Supplementary Material (ESI) for Chemical Communications

ELECTRONIC SUPPLEMENTARY INFORMATION FOR

Cyclizations and Cycloadditions of Acetylenic Sulfones on Solid Supports

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Preparation of 3-[4-(phenylselenosulfonyl)phenyl]propionyl resin 2.

Benzeneseleninic acid (1.89 g, 10 mmol) was added in portions over 15 min to 2.25 g of a suspension of 3-[4-(hydrazinosulfonyl)phenyl]propionyl AM resin **1** (NovaBiochem Inc., 1.5 mmol/g) in 20 mL of methanol-THF (1:1) at room temperature. Evolution of nitrogen was observed. After stirring at room temperature overnight, the product resin **2** was collected by filtration and washed with methanol, THF and ether, and dried under vacuum to afford 2.70 g of the yellow resin **2**: IR (KBr) 1669, 1292, 1119, 1068 cm^{-1}.

Preparation of 3-[4-(1-hexynylsulfonyl)phenyl]propionyl resin 4.

1-Hexyne (820 mg, 10.0 mmol), diphenyl diselenide (47 mg, 0.15 mmol) and AIBN (24 mg, 0.15 mmol) were added to a suspension of the resin **2** (1.00 g) in 20 mL of dry benzene. The mixture was refluxed for 24 h under nitrogen. The β-seleno vinyl sulfone resin was collected by filtration and washed with benzene, methanol, THF and ether, and then dried under vacuum to afford 1.11 g of a yellow resin **3**. The resin was suspended in THF (30 mL) and 30% hydrogen peroxide (3 mL) was added. The mixture was stirred for 2 h at 60 ^{o}C. The resin was filtered and washed with water, methanol, THF and ether, and dried under vacuum to afford 821 mg (0.90 mmol/g) of **4**, obtained as a white resin: IR (KBr) 2194, 1650, 1314, 1142, 1083, 1006 cm^{-1}.

***p*-(Bromomethyl)benzenesulfonhydrazide (5).**

p-(Bromomethyl)benzenesulfonyl chloride[1] (8.07 g, 30.0 mmol) was dissolved in 120 mL of THF. The stirred mixture was cooled in an ice bath and a solution of hydrazine hydrate (3.30 g, 66.0 mmol) in 3 mL of water was added dropwise. Stirring was continued for 15 min. The mixture was washed with brine, dried and filtered through Celite. The clear filtrate was evaporated under reduced pressure to afford 7.14 g (90%) of **5** as a white solid, mp 156-160 ^{o}C (dec.); IR (film) 3479, 3330, 1328, 1148 cm^{-1}; ^{1}H NMR (300 MHz) δ 7.91 (d, J = 8.2 Hz, 2 H), 7.59 (d, J = 8.7 Hz, 2 H), 5.68-5.57 (br s, 1 H), 4.52 (s, 2 H), 2.18-1.36 (br s, 2 H); ^{13}C NMR (75 MHz) δ 143.6, 136.3, 129.9, 128.7, 31.2. The crude product was used directly in the next step.

***Se*-Phenyl *p*-(bromomethyl)benzeneselenosulfonate (6).**

Benzeneseleninic acid (4.56 g, 24.1 mmol) was added in portions to sulfonhydrazide **5** (6.40 g, 24.2 mmol) in 80 mL of methanol over 25 min at 0 ^{o}C. Vigorous evolution of nitrogen was observed. The solution gradually turned clear yellow and toward the end of the addition a yellow precipitate formed. After cooling at -20 ^{o}C overnight, the product was filtered to afford 8.49 g (90%) of the selenosulfonate **6** as a yellow solid, mp 60-62 ^{o}C (from methanol); IR (film) 1292, 1128, 745 cm^{-1}; ^{1}H NMR (300 MHz) δ 7.58-7.32 (m, 9 H), 4.47 (s, 2 H); ^{13}C NMR (75 MHz) δ 144.8, 143.5, 137.2, 131.0, 129.7, 129.3, 127.8, 127.5, 31.3; MS (*m/z,* %) 390 (20, M^{+}), 233 (40), 217 (44), 157 (85), 90 (100). HRMS calcd for $C_{13}H_{11}{}^{79}BrO_2S^{80}Se$: 389.8828. Found: 389.8827. Anal. calcd for $C_{13}H_{11}BrO_2SSe$: C, 40.02; H, 2.84. Found: C, 40.08; H, 2.69.

(*E*)-1-[(*p*-Bromomethyl)phenyl]sulfonyl-2-phenylseleno-1-hexene (7a).

1-Hexyne (82 mg, 1.0 mmol) and selenosulfonate **6** (250 mg, 0.641 mmol) were dissolved in 4 mL of chloroform and irradiated for 1 h in a Rayonet reactor equipped with

six 300 nm lamps. The solvent was evaporated, and the residue was purified by flash chromatography (15% ethyl acetate-hexanes) to afford 268 mg (88%) of **7a** as a pale yellow oil: IR (film) 1317, 1305, 1146, 1085 cm^{-1}; ^1H NMR (300 MHz) δ 7.76 (d, *J* = 8.2 Hz, 2 H), 7.58-7.47 (m, 4 H), 7.47-7.33 (m, 3 H), 5.83 (s, 1 H), 4.49 (s, 2 H), 2.85 (t, *J* = 7.7 Hz, 2 H), 1.63-1.51 (m, 2 H), 1.43-1.30 (m, 2 H), 0.91 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (75 MHz) δ 162.9, 142.8, 142.2, 136.7, 130.1, 130.0, 129.7, 127.3, 125.7, 122.8, 33.0, 32.2, 31.5, 22.5, 13.7; MS (*m/z,* %) 472 (0.7, M^+), 89 (100). HRMS calcd for $C_{19}H_{21}{}^{79}BrO_2S^{80}Se$: 471.9611. Found: 471.9615. Anal. calcd for $C_{19}H_{21}BrO_2SSe$: C, 48.32; H, 4.48. Found: C, 48.46; H, 4.65.

(*E*)-1-[(*p*-Bromomethyl)phenyl]sulfonyl-2-phenyl-2-(phenylseleno)ethene (7b).

The same procedure as for **7a** was employed, using phenylacetylene, to afford 90% of **7b**: mp 128-129 °C (from ethyl acetate-hexanes); IR (film) 1305, 1273, 1131, 1082 cm^{-1}; ^1H NMR (300 MHz) δ 7.63-7.57 (d, *J* = 7.4 Hz, 2 H), 7.48-7.23 (m, 10 H), 7.16 (d, *J* = 6.7 Hz, 2 H), 6.18 (s, 1 H), 4.43 (s, 2 H); ^{13}C NMR (75 MHz) δ 158.3, 142.5, 141.4, 136.5, 134.3, 130.18, 130.15, 129.3, 129.1, 128.3, 127.9, 127.8, 126.6, 125.5, 31.6; MS (*m/z,* %) 492 (18, M^+), 259 (54), 157 (59), 90 (100). HRMS calcd for $C_{21}H_{17}{}^{79}BrO_2S^{80}Se$: 491.9298. Found: 491.9311. Anal. calcd for $C_{21}H_{17}BrO_2SSe$: C, 51.24; H, 3.48. Found: C, 51.11; H, 3.37.

(*E*)-1-[(*p*-Bromomethyl)phenyl]sulfonyl-2-phenylseleno-2-trimethylsilylethene (7c).

The same procedure as for **7a** was employed, using trimethylsilylacetylene, to afford 93% of **7c**: mp 99-101 °C (from ethyl acetate-hexanes); IR (film) 1320, 1304, 1247, 1147, 1085 cm^{-1}; ^1H NMR (300 MHz) δ 7.66 (d, *J* = 8.2 Hz, 2 H), 7.48 (d, *J* = 8.2 Hz, 2 H), 7.46-7.32 (m, 5 H), 6.03 (s, 1 H), 4.48 (s, 2 H), 0.50 (s, 9 H); ^{13}C NMR (75 MHz) δ 161.6, 142.7, 141.2, 136.8, 130.8, 130.2, 129.9, 129.6, 127.4, 126.6, 31.5, 0.4; MS (*m/z,* %) 488 (6, M^+), 473 (20), 182 (41), 73 (100). HRMS calcd for $C_{18}H_{21}{}^{79}BrO_2S^{80}SeSi$: 487.9380. Found: 487.9428. Anal. calcd for $C_{18}H_{21}BrO_2SSeSi$: C, 44.27; H, 4.33. Found: C, 44.19; H, 4.23.

Preparation of resins 9a-9d from 8.

Benzoic acid resin **8**[2] (1.50 g, 0.86 mmol/g, loading determined gravimetrically by conversion to the corresponding cesium carboxylate), prepared from Merrifield resin (1.2 mmol/g), was suspended in 30 mL of DMF under a nitrogen atmosphere. Bromide **7a** (1.54 g, 3.21 mmol), cesium iodide (0.78 g, 3.0 mmol) and ethyldiisopropylamine (0.39 g, 3.0 mmol) were added and the suspension was stirred at room temperature for 1 d. The mixture was filtered, washed with water, DMF, dichloromethane, methanol and ether, followed by drying under reduced pressure, to afford a yellow resin.

The latter was suspended in 25 mL of THF and 3.0 mL of 30% hydrogen peroxide was added. The mixture was stirred and heated at 60 °C for 2 h. The resin was filtered and washed with water, THF, dichloromethane, methanol and ether, followed by drying under reduced pressure to afford 1.76 g (0.65 mmol/g) of **9a**, obtained as a white resin; IR (KBr) 2198, 1720, 1599, 1333, 1268, 1160 cm^{-1}.

Resin **9b** (0.59 mmol/g) was obtained similarly from **8** and **7b**; IR (KBr) 2176, 1716, 1599, 1338, 1266, 1153 cm^{-1}.

Resin **9c** (0.39 mmol/g) was prepared similarly by esterification of **8** (3.00 g) with **7c**, followed by oxidation and selenoxide elimination conducted as follows. The

esterified resin was suspended in 70 mL of chloroform. MCPBA (3.36 g, 77%, 15.0 mmol) was added and the mixture was stirred for 10 h at room temperature and then refluxed for 5 h. The resin was filtered, washed with water, 10% aqueous K_2CO_3 solution, water, methanol and dichloromethane to afford 3.54 g of **9c** as a yellow resin; IR (KBr) 2122, 1718, 1598, 1338, 1269, 1162 cm^{-1}.

Resin **9c** (3.00 g) was suspended in a mixture of 20 mL of methanol and 20 mL of 30% aqueous K_2CO_3 solution, and the mixture was stirred at room temperature for 40 h. The resin was filtered, then washed with water, methanol, dichloromethane and ether, followed by drying under reduced pressure, to provide 2.71 g of the yellow resin **9d** (0.36 mmol/g); IR (KBr), 2119, 1717, 1368, 1270, 1162 cm^{-1}.

Hydrolysis of resins 9b and 9d.

Resin **9b** (1.00 g) was hydrolyzed in 20 mL of THF containing 2.0 mL of 5% aqueous LiOH solution at room temperature overnight to give 161 mg (0.59 mmol) of 1-[(*p*-hydroxymethyl)benzenesulfonyl]-2-phenylethyne as a pale yellow oil: IR (film) 3419, 2180, 1330, 1156 cm^{-1}; ^{1}H NMR (300 MHz) δ 8.05 (d, *J* = 8.2 Hz, 2 H), 7.59 (d, *J* = 8.7 Hz, 2 H), 7.56-7.43 (m, 3 H), 7.42-7.34 (m, 2 H), 4.84 (s, 2 H), 2.39-1.82 (br s, 1 H); ^{13}C NMR (75 MHz) δ 147.8, 140.6, 132.7, 131.6, 128.7, 127.7, 127.2, 117.8, 93.5, 85.3, 64.2.

Resin **9d** (1.00 g) was treated similarly to afford 67 mg (0.36 mmol) of (*p*-hydroxymethyl)phenyl methyl sulfone as a pale yellow oil: IR (film) 3491, 1303, 1146 cm^{-1}; ^{1}H NMR (300 MHz) δ 7.86 (d, *J* = 8.7 Hz, 2 H), 7.54 (d, *J* = 8.2 Hz, 2 H), 4.79 (s, 2 H), 3.03 (s, 3 H), 2.58-2.17 (br s, 1 H); ^{13}C NMR (75 MHz) δ 147.4, 139.2, 127.4, 127.2, 64.0, 44.5.

A similar attempt to hydrolyze resin **9a** afforded a complex mixture, thereby precluding the determination of its loading by this method.

Preparation of resin 10.

Benzoic acid resin **8**[2] (4.00 g, 0.86 mmol/g), prepared from Merrifield resin (1.2 mmol/g) was suspended in 50 mL of DMF under nitrogen. Sulfonhydrazide **5** (2.11 g, 7.96 mmol), cesium iodide (2.08 g, 8.00 mmol) and ethyldiisopropylamine (1.03 g, 7.97 mmol) were added and the suspension was stirred at room temperature for 1 d. The solid was filtered, washed with water, DMF, dichloromethane, methanol, dichloromethane and ether, followed by drying under reduced pressure, to yield 4.59 g of **10** as a white resin; IR 3365, 3269, 1717, 1335, 1267, 1154 cm^{-1}. Elemental analysis of the resin indicated it to contain 1.88% nitrogen, which corresponds to a loading of 0.67 mmol/g.

Alternative preparation of resins 9a-9d from 10.

Sulfonhydrazide resin **10** (4.00 g, 0.67 mmol/g) was stirred in 30 mL of THF-methanol (1:1). Benzeneseleninic acid (1.50 g, 7.9 mmol) was added in portions over 15 min at room temperature. Evolution of nitrogen was observed. After stirring at room temperature overnight, the yellow resin was filtered, washed with methanol, THF and ether, and then dried under vacuum to afford 4.32 g of the corresponding polymer-supported selenosulfonate.

The latter resin (0.80 g), 1-hexyne (0.39 g, 4.8 mmol), diphenyl diselenide (31 mg, 0.10 mmol) and AIBN (16 mg, 0.10 mmol) were refluxed under a nitrogen atmosphere for 24 h in 15 mL of dry benzene. The resulting β-selenovinyl sulfone resin was filtered, washed with benzene, methanol, THF and ether. The product was then

suspended in THF (30 mL) and 30% H_2O_2 (2 mL) was added at room temperature. The mixture was stirred for 2 h at 60 ^oC. The resin was filtered, washed with water, methanol, THF and ether, and then dried under vacuum to afford 0.77 g (0.67 mmol/g) of **9a**, obtained as a white resin.

The selenosulfonate resin (0.80 g), phenylacetylene (0.41 g, 4.0 mmol), diphenyl diselenide (31 mg, 0.10 mmol) and AIBN (16 mg, 0.10 mmol) were refluxed under a nitrogen atmosphere for 24 h in 15 mL of dry benzene. The resulting β-selenovinyl sulfone resin was filtered, washed with benzene, methanol, THF and ether. The product was then suspended in chloroform (20 mL) and MCPBA (0.67 g, 77%, 3.0 mmol) was added at room temperature. The mixture was refluxed for 3 h. The resin was filtered, washed with water, 10% aqueous K_2CO_3 solution, water, methanol, THF and ether, and then dried under vacuum to afford 0.76 g (0.59 mmol/g) of **9b** as a white resin.

The selenosulfonate resin (0.80 g), trimethysilylacetylene (0.41 g, 4.2 mmol), diphenyl diselenide (31 mg, 0.10 mmol) and AIBN (16 mg, 0.10 mmol) were refluxed under a nitrogen atmosphere for 24 h in 15 mL of dry benzene. The resulting β-selenovinyl sulfone resin was filtered, washed with benzene, methanol, THF and ether. The product was then suspended in chloroform (20 mL) and MCPBA (0.67 g, 77%, 3.0 mmol) was added at room temperature. The mixture was was refluxed for 3 h. The resin was filtered, washed with water, 10% aqueous K_2CO_3 solution, water, methanol, THF and ether. The resulting resin **9c** was then suspended in 10 mL of methanol and 10 mL of 30% aqueous K_2CO_3 solution, and the mixture was stirred at room temperature for 43 h. The resin was filtered, then washed with water, methanol, dichloromethane and ether, followed by drying under vacuum, to provide 0.70 g (0.47 mmol/g) of **9d** as a yellow resin.

Preparation of the products 15-22 shown in Scheme 6.

The yields and purities of the crude products are given in Scheme 6. Typical procedures and characterization data are given below. The characterization data are based on samples that were further purified by flash chromatography. All ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 300 or 75 MHz, respectively.

2-*n*-Butyl-3-(*p*-hydroxymethyl)benzenesulfonyl-1-(*p*-methoxybenzyl)-2,3-dehydropiperidine (15a).

The chloroamine **11**[3] was liberated from its hydrochloride (316 mg, 1.26 mmol) by treatment with aqueous KOH solution, extraction with dichloromethane, drying ($MgSO_4$), and concentration at reduced pressure and room temperature. A suspension of resin **9a** (690 mg, 0.65 mmol/g) and the free base **11** in 20 mL of benzene was refluxed for 2 d. The resin was filtered and washed with benzene, dichloromethane, methanol and ether, followed by drying under reduced pressure. The product was suspended in 15 mL of dry THF and 1.0 mmol of LDA in 5 mL of THF was added at -78 ^oC. The mixture was stirred at -78 ^oC for 1 h and was then quenched with 1.0 mL of 5% aqueous LiOH solution. The mixture was stirred at room temperature overnight, filtered and washed with THF and ether. The filtrate was concentrated to dryness and the residue was triturated with dichloromethane, washed with water, dried, filtered and evaporated to give 109 mg (57%) of **15a** of ca. 90% purity. Flash chromatography (30% hexanes-ethyl acetate) afforded a pale yellow oil: IR (film) 3442, 1558, 1283, 1252, 1124, 1078 cm^{-1}; ^1H NMR (300 MHz) δ 7.82 (d, J = 8.2 Hz, 2 H), 7.46 (d, J = 8.2 Hz, 2 H), 7.04 (d, J = 8.7

Hz, 2 H), 6.87 (d, *J* = 8.7 Hz, 2 H), 4.78 (s, 2 H), 4.33 (s, 2 H), 3.81 (s, 3 H), 3.05 (t, *J* = 6.2 Hz, 2 H), 2.77 (m, 2 H), 2.50 (t, *J* = 6.2 Hz, 2 H), 1.79-1.67 (m, 2 H), 1.55-1.22 (m, 4 H), 0.86 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (75 MHz) δ 159.0, 156.1, 144.7, 144.2, 129.3, 127.6, 126.8, 126.4, 114.2, 99.7, 64.4, 55.3, 53.2, 48.5, 31.6, 28.7, 24.9, 22.9, 21.6, 13.7; MS (*m/z,* %) 429 (0.6, M^+), 216 (26), 121 (100). HRMS calcd for $C_{24}H_{31}NO_4S$: 429.1974. Found: 429.1947.

3-(*p*-Hydroxymethyl)benzenesulfonyl-1-(*p*-methoxybenzyl)-2-phenyl-2,3-dehydropiperidine (15b).

The product was obtained from **9b** and **11** via a similar procedure to that used to prepare **15a** from **9a**; pale yellow oil; IR (film) 3464, 1355, 1289, 1246, 1138 cm^{-1}; ^{1}H NMR (300 MHz) δ 7.37 (d, *J* = 7.7 Hz, 2 H), 7.34-7.21 (m, 5 H), 7.14 (d, *J* = 7.2 Hz, 2 H), 6.97 (d, *J* = 8.2 Hz, 2 H), 6.81 (d, *J* = 8.2 Hz, 2 H), 4.67 (s, 2 H), 3.83 (s, 2 H), 3.77 (s, 3 H), 3.12 (t, *J* = 5.1 Hz, 2 H), 2.61 (t, *J* = 5.9 Hz, 2 H), 1.81 (quintet, *J* = 5.6 Hz, 2 H); ^{13}C NMR (75 MHz) δ 158.9, 154.8, 144.9, 143.0, 134.1, 129.7, 129.2, 128.7, 128.3, 127.7, 126.6, 126.3, 113.9, 103.9, 64.1, 55.2, 54.3, 47.2, 24.4, 21.5; MS (*m/z,* %) 449 (2, M^+), 156 (7), 121 (100). HRMS calcd for $C_{26}H_{27}NO_4S$: 449.1661. Found: 449.1659.

3-(*p*-Hydroxymethyl)benzenesulfonyl-1-(*p*-methoxybenzyl)-2,3-dehydropiperidine (15d).

The product was obtained from **9d** and **11** via a similar procedure to that used to prepare **15a** from **9a**. The product required purification by flash chromatography (30% hexanes-ethyl acetate) to afford **15d** as a pale yellow oil: IR (film) 3478, 1617, 1513, 1358, 1249, 1133 cm^{-1}; ^{1}H NMR (300 MHz) δ7.78 (d, *J* = 8.2 Hz, 2 H), 7.49 (s, 1 H), 7.45 (d, *J* = 8.2 Hz, 2 H), 7.12 (d, *J* = 8.7 Hz, 2 H), 6.88 (d, *J* = 8.7 Hz, 2 H), 4.76 (s, 2 H), 4.24 (s, 2 H), 3.81 (s, 3 H), 2.93 (t, *J* = 5.6 Hz, 2 H), 2.23 (br s, 1 H), 2.14 (t, *J* = 6.2 Hz, 2 H), 1.74 (quintet, *J* = 5.6 Hz, 2 H); ^{13}C NMR (75 MHz) δ 159.4, 145.0, 144.3, 141.6, 128.8, 128.2, 127.0, 126.9, 114.2, 100.3, 64.4, 59.2, 55.3, 44.7, 20.9, 19.6; MS (*m/z,* %) 373 (3, M^+), 205 (11), 121 (100). HRMS calcd for $C_{20}H_{23}NO_4S$: 373.1348. Found: 373.1353.

2-*n*-Butyl-1-(*p*-methoxybenzyl)piperidine (16a).

Chloroamine **11** was liberated from its hydrochloride (217 mg, 0.87 mmol) and added to resin **9a** (600 mg, 0.65 mmol/g) to effect conjugate addition and base-mediated cyclization as in the case of **15a**, except that LiHMDS was employed instead of LDA. The resulting resin was filtered, washed and dried as in the case of **15a**. It was then suspended in 25 mL of dichloromethane containing sodium cyanoborohydride (375 mg, 5.97 mmol). Trifluroacetic acid (0.44 mL, 5.7 mmol) was added dropwise and the mixture was stirred at room temperature for 50 min and refluxed for 50 min. The resin was filtered, washed with aqueous KOH solution, water, methanol, THF and ether, and then dried under vacuum. The product was suspended in 25 mL of dry THF and finely ground 5% sodium amalgam (4.44 g, 9.65 g-atoms of Na) was added. The mixture was refluxed under nitrogen for 30 h and filtered through Celite, followed by washing with THF. The filtrate was washed with water, dried and concentrated in vacuo to afford 50 mg (46%) of the product of ca. 90% purity. Flash chromatography (20% ethyl acetate-hexanes) afforded pure **16a** as a pale yellow oil: IR (film) 1612, 1509, 1245, 1039 cm^{-1};

^{1}H NMR (300 MHz) δ 7.25 (d, *J* = 8.7 Hz, 2 H), 6.85 (d, *J* = 8.7 Hz, 2 H), 3.93 (d, *J* = 13.3 Hz, 1 H), 3.81 (s, 3 H), 3.22 (d, *J* = 12.8 Hz, 1 H), 2.79-2.70 (m, 1 H), 2.32-2.21 (m, 1 H), 2.09-1.98 (m, 1 H), 1.75-1.22 (m, 12 H), 0.92 (t, *J* = 6.7 Hz, 3 H); ^{13}C NMR (75 MHz) δ 158.5, 130.2, 113.5, 60.7, 56.7, 55.2, 51.5, 31.3, 30.1, 27.7, 25.0, 23.6, 23.2, 14.1; MS (*m/z,* %) 261 (0.6, M^+), 261 (1.6, M^+-1), 204 (12), 121 (100); HRMS calcd for $C_{17}H_{26}NO$ (M^+- H): 260.2014. Found: 260.2001.

1-(*p*-Methoxybenzyl)-2-phenylpiperidine (16b).

The product was obtained from **9b** and **11** via a similar procedure to that used to prepare **16a** from **9a**: mp 82-83 ^{o}C (from hexane); IR (KBr) 1507, 1247, 1092, 1035 cm^{-1}; ^{1}H NMR (300 MHz) δ 7.51-7.45 (m, 2 H), 7.42-7.33 (m, 2 H), 7.30-7.20 (m, 1 H), 7.17 (d, *J* = 8.7 Hz, 2 H), 6.82 (d, *J* = 8.2 Hz, 2 H), 3.79 (s, 3 H), 3.76-3.66 (m, 1 H), 3.09 (d, *J* = 15 Hz, 1 H), 3.02-2.91 (m, 1 H), 2.77 (d, J = 13.4 Hz, 1 H), 1.93 (m, 1 H), 1.82-1.70 (m, 2 H), 1.67-1.48 (m, 3 H), 1.46-1.27 (m, 1 H); ^{13}C NMR (75 MHz) δ 158.3, 145.8, 131.7, 129.8, 128.5, 128.4, 127.4, 127.1, 126.8, 124.3, 113.44, 113.37, 69.1, 59.0, 55.2, 53.1, 37.0, 26.0, 25.2; MS (*m/z,* %) 281 (12, M^+), 204 (22), 160 (11), 121 (100). HRMS calcd for $C_{19}H_{23}NO$: 281.1780. Found: 281.1784.

4-*n*-Butyl-3-(*p*-hydroxymethyl)benzenesulfonyl-3,4-dehydroquinolizidine (17a).

The product was obtained from **9a** and **12**[4] via a similar procedure to that used to prepare **15a** from **9a**: pale yellow oil; IR (film) 3464, 1558, 1272, 1124, 1078 cm^{-1}; ^{1}H NMR (300 MHz) δ 7.77 (d, *J* = 8.2 Hz, 2 H), 7.43 (d, *J* = 8.2 Hz, 2 H), 4.75 (s, 2 H), 3.81-3.71 (m, 1 H), 3.10-2.97 (m, 1 H), 2.80-2.62 (m, 2 H), 2.54-2.42 (m, 1 H), 1.89-1.76 (m, 2 H), 1.72-1.22 (m, 12 H), 0.86 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (75 MHz) δ 155.9, 144.7, 144.4, 126.8, 126.2, 100.9, 64.5, 57.0, 48.2, 32.4, 31.1, 28.7, 28.6, 26.7, 24.5, 22.8, 22.3, 13.8; MS (*m/z,* %) 363 (7, M^+), 257 (100), 192 (93), 150 (62). HRMS calcd for $C_{20}H_{29}NO_3S$: 363.1868. Found: 363.1878.

3-(*p*-Hydroxymethyl)benzenesulfonyl-4-phenyl-3,4-dehydroquinolizidine (17b).

The product was obtained from **9b** and **12** via a similar procedure to that used to prepare **15a** from **9a**: pale yellow oil; IR (film) 3464, 1556, 1282, 1145, 1079 cm^{-1}; ^{1}H NMR (300 MHz) δ 7.37 (d, *J* = 8.2 Hz, 2 H), 7.34-7.24 (m, 5 H), 7.11-7.03 (m, 2 H), 4.68 (s, 2 H), 3.20-3.08 (m, 1 H), 3.00-2.83 (m, 1 H), 2.74-2.38 (m, 2 H), 2.00-1.85 (m, 1 H), 1.84-1.51 (m, 3 H), 1.50-1.28 (m, 4 H), 1.26-1.10 (m, 1 H); ^{13}C NMR (75 MHz) δ 154.7, 144.6, 143.4, 134.7, 129.8, 129.0, 128.4, 127.7, 127.5, 126.6, 126.3, 103.5, 64.3, 56.7, 49.6, 32.5, 28.9, 26.3, 24.3, 21.8; MS (*m/z,* %) 383 (36, M^+), 212 (81), 210 (100), 105 (43). HRMS calcd for $C_{22}H_{25}NO_3S$: 383.1555. Found: 383.1552.

3-(*p*-Hydroxymethyl)benzenesulfonyl-3,4-dehydroquinolizidine (17d).

The product was obtained from **9d** and **12** via a similar procedure to that used to prepare **15a** from **9a**: pale yellow oil; IR (film) 3478, 1616, 1513, 1277, 1247, 1132, 1092 cm^{-1}; ^{1}H NMR (300 MHz) δ 7.77 (d, *J* = 8.2 Hz, 2 H), 7.44 (d, *J* = 8.2 Hz, 2 H), 7.18 (s, 1 H), 4.76 (s, 2 H), 3.34 (dt, *J* = 12.3, 2.0 Hz, 1 H), 3.03 (td, *J* = 12.3, 3.1 Hz, 1 H), 2.93-2.82 (m, 1 H), 2.28-2.04 (m, 2 H), 1.98-1.78 (m, 2 H), 1.74-1.16 (m, 6 H); ^{13}C NMR (75 MHz) δ 145.0, 144.9, 141.3, 127.1, 126.9, 101.9, 64.4, 54.0, 53.0, 31.5, 28.7,

25.9, 23.9, 19.0; MS (*m/z,* %) 307 (7, M^+), 136 (23), 83 (24), 43 (100). HRMS calcd for $C_{16}H_{21}NO_3S$: 307.1242. Found: 307.1226.

***trans*-4-Phenylquinolizidine (18b).**[5]

The known product **18b** was obtained from **9b** and **12** via a similar procedure to that used to prepare **16a** from **9a**: colourless oil; ^{1}H NMR (300 MHz) δ 7.40-7.18 (m, 5 H), 2.90 (dd, *J* = 10.5 Hz, 3.3 Hz, 1 H), 2.66 (d, *J* = 10.7 Hz, 1 H), 1.93 (m, 1 H), 1.82-1.18 (m, 13 H); ^{13}C NMR (75 MHz) δ 145.5, 128.2, 127.5, 126.6, 70.5, 63.4, 53.7, 36.5, 33.9, 33.8, 26.2, 24.9, 24.8.

2-*n*-Butyl-3-(*p*-hydroxymethyl)benzenesulfonylnorbornadiene (19a).

A mixture of cyclopentadiene (1.0 mL) and resin **9a** (250 mg, 0.65 mmol/g) in 20 mL of benzene was refluxed for 30 h. The resin was filtered, washed with benzene, dichloromethane, methanol and ether, followed by drying under reduced pressure. The resin was suspended in 10 mL of THF and 1.0 mL of 5% aqueous LiOH was added. The mixture was then stirred at room temperature overnight and filtered, followed by washing with THF, chloroform and ether. The filtrate was concentrated to dryness and triturated with dichloromethane. The mixture was filtered and evaporated to give 27 mg (52%) of **19a** of ca. 95% purity. Flash chromatography (40% hexanes-ethyl acetate) afforded a colourless oil: IR (film) 3504, 1610, 1308, 1139 cm^{-1}; ^{1}H NMR (300 MHz) δ 7.77 (d, *J* = 8.2 Hz, 2 H), 7.50 (d, *J* = 8.2 Hz, 2 H), 6.54 (s, 2 H), 4.80 (s, 2 H), 3.69 (s, 1 H), 3.60 (s, 1 H), 3.83-3.70 (m, 2 H), 2.06 (d, *J* = 6.7 Hz, 2 H), 1.91 (d, *J* = 6.7 Hz, 2 H), 1.42-1.24 (m, 4 H), 0.94 (t, *J* = 6.9 Hz, 3 H); ^{13}C NMR (75 MHz) δ 170.6, 146.1, 144.6, 142.6, 139.7, 139.4, 127.5, 126.9, 70.6, 64.3, 56.4, 52.3, 28.9, 28.8, 22.6, 13.9; MS (*m/z,* %) 318 (32, M^+), 253 (33), 117 (72), 91 (94), 77 (100). HRMS calcd for $C_{18}H_{22}O_3S$: 318.1290. Found: 318.1275.

2-(*p*-Hydroxymethyl)benzenesulfonyl-3-phenylnorbornadiene (19b).

Product **19b** was prepared from resin **9b** via a similar procedure to that used for **19a**: pale yellow oil; IR (film) 3505, 1304, 1144, 1085 cm^{-1}; ^{1}H NMR (300 MHz) δ 7.56 (d, *J* = 8.2 Hz, 2 H), 7.46-7.41 (m, 2 H), 7.39-7.32 (m, 5 H), 6.77 (dd, *J* = 5.1 Hz, 2.6 Hz, 1 H), 6.59 (dd, *J* = 5.1 Hz, 2.6 Hz, 1 H), 4.73 (s, 2 H), 3.96 (s, 1 H), 3.87 (s, 1 H), 2.32 (d, *J* = 6.7 Hz, 1 H), 2.02 (d, *J* = 6.7 Hz, 1 H); ^{13}C NMR (75 MHz) δ 164.7, 146.3, 146.2, 142.8, 139.5, 138.5, 133.6, 129.2, 127.9, 127.8, 127.7, 126.6, 70.3, 64.2, 59.7, 54.0; MS (*m/z,* %) 338 (5, M^+) 273 (13), 167 (100). HRMS calcd for $C_{20}H_{18}O_3S$: 338.0977. Found: 338.0961.

2-(*p*-Hydroxymethyl)benzenesulfonylnorbornadiene (19d).

Product **19d** was prepared from resin **9d** via a similar procedure to that used for **19a**. The product solidified on standing, mp 62-65 ^{o}C; IR (film) 3505, 1297, 1162, 1141cm^{-1}; ^{1}H NMR (300 MHz) δ 7.71 (d, *J* = 8.7 Hz, 2 H), 7.48 (d, *J* = 7.7 Hz, 2 H), 7.48 (s, 1 H), 6.64-6.56 (m, 2 H), 4.76 (s, 2 H), 3.79 (s, 1 H), 3.66 (s, 1 H), 2.8-2.3 (br s, 1 H), 2.16 (d, *J* = 6.7, 1 H), 2.07 (d, *J* = 6.7, 1 H); ^{13}C NMR (75 MHz) δ 157.3, 153.5, 147.0, 142.4, 141.0, 137.5, 127.9, 127.0, 74.0, 64.0, 51.5, 50.8; MS (*m/z,* %) 262 (7, M^+), 91 (100). HRMS calcd for $C_{14}H_{14}O_3S$: 262.0664. Found: 262.0673.

2-Phenylnorbornadiene (20b).[6]

The cycloaddition of cyclopentadiene and resin **9b** was performed as in the preparation of **19a**. Desulfonylation of the product was achieved with 5% sodium amalgam, as in the preparation of **16b**, except that methanol was employed as the solvent, to afford the known product **20b** as a colourless oil; ^{1}H NMR (300 MHz) δ 7.45-7.40 (m, 2 H), 7.40-7.28 (m, 2 H), 7.27-7.13 (m, 1 H), 6.95-6.89 (m, 2 H), 6.83 (dd, *J* = 5.1, 3.1 Hz, 1 H), 3.98-3.91 (m, 1 H), 3.75-3.69 (m, 1 H), 2.18-2.06 (m, 2 H); ^{13}C NMR (75 MHz) δ 156.8, 143.5, 142.0, 136.2, 136.0, 128.4, 126.9, 124.7, 72.4, 51.5, 50.9.

5-*n*-Butyl-4-(*p*-hydroxymethyl)benzenesulfonyl-3-mesityl-1,2-oxazole (21a).

2,4,6-Trimethylbenzonitrile-*N*-oxide (**14**)[7] (91 mg, 0.57 mmol) and resin **9a** (300 mg, 0.65 mmol/g) were stirred for 30 h in 10 mL of ether. The resin was filtered and washed with ether, dichloromethane, methanol and ether, followed by drying under reduced pressure. The product was suspended in 10 mL of THF and 1.0 mL of 5% aqueous LiOH was added. The mixture was then stirred at room temperature overnight and filtered, followed by washing with THF, chloroform and ether. The filtrate was concentrated to dryness and triturated with dichloromethane. The mixture was filtered and evaporated to give 39 mg (48%) of the crude product **21a** of ca. 95% purity. Flash chromatography (40% hexanes-ethyl acetate) afforded a colourless oil: IR (film) 3441, 1570, 1330, 1161, 1134, 1057 cm^{-1}; ^{1}H NMR (300 MHz) δ 7.36 (d, *J* = 8.7 Hz, 2 H), 7.31 (d, *J* = 8.7 Hz, 2 H), 6.83 (s, 2 H), 4.77 (s, 2 H), 3.33, (t, *J* = 7.7 Hz, 2 H), 2.35 (s, 3 H), 1.96-1.85 (m, 2 H), 1.70 (s, 6 H), 1.58-1.46 (m, 2 H), 1.03 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (75 MHz) δ 177.6, 159.7, 147.0, 139.7, 139.5, 138.1, 128.04, 128.01, 126.5, 122.8, 117.6, 64.1, 29.8, 26.9, 22.4, 21.3, 19.6, 13.7; MS (*m/z,* %) 413 (40, M^+), 242 (46), 186 (59), 158 (90), 41 (100). HRMS calcd for $C_{23}H_{27}NO_4S$: 413.1661, found 413.1685.

4-(*p*-Hydroxymethyl)benzenesulfonyl-3-mesityl-5-phenyl-1,2-oxazole (21b).

Product **21b** was prepared from resin **9b** via a similar procedure to that used for **21a**. The product solidified on standing, mp 150-153 ^{o}C; IR (film) 3437, 1557, 1366, 1327, 1162 cm^{-1}; ^{1}H NMR (300 MHz) δ 7.99 (dd, *J* = 8.2, 1.5 Hz, 2 H), 7.64-7.55 (m, 3 H), 7.33 (d, *J* = 8.2 Hz, 2 H), 7.25 (d, *J* = 8.7 Hz, 2 H), 6.86 (s, 2 H), 4.73 (s, 2 H), 2.36 (s, 3 H), 1.86 (s, 6 H); ^{13}C NMR (75 MHz) δ 172.7, 160.6, 147.1, 139.8, 139.2, 138.1, 131.9, 130.1, 128.4, 128.10, 128.06, 126.4, 125.9, 123.0, 118.3, 64.1, 21.3, 19.9; MS (*m/z,* %) 433 (13, M^+), 243 (35), 105 (100), 91 (67), 77 (66). HRMS calcd for $C_{25}H_{23}NO_4S$: 433.1348. Found: 433.1351.

4-(*p*-Hydroxymethyl)benzenesulfonyl-3-mesityl-1,2-oxazole (21d).

Product **21d** was prepared from resin **9d** via a similar procedure to that used for **21a**. The product solidified on standing, mp 118-122 ^{o}C; IR (film) 3437, 1341, 1160, 1112 cm^{-1}; ^{1}H NMR (300 MHz) δ 8.10 (d, *J* = 8.7 Hz, 2 H), 7.64 (d, *J* = 8.7 Hz, 2 H), 6.94 (s, 2 H), 6.90 (s, 1 H), 4.86 (s, 2 H), 2.32 (s, 3 H), 2.09 (s, 6 H); ^{13}C NMR (75 MHz) δ 167.3, 162.5, 148.6, 139.8, 137.1, 136.9, 128.9, 128.7, 127.5, 123.9, 109.6, 64.1, 21.1, 20.3; MS (*m/z,* %) 357 (21, M^+), 186 (100), 158 (77). HRMS calcd for $C_{19}H_{19}NO_4S$: 357.1035. Found: 357.1059.

1-Hydroxy-3-imino-3-mesityl-1-phenyl-1-propene (22b).

The cycloaddition of **14** with resin **9b** was performed as in the preparation of **21b** and subsequent desulfonylation was prformed with 5% sodium amalgam in THF as in the preparation of **16b**. The crude product was purified by flash chromatography (30% ethyl acetate-hexanes) to afford **22b** as a colourless oil: IR (KBr) 3337, 1595, 1529, 1320, 1289 cm^{-1}; ^1H NMR (300 MHz) δ 10.51-10.28 (br s, 1 H), 7.91 (dd, *J* = 7.9, 1.2 Hz, 2 H), 7.50-7.37 (m, 3 H), 6.93 (s, 2 H), 5.79 (d, *J* = 1.0 Hz, 1 H), 5.22-5.10 (br s, 1 H), 2.34 (s, 6 H), 2.33 (s, 3 H); ^{13}C NMR (75 MHz) δ 190.1, 163.6, 140.1, 138.5, 135.1, 134.9, 131.0, 128.3, 128.2, 127.2, 93.6, 21.1, 19.3; MS (*m/z,* %) 265 (34, M^+), 250 (85), 236 (25), 146 (35), 121 (39), 105 (100). HRMS calcd for $C_{18}H_{19}NO$: 265.1467. Found: 265.1489.

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