Supporting Information Part A

Preparation of Chiral Allenes through Pd-Catalyzed Intermolecular Hydroamination of Conjugated Enynes: Enantioselective Synthesis Enabled by Catalyst Design

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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.

Reagents purchased and used as received

acetyl chloride (Sigma-Aldrich)
allyl palladium chloride dimer (Strem)
azepane (Sigma-Aldrich)
benzofuran-2-carbaldehyde (Beantown)
benzophenone imine (Chem-Impex)
bis[rhodium(α,α,α′,α′-tetramethyl-1,3-benzenedipropionic acid)] ($Rh_2(esp)_2$, Sigma-Aldrich)
2-bromobenzoyl chloride (Oakwood)
1-bromo-4-ethynylbenzene (Matrix)
(*Z*)-1-bromo-1-propene (Sigma-Aldrich)
2-bromopropene (Beantown)
2-bromo-3,3,3-trifluoro-1-propene (Alfa Aesar)
tert-butyl(ethynyl)dimethylsilane (TCI)
n-butyllithium (2.0 M in cyclohexane or 2.5 M in hexanes, Sigma-Aldrich)
t-butyllithium (1.7 M in pentane, Sigma-Aldrich)
citric acid (Fisher)
copper (I) Iodide (Strem)
cyclohexylacetylene (Alfa Aesar)
cyclohexylamine (Sigma-Aldrich)
diisoproyl azodicarboxylate (Alfa Aesar)
(*S*)-N,*α*-dimethylbenzylamine (Acros)
1-dodecyne (Beantown)
4-ethynylaniline (Chem-Impex)
4-ethynylanisole (TCI)
2-ethynyltoluene (Sigma-Aldrich)
3-ethynyltoluene (Alfa Aesar)
1-ethynyl-4-(trifluoromethyl)benzene (TCI)
ferrocene carboxylic acid (Chem-Impex)
indoline (Acros)
L-*tert*-leucinol (TCI)
methanesulfonyl chloride (Alfa Aesar)
N-methylbenzylamine (Sigma-Aldrich)
methyl 4-ethynylbenzoate (Sigma-Aldrich)
1-methylpiperazine (TCI)
(*R*)-2-methylpyrrolidine (Alfa Aesar)
morpholine (Sigma-Aldrich)
oxalyl chloride (Alfa Aesar)
4-pentyn-1-ol (Alfa Aesar)
phenylacetylene (Alfa Aesar)
4-phenyl-1-butyne (Acros)
piperidine (Sigma-Aldrich)
4-piperidone ethylene ketal (Alfa Aesar)
N-propargylphthalimide (Alfa Aesar)
n-propylamine (Alfa Aesar)
pyridine (Alfa Aesar)

pyrrolidine (Sigma-Aldrich)
silver tetrafluoroborate (Strem)
sodium tetrafluoroborate (Acros)
1,2,3,4-tetrahydroquinoline (Alfa Aesar)
Tetrabutylammonium fluoride (1.0 M in THF, Sigma-Aldrich)
tetrakis[(R)-(-)-[(1R)-1-(4-bromophenyl)-2,2-diphenylcyclopropanecarboxylato]dirhodium(II) (Rh_2(*R*-BTPCP)$_4$, Strem)
tetrakis[(R)-(+)-N-(p-dodecylphenylsulfonyl)prolinato]dirhodium(II) (Rh_2(*R*-DOSP)$_4$, Strem)
tetrakis[(S)-(+)-(1-adamantyl)-(N-phthalimido)acetato]dirhodium(II) (Rh_2(*S*-PTAD)$_4$, Strem)
tetrakis[5-t-butyl-phthaloyl-N-(S)-tert-leucinato]dirhodium (Rh_2(*S*-*tert*-PTTL)$_4$, Strem)
tetrakis(triphenylphosphine)palladium(0) (Strem)
p-toluenesulfonyl chloride (Alfa Aesar)
trimethylsilylacetylene (Chem-Impex)
vinyl bromide (1.0 M in THF, Sigma-Aldrich)

<u>Ligands purchased and used as received</u>
(R)-2,2'-bis[bis(3,5-trifluoromethylphenyl)phosphino]-4,4',6,6'-tetramethoxybiphenyl (*R*-BTFM-Garphos, Alfa Aesar)
(*S*,*S*)-2,3-bis(*tert*-butylmethylphosphino)quinoxaline (*S*,*S*-QuinoxP*, Strem)
(-)-1,2-bis((2S,5S)-2,5-dimethylphospholano)ethane (*S*,*S*-Me-BPE, Alfa Aesar)
(±)-2,2′-bis(diphenylphosphino)-1,1′-binaphthalene (*rac*-BINAP, Chem-Impex)
(*R*)-2,2′-bis(diphenylphosphino)-1,1′-binaphthalene (*R*-BINAP, Alfa Aesar)
1,4-bis(diphenylphosphino)butane (dppb, Alfa Aesar)
4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (xantphos, Strem)
(+)-1,2-bis((2R,5R)-2,5-diphenylphospholano)ethane (*S*,*S*-Ph-BPE, Strem)
(2*S*,4*S*)-2,4-bis(diphenylphosphino)pentane (*S*,*S*-BDPP, Strem)
1,3-bis(diphenylphosphino)propane (dppp, Sigma-Aldrich)
(R_P)-1-[(*R*)-|A-(Dimethylamino)-2-(diphenylphosphino)benzyl]-2-diphenylphosphinoferrocene
(R_P)-1-[(*R*)-|A-(Dimethylamino)-2-(diphenylphosphino)benzyl]-2-diphenylphosphinoferrocene ((*R*,*R*)-taniaphos, Strem)
(*R*)-1-[(S_P)-2-(diphenylphosphino)ferrocenyl]ethyldicyclohexylphosphine (*R*,*S*-josiphos, Strem)
ethylenebis(diphenylphosphine) (dppe, Strem)
1,1′-ferrocenediyl-bis(diphenylphosphine) (dppf, Sigma-Aldrich)
(oxydi-2,1-phenylene)bis(diphenylphosphine) (DPEphos, Strem)
triphenylphosphine (Alfa Aesar)

<u>Reagents distilled from CaH_2</u>
diethylamine (Beantown)
1,2,3,4-tetrahydroisoquinoline (THIQ, Sigma-Aldrich)
tetramethylethylenediamine (TMEDA, Alfa Aesar)
triethylamine (Sigma-Aldrich)

<u>The following alkynes were prepared by a previously described route through Sonogashira coupling of the corresponding aryl halides with trimethylsilylacetylene followed by deprotection.</u>[1]
4-ethynylbenzaldehyde
3-ethynylbenzonitrile

2-ethynylnaphthalene
2-ethynylphenol
3-ethynylpyridine
2-ethynylbenzofuran was prepared by a Corey-Fuchs reaction from the corresponding aldehyde as previously described.[2]

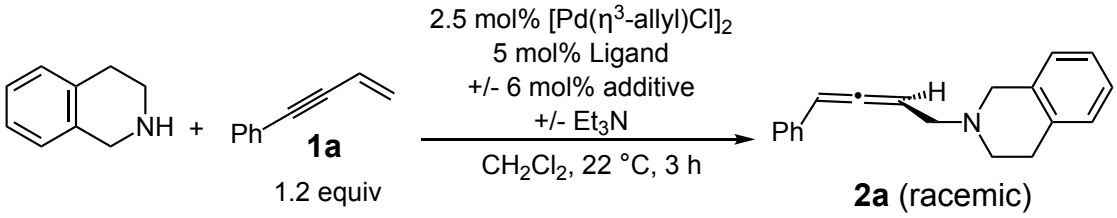
Other reagents prepared by previously described methods
2-bromooct-1-ene[3]
(1-bromovinyl)cyclohexane[3]
chlorobis(perfluorophenyl)phosphane[4]
methyl 2-diazo-2-phenylacetate[5]
sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($NaBAr_4^F$)[6]

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), toluene (Sigma-Aldrich), and diethyl ether (Sigma-Aldrich) were passed through two consecutive alumina columns. Hexanes (Fisher) and ethyl acetate (Fisher) were used for flash column chromatography and used as received. HPLC-grade hexanes (Sigma-Aldrich), isopropanol (Sigma-Aldrich), acetonitrile (Fischer), and methanol (Sigma-Aldrich) were used as received.

Instrumentation. ^{1}H NMR spectra were recorded on a Varian INOVA (400 MHz) or a Bruker (500 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_3OD: δ 3.29). 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) or a Bruker (500 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal reference ($CDCl_3$: δ 77.07, CD_3OD: δ 47.6, DMSO-d_6: δ 40.0). ^{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-3, Amylose-1, or Chiralpak 1A-3) 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. Elemental Analysis was performed at Atlantic Microlab. Specific rotation values were recorded on a Rudolph Autopol IV Polarimeter. Melting points were measured on an Electrothermal MelTemp® capillary melting point apparatus and are uncorrected. 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).

II. Supplemental Screening Data

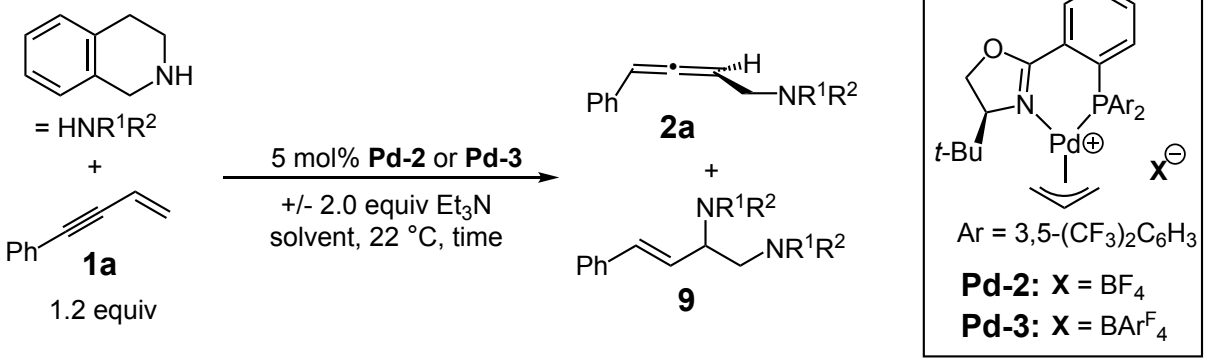
Table S1. Optimization of Non-Enantioselective Reaction[a]



entry	Ligand	additive (6 mol%)	base (equiv)	yield 2a (%)[b]
1	none	none	none	0
2	DPEphos	none	none	29
3	DPEphos	$NaBAr_4^F$	none	84
4	Xantphos	$NaBAr_4^F$	none	83
5	*rac*-BINAP	$NaBAr_4^F$	none	46
6	dppf	$NaBAr_4^F$	none	63
7	dppe	$NaBAr_4^F$	none	14
8	dppp	$NaBAr_4^F$	none	44
9	dppb	$NaBAr_4^F$	none	62
10	PPh_3 (10 mol%)	$NaBAr_4^F$	none	44
11	DPEphos	$NaBAr_4^F$	Et_3N (2.0)	84
12	DPEphos	$NaBF_4$	none	86
13[c]	DPEphos	$AgBF_4$	none	85
14	**Pd-1**	none	none	88

[a]Reactions run with 0.20 mmol THIQ in 0.25 mL CH_2Cl_2. [b]Isolated yield of pure **2a**.
[c]AgCl precipitate removed by filtration

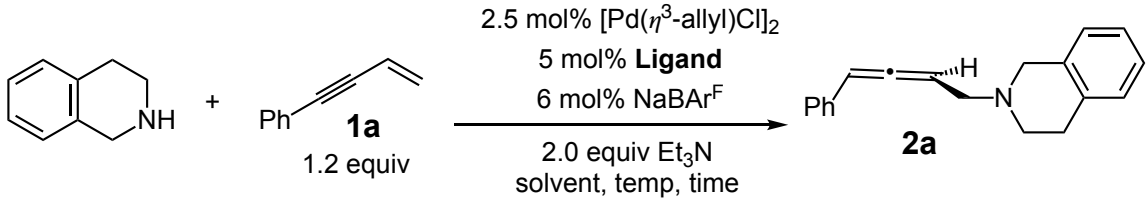
Table S2. Initial Investigations into Enantioselective Reaction with PHOX Ligands[a]



entry	Pd	solvent	base (equiv)	time (h)	2a:9[b]	yield 2a (%)[c]	er[d]
1	**Pd-2**	CH_2Cl_2	none	17	2:1	43	50:50
2	**Pd-2**	CH_2Cl_2	none	3	4:1	56	53.5:46.5
3	**Pd-2**	CH_2Cl_2	none	0.5	8:1	51	68:32
4	**Pd-2**	Et_2O	none	3	-	<5%	–
5	**Pd-3**	Et_2O	none	3	13:1	73	69.5:30.5
6	**Pd-2**	CH_2Cl_2	Et_3N (2.0)	3	19:1	71	63:37
7	**Pd-3**	Et_2O	Et_3N (2.0)	3	>20:1	23	80:20
8	**Pd-3**	CH_2Cl_2	Et_3N (2.0)	3	>20:1	65	84:16

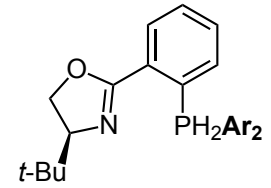
[a]Reactions run with 0.20 mmol THIQ in 0.25 mL solvent. [b]Determined by ^{1}H NMR analysis of unpurified reaction mixture. [c]Isolated yield of pure **2a**. [d]Determined by HPLC analysis of pure **2a** in comparison with an authentic racemic standard.

Table S3. Enantioselective Reaction Ligand Screening and Optimization[a]

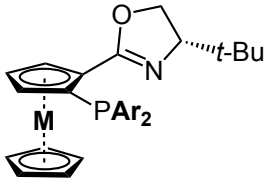


entry	ligand	solvent	temp (°C)	time (h)	yield 3a (%)[b]	er[c]
1	(*R*)-BINAP	Et_2O	22	3	82	50:50
2	(*R*,*S*)-Josiphos	Et_2O	22	3	30	50:50
3	(*S*,*S*)-Ph-BPE	Et_2O	22	3	85	70:30
4	(*S*,*S*)-Me-BPE	Et_2O	22	3	<5	–
5	(*S*,*S*)-BDPP	Et_2O	22	3	82	50:50
6	(*R*,*R*)-Taniaphos	Et_2O	22	3	83	50:50
7	(*R*)-BTFM-Garphos	Et_2O	22	3	19	80:20
8	(*S*,*S*)-QuinoxP*	Et_2O	22	3	34	66:34
9	**L4**	Et_2O	22	3	63	50:50
10	**L2**	Et_2O	22	3	75	79.5:20.5
11	**L5**	Et_2O	22	3	77	75:25
12	**L6**	Et_2O	22	3	75	50:50
13	**L3**	Et_2O	22	3	73	84.5:15.5
14	**L3**	CH_2Cl_2	22	3	66	86.5:13.5
15	**L3**	CH_2Cl_2	22	19	78	82.5:17.5
16	**L3**	CH_2Cl_2	0-4	3	33	93.5:6.5
17	**L3**	CH_2Cl_2	0-4	19	63	92.5:7.5
18	**L7**	CH_2Cl_2	0-4	3	37	92.5:7.5

[a]Reactions run with 0.20 mmol THIQ in 0.25 mL solvent. [b]Isolated yield of pure **3a**. [c]Determined by HPLC analysis of pure **2a** in comparison with an authentic racemic standard.

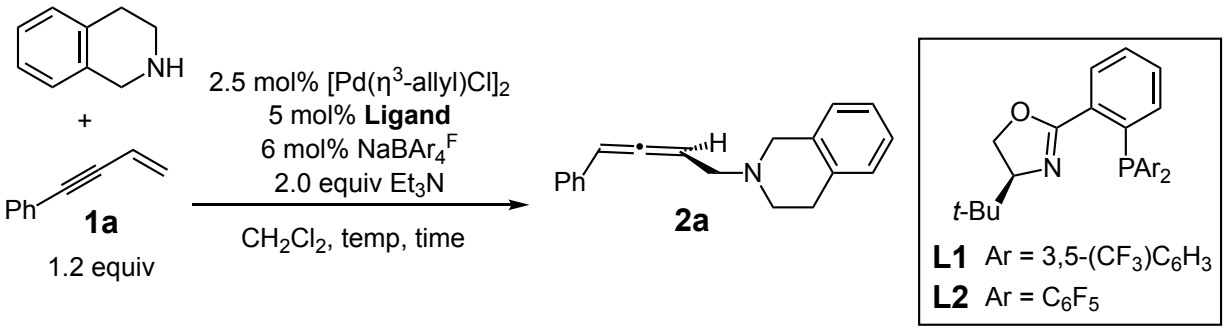


L2: **Ar** = C_6F_6
L4: **Ar** = 4-$(CF_3)C_6H_4$



L3: **Ar** = C_6F_5, **M** = Fe
L5: **Ar** = 4-$(CF_3)C_6H_4$, **M** = Fe
L6: **Ar** = 3,5-$(CF_3)_2C_6H_3$, **M** = Fe
L7: **Ar** = C_6F_5, **M** = Ru

Table S4. Experiments Performed in Duplicate or Triplicate to Compare Reaction Reproducibility with Different Ligand Electronics[a]

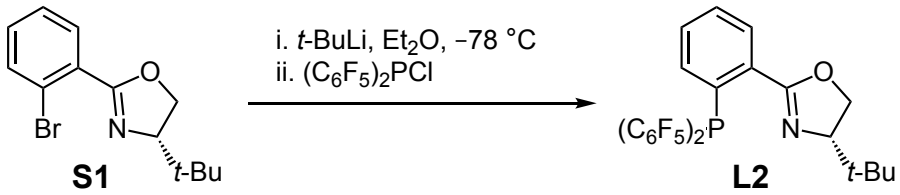


entry	ligand	solvent	temperature (°C)	time (h)	trial	yield 2a (%)[b]	er[c]
1	**L1**	Et_2O	22	3	1	73	74:26
					2	48	71.5:28.5
					3	70	51.5:48.5
2	**L1**	CH_2Cl_2	22	3	1	65	82:18
					2	65	54:46
					3	70	76.5:23.5
3	**L1**	CH_2Cl_2	22	20	1	68	61:39
					2	67	50:50
4	**L1**	CH_2Cl_2	0-4	20	1	50	86:14
					2	62	71:29
5	**L2**	CH_2Cl_2	22	3	1	67	82:18
					2	67	82.5:17.5
					3	73	82:18

[a]Reactions run with 0.20 mmol THIQ in 0.25 mL solvent. [b]Isolated yield of pure **2a**. [c]Determined by HPLC analysis of pure **2a** in comparison with an authentic racemic standard.

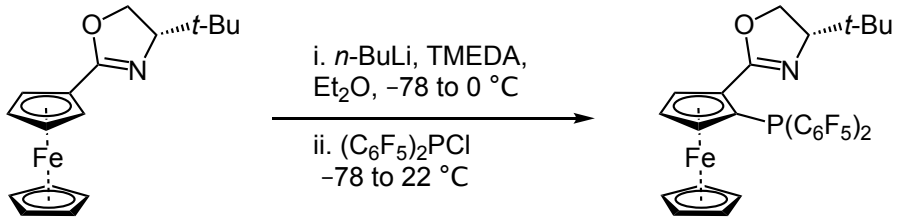
III. Ligand Synthesis

Ligands **L1** and **L4** were prepared as previously described.[7,8]



S1 was prepared by a known method.[9]

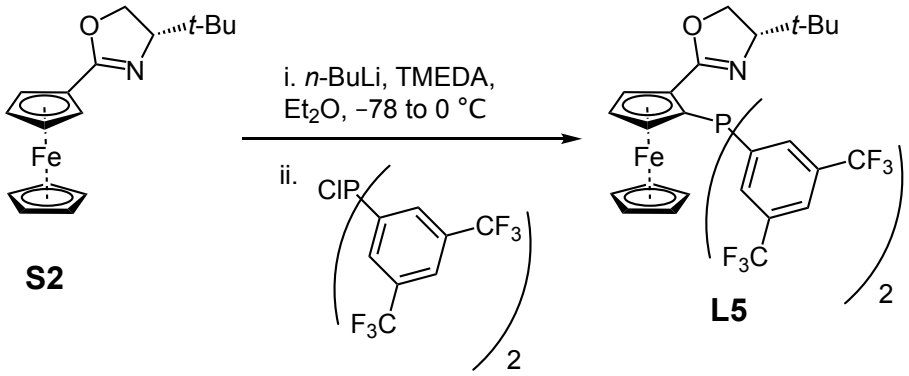
L2: To an oven dried 50-mL round-bottom flask equipped with a magnetic stirring rod was added **S1** (847 mg, 3.00 mmol, 1.00 equiv) and Et_2O (15 mL). The solution was allowed to cool to −78 °C and *t*-BuLi (1.7 M in pentane, 2.30 mL, 3.9 mmol, 1.30 equiv) was added dropwise via syringe. The reaction mixture was allowed to stir at −78 °C for 1 h and then chlorobis(pentafluorophenyl)phosphane (80% pure by wt., 1.95 g, 3.90 mmol, 1.30 equiv) [note: for this material the remaining 20 wt.% was tris(pentafluorophenyl)phosphine and does not affect reactivity] was added as a solution in Et_2O (3 mL) via cannula transfer. The mixture was allowed to warm to ambient temperature and stir for 1 h. The reaction was quenched with sat aq NH_4Cl (50 mL). The aqueous layer was separated from the organics and was washed with Et_2O (20 mL). The combined organic fractions were dried over $MgSO_4$, filtered, and concentrated. **L2** (1.37 g, 2.42 mmol, 80.7% yield) was obtained as a white solid after flash silica gel chromatography (99:1 to 95:5 hexanes:EtOAc). **IR** (neat, cm^{-1}) 2959 (w), 1650 (m), 1640 (m), 1513 (s), 1467 (s), 1381 (m), 1358 (m), 1309 (w), 1285 (m), 1256 (w), 1209 (w), 1138 (w), 1082 (s), 1051 (m), 1026 (w), 973 (s); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (1H, ddd, J = 7.7, 5.0, 1.4 Hz), 7.52–7.47 (1H, m), 7.39 (1H, td, J = 7.7, 1.4 Hz), 7.15 (1H, dd, J = 7.4, 3.7 Hz), 4.34 (1H, dd, J = 10.1, 8.7 Hz), 4.16 (1H, t, J = 8.7 Hz), 3.92 (1H, dd, J = 10.1, 8.8 Hz), 0.74 (9H, s); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.2 (d, J = 5.0 Hz), 149.2–148.3 (m), 147.0–146.3 (m), 143.6–142.5 (m), 141.5–140.5 (m), 138.9–138.1 (m), 136.9–136.0 (m), 132.4, 132.0 (d, J = 25.1 Hz), 131.3 (d, J = 22.1 Hz), 130.7, 129.6 (d, J = 1.8 Hz), 129.5, 112.2–111.4 (m), 77.1 (d, J = 1.5 Hz), 69.0, 33.5, 25.5 (note: aryl carbons show complex splitting due to ^{19}F and ^{31}P atoms); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -129.61 – -130.00 (2F, m), -130.19 – -130.63 (2F, m), -151.09 – -151.33 (1F, m), -151.53 – -151.80 (1F, m), -160.95 – -161.16 (2F, m), -161.17 – -161.44 (2F, m); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 75.2–74.2 (1P, m); **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{25}H_{16}F_{10}NOP$: 568.0883, found: 568.0886; **MP** = 61–65 °C.



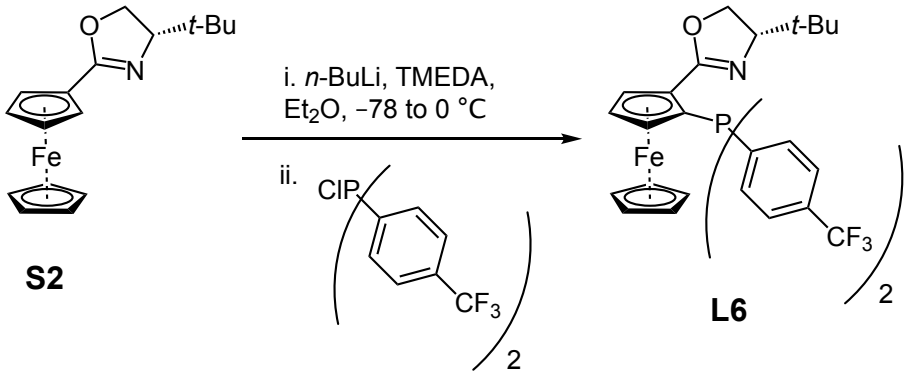
S2 **L3**

S2 was prepared from ferrocenecarboxylic acid and (*S*)-*tert*-leucinol by a previously reported method and spectral data match those previously reported.[10,11] The synthesis of all ferrocene and ruthenocene based ligands is based on a previously reported method for related ligands and the stereoisomer depicted is based on the observed diastereoselectivity for this related procedure.[10]

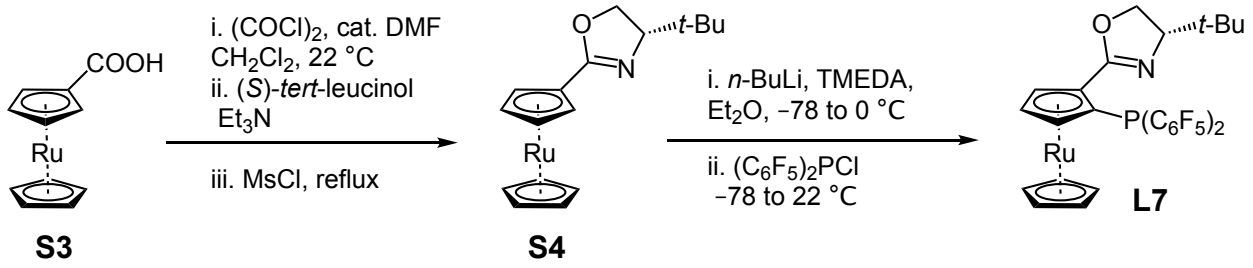
L3: To an oven-dried 50-mL round-bottom flask equipped with a magnetic stirring rod was added **S2** (622 mg, 2.00 mmol, 1.00 equiv), TMEDA (0.450 mL, 3.01 mmol, 1.51 equiv) and Et_2O (24 mL). The solution was then allowed to cool to −78 °C and subsequently *n*-BuLi (2.50 M in hexanes, 1.20 mL, 3.00 mmol, 1.50 equiv) was added dropwise via syringe. The mixture was allowed to stir at −78 °C for 0.5 h and then warm to 0 °C and stir for an additional 0.5 h. The resulting red solution was then allowed to cool to −78 °C and chlorobis(pentafluorophenyl)phosphane (94% pure by wt., 1.11 g, 2.60 mmol, 1.30 equiv) was added as a solution in Et_2O (4.0 mL) via cannula transfer. The resulting solution was allowed to warm gradually to ambient temperature and stir for 1 h. The reaction mixture was then quenched with sat aq $NaHCO_3$ (30 mL). The aqueous layer was separated from organics and washed with Et_2O (30 mL). The combined organic fractions were dried over $MgSO_4$, filtered, and concentrated. **L3** (986 mg, 1.46 mmol, 73.0% yield) was obtained as an orange solid after flash silica gel chromatography (98:2 to 95:5 hexanes:EtOAc). ^{1}H NMR analysis indicated **L3** was formed as a single detectable diastereomer. **IR** (neat, cm^{-1}) 2957 (w) 1657 (m), 1638 (w), 1513 (s), 1470 (s), 1382 (m), 1365 (w), 1285 (m), 1256 (w), 1171 (w), 1151 (m), 1084 (s); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.88 (1H, dt, J = 2.7, 1.4 Hz), 4.41 (1H, t, J = 2.6 Hz), 4.22–4.14 (2H, m), 4.17 (5H, s), 3.92 (1H, br s), 3.66 (1H, dd, J = 9.9, 7.4 Hz), 0.87 (9H, s); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 163.9 (d, J = 3.8 Hz), 149.5–149.0 (m), 148.3–147.8 (m), 147.5–147.1 (m), 146.2–141.7 (m), 138.9–138.5 (m), 138.1–137.7 (m), 136.9–136.5 (m), 136.2–135.6 (m), 76.3 (d, J = 1.9 Hz), 73.3, 73.2, 72.4, 72.4, 70.9, 70.9, 70.9, 69.0, 33.5, 29.6 (note: aryl carbons show complex splitting due to ^{19}F and ^{31}P atoms); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -127.0 – -127.5 (2F, m), -133.3 – -134.0 (2F, m), -148.7 – -148.9 (1F, m), -153.9 (1F, t, J_F = 20.6 Hz), -159.8 (2F, ddd, J_F = 23.8, 20.7, 9.3 Hz), -162.7 – -162.9 (2F, m); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 68.0–67.0 (1P, m); **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{29}H_{20}F_{10}[^{56}Fe]NOP$: 676.0545, found: 676.0546; **MP** = 75–80 °C.



L5: To an oven-dried 100-mL round-bottom flask equipped with a magnetic stirring rod was added **S2** (966 mg, 3.20 mmol, 1.00 equiv), TMEDA (0.620 mL, 4.16 mmol, 1.30 equiv) and Et_2O (35 mL). The solution was then allowed to cool to −78 °C and subsequently *n*-BuLi (2.00 M in cyclohexane, 2.10 mL, 4.16 mmol, 1.30 equiv) was added dropwise via syringe. The mixture was allowed to stir at −78 °C for 1 h and then warm to 0 °C and stir for an additional 0.5 h. Chlorobis[3,5-bis(trifluoromethyl)phenyl]phosphine (2.05 g, 4.16 mmol, 1.30 equiv) was then added as a solution in Et_2O (5.0 mL) via cannula transfer. The resulting solution was allowed to warm gradually to ambient temperature and stir for 1 h. The mixture was then quenched with sat aq NH_4Cl (30 mL). The aqueous layer was separated from the organics and washed with Et_2O (30 mL). The combined organic fractions were dried over $MgSO_4$, filtered, and concentrated. **L5** (2.07 g, 2.69 mmol, 84.1% yield) was obtained as an orange solid after flash silica gel chromatography (100% hexanes to 95:5 hexanes:EtOAc). ^{1}H NMR analysis indicated **L5** was formed as a single detectable diastereomer. **IR** (neat, cm^{-1}) 1656 (m), 1353 (s), 1277 (s), 1171 (m), 1120 (s), 1093 (m), 1037 (w), 984 (w); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (1H, s), 7.88 (1H, s), 7.87 (1H, s), 7.78 (1H, s), 7.66 (1H, s), 7.64 (1H, s), 4.94 (1H, dt, J = 2.7, 1.4 Hz), 4.44 (1H, t, J = 2.6 Hz), 4.21 (5H, s), 4.16 (1H, app. t, J = 8.9 Hz), 4.09 (1H, app. t, J = 7.5 Hz), 3.61 (1H, dd, J = 10.0, 7.4 Hz), 3.51–3.46 (1H, m), 0.88 (9H, s); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 163 (d, J = 3.3 Hz), 142.4 (d, J = 20.1 Hz), 141.6 (d, J = 20.8 Hz), 134.4 (dd, J = 22.1, 2.5 Hz), 132.5 (dd, J = 19.6, 2.4 Hz), 131.7 (qd, J = 32.9, 6.2 Hz), 131.3 (qd, J = 32.7, 6.2 Hz), 123.3 (q, J = 271 Hz), 123.2 (q, J = 271 Hz), 123.0 (t, J = 3.6 Hz), 122.3 (t, J = 3.7 Hz), 76.4, 76.3, 74.2 (d, J = 12.3 Hz), 73.3 (d, J = 5.3 Hz), 73.0 (d, J = 1.5 Hz), 71.4, 70.9, 68.6, 33.5, 25.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ −62.89, −62.98, **^{31}P NMR** (162 MHz, $CDCl_3$) δ −16.6; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{33}H_{26}F_{12}[^{56}Fe]NOP$: 768.0983, found: 768.0984; **MP** = 125–127 °C.



L6: To an oven-dried 100-mL round-bottom flask equipped with a magnetic stirring rod was added **S2** (966 mg, 3.20 mmol, 1.00 equiv), TMEDA (0.620 mL, 4.16 mmol, 1.30 equiv) and Et_2O (35 mL). The solution was then allowed to cool to −78 °C and subsequently *n*-BuLi (2.00 M in cyclohexane, 2.10 mL, 4.16 mmol, 1.30 equiv) was added dropwise via syringe. The mixture was allowed to stir at −78 °C for 1 h and then warm to 0 °C and stir for an additional 0.5 h. Chlorobis[4-(trifluoromethyl)phenyl]phosphine (1.48 g, 4.16 mmol, 1.30 equiv) was then added as a solution in Et_2O (5.0 mL) via cannula transfer. The resulting solution was allowed to warm gradually to ambient temperature and stir for 1 h. The mixture was then quenched with sat aq NH_4Cl (30 mL). The aqueous layer was separated from the organics and washed with Et_2O (30 mL). The combined organic fractions were dried over $MgSO_4$, filtered, and concentrated. **L6** (1.72 g, 2.73 mmol, 85.3% yield) was obtained as a yellow solid after flash silica gel chromatography (99:1 to 93:7 hexanes:EtOAc). ^{1}H NMR analysis indicated **L6** was formed as a single detectable diastereomer. **IR** (neat, cm^{-1}) 2965 (w), 1652 (m), 1604 (w), 1483 (w), 1394 (m), 1364 (w), 1323 (s), 1279 (w), 1254 (w), 1209 (w), 1165 (s), 1121 (s), 1058 (s), 1007 (m), 985 (m); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 (1H, d, J = 7.9 Hz), 7.56 (1H, t, J = 6.5 Hz), 7.47 (1H, d, J = 7.9 Hz), 7.29 (1H, t, J = 7.3 Hz), 4.94 (1H, dt, J = 2.6, 1.2 Hz), 4.39 (1H, t, J = 2.5 Hz), 4.20 (5H, s), 4.16 (1H, dd, J = 9.8, 8.6 Hz), 3.97 (1H, app. t, J = 7.5 Hz), 3.69 (1H, dd, J = 9.9, 7.4 Hz), 3.59–3.55 (1H, m), 0.818 (9H, s); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 163.6 (d, J = 2.9 Hz), 144.6 (d, J = 16.0 Hz), 143.1 (d, J = 17.0 Hz), 135.3 (d, J = 21.8 Hz), 132.5 (d, J = 19.3 Hz), 131.1 (q, J = 34.4 Hz), 130.0 (q, J = 32.0 Hz), 125.0 (dt, J = 10.3, 3.6 Hz), 124.7 (dt, J = 13.7, 3.7 Hz), 124.2 (q, J = 271 Hz), 124.0 (q, J = 271 Hz), 76.2, 76.2, 76.1 (d, J = 3.4 Hz), 73.6 (d, J = 4.8 Hz), 72.6 (d, J = 1.5 Hz), 71.0, 70.8, 68.5, 33.6, 25.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ –62.66, –62.75; **^{31}P NMR** (162 MHz, $CDCl_3$) δ –18.0; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{31}H_{28}F_6[^{56}Fe]NOP$: 632.1235, found: 632.1238; **MP** = 197–199 °C (decomp.).



Ruthenocenecarboxylic acid (**S3**) was prepared from ruthenocene by a known method.[12]

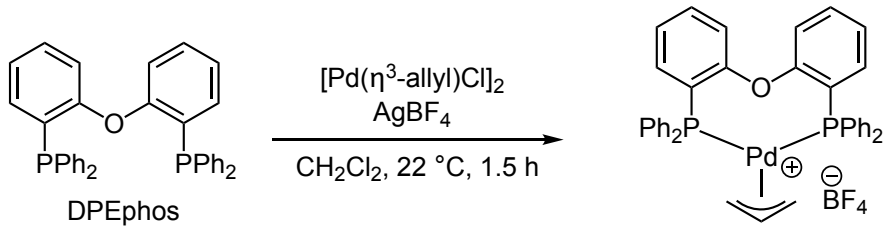
S4: To a dry 50-mL round-bottom flask equipped with a magnetic stirring rod was added ruthenocene carboxylic acid (**S3**, 743 mg, 2.70 mmol, 1.00 equiv), which was suspended in CH_2Cl_2 (7.5 mL) with one drop of DMF added. The suspension was then treated with oxalyl chloride (0.460 mL, 5.40 mmol, 2.00 equiv) and the resulting yellow solution was allowed to stir at ambient temperature for 1 h. Volatiles were then removed by mild vacuum distillation with gentle heating (warm water bath) to reveal the acid chloride as a yellow solid. The acid chloride was then dissolved in CH_2Cl_2 (7 mL) and added to a solution of (*S*)-*tert*-leucinol (333 mg, 2.84 mmol, 1.05 equiv) and Et_3N (1.90 mL, 13.5 mmol, 5.00 equiv) in CH_2Cl_2 (3 mL) via cannula transfer. The reaction mixture was allowed to stir at ambient temperature for 1.5 h, and then methanesulfonyl chloride (0.230 mL, 3.0 mmol, 1.10 equiv) was added. A reflux condenser was added to the flask and the reaction mixture was brought to reflux, which was maintained for 11 h. The reaction mixture was then allowed to cool to ambient temperature and was quenched with H_2O (20 mL). The aqueous layer was separated from the organics and washed with CH_2Cl_2 (3 X 10 mL). The combined organic fractions were dried over $MgSO_4$, filtered, and concentrated. **S4** (580 mg, 1.63 mmol, 60.3% yield) was obtained as a white solid after flash silica gel chromatography (85:15 hexanes:EtOAc). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.16–5.13 (1H, m), 5.04–5.02 (1H, m), 4.67–4.61 (2H, m), 4.55 (5H, s), 4.13 (1H, dd, J = 9.9, 8.6 Hz), 4.07 (1H, dd, J = 8.6, 7.0 Hz), 3.81 (1H, dd, J = 9.9, 7.0 Hz), 0.88 (9H, s). Spectral data match those previously reported.[13]

L7: To an oven-dried 25-mL round-bottom flask equipped with a magnetic stirring rod was added **S4** (178 mg, 0.500 mmol, 1.00 equiv), TMEDA (97.0 μL, 0.650 mmol, 1.30 equiv) and Et_2O (8 mL). The solution was then allowed to cool to −78 °C and subsequently *n*-BuLi (2.00 M in cyclohexane, 0.33 mL, 0.65 mmol, 1.30 equiv) was added dropwise via syringe. The mixture was allowed to stir at −78 °C for 1 h and then warm to 0 °C and stir for an additional 0.5 h. Chlorobis(pentafluorophenyl)phosphane (94% pure by wt., 277 mg, 0.650 mmol, 1.30 equiv) was then added as a solution in Et_2O (2.0 mL) via cannula transfer. The resulting solution was allowed to warm gradually to ambient temperature and stir for 1 h. The reaction mixture was then quenched with sat aq NH_4Cl (10 mL). The aqueous layer was separated from organics and washed with Et_2O (2 X 10 mL). The combined organic fractions were dried over $MgSO_4$, filtered, and concentrated. **L7** (218 mg, 0.290 mmol, 58.1% yield) was obtained as a pale yellow solid after flash silica gel chromatography (95:5 hexanes:EtOAc). ^{1}H NMR analysis indicated **L7** was formed as a single detectable diastereomer. **IR** (neat, cm^{-1}) 2953 (w), 1659 (m), 1638 (w), 1513 (s), 1468 (s), 1382 (m), 1365 (w), 1284 (m), 1254 (w), 1209 (w), 1170 (w), 1149 (m), 1083 (s), 1030 (w), 972 (s); **^{1}H NMR** (400 MHz, $CDCl_3$) δ; 5.21–5.19 (1H, m), 4.27–4.70 (1H, m), 5.43 (5H, s), 4.32–4.29 (1H, m), 4.16 (1H, app. t, J = 8.8 Hz), 4.11 (1H, dd, J = 8.7, 6.9 Hz), 3.65 (1H, dd, J = 9.6, 6.7 Hz), 0.81 (9H, s); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.7 (t, J = 3.9 Hz), 149.3–148.8 (m), 148.0–147.6

(m), 147.3–146.8 (m), 146.1–145.5 (m), 142.1–141.3 (m), 140.4–139.6 (m), 138.3–138.2 (m), 138.0–137.5 (m), 136.8–136.2 (m), 136.1–135.6 (m), 80.8–80.4 (m), 76.1–75.9 (m), 75.9–75.8 (m), 73.8, 73.2, 72.8, 68.8, 33.9, 25.3 (note: aryl carbons show complex splitting due to ^{19}F and ^{31}P atoms); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -127.67 – -127.88 (2F, m), -134.10 – -134.38 (2F, m), -148.95 – -149.15 (1F, m), -153.91 (1F, t, J_{CF} = 20.9 Hz), -159.99 – -160.21 (2F, m), -162.59 – -162.87 (2F, m); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 67.8–66.5 (1P, m); **HRMS** (ESI^+) $[M+H]^+$ calc'd for; $C_{29}H_{20}F_{10}NOP[^{102}Ru]$: 722.0239, found: 722.0243; **MP** = 83–88 °C.

IV. Pd Complex Synthesis

The synthesis of **Pd-2** and **Pd-3** have been reported previously.[7,14] **Pd-1** was prepared by an analogous procedure.

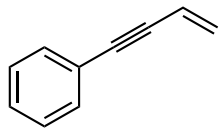


Pd-1

Pd-1: In an N_2-filled glovebox, to a dry 250-mL round-bottom flask equipped with a magnetic stirring rod was added (oxybis(2,1-phenylene))bis(diphenylphosphane) (DPEphos, 1.24 g, 2.30 mmol, 1.00 equiv), [Pd(η^3-allyl)Cl]$_2$ (420 mg, 1.15 mmol, 0.500 equiv), and CH_2Cl_2 (50 mL). The solution was allowed to stir at ambient temperature for 20 min and then $AgBF_4$ (493 mg, 2.53 mmol, 1.10 equiv) was added. Vigorous stirring was allowed to continue for 1 h during which time a white precipitate formed. The following work up took place outside of the glovebox. The heterogenous reaction mixture was filtered through a pad of celite eluting with CH_2Cl_2 (3 X 20 mL). The solution was then concentrated to reveal **Pd-1** as an off-white powder (1.77 g, 2.06 mmol, 89.7% yield). ^{1}H NMR analysis revealed **Pd-1** to be formed as a 1:1 adduct with CH_2Cl_2. **IR** (neat, cm^{-1}); 3057 (w), 1567 (w), 1479 (w), 1465 (m), 1434 (s), 1262 (m), 1215 (s), 1187 (w), 1092 (m), 1052 (s), 1020 (s), 958 (m); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.56–7.29 (18H, m), 7.26–7.18 (4H, m), 7.09–7.00 (4H, m), 6.61–6.52 (2H, m), 6.14–6.00 (1H, m), 5.72 (2H, s, CH_2Cl_2), 4.06–3.93 (2H, m), 3.70–3.54 (2H, m); **^{13}C NMR** (125 MHz, DMSO-d_6) δ 158.2 (t, J = 3.8 Hz), 134.4, 133.9 (t, J = 6.6 Hz), 133.7, 133.4 (t, J = 6.4 Hz), 131.7, 131.5, 129.5 (q, J = 5.3 Hz), 125.7, 123.7 (t, J = 5.0 Hz), 122.2, 122.0, 121.8, 121.3, 79.2, 79.1, 77.0, 55.4 (CH_2Cl_2); **^{19}F NMR** (376 MHz, DMSO-d_6) δ –148.31, –148.36; **^{31}P NMR** (162 MHz, DMSO-d_6) δ 13.0; **HRMS** (ESI$^+$) [M+H]$^+$ calc'd for $C_{39}H_{33}OP_2$[^{106}Pd]: 685.1036, found: 685.1055; **MP** = 255–260 °C (decomp.).

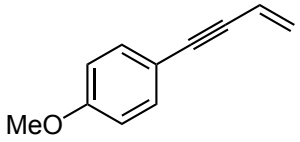
V. Substrate Synthesis

Enyne substrates were prepared by Sonogashira coupling[15] from their corresponding terminal alkynes with vinyl bromide by a slightly modified method. General Method A is exemplified by the synthesis of **1a**.



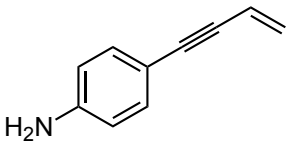
1a

but-3-en-1-yn-1-ylbenzene (1a): General Method A: In an N_2-filled glovebox, to an oven-dried 250-mL round-bottom flask equipped with a magnetic stirring bar was added $Pd(PPh_3)_4$ (462 mg, 0.400 mmol, 2.00 mol%) and CuI (381 mg, 2.00 mmol, 10.0 mol%). The flask was sealed with a rubber septum and removed from the glovebox. Vinyl bromide (1.0 M in THF, 50.0 mL, 2.50 equiv) was added followed by freshly distilled and degassed Et_2NH (10.4 mL, 100 mmol, 5.00 equiv). The mixture was allowed to stir at ambient temperature for *ca.* 5 min and subsequently phenylacetylene (2.20 mL, 20.0 mmol, 1.00 equiv) was added as a solution in THF (10 mL) dropwise over 1 h. The mixture was then allowed to stir at ambient temperature overnight (15–20 h). The reaction contents were then filtered through a pad of celite, eluting with Et_2O (3 X 20 mL). The solution was then concentrated *in vacuo*. **1a** was obtained by flash silica gel chromatography (99:1 hexanes:Et_2O) to afford a colorless oil (2.43 g, 18.9 mmol, 94.6%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48–7.41 (2H, m), 7.34–7.26 (3H, m), 6.01 (1H, dd, J = 17.6, 11.1), 5.73 (1H, dd, J = 17.6, 2.0 Hz), 5.54 (1H, dd, J = 11.1, 2.0 Hz). Spectral data match those previously reported.[15]



1b

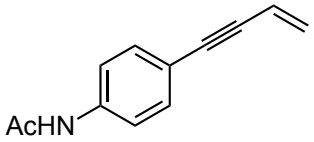
1-(but-3-en-1-yn-1-yl)-4-methoxybenzene (1b): Prepared by General Method A in 92.5% yield after flash silica gel chromatography (98:2 to 95:5 hexanes:EtOAc). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39–7.34 (2H, m), 6.86–6.80 (2H, m), 5.99 (1H, dd, J = 17.5, 11.1 Hz), 5.68 (1H, dd, J = 17.5, 2.0 Hz), 5.48 (1H, dd, J = 11.1, 2.0 Hz), 3.80 (3H, s). Spectral data match those previously reported.[16]



S5

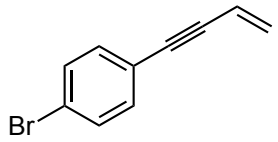
4-(but-3-en-1-yn-1-yl)aniline (S5): Prepared by General Method A in 89.0% yield after flash silica gel chromatography (80:20 hexanes:EtOAc). **IR** (neat, cm^{-1}) 3466 (m), 3376 (m), 3211 (w), 3033 (w), 3005 (w), 2212 (m), 2177 (m), 1618 (s), 1598(s), 1510 (s), 1432 (w), 1410 (w), 1284 (s), 1176 (s), 1127 (w), 1077 (w), 969 (m); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29–7.17 (2H, m),

6.61–6.55 (2H, m), 5.99 (1H, dd, J = 17.5, 11.1 Hz), 5.64 (1H, dd, J = 17.5, 2.1 Hz), 5.44 (1H, dd, J = 11.1, 2.1 Hz), 3.79 (2H, br s); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 146.7, 132.9, 125.4, 117.5, 114.7, 112.4, 90.8, 86.2; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{10}H_9N$: 144.0808, found: 144.0810.



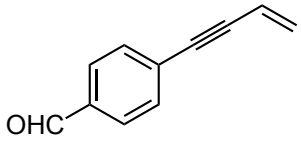
1c

***N*-(4-(but-3-en-1-yn-1-yl)phenyl)acetamide (1c):** Prepared from **S5** by the following procedure. To an oven-dried 25-mL round-bottom flask equipped with a magnetic stirring rod was add **S5** (430 mg, 3.00 mmol, 1.00 equiv), pyridine (0.480 mL, 5.96 mmol, 1.99 equiv), and CH_2Cl_2 (5.0 mL). The mixture was allowed to cool to 0 °C and acetyl chloride (0.430 mL, 6.05 mmol, 2.02 equiv) was added. The mixture was then allowed to warm to ambient temperature and stir for 3 h. The reaction was then quenched with sat aq $NaHCO_3$ (20 mL). The aqueous layer was separated from the organics and washed with CH_2Cl_2 (2 X 20 mL). The combined organic fractions were dried over $MgSO_4$, filtered, and concentrated. **1c** was obtained as a pale yellow solid (462 mg, 2.49 mmol, 83.2% yield) after purification by flash silica gel chromatography (60:40 hexanes:EtOAc). **IR** (neat, cm^{-1}) 3252 (w), 3103 (w), 1660 (m), 1594 (s), 1530 (s), 1505 (s), 1403 (m), 1369 (m), 1319 (s), 1296 (w), 1256 (m), 1178 (w), 1111 (w), 1080 (w), 1040 (w), 1012 (w), 966 (m); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 (2H, d, J = 8.6 Hz), 7.42–7.32 (3H, m), 5.99 (1H, dd, J = 17.5, 11.1), 5.70 (1H, dd, J = 17.5, 2.0 Hz), 5.51 (1H, dd, J = 11.1, 2.0 Hz), 2.16 (3H, s); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 168.7, 138.0, 132.3, 126.7, 119.5, 118.7, 117.1, 89.7, 87.8, 24.6; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{12}H_{11}NO$: 186.0913, found: 186.0917; **MP** = 144–147 °C.



1d

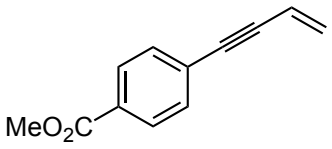
1-bromo-4-(but-3-en-1-yn-1-yl)benzene (1d): Prepared by General method A in 79.1% yield after flash silica gel chromatography (99:1 hexanes:Et_2O). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46–7.40 (2H, m), 7.31–7.26 (2H, m), 5.98 (1H, dd, J = 17.6, 11.1 Hz), 5.73 (1H, dd, J = 17.6, 2.0 Hz), 5.55 (1H, dd, J = 11.1, 2.0 Hz). Spectral data match those previously reported.[17]



1e

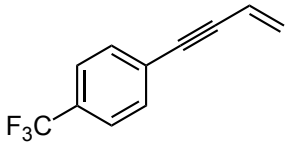
4-(but-3-en-1-yn-1-yl)benzaldehyde (1e): Prepared by General Method A in 86.6% yield after flash silica gel chromatography (95:5 hexanes:EtOAc). **IR** (neat, cm^{-1}) 2845 (w), 2744 (w), 2215 (w), 1693 (s), 1599 (s), 1556 (m), 1503 (w), 1413 (m), 1386 (m), 1300 (m), 1287 (m), 1265 (m), 1204 (s), 1163 (s), 1103 (m), 1013 (w), 1001 (w), 970 (m); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.99 (1H, s), 7.82 (2H, d, J = 8.2 Hz), 7.57 (2H, d, J = 8.2 Hz), 6.02 (1H, dd, J =17.6, 11.2 Hz), 5.79 (1H, dd, J = 17.6, 1.9 Hz), 5.62 (1H, dd, J = 11.2, 1.9 Hz); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 191.4,

135.4, 132.0, 129.5, 129.4, 128.4, 116.7, 92.0, 89.0; **HRMS** (ESI$^+$) [M+H]$^+$ calc'd for $C_{11}H_8O$: 157.0648, found: 157.0647.



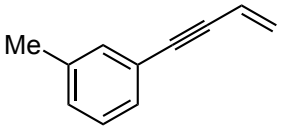
1f

methyl 4-(but-3-en-1-yn-1-yl)benzoate (1f): Prepared by General Method A in 83.0% yield after flash silica gel chromatography (95:5 hexanes:EtOAc). **IR** (neat, cm^{-1}) 2950 (w), 2850 (w), 1707 (s), 1605 (s), 1436 (s), 1406 (m), 1307 (w), 1271 (s), 1193 (w), 1174 (m), 1105 (s), 1015 (m), 961 (m); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00–7.94 (2H, m), 7.51–7.44 (2H, m), 6.01 (1H, dd, J = 17.5, 11.1 Hz), 5.76 (1H, dd, J = 17.5, 1.9 Hz), 5.59 (1H, dd, J = 11.1, 1.9 Hz), 3.89 (3H, s); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.5, 131.4, 129.4, 128.0, 127.8, 116.8, 90.9, 89.1, 52.2 (one sp^2 carbon missing due to overlap); **HRMS** (ESI$^+$) [M+H]$^+$ calc'd for $C_{12}H_{10}O_2$: 187.0754, found: 187.0756; **MP** = 34–36 °C.



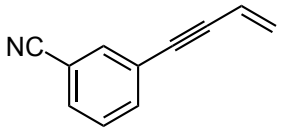
1g

1-(but-3-en-1-yn-1-yl)-4-(trifluoromethyl)benzene (1g): Prepared by General Method A in 99.0% yield after flash silica gel chromatography (99:1 hexanes:Et_2O). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (2H, AB_q, J_{AB} = 8.6 Hz), 7.52 (2H, AB_q, J_{AB} = 8.6 Hz), 6.01 (1H, dd, J = 17.5, 11.1 Hz), 5.78 (1H, dd, J = 17.5, 1.9 Hz), 5.60 (1H, dd, J = 11.1, 1.9 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –62.9. Spectral data match those previously reported.[16]



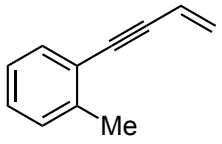
1h

1-(but-3-en-1-yn-1-yl)-3-methylbenzene (1h): Prepared by General Method A in 88.8% yield after flash silica gel chromatography (99:1 hexanes:Et_2O). **IR** (neat, cm^{-1}) 3008 (w), 2920 (w), 2202 (w), 1840 (w), 1607 (m), 1578 (w), 1484 (m), 1450 (w), 1380 (w), 1281 (w), 1181 (w), 1094 (w), 1080 (w), 1040 (w), 969 (m); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29–7.22 (2H, m), 7.19 (1H, dd, J = 7.5, 7.5 Hz), 7.14–7.09 (1H, m), 6.00 (1H, dd, J = 17.5, 11.2 Hz), 5.71 (1H, dd, J = 17.5, 2.0 Hz) 5.52 (1H, dd, J = 11.2, 2.0 Hz), 2.32 (3H, s); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 138.0, 132.2, 129.2, 128.7, 128.2, 126.7, 122.9, 117.3, 90.2, 87.8, 21.2; **EA** calc' for $C_{11}H_{10}$: C = 92.91%, H = 7.09%, found: C = 92.65%, H = 7.12%.



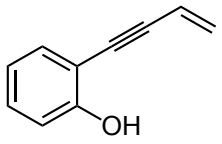
1i

3-(but-3-en-1-yn-1-yl)benzonitrile (1i): Prepared by General Method A in 87.5% yield after flash silica gel chromatography (95:5 hexanes:EtOAc). **IR** (neat, cm^{-1}) 3070 (w), 3012 (w), 2230 (m), 1850 (w), 1722 (w), 1600 (m), 1571 (w), 1477 (s), 1417 (w), 1407 (w), 1319 (w), 1288 (w), 1267 (w), 1167 (w), 1095 (w), 1082 (w), 969 (m); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (1H, dd, J = 1.6,1.6 Hz), 7.63 (1H, ddd, J = 7.8, 1.4, 1.4 Hz), 7.57 (1H, ddd, J = 7.8, 1.4, 1.4 Hz), 7.42 (1H, dd, J = 7.8, 7.8 Hz), 5.99 (1H, dd, J = 17.5, 11.1 Hz), 5.78 (1H, dd, J = 17.5, 1.8 Hz), 5.61 (1H, dd, J = 11.1, 1.8 Hz). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 135.6, 134.8, 131.4, 129.2, 128.5, 124.8, 118.0, 116.5, 112.8, 90.4, 87.4; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{11}H_7N$: 154.0651, found: 154.0649.



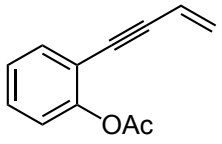
1j

1-(but-3-en-1-yn-1-yl)-2-methylbenzene (1j): Prepared by General Method A in 89.0% yield after flash silica gel chromatography (99:1 hexanes:Et_2O). **IR** (neat, cm^{-1}) 3009 (w), 2920 (w), 2212 (w), 1839 (w), 1605 (m), 1484 (m), 1455 (m), 1409 (w), 1379 (w), 1289 (w), 1256 (w), 1197 (w), 1158 (w), 1116 (m), 1042 (w), 968 (m); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (1H, d, J = 7.3 Hz), 7.23–7.16 (2H, m), 7.15–7.08 (1H, m), 6.05 (1H, dd, J = 17.5, 11.1 Hz), 5.72 (1H, dd, J = 17.5, 2.0 Hz), 5.53 (1H, dd, J = 11.1, 2.0 Hz), 2.44 (3H, s); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 140.2, 131.9, 129.4, 128.3, 126.5, 125.5, 122.9, 117.4, 92.0, 88.9, 20.7; **EA** calc' for $C_{11}H_{10}$: C = 92.91%, H = 7.09%, found: C = 91.58%, H = 6.89%.



S6

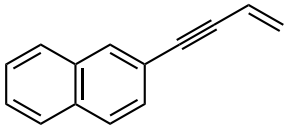
2-(but-3-en-1-yn-1-yl)phenol (S6): Prepared by General Method A in 61.2% yield after flash silica gel chromatography (95:5 hexanes:EtOAc). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 (1H, dd, J = 7.7, 1.6 Hz), 7.27–7.19 (1H, m), 6.94 (1H, dd, J = 8.3, 0.9 Hz), 6.86 (1H, td, J = 7.6, 1.1 Hz), 6.05 (1H, dd, J = 17.5, 11.2 Hz), 5.77 (1H, dd, J = 17.5, 1.8 Hz), 5.72 (1H, br s), 5.60 (1H, dd, J = 11.2, 1.8 Hz). Spectral data match those previously reported.[18]



1k

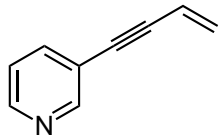
2-(but-3-en-1-yn-1-yl)phenyl acetate (1k): Prepared from **S6** by the following procedure. To an oven-dried 25-mL round-bottom flask equipped with a magnetic stirring rod was added **S6** (288 mg, 2.00 mmol, 1.00 equiv), pyridine (0.320 mL, 3.97 mmol 1.99 equiv), and CH_2Cl_2 (4.0 mL).

The solution was cooled to 0 °C and acetyl chloride (0.280 mL, 3.94 mmol, 1.97 equiv) was added. The solution was allowed to warm to ambient temperature and stir for 3 h. The reaction mixture was quenched with sat aq $NaHCO_3$ (20 mL) and the aquous layer was separated from the organics and washed with CH_2Cl_2 (2 X 20 mL). The combined organic fractions were dried over $MgSO_4$, filtered and concentrated. **1k** (342 mg, 1.84 mmol, 91.8% yield) was obtained as a colorless oil after flash silica gel chromatography (95:5 hexanes:EtOAc). **IR** (neat, cm^{-1}) 3010 (w), 1759 (s), 1590 (w), 1485 (m), 1445 (m), 1367 (m), 1290 (w), 1256 (w), 1207 (m), 1178 (s), 1106 (m), 1077 (w), 1034 (w), 1008 (m), 969 (w); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 (1H, dd, J = 7.7, 1.9 Hz), 7.33 (1H, ddd, J = 7.6, 7.6, 1.6 Hz), 7.19 (1H, ddd, J = 7.6, 7.6, 1.2 Hz), 7.08 (1H, dd, J = 8.1, 1.1 Hz), 6.00 (1H, dd, J = 17.6, 11.2 Hz), 5.71 (1H, dd, J = 17.6, 2.0 Hz), 5.55 (1H, dd, J = 11.2, 2.0 Hz), 2.33 (3H, s); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 168.9, 151.5, 133.0, 129.5, 127.5, 125.9, 122.3, 117.3, 116.9, 92.8, 84.7, 20.8; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{12}H_{10}O_2$: 187.0754, found: 187.0755.



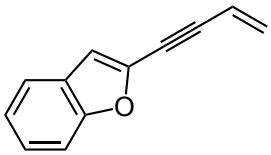
1l

2-(but-3-en-1-yn-1-yl)naphthalene (1l): Prepared by General Method A in 79.5% yield after flash silica gel chromatography (99:1 hexanes:EtOAc). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (1H, s), 7.86–7.70 (3H, m), 7.54–7.41 (3H, s), 6.06 (1H, dd, J = 17.5, 11.1 Hz), 5.78 (1H, dd, J = 17.5, 1.9 Hz), 5.57 (1H, dd, J = 11.1, 1.9 Hz). Spectral data match those previously reported.[19]



1m

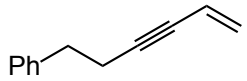
3-(but-3-en-1-yn-1-yl)pyridine (1m): Prepared by General Method A in 82.0% yield after flash silica gel chromatography (70:30 pentanes:Et_2O). **IR** (neat, cm^{-1}) 3030 (w), 1605 (m), 1578 (m), 1552 (m), 1475 (s), 1404 (s), 1327 (w), 1291 (w), 1268 (w), 1186 (m), 1121 (w), 1098 (w), 1021 (m), 969 (m); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.66 (1H, d, J = 1.8 Hz), 8.51 (1H, dd, J = 4.9, 1.6 Hz), 7.70 (1H, ddd, J = 7.9, 1.9, 1.9 Hz), 7.26–7.21 (1H, m), 6.01 (1H, dd, J = 17.6, 11.2 Hz), 5.77 (1H, dd, J = 17.6, 1.9 Hz), 5.60 (1H, dd, J = 11.2, 1.9 Hz); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 152.1, 148.5, 138.3, 128.0, 123.0, 120.3, 116.6, 91.2, 86.5; **HRMS** (ESI^+) $[M+H]^+$ calc'd for C_9H_7N 130.0651, found: 130.0653.



1n

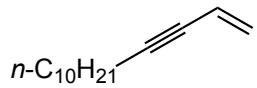
2-(but-3-en-1-yn-1-yl)benzofuran (1n): Prepared by General Method A in 76.1% yield after flash silica gel chromatography (100% hexanes). **IR** (neat, cm^{-1}) 3057 (w), 1854 (w), 1778 (w), 1608 (w), 1557 (w), 1473 (w), 1448 (m), 1408 (w), 1349 (w), 1305 (w), 1288 (w), 1267 (w), 1255 (m),

1200 (m), 1160 (m), 1143 (m), 1108 (m), 1073 (w), 966 (m); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (1H, d, J = 7.6 Hz), 7.44 (1H, d, J = 8.2 Hz), 7.32 (1H, ddd, J = 7.3, 7.3, 1.3 Hz), 7.23 (1H, dd, J = 7.4, 7.4 Hz), 6.93 (1H, s), 6.05 (1H, dd, J = 17.6, 11.3 Hz), 5.84 (1H, dd, J = 17.6, 1.8 Hz), 5.65 (1H, dd, J = 11.3, 1.8 Hz); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 154.9, 138.6, 128.7, 127.7, 125.7, 123.3, 121.2, 116.1, 111.7, 111.2, 93.9, 80.2; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{12}H_8O$: 169.0648, found: 169.0645.



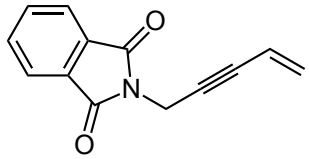
1o

hex-5-en-3-yn-1-ylbenzene (1o): Prepared by General Method A in 87.9% yield after flash silica gel chromatography (99:1 hexanes:Et_2O). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33–7.26 (2H, m), 7.25–7.18 (3H, m), 5.76 (1H, ddt, J = 17.6, 11.0, 2.0 Hz), 5.54 (1H, dd, J = 17.6, 2.2 Hz), 5.38 (1H, dd, J = 11.0, 2.2 Hz), 2.85 (2H, t, J = 7.6 Hz), 2.59 (2H, td, J = 7.6, 2.0 Hz). Spectral data match those previously reported.[20]



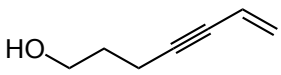
1p

tetradec-1-en-3-yne (1p): Prepared by General Method A in 95.0% yield after flash silica gel chromatography (100% hexanes). **IR** (neat, cm^{-1}) 2922 (s), 2853 (s), 2227 (w), 1608 (w), 1466 (m), 1378 (w), 1328 (w), 1162 (w), 971 (m); 911 (s); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.76 (1H, ddt, J = 17.5, 11.0, 2.0 Hz), 5.52 (1H, dd, J = 17.5, 2.2 Hz), 5.35 (1H, dd, J = 11.0, 2.2 Hz), 2.28 (2H, td, J = 7.1, 2.0 Hz), 1.56–1.47 (2H, m), 1.42–1.15 (14H, m), 0.86 (3H, t, J = 6.6 Hz); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 125.3, 117.6, 91.2, 79.3, 31.9, 29.6, 29.5, 29.3, 29.2, 28.9, 28.7, 22.7, 19.3, 14.1; **EA** calc' for $C_{14}H_{24}$: C = 87.42%, H = 12.58%, found: C = 87.44%, H = 12.65%.



1q

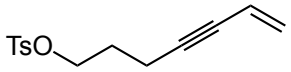
2-(pent-4-en-2-yn-1-yl)isoindoline-1,3-dione (1q): Prepared by General Method A in 82.8% yield after flash silica gel chromatography (80:20 hexanes:EtOAc). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90–7.83 (2H, m), 7.75–7.69 (2H, m), 5.72 (1H, ddt, J = 17.6, 10.8, 1.8 Hz), 5.62 (1H, dd, J = 17.6, 2.4 Hz), 5.45 (1H, dd, J = 10.8, 2.4 Hz), 4.55 (2H, d, J = 1.9 Hz). Spectral data match those previously reported.[21]



1r

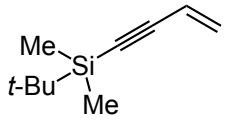
hept-6-en-4-yn-1-ol (1r): Prepared by General Method A in 92.2% yield after flash silica gel chromatography (70:30 to 50:50 pentanes:Et_2O). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.75 (1H, ddt, J = 17.5, 11.0, 2.0 Hz), 5.53 (1H, dd, J = 17.5, 2.2 Hz), 5.37 (1H, dd, J = 11.0, 2.2 Hz), 3.79–3.71

(2H, m), 2.42 (2H, td, J = 7.0, 2.0 Hz), 1.82–1.72 (2H, m), 1.55 (1H, br s). Spectral data match those previously reported.[22]



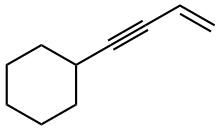
1s

hept-6-en-4-yn-1-yl 4-methylbenzenesulfonate (1s): Prepared from **1r** by the following procedure. To an oven-dried 50-mL round-bottom flask equipped with a magnetic stirring rod was added **1r** (551 mg, 5.00 mmol, 1.00 equiv), pyridine (1.60 mL, 19.9 mmol, 3.97 equiv), and CH_2Cl_2 (5.0 mL). The solution was allowed to cool to 0 °C and then *p*-toluenesulfonyl chloride (1.43 g, 7.50 mmol, 1.50 equiv) was added portionwise over 10 min. The reaction mixture was allowed to stir at 0 °C for 1 h and then partitioned between H_2O (50 mL) and Et_2O (50 mL). The aqueous layer was separated from the organics and washed with Et_2O (20 mL). The combined organic fractions were dried over $MgSO_4$, filtered and concentrated. **1s** (1.14 g, 4.30 mmol, 86.0% yield) was obtained as a pale yellow oil after flash silica gel chromatography (90:10 hexanes:EtOAc). **IR** (neat, cm^{-1}) 2960 (w), 2227 (w), 1598 (m), 1495 (w), 1433 (w), 1357 (s), 1307 (w), 1291 (w), 1188 (m), 1173 (s), 1120 (w), 1096 (m), 973 (m), 921 (s); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81–7.75 (2H, m), 7.32 (2H, d, J = 8.3 Hz), 5.65 (1H, ddt, J = 17.5, 11.0, 2.0 Hz), 5.46 (1H, dd, J = 17.5, 2.2 Hz), 5.35 (1H, dd, J = 11.0, 2.2 Hz), 4.12 (2H, t, J = 6.1 Hz), 2.42 (3H, s), 2.35 (2H, td, J = 6.9, 2.0 Hz), 1.84 (2H, dt, J = 6.4, 6.4 Hz); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 144.8, 132.8, 129.9, 127.9, 126.0, 117.2, 88.4, 80.3, 68.9, 27.8, 21.6, 15.5; **HRMS** (ESI^+) $[M+H]^+$ calc'd for: $C_{14}H_{16}O_3S$: 265.0893, found: 265.0896.



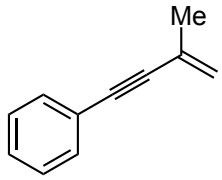
1t

but-3-en-1-yn-1-yl(*tert*-butyl)dimethylsilane (1t): Prepared by General Method A in 84.0% yield after flash silica gel chromatography (100% pentanes). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.80 (1H, dd, J = 17.6, 11.1 Hz), 5.67 (1H, dd, J = 17.6, 2.4 Hz), 5.48 (1H, dd, J = 11.1, 2.4 Hz), 0.93 (9H, s), 0.11 (6H, s). Spectral data match those previously reported.[17]



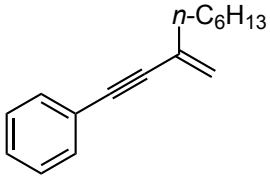
1u

but-3-en-1-yn-1-ylcyclohexane (1u): Prepared by General Method A in 82.7% yield after flash silica gel chromatography (99:1 pentanes:Et_2O). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.78 (1H, ddd, J = 17.5, 11.0, 1.9 Hz), 5.52 (1H, dd, J = 17.5, 2.2 Hz), 5.35 (1H, dd, J = 11.0, 2.2 Hz), 2.88–2.52 (1H, m), 1.98–0.97 (10H, m). Spectral data match those previously reported.[17]



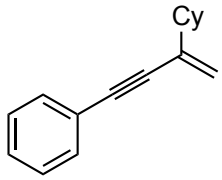
5a

(3-methylbut-3-en-1-yn-1-yl)benzene (5a): Prepared by General Method A in 91.3% yield after flash silica gel chromatography (99:1 hexanes:EtOAc) using 2-bromopropene (2.5 equiv) in place of vinyl bromide. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47–7.40 (2H, m), 7.34–7.27 (3H, m), 5.41–5.37 (1H, m), 5.31–5.27 (1H, m), 2.00–1.98 (3H, m). Spectral data match those previously reported.[23]



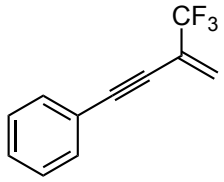
5b

(3-methylenenon-1-yn-1-yl)benzene (5b): Prepared by General Method A in 40.8% yield after flash silica gel chromatography (99:1 hexanes:EtOAc) using 2-bromooct-1-ene (2.5 equiv) in place of vinyl bromide. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.50–745 (2H, m), 7.36–7.29 (3H, m), 5.44 (1H, ABq, J = 1.9 Hz), 5.32 (1H, ABq, J = 1.9 Hz), 2.27 (2H, t, J = 7.6 Hz), 1.68–1.57 (2H, m), 1.43–1.28 (6H, m), 0.94 (3H, t, J = 6.9 Hz). Spectral data match those previously reported.[24]



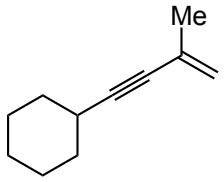
5c

(3-cyclohexylbut-3-en-1-yn-1-yl)benzene (5c): Prepared by General Method A in 83.2% yield after flash silica gel chromatography (99:1 hexanes:EtOAc) using (1-bromovinyl)cyclohexane (2.5 equiv) in place of vinyl bromide. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54–7.46 (2H, m), 7.39–7.30 (3H, m), 5.43 (1H, s), 5.34 (1H, s), 2.18 (1H, t, J = 10.9 Hz), 2.00–1.68 (4H, m), 1.49–1.15 (6H, m). Spectral data match those previously reported.[25]



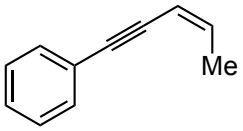
5d

(3-(trifluoromethyl)but-3-en-1-yn-1-yl)benzene (5d): Prepared by General Method A in 88.0% yield after flash silica gel chromatography (99:1 hexanes:EtOAc) using 2-bromo-3,3,3-trifluoroprop-1-ene (2.5 equiv) in place of vinyl bromide. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.46–7.35 (2H, m), 7.30–7.20 (3H, m), 6.00 (1H, s), 5.84 (1H, s). Spectral data match those previously reported.[26]



5e

(3-methylbut-3-en-1-yn-1-yl)cyclohexane (5e): Prepared by General Method A in 49.8% yield after flash silica gel chromatography (99:1 hexanes:EtOAc) using 2-bromopropene (2.5 equiv) in place of vinyl bromide. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.20–5.16 (1H, m), 5.13–5.09 (1H, m), 2.49–2.37 (1H, m), 1.85 (3H, s), 1.81–1.62 (4H, m), 1.56–1.36 (4H, m), 1.33–1.21 (2H, m). Spectral data match those previously reported.[27]



7

(*Z*)-pent-3-en-1-yn-1-ylbenzene (7): Prepared by General Method A in 91.1% yield after flash silica gel chromatography (99:1 pentane:Et_2O) using (*Z*)-1-bromo-1-propene (2.5 equiv) in place of vinyl bromide. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49–7.41 (2H, m), 7.35–7.27 (3H, m), 6.04 (1H, dq, J = 10.7, 6.8 Hz), 5.70 (1H, dq, J = 10.7, 1.6 Hz), 1.96 (3H, dd, J = 6.8, 1.6 Hz). Spectral data match those previously reported.[28]

VI. Substrate Scope

General Method B (non-enantioselective method): In an N_2-filled glovebox, to a 2-dram vial equipped with a magnetic stirring rod were added successively: **Pd-1** catalyst (8.6 mg, 0.01 mmol, 5 mol %), CH_2Cl_2 (0.25 mL), appropriate enyne (0.240 mmol, 1.20 equiv), and lastly appropriate amine nucleophile (0.200 mmol, 1.00 equiv). The reaction vials were then capped with a PTFE lined cap and allowed to stir at ambient temperature for the specified amount of time. The reaction contents were then diluted with 1:1 hexanes:EtOAc (1 mL) and passed through a short plug of either silica gel or neutral alumina, eluting with 1:1 hexanes:EtOAc (*ca.* 20 mL, in some cases 2% Et_3N was added to the eluent). The solution was then concentrated. The pure products were obtained by flash silica gel chromatography as described for each compound.

General Method C (*in situ* non-enantioselective method): In an N_2-filled glovebox, to a 2-dram vial equipped with a magnetic stirring rod were added successively: (1.8 mg, 5.0 μmol, 2.5 mol %), DPEphos (5.4 mg, 0.010 mmol, 5.0 mol %), and $NaBAr_4^F$ (10.6 mg, 0.012 mmol, 6.0 mol %). This mixture was dissolved in CH_2Cl_2 (0.25 mL) and then appropriate enyne (0.240 mmol, 1.20 equiv) was added followed by appropriate amine nucleophile (0.200 mmol, 1.00 equiv). The reaction vials were then capped with a PTFE lined cap and were allowed to stir at ambient temperature for the specified amount of time. The reactions were worked up and purified as described for General Method B.

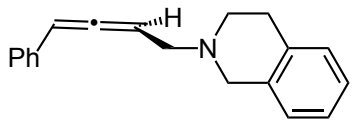
General Method D (enantioselective method for enyne scope): In an N_2-filled glovebox, to a 2-dram vial equipped with a magnetic stirring rod were added successively: $[Pd(\eta^3\text{-allyl})Cl]_2$ (1.8 mg, 5.0 μmol, 2.5 mol %), **L3** (6.8 mg, 0.010 mmol, 5.0 mol %), and $NaBAr_4^F$ (10.6 mg, 0.012 mmol, 6.0 mol %). The mixture was dissolved in CH_2Cl_2 (0.25 mL) and allowed to stir for *ca.* 5 min, resulting in a deep orange/red solution, and then appropriate enyne (0.240 mmol, 1.20 equiv) was added. The reaction vials were then capped with a PTFE lined cap, removed from the glovebox, and allowed to cool in an ice water bath at 0–4 °C for *ca.* 15 minutes before Et_3N (56.0 μL, 0.400 mmol, 2.00 equiv) and THIQ (25.0 μL, 0.200 mmol, 1.00 equiv) were added. The reactions were allowed to stir at 4 °C for 20 h and then worked up and purified as described for General Method B.

General Method E (enantioselecitve method for amine scope):
Catalyst stock solution: In an N_2-filled glovebox, to a 2-dram vial equipped with a magnetic stirring rod were added successively: $[Pd(\eta^3\text{-allyl})Cl]_2$ (7.3 mg, 0.020 mmol, 1.0 mol %), **L3** (27.0 mg, 0.040 mmol, 2.0 mol %), and $NaBAr_4^F$ (44.3 mg, 0.050 mmol, 2.5 mol %). The mixture was dissolved in Et_2O (2.50 mL) and allowed to stir for *ca.* 5 min, resulting in a deep orange solution.

To a 2-dram vial equipped with a magnetic stirring rod was added 0.50 mL of the above catalyst stock solution and then enyne **2a** (65.0 μL, 0.480 mmol, 1.20 equiv). The reaction vial was then capped with a PTFE lined cap, removed from the glovebox, and allowed to cool in an ice water bath at 0–4 °C for *ca.* 15 minutes before Et_3N (112 μL, 0.800 mmol, 2.00 equiv) and appropriate amine nucleophile (0.400 mmol, 1.00 equiv) were added. The reaction mixtures were maintained at 4 °C for 3–5 h and then worked up and purified as described for General Method B.

Important Notes About Substrate Scope:

- 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. In all cases the remainder of the mass balance is unreacted starting material and, unless otherwise noted, evidence of other competing side reactions was not observed.
- Some samples may contain ≤5% of the allylated starting amine (e.g. THIQ) that is generated upon pre-catalyst activation and which could not be separated from the desired product. Samples that contain this minor impurity are indicated with an asterisk (*) where the yields are reported.
- It was found early on that many of the products produced in this research exhibit only moderate stability if stored neat at ambient temperature. In most cases, products can be stored for up to 48 h at ambient temperature without detectable decomposition. It is advised that the allene products be stored in a –20 °C freezer, where they are generally stable for weeks. To avoid problems associated with decomposition and racemization, all products were purified immediately after workup and were analyzed by ^{1}H NMR and HPLC immediately after purification.



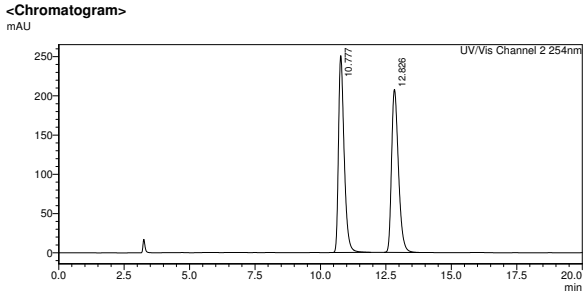
2a

2-(4-phenylbuta-2,3-dien-1-yl)-1,2,3,4-tetrahydroisoquinoline (2a): Prepared by General Method B using **Pd-1** at 22 ˚C for 3 h. The material was purified by flash silica gel chromatography (75:25 hexanes:EtOAc) to yield **2a** as a pale yellow oil (46.1 mg, 0.176 mmol, 88.2 % yield). **IR** (neat, cm^{-1}) 3026 (w), 2914 (w), 2787 (m), 2746 (w), 1947 (m), 1650 (w), 1597 (w), 1494 (m), 1456 (m), 1427 (w), 1360 (w), 1314 (w), 1277 (w), 1264 (w), 1232 (w), 1130 (m), 1089 (m); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36–7.30 (4H, m), 7.24–7.20 (1H, m), 7.15–7.09 (3H, m), 7.06–7.01 (1H, m), 6.24 (1H, dt, J = 6.4, 2.5 Hz), 5.71 (1H, ddd, J = 6.7, 6.7, 6.7 Hz), 3.79 (1H, AB_q, J_{AB} = 15.0 Hz), 3.73 (1H, AB_q, J_{AB} = 15.0 Hz), 3.36 (2H, dd, J = 7.2, 2.4 Hz), 2.98–2.91 (2H, m), 2.89–2.83 (2H, m); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 206.3, 134.7, 134.3, 134.2, 128.7, 128.7, 127.0, 126.8, 126.6, 126.2, 125.6, 94.9, 91.7, 57.2, 55.6, 50.4, 29.1; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{19}H_{19}N$: 262.1590, found: 262.1591.

Scaled Up Reaction: To an oven-dried 25-mL round-bottom flask equipped with a magnetic stirring rod was added $[Pd(\eta^3\text{-allyl})Cl]_2$ (18.3 mg, 0.0500 mmol, 1.00 mol %), DPEphos (53.9 mg, 0.100 mmol, 2.00 mol %), and $NaBAr_4^F$ (102 mg, 0.115 mmol, 2.30 mol %). This mixture was dissolved in CH_2Cl_2 (6.25 mL) which was then allowed to stir an ambient temperature for *ca.* 5 min. To this solution was added enyne **1a** (811 μL, 6.00 mmol, 1.20 equiv) and then 1,2,3,4-tetrahydroisoquinoline (634 μL, 5.00 mmol, 1.00 equiv). The reaction mixture was allowed to stir at ambient temperature for 3 h and then concentrated. The concentrated material was purified by flash silica gel chromatography (75:25 hexanes:EtOAc) to afford **2a** as a pale yellow oil (1.21 g, 4.61 mmol, 92.2% yield).

By General Method D: (*R*)-**2a** was isolated as a pale yellow oil (32.8 mg, 0.125 mmol, 62.7% yield). HPLC analysis indicated er = 92.5:7.5. $[\alpha]_D^{24}$ = –161.0 (c = 1.0, $CHCl_3$) for a sample of 92.5:7.5 er.

HPLC: Column: Cellulose-3 (3 μm, 4.6 mm X 250 mm). Mobile phase: 90:10 hexanes:*i*-PrOH, 1 mL/min. Detection wavelength: 254 nm. Er = 92.5:7.5.



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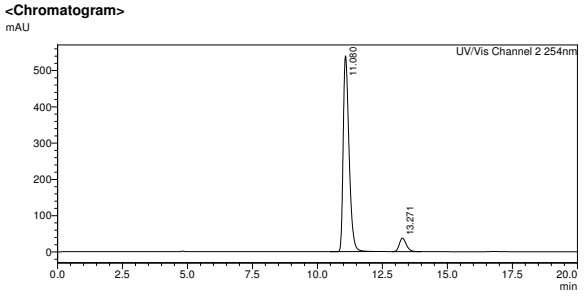

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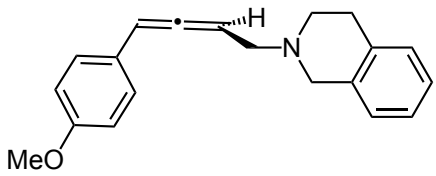
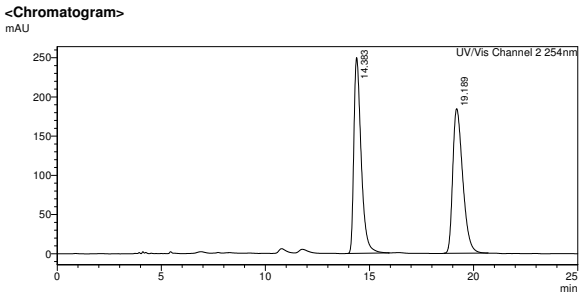


2b

2-(4-(4-methoxyphenyl)buta-2,3-dien-1-yl)-1,2,3,4-tetrahydroisoquinoline (2b): Prepared by General Method B using **Pd-1** at 22 ˚C for 3 h. The material was purified by flash silica gel chromatography (75:25 hexanes:EtOAc) to yield **2b** as a yellow oil (49.8 mg, 0.171 mmol, 85.4% yield). **IR** (neat, cm^{-1}) 3003 (w), 2916 (m), 2832 (w), 2786 (m), 2748 (w), 1946 (w), 1650 (w), 1605 (s), 1580 (w), 1509 (s), 1462 (m), 1439 (m), 1385 (w), 1358 (w), 1336 (w), 1301 (m), 1282 (w), 1241 (s), 1169 (s), 1130 (s), 1082 (m), 1060 (w), 1032 (s); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29–7.20 (2H, m), 7.17–7.08 (3H, m), 7.06–6.99 (1H, m), 6.90–6.84 (2H, m), 6.19 (1H, dt, J = 6.4, 2.3 Hz), 5.67 (1H, ddd, J = 6.8, 6.8, 6.8 Hz), 3.80 (3H, s), 3.77 (1H, AB_q, J_{AB} = 14.8 Hz), 3.71 (1H, AB_q, J_{AB} = 14.8 Hz), 3.34 (2H, dd, J = 7.2, 2.4 Hz), 2.98–2.89 (2H, m), 2.88–2.80 (2H, m); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 205.8, 158.8, 134.6, 134.2, 128.7, 127.9, 126.6, 126.5, 126.2, 125.6, 114.2, 94.3, 91.5, 57.5, 55.6, 55.3, 50.3, 29.1; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{20}H_{21}NO$: 292.1696, found: 292.1698.

By General Method D: (*R*)-**2b** was isolated as a pale yellow oil (37.0 mg, 0.127 mmol, 63.5% yield). HPLC analysis indicated er = 91:9. $[\alpha]_D^{25}$ = –116.3 (c = 1.0, $CHCl_3$) for a sample of 91:9 er.

HPLC: Column: Cellulose-3 (3 μm, 4.6 mm X 250 mm). Mobile phase: 70:30 hexanes:*i*-PrOH, 1 mL/min. Detection wavelength: 254 nm. Er = 91:9.



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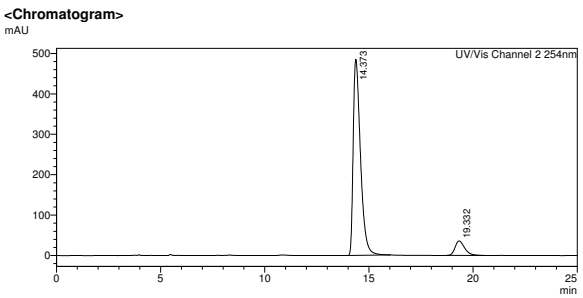

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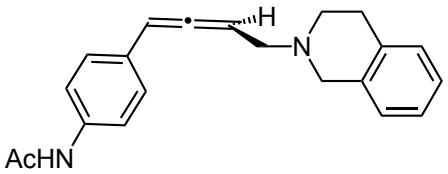
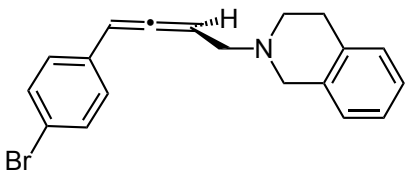


2c (racemic)

***N*-(4-(4-(3,4-dihydroisoquinolin-2(1*H*)-yl)buta-1,2-dien-1-yl)phenyl)acetamide** (**2c**): Prepared by General Method B using **Pd-1** at 22 ˚C for 3 h. The material was purified by flash silica gel chromatography (75:25 hexanes:EtOAc) to yield **2c** as a yellow semisolid (45.5 mg, 0.143 mmol, 71.5% yield). **IR** (neat, cm^{-1}) 3257 (m), 3023 (m), 2918 (m), 2801 (m), 2244 (w), 1947 (w), 1664 (s), 1599 (s), 1532 (s), 1511 (s), 1427 (m), 1368 (m), 1313 (s), 1262 (m), 1195 (w), 1176 (w), 1129 (w), 1088 (w), 1036 (w), 1007 (w); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (1H, br s), 7.49–7.42 (2H, m), 7.26–7.19 (2H, m), 7.15–7.06 (3H, m) 7.04–6.98 (1H, m), 6.17 (1H, dt, J = 6.4, 2.5 Hz), 5.67 (1H, ddd, J = 6.7, 6.7, 6.7 Hz), 3.74 (1H, AB_q, J_{AB} = 15.2 Hz), 3.70 (1H, AB_q, J_{AB} = 15.2 Hz), 3.32 (2H, dd, J = 7.1, 2.1 Hz), 2.96–2.87 (2H, m), 2.86–2.78 (2H, m), 2.13 (3H, s); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 206.2, 168.5, 136.9, 134.6, 134.1, 130.2, 128.7, 127.3, 126.6, 126.2, 125.7, 120.2, 94.4, 91.7, 57.2, 55.6, 50.3, 29.1, 24.6; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{21}H_{22}N_2O$: 319.1805, found: 319.1807.

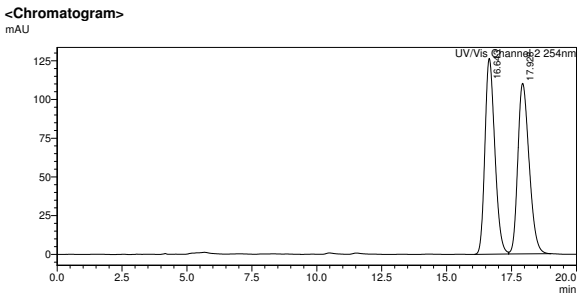


2d

2-(4-(4-bromophenyl)buta-2,3-dien-1-yl)-1,2,3,4-tetrahydroisoquinoline (2d): Prepared by General Method B using **Pd-1** at 22 ˚C for 3 h. The material was purified by flash silica gel chromatography (75:25 hexanes:EtOAc) to yield **2d** as a yellow solid (59.4 mg, 0.175 mmol, 87.3% yield). **IR** (neat, cm^{-1}) 3019 (w), 2924 (m), 2789 (m), 2743 (m), 1946 (m), 1907 (w), 1583 (w), 1485 (s), 1452 (m), 1426 (m), 1377 (w), 1359 (m), 1330 (m), 1308 (m), 1226 (w), 1192 (w), 1129 (m), 1089 (s), 1037 (s), 1007 (s), 932 (m); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46–7.40 (2H, m), 7.20–7.14 (2H, m), 7.14–7.07 (3H, m), 7.04–6.99 (1H, m), 6.16 (1H, dt, J = 6.4, 2.4 Hz), 5.68 (1H, ddd, J 6.9, 6.9, 6.9 Hz), 3.74 (1H, AB_q, J_{AB} = 15.8 Hz), 3.70 (1H, AB_q, J_{AB} = 15.8 Hz), 3.38–3.29 (2H, m), 2.97–2.89 (2H, m), 2.85–2.79 (2H, m); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 206.3, 134.6, 134.1, 133.4, 131.8, 128.8, 128.3, 126.6, 126.2, 125.7, 120.6, 94.1, 92.2, 57.0, 55.6, 50.4, 29.1; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{19}H_{18}NBr$: 340.0695, found: 340.0704; **MP** = 66–69 °C.

By General Method D: (*R*)-**2d** was isolated as a yellow solid (35.3 mg, 0.104 mmol, 51.9% yield). HPLC analysis indicated er = 94.5:5.5. $[\alpha]_D^{27}$ = –182.3 (*c* = 1.0, $CHCl_3$) for a sample of 94.5:5.5 er.

HPLC: Column: Cellulose-3 (3 μm, 4.6 mm X 250 mm). Mobile phase: 80:20 hexanes:*i*-PrOH, 1 mL/min. Detection wavelength: 254 nm. Er = 94.5:5.5.



<Peak Table>
UV/Vis Channel 2 254nm

Peak#	Ret. Time	Area	Area%
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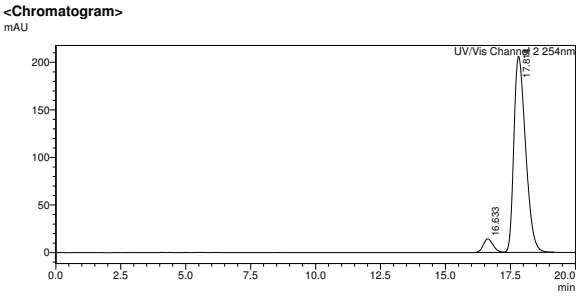
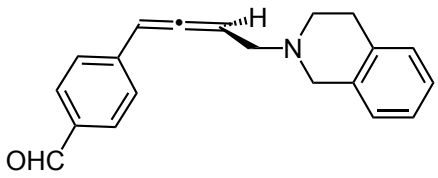
2	17.928	3341091	49.915
Total		6693531	100.000



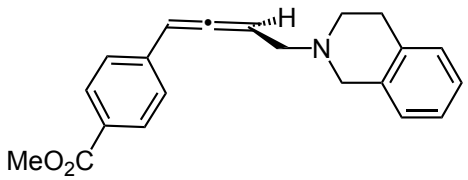
<Peak Table>
UV/Vis Channel 2 254nm

Peak#	Ret. Time	Area	Area%
1	16.633	372619	5.452
2	17.814	6462173	94.548
Total		6834793	100.000



2e (racemic)

4-(4-(3,4-dihydroisoquinolin-2(1*H*)-yl)buta-1,2-dien-1-yl)benzaldehyde (2e): Prepared by General Method B using **Pd-1** at 22 ˚C for 3 h. The material was purified by flash silica gel chromatography (70:30 hexanes:EtOAc) to yield **2e** as a yellow oil (38.9 mg, 0.134 mmol, 67.2% yield). **IR** (neat, cm^{-1}) 3021 (w), 2917 (w), 2801 (m), 2744 (w), 1945 (m), 1690 (s), 1600 (s), 1570 (w), 1497 (w), 1428 (w), 1384 (w), 1334 (w), 1303 (m), 1210 (m), 1163 (m), 1130 (w), 1091 (m), 1056 (w), 1038 (w), 1013 (w); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.96 (1H, s), 7.86–7.79 (2H, m), 7.48–7.41 (2H, m), 7.17–7.06 (3H, m), 7.04–6.98 (1H, m), 6.28 (1H, dt, J = 6.4, 2.4 Hz), 5.77 (1H, ddd, J = 6.7, 6.7, 6.7 Hz), 3.75 (1H, AB_q, J_{AB} = 15.1 Hz), 3.73 (1H, AB_q, J_{AB} = 15.1 Hz), 3.43–3.33 (2H, m), 2.97–2.89 (2H, m), 2.87–2.79 (2H, m); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 207.6, 191.6, 141.1, 135.0, 134.4, 134.0, 130.1, 128.7, 127.2, 126.6, 126.3, 125.7, 94.6, 92.2, 56.7, 55.5, 50.3, 29.0; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{20}H_{19}NO$: 290.1539, found: 290.1540.

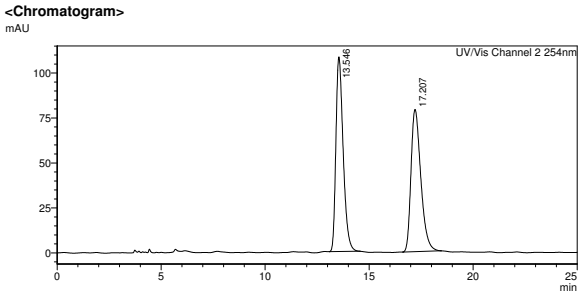


2f

methyl 4-(4-(3,4-dihydroisoquinolin-2(1*H*)-yl)buta-1,2-dien-1-yl)benzoate (2f): Prepared by General Method B using **Pd-1** at 22 ˚C for 3 h. The material was purified by flash silica gel chromatography (70:30 hexanes:EtOAc) to yield **2f** as a pale yellow oil (55.0 mg, 0.172 mmol, 86.1 % yield). **IR** (neat, cm^{-1}) 3026 (w), 2912 (w), 2806 (w), 1952 (w), 1713 (s), 1605 (m), 1497 (w), 1435 (m), 1362 (w), 1331 (w), 1276 (s), 1235 (w), 1192 (w), 1177 (m), 1109 (m), 1091 (m), 1014 (w), 1039 (w); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02–7.96 (2H, m), 7.39–7.32 (2H, m), 7.17–7.05 (3H, m), 7.04–6.98 (1H, m), 6.25 (1H, dt, J = 6.4, 2.3 Hz), 5.74 (1H, ddd, J = 6.7, 6.7, 6.7 Hz), 3.90 (3H, s), 3.76 (1H, AB_q, J_{AB} = 14.9 Hz), 3.70 (1H, AB_q, J_{AB} =14.9 Hz), 3.36 (2H, dt, J = 7.1, 2.0 Hz), 2.97–2.88 (2H, m), 2.87–2.77 (2H, m); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 207.2, 166.9, 139.4, 134.5, 134.0, 130.0, 128.7, 128.5, 126.6, 126.2, 125.7, 94.5, 92.1, 56.8, 55.5, 52.1, 50.3, 29.1 (note: one sp^2 carbon could not be identified due to overlap); **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{21}H_{21}NO_2$: 320.1645, found: 320.1645.

By General Method D: (*R*)-**2f** was isolated as a pale yellow oil (38.1 mg, 0.119 mmol, 59.6% yield). HPLC analysis standard indicated er = 95.5:4.5. $[\alpha]_D^{24}$ = –158.7 (c = 1.0, $CHCl_3$) for a sample of 94.5:5.5 er.

HPLC: Column: Cellulose-3 (3 μm, 4.6 mm X 250 mm). Mobile phase: 70:30 hexanes:*i*-PrOH, 1 mL/min. Detection wavelength: 254 nm. Er = 94.5:5.5.



<Peak Table>
UV/Vis Channel 2 254nm

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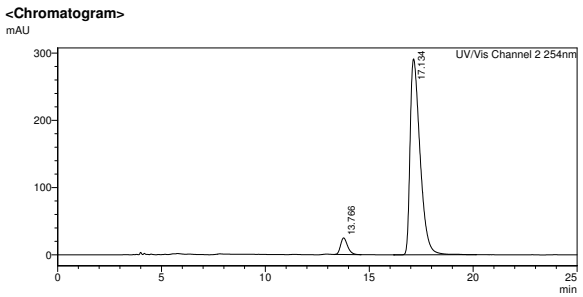
Total		5222734	100.000



<Peak Table>
UV/Vis Channel 2 254nm

Peak#	Ret. Time	Area	Area%
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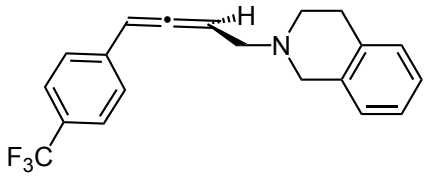
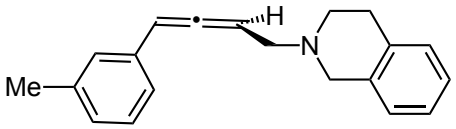
2	17.134	9706133	94.348
Total		10287548	100.000



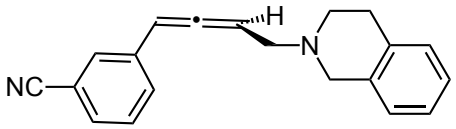
2g (racemic)

2-(4-(4-(trifluoromethyl)phenyl)buta-2,3-dien-1-yl)-1,2,3,4-tetrahydroisoquinoline (2g): Prepared by General Method B using **Pd-1** at 22 ˚C for 3 h. The material was purified by flash silica gel chromatography (80:20 hexanes:EtOAc) to yield **2g** as a yellow solid (58.7 mg, 0.178 mmol, 89.1 % yield). **IR** (neat, cm^{-1}) 3023 (w), 2925 (w), 2814 (w), 1951 (m), 1611 (m), 1581 (w), 1497 (w), 1464 (w), 1450 (w), 1438 (w), 1359 (w), 1322 (s), 1157 (s), 1113 (s), 1087 (m), 1063 (s), 1028 (w), 1014 (m); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (2H, d J = 8.2 Hz), 7.40 (2H, d, J = 8.2 Hz), 7.18–7.08 (3H, m), 7.06–6.99 (1H, m), 6.26 (1H, dt, J = 6.4, 2.3 Hz), 5.76 (1H, ddd, J = 6.8, 6.8, 6.8 Hz), 3.76 (1H, AB_q, J_{AB} = 15.7 Hz), 3.73 (1H, AB_q, J_{AB} = 15.7 Hz), 3.41–3.32 (2H, m), 2.99–2.90 (2H, m), 2.88–2.81 (2H, m); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 207.0, 138.3, 134.4, 134.0, 128.9 (q, J_{CF} = 32.0 Hz), 128.7, 126.9, 126.6 (q, J_{CF} = 3.2 Hz), 125.7, 125.6, 125.6, 124.2 (q, J_{CF} = 270.2 Hz), 94.1, 92.2, 56.8, 55.6, 50.3, 29.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ –62.4; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{20}H_{18}F_3N$: 330.1464, found: 330.1460; **MP** = 73–75 °C.



2h (racemic)

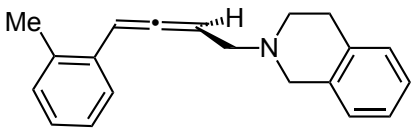
2-(4-(*m*-tolyl)buta-2,3-dien-1-yl)-1,2,3,4-tetrahydroisoquinoline (2h): Prepared by General Method B using **Pd-1** at 22 ˚C for 3 h. The material was purified by flash silica gel chromatography (75:25 hexanes:EtOAc) to yield **2h** as a pale yellow oil (48.2 mg, 0.175 mmol, 87.5% yield). **IR** (neat, cm^{-1}) 3021 (w), 2915 (m), 2792 (m), 2746 (w), 1947 (m), 1584 (m), 1603 (w), 1488 (m), 1453 (m), 1380 (w), 1359 (w), 1332 (m), 1306 (w), 1276 (w), 1232 (w), 1130 (m), 1091 (m), 1056 (w), 1038 (w); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26–7.20 (1H, m), 7.18–7.10 (5H, m), 7.07–7.02 (2H, m), 6.21 (1H, dt, J = 6.4, 2.3 Hz), 5.70 (1H, ddd, J = 7.0, 7.0, 7.0 Hz), 3.80 (1H, AB_q, J_{AB} = 14.8 Hz), 3.73 (1H, AB_q, J_{AB} = 14.8 Hz), 3.36 (2H, dd, J = 7.2, 2.4 Hz), 2.99–2.92 (2H, m), 2.90–2.83 (2H, m), 2.36 (3H, s); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 206.4, 138.2, 134.6, 134.2, 134.1, 128.7, 128.6, 127.8, 127.5, 126.6, 126.2, 125.7, 124.0, 94.8, 91.4, 57.2, 55.5, 50.3, 29.1, 21.4; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{20}H_{21}N$: 276.1747, found: 276.1749.



2i (racemic)

3-(4-(3,4-dihydroisoquinolin-2(1*H*)-yl)buta-1,2-dien-1-yl)benzonitrile (2i): Prepared by General Method B using **Pd-1** at 22 ˚C for 3 h. The material was purified by flash silica gel chromatography (65:35 hexanes:EtOAc) to yield **2i** as a pale yellow oil (53.8 mg, 0.188 mmol, 93.9% yield).* **IR** (neat, cm^{-1}) 3021 (w), 2917 (m), 2796 (m), 2229 (m), 1948 (m), 1597 (w), 1578

(w), 1497 (w), 1481 (m), 1463 (m), 1453 (m), 1434 (m), 1381 (w), 1359 (w), 1332 (m), 1305 (w), 1277 (w), 1226 (w), 1192 (w), 1130 (m), 1092 (m), 1056 (w); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (1H, s), 7.53–7.44 (2H, m), 7.40 (1H, dd J = 7.7, 7.7 Hz), 7.18–7.06 (3H, m), 7.05–6.99 (1H, m), 6.20 (1H, dt, J = 6.4, 2.4 Hz), 5.77 (1H, ddd, J = 6.9, 6.9, 6.9 Hz), 3.75 (1H, AB_q, J_{AB} = 15.2 Hz), 3.71 (1H, AB_q, J_{AB} =15.2 Hz), 3.42–3.30 (2H, m), 2.97–2.88 (2H, m), 2.86–2.78 (2H, m); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 206.6, 136.0, 134.4, 134.0, 130.9, 130.3, 130.1, 129.4, 128.7, 126.6, 126.2, 125.7, 118.7, 112.8, 93.5, 92.9, 56.8, 55.6, 50.4, 29.1; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{20}H_{18}N_2$: 287.1543, found: 287.1544.

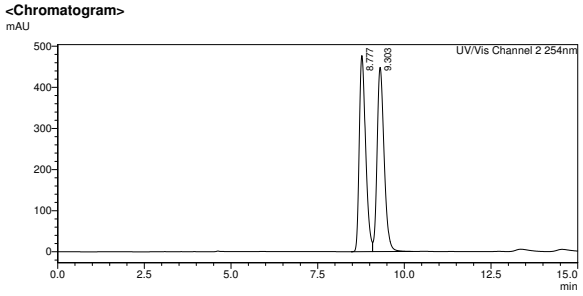


2j

2-(4-(*o*-tolyl)buta-2,3-dien-1-yl)-1,2,3,4-tetrahydroisoquinoline (2j): Prepared by General Method B using **Pd-1** at 22 ˚C for 3 h. The material was purified by flash silica gel chromatography (75:25 hexanes:EtOAc) to yield **2j** as a pale yellow oil (43.0 mg, 0.156 mmol, 78.1% yield). **IR** (neat, cm^{-1}) 3021 (w), 2915 (m), 2786 (m), 2746 (w), 1945 (m), 1655 (w), 1600 (w), 1491 (m), 1462 (m), 1381 (w), 1358 (w), 1334 (m), 1302 (w), 1276 (w), 1192 (w), 1127 (m), 1095 (m), 1037 (w); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (1H, d, J = 7.6 Hz), 7.22–7.09 (6H, m), 7.06–7.01 (1H, m), 6.43 (1H, dt, J = 6.4, 2.4 Hz), 5.67 (1H, ddd, J = 7.0, 7.0, 7.0 Hz), 3.77 (1H, AB_q, J_{AB} = 15.0 Hz), 3.72 (1H, AB_q, J_{AB} = 15.0 Hz), 3.36 (2H, dd, J = 7.1, 2.4 Hz), 2.98–2.91 (2H, m), 2.88–2.82 (2H, m), 2.38 (3H, s); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 207.0, 135.0, 134.6, 134.1, 132.5, 130.5, 128.7, 127.3, 126.9, 126.6, 126.2, 126.1, 125.7, 92.1, 90.8, 57.3, 55.6, 50.4, 29.1, 19.9; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{20}H_{21}N$: 276.1747, found: 276.1752.

By General Method D: (*R*)-**2j** was isolated as a pale yellow oil (32.7 mg, 0.119 mmol, 59.4% yield). HPLC analysis indicated er = 86:14. $[\alpha]_D^{27}$ = –102.2 (c = 1.0, $CHCl_3$) for a sample of 86:14 er.

HPLC: Column: Cellulose-3 (3 μm, 4.6 mm X 250 mm). Mobile phase: 90:10 hexanes:*i*-PrOH, 1 mL/min. Detection wavelength: 254 nm. Er = 86:14.



<Peak Table>
UV/Vis Channel 2 254nm

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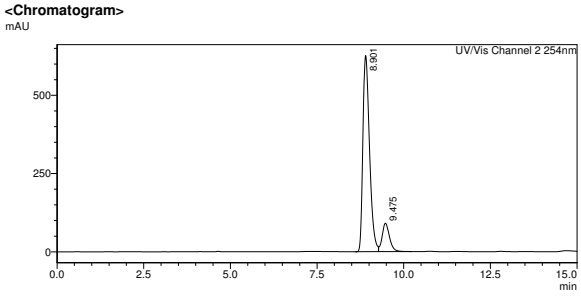
Total		12409012	100.000



<Peak Table>
UV/Vis Channel 2 254nm

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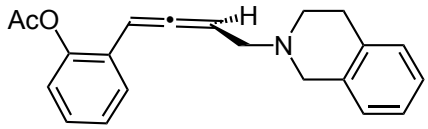
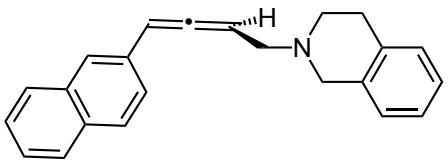
Total		9628578	100.000



2k (racemic)

2-(4-(3,4-dihydroisoquinolin-2(1*H*)-yl)buta-1,2-dien-1-yl)phenyl acetate (2k): Prepared by General Method B using **Pd-1** at 22 ˚C for 3 h. The material was purified by flash silica gel chromatography (75:25 hexanes:EtOAc) to yield **2k** as a pale yellow oil (42.9 mg, 0.134 mmol, 67.2% yield). **IR** (neat, cm^{-1}) 3021 (w), 2917 (m), 2789 (w), 1948 (m), 1762 (s), 1649 (w), 1604 (w), 1580 (w), 1490 (m), 1453 (w), 1367 (m), 1334 (w), 1307 (w), 1277 (w), 1194 (s), 1171 (s), 1131 (m), 1091 (s), 1038 (w), 1008 (m); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50–7.42 (1H, m), 7.29–7.18 (2H, m), 7.16–6.98 (5H, m), 6.28 (1H, dt, J = 6.5, 2.3 Hz), 5.70 (1H, ddd, J = 7.0, 7.0, 7.0 Hz), 3.75 (1H, AB_q, J_{AB} = 15.1 Hz), 3.71 (1H, AB_q, J_{AB} = 15.1 Hz), 3.40–3.29 (2H, m), 2.96–2.89 (2H, m), 2.87–2.78 (2H, m), 2.33 (3H, s); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 207.0, 169.2, 147.5, 134.6, 134.1, 128.7, 128.3, 127.9, 126.6, 126.5, 126.2, 125.6, 122.8, 91.5, 88.7, 57.0, 55.6, 50.4, 29.1, 20.9 (one sp^2 carbon could not be identified due to overlap); **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{21}H_{21}NO_2$: 320.1645, found: 320.1649.

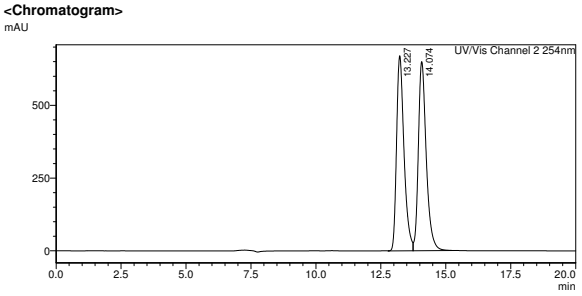


2l

2-(4-(naphthalen-2-yl)buta-2,3-dien-1-yl)-1,2,3,4-tetrahydroisoquinoline (2l): Prepared by General Method B using **Pd-1** at 22 ˚C for 3 h. The material was purified by flash silica gel chromatography (75:25 hexanes:EtOAc) to yield **2l** as a white solid (56.1 mg, 0.180 mmol, 90.1% yield). **IR** (neat, cm^{-1}) 2906 (w), 2808 (w), 1940 (w), 1596 (w), 1496 (w), 1448 (w), 1380 (w), 1356 (w), 1322 (w), 1270 (w), 1126 (w), 1082 (w); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89–7.73 (3H, m), 7.69 (1H, s), 7.58–7.39 (3H, m), 7.21–7.10 (3H, m), 7.10–6.98 (1H, m), 6.43 (1H, dt, J = 6.3, 2.6 Hz), 7.79 (1H, ddd, J = 6.9, 6.9, 6.9 Hz), 3.82 (1H, AB_q, J_{AB} = 14.8 Hz), 3.76 (1H, AB_q, J_{AB} = 14.8 Hz), 3.41 (2H, dt, J = 7.1, 2.1 Hz), 3.01–2.93 (2H, m), 2.92–2.84 (2H, m); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 206.9, 134.7, 134.2, 133.7, 132.7, 131.9, 128.8, 128.3, 127.8, 127.7, 126.7, 126.3, 126.2, 125.7, 125.7, 125.7, 124.7, 95.3, 92.0, 57.3, 55.7, 50.4, 29.2; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{23}H_{21}N$: 312.1747, found: 312.1744; **MP** = 101–104 °C.

By General Method D: (*R*)-**2l** was isolated as a white solid (40.0 mg, 0.128 mmol, 64.2% yield). HPLC analysis indicated er = 93.5:6.5. $[\alpha]_D^{26}$ = –198.8 (*c* = 1.0, $CHCl_3$) for a sample of 93.5:6.5 er.

HPLC: Column: Chiralpak 1A-3 (3 µm, 4.6 mm X 150 mm). Mobile phase: 98:2 *i*-PrOH:MeCN with 0.1% Et_2NH additive, 0.25 mL/min. Detection wavelength: 254 nm. Er = 93.5:6.5.



<Peak Table>
UV/Vis Channel 2 254nm

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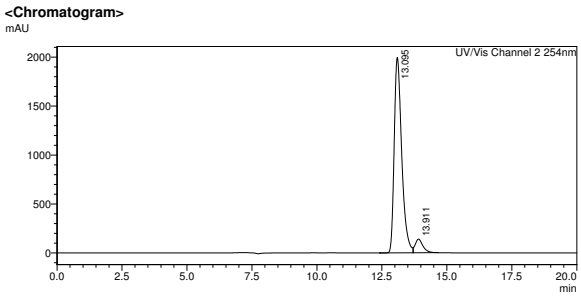

<Peak Table>
UV/Vis Channel 2 254nm

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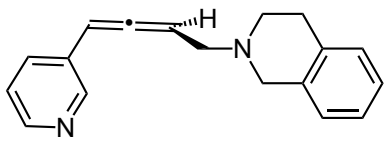
2	13.911	2894673	6.727
Total		43032116	100.000

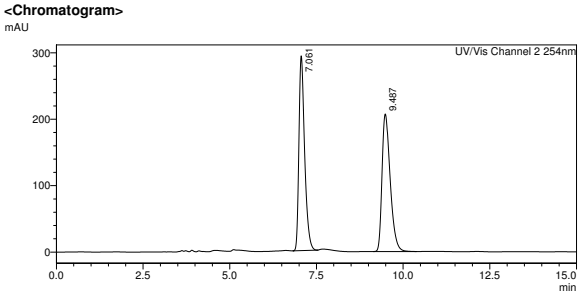


2m

2-(4-(pyridin-3-yl)buta-2,3-dien-1-yl)-1,2,3,4-tetrahydroisoquinoline (2m): Prepared by General Method B using **Pd-1** at 22 ˚C for 3 h. The material was purified by flash silica gel chromatography (70:30 hexanes:EtOAc with an additional 2% Et_3N additive) to yield **2m** as a pale yellow oil (42.3 mg, 0.161 mmol, 80.6% yield).* **IR** (neat, cm^{-1}) 3022 (w), 2917 (m), 2796 (m), 1948 (m), 1643 (w), 1584 (w), 1570 (m), 1497 (w), 1480 (m), 1445 (m), 1427 (m), 1383 (w), 1325 (m), 1232 (w), 1180 (w), 1129 (m), 1093 (m), 1056 (w), 1024 (m); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.52 (1H, d, J = 2.1 Hz), 8.42 (1H, dd, J = 4.8, 1.6 Hz), 7.58 (1H, ddd, J = 7.9, 1.8, 1.8 Hz), 7.25–7.19 (1H, m), 7.14–7.06 (3H, m), 7.03–6.98 (1H, m), 6.19 (1H, dt, J = 6.4, 2.4 Hz), 5.73 (1H, ddd, J = 6.9, 6.9, 6.9 Hz), 3.74 (1H, AB_q, J_{AB} = 15.2 Hz), 3.70 (1H, AB_q, J_{AB} = 15.2 Hz), 3.35 (2H, dd, J = 7.1, 2.4 Hz), 2.95–2.87 (2H, m), 2.86–2.79 (2H, m); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 206.5, 148.2, 148.0, 134.4, 134.0, 133.5, 130.3, 128.7, 126.6, 126.2, 125.7, 123.5, 92.4, 91.7, 56.8, 55.6, 50.3, 29.0; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{18}H_{18}N_2$: 263.1543, found: 263.1545.

By General Method D: (*R*)-**2m** was isolated as a pale yellow oil (16.0 mg, 0.0610 mmol, 30.5% yield). HPLC analysis indicated er = 91:9. $[\alpha]_D^{26}$ = –120.9 (c = 1.0, $CHCl_3$) for a sample of 91:9 er.

HPLC: Column: Cellulose-3 (3 μm, 4.6 mm X 250 mm). Mobile phase: 70:30 hexanes:*i*-PrOH, 1 mL/min. Detection wavelength: 254 nm. Er = 91:9.



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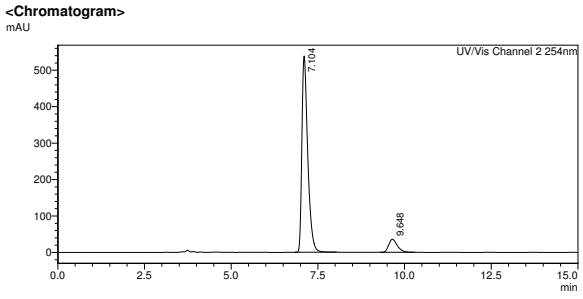

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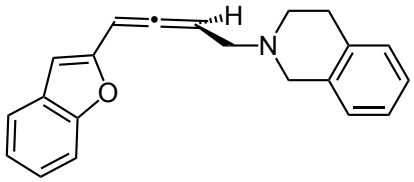
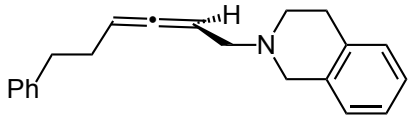


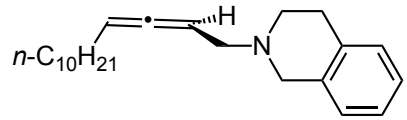
2n (racemic)

2-(4-(benzofuran-2-yl)buta-2,3-dien-1-yl)-1,2,3,4-tetrahydroisoquinoline (2n): Prepared by General Method B using **Pd-1** at 22 ˚C for 15 h. The material was purified by flash silica gel chromatography (75:25 hexanes:EtOAc) to yield **2n** as a pale yellow oil (38.9 mg, 0.129 mmol, 64.5% yield). **IR** (neat, cm^{-1}) 3021 (w), 2916 (m), 2796 (m), 1950 (w), 1679 (w), 1582 (w), 1497 (w), 1453 (m), 1382 (w), 1361 (w), 1279 (w), 1253 (m), 1220 (w), 1164 (w), 1130 (m), 1090 (m), 1007 (w); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53–7.47 (1H, m), 7.44 (1H, d, J = 8.0 Hz), 7.29–7.17 (2H, m), 7.16–7.08 (3H, m), 7.07–6.99 (1H, m), 6.59 (1H, s), 6.30 (1H, dt, J = 6.4, 2.3 Hz), 5.83 (1H, ddd, J = 6.9, 6.9, 6.9 Hz), 3.86 (1H, AB_q, J_{AB} = 14.9 Hz), 3.74 (1H, AB_q, J_{AB} = 14.9 Hz), 3.39 (2H, dd, J = 7.2, 2.4 Hz), 2.99–2.92 (2H, m), 2.92–2.86 (2H, m); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 207.1, 155.0, 150.8, 134.7, 134.2, 129.1, 128.8, 126.7, 126.2, 125.7, 124.1, 122.8, 120.5, 110.9, 104.0, 92.5, 85.9, 57.0, 55.6, 50.4, 29.2; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{21}H_{19}NO$: 302.1539, found: 302.1534.



2o (racemic)

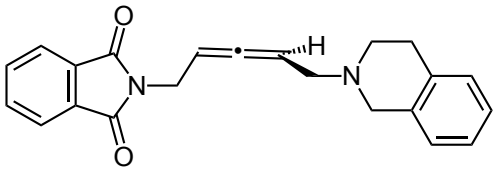
2-(6-phenylhexa-2,3-dien-1-yl)-1,2,3,4-tetrahydroisoquinoline (2o): Prepared by General Method C at 22 ˚C for 3 h. The material was purified by flash silica gel chromatography (80:20 hexanes:EtOAc) to yield **2o** as a pale yellow oil (50.3 mg, 0.174 mmol, 86.9% yield). **IR** (neat, cm^{-1}) 3023 (w), 2916 (m), 2789 (m), 2747 (w), 1961 (m), 1651 (m), 1603 (w), 1583 (w), 1496 (m), 1452 (m), 1385 (w), 1360 (w), 1333 (m), 1232 (w), 1192 (w), 1130 (m), 1091 (m), 1029 (w); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34–7.27 (2H, m), 7.24–7.17 (3H, m), 7.16–7.08 (3H, m), 7.05–7.00 (1H, m), 5.27–5.20 (2H, m), 3.69 (1H, AB_q, J_{AB} = 15.1 Hz), 3.64 (1H, AB_q, J_{AB} = 15.1 Hz), 3.18–3.12 (2H, m), 2.92 (2H, app. t, J = 5.9 Hz), 2.82–2.71 (4H, m), 2.42–2.31 (2H, m); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 205.5, 141.7, 134.7, 134.2, 128.7, 128.6, 128.3, 126.6, 126.1, 125.9, 125.6, 90.5, 88.0, 57.6, 55.5, 50.2, 35.5, 30.5, 29.0; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{21}H_{23}N$: 290.1903, found: 290.1902.



2p (racemic)

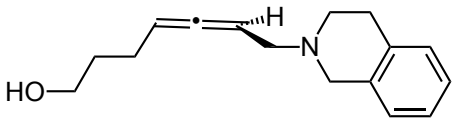
2-(tetradeca-2,3-dien-1-yl)-1,2,3,4-tetrahydroisoquinoline (2p): Prepared by General Method C at 22 ˚C for 3 h. The material was purified by flash silica gel chromatography (85:15 hexanes:EtOAc) to yield **2p** as a pale yellow oil (53.0 mg, 0.163 mmol, 81.4% yield). **IR** (neat, cm^{-1}) 2921 (s), 2851 (s), 2791 (m), 2747 (w), 1961 (w), 1658 (w), 1585 (w), 1498 (w), 1454 (m), 1397 (w), 1360 (w), 1333 (m), 1303 (w), 1232 (w), 1192 (w), 1193 (w), 1092 (m); **^{1}H NMR** (400

MHz, $CDCl_3$) δ 7.16–7.06 (3H, m), 7.05–6.99 (1H, m), 5.25–5.12 (2H, m), 3.71 (1H, AB_q, J_{AB} = 15.1 Hz), 3.66 (1H, AB_q, J_{AB} = 15.1 Hz), 3.19 (2H, dt, J = 6.9, 2.6 Hz), 2.94–2.89 (2H, m), 2.83–2.76 (2H, m), 2.07–1.95 (2H, m), 1.471.15 (16H, m), 0.872 (3H, t, J = 7.0 Hz); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 205.3, 134.7, 134.2, 128.7, 126.6, 126.1, 125.6, 91.3, 87.5, 57.8, 55.5, 50.2, 31.9, 29.7, 29.5, 29.4, 29.2, 29.1, 29.0, 28.7, 22.7, 14.1 (note: one sp^3 carbon could not be identified due to overlap); **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{23}H_{35}N$: 326.2842, found: 326.2841.



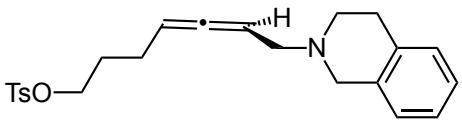
2q (racemic)

2-(5-(3,4-dihydroisoquinolin-2(1*H*)-yl)penta-2,3-dien-1-yl)isoindoline-1,3-dione (2q): Prepared by General Method C at 22 ˚C for 3 h. The material was purified by flash silica gel chromatography (50:50 hexanes:EtOAc) to yield **2q** as a yellow oil (54.4 mg, 0.158 mmol, 79.0% yield).* **IR** (neat, cm^{-1}) 2921 (w), 2792 (w), 1966 (w), 1771 (m), 1709 (s), 1613 (w), 1498 (w), 1466 (w), 1425 (m), 1388 (s), 1315 (s), 1189 (w), 1170 (w), 1129 (w), 1109 (m), 1088 (m), 1007 (w); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85–7.80 (2H, m), 7.71–7.66 (2H, m), 7.13–6.98 (3H, m), 6.92–6.84 (1H, m), 5.37–5.26 (2H, m), 4.34–4.23 (2H, m), 3.56 (1H, AB_q, J_{AB} = 15.5 Hz), 3.52 (1H, AB_q, J_{AB} = 15.5 Hz), 3.23–3.14 (1H, m), 3.12–3.02 (1H, m), 2.80–2.70 (2H, m), 2.61 (2H, app. t, J = 5.9 Hz); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 204.8, 167.7, 134.5, 134.0, 134.0, 132.1, 128.6, 126.6, 126.1, 125.5, 123.3, 91.2, 87.2, 56.9, 55.4, 50.1, 36.6, 29.0; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{22}H_{20}N_2O_2$: 345.1598, found: 345.1600.



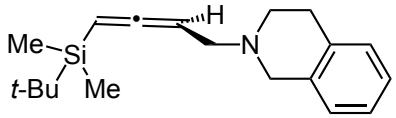
2r (racemic)

7-(3,4-dihydroisoquinolin-2(1*H*)-yl)hepta-4,5-dien-1-ol (2r): Prepared by General Method C at 22 ˚C for 3 h. The material was purified by flash silica gel chromatography (50:50 hexanes:EtOAc to 100% EtOAc) to yield **2r** as a colorless oil (28.5 mg, 0.117 mmol, 58.5% yield). **IR** (neat, cm^{-1}) 3283 (br m), 2917 (m), 2794 (m), 1960 (m), 1584 (w), 1498 (w), 1451 (m), 1385 (w), 1360 (w), 1333 (m), 1304 (m), 1233 (w), 1192 (w), 1130 (m), 1057 (s); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.13–7.06 (3H, m), 7.03–6.98 (1H, m), 5.26–5.13 (2H, m), 3.67 (2H, s), 3.61 (2H, t, J = 6.4 Hz), 3.21–3.11 (2H, m), 2.94–2.86 (2H, m), 2.81–2.73 (2H, m), 2.31 (1H, br s), 2.15–2.02 (2H, m), 1.72–1.57 (2H, m); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 205.4, 134.5, 134.1, 128.7, 126.6, 126.2, 125.6, 90.8, 87.9, 61.8, 57.5, 55.6, 50.4, 31.7, 28.9, 25.0; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{16}H_{21}NO$: 244.1696, found: 244.1694.



2s

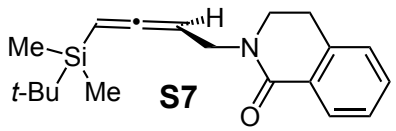
7-(3,4-dihydroisoquinolin-2(1*H*)-yl)hepta-4,5-dien-1-yl 4-methylbenzenesulfonate (2s): Prepared by General Method C at 22 ˚C for 3 h. The material was purified by flash silica gel chromatography (50:50 hexanes:EtOAc) to yield **2s** as a pale yellow oil (59.4 mg, 0.149 mmol, 74.7% yield). **IR** (neat, cm^{-1}) 2918 (w), 2791 (w), 1962 (w), 1650 (w), 1597 (w), 1496 (w), 1449 (m), 1356 (s), 1306 (w), 1232 (w), 1188 (m), 1173 (s), 1095 (m), 1033 (w), 1009 (m), 927 (s); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79–7.74 (2H, m), 7.31 (2H, d, J = 8.3 Hz), 7.13–7.04 (3H, m), 7.02–6.97 (1H, m), 5.26–5.15 (1H, m), 5.13–5.00 (1H, m), 4.06 (2H, t, J = 6.4 Hz), 3.65 (2H, s), 3.15 (2H, dd, J = 7.1, 2.4 Hz), 2.92–2.85 (2H, m), 2.79–2.71 (2H, m), 2.41 (3H, s), 2.10–2.00 (2H, m), 1.82–1.70 (2H, m); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 205.3, 144.7, 134.4, 134.0, 133.1, 129.8, 128.7, 127.9, 126.6, 126.2, 125.6, 89.7, 88.5, 69.7, 57.5, 55.5, 50.2, 28.9, 28.1, 24.3, 21.6; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{23}H_{27}NO_3S$: 398.1784, found: 398.1783.



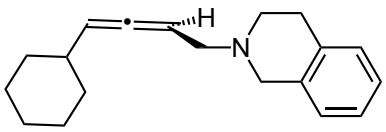
2t (racemic)

(*S*)-2-(4-(*tert*-butyldimethylsilyl)buta-2,3-dien-1-yl)-1,2,3,4-tetrahydroisoquinoline (2t): Prepared by General Method C at 22 ˚C for 15 h. The material was purified by flash silica gel chromatography (100% hexanes to 85:15 hexanes:EtOAc) to afford **2t** (60.6 mg, 0.202 mmol, 50.6% yield) as a yellow oil. **IR** (neat, cm^{-1}) 2950 (m), 2926 (m), 2855 (m), 2803 (w), 1937 (s), 1657 (w), 1498 (w), 1462 (m), 1376 (w), 1360 (m), 1323 (m), 1190 (w), 1129 (w), 1096 (m), 1056 (w), 936 (m); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.16–7.06 (3H, m), 7.04–6.99 (1H, m), 4.97 (1H, dt, J = 6.8, 2.9, Hz), 4.90 (1H, ddd, J = 7.2, 7.2, 7.2 Hz), 3.73 (1H, AB_q, J_{AB} = 15.0 Hz), 3.66 (1H, AB_q, J_{AB} = 15.0 Hz), 3.28–3.17 (2H, m), 2.95–2.87 (2H, m), 2.83–2.74 (2H, m), 0.903 (9H, s), 0.07 (6H, s); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 211.1, 134.5, 134.1, 128.7, 126.6, 126.2, 125.7, 79.8, 79.6, 57.2, 55.3, 50.1, 29.0, 26.3, 17.0, –5.56, –5.65; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{19}H_{29}NSi$: 300.2142, found: 300.2143.

The formation of **2t** was accompanied by the formation of *ca.* 5% of an oxidized side product that could not be separated and which we propose is **S7**. We have not fully characterized this minor side product and so cannot assign its structure with absolute certainty.



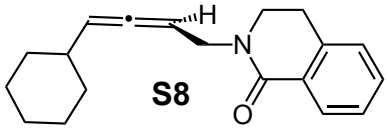
S7



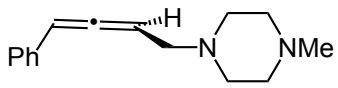
2u (racemic)

2-(4-cyclohexylbuta-2,3-dien-1-yl)-1,2,3,4-tetrahydroisoquinoline (2u): Prepared by General Method C at 22 ˚C for 15 h. The material was purified by flash silica gel chromatography (85:15 hexanes:EtOAc) to afford **2u** (84.6 mg, 0.316 mmol, 79.1% yield) as a yellow oil. **IR** (neat, cm^{-1}) 2920 (s), 2848 (s), 2789 (m), 2746 (w), 1959 (w), 1656 (m), 1605 (w), 1497 (w), 1479 (w), 1447 (s), 1385 (w), 1359 (w), 1329 (m), 1304 (m), 1231 (w), 1192 (w), 1130 (m), 1092 (m); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.15–7.05 (3H, m), 7.04–6.97 (1H, m), 5.23 (1H, ddd, J = 13.5, 7.0, 3.0 Hz), 5.19–5.13 (1H, m), 3.71 (1H, AB_q, J_{AB} = 15.1 Hz), 3.66 (1H, AB_q, J_{AB} = 15.1 Hz), 3.24–3.14 (2H, m), 2.95–2.87 (2H, m), 2.83–2.75 (2H, m), 2.07–1.93 (1H, m), 1.83–1.55 (5H, m), 1.36–1.01 (5H, m); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 204.2, 134.7, 134.2, 128.7, 126.6, 126.1, 125.6, 97.3, 88.5, 58.0, 55.6, 50.2, 37.2, 33.2, 33.1, 29.0, 26.2, 26.0 (note: one extra sp^3 carbon was observed, but this has been noted before with related cyclohexyl-substituted compounds[7,29]); **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{19}H_{25}N$: 268.2060, found: 268.2063.

The formation of **2u** was accompanied by the formation of *ca.* 5% of an oxidized side product that could not be separated and which we propose is **S8**. We have not fully characterized this minor side product and so cannot assign its structure with absolute certainty.



S8

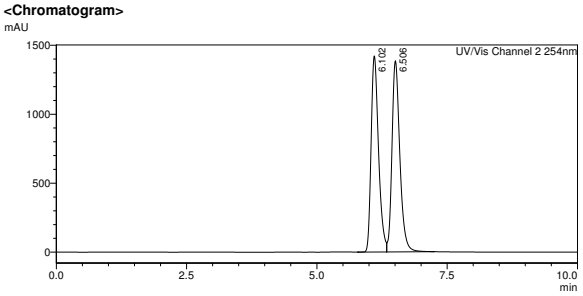


2v

1-methyl-4-(4-phenylbuta-2,3-dien-1-yl)piperazine (2v): Prepared by General Method B using **Pd-1** at 22 ˚C for 3 h. The material was purified by flash silica gel chromatography (95:5 CH_2Cl_2:MeOH with 5% Et_3N) to yield **2v** as a pale yellow oil (41.4 mg, 0.144 mmol, 71.8% yield). **IR** (neat, cm^{-1}) 2933 (w), 2791 (m), 1949 (w), 1454 (s), 1330 (s), 1280 (s), 1161 (s), 1141 (m), 1009 (s), 690 (s), (625 (m); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32–7.22 (4H, m), 7.21–7.15 (1H, m), 6.16 (1H, dt, J = 6.4, 2.4 Hz), 5.59 (1H, ddd, J = 7.1, 7.1, 7.1 Hz), 3.18 (2H, dd, J = 7.2, 2.4 Hz), 2.82–2.26 (8H, m), 2.25 (3H, s); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 206.2, 134.2, 128.6, 126.9, 126.8, 94.8, 91.3, 57.4, 55.0, 52.4, 45.9; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{15}H_{20}N_2$: 229.1699, found: 229.1704.

By General Method E: (*R*)-**2v** was isolated as a pale yellow wax (65.4 mg, 0.286 mmol, 71.6% yield). HPLC analysis indicated er = 94.5:5.5. **$[\alpha]_D^{26}$** = –204.5 (c = 1.0, $CHCl_3$) for a sample of 94.5:5.5 er

HPLC: Column: Chiralpak 1A-3 (3 μm, 4.6 mm X 150 mm). Mobile phase: 60:40 MeOH:*i*-PrOH with 0.1% Et_2NH additive, 0.4 mL/min. Detection wavelength: 254 nm. Er = 94.5:5.5.



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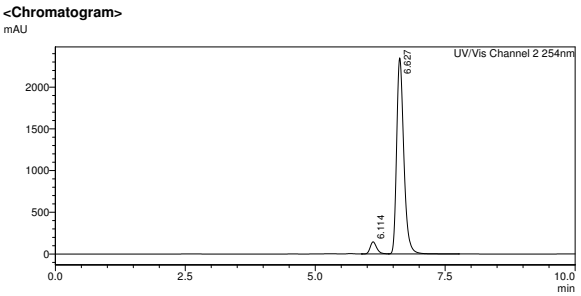
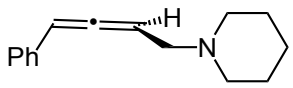


<Peak Table>
UV/Vis Channel 2 254nm

Peak#	Ret. Time	Area	Area%
1	6.114	1290073	5.379
2	6.627	22691807	94.621
Total		23981879	100.000

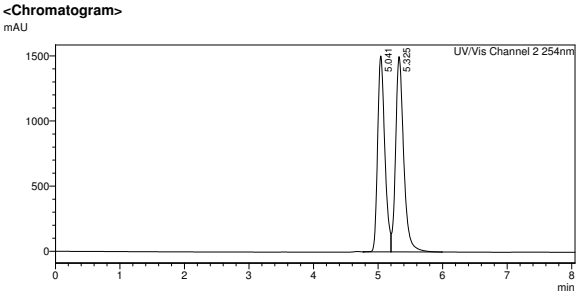


2w

1-(4-phenylbuta-2,3-dien-1-yl)piperidine (2w): Prepared by General Method B using **Pd-1** at 22 ˚C for 3 h. The material was purified by flash silica gel chromatography (85:15 hexanes:EtOAc with 5% Et_3N) to yield **2w** as a pale yellow oil (35.6 mg, 0.167 mmol, 83.4% yield). **IR** (neat, cm^{-1}) 2933 (s), 2788 (w), 1949 (m), 1457 (w), 1338 (w), 1109 (m), 789 (s), 769 (s), 690 (s); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33–7.23 (4H, m), 7.21–7.14 (1H, m), 6.14 (1H, dt, J = 6.2, 2.3 Hz), 5.61 (1H, ddd, J = 7.1, 7.1, 7.1 Hz), 3.15–3.13 (2H, m) 2.59–2.40 (4H, m), 1.68–1.56 (4H, m), 1.49–1.38 (2H, m); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 206.1, 134.5, 128.6, 126.9, 126.8, 94.5, 91.7, 58.3, 54.1, 26.1, 24.3; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{15}H_{19}N$: 214.1590, found: 214.1591.

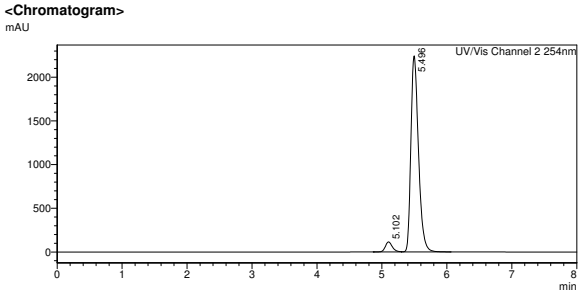
By General Method E: (*R*)-**2w** was isolated as a pale yellow oil (59.8 mg, 0.280 mmol, 70.1% yield). HPLC analysis indicated er = 95.5:4.5. $[\alpha]_D^{25}$ = –238.9 (c = 1.0, $CHCl_3$) for a sample of 95.5:4.5 er.

HPLC: Chiralpak 1A-3 (3 µm, 4.6 mm X 150 mm). Mobile phase: 100% MeOH with 0.1% Et_2NH additive, 0.5 mL/min. Detection wavelength: 254 nm. Er = 95.5:4.5.



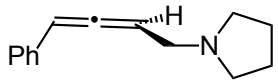
<Peak Table>
UV/Vis Channel 2 254nm

Peak#	Ret. Time	Area	Area%
1	5.041	11655202	47.288
2	5.325	12991878	52.712
Total		24647080	100.000



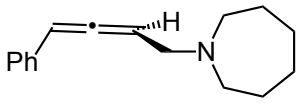
<Peak Table>
UV/Vis Channel 2 254nm

Peak#	Ret. Time	Area	Area%
1	5.102	875863	4.591
2	5.496	18200817	95.409
Total		19076680	100.000



2x (racemic)

1-(4-phenylbuta-2,3-dien-1-yl)pyrrolidine (2x): Prepared by General Method B using **Pd-1** at 22 ˚C for 3 h. The material was purified by flash silica gel chromatography (80:20 hexanes:EtOAc with 5% Et_3N) to yield **2x** as a pale yellow oil (28.9 mg, 0.145 mmol, 72.5% yield). **IR** (neat, cm^{-1}) 2962 (m), 2783 (m), 1949 (w), 1494 (w), 1458 (m), 1365 (m), 1344 (m), 1140 (m), 870 (m), 773 (s), 691 (s); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26–7.20 (4H, m), 7.15–7.10 (1H, m), 6.12 (1H, dt, J = 6.4, 2.5 Hz), 5.61 (1H, ddd, J = 6.9, 6.9, 6.9 Hz), 3.37–3.19 (2H, m), 2.73–2.52 (4H, m), 1.92–1.72 (4H, m); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 205.8, 134.3, 128.6, 126.9, 126.7, 94.8, 92.5, 54.6, 53.7, 23.6; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{14}H_{17}N$: 200.1434, found: 200.1435.

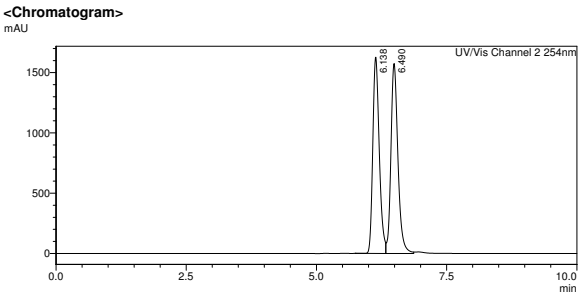


2y

1-(4-phenylbuta-2,3-dien-1-yl)azepane (2y): Prepared by General Method B using **Pd-1** at 22 ˚C for 3 h. The material was purified by flash silica gel chromatography (70:30 hexanes:EtOAc with 5% Et_3N) to yield **2y** as a pale yellow oil (35.3 mg, 0.155 mmol, 77.6% yield). **IR** (neat, cm^{-1}) 2919 (m), 2580 (w), 1945 (m), 1457 (m), 1315 (w), 1123 (w), 1077 (m), 871 (m), 771 (s), 689 (s), 630 (m); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32–7.25 (4H, m), 7.20–7.15 (1H, m), 6.15 (1H, dt, J = 6.4, 2.4 Hz), 5.62 (1H, ddd, J = 6.9, 6.9, 6.9 Hz), 3.30 (2H, dd, J = 7.0, 2.4 Hz), 2.79–2.64 (4H, m), 1.75–1.48 (8H, m); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 205.9, 134.6, 128.6, 126.8, 126.7, 94.5, 92.1, 57.8, 55.2, 28.3, 26.9; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{16}H_{21}N$: 228.1747, found: 228.1749.

By General Method E: (*R*)-**2y** was isolated as a pale yellow oil (54.1 mg, 0.238 mmol, 59.5% yield). HPLC analysis indicated er = 92:8. **$[\alpha]_D^{26}$** = –219.9 (c = 1.0, $CHCl_3$) for a sample of 92:8 er.

HPLC: Column: Chiralpak 1A-3 (3 μm, 4.6 mm X 150 mm). Mobile phase: 60:40 MeOH:*i*-PrOH with 0.1% Et_2NH additive, 0.4 mL/min. Detection wavelength: 254 nm. Er = 92:8.



<Peak Table>
UV/Vis Channel 2 254nm

Peak#	Ret. Time	Area	Area%
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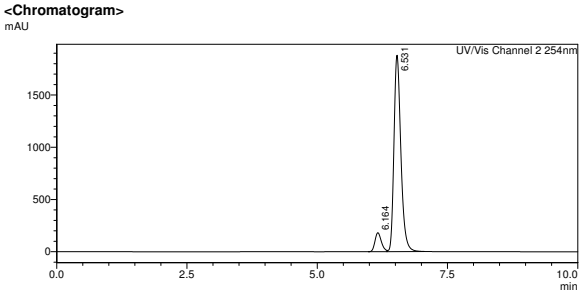
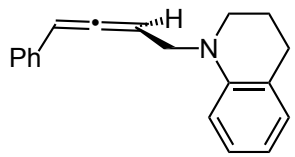
2	6.490	14796105	51.105
Total		28952553	100.000



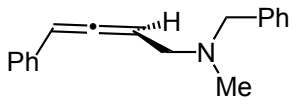
<Peak Table>
UV/Vis Channel 2 254nm

Peak#	Ret. Time	Area	Area%
1	6.164	1567761	8.237
2	6.531	17465644	91.763
Total		19033406	100.000



2z (racemic)

1-(4-phenylbuta-2,3-dien-1-yl)-1,2,3,4-tetrahydroquinoline (2z): Prepared by General Method B using **Pd-1** at 22 ˚C for 20 h. The material was purified by flash silica gel chromatography (99:1 hexanes:EtOAc with 5% Et_3N) to yield **2z** as a pale yellow oil (31.9 mg, 0.122 mmol, 61.0% yield). **IR** (neat, cm^{-1}) 2842 (w), 1942 (w), 1704 (w), 1599 (m), 1494 (m), 1456 (m), 1264 (m), 732 (s), 699 (s); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30–7.20 (4H, m), 7.20–7.14 (1H, m), 7.06–7.00 (1H, m), 6.96 (1H, d, J = 7.3 Hz), 6.69 (1H, d, J = 8.2 Hz), 6.62 (1H, dd, J = 7.3, 7.3 Hz), 6.17 (1H, dt, J = 5.8, 2.7 Hz), 5.58 (1H, ddd, J = 6.3, 6.3, 6.3 Hz), 4.02 (2H, dd, J = 6.2, 2.7 Hz), 3.34–3.29 (2H, m), 2.73 (2H, t, J = 6.4 Hz), 2.01–1.90 (2H, m); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 205.7, 144.7, 134.3, 129.2, 128.6, 127.1, 126.9, 126.8, 123.0, 116.3, 111.5, 95.7, 90.6, 50.3, 49.3, 28.1, 22.3; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{19}H_{19}N$: 262.1590, found: 262.1594.

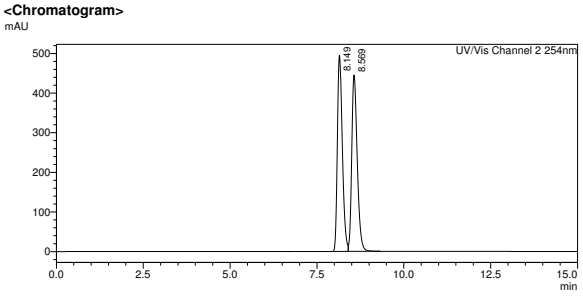


2aa

N-benzyl-N-methyl-4-phenylbuta-2,3-dien-1-amine (2aa): Prepared by General Method B using **Pd-1** at 22 ˚C for 3 h. The material was purified by flash silica gel chromatography (hexanes with 5% Et_3N) to yield **2aa** as a pale yellow oil (44.6 mg, 0.179 mmol, 89.4% yield). **IR** (neat, cm^{-1}) 3027(w), 2783 (w), 1946 (m), 1597 (w), 1493 (m), 1452 (s), 1205 (s), 772 (s), 780 (s), 690 (s), 619 (m). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37–7.23 (9H, m), 7.22–7.16 (1H, m), 6.19 (1H, dt, J = 6.4, 2.4 Hz), 3.62 (1H, AB_q, J_{AB} = 13.1 Hz), 3.58 (1H, AB_q, J_{AB} = 13.1 Hz), 3.25–3.20 (2H, m), 2.31 (3H, s); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 206.2, 138.9, 134.5, 129.1, 128.7, 128.3, 127.1, 126.9, 126.8, 94.7, 91.7, 61.2, 56.1, 41.9; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{18}H_{19}N$: 250.1590, found: 250.1592.

By General Method E: (*R*)-**2aa** was isolated as a clear oil (53.7 mg, 0.215 mmol, 53.8% yield). HPLC analysis indicated er = 93:7. **$[\alpha]_D^{25}$** = –209.1 (c = 1.0, $CHCl_3$) for a sample of 93:7 er.

HPLC: Column: Cellulose-3 (3 μm, 4.6 mm X 250 mm). Mobile phase: 99:1 hexanes:*i*-PrOH, 1 mL/min. Detection wavelength: 254 nm. Er = 93:7.



<Peak Table>
UV/Vis Channel 2 254nm

Peak#	Ret. Time	Area	Area%
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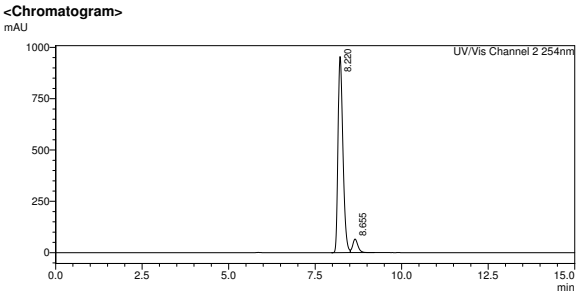
Total		9807671	100.000

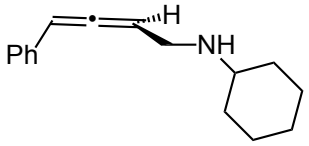


<Peak Table>
UV/Vis Channel 2 254nm

Peak#	Ret. Time	Area	Area%
1	8.220	9376263	93.066
2	8.655	698573	6.934
Total		10074835	100.000

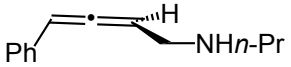
2ab (racemic)

N,N-diethyl-4-phenylbuta-2,3-dien-1-amine (2ab): Prepared by General Method B using **Pd-1** at 22 ˚C for 3 h. The material was purified by flash silica gel chromatography (90:10 hexanes:EtOAc with 5%Et_3N) to yield **2ab** as a pale yellow oil (31.1 mg, 0.154 mmol, 77.2% yield). **IR** (neat, cm^{-1}) 2967 (m), 1947 (w), 1494 (w), 1457 (m), 1199 (w), 1089 (m), 868 (w), 763 (s), 713 (s), 629 (m); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.46–7.13 (5H, m), 6.08 (1H, dt, J = 6.4, 2.3 Hz), 5.57 (1H, ddd, J = 6.8, 6.8, 6.8 Hz), 3.33 (2H, dd, J = 7.2, 2.0 Hz), 2.61 (4H, q, J = 7.2 Hz), 1.06 (6H, t, J = 7.2 Hz); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 205.9, 134.5, 128.6, 126.8, 126.7, 94.4, 90.6, 51.4, 46.7, 12.1; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{14}H_{19}N$: 202.1590, found: 202.1591.



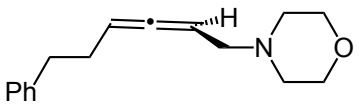
2ac (racemic)

N-(4-phenylbuta-2,3-dien-1-yl)cyclohexanamine (2ac): Prepared by General Method B using 10 mol% **Pd-1** at 22 ˚C for 3 h. The material was purified by flash silica gel chromatography (90:10:5 hexanes:EtOAc:Et_3N) to yield **2ac** as a colorless oil (26.6 mg, 0.117 mmol, 58.3% yield). **IR** (neat, cm^{-1}) 2925 (s), 2852 (m), 1944 (w), 1462 (w), 1450 (m), 1010 (w), 983 (w) 756 (m), 669 (m); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.27–7.21 (4H, m), 7.16–7.10 (1H, m), 6.15 (1H, dt, J = 6.1, 2.8 Hz), 5.57 (1H, ddd, J = 6.3, 6.3, 6.3 Hz), 3.34 (2H, dd, J = 6.3, 2.9 Hz), 2.53–2.44 (1H, m), 1.87–1.73 (2H, m), 1.71–1.58 (2H, m), 1.56–1.50 (1H, m), 1.25–0.92 (6H, m); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 204.8, 134.5, 128.6, 126.9, 126.7, 95.7, 94.6, 55.7, 45.2, 33.6, 33.4, 26.1, 25.1, 25.0 (note: two extra sp^3 carbon was observed, but this has been noted before with related cyclohexyl-substituted compounds[7,29]); **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{16}H_{21}N$: 228.1747, found: 228.1749.



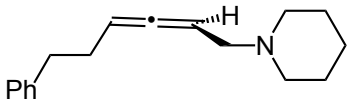
2ad (racemic)

4-phenyl-N-propylbuta-2,3-dien-1-amine (2ad): Prepared by General Method B using 10 mol% **Pd-1** at 22 ˚C for 3 h. The material was purified by flash silica gel chromatography (90:10:5 hexanes:EtOAc:Et_3N) to yield **2ad** as a colorless oil (22.1 mg, 0.118 mmol, 59.0% yield). **IR** (neat, cm^{-1}) 2957 (m), 2930 (m), 1946 (m), 1494 (s), 1458 (m), 1072 (m), 910 (w), 773 (m), 690 (s); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.24–7.17 (4H, m), 7.14–7.08 (1H, m), 6.09–6.05 (1H, m), 5.52 (1H, ddd, J = 6.9, 6.9, 6.9 Hz), 3.35–3.30 (2H, m), 2.53–2.49 (2H, m), 1.98 (1H, br. s), 1.50–1.41 (2H, m), 0.82 (3H, t, J = 7.9 Hz); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 206.1, 134.4, 128.6, 126.8, 126.7, 94.6, 91.2, 54.9, 52.4, 20.4, 11.9; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{13}H_{17}N$: 188.1434, found: 188.1431.



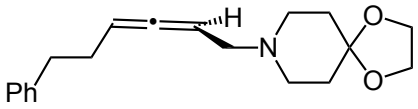
2ae (racemic)

1-(6-phenylhexa-2,3-dien-1-yl)morpholine (2ae): Prepared by General Method B using **Pd-1** at 22 ˚C for 3 h. The material was purified by flash silica gel chromatography (2:1 hexanes:EtOAc with 5% Et_3N) to yield **2ae** as a pale yellow oil (40.1 mg, 0.165 mmol, 82.4% yield). **IR** (neat, cm^{-1}) 2917 (w), 2851 (w), 2799 (w), 1945 (w), 1452 (m), 1295 (w), 1114 (s), 1004 (m), 861 (s), 697 (s); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.33–7.21 (2H, m), 7.20–7.14 (3H, m), 5.18–5.10 (2H, m), 3.03–2.85 (2H, m), 2.70 (2H, t, J = 7.8 Hz), 2.52–2.21 (6H, m), 1.69–1.49 (4H, m); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 205.6, 141.5, 128.5, 128.3, 125.9, 90.4, 87.4, 66.9, 58.4, 53.2, 35.5, 30.5; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{16}H_{21}NO$: 244.1696, found: 244.1696.



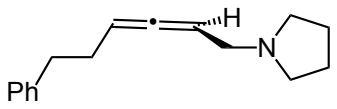
2af (racemic)

1-(6-phenylhexa-2,3-dien-1-yl)piperidine (2af): Prepared by General Method B using **Pd-1** at 22 ˚C for 3 h. The material was purified by flash silica gel chromatography (80:20 hexanes:EtOAc with 5% Et_3N) to yield **2af** as a pale yellow oil (36.4 mg, 0.151 mmol, 75.4% yield). **IR** (neat, cm^{-1}) 2930 (m), 1949 (w), 1495 (w), 1452 (m), 1440 (w),1336 (w), 1299 (w), 1108 (m), 743 (m), 696 (s); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23–7.16 (2H, m), 7.14–7.08 (3H, m), 5.17–5.10 (2H, m), 2.94–2.81 (2H, m), 2.64 (2H, app. t, J = 8.4 Hz), 2.34 (4H, br. s), 2..28–2.18 (2H, m), 1.52 (4H, app. p, J = 5.6 Hz); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 205.3, 141.7, 128.5, 128.3, 125.9, 90.2, 88.0, 58.7, 53.9, 35.5, 30.5, 25.9, 24.3; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{17}H_{23}N$: 242.1903, found: 242.1903.



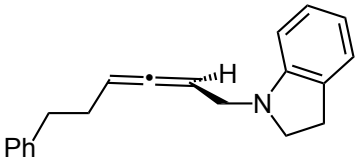
2ag (racemic)

8-(6-phenylhexa-2,3-dien-1-yl)-1,4-dioxa-8-azaspiro[4.5]decane (2ag): Prepared by General Method B using **Pd-1** at 22 ˚C for 3 h. The material was purified by flash silica gel chromatography (90:10 hexanes:EtOAc with 5% Et_3N) to yield **2ag** as a pale yellow oil (49.7 mg, 0.183 mmol, 91.6% yield). **IR** (neat, cm^{-1}) 2930 (w), 2850 (w), 2804 (w), 1947 (w), 1496 (m), 1451 (m), 1354 (m), 1268 (m), 1022 (s), 864 (s), 716 (s), 698 (s); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.25–7.17 (2H, m), 7.14–7.08 (3H, m), 5.14–5.02 (2H, m), 3.88 (4H, s), 2.98–2.87 (2H, m), 2.64 (2H, t, J = 7.7 Hz), 2.54–2.42 (4H, m), 2.28–2.20 (2H, m), 1.68 (4H, t, J = 5.6 Hz); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 205.3, 141.7, 128.5, 128.3, 125.9, 107.2, 90.4, 88.1, 64.2, 57.7, 50.8, 35.5, 34.9, 30.5; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{19}H_{25}NO_2$: 300.1598, found: 300.1594.



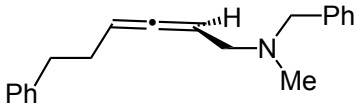
2ah (racemic)

1-(6-phenylhexa-2,3-dien-1-yl)pyrrolidine (2ah): Prepared by General Method B using **Pd-1** at 22 ˚C for 3 h. The material was purified by flash silica gel chromatography (2:1 hexanes:EtOAc with 5% Et_3N) to yield **2ah** as a pale yellow oil (33.9 mg, 0.122 mmol, 61.1% yield). **IR** (neat, cm^{-1}) 2925 (w), 2775 (w), 1943 (w), 1495 (w), 1453 (w), 1365 (w), 1123 (w), 866 (w), 743 (m), 697 (s); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.25–7.18 (2H, m), 7.13–7.10 (3H, m), 5.16–5.06 (2H, m), 3.05–2.95 (2H, m), 2.65 (2H, t, J = 7.2 Hz), 2.51–2.39 (4H, m) 2.34–2.18 (2H, m), 1.77–1.63 (4H, m); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 204.8, 141.8, 128.5, 128.3, 128.9, 90.5, 89.2, 55.2, 53.6, 35.5, 30.5, 23.6; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{16}H_{21}N$: 228.1747, found: 228.1747.



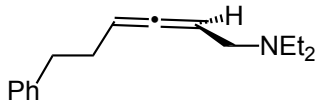
2ai (racemic)

1-(6-phenylhexa-2,3-dien-1-yl)indoline (2ai): Prepared by General Method B using **Pd-1** at 22 ˚C for 3 h. The material was purified by flash silica gel chromatography (hexanes with 5% Et_3N) to yield **2ai** as a pale red oil (41.6 mg, 0.151 mmol, 75.5% yield).* **IR** (neat, cm^{-1}) 3024 (w), 2918 (w), 2827 (w), 1959 (w), 1605 (m), 1486 (m), 1382 (w), 1331 (w), 906 (s), 695 (s), 648 (w); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.24–7.19 (2H, m), 7.14–7.09 (3H, m), 7.02–6.96 (2H, m), 6.58 (1H, dd, J = 7.2, 7.2 Hz), 6.41 (1H, d, J = 7.7 Hz), 5.15–5.09 (1H, m), 5.09–5.03 (1H, m), 3.67–3.57 (2H, m), 3.34–3.23 (2H, m), 2.87 (2H, t, J = 8.3 Hz), 2.68–2.58 (2H, m), 2.30–2.17 (2H, m); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 205.2, 151.7, 141.7, 130.4, 128.6, 128.3, 127.2, 125.9, 124.5, 117.7, 107.6, 91.2, 86.8, 52.6, 48.0, 35.4, 30.5, 28.5; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{20}H_{21}N$: 276.1747, found: 276.1753.



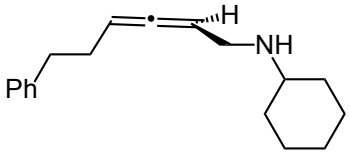
2aj (racemic)

N-benzyl-N-methyl-6-phenylhexa-2,3-dien-1-amine (2aj): Prepared by General Method B using **Pd-1** at 22 ˚C for 3 h. The material was purified by flash silica gel chromatography (hexanes with 5% Et_3N) to yield **2aj** as a pale yellow oil (50.2 mg, 0.181 mmol, 90.4% yield). **IR** (neat, cm^{-1}) 3022 (w), 2818 (w), 2703 (w), 1962 (m), 1612 (m), 1440 (m), 1212 (w), 912 (s), 884 (s), 698 (s); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.26–7.07 (10H, m), 5.23–5.17 (2H, m), 3.43 (2H, s), 2.98–2.90 (2H, m), 2.65 (2H, t, J = 7.7 Hz), 2.30–2.20 (2H, m), 2.13 (3H, s); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 205.3, 141.7, 139.0, 129.1, 128.5, 128.3, 128.2, 126.9, 125.9, 90.3, 88.2, 61.1, 56.6, 41.8, 35.5, 30.6; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{20}H_{23}N$: 276.1903, found: 276.1899.



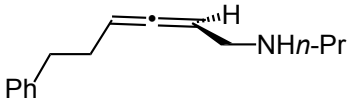
2ak (racemic)

N,N-diethyl-6-phenylhexa-2,3-dien-1-amine (2ak): Prepared by General Method B using **Pd-1** at 22 ˚C for 3 h. The material was purified by flash silica gel chromatography (80:20 hexanes:EtOAc with 5% Et_3N) to yield **2ak** as a pale yellow oil (34.8 mg, 0.152 mmol, 75.9% yield). **IR** (neat, cm^{-1}) 2968 (w), 2932 (w) 2807 (w), 1965 (w), 1453 (w), 1264 (m), 1199 (w), 1065 (w), 733 (s), 697 (s); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.24–7.17 (2H, m), 7.14–7.08 (3H, m), 5.10–5.00 (2H, m), 3.05 (2H, dd, J = 7.1, 2.4 Hz), 2.65 (2H, t, J = 8.2 Hz), 2.47 (4H, q, J = 7.2 Hz), 2.30–2.19 (2H, m), 0.96 (6H, t, J = 7.2 Hz); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 205.1, 141.7, 128.5, 128.3, 125.9, 90.0, 87.1, 51.8, 46.5, 35.5, 30.6, 11.9; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{16}H_{23}N$: 230.1903, found: 230.1904.



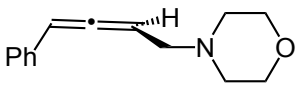
2al (racemic)

N-(6-phenylhexa-2,3-dien-1-yl)cyclohexanamine (2al): Prepared by General Method B using **Pd-1** at 22 ˚C for 3 h. The material was purified by flash silica gel chromatography (95:5 hexanes:EtOAc with 5% Et_3N) to yield **2al** as a pale yellow oil (28.2 mg, 0.124 mmol, 62.1% yield). **IR** (neat, cm^{-1}) 2998 (w), 2828 (m), 1956 (w), 1435 (m), 1234 (m), 1146 (s), 763 (s), 622 (m); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.24–7.19 (2H, m), 7.14–7.08 (3H, m), 5.18–5.08 (2H, m), 3.13 (2H, dd, J = 6.3, 2.9 Hz), 2.66 (2H, t, J = 7.7 Hz), 2.44–2.37 (1H, m), 2.30–2.23 (2H, m), 1.82–1.50 (4H, m), 1.24–0.90 (6H, m), 0.87 (1H, br. s); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 203.8, 141.7, 128.5, 128.3, 125.9, 91.5, 90.9, 55.7, 45.4, 35.4, 33.6, 33.5, 30.4, 26.2, 25.1 (note: one extra sp^3 carbon was observed, but this has been noted before with related cyclohexyl-substituted compounds[7,29]); **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{18}H_{25}N$: 256.2060, found: 256.2064.



2am (racemic)

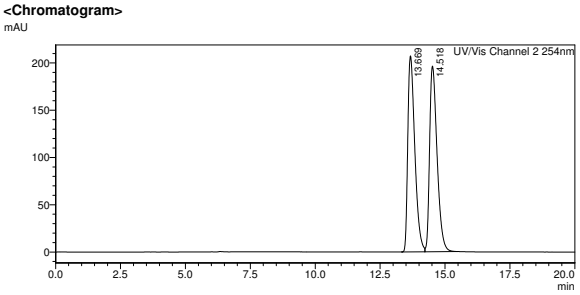
6-phenyl-N-propylhexa-2,3-dien-1-amine (2am): Prepared by General Method B using **Pd-1** at 22 ˚C for 3 h. The material was purified by flash silica gel chromatography (95:5 hexanes:EtOAc with 5% Et_3N) to yield **2am** as a pale yellow oil (22.0 mg, 0.109 mmol, 54.8% yield). **IR** (neat, cm^{-1}) 2956 (m), 1959 (w), 1495 (m), 1453 (s), 1334 (w), 1076 (m), 868 (w), 745 (m), 697 (s); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25–7.15 (2H, m), 7.13–7.08 (3H, m), 5.13–4.97 (2H, m), 3.09–2.99 (2H, m), 2.65 (2H, t, J = 7.7 Hz), 2.39–2.31 (2H, m), 2.29–2.19 (2H, m), 1.47–1.33 (2H, m), 0.80 (3H, t, J = 7.4 Hz); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 205.2, 141.7, 128.5, 128.3, 125.9, 90.1, 87.8, 54.7, 52.8, 35.5, 30.6, 20.3, 12.0; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{15}H_{21}N$: 216.1747, found: 216.1741.



2an

(*R*)-4-(4-phenylbuta-2,3-dien-1-yl)morpholine (2an): Prepared by General Method E. The material was purified by flash silica gel chromatography (70:30 hexanes:EtOAc with an additional 2% Et_3N additive v/v) to yield (*R*)-**2an** as a pale yellow oil (56.8 mg, 0.264 mmol, 66.0% yield). HPLC analysis indicated er = 95.5:4.5. **IR** (neat, cm^{-1}) 3030 (w), 2956 (m), 2852 (m), 2801 (m), 1949 (m), 1713 (w), 1596 (w), 1494 (m), 1453 (m), 1344 (m), 1330 (m), 1315 (m), 1287 (m), 1270 (m), 1204 (w), 1114 (s), 1070 (m), 1034 (w), 1004 (s); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33–7.23 (4H, m), 7.22–7.16 (1H, m), 6.18 (1H, dt, J = 6.4, 2.4 Hz), 5.58 (1H, ddd, J = 7.0, 7.0, 7.0 Hz), 3.74 (4H, t, J = 4.6 Hz), 3.15 (2H, dd, J = 7.2, 2.4 Hz), 2.59–2.48 (4H, m); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 206.3, 134.2, 128.6, 127.0, 126.7, 94.8, 91.2, 67.0, 57.8, 53.2; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{14}H_{17}NO$: 216.1383, found: 216.1381; **$[\alpha]_D^{26}$** = –185.6 (c = 1.0, $CHCl_3$) for a sample of 95.5:4.5 er.

HPLC: Column: Cellulose-3 (3 µm, 4.6 mm X 250 mm). Mobile phase: 99.9:0.1 hexanes:*i*-PrOH, 1 mL/min. Detection wavelength: 254 nm. Er = 95.5:4.5.



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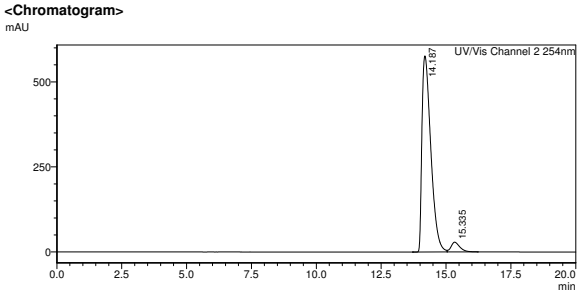

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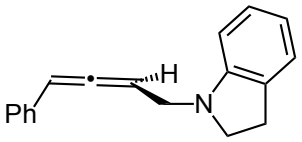
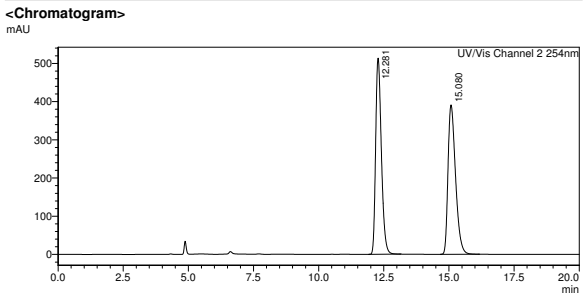


2ao

1-(4-phenylbuta-2,3-dien-1-yl)indoline (2ao): Prepared by General Method E. The material was purified by flash silica gel chromatography (100% hexanes to 98:2 hexanes:EtOAc) to yield (*R*)-**2ao** as a pale yellow oil (29.5 mg, 0.119 mmol, 59.6% yield).* HPLC analysis indicated er = 69.5:30.5. **IR** (neat, cm^{-1}) 3028 (w), 2920 (w), 2945 (w), 2846 (m), 1940 (m), 1604 (s), 1485 (m), 1469 (m), 1453 (m), 1384 (m), 1334 (m), 1305 (m), 1280 (m), 1261 (m), 1230 (m), 1199 (m), 1171 (m), 1151(m), 1140 (m), 1084 (m), 1068 (m), 1054 (m), 1020 (m), 985 (m); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32–7.23 (4H, m), 7.22–7.17 (1H, m), 7.10–7.03 (2H, m), 6.66 (1H, t, J = 7.4 Hz), 6.53 (1H, d, J = 7.8 Hz), 6.19 (1H, dt, J = 6.4, 2.4 Hz), 5.60 (1H, app. q, J = 6.7 Hz), 3.92 (1H, ddd, J = 14.7, 6.6, 2.5 Hz), 3.87 (1H, ddd, J = 14.8, 6.9, 2.5 Hz), 3.50–3.39 (2H, m), 2.98 (2H, t, J = 8.3 Hz); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 206.1, 151.5, 134.3, 130.5, 128.7, 127.4, 127.1, 127.0, 124.6, 118.0, 107.8, 95.4, 90.4, 52.8, 47.9, 28.7; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{18}H_{17}N$: 248.1434, found: 248.1432; **$[\alpha]_D^{27}$** = –59.3 (c = 1.0, $CHCl_3$) for a sample of 69.5:30.5 er.

HPLC: Column: Cellulose-3 (3 μm, 4.6 mm X 250 mm). Mobile phase: 90:10 hexanes:*i*-PrOH, 1 mL/min. Detection wavelength: 254 nm. Er = 69.5:30.5.



<Peak Table>
UV/Vis Channel 2 254nm

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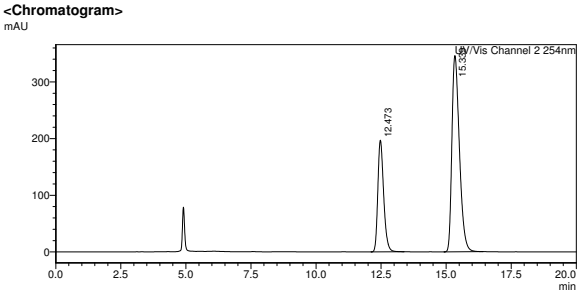

<Peak Table>
UV/Vis Channel 2 254nm

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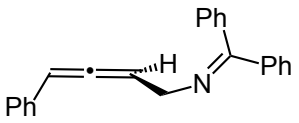
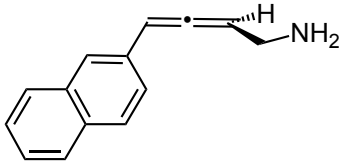


3 (racemic)

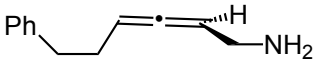
1,1-diphenyl-*N*-(4-phenylbuta-2,3-dien-1-yl)methanimine (3): To an oven-dried 2-dram vial equipped with a magnetic stirring rod was added **Pd-1** (42.9 mg, 0.0500 mmol, 5.00 mol%) and CH_2Cl_2 (1.25 mL). To this suspension was added enyne **1a** (162 μL, 1.20 mmol, 1.20 equiv), Et_3N (0.28 mL, 2.0 mmol, 2.0 equiv), and finally benzophenone imine (168 μL, 1.00 mmol, 1.00 equiv). This mixture was allowed to stir at ambient temperature for 24 h. During this time the suspension gradually became a homogenous solution. The reaction mixture was then passed through a short plug of neutral alumina eluting with 1:1 hexanes:EtOAc (*ca.* 20 mL) and the solution concentrated. The product was purified by flash silica gel chromatography (hexanes with 2% Et_3N additive v/v to 95:5 hexanes:EtOAc with 2% Et_3N additive v/v) to afford **3** as a yellow solid (273 mg, 0.882 mmol, 88.2% yield). **IR** (neat, cm^{-1}) 3053 (w), 2902 (w), 1947 (w), 1620 (m), 1596 (w), 1574 (w), 1488 (w), 1459 (w), 1444 (m), 1425 (w), 1315 (m), 1287 (m), 1273 (m), 1258 (m), 1176 (w), 1154 (w), 1073 (w), 1024 (w), 996 (m); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63–7.57 (2H, m), 7.43–7.24 (10H, m), 7.21–7.12 (3H, m), 6.20 (1H, dt, J = 6.4, 2.9 Hz), 5.85 (1H, ddd, J = 6.4, 6.4, 6.4 Hz), 4.16–4.12 (2H, m); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 205.5, 169.5, 139.8, 136.5, 134.5, 130.1, 128.6, 128.6, 128.5, 128.1, 127.9, 126.9, 126.9, 95.8, 94.4, 52.8 (note: one sp^2 carbon is missing due to overlap); **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{23}H_{19}N$: 310.1590, found: 310.1595; **MP** = 71–74 °C.



4a (racemic)

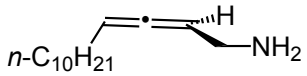
4-(naphthalen-2-yl)buta-2,3-dien-1-amine (4a): To an oven-dried 2-dram vial equipped with a magnetic stirring rod was added **Pd-1** (42.9 mg, 0.0500 mmol, 5.00 mol%) and CH_2Cl_2 (1.25 mL). To this suspension was added enyne **1l** (206 μL, 1.20 mmol, 1.20 equiv), Et_3N (0.28 mL, 2.0 mmol, 2.0 equiv), and finally benzophenone imine (168 μL, 1.00 mmol, 1.00 equiv). This mixture was allowed to stir at ambient temperature for 24 h. During this time the suspension gradually became a homogenous solution. After this time, the reaction mixture was transferred to a 50-mL round-bottom flask, diluted with THF (5 mL), and then treated with 10% aq citric acid (10 mL). The reaction mixture was allowed to stir vigorously for 6 h. TLC analysis revealed that hydrolysis was complete after this time. The reaction mixture was diluted with EtOAc (30 mL) and basified with 2 M aq NaOH (30 mL). The aqueous fraction was separated from the organics and washed with EtOAc (2 X 10 mL). The combined organic fractions were dried over $MgSO_4$, filtered, and concentrated. The product was purified by flash silica gel chromatography (95:5 CH_2Cl_2:MeOH to 95:5 CH_2Cl_2:MeOH with 2% Et_3N additive v/v) to afford **4a** as a yellow solid (136 mg, 0.696 mmol, 69.6% yield). **IR** (neat, cm^{-1}) 3300–2500 (br), 1944 (m), 1595 (m), 1506 (s), 1413 (w), 1364 (m), 1275 (m), 1250 (m), 1212 (m), 1144 (w), 1124 (w), 1006 (m), 949 (m); **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 7.87–7.80 (3H, m), 7.75 (1H, s), 7.53–7.39 (3H, m), 6.53 (1H, dt, J = 6.3, 2.8 Hz), 5.80 (1H, ddd, J = 6.1, 6.1, 6.1 Hz), 3.52 (2H, br s), 3.38–3.26 (2H, m); **^{13}C NMR** (125 MHz, DMSO-*d6*) δ 205.4, 133.7, 132.7, 131.8, 128.6, 128.1, 128.1, 126.9, 126.3, 126.0, 125.2, 96.9,

94.6 (note: one sp^3 carbon missing due to overlap with DMSO-*d6*); **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{14}H_{13}N$: 196.1121, found: 196.1123; **MP** = 170–176 °C (decomp.).



4b (racemic)

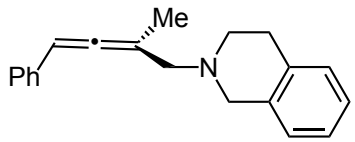
6-phenylhexa-2,3-dien-1-amine (4b): To an oven-dried 2-dram vial equipped with a magnetic stirring rod was added **Pd-1** (42.9 mg, 0.0500 mmol, 5.00 mol%) and CH_2Cl_2 (1.25 mL). To this suspension was added enyne **1o** (202 μL, 1.20 mmol, 1.20 equiv), Et_3N (0.28 mL, 2.0 mmol, 2.0 equiv), and finally benzophenone imine (168 μL, 1.00 mmol, 1.00 equiv). This mixture was allowed to stir at ambient temperature for 24 h. During this time the suspension gradually became a homogenous solution. After this time, the reaction mixture was transferred to a 50-mL round-bottom flask, diluted with THF (5 mL), and then treated with 10% aq citric acid (10 mL). The reaction mixture was allowed to stir vigorously for 6 h. The reaction mixture was diluted with Et_2O (20 mL) and basified with 2 M aq NaOH (30 mL). The aqueous fraction was separated from the organics and washed with Et_2O (20 mL). The combined organic fractions were washed with sat aq brine (30 mL), dried over $MgSO_4$, filtered, and concentrated. The product was purified by flash silica gel chromatography (100% CH_2Cl_2 to 90:10 CH_2Cl_2:MeOH) to afford **4b** as a pale yellow oil (100 mg, 0.579 mmol, 57.9% yield). NOTE: It is important that **4b** be purified *immediately* after work up since this compound is not stable for long in its unpurified form. **IR** (neat, cm^{-1}) 3025 (w), 2918 (m), 2853 (m), 1962 (m), 1602 (m), 1495 (m), 1453 (m), 1333 (w), 1278 (w), 1078 (w), 1029 (w), 863 (m); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.30–7.23 (2H, m), 7.21–7.14 (3H, m), 5.31–5.19 (2H, m), 3.16 (2H, dd, J = 5.3, 3.3 Hz), 2.80–2.65 (2H, m), 2.43–2.25 (2H, m), 2.14 (2H, br s); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 203.4, 141.5, 128.6, 128.3, 126.0, 93.3, 92.1, 40.0, 35.2, 30.3; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{12}H_{15}N$: 174.1277, found: 174.1281.



4c (racemic)

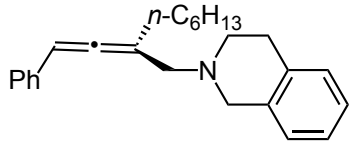
tetradeca-2,3-dien-1-amine (4c): To an oven-dried 2-dram vial equipped with a magnetic stirring rod was added **Pd-1** (42.9 mg, 0.0500 mmol, 5.00 mol%) and CH_2Cl_2 (1.25 mL). To this suspension was added enyne **1p** (288 μL, 1.20 mmol, 1.20 equiv), Et_3N (0.28 mL, 2.0 mmol, 2.0 equiv), and finally benzophenone imine (168 μL, 1.00 mmol, 1.00 equiv). This mixture was allowed to stir at ambient temperature for 24 h. During this time the suspension gradually became a homogenous solution. After this time, the reaction mixture was transferred to a 50-mL round-bottom flask, diluted with THF (5 mL), and then treated with 10% aq citric acid (10 mL). The reaction mixture was allowed to stir vigorously for 6 h. The reaction mixture was diluted with Et_2O (20 mL) and basified with 2 M aq NaOH (30 mL). The aqueous fraction was separated from the organics and washed with Et_2O (20 mL). The combined organic fractions were washed with sat aq brine (20 mL), dried over $MgSO_4$, filtered, and concentrated. The product was purified by flash silica gel chromatography (100% CH_2Cl_2 to 90:10 CH_2Cl_2:MeOH) to afford **4c** as a pale yellow wax (119 mg, 0.570 mmol, 57.0% yield). NOTE: It is important that **4c** be purified *immediately* after work up since this compound is not stable for long in its unpurified form. **IR** (neat, cm^{-1}) 2921 (s), 2852 (s), 1962 (w), 1598 (w), 1516 (w), 1465 (m), 1377 (w), 872 (m); **^{1}H NMR** (500

MHz, $CDCl_3$) δ 5.30–5.20 (2H, m), 3.28 (2H, dd, J = 5.2, 3.4 Hz), 2.87 (2H, dd, J = 5.2, 3.4 Hz), 2.87 (2H, br s), 2.04–1.96 (2H, m), 1.42–1.19 (16 H, m), 0.86 (3H, t, J = 6.6 Hz); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 203.3, 94.0, 91.4, 40.3, 31.9, 29.6, 29.6, 29.5, 29.3, 29.2, 29.1, 28.8, 22.7, 14.1; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{14}H_{27}N$: 210.2216, found: 210.2219.



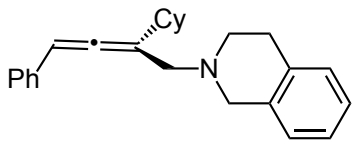
6a (racemic)

2-(2-methyl-4-phenylbuta-2,3-dien-1-yl)-1,2,3,4-tetrahydroisoquinolineamine (6a): Prepared by General Method B using **Pd-1** at 22 ˚C for 3 h. The material was purified by flash silica gel chromatography (95:5 hexanes:EtOAc) to yield **6a** as a pale yellow oil (33.7 mg, 0.122 mmol, 61.1% yield).* **IR** (neat, cm^{-1}) 3030 (w), 2931 (s), 2808 (m), 1956 (m), 1644 (m), 1451 (m), 1303 (w), 988 (s), 824 (s), 773 (s), 628 (w); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.27–7.19 (4H, m), 7.14–7.09 (1H, m), 7.06–6.99 (3H, m), 6.95–6.89 (1H, m), 6.08–6.02 (1H, m), 3.63 (1H, AB_q, J_{AB} = 14.9 Hz), 3.59 (1H, AB_q, J_{AB} = 14.9 Hz), 3.16 (1H, ABX_q, J_{AB} = 12.8 Hz, J_{BX} = 2.2 Hz), 3.12 (1H, ABX_q, J_{AB} = 12.8 Hz, J_{BX} = 2.2 Hz), 2.81 (2H, t, J = 5.9 Hz), 2.76–2.64 (2H, m), 1.81 (3H, d, J = 2.9 Hz); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 204.1, 135.4, 134.9, 134.5, 128.7, 128.6, 126.8, 126.7, 126.6, 126.0, 125.6, 100.9, 93.7, 61.8, 56.2, 50.5, 29.1, 17.1; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{20}H_{21}N$: 276.1747, found: 276.1748.



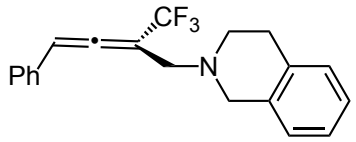
6b (racemic)

2-(2-(2-phenylvinylidene)octyl)-1,2,3,4-tetrahydroisoquinoline (6b): Prepared by General Method B using **Pd-1** at 22 ˚C for 3 h. The material was purified by flash silica gel chromatography (95:5 hexanes:EtOAc) to yield **6b** as a pale yellow oil (45.8 mg, 0.134 mmol, 67.0% yield). **IR** (neat, cm^{-1}) 3042 (m), 2899 (s), 1977 (m), 1503 (m), 1434 (m), 1206 (m), 1188 (m), 969 (s), 845 (m), 712 (s), 680 (w); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.27–7.21 (4H, m), 7.15–7.10 (1H, m), 7.06–7.02 (3H, m), 6.95–6.90 (1H, m), 6.17–6.08 (1H, m), 3.62 (1H, AB_q, J_{AB} = 14.9 Hz), 3.57 (1H, AB_q, J_{AB} = 14.9 Hz), 3.17 (1H, ABX_q, J_{AB} = 12.8 Hz, J_{BX} = 1.9 Hz), 3.12 (1H, ABX_q, J_{AB} = 12.8 Hz, J_{AX} = 1.9 Hz), 2.86–2.78 (2H, m), 2.77–2.62 (2H, m), 2.19–2.03 (2H, m), 1.50–1.36 (2H, m), 1.32–1.14 (4H, m), 0.86–0.71 (5H, m); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 203.6, 135.6, 135.1, 134.5, 134.4, 128.7, 128.6, 126.8, 126.6, 126.0, 125.5, 105.9, 95.1, 60.9, 56.3, 50.5, 31.7, 30.7, 29.2, 29.1, 27.7, 22.7, 14.1; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{25}H_{31}N$: 346.2526, found: 346.2529.



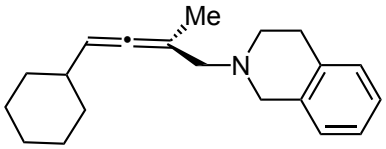
6c (racemic)

2-(2-cyclohexyl-4-phenylbuta-2,3-dien-1-yl)-1,2,3,4-tetrahydroisoquinoline (6c): Prepared by General Method B using **Pd-1** at 22 ˚C for 3 h. The material was purified by flash silica gel chromatography (95:5 hexanes:EtOAc) to yield **6c** as a pale yellow oil (38.0 mg, 0.106 mmol, 53.2% yield). **IR** (neat, cm^{-1}) 3027 (w), 2910 (s), 2848 (m), 1944 (w), 1597 (w), 1495 (m), 1446 (m), 1333 (m), 1086 (m), 933 (s), 820 (m), 738 (s), 692 (s), 649 (m), 626 (w); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.26–7.18 (4H, m), 7.14–7.07 (1H, m), 7.04–6.98 (3H, m), 6.93–6.87 (1H, m), 6.16–6.12 (1H, m), 3.62 (1H, AB_q, J_{AB} = 14.9 Hz), 3.53 (1H, AB_q, J_{AB} = 14.9 Hz), 3.18 (1H, ABX_q, J_{AB} = 13.0 Hz, J_{BX} = 2.2 Hz), 3.13 (1H, ABX_q, J_{AB} = 13.0 Hz, J_{BX} = 2.2 Hz), 2.82–2.60 (4H, m), 2.10–1.81 (3H, m), 1.68–1.50 (2H, m), 1.27–1.04 (6H, m); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 203.5, 135.7, 135.2, 134.7, 128.7, 128.6, 126.7, 126.6, 126.5, 126.0, 125.6, 111.4, 95.9, 59.7, 56.4, 50.6, 38.9, 32.9, 32.5, 29.2, 26.5, 26.4 (note: one extra sp^3 carbon was observed, but this has been noted before with related cyclohexyl-substituted compounds[7,29]); **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{25}H_{29}N$: 344.2373, found: 344.2377.



6d (racemic)

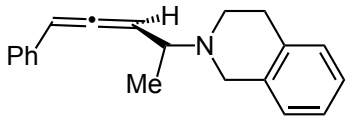
2-(4-phenyl-2-(trifluoromethyl)buta-2,3-dien-1-yl)-1,2,3,4-tetrahydroisoquinoline (6d): Prepared by General Method B using **Pd-1** at 22 ˚C for 3 h. The material was purified by flash silica gel chromatography (95:5 hexanes:EtOAc) to yield **6d** as a pale yellow oil (42.2 mg, 0.123 mmol, 61.4% yield). **IR** (neat, cm^{-1}) 3024 (w), 2922 (w), 2798 (w), 1957 (w), 1497 (m), 1462 (m), 1279 (m), 1174 (s), 1073 (w), 935 (w), 742 (s), 691 (s), 652 (w); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38–7.27 (5H, m), 7.13–7.01 (3H, m), 6.96–6.91 (1H, m), 6.70–6.63 (1H, m), 3.75 (1H, AB_q, J_{AB} = 14.9 Hz), 3.68 (1H, AB_q, J_{AB} = 14.9 Hz), 3.46 (1H, ABX_q, J_{AB} = 15.2 Hz, J_{BX} = 3.0 Hz), 3.41 (1H, ABX_q, J_{AB} = 15.2 Hz, J_{BX} = 3.0 Hz), 2.89–2.72 (4H, m); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 205.6 (q, J_{CF} = 4.3 Hz), 134.5, 134.2, 131.9, 131.5, 129.0, 128.7, 127.5, 126.6, 126.2, 125.7, 125.3 (q, J_{CF} = 273 Hz), 101.3, 100.0 (q, J_{CF} = 33.5 Hz), 55.8, 55.1, 50.3, 29.0; **^{19}F NMR** (376 MHz, $CDCl_3$) -62.46 (3F, d, J = 3.2 Hz); **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{20}H_{18}F_3N$: 330.1464, found: 330.1470.



6e (racemic)

2-(4-cyclohexyl-2-methylbuta-2,3-dien-1-yl)-1,2,3,4-tetrahydroisoquinoline (6e): Prepared by General Method B using **Pd-1** at 22 ˚C for 3 h. The material was purified by flash silica gel chromatography (95:5 hexanes:EtOAc) to yield **6e** as a pale yellow oil (43.9 mg, 0.156 mmol,

77.8% yield). **IR** (neat, cm^{-1}) 2902 (s), 2849 (m), 2791 (w), 1938 (w), 1497 (w), 1447 (m), 1367 (w), 1128 (w), 1089 (m), 933 (w), 908 (w), 739 (s); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.09–6.98 (3H, m), 6.98–6.91 (1H, m), 5.03–4.94 (1H, m), 3.57 (1H, AB_q, J_{AB} = 15.5 Hz), 3.53 (1H, AB_q, J_{AB} = 15.5 Hz), 3.03–2.96 (2H, m), 2.82 (2H, t, J = 5.9 Hz), 2.71–2.59 (1H, m), 1.76–1.60 (7H, m), 1.31–0.97 (6H, m); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 201.7, 135.2, 134.6, 128.7, 126.6, 125.9, 125.5, 97.3, 95.9, 62.6, 56.2, 50.3, 37.6, 33.3, 29.2, 26.3, 26.1, 22.7, 17.6 (note: one extra sp^3 carbon was observed, but this has been noted before with related cyclohexyl-substituted compounds[7,29]); **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{20}H_{27}N$: 282.2216, found: 282.2214.



8 (racemic)

5-phenylpenta-3,4-dien-2-yl)-1,2,3,4-tetrahydroisoquinoline (8): Prepared by General Method C (0.40 mmol scale) at 22 ˚C for 20 h. ^{1}H NMR analysis of the unpurified material revealed a 2:1 mixture of diastereomers. The material was purified by flash silica gel chromatography (85:15 hexanes:EtOAc) to yield **8** as a pale yellow oil (28.2 mg, 0.102 mmol, 25.6% yield). The diastereomers could not be separated and all characterization data is for material with 2:1 dr. **IR** (neat, cm^{-1}) 3027 (w), 2970 (w), 2918 (w), 2799 (w), 1944 (m), 1597 (m), 1495 (m), 1455 (m), 1374 (w), 1333 (w), 1279 (w), 1267 (w), 1232 (w), 1210 (w), 1193 (w), 1155 (w), 1134 (m), 1099 (m), 1078 (w), 1027 (w), 934 (m); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36–7.29 (4H, m), 7.24–7.18 (1H, m), 7.15–7.09 (3H, m), 7.07–7.02 (1H, m), 6.25 (0.33 H, dd, J = 6.4, 2.2 Hz), 6.22 (0.66 H, dd, J = 6.4, 1.9 Hz), 5.72–5.65 (1H, m), 3.89–3.75 (2H, m), 3.60–3.52 (1H, m), 3.00–2.77 (4H, m), 1.37 (1H, d, J = 6.7 Hz), 1.34 (2H, d, J = 6.7 Hz); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 205.0, 135.2, 135.1, 134.6, 134.6, 234.5, 134.5, 128.8. 128.7, 128.7, 126.9, 126.9, 126.8, 126.7, 126.7, 126.1, 125.6, 95.9, 95.6, 95.5, 95.3, 59.1, 59.1, 52.0, 51.9, 46.7, 46.7, 29.7, 17.6, 17.2 (note: one sp, two sp^2, and one sp^3 carbon were not detected due to overlap from complex mixture of diastereomers); **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{20}H_{21}N$: 276.1747, found: 276.1753.

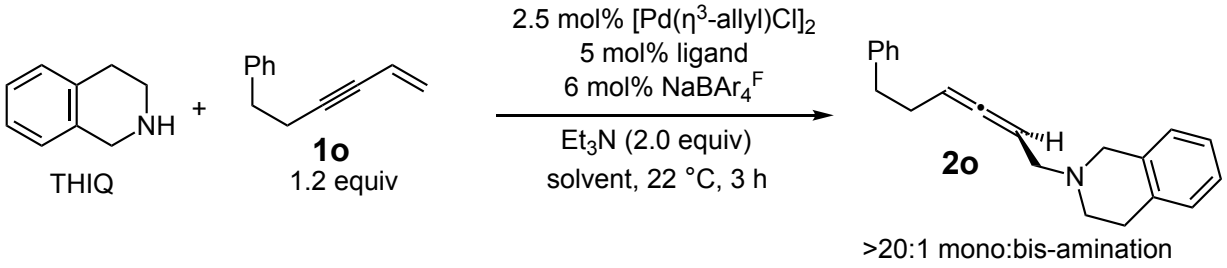
Following the procedure above (0.40 mmol scale) with addition of Et_3N (112 μL, 0.80 mmol, 2.0 equiv) to the reaction mixture, **8** is isolated as a pale yellow oil (65.3 mg, 0.237 mmol, 59.3% yield). ^{1}H NMR analysis of the unpurified material revealed a 1:1 mixture of diastereomers. These diastereomers were not separated by chromatography.

VII. Supplemental Substrate Screening

1. Enantioselective Reaction Screening with Alkyl-Substituted Enynes

Efforts to expand the enantioselective reaction scope to alkyl-substituted enynes was met with limited success. Although PHOX ligands, promote the reactions, yields and er are poor (Table S5).

Table S5. Investigation of Alkyl-Substituted Enynes in the Enantioselective Reaction

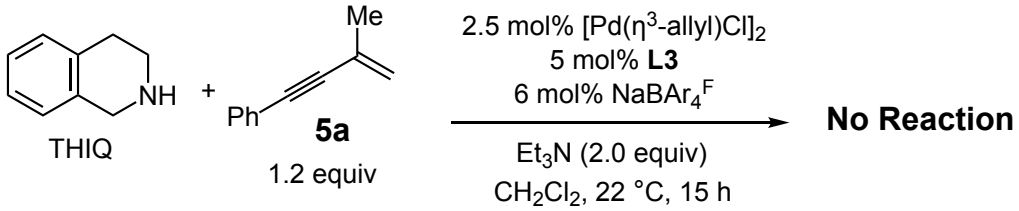


entry	ligand	solvent	yield (%)[b]	er[c]
1	**L1**	Et_2O	49	52:48
2	**L2**	CH_2Cl_2	40	61:39
3	**L3**	CH_2Cl_2	35	59:41

[a]Reactions run with 0.20 mmol THIQ in 0.25 mL solvent. [b]Isolated yield of pure **2o**. [c]Determined by HPLC analysis of pure **2o** in comparison with an authentic racemic standard.

2. Enantioselective Reaction Screening with 1,3-Disubstituted 1,3-Enynes

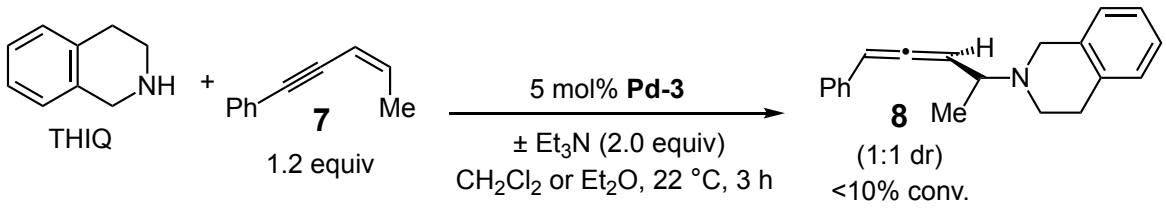
Efforts to expand the enantioselective reaction scope to 1,3-disubstituted enynes was met without success. Under standard reaction conditions, THIQ failed to add to enynes **5a**. Starting materials were recovered from this experiment and <5 % desired product formation was observed by ^{1}H NMR of the unpurified material.



3. Enantioselective Reaction Screening with 1,4-Disubstituted 1,3-Enynes

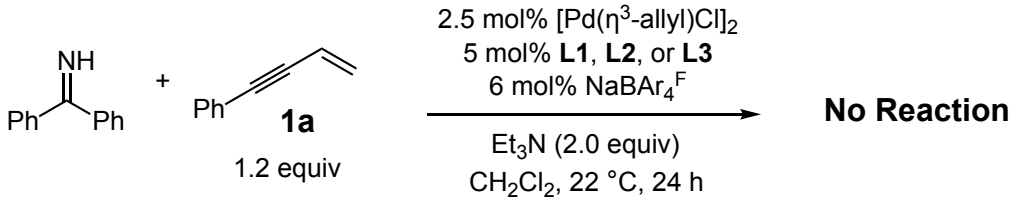
Efforts to expand the enantioselective reaction scope to 1,4-disubstituted enynes was met with little success. In the presence of a Pd-PHOX catalyst, the addition of THIQ to enyne **7** resulted in

< 10% conversion by ^{1}H NMR of the unpurified reaction mixture to a 1:1 mixture of diastereomers of **8**. The er of this product was not determined.



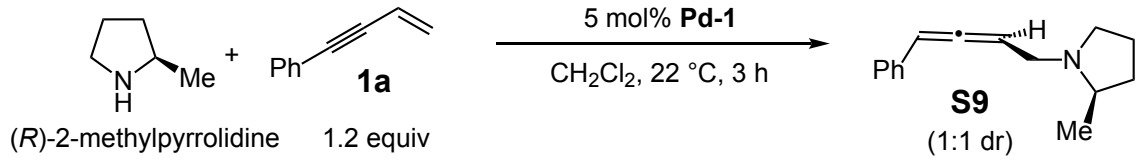
4. Enantioselective Reaction Screening with Benzophenone Imine

Efforts to expand the enantioselective reaction scope to benzophenone imine was met without success. Under standard reaction conditions with PHOX ligands **L1**, **L2** or **L3**, benzophenone imine failed to add to enyne **1a**. Starting materials were recovered from these experiments and <5 % desired product formation was observed by ^{1}H NMR of the unpurified material.



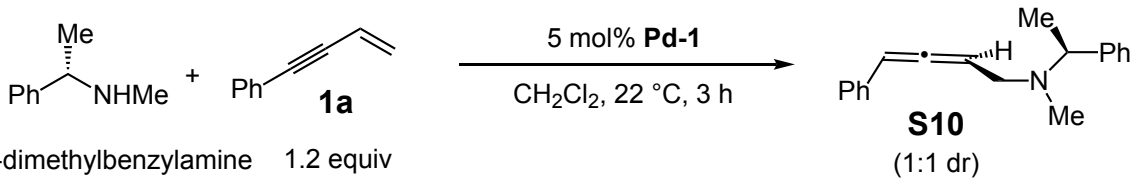
5. Addition of a Chiral Amine to Enyne **1a** Under Racemic Reaction Conditions

Experiments to determine if the chirality of the amine nucleophile can influence the stereochemistry of the allene in the product is presented below. When (*R*)-2-methylpyrrolidine (>99:1 er) or (*S*)-N,α-dimethylbenzylamine (>99:1 er) was added to enyne **1a** in the presence of 5 mol % **Pd-1**, the resulting products **S9** and **S10** were produced as 1:1 mixtures of diastereomers. Therefore, the chirality of amine nucleophiles has little to no influence on the stereochemistry of the allene.



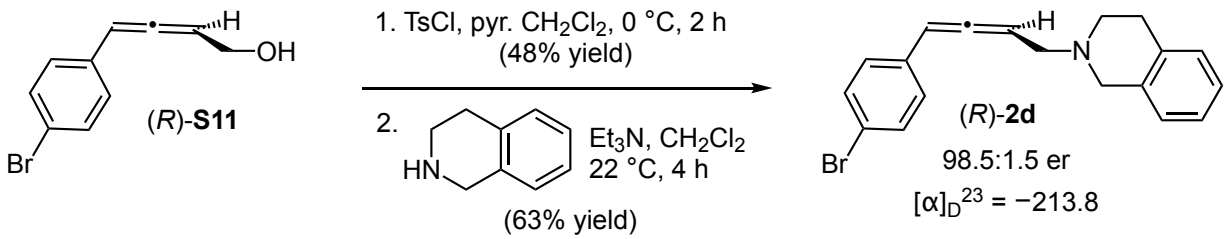
(*R*)-2-methyl-1-(4-phenylbuta-2,3-dien-1-yl)pyrrolidine (S9): Prepared by General Method B using **Pd-1** at 22 ˚C for 3 h. ^{1}H NMR analysis of the unpurified material revealed a 1:1 mixture of diastereomers. The material was purified by flash silica gel chromatography (60:40 hexanes:EtOAc with 2% v/v Et_3N additive) to yield **S9** as a pale yellow oil (34.7 mg, 0.163 mmol, 81.3% yield). The diastereomers could not be separated and all characterization data is for material

with 1:1 dr. **IR** (neat, cm^{-1}) 3030 (w), 2961 (m), 2869 (w), 2790 (m), 1949 (m), 1597 (w), 1495 (m), 1458 (m), 1375 (m), 1353 (w), 1308 (w), 1267 (w), 1220 (w), 1196 (w), 1167 (m), 1139 (m), 1071 (w), 1028 (w), 910 (m); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32–7.25 (4H, m), 7.21–7.15 (1H, m), 6.19–6.11 (1H, m), 5.68–5.60 (1H, m), 3.62–3.52 (1H, m), 3.22 (0.5 H, ddd, J = 8.8, 8.8, 2.7 Hz), 3.13 (0.5 H, ddd, J = 9.0, 9.0, 2.8 Hz), 3.01 (0.5 H, ddd, J = 13.4, 8.0, 2.0 Hz), 2.95 (0.5 H, ddd, J = 13.0, 8.4, 1.6 Hz), 2.50–2.37 (1H, m), 2.36–2.25 (1H, m), 1.99–1.88 (1H, m), 1.84–1.62 (2H, m), 1.50–1.38 (1H, m), 1.13 (1.5 H, d, J = 6.1 Hz), 1.11 (1.5 H, d, J = 6.1 Hz); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 205.8, 205.7, 134.6, 134.5, 128.6, 128.6, 126.8, 126.8, 126.7, 94.6, 94.5, 92.0, 91.9, 58.7, 58.4, 53.7, 53.5, 52.2, 51.8, 32.9, 32.9, 21.7, 21.6, 19.0, 18.9; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{15}H_{19}N$: 214.1590, found: 214.1596.



***N*-methyl-4-phenyl-*N*-((*S*)-1-phenylethyl)buta-2,3-dien-1-amine (S10):** Prepared by General Method B using **Pd-1** at 22 ˚C for 3 h. ^{1}H NMR analysis of the unpurified material revealed a 1:1 mixture of diastereomers. The material was purified by flash silica gel chromatography (85:15 hexanes:EtOAc) to yield **S10** as a pale yellow oil (35.5 mg, 0.135 mmol, 67.4% yield). The diastereomers could not be separated and all characterization data is for material with 1:1 dr. **IR** (neat, cm^{-1}) 3082 (w), 3061 (w), 3029 (w), 2973 (m), 2936 (w), 2874 (w), 2839 (w), 2782 (m), 1946 (m), 1599 (w), 1495 (m), 1458 (m), 1449 (m), 1418 (w), 1404 (w), 1369 (w), 1346 (w), 1313 (m), 1281 (w), 1200 (m), 1155 (w), 1122 (w), 1071 (m), 1054 (w), 1028 (m), 1013 (w), 999 (w), 954 (w); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36–7.15 (10H, m), 6.20–6.12 (1H, m), 5.64–5.54 (1H, m), 3.72–3.61 (1H, m), 3.39–3.25 (1H, m), 3.18–3.06 (1H, m), 2.30 (1.5 H, s), 2.30 (1.5H, s), 1.39 (1.5H, d, J = 6.5 Hz), 1.38 (1.5H, d, J = 6.6 Hz); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 206.0, 206.0, 144.1, 144.0, 134.6, 134.5, 128.6, 128.3, 127.6, 127.6, 127.0, 126.9, 126.8, 126.8, 126.7, 94.5, 91.6, 62.7, 62.6, 53.7, 53.6, 39.0, 38.9, 19.7, 19.6 (note: four sp^2 carbons could not be identified due to complex overlap of diastereomer peaks); **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{19}H_{21}N$: 264.1747, found: 264.1754.

VIII. Stereoproof



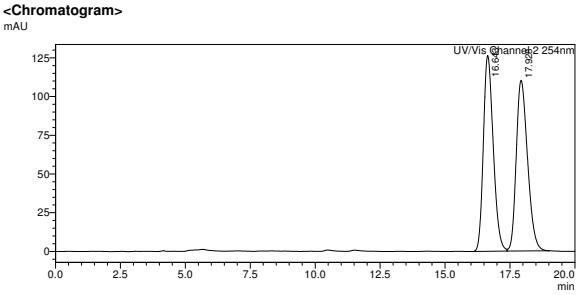
(*R*)-**S11** was prepared by a previously described method where the absolute configuration is known.[30]

(*R*)-4-(4-bromophenyl)buta-2,3-dien-1-yl 4-methylbenzenesulfonate (S12): To an oven-dried 2-dram vial equipped with a magnetic stirring rod was added (*R*)-**S11** (225 mg, 1.00 mmol, 1.00 equiv) and CH_2Cl_2 (1.0 mL). The reaction mixture was allowed to cool to 0 °C in an ice water bath, and then pyridine (161 μL, 2.00 mmol, 2.00 equiv) was added followed by *p*-TsCl (286 mg, 1.50 mmol, 1.50 equiv). The reaction mixture was allowed to stir at 0 °C for 2 h. The reaction contents were then partitioned between water (10 mL) and EtOAc (5 mL), and the aqueous layer was separated from the organics and washed with EtOAc (5 mL). The combined organic fractions were dried over $MgSO_4$, filtered, and concentrated. The product was then purified by flash silica gel chromatography (90:10 to 85:15 hexanes:EtOAc) to yield the tosylate (*R*-**S12**) as a colorless oil (183 mg, 0.482 mmol, 48.2 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83–7.75 (2H, m), 7.44–7.37 (2H, m), 7.31 (2H, d, J = 8.2 Hz), 7.11–7.04 (2H, m), 6.19 (1H, dt, J = 6.4, 2.1 Hz), 5.64 (1H, app. q, J = 6.9 Hz), 4.67–4.58 (2H, m), 2.43 (3H, s). This product was found to be particularly unstable and so was used immediately in the next step.

(R)-2-(4-(4-bromophenyl)buta-2,3-dien-1-yl)-1,2,3,4-tetrahydroisoquinoline (*R*-2d): The tosylate (*R*)-**S12** prepared above (114 mg, 0.300 mmol, 1.00 equiv) was added to an oven-dried 2-dram vial equipped with a magnetic stirring rod and dissolved in CH_2Cl_2 (1.0 mL). To this solution was added Et_3N (84.0 μL, 0.600 mmol, 2.00 equiv) and 1,2,3,4-tetrahydroisoquinoline (THIQ, 57.0 μL, 0.450 mmol, 1.50 equiv). The mixture was allowed to stir at ambient temperature for 4 h. The reaction contents were then partitioned between sat aq $NaHCO_3$ (10 mL) and EtOAc (5 mL). The aqueous layer was separated from the organics and washed with EtOAc (2 X 3 mL). The combined organic fractions were dried over $MgSO_4$, filtered, and concentrated. Flash silica gel chromatography (75:25 hexanes:EtOAc) then afforded (*R*)-**2d** as a yellow solid (64.0 mg, 0.188 mmol, 62.7% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46–7.40 (2H, m), 7.20–7.14 (2H, m), 7.14–7.07 (3H, m), 7.04–6.99 (1H, m), 6.16 (1H, dt, J = 6.4, 2.4 Hz), 5.68 (1H, ddd, J 6.9, 6.9, 6.9 Hz), 3.74 (1H, AB_q, J_{AB} = 15.8 Hz), 3.70 (1H, AB_q, J_{AB} = 15.8 Hz), 3.38–3.29 (2H, m), 2.97–2.89 (2H, m), 2.85–2.79 (2H, m); **$[\alpha]_D^{23}$** = –213.8 (c = 1.0, $CHCl_3$) for a sample of 98.5:1.5 er. The spectral data match those from (*R*)-**2d** as prepared by enyne hydroamination. The direction of the specific rotation and comparison of HPLC retention times confirm that the major enantiomer formed by enantioselective hydroamination of the corresponding 1,3-enyne with **L3** is the (*R*)-enantiomer. The absolute stereochemistry for all other allene products is based on the stereochemical assignment for (*R*)-**2d**.

HPLC: Column: Cellulose-3 (3 μm, 4.6 mm X 250 mm). Mobile phase: 80:20 hexanes:*i*-PrOH, 1 mL/min. Detection wavelength: 254 nm. Er = 98.5:1.5

<Chromatogram>

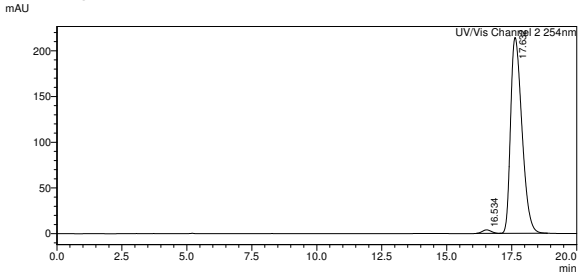


<Peak Table>

UV/Vis Channel 2 254nm

Peak#	Ret. Time	Area	Area%
1	16.643	3352440	50.085
2	17.928	3341091	49.915
Total		6693531	100.000

<Chromatogram>



<Peak Table>

UV/Vis Channel 2 254nm

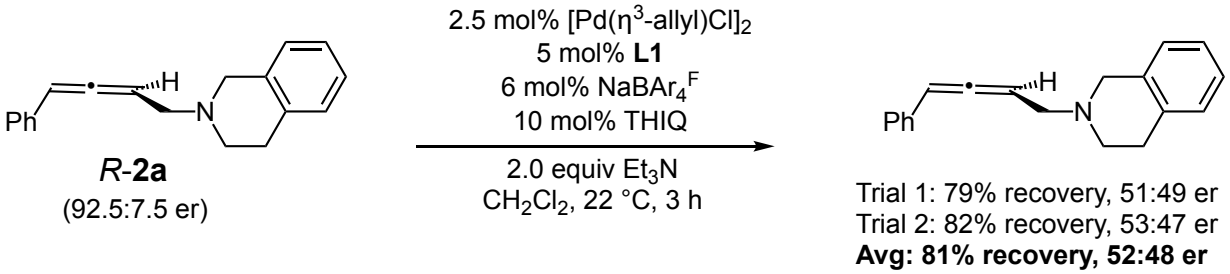
Peak#	Ret. Time	Area	Area%
1	16.534	93091	1.408
2	17.632	6517740	98.592
Total		6610831	100.000

IX. Transamination/Reaction Reversibility Studies

The following experiments were carried out to elucidate aspects of the mechanism pertaining to reaction reversibility and racemization of allene products, and were conducted based on the below general procedure.

General Procedure F (Reversibility Studies): In an N_2-filled glovebox, to a 2-dram vial equipped with a magnetic stirring rod were added successively: $[Pd(\eta^3\text{-allyl})Cl]_2$ (1.8 mg, 5.0 μmol, 2.5 mol %), appropriate ligand (0.010 mmol, 5.0 mol %), and $NaBAr_4^F$ (10.6 mg, 0.012 mmol, 6.0 mol %). To a separate 2-dram vial was added (*R*)-**2a** (52.3 mg, 0.200 mmol, 1.00 equiv, 92.5:7.5 er) and dissolved in CH_2Cl_2 (50 μL). The solution containing (*R*)-**2a** was added by micro syringe to the solution containing the Pd pre-catalyst (rinsing with an addition 50 μL CH_2Cl_2). To the resulting solution was added Et_3N (56 μL, 0.40 mmol, 2.0 equiv) followed by appropriate amine nucleophile (THIQ = 2.5 μL, 0.020 mmol, 10 mol % *or* morpholine = 17.0 μL, 0.200 mmol, 1.00 equiv). The solutions were allowed to stir at ambient temperature for 3 h and then worked up and purified as described for **2a** and **2an** as appropriate (see Substrate Scope section of SI).

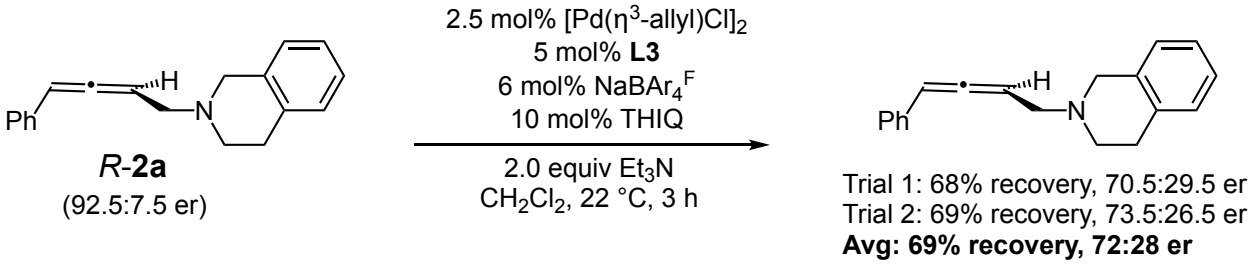
1. Reaction Reversibility Study with **L1**



R-**2a**
(92.5:7.5 er)

Trial 1: 79% recovery, 51:49 er
Trial 2: 82% recovery, 53:47 er
Avg: 81% recovery, 52:48 er

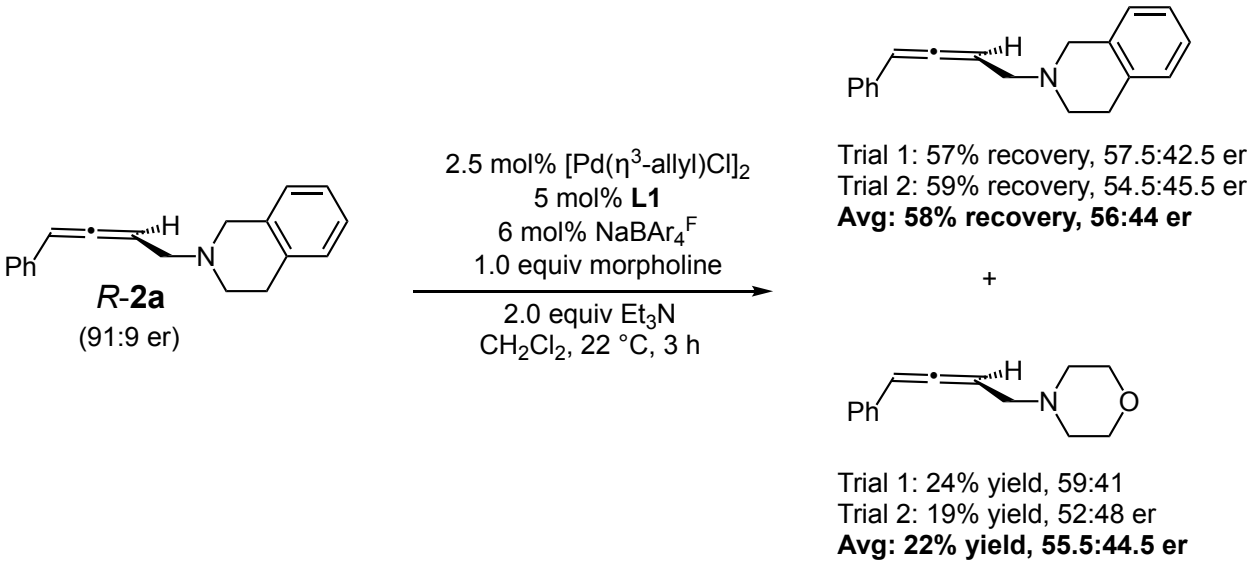
2. Reaction Reversibility Study with **L3**



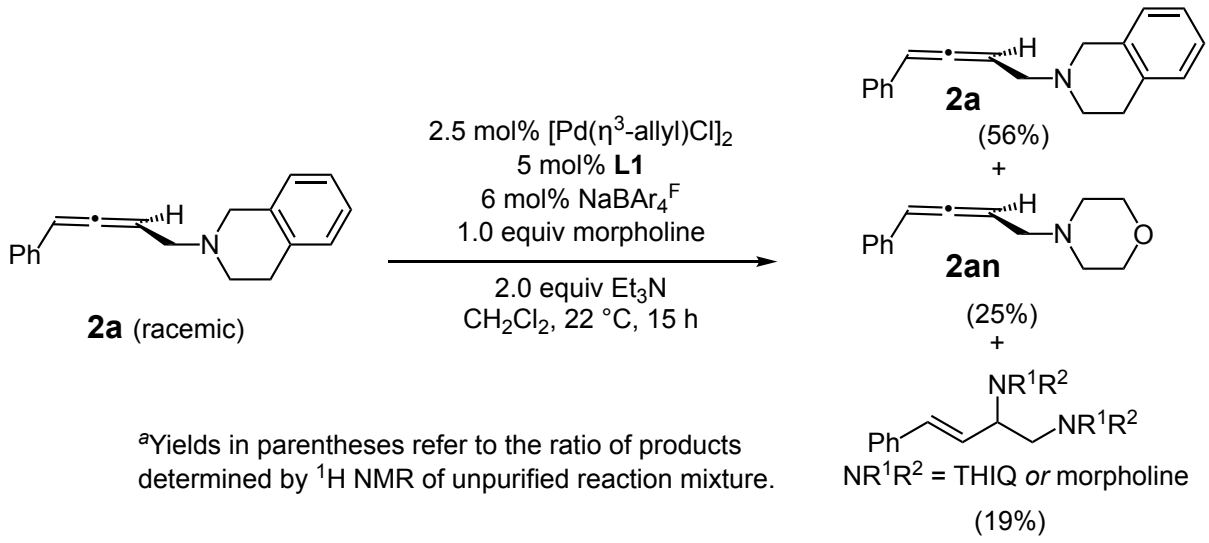
R-**2a**
(92.5:7.5 er)

Trial 1: 68% recovery, 70.5:29.5 er
Trial 2: 69% recovery, 73.5:26.5 er
Avg: 69% recovery, 72:28 er

3. Transamination Study with **L1** to Elucidate Mechanism of Racemization



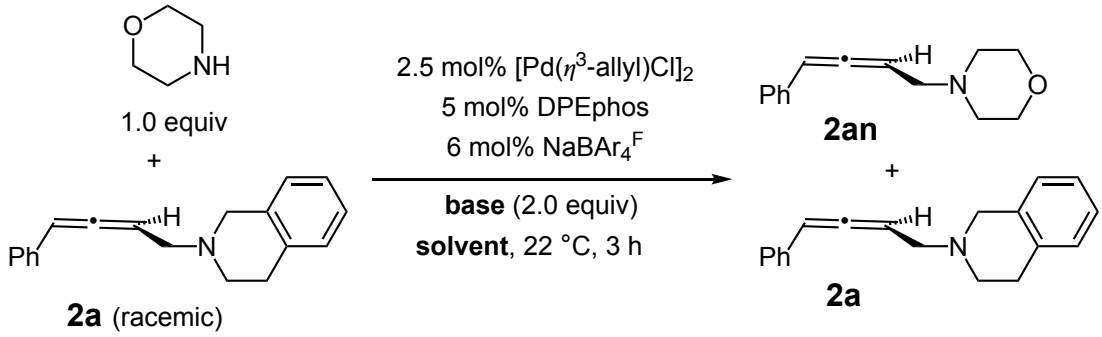
4. Prolonged Reaction Times for Transamination Experiments Results in Hydroamination of Allenes to Afford Bis-Amination Products.[a]



[a]Yields in parentheses refer to the ratio of products determined by ^{1}H NMR of unpurified reaction mixture.

5. Transamination with DPEphos Derived Pd Catalyst Reveals Approximately 1:1 Ratio of Morpholine:THIQ Adducts Under a Variety of Conditions (Table S6).

Table S6. Solvent and Base Screening of Transamination Reaction with DPEphos Pd Catalyst



entry	solvent	base	2an:2a[a]
1	Et_2O	Et_3N	1.5:1
2	CH_2Cl_2	Et_3N	1.3:1
3	THF	Et_3N	1.4:1
4	hexanes	Et_3N	1.2:1
5	cyclohexane	Et_3N	1.4:1
6	dioxane	Et_3N	1.3:1
7	toluene	Et_3N	1.3:1
8	MeCN	Et_3N	1.3:1
9	acetone	Et_3N	1.3:1
10	Et_2O	iPr_2NEt	1.5:1
11	Et_2O	DABCO	1.3:1
12	Et_2O	DBU[b]	>20:1
13	Et_2O	TMP	1.3:1
14	Et_2O	DMAP	0.9:1
15	Et_2O	TMG[b,c]	>20:1

[a]Determined by ^1H NMR of the unpurified reaction mixture.
[b]Base additive does not promote the hydroamination of 1,3-enynes.
[c]TMG = 1,1,3,3-tetramethylguanidine

X. Enantiomerization Kinetic Studies

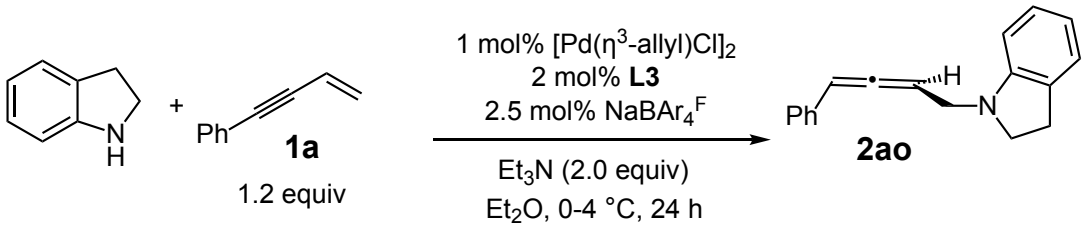
To better understand the kinetics of enantiomerization of our allene products, we performed experiments aimed at monitoring the er over time for several different amine products. We chose to study indoline (pK_a conjugate acid = 5.6 in H_2O),[31] morpholine (pK_a conjugate acid = 9.2 in DMSO and 8.5 in H_2O),[32] and piperidine (pK_a conjugate acid = 10.9 in DMSO and 11.1 in H_2O)[32] adducts **2ao**, **2an**, and **2w**, respectively, because these cover a broad range in terms pK_a and Lewis basicity.

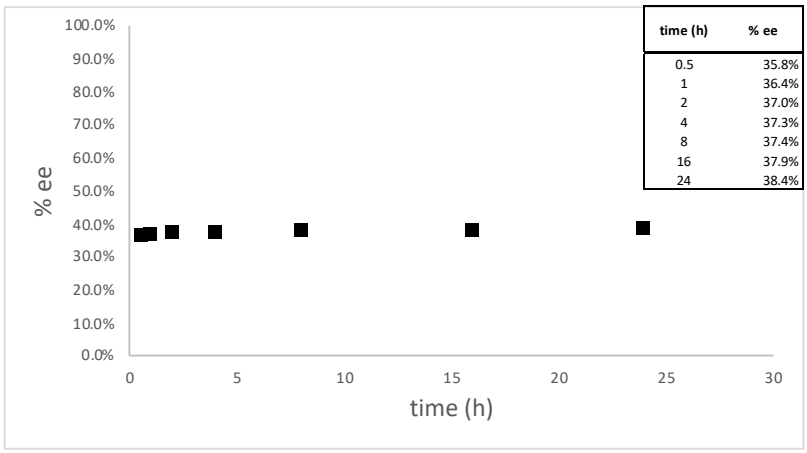
1. Enantiomerization of Allenes in the Forward Progression of the Reaction

We aimed to discover if the rate and extent of er deterioration over time for the optimized reaction. A general procedure for these experiments is found below:

General Procedure F: In an N_2-filled glovebox, to a 2-dram vial equipped with a magnetic stirring rod were added successively: $[Pd(\eta^3\text{-allyl})Cl]_2$ (3.7 mg, 10.0 μmol, 1.0 mol %), **L3** (13.5 mg, 0.020 mmol, 2.0 mol %), and $NaBAr_4^F$ (22.1 mg, 0.025 mmol, 2.5 mol %). The mixture was dissolved in Et_2O (1.25 mL) and allowed to stir for *ca.* 5 min, resulting in a deep orange/red solution, and then enyne **1a** (162 μL, 1.20 mmol, 1.20 equiv) was added. The reaction vials were then capped with a PTFE lined cap, removed from the glovebox, and allowed to cool in an ice water bath at 0–4 °C for *ca.* 15 minutes before Et_3N (279 μL, 2.00 mmol, 2.00 equiv) and appropriate amine nucleophile (1.00 mmol, 1.00 equiv) were added. The reactions were allowed to stir at 4 °C for 24 h with aliquots (0.15 mL) taken at: 30 min, 1 h, 2 h, 4 h, 8 h, 16 h, and 24 h. These aliquots were passed through a short plug of silica gel eluting with a solvent system appropriate for each amine (**2ao** = *ca.* 20 mL 90:10 hexanes:EtOAc, **2an** = *ca.* 20 mL 60:40 hexanes:EtOAc, and **2w** = *ca.* 20 mL 60:40 hexanes:EtOAc with 2% v/v Et_3N additive). The aliquots were then concentrated under reduced pressure and dissolved in HPLC grade solvents (**2ao** and **2an** = 10 mL 80:20 hexanes:IPA, **2w** = 10 mL MeOH) and analyzed promptly (within 2 h) by HPLC for enantiomeric ratio. For HPLC methods and representative chromatograms for each compound, see the "Substrate Scope" section for **2ao**, **2an**, and **2w**.

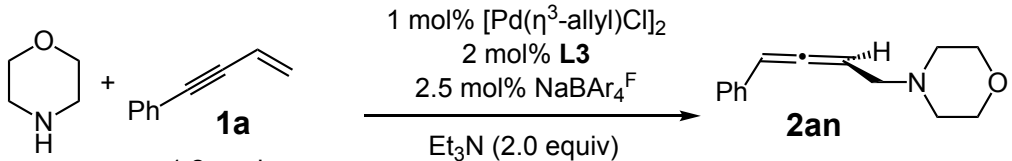
Chart S1. Enantiomeric Ratio of **2ao** During Course of Reaction

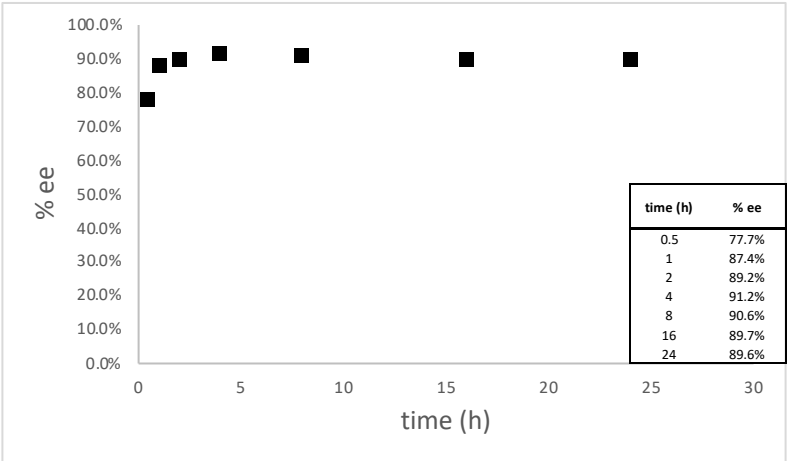




time (h)	% ee
0.5	35.8%
1	36.4%
2	37.0%
4	37.3%
8	37.4%
16	37.9%
24	38.4%

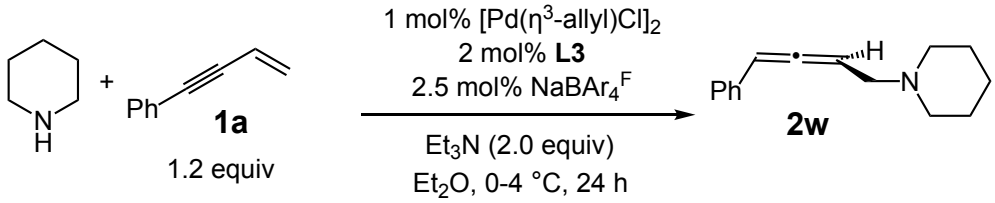
Chart S2. Enantiomeric Ratio of **2an** During Course of Reaction

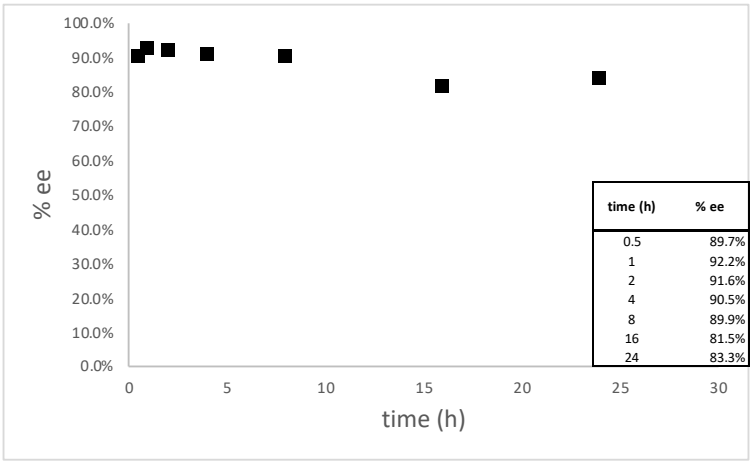




time (h)	% ee
0.5	77.7%
1	87.4%
2	89.2%
4	91.2%
8	90.6%
16	89.7%
24	89.6%

Chart S3. Enantiomeric Ratio of **2w** During Course of Reaction

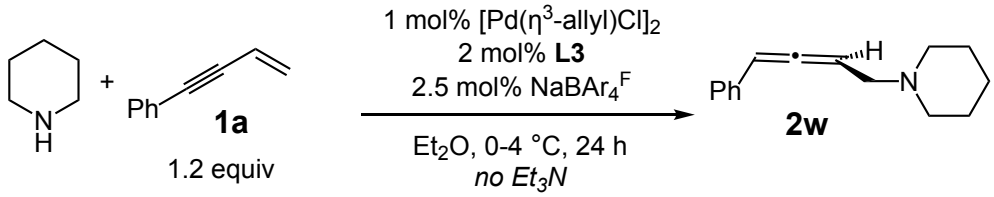


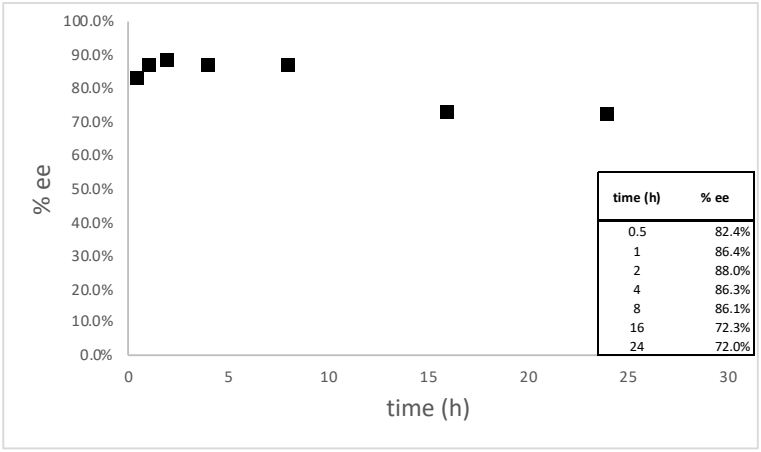


time (h)	% ee
0.5	89.7%
1	92.2%
2	91.6%
4	90.5%
8	89.9%
16	81.5%
24	83.3%

We additionally performed an experiment identical to Chart S3 but without Et_3N (following General Procedure F but without addition of Et_3N).

Chart S4. Enantiomeric Ratio of **2w** During Course of Reaction without Et_3N





time (h)	% ee
0.5	82.4%
1	86.4%
2	88.0%
4	86.3%
8	86.1%
16	72.3%
24	72.0%

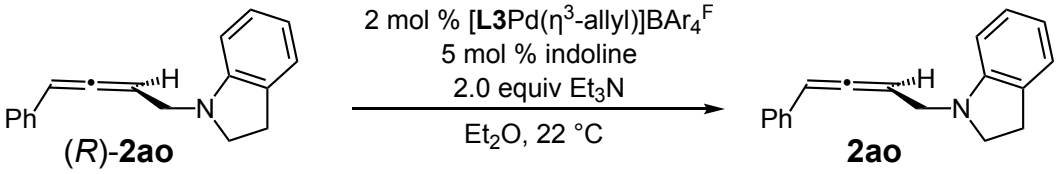
From the data above, we can conclude that an insignificant amount of enantiomerization occurs for indoline (**2ao**) and morpholine (**2an**) adducts (smaller pK_a values), whereas piperidine adduct **2w** demonstrates a very slow rate of enantiomerization (higher pK_a). It is unclear from the data above if Et_3N plays a significant role in the rate of enantiomerization, although slightly faster enantiomerization of **2w** occurs in its absence.

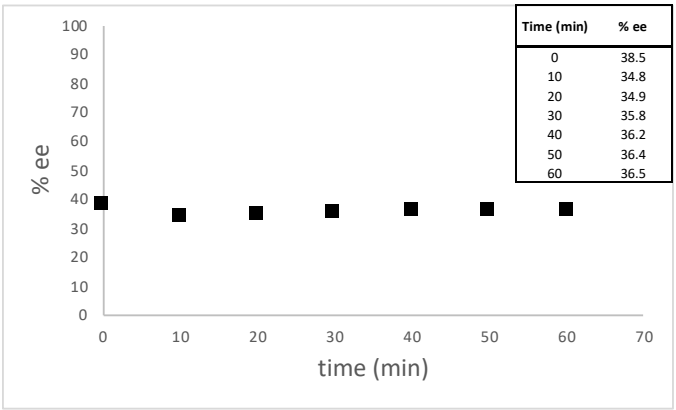
2. Isolated **2ao** Resubjected to Reaction Conditions

Given the unusually low enantioselectivity of indoline addition, we performed an experiment where (*R*)-**2ao** (69:31 er) was resubjected to the reaction conditions to measure the rate of enantiomerization.

In an N_2-filled glovebox, to a 1-dram vial was added [**L3**Pd(η^3-allyl)]BAr_4^F (3.4 mg, 2.0 μmol, 2.0 mol %). This vial was capped with a rubber septum and removed from the glovebox. To this vial was added a solution of (*R*)-**2ao** (24.7 mg, 0.100 mmol, 1.00 equiv), indoline (25μL of a freshly prepared 0.20 M solution in Et_2O, 5.0 μmol, 5.0 mol %), and Et_3N (28.0 μL, 0.200 mmol, 2.00 equiv) in Et_2O (2 x 0.50 mL) via cannula transfer at ambient temperature. Experiments that indicate they were performed in the absence of Et_3N did not include this component in above solution. Aliquots (*ca.* 50 μL) were taken at 10 min intervals during the reaction. These aliquots were immediately passed through a short plug of silica gel eluting with 80:20 hexanes:EtOAc (*ca.* 5–10 mL) and subsequently concentrated under reduced pressure. The concentrated aliquots were dissolved in HPLC grade 80:20 hexanes:IPA (*ca.* 1–2 mL) and analyzed promptly (within 2 h) by HPLC for enantiomeric ratio. For HPLC methods and representative chromatograms, see the "Substrate Scope" section for **2ao**.

Chart S5. Initial Rate of Enantiomerization of **2ao**

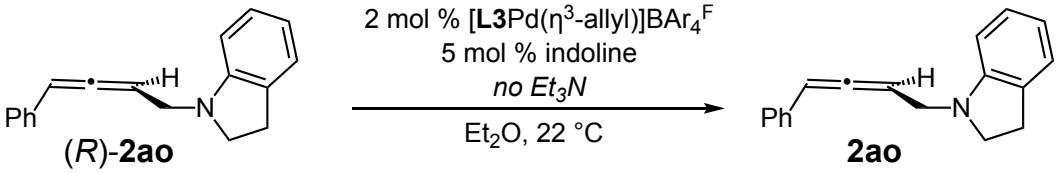


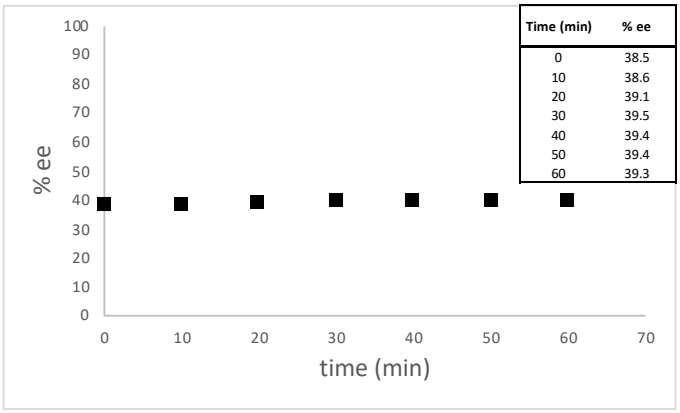


Time (min)	% ee
0	38.5
10	34.8
20	34.9
30	35.8
40	36.2
50	36.4
60	36.5

An additional aliquot was taken after 46 h, but the er remained unchanged (36.8% ee).

Chart S6. Initial Rate of Enantiomerization of **2ao** without Et_3N





Time (min)	% ee
0	38.5
10	38.6
20	39.1
30	39.5
40	39.4
50	39.4
60	39.3

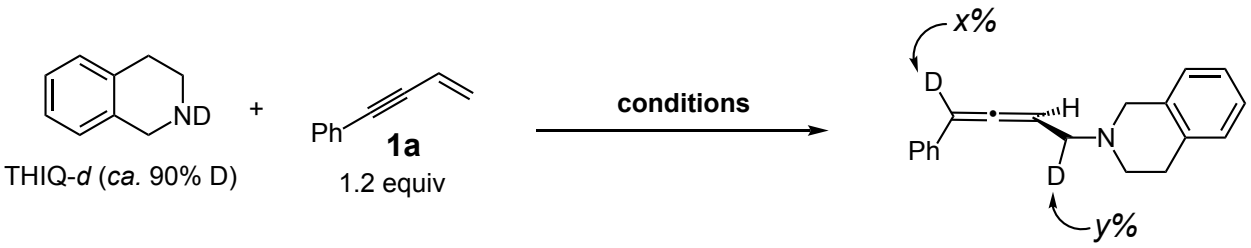
An additional aliquot was taken after 46 h, but the er remained unchanged (38.0% ee).

From the data in Charts S5 and S6 above, we can conclude that indoline adduct **2ao** does not significantly enantiomerize in the presence of a Pd catalyzed derived from **L3**. Therefore, the low enantioselectivity observed with indoline is likely due to kinetics of nucleophile addition and not post-reaction enantiomerization.

XI. Deuterium Labeling Studies

Deuterium labeling studies were carried out under standard non-enantioselective reaction conditions (General Method C) and enantioselective conditions (General Method D). All reactions performed on a 0.20 mmol scale with respect to THIQ-*d* and were otherwise carried out as described in "Substrate Scope" section of the SI (see above for **2a**). THIQ-*d* (*ca.* 90% deuterium incorporation) was prepared as previously described. Deuterium incorporation was measured based on disappearance of peaks in the ^{1}H NMR spectra of purified products using the AB quartet centered at *ca.* δ 3.76 (2H) in $CDCl_3$ as a reference for every measurement. An example ^{1}H NMR spectrum of ***d*-2a** can be found in the Supplementary Information Part B. Recovered starting material enyne from the reactions indicated <5% deuterium incorporation.

Table S7. Deuterium Labeling Experiments

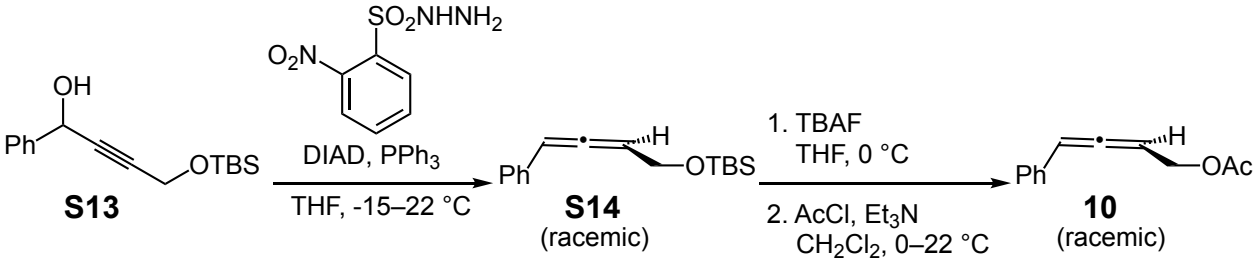


THIQ-*d* (*ca.* 90% D)

conditions	trial	yield (%)	e.r.	x%	y%
General Method C (DPEphos)	1	83	n/a	82%	<5%
	2	81	n/a	83%	<5%
	avg	**82**	**n/a**	**83%**	**<5%**
General Method D (**L3**)	1	73	91:9	80%	<5%
	2	72	91:9	79%	<5%
	avg	**73**	**91:9**	**80%**	**<5%**

XII. Allylic Substitution Experiments

The preparation of **S13** has been reported previously.[33]

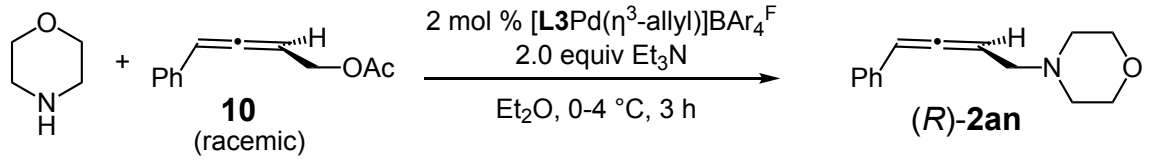


***tert*-butyldimethyl((4-phenylbuta-2,3-dien-1-yl)oxy)silane (S14):** Prepared by the method of Myers and co-workers.[34] To a 250-mL round-bottom flask equipped with a magnetic stirring rod was added triphenylphosphine (3.75 g, 14.3 mmol, 1.30 equiv) and dissolved in THF (40 mL). This solution was cooled to −15 °C and diisopropyl azodicarboxylate (2.82 mL, 14.3 mmol, 1.30 equiv) was added dropwise via syringe. After 10 min of stirring at this temperature, **S13** (3.04 g, 11.0 mmol, 1.00 equiv) was added as a solution in THF (40 mL) via cannula transfer. After an additional 10 min of stirring, 2-nitrobenzenesulfonohydrazide (3.11 g, 14.3 mmol, 1.30 equiv) was added as a solution in THF (40 mL) via cannula transfer. The resulting yellow solution was allowed to stir at −15 °C for 1 h and then warm to ambient temperature. Stirring was allowed to continue at ambient temperature for 13 h. After this time, the reaction mixture was concentrated under reduced pressure. Purification by flash silica gel chromatrography (99:1 hexanes:Et_2O) afforded **S14** as a yellow oil (1.20 g, 4.59 mmol, 41.7% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30–7.25 (4H, m), 7.21–7.15 (1H, m), 6.21 (dt, J = 6.4, 2.7 Hz), 5.67 (ddd, J = 6.3, 6.3, 6.3 Hz), 4.31–4.26 (2H, m), 0.89 (9H, s), 0.08 (3H, s), 0.07 (3H, s). Spectral data match those previously reported.[33]

4-phenylbuta-2,3-dien-1-ol (S15): To a 100-mL round-bottom flask equipped with a magnetic stirring rod was added **S14** (1.04 g, 4.00 mmol, 1.00 equiv) and dissolved in THF (12 mL) and then cooled to 0 °C. TBAF (1.0 M in THF, 6.0 mL, 1.5 equiv) was added dropwise via syringe and stirring was allowed to continue at 0 °C for 3 h. The reaction mixture was partitioned between sat aq brine (50 mL) and Et_2O (50 mL). The aqueous layer was separated from organics and washed with Et_2O (30 mL). The combined organic fractions were dried over Na_2SO_4, filtered, and concentrated. Purification by flash silica gel chromatography (80:20 to 70:30 hexanes:Et_2O) afforded **S15** as a yellow oil (464 mg, 3.17 mmol, 79.3% yield).). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33–7.26 (4H, m), 7.23–7.17 (1H, m), 6.31 (1H, dt, J = 6.4, 2.9 Hz), 5.78 (1H, ddd, J = 6.0, 6.0, 6.0 Hz), 4.28–4.20 (2H, m), 1.59–1.54 (1H, m). Spectral data match those previously reported.[35]

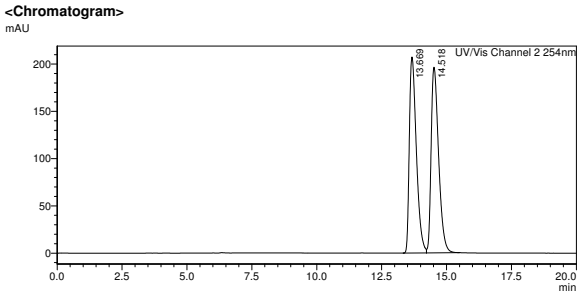
4-phenylbuta-2,3-dien-1-yl acetate (10): To a 50-mL round-bottom flask equipped with a magnetic stirring rod was added **S15** (421 mg, 2.88 mmol, 1.00 equiv) and dissolved in CH_2Cl_2 (10 mL). This solution was cooled to 0 °C and Et_3N (0.80 mL, 5.8 mmol, 2.0 equiv) was added followed by acetyl chloride (0.41 mL, 5.8 mmol, 2.0 equiv) dropwise via syringe. The reaction mixture was allowed to warm to ambient temperature and allowed to stir for 30 min. The reaction mixture was then poured into sat aq $NaHCO_3$ (20 mL). The aqueous layer was separated from organics and washed with CH_2Cl_2 (2 X 5 mL). The combined organic fractions were dried over $MgSO_4$, filtered, and concentrated. Purification by flash silica gel chromatography (90:10

hexanes:Et_2O) afforded pure **10** as a pale yellow oil (471 mg, 2.50 mmol, 86.9% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33–7.25 (4H, m), 7.23–7.18 (1H, m), 6.28 (1H, dt, J = 6.4, 2.5 Hz), 5.70 (1H, ddd, J = 6.5, 6.5, 6.5 Hz), 4.66 (2H, dd, J = 6.6, 2.5 Hz), 2.06 (3H, s). Spectral data match those previously reported.[36]



(*R*)-4-(4-phenylbuta-2,3-dien-1-yl)morpholine (2an): In an N_2-filled glovebox, to a dry 2-dram vial equipped with a magnetic stirring rod was added [(**L3**)Pd(η^3-allyl)]BAr_4^F (6.7 mg, 4.0 μmol, 2.0 mol %) and dissolved in Et_2O (0.50 mL). To this solution was added **10** (42.5 μL, 0.240 mmol, 1.20 equiv). At this point, the vial was capped with a PTFE lined cap and removed from the glovebox. The vial was allowed to cool in an ice bath (0 °C) for *ca.* 10 min before Et_3N (56 μL, 0.40 mmol, 2.0 equiv) was added followed by morpholine (17.5 μL, 0.200 mmol, 1.00 equiv). The reaction mixture was allowed to stir at 0–4 °C for 3 h and then passed through a plug of silica gel eluting with 1:1 hexanes:EtOAc with 2 % v/v Et_3N addition (*ca.* 20 mL) and concentrated under reduced pressure. Purification by flash silica gel chromatography (70:30 hexanes:EtOAc with 2% v/v Et_3N additive) afforded **2an** as a colorless semi-solid (18.8 mg, 0.0873 mmol, 43.7 %). HPLC analysis revealed this material to be 91:9 er with the same major enantiomer as obtained through hydroamination of **1a**.

HPLC: Column: Cellulose-3 (3 µm, 4.6 mm X 250 mm). Mobile phase: 99.9:0.1 hexanes:*i*-PrOH, 1 mL/min. Detection wavelength: 254 nm. Er = 91:1.



<Peak Table>
UV/Vis Channel 2 254nm

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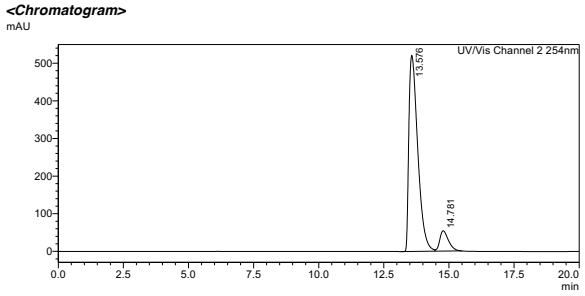
2	14.518	3924727	50.198
Total		7818563	100.000

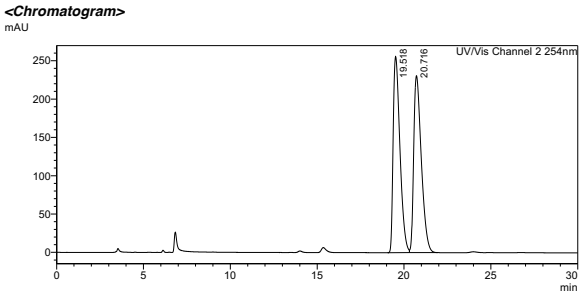


<Peak Table>
UV/Vis Channel 2 254nm

Peak#	Ret. Time	Area	Area%
1	13.576	12368629	90.775
2	14.781	1256943	9.225
Total		13625572	100.000

The starting material **10** was recovered from the above experiment (26.6 mg, 58.9% recovery based on 1.20 equiv used). This material was additionally analyzed by HPLC and determined to be racemic.

HPLC: Column: Cellulose-3 (3 µm, 4.6 mm X 250 mm). Mobile phase: 99.9:0.1 hexanes:*i*-PrOH, 1 mL/min. Detection wavelength: 254 nm.



<Peak Table>
UV/Vis Channel 2 254nm

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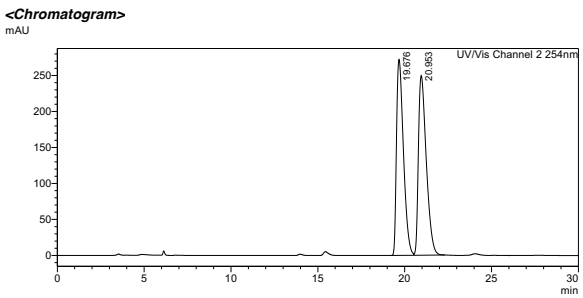
2	20.716	7046829	50.192
Total		14039629	100.000

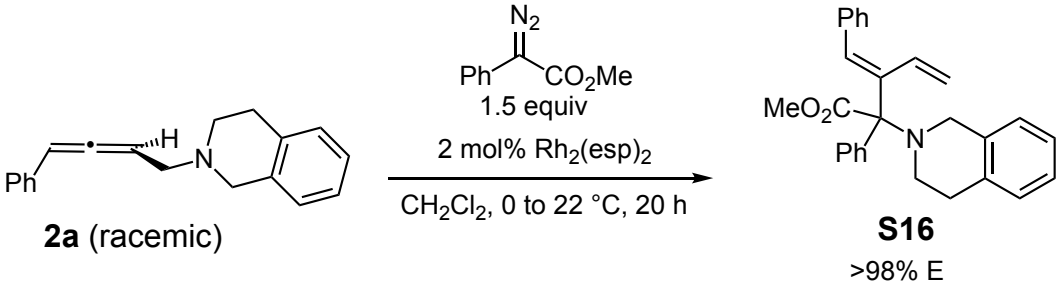


<Peak Table>
UV/Vis Channel 2 254nm

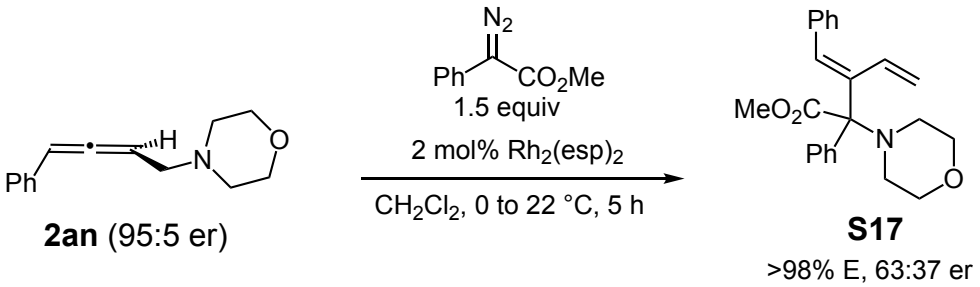
Peak#	Ret. Time	Area	Area%
1	19.676	7601528	49.032
2	20.953	7901761	50.968
Total		15503289	100.000

HPLC traces above show starting material allenyl acetate **10** (left) and **10** recovered from above allylic substitution reaction with morpholine (right). The recovered **10** is still a racemate indicating that kinetic resolution does not take place.

XIII. Derivatization of Allene Products



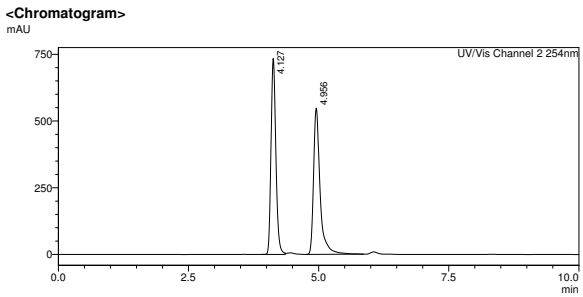
methyl (*E*)-3-benzylidene-2-(3,4-dihydroisoquinolin-2(1*H*)-yl)-2-phenylpent-4-enoate (S16): To an oven-dried 2-dram vial equipped with a magnetic stirring rod were added *rac*-**2a** (52.3 mg, 0.200 mmol, 1.00 equiv) and $Rh_2(esp)_2$ (3.0 mg, 4.0 μmol, 2.0 mol %). CH_2Cl_2 (0.50 mL) was added and the resulting solution was allowed to cool to 0 °C. Methyl 2-diazo-2-phenylacetate (53 mg, 0.30 mmol, 1.5 equiv) was added as a solution in CH_2Cl_2 (0.50 mL) dropwise via syringe. The reaction mixture was allowed to warm gradually to ambient temperature and then stir for 20 h. The reaction mixture was then passed through a short plug of neutral alumina, eluting with 1:1 hexanes:EtOAc (*ca.* 20 mL) and the solution was concentrated. ^{1}H NMR analysis of the unpurified reaction mixture indicated that the product was >98% *E*. The product was then purified by flash silica gel chromatography (90:10 hexanes:EtOAc) to afford **S16** as a white solid (68.1 mg, 0.166 mmol, 83.2% yield). **IR** (neat, cm^{-1}) 3021 (w), 2947 (w), 2829 (w), 2246 (w), 1720 (s), 1599 (w), 1492 (m), 1445 (m), 1429 (m), 1382 (w), 1226 (s), 1175 (s), 1077 (m), 1035 (m), 1010 (m), 906 (s); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65–7.58 (2H, m), 7.37–7.08 (12H, m), 6.96 (1H, d, J = 7.3 Hz), 6.41 (1H, dd, J = 18.0, 11.8 Hz), 5.05 (1H, dd, J = 18.0, 1.5 Hz), 5.01 (1H, dd, J = 12.0, 1.5 Hz), 3.83 (3H, s), 3.80 (1H, AB_q, J_{AB} = 15.0 Hz), 3.73 (1H, AB_q, J_{AB} = 15.0 Hz), 3.14–2.89 (3H, m), 2.76–2.68 (1H, m); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 169.5, 139.2, 138.6, 137.4, 135.9, 134.8, 133.3, 129.8, 129.7, 129.3, 128.8, 128.1, 127.5, 127.1, 127.0, 126.7, 126.1, 125.6, 119.3, 79.1, 51.3, 51.2, 47.2, 30.3; **HRMS** (ESI$^+$) $[M+H]^+$ calc'd for $C_{28}H_{27}NO_2$: 410.2115, found: 410.2120; **MP** = 40–44 °C.



methyl (*E*)-3-benzylidene-2-morpholino-2-phenylpent-4-enoate (S17): To an oven-dried 2-dram vial equipped with a magnetic stirring rod were added (*R*)-**2an** (32.3 mg, 0.150 mmol, 1.00 equiv, 95:5 er) and $Rh_2(esp)_2$ (2.3 mg, 3.0 μmol l, 2.0 mol %). CH_2Cl_2 (0.35 mL) was added and the resulting solution was allowed to cool to 0 °C. Methyl 2-diazo-2-phenylacetate (40 mg, 0.23 mmol, 1.5 equiv) was added as a solution in CH_2Cl_2 (0.40 mL) dropwise via syringe. The reaction mixture was allowed to warm gradually to ambient temperature and then stir for 5 h. The reaction mixture was then passed through a short plug of neutral alumina, eluting with 1:1 hexanes:EtOAc (*ca.* 20 mL) and the solution was concentrate. ^{1}H NMR analysis of the unpurified reaction mixture

indicated that the product was >98% *E*. The product was then purified by flash silica gel chromatography (90:10 hexanes:EtOAc) to afford **S17** as a colorless viscous oil (46.1 mg, 0.127 mmol, 84.5% yield). **IR** (neat, cm^{-1}) 3021 (w), 2951 (m), 2889 (w), 2848 (m), 2246 (w), 1721 (s), 1599 (w), 1492 (m), 1445 (m), 1432 (w), 1390 (w), 1291 (w), 1266 (m), 1227 (s), 1193 (s), 1113 (s), 1070 (w), 1008 (m), 908 (s); **^{1}H NMR** (400 MHz, $CDCl_3$) 7.56–7.49 (2H, m), 7.34–7.17 (8H, m), 7.04 (1H, s), 6.36 (1H, dd, J = 18.0, 11.9 Hz), 5.05 (1H, d, J = 17.9 Hz), 4.99 (1H, d, J = 11.8 Hz), 3.80 (3H, s), 3.80–3.73 (4H, m), 2.76–2.60 (2H, m), 2.57–2.42 (2H, m); δ **^{13}C NMR** (125 MHz, $CDCl_3$) δ 169.5, 138.3, 138.0, 137.2, 133.3, 130.6, 129.6, 129.3, 128.1, 127.5, 127.2, 127.1, 119.1, 78.8, 67.8, 51.2, 49.5; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{23}H_{25}NO_3$: 364.1907, found: 364.1914.

HPLC: Column: Amylose-1 (3 μm, 4.6 mm X 250 mm). Mobile phase: 90:10 hexanes:*i*-PrOH, 1 mL/min. Detection wavelength: 254 nm. Er = 62.5:37.5 er



<Peak Table>
UV/Vis Channel 2 254nm

Peak#	Ret. Time	Area	Area%
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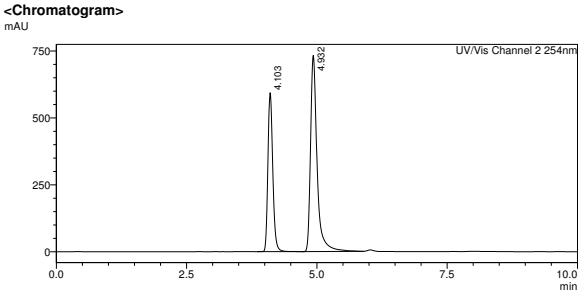
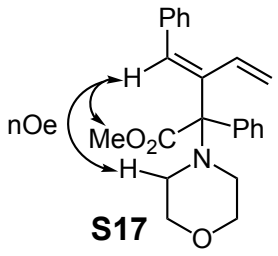
2	4.956	4748782	50.160
Total		9467256	100.000



<Peak Table>
UV/Vis Channel 2 254nm

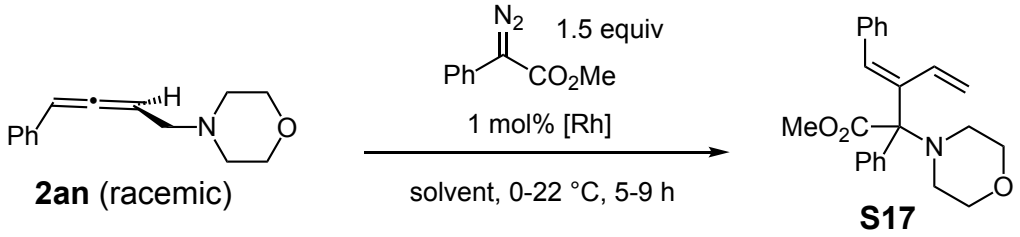
Peak#	Ret. Time	Area	Area%
1	4.103	3818924	37.343
2	4.932	6407644	62.657
Total		10226568	100.000

The olefin stereochemistry of **S17** was confirmed by NOESY analysis. Key nOe signals are depicted below:



Efforts to realize a stereoconvergent reaction starting from racemic **2an** with a chiral catalyst were largely unsuccessful. The relevant data are presented in Table S8.

Table S8. Screening of Chiral Rh-Based Catalysts with Racemic **2an**[a]



entry	[Rh]	solvent	time (h)	yield 7b (%)[b]	er[c]
1	Rh_2(*S*-PTAD)$_4$	CH_2Cl_2	9	(10)	ND
2	Rh_2(*R*-BTPCP)$_4$	CH_2Cl_2	9	<2	–
3	Rh_2(*S*-*tert*-PTTL)$_4$	CH_2Cl_2	9	34	51:49
4	Rh_2(*R*-DOSP)$_4$	CH_2Cl_2	9	72	53:47
5	Rh_2(*R*-DOSP)$_4$	pentane	5	77	65.5:34.5

[a]Reactions run with 0.20 mmol **2an** in 1.0 mL solvent. [b]Isolated yield of pure **S17**. Yields in parenthesis are conversions based on ^{1}H NMR of unpurified reaction mixture. [c]Determined by HPLC analysis of pure **S17** in comparison with an authentic racemic standard. ND = not determined.

XIV. References

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