Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Microwave-assisted benzyl-transfer reactions of commercially available 2-benzyloxy-1-methylpyridinium triflate

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General procedure (Alcohols and arene)

An oven-dried 10-mL microwave reaction vessel equipped with a magnetic stir bar was charged with 2-benzyloxy-1-methylpyridinium trifluoromethanesulfonate (**1**) (1.2–2.0 mmol, 1.2–2.0 equiv, see Table 1), *α*,*α*,*α*-trifluorotoluene (2 mL), and alcohol **2**[a] (1.0 mmol, 1.0 equiv).[b] The mixture was irradiated in an Anton Paar Monowave 300 microwave synthesis reactor at a constant temperature of 120 °C. After 20 minutes at 120 °C, the reaction vessel was cooled using a stream of compressed air, and the reaction mixture was suction-filtered through a pad of Celite. The Celite was washed with diethyl ether (2 x 10 mL). The filtrate was concentrated by rotary evaporation, and the resulting light brown oil was purified by flash column chromatography on silica gel to obtain the benzylated products as described in Table 1.

Notes: [a]*Used 5 equiv. of* ***2i****.* [b]*2 equiv. of MgO included with alcohols* ***2e*** *and* ***2f****; see Table 1.*

General procedure (Carboxylic Acid)

An oven-dried 10 mL microwave reaction vessel equipped with a magnetic stir bar was charged with carboxylic acid (1.0 mmol, 1.0 equiv.), 2-benzyloxy-1-methylpyridinium trifluoromethanesulfonate (**1**) (2.0 mmol, 2.0 equiv.), *α*,*α*,*α*-trifluorotoluene (2 mL) and triethylamine (2.0 mmol, 2.0 equiv.). The mixture was irradiated in an Anton Paar Monowave 300 microwave synthesis reactor at a constant temperature of 120 °C. After 20 minutes at 120 °C, the reaction vessel was cooled using a stream of compressed air. The sample was then diluted with water (5 mL) and extracted with ethyl acetate (2 × 10 mL). The combined organic phases were washed with water (10 mL) and brine (10 mL), dried over magnesium sulfate, filtered, and concentrated by rotary evaporation. The crude residue was purified by flash column chromatography on silica gel to provide the benzyl ester products as described in Table 1.

Characterization (analytical) data

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

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

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

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

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

2-Phenyl-2 Benzyloxy butane (3f*): 1HNMR (400MHz, CDCl3) δ 7.26-7.23 (m, 10H), 4.32-4.29(d, *J* = 12 Hz, 1H), 4.21-4.18 (d, *J* = 12Hz), 1.91-1.86 (q, J = 7.4 Hz, 2H), 1.61 (s, 3H), 0.84-0.80(t, J = 7.4 Hz, 3H). 13C NMR (100 MHz, CDCl3) δ 145.38, 139.60, 128.42, 128.27, 128.12, 127.80, 127.65, 127.24, 127.09, 126.79, 126.32, 79.65, 72.13, 64.50, 35.51, 23.15, 8.44. IR; 3062.36, 3029.89, 2936.10, 2975.55, 2878.42, 1602.71, 1494.87, 1446.73, 1381.34, 1295.97, 1229.74, 1156.91, 1130.84, 1088.65, 1063.32, 1027.25, 986.71, 892.06, 759.75, 732.12, 694.58

**NMR signals associated with the dibenzyl ether by-product have been omitted.*

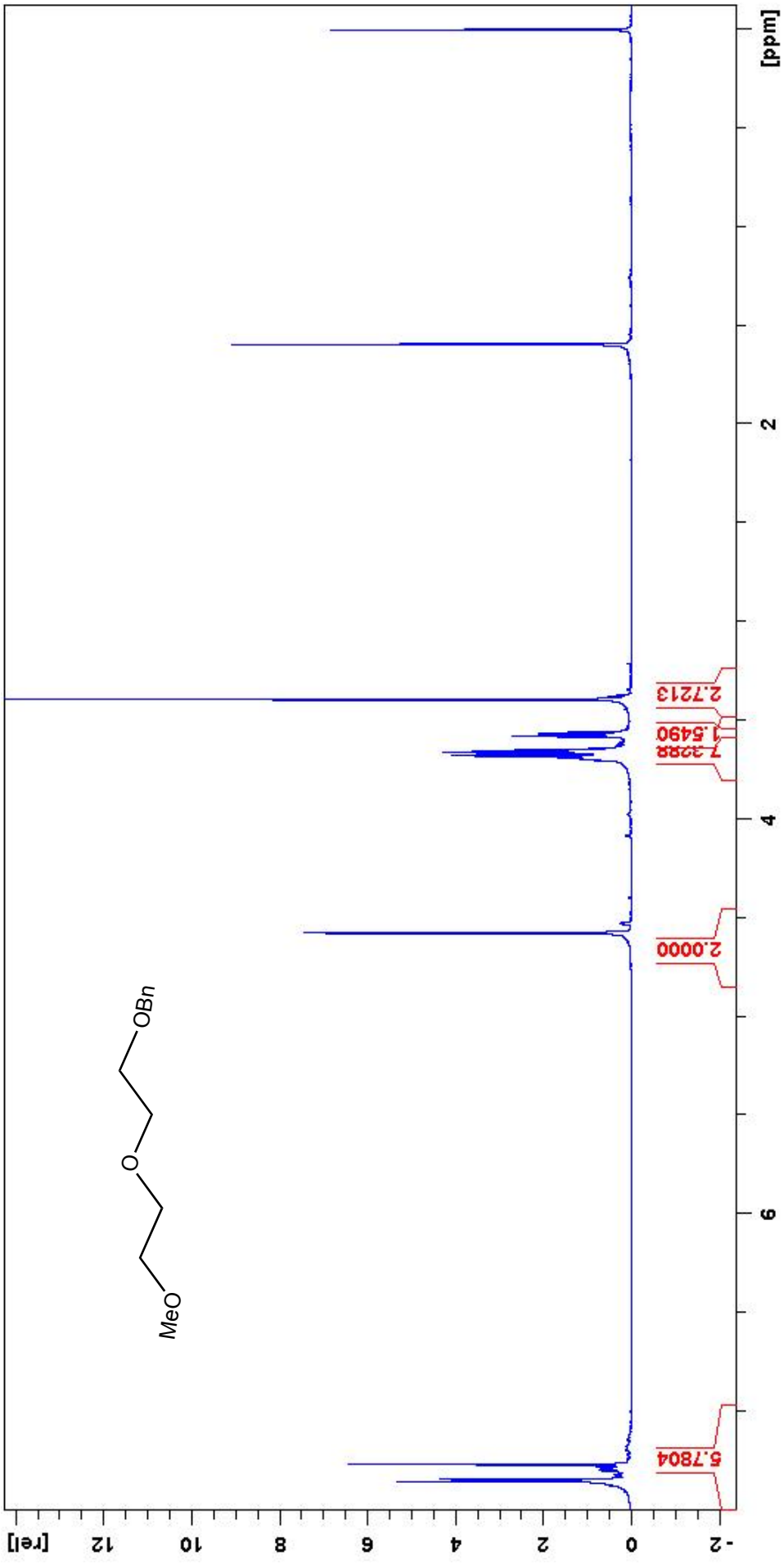
3-benzyloxy-3-methyl-butyne (3g): 1HNMR (400MHz, CDCl3) δ 7.39- 7.26 (m, 5H), 4.64 (s, 2H), 2.48 (s, 1H), 1.56 (s, 6H). 13C NMR (100 MHz, CDCl3) δ 138.85, 128.30, 127.73, 127.38, 86.08, 72.23, 70.47, 66.52, 28.84. IR 3032.22, 2985.75, 2936.01, 2867.77, 1605.69, 1497.72, 1454.38, 1380.38, 1360.84,1227.10, 1186.83, 1157.05, 1085.15, 1052.00, 1028.56, 1002.92, 942.42, 883.03,734.45, 710.56, 694.47

Benzoic acid benzyl ester (3h): Complete characterization data from Tummatorn, J.; Albiniak, P. A.; Dudley, G. B. *J. Org. Chem.* **2007**, *72*, 8962-8964.

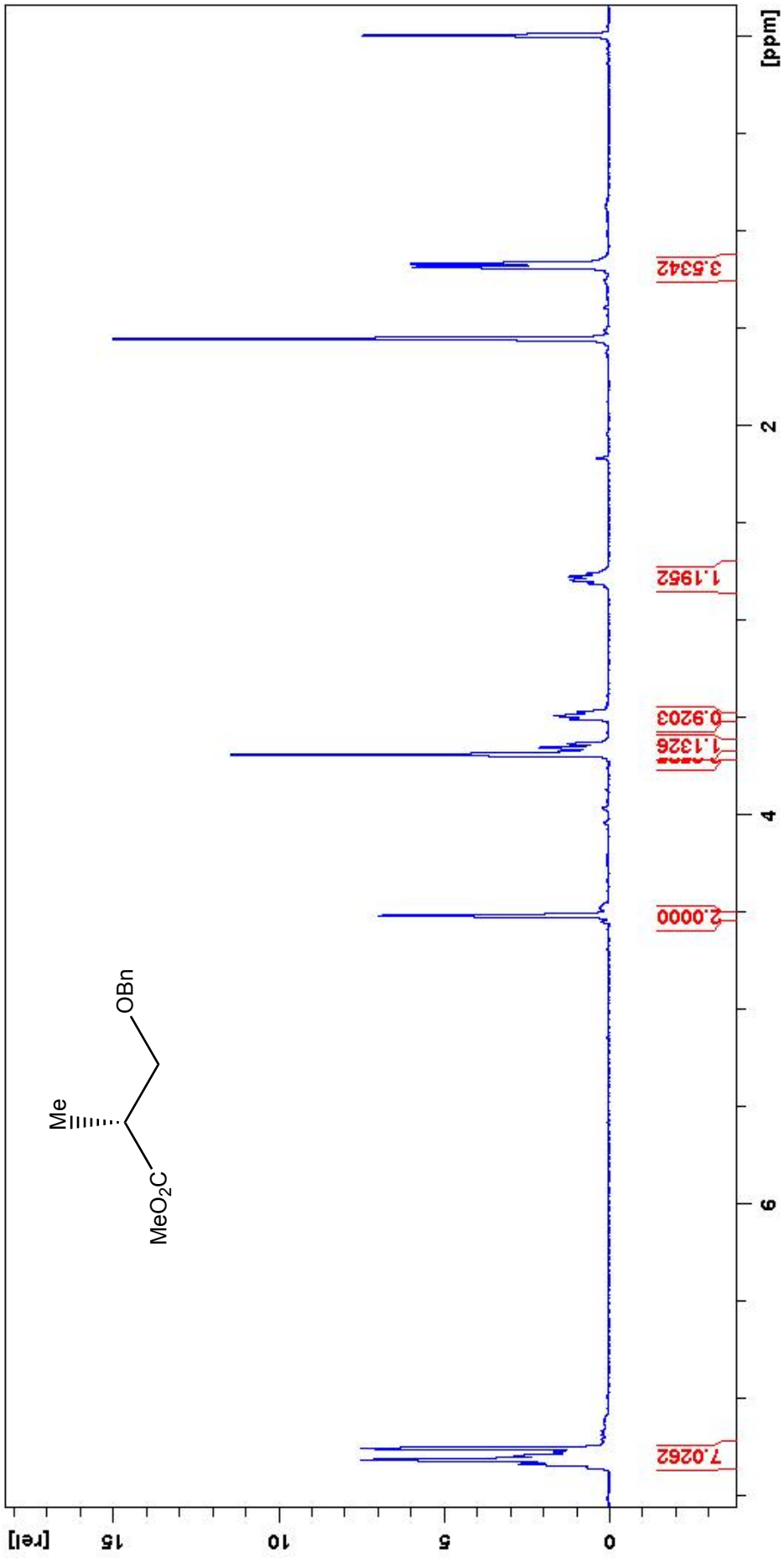
2-*tert*-Butoxycarbonoamino-3-hydroxy-propionic acid benzyl ester (3i): Crosignani, S.; White, P. D.; Linclau, B. *J. Org. Chem*. **2004**, 69, 5897 - 5905.

2-Benzyl anisole + 4-Benzyl anisole (3j): LI, Z.; CAO, L.; LI, C.-J.; Angew. Chem., Int. Ed. 46 (2007) 34, 6505-6507.

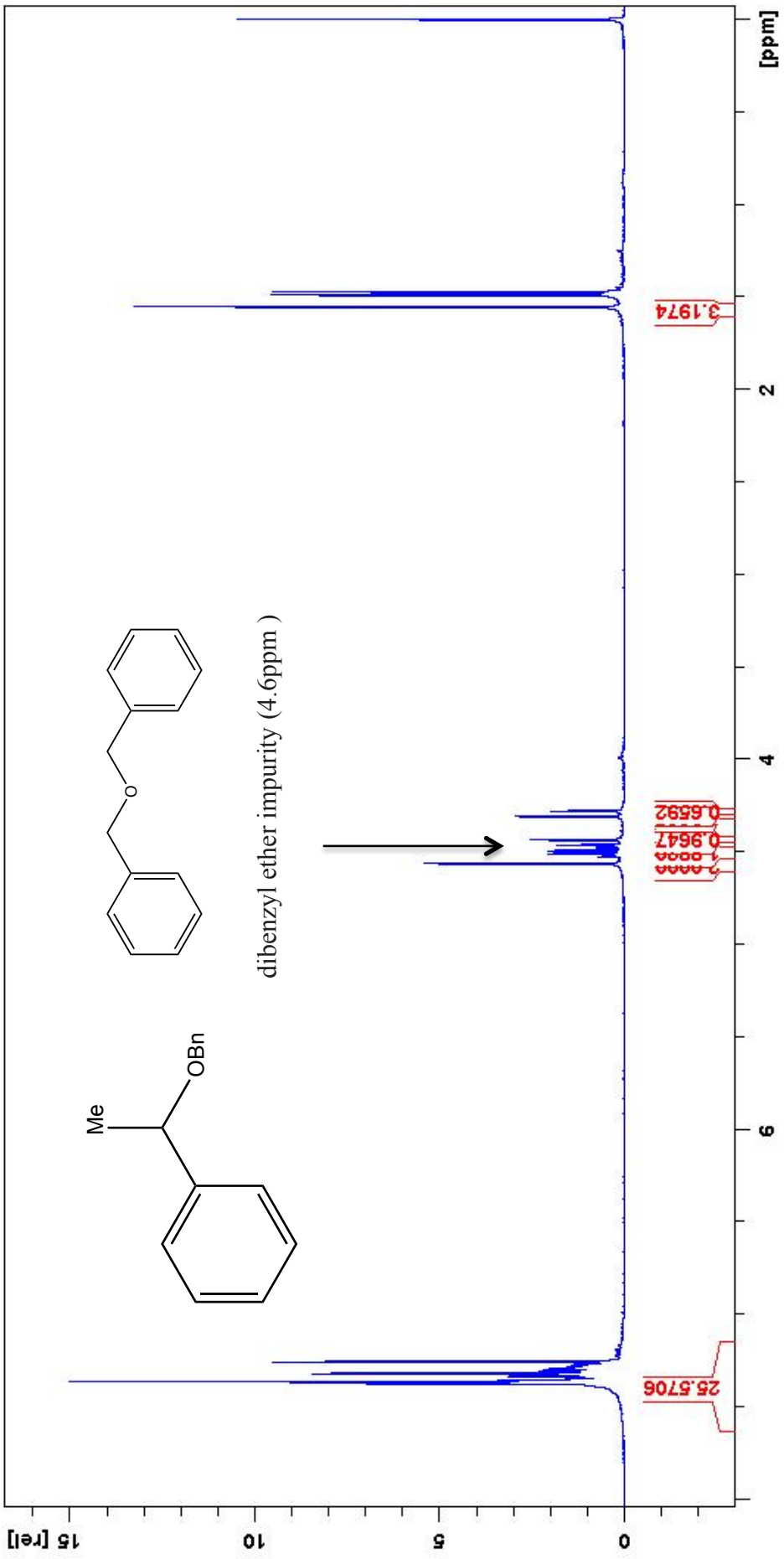
Diethylene glycol benzyl methyl ether (3a)



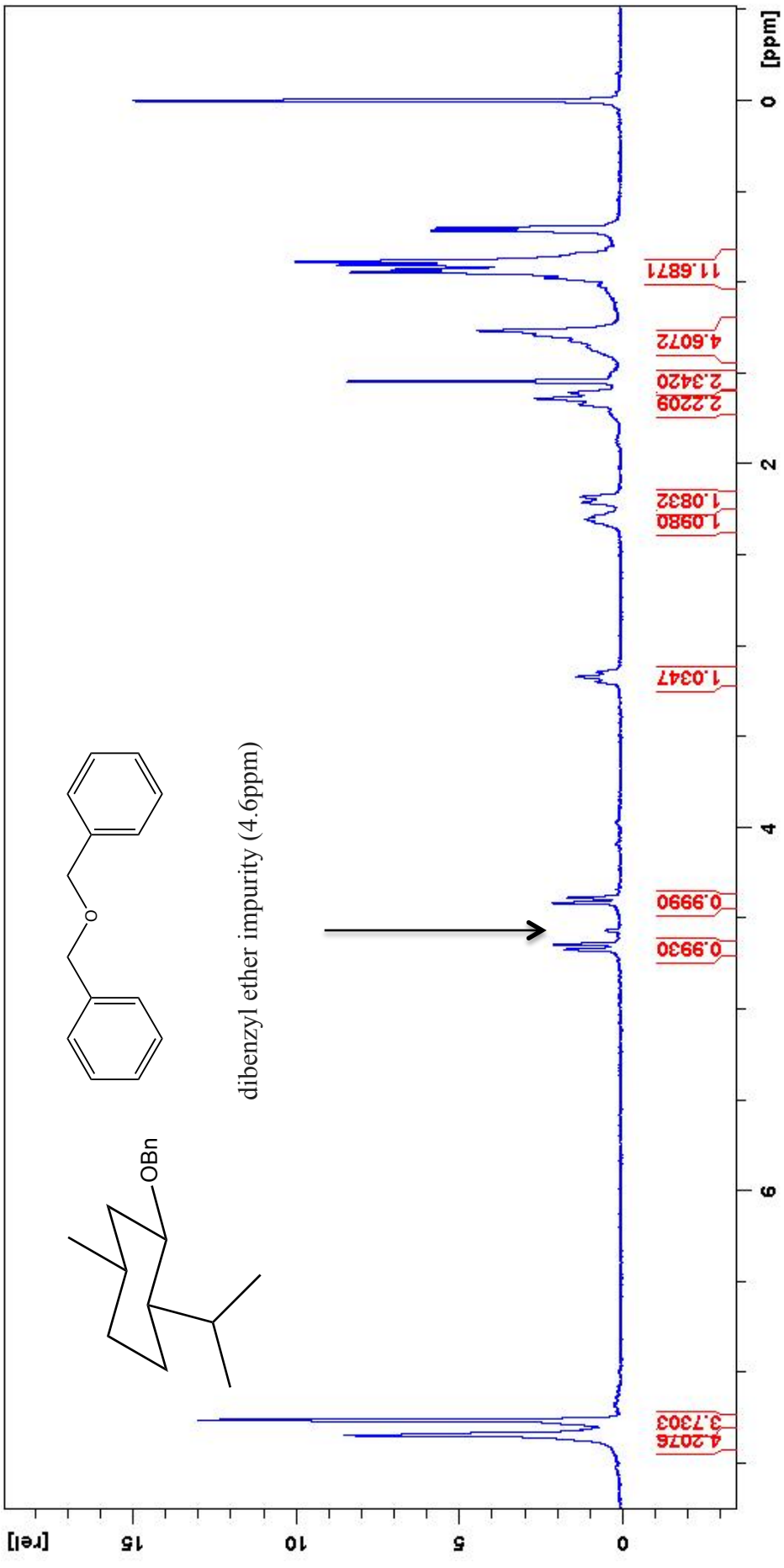
Methyl (2R)-3-(benzyloxy)-2-methylpropionate (3b)



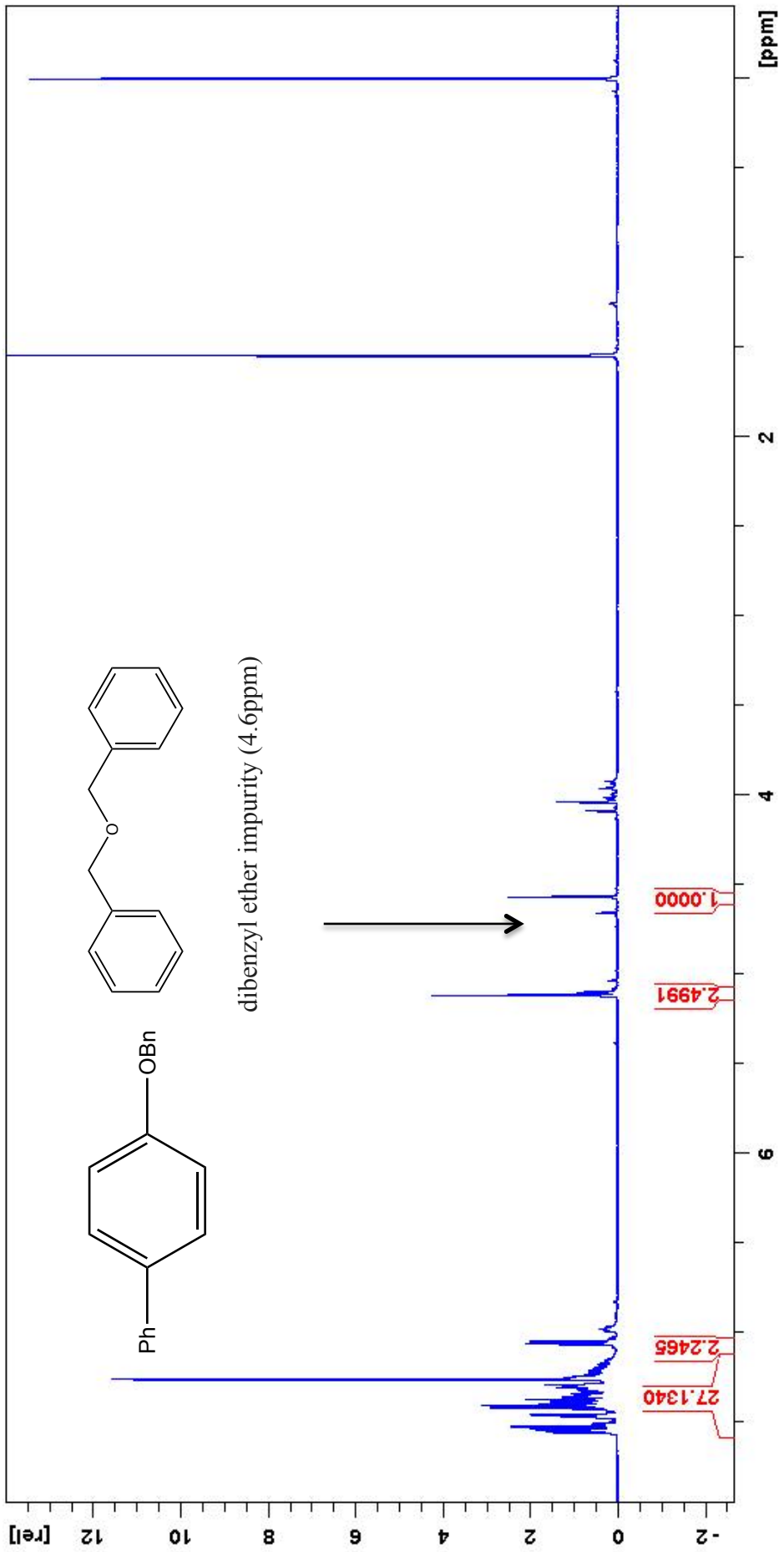
Benzyl α-methylbenzylether (3c) and dibenzyl ether



(1R,2S,5R)-(-)-O-Benzylmenthol (3d) and dibenzyl ether

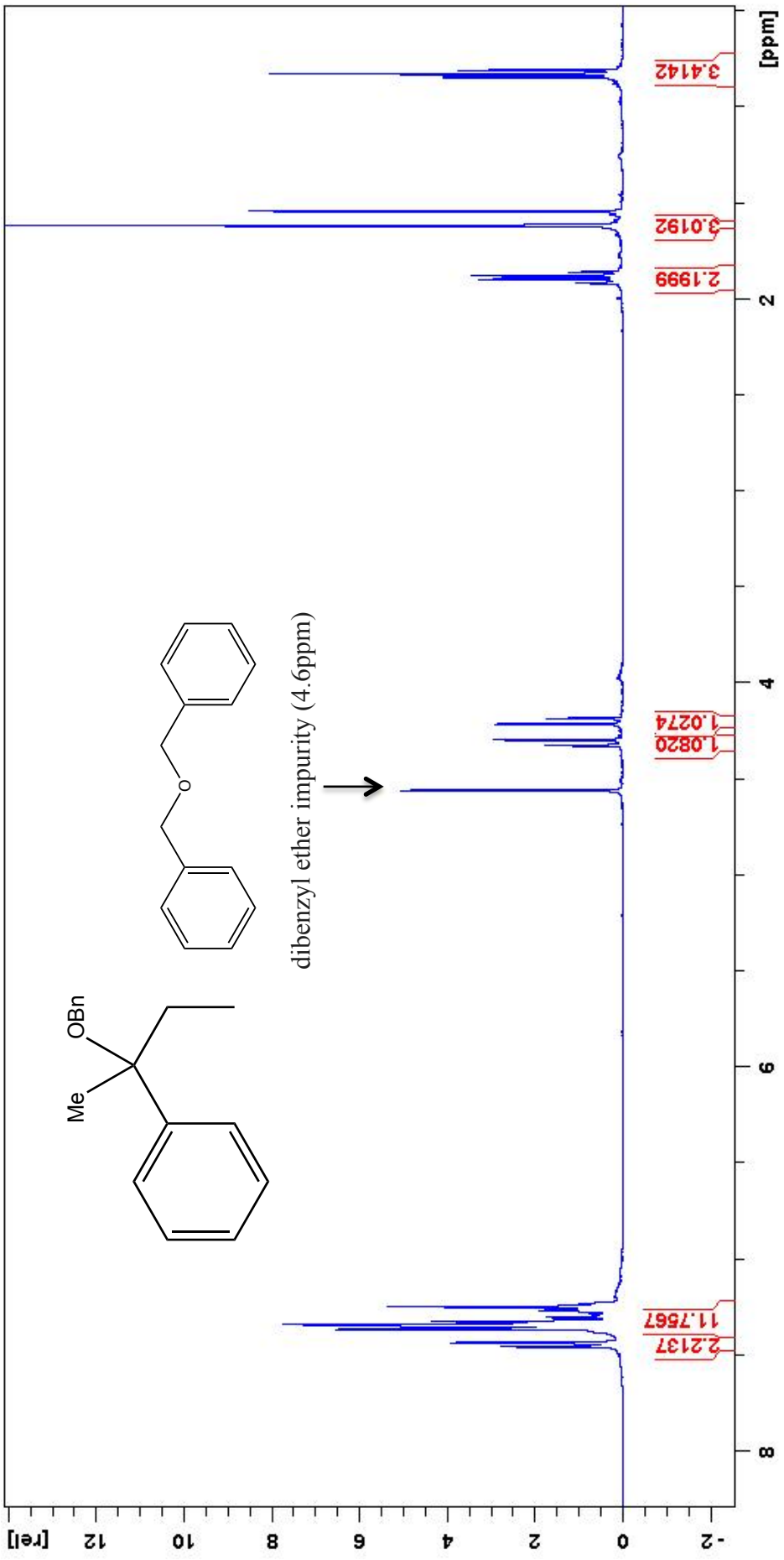


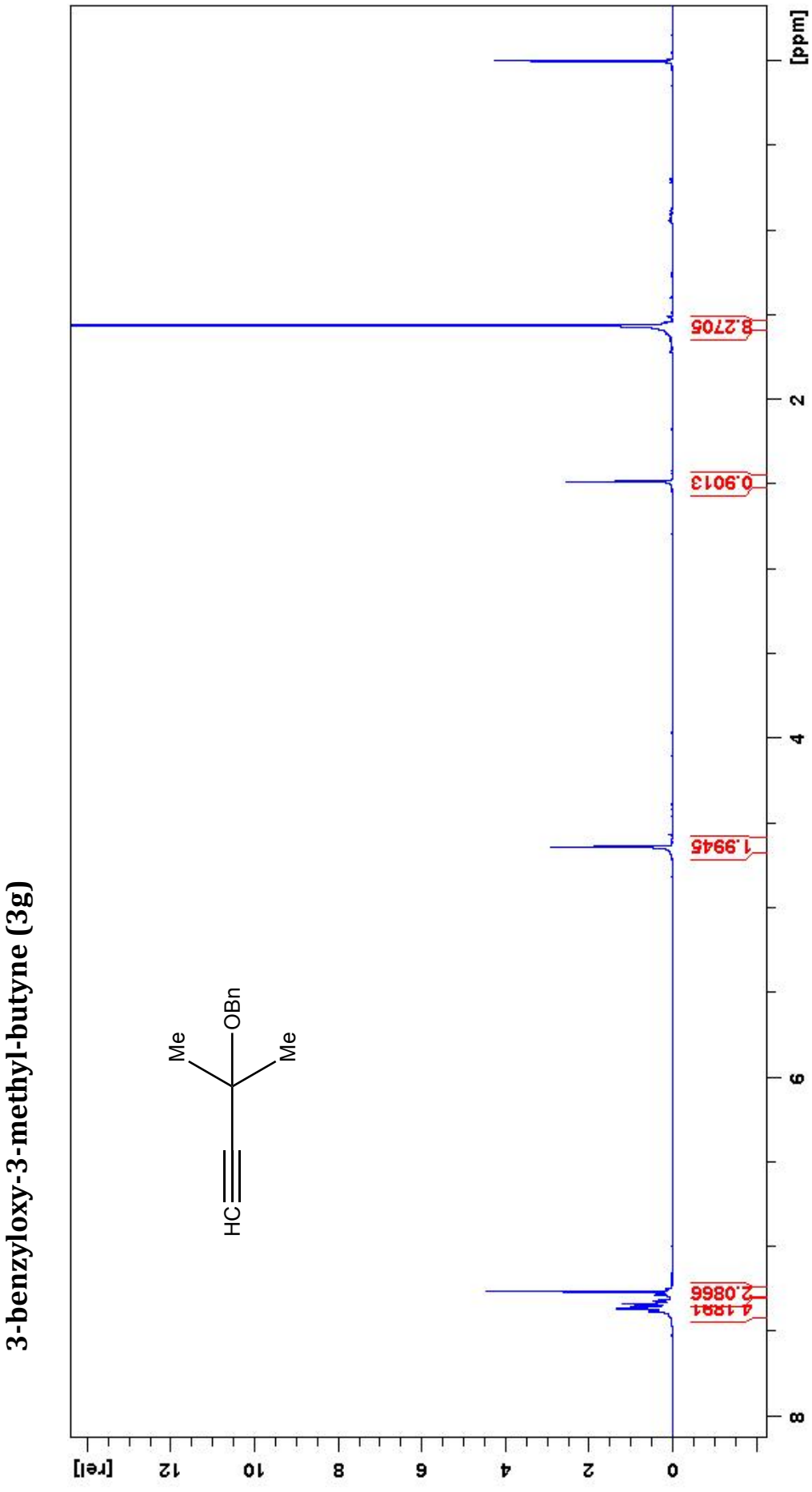
4-Benzyloxybiphenyl (3e) and dibenzyl ether



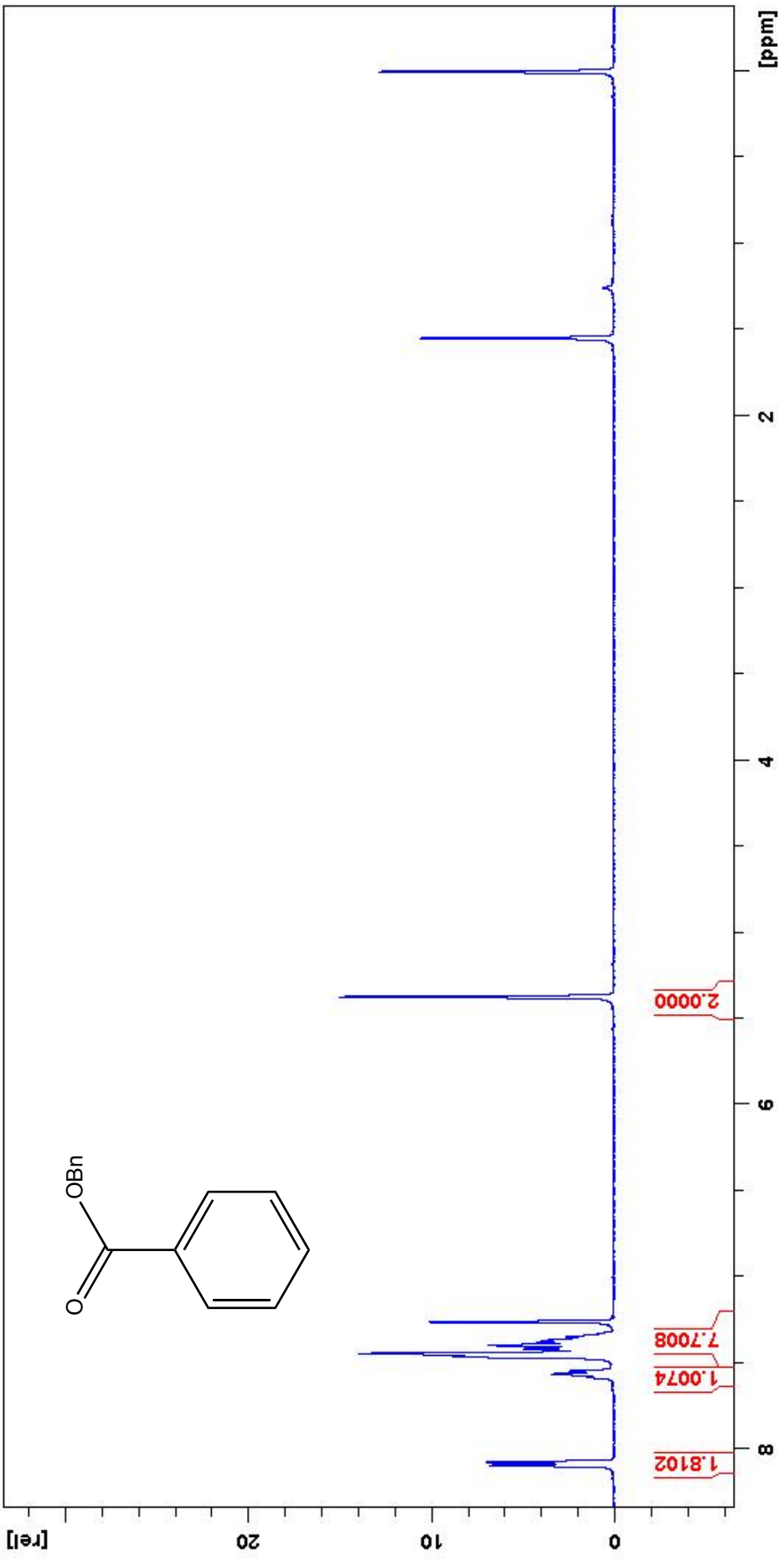
Notes: Additional peaks near 4.0 ppm represent various benzylation products of 4-phenylphenol and/or 4-benzyloxybiphenyl. This is consistent with the electron-rich nature of those arenes and with the modest yields of 4-benzyloxybiphenyl.

2-Phenyl-2 Benzyloxy butane (3f) and dibenzyl ether

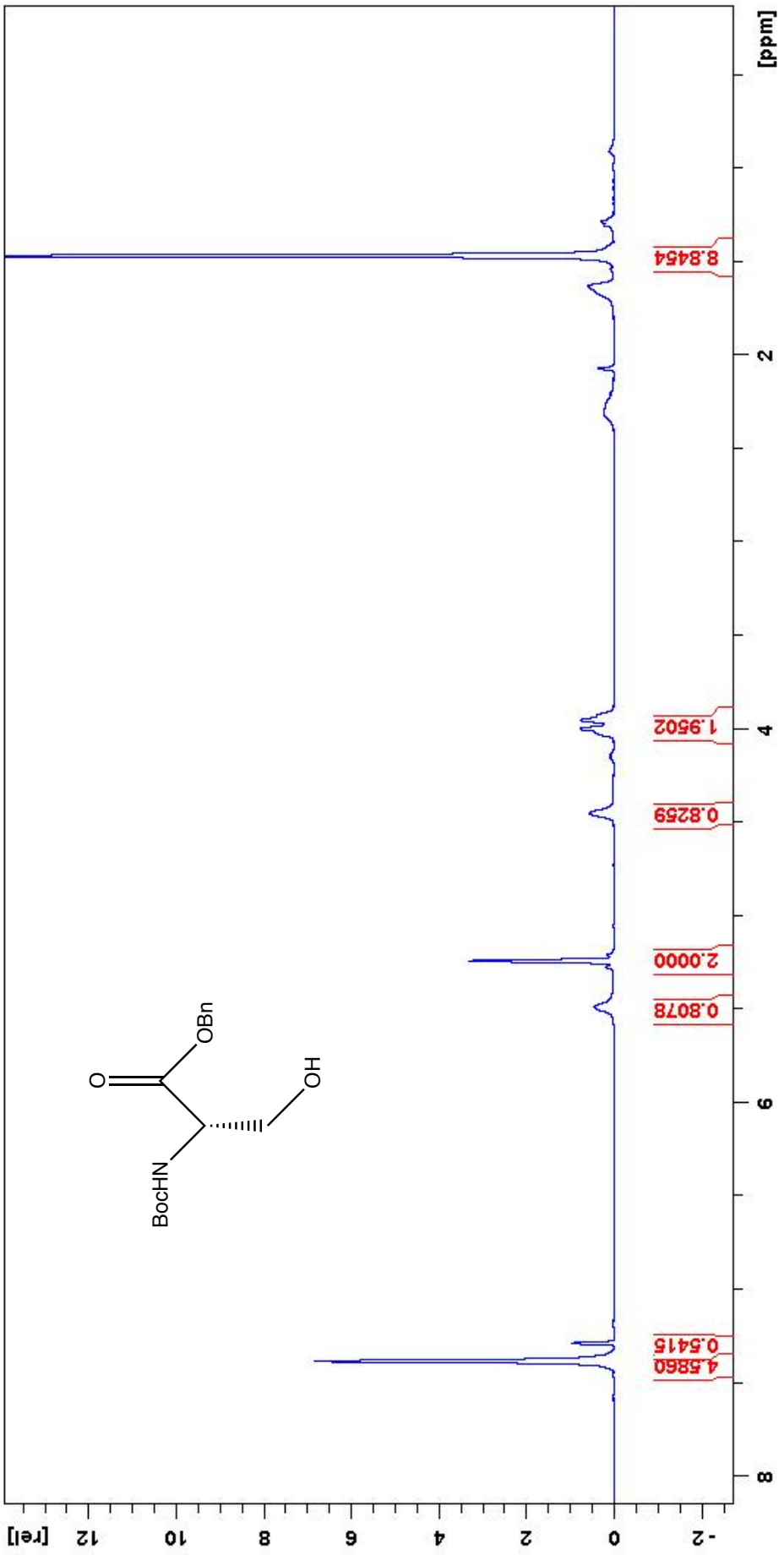




Benzoic acid benzyl ester (3h)



2-*tert*-Butoxycarbonoamino-3-hydroxy-propionic acid benzyl ester (3i)



Benzyl Anisole -mixture of regioisomers (3j)