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Supporting Information

for

Palladium-Catalyzed Intramolecular Hydroalkylation of Alkenyl- β-Keto Esters, α-Aryl Ketones, and Alkyl Ketones in the Presence of Me_3SiCl or HCl

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Experimental procedures, analytical and spectroscopic data for alkenyl ketones and spectroscopy for carbocycles and heterocycles. X-ray crystal structure data for *trans*-**23** (39 pages).

Experimental

General Methods. Catalytic reactions were performed under an atmosphere of dry nitrogen. NMR spectra were obtained at 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR in $CDCl_3$ unless otherwise noted. IR spectra were obtained on a Bomen MB-100 FT IR spectrometer. 2-Carboalkoxycyclohexanones existed as mixtures of enol and keto tautomers in $CDCl_3$ solution. The predominant tautomer for each carbocycle is noted and NMR data correspond to this predominant tautomer. Gas chromatography was performed on a Hewlett-Parkard 5890 gas chromatography equipped with a 25 m polydimethylsiloxane capillary column. Flash column chromatography was performed employing 200-400 mesh silica gel (EM). Thin layer chromatography (TLC) was performed on silica gel 60 F_{254} eluting with a 5:1 mixture of hexanes and ethyl acetate unless otherwise noted. Elemental analyses were performed by Complete Analysis Laboratories (Parsippany, NJ). 1,4-Dioxane (Aldrich, anhydrous) was used as received. $PdCl_2(CH_3CN)_2$ (**2**) was purchased (Aldrich) or was prepared from $PdCl_2$ (Strem) employing a literature procedure.[1] An authentic sample of 2-carbomethoxycyclohexanone (**5**) was purchased from Fluka

Alkenyl β-keto esters methyl 3-oxo-6-heptenoate (**4**),[2] ethyl 3-oxo-6-heptenoate,[3] benzyl 3-oxo-6-heptenoate,[3] isobutyl 3-oxo-6-heptenoate, (*E*)-methyl 3-oxo-6-nonenoate [(*E*)-**6**],[4] methyl 3-oxo-7-phenyl-6-heptenoate,[5] (*E*)-methyl 3-oxo-6-octenoate,[4] dimethyl 3,10-dioxo-6-dodecenedioate,[6] methyl 5-methyl-3-oxo-6-octenoate (**8**), methyl 6-methyl-3-oxo-6-heptenoate (**11**),[7] and methyl-3-oxo-7-octenoate (**16**),[8] were prepared via alkylation of a 3-oxo-butyrate dianion with the appropriate alkyl halide employing a published procedure.[2,9] (*Z*)-Methyl 3-oxo-6-nonenoate [(*Z*)-**6**][10] was synthesized via hydrogenation of methyl 3-oxo-6-nonynoate[11] with Lindlar catalyst. Benzyl 3-butenyl ketone (**18**),[12] benzyl 4-pentenyl ketone (**29**),[13] 3-butenyl heptyl ketone (**32**),[14] 1-(4-methoxyphenyl)-5-hexen-2-one (**34**),[15] 3-butenyl pentyl ketone[14] 3-butenyl phenethyl ketone,[16] 3-butenyl cyclohexyl ketone,[17] methyl 5-oxo-8-nonenate,[18] and 1-acetyl-1-allylcyclohexane (**36**)[19] were prepared by published procedures. 2-But-3-enyl-[1,3]dithiane was synthesized using a modified literature procedure.[20]

Alkenyl b -Keto Esters

Isobutyl 3-oxo-6-heptenoate (Table 2, entry 4). TLC: R_f = 0.51. ^{1}H NMR: δ 5.84-5.74 (m, 1 H), 5.08-4.97 (m, 2 H), 3.91 (d, *J* = 6.4 Hz, 2 H), 3.44 (s, 2 H), 2.65 (t, *J* = 7.4 Hz, 2 H), 2.37-2.32 (m, 2 H), 1.94 (m, 1 H), 0.92 (d, *J* = 6.8 Hz, 6 H). ^{13}C{^{1}H} NMR: δ 167.5, 136.9, 115.9, 71.8, 49.6, 42.4, 28.0, 27.7, 19.3. IR (neat, cm^{-1}): 3078, 2962, 2875, 1742, 1713, 1641, 1468, 1411, 1376, 1315, 1234, 1154, 1088, 1000, 915. Anal. Calcd. (found) for $C_{11}H_{18}O_3$: C, 66.64 (66.79); H, 9.15 (9.13).

(*E*)-Methyl 3-oxo-6-nonenoate [(*E*)-6].[4] TLC: R_f = 0.40. ^{1}H NMR (300 MHz): δ 5.55 (td, *J* = 6.0, 15.3 Hz, 1 H), 5.47 (td, *J* = 6.3, 15.3 Hz, 1 H), 3.82 (s, 3 H), 3.53 (s, 2 H), 2.68 (t, *J* = 7.2 Hz, 2 H), 2.42-2.33 (m, 2 H), 2.13-2.02 (m, 2 H), 1.03 (t, *J* = 7.2 Hz, 3 H). ^{13}C{^{1}H} NMR: δ 202.5, 167.9, 133.8, 127.0, 52.6, 49.4, 43.2, 26.7, 25.8, 14.0.

(*Z*)-Methyl 3-oxo-6-nonenoate [(*Z*)-6].[10] TLC: R_f = 0.41. ^{1}H NMR (300 MHz): δ 5.50 (ttd, *J* = 1.5, 7.2, 11.5 Hz, 1 H), 5.36 (ttd, *J* = 1.5, 7.2, 11.5 Hz, 1 H), 3.83 (s, 3 H), 3.55 (s, 2 H), 2.68 (t, *J* = 7.2 Hz, 2 H), 2.46-2.38 (m, 2 H), 2.19-2.09 (m, 2 H), 1.05 (t, *J* = 7.5 Hz, 3 H). ^{13}C{^{1}H} NMR: δ 202.5, 167.9, 133.6, 126.9, 52.7, 49.4, 43.3, 21.6, 20.8, 14.5.

Methyl 3-oxo-6-nonynoate.[11] TLC: R_f = 0.37. ^{1}H NMR: δ 3.73 (s, 3 H), 3.47 (s, 2 H), 2.73 (t, *J* = 7.4 Hz, 2 H), 2.44-2.40 (m, 2 H), 2.11 (tq, *J* = 2.4, 7.6 Hz, 2 H), 1.08 (t, *J* = 7.6 Hz, 3 H). ^{13}C{^{1}H} NMR: δ 201.4, 167.7, 82.9, 77.6, 52.7, 49.3, 42.7, 14.4, 13.6, 12.6.

Methyl 5-methyl-3-oxo-6-octenoate (8). TLC: R_f = 0.47. ^{1}H NMR: δ 5.47-5.38 (m, 1 H), 5.34-5.28 (m, 1 H), 3.71 (s, 3 H), 3.41 (s, 2 H), 2.65 (m, 1 H), 2.52 (dd, *J* = 7.2, 16.0 Hz, 1 H), 2.43 (dd, *J* = 7.2, 16.0 Hz, 1 H), 1.61 (m, 3 H), 0.98 (d, *J* = 6.4 Hz, 3 H). ^{13}C{^{1}H} NMR: δ 202.3, 167.9, 135.4, 124.5, 52.6, 50.4, 49.9, 32.7, 20.7, 18.2. IR (neat, cm^{-1}): 3024, 2957, 2932, 2876, 1746, 1714, 1650, 1632, 1453, 1436, 1406, 1319, 1239, 1157, 1011, 970. Anal. Calcd. (found) for $C_{10}H_{16}O_3$: C, 65.19 (64.83); H, 8.75 (8.77).

Alkenyl a **-Aryl Ketones**

1-(4-Tolyl)-5-hexen-2-one (Table 3, entry 1).[15] 1-(4-Methylphenyl)-5-hexen-2-one was synthesized in 60% as a pale yellow oil employing a procedure similar to that used to synthesize 1-biphenyl-4-yl-hex-5-en-2-one. ^{1}H NMR: δ 7.14 (br d, *J* = 7.6 Hz, 2 H), 7.09 (br d, *J* = 8.0 Hz, 2 H), 5.77 (td, *J* = 6.4, 10.0, 17.0 Hz, 1 H), 5.02-4.94 (m, 1 H), 3.05 (s, 2 H), 2.54 (t, *J* = 7.2 Hz, 2 H), 2.34 (s, 3 H), 2.33-2.27 (m, 2 H). ^{13}C {^{1}H} NMR: δ 208.1, 137.4, 136.9, 131.5, 129.7, 129.6, 115.5, 50.1, 41.2, 28.0, 21.4.

1-Biphenyl-4-yl-hex-5-en-2-one (Table 3, entry 2). *n*-BuLi (2.5 M in hexanes, 4.0 mL, 10.0 mmol) was added dropwise to a solution of 2-but-3-enyl-[1,3]dithiane (1.73 g, 9.95 mmol) in THF (30 mL) at –30 °C and stirred for 2 h. The resulting solution was cooled to –78 °C, treated with a solution of 1-bromomethyl-4-phenylbenzene (2.45 g, 9.95 mmol) in THF (5 mL), stirred for 10 min, warmed to room temperature, and stirred overnight. After quenching with saturated aqueous ammonium chloride, the reaction mixture was extracted with ether. The combined ether extracts were washed with brine, dried ($MgSO_4$), and concentrated under vacuum to give an oily residue that was dissolved in acetonitrile (20 mL) and added to a suspension of *N*-chlorosuccinimide (5.31 g, 39.8 mmol) and silver nitrate (7.60 g, 44.8 mmol) in acetonitrile/water (4/1, 100 mL) at room temperature. The cloudy white suspension was stirred for 45 min, treated sequentially with saturated aqueous Na_2SO_3 (20 mL), saturated aqueous Na_2CO_3 (20 mL), and brine (20 mL), and extracted with ether (2 ∞ 60 mL). The combined ether extracts were dried ($MgSO_4$) and concentrated under vacuum to give an oily residue that was chromatographed (hexanes–Et_2O = 20:1) to give 1-biphenyl-4-yl-hex-5-en-2-one as a white solid (1.79 g, 72%). mp 53-55 °C. TLC: R_f = 0.52. ^{1}H NMR: δ 7.58 (br t, *J* = 8.8 Hz, 4 H), 7.45 (br t, *J* = 8.0 Hz, 2 H), 7.35 (br t, *J* = 8.0 Hz, 1 H), 7.29 (br d, *J* = 8.0 Hz, 2 H), 5.80 (tdd, *J* = 6.4, 10.4, 17.6 Hz, 1 H), 5.04-4.97 (m, 2 H), 3.75 (s, 2 H), 2.61 (t, *J* = 7.4 Hz, 2 H), 2.37-2.32 (m, 2 H). ^{13}C {^{1}H} NMR: δ 207.8, 141.0, 140.3, 137.3, 133.5, 130.2, 129.1, 127.8, 127.6, 127.4, 115.6, 50.1, 41.5, 28.0. IR (neat, cm^{-1}): 3031, 2921, 1708, 1488, 1412, 1334, 1077, 913, 760, 740, 692. Anal. Calcd (found) for $C_{18}H_{18}O$: C, 86.36 (86.03); H, 7.25 (7.02).

1-(4-Fluorophenyl)-5-hexen-2-one (Table 3, entry 3). 1-(4-Fluorophenyl)-5-hexen-2-one was synthesized in 49% overall yield from 4-fluorophenylacetaldehyde as a colorless oil employing a procedure similar to that used to synthesize **24**.

For 1-(4-fluorophenyl)-5-hexen-2-ol: White solid. TLC: R_f = 0.42. ^{1}H NMR: δ 7.19-7.15 (m, 2 H), 7.03-6.97 (m, 2 H), 5.84 (tdd, *J* = 6.8, 10.0, 17.0 Hz, 1 H), 5.08-4.96 (m, 2 H), 3.84-3.78 (m, 1 H), 2.79 (dd, *J* = 4.2, 13.8 Hz, 1 H), 2.64 (dd, *J* = 8.2, 13.8 Hz, 1 H), 2.31-2.12 (m, 2 H), 1.67-1.53 (m, 3 H). ^{13}C{^{1}H} NMR: δ 162.0 (d, *J* = 243.1 Hz), 138.6, 134.5, 131.6 (d, *J* = 7.6 Hz), 115.6 (d, *J* = 20.8 Hz), 115.3, 72.5, 43.5, 36.1, 30.4. IR (neat, cm^{-1}): 3384, 3077, 2935, 1512, 1223, 1156, 1222, 1158, 913, 821. Anal. Calcd (found) for $C_{12}H_{15}FO$: C, 74.20 (74.09); H, 7.78 (7.66).

For 1-(4-fluorophenyl)-5-hexen-2-one: TLC: R_f = 0.44. ^{1}H NMR: δ 7.17-7.13 (m, 2 H), 7.04-6.98 (m, 2 H), 5.76 (tdd, *J* = 6.4, 10.0, 17.0 Hz, 1 H), 5.02-4.94 (m, 2 H), 3.66 (s, 2 H), 2.55 (t, *J* = 7.4 Hz), 2.33-2.28 (m, 2 H). ^{13}C{^{1}H} NMR: δ 207.5, 162.3 (d, *J* = 244 Hz), 137.2, 131.3 (d, *J* = 8.0 Hz), 130.1, 115.9 (d, *J* = 21.2 Hz), 115.7, 49.4, 41.4, 28.0. IR (neat, cm^{-1}): 3077, 2920, 1716, 1509, 1222, 1157, 915, 819. Anal. Calcd (found) for $C_{12}H_{13}FO$: C, 74.98 (74.96); H, 6.82 (6.79).

1-(4-Chlorophenyl)-5-hexen-2-one (Table 3, entry 4). 1-(4-Chlorophenyl)-5-hexen-2-one was synthesized in 46% as a pale yellow oil employing a procedure similar to that used to synthesize 1-biphenyl-4-yl-hex-5-en-2-one. TLC: R_f = 0.59. ^{1}H NMR: δ 7.29-7.26 (m, 2 H), 7.11-7.09 (m, 2 H), 5.74 (tdd, *J* = 6.4, 10.4, 17.2 Hz, 1 H), 5.00-4.93 (m, 2 H), 3.64 (s, 2 H), 2.53 (t, *J* = 7.4 Hz, 2 H), 2.31-2.26 (m, 2 H). ^{13}C{^{1}H} NMR: δ 207.2, 137.1, 133.3, 132.9, 131.1, 129.1, 115.7, 49.6, 41.5, 28.0. IR (neat, cm^{-1}): 3077, 2977, 2918, 1899, 1713, 1641, 1492, 1408, 1358, 1320, 1179, 1090, 1015, 998, 915, 801. Anal. Calcd (found) for $C_{12}H_{13}ClO$: C, 69.07 (68.81); H, 6.28 (6.13).

1-(4-Bromophenyl)-5-hexen-2-one (Table 3, entry 5). 1-(4-Bromophenyl)-5-hexen-2-one was prepared in 44% yield as a colorless oil employing a procedure similar to that used to synthesize 1-biphenyl-4-yl-hex-5-en-2-one. TLC: R_f = 0.52. ^{1}H NMR: δ 7.46-7.43 (m, 2 H), 7.08-7.06 (m, 2 H), 5.76 (tdd, *J* = 5.6, 10.2, 17.0 Hz, 1 H), 5.03-4.95 (m, 2 H), 3.65 (s, 2 H), 2.55 (t, *J* = 7.4 Hz, 2

H), 2.34-2.28 (m, 2 H). $^{13}C\{^1H\}$ NMR: δ 207.0, 137.1, 133.4, 132.1, 131.5, 121.4, 115.8, 49.6, 41.6, 28.0. IR (neat, cm^{-1}): 3077, 2976, 2917, 1897, 1713, 1640, 1590, 1487, 1405, 1358, 1262, 1186, 1107, 1070, 1012, 914, 797. Anal. calcd (found) for $C_{12}H_{13}BrO$: C, 56.94 (57.06); H, 5.18 (4.99).

1-(4-Iodophenyl)-5-hexen-2-one (Table 3, entry 6). 1-(4-Iodophenyl)-5-hexen-2-one was prepared in 11% yield as a pale yellow oil employing a procedure similar to that used to synthesize 1-biphenyl-4-yl-hex-5-en-2-one. TLC: R_f = 0.62. ^1H NMR: δ 7.66-7.63 (m, 2 H), 6.95-6.93 (m, 2 H), 5.76 (tdd, *J* = 6.6, 10.4, 16.8 Hz, 1 H), 5.02-4.95 (m, 2 H), 3.63 (s, 2 H), 2.55 (t, *J* = 7.4 Hz, 2 H), 2.33-2.28 (m , 2 H). $^{13}C\{^1H\}$ NMR: δ 207.0, 138.1, 137.1, 134.0, 131.8, 115.8, 92.8, 49.8, 41.6, 28.0. IR (neat, cm^{-1}): 3076, 2984, 2908, 1900, 1785, 1713, 1640, 1484, 1401, 1357, 1322, 1261, 1185, 1059, 1007, 914, 794. Anal. calcd (found) for $C_{12}H_{13}IO$: C, 48.02 (47.86); H, 4.37 (4.19).

1-(2-Trifluoromethylphenyl)-5-hexen-2-one. (Table 3, entry 7) 1-(2-Trifluoromethylphenyl)-5-hexen-2-one was obtained in 56% overall yield (2-trifluoromethylphenyl)acetaldehyde as a colorless oil employing a procedure similar to that used to synthesize **24**.

For 1-(2-trifluoromethylphenyl)-hex-5-en-2-ol: Yellow oil. TLC: R_f= 0.32. ^1H NMR: δ 7.65 (br d, *J* = 7.6 Hz, 1 H), 7.48 (br t, *J* = 7.4 Hz, 1 H), 7.42 (br d, *J* = 7.6 Hz, 1 H), 7.33 (br t, *J* = 7.6 Hz, 1 H), 5.85 (tdd, *J* = 6.8, 10.4, 16.8 Hz, 1 H), 5.09-4.97 (m, 2 H), 3.90-3.83 (m, 1 H), 3.06 (dd, *J* = 1.2, 14.0 Hz, 1 H), 2.79 (dd, *J* = 9.0, 14.2 Hz, 1 H), 2.32-2.13 (m, 2 H), 1.73-1.63 (m, 3 H). $^{13}C\{^1H\}$ NMR: δ 138.6, 137.9, 132.6, 131.9, 129.3 (q, *J* = 29.2 Hz), 126.8, 126.5 (br q, *J* = 5.5 Hz), 124.9 (q, *J* = 272.3 Hz), 72.0, 41.0, 36.8, 30.3. IR (neat, cm^{-1}): 3380, 3078, 2979, 2936, 1454, 1314, 1159, 1120, 1060, 1038, 913, 742. Anal. Calcd (found) for $C_{13}H_{15}F_3O$: C, 63.93 (63.83); H, 6.19 (6.07).

For 1-(2-trifluoromethylphenyl)-5-hexen-2-one: TLC: R_f= 0.45. ^1H NMR: δ 7.63 (br d, *J* = 8.0 Hz, 1 H), 7.48 (br t, *J* = 7.4 Hz, 1 H), 7.35 (br t, *J* = 8.0 Hz, 1 H), 7.24 (br d, *J* = 7.2 Hz, 1 H), 5.78 (tdd, *J* = 6.4, 10.2, 17.0 Hz, 1 H), 5.03-4.94 (m, 2 H), 3.87 (s, 2 H), 2.56 (t, , *J* = 7.2 Hz, 2

H), 2.34-2.29 (m, 2 H). $^{13}C\{^{1}H\}$ NMR: δ 206.1, 137.2, 133.1, 132.2, 129.1 (q, *J* = 29.6 Hz), 127.5, 126.4(d, *J* = 5.3 Hz), 126.0, 124.7 (q, *J* = 272.0 Hz), 115.7, 46.9, 41.8, 27.9. IR (neat, cm^{-1}): 3078, 2979, 2919, 1723, 1316, 1174, 1160, 1118, 1037, 915, 768. Anal. Calcd (found) for $C_{13}H_{13}F_3O$: C, 64.46 (64.39); H, 5.41 (5.37).

1-(3-Trifluoromethylphenyl)-5-hexen-2-one (Table 3, entry 8). 1-(3-Trifluoromethylphenyl)-5-hexen-2-one was obtained in 43% overall yield from (3-trifluoromethylphenyl)acetaldehyde as a yellow oil employing a procedure similar to that used to synthesize **24**.

For 1-(3-trifluoromethylphenyl)-5-hexen-2-ol: TLC: R_f = 0.32. ^{1}H NMR: δ 7.50-7.48 (m, 2 H), 7.44-7.41 (m, 2 H), 5.84 (tdd, *J* = 6.4, 10.4, 17.0 Hz, 1 H), 5.08-4.98 (m, 2 H), 3.89-3.83 (m, 1 H), 2.86 (dd, *J* = 4.4, 13.6, 1 H), 2.73 (dd, *J* = 8.2, 13.8 Hz, 1 H), 2.31-2.13 (m, 2 H), 1.72-1.55 (m, 3 H). $^{13}C\{^{1}H\}$ NMR: δ 140.0, 138.5, 133.2, 131.1 (q, *J* = 31.7 Hz), 129.2, 126.2 (q, *J* = 3.4 Hz), 124.5 (q, *J* = 270.6 Hz), 123.6 (q, *J* = 3.5 Hz), 115.4, 72.3, 44.0, 36.3, 30.4. IR (neat, cm^{-1}): 3376, 3077, 2924, 1641, 1449, 1331, 1201, 1164, 1125, 1074, 915, 798, 703. Anal. calcd. (found) for $C_{13}H_{15}F_3O$: H, 6.19 (6.28); C, 63.93 (63.68).

For 1-(3-trifluoromethylphenyl)-5-hexen-2-one: TLC: R_f = 0.54. ^{1}H NMR: δ 7.53 (br d, *J* = 7.6 Hz, 1 H), 7.47-7.43 (m, 2 H), 7.38 (br d, *J* = 8.0 Hz, 1 H), 5.77 (tdd, *J* = 6.4, 10.4, 16.8 Hz, 1 H), 5.04-4.96 (m, 2 H), 3.77 (s, 2 H), 2.59 (t, *J* = 7.4 Hz, 2 H), 2.36-2.31 (m, 2 H). $^{13}C\{^{1}H\}$ NMR: δ 206.6, 137.0, 135.3, 133.3, 131.3 (q, *J* = 32.0 Hz), 129.4, 126.5 (q, *J* = 3.4 Hz), 124.4 (q, *J* = 271.0 Hz), 124.2 (q, *J* = 3.4 Hz), 115.8, 49.7, 41.8, 27.9. IR (neat, cm^{-1}): 2918, 1718, 1332, 1164, 1124, 1075, 914, 702. Anal. calcd. (found) for $C_{13}H_{13}F_3O$: C, 64.46 (64.25); H, 5.41 (5.34).

1-(4-Trifluoromethylphenyl)-5-hexen-2-one (Table 3, entry 9). 1-(4-Trifluoromethylphenyl)-5-hexen-2-one was prepared in 12% yield as a pale yellow oil employing a procedure similar to that used to synthesize 1-biphenyl-4-yl-hex-5-en-2-one. TLC: R_f = 0.52. ^{1}H NMR: δ 7.59 (d, *J* = 8.0 Hz, 2 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 5.77 (tdd, *J* = 6.4, 10.4, 17.2 Hz, 1 H), 5.04-4.96 (m, 2 H), 3.77 (s, 2 H), 2.59 (t, *J* =7.4 Hz, 2 H), 2.36-2.30 (m, 2 H). $^{13}C\{^{1}H\}$ NMR:

δ 206.6, 138.4, 137.0, 130.2, 125.9 (q, J = 3.8 Hz), 125.8, 115.9, 49.9, 41.8, 28.0. ^{19}F NMR: δ –62.99. IR (neat, cm^{-1}): 3077, 2914, 1718, 1640, 1618, 1419, 1325, 1260, 1163, 1122, 1066, 1019, 915, 814. Anal. calcd (found) for $C_{13}H_{13}F_3O$: C, 64.46 (64.37); H, 5.41 (5.29).

1-(2-oxo-5-hexenyl)naphthalene (Table 3, entry 10). 1-(2-Oxo-5-hexenyl)naphthalene was obtained in 70% overall yield from 1-naphthylacetaldehyde as a pale yellow oil using a procedure similar to that used to synthesize **24**.

For 1-naphthalen-1-yl-5-hexen-2-ol: TLC: R_f = 0.42. ^{1}H NMR: δ 8.05 (m, 1 H), 7.88 (m, 1 H), 7.77 (m, 1 H), 7.56-7.48 (m, 2 H), 7.45-7.37 (m, 2 H), 5.88 (tdd, J = 6.8, 10.4, 17 Hz, 1 H), 5.11-4.99 (m, 2 H), 4.02 (m, 1 H), 3.36 (dd, J = 4.2, 13.8 Hz, 1 H), 3.08 (dd, J = 8.6, 13.8 Hz, 1 H), 2.38-2.18 (m, 2 H), 1.77-1.71 (m, 2 H), 1.58 (s, 1 H). ^{13}C{^{1}H} NMR: δ 138.7, 134.8, 134.2, 132.4, 129.1, 127.9, 127.6, 126.2, 125.9, 125.7, 124.1, 115.1, 71.7, 41.4, 36.5, 30.4. Anal. calcd. (found) for $C_{16}H_{18}O$: H, 8.02 (7.94); C, 84.91 (84.77).

For 1-(2-oxo-5-hexenyl)naphthalene: TLC: R_f = 0.53. ^{1}H NMR: δ 7.92-7.87 (m, 2 H), 7.82 (d, J = 8.0 Hz, 1 H), 7.56-7.44 (m, 3 H), 7.40 (d, J = 6.8 Hz, 1 H), 5.74 (tdd, J = 6.4, 10.4, 17.2 Hz, 1 H), 5.00-4.92 (m, 2 H), 4.13 (s, 2 H), 2.53 (t, J = 7.2 Hz, 2 H), 2.32-2.27 (m, 2 H). ^{13}C{^{1}H} NMR: δ 208.1, 137.2, 134.1, 132.4, 131.2, 129.0, 128.5, 128.3, 126.7, 126.1, 125.8, 124.1, 115 5, 48.7, 40.8, 27.9. Anal. calcd. (found) for $C_{16}H_{16}O$: C, 85.68 (85.81); H, 7.19 (7.03).

2-(2-Oxo-5-hexenyl)naphthalene (Table 3, entry 11). 2-(2-Oxo-5-hexenyl)naphthalene was synthesized in 64% overall yield from 2-naphthylacetaldehyde as a yellow solid employing a procedure similar to that used to synthesize **24**.

For 1-naphthalen-2-yl-5-hexen-2-ol: Yellow oil. TLC: R_f = 0.39. ^{1}H NMR: δ 7.85-7.81 (m, 3 H), 7.68 (s, 1 H), 7.51-7.44 (m, 2 H), 7.36 (dd, J = 1.4 Hz, 8.6 Hz, 1 H), 5.87 (tdd, J = 6.4, 10.4, 17.2 Hz, 1 H), 5.11-4.99 (m, 2 H), 3.97-3.92 (m, 1 H), 3.00 (dd, J = 4.4 Hz, 13.6 Hz, 1 H), 2.84 (dd, J = 8.4, 13.2 Hz, 1 H), 2.35-2.16 (m, 2 H), 1.74-1.60 (m, 3 H). ^{13}C{^{1}H} NMR: δ 136.6, 126.2, 133.8, 132.5, 128.4, 128.1, 128.0, 127.9, 127.7, 126.3, 125.7, 115.1, 72.3, 44.4, 36.1, 30.4. IR (neat, cm^{-1}): 3385, 3054, 2933, 2917, 1638, 1599, 1507, 909, 815, 748. Anal. Calcd (found) for $C_{16}H_{18}O$: C, 84.91 (84.82); H, 8.02 (7.97).

For 2-(2-oxo-5-hexenyl)naphthalene: TLC: R_f = 0.59. ^{1}H NMR: δ 7.84-7.79 (m, 3 H), 7.67 (s, 1 H), 7.51-7.44 (m, 2 H), 7.33 (dd, *J* = 1.6 Hz, 8.4 Hz, 1 H), 5.76 (tdd, *J* = 6.4, 10.4, 16.8 Hz, 1 H), 5.02-4.93 (m, 2 H), 3.86 (s, 2 H), 2.59 (t, *J* = 7.4 Hz, 2 H), 2.35-2.29 (m, 2 H). ^{13}C{^{1}H} NMR: δ 207.8, 137.2, 133.7, 132.6, 131.9, 128.6, 128.3, 127.9, 127.8, 127.7, 126.4, 126.0, 115.5, 50.6, 41.3, 27.9. IR (neat, cm^{-1}): 3060, 2940, 2921, 1712, 1443, 1407, 1318, 1000, 951, 909, 826, 757. Anal. Calcd (found) for $C_{16}H_{16}O$: C, 85.68 (85.76); H, 7.19 (7.23).

(*E*)-1-Phenyl-5-octen-2-one [(*E*)-20]. Compound (*E*)-**20** was synthesized in 39% overall yield from phenylacetaldehyde as a pale yellow oil employing a procedure similar to that used to synthesize **24**.

For (*E*)-1-phenyl-5-octen-2-ol: TLC: R_f = 0.42. ^{1}H NMR: δ 7.34-7.30 (m, 2 H), 7.26-7.21 (m, 3 H), 5.55-5.48 (m, 1 H), 5.46-5.38 (m, 1 H), 3.87-3.81 (m, 1 H), 2.83 (dd, *J* = 4.4, 13.6 Hz, 1 H), 2.66 (dd, *J* = 7.8, 13.6 Hz, 1 H), 2.24-2.07 (m, 2 H), 2.04-1.97 (m, 2 H), 1.62-1.57 (m, 3 H), 0.97 (t, *J* = 7.6 Hz, 3 H). ^{13}C{^{1}H} NMR: δ 138.9, 133.1, 129.8, 128.8, 126.8, 72.6, 44.3, 36.8, 29.3, 25.9, 14.2. IR (neat, cm^{-1}): 3386, 3083, 3060, 3025, 2959, 2930, 2870, 2848, 1601, 1494, 1451, 1079, 966. Anal. calcd (found) for $C_{14}H_{20}O$: C, 82.30 (82.18); H, 9.87 (9.69).

For (*E*)-20: TLC: R_f = 0.71. ^{1}H NMR: δ 7.30 (m, 2 H), 7.26-7.21 (m, 1 H), 7.17 (m, 2 H), 5.45-5.38 (m, 1 H), 5.33-5.25 (m, 1 H), 3.65 (s, 2 H), 2.48 (t, *J* = 7.4 Hz, 2 H), 2.24-2.18 (m, 2 H), 1.97-1.89 (m, 2 H), 0.90 (t, *J* = 7.6 Hz, 3 H). ^{13}C{^{1}H} NMR: δ 208.2, 134.6, 133.4, 129.7, 129.0, 127.5, 127.3, 50.6, 42.4, 27.0, 25.8, 14.1. IR (neat, cm^{-1}): 3062, 3028, 2961, 2930, 2872, 2848, 1943, 1868, 1713, 1602, 1495, 1454, 1407, 1361, 1188, 1076. Anal. calcd (found) for $C_{14}H_{18}O$: C, 83.12 (82.94); H, 8.97 (9.02).

(*Z*)-1-Phenyl-5-octen-2-one [(*Z*)-20]. Compound (*Z*)-**20** was obtained in 79% yield as a colorless oil via oxidation of (*Z*)-1-phenyl-5-octen-2-ol[21] employing a procedure similar to that used to synthesize **24**.

For (*Z*)-20: TLC: R_f = 0.72. ^{1}H NMR: δ 7.35-7.31 (m, 2 H), 7.28-7.24 (m, 1 H), 7.21-7.19 (m, 2 H), 5.40-5.33 (m, 1 H), 5.26-5.19 (m, 1 H), 3.68 (s, 2 H), 2.49 (t, *J* = 7.0 Hz, 2 H), 2.31-2.25 (m, 2 H), 2.06-1.98 (m, 2 H), 0.93 (t, *J* = 7.6 Hz, 3 H). ^{13}C{^{1}H} NMR: δ 208.2, 134.6,

133.2, 129.7, 129.0, 127.4, 127.3, 50.6, 42.2, 21.9, 20.8, 14.6. IR (neat, cm^{-1}): 3062, 3028, 2963, 2932, 2876, 1958, 1885, 1713, 1603, 1495, 1453, 1359, 1314, 1260, 1070, 1030, 970. Anal. calcd (found) for $C_{14}H_{18}O$: C, 83.12 (83.02); H, 8.97 (8.91).

(*E*)-1,6-Diphenyl-5-hexen-2-one [(*E*)-21]. (*E*)-**21** was obtained in 29% overall yield from phenylacetaldehydeas a pale yellow oil employing a procedure similar to that used to synthesize **24**.

For (*E*)-1,6-diphenyl-5-hexen-2-ol: White solid. mp 49-50.0 °C. TLC: R_f = 0.30. ^1H NMR: δ 7.37-7.31 (m, 5 H), 7.28-7.20 (m, 5 H), 6.43 (d, *J* = 15.6 Hz, 1 H), 6.25 (td, *J* = 6.8, 15.6 Hz, 1 H), 3,94-3.86 (m, 1 H), 2.87 (dd, *J* = 4.4, 13.6 Hz, 1 H), 2.71 (dd, *J* = 8.4, 13.6 Hz, 1 H), 2.49-2.31 (m, 2 H), 1.78-1.65 (m, 2 H), 1.60 (d, *J* = 3.6 Hz, 1 H). $^{13}C\{^1H\}$ NMR: δ 138.7, 138.0, 130.6, 130.5, 129.8, 128.9, 128.8, 127.3, 126.9, 126.3, 72.4, 44.5, 36.6, 29.7. IR (neat, cm^{-1}): 3418, 3081, 3025, 2934, 2917, 2849, 1942, 1888, 1867, 1747, 1715, 1651, 1539, 1494, 1453, 1081, 965. Anal. calcd (found) for $C_{18}H_{20}O$: C, 85.67 (85.39); H, 7.99 (7.86).

For (*E*)-21: TLC: R_f = 0.52. ^1H NMR: δ 7.38-7.29 (m, 7 H), 7.25-7.20 (m, 3 H), 6.38 (d, *J* = 15.6 Hz, 1 H), 6.16 (td, *J* = 6.8 Hz, 15.6 Hz, 1 H), 3.73 (s, 2 H), 2.65 (t, *J* = 7.2 Hz, 2 H), 2.48 (dt, *J* = 6.8, 7.2 Hz, 2 H). $^{13}C\{^1H\}$ NMR: δ 207.7, 137.7, 134.4, 131.0, 129.7, 129.0, 128.8, 127.4, 127.3, 126.3, 50.6, 41.7, 27.3. IR (neat, cm^{-1}): 3081, 3059, 3026, 2918, 1949, 1878, 1806, 1713, 1598, 1494, 1453, 1407, 1361, 1208, 1188, 1092, 1072. Anal. calcd (found) for $C_{18}H_{18}O$: C, 86.36 (86.17); H, 7.25 (7.33).

1,1-Diphenyl-5-hexen-2-one (24). Diphenyl acetaldehyde (2.16 g, 11.0 mmol) was added slowly to a solution of 3-butenyl magnesium bromide (0.5 M in THF, 24.2 mL, 12.1 mmol) in THF (30 mL) at room temperature, refluxed for 12 h, and quenched with saturated aqueous NH_4Cl. The resulting mixture was extracted with ether and the combined ether extracts were washed with brine, dried ($MgSO_4$), and concentrated under vacuum. The resulting residue was chromatographed (hexanes–EtOAc = 40:1) to give 1,1-diphenyl-5-hexen-2-ol (0.66 g, 24%) as a colorless oil.

A solution of DMSO (0.46 mL, 6.4 mmol) in CH_2Cl_2 (2 mL) was added dropwise to a solution of oxalyl chloride (0.27 mL, 3.08 mmol) in CH_2Cl_2 (10 mL) at −78 °C and stirred for 5 min. 1,1-Diphenyl-5-hexen-2-ol (0.648 g, 2.57 mmol) was added and the resulting solution was stirred for 1.5 h

and then treated with triethylamine (1.79 mL, 12.8 mmol). The resulting mixture was warmed to room temperature, poured into water, and extracted with CH_2Cl_2. The combined dichloromethane extracts were dried ($MgSO_4$), concentrated, and chromatographed (hexanes–EtOAc = 20:1) to give **24** as a yellow oil (0.52 g, 81%).

For 1,1-diphenyl-5-hexen-2-ol: TLC: R_f = 0.40. ^{1}H NMR: δ 7,38-7.36 (m, 2 H), 7.32-7.26 (m, 6 H), 7.23-7.16 (m, 2 H), 5.76 (tdd, *J* = 6.6, 10.4, 17.2 Hz, 1 H), 5.02-4.91 (m, 2 H), 4.35 (dt, *J* = 2.9, 8.8 Hz, 1 H), 3.87 (d, *J* = 8.4 Hz, 2 H), 2.32–2.25 (m, 1 H), 2.20-2.10 (m, 1 H), 1.63-1.54 (m, 2 H), 1.53-1.43 (m, 1 H). ^{13}C{^{1}H} NMR: δ 142.3, 141.4, 138.4, 128.8, 128.6, 128.2, 126.8, 126.5, 114.8, 73.1, 58.9, 34.2, 30.1. IR (neat, cm^{-1}): 3442, 3061, 3026, 2975, 2916, 2849, 1494, 1450, 1118, 1078, 913, 702. Anal. calcd. (found) for $C_{13}H_{20}O$: C, 85.67 (85.46); H, 7.99 (7.80).

For 24: TLC: R_f = 0.57. ^{1}H NMR: δ 7.33-7.29 (m, 4 H), 7.26-7.21 (m, 6 H), 5.75 (tdd, *J* = 6.6, 10.4, 17.0 Hz, 1 H), 5.12 (s, 1 H), 5.00-4.92 (m, 2 H), 2.64 (t, *J* = 7.4 Hz, 2 H), 2.35-2.30 (m, 2 H). ^{13}C{^{1}H} NMR: δ 207.7, 138.3, 136.9, 128.9, 128.7, 127.2, 115.4, 64.2, 41.9, 27.9. IR (neat, cm^{-1}): 3061, 3026, 1717, 1598, 1494, 1451, 1277, 1079, 1032, 1000, 916, 745, 701. Anal. calcd. (found) for $C_{13}H_{18}O$: C, 86.36 (86.33); H, 7.25 (7.22).

4-Methyl-1-phenyl-5-hexen-2-one (26). Compound **26** was prepared in 60% yield as a pale yellow oil employing a procedure similar to that used to synthesize 1-biphenyl-4-yl-hex-5-en-2-one. TLC: R_f = 0.58. ^{1}H NMR: δ 7.32-7.28 (m, 2 H), 7.26-7.22 (m, 1 H), 7.17-7.15 (m, 2 H), 5.69 (ddd, *J* = 6.8, 10.4, 17.4 Hz, 1 H), 4.96-4.87 (m, 2 H), 3.64 (s, 2 H), 2.74-2.64 (m, 1 H), 2.47 (dd, *J* = 6.8, 16.4 Hz, 1 H), 2.36 (dd, *J* = 6.8, 16.4 Hz, 1 H), 0.94 (d, *J* = 6.8 Hz, 3 H). ^{13}C{^{1}H} NMR: δ 207.6, 143.1, 134.4, 129.8, 129.0, 127.3, 113.4, 51.0, 48.8, 35.5, 20.0. IR (neat, cm^{-1}): 3081, 3063, 3028, 2961, 2928, 2886, 1947, 1713, 1638, 1601, 1584, 1558, 1540, 1495, 1453, 1415, 1371, 1354, 1275, 1186, 1111, 1079, 1047, 995, 914. Anal. calcd (found) for $C_{13}H_{16}O$: C, 82.94 (82.77); H, 8.57 (8.39).

1-(4-Methylphenyl)-6-hepten-2-one (Table 4, entry 1). *n*-BuLi (2.5 M in hexanes, 3.2 mL, 7.96 mmol) was added dropwise to a solution of 2-pent-4-enyl-[1,3]dithiane[9] (1.43 g, 7.58

mmol) in THF (25 mL) at –30 °C. The resulting solution was stirred for 2 h, cooled to –78 °C, and treated with a solution of 1-bromomethyl-4-methylbenzene (1.47 g, 7.96 mmol) in THF (10 mL). The reaction mixture was stirred for 10 min, warmed to room temperature overnight, quenched with saturated aqueous NH_4Cl, and extracted with ether. The combined ether extracts were washed with brine, dried ($MgSO_4$), and concentrated under vacuum to give crude 2-pent-4-enyl-2-(4-methylbenzyl)-[1,3]-dithiane that was used in the following step without further purification. A solution of crude 2-pent-4-enyl-2-(4-methylbenzyl)-[1,3]-dithiane in acetonitrile (15 mL) was added to a mixture of *N*-chlorosuccinomide (4.05 g, 30.3 mmol) and silver nitrate (5.80 g, 34.1 mmol) in acetonitrile/water (v/v = 4/1, 100 mL) at room temperature and stirred for 45 min. The resulting white suspension was treated with saturated aqueous Na_2SO_3, saturated aqueous Na_2CO_3, and brine. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic fractions were dried ($MgSO_4$), and concentrated under vacuum. The residue was purified by flash column chromatography (hexanes–ether = 50:1) to give 1-(4-methylphenyl)-6-hepten-2-one (0.69 g, 45 %) as a yellow oil. TLC: R_f = 0.63. ^{1}H NMR: δ 7.14 (br d, *J* = 8.0 Hz, 2 H), 7.09 (br d, *J* = 8.0 Hz, 2 H), 5.73 (tdd, *J* = 6.8, 10.2, 17.0 Hz, 1 H), 5.00-4.94 (m, 2 H), 3.64 (s, 2 H), 2.45 (t, *J* = 7.2 Hz, 2 H), 2.34 (s, 3 H), 2.04-1.99 (m, 2 H), 1.66 (quintet, *J* = 7.4, 2 H). ^{13}C{^{1}H} NMR: δ 208.7, 138.2, 136.8, 131.4, 129.6, 129.4, 115.4, 50.1, 41.2, 33.2, 22.9, 21.3. IR (neat, cm^{-1}): 2925, 1712, 1513, 1412, 1364, 993, 912, 805. Anal. Calcd (found) for $C_{14}H_{18}O$: C, 83.12 (82.98); H, 8.97 (8.82).

1-(3-Trifluoromethylphenyl)-6-hepten-2-one (Table 4, entry 2). 4-Bromo-1-butene (2.38 g, 15.9 mmol) in THF (20 mL) was added slowly to a suspension of Mg powder (0.48g, 19.9 mmol) in THF (15 mL) and the resulting suspension was refluxed for 1 h, treated with a solution of (3-trifluoromethylphenyl)acetaldehyde (1.50 g, 7.97 mmol) in THF (20 mL), and refluxed for 1 h. The reaction mixture was quenched with saturated aqueous NH_4Cl, and extracted with ether. The combined ether extracts were washed with brine, dried ($MgSO_4$), and concentrated under vacuum. The residue was chromoatographed (hexanes:ether = 20:1) to give 1-(3-trifluoromethylphenyl)-6-hepten-2-ol as a colorless oil (1.13 g, 55 %).

A solution of DMSO (anhydrous, 0.83 mL, 11.7 mmol) in dichloromethane (5 mL) was added dropwise to a solution of oxalyl chloride (0.48 mL, 5.45 mmol) in dichloromethane (20 mL) at –78 °C. The resulting solution was stirred 10 min, treated with 1-(3-trifluoromethylphenyl)-6-hepten-2-ol (1.01 g, 3.89 mmol), stirred for 1 h, and treated with triethylamine (3.30 mL, 23.4 mmol). The reaction mixture was warmed to room temperature, poured into water, and extracted with dichloromethane. The combined dichloromethane extracts were dried ($MgSO_4$), and concentrated under vacuum. The residue was chromatographed (hexanes:ether = 20:1) to give 1-(3-trifluoromethylphenyl)-6-hepten-2-one as a yellow oil (0.79 g, 79%).

For 1-(3-Trifluoromethylphenyl)-6-hepten-2-ol: Yellow oil. TLC: R_f = 0.26. ^{1}H NMR: δ 7.50-7.48 (m, 2 H), 7.42-7.40 (m, 2 H), 5.81 (tdd, *J* = 6.8, 10.4, 17.0 Hz, 1 H), 5.04-4.95 (m, 2 H), 3.86-3.80 (m, 1 H), 2.86 (dd, *J* = 4.2, 13.8 Hz, 1 H), 2.72 (dd, *J* = 8.4, 13.6 Hz, 1 H), 2.10-2.08 (m, 2 H), 1.65-1.45 (m, 5 H). ^{13}C{^{1}H} NMR δ 140.1, 138.8, 133.2, 131.1 (q, *J* = 31.9 Hz), 129.2, 126.4 (d, *J* = 3.4 Hz), 134.5 (q, *J* = 270.7 Hz), 123.6 (d, *J* = 3.4 Hz), 115.1, 72.6, 44.0, 36.7, 33.9, 25.2. IR (neat, cm^{-1}): 3384, 2934, 1449, 1331, 1163, 1125, 1073, 912, 797, 702. Anal. Calcd (found) for $C_{14}H_{17}F_3O$: C, 65.10 (65.08); H, 6.63 (6.47).

For 1-(3-Trifluoromethylphenyl)-6-hepten-2-one: Yellow oil. TLC: R_f = 0.49. ^{1}H NMR: δ 7.63 (d, *J* = 7.6 Hz, 1 H), 7.56-7.52 (m, 2 H), 7.48 (d, *J* = 7.6 Hz, 1 H), 5.83 (tdd, *J* = 6.8, 10.2, 17.0 Hz, 1 H), 5.10-5.05 (m, 2 H), 3.85 (s, 2 H), 2.60 (t, *J* = 7.2 Hz, 2 H), 2.13 (q, *J* = 7.2 Hz, 2 H), 1.79 (quintet, *J* = 7.2 Hz, 2 H). ^{13}C{^{1}H} NMR: δ 207.3, 138.1, 135.4, 133.2, 131.3 (q, *J* = 32.0 Hz), 129.4, 126.5 (d, *J* = 3.4 Hz), 124.4 (q, *J* = 270.7 Hz), 124.2 (d, *J* = 3.5 Hz), 115.7, 49.7, 41.8, 33.2, 22.9. IR (neat, cm^{-1}): 2935, 1716, 1331, 1163, 1124, 1075, 913, 702. Anal. Calcd (found) for $C_{14}H_{15}F_3O$: C, 65.62 (65.54); H, 5.90 (5.85).

1-(4-Trifluoromethylphenyl)-6-hepten-2-one (Table 4, entry 3). 1-(4-Trifluoromethylphenyl)-6-hepten-2-one was obtained in 43% overall yield from (4-trifluoromethylphenyl)acetaldehyde as a pale yellow oil employing a procedure simiar to that described above for the synthesis of 1-(3-trifluoromethylphenyl)-6-hepten-2-one (Table 4, enty 2).

For 1-(4-Trifluoromethylphenyl)-6-hepten-2-ol: Yellow oil. TLC: R_f = 0.39. ^{1}H NMR: δ 7.57 (br d, *J* = 8.0 Hz, 2 H), 7.33 (br d, *J* = 8.0 Hz, 2 H), 5.81 (tdd, *J* = 6.8, 10.2, 15.0 Hz, 1 H), 5.05-4.95 (m, 2 H), 3.87-3.81 (m, 1 H), 2.87 (dd, *J* = 4.0, 13.6 Hz, 1 H), 2.72 (dd, *J* = 8.4, 14.0 Hz, 1 H), 2.10-2.06 (m, 2 H), 1.65-1.43 (m, 5 H). ^{13}C{^{1}H} NMR: δ 143.2, 138.8, 130.1, 129.1 (q, *J* = 32.2 Hz), 125.7 (br d, *J* = 2.9 Hz), 124.1 (q, *J* = 270.2 Hz), 115.1, 72.7, 44.1, 36.7, 33.9, 25.3. IR (neat, cm^{-1}): 3349, 2934, 2859, 1618, 1417, 1328, 1162, 1120, 1067, 1019, 913, 819. Anal. Calcd (found) for $C_{14}H_{17}F_3O$: C, 65.10 (65.13); H, 6.63 (6.57).

For 1-(4-Trifluoromethylphenyl)-6-hepten-2-one: Pale yellow oil. TLC: R_f = 0.50. ^{1}H NMR: δ 7.58 (br d, *J* = 8.0 Hz, 2 H), 7.31 (br d, *J* = 8.0 Hz, 2 H), 5.74 (tdd, *J* = 6.8, 10.4, 17.0 Hz, 1 H), 5.00-4.95 (m, 2 H), 3.75 (s, 2 H), 2.49 (t, *J* = 7.2 Hz, 2 H), 2.03 (q, *J* = 7.2 Hz, 2 H), 1.68 (quintet, *J* = 7.2 Hz, 2 H). ^{13}C{^{1}H} NMR δ 207.3, 138.5, 138.1, 130.1, 129.6 (q, *J* = 32.2 Hz), 125.8 (br d, *J* = 3.0 Hz), 124.5, (q, *J* = 270.5 Hz), 115.6, 49.8, 41.8, 33.2, 22.9. IR (neat, cm^{-1}): 3077, 2937, 1714, 1418, 1326, 1164, 1124, 1067, 1020, 915. Anal. Calcd (found) for $C_{14}H_{15}F_3O$: C, 65.62 (65.43); H, 5.90 (5.94).

1-(4-Fluorophenyl)-6-hepten-2-one (Table 4, entry 4). 1-(4-Fluorophenyl)-6-hepten-2-one was obtained in 56% overall yield from (4-flurophenyl)acetaldehyde as a pale yellow oil employing a procedure simiar to that described above for the synthesis of 1-(3-trifluoromethylphenyl)-6-hepten-2-one (Table 4, enty 2).

For 1-(4-fluorophenyl)-6-hepten-2-ol: TLC: R_f = 0.38. ^{1}H NMR: δ 7.19-7.15 (m, 2 H), 7.03-6.97 (m, 2 H), 5.81 (tdd, *J* = 6.6, 10.4 17.2 Hz, 1 H), 5.04-4.94 (m, 2 H), 3.82-3.76 (m, 1 H), 7.80 (dd, *J* = 4.0, 13.6 Hz, 1 H), 2.63 (dd, *J* = 8.4, 13.6 Hz, 1 H), 2.11-2.06 (m, 2 H), 1.65-1.43 (m, 5 H). ^{13}C{^{1}H} NMR: δ 162.0 (d, *J* = 242.8 Hz), 138.9, 134.5, 131.1 (d, *J* = 7.6 Hz), 115.7 (d, *J* = 20.8 Hz), 115.0, 72.9, 43.5, 36.6, 34.0, 25.3. Anal. calcd. (found) for $C_{13}H_{15}FO$: C, 74.97 (75.10); H, 8.23 (8.32).

For 1-(4-Fluorophenyl)-6-hepten-2-one: TLC: R_f = 0.44. ^{1}H NMR: δ 7.17-7.12 (m, 2 H), 7.04-6.98 (m, 2 H), 5.72 (tdd, *J* = 6.6, 10.4, 17.0 Hz, 1 H), 4.99-4.93 (m, 2 H), 3.65 (s, 2 H), 2.46 (t, *J* = 7.2 Hz, 2 H), 2.04-1.99 (m, 2 H), 1.66 (quintet, *J* = 7.2 Hz, 2 H). ^{13}C{^{1}H} NMR: δ

208.2, 162.3 (d, J = 243.9 Hz), 138.1, 131.2 (d, J = 7.9 Hz), 130.3, 115.8 (d, J = 21.2 Hz), 115.6, 49.4, 41.5, 33.3, 23.0. Anal. calcd (found) for $C_{13}H_{15}FO$: C, 75.70 (75.61); H, 7.33 (7.28).

1-(4-Chlorophenyl)-6-hepten-2-one (Table 4, entry 5). 1-(4-Chlorophenyl)-6-hepten-2-one was obtained in 12% overall yield as a pale yellow oil from 1-brommethyl-4-chlorobenzene employing a procedure simiar to that described above for the synthesis of 1-(4-methylphenyl)-6-hepten-2-one (Table 4, enty 1). TLC: R_f = 0.59. ^{1}H NMR: δ 7.30-7.28 (m, 2 H), 7.13-7.11 (m, 2 H), 5.72 (tdd, J = 6.8, 10.4, 16.8, 1 H), 5.00-4.94 (m, 2 H), 3.65 (s, 2 H), 2.46 (t, J = 7.4 Hz, 2 H), 2.04-2.00 (m, 2 H), 1.70-1.63 (quintet, J = 7.2 Hz, 2 H). ^{13}C{^{1}H} NMR δ 207.9, 138.1, 133.3, 133.0, 131.1, 129.1, 115.6, 49.6, 41.6, 33.3, 23.0. IR (neat, cm^{-1}): 2932, 1714, 1491, 1407, 1089, 1015, 913. Anal. Calcd (found) for $C_{13}H_{15}ClO$: C, 70.11 (70.03); H, 6.79 (6.84).

1-(4-Bromophenyl)-6-hepten-2-one (Table 4, entry 6). 1-(4-Bromophenyl)-6-hepten-2-one was obtained in 33% overall yield as a pale yellow oil from 1-brommethyl-4-bromobenzene employing a procedure simiar to that described above for the synthesis of 1-(4-Methylphenyl)-6-hepten-2-one (Table 4, enty 1). TLC: R_f = 0.56. ^{1}H NMR: δ 7.46-7.42 (m, 2 H), 7.08-7.05 (m, 2 H), 5.73 (tdd, J = 6.8, 10.6, 17.0 Hz, 1 H), 5.00-4.93 (m, 2 H), 3.63 (s, 2 H), 2.46 (t, J = 7.4 Hz, 2 H), 2.04-1.99 (m, 2 H), 1.66 (quintet, J = 7.2 Hz, 2 H). ^{13}C{^{1}H} NMR: δ 207.8, 138.1, 133.5, 132.1, 131.4, 121.3, 115.6, 49.6, 41.6, 33.3, 23.0. Anal. calcd. (found) for $C_{13}H_{15}BrO$: C, 58.44 (58.59); H, 5.66 (5.65).

1-(4-Iodophenyl)-6-hepten-2-one (Table 4, entry 7). 1-(4-Iodophenyl)-6-hepten-2-one was obtained in 43% overall yield from (4-iodophenyl)acetaldehyde employing a procedure simiar to that described above for the synthesis of 1-(3-trifluoromethylphenyl)-6-hepten-2-one (Table 4, enty 2).

For 1-(4-Iodophenyl)-6-hepten-2-ol: White solid. TLC: R_f = 0.46. ^{1}H NMR: δ 7.75 (br d, J = 8.0 Hz, 2 H), 7.04 (br d, J = 8.0 Hz, 2 H), 5.82 (tdd, J = 6.4, 10.2, 17.2 Hz, 1 H), 5.10-5.04 (m, 2 H), 3.72 (s, 2 H), 2.56 (t, J = 7.4 Hz, 2 H), 2.12 (q, J = 6.8 Hz, 2 H), 1.76 (quintet, J = 7.2 Hz, 2 H). ^{13}C{^{1}H} NMR δ 207.8, 138.2, 138.1, 134.2, 131.8, 115.7, 92.8, 49.8, 41.6, 33.3, 23.0. IR (neat, cm^{-1}): 3073, 2931, 1714, 1633, 1484, 1400, 1059, 1007, 913. Anal. Calcd (found) for $C_{13}H_{15}IO$: C, 49.70 (49.92); H, 4.81 (4.73).

For 1-(4-Iodophenyl)-6-hepten-2-one: White solid. mp 35-37 °C. TLC: R_f = 0.46. ^{1}H NMR: δ 7.75 (br d, *J* = 8.0 Hz, 2 H), 7.04 (br d, *J* = 8.0 Hz, 2 H), 5.82 (tdd, *J* = 6.4, 10.2, 17.2 Hz, 1 H), 5.10-5.04 (m, 2 H), 3.72 (s, 2 H), 2.56 (t, *J* = 7.4 Hz, 2 H), 2.12 (q, *J* = 6.8 Hz, 2 H), 1.76 (quintet, *J* = 7.2 Hz, 2 H). ^{13}C{^{1}H} NMR δ 207.8, 138.2, 138.1, 134.2, 131.8, 115.7, 92.8, 49.8, 41.6, 33.3, 23.0. IR (neat, cm^{-1}): 3073, 2931, 1714, 1633, 1484, 1400, 1059, 1007, 913. Anal. Calcd (found) for $C_{13}H_{15}IO$: C, 49.70 (49.92); H, 4.81 (4.73).

1-(2-Oxo-6-heptenyl)naphthalene (Table 4, entry 8). 1-(2-Oxo-6-heptenyl)naphthalene was obtained in 54% overall yield as a yellow oil from 1-naphthylacetaldehyde employing a procedure simiar to that described above for the synthesis of 1-(3-trifluoromethylphenyl)-6-hepten-2-one (Table 4, enty 2)

For 1-Naphthalen-1-yl-hept-6-en-2-ol: TLC: R_f = 0.47. ^{1}H NMR: δ 8.05-8.03 (m, 1 H), 7.89-7.86 (m, 1 H), 7.77 (d, *J* = 8.0 Hz), 7.55-7.48 (m, 2 H), 7.45-7.37 (m, 2 H), 5.84 (tdd, *J* = 6.8, 10.2, 17 Hz, 1 H), 5.06-4.96 (m, 2 H), 4.03-3.96 (m, 1 H), 3.36 (dd, *J* = 4.0 Hz, 13.6 Hz, 1 H), 3.05 (dd, *J* = 8.8 14.0 Hz, 1 H), 2.15-2.09 (m, 2 H), 1.71-1.50 (m, 5 H). ^{13}C{^{1}H} NMR: δ 138.9, 134.9, 134.2, 132.4, 129.1, 127.8, 127.6, 126.2, 125.9, 125.7, 124.0, 114.0, 72.0, 41.5, 36.9, 34.0, 25.3. IR (neat, cm^{-1}): 3384, 3064, 2931, 1637, 1594, 1507, 1079, 995, 909, 776, 705. Anal. Calcd (found) for $C_{17}H_{20}O$: C, 84.96 (84.81); H, 8.39 (8.30).

For 1-(2-Oxo-6-heptenyl)naphthalene: TLC: R_f = 0.59. ^{1}H NMR: δ 7.91-7.87 (m, 2 H), 7.81 (d, *J* = 8.4 Hz, 1 H), 7.55-7.44 (m, 3 H), 7.39 (d, *J* = 6.8 Hz, 1 H), 5.68 (tdd, *J* = 6.8, 9.6, 17.6 Hz, 1 H), 4.94-4.89 (m, 2 H), 4.12 (s, 2 H), 2.44 (t, *J* = 7.2 Hz, 2 H), 2.00-1.94 (m, 2 H), 1.64 (quintet, *J* = 7.2 Hz, 2 H). ^{13}C{^{1}H} NMR δ 208.9, 138.1, 134.1, 132.5, 131.3, 129.0, 128.4, 128.2, 126.7, 126.1, 125.8, 124.1, 115.3, 48.7, 40.8, 33.1, 22.9. IR (neat, cm^{-1}): 3064, 2933, 1709, 1638, 1596, 1509, 1398, 912, 778. Anal. Calcd (found) for $C_{17}H_{18}O$: C, 85.67 (85.58); H, 7.61 (7.52).

1-Naphthalen-2-yl-hept-6-en-2-one (Table 4, entry 9). 1-Naphthalen-2-yl-hept-6-en-2-one was obtained in 64% overall yield from 2-naphthylacetaldehyde as a yellow solid employing a

procedure simiar to that described above for the synthesis of 1-(3-trifluoromethylphenyl)-6-hepten-2-one (Table 4, enty 2).

For 1-naphthalen-2-yl-hept-6-en-2-ol: TLC: R_f = 0.34. ^{1}H NMR: δ 7.85-7.81 (m, 3 H), 7.68 (s, 1 H), 7.52-7.45 (m, 2 H), 7.37 (m, 1 H), 5.85 (tdd, *J* = 6.8, 10.4, 17.0 Hz, 1 H), 5.08-4.97 (m, 2 H), 3.95-3.89 (m, 1 H), 3.00 (dd, *J* = 4.0, 13.6 Hz, 1 H), 2.82 (dd, *J* = 8.4, 13.4 Hz, 1 H), 2.14-2.09 (m, 2 H), 1.70-1.48 (m, 5 H). ^{13}C{^{1}H} NMR: δ 138.9, 136.3, 133.8, 132.5, 128.4, 128.1, 128.0, 127.9, 127.7, 126.3, 125.7, 114.9, 72.6, 44.5, 36.5, 33.9, 25.3. Anal. calcd. (found) for $C_{17}H_{20}O$: C, 84.96 (84.87); H, 8.39 (8.26).

For 1-Naphthalen-2-yl-hept-6-en-2-one : TLC: R_f = 0.42. ^{1}H NMR: δ 7.85-7.80 (m, 3 H), 7.68 (s, 1 H), 7.51-7.45 (m, 2 H), 7.33 (dd, *J* = 2.0, 8.4, 1 H), 5.73 (tdd, *J* = 6.8, 10.4, 16.8 Hz, 1 H), 4.99-4.93 (m, 2 H), 3.85 (s, 2 H), 2.51 (t, *J* = 7.4 Hz, 2 H), 2.04-1.99 (m, 2 H), 1.68 (quintet, *J* = 7.2 Hz, 2 H). ^{13}C{^{1}H} NMR: δ 208.6, 138.2, 133.9, 132.7, 132.2, 128.7, 128.4, 128.0, 127.9, 127.8, 126.5, 126.1, 115.5, 50.7, 41.5, 33.3, 23.0. IR (neat, cm^{-1}): 3053, 2935, 1712, 1411, 1313, 992, 952, 904, 828, 757. Anal. calcd. (found) for $C_{17}H_{18}O$: C, 85.67 (85.76); H, 7.61 (7.79).

Alkyl 3-Butenyl Ketones

1-Cyclohexyl-5-hexen-2-one (Table 5, entry 6). A solution of cyclohexylacetaldehyde (3.5 g, 28 mmol) in ether (10 mL) was added slowly to a solution of 3-butenyl magnesium bromide (0.5 N in THF, 70 mL, 35 mmol) at 0 °C. The resulting mixture was stirred for 1h, quenched by addition of HCl (1 N, 20 mL), and extracted with ether (2 x 50 mL). The combined organic fractions were dried ($MgSO_4$) and distilled (75-78 °C/60 mTorr) to give 1-cyclohexyl-5-hexen-2-ol (3.2 g, 17.6 mmol, 63%) that was 80% pure by GC and used in the next step without further purification. A solution of DMSO (0.8 mL, 11.6 mmol) in CH_2Cl_2 (5 mL) was added to a solution of oxalyl chloride (1.0 mL, 11.5 mmol) in CH_2Cl_2 (15 mL) at –78 °C, stirred for 5 min. A solution of 1-cyclohexyl-5-hexen-2-ol (2.0 g, 11.0 mmol) in CH_2Cl_2 (5 mL) was added slowly to the above solution and the resulting white suspension was stirred for 2 h, quenched with water (15 mL), and extracted with CH_2Cl_2 (2 x 40 mL).

The combined organic fractions were dried ($MgSO_4$), concentrated, and distilled (45 °C/15-20 mTorr) to give 1-cyclohexyl-5-hexen-2-one (1.5 g, 76%). TLC: R_f = 0.64. ^{1}H NMR: δ 5.78 (tdd, *J* = 6.4. 16.8 Hz, 1 H), 5.01 (qd, *J* = 1.6, 17.2 Hz, 1 H), 4.95 (tdd, *J* = 1.2, 1.6. 10.0 Hz, 1 H), 2.46 (t, *J* = 7.2 Hz, 2 H), 2.27-2.32 (m, 2 H), 2.25 (d, *J* = 6.8 Hz, 2 H), 1.76-1.86 (m, 1 H), 1.60-1.69 (m, 5 H), 1.19-1.31 (m, 2 H), 1.06-1.17 (m, 1 H), 0.85-0.95 (m, 2 H). ^{13}C{^{1}H} NMR: δ 210.3, 137.4, 115.3, 50.8, 42.6, 34.1, 33.4, 27.9, 26.4, 26.3. IR (neat, cm^{-1}): 2922, 2850, 1713, 1448. Anal. calcd. (found) for $C_{12}H_{20}O$: C, 79.94 (79.82); H, 11.18 (11.16).

1-Chloro-7-octen-4-one (Table 5, entry 9). 1-Chloro-7-octen-4-one was synthesized in 82% yield as a pale yellow oil as from reaction of 4-chlorobutyryl chloride and 3-butenyl magnesium bromide employing a procedure similar to that used to synthesize 1-phenoxy-7-octen-4-one. TLC: R_f = 0.45. ^{1}H NMR: δ 5.79 (tdd, *J* = 6.4, 10.4, 13.2 Hz, 1 H), 5.03 (qd, *J* = 1.6, 17.2 Hz, 1 H), 4.96-5.00 (m, 1 H), 3.57 (t, *J* = 6.4 Hz, 2 H), 2.61 (t, *J* = 7.2 Hz, 2 H), 2.53 (t, *J* = 7.2 Hz, 2 H), 2.30-2.36 (m, 2 H), 2.01-2.07 (m, 2 H). ^{13}C{^{1}H} NMR: δ 209.1, 137.1, 115.6, 44.7, 42.1, 39.5, 27.9, 26.4. IR (neat, cm^{-1}): 3078, 2961, 2922, 1716, 1640, 1411. Anal. calcd. (found) for $C_8H_{13}ClO$: C, 59.81 (59.74); H, 8.16 (8.11).

1-Phenoxy-7-octen-4-one (Table 5, entry 10). A solution of 3-butenyl magnesium bromide (0.5 N in THF, 9 mL) was added over 15 min to a suspension of CuI (0.9 g, 4.7 mmol), and 4-phenoxybutyryl chloride (1.0 g, 5.0 mmol) in THF (15 mL) at −78 °C. The resulting mixture was warmed slowly to room temperature, quenched with HCl (1 N, 20 mL), and extracted with ether (3 ∞ 30 mL). The combined organic extracts were dried ($MgSO_4$), concentrated, and chromatographed (hexanes−ether = 20:1 ∅ 5:1) to give 1-phenoxy-7-octen-4-one (0.89 g, 91%) as a colorless oil. TLC: R_f = 0.40. ^{1}H NMR (300 MHz): δ 7.23-7.27 (m, 2 H), 6.85-6.84 (m, 3 H), 5.79 (tdd, *J* = 6.6, 10.2, 17.1 Hz, 1 H), 4.94-5.05 (m, 2 H), 3.96 (t, *J* = 6.0 Hz, 2 H), 2.62 (t, *J* = 6.9 Hz, 2 H), 2.53 (t, *J* = 7.5 Hz, 2 H), 2.32 (1, *J* = 6.9 Hz, 2 H), 2.05 (quintet, *J* = 6.9 Hz, 2 H). ^{13}C{^{1}H} NMR (75 MHz): δ 208.9, 158.1, 136.4, 128.7, 120.0, 114.6, 113.7, 66.0, 41.2, 38.4, 27.1, 22.7. IR (neat, cm^{-1}): 3073, 3039, 2935, 1713, 1496. Anal. calcd. (found) for $C_{14}H_{18}O_2$: C, 77.03 (76.95); H, 8.31 (8.36).

1-Methoxy-7-octen-4-one (Table 5, entry 11). 1-Methoxy-7-octen-4-one was synthesized in 28% overall yield from 4-methoxy-butyraldehyde as a pale yellow oil employing a procedure similar to that used to synthesize 1-cyclohexyl-5-hexen-2-one.

For 1-methoxy-7-octen-4-ol: TLC: R_f = 0.23. ^{1}H NMR: δ 5.81 (tdd, *J* = 6.8, 10.4, 17.2 Hz, 1 H), 5.01 (qd, *J* = 1.6, 17.2 Hz, 1 H), 4.93 (tdd, *J* = 1.2, 2.0, 10.0 Hz, 1 H), 3.55-3.61 (m, 1 H), 3.75-3.41 (m, 2 H), 3.32 (s, 3 H), 2.66 (s, 1 H), 2.05-2.23 (m, 2 H), 1.38-1.71 (m, 6 H). ^{13}C{^{1}H} NMR: δ 138.9, 114.8, 73.2, 71.1, 58.7, 36.8, 35.0, 30.3, 26.4. IR (neat, cm^{-1}): 3411, 2931, 2250, 907. Anal. calcd (found) for $C_9H_{18}O_2$: C, 68.31 (68.32); H, 11.47 (11.29).

For 1-methoxy-7-octen-4-one: TLC: R_f = 0.25. ^{1}H NMR: δ 5.78 (tdd, *J* = 6.4, 10.0, 17.2 Hz, 1 H), 5.00 (qd, *J* = 1.6, 17.2 Hz, 1 H), 4.95 (tdd, *J* = 1.2, 2.0, 10.0 Hz, 1 H), 3.35 (t, *J* = 6.4 Hz, 2 H), 3.28 (s, 3 H), 2.46-2.51 (m, 4 H), 2.28-2.33 (m, 2 H), 1.82 (tt, *J* = 6.0, 7.2 Hz, 2 H). ^{13}C{^{1}H} NMR: δ 210.3, 137.3, 115.3, 71.9, 58.7, 42.0, 39.5, 28.0, 23.9. IR (neat, cm^{-1}): 3078, 2977, 2927, 2828, 1713, 1119. Anal. calcd. (found) for $C_9H_{16}O_2$: C, 69.19 (69.31); H, 10.32(10.18).

3-Methyl-1-dodecen-5-one (38). Compound **38** was synthesized in 93% yield as a colorless oil from reaction of 3-methyl-4-pentenoic chloride and *n*-heptyl magnesium bromide employing a procedure similar to that used to synthesize 1-phenoxy-7-octene-4-one. TLC: R_f = 0.72. ^{1}H NMR (300 MHz): δ 5.72 (ddd, *J* = 6.6, 10.2, 17.1 Hz, 1 H), 4.88-4.98 (m, 2 H), 2.63-2.72 (m, 1 H), 2.26-2.45 (m, 4 H), 1.47-1.54 (m, 2 H), 1.23 (bs, 8 H), 0.97 (d, *J* = 6.6 Hz, 3 H), 0.84 (t, *J* = 6.6 Hz, 3 H). ^{13}H{^{1}H} NMR (75 MHz): δ 209.6, 142.3, 112.2, 48.7, 42.8, 32.6, 31.0, 28.5, 28.4, 23.0, 21.9, 19.1, 13.4. IR (neat, cm^{-1}): 2956, 2927, 2870, 2855, 1714. HRMS calcd (found) for $C_{13}H_{24}O$: 196.1827 (196.1829).

Cyclohexanones

2-Carbomethoxycyclohexanone (5). TLC: R_f = 0.67. ^{1}H NMR (enol tautomer): δ 12.19 (s, 1 H), 3.75 (s, 3 H), 2.27 (t, *J* = 6.4 Hz, 2 H), 2.21 (t, *J* = 6.0 Hz, 2 H), 1.69-1.66 (m, 2 H), 1.62-1.58 (m, 2 H). ^{13}C{^{1}H} NMR (enol tautomer): δ 173.4, 172.5, 98.0, 51.7, 29.4, 22.8, 22.7, 22.2.

2-Carboethoxycyclohexanone (Table 2, entry 2).[22] TLC: R_f = 0.59. ^{1}H NMR (enol tautomer): δ 12.24 (s, 1 H), 4.20 (q, J = 7.2 Hz, 2 H), 2.27-2.20 (m, 4 H), 1.70-1.64 (m, 2 H), 1.62-1.58 (m, 2 H), 1.29 (t, J = 7.2 Hz, 3 H). ^{13}C{^{1}H} NMR (enol tautomer): δ 173.1, 172.3, 98.1, 60.5, 29.4, 22.8, 22.7, 22.3, 14.6.

2-Carbobenzyloxycyclohexanone (Table 2, entry 3).[23] TLC: R_f = 0.66. ^{1}H NMR (enol tautomer): δ 12.16 (s, 1 H), 7.38-7.31 (m, 5 H), 5.21 (s, 2 H), 2.30-2.27 (m, 4 H), 1.70-1.66 (m, 2 H), 1.64-1.58 (m, 2 H). ^{13}C{^{1}H} NMR (enol tautomer): δ 172.9, 172.8, 136.5, 128.9, 128.4, 128.2, 98.0, 66.0, 29.5, 22.7, 22.6, 22.2.

2-Carboisobutoxycyclohexanone (Table 2, entry 4). TLC: R_f = 0.80. ^{1}H NMR (enol tautomer): δ 12.21 (s, 1 H), 3.91 (d, J = 6.4 Hz, 2 H), 2.27-2.21 (m, 4 H), 1.96 (m, 1 H), 1.71-1.64 (m, 2 H), 1.63-1.57 (m, 2 H), 0.94 (d, J = 6.8 Hz, 6 H). ^{13}C{^{1}H} NMR (enol tautomer): δ 173.1, 172.3, 98.2, 70.5, 29.4, 28.1, 22.8, 22.7, 22.3, 19.4. IR (neat, cm^{-1}): 2933, 2872, 1744, 1715, 1655, 1613, 1469, 1448, 1420, 1402, 1385, 1359, 1295, 1258, 1218, 1174, 1081, 1058, 984, 830. Anal. Calcd. (found) for $C_{11}H_{18}O_3$: C, 66.64 (66.58); H, 9.15 (9.14).

2-Carbomethoxy-3-phenylcyclohexanone (Table 2, entry 6). TLC: R_f = 0.21. ^{1}H NMR (enol tautomer): δ 12.54 (s, 1 H), 7.28-7.24 (m, 3 H), 7.23-7.10 (m, 2 H), 3.89 (dd, J = 3.4, 5.4 Hz, 1 H), 3.51 (s, 3 H), 2.36-2.33 (m, 2 H), 1.90-1.83 (m, 1 H), 1.73-1.69 (m, 1 H), 1.56-1.51 (m, 2 H). ^{13}C{^{1}H} NMR (enol tautomer): δ 174.3, 173.3, 146.3, 128.3, 127.9, 126.1, 100.0, 51.8, 38.6, 31.8, 29.5, 17.1. IR (neat, cm^{-1}): 3059, 3025, 2947, 2867, 1951, 1876, 1746, 1713, 1656, 1613, 1492, 1440, 1380, 1359, 1314, 1267, 1221, 1084. Anal. Calcd. (found) for $C_{14}H_{16}O_3$: C, 72.39 (72.36); H, 6.94 (6.84).

Methyl 2-(4-methoxycarbonyl-3-oxo-butyl)-6-oxo-cyclohexanecarboxylate (Table 2, entry 8). TLC (hexanes–EtOAc = 1:1): R_f = 0.49. ^{1}H NMR (keto tautomer): δ 3.75 (s, 3 H), 3.73 (s, 3 H), 3.46 (s, 2 H), 3.12 (d, J = 10.8 Hz, 1 H), 2.64-2.55 (m, 2 H), 2.53-2.49 (m, 1 H), 2.28-2.24 (m, 2 H), 2.08-2.02 (m, 1 H), 1.86-1.77 (m, 1 H), 1.70-1.64 (m, 2 H), 1.61-1.48 (m, 2 H). ^{13}C{^{1}H} NMR (keto tautomer): δ 202.9, 202.2, 173.5, 170.4, 63.7, 52.7, 51.8, 49.2, 41.8, 40.5, 31.3, 29.3, 25.7, 17.3. IR (neat, cm^{-1}): 2999, 2951, 2868, 1754, 1746, 1730, 1713, 1643, 1620,

1441, 1414, 1358, 1316, 1221, 1151, 1068, 1021, 944. Anal. Calcd. (found) for $C_{14}H_{20}O_6$: C, 59.14 (59.18); H, 7.09 (7.04).

Cyclization of methyl 3-oxo-7-octenoate (16). A suspension of methyl 3-oxo-7-octenoate (**16**) (100 mg, 0.59 mmol), **2** (10 mol%), Me_3SiCl (2.0 equiv), and $CuCl_2$ (1 equiv) in dioxane was stirred at 55 °C for 8 h, cooled to room temperature, and concentrated under vacuum. The resulting oily residue was chromatographed (hexanes–Et_2O = 10:1 ∅ 5:1) to give 2-carbomethoxy-3-methylcyclohexanone (**17a**) (72 mg, 72%) as a pale yellow oil and 2-carbomethoxy-3-methyl-2-cyclohexenone (**17b**) (15 mg, 15%) as a colorless oil.

2-Carbomethoxy-3-methylcyclohexanone (17a).[24] TLC: R_f = 0.35. ^{1}H NMR (keto tautomer): δ 3.76 (s, 3 H), 3.05 (d, *J* = 11.2 Hz, 1 H), 2.49-2.44 (m, 1 H), 2.32-2.24 (m, 2 H), 2.08-2.01 (m, 1 H), 1.95-1.89 (m, 1 H), 1.79-1.57 (m, 2 H), 1.02 (d, *J* = 6.4 Hz, 3 H). ^{13}C{^{1}H} NMR (keto tautomer): δ 206.3, 170.5, 65.4, 52.3, 41.2, 37.0, 32.7, 25.3, 21.2.

2-Carbomethoxy-3-methyl-2-cyclohexenone (17b).[25] ^{1}H NMR: δ 3.81 (s, 3 H), 2.43-2.37 (m, 4 H), 2.02 (m, 2 H), 1.98 (s, 3 H). ^{13}C{^{1}H} NMR: δ 195.2, 167.5, 160.8, 133.2, 52.4, 37.0, 31.8, 22.4, 21.8.

***cis*-3,5-Dimethylcyclohexanone.**[26] ^{1}H NMR: δ 2.32 (bd, *J* = 12.0 Hz, 2 H), 1.92 (t, *J* = 12.8 Hz, 2 H), 1.76-1.86 (m, 3 H), 0.99-1.06 (m, 1 H), 1.02 (d, *J* = 6.4 Hz, 6 H). ^{13}C{^{1}H} NMR: δ 211.9, 49.5, 42.8, 33.4, 22.6.

(*E*)-Methyl (5,5-dimethyl-dihydrofuran-2-ylidene)acetate [(*E*)-13].[27] TLC (hexanes–EtOAc = 5:1): R_f = 0.44. ^{1}H NMR: δ 5.22(t, *J* = 1.8 Hz, 1 H), 3.65 (s, 3 H), 3.19 (dt, *J* = 1.8, 8.0 Hz, 2 H), 1.90 (d, *J* = 8.0 Hz, 2 H), 1.36 (s, 6 H). ^{13}C{^{1}H} NMR: δ 176.7, 169.6, 89.0, 87.9, 50.9, 36.2, 31.3, 27.3.

2-Phenylcyclohexanone (19).[28] ^{1}H NMR: δ 7.33-7.29 (m, 2 H), 7.25-7.21 (m, 1 H), 7.13-7.11 (m, 2 H), 3.59 (dd, *J* = 5.4, 12.2 Hz, 1 H), 2.54-2.43 (m, 2 H), 2.28-2.22 (m, 1 H), 2.16-2.10 (m, 1 H), 2.04-1.95 (m, 2 H), 1.83-1.77 (m, 2 H). ^{13}C{^{1}H} NMR: δ 210.6, 139.1, 128.8, 128.7, 127.2, 57.7, 42.5, 35.4, 28.1, 25.6.

2-(*p*-Tolyl)cyclohexanone (Table 3, entry 1).[29] ^{1}H NMR: δ 7.14-7.12 (m, 2 H), 7.02-7.00 (m, 2 H), 3.55 (dd, *J* = 5.2, 12.0 Hz, 1 H), 2.53-2.39 (m, 3 H), 2.31 (s, 3 H), 2.26-2.20 (m, 1 H), 2.15-2.10 (m, 1 H), 2.02-1.95 (m, 1 H), 1.83-1.77 (m, 2 H). ^{13}C{^{1}H} NMR: δ 210.9, 136.8, 136.0, 129.4, 128.7, 57.3, 42.5, 35.4, 28.1, 25.7, 21.4.

2-Biphenyl-4-yl-cyclohexanone (Table 3, entry 2).[30] White solid. ^{1}H NMR: δ 7.6-7.56 (m, 4 H), 7.42 (br t, *J* = 7.6 Hz, 2 H), 7.35-7.31 (m, 1 H), 7.22 (d, *J* = 8.0 Hz, 2 H), 3.65 (dd, J = 5.4, 12.2 Hz, 1 H), 2.63 - 2.45 (m, 2 H), 2.32 - 2.28 (m, 1 H), 2.19 - 1.99 (m, 3 H), 1.90 - 1.77 (m, 2 H). ^{13}C{^{1}H} NMR δ 210.6, 141.3, 140.1, 138.1, 129.2, 129.0, 127.4, 57.4, 42.5, 35.5, 28.1, 25.6.

2-(4-Fluorophenyl)cyclohexanone (Table 3, entry 3).[29] Yellow solid. TLC: R_f = 0.40. ^{1}H NMR: δ 7.11-7.08 (m, 2 H), 7.05-6.99 (m, 2 H), 3.60 (dd, *J* = 5.2, 12.0 Hz, 1 H), 2.56-2.41 (m, 2 H), 2.29-2.23 (m, 1 H), 2.20-2.14 (m, 1 H), 2.03-1.92 (m, 2 H), 1.92-1.78 (m, 2 H). ^{13}C{^{1}H} NMR: δ 210.4, 162.1 (d, *J* = 244), 134.8, 130.3 (d, *J* = 7.9 Hz), 115.5 (d, *J* = 20.0 Hz), 57.0, 42.5, 35.7, 28.1, 25.7.

2-(4-Chlorophenyl)cyclohexanone (Table 3, entry 4).[29] ^{1}H NMR: δ 7.30 (d, *J* = 8.4 Hz, 2 H), 7.07 (d, *J* = 8.4 Hz, 2 H), 3.59 (dd, *J* = 5.4, 12.2 Hz, 1 H), 2.56-2.42 (m, 2 H), 2.28-2.23 (m, 1 H), 2.19-2.15 (m, 1 H), 2.02-1.95 (m, 2 H), 1.85-1.79 (m, 2 H). ^{13}C{^{1}H} NMR: δ 210.1, 137.5, 133.0, 130.3, 128.5, 57.1, 42.5, 35.6, 28.1, 25.7.

2-(4-Bromophenyl)cyclohexanone (Table 3, entry 5).[31] ^{1}H NMR: δ 7.47-7.44 (m, 2 H), 7.03-7.00 (m, 2 H), 3.57 (dd, *J* = 5.2, 12.4 Hz, 1 H), 2.56-2.54 (m, 2 H), 2.29-2.23 (m, 1 H), 2.19-2.14 (m, 1 H), 2.02-1.95 (m, 2 H), 1.87-1.78 (m, 2 H). ^{13}C{^{1}H} NMR: δ 210.0, 138.1, 131.8, 130.6, 121.2, 57.2, 42.5, 35.5, 28.1, 25.7.

2-(4-Iodophenyl)cyclohexanone (Table 3, entry 6).[32] ^{1}H NMR: δ 7.67-7.64 (m, 2 H), 6.91-6.87 (m, 2 H), 3.56 (dd, *J* = 5.0, 12.4 Hz, 1 H), 2.56-2.41 (m, 2 H), 2.28-2.22 (m, 1 H), 2.20-2.13 (m, 1 H), 2.03-1.92 (m, 2 H), 1.84-1.78 (m, 2 H). ^{13}C{^{1}H} NMR: δ 210.0, 138.7, 137.7, 131.1, 92.8, 57.3, 42.5, 35.5, 28.1, 25.7.

2-(2-Trifluoromethylphenyl)cyclohexanone (Table 3, entry 7). Yellow oil. TLC: R_f = 0.37. ^{1}H NMR: δ 7.74 (br d, *J* = 8.0 Hz, 1 H), 7.64 (br t, *J* = 7.4 Hz, 1 H), 7.47-7.43 (m, 2 H), 4.16 (dd, *J* = 4.8, 12.0 Hz, 1 H), 2.67-2.57 (m, 2 H), 2.41-2.29 (m, 2 H), 2.15-2.05 (m, 2 H), 2.03-1.89 (m, 2 H). ^{13}C{^{1}H} NMR: δ 209.2, 138.0, 131.9, 130.8, 128.9 (q, *J* = 29.2 Hz), 127.1, 126.0 (d, *J* = 5.3 Hz), 124.8 (q, *J* = 272 Hz), 53.6, 42.6, 36.2, 28.2, 26.1. IR (neat, cm^{-1}): 2940, 2864, 1717, 1451, 1313, 1160, 1124, 1035, 767. Anal. Calcd (found) for $C_{13}H_{13}F_3O$: C, 64.46 (64.45); H, 5.41 (5.32).

2-(3-Trifluoromethylphenyl)cyclohexanone (Table 3, entry 8). Yellow oil. TLC: R_f = 0.33. ^{1}H NMR: δ 7.52 (br d, *J* = 7.6 Hz, 1 H), 7.48 (br t, *J* = 7.6 Hz, 1 H), 7.40 (s, 1 H), 7.33 (br d, *J* = 8.0 Hz, 1 H), 3.68 (dd, *J* = 5.6, 12.4 Hz, 1 H), 2.57-2.44 (m, 2 H), 2.32-2.27 (m, 1 H), 2.22-2.16 (m, 1 H), 2.06-1.96 (m, 2 H), 1.89-1.78 (m, 2 H). ^{13}C{^{1}H} NMR: δ 209.7, 140.0, 132.5, 130.9, (q, *J* = 31.7 Hz), 129.0, 125.7 (d, *J* = 3.4 Hz), 124.5 (q, *J* = 207.7 Hz), 124.8 (d, *J* = 3.4 Hz), 57.5, 42.5, 35.6, 28.1, 25.7. IR (neat, cm^{-1}): 2940, 2864, 1711, 1449, 1330, 1163, 1124, 1074, 799, 702. Anal. Calcd (found) for $C_{13}H_{13}F_3O$: C, 64.46 (64.29); H, 5.41 (5.25).

2-(4-Trifluoromethylphenyl)cyclohexanone (Table 3, entry 9).[33] ^{1}H NMR: δ 7.56 (d, *J* = 8.0 Hz, 2 H), 7.23-7.21 (m, 2 H), 3.64 (dd, *J* = 5.4, 12.2 Hz, 1 H), 2.55-2.41 (m, 2 H), 2.28-2.22 (m, 1 H), 2.20-2.13 (m, 1 H), 2.03-1.96 (m, 2 H), 1.84-1.78 (m, 2 H). ^{13}C{^{1}H} NMR: δ 209.7, 143.1, 143.0, 129.3, 125.6 (q, *J* = 3.8 Hz), 57.6, 42.6, 35.6, 28.1, 25.7. ^{19}F NMR: δ –62.93.

2-Naphthalen-1-yl-cyclohexanone (Table 3, entry 10).[28] ^{1}H NMR: δ 7.89-7.86 (m, 1 H), 7.80 (d, *J* = 8.0 Hz, 1 H), 7.75-7.73 (m, 1 H), 7.51-7.45 (m, 3 H), 7.38 (d, *J* = 7.2 Hz, 1 H), 4.37 (dd, *J* = 5.2, 12.4 Hz, 1 H), 2.71-2.62 (m, 2 H), 2.46-2.39 (m, 1 H), 2.34-2.24 (m, 2 H), 2.17-2.11 (m, 1 H), 2.01-1.86 (m, 2 H). ^{13}C{^{1}H} NMR: δ 210.2, 135.5, 134.1, 132.0, 129.3, 127.9, 126.1, 125.60, 125.57, 125.54, 123.5, 53.6, 42.9, 34.5, 28.1, 26.2.

2-Naphthalen-2-yl-cyclohexanone (Table 3, entry 11).[29] ^{1}H NMR: δ 7.89-7.86 (m, 1 H), 7.80 (d, *J* = 8.0 Hz, 1 H), 7.75-7.73 (m, 1 H), 7.51-7.45 (m, 3 H), 7.38 (d, *J* = 7.2 Hz, 1 H), 4.37 (dd, *J* = 5.2, 12.4 Hz, 1 H), 2.71-2.62 (m, 2 H), 2.46-2.39 (m, 1 H), 2.34-2.24 (m, 2 H), 2.17-

2.11 (m, 1 H), 2.01-1.86 (m, 2 H). $^{13}C\{^1H\}$ NMR: δ 210.2, 135.5, 134.1, 132.0, 129.3, 127.9, 126.1, 125.60, 125.57, 125.54, 123.5, 53.6, 42.9, 34.5, 28.1, 26.2.

***trans*-3-Ethyl-2-phenylcyclohexanone (*trans*-22).** TLC: R_f = 0.47. ^1H NMR: δ 7.36-7.32 (m, 2 H), 7.28-7.24 (m, 1 H), 7.08-7.06 (m, 2 H), 3.31 (d, *J* = 11.6 Hz, 1 H), 2.57-2.55 (m, 1 H), 2.53-2.51 (m, 1 H), 2.44 (dt, *J* = 6.0, 13.6 Hz, 1 H), 2.22-2.09 (m, 2 H), 2.03-1.93 (m, 1 H), 1.86-1.74 (m, 1 H), 1.27 (dqd, *J* = 3.2, 7.6, 13.6 Hz, 1 H), 1.08 (m, 1 H), 0.81 (t, *J* = 7.6 Hz, 3 H). $^{13}C\{^1H\}$ NMR: δ 210.6, 137.8, 129.7, 128.5, 127.1, 63.6, 46.7, 42.3, 30.4, 27.4, 26.2, 10.9. IR (neat, cm^{-1}): 3087, 3061, 3028, 2961, 2935, 2863, 1947, 1870, 1812, 1713, 1603, 1497, 1454, 1445, 1381, 1358, 1344, 1310, 1280, 1176, 1123. Anal. calcd (found) for $C_{14}H_{18}O$: C, 83.12 (83.05); H, 8.97 (8.92).

***trans*-2,3-Diphenylcyclohexanone (*trans*-23)**.[34] ^1H NMR: δ 7.17-7.12 (m, 4 H), 7.10-7.03 (m, 4 H), 6.93-6.91 (m, 2 H), 3.81 (d, *J* = 12.4 Hz, 1 H), 3.23 (dt, *J* = 4.0, 11.6 Hz, 1 H), 2.68-2.58 (m, 2 H), 2.29-2.21 (m, 1 H), 2.19-2.07 (m, 2 H), 2.02-1.90 (m, 1 H). $^{13}C\{^1H\}$ NMR: δ 209.7, 143.4, 137.0, 129.8, 128.6, 128.2, 127.6, 126.9 126.7, 63.9, 52.7, 42.4, 34.9, 26.5. Slow evaporation of an ether solution gave crystals of *trans*-**23** suitable for X-ray analysis (see below).

2,2-Diphenylcyclohexanone (25).[35] ^1H NMR: δ 7.32-7.27 (m, 4 H), 7.25-7.21 (m, 2 H), 7.05-7.02 (m, 4 H), 2.58 (t, *J* = 5.8 Hz, 2 H), 2.49 (t, *J* = 6.8 Hz, 2 H), 1.96-1.90 (m, 2 H), 1.85-1.79 (m, 2 H). $^{13}C\{^1H\}$ NMR: δ 211.3, 142.3, 128.5, 128.3, 126.8, 63.9, 40.7, 39.2, 27.8, 22.1.

Cyclization of 4-methyl-1-phenyl-5-hexen-2-one (26). A suspension of **26** (93 mg, 0.50 mmol), Me_3SiCl (0.19 mL, 1.5 mmol), **2** (13 mg, 0.050 mmol), and $CuCl_2$ (67 mg, 0.50 mmol) in dioxane (10 mL) was stirred at 70 °C for 3 h and cooled to room temperature. The resulting suspension was filtered through a plug of silica gel and eluted with ether. The resulting solution was concentrated and chromatographed (hexanes–ether = 20:1 ∅ 10:1) to give 5-methyl-2-phenyl cyclohexanone (**27**) (*cis*:*trans* = 1:4, 54 mg, 58%) as a colorless oil and 3-methyl-6-phenyl-2-cyclohexenone (**28**) (11 mg, 12 %) as a pale yellow oil.

For 27: TLC: R_f = 0.46. ^{1}H NMR (trans isomer): δ 7.36-7.12 (m, 5 H), 3.54 (dd, *J* = 5.6, 13.2 Hz, 1 H), 2.51 (m, 1 H), 2.29-1.97 (m, 5 H), 1.61-1.53 (m, 1 H), 1.09 (d, *J* = 6.0 Hz, 3 H). ^{13}C{^{1}H} NMR (trans isomer): δ 210.0, 139.0, 129.0, 128.6, 127.2, 57.1, 50.9, 35.8, 34.7, 34.6, 22.8. IR (neat, cm^{-1}): 1711 ($\nu_{C=O}$). Anal. calcd (found) for $C_{13}H_{16}O$: C, 82.94 (82.84); H, 8.57 (8.46).

For 28: TLC: R_f = 0.24. ^{1}H NMR: δ 7.35-7.31 (m, 2 H), 7.27-7.23 (m, 1 H), 7.17-7.15 (m, 2 H), 6.04-6.03 (m, 1 H), 3.53 (dd, *J* = 6.8, 9.0 Hz, 1 H), 2.49-2.22 (m, 4 H), 2.00 (s, 3 H). ^{13}C{^{1}H} NMR δ 199.6, 162.5, 140.0, 128.8, 128.6, 127.4, 127.2, 52.6, 30.9, 30.8, 24.7. IR (neat, cm^{-1}): 1665 ($\nu_{C=O}$). HRMS calcd (found) for $C_{13}H_{14}O$ (M^+): 186.1045 (186.1038).

Isomerization of *cis*-27 under reaction conditions. A 1.2:1 mixture of *cis*-**27**:*trans*-**27** was synthesized employing a procedure similar to that used to synthesize *cis*-**23**. A suspension of *cis*-**27** (*cis*:*trans* = 1.2:1, 55 mg, 0.29 mmol), Me_3SiCl (0.19 mL, 1.5 mmol), **2** (13 mg, 0.050 mmol), and $CuCl_2$ (67 mg, 0.50 mmol) in dioxane (10 mL) was stirred at 70 °C and monitored periodically by GC analysis. After 1.5 h, no further change in the cis:trans ratio was observed, and the reaction mixture was cooled to room temperature, filtered through a plug of silica gel and eluted with ether. The resulting solution was concentrated and chromatographed (hexanes–ether = 10:1) to give **27** (53 mg, 96%) as a colorless oil, which consisted of a 3.9:1 mixture of trans:cis isomers by ^{1}H NMR analysis.

***trans*-3-Methyl-2-phenylcyclohexanone (30).**[36] ^{1}H NMR: δ 7.32-7.28 (m, 2 H), 7.24-7.21 (m, 1 H), 7.05-7.03 (m, 2 H), 3.16 (d, *J* = 11.6 Hz, 1 H), 2.53-2.48 (m, 1 H), 2.41 (dt, *J* = 5.6, 13.6 Hz, 1 H), 2.15-2.05 (m, 2 H), 2.03-1.96 (m, 1 H), 1.80 (tq, *J* = 4.0, 13.2 Hz, 1 H), 1.61-1.51 (m, 1 H), 0.79 (d, *J* = 6.4 Hz, 3 H). ^{13}C{^{1}H} NMR δ 210.3, 137.8, 129.7, 128.6, 127.1, 65.5, 42.1, 41.0, 34.7, 26.3, 21.6.

***trans*-3-Methyl-2-(4-methylphenyl)cyclohexanone (Table 4, entry 1).** White solid. mp 56-58 °C. TLC: R_f = 0.44. ^{1}H NMR: δ 7.15 (br d, *J* = 7.6 Hz, 2 H), 6.96 (br d, *J* = 8.0 Hz, 2 H), 3.16 (d, *J* = 12.0 Hz, 1 H), 2.56-2.50 (m, 1 H), 2.48-2.38 (m, 1 H), 2.34 (s, 3 H), 2.18-2.00 (m, 3 H), 1.88-1.76 (m, 1 H), 1.63-1.53 (m, 1 H), 0.83 (d, *J* = 6.4 Hz, 3 H). ^{13}C{^{1}H} NMR δ 210.5, 136.6, 134.7, 129.4, 129.3, 65.1, 42.1, 40.9, 34.7, 26.3, 21.6, 21.5. IR (neat, cm^{-1}): 2951, 2924,

2866, 1711, 1515, 1456, 1182, 1121, 1047, 875, 797. Anal. Calcd (found) for $C_{14}H_{18}O$: H, 8.97 (8.86); C, 83.12 (82.99).

***trans*-3-Methyl-2-(3-trifluoromethylphenyl)cyclohexanone (Table 4, entry 2).** Colorless oil. TLC: R_f = 0.39. ^{1}H NMR: δ 7.49 (d, *J* = 7.6 Hz, 1 H), 7.42 (t, *J* = 7.6 Hz, 1 H), 7.29 (s, 1 H), 7.23 (d, *J* = 7.6 Hz, 1 H), 3.25 (d, *J* = 11.6 Hz, 1 H), 2.53-2.38 (m, 2 H), 2.17-1.99 (m, 3 H), 1.87-1.75 (m, 1 H), 1.63-1.52 (m, 1 H), 0.78 (d, *J* = 6.4 Hz, 3 H). ^{13}C{^{1}H} NMR: δ 209.5, 138.8, 133.1, 130.8 (q, *J* = 32 Hz), 129.0, 126.5 (d, *J* = 3.4 Hz), 124.6 (q, *J* = 271 Hz), 124.2 (d, *J* = 3.4 Hz), 65.3, 42.1, 41.1, 34.6, 26.3, 21.5. IR (neat, cm^{-1}): 2958, 2930, 2871, 1712, 1330, 1162, 1123, 1074, 795, 703, 667. Anal. Calcd (found) for $C_{14}H_{15}F_3O$: H, 5.90 (5.74); C, 65.62 (65.42).

***trans*-3-Methyl-2-(4-trifluoromethylphenyl)cyclohexanone (Table 4, entry 3).** Pale yellow oil. TLC: R_f = 0.36. ^{1}H NMR: δ 7.59 (br d, *J* = 8.0 Hz, 2 H), 7.19 (br d, *J* = 8.0 Hz, 2 H), 3.28 (d, *J* = 12.0 Hz, 1 H), 2.57-2.41 (m, 2 H), 2.20-2.02 (m, 3 H), 1.90-1.77 (m, 1 H), 1.66-1.56 (m, 1 H), 0.81 (d, *J* = 6.8 Hz, 3 H). ^{13}C{^{1}H} NMR: δ 209.5, 142.0, 130.1, 129.4 (q, *J* = 32.2 Hz), 125.5 (br d, *J* = 3.4 Hz), 124.6 (q, *J* = 270.1 Hz), 65.3, 42.0, 41.1, 34.6, 26.3, 21.4. IR (neat, cm^{-1}): 2963, 2930, 2872, 1707, 1421, 1328, 1158, 1112, 1069, 813. Anal. Calcd (found) for $C_{14}H_{15}F_3O$: C, 65.62 (65.54); H, 5.90 (5.84).

***trans*-2-(4-Fluorophenyl)-3-methylcyclohexanone (Table 4, entry 4).** White solid. TLC: R_f = 0.43. ^{1}H NMR: δ 7.03 (s, 2 H), 7.02 (s, 2 H), 3.20 (d, *J* = 11.6 Hz, 1 H), 2.55-2.40 (m, 2 H), 2.18-2.00 (m, 3 H), 1.87-1.75 (m, 1 H), 1.64-1.53 (m, 1 H), 0.81 (d, *J* = 6.4 Hz, 3 H). ^{13}C{^{1}H} NMR: δ 210.1, 162.1 (d, *J* = 243.2 Hz), 133.4, 131.0 (d, *J* = 7.9 Hz), 115.4 (d, *J* = 20.9 Hz), 64.7, 42.1, 41.3, 34.6, 26.3, 21.5. IR (neat, cm^{-1}): 2922, 2863, 1705, 1509, 1220, 1160, 1047, 807. Anal. calcd. (found) for $C_{13}H_{15}FO$: C, 75.70 (75.70); H, 7.33 (7.16).

***trans*-2-(4-Chlorophenyl)-3-methylcyclohexanone (Table 4, entry 5).** White solid. mp 69-71 °**C**. TLC: R_f = 0.38. ^{1}H NMR: δ 7.30 (br d, *J* = 8.4 Hz, 2 H), 7.00 (br d, *J* = 8.4 Hz, 2 H), 3.17 (d, *J* = 11.6 Hz, 1 H), 2.54-2.39 (m, 2 H), 2.18-2.00 (m, 3 H), 1.87-1.75 (m, 1 H), 1.63-1.53 (m, 1 H), 0.81 (d, *J* = 6.0 Hz, 3 H). ^{13}C{^{1}H} NMR: δ 209.8, 136.3, 132.9, 131.0, 128.8, 64.9,

42.1, 41.1, 34.6, 26.3, 21.5. Anal. Calcd (found) for $C_{13}H_{15}ClO$:: C, 70.11 (70.19); H, 6.79 (6.71).

***trans*-2-(4-Bromophenyl)-3-methylcyclohexanone (Table 4, entry 6).** White solid. mp 91-92 °C. TLC: R_f = 0.42. ^{1}H NMR: δ 7.47-7.44 (m, 2 H), 6.96-6.93 (m,2 H), 3.16 (d, *J* = 11.6 Hz, 1 H), 2.55-2.39 (m, 2 H), 2.18-2.00 (m, 3 H), 1.87-1.75 (m, 1 H), 1.63-1.53 (m, 1 H), 0.81 (d, *J* = 6.4 Hz, 3 H). ^{13}C{^{1}H} NMR: δ 209.8, 136.8, 131.7, 131.4, 121.1, 64.9, 42.1, 41.1, 34.6, 26.3, 21.5. IR (neat, cm^{-1}): 2955, 2921, 1707, 1320, 1046, 708. Anal. calcd. (found) for $C_{13}H_{15}BrO$: C, 58.44 (58.40); H, 5.66 (5.58).

***trans*-2-(4-Iodophenyl)-3-methylcyclohexanone (Table 4, entry 7).** White solid. mp 89-91 °C. TLC: R_f = 0.34. ^{1}H NMR: δ 7.65 (br d, *J* = 7.6 Hz, 2 H), 6.82 (br d, *J* = 8.0 Hz, 2 Hz), 3.14 (d, *J* = 11.6 Hz, 1 H), 2.54-2.38 (m, 2 H), 2.16-1.99 (m, 3 H), 1.85-1.74 (m, 1 H), 1.62-1.52 (m, 1 H), 0.81 (d, *J* = 6.4 Hz, 3 H). ^{13}C{^{1}H} NMR δ 209.7, 137.6, 137.5, 131.7, 92.7, 65.1, 42.0, 41.0, 34.6, 26.3, 21.5. IR (neat, cm^{-1}): 2952, 2923, 2865, 1710, 1463, 1456, 1182, 1005, 780. Anal. Calcd (found) for $C_{13}H_{15}IO$: C, 49.70 (49.82); H, 4.81 (4.81).

***trans*-3-Methyl-2-naphthalen-1-yl-cyclohexanone (Table 4, entry 8).** White solid. mp 92-95 °C. TLC: R_f = 0.40. ^{1}H NMR: δ 7.91-7.87 (m, 1 H), 7.83-7.79 (m, 2 H), 7.52-7.45 (m, 3 H), 7.31 (d, *J* = 7.6 Hz, 1 H), 3.96 (d, *J* = 11.6 Hz, 1 H), 2.67-2.42 (m, 3 H), 2.26-2.18 (m, 1 H), 2.16-2.10 (m, 1 H), 2.02-1.90 (m, 1 H), 1.76-1.66 (m, 1 H), 0.85 (d, *J* = 6.4 Hz, 3 H). ^{13}C{^{1}H} NMR: δ 209.7, 134.3, 134.2, 132.6, 129.3, 127.8, 127.3, 125.9, 125.5, 125.4, 123.8, 61.3, 42.2, 40.33, 34.9, 25.9, 21.6. Anal. Calcd (found) for $C_{17}H_{18}O$: C, 85.67 (85.64); H, 7.61 (7.78).

***trans*-3-Methyl-2-naphthalen-2-yl-cyclohexanone (Table 4, entry 9).** White solid. mp 87-89 °C. TLC: R_f = 0.42. ^{1}H NMR: δ 7.83-7.77 (m, 3 H), 7.52 (s, 1 H), 7.47-7.41 (m, 2 H), 7.22 (dd, *J* = 1.2, 8.4 Hz, 1 H), 3.35 (d, *J* = 12.0 Hz, 1 H), 2.57-2.42 (m, 2 H), 2.28 (m, 2 H), 2.06-2.01 (m, 1 H), 1.91-1.79 (m, 1 H), 1.66-1.56 (m, 1 H). 0.82 (d, *J* = 6.4 Hz, 3 H). ^{13}C{^{1}H} NMR: δ 210.5, 135.5, 133.7, 132.9, 128.7, 128.1, 128.0, 127.4, 126.1, 125.8, 65.6, 42.2, 40.8, 34.6, 26.3, 21.7. IR (neat, cm^{-1}): 3053, 2952, 29.25, 28.66, 1710, 1599, 1508, 1455, 1374, 1318, 1267,

1184, 1121, 1048, 962, 907, 851, 811, 745. Anal. calcd. (found) for $C_{17}H_{18}O$: C, 85.67 (85.44); H, 7.61 (7.85).

2-Hexylcyclohexanone (33).[37] ^{1}H NMR: δ 2.33-2.38 (m, 1 H), 2.20-2.30 (m, 2 H), 1.96-2.11 (m, 2 H), 1.57-1.85 (m, 2 H), 1.30-1.39 (m, 1 H), 1.13-1.29 (m, 9 H), 0.83 (t, *J* = 6.8 Hz, 3 H). ^{13}C{^{1}H} NMR: δ 213.8, 50.9, 42.1, 34.0, 31.9, 29.6, 29.6, 28.2, 27.3, 25.0, 22.8, 14.2.

(4-Methoxyphenyl)cyclohexanone (35).[38] ^{1}H NMR: δ 7.05-7.08 (m, 2 H), 6.86-6.90 (m, 2 H), 3.80 (s, 3 H), 3.56 (dd, *J* = 5.2, 12.4 Hz, 1 H), 2.40-2.55 (m, 2 H), 2.22- 2.29 (m, 1 H), 2.10-2.18 (m, 1 H), 1.95-2.05 (m, 1 H), 1.78-1.88 (m, 2 H). ^{13}C{^{1}H} NMR: δ 210.9, 158.6, 131.1, 129.6, 114.0, 56.8, 55.4, 42.4, 35.5, 28.1, 25.6.

2-Butylcyclohexanone (Table 5, entry 4).[39] ^{1}H NMR: δ 2.34-2.40 (m, 1 H), 2.21-2.31 (m, 2 H), 2.08-2.12 (m, 1 H), 2.00-2.03 (m, 1 H), 1.61-1.87 (m, 4 H), 0.90-1.60 (m, 6 H), 0.88 (t, *J* = 7.2 Hz, 3 H). ^{13}C{^{1}H} NMR: δ 213.8, 50.9, 42.1, 34.0, 29.6, 29.3, 28.2, 25.0, 23.0, 14.2.

2-Benzylcyclohexanone (Table 5, entry 5).[40] ^{1}H NMR: δ 7.25 (t, *J* = 7.2 Hz, 2 H), 7.17 (d, *J* = 6.8 Hz, 1 H), 7.13 (d, *J* = 7.6 Hz, 2 H), 3.21 (dd, *J* = 6.4, 11.2 Hz, 1 H), 2.49-2.57 (m, 1 H), 1.49-1.71 (m, 2 H), 1.33 (dq, *J* = 3.6, 12.4 Hz, 1 H). ^{13}C{^{1}H} NMR: δ 212.7, 140.6, 129.3, 128.5, 126.2, 52.7, 42.4, 35.7, 33.6, 28.3, 25.3.

2-Cyclohexylcyclohexanone (Table 5, entry 6).[41] ^{1}H NMR: δ 2.30-2.36 (m, 1 H), 2.18-2.26 (m, 1 H), 2.02-2.08 (m, 1H), 1.86-1.94 (m, 2 H), 1.47-1.83 (m, 10 H), 1.24 (tq, *J* = 3.2, 12.8 Hz, 2 H), 1.09 (tq, *J* = 2.2, 12.4 Hz, 1 H), 0.96 (dq, *J* = 3.2, 12.0 Hz, 1 H), 0.80-0.90 (m, 1 H). ^{13}C{^{1}H} NMR: δ 213.8, 56.7, 42.0, 36.2, 31.7, 29.5, 28.1, 26.7, 26.6, 24.2.

Spiro[5.5]undecan-1-one (37).[42] White crystals. mp 36-39 °C. ^{1}H NMR: δ 2.38 (t, *J* = 6.8 Hz, 2 H), 1.79-1.90 (m, 4 H), 1.65-1.74 (m, 4 H), 1.45-1.50 (m, 4 H), 1.29-1.42 (m, 4 H). ^{13}C{^{1}H} NMR: δ 217.1, 49.2, 38.8, 33.9, 28.4, 26.5, 22.2, 20.8.

Methyl 3-(2-oxo-cyclohexyl)propionate (Table 5, entry 8).[43] ^{1}H NMR: δ 3.61 (s, 3 H), 2.21-2.40 (m, 5 H), 1.96-2.01 (m, 3 H), 1.81-1.86 (m, 1 H), 1.58-1.68 (m, 2 H), 1.45-1.54 (m, 1 H), 1.34 (dq, *J* = 4.0, 12.4 Hz, 1 H). ^{13}C{^{1}H} NMR: δ 212.7, 174.2, 51.6, 49.9, 42.3, 34.3, 31.8, 28.2, 25.2, 25.0.

2-(2-Chloroethyl)cyclohexanone (Table 5, entry 9). Pale yellow oil. ^{1}H NMR: δ 3.59 (t, *J* = 6.4 Hz, 2 H), 2.52-2.60 (m, 1 H), 2.21-2.39 (m, 3 H), 2.04-2.14 (m, 2 H), 1.83-1.88 (m, 1 H), 1.48-1.74 (m, 3 H), 1.34 (dq, *J* = 3.6, 12.8 Hz, 1 H). ^{13}C{^{1}H} NMR: δ 212.4, 47.6, 43.5, 42.4, 34.3, 32.7, 28.2, 25.4. IR (neat, cm^{-1}): 2934, 2861, 1708, 1448. Anal. calcd. (found) for $C_8H_{13}ClO$: C, 59.81 (59.62); H, 8.16 (8.17).

2-(2-Phenoxyethyl)cyclohexanone (Table 5, entry 10). Colorless oil. TLC: R_f = 0.28. ^{1}H NMR: δ 7.21-7.27 (m, 2 H), 3.93-4.04 (m, 2 H), 2.55-2.63 (m, 1 H), 2.23-2.41 (m, 3 H), 2.13-2.19 (m, 1 H), 2.03-2.08 (m, 1H), 1.83-1.88 (m, 1 H), 1.58-1.71 (m, 1 H), 1.40 (dq, *J* = 4.0, 12.4 Hz, 1 H). ^{13}C{^{1}H} NMR: δ 213.0, 159.1, 120.8, 114.7, 65.8, 47.5, 42.5, 34.6, 29.5, 28.3, 25.4. IR (neat, cm^{-1}): 2933, 2860, 1708, 1244. Anal. Calcd. (found) for $C_{14}H_{18}O_2$: C, 77.03 (76.95); H, 8.31 (8.10).

2-(2-Methoxyethyl)cyclohexanone (Table 5, entry 11). Pale yellow oil. TLC: R_f = 0.14. ^{1}H NMR: δ 3.35-3.42 (m, 2 H), 3.28 (s, 3 H), 2.42-2.50 (m, 1 H), 2.25-2.40 (m, 2 H), 2.01-2.14 (m, 2 H), 1.78-1.87 (m, 1 H), 1.61-1.72 (m, 2 H), 1.34-1.42 (m, 2 H). ^{13}C{^{1}H} NMR: δ 213.2, 70.7, 58.7, 47.5, 42.4, 34.5, 29.6, 28.3, 25.3. IR (neat, cm^{-1}): 2932, 2861, 1708, 1118. Anal. calcd. (found) for $C_9H_{16}O_2$: C, 69.19 (69.28); H, 10.32 (10.21).

Cyclization of 1-allyl-1-acetylcyclohexane (36). A suspension of **36** (83 mg, 0.5 mmol), **2** (13 mg, 0.05 mmol), HCl (4.0 N in dioxane, 0.5 mL, 2.0 mmol), $CuCl_2$ (40 mg, 0.30 mmol), and dioxane (5 mL) was heated at 70 °C for 12 h in a sealed tube. GC analysis of the crude reaction mixture revealed formation of an 71:20 mixture of spiro[5.5]-undecan-1-one (**37**) and (*E*)-1-acetyl-1-(1-propenyl) cyclohexane. The resulting suspension was filtered through a short plug of silica gel and eluted with ether (20 mL). The resulting solution was concentrated and chromatographed (hexanes–ether = 40:1 ∅ 10:1) to give **37**[42] (46 mg, 55%) as white crystals. (*E*)-1-Acetyl-1-(1-propenyl) cyclohexane was isolated in 18% yield as a colorless oil from a similar experiment.

For (*E*)-1-acetyl-1-(1-propenyl) cyclohexane: ^{1}H NMR: δ 5.48 (qd, *J* = 6.4, 16.0 Hz, 1 H), 5.27 (qd, *J* = 1.2, 16.0 Hz, 1 H), 2.04 (s, 3 H), 1.85-1.90 (s, 2 H), 1.66 (dd, *J* = 2.0, 6.8 Hz, 3 H), 1.45-1.54 (m, 4 H), 1.30-1.36 (m, 4 H). ^{13}C{^{1}H} NMR: δ 211.2, 124.5, 126.9, 54.5, 33.3,

26.1, 25.6, 23.0, 18.6. IR (neat, cm^{-1}): 1705 ($\nu_{C=O}$). HRMS Calcd. (found) for $C_{11}H_{18}O$ (M^+): 166.1358 (166.1362).

Cyclization of 3-methyl-1-dodecen-5-one (38). A suspension of **38** (0.20 g, 1.0 mmol), **2** (26 mg, 0.1 mol), $CuCl_2$ (80 mg, 0.60 mmol), HCl (4 N in dioxane, 0.10 mL, 0.40 mmol) and dioxane (10 mL) was heated at 70 °C in a sealed tube for 8 h. GC analysis of the crude reaction mixture revealed formation of a 2.6:1 mixture of *trans*-**39** and *cis*-**39**. The reaction mixture was diluted with hexanes (20 mL), filtered through a plug of silica gel, and eluted with ether (20 mL). The resulting solution was concentrated and chromatographed (hexanes ∅ hexanes–ether = 5:1) to give *trans*-2-hexyl-5-methylcyclohexanone (*trans*-**39**) (60 mg, 31%) and *cis*-2-hexyl-5-methylcyclohexanone (*cis*-**39**) (25 mg, 13%) as colorless oils.

For *trans*-39: ^{1}H NMR: δ 2.33 (ddd, *J* = 2.0, 3.6, 12.4 Hz, 1 H), 2.06-2.20 (m, 2 H), 1.99 (dt, *J* = 0.8, 12. 8 Hz, 1 H), 1.70-1.88 (m, 3 H), 1.28-1.38 (m, 2 H), 1.25 (br s, 8 H), 1.09-1.16 (m, 1 H), 1.00 (d, *J* = 6.4 Hz, 3 H), 0.86 (t, *J* = 6.8 Hz, 3 H). ^{13}H{^{1}H} NMR: δ 213.0, 50.8, 50.0, 35.9, 34.3, 33.1, 32.0, 29.7, 29.1, 27.3, 22.8, 22.6, 14.3. IR (neat, cm^{-1}): 2953, 2925, 2857, 1712. HRMS calcd (found) for $C_{13}H_{24}O$: 196.1827 (196.1820).

For *cis*-39: ^{1}H NMR: δ 2.31-2.36 (m, 1 H), 2.27 (pent, *J* = 6.0 Hz, 1 H), 2.04-2.16 (m, 2 H), 1.82-1.89 (m, 1 H), 1.63-1.77 (m, 3 H), 1.48-1.55 (m, 1 H), 1.20-1.34 (m, 9 H), 0.96 (d, *J* = 6.8 Hz, 3 H), 0.86 (t, *J* = 7.2 Hz, 3 H). ^{13}H{^{1}H} NMR: δ 214.7, 50.1, 47.8, 33.8, 31.9, 30.6, 30.0, 29.8, 29.5, 27.4, 22.8. 21.0, 14.3. IR (neat, cm^{-1}): 2954, 2926, 2856, 1710. HRMS calcd (found) for $C_{13}H_{24}O$: 196.1827 (196.1824).

Table S1. X-ray crystal data and collection and refinement of parameters for *trans*-**23**.

empirical formula	$C_{18}H_{18}O$
fw	**1072.56**
crystal size, mm	**0.30 ´ 0.25 ´ 0.15**
crystal system	**monoclinic**
space group	$P2_1/n$
***a*, Å**	**17.0799(23)**
***b*, Å**	**9.6283(13)**
***c*, Å**	**18.0672(25)**
b**, deg**	**106.382(2)**
***V*, Å^3**	**2850.5(7)**
Z	**8**
scan mode	***w***
2q limits, deg	**5.0 < 2q < 50.0**
***D*$_c$ (mg cm^{-3})**	**1.167**
abs coeff (mm^{-1})	**0.07**
unique reflections	**5037**
data with I > 2.5 s(I)	**3282**
***F*(000)**	**1072.56**
***R*(*F*)**	**0.056**
***R*$_w$(*F*)**	**0.059**
GoF	**2.2614**
no. of parameters	**488**
max ²/ s	**0.000**
largest resid density (e/Å ^{3})	**0.380**

Figure S1. X-ray crystal structure of *trans*-**23**.

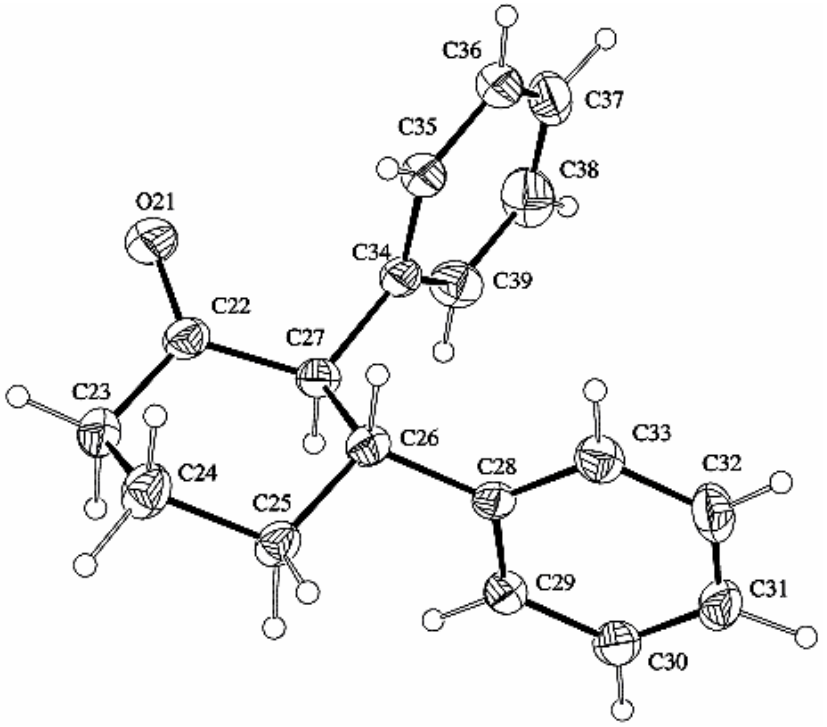

Table S2. Atomic coordinates for *trans*-**23**.

	x	y	z	Biso[a]
O1	0.70906(12)	0.10366(21)	0.97659(11)	4.86(10)
C2	0.70108(15)	0.0074 (3)	1.01652(14)	2.94(12)
C3	0.62752(18)	-0.0852 (3)	0.99347(16)	3.51(14)
C4	0.59590(17)	-0.1253 (3)	1.06104(16)	3.36(13)
C5	0.66423(16)	-0.1847 (3)	1.12691(15)	2.91(13)
C6	0.73372(15)	-0.0809 (3)	1.15547(14)	2.46(12)
C7	0.76818(15)	-0.0301 (3)	1.08960(13)	2.51(11)
C8	0.80163(14)	-0.13415(24)	1.22241(13)	2.27(11)
C9	0.84138(16)	-0.2594 (3)	1.21855(16)	2.89(12)
C10	0.90318(17)	-0.3064 (3)	1.28130(18)	3.62(15)
C11	0.92651(18)	-0.2291 (3)	1.34834(17)	3.88(14)
C12	0.88841(18)	-0.1053 (3)	1.35245(17)	3.80(15)
C13	0.82649(16)	-0.0580 (3)	1.29075(15)	2.86(12)
C14	0.82916(14)	0.08672(25)	1.11509(13)	2.39(11)
C15	0.91011(16)	0.0690 (3)	1.11821(14)	3.08(14)
C16	0.96588(18)	0.1756 (4)	1.14142(15)	3.88(16)
C17	0.94064(20)	0.3021 (4)	1.16309(17)	4.16(16)
C18	0.86049(20)	0.3200 (3)	1.16125(17)	3.87(16)
C19	0.80554(18)	0.2140 (3)	1.13745(16)	3.37(15)
O21	0.35521(14)	0.41803(21)	0.01359(13)	5.82(12)
C22	0.35007(17)	0.5172 (3)	0.05155(15)	3.42(13)
C23	0.41807(19)	0.6197 (3)	0.07474(17)	3.86(15)
C24	0.43838(18)	0.6512 (4)	0.16064(18)	4.36(16)
C25	0.36205(16)	0.7013 (3)	0.18118(18)	3.28(14)
C26	0.29293(16)	0.5963 (3)	0.15969(14)	2.93(12)
C27	0.27288(16)	0.5516 (3)	0.07390(15)	3.03(13)
C28	0.21702(15)	0.6500 (3)	0.17842(13)	2.74(12)
C29	0.17853(17)	0.7712 (3)	0.14481(16)	3.38(13)
C30	0.11061(18)	0.8223 (3)	0.16342(19)	4.18(16)
C31	0.07957(20)	0.7535 (4)	0.21492(19)	4.54(17)
C32	0.11618(20)	0.6325 (4)	0.24826(19)	4.66(17)
C33	0.18480(19)	0.5801 (3)	0.23015(16)	3.74(15)
C34	0.20903(17)	0.4379 (3)	0.05440(14)	3.03(12)
C35	0.22341(19)	0.3081 (3)	0.08836(18)	3.96(15)
C36	0.16359(25)	0.2060 (4)	0.06968(22)	4.87(19)
C37	0.0897 (3)	0.2328 (4)	0.01716(22)	5.56(22)
C38	0.07460(23)	0.3610 (5)	-0.01642(20)	5.39(20)
C39	0.13361(20)	0.4619 (4)	0.00272(17)	4.23(17)
H3a	0.5824 (17)	-0.027 (3)	0.9474 (16)	5.0 (6)
H3b	0.6480 (17)	-0.170 (3)	0.9736 (17)	5.8 (8)

H4a	0.5524 (15)	-0.195 (3)	1.0454 (13)	3.4 (6)
H4b	0.5730 (16)	-0.034 (3)	1.0813 (15)	5.1 (7)
H5a	0.6437 (14)	-0.2138 (24)	1.1709 (14)	3.5 (6)
H5b	0.6841 (15)	-0.270 (3)	1.1096 (14)	3.4 (6)
H6	0.7121 (14)	0.006 (3)	1.1717 (13)	3.6 (6)
H7	0.7972 (14)	-0.1180 (25)	1.0737 (13)	3.6 (6)

Table S2. Continued.

H9	0.8261 (14)	-0.3102 (24)	1.1710 (14)	3.3 (6)
H10	0.9276 (17)	-0.395 (3)	1.2722 (15)	4.6 (7)
H11	0.9752 (19)	-0.262 (3)	1.3920 (17)	5.7 (7)
H12	0.9023 (17)	-0.053 (3)	1.3962 (16)	4.7 (7)
H13	0.7980 (15)	0.028 (3)	1.2951 (13)	3.4 (6)
H15	0.9269 (15)	-0.016 (3)	1.1044 (14)	3.9 (7)
H16	1.0233 (18)	0.159 (3)	1.1433 (16)	5.2 (7)
H17	0.9770 (19)	0.371 (3)	1.1794 (17)	5.7 (8)
H18	0.8423 (18)	0.411 (3)	1.1737 (16)	5.6 (8)
H19	0.7472 (16)	0.229 (3)	1.1338 (13)	3.8 (6)
H23a	0.4656 (18)	0.585 (3)	0.0613 (16)	5.1 (7)
H23b	0.3965 (19)	0.720 (3)	0.0441 (17)	6.6 (8)
H24a	0.4545 (18)	0.556 (3)	0.1884 (17)	6.4 (8)
H24b	0.4827 (20)	0.730 (3)	0.1745 (17)	7.0 (9)
H25	0.3712 (15)	0.735 (3)	0.2288 (15)	3.8 (6)
H25b	0.3531 (13)	0.801 (3)	0.1720 (13)	2.7 (5)
H26	0.3110 (15)	0.505 (3)	0.1888 (14)	4.5 (6)
H27	0.2515 (15)	0.639 (3)	0.0441 (14)	4.1 (6)
H29	0.2014 (16)	0.821 (3)	0.1085 (16)	4.6 (7)
H30	0.0835 (20)	0.914 (3)	0.1387 (18)	6.6 (8)
H31	0.0297 (19)	0.783 (3)	0.2325 (17)	6.4 (8)
H32	0.1010 (19)	0.581 (3)	0.2866 (17)	5.7 (8)
H33	0.2109 (16)	0.493 (3)	0.2552 (15)	4.2 (6)
H35	0.2783 (19)	0.289 (3)	0.1324 (18)	6.6 (8)
H36	0.1816 (20)	0.119 (4)	0.0951 (18)	6.8 (9)
H37	0.0459 (19)	0.162 (3)	0.0059 (16)	5.8 (8)
H38	0.0220 (21)	0.381 (3)	-0.0490 (19)	6.6 (9)
H39	0.1244 (19)	0.550 (3)	-0.0169 (17)	5.8 (9)

[a]Biso is the Mean of the Principal Axes of the Thermal Ellipsoid.

Table S3. Bond lengths for *trans*-**23**.

O(1)-C(2)	1.205(3)	C(22)-C(23)	1.491(4)
C(2)-C(3)	1.501(4)	C(22)-C(27)	1.520(4)
C(2)-C(7)	1.528(3)	C(23)-C(24)	1.522(4)
C(3)-C(4)	1.517(4)	C(23)-H(23a)	0.97(3)
C(3)-H(3a)	1.11(3)	C(23)-H(23b)	1.12(3)
C(3)-H(3b)	0.99(3)	C(24)-C(25)	1.531(4)
C(4)-C(5)	1.524(4)	C(24)-H(24a)	1.04(3)
C(4)-H(4a)	0.98(3)	C(24)-H(24b)	1.05(3)
C(4)-H(4b)	1.07(3)	C(25)-C(26)	1.519(4)
C(5)-C(6)	1.526(3)	C(25)-H(25a)	0.89(3)
C(5)-H(5a)	1.00(3)	C(25)-H(25b)	0.98(3)
C(5)-H(5b)	0.97(3)	C(26)-C(27)	1.551(3)
C(6)-C(7)	1.548(3)	C(26)-C(28)	1.520(4)
C(6)-C(8)	1.510(3)	C(26)-H(26)	1.03(3)
C(6)-H(6)	0.99(3)	C(27)-C(34)	1.515(4)
C(7)-C(14)	1.514(3)	C(27)-H(27)	1.01(3)
C(7)-H(7)	1.060(25)	C(28)-C(29)	1.392(4)
C(8)-C(9)	1.395(4)	C(28)-C(33)	1.385(4)
C(8)-C(13)	1.395(3)	C(29)-C(30)	1.386(4)
C(9)-C(10)	1.389(4)	C(29)-H(29)	0.98(3)
C(9)-H(9)	0.958(25)	C(30)-C(31)	1.365(5)
C(10)-C(11)	1.381(5)	C(30)-H(30)	1.03(3)
C(10)-H(10)	0.99(3)	C(31)-C(32)	1.378(6)
C(11)-C(12)	1.370(5)	C(31)-H(31)	1.03(3)
C(11)-H(11)	1.02(3)	C(32)-C(33)	1.397(5)
C(12)-C(13)	1.380(4)	C(32)-H(32)	0.95(3)
C(12)-H(12)	0.91(3)	C(33)-H(33)	1.00(3)
C(13)-H(13)	0.98(3)	C(34)-C(35)	1.383(4)
C(14)-C(15)	1.378(4)	C(34)-C(39)	1.381(4)
C(14)-C(19)	1.386(4)	C(35)-C(36)	1.389(5)
C(15)-C(16)	1.383(4)	C(35)-H(35)	1.06(3)
C(15)-H(15)	0.92(3)	C(36)-C(37)	1.373(6)
C(16)-C(17)	1.385(5)	C(36)-H(36)	0.96(3)
C(16)-H(16)	0.98(3)	C(37)-C(38)	1.367(7)
C(17)-C(18)	1.371(5)	C(37)-H(37)	0.99(3)
C(17)-H(17)	0.90(3)	C(38)-C(39)	1.372(5)
C(18)-C(19)	1.371(4)	C(38)-H(38)	0.94(4)
C(18)-H(18)	0.98(3)	C(39)-H(39)	0.91(3)
C(19)-H(19)	0.99(3)	H(5a)-H(5b)	1.56(3)
O(21)-C(22)	1.193(3)	H(25a)-H(25b)	1.17(3)

Table S4. Bond angles for *trans*-**23**.

O(1)-C(2)-C(3)	121.19(23)	C(23)-C(22)-C(27)	116.53(24)
O(1)-C(2)-C(7)	121.02(23)	C(22)-C(23)-C(24)	110.7(3)
C(3)-C(2)-C(7)	117.67(22)	C(22)-C(23)-H(23a)	109.9(16)
C(2)-C(3)-C(4)	112.84(22)	C(22)-C(23)-H(23b)	108.0(15)
C(2)-C(3)-H(3a)	104.9(13)	C(24)-C(23)-H(23a)	110.9(16)
C(2)-C(3)-H(3b)	103.6(16)	C(24)-C(23)-H(23b)	106.3(15)
C(4)-C(3)-H(3a)	113.7(13)	H(23a)-C(23)-H(23b)	110.9(23)
C(4)-C(3)-H(3b)	108.9(17)	C(23)-C(24)-C(25)	110.20(25)
H(3a)-C(3)-H(3b)	112.5(21)	C(23)-C(24)-H(24a)	105.5(16)
C(3)-C(4)-C(5)	110.84(23)	C(23)-C(24)-H(24b)	109.1(17)
C(3)-C(4)-H(4a)	110.8(13)	C(25)-C(24)-H(24a)	106.8(16)
C(3)-C(4)-H(4b)	108.4(14)	C(25)-C(24)-H(24b)	108.7(17)
C(5)-C(4)-H(4a)	108.7(13)	H(24a)-C(24)-H(24b)	116.4(23)
C(5)-C(4)-H(4b)	108.4(14)	C(24)-C(25)-C(26)	112.44(25)
H(4a)-C(4)-H(4b)	109.8(19)	C(24)-C(25)-H(25a)	114.8(16)
C(4)-C(5)-C(6)	111.68(22)	C(24)-C(25)-H(25b)	111.8(13)
C(4)-C(5)-H(5a)	111.4(13)	C(26)-C(25)-H(25a)	113.8(17)
C(4)-C(5)-H(5b)	109.0(14)	C(26)-C(25)-H(25b)	122.4(13)
C(6)-C(5)-H(5a)	109.3(13)	H(25a)-C(25)-H(25b)	77.3(21)
C(6)-C(5)-H(5b)	110.7(14)	C(25)-C(26)-C(27)	112.14(22)
H(5a)-C(5)-H(5b)	104.7(19)	C(25)-C(26)-C(28)	111.52(21)
C(5)-C(6)-C(7)	112.02(20)	C(25)-C(26)-H(26)	109.9(14)
C(5)-C(6)-C(8)	113.38(20)	C(27)-C(26)-C(28)	110.80(20)
C(5)-C(6)-H(6)	109.5(14)	C(27)-C(26)-H(26)	102.8(14)
C(7)-C(6)-C(8)	110.50(19)	C(28)-C(26)-H(26)	109.2(14)
C(7)-C(6)-H(6)	102.4(13)	C(22)-C(27)-C(26)	111.24(21)
C(8)-C(6)-H(6)	108.4(13)	C(22)-C(27)-C(34)	113.74(22)
C(2)-C(7)-C(6)	112.58(20)	C(22)-C(27)-H(27)	104.4(14)
C(2)-C(7)-C(14)	111.78(20)	C(26)-C(27)-C(34)	112.00(21)
C(2)-C(7)-H(7)	104.4(12)	C(26)-C(27)-H(27)	104.1(13)
C(6)-C(7)-C(14)	112.27(19)	C(34)-C(27)-H(27)	110.6(14)
C(6)-C(7)-H(7)	105.3(12)	C(26)-C(28)-C(29)	121.04(23)
C(14)-C(7)-H(7)	109.9(12)	C(26)-C(28)-C(33)	120.74(24)
C(6)-C(8)-C(9)	121.89(22)	C(29)-C(28)-C(33)	118.2(3)
C(6)-C(8)-C(13)	120.25(22)	C(28)-C(29)-C(30)	121.1(3)
C(9)-C(8)-C(13)	117.86(23)	C(28)-C(29)-H(29)	118.1(16)
C(8)-C(9)-C(10)	120.6(3)	C(30)-C(29)-H(29)	120.8(16)
C(8)-C(9)-H(9)	118.2(14)	C(29)-C(30)-C(31)	120.4(3)
C(10)-C(9)-H(9)	121.2(14)	C(29)-C(30)-H(30)	120.0(18)
C(9)-C(10)-C(11)	120.4(3)	C(31)-C(30)-H(30)	119.6(18)
C(9)-C(10)-H(10)	114.0(15)	C(30)-C(31)-C(32)	119.5(3)
C(11)-C(10)-H(10)	125.7(15)	C(30)-C(31)-H(31)	126.2(16)

C(10)-C(11)-C(12)	119.5(3)	C(32)-C(31)-H(31)	114.3(16)
C(10)-C(11)-H(11)	118.5(16)	C(31)-C(32)-C(33)	120.7(3)
C(12)-C(11)-H(11)	121.8(16)	C(31)-C(32)-H(32)	125.3(18)
C(11)-C(12)-C(13)	120.7(3)	C(33)-C(32)-H(32)	113.9(18)
C(11)-C(12)-H(12)	121.2(17)	C(28)-C(33)-C(32)	120.1(3)
C(13)-C(12)-H(12)	118.1(17)	C(28)-C(33)-H(33)	120.2(15)
C(8)-C(13)-C(12)	121.0(3)	C(32)-C(33)-H(33)	119.7(15)
C(8)-C(13)-H(13)	118.9(14)	C(27)-C(34)-C(35)	121.6(3)

Table S4. Continued.

C(12)-C(13)-H(13)	120.1(14)	C(27)-C(34)-C(39)	120.6(3)
C(7)-C(14)-C(15)	121.12(23)	C(35)-C(34)-C(39)	117.8(3)
C(7)-C(14)-C(19)	120.93(22)	C(34)-C(35)-C(36)	120.3(3)
C(15)-C(14)-C(19)	117.94(24)	C(34)-C(35)-H(35)	119.8(16)
C(14)-C(15)-C(16)	121.2(3)	C(36)-C(35)-H(35)	119.6(16)
C(14)-C(15)-H(15)	118.8(16)	C(35)-C(36)-C(37)	120.3(4)
C(16)-C(15)-H(15)	120.0(16)	C(35)-C(36)-H(36)	112.7(20)
C(15)-C(16)-C(17)	119.7(3)	C(37)-C(36)-H(36)	126.9(19)
C(15)-C(16)-H(16)	119.1(16)	C(36)-C(37)-C(38)	119.9(3)
C(17)-C(16)-H(16)	121.2(16)	C(36)-C(37)-H(37)	120.4(17)
C(16)-C(17)-C(18)	119.5(3)	C(38)-C(37)-H(37)	119.6(17)
C(16)-C(17)-H(17)	119.9(19)	C(37)-C(38)-C(39)	119.6(4)
C(18)-C(17)-H(17)	120.6(19)	C(37)-C(38)-H(38)	118.9(20)
C(17)-C(18)-C(19)	120.3(3)	C(39)-C(38)-H(38)	121.3(20)
C(17)-C(18)-H(18)	119.2(17)	C(34)-C(39)-C(38)	122.0(3)
C(19)-C(18)-H(18)	120.4(17)	C(34)-C(39)-H(39)	116.3(19)
C(14)-C(19)-C(18)	121.3(3)	C(38)-C(39)-H(39)	121.6(20)
C(14)-C(19)-H(19)	118.5(14)	C(5)-H(5a)-H(5b)	37.1(12)
C(18)-C(19)-H(19)	120.1(14)	C(5)-H(5b)-H(5a)	38.2(13)
O(21)-C(22)-C(23)	120.9(3)	C(25)-H(25a)-H(25b)	54.7(19)
O(21)-C(22)-C(27)	122.5(3)	C(25)-H(25b)-H(25a)	48.0(17)

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