An Efficient Synthesis of Vinyl Ethers using the Julia Olefination

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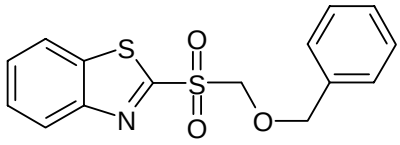
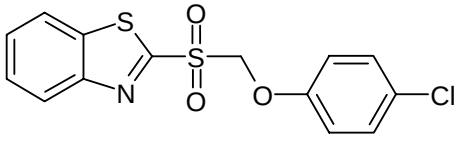
Supporting Information

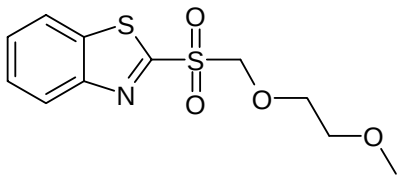
General. All reactions were carried out under a nitrogen atmosphere using dry glassware which had been flame-dried under a stream of nitrogen. All solvents came from Aldrich Sure-Seal bottle and used as received. Commercially available reagents were used as received. We used LiHMDS (1M/Hexanes) or (1M/THF), NaHMDS (1M/THF), KHMDS (0.5M/Toluene) and BOMCl was purchased from TCI-US (90% purity). Reactions were monitored by thin-layer chromatography (TLC) using 0.25-mm E. Merck precoated silica gel plates. Visualization was accomplished with UV light and aqueous ceric ammonium molybdate solution followed by charring on a hot-plate. Reactions were purified using a Isco Combi-Flash Sq16x system or by chromatography column performed with the indicated solvents using silica gel 60 (particle size 0.040-0.063 mm) desactivated with 5% Et_3N in the case of aldehydes. Yields refer to chromatographically and spectroscopically pure compounds. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX-500 MHz spectrometer at ambient temperature. ^{1}H and ^{13}C NMR data are reported as δ values relative to tetramethylsilane.



2-{[(benzyloxy)methyl]sulfonyl}-1,3-benzothiazole (2a). To a solution of 2-mercaptobenzothiazole (10 g, 60 mmol, 1 eq) in N,N-dimethylformamide (300 mL, 0.2M) at 0°C, was added sodium hydride 60% (2.6 g, 66 mmol, 1.1 eq) portionwise over 5 min. When gas evolution stopped, benzyl chloromethyl ether (9.2 mL, 66 mmol, 1.1 eq) was added dropwise over 5 min. The reaction was stirred at 21°C for 1.5 h. The reaction mixture was quenched with a saturated NH_4Cl solution at 0°C, diluted with EtOAc and the mixture was extracted 3 times with EtOAc. The combined organic layers were washed with water 2 times, with a saturated NaCl solution, dried over $MgSO_4$ and concentrated. The crude product was purified by Combi-Flash (0 to 20% EtOAc/Hexanes over 30min, 120g silica gel cartridge) to give the desired thioether (15.26 g, 89%) as a yellowish oil which was oxidized by the following procedure. To a solution of 2-{[(benzyloxy)methyl]thio}-1,3-benzothiazole (5 g, 17.4 mmol, 1 eq) in methanol (311 mL, 0.056M) at 0°C, was added sodium tungstate dihydrate (2.9 g, 8.7 mmol, 0.5 eq) and 5 minutes later, hydrogen peroxide 30% (7.2 mL, 70 mmol, 4 eq). The reaction was stirred at 21°C overnight. The reaction mixture was quenched with 10 g of sodium metabisulfite in 100 mL of water at 0°C and diluted with 600 mL of CH_2Cl_2. The mixture was extracted 3 times with 250 mL of CH_2Cl_2. The combined organic layers were washed with 100 mL of brine, dried over $MgSO_4$ and concentrated. The crude product was purified by Combi-Flash (0 to 30 % EtOAc/Hexanes over 35 min, 120g silica gel cartridge) to give the desired product **2a** (4.1 g, 76%) as a white solid. ^{1}H NMR (500 MHz, Acetone-d_6): δ 8.27 (d, J = 7.4 Hz, 1H), 8.23 (d, J = 7.8 Hz, 1H), 7.73-7.67 (m, 2H), 7.29 (m, 5H), 5.24 (s, 2H), 4.94 (s, 2H). ^{13}C NMR (125 MHz, Acetone-d_6): δ 166.26, 153.77, 137.95, 137.26, 129.22, 129.06, 128.73, 125.99, 123.86, 85.32, 75.49. HRMS (FAB) calcd. for $C_{15}H_{14}NO_3S_2$ 320.0415, found 320.0416.

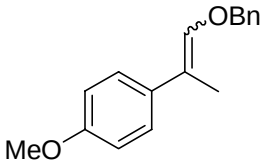


2-{[(4-chlorophenoxy)methyl]sulfonyl}-1,3-benzothiazole (2b). ^{1}H NMR (500 MHz, Acetone-d_6): δ 7.96 (d, J = 8.0 Hz, 1H), 7.86 (d, J = 8.1 Hz, 1H), 7.65 (m, 2H), 7.48 (d, J = 7.1 Hz, 2H), 7.38 (d, J = 7.3 Hz, 2H), 5.94 (s, 2H). ^{13}C NMR (125 MHz, Acetone-d_6): δ 165.55, 156.68, 153.66, 138.06, 130.21, 129.22, 128.82, 128.52, 126.02, 123.88, 118.75, 82.87. HRMS (FAB) calcd. for $C_{14}H_{11}NO_3S_2Cl$ 339.9867, found 339.9868.

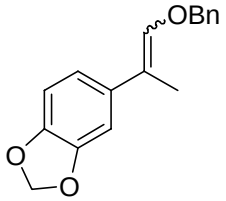


2-{[(2-methoxyethoxy)methyl]sulfonyl}-1,3-benzothiazole (2c). ^{1}H NMR (500 MHz, Acetone-d_6): 8.29 (d, J = 7.5 Hz, 1H), 8.24 (d, J = 7.5 Hz, 1H), 7.71 (m, 2H), 5.20 (s, 2H), 3.99 (t, J = 3.0 Hz, 2H), 3.46 (t, J = 3.0 Hz, 2H), 3.21 (s, 3H).

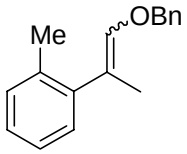
General procedure for the synthesis of vinyl ether. To a solution of sulfone (1.56 mmol, 1.2 eq) and ketone or aldehyde (1.3 mmol, 1.0 eq) in THF (15 mL, 0.085M) at 0°C, was added LiHMDS (3.1 mL, 3.1 mmol, 2.4 eq, 1M in THF) dropwise over 2 min. The reaction was stirred at 0°C for 90 min and quenched with 20 mL of NH_4Cl sat., extracted 3 times with 50 mL of EtOAc, washed with 20 mL of brine, dried over $MgSO_4$ and concentrated. The crude product was purified by combi-flash or flash chromatography to afford the desired vinyl ether.



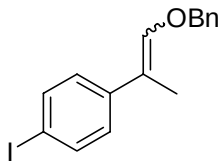
1-[-2-(benzyloxy)-1-methylvinyl]-4-methoxybenzene (3). ^{1}H NMR (500 MHz, Acetone-d_6): δ (trans) 7.42-7.34 (m, 5H), 7.23 (d, J = 7.2 Hz, 2H), 6.84 (m, 2H), 6.66 (s, 1H), 4.94 (s, 2H), 3.74 (s, 3H), 1.96 (s, 3H). δ (cis) 7.63 (d, J = 7.3 Hz, 2H), 7.42-7.29 (m, 5H), 6.84 (m, 2H), 6.33 (s, 1H), 4.91 (s, 2H), 3.76 (s, 3H), 1.86 (s, 3H). ^{13}C NMR (125 MHz, Acetone-d_6): δ (mixture of cis and trans) 153.03, 158.68, 143.69, 143.19, 139.06, 138.90, 133.72, 131.77, 129.39, 128.25, 128.59, 128.31, 128.23, 126.59, 114.49, 113.90, 110.88, 74.86, 74.39, 55.40, 55.33, 18.46, 12.93. HRMS (FAB) calcd. for $C_{17}H_{19}O_2$ 255.1385, found 255.1385.



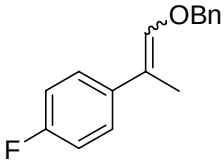
5-[-2-(benzyloxy)-1-methylvinyl]-1,3-benzodioxole (4). ^{1}H NMR (500 MHz, Acetone-d_6): δ (trans) 7.42-7.34 (m, 5H), 7.30 (d, J = 6.4 Hz, 1H), 6.84 (s, 1H), 6.77 (d, J = 6.4 Hz, 1H), 5.93 (s, 2H), 4.96 (s, 2H), 1.93 (s, 3H). δ (cis) 7.42-7.34 (m, 5H), 7.06 (d, J = 8.2 Hz, 1H), 6.77 (d, J = 8.2 Hz, 1H), 6.68 (s, 1H), 5.93 (s, 2H), 4.93 (s, 2H), 1.84 (s, 3H). ^{13}C NMR (125 MHz, Acetone-d_6) δ (mixture of cis and trans) 148.68, 148.10, 146.76, 146.41, 144.16, 143.67, 138.99, 138.77, 135.73, 133.45, 129.29, 129.25, 129.07, 128.68, 128.61, 128.34, 128.31, 128.25, 121.38, 118.83, 114.68, 110.91, 109.04, 108.74, 108.30, 106.04, 101.72, 101.62, 74.99. 74.47, 69.86, 18.70, 13.09. HRMS (FAB) calcd. for $C_{17}H_{17}O_3$ 269.1178, found 269.1178.



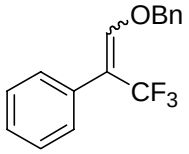
Benzyl-2-(2-methylphenyl)prop-1-en-1-yl ether (5). ^{1}H NMR (500 MHz, Acetone-d_6): δ (trans) 7.43-7.04 (m, 9H), 6.26 (s, 1H), 4.75 (s, 2H), 2.22 (s, 3H), 1.79 (s, 3H). δ (cis) 7.43-7.04 (m, 9H), 6.12 (s, 1H), 4.91 (s, 2H), 2.22 (s, 3H), 1.90 (s, 3H). ^{13}C NMR (125 MHz, Acetone-d_6): δ (mixture of cis and trans) 145.04, 142.00, 141.84 140.51, 139.11, 138.93, 136.82, 136.56, 130.88, 130.44, 130.19, 129.35, 129.25, 129.14, 128.59, 128.51, 128.34, 128.32, 127.40, 127.23, 126.38, 126.20, 115.83, 114.11, 74.18, 73.99, 30.74, 30.33, 30.17, 29.56, 29.40, 20.26, 19.90, 19.87, 15.55. HRMS (FAB) calcd. for $C_{12}H_{19}O$ 239.1436, found 239.1436.



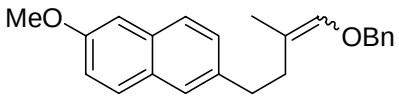
Benzyl-2-(4-iodophenyl)prop-1-en-1-yl ether (6). ^{1}H NMR (500 MHz, Acetone-d_6): δ (trans) 7.59 (d, J = 8.1 Hz, 2H), 7.49-7.31 (m, 5H), 7.14 (d, J = 8.1 Hz, 2H), 6.87 (s, 1H), 5.00 (s, 2H), 1.95 (s, 3H). δ (cis) 7.64 (d, J = 8.1 Hz, 2H), 7.49-7.31 (m, 5H), 7.42 (d, J = 8.1 Hz, 2H), 6.48 (s, 1H), 4.96 (s, 2H), 1.86 (s, 3H). ^{13}C NMR (125 MHz, Acetone-d_6): δ (mixture of cis and trans) 145.74, 145.49, 138.08, 137.65, 130.39, 129.34, 129.31, 128.75, 128.72, 128.36, 128.30, 127.56, 75.22, 74.73, 18.02, 12.39. HRMS (FAB) calcd. for $C_{16}H_{16}OI$ 351.0246, found 351.0247.



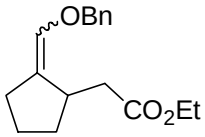
Benzyl-2-(4-fluorophenyl)prop-1-en-1-yl ether (7). ^{1}H NMR (500 MHz, Acetone-d_6): δ 7.43-7.30 (m, 7H), 7.06-7.00 (m, 2H), 6.75 (s, 1H), 4.99 (s, 2H), 1.88 (s, 3H). δ (cis) 7.70 (t, J = 7.2 Hz, 2H), 7.43-7.30 (m, 5H), 7.06-7.00 (m, 2H), 6.43 (s, 1H), 4.95 (s, 2H), 1.96 (s, 3H). ^{13}C NMR (125 MHz, Acetone-d_6): δ (mixture of cis and trans) 144.95, 144.32, 138.89, 138.69, 130.07, 130.00, 129.31, 129.28, 129.11, 128.70, 128.66, 128.34, 128.29, 127.22, 127.16, 115.76, 115.59, 115.23, 115.06, 113.88, 110.24, 75.04, 74.57, 18.40, 12.87. HRMS (FAB) calcd. for $C_{16}H_{16}OF$ 243.1185, found 243.1185.



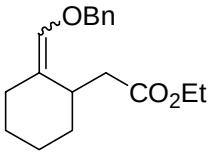
Benzyl-3,3,3-trifluoro-2-phenylprop-1-en-1-yl ether (8). ^{1}H NMR (500 MHz, Acetone-d_6): δ (trans) 7.46-7.28 (m, 11H), 5.20 (s, 2H). δ (cis) 7.46-7.28 (m, 10H), 6.96 (s, 1H), 5.17 (s, 2H). ^{13}C NMR (125 MHz, Acetone-d_6): δ (mixture of cis and trans) 154.68, 154.66, 152.12, 152.06, 137.55, 137.39, 133.84, 131.30, 129.49, 129.46, 129.25, 129.17, 129.06, 128.66, 128.50, 128.42, 76.73, 76.56. HRMS (FAB) calcd. for $C_{16}H_{14}OF_3$ 279.0997, found 279.0997.



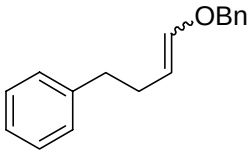
2-[4-(benzyloxy)but-3-en-1-yl]-6-methoxynaphthalene (9). ^{1}H NMR (500 MHz, Acetone-d_6): δ (trans) 7.70 (m, 2H), 7.58 (d, J = 7.5 Hz, 1H), 7.34-7.23 (m, 7H), 7.09 (m, 1H), 6.00 (s, 1H), 4.70 (s, 2H), 3.88 (s, 3H), 2.82 (t, J = 7.9 Hz, 2H), 2.47 (t, J = 7.9 Hz, 2H), 1.67 (s, 3H). δ (cis) 7.70 (m, 2H), 7.58 (d, J = 7.5 Hz, 1H), 7.34-7.23 (m, 7H), 7.09 (m, 1H), 5.97 (s, 1H), 4.67 (s, 2H), 3.88 (s, 3H), 2.82 (t, J = 7.9 Hz, 2H), 2.24 (t, J = 7.8 Hz, 2H), 1.54 (s, 3H). ^{13}C NMR (125 MHz, Acetone-d_6) : δ (mixture of cis and trans) 158.11, 142.19, 141.73, 139.27, 138.46, 138.21, 134.10, 130.04, 129.67, 129.12, 128.71, 128.62, 128.35, 128.15, 128.07, 127.49, 127.43, 127.02, 126.92, 119.32, 119.28, 114.22, 113.76, 106.43, 73.73, 55.51, 36.74, 35.43, 34.30, 31.77, 17.51, 13.33. HRMS (FAB) calcd. for $C_{23}H_{25}O_2$ 333.1855, found 333.1856.



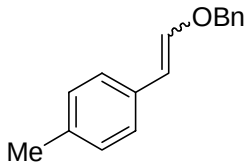
Ethyl {2-[(benzyloxy)methylene]cyclopentyl}acetate (10). ^{1}H NMR (500 MHz, Acetone-d_6) δ (mixture of cis and trans) 7.35-7.26 (m, 5H), 6.14 (s, 1H), 4.77 (s, 2H), 4.07-4.02 (m, 2H), 3.05 (m, 1H), 2.41-2.08 (m, 4H), 1.91-1.82 (m, 1H), 1.73-1.62 (m, 1H), 1.56-1.38 (m, 2H), 1.20-1.16 (m, 3H). ^{13}C NMR (125 MHz, Acetone-d_6) δ (mixture of cis and trans) 173.04, 172.74, 139.69, 139.47, 139.29, 139.17, 129.18, 129.13, 128.48, 128.40, 128.22, 128.17, 123.78, 123.31, 74.08, 73.96, 60.41, 60.28, 40.41, 38.76, 38.51, 37.27, 34.11, 33.57, 27.85, 25.88, 24.55, 14.57, 14.55. HRMS (FAB) calcd. for $C_{17}H_{23}O_3$ 275.1647, found 275.1643.



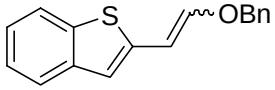
Ethyl {2-[(benzyloxy)methylene]cyclohexyl}acetate (11). ^{1}H NMR (500 MHz, Acetone-d_6) δ (mixture of cis and trans) 7.36-7.27 (m, 5H), 5.96 (s, 1H), 4.75* or 4.73‡(s, 2H), 4.03 (m, 2H), 3.37 (m, 1H), 2.48-2.26 (m, 2H), 2.13-1.84 (m, 2H), 1.69-1.28 (m, 6H), 1.16 (m, 3H). *denotes cis proton; ‡denotes trans proton. ^{13}C NMR (125 MHz, Acetone-d_6) δ (mixture of cis and trans) 172.73, 172.70, 139.43, 139.18, 138.95, 129.11, 128.39, 128.19, 120.50, 119.83, 73.92, 73.87, 60.42, 60.34, 38.28, 37.21, 37.06, 34.12, 31.59, 31.21, 28.94, 27.71, 27.56, 24.50, 24.33, 22.31, 14.57. HRMS (FAB) calcd. for $C_{18}H_{25}O_3$ 289.1804, found 289.1798.



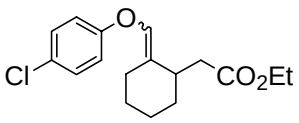
Benzyl-4-phenylbut-1-en-1-yl ether (12). ^{1}H NMR (500 MHz, Acetone-d_6): δ (trans) 7.34–7.17 (m, 10H), 6.38 (d, J = 12.5 Hz, 1H), 4.92-4.87 (m, 1H), 4.79 (s, 2H), 2.62 (t, J = 7.6 Hz, 2H), 2.39 (t, J = 7.5 Hz, 2H). δ (cis) 7.34–7.17 (m, 10H), 6.10 (d, J = 6.2 Hz, 1H), 4.71 (s, 2H), 4.39 (t, J = 6.9 Hz, 1H), 2.62 (t, J = 7.6 Hz, 2H), 2.22 (t, J = 7.5 Hz, 2H). ^{13}C NMR (125 MHz, Acetone-d_6) δ (mixture of cis and trans) 147.44, 146.17, 143.08, 142.78, 139.06, 138.63, 129.31, 129.20, 129.14, 129.03, 128.99, 128.48, 128.42, 128.26, 128.14, 126.52, 126.46, 106.72, 104.52, 74.03, 71.42, 37.94, 36.54, 30.66, 26.69. HRMS (FAB) calcd. for $C_{17}H_{19}O$ 239.1436, found 239.1436.



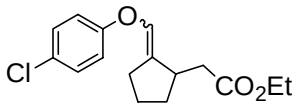
Benzyl-2-(4-methylphenyl)vinyl ether (13). ^{1}H NMR (500 MHz, Acetone-d_6) δ (trans) 7.42-7.36 (m, 5H), 7.18 (d, J = 13.1 Hz, 1H), 7.16 (d, J = 6.3 Hz, 2H), 7.04 (d, J = 8.6 Hz, 2H), 5.95 (d, J = 13.2 Hz, 1H), 4.93 (s, 2H), 2.25 (s, 3H). δ (cis) 7.50 (d, J = 6.2 Hz, 2H), 7.42-7.36 (m, 5H), 7.32 (d, J = 4.7 Hz, 2H), 6.36 (d, J = 7.1 Hz, 1H), 5.22 (d, J = 7.1 Hz, 1H), 5.03 (s, 2H), 2.26 (s, 3H). ^{13}C NMR (125 MHz, Acetone-d_6) δ (mixture of cis and trans) 148.25, 146.92, 138.32, 135.69, 134.50, 134.33, 129.96, 129.52, 129.33, 129.24, 129.00, 128.75, 128.66, 128.49, 128.24, 125.76, 107.34, 106.51, 75.44, 72.40, 21.12, 20.98. HRMS (FAB) calcd. for $C_{16}H_{17}O$ 225.1279, found 225.1279.



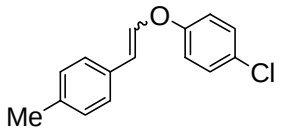
2-(1-benzothien-2-yl)vinyl benzyl ether (14). ^{1}H NMR (500 MHz, Acetone-d_6) δ (trans) 7.75 (d, J = 7.8 Hz, 1H), 7.63 (d, J = 7.7 Hz, 1H), 7.51-7.21 (m, 8H), 7.08 (s, 1H), 6.31 (d, J = 12.7 Hz, 1H), 5.00 (s, 2H). δ (cis) 7.81 (d, J = 7.8 Hz, 1H), 7.69 (d, J = 7.8 Hz, 1H), 7.51-7.21 (m, 8H), 6.58 (d, J = 6.5 Hz, 1H), 5.80 (d, J = 6.5 Hz, 1H), 5.14 (s, 2H). ^{13}C NMR (125 MHz, Acetone-d_6) δ (mixture of cis and trans) 150.47, 147.71, 141.44, 141.16, 140.78, 140.49, 139.78, 138.38, 138.30, 137.80, 129.37, 129.33, 129.16, 128.90, 128.87, 128.84, 128.72, 128.65, 128.57, 128.31, 125.23, 125.00, 124.93, 124.66, 124.54, 124.38, 123.53, 123.29, 122.68, 122.63, 121.54, 120.57, 102.54, 101.68, 75.68, 72.99. HRMS (FAB) calcd. for $C_{17}H_{15}OS$ 267.0844, found 267.0837.



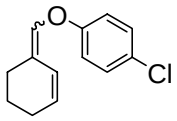
Ethyl {2-[(4-chlorophenoxy)methylene]cyclohexyl}acetate (15). ^{1}H NMR (500 MHz, Acetone-d_6) δ (mixture of cis and trans) 7.32 (m, 2H), 7.01 (m, 2H), 6.30* (s, 1H) or 6.29‡(m, 1H), 4.11‡(m, 2H) or 3.97* (m, 2H), 2.75 (m, 9H), 1.20‡(t, J = 7.1 Hz, 3H) or 1,12* (t, J = 7.1 Hz, 3H). *denotes cis proton; ‡denotes trans proton. HRMS (FAB) calcd. for $C_{17}H_{22}ClO_3$ 309.1257, found 309.1252.



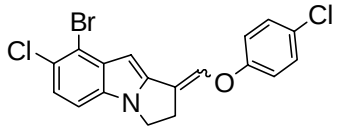
Ethyl {2-[(4-chlorophenoxy)methylene]cyclopentyl}acetate (16). ^{1}H NMR (500 MHz, Acetone-d_6): δ (trans) 7.34-7.31 (m, 2H), 7.04-7.01 (m, 2H), 6.49 (s, 1H), 4.11 (q, J = 7.1 Hz, 2H), 3.15 (m, 1H), 2.74 (m, 1H), 2.37 (m, 3H), 1.94 (m, 2H), 1.57 (m, 2H), 1.21 (t, J = 7.1 Hz, 3H). δ (cis) 7.34-7.31 (m, 2H), 7.04-7.01 (m, 2H), 6.49 (s, 1H), 4.02 (q, J = 7.0 Hz, 2H), 2.96 (m, 1H), 2.59 (m, 1H), 2.37 (m, 2H), 2.25 (m, 1H), 1.75 (m, 2H), 1.46 (m, 2H), 1.16 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, Acetone-d_6) δ (mixture of cis and trans) 172.73, 172.63, 157.37, 157.26, 134.76, 134.50, 131.69, 131.17, 130.29, 130.03, 127.39, 127.18, 118.18, 118.04, 60.60, 60.43, 39.90, 38.74, 37.44, 33.93, 33.43, 27.93, 25.68, 24.44, 14.46, 14.50. HRMS (FAB) calcd. for $C_{16}H_{20}O_3Cl$ 295.1101, found 295.1100. Anal. Calcd for $C_{16}H_{19}O_3Cl$: C, 65.19%; H, 6.50%; found: C, 64.72%; H, 6.78%.



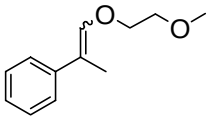
4-chlorophenyl-2-(4-methylphenyl)vinyl ether (17). ^{1}H NMR (500 MHz, Acetone-d_6) δ (trans) 7.41-7.36 (m, 2H), 7.31 (d, J = 7.4 Hz, 2H), 7.20-7.11 (m, 5H), 6.35 (d, J = 12.4 Hz, 1H), 2.29 (s, 3H). δ (cis) 7.56 (d, J = 7.5 Hz, 2H), 7.38 (d, J = 7.7 Hz, 2H), 7.20-7.11 (m, 4H), 6.70 (d, J = 6.5 Hz, 1H), 5.70 (d, J = 6.5 Hz, 1H), 2.29 (s, 3H). ^{13}C NMR (125 MHz, Acetone-d_6) δ (mixture of cis and trans) 156.89, 156.82, 143.10, 141.29, 137.17, 137.13, 132.91, 130.57, 130.47, 130.09, 129.79, 129.55, 128.56, 128.25, 126.60, 118.93, 115.00, 111.74, 21.21, 21.12. HRMS (FAB) calcd. for $C_{15}H_{14}OCl$ 245.0733, found 245.0734.



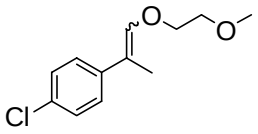
4-chlorophenylcyclohex-2-en-1-ylidenemethyl ether (18). ^{1}H NMR (500 MHz, Acetone-d_6) δ (trans) 7.33-7.29 (m, 2H), 7.06-7.00 (m, 2H), 6.57 (m, 1H), 6.33 (m, 1H), 5.83 (m, 1H), 2.30 (m, 2H), 2.13 (m, 2H), 1.67 (m, 2H). δ (cis) 7.33-7.29 (m, 2H), 7.06-7.00 (m, 2H), 6.54 (m, 1H), 6.12 (m, 1H), 5.74 (m, 1H), 2.45 (m, 2H), 2.13 (m, 2H), 1.67 (m, 2H). ^{13}C NMR (125 MHz, Acetone-d_6) δ (mixture of cis and trans) 157.26, 157.09, 138.13, 135.12, 130.38, 130.33, 128.18, 127.75, 127.55, 126.02, 122.44, 122.16, 120.68, 118.31, 118.20, 26.64, 26.03, 23.59, 23.06, 22.39. HRMS (FAB) calcd. for $C_{13}H_{14}OCl$ 221.0733, found 221.0733.



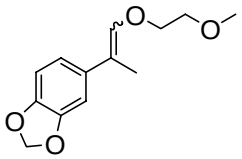
8-bromo-7-chloro-1-[(4-chlorophenoxy)methylene]-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole (19). ^{1}H NMR (500 MHz, Acetone-d_6): δ (trans) 7.68 (s, 1H), 7.42 (d, J = 8.9 Hz, 2H), 7.33 (d, J = 8.6 Hz, 1H), 7.23 (d, J = 8.9 Hz, 2H), 7.19, (d, J = 8.5 Hz, 2H), 6.49 (s, 1H), 4.31 (t, J = 6.9 Hz, 2H), 3.44 (t, J = 6.7 Hz, 2H). HRMS (FAB) calcd. for $C_{18}H_{13}NOCl_2Br$ 407.9558, found 407.9550.



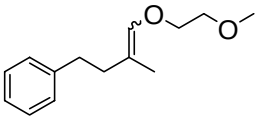
(2-methoxyethoxy-1-methylvinyl)benzene (20). See Kluge, A. F.; Cloudsdale, I. S. *J. Org. Chem.* **1979**, *44*, 4847.



1-chloro-4-[2-methoxyethoxy-1-methylvinyl]benzene (21). ^{1}H NMR (500 MHz, Acetone-d_6): δ (trans) 7.38-7.27 (m, 4H), 6.80 (s, 1H), 4.08 (t, *J* = 3.0 Hz, 2H), 3.60 (t, *J* = 3.0 Hz, 2H), 3.34 (s, 3H), 1.95 (s, 3H). δ (cis) 7.38-7.27 (m, 4H), 6.40 (s, 1H), 4.03 (t, *J* = 3.0 Hz, 2H), 3.60 (t, *J* = 3.0 Hz, 2H), 3.31 (s, 3H), 1.90 (s, 3H).



5-[2-methoxyethoxy-1-methylvinyl]-1,3-benzodioxole (22). ^{1}H NMR (500 MHz, Acetone-d_6): δ (trans) 6.86 (s, 1H), 6.75 (m, 2H), 6.60 (s, 1H), 5.93 (s, 2H), 3.95 (m, 2H), 3.57 (m, 2H), 3.34 (s, 3H), 1.90 (s, 3H). δ (cis) 7.38 (s, 1H), 7.05 (d, *J* = 6.9 Hz, 1H), 6.75 (m, 1H), 6.25 (s, 1H), 5.93 (s, 2H), 3.95 (m, 2H), 3.57 (m, 2H), 3.34 (s, 3H), 1.84 (s, 3H).



[4-(2-methoxyethoxy)-3-methylbut-3-en-1-yl]benzene (23). ^{1}H NMR (500 MHz, Acetone-d_6): δ (trans) 7.25–7.15 (m, 5H), 5.88 (s, 1H), 3.73 (t, *J* = 3.0 Hz, 2H), 3.44 (t, *J* = 3.0 Hz, 2H), 3.27 (s, 3H), 2.65 (t, *J* = 3.3 Hz, 2H), 2.33 (t, *J* = 3.3 Hz, 2H), 1.52 (s, 3H). δ (cis) 7.25–7.15 (m, 5H), 5.61 (s, 1H), 3.73 (t, *J* = 3.0 Hz, 2H), 3.44 (t, *J* = 3.0 Hz, 2H), 3.25 (s, 3H), 2.65 (t, *J* = 3.3 Hz, 2H), 2.14 (t, *J* = 3.3 Hz, 2H), 1.60 (s, 3H).