Selenophosphoramide-Catalyzed Diamination and Oxyamination of Alkenes

Supporting Information

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I. General Procedures

All reactions were performed under a nitrogen atmosphere using flame-dried glassware unless otherwise indicated. Infrared spectra were acquired using a Perkin Elmer Spectrum RX I Spectrometer. Mass spectra were acquired using a Bruker Esquire 1100 Liquid Chromatograph-Ion Trap Mass Spectrometer or a Hewlett Packard 5971A Gas Chromatograph - Mass Spectrometer. Column chromatography was performed using silica gel (Whatman, 60 Å, 230-400 mesh). NMR spectra were recorded on a Bruker AV-300, AV-301, DRX-499 or AV-500 Spectrometer. ^{1}H NMR chemical shifts (δ) are reported in parts per million (ppm) and are referenced relative to TMS (0.0 ppm), residual $CHCl_3$ (7.26 ppm), DCM (5.32 ppm) or acetone (2.05 ppm). ^{13}C NMR chemical shifts (δ) are reported in parts per million (ppm) relative to the carbon resonance of $CDCl_3$ (77.16 ppm), CD_2Cl_2 (53.84 ppm) or acetone-d_6 (29.84 ppm). Melting points were taken on a MEL-TEMP melting point apparatus and are uncorrected.

II. Materials

All commercial reagents were used as received, unless otherwise noted. All solvents were degassed and dried on solvent columns of neutral alumina. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc., stored over 4Å molecular sieves, and were used without further purification. 2-methyl-3-buten-1-ol, 4-phenyl-1-butene, beta-methylstyrene, 6-bromo-1-

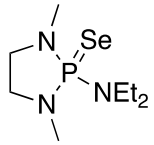
hexene, 1-hexadecene, allylcyclohexane, 4-octene, 3-octene, 2-octene, 2-heptene, allyl chloride, trans-stilbene, 4-bromo-1-butene and *N*-fluorobenzenesulfonimide were purchased from commercial sources and used without further purification. Trimethylsilyl trifluoromethanesulfonate was purified by vacuum distillation and stored under an atmosphere of nitrogen. 4-[(Tert-butyldiphenylsilyl)oxy]-1-butene[1], 5-(4-methoxyphenyl)-1-pentene[2], 6-(4-methylphenyl)-1-hexene[3], trans-4-hexenyl benzoate[4], 4-pentenyl benzoate[5], allyl p-methoxybenzoate[6], homoallyl p-methoxybenzoate[7], (2-methyl-3-butenyl)-p-methoxybenzoate[8], 3-butenyl-trifluoroacetate[9], hex-4-enyl methanesulfonate[10], triethylammonium benzenesulfonimide[11], and all phosphine selenide catalysts (unless otherwise noted)[11] were prepared according to previously published procedures and their respective spectroscopic signatures (^{1}H NMR) were found to be consistent with values reported therein.

III. Synthesis of Starting Materials

General Procedure A: To a flame-dried flask under nitrogen atmosphere, DMAP (776 mg, 12.7 mmol) and triethylamine (3.2 mL, 22.86 mmol) were added to a solution of alcohol (12.7 mmol) in DCM (63.5 mL, 0.2 M). Next, *p*-methoxybenzoyl chloride (2.4 mL, 17.8 mmol) was slowly added to at 0 °C. The reaction was stirred at room temperature overnight. The resulting mixture was quenched with water (50 mL) and washed with DCM (3×50 mL). The combined organic layers were washed with 1 M HCl (100 mL), $NaHCO_3$ (sat. aq., 100 mL) and brine (100 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The products were purified by flash chromatography.

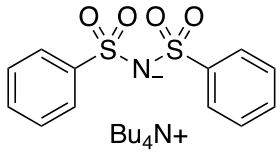
General Procedure B: *n*-Butyllithium (12 mL, 2 M in hexanes, 24 mmol) was added dropwise to a solution of alcohol (20 mmol) in THF (20 mL, 1 M) at 0 °C. The reaction mixture was stirred for 2 hours. The reaction was then quenched by pouring onto ice. The aqueous layer was extracted with ether (3x50 mL). The ether layers were combined and washed with brine, then dried over magnesium sulfate. The products were purified by flash chromatography on silica gel.

General Procedure C: Carboxylic acid (10 mmol), 4-hexen-1-ol (1.1 mL, 10 mmol), DMAP (122 mg, 1 mmol) and DCC (2 g, 10 mmol) were dissolved in anhydrous DCM (25 mL, 0.4 M), and the mixture was stirred at room temperature for 24 h. The suspension was filtered, and the filtrate was concentrated in vacuo. The products were purified by silica gel chromatography.

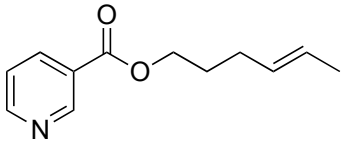


1,3-dimethyl-2-(pentan-3-yl)-1,3,2-diazaphospholidine selenide (4f). To a flame-dried round-bottomed flask under an atmosphere of nitrogen was added ether (200 mL, 0.15 M) followed by phosphorus trichloride (2.6 mL, 30 mmol). This mixture was cooled to -78 °C and *N*,*N*'-dimethylethylenediamine (3.2 mL, 30 mmol) then triethylamine (15 mL, 108 mmol) were added dropwise. The reaction was allowed to warm to room temperature with stirring for 1 hour. The reaction was cooled again to -78 °C and diethylamine (3.1 mL, 30 mmol) was added dropwise. Again, the reaction was allowed to warm to room temperature with stirring overnight. The mixture was filtered over a pad of celite and the filtrate was concentrated in vacuo to give 1,3-dimethyl-2-(pentan-3-yl)-1,3,2-diazaphospholidine as a yellow oil. The crude triaminophosphine was added to a round bottom flask along with selenium powder (2.8 g, 36 mmol) and DCM (60 mL, 0.5 M). This mixture was stirred under nitrogen at room temperature overnight. The mixture was then filtered

through a pad of silica gel with ethyl acetate and the filtrate was concentrated in vacuo to give a beige solid. The solid was recrystallized from ethyl acetate to yield the final product as large colorless crystals. (6.1 g, 76% yield). **MP:** 59.2-60.7 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 3.33 – 3.10 (m, 6H), 3.10 – 2.88 (m, 2H), 2.47 (d, *J* = 12.8 Hz, 6H), 1.06 (t, *J* = 7.0 Hz, 6H). **^{13}C NMR (126 MHz, CDCl3)**: δ 47.70 (d, *J* = 8.8 Hz), 39.64 (d, *J* = 5.0), 32.11 (d, *J* = 7.6 Hz), 14.65 (d, *J* = 1.3 Hz). **^{31}P NMR (121 MHz, $CDCl_3$):** δ 75.49 (J^{Se-P} = 791 Hz). **IR (thin film):** 2966.7, 2927.0, 2868.5, 2807.9, 1460.4, 1375.8, 1233.1, 1205.0, 1171.7, 1022.1, 939.7, 786.5, 736.3, 674.0, 525.8 cm^{-1}. **(ESI, positive mode):** 291.9 [M+Na]. **HRMS** (ESI): Calculated for $C_8H_{21}N_3PSe^+$ $[M+H]^+$: 270.0633, Found: 270.0631.

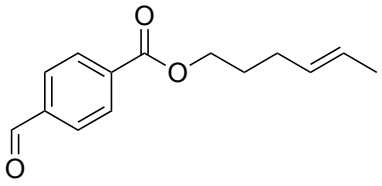


Tetrabutylammonium benzenesulfonimide. To a flame dried 1000 mL RBF was added sodium hydride mineral oil dispersion (8.8 g, 220 mmol) and benzenesulfonamide (15.7 g, 100 mmol). THF (400 mL, 0.25 M) was added and the flask was allowed to stir at room temperature for 3 hours, then benzenesulfonyl chloride (15.3 mL, 120 mmol) was added. The cloudy mixture was allowed to stir overnight. Solvent was removed in vacuo to give a white solid. Saturated sodium bicarbonate was added and the slurry was filtered with a fritted funnel (to remove any unreactive amide). The filtrate was reacidified with 6 M HCl (until pH = 2), and the product was extracted 3x with ether. The combined ether layers were washed with brine, dried over magnesium sulfate, and concentrated in vacuo to give a white solid. A minimal amount of 1 M NaOH solution was added slowly to the solid until the solid was dissolved and the pH reached 7-8. (If necessary, the mixture can be filtered to remove undissolved particles.) Next, tetrabutylammonium chloride (27.8 g, 100 mmol) dissolved in a minimum amount of deionized water was pipetted into the mixture and a white solid started to precipitate. The solid continued to precipitate overnight in the fridge. The solid was collected in a fritted funnel, washed with water and dried on the high vac. The resulting solid was recrystallized twice from a minimum amount of ethyl acetate to give large, almost transparent crystals. The crystals were crushed and dried under vacuum at 40 °C overnight. (36 g, 67% yield). **MP:** 110-113.2 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.71 (d, *J* = 7.6 Hz, 4H), 7.32 – 7.22 (m, 2H), 7.18 (t, *J* = 7.4 Hz, 4H), 3.35 – 3.13 (m, 8H), 1.72 – 1.51 (m, 8H), 1.51 – 1.30 (m, 8H), 0.98 (t, *J* = 7.2 Hz, 12H). **^{13}C NMR (126 MHz, CDCl3):** δ 145.60, 129.94, 127.71, 126.77, 58.63, 23.99, 19.68, 13.75. **IR (thin film):** 2960.8, 2874.4, 1478.6, 1444.6, 1381.1, 1279.8, 1155.0, 1132.9, 1086.9, 1054.5, 1023.7, 882.6, 791.1, 751.7, 719.5, 690.8, 593.1, 572.6, 554.0 cm^{-1}. **(ESI, negative mode):** 295.9 [$^-$N$(SO_2Ph_2)_2$]. **HRMS** (ESI): Calculated for $C_{16}H_{36}N^+$ $[Bu_4N]^+$: 242.2842, Found: 242.2841. Calculated for $C_{12}H_{10}NO_4S_2^-$ $[N(SO_2Ph)_2]^-$: 296.0046, Found: 296.001.

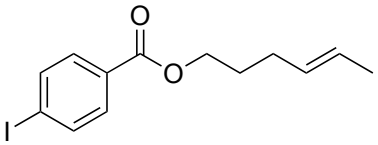


(*E*)-hex-4-enyl nicotinate (1g). Prepared according to General Procedure C and purified by silica gel chromatography (10% ethyl acetate/ 90% hexanes) to yield the product as a clear, yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 9.23 (s, 1H), 8.86 – 8.66 (m, 1H), 8.39 – 8.19 (m, 1H), 7.51 – 7.33 (m,

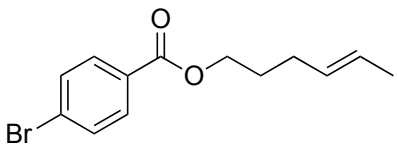
1H), 5.60 – 5.36 (m, 2H), 4.36 (td, *J* = 6.6, 1.5 Hz, 2H), 2.15 (m, 2H), 1.92 – 1.78 (m, 2H), 1.65 (d, *J* = 5.8 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 165.42, 153.47, 151.05, 137.12, 129.87, 126.45, 126.22, 123.37, 65.07, 29.06, 28.56, 18.01. **IR (thin film):** 3021, 2958, 2937, 2918, 2854, 1725, 1591, 1450, 1419, 1388, 1327, 1284, 1237, 1193, 1113, 1025, 967, 741, 703 cm^{-1}. **(ESI, positive mode):** 206.0 [M+1]. **HRMS** (ESI): Calculated for $C_{12}H_{16}NO_2^+$ $[M+H]^+$: 206.1176, Found: 206.1174.



(*E*)-hex-4-enyl 4-formylbenzoate (1i). Prepared according to General Procedure C and purified by silica gel chromatography (5% ethyl acetate/ 95% hexanes) to yield the product as a clear oil. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 10.11 (s, 1H), 8.25 – 8.11 (m, 2H), 8.01 – 7.90 (m, 2H), 5.63 – 5.33 (m, 2H), 4.36 (t, *J* = 6.6 Hz, 2H), 2.15 (dd, *J* = 13.2, 6.8 Hz, 2H), 1.96 – 1.80 (m, 2H), 1.65 (d, *J* = 5.8 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 191.78, 165.72, 139.24, 135.60, 130.29, 129.91, 129.63, 126.21, 65.27, 29.10, 28.58, 18.03. **IR (thin film):** 2958, 2937, 2853, 2733, 1722, 1705, 1699, 1695, 1684, 1386, 1275, 1202, 1117, 1106, 1016, 967, 855, 818, 759, 689 cm^{-1}. **GC-MS (m/z):** 233.1 (1, M+1), 133.0 (671, $C_8H_5O_2^+$), 83.10 (74.04, C_6H11^+), 67.10 (1,250, $C_5H_7^+$). **HRMS** (ESI): Calculated for $C_{14}H_{17}O_3^+$ $[M+H]^+$: 233.1172, Found: 233.1169.

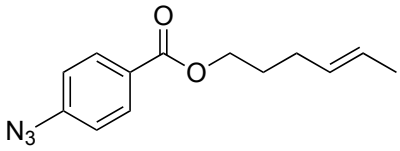


(*E*)-hex-4-enyl 4-iodobenzoate (1k). Prepared according to Genera Procedure C and purified by silica gel chromatography (5% ethyl acetate/ 95% hexanes) to yield the product as a clear oil. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.79 (dd, *J* = 8.4, 1.7 Hz, 2H), 7.74 (dd, *J* = 8.3, 1.6 Hz, 2H), 5.60 – 5.31 (m, 2H), 4.30 (td, *J* = 6.6, 1.2 Hz, 2H), 2.13 (m, 2H), 1.93 – 1.72 (m, 2H), 1.65 (d, *J* = 5.6 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 166.23, 137.81, 131.13, 130.09, 129.98, 126.11, 100.69, 64.88, 29.09, 28.60, 18.03. **IR (thin film):** 3020, 2955, 2935, 2851, 1719, 1587, 1482, 1465, 1456, 1448, 1437, 1393, 1306, 1269, 1176, 1115, 1103, 1083, 1008, 966, 845, 753 cm^{-1}. **(ESI, positive mode):** 353.1 [M+Na]. **HRMS** (ESI): Calculated for $C_{13}H_{16}IO_2^+$ $[M+H]^+$: 331.0189, Found: 331.0188.

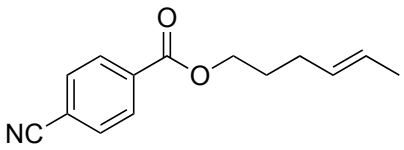


(*E*)-hex-4-enyl 4-bromobenzoate (1l). Prepared according to General Procedure C and purified by silica gel chromatography (5% ethyl acetate/ 95% hexanes) to yield the product as a clear oil. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.90 (dd, *J* = 6.8, 1.8 Hz, 2H), 7.57 (dd, *J* = 8.4, 1.5 Hz, 2H), 5.58 – 5.31 (m, 2H), 4.31 (t, *J* = 6.6 Hz, 2H), 2.13 (m, 2H), 1.88 – 1.74 (m, 2H), 1.65 (d, *J* = 5.5 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 166.02, 131.81, 131.22, 129.99, 129.53, 128.05, 126.13, 64.91, 29.11, 28.61, 18.04. **IR (thin film):** 3020, 2957, 2936, 2853, 1718, 1591, 1398, 1271, 1173, 1116,

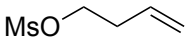
1103, 1069, 1012, 966, 847, 756 cm^{-1}. **(ESI, positive mode):** 305.1 [M+Na]. **HRMS** (ESI): Calculated for $C_{13}H_{16}{}^{79}BrO_2^+$ [M+H]$^+$: 283.0328, Found: 283.0325.



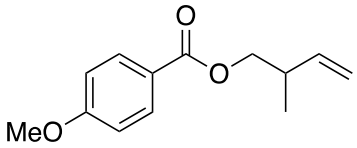
(*E*)-hex-4-enyl 4-azidobenzoate (1m). Prepared according to General Procedure C and purified by silica gel chromatography (5% ethyl acetate/ 95% hexanes) to yield the product as a clear, yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.03 (dd, *J* = 6.8, 1.9 Hz, 2H), 7.11 – 6.93 (m, 2H), 5.58 – 5.35 (m, 2H), 4.31 (t, *J* = 6.6 Hz, 2H), 2.14 (m, 2H), 1.90 – 1.76 (m, 2H), 1.65 (d, *J* = 4.7 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 165.93, 144.76, 131.49, 130.04, 127.19, 126.07, 118.92, 64.71, 29.12, 28.66, 18.03. **IR (thin film):** 3020, 2937, 2853, 2413, 2258, 2123, 1719, 1603, 1504, 1274, 1173, 1131, 1109, 1015, 967, 850, 766, 690 cm^{-1}. **(ESI, positive mode):** 268.0 [M+Na].



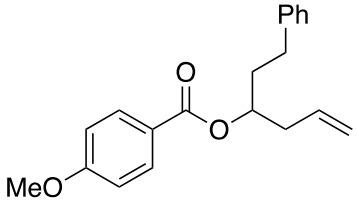
(*E*)-hex-4-enyl 4-cyanobenzoate (1n). Prepared according to General Procedure C and purified by silica gel chromatography (5% ethyl acetate/ 95% hexanes) to yield the product as a clear oil. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.21 – 8.05 (m, 2H), 7.82 – 7.64 (m, 2H), 5.61 – 5.25 (m, 2H), 4.36 (td, *J* = 6.6, 1.2 Hz, 2H), 2.14 (dd, *J* = 13.5, 6.9 Hz, 2H), 1.84 (quin, *J* = 6.6 Hz, 2H), 1.65 (d, *J* = 5.8 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 165.06, 134.40, 132.31, 130.17, 129.80, 126.25, 118.11, 116.42, 65.44, 29.04, 28.51, 18.00. **IR (thin film):** 3098, 3052, 2958, 2937, 2918, 2854, 2231, 1719, 1450, 1405, 1388, 1310, 1275, 1177, 1119, 1108, 1019, 967, 862, 768, 692, 546 cm^{-1}. **(ESI, positive mode):** 252.0 [M+Na]. **HRMS** (ESI): Calculated for $C_{14}H_{16}NO_2^+$ [M+H]$^+$: 230.1176, Found: 230.1172.



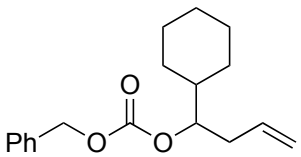
but-3-enyl methanesulfonate (1t). To a flame dried 100 mL round bottom flask was added 3-buten-1-ol (1.72 mL, 20 mmol) and DCM (20 mL, 1 M). The reaction was cooled to 0 ^{oC} and triethylamine (4.18 mL, 30 mmol) then methanesulfonyl chloride (2.32 mL, 30 mmol) were added dropwise. The reaction was stirred at 0 ^{o}C for 1 hour then at room temperature overnight. Saturated ammonium chloride (20 mL) was added and the mixture was extracted with ether (2x50 mL). The combined ether layers were dried over magnesium sulfate and concentrated in vacuo to give a yellow oil. The crude product was purified by silica gel chromatography (5% ethyl acetate/ 95% hexanes) to yield the product as a clear oil. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 5.89 – 5.69 (m, 1H), 5.23 – 5.10 (m, 2H), 4.27 (td, *J* = 6.7, 1.5 Hz, 2H), 3.01 (s, 3H), 2.60 – 2.40 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)**: δ 132.53, 118.59, 68.97, 37.60, 33.52. **IR (thin film):** 3081, 3028, 2984, 2942, 1643, 1353, 1174, 976, 954, 910, 835, 805, 528 cm^{-1}. **(ESI, positive mode):** 172.8 [M+Na]. **HRMS** (ESI): Calculated for $C_5H_{11}O_3S^+$ [M+H]$^+$: 151.0423, Found: 151.0418.



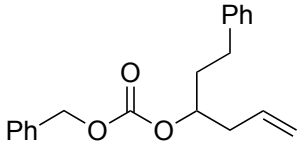
2-methyl-but-3-en-1-yl 4-methoxybenzoate (1ag). Prepared according to General Procedure A and purified by column chromatography (5% EtOAc in hexane) to give the product as a colorless oil (2.3 g, 69%). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.99 (d, *J* = 8.9 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 5.83 (ddd, *J* = 17.3, 10.4, 7.0 Hz, 1H), 5.13 (dd, *J* = 17.3, 1.3 Hz, 1H), 5.07 (dd, *J* = 10.4 Hz, 0.9 Hz, 1H), 4.32 – 4.00 (m, 2H), 3.86 (s, 3H), 2.74 – 2.58 (m, 1H), 1.12 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 166.41, 163.46, 140.30, 131.70, 122.99, 115.11, 113.73, 68.61, 55.55, 37.30, 16.62. **IR (thin film):** 3079, 2966, 2839, 1714, 1607, 1511, 1316, 1276, 1257, 1168, 1114, 1102, 1031, 847, 770, 697, 613 cm^{-1}. **(ESI, positive mode):** 242.9 [M+Na]. **HRMS** (ESI): Calculated for $C_{13}H_{17}O_3^+$ $[M+H]^+$: 221.1172, Found: 221.1169.



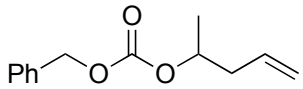
1-phenylhex-5-en-3-yl 4-methoxybenzoate (1ah). Prepared according to General Procedure A and purified by column chromatography (5 % EtOAc, 95% Hexane) to give the product as a colorless oil (2.3 g, 58%). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.00 (d, *J* = 8.8 Hz, 2H), 7.28 – 7.23 (m, 2H), 7.17 (m, 3H), 6.92 (dd, *J* = 8.9, 2.0 Hz, 2H), 5.88 – 5.76 (m, 1H), 5.19 (m, 1H), 5.10 (d, *J* = 17.1 Hz, 1H), 5.06 (d, *J* = 10.2 Hz, 1H), 3.86 (s, 3H), 2.83 – 2.61 (m, 2H), 2.47 (t, *J* = 6.5 Hz, 2H), 2.13 – 1.88 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 166.07, 163.46, 141.75, 133.66, 131.72, 128.55, 128.48, 126.04, 123.16, 118.06, 113.73, 73.26, 55.57, 38.91, 35.60, 31.92. **IR (thin film):** 3078, 3025, 3004, 2952, 2839, 1707, 1606, 1511, 1316, 1274, 1256, 1167, 1114, 1102, 1031, 1009, 919, 848, 770, 698, 613 cm^{-1}. **MS (ESI, positive mode):** 310.9 [M+1], 333.0 [M+Na]. **HRMS** (ESI): Calculated for $C_{20}H_{23}O_3^+$ $[M+H]^+$: 331.1642, Found: 311.1642.



benzyl 1-cyclohexylbut-3-enyl carbonate (6a). Prepared according to general procedure B and purified by silica gel chromatography (5% ethyl acetate/ 95% hexanes) to yield the product as a clear oil. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.42 – 7.28 (m, 5H), 5.87 – 5.68 (m, 1H), 5.16 (d, *J* = 12.2 Hz, 1H), 5.12 (d, *J* = 12.2 Hz, 1H), 5.07 (d, *J* = 17.1 Hz, 1H), 5.03 (d, *J* = 10.2 Hz, 1H), 4.61 (m, 1H), 2.44 – 2.26 (m, 2H), 1.82 – 1.60 (m, 5H), 1.60 – 1.47 (m, 1H), 1.27 – 1.09 (m, 3H), 1.09 – 0.95 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 155.36, 135.69, 133.84, 128.66, 128.49, 128.26, 117.87, 81.90, 69.47, 40.94, 35.96, 28.96, 28.04, 26.40, 26.16, 26.04. **IR (thin film):** 3067, 3034, 2929, 2853, 1741, 1643, 1498, 1451, 1385, 1352, 1332, 1258, 1185, 1099, 1081, 1029, 973, 915, 859, 787, 753, 738, 697 cm^{-1}. **(ESI, positive mode):** 311.0 [M+Na]. **HRMS** (ESI): Calculated for $C_{18}H_{25}O_3^+$ $[M+H]^+$: 289.1798, Found: 289.1796.

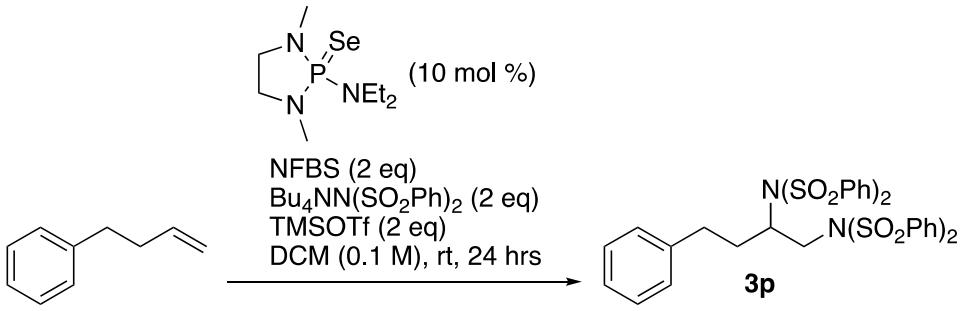


benzyl 1-phenylhex-5-en-3-yl carbonate (6b). Prepared according to General Procedure B and purified by column chromatography (5% EtOAc in hexane) to give the product as a a clear oil (851 mg, 14% yield). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.41 – 7.30 (m, 5H), 7.26 (t, *J* = 8.0 Hz, 2H), 7.21 – 7.09 (m, 3H), 5.84 – 5.67 (m, 1H), 5.16 (s, 2H), 5.12 – 5.00 (m, 2H), 4.86 – 4.68 (m, 1H), 2.75 – 2.66 (m, 1H), 2.66 – 2.56 (m, 1H), 2.40 (t, *J* = 6.4 Hz, 2H), 2.00 – 1.81 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 155.04, 141.43, 135.55, 133.11, 128.72, 128.61, 128.57, 128.48, 128.38, 126.13, 118.41, 77.51, 69.60, 38.76, 35.41, 31.69. **IR (thin film):** 3064, 3028, 2953, 2861, 1740, 1735, 1496, 1454, 1385, 1261, 1029, 994, 916, 859, 789, 750, 698 cm^{-1}. **(ESI, positive mode):** 333.1 [M+Na]. **HRMS** (ESI): Calculated for $C_{20}H_{22}O_3Na^+$ $[M+Na]^+$: 333.1461, Found: 333.1460.



benzyl pent-4-en-2-yl carbonate (6c). Prepared according to General Procedure B and purified by silica gel chromatography (5% ethyl acetate/ 95% hexanes) to yield the product as a clear oil. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.41 – 7.29 (m, 5H), 5.86 – 5.62 (m, 1H), 5.14 (s, 2H), 5.13 – 5.05 (m, 2H), 4.91 – 4.74 (m, 1H), 2.46 – 2.36 (m, 1H), 2.36 – 2.22 (m, 1H), 1.28 (d, *J* = 6.3 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 154.83, 135.54, 133.34, 128.70, 128.58, 128.41, 118.25, 74.69, 69.49, 40.35, 19.55. **IR (thin film):** 3068, 3034, 2980, 2935, 1743, 1456, 1382, 1350, 1262, 1128, 1051, 994, 913, 791, 753, 697 cm^{-1}. **(ESI, positive mode):** 242.9 [M+Na]. **HRMS** (ESI): Calculated for $C_{13}H_{17}O_3^+$ $[M+H]^+$: 221.1172, Found: 221.1169.

IV. Control Experiments



Deviation from above conditions	% Yield of **3p**
None	56%
Omit Catalyst	Not Observed
Omit NFBS	Not Observed
Omit $Bu_4NN(SO_2Ph)_2$	Not Observed
Omit TMSOTf	Not Observed
Se grey (10 mol %) as catalyst	Not Observed

V. General Procedure and Characterization of Products

a. Standard Conditions A

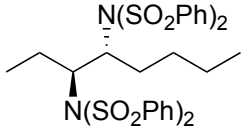
A flame-dried 1-dram vial was allowed to cool under positive pressure of nitrogen. To the vial was added phosphine selenide catalyst (5.4 mg, 0.02 mmol) and tetrabutylammonium benzenesulfonimide (215.5 mg, 0.4 mmol). Next, DCM (2 mL, 0.1 M), alkene (0.2 mmol), TMSOTf (72.4 uL, 0.4 mmol) and NFBS (126.1 mg, 0.4 mmol) were added in that order. The vial was flushed with nitrogen, capped with a Teflon-lined cap and allowed to stir at room temperature for 24 hours. After 24 hours, dimethyl sulfide (60 uL) and water (0.5 mL) were added and the vial was capped and shaken. The mixture was diluted with DCM (2 mL) followed by ether (30 mL). The organic layer was washed 1 M citric acid (30 mL), saturated sodium bicarbonate (30 mL) and brine (30 mL), dried over magnesium sulfate, filtered and concentrated in vacuo.

b. Standard Conditions B

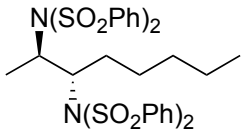
A flame-dried 1-dram vial was allowed to cool under positive pressure of nitrogen. To the vial was added phosphine selenide catalyst (5.4 mg, 0.02 mmol) and tetrabutylammonium benzenesulfonimide (107.8 mg, 0.2 mmol). Next, DCM (2 mL, 0.1 M), alkene (0.2 mmol), TMSOTf (72.4 uL, 0.4 mmol) and NFBS (94.6 mg, 0.3 mmol) were added in that order. The vial was flushed with nitrogen, capped with a Teflon-lined cap and allowed to stir at room temperature for 24 hours. After 24 hours, dimethyl sulfide (60 uL) and water (0.5 mL) were added and the vial was capped and

shaken. The mixture was diluted with DCM (2 mL) followed by ether (30 mL). The organic layer was washed 1 M citric acid (30 mL), saturated sodium bicarbonate (30 mL) and brine (30 mL), dried over magnesium sulfate, filtered and concentrated in vacuo.

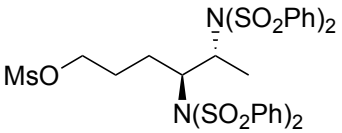
c. Characterization of Products



***N,N'*-(octane-3,4-diyl)bis(benzenesulfonimide) (3a).** Prepared according to Standard Conditions A and purified by silica gel chromatography (20% ethyl acetate/ 80% hexanes) to yield the product as an off-white solid (122.5 mg, 88% yield). **Mp:** 174.1-177.6 °C. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.24 – 7.92 (m, 8H), 7.67 – 7.59 (m, 4H), 7.59 – 7.46 (m, 8H), 5.14 – 4.59 (m, 2H), 1.74 – 1.61 (m, 1H), 1.57 – 1.46 (m, 1H), 1.46 – 1.34 (m, 1H), 1.34 – 1.23 (m, 1H), 0.66 – 0.45 (m, 4H), 0.42 (t, *J* = 7.0 Hz, 3H), 0.35 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 141.27, 141.09, 139.18, 139.13, 134.27, 133.98, 129.74, 129.68, 129.29, 129.17, 128.91, 128.85, 128.83, 67.86, 67.36, 30.86, 28.40, 23.68, 22.38, 13.81, 10.85. **IR (thin film):** 3103, 3067, 2958, 2931, 2872, 1584, 1448, 1366, 1170, 1082, 993, 910, 845, 753, 730, 719, 686, 654, 592, 583, 555 cm^{-1}. **MS (ESI, positive mode):** 727.1 [M+Na]. **HRMS** (ESI): Calculated for $C_{32}H_{36}N_2O_8S_4Na^+$ $[M+Na]^+$: 727.1247, Found: 727.1253.

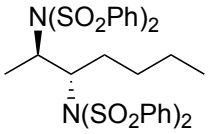


***N,N'*-(octane-2,3-diyl)bis(benzenesulfonimide) (3b).** Prepared according to Standard Conditions A and purified by silica gel chromatography (15% ethyl acetate/ 85% hexanes) to yield the product as a tan solid (114.7 mg, 83% yield). **Mp:** 176.8-177.9 °C. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.19 (d, *J* = 8.8 Hz, 2H), 8.17 (d, *J* = 8.1 Hz, 2H), 8.08 (d, *J* = 7.5 Hz, 2H), 8.00 (d, *J* = 7.4 Hz, 2H), 7.69 – 7.47 (m, 12H), 5.11 (td, *J* = 11.2, 3.4 Hz, 1H), 4.90 (dq, *J* = 10.3, 7.0 Hz, 1H), 1.77 – 1.55 (m, 2H), 1.09 – 0.83 (m, 4H), 0.83 – 0.69 (m, 8H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 141.46, 141.08, 139.05, 138.52, 134.28, 133.99, 133.94, 129.77, 129.31, 129.23, 129.00, 128.92, 128.88, 128.82, 128.67, 65.60, 62.68, 31.68, 30.25, 26.23, 22.52, 16.94, 14.16. **IR (thin film):** 3164, 3101, 3067, 2955, 2929, 2871, 1583, 1448, 1367, 1170, 1083, 911, 861, 753, 732, 721, 686, 652, 586, 555 cm^{-1}. **MS (ESI, positive mode):** 727.1 [M+Na]. **HRMS** (ESI): Calculated for $C_{32}H_{36}N_2O_8S_4Na^+$ $[M+Na]^+$: 727.1247, Found: 727.1255.



4,5-bis(benzenesulfonimido)hexyl methanesulfonate (3c). Prepared according to Standard Conditions A and purified by silica gel chromatography (20% ethyl acetate/ 80% hexanes) to yield the product as an off-white solid (142.7 mg, 88% yield). **Mp:** 145-147 °C. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.16 (d, *J* = 7.7 Hz, 4H), 8.03 (d, *J* = 8.2 Hz, 2H), 7.93 (d, *J* = 8.2 Hz, 2H), 7.74 – 7.57

(m, 8H), 7.53 (t, J = 7.7 Hz, 4H), 5.13 (td, J = 10.4, 3.8 Hz, 1H), 4.97 – 4.87 (m, 1H), 3.86 (t, J = 5.8 Hz, 2H), 2.89 (s, 3H), 1.94 – 1.72 (m, 2H), 1.61 – 1.42 (m, 1H), 1.38 – 1.16 (m, 1H), 0.73 (d, J = 6.9 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 141.16, 140.75, 138.60, 138.05, 134.57, 134.39, 134.22, 129.70, 129.44, 129.21, 129.19, 129.14, 129.03, 128.84, 128.62, 69.49, 64.72, 62.18, 37.45, 26.47, 26.28, 16.54. **IR (thin film):** 3069, 2926, 2854, 1583, 1449, 1367, 1169, 1083, 961, 912, 860, 732, 722, 686, 651, 587, 555 cm^{-1}. **MS (ESI, positive mode):** 788.0 [M+NH_4], 793.0 [M+Na]. **HRMS** (ESI): Calculated for $C_{31}H_{34}N_2O_{11}S_5Na^+$ [M+Na]$^+$: 793.0658, Found: 793.0665.



***N*,*N*'-(heptane-2,3-diyl)bis(benzenesulfonimide) (3d).** Prepared according to Standard Conditions A and purified by silica gel chromatography (20% ethyl acetate/ 80% hexanes) to yield the product as a white solid (110.3 mg, 88% yield). **Mp:** 190.2-199.1 °C. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.18 (m, 4H), 8.08 (dd, J = 8.4, 1.0 Hz, 2H), 8.00 (dd, J = 8.4, 1.0 Hz, 2H), 7.70 – 7.45 (m, 12H), 5.11 (td, J = 11.1, 3.5 Hz, 1H), 4.90 (dq, J = 10.3, 7.0 Hz, 1H), 1.80 – 1.49 (m, 2H), 1.06 – 0.77 (m, 4H), 0.75 (d, J = 7.0 Hz, 3H), 0.61 (t, J = 7.2 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 141.46, 141.06, 139.05, 138.52, 134.29, 134.01, 133.95, 129.78, 129.32, 129.24, 129.01, 128.92, 128.89, 128.81, 128.67, 65.57, 62.69, 29.97, 28.59, 22.53, 16.91, 13.97. **IR (thin film):** 3067, 3029, 2956, 2871, 1583, 1448, 1367, 1170, 1083, 1045, 859, 753, 731, 720, 686, 652, 585, 554 cm^{-1}. **MS (ESI, positive mode):** 713.1 [M+Na]. **HRMS** (ESI): Calculated for $C_{31}H_{34}N_2O_8S_4Na^+$ [M+Na]$^+$: 713.1090, Found: 713.1096.

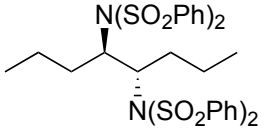
In order to determine the relative stereochemistry of the products derived from internal olefins, the above product (**3d**) was compared to the analogous diaddition products, **8d** (trans) and **8k'** (cis), from Muniz's paper.[13] These products contain p-toluenesulfonimide groups instead of benzenesulfonimide groups, but are in all other ways identical to **3d**. The alkene resonances of **3d** for both ^{1}H and ^{13}C NMR are consistent with a trans-1,2-diamination product.

3d: **^{1}H NMR (500 MHz, $CDCl_3$):** δ 5.11 (td, J = 11.1, 3.5 Hz, 1H), 4.90 (dq, J = 10.3, 7.0 Hz, 1H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 65.57, 62.69.

8d: **^{1}H NMR (500 MHz, $CDCl_3$):** δ 5.0 – 5.1 (m, 1H), 4.85 (dq, J = 10.3, 7.0 Hz, 1H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 65.4, 62.5.

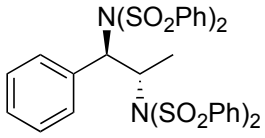
8k': **^{1}H NMR (500 MHz, $CDCl_3$):** δ 5.2 – 5.3 (m, 2H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 69.5, 64.8.

The stereochemistry for all other products derived from trans-1,2-olefins was assigned on the same basis.

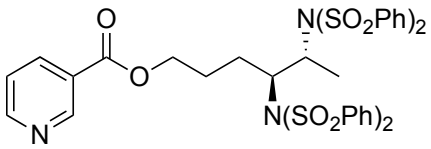


***N*,*N*'-(octane-4,5-diyl)bis(benzenesulfonimide) (3e).** Prepared according to Standard Conditions A and purified by silica gel chromatography (20% ethyl acetate/ 70% hexanes) to yield the product as a tan solid (100.8 mg, 74% yield). **Mp:** 204.5-206.4 °C. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.15 (d, J = 7.5 Hz, 2H), 8.13 (d, J = 8.3 Hz, 2H), 7.68 – 7.61 (m, 4H), 7.55 (t, J = 7.7 Hz, 8H), 5.03 – 4.93 (m, 2H), 1.46 – 1.31 (m, 2H), 1.29 – 1.16 (m, 2H), 0.82 – 0.57 (m, 4H), 0.29 (t, J = 7.3 Hz, 6H). **^{13}C**

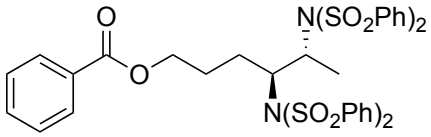
NMR (126 MHz, $CDCl_3$): δ 141.18, 139.16, 134.28, 133.97, 129.72, 129.14, 128.94, 128.80, 66.93, 32.78, 19.60, 13.65. **IR (thin film):** 2963, 2872, 1449, 1366, 1169, 1082, 1058, 1020, 972, 913, 884, 843, 730, 719, 685, 667, 653, 594, 572, 553 cm^{-1}. **MS (ESI, positive mode):** 727.1 [M+Na]. **HRMS** (ESI): Calculated for $C_{32}H_{36}N_2O_8S_4Na^+$ $[M+Na]^+$: 727.1247, Found: 727.1254.



***N*,*N*'-(1-phenylpropane-1,2-diyl)bis(benzenesulfonimide) (3f).** Prepared according to Standard Conditions A and purified by silica gel chromatography (20% ethyl acetate/ 80% hexanes) to yield the product as an off-white solid (114.8 mg, 85% yield). **Mp:** 173.5-181.5 °C. **^{1}H NMR (500 MHz, Acetone):** δ 8.23 – 8.17 (m, 2H), 8.05 – 8.02 (m, 2H), 7.85 – 7.76 (m, 4H), 7.74 – 7.66 (m, 4H), 7.60 – 7.50 (m, 4H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.38 – 7.28 (m, 6H), 7.22 – 7.16 (m, 2H), 6.48 (d, *J* = 10.9 Hz, 1H), 6.00 (dq, *J* = 11.0, 6.9 Hz, 1H), 0.86 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR (126 MHz, Acetone):** δ 206.11, 142.29, 142.27, 139.96, 139.66, 135.77, 135.61, 135.26, 134.56, 134.38, 132.04, 130.39, 130.32, 130.15, 130.04, 129.74, 129.62, 129.21, 128.72, 128.34, 66.61, 60.35, 29.99, 29.84, 29.69, 17.63. **IR (thin film):** 2918, 2849, 1448, 1371, 1352, 1168, 1082, 846, 752, 733, 721, 684, 578, 554 cm^{-1}. **MS (ESI, positive mode):** 733.0 [M+Na]. **HRMS** (ESI): Calculated for $C_{33}H_{30}N_2O_8S_4Na^+$ $[M+Na]^+$: 733.0777, Found: 733.0776.

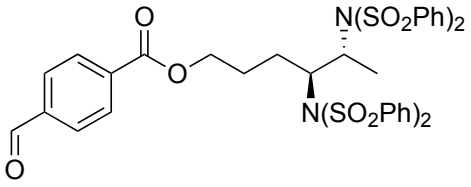


4,5-bis(benzenesulfonimido)hexyl nicotinate (3g). Prepared according to Standard Conditions A and purified by silica gel chromatography (30% ethyl acetate/ 70% hexanes) to yield the product as an off-white solid (63.1 mg, 40% yield). **Mp:** 191.2-196.1 °C. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 9.15 (s, 1H), 8.79 (s, 1H), 8.24 – 8.12 (m, 4H), 8.05 (d, *J* = 8.1 Hz, 2H), 7.99 (d, *J* = 7.5 Hz, 2H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.64 – 7.42 (m, 12H), 7.40 – 7.32 (m, 1H), 5.16 (t, *J* = 10.9 Hz, 1H), 5.06 – 4.79 (m, 1H), 4.13 – 3.92 (m, 1H), 3.92 – 3.71 (m, 1H), 2.01 – 1.88 (m, 1H), 1.88 – 1.75 (m, 1H), 1.61 – 1.45 (m, 1H), 1.33 – 1.14 (m, 1H), 0.82 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 165.06, 153.44, 150.97, 141.32, 141.00, 138.74, 138.37, 137.26, 134.47, 134.36, 134.28, 133.99, 129.71, 129.28, 129.15, 129.02, 128.91, 128.65, 123.51, 65.18, 64.56, 62.37, 26.78, 25.75, 16.95. **IR (thin film):** 3067, 2953, 2894, 1723, 1591, 1448, 1367, 1285, 1169, 1083, 912, 859, 730, 721, 686, 651, 586, 554 cm^{-1}. **MS (ESI, positive mode):** 798.2 [M+H], 800.1 [M+NH_4]. **HRMS** (ESI): Calculated for $C_{36}H_{36}N_3O_{10}S_4^+$ $[M+H]^+$: 798.1278, Found: 798.1282.

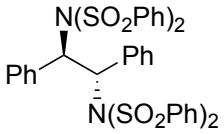


4,5-bis(benzenesulfonimido)hexyl benzoate (3h). Prepared according to Standard Conditions A and purified by silica gel chromatography (20% ethyl acetate/ 80% hexanes) to yield the product as a tan solid (142.7 mg, 90% yield). **Mp:** 188.5-191.2 °C. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.21 – 8.15

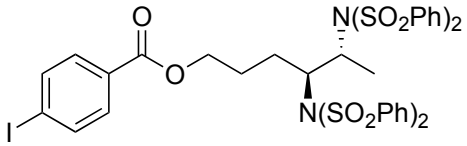
(m, 4H), 8.09 – 8.05 (m, 2H), 8.01 (dd, *J* = 8.4, 1.1 Hz, 2H), 7.95 – 7.91 (m, 2H), 7.68 – 7.37 (m, 15H), 5.17 (td, *J* = 11.7, 3.1 Hz, 1H), 4.95 (dq, *J* = 10.4, 7.0 Hz, 1H), 4.02 – 3.88 (m, 1H), 3.83 – 3.66 (m, 1H), 2.00 – 1.88 (m, 1H), 1.85 – 1.73 (m, 1H), 1.58 – 1.45 (m, 1H), 1.32 – 1.16 (m, 1H), 0.84 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 166.42, 141.36, 140.95, 138.72, 138.33, 134.45, 134.35, 134.24, 133.94, 133.00, 130.28, 129.72, 129.70, 129.27, 129.12, 129.02, 128.99, 128.98, 128.91, 128.54, 128.49, 65.24, 64.15, 62.42, 26.91, 25.88, 16.95. **IR (thin film):** 3165, 3067, 2954, 2892, 1718, 1449, 1367, 1276, 1170, 1083, 912, 860, 753, 731, 721, 686, 651, 586, 554 cm^{-1}. **MS (ESI, positive mode):** 814.2 [M+NH_4], 819.3 [M+Na]. **HRMS** (ESI): Calculated for $C_{37}H_{36}N_2O_{10}S_4Na^+$ [M+Na]$^+$: 819.1145, Found: 819.1150.



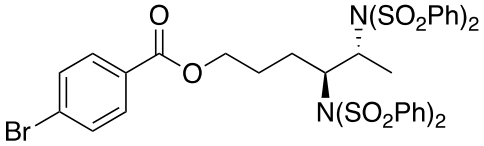
4,5-bis(benzenesulfonimido)hexyl 4-formylbenzoate (3i). Prepared according to Standard Conditions A and purified by silica gel chromatography (30% ethyl acetate/ 70% hexanes) to yield the product as an off-white solid (159.1 mg, 96% yield). **Mp:** 206-201.2 °C. **^{1}H NMR (500 MHz, CD_2Cl_2):** δ 10.10 (s, 1H), 8.16 (d, *J* = 8.2 Hz, 2H), 8.13 (d, *J* = 8.2 Hz, 2H), 8.10 (d, *J* = 8.0 Hz, 2H), 8.04 (d, *J* = 8.1 Hz, 2H), 7.93 (d, *J* = 9.2 Hz, 2H), 7.92 (d, *J* = 8.7 Hz, 2H), 7.74 – 7.50 (m, 10H), 7.47 (t, *J* = 7.6 Hz, 2H), 5.17 (t, *J* = 10.9 Hz, 1H), 5.04 – 4.86 (m, 1H), 4.11 – 3.97 (m, 1H), 3.87 – 3.76 (m, 1H), 2.03 – 1.91 (m, 1H), 1.86 – 1.73 (m, 1H), 1.63 – 1.48 (m, 1H), 1.34 – 1.17 (m, 1H), 0.84 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 191.83, 165.42, 141.34, 141.00, 139.22, 138.72, 138.33, 135.24, 134.49, 134.37, 134.28, 133.92, 130.36, 129.71, 129.65, 129.29, 129.15, 129.01, 128.90, 128.66, 65.20, 64.68, 62.42, 26.83, 25.78, 16.87. **IR (thin film):** 3067, 2951, 2853, 2738, 1722, 1705, 1610, 1577, 1449, 1367, 1313, 1277, 1202, 1170, 1118, 1083, 1044, 955, 858, 755, 730, 721, 686, 651, 586, 554 cm^{-1}. **MS (ESI, positive mode):** 847.0 [M+Na]. **HRMS** (ESI): Calculated for $C_{38}H_{37}N_2O_{11}S_4^+$ [M+H]$^+$: 825.1275, Found: 825.1281.



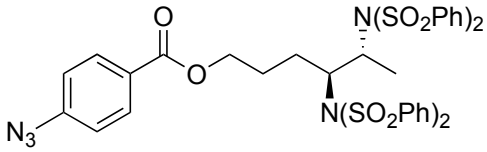
***N*,*N*'-(1,2-diphenylethane-1,2-diyl)bis(benzenesulfonimide) (3j).** Prepared according to Standard Conditions A and purified by silica gel chromatography (20% ethyl acetate/ 80% hexanes) to yield the product as a yellow solid (116 mg, 75% yield). **Mp:** 159.5-161.8 °C. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.77 (s, 4H), 7.49 (d, *J* = 7.5 Hz, 4H), 7.40 – 7.30 (m, 4H), 7.21 (s, 2H), 7.14 – 7.06 (m, 14H), 7.01 (t, *J* = 7.4 Hz, 4H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 141.30, 138.69, 135.06, 133.36, 133.07, 128.92, 128.54, 128.51, 128.43, 128.10, 66.60. **IR (thin film):** 3100, 3065, 3034, 1584, 1500, 1448, 1370, 1337, 1166, 1081, 985, 910, 843, 751, 734, 721, 703, 684, 605, 582, 552 cm^{-1}. **MS (ESI, positive mode):** 795.1 [M+Na]. **HRMS** (ESI): Calculated for $C_{38}H_{32}N_2O_8S_4Na^+$ [M+Na]$^+$: 795.0934, Found: 795.0939.



4,5-bis(benzenesulfonimido)hexyl 4-iodobenzoate (3k). Prepared according to Standard Conditions A and purified by silica gel chromatography (100% DCM) to yield the product as a white solid (182.2 mg, 93% yield). **Mp:** 219.5-226.3 °C. **^{1}H NMR (500 MHz, CD_2Cl_2):** δ 8.14 (d, *J* = 8.1 Hz, 2H), 8.11 (d, *J* = 8.2 Hz, 2H), 8.08 (d, *J* = 8.3 Hz, 2H), 7.97 (d, *J* = 8.1 Hz, 2H), 7.86 (d, *J* = 8.3 Hz, 2H), 7.78 – 7.56 (m, 12H), 7.53 (t, *J* = 7.8 Hz, 2H), 5.19 (t, *J* = 11.0 Hz, 1H), 4.99 (m, 1H), 4.10 – 3.95 (m, 1H), 3.87 – 3.71 (m, 1H), 2.06 – 1.88 (m, 1H), 1.88 – 1.69 (m, 1H), 1.68 – 1.43 (m, 1H), 1.40 – 1.18 (m, 1H), 0.88 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (126 MHz, CD_2Cl_2):** δ 166.19, 141.68, 141.38, 139.18, 138.70, 138.35, 135.06, 134.97, 134.83, 134.53, 131.58, 130.45, 130.06, 129.81, 129.52, 129.27, 129.07, 101.05, 65.79, 64.76, 62.76, 27.25, 26.31, 17.23. **IR (thin film):** 3066, 2955, 1719, 1586, 1448, 1367,1280, 1270, 1169, 1083, 860, 753, 685, 585, 554 cm^{-1}. **MS (ESI, positive mode):** 944.9 [M+Na]. **HRMS** (ESI): Calculated for $C_{37}H_{35}IN_2O_{10}S_4Na^+$ [M+Na]$^+$: 945.0111, Found: 945.0121.

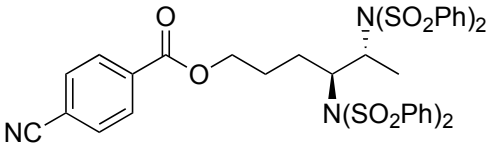


4,5-bis(benzenesulfonimido)hexyl 4-bromobenzoate (3l). Prepared according to Standard Conditions A and purified by silica gel chromatography (100% DCM) to yield the product as a white solid (145.5 mg, 83% yield). **Mp:** 212.9-217.6 °C. **^{1}H NMR (500 MHz, CD_2Cl_2):** δ 8.18 – 8.07 (m, 4H), 8.02 (d, *J* = 7.2 Hz, 2H), 7.91 (d, *J* = 7.5 Hz, 2H), 7.80 (d, *J* = 8.6 Hz, 2H), 7.72 – 7.50 (m, 12H), 7.47 (t, *J* = 7.9 Hz, 2H), 5.18 – 5.07 (m, 1H), 5.00 – 4.85 (m, 1H), 3.98 (dt, *J* = 10.9, 5.5 Hz, 1H), 3.75 (ddd, *J* = 10.9, 8.4, 5.4 Hz, 1H), 1.98 – 1.87 (m, 1H), 1.81 – 1.68 (m, 1H), 1.59 – 1.43 (m, 1H), 1.32 – 1.08 (m, 1H), 0.82 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (126 MHz, CD_2Cl_2):** δ 165.95, 141.68, 141.38, 139.18, 138.70, 135.06, 134.97, 134.83, 134.53, 132.30, 131.70, 130.06, 129.90, 129.81, 129.53, 129.26, 129.08, 128.39, 65.80, 64.78, 62.76, 27.25, 26.31, 17.23. **IR (thin film):** 3068, 2956, 1716, 1590, 1449, 1367, 1273, 1169, 1083, 860, 754, 721, 685, 586, 555 cm^{-1}. **MS (ESI, positive mode):** 897.0 [M+Na]. **HRMS** (ESI): Calculated for $C_{37}H_{35}{}^{79}BrN_2O_{10}S_4Na$ [M+Na]$^+$: 897.0250, Found: 897.0257.



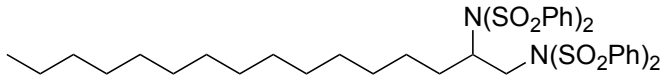
4,5-bis(benzenesulfonimido)hexyl 4-azidobenzoate (3m). Prepared according to Standard Conditions A and purified by silica gel chromatography (30% ethyl acetate/ 70% hexanes) to yield the product as a yellow solid (143 mg, 84% yield). **Mp:** 191.8-194 °C. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.19 (d, *J* = 6.5 Hz, 2H), 8.17 (d, *J* = 7.1 Hz, 2H), 8.06 (d, *J* = 7.6 Hz, 2H), 8.00 (d, *J* = 7.6 Hz, 2H), 7.92 (d, *J* = 8.5 Hz, 2H), 7.70 – 7.39 (m, 12H), 7.03 (d, *J* = 8.5 Hz, 2H), 5.16 (t, *J* = 10.9 Hz, 1H), 5.01 – 4.83 (m, 1H), 4.03 – 3.88 (m, 1H), 3.84 – 3.62 (m, 1H), 1.97 (t, *J* = 13.6 Hz, 1H), 1.88 – 1.70 (m, 1H), 1.62 – 1.38 (m, 1H), 1.35 – 1.14 (m, 1H), 0.83 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 165.59, 144.79, 141.37, 140.97, 138.72, 138.32, 134.45, 134.35, 134.24, 133.91,

131.56, 129.69, 129.27, 129.12, 128.99, 128.90, 128.60, 126.82, 118.96, 65.25, 64.17, 62.40, 26.87, 25.83, 16.90. **IR (thin film):** 3067, 2953, 2124, 1715, 1603, 1448, 1382, 1367, 1275, 1169, 1083, 858, 731, 721, 686, 586, 555 cm^{-1}. **MS (ESI, positive mode):** 838.0 [M+H]. **HRMS** (ESI): Calculated for $C_{37}H_{36}N_5O_{10}S$ $[M+H]^+$: 838.1340, Found: 838.1348.



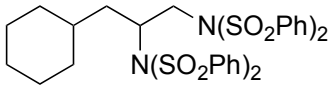
4,5-bis(benzenesulfonimido)hexyl 4-cyanobenzoate (3n). Prepared according to Standard Conditions A and purified by silica gel chromatography (30% ethyl acetate/ 70% hexanes) to yield the product as an off-white solid (141.7 mg, 87% yield). **Mp:** 219.6-223.5 °C. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.28 – 8.10 (m, 4H), 8.10 – 7.90 (m, 6H), 7.79 – 7.38 (m, 14H), 5.23 – 5.09 (m, 1H), 4.94 (dq, *J* = 10.3, 7.0 Hz, 1H), 4.10 (dt, *J* = 10.7, 5.4 Hz, 1H), 3.85 – 3.72 (m, 1H), 2.20 – 2.01 (m, 1H), 1.95 – 1.78 (m, 1H), 1.69 – 1.49 (m, 1H), 1.37 – 1.11 (m, 1H), 0.79 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 164.84, 141.33, 141.04, 138.73, 138.30, 134.51, 134.40, 134.31, 134.10, 133.90, 132.36, 130.28, 129.73, 129.32, 129.17, 129.06, 129.03, 129.01, 128.88, 128.73, 118.16, 116.40, 65.17, 64.81, 62.47, 26.80, 25.79, 16.78. **IR (thin film):** 3067, 2957, 2230, 1724, 1449, 1367, 1277, 1169, 1083, 860, 686, 586, 555 cm^{-1}. **MS (ESI, positive mode):** 844.0 [M+Na]. **HRMS** (ESI): Calculated for $C_{38}H_{35}N_3O_{10}S_4Na^+$ $[M+Na]^+$: 844.1097, Found: 844.1102.

***N*,*N*'-(4-phenylbutane-1,2-diyl)bis(benzenesulfonimide) (3p).** Prepared according to Standard Conditions A and purified by silica gel chromatography (20% ethyl acetate/ 80% hexanes) to yield the product as an off-white solid (79.8 mg, 56% yield). **Mp:** 189.5-199.2 °C. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.18 (dd, *J* = 11.8, 7.9 Hz, 4H), 8.05 (d, *J* = 7.7 Hz, 4H), 7.69 – 7.46 (m, 12H), 7.14 (t, *J* = 7.3 Hz, 3H), 6.60 (d, *J* = 6.5 Hz, 2H), 4.99 – 4.85 (m, 1H), 4.77 (dd, *J* = 14.4, 11.5 Hz, 1H), 3.74 (dd, *J* = 14.5, 3.8 Hz, 1H), 2.18 – 1.98 (m, 2H), 1.95 – 1.84 (m, 1H), 1.78 (dt, *J* = 19.0, 4.8 Hz, 1H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 141.09, 140.55, 139.72, 139.35, 134.30, 134.27, 134.10, 129.34, 129.30, 129.19, 129.05, 128.97, 128.63, 128.26, 128.18, 126.02, 62.15, 51.47, 32.41, 30.27. **IR (thin film):** 3065, 3028, 2942, 1448, 1379, 1358, 1170, 1084, 911, 895, 860, 795, 753, 735, 720, 686, 651, 281, 554 cm^{-1}. **MS (ESI, positive mode):** 747.2 [M+Na]. **HRMS** (ESI): Calculated for $C_{34}H_{32}N_2O_8S_4Na^+$ $[M+Na]^+$: 747.0934, Found: 747.0939.

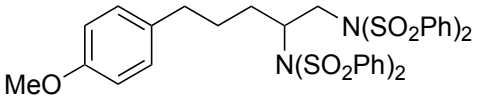


***N*,*N*'-(hexadecane-1,2-diyl)bis(benzenesulfonimide) (3q).** Prepared according to Standard Conditions A and purified by silica gel chromatography (20% ethyl acetate/ 80% hexanes) to yield the product as a tan oil (82.4 mg, 51% yield). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.16 (d, *J* = 7.4 Hz, 4H), 8.06 (d, *J* = 7.4 Hz, 4H), 7.68 – 7.59 (m, 4H), 7.54 (td, *J* = 7.9, 5.0 Hz, 8H), 4.78 (tt, *J* = 11.3, 3.3 Hz, 1H), 4.70 (dd, *J* = 14.0, 11.5 Hz, 1H), 3.71 (dd, *J* = 14.1, 3.5 Hz, 1H), 1.85 – 1.69 (m, 1H), 1.47 – 1.36 (m, 1H), 1.36 – 1.19 (m, 15H), 1.19 – 1.11 (m, 2H), 1.08 – 0.97 (m, 2H), 0.89 (t, *J* = 6.9

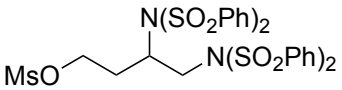
Hz, 3H), 0.85 – 0.73 (m, 2H), 0.73 – 0.57 (m, 2H), 0.57 – 0.42 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 140.95, 139.98, 139.48, 134.21, 134.09, 133.98, 129.30, 129.19, 128.96, 128.94, 128.88, 128.58, 127.92, 62.11, 51.64, 32.05, 29.84, 29.83, 29.80, 29.78, 29.69, 29.57, 29.50, 29.45, 29.17, 28.67, 26.36, 22.82, 14.25. **IR (thin film):** 3067, 2924, 2856, 1448, 1379, 1359, 1170, 1084, 753, 731, 720, 686, 585, 555 cm^{-1}. **MS (ESI, positive mode):** 834.4 $[M+NH_4]$, 839.3 [M+Na]. **HRMS** (ESI): Calculated for $C_{40}H_{52}N_2O_8S_4Na^+$ $[M+Na]^+$: 839.2499, Found: 839.2505.



***N*,*N*'-(3-cyclohexylpropane-1,2-diyl)bis(benzenesulfonimide) (3r).** Prepared according to Standard Conditions A and purified by silica gel chromatography (20% ethyl acetate/ 80% hexanes) to yield the product as white solid (79.4 mg, 54% yield). **Mp:** 210.8-213.8 °C. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.20 (d, *J* = 7.4 Hz, 2H), 8.19 (d, *J* = 7.4 Hz, 2H), 8.03 (d, *J* = 7.5 Hz, 4H), 7.72 – 7.60 (m, 4H), 7.60 – 7.47 (m, 8H), 4.99 – 4.84 (m, 1H), 4.64 (dd, *J* = 14.7, 11.1 Hz, 1H), 3.77 (dd, *J* = 14.7, 3.6 Hz, 1H), 1.75 (t, *J* = 12.8 Hz, 1H), 1.55 (d, *J* = 12.0 Hz, 1H), 1.49 – 1.36 (m, 3H), 1.36 – 1.19 (m, 1H), 0.97 – 0.78 (m, 3H), 0.78 – 0.58 (m, 2H), 0.58 – 0.44 (m, 1H), 0.16 (dd, *J* = 21.0, 10.0 Hz, 1H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 141.17, 140.37, 139.43, 134.22, 134.02, 133.96, 129.28, 129.19, 129.01, 128.98, 128.91, 128.72, 59.63, 52.09, 35.84, 33.66, 33.51, 31.73, 26.36, 26.22, 25.78. **IR (thin film):** 3067, 2924, 2851, 1448, 1378, 1170, 1084, 911, 883, 867, 825, 796, 753, 732, 720, 686, 652, 586, 553 cm^{-1}. **MS (ESI, positive mode):** 739.3 [M+Na]. **HRMS** (ESI): Calculated for $C_{33}H_{36}N_2O_8S_4Na^+$ $[M+Na]^+$: 739.1247, Found: 739.1251.

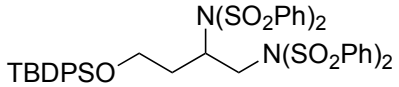


***N*,*N*'-(5-(4-methoxyphenyl)pentane-1,2-diyl)bis(benzenesulfonimide) (3s).** Prepared according to Standard Conditions A and purified by silica gel chromatography (20% ethyl acetate/ 80% hexanes) to yield the product as a yellow resin (75.8 mg, 48% yield). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.15 (d, *J* = 7.4 Hz, 2H), 8.14 (d, *J* = 6.2 Hz, 2H), 8.04 (d, *J* = 7.4 Hz, 4H), 7.67 – 7.46 (m, 12H), 6.75 (d, *J* = 2.2 Hz, 4H), 4.79 (tt, *J* = 11.2, 3.3 Hz, 1H), 4.71 (dd, *J* = 14.0, 11.4 Hz, 1H), 3.78 (s, 3H), 3.72 (dd, *J* = 14.0, 3.5 Hz, 1H), 2.10 – 2.00 (m, 1H), 1.98 – 1.85 (m, 2H), 1.59 – 1.48 (m, 1H), 1.01 – 0.88 (m, 1H), 0.88 – 0.73 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 157.81, 140.95, 139.85, 139.42, 134.25, 134.15, 134.08, 133.86, 129.32, 129.21, 129.05, 128.98, 128.85, 128.55, 113.73, 61.79, 55.40, 51.60, 34.52, 28.60, 28.55. **IR (thin film):** 3067, 3006, 2935, 2860, 1512, 1448, 1378, 1358, 1246, 1170, 1084, 908, 753, 731, 720, 686, 585, 554 cm^{-1}. **MS (ESI, positive mode):** 786.2 $[M+NH_4]$, 791.2 [M+Na]. **HRMS** (ESI): Calculated for $C_{36}H_{36}N_2O_9S_4Na^+$ $[M+Na]^+$: 791.1196, Found: 791.1202.

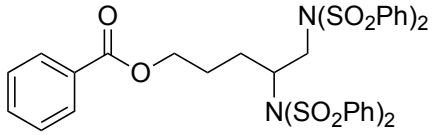


3,4-bis(benzenesulfonimido)butyl methanesulfonate (3t). Prepared according to Standard Conditions A and purified by silica gel chromatography (100% DCM) to yield the product as a white solid (114.6 mg, 76% yield). **Mp:** 175.8-184.7 °C. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.14 – 8.07 (m, 4H), 8.01 (d, *J* = 7.4 Hz, 4H), 7.75 – 7.63 (m, 4H), 7.60 (t, *J* = 7.7 Hz, 6H), 7.55 (t, *J* = 7.9 Hz, 2H), 5.06 (tt, *J* = 11.5, 3.6 Hz, 1H), 4.62 (dd, *J* = 14.7, 11.3 Hz, 1H), 3.90 (dt, *J* = 10.0, 5.1 Hz, 1H), 3.65

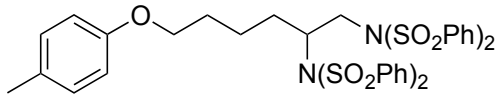
(dd, J = 14.6, 4.0 Hz, 1H), 3.58 (td, J = 9.6, 4.5 Hz, 1H), 2.91 (s, 3H), 2.47 (ddt, J = 16.0, 11.6, 4.5 Hz, 1H), 2.33 – 2.21 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 140.38, 139.12, 138.69, 134.62, 134.59, 129.52, 129.44, 129.38, 128.95, 128.82, 128.75, 66.27, 58.13, 50.21, 37.20, 28.51. **IR (thin film):** 3067, 3032, 2939, 1583, 1449, 1376, 1359, 1083, 950, 909, 859, 754, 732, 720, 686, 650, 586, 554 cm^{-1}. **MS (ESI, positive mode):** 760.2 [M+NH_4], 765.2 [M+Na]. **HRMS** (ESI): Calculated for $C_{29}H_{30}N_2O_{11}S_5Na^+$ [M+Na]$^+$: 765.0345, Found: 765.0348.



***N*,*N*'-(4-(*tert*-butyldiphenylsilyloxy)butane-1,2-diyl)bis(benzenesulfonimide) (3u).** Prepared according to Standard Conditions A and purified by silica gel chromatography (30% ethyl acetate/ 70% hexanes) to yield the product as a yellow resin (109 mg, 60% yield). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.09 (d, J = 7.5 Hz, 2H), 8.02 (m, 6H), 7.59 – 7.49 (m, 6H), 7.47 – 7.31 (m, 16H), 5.00 (tt, J = 11.5, 3.8 Hz, 1H), 4.69 (dd, J = 14.7, 11.2 Hz, 1H), 3.69 (dd, J = 14.7, 4.2 Hz, 1H), 3.24 (td, J = 10.1, 4.0 Hz, 1H), 2.89 (dd, J = 17.9, 7.7 Hz, 1H), 2.32 (dddd, J = 15.5, 11.7, 7.6, 4.1 Hz, 1H), 2.02 (dtd, J = 11.6, 8.0, 3.5 Hz, 1H), 0.96 (s, 9H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 140.87, 139.33, 138.86, 135.60, 135.57, 134.27, 134.13, 133.99, 133.94, 133.59, 129.70, 129.23, 129.14, 129.01, 128.87, 128.83, 128.81, 127.84, 127.78, 60.44, 59.02, 50.55, 31.93, 26.98, 19.30. **IR (thin film):** 3070, 2957, 2930, 2857, 1584, 1448, 1378, 1360, 1171, 1111, 1084, 909, 856, 785, 753, 731, 720, 704, 686, 650, 585, 555 cm^{-1}. **MS (ESI, positive mode):** 925.2 [M+Na]. **HRMS** (ESI): Calculated for $C_{44}H_{46}N_2O_9S_4SiNa^+$ [M+X]$^+$: 925.1748, Found: 925.1757.

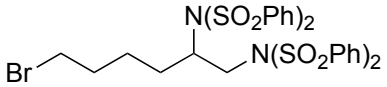


4,5-bis(benzenesulfonimido)pentyl benzoate (3v). Prepared according to Standard Conditions A and purified by silica gel chromatography (20% ethyl acetate/ 80% hexanes) to yield the product as a clear oil (99.8 mg, 64% yield). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.20 – 8.13 (m, 4H), 8.03 (d, J = 7.9 Hz, 4H), 7.93 (d, J = 7.9 Hz, 2H), 7.63 (t, J = 7.4 Hz, 2H), 7.61 – 7.50 (m, 7H), 7.50 – 7.38 (m, 6H), 4.83 (t, J = 11.4 Hz, 1H), 4.79 – 4.70 (m, 1H), 3.85 (dt, J = 11.3, 5.8 Hz, 1H), 3.76 – 3.68 (m, 2H), 2.03 – 1.89 (m, 1H), 1.78 – 1.67 (m, 1H), 1.21 – 1.11 (m, 1H), 1.11 – 0.99 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 166.28, 140.80, 139.59, 139.33, 134.30, 134.27, 134.24, 133.05, 130.30, 129.70, 129.29, 129.10, 128.92, 128.84, 128.52, 128.49, 128.28, 63.74, 61.65, 51.44, 25.67, 25.35. **IR (thin film):** 3166, 3067, 3007, 2959, 2894, 1717, 1602, 1584, 1449, 1379, 1 358, 1314m 1275, 1170, 1084, 908, 754, 732, 686, 651, 584, 555 cm^{-1}. **MS (ESI, positive mode):** 805.2 [M+Na]. **HRMS** (ESI): Calculated for $C_{36}H_{34}N_2O_{10}S_4Na^+$ [M+Na]$^+$: 805.0988, Found: 805.0944.

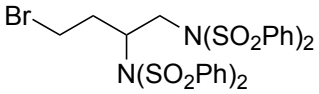


***N*,*N*'-(6-(*p*-tolyloxy)hexane-1,2-diyl)bis(benzenesulfonimide) (3w).** Prepared according to Standard Conditions A and purified by silica gel chromatography (30% ethyl acetate/ 70% hexanes) to yield the product as a tan solid (101.5 mg, 65% yield). **Mp:** 68.4-74.2 ^{o}C. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.16 (d, J = 8.8 Hz, 2H), 8.14 (d, J = 7.8 Hz, 2H), 8.05 (d, J = 7.4 Hz, 4H), 7.65 – 7.55

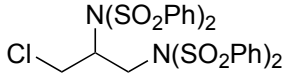
(m, 4H), 7.55 – 7.46 (m, 6H), 7.08 (d, *J* = 8.3 Hz, 2H), 6.69 (d, *J* = 8.5 Hz, 2H), 4.83 – 4.76 (m, 1H), 4.76 – 4.67 (m, 1H), 3.72 (dd, *J* = 13.7, 3.2 Hz, 1H), 3.56 – 3.40 (m, 2H), 2.30 (s, 3H), 1.98 – 1.76 (m, 1H), 1.58 – 1.42 (m, 1H), 1.32 – 1.21 (m, 1H), 1.21 – 1.09 (m, 1H), 0.88 – 0.75 (m, 1H), 0.73 – 0.59 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 156.87, 140.87, 139.72, 139.37, 134.28, 134.18, 134.09, 129.94, 129.79, 129.32, 129.22, 129.02, 128.97, 128.92, 128.86, 128.54, 114.41, 67.45, 61.89, 51.51, 28.76, 28.49, 22.97, 20.59. **IR (thin film):** 3066, 3032, 3006, 2925, 2869, 1612, 1584, 1511, 1488, 1378, 1358, 1243, 1170, 1084, 1043, 999, 910, 890, 851, 793, 753, 720, 686, 651, 585, 555 cm^{-1}. **MS (ESI, positive mode):** 800.3 [M+NH_4], 805.2 [M+Na]. **HRMS** (ESI): Calculated for $C_{37}H_{38}N_2O_9S_4Na$ [M+Na]$^+$: 805.1352, Found: 805.1360.



***N*,*N*'-(6-bromohexane-1,2-diyl)bis(benzenesulfonimide) (3x).** Prepared according to Standard Conditions A and purified by silica gel chromatography (30% ethyl acetate/ 70% hexanes) to yield the product as an off-white solid (111.4 mg, 75% yield). **Mp:** 63.4-71.2 °C. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.15 (d, *J* = 9.3 Hz, 2H), 8.14 (d, *J* = 8.4 Hz, 2H), 8.04 (d, *J* = 7.9 Hz, 4H), 7.66 (dt, *J* = 10.3, 7.3 Hz, 4H), 7.55 (dd, *J* = 14.2, 7.3 Hz, 6H), 4.76 (tt, *J* = 11.0, 3.0 Hz, 1H), 4.73 – 4.66 (m, 1H), 3.72 (dd, *J* = 13.9, 3.2 Hz, 1H), 3.04 – 2.87 (m, 2H), 1.84 (dtd, *J* = 15.4, 11.4, 4.2 Hz, 1H), 1.50 – 1.40 (m, 1H), 1.40 – 1.30 (m, 1H), 1.30 – 1.18 (m, 1H), 0.86 – 0.74 (m, 1H), 0.72 – 0.59 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 140.96, 139.66, 139.37, 134.34, 134.25, 134.14, 129.36, 129.28, 129.08, 128.92, 128.87, 128.57, 61.72, 51.47, 32.93, 32.29, 27.96, 25.01. **IR (thin film):** 3067, 2959, 1584, 1448, 1378, 1358, 1171, 1084, 907, 754, 731, 720, 686, 584, 554 cm^{-1}. **MS (ESI, positive mode):** 777.1 [M+Na]. **HRMS** (ESI): Calculated for $C_{30}H_{31}BrN_2O_8S_4Na^+$ [M+Na]$^+$: 777.0039, Found: 777.0043.

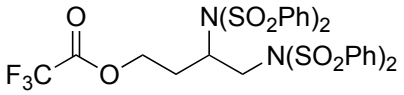


***N*,*N*'-(4-bromobutane-1,2-diyl)bis(benzenesulfonimide) (3y).** Prepared according to Standard Conditions A and purified by silica gel chromatography (20% ethyl acetate/ 80% hexanes) to yield the product as an off-white resin (114.7 mg, 70% yield). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.17 – 8.11 (m, 4H), 8.02 (dd, *J* = 7.5, 1.0 Hz, 4H), 7.72 – 7.63 (m, 4H), 7.63 – 7.51 (m, 8H), 4.82 (t, *J* = 11.3 Hz, 1H), 4.68 (dd, *J* = 14.6, 11.3 Hz, 1H), 3.62 (dd, *J* = 14.6, 4.0 Hz, 1H), 2.73 (td, *J* = 10.1, 4.4 Hz, 1H), 2.63 (m, 1H), 2.59 – 2.43 (m, 1H), 2.16 – 2.00 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 140.44, 139.36, 139.01, 134.50, 134.45, 129.44, 129.42, 129.37, 128.91, 128.85, 128.70, 60.53, 50.77, 32.62, 27.79. **IR (thin film):** 3067, 2927, 1448, 1378, 1171, 1084, 753, 731, 720, 685, 583, 554 cm^{-1}. **MS (ESI, positive mode):** 749.1 [M+Na]. **HRMS** (ESI): Calculated for $C_{28}H_{27}{}^{79}BrN_2O_8S_4Na^+$ [M+Na]$^+$: 748.9726, Found: 748.9733.

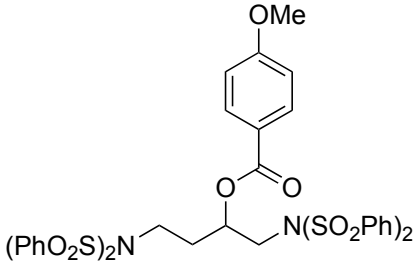


***N*,*N*'-(3-chloropropane-1,2-diyl)bis(benzenesulfonimide) (3z).** Prepared according to Standard Conditions A and purified by silica gel chromatography (20% ethyl acetate/ 80% hexanes) to yield the product as an off-white solid (57.5 mg, 43% yield). **Mp:** 196.8-204.9 °C. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.17 (d, *J* = 7.9 Hz, 2H), 7.99 (d, *J* = 7.9 Hz, 6H), 7.69 (t, *J* = 7.5 Hz, 3H), 7.64 (t, *J* = 7.5

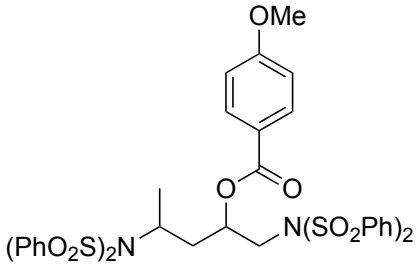
Hz, 1H), 7.61 – 7.54 (m, 6H), 7.51 (t, *J* = 7.8 Hz, 2H), 4.99 (tt, *J* = 11.0, 4.1 Hz, 1H), 4.62 (dd, *J* = 14.9, 11.4 Hz, 1H), 4.05 (dd, *J* = 12.6, 11.1 Hz, 1H), 3.89 (dd, *J* = 14.9, 4.4 Hz, 1H), 3.67 (dd, *J* = 12.7, 3.9 Hz, 1H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 140.17, 138.65, 138.53, 134.61, 134.49, 134.34, 129.51, 129.40, 129.21, 129.15, 129.14, 128.99, 128.93, 128.67, 62.38, 49.56, 41.39. **IR (thin film):** 3067, 2927, 1449, 1378, 1360, 1170, 1084, 753, 732, 720, 685, 583, 554 cm^{-1}. **MS (ESI, positive mode):** 691.0 [M+Na]. **HRMS** (ESI): Calculated for $C_{27}H_5ClN_2O_8S_4Na$ [M+Na]$^+$: 691.0074, Found: 691.0079.



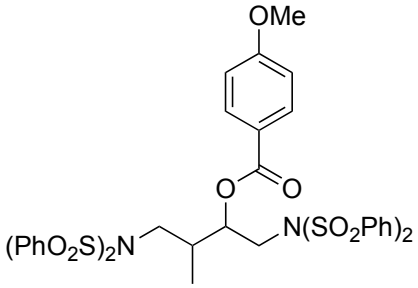
3,4-bis(benzenesulfonimido)butyl 2,2,2-trifluoroacetate (3aa). Prepared according to Standard Conditions A and purified by silica gel chromatography (20% ethyl acetate/ 80% hexanes) to yield the product as a yellow resin (103.6 mg, 68% yield). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.12 (d, *J* = 7.8 Hz, 2H), 8.08 (d, *J* = 7.7 Hz, 2H), 7.99 (d, *J* = 7.7 Hz, 4H), 7.72 – 7.62 (m, 4H), 7.62 – 7.47 (m, 8H), 4.92 (tt, *J* = 11.6, 3.8 Hz, 1H), 4.67 (dd, *J* = 14.7, 11.2 Hz, 1H), 3.91 – 3.75 (m, 2H), 3.59 (dd, *J* = 14.7, 4.3 Hz, 2H), 2.51 – 2.34 (m, 1H), 2.14 (dtd, *J* = 11.5, 8.1, 3.4 Hz, 1H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 156.92 (q, *J* = 42.4 Hz), 140.39, 138.84, 138.68, 134.54, 134.34, 129.45, 129.37, 129.30, 129.10, 128.88, 128.77, 128.70, 114.50 (q, *J* = 285.8 Hz) ,77.36, 64.20, 60.47, 58.15, 50.01, 27.49, 21.14, 14.29. **IR (thin film):** 3167, 3069, 2960, 1789, 1449, 1377, 1361, 1221, 1170, 1083, 911, 879, 818, 780, 753, 733, 721, 686, 651, 584, 554 cm^{-1}. **MS (ESI, positive mode):** 783.1 [M+Na]. **HRMS** (ESI): Calculated for $C_{30}H_7F_3N_2O_{10}S_4Na^+$ [M+Na]$^+$: 783.0393, Found: 783.0396.



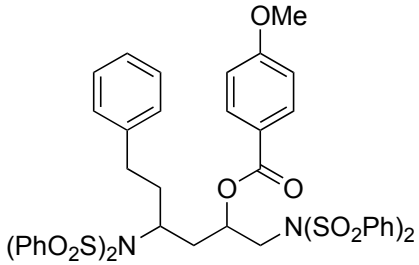
1,4-bis(benzenesulfonimido)butan-2-yl 4-methoxybenzoate (5ae). Prepared according to Standard Conditions B and purified by silica gel chromatography (25% ethyl acetate/ 75% hexanes) to yield the product as a white solid (147.1 mg, 92% yield). **Mp:** 115.7-120.9 °C. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.03 – 7.96 (m, 6H), 7.92 (dd, *J* = 8.4, 1.1 Hz, 4H), 7.64 – 7.54 (m, 4H), 7.47 (m, 8H), 6.96 – 6.87 (m, 2H), 5.36 – 5.18 (m, 1H), 4.12 (dd, *J* = 15.4, 7.5 Hz, 1H), 3.91 – 3.83 (m, 1H), 3.85 (s, 3H), 3.75 (m, 2H), 2.26 – 2.16 (m, 1H), 2.16 – 2.05 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 165.51, 163.80, 139.53, 139.29, 134.13, 134.04, 132.08, 129.27, 129.23, 128.40, 128.23, 121.84, 113.79, 69.79, 55.58, 50.51, 45.39, 32.97. **IR (thin film):** 3067, 3007, 2960, 2934, 2841, 1712, 1606, 1512, 1448, 1374, 1355, 1259, 1170, 1085, 1026, 912, 842, 753, 736, 720, 686, 582, 551 cm^{-1}. **MS (ESI, positive mode):** 816.5 [M+NH_4], 821.5 [M+Na]. **HRMS** (ESI): Calculated for $C_{36}H_{34}N_2O_{11}S_4Na^+$ [M+Na]$^+$: 821.0938, Found: 821.0944.



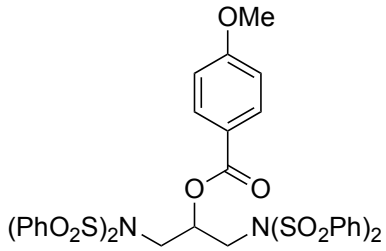
1,4-bis(benzenesulfonimido)pentan-2-yl 4-methoxybenzoate (5af). Prepared according to Standard Conditions B and purified by silica gel chromatography (25% ethyl acetate/ 75% hexanes) to yield the product as a yellow resin (110.8 mg, 68% yield, 2.3:1 dr). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.09 – 7.84 (m, 22H, Major+Minor), 7.66 – 7.37 (m, 22H, Major+Minor), 6.95 (d, *J* = 9.0 Hz, 2H, Major), 6.90 (d, *J* = 8.9 Hz, 2H, Minor), 5.29 – 5.09 (m, 2H, Major+Minor), 4.39 – 4.28 (m, 1H, Minor), 4.28 – 4.18 (m, 1H, Major), 4.07 (dd, *J* = 15.4, 7.0 Hz, 1H, Major), 4.02 (dd, *J* = 15.9, 7.8 Hz, 1H, Minor), 3.92 (dd, *J* = 15.3, 5.0 Hz, 1H, Major), 3.87 (s, 3H, Major), 3.85 (s, 3H, Minor), 3.79 (dd, *J* = 15.9, 3.1 Hz, 1H, Minor), 2.71 – 2.61 (m, 1H, Major), 2.52 – 2.41 (m, 1H, Minor), 2.24 – 2.14 (m, 1H, Minor), 2.13 – 2.03 (m, 1H, Major), 1.42 (d, *J* = 6.8 Hz, 3H, Minor), 1.23 (d, *J* = 6.8 Hz, 3H, Major). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 165.76, 165.37, 163.90, 163.70, 139.39, 139.25, 134.14, 134.08, 132.20, 132.03, 129.26, 129.17, 128.47, 128.43, 122.10, 121.75, 113.81, 113.73, 71.63, 69.01, 56.64, 56.16, 55.60, 55.56, 50.91, 50.70, 39.86, 38.70, 29.78, 20.03, 18.42. **IR (thin film):** 3068, 3006, 2935, 2842, 1711, 1606, 1512, 1448, 1370, 1259, 1169, 1085, 1030, 910, 753, 733, 721, 686, 583, 551 cm^{-1}. **MS (ESI, positive mode):** 835.0 [M+Na]. **HRMS** (ESI): Calculated for $C_{37}H_{36}N_2O_{11}S_4Na^+$ [M+X]$^+$: 835.1094, Found: 835.1085.



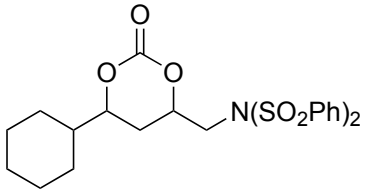
3-methyl-1,4-bis(benzenesulfonimido)butan-2-yl 4-methoxybenzoate (5ag). Prepared according to Standard Conditions B and purified by silica gel chromatography (25% ethyl acetate/ 75% hexanes) to yield the product as a yellow resin (144.1 mg, 89% yield, 1:1 dr). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.05 – 7.96 (m, 14H, A+B), 7.95 (dd, *J* = 8.4, 0.9 Hz, 4H, A+B), 7.89 (dd, *J* = 8.4, 0.9 Hz, 4H, A+B), 7.65 – 7.53 (m, 8H, A+B), 7.53 – 7.39 (m, 14H, A+B), 6.92 (dd, *J* = 8.8, 1.2 Hz, 4H, A+B), 5.40 (m, 2H, A+B), 4.22 (dd, *J* = 15.7, 9.1 Hz, 1H, A), 4.10 (dd, *J* = 15.4, 7.9 Hz, 1H, B), 3.93 (dd, *J* = 15.4, 4.7 Hz, 1H, B), 3.89 – 3.82 (m, 8H, A+B), 3.77 (dd, *J* = 14.6, 4.2 Hz, 2H, A+B), 3.65 (dd, *J* = 14.8, 10.4 Hz, 1H, B), 2.61 – 2.46 (m, 2H, A+B), 1.03 (d, *J* = 7.0 Hz, 3H, A), 0.96 (d, *J* = 7.0 Hz, 3H, B). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 165.42, 165.26, 163.74, 163.71, 139.44, 139.31, 139.27, 134.10, 134.01, 132.18, 132.10, 129.22, 129.20, 129.14, 128.47, 128.41, 128.31, 122.00, 113.77, 113.72, 77.36, 74.00, 72.74, 60.47, 55.57, 51.74, 50.41, 49.80, 48.78, 36.29, 35.18, 29.78, 21.14, 14.30, 13.86, 11.65. **IR (thin film):** 3067, 2971, 2935, 2842, 1712, 1605, 1512, 1448, 1374, 1355, 1259, 1169, 1085, 1031, 912, 794, 782, 753, 738, 720, 686, 583, 551 cm^{-1}. **MS (ESI, positive mode):** 835.3 [M+Na]. **HRMS** (ESI): Calculated for $C_{37}H_{36}N_2O_{11}S_4Na^+$ [M+Na]$^+$: 835.1094, Found: 835.1100.



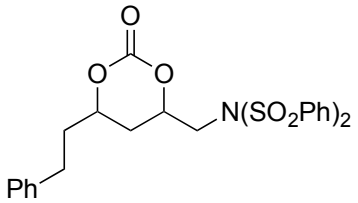
6-phenyl-1,4-bis(benzenesulfonimido)hexan-2-yl 4-methoxybenzoate (5ah). Prepared according to Standard Conditions B and purified by silica gel chromatography (25% ethyl acetate/ 75% hexanes) to yield the product as an off-white resin (102.6 mg, 57% yield, 2.1:1 dr). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.21 – 7.90 (m, 20H, Major+Minor), 7.80 (d, *J* = 7.8 Hz, 2H, Major), 7.69 – 7.31 (m, 22H, Major+Minor), 7.29 – 7.21 (m, 2H, Minor), 7.21 – 7.06 (m, 4H, Major+Minor), 6.97 (d, *J* = 8.0 Hz, 4H, Major), 6.91 (d, *J* = 7.8 Hz, 2H, Minor), 6.75 (d, *J* = 7.0 Hz, 2H, Minor), 5.36 – 5.29 (m, 1H, Minor), 5.29 – 5.18 (m, 1H, Major), 4.36 – 4.25 (m, 1H, Minor), 4.24 – 4.14 (m, 1H, Major), 4.07 (dd, *J* = 15.7, 6.7 Hz, 1H, Major), 3.99 – 3.91 (m, 1H, Minor), 3.91 – 3.83 (m, 7H, Major+Minor), 3.78 – 3.68 (m, 1H, Minor), 2.64 – 2.52 (m, 1H, Major), 2.43 – 2.32 (m, 1H, Minor), 2.32 – 2.11 (m, 2H, Major+Minor), 2.11 – 1.97 (m, 4H, Major+Minor), 1.94 – 1.76 (m, 4H, Major+Minor). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 165.79, 165.55, 163.93, 163.74, 141.50, 141.29, 140.86, 139.49, 139.13, 138.83, 134.16, 134.10, 133.80, 132.27, 132.09, 131.77, 129.47, 129.28, 129.21, 129.17, 129.05, 128.85, 128.61, 128.58, 128.51, 128.44, 128.38, 128.35, 128.33, 128.29, 126.04, 122.15, 121.81, 113.86, 113.78, 77.36, 71.59, 68.88, 61.46, 61.25, 60.48, 55.61, 55.59, 51.04, 50.59, 38.64, 36.28, 34.37, 33.57, 32.86, 21.15, 14.30. **IR (thin film):** 3064, 3026, 2935, 2843, 2360, 2340, 1710, 1605, 1448, 1373, 1355, 1259, 1169, 1084, 1026, 910, 753, 732, 720, 686, 582, 551 cm^{-1}. **MS (ESI, positive mode):** 920.2 [M+NH_4], 925.2 [M+Na]. **HRMS** (ESI): Calculated for $C_{44}H_{42}N_2O_{11}S_4Na^+$ [M+Na]$^+$: 925.1564, Found: 925.1561.



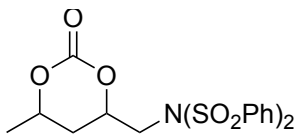
1,3-bis(benzenesulfonimido)propan-2-yl 4-methoxybenzoate (5ai). Prepared according to Standard Conditions B and purified by silica gel chromatography (25% ethyl acetate/ 75% hexanes) to yield the product as a white solid (128.8 mg, 82% yield). **Mp:** 153.7-159.1 °C. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.01 – 7.93 (m, 10H), 7.57 (t, *J* = 7.5 Hz, 4H), 7.45 (t, *J* = 7.9 Hz, 8H), 6.86 (d, *J* = 9.0 Hz, 2H), 5.58 (tt, *J* = 7.3, 4.7 Hz, 1H), 4.21 (dd, *J* = 15.8, 7.3 Hz, 2H), 4.10 (dd, *J* = 15.8, 4.6 Hz, 2H), 3.82 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 165.34, 163.66, 139.08, 134.13, 132.23, 129.20, 128.55, 121.81, 113.65, 69.71, 55.52, 48.96. **IR (thin film):** 3067, 3007, 2936, 2841, 1718, 1605, 1448, 1374, 1259, 1170, 1085, 784, 753, 736, 721, 685, 583, 551 cm^{-1}. **MS (ESI, positive mode):** 802.2 [M+NH_4], 807.4 [M+Na]. **HRMS** (ESI): Calculated for $C_{35}H_{32}N_2O_{11}S_4Na^+$ [M+Na]$^+$: 807.0781, Found: 807.0784.



***N*-((6-cyclohexyl-2-oxo-1,3-dioxan-4-yl)methyl)-benzenesulfonimide (7a).** Prepared according to Standard Conditions A and purified by silica gel chromatography (30% ethyl acetate/ 70% hexanes) to yield the product as a tan solid (89 mg, 89% yield, 1.16:1 dr). **Mp:** 68.9-72.5 °C. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.06 (d, *J* = 7.8 Hz, 4H, minor), 8.02 (d, *J* = 7.9 Hz, 4H, major), 7.68 (d, *J* = 6.5 Hz, 2H, minor), 7.67 (d *J* = 6.0 Hz, 2H, minor), 7.56 (t, *J* = 7.8 Hz, 8H, major+minor), 4.82 (quin, *J* = 5.9 Hz, 1H, major), 4.78 – 4.66 (m, 1H, ,minor), 4.23 (q, *J* = 6.5 Hz, 1H, major), 4.11 (m, 3H, major+minor), 3.82 – 3.67 (m, 2H, major+minor), 2.09 – 1.91 (m, 4H, major+minor), 1.91 – 1.46 (m, 10H, major+minor), 1.35 – 1.09 (m, 8H, major+minor), 1.09 – 0.91 (m, 4H, major+minor). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 148.36, 148.26, 138.94, 138.86, 134.44, 134.38, 129.32, 129.28, 128.81, 128.72, 82.75, 80.09, 77.36, 77.12, 74.85, 51.62, 50.56, 42.06, 41.54, 28.30, 27.99, 27.84, 27.75, 26.18, 26.11, 25.74, 25.63, 25.55. **IR (thin film):** 3067, 2930, 2854, 2360, 2341, 1749, 1448, 1375, 1169, 735, 721, 686, 582, 550 cm^{-1}. **MS (ESI, positive mode):** 511.3 [M+NH_4], 516.2 [M+Na]. **HRMS** (ESI): Calculated for $C_{23}H_{31}N_2O_7S_2^+$ [M+NH_4]$^+$: 511.1567, Found: 511.1570.



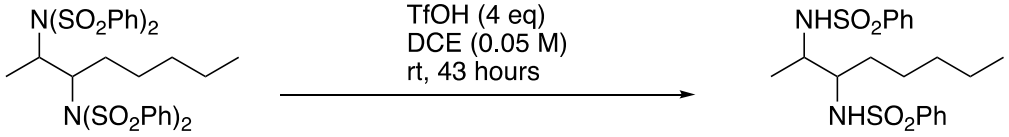
***N*-((2-oxo-6-phenethyl-1,3-dioxan-4-yl)methyl)-benzenesulfonimide (7b).** Prepared according to Standard Conditions A and purified by silica gel chromatography (25% ethyl acetate/ 75% hexanes) to yield the product as a yellow resin (77.9 mg, 76% yield, 1.25:1 dr). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.10 – 7.91 (m, 8H, major+minor), 7.74 – 7.60 (m, 4H, major+minor), 7.55 (t, *J* = 7.6 Hz, 8H, major+minor), 7.38 – 7.14 (m, 10H, major+minor), 4.83 (quin, *J* = 6.1 Hz, 1H, major), 4.78 – 4.69 (m, 1H, minor), 4.54 – 4.44 (m, 1H, major), 4.34 – 4.23 (m, 1H, minor), 4.09 (dd, *J* = 15.8, 6.7 Hz, 2H, major+minor), 3.70 (dt, *J* = 15.6, 6.6 Hz, 2H, major+minor), 2.88 – 2.64 (m, 4H, major+minor), 2.10 – 1.74 (m, 6H, major+minor), 1.70 – 1.54 (m, 2H, major+minor). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 148.04, 147.96, 140.29, 138.73, 134.50, 134.44, 129.35, 129.28, 128.84, 128.73, 128.55, 126.43, 77.46, 77.36, 75.42, 74.55, 51.48, 50.52, 36.86, 36.44, 30.96, 30.61, 30.50, 28.39. **IR (thin film):** 3064, 3027, 2926, 2852, 1749, 1448, 1375, 1355, 1203, 1169, 1130, 1084, 754, 738, 721, 686, 582, 551 cm^{-1}. **MS (ESI, positive mode):** 538.1 [M+Na]. **HRMS** (ESI): Calculated for $C_{25}H_{25}NO_7S_2Na^+$ [M+Na]$^+$: 538.0965, Found: 538.0964.



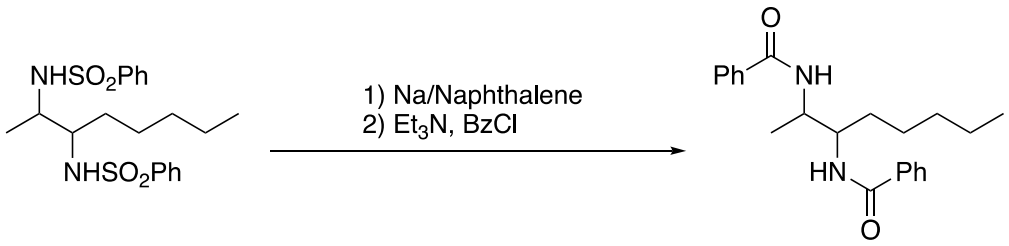
***N*-((6-methyl-2-oxo-1,3-dioxan-4-yl)methyl)-benzenesulfonimide (7c).** Prepared according to Standard Conditions A and purified by silica gel chromatography (30% ethyl acetate/ 70% hexanes) to yield the product as an off-white solid (77.3 mg, 90% yield, 1.3:1 dr). **Mp:** 58-62.4 °C. **^{1}H NMR**

(500 MHz, $CDCl_3$): δ 8.04 (d, *J* = 7.4 Hz, 8H, major+minor), 7.67 (t, *J* = 6.7 Hz, 4H, major+minor), 7.56 (t, *J* = 6.1 Hz, 8H, major+minor), 4.90 – 4.82 (m, 1H, major), 4.82 – 4.74 (m, 1H, minor), 4.73 – 4.63 (m, 1H, major), 4.53 – 4.43 (m, 1H, minor), 4.12 (td, *J* = 16.3, 6.8 Hz, 2H, major+minor), 3.73 (td, *J* = 15.6, 5.4 Hz, 2H, major+minor), 2.19 – 2.01 (m, 2H, major+minor), 1.95 – 1.83 (m, 1H, major), 1.59 (m, 1H, minor), 1.36 (d, *J* = 6.2 Hz, 6H, major+minor). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 148.07, 147.96, 138.73, 138.68, 134.48, 134.43, 129.32, 129.26, 128.82, 128.72, 77.26, 75.12, 74.36, 72.79, 51.48, 50.63, 32.18, 29.61, 21.19, 20.64. **IR (thin film):** 3067, 2983, 2935, 1750, 1449, 1373, 1355, 1247, 1203, 1170, 1128, 1084, 913, 822, 755, 736, 721, 686, 583, 551 cm^{-1}. **MS (ESI, positive mode):** 488.1 [M+Na]. **HRMS** (ESI): Calculated for $C_{18}H_9NO_7S_2Na$ $[M+Na]^+$: 448.0495, Found: 448.0492.

VI. Deprotection of Products



A flame dried round bottom flask equipped with a stir bar and a rubber septum was charged with bis-benzenesulfonimide substrate (956 mg, 1.36 mmol), DCE (34 mL, 0.04 M), and triflic acid (480 uL, 5.43 mmol) at 0 °C under nitrogen. The mixture was stirred at room temperature for 43 hours and then quenched with 15 drops of neat ethylenediamine and subsequently diluted with 1.0 M NaOH aq. solution. The resulting biphasic mixture was extracted with DCM (3x). The combined organic extracts were dried over Na2SO4, filtered, and then concentrated in vacuo. The product was purified via silica gel flash column chromatography (30% pentane/ 70% ether) to yield the product as a yellow resin (496 mg, 86% yield).[14] **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 7.86 (d, *J* = 7.4 Hz, 2H), 7.80 (d, *J* = 7.4 Hz, 2H), 7.64 – 7.56 (m, 2H), 7.56 – 7.44 (m, 4H), 5.40 (d, *J* = 9.0 Hz, 1H), 4.96 (d, *J* = 8.9 Hz, 1H), 3.34 – 3.19 (m, 1H), 3.00 – 2.87 (m, 1H), 1.24 – 1.15 (m, 1H), 1.12 – 1.05 (m, 1H), 1.05 – 0.96 (m, 2H), 0.94 (d, *J* = 6.8 Hz, 3H), 0.93 – 0.74 (m, 4H), 0.72 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 140.84, 140.09, 133.00, 132.74, 129.25, 129.24, 127.38, 127.30, 57.84, 52.33, 31.56, 31.08, 25.25, 22.33, 16.59, 13.93. **IR (thin film):** 3278, 3066, 2955, 2931, 2860, 1586, 1448, 1385, 1325, 1263, 1162, 1092, 1024, 905, 801, 756, 721, 690, 597, 559, 457 cm^{-1}. **MS (ESI, positive mode):** 425.1 [M+1], 447.1 [M+Na].



An oven dried, two-neck flask was charged with naphthalene (621 mg, 4.85 mmol) in THF (12.13 mL, 0.08 M) and cut-up Na (112 mg, 4.85 mmol) was gradually added. The solution quickly turned dark green, and was stirred at room temperature for 4h. The bis-benzenesulfonamide (412 mg, 0.97 mmol) in THF (12.13 mL, 0.08 M) was then added to the above solution via syringe at 0 °C, and the mixture was stirred overnight at room temperature. Water (0.7 mL) was added to quench reaction and the mixture was diluted with EtOAc. The organic layer was dried over $MgSO_4$ and filtered. The

organic solution was concentrated and then diluted in DCM (25 mL) and triethylamine (811 uL, 5.82 mmol) and benzoyl chloride (676 uL, 5.82 mmol) were added. The reaction was allowed to stir for 3 hours then water was added. The mixture was extracted DCM (3x). The combined organic layers were dried over $MgSO_4$, filtered and concentrated in vacuo. The resulting solid was purified by silica gel flash column chromatography (70% hexane /30% EtOAc) to yield the product as a white solid (209.2 mg, 61% yield).[15] **MP:** 228.9-230.8 ^oC. **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 7.98 (d, *J* = 6.1 Hz, 1H), 7.90 (d, *J* = 7.2 Hz, 2H), 7.85 (d, *J* = 7.4 Hz, 2H), 7.53 (M, 2H), 7.49 – 7.43 (m, 4H), 6.51 (d, *J* = 7.5 Hz, 1H), 4.28 (dd, *J* = 11.9, 5.7 Hz, 2H), 1.75 – 1.62 (m, 1H), 1.62 – 1.51 (m, 1H), 1.51 – 1.39 (m, 2H), 1.38 – 1.29 (m, 4H), 1.26 (d, *J* = 6.6 Hz, 3H), 0.88 (t, *J* = 6.7 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 169.24, 167.15, 134.58, 132.03, 131.47, 128.92, 128.69, 127.28, 127.19, 55.12, 51.27, 32.45, 31.74, 26.39, 22.64, 15.25, 14.12. **IR (thin film):** 3287, 2954, 2924, 2856, 2360, 1630, 1622, 1532, 1479, 1449, 1336, 1155, 696 cm^{-1}. **MS (ESI, positive mode):** 375.2 [M+Na].

VII. References

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