Supporting Information

Mild preparation of alkenes from phenyl sulfides: one-pot elimination of phenylthio group via sulfilimine at ambient temperature

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General. Infrared (IR) spectra were recorded on a Shimadzu FTIR-8100. ¹H NMR spectra were recorded on a JEOL EX270 (270 MHz) or a JEOL GSX500 (500 MHz) spectrometer; chemical shifts (δ) are reported in parts per million relative to tetramethylsilane. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. ¹³C NMR spectra were recorded on a JEOL JNM EX270 (67.5 MHz) or a JEOL GSX500 (125 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in parts per million relative to tetramethylsilane with the solvent resonance as the internal standard (CDCl₃; δ 77.0 ppm). High resolution mass spectra (HRMS) were recorded on a JEOL JMS-SX-102A mass spectrometer. Elemental analysis was recorded on a Yanaco CHN Corder MT-5. Analytical TLC was performed on Merck precoated TLC plates (silica gel 60 GF254, 0.25 mm). Silica-gel column chromatography was carried out on silica gel 60N (Kanto Kagaku Co., Ltd., spherical, neutral, 63–210 μm). Preparative thin-layer chromatography (PTLC) was carried out on silica gel Wakogel B-5F. THF, toluene, and Et₂O were distilled under argon from sodium/benzophenone ketyl. CH2Cl2, CH3CN, MeNO2, and DMF were freshly distilled from CaH2. Potassium carbonate, CsF , and molecular sieves 4A were dried in vacuo at 150 °C for 5 h. Diisopropylethylamine, DBU, and t-BuOK were used without purification. All elimination reactions were carried out under nitrogen in dried glassware with magnetic stirring.

Dry *O*-mesitylenesulfonylhydroxylamine (MSH) was prepared by Johnson's procedure.¹ Phenyl sulfides (**6** and **11a-c**) were prepared by the following method (Scheme 2). Phenyl sulfides (**13** and **16**) were prepared by the reported procedure.² Phenyl sulfides (**17a-c**) were prepared by benzenesulfenylation of the corresponding carbonyl compounds according to Trost's procedure.³



Scheme 2. Preparation of phenyl sulfides (6 and 11a-c).

¹ Johnson, C. R.; Kirchhoff, R. A.; Corkins, H. G. J. Org. Chem. 1974, 39, 2458–2459.

² Tsujihara, K.; Harada, K.; Furukawa, N.; Oae, S. *Tetrahedron* **1971**, *27*, 6101-6108.

³ Trost, B. M.; Salzman, T. N.; Hiroi, K. J. Am. Chem. Soc. 1976, 98, 4887–4902.



To a stirred solution of 1,5-pentanediol (5.0 g, 48 mmol) and triethylamine (7.4 mL, 53 mmol) in dry CH_2Cl_2 (80 mL) was added a solution of benzoyl chloride (5.6 mL, 48 mmol) in CH_2Cl_2 (5 mL) at 0 $^{\circ}C$, and the mixture was stirred for 20 min at 0 $^{\circ}C$ and for 50 min at room temperature. The mixture was extracted with ether, and the organic extracts were washed with brine, dried over anhydrous Na_2SO_4 , filtered, and concentrated. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate = 3/1) to afford **19**⁴ (4.51 g, 21.7 mmol, 45%) as a colorless oil.

¹H NMR (500 HHz, CDCl₃) δ 1.35 (brs, 1H), 1.51-1.57 (m, 2H), 1.63-1.69 (m, 2H), 1.79-1.85 (m, 2H), 3.68 (t, *J* = 6.4 Hz, 2H), 4.34 (t, *J* = 6.4 Hz, 2H), 7.42-7.45 (m, 2H), 7.54-7.57 (m, 1H), 8.04 (dd, *J* = 7.3, 1.2 Hz, 2H); ¹³C NMR (67.8 MHz, CDCl₃) δ 22.3, 28.5, 32.2, 62.5, 64.8, 128.2, 129.5, 130.3, 132.8, 166.6.



To a stirred solution of **19** (4.5 g, 21.7 mmol) and triehylamine (6.0 mL, 43 mmol) in CH_2Cl_2 (80 mL) was added methanesulfonyl chloride (4.5 mL, 58 mmol) at 0 °C, and the mixture was stirred for 30 min at 0 °C. After adding water, the mixture was extracted with ether, and organic extracts were washed with brine, dried over anhydrous Na₂SO₄, filtered, and concentrated. The crude mesylate (8.45 g) was obtained as a pale yellow oil.

A suspension of thus obtained mesylate (8.45 g) and NaI (8.8 g, 58.7 mmol) in acetone (140 mL) was refluxed for 2 h, and aqueous Na₂SO₃ was added. After acetone was evaporated, the mixture was extracted with ethyl acetate, and organic extracts were washed with brine, dried over anhydrous Na₂SO₄, filtered, and concentrated. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate = 5/1) to afford **20**⁵ (5.1 g, 16.0 mmol, 54%) as a colorless oil. ¹H NMR (270 HHz, CDCl₃) δ 1.53-1.64 (m, 2H), 1.75-1.96 (m, 4H), 3.22 (t, *J* = 6.9 Hz, 2H), 4.34 (t,

J = 6.5 Hz, 2H), 7.42-7.59 (m, 3H), 8.04 (d, J = 8.1 Hz, 2H); ¹³C NMR (67.8 MHz, CDCl₃) δ 6.4, 27.0, 27.6, 32.9, 64.5, 128.3, 129.5, 130.3, 132.8, 166.5.

⁴ Iwasaki, F.; Maki, T.; Onomura, O.; Nakashima, W.; Matsumura, Y. *J. Org. Chem.* **2000**, *65*, 996-1002.

⁵ Kabalka, G. W.; Eugene Gooch III, E. J. Org. Chem. **1980**, 45, 3578-3580.



To a stirred suspension of NaH (0.68 g, 17 mmol) in DMF (50 mL) was added benzenethiol (1.8 mL, 17.6 mmol) and **20** (5.1 g, 16 mmol) at room temperature, and the mixture was refluxed for 1 h. After cooling to room temperature, water was added to the reaction mixture and the resulting mixture was extracted with ethyl acetate. The combined organic extracts were washed thoroughly with water, and brine, dried over anhydrous Na₂SO₄, filtered, and concentrated. The crude product was purified by column chromatography on silica gel (hexane/ether = 50/1) to afford **6** (4.7 g, 15.6 mmol, 97%) as a colorless oil.

¹H NMR (270 HHz, CDCl₃) δ 1.59-1.82 (m, 6H), 2.96 (t, *J* = 7.0 Hz, 2H), 4.31 (t, *J* = 6.5 Hz, 2H), 7.16-7.35 (m, 8H), 8.02-8.05 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 25.2, 28.3, 28.8, 33.5, 64.7, 125.8, 128.3, 128.8, 129.1, 129.5, 130.4, 132.8, 136.6, 166.5; IR (CHCl₃, cm⁻¹) 1713, 1279, 1119; HRMS (EI) Calculated for C₁₈H₂₀O₂S: 300.11840. Found 300.11885.



A mixture of **6** (486 mg, 1.62 mmol), KOH (915 mg, 16.3 mmol), EtOH (1 mL), and H_2O (5 mL) was stirred for 2 h at room temperature. After evaporation of EtOH, the mixture was extracted with ether, and combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4 , filtered, and concentrated. The crude product was purified by column chromatography on silica gel to afford 5-phenylthiopentanol (289 mg) as a colorless oil.

To a stirred suspension of NaH (60%, 88.6 mg, 2.22 mmol) in DMF (4 mL) was added a solution of 5-phenylthiopentanol (289 mg, 1.47 mmol) in DMF (1.5 mL) at room temperature, and the mixture was stirred for 20 min. *p*-Methoxybenzyl chloride (0.3 mL, 2.20 mmol) was then added and the mixture was stirred for 1 h at room temperature. After the addition of saturated aqueous NaHCO₃, the mixture was extracted with ether, and combined organic extracts were washed with water (four times) and brine, dried over anhydrous Na₂SO₄, filtered, and concentrated. The crude product was purified by column chromatography on silica gel to afford **11a** as a colorless oil.

¹H NMR (500 HHz, CDCl₃) δ 1.47-1.69 (m, 6H), 2.91 (t, *J* = 7.3 Hz, 2H), 3.43 (t, *J* = 6.4 Hz, 2H), 3.80 (s, 3H), 4.41 (s, 2H), 6.87 (d, *J* = 8.5 Hz, 2H), 7.14-7.15 (m, 1H), 7.24-7.32 (m, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 25.5, 29.0, 29.3, 33.5, 55.3, 69.8, 72.6, 113.8, 125.7, 128.8, 128.9, 129.2, 130.7,

136.9, 159.1; IR (CHCl₃, cm⁻¹) 1514, 1223, 1091, 1035; HRMS (EI) Calculated for $C_{19}H_{24}O_2S$: 316.14970. Found 316.14948.



To a stirred solution of 5-phenylthiopentanol (500 mg, 2.38 mmol) and diisopropylethylamine (1.24 mL, 7.12 mmol) in CH_2Cl_2 (5 mL) was added BOMCl (0.49 mL, 3.57 mmol) at 0 °C, and the mixture was stirred for 1.5 h at room temperature. After the addition of saturated aqueous NaHCO₃, the mixture was extracted with ethyl acetate, and combined organic extracts were washed with brine, dried over anhydrous Na₂SO₄, filtered, and concentrated. The crude product was purified by column chromatography on silica gel to afford **11b** as a colorless oil.

¹H NMR (270 HHz, CDCl₃) δ 1.48-1.71 (m, 6H), 2.92 (t, J = 7.3 Hz, 2H), 3.57 (t, J = 6.2 Hz, 2H), 4.59 (s, 2H), 4.74 (s, 2H), 7.13-7.18 (m, 1H), 7.24-7.35 (m, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 25.5, 29.0, 29.3, 33.5, 67.8, 69.3, 94.6, 125.7, 127.7, 127.8, 128.4, 128.8, 129.0, 136.8, 138.0; IR (CHCl₃, cm⁻¹) 2940, 1482, 1042; HRMS (EI) Calculated for C₁₉H₂₄O₂S: 316.14970. Found 316.14963.



To a stirred solution of 5-phenylthiopentanol (305 mg, 1.55 mmol) and imidazole (324 mg, 4.76 mmol) in DMF (3 mL) was added TBDPSCl (0.8 mL, 3.11 mmol) at room temperature, and the mixture was stirred for 9 h. After the addition of water, the mixture was extracted with ether, and combined organic extracts were washed with water and brine, dried over anhydrous Na_2SO_4 , filtered, and concentrated. The crude product was purified by column chromatography on silica gel to afford **11c** (468 mg, 1.08 mmol, 69%) as a colorless oil.

¹H NMR (270 HHz, CDCl₃) δ 1.49 (m, 6H), 2.89 (t, *J* = 7.1 Hz, 2H), 3.65 (t, *J* = 6.0 Hz, 2H), 7.12-7.41 (m, 11H), 7.66-7.67 (m, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 19.2, 25.0, 26.9, 28.9, 32.0, 33.6, 63.7, 125.6, 127.6, 128.8, 128.9, 129.5, 134.1, 135.5, 137.0; IR (CHCl₃, cm⁻¹) 2932, 1428, 1210, 1111, 505; HRMS (EI) Calculated for C₂₇H₃₄OSiS: 434.20997. Found 434.21087.

Compound 11d was prepared by the following procedure shown in Scheme 3.



Scheme 3. Preparation of 11d.

11d

Colorless plates: mp 91.0-91.5 °C (Hexanes-AcOEt); ¹H NMR (500 HHz, CDCl₃) δ 1.98 (quint, J = 6.8 Hz, 2H), 3.03 (t, J = 6.9 Hz, 2H), 3.60 (dt, J = 6.5, 6.8 Hz, 2H), 6.28 (brs, 1H), 7.18-7.51 (m, 8H), 7.72-7.74 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 28.9, 31.5, 39.0, 126.3, 126.8, 128.6, 129.0, 129.5, 131.4, 134.5, 136.0, 167.6; IR (CHCl₃, cm⁻¹) 1659, 1522, 699; Anal. Calcd for C₁₆H₁₇NOS: C, 70.81; H, 6.31; N, 5.16. Found: C, 70.46; H, 6.37; N, 5.21.

Compound **11e** was prepared by benzoylation of 2-phenylthioethanamine.⁶

11e

Colorless powder: mp 98.5-99.0 °C (Hexanes-AcOH); ¹H NMR (500 HHz, CDCl₃) δ 3.20 (t, *J* = 6.1 Hz, 2H), 3.69 (dt, *J* = 6.1, 6.1 Hz, 2H), 6.50 (brs, 1H), 7.20-7.51 (m, 8H), 7.69-7.70 (m, 2H); ¹³C NMR (67.8 MHz, CDCl₃) δ 33.7, 39.1, 126.6, 126.9, 128.5, 129.2, 129.9, 131.5, 134.3, 134.9, 167.5; IR (CHCl₃, cm⁻¹) 3011, 1659, 1520; Anal. Calcd for C₁₅H₁₅NOS: C, 70.01; H, 5.87; N, 5.44. Found: C, 69.98; H, 5.91; N, 5.39.

MeO SPh Ph Ph 13

Colorless solid: mp 96.5-97.5 (lit.⁷ 94.0-95.5 °C); ¹H NMR (270 HHz, CDCl₃) & 3.22 (s, 3H), 4.36 (d,

⁶ Ishibashi, H.; Uegaki, M.; Sakai, M.; Takeda, Y. *Tetrahedron* **2001**, *57*, 2115-2120.

⁷ Tsujihara, K.; Harada, K.; Furukawa, N.; Oae, S. *Tetrahedron* **1971**, *27*, 6101-6108.

J = 5.4 Hz, 1H), 4.61 (d, *J* = 5.4 Hz, 1H), 7.09-7.26 (m, 15H); ¹³C NMR (125 MHz, CDCl₃) δ 57.4, 60.2, 86.1, 126.8, 127.1, 127.5, 127.7, 127.9, 127.9, 128.6, 129.3, 131.9, 135.4, 138.7, 138.9.

Colorless solid: mp 57.0-57.5 (lit.⁷ 55.0-55.5 °C); ¹H NMR (500 HHz, CDCl₃) δ 3.29 (s, 3H), 4.45 (d, J = 7.6 Hz, 1H), 4.51 (d, J = 7.6 Hz, 1H), 7.07-7.13 (m, 10H), 7.19-7.21 (m, 5H), ¹³C NMR (125 MHz, CDCl₃) δ 57.2, 60.7, 87.1, 126.7, 127.0, 127.6, 127.8, 127.8, 127.9, 128.5, 128.9, 132.2, 135.1, 138.9, 139.3.



17a

Colorless oil; ¹H NMR (500 HHz, CDCl₃) δ 1.00 (t, J = 7.3 Hz, 3H), 1.77-1.82 (m, 1H), 1.88-1.94 (m, 1H), 3.59 (dd, J = 6.7, 8.3 Hz, 1H), 3.81 (s, 3H), 5.02 (d, J = 12.0 Hz, 1H), 5.05 (d, J = 12.2 Hz, 1H), 6.84-6.86 (m, 2H), 7.19-7.21 (m, 2H), 7.24-7.26 (m, 3H), 7.37-7.39 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 11.8, 25.1, 52.5, 55.2, 66.6, 113.8, 127.7, 127.7, 128.8, 130.1, 132.8, 133.4, 159.6, 172.1; IR (CHCl₃, cm⁻¹) 1728, 1516, 1250, 11215; HRMS (EI) Calculated for C₁₂H₁₄O₃: 206.09430. Found 206.09383.



17b

Colorless oil; ¹H NMR (500 HHz, CDCl₃) δ 1.25-1.38 (m, 3H), 1.46-1.48 (m, 1H), 1.62-1.73 (m, 4H), 2.10-2.13 (m, 2H), 3.80 (s, 3H), 5.02 (s, 2H), 6.86-6.88 (m, 2H), 7.21-7.24 (m, 4H), 7.30-7.32 (m, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 23.4, 25.3, 34.2, 55.2, 55.5, 66.3, 113.8, 128.0, 128.5, 129.2, 130.1, 130.5, 136.9, 159.5, 172.5; IR (CHCl₃, cm⁻¹) 1725, 1516, 1250, 1130; HRMS (EI) Calculated for C₂₁H₂₄O₃S: 356.14462. Found 356.14476.



Colorless fine needles; ¹H NMR (500 HHz, CDCl₃) δ 0.91 (t, *J* = 7.3 Hz, 3H), 1.75-1.80 (m, 1H), 2.05-2.11 (m, 1H), 3.70 (dd, *J* = 5.6, 8.5 Hz, 1H), 4.18 (d, *J* = 14.6 Hz, 1H), 4.27 (d, *J* = 17.6 Hz, 1H), 4.58 (d, *J* = 17.6 Hz, 1H), 5.08 (d, *J* = 14.6 Hz, 1H), 7.10 (d, *J* = 7.3 Hz, 2H), 7.20-7.37 (m, 13H); ¹³C NMR (125 MHz, CDCl₃) δ 12.2, 26.2, 49.1, 49.5, 50.0, 126.3, 127.5, 127.6, 128.1, 128.5, 128.6, 128.9, 129.0, 132.9, 133.8, 136.8, 137.3, 171.7; IR (CHCl₃, cm⁻¹) 1646, 1439; Anal. Calcd for C₂₄H₂₅NOS: C, 76.76; H, 6.71; N, 3.73. Found: C, 76.58; H, 6.75; N, 3.69.

Typical procedure for one pot elimination of phenyl sulfides to alkenes (Table 3, entry 1)



To a stirred solution of **11a** (46.1 mg, 0.146 mmol) in dry CH_2Cl_2 (1 mL) was added MSH (37.6 mg, 0.175 mmol) at room temperature. After the mixture was stirred for 30 min, K_2CO_3 (203.1 mg, 1.47 mmol) was added at room temperature, and the mixture was stirred for 6 h. The reaction was quenched with saturated aqueous NaHCO₃ solution (5 mL), and the mixture was extracted with AcOEt. The organic extracts were washed with 0.12 N aqueous NaOCl solution (3 mL), 10% aqueous Na₂S₂O₃ solution (3 mL), and brine, dried over anhydrous Na₂SO₄, filtered, and concentrated in vacuo. The crude product was purified by thin layer chromatography on silica gel (hexane/ethyl acetate = 15/1 then 10/1) to afford **12a** (25 mg, 0.121 mmol, 83%) as a pale yellow oil.

Characterization data for olefins (9 and 12a-e) are listed below.

Colorless oil; ¹H NMR (500 HHz, CDCl₃) δ 1.85-1.91 (m, 2H), 2.22 (dt, *J* = 6.7, 7.3 Hz, 2H), 4.34 (t, *J* = 6.7 Hz, 2H), 5.02 (d, *J* = 10 Hz, 1H), 5.07 (dd, *J* = 17, 1.5 Hz, 1H), 5.81-5.90 (m, 1H), 7.44 (t, *J* = 7.3 Hz, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 8.05 (d, *J* = 7.3 Hz, 2H); ¹³C NMR (67.8 MHz, CDCl₃) δ 27.9, 30.2, 64.3, 115.4, 128.3, 129.5, 130.4, 132.8, 137.5, 166.6.

⁸ Nishimura, T.; Kakiuchi, N.; Onoue, T.; Ohe, K.; Uemura, S. J. Chem. Soc., Perkin Trans. 1, **2000**, 1915-1918.

PMBO 12a

Colorless oil; ¹H NMR (500 HHz, CDCl₃) δ 1.70 (quint, *J* = 7.3 Hz, 2H), 2.13 (dt, *J* = 7.1, 7.5 Hz, 2H), 3.46 (t, *J* = 6.6 Hz, 2H), 3.81 (s, 3H), 4.43 (s, 2H), 4.94-5.05 (m, 2H), 5.76-5.86 (m, 1H), 6.86-6.89 (m, 2H), 7.25-7.28 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 29.0, 30.3, 55.3, 69.4, 72.5, 113.8, 114.7, 129.2, 130.7, 138.3, 159.1; IR (CHCl₃, cm⁻¹) 1514, 1209, 1095, 1036; HRMS (EI) Calculated for C₁₃H₁₈O₂: 206.13068. Found 206.13094.



Colorless oil; ¹H NMR (500 HHz, CDCl₃) δ 1.54-1.74 (m, 2H), 2.13-2.17 (m, 2H), 3.60 (t, *J* = 6.6 Hz, 2H), 4.60 (s, 2H), 4.76 (s, 2H), 4.97-5.06 (m, 2H), 5.79-5.87 (m, 1H), 7.28-7.30 (m, 3H), 7.35 (d, J = 4.6 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 28.9, 30.3, 67.4, 69.3, 94.6, 114.8, 127.7, 127.9, 128.4, 138.0, 138.1; IR (CHCl₃, cm⁻¹) 2941, 1454, 1041, 916; HRMS (EI) Calculated for C₁₃H₁₈O₂: 206.13068. Found 206.12908.

TBDPSO

¹H NMR (270 HHz, CDCl₃) δ 1.05 (s, 9H), 1.66 (quint, J = 7.9 Hz, 2H), 2.13-2.17 (m, 2H), 3.67 (t, J = 6.4 Hz, 2H), 4.93 (d, J = 10.3 Hz, 1H), 4.99 (dd, J = 15.9, 1.2 Hz, 1H), 5.76-5.84 (m, 1H), 7.36-7.43 (m, 6H), 7.66-7.68 (m, 4H); ¹³C NMR (67.8 MHz, CDCl₃) δ 19.2, 26.9, 30.1, 31.8, 63.3, 114.5, 127.6, 127.6, 129.5, 134.1, 135.5, 135.6, 138.5.

¹H NMR (500 HHz, CDCl₃) δ 4.07-4.10 (m, 2H), 5.18 (dd, *J* = 10.4, 1.2 Hz, 1H), 5.26 (dd, *J* = 17.1, 1.2 Hz, 1H), 5.91-5.97 (m, 1H), 6.33 (brs, 1H), 7.41-7.51 (m, 3H), 7.77-7.79 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 42.4, 116.6, 126.9, 128.5, 131.4, 134.1, 134.5, 167.3.

⁹ Dakin, L.A.; Langille, N. F.; Panek, J. S. J. Org. Chem. **2002**, 67, 6812-6815.

¹⁰ Fisher, L. E.; Muchowski, J. M.; Clark, R. D. J. Org. Chem. **1992**, 57, 2700-2705.



Colorless powder: mp 102.5-103.0 °C; ¹H NMR (500 HHz, CDCl₃) δ 4.54 (d, *J* = 8.8 Hz, 1H), 4.77 (d, *J* = 15.9 Hz, 1H), 7.17-7.24 (m, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.75 (brs, 1H), 7.81 (d, *J* = 7.6 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 96.0, 127.1, 128.8, 129.0, 132.1, 133.5, 164.5; IR (CHCl₃, cm⁻¹) 1674, 1644, 1507, 1485, 1267; Anal. Calcd for C₉H₉NO: C, 73.45; H, 6.16; N, 9.52. Found: C, 73.55; H, 6.26; N, 9.50.

Typical procedure for the one-pot elimination of α -phenylthio carbonyl compounds to α , β -unsaturated carbonyl compounds (Table 4, entry 1)



To a stirred solution of **17a** (55.3 mg, 0.175 mmol) in dry CH_2Cl_2 (1 mL) was added MSH (43.3 mg, 0.201 mmol) at 0 °C, and the mixture was stirred for 45 min at 0 °C. Compound **17a** was not detected by TLC analysis after that period. Potassium carbonate (245 mg, 1.77 mmol) was added, and the mixture was stirred for 0 °C for 30 min and for 6 h at room temperature. The reaction was quenched with saturated aqueous NaHCO₃ solution, and the mixture was extracted with ethyl acetate. The combined organic extracts were washed with brine, dried over anhydrous Na₂SO₄, filtered, and concentrated in vacuo. The crude product was purified by thin layer chromatography on silica gel (benzene/hexane = 4/1) to afford **18a** (31.3 mg, 0.152 mmol, 87%) as a pale yellow oil.





Colorless oil; ¹H NMR (500 HHz, CDCl₃) δ 1.87 (dd, J = 1,7, 6.8 Hz, 3H), 3.81 (s, 3H), 5.10 (s, 2H), 5.87 (dq, J = 1.7, 13.9 Hz, 1H), 6.89 (d, J = 8.8 Hz, 2H), 6.99 (qd, J = 6.8, 15.5 Hz, 1H), 7.30-7.32 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 17.9, 55.2, 65.7, 113.9, 122.6, 128.3, 130.0, 144.9, 159.6, 166.4; IR (CHCl₃, cm⁻¹) 1713, 1659, 1615, 1516, 1250, 1172, 1103, 1036, 970; HRMS (EI) Calculated for C₁₂H₁₄O₃: 206.09430. Found 206.09383.



18b

Colorless oil; ¹H NMR (500 HHz, CDCl₃) δ 1.56-1.67 (m, 4H), 2.15-2.19 (m, 2H), 2.25-2.28 (m, 2H), 3.80 (s, 3H), 5.11 (s, 2H), 6.87-6.90 (m, 2H), 6.99-7.01 (m, 1H), 7.30-7.32 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 21.4, 22.0, 24.1, 25.7, 55.2, 65.7, 113.9, 128.6, 129.8, 130.3, 139.9, 159.5, 167.4; IR (CHCl₃, cm⁻¹) 1703, 1516, 1213; HRMS (EI) Calculated for C₁₅H₁₈O₃: 246.12560. Found 246.12470.

Colorless oil; ¹H NMR (500 HHz, CDCl₃) δ 1.86 (dd, J = 1,8, 6.8 Hz, 3H), 4.50 (s, 2H), 4.63 (s, 2H), 6.28-6.32 (m, 1H), 7.04-7.11 (m, 1H), 7.16-7.35 (m, 10H); ¹³C NMR (125 MHz, CDCl₃) δ 18.2, 48.4, 49.8, 121.6, 126.5, 127.3, 127.6, 128.3, 128.5, 128.9, 136.8, 137.4, 142.9, 167.3; IR (CHCl₃, cm⁻¹) 1661, 1613, 1449, 1210, 963; HRMS (EI) Calculated for C₁₈H₁₉ON: 265.14667. Found 265.14695.



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BZO-OH 13C



BZO-I



BZO-I



S-Ph

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SPh-256



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