ROMPgel-supported Thiazolium Iodide: An Efficient Supported Organic Catalyst For Parallel Stetter Reactions

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1. Experimental Procedures and Data

General Information

All reagents were obtained from commercial suppliers and used without further purification unless otherwise stated. Where solvents have been described they had been vigorously dried over CaH_2 (CH_2Cl_2), $\text{Na}/\text{Ph}_2\text{CO}$ (Et_2O), Mg (MeOH) or $\text{K}/\text{Ph}_2\text{CO}$ (THF). All reactions were carried out in flame-dried or oven-dried glassware under a dry nitrogen atmosphere at ambient temperature unless otherwise stated. Flash column chromatography was carried out on BDH silica gel 60, grade 40-63 μm . Reactions were monitored by thin layer chromatography (TLC) using Merck Kieselgel 60 F_{254} aluminum sheets. Visualization was effected with short wavelength UV light (254 nm) or chemical staining using either a solution of basic KMnO_4 or a solution of vanillin and concentrated sulfuric acid in ethanol.

Preparation of 5-Bicyclo[2.2.1]hept-5-en-2-yl)-4-methyl-1,3-thiazole (2).

Cyclopentadiene (5.77g, 87.3 mmol) was added to **1** (1 mL, 8.73 mmol) and the reaction mixture heated to 200 °C for 1 h, 230 °C for 0.5 h and 200 °C for 1.5 h. The mixture was cooled to 24 °C and concentrated *in vacuo*. Flash column chromatography (30 : 70; EtOAc : hexanes) gave 5-bicyclo[2.2.1]hept-5-en-2-yl)-4-methyl-1,3-thiazole (**2**) (1.19 g, 53% yield) a clear colorless oil, as a mixture of (1 : 9.5) *exo* : *endo* isomers: *R_f* 0.38 (EtOAc : hexanes 2 : 3); IR (thin film) 1532, 1447, 1416, 1376, 1340, 1247, 925, 844, 785, 730 cm⁻¹; 5-*endo*-bicyclo[2.2.1]hept-5-en-2-yl)-4-methyl-1,3-thiazole (**2a**) ¹H NMR (500 MHz, CDCl₃) δ 8.45 (s, 1H), 6.35 (dd, *J* = 5.6 Hz, *J* = 3.0 Hz, 1H), 5.91 (dd, *J* = 5.6 Hz, *J* = 3.0 Hz, 1H), 3.57 (m, 1H), 3.02 (s, 1H), 2.96 (s, 1H), 2.45 (s, 3H), 2.40 - 2.33 (m, 1H), 1.58 - 1.55 (m, 1H), 1.47 - 1.45 (m, 1H), 1.02 (ddd, *J* = 11.9 Hz, *J* = 4.5 Hz, *J* = 2.7 Hz, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 148.5, 148.0, 138.9, 136.9, 132.8, 50.3, 47.9, 43.3, 37.7, 36.2, 15.3; 5-*exo*-bicyclo[2.2.1]hept-5-en-2-yl)-4-methyl-1,3-thiazole (**2b**) ¹H NMR (500 MHz, CDCl₃) δ 8.52 (s, 1H), 6.24 (dd, *J* = 5.6 Hz, *J* = 3.0 Hz, 1H), 6.15 (dd, *J* = 5.6 Hz, *J* = 3.0 Hz, 1H), 3.00 (s, 1H), 2.86 (dd, *J* = 8.3 Hz, *J* = 4.4 Hz, 1H), 2.79 (s, 1H), 2.40 (s, 3H), 1.81 - 1.76 (m, 1H), 1.65 - 1.63 (m, 1H), 1.61 - 1.50 (m, 1H), 1.46 (m, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 148.2, 148.0, 137.4, 137.0, 136.6, 49.4, 46.2, 42.2, 36.5, 36.4, 15.3; MS (CI, NH₃) *m/z* 192 (M + H)⁺; HRMS (CI, NH₃) *m/z* calc for C₁₁H₁₄NS: 192.0847; found: 192.0841. Anal. calc for C₁₁H₁₃NS: C, 69.07; H, 6.85; N, 7.32. Found: C, 68.93; H, 6.74; N, 7.21.

Preparation of 5-endo-Bicyclo[2.2.1]hept-5-en-2-yl)-3,4-dimethyl-1,3-thiazol-3-ium Iodide (3a).

MeI (0.05 mL, 0.74 mmol) was added to **2a** (94.4 mg, 0.49 mmol) in *n*-BuOH (2.5 mL) and the mixture heated to 70 °C. After 58 h, the reaction mixture was concentrated *in vacuo*. The crude solid was recrystallized (CH₂Cl₂ : Et₂O) to give 5-*endo*-bicyclo[2.2.1]hept-5-en-2-yl)-3,4-dimethyl-1,3-thiazol-3-ium iodide **3a** (143.3 mg, 87%) as yellow crystals: mp 155 - 160 °C; IR (solid) 1591, 1479, 1336, 738 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 10.8 (s, 1H), 6.53 (m, 1H), 6.01 (m, 1H), 4.38 (m, 3H), 3.68 (m, 1H), 3.11 (s, 2H), 2.61 (s, 3H), 2.55 - 2.46 (m, 1H), 1.71 - 1.68 (m, 1H), 1.56 - 1.54 (m, 1H), 1.14 - 1.09 (m, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 155.6, 143.7, 141.0, 140.9, 132.3, 50.7, 48.0, 43.4, 41.7, 37.9, 37.1, 12.7; MS (FAB +) *m/z* 206 (M - I)⁺; HRMS (FAB +) *m/z* calc for C₁₂H₁₆NS: 206.1003; found: 206.1013. Anal. calc for C₁₂H₁₆INS: C, 43.25; H, 4.84; N, 4.20. Found: C, 43.30; H, 4.71; N, 4.13.

Preparation of 3,4-Dimethyl-1,3-thiazol-3-ium Iodide Functionalized ROMPgel (**6**).

1,3-Dimesityl-4,5-dihydroimidazol-2-ylidene ruthenium benzyldiene (**5**) (12.0 mg, 0.01 mmol) in $\text{ClCH}_2\text{CH}_2\text{Cl}$ (0.25 mL) was added to **3a** (426.3 mg, 1.28 mmol) and cross-linker **4** (37.3 mg, 0.14 mmol) in $\text{ClCH}_2\text{CH}_2\text{Cl}$ (2 mL) at 50 °C. After 16 h CH_3CN (2 mL) and Et_2O (2 mL) were added and the reaction mixture was heated to 50 °C for 2 h. The ROMPgel was filtered off and rinsed repeatedly with alternating Et_2O (6×10 mL) and CH_2Cl_2 (6×10 mL). The ROMPgel was dried under high vacuum to a yellow ROMPgel **6** (94% yield): IR (solid) 1456, 975, 923 cm^{-1} . Anal. Found: C, 48.57; H, 5.23; N, 3.54.

General Procedure for the Synthesis of 1,4-Dicarbonyl Compounds (9).

In a typical experiment, DMF (2 mL) was added to the α,β -unsaturated ketone **8** (222 mg, 0.92 mmol) and 3,4-dimethyl-1,3-thiazol-3-ium iodide functionalized ROMPgel (**6**) (59.3 mg, 0.15 mmol). Aldehyde **7c** (0.11 mL, 0.92 mmol) was added to the reaction mixture, followed by Et₃N (1.02 mL, 7.33 mmol) and the reaction heated at 80 °C for 22 h. When the transformation was complete (GC-MS), the mixture was concentrated *in vacuo* and filtered through a plug of silica with hexanes. Concentration of the filtrate gave the corresponding 1,4-dicarbonyl compound **9**.

1,3-Diphenylnonane-1,4-dione (9a)¹

1,3-Diphenylnonane-1,4-dione (121 mg, 89% yield, 90% purity) was obtained as a yellow oil: R_f 0.73 (Et₂O); IR (thin film) 1713, 1684, 1449, 752, 702, 690 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.97 - 7.95 (m, 2H), 7.57 - 7.26 (m, 8H), 4.42 (dd, J = 10.2 Hz, J = 3.6 Hz, 1H), 4.04 (dd, J = 18.0 Hz, J = 10.2 Hz, 1H), 3.12 (dd, J = 18.0 Hz, J = 3.6 Hz, 1H), 2.65 - 2.57 (m, 1H), 2.51 - 2.43 (m, 1H), 1.68 - 1.49 (m, 2H), 1.31 - 1.13 (m, 4H), 0.83 (t, J = 7.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 209.5, 198.2, 138.2, 136.5, 133.2, 129.1, 128.5, 128.3, 128.1, 127.5, 53.3, 42.3, 41.8, 31.1, 23.3, 22.5, 14.0; MS (CI, NH₃) m/z 326 (M+NH₄)⁺, 309 (M+H)⁺; HRMS (CI, NH₃) m/z calc for C₂₁H₂₅O₂: 309.1855; found: 309.1862.

1-(4-Chlorophenyl)-3-phenylnonane-1,4-dione (9b)

1-(4-Chlorophenyl)-3-phenylnonane-1,4-dione (342 mg, 92% yield, 95% purity) was obtained as a orange oil: R_f 0.71 (Et₂O); IR (thin film) 1713, 1682, 1590, 1401, 1091, 700 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.86 (d, J = 8.5 Hz, 2H), 7.37 - 7.26 (m, 7H), 4.41 (dd, J = 10.1 Hz, J = 3.3 Hz, 1H), 3.99 (dd, J = 18.0 Hz, J = 10.1 Hz, 1H), 3.04 (dd, J = 18.0 Hz, J = 3.3 Hz, 1H), 2.64 - 2.39 (m, 2H), 1.60 - 1.46 (m, 2H), 1.34 - 1.17 (m, 4H), 0.81 (t, J = 6.8 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 209.1, 196.9, 139.5, 138.1, 134.9, 129.5, 129.1, 128.8, 128.3, 127.6, 53.3, 42.3, 41.7, 31.2, 23.3, 22.4, 13.9; MS (CI, NH₃) m/z 368 (M+NH₄)⁺, 343 (M+H)⁺; HRMS (CI, NH₃) m/z calc for C₂₁H₂₄O₂Cl: 343.1465; found: 343.1465.

3-(4-Chlorophenyl)-1-phenylnonane-1,4-dione (9c)

3-(4-Chlorophenyl)-1-phenylnonane-1,4-dione (308 mg, 98% yield, 95% purity) was obtained as a yellow oil: R_f 0.71 (Et₂O); IR (thin film) 1713, 1682, 1489, 1015, 754, 689 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.94 (d, J = 7.2 Hz, 2H), 7.55 - 7.50 (m, 1H), 7.44 - 7.39 (m, 2H), 7.31 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 8.4 Hz, 2H), 4.40 (dd, J = 9.9 Hz, J = 3.6 Hz, 1H), 4.00 (dd, J = 18.0 Hz, J = 9.9 Hz, 1H), 3.11 (dd, J = 18.0 Hz, J = 3.6 Hz, 1H), 2.68 - 2.40 (m, 2H), 1.61 - 1.45 (m, 2H), 1.35 - 1.15 (m, 4H), 0.83 (t, J = 6.9 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 209.0, 197.8, 136.8, 136.4, 133.5, 133.3, 129.7, 129.2, 128.6, 128.1, 52.6, 42.3, 41.9, 31.2, 23.3, 22.4, 13.9; MS (CI, NH₃) m/z 360 (M+NH₄)⁺, 343 (M+H)⁺; HRMS (CI, NH₃) m/z calc for C₂₁H₂₄O₂Cl: 343.1465; found: 343.1460. Anal. calc for C₂₁H₂₃O₂Cl: C, 73.57; H, 6.76. Found: C, 73.36; H, 6.87.

3-(2-Chlorophenyl)-1-phenylnonane-1,4-dione (9d)

3-(2-Chlorophenyl)-1-phenylnonane-1,4-dione (361mg, 97% yield, 95% purity) was obtained as an orange oil: R_f 0.69 (Et₂O); IR (thin film) 1716, 1686, 754 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.95 (d, J = 7.7 Hz, 2H), 7.54 - 7.38 (m, 4H), 7.23 - 7.19 (m, 3H), 5.00 (dd, J = 10.1 Hz, J = 3.1 Hz, 1H), 3.98 (dd, J = 17.9 Hz, J = 10.1 Hz, 1H), 3.09 (dd, J = 17.9 Hz, J = 3.1 Hz, 1H), 2.69 - 2.38 (m, 2H), 1.67 - 1.42 (m, 2H), 1.34 - 1.21 (m, 4H), 0.84 (t, J = 6.7 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 208.8, 197.6, 136.4, 136.0, 134.1, 133.2, 130.2, 129.3, 128.8, 128.6, 128.1, 127.5, 49.2, 42.1, 41.1, 31.2, 23.4, 22.4, 13.9; MS (CI, NH₃) m/z 360 (M+NH₄)⁺, 343 (M+H)⁺; HRMS (CI, NH₃) m/z calc for C₂₁H₂₄O₂Cl: 343.1465; found: 343.1453. Anal. calc for C₂₁H₂₃O₂Cl: C, 73.57; H, 6.76. Found: C, 73.39; H, 6.96.

1,3-Di(4-chlorophenyl)nonane-1,4-dione (9e)

1,3-Di(4-chlorophenyl)nonane-1,4-dione (345 mg, 92% yield, 95% purity) was obtained as a yellow oil: R_f 0.73 (Et₂O); IR (thin film) 1713, 1682, 1590, 1488, 1092, 1014, 820 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.87 (d, J = 8.3 Hz, 2H), 7.38 (d, J = 8.3 Hz, 2H), 7.30 (d, J = 8.2 Hz, 2H), 7.21 (d, J = 8.2 Hz, 2H), 4.38 (dd, J = 10.0 Hz, J = 3.2 Hz, 1H), 3.95 (dd, J = 18.0 Hz, J = 10.0 Hz, 1H), 3.05 (dd, J = 18.0 Hz, J = 3.2 Hz, 1H), 2.64 - 2.38 (m, 2H), 1.60 - 1.18 (m, 6H), 0.82 (t, J = 6.8 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 208.9, 196.6, 139.7, 136.5, 134.7, 133.6, 129.7, 129.5, 129.3, 128.9, 52.6, 42.2, 41.8, 31.2, 23.3, 22.4, 13.9; MS (CI, NH₃) m/z 394 (M+NH₄)⁺, 377 (M+H)⁺; HRMS (CI, NH₃) m/z calc for C₂₁H₂₃O₂Cl₂: 377.1075; found: 377.1086

1,3-Di(4-methoxyphenyl)nonane-1,4-dione (9f)

1,3-Di(4-methoxyphenyl)nonane-1,4-dione (317 mg, 86% yield, 95% purity) was obtained as a clear colorless oil: R_f 0.10 (1 : 4; Et₂O : hexanes); IR (thin film) 1713, 1678, 1600, 1253, 1169, 1032, 831 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.93 (d, J = 8.8 Hz, 2H), 7.20 (d, J = 8.5 Hz, 2H), 6.89 (d, J = 6.9 Hz, 2H), 6.87 (d, J = 6.9 Hz, 2H), 4.35 (dd, J = 10.1 Hz, J = 3.6 Hz, 1H), 3.95 (dd, J = 17.8 Hz, J = 10.1 Hz, 1H), 3.82 (s, 3H), 3.78 (s, 3H), 3.05 (dd, J = 17.8 Hz, J = 3.6 Hz, 1H), 2.63 - 2.41 (m, 2H), 1.61 - 1.46 (m, 2H), 1.29 - 1.14 (m, 4H), 0.83 (t, J = 6.9 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 209.8, 196.8, 163.5, 159.0, 130.3, 129.7, 129.4, 114.4, 113.7, 55.4, 55.3, 52.5, 42.1, 41.7, 31.2, 23.4, 22.4, 13.9; MS (CI, NH₃) m/z 369 (M+H)⁺; HRMS (CI, NH₃) m/z calc for C₂₃H₂₉O₄: 369.2066; found: 369.2054. Anal. calc for C₂₃H₂₈O₄: C, 74.97; H, 7.66. Found: C, 74.98; H, 7.69.

4-Phenyldecane-2,5-dione (9g)

4-Phenyldecane-2,5-dione (166 mg, 95% yield, 95% purity) was obtained as a yellow oil: R_f 0.68 (Et₂O); IR (thin film) 1713, 701 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.35 - 7.17 (m, 5H), 4.22 (dd, J = 10.3 Hz, J = 3.6 Hz, 1H), 3.46 (dd, J = 17.9 Hz, J = 10.3 Hz, 1H), 2.57 (dd, J = 17.9 Hz, J = 3.6 Hz, 1H), 2.49 - 2.38 (m, 2H), 2.16 (s, 3H), 1.64 - 0.90 (m, 6H), 0.82 (t, J = 6.9 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 209.5, 206.9, 138.0, 129.1, 128.2, 127.5, 53.3, 46.6, 41.5, 31.1, 30.0, 23.3, 22.3, 13.9; MS (CI, NH₃) m/z 264 (M+NH₄)⁺, 247 (M+H)⁺; HRMS (CI, NH₃) m/z calc for C₁₆H₂₃O₂: 247.1698; found: 247.1696. Anal. calc for C₁₆H₂₂O₂: C, 78.01; H, 9.00. Found: C, 77.87; H, 9.08.

4-Phenylpentadecane-2,5-dione (9h)

4-Phenylpentadecane-2,5-dione (334 mg, 95% yield, 90% purity) was obtained as a yellow oil: R_f 0.68 (Et₂O); IR (thin film) 1715, 701 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.35 - 7.19 (m, 5H), 4.22 (dd, J = 10.3 Hz, J = 3.6 Hz, 1H), 3.47 (dd, J = 18.0 Hz, J = 10.3 Hz, 1H), 2.57 (dd, J = 18.0 Hz, J = 3.6 Hz, 1H), 2.49 - 2.38 (m, 2H), 2.17 (s, 3H), 1.52 - 1.18 (m, 16H), 0.88 (t, J = 6.9 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 209.5, 206.9, 138.0, 129.1, 128.2, 127.5, 53.3, 46.6, 41.6, 31.9, 30.0, 29.5, 29.4, 29.3, 29.0, 23.6, 22.7, 14.1; MS (CI, NH₃) m/z 334 (M+NH₄)⁺, 317 (M+H)⁺; HRMS (CI, NH₃) m/z calc for C₂₁H₃₃O₂: 317.2481; found: 317.2480.

3-(4-Methoxyphenyl)-1-(2-naphthyl)nonane-1,4-dione (9i)

3-(4-Methoxyphenyl)-1-(2-naphthyl)nonane-1,4-dione (350 mg, 98% yield, 85% purity) was obtained as a yellow oil: R_f 0.66 (Et_2O); IR (thin film) 1713, 1682, 1505, 1463, 1367, 1302, 1250, 1178 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 8.48 (s, 1H), 8.01 (d, $J = 8.6$ Hz, 1H), 7.90 (d, $J = 7.9$ Hz, 1H), 7.83 (d, $J = 9.3$ Hz, 2H), 7.62 - 7.48 (m, 2H), 7.26 (d, $J = 7.8$ Hz, 2H), 6.91 (d, $J = 7.8$ Hz, 2H), 4.45 (dd, $J = 9.8$ Hz, $J = 2.7$ Hz, 1H), 4.16 (dd, $J = 17.8$ Hz, $J = 10.0$ Hz, 1H), 3.79 (s, 3H), 3.24 (dd, $J = 17.8$ Hz, $J = 2.7$ Hz, 1H), 2.68 - 2.47 (m, 2H), 1.69 - 1.53 (m, 2H), 1.37 - 1.23 (m, 4H), 0.91 - 0.84 (m, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 209.8, 198.2, 159.1, 135.6, 133.9, 132.5, 130.3, 129.9, 129.6, 129.5, 128.5, 128.4, 127.8, 126.7, 123.8, 114.5, 55.3, 52.6, 42.5, 41.7, 31.3, 23.4, 22.5, 14.0; MS (CI, NH_3) m/z 406 ($\text{M}+\text{NH}_4$) $^+$, 389 ($\text{M}+\text{H}$) $^+$; HRMS (CI, NH_3) m/z calc for $\text{C}_{26}\text{H}_{29}\text{O}_3$: 389.2117; found: 389.2122.

1-(1-Methyl-1H-indol-2-yl)nonane-1,4-dione (9j)

1-(1-Methyl-1H-indol-2-yl)nonane-1,4-dione (158 mg, 86% yield, 94% purity) was obtained as a white solid: mp 58.5 - 59.5 $^\circ$ (1 : 9; Et_2O , hexanes). R_f 0.68 (Et_2O); IR (CHCl_3) 1712, 1665, 1512, 1465, 1396, 751 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.72 (d, $J = 8.1$ Hz, 1H), 7.39 (m, 3H), 7.19 - 7.16 (m, 1H), 4.07 (s, 3H), 3.34 (t, $J = 6.4$ Hz, 2H), 2.87 (t, $J = 6.4$ Hz, 2H), 2.54 (t, $J = 7.4$ Hz, 2H), 1.67 - 1.62 (m, 2H), 1.34 - 1.33 (m, 4H), 0.92 (m, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 209.8, 192.5, 140.0, 134.5, 125.9, 123.0, 120.7, 111.4, 110.3, 43.0, 36.4, 33.4, 32.2, 31.4, 23.6, 22.5, 14.0; MS (CI, NH_3) m/z 286 ($\text{M}+\text{H}$) $^+$; HRMS (CI, NH_3) m/z calc for $\text{C}_{18}\text{H}_{24}\text{NO}_2$: 286.1807; found: 286.1814.

2-(2-Oxo-1-phenylheptyl)-3,4-dihydronaphthalen-1(2H)-one (9k)

2-(2-Oxo-1-phenylheptyl)-3,4-dihydronaphthalen-1(2H)-one (300 mg, 69% yield, purity 66%) was obtained as a yellow oil: R_f 0.18 (1 : 9; Et_2O : hexanes); IR (thin film) 1713, 1682, 1599, 1455, 1296, 1219, 741, 702 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.99 (d, $J = 7.8$ Hz, 1H), 7.54 - 7.20 (m, 8H), 4.01 (d, $J = 10.0$ Hz, 1H), 3.69 - 3.59 (m, 1H), 3.10 - 2.80 (m, 4H), 2.61 - 2.50 (m, 2H), 1.74 - 1.23 (m, 6H), 0.86 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 209.5, 199.5, 144.0, 136.4, 133.4, 129.0, 128.9, 128.7, 128.2, 127.5, 127.4, 126.6, 58.6, 51.3, 42.4, 31.2, 29.8, 27.2, 23.2, 22.5, 13.9; MS (CI, NH_3) m/z 352 ($\text{M}+\text{NH}_4$) $^+$, 335 ($\text{M}+\text{H}$) $^+$; HRMS (CI, NH_3) m/z calc for $\text{C}_{23}\text{H}_{27}\text{O}_2$: 335.2011; found: 335.1998.

1-Cyclohexyl-2-phenylpentane-1,4-dione (9l)

1-Cyclohexyl-2-phenylpentane-1,4-dione (229 mg, 82% yield, 82% purity) was obtained as a yellow oil: R_f 0.70 (Et_2O); IR (thin film) 1708, 1450, 700 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.43 - 7.17 (m, 5H), 4.38 (dd, $J = 10.3$ Hz, $J = 3.6$ Hz, 1H), 3.44 (dd, $J = 17.9$ Hz, $J = 10.3$ Hz, 1H), 2.54 (dd, $J = 17.9$ Hz, $J = 3.6$ Hz, 1H), 2.48 - 2.30 (m, 1H), 2.16 (s, 3H), 2.12 - 2.05 (m, 4H), 1.87 - 1.06 (m, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 212.4, 206.9, 138.0, 129.0, 128.3, 127.4, 51.9, 49.7, 47.0, 30.1, 29.4, 28.3, 25.9, 25.8, 25.3; MS (CI, NH_3) m/z 276 ($\text{M}+\text{NH}_4$) $^+$, 259 ($\text{M}+\text{H}$) $^+$; HRMS (CI, NH_3) m/z calc for $\text{C}_{17}\text{H}_{26}\text{NO}_2$: 276.1964; found: 276.1970.

1,2,4-Triphenylbutane-1,4-dione (9m)²

1,2,4-Triphenylbutane-1,4-dione (88.1 mg, 68% yield, 73% purity) was obtained as a yellow oil: R_f 0.62 (Et_2O); IR (thin film) 1678, 1597, 1448, 1230, 754, 698 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 8.08 - 8.00 (m, 4H), 7.58 - 7.56 (m, 1H), 7.52 - 7.23 (m, 9H), 5.36 (dd, $J = 10.1$ Hz, $J = 3.5$ Hz, 1H), 4.25 (dd, $J = 18.1$ Hz, $J = 10.1$ Hz, 1H), 3.34 (dd, $J = 18.1$ Hz, $J = 3.5$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 199.0, 198.1, 138.7, 136.5, 133.3, 132.9, 129.2, 129.0, 128.7, 128.6, 128.5, 128.3, 128.2, 127.4, 48.7, 43.9; MS (CI, NH_3) m/z 332 ($\text{M}+\text{NH}_4$) $^+$, 315 ($\text{M}+\text{H}$) $^+$; HRMS (CI, NH_3) m/z calc for $\text{C}_{22}\text{H}_{19}\text{O}_2$: 315.1385; found: 315.1390.

(2) (a) Henrick, C. A.; Ridley, D. D.; Ritchie, E.; Taylor, W. C. *Aust. J. Chem.*, **1970**, 23, 329-339. (b) Zdrojewski, T.; Jonczyk, A. *Synthesis* **1990**, 224-233. (c) Mattson, A. E.; Bharadwaj, A. R.; Scheidt, K. A. *J. Am. Chem. Soc.* **2004**, 126, 2314-2315.

1-(4-Chlorophenyl)-3-phenyltetradecane-1,4-dione (9n)

1-(4-Chlorophenyl)-3-phenyltetradecane-1,4-dione (339 mg, 97% yield, 95% purity) was obtained as a colorless oil: R_f 0.17 (1 : 9; Et₂O : hexanes); IR (thin film) 1713, 1682, 1590, 1401, 1092, 700 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.91 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 7.40 - 7.27 (m, 5H), 4.43 (dd, J = 10.1 Hz, J = 3.4 Hz, 1H), 4.01 (dd, J = 17.9 Hz, J = 10.1 Hz, 1H), 3.08 (dd, J = 17.9 Hz, J = 3.4 Hz, 1H), 2.64 - 2.42 (m, 2H), 1.57 - 1.53 (m, 2H), 1.21 (br s, 14H), 0.89 (t, J = 6.4 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 209.4, 197.0, 139.6, 138.1, 134.9, 129.5, 129.1, 128.9, 128.3, 127.6, 53.4, 42.3, 41.8, 31.9, 29.6, 29.5, 29.3, 29.0, 23.7, 22.7, 14.1; MS (CI, NH₃) m/z 430 (M+NH₄)⁺, 413 (M+H)⁺; HRMS (CI, NH₃) m/z calc for C₂₆H₃₄O₂Cl: 413.2247; found: 413.2264; Anal. calc for C₂₆H₃₃O₂Cl: C, 75.61; H, 8.05. Found: C, 75.69; H, 7.85.

3-(4-Chlorophenyl)-1-phenyltetradecane-1,4-dione (9o)

3-(4-Chlorophenyl)-1-phenyltetradecane-1,4-dione (342 mg, 99% yield, 95% purity) was obtained as a yellow oil: R_f 0.19 (1 : 9; Et₂O : hexanes); IR (thin film) 1715, 1682, 1489, 1449, 1092, 1015, 689 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.96 (d, J = 7.9 Hz, 2H), 7.58 - 7.54 (m, 1H), 7.47 - 7.42 (m, 2H), 7.33 (d, J = 8.3 Hz, 2H), 7.24 (d, J = 8.3 Hz, 2H), 4.42 (dd, J = 9.9 Hz, J = 3.6 Hz, 1H), 4.01 (dd, J = 18.0 Hz, J = 9.9 Hz, 1H), 3.13 (dd, J = 18.0 Hz, J = 3.6 Hz, 1H), 2.66 - 2.42 (m, 2H), 1.57 - 1.53 (m, 2H), 1.25 - 1.22 (m, 14H), 0.89 (t, J = 6.4 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 209.1, 197.9, 136.7, 136.4, 133.5, 133.3, 129.7, 129.3, 128.6, 128.1, 52.6, 42.3, 42.0, 31.9, 29.6, 29.5, 29.3, 29.0, 23.6, 22.7, 14.2; MS (CI, NH₃) m/z 430 (M+NH₄)⁺, 413 (M+H)⁺; HRMS (CI, NH₃) m/z calc for C₂₆H₃₄O₂Cl: 413.2247; found: 413.2263; Anal. calc for C₂₆H₃₃O₂Cl: C, 75.61; H, 8.05. Found: C, 75.74; H, 8.10.

1-(4-Methoxyphenyl)-3-phenyltetradecane-1,4-dione (9p)

1-(4-Methoxyphenyl)-3-phenyltetradecane-1,4-dione (316 mg, 94% yield, 95% purity) was obtained as a yellow oil: R_f 0.57 (Et_2O); IR (thin film) 1714, 1676, 1601, 1576, 1509, 1258, 1168, 701 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.95 (d, $J = 8.8$ Hz, 2H), 7.38 - 7.29 (m, 5H), 6.92 (d, $J = 8.8$ Hz, 2H), 4.43 (dd, $J = 10.1$ Hz, $J = 3.3$ Hz, 1H), 4.00 (dd, $J = 17.8$ Hz, $J = 10.1$ Hz, 1H), 3.86 (s, 3H), 3.09 (dd, $J = 17.8$ Hz, $J = 3.3$ Hz, 1H), 2.66 - 2.43 (m, 2H), 1.60 - 1.53 (m, 2H), 1.21 (m, 14H), 0.89 (m, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 209.6, 196.7, 163.6, 138.4, 130.4, 129.7, 129.1, 128.4, 127.4, 113.7, 55.4, 53.4, 42.1, 41.9, 31.9, 29.6, 29.5, 29.3, 29.0, 23.7, 22.7, 14.1; MS (CI, NH_3) m/z 409 ($\text{M}+\text{H}^+$); HRMS (CI, NH_3) m/z calc for $\text{C}_{27}\text{H}_{37}\text{O}_3$: 409.2743; found: 409.2741.

3-(4-Methoxyphenyl)-1-phenyltetradecane-1,4-dione (9q)

3-(4-Methoxyphenyl)-1-phenyltetradecane-1,4-dione (295 mg, 87% yield, 95% purity) was obtained as an orange oil: R_f 0.14 (1 : 9; Et_2O : hexanes); IR (thin film) 1714, 1685, 1511, 1254 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.97 (d, $J = 7.2$ Hz, 2H), 7.57 - 7.42 (m, 3H), 7.21 (d, $J = 8.6$ Hz, 2H), 6.89 (d, $J = 8.6$ Hz, 2H), 4.38 (dd, $J = 10.0$ Hz, $J = 3.5$ Hz, 1H), 4.01 (dd, $J = 18.0$ Hz, $J = 10.0$ Hz, 1H), 3.80 (s, 3H), 3.11 (dd, $J = 18.0$ Hz, $J = 3.5$ Hz, 1H), 2.64 - 2.43 (m, 2H), 1.60 - 1.51 (m, 2H), 1.28 - 1.22 (m, 14H), 0.91 - 0.87 (m, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 209.7, 198.4, 159.0, 136.6, 133.1, 130.2, 129.4, 128.5, 128.1, 114.5, 55.3, 55.2, 52.5, 42.4, 41.7, 31.9, 29.6, 29.5, 29.3, 29.1, 23.7, 22.7, 14.1; MS (CI, NH_3) m/z 426 ($\text{M}+\text{NH}_4^+$), 409 ($\text{M}+\text{H}^+$); HRMS (CI, NH_3) m/z calc for $\text{C}_{27}\text{H}_{37}\text{O}_3$: 409.2743; found: 409.2729; Anal. calc for $\text{C}_{27}\text{H}_{36}\text{O}_3$: C, 79.37; H, 8.88. Found: C, 79.45; H, 9.00.

2. Additional Spectra

5-*exo*-bicyclo[2.2.1]hept-5-en-2-yl)-4-methyl-1,3-thiazole (2a) ^1H NMR

5-*exo*-bicyclo[2.2.1]hept-5-en-2-yl)-4-methyl-1,3-thiazole (2a) ^{13}C NMR

5-endo-bicyclo[2.2.1]hept-5-en-2-yl)-4-methyl-1,3-thiazole (2b) ^1H NMR

5-endo-bicyclo[2.2.1]hept-5-en-2-yl)-4-methyl-1,3-thiazole (2b) ^{13}C NMR

5-endo-bicyclo[2.2.1]hept-5-en-2-yl)-3,4-dimethyl-1,3-thiazol-3-ium iodide (3a) ¹H NMR

5-endo-bicyclo[2.2.1]hept-5-en-2-yl)-3,4-dimethyl-1,3-thiazol-3-ium iodide (3a) ¹³C NMR

1,3-Diphenylnonane-1,4-dione (9a) ^1H NMR

1,3-Diphenylnonane-1,4-dione (9a) ^{13}C NMR

1-(4-Chlorophenyl)-3-phenylnonane-1,4-dione (9b) ^1H NMR

1-(4-Chlorophenyl)-3-phenylnonane-1,4-dione (9b) ^{13}C NMR

3-(4-Chlorophenyl)-1-phenylnonane-1,4-dione (9c) ^1H NMR

3-(4-Chlorophenyl)-1-phenylnonane-1,4-dione (9c) ^{13}C NMR

3-(2-Chlorophenyl)-1-phenylnonane-1,4-dione (9d) ^1H NMR

3-(2-Chlorophenyl)-1-phenylnonane-1,4-dione (9d) ^{13}C NMR

1,3-Di(4-chlorophenyl)nonane-1,4-dione (9e) ^1H NMR

1,3-Di(4-chlorophenyl)nonane-1,4-dione (9e) ^{13}C NMR

1,3-Di(4-methoxyphenyl)nonane-1,4-dione (9f) ^1H NMR

1,3-Di(4-methoxyphenyl)nonane-1,4-dione (9f) ^{13}C NMR