

Supporting Information for
Oxidative Debenzylation of *N*-Benzyl Amides and *O*-Benzyl Ethers Using Alkali Metal Bromide

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1. General Methods. ^1H NMR spectra were measured on a JEOL ECS-400 (400 MHz) spectrometer at ambient temperature. Data were recorded as follows: chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (s = singlet; d = doublet; t = triplet; q = quartet; sep = septet; m = multiplet; br = broad), coupling constant (Hz), integration, and assignment. ^{13}C NMR spectra were measured on a JEOL ECS-400 (100 MHz) spectrometer. Chemical shifts were recorded in ppm from the solvent resonance employed as the internal standard (deuteriochloroform at 77.0 ppm). High-resolution mass spectra were recorded by Thermo Fisher Scientific Exactive Orbitrap mass spectrometers. Infrared (IR) spectra were recorded on a JASCO FT/IR 4100 spectrometer. For thin-layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60GF254 0.25 mm) were used. The products were purified by neutral column chromatography on silica gel (Kanto Chemical Co., Inc. silica gel 60N, Prod. No. 37560-84; Merck silica gel 60, Prod. No. 1.09385.9929). Visualization was accomplished by UV light (254 nm), anisaldehyde, KMnO_4 , and phosphomolybdic acid. In experiments that required dry solvents such as nitromethane and acetonitrile were distilled in prior to use.

2. General procedure for Oxidative Debenzylation of *N*-Benzyl Amides **1** Using Alkali Metal Bromide (Scheme 1, eq 1 and Scheme 2).

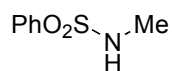
To the solution of **1a** (65.3mg, 0.25 mmol) and KBr (29.8 mg, 0.25 mmol) in MeNO_2 (1.5 mL) was added Oxone[®] (230.5 mg, 0.375 mmol) at room temperature, and was stirred at 30 °C for 24 h. Saturated Na_2SO_3 aqueous solution (10 mL) was added to the reaction mixture, and the product was extracted with AcOEt (15 mL $\times$ 3). The combined extracts were washed by brine (10 mL) and dried over Na_2SO_4 . The organic phase was concentrated under reduced pressure and the crude product was purified by silica gel column chromatography (eluent: hexane/AcOEt = 5/1), to give the desired product **2a** (42.6 mg, >99% yield).

Table S1. Screening of Oxidative Debenzylation of Benzylamide **1a**.

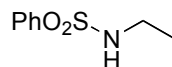
$ \begin{array}{ccc} \text{PhO}_2\text{S}-\text{N}(\text{Me})-\text{CH}_2\text{Ph} & \xrightarrow[\text{Solvent, 50 } ^\circ\text{C, 24 h}]{\text{M}^+\text{X}^-\text{Oxidant}} & \text{PhO}_2\text{S}-\text{N}(\text{H})-\text{CH}_2\text{Ph} \\ \mathbf{1a} & & \mathbf{2a} \end{array} $				
Entry	MX (equiv.)	Oxidant (equiv.)	Solvent	Yield (%) ^a
1	KBr (1.0)	Oxone [®] (1.2)	MeNO_2	95 (5)
2	KBr (1.0)	Oxone [®] (1.2)	MeCN	92

3	KBr (1.0)	Oxone [®] (1.2)	AcOEt	52 (48)
4	KBr (1.0)	Oxone [®] (1.2)	THF	0 (>99)
5	KBr (1.0)	Oxone [®] (1.2)	ClCH ₂ CH ₂ Cl	74 (26)
6	KBr (1.0)	<i>m</i> CPBA (1.2)	MeNO ₂	0 (95)
7	KBr (1.0)	<i>t</i> -BuOCl (1.2)	MeNO ₂	0 (>99)
8	KBr (1.0)	PhI(OAc) ₂ (1.2)	MeNO ₂	0 (99)
9	KBr (1.0)	H ₂ O ₂ (1.2)	MeNO ₂	0 (>99)
10	NaBr (1.0)	Oxone [®] (1.2)	MeNO ₂	94 (6)
11	CaBr ₂ (1.0)	Oxone [®] (1.2)	MeNO ₂	0 (>99)
12	TBABr (1.0)	Oxone [®] (1.2)	MeNO ₂	0 (97)
13	KCl (1.0)	Oxone [®] (1.2)	MeNO ₂	12 (88)
14	KI (1.0)	Oxone [®] (1.2)	MeNO ₂	0 (>99)
15	KBr (1.0)	Oxone [®] (1.5)	MeNO ₂	>99
16	NBS (1.0)	-	MeNO ₂	3 (45)
17	Br ₂ (1.0)	-	MeNO ₂	25 (58)
18	-	Oxone [®] (1.2)	MeNO ₂	0 (>99)
19 ^b	KBr (1.0)	Oxone [®] (1.5)	MeNO ₂	54 (46)
20 ^c	KBr (1.0)	Oxone [®] (1.5)	MeNO ₂	>99

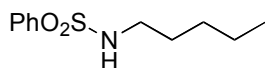
^a Number in the parentheses indicate the recovery of **1a**. ^b The reaction was carried out under the dark conditions. ^c The reaction was carried out at 30 °C.



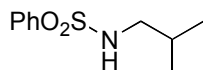
***N*-Methylbenzenesulfonamide (2a, commercially available):** Colorless oil, ¹H NMR (400 MHz, CDCl₃) δ 2.66 (d, *J* = 5.5 Hz, 3H), 4.72 (brs, 1H), 7.50-7.56 (m, 2H), 7.57-7.62 (m, 1H), 7.86-7.90 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 29.3, 127.2 (2C), 129.1 (2C), 132.7, 138.7. IR (neat) 3290, 2924, 1309, 1155, 1092 cm⁻¹. MS (ESI) calcd for C₇H₁₀NO₂S [M+H]⁺ 172.0427, found 172.0428.



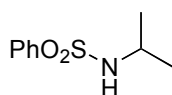
***N*-Ethylbenzenesulfonamide (2b):** White solid, ¹H NMR (400 MHz, CDCl₃) δ 1.11 (t, *J* = 7.3 Hz, 3H), 3.02 (qd, *J* = 7.3, 6.1 Hz, 2H), 4.57 (brs, 1H), 7.49-7.55 (m, 2H), 7.56-7.61 (m, 1H), 7.87-7.90 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 15.1, 38.2, 127.0 (2C), 129.1 (2C), 132.6, 140.0. IR (neat) 3248, 2979, 1321, 1156, 1089 cm⁻¹. MS (ESI) calcd for C₈H₁₂NO₂S [M+H]⁺ 186.0583, found 186.0585.



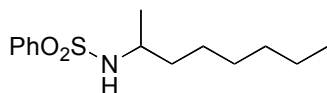
N-Pentylbenzenesulfonamide (2c): Colorless oil, ^1H NMR (400 MHz, CDCl_3) δ 0.83 (t, J = 7.2 Hz, 3H), 1.17-1.30 (m, 4H), 1.45 (quin, J = 7.2 Hz, 2H), 2.94 (q, J = 7.2 Hz, 2H), 4.80 (brs, 1H), 7.48-7.55 (m, 2H), 7.55-7.61 (m, 1H), 7.86-7.91 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 13.8, 22.1, 28.6, 29.3, 43.2, 127.0 (2C), 129.1 (2C), 132.6, 140.0. IR (neat) 3282, 2931, 1322, 1156, 1092 cm^{-1} . MS (ESI) calcd for $\text{C}_{11}\text{H}_{18}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$ 228.1053, found 228.1054.



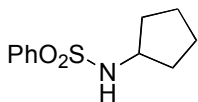
N-Isobutylbenzenesulfonamide (2d): Colorless oil, ^1H NMR (400 MHz, CDCl_3) δ 0.87 (d, J = 6.9 Hz, 6H), 1.64-1.79 (m, 1H), 2.76 (t, J = 6.9 Hz, 2H), 4.87-4.95 (br, 1H), 7.48-7.55 (m, 2H), 7.55-7.61 (m, 1H), 7.86-7.91 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 19.8 (2C), 28.4, 50.5, 126.9 (2C), 127.0 (2C), 132.5, 140.0. IR (neat) 3287, 2960, 1321, 1156, 1092 cm^{-1} . MS (ESI) calcd for $\text{C}_{10}\text{H}_{16}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$ 214.0896, found 214.0898.



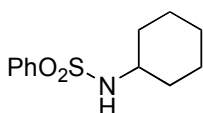
N-Isopropylbenzenesulfonamide (2e): Colorless oil, ^1H NMR (400 MHz, CDCl_3) δ 1.08 (d, J = 6.6 Hz, 6H), 3.41-3.54 (m, 1H), 4.56-4.69 (br, 1H), 7.48-7.54 (m, 2H), 7.54-7.60 (m, 1H), 7.88-7.92 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 27.3 (2C), 46.1, 126.9 (2C), 129.0 (2C), 132.4, 141.1. IR (neat) 3278, 2975, 1305, 1141, 1092 cm^{-1} . MS (ESI) calcd for $\text{C}_9\text{H}_{14}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$ 200.0740, found 200.0740.



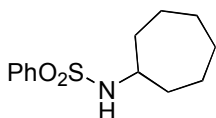
N-(1-Methylheptyl)benzenesulfonamide (2f): Colorless oil, ^1H NMR (400 MHz, CDCl_3) δ 0.85 (t, J = 7.2 Hz, 3H), 1.04 (d, J = 6.6 Hz, 3H), 1.07-1.28 (m, 8H), 1.29-1.38 (m, 2H), 3.32 (tq, J = 8.2, 6.6 Hz, 1H), 4.29 (brs, 1H), 7.47-7.53 (m, 2H), 7.53-7.60 (m, 1H), 7.86-7.91 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 14.0, 21.9, 22.5, 25.4, 28.8, 31.6, 37.5, 50.1, 127.0 (2C), 129.0 (2C), 132.4, 141.2. IR (neat) 3278, 2928, 1322, 1161, 1093 cm^{-1} . MS (ESI) calcd for $\text{C}_{14}\text{H}_{24}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$ 270.1522, found 270.1521.



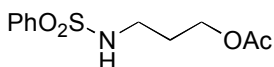
N-Cyclopentylbenzenesulfonamide (2g): White solid, ^1H NMR (400 MHz, CDCl_3) δ 1.29-1.39 (m, 2H), 1.44-1.55 (m, 2H), 1.57-1.68 (m, 2H), 1.74-1.84 (m, 2H), 3.62 (sext, $J = 6.9$ Hz, 1H), 4.36-4.46 (br, 1H), 7.49-7.55 (m, 2H), 7.55-7.61 (m, 1H), 7.86-7.91 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 23.1 (2C), 33.5 (2C), 55.2, 127.0 (2C), 129.0 (2C), 132.5, 140.8. IR (neat) 3274, 2959, 1308, 1152, 1092 cm^{-1} . IR (neat) 3274, 2959, 1308, 1152, 1092 cm^{-1} . MS (ESI) calcd for $\text{C}_{11}\text{H}_{16}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$ 226.0896, found 226.0898.



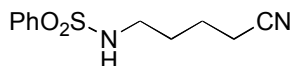
N-Cyclohexylbenzenesulfonamide (2h): White solid, ^1H NMR (400 MHz, CDCl_3) δ 1.05-1.30 (m, 5H), 1.47-1.57 (m, 1H), 1.58-1.68 (m, 2H), 1.71-1.80 (m, 2H), 3.11-3.21 (m, 1H), 4.47 (brs, 1H), 7.48-7.54 (m, 2H), 7.54-7.60 (m, 1H), 7.87-7.91 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 24.6 (2C), 25.1, 33.9 (2C), 52.6, 126.8 (2C), 129.0 (2C), 132.4, 141.4. IR (neat) 3246, 2932, 1318, 1156, 1080 cm^{-1} . MS (ESI) calcd for $\text{C}_{12}\text{H}_{18}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$ 240.1053, found 240.1052.



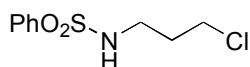
N-Cycloheptylbenzenesulfonamide (2i): White solid, ^1H NMR (400 MHz, CDCl_3) δ 1.30-1.61 (m, 10H), 1.71-1.82 (m, 2H), 3.31-3.42 (m, 1H), 4.41-4.56 (br, 1H), 7.51 (t, $J = 7.3$ Hz, 2H), 7.57 (t, $J = 7.3$ Hz, 1H), 7.88 (t, $J = 7.3$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 23.5 (2C), 27.9 (2C), 35.9 (2C), 54.8, 126.9 (2C), 129.0 (2C), 132.4, 141.2. IR (neat) 3249, 2926, 1308, 1152, 1092, 1040 cm^{-1} . MS (ESI) calcd for $\text{C}_{13}\text{H}_{20}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$ 254.1209, found 254.1208.



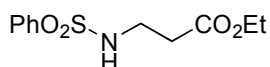
N-(2-(Acetoxy)propyl)benzenesulfonamide (2j): Colorless oil, ^1H NMR (400 MHz, CDCl_3) δ 1.81 (quin, $J = 6.4$ Hz, 2H), 2.02 (s, 3H), 3.04 (q, $J = 6.4$ Hz, 2H), 4.10 (t, $J = 6.4$ Hz, 2H), 4.80-4.88 (br, 1H), 7.53 (t, $J = 7.3$ Hz, 2H), 7.59 (t, $J = 7.3$ Hz, 1H), 7.87 (d, $J = 7.3$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 20.8, 28.9, 40.1, 61.3, 127.0 (2C), 129.1 (2C), 132.7, 139.9, 171.1. IR (neat) 3276, 2927, 1733, 1325, 1239, 1155, 1049 cm^{-1} . MS (ESI) calcd for $\text{C}_{11}\text{H}_{16}\text{NO}_4\text{S}$ $[\text{M}+\text{H}]^+$ 258.0795, found 258.0793.



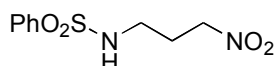
***N*-(4-Cyanobutyl)benzenesulfonamide (2k):** Colorless oil, ^1H NMR (400 MHz, CDCl_3) δ 1.59-1.76 (m, 4H), 2.35 (t, $J = 6.8$ Hz, 2H), 3.00 (q, $J = 6.4$ Hz, 2H), 4.76-4.86 (br, 1H), 7.51-7.57 (m, 2H), 7.58-7.64 (m, 1H), 7.85-7.89 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 16.7, 22.2, 28.5, 42.2, 119.2, 127.0 (2C), 129.2 (2C), 132.8, 139.7. IR (neat) 3276, 2925, 2247, 1323, 1154, 1092 cm^{-1} . MS (ESI) calcd for $\text{C}_{11}\text{H}_{15}\text{N}_2\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$ 239.0849, found 239.0847.



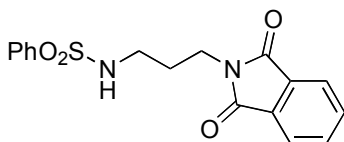
***N*-(3-Chloropropyl)benzenesulfonamide (2l):** Colorless oil, ^1H NMR (400 MHz, CDCl_3) δ 1.96 (quin, $J = 6.4$ Hz, 2H), 3.15 (q, $J = 6.4$ Hz, 2H), 3.58 (t, $J = 6.4$ Hz, 2H), 4.62-4.71 (br, 1H), 7.51-7.57 (m, 2H), 7.58-7.64 (m, 1H), 7.86-7.91 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 32.2, 40.4, 41.8, 127.0 (2C), 129.2 (2C), 132.8, 139.7. IR (neat) 3279, 2965, 1321, 1153, 1092, 752, 687 cm^{-1} . MS (ESI) calcd for $\text{C}_9\text{H}_{13}\text{ClNO}_2\text{S}$ $[\text{M}+\text{H}]^+$ 234.0350, found 234.0350.



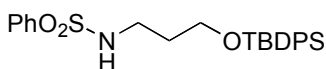
***N*-Benzenesulfonyl- β -alanine ethyl ester (2m):** Colorless oil, ^1H NMR (400 MHz, CDCl_3) δ 1.24 (t, $J = 7.3$ Hz, 3H), 2.53 (t, $J = 6.2$ Hz, 2H), 3.21 (q, $J = 6.2$ Hz, 2H), 4.12 (q, $J = 7.3$ Hz, 2H), 5.15-5.28 (br, 1H), 7.49-7.56 (m, 2H), 7.56-7.62 (m, 1H), 7.85-7.90 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 14.1, 34.0, 38.8, 61.0, 126.9 (2C), 129.2 (2C), 132.7, 139.9, 172.1. IR (neat) 3283, 2985, 1725, 1325, 1155, 1092 cm^{-1} . MS (ESI) calcd for $\text{C}_{11}\text{H}_{16}\text{NO}_4\text{S}$ $[\text{M}+\text{H}]^+$ 258.0795, found 258.0794.



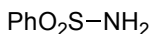
***N*-(3-Nitropropyl)benzenesulfonamide (2n):** White solid, ^1H NMR (400 MHz, CDCl_3) δ 2.22 (quin, $J = 6.6$ Hz, 2H), 3.11 (q, $J = 6.6$ Hz, 2H), 4.50 (t, $J = 6.6$ Hz, 2H), 4.61-4.67 (br, 1H), 7.52-7.57 (m, 2H), 7.58-7.65 (m, 1H), 7.84-7.88 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 27.4, 39.9, 72.2, 127.0 (2C), 129.3 (2C), 133.0, 139.3. IR (neat) 3270, 2974, 1550, 1316, 1158, 1069 cm^{-1} . MS (ESI) calcd for $\text{C}_9\text{H}_{13}\text{N}_2\text{O}_4\text{S}$ $[\text{M}+\text{H}]^+$ 245.0591, found 245.0590.



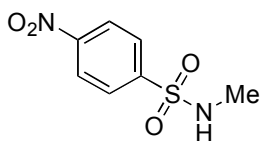
N-(3-(1,3-Dioxoisindolin-2-yl)propyl)benzenesulfonamide (2o): White solid, ^1H NMR (400 MHz, CDCl_3) δ 1.84 (quin, $J = 6.4$ Hz, 2H), 2.96 (q, $J = 6.4$ Hz, 2H), 3.75 (t, $J = 6.4$ Hz, 2H), 5.27-5.35 (br, 1H), 7.46-7.57 (m, 3H), 7.70-7.75 (m, 2H), 7.79-7.85 (m, 2H), 7.86-7.90 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 28.8, 34.5, 39.9, 123.4 (2C), 127.0 (2C), 129.1 (2C), 131.8, 132.5 (2C), 134.2 (2C), 140.1, 168.6 (2C). IR (neat) 3269, 2973, 1709, 1338, 1162, 1044 cm^{-1} . MS (ESI) calcd for $\text{C}_{17}\text{H}_{17}\text{N}_2\text{O}_4\text{S}$ $[\text{M}+\text{H}]^+$ 345.0904, found 345.0902.



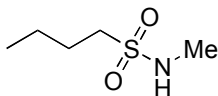
N-(3-((*tert*-Butyldiphenylsilyloxy)propyl)benzenesulfonamide (2p): Colorless oil, ^1H NMR (400 MHz, CDCl_3) δ 1.04 (s, 9H), 1.64-1.73 (m, 2H), 3.15 (q, $J = 6.2$ Hz, 2H), 3.67 (t, $J = 5.5$ Hz, 2H), 5.04-5.13 (br, 1H), 7.34-7.40 (m, 4H), 7.41-7.46 (m, 2H), 7.46-7.52 (m, 2H), 7.55-7.61 (m, 5H), 7.79-7.84 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 19.0, 26.8 (3C), 31.1, 41.9, 62.8, 127.0 (2C), 127.8 (4C), 129.0 (2C), 129.8 (2C), 132.4, 133.0 (2C), 135.4 (4C), 134.0. IR (neat) 3285, 1326, 1160, 1109, 1090 cm^{-1} . MS (ESI) calcd for $\text{C}_{25}\text{H}_{32}\text{NO}_3\text{SSi}$ $[\text{M}+\text{H}]^+$ 454.1867, found 454.1862.



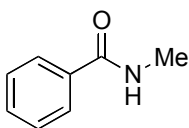
Benzenesulfonamide (2q, commercially available): White solid, ^1H NMR (400 MHz, CDCl_3) δ 4.85 (brs, 2H), 7.50-7.57 (m, 2H), 7.57-7.63 (m, 1H), 7.92-7.97 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 126.4 (2C), 129.2 (2C), 132.8, 141.9. IR (neat) 3346, 3251, 1722, 1688, 1310, 1274, 1154 cm^{-1} . MS (ESI) calcd for $\text{C}_6\text{H}_7\text{NNaO}_2\text{S}$ $[\text{M}+\text{Na}]^+$ 180.0090, found 180.0089.



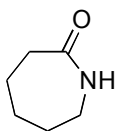
N-Methyl-4-nitrobenzenesulfonamide (2r): White solid, ^1H NMR (400 MHz, CDCl_3) δ 2.74 (d, $J = 5.2$ Hz, 3H), 4.50-4.75 (br, 1H), 8.06 (dt, $J = 9.0, 2.3$ Hz, 2H), 8.38 (dt, $J = 9.0, 2.3$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 29.3, 124.4 (2C), 128.4 (2C), 144.9, 150.1. IR (neat) 3302, 2971, 1530, 1306, 1160, 1090 cm^{-1} . MS (ESI) calcd for $\text{C}_7\text{H}_7\text{N}_2\text{O}_4\text{S}$ $[\text{M}-\text{H}]^-$ 215.0121, found 215.0132.



N-Methyl-1-butanethiosulfonamide (2s): Colorless oil, ^1H NMR (400 MHz, CDCl_3) δ 0.96 (t, J = 7.4 Hz, 3H), 1.47 (sext, J = 7.4 Hz, 2H), 1.74-1.84 (m, 2H), 2.81 (d, J = 5.5 Hz, 3H), 2.98-3.05 (m, 2H), 4.21-4.37 (br, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 13.6, 21.5, 25.6, 29.3, 51.1. IR (neat) 3296, 2962, 1314, 1128, 1074 cm^{-1} . MS (ESI) calcd for $\text{C}_5\text{H}_{13}\text{NNaO}_2\text{S}$ $[\text{M}+\text{Na}]^+$ 174.0559, found 174.0560.



N-Methylbenzamide (2t, commercially available): White solid, ^1H NMR (400 MHz, CDCl_3) δ 3.02 (d, J = 5.2 Hz, 3H), 6.15 (brs, 1H), 7.39-7.46 (m, 2H), 7.46-7.53 (m, 1H), 7.73-7.79 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 26.8, 126.8 (2C), 128.5 (2C), 131.3, 134.6, 168.2. IR (neat) 3321, 2939, 1633, 1547, 1302, 1163 cm^{-1} .

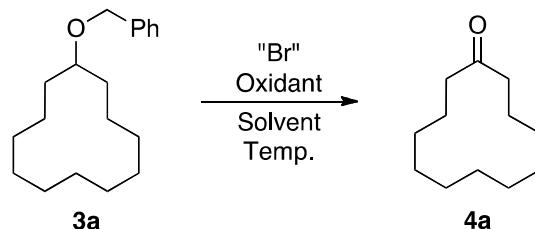


ϵ -Caprolactam (2u): White solid, ^1H NMR (400 MHz, CDCl_3) δ 1.60-1.82 (m, 6H), 2.43-2.51 (m, 2H), 3.21 (dd, J = 10.0, 6.2 Hz, 2H), 6.08 (brs, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 23.2, 29.8, 30.6, 36.6, 42.9, 178.9. IR (neat) 3197, 3072, 2927, 1652, 1416, 1198 cm^{-1} .

3. General procedure for Oxidative Debenzylation of *O*-Benzyl Ethers **3** Using Alkali Metal Bromide (Scheme 1, eq 2 and Scheme 3)

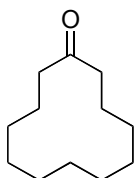
To the solution of **3a** (68.6mg, 0.25 mmol) and KBr (29.8 mg, 0.25 mmol) in MeCN (1.5 mL) was added Oxone[®] (230.5 mg, 0.375 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 30 min, and then at 30 °C for 24 h. Saturated Na_2SO_3 aqueous solution (10 mL) was added to the reaction mixture, and the product was extracted with AcOEt (15 mL $\times$ 3). The combined extracts were washed by brine (10 mL) and dried over Na_2SO_4 . The organic phase was concentrated under reduced pressure and the crude product was purified by silica gel column chromatography (eluent: hexane/AcOEt = 30/1), to give the desired product **4a** (43.5 mg, 95% yield).

Table S1. Screening for Oxidation involved Debenzylation of Benzyl cyclododecylether **3a**.

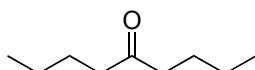


Entry	MX (equiv)	Oxone [®] (equiv)	Solvent	Temp. (°C)	Yield (%)
1	KBr (1.0)	1.5	MeNO ₂	30	40 (15) ^a (15) ^b
2	KBr (1.0)	1.5	MeNO ₂	r.t.	44 (4) ^a (19) ^b
3	KBr (1.0)	3.0	MeNO ₂	30	27
4	KBr (1.2)	2.0	MeNO ₂	30	74
5	KBr (1.2)	2.0	MeCN	30	42 (22) ^a
6	KBr (1.2)	2.0	MeCN	0 to 30	75
7	KBr (1.2)	2.0	MeNO ₂	0 to 30	38 (7) ^a
8	KBr (1.2)	2.0	MeCN	0	0 (86) ^a
9	KBr (1.0)	1.5	MeCN	0 to 30	69 (6) ^c
10	KBr (1.0)	1.2	MeCN	0 to 30	32 (19) ^a (36) ^c
11 ^d	KBr (1.0)	1.5	MeCN	0 to 30	95
12	KCl (1.0)	1.5	MeCN	0 to 30	34 (10) ^a (19) ^e
13	KI (1.0)	1.5	MeCN	0 to 30	0 (>99) ^a

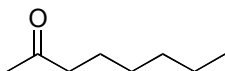
^a Number in the parentheses indicates the recovery of **3a**. ^b Number in the parentheses indicates the yield of cyclododecyl alcohol. ^c Number in the parentheses indicates the yield of α -bromo-cyclododecanone. ^d Reaction was carried out under the dark conditions. ^e Number in the parenthesis indicates the yield of α -chloro-cyclododecanone.



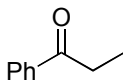
Cyclododecanone (4a, commercially available): White solid, ¹H NMR (400 MHz, CDCl₃) δ 1.22-1.37 (m, 14H), 1.67-1.76 (m, 4H), 2.44-2.49 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 22.3, 22.5 (2C), 24.2 (2C), 24.6 (2C), 24.7 (2C), 40.3 (2C), 212.9. IR (neat) 2927, 1702, 1470, 1362, 1204, 1131 cm⁻¹.



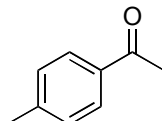
5-Nonanone (4b, commercially available): Colorless oil, ^1H NMR (400 MHz, CDCl_3) δ 0.90 (t, $J = 7.6$ Hz, 6H), 1.31 (sext, $J = 7.6$ Hz, 4H), 1.55 (quin, $J = 7.6$ Hz, 4H), 2.39 (t, $J = 7.6$ Hz, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ 13.8 (2C), 22.3 (2C), 26.0 (2C), 42.5 (2C), 211.7. IR (neat) 2958, 1712, 1465, 1379, 1133, 1043 cm^{-1} .



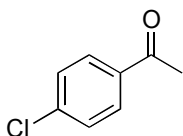
2-Octanone (4c, commercially available): Colorless oil, ^1H NMR (400 MHz, CDCl_3) δ 0.88 (t, $J = 6.9$ Hz, 3H), 1.24-1.36 (m, 6H), 1.52-1.62 (m, 2H), 2.13 (s, 3H), 2.42 (t, $J = 7.6$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 14.0, 22.4, 23.8, 28.8, 29.8, 31.5, 43.7, 209.3. IR (neat) 2928, 1715, 1410, 1359, 1226, 1164 cm^{-1} .



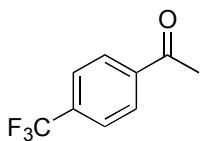
Propiophenone (4d, commercially available): Colorless oil, ^1H NMR (400 MHz, CDCl_3) δ 1.23 (t, $J = 7.3$ Hz, 3H), 3.00 (q, $J = 7.3$ Hz, 2H), 7.45 (t, $J = 7.8$ Hz, 2H), 7.55 (t, $J = 7.8$ Hz, 1H), 7.97 (d, $J = 7.8$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 8.2, 31.7, 127.9 (2C), 128.5 (2C), 132.8, 136.8, 200.7. IR (neat) 2979, 1685, 1597, 1448, 1351, 1218 cm^{-1} .



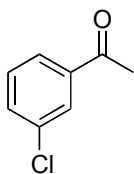
4-Methylacetophenone (4e, commercially available): Colorless oil, ^1H NMR (400 MHz, CDCl_3) δ 2.41 (s, 3H), 2.58 (s, 3H), 7.26 (d, $J = 8.2$ Hz, 2H), 7.86 (d, $J = 8.2$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 21.6, 26.5, 128.4 (2C), 129.2 (2C), 134.7, 143.8, 197.8. IR (neat) 1679, 1605, 1574, 1265, 1181 cm^{-1} .



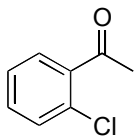
4-Chloroacetophenone (4f, commercially available): White solid, ^1H NMR (400 MHz, CDCl_3) δ 2.59 (s, 3H), 7.44 (d, $J = 8.9$ Hz, 2H), 7.90 (d, $J = 8.9$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 26.6, 128.9 (2C), 129.7 (2C), 135.4, 139.6, 196.8. IR (neat) 1683, 1587, 1357, 1258, 1092 cm^{-1} .



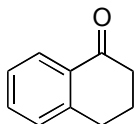
4-Trifluoromethylacetophenone (4g, commercially available): White solid, ^1H NMR (400 MHz, CDCl_3) δ 2.66 (s, 3H), 7.74 (d, $J = 8.2$ Hz, 2H), 8.07 (d, $J = 8.2$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 26.7, 123.6 (q, $J_{\text{C-F}} = 274.0$ Hz), 125.6 (q, $J_{\text{C-F}} = 3.8$ Hz) (2C), 128.6 (2C), 134.4 (q, $J_{\text{C-F}} = 32.6$ Hz), 139.6, 196.9. IR (neat) 2971, 1690, 1321, 1164, 1125, 1110, 1060 cm^{-1} .



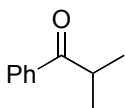
3-Chloroacetophenone (4h, commercially available): Colorless oil, ^1H NMR (400 MHz, CDCl_3) δ 2.60 (s, 3H), 7.41 (t, $J = 8.0$ Hz, 1H), 7.54 (ddd, $J = 8.0, 2.0, 1.2$ Hz, 1H), 7.83 (ddd, $J = 8.0, 2.0, 1.2$ Hz, 1H), 7.93 (t, $J = 2.0$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 26.6, 126.4, 128.4, 129.9, 133.0, 134.9, 138.5, 196.7. IR (neat) 1688, 1572, 1422, 1358, 1251 cm^{-1} .



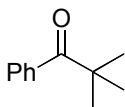
2-Chloroacetophenone (4i, commercially available): White solid, ^1H NMR (400 MHz, CDCl_3) δ 2.65 (s, 3H), 7.32 (ddd, $J = 7.8, 7.1, 1.8$ Hz, 1H), 7.36-7.44 (m, 2H), 7.55 (dd, $J = 7.8, 1.8$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 30.7, 126.9, 129.4, 130.6, 131.3, 132.0, 139.1, 200.5. IR (neat) 1695, 1432, 1357, 1276, 1240, 1095 cm^{-1} .



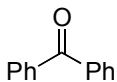
α -Tetralone (4j, commercially available): Colorless oil, ^1H NMR (400 MHz, CDCl_3) δ 2.14 (quin, $J = 6.4$ Hz, 2H), 2.66 (t, $J = 6.4$ Hz, 2H), 2.97 (t, $J = 6.4$ Hz, 2H), 7.25 (d, $J = 7.6$ Hz, 1H), 7.30 (t, $J = 8.0$ Hz, 1H), 7.47 (td, $J = 7.6, 1.4$ Hz, 1H), 8.03 (dd, $J = 8.0, 1.4$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 23.4, 29.7, 39.1, 126.6, 127.1, 128.7, 132.6, 133.4, 144.4, 198.4. IR (neat) 2944, 1679, 1600, 1324, 1284 cm^{-1} .



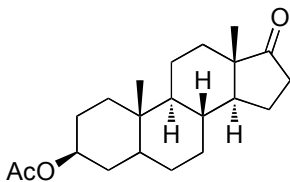
Isobutyrophenone (4k, commercially available): Colorless oil, ^1H NMR (400 MHz, CDCl_3) δ 1.22 (d, $J = 6.9$ Hz, 6H), 3.56 (sept, $J = 6.9$ Hz, 1H), 7.46 (t, $J = 7.3$ Hz, 2H), 7.55 (t, $J = 7.3$ Hz, 1H), 7.96 (d, $J = 7.3$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 19.2 (2C), 35.4, 128.4 (2C), 128.7 (2C), 132.9, 136.3, 204.6. IR (neat) 2972, 1684, 1465, 1383, 1225, 1161 cm^{-1} .



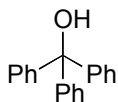
Pivalophenone (4l, commercially available): Colorless oil, ^1H NMR (400 MHz, CDCl_3) δ 1.35 (s, 9H), 7.39 (tt, $J = 7.3$, 1.6 Hz, 2H), 7.45 (tt, $J = 7.3$, 1.6 Hz, 1H), 7.68 (dt, $J = 7.3$, 1.6 Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 27.9 (3C), 44.1, 127.8 (2C), 128.0 (2C), 130.7, 138.5, 209.2. IR (neat) 2969, 1674, 1476, 1366, 1277, 1175 cm^{-1} .



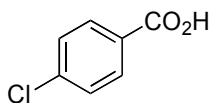
Benzophenone (4m, commercially available): White solid, ^1H NMR (400 MHz, CDCl_3) δ 7.49 (t, $J = 7.8$ Hz, 4H), 7.60 (t, $J = 7.8$ Hz, 2H), 7.81 (d, $J = 7.8$ Hz, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ 128.2 (4C), 130.0 (4C), 132.2 (2C), 137.6 (2C), 196.7. IR (neat) 3055, 1652, 1596, 1319, 1278 cm^{-1} .



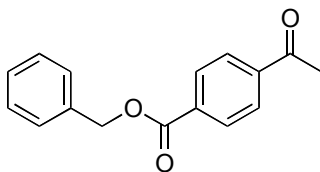
(3 β ,5 α)-3-(Acethyloxy)-androstan-17-one (5n): White solid, ^1H NMR (400 MHz, CDCl_3) δ 0.67-0.76 (m, 1H), 0.85 (s, 3H), 0.86 (s, 3H), 0.91-1.10 (m, 2H), 1.14-1.42 (m, 7H), 1.43-1.58 (m, 3H), 1.58-1.70 (m, 2H), 1.70-1.87 (m, 4H), 1.88-1.98 (m, 1H), 2.02 (s, 3H), 2.01-2.12 (m, 1H), 2.43 (dd, $J = 19.5$, 8.2 Hz, 1H), 4.63-4.74 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 12.2, 13.8, 20.4, 21.4, 21.7, 27.4, 28.2, 30.8, 31.5, 33.9, 35.0, 35.6, 35.8, 36.7, 44.6, 47.7, 51.3, 54.3, 73.5, 170.6, 221.2. IR (neat) 2939, 1743, 1730, 1367, 1242, 1234, 1021 cm^{-1} . MS (ESI) calcd for $\text{C}_{21}\text{H}_{32}\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$ 355.2244, found 355.2239.



Triphenylmethanol (5o, commercially available): White solid, ^1H NMR (400 MHz, CDCl_3) δ 2.80 (s, 1H), 7.25-7.35 (m, 15H). ^{13}C NMR (100 MHz, CDCl_3) δ 82.1, 127.4 (3C), 128.01 (6C), 128.03 (6C), 146.9 (3C). IR (neat) 3467, 2924, 1444, 1156, 1010 cm^{-1} .



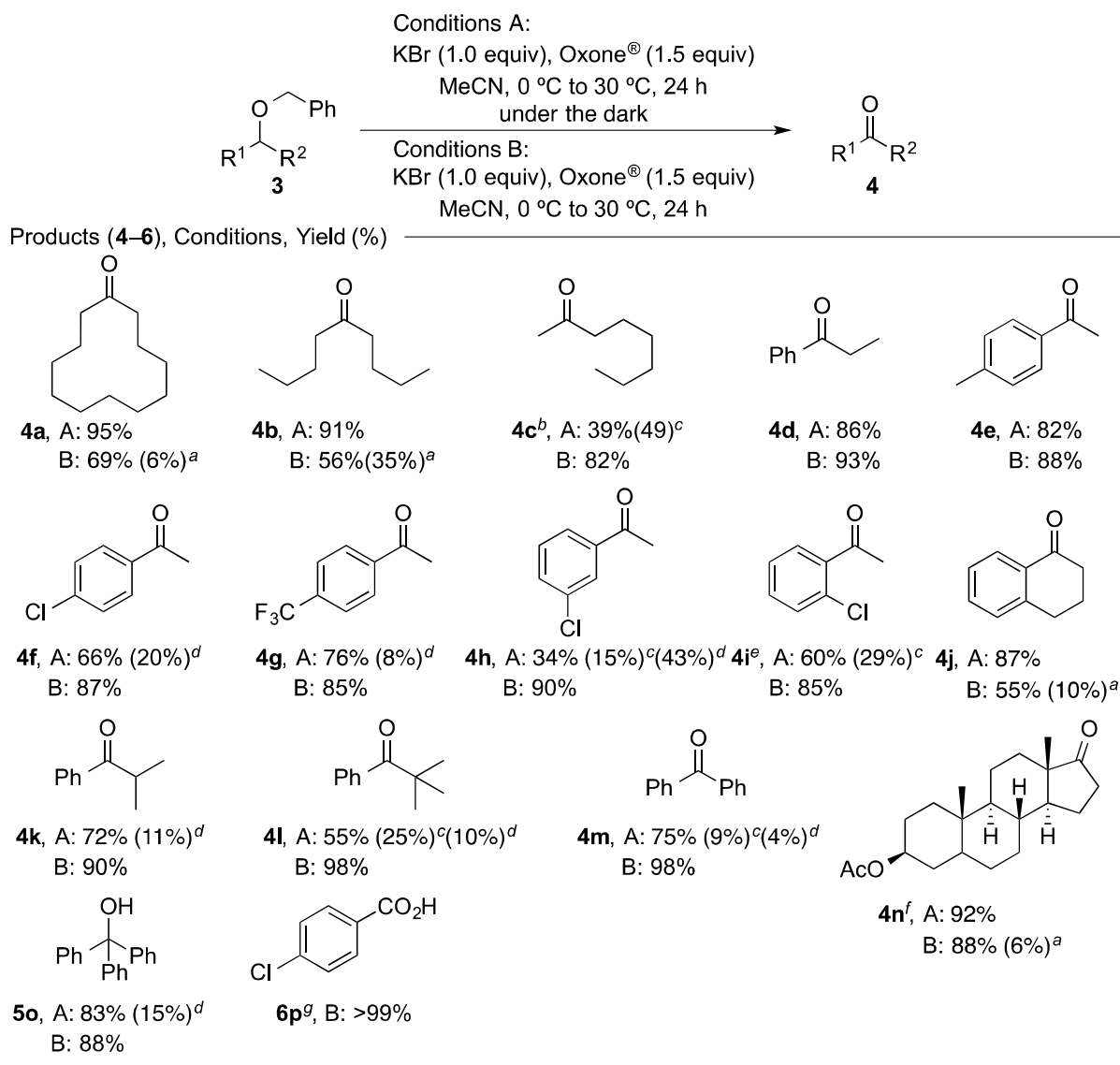
4-Chlorobenzoic acid (6p, commercially available): White solid, ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 3.35 (brs, 1H), 7.58 (d, $J = 8.6$ Hz, 2H), 7.94 (d, $J = 8.6$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 128.8 (2C), 129.6, 131.2 (2C), 137.8, 166.5. IR (neat) 2839, 1685, 1592, 1425, 1324, 1092 cm^{-1} .



Benzyl 4-acetylbenzoate (4r): White solid, ^1H NMR (400 MHz, CDCl_3) δ 2.64 (s, 3H), 5.39 (s, 2H), 7.33-7.48 (m, 5H), 8.00 (dt, $J = 8.7, 1.8$ Hz, 2H), 8.16 (dt, $J = 8.7, 1.8$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 26.9, 67.2, 128.2 (2C), 128.3 (2C), 128.4, 128.7 (2C), 129.9 (2C), 133.9, 135.6, 140.3, 165.6, 197.5. IR (neat) 1719, 1686, 1258, 1102, 1015 cm^{-1} . MS (ESI) calcd for $\text{C}_{16}\text{H}_{16}\text{O}_3$ $[\text{M}+\text{H}]^+$ 255.1016, found 255.1017.

4. A Comparative Experiment for Debenzylation of *O*-Benzyl Ethers under the Dark Conditions or not

Scheme S1. A Comparative Experiment for Debenzylation of Ethers **3** under the Dark Conditions (Conditions A) or not (Conditions B).



^a Number in parentheses indicates the yield of α -bromo ketones. ^b KBr (1.2 equiv) and Oxone[®] (1.8 equiv) were used. ^c Number in parentheses indicates the yield of alcohols. ^d Number in parentheses indicates the recovery of **3**. ^e KBr (1.0 equiv) and Oxone[®] (1.8 equiv) were used. ^f The reaction was carried out for 28 h. ^g KBr (2.0 equiv) and Oxone[®] (3.0 equiv) were used.

5. Mechanistic Study of the Oxidative Debenzylation of *N*-Benzylamide (**1a**) and *O*-Benzyl Ether (**3a**) Using Alkali Metal Bromide

Treatment of **1a** with KBr (1.0 equiv.) and Oxone[®] (1.5 equiv.) in MeNO₂ at 30 °C for 24 h gave the desired product **2a** (99%) together with benzoic acid (93%) (Scheme S2, eq S1). Reaction of **3a** with KBr (1.0 equiv.) and Oxone[®] (1.5 equiv.) in MeCN at 0 °C to 30 °C for 24 h also provided the desired ketone **4a** (95%) together with benzaldehyde (30%) and benzoic acid (15%) (Scheme S2, eq. S2). It is noteworthy that benzaldehyde easily oxidize to benzoic acid by a redundant amount of potassium peroxymonosulfate (Oxone[®] = 2KHSO₅•KHSO₄•K₂SO₄) during the oxidative debenzylation.

Scheme S2. The Oxidative Debenzylation of **1a** and **3a** Using Alkali Metal Bromide.

