Supporting Information

Effective Acceleration of Atom Transfer Carbonylation of Alkyl Iodides by Metal Complexes. Application to the Synthesis of Hinokinin Precursor and Dihydrocapsaicin

Takahide Fukuyama, Satoshi Nishitani, Takaya Inouye, Keisuke Morimoto, and Ilhyong Ryu*

Department of Chemistry, Graduate School of Science, Osaka Prefecture University

Sakai, Osaka 599-8531, Japan

ryu@c.s.osakafu-u.ac.jp

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General information. ^1H NMR spectra were recorded with a JEOL JMN ECP-500 (500 MHz) spectrometer in CDCl_3 . Chemical shifts are reported in parts per million (δ) downfield from internal TMS at 0.00. ^{13}C NMR spectra were recorded with a JEOL JMN ECP-500 (125 MHz) spectrometer and referenced to the solvent peak at 77.00 ppm. Infrared spectra were obtained on a JASCO FT/IR 4100 spectrometer; absorptions are reported in reciprocal centimeters. Both conventional and high resolution mass spectra were recorded with a JEOL MS700 spectrometer. Benzene was distilled from benzophenone prior to use. The products were purified by flash chromatography on silica gel (NACALAI TESQUE, INC., Silica Gel 60, 70-230 mesh) and, if necessary, were further purified by recycling preparative HPLC (Japan Analytical Industry Co., Ltd., LC-908) equipped with GPC columns (JAIGEL-1H + JAIGEL-2H columns) using CHCl_3 as eluent. Photolysis were carried out using a stainless autoclave with quartz windows glass lined with a 30 mm ϕ Pyrex glass liner and using a 500 W Xenon short arc lamp (Ushio Co. Ltd., lamp house: SX-UI500XQ, Xenon short arc lamp: UXL-500SX, power supply: BA-X500). Alkyl iodides **1b**, **1c**, **1d**, **1f**, **1g**, **1i** were preparation from the corresponding alcohol.

General procedure. A magnetic stirring bar, **1b** (0.051 g, 0.28 mmol), BuOH (0.095 g, 1.3 mmol), NEt₃ (0.048 g, 0.47 mmol), 4-dimethylaminopyridine (0.002 g, 0.016 mmol), Pd(PPh₃)₄ (0.018 g, 0.016 mmol) and benzene (3.0 mL) were placed in a stainless steel autoclave for photoreaction equipped with an inserted Pyrex glass liner. The autoclave was closed, purged three times with carbon monoxide, pressurized with 45 atm of CO and then irradiated by Xenon arc lamp (500 W) with stirring for 16 h. Excess CO was discharged at room temperature after the reaction. The reaction mixture was added to water (20 mL) and extracted with ether (20 mL × 3). The ether layer was washed with brine, and dried over MgSO₄, then filtered and concentrated *in vacuo* to give a residue, which was subjected to silica gel column chromatography using hexane/EtOAc = 20/1 as eluent affording **2b** (0.036 g, 83%).

Ethyl nonanoate (2a)

Procedure for **2a** carried out by the method described for **2b**. K₂CO₃ (2.0 equivalent) and EtOH (1.0 M) were used as the base and solvent instead of NEt₃, 4-dimethylaminopyridine and benzene. This product is commercially available and the ¹H- and ¹³C-NMR spectra are consistent with those of the authentic sample.

¹H NMR (CDCl₃, 500 MHz) δ 4.12 (q, *J* = 7.03 Hz, 2H), 2.28 (t, *J* = 7.56 Hz, 2H), 1.63-1.59 (m, 2H), 1.32-1.24 (m, 13H), 0.88 (t, *J* = 6.64 Hz, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ 14.04, 14.20, 22.60, 24.95, 29.11, 29.19, 31.78, 34.36, 60.09, 173.87.

Butyl 3-pentenoate (2b)

¹H NMR (CDCl₃, 500 MHz) δ 5.86-5.79 (m, 1H), 5.00 (d, *J* = 10.1 Hz, 1H), 5.05 (d, *J* = 17.4 Hz, 1H), 4.08 (t, *J* = 6.7 Hz, 2H), 2.40-2.35 (m, 4H), 1.74 (quint, *J* = 7.3 Hz, 2H), 1.24-1.58 (m, 2H), 0.88 (t, *J* = 6.9 Hz, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ 13.69, 19.13, 28.92, 30.61, 33.61, 64.27, 115.41, 136.75, 173.16; IR (neat) 1642 cm⁻¹, 1725 cm⁻¹; MS (relative intensity) *m/z* 156 (M⁺, 6), 100 (100), 83 (64), 82 (17), 57 (35), 56 (32), 55 (69), 54 (28); HRMS (EI) *m/z* calcd for C₉H₁₆O₂ 156.1150, found 156.1146.

3-Ethyl-4-propyl-γ-butyrolactone (2c)

Procedure for **2c** carried out by the method described for **2b**. Obtained as a cis/trans-mixture in a 34/66 ratio, as determined by ¹H NMR analysis of the crude mixture before being submitted chromatography separation. ¹H NMR (CDCl₃, 500 MHz) δ 4.51-4.49 (m, cis 1H), 4.12-4.10 (m, trans 1H), 2.66 (dd, *J* = 8.5, 9.2 Hz, trans 1H), 2.57 (dd, *J* = 7.8, 9.2 Hz, cis 1H), 2.37-2.42 (m, cis 1H), 2.29 (dd, *J* = 6.0, 9.2 Hz, cis 1H), 2.21 (dd, *J* = 8.0, 8.7 Hz, trans 1H), 2.03-2.08 (m, trans 1H), 1.20-1.66 (m, cis 6H and trans 6H), 0.92-0.98 (m, cis 6H and

trans 6H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 11.82(trans), 11.97(cis), 13.78(two superimposed), 18.90(trans), 19.13(cis), 21.15(cis), 25.94(trans), 31.81(cis), 34.03(trans), 36.80(trans), 40.37(cis), 42.64(trans), 83.20(cis), 85.57(trans), 176.66(cis), 176.86(cis); IR (neat) 1776 cm^{-1} ; MS (relative intensity) m/z cis 156 (M^+ , 1), 138 (3), 128 (3), 113(100), 85 (23), 73 (13), 67 (14), 56 (67); trans 156 (M^+ , 1), 138 (2), 128 (2), 113(100), 85 (22), 73 (7), 67 (13), 56 (37); HRMS (EI) m/z calcd for $\text{C}_9\text{H}_{16}\text{O}_2$ 156.1150, found cis:156.1134, trans:156.1162.

Butyl 2-methyl octanoate (2d)

Procedure for **2d** carried out by the method described for **2b**. ^1H NMR (CDCl_3 , 500 MHz) δ 4.09-4.06 (m, 2H), 2.42 (sext, $J = 7.1\text{ Hz}$, 1H), 1.67-1.58 (m, 3H), 1.56-1.34 (m, 3H), 1.27-1.24 (m, 8H), 1.14 (d, $J = 6.9\text{ Hz}$, 3H), 0.94 (t, $J = 7.6\text{ Hz}$, 3H), 0.88 (t, $J = 6.9\text{ Hz}$, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 13.62, 13.98, 17.05, 19.09, 22.51, 27.17, 29.12, 30.69, 31.65, 33.79, 39.56, 63.86, 176.88; IR (neat) 1736 cm^{-1} ; MS (relative intensity) m/z 214 (M^+ , 1), 159 (83), 141 (34), 130 (37), 87 (29), 74 (100), 71 (46), 57 (73), 56 (42), 55 (24); HRMS (EI) m/z calcd for $\text{C}_{13}\text{H}_{26}\text{O}_2$ 214.1933, found 214.1926.

Butyl 1-adamantanoate (2e)

Procedure for **2e** carried out by the method described for **2b**. ^1H NMR (CDCl_3 , 500 MHz) δ 4.05 (t, $J = 6.6\text{ Hz}$, 2H), 2.01 (m, 3H), 1.89-1.88 (m, 6H), 1.79-1.68 (m, 6H), 1.60 (quint, $J = 7.2\text{ Hz}$, 2H), 1.38 (sext, $J = 7.4\text{ Hz}$, 2H), 0.94 (t, $J = 7.3\text{ Hz}$, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 13.59, 19.02, 27.85, 30.59, 36.39, 38.71, 40.51, 63.65, 177.46; IR (neat) 1728 cm^{-1} ; MS (relative intensity) m/z 235 (M^+ , 1), 181 (10), 136 (11), 135 (100), 93 (15), 79 (18); HRMS (EI) m/z calcd for $\text{C}_{15}\text{H}_{24}\text{O}_2$ 236.1776, found 236.1768.

Transition-metal Accelerated Atom Transfer Carbonlation with Diethylamine.

General Procedure. A magnetic stirring bar, **1a** (0.122 g, 0.51 mmol), HNEt_2 (0.187 g, 2.6 mmol), $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (0.015 g, 0.014 mmol), $(p\text{-MeOC}_6\text{H}_4)_3\text{P}$ (0.019 g, 0.054 mmol) and benzene (5.1 mL) were placed in a stainless steel autoclave for photoreaction equipped with an inserted Pyrex glass liner. The autoclave was closed, purged three times with carbon monoxide, pressurized with 75 atm of CO and then irradiated by Xenon arc lamp (500 W) with stirring for 16 h. Excess CO was discharged at room temperature after the reaction. The reaction mixture was added to water (20 mL) and extracted with ether (20 mL $\times$ 3). The ether layer was washed with brine and dried over MgSO_4 , then filtered and concentrated *in vacuo* to give a residue, which was subjected to silica gel column chromatography using hexane/EtOAc = 5/1 as eluent affording **3a** (0.013 g, 11%) and **4a** (0.082 g, 64%). **3a** was obtained in 91% yield (0.096 g) when $\text{Mn}_2(\text{CO})_{10}$ was used as the catalyst.

N,N-Diethyl nonanamide (3a)

This product is commercially available and the ^1H - and ^{13}C -NMR spectra are consistent with those of the authentic sample.

^1H NMR (CDCl_3 , 500 MHz) δ 3.37 (q, $J = 7.2$ Hz, 2H), 3.30 (q, $J = 7.2$ Hz, 2H), 2.28 (t, $J = 7.8$ Hz, 2H), 1.67-1.61 (m, 2H), 1.31- 1.26 (m, 10H), 1.17 (t, $J = 7.1$ Hz, 3H), 1.11 (t, $J = 7.1$ Hz, 3H), 0.88 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 13.03, 14.00, 14.33, 22.60, 25.46, 29.14, 29.42, 29.49, 31.81, 33.10, 39.85, 41.92, 172.19.

***N,N*-Diethyl-2-oxodecanamide (4a)**

^1H NMR (CDCl_3 , 500 MHz) δ 3.42 (q, $J = 7.2$ Hz, 2H), 3.26 (q, $J = 7.2$ Hz, 2H), 2.75 (t, $J = 7.6$ Hz, 2H), 1.66-1.60 (m, 2H), 1.30- 1.17 (m, 16H), 0.88 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 12.66, 14.09, 14.45, 22.65, 22.89, 29.12, 29.32, 31.81, 39.34, 40.00, 42.05, 166.98, 201.66; IR (neat) 1640 cm^{-1} , 1712 cm^{-1} ; MS (relative intensity) m/z 241 (M^+ , 4), 100 (100), 72 (23); HRMS (EI), m/z calcd for $\text{C}_{14}\text{H}_{27}\text{NO}_2$ 241.2042, found 241.2037.

***N,N*-Diethyl-4-pentenamide (3b)**

^1H NMR (CDCl_3 , 500 MHz) δ 5.83-5.41 (m, 1H), 5.06 (d, $J = 17.4$ Hz, 1H), 4.99 (d, $J = 10.1$ Hz, 1H), 3.38 (q, $J = 7.0$ Hz, 2H), 3.31 (q, $J = 7.2$ Hz, 2H), 2.43-2.37 (m, 4H), 1.17 (t, $J = 7.1$ Hz, 3H), 1.11 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 12.99, 14.24, 29.36, 32.25, 39.98, 41.81, 114.90, 137.61, 171.23; IR (neat) 1640 cm^{-1} ; MS (relative intensity) m/z 156 ($\text{M}^+ + 1$, 35), 155 (M^+ , 58), 126 (34), 100 (57), 72 (50), 70 (100), 55 (86); HRMS (EI) m/z calcd for $\text{C}_9\text{H}_{17}\text{NO}$ 155.1310, found 155.1291

***N,N*-Diethyl-2-oxohexenamide (4b)**

^1H NMR (CDCl_3 , 500 MHz) δ 5.87-5.79 (m, 1H), 5.08 (d, $J = 16.8$ Hz, 1H), 5.01 (d, $J = 10.5$ Hz, 1H), 3.42 (q, $J = 7.2$ Hz, 2H), 3.26 (q, $J = 7.6$ Hz, 2H), 2.89 (t, $J = 7.3$ Hz, 2H), 2.39 (q, $J = 7.0$ Hz, 2H), 1.22-1.17 (m, 6H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 12.55, 14.38, 26.80, 38.93, 39.41, 42.04, 115.65, 136.39, 166.53, 200.57; IR (neat) 1639 cm^{-1} , 1712 cm^{-1} ; MS (relative intensity) m/z 183 (M^+ , 3), 155 (21), 100 (100), 72 (50), 55 (22); HRMS (EI) m/z calcd for $\text{C}_{10}\text{H}_{17}\text{NO}_2$ 183.1259, found.183.1257.

***N,N*-Diethyl-4-phenylbutanamide (3f)**

This product is commercially available and the ^1H - and ^{13}C -NMR spectra are consistent with those of the authentic sample.

^1H NMR (CDCl_3 , 500 MHz) δ 7.29-7.16 (m, 5H), 3.37 (q, J = 7.0 Hz, 2H), 3.23 (q, J = 7.2 Hz, 2H), 2.68 (t, J = 7.6 Hz, 2H), 2.30 (t, J = 7.6 Hz, 2H), 1.99 (quint, J = 7.6 Hz, 2H), 1.13- 1.09 (m, 6H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 13.17, 14.36, 26.93, 32.21, 35.38, 40.14, 41.98, 125.89, 128.37, 128.56, 141.92, 171.88.

***N,N*-Diethyl-2-oxo-5-phenylpentanamide (4f)**

^1H NMR (CDCl_3 , 500 MHz) δ 7.30-7.17 (m, 5H), 3.40 (q, J = 7.2 Hz, 2H), 3.23 (q, J = 7.0 Hz, 2H), 2.78 (t, J = 7.3 Hz, 2H), 2.67 (t, J = 7.6 Hz, 2H), 1.98 (quint, J = 7.6 Hz, 2H), 1.19-1.16 (m, 6H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 12.74, 14.52, 24.53, 35.08, 39.28, 39.47, 42.14, 126.11, 128.50, 141.36, 166.85, 201.25; IR (neat) 1639 cm^{-1} , 1710 cm^{-1} ; MS (relative intensity) m/z 247 (M^+ , 2), 219 (19), 191 (35), 147 (38), 100 (100), 91 (60), 72 (45); HRMS (EI), m/z calcd for $\text{C}_{15}\text{H}_{21}\text{NO}_2$ 247.1572, found 247.1567.

***N,N*-Diethyl-2-methyloctanamide (3d)**

^1H NMR (CDCl_3 , 500 MHz) δ 3.45-3.26 (m, 4H), 2.59 (sextet, J = 6.8 Hz, 1H), 1.71-1.64 (m, 1H), 1.39-1.26 (m, 9H), 1.18 (t, J = 7.1 Hz, 3H), 1.12-1.09 (m, 6H), 0.87(t, J = 6.6 Hz, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 13.15, 14.09, 15.00, 18.16, 22.64, 27.62, 29.49, 31.81, 34.58, 35.64, 40.33, 41.85, 176.06; IR (neat) 1643 cm^{-1} ; MS (relative intensity) m/z 213 (M^+ , 7), 142 (28), 129 (100), 100 (41), 72 (23), 58 (26); HRMS (EI), m/z calcd for $\text{C}_{13}\text{H}_{27}\text{NO}$ 213.2093, found 213.2083.

***N,N*-Diethyl-3-methyl-2-oxononanamide (4d)**

^1H NMR (CDCl_3 , 500 MHz) δ 3.43(q, J = 7.1 Hz, 2H), 3.24 (q, J = 7.1 Hz, 2H), 3.14-3.08 (m, 1H), 1.76-1.74 (m, 1H), 1.36-1.17 (m, 15H), 1.13 (t, J = 6.9 Hz, 3H), 0.88 (t, J = 6.9 Hz, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 12.61, 14.10, 14.33, 14.68, 22.63, 27.09, 29.30, 31.55, 31.74, 39.23, 42.02, 42.70, 167.10, 204.45; IR (neat) 1640 cm^{-1} , 1710 cm^{-1} ; MS (relative intensity) m/z 241 (M^+ , 16), 100 (100), 72 (40), 71 (23), 57 (22); HRMS (EI), m/z calcd for $\text{C}_{14}\text{H}_{27}\text{NO}_2$ 241.2042, found 241.2039.

***N,N*-Diethyl-1-adamantanamide (3e)**

This product is commercially available and the ^1H - and ^{13}C -NMR spectra are consistent with those of the authentic sample.

^1H NMR (CDCl_3 , 500 MHz) δ 3.42 (m, 4H), 1.99-1.97 (m, 3H), 1.99 (m, 6H), 1.75-1.70 (m, 6H), 1.13 (t, J = 6.9 Hz, 6H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 13.74, 28.61, 36.70, 39.17, 41.79, 41.85.

***N,N*-Diethyl-2-adamantanatyl-2-oxo-acetamide (4e)**

^1H NMR (CDCl_3 , 500 MHz) δ 3.41 (q, J = 7.2 Hz, 2H), 3.12 (q, J = 7.2 Hz, 2H), 2.05 (m, 3H), 1.94-1.92 (m, 6H), 1.77-1.71 (m, 6H), 1.18 (t, J = 7.1 Hz, 6H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 12.68, 12.72, 13.89, 13.93, 27.82, 36.40, 38.14, 41.92, 45.02, 167.03, 207.63; IR (KBr) 1634 cm^{-1} , 1699 cm^{-1} ; mp 40-41 degrees; MS (relative intensity) m/z 263 (M^+ , 2), 135 (100), 100 (19), 93 (15), 79 (19); HRMS (EI), m/z calcd for $\text{C}_{16}\text{H}_{25}\text{NO}_2$ 263.1885, found 263.1884.

***N,N*-Diethyl-hexenamide (3g)**

^1H NMR (CDCl_3 , 500 MHz) δ 5.85-5.77 (m, 1H), 5.03 (d, J = 17.0 Hz, 1H), 4.98 (d, J = 10.1 Hz, 1H), 3.37 (q, J = 7.0 Hz, 2H), 3.29 (q, J = 7.2 Hz, 2H), 2.30 (t, J = 7.6 Hz, 2H), 2.11 (q, J = 7.0 Hz, 2H), 1.76 (quint, J = 7.4 Hz, 2H), 1.17 (t, J = 7.1 Hz, 3H), 1.11 (t, J = 7.1 Hz, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 13.06, 14.37, 24.45, 32.19, 33.33, 40.02, 41.89, 114.99, 138.25, 171.90; IR (neat) 1640 cm^{-1} ; MS (relative intensity) m/z 169 (M^+ , 69), 128 (21), 115 (87), 100 (100), 87 (20), 86 (35), 85 (62); HRMS (EI), m/z calcd for $\text{C}_{10}\text{H}_{19}\text{NO}$ 169.1467, found. 169.1478.

Synthesis of (-)-hinokinin Precursor.

A magnetic stirring bar, **1h** (0.162 g, 0.51 mmol), NEt_3 (0.063 g, 0.62 mmol), 4-Dimethylaminopyridine (0.007 g, 0.054 mmol), $\text{Pd}(\text{PPh}_3)_4$ (0.036 g, 0.026 mmol), and benzene (3 mL) were placed in a stainless steel autoclave for photoreaction equipped with an inserted Pyrex glass liner. The autoclave was closed, purged three times with carbon monoxide, pressurized with 45 atm of CO and then irradiated by Xenon arc lamp (500 W) with stirring for 16 h. Excess CO was discharged at room temperature after the reaction. The reaction mixture was added to water (20mL) and extracted with ether (20 mL $\times$ 3). The ether layer was washed with sodium thiosulfate solution and brine. Dried over MgSO_4 , then filtered and concentrated *in vacuo* to give a residue, which was subjected to silica gel column chromatography using hexane/EtOAc = 4/1 as eluent to give **2h** (0.085 g, 76%).

3-Benzo[1,3]dioxol-5-yl-2-iodomethyl-propan-1-ol (1h)

This compound was prepared from the Ito's chiral intermediate, Itoh, T.; Chika, J.; Takagi, Y.; Nishiyama, S. *J. Org. Chem.* **1993**, 58, 5717, (R)-3-hydroxy-2-[[3,4-(methylenedioxy)phenyl]methyl]propyl acetate by three steps in 70% overall yield. (1) MsCl, CH₂Cl₂, NEt₃, 0 degree, (2) NaI, acetone, 50 degrees, 7 h, (3) NaOMe, MeOH, r.t., 1.5 h.

¹H-NMR (500 MHz, CDCl₃) δ 1.38-1.45 (m, 1H), 1.64-1.69 (m, 1H), 2.51 (dd, *J* = 13.7, 8.2 Hz, 1H), 2.61 (dd, *J* = 13.7, 6.4 Hz, 1H), 3.19 (dd, *J* = 10.1, 10.1 Hz, 1H), 3.35 (dd, *J* = 9.6, 4.6 Hz, 1H), 3.54 (dd, *J* = 10.8, 6.6 Hz, 1H), 3.67 (dd, *J* = 10.6, 5.1 Hz, 1H), 5.93 (s, 2H), 6.65-6.74 (m, 3H); ¹³C-NMR (125 MHz, CDCl₃) δ 11.6, 36.8, 43.6, 65.0, 101.0, 108.4, 109.5, 122.0, 132.8, 146.2, 147.8; IR (neat) 3347, 2886, 1607, 1487, 1245, 1039, 926, 811, 770 cm⁻¹; MS (relative intensity) *m/z* 320 (M⁺, 48), 263 (20), 262 (97), 183 (59), 135 (100), 108 (19), 77 (19), 69 (26); HRMS (EI) *m/z* calcd for C₁₁H₁₃IO₃ 319.9909, found 319.9918.

(R)-3-[[3,4-(methylenedioxy)phenyl]methyl]-4,5-dihydrofuran-2-(3H)-one (2h)

This compound is known. See the reference; Itoh, T.; Chika, J.; Takagi, Y.; Nishiyama, S. *J. Org. Chem.* **1993**, 58, 5717.

Synthesis of Dihydrocapsaicin (6).

A magnetic stirring bar, **1i** (0.075 g, 0.30 mmol), 4-hydroxy-3-methoxybenzylamine hydrochloride (0.140 g, 0.738 mmol), hexamethyldisilazane (0.153 mL, 0.948 mmol), K₂CO₃ (0.128 g, 0.926 mmol), Pd(PPh₃)₄ (0.017 g, 0.015 mmol), and Benzene (3.0 mL) were placed in a stainless steel autoclave for photoreaction equipped with an inserted Pyrex glass liner. The autoclave was closed, purged three times with carbon monoxide, pressurized with 45 atm of CO and then irradiated by Xenon arc lamp (500 W) with stirring for 16 h. Excess CO was discharged at room temperature after the reaction. The reaction mixture was added to water (20mL) and extracted with ether (20 mL × 3). The ether layer was washed with brine, and dried over MgSO₄, then filtered and concentrated *in vacuo*. The residue was treated with Tetrabutyl-ammonium fluoride (1.0 M THF solution; 1.5 mL, 1.5 mmol) in CHCl₃ (10 mL) at room temperature for 3 h. After that, the reaction mixture was added to water (20mL) and extracted with ether (20 mL × 3). The ether layer was washed with brine (20 mL) and dried over MgSO₄, then filtered and concentrated *in vacuo* to give a residue, which was subjected to silica gel column chromatography using hexane/EtOAc = 1/1 as eluent, affording **6** (0.082 g, 82%).

Dihydrocapsaicin (6)

^1H NMR (CDCl_3 , 500 MHz) δ 6.84 (d, $J = 7.80$ Hz, 1H), 6.79 (s, 1H), 6.73 (d, $J = 7.80$ Hz, 1H), 5.94 (brs, 1H), 4.32 (d, $J = 5.50$ Hz, 2H), 3.85 (s, 3H), 2.19 (t, $J = 7.80$ Hz, 2H), 1.64 (quint, $J = 7.40$ Hz, 2H), 1.26-1.32 (m, 7H), 1.13-1.15 (m, 2H), 0.85 (d, $J = 6.90$ Hz, 6H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 22.54, 25.75, 27.17, 27.85, 29.29, 29.55, 36.74, 38.86, 43.42, 55.81, 110.66, 114.39, 120.63, 130.20, 145.11, 146.74, 173.03; IR (neat) 1642 cm^{-1} ; MS (relative intensity) m/z 307 (M^+ , 32), 152 (15), 137 (100); HRMS (EI), m/z calcd for $\text{C}_{18}\text{H}_{29}\text{NO}_3$ 307.2147, found 307.2144.

[illegible]

JEOL

JEOL CORPORATION
 1000 N. 17th St.
 Avondale, AZ 85009
 (602) 885-8800
 FAX (602) 885-8801
 E-MAIL: JEOL@JEOL.COM
 WWW: JEOL.COM
 JEOL (UK) LTD.
 1000 N. 17th St.
 Avondale, AZ 85009
 (602) 885-8800
 FAX (602) 885-8801
 E-MAIL: JEOL@JEOL.COM
 WWW: JEOL.COM
 JEOL (EUROPE) LTD.
 1000 N. 17th St.
 Avondale, AZ 85009
 (602) 885-8800
 FAX (602) 885-8801
 E-MAIL: JEOL@JEOL.COM
 WWW: JEOL.COM

Butyl 3-mercaptopropionate (2b)

1-Ethyl-4-propyl-γ-butyrolactone (2c)

3-Ethyl-4-propyl- γ -butyrolactone (2e)

[illegible]

Butyl Cadmate: 200 (2e)

[illegible]

N,N-Diethyl nonanamide (3a)

N,N-Diethyl-2-oxodecanamide (4a)

NAME: N,N-Diethyl-2-oxo-5-hexenamide (4b)
 ANALYST: M. J. ...
 INSTRUMENT: JEOL JNM-500
 PULPROG: zgpg30
 F2: 500.136 MHz (1H)
 F1: 125.761 MHz (13C)
 AQ: 1.00000000
 RG: 327.680
 SD: 3.00000000
 DE: 1.00000000
 TE: 300.2 K
 D1: 1.00000000
 D2: 0.05000000
 D3: 0.05000000
 D4: 0.05000000
 D5: 0.05000000
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 D96: 0.05000000
 D97: 0.05000000
 D98: 0.05000000
 D99: 0.05000000
 D100: 0.05000000

N,N-Diethyl-2-oxo-5-hexenamide (4b)

1H NMR (CDCl₃)

[illegible]

N,N-Diethyl-2-oxo-5-phenylpentanamide (40)

N,N'-Diethyl-2-methyloctanamide (3d)

N,N-Diethyl-3-methyl-2-oxooxanamide (4d)

N,N-Diethyl-1-adamantanamide (3a)

N,N'-Diethyl-3-adamantanylt-2-oxoacetamide (4e)

[illegible]

N,N'-Diethyl-2-adamantyl-2'-oxoacetamide (4e)

N,N-Diethyl-benzamide (3g)

X = parts per Million = 111

[illegible]

[illegible]

3-Benzof[1,3]dioxol-5-yl-2-iodomethyl-propan-1-ol (14)

X : parts par million : 100

[illegible]

3-Benzyl[1,3-bisoxol-5-yl]-2-iodomethyl-propan-1-ol (1h)