Facile Synthesis of 2-Methylene-cyclobutanones via Ca(OH)$_2$-Catalyzed Direct Condensation of Cyclobutanone with Aldehydes and (PhSe)$_2$-Catalyzed Baeyer-Villiger Oxidation to 4-Methylenebutanolides

Lei Yu,*$^{a,b,c}$ Yulan Wu,$^a$ Hongen Cao,$^a$ Xu Zhang,$^{a,b}$ Xinkang Shi,$^b$ Jie Luan,$^a$ Tian Chen,$^a$ Yi Pan$^c$ and Qing Xu*,$^{b,c}$

$^a$ School of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou, Jiangsu 225002, People’s Republic of China
Fax: (+86)-514-8797-5244; phone: (+86)-136-652-95901; e-mail: yulei@yzu.edu.cn

$^b$ College of Chemistry and Materials Engineering, Wenzhou University, Wenzhou, Zhejiang 325035, People’s Republic of China
Fax: (+86)-577-8668-9302; phone: (+86)-138-577-45327; e-mail: qing-xu@wzu.edu.cn

$^c$ School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, Jiangsu 210089, People’s Republic of China

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Experimental Section

General Methods. The chemicals, cyclobutanone, aldehydes, bases, solvents, and organoselenium catalysts were all purchased. Liquid aldehydes were redistilled under vacuum before use. Solid aldehydes were recrystallized in EtOH/H₂O under N₂ before use. All reactions were monitored by TLC and/or GC analysis. GC yields were calculated according to the internal standard curve. (E)-2-Methylenecyclobutanones and (E)-4-methylenebutanolides were all purified by column chromatogram. ^1H and ^13C NMR and NOESY spectra were recorded on a Bruker Avance 600 instrument (600 MHz for ^1H and 150 MHz for ^13C NMR spectroscopy) by using CDCl₃ as the solvent and Me₄Si as the internal standard. Chemical shifts for ^1H and ^13C NMR were referred to internal Me₄Si (0 ppm) and J-values were shown in Hz. ^77Se NMR were recorded on an Agilent DD2 600 instrument (114 MHz) by using D₂O as the solvent. Melting points were measured using a WRS-2A digital instrument. Mass spectra were measured on a Thermo Trace DSQ II or a Shimadzu GCMS-QP2010 Ultra spectrometer (EI). Elemental analysis was performed on an Elementar Vario EL cube instrument. HRMS (ESI) analysis was measured on a Bruker microTOF-Q II instrument.

General Procedure for Preparation of (E)-2-MCBones. To a 10 mL round-bottomed flask was added 0.1 mmol of Ca(OH)₂. A solution of aldehyde (1.0 mmol) and cyclobutanone (3.0 mmol) in 3 mL of anhydrous ethanol were then injected via a syringe under N₂. The mixture was then stirred at 80 °C for 24 hours under N₂. The solvent was evaporated under vacuum and the residue was purified through flash column chromatogram (eluent: petroleum ether: EtOAc 9:1) to give (E)-3.

General Procedure for (PhSe)₂-Catalyzed Baeyer-Villiger Oxidation of (E)-2-MCBones to (E)-4-Methylenebutanolides with H₂O₂. (E)-2-MCBones (0.3 mmol) and (PhSe)₂ (0.015 mmol) were added to a reaction tube. A solution of H₂O₂ (1.5 mmol) in 1 mL of CH₃CN was then injected via a syringe. The mixture was then stirred at room temperature (ca. 30 °C) for 24 h. After the reaction completed as monitored by TLC, 2 mL of water was added and the mixture was extracted with EtOAc (2 mL × 3). The combined organic layer was dried over Na₂SO₄ and the solvent evaporated under vacuum. The residue was purified by flash column chromatogram (eluent: petroleum ether: EtOAc 8:1) to give (E)-4.
Table S1. Detailed Optimization of the Reaction Conditions for Preparation of \((E)-2\text{-MCBones} 3^a\).

![Chemical Structure](image)

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\(^b\) \(\text{NOE}_{\text{cat. base, solvent}}\)
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As indicated in the table, the mixture of excess 1, freshly distilled 2a (1 mmol), and catalytic amount of a base in a solvent was heated under N₂ and then monitored by GC. ^b^ GC yields (shown outside the parenthesis, using biphenyl as the internal standard) and isolated yields (shown in parenthesis) are based on 2a. As determined by NOESY analysis, only the (E)-stereomer of 3a was obtained.
Characterization of the Products

\( \text{Ph} \)

**(E)-2-Benzylidencyclobutanone ((E)-3a).** Soild. m.p. 88.7-90.3 °C. IR (KBr): 2976, 2932, 2866, 1737, 1645, 1449, 1384, 1228, 1176, 1113, 934, 759, 685 cm\(^{-1}\); \(^1\)H NMR (600 MHz, CDCl\(_3\), TMS): \(\delta\) 7.52–7.40 (m, 5H), 7.04 (t, \(J = 2.7\) Hz, 1H), 3.15 (t, \(J = 7.8\) Hz, 2H), 2.99 (dt, \(J = 2.4\) Hz, \(J = 8.4\) Hz, 2H); \(^13\)C NMR (150 MHz, CDCl\(_3\)): \(\delta\) 199.7, 146.2, 134.6, 130.1, 130.0, 128.9, 126.5, 45.8, 23.6; Anal. Calcd for C\(_{11}\)H\(_{10}\)O: C, 83.51; H, 6.37. Found: C, 83.67; H, 6.22. Known compound.\(^1\)

\( \text{Me} \)

**(E)-2-(4-Methylphenyl)methylenecyclobutanone ((E)-3b).** Soild. m.p. 84.3-85.7 °C. IR (KBr): 2928, 1736, 1646, 1603, 1448, 1103, 919, 810, 523, 498 cm\(^{-1}\); \(^1\)H NMR (600 MHz, CDCl\(_3\), TMS): \(\delta\) 7.41 (d, \(J = 8.4\) Hz, 2H), 7.21 (d, \(J = 7.8\) Hz, 2H), 7.02 (t, \(J = 2.7\) Hz, 1H), 3.13 (t, \(J = 7.8\) Hz, 2H), 2.97 (dt, \(J = 2.4\) Hz, \(J = 7.8\) Hz, 2H), 2.38 (s, 3H); \(^13\)C NMR (150 MHz, CDCl\(_3\)): \(\delta\) 199.7, 145.1, 140.6, 131.8, 130.1, 129.7, 126.6, 45.7, 23.5, 23.6; MS (EI, 70 eV): \(m/z\) (%) 172 (12, M\(^+\)), 157 (58), 129 (100); Anal. Calcd for C\(_{12}\)H\(_{12}\)O: C, 83.69; H, 7.02. Found: C, 83.84; H, 6.90.

\( \text{Me} \)

**(E)-2-(2-Methylphenyl)methylenecyclobutanone ((E)-3c).** Soild. m.p. 69.0-70.2 °C. IR (KBr): 2975, 2870, 1732, 1639, 1595, 1481, 1387, 1291, 1260, 1126, 1089, 1033, 889, 799, 763, 711, 491, 463 cm\(^{-1}\); \(^1\)H NMR (600 MHz, CDCl\(_3\), TMS): \(\delta\) 7.46 (d, \(J = 7.8\) Hz, 1H), 7.19–7.09 (m, 4H), 3.00 (t, \(J = 7.8\) Hz, 2H), 2.84 (dt, \(J = 3.0\) Hz, \(J = 7.8\) Hz, 2H), 2.29 (s, 3H); \(^13\)C NMR (150 MHz, CDCl\(_3\)): \(\delta\) 198.6, 145.4, 138.4, 131.8, 129.9, 128.9, 126.8, 125.2, 122.5, 44.5, 22.5, 18.7; MS (EI, 70 eV): \(m/z\) (%) 172 (12, M\(^+\)), 158 (12), 157 (100), 143 (10), 129 (90), 128 (46), 127 (15), 116 (31), 115 (65), 105 (14), 89 (9). HRMS calcd for C\(_{12}\)H\(_{13}\)O ([M+H\(^+\)]: 173.0961; found: 173.0975.
(E)-2-(2,4,6-Trimethylphenyl)methylene cyclobutanone ((E)-3d). Oil. IR (film): 2937, 1754, 1652, 1446, 1394, 1225, 1178, 1100, 1033, 852, 736, 668, 591, 564, 561 cm\(^{-1}\); \(^1\)H NMR (600 MHz, CDCl\(_3\), TMS): \(\delta\) 7.20 (t, \(J = 1.8\) Hz, 1H), 6.89 (s, 2H), 3.02 (t, \(J = 7.8\) Hz, 2H), 2.55 (dt, \(J = 2.4\) Hz, \(J = 7.8\) Hz, 2H), 2.29 (s, 3H), 2.25 (s, 6H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)):\(\delta\) 199.8, 149.1, 138.1, 136.6, 129.9, 128.6, 126.8, 44.1, 23.0, 21.1, 20.5; MS (EI, 70 eV): \(m/z\) (%) 200 (16, M\(^+\)), 185 (100), 157 (98); Anal. Calcd for C\(_{14}\)H\(_{16}\)O: C, 83.96; H, 8.05. Found: C, 83.79; H, 8.11.

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\[\text{Bu}^t\]

(E)-2-(4-tert-Butyl)methylene cyclobutanone ((E)-3e). Soild. m.p. 98.3-99.5 °C. IR (KBr): 2961, 2869, 1744, 1644, 1605, 1509, 1464, 1394, 1364, 1127, 1096, 900, 829, 561 cm\(^{-1}\); \(^1\)H NMR (600 MHz, CDCl\(_3\), TMS): \(\delta\) 7.47–7.42 (m, 4H), 7.02 (s, 1H), 3.13 (t, \(J = 7.5\) Hz, 2H), 2.97 (dt, \(J = 2.4\) Hz, \(J = 7.5\) Hz, 2H), 1.33 (s, 9H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)):\(\delta\) 199.7, 153.6, 145.3, 131.8, 130.0, 126.5, 126.0, 45.7, 35.0, 31.2, 23.5; MS (EI, 70 eV): \(m/z\) (%) 214 (9, M\(^+\)), 171 (36), 157 (100), 130 (34), 129 (91), 128 (38), 115 (38), 57 (32). HRMS calcd for C\(_{15}\)H\(_{19}\)O ([M+H\(^+\)]\(^{+}\)): 215.1430; found: 215.1428.

O
\[\text{OMe}\]

(E)-2-(4-Methoxyl)methylene cyclobutanone ((E)-3f). Soild. m.p. 79.0-79.6 °C. IR (KBr): 2932, 2840, 1731, 1644, 1600, 1569, 1512, 1462, 1423, 1388, 1305, 1259, 1175, 1122, 1026, 942, 902, 824, 761, 717, 589, 533, 501 cm\(^{-1}\); \(^1\)H NMR (600 MHz, CDCl\(_3\), TMS): \(\delta\) 7.43 (d, \(J = 8.4\) Hz, 2H), 6.95 (s, 1H), 6.90 (d, \(J = 8.4\) Hz, 2H), 3.81 (s, 3H), 3.07 (t, \(J = 7.8\) Hz, 2H), 2.88 (dt, \(J = 2.4\) Hz, \(J = 7.8\) Hz, 2H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)):\(\delta\) 198.8, 160.6, 143.1, 131.3, 126.7, 125.7, 114.0, 54.8, 45.0, 22.7; MS (EI, 70 eV): \(m/z\) (%) 188 (57, M\(^+\)), 187 (24), 160 (87), 159 (69), 157 (71), 145 (100), 129 (51), 117 (78), 115 (40), 89 (40), 77 (20), 63 (22). HRMS calcd for C\(_{12}\)H\(_{13}\)O\(_2\) ([M+H\(^+\)]\(^{+}\]): 189.0910; found: 189.0944.

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(E)-2-(Furan-2-yl)methylene cyclobutanone ((E)-3g). Soild. m.p. 59.4-60.5 °C. IR (KBr): 3116, 2937, 2251, 1734, 1639, 1474, 1390, 1328, 1224, 1177, 1108, 1016, 911, 819, 741, 684, 591, 534 cm\(^{-1}\); \(^1\)H NMR (600 MHz, CDCl\(_3\), TMS): \(\delta\) 7.56 (s, 1H), 6.85 (t, \(J = 3.0\) Hz, 1H), 6.66 (d, \(J = 3.0\) Hz, 1H).
Hz, 1H), 6.51 (t, J = 1.8 Hz, 1H), 3.08 (t, J = 7.8 Hz, 2H), 2.92 (dt, J = 2.4 Hz, J = 7.8 Hz, 2H); 
$^{13}$C NMR (150 MHz, CDCl$_3$): δ 199.1, 151.3, 145.3, 143.8, 115.9, 113.4, 112.5, 45.0, 22.9. MS (EI, 70 eV): m/z (%) 148 (39, M$^+$), 120 (85), 91 (100); Anal. Calcd for C$_9$H$_8$O$_2$: C, 72.96; H, 5.44. Found: C, 72.87; H, 5.48.

**O**

(\textit{E})-2-(Pyridine-2-yl)methylenecyclobutanone ((\textit{E})-3h). Soild. m.p. 81.6-82.9 °C. IR (KBr): 2978, 2934, 2870, 1777, 1750, 1654, 1584, 1467, 1434, 1386, 1294, 1224, 1109, 1084, 1020, 950, 907, 844, 777, 745, 612, 510 cm$^{-1}$; $^1$H NMR (600 MHz, CDCl$_3$, TMS): δ 8.68 (d, J = 4.2 Hz, 1H), 7.72 (t, J = 7.5 Hz, 1H), 7.47 (d, J = 7.8 Hz, 1H), 7.26-7.24 (m, 1H), 7.05 (d, J = 2.4 Hz, 1H), 3.17-3.11 (m, 4H); $^{13}$C NMR (150 MHz, CDCl$_3$): δ 200.1, 154.0, 150.6, 150.3, 136.4, 125.4, 125.1, 123.5, 46.0, 24.2; MS (EI, 70 eV): m/z (%) 159 (3, M$^+$), 131 (56), 130 (100), 103 (20), 78 (9), 77 (9), 76 (9), 52 (8), 51 (13). HRMS calcd for C$_{10}$H$_{10}$NO ([M+H$^+$]): 160.0757; found: 160.0745.

O

(\textit{E})-2-(Naphthalen-1-yl)methylenecyclobutanone ((\textit{E})-3i). Soild. m.p. 98.1-99.2 °C. IR (KBr): 3050, 2932, 1739, 1638, 1508, 1387, 1327, 1227, 1177, 1104, 881, 783, 735, 542, 429 cm$^{-1}$; $^1$H NMR (600 MHz, CDCl$_3$, TMS): δ 8.17 (d, J = 8.4 Hz, 1H), 7.91-7.88 (m, 3H), 7.80 (d, J = 4.2 Hz, 1H), 7.59-7.50 (m, 3H), 3.18 (t, J = 7.8 Hz, 2H), 3.02 (dt, J = 2.4 Hz, J = 7.8 Hz, 2H); $^{13}$C NMR (150 MHz, CDCl$_3$): δ 199.6, 147.6, 133.8, 132.5, 130.6, 129.0, 127.0, 126.6, 126.3, 125.3, 123.2, 122.6, 45.5, 23.7; MS (EI, 70 eV): m/z (%) 208 (47, M$^+$), 179 (100), 165 (88); Anal. Calcd for C$_{15}$H$_{12}$O: C, 86.51; H, 5.81. Found: C, 86.70; H, 5.66.

O

(\textit{E})-2-(4-Fluorophenyl)methylenecyclobutanone ((\textit{E})-3j). Soild. m.p. 89.1-90.1 °C. IR (KBr): 2935, 1735, 1644, 1594, 1507, 1392, 1294, 1225, 1159, 1106, 905, 833, 775, 526 cm$^{-1}$; $^1$H NMR (600 MHz, CDCl$_3$, TMS): δ 7.52-7.50 (m, 2H), 7.12-7.09 (m, 2H), 7.01 (t, J = 2.7 Hz, 1H), 3.16
(E)-2-(4-Chlorophenyl)methylene cyclobutanone ((E)-3k). Soild. m.p. 95.7-97.3 °C. IR (KBr): 2932, 1732, 1645, 1587, 1490, 1403, 1180, 1089, 1011, 892, 817, 703, 518, 491 cm⁻¹; ¹H NMR (600 MHz, CDCl₃, TMS): δ 7.44 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H), 6.98 (t, J = 2.7 Hz, 1H), 3.16 (t, J = 8.1 Hz, 2H), 2.97 (dt, J = 2.4 Hz, J = 8.4 Hz, 2H); ¹³C NMR (150 MHz, CDCl₃): δ 199.4, 163.6 (d, JCF = 250.7 Hz), 145.7, 132.0 (d, JCF = 8.4 Hz), 130.8 (d, JCF = 3.3 Hz), 125.2, 116.2 (d, JCF = 21.8 Hz), 45.8, 23.4; MS (EI, 70 eV): m/z (%) 176 (27, M⁺), 148 (100), 133 (96); Anal. Calcd for C₁₁H₉FO: C, 74.99; H, 5.15. Found: C, 75.08; H, 5.10.

(E)-2-(4-Bromophenyl)methylene cyclobutanone ((E)-3l). Soild. m.p. 62.1-63.5 °C. IR (KBr): 2927, 1780, 1728, 1640, 1484, 1396, 1176, 1117, 1093, 1069, 1006, 892, 813, 697, 515, 490 cm⁻¹; ¹H NMR (600 MHz, CDCl₃, TMS): δ 7.54 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H), 6.97 (t, J = 2.7 Hz, 1H), 3.16 (t, J = 8.1 Hz, 2H), 2.97 (dt, J = 2.4 Hz, J = 8.4 Hz, 2H); ¹³C NMR (150 MHz, CDCl₃): δ 199.3, 146.7, 136.0, 133.1, 131.2, 129.2, 125.1, 45.9, 23.5; MS (EI, 70 eV): m/z (%) 192 (8, M⁺), 157 (39), 129 (100). Known Compound.

(E)-2-(2-Bromophenyl)methylene cyclobutanone ((E)-3m). Oil. IR (film): 2926, 2177, 1740, 1637, 1461, 1429, 1388, 1277, 1229, 1172, 1126, 1087, 1020, 891, 755, 696, 501, 450 cm⁻¹; ¹H NMR (600 MHz, CDCl₃, TMS): δ 7.63 (t, J = 6.0 Hz, 2H), 7.44 (t, J = 2.7 Hz, 1H), 7.34 (t, J = 7.5 Hz, 1H), 7.23 (t, J = 7.5 Hz, 1H), 3.16 (t, J = 8.1 Hz, 2H), 2.97 (dt, J = 3.0 Hz, J = 8.4 Hz, 2H); ¹³C NMR (150 MHz, CDCl₃): δ 199.1, 148.2, 134.0, 133.7, 131.0, 129.1, 127.5, 127.1, 125.0, 45.8, 23.4; MS (EI, 70 eV): m/z (%) 236 (2, M⁺), 157 (54), 129 (100); Anal. Calcd for C₁₁H₉BrO: C, 55.72; H, 3.83. Found: C, 55.86; H, 3.91.
C_{11}H_{9}BrO: C, 55.72; H, 3.83. Found: C, 55.88; H, 3.84.

**(E)-2-(3-Bromophenyl)methylene cyclobutanone (**E-3n**).** Oil. IR (film): 1781, 1737, 1640, 1463, 1126, 1089, 1023, 757, 509, 450 cm\(^{-1}\); \(^1\)H NMR (600 MHz, CDCl\(_3\), TMS): \(\delta\) 7.63 (t, \(J = 6.0\) Hz, 2H), 7.44 (t, \(J = 2.7\) Hz, 1H), 7.34 (t, \(J = 7.2\) Hz, 1H), 7.23 (t, \(J = 7.8\) Hz, 1H), 3.16 (t, \(J = 7.8\) Hz, 2H), 2.97 (dt, \(J = 2.4\) Hz, \(J = 7.8\) Hz, 2H); \(^1\)C NMR (150 MHz, CDCl\(_3\)):

\(\delta\) 199.1, 148.2, 134.0, 133.7, 131.0, 129.1, 127.5, 127.1, 125.0, 45.8, 23.4; MS (EI, 70 eV): \(m/z\) (%) 236 (1, M\(^+\)), 157 (48), 129 (100); **Anal. Calcd for C_{11}H_{9}BrO: C, 55.72; H, 3.83. Found: C, 55.57; H, 3.68.**

**(E)-2-(4-Trifluoromethylphenyl)methylene cyclobutanone (**E-3o**).** Soild. m.p. 92.3-93.7 °C. IR (KBr): 2935, 1734, 1643, 1417, 1321, 1235, 1164, 1113, 1063, 1013, 910, 834, 735, 685, 596, 498 cm\(^{-1}\); \(^1\)H NMR (600 MHz, CDCl\(_3\), TMS): \(\delta\) 7.66 (d, \(J = 8.4\) Hz, 2H), 7.62 (d, \(J = 7.8\) Hz, 2H), 7.04 (t, \(J = 2.7\) Hz, 1H), 3.21 (t, \(J = 7.8\) Hz, 2H), 3.04 (dt, \(J = 2.4\) Hz, \(J = 7.8\) Hz, 2H); \(^1\)C NMR (150 MHz, CDCl\(_3\)):

\(\delta\) 199.1, 148.7, 138.0, 131.3 (d, \(J_{CF} = 32.7\) Hz), 130.0, 125.8 (m), 124.6, 46.1, 23.7; MS (EI, 70 eV): \(m/z\) (%) 226 (10, M\(^+\)), 198 (15), 170 (50), 157 (100). Known Compound.\(^1\)

**(E,E)-2-(3-Phenyl-allylidene)-cyclobutanone (**E,E-3p**).** Soild. m.p. 72.5-73.5 °C. IR (KBr): 3061, 3027, 2973, 2933, 1724, 1675, 1626, 1449, 1391, 1103, 970, 737, 688, 515 cm\(^{-1}\); \(^1\)H NMR (600 MHz, CDCl\(_3\), TMS): \(\delta\) 7.40-7.22 (m, 5H), 6.85 (d, \(J = 15.6\) Hz, 1H), 6.73 (d, \(J = 11.4\) Hz, 1H), 6.66 (dd, \(J = 11.4\) Hz, \(J = 15.0\) Hz, 1H); \(^1\)C NMR (150 MHz, CDCl\(_3\)):

\(\delta\) 199.1, 147.6, 142.5, 136.2, 129.2, 128.9, 127.2, 126.6, 123.5, 43.8, 20.8; MS (EI, 70 eV): \(m/z\) (%) 184 (70, M\(^+\)), 156 (83), 155 (66), 141 (100), 128 (95), 127 (40), 115 (67), 102 (27), 91 (40), 78 (27), 77 (28). HRMS calcd for C_{13}H_{13}O ([M+H]\(^+\]): 185.0961; found: 185.0983.
(E)-2-Cyclohexylcyclobutanone ((E)-3q). Oil. IR (film): 2928, 2853, 1756, 1665, 1448, 1393, 1231, 1110, 1088, 963, 901, 734 cm⁻¹; ¹H NMR (600 MHz, CDCl₃, TMS): δ 6.15 (dt, J = 2.7 Hz, J = 8.4 Hz, 1H), 2.92 (t, J = 7.8 Hz, 2H), 2.63 (td, J = 2.4 Hz, J = 7.8 Hz, 2H), 2.15-2.10 (m, 1H), 1.76-1.71 (m, 4H), 1.33-1.18 (m, 6H); ¹³C NMR (150 MHz, CDCl₃): δ 200.1, 146.0, 135.7, 43.8, 38.2, 31.7, 25.8, 25.5, 20.6; MS (EI, 70 eV): m/z (%) 164 (9, M⁺), 163 (14), 136 (17), 135 (100), 107 (26), 93 (22), 81 (32), 80 (14), 79 (54), 67 (22), 55 (21). HRMS calcd for C₁₁H₁₇O ([M+H]⁺): 165.1274; found: 165.1275.

(E)-4-Benzylidenebutanolide ((E)-4a). Soild. m.p. 94.2-95.7 °C. IR (KBr): 2944, 1801, 1676, 1445, 1371, 1295, 1233, 1173, 1125, 1012, 935, 912, 871, 821, 757, 693, 611, 570, 548, 516, 468, 446, 425 cm⁻¹; ¹H NMR (600 MHz, CDCl₃, TMS): δ 7.36-7.33 (m, 2H), 7.23-7.22 (m, 3H), 6.33 (t, J = 1.8 Hz, 1H), 3.17 (dt, J = 1.8 Hz, J = 8.4 Hz, 2H), 2.75 (t, J = 8.7 Hz, 2H). ¹³C NMR (150 MHz, CDCl₃): δ 174.2, 151.1, 134.4, 128.7, 127.8, 126.7, 107.1, 27.8, 25.1; MS (EI, 70 eV): m/z (%) 174 (100, M⁺), 145 (46); Anal. Calcd for C₁₁H₁₀O₂: C, 75.84; H, 5.79. Found: C, 75.93; H, 5.88. Known Compound.²,³

(E)-4-(4-Methylphenyl)methylenebutanolide ((E)-4b). Soild. m.p. 91.3-92.5 °C. IR (KBr): 2922, 1796, 1671, 1609, 1513, 1443, 1417, 1292, 1210, 1170, 1125, 933, 886, 808, 715, 520, 488 cm⁻¹; ¹H NMR (600 MHz, CDCl₃, TMS): δ 7.15 (d, J = 7.8 Hz, 2H), 7.12 (d, J = 7.8 Hz, 2H), 6.29 (s, 1H), 3.14 (t, J = 8.4 Hz, 2H), 2.74 (t, J = 8.4 Hz, 2H), 2.34 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ 174.3, 150.5, 136.5, 130.2, 129.4, 127.7, 107.0, 27.8, 25.1, 21.2; MS (EI, 70 eV): m/z (%) 188 (100, M⁺), 145 (52), 132 (78); Anal. Calcd for C₁₂H₁₂O₂: C, 76.57; H, 6.43. Found: C, 76.75; H, 6.50.
\textbf{(E)-4-(2-Methylphenyl)methylenebutanolide ((E)-4c).} Oil. IR (film): 2930, 1803, 1730, 1675, 1601, 1485, 1460, 1415, 1381, 1293, 1161, 1121, 1090, 932, 842, 752, 725, 664, 617, 546, 494, 450 cm\(^{-1}\); \(^1\)H NMR (600 MHz, CDCl\(_3\), TMS): \(\delta\) 7.13-7.08 (m, 4H), 6.30 (s, 1H), 2.96 (dt, \(J = 1.8\) Hz, \(J = 8.4\) Hz, 2H), 2.63 (t, \(J = 8.4\) Hz, 2H), 2.21 (s, 3H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)): \(\delta\) 174.4, 151.0, 136.7, 133.0, 127.5, 127.1, 125.9, 105.2, 27.9, 24.7, 20.0; MS (EI, 70 eV): \(m/z\) (%) 188 (100, M\(^+\)), 145 (48), 132 (21), 129 (19), 128 (20), 117 (20), 105 (36), 104 (53), 103 (22), 78 (26), 77 (21). HRMS calcld for \(\text{C}_{12}\text{H}_{13}\text{O}_2\) ([M+H]\(^+\)) 189.0910; found: 189.0944.

\begin{center}
\includegraphics[width=0.2\textwidth]{image1.png}
\end{center}

\textbf{(E)-4-(2,4,6-Trimethylphenyl)methylenebutanolide ((E)-4d).} Soild. m.p. 93.6-94.5 °C. IR (KBr): 2922, 1803, 1690, 1612, 1446, 1380, 1340, 1291, 1161, 1106, 1026, 923, 852, 740, 671, 564, 473 cm\(^{-1}\); \(^1\)H NMR (600 MHz, CDCl\(_3\), TMS): \(\delta\) 6.88 (s, 2H), 6.15 (s, 1H), 2.66 (t, \(J = 8.4\) Hz, 2H), 2.55 (dt, \(J = 2.4\) Hz, \(J = 8.4\) Hz, 2H), 2.28 (s, 3H), 2.20 (s, 6H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)): \(\delta\) 174.8, 150.6, 136.9, 136.7, 129.2, 128.3, 104.0, 27.9, 23.7, 21.0, 20.3; MS (EI, 70 eV): \(m/z\) (%) 216 (100, M\(^+\)), 173 (44), 157 (52); \textit{Anal.} Calcld for \(\text{C}_{14}\text{H}_{16}\text{O}_2\): C, 77.75; H, 7.46. Found: C, 77.89; H, 7.58.

\begin{center}
\includegraphics[width=0.2\textwidth]{image2.png}
\end{center}

\textbf{(E)-4-(4-tert-Butylphenyl)methylenebutanolide ((E)-4e).} Soild. m.p. 92.6-93.5 °C. IR (KBr): 2963, 2868, 1800, 1737, 1676, 1602, 1512, 1461, 1361, 1292, 1266, 1171, 1104, 1015, 936, 888, 807, 559 cm\(^{-1}\); \(^1\)H NMR (600 MHz, CDCl\(_3\), TMS): \(\delta\) 7.36 (d, \(J = 8.4\) Hz, 2H), 7.16 (d, \(J = 7.8\) Hz, 2H), 6.30 (s, 1H), 3.16 (dt, \(J = 1.8\) Hz, \(J = 8.4\) Hz, 2H), 2.74 (t, \(J = 8.4\) Hz, 2H), 1.32 (s, 9H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)): \(\delta\) 174.3, 150.6, 149.7, 131.4, 127.5, 125.6, 106.8, 34.6, 31.3, 27.8, 25.1; MS (EI, 70 eV): \(m/z\) (%) 230 (27, M\(^+\)), 216 (16), 215 (100), 159 (13), 145 (9), 131 (13), 115 (10), 91 (9), 55 (8). HRMS calcld for \(\text{C}_{15}\text{H}_{19}\text{O}_2\) ([M+H]\(^+\)) 231.1380; found: 231.1375.

\begin{center}
\includegraphics[width=0.2\textwidth]{image3.png}
\end{center}
**O**

**OMe**

(E)-4-(4-Methoxyphenyl)methylenebutanolide ((E)-4f). Oil. IR (film): 2938, 2836, 1795, 1679, 1603, 1511, 1443, 1360, 1297, 1233, 1178, 1101, 1033, 939, 828, 733, 523 cm⁻¹; ¹H NMR (600 MHz, CDCl₃, TMS): δ 7.14 (d, J = 8.4 Hz, 2H), 6.88 (d, J = 9.0 Hz, 2H), 6.27 (s, 1H), 3.81 (s, 3H), 3.11 (dt, J = 1.8 Hz, J = 8.4 Hz, 2H), 2.73 (t, J = 8.4 Hz, 2H); ¹³C NMR (150 MHz, CDCl₃): δ 174.7, 149.9, 129.0, 116.1, 114.9, 114.2, 106.6, 55.8, 42.0, 25.0; MS (EI, 70 eV): m/z (%) 204 (100, M⁺), 148 (66), 134 (32), 133 (16), 121 (24), 120 (50), 119 (12), 91 (27), 77 (27), 51 (19). HRMS calcd for C₁₂H₁₃O₃ ([M+H⁺]): 205.0859; found: 205.0872.

**O**

**O**

(E)-4-(Naphthalen-1-yl)methylenebutanolide ((E)-4i). Solid. m.p. 102.3-103.6 °C. IR (KBr): 2977, 2902, 1803, 1675, 1453, 1400, 1293, 1259, 1166, 1106, 1081, 1048, 927, 880, 780 cm⁻¹; ¹H NMR (600 MHz, CDCl₃, TMS): δ 7.35-7.99 (m, 7H), 6.85 (s, 1H), 3.01-3.04 (t, J = 8.4 Hz, 2H), 2.70-2.73 (t, J = 8.4 Hz, 2H); ¹³C NMR (150 MHz, CDCl₃): δ 174.5, 152.0, 131.0, 128.6, 127.8, 126.3, 126.1, 125.7, 125.3, 124.3, 104.2, 27.8, 24.6; MS (EI, 70 eV): m/z (%) 224 (3, M⁺), 207 (38), 57 (100); Anal. Calcd for C₁₅H₁₂O₂: C, 80.34; H, 5.39. Found: C, 80.46; H, 5.18.

**O**

**F**

(E)-4-(4-Fluorophenyl)methylenebutanolide ((E)-4j). Solid. m.p. 93.5-94.6 °C. IR (KBr): 2929, 2268, 1788, 1672, 1508, 1416, 1292, 1220, 1176, 1105, 929, 878, 837, 741, 655, 524, 483 cm⁻¹; ¹H NMR (600 MHz, CDCl₃, TMS): δ 7.17-7.20 (m, 2H), 7.03-7.06 (m, 2H), 6.30 (s, 1H), 3.13 (dt, J = 1.8 Hz, J = 8.4 Hz, 2H), 2.75-2.78 (t, J = 8.4 Hz, 2H); ¹³C NMR (150 MHz, CDCl₃): δ 174.0, 161.4 (d, J_CF = 245.4 Hz), 150.8, 130.4 (d, J_CF = 3.3 Hz), 129.3 (d, J_CF = 7.8 Hz), 115.6 (d, J_CF = 21.3 Hz), 106.0, 27.7, 25.0; MS (EI, 70 eV): m/z 192 (88, M⁺), 136 (82), 108 (100); Anal. Calcd for C₁₁H₉FO₂: C, 68.74; H, 4.72. Found: C, 68.58; H, 4.63.

S12.
(E)-4-(4-Bromophenyl)methylenebutanolide ((E)-4I). Solid. m.p. 67.3-68.4 °C. IR (KBr): 2927, 1803, 1587, 1489, 1443, 1402, 1293, 1167, 1098, 1075, 1009, 969, 942, 912, 873, 832, 805, 740, 651, 559, 512 cm⁻¹; ¹H NMR (600 MHz, CDCl₃, TMS): δ 7.46 (d, J = 8.4 Hz, 2H), 7.08 (d, J = 8.4 Hz, 2H), 6.26 (s, 1H), 3.13 (t, J = 7.8 Hz, 2H), 2.77 (t, J = 8.7 Hz, 2H); ¹³C NMR (150 MHz, CDCl₃): δ 173.9, 151.7, 133.3, 131.8, 129.8, 129.3, 106.1, 27.6, 25.1; MS (EI, 70 eV): m/z 252 (18, M⁺), 89 (100); Anal. Calcd for C₁₁H₉BrO₂: C, 52.20; H, 3.58. Found: C, 52.08; H, 3.43.

(E)-4-(2-Bromophenyl)methylenebutanolide ((E)-4m). Oil. IR (film): 2976, 1806, 1676, 1563, 1468, 1437, 1297, 1161, 1123, 1102, 1025, 935, 837, 757, 662, 507 cm⁻¹; ¹H NMR (600 MHz, CDCl₃, TMS): δ 7.61 (d, J = 7.2 Hz, 1H), 7.24-7.29 (m, 2H), 7.10-7.13 (m, 1H), 6.50 (s, 1H), 3.04-3.08 (m, 2H), 2.72-2.75 (m, 2H); ¹³C NMR (150 MHz, CDCl₃): δ 174.0, 152.2, 134.3, 133.1, 128.8, 128.4, 127.3, 124.5, 106.6, 27.6, 24.7; MS (EI, 70 eV): m/z 252 (32, M⁺), 296 (38), 89 (100); Anal. Calcd for C₁₁H₉BrO₂: C, 52.20; H, 3.58. Found: C, 52.37; H, 3.62.

(E)-4-(3-Bromophenyl)methylenebutanolide ((E)-4n). Oil. IR (film): 2974, 1806, 1676, 1468, 1437, 1297, 1161, 1123, 1102, 1024, 934, 836, 757, 663, 507, 447 cm⁻¹; ¹H NMR (600 MHz, CDCl₃, TMS): δ 7.61 (d, J = 2.4 Hz, 1H), 7.25-7.29 (m, 2H), 7.10-7.12 (m, 1H), 6.50 (s, 1H), 3.05 (dt, J = 2.4 Hz, J = 7.8 Hz, 2H), 2.73 (t, J = 7.2 Hz, 2H); ¹³C NMR (150 MHz, CDCl₃): δ 172.1, 150.4, 132.4, 131.2, 126.9, 126.5, 125.4, 122.6, 104.7, 25.7, 22.8; MS (EI, 70 eV): m/z 252 (31, M⁺), 196 (20), 89 (100); Anal. Calcd for C₁₁H₉BrO₂: C, 52.20; H, 3.58. Found: C, 52.28; H, 3.73.
(E)-4-Cyclopropylidenebutanolide ((E)-4q). Oil. IR (film): 2925, 2851, 1797, 1696, 1447, 1418, 1379, 1345, 1295, 1238, 1175, 1139, 1091, 1012, 975, 911, 839, 664, 581, 536, 454 cm⁻¹; ¹H NMR (600 MHz, CDCl₃, TMS): δ 5.09 (d, J = 10.2 Hz, 1H), 2.84 (t, J = 8.4 Hz, 2H), 2.66 (t, J = 8.4 Hz, 2H), 1.99-1.93 (m, 1H), 1.74-1.64 (m, 4H), 1.31-1.08 (m, 6H); ¹³C NMR (150 MHz, CDCl₃): δ 175.1, 147.9, 110.7, 35.4, 33.3, 27.8, 25.9, 22.6; MS (EI, 70 eV): m/z (%) 180 (43, M⁺), 137 (100), 109 (56), 95 (65), 82 (66), 81 (92), 80 (51), 67 (50), 55 (67). HRMS calcd for C₁₁H₁₇O₂ ([M+H]+): 181.1223; found: 181.1229.

References
2. WSS: Spectral data were obtained from Wiley Subscription Services, Inc. (US).
NOESY Spectra of Product (E)-3a and Determination of the Products’ Stereochemistry

1) As shown in the following NOESY spectra of 3a, the strong correlation between an aromatic proton (7.40 ppm) and the protons of cyclic CH\textsubscript{2} (2.99 ppm) confirmed that they are in a syn-position, indicating that product 3a is the (E)-stereomer.

2) On the contrary, obviously there is no correlation between the vinylic proton (7.04 ppm) and the protons of cyclic CH\textsubscript{2} (2.99 ppm), implying that they are in an anti-position, which also indicated that product 3a is the (E)-stereomer.

3) The stereochemistry of products (E)-3a, 3g, and 3k were also confirmed by the literature data (J. Am. Chem. Soc. 2005, 127, 9708).

4) The stereochemistry of other products (E)-3 can be inferred analogously by comparing their NMR spectra and chemical shifts of the corresponding protons with those of 3a, 3g and 3k.
**77Se NMR Spectroscopic Analysis of the Involved Organoselenium Species**

**Step 1.** Determined chemical shift of pure benzeneseleninic acid PhSe(O)OH (A) in D₂O is 1171 ppm, which is consistent with the literature data (1182 ppm, see: D. Dowd, P. Gettins, *Magn. Reson. Chem.* 1988, 26, 1).

![Diagram of benzeneseleninic acid PhSe(O)OH (A)](image)

**Step 2.** Literature chemical shift of the unstable benzeneseleninoperoxoic acid PhSe(O)OOH (B) is not available, but it was reported that B could be obtained from A by treatment with H₂O₂ (see: L. Syper, J. Mlochowski, *Tetrahedron* 1987, 43, 207). As shown below, by treating A with H₂O₂ in D₂O, a new peak at 1024 ppm was detected, which is most possibly the chemical shift of B.

![Diagram of reactions involving PhSe(O)OH (A) and H₂O₂ to form PhSe(O)OOH (B)](image)
Step 3. By treating (PhSe)$_2$ with H$_2$O$_2$ in D$_2$O, a new peak at 1248 ppm was detected, which, consists with the literature data (1241 ppm, see: http://www.chem.wisc.edu/areas/reich/handouts/nmr/se-data.htm) of benzeneseleninoperoxoic anhydride [PhSe(O)O]$_2$O (C), is thus most possibly the chemical shift of C.

\[
\begin{align*}
(\text{PhSe})_2 + \text{H}_2\text{O}_2, \text{ in D}_2\text{O} & \rightarrow [\text{PhSe(O)}\text{O}]_2\text{O} (C) \\
\text{Detd.: 1248 ppm} & \\
\text{Lit.:}^{25} 1241 \text{ ppm}
\end{align*}
\]

Step 4. After standing for 24 h, the chemical shifts of the above sample (in step 3) changed a lot. As shown below, the peak of [PhSe(O)O]$_2$O (C) disappeared and that of B (1024 ppm) appeared as the major one, with generation of small amounts of A (1173 ppm).

\[
\begin{align*}
[\text{PhSe(O)}\text{O}]_2\text{O} (C) + \text{H}_2\text{O} & \rightarrow \text{B} \quad \text{standing, 24 h} \\
\text{B} & \rightarrow \text{A}
\end{align*}
\]
Step 5. On the other hand, as shown below, vigorous stirring of the mixture of (PhSe)$_2$ and H$_2$O$_2$ (5 equiv.) in CH$_3$CN for 4 h could directly afford A and B without the detection of C.

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$^1$H and $^{13}$C NMR Spectra of Products (E)-3 and (E)-4

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$\text{CDCl}_3$, 600 MHz

$\text{CDCl}_3$, 150 MHz

S3
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S40.