Supplementary Material

General. IR spectra were recorded on a Shimadzu IR-408 spectrometer. NMR spectra were obtained on a JEOL JNM-FX-100, a JEOL JNM-EX-270, or a JEOL JNM-A-500 spectrometer. Chemical shift value were given in ppm relative to internal Me_4Si (for ^1H and ^{13}C NMR: δ-value) or internal C_6F_6 (for ^{19}F NMR). Mass spectra were taken with a JEOL JMS-DX-300 spectrometer. Elemental analyses were performed with a YANAKO MT-3 CHN Corder apparatus. THF was distilled from sodium benzophenone ketyl prior to use. HFIP from Central Glass Co., Ltd (purity 99.9%) was distilled from and stored over 3A molecular sieves.

Synthesis of 5-Methylene-3-fluoro-2-cyclopentenone 1.

2-Butyl-1,1-difluoro-4-metyl-1,4-pentadien-3-one. Butyllithium (20 ml, 1.63 M in hexane, 33 mmol) was added to a tetrahydrofuran (THF, 80ml) solution of 2,2,2-trifluoroethyl *p*-toluenesulfonate (4.0 g, 15.7 mmol) at –78 °C over 10 min under a nitrogen atmosphere. The reaction mixture was stirred for 30 min and then tributylborane (17.3 ml, 1.0M in THF, 17.3 mmol) was added at –78 °C. After being stirred for 1 h, the reaction mixture was warmed up to room temperature and stirred for an additional 3 h. The solution was treated with hexamethylphosphoric triamide (HMPA, 18 ml) and cuprous iodide (6.0 g, 31 mmol) at 0 °C and stirred for 30 min at the same temperature. To the resulting solution was added methacryloyl chloride (1.84 ml, 18.8 mmol), and the mixture was stirred at room temperature for 1 h. The reaction was quenched with phosphate buffer (pH 7), followed by addition of a large quantity of ice-cold water (about 100 ml). To the resulting mixture was added aqueous hydrogen peroxide (7 ml, 30%) dropwise at 0 °C. After being stirred for 15 min at room temperature, the mixture was filtered. Organic materials were extracted with CH_2Cl_2 three times. The combined extracts were washed with aqueous $Na_2S_2O_3$ and water, and then dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel

(hexane–Et_2O 30:1), followed by bulb-to-bulb distillation (65 °C/28 mmHg) to give the title compound (1.61 g, 8.48 mmol, 54%) as a colorless liquid. ^1H NMR (500 MHz, $CDCl_3$) δ 0.90 (3H, t, J = 7.0 Hz), 1.24–1.42 (4H, m), 1.94 (3H, br s), 2.25–2.32 (2H, m), 5.78 (1H, m), 5.79 (1H, m). ^{13}C NMR (126 MHz, $CDCl_3$) δ 13.7, 17.3, 22.3, 25.1, 30.3 (t, J_{CF} = 3 Hz), 94.1 (dd, J_{CF} = 17, 11 Hz), 125.7 (d, J_{CF} = 3 Hz), 145.0, 156.7 (t, J_{CF} = 296 Hz), 194.8 (dd, J_{CF} = 8, 3 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) 78.3 (1F, dt, J_{FF} = 24 Hz, J_{FH} = 3 Hz), 86.2 (1F, dt, J_{FF} = 24 Hz, J_{FH} = 2 Hz) ppm. IR (neat) 2960, 1720, 1655, 1345, 1270, 1135, 1080, 960 cm^{-1}. MS (20 eV) *m/z* 188 (M^+), 187, 147 (base peak), 145, 69. HRMS calcd for $C_{10}H_{14}OF_2$ 188.1013 (M^+); found 188.1052.

2-Butyl-3-fluoro-5-methylene-2-cyclopenten-1-one (1a). TMSOTf (56 μl, 0.31 mmol) was added to a solution of 2-butyl-1,1-difluoro-4-metyl-1,4-pentadien-3-one (54 mg, 0.29 mmol) in CH_2Cl_2–HFIP (1:1, 4.0 ml) at room temperature under a nitrogen atmosphere. After the reaction mixture was stirred for 8 min, phosphate buffer (pH 7) was added to quench the reaction. Organic materials were extracted with CH_2Cl_2 three times. The combined extracts were washed with water, and then dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by thin layer chromatography on silica gel (hexane–Et_2O 7:1) to give **1a** (35 mg, 0.21 mmol, 73%) as a colorless liquid. ^1H NMR (270 MHz, $CDCl_3$) δ 0.91 (3H, t, J = 7.3 Hz), 1.23–1.42 (2H, m), 1.41–1.56 (2H, m), 2.25 (2H, t, J = 7.4 Hz), 3.28 (2H, dd, J_{HF} = 3.3 Hz, J = 1.7 Hz), 5.42 (1H, s), 6.17 (1H, dt, J = 4.0 Hz, J = 1.7 Hz). ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.7, 20.8, 22.5, 29.5, 31.0 (d, J_{CF} = 18 Hz), 116.9 (d, J_{CF} = 5 Hz), 124.8 (d, J_{CF} = 4 Hz), 139.6, 182.5 (d, J_{CF} = 300 Hz), 192.8 (d, J_{CF} = 13 Hz). ^{19}F NMR (94 MHz, $CDCl_3$–CCl_4) 69.7 (1F, br s) ppm. IR (neat) 2960, 1710, 1685, 1645, 1425, 1355, 1200, 1120, 1055, 965, 935 cm^{-1}. MS (70 eV) *m/z* 168 (M^+), 139, 126 (base peak), 97, 69. HRMS calcd for $C_{10}H_{13}OF$ 168.0950 (M^+); found 168.0952. Anal. Calcd for $C_{10}H_{13}OF$: C, 71.40; H, 7.79. Found: C, 71.08; H, 7.82.

Synthesis of 2,3-disubstituted 4-methylene-2-cyclopentenones 2.

2-Butyl-3-methyl-4-methylene-2-cyclopenten-1-one (2a). To a mixture of **1a** (40 mg, 0.24 mmol) and CuI (45 mg, 0.24 mmol) in THF (4.0 ml) was added methyllithium (0.43 ml, 1.10 M in Et_2O, 0.48 mmol) at –78 °C under a nitrogen atmosphere. After the reaction mixture was stirred for 8 min, phosphate buffer (pH 7) was then added to quench the reaction. Organic materials were extracted with Et_2O three times. The combined extracts were washed with water, and then dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by thin layer chromatography on silica gel (hexane–Et_2O 3:1) to give **2a** (34 mg, 0.21 mmol, 87%) as a colorless liquid. ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.91 (3H, m), 1.20–1.47 (4H, m), 2.09 (3H, s), 2.28 (2H, t , *J* = 7.4 Hz), 2.95 (2H, br s) 5.14 (1H, br t, *J* = 1.0 Hz), 5.31 (1H, br t, *J* = 1.7 Hz). ^{13}C NMR (68 MHz, $CDCl_3$) δ 11.5, 13.9, 22.8, 23.3, 30.5, 39.5, 107.5, 144.7, 145.3, 162.1, 204.8. IR (neat) 2940, 1705, 1645, 1290, 1265, 1230, 1200, 1110, 885. cm^{-1}. MS (70 eV) *m/z* (rel intensity) 164 (M^+; 37), 149 (39), 135 (30), 122(100), 91 (28), 79 (31). HRMS calcd for $C_{11}H_{16}O$ 164.1201 (M^+); found 164.1218.

2,3-Dibutyl-4-methylene-2-cyclopenten-1-one (2b). To a mixture of cerium trichloride (330 mg, 1.34 mmol) in THF (3.3 ml) was added butyllithium (0.85 ml, 1.57 M in hexane, 1.34 mmol) at –78 °C over 10 min under a nitrogen atmosphere. The reaction mixture was stirred for 30 min, and **1a** (112 mg, 0.67 mmol) was added. After stirring for 8 min, phosphate buffer (pH 7) was added to quench the reaction. Organic materials were extracted with Et_2O three times. The combined extracts were washed with water, and then dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by thin layer chromatography on silica gel (hexane–Et_2O 5:1) to give **2b** (104 mg, 0.506 mmol, 76%) as a colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.91 (3H, t, *J* = 7.5 Hz), 0.96 (3H, t, *J* = 7.5 Hz), 1.28–1.56 (8H, m), 2.26 (2H, t, *J* = 7.5 Hz), 2.51 (2H, t, *J* = 7.5 Hz), 3.00 (2H, S), 5.14 (1H, dd, *J* = 1.1, 1.1 Hz), 5.32

(1H, dd, *J* = 1.7, 1.7 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 13.9, 13.9, 23.0, 23.1, 23.6, 25.8, 30.7, 31.4, 39.8, 107.5, 143.7, 145.0, 166.3, 205.3. IR (neat) 2925, 1715, 1680, 1460, 1435, 1340, 1215, 1125, 990 cm^{-1}. HRFABMS calcd for $C_{14}H_{23}O$ 207.1749 ($M+1^+$); found 207.1766.

2-Butyl-4-methylene-3-phenyl-2-cyclopenten-1-one (2c). Compound **2c** was prepared by the method described above for **2b** using cerium trichloride (517 mg, 1.39 mmol), phenyllithium (1.37 ml, 0.99 M in cyclohexane–Et_2O, 1.39 mmol), and **1a** (117 mg, 0.69 mmol). Purification by thin layer chromatography on silica gel (hexane–Et_2O 5:1) gave **2c** (127 mg, 0.615 mmol, 79%) as a colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.79 (3H, t, *J* = 7.3 Hz), 1.22 (2H, tq, *J* = 7.3, 7.3 Hz), 1.37 (2H, tt, *J* = 7.3, 7.3 Hz), 2.24 (2H, t, *J* = 7.3 Hz), 3.13 (2H, dd, *J* = 1.4, 1.4 Hz), 5.11 (1H, S), 5.23 (1H, S), 7.24–7.29 (2H, m), 7.39–7.49 (3H, m). ^{13}C NMR (126 MHz, $CDCl_3$) δ 13.7, 22.8, 23.7, 30.5, 39.9, 110.9, 128.3, 128.4, 128.6, 133.4, 144.1, 145.4, 164.8, 205.1. IR (neat) 2925, 1705, 1370, 1270, 1215, 1110, 890, 770, 740 cm^{-1}. HRFABMS calcd for $C_{16}H_{19}O$ 227.1436 ($M+1^+$); found 227.1449.

Synthesis of 2,5-Disubstituted 3-fluoro-2-cyclopentenones 5.

2-Butyl-5-ethyl-3-fluoro-2-cyclopenten-1-one (5a). To a suspension of copper thiocyanate (38.1 mg, 0.30 mmol) in THF (1.0 ml) was added methyllithium (0.6 ml, 1.05 M in cyclohexane–Et_2O, 0.60 mmol) at –45 °C over 10 min under a nitrogen atmosphere. After being stirred for 30 min, the reaction mixture was cooled to –78 °C. A mixture of **1a** (50 mg, 0.30 mmol) and boron trifluoride–diethylether (1/1) (74 μl, 0.59 mmol) was added and stirred for 18 min at –45 °C. Phosphate buffer (pH 7) was then added to quench the reaction. Organic materials were extracted with Et_2O three times. The combined extracts were washed with water, and then dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane–Et_2O 2:1) to give **5a** (50 mg, 0.27 mmol, 91%) as a colorless liquid. ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.90 (3H, t, *J* = 7.3 Hz), 0.94

(3H, t, J = 7.3 Hz), 1.29 (2H, tq, J = 7.3, 7.3 Hz), 1.44 (2H, tt, J = 7.3, 7.3 Hz), 1.49 (1H, dq, J = 15.0, 7.3 Hz), 1.81–1.91 (1H, m), 2.15 (2H, t, J = 7.3 Hz), 2.33 (1H, br d, J = 17.7 Hz), 2.48–2.54 (1H, m), 2.78 (1H, ddd, J = 17.7, 6.7, 1.2 Hz). ^{13}C NMR (68 MHz, $CDCl_3$) δ 11.0, 13.7, 20.6, 22.5, 24.1, 29.5, 31.3 (d, J_{CF} = 16 Hz), 47.2, 122.8 (d, J_{CF} = 4 Hz), 184.7 (d, J_{CF} = 301 Hz), 206.8 (d, J_{CF} = 15 Hz). ^{19}F NMR (470 MHz, $CDCl_3$–CCl_4) 74.3 (1F, s) ppm. IR (neat) 2960, 1720, 1680, 1465, 1445, 1355, 1215, 1135, 840 cm^{-1}. MS (70 eV) *m/z* (rel intensity)184 (M^+; 28), 167 (37), 156 (47), 149 (100), 142 (49), 113 (34). HRMS calcd for $C_{11}H_{17}OF$ 184.1263 (M^+); found 184.1264.

2-Butyl-3-fluoro-5-pentyl-2-cyclopenten-1-one (5b). Compound **5b** was prepared by the method described for **5a** using copper thiocyanate (50 mg, 0.36 mmol), butyllithium (0.51 ml, 1.55 M in hexane, 0.79 mmol), **1a** (60 mg, 0.36 mmol), and boron trifluoride–diethylether (1/1) (88 μl, 0.70 mmol). Purification by thin layer chromatography on silica gel (hexane–Et_2O 6:1) gave **5b** (67 mg, 0.30 mmol, 83%) as a colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (3H, t, J = 7.3 Hz), 0.90 (3H, t, J = 7.0 Hz), 1.25–1.48 (11H, m), 1.80–1.87 (1H, m), 2.14 (2H, t, J = 7.6 Hz), 2.33 (1H, d, J = 18.0 Hz), 2.51–2.57 (1H, m), 2.79 (1H, ddt, J = 18.0, 7.0, 1.5 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 13.7, 14.0, 20.6, 22.5, 26.7, 29.5, 31.1, 31.8, 31.8 (d, J_{CF} = 12 Hz), 45.9, 122.6, 184.7 (d, J_{CF} = 302 Hz), 207.1 (d, J_{CF} = 16 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) 74.9 (1F, s) ppm. IR (neat) 2925, 1715, 1675, 1460, 1445, 1345, 1390, 1210, 1130 cm^{-1}. MS (70 eV) *m/z* (rel intensity) 226 (M^+; 15), 207 (19), 156 (142), 113 (100). HRMS calcd for $C_{14}H_{23}OF$ 226.1733 (M^+); Found 226.1732.

5-benzyl-2-butyl-3-fluoro-2-cyclopenten-1-one (5c). Compound **5c** was prepared by the method described for **5a** using copper thiocyanate (50 mg, 0.36 mmol), phenyllithium (0.71 ml, 1.01 M in cyclohexane–Et_2O, 0.72 mmol), **1a** (60 mg, 0.36 mmol), and boron trifluoride–diethylether (1/1) (88 μl, 0.70 mmol). Purification by thin layer chromatography on

silica gel (hexane–Et_2O 10:1) gave **5c** (62 mg, 0.25 mmol, 69%) as a colorless liquid. ^1H NMR (500 MHz, $CDCl_3$) δ 0.89 (3H, t, *J* = 7.3 Hz), 1.26 (2H, tq, *J* = 7.3, 7.3 Hz), 1.42 (2H, tt, *J* = 7.3, 7.3 Hz), 2.14 (2H, t, *J* = 7.3 Hz), 2.38 (1H, d, *J* = 18.0 Hz), 2.61–2.70 (2H, m), 2.88 (1H, ddt, *J* = 13.9, 7.1, 2.4 Hz), 3.21 (1H, ddd, *J* = 14.0, 4.0, 1.5 Hz), 7.16 (1H, d, *J* = 7.5 Hz), 7.22 (2H, t, *J* = 7.3 Hz), 7.29 (2H, t, *J* = 7.3 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 13.7, 20.5, 22.4, 29.4, 30.8 (d, J_{CF} = 17 Hz), 36.6, 47.0, 122.7 (d, J_{CF} = 15 Hz), 126.6, 128.6, 128.9, 138.6, 184.7 (d, J_{CF} = 301 Hz), 206.1 (d, J_{CF} = 17 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) 75.9 (1F, s) ppm. IR (neat) 2925, 1710, 1665, 1500, 1465, 1340, 1210, 1130, 1075 cm^{-1}. MS (70 eV) *m/z* (rel intensity) 246 (M^+; 100), 155 (51), 113 (36), 91 (205). HRMS calcd for $C_{16}H_{19}OF$ 246.1420 (M^+); found 246.1415.

Synthesis of 2-Butyl-4-ethyl-3-methyl-2-cyclopenten-1-one (4). Compound **4** was prepared by the method described for **2a** using **5a** (49 mg, 0.266 mmol), CuI (50 mg, 0.266 mmol), and methyllithium (0.47 ml, 1.13 M in Et_2O, 0.53 mmol). Purification by thin layer chromatography on silica gel (hexane–Et_2O 3:1) gave **4** (47 mg, 0.261mmol, 98%) as a colorless liquid. ^1H NMR (270 MHz, $CDCl_3$) δ 0.87 (3H, t, *J* = 7.2 Hz), 0.89 (3H, t, *J* = 7.2 Hz), 1.18–1.43 (5H, m), 1.73–1.92 (1H, m), 1.99 (3H, s), 2.05 (1H, dd, *J* = 18.5 Hz, 1.7 Hz), 2.17 (2H, m), 2.48 (1H, dd, *J* = 18.5, 6.6 Hz), 2.58–2.69 (1H, m). ^{13}C NMR (68 MHz, $CDCl_3$) δ 10.6, 13.9, 15.0, 22.7, 22.8, 25.4, 30.6, 40.0, 43.7, 141.1, 172.6, 208.8. IR (neat) 2950, 1700, 1645, 1460, 1385, 1075, 665 cm^{-1}. MS (70 eV) *m/z* (rel intensity) 180 (M^+; 30), 165 (28), 152 (37), 138(70), 109 (100), 81 (23). HRMS calcd for $C_{12}H_{20}O$ 180.1514 (M^+); found 180.1506.

Synthesis of 2,3-Disubstituted-5-methylene-2-cyclopentenones 6.

2-Butyl-3-methyl-5-methylene-2-cyclopenten-1-one (6a). Trimethylaluminium (0.61ml, 1.02 M in hexane, 0.63 mmol) was added dropwise to a CH_2Cl_2 (5 ml) solution of 2,6-diphenylphenol (462 mg, 1.88 mmol) at room temperature under an argon atmosphere. The reaction mixture was stirred for 30 min to furnish aluminium tris(2,6-diphenylphenoxide) (ATPH) in hexane–CH_2Cl_2.

The solution was cooled to –78 °C and **1a** (70 mg, 0.42 mmol) in CH_2Cl_2 (0.5 ml) was added to generate enone/ATPH complex. After stirring for 5min, methyllithium (0.75 ml, 1.11 M in Et_2O, 0.83 mmol) was added to the enone/ATPH complex at –78 °C. After the resulting mixture was stirred for 2 h, the reaction was quenched with 1M aqueous HCl. Organic materials were extracted with Et_2O and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by thin layer chromatography on silica gel (benzene–Et_2O 30:1) to give **6a** (27 mg, 0.145 mmol, 39%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.90 (3H, t, *J* = 7.3 Hz), 1.30 (2H, tq, *J* = 7.3, 7.3 Hz), 1.36–1.44 (2H, m), 2.09 (3H, s), 2.26 (2H, t, *J* = 7.3 Hz), 3.09 (2H, s), 5.33 (1H, dd *J* = 1.2, 1.2 Hz), 6.03 (1H, dd, *J* = 3.1, 1.8 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 13.9, 16.7, 22.7, 23.1, 30.4, 36.9, 114.9, 141.7, 142.6, 164.1, 196.0. IR (neat) 2930, 1690, 1650, 1625, 1385, 1345, 1285, 1060, 935, 815 cm^{-1}. MS (70 eV) *m/z* (rel intensity) 164 (M^+; 57), 122 (100), 79 (46). HRMS calcd for $C_{11}H_{16}O$ 164.1201 (M^+); found 164.1201.

2-Butyl-3-phenyl-5-methylene-2-cyclopenten-1-one (6b). Compound **6b** was prepared by the method described for **6a** using trimethylaluminium (0.53 ml, 1.02 M in hexane, 0.54 mmol), 2,6-diphenylphenol (396 mg, 1.61 mmol) in CH_2Cl_2 (4 ml), **1a** (60 mg, 0.36 mmol), and phenyllithium (0.71 ml, 1.01 M in cyclohexane–Et_2O, 0.72 mmol). Purification by thin layer chromatography on silica gel (benzene–Et_2O 30:1) gave **6b** (33 mg, 0.15mmol, 43%) as a colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.89 (3H, t, *J* = 7.3 Hz), 1.35 (2H, tq, *J* = 7.3, 7.3 Hz), 1.51 (2H, tt, *J* = 7.3, 7.3 Hz), 2.49 (2H, t, *J* = 7.3 Hz), 3.51 (2H, t, *J* = 1.4 Hz), 5.47 (1H, t, *J* = 1.2 Hz), 6.17 (1H, dd, *J* = 2.7, 1.8 Hz), 7.40–7.52 (5H, m). ^{13}C NMR (126 MHz, $CDCl_3$) δ 13.9, 23.0, 24.3, 30.3, 35.4, 116.1, 127.5, 128.7, 129.5, 136.0, 141.5, 143.2, 161.1, 196.2. IR (neat) 2955, 1685, 1650, 1610, 1360, 1270, 1180, 1030, 930, 815, 760 cm^{-1}. MS (70 eV) *m/z* (rel intensity) 226 (M^+; 100), 197 (23). HRMS calcd for $C_{16}H_{18}O$ 226.1358 (M^+); found 226.1369.

2-Butyl-3-methoxy-5-methylene-2-cyclopenten-1-one (6c). TfOH (45 μl, 0.50 mmol) was added to a solution of **1a** (85 mg, 0.50 mmol) and methanol (20 μl, 0.50 mmol) in CH_2Cl_2 (5.0 ml) at room temperature under a nitrogen atmosphere. After the reaction mixture was stirred for 8 min, phosphate buffer (pH 7) was added to quench the reaction. Organic materials were extracted with CH_2Cl_2 three times. The combined extracts were washed with water, and then dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by thin layer chromatography on silica gel (Et_2O) to give **6c** (74 mg, 0.41 mmol, 82%) as a colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.89 (3H, t, *J* = 7.3 Hz), 1.30 (2H, tq, *J* = 7.3, 7.3 Hz), 1.41 (2H, tt, *J* = 7.3, 7.3 Hz), 2.20 (2H, t, *J* = 7.3 Hz), 3.28 (2H, s), 3.95 (3H, s), 5.29 (1H, d, *J* = 0.9 Hz), 6.05 (1H, br s). ^{13}C NMR (126 MHz, $CDCl_3$) δ 13.9, 21.2, 22.7, 30.1, 30.2, 56.7, 114.1, 123.3, 140.3, 181.0, 192.9. IR (neat) 2950, 1690, 1610, 1465, 1375, 1235, 1125, 1075, 1010, 930 cm^{-1}. MS (70 eV) *m/z* (rel intensity) 180 (M^+; 41), 151 (47), 138 (100), 123 (43), 109 (64). HRMS calcd for $C_{11}H_{16}O_2$ 180.1150 (M^+); found 180.1147.

2-Butyl-3-cyclohexyloxy-5-methylene-2-cyclopenten-1-one (6d). Compound **6d** was prepared by the method described for **6c** using TfOH (37 μl, 0.42 mmol), **1a** (70 mg, 0.42 mmol), and cyclohexanol (42 mg, 0.41 mmol) in CH_2Cl_2 (2.0 ml). Purification by thin layer chromatography on silica gel (Et_2O) gave **6d** (81 mg, 0.33 mmol, 79%) as a colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.89 (3H, t, *J* = 7.3 Hz), 1.29 (2H, tq, *J* = 7.3, 7.3 Hz), 1.32–1.48 (5H, m), 1.52–1.65 (3H, m), 1.76–1.92 (4H, m), 2.22 (2H, t, *J* = 7.3 Hz), 3.27 (2H, s), 4.32 (1H, tt, *J* = 8.5, 4.3 Hz), 5.25 (1H, d, *J* = 0.9 Hz), 6.01 (1H, d, *J* = 0.9 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 13.9, 21.2, 22.5, 23.4, 25.2, 29.9, 30.6, 32.8, 77.9, 113.4, 123.7, 140.7, 180.2, 193.0. IR (neat) 2930, 1685, 1605, 1450, 1390, 1370, 1220, 1125, 1015, 920 cm^{-1}. MS (70 eV) *m/z* (rel intensity) 248 (M^+; 19), 167 (62), 124 (100), 83 (19). HRMS calcd for $C_{16}H_{24}O_2$ 248.1776 (M^+); found 248.1796.

2-Butyl-5-methylene-3-(2-propynyloxy)-2-cyclopenten-1-one (6e). Compound **6e** was

prepared by the method described for **6c** using TfOH (34 μl, 0.39 mmol), **1a** (65 mg, 0.39 mmol), and 2-propynol (23 μl, 0.39 mmol) in CH_2Cl_2 (2.0 ml). Purification by thin layer chromatography on silica gel (Et_2O) gave **6e** (67 mg, 0.33 mmol, 85%) as a colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.89 (3H, t, *J* = 7.3 Hz), 1.30 (2H, tq, *J* = 7.3, 7.3 Hz), 1.43 (2H, tt, *J* = 7.3, 7.3 Hz), 2.22 (2H, t, *J* = 7.3 Hz), 2.66 (1H, t, *J* = 2.4 Hz), 3.41 (2H, d, *J* = 1.2 Hz), 4.79 (2H, d, *J* = 2.4 Hz), 5.31 (1H, d, *J* = 0.6 Hz), 6.06 (1H, d, *J* = 0.6 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 13.9, 21.2, 22.6, 30.0, 30.2, 56.9, 77.0, 77.6, 114.5, 124.8, 140.3, 179.1, 192.9. IR (neat) 3220, 2950, 2150, 1685, 1615, 1395, 1350, 1315, 1205, 1000, 925 cm^{-1}. MS (70 eV) *m/z* (rel intensity) 204 (M^+; 24), 162 (44), 123 (100), 77 (26). HRMS calcd for $C_{13}H_{16}O_2$ 204.1150 (M^+); found 204.1141.

2-Butyl-3-ethylthio-5-methylene-2-cyclopenten-1-one (6f). Compound **6f** was prepared by the method described for **6c** using TfOH (34 μl, 0.39 mmol), **1a** (65 mg, 0.39 mmol), and ethanethiol (29 μl, 0.39 mmol) in CH_2Cl_2–HFIP (1:1, 2.0 ml). Purification by thin layer chromatography on silica gel (hexane–Et_2O 1:1) gave **6f** (68 mg, 0.32 mmol, 84%) as a colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.91 (3H, t, *J* = 7.3 Hz), 1.32 (2H, tq, *J* = 7.3, 7.3 Hz), 1.38 (3H, t, *J* = 7.3 Hz), 1.41–1.48 (2H, m), 2.30 (2H, t, *J* = 7.3 Hz), 2.99 (2H, q, *J* = 7.3 Hz), 3.39 (2H, dd, *J* = 1.2, 1.2 Hz), 5.33 (1H, d, *J* = 0.9 Hz), 6.00 (1H, d, *J* = 0.9 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 13.9, 15.2, 22.8, 24.0, 24.8, 29.2, 34.4, 114.0, 140.9, 141.0, 166.6, 191.6. IR (neat) 2925, 1685, 1675, 1640, 1570, 1340, 1190, 1080, 1025, 925, 810 cm^{-1}. MS (70 eV) *m/z* (rel intensity) 210 (M^+; 4), 181 (100), 139 (22), 77 (7). HRMS calcd for $C_{12}H_{18}OS$ 210.1078 (M^+); found 210.1097.

2-Butyl-5-methylene-3-phenylthio-2-cyclopenten-1-one (6g). Compound **6g** was prepared by the method described for **6c** using TfOH (90 μl, 1.02 mmol), **1a** (86 mg, 0.51 mmol), and benzenethiol (53 μl, 0.51 mmol) in CH_2Cl_2–HFIP (1:1, 2.5 ml). Purification by thin layer chromatography on silica gel (hexane–Et_2O 5:1) gave **6g** (110 mg, 0.44mmol, 85%) as a

colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.95 (3H, t, *J* = 7.3 Hz), 1.38 (2H, tq, *J* = 7.3, 7.3 Hz), 1.52 (2H, tt, *J* = 7.3, 7.3 Hz), 2.40 (2H, t, *J* = 7.3 Hz), 2.90 (2H, s), 5.17 (1H, s), 5.95 (1H, d, *J* = 1.8 Hz), 7.40–7.49 (3H, m), 7.56 (2H, dd, *J* = 8.2, 1.5 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 13.9, 22.7, 24.0, 29.3, 35.2, 114.2, 128.4, 129.4, 129.8, 135.4, 140.9, 141.1, 165.9, 191.8. IR (neat) 2940, 1690, 1650, 1575, 1340, 1080, 1025, 950, 925, 750 cm^{-1}. MS (70 eV) *m/z* (rel intensity) 259 (M^++1; 100), 181 (73), 149 (37), 77 (24). HRMS calcd for $C_{16}H_{18}OS$ 258.1078 (M^+); found 258.1090.