Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

SUPPORTING INFORMATION

On the Nature of the Reactive Intermediates in Gold Catalyzed Cycloisomerization Reactions

Alois Fürstner and Louis Morency*

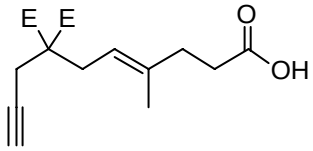
Max-Planck-Institut für Kohlenforschung, D-45470 Mülheim/Ruhr, Germany

E-mail: fuerstner@mpi-muelheim.mpg.de

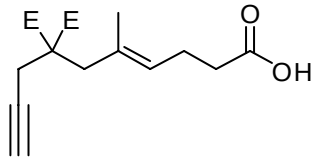
General. All reactions were carried out under Ar. The solvents used were purified by distillation over the drying agents indicated and were transferred under Ar: CH_2Cl_2 (P_4O_{10}), toluene (Na/K). Flash chromatography: Merck silica gel 60 (230–400 mesh). NMR: Spectra were recorded on a DPX 300, AV 400 or DMX 600 spectrometer (Bruker) in the solvents indicated; chemical shifts (δ) are given in ppm relative to residual solvent peaks, coupling constants (*J*) in Hz. IR: Nicolet FT-7199 spectrometer, wavenumbers in cm^{-1}. MS (EI): Finnigan MAT 8200 (70 eV), ESI: Finnigan MAT 95, accurate mass determination: Finnigan MAT 95, Bruker APEX III FT-ICR-MS (7 T magnet). Melting points: Büchi melting point apparatus (corrected). Elemental analyses: H. Kolbe, Mülheim/Ruhr.

Starting Materials

Compound 8. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.98 (t, *J* = 6.5 Hz, 1H), 3.73 (s, 6H), 2.79 (d, *J* = 8.0 Hz, 2H), 2.75 (d, *J* = 2.7 Hz, 2H), 2.47-2.42 (m, 2H), 2.34-2.29 (m, 2H), 2.01 (t, *J* = 2.6 Hz, 1H), 1.67 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 179.6, 179.5, 170.7, 138.9, 118.5, 79.5, 71.7, 57.4, 53.1, 34.9, 33.1, 31.0, 23.0, 16.5; IR (film): $\tilde{\nu}$ = 3500-2500, 3289, 2955, 2122, 1738, 1437, 1224 cm^{-1}; MS (EI): *m/z* (%): 265 (8) [M^+ -OMe], 257 (34), 236 (57), 225 (100), 204 (69), 170 (91); HRMS: *m/z*: calcd for $C_{15}H_{20}O_6$+Na: 319.11521; found: 319.11498.



Compound *E*-10. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.60 (br s, 1H), 5.31 (t, *J* = 5.9 Hz, 1H), 3.72 (s, 6H), 2.80 (s, 2H), 2.76 (d, *J* = 2.6 Hz, 2H), 2.41-2.36 (m, 1H), 2.37 (d, *J* = 5.7 Hz, 1H), 2.34-2.30 (m, 2H), 2.03 (t, *J* = 2.6 Hz, 1H), 1.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 179.0, 170.6, 131.1, 128.6, 79.2, 71.7, 56.7, 52.7, 41.4, 33.7, 23.3, 22.5, 16.7; IR (film): $\tilde{\nu}$ = 3290, 2954, 1735, 1709, 1436, 1289, 1200 cm^{-1}; MS (EI): *m/z* (%): 257 (1) [M^+ -CH_2CCH], 247 (32), 236 (32), 219 (14), 205 (47), 187 (28), 177 (54) 170 (100); HRMS: *m/z*: calcd for $C_{15}H_{20}O_6$+Na: 319.11521; found: 319.11524.



Compound *Z*-10. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.26 (t, *J* = 5.6 Hz, 1H), 3.68 (s, 6H), 2.85 (s, 2H), 2.71 (d, *J* = 2.6 Hz, 2H), 2.37-2.29 (m, 4H), 1.97 (t, *J* = 2.6 Hz, 1H), 1.53 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 178.8, 170.7, 130.8, 129.5, 79.3, 71.7, 56.5, 52.8, 34.0, 23.9, 23.4, 22.8; IR (film): $\tilde{\nu}$ 3292, 2955, 1736, 1201 cm^{-1}; MS (EI): *m/z* (%): 237 (18) [M^+ -CO_2Me], 253 (14), 219 (17), 205 (52), 187 (52), 177 (56), 170 (100); HRMS: *m/z*: calcd for $C_{15}H_{20}O_6$+Na: 319.11521; found: 319.11506.

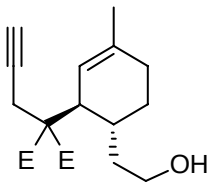
Compound 13. White solid; m.p. = 110-112 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 5.90-5.88 (m, 1H), 5.64-5.61 (m, 1H), 3.72 (s, 6H), 2.94 (dd, *J* = 17.4, 2.7 Hz, 1H), 2.87 (dd, *J* = 17.4, 2.7 Hz, 1H), 2.80 (s, 1H), 2.58-2.56 (m, 1H), 2.48 (dd, *J* = 14.8, 6.0 Hz, 1H), 2.37 (dd, *J* = 14.9, 9.4 Hz, 1H), 2.01 (t, *J* = 2.7 Hz, 1H), 1.95-1.94 (m, 1H), 1.93-1.91 (m, 1H), 1.56-1.54 (m, 1H), 1.35-1.29 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 178.3, 170.3, 169.9, 130.3, 123.5, 78.9, 71.8, 60.7, 52.7, 52.6, 41.2, 38.7, 29.6, 23.4, 22.1, 20.0; IR (film): $\tilde{\nu}$ = 3500-2200, 3290,2953, 2122, 1733, 1708, 1228, 707 cm^{-1}; MS (EI): *m/z* (%): 269 (7) [M^+-CH_2CCH], 249 (27), 248 (37), 216 (60), 170 (100), 129 (54); HRMS: *m/z*: calcd for $C_{16}H_{19}O_6$: 307.11864; found: 307.11872; elemental analysis calcd (%) for $C_{16}H_{20}O_6$: C 62.33; H 6.54, found: C 62.30; H 6.48.

Compound 16. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.52 (s, 1H), 3.74 (s, 3H), 3.67 (s, 3H), 2.91-2.89 (m, 3H), 2.50-2.47 (m, 1H), 2.34 (d, *J* = 5.1 Hz, 1H), 2.32 (d, *J* = 6.6 Hz, 1H), 2.00 (t, *J* = 2.6 Hz, 1H), 1.93 (s, 2H), 1.68 (d, *J* = 1.4 Hz, 3H), 1.63-1.54 (m, 1H), 1.48-1.40 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.9, 170.9, 170.6, 131.0, 125.6, 79.6, 71.2, 60.8, 52.7, 52.2, 45.7, 38.2, 30.1, 25.3, 24.4, 20.7, 20.6; IR (film): $\tilde{\nu}$ = 3285, 2952, 1730, 1706, 1202, 1179 cm^{-1}; MS (EI): *m/z* (%): 322 (1) [M^+], 291 (3), 283 (5), 263 (18), 231 (7), 203 (10), 170 (40), 93 (100); HRMS: *m/z*: calcd for $C_{17}H_{22}O_6$+Na: 345.13086; found: 345.13067.

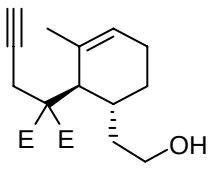
Compound 18. White solid; m.p. = 119-122°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.30-5.29 (m, 1H), 3.72 (s, 3H), 3.71 (s, 3H), 2.88 (dd, *J* = 17.3, 2.7 Hz, 1H), 2.83 (dd, *J* = 17.3, 2.7 Hz, 1H), 2.80 (s, 1H), 2.53-2.49 (m, 1H), 2.48-2.43 (m, 1H), 2.32 (dd, *J* = 14.6, 9.2 Hz, 1H), 2.00 (t, *J* = 2.6 Hz, 1H), 1.95-1.86 (m, 1H), 1.76 (dd, *J* = 18.0, 5.4 Hz, 1H), 1.68 (s, 3H), 1.58-1.53 (m, 1H), 1.41-1.32 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.8, 170.5, 170.0, 137.4, 79.2, 71.5, 60.8, 52.6, 41.8, 38.7, 29.1, 24.9, 24.2, 23.3, 22.8; IR (film): $\tilde{\nu}$ = 3287, 2953, 1729, 1706, 1227, 1202 cm^{-1}; MS (EI): *m/z* (%): 322 (2) [M^+], 304 (4), 283 (2), 263 (14), 262 (29), 251 (32), 230 (47), 202 (32), 93 (100); HRMS: *m/z*: calcd for $C_{17}H_{22}O_6$+Na: 345.13086; found: 345.13084.

Compound 20a. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.86-5.82 (m, 1H), 5.49-5.46 (m, 1H), 3.80-3.79 (m, 1H), 3.68 (s, 3H), 3.66 (s, 3H), 3.66-3.64 (m, 1H), 2.94 (dd, *J* = 17.3, 2.7 Hz, 1H), 2.85 (s, 1H), 2.77 (dd, *J* = 17.4, 2.7 Hz, 1H), 2.35 (br s, 1H), 2.26-2.24 (m, 1H), 1.97 (t, *J* = 2.7 Hz, 1H), 1.90-1.85 (m, 2H), 1.55-1.51 (m, 2H), 1.35-1.30 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.7, 169.8, 130.5, 122.7, 78.7, 71.2, 60.1, 59.8, 52.4, 52.3, 38.7, 36.4, 27.6, 23.3, 23.0, 19.9; IR (film): $\tilde{\nu}$ = 3553, 3288, 2951, 1731, 1226 cm^{-1}; MS (EI): *m/z* (%): 294 (10) [M^+], 255 (30), 235 (35), 223 (92), 217 (17), 202 (35), 191 (65), 79 (100); HRMS: *m/z*: calcd for $C_{16}H_{22}O_5$+Na: 317.13594; found: 317.13624; elemental analysis calcd (%) for $C_{16}H_{22}O_5$: C 65.29; H 7.53, found: C 65.22; H 7.76.

Compound 20b. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.21-5.30 (m, 1H), 3.91-3.84 (m, 1H), 3.75 (s, 3H), 3.73-3.66 (m, 1H), 3.72 (s, 3H), 3.01 (dd, *J* = 17.3, 2.7 Hz, 1H), 2.92 (br s, 1H), 2.80 (dd, *J* = 17.3, 2.6 Hz, 1H), 2.28-2.27 (m, 1H), 2.03 (t, *J* = 2.7 Hz, 1H), 1.92-1.87 (m, 1H), 1.77-1.73 (m, 1H), 1.69 (s, 3H), 1.57-1.41 (m, 2H), 1.44-1.40 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3, 170.4, 138.0, 116.9, 79.3, 71.4, 60.6, 60.2, 52.8, 52.6, 39.5, 36.8, 27.4, 25.2, 24.5, 24.3, 23.2; IR (film): $\tilde{\nu}$ = 2952, 1731, 1435, 1269, 1221 cm^{-1}.

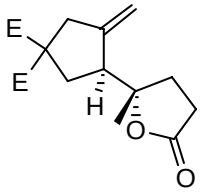


Compound 22. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.51 (s, 1H), 3.77-3.71 (m, 1H), 3.73 (s, 3H), 3.70-3.63 (m, 1H), 3.66 (s, 3H), 2.93 (s, 1H), 2.89 (d, *J* = 2.7 Hz, 2H), 2.18-2.13 (m, 1H), 2.02 (t, *J* = 2.6 Hz, 1H), 1.94-1.87 (m, 2H), 1.80 (s, 1H), 1.67 (q, *J* = 1.7 Hz, 3H), 1.65-1.59 (m, 1H), 1.51 (dd, *J* = 6.5 Hz, 2H), 1.36-1.31 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.2, 130.7, 126.3, 80.1, 71.1, 60.8, 60.7, 52.7, 52.3, 44.5, 36.5, 29.1, 25.5, 24.1, 21.7, 20.9; IR (film): $\tilde{\nu}$ = 3285, 2951, 1729, 1274, 1261, 1202 cm^{-1}; MS (EI): *m/z* (%): 308 (4) [M^+], 277 (2), 269 (4), 249 (26), 217 (11), 171 (45), 138 (100); HRMS: *m/z*: calcd for $C_{17}H_{24}O_5$+Na: 331.15160; found: 331.15193.

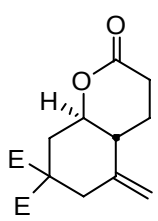


Gold Catalyzed Cycloisomerization Reactions

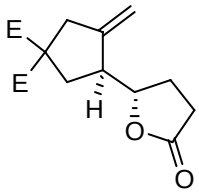
Representative Procedure. Preparation of Compound 9. A solution of [Au(PPh_3)Cl] (5 mg, 0.01 mmol) and $AgSbF_6$ (4 mg, 0.01 mmol) in dichloromethane (7 mL) was added via cannula to enyne **8** (112 mg, 0.37 mmol) and the resulting mixture was stirred for 30 minutes at room temperature. The reaction was filtered through a plug of SiO_2, the filtrate was evaporated and the crude product purified by flash column chromatography (30% *v/v* EtOAc in hexanes) to afford compound **9** as a colorless oil (92 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.06 (s, 1H), 4.99 (s, 1H), 3.68 (s, 3H), 3.67 (s, 3H), 3.01-2.94 (m, 1H), 2.88 (td, *J* = 15.8, 1.7 Hz, 1H), 2.82 (dq, *J* = 15.8, 2.4 Hz, 1H), 2.65-2.59 (m, 1H), 2.61-2.54 (m, 1H), 2.52-2.47 (m, 1H), 2.10 (dt, *J* = 12.8, 9.8 Hz, 1H), 1.97-1.88 (m, 1H), 1.82 (dd, *J* = 13.5, 10.0 Hz, 1H), 1.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.0, 171.1, 170.0, 145.9, 112.2, 87.6, 58.1, 52.6, 52.5, 49.5, 43.0, 35.7, 29.8, 28.8, 24.4, ; IR (film): $\tilde{\nu}$ = 2955, 1773, 1734, 1435, 1275, 1204, 903 cm^{-1}; MS (EI): *m/z* (%): 296 (4) [M^+], 237 (3), 236 (4), 205 (4), 177 (2), 99 (100); HRMS: *m/z*: calcd for $C_{15}H_{20}O_6$+Na: 319.11521; found: 319.11495.



Compounds 6 and 7. Prepared analogously from enyne **5** (117 mg, 0.41 mmol). The crude product mixture was purified by flash column chromatography (EtOAc/hexanes, 30% → 50% *v/v*) to afford compound **6** (22.5 mg, 19%) and compound **7** (12.9 mg, 11%) as colorless oils each. Analytical and spectroscopic data of compound **6**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.95 (s, 1H), 4.76 (s, 1H), 4.09 (td, *J* = 11.2, 4.6 Hz, 1H), 3.69 (s, 3H), 3.65 (s, 3H), 2.93 (dd, *J* = 13.8, 2.3 Hz, 1H), 2.77 (ddd, *J* = 13.1, 4.6, 2.3 Hz, 1H), 2.71 (dd, *J* = 18.4, 7.4, 2.6 Hz, 1H), 2.59-2.49 (m, 1H), 2.52 (d, *J* = 14.8 Hz, 1H), 2.10-2.04 (m, 1H), 2.00-1.95 (m, 1H), 1.82 (dd, *J* = 13.1, 11.4 Hz, 1H), 1.80-1.72 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.3, 169.8, 169.6, 141.0, 111.9, 79.4, 55.1, 52.8, 52.4, 42.5, 39.7, 36.2, 29.1, 21.7; IR (film): $\tilde{\nu}$ = 2955,

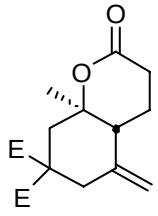


1735, 1212, 1436, 909 cm^{-1}; MS (EI): *m/z* (%): 282 (17) [M^+], 264 (8), 251 (25), 236 (15), 223 (97), 222 (100), 205 (61), 191 (60), 163 (55); HRMS: *m/z*: calcd for $C_{14}H_{18}O_6$+Na: 305.09956; found: 305.09939; elemental analysis calcd (%) for $C_{14}H_{18}O_6$: C 59.57; H 6.43, found: C 59.50; H 6.37.

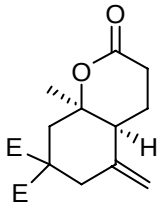


Analytical and spectroscopic data of compound **7**: ^{1}H NMR (600 MHz, $CDCl_3$): δ = 5.03 (q, *J* = 2.0 Hz, 1H), 4.90 (q, *J* = 2.0 Hz, 1H), 4.49 (dd, *J* = 8.6, 6.3 Hz, 1H), 3.67 (s, 6H), 2.91 (dd, *J* = 4.4, 2.4 Hz, 2H), 2.88-2.82 (m, 1H), 2.59 (dd, *J* = 13.4, 8.9 Hz, 1H), 2.48 (dd, *J* = 10.2, 6.8 Hz, 2H), 2.28 (dd, *J* = 12.8, 6.5 Hz, 1H), 2.01 (dd, *J* = 13.4, 9.3 Hz, 1H), 1.96-1.87 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 176.7, 171.8, 171.5, 146.9, 109.8, 81.8, 58.5, 52.9, 46.3, 41.8, 35.3, 30.9, 29.0, 26.4; IR (film): $\tilde{\nu}$ = 2955, 1776, 1733, 1272, 1177 cm^{-1}; MS (EI): *m/z* (%): 282 (8) [M^+], 251 (13), 223 (23), 222 (56), 205 (10), 191 (34), 85 (100); HRMS: *m/z*: calcd for $C_{14}H_{18}O_6$+Na: 305.09956; found: 305.09939; elemental analysis calcd (%) for $C_{14}H_{18}O_6$: C 59.57; H 6.43, found: C 59.44; H 6.37.

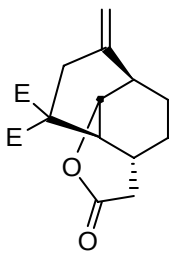
Compound 11. Prepared analogously from compound ***E*-10** (79 mg, 0.27 mmol) as the substrate. White solid (63.4 mg, 80%); m.p. 110-113°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.10 (s, 1H), 4.75 (s, 1H), 3.68 (s, 3H), 3.66 (s, 3H), 3.13 (dd, *J* = 13.8, 2.2 Hz, 1H), 2.73-2.71 (m, 1H), 2.68-2.66 (m, 1H), 2.58 (q, *J* = 9.6 Hz, 1H), 2.39 (d, *J* = 13.9 Hz, 1H), 2.30-2.25 (m, 2H), 1.88-1.81 (m, 2H), 1.03 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 171.0, 170.6, 170.0, 141.6, 112.7, 82.3, 54.4, 53.2, 52.6, 45.9, 42.9, 39.9, 29.1, 20.5, 18.7; IR (film): $\tilde{\nu}$ = 3006, 2990, 1733, 1275, 1260 cm^{-1}; MS (EI): *m/z* (%): 296 (25) [M^+], 281 (3), 265 (15), 237 (46), 219 (14), 207 (45), 205 (46), 157 (90), 43 (100); HRMS: *m/z*: calcd for $C_{15}H_{20}O_6$+Na: 319.11521; found: 319.11498; elemental analysis calcd (%) for $C_{15}H_{20}O_6$: C 60.80; H 6.80, found: C 61.00; H 6.73.



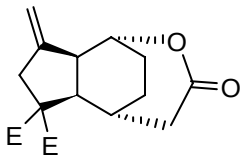
Compound 12. Prepared analogously from compound ***Z*-10** (21 mg, 0.07 mmol) as the substrate. White solid (13 mg, 62%); m.p. = 135-136°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.19 (s, 1H), 5.00 (s, 1H), 3.71 (s, 6H), 2.89 (d, *J* = 13.9 Hz, 1H), 2.67-2.61 (m, 2H), 2.49-2.40 (m, 1H), 2.49 (d, *J* = 12.9 Hz, 1H), 2.37 (d, *J* = 14.8 Hz, 1H), 2.33 (t, *J* = 5.2 Hz, 1H), 2.21-2.11 (m, 1H), 2.08-2.00 (m, 1H), 1.40 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.3, 170.4, 169.6, 140.7, 115.0, 82.5, 53.6, 52.9, 52.8, 43.6, 40.6, 37.7, 27.7, 26.6, 19.6; IR (film): $\tilde{\nu}$ = 2988, 1729, 1275, 1260 cm^{-1}; MS (EI): *m/z* (%): 296 (4) [M^+], 281 (3), 265 (12), 237 (100), 205 (51) 177 (49); HRMS: *m/z*: calcd for $C_{15}H_{20}O_6$+Na: 319.11521; found: 319.11522.



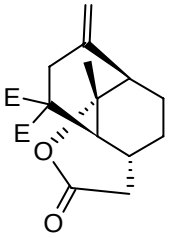
Compounds 14 and 15. Prepared analogously from compound **13** (61.8 mg, 0.2 mmol) as the substrate. Analytical and spectroscopic data of compound **14**: white solid (37 mg, 60%); m.p. = 130-132 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 4.88 (dd, *J* = 1.9 Hz, 1H), 4.84 (dd, *J* = 1.8 Hz, 1H), 4.73-4.71 (m, 1H), 3.74 (s, 3H), 3.73 (s, 3H), 3.32 (dt, *J* = 16.5, 2.3 Hz, 1H), 2.92-2.90 (m, 1H), 2.86 (d, *J* = 16.6 Hz, 1H), 2.80 (ddd, *J* = 18.2, 6.3, 1.5 Hz, 1H), 2.77-2.74 (m, 1H), 2.51 (dd, *J* = 18.2, 1.4 Hz, 1H), 2.18-2.10 (m, 1H), 2.01-1.97 (m, 1H), 1.96-1.89 (m, 1H), 1.61 (dd, *J* = 14.9, 6.6 Hz, 1H), 1.50 (dd, *J* = 15.1, 6.9 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 170.7, 170.5, 169.7, 144.4, 113.7, 77.5, 58.6, 53.2, 42.5, 39.6, 36.2, 35.7, 28.9, 25.8, 21.2; IR (film): $\tilde{\nu}$ = 2924, 1734, 1646, 1269 cm^{-1}; MS (EI): *m/z* (%): 308 (17) [M^+], 277 (2), 248 (100), 216 (10),188 (18), 145 (10), 91 (17); HRMS: *m/z*: calcd for $C_{16}H_{20}O_6$+Na: 331.11493; found: 331.11521; elemental analysis calcd (%) for $C_{16}H_{20}O_6$: C 62.33; H 6.54, found: C 62.30; H 6.47.



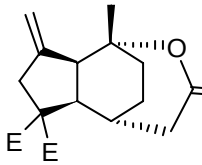
Analytical and spectroscopic data of compound **15**: white solid (7 mg, 11%); m.p = 120-122 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 5.14-5.13 (m, 1H), 4.94-4.93 (m, 1H), 4.47 (ddd, *J* = 5.4, 3.8, 1.6 Hz, 1H), 3.74 (s, 3H), 3.71 (s, 3H), 3.62-3.58 (m, 1H), 3.45 (dq, *J* = 17.5, 2.9 Hz, 1H), 3.27 (d, *J* = 9.6 Hz, 1H), 3.04 (ddd, *J* = 18.8, 5.0, 2.5 Hz, 1H), 2.83-2.82 (m, 1H), 2.80-2.79 (m, 1H), 2.17-2.11 (m, 1H), 2.10-2.03 (m, 1H), 1.79-1.73 (m, 1H), 1.71-1.68 (m, 1H), 1.66-1.60 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 172.6, 171.8, 170.0, 147.3, 111.0, 77.5, 64.4, 53.1, 52.8, 46.2, 45.2, 44.9, 41.2, 28.8, 22.7, 21.8; IR (film): $\tilde{\nu}$ = 2924, 2854, 1731, 1276, 1227 cm^{-1}; MS (EI): *m/z* (%): 308 (52) [M^+], 290 (17), 277 (29), 248 (100), 188 (92), 91 (79); HRMS: *m/z*: calcd for $C_{16}H_{20}O_6$+Na: 331.11493; found: 331.11516; elemental analysis calcd (%) for $C_{16}H_{20}O_6$: C 62.33; H 6.54, found: C 62.40; H 6.43.



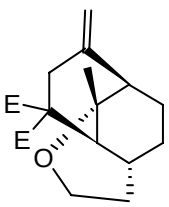
Compound 17. Prepared analogously from compound **16** (70 mg, 0.216 mmol) as the substrate. White solid (55 mg, 80%); m.p. = 123-124°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.87 (d, *J* = 1.6 Hz, 1H), 4.81 (d, *J* = 1.4 Hz, 1H), 3.72 (s, 6H), 3.21 (s, 2H), 3.05 (s, 1H), 2.76 (ddd, *J* = 18.1, 5.9, 1.5 Hz, 1H), 2.45 (dd, *J* = 18.0, 1.5 Hz, 1H), 2.41-2.40 (m, 1H), 2.12-2.07 (m, 1H), 2.06-1.98 (m, 1H), 1.96-1.90 (m, 1H), 1.59 (dd, *J* = 14.4, 5.8 Hz, 1H), 1.42 (dd, *J* = 13.9, 5.6 Hz, 1H), 1.18 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 171.0, 170.5, 169.7, 145.0, 113.5, 83.5, 58.7, 53.4, 53.3, 48.0, 41.1, 39.3, 33.9, 30.4, 27.1, 25.0, 23.8; IR (film): $\tilde{\nu}$ = 2951, 1728, 1257, 1202, 1093 cm^{-1}; MS (EI): *m/z* (%): 322 (20) [M^+], 291 (3), 264 (14), 263 (71), 262 (100), 220 (10), 202 (19); HRMS: *m/z*: calcd for $C_{17}H_{22}O_6$+Na: 345.13086; found: 345.13093.



Compound 19. Prepared analogously from compound **18** (48 mg, 0.15 mmol). White solid (26 mg, 54%); m.p. = 184-186°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.13 (s, 1H), 5.03 (s, 1H), 3.73 (s, 3H), 3.70 (s, 3H), 3.34 (d, *J* = 12.1 Hz, 1H), 3.33 (s, 2H), 3.00 (ddd, *J* = 18.9, 5.0, 2.1 Hz, 1H), 2.77 (dd, *J* = 18.7, 2.6 Hz, 1H), 2.73 (d, *J* = 15.6 Hz, 1H), 2.11-2.03 (m, 1H), 1.90-1.81 (m, 2H), 1.67-1.61 (m, 2H), 1.45 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 172.3, 171.4, 169.9, 146.1, 114.1, 83.0, 64.1, 53.1, 52.8, 50.7, 45.7, 44.8, 42.4, 29.6, 29.3, 28.1, 23.0; IR (film): $\tilde{\nu}$ = 2953, 1728, 1253, 1221, 1158 cm^{-1}; MS (EI): *m/z* (%): 322 (45) [M^+], 304 (26), 290 (46), 275 (29), 258 (42), 230 (45), 204 (73); HRMS: *m/z*: calcd for $C_{17}H_{22}O_6$+Na: 345.13086; found: 345.13110; elemental analysis calcd (%) for $C_{17}H_{22}O_6$: C 63.34; H 6.88, found: C 63.26; H 6.84.



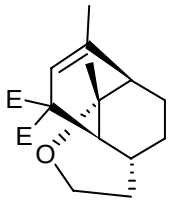
Compound 21b. Prepared analogously from compound **20b** (52.5 mg, 0.17 mmol). Colorless oil (37.2 mg, 71%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.00 (s, 1H), 4.86 (s, 1H), 3.78 (dd, *J* = 16.8, 5.0 Hz, 2H), 3.71 (s, 3H), 3.67 (s, 3H), 3.31 (dd, *J* = 9.4, 0.9 Hz, 1H), 3.19 (ddd, *J* = 15.0, 4.6, 2.5 Hz, 1H), 2.91 (d, *J* = 9.3 Hz, 1H), 2.62 (d, *J* = 15.0 Hz, 1H), 1.90-1.63 (m, 5H), 1.57-1.42 (m, 2H), 1.19 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 172.1, 170.6, 148.3, 112.8, 77.6, 64.4, 61.9, 52.9, 52.4, 51.1, 47.7, 43.0, 40.0, 31.1, 29.8, 28.1, 22.4; IR (film): $\tilde{\nu}$ = 2934, 1733, 1254, 1220, 1109 cm^{-1}; MS (EI): *m/z* (%): 308 (98) [M^+], 290 (10), 276 (34), 250 (25), 230 (12), 216 (31), 43 (100); HRMS: *m/z*: calcd for $C_{17}H_{24}O_5$+Na: 331.15159; found: 331.15166; elemental analysis calcd (%) for $C_{17}H_{24}O_5$: C 66.21; H 7.84, found: C 66.08; H 7.79.



Compounds 23a/b. Prepared analogously from compound **22** (66 mg, 0.21 mmol). The crude product mixture was purified by flash chromatography (20% *v/v* EtOAc in hexanes) to afford compound **23a** (28 mg, 43%) and compound **23b** (13 mg, 19%) as colorless oils each. Analytical and spectroscopic data of compound **23a**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.72 (t, *J* = 2.0 Hz, 1H), 4.69 (t, *J* = 2.0 Hz, 1H), 3.90-3.80 (m, 2H), 3.71 (s, 6H), 3.20

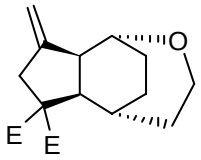
(dt, J = 16.5, 2.4 Hz, 1H), 3.11 (d, J = 16.5 Hz, 1H), 2.99 (s, 1H), 2.38-2.30 (m, 1H), 2.22 (d, J = 5.8 Hz, 1H), 2.08-1.97 (m, 2H), 1.91-1.88 (m, 1H), 1.71-1.64 (m, 1H), 1.48 (dd, J = 14.1, 7.8 Hz, 1H), 1.32 (dd, J = 14.7,7.8 Hz, 1H), 0.95 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 171.3, 170.5, 147.9, 110.7, 73.7, 59.8, 59.2, 53.1, 53.0, 49.2, 40.7, 34.9, 34.3, 29.1, 26.9, 26.0, 25.7; IR (film): $\tilde{\nu}$ = 2949, 1734, 1223, 1093 cm^{-1}; MS (EI): *m/z* (%): 308 (61) [M^+], 293 (16), 280 (7), 249 (100), 189 (27); HRMS: *m/z*: calcd for $C_{17}H_{24}O_5$+Na: 331.15159; found: 331.15170; elemental analysis calcd (%) for $C_{17}H_{24}O_5$: C 66.21; H 7.84, found: C 66.08; H 7.86.

Analytical and spectroscopic data of compound **23b**: ^{1}H NMR (600 MHz, $CDCl_3$): δ = 5.72-5.71 (m, 1H),



3.91 (ddd, J = 11.8, 10.5, 5.7 Hz, 1H), 3.78 (ddd, J = 11.8, 7.6, 3.0 Hz, 1H), 3.71 (s, 3H), 3.70 (s, 3H), 3.10-3.08 (m, 1H), 2.19 (tt, J = 13.4, 4.9 Hz, 1H), 1.99 (dddd, J = 13.0, 9.1, 5.7, 2.9 Hz, 1H), 1.88-1.86 (m, 1H), 1.76 (d, J = 2.4 Hz, 3H), 1.74-1.73 (m, 1H), 1.72-1.65 (m, 2H), 1.30-1.26 (m, 1H), 1.04-1.02 (m, 1H), 1.00 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 170.7, 170.5, 139.4, 117.8, 73.7, 60.5, 58.8, 53.0, 52.7, 46.4, 37.0, 32.4, 28.6, 26.4, 23.6, 23.2, 20.7; IR (film): $\tilde{\nu}$ = 2929, 1735, 1433, 1227, 1174, 1089 cm^{-1}; MS (EI): *m/z* (%): 308 (45) [M^+], 293 (35), 276 (15), 265 (12), 249 (100), 217 (25), 97 (64), 43 (86); HRMS: *m/z*: calcd for $C_{17}H_{24}O_5$+Na: 331.15159; found: 331.15145.

Compound 21a. A mixture of compound **20a** (38 mg, 0.13 mmol) and $PtCl_2$ (3.4 mg, 0.013 mmol) in



toluene (3 mL) was stirred for 30 minutes at room temperature. The reaction was filtered through a plug of SiO_2, the filtrate was evaporated, and the crude product purified by flash column chromatography (5% → 10% *v/v* EtOAc in hexanes) to afford compound **21a** as a white solid (23 mg, 60%). m.p. = 92-95°C; ^{1}H NMR (600 MHz, acetone-d_6): δ = 5.02-5.01 (m, 1H), 4.85-4.84 (m, 1H), 3.91-3.89 (m, 1H), 3.79-3.75 (m, 1H), 3.73-3.68 (m, 1H), 3.70 (s, 3H), 3.66 (s, 3H), 3.30 (dq, J = 16.4, 3.0 Hz, 1H), 3.20 (d, J = 9.6 Hz, 1H), 3.15-3.12 (m, 1H), 2.67 (dq, J = 16.4, 1.0 Hz, 1H), 1.83-1.79 (m, 2H), 1.78-1.77 (m, 1H), 1.76-1.74 (m, 2H), 1.73-1.70 (m, 1H), 1.54-1.52 (m, 1H); ^{13}C NMR (150 MHz, acetone-d_6): δ = 172.7, 171.0, 150.8, 109.8, 77.7, 65.5, 62.3, 53.0, 52.6, 47.7, 47.5, 42.6, 40.4, 32.0, 22.0, 21.8; IR (film): $\tilde{\nu}$ = 2924, 1735, 1267, 1157 cm^{-1}; MS (EI): *m/z* (%): 294 (85) [M^+], 276 (8), 263 (21), 250 (21), 235 (42), 234 (100), 216 (23), 202 (62); HRMS: *m/z*: calcd for $C_{16}H_{22}O_5$+Na: 317.13595; found: 317.13609; elemental analysis calcd (%) for $C_{16}H_{22}O_5$: C 65.29; H 7.53, found: C 65.24; H 7.45.

Crystallographic Summaries

X-ray Crystal Structure Analysis of Compound 17: $C_{17}H_{22}O_6$, M_r = 322.35 g·mol^{-1}, colorless plate, crystal size 0.55 x 0.36 x 0.22 mm, triclinic, space group $P\bar{1}$, a = 7.7836(13) Å, b = 10.5368(18) Å, c = 10.9036(18) Å, α = 71.566(7)°, β = 72.110(7)°, γ = 77.918(7)°, V = 801.1(2) Å^3, T = 150 K, Z = 2, D_{calc} = 1.336 g·cm^3, λ = 1.54178 Å, μ(*Cu-K*$_\alpha$) = 0.841 mm^{-1}, Semi-empirical absorption correction (T_{min} = 0.72, T_{max} = 0.88), Bruker AXS Proteum X8 diffractometer, 5.37 < θ < 63.14°, 17343 measured reflections, 2538 independent reflections, 2329 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.043 [$I > 2\sigma(I)$], wR_2 = 0.115, 209 parameters, H atoms riding, S = 1.063, Extinction coefficient = 0.0095(12), residual electron density 0.3 / –0.2 e Å^{-3}.

X-ray Crystal Structure Analysis of Compound 19: $C_{17}H_{22}O_6$, M_r = 322.35 g·mol^{-1}, colorless plate, crystal size 0.26 x 0.22 x 0.22 mm, monoclinic, space group $P2_1/n$, a = 7.7663(2) Å, b = 17.8875(5) Å, c

= 11.1165(3) Å, β = 94.6330(10)°, V = 1539.25(7) Å^3, T = 100 K, Z = 4, D_{calc} = 1.391 g·cm^3, λ = 0.71073 Å, μ(*Mo-K*$_\alpha$) = 0.105 mm^{-1}, Semi-empirical absorption correction (T_{min} = 0.95, T_{max} = 1.00), Nonius KappaCCD diffractometer, 2.93< θ < 32.97°, 35378 measured reflections, 5741 independent reflections, 5078 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.038 [$I > 2\sigma(I)$], wR_2 = 0.109, 208 parameters, H atoms riding, S = 1.047, residual electron density 0.4 / –0.3 e Å^{-3}.

X-ray Crystal Structure Analysis of Compound 21a: $C_{16}H_{22}O_5$, M_r = 294.34 g · mol^{-1}, colorless plate, crystal size 0.22 x 0.18 x 0.16 mm, triclinic, space group $P\bar{1}$, a = 7.2093(3) Å, b = 9.0792(3) Å, c = 11.4929(5) Å, α = 84.625(2)°, β = 81.086(2)°, γ = 77.933(2)°, V = 725.29(5) Å^3, T = 100 K, Z = 2, D_{calc} = 1.348 g·cm^3, λ = 0.71073 Å, μ(*Mo-K*$_\alpha$) = 0.099 mm^{-1}, Gaussian absorption correction (T_{min} = 0.98, T_{max} = 0.99), Nonius KappaCCD diffractometer, 5.30 < θ < 33.16°, 14528 measured reflections, 5499 independent reflections, 4766 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.043 [$I > 2\sigma(I)$], wR_2 = 0.111, 190 parameters, H atoms riding, S = 1.032, residual electron density 0.5 / –0.3 e Å^{-3}.