Supporting Information

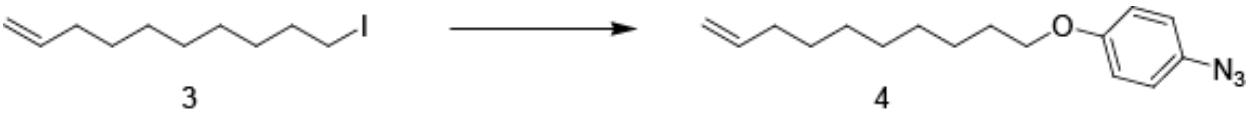
1 2

Dec-9-enyl 4-methylbenzenesulfonate (2). A flame-dried 50 mL round-bottom flask containing a spin bar and sealed with a septum was flushed with argon for 15 minutes. 9-Decene-1-ol (compound 1, 5.7mL, 31.9mmol), triethylamine (TEA) (15.5mL, 111.9 mmol, 5.65 eq), 4-dimethylaminopyridine (DMAP) (0.394 g, 3.23 mmol, 0.16 eq), and 49 mL dichloromethane (DCM) were added to the flask using a syringe. The mixture was stirred for 5 minutes. This mixture was added to another flame-dried flask containing p-toluenesulfonyl chloride (12.1g, 64.0 mmol, 2.0 eq) and 50 mL of dichloromethane using a syringe. A 13 mL DCM rinse was also added to flask via a syringe. The mixture was set to stir at room temperature for at least 7 hours. The reaction mixture was quenched with 25 mL of DCM, washed with 1M NH_4Cl until the aqueous layer was no longer milky. The organic layer was dried with magnesium sulfate and the solvent was evaporated under reduced pressure, giving a yellow solution. The solution was passed through a silica plug, yielding 6.45 g (21 mmol, 65.1%) of essentially pure product as yellow oil at room temperature. TLC R_f 0.6 (9:1 hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.26 (m, 10 H), 1.60 (p, 2 H, J = 7 Hz), 1.99 (q, 2 H, J = 7 Hz), 2.42 (s, 3 H), 3.99 (t, 2 H, 7 Hz), 4.89 (d, 1 H, 10 Hz), 4.97 (d, 1 H, 17 Hz), 5.75 (m, 1 H), 7.32 (d, 2 H, 8 Hz), 7.76 (d, 2 H, 8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.5, 25.2, 28.7, 28.7, 28.7, 28.8, 28.9, 29.1, 33.6, 70.6, 127.9, 129.9, 133.1, 138.9, 144.5. IR (KBr, cm^{-1}): 3063.2, 2976.9, 2920.4, 2851.3, 1596.2, 1355.9, 1189.4, 1174.0, 1019.4.; HRMS (Electrospray) calcd for $C_{17}H_{26}O_3S$: 310.1603, found 311.1690 $(M+H)^+$.

2 3

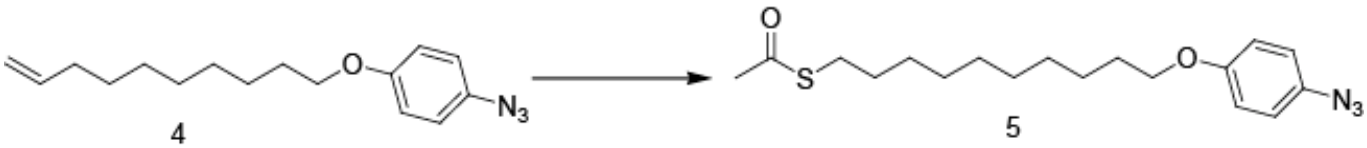
10-Iododecene (3). To a flame dried flask equipped with a spin bar, compound 2 (2.00 g, $6.4x10^{-3}$ mol) in 30 mL of reagent grade acetone was added. The flask was subsequently sealed using a rubber septum. In a separate vessel, NaI (4.83 g, $3.22x10^{-2}$ mol) in 30 mL of acetone was prepared and added to the sealed flask using a syringe. The mixture was kept stirring for 24 hours. The mixture was quenched with hexanes, and a brown precipitate immediately formed. The mixture was washed 3 times using 100 mL portions of saturated $NaHCO_3$ solution and three times with saturated NaCl solution. The organic layer was dried with anhydrous $MgSO_4$ and was concentrated under reduced pressure. The solution was passed through a silica plug, yielding 1.40 g ($5.30x10^{-3}$ mol, 82.4%) of compound 3 as oil at room temperature. TLC R_f = 0.5

(hexanes). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.37 (m, 10 H), 1.80 (p, 2 H, J = 7 Hz), 2.05 (q, 2 H, J = 7 Hz), 3.17 (t, 2 H, 7 Hz), 4.91 (d, 1 H, 10 Hz), 4.98 (d, 1 H, 17 Hz), 5.78 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 7.09, 28.4, 28.8, 28.85, 28.91, 29.0, 30.4, 33.5, 33.7, 114.1, 138.9. IR (Neat, cm^{-1}): 3074.6, 2974.4, 2925.7, 2853.2, 1462.6, 1193.1, 993.4.; HRMS (CI) calcd for $C_{10}H_{19}I$: 267.0531, found 267.0611.



3 4

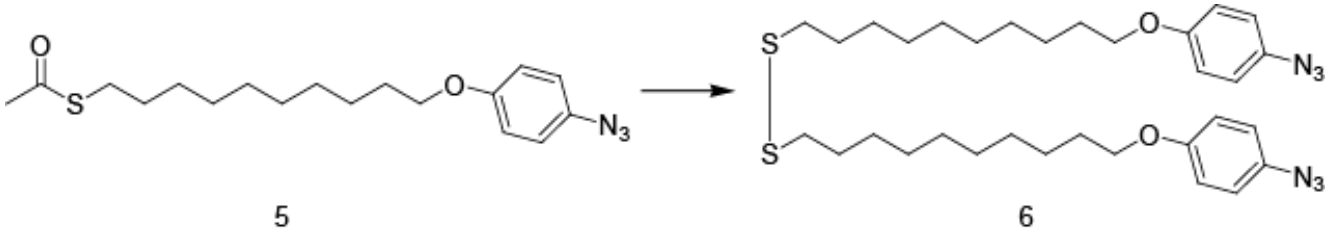
10-(p-Azidophenoxyl)decene (4). To a flame dried flask, 3 (3.00 g, $1.13x10^{-2}$ mol), 4-azidophenol (compound 9, 0.310g, $2.29x10^{-3}$), 0.436 g of K_2CO_3 and 30 mL reagent grade acetone were added with a spin bar. The mixture was refluxed for 7.5 hours. The mixture was cooled to room temperature and quenched with 50 mL of hexanes. The mixture was filtered and concentrated under reduced pressure. The concentrate was loaded into a silica plug. 420mg ($1.4x10^{-3}$ mol, 67.3%) of 4 was obtained as oil. TLC R_f = 0.2 (hexanes). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.37 (m, 10 H), 1.78 (p, 2 H, J = 7 Hz), 2.05 (q, 2 H, J = 7 Hz), 3.92 (t, 2 H, 7 Hz), 4.94 (d, 1 H, 10 Hz), 5.03 (d, 1 H, 17 Hz), 5.83 (m, 1 H), 6.88 (d, 2 H, 9 Hz), 6.95 (d, 2 H, 9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 25.9, 28.8, 28.9, 29.15, 29.25, 29.2, 33.7, 68.3, 114.1, 115.6, 119.8, 131.9, 139.0, 156.5. (Neat, cm^{-1}): 3075.4, 2927.2, 2855.0, 2111.8, 1607.9, 1584.2, 1505.2, 1471.8, 1392.6, 1282.0, 1245.4, 1172.4, 1027.4, 994.0; HRMS (EI) calcd for $C_{16}H_{23}N_3O$: 273.1841, found 273.1837.



4 5

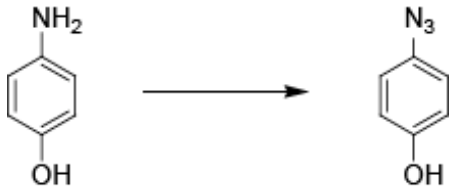
S-10-(4-Azidophenoxy)decyl ethanethioate (5). Compound 4 (0.177g, $2.79x10^{-4}$ mol), azobisisobutyronitrile (0.086g, $5.26x10^{-4}$ mol, 2 eq), thioacetic acid (0.140mL, d = 1.065, $1.96x10^{-3}$ mol, 7 eq), and 5 mL of toluene were added to a flame dried 2-head flask, which was equipped with a spin bar. A condenser was first attached to the setup and the mixture was refluxed for 30 minutes. The reaction mixture was subsequently cooled to room temperature and was quenched with 5 mL of 1M $NaHCO_3$. The organics were extracted using ethyl acetate. The organic extract was washed with 30 mL of 1M $NaHCO_3$ three times, dried and concentrated under reduced pressure. The crude was purified using preparatory TLC with a 9:1 hexanes/ethyl acetate solvent system. 181mg ($5.18x10^{-4}$ mol, 79.7%) of 5 was obtained as solid. TLC R_f = 0.4. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.28 (m, 8 H), 1.43 (p, 2 H, J = 8 Hz), 1.55 (p, 2 H, J = 8 Hz), 1.75 (p, 2 H, J = 8 Hz), 2.31 (s, 3 H), 2.85 (t, 2 H, 7 Hz), 3.91 (t, 2 H, 7 Hz), 6.86 (d, 2 H, 8 Hz), 6.92 (d, 2 H, 8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 25.9, 28.7,

28.95, 29.02, 29.11, 29.21, 29.26, 29.33, 29.4, 30.5, 68.3, 115.6, 120.0, 132.0, 156.4, 195.9. IR (KBr, cm^{-1}): 3031.5, 2920.5, 2851.7, 2116.0, 1694.8, 1507.6, 1472.2, 1352.7, 1292.4, 1248.4, 1130.3, 1113.4, 1013.9.; HRMS (Electrospray) calcd for $C_{18}H_{27}N_3O_2S$: 349.1824, found 349.1829. M. P. 41.6-43.4ºC.



5 6

1,2-bis(10-(4-Azidophenoxy)decyl)disulfane (7). Compound 6 (29.0 mg, $8.3x10^{-5}$ mol), 1.8 ml of tetrahydrofuran was added to a round bottom flask equipped with a spin bar and the mixture was cooled to 0ºC. The flask was sealed and purged with argon. 1.2 ml of pre-chilled 1M NaOH solution was added to the flask using a syringe and an emulsion formed immediately. To make the solution homogenous, 1mL of pre-chilled tetrahydrofuran and 0.3 mL of pre-chilled deionized water were added to the flask. The mixture was left stirring for 6 hours with temperature maintained at 0°C. The pH of the mixture was subsequently adjusted to 5.0 using 1M hydrochloric acid. The mixture was extracted with 10 mL of ethyl acetate twice, washed with brine three times and solvents were concentrated for purification using preparatory thin-layered chromatography. 7 mg of compound 7 was obtained ($1.14x10^{-5}$ mol, 27.5%). TLC R_f = 0.6. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.29 (m, 16 H), 1.44 (p, 4 H, J = 8 Hz), 1.56 (p, 4 H, J = 8 Hz), 1.76 (p, 4 H, J = 8 Hz), 2.51 (q, 4 H, 7 Hz), 3.91 (t, 4 H, 7 Hz), 6.86 (d, 4 H, 8 Hz), 6.94 (d, 4 H, 8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 24.5, 25.9, 28.2, 28.9, 29.1, 29.2, 29.3, 29.4, 33.9, 68.3, 115.6, 119.8, 132.0, 156.4. IR (KBr, cm^{-1}): 3031.5, 2920.5, 2851.7, 2116.0, 1507.6, 1472.2, 1352.7, 1292.4, 1248.4, 1130.3, 1113.4, 1013.9.; HRMS (ACPI) calcd for $C_{18}H_{27}N_3O_2S$: 612.3280, found ions 585.3, 557.4, 280.2, 246.3. M. P. 43.8 – 48.3ºC.



7 8

4-Azidophenol (9). 4-Aminophenol (8) (1.0169 g, $1.0x10^{-2}$ mol), 30 mL of deionized water, 10 mL of 12 M HCl solution were mixed and cooled in an ice bath for 15 minutes. Separate aqueous solutions of $NaNO_2$ (0.65 g, $9.4x10^{-3}$ mol) and NaN_3 (0.65 g, $1.0x10^{-2}$ mol) in 10 mL of deionized water were also prepared and chilled in ice for 15 minutes. The $NaNO_2$ solution

was added first drop-wise, followed by 15 minutes of stirring on ice. The NaN_3 solution was then introduced drop-wise as well. The reaction mixture was brought to room temperature and neutralized using saturated sodium hydroxide solution. The aqueous layer was extracted thrice using 25 mL portions of diethyl ether, washed with 50 mL of ammonium chloride and 50 mL of brine. The organics were concentrated under reduced pressure, and purified using a silica gel column with a 0.85:0.15 hexane/ethyl acetate solvent system (TLC R_f = 0.4). 0.680 g ($5x10^{-3}$ mol, 50.0%) of 9 was obtained as oil. ^1H NMR (500 MHz, CD_3OD): δ 4.85 (s, 1 H), 6.76 (d, 2 H, 9 Hz), 6.94 (d, 2 H, 9 Hz); ^{13}C NMR (125 MHz, CD_3OD): δ 115.9, 119.5, 130.8, 154.6. IR (Neat, cm^{-1}): 3382.3, 3031.8, 2109.5, 2065.1, 1504.9, 1445.3.2, 1368.3, 1290.0, 1233.1, 1130.3, 1107.6, 833.7; HRMS (EI) calcd for $C_6H_5N_3O$: 135.0433, found 135.043.

Source of compounds

9-decene-1-ol, tiethylamine, 4-dimethylaminopyridine, p-toluenesulfonyl chloride, 4-aminophenol, azobisisobutyronitrile, thioacetic acid, sodium nitrite, sodium iodide and sodium azide were obtained from Sigma-Aldrich. Dichloromethane, acetone, hexanes, ammonium chloride, and tetrhydrofuran, ethyl acetate, hydrochloric acid, and diethyl ether were obtained from EMScience. Dichloromethane was distilled over calcium hydride before use. Sodium bicarbonate, magnesium sulfate anhydrous, potassium carbonate, and sodium hydroxide were obtained from Fisher Scientific. Chloroform-d and methanol-d_4 were obtained from Cambridge Isotope Lab.