Diastereoselective metal-catalyzed [4+2+2] carbocyclization reactions utilizing a rhodium(I) N-heterocyclic carbene (NHC) complex: the first example of a rhodium(I)-NHC-catalyzed [m+n+o] carbocyclization

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Representative Experimental Procedures and Supplemental Data

**RhCl(IMes)(COD).** Silver oxide (231 mg, 1.0 mmol) was added to a stirred solution of 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride (685 mg, 2.0 mmol) in dichloromethane (15 mL) at room temperature and allowed to stir for an additional 2 hours. The resulting suspension was filtered through a small plug of celite® into a solution of [Rh(COD)Cl]₂ (490 mg, 1.0 mmol) and dichloromethane (5 mL). The yellow solution was stirred at room temperature for ca. 18 hours and the solvent was concentrated *in vacuo* to afford a crude solid. Purification by flash chromatography (10-50% gradient elution with ether/pentane) afforded Rh(IMes)(COD)Cl (938 mg, 86%) as orange-yellow crystals.

**MP** 212-214 °C (Uncorrected)

**¹H NMR** (400 MHz, CDCl₃) δ 7.04 (s, 2H), 6.99 (s, 2H), 6.93 (s, 2H), 4.50 (s, 2H), 3.27 (s, 2H), 2.38 (s, 6H), 2.37 (s, 6H), 2.09 (s, 6H), 1.89-1.78 (m, 4H), 1.58-1.52 (m, 4H).

**¹³C NMR** (100 MHz, C₆D₆) δ 183.69 (d, ¹J_RhC = 51.9 Hz, e), 138.77 (e), 137.70 (e), 136.38 (e) 134.46 (e), 129.81 (o), 128.23 (o), 123.63 (o), 96.21 (d, ¹J_RhC = 7.6 Hz, o), 67.93 (d, ¹J_RhC = 14.5 Hz, o), 32.83 (e), 28.50 (e), 21.25 (o), 19.92 (o), 18.24 (o).

**IR** (neat) 3116 (w), 3084 (w), 2911 (m), 2874 (m), 2829 (w), 1483 (s), 1317 (s), 1261 (s), 848 (s), 738 (s), 708 (vs) cm⁻¹.

**HRMS** (FAB, M⁺) calcd for C₂₉H₃₆ClN₂Rh 550.1620, found 550.1624.
**N-But-2-yn-1-yl-4-methyl-N-(1-methylprop-2-en-1-yl)benzene sulfonamide 1a.**

**1H NMR** (400 MHz, C\textsubscript{6}D\textsubscript{6}) $\delta$ 7.83 (m, 2H), 6.87 (d, $J = 7.6$ Hz, 2H), 5.71-5.62 (m, 1H), 4.91 (d, $J = 16.5$ Hz, 1H), 4.88 (d, $J = 10.4$ Hz, 1H), 4.63-4.60 (m, 1H), 4.10-4.05 (m, 1H), 3.79-3.73 (m, 1H), 1.97 (s, 3H), 1.33 (t, $J = 2.3$ Hz, 3H), 1.08 (dd, $J = 7.0, 2.4$ Hz, 3H).

**13C NMR** (100 MHz, C\textsubscript{6}D\textsubscript{6}) $\delta$ 142.60 (e), 139.22 (e), 138.22 (e), 129.34 (o), 127.92 (o), 116.40 (e), 80.09 (e), 76.09 (e), 55.05 (o), 33.09 (e), 21.15 (o), 17.20 (o), 3.14 (o).

**IR** (neat) 3087 (w), 3066 (w), 2981 (m), 2921 (m), 2230 (w), 1640 (w), 1598 (m), 1336 (vs), 1157 (vs), 1095 (vs) cm\textsuperscript{-1}.

**HRMS** (EI, M$^+$) calcd for C\textsubscript{15}H\textsubscript{19}NO\textsubscript{2}S 277.1136, found 277.1115.

**N-(1-benzylprop-2-en-1-yl)-N-but-2-yn-1-yl-4-methylbenzene sulfonamide 1b.**

**1H NMR** (400 MHz, C\textsubscript{6}D\textsubscript{6}) $\delta$ 7.76 (d, $J = 8.2$ Hz, 2H), 7.09-7.01 (m, 5H), 6.72 (d, $J = 7.9$ Hz, 2H), 5.74 (ddd, $J = 17.1, 10.3, 6.3$ Hz, 1H), 4.95-4.84 (m, 3H), 4.15 (dd, A of ABX, $J_{AB} = 18.3$ Hz, $J_{AX} = 2.4$ Hz, 1H), 3.87 (dd, B of ABX, $J_{AB} = 18.2$ Hz, $J_{BX} = 2.4$ Hz, 1H), 3.05 (dd, A of ABX, $J_{AB} = 13.6$ Hz, $J_{AX} = 6.2$ Hz, 1H), 2.84 (dd, B of ABX, $J_{AB} = 13.6$ Hz, $J_{BX} = 9.0$ Hz, 1H), 1.86 (s, 3H), 1.31 (t, $J = 2.4$ Hz, 3H).

**13C NMR** (100 MHz, C\textsubscript{6}D\textsubscript{6}) $\delta$ 142.58 (e), 139.16 (e), 138.47 (e), 135.48 (o), 129.65 (o), 129.23 (o), 128.61 (o), 126.59 (o), 118.13 (e), 80.48 (e), 75.86 (e), 61.86 (o), 39.64 (e), 34.06 (e), 21.09 (o), 3.12 (o).

**IR** (neat) 3086 (w), 3064 (w), 3028 (w), 2921 (w), 2856 (w), 1598 (w), 1496 (w), 1455 (w), 1337 (m), 1160 (vs), 1094 (m) cm\textsuperscript{-1}.

**HRMS** (EI, M$^+$) calcd for C\textsubscript{21}H\textsubscript{23}NO\textsubscript{2}S 353.1449, found 353.1442.
**N-But-2-yn-1-yl-4-methyl-N-[1-(2-phenylethyl)prop-2-en-1-yl]benzenesulfonamide 1c.**

**1H NMR** (400 MHz, C\textsubscript{6}D\textsubscript{6}) δ 7.81 (d, J = 8.2 Hz, 2H), 7.15-7.13 (m, 2H), 7.07-7.05 (m, 3H), 6.76 (d, J = 7.9 Hz, 2H), 5.59 (ddd, J = 17.3, 10.6, 5.8 Hz, 1H), 4.88 (dt, J = 17.3, 1.3 Hz, 1H), 4.85 (dt, J = 10.5, 1.2 Hz, 1H), 4.57-4.51 (m, 1H), 4.12 (dd, A of ABX, J\textsubscript{AB} = 18.3 Hz, J\textsubscript{AX} = 2.3 Hz, 1H), 3.79 (dd, B of ABX, J\textsubscript{AB} = 18.3 Hz, J\textsubscript{BX} = 2.4 Hz, 1H), 2.76 (ddd, A of ABMX, J\textsubscript{AB} = 15.0 Hz, J\textsubscript{AX} = 10.6 Hz, J\textsubscript{AM} = 5.5 Hz, 1H), 2.52 (ddd, B of ABMX, J\textsubscript{AB} = 15.0 Hz, J\textsubscript{BX} = 10.9 Hz, J\textsubscript{BM} = 5.4 Hz, 1H), 2.00-1.90 (m, 1H), 1.87 (s, 3H), 1.80-1.71 (m, 1H), 1.32 (t, J = 2.4 Hz, 3H).

**13C NMR** (100 MHz, C\textsubscript{6}D\textsubscript{6}) δ 142.65 (e), 142.11 (e), 139.28 (e), 136.45 (o), 129.30 (o), 128.73 (o), 128.61 (o), 127.97 (o), 126.14 (o), 117.44 (e), 79.95 (e), 76.01 (e), 59.90 (o), 33.88 (e), 33.33 (e), 32.98 (e), 21.09 (o), 3.15 (o).

**IR** (neat) 3085 (w), 3063 (w), 3027 (w), 2921 (w), 2859 (w), 1599 (w), 1496 (w), 1455 (w), 1338 (s), 1160 (vs), 1094 (m) cm\textsuperscript{-1}.

**HRMS** (EI, M\textsuperscript{+}) calcd for C\textsubscript{22}H\textsubscript{25}NO\textsubscript{2}S 367.1606, found 367.1605.

**N-But-2-yn-1-yl-N-(1-isopropylprop-2-en-1-yl)-4-methylbenzene sulfonamide 1d.**

**1H NMR** (400 MHz, C\textsubscript{6}D\textsubscript{6}) δ 7.80 (d, J = 8.2 Hz, 2H), 6.83 (d, J = 7.9 Hz, 2H), 5.63 (ddd, J = 17.1, 10.4, 9.2 Hz, 1H), 4.85 (d, J = 16.5 Hz, 1H), 4.84 (d, J = 11.0 Hz, 1H), 4.02 (t, J = 9.8 Hz, 1H), 4.00-3.85 (m, 2H), 1.93 (s, 3H), 1.81-1.75 (m, 1H), 1.33 (t, J = 2.2 Hz, 3H), 1.05 (d, J = 6.7 Hz, 3H), 0.76 (t, J = 6.7 Hz, 3H).

**13C NMR** (100 MHz, C\textsubscript{6}D\textsubscript{6}) δ 142.53 (e), 139.25 (e), 135.20 (o), 129.12 (o), 128.15 (o), 118.52 (e), 80.24 (e), 75.60 (e), 67.85 (o), 33.88 (e), 30.07 (o), 21.12 (o), 20.46 (o), 20.32 (o), 3.09 (o).
IR (neat) 3077 (w), 2963 (m), 2923 (m), 2874 (w), 1599 (w), 1337 (s), 1159 (s), 1092 (s) cm\(^{-1}\).

HRMS (EI, M\(^+\)) calcd for C\(_{17}\)H\(_{23}\)NO\(_2\)S 305.1449, found 305.1432.

\[ \text{N-But-2-yn-1-yl-N-(1-cyclohexylprop-2-en-1-yl)-4-methylbenzene sulfonamide 1e.} \]

\[ ^1H\text{ NMR} \quad (400 \text{ MHz, C}_6D_6) \delta \]
\[ 7.84 \text{ (d, } J = 8.2 \text{ Hz, 2H)}, \]
\[ 6.77 \text{ (d, } J = 8.2 \text{ Hz, 2H)}, \]
\[ 5.61 \text{ (dt, } J = 18.1, 9.1 \text{ Hz, 1H)}, \]
\[ 4.90 \text{ (d, } J = 15.8 \text{ Hz, 1H)}, \]
\[ 4.85 \text{ (d, } J = 11.5 \text{ Hz, 1H)}, \]
\[ 4.18 \text{ (t, } J = 9.5 \text{ Hz, 1H)}, \]
\[ 3.95 \text{ (dq, } A \text{ of ABX, } J_{AB} = 18.4 \text{ Hz, } J_{AX} = 2.4 \text{ Hz, 1H)}, \]
\[ 3.85 \text{ (dq, } B \text{ of ABX, } J_{AB} = 18.2 \text{ Hz, } J_{BX} = 2.4 \text{ Hz, 1H)}, \]
\[ 1.88 \text{ (s, 3H)}, \]
\[ 1.72-1.47 \text{ (m, 5H)}, \]
\[ 1.33 \text{ (t, } J = 2.4 \text{ Hz, 3H)}, \]
\[ 0.78-0.69 \text{ (m, 1H)} \]

\[ ^{13}C\text{ NMR} \quad (100 \text{ MHz, C}_6D_6) \delta \]
\[ 142.36 \text{ (e)}, \]
\[ 139.48 \text{ (e)}, \]
\[ 135.01 \text{ (o)}, \]
\[ 129.07 \text{ (o)}, \]
\[ 128.17 \text{ (o)}, \]
\[ 118.53 \text{ (e)}, \]
\[ 80.07 \text{ (e)}, \]
\[ 75.70 \text{ (e)}, \]
\[ 66.72 \text{ (o)}, \]
\[ 39.13 \text{ (o)}, \]
\[ 33.84 \text{ (e)}, \]
\[ 30.91 \text{ (e)}, \]
\[ 26.66 \text{ (e)}, \]
\[ 26.41 \text{ (e)}, \]
\[ 26.32 \text{ (e)}, \]
\[ 21.09 \text{ (o)}, \]
\[ 3.09 \text{ (o)} \]

IR (neat) 3076 (w), 2923 (s), 2852 (s), 1599 (w), 1450 (m), 1337 (s), 1156 (s), 1094 (m), 1040 (m) cm\(^{-1}\).

HRMS (EI, M\(^+\)) calcd for C\(_{20}\)H\(_{27}\)NO\(_2\)S 345.1762, found 345.1749.

\[ \text{N-But-2-yn-1-yl-N-[1-(hydroxymethyl)prop-2-en-1-yl]-4-methyl benzenesulfonamide 1f.} \]

\[ ^1H\text{ NMR} \quad (400 \text{ MHz, C}_6D_6) \delta \]
\[ 7.83 \text{ (d, } J = 8.2 \text{ Hz, 2H)}, \]
\[ 6.87 \text{ (d, } J = 8.2 \text{ Hz, 2H)}, \]
\[ 5.56 \text{ (ddd, } J = 16.8, 10.7, 5.5 \text{ Hz, 1H)}, \]
\[ 4.99 \text{ (d, } J = 17.4 \text{ Hz, 1H)}, \]
\[ 4.92 \text{ (d, } J = 10.7 \text{ Hz, 1H)}, \]
\[ 4.66 \text{ (dd, } J = 13.7, 5.8 \text{ Hz, 1H)}, \]
\[ 4.20 \text{ (dd, } A \text{ of ABX, } J_{AB} = 18.3 \text{ Hz, } J_{AX} = 2.4 \text{ Hz, 1H)}, \]
\[ 3.80 \text{ (dd, } B \text{ of ABX, } J_{AB} = 18.3 \text{ Hz, } J_{BX} = 2.1 \text{ Hz, 1H)}, \]
\[ 3.75-3.72 \text{ (m, 1H)}, \]
\[ 3.69-3.63 \text{ (m, 1H)}, \]
\[ 2.57 \text{ (bs, 1H)}, \]
\[ 1.95 \text{ (s, 3H)}, \]
\[ 1.30 \text{ (t, } J = 2.3 \text{ Hz, 3H)}. \]
\(^{13}\)C NMR (100 MHz, C\(_6\)D\(_6\)) \(\delta\) 143.11 (e), 138.69 (e), 133.17 (o), 129.43 (o), 128.02 (o), 118.69 (e), 80.74 (e), 75.62 (e), 62.74 (e), 62.00 (o), 33.70 (e), 21.15 (o), 2.97 (o).

IR (neat) 3538 (bs), 2922 (w), 2882 (w), 1598 (w), 1428 (w), 1333 (m), 1159 (s), 1094 (s), 1054 (m) cm\(^{-1}\).

HRMS (EI, M\(^+\)) calcd for C\(_{15}\)H\(_{19}\)NO\(_3\)S 293.1086, found 293.1086.

\(N\)-{[Benzyloxy)methyl]prop-2-en-1-yl}-\(N\)-but-2-yn-1-yl-4-methylbenzenesulfonamide 1g.

\(^1\)H NMR (400 MHz, C\(_6\)D\(_6\)) \(\delta\) 7.86 (d, \(J = 8.1\) Hz, 2H), 7.15-7.06 (m, 5H), 6.73 (d, \(J = 8.1\) Hz, 2H), 5.81 (ddd, \(J = 16.8, 10.4, 5.5\) Hz, 1H), 5.12 (d, \(J = 17.4\) Hz, 1H), 5.00 (d, \(J = 10.6\) Hz, 1H), 4.86 (q, \(J = 6.1\) Hz, 1H), 4.24 (dq, \(J = 18.0\) Hz, \(J = 2.0\) Hz, 1H), 4.18 (d, \(J = 11.2\) Hz, 1H), 4.15 (d, \(J = 11.9\) Hz, 1H), 4.02 (dq, \(J = 18.0\) Hz, \(J = 2.4\) Hz, 1H), 3.61 (dd, \(J = 9.9\) Hz, \(J = 6.0\) Hz, 1H), 3.53 (dd, \(J = 9.9\) Hz, \(J = 6.2\) Hz, 1H), 1.88 (s, 3H), 1.28 (t, \(J = 2.4\) Hz, 3H)

\(^{13}\)C NMR (100 MHz, C\(_6\)D\(_6\)) \(\delta\) 142.41 (e), 139.33 (e), 138.61 (e), 134.27 (o), 129.13 (o), 128.46 (o), 128.11 (o), 127.64 (o), 118.31 (e), 80.01 (e), 75.87 (e), 73.02 (e), 71.09 (e), 59.50 (o), 34.53 (e), 21.09 (o), 3.09 (o).

IR (neat) 3064 (m), 3030 (m), 2920 (m), 2861 (m), 1641 (m), 1598 (m), 1496 (m), 1455 (m), 1336 (s), 1159 (vs), 1094 (s).

HRMS (CI, M\(^+\)) calcd for C\(_{22}\)H\(_{26}\)NO\(_3\)S 384.1633, found 384.1635.

\(N\)-[1-{[\textit{tert}-Butyl(dimethyl)silyl]oxy}methyl]prop-2-en-1-yl]-\(N\)-but-2-yn-1-yl-4-methylbenzenesulfonamide 1h.

\(^1\)H NMR (400 MHz, C\(_6\)D\(_6\)) \(\delta\) 7.85 (d, \(J = 8.2\) Hz, 2H), 6.77 (d, \(J = 8.2\) Hz, 2H), 5.88 (ddd, \(J = 17.0, 10.6, 6.1\) Hz, 1H), 5.13 (dt, \(J = 8.2\) Hz, 2H), 5.09 (d, \(J = 11.2\) Hz, 1H), 4.20 (dq, \(J = 18.0\) Hz, \(J = 2.4\) Hz, 1H), 4.15 (d, \(J = 11.9\) Hz, 1H), 4.02 (dq, \(J = 18.0\) Hz, \(J = 2.4\) Hz, 1H), 3.61 (dd, \(J = 9.9\) Hz, \(J = 6.2\) Hz, 1H), 1.88 (s, 3H), 1.28 (t, \(J = 2.4\) Hz, 3H)
17.4, 1.5 Hz, 1H), 5.02 (dt, J = 10.6, 1.4 Hz, 1H), 4.65 (q, J = 6.3 Hz, 1H), 4.26 (dq, A of ABX, $J_{AB} = 18.0$, $J_{AX} = 2.3$ Hz, 1H), 4.05 (dd, B of ABX, $J_{AB} = 18.0$, $J_{BX} = 2.3$ Hz, 1H), 3.90 (dd, A of ABX, $J_{AB} = 10.3$ Hz, $J_{AX} = 6.7$ Hz, 1H), 3.86 (dd, B of ABX, $J_{AB} = 10.3$, $J_{BX} = 6.0$ Hz, 1H), 1.89 (s, 3H), 1.32 (t, $J = 2.3$ Hz, 3H), 0.90 (s, 9H), 0.01 (s, 6H).

$^{13}$C NMR (100 MHz, C$_6$D$_6$) δ 142.55 (e), 139.39 (e), 134.26 (o), 129.29 (o), 118.72 (e), 80.18 (e), 76.09 (e), 64.90 (e), 61.65 (o), 34.92 (e), 26.04 (o), 21.11 (o), 18.44 (e), 3.16 (o), -5.37 (o).

IR (neat) 2955 (m), 2929 (m), 2885 (m), 2857 (m), 1598 (w), 1495 (w), 1472 (m), 1338 (s), 1161 (vs), 1094 (s) cm$^{-1}$.

HRMS (ESI, M+Na$^+$) calcd for C$_{21}$H$_{33}$NNaO$_3$Si 430.1848, found 430.1850.

Methyl 2-{but-2-yn-1-yl[(4-methylphenyl)sulfonyl]amino}but-3-enoate 1i.

$^1$H NMR (400 MHz, C$_6$D$_6$) δ 7.84 (d, J = 8.2 Hz, 2H), 6.73 (d, J = 8.2 Hz, 2H), 6.07 (ddd, J = 16.8, 10.4, 6.1 Hz, 1H), 5.28 (d, J = 6.1 Hz, 1H), 5.19 (d, J = 17.1 Hz, 1H), 5.04 (d, J = 10.4 Hz, 1H), 4.29 (dq, A of ABX, $J_{AB} = 18.0$ Hz, $J_{AX} = 2.4$ Hz, 1H), 4.13 (dq, B of ABX, $J_{AB} = 18.0$ Hz, $J_{BX} = 2.4$ Hz, 1H), 3.19 (s, 3H), 1.85 (s, 3H), 1.26 (t, J = 2.4 Hz, 3H).

$^{13}$C NMR (100 MHz, C$_6$D$_6$) δ 170.00 (e), 142.97 (e), 138.25 (e), 131.53 (o), 129.27 (o), 128.17 (o), 120.10 (e), 80.92 (e), 74.71 (e), 61.95 (o), 51.76 (o), 35.93 (e), 21.08 (o), 3.11 (o).

IR (neat) 3030 (w), 2954 (m), 2922 (m), 1746 (vs), 1598 (w), 1436 (m), 1349 (s), 1162 (s), 1093 (s) cm$^{-1}$.

HRMS (EI, M$^+$) calcd for C$_{16}$H$_{19}$NO$_4$S 321.1035, found 321.1021.
N-But-2-yn-1-yl-4-methyl-N-(1-vinylprop-2-en-1-yl)benzenesulfonamide 1j.

$^1$H NMR (400 MHz, C$_6$D$_6$) $\delta$ 7.86 (d, $J = 8.3$ Hz, 2H), 6.76 (d, $J = 8.2$ Hz, 2H), 5.79 (2ddd, $J = 17.1$, 10.3, 5.9 Hz, 2H), 5.17-5.14 (m, 1H), 5.02 (2dt, $J = 17.3$, 1.2 Hz, 2H), 4.94 (2dt, $J = 10.5$, 1.2 Hz, 2H), 4.00 (q, $J = 2.3$ Hz, 2H), 1.88 (s, 3H), 1.27 (t, $J = 2.4$ Hz, 3H).

$^{13}$C NMR (100 MHz, C$_6$D$_6$) $\delta$ 142.59 (e), 139.36 (e), 135.42 (o), 129.17 (o), 118.30 (e), 80.49 (e), 75.78 (e), 62.44 (o), 34.39 (e), 21.15 (o), 3.15 (o).

IR (neat) 2922 (s), 2852 (m), 1598 (w), 1337 (m), 1160 (vs), 1093 (s) cm$^{-1}$.

HRMS (EI, M$^+$) calcd for C$_{16}$H$_{19}$NO$_2$S 289.1136, found 289.1127.

N-But-2-yn-1-yl-4-methyl-N-(1-vinylbut-3-en-1-yl)benzenesulfonylamine 1k.

$^1$H NMR (400 MHz, C$_6$D$_6$) $\delta$ 7.78 (d, $J = 8.2$ Hz, 2H), 6.88 (d, $J = 7.6$ Hz, 2H), 5.70-5.60 (m, 2H), 4.96-4.92 (m, 2H), 4.91-4.88 (m, 2H), 4.53-4.51 (m, 1H), 4.03 (dt, A of ABX, $J_{AB} = 18.3$ Hz, $J_{AX} = 2.1$ Hz, 1H), 3.84 (dt, B of ABX, $J_{AB} = 18.3$ Hz, $J_{BX} = 2.1$ Hz, 1H), 2.36 (dt, A of ABX, $J_{AB} = 14.3$ Hz, $J_{AX} = 7.6$ Hz, 1H), 2.26 (dt, B of ABX, $J_{AB} = 14.3$ Hz, $J_{BX} = 7.3$ Hz, 1H), 1.97 (s, 3H), 1.34 (t, $J = 2.1$ Hz, 3H).

$^{13}$C NMR (100 MHz, C$_6$D$_6$) $\delta$ 142.86 (e), 139.12 (e), 135.42 (o), 129.17 (o), 127.97 (o), 117.58 (e), 117.20 (e), 80.35 (e), 75.71 (e), 59.95 (o), 36.85 (e), 33.51 (e), 21.15 (o), 3.12 (o).

IR (neat) 3078 (m), 2980 (s), 2921 (m), 2856 (m), 1642 (w), 1598 (w), 1441 (w), 1338 (m), 1160 (vs), 1093 (s) cm$^{-1}$.

HRMS (EI, M$^+$) calcd for C$_{17}$H$_{21}$NO$_2$S 303.1293, found 303.1254.
N-But-2-yn-1-yl-4-methyl-N-(1-phenylprop-2-en-1-yl)benzene sulfonamide 1l.

\(^1H\) NMR (400 MHz, \(C_6D_6\)) \(\delta\) 7.87 (d, \(J = 8.2\) Hz, 2H), 7.37 (d, \(J = 7.6\) Hz, 2H), 7.10-7.00 (m, 3H), 6.77 (d, \(J = 8.2\) Hz, 2H), 6.11 (ddd, \(J = 17.4, 10.7, 7.9\) Hz, 1H), 5.80 (d, \(J = 7.6\) Hz, 1H), 4.97 (d, \(J = 10.4\) Hz, 1H), 4.95 (d, \(J = 17.1\) Hz, 1H), 4.13 (dq, A of ABX, \(J_{AB} = 18.2\) Hz, \(J_{AX} = 4.8\) Hz, 1H), 3.74 (dq, B of ABX, \(J_{AB} = 18.2\) Hz, \(J_{BX} = 4.6\) Hz, 1H), 1.89 (s, 3H), 1.21 (t, \(J = 2.4\) Hz, 3H).

\(^13C\) NMR (100 MHz, \(C_6D_6\)) \(\delta\) 142.57 (e), 139.25 (e), 139.00 (e), 134.76 (o), 129.06 (o), 128.65 (o), 128.47 (o), 128.35 (o), 118.80 (e), 80.61 (e), 75.42 (e), 63.98 (o), 34.64 (e), 24.113 (o), 3.05 (o).

IR (neat) 3026 (m), 2929 (m), 2855 (m), 1651 (w), 1599 (m), 1495 (m), 1455 (m), 1344 (s), 1161 (vs), 1095 (s) cm\(^{-1}\).

HRMS (Cl, M+H\(^+\)) calcd for C\(_{20}\)H\(_{22}\)O\(_2\)NS 340.1371, found 340.1371.

\((6Z,9E)-3,9\)-Dimethyl-2-[\(4\)-methylphenyl)sulfonyl]-2,3,3a,4,5,8-hexahydro-1H-cycloocta[c]pyrrole 2a.

**Representative Procedure for Intermolecular Rhodium(I)-Catalyzed [4+2+2] Carbocyclization:** Silver triflate (13.0 mg, 0.05 mmol) was added to RhCl(IMes)(COD) (14.0 mg, 0.025 mmol) in anhydrous toluene (5.0 mL) under an atmosphere of nitrogen in a sealed tube. The catalyst was allowed stir in the dark for ca. 15 minutes. Enyne 1a (69.0 mg, 0.25 mmol) was then added to the catalyst under a stream of nitrogen. The sealed tube was evacuated and refilled with 1,3-butadiene three times. The sealed tube was then heated in a 110 °C oil bath overnight. The resulting mixture was purified by flash chromatography (eluting with 5-10% ethyl acetate/hexanes) furnishing 2a (62 mg, 75%) as a clear thick oil.
$^1$H NMR (400 MHz, C$_6$D$_6$) δ 7.81 (d, $J = 7.9$ Hz, 2H), 6.79 (d, $J = 8.2$ Hz, 2H), 5.52 (ddd, $J = 11.5, 7.2, 4.8$ Hz, 1H), 5.29-5.23 (m, 1H), 4.08 (d, A of AB, $J_{AB} = 13.7$ Hz, 1H), 3.86 (dd, B of ABX, $J_{AB} = 14.0$ Hz, $J_{BX} = 1.2$ Hz, 1H), 3.68 (dq, $J = 6.4, 1.2$ Hz, 1H), 2.70-2.63 (m, 2H), 2.18 (dd, B of ABX, $J_{AB} = 17.6$ Hz, $J_{BX} = 3.9$ Hz, 1H), 1.99 (dt, A of ABX, $J_{AB} = 13.6$ Hz, $J_{AX} = 4.2$ Hz, 1H), 1.88 (s, 3H), 1.71 (ddd, B of ABMX, $J_{AB} = 13.0$ Hz, $J_{BX} = 9.8$ Hz, $J_{BM} = 6.4$ Hz, 1H), 1.23 (d, $J = 6.5$ Hz, 3H), 1.17-1.09 (m, 1H), 0.80-0.71 (m, 1H).

$^{13}$C NMR (100 MHz, C$_6$D$_6$) δ 142.62 (e), 137.34 (e), 130.78 (e), 130.32 (o), 129.94 (e), 129.55 (o), 129.00 (o), 127.73 (o), 63.18 (o), 50.42 (e), 48.92 (o), 35.91 (e), 29.35 (e), 25.36 (e), 21.86 (o), 21.07 (o) 20.83 (o).

IR (neat) 3017 (w), 2929 (m), 2865 (m), 1710 (w), 1652 (w), 1598 (w), 1495 (w), 1455 (m), 1377 (m), 1341 (vs), 1305 (m), 1289 (m), 1163 (vs), 1095 (s), 1050 (m), 1018 (m), 756 (m), 666 (vs), 549 (s) cm$^{-1}$.

HRMS (EI, M$^+$) calcd. For C$_{19}$H$_{25}$NO$_2$S 331.1606, found 331.1590.

(6Z,9E)-3-Benzyl-9-methyl-2-[(4-methylphenyl)sulfonyl]-2,3,3a,4,5,8-hexahydro-1H-cycloocta[c]pyrrole 2b.

$^1$H NMR (400 MHz, C$_6$D$_6$) δ 7.82 (d, $J = 8.2$ Hz, 2H), 7.21 (d, $J = 7.3$ Hz, 2H), 7.10 (t, $J = 7.5$ Hz, 2H), 7.03-7.01 (m, 1H), 6.79 (d, $J = 8.2$ Hz, 2H), 5.46 (ddd, $J = 11.3, 6.7, 4.8$ Hz, 1H), 5.16-5.09 (m, 1H), 4.02 (dd, $J = 8.9, 3.7$ Hz, 1H), 3.98 (d, A of AB, $J_{AB} = 14.0$ Hz, 1H), 3.88-3.83 (m, 1H), 3.15 (dd, A of ABX, $J_{AB} = 13.1$ Hz, $J_{AX} = 3.7$ Hz, 1H), 3.00 (dd, $J = 11.8, 4.5$ Hz, 1H), 2.83 (dd, B of ABX, $J_{AB} = 13.1$ Hz, $J_{BX} = 8.5$ Hz, 1H), 2.67 (dd, A of ABX, $J_{AB} = 18.5$ Hz, $J_{AX} = 6.6$ Hz, 1H), 2.19 (dd, B of ABX, $J_{AB} = 18.3$ Hz, $J_{BX} = 2.1$ Hz, 1H), 1.99-1.89 (m, 1H), 1.87 (s, 3H), 1.58-1.51 (m, 1H), 1.22 (s, 3H), 0.95 (tt, A of ABX, $J_{AB} = 12.4$ Hz, $J_{AX} = 4.2$ Hz, 1H), 0.63 (tt, B of ABX, $J_{AB} = 12.5$ Hz, $J_{BX} = 4.7$ Hz, 1H).
\(^{13}\text{C NMR}\) (100 MHz, C\(_6\)D\(_6\)) \(\delta\) 142.71 (e), 138.68 (e), 137.43 (e), 130.82 (e), 130.14 (o), 129.91 (o), 129.59 (o), 129.18 (e), 128.53 (o), 128.49 (o), 127.67 (o), 126.57 (o), 68.55 (o), 50.71 (e), 44.80 (o), 42.75 (e), 36.37 (e), 29.15 (e), 24.85 (e), 21.06 (o), 20.84 (o).

\(\text{IR (neat)}\) 3062 (w), 3025 (w), 2928 (m), 2854 (w), 1731 (w), 1654 (w), 1598 (w), 1494 (m), 1454 (m), 1343 (vs), 1161 (vs), 1096 (s), 1056 (m), 1017 (w), 751 (s), 668 (s), 547 (s) cm\(^{-1}\).

\(\text{HRMS (CI, M+H}^+\) calcd for C\(_{25}\)H\(_{30}\)NO\(_2\)S 408.1992, found 408.1982.

(6Z,9E)-9-Methyl-2-[(4-methylphenyl)sulfonyl]-3-(2-phenylethyl)-2,3,3a,4,5,8-hexahydro-1\(H\)-cycloocta[c]pyrrole 2c.

\(^{1}\text{H NMR}\) (400 MHz, C\(_6\)D\(_6\)) \(\delta\) 7.79 (d, \(J = 8.2\) Hz, 2H), 7.17-7.05 (m, 5H), 6.76 (d, \(J = 8.1\) Hz, 2H), 5.52 (ddd, \(J = 11.4, 7.2, 4.7\) Hz, 1H), 5.25 (q, \(J = 9.0\) Hz, 1H), 4.10 (d, A of AB, \(J_{AB} = 14.1\) Hz, 1H), 3.95 (dd, B of ABX, \(J_{AB} = 14.2\) Hz, \(J_{BX} = 1.1\) Hz, 1H), 3.72 (dd, \(J = 7.3, 5.1\) Hz, 1H), 2.87 (dd, \(J = 11.8, 3.7\) Hz, 1H), 2.76-2.63 (m, 3H), 2.23-2.09 (m, 2H), 2.05-1.96 (m, 1H), 1.91-1.82 (m, 1H), 1.86 (s, 3H), 1.73-1.65 (m, 1H), 1.28 (s, 3H), 1.09 (tt, A of ABX, \(J_{AB} = 12.3\) Hz, \(J_{AX} = 4.0\) Hz, 1H), 0.63 (tt, B of ABX, \(J_{AB} = 12.5\) Hz, \(J_{BX} = 4.7\) Hz, 1H).

\(^{13}\text{C NMR}\) (100 MHz, C\(_6\)D\(_6\)) \(\delta\) 142.82 (e), 142.08 (e), 137.17 (e), 131.24 (e), 130.51 (o), 129.70 (o), 129.63 (o), 128.84 (o), 128.81 (o), 128.67 (o), 127.78 (e), 126.11 (o), 67.22 (o), 50.96 (e), 46.29 (o), 38.22 (e), 36.19 (e), 32.59 (e), 29.58 (e), 25.30 (e), 21.11 (o), 20.92 (o).

\(\text{IR (neat)}\) 3062 (w), 3024 (m), 2927 (m), 2856 (m), 1652 (w), 1599 (w), 1496 (m), 1454 (m), 1343 (s), 1305 (m), 1290 (w), 1161 (vs), 1095 (m), 1050 (m), 1017 (w), 753 (m), 668 (s), 548 (m) cm\(^{-1}\).

\(\text{HRMS (CI, M+H}^+\) calcd for C\(_{26}\)H\(_{32}\)NO\(_2\)S 422.2148, found 422.2138.
(6Z,9E)-3-Isopropyl-9-methyl-2-[(4-methylphenyl)sulfonyl]-2,3,3a,4,5,8-hexahydro-1H-cycloocta[c]pyrrole 2d.

$^1$H NMR (400 MHz, C$_6$D$_6$) $\delta$ 7.84 (d, $J = 8.2$ Hz, 2H), 6.78 (d, $J = 7.9$ Hz, 2H), 5.51 (ddd, $J =$ 11.3, 7.0, 4.6 Hz, 1H), 5.24 (q, $J =$ 9.0 Hz, 1H), 4.11 (d, A of AB, $J_{AB} =$ 14.3 Hz, 1H), 3.99 (d, B of AB, $J_{AB} =$ 14.0 Hz, 1H), 3.65 (d, $J =$ 4.6 Hz, 1H), 2.98 (dd, $J =$ 11.6, 4.0 Hz, 1H), 2.68 (dd, A of ABX, $J_{AB} =$ 18.2 Hz, $J_{AX} =$ 6.6 Hz, 1H), 2.30-2.19 (m, 2H), 2.08-1.97 (m, 1H), 1.86 (s, 3H), 1.70-1.64 (m, 1H), 1.28 (s, 3H), 1.08 (tt, A of ABX, $J_{AB} =$ 12.4 Hz, $J_{BX} =$ 4.2 Hz, 1H), 0.92 (d, $J =$ 7.0 Hz, 3H), 0.87 (d, $J =$ 6.7 Hz, 3H), 0.63 (tt, B of ABX, $J_{AB} =$ 12.7 Hz, $J_{BX} =$ 4.4 Hz, 1H).

$^{13}$C NMR (100 MHz, C$_6$D$_6$) $\delta$ 142.70 (e), 137.12 (e), 132.23 (e), 130.44 (o), 129.55 (o), 128.61 (o), 128.08 (e), 127.85 (o), 73.08 (o), 51.89 (e), 41.88 (o), 36.24 (e), 34.16 (o), 30.34 (e), 25.08 (e), 21.07 (o), 20.89 (o), 19.49 (o), 17.22 (o).

IR (neat) 3017 (w), 2960 (m), 2929 (m), 2871 (m), 1653 (w), 1599 (w), 1494 (w), 1463 (m), 1388 (w), 1344 (s), 1305 (m), 1290 (m), 1162 (vs), 1094 (m), 1051 (m), 1017 (m), 669 (s) cm$^{-1}$.

HRMS (CI, M+H$^+$) calcd for C$_{21}$H$_{30}$NO$_2$S 360.1992, found 360.2007.

(6Z,9E)-3-Cyclohexyl-9-methyl-2-[(4-methylphenyl)sulfonyl]-2,3,3a,4,5,8-hexahydro-1H-cycloocta[c]pyrrole 2e.

$^1$H NMR (400 MHz, C$_6$D$_6$) $\delta$ 7.86 (d, $J =$ 8.2 Hz, 2H), 6.78 (d, $J =$ 7.9 Hz, 2H), 5.53 (ddd, $J =$ 11.3, 6.9, 4.8 Hz, 1H), 5.31-5.24 (m, 1H), 4.09 (d, A of AB, $J_{AB} =$ 14.0 Hz, 1H), 4.05-4.01 (m, 1H), 3.67 (d, $J =$ 4.9 Hz, 1H), 3.05 (dd, $J =$ 11.8, 3.9 Hz, 1H), 2.71 (dd, A of ABX, $J_{AB} =$ 18.0 Hz, $J_{AX} =$ 6.7 Hz, 1H), 2.22 (d, B of AB, $J_{AB} =$ 18.0 Hz, 1H), 2.10-2.00 (m, 1H), 1.95-1.89 (m, 1H), 1.86 (s, 3H), 1.79-1.56 (m, 6H), 1.29 (s, 3H), 1.26-0.95 (m, 6H), 0.65 (tt, B of ABX, $J_{AB} =$ 12.5 Hz, $J_{BX} =$ 4.8 Hz, 1H).
\textbf{13C NMR} (100 MHz, C$_6$D$_6$) \(\delta\) 142.64 (e), 137.40 (e), 132.43 (e), 130.46 (o), 129.53 (o), 129.79 (o), 128.12 (e), 127.86 (o), 72.89 (o), 51.91 (e), 44.34 (o), 42.86 (o), 36.27 (e), 30.44 (e), 30.19 (e), 28.36 (e), 26.83 (o), 26.66 (e), 25.22 (e), 21.06 (o), 20.90 (o).

\textbf{IR} (neat) 3018 (w), 2926 (vs), 2853 (s), 1654 (w), 1598 (w), 1494 (w), 1449 (m), 1342 (m), 1304 (m), 1289 (m), 1161 (vs), 1094 (m), 1052 (m), 1017 (w), 756 (m), 670 (m), 546 (m) cm\(^{-1}\).

\textbf{HRMS} (CI, M+H\(^{+}\)) calcd for C$_{24}$H$_{34}$NO$_2$S 400.2305, found 400.2314.

\{3\textit{aE,6Z}-4-Methyl-2-[(4-methylphenyl)sulfonyl]-2,3,5,8,9,9\textit{a-hexahydro-1\textit{H}}-cycloocta[c]pyrrol-1-yl\}methanol 2f.

\textbf{1H NMR} (400 MHz, C$_6$D$_6$) \(\delta\) 7.78 (d, \(J = 8.2\) Hz, 2H), 6.77 (d, \(J = 8.1\) Hz, 2H), 5.50 (ddd, \(J = 11.5, 7.3, 4.9\) Hz, 1H), 5.21 (q, \(J = 8.9\) Hz, 1H), 4.14 (d, A of AB, \(J_{AB} = 14.0\) Hz, 1H), 3.83 (d, B of AB, \(J_{AB} = 14.0\) Hz, 1H), 3.74 (dd, \(J = 12.5, 8.2\) Hz, 1H), 3.56-3.55 (m, 2H), 2.99 (d, \(J = 9.4\) Hz, 1H), 2.68 (dd, A of ABX, \(J_{AB} = 17.4\) Hz, \(J_{AX} = 7.3\) Hz, 1H), 2.50 (bs, 1H), 2.11 (dd, B of ABX, \(J_{AB} = 17.0\) Hz, \(J_{BX} = 4.3\) Hz, 1H), 1.96-1.86 (m, 1H), 1.85 (s, 3H), 1.73-1.65 (m, 1H), 1.26 (s, 3H), 1.07 (tt, A of ABX, \(J_{AB} = 11.0\) Hz, \(J_{AX} = 3.8\) Hz, 1H), 0.46 (ddt, B of ABMX, \(J_{AB} = 11.5\) Hz, \(J_{BX} = 5.9\) Hz, \(J_{BM} = 4.0\) Hz, 1H).

\textbf{13C NMR} (100 MHz, C$_6$D$_6$) \(\delta\) 143.20 (e), 135.83 (e), 130.72 (o), 130.37 (e), 130.11 (e), 129.71 (o), 128.74 (o), 127.92 (o), 69.12 (o), 65.61 (e), 51.62 (e), 44.05 (o), 35.83 (e), 29.63 (e), 25.40 (e), 21.08 (o), 20.80 (o).

\textbf{IR} (neat) 3512 (bs), 3017 (m), 2930 (m), 2855 (m), 1598 (w), 1494 (w), 1453 (m), 1400 (w), 1380 (w), 1340 (s), 1306 (m), 1290 (m), 1216 (w), 1161 (vs), 1095 (s), 1054 (m), 1017 (m), 756 (m), 668 (s), 547 (m) cm\(^{-1}\).

\textbf{HRMS} (EI, M-OCH$_3$\(^{+}\)) calcd for C$_{18}$H$_{22}$NO$_2$S 316.1371, found 316.1374.
(6Z,9E)-3-[(Benzyloxy)methyl]-9-methyl-2-[(4-methylphenyl)sulfonyl]-2,3,3a,4,5,8-hexahydro-1H-cycloocta[c]pyrrole 2g.

$^{1}$H NMR (400 MHz, C$_6$D$_6$) $\delta$ 7.80 (d, $J = 8.2$ Hz, 2H), 7.22 (d, $J = 7.3$ Hz, 2H), 7.16-7.13 (m, 2H), 7.07 (t, $J = 7.3$ Hz, 1H), 6.74 (d, $J = 8.2$ Hz, 2H), 5.53 (ddd, $J = 11.3$, 7.0, 4.6 Hz, 1H), 5.24 (q, $J = 9.1$ Hz, 1H), 4.33 (d, A of AB, $J_{AB} = 12.2$ Hz, 1H), 4.26 (d, B of AB, $J_{AB} = 12.2$ Hz, 1H), 4.12 (d, A of AB, $J_{AB} = 13.7$ Hz, 1H), 3.94-3.88 (m, 2H), 3.83 (dd, $J = 9.1$, 4.2 Hz, 1H), 3.42 (t, $J = 8.7$ Hz, 1H), 3.33 (dd, $J = 11.8$, 3.9 Hz, 1H), 2.73 (dd, A of ABX, $J_{AB} = 17.7$ Hz, $J_{AX} = 7.0$ Hz, 1H), 2.19 (dd, B of ABX, $J_{AB} = 17.9$ Hz, $J_{BX} = 3.6$ Hz, 1H), 2.00 (ddd, A of ABX, $J_{AB} = 13.3$ Hz, $J_{AX} = 11.3$ Hz, $J_{AM} = 4.0$ Hz, 1H), 1.84 (s, 3H), 1.75-1.68 (m, 1H), 1.26 (s, 3H), 1.20 (tt, A of ABX, $J_{AB} = 12.2$ Hz, $J_{AX} = 4.0$ Hz, 1H), 0.62 (tt, B of ABX, $J_{AB} = 12.5$ Hz, $J_{AX} = 4.8$ Hz, 1H).

$^{13}$C NMR (100 MHz, C$_6$D$_6$) $\delta$ 142.81 (e), 139.06 (e), 136.80 (e), 130.92 (e), 130.49 (o), 129.63 (e), 129.58 (o), 128.75 (o), 128.48 (o), 128.29 (o), 127.70 (o), 127.61 (o), 73.24 (e), 73.18 (e), 66.60 (o), 51.17 (e), 44.23 (o), 36.16 (e), 29.56 (e), 25.35 (e), 21.08 (o), 20.86 (o).

IR (neat) 3063 (w), 3026 (w), 2928 (m), 2857 (m), 1723 (w), 1652 (w), 1598 (w), 1454 (m), 1400 (w), 1345 (vs), 1306 (m), 1163 (vs), 1096 (s), 739 (m), 667 (s), 547 (m) cm$^{-1}$.

HRMS (CI, M$^+$H$^+$) calcd for C$_{26}$H$_{32}$NO$_3$S 438.2097, found 438.2093.

(6Z,9E)-3-{{[tert-Butyl(dimethyl)silyl]oxy}methyl}-9-methyl-2-[(4-methylphenyl)sulfonyl]-2,3,3a,4,5,8-hexahydro-1H-cycloocta[c]pyrrole 2h.

$^{1}$H NMR (400 MHz, C$_6$D$_6$) $\delta$ 7.80 (d, $J = 8.2$ Hz, 2H), 6.77 (d, $J = 7.9$ Hz, 2H), 5.55 (ddd, $J = 11.3$, 7.2, 4.5 Hz, 1H), 5.29-5.22 (m, 1H), 4.16 (d, A of AB, $J_{AB} = 13.7$ Hz, 1H), 4.00 (dd, $J = 9.8$, 3.7 Hz, 1H), 3.89 (dd, B of ABX, $J_{AB} = 13.7$ Hz,
$J_{BX} = 1.2$ Hz 1H), 3.76 (dd, A of ABX, $J_{AB} = 7.9$ Hz, $J_{AX} = 3.4$ Hz, 1H), 3.61 (dd, B of ABX, $J_{AB} = 9.8$ Hz, $J_{BX} = 8.3$ Hz, 1H), 3.34 (dd, $J = 11.9$, 3.7 Hz, 1H), 2.77 (dd, A of ABX, $J_{AB} = 18.3$ Hz, $J_{AX} = 7.0$ Hz, 1H), 2.24 (d, B of AB, $J_{AB} = 18.0$ Hz, 1H), 2.09-1.88 (m, 1H), 1.86 (s, 3H), 1.74 (ddt, $J = 11.9$, 7.8, 4.2 Hz, 1H), 1.30 (s, 3H), 1.21(tt, A of ABX, $J_{AB} = 12.2$ Hz, $J_{AX} = 3.8$ Hz, 1H), 0.93 (s, 9H), 0.61 (tt, B of ABX, $J_{AB} = 12.5$ Hz, $J_{BX} = 4.7$ Hz, 1H), 0.06 (s, 3H), 0.05 (s, 3H).

$^{13}$C NMR (100 MHz, C$_6$D$_6$) δ 142.79 (e), 136.79 (e), 131.08 (e), 130.45 (o), 129.60 (o), 129.20 (e), 128.78 (o), 127.78 (e), 68.46 (o), 66.32 (e), 51.58 (e), 43.47 (o), 36.23 (e), 29.76 (e), 25.98 (o), 25.33 (e), 21.07 (o), 20.93 (e), 18.32 (e), -5.22 (o), -5.41 (o).

IR (neat) 3018 (m), 2929 (vs), 2857 (s), 1920 (w), 1718 (w), 1655 (w), 1599 (m), 1494 (w), 1463 (m), 1384 (w), 1346 (s) 1255 (s), 1215 (w), 1163 (vs), 1096 (vs), 1017 (m), 1006 (m) cm$^{-1}$.

HRMS (CI, M+H$^+$) calcd for C$_{25}$H$_{40}$NO$_3$SSi 462.2493, found 462.2493.

Methyl (3aE,6Z)-4-methyl-2-[(4-methylphenyl)sulfonyl]-2,3,5,8,9,9a-hexahydro-1H-cycloocta[c]pyrrole-1-carboxylate 2i.

$^1$H NMR (400 MHz, C$_6$D$_6$) δ 7.87 (d, $J = 8.2$ Hz, 2H), 6.79 (d, $J = 7.9$ Hz, 2H), 5.46 (ddd, $J = 11.5$, 7.6, 4.6 Hz, 1H), 5.26-5.19 (m, 1H), 4.54 (d, $J = 0.9$ Hz, 1H), 4.25 (d, A of AB, $J_{AB} = 12.8$ Hz, 1H), 4.12 (d, B of AB, $J_{AB} = 13.1$ Hz, 1H), 3.43-3.37 (m, 1H), 3.18 (s, 3H), 2.53 (dd, A of ABX, $J_{AB} = 18.3$ Hz, $J_{AX} = 7.3$ Hz, 1H), 2.18 (d, B of AB, $J_{AB} = 18.0$ Hz, 1H), 2.07-1.97 (m, 1H), 1.87 (s, 3H), 1.76-1.69 (m, 1H), 1.39 (tt, A of ABX, $J_{AB} = 12.2$ Hz, $J_{AX} = 4.1$ Hz, 1H), 1.31-1.15 (m, 1H), 1.18 (s, 3H).

$^{13}$C NMR (100 MHz, C$_6$D$_6$) δ 172.07 (e), 142.92 (e), 137.40 (e), 130.21 (e), 129.82 (o), 129.55 (o), 129.18 (o), 67.78 (o), 51.64 (o), 51.26 (e), 45.91 (o), 35.87 (e), 30.34 (e), 25.16 (e), 21.06 (o), 20.97 (o).
IR (neat) 3021 (w), 2932 (w), 2857 (w), 1743 (s), 1598 (w), 1495 (w), 1437 (m), 1347 (vs), 1306 (w), 1289 (m), 1163 (vs), 1096 (s), 1070 (m), 1018 (w), 755 (m), 670 (s), 549 (m) cm\(^{-1}\).

**HRMS (CI, M+H\(^{+}\))** calcd for C\(_{20}\)H\(_{26}\)NO\(_4\)S 376.1577, found 376.1584.

\((6Z,9E)-9\text{-methyl}-2-[(4\text{-methylphenyl})\text{sulfonyl}]-3\text{-vinyl}-2,3,3a,4,5,8\text{-hexahydro}-1\text{H}\text{-cycloocta}[c]\text{pyrrole} \ 2j.\)

\(^1\text{H} \text{NMR}\) (400 MHz, C\(_6\)D\(_6\)) \(\delta\) 7.83 (d, \(J = 8.2\) Hz, 2H), 6.79 (d, \(J = 7.9\) Hz, 2H), 5.70 (ddd, \(J = 17.1, 10.3, 7.0\) Hz, 1H), 5.51 (ddd, \(J = 11.5, 7.3, 4.9\) Hz, 1H), 5.31-5.24 (m, 1H), 5.21 (dt, \(J = 17.1, 1.2\) Hz, 1H), 4.95 (dt, \(J = 10.4, 1.1\) Hz, 1H), 4.05-4.01 (m, 2H), 3.96-3.92 (m, 1H), 2.86 (d, \(J = 10.4\) Hz, 1H), 2.64 (dd, A of ABX, \(J_{AB} = 17.1\) Hz, \(J_{AX} = 7.3\) Hz, 1H), 2.16 (dd, B of ABX, \(J_{AB} = 17.4\), \(J_{BX} = 4.3\) Hz, 1H), 2.01 (dd, A of ABMX, \(J_{AB} = 18.6\) Hz, \(J_{AX} = 13.7\) Hz, \(J_{AM} = 4.0\) Hz, 1H), 1.88 (s, 3H), 1.81-1.73 (m, 1H), 1.32-1.27 (m, 1H), 1.26 (s, 3H), 1.05-0.97 (m, 1H).

\(^{13}\text{C} \text{NMR}\) (100 MHz, C\(_6\)D\(_6\)) \(\delta\) 142.71 (e), 138.21 (o), 136.99 (e), 130.52 (e), 130.05 (o), 129.93 (e), 129.44 (o), 129.30 (o), 128.12 (o), 115.17 (e), 69.58 (o), 50.97 (e), 47.85 (o), 35.67 (e), 29.09 (e), 25.42 (e), 21.09 (o), 20.87 (o).

IR (neat) 3015 (w), 2027 (m), 2856 (w), 1645 (w), 1598 (w), 1494 (w), 1452 (w), 1345 (vs), 1163 (vs), 1095 (s), 1058 (m), 1017 (m), 669 (s) cm\(^{-1}\).

**HRMS (EI, M\(^{+}\))** calcd for C\(_{20}\)H\(_{25}\)NO\(_2\)S 343.1606, found 343.1600.

\((6Z,9E)-3\text{-allyl}-9\text{-methyl}-2-[(4\text{-methylphenyl})\text{sulfonyl}]-2,3,3a,4,5,8\text{-hexahydro}-1\text{H}\text{-cycloocta}[c]\text{pyrrole} \ 2k.\)

\(^1\text{H} \text{NMR}\) (400 MHz, C\(_6\)D\(_6\)) \(\delta\) 7.81 (d, \(J = 8.2\) Hz, 2H), 6.81 (d, \(J = 8.2\) Hz, 2H), 5.78 (ddt, \(J = 17.1, 10.1, 7.0\) Hz, 1H), 5.50 (ddd, \(J = 11.3, 7.0, 4.6\) Hz, 1H), 5.28-5.21 (m, 1H), 5.00 (dd, \(J = 17.1, 1.5\) Hz, 1H), 4.97 (d, \(J = 10.4\) Hz, 1H).
**1H NMR** (400 MHz, C$_6$D$_6$) δ 7.63 (d, J = 8.2 Hz, 2H), 7.24 (d, J = 7.3 Hz, 2H), 7.08-7.00 (m, 3H), 6.69 (d, J = 7.9 Hz, 2H), 5.38 (ddd, J = 11.4, 7.1, 4.8 Hz, 1H), 5.26-5.20 (m, 1H), 4.85 (s, 1H), 4.20 (s, 2H), 3.15 (dd, J = 11.4, 3.6 Hz, 1H), 2.50 (dd, A of ABX, $J_{AB} = 18.1$ Hz, $J_{AX} = 6.8$ Hz, 1H), 2.13-2.03 (m, 2H), 1.84 (s, 3H), 1.77-1.71 (m, 1H), 1.44 (tt, A of ABX, $J_{AB} = 12.3$ Hz, $J_{AX} = 4.1$ Hz, 1H), 1.28 (s, 3H), 1.20-1.12 (m, 1H).

**13C NMR** (100 MHz, C$_6$D$_6$) δ 143.60(e), 142.47(e), 137.23(e), 130.84 (e), 130.16 (o), 129.91 (e), 129.31 (o), 128.82 (o), 128.67 (o), 127.36 (o), 126.79 (o), 70.80 (o), 51.57 (e), 50.59 (o), 35.93 (e), 30.14 (e), 25.19 (e), 21.05 (o), 21.02 (o).

**(6Z,9E)-9-Methyl-2-[(4-methylphenyl)sulfonyl]-3-phenyl-2,3,3a,4,5,8-hexahydro-1H-cycloocta[c]pyrrole 2I.**

**1H NMR** (400 MHz, C$_6$D$_6$) δ 7.63 (d, J = 8.2 Hz, 2H), 7.24 (d, J = 7.3 Hz, 2H), 7.08-7.00 (m, 3H), 6.69 (d, J = 7.9 Hz, 2H), 5.38 (ddd, J = 11.4, 7.1, 4.8 Hz, 1H), 5.26-5.20 (m, 1H), 4.85 (s, 1H), 4.20 (s, 2H), 3.15 (dd, J = 11.4, 3.6 Hz, 1H), 2.50 (dd, A of ABX, $J_{AB} = 18.1$ Hz, $J_{AX} = 6.8$ Hz, 1H), 2.13-2.03 (m, 2H), 1.84 (s, 3H), 1.77-1.71 (m, 1H), 1.44 (tt, A of ABX, $J_{AB} = 12.3$ Hz, $J_{AX} = 4.1$ Hz, 1H), 1.28 (s, 3H), 1.20-1.12 (m, 1H).

**13C NMR** (100 MHz, C$_6$D$_6$) δ 143.60(e), 142.47(e), 137.23(e), 130.84 (e), 130.16 (o), 129.91 (e), 129.31 (o), 128.82 (o), 128.67 (o), 127.36 (o), 126.79 (o), 70.80 (o), 51.57 (e), 50.59 (o), 35.93 (e), 30.14 (e), 25.19 (e), 21.05 (o), 21.02 (o).
IR (neat) 3063 (w), 3026 (w), 2929 (m), 2855 (m), 1650 (w), 1599 (w), 1495 (w), 1455 (m), 1400 (w), 1344 (vs), 1306 (m), 1290 (m), 1163 (vs), 1095 (s), 1071 (m), 1031 (m), 1017 (m), 756 (vs), 670 (vs) cm\(^{-1}\).

**HRMS** (EI, M\(^{+}\)) calcd. for C\(_{24}\)H\(_{27}\)NO\(_2\)S 393.1762, found 393.1753.

\[
N-((2Z)-4-\{[\text{tert-Butyl(dimethyl)silyl]oxy}]\}-1-methylbut-2-en-1-yl)-
4-methyl-\[\text{N-(3-phenylprop-2-yn-1-yl)}\]benzenesulfonamide 4.
\]

\[^{1}\text{H NMR}\] (400 MHz, CDCl\(_3\)) \(\delta\) 7.80 (d, \(J = 8.3\) Hz, 2H), 7.28-7.17 (m, 7H), 5.59-5.52 (m, 2H), 4.85 (dq, \(J = 10.6, 7.0\) Hz, 1H), 4.32 (s, 2H), 4.29-4.24 (m, 1H), 4.15-4.10 (m, 1H), 2.33 (s, 3H), 1.29 (d, \(J = 6.8\) Hz, 3H), 0.05 (s, 3H), 0.04 (s, 3H).

\[^{13}\text{C NMR}\] (100 MHz, CDCl\(_3\)) \(\delta\) 143.22 (e), 138.12 (e), 133.03 (o), 131.51 (o), 129.45 (o), 128.80 (o), 128.48 (o), 128.33 (o), 127.82 (o), 122.69 (e), 85.44 (e), 84.59 (e), 59.51 (e), 51.03 (o), 33.63 (e), 26.03 (o), 21.58 (o), 20.34 (o), -5.12 (o)

IR (neat) 3025 (m), 2955 (s), 2929 (s), 2857 (s), 1599 (m), 1491 (m), 1349 (vs), 1165 (vs), 1092 (vs), 838 (vs), 660 (s) cm\(^{-1}\).

**HRMS** (CI, M\(^{+}\)) calcd. for C\(_{27}\)H\(_{37}\)NO\(_3\)SSi 483.2263, found 483.2273.

\[
(6Z,9Z)-4-\{[\text{tert-Butyl(dimethyl)silyl]oxy}]\text{methyl}\}\) \(3\)-methyl-2-
[\(\text{[4-methylphenyl)sulfonyl]}\]9-phenyl-2,3,3a,4,5,8-hexahydro-1\(H\)-
cycloocta[c]pyrrole 5.
\]

\[^{1}\text{H NMR}\] (400 MHz, C\(_6\)D\(_6\)) \(\delta\) 7.62 (d, \(J = 7.9\) Hz, 2H), 7.07 (t, \(J = 7.3\) Hz, 2H), 7.02-6.95 (m, 3H), 6.67 (d, \(J = 7.9\) Hz, 2H), 5.80-5.74 (m, 1H), 5.68-5.62 (m, 1H), 4.02 (d, \(A\) of AB, \(J_{AB} = 13.7\) Hz, 1H), 3.94 (d, \(B\) of AB, \(J_{AB} = 13.7\) Hz, 1H), 3.73 (dq, \(J = 9.8, 3.8\) Hz, 1H), 3.66 (dd, \(J = 9.5, 4.0\) Hz, 1H), 3.54 (t, \(J = 10.4\) Hz, 1H), 3.18 (dd, \(A\) of ABX, \(J_{AB} = 13.6\) Hz, \(J_{AX} = 9.1\) Hz, 1H), 2.99 (bs, 1H), 2.67-2.56 (m, 2H), 2.42
(dd, B of ABX, $J_{AB} = 14.0$ Hz, $J_{RX} = 6.3$ Hz, 1H), 1.97-1.93 (m, 1H), 1.86 (s, 3H), 1.28 (d, $J = 6.1$ Hz, 3H), 0.99 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H).

$^{13}$C NMR (100 MHz, C$_6$D$_6$) δ 142.77 (e), 138.16 (e), 136.14 (e), 132.04 (o), 131.60 (e), 129.69 (o), 128.93 (o), 128.41 (e), 128.35 (o), 127.96 (o), 127.54 (o), 127.40 (o), 62.43 (o), 61.81 (e), 53.24 (e), 42.91 (o), 35.79 (e), 30.43 (e), 26.16 (o), 21.85 (o), 21.18 (o), 18.44 (e), -5.15 (o), -5.35 (o).

IR (Neat): 3024 (s), 2929 (s), 2858 (s), 1752 (m), 1647 (w), 1599 (s), 1494 (s), 1462 (s), 1347 (vs), 1254 (s), 1163 (vs), 1094 (s), 838 (vs), 758 (vs), 593 (s) cm$^{-1}$.

HRMS (FAB, M+H$^+$): calcd for C$_{31}$H$_{44}$NO$_3$SSi 538.2811, found 538.2819.
The sample was submitted by Erich Baum (research group of Prof. P. A. Evans, Department of Chemistry, Indiana University). A preliminary set of cell constants was calculated from reflections harvested from three sets of 20 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced initial orientation matrices determined from 339 reflections. The data collection was carried out using Mo Ka radiation (graphite monochromator) with a frame time of 15 seconds and a detector distance of 5.09 cm. A randomly oriented region of reciprocal space was surveyed to the extent of a quadrant. Two major sections of frames were collected with 0.30° steps in w at two different f settings and a detector position of −43° in 2q. An additional set of 80 frames was collected in order to model decay. Data to a resolution of 0.71 Å were considered in the reduction. Final cell constants were calculated from the xyz centroids of 7032 strong reflections from the actual data collection after integration. The intensity data were corrected for absorption.

The structure was found as proposed. C-H…X hydrogen bonds were observed.

Complete data are available at http://bl-chem-iumsc110.chem.indiana.edu/recipnet/showsample.jsp?sampleId=59057656
Indiana University Molecular Structure Center

Report 03220: C_{26}H_{27}N_{3}O_{8}S; CH_{2}Cl_{2}; 3,5-Dinitrobenzoate of 2f

John C. Huffman
October 23, 2003

Empirical Formula: C_{27}H_{29}Cl_{2}N_{3}O_{8}S
Color of Crystal: pale yellow
Crystal System: Monoclinic
Space Group: P2(1)/n
Cell Dimensions (at 118(2) K; 990 data)
\[ a = 11.1295(9) \]
\[ b = 10.5003(9) \]
\[ c = 24.1594(18) \]
\[ \alpha = 90 \]
\[ \beta = 94.137(2) \]
\[ \gamma = 90 \]

Z (Molecules/cell): 4
Volume: 2816.0(4)
Calculated Density: 1.478
Molecular Weight: 626.49
Linear Absorption Coefficient: 0.360
Final residuals are:
\[ R(F) \text{ (observed data)} = 0.0465 \]
\[ Rw(F^2) \text{ (refinement data)} = 0.1423 \]

The sample was submitted by Aleem Fazal from the research group of Prof. P. A. Evans, Department of Chemistry, Indiana University. The crystals occur as pale yellow layered prisms that cleaved easily. A fragment of one of the plates of approximate dimensions 0.30 \times 0.30 \times 0.25 mm onto the tip of a 0.15 mm diameter glass fiber which was subsequently mounted on a SMART6000 (Bruker) and cooled to 118(2) K.

A preliminary set of cell constants was calculated from reflections obtained from three nearly orthogonal sets of 30 frames. The data collection was carried out using graphite monochromated Mo Kα radiation with a frame time of 2 seconds and a detector distance of 5.0 cm. A randomly oriented region of a sphere in reciprocal space was surveyed. Six sections of 606 frames were collected with 0.30° steps in \( \omega \) at different \( \phi \) settings with the detector set at \(-43°\) in \( 2\theta \). Final cell constants were calculated from the xyz centroids of 990 strong reflections from the actual data collection after integration (SAINT).

Complete data are available at
http://bl-chem-iiumsc110.chem.indiana.edu/recipnet/showsample.jsp?sampleId=59057303&sampleHistoryId=-1
Indiana University Molecular Structure Center

Report 03228: C₃₂H₃₁N₃O₈S; 3,5-Dinitrobenzoate of 5

John C. Huffman
October 31, 2003

Empirical Formula: C₃₂H₃₁N₃O₈S
Color of Crystal: colorless
Crystal System: Monoclinic
Space Group: P2(1)/c
Cell Dimensions (at 110(2) K; 911 data)
a = 13.3244(14)
b = 7.2183(8)
c = 30.905(3)
alpha = 90
beta = 100.270(3)
gamma = 90
Z (Molecules/cell): 4
Volume: 2924.8(5)
Calculated Density: 1.403
Molecular Weight: 617.66
Linear Absorption Coefficient: 0.169
Final residuals are:
R(F) (observed data) = 0.0405
Rw(F2) (refinement data) = 0.1045

The sample was submitted by Aleem Fazal from the research group of Prof. P. A. Evans, Department of Chemistry, Indiana University. The crystals occur as elongated transparent prisms plates that tend to grow in clumps. A well-formed typical sample was cleaved to form a fragment of dimensions 0.25 × 0.14 × 0.10 mm onto the tip of a 0.1 mm diameter glass fiber which was subsequently mounted on a SMART6000 (Bruker) and cooled to 11(02) K.

A preliminary set of cell constants was calculated from reflections obtained from three nearly orthogonal sets of 30 frames. The data collection was carried out using graphite monochromated Mo Kα radiation with a frame time of 15 seconds and a detector distance of 5.0 cm. A randomly oriented region of a sphere in reciprocal space was surveyed. Four sections of 606 frames were collected with 0.30º steps in ω at different φ settings with the detector set at −43º in 2θ. Final cell constants were calculated from the xyz centroids of 911 strong reflections from the actual data collection after integration (SAINT).

Complete data are available at
http://bl-chem-iumsc110.chem.indiana.edu/recipnet/jamm.jsp?sampleId=59057557&sampleHistoryId=–1