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Aqueous Catalytic Pauson–Khand-Type Reactions of Enynes Using Formaldehyde: Transfercarbonylation Involving an Aqueous Decarbonylation and a Micellar Carbonylation

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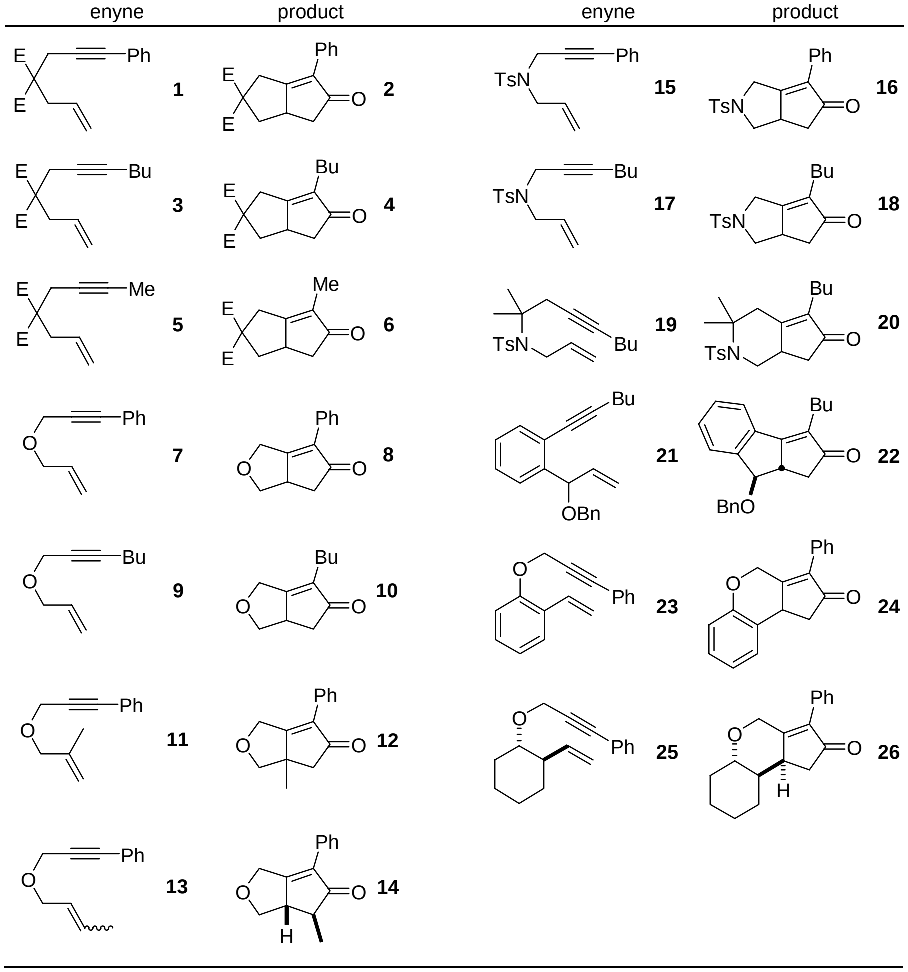
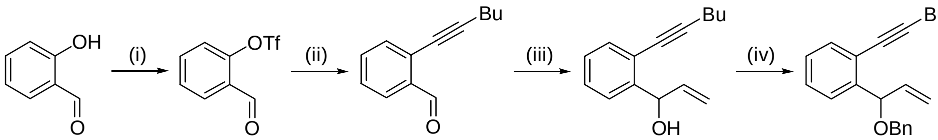
General Information. ^{1}H NMR and ^{13}C NMR were recorded on a JEOL JNM-ECP500 spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), coupling constant (Hz), integration, and interpretation. Infrared spectra (IR) were obtained on a JASCO FT/IR-420 spectrometer; absorption peaks are reported in reciprocal centimeters with the following relative intensities: s (strong), m (medium), or w (weak). Mass spectra were obtained on a SHIMADZU GCMS-QP 5000 instrument with ionization voltages of 70 eV. High resolution mass spectra (HRMS) were obtained on a JEOL JMS-700. Analytical GC was carried out on a HITACHI G-3900 gas chromatography, equipped with a flame ionization detector. Column chromatography was performed on SiO_2 (MERCK Silica gel 60).

Materials. $[RhCl(cod)]_2$ was prepared using the method reported.[1] 1,3-Bis(diphenylphosphino)propane (dppp), triphenylphosphine-3,3’,3’’-trisulfonic acid trisodium salt (TPPTS), and sodium dodecylsulfate (SDS) were purchased from Aldrich, Fluka, and WAKO, respectively. Formalin was used as a 37% aqueous solution (including 8% of methanol) purchased from Nacalai Tesque. 3-Bromo-1-phenyl-1-propyne (for synthesis of enyne **23**) was synthesized by bromination of 3-phenyl-2-propyn-1-ol using a modification of the reported method, respectively.[2] 3-Phenyl-2-propyn-1-ol was prepared by the reaction of phenylacetylene with paraformaldehyde using butyllithium as a base, respectively.[3] Enynes **1**, **3**, **5**, **7**, **9**, **11**, **13**, **15**, **17**, **19**, and **25** were synthesized using the procedure described previously.[4] Enynes **21** and **23** were prepared as described bellow.



Benzene, 2-(1-hexynyl)-1-[1-(phenylmethyl)oxy-2-propenyl]-, (21) (Table 2, entry 11)



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(i) *O*-trifluoromethanesulfonyl salicylaldehyde was prepared using the method of Stille as follows.[5] To a cold (0 °C) solution of salicylaldehyde (6.142 g, 50.3 mmol) and pyridine (12.6 mL, 75 mmol) in CH_2Cl_2 (25 mL) was added dropwise triflic anhydride (8.1 mL, 100 mmol) over a period of

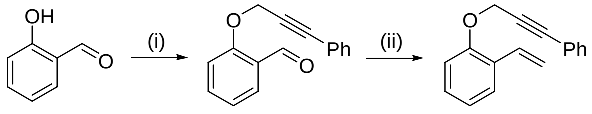
15 min, and the mixture was stirred at room temperature for 12 h. The reaction mixture was poured into water (60 mL), and the organic layer was separated. The aqueous layer was extracted with ether (3 x 50 mL), and the combined organic layers were dried over $MgSO_4$ and evaporated. The residue was purified by column chromatography on silica-gel (eluent; hexane/AcOEt=6/1, R_f 0.30) to give *O*-trifluoromethanesulfonyl salicylaldehyde (8.906 g, 35.0 mmol) in 70% yield.

(ii) Ethynylation of *O*-trifluoromethanesulfonyl salicylaldehyde was carried out using the method of Chen as follows.[6] A mixture of $PdCl_2(PPh_3)_2$ (348 mg, 0.50 mmol), *O*-trifluoromethanesulfonyl salicylaldehyde (7.291 g, 28.7 mmol), 1-hexyne (4.6 mL, 40.0 mmol), triethylamine (10 mL) and DMF (10 mL) was stirred at 80 °C for 3 h. After cooling the reaction mixture to room temperature, water (50 mL) and ether (50 mL) were added, and the organic layer was separated. The aqueous layer was extracted with ether (4 x 30 mL), and the combined organic layers were washed with water (2 x 10 mL) and brine (10 mL), dried over $MgSO_4$, and evaporated. The residue was purified by column chromatography on silica-gel (eluent; hexane/AcOEt=30/1, R_f 0.22) to give 2-(1-hexynyl)benzaldehyde (3.408 g, 18.3 mmol) in 64% yield.

(iii) To a cold (0 °C) solution of vinylmagnesium bromide in THF (1.0 M solution, 19 mL, 19 mmol) was added dropwise a solution of 2-(1-hexynyl)benzaldehyde (2.496 g, 12.9 mmol) in THF (11 mL) over a period of 15 min, and the mixture was stirred at 0 °C for 15 min and at room temperature for 3 h. The reaction mixture was cooled to 0 °C, and 1*N* HCl aqueous solution (20 mL) was added slowly. After separation of the organic layer, the aqueous layer was extracted with ether (3 x 40 mL). The combined organic layers were washed with saturated $NaHCO_3$ aqueous solution (2 x 10 mL) and brine (10 mL), dried over $MgSO_4$, and evaporated. The residue was purified by column chromatography on silica-gel (eluent; hexane/AcOEt=10/1, R_f 0.16) to give the desired allylic alcohol (2.424 g, 11.3 mmol) in 87% yield.

(iv) To a 10 mL two-necked flask were placed NaH (123 mg, 3.08 mmol), washed with haxane, and THF (2 mL). A solution of the allylic alcohol (214.3 mg, 1.00 mmol) in THF (2 mL) was added dropwise at room temperature over a period of 10 min, and the mixture was stirred for 1 h and then cooled to 0 °C. To the mixture was added dropwise a solution of benzyl bromide (257 mg, 1.50 mmol) in THF (2 mL) at 0 °C over 10 min, and the mixture was allowed to warm to room temperature and stirred at room temperature for 1.5 h and then at 60 °C for 12 h. Ater quenching of excess NaH with water (10 mL), an organic layer was separated. The aqueous layer was extracted with ether (3 x 10 mL), and the combined organic layers were washed with water (2 x 2 mL) and brine (2 mL), dried over $MgSO_4$, and evaporated. The residue was purified by column chromatography on silica-gel (eluent; hexane/AcOEt=20/1, R_f 0.28) to give the enyne **21** (298.5 mg, 0.982 mmol) in 98% yield. Colorless oil; R_f 0.28 (hexane/AcOEt=20/1); ^{1}H NMR ($CDCl_3$) δ 0.93 (t, *J* = 7.3 Hz, 3H), 1.45 (m, 2H), 1.54 (m, 2H), 2.40 (t, *J* = 7.3 Hz, 2H), 4.51 (dd, *J* = 12 Hz, *J* = 15 Hz, 2H), 5.17 (ddd, *J* = 1.2 Hz, *J* = 1.2 Hz, *J* = 10 Hz, 1H), 5.34 (ddd, *J* = 1.2 Hz, *J* = 1.2 Hz, *J* = 17 Hz, 1H), 5.43 (d, *J* = 6.1 Hz, 1H), 5.98 (ddd, *J* = 6.1 Hz, *J* = 10 Hz, *J* = 17 Hz, 1H), 7.20-7.54 (m, 9H); ^{13}C NMR ($CDCl_3$) δ 13.6, 19.2, 22.0, 30.8, 70.3, 78.3, 79.3, 99.6, 115.6, 122.9, 126.2, 127.2, 127.4, 127.7, 128.0, 128.2, 132.1, 138.1, 142.4; IR (neat) 2957 m, 2861 m, 2229 w, 1869 w, 1793 w, 1699 m, 1653 m, 1558 s, 1541 s, 1507 m, 1456 w, 1338 w, 1243 w, 1066 m, 924 w, 760 m, 697 m, 668 m; MS, m/z (relative intensity, %) 304 (M^+, 3), 247 (11), 214 (10), 213 (61), 198 (13), 195 (12), 185 (20), 183 (12), 171 (32), 170 (13), 169 (19), 167 (18), 165 (18), 158 (10), 157 (39), 156 (21), 155 (74), 154 (18), 153 (35), 152 (30), 145 (14), 144 (11), 143 (42), 142 (33), 141 (97), 131 (13), 130 (12), 129 (78), 128 (51), 127 (17), 117 (21), 116 (10), 115 (48), 105 (21), 97 (12), 95 (10), 92 (23), 91 (100), 85 (10), 83 (12), 81 (12), 79 (10), 77 (22), 71 (14), 69 (28), 65 (20), 57 (29), 55 (26); exact mass calcd for $C_{22}H_{24}O$ 304.1827, found 304.1817.

Benzene, 2-ethenyl-1-(3-phenyl-1-propynyl)oxy-, (23) (Table 2, entry 12).



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(i) *O*-3-Phenyl-2-propnyl salicylaldehyde was prepared using a modification of the method reported by Buchwald as follows.[7] To a 100 mL two-necked flask equipped with a reflux condenser were placed 3-bromo-1-phenyl-1-propyne (4.294 g, 22.0 mmol), salicylaldehyde (2.447 g, 20.0 mmol),

Na_2CO_3 (4.255 g, 40.1 mmol), DME (20 mL), and DMF (20 mL), and the mixture was stirred at 80 °C for 4 h. After filtration of the reaction mixture and concentration of the filtrate, the residue was dissolved in 50 mL of ether. 50 mL of water was added, and the organic layer was separated. The aqueous layer was extracted with ether (3 x 30 mL), and the combined organic layers were washed with water (3 x 10 mL) and brine (10 mL), dried over $MgSO_4$, and concentrated *in vacuo* to give a pale yellow solid. This solid was crystallized from hexane to afford a needle crystal (4.211 g, 17.8 mmol) in 89% yield.

(ii) Ethenylation of *O*-3-phenyl-2-propnyl salicylaldehyde was carried out as follows.[8] To a 100 mL two-necked flask were placed triphenylphosphonium bromide (9.290 g, 26.0 mmol) and THF (40 mL), and the mixture was cooled to 0 °C. BuLi (1.60 M hexane solution, 15.0 mL, 24.0 mmol) was added dropwise at 0 °C over a period of 20 min, and then the resulting orange solution was stirred at room temperature for 30 min. To the re-cooled (0 °C) mixture was added dropwise a solution of *O*-3-phenyl-2-propnyl salicylaldehyde (2.863 g, 12.1 mmol) in THF (10 mL) over a period of 15 min, and the mixture was stirred at 0 °C for 15 min and at room temperature for 2 h. After quenching with MeOH (1 mL), the precipitate was removed by filtration, and washed with ether (100 mL). The combined filtrate was concentrated *in vacuo*, and ether (50 mL) was added to the residue. After filtration and evaporation, the residue was purified by column chromatography on silica-gel (eluent; hexane/AcOEt=20/1, R_f 0.37) to give the desired enyne **23** (2.044 g, 8.72 mmol) in 72% yield. Colorless oil; R_f 0.37 (hexane/AcOEt=30/1); ^1H NMR ($CDCl_3$) δ 4.92 (s, 2H), 5.28 (dd, J = 1.2 Hz, J = 11 Hz, 1H), 5.75 (dd, J = 1.2 Hz, J = 18 Hz, 1H), 6.89 (dd, J = 11 Hz, J = 18 Hz, 1H), 7.05-7.51 (m, 9H); ^{13}C NMR ($CDCl_3$) δ 57.2, 84.0, 87.1, 113.0, 114.6, 121.5 (two overlapping signals), 122.3, 126.5, 127.5, 128.2, 128.6, 128.7, 131.5, 131.8, 155.0; IR (neat) 3062 w, 2919 w, 2289 w, 1626 m, 1598 m, 1487 s, 1455 s, 1415 w, 1372 m, 1294 m, 1261 m, 1219 s, 1108 s, 1017 s, 999 s, 961 w, 913 m, 754 s, 691 s; MS, m/z (relative intensity, %) 234 (M^+, 5), 233 (14), 219 (10), 116 (11), 115 (100), 89 (13), 65 (15), 63 (11); exact mass calcd for $C_{17}H_{14}O$ 234.1045, found 234.1044.

Typical Procedure for Aqueous Catalytic Pauson-Khand-Type Reaction of Enynes with Formaldehyde (Table 1, entry 12). In a 5-mL two-necked flask equipped a reflux condenser were placed $[RhCl(cod)]_2$ (6.16 mg, 0.0125 mmol), dppp (13.55 mg, 0.025 mmol), TPPTS (14.21 mg, 0.025 mmol) and water (0.5 mL), and the mixture was stirred at room temperature for 15 min and turned out to a light yellow suspension. After SDS (144.2 mg, 0.5 mmol), formalin (0.1 mL, 1.25 mmol), enyne **1** (78.6 mg, 0.25 mmol) and water (1.4 mL) were added, the mixture was degassed, charged with N_2, and stirred at 100 °C under N_2 until **1** was consumed. The reaction was pursued by monitoring with TLC. Ether (10 mL) was added to the reaction mixture, and the biphasic mixture was stirred for 15 min. The separated aqueous layer was extracted with ether (3 x 10 mL), and the combined organic layers were dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica-gel (eluent; hexane/AcOEt=4/1) to give bicyclic cyclopentenone **2** (82.1 mg, 0.240 mmol) in 96% yield as colorless oil.

Procedure for the Reaction of Enyne 1 with Paraformaldehyde in water (Table 1, entry 13). In a 5-mL two-necked flask equipped a reflux condenser were placed $[RhCl(cod)]_2$ (6.16 mg, 0.0125 mmol), dppp (13.55 mg, 0.025 mmol), TPPTS (14.21 mg, 0.025 mmol) and water (0.5 mL), and the mixture was stirred at room temperature for 15 min and turned out to a light yellow suspension. After SDS (144.2 mg, 0.5 mmol), paraformaldehyde (37.5 mg, 1.25 mmol), enyne **1** (78.6 mg, 0.25 mmol) and water (1.5 mL) were added, the mixture was degassed, charged with N_2, and stirred at 100 °C under N_2 until **1** was consumed. The reaction was pursued by monitoring with TLC. Ether (10 mL) was added to the reaction mixture, and the biphasic mixture was stirred for 15 min. The separated aqueous layer was extracted with ether (3 x 10 mL), and the combined organic layers were dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica-gel (eluent; hexane/AcOEt=4/1) to give bicyclic cyclopentenone **2** (83.1 mg, 0.243 mmol) in 97% yield as colorless oil.

Procedure for the Reaction of Enyne 1 with Paraformaldehyde in Xylene. In a 5-mL two-necked flask equipped a reflux condenser were placed $[RhCl(cod)]_2$ (6.16 mg, 0.0125 mmol), dppp (13.55 mg, 0.025 mmol), and xylene (0.5 mL), and the mixture was stirred at room temperature for 15 min and turned out to a light yellow suspension. After paraformaldehyde (75.1 mg, 2.50 mmol), enyne **1** (78.6 mg, 0.250 mmol) and xylene (1.5 mL) were added, the mixture was degassed, charged with N_2, and stirred at 130 °C under N_2 for 24. The reaction was pursued by monitoring with TLC. The reaction mixture was concentrated *in vacuo*, and the residue was purified by column chromatography on silica-gel (eluent; hexane/AcOEt=4/1) to give bicyclic cyclopentenone **2** (45.5 mg, 0.133 mmol) in 53% yield and unreacted **1** (11.0 mg, 0.035 mmol) in 14%.

3,3a,4,5-Tetrahydro-2,2(1*H*)-pentalenedicarboxylic acid, 5-oxo-6-phenyl-, diethyl ester, (2).[9] Colorless oil; R_f 0.20 (hexane/AcOEt=4/1); ^{1}H NMR ($CDCl_3$) δ 1.20 (t, *J* = 7.3 Hz, 3H), 1.29 (t, *J* = 7.3 Hz, 3H), 1.74 (t, *J* = 12 Hz, 1H), 2.29 (dd, *J* = 3.7 Hz, *J* = 18 Hz, 1H), 2.79 (dd, *J* = 8.5 Hz, *J* = 18 Hz, 1H), 2.82 (dd, *J* = 7.9 Hz, *J* = 12 Hz, 1H), 3.08-3.15 (m, 1H), 3.27 (d, *J* = 19 Hz, 1H), 3.63 (d, *J* = 19 Hz, 1H), 4.15 (dq, *J* = 3.7 Hz, *J* = 7.3 Hz, 2H), 4.26 (q, *J* = 7.3 Hz, 2H), 7.28-7.56 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 13.8, 13.9, 35.8, 38.6, 42.5, 42.7, 61.2, 61.8, 62.0, 128.0, 128.3, 130.8, 135.3, 170.6, 171.4, 178.9, 207.0; IR (neat) 2981 m, 2937 m, 1730 s, 1651 m, 1600 w, 1496 w, 1446 m, 1413 m, 1389 m, 1367 m, 1347 w, 1272 s, 1159 s, 1119 m, 1096 m, 1063 s, 1039 m, 1016 m, 930 w, 887 w, 858 w, 765 m, 698 s, 607 m; MS, m/z (relative intensity, %) 342 (M^+, 30), 269 (20), 268 (93), 196 (18), 195 (100), 194 (11), 167 (48), 166 (18), 165 (27), 153 (12), 152 (19), 141 (10), 115 (13); exact mass calcd for $C_{20}H_{22}O_5$ 342.1468, found 342.1470.

3,3a,4,5-Tetrahydro-2,2(1*H*)-pentalenedicarboxylic acid, 6-butyl-5-oxo-, diethyl ester, (4).[10] Colorless oil; R_f 0.30 (hexane/AcOEt=4/1); ^{1}H NMR ($CDCl_3$) δ 0.83 (t, *J* = 7.3 Hz, 3H), 1.20 (t, *J* = 7.3 Hz, 3H), 1.23 (t, *J* = 7.3 Hz, 3H), 1.35 (m, 2H), 1.60 (t, *J* = 7.3 Hz, 2H), 2.03 (dd, *J* = 3.1 Hz, *J* = 18 Hz, 1H), 2.05 (td, *J* = 7.3 Hz, *J* = 15 Hz, 1H), 2.19 (td, *J* = 7.3 Hz, *J* = 15 Hz, 1H), 2.58 (dd, *J* = 6.7 Hz, *J* = 18 Hz, 1H), 2.74 (dd, *J* = 7.9 Hz, *J* = 12 Hz, 1H), 2.89-2.96 (m, 1H), 3.16 (d, *J* = 20 Hz, 1H), 3.20

(d, *J* = 20 Hz, 1H), 4.16 (q, *J* = 7.3 Hz, 2H), 4.20 (q, *J* = 7.3 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.7, 13.8, 13.9, 22.5, 23.4, 29.9, 34.1, 39.0, 41.4, 42.6, 60.9, 61.7, 61.9, 137.1, 170.9, 171.5, 177.5, 209.1; IR (neat) 2958 s, 2934 s, 2872 m, 1731 s, 1668 s, 1466 m, 1366 m, 1263 s, 1191 s, 1154 s, 1096 s, 1065 s, 1041 s, 860 m; MS, m/z (relative intensity, %) 322 (M^+, 39), 277 (21), 276 (13), 250 (17), 249 (100), 248 (81), 233 (14), 230 (10), 220 (11), 219 (34), 207 (10), 206 (52), 202 (19), 177 (17), 176 (15), 174 (26), 173 (25), 162 (19), 161 (12), 160 (11), 149 (38), 148 (15), 147 (34), 145 (11), 134 (12), 133 (40), 132 (10), 131 (11), 119 (14), 117 (14), 105 (39), 103 (12), 91 (47), 79 (32), 78 (11), 77 (32), 65 (14), 55 (24), 53 (10); exact mass calcd for $C_{18}H_{26}O_5$ 322.1780, found 322.1778

3,3a,4,5-Tetrahydro-2,2(1*H*)-pentalenedicarboxylic acid, 6-methyl-5-oxo-, diethyl ester, (6).[11] Colorless oil; R_f 0.29 (hexane/AcOEt=2/1); ^{1}H NMR ($CDCl_3$) δ 1.24 (t, *J* = 7.3 Hz, 3H), 1.26 (t, *J* = 7.3 Hz, 3H), 1.63 (t, *J* = 12 Hz, 1H), 1.69 (s, 3H), 2.06 (dd, *J* = 3.1 Hz, *J* = 18 Hz, 1H), 2.62 (dd, *J* = 6.1 Hz, *J* = 18.3 Hz, 1H), 2.76 (dd, *J* = 7.3 Hz, *J* = 12 Hz, 1H), 2.92-3.00 (m, 1H), 3.15 (d, *J* = 19 Hz, 1H), 3.22 (d, *J* = 19 Hz, 1H), 4.19 (q, *J* = 7.3 Hz, 2H), 4.23 (q, *J* = 7.3 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 8.5, 13.9, 14.0, 33.9, 39.1, 41.3, 42.6, 60.9, 61.9, 62.0, 132.9, 170.9, 171.6, 177.7, 209.4; IR (neat) 2982 m, 1733 s, 1674 s, 1447 m, 1418 m, 1395 m, 1366 m, 1270 s, 1194 s, 1095 m, 1065 m, 1040 m, 936 w, 859 m, 665 m; MS, m/z (relative intensity, %) 280 (M^+, 32), 235 (13), 234 (14), 207 (12), 206 (71), 178 (26), 177 (11), 134 (16), 133 (100), 132 (10), 105 (36), 91 (23), 79 (18), 77 (16); exact mass calcd for $C_{15}H_{20}O_5$ 280.1310, found 280.1314.

3a,4-Dihydro-1*H*-cyclopenta[c]furan-5(3*H*)-one, 6-phenyl-, (8).[11] Colorless oil; R_f 0.23 (hexane/AcOEt=2/1); ^{1}H NMR ($CDCl_3$) δ 2.34 (dd, *J* = 3.7 Hz, *J* = 18 Hz, 1H), 2.85 (dd, *J* = 6.1 Hz, *J* = 18 Hz, 1H), 3.24 (dd, *J* = 7.9 Hz, *J* = 12 Hz, 1H), 3.29-3.37 (m, 1H), 4.37 (t, *J* = 7.9 Hz, 1H), 4.59 (d, *J* = 17 Hz, 1H), 4.94 (d, *J* = 17 Hz, 1H), 7.33-7.55 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 40.3, 43.3, 66.3, 71.3, 128.0, 128.0, 128.5, 128.6, 130.6, 134.7, 177.4, 206.8; IR (neat) 2940 w, 2852 m, 1716 s, 1418 m, 1397 w, 1362 w, 1301 w, 1166 w, 1120 m, 1026 m, 907 m, 890 m, 832 w, 768 m, 697 m, 668 m, 604 w; MS, m/z (relative intensity, %) 200 (M^+, 64), 171 (12), 170 (28), 169 (32), 158 (53), 143 (16), 142 (47), 141

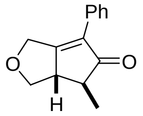
(100), 130 (10), 129 (29), 128 (42), 127 (10), 115 (56), 103 (21), 102 (14), 89 (12), 77 (22), 70 (27), 65 (10), 63 (20), 57 (13), 55 (13), 51 (16); exact mass calcd for $C_{13}H_{12}O_2$ 200.0837, found 200.0827

3a,4-Dihydro-1*H*-cyclopenta[c]furan-5(3*H*)-one, 6-butyl-, (10).[4] Colorless oil; R_f 0.31 (hexane/AcOEt=4/1); ^{1}H NMR ($CDCl_3$) δ 0.87 (t, *J* = 7.3 Hz, 3H), 1.22-1.31 (m, 2H), 1.35-1.46 (m, 2H), 2.10 (q, *J* = 7.3 Hz, 2H), 2.22-2.28 (m, 1H), 2.63 (dd, *J* = 5.5 Hz, *J* = 18 Hz, 1H), 3.15 (dd, *J* = 12 Hz, *J* = 18 Hz, 1H), 3.16 (dd, *J* = 4.9 Hz, *J* = 12 Hz, 1H), 4.28 (t, *J* = 4.9 Hz, 1H), 4.49 (d, *J* = 16 Hz, 1H), 4.58 (d, *J* = 16 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.7, 22.5, 23.9, 29.8, 38.8, 43.3, 64.8, 71.7, 136.9, 176.0, 209.1; IR (neat) 2958 m, 1716 s, 1651 s, 1558 m, 1541 m, 1522 m, 1458 m, 1419 w, 1174 w, 1043 m, 669 m; MS, m/z (relative intensity, %) 180 (M^+, 100), 150 (13), 149 (80), 148 (10), 138 (12), 137 (14), 135 (31), 133 (26), 123 (17), 122 (12), 121 (16), 120 (13), 110 (12), 109 (30), 108 (30), 107 (42), 105 (13), 96 (13), 95 (43), 94 (17), 93 (38), 91 (32), 81 (33), 80 (33), 79 (94), 78 (20), 77 (73), 69 (14), 67 (34), 66 (16), 65 (24), 55 (39), 53 (42), 52 (15), 51 (24); exact mass calcd for $C_{11}H_{16}O_2$ 180.1150, found 180.1136.

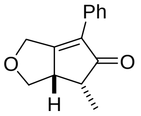
3a,4-Dihydro-1*H*-cyclopenta[c]furan-5(3*H*)-one, 3a-methyl-6-phenyl-, (12).[12] Colorless oil; R_f 0.15 (hexane/AcOEt=5/1); ^{1}H NMR ($CDCl_3$) δ 1.39 (s, 3H), 2.54 (d, *J* = 17 Hz, 1H), 2.60 (d, *J* = 17 Hz, 1H), 3.43 (d, *J* = 7.9 Hz, 1H), 4.03 (d, *J* = 7.9 Hz, 1H), 4.60 d, *J* = 17 Hz, 1H), 4.98 (d, *J* = 17 Hz, 1H), 7.33-7.51 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 24.7, 47.8, 48.7, 65.3, 76.5, 128.1, 128.6, 128.7, 130.5, 133.2, 180.6, 206.7; IR (neat) 2968 m, 2929 m, 2870 m, 1712 s, 1653 s, 1495 m, 1450 m, 1375 m, 1294 m, 1151 m, 1074 m, 1024 m, 918 w, 895 m, 847 w, 766 s, 696 s, 648 w; MS, m/z (relative intensity, %) 214 (M^+, 82), 185 (21), 184 (51), 183 (21), 173 (12), 172 (97), 171 (18), 169 (44), 157 (26), 156 (33), 155 (27), 153 (14), 143 (18), 142 (27), 141 (100), 129 (53), 128 (40), 127 (15), 116 (14), 115 (81), 103 (26), 102 (13), 91 (20), 89 (16), 85 (16), 78 (10), 77 (36), 76 (18), 71 (25), 69 (18), 65 (13), 64 (13), 63 (23), 58 (11), 55 (10), 51 (23); exact mass calcd for $C_{14}H_{14}O_2$ 214.0994, found 214.0997

3a,4-Dihydro-1*H*-cyclopenta[c]furan-5(3*H*)-one, 4-methyl-6-phenyl-, (14).[13] GC analysis of the crude reaction mixture showed that a mixture of *cis*-**14** and *trans*-**14** was produced in a ratio of

64:36. Both isomers can be separated easily by column chromatography on silica-gel (eluent; hexane/AcOEt=4/1). (*cis*-**14**): White solid; mp 62-65 °C (hexane); R_f 0.17 (hexane/AcOEt=4/1); ^{1}H NMR ($CDCl_3$) δ 1.28 (d, *J* = 7.3 Hz, 3H), 2.29 (qd, *J* = 7.3 Hz, *J* = 11 Hz, 1H), 2.96-3.03 (m, 1H), 3.22 (dd, *J* = 7.9 Hz, *J* = 11 Hz, 1H), 4.36 (t, *J* = 7.9 Hz, 1H), 4.54 (d, *J* = 16 Hz, 1H), 4.87 (d, *J* = 16 Hz, 1H), 7.26-7.47 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 13.7, 47.4, 52.0, 66.4, 71.1, 127.9, 128.5, 128.6, 130.7, 174.7, 208.7; IR (KBr) 2939 w, 2864 w, 1697 s, 1651 m, 1635 m, 1558 m, 1541 m, 1493 m, 1456 m, 1398 w, 1358 w, 1292 w, 1167 w, 1124 w, 1028 s, 895 m, 779 m, 748 m, 696 m, 667 w; MS, m/z (relative intensity, %) 214 (M^+, 100), 186 (18), 185 (19), 184 (36), 183 (24), 171 (15), 169 (48), 159 (14), 158 (99), 157 (26), 156 (40), 155 (43), 153 (18), 152 (12), 143 (19), 142 (33), 141 (95), 131 (11), 130 (18), 129 (61), 128 (55), 127 (20), 116 (16), 115 (94), 103 (27), 102 (20), 91 (31), 89 (17), 78 (19), 77 (45), 76 (22), 75 (11), 69 (13), 65 (15), 64 (21), 63 (29), 55 (22), 53 (10), 51 (33), 50 (11); exact mass calcd for $C_{14}H_{14}O_2$ 214.0994, found 214.0986. (*trans*-**14**): Colorless oil; R_f 0.13 (hexane/AcOEt=4/1); ^{1}H NMR ($CDCl_3$) δ 1.17 (d, *J* = 7.3 Hz, 3H), 2.80 (qd, *J* = 7.3 Hz, *J* = 11 Hz, 1H), 3.12-3.17 (m, 1H), 3.45 (d, *J* = 9.2 Hz, 1H), 3.51 (dd, *J* = 9.2 Hz, *J* = 11 Hz, 1H), 4.02 (d, *J* = 9.8 Hz, 1H), 4.18 (dd, *J* = 7.9 Hz, *J* = 9.8 Hz, 1H), 7.30-7.54 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 14.2, 40.4, 41.0, 60.4, 68.4, 127.2, 128.5, 128.7, 130.2, 133.7, 174.7, 208.7; IR (neat) 2933 w, 1701 s, 1651 m, 1558 m, 1541 m, 1506 m, 1456 m, 1419 w, 1398 w, 1144 w, 1038 m, 887 w, 752 m, 698 m, 667m; MS, m/z (relative intensity, %) 214 (M^+, 0.4), 196 (13), 182 (12), 180 (52), 166 (12), 153 (13), 151 (13), 150 (11), 149 (33), 139 (16), 138 (12), 137 (17), 135 (19), 126 (21), 125 (15), 124 (20), 123 (27), 121 (16), 112 (15), 111 (43), 110 (21), 109 (33), 108 (16), 107 (19), 98 (13), 97 (19), 96 (25), 95 (36), 94 (17), 93 (19), 91 (18), 86 (10), 85 (78), 83 (19), 82 (12), 81 (23), 80 (14), 79 (39), 77 (29), 71 (10), 69 (67), 68 (17), 67 (34), 66 (12), 65 (16), 57 (100), 55 (38), 53 (25), 51 (10); exact mass calcd for $C_{14}H_{14}O_2$ 214.0994, found 214.0991.



major (*cis*-**14**)



minor (*trans*-**14)**

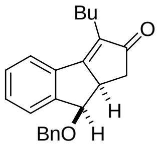
2,3,3a,4-Tetrahydro-cyclopenta[c]pyrrol-5(1*H*)-one, 2-[(4-methylphenyl)sulfonyl]-6-phenyl-, (16).[9] White solid; mp 160-163 °C (hexane/AcOEt); R_f 0.22 (hexane/AcOEt=2/1); ^{1}H NMR ($CDCl_3$) δ 2.26 (d, *J* = 18 Hz, 1H), 2.41 (s, 3H), 2.62 (dd, *J* = 9.2 Hz, *J* = 12 Hz, 1H), 2.79 (dd, *J* = 6.1 Hz, *J* = 18 Hz, 1H), 3.17-3.25 (m, 1H), 4.08 (d, *J* = 17 Hz, 1H), 4.09 (d, *J* = 12 Hz, 1H), 4.63 (d, *J* = 17 Hz, 1H), 7.31 (d, *J* = 6.7 Hz, 2H), 7.34-7.48 (m, 5H), 7.72 (d, *J* = 6.7 Hz, 2H); ^{13}C NMR ($CDCl_3$) ? 21.5, 40.7, 41.9, 48.4, 52.0, 127.4, 128.2, 128.7, 129.0, 130.0, 136.1, 171.8, 206.1; IR (KBr) 2941 w, 1711 s, 1653 m, 1541 m, 1522 m, 1508 m, 1473 w, 1458 m, 1340 s, 1302 w, 1163 s, 1095 m, 1061 m, 901 m, 812 m, 764 w, 694 m, 661 m; MS, m/z (relative intensity, %) 353 (M^+, 11), 199 (14), 198 (100), 197 (50), 171 (60), 170 (48), 169 (47), 168 (35), 155 (11), 143 (39), 142 (22), 141 (59), 129 (17), 128 (44), 127 (10), 115 (34), 91 (60), 89 (10), 77 (12), 67 (10), 65 (31), 63 (10); exact mass calcd for $C_{20}H_{19}NO_3S$ 353.1086, found 353.1077.

2,3,3a,4-Tetrahydro-cyclopenta[c]pyrrol-5(1*H*)-one, 6-butyl-2-[(4-methylphenyl)sulfonyl]-, (18).[4] White solid; mp 117-118 °C (hexane/ether); R_f 0.18 (hexane/AcOEt=3/1); ^{1}H NMR ($CDCl_3$) δ 0.84 (t, *J* = 7.3 Hz, 3H), 1.14-1.23 (m, 2H), 1.28-1.37 (m, 2H), 2.01 (dd, *J* = 3.7 Hz, *J* = 18 Hz, 1H), 2.03 (td, *J* = 7.3 Hz, *J* = 15 Hz, 1H), 2.17 (td, *J* = 7.9 Hz, *J* = 15 Hz, 1H), 2.42 (s, 3H), 2.55 (dd, *J* = 9.2 Hz, *J* = 12 Hz, 1H), 2.58 (dd, *J* = 6.7 Hz, *J* = 18 Hz, 1H), 2.96-3.04 (m, 1H), 3.97 (t, *J* = 9.2 Hz, 1H), 3.99 (d, *J* = 16 Hz, 1H), 4.23 (d, *J* = 16 Hz, 1H), 7.33 (d, *J* = 7.9 Hz, 2H), 7.72 (d, *J* = 7.9 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.6, 21.5, 22.5, 23.3, 30.0, 39.2, 41.6, 46.8, 52.5, 127.4, 130.0, 133.4, 138.3, 144.0, 170.8, 207.6; IR (KBr) 2954 m, 1701 s, 1674 s, 1651 s, 1558 m, 1541 m, 1522 m, 1458 m, 1419 w, 1348 m, 1163 m, 1092 w, 1043 m, 814 w, 712 w, 665 s; MS, m/z (relative intensity, %) 333 (M^+, 16), 197 (10), 179 (12), 178 (100), 155 (11), 150 (31), 149 (22), 148 (10), 136 (10), 108 (10), 107 (15), 93 (16), 92 (10), 91 (67), 81 (11), 80 (10), 79 (30), 77 (21), 67 (15), 65 (29), 55 (16); exact mass calcd for $C_{18}H_{23}NO_3S$ 333.1398, found 333.1390.

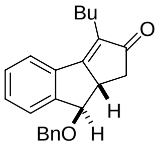
1,2,3,4,7,7a-Hexahydro-cyclopenta[c]pyridin-6(6*H*)-one, 5-butyl-3,3-dimethyl-2-[(4-methylphenyl)sulfonyl]-, (20).[4] White solid; mp 176-178 °C (hexane); R_f 0.15 (hexane/AcOEt=4/1);

^{1}H NMR ($CDCl_3$) δ 0.87 (t, *J* = 7.3 Hz, 3H), 0.98 (s, 3H), 1.25-1.35 (m, 4H), 1.57 (s, 3H), 1.97 (d, *J* = 19 Hz, 1H), 2.06-2.19 (m, 2H), 2.43 (s, 3H), 2.52 (d, *J* = 19 Hz, 1H), 2.55 (d, *J* = 19 Hz, 1H), 2.56 (d, *J* = 19 Hz, 1H), 2.78 (dd, *J* = 12 Hz, *J* = 12 Hz, 1H), 2.87-2.95 (m, 1H), 4.55 (dd, *J* = 6.1 Hz, *J* = 12 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.71 (d, *J* = 8.0 H z, 2H); ^{13}C NMR ($CDCl_3$) δ 13.7, 21.4, 22.3, 22.6, 23.3, 29.9, 30.8, 37.6, 39.3, 43.0, 49.3, 59.0, 126.8, 129.6, 139.8, 140.3, 143.1, 169.2, 206.8; IR (KBr) 2949 w, 1828 w, 1697 s, 1651 s, 1540 m, 1522 m, 1458 m, 1419 w, 1373 w, 1331 w, 1155 m, 1070 w, 1045 w, 955 w, 914 w, 812 m, 706 w, 669 m; MS, m/z (relative intensity, %) 375 (M^+, 33), 361 (13), 360 (57), 281 (11), 224 (61), 221 (17), 220 (100), 212 (23), 207 (25), 192 (21), 177 (19), 163 (10), 155 (33), 149 (10), 91 (55), 77 (11), 71 (14), 70 (56), 65 (10); exact mass calcd for $C_{21}H_{29}NO_3S$ 375.1868, found 375.1868.

8,8a-Dihydro-cyclopenta[a]inden-2-one, 3-butyl-8-(phenylmethyl)oxy-, (22). GC analysis of the crude reaction mixture showed that a mixture of *trans*-**22** and *cis*-**22** was produced in a ratio of 2.4:1. Because both isomers cannot be separated by column chromatography on silica-gel (eluent; hexane/AcOEt=10/1), the following spectra were obtained as a mixture of them. Each signal on the NMR spectra was assigned by referring to the *O*-TBS derivatives.[4] Colorless oil; R_f 0.22 (hexane/AcOEt=10/1); ^{1}H NMR ($CDCl_3$) δ 0.92 (t, *J* = 7.3 Hz, 3H, *cis*), 0.93 (t, *J* = 7.3 Hz, 3H, *trans*), 1.32-1.44 (m, 2H and 2H, *trans* and *cis*), 1.44-1.64 (m, 2H and 2H, *trans* and *cis*), 2.33-2.58 (m, 2H and 2H, *trans* and *cis*), 2.42 (dd, *J* = 4.9 Hz, *J* = 17 Hz, 1H, *cis*), 2.61 (dd, *J* = 6.7 Hz, *J* = 18 Hz, 1H, *trans*), 2.69 (dd, *J* = 6.7 Hz, *J* = 17 Hz, 1H, *cis*), 2.84 (dd, *J* = 4.9 Hz, *J* = 18 Hz, 1H, *trans*), 3.37 (bq, *J* = 5.5 Hz, 1H, *trans*), 3.45 (bq, *J* = 6.1 Hz, 1H, *cis*), 4.58 (s, 2H and 2H, *trans*), 4.73 (d, *J* = 6.1 Hz, 1H, *cis*), 4.76 (d, J = 18 Hz, 1H, *cis*), 4.81 (d, *J* = 5.5 Hz, 1H, *trans*), 4.84 (d, J = 18 Hz, 1H, *cis*), 7.24-7.73 (m, 9H and 9H, *trans* and *cis*); ^{13}C NMR ($CDCl_3$) δ 13.9 (*cis*), 14.0 (*trans*), 22.7 (*cis*), 22.8 (*trans*), 23.3 (*cis*), 23.5 (*trans*), 30.8 (*cis*), 30.9 (*trans*), 36.5 (*trans*), 41.0 (*cis*), 49.2 (*trans*), 53.9 (*trans*), 63.1 (*cis*), 65.3 (*cis*), 70.6 (*trans*), 71.9 (*cis*), 123.9 (*cis*), 124.9 (*trans*), 125.4 (*cis*), 126.9 (*cis*), 127.0 (*trans*), 127.5 (*trans*), 127.6 (*trans*), 127.7 (*cis*), 128.0 (*cis*), 128.4 (*trans*), 128.5 (*cis*), 128.6 (*trans*), 128.8 (*cis*), 129.5 (*trans*), 130.5 (*trans*), 131.2 (*cis*), 136.5 (*trans*), 136.6 (*cis*), 137.8 (*cis*), 138.0 (*trans*), 147.5 (*trans*), 147.9 (*cis*), 170.5 (*cis*), 172.8 (*trans*), 208.8 (*cis*), 219.9 (*trans*); IR (neat) 2955 s, 2928 s, 2859 m, 1699 s, 1653 s, 1496 w, 1455 m, 1351 m, 1269 m, 1205 w, 1170 m, 1097 s, 1027 m, 922 w, 755 s, 698 m, 607w; MS, m/z (relative intensity, %) 332 (M$^+$, 3), 241 (38), 183 (11), 181 (18), 153 (14), 152 (11), 141 (11), 129 (10), 128 (13), 115 (11), 91 (100), 77 (10), 65 (13), 55 (11) (*trans*); MS, m/z (relative intensity, %) 332 (M$^+$, 4), 241 (36), 181 (14), 128 (11), 115 (10), 91 (100), 65 (13) (*cis*); exact mass calcd for $C_{23}H_{24}O_2$ 332.1776, found 332.1766.



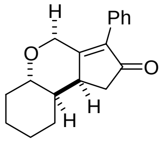
major (*trans*-**22**)



minor (*cis*-**22**)

1,9b-Dihydro-cyclopenta[c]chromen-2(4*H*)-one, 3-phenyl,- (24). Colorless oil; R_f 0.21 (hexane/AcOEt=4/1); ^{1}H NMR (CDCl$_3$) δ 2.78 (dd, J = 3.7 Hz, J = 18.3 Hz, 1H), 3.20 (dd, J = 6.7 Hz, J = 18.3 Hz, 1H), 4.20 (m, 1H), 5.19 (dd, J = 15 Hz, J = 20 Hx, 2H), 6.91-7.45 (m, 9H); ^{13}C NMR (CDCl$_3$) δ 37.2, 41.0, 65.2, 117.0, 122.0, 127.0, 128.4, 128.51, 128.55, 128.8, 130.1, 138.0, 153.6, 165.4, 204.6; IR (KBr) 3057 w, 2925 m, 1705 s, 1606 w, 1580 m, 1486 s, 1456 m, 1404 w, 1345 m, 1308 m, 1227 s, 1129 m, 1079 w, 1040 m, 989 m, 918 m, 831 w, 752 m, 698 m, 631 w, 600 w; MS, m/z (relative intensity, %) 262 (M$^+$, 91), 261 (23), 260 (32), 259 (12), 235 (10), 234 (49), 233 (75), 232 (13), 231 (32), 220 (48), 219 (100), 218 (18), 215 (15), 205 (12), 203 (17), 202 (28), 194 (15), 191 (15), 189 (18), 165 (14), 131 (15), 128 (14), 116 (14), 115 (58), 105 (20), 103 (13), 102 (11), 101 (16), 91 (16), 89 (28), 88 (10), 77 (25), 76 (10), 65 (16), 63 (21), 51 (12); exact mass calcd for $C_{18}H_{14}O_2$ 262.0994, found 262.0996.

1,5a,6,7,8,9,9a,9b-Octahydro-cyclopenta[c]chromen-2(4*H*)-one, 3-phenyl-, (26).[4] White solid; mp 160-162 °C (hexane/ether); R_f 0.20 (hexane/AcOEt=5/1); ^{1}H NMR (CDCl$_3$) δ 1.10-1.40 (m, 5H), 1.72 (d, J = 14 Hz, 1H), 1.84 (t, J = 14 Hz, 2H), 1.90-2.00 (m, 1H), 2.22 (dd, J = 3.1 Hz, J = 19 Hz, 1H), 2.58-2.63 (m, 1H), 2.71 (dd, J = 6.7 Hz, J = 19 Hz, 1H), 3.27 (dt, J = 4.3 Hz, J = 9.8 Hz, 1H), 4.33 (d, J = 14 Hz, 1H), 4.84 (d, J = 14 Hz, 1H), 7.20-7.40 (m, 5H); ^{13}C NMR (CDCl$_3$) δ 24.6, 25.2, 30.2, 31.8, 39.7, 43.2, 50.0, 65.6, 80.4, 128.1, 128.3, 129.0, 130.2, 137.6, 169.0, 205.9; IR (KBr) 2929 m, 2858 m, 1697 s, 1651 m, 1558 m, 1541 m, 1522 m, 1456 m, 1417 w, 1273 w, 1134 w, 1076 m, 987 w, 845 w, 764 w, 702 m, 669 w; MS, m/z (relative intensity, %) 268 (M^+, 100), 241 (13), 240 (66), 239 (34), 172 (11), 171 (39), 170 (22), 169 (16), 165 (12), 160 (67), 159 (13), 158 (40), 157 (43), 155 (11), 153 (14), 152 (11), 145 (10), 144 (20), 143 (14), 142 (35), 141 (50), 133 (10), 132 (11), 131 (48), 130 (15), 129 (64), 128 (46), 127 (16), 116 (11), 115 (67), 103 (17), 102 (11), 91 (25), 89 (15), 81 (16), 79 (15), 77 (25), 69 (11), 67 (38), 65 (14), 63 (11), 55 (29), 53 (10), 51 (10); exact mass calcd for $C_{18}H_{20}O_2$ 268.1463, found 268.1454.



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