Supporting Information

The First Tandem [2 + 2] Cycloaddition-Michael Reaction Using Ynolates: Facile Construction of Substituted Carbocycles

Mitsuru Shindo,* Kenji Matsumoto, Yusuke Sato, and Kozo Shishido

Institute for Medicinal Resources, University of Tokushima

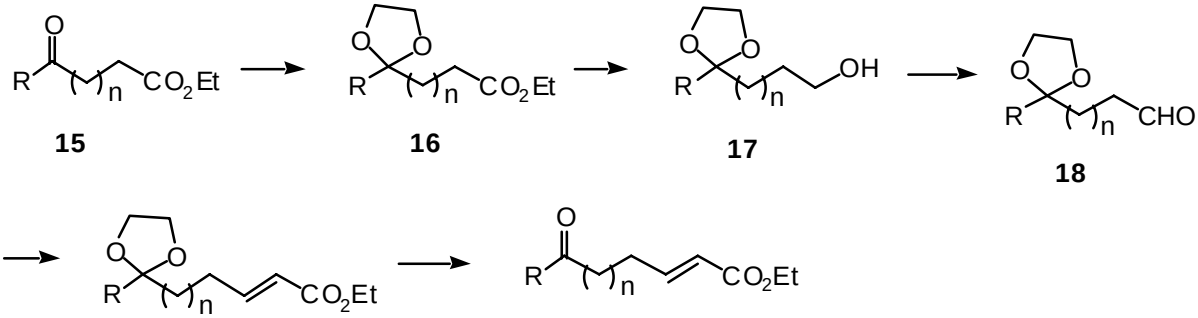
TOREST, Japan Science and Technology Corporation (JST)

Sho-machi 1, Tokushima 770-8505, Japan

Materials. Tetrahydrofuran was freshly distilled from sodium benzophenone ketyl. *tert*-Butyllithium, purchased from Kanto Chemical Co., Inc., was titrated with diphenylacetic acid.

General Procedures. ^{1}H NMR were measured in $CDCl_3$ solution and referenced to TMS (0.00 ppm). ^{13}C NMR were measured in $CDCl_3$ solution and referenced to $CDCl_3$ (77.0 ppm). Melting points are uncorrected. All reactions were performed in oven-dried glassware under positive pressure of argon, unless otherwise noted. Reaction mixtures were stirred magnetically. Solutions of alkyllithium reagents were transferred by syringe or cannula and were introduced into reaction vessels through rubber septa.

General Procedure for Preparation of 5:



(An example for preparation of **5a** (R = Ph, n = 1)): A solution of **15a**[1] (11.3 g, 55 mmol), ethylene glycol (6.83 g, 110 mmol), and pTsOH (107 mg, 0.56 mmol) in benzene (250 mL) was refluxed for 18 h under N_2 using Dean-Stark trap. After cooling, the mixture was successively washed with saturated aqueous $NaHCO_3$ solution, brine, dried over $MgSO_4$, and concentrated. The residue was chromatographed over silica gel to afford 11.2 g (81%) of **16a**.[2] To a suspension of $LiAlH_4$ (1.03 g, 27.1 mmol) in THF (100 mL) was added a solution of **16a** (3.39 g, 13.5 mmol) dropwise at 0 ˚C. After stirring for 1.5 h at 0 ˚C, water (1.1 mL), 15% NaOH solution (1.1 mL), and water (3.3 mL) were successively added. After stirring for 0.5 h, the mixture was filtered through celite pad. The filtrate was concentrated and the residue was distilled to afford 914 mg (95%) of **17a**[3] as a colorless oil. To a suspension of PDC (10.2 g,

[1] Yasuda, M.; Oh-hata, T.; Shibata, I.; Baba, A.; Matsuda, H. *J. Chem. Soc., Perkin Trans.1*. **1993**, 859-865.

[2] Best, W. M.; Widdowson, D. A. *Tetrahedron* **1989**, *45*, 5943-5954.

[3] Dhokte, U. P.; rao, A. S. *Org. Prep. Proced. Int.*, **1992**, *24*, 13-20.

27.1 mmol) in CH_2Cl_2 (200 mL) was added a solution of 17a in CH_2Cl_2 (50 mL) dropwise under N_2. After stirring for 15 h at room temperature, ether (500 mL) and florisil (25 g) were added to the mixture. After 2 h, the mixture was filtered through celite pad and the filtrate was concentrated. The residue was purified by column chromatography (SiO_2) to afford 2.15 g (77%) of **18a** as a colorless oil. To a solution of **18a** (2.15 g, 10.4 mmol) in THF (110 mL) was added ethyl diethylphosphonoacetate (2.57 g, 11.5 mmol) and $LiOH•H_2O$ (0.48 g, 11.5 mmol) and the mixture was stirred for 45 h at room temperature. The reaction mixture was diluted with CH_2Cl_2 (200 mL) and the organic phase was successively washed with water (200 mL) and brine (200 mL), dried over $MgSO_4$ and concedntrated. The residue was purified by column chromatography (SiO_2) to give 2.20 g (77%) of **19a**[4] as a colorless oil. A solution of **19a** (2.20 g, 7.98 mmol) and pTsOH (24 mg, 0.13 mmol) in acetone (70 mL) was refluxed for 67 h under N_2. After concentration, the residue was diluted with CH_2Cl_2 (50m L) and the solution was washed with a saturated aqueous $NaHCO_3$ solution and brine, dried over $MgSO_4$, and concentrated. The residue was chromatographed over silica gel to afford 1.64 g (89%) of **5a** as colorless crystals (mp. 42.2-42.5 ˚C). ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.29 (t, *J* = 7.2 Hz, 3H), 2.66 (m, 2H), 3.16 (t, *J* = 7.3 Hz, 2H), 4.19 (q, *J* = 7.2 Hz, 2H), 5.90 (d, *J* = 15.6 Hz, 1H), 7.03 (dt, *J* = 7.0 Hz, 15.6 Hz, 1H), 7.47 (dd, *J* = 7.2 Hz, 7.3 Hz, 2H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.96 (dd, *J* = 1.3 Hz, 7.2 Hz, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 14.2 (q), 26.2 (t), 36.6 (t), 60.2 (t), 122.1 (d), 127.9 (d), 128.6 (d), 133.2 (d), 136.5 (s), 147.4 (d), 166.4 (s), 198.2 (s). IR ($CHCl_3$): 1711, 1687 cm^{-1}. MS (EI) *m/z* 232 (M^+), 187 (M-45), 105 (100%). Anal. Clcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.33; H, 7.01.

General Procedure. Synthesis of ethyl (2-methyl-3-phenyl-2-cyclopentenyl)acetate (**9a** (R = Me, R' = Ph, n = 1) Table 1, entry 4). To a solution of ethyl 2,2-dibromopropionate (260 mg, 1.0 mmol) in THF (6 mL), cooled to –78 ˚C under argon, was added dropwise a solution of *tert*-butyllithium (2.82 mL, 4.0 mmol, 1.42 M in pentane). The yellow solution was stirred for 3 h at –78 ˚C and allowed to warm to 0 ˚C. After 30 min, the resulting colorless reaction mixture was cooled to –78 ˚C and a solution of (*E*)-ethyl 6-oxo-6-phenyl-2-hexenoate (**5a** (n = 1, R' = phenyl), 186 mg, 0.80 mmol) in THF (2 mL) was added dropwise. After 0.5 h at –78 ˚C, a saturated aqueous NH_4Cl solution was added and the resulting mixture was extracted with ethyl acetate (3 x 20 mL). The organic phase was successively washed with saturated solutions of $NaHCO_3$ and NaCl, dried over $MgSO_4$, filtered, and concentrated to afford a yellow oil. This crude mixture was dissolved in benzene (15 mL), and 72 mg of silica gel was added. The reaction mixture was heated at reflux for 9 h and then allowed to cool to room temperature before filtering. The filtrate was concentrated to afford a yellow oil, which was chromatographed over silica gel (5% ethyl acetate in hexane) to yield 163 mg (84%) of **9a**.

Pale yellow oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.28 (t, *J* = 7.2 Hz, 3H), 1.59-1.68 (m, 1H), 1.80 (s,3H), 2.17-2.29 (m, *J* = 9.9 Hz, 14,9 Hz, 2H), 2.61-2.72 (m, *J* = 4.4 Hz, 14.9 Hz, 3H), 3.08 (m, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 7.19-7.36 (m, 5H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 13.6 (q), 14.2 (q), 28.7 (t), 35.2 (t), 38.7 (t), 47.6 (d), 60.2 (t), 126.3 (d), 127.6 (d), 127.9 (d), 136.0 (s), 136.3 (s), 138.3 (s), 173.1 (s). IR (Neat): 1733, 1599, 1493, 763, 700 cm^{-1}. MS (EI) *m/z* 244 (M+), 173 (100%). HRMS (EI) calcd for $C_{16}H_{20}O_2$ 244.1463, found: 244.1478.

Ethyl (2,3-dimethyl-2-cyclopentenyl)acetate (Table 1, entry 1). Colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.26 (t, *J* = 7.2 Hz, 3H), 1.42-1.53 (m, 1H), 1.56 (s, 3H), 1.61 (s, 3H), 2.01-2.12 (m, *J* = 10.0 Hz, 14.7 Hz, 2H), 2.22 (m, 2H), 2.52 (d, *J* = 4.4 Hz, 14.7 Hz, 1H), 2.88 (m, 1H), 4.13 (q, *J* = 7.3 Hz, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 11.8 (q), 13.9 (q), 14.2 (q), 28.5 (t), 36.4 (t), 39.0 (t), 46.4 (d), 60.0 (t), 132.2 (s), 132.4 (s), 173.4 (s). IR (Neat): 1737 cm^{-1}. MS (EI) *m/z* 182 (M^+), 95 (70%). HRMS (EI) calcd for $C_{11}H_{18}O_2$ 182.1307, found: 182.1283.

Ethyl (2-butyl-3-methyl-2-cyclopentenyl)acetate (Table 1, entry 2)
Colorless oil.^{1}H-NMR (300 MHz, $CDCl_3$, TMS) δ: 0.89 (m, 3H), 1.26 (m, *J* = 7.2 Hz, 7H), 1.44-1.53 (m, 1H), 1.61 (s, 3H), 1.84 (m, 1H), 2.05 (m, *J* = 10.4 Hz, 14.8 Hz, 2H), 2.11-2.28 (m, 3H), 2.52 (dd, *J* = 4.1

[4] Johnson, S. J.; Kesten, S. R.; Wise, L. D. *J. Org. Chem*. **1992**, *57*, 4746-4749.

Hz, 14.8 Hz, 1H), 2.99 (m, 1H), 4.13 (q, *J* = 7.2 Hz, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 13.9 (q), 14.0 (q), 14.2 (q), 22.6 (t), 25.8 (t), 28.6 (t), 30.2 (t), 36.4 (t), 38.9 (t), 43.8 (d), 60.0 (t), 132.6 (s), 136.7 (s), 173.4 (s). IR (Neat): 1737 cm^{-1}. MS (EI) *m/z* 224 (M^+), 137 (100%).
HRMS (EI) calcd for $C_{14}H_{24}O_2$ 224.1776, found: 224.1806.

Ethyl (2-cyclohexyl-3-methyl-2-cyclopentenyl)acetate (Table 1, entry 3)
Colorless oil.^{1}H-NMR (300 MHz, CDCl3, TMS) δ: 1.26 (m, *J* = 7.2 Hz, 7H), 1.51-1.74 (m, 10H), 1.89-1.96 (m, 1H), 2.09 (m, *J* = 11.1 Hz, 14.9 Hz, 1H), 2.23 (m, 1H), 2.32 (m, 1H), 2.57 (dd, *J* = 3.3Hz, 14.9 Hz, 1H), 3.02 (m, 1H), 4.13 (q, *J* = 7.2 Hz, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 14.2 (q), 26.2 (t), 26.8 (t), 27.1 (t), 29.0 (t), 31.2 (t), 32.6 (t), 36.5 (t), 38.2 (d), 39.6 (t), 43.6 (d), 60.0 (t), 132.4 (s), 141.3 (s), 173.4 (s). IR (Neat): 1737 cm^{-1}. MS (EI) *m/z* 250 (M^+), 162 (100%). HRMS (EI) calcd for $C_{16}H_{26}O_2$ 250.1933, found: 250.1929.

Ethyl (2-buthyl-3-phenyl-2-cyclopentenyl)acetate (Table 1, entry 5)
Pale yellow oil. ^{1}H-NMR (300 MHz, $CDCl_3$, TMS) δ: 0.85 (t, *J* = 7.2 Hz, 3H), 1.28 (m, *J* = 7.2 Hz, 7H), 1.61-1.68 (m, 1H), 1.96 (m, 1H), 2.14-2.25 (m, *J* = 10.6 Hz, 14.9 Hz, 2H), 2.38 (m, 1H), 2.59-2.71 (m, *J* = 4.0 Hz, 14.9 Hz, 3H), 3.22 (m, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 7.19-7.35 (muti, 5H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 13.8 (q), 14.2 (q), 22.7 (t), 26.6 (t), 28.8 (t), 30.2 (t), 35.7 (t), 38.5 (t), 44.5 (d), 60.2 (t), 126.3 (d), 127.7 (d), 128.0 (d), 136.7 (s), 138.7 (s), 140.5 (s), 173.2 (s). IR (Neat): 1736, 762, 699 cm^{-1}. MS (EI) *m/z* 286 (M^+), 199 (100%). HRMS (EI) calcd for $C_{19}H_{26}O_2$ 286.1933, found: 286.1927.

Ethyl (2-cyclohexyl-3-phenyl-2-cyclopentenyl)acetate (Table 1, entry 6)
Pale yellow oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.11-1.43 (m, *J* = 7.2 Hz, 9H), 1.60-1.72 (m, 5H), 2.06-2.18 (m, 1H), 2.28 (dd, *J* = 11.2 Hz, 15.0 Hz, 1H), 2.46 (m, 1H), 2.57-2.68 (m, 2H), 2.75 (dd, *J* = 3.3 Hz, 15.0 Hz, 1H), 3.24 (m, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 7.18-7.35 (muti, 5H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 14.3 (q), 26.1 (t), 26.5 (t), 26.7 (t), 29.8 (t), 31.6 (t). 33.2 (t), 35.9 (t), 38.7 (d), 39.4 (t), 43.4 (d), 60.2 (t), 126.3 (d), 127.8 (d), 128.0 (d), 137.0 (s), 139.1 (s), 145.1 (s), 173.1 (s). IR (Neat): 1732, 761, 700 cm^{-1}. MS (EI) *m/z* 312 (M+), 224 (100%). HRMS (EI) calcd for $C_{21}H_{28}O_2$ 312.2089, found: 312.2117.

Ethyl (2,3-dimethyl-2-cyclohexenyl)acetate (Table 1, entry 7)
Colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.26 (t, *J* = 7.2 Hz, 3H), 1.55 (m, 4H), 1.59 (s, 3H), 1.62 (s,3H), 1.90 (m, 2H), 2.17 (dd, *J* = 10.3 Hz, 14.5 Hz, 1H), 2.40 (m, 1H), 2.51 (dd, *J* = 3.5 Hz, 14.5 Hz, 1H), 4.14 (q, *J* = 7.2 Hz, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 14.2 (q), 17.3 (q), 19.2 (t), 19.5 (q), 27.9 (t), 31.8 (t), 37.0 (d), 38.2 (t), 60.1 (t), 127.1 (s), 127.9 (s), 173.5 (s). IR (Neat): 1737 cm^{-1}. MS (EI) *m/z* 196 (M^+), 109. HRMS (EI) calcd for $C_{12}H_{20}O_2$ 196.1463, found: 196.1468.

Ethyl (2-buthyl-3-mthyl-2-cyclohexenyl)acetate (Table 1, entry 8)
Colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 0.90 (t, *J* = 7.2 H, 3H), 1.26 (m, *J* = 7.2 Hz, 7H), 1.56 (m, 4H), 1.60 (s, 3H), 1.78 (m, 1H), 1.89 (m, 2H), 2.18 (m, *J* = 10.3 Hz, 14.3 Hz, 2H), 2.49 (m, *J* = 3.3 Hz, 14.3 Hz, 2H), 4.14 (q, *J* = 7.2 Hz, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 13.9 (q), 14.2 (q), 18.6 (t), 19.2 (q), 22.9 (t), 27.6 (t), 30.8 (t), 31.1 (t), 31.8 (t), 34.3 (d), 38.2 (t), 60.0 (t), 127.9 (s), 132.2 (s), 173.5 (s). IR (Neat): 1737 cm^{-1}. MS (EI) *m/z* 238 (M^+), 150, 108 (100%). HRMS (EI) calcd for $C_{15}H_{26}O_2$ 238.133, found: 238.1905.

Ethyl (2-cyclohexyl-3-methyl-2-cyclohexenyl)acetate (Table 1, entry 9)
Colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.27 (m, *J* = 7.2 Hz, 9H), 1.51-1.75 (m, 11H), 1.93 (m, 2H), 2.16-2.34 (m, *J* = 11.3 Hz, 15.3 Hz, 2H), 2.48 (dd, *J* = 2.3 Hz, 15.3 Hz, 1H), 2.60 (m, 1H), 4.14 (q, *J* = 7,2 Hz, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 14.2 (q), 17.5 (t), 19.5 (q), 26.2 (t), 27.1 (t), 27.3 (t), 30.8 (t), 31.9 (d), 32.1 (t), 32.2 (t), 38.6 (t), 42.0 (d), 60.0 (t), 127.5 (s), 136.4 (s), 173.2 (s). IR (Neat): 1736 cm^{-1}. MS (EI) *m/z* 264 (M^+), 176 (100%). HRMS (EI) calcd for $C_{17}H_{28}O_2$ 264.2089, found: 264.2115.

Ethyl (2-butyl-3-phenyl-2-cyclohexenyl)acetate (Table 1, entry 10)

Yellow oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 0.74 (t, *J* = 7.2 Hz, 3H), 1.05-1.19 (m, 2H), 1.26-1.31 (m, *J* = 7.2 Hz, 5H), 1.61-1.74 (m, 5H), 1.96-2.02 (m, 1H), 2.18 (m, 2H), 2.30 (dd, *J* = 10.5 Hz, 15.0 Hz, 1H), 2.59 (dd, *J* = 3.7 Hz, 15.0 Hz, 1H), 2.71 (m, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 7.07 (dd, *J* = 1.5 Hz, 7.3 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.29 (t, *J* = 7.3 Hz, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 13.9 (q), 14.3 (q), 19.2 (t), 22.5 (t), 27.8 (t), 30.7 (t), 30.8 (t), 32.7 (t), 32.9 (d), 38.3 (t), 60.3 (t), 125.9 (d), 128.0 (d), 128.2 (d), 134.9 (s), 135.2 (s), 144.5 (s), 173.4 (s). IR (Neat): 1733, 762, 702 cm^{-1}. MS (EI) *m/z* 300 (M^+, 100%). HRMS (EI) calcd for $C_{20}H_{28}O_2$ 300.2089, found: 300.2113.

Ethyl (2-butyl-3-methyl-2-cycloheptenyl)acetate (Table 1, entry 11)
Colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 0.91 (m, 3H), 1.21-1.32 (m, *J* = 7.2 Hz, 9H), 1.50-1.63 (m, 4H), 1.66 (s, 3H), 1.86 (m, 1H), 2.04 (m, 2H), 2.21 (m, 1H), 2.50 (dd, *J* = 6.3 Hz, 14.6 Hz, 1H), 2.54 (dd, *J* = 9.6 Hz, 14.6 Hz, 1H), 2.75 (m, 1H), 4.13 (q, *J* = 7.2 Hz, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 14.1 (q), 14.3 (q), 22.2 (t), 22.9 (t), 26.1 (t), 30.8 (t), 31.1 (t), 34.2 (t), 34.5 (t), 36.6 (t), 40.4 (d), 60.1 (t), 132.0 (s), 136.6 (s), 173.4 (s). IR (Neat): 1738 cm^{-1}. MS (EI) *m/z* 252 (M^+), 164 (100%). HRMS (EI) calcd for $C_{16}H_{28}O_2$ 252.2089, found: 252.2108.

Ethyl (2-butylbicyclo[4.4.0]dec-1-en-3-yl)acetate (**11**)
Colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 0.88-0.93 (m, 3H), 1.18-1.46 (m, *J* = 7.2 Hz, 12H), 1.54-1.86 (m, 8H), 2.15-2.26 (m, 2H), 2.42-2.52 (m, 2H), 2.59 (m, 1H), 4.13 (q, *J* = 7.2 Hz, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 14.1 (q), 14.3 (q), 23.0 (t), 24.4 (t), 25.5 (t), 27.1 (t), 28.7 (t), 30.6 (t), 30.7 (t), 32.1 (t), 35.1 (d), 35.6 (t), 37.9 (t), 38.0 (d), 60.1 (t), 130.1 (s), 135.9 (s), 173.6 (s). IR (Neat):1732 cm^{-1}. MS (EI) *m/z* 278(M+), 190(100%). HRMS (EI) calcd for $C_{18}H_{30}O_2$ 278.2246, found: 278.2249.

(2-Butylbicyclo[4.4.0]dec-1-en-3-yl)acetic acid(11')
Colorless prisms (m.p. 72.0-74.8 ˚C). ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 0.88-0.93 (m, 3H), 1.15-1.42 (m, 9H), 1.56-1.84 (m, 8H), 2.18-2.32 (m, 2H), 2.50-2.61 (m, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$). IR ($CHCl_3$): 1732 cm^{-1}. MS (EI) *m/z* 250 (M^+), 133 (100%). Anal. Calcd for $C_{16}H_{26}O_2$: C, 76.75; H, 10.47. Found: C, 76.50; H, 10.45.

Ethyl (3,4-dimethyl-1,2-dihydronaphthalen-2-yl)acetate (**13**)
Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.24 (t, *J* = 7.1 Hz, 3H), 1.93 (s, 3H), 2.01 (s, 3H), 2.12 (dd, *J* = 10.1 Hz, 15.1 Hz, 1H), 2.20 (dd, *J* = 4.6 Hz, 15.1 Hz, 1H), 2.60-2.68 (m, *J* = 15.6 Hz, 2H), 2.99 (dd, *J* = 6.3 Hz, 15.6 Hz, 1H), 4.07-4.15 (m, 2H), 7.08-7.12 (m, 2H), 7.18-7.24 (m, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 14.3 (q), 14.5 (q), 19.0 (q), 32.9 (t), 34.8 (t), 36.9 (d), 60.2 (t), 122.4 (d), 125.8 (s), 125.9 (d), 126.3 (d), 128.1 (d), 132.6 (s), 133.5 (s), 136.0 (s), 172.7 (s). IR (Neat): 1731, 761 cm^{-1}. MS (EI) *m/z* 244 (M^+), 156 (100%). HRMS (EI) calcd for $C_{16}H_{20}O_2$ 244.1463, found: 244.1446.

Ethyl (3,4-dimethylnaphthalen-2-yl)acetate (**14**). To a solution of 13 (50 mg, 0.20 mmol) in toluene (2 mL) was added DDQ (61 mg, 0.27 mmol) and the suspension was refluxed for 1 h. The mixture was dilutied with CH_2Cl_2 (200 mL) and the solution was successively washed with saturated aqueous NaHCO3 solution, brine, and dried over $MgSO_4$, filtered and concentrated to afford 44 mg of a dark oil, which was chromatographed over silica gel to give 20 mg (40%) of **14** as a yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.25 (t, *J* = 7.1 Hz, 3H), 2.40 (s, 3H), 2.62 (s, 3H), 3.82 (s, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 7.40 (t, *J* = 7.8 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 1H), 7.56 (s, 1H), 7.74 (d, *J* = 7.8 Hz, 1H), 8.00 (d, *J* = 7.8 Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 14.2 (q), 15.1 (q), 16.5 (q), 40.8 (t), 60.8 (t), 123.8 (d), 124.8 (d), 125.6 (d), 127.5 (d), 128.1 (d), 131.6 (s) 131.8 (s), 132.0 (s), 132.2 (s), 132.6 (s), 171.8 (s). IR (Neat): 1732, 761 cm^{-1}. MS (EI) *m/z* 242 (M^+), 169 (100%). HRMS (EI) calcd for C16H18O2 242.1307, found: 242.1319.

Crystal Data for **11'**: $C_{16}H_{26}O_2$, Mr = 250.38, triclinic, space group *P*1, *a* = 8.5557(9) Å, *b* = 13.195(1) Å, *c* = 7.1967(8) Å, α= 90.532(9)°, β= 99.287(9)°, g= 71.156(7)°, *V* = 758.0(1) Å^3, *Z* = 2, Dc = 1.097Mgm^{-3}, F(000) = 276, μ(Mo*K*α) = 0.699cm^{-1}.

The crystal used for data collection was a colourless prism with the approximate dimensions 0.5 × 0.5 × 0.3 mm. All data were obtained Rigaku AFC-5S automated four circle diffractometer with graphite-monochromated Mo *Ka* radiation. Unit cell parameters were determined by least squares refinement of the optimized setting angles of 25 reflections in the range 12.5º< θ <14.5º. The intensities were measured using $\omega/2\theta$ scan up to 55°. Three standard reflections were monitored every 150 measurements. The data were corrected for Lorentz and polarization factors. Absorption (ψ-scan[1], transmission factor = 0.967 – 1.000) and decay (-3.9% decline) correction was applied. Of the 3493 independent reflections which collected, 2964 reflections with $I>0.1\sigma(I)$ were used for structure determination and refinement. The structure was solved by direct method using TEXSAN crystallographic software package.[2] All non-H atoms were found in Fourier map. The refinement of atomic parameters were carried out by the full matrix least-squares refinement, using anisotropically temperature factors for all non-H atoms. All H atoms were located from difference Fourier maps, and included in the refinement calculations with isotropic temperature factors. The final refinement converged with *R*=0.041 and *Rw*=0.051 (*R* and *Rw* were calculated by 2133 reflections with $I>2.0\sigma(I)$.) for 268 parameters. Atomic scattering factors were taken from "International Tables for X-ray Crystallography. ".[3]

References and Notes

1) North, A. C. T.,; Phillips, D. C.,; Mathews, F. S. Acta Cryst. **1968**, A24, 351-359

2) Molecular Structure Corporation. (1995). teXsan. Single Crystal Structure Analysis Software. Version 1.7. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

3)" *International Tables for X-ray Crystallography*," Vol. **C,** Kynoch Press, Birmingham, England, 1992.

Positional parameters and B(eq)

atom	x	y	z	B(eq)	
O(17)	0.4468(1)	0.40044(8)	0.0718(2)	5.28(3)	
O(18)	0.4120(2)	0.55536(9)	0.2112(2)	5.36(3)	
C(1)	0.0623(2)	0.2907(1)	0.4933(2)	4.03(3)	
C(2)	0.0139(3)	0.2414(2)	0.6543(3)	5.34(4)	
C(3)	-0.0401(3)	0.1458(2)	0.5868(3)	6.34(5)	
C(4)	-0.1820(3)	0.1774(2)	0.4199(4)	7.08(6)	
C(5)	-0.1368(2)	0.2320(2)	0.2611(3)	5.78(5)	
C(6)	-0.0798(2)	0.3267(1)	0.3280(2)	4.78(4)	

C(7)	-0.0369(2)	0.3852(2)	0.1722(3)	5.78(5)
C(8)	0.1400(2)	0.3302(1)	0.1385(2)	4.82(4)
C(9)	0.2669(2)	0.3283(1)	0.3141(2)	3.86(3)
C(10)	0.2167(2)	0.2939(1)	0.4906(2)	3.74(3)
C(11)	0.3566(2)	0.2581(1)	0.6574(2)	4.45(4)
C(12)	0.4544(2)	0.1399(1)	0.6735(3)	4.98(4)
C(13)	0.5959(3)	0.1112(2)	0.8420(3)	6.59(5)
C(14)	0.6990(4)	-0.0058(3)	0.8616(6)	9.69(9)
C(15)	0.3010(2)	0.4352(1)	0.3371(2)	4.64(4)
C(16)	0.3936(2)	0.4603(1)	0.1935(2)	4.10(3)
H(19)	0.457(3)	0.567(2)	0.111(3)	9.4(6)
H(20)	-0.174(2)	0.375(1)	0.381(2)	5.7(4)
H(21)	0.377(2)	0.274(1)	0.301(2)	4.2(3)
H(22)	0.786(4)	-0.014(3)	0.970(4)	13.8(10)
H(23)	0.622(4)	-0.048(3)	0.870(4)	14(1)
H(24)	0.726(4)	-0.013(2)	0.737(5)	14(1)
H(25)	0.665(3)	0.158(2)	0.832(3)	8.5(6)
H(26)	0.556(2)	0.125(1)	0.964(3)	7.4(5)
H(27)	0.383(2)	0.094(1)	0.680(2)	6.1(4)
H(28)	0.492(2)	0.114(1)	0.556(2)	5.5(4)
H(29)	0.368(2)	0.438(1)	0.458(2)	5.7(4)
H(30)	0.194(2)	0.495(2)	0.326(2)	6.9(5)
H(31)	0.314(2)	0.279(1)	0.775(2)	5.0(3)
H(32)	0.438(2)	0.296(1)	0.649(2)	5.2(3)
H(33)	-0.215(3)	0.113(2)	0.368(3)	9.7(6)
H(34)	-0.276(3)	0.231(2)	0.459(3)	9.4(6)
H(35)	-0.071(2)	0.114(1)	0.693(3)	6.9(4)
H(36)	0.059(2)	0.091(2)	0.549(3)	7.0(5)
H(37)	0.168(2)	0.364(1)	0.030(2)	4.9(3)
H(38)	0.150(2)	0.254(1)	0.108(2)	5.0(3)
H(39)	0.109(2)	0.217(1)	0.760(2)	6.2(4)
H(40)	-0.078(2)	0.297(1)	0.701(2)	7.2(5)
H(41)	-0.111(2)	0.388(1)	0.059(3)	6.7(4)
H(42)	-0.047(2)	0.462(2)	0.210(3)	8.0(5)
H(43)	-0.232(2)	0.255(1)	0.154(3)	6.9(4)
H(44)	-0.044(2)	0.178(1)	0.209(2)	6.2(4)

Intramolecular Distances Involving the Nonhydrogen Atoms

atom	atom	distance	atom	atom	distance
O(17)	C(16)	1.217(2)	C(7)	C(8)	1.511(3)
O(18)	C(16)	1.317(2)	C(8)	C(9)	1.522(2)
C(1)	C(2)	1.509(2)	C(9)	C(10)	1.522(2)
C(1)	C(6)	1.513(2)	C(9)	C(15)	1.533(2)
C(1)	C(10)	1.338(2)	C(10)	C(11)	1.510(2)
C(2)	C(3)	1.528(3)	C(11)	C(12)	1.509(2)
C(3)	C(4)	1.517(3)	C(12)	C(13)	1.523(3)
C(4)	C(5)	1.521(3)	C(13)	C(14)	1.505(3)
C(5)	C(6)	1.529(2)	C(15)	C(16)	1.498(2)
C(6)	C(7)	1.524(2)			

Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Intramolecular Distances Involving the Hydrogen Atoms

atom	atom	distance	atom	atom	distance
O(18)	H(19)	0.90(2)	C(8)	H(38)	1.01(2)
C(2)	H(39)	0.99(2)	C(9)	H(21)	1.00(1)
C(2)	H(40)	0.99(2)	C(11)	H(31)	0.98(2)
C(3)	H(35)	0.98(2)	C(11)	H(32)	0.99(2)
C(3)	H(36)	1.00(2)	C(12)	H(27)	0.99(2)
C(4)	H(33)	1.02(2)	C(12)	H(28)	0.97(2)
C(4)	H(34)	0.96(2)	C(13)	H(25)	0.99(2)
C(5)	H(43)	1.00(2)	C(13)	H(26)	0.99(2)
C(5)	H(44)	1.00(2)	C(14)	H(22)	0.97(3)
C(6)	H(20)	0.98(2)	C(14)	H(23)	1.00(3)
C(7)	H(41)	0.94(2)	C(14)	H(24)	0.96(3)
C(7)	H(42)	1.03(2)	C(15)	H(29)	0.97(2)
C(8)	H(37)	1.00(2)	C(15)	H(30)	0.99(2)

Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Intramolecular Bond Angles Involving the Nonhydrogen Atoms

atom	atom	atom	angle	atom	atom	atom	angle
C(2)	C(1)	C(6)	112.0(1)	C(8)	C(9)	C(15)	112.1(1)
C(2)	C(1)	C(10)	124.0(1)	C(10)	C(9)	C(15)	111.6(1)
C(6)	C(1)	C(10)	123.8(1)	C(1)	C(10)	C(9)	122.2(1)
C(1)	C(2)	C(3)	109.7(1)	C(1)	C(10)	C(11)	123.0(1)
C(2)	C(3)	C(4)	111.6(2)	C(9)	C(10)	C(11)	114.8(1)
C(3)	C(4)	C(5)	111.2(2)	C(10)	C(11)	C(12)	115.5(1)
C(4)	C(5)	C(6)	112.2(2)	C(11)	C(12)	C(13)	112.1(2)
C(1)	C(6)	C(5)	109.9(1)	C(12)	C(13)	C(14)	113.9(2)
C(1)	C(6)	C(7)	112.2(1)	C(9)	C(15)	C(16)	114.7(1)
C(5)	C(6)	C(7)	113.9(1)	O(17)	C(16)	O(18)	122.5(1)
C(6)	C(7)	C(8)	111.4(1)	O(17)	C(16)	C(15)	124.6(1)
C(7)	C(8)	C(9)	111.2(1)	O(18)	C(16)	C(15)	112.9(1)
C(8)	C(9)	C(10)	111.9(1)				

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

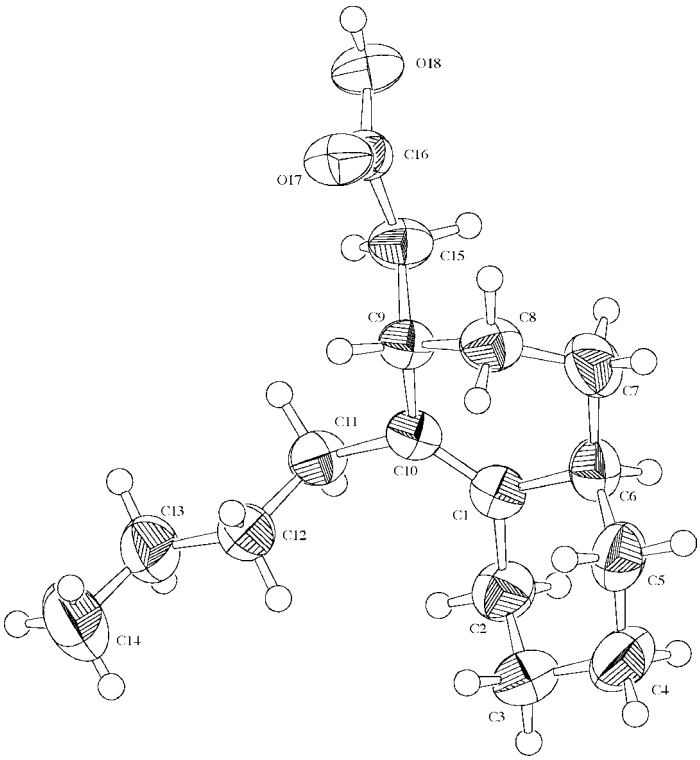
Intramolecular Bond Angles Involving the Hydrogen Atoms

atom	atom	atom	angle	atom	atom	atom	angle
C(16)	O(18)	H(19)	107(1)	H(37)	C(8)	H(38)	108(1)
C(1)	C(2)	H(39)	111(1)	C(8)	C(9)	H(21)	109.0(8)
C(1)	C(2)	H(40)	108(1)	C(10)	C(9)	H(21)	106.2(8)
C(3)	C(2)	H(39)	109(1)	C(15)	C(9)	H(21)	105.6(8)
C(3)	C(2)	H(40)	111(1)	C(10)	C(11)	H(31)	110.7(9)
H(39)	C(2)	H(40)	108(1)	C(10)	C(11)	H(32)	108.9(9)
C(2)	C(3)	H(35)	109(1)	C(12)	C(11)	H(31)	108.7(9)
C(2)	C(3)	H(36)	108(1)	C(12)	C(11)	H(32)	106.7(9)
C(4)	C(3)	H(35)	112(1)	H(31)	C(11)	H(32)	106(1)
C(4)	C(3)	H(36)	109(1)	C(11)	C(12)	H(27)	113(1)
H(35)	C(3)	H(36)	107(2)	C(11)	C(12)	H(28)	111.6(9)
C(3)	C(4)	H(33)	113(1)	C(13)	C(12)	H(27)	109.3(9)
C(3)	C(4)	H(34)	108(1)	C(13)	C(12)	H(28)	112.8(9)
C(5)	C(4)	H(33)	109(1)	H(27)	C(12)	H(28)	97(1)
C(5)	C(4)	H(34)	105(1)	C(12)	C(13)	H(25)	108(1)
H(33)	C(4)	H(34)	111(2)	C(12)	C(13)	H(26)	113(1)
C(4)	C(5)	H(43)	111(1)	C(14)	C(13)	H(25)	112(1)
C(4)	C(5)	H(44)	109(1)	C(14)	C(13)	H(26)	103(1)
C(6)	C(5)	H(43)	110(1)	H(25)	C(13)	H(26)	106(2)
C(6)	C(5)	H(44)	109.0(9)	C(13)	C(14)	H(22)	106(2)
H(43)	C(5)	H(44)	106(1)	C(13)	C(14)	H(23)	108(2)
C(1)	C(6)	H(20)	104.8(9)	C(13)	C(14)	H(24)	98(2)
C(5)	C(6)	H(20)	105.2(9)	H(22)	C(14)	H(23)	116(3)
C(7)	C(6)	H(20)	110.1(9)	H(22)	C(14)	H(24)	120(3)
C(6)	C(7)	H(41)	110(1)	H(23)	C(14)	H(24)	107(3)
C(6)	C(7)	H(42)	109(1)	C(9)	C(15)	H(29)	112.0(9)
C(8)	C(7)	H(41)	109(1)	C(9)	C(15)	H(30)	110(1)
C(8)	C(7)	H(42)	108(1)	C(16)	C(15)	H(29)	105(1)
H(41)	C(7)	H(42)	109(1)	C(16)	C(15)	H(30)	106(1)
C(7)	C(8)	H(37)	112.8(8)	H(29)	C(15)	H(30)	108(1)
C(7)	C(8)	H(38)	107.5(9)				
C(9)	C(8)	H(37)	109.2(8)				
C(9)	C(8)	H(38)	108.1(8)				

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Anisotropic Displacement Parameters for Dr. M. Shindo Tokushima Univ. 2000.11.16

atom	U11	U22	U33	U12	U13	U23
O(17)	0.0830(8)	0.0558(6)	0.0741(7)	-0.0312(6)	0.0297(6)	-0.0092(5)
O(18)	0.0905(8)	0.0633(7)	0.0679(7)	-0.0460(6)	0.0209(6)	-0.0114(5)
C(1)	0.0577(9)	0.0480(8)	0.0478(8)	-0.0162(6)	0.0113(7)	-0.0073(6)
C(2)	0.069(1)	0.075(1)	0.064(1)	-0.0233(9)	0.0245(9)	-0.0046(9)
C(3)	0.075(1)	0.083(1)	0.096(1)	-0.038(1)	0.023(1)	0.008(1)
C(4)	0.068(1)	0.092(2)	0.123(2)	-0.042(1)	0.019(1)	-0.008(1)
C(5)	0.054(1)	0.079(1)	0.084(1)	-0.0229(9)	0.0014(10)	-0.012(1)
C(6)	0.0489(9)	0.0594(9)	0.067(1)	-0.0092(7)	0.0085(8)	-0.0066(8)
C(7)	0.071(1)	0.072(1)	0.065(1)	-0.0195(9)	-0.0127(9)	0.0115(9)
C(8)	0.075(1)	0.071(1)	0.0433(8)	-0.0334(9)	0.0041(7)	0.0021(7)
C(9)	0.0583(9)	0.0478(8)	0.0436(7)	-0.0218(7)	0.0068(6)	-0.0030(6)
C(10)	0.0581(9)	0.0444(7)	0.0409(7)	-0.0194(6)	0.0059(6)	-0.0051(6)
C(11)	0.0638(10)	0.0659(10)	0.0435(8)	-0.0290(8)	0.0034(7)	-0.0009(7)
C(12)	0.062(1)	0.067(1)	0.059(1)	-0.0215(8)	0.0054(8)	0.0059(8)
C(13)	0.068(1)	0.097(2)	0.077(1)	-0.019(1)	0.001(1)	0.020(1)
C(14)	0.093(2)	0.114(2)	0.131(3)	0.001(2)	0.002(2)	0.046(2)
C(15)	0.076(1)	0.0565(10)	0.0519(9)	-0.0325(9)	0.0111(8)	-0.0049(7)
C(16)	0.0554(8)	0.0499(8)	0.0514(8)	-0.0224(7)	-0.0002(7)	0.0025(7)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