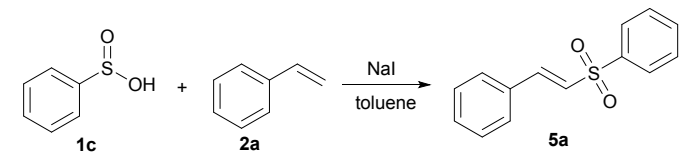


Supporting Information for:

Three-component oxysulfenylation reaction: two simple and convenient approaches to β -alkoxy sulfides

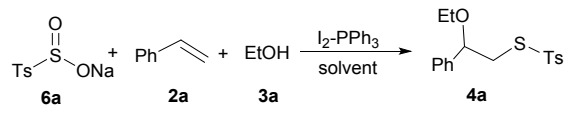
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Table S1 Optimization of reaction conditions^a

					
Entry	1c (eq.)	NaI (eq.)	HBr (eq.)	Temp (°C)	Yield ^b (%)
1	1	1.8	1.5	110	11
2	1	1.8	-	110	45
3	1	1.5	-	110	47
4	1.5	1.5	-	110	60
5	2.0	1.5	-	110	59
6	1.5	1.5	-	80	42

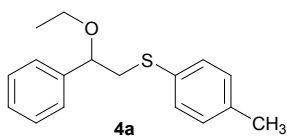
^aReaction conditions: sodium arenesulfonates **1c**, alkene **2** (0.20 mmol) and NaI in toluene (2.0 mL), 12 h, in air. ^bYield of isolated product.

Table S2 Optimization of reaction conditions^a

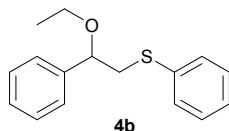
				
Entry	I ₂ (eq.)	PPh ₃ (eq.)	Solvent	Yield ^b (%)
1	1	1	DMF	trace
2	1	1	DMSO	trace
3	1	1	DCE	24
4	1	1	DME	15
5	1	1	EtOH	32
6	1	1	CH ₃ CN	27
7	1	1	Toluene	62
8	1	1.2	Toluene	65
9	1.2	1	Toluene	64
10 ^c	1	1.2	Toluene	55

^aReaction conditions: sodium arenesulfonates **1** (0.20 mmol), alkene **2** (0.24 mmol), alcohol **3** (60 μ L), I₂, PPh₃, toluene (1.5 mL), 75 °C, 24 h, in air. ^bYield of isolated product. ^c 15h.

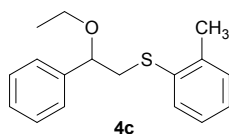
Analytical Data for the Products 4 and 5



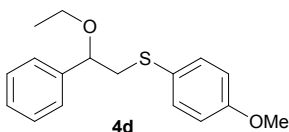
4a¹: colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.34-7.25 (m, 7H), 7.17-7.13 (m, 2H), 4.39-4.35 (m, 1H), 3.40-3.26 (m, 3H), 3.09-3.05 (m, 1H), 2.32 (s, 3H), 1.18 (t, J = 12.0 Hz, 3H).



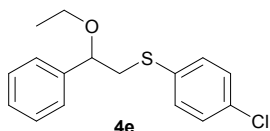
4b¹: colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.34-7.23 (m, 9H), 7.17-7.13 (m, 1H), 4.41-4.38 (m, 1H), 3.42-3.29 (m, 3H), 3.13-3.09 (m, 1H), 1.17 (t, J = 8.0 Hz, 3H).



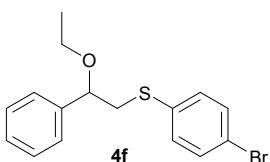
4c: colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.33-7.25 (m, 6H), 7.14-7.08 (m, 3H), 4.46-4.39 (m, 1H), 3.42-3.27 (m, 3H), 3.10-3.06 (m, 1H), 2.37 (s, 3H), 1.19 (t, J = 8.0 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 141.4, 137.8, 136.0, 130.0, 128.5, 128.4, 127.9, 126.6, 126.3, 125.7, 80.7, 64.6, 41.1, 20.4, 15.2. HRMS (ESI) m/z: calcd for C₁₇H₁₉OS: 271.1162 [M-H]⁻; found: 271.1167.



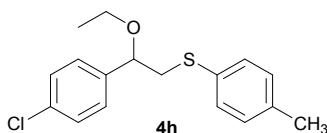
4d¹: colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.35-7.25 (m, 7H), 6.82 (d, J = 8.0 Hz, 2H), 4.34-4.31 (m, 1H), 3.79 (s, 3H), 3.40-3.20 (m, 3H), 3.03-2.98 (m, 1H), 1.17 (t, J = 8.0 Hz, 3H).



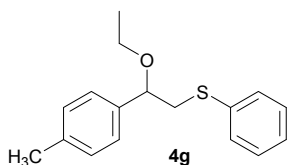
4e: colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.35-7.22 (m, 9H), 4.40-4.35 (m, 1H), 3.43-3.27 (m, 3H), 3.11-3.06 (m, 1H), 1.17 (t, J = 8.0 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 141.0, 135.3, 131.8, 130.6, 128.9, 128.5, 128.1, 126.6, 80.66, 64.7, 41.8, 15.2. HRMS (ESI) m/z: calcd for C₁₆H₁₆ClOS: 291.0616 [M-H]⁻; found: 291.0628.



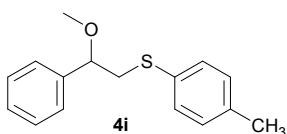
4f¹: colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.37-7.30 (m, 7H), 7.19 (d, J = 4.0 Hz, 2H), 4.40-4.35 (m, 1H), 3.43-3.27 (m, 3H), 3.11-3.07 (m, 1H), 1.17 (t, J = 4.0 Hz, 3H).



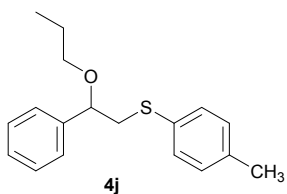
4h¹: colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.30-7.23 (m, 6H), 7.07 (m, 8.0 Hz, 2H), 4.34-4.31 (m, 1H), 3.36-3.23 (m, 3H), 3.04-3.00 (m, 1H), 2.31 (s, 3H), 1.16 (t, J = 12.0 Hz, 3H).



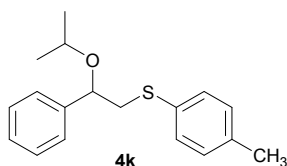
4g²: colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.34 (d, J = 4.0 Hz, 2H), 7.27-7.14 (m, 7H), 4.38-4.33 (m, 1H), 3.42-3.30 (m, 3H), 3.12-3.08 (m, 1H), 2.34 (s, 3H), 1.16 (t, J = 4.0 Hz, 3H).



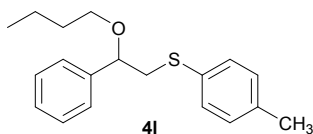
4i³: colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.37-7.25 (m, 7H), 7.08 (d, J = 8.0 Hz, 2H), 4.27-4.24 (m, 1H), 3.30-3.26 (m, 1H), 3.24 (s, 3H), 3.10-3.05 (m, 1H), 2.31 (s, 3H).



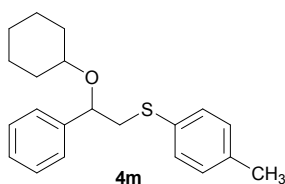
4j: colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.36-7.25 (m, 7H), 7.08 (d, J = 8.0 Hz, 2H), 4.38-4.34 (m, 1H), 3.32-3.22 (m, 3H), 3.09-3.05 (m, 1H), 2.31 (s, 3H), 1.61-1.55 (m, 2H), 0.90 (t, J = 4.0 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 141.4, 136.0, 133.2, 130.0, 129.6, 128.4, 127.8, 126.7, 80.9, 71.0, 42.4, 23.0, 20.9, 10.6. HRMS (ESI) m/z: calcd for C₁₈H₂₁OS: 285.1319 [M-H]⁻; found: 285.1314.



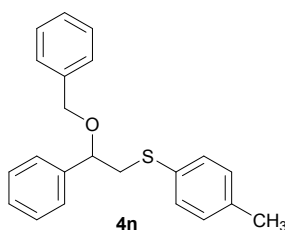
4k¹: colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.33-7.25 (m, 7H), 7.08 (d, J = 8.0 Hz, 2H), 4.50-4.47 (m, 1H), 3.52-3.49 (m, 1H), 3.25-3.22 (m, 1H), 3.08-3.04 (m, 1H), 2.31 (s, 3H), 1.15 (d, J = 4.0 Hz, 3H), 1.08 (d, J = 8.0 Hz, 3H).



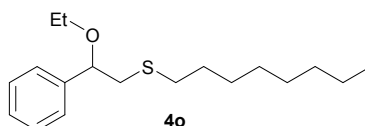
4l¹: colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.34-7.25 (m, 7H), 7.08 (d, J = 8.0 Hz, 2H), 4.37-4.34 (m, 1H), 3.35-3.26 (m, 3H), 3.09-3.05 (m, 1H), 2.31 (s, 3H), 1.56-1.52 (m, 2H), 1.37-1.36 (m, 2H), 0.88 (t, J = 8.0 Hz, 3H).



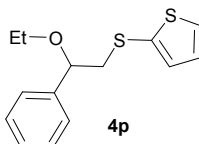
4m: colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.33-7.25 (m, 7H), 7.08 (d, J = 8.0 Hz, 2H), 4.56-4.53 (m, 1H), 3.28-3.17 (m, 3H), 3.08-3.04 (m, 1H), 2.31 (s, 3H), 1.90 (d, J = 8.0 Hz, 1H), 1.76-1.67 (m, 3H), 1.48-1.29 (m, 3H), 1.22-1.11 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 142.3, 135.8, 133.3, 129.6, 129.5, 128.3, 127.7, 126.6, 42.8, 33.3, 31.4, 25.8, 24.0, 21.0. HRMS (ESI) m/z : calcd for $\text{C}_{21}\text{H}_{25}\text{OS}$: 325.1632 $[\text{M}-\text{H}]^-$; found: 325.1628.



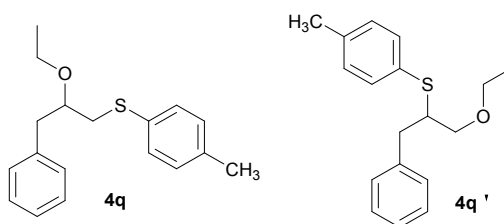
4n³: colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.48-7.20 (m, 12H), 7.05 (d, J = 8.0 Hz, 2H), 4.49 (d, J = 12.0 Hz, 2H), 4.30 (d, J = 12.0 Hz, 2H), 3.38-3.33 (m, 1H), 3.12-3.08 (m, 1H), 2.30 (s, 3H).



4o³: colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.37-7.27 (m, 5H), 4.39-4.36 (m, 1H), 3.40-3.38 (m, 2H), 2.95-2.90 (m, 1H), 2.71-2.66 (m, 1H), 2.47 (t, J = 8.0 Hz, 2H), 1.62-1.50 (m, 2H), 1.29-1.16 (m, 13H), 0.87 (t, J = 8.0 Hz, 3H).

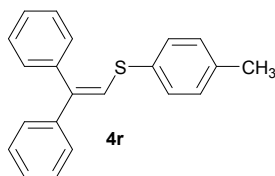


4p: colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.35-7.25 (m, 6H), 7.11 (d, J = 4.0 Hz, 1H), 6.97-6.94 (m, 1H), 4.40-4.37 (m, 1H), 3.42-3.36 (m, 2H), 3.18-3.16 (m, 1H), 3.01-2.96 (m, 1H), 1.20 (t, J = 4.0 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 141.1, 135.0, 133.4, 129.1, 128.5, 128.0, 127.5, 126.7, 80.5, 64.7, 46.5, 15.3. HRMS (ESI) m/z : calcd for $\text{C}_{14}\text{H}_{15}\text{OS}_2$: 263.0570 $[\text{M}-\text{H}]^-$; found: 263.0571.

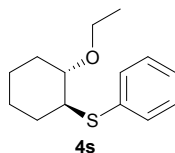


4q and **4q¹**, obtained as a 1:2 mixture of regioisomers, colorless oil; **4p**: ^1H NMR (400 MHz, CDCl_3) δ 7.31-7.18 (m, 7H), 7.08 (d, J = 8.0 Hz, 2H), 3.60-3.56 (m, 1H), 3.46-3.41 (m, 2H), 3.10-3.06 (m, 1H), 3.00-2.84 (m, 3H), 2.32 (s, 3H), 1.09 (t, J = 7.2 Hz, 3H). **4p'**: δ 7.31-7.18 (m, 7H), 7.08 (d, J =

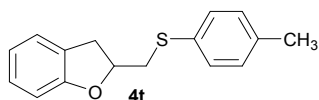
8.4 Hz, 2H), 3.46–3.41 (m, 5H), 2.87–2.84 (m, 2H), 2.32 (s, 3H), 1.19 (t, $J = 4.0$ Hz, 3H).



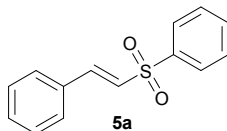
4r¹: white solid; ^1H NMR (400 MHz, CDCl_3) δ 7.43–7.12 (m, 12H), 7.13 (d, $J = 8.0$ Hz, 2H), 6.82 (s, 1H), 2.33 (s, 3H).



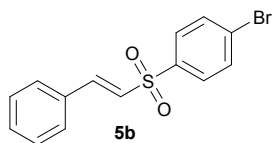
4s: colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.45 (d, $J = 4.0$ Hz, 2H), 7.29–7.18 (d, $J = 8.4$ Hz, 3H), 3.64–3.60 (m, 1H), 3.52–3.48 (m, 1H), 3.21–3.16 (m, 2H), 2.11–2.02 (m, 2H), 1.71–1.63 (m, 2H), 1.41–1.26 (m, 4H), 1.16 (t, $J = 8.0$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 140.5, 135.8, 132.0, 128.6, 126.5, 80.4, 64.6, 51.4, 31.5, 31.0, 24.8, 23.5, 15.6. HRMS (ESI) m/z : calcd for $\text{C}_{14}\text{H}_{20}\text{OSNa}$: 259.1127 $[\text{M}+\text{Na}]^+$; found: 259.1113.



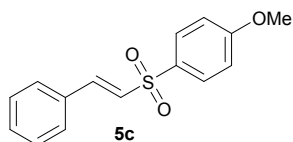
4t¹, colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.34 (d, $J = 4.0$ Hz, 2H), 7.16–7.11 (m, 4H), 6.87–6.83 (m, 1H), 6.77–6.74 (m, 1H), 4.92–4.86 (m, 1H), 3.35–3.31 (m, 2H), 3.07–3.03 (m, 2H), 2.33 (s, 3H).



5a⁵, pale yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ 7.97 (d, $J = 12.0$ Hz, 2H), 7.69 (d, $J = 16.0$ Hz, 1H), 7.61 (d, $J = 8.0$ Hz, 1H), 7.57–7.53 (m, 2H), 7.49–7.47 (m, 2H), 7.40–7.36 (m, 3H), 6.87 (d, $J = 16$ Hz, 1H).



5b⁶, white solid; ^1H NMR (400 MHz, CDCl_3) δ 7.81 (d, $J = 8.0$ Hz, 2H), 7.69 (d, $J = 16.0$ Hz, 3H), 7.49–7.40 (m, 5H), 6.83 (d, $J = 16.0$ Hz, 1H).



5b⁷, white solid; ^1H NMR (400 MHz, CDCl_3) δ 7.86 (d, $J = 8.0$ Hz, 2H), 7.62 (d, $J = 12.0$ Hz, 1H), 7.45 (d, $J = 4.0$ Hz, 2H), 7.38 (s, 2H), 7.99 (d, $J = 8.0$ Hz, 2H), 6.84 (d, $J = 16.0$ Hz, 1H), 3.85 (s, 3H).

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