with Et_2O. The combined organic solutions were washed with aqueous HCl (1.0 M, 20 mL),

water (20 mL) and sat. aq. brine (20 mL) and then dried over $MgSO_4$. After filtration, solvent was evaporated under reduced pressure to give the residue which was purified by silica gel chromatography (eluting with hexanes) to afford (1*E*,3*Z*)-1-phenyl-1,3-pentadiene as a colorless oil (1.07 g, 7.39 mmol, 69.0% yield). **^{1}H NMR** (400 MHz, $CDCl_3$, *E,Z*-**1a**) δ 7.41 (2H, d, J = 7.4 Hz), 7.31 (2H, t, J = 7.6 Hz), 7.20 (1H, t, J = 7.2 Hz), 7.08 (1H, ddd, J = 15.4, 11.1, 1.2 Hz), 6.51 (1H, d, J = 15.5 Hz), 6.17 (1H, td, J = 11.1, 1.2 Hz) 5.64–5.54 (1H, m), 1.85 (3H, dd, J = 7.2, 1.7 Hz). Spectral data matched those previously reported.[3]



1:99 *E,E*:*E,Z*

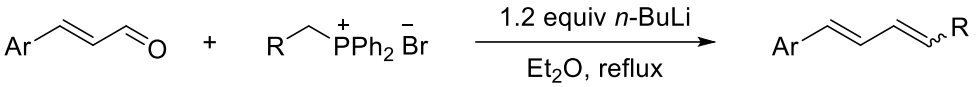
(2Z,4E)-Undeca-2,4-diene: Prepared by General Method A for 12 h. The material was purified by flash silica gel chromatography (100% hexanes) to yield as a colorless oil (608 mg, 3.99 mmol, 76.9% yield). *E,Z*-isomer (major): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.34-6.24 (1H, m), 5.95 (1H, t, J = 10.8 Hz), 5.67-5.58 (1H, m), 5.41-5.32 (1H, m), 2.15-1.90 (2H, m), 1.72 (3H, d, J = 7.1 Hz), 1.46-1.16 (m, 8H), 0.89 (3H, t, J = 7 Hz). Spectral data matched those previously reported.[4]



42% yield
E,E-**1a**

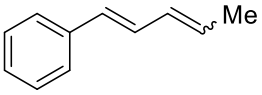
(1*E*, 3*E*)-1-Phenyl-1,3-pentadiene ((*E,E*)-1a): *trans*-1-Bromo-1-propene (172 μL, 2.00 mmol), (*E*)-styrylboronic acid (444 mg, 3.00 mmol), $Pd(OAc)_2$ (22.5 mg, 0.100 mmol), Cs_2CO_3 (1.95 g, 6.00 mmol) and acetone (10 mL) were added to Schlenk tube and allowed to stir at 100 °C for 12 h. The mixture was then poured into EtOAc (ca. 10 mL) and washed with sat. aq. brine (3 x 10 mL). The organic layer was dried over $MgSO_4$. The solvent was evaporated under reduced pressure to afford the residue which was purified by silica gel chromatography (eluting with hexanes) to afford (*E*)-pent-1-en-3-yn-1-ylbenzene as a colorless oil (120 mg, 0.840 mmol, 42.0 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 (2H, d, J = 7.8 Hz), 7.28 (2H, t, J = 7.7 Hz), 7.18 (1H, t, J = 7.3 Hz), 6.74 (1H, dd, J = 15.7 Hz, 10.4 Hz), 6.41 (1H, d, J = 15.7 Hz), 6.26–6.16 (2H, m), 5.82 (1H, dd, J = 15.0 Hz, 6.9 Hz), 1.81 (3H, dd, J = 6.7 Hz, 1.3 Hz). Spectral data match those previously reported.[5]

2. Preparation of internal dienes through Wittig olefination



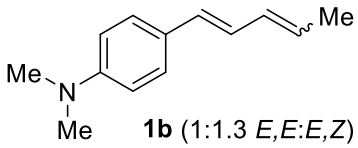
Cinnamaldehydes were prepared from commercially available cinnamic acids according to their availability by the same route as Doye *et al* (**1e**-**1h**).[6]

General Method B: (1*E*)-Penta-1,3-dien-1-ylbenzene (1a): To a dry 250-mL round-bottom flask with a magnetic stirring rod was added triphenylphosphonium bromide (25.0 mmol, 1.25 equiv) and then equipped with reflux condenser and added diethyl ether (80 mL). The mixture was allowed to stir and then heated to 55 °C for 10 min. The solution was treated with *n*-BuLi (12.5 mL, 25.0 mmol, 1.25 equiv), allowed to stir for 15 min, and then added aldehyde (20.0 mmol, 1.00 equiv), continued stirring for the specified amount of time. The reaction mixture was allowed to cool to ambient temperature and poured into a separatory funnel filled with water (100 mL). The organics were extracted with Et_2O (3 X 50 mL). The combined organic fractions were dried over $MgSO_4$, filtered, and concentrated. The residue was purified by silica gel column chromatography to give **1** starting materials.



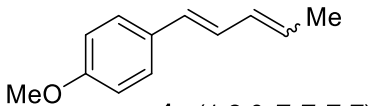
1a (1:1.8 *E,E*:*E,Z*)

((1E)-Penta-1,3-dien-1-yl)benzene (1a): Prepared by General Method B for 2 h. The material was purified by flash silica gel chromatography (100% hexanes) to yield **1a** as a colorless oil (2.52 g, 17.5 mmol, 87.4%). *E,Z*-isomer (major): **^{1}H NMR** (400 MHz, $CDCl_3$,) δ 7.42 (2H, d, J = 7.7 Hz), 7.35–7.26 (2H, m), 7.24–7.16 (1H, m), 7.09 (1H, dd, J = 15.6, 11.1 Hz), 6.53 (1H, d, J = 15.6 Hz), 6.27–6.13 (1H, m), 5.65–5.55 (1H, m), 1.87 (3H, dd, J = 7.2, 1.7 Hz). *E,E*-isomer (minor): **^{1}H NMR** (400 MHz, $CDCl_3$,) δ 7.37 (2H, d, J = 7.7 Hz), 7.35–7.26 (2H, m), 7.24–7.16 (1H, m), 6.75 (1H, dd, J = 15.6, 10.6 Hz), 6.43 (1H, J =15.7 Hz), 6.27–6.13 (2H, m), 5.84 (1H, dd, J = 14.8, 6.9 Hz), 1.83 (3H, d, J = 6.5 Hz); Spectral data matched those previously reported.[3,5]



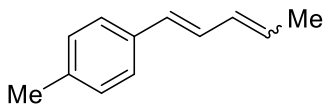
1b (1:1.3 *E,E*:*E,Z*)

***N,N*-Dimethyl-4-((1*E*)-penta-1,3-dien-1-yl)aniline (1b) :** Prepared by General Method B for 12 h. The material was purified by flash silica gel chromatography (100% hexanes to 10:90 hexanes:EtOAc) to yield **1b** as a colorless oil (768 mg, 4.10 mmol, 82.0% yield). **IR** (neat, cm^{-1}) 3006 (m), 2910 (m), 2804 (m), 1602 (s), 1517 (s), 1355 (s), 1184 (m), 1024 (s), 942 (s), 809 (s); *E,Z*-isomer (major): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39–7.32 (2H, m), 6.93 (1H, dd, *J* = 15.5 Hz, 11.0 Hz), 6.75–6.66 (2H, m), 6.48 (1H, d, *J* = 15.5 Hz), 6.28–6.13 (1H, m), 5.50 (1H, dq, *J* = 14.1 Hz, 7.1 Hz), 2.98 (3H, s), 2.97 (3H, s), 1.87 (3H, d, *J* = 7.1 Hz); *E,E*-isomer (minor): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 (2H, dd, *J* = 8.6, 1.6 Hz), 6.75–6.66 (2H, m), 6.61 (1H, dd, *J* = 15.5, 10.4 Hz), 6.38 (1H, d, *J* = 15.7 Hz), 6.28–6.13 (1H, m), 5.75 (1H, dq, *J* = 14.5, 6.7 Hz), 2.96 (6H, s), 1.83 (3H, d, *J* = 6.7 Hz); *E,Z*- and *E,E*-isomer mixture : **^{13}C NMR** (125 MHz, $CDCl_3$) δ 150.0, 132.4, 132.1, 127.6, 127.4, 127.2, 126.2, 125.4, 124.6, 120.3, 112.5, 40.5, 18.4, 13.6; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{13}H_{17}N$: 188.1434, found: 188.1435.



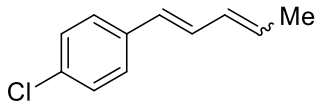
1c (1:2.0 *E,E*:*E,Z*)

1-Methoxy-4-((1*E*,3*E*)-penta-1,3-dien-1-yl)benzene (1c): Prepared by General Method B for 12 h. The material was purified by flash silica gel chromatography (100% hexanes to 15:85 hexanes:EtOAc) to yield **1c** as a colorless oil (1.23 g, 7.03 mmol, 70.3% yield). *E,Z*-isomer (major): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 (2H, d, *J* = 8.7 Hz), 6.94 (1H, dd, *J* = 15.6, 11.0 Hz), 6.85–6.81 (2H, m), 6.46 (1H, d, *J* = 15.5 Hz), 6.21–6.12 (1H, m), 5.53 (1H, dq, *J* = 11.0, 6.9 Hz), 3.80 (3H, s), 1.83 (3H, dd, *J* = 7.2, 1.6 Hz); *E,E*-isomer (minor): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 (2H, d, *J* = 8.8 Hz), 6.85–6.81 (2H, m), 6.61 (1H, dd, *J* = 15.5, 10.3 Hz), 6.36 (1H,d, *J* = 15.9 Hz), 6.21–6.12 (1H, m), 5.76 (1H, dq, *J* = 14.0, 6.9 Hz), 3.79 (3H, s), 1.80 (3H, d, *J* = 6.9 Hz). Spectral data matched those previously reported.[7]



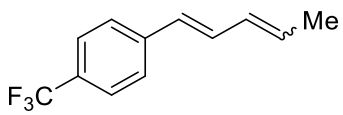
1d (1:1.5 *E,E*:*E,Z*)

1-Methyl-4-((1*E*)-penta-1,3-dien-1-yl)benzene (1d) : Prepared by General Method B for 12 h. The material was purified by flash silica gel chromatography (100% hexanes) to yield **1d** as a colorless oil (467 mg, 2.95 mmol, 59.0% yield). *E,Z*-isomer (major): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 (2H, d, J = 8.1 Hz), 7.11 (2H, d, J = 7.7 Hz), 7.03 (1H, dd, J = 15.5, 11.1 Hz), 6.49 (1H, d, J = 15.6 Hz), 6.26–6.11 (1H, m), 5.56 (1H, dq, J = 10.3, 7.1 Hz), 2.33 (3H, s), 1.85 (3H, dd, J = 7.2, 1.7 Hz); *E,E*-isomer (minor): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 (2H, d, J = 8.0 Hz), 7.31 (2H, d, J = 8.1 Hz), 6.69 (1H, dd, J = 15.7, 10.4 Hz), 6.39 (1H, d, J = 15.7 Hz), 6.26–6.11 (1H, m), 5.79 (1H, dq, J = 13.6, 6.7 Hz), 2.32 (3H, s), 1.81 (3H, dd, J = 6.8, 1.3 Hz). Spectral data matched those previously reported.[8]



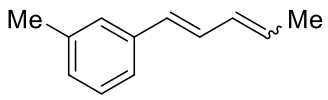
1e (1:2.8 *E,E*:*E,Z*)

1-Chloro-4-((1*E*)-penta-1,3-dien-1-yl)benzene (1e) : Prepared by General Method B for 12 h. The material was purified by flash silica gel chromatography (100% hexanes to 15:85 hexanes:EtOAc) to yield **1e** as a colorless oil (557 mg, 3.12 mmol, 53.0% yield); *E,Z*-isomer (major): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33–7.24 (4H, m), 7.04 (1H, dd, J = 15.9, 11.5 Hz), 6.45 (1H, d, J = 15.7 Hz), 6.25–6.08 (1H, m), 5.61 (1H, dq, J = 10.5, 6.9 Hz), 1.84 (3H, dd, J = 7.2, 1.7 Hz); *E,E*-isomer (minor): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33–7.24 (4H, m), 6.69 (1H, dd, J = 15.7, 10.4 Hz), 6.35 (1H, d, J = 15.7 Hz), 6.25–6.08 (1H, m), 5.89–5.77 (1H, m), 1.81 (3H, d, J = 7.3 Hz). Spectral data matched those previously reported.[8]



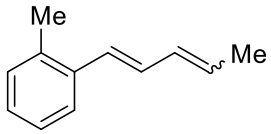
1f (1:2.5 *E,E*:*E,Z*)

1-((1*E*)-Penta-1,3-dien-1-yl)-4-(trifluoromethyl)benzene (1f) : Prepared by General Method B for 12 h. The material was purified by flash silica gel chromatography (100% hexanes to 15:85 hexanes:EtOAc) to yield **1f** as a colorless oil (628 mg, 2.96 mmol, 52.4% yield). *E*,*Z*-isomer (major): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59–7.28 (4H, m), 7.17 (1H, dd, J = 15.6, 11.1 Hz), 6.52 (1H, d, J = 15.6 Hz), 6.29–6.13 (1H, m), 5.69 (1H, dq, 10.5, 7.1 Hz), 1.88 (3H, dd, J = 7.2, 1.6 Hz); *E*,*E*-isomer (minor): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59–7.28 (4H, m), 6.81 (1H, dd, J = 15.6, 10.4 Hz), 6.42 (1H, d, J = 15.6 Hz), 6.29–6.13 (1H, m), 5.91 (1H, dq, J = 13.9, 6.8 Hz), 1.84 (3H, J = 6.8 Hz). Spectral data matched those previously reported.[9]



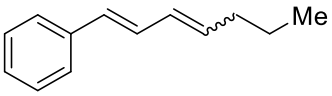
1g (1:1.4 *E*,*E*:*E*,*Z*)

1-Methyl-3-((1*E*)-penta-1,3-dien-1-yl)benzene (1g) : Prepared by General Method B for 12 h. The material was purified by flash silica gel chromatography (100% hexanes) to yield **1g** as a colorless oil (430 mg, 2.72 mmol, 36.7% yield). **IR** (neat, cm^{-1}) 3014 (m), 2912 (m), 2852 (w), 1599 (m), 1445 (m), 982 (s), 941 (s), 718 (s), 690 (s); *E*,*Z*-isomer (major): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24–7.00 (4H, m), 6.76–6.68 (1H, m), 6.37 (1H, d, J = 15.4 Hz), 6.27–6.11 (1H, m), 5.88–5.73 (1H, m), 2.33 (3H, s), 1.80 (3H, d, J = 5.3 Hz); *E*,*E*-isomer (minor): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24–7.00 (5H, m), 6.47 (1H, d, J = 16.0 Hz), 6.27–6.11 (1H, m), 5.63–5.50 (1H, m), 2.31 (3H, s), 1.84 (3H, s); *E*,*Z*- and *E*,*E*-isomer mixture : **^{13}C NMR** (125 MHz, $CDCl_3$) δ 138.1, 137.7, 132.1, 132.0, 130.1, 129.9, 129.8, 129.2, 128.5, 128.2, 128.0, 127.1, 127.0, 126.7, 124.0, 123.6, 123.4, 21.5, 18.4, 13.7; Elemental Analysis calc'd for $C_{12}H_{14}$: C, 91.08; H, 8.92. found : C, 90.79; H, 8.88.



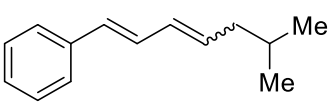
1h (1:2.4 *E*,*E*:*E*,*Z*)

1-Methyl-2-((1*E*)-penta-1,3-dien-1-yl)benzene (1h) : Prepared by General Method B for 12 h. The material was purified by flash silica gel chromatography (100% hexanes) to yield **1h** as a colorless oil (656 mg, 4.15 mmol, 50.9% yield). **IR** (neat, cm^{-1}) 3022 (m), 2911 (m), 1599 (w), 1481 (m), 980 (s), 942 (s), 745 (s); *E*,*Z*-isomer (major): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 (1H, d, J = 7.2 Hz), 7.26–7.07 (3H, m), 6.98 (1H, dd, J = 15.4, 11.1 Hz), 6.72 (1H, d, J = 15.5 Hz), 6.32–6.15 (1H, m), 5.59 (1H, dq, J = 10.6, 7.1 Hz), 2.34 (3H, s), 1.84 (3H, dd, J = 7.1, 1.8 Hz); *E*,*E*-isomer (minor): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (1H, d, J = 7.1 Hz), 7.26–7.07 (4H, m), 6.63 (1H, d, J = 7.5 Hz), 6.31–6.15 (1H, m), 5.82 (1H, dq, J = 13.5, 7.0 Hz), 2.33 (3H, s), 1.81 (3H, dd, J = 6.9 Hz, 1.7 Hz); *E*,*Z*- and *E*,*E*-isomer mixture : **^{13}C NMR** (125 MHz, $CDCl_3$) δ 136.6, 135.5, 132.3, 130.5, 130.4, 130.2, 130.0, 129.6, 127.5, 127.3, 127.1, 126.1, 125.4, 125.2, 125.0, 19.9, 18.4, 13.7; Elemental Analysis calc'd for $C_{12}H_{14}$: C, 91.08; H, 8.92; found : C, 90.79; H, 8.98.



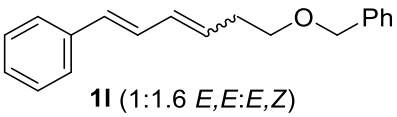
1i (1:1 *E*,*E*:*E*,*Z*)

((1*E*)-Hepta-1,3-dien-1-yl)benzene (1i) : Prepared by General Method B for 12 h. The material was purified by flash silica gel chromatography (100% hexanes) to yield **1i** as a colorless oil (1.13 g, 6.53 mmol, 65.3% yield); *E*,*Z*-isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44–7.34 (2H, m), 7.34–7.25 (2H, m), 7.23–7.14 (1H, m), 6.75 (1H, dd, J = 15.7, 10.4 Hz), 6.43 (1H, d, J = 15.6 Hz), 6.25–6.11 (1H, m), 5.82 (1H, dt, J = 14.6, 7.0 Hz), 2.12 (2H, dt, J = 7.3, 7.3 Hz), 0.93 (3H, t, J = 7.4 Hz); *E*,*E*-isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44–7.34 (2H, m), 7.34–7.25 (2H, m), 7.23–7.14 (1H, m), 7.06 (1H, dd, J = 15.6, 11.1 Hz), 6.52 (1H, d, J = 15.6 Hz), 6.25–6.11 (1H, m), 5.53 (1H, dt, J = 10.5, 7.7 Hz), 2.27 (2H, dt, J = 7.5, 7.5 Hz), 1.53–1.39 (2H, m), 0.95 (3H, t, J = 7.4 Hz). Spectral data matched those previously reported.[10]



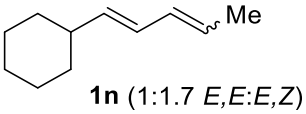
1j (1:1 *E*,*E*:*E*,*Z*)

((1*E*)-6-Methylhepta-1,3-dien-1-yl)benzene (1j) : Prepared by General Method B for 12 h. The material was purified by flash silica gel chromatography (100% hexanes) to yield **1j** as a colorless oil (1.32 g, 7.10 mmol, 71.0% yield). **IR** (neat, cm^{-1}) 3023 (m), 293 (s), 2924 (m), 2867 (m), 1595 (m), 1464 (m), 985 (s), 946 (s), 742 (s); *E,Z*- and *E,E*-isomer mixture: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46–7.37 (4H, m), 7.37–7.27 (4H, m), 7.27–7.17 (2H, m), 7.09 (1H, dd, *J* = 15.5, 11.2 Hz), 6.79 (1H, dd, *J* = 15.7, 10.4 Hz), 6.55 (1H, d, *J* = 15.6 Hz), 6.46 (1H, d, 15.7 Hz), 6.28–6.14 (2H, m), 5.83 (1H, dt, *J* = 15.0, 7.4 Hz), 5.57 (1H, dt, *J* = 10.7, 7.8 Hz), 2.20 (2H, td, *J* = 7.3, 1.5 Hz), 2.06 (2H, dd, *J* = 7.0, 7.0 Hz), 1.79–1.64 (2H, m), 0.97 (6H, d, *J* = 6.7 Hz), 0.94 (6H, d, *J* = 6.7 Hz); *E,Z*- and *E,E*-isomer mixture : **^{13}C NMR** (125 MHz, $CDCl_3$) δ 137.8, 134.7, 132.1, 131.7, 130.0, 129.5, 128.6, 127.4, 127.1, 126.4, 126.2, 124.7, 42.3, 37.2, 28.9, 28.7, 22.5, 22.4; Elemental Analysis calc'd for $C_{14}H_{18}$: C, 90.26; H, 9.74. found : C, 89.76; H, 9.82.



1l (1:1.6 *E,E*:*E,Z*)

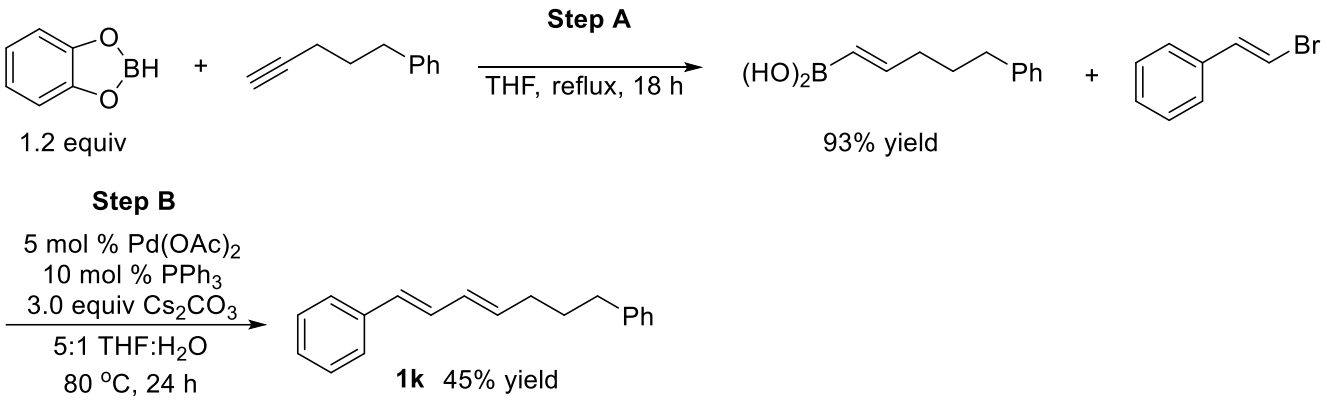
((1*E*)-6-(Benzyloxy)hexa-1,3-dien-1-yl)benzene (1l) : Prepared by General Method B for 12 h. The material was purified by flash silica gel chromatography (100% hexanes to 20:80 hexanes:EtOAc) to yield **1l** as a colorless oil (1.11 g, 4.21 mmol, 98.2% yield). *E,Z*-isomer (major): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43–7.16 (10H, m), 7.06 (1H, dd, *J* = 15.5, 11.2 Hz), 6.54 (1H, d, *J* = 15.6 Hz), 6.31–6.20 (1H, m), 5.56 (1H, dt, *J* = 10.4, 7.6 Hz), 2.54 (2H, s), 3.55 (2H, t, *J* = 6.9 Hz), 2.62 (2H, q, *J* = 7.1 Hz); *E,E*-isomer (minor): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43-7.16 (10H, m), 6.75 (1H, dd, *J* = 15.6, 10.5 Hz), 6.45 (1H, d, *J* = 15.7 Hz), 6.31–6.20 (1H, m), 5.83 (1H, dt, *J* = 14.6, 7.0 Hz), 4.53 (2H, s), 3.55 (2H, t, *J* = 6.8 Hz), 2.47 (2H, dt, *J* = 6.9, 6.9 Hz). Spectral data match those previously reported.[11]



1n (1:1.7 *E,E*:*E,Z*)

((1*E*)-Penta-1,3-dien-1-yl)cyclohexane (1n) : Prepared by General Method B for 12 h. The material was purified by flash silica gel chromatography (100% hexanes) to yield **1n** as a colorless oil (393 mg, 2.62 mmol, 27.1% yield). *E,Z*-isomer (major): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.29 (1H, dd, J = 15.3, 11.0 Hz), 6.03–5.92 (1H, m), 5.65–5.46 (1H, m), 5.37 (1H, dq, J = 14.1, 7.1 Hz), 1.74–0.82 (14H, m); *E,E*-isomer (minor): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.03–5.92 (2H, m), 5.65–5.46 (2H, m), 1.74–0.82 (14H, m). Spectral data matched those previously reported.[12]

3. Preparation of other internal diene derivatives

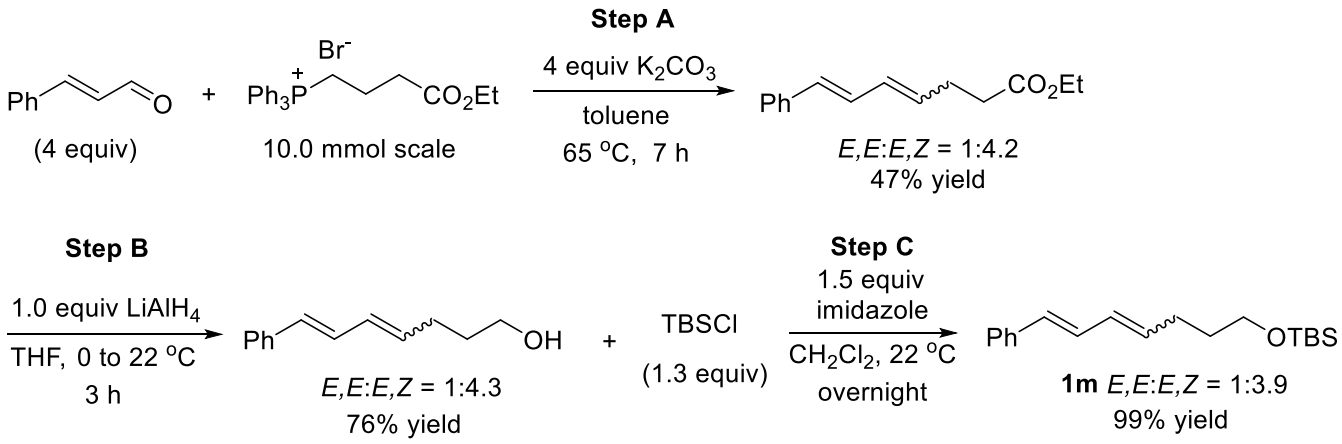


Step A: To a 2-neck 25-mL round-bottom flask fitted with a reflux condenser and equipped with a magnetic stirring rod was added 5-phenyl-1-pentyne (720 mg, 5.0 mmol, 1.0 equiv), catecholborane (720 mg, 6.00 mmol, 1.20 equiv) and THF (1 mL). The mixture was allowed to stir and then heated to 70 °C for 18 h. The reaction mixture was allowed to cool to ambient temperature and the solvent was then removed *in vacuo*. Then H_2O (3 mL) was added and the suspension was vigorously stirred for 4 h at room temperature. The solid was filtered and then recrystallized from water. The resulting vinylboronic acid was then filtered and dried *in vacuo* to give (*E*)-(5-phenylpent-1-en-1-yl)boronic acid (882 mg, 4.63 mmol, 92.8%) as a white solid.

Step B: In a glovebox, to a 25-mL screw-type flask equipped with a magnetic stirring rod was added palladium acetate (22.5 mg, 0.100 mmol, 5.00 mol %), triphenylphosphine (52.5 mg, 0.200 mmol, 10.0 mol %), Cs_2CO_3 (1.95 g, 6.00 mmol, 3.00 eqiuv), (*E*)-(5-phenylpent-1-en-1-yl)boronic acid (418 mg, 2.20 mmol, 1.10 equiv) and *trans-*β –bromostyrene (360 mg, 2.00 mmol, 1.00 equiv) with 5:1

THF:H_2O (6 mL) in the glovebox. The reaction flask was removed from the glovebox and then heated to 80 °C for 24 h. The reaction mixture was allowed to cool to ambient temperature and poured into a separatory funnel filled with water (20 mL). The organics were extracted with Et_2O (3 X 20 mL). The combined organic fractions were dried over $MgSO_4$, filtered, and concentrated. The residue was purified by silica gel column chromatography (hexanes) to give **1k** (224.0 mg, 0.901 mmol, 45.1%) as a white solid.

((1*E*,3*E*)-Hepta-1,3-diene-1,7-diyl)dibenzene (1k) : Modified from published procedure.[13,14] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52–7.14 (10H, m), 6.85 (1H, dd, *J* = 15.6, 10.4 Hz), 6.51 (1H, d, *J* = 15.6 Hz), 6.29 (1H, dd, *J* = 15.0, 10.4 Hz), 5.91 (1H, dt, *J* = 15.0, 7.0 Hz), 2.73 (2H, t, *J* = 7.5 Hz), 2.26 (2H, td, *J* = 7.5, 7.0 Hz), 1.84 (2H, t, *J* = 7.5 Hz). Spectral data matched those previously reported.[15]



Step A: To a 100-mL round-bottom flask equipped with a magnetic stirring rod was added [3-(ethoxycarbonyl)propyl]triphenylphosphonium bromide (4.57 g, 10.0 mmol, 1.00 equiv), K_2CO_3 (5.53 g, 40.0 mmol, 4.00 equiv) and toluene (20 mL). The mixture was allowed to stir and then heated to 65 °C. After 10 min, *trans*-cinnamaldehyde (5.3 mL, 40 mmol, 4.0 equiv) was added and the mixture was allowed to continue stirring for 7 h. The reaction mixture was then allowed to cool to ambient temperature and poured into a separatory funnel filled with water (100 mL). The organics were extracted with EtOAc (3 X 50 mL). The combined organic fractions were dried over $MgSO_4$, filtered, and concentrated. The residue was purified by silica gel column chromatography (100% hexanes to 80:20 hexanes:EtOAc) to give ethyl (6*E*)-7-phenylhepta-4,6-dienoate (1.09 g, 4.73 mmol, 47.3%) as a colorless oil.

Ethyl (6*E*)-7-phenylhepta-4,6-dienoate : *E,Z*-isomer (major): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (2H, d, J = 8.0 Hz), 7.33–7.25 (2H, m), 7.24–7.16 (1H, m), 7.05 (1H, dd, J = 15.5, 11.2 Hz), 6.53 (1H, d, J = 15.5 Hz), 6.18 (1H, t, J = 11.9 Hz), 5.47 (1H, dt, J = 11.1, 7.7 Hz), 4.12 (2H, q, J = 7.1 Hz), 2.61 (2H, q, J = 7.4 Hz), 2.42 (2H, t, J = 7.5 Hz), 1.24 (3H, t, J = 7.3 Hz) ; *E,E*-isomer (minor): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 (2H, d, J = 8.2 Hz), 7.33–7.25 (2H, m), 7.24–7.16 (1H, m), 6.77 (1H, dd, J = 15.8, 10.5 Hz), 6.45 (1H, d, J = 15.7 Hz), 6.28–6.22 (1H, m), 5.84–5.74 (1H, m), 4.13 (2H, q, J = 7.2 Hz), 2.63–2.58 (2H, m), 2.47–2.40 (2H, m), 1.24 (3H, t, J = 7.1 Hz). Spectral data matched those previously reported.[16]

Step B: In a 25-mL round-bottom flask with stir bar, lithium aluminum hydride (125 mg, 3.30 mmol, 1.10 equiv) was suspended in THF (4 mL). The suspension was allowed to stir and cool to 0 ^{o}C. A solution of ethyl (6*E*)-7-phenylhepta-4,6-dienoate (692 mg, 3.00 mmol, 1.00 equiv) in THF (3 mL) was added by cannula. The reaction mixture was allowed to warm to room temperature and stirr for 3 h. To this reaction mixture were added water (1 mL), 3.0 M aqueous sodium hydroxide (10 mL), and water (10 mL) successively. After stirring for 15 min, the resulting suspension was filtered through a celite pad, which was rinsed with ethyl acetate. The filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (100% hexanes to 80:20 hexanes:EtOAc) to give (6*E*)-7-phenylhepta-4,6-dien-1-ol (428 mg, 2.27 mmol, 75.8%) as a colorless oil.

(6*E*)-7-Phenylhepta-4,6-dien-1-ol : *E,Z*-isomer (major): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (2H, d, J = 7.7 Hz), 7.30 (2H, t, J = 6.8 Hz), 7.25–7.15 (1H, m), 7.07 (1H, dd, J = 15.5, 11.1 Hz), 6.53 (1H, d, J = 15.5 Hz), 6.18 (1H, t, J = 10.9 Hz), 5.52 (1H, q, J = 9.1, 8.5 Hz), 3.68 (2H, td, J =6.2, 1.8 Hz), 2.38 (2H, q, J = 7.5 Hz), 1.73–1.66 (2H, m), 1.38 (1H, s); *E,E*-isomer (minor): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 (2H, d, J = 7.6 Hz), 7.34–7.26 (2H, m), 7.25–7.15 (1H, m), 6.74 (1H, dd, J = 15.1, 10.2 Hz), 6.44 (1H, d, J = 15.4 Hz), 6.26–6.16 (1H, m), 5.81 (1H, dt, J = 15.6, 7.3 Hz), 3.70–3.65 (2H, m), 2.23 (2H, q, J = 7.0 Hz), 1.73–1.66 (3H, m). Spectral data matched those previously reported.[17]

Step C: In a 25-mL round-bottom flask with stir bar, (6*E*)-7-phenylhepta-4,6-dien-1-ol (188 mg, 1.00 mmol, 1.00 equiv) in dichloromethane (5 mL) was treated with *tert*-butyldimethylsilyl chloride (196 mg, 1.30 mmol, 1.30 equiv) and imidazole (102 mg, 1.50 mmol, 1.50 equiv). The resulting solution was allowed to stir overnight and then treated with water (10 mL). The organic layer was separated, and the aqueous layer was washed with hexanes (3 x 20 mL). The combined organic layerss were washed with water (50 mL), and saturated aqueous sodium bicarbonate (50 mL) and then dried over

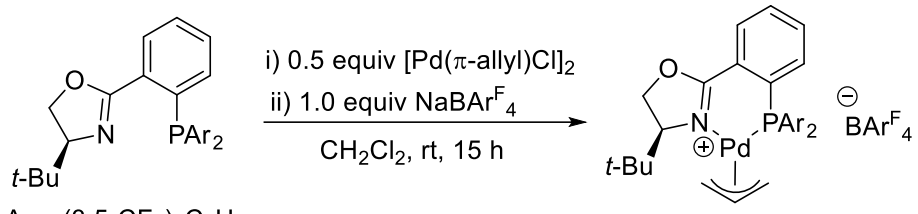
$MgSO_4$. After filtration, the solvent was removed under reduced pressure.The residue was purified by silica gel column chromatography (hexanes) to give **1m** (300 mg, 0.992 mmol, 99.2%) as a colorless oil.

***tert*-Butyldimethyl(((6*E*)-7-phenylhepta-4,6-dien-1-yl)oxy)silane (1m):** *E,Z*-isomer (major): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 (2H, d, J = 8.0 Hz), 7.29 (2H, t, J = 7.5 Hz), 7.20 (1H, t, J = 7.3 Hz), 7.06 (1H, dd, J = 15.5, 11.1 Hz), 6.51 (1H, d, J = 15.6 Hz), 6.17 (1H, t, J = 11.0 Hz), 5.57–5.47 (1H, m), 3.64 (2H, t, J = 6.4 Hz), 2.35 (2H, q, J = 5.5 Hz), 1.64 (2H, p, J = 6.6 Hz), 0.89 (9H, s), 0.04 (6H, s); *E,E*-isomer (minor): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 (2H, d, J = 7.7 Hz), 7.31–7.26 (2H, m), 7.21-7.16 (1H, m), 6.74 (1H, dd, J = 15.6, 10.5 Hz), 6.42 (1H, d, J = 15.8 Hz), 6.24–6.13 (1H, m), 5.81 (1H, dt, J = 14.4, 6.8 Hz), 3.66–3.61 (2H, m), 2.19 (2H, q, J = 7.0 Hz), 1.67–1.60 (2H, m), 0.89 (9H, s), 0.04 (6H, s). Spectral data matched those previously reported.[18]

III. Preparation of Pd-1

1. Preparation of Pd–PHOX complex of the type [L(η^3-allyl)Pd]BAr$^F_4$

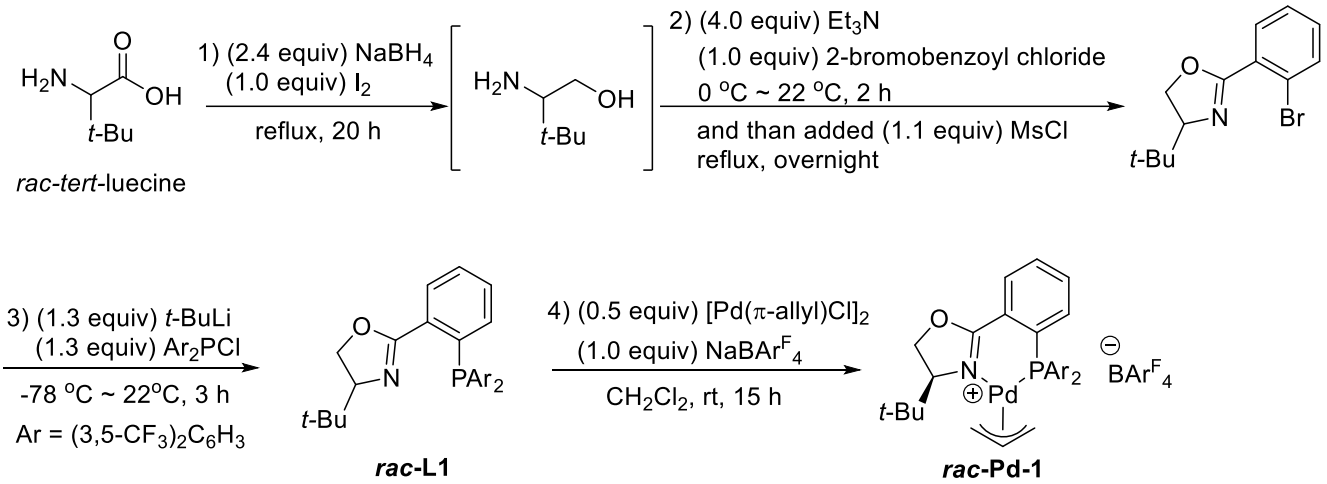
General Procedure: This method is exemplified by the preparation of **Pd-1**:



Pd-1: To a 100-mL round-bottom flask, equipped with a magnetic stirring rod, inside an N_2-filled glovebox, was added [Pd(η^3-allyl)Cl]$_2$ (173 mg, 0.500 mmol, 0.500 equiv), **L1**[19] (543 mg, 1.00 mmol, 1.00 equiv), and CH_2Cl_2 (25 mL). The resulting yellow solution was allowed to stir at ambient temperature for *ca.* 20 min before NaBAr$^F_4$ (886 mg, 1.00 mmol, 1.00 equiv). The reaction was allowed to stir vigorously until becoming cloudy and black in color. After 15 h, the reaction flask was removed from the glovebox and the mixture concentrated *in vacuo*. The resulting gray solid dissociated in CH_2Cl_2 and then washed water. The organic layer was dried over $MgSO_4$, filtered and then the solvent evaporated under reduced pressure. The resulting white to gray solid was used directly without further purification (1.58 g, 0.948 mmol, 94.8% yield). Product exists as a mixture of *exo* and *endo* complexes (*ca.* 70:30 mixture) that will hereby be referred to as major and minor, respectively. See Adamson *et al.* for a similar analysis of a related complex with a BF_4 counterion.[20] **IR** (neat, cm^{-1}) 1613 (m), 1353 (s), 1273 (s), 1113 (s), 886 (m), 838 (m), 712 (m), 681 (s); **^{1}H NMR** (400 MHz, CD_2Cl_2) δ 8.40–7.55 (21H, m, major + minor), 7.09 (0.7H, ddd, J = 11.2, 7.7, 1.4 Hz, major), 7.00 (0.3H, ddd, J = 11.3, 7.8, 1.4 Hz, minor), 5.94–5.77 (1H, m, major + minor), 4.97 (0.7H, ddd, J = 7.8, 5.7, 2.5 Hz, major), 4.86 (0.3H, td, J = 7.6, 2.4 Hz, minor), 4.65–4.31 (2H, m, major + minor), 4.11–3.96 (2H, m, major + minor), 3.74–3.66 (1H, m, major + minor), 3.37–3.26 (0.3H, m, minor), 2.80 (0.7H, d, J = 12.2 Hz, major), 0.64 (2.5H, s, minor), 0.56 (6.5H, s, major); **^{13}C NMR** (125 MHz, CD_2Cl_2) δ {C–F decoupled} (note: spectrum is complex due to mixture of diastereomeric species and as a result many peaks overlap) 166.1, 162.9, 162.5, 162.1, 161.7, 135.4, 134.7, 134.5, 134.3, 134.2,

132.9, 132.8, 129.4, 127.9, 127.3, 125.1, 124.1, 123.1, 122.9, 122.7, 118.0, 84.5, 84.3, 82.8, 82.1, 81.4, 81.2, 70.5, 70.4, 66.3, 61.4, 54.3, 54.1, 53.8, 53.6, 53.4, 34.9, 25.4, 14.9.; **^{19}F NMR** (376 MHz, CD_2Cl_2) δ -62.9 (major), -63.2 (minor), -63.6 (medium); **^{31}P NMR** (162 MHz, CD_2Cl_2) δ 25.3 (minor), 24.1 (major); **MALDI-MS** $[M]^+$ calc'd for $C_{32}H_{27}F_{12}NOP[^{106}Pd]$: 806.0668, found: 806.0688.

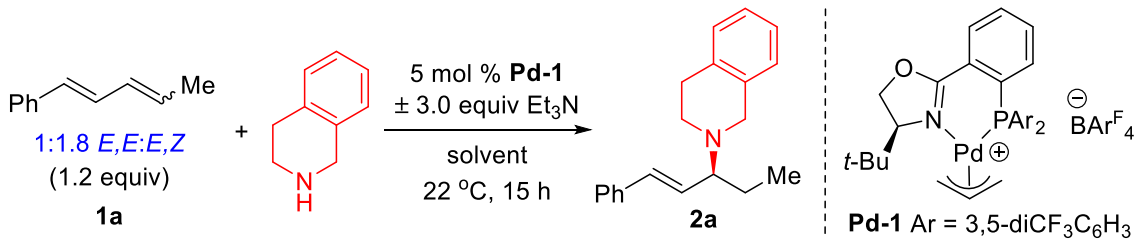
2. Preparation of Pd–*rac*-PHOX complex of the type [L(η^3-allyl)Pd]BAr$^F_4$



Step 1: This procedure was adapted from: Krout, M. R.; Mohr, J. T.; Stoltz, B. M. *Org. Synth*. **2009,** *86,* 181. The 250 mL round-bottom flask was charged with *rac*-*tert*-leucine (1.31 g, 10.0 mmol, 1.00 equv) and THF (30 mL) under a positive pressure of nitrogen. The resulting slurry was cooled to 0 ºC in a dry ice-acetone bath and $NaBH_4$ (908 mg, 24.0 mmol, 2.40 equiv) was added in one portion. A solution of I_2 (2.54 g, 10.0 mmol, 1.00 equiv) in THF (10 mL) was transferred dropwise over 1 hours. After the addition was complete, the cooling bath was removed and replaced by a condenser and the reaction was heat to reflux (80 °C oil bath). After 20 h the reaction was allowed to cool to ambient temperature and methanol (10 mL) was added slowly, resulting in an almost clear solution. After stirring for 30 min the solution was quantitatively transferred to a 250 mL round-bottom flask with MeOH (5 mL) and concentrated on a rotary evaporator under reduced pressure (40 °C) to a white semi-solid. The resulting material was dissolved in 20 wt % aqueous KOH (25 mL) and stirred for 12 h at ambient temperature. The aqueous phase was extracted with CH_2Cl_2 (5 × 30 mL) and the combined organic extracts were dried over $MgSO_4$, filtered, and concentrated on a rotary evaporator under reduced pressure and dried under vacuum to give crude (*S*)-*tert*-leucinol (628 mg, 5.36 mmol, 53.6%) as a colorless oil. This material was used in the following step without further purification. Step 2, 3 and 4 were prepared by previously methods.[19]

IV. Supplemental Screening Data

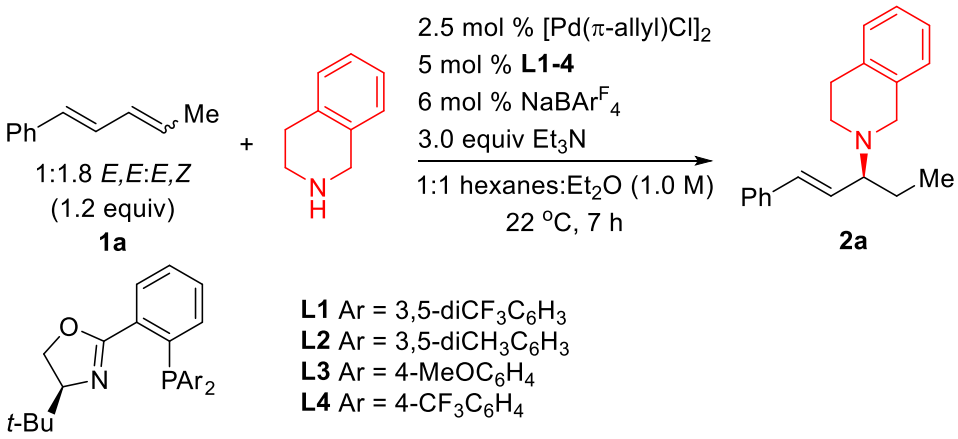
Table S1. Reaction optimization



entry	solvent	3 equiv Et_3N (Y/N)	yield (%)[a]	*er*[b]
1	CH_2Cl_2	Y	43	54:46
2	Et_2O	Y	42	94:6
3	THF	Y	5	94:6
4	1,4-dioxane	Y	27	89:11
5	cyclopentyl methyl ether	Y	34	94:6
6	*t*-butyl methyl eher	Y	20	95:5
7[c]	hexanes	Y	27	91:9
8	hexanes	Y	62	80:20
9[d]	hexanes	Y	65	65:35
10	hexanes	N	11	85:15
11[e]	hexanes	Y	27	90:10
12	1:1 hexanes:Et_2O	N	13	93:7
13	1:1 hexanes:Et_2O	Y	65	93:7
14[f]	1:1 hexanes:Et_2O	Y	63	96.5:3.5

Reaction conditions: **1a** (0.24 mmol), THIQ (0.2 mmol), Et_3N (0.6 mmol) and **Pd-1** were allowed to stir in solvent (0.2 mL, 1.0 M) at room temperature under N_2.[a]Isolated yield. [b]Enantiomeric ratio determined by HPLC analysis of purified products in comparison with authentic racemic standards. [c]Use of 2.5 mol % **Pd-1**. [d]Use of 10 mol % **Pd-1**. [e]Reaction temperature : 0 °C. [f]Reaction time : 7 h.

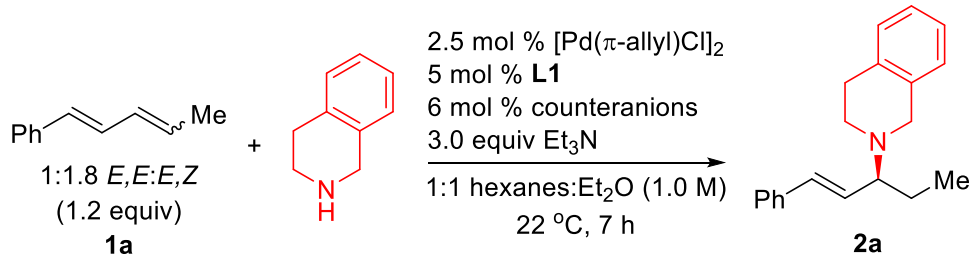
Table S2. Other PHOX ligand screened



entry	PHOX ligands	yield (%)[a]	er[b]
1	**L1**	56	96.5:3.5
2	**L2**	45	92:8
3	**L3**	23	90:10
4	**L4**	47	85:15

Reaction conditions: **1a** (0.24 mmol), THIQ (0.2 mmol) and Et_3N (0.6 mmol) in the presence of $[Pd(\pi\text{-allyl})Cl]_2$ (2.5 mol %), PHOX ligands (5 mol %) and $NaBAr^F_4$ (6 mol %) were allowed to stir in 1:1 hexanes:Et_2O (0.2 mL) under N_2. [a]Isolated yield. [b]Enantiomeric ratio determined by HPLC analysis of purified products in comparison with authentic racemic standards.

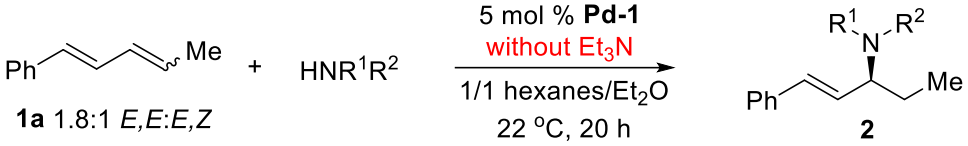
Table S3. Other counteranions screened



entry	counteranions	yield (%)	er
1	AgOTf	<5	-
2	$AgAbF_6$	<5	-
3	$AgPF_4$	<5	-
4	$AgBF_4$	<5	-

Reaction conditions: **1a** (0.24 mmol), THIQ (0.2 mmol) and Et_3N (0.6 mmol) in the presence of $[Pd(\pi\text{-allyl})Cl]_2$ (2.5 mol %), **L1** (5 mol %) and counter anion (6 mol %) were allowed to stir in 1:1 hexanes:Et_2O (0.2 mL) under N_2.

Table S4. Hydroamination reactions under the optimum reactions without Et_3N

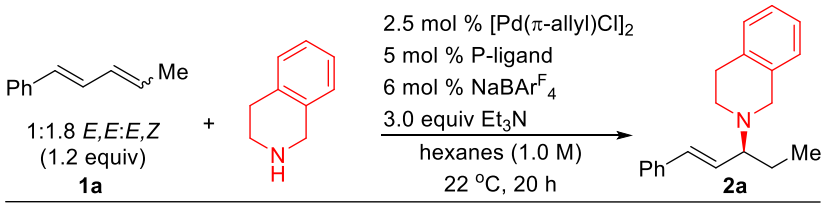


1a 1.8:1 *E,E*:*E,Z* **2**

entry	HNR^1R^2	yield (%)[a]	er[b]
1	THIQ	13	93:7
2	morpholine	38	95:5
3	*N*-methylbenzylamine	28	77:23
4	indoline	48	95:5
5	aniline	7	94:6

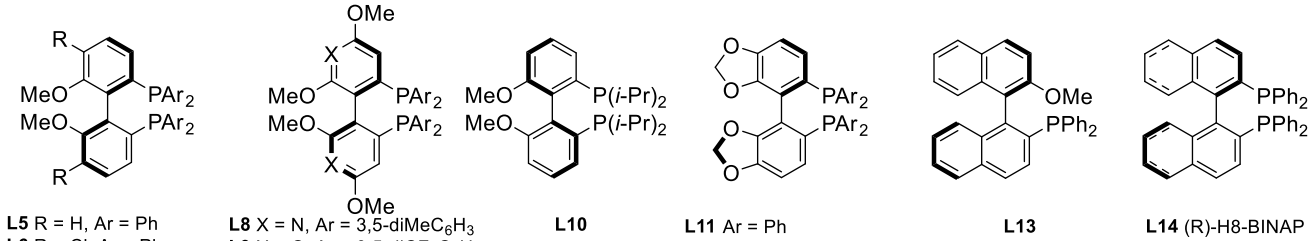
Reaction conditions: **1a** (0.24 mmol), amine (0.2 mmol), Et_3N (0.6 mmol) and **Pd-1** were allowed to stir in solvent (0.2 mL, 1.0 M) at room temperature under N_2.[a]Isolated yield. [b]Enantiomeric ratio determined by HPLC analysis of purified products in comparison with authentic racemic standards.

Table S5. Other chiral phosphine ligands screened



entry	Phosphine ligands	conv. (%)	yield (%)[a]	er[b]
1	**L5** (*R*)-MeO-BIPHEP	44	31	75 : 25
2	**L6** (*R*)-Cl-MeO-BIPHEP	58	43	72 : 28
3	**L7** (*R*)-DTBM-MeO-BIPHEP	16	4	49 : 51
4	**L8** (*R*)-Xylyl-P-Phos	23	4	49 : 51
5	**L9** (*R*)-BTFM-GarPhos	23	4	53 : 47
6	**L10** (*S*)-*i*Pr-MeO-BIPHEP	13	13	56 : 44
7	**L11** (*R*)-SEGPhos	58	40	73 : 27
8	**L12** (*R*)-DTBM-SEGPhos	<5	2	38 : 62
9	**L13** (*R*)-MOP	44	36	47 : 53
10	**L14** (*R*)-H8-BINAP	33	13	60 : 40
11	**L15** (*R*)-BINAP	37	31	60 : 40
12	**L16** (*R*,*R*)-Taniaphos	51	36	47 : 53
13	**L17** Josiphos	13	6	33 : 67
14	**L18** (*R*,*R*)-QuinoxP	13	5	84 : 16
15	**L19** (*R*,*R*)-Me-DuPhos	<2	-	-
16	**L20** (*S*,*S*)-DIPAMP	<2	-	-
17	**L21** (*S*,*S*)-BDPP	40	27	56 : 44

Reaction conditions : **1a** (0.24 mmol), THIQ (0.2 mmol) and Et_3N (0.6 mmol) in the presence of $[Pd(\pi\text{-allyl})Cl]_2$ (2.5 mol %), phosphine ligands (5 mol %) and $NaBAr^F_4$ (6 mol %) were allowed to stir in hexanes (0.2 mL) under N_2. [a]Isolated yield. [b]Enantiomeric ratio determined by HPLC analysis of purified products in comparison with authentic racemic standards.



L5 R = H, Ar = Ph
L6 R = Cl, Ar = Ph
L7 R = H, Ar = (3,5-DTBM)C_6H_2

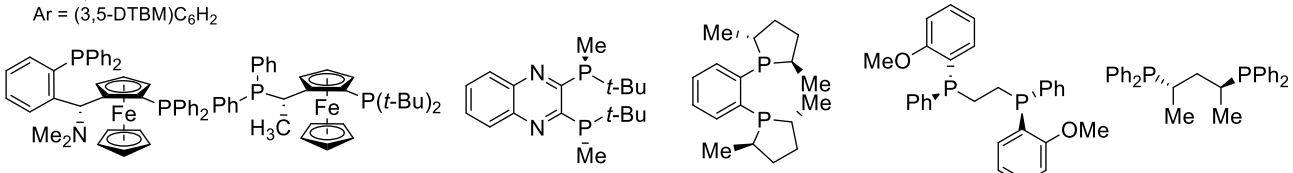
L8 X = N, Ar = 3,5-diMeC_6H_3
L9 X = C, Ar = 3,5-di$CF_3C_6H_3$

L10

L11 Ar = Ph
L12 Ar = (3,5-DTBM)C_6H_2

L13

L14 (R)-H8-BINAP
L15 (R)-BINAP



L16

L17

L18

L19

L20

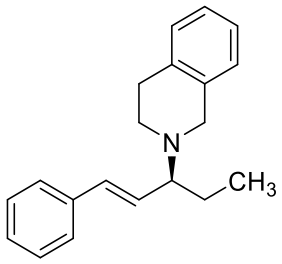
L21

V. Substrate Scope

Hydroamination of Internal Dienes

General Method C: Inside an N_2-filled glovebox, to a microwave vial equipped with a magnetic stirring rod was added successively: **Pd-1** catalyst (0.01 mmol, 5 mol%), appropriate nucleophile (0.20 mmol, 1.0 equiv), 1:1 hexanes:Et_2O (0.2 mL), appropriate diene (0.24 mmol, 1.20 equiv), and lastly Et_3N (84 μL, 0.60 mmol, 3.0 equiv). Reactions were allowed to stir at room temperature for the specified amount of time, then diluted with 1.0 mL of 1:1 hexanes:EtOAc, and filtered through a short plug of neutral alumina, eluting with ca. 10 mL of 1:1 hexanes:EtOAc. The solution was then concentrated in vacuo and the unpurified material was analyzed by ^{1}H NMR to determine the regiomeric ratio. The material was purified by flash silica gel chromatography.

The results for the substrate scope in the manuscript are an average of two runs, but for clarity, the results shown below are one of the two runs.



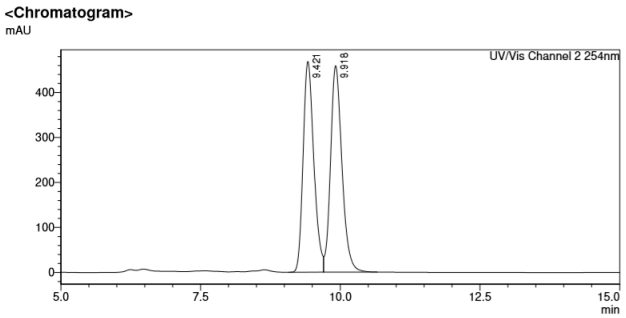
2a

(*S*,*E*)-2-(1-Phenylpent-1-en-3-yl)-1,2,3,4-tetrahydroisoquinoline (2a): Prepared by General Method C using **Pd-1** at 22 ˚C for 7 h. The material was purified by flash silica gel chromatography (100% hexanes to 80:20 hexanes:EtOAc) to yield **2a** as a colorless oil (35.0 mg, 0.126 mmol, 63.0 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (2H, d, J = 8.2 Hz), 7.32 (2H, t, J = 7.6 Hz), 7.27–7.20 (1H, m), 7.15–6.99 (4H, m), 6.52 (1H, d, J = 15.9 Hz), 6.21 (1H, dd, J = 15.9, 8.9 Hz), 3.87–3.72 (2H, m), 3.05–2.74 (4H, m), 1.95–185 (1H, m), 1.71–1.60 (1H, m), 0.96 (3H, t, J = 7.4 Hz); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 137.1, 135.3, 134.7, 132.8, 129.8, 128.7, 128.6, 127.4, 125.5, 69.0, 53.2, 47.2, 29.6, 25.3, 11.1. Spectral data match those previously reported.[19, 21]

$[\alpha]_D^{27}$ = –30.3 (c = 1.0, $CHCl_3$) for a sample of 96.5:3.5 er.

Compound **2a** was prepared in reference 21 in enantiomerically enriched form. The sign of the rotation is the same as we observed for **2a** in hydroamination. Thus, we have assigned **2a** as the (*S*)-enantiomer and make all other stereochemical assignments by inference. The observed enantiomer matches that in our terminal diene hydroamination as well; see reference 19.

HPLC: Column: Chiralpak 1-A3 (3 μm, 4.6 mm X 150 mm). Mobile phase: 95:5 *i*-PrOH (with 0.1% Et_2NH):MeCN, 0.3 mL/min. Detection wavelength: 254 nm. Er = 96.5:3.5.



<Peak Table>
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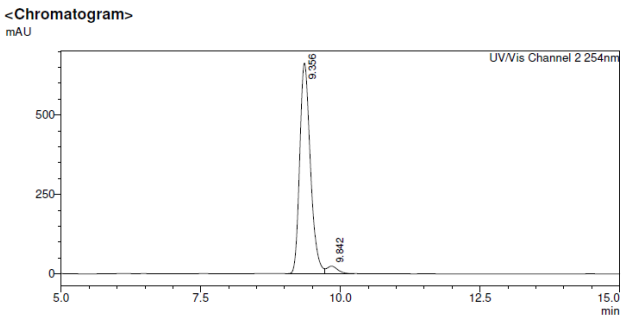

<Peak Table>
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2	9.842	317329	3.464
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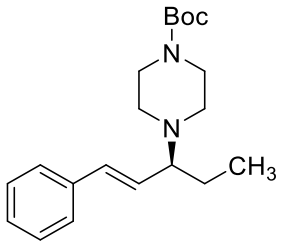
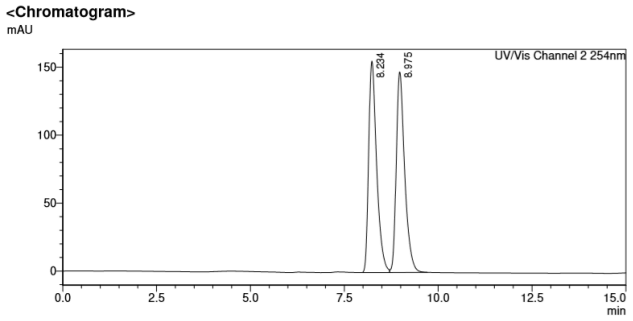


2b

***tert*-Butyl (*S*,*E*)-4-(1-phenylpent-1-en-3-yl)piperazine-1-carboxylate (2b):** Prepared by General Method C using **Pd-1** at 22 ˚C for 20 h. The material was purified by flash silica gel chromatography (100% hexanes to 50:50 hexanes:EtOAc) to yield **2b** as colorless oil (35.0 mg, 0.106 mmol, 53.0 % yield).* **IR** (neat, cm^{-1}) 2969 (m), 2956 (m), 2927 (m), 2893 (m), 2866 (m), 2820 (m), 1678 (s), 1478 (s), 1248 (s), 1213 (br), 1129 (s), 972 (m); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 (2H, d, J = 7.1 Hz), 7.29 (2H, t, J = 7.5 Hz), 7.21 (1H, t, J = 7.2 Hz), 6.41 (1H, d, J = 15.9 Hz), 6.06 (1H, dd, J = 15.9, 9.0 Hz), 3.43–3.38 (4H, m), 2.80 (1H, td, J = 8.9, 4.6 Hz), 2.63–2.35 (4H, m), 1.74 (1H, ddd, J = 14.8, 7.4, 3.6 Hz), 1.59–1.46 (1H, m), 1.42 (9H, s), 0.89 (3H, t, J = 7.4 Hz) ; **^{13}C NMR** (125 MHz, $CDCl_3$) δ 154.7, 136.9, 132.9, 129.4, 128.6, 127.5, 126.3, 79.5, 69.6, 49.8, 44.2, 28.4, 25.0, 10.9; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{20}H_{30}N_2O_2$: 330.2307, found: 330.2308.

$[\alpha]_D^{27}$ = –15.1 (c = 1.0, $CHCl_3$) for a sample of 96:4 er.

HPLC: Column: Chiralpak 1-A3 (3 μm, 4.6 mm X 150 mm). Mobile phase: 70:30 *i*-PrOH (with 0.1% Et_2NH):MeOH, 0.3 mL/min. Detection wavelength: 254 nm. Er = 96:4.



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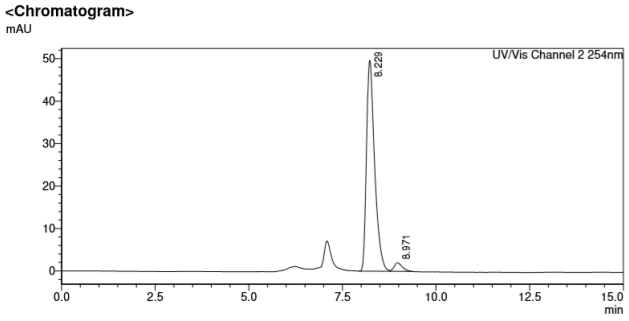

<Peak Table>
UV/Vis Channel 2 254nm

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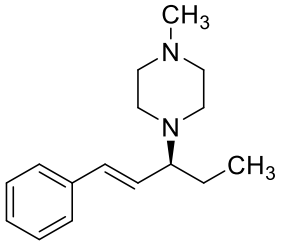
2	8.971	30695	3.935
Total		780150	100.000

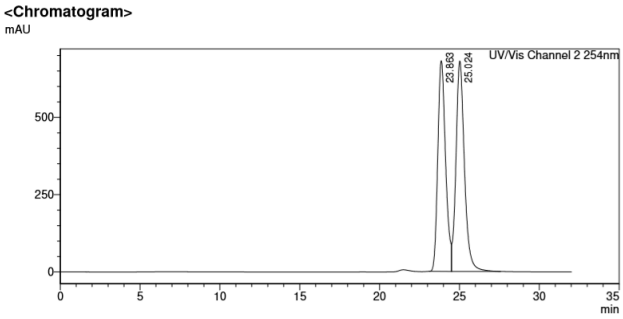


2c

(*S*,*E*)-1-Methyl-4-(1-phenylpent-1-en-3-yl)piperazine (2c): Prepared by General Method C using **Pd-1** at 22 ˚C for 20 h. The material was purified by flash silica gel chromatography (100% hexanes to 50:50 hexanes:EtOAc) to yield **2b** as a colorless oil (26.0 mg, 0.106 mmol, 53.2 % yield). **IR** (neat, cm^{-1}) 2960 (m), 2931 (s), 2873 (w), 279 (s), 1493 (m), 1451 (s), 1283 (s), 1160 (s), 967 (S); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 (2H, d, J = 7.1 Hz), 7.27 (2H, J = 7.1 Hz), 7.18 (1H, t, J = 15.9 Hz), 6.41 (1H, d, J = 15.9 Hz), 6.08 (1H, dd, J = 15.9, 9.0 Hz), 2.75 (1H, td, J = 9.1, 4.3 Hz), 2.70–2.29 (8H, m), 2.25 (3H, s), 1.83–1.67 (1H, m), 1.57–1.41 (1H, m), 0.87 (3H, t, J = 7.4 Hz); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 137.1, 132.7, 130.0, 128.5, 127.3, 126.3, 69.6, 55.5, 50.0, 46.0, 25.0, 11.0; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{16}H_{24}N_2$: 244.1939, found: 244.1940.

$[\alpha]_D^{27}$ = –15.4 (c = 1.0, $CHCl_3$) for a sample of 90.5:9.5 er.

HPLC: Column: Chiralpak 1-A3 (3 μm, 4.6 mm X 150 mm). Mobile phase: 70:30 *i*-PrOH (with 0.1% Et_2NH):MeOH, 0.1 mL/min. Detection wavelength: 254 nm. Er = 90.5:9.5.



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UV/Vis Channel 2 254nm

Peak#	Ret. Time	Area	Area%
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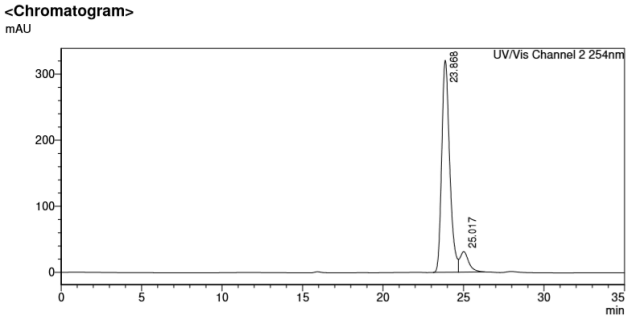

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UV/Vis Channel 2 254nm

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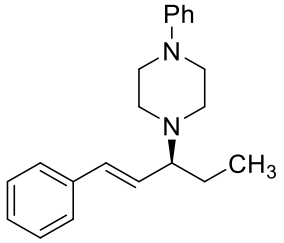
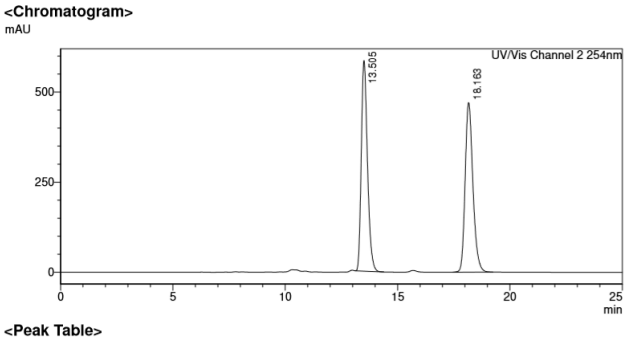


2d

(*S*,*E*)-1-Phenyl-4-(1-phenylpent-1-en-3-yl)piperazine (2d): Prepared by General Method C using **Pd-1** at 22 ˚C for 20 h. The material was purified by flash silica gel chromatography (100% hexanes to 50:50 hexanes:EtOAc) to yield **2d** as white solid (40.0 mg, 0.131 mmol, 65.3 % yield). **IR** (neat, cm^{-1}) 2965 (m), 2923 (m), 2873 (m), 2832 (m), 2806 (m), 1595 (s), 1492 (s), 1453 (s), 1228 (m), 1138 (s), 1007 (s), 969 (s); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (2H, d, J = 7.2 Hz), 7.32 (2H, t, J = 7.6 Hz), 7.30–7.21 (3H, m), 6.93 (2H, d, J = 7.9 Hz), 6.85 (1H, t, J = 7.2 Hz), 6.49 (1H, d, J = 15.9 Hz), 6.15 (1H, dd, J = 15.9, 9.1 Hz), 3.30–3.12 (4H, m), 2.92–2.57 (5H, m), 1.84 (1H, dtt, J = 14.9, 7.4, 3.7 Hz), 1.64–1.49 (1H, m), 0.94 (3H, t, J = 7.4 Hz); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 151.4, 137.0, 132.9, 129.8, 129.1, 128.6, 127.5, 126.3, 119.7, 116.1, 69.7, 50.1, 49.6, 25.1, 11.0; **MP** = 86–88 ºC; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{21}H_{26}N_2$: 306.2096, found: 306.2099.

$[\alpha]_D^{27}$ = –15.5 (c = 1.0, $CHCl_3$) for a sample of 94.5:5.5 er.

HPLC: Column: Chiralpak 1-A3 (3 μm, 4.6 mm X 150 mm). Mobile phase: 70:30 *i*-PrOH (with 0.1% Et_2NH):MeOH, 0.3 mL/min. Detection wavelength: 254 nm. Er = 94.5:5.5.



<Peak Table>
UV/Vis Channel 2 254nm

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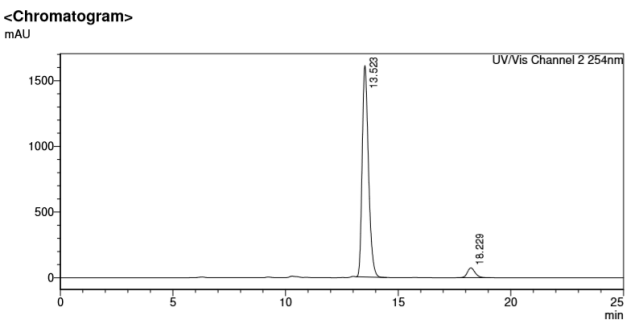
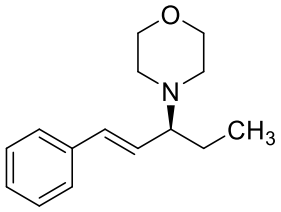


<Peak Table>
UV/Vis Channel 2 254nm

Peak#	Ret. Time	Area	Area%
1	13.523	31305878	94.553
2	18.229	1803320	5.447
Total		33109199	100.000

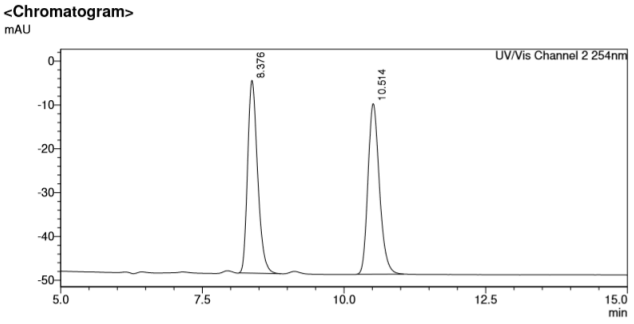


2e

(*S*,*E*)-4-(1-Phenylpent-1-en-3-yl)morpholine (2e): Prepared by General Method C using **Pd-1** at 22 ˚C for 20 h. The material was purified by flash silica gel chromatography (100% hexanes to 80:20 hexanes:EtOAc) to yield **2e** as colorless oil (33.0 mg, 0.143 mmol, 71.3 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 (2H, d, J = 7.7 Hz), 7.30 (2H, t, J = 7.5 Hz), 7.24–7.19 (1H, m), 6.43 (1H, d, J = 15.9 Hz), 6.07 (1H, dd, J = 15.9, 9.0 Hz), 3.70 (4H, t, J = 4.5 Hz), 2.74 (1H, td, J = 9.0, 4.4 Hz), 2.63–2.52 (4H, m), 1.76 (1H, dtt, J = 14.9, 7.4, 4.3 Hz), 1.54–1.41 (1H, m); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 136.9, 133.0, 129.7, 128.6, 127.5, 126.3, 70.1, 67.3, 50.8, 24.7, 10.8. Spectral data match those previously reported.[22]

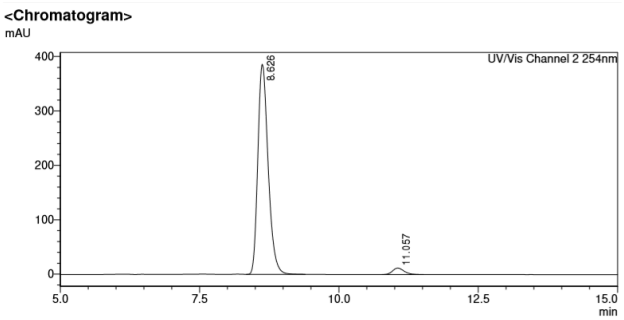
$[\alpha]_D^{27}$ = –24.7 (c = 1.0, $CHCl_3$) for a sample of 96.5:3.5 er.

HPLC: Column: Chiralpak 1-A3 (3 μm, 4.6 mm X 150 mm). Mobile phase: 95:5 *i*-PrOH (with 0.1% Et_2NH):MeCN, 0.3 mL/min. Detection wavelength: 254 nm. Er = 96.5:3.5.



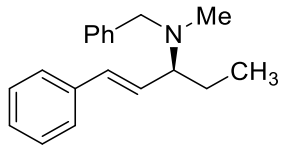
<Peak Table>
UV/Vis Channel 2 254nm

Peak#	Ret. Time	Area	Area%
1	8.376	543371	49.897
2	10.514	545614	50.103
Total		1088986	100.000



<Peak Table>
UV/Vis Channel 2 254nm

Peak#	Ret. Time	Area	Area%
1	8.626	4946049	96.621
2	11.057	172959	3.379
Total		5119008	100.000

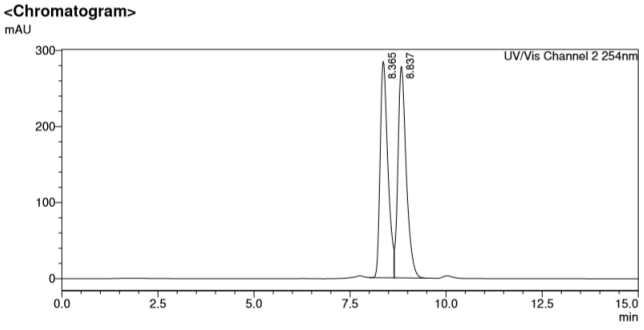


2f

(*S*,*E*)-*N*-Benzyl-N-methyl-1-phenylpent-1-en-3-amine (2f): Prepared by General Method C using **Pd-1** at 22 ˚C for 15 h. The material was purified by flash silica gel chromatography (100% hexanes to 80:20 hexanes:EtOAc) to yield **2f** as colorless oil (33.0 mg, 0.124 mmol, 62.2 % yield). **IR** (neat, cm^{-1}) 3060 (w), 3025 (m), 2959 (m), 2929 (m), 2872 (m), 2786 (m), 1739 (m), 1450 (s), 1239 (s), 967 (s); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (2H, d, J = 7.2 Hz), 7.37–7.27 (6H, m), 7.27–7.20 (2H, m), 6.44 (1H, d, J = 15.9 Hz), 6.21 (1H, dd, J = 15.9, 8.9 Hz), 3.71 (1H, d, J = 13.3 Hz), 3.48 (1H, J = 13.3 Hz), 3.01 (1H, td, J = 8.5, 5.9 Hz), 2.22 (3H, s), 1.86–1.74 (1H, m), 1.60 (1H, dt, J =13.6, 7.6 Hz), 0.95 (3H, t, 7.4 Hz); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 140.0, 137.3, 132.8, 129.1, 128.9, 128.6, 128.2, 127.4, 126.8, 126.3, 67.6, 58.3, 37.8, 25.8, 11.2; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{19}H_{23}N$: 265.1830, found: 265.1827.

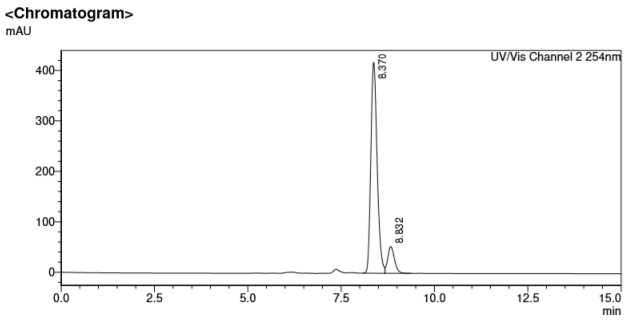
$[\alpha]_D^{27}$ = –15.6 (c = 1.0, $CHCl_3$) for a sample of 88.5:11.5 er.

HPLC: Column: Chiralpak 1-A3 (3 μm, 4.6 mm X 150 mm). Mobile phase: 70:30 *i*-PrOH (with 0.1% Et_2NH):MeOH, 0.3 mL/min. Detection wavelength: 254 nm. Er = 88.5:11.5.



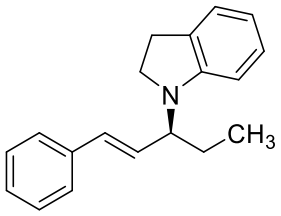
<Peak Table>
UV/Vis Channel 2 254nm

Peak#	Ret. Time	Area	Area%
1	8.365	4004046	49.079
2	8.837	4154281	50.921
Total		8158326	100.000



<Peak Table>
UV/Vis Channel 2 254nm

Peak#	Ret. Time	Area	Area%
1	8.370	4957971	88.269
2	8.832	658897	11.731
Total		5616868	100.000

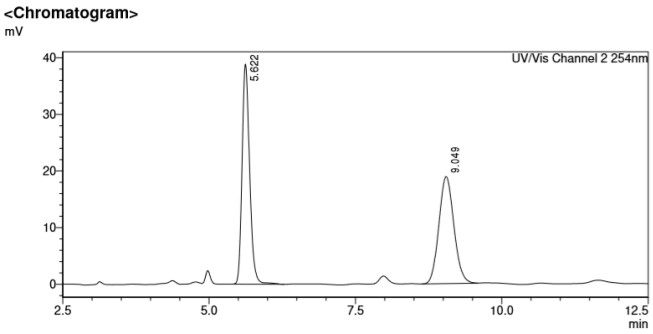


2g

(*S*,*E*)-1-(1-Phenylpent-1-en-3-yl)indoline (2g): Prepared by General Method C using **Pd-1** at 22 ˚C for 1 h. The material was purified by flash silica gel chromatography (100% hexanes to 80:20 hexanes:EtOAc) to yield **2g** as colorless oil (41.0 mg, 0.156 mmol, 77.8 % yield). **IR** (neat, cm^{-1}) 3023 (w), 2960 (m), 2927 (m), 2871 (w), 2843 (w), 1605 (s), 1486 (s), 1384 (m), 1157 (m), 1022 (m), 963 (s); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 (2H, d, J = 7.8 Hz), 7.29 (2H, t, J = 7.5 Hz), 7.22 (1H, t, J = 7.2 Hz), 7.05 (2H, t, J = 7.6 Hz), 6.60 (1H, t, J = 7.3 Hz), 6.55 (1H, d, J = 16.0 Hz), 6.50 (1H, d, J = 7.8 Hz), 6.21 (1H, dd, J = 16.0, 7.0 Hz), 4.03 (1H, q, J = 7.1 Hz), 3.53–3.40 (2H, m), 2.98 (2H, t, J = 8.4 Hz), 1.90–1.74 (2H, m), 1.04 (3H, t, J = 7.4 Hz); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 151.5, 137.0, 131.9, 129.9, 128.5, 128.2, 127.4, 127.3, 126.4, 124.5, 116.8, 107.2, 59.0, 46.9, 28.3, 25.2, 11.4; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{19}H_{21}N$: 263.1674, found: 263.1674.

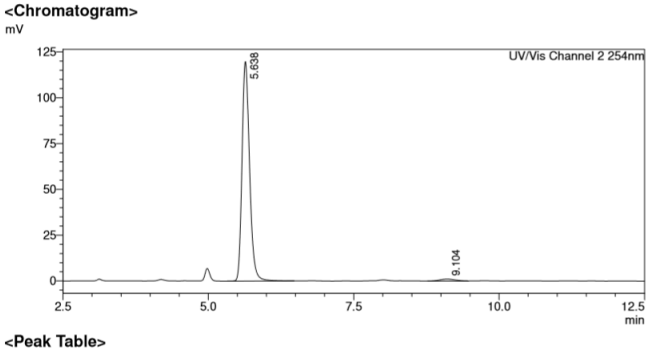
$[\alpha]_D^{27}$ = –17.0 (c = 1.0, $CHCl_3$) for a sample of 98.5:1.5 er.

HPLC: Column: Cellulose III (3 μm, 4.6 mm X 250 mm). Mobile phase: 10:90 *i*-PrOH:hexanes, 1.0 mL/min. Detection wavelength: 254 nm. Er = 98.5:1.5.



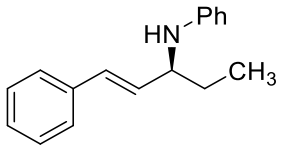
<Peak Table>
UV/Vis Channel 2 254nm

Peak#	Ret. Time	Area	Area%
1	5.622	348268	50.761
2	9.049	337830	49.239
Total		686098	100.000



<Peak Table>
UV/Vis Channel 2 254nm

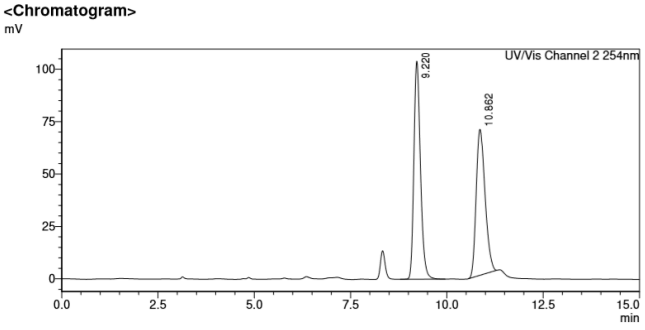
Peak#	Ret. Time	Area	Area%
1	5.638	1076317	98.256
2	9.104	19100	1.744
Total		1095417	100.000



2h

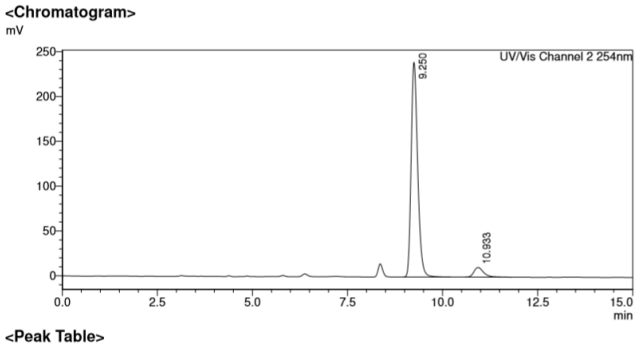
(*S*,*E*)-*N*-(1-Phenylpent-1-en-3-yl)aniline (2h): Prepared by General Method C using **Pd-1** at 22 ˚C for 20 h. The material was purified by flash silica gel chromatography (100% hexanes) to yield **2h** as colorless oil (25.0 mg, 0.105 mmol, 52.7 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35–7.12 (7H, m), 6.68–6.54 (4H, m), 6.12 (1H, dd, J = 15.9, 6.4 Hz), 3.88 (1H, q, J = 6.1 Hz), 3.72 (1H, s), 1.77–1.66 (2H, m), 1.02 (3H, t, J =7.4 Hz); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 147.7, 137.1, 132.0, 130.4, 129.2, 128.5, 127.4, 126.4, 117.3, 113.4, 57.2, 29.2, 10.6. Spectral data matched those previously reported.[15] **$[\alpha]_D^{27}$** = –15.8 (c = 1.0, $CHCl_3$) for a sample of 94:6 er.

HPLC: Column: Cellulose III (3 μm, 4.6 mm X 250 mm). Mobile phase: 10:90 *i*-PrOH:hexanes, 1.0 mL/min. Detection wavelength: 254 nm. Er = 94:6.



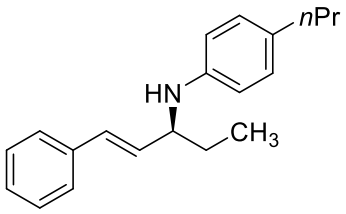
<Peak Table>
UV/Vis Channel 2 254nm

Peak#	Ret. Time	Area	Area%
1	9.220	1241683	52.778
2	10.862	1110988	47.222
Total		2352671	100.000



<Peak Table>
UV/Vis Channel 2 254nm

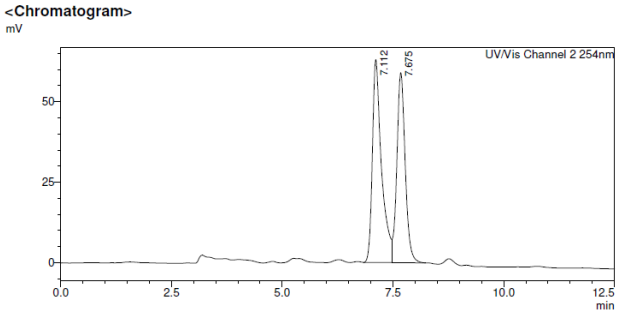
Peak#	Ret. Time	Area	Area%
1	9.250	2879024	93.779
2	10.933	190987	6.221
Total		3070012	100.000



2i

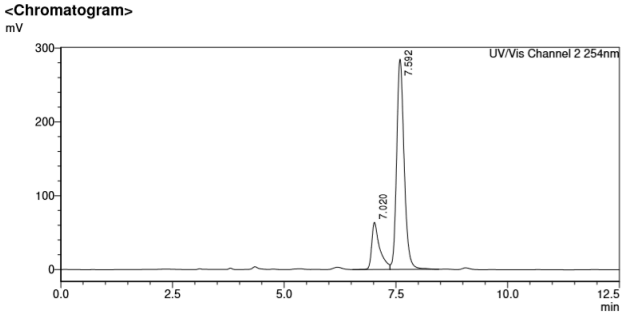
(*S*,*E*)-*N*-(1-Phenylpent-1-en-3-yl)-4-propylaniline (2i): Prepared by General Method C using **Pd-1** at 22 ˚C for 20 h. The material was purified by flash silica gel chromatography (100% hexanes) to yield **2i** as colorless oil (29.0 mg, 0.104 mmol, 51.9 % yield). Contains <5% *N*-allyl 4-propylaniline; **IR** (neat, cm^{-1}) 2958 (m), 2926 (m), 2870 (w), 2858 (w), 1614 (m), 1493 (s), 1339 (m), 964 (s); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 (2H, d, J = 7.2 Hz), 7.28 (2H, t, J = 7.6 Hz), 7.21 (1H, d, J = 7.2 Hz), 6.96 (2H, d, J = 8.4 Hz), 6.59–6.55 (2H, m), 6.23 (1H, dd, J = 15.9, 6.4 Hz), 3.85 (1H, q, J = 6.3 Hz), 3.62 (1H, brs), 2.45 (2H, t, J = 8.0 Hz), 1.75–1.65 (2H, m), 1.57 (2H, dq, J = 14.8, 7.3 Hz), 1.01 (3H, t, J = 7.4 Hz), 0.91 (3H, t, J = 7.3 Hz); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 145.6, 137.1, 132.3, 131.5, 130.3, 129.1, 128.5, 127.3, 126.4, 113.4, 57.5, 37.2, 29.2, 24.9, 13.9, 10.6; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{20}H_{25}N$: 279.1987, found: 279.1990. **$[\alpha]_D^{27}$** = –16.3 (c = 1.0, $CHCl_3$) for a sample of 81:19 er.

HPLC: Column: Cellulose III (3 μm, 4.6 mm X 250 mm). Mobile phase: 10:90 MeOH:hexanes, 1.0 mL/min. Detection wavelength: 254 nm. Er = 81:19.



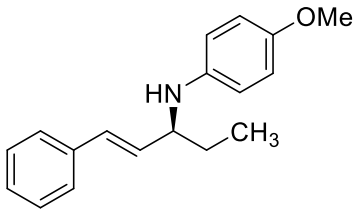
<Peak Table>
UV/Vis Channel 2 254nm

Peak#	Ret. Time	Area	Area%
1	7.112	902197	53.860
2	7.675	772866	46.140
Total		1675063	100.000



<Peak Table>
UV/Vis Channel 2 254nm

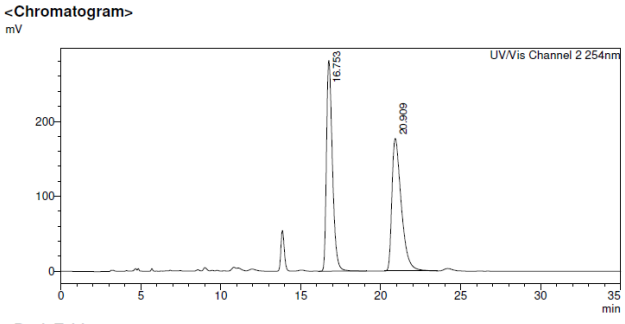
Peak#	Ret. Time	Area	Area%
1	7.020	794986	19.250
2	7.592	3334856	80.750
Total		4129842	100.000



2j

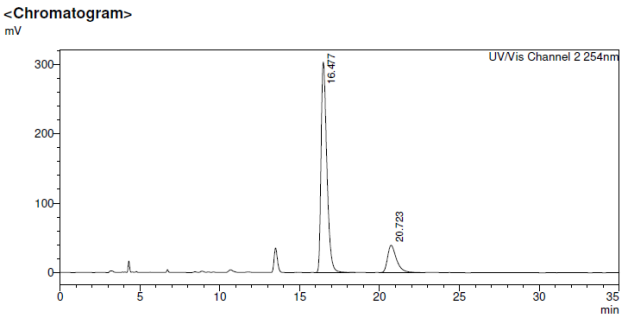
(*S*,*E*)-4-Methoxy-N-(1-phenylpent-1-en-3-yl)aniline (2j): Prepared by General Method C using **Pd-1** at 22 ˚C for 20 h. The material was purified by flash silica gel chromatography (100% hexanes to 80:20 hexanes:EtOAc) to yield **2j** as colorless oil (31.0 mg, 0.116 mmol, 58.0 % yield). Contains <5% *N*-allyl 4-methoxyaniline; **IR** (neat, cm^{-1}) 3394 (w), 3024 (w), 2959 (m), 2929 (m), 2830 (w), 1508 (s), 1461 (m), 1229 (s), 1035 (s), 965 (s); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 (2H, d, J = 7.1Hz), 7.28 (2H, t, J = 7.5 Hz), 7.19 (1H, t, J = 7.2 Hz), 6.79–6.70 (2H, m), 6.64–6.58 (2H, m), 6.55 (1H, d, J = 16.0 Hz), 6.11 (1H, dd, J = 15.9, 6.6 Hz), 3.80 (1H, qd, J = 6.3, 1.2 Hz), 3.72 (3H, s), 3.47 (1H, brs), 1.78–1.61 (2H, m), 1.01 (3H, t, J = 7.4 Hz); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 152.1, 149.3, 137.1, 132.4, 130.4, 128.6, 127.3, 126.4, 114.9, 114.4, 58.3, 55.9, 29.2, 10.5; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{18}H_{21}NO$: 267.1623, found: 267.1620. **$[\alpha]_D^{27}$** = –16.0 (c = 1.0, $CHCl_3$) for a sample of 83.5:16.5 er.

HPLC: Column: Cellulose III (3 μm, 4.6 mm X 250 mm). Mobile phase: 10:90 MeOH:hexanes, 1.0 mL/min. Detection wavelength: 254 nm. Er = 83.5:16.5.



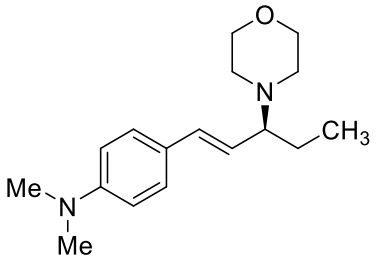
<Peak Table>
UV/Vis Channel 2 254nm

Peak#	Ret. Time	Area	Area%
1	16.753	7250977	50.077
2	20.909	7228726	49.923
Total		14479703	100.000



<Peak Table>
UV/Vis Channel 2 254nm

Peak#	Ret. Time	Area	Area%
1	16.477	7644742	83.267
2	20.723	1536212	16.733
Total		9180954	100.000

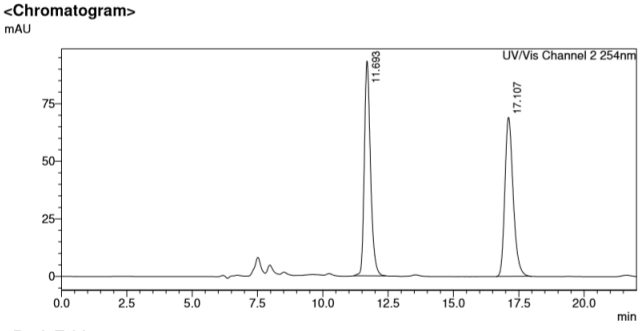


3a

(*S*,*E*)-*N*,*N*-Dimethyl-4-(3-morpholinopent-1-en-1-yl)aniline (3a): Prepared by General Method C using **Pd-1** at 22 ˚C for 20 h. The material was purified by flash silica gel chromatography (100% hexanes to 50:50 hexanes:EtOAc) to yield **3a** as colorless oil (36.0 mg, 0.131 mmol, 65.5 % yield). **IR** (neat, cm^{-1}) 2957 (m), 2928 (w), 2850 (m), 2802 (m), 1737 (s), 1608 (s), 1520 (s), 1447 (m), 1350 (s), 1237 (s), 1116 (s), 1003 (s); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 (2H, d, J = 8.8 Hz), 6.67 (2H, d, J = 8.8 Hz), 6.34 (1H, d, J = 15.8 Hz), 5.84 (1H, dd, J = 15.8, 9.1 Hz), 3.77–3.64 (4H, m), 2.93 (6H, s), 2.68 (1H, td, J = 9.1, 4.2 Hz), 2.64–2.43 (4H, m), 1.75 (1H, ddt, J = 14.9, 7.4, 4.4 Hz), 1.53–1.40 (1H, m), 0.88 (3H, t, J = 7.4 Hz); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 150.1, 132.9, 127.2, 125.5, 125.1, 112.5, 70.3, 67.3, 50.8, 40.6, 24.8, 10.9; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{17}H_{26}N_2O$: 274.2045, found: 274.2047.

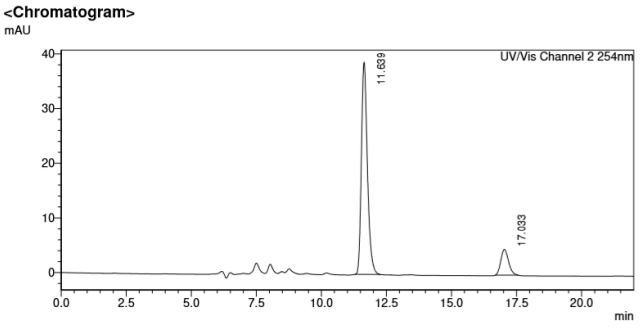
$[\alpha]_D^{27}$ = –15.6 (c = 1.0, $CHCl_3$) for a sample of 86.5:13.5 er.

HPLC: Column: Chiralpak 1-A3 (3 μm, 4.6 mm X 150 mm). Mobile phase: 95:5 *i*-PrOH (with 0.1% Et_2NH):MeCN, 0.3 mL/min. Detection wavelength: 254 nm. Er = 86.5:13.5.



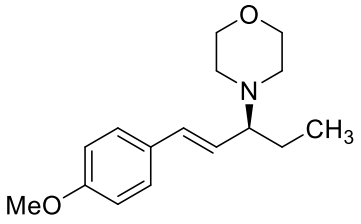
<Peak Table>
UV/Vis Channel 2 254nm

Peak#	Ret. Time	Area	Area%
1	11.693	1536593	50.119
2	17.107	1529288	49.881
Total		3065881	100.000



<Peak Table>
UV/Vis Channel 2 254nm

Peak#	Ret. Time	Area	Area%
1	11.639	622285	86.534
2	17.033	96837	13.466
Total		719122	100.000

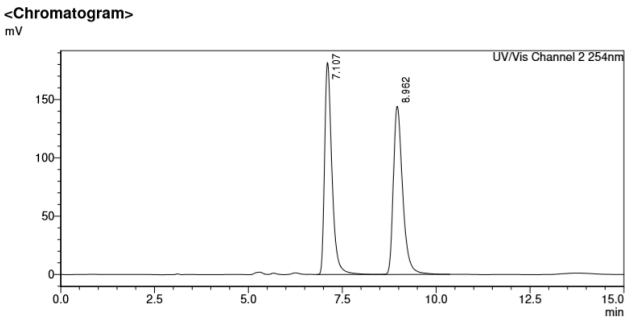


3b

(*S*,*E*)-4-(1-(4-Methoxyphenyl)pent-1-en-3-yl)morpholine (3b): Prepared by General Method C using **Pd-1** at 22 ˚C for 20 h. The material was purified by flash silica gel chromatography (100% hexanes to 80:20 hexanes:EtOAc) to yield **3b** as colorless oil (40.0 mg, 0.153 mmol, 76.5 % yield). **IR** (neat, cm^{-1}) 2949 (m), 2925 (w), 2850 (m), 2805 (m), 1604 (s), 1512 (s), 1454 (s), 1297 (s), 1135 (s), 1005 (s); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 (2H, d, J = 8.7 Hz), 6.84 (2H, d, J = 8.7 Hz), 6.37 (1H, d, J = 15.9 Hz), 5.91 (1H, dd, J = 15.9, 9.0 Hz), 3.79 (3H, s), 3.74–3.64 (4H, m), 2.70 (1H, td, J = 9.0, 4.2 Hz), 2.64–2.41 (4H, m), 1.75 (1H, ddt, J = 14.6, 7.2, 3.6 Hz), 1.55–1.39 (1H, m), 0.88 (3H, t, J = 7.4 Hz); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 159.1, 132.4, 129.8, 127.4, 114.0, 70.2, 67.3, 55.4, 50.8, 24.7, 10.9; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{16}H_{23}NO_2$: 261.1729, found: 261.1729.

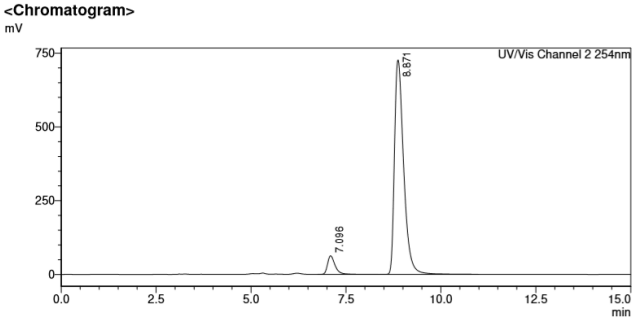
$[\alpha]_D^{27}$ = –15.5 (c = 1.0, $CHCl_3$) for a sample of 93:7 er.

HPLC: Column: Cellulose III (3 μm, 4.6 mm X 250 mm). Mobile phase: 10:90 *i*-PrOH:Hexanes, 1.0 mL/min. Detection wavelength: 254 nm. Er = 93:7.



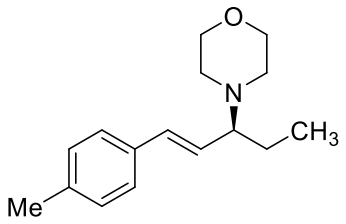
<Peak Table>
UV/Vis Channel 2 254nm

Peak#	Ret. Time	Area	Area%
1	7.107	2492901	50.139
2	8.962	2479049	49.861
Total		4971951	100.000



<Peak Table>
UV/Vis Channel 2 254nm

Peak#	Ret. Time	Area	Area%
1	7.096	883381	6.786
2	8.871	12133517	93.214
Total		13016899	100.000

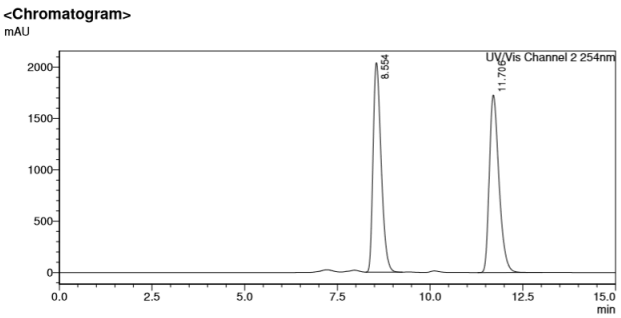


3c

(*S*,*E*)-4-(1-(*p*-Tolyl)pent-1-en-3-yl)morpholine (3c): Prepared by General Method C using **Pd-1** at 22 ˚C for 20 h. The material was purified by flash silica gel chromatography (100% hexanes to 80:20 hexanes:EtOAc) to yield **3c** as colorless oil (32.0 mg, 0.130 mmol, 65.2 % yield). **IR** (neat, cm^{-1}) 2957 (m), 2926 (w), 2889 (w), 2872 (w), 2851 (m), 2805 (m), 1513 (m), 1450 (m), 1268 (m), 1115 (s), 970 (s); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 (2H, d, J = 7.8 Hz), 7.11 (2H, J = 7.9 Hz), 6.40 (1H, d, J = 15.9 Hz), 6.01 (1H, dd, J = 15.9, 9.0 Hz), 3.70 (4H, q, J = 7.8, 6.2 Hz), 2.72 (1H, td, J = 9.0, 4.3 Hz), 2.66–2.44 (4H, m), 2.32 (3H, s), 1.82–1.71 (1H, m), 1.56–1.41 (1H, m), 0.88 (3H, t, J = 7.3 Hz); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 137.3, 134.2, 132.9, 129.3, 128.7, 126.2, 70.1, 67.4, 50.8, 24.7, 21.2, 10.8; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{16}H_{23}NO$: 245.1780, found: 245.1784.

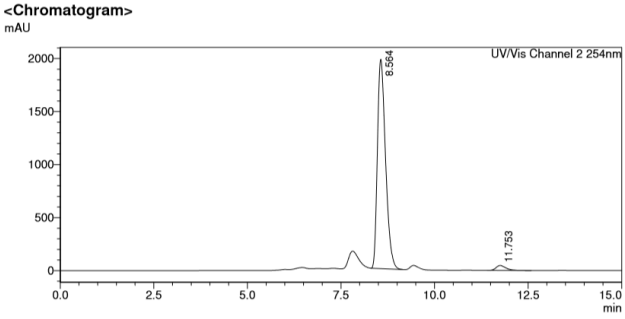
$[\alpha]_D^{27}$ = –15.1 (c = 1.0, $CHCl_3$) for a sample of 97:3 er.

HPLC: Column: Chiralpak 1-A3 (3 μm, 4.6 mm X 150 mm). Mobile phase: 90:10 *i*-PrOH (with 0.1% Et_2NH):MeCN, 0.3 mL/min. Detection wavelength: 254 nm. Er = 97:3.



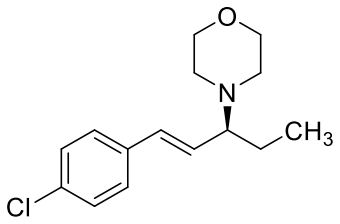
<Peak Table>
UV/Vis Channel 2 254nm

Peak#	Ret. Time	Area	Area%
1	8.554	31046489	49.755
2	11.706	31352529	50.245
Total		62399017	100.000



<Peak Table>
UV/Vis Channel 2 254nm

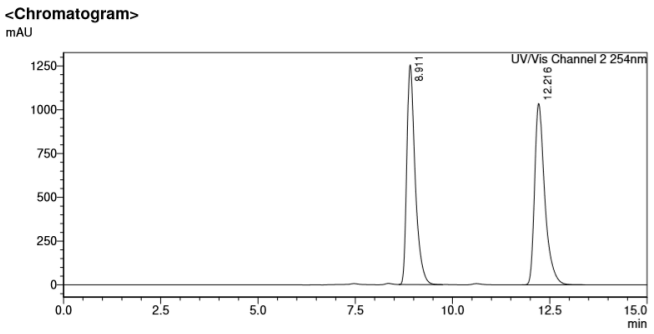
Peak#	Ret. Time	Area	Area%
1	8.564	29996186	97.220
2	11.753	857623	2.780
Total		30853809	100.000



3d

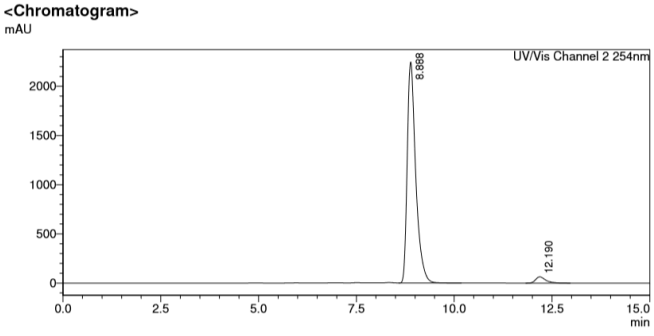
(*S*,*E*)-4-(1-(4-Chlorophenyl)pent-1-en-3-yl)morpholine (3d): Prepared by General Method C using **Pd-1** at 22 ˚C for 20 h. The material was purified by flash silica gel chromatography (100% hexanes to 80:20 hexanes:EtOAc) to yield **3d** as colorless oil (42.0 mg, 0.158 mmol, 79.0 % yield). **IR** (neat, cm^{-1}) 2958 (m), 2929 (w), 2852 (m), 2806 (m), 1490 (s), 1451 (s), 1115 (s), 1011 (s), 837 (m); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30–7.22 (4H, m), 6.73 (1H, d, J = 15.9 Hz), 6.64 (1H, dd, J = 15.9, 9.1 Hz), 3.68 (4H, q, J = 8.3, 6.3 Hz), 2.73 (1H, td, J = 9.0, 4.4 Hz), 2.64–2.44 (4H, m), 1.81–1.67 (1H, m), 1.55–1.39 (1H, m), 0.87 (3H, t, J = 7.4 Hz); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 135.4, 133.0, 131.7, 130.5, 128.7, 127.5, 69.9, 67.3, 50.7, 24.5, 10.8; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{15}H_{20}ClNO$: 265.1233, found: 265.1231. **$[\alpha]_D^{27}$** = –15.4 (c = 1.0, $CHCl_3$) for a sample of 97:3 er.

HPLC: Column: Chiralpak 1-A3 (3 μm, 4.6 mm X 150 mm). Mobile phase: 90:10 *i*-PrOH (with 0.1% Et_2NH):MeCN, 0.3 mL/min. Detection wavelength: 254 nm. Er = 97:3.



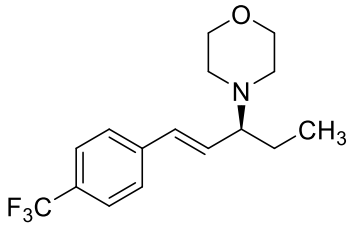
<Peak Table>
UV/Vis Channel 2 254nm

Peak#	Ret. Time	Area	Area%
1	8.911	18690326	49.935
2	12.216	18739183	50.065
Total		37429508	100.000



<Peak Table>
UV/Vis Channel 2 254nm

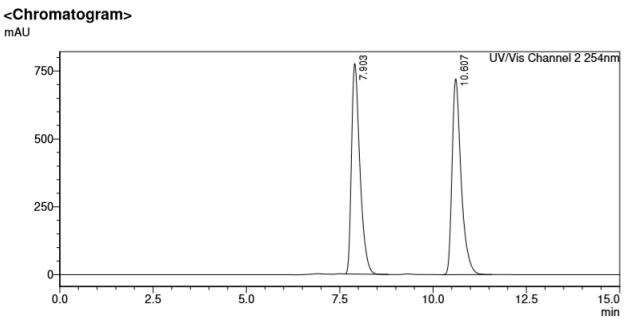
Peak#	Ret. Time	Area	Area%
1	8.888	33678826	96.748
2	12.190	1131904	3.252
Total		34810731	100.000



3e

(*S*,*E*)-4-(1-(4-(Trifluoromethyl)phenyl)pent-1-en-3-yl)morpholine (3e): Prepared by General Method C using **Pd-1** at 22 ˚C for 20 h. The material was purified by flash silica gel chromatography (100% hexanes to 70:30 hexanes:EtOAc) to yield **3e** as colorless oil (25.0 mg, 0.084 mmol, 41.8 % yield). **IR** (neat, cm^{-1}) 2961 (w), 2930 (w), 2855 (w), 2811 (w), 1615 (m), 1322 (s), 1115 (s), 1066 (s), 752 (s); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (2H, d, J = 7.0 Hz), 7.44 (2H, d, J = 7.4 Hz), 6.47 (1H, d, J = 15.9 Hz), 6.18 (1H, dd, J = 15.9, 9.0 Hz), 3.70 (4H, brs), 2.86–2.68 (1H, m), 2.67–2.41 (4H, m), 1.88–1.68 (1H, m), 1.58–1.40 (1H, m), 0.88 (3H, t, J = 7.4 Hz) ; **^{13}C NMR** (125 MHz, $CDCl_3$) δ 140.4, 132.7, 131.6, 128.8, 126.4, 125.6, 69.8, 67.3, 50.7, 28.2 (q, J = 18.1 Hz), 24.5, 10.7; **^{19}F NMR** (400 MHz, $CDCl_3$) δ -65.5 Hz; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{16}H_{20}F_3NO$: 299.1497, found: 299.1497. **$[\alpha]_D^{27}$** = –15.1 (c = 1.0, $CHCl_3$) for a sample of 86.5:13.5 er.

HPLC: Column: Chiralpak 1-A3 (3 μm, 4.6 mm X 150 mm). Mobile phase: 90:10 *i*-PrOH (with 0.1% Et_2NH):MeCN, 0.3 mL/min. Detection wavelength: 254 nm. Er = 86.5:13.5.



<Peak Table>
UV/Vis Channel 2 254nm

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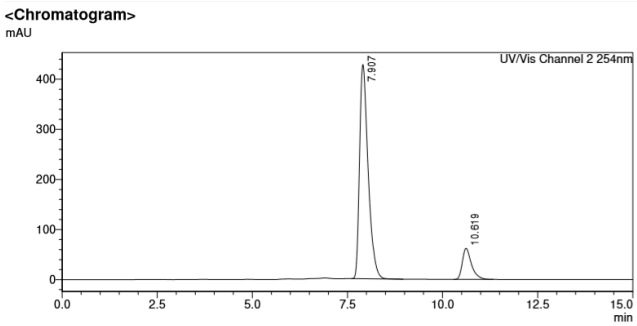
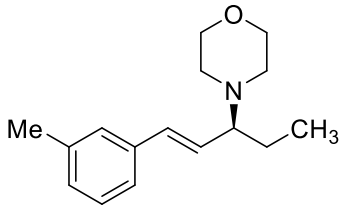
2	10.607	12257673	50.118
Total		24457605	100.000



<Peak Table>
UV/Vis Channel 2 254nm

Peak#	Ret. Time	Area	Area%
1	7.907	6716715	86.557
2	10.619	1043175	13.443
Total		7759890	100.000

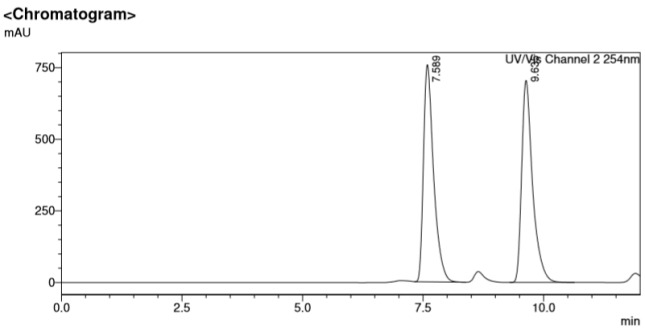


3f

(*S*,*E*)-4-(1-(*m*-Tolyl)pent-1-en-3-yl)morpholine (3f): Prepared by General Method C using **Pd-1** at 22 ˚C for 20 h. The material was purified by flash silica gel chromatography (100% hexanes to 80:20 hexanes:EtOAc) to yield **3f** as colorless oil (30.0 mg, 0.122 mmol, 61.1 % yield). **IR** (neat, cm^{-1}) 2957 (s), 2926 (m), 2873 (w), 2851 (m), 2805 (m), 1450 (m), 1270 (m), 1116 (s), 969 (s); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25–7.13 (3H, m), 7.04 (1H, d, J = 6.9 Hz), 6.40 (1H, d, 15.9 Hz), 6.50 (1H, dd, J = 15.9, 9.1 Hz), 3.82–3.60 (4H, m), 2.73 (1H, td, J = 9.0, 4.3 Hz), 2.64–2.42 (4H, m), 2.33 (3H, s), 1.85–1.69 (1H, m), 1.57–1.39 (1H, m), 0.88 (3H, t, J = 7.4 Hz); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 138.1, 136.9, 133.1, 129.5, 128.5, 128.3, 127.0, 123.5, 70.0, 67.3, 50.7, 24.7, 21.4, 10.8; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{16}H_{23}NO$: 245.1780, found: 245.1780.

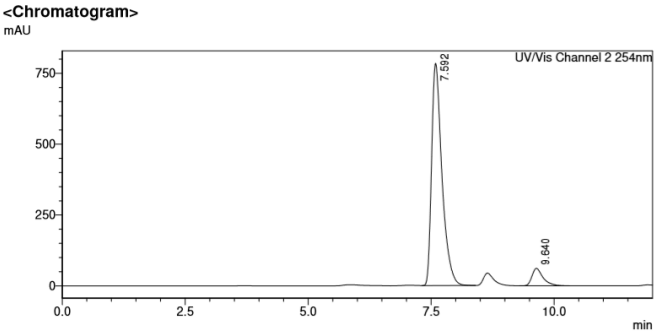
$[\alpha]_D^{27}$ = –15.4 (c = 1.0, $CHCl_3$) for a sample of 92.5:7.5 er.

HPLC: Column: Chiralpak 1-A3 (3 μm, 4.6 mm X 150 mm). Mobile phase: 90:10 *i*-PrOH (with 0.1% Et_2NH):MeCN, 0.3 mL/min. Detection wavelength: 254 nm. Er = 92.5:7.5.



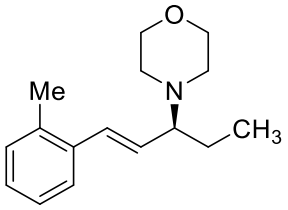
<Peak Table>
UV/Vis Channel 2 254nm

Peak#	Ret. Time	Area	Area%
1	7.589	11100500	49.913
2	9.635	11139201	50.087
Total		22239701	100.000



<Peak Table>
UV/Vis Channel 2 254nm

Peak#	Ret. Time	Area	Area%
1	7.592	11487525	92.302
2	9.640	958028	7.698
Total		12445553	100.000

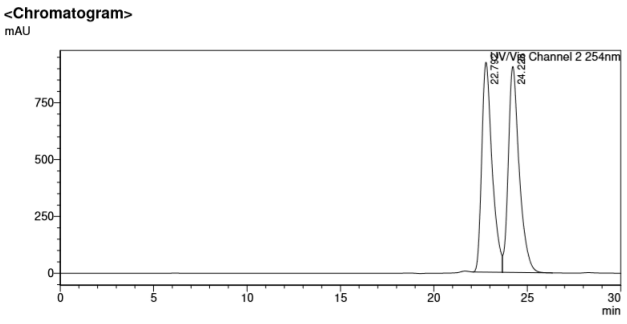


3g

(*S*,*E*)-4-(1-(*o*-Tolyl)pent-1-en-3-yl)morpholine (3g): Prepared by General Method C using **Pd-1** at 22 ˚C for 20 h. The material was purified by flash silica gel chromatography (100% hexanes to 80:20 hexanes:EtOAc) to yield **3g** as colorless oil (28.0 mg, 0.114 mmol, 57.1 % yield). **IR** (neat, cm^{-1}) 2956 (m), 2924 (w), 2872 (m), 2804 (w), 1451 (s), 1116 (s), 969 (s); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46–7.36 (1H, m), 7.22–7.09 (3H, m), 6.64 (1H, d, J = 15.8 Hz), 5.92 (1H, dd, J = 15.8, 9.0 Hz), 3.77–3.65 (4H, m), 2.77 (1H, td, J = 9.1, 4.3 Hz), 2.67–2.44 (4H, m), 2.34 (3H, s), 1.88–1.69 (1H, m), 1.61–1.40 (1H, m), 0.91 (3H, t, J = 7.4 Hz); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 136.3, 135.2, 131.1, 131.0, 130.3, 127.4, 126.1, 125.8, 70.2, 67.3, 50.7, 24.7, 20.0, 10.9; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{16}H_{23}NO$: 245.1780, found: 245.1781.

$[\alpha]_D^{27}$ = –15.2 (c = 1.0, $CHCl_3$) for a sample of 84.5:15.5 er.

HPLC: Column: Chiralpak 1-A3 (3 μm, 4.6 mm X 150 mm). Mobile phase: 90:10 *i*-PrOH (with 0.1% Et_2NH):MeCN, 0.3 mL/min. Detection wavelength: 254 nm. Er = 84.5:15.5.



<Peak Table>
UV/Vis Channel 2 254nm

Peak#	Ret. Time	Area	Area%
1	22.792	35640127	49.130
2	24.228	36901628	50.870
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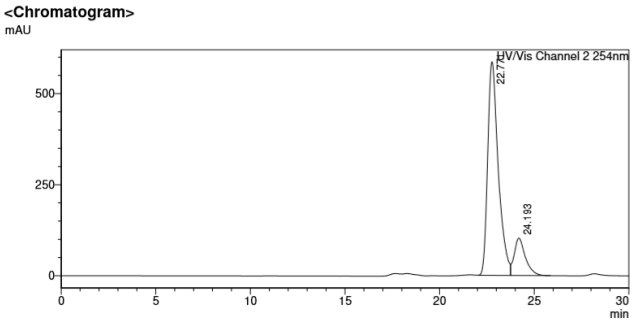

<Peak Table>
UV/Vis Channel 2 254nm

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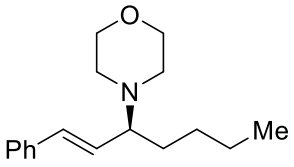
2	24.193	4220581	15.627
Total		27008384	100.000

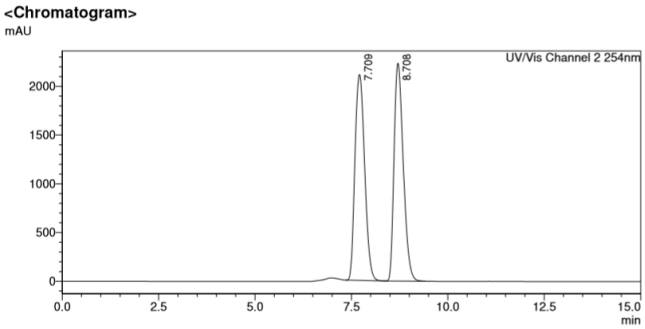


3h

(*S*,*E*)-4-(1-Phenylhept-1-en-3-yl)morpholine (3h): Prepared by General Method C using **Pd-1** at 22 ˚C for 20 h. The material was purified by flash silica gel chromatography (100% hexanes to 80:20 hexanes:EtOAc) to yield **3h** as colorless oil (29.0 mg, 0.112 mmol, 56.0 % yield). Regiomeric ratio: 83:17; **IR** (neat, cm^{-1}) 2955 (m), 2926 (m), 2855 (m), 2811 (w), 1451 (m), 1116 (s), 970 (S); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40–7.35 (2H, m), 7.33–7.27 (2H, m), 7.25–7.19 (1H, m), 6.42 (1H, d, J = 15.9 Hz), 6.08 (1H, dd, J = 15.9 Hz, 9.1 Hz), 3.81–3.60 (4H, m), 2.82 (1H, td, J = 9.1, 4.3 Hz), 2.66–2.47 (4H, m), 1.80–0.79 (9H, m); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 136.9, 132.8, 129.9, 128.6, 127.5, 126.3, 68.5, 67.3, 50.7, 31.7, 28.6, 22.9, 14.1; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{17}H_{25}NO$: 259.1936, found: 259.1939.

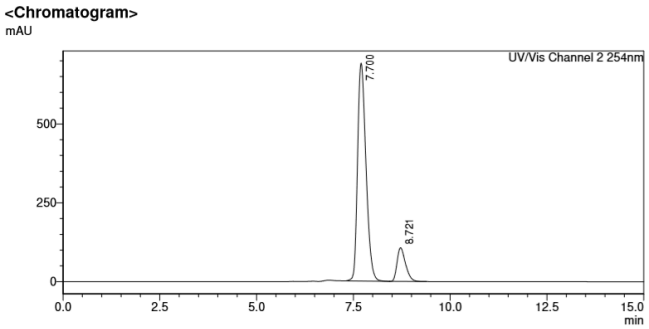
$[\alpha]_D^{27}$ = –15.1 (c = 1.0, $CHCl_3$) for a sample of 86.5:13.5 er.

HPLC: Column: Chiralpak 1-A3 (3 μm, 4.6 mm X 150 mm). Mobile phase: 90:10 *i*-PrOH (with 0.1% Et_2NH):MeCN, 0.3 mL/min. Detection wavelength: 254 nm. Er = 86.5:13.5.



<Peak Table>
UV/Vis Channel 2 254nm

Peak#	Ret. Time	Area	Area%
1	7.709	37212588	49.999
2	8.708	37214147	50.001
Total		74426735	100.000



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UV/Vis Channel 2 254nm

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1	7.700	10497580	86.552
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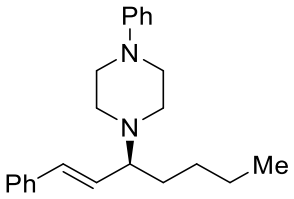
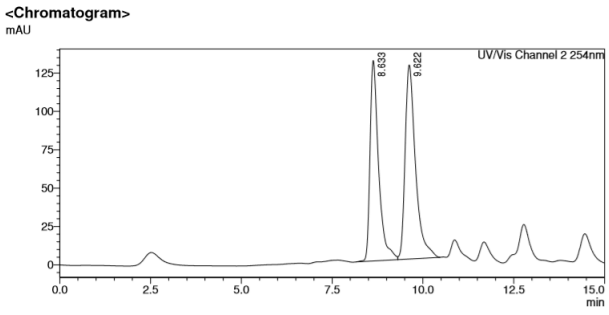


3i

(*S*,*E*)-1-Phenyl-4-(1-phenylhept-1-en-3-yl)piperazine (3i): Prepared by General Method C using **Pd-1** at 22 ˚C for 20 h. The material was purified by flash silica gel chromatography (100% hexanes to 80:20 hexanes:EtOAc) to yield **3i** as colorless oil (41.0 mg, 0.123 mmol, 61.3 % yield). Regiomeric ratio: 94:6; **IR** (neat, cm^{-1}) 3024 (w), 2954 (m), 2930 (m), 2820 (m), 1599 (s), 1494 (s), 1450 (s), 1354 (m), 1232 (s), 1136 (s), 969 (m); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43–7.32 (2H, m), 7.32 (2H, t, J = 7.6 Hz), 7.30–7.09 (3H, m), 6.93 (2H, d, J = 8.7 Hz), 6.85 (1H, t, J = 7.3 Hz), 6.47 (1H, d, J = 15.9 Hz), 6.16 (1H, dd, J = 15.9, 9.1 Hz), 3.28–3.16 (4H, m), 2.94 (1H, td, J = 9.1, 4.3 Hz), 2.89–2.66 (4H, m), 1.85–1.71 (1H, m), 1.65–1.49 (1H, m), 1.43–1.23 (4H, m), 0.91 (3H, t, J = 6.3 Hz); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 151.4, 137.0, 132.7, 130.0, 129.1, 128.6, 127.4, 126.3, 120.0, 116.1, 68.1, 50.0, 49.6, 32.0, 28.7, 22.9, 14.1; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{23}H_{30}N_2$: 334.2409, found: 334.2409.

$[\alpha]_D^{27}$ = –15.3 (c = 1.0, $CHCl_3$) for a sample of 99:1 er.

HPLC: Column: Chiralpak 1-A3 (3 μm, 4.6 mm X 150 mm). Mobile phase: 90:10 *i*-PrOH (with 0.1% Et_2NH):MeCN, 0.3 mL/min. Detection wavelength: 254 nm. Er = 99:1.



<Peak Table>
UV/Vis Channel 2 254nm

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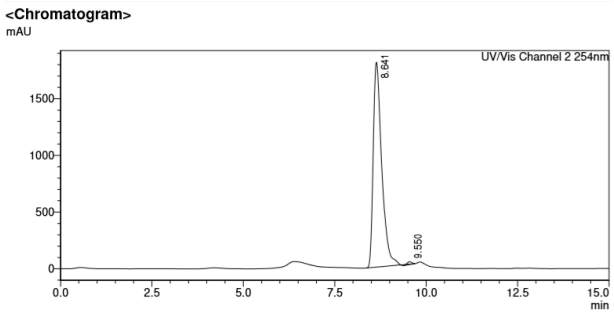
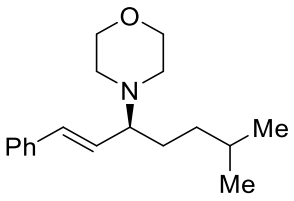
1	8.633	2148432	46.112
2	9.622	2510698	53.888
Total		4659130	100.000



<Peak Table>
UV/Vis Channel 2 254nm

Peak#	Ret. Time	Area	Area%
1	8.641	29154028	99.231
2	9.550	226008	0.769
Total		29380036	100.000

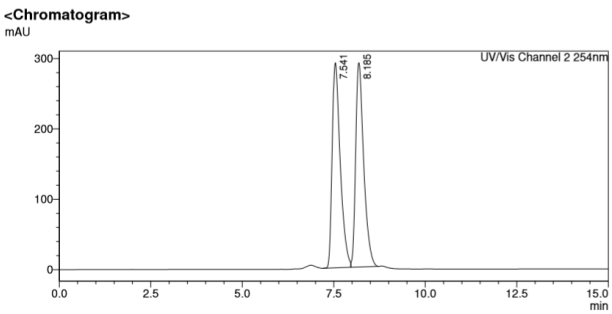


3j

(*S,E*)-4-(6-Methyl-1-phenylhept-1-en-3-yl)morpholine (3j): Prepared by General Method C using **Pd-1** at 22 ˚C for 20 h. The material was purified by flash silica gel chromatography (100% hexanes to 80:20 hexanes:EtOAc) to yield **3j** as colorless oil (33.5 mg, 0.124 mmol, 62.0 % yield). Regiomeric ratio: 91:9; **IR** (neat, cm^{-1}) 2952 (s), 2928 (m), 2851 (m), 2806 (m), 1450 (m), 1116 (s), 968 (m); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 (2H, d, J = 7.1 Hz), 7.30 (2H, t, J = 7.6 Hz), 7.27–7.09 (1H, m), 6.42 (1H, d, J = 15.9 Hz), 6.07 (1H, dd, J = 15.9, 9.1 Hz), 3.78–3.63 (4H, m), 2.80 (1H, td, J = 9.1, 4.3 Hz), 2.67–2.47 (4H, m), 1.85–1.66 (1H, m), 1.56–1.42 (2H, m), 1.27–1.08 (2H, m), 0.86 (6H, dt, J = 6.5, 3.2 Hz); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 137.0, 132.8, 129.9, 128.6, 127.5, 126.3, 68.7, 67.4, 50.7, 35.5, 29.8, 28.3, 22.8, 22.5; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{16}H_{27}NO$: 273.2093, found: 273.2094.

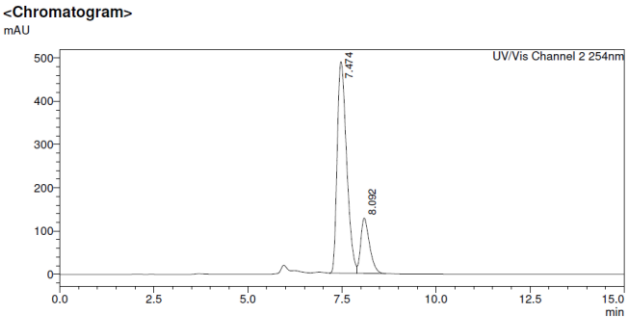
$[\alpha]_D^{27}$ = –15.2 (c = 1.0, $CHCl_3$) for a sample of 80.5:19.5 er.

HPLC: Column: Chiralpak 1-A3 (3 μm, 4.6 mm X 150 mm). Mobile phase: 90:10 *i*-PrOH (with 0.1% Et_2NH):MeCN, 0.3 mL/min. Detection wavelength: 254 nm. Er = 80.5:19.5.



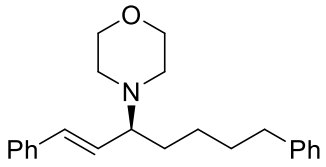
<Peak Table>
UV/Vis Channel 2 254nm

Peak#	Ret. Time	Area	Area%
1	7.541	4453075	50.327
2	8.185	4395150	49.673
Total		8848224	100.000



<Peak Table>
UV/Vis Channel 2 254nm

Peak#	Ret. Time	Area	Area%
1	7.474	8458275	80.367
2	8.092	2066352	19.633
Total		10524626	100.000

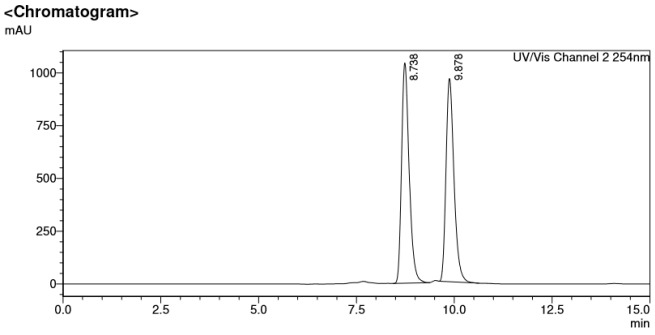


3k

(*S*,*E*)-4-(1,7-Diphenylhept-1-en-3-yl)morpholine (3k): Prepared by General Method C using **Pd-1** at 22 ˚C for 20 h. The material was purified by flash silica gel chromatography (100% hexanes to 80:20 hexanes:EtOAc) to yield **3k** as colorless oil (37.0 mg, 0.110 mmol, 55.1 % yield). Regiomeric ratio: 95:5; **IR** (neat, cm^{-1}) 3059(w), 3024 (w), 2927 (s), 2852 (m), 2806 (w), 1495 (m), 1451 (m), 1116 (s), 969 (m); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39–7.34 (2H, m), 7.34–7.28 (2H, m), 7.27–7.20 (2H, m), 7.18–7.11 (4H, m), 6.41 (1H, d, J = 15.9 Hz), 6.07 (1H, dd, J = 15.9, 9.1 Hz), 3.77–3.64 (4H, m), 2.83 (1H, td, J = 9.2 Hz, 4.6 Hz), 2.67–2.46 (4H, m), 1.81–1.69 (1H, m), 1.69–1.46 (4H, m), 1.40–1.26 (3H, m); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 142.6, 136.9, 132.9, 129.7, 128.6, 128.4, 128.3, 127.5, 126.3, 125.7, 68.3, 67.3, 50.6, 35.9, 31.7, 31.6, 26.0; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{23}H_{29}NO$: 335.2249, found: 335.2253.

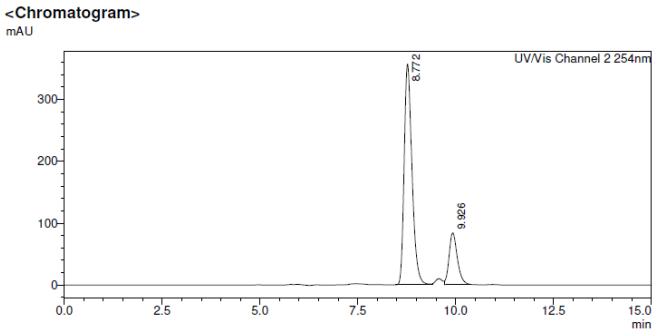
$[\alpha]_D^{27}$ = –15.1 (c = 1.0, $CHCl_3$) for a sample of 80:20 er.

HPLC: Column: Chiralpak 1-A3 (3 μm, 4.6 mm X 150 mm). Mobile phase: 90:10 *i*-PrOH (with 0.1% Et_2NH):MeCN, 0.3 mL/min. Detection wavelength: 254 nm. Er = 80:20.



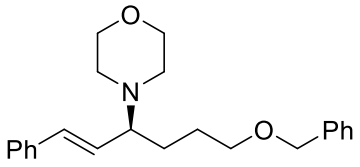
<Peak Table>
UV/Vis Channel 2 254nm

Peak#	Ret. Time	Area	Area%
1	8.738	14080924	50.599
2	9.878	13747675	49.401
Total		27828598	100.000



<Peak Table>
UV/Vis Channel 2 254nm

Peak#	Ret. Time	Area	Area%
1	8.772	4943298	80.145
2	9.926	1224661	19.855
Total		6167959	100.000

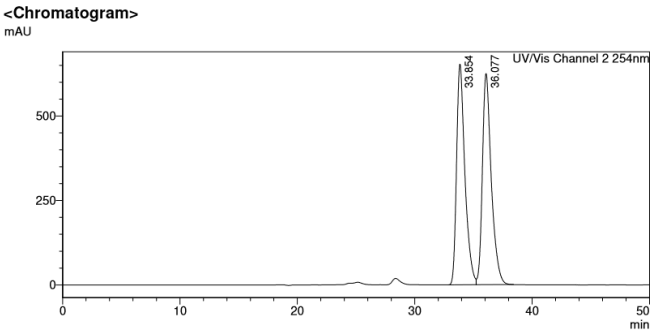


3l

(*S*,*E*)-4-(6-(Benzyloxy)-1-phenylhex-1-en-3-yl)morpholine (3l): Prepared by General Method C using **Pd-1** at 22 ˚C for 20 h. The material was purified by flash silica gel chromatography (100% hexanes to 80:20 hexanes:EtOAc) to yield **3l** as colorless oil (56.0 mg, 0.159 mmol, 79.7 % yield). Regiomeric ratio: 95:5; **IR** (neat, cm^{-1}) 2952 (w), 2922 (m), 2853 (m), 2810 (w), 1452 (m), 1357 (m), 1115 (s), 1002 (m), 746 (s); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41–7.17 (10H, m), 6.42 (1H, d, J = 15.9 Hz), 6.08 (1H, dd, J = 15.9, 9.1 Hz), 4.48 (2H, s), 3.78–3.59 (4H, m), 3.47 (2H, t, J = 6.2 Hz), 2.92–2.80 (1H, m), 2.71–2.45 (4H, m), 1.91–1.77 (1H, m), 1.75–1.47 (3H, m); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 138.6, 136.8, 133.1, 129.6, 129.5, 128.6, 128.4, 127.6, 127.5, 126.3, 72.9, 70.3, 68.2, 67.3, 50.6, 28.4, 26.6; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{23}H_{29}NO_2$: 351.2198, found: 351.2200.

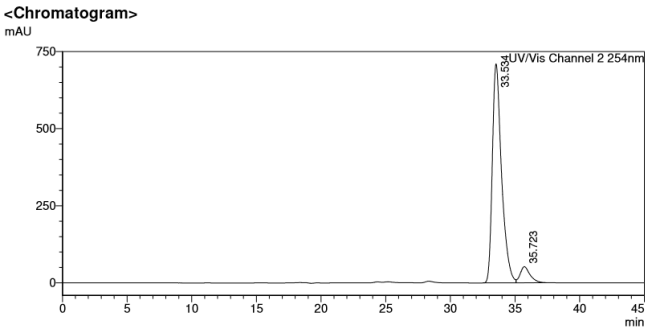
$[\alpha]_D^{27}$ = –15.1 (c = 1.0, $CHCl_3$) for a sample of 93:7 er.

HPLC: Column: Chiralpak 1-A3 (3 μm, 4.6 mm X 150 mm). Mobile phase: 95:5 *i*-PrOH (with 0.1% Et_2NH):MeCN, 0.1 mL/min. Detection wavelength: 254 nm. Er = 93:7.



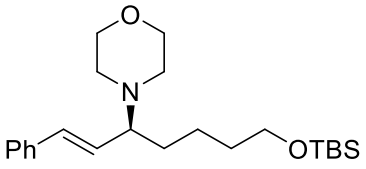
<Peak Table>
UV/Vis Channel 2 254nm

Peak#	Ret. Time	Area	Area%
1	33.854	32331277	49.518
2	36.077	32960508	50.482
Total		65291785	100.000



<Peak Table>
UV/Vis Channel 2 254nm

Peak#	Ret. Time	Area	Area%
1	33.534	35207884	92.734
2	35.723	2758787	7.266
Total		37966671	100.000

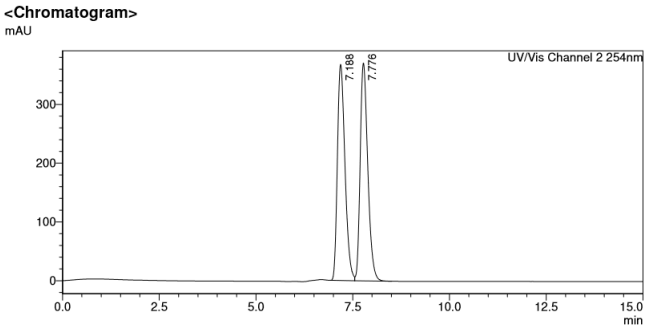


3m

(*S*,*E*)-4-(7-((*tert*-Butyldimethylsilyl)oxy)-1-phenylhept-1-en-3-yl)morpholine (3m): Prepared by General Method C using **Pd-1** at 22 ˚C for 20 h. The material was purified by flash silica gel chromatography (100% hexanes to 80:20 hexanes:EtOAc) to yield **3m** as colorless oil (42.0 mg, 0.108 mmol, 53.9 % yield). Regiomeric ratio: 95:5; **IR** (neat, cm^{-1}) 2951 (m), 2927 (m), 2891 (w), 2854 (s), 2807 (w), 1450 (m), 1251 (m), 1117 (s), 1098 (s), 968 (m), 833 (s); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 (2H, d, J = 7.3 Hz), 7.29 (2H, t, J = 7.6 Hz), 7.22 (1H, d, J = 7.3 Hz), 6.42 (1H, d, J = 15.9 Hz), 6.07 (1H, dd, J = 15.9, 9.0 Hz), 3.74–3.66 (4H, m), 3.57 (2H, t, J = 6.5 Hz), 2.88–2.78 (1H, m), 2.65–2.45 (4H, m), 1.79–1.66 (1H, m), 1.59–1.25 (5H, m), 0.84 (9H, s), 0.00 (6H, s); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 136.9, 133.0, 129.7, 128.6, 127.5, 126.3, 68.4, 67.3, 63.1, 50.7, 33.0, 31.7, 26.0, 22.7, 18.4, -5.2; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{23}H_{39}NO_2Si$: 389.2750, found: 389.2753.

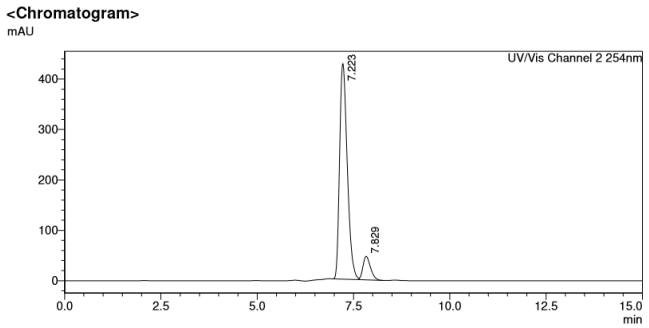
$[\alpha]_D^{27}$ = –15.1 (c = 1.0, $CHCl_3$) for a sample of 90:10 er.

HPLC: Column: Chiralpak 1-A3 (3 μm, 4.6 mm X 150 mm). Mobile phase: 90:10 *i*-PrOH (with 0.1% Et_2NH):MeCN, 0.3 mL/min. Detection wavelength: 254 nm. Er = 90:10.



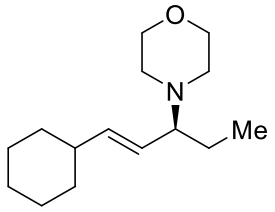
<Peak Table>
UV/Vis Channel 2 254nm

Peak#	Ret. Time	Area	Area%
1	7.188	5042232	49.764
2	7.776	5090122	50.236
Total		10132355	100.000



<Peak Table>
UV/Vis Channel 2 254nm

Peak#	Ret. Time	Area	Area%
1	7.223	5947168	90.265
2	7.829	641381	9.735
Total		6588549	100.000

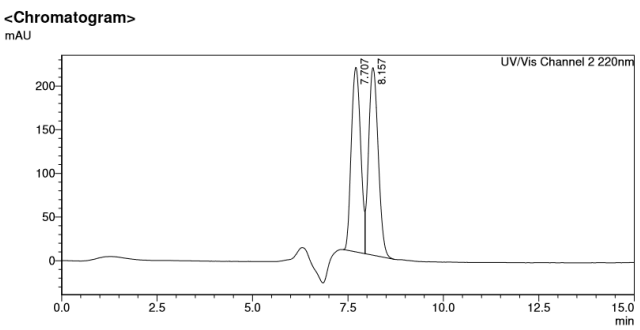


3n

(*S*,*E*)-4-(1-Cyclohexylpent-1-en-3-yl)morpholine (3n): Prepared by General Method C using **Pd-1** at 22 ˚C for 20 h. The material was purified by flash silica gel chromatography (100% hexanes to 80:20 hexanes:EtOAc) to yield **3n** as colorless oil (29.0 mg, 0.122 mmol, 61.1 % yield). **IR** (neat, cm^{-1}) 2956 (w), 2921 (s), 2874 (w), 2849 (s), 2805 (w), 1448 (s), 1268 (m), 1117 (s), 1004 (s), 972 (s), 859 (m); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.42 (1H, dd, J = 15.5, 6.6 Hz), 5.15 (1H, dd, J = 15.5, 9.0 Hz), 3.76–3.60 (4H, m), 2.59–2.30 (4H, m), 1.76–1.55 (7H, m), 1.41–0.98 (7H, m), 0.80 (3H, t, J = 7.4 Hz); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 140.6, 126.2, 69.9, 67.4, 50.5, 40.7, 33.3, 33.2, 26.1, 24.7, 10.9; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{15}H_{27}NO$: 237.2093, found: 237.2095.

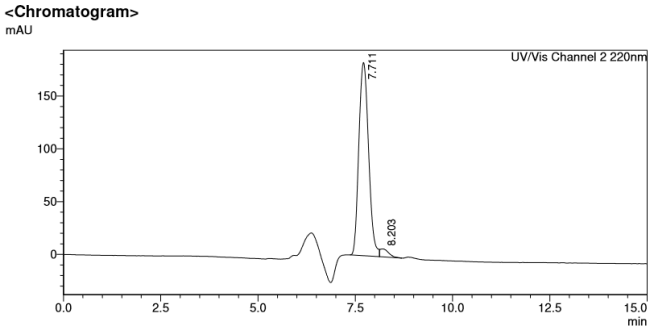
$[\alpha]_D^{27}$ = –15.1 (c = 1.0, $CHCl_3$) for a sample of 96:4 er.

HPLC: Column: Chiralpak 1-A3 (3 μm, 4.6 mm X 150 mm). Mobile phase: 90:10 *i*-PrOH (with 0.1% Et_2NH):MeCN, 0.3 mL/min. Detection wavelength: 220 nm. Er = 96:4.



<Peak Table>
UV/Vis Channel 2 220nm

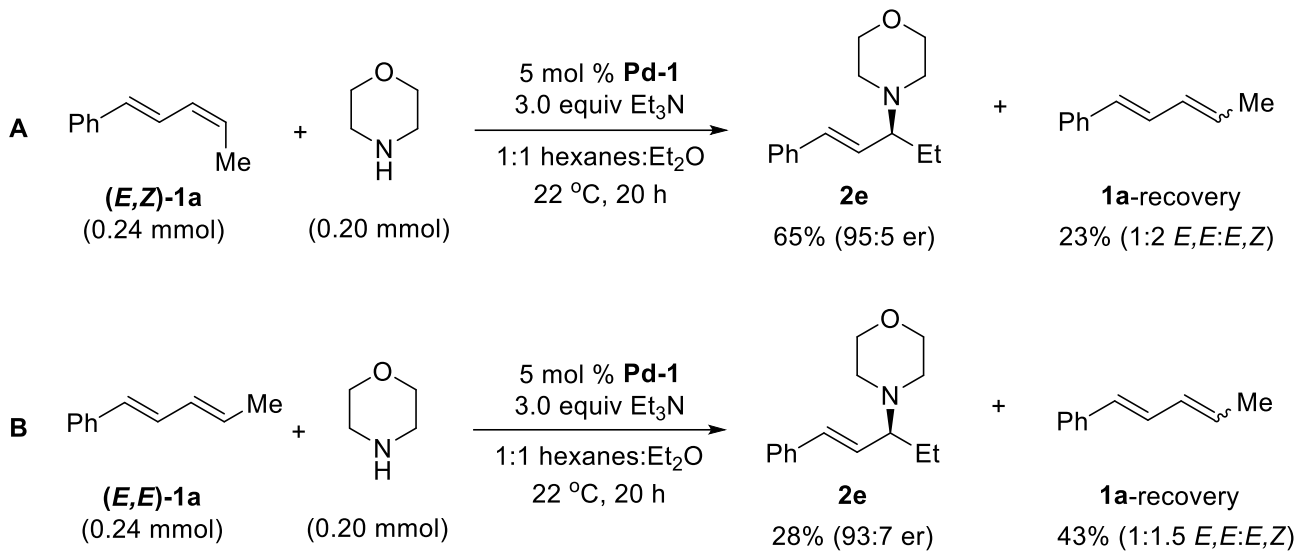
Peak#	Ret. Time	Area	Area%
1	7.707	3631619	49.394
2	8.157	3720775	50.606
Total		7352394	100.000



<Peak Table>
UV/Vis Channel 2 220nm

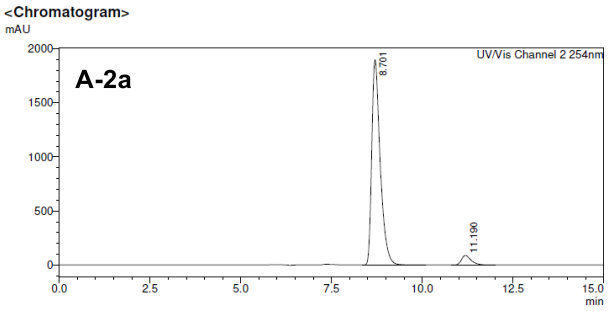
Peak#	Ret. Time	Area	Height%
1	7.711	3204890	96.058
2	8.203	114292	3.942
Total		3319182	100.000

VI. Reaction Outcome Dependence on Diene Stereochemistry



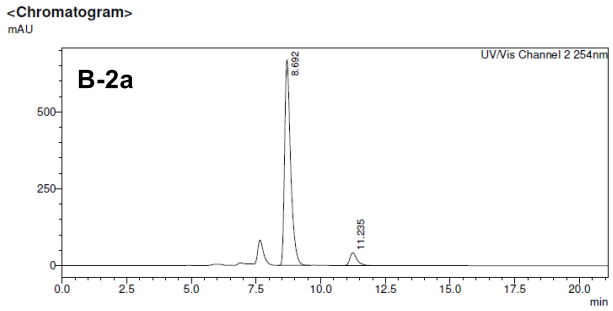
Reactions were carried as described in General Method C at 22 ºC for 20 h. Products **2e** and **1a**-recovery were then purified by flash silica gel chromatography (100% hexanes to 80:20 hexanes:EtOAc).

HPLC: Column: Chiralpak 1-A3 (3 μm, 4.6 mm X 150 mm). Mobile phase: 95:5 *i*-PrOH (with 0.1% Et_2NH):MeCN, 0.3 mL/min. Detection wavelength: 254 nm. **A-2e**: Er = 95:5; **B-2e**: Er = 93:7.



<Peak Table>
UV/Vis Channel 2 254nm

Peak#	Ret. Time	Area	Area%
1	8.701	30787879	94.850
2	11.190	1671588	5.150
Total		32459468	100.000

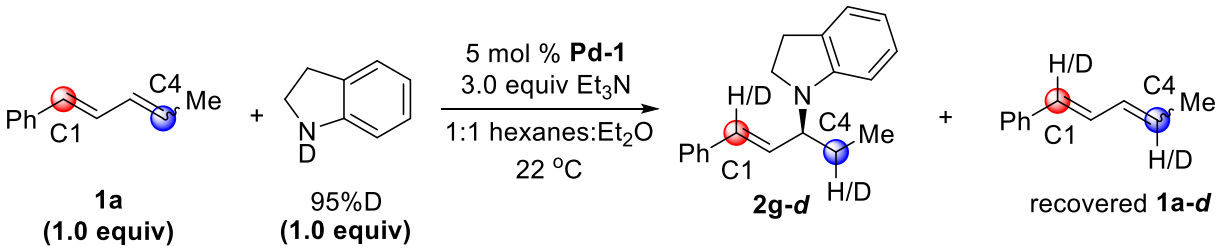


<Peak Table>
UV/Vis Channel 2 254nm

Peak#	Ret. Time	Area	Area%
1	8.692	10823169	93.113
2	11.235	800583	6.887
Total		11623751	100.000

VII. Deuterium Labelling Studies

Table S6. Deuterium labelling studies in indoline addition to diene **1a**[a]



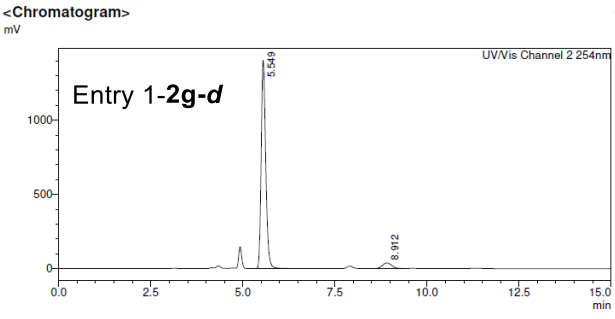
1a (1.0 equiv) | 95%D (1.0 equiv) | **2g-*d*** | recovered **1a-*d***

entry	time (h)	yield **2g-d** (%)[b] (er)	C4 % D in **2g-*d***[c,d]	1D/2D % in **2g-*d***[e]	recovered **1a-*d*** (%)[b] (*E,E*:*E,Z*)[c]	C1; C4 % D in *E,E*- & *E,Z*-**1a-*d***[c]
1	2	13 (95:5 er)	24	31/0	79 (1.4:1)	*E,E*: 15; 15 *E,Z*: 38; 48
2	20	28 (91:1 er)	22	40/8	56 (1.8:1)	*E,E*: 15; 19 *E,Z*: 45; 61

D-Indoline was prepared by a known previously established method.[23] [a]1:1.8 *E,E*:*E,Z* mixture of diene **1a**. [b]Isolated purified compound. [c]Determined by 400 MHz ^{1}H-NMR spectroscopy of purified compound. [d]Deuterium contant at C1 in **2g-*d*** could not be accurately determined due to overlap of the C1 proton with indoline aryl protons. [e]Determined by high resolution mass spectrometry of purified compound.

Reactions were carried as described in General Method C at 22 ºC. Products **2g-*d*** and recovered **1a-*d*** were then purified by flash silica gel chromatography (100% hexanes to 80:20 hexanes:EtOAc).

HPLC: Column: Cellulose III (3 μm, 4.6 mm X 250 mm). Mobile phase: 10:90 *i*-PrOH:hexanes, 1.0 mL/min. Detection wavelength: 254 nm. Entry 1-**2g-*d***: Er = 95:5; Entry 2-**2g-*d***: Er = 91:9.



<Peak Table>
UV/Vis Channel 2 254nm

Peak#	Ret. Time	Area	Area%
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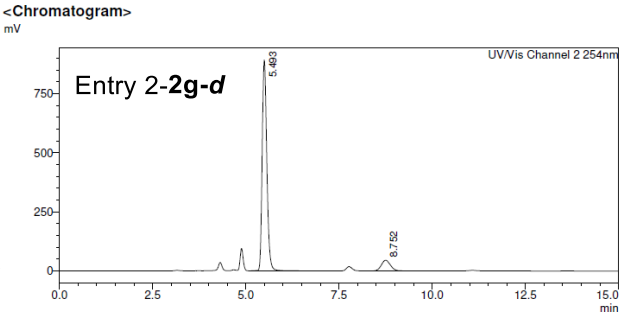
2	8.912	671420	5.270
Total		12740396	100.000



<Peak Table>
UV/Vis Channel 2 254nm

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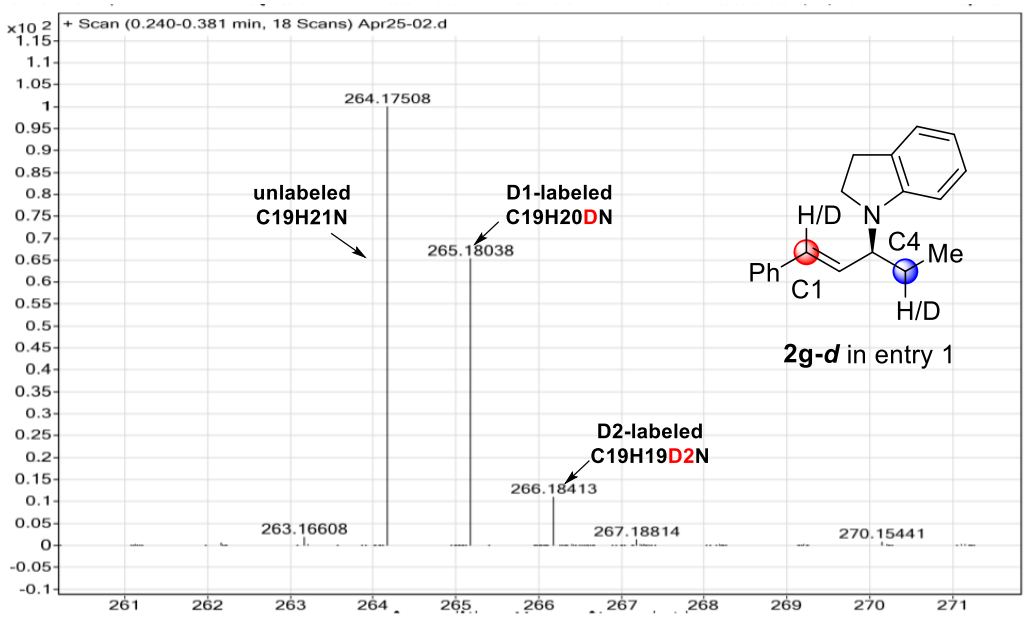
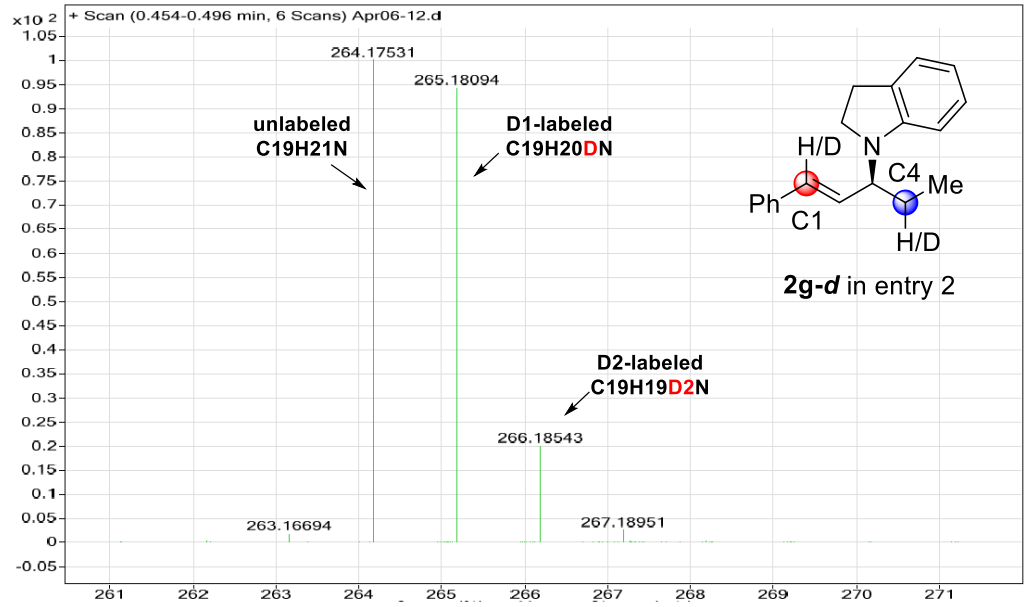
1	5.493	7622471	90.892
2	8.752	763857	9.108
Total		8386328	100.000

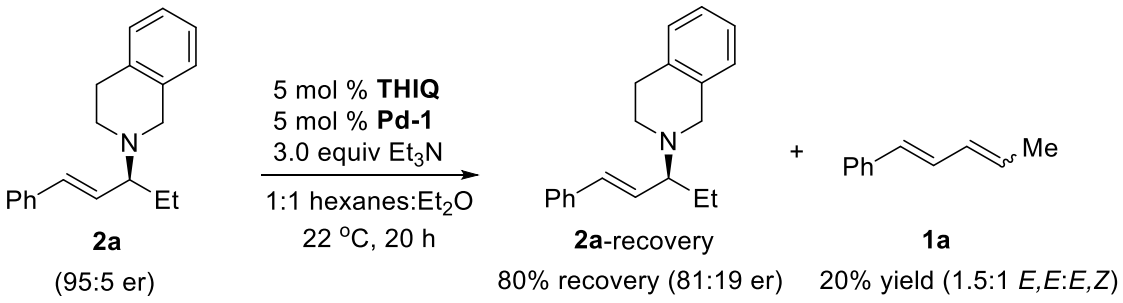


Mol Formula	Calculated Mass	Observed Mass	Error (ppm)	ion	Peak Area	% Area	Theoretical M+1 Peak Area	Corrected Peak Area	Corrected %Area
C19H21N	264.17468	264.17546	-2.97	[M+H]+	2489698	56.6		2489698	69.4
C19H20DN	265.18095	265.18082	-0.06	[M+H]+	1630501	37.1	527069.0666	1103431.933	30.8
C19H19D2N	266.18723	266.18465	9.69	[M+H]+	278465	6.3	286516.7645	-8051.764507	-0.2



Mol Formula	Calculated Mass	Observed Mass	Error (ppm)	ion	Peak Area	% Area	Theoretical M+1 Peak Area	Corrected Peak Area	Corrected %Area
C19H21N	264.17468	264.17531	-2.4	[M+H]+	22630454.3	43.0		22630454.3	51.9
C19H20DN	265.18095	265.18094	0.05	[M+H]+	22397309.2	42.6	4790867.175	17606442.06	40.4
C19H19D2N	266.18723	266.18543	6.76	[M+H]+	7575560.57	14.4	4207551.817	3368008.753	7.7

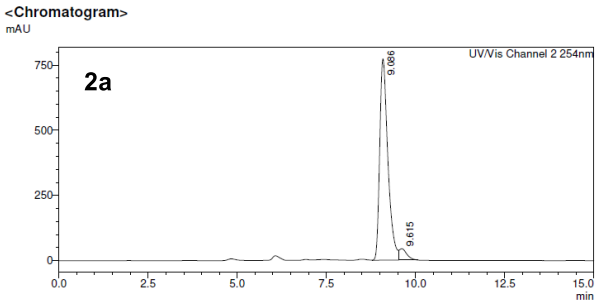
VII. Reaction Reversibility and Transamination Studies



2a (95:5 er) → **2a**-recovery (80% recovery (81:19 er)) + **1a** (20% yield (1.5:1 *E,E*:*E,Z*))

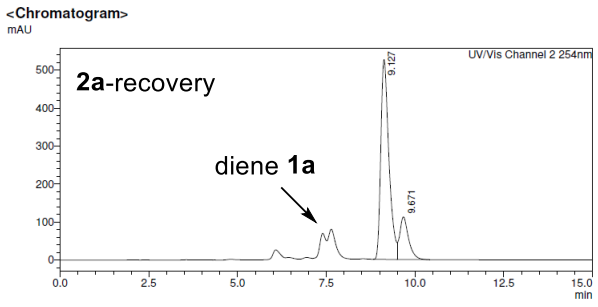
General Method D: Inside an N_2-filled glovebox, to a microwave vial equipped with a magnetic stirring rod was added successively: **Pd-1** catalyst (0.01 mmol, 5 mol%), **2** (0.20 mmol, 1.0 equiv), Et_2O/hexanes = 1/1 (0.2 mL), amine (0.01 mmol, 5 mol %) and lastly Et_3N (84 μL, 0.60 mmol, 3.0 equiv). Reactions were allowed to stir at room temperature for 20 h and then diluted with 1.0 mL of 1:1 hexanes:EtOAc, and finally filtered through a short plug of neutral alumina, eluting with ca. 10 mL of 1:1 hexanes:EtOAc. The solution was then concentrated *in vacuo* and the unpurified material was analyzed by ^{1}H NMR to determine *E*,*E*/*E*,*Z*-isomer ratio of **1a** and the yield of **1a** and **2** using CH_2Br_2 as an internal standard. And also, unpurified material was analyzed by HPLC to determine enantiomer ratio of **2.**

HPLC: Column: Chiralpak 1-A3 (3 μm, 4.6 mm X 150 mm). Mobile phase: 95:5 *i*-PrOH (with 0.1% Et_2NH):MeCN, 0.3 mL/min. Detection wavelength: 254 nm. **2a**: Er = 95:5; **2a**-recovery: Er = 81:19.



<Peak Table>
UV/Vis Channel 2 254nm

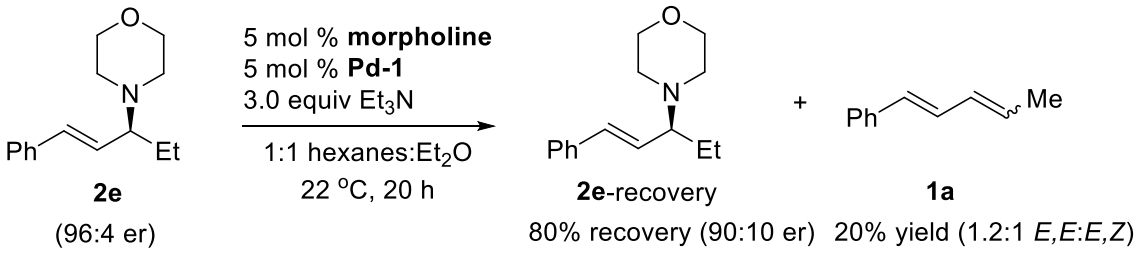
Peak#	Ret. Time	Area	Area%
1	9.086	12375294	94.993
2	9.615	652243	5.007
Total		13027537	100.000



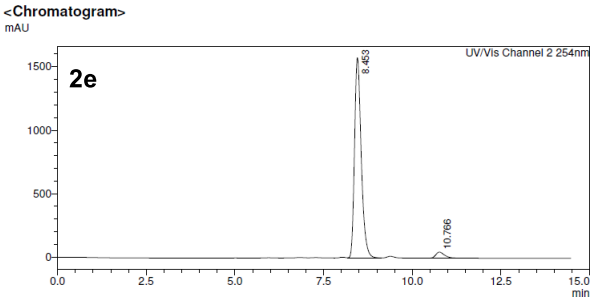
<Peak Table>
UV/Vis Channel 2 254nm

Peak#	Ret. Time	Area	Area%
1	9.127	8411836	81.229
2	9.671	1943819	18.771
Total		10355655	100.000

Additional experiment:

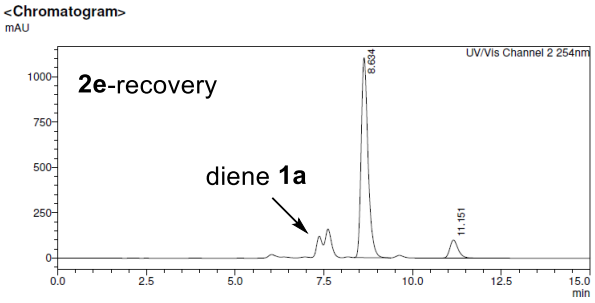


HPLC: Column: Chiralpak 1-A3 (3 μm, 4.6 mm X 150 mm). Mobile phase: 95:5 *i*-PrOH (with 0.1% Et_2NH):MeCN, 0.3 mL/min. Detection wavelength: 254 nm. **2e**: Er = 96:4; **2e**-recovery: Er = 90:10.



<Peak Table>
UV/Vis Channel 2 254nm

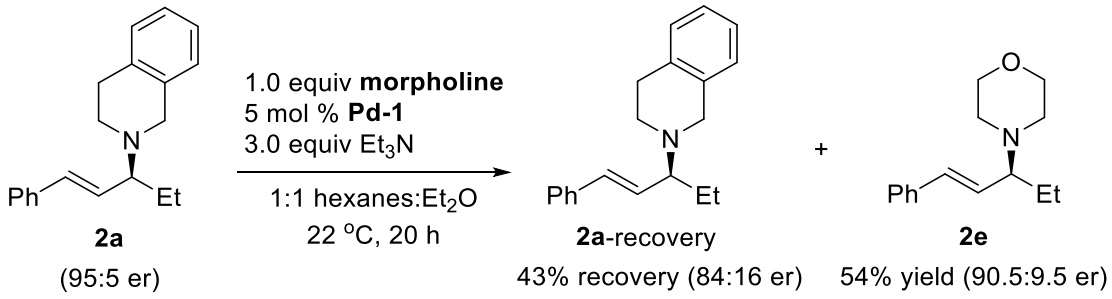
Peak#	Ret. Time	Area	Area%
1	8.453	20794000	96.225
2	10.766	815874	3.775
Total		21609874	100.000



<Peak Table>
UV/Vis Channel 2 254nm

Peak#	Ret. Time	Area	Area%
1	8.634	14879019	90.145
2	11.151	1626550	9.855
Total		16505569	100.000

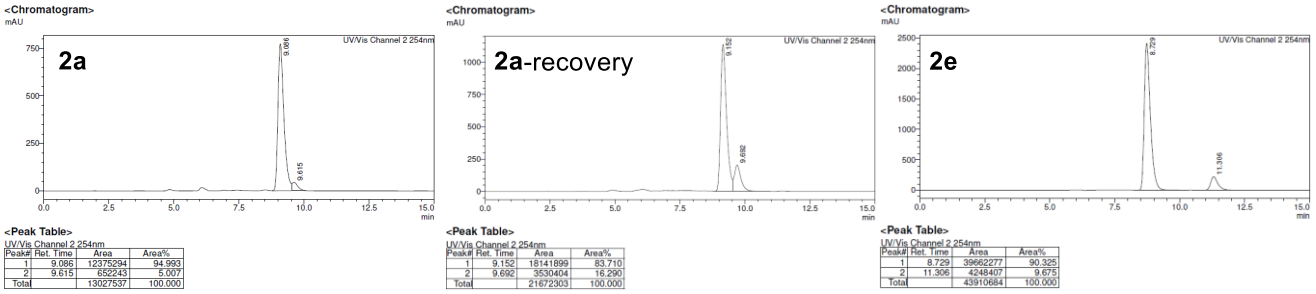
A)



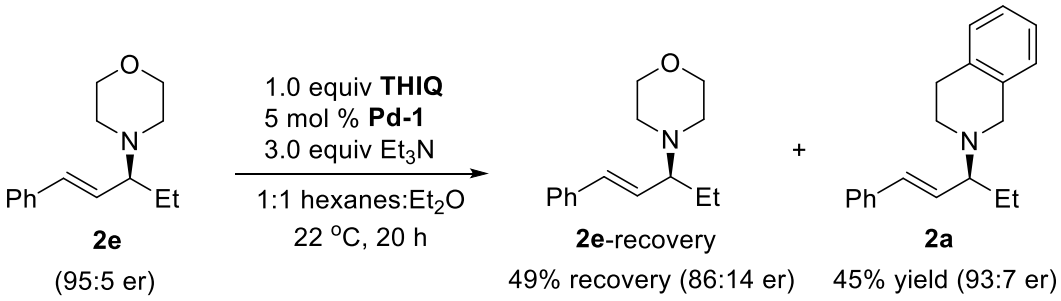
General Method E: Inside an N_2-filled glovebox, to a microwave vial equipped with a magnetic stirring rod was added successively: **Pd-1** catalyst (0.01 mmol, 5 mol%), **2** (0.20 mmol, 1.0 equiv), Et_2O/hexanes = 1/1 (0.2 mL), amine (0.20 mmol, 1.0 equiv) and lastly Et_3N (84 μL, 0.60 mmol, 3.0 equiv). Reactions were allowed to stir at room temperature for 20 h and then diluted with 1.0 mL of 1:1 hexanes:EtOAc, and finally filtered through a short plug of neutral alumina, eluting with ca. 10 mL of 1:1 hexanes:EtOAc. The solution was then concentrated *in vacuo* and the unpurified material was

analyzed by ^{1}H NMR to determine *E*,*E*/*E*,*Z*-isomer ratio of **1a** and the yield of **1a** and **2** using CH_2Br_2 as an internal standard. The material was purified by flash silica gel chromatography (100% hexanes to 80:20 hexanes:EtOAc). The purified material was analyzed by HPLC to determine enantiomer ratio of the two allylic amines separately.

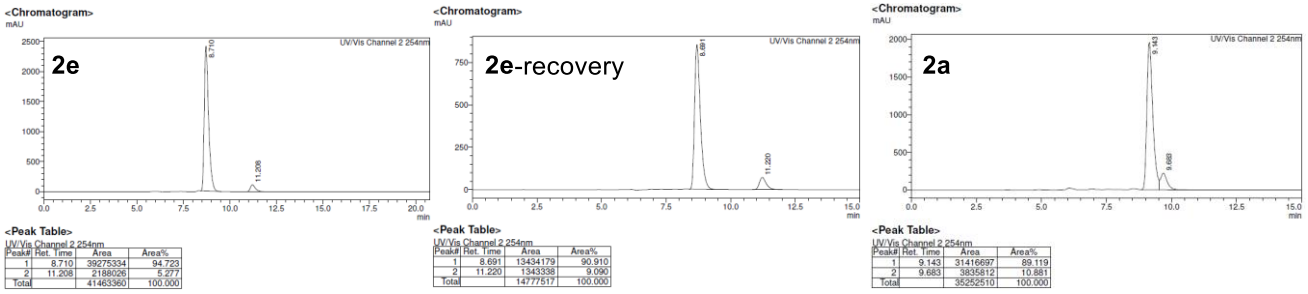
HPLC: Column: Chiralpak 1-A3 (3 μm, 4.6 mm X 150 mm). Mobile phase: 95:5 *i*-PrOH (with 0.1% Et_2NH):MeCN, 0.3 mL/min. Detection wavelength: 254 nm. **2a**: Er = 98.5:1.5; **2a**-recovery: Er = 84:16; **2e**: Er = 90.5:10.5.



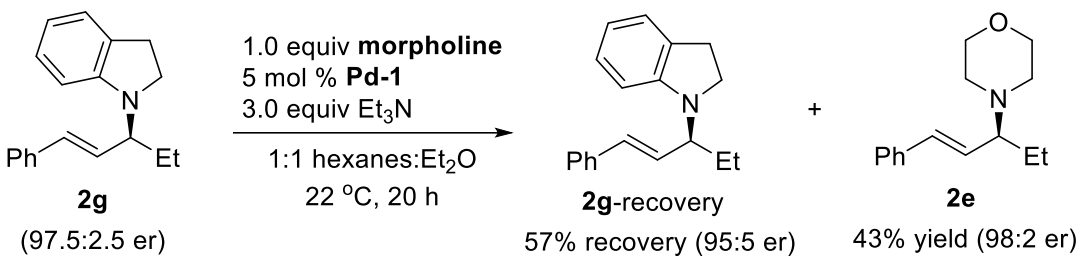
B)



HPLC: Column: Chiralpak 1-A3 (3 μm, 4.6 mm X 150 mm). Mobile phase: 95:5 *i*-PrOH (with 0.1% Et_2NH):MeCN, 0.3 mL/min. Detection wavelength: 254 nm. **2e**: Er = 95:5; **2e**-recovery: Er = 91:9; **2a**: Er = 89:11.

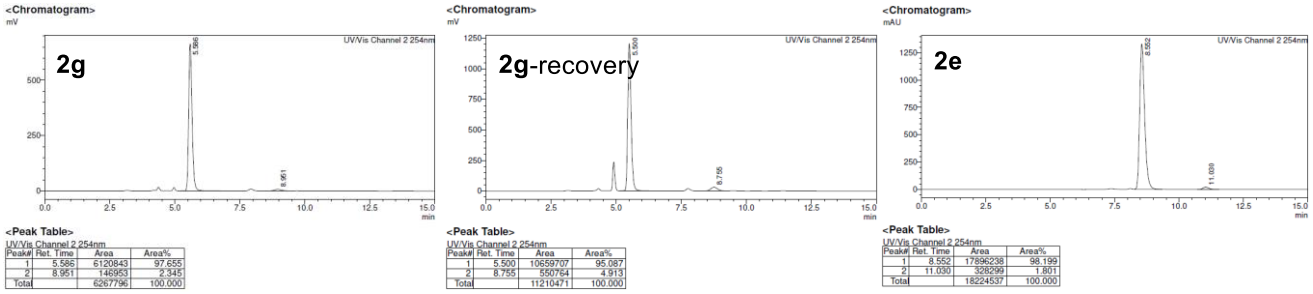


C)

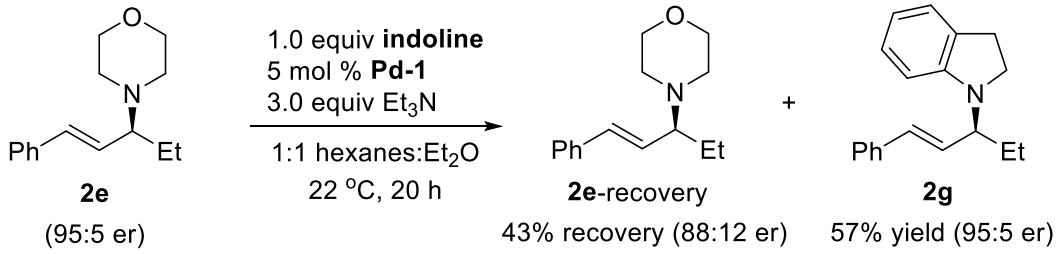


2g (97.5:2.5 er) → **2g**-recovery (57% recovery (95:5 er)) + **2e** (43% yield (98:2 er))

HPLC: Column 1: Cellulose III (3 μm, 4.6 mm X 250 mm). Mobile phase: 10:90 *i*-PrOH:hexanes, 1.0 mL/min. Detection wavelength: 254 nm. **2g**: Er = 97.5:2.5; **2g**-recovery: Er = 95:5; Column 2: Chiralpak 1-A3 (3 μm, 4.6 mm X 150 mm). Mobile phase: 95:5 *i*-PrOH (with 0.1% Et_2NH):MeCN, 0.3 mL/min. Detection wavelength: 254 nm. **2e**: Er = 98:2.

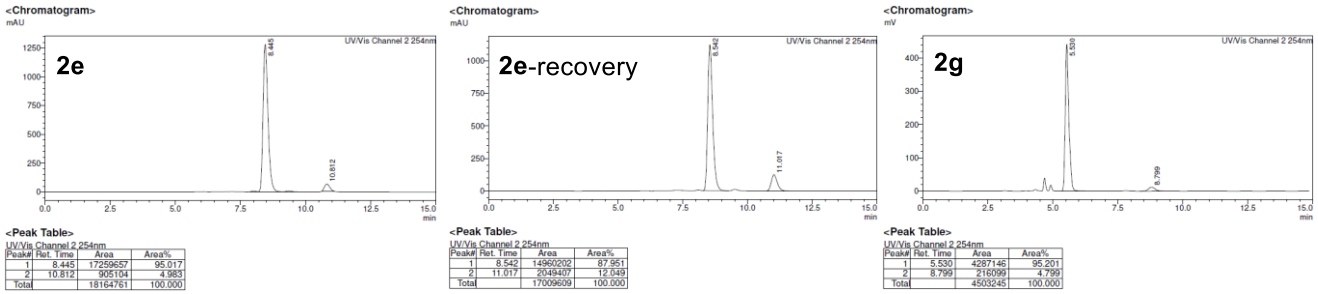


D)

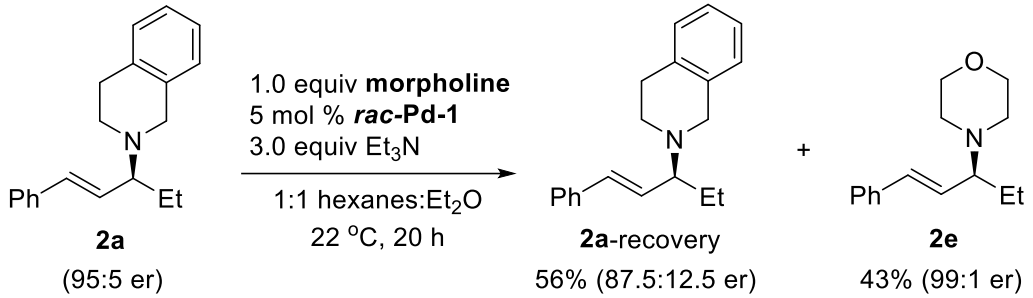


2e (95:5 er) → **2e**-recovery (43% recovery (88:12 er)) + **2g** (57% yield (95:5 er))

HPLC: Column 1: Chiralpak 1-A3 (3 μm, 4.6 mm X 150 mm). Mobile phase: 95:5 *i*-PrOH (with 0.1% Et_2NH):MeCN, 0.3 mL/min. Detection wavelength: 254 nm. **2e**: Er = 95:5; **2e**-recovery: Er = 88:12; Column 2: Cellulose III (3 μm, 4.6 mm X 250 mm). Mobile phase: 10:90 *i*-PrOH:hexanes, 1.0 mL/min. Detection wavelength: 254 nm. **2g**: Er = 95:5.



E)

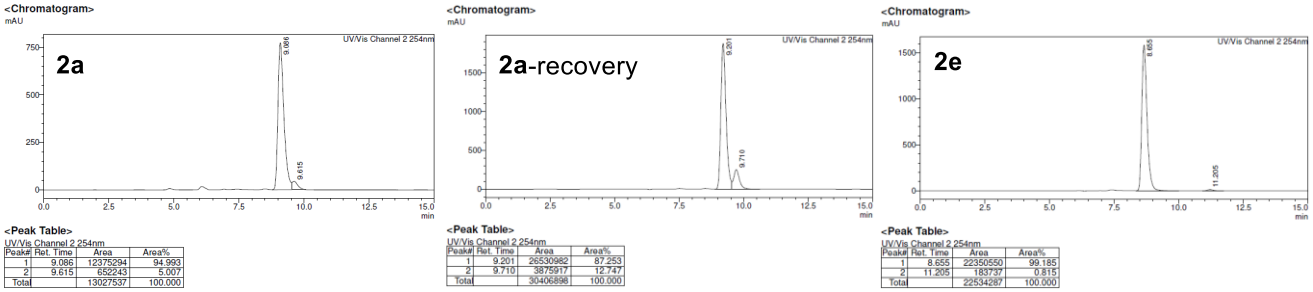


2a (95:5 er)

2a-recovery 56% (87.5:12.5 er)

2e 43% (99:1 er)

HPLC: Column: Chiralpak 1-A3 (3 μm, 4.6 mm X 150 mm). Mobile phase: 95:5 IPA (with 0.1% Et_2NH):MeCN, 0.3 mL/min. Detection wavelength: 254 nm. **2a**-racemic: E.r. = 95:5; **2a**-recovery: E.r. = 87.5:12.5; **2e**: E.r. = 99:1.



<Peak Table> UV/Vis Channel 2 254nm

Peak#	Ret. Time	Area	Area%
1	9.086	12375294	94.993
2	9.615	652243	5.007
Total		13027537	100.000

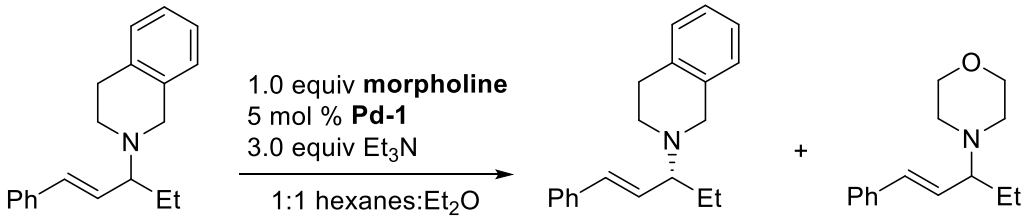
<Peak Table> UV/Vis Channel 2 254nm

Peak#	Ret. Time	Area	Area%
1	9.201	26530982	87.253
2	9.710	3875917	12.747
Total		30406898	100.000

<Peak Table> UV/Vis Channel 2 254nm

Peak#	Ret. Time	Area	Area%
1	8.655	22350550	99.185
2	11.205	183737	0.815
Total		22534287	100.000

Additional experiment:

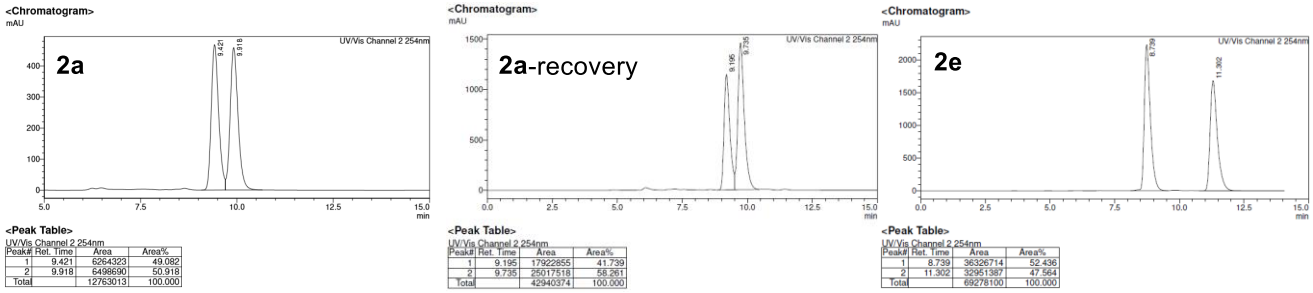


2a (racemic)

2a-recovery 42% (58:42 er)

2e 58% (52.5:47.5 er)

HPLC: Column: Chiralpak 1-A3 (3 μm, 4.6 mm X 150 mm). Mobile phase: 95:5 IPA (with 0.1% Et_2NH):MeCN, 0.3 mL/min. Detection wavelength: 254 nm. **2a**-racemic: E.r. = 95:5; **2a**-recovery: E.r. = 42:58; **2e**: E.r. = 52.5:47.5.



<Peak Table> UV/Vis Channel 2 254nm

Peak#	Ret. Time	Area	Area%
1	9.421	6264323	49.082
2	9.918	6498690	50.918
Total		12763013	100.000

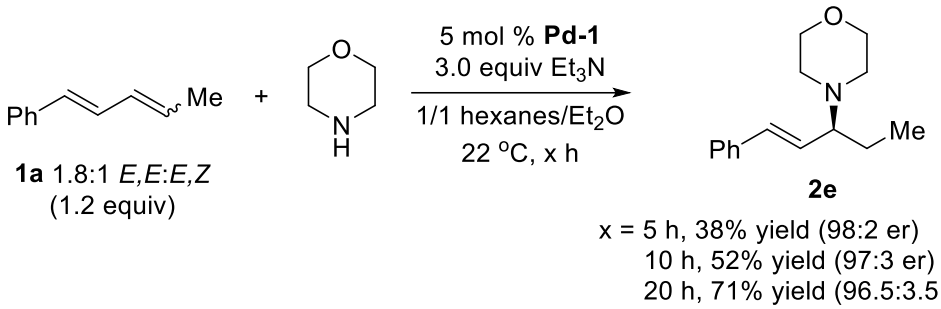
<Peak Table> UV/Vis Channel 2 254nm

Peak#	Ret. Time	Area	Area%
1	9.195	17922855	41.739
2	9.735	25017518	58.261
Total		42940374	100.000

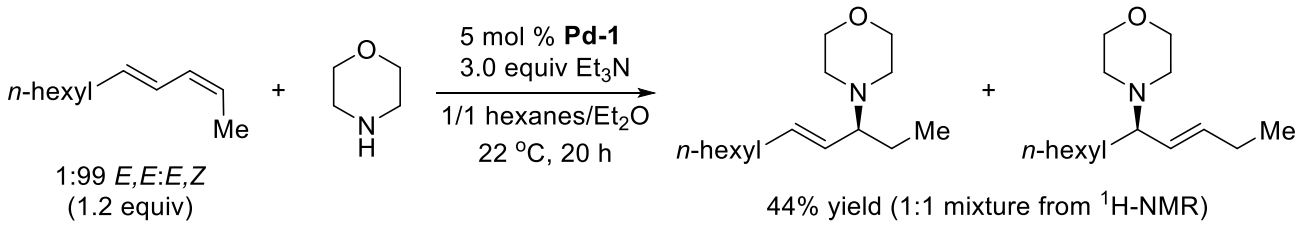
<Peak Table> UV/Vis Channel 2 254nm

Peak#	Ret. Time	Area	Area%
1	8.739	36326714	52.436
2	11.302	32951387	47.564
Total		69278100	100.000

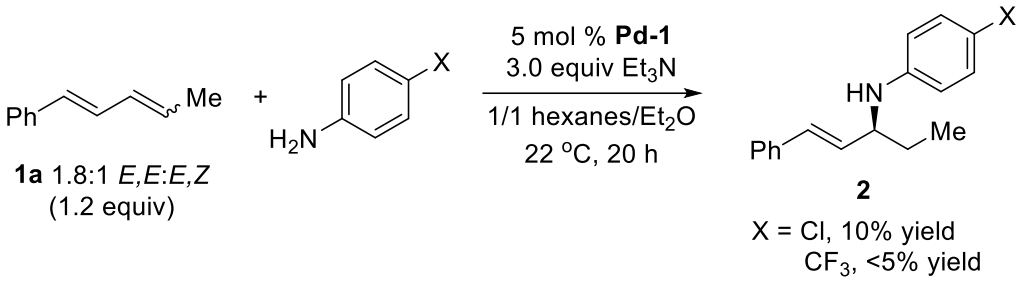
IX. Additonal Experiments



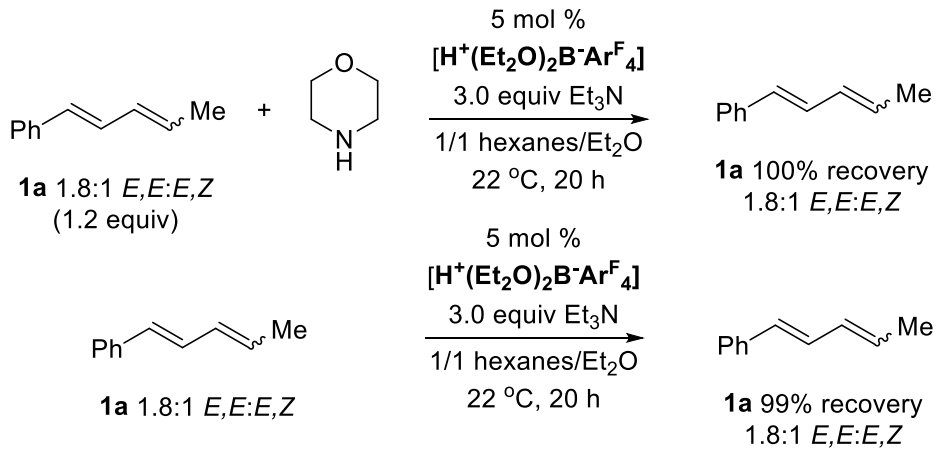
Scheme S1. Reactivity and enantioselectivity of morpholine addition to **1a** over time



Scheme S2. Hydroamination of another 1,4-dialkyldiene derivative with morpholine



Scheme S3. Hydroamination of internal diene **1a** with other aniline derivatives



Scheme S4. Control experiments with Brookhart's acid

X. References

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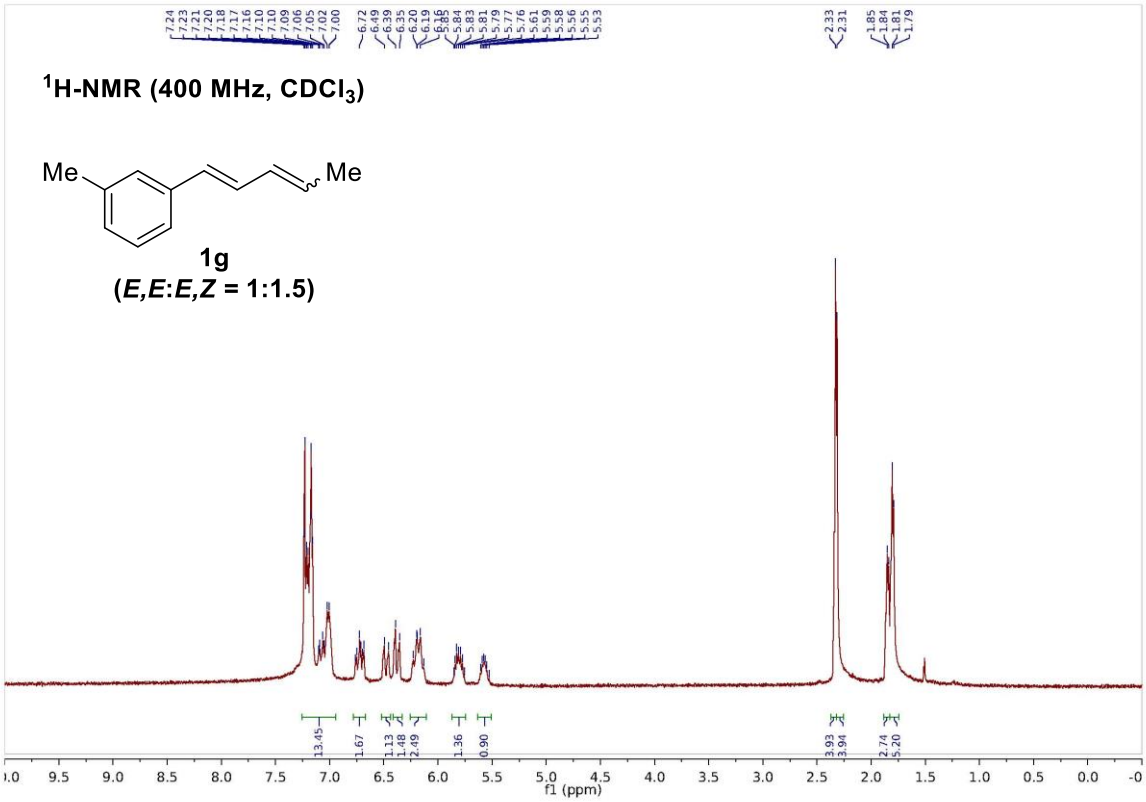
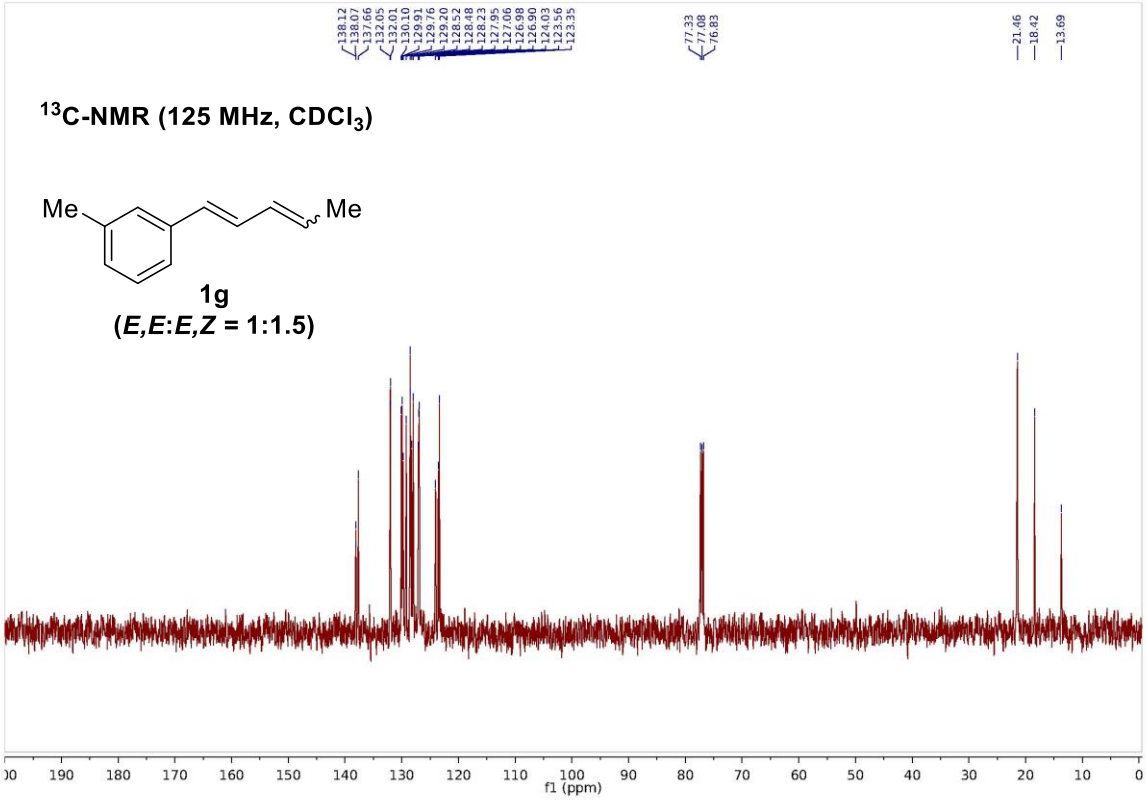
XI. NMR Spectra



^{1}H-NMR (400 MHz, $CDCl_3$)

1g

(*E*,*E*:*E*,*Z* = 1:1.5)

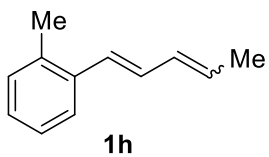


^{13}C-NMR (125 MHz, $CDCl_3$)

1g

(*E*,*E*:*E*,*Z* = 1:1.5)

^{1}H-NMR (400 MHz, $CDCl_3$)



1h

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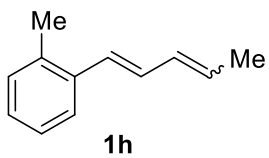

1h

(*E*,*E*:*E*,*Z* = 1:2.4)

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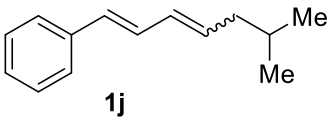
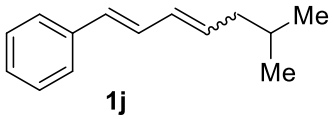
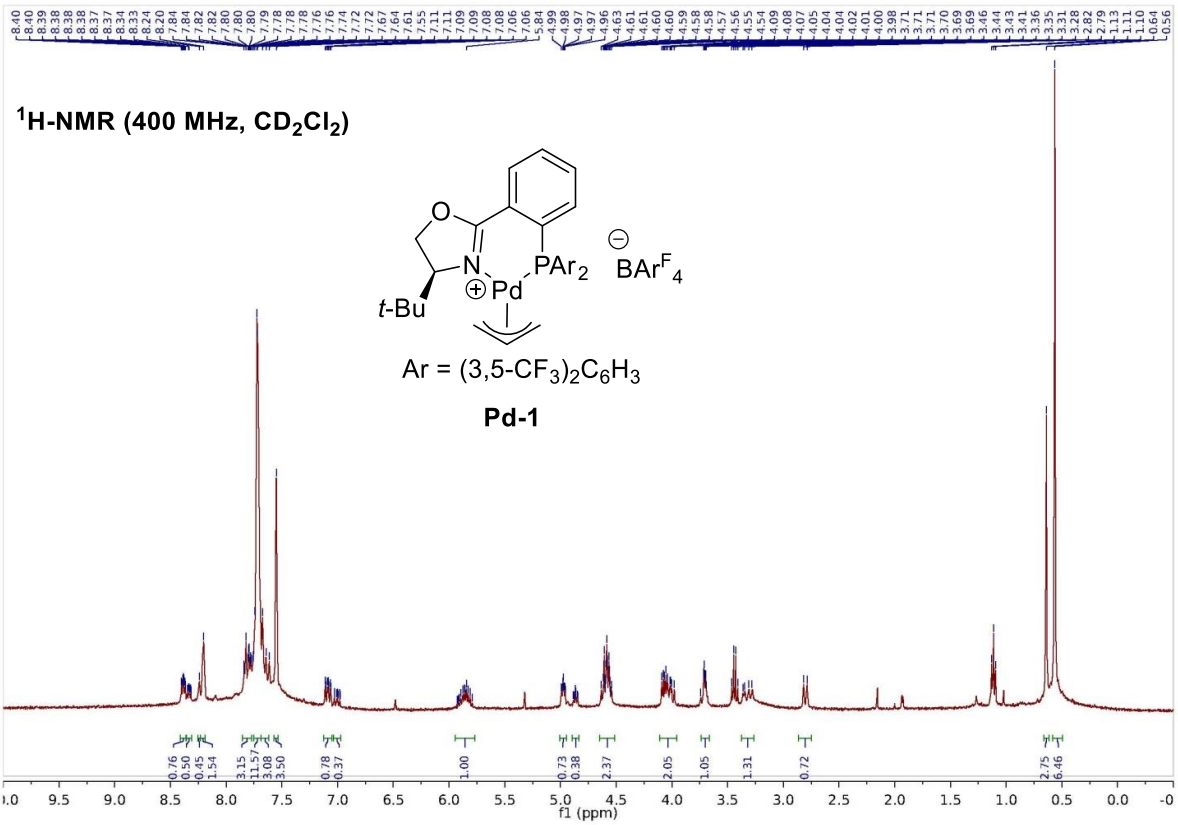


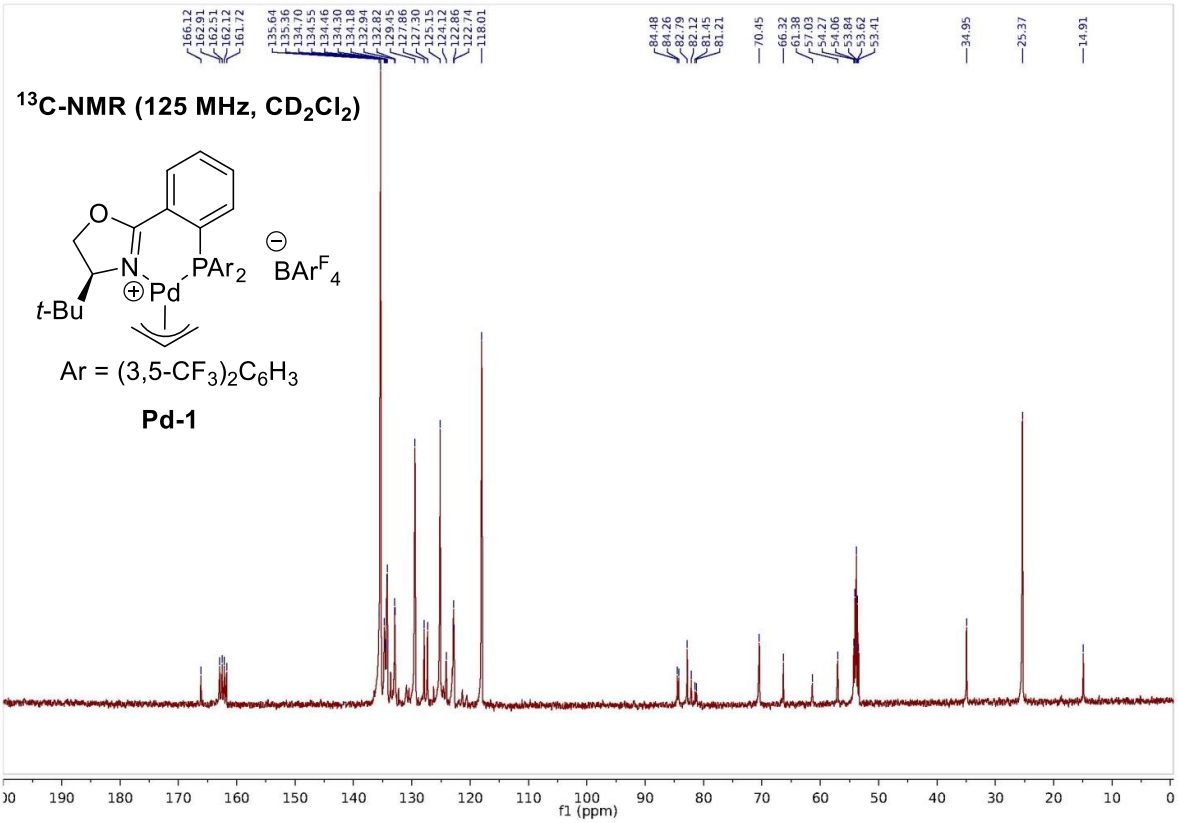
1j
(*E,E*:*E,Z* = 1:1)

^{13}C-NMR (125 MHz, $CDCl_3$)

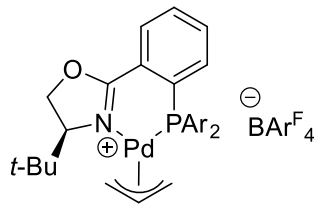


1j
(*E,E*:*E,Z* = 1:1)


^{1}H-NMR (400 MHz, CD_2Cl_2)
O
N
PAr$_2$
Pd
t-Bu
BAr$^F_4$
Ar = (3,5-CF_3)$_2$$C_6H_3$
Pd-1
f1 (ppm)


^{13}C-NMR (125 MHz, CD_2Cl_2)
O
N
PAr$_2$
Pd
t-Bu
BAr$^F_4$
Ar = (3,5-CF_3)$_2$$C_6H_3$
Pd-1
f1 (ppm)

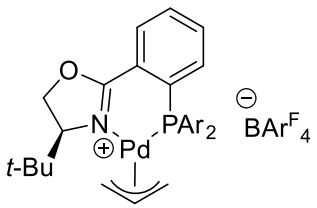
^{19}F-NMR (376 MHz, CD_2Cl_2)



Ar = $(3,5\text{-}CF_3)_2C_6H_3$

Pd-1

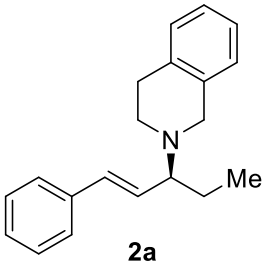
^{31}P-NMR (162 MHz, CD_2Cl_2)



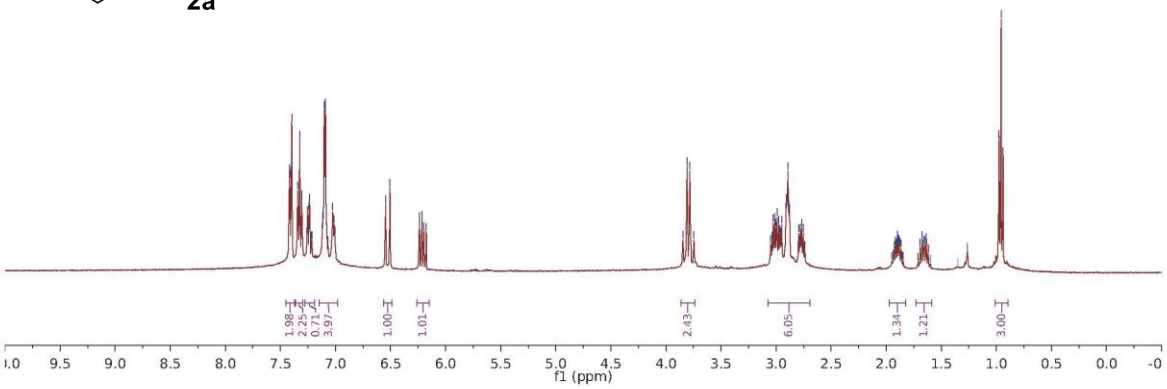
Ar = $(3,5\text{-}CF_3)_2C_6H_3$

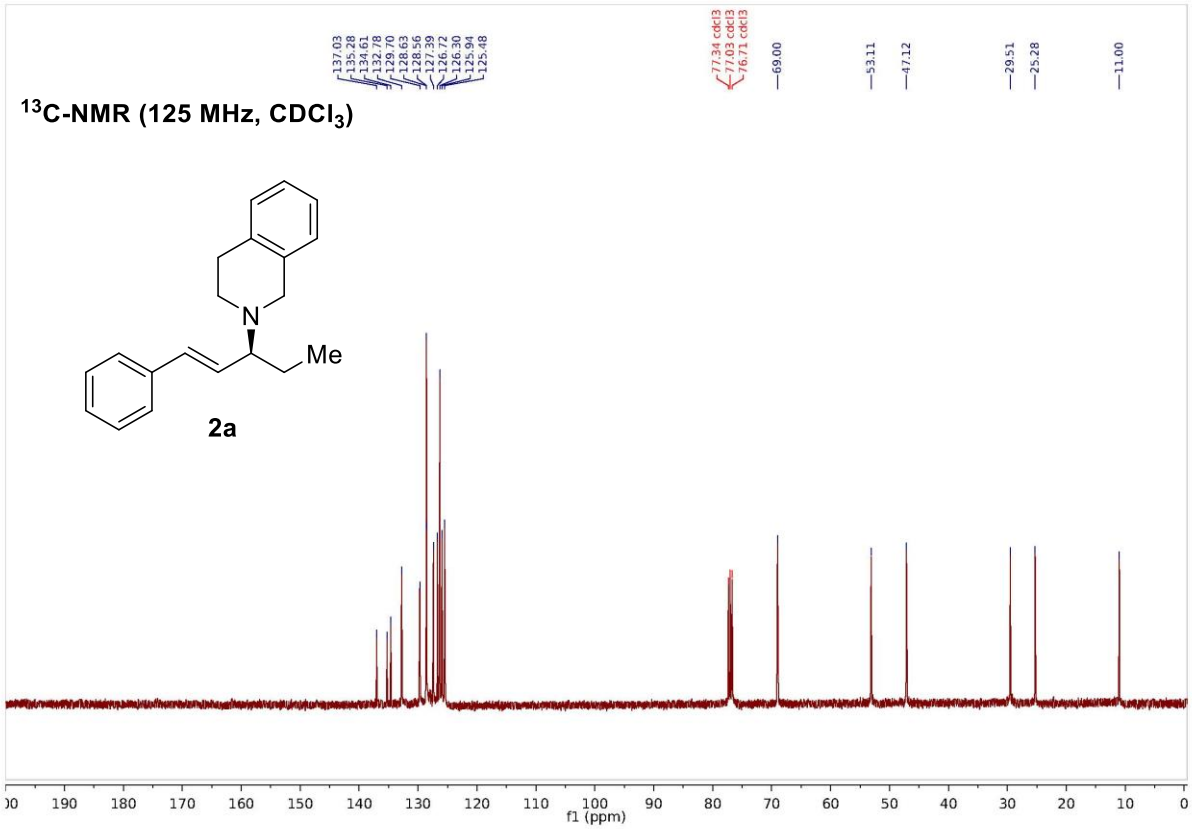
Pd-1

^{1}H-NMR (400 MHz, $CDCl_3$)



2a

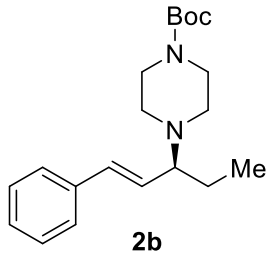




^{13}C-NMR (125 MHz, $CDCl_3$)

2a

^{1}H-NMR (400 MHz, $CDCl_3$)

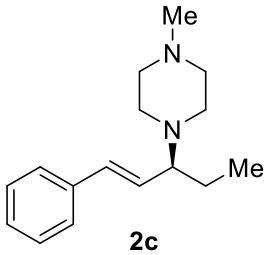


2b

^{13}C-NMR (125 MHz, $CDCl_3$)

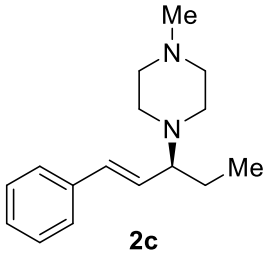
2b

^{1}H-NMR (400 MHz, $CDCl_3$)



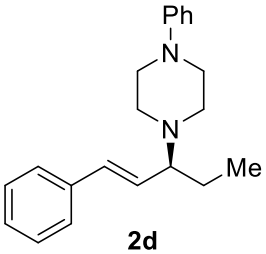
2c

^{13}C-NMR (125 MHz, $CDCl_3$)



2c

^{1}H-NMR (400 MHz, $CDCl_3$)



2d

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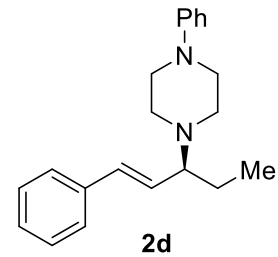
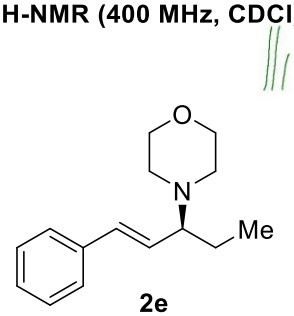


2d

^{1}H-NMR (400 MHz, $CDCl_3$)



2e

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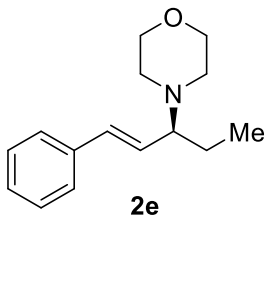
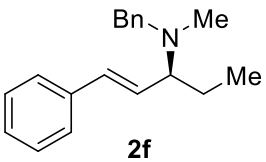


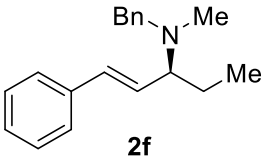
2e

^{1}H-NMR (400 MHz, $CDCl_3$)

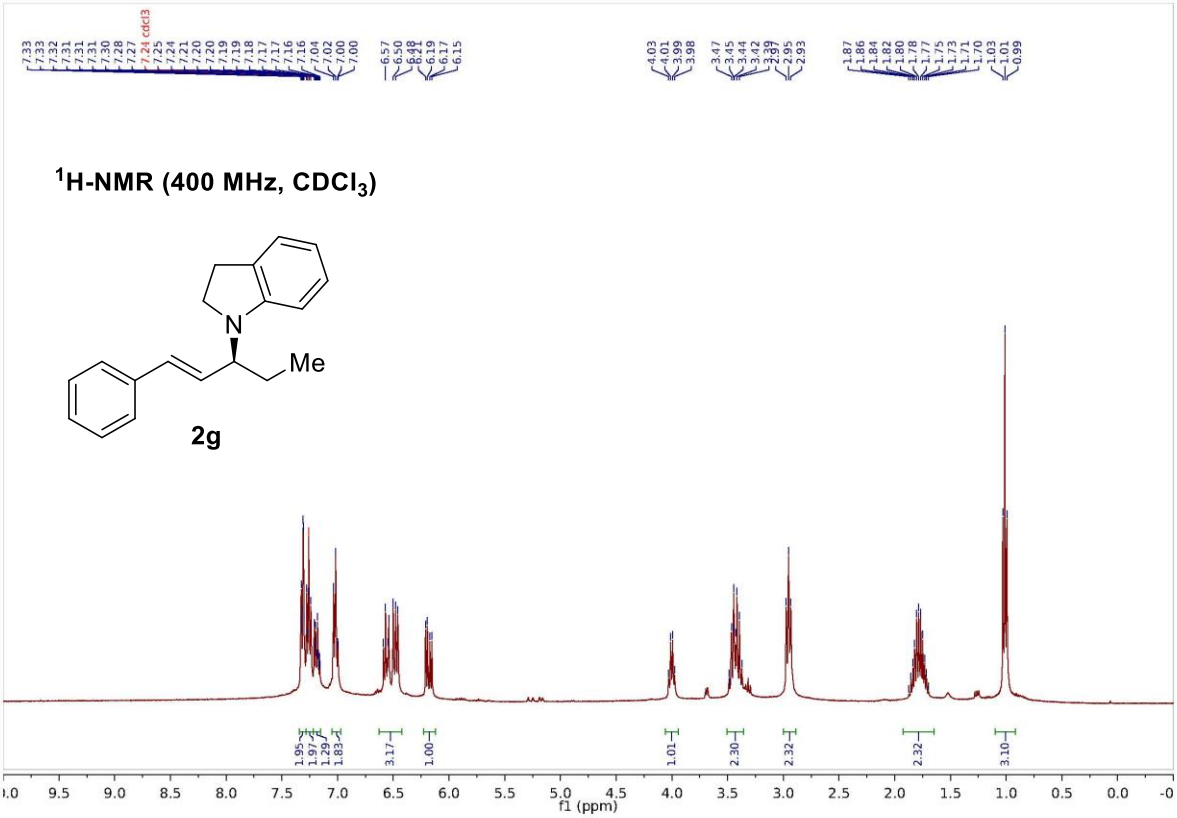


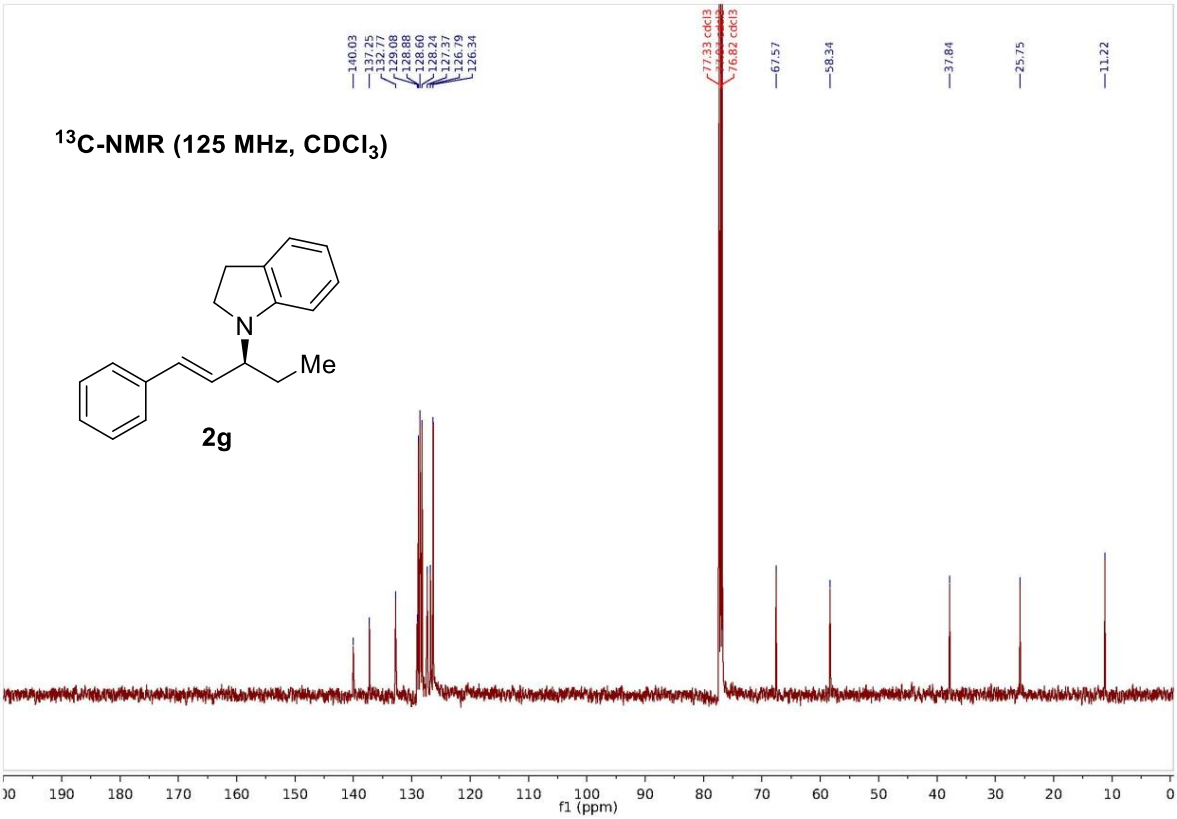
2f

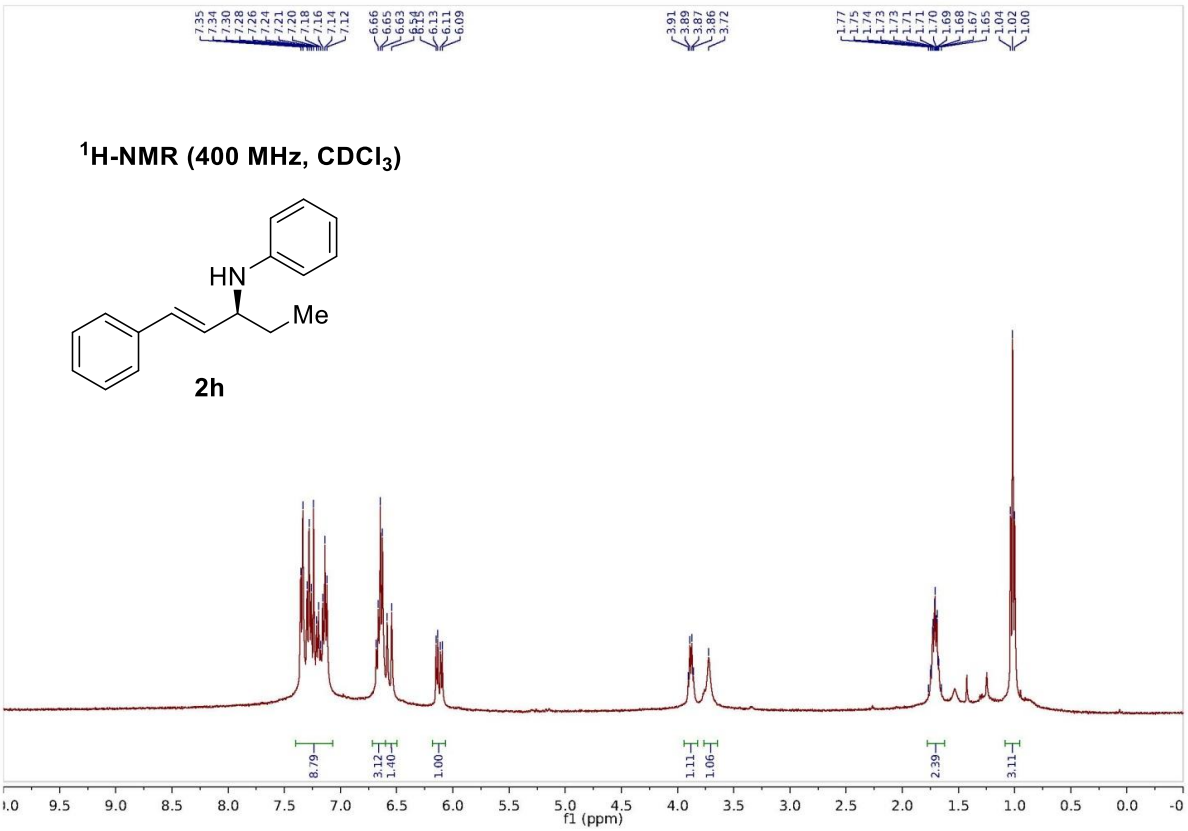
^{13}C-NMR (125 MHz, $CDCl_3$)

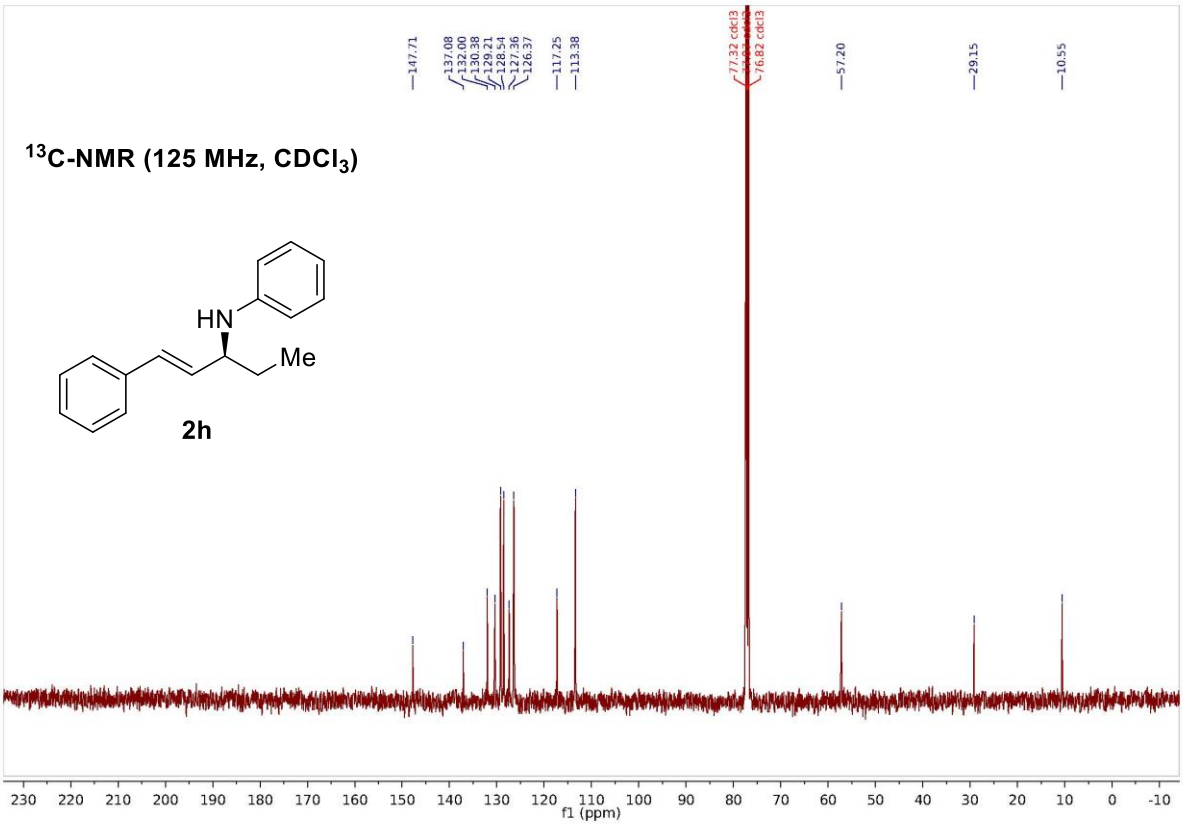


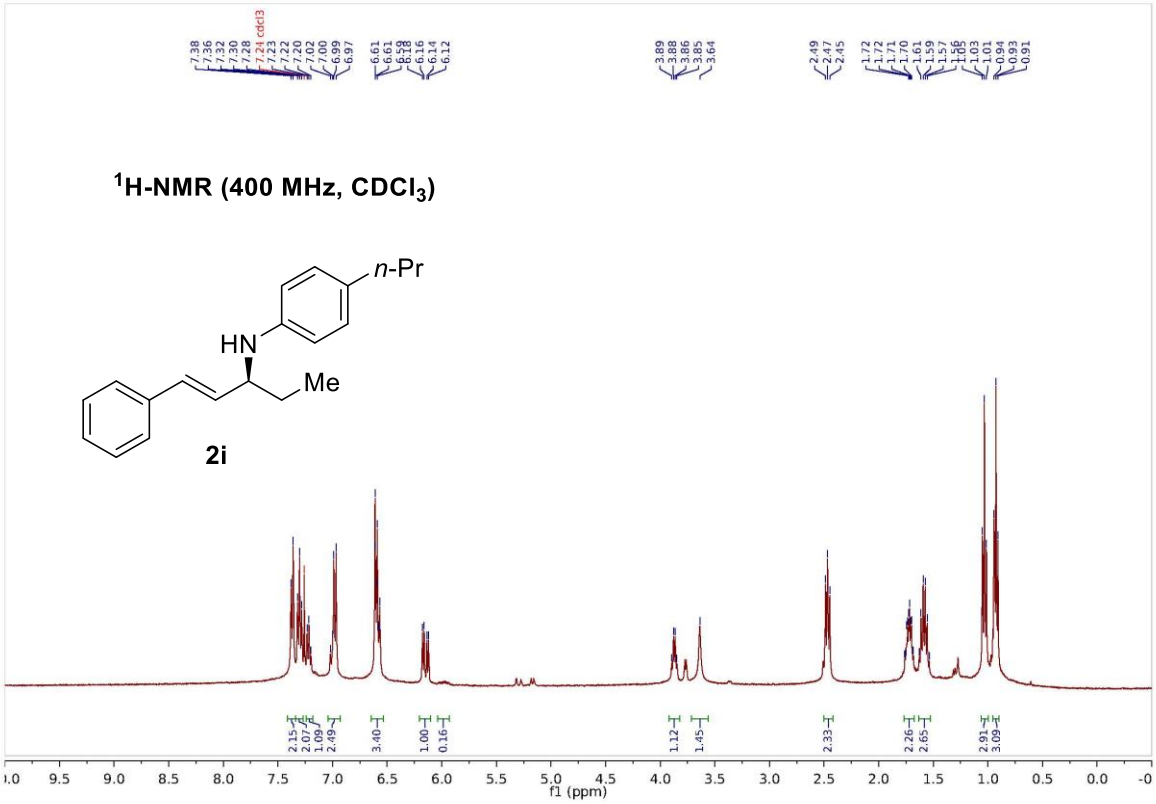
2f

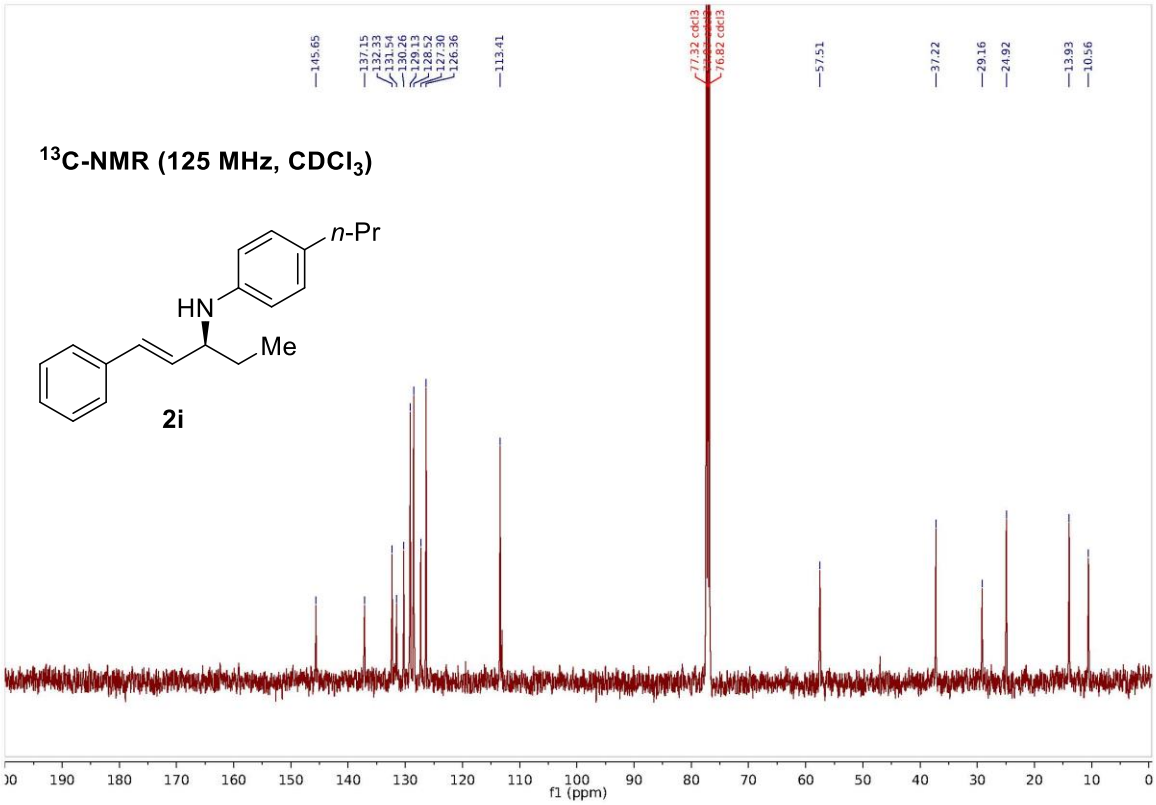

1H-NMR (400 MHz, CDCl3)
N
Me
2g
f1 (ppm)

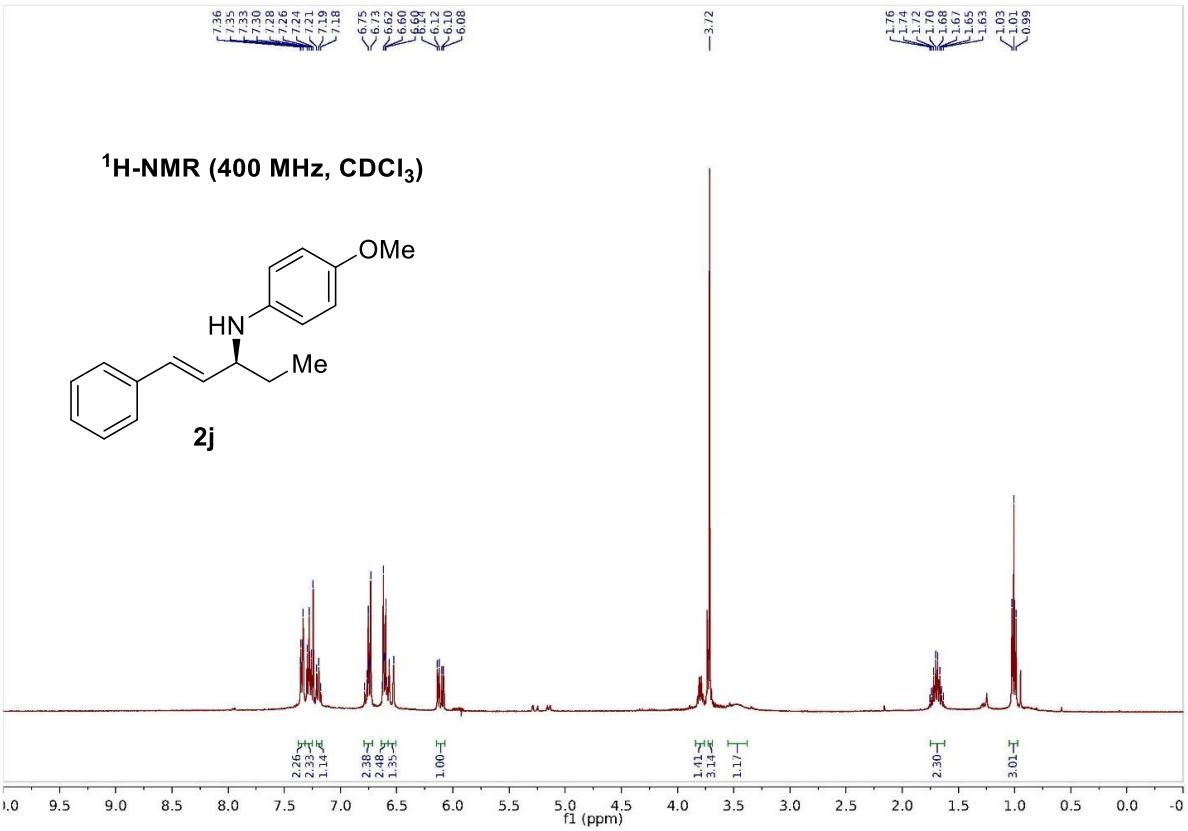

13C-NMR (125 MHz, CDCl3)
N
Me
2g
f1 (ppm)

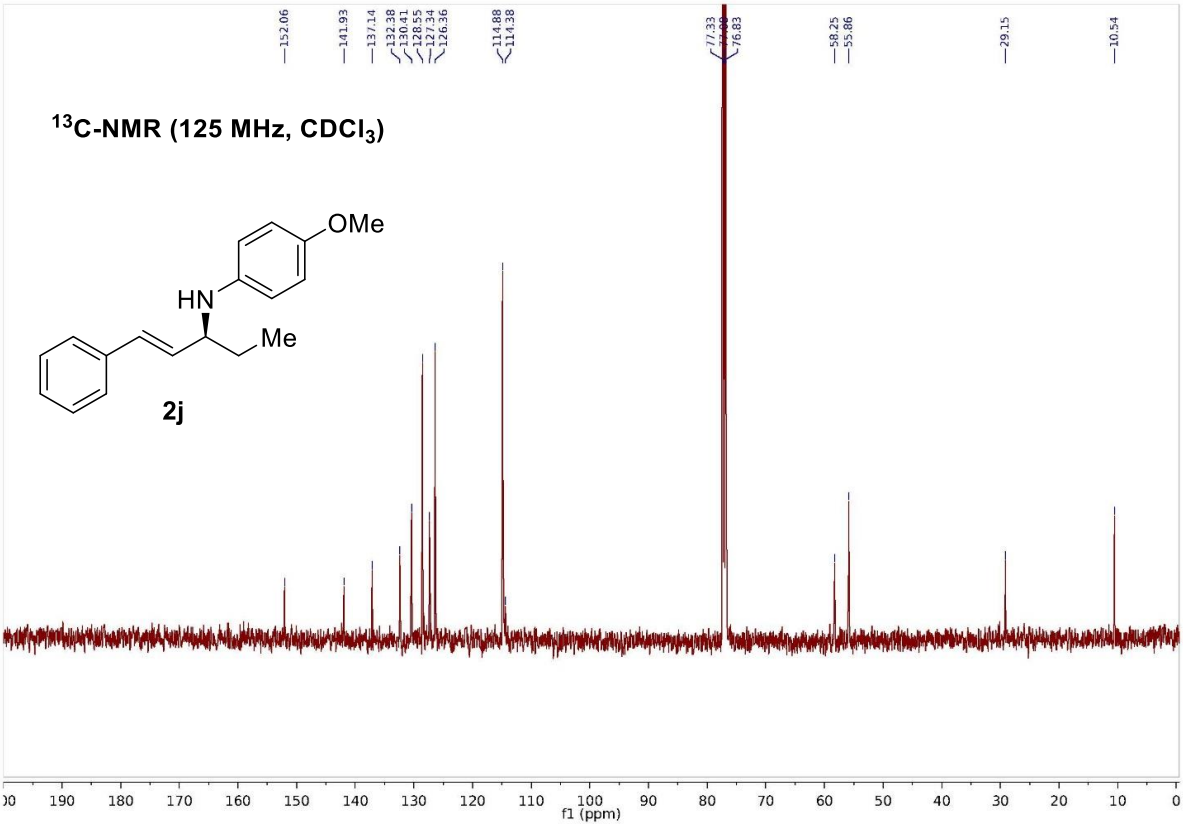

7.35
7.34
7.30
7.28
7.26
7.24
7.21
7.20
7.18
7.16
7.14
7.12
6.66
6.65
6.63
6.54
6.53
6.13
6.11
6.09
3.91
3.89
3.87
3.86
3.72
1.77
1.75
1.74
1.73
1.73
1.71
1.71
1.70
1.69
1.68
1.67
1.65
1.04
1.02
1.00
^{1}H-NMR (400 MHz, CDCl$_3$)
HN
Me
2h
8.79
3.12
1.40
1.00
1.11
1.06
2.39
3.11
f1 (ppm)

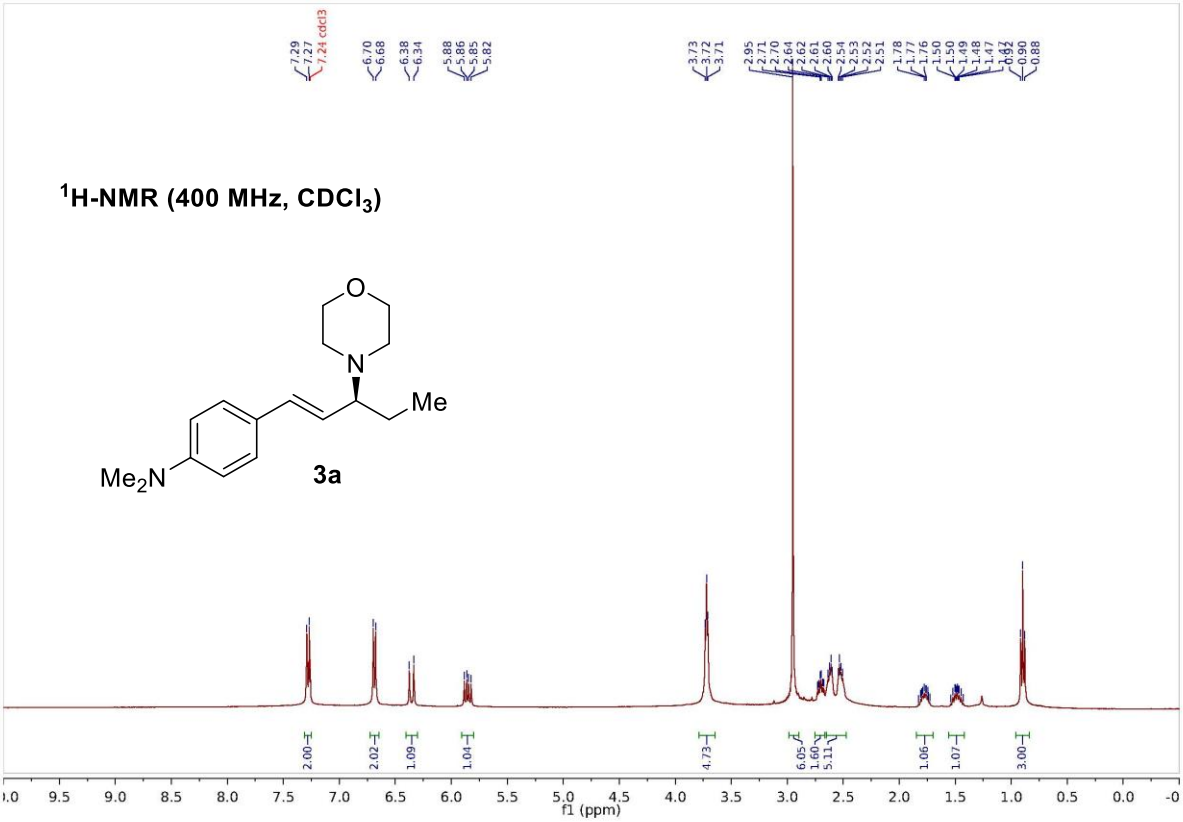

147.71
137.08
132.00
130.38
129.21
128.54
127.36
126.37
117.25
113.38
77.32 cdcl3
76.82 cdcl3
57.20
29.15
10.55
^{13}C-NMR (125 MHz, CDCl$_3$)
HN
Me
2h
f1 (ppm)


7.38
7.36
7.32
7.30
7.28
7.24 cdcl3
7.23
7.22
7.20
7.02
7.00
6.99
6.97
6.61
6.61
6.18
6.16
6.14
6.12
3.89
3.88
3.86
3.85
3.64
2.49
2.47
2.45
1.72
1.72
1.71
1.70
1.61
1.59
1.57
1.03
1.01
0.94
0.93
0.91
1H-NMR (400 MHz, CDCl3)
n-Pr
HN
Me
2i
2.15
2.07
1.09
2.49
3.40
1.00
0.16
1.12
1.45
2.33
2.26
2.65
2.91
3.09
f1 (ppm)


145.65
137.15
132.33
131.54
130.26
129.13
128.52
127.30
126.36
113.41
77.32 cdcl3
76.82 cdcl3
57.51
37.22
29.16
24.92
13.93
10.56
13C-NMR (125 MHz, CDCl3)
n-Pr
HN
Me
2i
f1 (ppm)

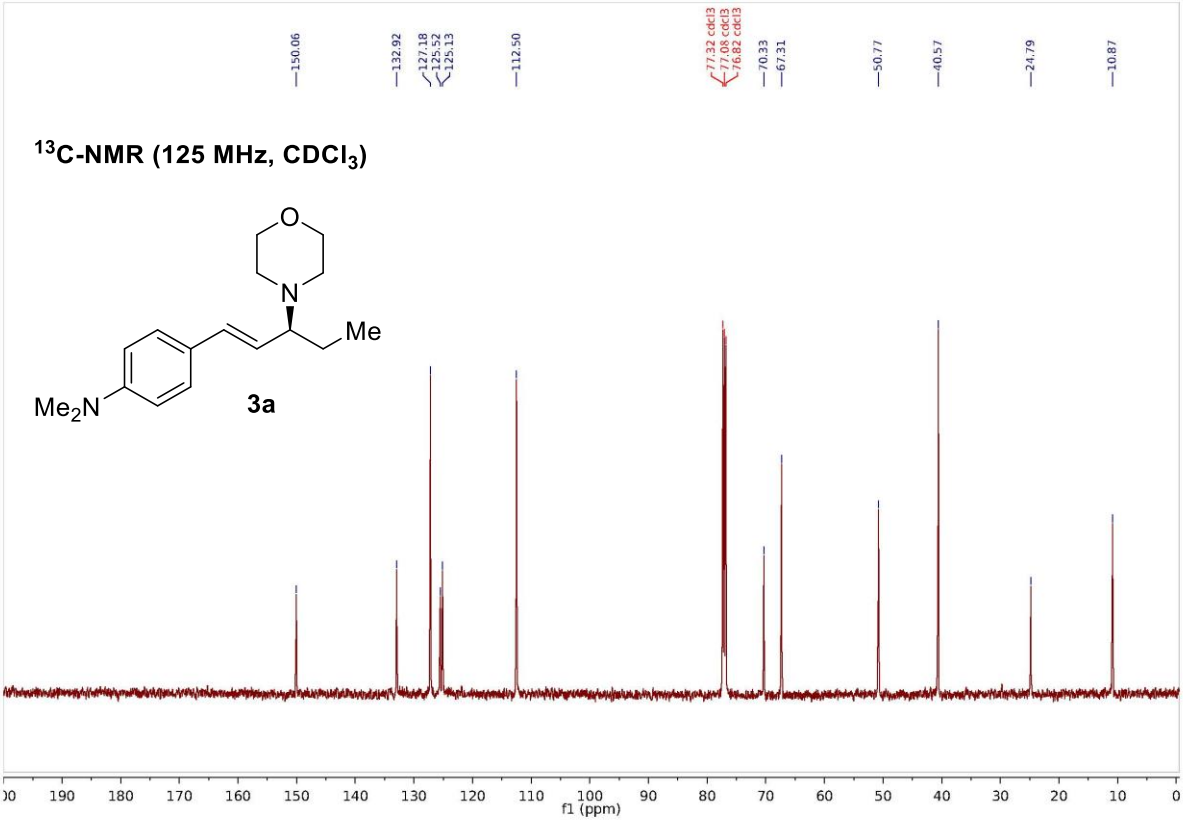

^{1}H-NMR (400 MHz, $CDCl_3$)
OMe
HN
Me
2j
f1 (ppm)


^{13}C-NMR (125 MHz, $CDCl_3$)
OMe
HN
Me
2j
f1 (ppm)



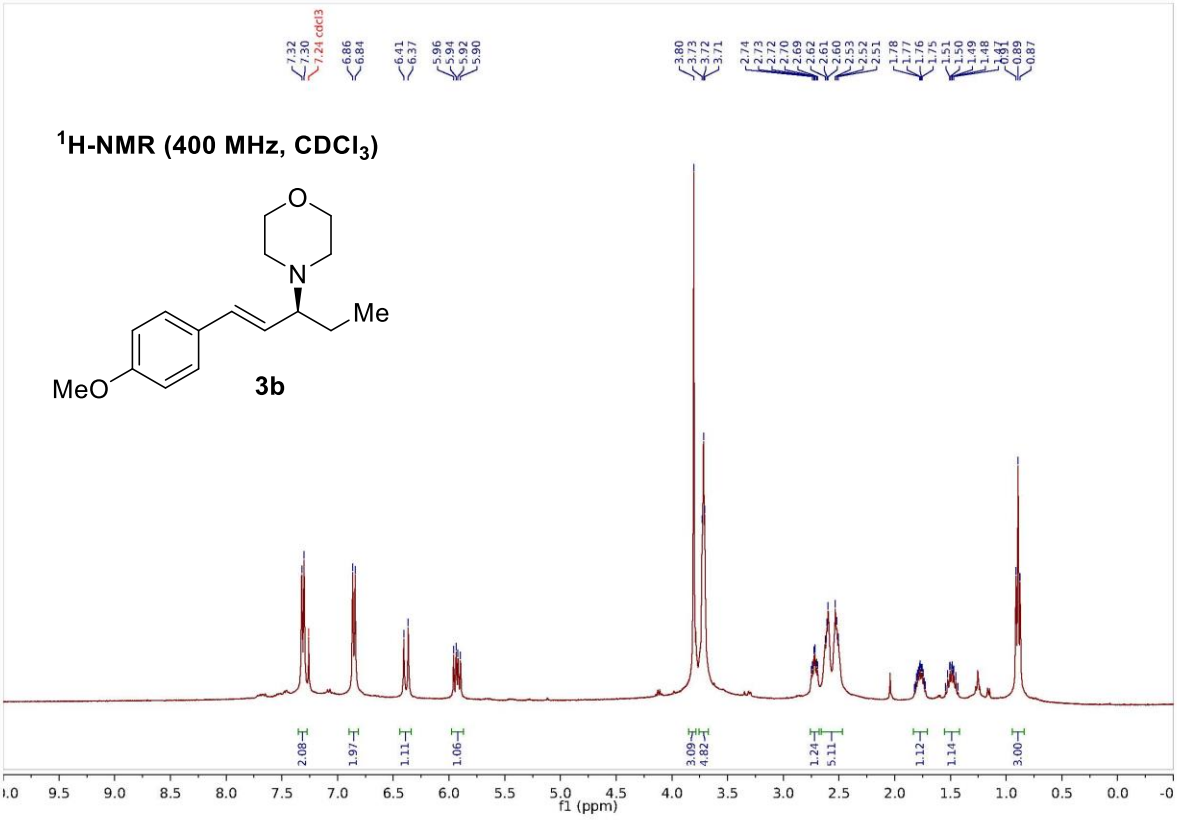
^{1}H-NMR (400 MHz, $CDCl_3$)

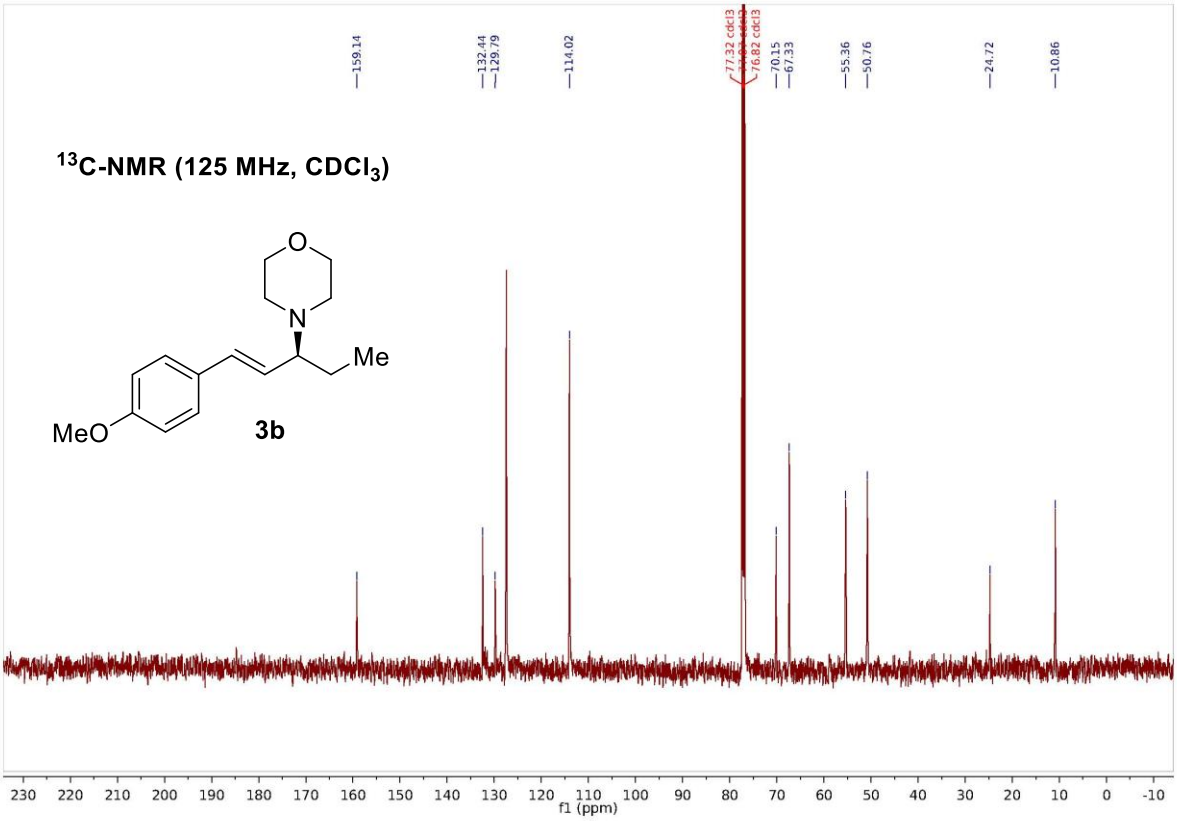
3a

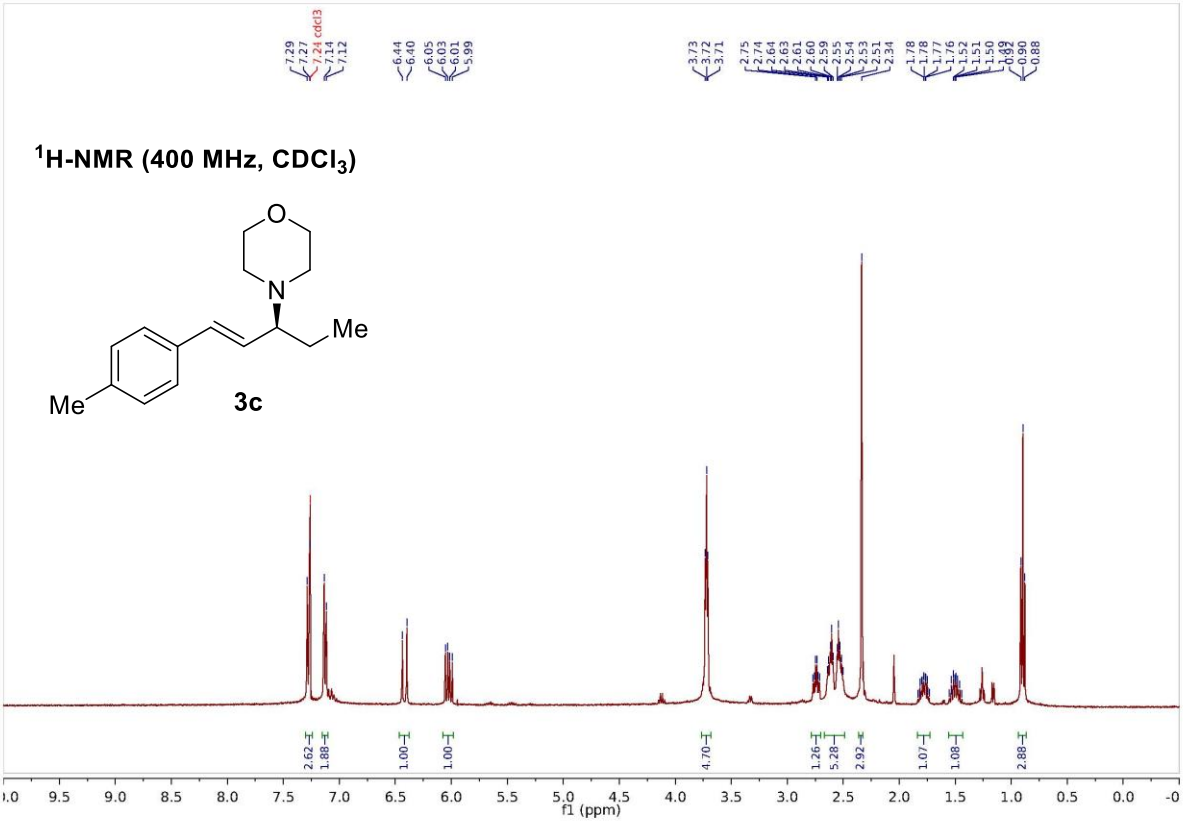


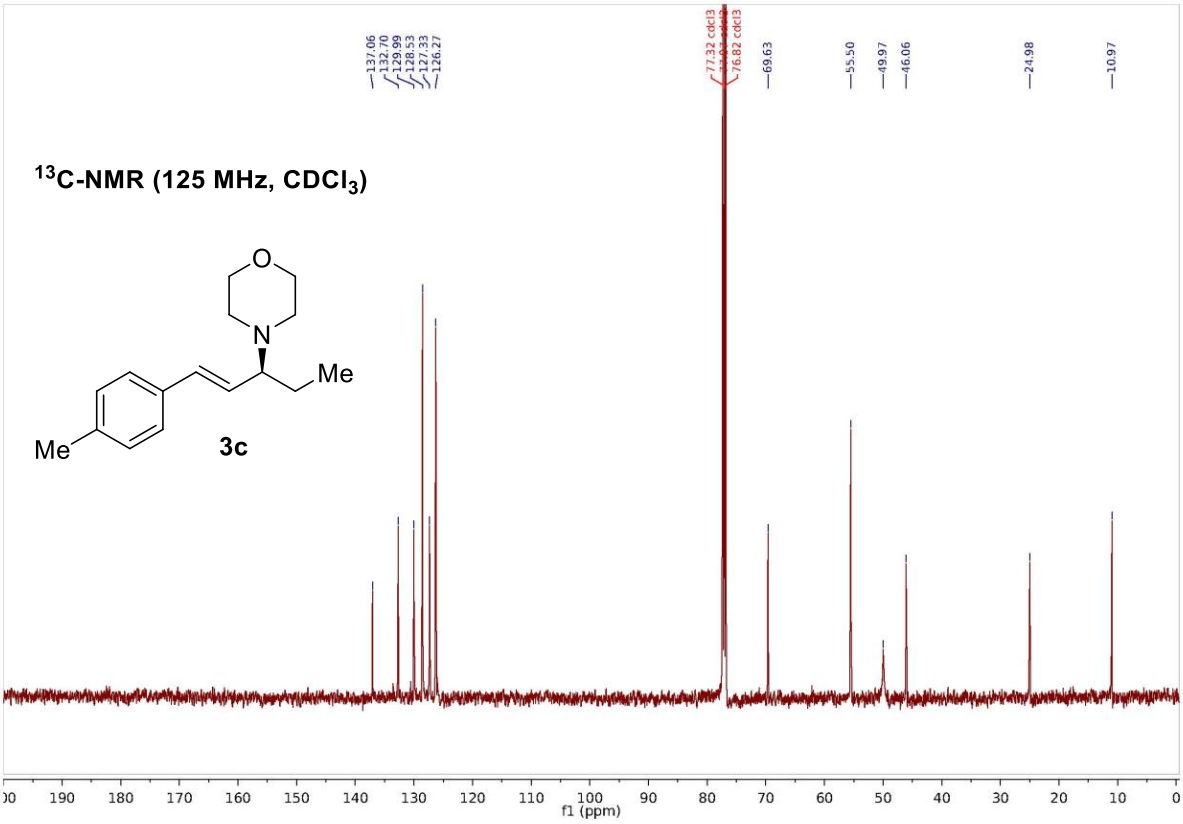
^{13}C-NMR (125 MHz, $CDCl_3$)

3a

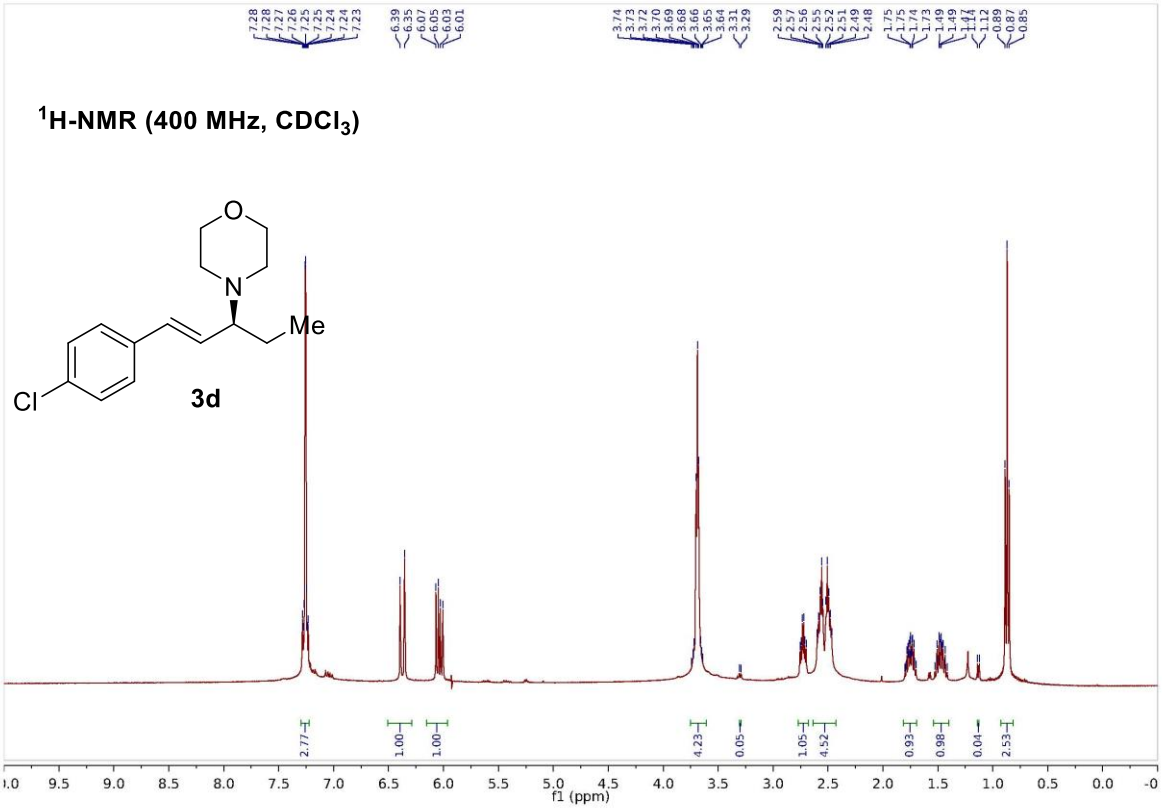

^{1}H-NMR (400 MHz, $CDCl_3$)
O
N
Me
MeO
3b
f1 (ppm)


^{13}C-NMR (125 MHz, $CDCl_3$)
O
N
Me
MeO
3b
f1 (ppm)

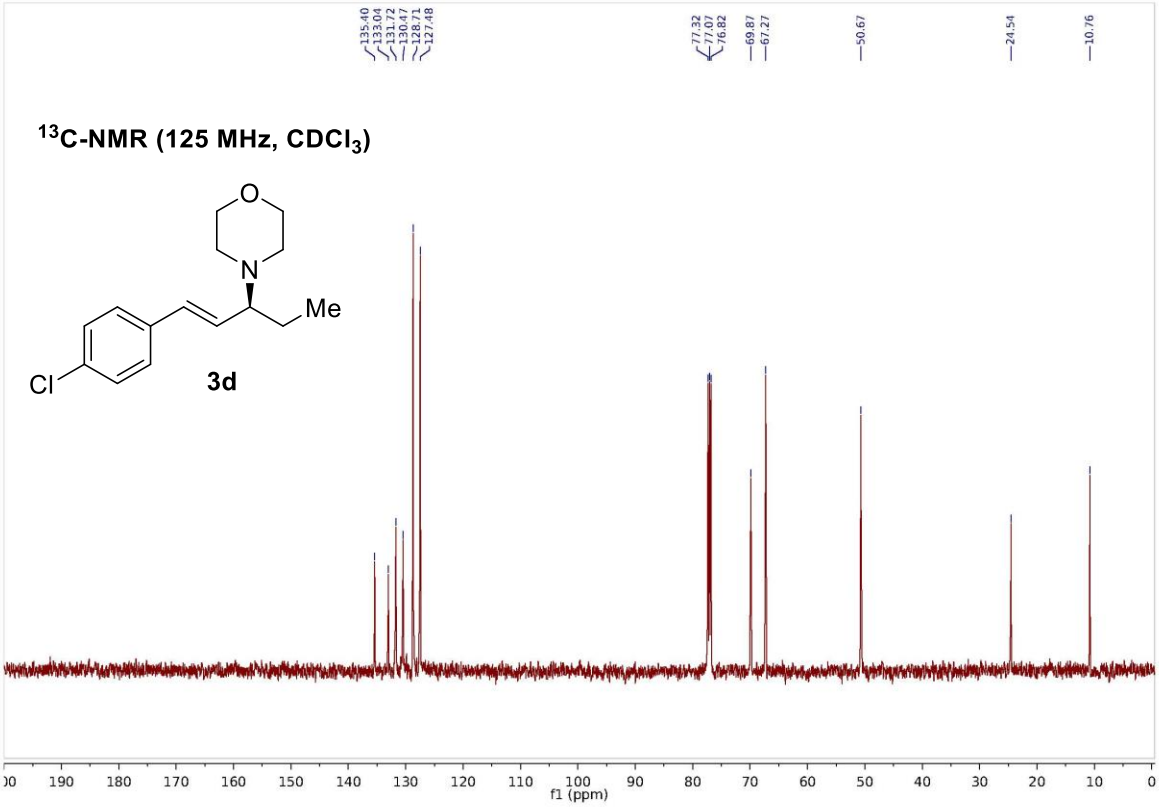

^{1}H-NMR (400 MHz, $CDCl_3$)
Me
Me
3c
f1 (ppm)


^{13}C-NMR (125 MHz, $CDCl_3$)
Me
Me
3c
f1 (ppm)

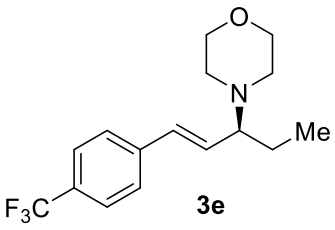
^{1}H-NMR (400 MHz, $CDCl_3$)



^{13}C-NMR (125 MHz, $CDCl_3$)

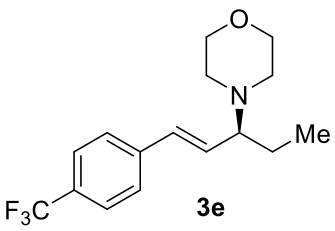


^{1}H-NMR (400 MHz, $CDCl_3$)

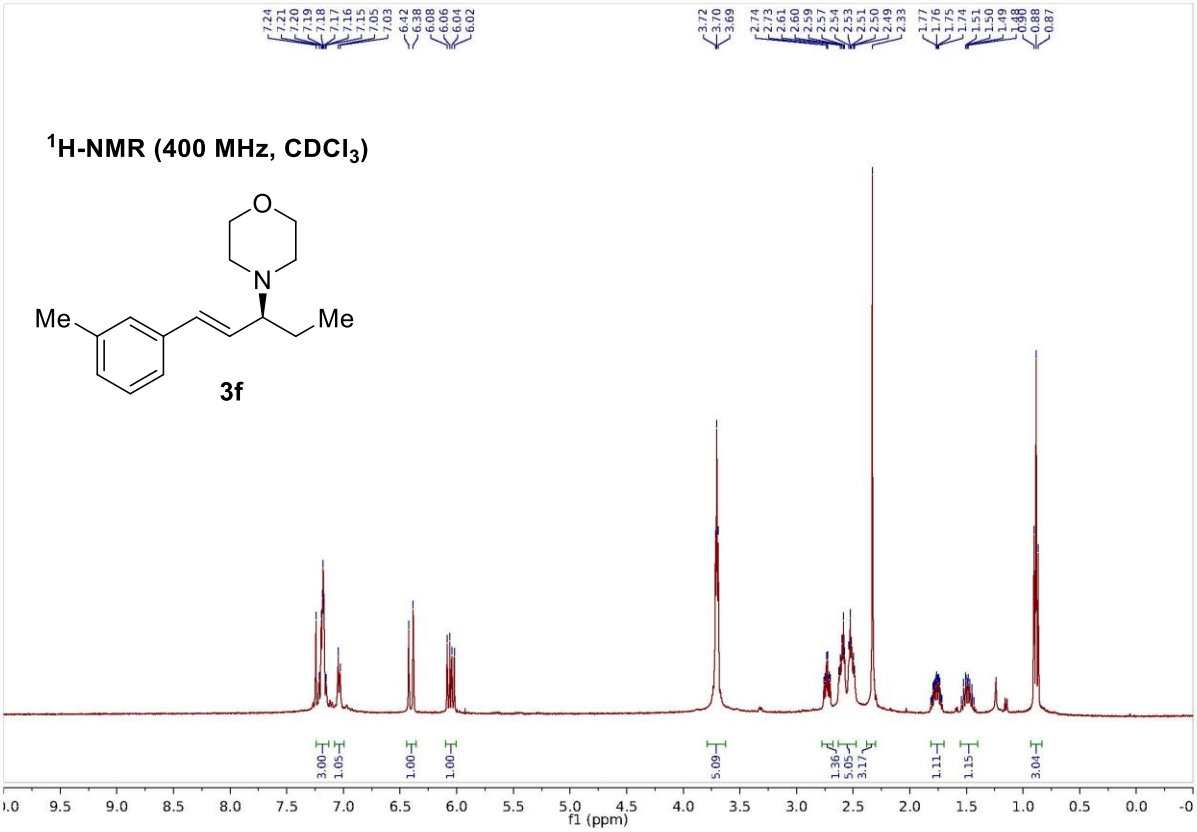


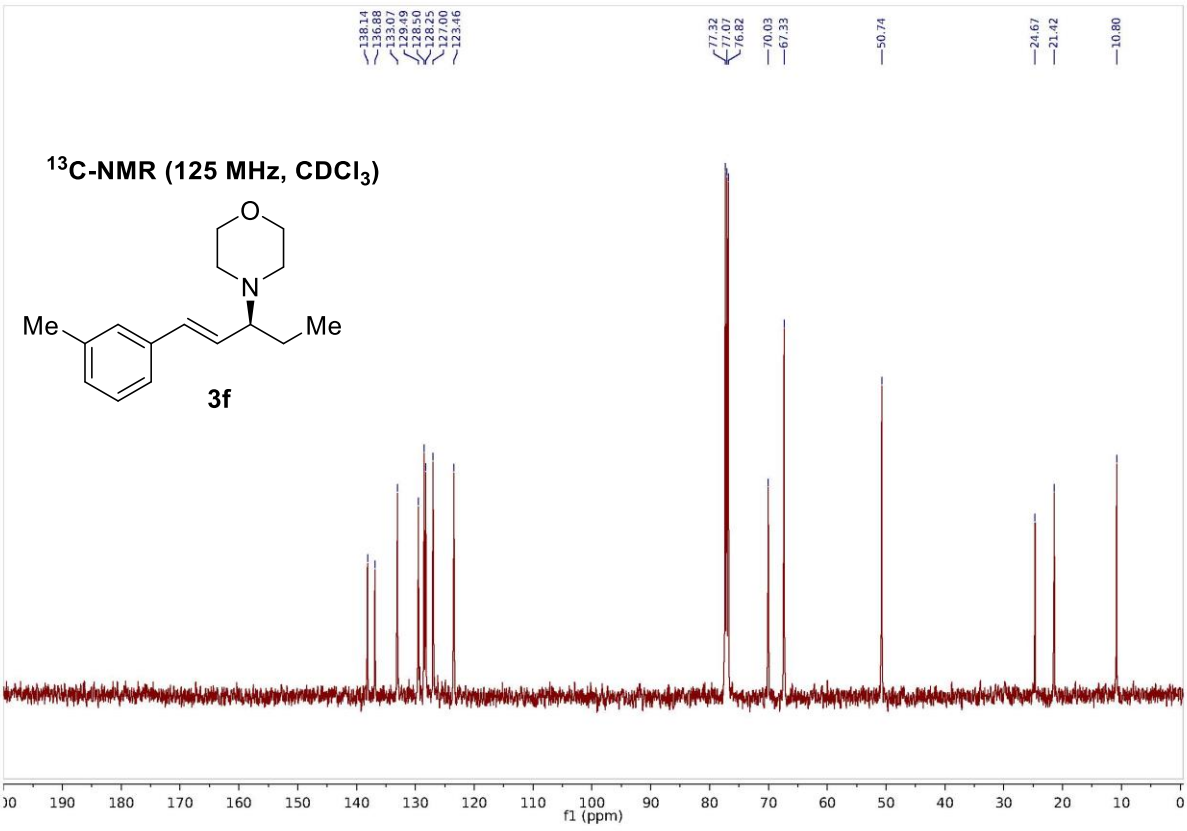
3e

^{13}C-NMR (125 MHz, $CDCl_3$)

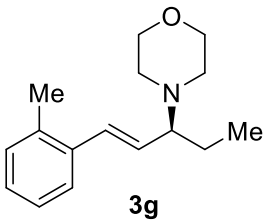


3e


^{1}H-NMR (400 MHz, $CDCl_3$)
Me
Me
3f
f1 (ppm)

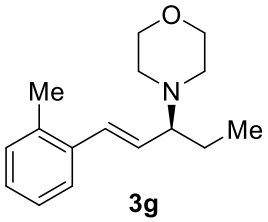

^{13}C-NMR (125 MHz, $CDCl_3$)
Me
Me
3f
f1 (ppm)

^{1}H-NMR (400 MHz, $CDCl_3$)

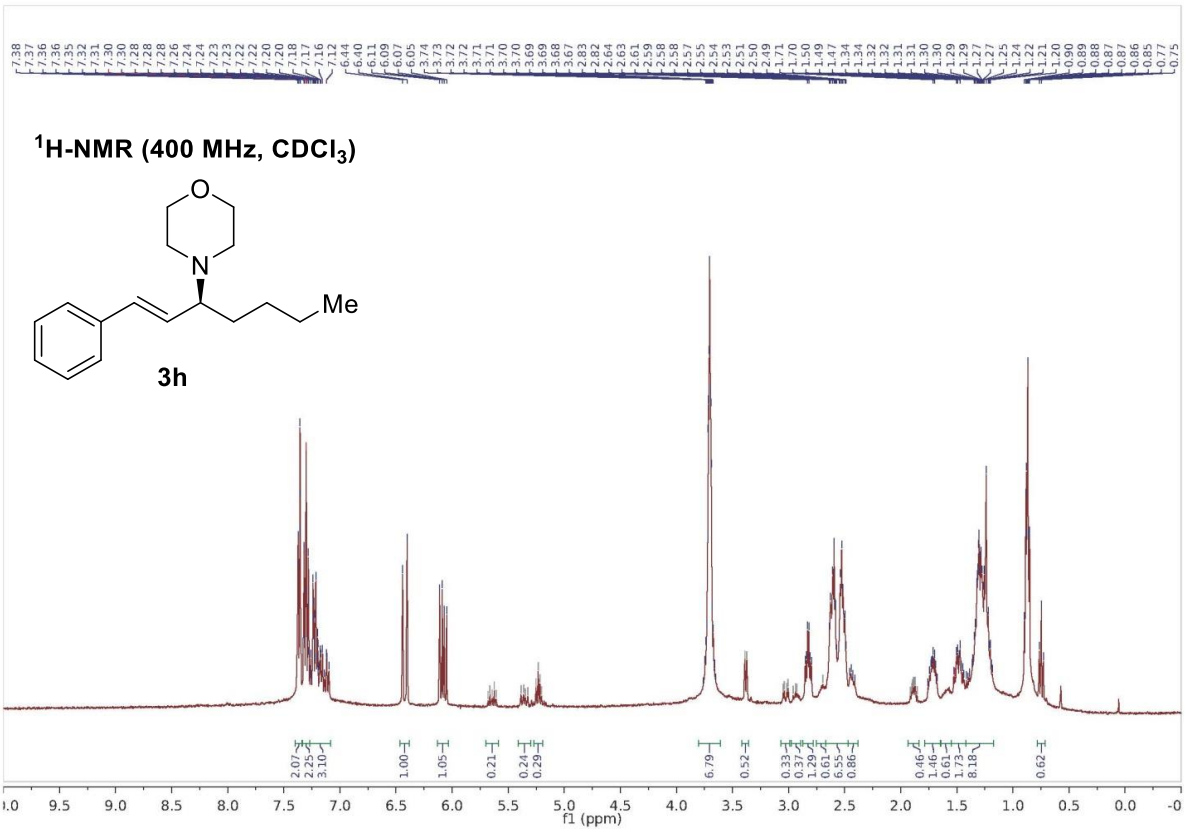


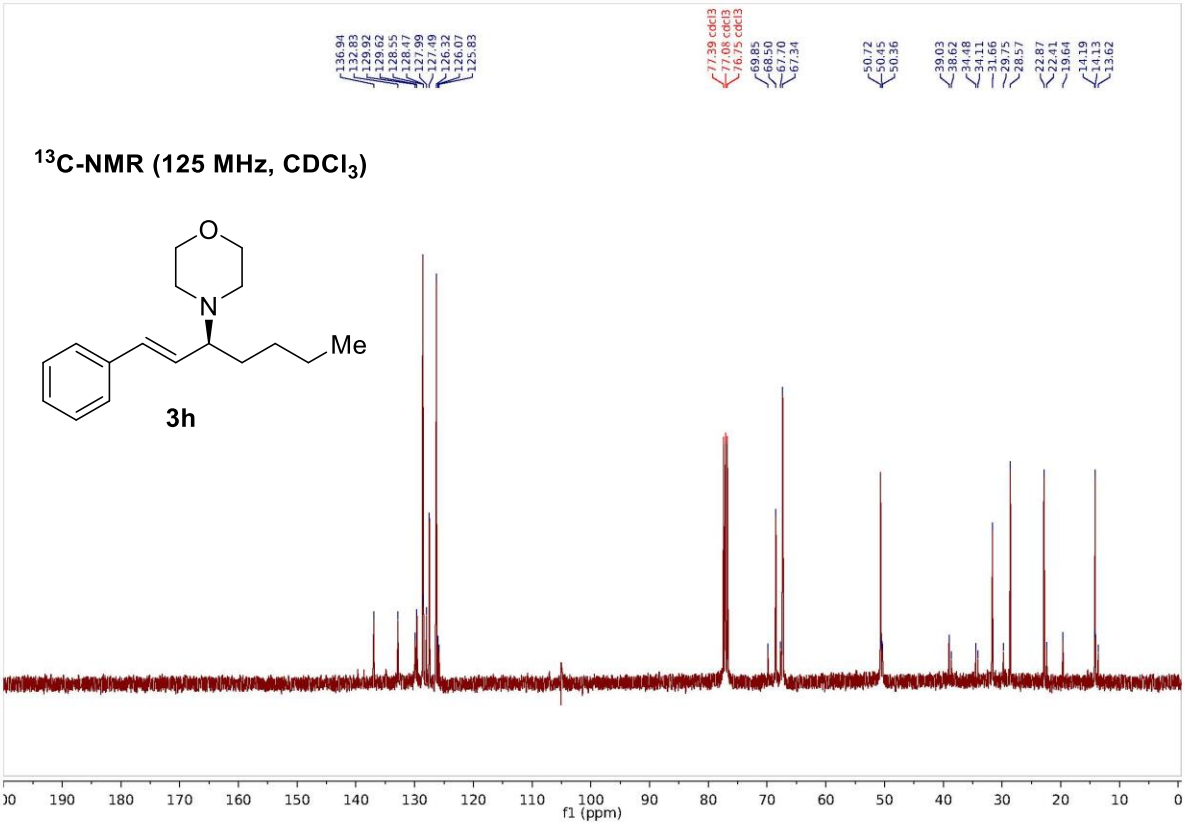
3g

^{13}C-NMR (125 MHz, $CDCl_3$)

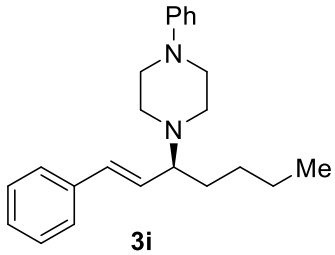


3g


^{1}H-NMR (400 MHz, $CDCl_3$)
O
N
Me
3h
f1 (ppm)

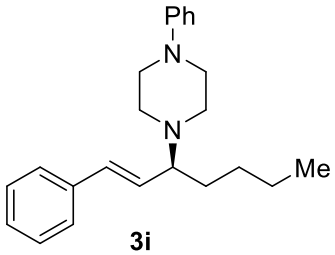

^{13}C-NMR (125 MHz, $CDCl_3$)
O
N
Me
3h
f1 (ppm)

^{1}H-NMR (400 MHz, $CDCl_3$)



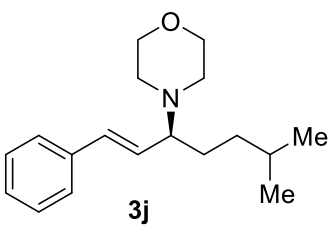
3i

^{13}C-NMR (125 MHz, $CDCl_3$)



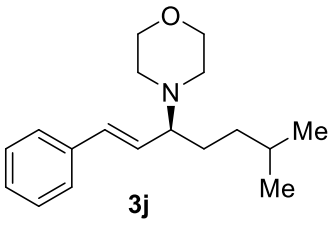
3i

^{1}H-NMR (400 MHz, $CDCl_3$)

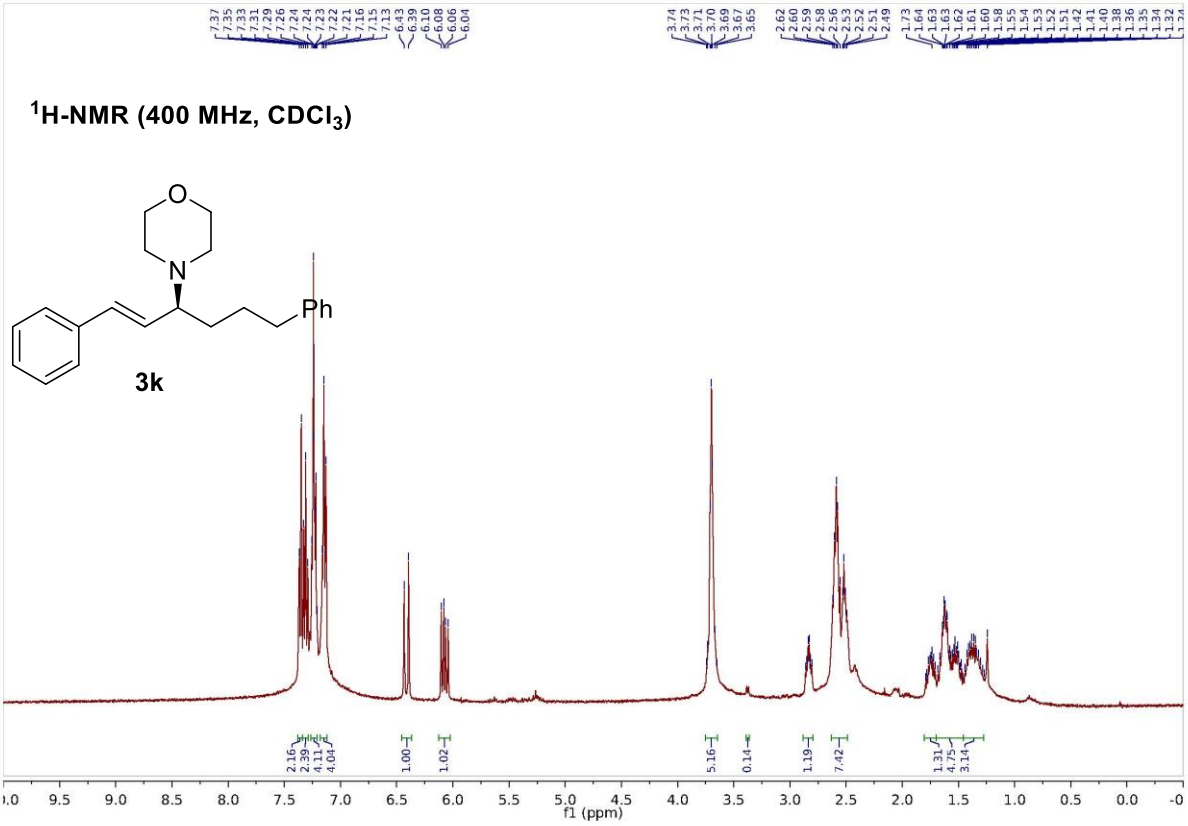


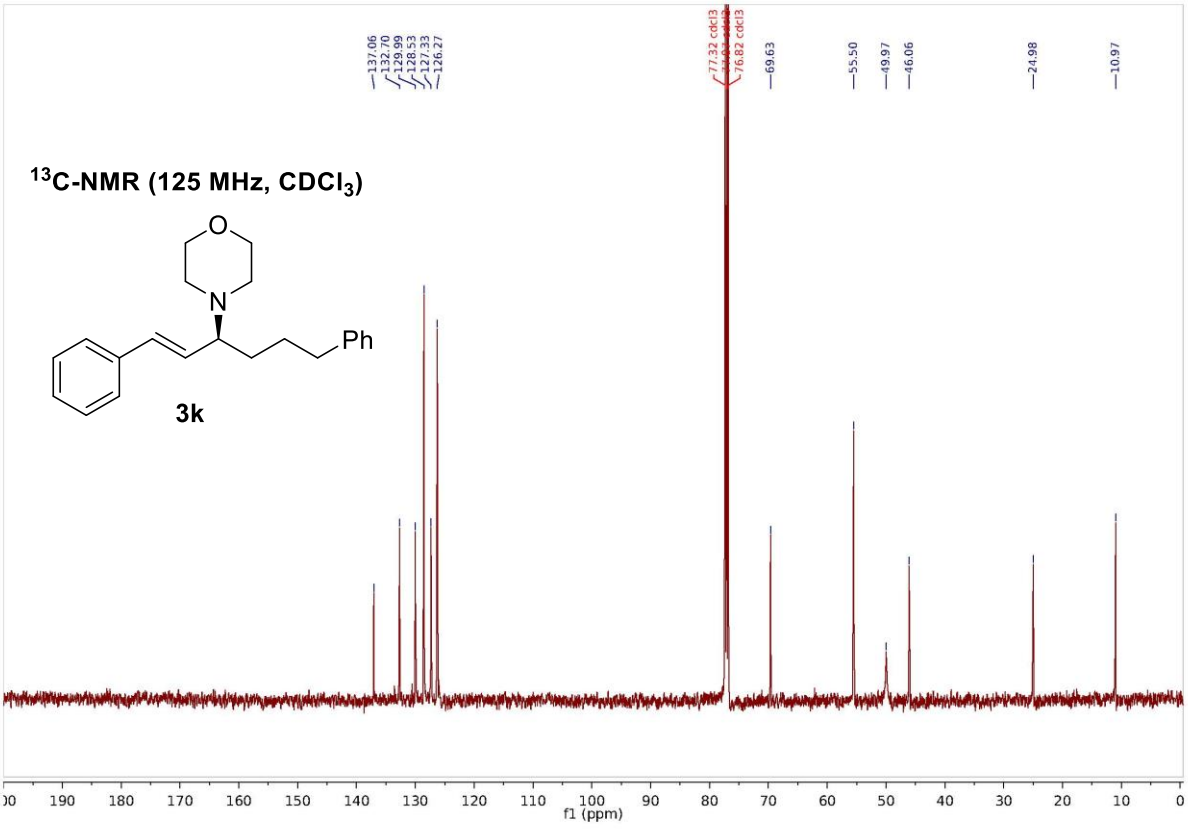
3j

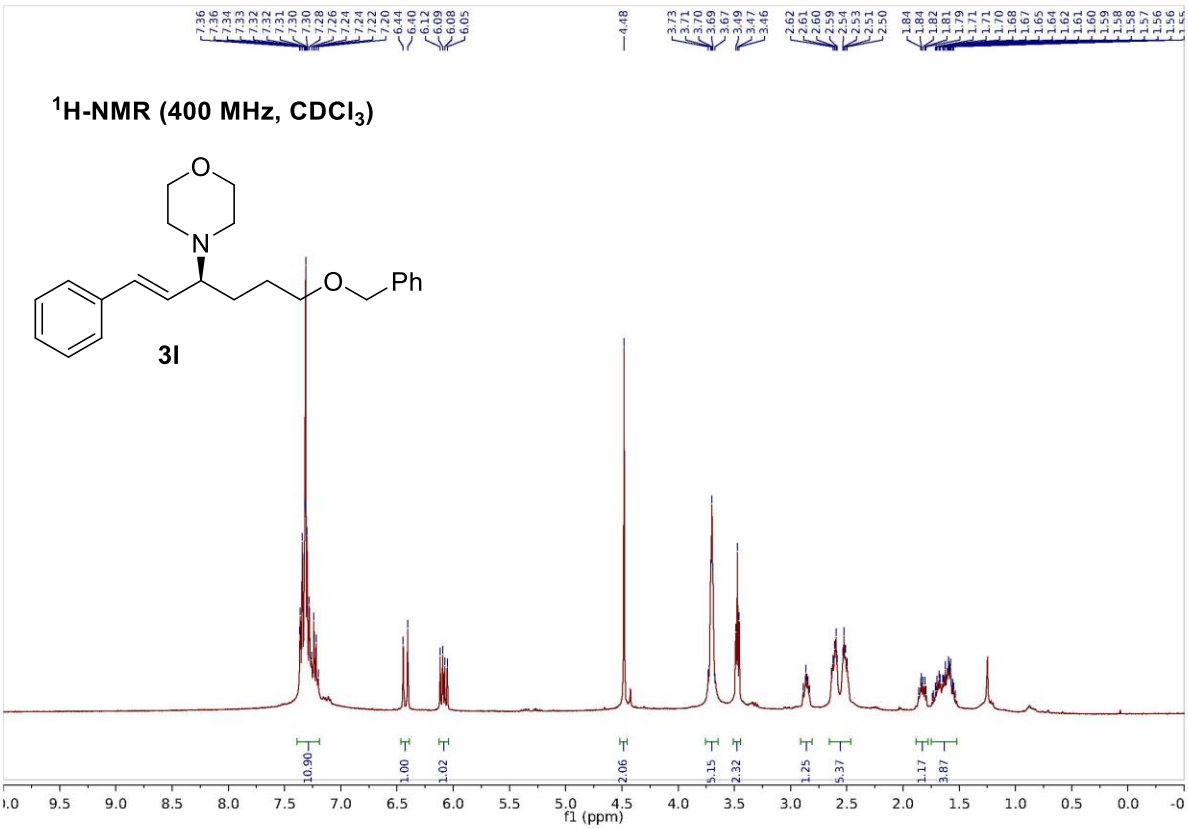
^{13}C-NMR (125 MHz, $CDCl_3$)

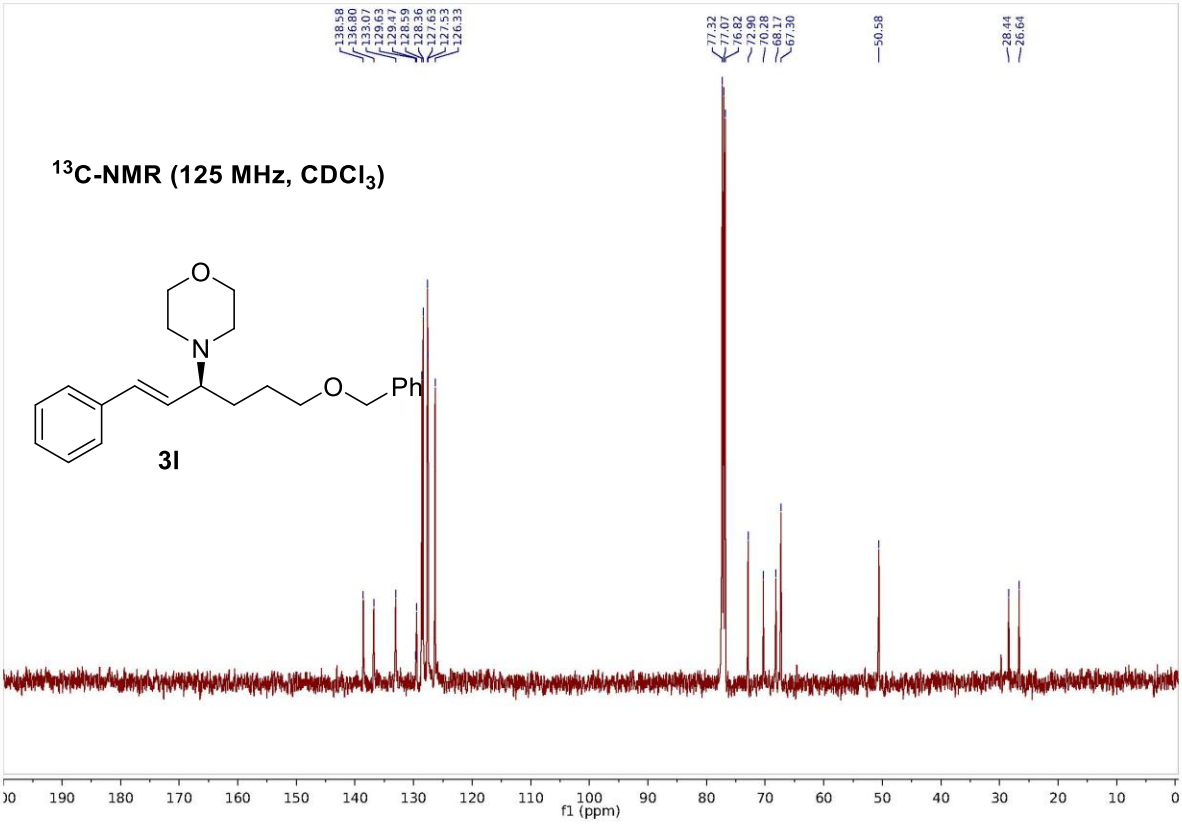


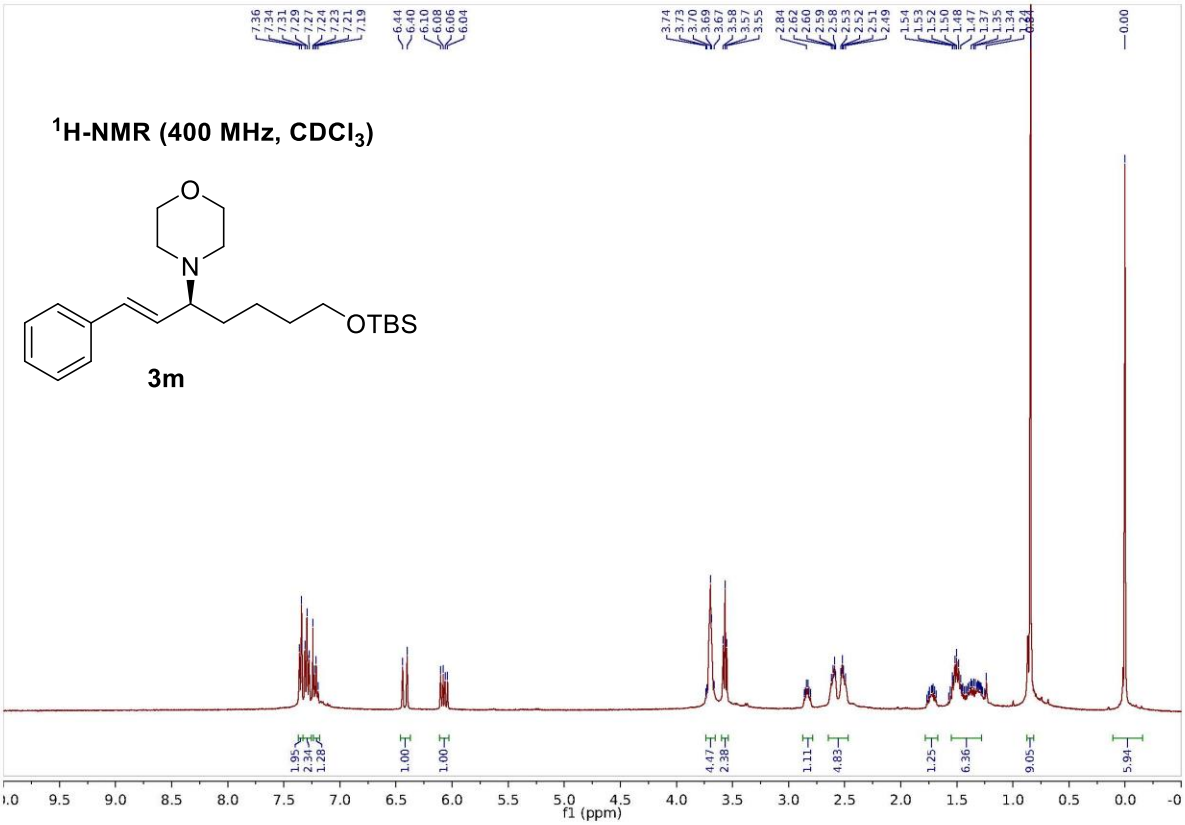
3j

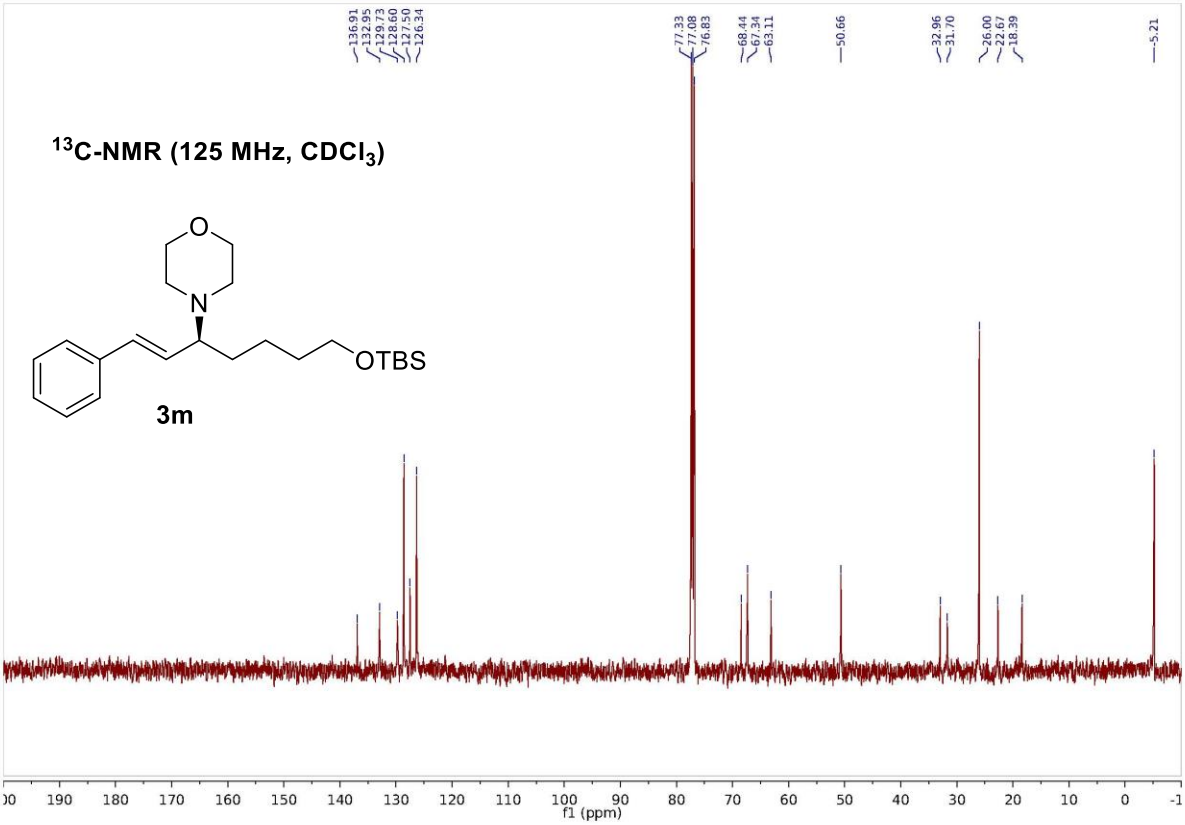

^{1}H-NMR (400 MHz, $CDCl_3$)
O
N
Ph
3k
f1 (ppm)


^{13}C-NMR (125 MHz, $CDCl_3$)
O
N
Ph
3k
f1 (ppm)

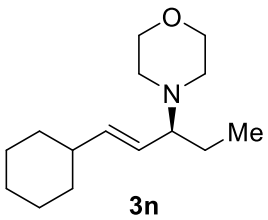

^{1}H-NMR (400 MHz, $CDCl_3$)
O
N
O
Ph
3l
f1 (ppm)


^{13}C-NMR (125 MHz, $CDCl_3$)
O
N
O
Ph
3l
f1 (ppm)


^{1}H-NMR (400 MHz, CDCl$_3$)
O
N
OTBS
3m
f1 (ppm)

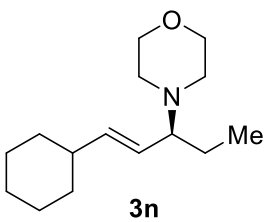

^{13}C-NMR (125 MHz, CDCl$_3$)
O
N
OTBS
3m
f1 (ppm)

^{1}H-NMR (400 MHz, $CDCl_3$)

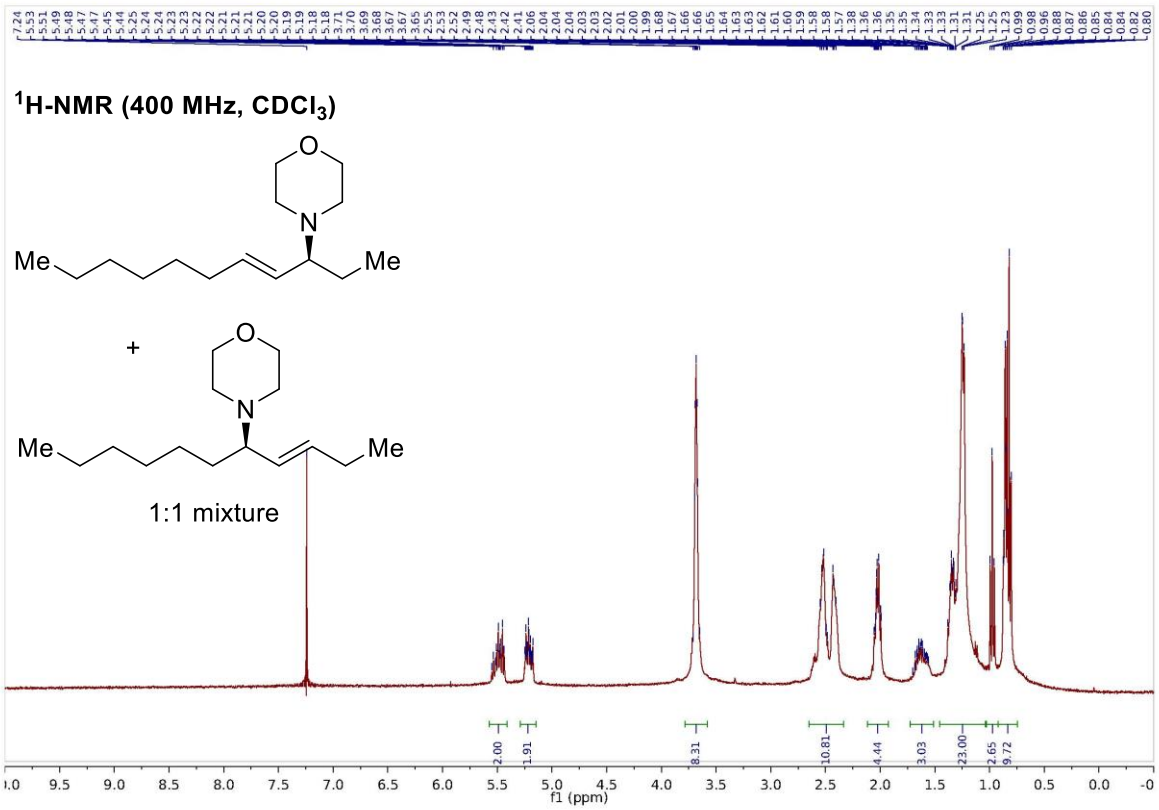


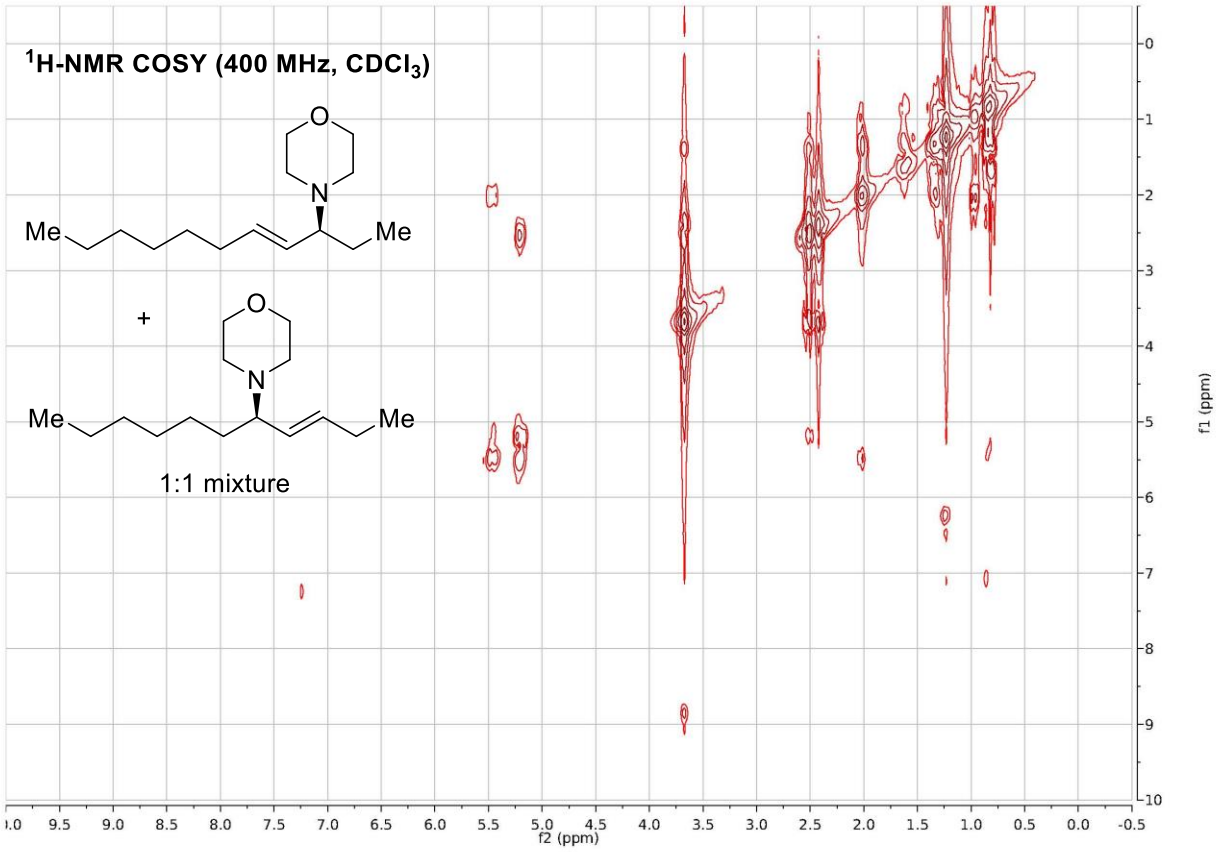
3n

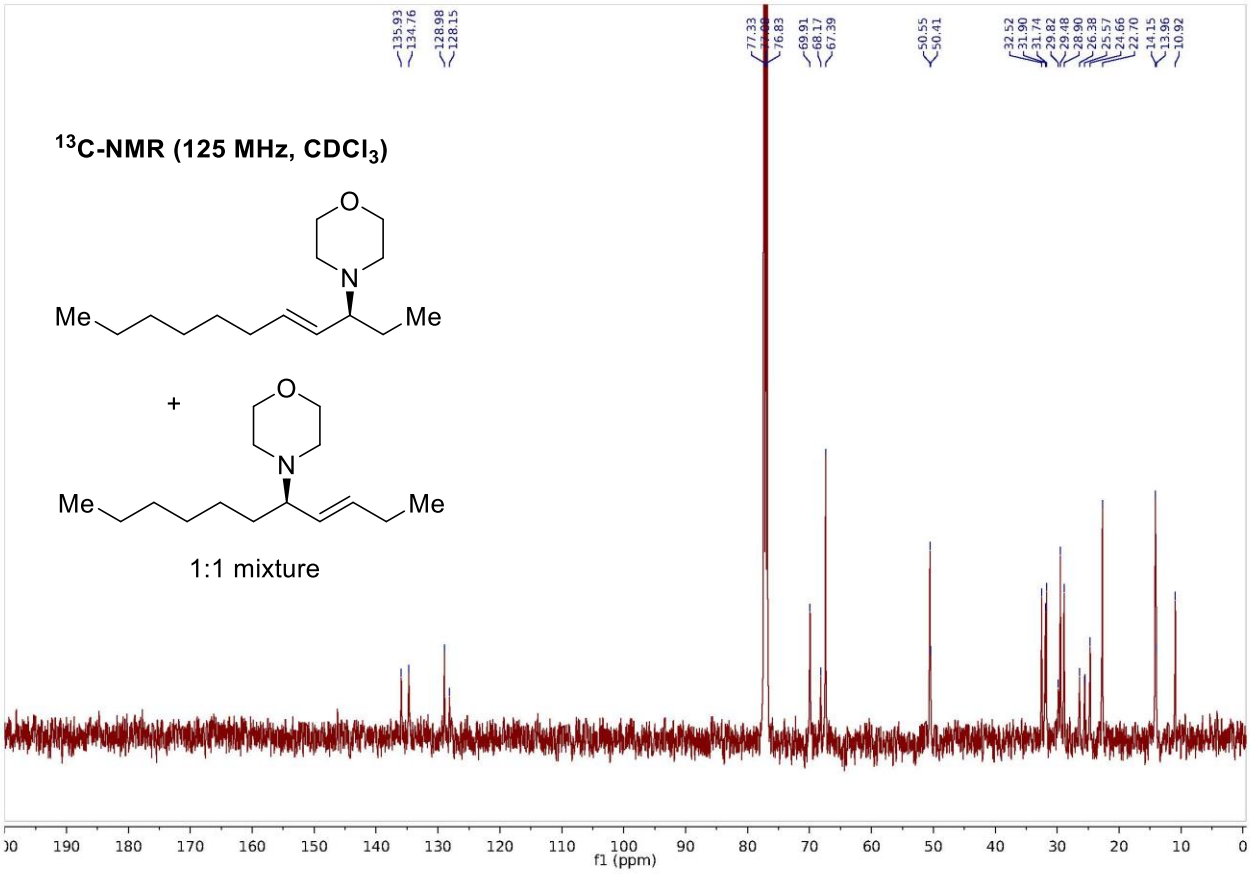
^{13}C-NMR (125 MHz, $CDCl_3$)



3n


^{1}H-NMR (400 MHz, $CDCl_3$)
O
N
Me
Me
+
O
N
Me
Me
1:1 mixture
2.00
1.91
8.31
10.81
4.44
3.03
23.00
2.65
9.72
f1 (ppm)


^{1}H-NMR COSY (400 MHz, $CDCl_3$)
O
N
Me
Me
+
O
N
Me
Me
1:1 mixture
f2 (ppm)
f1 (ppm)


135.93
134.76
128.98
128.15
77.33
77.08
76.83
69.91
68.17
67.39
50.55
50.41
32.52
31.90
31.74
29.62
29.48
28.90
26.38
25.57
24.66
22.70
14.15
13.96
10.92
13C-NMR (125 MHz, CDCl3)
O
N
Me
Me
+
O
N
Me
Me
1:1 mixture
f1 (ppm)