

## Supporting Information

# Metallotropic Equilibrium and Configurational Stability of 3-Chloro-1-(trimethylsilyl)propargyl and -allenyl Metals: Comparative Study among Lithium, Titanium, and Zinc

*Joseph Bejjani, Candice Botuha, Fabrice Chemla\*, Franck Ferreira\*, Sarah Magnus and Alejandro Pérez-Luna*

UPMC–Univ Paris 06, UMR CNRS 7201, Institut Parisien de Chimie Moléculaire, Institut de Chimie Moléculaire (FR 2769), case 183, 4 place Jussieu, 75252 Paris Cedex 05, France.

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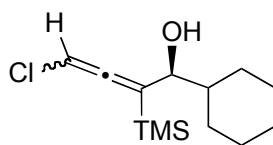
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## I. General Information

Experiments involving organometallics were carried out in dried glassware under a positive pressure of dry nitrogen. Liquid nitrogen was used as a cryoscopic fluid. A three-necked, round-bottomed flask equipped with an internal thermometer, a septum cap and a nitrogen inlet was used. Anhydrous THF and Et<sub>2</sub>O were obtained by distillation over sodium–benzophenone ketyl. CH<sub>2</sub>Cl<sub>2</sub> and TMEDA were obtained by distillation over CaH<sub>2</sub>. (+)-Camphor was sublimed prior to use. Commercial zinc bromide was melted under argon and immediately after cooling to room temperature dissolved in anhydrous THF or Et<sub>2</sub>O. *n*-BuLi (2.50 M commercial solution in hexane) was titrated with *N*-pivaloyl-*o*-toluidine.<sup>51</sup> All other reagents and solvents were of commercial quality and were used without further purification. Flash chromatographies were carried out over silica gel (230–400 mesh). <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with a dual probe (<sup>13</sup>C/<sup>1</sup>H). Chemical shifts are reported in δ units relative to an internal standard of residual chloroform (δ = 7.27 ppm for <sup>1</sup>H NMR and δ = 77.16 ppm for <sup>13</sup>C NMR) or C<sub>6</sub>D<sub>6</sub> (δ = 7.15 ppm for <sup>1</sup>H NMR and δ = 128.6 ppm for <sup>13</sup>C NMR). Elemental analyses were performed at the Service de Microanalyses de l'Université Pierre et Marie Curie–Paris 6, case 55, 4 place Jussieu, 75252 Paris Cedex 05.

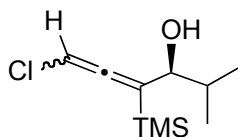
## II. Data for Allenic Alcohols 3 (Table 1)

### 2.1. (±)-4-Chloro-1-cyclohexyl-2-(trimethylsilyl)butan-2,3-dien-1-ol



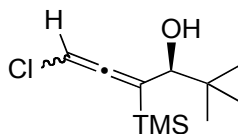
Colourless oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 25 °C): δ = 6.02 (d, *J* = 1.8 Hz, 1 H), 4.04 (d, *J* = 4.0 Hz, 1 H), 1.85–1.53 (m, 3 H), 1.70–1.60 (m, 3 H), 1.51–1.43 (m, 1 H), 1.32–1.12 (m, 4 H), 1.07–0.97 (m, 1 H), 0.19 (s, 9 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, 25 °C): δ = 202.1, 114.6, 88.2, 75.5, 43.4, 30.5, 26.56, 26.50, 26.2, –0.8; IR (neat): ν = 3446, 2924, 2852, 1932, 1450, 1305, 1248, 1099, 1011, 838, 735, 624 cm<sup>–1</sup>; HMRS (ESI): *m/z* calcd for C<sub>13</sub>H<sub>23</sub>OSi+Na<sup>+</sup>: 281.1099 [*M*+Na<sup>+</sup>]; found 281.1099.

## 2.2. (±)-6-Chloro-2-methyl-4-(trimethylsilyl)hexa-4,5-dien-3-ol



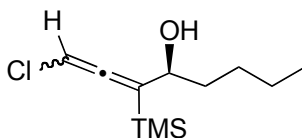
Colourless oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 25 °C):  $\delta$  = 6.04 (d,  $J$  = 1.8 Hz, 1 H), 4.07–4.02 (m, 1 H), 1.88–1.76 (m, 1 H), 1.63 (d,  $J$  = 6.6 Hz, 1 H), 1.00 (d,  $J$  = 6.8 Hz, 3 H), 0.92 (d,  $J$  = 6.6 Hz, 3 H), 0.19 (s, 9 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, 25 °C):  $\delta$  = 202.1, 114.9, 88.4, 75.8, 33.5, 20.1, 16.0, –0.9; IR (neat):  $\nu$  = 3451, 3060, 2959, 2899, 2873, 1933, 1467, 1305, 1249, 1014, 839, 736, 628  $\text{cm}^{-1}$ ; elemental analysis calcd (%) for  $\text{C}_{10}\text{H}_{19}\text{ClOSi}$ : C 54.89, H 8.75; found: C 54.84, H, 8.93.

## 2.3. (±)-6-Chloro-2,2-dimethyl-4-(trimethylsilyl)hexa-4,5-dien-3-ol



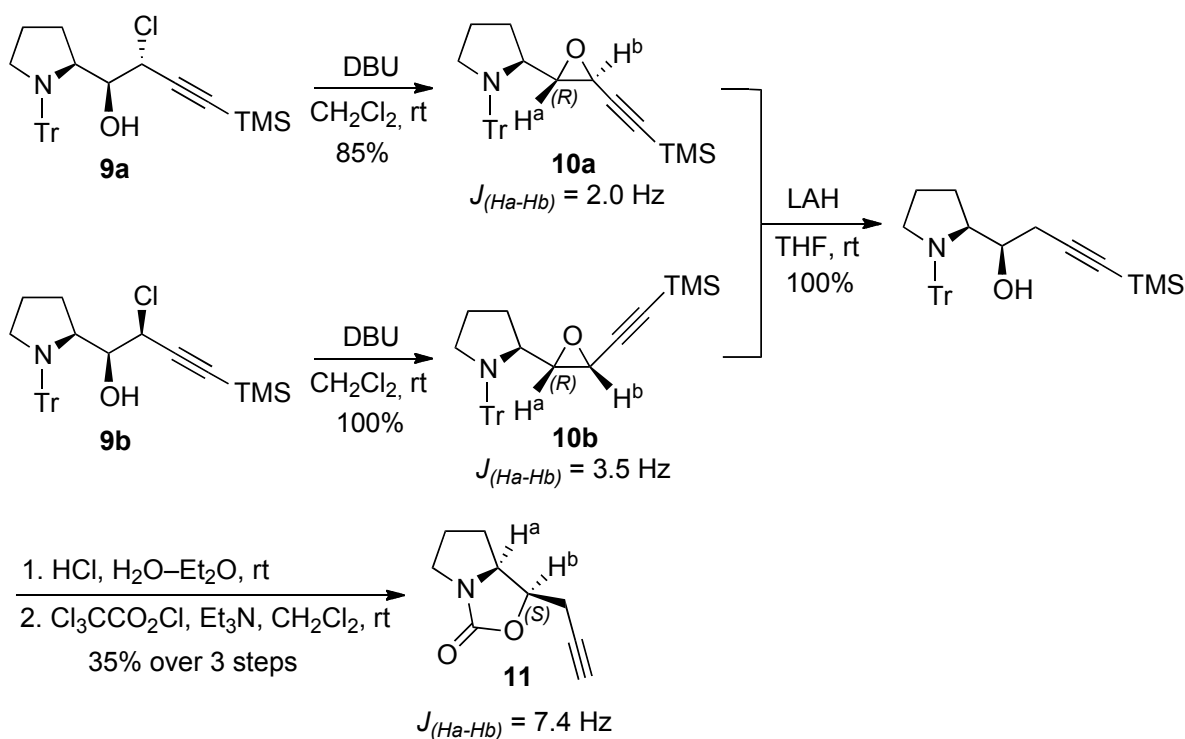
Colourless oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 25 °C):  $\delta$  = 6.00 (d,  $J$  = 1.0 Hz, 1 H), 3.89 (s, 1 H), 1.65 (bs, 1 H), 0.97 (s, 9 H), 0.19 (s, 9 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, 25 °C):  $\delta$  = 203.3, 113.1, 89.1, 78.1, 36.9, 26.0, –0.6; IR (neat):  $\nu$  = 3473, 3059, 2995, 2903, 2871, 1928, 1478, 1394, 1364, 1297, 1249, 1052, 1005, 838, 737, 627  $\text{cm}^{-1}$ ; elemental analysis calcd (%) for  $\text{C}_{11}\text{H}_{21}\text{ClOSi}$ : C 56.75, H 9.09; found: C 56.64, H 9.19.

## 2.4 (±)-1-Chloro-3- (trimethylsilyl)octa-1,2-dien-4-ol



Colourless oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 25 °C):  $\delta$  = 6.00 (d,  $J$  = 1.8 Hz, 1 H), 4.27 (d,  $J$  = 4.8 Hz, 1 H), 1.73–1.61 (m, 2 H), 1.60–1.50 (m, 1 H), 1.47–1.28 (m, 4 H), 0.91 (t,  $J$  = 7.1 Hz, 3 H), 0.19 (s, 9 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, 25 °C):  $\delta$  = 202.0, 115.6, 88.0, 71.2, 37.4, 27.7, 22.7, 14.2, –0.8; IR (neat):  $\nu$  = 3394, 2957, 2933, 2861, 1933, 1302, 1249, 1014, 838, 748, 625  $\text{cm}^{-1}$ ; elemental analysis calcd (%) for  $\text{C}_{11}\text{H}_{21}\text{ClOSi}$ : C 56.75, H 9.09; found: C 56.71, H 9.10.

### III. Determination of the Configurations of Compounds **9a** and **9b**



**(-)-(1*S*,2*S*,2'*S*)-2-[*N*-(Triphenylmethyl)pyrrolidin-2'-yl]-3-trimethylsilyl)ethynyloxirane (**10a**):** At room temperature, DBU (0.18 mL, 1.17 mmol) was added to a solution of **9a** (0.19 g, 0.39 mmol) in  $\text{CH}_2\text{Cl}_2$  (2 mL). After 3 h of stirring, a 2:1 mixture of a saturated aqueous  $\text{NH}_4\text{Cl}$  solution and  $\text{NH}_3$  was added (10 mL). The layers were separated and the aqueous one extracted with  $\text{CH}_2\text{Cl}_2$  (2  $\times$  10 mL). The combined organic layers were dried over anhydrous  $\text{MgSO}_4$ , filtered and concentrated in vacuo. The crude material was filtered on silica gel (4.9%/0.1%  $\text{EtOAc}/\text{Et}_3\text{N}/\text{cyclohexane}$ ) and the solvents were removed under reduced pressure to afford **10a** (0.15 g, 85%) as a white solid. M.p. 59–60 °C;  $[\alpha]_{\text{D}}^{20} = -123.0$  ( $c = 1.18$  in  $\text{CHCl}_3$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 25 °C):  $\delta = 7.59$  (d,  $J = 7.7$  Hz, 6 H), 7.27 (t,  $J = 7.7$  Hz, 6 H), 7.17 (t,  $J = 7.2$  Hz, 3 H), 3.38–3.30 (m, 1 H), 3.27 (dd,  $J = 7.6, 1.8$  Hz, 1 H), 2.98–2.89 (m, 2 H), 2.80 (d,  $J = 2.0$  Hz, 1 H), 1.59–1.45 (m, 2 H), 0.93–0.84 (m, 1 H), 0.79–0.69 (m, 1 H), 0.25 (s, 9 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, 25 °C):  $\delta = 144.7, 130.0, 127.7, 126.3, 102.0, 89.6, 77.3, 63.6, 61.4, 50.5, 49.1, 29.2, 24.2, -0.1$ ; IR ( $\text{CHCl}_3$ ):  $\nu = 3056, 2957, 2875, 2177, 1647, 1595, 1488, 1447, 1249, 1055, 1031, 1019, 841, 761, 744, 708, 629 \text{ cm}^{-1}$ ; elemental analysis calcd (%) for  $\text{C}_{30}\text{H}_{33}\text{NOSi}$ : C 79.77, H 7.36, N 3.10; found: C 79.71, H 7.47, N 3.11.

The *anti* relationship between H<sup>a</sup> and H<sup>b</sup> in **9a** could be deduced from the coupling constant  $J_{(Ha-Hb)} = 2.0$  Hz in **10a** which is characteristic of a *trans* oxirane.

**(-)-(1*R*,2*S*,2'*S*)-2-[*N*-(Triphenylmethyl)pyrrolidin-2'-yl]-3-trimethylsilyl)ethynyloxirane (10b):**

Pale yellow oil (0.036 g, 100%) obtained from **9b** (0.040 g, 0.08 mmol) following the above procedure.

$[\alpha]_D^{20} = -16.5$  ( $c = 0.80$  in  $\text{CHCl}_3$ );  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 200 MHz, 25 °C):  $\delta = 7.66$  (d,  $J = 7.4$  Hz, 6 H), 7.14 (t,  $J = 7.4$  Hz, 6 H), 7.01 (t,  $J = 7.1$  Hz, 3 H), 3.65 (dt,  $J = 7.4, 2.8$  Hz, 1 H), 3.29 (d,  $J = 3.7$  Hz, 1 H), 3.17 (dd,  $J = 7.1, 3.7$  Hz, 1 H), 2.88–2.75 (m, 1 H), 1.95–1.77 (m, 1 H), 1.42–1.34 (m, 2 H), 0.86–0.78 (m, 2 H), 0.08 (s, 9 H);  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , 50 MHz, 25 °C):  $\delta = 145.6, 130.2, 128.2, 126.7, 101.4, 91.5, 77.0, 62.8, 58.2, 51.3, 48.2, 30.5, 24.9, -0.2$ ; IR (neat):  $\nu = 3056, 2955, 2880, 2179, 1725, 1595, 1487, 1447, 1248, 1069, 1055, 1031, 900, 836, 756, 707, 698, 628\text{ cm}^{-1}$ ; HMRS (ESI):  $m/z$  calcd for  $\text{C}_{30}\text{H}_{33}\text{NOSi} + \text{H}^+$ : 452.2410 [ $M + \text{H}^+$ ]; found: 452.2401.

The *syn* relationship between H<sup>a</sup> and H<sup>b</sup> in **9b** could be deduced from the coupling constant  $J_{(Ha-Hb)} = 3.5$  Hz in **10b** which is characteristic of a *cis* oxirane.

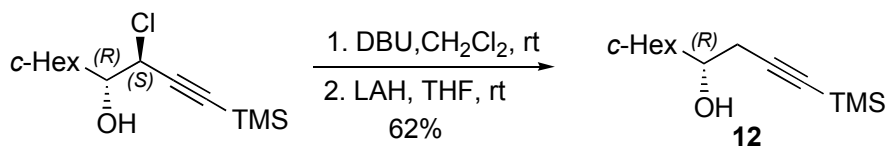
**(-)-(4*R*,5*S*)-4-Prop-2-ynyl-3,1-oxazabicyclo[3.3.0]octan-2-one (11):** At room temperature, under nitrogen atmosphere,  $\text{LiAlH}_4$  (0.06 g, 1.60 mmol) was added to **10a** or **10b** (0.18 g, 0.40 mmol) in THF (7 mL). After 22 h of stirring a 1 M aqueous solution of Seignette salt (15 mL) was added. The layers were separated and the aqueous one extracted with  $\text{Et}_2\text{O}$  ( $2 \times 15$  mL). The combined organic layers were dried over anhydrous  $\text{MgSO}_4$ , filtered and concentrated in vacuo. The crude material was filtered on silica gel (2%  $\text{Et}_3\text{N}/\text{Et}_2\text{O}$ ) and the solvents were removed under reduced pressure.

The residue (0.13 g) was taken up in  $\text{Et}_2\text{O}$  (4 mL) and a 5 M aqueous HCl solution (4 mL) was added to the solution at room temperature. After 3 h of vigorous stirring, the two layers were separated and the aqueous one washed with  $\text{Et}_2\text{O}$  ( $3 \times 3$  mL). The aqueous layer was cooled to 0 °C, made alkaline by careful addition of aqueous NaOH, and then extracted with  $\text{CHCl}_3$  ( $3 \times 3$  mL). The combined extracts were dried over anhydrous  $\text{Na}_2\text{SO}_4$  filtered and evaporated in vacuo.

The residue (0.03 g) was dissolved in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (3 mL). At room temperature, Et<sub>3</sub>N (0.16 mL, 1.00 mmol) and trichloromethyl chloroformate (24 µl, 0.20 mmol) were successively added. The resulting mixture was stirred for 20 h at which time it was hydrolyzed with a saturated aqueous NaHCO<sub>3</sub> solution (3 mL). The layers were separated and the aqueous one extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 × 3 mL). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated in vacuo to afford **11** (0.02 g, 35% over three steps) as a yellow oil.  $[\alpha]_D^{20} = -103.0$  ( $c = 0.59$  in CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 25 °C):  $\delta = 4.83$  (ddd,  $J = 9.5, 7.4, 5.6$  Hz, 1 H), 3.96 (ddd,  $J = 10.7, 7.4, 5.1$  Hz, 1 H), 3.64 (dt,  $J = 11.1, 8.0$ , 1 H), 3.21 (ddd,  $J = 11.1, 9.3, 3.5$  Hz, 1 H), 2.78 (ddd,  $J = 16.4, 5.4, 2.7$  Hz, 1 H), 2.52 (ddd,  $J = 16.4, 9.6, 2.7$  Hz, 1 H), 2.05 (t,  $J = 2.7$  Hz, 1 H), 2.17–1.84 (m, 3 H), 1.61–1.50 (m, 1 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, 25 °C):  $\delta = 160.9, 78.0, 73.6, 71.4, 62.9, 45.8, 25.4, 25.0, 20.8$ ; HMRS (ESI):  $m/z$  calcd for C<sub>9</sub>H<sub>11</sub>NO<sub>2</sub>+H<sup>+</sup>: 166.0868 [ $M$ +H<sup>+</sup>]; found: 166.0869.

The *cis* relationship between H<sup>a</sup> and H<sup>a</sup> was deduced from the coupling constant  $J_{(H^a-H^b)} = 7.4$  Hz.<sup>1</sup> This allowed to assign unambiguously the (*R*) configuration to carbon atom C5 of **11**. As a consequence, the *S* configuration could be assigned to carbon atom C2 of **9a** and **9b**.

#### IV. Kinetic Resolution: Determination of the Absolute Configuration of the Chlorohydrin



At room temperature, to a solution of chlorohydrin (148 mg, 0.57 mmol, er = 63:37, *anti:syn* = 84:16) in CH<sub>2</sub>Cl<sub>2</sub> (3 mL) was added DBU (0.26 mL, 1.70 mmol). The mixture was stirred for 2 h and hydrolyzed with a 0.3 M aqueous HCl solution (1 mL). The layers were separated, and the aqueous one extracted

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- (1) (a) D. H. Rich, E. T. O. Sun, E. Ulm, *J. Med. Chem.* **1980**, 23, 27–33; (b) M.-N. Dufour, P. Jouin, J. Poncet, A. Pantaloni, B. Castro, *J. Chem. Soc., Perkin Trans. 1* **1986**, 1895–1899; (c) S. Kiyooka, H. Nakano, F. Shiota, R. Fujiyama, *J. Org. Chem.* **1989**, 54, 5409–5411; (d) T. Ibuka, H. Habashita, A. Otaka, N. Fujii, Y. Oguchi, T. Uyehara, Y. Yamamoto, *J. Org. Chem.* **1991**, 56, 4370–4382; (e) F. Roux, I. Maugras, J. Poncet, G. Niel, P. Jouin, *Tetrahedron* **1994**, 50, 5345–5360.

with Et<sub>2</sub>O (2 × 2 mL). The combined organic layers were dried over anhydrous MgSO<sub>4</sub> filtered and the solvent removed in vacuo.

The residue (0.12 g) was taken up in THF (6 mL) and added to a suspension of LiAlH<sub>4</sub> (0.07 g, 1.89 mmol) in THF (2 mL) at 0 °C. The mixture was warmed to room temperature and stirred for 26 h. After cooling to 0 °C, a 2 M aqueous NaOH solution (1 mL) was added, the resulting suspension filtered through a pad of celite, and the filtrate concentrated in vacuo. The crude material was purified by flash chromatography (10% EtOAc/cyclohexane) to afford homoallylic alcohol **12** as a pure product (53 mg, 62% for two steps). The data of **12** were found to be identical to those reported in literature.<sup>2</sup> [ $\alpha$ ]<sub>D</sub><sup>20</sup> = +1.6 (er = 63:37, *c* = 2.3 in CHCl<sub>3</sub>) [Lit.<sup>[2]</sup> [ $\alpha$ ]<sub>D</sub><sup>20</sup> = +9.6 (er = 99.5:0.5, *c* = 1 in CHCl<sub>3</sub>)].

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(2) N. Ikeda, I. Arai, H. Yamamoto, *J. Am. Chem. Soc.* **1986**, *108*, 483–486.

## V. NMR Spectra ( $^1\text{H}$ NMR and $^{13}\text{C}$ NMR)

