SUPPORTING INFORMATION

Title: Borax as an Efficient Metal-Free Catalyst for Hetero-Michael Reactions in an Aqueous Medium
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**Experimental**

**General:** Reagents and solvents were used as purchased. All reactions were monitored by TLC on silica gel 60 F254 (0.25mm), visualization was effected with UV and/or by developing in iodine. Chromatography refers to open column chromatography on silica gel (60-120 mesh). Organic extracts were dried over Na2SO4 (anhydrous). Solvents were removed in a rotary evaporator under reduced pressure. Crystalline borax was used for the reaction. Melting points were recorded with a Buchi B-545 melting point apparatus and were uncorrected. 1H NMR and 13C NMR were recorded on Bruker 200MHz and Varian 400MHz spectrometers. Chemical shifts are reported in (ppm) relative to TMS (1H) or CDCl3 and DMSO-d6 (13C) as internal standards. IR spectra were recorded in KBr or neat with a Nicolet Impact 410 spectrophotometer. GC-MS spectra were recorded on Perkin-Elmer Precisely Clarus 500 instrument using a capillary column (30×0.25×0.25 mm). Elemental analyses were carried out on a Perkin-Elmer 2400 automatic carbon, hydrogen, nitrogen and sulfur analyzer.

The following β-thio and amino compounds have been reported in literature: 1a, 2a, 4a, 6a, 7a, 9a, 12a, 13a, 14a, 15a, 16a, 17a, 19a, 21a, 22a, 23a, 24a, 25a, 28a, 29a (1b, 2b, 7b)12,13.

**Spectral Data for the β-thio and amino compounds (Michael adducts)**

**Product 3a.** Yield: 0.443 g, 92%, light yellow solid (mp 56–57 °C), IR (KBr) ν(tilde) = 1340 and 1511 (NO2), 1733 (C=O) cm\(^{-1}\); 1H NMR (400MHz, CDCl3) δ = 2.71(t, J = 7.6Hz, 2H), 3.30(t, J = 7.2Hz, 2H), 3.71(s, 3H), 7.34(d, J = 8.8Hz, 2H), 8.12(d, J = 8.8Hz, 2H); 13C NMR (100MHz, CDCl3) δ: 27.39, 33.73, 52.37, 124.20(2C), 126.76(2C), 145.21, 146.27, 171.89; C10H11NO4S (241.27): calcd. C 49.78, H 4.60, N 5.81, S 13.29, found C 49.62, H 4.65, N 5.85, S 13.25.
4a. Yield: 0.264 g, 89%, pale yellow liquid, IR(neat) ν(tilde) = 1744 (C=O) cm⁻¹; ¹H NMR (400MHz, CDCl₃) δ = 1.24(t, J = 7.2Hz, 3H), 2.54(q, J = 7.2Hz, 2H), 2.59(t, J = 7.6Hz, 2H), 2.77(t, J = 7.6Hz, 2H), 3.67(s, 3H); ¹³C NMR (100MHz, CDCl₃) δ = 14.87, 26.11, 26.67, 34.83, 51.84, 172.24; C₆H₁₂O₂S (148.23): calcd: C 48.62 H 8.16, S 21.63, found C 48.47, H 8.20, S 21.55.

5a. Yield: 0.433 g, 75%, colorless oil, IR (neat) ν(tilde) = 1747 (C=O) cm⁻¹; ¹H NMR (400MHz, CDCl₃) δ = 0.87(t, J = 6.4Hz, 3H), 1.25-1.59(m, 20H), 2.51(t, J = 7.6Hz, 2H), 2.60(t, J = 7.2Hz, 2H), 2.77(t, J = 7.2Hz, 2H), 3.69(s, 3H); ¹³C NMR (100MHz, CDCl₃) δ = 14.80, 23.36, 27.66, 29.53, 29.88, 29.99(2C), 30.18(2C), 30.25(2C), 32.56, 32.86, 35.40, 52.37, 172.38; C₁₆H₃₂O₂S (288.50): calcd. C 66.61, H 11.18, S 11.11, found C 66.52, H 11.25, S 11.07.

8a. Yield: 0.368 g, 72%, colorless oil, IR(neat) ν(tilde) = 2340 cm⁻¹ (CN); ¹H NMR (400MHz, CDCl₃) δ = 0.87(t, J = 6.8Hz,3H), 1.25–1.60(m, 20H), 2.58(t, J = 8Hz, 2H), 2.62(t, J = 7.2Hz, 2H), 2.77(t, J = 7.2Hz, 2H); ¹³C NMR (100MHz, CDCl₃) δ = 14.24, 19.05, 22.79, 27.76, 28.87, 29.28, 29.43, 29.57(2C), 29.72(3C), 32.00, 32.44, 118.25; C₁₅H₂₉NS (255.47): calcd. C 70.52, H 11.44, N 5.48, S 12.55, found C 70.32, H 11.49, N 5.49, S 12.48.

10a. Yield: 0.280 g, 87%, white solid: (mp 78°C) IR(KBr) ν(tilde) = 1657 (C=O), 3197 and 3374 (NH₂) cm⁻¹; ¹H NMR (400MHz, CDCl₃) δ = 0.91(t, J = 7.6Hz, 3H), 1.41(sex, J = 7.6Hz, 2H), 1.57(quin, J = 7.6Hz, 2H), 2.48–2.56(m, 4H), 2.79(t, J = 7.2Hz, 2H), 6.02(bs, NH), 6.02(bs, NH); ¹³C NMR (100MHz, CDCl₃) δ = 13.95, 22.21, 27.71, 31.85, 32.24, 36.23, 174.14; C₇H₁₃NOS (161.27): calcd. C 54.14, H 9.38, N 8.69, S 19.88, found C 52.09, H 9.39, N 8.72, S 19.79.

18a. Yield: 0.442 g, 88%, yellow solid: (mp 70°C); IR(KBr) ν(tilde) = 1340 and 1508 (NO₂), 1717 (C=O) cm⁻¹; ¹H NMR (400MHz, CDCl₃) δ = 1.81–1.89(m, 2H), 2.15–2.26(m, 2H), 2.39–2.49(m, 3H), 2.76–2.80(dd, J₁ = 4.4Hz, J₂ = 14Hz, 1H), 3.68–3.75(m,
1H), 7.399(d, J = 8.4Hz, 2H), 8.12(d, J = 8.4Hz, 2H); $^{13}$C NMR(100MHz, CDCl$_3$) δ = 24.25, 31.22, 41.09, 44.73, 47.50, 124.22(2C), 129.21(2C), 144.28, 146.04, 207.27; C$_{12}$H$_{13}$NO$_3$S (251.31): calcd. C 57.35, H 5.21, N 5.57, 12.76, found C 57.17, H 5.27, N 5.60, S 12.73.

20a. Yield: 0.417 g, 70%, colorless oil, IR(neat) ν(tilde) = 1717 (C=O) cm$^{-1}$; $^1$HNMR (400MHz, CDCl$_3$) δ = 0.87(t, J = 6.4Hz, 3H), 1.25–1.59(m, 20H), 1.67–1.73(m, 2H), 2.10–2.15(m, 2H), 2.32–2.39(m, 3H), 2.53(t, J = 7.6Hz, 2H), 2.67–2.72(m, 1H) 3.10–3.11(m, 1H); $^{13}$C NMR (100MHz, CDCl$_3$) δ = 14.80, 23.35, 24.96, 29.61, 29.86, 29.99, 30.15, 30.27(2C), 30.39(2C), 31.24, 32.36, 32.55, 41.59, 43.41, 48.89, 209.22; C$_{18}$H$_{34}$OS (298.54): calcd. C 72.42, H 11.48, S 10.74, found C 72.20, H 11.54, S 10.71.

26a. Yield: 0.217 g, 92%, white solid, (mp 179–181°C); IR(KBr) ν(tilde) = 1646 (C=O), 3200 and 3395 (NH$_2$) cm$^{-1}$; $^1$HNMR (400MHz, DMSO-d$_6$) δ = 2.32(t, J = 7.2Hz, 4H), 2.68–2.71(m, 6H), 6.83(bs, NH), 7.33(bs, NH); $^{13}$C NMR (100MHz, DMSO-d$_6$) δ = 26.87(2C), 31.27(2C), 35.65(2C), 172.22(2C); C$_8$H$_{16}$N$_2$O$_2$S$_2$ (236.36): calcd. C 40.65, H 6.82, N 11.85, S 27.13, found C 40.54, H 6.88, N 11.90, S 27.10.

27a. Yield: 0.235 g, 94%, white solid, (mp 147–149 °C); IR(KBr) ν(tilde) = 1648 (C=O), 3200 and 3397 (NH$_2$) cm$^{-1}$; $^1$HNMR (400MHz, DMSO-d$_6$) δ = 1.74(quin, J = 7.2Hz, 2H), 2.30(t, J = 7.2Hz, 4H), 2.55(t, J = 7.2Hz, 4H), 2.64(t, J = 7.6Hz, 4H), 6.81(bs, NH), 7.31(bs, NH); $^{13}$C NMR (100MHz, DMSO-d$_6$) δ = 26.88(2C), 29.03, 29.89(2C), 35.54(2C), 172.21(2C); C$_9$H$_{18}$N$_2$O$_2$S$_2$ (250.38): calcd. C 43.17, H 7.25, N 11.19, S 25.61, found C 43.05, H 7.29, N 11.17, S 25.53.

30a. Yield: 0.229 g, 86%, colorless oil, IR(neat) ν(tilde) = 1732 (C=O) cm$^{-1}$; $^1$HNMR (400MHz, CDCl$_3$) δ = 2.62(t, J = 7.2Hz, 4H), 2.74(s, 4H), 2.82(t, J = 7.2Hz 4H), 3.69(s, 6H); $^{13}$C NMR (100MHz, CDCl$_3$) δ = 27.33(2C), 32.39(2C), 34.96(2C), 52.12(2C), 171.22(2C); C$_{10}$H$_{18}$O$_4$S$_2$ (266.38): calcd. C 45.09, H 6.81, S 24.07, found C 44.94, H 6.85, S 24.11.
31a. Yield: 0.238 g, 85%, colorless oil, IR(neat) ν(tilde) = 1735 (C=O) cm⁻¹; ¹H NMR (400MHz, CDCl₃) δ = 1.85(quin, J = 7.2Hz, 2H), 2.60(t, J = 7.6 Hz, 4H), 2.62(t, J = 7.6Hz, 4H), 2.76(t, J = 7.2Hz, 4H), 3.68(s, 6H); ¹³C NMR (100MHz,CDCl₃) δ = 27.26(2C), 29.32, 31.14(2C), 34.93(2C), 52.04(2C), 172.28(2C); C₁₁H₂₀O₄S₂ (280.41): calcd. C 47.12, H 7.19, S 22.87, found C 47.02, H 7.25, S 22.79.

3b. Yield: 0.344 g, 89%, colorless liquid, IR(neat) ν(tilde) = 3467 (N-H) 1742(C=O) cm⁻¹; ¹H NMR (CDCl₃, 400MHz) δ = 1.87(s, 1NH), 2.52(t, J = 6.8Hz, 2H), 2.88(t, J = 6Hz, 2H), 3.66(s, 2H), 3.79(s, 3H), 7.20–7.30(m, 5H); C₁₁H₁₅NO₂ (193.25): C 68.37, H 7.28, N 7.25; found C 68.32, H 7.33, N 7.29.

4b. Yield: 0.396 g, 92%, colorless liquid, IR(neat) ν(tilde) = 1743(C=O) cm⁻¹; ¹H NMR: (CDCl₃, 400MHz) δ = 0.90(t, J = 6.8Hz, 6H), 1.26–1.44(m, 8H), 2.39(t, J = 7.2Hz, 2H), 2.60(t, J = 7.2Hz, 2H), 2.77(t, J = 7.6Hz, 2H), 3.66(s, 3H); ¹³C NMR (CDCl₃, 100MHz) δ = 14.50, 21.04, 29.70, 32.68, 47.18, 49.70, 50.17, 51.82, 54.00, 173.42; MS (EI): m/z 215(M⁺), 172(100%); C₁₂H₂₅NO₂ (215.34): calcd. C 66.93, H 11.70, N 6.50; found C 66.78, H 11.69, N 6.52.

5b. Yield: 0.248 g, 90%, colourless liquid, IR(KBr) ν(tilde) = 2259 (CN) cm⁻¹; ¹H NMR: (CDCl₃, 200MHz) δ = 1.44–1.49(m, 2H), 1.57–1.65(m, 4H), 2.40–2.50(m, 6H), 2.62–2.69(m, 2H); MS (EI): m/z 138(M⁺), 98(100%); C₈H₁₄N₂ (138.21): C 69.52, H 10.21, N 20.27; found C 69.49, H 10.25; N 20.29.

6b. Yield: 0.275 g, 86%, colorless liquid, IR(neat) ν(tilde) = 3334 (N–H), 2254 (CN) cm⁻¹; ¹H NMR: (CDCl₃, 200MHz) δ = 1.50(s, 1NH), 2.47(t, J = 4.4Hz, 2H), 2.90(t, J = 4.6Hz, 2H), 3.81(s, 2H), 7.24–7.28(m, 5H); MS (EI): m/z 160(M⁺), 91(100%); C₁₀H₁₂N₂ (160.22): C 74.97, H 7.55, N 17.48; found C 74.77 H 7.61; N 17.52.
$^1$H and $^{13}$C NMR spectra of β-amino compounds:

3a
3b

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\begin{align*}
\text{Ph} & \quad \text{H} & \quad \text{H} & \quad \text{C} & \quad \text{O} \quad \text{OMe} \\
\end{align*}
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4b

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\begin{align*}
\text{n-Bu} & \quad \text{H} & \quad \text{H} & \quad \text{C} & \quad \text{O} \quad \text{OMe} \\
\end{align*}
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References


