Enantioselective Transfer Aminoallylation: Synthesis of Optically Active Homoallylic Primary Amines

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Experimental Details and Physical Data

General Methods: ¹H and ¹³C NMR spectra were recorded on JEOL JNM-ECX400 or JNM-ECX600 spectrometer in CDCl₃ unless otherwise noted. Tetramethylsilane (TMS) served as an internal standard (δ = 0) for ¹H NMR and CDCl₃ was used as an internal standard (δ = 77.0) for ¹³C NMR. Electrospray ionization high-resolution mass spectra (ESI-HRMS) were measured with BRUKER DALTONICS BioTOF II mass spectrometer. Optical rotations

were recorded on JASCO P-1010 polarimeter. Preparative thin-layer chromatography (PTLC) was carried out using Wakogel B-5F. Ethanol was distilled from sodium and stored over 3 Å MS. 1,2-Dichloroethane (DCE) was distilled from P₂O₅ and then from CaH₂ and stored over 4 Å MS. Purified water was obtained by MILLIPORE water purification system. All other solvents were purified based on standard procedures.

Chemicals: (1*R*)-(-)-Camphorquinone was purchased from Tokyo Kasei Kogyo Co., Ltd. and used without further purification. Allylboronoic acid pinacol ester was prepared according to the literature.¹ Methanolic ammonia (ca. 7 M) was purchased from Aldrich Chemical Company. Glyoxylic acid monohydrate (**2a**) was purchased from Wako Pure Chemical Industries, Ltd. and used without further purification. Aldehydes **2b-i**, **2k**, and **2m** were purchased from Tokyo Kasei Kogyo Co., Ltd. and freshly distilled or recrystallized (for **2c** and **2d**) before use. Aldehydes **2j**, **2l**, and **2o** were purchased from Aldrich Chemical Company and freshly distilled prior to use. Aldehyde **2n** was prepared by Swern oxidation of 3-benzyloxy-1-propanol. All other chemicals were purified based on standard procedures.

Preparation of (1*R*,3*R*,4*S*)-3-allyl-3-amino-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one (1a**)**

To a solution of (1*R*)-(-)-camphorquinone (1.33 g, 8.0 mmol) in methanolic ammonia (ca. 7 M, 12 mL), allylboronoic acid pinacol ester (2.02 g, 12.0 mmol) was added dropwise at rt. After being stirred for 24 h at that temperature, 3 N hydrochloric acid was added slowly to adjust pH ca. 1. After being stirred for 30 min, the aqueous layer was washed with dichloromethane (3×), basified with 6 N aqueous NaOH (pH ca. 10), and extracted with dichloromethane (3×). The later dichloromethane layers were dried over anhydrous Na₂CO₃, filtered, evaporated, and purified by silica gel column chromatography (hexane/ethyl acetate = 3/1) to give amine **1a** (1.32 g, 80% yield, >99% de).

(1*R*,3*R*,4*S*)-3-Allyl-3-amino-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one (1a**)**

$[\alpha]_D^{23} +151.6$ (c 1.26, CHCl₃, >99% de); ¹H NMR (400 MHz, CDCl₃) δ 5.85 (dddd, *J* = 16.9, 10.3, 8.0, 6.4 Hz, 1H), 5.22-5.12 (m, 2H), 2.25 (dd, *J* = 14.6, 6.2 Hz, 1H), 2.11 (dd, *J* = 14.6, 7.8 Hz, 1H), 1.94-1.83 (m, 1H), 1.85 (d, *J* = 3.2 Hz, 1H), 1.72-1.62 (m, 2H), 1.52-1.44 (m,

1H), 1.41 (brs, 2H), 1.07 (s, 3H), 1.00 (s, 3H), 0.91 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 222.8, 133.3, 119.3, 61.9, 58.6, 52.5, 46.3, 42.5, 30.2, 23.3, 23.0, 20.9, 9.8; ESI-HRMS calcd for C₁₃H₂₂NO (M+H⁺) 208.1696, found 208.1689.

Assignment of the relative configuration of **1a**

A mixture of **1a** (29.5 mg, 0.14 mmol), triethylamine (1.6 equiv), DMAP (0.05 equiv), and *p*-bromobenzoyl chloride (37.0 mg, 1.2 equiv) in dichloromethane (1.4 mL) was stirred at rt for 24 h. The mixture was concentrated and directly purified by preparative TLC (hexane/ethyl acetate = 5/1) to give the corresponding *p*-bromobenzamide (36.7 mg, 66% yield). A NOESY experiment of this *p*-bromobenzamide confirmed the 3*R* configuration (Chart S-1 and Figure S-1).

Chart S-1. NOESY spectrum of *p*-bromobenzamide of **1a**

p*-Bromobenzamide of **1a*

^1H NMR (600 MHz, CDCl_3) δ 7.52-7.47 (m, 4H; Ph), 6.01 (brs, 1H; NH), 5.88 (dddd, $J = 17.8, 9.6, 8.9, 5.5$ Hz, 1H; 2'-H), 5.02-4.97 (m, 2H; 3'-H), 3.30 (d, $J = 4.1$ Hz, 1H; 4-H), 2.95 (dd, $J = 14.5, 8.9$ Hz, 1H; 1'-H_b), 2.26 (dd, $J = 14.5, 5.5$ Hz, 1H; 1'-H_a), 1.98 (dddd, $J = 13.7, 11.4, 5.5, 4.1$ Hz, 1H; 5-H _{β}), 1.82-1.71 (m, 2H; 5-H _{α} , 6-H _{β}), 1.58 (ddd, $J = 14.4, 8.9, 5.5$ Hz, 1H; 6-H _{α}), 1.00 (s, 3H; CH₃), 0.93 (s, 3H; CH₃), 0.91 (s, 3H; CH₃); ^{13}C NMR (150 MHz, CDCl_3) δ 217.7, 165.7, 134.1, 133.1, 131.8, 128.3, 126.0, 118.7, 64.3, 58.6, 49.1, 46.6, 38.9, 29.5, 22.4, 22.0, 20.7, 9.8; ESI-HRMS calcd for $\text{C}_{20}\text{H}_{25}\text{BrNO}_2$ ($\text{M}+\text{H}^+$) 390.1063, found 390.1057.

Figure S-1. The NOESY correlation of *p*-bromobenzamide of **1a**

Transfer aminoallylation of glyoxylic acid (2a**)**

To a solution of chiral amine **1a** (98.6 mg, 0.48 mmol) in ethanol (0.6 mL), a solution of glyoxylic acid monohydrate (**2a**) (42.8 mg, 0.46 mmol) in ethanol (0.6 mL) was added dropwise at -40 °C. The mixture was stirred for 4 days at that temperature and quenched with 1 N hydrochloric acid (5 mL). After being stirred for 1 h at rt, the mixture was washed with dichloromethane (2 $\times$) and diethyl ether (1 $\times$). The aqueous layer was concentrated to ca. 2 mL and charged on a cationic ion exchange resin column (DOWEX 50W-X2, 50-100 mesh, H^+ form; ca. 7 g/wet) with purified water. After being washed with purified water (100 mL), the product was eluted with 1 N aqueous ammonia (100 mL). The eluant was concentrated to ca. 2 mL and charged on an anionic ion exchange resin column (Amberlite IRA 400, OH^- form; ca. 7 g/wet) with purified water. After being washed with purified water (100 mL), the product was eluted with 1 N hydrochloric acid (100 mL). The eluant was concentrated to dryness to give (*S*)-allylglycine hydrochloride (**3a**) (44.1 mg, 63% yield, 93% ee).

(*S*)-2-Allylglycine hydrochloride (3a**)**

NMR and MS data were identical to the previous report.² The absolute configuration was assigned on comparison of the retention times of HPLC analysis with an authentic sample (obtained from Tokyo Kasei Kogyo Co., Ltd.); HPLC (CROWNPAK CR(+), 0.4 cm ϕ $\times$ 25 cmL, 0.1 M HClO₄ aqueous solution, flow rate 0.5 mL/min, UV detection at 200 nm) t_R = 3.9 min (*R*), t_R = 5.5 min (*S*).

General procedures for transfer aminoallylation using **1a** (Tables 1 and 2)

To a solution of chiral amine **1a** (103.6 mg, 0.5 mmol) and an aldehyde **2** (0.5 mmol) in 1,2-dichloroethane (1 mL) was added camphorsulfonic acid (11.6 mg, 10 mol%) at 0 °C or rt. The mixture was stirred at the indicated temperature for the indicated time. Then, a solution of HONH₂•AcOH in methanol [0.5 M, 2 mL, prepared from HONH₂•HCl, NaOH (solid, 1 equiv), and AcOH (1 equiv) in methanol] was added to the solution. After being stirred at 50 °C for 3 h, the mixture was cooled to rt, acidified with 1 N aqueous HCl (pH ca. 1). The mixture was washed with dichloromethane (3 $\times$), basified with 6 N aqueous NaOH (pH ca. 10), and extracted with dichloromethane (3 $\times$). The later dichloromethane layers were dried over anhydrous Na₂CO₃, filtered, and evaporated to give almost pure amine **3**. The crude product was purified by preparative TLC (developed with hexane/ethyl acetate = 1/1 or ethyl acetate, and then eluted with hexane/isopropylamine = 10/1 or 7/1) to give amine **3**.

(*S*)-1-Phenylbut-3-en-1-amine (**3b**)

Obtained from benzaldehyde (**2b**). NMR and MS data were identical to the previous report.² The absolute configuration was assigned according to the literature³: [α]_D²⁵ -50.0 (c 1.13, CHCl₃, 96% ee (*S*)); HPLC (CHIRALCEL OD-H, 0.46 cm ϕ $\times$ 25 cmL, hexane/2-propanol/diethylamine = 95/5/0.05, flow rate 1.0 mL/min, UV detection at 254 nm) t_R = 7.3 min (*R*), t_R = 9.9 min (*S*).

(*S*)-1-(4-Nitrophenyl)but-3-en-1-amine (**3c**)

Obtained from *p*-nitrobenzaldehyde (**2c**). NMR and MS data were identical to the previous report.² The absolute configuration was assigned according to the literature⁴: $[\alpha]_{\text{D}}^{22} -40.0$ (c 1.52, CHCl₃, 97% ee (*S*)); HPLC (CHIRALCEL OD-H, 0.46 cm $\varnothing$ $\times$ 25 cmL, hexane/2-propanol/diethylamine = 95/5/0.05, flow rate 1.0 mL/min, UV detection at 254 nm) t_{R} = 15.5 min (*R*), t_{R} = 16.8 min (*S*).

(*S*)-1-(4-Bromophenyl)but-3-en-1-amine (3d)

Obtained from *p*-bromobenzaldehyde (**2d**). NMR and MS data were identical to the previous report.² The absolute configuration was tentatively assigned on the basis of analogy: $[\alpha]_{\text{D}}^{23} -40.1$ (c 1.16, CHCl₃, 98% ee (*S*)); HPLC (CHIRALCEL OD-H, 0.46 cm $\varnothing$ $\times$ 25 cmL, hexane/2-propanol/diethylamine = 95/5/0.05, flow rate 0.5 mL/min, UV detection at 254 nm) t_{R} = 15.9 min (*R*), t_{R} = 17.1 min (*S*).

(*S*)-1-(4-Methoxyphenyl)but-3-en-1-amine (3e)

Obtained from *p*-anisaldehyde (**2e**). NMR and MS data were identical to the previous report.² The absolute configuration was assigned according to the literature³: $[\alpha]_{\text{D}}^{23} -42.3$ (c 0.81, CHCl₃, 97% ee (*S*)); HPLC (CHIRALCEL OD-H, 0.46 cm $\varnothing$ $\times$ 25 cmL, hexane/2-propanol/diethylamine = 95/5/0.05, flow rate 1.0 mL/min, UV detection at 254 nm) t_{R} = 9.8 min (*R*), t_{R} = 12.2 min (*S*).

(*S*)-1-(Thiophen-2-yl)but-3-en-1-amine (3f)

Obtained from 2-thiophencarboxaldehyde (**2f**). NMR and MS data were identical to the previous report.² The absolute configuration was assigned according to the literature³: $[\alpha]_{\text{D}}^{24} -23.8$ (c 0.72, CHCl₃, 95% ee (*S*)); HPLC (CHIRALCEL OD-H, 0.46 cm $\varnothing$ $\times$ 25 cmL,

hexane/2-propanol/diethylamine = 95/5/0.05, flow rate 1.0 mL/min, UV detection at 254 nm)
 $t_R = 7.7$ min (*R*), $t_R = 9.4$ min (*S*).

(S)-1-(Furan-2-yl)but-3-en-1-amine (3g)

Obtained from 2-furancarboxaldehyde (**2g**). The absolute configuration was assigned according to the literature³: $[\alpha]_D^{23} -37.1$ (c 0.85, CHCl₃, 94% ee (*S*)); ¹H NMR (400 MHz, CDCl₃) δ 7.32 (dd, $J = 1.8, 0.9$ Hz, 1H), 6.28 (dd, $J = 3.2, 1.8$ Hz, 1H), 6.11 (dd, $J = 3.2, 0.9$ Hz, 1H), 5.74 (dddd, $J = 16.9, 10.1, 7.4, 6.8$ Hz, 1H), 5.16-5.04 (m, 2H), 3.98 (dd, $J = 7.8, 5.5$ Hz, 1H), 2.60-2.50 (m, 1H), 2.44-2.34 (m, 1H), 1.53 (brs, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 158.5, 141.3, 134.7, 117.9, 110.0, 104.4, 49.2, 40.9; ESI-HRMS calcd for C₈H₁₂NO (*M*+*H*⁺) 138.0913, found 138.0918; HPLC (CROWNPAK CR(+), 0.4 cm ϕ $\times$ 25 cmL, 0.1 M HClO₄ aqueous solution, flow rate 0.5 mL/min, UV detection at 200 nm; $t_R = 25.9$ min (*S*), $t_R = 30.1$ min (*R*).

(S)-1-(Pyridin-3-yl)but-3-en-1-amine (3h)

Obtained from 3-pyridinecarboxaldehyde (**2h**). The absolute configuration was assigned according to the literature⁵: $[\alpha]_D^{26} -59.6$ (c 0.66, CHCl₃, 98% ee (*S*)); ¹H NMR (400 MHz, CDCl₃) δ 8.56 (d, $J = 1.8$ Hz, 1H), 8.48 (dd, $J = 5.0, 1.8$ Hz, 1H), 7.69 (ddd, $J = 7.8, 1.8, 1.8$ Hz, 1H), 7.24 (dd, $J = 7.8, 5.0$ Hz, 1H), 5.71 (dddd, $J = 17.0, 10.5, 7.8, 6.4$ Hz, 1H), 5.17-5.06 (m, 2H), 4.04 (dd, $J = 7.8, 5.5$ Hz, 1H), 2.50-2.31 (m, 2H), 1.74 (brs, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 148.5, 140.6, 134.5, 133.9, 123.4, 118.4, 53.0, 43.9; ESI-HRMS calcd for C₉H₁₃N₂ (*M*+*H*⁺) 149.1073, found 149.1071; HPLC (CROWNPAK CR(+), 0.4 cm ϕ $\times$ 25 cmL, 0.1 M HClO₄ aqueous solution, flow rate 0.2 mL/min, UV detection at 257 nm; $t_R = 12.0$ min (*S*), $t_R = 14.3$ min (*R*).

(R)-1-Phenylhex-5-en-3-amine (3i)

Obtained from 3-phenylpropionaldehyde (**2i**). NMR and MS data were identical to the previous report.^{2,6} The absolute configuration was assigned according to the literature⁶: $[\alpha]_D^{25} +12.1$ (c 0.81, CHCl₃, 96% ee (*R*)); HPLC (CHIRALCEL OD-H, 0.46 cmø × 25 cmL, hexane/2-propanol/diethylamine = 90/10/0.05, flow rate 1.0 mL/min, UV detection at 254 nm) $t_R = 7.4$ min (*S*), $t_R = 10.0$ min (*R*).

(S)-1-Phenylpent-4-en-2-amine (3j)

Obtained from phenylacetaldehyde (**2j**). The absolute configuration was tentatively assigned on the basis of analogy: $[\alpha]_D^{21} +28.3$ (c 1.59, CHCl₃, 93% ee (*S*)); ¹H NMR (400 MHz, CDCl₃) δ 7.35-7.18 (m, 5H), 5.83 (dddd, *J* = 17.0, 10.3, 7.8, 6.4 Hz, 1H), 5.19-5.08 (m, 2H), 3.09 (dddd, *J* = 8.2, 7.8, 5.0, 5.0 Hz, 1H), 2.80 (dd, *J* = 13.3, 5.0 Hz, 1H), 2.55 (dd, *J* = 13.3, 8.2 Hz, 1H), 2.30 (ddd, *J* = 13.7, 6.4, 5.0 Hz, 1H), 2.09 (ddd, *J* = 13.7, 7.8, 7.8 Hz, 1H), 1.66 (brs, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 139.4, 135.6, 129.3, 128.5, 126.3, 117.6, 52.1, 44.1, 41.9; ESI-HRMS calcd for C₁₁H₁₆N (M+H⁺) 162.1277, found 162.1278; HPLC (CHIRALCEL OD-H, 0.46 cmø × 25 cmL, hexane/2-propanol/diethylamine = 99.8/0.2/0.05, flow rate 1.0 mL/min, UV detection at 254 nm) $t_R = 13.5$ min (*S*), $t_R = 14.9$ min (*R*).

(R)-Undec-1-en-4-amine (3k)

Obtained from octanal (**2k**). The absolute configuration was tentatively assigned on the basis of analogy: $[\alpha]_D^{27} +5.9$ (c 1.17, CHCl₃, 93% ee (*R*)); ¹H NMR (400 MHz, CDCl₃) δ 5.77 (dddd, *J* = 16.7, 10.5, 8.2, 6.4 Hz, 1H), 5.10-5.02 (m, 2H), 2.78-2.69 (m, 1H), 2.25-2.15 (m, 1H), 1.99-1.89 (m, 1H), 1.44-1.14 (m, 14H), 0.85 (t, *J* = 6.9 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 136.0, 117.1, 50.6, 42.6, 37.7, 31.8, 29.7, 29.3, 26.2, 22.6, 14.1; ESI-HRMS calcd for C₁₁H₂₄N (M+H⁺) 170.1903, found 170.1902.

Benzamide of 3k

For determination of the enantiomeric excess, **3k** was converted to the corresponding benzamide under the usual procedure [benzoyl chloride (1.2 equiv) and triethylamine (1.5 equiv) in dichloromethane at rt]: ^1H NMR (400 MHz, CDCl_3) δ 7.72 (apparent d, $J = 8.0$ Hz, 2H), 7.50-7.35 (m, 3H), 5.94 (d, $J = 8.7$ Hz, 1H), 5.81 (dddd, $J = 17.4, 10.3, 6.9, 6.0$ Hz, 1H), 5.13-5.05 (m, 2H), 4.25-4.13 (m, 1H), 2.36 (ddd, $J = 14.0, 6.0, 6.0$ Hz, 1H), 2.28 (ddd, $J = 14.0, 6.9, 6.9$ Hz, 1H), 1.63-1.42 (m, 2H), 1.42-1.17 (m, 10H), 0.84 (t, $J = 6.6$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.0, 135.0, 134.4, 131.2, 128.5, 126.8, 117.9, 49.0, 39.2, 34.5, 31.7, 29.5, 29.2, 26.0, 22.6, 14.0; ESI-HRMS calcd for $\text{C}_{18}\text{H}_{28}\text{NO}$ ($\text{M}+\text{H}^+$) 274.2165, found 274.2167; HPLC (CHIRALCEL OD-H, $0.46\text{ cm}\phi \times 25\text{ cmL}$, hexane/2-propanol/diethylamine = 95/5/0.05, flow rate 1.0 mL/min, UV detection at 254 nm) $t_R = 9.2\text{ min}$ (*R*), $t_R = 12.3\text{ min}$ (*S*).

(4*S*,6*S*)-6,10-Dimethylundeca-1,9-dien-4-amine (3l**)**

Obtained from (*S*)-citronellal (**2l**) [95% ee (*S*)]. Due to the high hydrophobicity of **3l**, it was difficult to extract **3l** completely into the acidic aqueous layer. Therefore, **3l** was extracted with dichloromethane directly from the reaction mixture (basified with 6 N aqueous NaOH), and then purified by PTLC. The relative configuration was tentatively assigned on the basis of analogy, and the diastereomeric excess was estimated by ^{13}C NMR analysis (93% de): $[\alpha]_D^{23} +15.9$ (c 0.99, CHCl_3 , 93% de); ^1H NMR (600 MHz, CDCl_3) δ 5.79 (dddd, $J = 16.5, 10.3, 8.0, 6.5$ Hz, 1H), 5.12-5.06 (m, 3H), 2.88 (ddt, $J = 8.9, 8.0, 4.6$ Hz, 1H), 2.23-2.16 (m, 1H), 2.05-1.92 (m, 3H), 1.66 (s, 3H), 1.60 (brs, 4H), 1.46-1.34 (m, 2H), 1.34-1.26 (m, 2H), 1.22-1.13 (m, 2H), 0.89 (d, $J = 6.2$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 135.91, 131.13, 124.73, 117.17, 47.90, 45.14, 43.45, 37.89, 29.15, 25.66, 25.44, 19.09, 17.61; ESI-HRMS calcd for $\text{C}_{13}\text{H}_{26}\text{N}$ ($\text{M}+\text{H}^+$) 196.2060, found 196.2060.

(4*R*,6*S*)-6,10-Dimethylundeca-1,9-dien-4-amine (3l**)**

Obtained from (*S*)-citronellal (**2l**) [95% ee (*S*)] and the enantiomer of **1a** [prepared from (1*S*)-camphorquinone]. The product was isolated as described above. The relative configuration was tentatively assigned on the basis of analogy, and the diastereomeric excess was estimated by ^{13}C NMR analysis (92% de): $[\alpha]_D^{23} -3.9$ (c 0.99, CHCl_3 , 91% de); ^1H NMR (600 MHz, CDCl_3) δ 5.79 (dddd, $J = 16.5, 10.6, 8.3, 6.5$ Hz, 1H), 5.14-5.06 (m, 3H), 2.89 (apparent ddt, J

= 7.6, 6.8, 4.1 Hz, 1H), 2.28-2.20 (m, 1H), 2.06-1.89 (m, 3H), 1.68 (s, 3H), 1.60 (s, 3H), 1.59-1.52 (m, 3H), 1.40-1.08 (m, 4H), 0.91 (d, J = 6.8 Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 135.79, 131.17, 124.71, 117.28, 48.03, 45.30, 42.45, 36.66, 29.24, 25.65, 25.26, 20.15, 17.60; ESI-HRMS calcd for $\text{C}_{13}\text{H}_{26}\text{N}$ ($\text{M}+\text{H}^+$) 196.2060, found 196.2053.

Determination of the enantiomeric excess of (*S*)-citronellal (**2l**)

The enantiomeric excess of (*S*)-citronellal (purchased from Aldrich Chemical Company) was determined by HPLC analysis after conversion to the corresponding *N'*-benzoylhydrazone [treatment with *N*-benzoylhydrazine (1 equiv) in THF at rt for 5 h]. HPLC (CHIRALCEL OD, 0.46 cm ϕ $\times$ 25 cmL, hexane/2-propanol = 19/1, flow rate 1.0 mL/min, UV detection at 254 nm) t_R = 30.3 min (*S*), t_R = 35.7 min (*R*).

(*S*)-1-Cyclohexylbut-3-en-1-amine (**3m**)

Obtained from cyclohexanecarboxaldehyde (**2m**). NMR and MS data were identical to the previous report.² The absolute configuration was assigned according to the literature⁴: $[\alpha]_{\text{D}}^{26}$ +4.5 (c 1.04, CHCl_3 , 95% ee (*S*)).

Benzamide of **3m**

For determination of the enantiomeric excess, **3m** was converted to the corresponding benzamide under the usual procedure (see the procedure for **3k**): ^1H NMR (400 MHz, CDCl_3) δ 7.72 (dd, J = 8.2, 1.4 Hz, 2H), 7.50-7.37 (m, 3H), 5.91 (brd, J = 9.2 Hz, 1H), 5.80 (dddd, J = 17.2, 10.0, 7.3, 6.9 Hz, 1H), 5.14-4.99 (m, 2H), 4.15-4.02 (m, 1H), 2.39 (ddd, J = 14.4, 6.9, 5.5 Hz, 1H), 2.26 (ddd, J = 14.4, 7.3, 7.3 Hz, 1H), 1.83-1.69 (m, 4H), 1.64 (brd, J = 11.0 Hz, 1H), 1.55-1.42 (m, 1H), 1.29-0.95 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.1, 135.1, 134.8, 131.2, 128.5, 126.8, 117.6, 53.2, 41.3, 36.4, 29.7, 28.8, 26.3, 26.14, 26.12; ESI-HRMS calcd for $\text{C}_{17}\text{H}_{24}\text{NO}$ ($\text{M}+\text{H}^+$) 258.1852, found 258.1857; HPLC (CHIRALCEL OD-H, 0.46 cm ϕ $\times$ 25 cmL, hexane/2-propanol/diethylamine = 95/5/0.05, flow rate 0.5 mL/min, UV detection at 254 nm) t_R = 18.8 min (*R*), t_R = 20.3 min (*S*).

(S)-1-(Benzyloxy)hex-5-en-3-amine (**3n**)

Obtained from 3-(benzyloxy)propanal (**2n**). The absolute configuration was tentatively assigned on the basis of analogy: $[\alpha]_D^{25} +26.8$ (c 1.27, CHCl_3 , 96% ee (*S*)); ^1H NMR (400 MHz, CDCl_3) δ 7.36-7.22 (m, 5H), 5.76 (dddd, $J = 15.4, 11.7, 7.8, 6.9$ Hz, 1H), 5.10-5.02 (m, 2H), 4.49 (s, 2H), 3.63-3.52 (m, 2H), 2.97 (dddd, $J = 8.7, 8.0, 4.7, 4.6$ Hz, 1H), 2.21 (ddd, $J = 13.7, 6.9, 4.7$ Hz, 1H), 1.99 (ddd, $J = 13.7, 8.0, 7.8$ Hz, 1H), 1.75 (dddd, $J = 14.2, 6.9, 6.9, 4.6$ Hz, 1H), 1.55 (dddd, $J = 14.2, 8.7, 6.0, 6.0$ Hz, 1H), 1.29 (brs, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 138.4, 135.6, 128.3, 127.6, 127.5, 117.4, 73.0, 68.0, 48.4, 42.8, 37.3; ESI-HRMS calcd for $\text{C}_{13}\text{H}_{20}\text{NO}$ ($\text{M}+\text{H}^+$) 206.1539, found 206.1542; HPLC (CHIRALCEL OD-H, 0.46 cm $\varnothing$ $\times$ 25 cmL, hexane/2-propanol/diethylamine = 95/5/0.05, flow rate 1.0 mL/min, UV detection at 254 nm) $t_R = 8.2$ min (*S*), $t_R = 9.2$ min (*R*).

(S)-1-(Benzyloxy)pent-4-en-2-amine (**3o**)

Obtained from 3-(benzyloxy)acetaldehyde (**2o**). The absolute configuration was tentatively assigned on the basis of analogy: $[\alpha]_D^{25} +7.1$ (c 1.14, CHCl_3 , 92% ee (*S*)); ^1H NMR (400 MHz, CDCl_3) δ 7.12-6.97 (m, 5H), 5.52 (dddd, $J = 17.0, 10.1, 7.6, 6.9$ Hz, 1H), 4.88-4.77 (m, 2H), 4.26 (s, 2H), 3.19 (dd, $J = 8.7, 4.1$ Hz, 1H), 3.02 (dd, $J = 8.7, 7.8$ Hz, 1H), 2.80 (dddd, $J = 7.8, 7.8, 5.3, 4.1$ Hz, 1H), 1.97 (ddd, $J = 13.8, 6.9, 5.3$ Hz, 1H), 1.78 (ddd, $J = 13.8, 7.8, 7.6$ Hz, 1H), 1.15 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 138.3, 135.2, 128.3, 127.6, 127.5, 117.4, 75.3, 73.2, 50.3, 38.8; ESI-HRMS calcd for $\text{C}_{12}\text{H}_{18}\text{NO}$ ($\text{M}+\text{H}^+$) 192.1383, found 192.1382; HPLC (CHIRALCEL OD-H, 0.46 cm $\varnothing$ $\times$ 25 cmL, hexane/2-propanol/diethylamine = 95/5/0.05, flow rate 1.0 mL/min, UV detection at 254 nm) $t_R = 9.8$ min (*R*), $t_R = 11.7$ min (*S*).

Isolation of intermediate **4b**

A mixture of chiral amine **1a** (103.3 mg, 0.5 mmol) and benzaldehyde (**2b**) (0.6 mmol), in 1,2-dichloroethane (1 mL) was stirred at 50 °C for 6 h. After evaporation of the solvent, the residue was purified by neutral silica gel column chromatography (hexane/ethyl acetate = 10/1) to give imine **4b** (130.4 mg, 89% yield).

(*E*,1*R*,3*R*,4*S*)-3-Allyl-3-(benzylideneamino)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one

(4b). ^1H NMR (400 MHz, CDCl_3) δ 8.57 (s, 1H), 7.74–7.67 (m, 2H), 7.40–7.34 (m, 3H), 5.73 (dddd, $J = 17.0, 10.1, 7.3, 6.9$ Hz, 1H), 5.06–4.95 (m, 2H), 2.56 (dd, $J = 14.8, 6.9$ Hz, 1H), 2.52 (d, $J = 3.7$ Hz, 1H), 2.40 (dd, $J = 14.8, 7.3$ Hz, 1H), 2.03–1.91 (m, 1H), 1.81–1.68 (m, 2H), 1.56–1.48 (m, 1H), 1.01 (s, 3H), 0.91 (s, 3H), 0.75 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 219.9, 159.5, 136.7, 132.5, 130.5, 128.4, 128.0, 118.8, 71.9, 58.3, 51.3, 46.7, 42.1, 31.3, 22.7, 22.2, 20.6, 9.7; ESI-HRMS calcd for $\text{C}_{20}\text{H}_{26}\text{NO}$ ($\text{M}+\text{H}^+$) 296.2009, found 296.2006.

Isolation of intermediate 5b

A mixture of chiral amine **1a** (189.8 mg, 0.9 mmol), benzaldehyde (**2b**) (0.9 mmol), and camphorsulfonic acid (22.4 mg, 11 mol%) in 1,2-dichloroethane (1.8 mL) was stirred at 50 °C for 48 h. After evaporation of the solvent, the residue was directly purified by PTLC (hexane/ethyl acetate = 6 / 1) to give rearranged products (*E*)-**5b** (182.6 mg, 68% yield) and (*Z*)-**5b** (27.3 mg, 10% yield).

(*E*,1*R*,4*S*)-3-((*S*)-1-Phenylbut-3-enylimino)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one

[(*E*)-5b**]** ^1H NMR (600 MHz, C_6D_6) δ 7.32 (apparent d, $J = 8.2$ Hz, 2H; Ph), 7.05 (apparent t, $J = 7.9$ Hz, 2H; Ph), 6.95 (apparent t, $J = 7.6$ Hz, 1H; Ph), 5.57 (dddd, $J = 17.2, 10.3, 7.6, 6.9$ Hz, 1H; 3'-H), 4.88 (dddd, $J = 17.2, 2.0, 1.4, 1.4$ Hz, 1H; 4'- H_{trans}), 4.81 (apparent dd, $J = 10.3, 2.0$ Hz, 1H; 4'- H_{cis}), 4.23 (dd, $J = 8.3, 5.5$ Hz, 1H; 1'-H), 2.70–2.64 (m, 1H; 2'- H_a), 2.54–2.48 (m, 1H; 2'- H_b), 2.41 (d, $J = 4.8$ Hz, 1H; 4-H), 1.21 (dddd, $J = 13.1, 11.7, 4.8, 4.8$ Hz, 1H; 5- H_β), 1.01 (ddd, $J = 13.7, 11.7, 4.1$ Hz, 1H; 6- H_β), 0.84 (ddd, $J = 13.7, 8.9, 4.8$ Hz, 1H; 6- H_α), 0.78 (s, 3H; 1- CH_3), 0.63 (ddd, $J = 13.1, 8.9, 4.1$ Hz, 1H; 5- H_α), 0.55 (s, 3H; 7- CH_3), 0.40 (s, 3H; 7- CH_3); ^{13}C NMR (150 MHz, C_6D_6) δ 204.4, 170.1, 143.7, 135.6, 128.3, 127.7, 127.5, 117.3, 68.1, 57.6, 49.0, 43.92, 43.88, 29.8, 23.5, 20.9, 17.5, 9.2; ESI-HRMS calcd for $\text{C}_{20}\text{H}_{26}\text{NO}$ ($\text{M}+\text{H}^+$) 296.2009, found 296.2005. The configuration was determined by a NOESY experiment (Chart S-2).

(*Z*,1*R*,4*S*)-3-((*S*)-1-Phenylbut-3-enylimino)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one

[(*Z*)-5b**]** ^1H NMR (600 MHz, C_6D_6) δ 7.49 (apparent d, $J = 8.2$ Hz, 2H; Ph), 7.06 (apparent t,

$J = 7.9$ Hz, 2H; Ph), 6.93 (apparent t, $J = 7.6$ Hz, 1H; Ph), 6.36 (dd, $J = 8.2, 4.9$ Hz, 1H; 1'-H), 5.71 (dddd, $J = 17.2, 10.3, 7.6, 6.2$ Hz, 1H; 3'-H), 4.90 (dddd, $J = 17.2, 2.1, 1.4, 1.4$ Hz, 1H; 4'-H_{trans}), 4.82 (apparent dd, $J = 10.3, 2.1$ Hz, 1H; 4'-H_{cis}), 2.70-2.42 (m, 2H; 2'-H), 2.35 (d, $J = 4.8$ Hz, 1H; 4-H), 1.56 (dddd, $J = 13.1, 11.7, 5.5, 4.8$ Hz, 1H; 5-H_β), 1.36 (ddd, $J = 13.1, 8.9, 4.8$ Hz, 1H; 5-H_α), 1.17 (ddd, $J = 13.7, 11.7, 4.8$ Hz, 1H; 6-H_α), 1.13 (ddd, $J = 13.7, 8.9, 5.5$ Hz, 1H; 5-H_β), 0.69 (s, 3H; 1-CH₃), 0.331 (s, 3H; 7-CH₃), 0.325 (s, 3H; 7-CH₃); ¹³C NMR (150 MHz, C₆D₆) δ 203.6, 167.4, 144.7, 135.9, 128.6, 127.7, 127.1, 117.0, 62.5, 59.9, 55.5, 44.4, 43.8, 29.9, 25.4, 20.1, 17.7, 9.2. The configuration was determined by a NOESY experiment (Chart S-3).

Chart S-2. NOESY spectrum of (*E*)-**5b** (Z:E = 5:95)

Chart S-3. NOESY spectrum of (Z)-**5b** (*Z:E* = 80:20)

NMR analysis of reaction of **4b** in CDCl₃

A reaction of imine **4b** (127.1 mg, 0.43 mmol) and camphorsulfonic acid (9.1 mg, 9 mol%) in deuterated chloroform (0.9 mL) at 50 °C was monitored by ¹H NMR spectroscopy until 48 h (Chart S-4). The reaction reached equilibrium within 48 h [**2b:4b:(Z)-5b:(E)-5b** = 2:6:18:74].

Chart S-4. NMR monitoring of reaction of **4b**

NMR analysis of reaction of **5b** in CDCl_3

A reaction of imine **5b** (104.7 mg, 0.35 mmol) and camphorsulfonic acid (7.6 mg, 9 mol%) in deuterated chloroform (0.7 mL) at 50 °C was monitored by ^1H NMR spectroscopy until 48 h (Chart S-5). The reaction reached equilibrium within 48 h [**2b**:**4b**:(*Z*)-**5b**:(*E*)-**5b** = 1:5:18:76].

Chart S-5. NMR monitoring of reaction of **5b**

NMR analysis of reaction of 2-thiophenecarboxaldehyde (2f**) with **1a** in CDCl_3**

A mixture of chiral amine **1a** (99.9 mg, 0.48 mmol) and 2-thiophenecarboxaldehyde (**2f**) (55.2 mg, 0.49 mmol) in deuterated chloroform (1.0 mL) was stood for 24 h at 50 °C in a NMR tube. No rearranged product was observed at that stage. Then camphorsulfonic acid (11.8 mg, 11 mol%) was added to the mixture and the reaction was monitored by ^1H NMR spectroscopy at 50 °C until 48 h (Chart S-6). The reaction reached equilibrium within 48 h [**2f**:**4f**:(*Z*)-**5f**:(*E*)-**5f** = 4:35:18:43].

Chart S-6. NMR monitoring of reaction of **2f** with **1a**

References

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RGAIN 34

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RGAIN 40

p-Bromobenzamide of **1a**

DFILE
COMNT
DATIM
OBNUC
EXMOD
OBFRQ
OBSET
OBFIN
POINT
FREQU
SCANS
ACQTM
PD
PW1
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN

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2.0000 sec
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1H
20.1 c
CDCL3
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0.12 Hz
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p-Bromobenzamide of 1a

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RGAIN 34

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PD 2.0000 sec
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POINT 13107
FREQU 6002.31 Hz
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PD 2.0000 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 23.6 c
SLVNT CDCL3
EXREF 7.24 ppm
BF 0.12 Hz
RGAIN 38

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PD 2.0000 sec
PW1 3.33 usec
IRNUC 1H
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SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 54

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PD 2.0000 sec
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IRNUC 1H
CTEMP 24.8 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 50

DFILE
COMNT
DATIM
OBNUC
EXMOD
OBFRQ
OBSET
OBFIN
POINT
FREQU
SCANS
ACQTM
PD
PW1
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN

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1H
22.5 c
CDCL3
7.24 ppm
0.12 Hz
34

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PD 2.0000 sec
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IRNUC 1H
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PD 2.0000 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 23.2 c
SLVNT CDCL3
EXREF 7.24 ppm
BF 0.12 Hz
RGAIN 28

DFILE
COMNT
DATIM
OBNUC
EXMOD
OBFRQ
OBSET
OBFIN
POINT
FREQU
SCANS
ACQTM
PD
PW1
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN

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32768
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CDCL3
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(4S,6S)-3I

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EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 60

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OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.31 Hz
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ACQTM 2.1837 sec
PD 2.0000 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 22.7 c
SLVNT CDCL3
EXREF 7.24 ppm
BF 0.12 Hz
RGAIN 32

Benzamide of 3m

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EXMOD single_pulse_dec
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OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 32768
FREQU 31407.04 Hz
SCANS 39
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PD 2.0000 sec
PW1 3.33 usec
IRNUC 1H
CTEMP 23.0 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 50

Benzamide of **3m**

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OBFIN 7.29 Hz
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FREQU 6002.31 Hz
SCANS 8
ACQTM 2.1837 sec
PD 2.0000 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 21.7 c
SLVNT CDCL3
EXREF 7.24 ppm
BF 0.12 Hz
RGAIN 32

DFILE C:\Documents and Settings\delta\My Documents\I
COMNT cm3-48-pure-13C
DATIM 07-04-2006 15:44:12
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 32768
FREQU 31407.04 Hz
SCANS 284
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.33 usec
IRNUC 1H
CTEMP 22.2 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 54

DFILE C:\Documents and Settings\delta\My Documents\I
COMNT cm3-31-OH-pure
DATIM 21-03-2006 17:23:46
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.31 Hz
SCANS 8
ACQTM 2.1837 sec
PD 2.0000 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 22.2 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 28

C:\Documents and Settings\My Documents\Personal Folder\Morichie\cm3-30\cm3-31-OH-pure-13C.als
cm3-31-OH-pure-13C

DFILE C:\Documents and Settings\My Documents\I
COMNT cm3-31-OH-pure-13C
DATIM 21-03-2006 17:28:13
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 32768
FREQU 31407.04 Hz
SCANS 69
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.33 usec
IRNUC 1H
CTEMP 22.6 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 50

DFILE C:\Documents and Settings\delta\My Documents\I
COMNT cm3-69-1H
DATIM 19-04-2006 10:04:25
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.31 Hz
SCANS 8
ACQTM 2.1837 sec
PD 2.0000 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 23.4 c
SLVNT CDCL3
EXREF 7.24 ppm
BF 0.12 Hz
RGAIN 34

DFILE C:\Documents and Settings\delta\My Documents\I
COMNT cm3-69-13C-1
DATIM 19-04-2006 10:25:30
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 32768
FREQU 31407.04 Hz
SCANS 201
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.33 usec
IRNUC 1H
CTEMP 23.9 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 50

4b

DFILE
COMNT
DATIM
OBNUC
EXMOD
OBFRQ
OBSET
OBFIN
POINT
FREQU
SCANS
ACQTM
PD
PW1
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN

C:\Documents and Settings\All Users\cm3-85-down
02-05-2006 01:06:22
1H
single_pulse.ex2
600.17 MHz
5.30 KHz
5.47 Hz
13107
9008.87 Hz
16
1.4549 sec
4.0000 sec
7.30 usec
1H
20.3 c
C6D6
0.00 ppm
0.12 Hz
42

(E)-5b
(95% E)

DFILE
COMNT
DATIM
OBNUC
EXMOD
OBFRQ
OBSET
OBFIN
POINT
FREQU
SCANS
ACQTM
PD
PW1
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN

C:\Documents and Settings\All Users\cm3-85-down
02-05-2006 03:45:38
13C
single_pulse_dec
150.92 MHz
8.52 KHz
1.74 Hz
32768
47348.48 Hz
1024
0.6921 sec
2.0000 sec
3.83 usec
1H
20.6 c
C6D6
128.00 ppm
0.12 Hz
58

DFILE
COMNT
DATIM
OBNUC
EXMOD
OBFRQ
OBSET
OBFIN
POINT
FREQU
SCANS
ACQTM
PD
PW1
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN

C:\Documents and Settings\All Users\cm3-85-up
01-05-2006 22:04:19
1H
single_pulse.ex2
600.17 MHz
5.30 KHz
5.47 Hz
13107
9008.87 Hz
16
1.4549 sec
4.0000 sec
7.30 usec
1H
20.4 c
C6D6
0.00 ppm
0.12 Hz
40

(Z)-5b
(80% Z)

DFILE
COMNT
DATIM 02-05-2006 00:43:11
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 150.92 MHz
OBSET 8.52 KHz
OBFIN 1.74 Hz
POINT 32768
FREQU 47348.48 Hz
SCANS 1024
ACQTM 0.6921 sec
PD 2.0000 sec
PW1 3.83 usec
IRNUC 1H
CTEMP 21.0 c
SLVNT C6D6
EXREF 128.00 ppm
BF 0.12 Hz
RGAIN 58

(Z)-5b
(80% Z)