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Supporting Information

Phenyl sulfones 2a-f and iodobenzaldehyde 3g-i were prepared from the corresponding benzyl bromides and benzyl alcohols, respectively.

Preparation of 2-bromobenzyl phenyl sulfone (2a) (representative). A DMF solution (50 mL) of 2-bromobenzyl bromide (5.0 g, 20.0 mmol) and PhSO2Na (dihydrate, 4.80 g, 24.0 mmol) was heated at 80 °C for 12 h. After usual workup with CH2Cl2/water, the combined CH2Cl2 layer was washed with water (three times) and NaClaq, dried over MgSO4, filtered and evaporated. The crude mixture was dissolved in a small amount of CH2Cl2 by heating, and, after addition of hexane, the solution was kept in the refrigerator. 2-Bromobenzyl phenyl sulfone (2a) was obtained as colorless...
crystals in 88%. Bromo derivatives 2b and 2c were prepared in the same procedure.

**2-Bromobenzyl phenyl sulfone (2a):**[1] 88%; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 4.59 (s, 2H), 7.19 (t, $J = 8.5$ Hz, 1H), 7.33 (t, $J = 7.7$ Hz, 1H), 7.42-7.52 (m, 4H), 7.63 (t, $J = 8.9$ Hz, 3H).

**3-Bromobenzyl phenyl sulfone (2b):**[2] 93%; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 4.26 (s, 2H), 7.05 (d, $J = 7.7$ Hz, 1H), 7.15 (t, $J = 7.9$ Hz, 1H), 7.19 (s,1H), 7.43-7.54 (m, 3H), 7.65 (t, $J = 7.6$ Hz, 3H).

**4-Bromobenzyl phenyl sulfone (2c):**[2] 94%; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 4.26 (s, 2H), 6.96 (d, $J = 8.4$ Hz, 2H), 7.40 (d, $J = 8.4$ Hz, 2H), 7.48 (t, $J = 7.9$ Hz, 2H), 7.60-7.68 (m, 3H).

**Preparation of 2-iodobenzyl phenyl sulfone (2d) (representative).** To a CCl$_4$ solution (100 mL) of 2-iodotoluene (4.36 g, 20.0 mmol) and NBS (3.92 g, 22.0 mmol) was added benzoyl peroxide (484.5 mg, 2.0 mmol), and the mixture was heated at reflux for 12 h. After filtration of the mixture, the solid obtained was washed with CH$_2$Cl$_2$, and the filtrate was washed with NaHCO$_3$. The combined aqueous layer was extracted with AcOEt, and the CH$_2$Cl$_2$ and AcOEt layers were combined, dried over MgSO$_4$ and evaporated. The crude products were dissolved in AcOEt by heating, and, after addition of hexane, the solution was kept at r.t. 2-Iodobenzyl bromide was obtained as colorless crystals. A DMF solution (80 mL) of 2-iodobenzyl bromide obtained and PhSO$_2$Na (dihydrate, 4.80 g, 24.0 mmol) was heated at 80 °C for 12 h. After usual workup with CH$_2$Cl$_2$/water, the combined CH$_2$Cl$_2$ layer was washed with water (three times) and NaClaq, dried over MgSO$_4$, filtered and evaporated. The crude mixture was dissolved in a small amount of CH$_2$Cl$_2$ by heating, and, after addition of hexane, the solution was kept in the refrigerator. 2-Iodobenzyl phenyl sulfone (2d) was obtained as colorless crystals in 73%. Iodo derivatives 2e and 2f were prepared in the same procedure.

**2-Iodobenzyl phenyl sulfone (2d):**[3] 73%; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 4.59 (s, 2H), 7.02 (t, $J = 7.7$ Hz, 1H), 7.36 (t, $J = 7.7$ Hz, 1H), 7.43-7.53 (m, 3H), 7.61-7.67 (m, 3H), 7.74 (d, $J = 8.0$ Hz, 1H).
3-Iodobenzyl phenyl sulfone (2e): 74%; $^1$H NMR (300 MHz, CDCl$_3$) δ 4.23 (s, 2H), 7.02 (t, $J = 7.7$ Hz, 1H), 7.10 (d, $J = 7.2$ Hz, 1H), 7.35 (s, 1H), 7.47-7.52 (m, 2H), 7.62-7.67 (m, 4H).

4-Iodobenzyl phenyl sulfone (2f): 75%; $^1$H NMR (300 MHz, CDCl$_3$) δ 4.24 (s, 2H), 6.96 (d, $J = 8.3$ Hz, 2H), 7.49 (t, $J = 8.0$ Hz, 2H), 7.58-7.67 (m, 5H).

Preparation of 2-iodobenzaldehyde (3g) (representative). A suspension of 2-iodobenzyl alcohol (4.68 g, 20.0 mmol) and manganese oxide (6.96 g, 80.0 mmol) in pyridine (30 mL) was heated at 60 °C for 20 h. After filtration through a celite pad, the solid obtained was washed with water, and the aqueous layer was extracted with AcOEt. The combined organic layer was washed with NaClaq, dried over MgSO$_4$, filtered and evaporated. The crude mixture was subjected to column chromatography on silica gel (5% AcOEt/hexane) to furnish 3g in pure form (4.27 g, 92%). Iodo derivatives 3h and 3i were prepared in the same procedure.

2-Iodobenzaldehyde (3g):$^{[4]}$ 92%; $^1$H NMR (300 MHz, CDCl$_3$) δ 7.29 (t, $J = 7.7$ Hz, 1H), 7.47 (t, $J = 7.7$ Hz, 1H), 7.89 (d, $J = 7.7$ Hz, 1H), 7.96 (d, $J = 7.7$ Hz, 1H), 10.08 (s, 1H).

3-Iodobenzaldehyde (3h): 96%; $^1$H NMR (300 MHz, CDCl$_3$) δ 7.29 (t, $J = 7.7$ Hz, 1H), 7.85 (d, $J = 7.7$ Hz, 1H), 7.96 (d, $J = 7.7$ Hz, 1H), 8.21 (s, 1H), 9.93 (s, 1H).

4-Iodobenzaldehyde (3i):$^{[5]}$ 96%; $^1$H NMR (300 MHz, CDCl$_3$) δ 7.59 (d, $J = 8.2$ Hz, 2H), 7.92 (d, $J = 8.2$ Hz, 2H), 9.96 (s, 1H).
One-pot process for dihalo-substituted diphenylacetylene derivatives

![Chemical Reaction Diagram]

GLC analysis of crude products

![GLC Chromatograms]


