**Mix-and-Heat Benzylation of Alcohols using a Bench-
Stable Pyridinium Salt**

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Supporting Information

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Experimental Section

All the chemicals were used as received unless otherwise stated. MgO was dried in an oil bath at 140 °C for 6 h under vacuum and stored in a round bottom flask under argon. Purifications of the compounds were performed on flash chromatography using silica gel F-254 (230-400 mesh particle size).

2-Benzyloxy-1-methylpyridinium triflate (1): ¹HNMR (300MHz, CDCl₃) δ 8.49 (d, *J* = 7.8 Hz, 1H), 8.34 (apparent t, *J* = 8.3 Hz, 1H), 7.59 (d, *J* = 9.0 Hz, 1H), 7.53–7.42 (m, 6H), 5.58 (s, 2H), 4.13 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 159.6, 148.0, 143.8, 132.5, 129.6, 129.1, 128.5, 119.0, 112.1, 74.5, 42.0. HRMS (ESI+) found 200.1070 (M–OTf)⁺ (calcd for C₁₃H₁₄NO⁺: 200.1075).

1-Benzyloxy-3-phenylpropane (3a): Sajiki, H.; Hirota, K. *Tetrahedron* **1998**, *54*, 13981–13996.

1-Benzyloxy-4-(*p*-methoxyphenyl) butane (3b): ¹HNMR (300MHz, CDCl₃) δ 7.38–7.27 (m, 5H), 7.09 (d, *J* = 8.4 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 4.49 (s, 2H), 3.79 (s, 3H), 3.48 (apparent t, *J* = 5.9 Hz, 2H), 2.57 (t, *J* = 7.2 Hz, 2H) 1.69–1.62 (m, 4H); ¹³C NMR (75 MHz, CDCl₃) δ 157.6, 138.6, 134.5, 129.2, 128.2, 127.5, 127.4, 113.6, 72.8, 70.2, 55.1, 34.7, 29.3, 28.2. HRMS (EI+) found 270.1619 (M⁺) (calcd for C₁₈H₂₂O: 270.1620).

(1*E*)-3-Benzyloxy-1-phenylpropene (3c): Kim, H.; Lee, C. *Org. Lett.* **2002**, *4*, 4639–4371.

Diethylene glycol benzyl methyl ether (3d): Grobelny, Z.; Stolarzewicz, A.; Maercker, A.; Krompiec, S.; Kasperczyk, J.; Rzepa, J. *J. Organomet. Chem.* **2004**, *689*, 1580–1585.

Methyl (2*R*)-3-(benzyloxy)-2-methylpropionate (3e): White, J. D.; Kawasaki, M. *J. Org. Chem.* **1992**, *57*, 5292–5300.

Benzyl α-methylbenzylether (3f): Kim, S.; Chung, K. N.; Yang, S. *J. Org. Chem.* **1987**, *52*, 3917–3919.

(1*R*, 2*S*, 5*R*)-(-)-*O*-Benzylmenthol (3g): Johnson, D. C., II; Widlanski, T. S. *Org. Lett.* **2004**, *6*, 4643–4646.

5 α -Cholester-3 β -yl Benzyl Ether (3h): Jang, D. O.; Song, S. H.; Cho, D. H. *Tetrahedron* **1999**, *55*, 3479–3488.

Benzyl Adamantyl Ether (3i): Hartz, N.; Prakash, G. K. S.; Olah, G. A. *Synlett* **1992**, 569–572.

2-Phenyl-2-benzyloxypropane (3j): a) Gevorgyan, V.; Liu, J. X.; Rubin, M.; Benson, S.; Yamamoto, Y. *Tetrahedron Lett.* **1999**, *40*, 8919–8922. b) Gevorgyan, V.; Liu, J. X.; Rubin, M.; Benson, S.; Yamamoto, Y. *J. Org. Chem.* **2000**, *65*, 6179–6186.

4-Benzyloxybiphenyl (3k): Percec, V.; Golding, G. M.; Smidrkal, J.; Weichold, O. *J. Org. Chem.* **2004**, *69*, 3447–3452.

TBS ether (8): ^1H NMR (300MHz, CDCl_3) δ 7.09 (d, J = 8.7 Hz, 2H), 6.82 (d, J = 8.7 Hz, 2H), 3.79 (s, 3H), 3.62 (t, J = 6.3 Hz, 2H), 2.57 (apparent t, J = 7.4 Hz, 2H) 1.68-1.50 (m, 4H), 0.89 (s, 9H), 0.04 (s, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 157.6, 134.7, 129.2, 113.6, 63.0, 55.2, 34.7, 32.4, 27.8, 26.0, 18.4, -5.28. HRMS (EI+) found 294.2017 (M^+) (calcd for $\text{C}_{17}\text{H}_{30}\text{O}_2\text{Si}$: 294.2015).

2-Methoxypyridinium triflate (10): Mp: 114–125 °C. ^1H NMR (300MHz, acetone- d_6) δ 8.73 (d, J = 6.3 Hz, 1H), 8.61 (apparent t, J = 8.1 Hz, 1H), 7.86 (d, J = 8.7 Hz, 1H),

7.65 (t, $J = 6.9$ Hz, 1H), 4.44 (s, 3H), 4.22 (s, 3H); ^{13}C NMR (75 MHz, D_6 acetone) δ 149.0, 145.7, 120.5, 113.1, 61.0, 43.2. HRMS (ESI+) found 124.0768 (M-OTf^+) (calcd for $\text{C}_7\text{H}_{10}\text{NO}^+$: 124.0762).

2-(Trimethylsilyl)ethanol, benzyl ether (**14**): ^1H NMR (300MHz, CDCl_3) δ 7.38-7.28 (m, 5H), 4.49 (s, 2H), 3.58 (apparent t, $J = 8.3$ Hz, 2H), 1.00 (apparent t, $J = 8.3$ Hz, 2H), 0.02 (s, 9H).

2-benzyloxy-1-methylpyridinium triflate (**1**)

1-Benzyloxy-3-phenylpropane (3a) and dibenzyl ether (diagnostic singlet: 4.567, 4H)

1-Benzyloxy-4-(*p*-methoxyphenyl) butane (3b) and dibenzyl ether (diagnostic singlet: 4.567, 4H)

**(1E)-3-Benzyloxy-1-phenylpropene (3c) and dibenzyl ether (diagnostic singlet:
4.567, 4H)**

Diethylene glycol benzyl methyl ether (3d)

Methyl (2*R*)-3-(benzyloxy)-2-methylpropionate (3e)

Benzyl α -methylbenzylether (3f) and dibenzyl ether (diagnostic singlet: 4.567, 4H)

(1*R*, 2*S*, 5*R*)-(-)-*O*-Benzylmenthol (3g)

5α-Cholester-3β-yl Benzyl Ether (3h)

Benzyl Adamantyl Ether (3i) and dibenzyl ether (diagnostic singlet: 4.567, 4H)

2-Phenyl-2-benzyloxypropane (3j) and dibenzyl ether (diagnostic singlet: 4.567, 4H)

4-Benzyloxybiphenyl (3k) and dibenzyl ether (diagnostic singlet: 4.567, 4H)

TBS ether (8)

2-methoxypyridinium triflate (10)

2-(Trimethylsilyl)ethanol benzyl ether (14)

crude product from reaction mixture of Bn-OPT and 2-(Trimethylsilyl) ethanol

crude product from reaction mixture of benzyltrichloroacetimidate, TfOH and 2-(Trimethylsilyl) ethanol