Supplementary Information

“Enantioselective Reductive Coupling of Acetylene to *N*-Arylsulfonyl Imines via Rhodium Catalyzed C-C Bond Forming Hydrogenation: (*Z*)-Dienyl Allylic Amines”

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Table of Contents

I. Experimental Section

General-----	S2
Experimental Apparatus-----	S3
General Experimental Procedure-----	S4
Spectroscopic Data for Imines-----	S5 - S13
Spectroscopic Data for Coupling Products Including HPLC Data-----	S14 - S61
Spectroscopic Data for Derivatization Products-----	S62 – S89
Determination of Absolute Stereochemistry-----	S90

I. Experimental Section

General. All reactions were run under an atmosphere of argon, unless otherwise indicated. Anhydrous solvents were transferred by an oven-dried syringe. Flasks were flame-dried and cooled under a stream of nitrogen. Toluene was distilled from sodium and benzophenone. BIPHEP was used as received from Strem Chemicals. (S)-Cl₃MeO-BIPHEP was used as received from Solvias. *M*-NO₂-benzoic acid was used as received from Aldrich. Acetylene Gas was used as received from PRAXAIR (Atomic Absorption Grade). [Rh(cod)₂]SbF₆, and [Rh(cod)₂]BARF¹ were prepared in analogy with the previously reported procedures. Analytical thin-layer chromatography (TLC) was carried out using 0.2-mm commercial silica gel plates (DC-Fertigplatten Kieselgel 60 F₂₅₄). Preparative column chromatography employing silica gel was performed according to the method of Still.² Solvents for chromatography are listed as volume/volume ratios. Infrared spectra were recorded on a Perkin-Elmer 1600 spectrometer. High-resolution mass spectra (HRMS) were obtained on a Karatos MS9 and are reported as m/z (relative intensity). Accurate masses are reported for the molecular ion (M + 1) or a suitable fragment ion. Melting points were obtained on a Thomas-Hoover Unimelt apparatus and are uncorrected. Optical rotation was obtained on a Atago POLAX-2L polarimeter. Proton nuclear magnetic resonance (¹H-NMR) spectra were recorded with a Varian Gemini (400 MHz or 300MHz) spectrometer. Chemical shifts are reported in delta (δ) units, parts per million (ppm) downfield from trimethylsilane. Coupling constants are reported in Hertz (Hz). Carbon-13 nuclear magnetic resonance (¹³C-NMR) spectra were recorded with a Varian Gemini 300 (75 MHz) or 400 (100 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, ppm relative to the center of the triplet at 77.0 ppm for deuteriochloroform. ¹³C NMR spectra were routinely run with broadband decoupling

¹ Guzel, B.; Omary, M.; Fackler, JP, Jr.; Akegerman, A. *Inorg. Chim. Acta* **2001**, 325, 45

² Still, W.C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, 43, 2923

Experimental Apparatus

- 1) Reaction Vessel: 2.0 cm (Diameter) * 13.0 cm (Length)
- 2) Gas Bag: Tedlar® Gas Sampling Bag (Aldrich)
- 3) Cannula (Double-Tipped Needle): 24 in. (Length) – 20 (Gauge)

Preparation of Imines Aryl imines were prepared according to the literature procedures reported by Stalick.³ Cyclohexyl imine and isopropyl imine were prepared according to the literature procedures reported by Chemla.⁴ Cyclopropyl imine was prepared according to the literature procedure reported by Trost.⁵

Representative Procedure for The Synthesis of Aryl Imine: Sulfonamide (3.44 mmol), tetraethyl orthosilicate (3.44 mmol), and respective aldehyde (3.44 mmol) were combined in a reaction vessel equipped with short still head and a receiving flask. The reaction mixture was stirred at 165°C for 5 hours, and ethanol, upon formation was collected in the receiving flask. After cooling, the reaction was diluted with ether, suction filtered and filtrates washed with cold ether (3 x 10 mL). The crude compound was recrystallized from EtOAc/hexanes to furnish imines of >95% purity as determined by ¹H NMR.

General Procedure Enantioselective Reductive Coupling of Acetylene to N-Arylsulfonyl Imines: To the reaction vessel charged with [Rh(cod)₂]BARF (5 mol%), (*S*)-Cl₂MeO-BIPHEP (5 mol%), *m*-nitrobenzoic acid (5 mol%), Na₂SO₄ (200 mol%), corresponding imine (0.2 mmol, 100 mol%) was added toluene (2.0 mL, 0.1 M). An equimolar mixture of hydrogen and acetylene gas was introduced into the solution *via* cannula. The mixture was stirred at an indicated temperature under 1 atm of the hydrogen and acetylene gas mixture for 16 hours (unless otherwise indicated). The reaction mixture was evaporated and the residue was purified by flash silica gel column chromatography.

³ Wynne, H. J.; Price, E. S.; Rorer, R. J.; Stalick, M. W. *Synth. Comm.* **2003**, 33, 341

⁴ Chelma, F.; Hebbe, V.; Normant, J. F. *Synthesis* **2000**, 75

⁵ Trost, B.; M.; Marrs, C. *J. Org. Chem.* **1991**, 56, 6468

(3-bromo-4-fluorophenyl)-*N*-tosylmethanimine

¹H NMR (400 MHz, CDCl₃): 8.94 (s, 1H), 8.18 (d, $J = 6.2$ Hz, 1H), 7.88 -7.84 (m, 3H) 7.35 (d, $J = 8$ Hz, 2H), 7.23 (t, $J = 8.2$ Hz, 1H), 2.44 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): 167.2, 164.2 (d, $J_{F-C} = 258.8$ Hz), 144.9, 136.0, 134.6, 132.6 (d, $J_{F-C} = 8.9$ Hz), 129.9 (d, $J_{F-C} = 3.7$ Hz), 129.9, 128.1, 117.3 (d, $J_{F-C} = 23.2$ Hz), 110.6 (d, $J_{F-C} = 21.7$ Hz), 21.6.

HRMS Calcd. for C₁₄H₁₂NO₂FSBr(M+1): 355.9756, Found: 355.9756

FTIR (neat): 3440, 3210, 1607, 1593, 1491, 1399, 1324, 1260, 1159, 1089, 823, 773, 665 cm⁻¹.

M.P. 126 - 128°C

(3-nitro-4-bromophenyl)-*N*-benzensulfonylmethanimine

¹H NMR (400 MHz, CDCl₃): 9.03 (s, 1H), 8.35 (s, 1H), 7.99 (d, *J* = 7.8 Hz, 1H), 7.94 – 7.87 (m, 3H), 7.67 (t, *J* = 7.6 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃): 166.7, 137.1, 136.2, 134.3, 134.2, 132.7, 129.4, 128.3, 126.9, 121.3.

HRMS Calcd. for C₁₃H₁₀N₂O₄S Br(M+1): 368.9545, Found: 368.9550

FTIR (neat): 3420, 2945, 1597, 1540, 1320, 1160, 1090, 796 cm⁻¹.

M.P. 159 - 161°C

(5-nitrothiophen-2-yl)-*N*-tosylmethanimine

¹H NMR (400 MHz, CDCl₃): 9.05 (s, 1H), 7.90 (d, *J* = 4.3 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 4.3 Hz, 1H), 7.35 (d, *J* = 8.2 Hz, 2H), 2.44 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): 161.6, 145.7, 142.7, 136.1, 134.3, 130.2, 128.6, 128.4, 21.9.

HRMS Calcd. for C₁₂H₁₀N₂O₄S₂ (M+1): 310.0082, Found: 310.0082

FTIR (neat): 3108, 1596, 1582, 1508, 1344, 1235, 1162, 1087, 821, 760 cm⁻¹.

M.P. 196 - 199°C

(Z)-N-(4-nitrobenzensulfonyl)-1-phenylpenta-2,4-dien-1-amine

General procedure was used. To a reaction vessel charged with [Rh(cod)₂]BARF (11.8 mg, 0.01 mmol, 5 mol%), (S)-Cl₂MeO-BIPHEP (6.5 mg, 0.01 mmol, 5 mol%), *m*-nitrobenzoic acid (1.7 mg, 0.01 mmol, 5 mol%), Na₂SO₄ (58 mg, 0.4 mmol, 200 mol%), and imine (58 mg, 0.2 mmol, 100 mol%) was added toluene (0.2 mL, 0.1 M). An equimolar mixture of hydrogen and acetylene gas was introduced into the solution *via* cannula. The mixture was stirred at room temperature under 1 atm of the hydrogen and acetylene gas mixture for 16 hours. The reaction mixture was evaporated and the residue was purified by flash column chromatography (SiO₂: R_f = 0.3, petroleum ether/CHCl₃/EtOAc = 6/3/1) to furnish 58.9 mg of the title compound as a white solid (86% yield).

¹H NMR (400 MHz, CDCl₃): 8.17 (d, *J* = 9 Hz, 2H), 7.84 (d, *J* = 9 Hz, 2H), 7.21 – 7.16 (m, 5H), 6.59 (dt, *J* = 16.6 Hz, 10.2 Hz, 1H), 5.98 (t, *J* = 10.4 Hz, 1H), 5.49 (dd, *J* = 9.0 Hz, 6.8 Hz, 1H), 5.32 – 5.16 (m, 4H).

¹³C NMR (100 MHz, CDCl₃): 149.7, 146.5, 138.9, 131.9, 130.5, 128.8, 128.5, 128.4, 128.1, 126.7, 123.9, 121.6, 55.1.

HRMS Calcd. for C₁₇H₁₇N₂O₄S (M+1): 345.0909, Found: 345.0912

HPLC (Chiralcel OD-H column, 5% *i*-PrOH/hexanes, 0.5 mL/min, 220 nm), *t*_{minor} = 71.4 min, *t*_{major} = 76.6 min; ee = 93%

FTIR (neat): 3266, 3102, 2890, 1528, 1432, 1349, 1311, 1164, 1091, 916, 748 cm⁻¹.

M.P. 127 - 128°C

Instrument (Inj): ipo 1

Calibration Level: N/A

Verification Tolerance: N/A

Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		50.9924	72.464	0.000	18025200	0.00	BB	122.8		0
2		49.0076	79.044	0.000	17323566	0.00	BB	135.3		0
Totals		100.0000		0.000	35348768					

Data File: d:\chromatograms\edves-3-117-chiral1.r

Channel: 1 = INTGR 1 RESULTS

Sample ID: es-3-117-chiral1

Operator (Inj):

Injection Date: 02/01/07 03:30:27 PM

Injection Method: c:\star\ed.mth

Run Time (min): 99.312

Workstation:

Instrument (Inj): ipo 1

Operator (Calc):

Calc Date: 02/01/07 05:10:59 PM

Times Calculated: 2

Calculation Method: c:\star\ed.mth

Instrument (Calc): ipo 1

Run Mode: Analysis

Peak Measurement: Peak Area

Calculation Type: Percent

Calibration Level: N/A

Verification Tolerance: N/A

Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		3.5893	71.389	0.000	1495456	0.00	BB	79.2		0
2		96.4107	76.601	0.000	40168316	0.00	BB	136.9		0
Totals		100.0000		0.000	41663772					

(Z)-N-(4-nitrobenzensulfonyl)-1-*p*-tolylpenta-2,4-dien-1-amine

General procedure was used. To a reaction vessel charged with [Rh(cod)₂]BARF (11.8 mg, 0.01 mmol, 5 mol%), (S)-Cl₂MeO-BIPHEP (6.5 mg, 0.01 mmol, 5 mol%), *m*-nitrobenzoic acid (1.7 mg, 0.01 mmol, 5 mol%), Na₂SO₄ (58 mg, 0.4 mmol, 200 mol%), and imine (61 mg, 0.2 mmol, 100 mol%) was added toluene (2.0 mL, 0.1 M). An equimolar mixture of hydrogen and acetylene gas was introduced into the solution *via* cannula. The mixture was stirred at room temperature under 1 atm of the hydrogen and acetylene gas mixture for 16 hours. The reaction mixture was evaporated and the residue was purified by flash column chromatography (SiO₂: R_f = 0.4, petroleum ether/CHCl₃/EtOAc = 6/3/1) to furnish 51 mg of the title compound as a white solid (86% yield).

¹H NMR (400 MHz, CDCl₃): 8.16 (d, *J* = 9 Hz, 2H), 7.84 (d, *J* = 9 Hz, 2H), 7.06 – 6.99 (m, 4H), 6.59 (dt, *J* = 16.6 Hz, 10.2 Hz, 1H), 5.96 (t, *J* = 10.4 Hz, 1H), 5.44 (dd, *J* = 9.4 Hz, 6.6 Hz, 1H), 5.32 – 5.22 (m, 3H), 5.15 (d, *J* = 6.5 Hz, 1H), 2.25 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): 149.7, 146.6, 138.1, 136.0, 131.7, 130.6, 129.5, 129.1, 129.0, 128.7, 128.5, 126.7, 123.9, 123.8, 121.4, 54.9, 20.9

HRMS Calcd. for C₁₈H₁₉N₂O₄S (M+1): 359.1066, Found: 359.1071

HPLC (Chiralcel OD-H column, 15% *i*-PrOH/hexanes, 0.5 mL/min, 220 nm), *t*_{minor} = 22.0 min, *t*_{major} = 30.1 min; ee = 98%

FTIR (neat): 3267, 3098, 2982, 1530, 1312, 1164, 1091, 1014, 922, 854, 737 cm⁻¹.

M.P. 98 - 100°C

Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		51.1351	22.675	0.000	15048450	0.00	BB	40.9		0
2		48.8649	30.564	0.000	14380383	0.00	BB	50.4		0
Totals		100.0000		0.000	29428832					

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 Run Time (min): 82.849
 Workstation:
 Instrument (Inj): ipo 1

Operator (Calc):
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 Times Calculated: 4
 Calculation Method: c:\star\ed.mth
 Instrument (Calc): ipo 1
 Run Mode: Analysis
 Peak Measurement: Peak Area
 Calculation Type: Percent
 Calibration Level: N/A
 Verification Tolerance: N/A

Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		0.6541	22.056	0.000	34445	0.00	BB	0.1		0
2		99.3459	30.141	0.000	5231666	0.00	BB	55.2		0
Totals		100.0000		0.000	5266111					

(Z)-N-benzensulfonyl-1-(4-nitrophenyl)penta-2,4-dien-1-amine

General procedure was used. To a reaction vessel charged with [Rh(cod)₂]BARF (11.8 mg, 0.01 mmol, 5 mol%), (S)-Cl₂MeO-BIPHEP (6.5 mg, 0.01 mmol, 5 mol%), *m*-nitrobenzoic acid (1.7 mg, 0.01 mmol, 5 mol%), Na₂SO₄ (58 mg, 0.4 mmol, 200 mol%), and imine (58 mg, 0.2 mmol, 100 mol%) was added toluene (2.0 mL, 0.1 M). An equimolar mixture of hydrogen and acetylene gas was introduced into the solution *via* cannula. The mixture was stirred at room temperature under 1 atm of the hydrogen and acetylene gas mixture for 16 hours. The reaction mixture was evaporated and the residue was purified by flash column chromatography (SiO₂: R_f = 0.3, petroleum ether/CHCl₃/EtOAc = 6/3/1) to furnish 56.5 mg of the title compound as a light yellow oil (83% yield).

¹H NMR (400 MHz, CDCl₃): 8.06 (d, *J* = 8.8 Hz, 2H), 7.74 (d, *J* = 8.8 Hz, 2H), 7.54 – 7.50 (m, 1H), 7.42 – 7.39 (m, 4H), 6.37 (dt, *J* = 16.6, 10.4 Hz, 1H), 6.02 (t, *J* = 10.6 Hz, 1H), 5.43 (dd, *J* = 9.6, 6.4 Hz, 1H), 5.30 – 5.20 (m, 3H), 5.12 (d, *J* = 6.4 Hz).

¹³C NMR (100 MHz, CDCl₃): 147.3, 147.2, 140.0, 132.9, 132.5, 130.1, 129.0, 127.6, 127.5, 127.2, 123.8, 122.1, 54.2.

HRMS Calcd. for C₁₇H₁₇N₂O₄S (M+1): 345.0909, Found: 345.0905

HPLC (Chiralcel OD-H column, 20% *i*-PrOH/hexanes, 0.5 mL/min, 254 nm), *t*_{minor} = 16.8 min, *t*_{major} = 27.0 min; ee = 97%

FTIR (neat): 3276, 3067, 2906, 1599, 1520, 1448, 1347, 1161, 1092, 923, 853 cm⁻¹.

Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		50.1630	16.108	0.000	14586948	0.00	BB	28.1		0
2		49.8370	26.822	0.000	14492138	0.00	BB	52.3		0
Totals		100.0000		0.000	29079086					

Data File: d:\chromatograms\edves-3-71-1-s-enam.r
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 Run Time (min): 42.318
 Workstation:
 Instrument (Inj): ipo 1

Operator (Calc):
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 Times Calculated: 2
 Calculation Method: c:\star\ming.mth
 Instrument (Calc): ipo 1
 Run Mode: Analysis
 Peak Measurement: Peak Area
 Calculation Type: Percent
 Calibration Level: N/A
 Verification Tolerance: N/A

Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		1.4506	16.793	0.000	123709	0.00	BB	26.6		0
2		98.5494	27.015	0.000	8404363	0.00	BB	47.4		0
Totals		100.0000		0.000	8528072					

Methyl 4-((Z)-N-(*p*-tolylsulfonyl)-1-aminopenta-2,4-dienyl)benzoate

General procedure was used. To a reaction vessel charged with [Rh(cod)₂]BARF (11.8 mg, 0.01 mmol, 5 mol%), (S)-Cl₂MeO-BIPHEP (6.5 mg, 0.01 mmol, 5 mol%), *m*-nitrobenzoic acid (1.7 mg, 0.01 mmol, 5 mol%), Na₂SO₄ (58 mg, 0.4 mmol, 200 mol%), and imine (63 mg, 0.2 mmol, 100 mol%) was added toluene (2.0 mL, 0.1 M). An equimolar mixture of hydrogen and acetylene gas was introduced into the solution *via* cannula. The mixture was stirred at room temperature under 1 atm of the hydrogen and acetylene gas mixture for 16 hours. The reaction mixture was evaporated and the residue was purified by flash column chromatography (SiO₂: R_f = 0.2, petroleum ether/CHCl₃/EtOAc = 6/3/1) to furnish 56 mg of the title compound as a clear oil (75% yield).

¹H NMR (400 MHz, CDCl₃): 7.87 (d, *J* = 8.2 Hz, 2H), 7.60 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.2 Hz, 2H), 7.17 (d, *J* = 8.2 Hz, 2H), 6.43 (dt, *J* = 16.8, 10.2 Hz, 1H), 5.98 (t, *J* = 10.6 Hz, 1H), 5.38 (dd, *J* = 9.6, 6.2 Hz, 1H), 5.30 – 5.17 (m, 3H), 4.97 (d, *J* = 6.2 Hz, 1H), 3.88 (s, 3H), 2.36 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): 166.6, 144.9, 143.5, 137.3, 131.9, 130.6, 129.9, 129.5, 128.7, 127.3, 126.7, 121.3, 54.6, 52.1, 21.5.

HRMS Calcd. for C₂₀H₂₂NO₄S (M+1): 372.1270, Found: 372.1268

HPLC (Chiralcel OD-H column, 10% *i*-PrOH/hexanes, 0.5 mL/min, 220 nm), *t*_{minor} = 26.8 min, *t*_{major} = 35.3 min; ee = 95%

FTIR (neat): 3270, 2994, 1770, 1720, 1610, 1436, 1374, 1280, 1245, 1160, 1060, 913 cm⁻¹.

Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		49.3965	27.284	0.000	19718454	0.00	BB	47.3		0
2		50.6035	36.049	0.000	20200266	0.00	BB	63.3		0
Totals		100.0000		0.000	39918720					

Data File: d:\chromatograms\edves-3-120-exp1-1.r
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 Injection Method: c:\star\ed.mth
 Run Time (min): 44.921
 Workstation:
 Instrument (Inj): ipo 1

Operator (Calc):
 Calc Date: 02/05/07 02:25:22 PM
 Times Calculated: 2
 Calculation Method: c:\star\ed.mth
 Instrument (Calc): ipo 1
 Run Mode: Analysis
 Peak Measurement: Peak Area
 Calculation Type: Percent
 Calibration Level: N/A
 Verification Tolerance: N/A

Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		2.6863	26.870	0.000	749918	0.00	BB	60.4		0
2		97.3137	35.753	0.000	27166190	0.00	BB	63.6		0
Totals		100.0000		0.000	27916108					

(Z)-N-(4-nitrobenzensulfonyl)-1-(3-methoxyphenyl)penta-2,4-dien-1-amine

General procedure was used. To a reaction vessel charged with [Rh(cod)₂]BARF (11.8 mg, 0.01 mmol, 5 mol%), (S)-Cl₂MeO-BIPHEP (6.5 mg, 0.01 mmol, 5 mol%), *m*-nitrobenzoic acid (1.7 mg, 0.01 mmol, 5 mol%), Na₂SO₄ (58 mg, 0.4 mmol, 200 mol%), and imine (75 mg, 0.2 mmol, 100 mol%) was added toluene (2.0 mL, 0.1 M). An equimolar mixture of hydrogen and acetylene gas was introduced into the solution *via* cannula. The mixture was stirred at room temperature under 1 atm of the hydrogen and acetylene gas mixture for 16 hours. The reaction mixture was evaporated and the residue was purified by flash column chromatography (SiO₂: R_f = 0.3, petroleum ether/CHCl₃/EtOAc = 6/3/1) to furnish 54 mg of the title compound as a light yellow solid (72% yield).

¹H NMR (400 MHz, CDCl₃): 8.16 (d, *J* = 9.0 Hz, 2H), 7.83 (d, *J* = 9.0 Hz, 2H), 7.13 (t, *J* = 8.0 Hz, 1H), 6.76 – 6.53 (m, 4H), 5.98 (t, *J* = 10.6 Hz, 1H), 5.44 (dd, *J* = 9.4, 6.6 Hz, 1H), 5.30 – 5.19 (m, 4H), 3.68 (s, 3H)

¹³C NMR (100 MHz, CDCl₃): 159.84, 149.7, 146.5, 140.5, 131.9, 130.5, 129.9, 128.4, 128.4, 123.8, 121.6, 118.9, 112.9, 112.7, 55.2, 55.0.

HRMS Calcd. for C₁₈H₁₉N₂O₅S (M+1): 375.1015, Found: 375.1016

HPLC (Chiralcel AD-H column, 15% *i*-PrOH/hexanes, 0.5 mL/min, 220 nm), t_{major} = 47.1 min, t_{minor} = 75.9 min; ee = 97%

FTIR (neat): 3266, 2878, 2331, 1603.6, 1529, 1432, 1344, 1312, 1263, 1160, 1091, 1042, 910, 853, 735 cm⁻¹.

M.P. 104 – 105°C

Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		51.8100	47.135	0.000	3888627	0.00	BB	68.3		0
2		48.1900	76.170	0.000	3616919	0.00	BB	107.2		0
Totals		100.0000		0.000	7505546					

Data File: d:\chromatograms\edves-3-133-exp1-2.r
Channel: 1 = INTEGR 1 RESULTS
Sample ID: es-3-133-exp1-2
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Injection Method: c:\star\ed.mth
Run Time (min): 81.762
Workstation:
Instrument (Inj): ipo 1

Operator (Calc):
Calc Date: 02/13/07 06:34:32 PM
Times Calculated: 2
Calculation Method: c:\star\ed.mth
Instrument (Calc): ipo 1
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
Calibration Level: N/A
Verification Tolerance: N/A

Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		98.4078	47.116	0.000	15702000	0.00	BB	66.4		0
2		1.5922	75.931	0.000	254052	0.00	BB	42.9		0
Totals		100.0000		0.000	15956052					

(Z)-N-(*p*-tolylsulfonyl)-1-(3-bromo-fluorophenyl)penta-2,4-dien-1-amine

General procedure was used. To a reaction vessel charged with [Rh(cod)₂]BARF (11.8 mg, 0.01 mmol, 5 mol%), (S)-Cl₂MeO-BIPHEP (6.5 mg, 0.01 mmol, 5 mol%), *m*-nitrobenzoic acid (1.7 mg, 0.01 mmol, 5 mol%), Na₂SO₄ (58 mg, 0.4 mmol, 200 mol%), imine (71 mg, 0.2 mmol, 100 mol%) was added toluene (2.0 mL, 0.1 M). An equimolar mixture of hydrogen and acetylene gas was introduced into the solution *via* cannula. The mixture was stirred at room temperature under 1 atm of the hydrogen and acetylene gas mixture for 16 hours. The reaction mixture was evaporated and the residue was purified by flash column chromatography (SiO₂: R_f = 0.2, petroleum ether/CHCl₃/EtOAc = 6/3/1) to furnish 59 mg of the title compound as a clear oil (70% yield).

¹H NMR (400 MHz, CDCl₃): 7.57 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 6.5 Hz, 1H), 7.18 (d, *J* = 8.2 Hz, 2H), 7.16 – 7.12 (m, 1H), 6.95 (t, *J* = 8.2 Hz, 1H), 6.41 (dt, *J* = 16.6, 10.2 Hz, 1H), 5.98 (t, *J* = 10.2 Hz, 1H), 5.31 – 5.18 (m, 4H), 4.98 (d, *J* = 6.2 Hz, 1H), 2.38 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): 158.4 (d, *J*_{F-C} = 247 Hz), 143.7, 137.3 (d, *J*_{F-C} = 3.7 Hz), 137.1, 131.9 (d, *J*_{F-C} = 6.7 Hz), 130.5, 129.5, 128.4, 127.5 (d, *J*_{F-C} = 7.5 Hz), 127.2, 121.5, 116.4 (d, *J*_{F-C} = 22.4 Hz), 109.1 (d, *J*_{F-C} = 21.7 Hz), 53.7, 21.5.

HRMS Calcd. for C₁₈H₁₈NO₂FSBr (M+1): 410.0026, Found: 410.0230

HPLC (Chiralcel OD-H column, 5% *i*-PrOH/hexanes, 0.5 mL/min, 220 nm), *t*_{minor} = 28.6 min, *t*_{major} = 36.6 min; ee = 97%

FTIR (neat): 3265, 2970, 2923, 1597, 1494, 1436, 1329, 1246, 1160, 1093, 1047, 921, 813 cm⁻¹.

Injection Method: c:\star\ed.mth
 Run Time (min): 52.649
 Workstation:
 Instrument (Inj): ipo 1

Run Mode: Analysis
 Peak Measurement: Peak Area
 Calculation Type: Percent
 Calibration Level: N/A
 Verification Tolerance: N/A

Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		50.6294	27.635	0.000	22638574	0.00	BB	40.7		0
2		49.3706	35.395	0.000	22075750	0.00	BB	56.7		0
Totals		100.0000		0.000	44714324					

Data File: d:\chromatograms\ed\es-3-112-2.run
 Channel: 1 = INTGR 1 RESULTS
 Sample ID: es-3-112-2
 Operator (Inj):
 Injection Date: 01/29/07 11:37:42 AM
 Injection Method: c:\star\ed.mth
 Run Time (min): 54.087
 Workstation:
 Instrument (Inj): ipo 1

Operator (Calc):
 Calc Date: 01/29/07 12:32:24 PM
 Times Calculated: 2
 Calculation Method: c:\star\ed.mth
 Instrument (Calc): ipo 1
 Run Mode: Analysis
 Peak Measurement: Peak Area
 Calculation Type: Percent
 Calibration Level: N/A
 Verification Tolerance: N/A

Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		1.3625	28.633	0.000	75378	0.00	BB	0.2		0
2		98.6375	36.603	0.000	5456796	0.00	BB	57.0		0
Totals		100.0000		0.000	5532174					

(Z)-N-(benzensulfonyl)-1-(4-bromo-3-nitrophenyl)penta-2,4-dien-amine

General procedure was used. To a reaction vessel charged with [Rh(cod)₂]BARF (11.8 mg, 0.01 mmol, 5 mol%), (S)-Cl₂MeO-BIPHEP (6.5 mg, 0.01 mmol, 5 mol%), *m*-nitrobenzoic acid (1.7 mg, 0.01 mmol, 5 mol%), Na₂SO₄ (58 mg, 0.4 mmol, 200 mol%), and imine (74 mg, 0.2 mmol, 100 mol%) was added toluene (2.0 mL, 0.1 M). An equimolar mixture of hydrogen and acetylene gas was introduced into the solution *via* cannula. The mixture was stirred at room temperature under 1 atm of the hydrogen and acetylene gas mixture for 16 hours. The reaction mixture was evaporated and the residue was purified by flash column chromatography (SiO₂: R_f = 0.3, petroleum ether/CHCl₃/EtOAc = 6/3/1) to furnish 60 mg of the title compound as a yellow oil (71% yield).

¹H NMR (400 MHz, CDCl₃): 7.72 (d, *J* = 7.2 Hz, 2H), 7.62 – 7.51 (m, 3H), 7.41 (t, *J* = 8 Hz, 2H), 7.34 (d, *J* = 8 Hz, 1H), 6.34 (dt, *J* = 16.6, 10.8 Hz, 1H), 6.04 (t, *J* = 10.2 Hz, 1H), 5.39 – 5.19 (m, 4H), 5.04 (d, *J* = 6.4 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃): 149.9, 141.6, 140.1, 135.5, 133.2, 133.2, 131.9, 130.2, 129.3, 127.4, 127.1, 124.2, 122.8, 113.8, 53.9.

HRMS Calcd. for C₁₇H₁₆N₂O₄SBr (M+1): 423.0014, Found: 423.0014

HPLC (Chiralcel OD-H column, 20% *i*-PrOH/hexanes, 0.5 mL/min, 220 nm), *t*_{minor} = 15.2 min, *t*_{major} = 22.4 min; ee = 94%.

FTIR (neat): 3320, 3210, 2946, 1538, 1473, 1448, 1332, 1162, 1092, 1032, 922 cm⁻¹.

Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		48.8427	15.005	0.000	12898868	0.00	BB	23.6		0
2		51.1573	22.148	0.000	13510145	0.00	BB	38.9		0
Totals		100.0000		0.000	26409012					

Data File: d:\chromatograms\ed\es-3-134-exp1.run
 Channel: 1 = INTGR 1 RESULTS
 Sample ID: es-3-134-exp1
 Operator (Inj):
 Injection Date: 02/19/07 12:40:52 PM
 Injection Method: c:\star\ming.mth
 Run Time (min): 43.915
 Workstation:
 Instrument (Inj): ipo 1

Operator (Calc):
 Calc Date: 02/19/07 01:25:33 PM
 Times Calculated: 2
 Calculation Method: c:\star\ming.mth
 Instrument (Calc): ipo 1
 Run Mode: Analysis
 Peak Measurement: Peak Area
 Calculation Type: Percent
 Calibration Level: N/A
 Verification Tolerance: N/A

Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		2.9574	15.165	0.000	765728	0.00	BB	23.7		0
2		97.0426	22.477	0.000	25125866	0.00	BB	40.3		0
Totals		100.0000		0.000	25891594					

(Z)-N-(*p*-tolylsulfonyl)-1-(4-chlorophenyl)penta-2,4-dien-1-amine

General procedure was used. To a reaction vessel charged with [Rh(cod)₂]BARF (11.8 mg, 0.01 mmol, 5 mol%), (*S*)-Cl₂MeO-BIPHEP (6.5 mg, 0.01 mmol, 5 mol%), *m*-nitrobenzoic acid (1.7 mg, 0.01 mmol, 5 mol%), Na₂SO₄ (58 mg, 0.4 mmol, 200 mol%), and imine (59 mg, 0.2 mmol, 100 mol%) was added toluene (2.0 mL, 0.1 M). An equimolar mixture of hydrogen and acetylene gas was introduced into the solution *via* cannula. The mixture was stirred at room temperature under 1 atm of the hydrogen and acetylene gas mixture for 16 hours. The reaction mixture was evaporated and the residue was purified by flash column chromatography (SiO₂: R_f = 0.3, petroleum ether/CHCl₃/EtOAc = 6/3/1) to furnish 51.4 mg of the title compound as a clear oil (74% yield).

¹H NMR (400 MHz, CDCl₃): 7.59 (d, *J* = 8.2 Hz, 2H), 7.19 – 7.12 (m, 6H), 6.41 (dt, *J* = 16.4, 10.2 Hz, 1H), 5.95 (t, *J* = 10.2 Hz, 1H), 5.32 – 5.13 (m, 4H), 4.95 (d, *J* = 5.8 Hz, 1H), 2.38 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): 143.5, 138.4, 137.3, 133.5, 131.5, 130.6, 129.4, 128.9, 128.7, 128.1, 127.3, 121.0, 54.2, 21.5.

HRMS Calcd. for C₁₈H₁₉NO₂SCl (M+1): 348.0825, Found: 348.0823

HPLC (Chiralcel OD-H column, 10% *i*-PrOH/hexanes, 0.5 mL/min, 220 nm), *t*_{minor} = 17.4 min, *t*_{major} = 23.4 min; ee = 95%.

FTIR (neat): 3265, 3029, 2923, 1597, 1491, 1435, 1329, 1160, 1092, 1013, 920, 813, 673 cm⁻¹.

Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		49.8254	17.598	0.000	11314039	0.00	BB	26.7		0
2		50.1746	23.592	0.000	11393324	0.00	BB	36.3		0
Totals		100.0000		0.000	22707364					

Data File: d:\chromatograms\ved\es-3-148-1.run
Channel: 1 = INTGR 1 RESULTS
Sample ID: es-3-148-1
Operator (Inj):
Injection Date: 02/23/07 11:36:18 AM
Injection Method: c:\star\cisco.mth
Run Time (min): 25.557
Workstation:
Instrument (Inj): ipo 1

Operator (Calc):
Calc Date: 02/23/07 12:02:35 PM
Times Calculated: 2
Calculation Method: c:\star\cisco.mth
Instrument (Calc): ipo 1
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
Calibration Level: N/A
Verification Tolerance: N/A

Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		2.4534	17.446	0.000	359170	0.00	BB	43.3		0
2		97.5466	23.376	0.000	14280295	0.00	BB	36.4		0
Totals		100.0000		0.000	14639465					

(Z)-N-(*p*-tolylsulfonyl)-1-(5-nitrothiophen-2-yl)penta-2,4-dien-1-amine

General procedure was used. To a reaction vessel charged with [Rh(cod)₂]BARF (11.8 mg, 0.01 mmol, 5 mol%), (S)-Cl₂MeO-BIPHEP (6.5 mg, 0.01 mmol, 5 mol%), *m*-nitrobenzoic acid (1.7 mg, 0.01 mmol, 5 mol%), Na₂SO₄ (58 mg, 0.4 mmol, 200 mol%), and imine (62 mg, 0.2 mmol, 100 mol%) was added toluene (2 mL, 0.1 M). An equimolar mixture of hydrogen and acetylene gas was introduced into the solution *via* cannula. The mixture was stirred at room temperature under 1 atm of the hydrogen and acetylene gas mixture for 16 hours. The reaction mixture was evaporated and the residue was purified by flash column chromatography (SiO₂: R_f = 0.2, petroleum ether/CHCl₃/EtOAc = 6/3/1) to furnish 53 mg of the title compound as a brown oil (74% yield).

¹H NMR (400 MHz, CDCl₃): 7.69 – 7.62 (m, 3H), 7.24 (d, *J* = 10.8 Hz, 2H), 6.83 (d, *J* = 4.1 Hz, 1H), 6.32 (dt, *J* = 16.6, 9.8 Hz, 1H), 6.04 (t, *J* = 10.8 Hz, 1H), 5.57 – 5.45 (m, 1H), 5.32 – 5.13 (m, 4H), 2.39 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): 153.3, 151.1, 144.2, 136.8, 133.2, 129.8, 129.7, 128.5, 127.2, 126.3, 124.4, 122.5, 51.0, 21.5.

HRMS Calcd. for C₁₆H₁₇N₂O₄S₂ (M+1): 365.0630, Found: 365.0629

HPLC (Chiralcel OD-H column, 15% *i*-PrOH/hexanes, 0.5 mL/min, 220 nm), *t*_{minor} = 21.2 min, *t*_{major} = 37.1 min; ee = 95%

FTIR (neat): 3260, 3106, 2924, 1597, 1503, 1434, 1337, 1161, 1092, 922, 815, 734, 675 cm⁻¹.

Injection Date: 01/20/07 02:00:27 PM
Injection Method: c:\star\ming.mth
Run Time (min): 105.882
Workstation:
Instrument (Inj): ipo 1

Instrument (Calc): ipo 1
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
Calibration Level: N/A
Verification Tolerance: N/A

Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		49.4581	20.900	0.000	8396639	0.00	BB	35.9		0
2		50.5419	36.490	0.000	8580626	0.00	BB	67.1		0
Totals		100.0000		0.000	16977264					

Data File: d:\chromatograms1\edves-3-90-exp2-5.rur
Channel: 1 = INTGR 1 RESULTS
Sample ID: es-3-90-exp2-5
Operator (Inj):
Injection Date: 01/20/07 02:07:50 PM
Injection Method: c:\star\ed.mth
Run Time (min): 40.752
Workstation:
Instrument (Inj): ipo 1

Operator (Calc):
Calc Date: 01/20/07 02:49:22 PM
Times Calculated: 2
Calculation Method: c:\star\ed.mth
Instrument (Calc): ipo 1
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
Calibration Level: N/A
Verification Tolerance: N/A

Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		2.5393	21.264	0.000	178840	0.00	BB	29.2		0
2		97.4607	37.140	0.000	6863972	0.00	BB	68.0		0
Totals		100.0000		0.000	7042812					

(Z)-N-(1-Cyclohexyl-penta-2,4-dienyl)-4-methyl-benzenesulfonamide (10b)

General procedure was used. To a reaction vessel charged with [Rh(cod)₂]BARF (11.8 mg, 0.01 mmol, 5 mol%), (S)-Cl₂MeO-BIPHEP (6.5 mg, 0.01 mmol, 5 mol%), *m*-nitrobenzoic acid (1.7 mg, 0.01 mmol, 5 mol%), Na₂SO₄ (58 mg, 0.4 mmol, 200 mol%), imine (53.1 mg, 0.2 mmol, 100 mol%) was added toluene (2.0 mL, 0.1M). An equimolar mixture of hydrogen and acetylene gas was introduced into the solution *via* cannula. The mixture was stirred at room temperature under 1 atm of the hydrogen and acetylene gas mixture for 24 hours. The reaction mixture was evaporated and the residue was purified by flash column chromatography (SiO₂: R_f = 0.3, hexane CHCl₃/EtOAc = 8/3/1) to furnish 43.2 mg of the title compound as a white solid (68% yield).

¹H NMR (300 MHz, CDCl₃): 7.66 (d, *J* = 8.1 Hz, 2H), 7.19 (d, *J* = 8.1 Hz, 2H), 6.33 (dt, *J* = 16.5 Hz, 10.7 Hz, 1H), 5.80 (t, *J* = 10.9 Hz, 1H), 5.10 (d, *J* = 16.5 Hz, 1H), 5.05 (d, *J* = 11.1 Hz, 1H), 4.96 (t, *J* = 10.4 Hz, 1H), 4.73 (d, *J* = 8.1 Hz, 1H), 3.97 (dd, *J* = 17.1, 7.5 Hz, 1H), 2.36 (s, 3H), 1.79 – 1.59 (m, 5H), 1.42 – 1.30 (m, 1H), 1.23 – 1.03 (m, 3H), 0.96 – 0.84 (m, 2H).

¹³C NMR (75 MHz, CDCl₃): 142.9, 138.0, 131.4, 131.0, 129.4, 129.3, 127.2, 119.1, 55.9, 43.0, 29.1, 28.5, 26.2, 25.9, 25.8, 21.4.

HRMS Calcd. for C₁₈H₂₆NO₂S (M+1): 320.1684, Found: 320.1687

FTIR (neat): 3273, 2925, 2852, 1652, 1598, 1558, 1540, 1506, 1448, 1327, 1158, 1093, 1042, 905, 812, 674 cm⁻¹.

HPLC (Chiralcel OD-H column, 5% *i*-PrOH/hexanes, 0.5 mL/min, 220 nm), t_{minor} = 16.7 min, t_{major} = 21.8 min; ee = 97%

MP : 113 - 114 °C

Data File: c:\star\010206163.run
Channel: 1 = INTGR 1 RESULTS
Sample ID: Manual Sample
Operator (Inj):
Injection Date: 12/18/06 06:46:51 PM
Injection Method: c:\star\kong\kong.mth
Run Time (min): 36.369
Workstation:
Instrument (Inj): ipo 1

Operator (Calc):
Calc Date: 12/18/06 07:24:01 PM
Times Calculated: 2
Calculation Method: c:\star\kong\kong.mth
Instrument (Calc): ipo 1
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
Calibration Level: N/A
Verification Tolerance: N/A

Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		49.7672	16.763	0.000	10939533	0.00	BB	37.3		0
2		50.2328	21.965	0.000	11041897	0.00	BB	46.7		0
Totals		100.0000		0.000	21981430					

Data File: c:\star\010206162.run
Channel: 1 = INTGR 1 RESULTS
Sample ID: Manual Sample
Operator (Inj):
Injection Date: 12/18/06 06:18:41 PM
Injection Method: c:\star\kong\kong.mth
Run Time (min): 23.891
Workstation:
Instrument (Inj): ipo 1

Operator (Calc):
Calc Date: 12/18/06 06:43:06 PM
Times Calculated: 2
Calculation Method: c:\star\kong\kong.mth
Instrument (Calc): ipo 1
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
Calibration Level: N/A
Verification Tolerance: N/A

Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		1.4978	16.668	0.000	190890	0.00	BB	21.2		0
2		98.5022	21.789	0.000	12554127	0.00	BB	45.7		0
Totals		100.0000		0.000	12745017					

(Z)- N-(1-Isopropyl-penta-2,4-dienyl)-4-methyl-benzenesulfonamide (11b)

General procedure was used. To a reaction vessel charged with [Rh(cod)₂]BARF (11.8 mg, 0.01 mmol, 5 mol%), (S)-Cl₂MeO-BIPHEP (6.5 mg, 0.01 mmol, 5 mol%), *m*-Nitrobenzoic acid (1.7 mg, 0.01 mmol, 5 mol%), Na₂SO₄ (174 mg, 1.2 mmol, 600 mol%), imine (45.1 mg, 0.2 mmol, 100 mol%) was added toluene (2.0 mL, 0.1M). An equimolar mixture of hydrogen and acetylene gas was introduced into the solution *via* cannula. The mixture was stirred at room temperature under 1 atm of the hydrogen and acetylene gas mixture for 24 hours. The reaction mixture was evaporated and the residue was purified by flash column chromatography (SiO₂: R_f = 0.3, Hexane CHCl₃/EtOAc = 8/3/1) to furnish 39.2 mg of the title compound as a white solid (70% yield).

¹H NMR (400 MHz, CDCl₃): 7.68 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 6.35 (dtd, *J* = 16.8 Hz, 10.6, 0.4 Hz, 1H), 5.85 (t, *J* = 10.8 Hz, 1H), 5.14 (d, *J* = 16.8 Hz, 1H), 5.09 (d, *J* = 10.0 Hz, 1H), 4.99 (t, *J* = 10.4 Hz, 1H), 4.60 (d, *J* = 8.0 Hz, 1H), 4.02 – 3.96 (m, 1H), 2.39 (s, 3H), 1.79 – 1.70 (m, 1H), 0.89 (d, *J* = 6.8 Hz, 3H), 0.85 (d, *J* = 6.4, 3H).

¹³C NMR (75 MHz, CDCl₃): 142.9, 137.9, 131.3, 131.3, 129.3, 128.9, 127.2, 119.2, 56.5, 33.4, 21.4, 18.5, 17.9.

HRMS Calcd. for C₁₅H₂₂NO₂S (M+1): 280.1371, Found: 280.1374

FTIR (neat): 3273, 2962, 2927, 2874, 1916, 1802, 1647, 1598, 1495, 1434, 1328, 1304, 1158, 1093, 1047, 915, 813, 788, 706, 676 cm⁻¹.

HPLC (Chiralcel OD-H column, 5% *i*-PrOH/hexanes, 0.5 mL/min, 220 nm), t_{minor} = 18.1 min, t_{major} = 20.6 min; ee = 98%

MP : 71 - 72 °C

Data File: e:\chromatograms2\visco\test033.run
Channel: 1 = INTGR 1 RESULTS
Sample ID: Manual Sample
Operator (Inj):
Injection Date: 01/16/07 12:52:20 PM
Injection Method: c:\star\kong\kong.mth
Run Time (min): 11.291
Workstation:
Instrument (Inj): ipo 1

Operator (Calc):
Calc Date: 01/16/07 02:05:13 PM
Times Calculated: 4
Calculation Method: c:\star\kong\kong.mth
Instrument (Calc): ipo 1
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
Calibration Level: N/A
Verification Tolerance: N/A

Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		49.5761	17.965	0.000	11878390	0.00	BB	39.3		0
2		50.4239	20.373	0.000	12081541	0.00	BB	53.7		0
Totals		100.0000		0.000	23959932					

Data File: e:\chromatograms2\visco\test037.run
Channel: 1 = INTGR 1 RESULTS
Sample ID: Manual Sample
Operator (Inj):
Injection Date: 01/16/07 02:34:30 PM
Injection Method: c:\star\kong\kong.mth
Run Time (min): 32.986
Workstation:
Instrument (Inj): ipo 1

Operator (Calc):
Calc Date: 01/16/07 03:07:57 PM
Times Calculated: 2
Calculation Method: c:\star\kong\kong.mth
Instrument (Calc): ipo 1
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
Calibration Level: N/A
Verification Tolerance: N/A

Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		1.1388	18.135	0.000	127315	0.00	BB	25.3		0
2		98.8612	20.635	0.000	11052369	0.00	BB	53.9		0
Totals		100.0000		0.000	11179684					

(Z)- N-(1-Cyclopropyl-penta-2,4-dienyl)-4-methyl-benzenesulfonamide

General procedure was used. To a reaction vessel charged with [Rh(cod)₂]BARF (11.8 mg, 0.01 mmol, 5 mol%), (*S*)-Cl₂MeO-BIPHEP (6.5 mg, 0.01 mmol, 5 mol%), *m*-nitrobenzoic acid (1.7 mg, 0.01 mmol, 5 mol%), Na₂SO₄ (174 mg, 1.2 mmol, 600 mol%), imine (44.7 mg, 0.2 mmol, 100 mol%) was added toluene (2.0 mL, 0.1 M) were added to the reaction vessel. An equimolar mixture of hydrogen and acetylene gas was introduced into the solution *via* cannula. The mixture was stirred at room temperature under 1 atm of the hydrogen and acetylene gas mixture for 24 hours. The reaction mixture was evaporated and the residue was purified by flash column chromatography (SiO₂: R_f = 0.3, hexane/CHCl₃/EtOAc = 8/3/1) to furnish 36.1 mg of title compound as a clear oil (65% yield).

¹H NMR (300 MHz, CDCl₃): 7.72 (dd, *J* = 6.5, 1.7 Hz, 2H), 7.27 (d, *J* = 8.7 Hz, 2H), 6.41 (dtd, *J* = 17.1 Hz, 10.2, 0.9 Hz, 1H), 5.91 (td, *J* = 11.1, 0.9 Hz, 1H), 5.22 (d, *J* = 16.5 Hz, 1H), 5.15 (d, *J* = 9.9 Hz, 1H), 5.08 (t, *J* = 10.5 Hz, 1H), 4.61 (s, br, 1H), 3.82 – 3.74 (m, 1H), 2.43 (s, 3H), 1.00 – 0.89 (m, 1H), 0.50 – 0.43 (m, 2H), 0.27 – 0.21 (m, 2H).

¹³C NMR (75 MHz, CDCl₃): 143.2, 137.9, 131.2, 130.9, 129.4, 129.2, 127.3, 119.7, 55.0, 21.5, 16.6, 3.5, 2.5.

HRMS Calcd. for C₁₅H₂₀NO₂S (M+1): 278.1215, Found: 278.1215

FTIR (neat): 3265, 3078, 3008, 2918, 2848, 1598, 1431, 1325, 1157, 1093, 1028, 911, 813 cm⁻¹.

HPLC (Chiralcel OD-H column, 5% *i*-PrOH/hexanes, 0.5 mL/min, 220 nm), *t*_{minor} = 24.5 min, *t*_{major} = 27.7 min; ee = 97%

Data File:	e:\chromatograms2\cisco\test059.run	Operator (Calc):	
Channel:	1 = INTGR 1 RESULTS	Calc Date:	02/09/07 05:49:10 PM
Sample ID:	Manual Sample	Times Calculated:	6
Operator (Inj):		Calculation Method:	c:\star\kong\kong.mth
Injection Date:	02/09/07 04:28:49 PM	Instrument (Calc):	ipo 1
Injection Method:	c:\star\kong\kong.mth	Run Mode:	Analysis
Run Time (min):	77.265	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	ipo 1	Calibration Level:	N/A
		Verification Tolerance:	N/A

Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		50.7476	24.813	0.000	14999916	0.00	BB	48.7		0
2		49.2524	28.205	0.000	14557996	0.00	BB	79.0		0
Totals		100.0000		0.000	29557912					

Data File:	e:\chromatograms2\cisco\test061.run	Operator (Calc):	
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Sample ID:	Manual Sample	Times Calculated:	2
Operator (Inj):		Calculation Method:	c:\star\kong\kong.mth
Injection Date:	02/10/07 01:13:45 PM	Instrument (Calc):	ipo 1
Injection Method:	c:\star\kong\kong.mth	Run Mode:	Analysis
Run Time (min):	34.040	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	ipo 1	Calibration Level:	N/A
		Verification Tolerance:	N/A

Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		1.3477	24.521	0.000	280283	0.00	BB	31.1		0
2		98.6523	27.695	0.000	20517508	0.00	BB	82.0		0
Totals		100.0000		0.000	20797792					

(Z)- N-But-3-enyl-N-(1-cyclohexyl-penta-2,4-dienyl)-4-methyl-benzenesulfonamide

Amine (34.2 mg, 0.108 mmol, 100 mol%), Cs₂CO₃ (176.2 mg, 1.08 mmol, 1000 mol%), and homoallyl bromide (73.0 mg, 1.08 mmol, 10 mol%) were suspended in 0.35 mL of DMF and the mixture stirred overnight at 70 °C. Water and ether were added to the suspension, and the aqueous layer was extracted three times with ether. The combined organic layers were dried with Na₂SO₄, and the solvent was removed under low pressure. The residue was purified by flash column chromatography (R_f = 0.4, hexane/EtOAc = 10/1) to furnish 28.9 mg of the title compound as a clear oil (84% yield).

¹H NMR (300 MHz, CDCl₃): 7.60 (d, *J* = 8.1 Hz, 2H), 7.17 (d, *J* = 7.8 Hz, 2H), 6.64 (dt, *J* = 16.8 Hz, 10.2 Hz, 1H), 6.00 (t, *J* = 11.1 Hz, 1H), 5.73 – 5.60 (m, 1H), 5.25 – 5.17 (m, 3H), 5.04 – 4.97 (m, 2H), 4.52 (t, *J* = 10.5 Hz, 1H), 3.16 – 2.95 (m, 2H), 2.49 – 2.39 (m, 1H), 2.35 (s, 3H), 2.30 – 2.18 (m, 1H), 2.01 (d, *J* = 12.6 Hz, 1H), 1.76 – 1.62 (m, 4H), 1.44 – 1.33 (m, 1H), 1.23 – 0.99 (m, 4H), 0.90 – 0.77 (m, 1H).

¹³C NMR (75 MHz, CDCl₃): 142.7, 137.7, 135.0, 132.5, 132.0, 129.2, 127.5, 127.2, 119.7, 116.7, 60.5, 43.8, 40.3, 35.1, 30.5, 30.2, 26.3, 26.1, 25.9, 21.5.

HRMS Calcd. for C₂₂H₃₂NO₂S (M+1): 374.2154, Found: 374.2151

FTIR (neat): 2924, 2851, 1641, 1598, 1450, 1337, 1154, 1090, 917, 812, 750, 663 cm⁻¹.

6-Cyclohexyl-1-(toluene-4-sulfonyl)-1,2,3,6-tetrahydro-pyridine

The triene (17.6 mg, 0.047 mmol, 100 mol%) was dissolved in dry degassed DCM (0.5 mL, 0.1 M) in a round-bottom flask under argon. The Grubb's II catalyst (2.0 mg, 0.0024 mmol, 5 mol%) was added, and the solution was stirred at reflux until the starting material was totally consumed. The solvent was evaporated, and the crude residue was purified by flash column chromatography (SiO₂: R_f = 0.4, hexane/EtOAc = 10/1) to furnish 14.3 mg of the title compound as a clear oil (95% yield).

¹H NMR (400 MHz, CDCl₃): 7.67 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 5.73 - 5.69 (m, 1H), 5.53 (d, *J* = 10.8 Hz, 1H), 3.98 (s, br, 1H), 3.84 - 3.79 (m, 1H), 3.17 - 3.09 (m, 1H), 1.92 (d, *J* = 12.8 Hz, 1H), 1.75 - 1.47 (m, 6H), 1.23 - 1.01 (m, 6H)

¹³C NMR (75 MHz, CDCl₃): 142.8, 138.8, 129.4, 127.1, 126.2, 125.1, 58.3, 43.1, 39.1, 30.2, 29.8, 26.3, 26.2, 26.1, 22.4, 21.5.

HRMS Calcd. for C₁₈H₂₆NO₂S (M+1): 320.1684, Found: 320.1688

FTIR (neat): 3036, 2924, 2851, 1598, 1494, 1449, 1342, 1283, 1212, 1159, 1059, 1041, 963, 925, 814, 717, 649 cm⁻¹.

(Z)-N-Allyl-N-(1-cyclohexyl-penta-2,4-dienyl)-4-methyl-benzenesulfonamide

Amine (104.3 mg, 0.33 mmol, 100 mol%), K_2CO_3 (68.4 mg, 0.49 mmol, 150 mol%), and allyl bromide (60.0 mg, 0.49 mmol, 150 mol%) were suspended in 1.1 mL of DMF and the mixture stirred overnight at room temperature. Water and ether were added to the suspension, and the aqueous layer was extracted three times with ether. The combined organic layers were dried with Na_2SO_4 , and the solvent was removed under low pressure. The residue was purified by flash column chromatography (SiO_2 : R_f = 0.4, hexane/EtOAc = 10/1) to furnish 118.6 mg of the title compound as a clear oil (100% yield).

1H NMR (400 MHz, $CDCl_3$): 7.60 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 6.65 (dt, J = 16.8 Hz, 10.8 Hz, 1H), 6.00 (t, J = 11.2 Hz, 1H), 5.80 – 5.70 (m, 1H), 5.28 (t, J = 11.0 Hz, 1H), 5.22 (dt, J = 16.4 Hz, 1H), 5.17 (d, J = 10.4 Hz, 1H), 5.10 (dd, J = 17.4, 1.4 Hz, 1H), 5.01 (dd, J = 9.8, 1.4 Hz, 1H), 4.53 (t, J = 10.6 Hz, 1H), 3.75 (dd, J = 16.4, 7.4 Hz, 1H), 3.66 (ddt, J = 16.2, 5.8, 1.4 Hz, 1H), 1.96 (d, J = 12.8 Hz, 1H), 1.74 – 1.56 (m, 4H), 1.50 – 1.40 (m, 1H), 1.23 – 0.93 (m, 4H), 0.85 – 0.71 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): 142.7, 137.7, 135.8, 132.2, 131.9, 129.1, 127.8, 127.5, 119.5, 117.0, 60.3, 47.0, 39.6, 30.1, 26.2, 26.0, 25.7, 21.4.

HRMS Calcd. for $C_{21}H_{30}NO_2S$ ($M+1$): 360.1997, Found: 360.1995

FTIR (neat): 2923, 2852, 1738, 1593, 1492, 1449, 1337, 1262, 1155, 1090, 1037, 1007, 921, 812, 767, 662 cm^{-1} .

1-Cyclohexyl-2-(toluene-4-sulfonyl)-2,3,3a,4,5,7a-hexahydro-1H-isoindole

(Note: The ratio of two diastereomers was determined by HPLC using the racemic product. In addition, the relative stereochemistry of the major diastereomer was assigned based on the report by Livinghouse⁶.)

A flame-dried 10 mL Schlenk tube was charged with [Rh(COD)₂]SbF₆ (3.1 mg, 0.0057 mmol, 5 mol%) and PPh₃ (4.5 mg, 0.017 mmol, 15 mol%), and fitted with a rubber septum. The flask was evacuated under high vacuum and back filled with argon. The precatalyst was dissolved in toluene (0.6 mL), allowed to stir for 5 min, then purged with H₂ and rapidly stirred for an additional 30 min. The H₂ was removed and followed by back filling with argon. The triene (40.7 mg, 0.113 mmol, 100 mol%) in toluene (0.6 mL) was then added by syringe and the reaction mixture was warmed to 80 °C with stirring 20 min. After the cycloaddition was complete (TLC), the solvent was evaporated, and the crude residue was purified by flash column chromatography (SiO₂: R_f = 0.4, hexane/EtOAc = 10/1) to furnish 35.5 mg of the title compound as a clear oil (87% yield, 9:1 dr).

¹H NMR (400 MHz, CDCl₃): 7.65 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 5.10 - 5.08 (m, 1H), 4.93 (d, *J* = 10.4 Hz, 1H), 3.36 (dd, *J* = 9.6, 7.6 Hz, 1H), 3.20 (d, *J* = 3.6 Hz, 1H), 3.01 (t, *J* = 9.0 Hz, 1H), 2.45 – 2.43 (m, 2H), 1.81 – 1.56 (m, 7H), 1.51 – 1.34 (m, 2H), 1.31 - 1.05 (m, 6H).

¹³C NMR (75 MHz, CDCl₃): 142.8, 138.8, 129.1, 128.1, 127.7, 126.5, 71.3, 50.5, 43.0, 39.6, 34.8, 30.4, 28.0, 26.6, 26.4, 26.2, 21.5, 20.9, 20.2.

HRMS Calcd. for C₂₁H₃₀NO₂S (M+1): 360.1997, Found: 360.1995

FTIR (neat): 3018, 2928, 2848, 1598, 1449, 1342, 1304, 1160, 1405, 1090, 1032, 988, 915, 846, 814, 709, 665 cm⁻¹.

⁶ O'Mahony, D. J. R.; Belanger, D. B.; Livinghouse, T. *Org. Biomol. Chem.* **2003**, *1*, 2038

Data File: e:\chromatograms2\abbas\test022.run
Channel: 1 = INTGR 1 RESULTS
Sample ID: Manual Sample
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Run Time (min): 28.287
Workstation:
Instrument (Inj): ipo 1

Operator (Calc):
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Times Calculated: 2
Calculation Method: c:\star\kong\kong.mth
Instrument (Calc): ipo 1
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
Calibration Level: N/A
Verification Tolerance: N/A

Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
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2		90.1501	21.049	0.000	46498672	0.00	BB	59.3		0
Totals		100.0000		0.000	51579144					

N-*tert*-Butoxycarbonyl-N(1-Cyclohexyl-penta-2,4-dienyl)-4-methyl-benzenesulfonamide

A solution of amine (61.0 mg, 0.19 mmol, 100 mol%) and Boc₂O (52.0 mg, 0.23 mmol, 120 mol%) in MeCN (1 mL, 0.2M) was treated with DMAP (2.4 mg, 0.019 mmol, 10 mol%) and left overnight under argon. Water and ether were added to the suspension, and the aqueous layer was extracted three times with ether. The combined organic layers were dried with Na₂SO₄, and the solvent was removed under low pressure. The residue was purified by flash column chromatography (SiO₂: R_f = 0.4, hexane/EtOAc = 10/1) to furnish 81.0 mg of the title compound as a clear oil (100% yield).

¹H NMR (300 MHz, CDCl₃): 7.67 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 6.85 (dt, *J* = 16.8 Hz, 10.6 Hz, 1H), 6.23 (t, *J* = 10.9 Hz, 1H), 5.86 (t, *J* = 10.4 Hz, 1H), 5.32 (d, *J* = 16.5 Hz, 1H), 5.23 (d, *J* = 10.2 Hz, 1H), 5.08 (t, *J* = 10.1 Hz, 1H), 2.38 (s, 3H), 2.11 - 2.00 (m, 1H), 1.90 - 1.78 (m, 2H), 1.72 - 1.63 (m, 3H), 1.28 (s, 9H), 1.37 - 1.00 (m, 4H), 0.89 - 0.78 (m, 1H).

¹³C NMR (75 MHz, CDCl₃): 150.6, 143.5, 137.8, 133.2, 132.1, 129.2, 129.0, 127.7, 120.0, 84.0, 60.7, 39.5, 31.1, 29.8, 27.9, 26.2, 25.9, 25.8, 21.5.

HRMS Calcd. for C₂₃H₃₄NO₄S (M+1): 420.2209, Found: 420.2206

FTIR (neat): 2929, 1724, 1597, 1495, 1450, 1393, 1355, 1278, 1256, 1162, 1087, 991, 813, 706, 665 cm⁻¹.

N-tert-Butoxycarbonyl-N-(1-Cyclohexyl-4-oxo-but-2-enyl)-4-methylbenzenesulfonamide

To a mixture of 1.2 mL of water and 2.9 mL of THF, OsO₄ (2.5 mg, 0.01 mmol, 5 mol%) and diene (85.2 mg, 0.20 mmol, 100 mol%) was added and then stirred for 5 minutes. While the temperature of the stirred mixture was maintained at 24 – 26 °C, NaIO₄ (95.5 mg, 0.45 mmol, 220 mol%) was added in portions over a period of 40 minutes. The solution was stirred for an additional 2 hours. The mixture was extracted thoroughly with ether and the combined organic layers were dried with Na₂SO₄. The solvent was removed *in vacuo*. Purification of the residue by flash chromatography (SiO₂: R_f = 0.4, EtOAc/hexane = 1/6) provides 70.3 mg of the title compound as a colorless oil (83% yield).

¹H NMR (300 MHz, CDCl₃): 10.2 (d, *J* = 8.1 Hz), 7.69 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 7.5 Hz, 2H), 7.04 (t, *J* = 10.9 Hz, 1H), 6.18 (dd, *J* = 10.8, 8.1 Hz, 1H), 5.54 (t, *J* = 10.5 Hz, 1H), 2.25 (m, 1H)- 2.06 (s, 3H), 1.89 – 1.65 (m, 5H), 1.34 (s, 9H), 1.30 – 0.88 9m, 5H).

¹³C NMR (75 MHz, CDCl₃): 191.3, 150.3, 147.2, 144.3, 137.0, 132.4, 129.3, 127.9, 85.0, 59.3, 38.5, 31.3, 29.6, 27.8, 26.0, 25.7, 25.6, 21.6.

HRMS Calcd. for C₂₂H₃₂NO₅S (M+1): 422.2001, Found: 422.2004

FTIR (neat): 2930, 2853, 1725, 1683, 1597, 1450, 1348, 1281, 1150, 1087, 1022, 943, 812, 768, 665 cm⁻¹.

N-*tert*-Butoxycarbonyl-N-4-Cyclohexyl-4-(toluene-4-sulfonylamino)-but-2-enoic acid methyl ester

To a solution of aldehyde (31.8 mg, 0.075 mmol, 100 mol%) in MeOH (1.4 mL, 0.05 M) was added manganese dioxide (154 mg, 1.5 mmol, 20 eq.) and sodium cyanide (15.5 mg, 0.30 mmol, 400 mol%). The resulting suspension was stirred at room temperature for 3 hrs, filtered and the filtrate evaporated. The residue was redissolved in water and extracted with ether, the combined organic extracts were dried with Na₂SO₄ and evaporated. The residue was purified by flash silica gel chromatography (R_f = 0.4, EtOAc/hexane = 1/6) to afford 26.3 mg as a colorless oil (77% yield).

¹H NMR (300 MHz, CDCl₃): 7.75 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 7.8 Hz, 2H), 6.63 (dd, *J* = 11.9, 10.0 Hz, 1H), 6.00 (dd, *J* = 11.7, 0.6 Hz, 1H), 5.92 (t, *J* = 10.2 Hz, 1H), 3.78 (s, 3H), 2.43 (s, 3H), 2.14 – 2.03 (m, 1H), 1.84 – 1.64 (m, 5H), 1.37 (s, 9H), 1.34 – 1.04 (m, 5H).

¹³C NMR (75 MHz, CDCl₃): 166.0, 150.8, 144.1, 143.7, 137.3, 129.0, 127.9, 122.5, 84.3, 60.0, 51.5, 39.4, 30.3, 29.7, 27.9, 26.1, 26.0, 26.0, 21.5.

HRMS Calcd. for C₂₃H₃₄NO₆S (M+1): 452.2107, Found: 452.2110

FTIR (neat): 2930, 2852, 1726, 1648, 1598, 1450, 1357, 1277, 1167, 1152, 1087, 988, 814, 668 cm⁻¹.

(,2*E*,4*Z*)-6-*N*-*p*-tolylsulfonyl-amino-6-cyclohexylhexa-2,4-dienyl acetate

Amine (25 mg, 0.078 mmol, 100 mol%) was dissolved in anhydrous DCM (0.4 mL) and 1,4-acetate-2-butene (40 mg, 0.234 mmol, 300 mol%) was added, following by Grubb's II catalyst (3.3 mg, 0.0039 mmol, 5 mol%). The reaction mixture was stirred for 14 hours, at which point the reaction mixture was deposited atop a silica gel column. The title compound was purified by flash column chromatography (SiO₂: R_f = 0.2, petroleum ether/CHCl₃/EtOAc = 6/3/1) to afford 22 mg (6:1 *E*:*Z*) as a clear oil (72 % yield).

¹H NMR (400 MHz, CDCl₃): 7.64 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.2 Hz, 2H), 6.24 (dd, *J* = 15.0, 11.2 Hz, 1H) 5.82 (t, *J* = 10.9 Hz, 1H), 5.64 (dt, *J* = 15.0, 6.5 Hz, 1H), 5.02 (t, *J* = 10.6 Hz, 1H), 4.53 (d, *J* = 6.5 Hz, 1H), 4.65 (d, *J* = 7.8 Hz, 2H), 3.94 (dt, *J* = 10.2, 7.2 Hz, 1H), 2.37 (s, 3H), 2.08 (s, 3H), 1.77 – 1.59 (m, 5H), 1.39 – 1.32 (m, 1H), 1.17 – 1.04 (m, 3H), 0.95 – 0.85 (m, 2H).

¹³C NMR (100 MHz, CDCl₃): 170.7, 143.1, 137.9, 130.1, 129.6, 129.4, 128.8, 128.2, 127.2, 64.5, 55.9, 42.9, 29.1, 28.5, 26.2, 25.9, 25.8, 21.5, 20.9

HRMS Calcd. for C₂₁H₃₀NO₄S (M+1): 392.1896, Found: 392.1891

FTIR (neat): 3270, 2926, 2852, 1740, 1598, 1448, 1330, 1240, 1160, 1093, 1027, 956, 814 cm⁻¹.

(S)-N-(4-nitrobenzylsulfonyl)-1-phenylpentan-1-amine

To the solution of diene (40 mg, 0.0114 mmol, 100 mol%) in DCM (1.2 mL, 0.1 M) at ambient temperature was added Crabtree's catalyst (7 mg, 0.0087 mmol, 7.5 mol%). The reaction was purged with argon followed by hydrogen. The reaction was allowed to stir at ambient temperature under 1 atm of hydrogen for 30 h. The volatiles were removed under reduced pressure. The title compound was purified by flash chromatography (SiO₂: rf = 0.4, 60/30/10 petroleum ether/CHCl₃/EtOAc) to afford 39.9 mg as a clear oil (99 % yield).

¹H NMR (400 MHz, CDCl₃): 8.04 (d, *J* = 8.9 Hz, 2H), 7.66 (d, *J* = 8.9 Hz, 2H), 7.11 – 7.05 (m, 3H), 6.92 (d, *J* = 7.5 Hz, 2H), 5.02 (d, *J* = 7.2 Hz, 1H), 4.37 (q, *J* = 7.2 Hz, 1H), 1.82 – 1.61 (m, 2H), 1.30 – 1.09 (m, 4H), 0.82 (t, *J* = 6.8 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): 149.5, 146.6, 140.0, 128.5, 128.1, 127.8, 126.5, 123.7, 58.8, 37.3, 27.9, 22.1, 13.8.

HRMS Calcd. for C₁₇H₂₁N₂O₄S (M+1): 349.1222, Found: 349.1223

FTIR (neat): 3280, 2932, 2874, 1529, 1456, 1349, 1164, 1092, 913, 744 cm⁻¹.

(S)-1-phenylpentan-1-amine

A mixture of substrate (74 mg, 0.212 mmol, 100 mol%), PhSH (0.087 mL, 0.848 mmol, 400 mol%), and K_2CO_3 (176 mg, 1.272 mmol, 600 mol%) were dissolved in MeCN (2.12 mL, 0.1 M).⁷ The reaction mixture was stirred at 50°C for 24 h under an atmosphere of argon. The title compound was purified by flash chromatography (SiO₂: rf = 0.05, 50/50/1 petroleum ether/EtOAc/TEA) to furnish 22.6 mg of the title compound as a clear oil (66 % yield).

¹H NMR (400 MHz, CDCl₃): 7.33 – 7.20 (m, 5H), 3.85 (t, J = 6.8 Hz, 1H), 1.67 – 1.30 (m, 4H), 1.29 – 1.17 (m, 4H), 0.85 (t, J = 7.2 Hz, 3H).

$[\alpha]_D = -17.2$ (c = 0.67, DCM, 94% ee) compared to $[\alpha]_D = -17.4$ (1.19, DCM, 94 % ee)⁸

⁷ Maligres, E., P.; See, M., M.; Askin, D.; Reider, J., P. *Tet. Lett.* **1997**, 38, 5253

⁸ Gonzalez, Z., A.; Soderquist, A.; J. *Org. Lett.* **2007**, ASAP