SUPPORTING INFORMATION

γ,δ-Unsaturated β-Diketones by Acylation of Ketones

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General Experimental Details. All reactions were carried out under a nitrogen atmosphere and solvents were dried according to standard procedures. Ketones, carboxylic acids and benzotriazole were purchased and used without further purification. Purification by column chromatography was carried out using silica gel. Melting points are uncorrected. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded in $CDCl_3$ (with TMS for ^{1}H and chloroform-*d* for ^{13}C as the internal standard) except for **2e**, which was recorded in DMSO-d_6.

General Procedure for Preparation of Unsaturated *N*-Acylbenzotriazoles 2a–e. To a solution of 1*H*-1,2,3-benzotriazole (11.9 g, 100 mmol) in CH_2Cl_2 (125 mL), $SOCl_2$ (1.9 mL, 25 mmol) was added dropwise with stirring at room temperature. After 30 min, unsaturated acid (25 mmol) was added. The reaction was continued for 3 h and the precipitated solid was filtered and washed with CH_2Cl_2 (50 mL). The combined filtrate was washed with aq NaOH (2N, 2×100 mL), water (100 mL) and brine (30 mL). The organic layer was dried over anhyd Na_2SO_4 and the solvent evaporated to obtain a solid, that was recrystallized from an appropriate solvent to give *N*-acylbenzotriazoles (**2a**–**e**).

(*E*)-1-(1*H*-1,2,3-Benzotriazol-1-yl)-3-phenyl-2-propen-1-one (2a). Yield 94%; colorless needles (from hexane/EtOAc); mp 152–153 ^{o}C (Lit.[1] mp 151–152 ^{o}C).

(*E*)-1-(1*H*-1,2,3-Benzotriazol-1-yl)-3-(2-furyl)-2-propen-1-one (2b). Yield 90%; light pink needles (from hexane/CH_2Cl_2); mp 142–143 ^{o}C (Lit.[2] mp 142–144 ^{o}C).

(*E*)-1-(1*H*-1,2,3-Benzotriazol-1-yl)-3-(2-thienyl)-2-propen-1-one (2c). Yield 95%; yellow plates (from hexane/EtOAc); mp 169–170 ^{o}C (Lit.[2] mp 169–170 ^{o}C).

1-(1*H*-1,2,3-Benzotriazol-1-yl)-3-phenyl-2-propyn-1-one (2d). Yield 90%; colorless needles (from hexane/CH_2Cl_2); mp 123–124 ^{o}C (Lit.[1] mp 124–125 ^{o}C).

1-(1*H*-1,2,3-Benzotriazol-1-yl)-3-methyl-2-buten-1-one (2e). Yield 90%; colorless needles (from hexane); mp 95–97 °C; ^{1}H NMR δ 2.16 (d, *J* = 0.9 Hz, 3H), 2.42 (d, *J* = 0.6 Hz, 3H), 7.37–7.38 (m, 1H), 7.46–7.51 (m, 1H), 7.61–7.66 (m, 1H), 8.11 (d, *J* = 8.4 Hz, 1H), 8.37 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (DMSO-d_6) δ 21.3, 28.0, 114.0, 114.2, 119.9, 126.2, 130.4, 130.9, 145.5, 162.7, 164.8. Anal. Calcd for $C_{11}H_{11}N_3O$: C, 65.66; H, 5.51; N, 20.88. Found: C, 65.86; H, 5.50; N, 21.08.

General Procedure for Acylation with Unsaturated *N*-Acylbenzotriazoles. To a solution of diisopropylamine (0.38 mL, 2.7 mmol) in THF (3 mL) under nitrogen atmosphere was added *n*-BuLi (1.7 mL, 2.6 mmol, 1.6M) dropwise with stirring at –15 °C. The solution was cooled to –78 °C and a solution of ketone **1a**–**f** (2.6 mmol) in THF (10 mL) was added dropwise and the mixture was stirred for 1 h at –78 °C. A solution of *N*-acylbenzotriazole **2a**–**e** (2 mmol) in THF (10 mL) was added at –78 °C and the reaction was continued for 3 h. The reaction was quenched with water (20 mL) at –78 °C and the mixture was diluted with diethyl ether (40 mL). Aqueous work-up gave a residue that was purified by column chromatography on silica gel using hexanes/ethyl acetate (9.8:0.2) to give γ,δ-unsaturated β-diketones **3a**–**p**.

4-(*tert*-Butyl)-2-[(*E*)-3-(2-furyl)-2-propenoyl]cyclohexanone (3b). Yield 0.22 g (51%); yellow needles (from hexane); mp 92–94 °C; ^{1}H NMR δ 0.97 (s, 9H), 1.30–1.37 (m, 2H), 1.89–1.94 (m, 1H), 2.14–2.23 (m, 1H), 2.40–2.54 (m, 2H), 2.59–2.65 (m, 1H), 6.48–6.49 (dd, *J* = 3.0, 1.8 Hz, 1H), 6.62 (d, *J* = 3.6 Hz, 1H), 6.83 (d, *J* = 15.3 Hz, 1H), 7.46 (d, *J* = 15.3 Hz, 1H), 7.51 (s, 1H), 16.78 (s, 1H); ^{13}C NMR δ 23.1, 25.2, 27.6, 32.7, 35.1, 44.9, 107.3, 112.7, 115.2, 117.6, 127.7, 144.8, 152.3, 180.5, 193.5. Anal. Calcd for $C_{17}H_{22}O_3$: C, 74.42; H, 8.08. Found: C, 74.52; H, 8.25.

4-(*tert*-Butyl)-2-(3-methyl-2-butenoyl)cyclohexanone (3e). Yield 0.18 g (38%); yellow needles (from hexane); mp 67–68 °C; ^{1}H NMR δ 0.93 (s, 9H), 1.23–1.30 (m, 2H), 1.86–1.89 (m, 1H), 1.96 (s, 3H), 1.99–2.07 (m, 1H), 2.17 (s, 3H), 2.38–2.43 (m, 3H), 6.07 (s, 1H), 16.80 (s, 1H); ^{13}C NMR δ 21.3, 23.1, 25.6, 27.5, 28.5, 32.6, 33.3, 44.9, 106.9, 119.6, 154.6, 185.8, 189.5. Anal. Calcd for $C_{15}H_{24}O_2$: C, 76.22; H, 10.23. Found: C, 76.06; H, 10.50.

3-Methyl-6-[(*E*)-3-phenyl-2-propenoyl]-2-cyclohexen-1-one (3f). Yield 0.21 g (44%); yellow needles (from hexane); mp 128 °C; ^{1}H NMR δ 2.00 (s, 3H), 2.33 (t, *J* = 7.2 Hz, 2H), 2.74 (t, *J* = 7.2 Hz, 2H), 5.97–5.98 (m, 1H), 6.93 (d, *J* = 15.6 Hz, 1H), 7.30–7.40 (m, 3H), 7.52–7.54 (m, 2H), 7.59 (d, *J* = 15.6 Hz, 1H), 15.76 (s, 1H); ^{13}C NMR δ 22.4, 24.4, 30.3, 105.1, 118.9, 126.2, 127.9, 129.0, 129.6, 136.0, 138.5, 160.0, 168.6, 191.3. Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 80.29; H, 6.91.

6-[(*E*)-3-(2-Furyl)-2-propenoyl]-3-methyl-2-cyclohexen-1-one (3g). Yield 0.24 g (52%); yellow prisms (from hexane); mp 112–114 °C; ^{1}H NMR δ 2.00 (s, 3H), 2.32 (t, *J* = 7.2 Hz, 2H), 2.73 (t, *J* = 7.2 Hz, 2H), 5.97 (d, *J* = 1.2 Hz), 6.45–6.47 (m, 1H), 6.53 (d, *J* = 3.3 Hz, 1H), 6.82 (d, *J* = 15.0 Hz, 1H), 7.34 (d, *J* = 15.0 Hz, 1H), 7.46 (s, 1H), 15.68 (s, 1H); ^{13}C NMR δ 22.4, 24.5, 30.3, 105.2, 112.6, 113.7, 117.0, 125.0, 126.3, 144.2, 152.6, 159.9, 168.4, 191.2. Anal. Calcd for $C_{14}H_{14}O_3$: C, 73.02; H, 6.13. Found: C, 73.11; H, 6.26.

3-Methyl-6-[(*E*)-3-(2-thienyl)-2-propenoyl]-2-cyclohexen-1-one (3h). Yield 0.21 g (42%); yellow plates (from hexane); mp 110–112 °C; ^{1}H NMR δ 1.99 (s, 3H), 2.32 (t, *J* = 7.2 Hz, 2H), 2.70 (t, *J* = 7.2 Hz, 2H), 5.97 (d, *J* = 0.9 Hz, 1H), 6.70 (d, *J* = 15.3 Hz, 1H), 7.03 (dd, *J* = 4.8, 3.6 Hz, 1H), 7.19 (d, *J* = 3.6 Hz, 1H), 7.32 (d, *J* = 4.8 Hz, 1H), 7.69 (d, *J* = 15.3 Hz, 1H), 15.76

(s, 1H); ^{13}C NMR δ 22.4, 24.4, 30.3, 104.9, 118.1, 126.2, 127.5, 128.3, 129.9, 131.3, 141.6, 159.8, 168.4, 191.0. Anal. Calcd for $C_{14}H_{14}O_2S$: C, 68.26; H, 5.73. Found: C, 68.00; H, 5.86.

3,5-Dimethyl-6-[(*E*)-3-phenyl-2-propenoyl]-2-cyclohexen-1-one (3i). Yield 0.23 g (45%); yellow microcrystals (from hexane); mp 81–82 ^{o}C; ^{1}H NMR δ 1.15 (d, *J* = 7.2 Hz, 3H), 1.99 (s, 3H), 2.10 (dd, *J* = 17.7, 0.9 Hz, 1H), 2.67 (br dd, *J* = 18.1, 6.1 Hz, 1H), 3.19 (quintet, *J* = 6.8 Hz, 1H), 5.98 (q, *J* = 1.2 Hz, 1H), 6.92 (dd, *J* = 15.6, 0.9 Hz, 1H), 7.33–7.41 (m, 3H), 7.53–7.56 (m, 2H), 7.63 (d, *J* = 15.6 Hz, 1H), 16.11 (d, *J* = 0.9 Hz, 1H); ^{13}C NMR δ 22.5, 24.9, 27.7, 37.6, 110.6, 118.7, 124.9, 128.0, 129.0, 129.7, 136.0, 139.1, 157.2, 170.1, 189.8. Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.30; H, 7.28.

3,5-Dimethyl-6-[(*E*)-3-(2-thienyl)-2-propenoyl]-2-cyclohexen-1-one (3j). Yield 0.22 g (42%); yellow prisms (from hexane/EtOAc); mp 81–82 ^{o}C; ^{1}H NMR δ 1.14 (d, *J* = 7.2 Hz, 3H), 1.98 (s, 3H), 2.09 (d, *J* = 16.8 Hz, 1H), 2.66 (br dd, J = 18.0, 5.6 Hz, 1H), 3.13 (quintet, *J* = 6.8 Hz, 1H), 5.96–5.97 (q, *J* = 1.2 Hz, 1H), 6.68 (d, *J* = 15.0 Hz, 1H), 7.04 (dd, *J* = 4.9, 3.4 Hz, 1H), 7.21(d, *J* = 3.3 Hz, 1H), 7.33 (d, *J* = 5.4 Hz, 1H), 7.73 (d, *J* = 15.0 Hz, 1H), 16.10 (s, 1H); ^{13}C NMR δ 22.5, 25.0, 27.7, 37.6, 110.5, 117.9, 124.9, 127.6, 128.4, 130.0, 131.8, 141.6, 157.1, 170.0, 189.6. Anal. Calcd for $C_{15}H_{16}O_2S$: C, 69.20; H, 6.19. Found: C, 69.47; H, 6.34.

2-[(*E*)-3-Phenyl-2-propenoyl]-1-indanone (3k). Yield 0.28 g (53%); yellow needles (from hexane/EtOAc); mp 121–122 ^{o}C; ^{1}H NMR δ 3.78 (s, 2H), 6.72 (d, *J* = 15.9 Hz, 1H), 7.34–7.46 (m, 4H), 7.53–7.59 (m, 4H), 7.66 (d, *J* = 15.9 Hz, 1H), 7.86 (d, *J* = 7.8 Hz, 1 H), 13.65 (br s, 1H); ^{13}C NMR δ 29.8, 111.7, 119.7, 123.6, 126.1, 127.7, 128.1, 129.1, 130.1, 133.6, 135.6, 139.1, 139.4, 148.5, 165.6, 196.3. Anal. Calcd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 82.06; H, 5.50.

2-[(*E*)-3-(2-Furyl)-2-propenoyl]-1-indanone (3l). Yield 0.20 g (40%); yellow needles (from hexane); mp 124–125 ^{o}C; ^{1}H NMR δ 3.74 (s, 2H), 6.48–6.50 (m, 1H), 6.58–6.63 (m, 2H), 7.53–7.44 (m, 2H), 7.51–7.59 (m, 3H), 7.84 (d, *J* = 7.8 Hz, 1H), 13.58 (br s, 1H); ^{13}C NMR δ 29.8, 111.8, 112.8, 114.5, 117.7, 123.5, 125.7, 126.1, 127.6, 133.5, 139.3, 144.8, 148.5, 152.2, 165.5, 196.0. Anal. Calcd for $C_{16}H_{12}O_3$: C, 76.18; H, 4.79. Found: C, 76.20; H, 4.80.

(3*R*)-3-Methyl-6-(1-methylethylidene)-2-[(*E*)-3-phenyl-2-propenoyl]cyclohexanone (3m). Yield 0.29 g (51%); yellow microcrystals (from hexane); mp 106–107 ^{o}C; ^{1}H NMR δ 1.15 (d, *J* = 6.9 Hz, 3H), 1.73–1.79 (m, 2H), 1.89 (s, 3H), 2.28 (s, 3H), 2.49 (br d, *J* = 6.3 Hz, 2H), 3.04–3.11 (m, 1H), 7.04 (d, *J* = 15.6 Hz, 1H), 7.31–7.41 (m, 3H), 7.54–7.57 (m, 2H), 7.67 (d, *J* = 15.6 Hz, 1H), 17.43 (s, 1H); ^{13}C NMR δ 20.8, 24.1, 24.5, 24.6, 28.4, 28.9, 115.1, 120.2, 127.6, 128.1, 129.0, 129.7, 136.1, 139.5, 148.2, 175.8, 189.8. Anal. Calcd for $C_{16}H_{12}O_3$: C, 80.81; H, 7.85. Found: C, 80.87; H, 8.12.

(*E*)-1,5-Diphenyl-4-pentene-1,3-dione (3n). Yield 0.33 g (66%); yellow microcrystals (from hexane/diethyl ether); mp 97–98 ^{o}C (Lit.[3] mp 111–112 ^{o}C); ^{1}H NMR δ 6.35 (s, 1H), 6.65 (d, *J* = 15.6 Hz, 1H), 7.35–7.43 (m, 3H), 7.45–7.50 (m, 2H), 7.53–7.58 (m, 3H), 7.69 (d, *J* = 15.9 Hz, 1H), 7.96 (d, *J* = 7.5 Hz, 2H), 16.12 (br s, 1H); ^{13}C NMR δ 97.9, 123.5, 127.6, 128.2, 128.9, 129.1, 130.2, 132.8, 135.2, 136.5, 140.2, 179.6, 189.6. Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found: C, 81.21; H, 5.64.

3-Methyl-6-(3-phenyl-2-propynoyl)-2-cyclohexen-1-one (3p). Yield 0.12 g (25%); pale yellow needles (from EtOAc); mp 107–109 ^{o}C; ^{1}H NMR δ 2.00 (s, 3H), 2.35 (t, *J* = 9.3 Hz, 2H), 2.78 (t, *J* = 9.3 Hz, 2H), 6.06–6.08 (m, 1H), 6.74 (s, 1H), 7.46–7.49 (m, 3H), 7.74–7.77 (m, 2H); ^{13}C NMR δ 18.2, 23.6, 28.4, 110.97, 111.0, 115.9, 116.0, 125.6, 128.9, 130.8, 131.7,

150.3, 160.0, 161.2, 178.4. Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.36; H, 5.95.

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