

## Supporting Information

### The spectral Data of the Substrate

**4-Acetoxy-2-butynyl 2-allyloxyphenyl ether (4a).** A colorless oil; IR (neat) 1748, 1648, 1224  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$  2.05 (s, 3 H), 4.58 (br d,  $J = 5.1$  Hz, 2 H), 4.68 (t,  $J = 2.0$  Hz, 2 H), 4.77 (t,  $J = 2.0$  Hz, 2 H), 5.26 (br d,  $J = 10.7$  Hz, 1 H), 5.39 (br d,  $J = 17.0$  Hz, 1 H), 6.07 (ddt,  $J = 17.0, 10.7, 5.1$  Hz, 1 H), 6.86-7.04 (m, 4 H);  $^{13}\text{C}$  NMR (67.8 MHz,  $\text{CDCl}_3$ )  $\delta$  20.4, 51.9, 57.0, 69.6, 81.2, 81.7, 113.9, 115.3, 117.5, 120.6, 121.9, 133.2, 147.2, 148.7, 169.9; LRMS  $m/z$  260 ( $\text{M}^+$ ), 150, 109, 43; EI-HRMS  $m/z$  calcd for  $\text{C}_{15}\text{H}_{16}\text{O}_4$  ( $\text{M}^+$ ) 260.1049, found 260.1064.

**2-Allyloxyphenyl 2-butynyl ether (4b).** A colorless oil; IR (neat) 2228, 1648, 1248  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$  1.81 (t,  $J = 2.4$  Hz, 3 H), 4.58 (br d,  $J = 5.1$  Hz, 2 H), 4.70 (q,  $J = 2.4$  Hz, 2 H), 5.25 (br d,  $J = 10.7$  Hz, 1 H), 5.38 (br d,  $J = 17.0$  Hz, 1 H), 6.07 (ddt,  $J = 17.0, 10.7, 5.1$  Hz, 1 H), 6.86-7.06 (m, 4 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  35.8, 57.3, 69.7, 74.2, 83.5, 113.8, 114.7, 117.4, 120.9, 121.5, 133.2, 147.4, 148.5; LRMS  $m/z$  202 ( $\text{M}^+$ ), 161, 149, 109, 77, 53, 41; EI-HRMS  $m/z$  calcd for  $\text{C}_{13}\text{H}_{14}\text{O}_2$  ( $\text{M}^+$ ) 202.0994, found 202.0992.

**N-Allyl-N-(2-butynoxyphenyl)-(p-toluenesulfonyl)amide (4c).** A colorless oil; IR (nujol) 2230, 1644, 1346, 1238, 1164  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.78 (br s, 3 H), 2.38 (s, 3 H), 4.17 (br s, 2 H), 4.20 (br s, 2 H), 4.97 (d,  $J = 10.0$  Hz, 1 H), 5.07 (d,  $J = 16.7$  Hz, 1 H), 5.67 (ddt,  $J = 16.7, 10.0, 6.5$  Hz, 1 H), 6.87-6.94 (m, 2 H), 7.20 (d,  $J = 7.9$  Hz, 2 H), 7.22-7.30 (m, 2 H), 7.57 (d,  $J = 7.9$  Hz, 2 H);  $^{13}\text{C}$  NMR (67.8 MHz,  $\text{CDCl}_3$ )  $\delta$  3.5, 21.3, 52.4, 55.9, 73.4, 83.4, 112.6, 117.8, 120.6, 126.5, 127.3, 128.7, 129.2, 133.3, 133.3, 137.0, 142.5, 154.4; LRMS  $m/z$  355 ( $\text{M}^+$ ), 302, 200, 155, 147, 120, 91, 53, 41; EI-HRMS  $m/z$  calcd for  $\text{C}_{20}\text{H}_{21}\text{NO}_3\text{S}$  ( $\text{M}^+$ ) 355.1242, found 355.1247.

**N-Allyl-N'-2-butynyl-1,2-bis-(p-toluenesulfonylamino)benzene (4d).** Colorless crystals; mp 138-140  $^{\circ}\text{C}$ . IR (nujol) 2226, 1636, 1350, 1158  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.55 (t,  $J = 2.4$  Hz, 3 H), 2.44 (s, 3 H), 2.45 (s, 3 H), 4.42 (br s, 2 H),

4.59 (br s, 2 H), 5.02 (d,  $J = 10.3$  Hz, 1 H), 5.07 (d,  $J = 17.0$  Hz, 1 H), 5.83 (ddt,  $J = 17.0, 10.3, 7.0$  Hz, 1 H), 7.06 (m, 1 H), 7.25 (m, 1 H), 7.23-7.27 (m, 2 H), 7.30 (d,  $J = 8.2$  Hz, 2 H), 7.32 (d,  $J = 8.2$  Hz, 2 H), 7.74 (d,  $J = 8.2$  Hz, 2 H), 7.78 (d,  $J = 8.2$  Hz, 2 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  3.4, 21.5, 21.6, 41.8, 54.7, 73.4, 81.7, 119.2, 128.0, 128.6, 128.8, 128.8, 129.4, 130.7, 131.2, 132.8, 136.8, 137.1, 139.1, 139.4, 143.4, 143.5; LRMS  $m/z$  508 ( $\text{M}^+$ ), 353, 198, 183, 171, 157, 155, 119, 91, 41, 39; EI-HRMS  $m/z$  calcd for  $\text{C}_{27}\text{H}_{28}\text{N}_2\text{O}_4\text{S}_2$  ( $\text{M}^+$ ) 508.1490, found 508.1498.

***N*-Allyl-*N'*-propargyl-1,2-bis-(*p*-toluenesulfonylamino)benzene (4e).** Colorless crystals; mp 178-180 °C. IR (nujol) 2118, 1654, 1350, 1158  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$  2.06 (t,  $J = 2.4$  Hz, 1 H), 2.45 (s, 6 H), 4.39 (br s, 2 H), 4.73 (br s, 2 H), 5.02 (d,  $J = 10.1$  Hz, 1 H), 5.08 (d,  $J = 17.0$  Hz, 1 H), 5.82 (ddt,  $J = 17.0, 10.1, 6.9$  Hz, 1 H), 6.91 (m, 1 H), 7.20-7.29 (m, 3 H), 7.31 (d,  $J = 8.3$  Hz, 2 H), 7.34 (d,  $J = 8.3$  Hz, 2 H), 7.73 (d,  $J = 8.3$  Hz, 2 H), 7.79 (d,  $J = 8.3$  Hz, 2 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  21.6, 21.6, 41.1, 54.7, 74.1, 78.3, 119.3, 128.1, 128.7, 128.7, 129.0, 129.2, 129.5, 130.9, 131.2, 132.7, 136.6, 136.9, 139.0, 139.1, 143.6, 143.8; LRMS  $m/z$  495 ( $\text{M}^+$ ), 339, 183, 169, 157, 143; EI-HRMS  $m/z$  calcd for  $\text{C}_{26}\text{H}_{26}\text{N}_2\text{O}_4\text{S}_2$  ( $\text{M}^+$ ) 494.1334, found 494.1354.

***N*-2-butynyl-*N'*-homoallyl-1,2-bis-(*p*-toluenesulfonylamino)benzene (6).** Colorless crystals; mp 149-151 °C. IR (nujol) 2230, 1637, 1342, 1164  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$  1.55 (t,  $J = 2.4$  Hz, 3 H), 2.32 (dt,  $J = 7.9, 7.2$  Hz, 2 H), 2.46 (s, 6 H), 3.79 (br, 2 H), 4.57 (br, 2 H), 4.97 (dd,  $J = 10.3, 1.6$  Hz, 1 H), 5.00 (dd,  $J = 17.4, 1.6$  Hz, 1 H), 5.61 (ddt,  $J = 17.4, 10.3, 7.2$  Hz, 1 H), 7.02 (dd,  $J = 2.4, 7.1$  Hz, 1 H), 6.98-7.01 (m, 1 H), 7.23-7.28 (m, 2 H), 7.32 (dd,  $J = 8.3, 3.2$  Hz, 4 H), 7.75 (d,  $J = 8.3$  Hz, 2 H), 7.81 (d,  $J = 8.3$  Hz, 2 H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  3.3, 21.5, 21.5, 32.5, 41.8, 51.1, 73.4, 81.8, 116.7, 126.1, 128.0, 128.6, 129.0, 129.0, 129.1, 129.6, 130.9, 131.0, 134.9, 137.1, 139.3, 139.6, 143.5, 143.6; LRMS  $m/z$  523 ( $\text{M}^+\text{+H}$ ), 481, 367, 325, 212, 197, 171, 156, 119, 91,.; EI-HRMS  $m/z$  calcd for  $\text{C}_{25}\text{H}_{25}\text{N}_2\text{O}_4\text{S}_2$  ( $\text{M}^+\text{-C}_3\text{H}_5$ ) 481.1256, found 481.1271.

***trans*-N-Allyl-N'-2-butynyl-1,2-bis-(*p*-toluenesulfonylamino)cyclohexane (11a).**

Amorphous solid; IR (film) 2224, 1640, 1352, 1156  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$  1.13-1.28 (m, 2 H), 1.54 (t,  $J = 2.4$  Hz, 3 H), 1.61-1.76 (m, 6 H), 2.41 (s, 6 H), 3.77-3.93 (m, 4 H), 4.01-4.09 (m, 1 H), 4.16-4.23 (m, 1 H), 5.00 (d,  $J = 10.3$  Hz, 1 H), 5.15 (d,  $J = 17.0$  Hz, 1 H), 5.67-5.82 (m 1 H), 7.28 (d,  $J = 8.3$  Hz, 2 H), 7.28 (d,  $J = 8.3$  Hz, 2 H), 7.74 (d,  $J = 8.3$  Hz, 2 H), 7.82 (d,  $J = 8.3$  Hz, 2 H);  $^{13}\text{C}$  NMR (67.8 MHz,  $\text{CDCl}_3$ )  $\delta$  3.3, 21.4, 25.4, 25.5, 31.1, 32.5, 33.0, 47.0, 57.9, 58.4, 75.0, 80.5, 116.9, 127.5, 127.9, 128.9, 129.4, 136.3, 138.4, 138.5, 142.9, 143.0; LRMS  $m/z$  508 ( $\text{M}^+$ ), 353, 198, 183, 171, 157, 155, 119, 91, 41, 39; EI-HRMS  $m/z$  calcd for  $\text{C}_{20}\text{H}_{27}\text{N}_2\text{O}_2\text{S}$  ( $\text{M}^+$ -Ts) 359.1793, found 359.1809.

***cis*-N-Allyl-N'-2-butynyl-1,2-bis-(*p*-toluenesulfonylamino)cyclohexane (11b).**

Amorphous solid; IR (film) 2214, 1636, 1354, 1158  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$  1.37 (br, 2 H), 1.61 (t,  $J = 2.2$  Hz, 3 H), 1.52-1.65 (m, 2 H), 1.73-1.86 (m, 4 H), 2.41 (s, 6 H), 3.93-4.00 (m, 1 H), 4.03-4.21 (m, 4 H), 4.43 (dd,  $J = 8.8, 2.2$  Hz, 1 H), 5.07 (dd,  $J = 10.1, 1.2$  Hz, 1 H), 5.17 (dd,  $J = 17.2, 1.2$  Hz, 1 H), 5.84 (ddt,  $J = 17.2, 10.1, 6.7$  Hz 1 H), 7.26 (d,  $J = 8.7$  Hz, 2 H), 7.28 (d,  $J = 8.7$  Hz, 2 H), 7.76 (d,  $J = 8.7$  Hz, 2 H), 7.79 (d,  $J = 8.7$  Hz, 2 H);  $^{13}\text{C}$  NMR (67.8 MHz,  $\text{CDCl}_3$ )  $\delta$  3.3, 21.4, 22.5, 24.0, 27.3, 27.9, 36.8, 49.3, 57.2, 58.4, 74.8, 80.8, 117.1, 127.4, 127.8, 129.0, 129.4, 135.9, 137.8, 138.4, 142.9, 142.9; LRMS  $m/z$  508 ( $\text{M}^+$ ), 353, 198, 183, 171, 157, 155, 119, 91, 41, 39; EI-HRMS  $m/z$  calcd for  $\text{C}_{20}\text{H}_{27}\text{N}_2\text{O}_2\text{S}$  ( $\text{M}^+$ -Ts) 359.1793, found 359.1799.

***N*-Allyl-N'-2-butynyl-1,2-bis-(*p*-toluenesulfonylamino)ethane (11c).**

Colorless crystals; mp 120-122  $^{\circ}\text{C}$ . IR (nujol) 2230, 1634, 1364, 1160  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$  1.59 (t,  $J = 2.4$  Hz, 3 H), 2.43 (s, 6 H), 3.33 (br, 4 H), 3.83 (d,  $J = 6.5$  Hz, 2 H), 4.02 (q,  $J = 2.4$  Hz, 2 H), 5.19 (dd,  $J = 9.9, 1.4$  Hz, 1 H), 5.23 (dd,  $J = 17.0, 1.4$  Hz, 1 H), 5.66 (ddt,  $J = 17.0, 9.9, 6.5$  Hz 1 H), 7.29 (d,  $J = 8.5$  Hz, 2 H), 7.31 (d,  $J = 8.5$  Hz, 2 H), 7.71 (d,  $J = 8.5$  Hz, 2 H), 7.72 (d,  $J = 8.5$  Hz, 2 H);  $^{13}\text{C}$  NMR (67.8 MHz,  $\text{CDCl}_3$ )  $\delta$  3.3, 21.5, 38.5, 45.8, 51.6, 71.9, 81.8, 119.6, 127.2, 127.8, 129.3,

129.7, 132.8, 135.5, 136.4, 143.5; LRMS  $m/z$  305 ( $M^+$ ), 236, 226, 184, 155; EI-HRMS  $m/z$  calcd for  $C_{16}H_{21}N_2O_2S$  ( $M^+$ -Ts) 305.1324, found 305.1335.

***N*-Allyl-*N*-(2-butynoxyethyl)-(p-toluenesulfonyl)amide (11d).** A colorless oil; IR (nujol) 2220, 1642, 1344, 1158, 1138  $cm^{-1}$ ;  $^1H$  NMR (270MHz,  $CDCl_3$ )  $\delta$  1.84 (t,  $J$  = 2.4 Hz, 3 H), 2.42 (s, 3 H), 3.33 (t,  $J$  = 6.3 Hz, 2 H), 3.62 (t,  $J$  = 6.3 Hz, 2 H), 3.87 (ddd,  $J$  = 6.3, 1.2, 1.2 Hz, 2 H), 4.04 (q,  $J$  = 2.4 Hz, 2 H), 5.14 (dddd,  $J$  = 10.1, 1.2, 1.2, 1.2 Hz, 1 H), 5.18 (dddd,  $J$  = 17.2, 1.2, 1.2, 1.2 Hz, 1 H), 5.67 (ddt,  $J$  = 17.2, 10.1, 6.3 Hz, 1 H), 7.29 (d,  $J$  = 8.3 Hz, 2 H), 7.71 (d,  $J$  = 8.3 Hz, 2 H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  3.5, 21.4, 46.2, 51.4, 58.6, 68.1, 74.6, 82.5, 118.7, 126.9, 129.4, 132.9, 136.8, 143.0; LRMS  $m/z$  307 ( $M^+$ ), 266, 252, 238, 224, 155, 152, 91, 84; EI-HRMS  $m/z$  calcd for  $C_{16}H_{21}NO_3S$  ( $M^+$ ) 307.1242, found 307.1272.

***N*-2-Butynyl-*N*-5-hexenyl-(p-toluenesulfonyl)amide (11e).** A pale yellow oil; IR (neat) 2221, 1654, 1346, 1160  $cm^{-1}$ ;  $^1H$  NMR (270 MHz,  $CDCl_3$ )  $\delta$  1.39-1.47 (m, 2 H), 1.51-1.59 (m, 4 H), 1.55 (t,  $J$  = 2.4 Hz, 3 H), 2.07 (dt,  $J$  = 6.7, 7.1 Hz, 2 H), 2.42 (s, 3 H), 3.16 (t,  $J$  = 7.1 Hz, 2 H), 4.04 (q,  $J$  = 2.4 Hz, 2 H), 4.95 (dd,  $J$  = 10.3, 1.6 Hz, 1 H), 5.00 (dd,  $J$  = 17.0, 1.6 Hz, 1 H), 5.78 (ddt,  $J$  = 17.0, 10.3, 6.7 Hz 1 H), 7.28 (d,  $J$  = 8.3 Hz, 2 H), 7.72 (d,  $J$  = 8.3 Hz, 2 H);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$  3.2, 21.5, 25.8, 26.9, 33.2, 36.6, 46.1 71.8, 81.3, 114.8, 127.8, 129.2, 136.2, 138.4, 143.0; LRMS  $m/z$  305 ( $M^+$ ), 236, 184, 155, 150, 139, 91; EI-HRMS  $m/z$  calcd for  $C_{17}H_{23}NO_2S$  ( $M^+$ ) 305.1449, found 305.1461.

### General Procedure for Synthesis of Eight-Membered Ring Compound

A  $CH_2Cl_2$  solution of the substrate and ruthenium carbene complex **1** (10 mol %) was stirred at room temperature under argon gas. The solution was concentrated and the residue was purified by column chromatography on silica gel to give eight-membered ring compound.

**7-(1-Acetoxymethylvinyl)-5,10-dioxo-5,6,9,10-tetrahydrobenzocyclooctene (5a).**

A colorless oil; IR (neat) 1740, 1654, 1598, 1234  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$  1.99 (s, 3 H), 4.67 (br s, 1 H), 4.67 (br s, 1 H), 4.97 (d,  $J = 5.5$  Hz, 1 H), 4.97 (d,  $J = 5.5$  Hz, 1 H), 5.14 (br s, 1 H), 5.14 (br s, 1 H), 5.25 (br s, 1 H), 5.32 (br s, 1 H), 5.32 (br s, 1 H), 6.93-6.97 (m, 4 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  64.9, 69.8, 70.9, 115.4, 122.0, 122.3, 123.6, 123.9, 126.1, 137.3, 141.2, 147.8, 148.2, 170.4; LRMS  $m/z$  260 ( $\text{M}^+$ ), 121, 108, 92, 43; EI-HRMS  $m/z$  calcd for  $\text{C}_{15}\text{H}_{16}\text{O}_4$  ( $\text{M}^+$ ) 260.1049, found 260.1040.

**7-Isopropenyl-5,10-dioxa-5,6,9,10-tetrahydrobenzocyclooctene (5b).**

A colorless oil; IR (neat) 1608, 1582, 1234  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$  1.84 (s, 3 H), 4.97 (br s, 1 H), 5.01 (d,  $J = 6.1$  Hz, 1 H), 5.01 (d,  $J = 6.1$  Hz, 1 H), 5.09 (br s, 1 H), 5.15 (br s, 1 H), 5.15 (br s, 1 H), 5.89 (dd,  $J = 6.1, 6.1$  Hz, 1 H), 6.92-6.97 (m, 4 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  21.2, 69.3, 71.3, 113.1, 122.0, 122.3, 123.5, 123.7, 124.5, 140.1, 141.7, 148.1, 148.2; LRMS  $m/z$  202 ( $\text{M}^+$ ), 121, 93, 77, 41; EI-HRMS  $m/z$  calcd for  $\text{C}_{13}\text{H}_{14}\text{O}_2$  ( $\text{M}^+$ ) 202.0994, found 202.0986.

**5-Aza-8-isopropenyl-10-oxa-5-(*p*-toluenesulfonyl)-5,6,9,10-**

**tetrahydrobenzocyclooctene (5c).** Colorless crystals; mp 125-128  $^\circ\text{C}$ . IR (nujol) 1654, 1598, 1344, 1224, 1162  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.63 (s, 3 H), 2.33 (s, 3 H), 4.37 (d,  $J = 7.0$  Hz, 1 H), 4.37 (d,  $J = 7.0$  Hz, 1 H), 4.79 (s, 1 H), 4.79 (s, 1 H), 4.79 (s, 1 H), 4.84 (s, 1 H), 5.68 (dd,  $J = 7.0, 7.0$  Hz, 1 H), 6.80 (m, 1 H), 6.92 (m, 1 H), 7.09 (m, 1 H), 7.15 (d,  $J = 7.9$  Hz, 2 H), 7.17 (m, 1 H), 7.42 (d,  $J = 7.9$  Hz, 2 H);  $^{13}\text{C}$  NMR (67.8 MHz,  $\text{CDCl}_3$ )  $\delta$  20.9, 21.6, 48.5, 69.7, 113.1, 121.7, 123.0, 123.4, 127.4, 128.9, 129.3, 130.0, 135.2, 140.6, 141.7, 143.4, 153.6; LRMS  $m/z$  355 ( $\text{M}^+$ ), 200, 155, 91, 53, 41; EI-HRMS  $m/z$  calcd for  $\text{C}_{20}\text{H}_{21}\text{NO}_3\text{S}$  ( $\text{M}^+$ ) 355.1242, found 355.1230.

**5,10-Diaza-7-isopropenyl-5,10-bis(*p*-toluenesulfonyl)-5,6,9,10-**

**tetrahydrobenzocyclooctene (5d).** Colorless crystals; mp 178-180  $^\circ\text{C}$ . IR (nujol) 1654, 1596, 1376, 1162  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.62 (s, 3 H), 2.40 (s, 3 H), 2.42 (s, 3 H), 4.17 (br s, 2 H), 4.52 (br s, 2 H), 4.90 (s, 1 H), 5.18 (s, 1 H), 5.50

(dd,  $J = 5.6, 5.6$  Hz, 1 H), 7.03 (m, 1 H), 7.16 (m, 1 H), 7.23 (m, 1 H), 7.28 (d,  $J = 8.2$  Hz, 2 H), 7.33 (d,  $J = 8.2$  Hz, 2 H), 7.42 (m, 1 H), 7.59 (d,  $J = 8.2$  Hz, 2 H), 7.78 (d,  $J = 8.2$  Hz, 2 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  20.6, 21.6, 21.6, 47.3, 48.5, 114.0, 123.7, 127.4, 127.6, 128.0, 128.0, 128.3, 129.5, 129.5, 129.7, 134.9, 135.5, 135.5, 136.7, 139.0, 141.1, 143.6, 143.7; LRMS  $m/z$  508 ( $\text{M}^+$ ), 353, 197, 183, 155, 91, 41; EI-HRMS  $m/z$  calcd for  $\text{C}_{27}\text{H}_{28}\text{N}_2\text{O}_4\text{S}_2$  ( $\text{M}^+$ ) 508.1490, found 508.1520.

**5,10-Diaza-7-vinyl-5,10-bis(*p*-toluenesulfonyl)-5,6,9,10-**

**tetrahydrobenzocyclooctene (5e).** Colorless crystals; mp 89-91 °C. IR (nujol) 1654, 1596, 1350, 1162  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$  2.42 (s, 3 H), 2.43 (s, 3 H), 4.17 (d,  $J = 5.9$  Hz, 2 H), 4.46 (s, 2 H), 5.02 (d,  $J = 11.1$  Hz, 1 H), 5.35 (d,  $J = 17.0$  Hz, 1 H), 5.46 (dd,  $J = 5.9, 5.9$  Hz, 1 H), 6.04 (dd,  $J = 11.1, 17.0$  Hz, 1 H), 7.09 (dd,  $J = 7.5, 1.6$  Hz, 1 H), 7.17 (ddd,  $J = 7.5, 7.5, 1.6$  Hz, 1 H), 7.24 (ddd,  $J = 7.5, 7.5, 1.6$  Hz, 1 H), 7.33 (d,  $J = 8.5$  Hz, 2 H), 7.37 (d,  $J = 8.5$  Hz, 2 H), 7.60 (d,  $J = 8.5$  Hz, 2 H), 7.76 (d,  $J = 8.5$  Hz, 2 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  21.7, 21.7, 45.8, 48.4, 114.5, 127.5, 127.5, 127.8, 128.1, 128.1, 128.4, 129.5, 129.6, 129.6, 135.0, 135.4, 135.6, 136.5, 136.6, 137.5, 143.8, 143.8; LRMS  $m/z$  494 ( $\text{M}^+$ ), 339, 183, 156, 118, 91; EI-HRMS  $m/z$  calcd for  $\text{C}_{26}\text{H}_{26}\text{N}_2\text{O}_4\text{S}_2$  ( $\text{M}^+$ ) 494.1334, found 494.1357.

**5,11-Diaza-7-isopropenyl-5,11-bis(*p*-toluenesulfonyl)-5,6,9,10,11-**

**hexahydrobenzo[9]-annulene (7).** Amorphous solid; IR (film) 1656, 1595, 1348, 1158  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$  1.38 (s, 3 H), 2.10 (br, 1 H), 2.45 (s, 6 H), 2.87 (br, 2 H), 3.93 (br, 1 H), 4.52 (d,  $J = 11.7$  Hz, 1 H), 4.69 (d,  $J = 11.7$  Hz, 1 H), 4.78 (s, 1 H), 4.97 (s, 1 H), 5.61 (dd,  $J = 8.1, 8.1$  Hz, 1 H), 6.60 (d,  $J = 8.1$  Hz, 1 H), 7.10 (dd,  $J = 6.4, 6.4$  Hz, 1 H), 7.20 (dd,  $J = 6.4, 6.4$  Hz, 2 H), 7.29 (d,  $J = 8.3$  Hz, 2 H), 7.37 (d,  $J = 8.3$  Hz, 2 H), 7.66 (d,  $J = 8.3$  Hz, 2 H), 8.10 (d,  $J = 8.3$  Hz, 2 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  20.7, 21.6, 21.7, 29.3, 45.4, 51.7, 114.0, 127.2, 127.2, 127.8, 128.5, 129.0, 129.3, 129.4, 129.4, 132.7, 135.7, 136.5, 136.9, 138.2, 139.9, 140.7, 143.4, 143.5; LRMS  $m/z$  522 ( $\text{M}^+$ ), 428, 367, 273, 155, 118, 91; EI-HRMS  $m/z$  calcd for  $\text{C}_{21}\text{H}_{23}\text{N}_2\text{O}_2\text{S}$  ( $\text{M}^+$ -Ts) 367.1480, found 367.1467.

**5,11-Diaza-7-vinylidene-5,11-bis(*p*-toluenesulfonyl)-5,6,7,10,11-**

**hexahydrobenzo[9]-annulene (8).** Amorphous solid; IR (film) 1655, 1596, 1352, 1160  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$  1.51 (t,  $J = 6.9$  Hz, 3 H), 2.43 (s, 3 H), 2.46 (s, 3 H), 4.30 (s, 2 H), 4.38 (d,  $J = 8.5$  Hz, 2 H), 5.13 (dt,  $J = 11.9, 8.5$  Hz, 1 H), 5.46 (q,  $J = 6.9$  Hz, 1 H), 5.79 (d,  $J = 11.9$  Hz, 1 H), 6.78 (dd,  $J = 7.9, 1.6$  Hz, 1 H), 7.10 (ddd,  $J = 7.9, 7.9, 1.6$  Hz, 1 H), 7.24 (ddd,  $J = 7.9, 7.9, 1.6$  Hz, 1 H), 7.33-7.37 (m, 5 H), 7.78 (d,  $J = 8.3$  Hz, 2 H), 7.93 (d,  $J = 8.3$  Hz, 2 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  13.7, 21.7, 45.9, 47.2, 121.2, 126.7, 128.5, 129.4, 129.4, 129.5, 129.8, 131.1, 133.6, 135.4, 135.5, 136.5, 137.0, 139.8, 143.5, 143.6; LRMS  $m/z$  508 ( $\text{M}^+$ ), 353, 261, 211, 197, 183, 169, 155, 131, 119, 91; EI-HRMS  $m/z$  calcd for  $\text{C}_{27}\text{H}_{28}\text{N}_2\text{O}_4\text{S}_2$  ( $\text{M}^+$ ) 508.1492, found 508.1493.

**Dimer of 6 (9).** Amorphous solid; IR (film) 2228, 1653, 1348, 1160  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$  1.55 (s, 3 H), 1.56 (s, 3 H), 2.13-2.23 (m, 4 H), 2.42 (s, 3 H), 2.43 (s, 3 H), 2.46 (s, 6 H), 3.64 (br, 4 H), 4.50 (br, 2 H), 4.70 (br, 2 H), 5.09-5.11 (m, 2 H), 6.92-6.95 (m, 2 H), 7.14-7.17 (m, 2 H), 7.22-7.25 (m, 4 H), 7.32 (d,  $J = 8.1$  Hz, 8 H), 7.70 (d,  $J = 8.1$  Hz, 4 H), 7.81 (d,  $J = 8.1$  Hz, 4 H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  3.4, 21.5, 21.6, 29.5, 31.3, 41.9, 73.5, 81.8, 126.5, 128.0, 128.6, 128.8, 129.0, 129.1, 129.6, 129.7, 130.9, 131.1, 137.1, 137.2, 139.4, 143.5, 143.7; LRMS  $m/z$  1039 ( $\text{M}^+ + \text{Na}$ ), 883, 729, 571, 513, 449, 419, 349, 335, 301; EI-HRMS  $m/z$  calcd for  $\text{C}_{54}\text{H}_{56}\text{N}_4\text{O}_8\text{S}_8\text{Na}$  ( $\text{M}^+ + \text{Na}$ ) 1039.2879, found 1039.2910.

***trans*-2,7-Diaza-4-isopropenyl-2,7-bis(*p*-toluenesulfonyl)bicyclo[6.4.0]-4-**

**dodecene (12a).** Amorphous solid; IR (film) 1653, 1598, 1361, 1156  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.10-1.29 (m, 2 H), 1.54-1.73 (m, 4 H), 1.76 (s, 3 H), 1.82-1.93 (m, 2 H), 2.39 (s, 6 H), 3.69 (ddd,  $J = 11.1, 11.1, 3.2$  Hz, 1 H), 4.00-4.07 (m, 1 H), 4.00 (dd,  $J = 6.5, 16.4$  Hz, 1 H), 4.07 (d,  $J = 15.5$  Hz, 1 H), 4.16 (dd,  $J = 6.5, 16.4$  Hz, 1 H), 4.25 (d,  $J = 15.5$  Hz, 1 H), 4.93 (s, 1 H), 4.99 (s, 1 H), 5.75 (dd,  $J = 6.5, 6.5$  Hz, 1 H), 7.26 (d,  $J = 8.2$  Hz, 4 H), 7.74 (d,  $J = 8.2$  Hz, 2 H), 7.79 (d,  $J = 8.2$  Hz, 2 H);  $^{13}\text{C}$  NMR (67.8 MHz,  $\text{CDCl}_3$ )  $\delta$  21.3, 21.4, 25.1, 25.8, 31.4, 31.5, 43.3, 46.9, 62.0,

63.6, 112.6, 125.5, 127.2, 127.5, 129.3, 129.4, 138.7, 139.2, 140.9, 142.8, 142.9, 143.0; LRMS  $m/z$  514 ( $M^+$ ), 433, 359, 204, 155; EI-HRMS  $m/z$  calcd for  $C_{20}H_{27}N_2O_2S$  ( $M^+$ ) 359.1793, found 359.1809.

***cis*-2,7-Diaza-4-isopropenyl-2,7-bis(*p*-toluenesulfonyl)bicyclo[6.4.0]-4-dodecene (12b).** Amorphous solid; IR (film) 1653, 1598, 1336, 1156  $cm^{-1}$ ;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  1.28-1.47 (m, 4 H), 1.56-1.70 (m, 2 H), 1.77-1.85 (m, 1 H), 1.90 (s, 3 H), 2.00-2.04 (m, 1 H), 2.44 (s, 6 H), 3.87-3.91 (m, 1 H), 4.03-4.17 (m, 3 H), 4.59 (dd,  $J$  = 16.1, 7.6 Hz, 2 H), 4.97 (s, 1 H), 5.04 (s, 1 H), 5.89 (t,  $J$  = 7.3 Hz, 1 H), 7.31 (d,  $J$  = 7.9 Hz, 4 H), 7.64 (d,  $J$  = 7.9 Hz, 2 H), 7.65 (d,  $J$  = 7.9 Hz, 2 H);  $^{13}C$  NMR (67.8 MHz,  $CDCl_3$ )  $\delta$  21.5, 21.6, 22.6, 24.0, 28.9, 30.8, 43.7, 45.0, 57.4, 57.6, 112.8, 124.4, 126.8, 126.9, 129.8, 129.8, 137.1, 137.3, 139.0, 142.6, 143.3, 143.4; LRMS  $m/z$  514 ( $M^+$ ), 449, 433, 359, 204, 155; EI-HRMS  $m/z$  calcd for  $C_{20}H_{27}N_2O_2S$  ( $M^+$ -Ts) 359.1793, found 359.1804.

**1,6-Diaza-3-isopropenyl-1,6-bis(*p*-toluenesulfonyl)-3-cyclooctene (12c).** Colorless needles; mp 126-128  $^{\circ}C$ . IR (nujol) 1652, 1595, 1354, 1164  $cm^{-1}$ ;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  1.82 (s, 3 H), 2.42 (s, 3 H), 2.43 (s, 3 H), 3.37 (dd,  $J$  = 7.0, 7.0 Hz, 2 H), 3.38 (dd,  $J$  = 7.0, 7.0 Hz, 2 H), 4.05 (s, 2 H), 4.06 (d,  $J$  = 7.9 Hz, 2 H), 4.97 (s, 1 H), 5.03 (s, 1 H), 5.90 (dd,  $J$  = 7.9, 7.9 Hz, 1 H), 7.30 (d,  $J$  = 7.9 Hz, 2 H), 7.32 (d,  $J$  = 7.9 Hz, 2 H), 7.64 (d,  $J$  = 7.9 Hz, 2 H), 7.79 (d,  $J$  = 7.9 Hz, 2 H);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$  21.3, 21.4, 21.4, 44.5, 47.3, 47.8, 48.8, 113.8, 124.3, 127.0, 127.1, 129.8, 129.9, 135.0, 136.1, 138.4, 142.1, 143.5, 143.8; LRMS  $m/z$  460 ( $M^+$ ), 305, 276, 150, 135, 120, 108; EI-HRMS  $m/z$  calcd for  $C_{23}H_{28}N_2O_4S_2$  ( $M^+$ ) 460.1490, found 460.1471.

**6-Aza-1-oxa-3-isopropenyl-6-(*p*-toluenesulfonyl)-3-cyclooctene (12d).** A colorless oil; IR (film) 1654, 1598, 1334, 1162, 1142  $cm^{-1}$ ;  $^1H$  NMR (270 MHz,  $CDCl_3$ )  $\delta$  1.77 (s, 3 H), 2.42 (s, 3 H), 3.36 (dd,  $J$  = 4.6, 4.6 Hz, 2 H), 3.79 (dd,  $J$  = 4.6, 4.6 Hz, 2 H), 4.21 (d,  $J$  = 8.5 Hz, 2 H), 4.43 (s, 2 H), 4.83 (s, 1 H), 4.91 (s, 1 H), 5.70 (dd,  $J$  = 8.5, 8.5 Hz, 1 H), 7.30 (d,  $J$  = 8.1 Hz, 2 H), 7.69 (d,  $J$  = 8.1 Hz, 2 H);  $^{13}C$  NMR (67.8

MHz, CDCl<sub>3</sub>)  $\delta$  21.4, 44.0, 46.2, 70.4, 70.8, 112.6, 120.8, 127.1, 129.7, 136.5, 141.7, 142.1, 143.3; LRMS  $m/z$  307 (M<sup>+</sup>), 226, 198, 155, 152, 91; EI-HRMS  $m/z$  calcd for C<sub>16</sub>H<sub>21</sub>NO<sub>3</sub>S (M<sup>+</sup>) 307.1242, found 307.1253.

**6-Aza-1-oxa-3-isopropenyl-6-(*p*-toluenesulfonyl)-2-cyclooctene (13).** A colorless oil; IR (film) 1655, 1630, 1597, 1338, 1156, 1125 cm<sup>-1</sup>; <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>)  $\delta$  1.85 (s, 3 H), 2.41 (s, 3 H), 2.64 (dd,  $J$  = 5.7, 5.7 Hz, 2 H), 3.26 (dd,  $J$  = 5.7, 5.7 Hz, 2 H), 3.34 (dd,  $J$  = 4.6, 4.6 Hz, 2 H), 3.92 (dd,  $J$  = 4.6, 4.6 Hz, 2 H), 4.87 (s, 1 H), 4.95 (s, 1 H), 6.51 (s, 1 H), 7.28 (d,  $J$  = 8.1 Hz, 2 H), 7.65 (d,  $J$  = 8.1 Hz, 2 H); <sup>13</sup>C NMR (68 MHz, CDCl<sub>3</sub>)  $\delta$  20.5, 21.5, 25.8, 48.5, 48.8, 72.0, 111.9, 126.9, 129.6, 130.7, 136.9, 139.3, 143.1, 144.0; LRMS  $m/z$  307 (M<sup>+</sup>), 152, 91; EI-HRMS  $m/z$  calcd for C<sub>16</sub>H<sub>21</sub>NO<sub>3</sub>S (M<sup>+</sup>) 307.1242, found 307.1259.

**1-Aza-3-isopropenyl-1-(*p*-toluenesulfonyl)-3-cyclooctene (12e).** A pale yellow oil; IR (film) 1655, 1598, 1344, 1160 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.37-1.42 (m, 2 H), 1.45-1.48 (m, 2 H), 1.89 (s, 3 H), 2.26-2.31 (m, 2 H), 2.44 (s, 3 H), 3.34 (m, 2 H), 4.03 (s, 2 H), 4.97 (s, 1 H), 5.23 (s, 1 H), 6.03 (dd,  $J$  = 8.5, 8.5 Hz, 1 H), 7.31 (d,  $J$  = 8.2 Hz, 2 H), 7.71 (d,  $J$  = 8.2 Hz, 2 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  21.0, 21.5, 25.9, 26.4, 27.6, 43.6, 46.1, 112.8, 127.1, 129.5, 130.9, 134.6, 136.3, 141.2, 142.9; LRMS  $m/z$  305 (M<sup>+</sup>), 184, 155, 150, 91; EI-HRMS  $m/z$  calcd for C<sub>17</sub>H<sub>23</sub>NO<sub>2</sub>S (M<sup>+</sup>) 305.1449, found 305.1441.

**Dimer of 11e (14).** A pale yellow oil; IR (neat) 2226, 1655, 1346, 1160 cm<sup>-1</sup>; <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>)  $\delta$  1.35-1.43 (m, 4 H), 1.49-1.59 (m, 4 H), 1.54 (t,  $J$  = 2.2 Hz, 6 H), 1.97-2.03 (m, 4 H), 2.42 (s, 6 H), 3.15 (dt,  $J$  = 2.4, 7.1 Hz, 4 H), 4.04 (q,  $J$  = 2.2 Hz, 4 H), 5.32-5.38 (m, 2 H), 7.28 (d,  $J$  = 8.3 Hz, 4 H), 7.72 (d,  $J$  = 8.3 Hz, 4 H); <sup>13</sup>C NMR (67.8 MHz, CDCl<sub>3</sub>)  $\delta$  3.2, 21.4, 26.4, 27.0, 32.0, 36.6, 46.1, 71.8, 81.3, 127.8, 129.2, 130.2, 136.2, 143.0; LRMS  $m/z$  582 (M<sup>+</sup>), 427, 236, 184, 155, 139, 91; EI-HRMS  $m/z$  calcd for C<sub>32</sub>H<sub>42</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub> (M<sup>+</sup>) 582.2586, found 582.2615.