Palladium nanoparticles as efficient catalyst for C-S bond formation reactions

Mei-Na Zhang, Shahid Khan, Junjie Zhang and Ajmal Khan*

Department of Applied Chemistry, School of Science, and Xi’an Key Laboratory of Sustainable Energy Materials Chemistry, MOE Key Laboratory for Nonequilibrium Synthesis and Modulation of Condensed Matter Xi’an Jiaotong University, Xi’an 710049, P. R. China

E-mail: ajmalkhan@xjtu.edu.cn

Table of Contents

General experimental details .................................................................S2
General procedure for PdNPs catalyzed cross coupling of allylic cyclic carbonate 1 with sodium sulfinates 2 ..................................................................................................................S3
Characterization of products 3 ..............................................................S3-S18
X-ray crystallography of 3ba ......................................................................S18-S20
References ..........................................................................................S20
Transmission Electron Microscopy (TEM) analysis ....................................S21
NMR charts .........................................................................................S22-S65
General experimental details

Analytical thin-layer chromatography (TLC) was carried out using 0.2 mm commercial silica gel plates (Yantai Jiangyou Silica Gel Development Co., Ltd., silica gel HSGF 254). Preparative column chromatography employing silica gel (Qingdao Shenghai Fine Silica Gel Chemical Co., Ltd., 200-300 mesh) was performed according to the method of Still. Solvents for the chromatography are listed as volume/volume ratios. High-resolution mass spectra (HRMS) were performed at Instrumental Analysis Center of Xi’an Jiao Tong University using ESI method. Proton nuclear magnetic resonance (\(^1\)H NMR) spectra were recorded with a Varian Mercuryplus 400 (400 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, parts per million (ppm) downfield from tetramethylsilane or ppm relative to the center of the singlet at 7.26 ppm for deuteriochloroform. Coupling constants are reported in Hertz (Hz). Carbon-13 nuclear magnetic resonance (\(^{13}\)C NMR) spectra were recorded with a Varian Gemini 400 (100 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, ppm relative to the center of the triplet at 77.0 ppm for deuteriochloroform. \(^{13}\)C NMR spectra were routinely run with broadband decoupling. Pd\(_2\)(dba)\(_3\) and other palladium catalysts were purchased from Energy Chemicals and Aladin/Sigma-Aldrich companies and used as received. Substituted vinyl ethylene carbonates (VECs) were synthesized according to the previously reported procedure. Sodium sulfinates were prepared according to a method reported in the literature. All other chemicals were used as received from commercial resources.
General procedure for PdNPs catalyzed cross coupling of allylic cyclic carbonate 1 with sodium sulfinites

To an oven dried screw-cap reaction tube equipped with a magnetic stir bar, Pd$_2$(dba)$_3$ (2 mol%), allylic cyclic carbonate 1a (0.2 mmol), sodium benzenesulfinate (0.3 mmol) and THF (1 mL) were added. The resulting mixture was stirred at room temperature for 15 hours. After the completion of reaction, the product 3aa was isolated either by using flash column chromatography or by simple filtration. The $Z/E$ ratio of the products were determined by $^1$H-NMR analysis.

Scale-up Experiment: To an oven dried screw-cap reaction tube equipped with a magnetic stir bar, Pd$_2$(dba)$_3$ (2 mol%), vinyl cyclic carbonate 1a (5.0 mmol, 0.951 g), sodium benzenesulfinate (7.5 mmol, 1.23 g) and THF (10 mL) were added. The resulting mixture was stirred at room temperature for 15 hours. After the completion of reaction, the residue was purified by flash column chromatography to afford the product 3aa in 90% yield (1.3 g).

(Z)-2-phenyl-4-(phenylsulfonyl)but-2-en-1-ol (3aa) was prepared according to the general procedure from 1a and 2a. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a yellow solid in 92% yield (53.0 mg). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.91–7.88 (m, 2H), 7.68–7.64 (m, 1H), 7.58–7.53 (m, 2H), 7.41–7.38 (m, 2H), 7.35–7.29 (m, 3H), 5.70 (t, $J = 8.4$ Hz, 1H), 4.37 s, 2H), 4.14 (d, $J = 8.4$ Hz, 2H), 2.76 (brs, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 148.9, 139.8, 138.5, 134.0, 129.3, 128.5, 128.2, 128.1, 126.3, 115.0, 60.0, 55.9; HRMS (ESI-MS): Calcd. for C$_{16}$H$_{16}$O$_3$S (M + Na): 311.0718, Found: 311.0724.

(Z)-2-phenyl-4-tosylbut-2-en-1-ol (3ab) was prepared according to the general procedure from 1a and 2b. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a white solid in 90% yield (44.4 mg). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.80–7.77 (m, 2H), 7.44–7.41 (m, 2H), 7.38–7.31 (m, 5H), 5.71 (t, $J = 8.4$ Hz, 1H), 4.42 (d, $J = 6.4$ Hz, 2H), 4.12 (d, $J = 8.4$ Hz, 2H), 2.68 (brt, 1H), 2.45 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 149.0, 145.2, 139.9, 135.7, 130.0, 128.5, 128.4,
128.3, 126.4, 115.2, 60.2, 56.0, 21.6; HRMS (ESI-MS): Calcd. for C_{17}H_{18}O_{3}S (M + Na): 325.0874, Found: 325.0891.

(Z)-4-[[1,1'-biphenyl]-4-ylsulfonyl]-2-phenylbut-2-en-1-ol (3ac) was prepared according to the general procedure from 1a and 2c. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a white solid in 93% yield (67.8 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.99–7.96 (m, 2H), 7.80–7.77 (m, 2H), 7.63–7.60 (m, 2H), 7.52–7.43 (m, 5H), 7.37–7.32 (m, 3H), 5.76 (t, $J$ = 8.4 Hz, 1H), 4.47 (d, $J$ = 6.4 Hz, 2H), 4.19 (d, $J$ = 8.4 Hz, 2H), 2.66 (brt, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 149.3, 147.1, 139.9, 138.9, 137.2, 129.1, 128.9, 128.8, 128.4, 127.9, 127.4, 126.5, 115.0, 60.4, 56.1; HRMS (ESI-MS): Calcd. for C$_{22}$H$_{20}$O$_3$S (M + Na): 387.1031, Found: 387.1023.

(Z)-4-((4-chlorophenyl)sulfonyl)-2-phenylbut-2-en-1-ol (3ad) was prepared according to the general procedure from 1a and 2d. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a white solid in 88% yield (56.8 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.87–7.84 (m, 2H), 7.58–7.54 (m, 2H), 7.44–7.42 (m, 2H), 7.39–7.33 (m, 3H), 5.70 (t, $J$ = 8.4 Hz, 1H), 4.46 (d, $J$ = 6.4 Hz, 2H), 4.16 (d, $J$ = 8.4 Hz, 2H), 2.58 (brt, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 149.4, 141.0, 139.7, 137.2, 129.9, 129.7, 128.7, 128.5, 126.4, 114.6, 60.4, 56.1; HRMS (ESI-MS): Calcd. for C$_{16}$H$_{15}$ClO$_3$S (M + Na): 345.0328, Found: 345.0336.

(Z)-4-((4-fluorophenyl)sulfonyl)-2-phenylbut-2-en-1-ol (3ae) was prepared according to the general procedure from 1a and 2e. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a white solid in 82% yield (50.2 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.95–7.90 (m, 2H), 7.43–7.39 (m, 2H), 7.37–7.31 (m, 3H), 7.27–7.22 (m, 2H), 5.69 (t, $J$ = 8.4 Hz, 1H), 4.42 (s, 2H), 4.15 (d, $J$ = 8.4 Hz, 2H), 2.71 (brs, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.3, 164.7, 149.2, 139.7, 134.6,
(Z)-4-(((4-nitrophenyl)sulfonyl)-2-phenylbut-2-en-1-ol (3af) was prepared according to the general procedure from 1a and 2f. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a white solid in 94% yield (62.7 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.41 (d, $J$ = 8.4 Hz, 2H), 8.13 (d, $J$ = 8.4 Hz, 2H), 7.41–7.35 (m, 5H), 5.70 (t, $J$ = 8.4 Hz, 1H), 4.46 (s, 2H), 4.25 (d, $J$ = 8.4 Hz, 2H), 2.44 (brs, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 151.0, 149.9, 144.3, 139.5, 130.0, 128.7, 128.6, 126.4, 124.5, 113.9, 60.6, 55.9; HRMS (ESI-MS): Calcd. for C$_{16}$H$_{15}$OFOS (M + Na): 329.0624, Found: 329.0632.

(Z)-4-(((2,4-dimethoxyphenyl)sulfonyl)-2-phenylbut-2-en-1-ol (3ag) was prepared according to the general procedure from 1a and 2g. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a white solid in 95% yield (66.2 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.52 (dd, $J$ = 2.1, 8.4 Hz, 1H), 7.46–7.42 (m, 2H), 7.37–7.31 (m, 3H), 7.29 (d, $J$ = 2.1 Hz, 1H), 6.99 (d, $J$ = 8.5 Hz, 1H), 5.71 (t, $J$ = 8.4 Hz, 1H), 4.43 (s, 2H), 4.14 (d, $J$ = 8.4 Hz, 2H), 3.96 (s, 3H), 3.84 (s, 3H), 2.77 (brs, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 153.6, 149.2, 148.7, 139.9, 130.1, 128.5, 128.3, 126.3, 122.5, 115.6, 110.8, 110.5, 60.1, 56.2, 56.1; HRMS (ESI-MS): Calcd. for C$_{18}$H$_{20}$O$_5$S (M + Na): 371.0929, Found: 371.0937.

(Z)-4-(((3,4-dichlorophenyl)sulfonyl)-2-phenylbut-2-en-1-ol (3ah) was prepared according to the general procedure from 1a and 2h. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a white solid in 92% yield (65.7 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.02 (d, $J$ = 2.1 Hz, 1H), 7.74 (dd, $J$ = 2.1, 8.4 Hz, 1H), 7.66 (d, $J$ = 8.4 Hz, 1H), 7.43–7.33 (m, 5H), 5.70 (t, $J$ = 8.4 Hz, 1H), 4.46 (s, 2H), 4.18 (d, $J$ = 8.3 Hz, 2H), 2.58 (brs, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 149.7,
(Z)-4-((3,5-bis(trifluoromethyl)phenyl)sulfonyl)-2-phenylbut-2-en-1-ol (3ai) was prepared according to the general procedure from 1a and 2i. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a white solid in 93% yield (78.9 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.41 (s, 2H), 8.20 (s, 1H), 7.43–7.31 (m, 5H), 5.72 (t, $J = 8.4$ Hz, 1H), 4.45 (s, 2H), 4.32 (d, $J = 8.4$ Hz, 2H), 2.31 (brs, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 150.0, 141.4, 139.3, 133.4, 133.0, 129.0, 128.7, 127.6, 126.4, 123.7, 120.9, 113.9, 60.7, 55.9; HRMS (ESI-MS): Calcd. for C$_{16}$H$_{14}$F$_6$O$_3$S (M + Na): 378.9938, Found: 378.9932.

(Z)-4-((3-bromophenyl)sulfonyl)-2-phenylbut-2-en-1-ol (3aj) was prepared according to the general procedure from 1a and 2j. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a white solid in 82% yield (60.2 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.07 (t, $J = 1.8$ Hz, 1H), 7.85–7.84 (m, 1H), 7.82–7.80 (m, 1H), 7.46 (t, $J = 8.0$ Hz, 1H), 7.42–7.41 (m, 2H), 7.37–7.33 (m, 3H), 5.70 (t, $J = 8.4$ Hz, 1H), 4.43 (s, 2H), 4.17 (d, $J = 8.4$ Hz, 2H), 2.60 (brs, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 149.5, 140.5, 139.7, 137.2, 131.3, 130.9, 128.6, 128.5, 126.9, 126.5, 123.4, 114.5, 60.3, 55.9; HRMS (ESI-MS): Calcd. for C$_{16}$H$_{15}$BrO$_3$S (M + Na): 388.9823, Found: 388.9831.

(Z)-4-((2-chlorophenyl)sulfonyl)-2-phenylbut-2-en-1-ol (3ak) was prepared according to the general procedure from 1a and 2k. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a white solid in 85% yield (54.8 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.10 (d, $J = 7.7$ Hz, 1H),
7.62–7.58 (m, 2H), 7.50–7.47 (m, 1H), 7.40–7.38 (m, 2H), 7.34–7.29 (m, 3H), 5.74 (t, J = 8.4 Hz, 1H), 4.52 (s, 2H), 4.47 (d, J = 8.4 Hz, 2H), 2.64 (brs, 1H); 13C NMR (100 MHz, CDCl3) δ 149.8, 139.8, 136.4, 135.1, 132.7, 132.1, 132.0, 128.5, 128.4, 127.6, 126.5, 114.0, 60.3, 53.8; HRMS (ESI-MS): Calcd. for C16H15ClO3S (M + Na): 345.0328, Found: 345.0336.

(Z)-4-((2-fluorophenyl)sulfonyl)-2-phenylbut-2-en-1-ol (3al) was prepared according to the general procedure from 1a and 2l. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a white solid in 81% yield (49.6 mg). 1H NMR (400 MHz, CDCl3) δ 7.94–7.91 (m, 1H), 7.70–7.66 (m, 1H), 7.41–7.39 (m, 2H), 7.36–7.27 (m, 5H), 5.76 (t, J = 8.4 Hz, 1H), 4.51 (s, 2H), 4.36 (d, J = 8.4 Hz, 2H), 2.64 (brs, 1H); 13C NMR (100 MHz, CDCl3) δ 160.4, 158.7, 149.8, 139.8, 136.6, 130.9, 128.5, 128.4, 126.5, 124.9, 117.3, 117.2, 113.9, 60.3, 55.2; HRMS (ESI-MS): Calcd. for C16H15FO3S (M + Na): 329.0624, Found: 329.0622.

(Z)-4-(naphthalen-2-ylsulfonyl)-2-phenylbut-2-en-1-ol (3am) was prepared according to the general procedure from 1a and 2m. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a white solid in 92% yield (62.3 mg). 1H NMR (400 MHz, CDCl3) δ 8.49 (s, 1H), 8.03–7.87 (m, 4H), 7.72–7.63 (m, 2H), 7.43–7.39 (m, 2H), 7.36–7.30 (m, 3H), 5.74 (t, J = 8.4 Hz, 1H), 4.43 (d, J = 8.0 Hz, 2H), 4.22 (d, J = 8.4 Hz, 2H), 2.69 (brt, 1H); 13C NMR (100 MHz, CDCl3) δ 149.2, 139.9, 135.5, 135.4, 132.1, 130.3, 129.6, 129.5, 129.4, 128.6, 128.3, 128.0, 127.9, 126.4, 122.8, 115.0, 60.3, 56.1; HRMS (ESI-MS): Calcd. for C20H16O3S (M + Na): 361.0874, Found: 361.0879.

(Z)-2-phenyl-4-(pyridin-3-ylsulfonyl)but-2-en-1-ol (3an) was prepared according to the general procedure from 1a and 2n. The crude product was purified by flash column chromatog-
raphy (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a white solid in 93% yield (53.8 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.09 (d, $J = 2.0$ Hz, 1H), 8.86 (dd, $J = 1.5$, 4.8 Hz, 1H), 7.52–7.45 (m, 2H), 7.39–7.37 (m, 2H), 7.35–7.31 (m, 3H), 5.70 (t, $J = 8.4$ Hz, 1H), 4.39 (s, 2H), 4.23 (d, $J = 8.4$ Hz, 2H), 2.93 (brs, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 154.4, 149.2, 139.6, 136.2, 135.1, 132.0, 128.6, 128.4, 126.4, 123.8, 114.3, 60.3, 56.2; HRMS (ESI-MS): Calcd. for C$_{15}$H$_{15}$NO$_3$S ($M + Na$): 312.0670, Found: 312.0678.

(Z)-2-phenyl-4-(thiophen-2-ylsulfonyl)but-2-en-1-ol (3ao) was prepared according to the general procedure from 1a and 2o. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a white solid in 92% yield (66.0 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.75 (dd, $J = 1.3$, 5.0 Hz, 1H), 7.69 (dd, $J = 1.3$, 5.0 Hz, 1H), 7.46–7.42 (m, 2H), 7.39–7.32 (m, 3H), 7.17 (dd, $J = 3.8$, 5.2 Hz, 1H), 5.77 (t, $J = 8.4$ Hz, 1H), 4.43 (s, 2H), 4.25 (d, $J = 8.4$ Hz, 2H), 2.53 (brs, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 149.2, 139.7, 139.3, 134.7, 128.6, 128.3, 128.0, 126.5, 115.1, 60.2, 57.1; HRMS (ESI-MS): Calcd. for C$_{14}$H$_{14}$O$_3$S ($M + Na$): 317.0282, Found: 317.0276.

(Z)-4-(methylsulfonyl)-2-phenylbut-2-en-1-ol (3ap) was prepared according to the general procedure from 1a and 2p. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a colorless oil in 82% yield (37.1 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.50–7.46 (m, 2H), 7.38–7.32 (m, 3H), 5.92 (t, $J = 8.4$ Hz, 1H), 4.56 (s, 2H), 4.09 (d, $J = 8.4$ Hz, 2H), 3.07 (brs, 1H), 2.94 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 149.0, 139.9, 132.0, 128.6, 126.4, 115.1, 60.5, 54.4, 40.1; HRMS (ESI-MS): Calcd. for C$_{11}$H$_{16}$O$_3$S ($M + Na$): 249.2798, Found: 249.2804.

(Z)-4-(ethylsulfonyl)-2-phenylbut-2-en-1-ol (3aq) was prepared according to the general procedure from 1a and 2q. The crude product was purified by flash column chromatography.
(Petroleum ether/EtOAc = 5:1) on silica gel to provide the title compound as a colorless oil in 86% yield (41.3 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.52–7.49 (m, 2H), 7.39–7.31 (m, 3H), 5.90 (t, $J = 8.4$ Hz, 1H), 4.56 (s, 2H), 4.06 (d, $J = 8.4$ Hz, 2H), 3.07 (dd, $J = 7.5$, 15.0 Hz, 2H), 2.87 (brs, 1H), 1.44 (t, $J = 7.5$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 149.4, 140.0, 128.6, 128.4, 114.5, 60.6, 51.9, 47.0, 6.53; HRMS (ESI-MS): Calcd. for C$_{12}$H$_{16}$O$_3$S (M + Na): 263.0718, Found: 263.0726.

(Z)-4-(isopropylsulfonyl)-2-phenylbut-2-en-1-ol (3ar) was prepared according to the general procedure from 1a and 2r. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 5:1) on silica gel to provide the title compound as a colorless oil in 90% yield (45.3 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.52–7.49 (m, 2H), 7.38–7.31 (m, 3H), 5.89 (t, $J = 8.4$ Hz, 1H), 4.53 (s, 2H), 4.04 (d, $J = 8.4$ Hz, 2H), 3.25–3.15 (m, 1H), 3.10 (brs, 1H), 1.44 (s, 3H), 1.42 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 149.2, 140.1, 128.5, 128.2, 126.4, 114.3, 60.4, 53.0, 49.4, 15.2; HRMS (ESI-MS): Calcd. for C$_{13}$H$_{18}$O$_3$S (M + Na): 277.0874, Found: 277.0878.

(Z)-4-(cyclopropylsulfonyl)-2-phenylbut-2-en-1-ol (3as) was prepared according to the general procedure from 1a and 2s. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 5:1) on silica gel to provide the title compound as a colorless oil in 87% yield (44.0 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.54–7.49 (m, 2H), 7.40–7.31 (m, 3H), 5.97 (t, $J = 8.4$ Hz, 1H), 4.57 (s, 2H), 4.11 (d, $J = 8.4$ Hz, 2H), 2.87 (brs, 1H), 2.51–2.45 (m,1H), 1.33–1.26 (m, 2H), 1.12–1.06 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 148.9, 140.0, 128.6, 128.3, 114.9, 60.4, 29.7, 4.9; HRMS (ESI-MS): Calcd. for C$_{13}$H$_{16}$O$_3$S (M + Na): 275.0718, Found: 275.0723.
methyl (Z)-3-((4-hydroxy-3-phenylbut-2-en-1-yl)sulfonyl)propanoate (3at) was prepared according to the general procedure from 1a and 2t. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 5:1) on silica gel to provide the title compound as a colorless oil in 82% yield (49.0 mg). 1H NMR (400 MHz, CDCl3) δ 7.51–7.47 (m, 2H), 7.38–7.33 (m, 3H), 5.93 (t, J = 8.4 Hz, 1H), 4.56 (s, 2H), 4.12 (d, J = 8.4 Hz, 2H), 3.73 (s, 3H), 3.39 (t, J = 7.3 Hz, 2H), 3.05 (brs, 1H), 2.90 (t, J = 7.3 Hz, 2H); 13C NMR (100 MHz, CDCl3) δ 171.03, 149.1, 139.9, 132.0, 128.5, 126.4, 114.7, 60.5, 53.5, 52.5, 47.7, 26.8; HRMS (ESI-MS): Calcd. for C14H10O3S (M + Na): 321.0773, Found: 321.0781.

(Z)-4-(phenylsulfonyl)-2-(p-tolyl)but-2-en-1-ol (3ba) was prepared according to the general procedure from 1b and 2a. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a yellow solid in 92% yield (55.6 mg). 1H NMR (400 MHz, CDCl3) δ 7.92–7.89 (m, 2H), 7.70–7.66 (m, 1H), 7.60–7.55 (m, 2H), 7.33–7.30 (m, 2H), 7.17–7.14 (m, 2H), 5.68 (t, J = 8.4 Hz, 1H), 4.38 (s, 2H), 4.13 (d, J = 8.4 Hz, 2H), 2.62 (brs, 1H), 2.35 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 148.8, 138.6, 138.3, 136.8, 134.0, 129.3, 129.2, 128.3, 126.3, 114.1, 60.1, 56.0, 21.1; HRMS (ESI-MS): Calcd. for C17H18O3S (M + Na): 325.0874, Found: 325.0892.

(Z)-2-(4-(tert-butyl)phenyl)-4-(phenylsulfonyl)but-2-en-1-ol (3ca) was prepared according to the general procedure from 1c and 2a. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a yellow solid in 94% yield (64.8 mg). 1H NMR (400 MHz, CDCl3) δ 7.93–7.90 (m, 2H), 7.71–7.66 (m, 1H), 7.61–7.56 (m, 2H), 7.41–7.34 (m, 4H), 5.70 (t, J = 8.4 Hz, 1H), 4.41 (s, 2H), 4.15 (d, J = 8.4 Hz, 2H), 2.58 (brs, 1H), 1.32 (s, 9H); 13C NMR (100 MHz, CDCl3) δ 151.5, 148.7, 138.6, 136.7, 134.0, 129.3, 128.4, 126.1, 125.5, 114.1, 60.0, 56.0, 34.6, 31.2; HRMS (ESI-MS): Calcd. for C20H23O3S (M + Na): 367.1344, Found: 367.1352.
(Z)-2-(4-bromophenyl)-4-(phenylsulfonyl)but-2-en-1-ol (3da) was prepared according to the general procedure from 1d and 2a. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a yellow solid in 88% yield (64.5 mg). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.94–7.89 (m, 2H), 7.72–7.68 (m, 1H), 7.61–7.57 (m, 2H), 7.48–7.45 (m, 2H), 7.34–7.29 (m, 2H), 5.71 (t, \(J = 8.4\) Hz, 1H), 4.39 (s, 2H), 4.13 (d, \(J = 8.4\) Hz, 2H), 2.76 (brs, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 148.1, 138.8, 138.6, 134.2, 131.6, 129.4, 128.3, 128.0, 122.5, 115.4, 59.9, 55.9; HRMS (ESI-MS): Calcd. for C\(_{16}\)H\(_{15}\)BrO\(_3\)S (M + Na): 388.9823, Found: 388.9826.

(Z)-2-(4-chlorophenyl)-4-(phenylsulfonyl)but-2-en-1-ol (3ea) was prepared according to the general procedure from 1e and 2a. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a yellow solid in 91% yield (58.7 mg). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.91–7.88 (m, 2H), 7.71–7.67 (m, 1H), 7.60–7.56 (m, 2H), 7.38–7.29 (m, 4H), 5.70 (t, \(J = 8.4\) Hz, 1H), 4.38 (s, 2H), 4.13 (d, \(J = 8.4\) Hz, 2H), 2.75 (brs, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 148.0, 138.6, 138.3, 134.2, 134.1, 129.4, 128.7, 128.3, 127.7, 115.4, 60.0, 55.9; HRMS (ESI-MS): Calcd. for C\(_{16}\)H\(_{15}\)ClO\(_3\)S (M + Na): 345.0328, Found: 345.0336.

(Z)-2-(4-fluorophenyl)-4-(phenylsulfonyl)but-2-en-1-ol (3fa) was prepared according to the general procedure from 1f and 2a. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a yellow solid in 82% yield (50.2 mg). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.92–7.89 (m, 2H), 7.71–7.66 (m, 1H), 7.60–7.56 (m, 2H), 7.43–7.39 (m, 2H), 7.06–6.99 (m, 2H), 5.67 (t, \(J = 8.4\) Hz, 1H), 4.38 (s, 2H), 4.13 (d, \(J = 8.4\) Hz, 2H), 2.82 (brs, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 163.9, 161.5, 148.1, 138.5, 136.0, 135.9, 134.1, 129.4, 128.3, 128.2, 128.1, 122.5, 115.5, 115.3, 114.8, 60.0, 55.9; HRMS (ESI-MS): Calcd. for C\(_{16}\)H\(_{15}\)FO\(_3\)S (M + Na): 329.0624, Found: 329.0628.

S11
(Z)-4-(phenylsulfonyl)-2-(4-(trifluoromethyl)phenyl)but-2-en-1-ol (3ga) was prepared according to the general procedure from 1g and 2a. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a yellow solid in 82% yield (58.4 mg). 1H NMR (400 MHz, CDCl₃) δ 7.92–7.91 (m, 2H), 7.72–7.69 (m, 1H), 7.61–7.54 (m, 6H), 5.78 (t, J = 8.4 Hz, 1H), 4.44 (s, 2H), 4.15 (d, J = 8.4 Hz, 2H), 2.85 (brs, 1H); 13C NMR (100 MHz, CDCl₃) δ 148.1, 143.5, 138.5, 134.3, 129.5, 128.5, 128.3, 125.5, 116.9, 59.9, 55.8; HRMS (ESI-MS): Calcd. for C₁₅H₁₂F₄O₃S (M + Na): 379.0592, Found: 379.0598.

(Z)-2-(3-methoxyphenyl)-4-(phenylsulfonyl)but-2-en-1-ol (3ha) was prepared according to the general procedure from 1h and 2a. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a yellow solid in 92% yield (58.5 mg). 1H NMR (400 MHz, CDCl₃) δ 7.94–7.91 (m, 2H), 7.71–7.67 (m, 1H), 7.61–7.57 (m, 2H), 7.28–7.24 (m, 1H), 7.01–6.95 (m, 2H), 6.88–6.85 (m, 1H), 5.70 (t, J = 8.4 Hz, 1H), 4.40 (s, 2H), 4.14 (d, J = 8.4 Hz, 2H), 3.81 (s, 3H), 2.61 (brs, 1H); 13C NMR (100 MHz, CDCl₃) δ 159.7, 149.1, 141.4, 138.6, 134.1, 129.6, 129.4, 128.4, 118.9, 115.2, 113.7, 112.2, 60.3, 55.9, 55.3; HRMS (ESI-MS): Calcd. for C₁₅H₁₈O₃S (M + Na): 341.0823, Found: 341.0816.

(Z)-2-(3-nitrophenyl)-4-(phenylsulfonyl)but-2-en-1-ol (3ia) was prepared according to the general procedure from 1i and 2a. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a yellow solid in 96% yield (64.0 mg). 1H NMR (400 MHz, CDCl₃) δ 8.27 (t, J = 2.0 Hz, 1H), 8.18–8.16 (m, 1H), 7.94–7.92 (m, 2H), 7.85–7.83 (m, 1H), 7.75–7.71 (m, 1H), 7.64–7.60 (m, 2H), 7.54 (t, J = 8.0 Hz, 1H), 5.82 (t, J = 8.4 Hz, 1H), 4.48 (s, 2H), 4.18 (d, J = 8.4 Hz, 2H), 3.01 (brs, 1H); 13C NMR (100 MHz, CDCl₃) δ 148.3, 147.2, 141.6, 138.4, 134.4, 132.5, 129.6, 129.5, 128.2, 123.0, 121.4, 117.4, 59.8, 55.7; HRMS (ESI-MS): Calcd. for C₁₆H₁₅NO₃S (M + Na): 356.0569, Found: 356.0574.
(Z)-2-(2-methoxyphenyl)-4-(phenylsulfonyl)but-2-en-1-ol (3ja) was prepared according to the general procedure from 1j and 2a. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a yellow solid in 87% yield (55.4 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.95 (d, $J =$ 7.8 Hz, 2H), 7.68–7.55 (m, 3H), 7.30–7.27 (m, 1H), 7.11–7.08 (m, 1H), 6.95–6.85 (m, 2H), 5.82 (t, $J =$ 8.4 Hz, 1H), 4.15 (d, $J =$ 8.4 Hz, 2H), 4.13, (s, 2H), 3.79 (s, 3H), 2.50 (brs, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 156.1, 148.4, 138.6, 133.7, 130.2, 129.9, 129.3, 129.0, 128.4, 120.9, 118.1, 110.5, 60.8, 55.6, 55.4; HRMS (ESI-MS): Calcd. for C$_{17}$H$_{18}$O$_4$S (M + Na): 341.0823, Found: 341.0831.

(Z)-2-(2,4-dimethoxyphenyl)-4-(phenylsulfonyl)but-2-en-1-ol (3ka) was prepared according to the general procedure from 1k and 2a. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a yellow solid in 92% yield (64.1 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.97–7.94 (m, 2H), 7.93–7.89 (m, 1H), 7.60–7.56 (m, 2H), 7.05 (d, $J =$ 8.2 Hz, 1H), 6.48–6.44 (m, 2H), 5.57 (t, $J =$ 8.4 Hz, 1H), 4.15 (d, $J =$ 8.4 Hz, 2H), 4.13, (s, 2H), 3.81 (s, 3H), 3.79 (s, 3H), 2.33 (brs, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 161.0, 157.2, 148.2, 138.8, 133.8, 130.6, 129.1, 128.5, 123.0, 117.4, 104.6, 98.7, 61.0, 55.8, 55.5, 55.4; HRMS (ESI-MS): Calcd. for C$_{18}$H$_{20}$O$_5$S (M + Na): 371.0929, Found: 371.0936.

(Z)-2-(2,4-difluorophenyl)-4-(phenylsulfonyl)but-2-en-1-ol (3la) was prepared according to the general procedure from 1l and 2a. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a yellow solid in 91% yield (59.0 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.95–7.92 (m, 2H), 7.72–7.68 (m, 1H), 7.63–7.58 (m, 2H), 7.32–7.27 (m, 1H), 6.89–6.77 (m, 2H), 5.64 (t, $J =$ 8.4 Hz, 1H),
4.29 (s, 2H), 4.16 (d, \( J = 8.4 \text{ Hz}, 2H \)), 2.46 (brs, 1H); \(^{13}\text{C} \text{ NMR} (100 \text{ MHz, CDCl}_3) \delta 163.9, 163.8, 161.4, 161.3, 161.0, 160.9, 158.5, 158.4, 144.2, 138.4, 134.1, 131.0, 130.0, 129.3, 128.3, 118.9, 111.6, 111.4, 104.4, 104.1, 103.9, 60.8, 60.7, 50.6; HRMS (ESI-MS): Calcd. for \( \text{C}_{18}\text{H}_{14}\text{F}_2\text{O}_3\text{S} (\text{M} + \text{Na}) \): 347.0529, Found: 347.0534.

(Z)-2-(3,4-dichlorophenyl)-4-(phenylsulfonyl)but-2-en-1-ol (3ma) was prepared according to the general procedure from 1m and 2a. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a yellow solid in 90% yield (64.3 mg). \(^{1}\text{H} \text{NMR} (400 \text{ MHz, CDCl}_3) \delta 7.91–7.89 (m, 2H), 7.73–7.69 (m, 1H), 7.62–7.53 (m, 3H), 7.40 (d, \( J = 8.0 \text{ Hz}, 1H \)), 7.30–7.27 (m, 1H), 5.71 (t, \( J = 8.4 \text{ Hz}, 1H \)), 4.38 (s, 2H), 4.13 (d, \( J = 8.4 \text{ Hz}, 2H \)), 2.85 (brs, 1H); \(^{13}\text{C} \text{ NMR} (100 \text{ MHz, CDCl}_3) \delta 147.1, 139.9, 138.5, 134.3, 132.6, 132.3, 130.4, 129.5, 128.4, 128.2, 125.7, 116.4, 59.8, 55.8; HRMS (ESI-MS): Calcd. for \( \text{C}_{16}\text{H}_{14}\text{Cl}_2\text{O}_3\text{S} (\text{M} + \text{Na}) \): 378.9938, Found: 378.9942.

(Z)-2-(benzo[d][1,3]dioxol-5-yl)-4-(phenylsulfonyl)but-2-en-1-ol (3na) was prepared according to the general procedure from 1n and 2a. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a yellow solid in 86% yield (57.2 mg). \(^{1}\text{H} \text{NMR} (400 \text{ MHz, CDCl}_3) \delta 7.92–7.90 (m, 2H), 7.72–7.67 (m, 1H), 7.62–7.57 (m, 2H), 6.94 (dd, \( J = 1.8, 9.6 \text{ Hz}, 2H \)), 6.78 (d, \( J = 8.1 \text{ Hz}, 1H \)), 5.97 (s, 2H), 5.61 (t, \( J = 8.4 \text{ Hz}, 1H \)), 4.37 (s, 2H), 4.11 (d, \( J = 8.4 \text{ Hz}, 2H \)), 2.63 (brs, 1H); \(^{13}\text{C} \text{ NMR} (100 \text{ MHz, CDCl}_3) \delta 148.7, 147.9, 147.8, 138.6, 134.1, 134.0, 129.4, 128.4, 120.3, 113.8, 108.3, 106.9, 101.2, 60.2, 56.0; HRMS (ESI-MS): Calcd. for \( \text{C}_{17}\text{H}_{16}\text{O}_5\text{S} (\text{M} + \text{Na}) \): 355.0616, Found: 355.0623.

(Z)-2-(naphthalen-1-yl)-4-(phenylsulfonyl)but-2-en-1-ol (3oa) was prepared according to the general procedure from 1o and 2a. The crude product was purified by flash column chro-
matography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a yellow solid in 89% yield (60.2 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.98–7.96 (m, 2H), 7.86–7.82 (m, 1H), 7.80–7.78 (m, 2H), 7.69–7.65 (m, 1H), 7.59–7.55 (m, 2H), 7.50–7.39 (m, 3H), 7.26–7.24 (m, 1H), 5.55 (t, J = 8.4 Hz, 1H), 4.43 (s, 2H), 4.30 (d, J = 8.4 Hz, 2H), 2.59 (brs, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 149.6, 138.7, 138.5, 134.0, 133.6, 131.3, 131.1, 129.3, 128.4, 128.3, 128.2, 126.3, 125.9, 125.8, 125.2, 117.8, 62.7, 55.5; HRMS (ESI-MS): Calcd. for C₂₀H₁₈O₃S (M + Na): 361.0874, Found: 361.0876.

(Z)-2-(naphthalen-2-yl)-4-(phenylsulfonyl)but-2-en-1-ol (3pa) was prepared according to the general procedure from 1p and 2a. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a yellow solid in 85% yield (57.5 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.94–7.90 (m, 3H), 7.83–7.88 (m, 3H), 7.69–7.64 (m, 1H), 7.58–7.45 (m, 5H), 5.83 (t, J = 8.4 Hz, 1H), 4.51 (s, 2H), 4.18 (d, J = 8.4 Hz, 2H), 2.82 (brs, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 148.9, 138.6, 137.0, 134.1, 133.2, 133.0, 129.3, 128.3, 128.2, 128.1, 127.5, 126.4, 126.3, 125.6, 124.1, 115.4, 60.1, 56.1; HRMS (ESI-MS): Calcd. for C₁₄H₁₄O₃S (M + Na): 317.0282, Found: 317.0286.

(E)-4-(phenylsulfonyl)-2-(thiophen-2-yl)but-2-en-1-ol (3qa) was prepared according to the general procedure from 1q and 2a. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a yellow solid in 86% yield (50.6 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.92–7.89 (m, 2H), 7.72–7.67 (m, 1H), 7.61–7.56 (m, 2H), 7.24–7.21 (m, 2H), 7.02 (dd, J = 3.7, 5.2 Hz, 1H), 5.77 (t, J = 8.4 Hz, 1H), 4.46 (d, J = 5.4 Hz, 2H), 4.12 (d, J = 8.4 Hz, 2H), 2.77 (brt, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 143.0, 142.5, 138.6, 134.1, 129.4, 128.4, 127.8, 125.6, 125.4, 112.7, 60.0, 55.8; HRMS (ESI-MS): Calcd. for C₁₄H₁₂O₂S₂ (M + Na): 317.0282, Found: 317.0286.
(Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a colorless oil in 75% yield (33.9 mg). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.90–7.87 (m, 2H), 7.70–7.65 (m, 1H), 7.60–7.56 (m, 2H), 5.23 (t, \(J = 8.4\) Hz, 1H), 3.98 (s, 2H), 3.94 (d, \(J = 8.4\) Hz, 2H), 2.56 (brs, 1H), 1.85 (s, 3H); \(^1\)^C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 146.9, 138.7, 133.8, 129.2, 128.2, 111.8, 67.9, 61.8, 25.5; HRMS (ESI-MS): Calcd. for C\(_{11}\)H\(_{14}\)O\(_3\)S (M + Na): 249.0561, Found: 249.0554.

\(\text{Me}^\text{3s}\)a

\(\text{3s}\)a

(Z)-2-(2-(phenylsulfonyl)ethylidene)tridecan-1-ol (3sa) was prepared according to the general procedure from 1s and 2a. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a yellow solid in 80% yield (58.5 mg). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.90–7.87 (m, 2H), 7.70–7.65 (m, 1H), 7.59–7.56 (m, 2H), 5.20 (t, \(J = 8.4\) Hz, 1H), 4.01 (s, 2H), 3.97 (d, \(J = 8.4\) Hz, 2H), 2.39 (brs, 1H), 2.15 (t, \(J = 7.4\) Hz, 2H), 1.43–1.20 (m, 18H), 1.20 (s, 3H), 2.15 (t, \(J = 7.4\) Hz, 2H), 1.43–1.20 (m, 18H), 1.20 (s, 3H), 2.15 (t, \(J = 7.4\) Hz, 2H); \(^1\)^C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 151.1, 138.7, 133.9, 129.2, 128.3, 128.2, 128.3, 111.8, 60.7, 55.3, 35.9, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 27.8, 22.6, 14.1; HRMS (ESI-MS): Calcd. for C\(_{21}\)H\(_{34}\)O\(_3\)S (M + Na): 389.2126, Found: 389.2134.

\(\text{3ta}\)

(Z)-2-phenethyl-4-(phenylsulfonyl)but-2-en-1-ol (3ta) was prepared according to the general procedure from 1t and 2a. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a colorless oil in 82% yield (52.0 mg). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.82–7.80 (m, 2H), 7.68–7.63 (m, 1H), 7.57–7.52 (m, 2H), 7.30–7.27 (m, 2H), 7.22–7.16 (m, 3H), 5.22 (t, \(J = 8.4\) Hz, 1H), 4.04 (s, 2H), 3.94 (d, \(J = 8.4\) Hz, 2H), 2.75 (t, \(J = 7.4\) Hz, 2H), 2.53 (brs, 1H), 2.49 (t, \(J = 7.4\) Hz, 2H); \(^1\)^C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 150.0, 141.1, 138.6, 133.9, 129.2, 128.4, 128.3, 128.2, 126.0, 112.7, 60.6, 55.2, 37.5, 34.2; HRMS (ESI-MS): Calcd. for C\(_{18}\)H\(_{20}\)O\(_3\)S (M + Na): 339.1031, Found: 339.1026.

\(\text{3ua}\)

(Z)-2-(3,4-dimethoxybenzyl)-4-(phenylsulfonyl)but-2-en-1-ol (3ua) was prepared according to the general procedure from 1u and 2a. The crude product was purified by flash col-

S16
umn chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a white solid in 92% yield (66.7 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.85–7.83 (m, 2H), 7.66–7.63 (m, 1H), 7.54–7.51 (m, 2H), 6.78 (d, $J$ = 8.0 Hz, 1H), 6.71–6.68 (m, 2H), 5.24 (t, $J$ = 8.4 Hz, 1H), 3.99 (s, 2H), 3.98 (d, $J$ = 8.4 Hz, 2H), 3.86 (s, 6H), 2.45 (s, 2H), 2.42 (brs, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 150.2, 148.9, 147.6, 138.6, 133.9, 130.7, 129.2, 128.2, 121.1, 113.4, 112.2, 111.1, 60.1, 55.9, 55.2, 41.4; HRMS (ESI-MS): Calcd. for C$_{19}$H$_{22}$O$_3$S (M + Na): 385.1086, Found: 385.1082.

(Z)-2-(2-(benzyloxy)ethyl)-4-(phenylsulfonyl)but-2-en-1-ol (3va) was prepared according to the general procedure from 1v and 2a. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a colorless oil in 86% yield (59.5 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.86–7.82 (m, 2H), 7.63–7.59 (m, 1H), 7.51–7.45 (m, 2H), 7.36–7.27 (m, 5H), 5.31 (t, $J$ = 8.4 Hz, 1H), 4.48 (s, 2H), 3.92 (d, $J$ = 8.4 Hz, 2H), 3.91 (m, 2H), 3.56 (t, $J$ = 7.4 Hz, 2H), 2.99 (brs, 1H), 2.45 (t, $J$ = 7.4 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 147.9, 138.4, 137.6, 133.7, 129.0, 128.4, 128.3, 127.7, 127.6, 113.9, 73.1, 69.2, 60.2, 55.2, 36.0; HRMS (ESI-MS): Calcd. for C$_{19}$H$_{22}$O$_3$S (M + Na): 369.1136, Found: 369.1144.

(Z)-2-cyclohexyl-4-(phenylsulfonyl)but-2-en-1-ol (3wa) was prepared according to the general procedure from 1w and 2a. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a white solid in 95% yield (55.3 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.89–7.87 (m, 2H), 7.69–7.67 (m, 1H), 7.59–7.57 (m, 2H), 5.19 (t, $J$ = 8.4 Hz, 1H), 3.99 (s, 2H), 3.96 (d, $J$ = 8.4 Hz, 2H), 2.39 (brs, 1H), 2.07 (t, $J$ = 7.4 Hz, 2H), 1.78–1.67 (m, 4H), 1.31–1.08 (m, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 155.7, 138.5, 133.9, 129.2, 128.4, 111.1, 59.9, 55.4, 43.9, 32.1, 26.5, 26.1; HRMS (ESI-MS): Calcd. for C$_{16}$H$_{22}$O$_3$S (M + Na): 317.1187, Found: 317.1193.
(Z)-2,3-dimethyl-4-(phenylsulfonyl)but-2-en-1-ol (3xa) was prepared according to the general procedure from 1x and 2a. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a colorless oil in 77% yield (37.0 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.93–7.90 (m, 2H), 7.71–7.66 (m, 1H), 7.61–7.56 (m, 2H), 3.99 (s, 2H), 3.98 (s, 2H), 1.85 (s, 3H), 1.70 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 147.1, 140.4, 139.3, 133.9, 129.4, 128.3, 63.8, 61.2, 22.7, 14.1; HRMS (ESI-MS): Calcd. for C$_{12}$H$_{16}$O$_3$S (M + Na): 263.0718, Found: 263.726.

X-ray crystallography of 3ab

A single-crystal of 3ab was obtained from ethyl acetate/hexane solvent system at room temperature. A specimen of C$_{17}$H$_{18}$O$_3$S was used for the X-ray crystallographic analysis. The X-ray intensity data were measured ($\lambda = 1.34139$ Å). The total exposure time was 0.14 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 7276 reflections to a maximum $\theta$ angle of 56.67° (0.80 Å resolution), of which 2773 were independent (average redundancy 2.624, completeness = 99.3%, $R_{int} = 6.23\%$, $R_{sig} = 7.42\%$) and 2576 (92.90%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 5.5164(3)$ Å, $b = 8.0709(5)$ Å, $c = 17.2124(11)$ Å, $\beta = 96.454(2)^\circ$, volume = 761.48(8) Å$^3$, are based upon the refinement of the XYZ-centroids of 6767 reflections above 20 $\sigma(I)$ with 8.996° < $2\theta$ < 113.1°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.643. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 c 1, with Z = 2 for the formula unit, C$_{17}$H$_{18}$O$_3$S. The final anisotropic full-matrix least-squares refinement on $F^2$ with 192 variables converged at R1 = 4.93%, for the observed data and wR2 = 13.70% for all data. The good-
ness-of-fit was 0.854. The largest peak in the final difference electron density synthesis was 0.308 e/Å³ and the largest hole was -0.401 e/Å³ with an RMS deviation of 0.061 e/Å³. On the basis of the final model, the calculated density was 1.319 g/cm³ and F(000), 320 e⁻. The crystallographic data is summarized in Table F1 and the diagram is shown in Figure F1.

**Table F1. Crystal data and structure refinement for 3ab.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identification code</td>
<td>xb2305_4</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C17H18O3S</td>
</tr>
<tr>
<td>Formula weight</td>
<td>302.37 g/mol</td>
</tr>
<tr>
<td>Temperature</td>
<td>186(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>1.34139 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>space group</td>
<td>P 1 c 1</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 5.5164(3) Å   α = 90°</td>
</tr>
<tr>
<td></td>
<td>b = 8.0709(5) Å   β = 96.454(2)°</td>
</tr>
<tr>
<td></td>
<td>c = 17.2124(11) Å  γ = 90°</td>
</tr>
<tr>
<td>Volume</td>
<td>761.48(8) Å³</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>Calculated density</td>
<td>1.319 g/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>1.275 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>320</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.35 x 0.27 x 0.14 mm³</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>4.50 to 56.67°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-6≤h≤6, -10≤k≤10, -21≤l≤21</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>7276</td>
</tr>
<tr>
<td>Completeness to theta = 25.08</td>
<td>99.3 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Multi-Scan</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.9648 and 0.9159</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
</tbody>
</table>

S19
Data / restraints / parameters: 2773 / 2 / 192

Goodness-of-fit on $F^2$: 0.854

Final R indices [I>2sigma(I)]: $R_1 = 0.0493$, $wR_2 = 0.1311$

R indices (all data): $R_1 = 0.0553$, $wR_2 = 0.1370$

Absolute structure parameter: 0.07(2)

Largest diff. peak and hole: 0.308 and -0.401 eÅ$^{-3}$

Figure F1. Molecular structure of 3ab.

References:
2. B. Du, P. Qian, Y. Wang, H. Mei, J. Han, Y. Pan, Org. Lett. 2016, 18, 4144.
TEM study of PdNPs for the coupling reaction of 1a with 2a in THF.

**Figure S1.** TEM image. A sample taken after 30 minutes of the reaction in THF.

**Figure S2.** TEM image. A sample taken after 15 hours of the reaction in THF.
S34
S45