

Synthetic Procedures for BmtBr, BmtCO₂H, and BmtCO₂Li·2THF

Materials. Magnesium chloride, lithium chloride, lithium wire, cupric chloride, *n*-butyllithium (1.6 M), and *tert*-butyllithium (1.7 M) were purchased from Aldrich Chemical Co. Carbon dioxide (bone dry) was procured from Matheson Gas Products, Inc. Elemental analyses were determined by Atlantic Microlabs, Inc. Solvents were dried and distilled according to standard purification methods.¹ All air sensitive reactions were performed either in a Vacuum Atmospheres inert-atmosphere glovebox under a N₂ atmosphere or by using standard Schlenk and vacuum line techniques.

BmtBr. This compound was synthesized following a modification of the published procedure.² To a batch of activated magnesium³ (3.70 g, 38.9 mmol) in 100 mL thf was slowly added 1,3-bis(2,6-dimethylphenyl)-2-iodobenzene⁴ (10.0 g, 24.3 mmol) under dry dinitrogen. This solution was stirred 14 h then filtered through celite. The filtrate was cooled to 0°C and to this was added a solution of 2,6-bis(bromomethyl)-4-*tert*-butylbromobenzene⁵ (3.23 g, 8.1 mmol), CuCl₂ (0.551 g, 4.1 mmol), and LiCl (0.343 g, 8.1 mmol) in 50 mL thf over 90 min. The mixture was stirred at room temperature for 30 min then heated to reflux for 14 h. The mixture was then allowed to cool to room temperature and 30 mL 10% HCl was added. The solution was transferred to a separatory funnel and 200 mL CH₂Cl₂ was added. The mixture was shaken and the organic layer separated. The aqueous layer was additionally extracted twice with 100 mL of CH₂Cl₂ and the pooled organic extracts were dried over Na₂SO₄. Evaporation of the solvent resulted in a residue which was redissolved in 300 mL of hexanes and heated to boiling. This solution was filtered, concentrated to 100 mL, and allowed to slowly cool to room temperature. The crystallization solution was then cooled to -20 °C and after 1 day crystals were collected. Yield: 4.59 g (70 %). Spectroscopic and analytical data for BmtBr are identical to that which was published previously.²

BmtCO₂H (3-H). To a stirring solution of 1.2 g (1.42 mmol) BmtBr in 300 mL ether at -50 °C was added 2.1 equiv (2.99 mmol) ^tBuLi. After 3 h, CO₂ (g) was bubbled into the reaction mixture for 5 min followed by sparging with dry HCl for 5 min. The solvent was then evaporated and the residue was extracted with 75 mL CH₂Cl₂. The solid obtained after removal of CH₂Cl₂ from the extract was loaded onto a silica column and eluted with 1:5 ethyl acetate:hexanes. The second band was collected and the solvent was removed to afford BmtCO₂H. Recrystallization from hexanes afforded analytically pure material. Yield: 770 mg (70%). ¹H NMR (CDCl₃, 300 MHz): δ 0.98 (s, 9H), 1.94 (s, 24H), 3.49 (s, 4H), 6.39 (s, 2H), 6.87 (m, 8H), 7.02 (m, 8H), 7.35 (t, 2H) ppm. ¹³C NMR (CDCl₃, 75 MHz): δ 21.14, 27.23, 31.07, 33.74, 34.85, 124.13, 127.63, 127.82,

128.72, 129.47, 136.00, 137.01, 138.41, 140.59, 142.36, 150.10, 171.21 ppm. IR (KBr pellet, cm^{-1}): 2423 (m), 3023 (s), 2932 (vs), 1715 (vs, ν_{CO}), 1603 (s), 1575 (s), 1455 (vs), 1377 (s), 1272 (s), 1208 (m), 1167 (m), 1082 (s), 1033 (m), 934 (m), 879 (w), 766 (vs), 633 (w), 548 (m). FAB-MS (MNBA), m/z (relative intensity, assignment): 775.7 (67, $[\text{BmtCO}_2\text{H}]^+$); 797.2 (100, $[\text{BmtCO}_2\text{Na}]^+$). Anal. Calcd for $\text{C}_{29}\text{H}_{34}\text{O}_2$: C, 88.33; H, 7.54. Found: C, 88.11; H, 7.43.

LiBmtCO₂·2thf. To a solution of 1.00 g (1.29 mmol) BmtCO₂H in 4 mL thf was slowly added ⁿBuLi (1.42 mmol, 1.1 equiv). The solution was stirred 30 min then the solvent was evaporated in vacuo. The remaining residue was redissolved in 2 mL thf and filtered. Pentane was diffused in and after 3 days, crystals were collected and placed under high vacuum for 30 min. Yield: 651 mg (54.6 %). ¹H NMR (CDCl₃, 300 MHz): δ 0.95 (s, 9H), 1.86 (m, 8H, thf), 1.91 (s, 24H), 3.44 (s, 4H), 3.74 (m, 8H, thf), 6.32 (s, 2H), 6.84 (m, 8H), 6.95 (m, 8H), 6.97 (m, 8H), 7.32 (t, 2H) ppm. ¹³C NMR (CDCl₃, 75 MHz): δ 21.05, 25.58, 31.03, 33.74, 33.58, 34.38, 68.03, 122.75, 126.46, 126.64, 127.27, 129.11, 134.93, 135.68, 137.16, 137.83, 140.75, 142.52, 145.53, 175.34 ppm. IR (KBr pellet, cm^{-1}): 3424 (br, s), 3061 (m), 2952 (s), 2869 (m), 1585 (s, ν_{CO}), 1459 (s), 1459 (s), 1390 (s), 1164 (m), 1082 (w), 1051 (m), 915 (w), 803 (m), 769 (s), 740 (m), 696 (m), 577 (m), 551 (m). Anal. Calcd for $\text{C}_{66}\text{H}_{73}\text{O}_4\text{Li}$: C, 84.58 ; H, 7.85. Found: C, 84.69; H, 7.75.

Summary of Characterization Data for All New Compounds

BmtCO₂H (**3-H**): colorless crystals (hexanes, 74%). ¹H NMR (CDCl₃): δ 0.98 (s, 9H), 1.94 (s, 24H), 3.49 (s, 4H), 6.39 (s, 2H), 6.87 (m, 8H), 7.02 (m, 8H), 7.35 (t, 2H) ppm; ¹³C{¹H} NMR (CDCl₃): δ 21.1, 27.2, 31.1, 33.7, 34.9, 124.1, 127.6, 127.8, 128.7, 129.5, 136.0, 137.0, 138.4, 140.6, 142.4, 150.1, 171.2 ppm; FTIR (KBr) 1715 cm^{-1} (ν_{CO}); FAB-MS (MNBA), m/z (relative intensity, assignment): 775.7 (67, $[\text{BmtCO}_2\text{H}]^+$); 797.2 (100, $[\text{BmtCO}_2\text{Na}]^+$). Anal. Calcd (found) for $\text{C}_{57}\text{H}_{58}\text{O}_2$: C, 88.33 (88.11); H, 7.54 (7.43). LiBmtCO₂·2thf: colorless crystals (thf/pentane, 55%); ¹H NMR (CDCl₃): δ 0.95 (s, 9H), 1.86 (m, 8H, thf), 1.91 (s, 24H), 3.44 (s, 4H), 3.74 (m, 8H, thf), 6.32 (s, 2H), 6.84 (m, 8H), 6.95 (m, 8H), 6.97 (m, 8H), 7.32 (t, 2H) ppm; ¹³C{¹H} NMR (CDCl₃): δ 21.1, 25.6, 31.0, 33.7, 33.6, 34.4, 68.0, 122.8, 126.5, 126.6, 127.3, 129.1, 134.9, 135.7, 137.2, 137.8, 140.8, 142.5, 145.5, 175.3 ppm. Anal. Calcd (found) for $\text{C}_{66}\text{H}_{73}\text{O}_4\text{Li}$: C, 84.58 (84.69); H, 7.85 (7.75). $[\text{Fe}(\text{BmtCO}_2)_2(\text{MeOH})_4]\cdot 4\text{MeOH}$: colorless crystals ($\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$, 73%). FTIR (KBr pellet, cm^{-1}): 2951 (s), 3427 (br, m), 1600 (m), 1562 (m), 1461 (s), 1163 (m), 1081 (m), 1031 (m), 802 (m), 769 (s), 740 (m). Anal. Calcd (Found) for $\text{C}_{122}\text{H}_{146}\text{O}_{12}\text{Fe}$: C, 78.77 (78.30); H, 7.91(7.23). $[\text{Cu}(\text{BmtCO}_2)_2(\text{MeOH})_2]$: light green crystals ($\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$,

63%). FTIR (KBr pellet, cm^{-1}): 3447 (br, m), 3061 (m), 2962 (s), 2922 (s), 2870 (m), 1602 (m), 1579 (m), 1459 (s), 1362 (vs), 1328 (m), 1262 (s), 1161 (m), 1083 (s), 1031 (s), 802 (s), 771 (s), 756 (m), 740 (m). UV-vis (CH_2Cl_2) [λ_{max} , nm (e, $\text{M}^{-1} \text{cm}^{-1}$): 685 (63), 800 (sh, 45). Anal. Calcd (found) for $\text{C}_{118}\text{H}_{122}\text{O}_6\text{Cu}$: C, 83.38 (82.91); H, 7.23 (7.20). EPR (1:10 $\text{CH}_3\text{OH}:\text{CH}_2\text{Cl}_2$, 20 K, 9.60 GHz): $g_{\perp} = 2.066$, $g_{\parallel} = 2.34$, $A_{\parallel} = 144$ G.

References

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