Supporting Information

Synthetic Utility of Stannyl Enolates as Radical Alkylating Agents

Katsukiyo Miura, Naoki Fujisawa, Hiroshi Saito, Di Wang, and Akira Hosomi*

Department of Chemistry, Graduate School of Pure and Applied Sciences
University of Tsukuba
Tsukuba, Ibaraki 305-8571, Japan

* For inquiries please address to
Professor Akira HOSOMI
phone: +81-298-53-4237
facsimile: +81-298-53-6503
e-mail: hosomi@chem.tsukuba.ac.jp

1. General Method

Unless otherwise noted, all reactions and distillation of solvents were carried out under N_2. Solvents were dried by distillation from sodium metal/benzophenone ketyl (THF, Et_2O) and CaH_2 (benzene, hexane, CH_2Cl_2). Bu_3SnCl was simply distilled in vacuo. All other commercial reagents were used as received. Boiling points determined with Kugelrohr distillation apparatus are indicated by air-bath temperature (bath temp). ^1H and ^{13}C NMR were recorded in $CDCl_3$ or C_6D_6 at 270 and 67.7 MHz, respectively. The chemical shifts (δ) are reported with reference at 0.00 ppm (Me_4Si) or 7.26 ppm ($CHCl_3$) for the proton and at 77.00 ppm (centered on the signal of $CDCl_3$) or 128.00 ppm (centered on the signal of C_6D_6) for the carbon.

2. Synthesis of Tributylstannyl Enolates

Tributylstannyl enolates **1a-e** were prepared by the reaction of the corresponding vinyl acetates with tributylmethoxystannane[1] (Bu_3SnOMe, [1067-52-3][2], commercially available from Aldrich). Vinyl acetates were synthesized from the corresponding ketones by the TsOH-catalyzed reaction with isopropenyl acetate.[3] The procedures for the syntheses of 1-phenylethenyl acetate and stannyl enolate **1c** are shown below.

1-Cyclohexenyl Acetate: [1424-22-2][1], commercially available from Aldrich; bp 92–94 °C (36 Torr). ^1H NMR ($CDCl_3$) δ 1.55–1.64 (m, 2H), 1.68–1.78 (m, 2H), 2.05–2.16 (m, 7H) including 2.11 (s), 5.34–5.37 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 20.93 (CH_3), 21.54 (CH_2), 22.48 (CH_2), 23.47 (CH_2), 26.67 (CH_2), 113.86 (CH), 148.25 (C), 169.35 (C).

1-Ethyl-1-propenyl Acetate (*Z*:*E* = 67:33):[1] bp 68–70 °C (25 Torr). ^1H NMR ($CDCl_3$) for *Z*-

isomer δ 1.03 (t, *J* = 7.4 Hz, 3H), 1.49 (dt, *J* = 6.8, 1.5 Hz, 3H), 2.17 (s, 3H), 2.18 (qqd, *J* = 7.4, 1.5, 1.2 Hz, 2H), 5.07 (qt, *J* = 6.8, 1.2 Hz, 1H), for *E*-isomer δ 1.01 (t, *J* = 7.4 Hz, 3H), 1.65 (d, *J* = 7.1 Hz, 3H), 2.12 (s, 3H), 2.28 (q, *J* = 7.4 Hz, 2H), 5.12 (q, *J* = 7.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) for major isomer δ 10.32 (CH_3), 10.83 (CH_3), 20.35 (CH_3), 26.27 (CH_2), 109.17 (CH), 150.34 (C), 168.45 (C), for minor isomer δ 11.03 (CH_3), 11.23 (CH_3), 20.61 (CH_3), 21.68 (CH_2), 111.15 (CH), 150.34 (C), 169.59 (C).

1-Phenylethenyl Acetate.[3] A mixture of isopropenyl acetate (39.5 mL, 363 mmol), acetophenone (23.3 mL, 200 mmol), and TsOH•H_2O (270 mg, 1.42 mmol) was stirred for 9 h at 110 °C. The acetone formed was continuously distilled off. The reaction mixture was cooled to room temperature and diluted with Et_2O (100 mL) and water (50 mL). The organic layer was washed with 10% aqueous Na_2CO_3 (2 × 50 mL). The aqueous layer was extracted with Et_2O (2 × 50 mL). The combined organic layer was dried over Na_2SO_4 and evaporated. Distillation of the residual oil gave 1-phenylethenyl acetate (10.4 g, 64.1 mmol) in 32% yield. 1-Phenylethenyl acetate: [2206-94-2][1]; bp 58–60 °C (0.50 Torr). ^{1}H NMR ($CDCl_3$) δ 2.28 (s, 3H), 5.03 (d, *J* = 2.2 Hz, 1H), 5.48 (d, *J* = 2.2 Hz, 1H), 7.32–7.39 (m, 3H), 7.45–7.50 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 20.84 (CH_3), 102.04 (CH_2), 124.73 (CH × 2), 128.42 (CH × 2), 128.85 (CH), 134.11 (C), 152.81 (C), 168.97 (C).

1-Phenyl-1-propenyl Acetate (*Z*:*E* = 94 : 6): bp 60–62 °C (0.50 Torr). ^{1}H NMR ($CDCl_3$) δ 1.72 (d, *J* = 7.1 Hz, 2.82H), 1.81 (d, *J* = 7.4 Hz, 0.18H), 2.14 (s, 0.18H), 2.30 (s, 2.82H), 5.53 (q, *J* = 7.4 Hz, 0.06H), 5.90 (q, *J* = 7.1 Hz, 0.94H), 7.26–7.41 (m, 5H); ^{13}C NMR ($CDCl_3$) for *Z*-isomer δ 11.45 (CH_3), 20.47 (CH_3), 112.51 (CH), 124.12 (CH × 2), 127.91 (CH), 128.36 (CH × 2), 134.87 (C), 146.79 (C), 168.49 (C).

1,2-Dihydro-4-naphthyl Acetate: mp 58–59 °C (hexane-AcOEt). IR (KBr) 1755 (C=O), 1207 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.29 (s, 3H), 2.45 (td, *J* = 8.2, 4.7 Hz, 2H), 2.87 (t, *J* = 8.2 Hz, 2H), 5.70 (t, *J* = 4.6 Hz, 1H), 7.06–7.19 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 20.80 (CH_3), 21.96 (CH_2), 27.38 (CH_2), 115.41 (CH), 120.64 (CH), 126.32 (CH), 127.53 (CH), 127.86 (CH), 130.36 (C), 136.34 (C), 145.56 (C), 169.16 (C). Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43%. Found: C, 76.38; H, 6.41%.

1-Tributylstannyloxy-1-cyclohexene (1a, keto:enol = <1:99): [17851-97-7][1]; bp 124–126 °C (0.50 Torr). ^{1}H NMR (C_6D_6) δ 0.90–1.79 (m, 31H), 2.22–2.37 (m, 4H), 4.75 (tt, *J* = 3.9, 1.2 Hz, 1H); ^{13}C NMR (C_6D_6) δ 13.81 (CH_3 × 3), 15.59 (CH_2 × 3), 23.55 (CH_2), 24.19 (CH_2), 24.85 (CH_2), 27.35 (CH_2 × 3), 28.27 (CH_2 × 3), 31.87 (CH_2), 96.75 (CH), 157.51 (C).

(*E*)- and (*Z*)-3-Tributylstannyloxy-2-pentene (enol) and 2-Tributylstannyl-3-pentanone (keto) (1b, (*E*)-enol:(*Z*)-enol:keto = 60:15:25): [17795-74-3][1] (enol form); [17795-75-4][1] (keto form); bp 102–105 °C (0.50 Torr). ^{1}H NMR (C_6D_6) δ 0.91–1.92 (m, 33H), 2.02–2.30 (m, 1.7H), 2.36 (q, *J* = 7.4 Hz, 0.30H), 2.64 (q, *J* = 6.8 Hz, 0.25H including satellite peaks), 4.41 (q, *J* = 6.6 Hz, 0.15 H), 4.60 (qt, *J* = 6.5, 0.9 Hz, 0.60 H); ^{13}C NMR (C_6D_6) δ 7.59–35.07 (35 peaks were detected), for (*E*)-enol form δ 95.81 (CH), 159.03 (C), for (*Z*)-enol form δ 92.23 (CH), 160.39 (C), for keto form δ 37.53 (CH), 208.72 (C).

1-Phenyl-2-tributylstannyl-1-ethanone and 1-Phenyl-1-(tributylstannyloxy)ethene (1c,

keto:enol = 74:26). A mixture of 1-phenylethenyl acetate (4.05 g, 25.0 mmol) and Bu_3SnOMe (8.03 g, 25.0 mmol) was heated to 100 °C and stirred for 4 h. The methyl acetate formed was continuously distilled off. The resultant reaction mixture was cooled to room temperature and distilled under reduced pressure to give the title compound **1c** (7.12 g, 17.4 mmol) in 70% yield. **1c**: [17851-98-8][1] (enol form); [17851-99-9][1] (keto form); bp 144–146 °C (0.50 Torr). ^{1}H NMR (C_6D_6) δ 0.81–1.76 (m, 27H), 2.85 (s, 1.48 H), 4.26 (d, *J* = 1.2 Hz, 0.26H), 4.89 (d, *J* = 1.2 Hz, 0.26H), 7.15–7.30 (m, 3H), 7.98–8.06 (m, 2H); ^{13}C NMR (C_6D_6) for keto form δ 10.78 ($CH_2 \times 3$), 13.82 ($CH_3 \times 3$), 15.96 (CH_2), 27.54 ($CH_2 \times 3$), 29.10 ($CH_2 \times 3$), 128.16 (CH × 2), 128.48 (CH × 2), 132.04 (CH), 138.87 (C), 198.01 (C), for enol form δ 13.82 ($CH_3 \times 3$), 25.25 ($CH_2 \times 3$), 27.37 ($CH_2 \times 3$), 28.24 ($CH_2 \times 3$), 84.75 (CH_2), 125.96 (CH × 2), 127.74 (CH), 128.00 (CH × 2), 140.75 (C), 162.54 (C).

(*Z*)-1-Phenyl-1-tributylstannyloxy-1-propene (1d, keto:enol = <1:99). The *Z*-configuration was determined by an NOE experiment. Upon irradiation of the para protons, a 10% enhancement of the olefinic proton was observed. **1d:** [116425-53-7][4]; bp 133–134 °C (0.45 Torr). ^{1}H NMR (C_6D_6) δ 0.87–1.81 (m, 27H), 2.01 (d, *J* = 6.8 Hz, 3H), 5.30 (q, *J* = 6.8 Hz, 1H), 7.10–7.28 (m, 3H), 7.74–7.78 (m, 2H); ^{13}C NMR (C_6D_6) δ 11.89 (CH_3), 13.78 ($CH_3 \times 3$), 16.06 ($CH_2 \times 3$), 27.46 ($CH_2 \times 3$), 28.15 ($CH_2 \times 3$), 100.59 (CH), 125.79 (CH × 2), 127.06 (CH), 128.20 (CH × 2), 142.71 (C), 156.49 (C).

4-Tributylstannyloxy-1,2-dihydronaphthalene (1e, keto:enol = <1:99): bp 142–144 °C (0.40 Torr). IR (neat) 1624 (C=C), 1255 cm^{-1}; ^{1}H NMR (C_6D_6) δ 0.91 (t, *J* = 7.2 Hz, 9H), 1.20–1.80 (m, 18H), 2.36 (td, *J* = 7.8, 4.6, 2H), 2.77 (t, *J* = 7.8 Hz, 2H), 5.03 (t, *J* = 4.4 Hz, 1H), 7.08–7.17 (m, 2H), 7.30 (t, *J* = 7.3 Hz, 1H), 8.09 (d, *J* = 7.7 Hz, 1H); ^{13}C NMR (C_6D_6) δ 13.81 ($CH_3 \times 3$), 15.81 ($CH_2 \times 3$), 23.08 (CH_2), 27.36 ($CH_2 \times 3$), 28.22 ($CH_2 \times 3$), 29.43 (CH_2), 99.25 (CH), 122.78 (CH), 126.41 (CH), 127.07 (CH), 127.18 (CH), 136.43 (C), 137.71 (C), 154.77 (C). Anal. Calcd for $C_{22}H_{36}OSn$: C, 60.71; H, 8.34%. Found: C, 60.33; H, 8.32%.

3. Synthesis of Radical Precursors

Organic halides **2a-j** were commercially available. Iodide **2k** was prepared from 3-chloro-1-propanol by acetylation with AcCl and pyridine followed by iodination with NaI. The TsOH-catalyzed etheration of 3-chloro-1-propanol with 3,4-dihydro-2*H*-pyran and the subsequent iodination with NaI were carried out for the synthesis of **2l**. Methyl phenylthioacetate (**2m**) was obtained by the reaction of **2a** with thiophenol. To synthesize phenyl thiocarbonates **2n-o**, the reactions of methyl hydroxyacetate and 2-propanol with phenyl chlorothionoformate were employed.[5]

3-Iodopropyl Acetate (2k). Acetyl chloride (393 mg, 5.00 mmol) was slowly added to a solution of 3-chloro-1-propanol (423 mg, 5.00 mmol) and pyridine (396 mg, 5.00 mmol) in Et_2O (5 mL) at room temperature. The mixture was warmed to reflux and stirred for 2 h. The resultant mixture was subjected to a usual aqueous work-up. Purification by silica gel column chromatography (hexane-AcOEt 5:1) gave 3-chloropropyl acetate (574 mg, 4.20 mmol) in 84% yield. 3-Chloropropyl acetate: [628-09-1], commercially available from Aldrich; bp 80 °C (30 Torr, bath temp). ^{1}H NMR ($CDCl_3$) δ 2.06 (s, 3H), 2.10 (tt, *J* = 6.3, 6.1 Hz, 2H), 3.62 (t, *J* = 6.3 Hz, 2H), 4.22 (t, *J* = 6.1 Hz, 2H). A solution

of 3-chloropropyl acetate (574 mg, 4.20 mmol) and NaI (150 mg, 10.0 mmol) in acetone (10 mL) was stirred at reflux for 24 h. The resultant mixture was subjected to a usual aqueous work-up. Purification by silica gel column chromatography (hexane-AcOEt 5:1) gave the title compound (746 mg, 3.27 mmol) in 79% yield. **2k**: [62116-24-9]; bp 120 °C (30 Torr, bath temp). ^{1}H NMR ($CDCl_3$) δ 2.06 (s, 3H), 2.14 (tt, *J* = 6.8, 6.2 Hz, 2H), 3.23 (t, *J* = 6.8 Hz, 2H), 4.14 (t, *J* = 6.2 Hz, 2H).

2-(3-Iodopropoxy)tetrahydropyran (2l). TsOH•H_2O (102 mg, 0.54 mmol) was added to a solution of 3-chloro-1-propanol (42 mL, 0.50 mol) and 3,4-dihydro-2*H*-pyran (48 mL, 0.53 mol) in CH_2Cl_2 (500 mL) at 0 °C. The mixture was stirred for 30 min and warmed to room temperature. After being stirred for 2 h, the mixture was quenched with saturated aqueous $NaHCO_3$ (100 mL). The organic layer was removed and the aqueous layer was extract with CH_2Cl_2 (100 mL). The combined organic layer was dried over Na_2SO_4 and evaporated. Purification by distillation gave 2-(3-chloropropoxy)tetrahydropyran (84.9 g, 475 mmol) in 95% yield. 2-(3-Chloropropoxy)tetrahydropyran: [42330-88-1], commercially available from Aldrich; bp 70–75 °C (3.5 Torr). ^{1}H NMR ($CDCl_3$) δ 1.46–1.91 (m, 6H), 2.01–2.10 (m, 2H), 3.48–3.57 (m, 2H), 3.67 (t, *J* = 6.4 Hz, 2H), 3.82–3.92 (m, 2H), 4.60 (t, *J* = 2.9 Hz, 1H). 2-(3-Chloropropoxy)tetrahydropyran was converted into the title compound by a similar procedure as above (NaI (3 equiv.), acetone, reflux, 59 h). The reaction mixture was quenched with saturated aqueous $NaHCO_3$. The crude product was purified by silica gel column chromatography (hexane-AcOEt 10:1, 69% yield). **2l:** [52103-12-5]; ^{1}H NMR ($CDCl_3$) δ 1.52–1.90 (m, 6H), 2.05–2.14 (m, 2H), 3.30 (t, *J* = 6.8 Hz, 2H), 3.41–3.56 (m, 2H), 3.77–3.91 (m, 2H), 4.60 (t, *J* = 3.1 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 3.37 (CH_2), 19.41 (CH_2), 25.37 (CH_2), 30.53 (CH_2), 33.51 (CH_2), 62.21 (CH_2), 66.76 (CH_2), 98.82 (CH).

Methyl Phenylthioacetate (2m). A mixture of thiophenol (1.00 mL, 10.0 mmol), Et_3N (1.40 mL, 10.0 mmol), methyl bromoacetate (**2a**, 1.53 g, 10.0 mmol), and benzene (13 mL) was stirred at room temperature for 4 h. The reaction mixture was subjected to a usual aqueous work-up. Purification of the crude product by silica gel column chromatography (hexane-AcOEt 10:1) gave the title compound (1.74 g, 9.56 mmol) in 96% yield. **2m:** [17277-58-6], commercially available from Tokyo Chemical Industry (TCI); bp 75 °C (0.50 Torr, bath temp). ^{1}H NMR ($CDCl_3$) δ 3.65 (s, 2H), 3.72 (m, 3H), 7.20–7.33 (m, 3H), 7.39–7.43 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 36.27 (CH_2), 52.34 (CH_3), 126.80 (CH), 128.90 (CH × 2), 129.69 (CH × 2), 134.80 (C), 169.95 (C).

Methoxycarbonylmethyl Phenyl Thiocarbonate (2n).[5] Pyridine (0.41 mL, 5.0 mmol) was added to a solution of methyl hydroxyacetate (227 mg, 2.50 mmol) and phenyl chlorothionoformate (0.415 mL, 2.80 mmol) in CH_2Cl_2 (15 mL) at room temperature. After being stirred for 2 h, the resultant mixture was washed with 1 M aqueous HCl, water, saturated aqueous $NaHCO_3$, and brine. The organic layer obtained was dried over Na_2SO_4 and evaporated. Purification of the residue by silica gel column chromatography (hexane-AcOEt 6:1) gave the title compound (564 mg, 2.49 mmol) in a quantitative yield. **2n:** bp 135 °C (0.70 Torr, bath temp). IR (neat) 1765 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.83 (s, 3H), 5.10 (s, 2H), 7.12–7.17 (m, 2H), 7.27–7.34 (m, 1H), 7.39–7.47 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 52.38 (CH_3), 67.97 (CH_2), 121.61 (CH × 2), 126.67 (CH), 129.51 (CH × 2), 153.39

(C), 166.76 (C), 194.85 (C); MS *m/z* (relative intensity) 226 (M^+, 0.5), 195 ($M^+ - CH_3O$, 4.7), 45 (100). Anal. Calcd for $C_{10}H_{10}O_4S$: C, 53.09; H, 4.45%. Found: C, 53.10; H, 4.59%.

Isopropyl Phenyl Thiocarbonate (2o). The title compound was prepared from 2-propanol by the same procedure as above (92% yield). **2o:** bp 115 °C (0.70 Torr, bath temp). IR (neat) 1294, 1203 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.45 (d, *J* = 6.5 Hz, 6H), 5.48 (sept, *J* = 6.5 Hz, 1H), 7.08–7.12 (m, 2H), 7.27–7.32 (m, 1H), 7.38–7.44 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 21.11 ($CH_3 \times 2$), 78.74 (CH), 121.96 ($CH \times 2$), 126.32 (CH), 129.35 ($CH \times 2$), 153.23 (C), 194.25 (C); MS *m/z* (relative intensity) 137 ($M^+ - C_3H_7O$, 1.0), 94 (100). Anal. Calcd for $C_{10}H_{12}O_2S$: C, 61.20; H, 6.16%. Found: C, 61.02; H, 6.08%.

4. Reaction of Radical Precursors with Stannyl Enolates

Et_3B-Initiated Reaction (General Procedure). Et_3B (1.02 M in hexane, 0.05 mL, 0.05 mmol) was added to a solution of a radical precursor (0.50 mmol) and a stannyl enolate (0.60 or 1.00 mmol) in hexane (2.5 mL) at room temperature. After addition of dry air (10 mL), the mixture was stirred for 9 h. The reaction mixture was treated with wet Et_2O (5 mL) and DBU (0.36 mL, 2.4 mmol) for 5 min, passed through a short silica gel column, and evaporated. The crude product was purified by silica gel column chromatography.

AIBN-Initiated Reaction (General Procedure). A radical precursor (0.50 mmol) and a stannyl enolate (0.60, 1.00, or 2.00 mmol) were added to a solution of AIBN (4.1 mg, 0.025 mmol) in benzene (2.5 mL). The mixture was warmed to 80 °C and stirred for 4 h. The resultant mixture was subjected to the same work-up and purification as above.

Methyl (2-Oxocyclohexyl)acetate (3aa): bp 125 °C (21 Torr, bath temp). IR (neat) 1728 (C=O, ester), 1700 (C=O, ketone) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.33–1.50 (m, 1H), 1.55–1.94 (m, 3H), 2.06–2.19 (m, 3H), 2.30–2.48 (m, 2H), 2.74–2.93 (m, 2H), 3.68 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 24.94 (CH_2), 27.53 (CH_2), 33.64 (CH_2), 33.93 (CH_2), 41.55 (CH_2), 46.83 (CH), 51.36 (CH_3), 172.74 (C), 210.67 (C); MS *m/z* (relative intensity) 170 (M^+, 5.8), 139 ($M^+ - CH_3O$, 20), 55 (100). Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29%. Found: C, 63.61; H, 8.09%.

(2-Oxocyclohexyl)acetonitrile (3ab): bp 100 °C (0.90 Torr, bath temp). IR (neat) 2249 (CN), 1712 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.40–1.83 (m, 3H), 1.92–2.04 (m, 1H), 2.10–2.20 (m, 1H), 2.28–2.54 (m, 4H), 2.62–2.75 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 17.67 (CH_2), 24.69 (CH_2), 27.38 (CH_2), 33.24 (CH_2), 41.43 (CH_2), 46.64 (CH), 118.46 (C), 208.54 (C); MS *m/z* (relative intensity) 137 (M^+, 4.3), 55 (100). Anal. Calcd for $C_8H_{11}NO$: C, 70.04; H, 8.08; N, 10.21%. Found: C, 70.13; H, 7.98; N, 10.04%.

Ethyl 2-(2-Oxocyclohexyl)propanoate (3ac, dr = 80:20): bp 135 °C (18 Torr, bath temp). IR (neat) 1732 (C=O, ester), 1711 (C=O, ketone) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.12 (d, *J* = 6.6 Hz, 2.4H), 1.18 (d, *J* = 6.9 Hz, 0.6H), 1.25 (t, *J* = 7.2 Hz, 0.6H), 1.26 (t, *J* = 7.2 Hz, 2.4H), 1.33–1.48 (m, 1H), 1.53–1.78 (m, 2H), 1.89–2.24 (m, 3H), 2.28–2.43 (m, 2H), 2.58–2.81 (m, 2H), 4.08–4.23 (m, 2H); ^{13}C NMR ($CDCl_3$) for major isomer δ 14.11 (CH_3), 14.14 (CH_3), 25.15 (CH_2), 27.68 (CH_2), 30.13 (CH_2),

38.72 (CH), 42.00 (CH_2), 52.82 (CH), 60.31 (CH_2), 176.40 (C), 211.32 (C), for minor isomer δ 14.17 (CH_3), 14.77 (CH_3), 24.95 (CH_2), 28.29 (CH_2), 31.18 (CH_2), 39.32 (CH), 42.18 (CH_2), 53.29 (CH), 60.27 (CH_2), 175.33 (C), 210.86 (C); MS *m/z* (relative intensity) for major isomer 198 (M^+, 2.5), 55 (100), for minor isomer 198 (M^+, 1.9), 55 (100).

2-(2-Oxocyclohexyl)propanenitrile (3ad, dr = 57:43): bp 150 °C (20 Torr, bath temp). IR (neat) 2239 (CN), 1711 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30 (d, *J* = 7.1 Hz, 1.29H), 1.33 (d, *J* = 7.1 Hz, 1.71H), 1.54–1.81 (m, 2H), 1.94–2.52 (m, 6.57H), 2.62 (dtd, *J* = 12.5, 4.6, 1.2 Hz, 0.43H), 3.08 (qd, *J* = 7.1, 4.6 Hz, 0.43H), 3.20 (dt, *J* = 7.1, 6.1 Hz, 0.57H); ^{13}C NMR ($CDCl_3$) for major isomer δ 16.51 (CH_3), 24.84 (CH_2), 24.98 (CH), 27.63 (CH_2), 31.16 (CH_2), 41.98 (CH_2), 52.84 (CH), 121.43 (C), 208.69 (C), for minor isomer δ 14.28 (CH_3), 24.76 (CH), 24.78 (CH_2), 27.25 (CH_2), 29.79 (CH_2), 41.89 (CH_2), 52.07 (CH), 122.29 (C), 208.24 (C); MS *m/z* (relative intensity) for major isomer 151 (M^+, 2.2), 55 (100), for minor isomer 151 (M^+, 1.3), 55 (100).

Dimethyl 2-(2-Oxocyclohexyl)malonate (3ae): bp 110 °C (0.9 Torr, bath temp). IR (neat) 1738 (C=O, ester), 1712 (C=O, ketone) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.46–1.81 (m, 3H), 1.89–2.17 (m, 3H), 2.34–2.47 (m, 2H), 3.20 (ddd, *J* = 12.7, 9.7, 5.1 Hz, 1H), 3.69 (d, *J* = 9.6 Hz, 1H), 3.736 (s, 3H), 3.740 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 24.86 (CH_2), 27.59 (CH_2), 31.05 (CH_2), 41.70 (CH_2), 50.23 (CH), 51.78 (CH), 52.42 (CH_3), 52.49 (CH_3), 168.60 (C), 168.74 (C), 209.44 (C); MS *m/z* (relative intensity) 228 (M^+, 3.4), 197 ($M^+ - CH_3O$, 14), 97 (100). Anal. Calcd for $C_{11}H_{16}O_5$: C, 57.89; H, 7.07%. Found: C, 57.84; H, 7.20%.

Methyl 3-Methyl-4-oxohexanoate (3ba): bp 100 °C (20 Torr, bath temp). IR (neat) 1734 (C=O, ester), 1714 (C=O, ketone) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.07 (t, *J* = 7.3 Hz, 3H), 1.13 (d, *J* = 7.3 Hz, 3H), 2.30 (dd, *J* = 16.8, 5.3 Hz, 1H), 2.54 (dq, *J* = 17.8, 7.3 Hz, 1H), 2.58 (dq, *J* = 17.8, 7.3 Hz, 1H), 2.79 (dd, *J* = 16.8, 8.9 Hz, 1H), 3.02 (dqd, *J* = 8.9, 7.3, 5.3 Hz, 1H), 3.65 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 7.58 (CH_3), 16.73 (CH_3), 34.20 (CH_2), 36.68 (CH_2), 41.60 (CH), 51.52 (CH_3), 172.73 (C), 213.38 (C); MS *m/z* (relative intensity) 129 ($M^+ - C_2H_5$, 12), 127 ($M^+ - CH_3O$, 4.3), 57 (100). Anal. Calcd for $C_8H_{14}O_3$: C, 60.74; H, 8.92%. Found: C, 60.75; H, 9.21%.

3-Methyl-4-oxohexanenitrile (3bb): bp 110 °C (20 Torr, bath temp). IR (neat) 2249 (CN), 1714 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.09 (t, *J* = 7.4 Hz, 3H), 1.32 (d, *J* = 7.1 Hz, 3H), 2.45 (dd, *J* = 16.9, 7.7 Hz, 1H), 2.47 (dq, *J* = 18.1, 7.4 Hz, 1H), 2.61 (dd, *J* = 16.9, 5.9 Hz, 1H), 2.62 (dq, *J* = 18.1, 7.4 Hz, 1H), 2.89 (dqd, *J* = 7.7, 7.1, 5.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 7.38 (CH_3), 16.37 (CH_3), 19.56 (CH_2), 33.63 (CH_2), 42.13 (CH), 118.30 (C), 210.44 (C); MS *m/z* (relative intensity) 125 (M^+, 3.3), 57 (100). Anal. Calcd for $C_7H_{11}NO$: C, 67.17; H, 8.86; N, 11.19%. Found: C, 66.82; H, 9.09; N, 11.01%.

Methyl 4-Oxo-4-phenylbutanoate (3ca): bp 100 °C (0.55 Torr, bath temp). IR (neat) 1738 (C=O, ester), 1687 (C=O, ketone) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.78 (t, *J* = 6.6 Hz, 2H), 3.33 (t, *J* = 6.6 Hz, 2H), 3.71 (s, 3H), 7.45–7.50 (m, 2H), 7.55–7.61 (m, 1H), 7.97–8.00 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 27.84 (CH_2), 33.23 (CH_2), 51.63 (CH_3), 127.85 (CH × 2), 128.45 (CH × 2), 133.06 (CH), 136.37 (C), 173.19 (C), 197.88 (C); MS *m/z* (relative intensity) 192 (M^+, 5.5), 105 (100). Anal. Calcd for $C_{11}H_{12}O_3$: C, 68.74; H, 6.29%. Found: C, 68.73; H, 6.05%.

4-Oxo-4-phenylbutanenitrile (3cb): mp 73.5–74.0 °C (hexane-AcOEt). IR (KBr) 2250 (CN), 1684 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.78 (t, *J* = 7.1 Hz, 2H), 3.39 (t, *J* = 7.1 Hz, 2H), 7.47–7.53 (m, 2H), 7.59–7.65 (m, 1H), 7.94–7.98 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 11.57 (CH_2), 34.03 (CH_2), 119.16 (C), 127.83 (CH × 2), 128.67 (CH × 2), 133.67 (CH), 135.43 (C), 195.29 (C); MS *m/z* (relative intensity) 159 (M^+, 10), 105 (100). Anal. Calcd for $C_{10}H_9NO$: C, 75.45; H, 5.70; N, 8.80%. Found: C, 75.30; H, 5.86; N, 8.81%.

Ethyl 2-Methyl-4-oxo-4-phenylbutanoate (3cc): bp 85 °C (0.63 Torr, bath temp). IR (neat) 1730 (C=O, ester), 1687 (C=O, ketone) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.27 (t, *J* = 7.1 Hz, 3H), 1.28 (d, *J* = 7.1 Hz, 3H), 3.04 (dd, *J* = 17.2, 5.6 Hz, 1H), 3.11 (dqd, *J* = 7.7, 7.1, 5.6 Hz, 1H), 3.48 (dd, *J* = 17.2, 7.7 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 7.43–7.50 (m, 2H), 7.54–7.60 (m, 1H), 7.95–8.00 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 13.98 (CH_3), 17.11 (CH_3), 34.88 (CH), 41.75 (CH_2), 60.36 (CH_2), 127.84 (CH × 2), 128.41 (CH × 2), 132.96 (CH), 136.57 (C), 175.72 (C), 197.88 (C); MS *m/z* (relative intensity) 220 (M^+, 1.1), 105 (100). Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32%. Found: C, 70.84; H, 7.51%.

2-Methyl-4-oxo-4-phenylbutanenitrile (3cd): bp 90 °C (0.63 Torr, bath temp). IR (neat) 2241 (CN), 1687 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.43 (d, *J* = 6.8 Hz, 3H), 3.18–3.47 (m, 3H), 7.47–7.52 (m, 2H), 7.59–7.64 (m, 1H), 7.93–7.97 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 17.67 (CH_3), 20.34 (CH), 42.04 (CH_2), 122.50 (C), 127.83 (CH × 2), 128.64 (CH × 2), 133.63 (CH), 135.70 (C), 195.11 (C); MS *m/z* (relative intensity) 173 (M^+, 8.4), 105 (100). Anal. Calcd for $C_{11}H_{11}NO$: C, 76.28; H, 6.40; N, 8.09%. Found: C, 75.91; H, 6.51; N, 8.16%.

Dimethyl 2-Phenacylmalonate (3ce): bp 100 °C (0.63 Torr, bath temp). IR (neat) 1737 (C=O, ester), 1687 (C=O, ketone) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.65 (d, *J* = 7.1 Hz, 2H), 3.79 (s, 6H), 4.10 (t, *J* = 7.1 Hz, 1H), 7.44–7.51 (m, 2H), 7.56–7.60 (m, 1H), 7.96–8.00 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 37.75 (CH_2), 46.67 (CH), 52.70 (CH_3 × 2), 127.99 (CH × 2), 128.55 (CH × 2), 133.44 (CH), 135.80 (C), 169.26 (C × 2), 196.28 (C); MS *m/z* (relative intensity) 219 ($M^+ - CH_3O$, 1.6), 105 (100). Anal. Calcd for $C_{13}H_{14}O_5$: C, 62.39; H, 5.64%. Found: C, 62.46; H, 5.79%.

1,4-Diphenyl-1,4-butanedione (3cf): [495-71-6], commercially available from Lancaster. ^1H NMR ($CDCl_3$) δ 3.47 (s, 4H), 7.45–7.52 (m, 4H), 7.55–7.62 (m, 2H), 8.03–8.07 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 32.46 (CH_2 × 2), 128.00 (CH × 4), 128.48 (CH × 4), 133.02 (CH × 2), 136.67 (C × 2), 198.52 (C × 2).

1-Phenyl-1-butanone (Butyrophenone, 3cg): [495-40-9], commercially available from Aldrich. ^1H NMR ($CDCl_3$) δ 1.01 (t, *J* = 7.3 Hz, 3H), 1.78 (sext, *J* = 7.3 Hz, 2H), 2.95 (t, *J* = 7.3 Hz, 2H), 7.42–7.49 (m, 2H), 7.52–7.59 (m, 1H), 7.94–7.99 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 13.81 (CH_3), 17.70 (CH_2), 40.44 (CH_2), 127.96 (CH × 2), 128.47 (CH × 2), 132.78 (CH), 137.06 (C), 200.33 (C); MS *m/z* (relative intensity) 148 (M^+, 11), 105 (100).

3-Methyl-1-phenyl-1-butanone (Isovalerophenone, 3ch): [582-62-7], commercially available from Aldrich. IR (neat) 1685 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.00 (d, *J* = 6.8 Hz, 6H), 2.30 (t-sept, *J* = 6.9, 6.8 Hz, 1H), 2.84 (d, *J* = 6.9 Hz, 2H), 7.42–7.49 (m, 2H), 7.52–7.58 (m, 1H), 7.93–7.98 (m,

2H); ^{13}C NMR ($CDCl_3$) δ 22.70 (CH_3 × 2), 25.08 (CH), 47.43 (CH_2), 128.02 (CH × 2), 128.47 (CH × 2), 132.78 (CH), 137.32 (C), 200.20 (C); MS *m/z* (relative intensity) 162 (M^+, 8.1), 105 (100).

3,3-Dimethyl-1-phenyl-1-butanone (3cj): bp 165 °C (104 Torr, bath temp). IR (neat) 1674 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.07 (s, 9H), 2.86 (s, 2H), 7.41–7.47 (m, 2H), 7.51–7.57 (m, 1H), 7.92–7.95 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 30.00 (CH_3 × 3), 31.30 (C), 49.96 (CH_2), 128.12 (CH × 2), 128.38 (CH × 2), 132.60 (CH), 138.51 (C), 200.31 (C); MS *m/z* (relative intensity) 176 (M^+, 8.9), 105 (100). Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15%. Found: C, 81.85; H, 9.28%.

5-Oxo-5-phenylpentyl Acetate (3ck): mp 45.0–46.0 °C (hexane-AcOEt). IR (neat) 1736 (C=O, ester), 1685 (C=O, ketone) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.68–1.89 (m, 4H), 2.04 (s, 3H), 3.02 (t, *J* = 7.2 Hz, 2H), 4.11 (t, *J* = 6.1 Hz, 2H), 7.43–7.49 (m, 2H), 7.52–7.60 (m, 1H), 7.94–7.98 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 20.53 (CH_2), 20.88 (CH_3), 28.10 (CH_2), 37.79 (CH_2), 64.06 (CH_2), 127.92 (CH × 2), 128.53 (CH × 2), 132.95 (CH), 136.86 (C), 171.07 (C), 199.66 (C); MS *m/z* (relative intensity) 160 (M^+ – CH_3CO_2H, 10), 105 (100). Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32%. Found: C, 71.03; H, 7.26%.

1-Phenyl-5-(2-tetrahydropyranyloxy)-1-pentanone (3cl): bp 150 °C (0.95 Torr, bath temp). IR (neat) 1685 (C=O), 1034 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.51–1.91 (m, 10H), 3.02 (t, *J* = 7.2 Hz, 2H), 3.40–3.54 (m, 2H), 3.76–3.91 (m, 2H), 4.59 (dd, *J* = 4.1, 2.8 Hz, 1H), 7.42–7.48 (m, 2H), 7.52–7.59 (m, 1H), 7.95–7.99 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 19.50 (CH_2), 21.05 (CH_2), 25.35 (CH_2), 29.18 (CH_2), 30.61 (CH_2), 38.14 (CH_2), 62.17 (CH_2), 67.07 (CH_2), 98.72 (CH), 127.90 (CH × 2), 128.41 (CH × 2), 132.76 (CH), 136.91 (C), 200.04 (C); MS *m/z* (relative intensity) 177 (M^+ – C_5H_9O, 2.2), 105 (93), 55 (100). Anal. Calcd for $C_{16}H_{22}O_3$: C, 73.25; H, 8.45%. Found: C, 73.13; H, 8.43%.

Methyl 3-Methyl-4-oxo-4-phenylbutanoate (3da): bp 90 °C (0.63 Torr, bath temp). IR (neat) 1737 (C=O, ester), 1682 (C=O, ketone) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.23 (t, *J* = 7.1 Hz, 3H), 2.46 (dd, *J* = 16.7, 5.7 Hz, 1H), 2.97 (dd, *J* = 16.7, 8.2 Hz, 1H), 3.65 (s, 3H), 3.95 (dqd, *J* = 8.2, 7.1, 5.7 Hz, 1H), 7.44–7.51 (m, 2H), 7.54–7.60 (m, 1H), 7.97–8.01 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 17.70 (CH_3), 37.08 (CH_2, CH), 51.52 (CH_3), 128.29 (CH × 2), 128.54 (CH × 2), 132.92 (CH), 135.74 (C), 172.62 (C), 202.53 (C); MS *m/z* (relative intensity) 206 (M^+, 3.4), 175 (M^+ – CH_3O, 3.5), 105 (100). Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84%. Found: C, 69.89; H, 6.80%.

3-Methyl-4-oxo-4-phenylbutanenitrile (3db): bp 125 °C (0.52 Torr, bath temp). IR (neat) 2249 (CN), 1682 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.41 (d, *J* = 7.2 Hz, 3H), 2.64 (dd, *J* = 17.0, 8.1 Hz, 1H), 2.74 (dd, *J* = 17.0, 5.9 Hz, 1H), 3.81 (dqd, *J* = 8.1, 7.2, 5.9 Hz, 1H), 7.48–7.54 (m, 2H), 7.59–7.65 (m, 1H), 7.93–7.97 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 17.83 (CH_3), 20.10 (CH_2), 37.82 (CH), 118.47 (C), 128.26 (CH × 2), 128.74 (CH × 2), 133.56 (CH), 134.53 (C), 199.78 (C); MS *m/z* (relative intensity) 173 (M^+, 1.1), 105 (100). Anal. Calcd for $C_{11}H_{11}NO$: C, 76.28; H, 6.40; N, 8.09%. Found: C, 76.03; H, 6.40; N, 8.03%.

Ethyl 2,3-Dimethyl-4-oxo-4-phenylbutanoate (3dc, dr = 57:43): bp 110 °C (0.57 Torr, bath temp). IR (neat) 1730 (C=O, ester), 1684 (C=O, ketone) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.14 (d, *J* = 7.1 Hz, 1.29H), 1.17 (t, *J* = 7.2 Hz, 1.71H), 1.18 (d, *J* = 7.2 Hz, 1.71H), 1.19 (d, *J* = 7.1 Hz, 1.29H), 1.25 (d, *J*

= 7.2 Hz, 1.71H), 1.28 (t, *J* = 7.1 Hz, 1.29H), 2.90–3.02 (m, 1H), 3.68–3.82 (m, 1H), 4.02–4.11 (m, 2H), 7.26–7.61 (m, 3H), 7.96–7.99 (m, 2H); ^{13}C NMR ($CDCl_3$) for major isomer δ 13.82 (CH_3), 13.89 (CH_3), 14.29 (CH_3), 41.56 (CH), 42.83(CH), 60.26 (CH_2), 128.14 (CH × 2), 128.40 (CH × 2), 132.68 (CH), 135.90 (C), 175.42 (C), 203.11 (C); for minor isomer δ 13.98 (CH_3), 15.85 (CH_3), 16.20 (CH_3), 42.55 (CH), 43.34 (CH), 60.18 (CH_2), 128.07 (CH × 2), 128.51 (CH × 2), 132.95 (CH), 136.53 (C), 175.19 (C), 202.24 (C); MS *m/z* (relative intensity) for major isomer 189 ($M^+ - C_2H_5O$, 5.7), 105 (100), for minor isomer 189 ($M^+ - C_2H_5O$, 3.7), 105 (100). Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74%. Found: C, 72.00; H, 7.84%.

2,3-Dimethyl-4-oxo-4-phenylbutanenitrile (3dd, major isomer): bp 110 °C (0.38 Torr, bath temp). IR (neat) 2241 (CN), 1682 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.34 (d, *J* = 7.2 Hz, 3H), 1.38 (d, *J* = 7.2 Hz, 3H), 3.07 (qd, *J* = 7.2, 6.7 Hz, 1H), 3.70 (qd, *J* = 7.2, 6.7 Hz, 1H), 7.47–7.54 (m, 2H), 7.58–7.64 (m, 1H), 7.92–7.96 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.64 (CH_3), 15.09 (CH_3), 27.42 (CH), 43.33 (CH), 121.85 (C), 128.30 (CH × 2), 128.84 (CH × 2), 133.58 (CH), 135.25 (C), 200.11 (C); MS *m/z* (relative intensity) 187 (M^+, 0.7), 105 (100). Anal. Calcd for $C_{12}H_{13}NO$: C, 76.98; H, 7.00; N, 7.48%. Found: C, 76.69; H, 7.22; N, 7.38%.

2,3-Dimethyl-4-oxo-4-phenylbutanenitrile (3dd, minor isomer): bp 110 °C (0.38 Torr, bath temp). IR (neat) 2241 (CN), 1684 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.30 (d, *J* = 7.1 Hz, 3H), 1.43 (d, *J* = 7.1 Hz, 3H), 3.22 (dq, *J* = 9.2, 7.1 Hz, 1H), 3.59 (dq, *J* = 9.2, 7.1 Hz, 1H), 7.48–7.54 (m, 2H), 7.59–7.65 (m, 1H), 7.93–7.96 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 16.92 (CH_3), 17.25 (CH_3), 28.43 (CH), 43.92 (CH), 121.83 (C), 128.29 (CH × 2), 128.90 (CH × 2), 133.76 (CH), 135.40 (C), 200.10 (C); MS *m/z* (relative intensity) 187 (M^+, 0.7), 105 (100). Anal. Calcd for $C_{12}H_{13}NO$: C, 76.98; H, 7.00; N, 7.48%. Found: C, 76.60; H, 7.17; N, 7.39%.

2,3-Dimethyl-1-phenyl-1-butanone (3dh): bp 70 °C (1.0 Torr, bath temp). IR (neat) 1682 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.90 (d, *J* = 6.8 Hz, 3H), 0.94 (d, *J* = 6.8 Hz, 3H), 1.14 (d, *J* = 6.9 Hz, 3H), 2.00–2.17 (m, 1H), 3.29 (qd, *J* = 6.9, 6.4 Hz, 1H), 7.43–7.58 (m, 3H), 7.93–7.95 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 13.36 (CH_3), 18.60 (CH_3), 21.56 (CH_3), 30.68 (CH), 46.85 (CH), 128.18 (CH × 2), 128.56 (CH × 2), 132.69 (CH), 137.31 (C), 204.76 (C); MS *m/z* (relative intensity) 176 (M^+, 10), 105 (100). Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15%. Found: C, 81.96; H, 9.36%.

Methyl (3,4-Dihydro-1-oxo-2(2*H*)-naphthyl)acetate (3ea): bp 105 °C (0.50 Torr, bath temp). IR (neat) 1738 (C=O, ester), 1684 (C=O, ketone) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.90–2.07 (m, 1H), 2.22–2.28 (m, 1H), 2.39–2.48 (m, 1H), 2.95–3.22 (m, 4H), 3.73 (s, 3H), 7.22–7.33 (m, 2H), 7.48 (td, *J* = 7.4, 1.5 Hz, 1H), 8.03 (dd, *J* = 7.9, 1.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 29.03 (CH_2 × 2), 34.64 (CH_2), 44.57 (CH), 51.51 (CH_3), 126.42 (CH), 127.32 (CH), 128.56 (CH), 131.89 (C), 133.21 (CH), 143.79 (C), 172.76 (C), 198.08 (C); MS *m/z* (relative intensity) 187 ($M^+ - CH_3O$, 21), 77 (100). Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47%. Found: C, 71.31; H, 6.46%.

(3,4-Dihydro-1-oxo-2(2*H*)-naphthyl)acetonitrile (3eb): bp 120 °C (0.48 Torr, bath temp). IR (neat) 2247 (CN), 1684 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.05 (dddd, *J* = 13.6, 13.0, 12.2, 5.1 Hz, 1H), 2.50 (dtd, *J* = 13.0, 4.4, 2.9 Hz, 1H), 2.62 (dd, *J* = 16.9, 8.5 Hz, 1H), 2.87 (ddt, *J* = 13.6, 8.5, 4.4 Hz,

1H), 3.06 (dd, *J* = 16.9, 4.4 Hz, 1H), 3.08 (ddd, *J* = 17.0, 5.1, 2.9 Hz, 1H), 3.16 (ddd, *J* = 17.0, 12.2, 4.4 Hz, 1H), 7.29–7.36 (m, 2H), 7.52 (td, *J* = 7.4, 1.3 Hz, 1H), 8.04 (dd, *J* = 7.9, 1.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 18.15 (CH_2), 28.46 (CH_2), 28.62 (CH_2), 44.19 (CH), 118.36 (C), 126.70 (CH), 127.31 (CH), 128.72 (CH), 131.30 (C), 133.78 (CH), 143.62 (C), 195.75 (C); MS *m/z* (relative intensity) 185 (M^+, 27), 118 (100). Anal. Calcd for $C_{12}H_{11}NO$: C, 77.81; H, 5.99; N, 7.56%. Found: C, 77.62; H, 6.19; N, 7.54%.

Ethyl 2-(3,4-Dihydro-1-oxo-2(2*H*)-naphthyl)propanoate (3ec, dr = 59:41): bp 130 °C (0.48 Torr, bath temp). IR (neat) 1732 (C=O, ester), 1684 (C=O, ketone) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.17 (d, *J* = 7.1 Hz, 1.77H), 1.19 (t, *J* = 7.2 Hz, 1.23H), 1.26 (d, *J* = 7.2 Hz, 1.23H), 1.29 (t, *J* = 7.2 Hz, 1.77H), 1.86–2.23 (m, 2H), 2.83-3.25 (m, 4H), 4.12 (q, *J* = 7.2 Hz, 0.82H), 4.20 (q, *J* = 7.1 Hz, 1.18H), 7.22–7.33 (m, 2H), 7.44–7.50 (m, 1H), 8.00–8.04 (m, 1H); ^{13}C NMR ($CDCl_3$) for major isomer δ 13.41 (CH_3), 14.04 (CH_3), 25.85 (CH_2), 28.99 (CH_2), 39.17 (CH), 50.53 (CH), 60.39 (CH_2), 126.59 (CH), 127.41 (CH), 128.54 (CH), 132.53 (C), 133.22 (CH), 143.67 (C), 174.58 (C), 197.86 (C), for minor isomer δ 13.09 (CH_3), 14.16 (CH_3), 25.19 (CH_2), 29.32 (CH_2), 38.69 (CH), 50.20 (CH), 60.45 (CH_2), 126.59 (CH), 127.41 (CH), 128.60 (CH), 132.37 (C), 133.31 (CH), 143.90 (C), 176.04 (C), 198.02 (C); MS *m/z* (relative intensity) for major isomer 246 (M^+, 1.8), 90 (100), for minor isomer 246 (M^+, 1.5), 144 (100). Anal. Calcd for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37%. Found: C, 73.14; H, 7.40%.

2-(3,4-Dihydro-1-oxo-2(2*H*)-naphthyl)propanenitrile (3ed, major isomer): bp 110 °C (0.50 Torr, bath temp). IR (neat) 2239 (CN), 1682 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.46 (d, *J* = 7.4 Hz, 3H), 2.15 (tt, *J* = 13.2, 8.2 Hz, 1H), 2.43 (ddt, *J* = 13.2, 4.3, 4.0 Hz, 1H), 2.56 (dt, *J* = 13.2, 4.3 Hz, 1H), 3.11 (dd, *J* = 8.2, 4.0 Hz, 2H), 3.64 (qd, *J* = 7.4, 4.3 Hz, 1H), 7.28–7.36 (m, 2H), 7.51 (td, *J* = 7.4, 1.5 Hz, 1H), 8.05 (dd, *J* = 7.7, 1.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 16.13 (CH_3), 24.86 (CH), 25.24 (CH_2), 28.64 (CH_2), 50.32 (CH), 121.03 (C), 126.81 (CH), 127.59 (CH), 128.70 (CH), 131.74 (C), 133.81 (CH), 143.42 (C), 195.76 (C); MS *m/z* (relative intensity) 199 (M^+, 13), 90 (100). Anal. Calcd for $C_{13}H_{13}NO$: C, 78.36; H, 6.58; N, 7.03%. Found: C, 78.26; H, 6.65; N, 7.10%.

2-(3,4-Dihydro-1-oxo-2(2*H*)-naphthyl)propanenitrile (3ed, minor isomer): bp 110 °C (0.50 Torr, bath temp). IR (neat) 2241 (CN), 1684 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.29 (d, *J* = 7.1 Hz, 3H), 2.12 (dddd, *J* = 14.0, 12.8, 6.4, 4.1 Hz, 1H), 2.41 (dtd, *J* = 12.8, 4.3, 3.1 Hz, 1H), 2.90 (ddd, *J* = 14.0, 4.3, 3.1 Hz, 1H), 3.08–3.21 (m, 2H), 3.69 (qd, *J* = 7.1, 3.1 Hz, 1H), 7.26–7.36 (m, 2H), 7.51 (td, *J* = 7.5, 1.5 Hz, 1H), 8.04 (dd, *J* = 7.9, 1.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.38 (CH_3), 24.63 (CH_2), 24.86 (CH), 29.03 (CH_2), 49.58 (CH), 122.55 (C), 126.92 (CH), 127.61 (CH), 128.85 (CH), 131.90 (C), 133.97 (CH), 143.83 (C), 195.19 (C); MS *m/z* (relative intensity) 199 (M^+, 5.0), 90 (100). Anal. Calcd for $C_{13}H_{13}NO$: C, 78.36; H, 6.58; N, 7.03%. Found: C, 78.59; H, 6.65; N, 7.28%.

3,4-Dihydro-2-isopropyl-1(2*H*)-naphthalenone (3eh): bp 125 °C (2.9 Torr, bath temp). IR (neat) 1684 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.91 (d, *J* = 6.8 Hz, 3H), 1.01 (d, *J* = 6.9 Hz, 3H), 1.95 (dddd, *J* = 13.3, 11.2, 9.9, 5.1 Hz, 1H), 2.16 (ddt, *J* = 13.3, 4.8, 4.6 Hz, 1H), 2.33 (ddd, *J* = 11.2, 4.8, 4.6 Hz, 1H), 2.53 (sept-d, *J* = 6.9, 4.8 Hz, 1H), 2.95 (ddd, *J* = 16.8, 9.9, 4.6 Hz, 1H), 3.03 (ddd, *J* = 16.8, 5.1, 4.8 Hz, 1H), 7.21–7.32 (m, 2H), 7.45 (td, *J* = 7.4, 1.5 Hz, 1H), 8.03 (dd, *J* = 7.7, 1.5 Hz, 1H); ^{13}C

NMR ($CDCl_3$) δ 18.49 (CH_3), 20.67 (CH_3), 23.47 (CH_2), 26.15 (CH), 28.52 (CH_2), 53.72 (CH), 126.49 (CH), 127.40 (CH), 128.57 (CH), 132.96 (CH and C), 143.91 (C), 199.89 (C); MS *m/z* (relative intensity) 188 (M^+, 8.9), 146 (100). Anal. Calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57%. Found: C, 82.59; H, 8.71%.

5. Three Component Coupling Reaction

General Procedure. A radical precursor (0.50 mmol), an alkene (1.00 mmol), and a stannyl enolate (1.00 mmol) were added to a solution of AIBN (4.1 mg, 0.025 mmol) in benzene (2.5 mL). The mixture was warmed to 80 °C and stirred for 4 h. The resultant mixture was subjected to the same work-up and purification as described in the method for the AIBN-initiated reaction of radical precursors with stannyl enolates.

Methyl 2-Phenacylpentanoate (5a): bp 105 °C (0.53 Torr, bath temp). IR (neat) 1733 (C=O, ester), 1687 (C=O, ketone) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.94 (t, *J* = 7.2 Hz, 3H), 1.31–1.45 (m, 2H), 1.50–1.74 (m, 2H), 3.01–3.12 (m, 2H), 3.46 (dd, *J* = 18.8, 10.0 Hz, 1H), 3.70 (s, 3H), 7.42–7.48 (m, 2H), 7.53–7.60 (m, 1H), 7.94–7.97 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 13.79 (CH_3), 20.28 (CH_2), 34.24 (CH_2), 40.01 (CH), 40.37 (CH_2), 51.57 (CH_3), 127.92 (CH × 2), 128.47 (CH × 2), 133.05 (CH), 136.60 (C), 176.00 (C), 198.12 (C); MS *m/z* (relative intensity) 234 (M^+, 0.7), 105 (100). Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74%. Found: C, 71.77; H, 8.03%.

Methyl 4-Methyl-2-phenacylpentanoate (5b): bp 110 °C (0.53 Torr, bath temp). IR (neat) 1736 (C=O, ester), 1687 (C=O, ketone) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.91 (d, *J* = 6.4 Hz, 3H), 0.97 (d, *J* = 6.5 Hz, 3H), 1.32–1.44 (m, 1H), 1.57–1.69 (m, 2H), 3.01–3.17 (m, 2H), 3.44 (dd, *J* = 16.9, 8.3 Hz, 1H), 3.70 (s, 3H), 7.43–7.49 (m, 2H), 7.54–7.60 (m, 1H), 7.94–7.98 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 22.18 (CH_3), 22.50 (CH_3), 25.84 (CH), 38.40 (CH), 40.85 (CH_2), 41.37 (CH_2), 51.57 (CH_3), 127.89 (CH × 2), 128.45 (CH × 2), 133.06 (CH), 136.51 (C), 176.32 (C), 198.08 (C); MS *m/z* (relative intensity) 248 (M^+, 0.5), 105 (100). Anal. Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12%. Found: C, 72.55; H, 7.87%.

Methyl 4,4-Dimethyl-2-phenacylpentanoate (5c): bp 125 °C (0.47 Torr, bath temp). IR (neat) 1736 (C=O, ester), 1687 (C=O, ketone) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.93 (s, 9H), 1.36 (dd, *J* = 14.1, 3.8 Hz, 1H), 1.48 (dd, *J* = 14.1, 7.8 Hz, 1H), 3.05–3.16 (m, 2H), 3.39 (dd, *J* = 18.9, 9.5 Hz, 1H), 3.68 (s, 3H), 7.43–7.49 (m, 2H), 7.53–7.59 (m, 1H), 7.93–7.96 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 29.37 (CH_3 × 3), 30.96 (C), 37.08 (CH), 43.07 (CH_2), 46.07 (CH_2), 51.82 (CH_3), 128.02 (CH × 2), 128.61 (CH × 2), 133.22 (CH), 136.62 (C), 177.19 (C), 197.97 (C); MS *m/z* (relative intensity) 231 ($M^+ - CH_3O$, 2.6), 105 (100). Anal. Calcd for $C_{16}H_{22}O_3$: C, 73.25; H, 8.45%. Found: C, 72.99; H, 8.48%.

2-Phenacylpentanenitrile (5d): bp 140 °C (1.0 Torr, bath temp). IR (neat) 2241 (CN), 1687 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.99 (t, *J* = 6.9 Hz, 3H), 1.49–1.71 (m, 4H), 3.18–3.45 (m, 3H), 7.46–7.52 (m, 2H), 7.58–7.64 (m, 1H), 7.93–7.98 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 13.33 (CH_3), 20.28 (CH_2), 25.94 (CH), 33.81 (CH_2), 40.65 (CH_2), 121.76 (C), 127.84 (CH × 2), 128.67 (CH × 2), 133.64 (CH), 135.78 (C), 195.24 (C); MS *m/z* (relative intensity) 201 (M^+, 1.0), 105 (100). Anal. Calcd for $C_{13}H_{15}NO$: C, 77.58; H, 7.51; N, 6.96%. Found: C, 77.40; H, 7.45; N, 6.99%.

4-Methyl-2-phenacylpentanenitrile (5e): mp 69.5–70.0 °C (hexane-AcOEt). IR (KBr) 2237 (CN), 1685 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.99 (d, *J* = 6.6 Hz, 3H), 1.01 (d, *J* = 6.4 Hz, 3H), 1.40 (ddd, *J* = 13.3, 9.6, 4.9 Hz, 1H), 1.67 (ddd, *J* = 13.3, 10.2, 4.8 Hz, 1H), 1.85–2.00 (m, 1H), 3.15–3.46 (m, 3H), 7.46–7.52 (m, 2H), 7.58–7.64 (m, 1H), 7.93–7.98 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 21.09 (CH_3), 22.80 (CH_3), 24.35 (CH), 26.11 (CH), 40.73 (CH_2), 41.06 (CH_2), 121.78 (C), 127.84 (CH × 2), 128.64 (CH × 2), 133.60 (CH), 135.75 (C), 195.18 (C); MS *m/z* (relative intensity) 215 (M^+, 0.5), 105 (100). Anal. Calcd for $C_{14}H_{17}NO$: C, 78.10; H, 7.96; N, 6.51%. Found: C, 78.07; H, 8.05; N, 6.40%.

4,4-Dimethyl-2-phenacylpentanenitrile (5f): mp 78.0–78.5 °C (hexane-AcOEt). IR (KBr) 2241 (CN), 1693 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.06 (s, 9H), 1.41 (dd, *J* = 13.8, 2.1Hz, 1H), 1.76 (dd, *J* = 13.8, 10.4 Hz, 1H), 3.20–3.48 (m, 3H), 7.46–7.52 (m, 2H), 7.58–7.64 (m, 1H), 7.93–7.97 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 21.82 (CH), 29.23 (CH_3 × 3), 30.87 (C), 42.47 (CH_2), 45.88 (CH_2), 123.13 (C), 127.89 (CH × 2), 128.70 (CH × 2), 133.66 (CH), 135.85 (C), 195.09 (C); MS *m/z* (relative intensity) 214 ($M^+ - CH_3$, 2.6), 105 (100). Anal. Calcd for $C_{15}H_{19}NO$: C, 78.56; H, 8.35; N, 6.11%. Found: C, 78.38; H, 8.43; N, 6.02%.

Dimethyl 2-Ethyl-3-phenacylbutanedioate (5g, dr = 74:26): bp 140 °C (0.74 Torr, bath temp). IR (neat) 1738 (C=O, ester), 1687 (C=O, ketone) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.94 (t, *J* = 7.4 Hz, 3H), 1.48–1.61 (m, 1H), 1.68–1.83 (m, 1H), 2.75–2.83 (m, 1H), 3.03 (dd, *J* = 17.5, 3.0 Hz, 0.74H), 3.16 (dd, *J* = 16.6, 2.8 Hz, 0.26H), 3.38 (ddd, *J* = 10.2, 6.9, 3.0 Hz, 0.74H), 3.43–3.60 (m, 1.26H) including 3.54 (dd, *J* = 17.5, 10.2 Hz), 3.69 (s, 0.78H), 3.70 (s, 3H), 3.71 (s, 2.22H), 7.43–7.49 (m, 2H), 7.54–7.60 (m, 1H), 7.94–7.97 (m, 2H); ^{13}C NMR ($CDCl_3$) for major isomer δ 11.80 (CH_3), 23.19 (CH_2), 37.78 (CH_2), 42.12 (CH), 48.48 (CH), 51.75 (CH_3), 52.01 (CH_3), 128.06 (CH × 2), 128.56 (CH × 2), 133.26 (CH), 136.40 (C), 174.00 (C), 174.06 (C), 197.76 (C), for minor isomer δ 12.09 (CH_3), 22.14 (CH_2), 37.09 (CH_2), 41.75 (CH), 48.01 (CH), 51.79 (CH_3), 52.08 (CH_3), 128.02 (CH × 2), 128.56 (CH × 2), 133.26 (CH), 136.52 (C), 173.65 (C), 174.25 (C), 197.71 (C); MS *m/z* (relative intensity) for major isomer 261 ($M^+ - CH_3O$, 1.6), 105 (100), for minor isomer 261 ($M^+ - CH_3O$, 3.7), 105 (100). Anal. Calcd for $C_{16}H_{20}O_5$: C, 65.74; H, 6.90%. Found: C, 65.84; H, 7.10%.

Dimethyl 2-Isopropyl-3-phenacylbutanedioate (5h, major isomer): bp 130 °C (0.55 Torr, bath temp). IR (neat) 1738 (C=O, ester), 1687 (C=O, ketone) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.977 (d, *J* = 6.8 Hz, 3H), 0.982 (d, *J* = 6.4 Hz, 3H), 1.90–2.03 (m, 1H), 2.67 (dd, *J* = 8.6, 6.1 Hz, 1H), 3.02 (dd, *J* = 16.6, 1.8 Hz, 1H), 3.48 (ddd, *J* = 11.0, 6.1, 1.8 Hz, 1H), 3.58 (dd, *J* = 16.6, 11.0 Hz, 1H), 3.68 (s, 3H), 3.70 (s, 3H), 7.43–7.49 (m, 2H), 7.54–7.60 (m, 1H), 7.95–8.00 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 19.98 (CH_3), 20.14 (CH_3), 27.87 (CH), 36.59 (CH_2), 40.39 (CH), 51.36 (CH_3), 51.90 (CH_3), 53.29 (CH), 127.95 (CH × 2), 128.42 (CH × 2), 133.13 (CH), 136.30 (C), 173.29 (C), 174.20 (C), 197.90 (C); MS *m/z* (relative intensity) 275 ($M^+ - CH_3O$, 1.7), 105 (100). Anal. Calcd for $C_{17}H_{22}O_5$: C, 66.65; H, 7.24%. Found: C, 66.44; H, 7.32%.

Dimethyl 2-Isopropyl-3-phenacylbutanedioate (5h, minor isomer): bp 150 °C (0.70 Torr, bath temp). IR (neat) 1738 (C=O, ester), 1687 (C=O, ketone) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.93 (d, *J* = 6.6 Hz, 3H), 1.06 (d, *J* = 6.8, Hz, 3H), 2.03–2.17 (m, 1H), 2.56 (dd, *J* = 8.6, 4.9 Hz, 1H), 3.12–3.22 (m, 1H),

3.48–3.60 (m, 2H), 3.68 (s, 3H), 3.69 (s, 3H), 7.43–7.49 (m, 2H), 7.54–7.61 (m, 1H), 7.93–7.98 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 20.17 (CH_3), 20.76 (CH_3), 27.86 (CH), 38.09 (CH_2), 39.94 (CH), 51.54 (CH_3), 52.00 (CH_3), 53.99 (CH), 128.06 (CH × 2), 128.60 (CH × 2), 133.28 (CH), 136.55 (C), 173.66 (C), 173.84 (C), 197.67 (C). MS *m/z* (relative intensity) 275 ($M^+ - CH_3O$, 1.5), 105 (100). Anal. Calcd for $C_{17}H_{22}O_5$: C, 66.65; H, 7.24%. Found: C, 66.95; H, 7.32%.

Dimethyl 2-*t*-Butyl-3-phenacylbutanedioate (5i): bp 160 °C (0.74 Torr, bath temp). IR (neat) 1732 (C=O, ester), 1687 (C=O, ketone) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.05 (s, 9H), 2.80 (d, *J* = 5.4 Hz, 1H), 3.16 (d, *J* = 15.0 Hz, 1H), 3.45 (dd, *J* = 11.0, 5.6 Hz, 1H), 3.50 (dd, *J* = 15.0, 11.0 Hz, 1H), 3.68 (s, 3H), 3.69 (s, 3H), 7.43–7.48 (m, 2H), 7.53–7.59 (m, 1H), 7.93–7.96 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 27.93 (CH_3 × 3), 33.51 (C), 38.94 (CH), 39.24 (CH_2), 51.16 (CH_3), 52.05 (CH_3), 55.90 (CH), 127.96 (CH × 2), 128.48 (CH × 2), 133.17 (CH), 136.32 (C), 173.33 (C), 174.91 (C), 197.71 (C); MS *m/z* (relative intensity) 288 ($M^+ - CH_3OH$, 7.6), 263 ($M^+ - C_4H_9$, 5.3), 105 (100). Anal. Calcd for $C_{18}H_{24}O_5$: C, 67.48; H, 7.55%. Found: C, 67.26; H, 7.56%.

4-Methyl-2-(1-methylphenacyl)pentanenitrile (5j, major isomer): bp 130 °C (0.45 Torr, bath temp). IR (neat) 2237 (CN), 1684 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.93 (d, *J* = 6.6 Hz, 3H), 0.97 (d, *J* = 6.6 Hz, 3H), 1.20 (ddd, *J* = 13.3, 10.0, 4.1 Hz, 1H), 1.43 (d, *J* = 7.2 Hz, 3H), 1.56 (ddd, *J* = 13.3, 11.4, 4.3 Hz, 1H), 1.90 (d-sept-d, *J* = 10.0, 6.6, 4.3 Hz, 1H), 3.23 (ddd, *J* = 11.4, 9.1, 4.1 Hz, 1H), 3.61 (dq, *J* = 9.1, 7.2 Hz, 1H), 7.48–7.54 (m, 2H), 7.59–7.65 (m, 1H), 7.93–7.96 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 17.25 (CH_3), 20.87 (CH_3), 23.13 (CH_3), 26.46 (CH), 32.82 (CH), 40.04 (CH_2), 43.01 (CH), 121.05 (C), 128.29 (CH × 2), 128.90 (CH × 2), 133.73 (CH), 135.42 (C), 200.22 (C); MS *m/z* (relative intensity) 229 (M^+, 0.5), 105 (100). Anal. Calcd for $C_{15}H_{19}NO$: C, 78.56; H, 8.35; N, 6.11%. Found: C, 78.35; H, 8.38; N, 6.00%.

4-Methyl-2-(1-methylphenacyl)pentanenitrile (5j, minor isomer): bp 130 °C (0.55 Torr, bath temp). IR (neat) 2237 (CN), 1684 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.91 (d, *J* = 6.6 Hz, 3H), 0.98 (d, *J* = 6.7 Hz, 3H), 1.31 (ddd, *J* = 13.5, 10.2, 4.4 Hz, 1H), 1.35 (d, *J* = 7.2 Hz, 3H), 1.67 (ddd, *J* = 13.5, 11.5, 4.1 Hz, 1H), 1.90 (d-sept-d, *J* = 10.2, 6.6, 4.1 Hz, 1H), 3.00 (ddd, *J* = 11.5, 6.6, 4.4 Hz, 1H), 3.72 (qd, *J* = 7.2, 6.6 Hz, 1H), 7.47–7.52 (m, 2H), 7.58–7.64 (m, 1H), 7.92–7.95 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 15.59 (CH_3), 21.00 (CH_3), 23.19 (CH_3), 26.25 (CH), 32.11 (CH), 37.59 (CH_2), 42.74 (CH), 120.98 (C), 128.29 (CH × 2), 128.85 (CH × 2), 133.56 (CH), 135.40 (C), 200.25 (C); MS *m/z* (relative intensity) 229 (M^+, 0.7), 105 (100). Anal. Calcd for $C_{15}H_{19}NO$: C, 78.56; H, 8.35; N, 6.11%. Found: C, 78.67; H, 8.45; N, 6.35%.

4,4-Dimethyl-2-(1-methylphenacyl)pentanenitrile (5k, major isomer): bp 120 °C (0.41 Torr, bath temp). IR (neat) 2239 (CN), 1684 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.01 (s, 9H), 1.21 (dd, *J* = 13.8, 2.0 Hz, 1H), 1.43 (d, *J* = 7.2 Hz, 3H), 1.68 (dd, *J* = 13.8, 10.9 Hz, 1H), 3.17 (ddd, *J* = 10.9, 9.2, 2.0 Hz, 1H), 3.61 (dq, *J* = 9.2, 7.1 Hz, 1H), 7.48–7.54 (m, 2H), 7.59–7.65 (m, 1H), 7.92–7.96 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.98 (CH_3), 29.14 (CH_3 × 3), 29.42 (CH), 30.64 (C), 42.37 (CH_2), 43.63 (CH), 122.37 (C), 128.29 (CH × 2), 128.89 (CH × 2), 133.55 (CH), 135.47 (C), 200.11 (C); MS *m/z* (relative

intensity) 228 ($M^+ - CH_3$, 2.1), 105 (100). Anal. Calcd for $C_{16}H_{21}NO$: C, 78.97; H, 8.70 N, 5.76%. Found: C, 78.78; H, 8.96; N, 5.65%.

4,4-Dimethyl-2-(1-methylphenacyl)pentanenitrile (5k, minor isomer): mp 81.5–82.0 °C (hexane-AcOEt). IR (KBr) 2241 (CN), 1676 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.96 (s, 9H), 1.37 (dd, *J* = 14.2, 2.0 Hz, 1H), 1.37 (d, *J* = 7.1 Hz, 3H), 1.75 (dd, *J* = 14.2, 10.5 Hz, 1H), 2.90 (ddd, *J* = 10.5, 5.6, 2.0 Hz, 1H), 3.71 (qd, *J* = 7.1, 5.6 Hz, 1H), 7.47–7.52 (m, 2H), 7.57–7.64 (m, 1H), 7.91–7.94 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.99 (CH_3), 29.14 ($CH_3 \times 3$), 29.42 (CH), 30.65 (C), 42.36 (CH_2), 43.63 (CH), 122.38 (C), 128.29 (CH × 2), 128.90 (CH × 2), 133.56 (CH), 135.46 (C), 200.11 (C); MS *m/z* (relative intensity) 228 ($M^+ - CH_3$, 2.9), 105 (100). Anal. Calcd for $C_{16}H_{21}NO$: C, 78.97; H, 8.70 N, 5.76%. Found: C, 78.72; H, 8.71; N, 5.82%.

Methyl 2-(3,4-Dihydro-1-oxo-2(2*H*)-naphthyl)-4-methylpentanoate (5l, dr = 64:36): bp 135 °C (0.43 Torr, bath temp). IR (neat) 1732 (C=O, ester), 1682 (C=O, ketone) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.91 (d, *J* = 6.4 Hz, 1.92H), 0.92 (d, *J* = 6.6 Hz, 1.08H), 0.94 (d, *J* = 6.6 Hz, 1.08H), 0.96 (d, *J* = 6.4 Hz, 1.92H), 1.17 (ddd, *J* = 13.0, 8.9, 3.6 Hz, 0.64H), 1.38 (ddd, *J* = 13.3, 7.6, 6.3 Hz, 0.36H), 1.49–1.63 (m, 1H), 1.66 (ddd, *J* = 13.0, 10.9, 4.5 Hz, 0.64H), 1.78 (ddd, *J* = 13.3, 8.6, 6.3 Hz, 0.36H) 1.92 (tdd, *J* = 13.3, 11.0, 5.9 Hz, 0.64H), 2.03–2.20 (m, 0.72H), 2.26 (dtd, *J* = 13.3, 4.3, 3.5 Hz, 0.64H), 2.69 (dt, *J* = 11.4, 5.3 Hz, 0.36H), 2.91 (ddd, *J* = 13.3, 5.9, 4.3 Hz, 0.64H), 2.95–3.10 (m, 2H), 3.17 (ddd, *J* = 10.9, 5.9, 3.6 Hz, 0.64H), 3.29 (ddd, *J* = 8.6, 6.3, 5.3 Hz, 0.36H), 3.65 (s, 1.08H), 3.74 (s, 1.92H), 7.22–7.33 (m, 2H), 7.43–7.50 (m, 1H), 8.00–8.05 (m, 1H); ^{13}C NMR ($CDCl_3$) for major isomer δ 21.35 (CH_3), 23.43 (CH_3), 25.42 (CH_2), 26.32 (CH), 29.18 (CH_2), 37.60 (CH_2), 42.36 (CH), 50.44 (CH), 51.46 (CH_3), 126.50 (CH), 127.37 (CH), 128.48 (CH), 132.24 (C), 133.23 (CH), 143.68 (C), 176.21 (C), 197.61 (C), for minor isomer δ 22.14 (CH_3), 22.47 (CH_3), 25.32 (CH_2), 26.06 (CH), 28.82 (CH_2), 38.44 (CH_2), 42.00 (CH), 49.58 (CH), 51.34 (CH_3), 126.50 (CH), 127.31 (CH), 128.48 (CH), 132.35 (C), 133.16 (CH), 143.46 (C), 175.04 (C), 198.15 (C); MS *m/z* (relative intensity) for major isomer 274 (M^+, 0.7), 146 (100), for minor isomer 274 (M^+, 0.4), 146 (100). Anal. Calcd for $C_{17}H_{22}O_3$: C, 74.42; H, 8.08%. Found: C, 74.43; H, 7.80%.

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