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$BtCH_2TMS$ Assisted Homologation of Carboxylic Acids: A Safe Alternative to the Arndt-Eistert Reaction

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Supporting Information

General procedure for the preparation of α-Bt ketones 3. To a solution of $BtCH_2TMS$ (10 mmol) in 50 mL of dry THF, acyl chloride (10 mmol) was added. The reaction mixture was refluxed for 24 h. The solvent was evaporated *in vacuo*. The solid product formed was recrystallized from THF to give colorless crystals in 85–95% yield.

2-(1*H*-1,2,3-Benzotriazol-1-yl)-1-phenyl-1-ethanone (3a). White crystals, mp 114-114.5 °C (90%, ethanol) (Lit.[7]: 113-114 °C).

2-(1*H*-1,2,3-Benzotriazol-1-yl)-1-(4-chlorophenyl)-1-ethanone (3b). White crystals, mp 154-154.5 °C (90%, ethanol); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 (1H, d, J = 7.8 Hz, Bt), 8.06 (2H, d, J = 7.1 Hz, Bt), 7.41–7.53 (3H, m), 7.40 (2H, d , J = 7.1 Hz), 6.06 (2H, s, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.2 (s, CO), 146.0 (s), 141.1 (s), 133.6 (s),

132.2 (s), 129.6 (d), 129.6 (d), 129.5 (d), 129.5 (d), 127.9 (d), 124.1 (d), 120.1 (d), 109.3 (d), 53.8 (t). Anal. Calcd. for $C_{14}H_{10}ClN_3O$: C, 61.89; H, 3.71; N, 15.47. Found: C, 61.70; H, 3.59; N, 15.40.

2-(1*H*-1,2,3-Benzotriazol-1-yl)-1-(4-methylphenyl)-1-ethanone (3c). White crystals, mp 133-135°C (91%, ethanol) (Lit.[7]: 133-135 °C).

2-(1*H*-1,2,3-Benzotriazol-1-yl)-propan-2-one (d). White crystals, mp 126-128 °C (83%, ethanol) (Lit.[7]: 126-127 °C).

1-(1H-1,2,3-benzotriazol-1-yl)-4,4-dimethyl-2-pentanone (3e). White needles, mp 60–61 °C (95%, hexane-ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10 (1H, d, *J* = 7.6Hz), 7.42-7.55 (3H, m), 5.45 (2H, s), 2.45 (2H, s), 1.05 (9H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.0 (s), 145.0 (s), 133.5 (s), 128.1 (d), 124.5 (d), 119.7 (d), 109.4 (d), 57.9 (t), 51.7 (t), 313 (s), 29.6 (q, $3CH_3$). Anal. Calcd. for $C_{13}H_{17}N_3O$: C, 67.51; H, 7.41; N, 18.17. Found: C, 67.34; H, 7.32; N, 18.20.

1-(1*H*-1,2,3-Benzotriazol-1-yl)-2-nonanone (3f). White crystals, mp 86-88 °C (95%, ethanol); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10 (1H, d, J = 7.6 Hz), 7.42–7.55 (3H, m), 5.54 (2H, s), 2.53 (2H, t, *J* = 7.3 Hz), 1.61 (2H, m), 1.25 (8H, m), 0.87 (3H, t, *J* = 6.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ202.0, 147.4, 133.9, 128.7, 125.4, 119.7, 110.0, 57.0, 40.2, 31.8, 29.2, 29.2, 23.5, 22.8, 14.3.

Typical Procedure for the Preparation of 4. To a cooled (0 °C) solution of **3a-f** (10 mmol) and 2,6-lutidine (3.47 mL, 20 mmol) in 20 mL of dry CH_2Cl_2, Tf_2O (3.36 mL, 4 mmol) was added dropwise. After stirring for 10 min, the ice bath was removed, the reaction mixture was allowed to warm up to 25 °C and stirred overnight. Hexane (20 mL)

was added to the reaction mixture. The pyridium salt was filtered off, and the precipitate was washed with ethyl acetate. The filtrate was washed with sat. NH_4Cl, sat. NaCl and H_2O, dried over $MgSO_4$, concentrated *in vacuo* to dryness. The residue was recrystallized form hexane-ethyl acetate to afford white crystals of **4a-f** in yields of 90-95%.

(*E*)-2-(1*H*-1,2,3-Benzotriazol-1-yl)-1-phenylethenyl trifluoromethanesulfonate (4a). White needles, mp 98-99 °C (95%, hexane-ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.13 (1H, dd, J = 8.3, 0.7 Hz, Bt), 7.70–7.75 (2H, m), 7.62–7.63 (2H, m), 7.60 (1H, s, CH=), 7.45–7.55 (4H, m); ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.3 (s), 142.3 (s), 132.4 (s), 131.0 (d), 129.2 (d), 129.2 (d), 128.8 (d), 126.2 (d), 126.2 (d), 124.9 (d), 120.5 (d), 118.2 (q, J = 319 Hz, CF_3), 113.8 (d), 109.9 (d). Anal. Calcd for $C_{15}H_{10}F_3N_3O_3S$: C, 48.78; H, 2.73; N, 11.38. Found: C, 48.89; H, 2.55; N, 11.33.

(*E*)-2-(1*H*-1,2,3-Benzotriazol-1-yl)-1-(4-chlorophenyl)ethenyl trifluoromethanesulfonate (4b). White needles, mp 156.0-156.5 °C (95%, hexane-ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (1H, d, J = 8.3 Hz, Bt), 7.64–7.67 (5H, m), 7.51–7.17 (3H, m); ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.3 (s), 140.9 (s), 137.2 (s), 132.4 (s), 129.6 (s), 129.5 (d), 129.5 (d), 128.8 (d), 127.4 (d), 127.4 (d), 125.0 (d), 120.5 (d), 118.0 (q, J = 319 Hz, CF_3), 114 (d), 109.7 (d). Anal. Calcd for $C_{15}H_9ClF_3N_3O_3S$: C, 44.62; H, 2.25; N, 10.14. Found: C, 44.49; H, 2.19; N, 10.22.

(E)–2– (1H–1,2,3–benzotriazol–1–yl)–1– (4–methylphenyl)ethenyl trifluoromethanesulfonate (4c). White needles, mp 147–148 °C (90%, hexane –ethyl acetate); ^{1}H NMR δ 8.10 (1H, dd, J = 8.3, 1.0 Hz, Bt), 7.59–7.62 (4H, m, Bt and aromatic proton), 7.56 (1H, s, CH =), 7.42–7.48 (1H, m, Bt), 7.31 (2H, d, J = 8.1 Hz), 2.42 (3H, s, CH_3); ^{13}C NMR δ 145.2 (s), 142.8 (s), 141.5 (s), 132.5 (s), 129.9 (d, 2×CH), 128.7 (d),

128.0 (s), 126.1 (d, 2×CH), 124.8 (d), 120.3 (d), 118.0 (q, J = 319 Hz, CF_3), 113.0 (d), 109.9 (d), 21.4 (q). Anal. Calcd for $C_{16}H_{12}F_3N_3O_3S$: C, 50.13; H, 3.16; N, 10.96. Found: C, 50.19; H, 2.97; N, 10.92.

(E)–2– (1H–1,2,3–benzotriazol–1–yl)–1–methylethenyl trifluoromethanesulfonate (4d). Crystals, mp 115–116 °C (88%, hexane –ethyl acetate); ^{1}H NMR δ 8.11 (1H, dd, J = 8.21, 0.9 Hz, Bt), 7.49–7.62 (2H, m), 7.41–7.47 (1H, m), 7.13 (1H, q , J = 1.2 Hz, CH =), 2.43 (3H, d, J = 1.2 Hz, CH_3); ^{13}C NMR δ 145.2 (s), 142.4 (s), 132.3 (s), 128.6 (d), 124.7 (d), 120.3 (d), 118.5 (q, J = 319 Hz, CF_3), 114.1 (d), 109.8 (d), 18.8 (q). Anal. Calcd for $C_{10}H_8F_3N_3O_3S$: C, 39.09; H, 2.62; N, 13.68. Found: C, 39.49; H, 2.45; N, 13.59.

(E)–2– (1H–1,2,3–benzotriazol–1–yl)–1–neopentylethenyl trifluoromethanesulfonate (4e). White needles, mp 97–99 °C (95%, hexane-ethyl acetate); ^{1}H NMR δ 8.10 (1H, d, J = 8.3 Hz, Bt), 7.58 (1H, t, J = 8.3 Hz, Bt), 7.51 (1H, d, J = 8.2 Hz, Bt), 7.43 (1H, t, J = 8.2 Hz, Bt), 7.20 (1H, s, CH =), 2.55 (2H, s), 1.15 (9H, s); ^{13}C NMR δ 145.1 (s), 144.3 (s), 132.2 (s), 128.6 (d), 124.6 (d), 120.1 (d), 118.0 (q, J = 319 Hz, CF3), 116.0 (d), 109.9 (d), 46.2 (t), 31.7 (s), 29.3 (q, 3×CH_3). Anal. Calcd for $C_{14}H_{16}F_3N_3O_3S$: C, 46.28; H, 4.44; N, 11.56. Found: C, 46.29; H, 4.14; N, 11.43.

(*E*)-2-(1*H*-1,2,3-benzotriazol-1-yl)-1-heptylethenyl trifluoromethanesulfonate (4f). White needles, mp 76.5–78.0 °C (90%, hexane-ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 (1H, d, J = 8.3, Bt), 7.57 (1H, d, J = 8.3 Hz, Bt), 7.50 (1H, t, J = 8.3 Hz, Bt), 7.43 (1H, t, J = 8.2 Hz, Bt), 7.14 (1H, s, CH=), 2.67 (2H, t, J = 7.1 Hz, =C(OTf) CH_2), 1.78 (2H, m, CH_2), 1.33–1.48 (8H, m , 4 × CH_2), 0.91 (3H, t, J = 6.6 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.6 (s), 145.5 (s), 132.6 (s), 128.8 (d), 124.9 (d), 120.6 (d),

118.0 (q, J = 319 Hz, CF_3), 114.1 (d), 110.2 (d), 32.9 (t), 31.8 (t), 29.0 (t), 28.9 (t), 26.6 (t), 22.8 (t), 14.3 (q). Anal. Calcd for $C_{15}H_{10}F_3N_3O_3S$: C, 49.10; H, 5.15; N, 10.74. Found: C, 48.98; H, 5.17; N, 10.17.

Typical Procedure for the Preparation of 5. To a solution of **4a-f** (5 mmol) in 10 mL of THF, 5 mL of 10% NaOH were added at room temperature. After stirring for 30 min, the reaction mixture was diluted with Et_2O (60 mL), washed with sat. NaCl, H_2O, dried over $MgSO_4$, and concentrated *in vacuo* to dryness. The residue was purified by column chromatography on silica gel using hexane-ethyl acetate (10:1) to afford colorless oils of **5a-f** in the yields of 90-98%.

1-(2-Phenylethynyl)-1*H*-benzotriazole (5a). White crystals, mp 78-78.5 °C (lit.[9]: 77-78 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 (1H, d, J = 8.3 Hz), 7. 74 (1H, d, J = 8.3 Hz), 7.60–7.66 (3H, m), 7.46 (1H, t, J = 8.3 Hz), 7.41–7.43 (3H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.9 (s), 134.2 (s), 131.8 (d), 131.8 (d), 129.4 (d), 129.3 (d), 128.5 (d), 128.5 (d), 125.2 (d), 120.5 (d), 110.1 (d), 79.7 (s), 75.7 (s).

1-[2-(4-Chlorophenyl)ethynyl)-1*H*-benzotriazole (5b). White crystals, 146-146.6 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (1H, d, J = 8.3 Hz, Bt), 7.74 (1H, d, J = 8.3 Hz, Bt), 7.66 (1H, dt, J = 0.9, 8.3 Hz, Bt), 7.57 (2H, dd, J = 1.8, 8.4 Hz), 7.50 (1H, dt, J = 0.9, 8.3 Hz, Bt), 7.42 (2H, dd, J = 1.8, 8.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.8 (s), 135.5 (s), 134.0 (s), 132.9 (d), 132.9 (d), 129.4 (d), 128.8 (d), 128.8 (d), 125.3 (d), 120.5 (d), 119.0 (s), 109.9 (d), 78.7 (s).

1–[2– (4–methylphenyl)ethynyl]–1H–1,2,3–benzotriazole (5c). Solid, mp 84–85 °C (lit.[9]: 82–85 °C) (95%); ^{1}H NMR δ 8.13 (1H, d, J = 8.3 Hz, Bt), 7.74 (1H, d, J = 8.3 Hz,

Bt), 7.64 (1H, t, J = 8.1 Hz, Bt), 7.54 (2H, d, J = 8.1 Hz), 7.47 (1H, t, J = 8.1 Hz, Bt), 7.22 (2H, d, J = 8.2 Hz), 2.41 (3H, s); ^{13}C NMR δ 143.9 (s), 139.9 (s), 134.3 (s), 131.8 (d, 2×CH), 129.4 (d, 2×CH), 129.2 (d), 125.2 (d), 120.5 (d), 117.5 (s), 110.2 (d), 79.9 (s), 75.2 (s), 21.6 (q).

1– (1–propynyl)–1H–1,2,3–benzotriazole (5d). Solid (90%); ^{1}H NMR δ 8.08 (1H, d, J = 8.3 Hz, Bt), 7.65 (1H, d, J = 8.3 Hz, Bt), 7.58 (1H, t, J = 8.3 Hz, Bt), 7.42 (1H, t, J = 8.3 Hz, Bt), 2.23 (3H, s); ^{13}C NMR δ 143.5 (s), 134.1 (s), 128.9 (d), 124.9 (d), 120.2 (d), 109.9 (d), 76.3 (s), 66.8 (s), 3.5 (q, CH_3). Anal. Calcd for $C_9H_7N_3$: C, 68.77; H, 4.49. Found: C, 69.10; H, 4.86.

1– (4,4–dimethyl–1–pentynyl)–1H–1,2,3–benzotriazole (5e). Solid (95%); ^{1}H NMR δ 8.08 (1H, d, J = 8.3 Hz, Bt), 7.62 (1H, d, J = 8.3 Hz, Bt), 7.58 (1H, t, J = 8.3 Hz, Bt), 7.42 (1H, t, J = 8.3 Hz, Bt), 2.48 (2H, s, CH_2), 1.13 (9H, s, 3×CH_3); ^{13}C NMR δ 143.6 (s), 134.3 (s), 128.9 (d), 124.9 (d), 120.2 (d), 109.9 (d), 78.9 (s), 69.2 (s), 33.5 (t), 31.4 (s), 29.0 (q). Anal. Calcd for $C_{13}H_{15}N_3$: C, 73.21; H, 7.09; N, 19.70. Found: C, 73.09; H, 6.97; N, 20.04.

1-(1-nonynyl)-1*H*-benzotriazole (5f). Oil, ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (1H, d, J = 8.3 Hz, Bt), 7.64 (1H, d, J = 8.3 Hz, Bt), 7.58 (1H, t, J = 8.3 Hz, Bt), 7.45 (1H, t, J = 8.3 Hz, Bt), 2.59 (2H, t, J = 7.1Hz, CH_2), 1.70 (2H, m, CH_2), 1.50 (2H, m , CH_2), 1.13 (6H, m), 0.89 (3H, t, J = 6.6 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.6 (s), 134.3 (s), 128.9 (d), 124.9 (d), 120.2 (d), 109.9 (d), 80.5 (s), 67.8 (s), 31.6 (t), 28.8 (t), 28.7 (t), 28.2 (t), 22.5 (t), 18.5 (t), 14.0 (q). Anal. Calcd for $C_{15}H_{19}N_3$: C, 74.65; H, 7.94; N, 17.41. Found: C, 74.42; H, 8.19; N, 17.66.

Procedures for the preparation of (1-[(*Z*)-1-methoxy-2-phenylethenyl]-1*H*-1,2,3-benzotriazole) (*Z*-6a) and (1-[(*E*)-1-methoxy-2-phenylethenyl]-1*H*-1,2,3-benzotriazole) (*E*-6a).

Method A: To a solution of **4a** (0.2 g, 0.54 mmol) in acetonitrile, solid $NaOCH_3$ (2.2 mmol, 59.4 mg) was added at room temperature. Then the reaction mixture was refluxed for 2 h, and allowed to cool down to room temperature. The reaction mixture was diluted with Et_2O, washed with sat. NaCl, H_2O, dried over $MgSO_4$, and evaporated *in vacuo* to dryness. The residue was purified by column chromatography on silica gel using hexane-ethyl acetate (10:1) giving 31 mg of *Z*-**6a** and 88 mg of *E*-**6a** as colorless oil (total yield 87%).

Method B: To a solution of **5a** (219 mg, 1 mmol) in acetonitrile, solid $NaOCH_3$ (1.1 mmol, 59.4 mg) was added at room temperature. The reaction mixture was refluxed for 2 h, and cooled down to room temperature. Then the reaction mixture was diluted with Et_2O, washed with sat. NaCl, H_2O, the organic fraction was dried over $MgSO_4$, and evaporated *in vacuo* to dryness. The residue was purified by column chromatography on silica gel using hexane-ethyl acetate (10:1) gave 51 mg of *Z*-**6a** and 194 mg of *E*-**6a** as colorless oil (total yield 98%).

***Z*-6a**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (1H, dd, J = 1.0, 7.6 Hz), 7.78 (1H, dd, J = 1.0, 7.6 Hz), 7.72 (2H, d, J = 7.3 Hz), 7.58 (1H, ddd, J = 1.0, 7.6, 7.6 Hz), 7.39–7.47 (3H, m), 7.30 (1H, ddd, J = 1.0, 7.6, 7.6 Hz), 6.29 (1H, s), 3.65 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$); δ 146.0 (s), 144.7 (s), 133.5 (s), 132.6 (s), 129.0 (d, 3 × CH), 128.9 (d, 2 × CH), 128.0 (d), 124.9 (d), 120.5 (d), 111.4 (d), 108.3 (d), 58.2 (q).

***E*-6a**. ^{1}H NMR (300 MHz, $CDCl_3$); δ 8.07 (1H, dd, J = 1.6, 8.6 Hz), 7.33–7.38 (2H, m), 7.20–7.26 (1H, m), 6.99–7.03 (3H, m), 6.62–6.68 (2H, m), 6.11 (1H, s), 3.98 (3H, s). ^{13}C NMR (75 MHz, $CDCl_3$); δ 145.4 (s), 145.1 (s), 132.7 (s), 132.2 (s), 128.4 (d, 2 x CH), 128.3 (d), 127.5 (d, 2 x CH), 126.8 (d), 124.3 (d), 120.0 (d), 110.4 (d), 101.1 (d), 56.9 (q).

Typical procedure for the preparation of 1-(1*H*-1,2,3-Benzotriazol-1-yl)-1-nonenyl 4-methylbenzenesulfonate (8d-f). To solution of **5d-f** (241 mg, 1 mmol) in 10 mL of acetonitrile, *p*-toluenesulfonic acid monohydrate (190 mg, 1 mmol) was added at room temperature. The reaction mixture was stirred under reflux for 4 h. After TLC showed no starting material, the reaction mixture was concentrated in vacuo to dryness, and the residue was purified by column chromatography on silica gel using hexane-EtOAc (10:1) to afford compound **8d-f** in the yield 62-75%.

1– (1H–1,2,3–benzotriazol–1–yl)– –1–propenyl 4–methylbenzenesulfonate (8d). White needles, mp 78–80 °C (62%, hexane-ethyl acetate); ^{1}H NMR δ 7.94 (1H, d, J = 8.2 Hz), 7.50–7.44 (2H, m), 7.43 (2H, d, J = 8.2 Hz), 7.33-7.39 (1H, m), 6.98 (2H, d, J = 8.2 Hz), 6.03 (1H, q, J = 7.3 Hz), 2.27 (3H, s), 1.69 (3H, d, J = 7.3 Hz); ^{13}C NMR δ 145.5 (s), 144.9 (s), 135.3 (s), 132.3 (s), 131.6 (s), 129.3 (d, 2×CH), 128.6 (d), 127.8 (d, 2×CH), 124.4 (d), 119.8 (d), 117.9 (d), 110.6 (d), 21.5 (q), 11.9 (q, 3×CH_3). Anal. Calcd for $C_{16}H_{15}N_3O_3S$: C, 58.34; H, 4.59; N, 12.76. Found: C, 58.44; H, 4.72; N, 12.68.

1– (1H–1,2,3–benzotriazol–1–yl)–4,4–dimethyl–1–pentenyl 4–methylbenzenesulfonate (8e). Crystal, mp 56-59 °C (67%, hexane-ethyl acetate); ^{1}H NMR δ 7.94 (1H, d, J = 8.3 Hz, Bt), 7.51–7.45 (4H, m), 7.38-7.33 (1H, m), 7.00 (2H, d, J

= 7.8 Hz), 6.03 (1H, t, J = 7.4 Hz), 2.27 (3H, s), 1.91 (2H, d, J = 7.4 Hz), 0.84 (9H, s); ^{13}C NMR δ 145.4 (s), 144.7 (s), 135.1 (s), 132.2 (s), 131.5 (s), 129.2 (d, 2×CH), 128.5 (d), 127.7 (d, 2×CH), 124.3 (d), 120.9 (d), 119.6 (d), 110.4 (d), 39.8, 31.0, 28.9 (q, 3×CH_3), 21.3 (q). Anal. Calcd for $C_{20}H_{23}N_3O_3S$: C, 62.32; H, 6.01; N, 10.90. Found: C, 62.68; H, 6.28; N, 11.05.

1-(1*H*-1,2,3-Benzotriazol-1-yl)-1-nonenyl 4-methylbenzenesulfonate (8f). pale yellow oil, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (1H, d, J = 8.2 Hz), 7.4–7.53 (4H, m), 7.38 (1H, m), 7.0 (2H, d, J = 8.2 Hz), 5.94 (1H, t, J = 8.0 Hz), 2.28 (3H, s), 1.99 (2H, m), 1.40 (2H, m), 1.16–1.22 (8H, m), 0.82 (3H, t, J = 7.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.5 9s), 144.7 (s), 134.5 (s), 132.2 (s), 131.4 (s), 129.2 (d), 129.2 (d), 128.5 (d), 127.7 (d), 127.7 (d), 124.3 (d), 123.1 (d), 119.6 (d), 110.4 (d), 31.4 (t), 28.6 (t), 28.6 (t), 28.5 (t), 26.1 (t), 22.3 (t), 21.3 (q), 13.8 (q).