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Supporting Information

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Gold(I)-Catalyzed 5-*endo-dig* Carbocyclization of β-Acetylinic Dicarbonyl Compounds.

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General Information. Unless otherwise noted all commercial materials were used without purification. Small scale reactions (< 3mL) were carried out in Fisher Scientific disposable scintillation vials. Dichloromethane (CH_2Cl_2) was obtained from EMD. Silver trifluoromethanesulfonate (AgOTf) and chloro(triphenylphosphine)gold ($AuCl(PPh_3)$) were obtained from Aldrich Chemical Company and Strem Chemicals respectively. Substrates **1**, **3**, **5**, **7**, **9**, **11**, **13** and **29** were prepared by the alkylation method described by Malacria (general procedure A).[1] Substrates **21** and **27** were prepared by $TiCl_4$ mediated conjugate addition of triphenylallenylstannane (general procedure B).[2] Substrates **15**, **17**, **19** were prepared by C-H insertion/annulation of the corresponding β-diazo trimethylsilyl protected alkynes. Substrate **23** was prepared by a sequence similar to that described by Wulff.[3] Iodoalkynes **31** and **33** were prepared by iodination of the corresponding terminal or trimethylsilyl protected alkynes as described by Denmark.[4] TLC analysis of reaction mixtures was performed on Merck silica gel 60 F_{254} TLC plates. Flash chromatography was carried out on Merck 60 silica gel (32-63 μm). ^1H and ^{13}C NMR spectra were recorded with Bruker AVB-400, and AVQ-400 spectrometers and referenced to $CDCl_3$ unless otherwise noted. Mass spectral and analytical data were obtained via the Micro-Mass/Analytical Facility operated by the College of Chemistry, University of California, Berkeley.

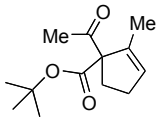
General Procedure A.[1] To a suspension of NaH (60 wt. %, 260 mg, 6.5 mmol) in 8 mL of a 1:1 mixture of THF:DMF was added potassium iodide (600 mg, 3.6 mmol). The solution was cooled to 0ºC and treated dropwise with 3-oxo-butyric acid prop-2-ynl ester[1] (1.00 g, 7.14 mmol). The resulting yellow solution was warmed to RT, stirred for 30 min then treated with methanesulfonic acid pent-3-ynyl ester[5] (1.17 g, 6.1 mmol). The whole was heated to 95ºC for 8 hours, quenched with 5 mL of 1N HCl, and extracted with ether (3 x 10 mL). The combined organics were washed with brine (2 x 10 mL), dried over $MgSO_4$, concentrated and purified by flash chromatography (hexanes:EtOAc, 7:1) to yield **5** as a colorless oil (365 mg, 30%). Data for the keto tautomer: ^1H NMR (400 MHz, $CDCl_3$) δ 4.74 (d, J = 2.4, 2H), 3.75 (t, J = 7.2, 1H), 2.51 (t, J = 2.4, 1H), 2.29 (s, 3H), 2.21 (m, 2H), 2.00 (app q, J = 6.9, 2H), 1.77 (t, J = 2.5, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.2, 168.7, 78.6, 76.9, 75.4, 74.8, 57.8, 52.7, 29.4, 27.0, 16.6, 3.4.

[1] P. Cruciani, R. Stammler, C. Aubert, M. Malacria, *J. Org. Chem.* **1996**, *61*, 2699.
[2] J. Haruta, K. Nishi, S. Matsuda, S. Akai, Y. Tamura, Y. Kita, *J. Org. Chem.* **1990**, *55*, 4853.
[3] W. D. Wulff, J. Su, P.-C. Tang, X. Yao-Chang, *Synthesis* **1999**, *3*, 415.
[4] S. E. Denmark, S.-M. Yang, *J. Am. Chem. Soc.* **2002**, *124*, 15196.
[5] A. T. Hewson, D. T.; MacPherson, *J. Chem. Soc., Perkin Trans. 1* **1985**, *12*, 2625.

HRMS (EI) calc. for $[C_{12}H_{14}O_3]^+$ 206.0943, found 206.0941; Anal. Calcd.: C, 69.88; H, 6.84, found: C, 70.24; H, 6.87.

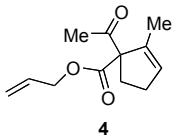
General Procedure B.[2] To a cold (-78°C) solution of 2-(ethoxycarbonyl)-2-cyclohexenone (384 mg, 2.3 mmol) in 4 mL dichloromethane was added $TiCl_4$ dropwise (1M in dichloromethane, 3.0 mL, 3.0 mmol). After 10 min a solution of triphenylallenyl tin (1.85 g, 4.6 mmol) in 4 mL dichloromethane. The resulting solution was allowed to gradually reach RT over 2 hours and stirred overnight. The reaction was quenched with 10 mL water and extracted with EtOAc (3 x 10 mL). The combined extracts were dried over Na_2SO_4, concentrated, taken up in 20 mL of diethyl ether, and treated with 10 mL of saturated KF. The resulting suspension was stirred at RT for 1 hour, filtered, and extracted with ethyl acetate (3 x 10 mL). The combined extracts were dried over Na_2SO_4, and concentrated to yield a crude oil which was purified by flash chromatography (hexanes:ether, 3:1) to yield **27** as a colorless oil (343 mg, 72%). Data for the keto tautomer: ^{1}H NMR (400 MHz, $CDCl_3$) □ 4.23 (m, 2H), 2.76 (m, 1H), 2.50 (dt, *J* = 16.8, 2.7, 1H), 2.28 (m, 2H), 2.20-2.05 (m, 2H), 1.97 (t, *J* = 2.6, 1H), 1.80-1.52 (m, 4H), 1.31 (t, *J* = 7.1, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) □ 173.9, 172.4, 100.68, 83.6, 69.0, 60.4, 37.6, 29.3, 25.7, 23.5, 17.0 ,14.3. LRMS (EI) 208 (M^+).

General procedure for Gold(I)-catalyzed 5-*endo-dig* carbocyclization. To a small screw-cap scintillation vial equipped with a magnetic stir bar and charged with a solution of alkynyl □-dicarbonyl compound (~150 mg, 1 eq) in CH_2Cl_2 (0.4M) was added $AuCl(PPh_3)$ (1 mol%) followed by AgOTf (1 mol%). The cloudy white reaction mixture was then stirred at RT and monitored periodically by TLC. Upon completion, the reaction mixture was loaded directly on to a silica gel column and chromatographed with the appropriate mixture of hexanes and EtOAc to give the cycloisomerized products.



2

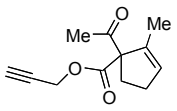
1-Acetyl-2-methyl-cyclopent-2-enecarboxylic acid *tert*-butyl ester (2). IR (thin film) 2978 (m), 1712 (s), 1254 (s) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) □ 5.66 (br s, 1H), 2.58 (m, 1H), 2.42-2.24 (m, 2H), 2.16 (s, 3H), 2.11 (m, 1H), 1.81 (q, *J* = 2.4, 3H), 1.47 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) □ 205.0, 170.6, 137.6, 131.5, 81.7, 75.2, 32.4, 30.1, 27.8, 26.7, 14.8; Anal. Calcd.: C, 69.61; H, 8.99, found: C, 69.89; H, 9.18.



4

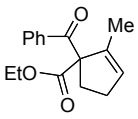
1-Acetyl-2-methyl-cyclopent-2-enecarboxylic acid allyl ester (4). IR (thin film) 2944 (m), 1714 (s), 1650 (w), 1625 (w), 1242 (s) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) □ 5.90 (m, 1H), 5.70 (br d, *J* = 1.2, 1H), 5.32 (dd, *J* = 17.2, 1.2, 1H), 5.24 (dd, *J* = 7.8, 1.2, 1H), 4.65 (dd, *J* = 4.8, 1.2, 2H), 2.63 (m, 1H), 2.46-2.30

(m, 2H), 2.24 (m, 1H), 2.17 (s, 3H), 1.81 (q, J = 1.6, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.8, 171.2, 137.3, 132.1, 131.6, 118.7, 74.6, 65.7, 32.7, 30.3, 26.6, 14.7; HRMS (EI) calc. for $[C_{12}H_{16}O_3]^+$ 208.1100, found 208.1102; Anal. Calcd.: C, 69.21; H, 7.74, found: C, 69.46; H, 7.85.



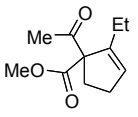
6

1-Acetyl-2-methyl-cyclopent-2-enecarboxylic acid prop-2-ynyl ester (6) IR (thin film) 2949 (m), 2128 (w), 1742 (s), 1711 (s), 1240 (br m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.74 (br s, 1H), 4.77 (d, J = 2.4, 2H), 2.64 (ddd, J = 5.0, 8.4, 13.4, 1H), 2.50 (t, J = 2.5, 1H), 2.47-2.33 (m, 2H), 2.25 (ddd, J = 5.6, 8.4, 13.4, 1H), 2.20 (s, 3H), 1.85 (br s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.62, 170.90, 137.16, 132.56, 77.12, 75.19, 74.65, 52.49, 32.74, 30.43, 26.67, 14.79. Calcd.: C, 69.88; H, 6.84, found: C, 70.07; H, 6.54.



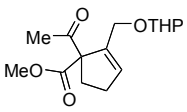
8

1-Benzoyl-2-methyl-cyclopent-2-enecarboxylic acid ethyl ester (8) IR (thin film) 2978 (m), 1728 (s), 1680 (s), 1597 (m), 1580 (m), 1447 (s), 1256 (s), 1216 (s) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (m, 2H), 7.50 (br t, J = 7.4, 1H), 7.39 (br t, J = 7.4, 2H), 5.73 (app d, J = 1.4, 1H), 4.08 (m, 2H), 3.06 (ddd, J = 4.5, 8.7, 13.2, 1H), 2.50 (m, 1H), 2.35 (m, 1H), 2.25 (ddd, J = 5.0, 9.1, 13.2, 1H), 1.83 (br s, 3H), 1.00 (t, J = 7.1, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.07, 172.25, 137.99, 135.57, 132.68, 131.62, 128.57, 128.44, 72.14, 61.35, 33.88, 30.89, 14.89, 13.82. HRMS (FAB) calc. for $[C_{16}H_{19}O_3]^+$ 259.1334, found 259.1333; Anal. Calcd.: C, 74.39; H, 7.02, found: C, 74.25; H, 6.99.



10

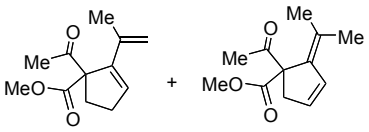
1-Acetyl-2-ethyl-cyclopent-2-enecarboxylic acid methyl ester (10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.75 (quintet, J = 2.0, 1H), 3.77 (s, 3H), 2.64 (m, 1H), 2.74 (m, 1H), 2.42 (m, 2H), 2.28-2.06 (m, 3H), 2.18 (s, 3H), 1.12 (t, J = 7.2, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.2, 172.3, 143.9, 129.3, 74.9, 52.2, 32.9, 30.4, 26.6, 21.7, 12.3; HRMS (EI) calc. for $[C_{11}H_{16}O_3]^+$ 196.1100, found 196.1102; Anal. Calcd.: C, 67.32; H, 8.22, found: C, 67.72; H, 8.42.



12

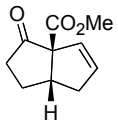
1-Acetyl-2-(tetrahydro-pyran-2-yloxymethyl)-cyclopent-2-enecarboxylic acid methyl ester (12) 1:1 mixture of diastereomers. IR (thin film) 2948 (m), 1724 (s), 1723 (s), 1256 (br m) cm^{-1}. ^{1}H NMR (400

MHz, $CDCl_3$) δ 6.01 (br s, 1H), 4.56 (br s, 1H), 4.43 (br d, J = 11.7, 0.5H), 4.37 (d, J = 13.0, 0.5H), 4.16 (d, J = 13.0, 0.5H), 4.07 (d, J = 11.7, 0.5H), 3.80 (br t, J = 9.4, 1H), 3.72 (s, 3H), 3.47 (m, 1H), 2.66 (m, 1H), 2.43 (m, 1H), 2.24 (m, 1H), 2.18 (s, 1.5H), 2.16 (s, 1.5H), 1.76-1.44 (br m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.14, 204.96, 172.17, 171.97, 139.12, 139.05, 134.31, 98.25, 97.79, 73.31, 73.27, 64.59, 64.31, 62.14, 61.72, 52.34, 52.31, 32.74, 32.37, 30.42, 30.32, 30.20, 26.26, 25.35, 19.38, 19.06. HRMS (FAB) calc. for $[C_{15}H_{23}O_5]^+$ 283.1545, found 283.1554; Anal. Calcd.: C, 63.81; H, 7.85, found: C, 63.85; H, 7.87.



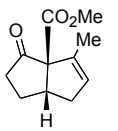
14a **14b**

1-Acetyl-2-isopropenyl-cyclopent-2-enecarboxylic acid methyl ester (14a) ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.15 (br s, 1H), 5.03 (br s, 1H), 4.92 (br s, 1H), 3.75 (s, 3H), 2.72-2.48 (m, 3H), 2.25 (s, 3H), 1.97 (s, 3H). The following resonances could be observed for the minor component **1-Acetyl-2-isopropylidene-cyclopent-3-enecarboxylic acid methyl ester (14b)** 6.42 (br s, 1H), 5.88 (br s, 1H), 3.78 (s, 3H), 3.28 (d, J = 18.3, 1H), 2.92 (d, J = 18.3, 1H), 2.18 (s, 3H), 1.90 (s, 3H), 1.72 (s, 3H). **(14a)** ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.82, 172.54, 143.13, 137.27, 134.75, 115.20, 73.19, 52.32, 35.53, 31.08, 26.71, 22.32. The following resonances could be observed for the minor isomer **(14b)** 131.73, 129.89, 68.37, 42.58, 25.47. IR cm^{-1} 2950 (m), 1732 (s), 1709 (s), 1246 (s). HRMS (EI) calc. for $[C_{12}H_{16}O_3]^+$ 208.1099, found 208.1093; Anal. Calcd.: C, 69.21; H, 7.74, found: C, 69.21; H, 7.56.



16

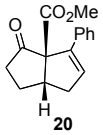
3-Oxo-2,3,6,6a-tetrahydro-1*H*-pentalene-3a-carboxylic acid methyl ester (16). IR (thin film) 2955 (m), 1738 (s), 1244 (s) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.90 (dt, J = 5.6, 2.4, 1H), 5.71 (dt, J = 5.6, 2.4, 1H), 3.71 (s, 3H), 3.25 (dq, J = 8.0, 2.4, 1H), 2.81 (qt, J = 8.4, 2.0, 1H), 2.50-2.20 (m, 4H), 1.55 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.6, 171.2, 134.7, 127.3, 73.3, 52.4, 44.1, 39.9, 37.8, 27.3; HRMS (EI) calc. for $[C_{10}H_{12}O_3]^+$ 180.0786, found 180.0790; Anal. Calcd.: C, 66.65; H, 6.71, found: C, 66.53; H, 7.01.



18

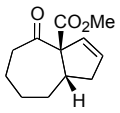
4-Methyl-3-oxo-2,3,6,6a-tetrahydro-1*H*-pentalene-3a-carboxylic acid methyl ester (18). IR (thin film) 2955 (m), 1745 (br s), 1239 (s) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.61 (br s, 1H), 3.74 (s, 3H), 3.24 (dq, J = 8.0, 2.4, 1H), 2.74 (m, 1H), 2.50-2.10 (m, 4H), 1.84 (q, J = 2.0, 1H), 1.63 (m, 1H); ^{13}C NMR (100

MHz, $CDCl_3$) δ 211.7, 171.6, 136.0, 130.1, 73.7, 52.4, 46.6, 38.3, 38.2, 27.8, 13.5; HRMS (EI) calc. for $[C_{11}H_{14}O_3]^+$ 194.0943, found 194.0943; Anal. Calcd.: C, 68.02; H, 7.27, found: C, 68.24; H, 7.52.



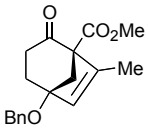
20

3-Oxo-4-phenyl-2,3,6,6a-tetrahydro-1*H*-pentalene-3a-carboxylic acid methyl ester (20). IR (thin film) 2953 (m), 1731 (s), 1250 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.54 (m, 2H), 7.28 (m, 3H), 6.36 (t, *J* = 2.8, 1H), 3.75 (s, 3H), 3.34 (m, 1H), 2.95 (ddd, *J* = 18.0, 8.0, 2.4, 1H), 2.58-2.27 (m, 4H), 1.79 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.2, 172.5, 140.2, 134.0, 132.2, 128.0, 127.5, 127.3, 72.6, 52.6, 49.3, 38.6, 38.3, 27.0; HRMS (EI) calc. for $[C_{16}H_{16}O_3]^+$ 256.1100, found 256.1106; Anal. Calcd.: C, 74.98; H, 6.29, found: C, 74.61; H, 6.47.



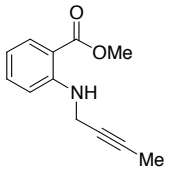
22

4-Oxo-4,5,6,7,8,8a-hexahydro-1*H*-azulene-3a-carboxylic acid methyl ester (22) ^1H NMR (400 MHz, $CDCl_3$) δ 5.96 (m, 1H), 5.78 (m, 1H), 3.76 (s, 3H), 3.12 (m, 1H), 2.92 (ddt, *J* = 2.3, 8.7, 17.1, 1H), 2.51 (m, 1H), 2.16 (app d, *J* = 17.1, 1H), 1.82 (m, 4H), 1.58 (m, 2H), 1.38 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.22, 172.42, 134.30, 128.36, 76.87, 52.73, 41.63, 41.29, 41.09, 33.26, 27.65, 26.04. HRMS (EI) calc. for $[C_{12}H_{16}O_3]^+$ 208.1099, found 208.1104; Anal. Calcd.: C, 69.21; H, 7.74, found: C, 69.49; H, 7.99.

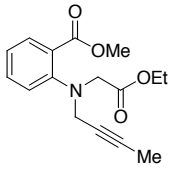


24

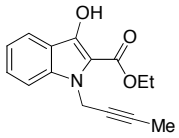
5-Benzyloxy-7-methyl-2-oxo-bicyclo[3.2.1]oct-6-ene-1-carboxylic acid methyl ester (24). IR (thin film) 2953 (m), 1725 (s), 1261 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.31 (m, 5H), 5.96 (s, 1H), 4.60 (m, 1H), 3.78 (s, 3H), 2.88 (dd, *J* = 11.2, 3.2, 1H), 2.57 (m, 2H), 2.37 (d, *J* = 11.2, 1H), 2.24 (m, 1H), 2.09 (m, 1H), 1.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.6, 168.9, 141.2, 138.6, 135.1, 128.4, 127.5, 127.3, 83.1, 69.7, 66.1, 52.1, 45.1, 34.5, 32.0, 15.1; HRMS (FAB) calc. for $[C_{18}H_{20}O_4]^+$ 300.1362, found 300.1363; Anal. Calcd.: C, 71.98; H, 6.71, found: C, 68.79; H, 6.40.



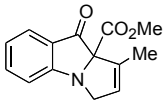
2-But-2-ynylamino-benzoic acid methyl ester. Prepared according to the method of Kundu by alkylation of methyl anthranilate with 1-bromo-2-butyne (65% yield). Kundu, N.G.; Chaudhuri, G. *Tetrehedron*, **2001**, *57*, 6833.



2-(But-2-ynyl-ethoxycarbonylmethyl-amino)-benzoic acid methyl ester. Prepared under identical conditions with ethyl bromoacetate (31% yield). Kundu, N.G.; Chaudhuri, G. *Tetrehedron*, **2001**, *57*, 6833.



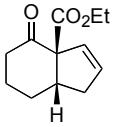
1-But-2-ynyl-3-hydroxy-1*H*-indole-2-carboxylic acid ethyl ester (25). To a solution of of potassium *tert*-butoxide (247 mg, 2.20 mmol) in THF (8.8 mL) at 0 °C was added 2-(But-2-ynyl-ethoxycarbonylmethyl-amino)-benzoic acid methyl ester (330 mg, 1.10 mmol) in THF (1 mL) dropwise. After 10 min a saturated solution ammonium chloride was added (5 mL), the mixture was then diluted with Et_2O, washed with H_2O, and then brine. The organic layer was seperated and dried with $MgSO_4$ before being concentrated *in vacuo* and chromatorgraphed (1:10 EtOAc / Hexanes) to give indole (shown above) (180 mg, 61%) as a pale yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$) 8.70 (bs, 1H), 7.75 (d, J = 8.1, 1H), 7.37 (m, 2H), 7.10 (t, J = 7.2, 1H), 5.08 (d, J = 2.1, 2H), 4.48 (q, J = 6.9, 2H), 1.72 (t, J = 2.1, 3H), 1.46 (t, J = 6.9, 3H).



26

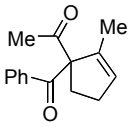
1-Methyl-8-oxo-3*H*,8*H*-3a-aza-cyclopenta[*a*]indene-8a-carboxylic acid ethyl ester (26). IR (thin film) 2980 (w), 2922 (w), 2868 (w), 1739 (s), 1709 (s), 1608 (s), 1475 (m), 1460 (m), 1242 (s) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) 7.64 (d, J = 2.8, 1H), 7.59 (t, J = 3.6, 1H), 7.05 (t, J = 3.6, 1H), 5.56 (s, 1H), 4.37 (d, J = 14.8, 1H), 4.22 (m, 2H), 4.37 (d, J = 14.8, 1H), 2.01 (s, 3H), 1.26 (t, J = 7.2, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 196.3, 167.9, 166.2, 137.3, 135.4, 125.4, 124.8, 123.1, 122.1, 115.4, 86.5, 62.0, 59.2, 14.0, 12.2;

HRMS (EI) calc. for $[C_{15}H_{15}NO_3]^+$ 257.1052, found 257.1052; Anal. Calcd.: C, 70.02; H, 5.88; N, 5.44 found: C, 69.83; H, 6.04; N, 5.33.



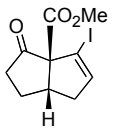
28

4-Oxo-1,4,5,6,7,7a-hexahydro-indene-3a-carboxylic acid ethyl ester (28). IR (thin film) 2939 (m), 1714 (br s), 1241 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 6.00 (dt, *J* = 2.3, 5.7, 1H), 5.90 (dt, *J* = 2.0, 5.7, 1H), 4.20 (m, 2H), 3.07 (app pentet, *J* = 6.0, 1H), 2.63-2.52 (m, 2H), 2.37 (dt, *J* = 5.5, 15.9, 1H), 2.19 (ddt, *J* = 2.2, 7.0, 16.7, 1H), 2.12-2.02 (m, 1H), 2.02-1.82 (m, 2H), 1.64 (m, 1H), 1.28 (t, *J* = 6.8, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.27, 171.83, 134.00, 130.42, 71.26, 61.56, 44.12, 39.23, 37.75, 26.99, 21.29, 14.09. HRMS (EI) calc. for $[C_{12}H_{16}O_3]^+$ 208.1099, found 208.1103; Anal. Calcd.: C, 69.21; H, 7.74, found: C, 69.17; H, 7.67.



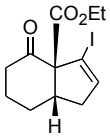
30

1-(1-Benzoyl-2-methyl-cyclopent-2-enyl)-ethanone (30). IR (thin film) 2936 (m), 1706 (s), 1679 (br s), 1246 (s). 1619 (m), 1597 (m), 1580 (m), 1448 (m), 1247 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 3.2, 2H), 7.53 (t, *J* = 3.2, 1H), 7.43 (t, *J* = 3.2, 2H), 5.81 (br d, *J* = 1.2, 1H), 2.86 (m, 1H), 2.50 (m, 2H), 2.35 (m, 1H), 2.23 (s, 3H), 1.85 (bd, *J* = 1.2, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.4, 199.5, 138.2, 135.5, 132.8, 132.2, 128.9, 128.5, 79.4, 33.4, 31.0, 27.6, 15.1; HRMS (EI) calc. for $[C_{15}H_{16}O_2]^+$ 228.1150, found 228.1151; Anal. Calcd.: C, 78.92; H, 7.06, found: C, 78.96; H, 7.15.



32

4-Iodo-3-oxo-2,3,6,6a-tetrahydro-1*H*-pentalene-3a-carboxylic acid methyl ester (32). IR (thin film) 2951 (m), 1737 (s), 1248 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 6.41 (t, *J* = 2.4, 1H), 3.73 (s, 3H), 3.34 (dq, *J* = 7.6, 2.0, 1H), 2.77 (ddd, *J* = 17.6, 8.0, 2.4, 1H), 2.46 (m, 2H), 2.24 (m, 2H), 1.60 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.8, 170.4, 145.6, 88.6, 73.6, 52.7, 46.4, 41.3, 38.4, 27.4; HRMS (FAB) calc. for $[C_{10}H_{11}IO_3 + H]^+$ 306.9831, found 306.9831; Anal. Calcd.: C, 39.24; H, 3.62, found: C, 39.51; H, 3.81.



34

3-Iodo-4-oxo-1,4,5,6,7,7a-hexahydroindene-3a-carboxylic acid ethyl ester (34) ^{1}H NMR (400 MHz, $CDCl_3$) 6.54 (t, *J* = 2.5, 1H), 4.29 (m, 2H), 3.31 (quintet, *J* = 6.2, 1H), 2.58 (quintet, *J* = 7.1, 1H), 2.49 (ddd, *J* = 2.7, 7.55, 16.4, 1H), 2.15 (m, 1H), 2.03-1.89 (m, 4H), 1.68 (m, 1H), 1.35 (t, *J* = 7.1, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) 206.88, 170.66, 144.77, 90.08, 73.72, 62.04, 46.62, 40.12, 38.79, 27.28, 22.68, 14.21. Anal. Calcd.: C, 43.13; H, 4.52, found: C, 45.08; H, 4.88.