

## Supporting Information 1

### Rh(I)-Catalyzed CO Gas-Free Carbonylative Cyclization Reactions of Alkynes with 2-Bromophenylboronic Acids Using Formaldehyde

Tsumoru Morimoto,<sup>\*,†</sup> Kae Yamasaki,<sup>†</sup> Akihisa Hirano,<sup>†</sup> Ken Tsutsumi,<sup>†</sup> Natsuko Kagawa,<sup>†</sup> Kiyomi Kakiuchi,<sup>†</sup> Yasuyuki Harada,<sup>‡</sup> Yoshiya Fukumoto,<sup>‡</sup> Naoto Chatani,<sup>\*,‡</sup> and Takanori Nishioka<sup>§</sup>

<sup>†</sup> Graduate School of Materials Science, Nara Institute of Science and Technology (NAIST), Takayama, Ikoma, Nara 630-0192, Japan

<sup>‡</sup> Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565-0871, Japan

<sup>§</sup> Department of Material Science, Graduate School of Science, Osaka City University, Sumiyoshi-ku, Osaka, 558-8585, Japan

**General Information.**  $^1\text{H}$  NMR and  $^{31}\text{P}$  NMR were recorded on a JEOL JNM-ECP500 spectrometer in  $\text{CDCl}_3$  using tetramethylsilane (0 ppm) as an internal standard and  $\text{CD}_2\text{Cl}_2$  with phosphoric acid (0 ppm) as an external standard.  $^{103}\text{Rh}$  NMR was recorded on a JEOL Lambda300WB spectrometer using  $\text{CD}_2\text{Cl}_2$  with  $[\text{C}_5\text{M}_5\text{RhCl}_2]_2$  (3678 ppm) as an external standard.<sup>1</sup> Data are reported as follows: chemical shift in ppm ( $\delta$ ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and c = complex), coupling constant (Hz), integration, and interpretation. Analytical GC was carried out on a HITACHI G-3900 gas chromatograph, equipped with a flame ionization detector. Column chromatography was performed using a  $\text{SiO}_2$  (MERCK Silica gel 60).

**Materials.**  $[\text{RhCl}(\text{cod})]_2$  was prepared using the reported method.<sup>2</sup> 1,1'-(Bis(diphenylphosphino)-2,2'-binaphthyl (BINAP), 1,1'-bis(diphenylphosphino)-2,2'-biphenyl

(BIPHEP), 1,2-bis(diphenylphosphino)ethane (dppe), 1,3-bis(diphenylphosphino)propane (dppp), 1,4-bis(diphenylphosphino)butane (dppb), 1,1-bis(diphenylphosphino)ferrocene (dppf), and triphenylphosphine were purchased from Strem Chemicals Inc. Paraformaldehyde, which was purchased from Nacalai Tesque, Inc., was dried over  $P_2O_5$  under vacuum, before it was used. 4-octyne (**1**), 1-phenyl-2-(trimethylsilyl)acetylene, 2-bromophenylboronic acid (**2**), 2-bromo-4,5-difluorophenylboronic acid, 2-bromo-6-fluorophenylboronic acid, 2-chlorophenylboronic acid, and 3-methoxyphenylboronic acid were purchased from Aldrich Chemical Co. Diphenyl acetylene and 1-phenyl-1-butyne were purchased from Tokyo Kasei Kogyo Co. 1,4-Dioxane (dehydrated), sodium carbonate, 1-phenyl-1-propyne, 1-(trimethylsilyl)-1-propyne, methyl propiolate, ethyl 3-(trimethylsilyl)propiolate and 2,5-dichlorophenylboronic acid were purchased from Wako Pure Chemical Industries, Ltd. 2-Bromo-5-methoxyphenylboronic acid was prepared using a method reported by Kuivila.<sup>3</sup>

**$^{31}P$  NMR Experiments.** All the operations were conducted in a glove-box. The  $^{31}P$  NMR analysis revealed that the treatment of 10  $\mu\text{mol}$  of  $[\text{RhCl}(\text{cod})]_2$  with 4  $\mu\text{mol}$  of BINAP in 0.65 mL of  $\text{CD}_2\text{Cl}_2$  afforded a doublet signal at 49.5 ppm (d,  $J_{P-\text{Rh}} = 199$  Hz). The signal was consistent with that of  $[\text{RhCl}(\text{BINAP})]_2$ , which was prepared using the reported method.<sup>4</sup> See the page S1-9.

**$^{103}\text{Rh}$  NMR experiments.** All the operations were conducted in a glove-box. It was clarified that, from  $^{103}\text{Rh}$  NMR, the treatment of 0.406 mmol of  $[\text{RhCl}(\text{cod})]_2$  with 0.162 mmol of BINAP in 0.65 mL of  $\text{CD}_2\text{Cl}_2$  and 4 mL of  $\text{CH}_2\text{Cl}_2$  afforded two signals: one was the singlet at 2438 ppm and the other was the triplet at 1620 ppm ( $J_{\text{Rh}-P} = 199$  Hz), as shown in page S1-10 and 11. Although the  $^{103}\text{Rh}$  NMR analysis of  $[\text{RhCl}(\text{BINAP})]_2$  failed because of extremely low solubility in all solvents tested ( $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ , acetone, benzene, and toluene), the latter could be assigned to that of  $[\text{RhCl}(\text{BINAP})]_2$  from its coupling constant.

**Typical Procedure for an Rh(I)-Catalyzed Carbonylative Cyclization Reaction of Alkynes with 2-Bromoarylboronic Acid Using Paraformaldehyde (Table 1, entry 2).** In a 7-mL screw-capped tube were placed 4-octyne (110 mg, 1 mmol), 2-bromophenylboronic acid (602 mg, 3 mmol),  $[\text{RhCl}(\text{cod})]_2$  (12.3 mg, 0.025 mmol), BINAP (6.23 mg, 0.01 mmol),  $\text{Na}_2\text{CO}_3$  (212 mg, 2 mmol), and 1,4-dioxane/water (100/1, 2 mL). The mixture was then degassed, charged with  $\text{N}_2$ , sealed, and stirred at 100 °C. After 30 h, the reaction mixture was filtered, and the filtered cake was washed with ethyl acetate (10 mL X 3). The combined filtrates were concentrated in vacuo, and the residue was purified by column chromatography on silica-gel (eluent; hexane/AcOEt=30/1) to give 2,3-dipropyl-1*H*-inden-1-one (**2**) ( $R_f$  0.20, 178 mg, 0.83 mmol) in 83% yield as yellow oil.

**Procedure for an Rh(I)-Catalyzed Carbonylative Cyclization Reaction of 2-Bromophenyl(trimethylsilyl)acetylene (**21**) with Phenylboronic Acid Using Paraformaldehyde (Scheme 3).** In a 7-mL screw-capped tube were placed 2-bromophenyl(trimethylsilyl)acetylene (**21**) (253 mg, 1 mmol), phenylboronic acid (366 mg, 3 mmol),  $[\text{RhCl}(\text{cod})]_2$  (12.3 mg, 0.025 mmol), BINAP (6.23 mg, 0.01 mmol),  $\text{Na}_2\text{CO}_3$  (212 mg, 2 mmol), styrene (208 mg, 2 mmol), and 1,4-dioxane/water (100/1, 2 mL). The mixture was then degassed, charged with  $\text{N}_2$ , sealed, and stirred at 100 °C. After 30 h, the reaction mixture was filtered, and the filtered cake was washed with ethyl acetate (10 mL X 3). The combined filtrates were concentrated in vacuo, and the residue was purified by column chromatography on silica-gel (eluent; hexane/AcOEt=20/1) to give 3-phenyl-2-(trimethylsilyl)-1*H*-inden-1-one (**8**) ( $R_f$  0.30, 161 mg, 0.58 mmol) in 58% yield as yellow oil.

**Products.** All the compounds are known and their spectral data were compared with those of authentic specimen.<sup>5-8</sup> Their  $^1\text{H}$  and  $^{13}\text{C}$  NMR data are shown as follows:

**2,3-Dipropyl-1*H*-inden-1-one (**2**).<sup>5</sup>** Yellow oil.  $R_f$  0.20 (hexane/AcOEt = 30/1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 0.94 (t,  $J$  = 7.3 Hz, 3H), 1.03 (t,  $J$  = 7.3 Hz, 3H), 1.65 (qt,  $J$  = 7.3 Hz, 7.6 Hz, 2H), 2.24 (qt,  $J$  = 7.3 Hz, 7.6 Hz, 2H), 2.53 (t,  $J$  = 7.6 Hz, 2H), 2.40 (t,  $J$  = 7.6 Hz, 2H), 7.03 (dd,  $J$  = 1.2 Hz, 7.3 Hz, 1H), 7.15

(ddd,  $J = 1.2$  Hz, 7.3 Hz, 7.3 Hz, 1H), 7.30 (ddd,  $J = 1.2$  Hz, 7.3 Hz, 7.3 Hz, 1H), 7.37 (d,  $J = 7.3$  Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 14.1, 14.3, 21.2, 22.4, 24.8, 28.2, 118.9, 121.6, 127.8, 131.1, 133.1, 134.8, 145.6, 157.6, 198.7.

**2,3-Diphenyl-1*H*-inden-1-one (4).**<sup>6</sup> Orange solid.  $R_f$  0.18 (hexane/AcOEt = 20/1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 7.11 (d,  $J = 7.3$  Hz, 1H), 7.21-7.25 (c, 6H), 7.31-7.37 (c, 6H), 7.55 (d,  $J = 7.3$  Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 121.2, 122.9, 127.7, 128.0, 128.7, 128.9, 129.2, 129.9, 130.1, 132.3, 133.4, 145.1, 155.2, 196.1.

**3-Methyl-2-phenyl-1*H*-inden-1-one (5).**<sup>7</sup> Orange solid.  $R_f$  0.20 (hexane/AcOEt = 20/1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 2.33 (s, 3H), 7.17 (d,  $J = 7.3$  Hz, 1H), 7.27 (dd,  $J = 6.7$  Hz, 7.3 Hz, 1H), 7.35 (dd,  $J = 1.9$  Hz, 1.9 Hz, 6.7 Hz, 6.7 Hz, 1H), 7.41-7.46 (c, 5H), 7.49 (d,  $J = 7.3$  Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 12.4, 119.3, 121.8, 127.5, 128.1, 128.7, 129.3, 130.1, 131.0, 133.1, 145.6, 154.6, 196.2.

**3-Butyl-2-phenyl-1*H*-inden-1-one (6) and 2-butyl-3-phenyl-1*H*-inden-1-one (6').**<sup>8</sup> Orange oil.  $R_f$  0.28 (hexane/AcOEt = 20/1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : [0.84 (t,  $J = 7.3$  Hz, 3H, **6'**), 0.93 (t,  $J = 7.3$  Hz, 3H, **6**)], [1.27-1.50 (c, 4H, **6'**), 1.44 (tq,  $J = 7.3$  Hz, 7.4 Hz, 2H, **6**)], 1.68 (tt,  $J = 7.4$  Hz, 8.2 Hz, 2H, **6**)], [2.34 (t,  $J = 7.9$  Hz, 2H, **6'**), 2.71 (t,  $J = 8.2$  Hz, 2H, **6**)], [7.00 (d, 1H, **6'**), 7.24-7.51 (c, 9H, **6** and c, 8H, **6'**)].  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 13.6, 22.6 (**6'**), 22.8, 26.3, 30.1, 31.2 (**6'**), 119.7, 120.3 (**6'**), 122.0, 122.1 (**6'**), 127.4, 127.5 (**6'**), 128.0 (**6'**), 128.5, 128.9, 129.2 (**6+6'**), 130.5, 130.7 (**6'**), 131.1, 132.6 (**6'**), 132.9 (**6'**), 133.0, 133.3, 135.2 (**6'**), 144.9, 145.6 (**6'**), 154.8 (**6'**), 158.7, 196.4, 198.0 (**6'**).

**3-Methyl-2-(trimethylsilyl)-1*H*-inden-1-one (7).**<sup>8</sup> Orange solid.  $R_f$  0.28 (hexane/AcOEt = 20/1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 0.29 (s, 9H), 2.30 (s, 3H), 7.13 (d,  $J = 7.3$  Hz, 1H), 7.24 (dd,  $J = 6.7$  Hz, 7.9 Hz, 1H), 7.37 (dd,  $J = 6.7$  Hz, 7.3 Hz, 1H), 7.40 (d,  $J = 6.7$  Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : -0.3, 14.3, 118.7, 121.1, 128.7, 132.2, 132.7, 147.0, 168.8, 201.6.

**3-Phenyl-2-(trimethylsilyl)-1*H*-inden-1-one (8).**<sup>5</sup> Orange oil.  $R_f$  0.30 (hexane/AcOEt = 20/1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 0.05 (s, 9H), 6.89 (d,  $J$  = 6.7 Hz, 1H), 7.24-7.50 (c, 8H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : -0.2, 120.7, 122.1, 127.5, 128.2, 128.9, 129.0, 132.2, 132.8, 134.6, 134.8, 147.1, 170.6, 201.6.

**1-Oxo-3-Phenyl-1*H*-indene-2-carboxylic acid methyl ester (9<sub>major</sub>).**<sup>8</sup> Yellow solid.  $R_f$  0.20 (hexane/AcOEt = 5/1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 3.75 (s, 9H), 7.20 (m, 1H), 7.41-7.62 (c, 8H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 51.8, 123.3, 123.4, 128.0, 128.3, 130.3, 130.5, 131.1, 131.2, 133.5, 142.9, 163.3, 165.6, 191.9.

**1-Oxo-2-Phenyl-1*H*-indene-3-carboxylic acid methyl ester (9<sub>minor</sub>).**<sup>8</sup> Orange solid.  $R_f$  0.27 (hexane/AcOEt = 5/1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 3.84 (s, 9H), 7.31-7.58 (c, 9H).

**1-Oxo-2-(Trimethylsilyl)-1*H*-indene-3-carboxylic acid ethyl ester (10<sub>major</sub>).**<sup>8</sup> Yellow oil.  $R_f$  0.44 (hexane/AcOEt = 5/1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 0.29 (s, 9H), 1.44 (t,  $J$  = 7.0 Hz, 3H), 4.42 (q,  $J$  = 7.1 Hz, 2H), 7.25-7.49 (c, 4H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : -0.8, 14.1, 61.6, 121.8, 123.0, 129.2, 131.4, 133.7, 141.6, 143.5, 157.7, 165.4, 200.7.

**1-Oxo-3-(Trimethylsilyl)-1*H*-indene-2-carboxylic acid ethyl ester (10<sub>minor</sub>).**<sup>8</sup> Yellow oil.  $R_f$  0.40 (hexane/AcOEt = 5/1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 0.39 (s, 9H), 1.37 (t,  $J$  = 7.0 Hz, 3H), 4.32 (q,  $J$  = 7.1 Hz, 2H), 7.29 (dd,  $J$  = 7.3 Hz, 7.9 Hz, 1H), 7.34 (d,  $J$  = 7.3 Hz, 1H), 7.40 (ddd,  $J$  = 1.2 Hz, 7.3 Hz, 7.9 Hz, 1H), 7.49 (d,  $J$  = 7.3 Hz, 1H).

**5-Methoxy-2,3-dipropyl-1*H*-inden-1-one (11).**<sup>8</sup> Yellow oil.  $R_f$  0.18 (hexane/AcOEt = 20/1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 0.93 (t,  $J$  = 7.3 Hz, 3H), 1.02 (t,  $J$  = 7.3 Hz, 3H), 1.49 (tq,  $J$  = 7.3 Hz, 7.9 Hz, 2H), 1.63 (tq,  $J$  = 7.3 Hz, 7.9 Hz, 2H), 2.23 (t,  $J$  = 7.9 Hz, 2H), 2.48 (t,  $J$  = 7.9 Hz, 2H), 3.84 (s, 3H), 6.53 (dd,  $J$  = 1.8 Hz, 7.9 Hz, 1H), 6.60 (d,  $J$  = 1.8 Hz, 1H), 7.33 (d,  $J$  = 7.9 Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 14.1, 14.3, 21.4, 22.5, 25.0, 28.0, 55.6, 108.5, 108.6, 123.4, 123.9, 136.4, 148.3, 155.2, 164.3, 197.2.

**5-Methoxy-3-methyl-2-(trimethylsilyl)-1*H*-inden-1-one (12).<sup>8</sup>** Yellow solid.  $R_f$  0.23 (hexane/AcOEt = 20/1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 0.27 (s, 9H), 2.23 (s, 3H), 3.83 (s, 3H), 6.61 (dd,  $J$  = 1.8 Hz, 7.9 Hz, 1H), 6.65 (d,  $J$  = 1.8, 1H), 7.32 (d,  $J$  = 7.9 Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : -0.2, 14.2, 55.6, 107.5, 110.4, 123.0, 125.1, 134.6, 149.9, 164.1, 166.5, 200.6.

**5-Methoxy-3-phenyl-2-(trimethylsilyl)-1*H*-inden-1-one (13).<sup>8</sup>** Yellow solid.  $R_f$  0.25 (hexane/AcOEt = 20/1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 0.04 (s, 9H), 3.78 (s, 3H), 6.43 (d,  $J$  = 1.8 Hz, 1H), 6.65 (dd,  $J$  = 1.8 Hz, 7.9 Hz, 1H), 7.33-7.35 (c, 2H), 7.44-7.49 (c, 4H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : -0.2, 55.7, 109.4, 110.8, 124.0, 125.1, 127.7, 128.3, 129.0, 134.8, 136.6, 149.9, 164.1, 168.5, 200.4.

**5,6-Difluoro-2,3-dipropyl-1*H*-inden-1-one (14).<sup>8</sup>** Yellow oil.  $R_f$  0.33 (hexane/AcOEt = 20/1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 0.93 (t,  $J$  = 7.3 Hz, 3H), 1.03 (t,  $J$  = 7.3 Hz, 3H), 1.48 (tq,  $J$  = 7.3 Hz, 7.6 Hz, 2H), 1.62 (tq,  $J$  = 7.3 Hz, 7.6 Hz, 2H), 2.23 (t,  $J$  = 7.6 Hz, 2H), 2.48 (t,  $J$  = 7.6 Hz, 2H), 6.85 (dd,  $J$  = 6.5 Hz, 9.5 Hz, 1H), 7.21 (dd,  $J$  = 7.7 Hz, 7.9 Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 14.0, 14.1, 21.0, 22.3, 25.0, 28.1, 109.3 (d,  $J$  = 20.1 Hz), 112.0 (dd,  $J$  = 1.9 Hz, 20.1 Hz), 127.1 (dd,  $J$  = 4.8 Hz), 136.0 (d,  $J$  = 4.8 Hz), 142.4 (dd,  $J$  = 3.8 Hz, 6.7 Hz), 149.5 (dd,  $J$  = 13.7 Hz, 218.1 Hz), 153.2 (dd,  $J$  = 13.6 Hz, 221.5 Hz), 155.6, 195.42.

**5,6-Difluoro-3-methyl-2-(trimethylsilyl)-1*H*-inden-1-one (15).<sup>8</sup>** Yellow solid.  $R_f$  0.35 (hexane/AcOEt = 20/1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 0.28 (s, 9H), 2.27 (s, 3H), 6.94 (dd,  $J$  = 6.4 Hz, 8.8 Hz, 1H), 7.23 (dd,  $J$  = 7.3 Hz, 8.6 Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : -0.3, 14.6, 108.9 (d,  $J$  = 20.2 Hz), 111.6 (d,  $J$  = 18.2 Hz), 128.6 (dd,  $J$  = 3.8 Hz, 4.8 Hz), 134.5 (d,  $J$  = 4.8 Hz), 143.9 (dd,  $J$  = 3.8 Hz, 6.7 Hz), 149.8 (dd,  $J$  = 14.3 Hz, 229.7 Hz), 153.0 (dd,  $J$  = 14.4 Hz, 233.5 Hz), 166.7, 198.9.

**5,6-Difluoro-3-phenyl-2-(trimethylsilyl)-1*H*-inden-1-one (16).<sup>8</sup>** Yellow solid.  $R_f$  0.33 (hexane/AcOEt = 20/1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 0.05 (s, 9H), 6.71 (dd,  $J$  = 6.1 Hz, 9.2 Hz, 1H), 7.28-7.35

(c, 3H), 7.46-7.52 (c, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : -0.4, 110.7 (d,  $J = 21.2$  Hz), 112.3 (d,  $J = 21.2$  Hz), 127.4, 128.6, 129.5, 134.0, 136.1 (d,  $J = 4.8$  Hz), 143.8 (dd,  $J = 3.8$  Hz, 6.7 Hz), 150.9 (dd,  $J = 14.4$  Hz, 248.6 Hz), 153.0 (dd,  $J = 14.4$  Hz, 256.2 Hz), 168.6, 198.7.

**4-Fluoro-2,3-dipropyl-1*H*-inden-1-one (17).**<sup>8</sup> Yellow oil.  $R_f$  0.28 (hexane/AcOEt = 20/1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 0.93 (t,  $J = 7.3$  Hz, 3H), 1.03 (t,  $J = 7.3$  Hz, 3H), 1.48 (tq,  $J = 7.3$  Hz, 7.6 Hz, 2H), 1.65 (tq,  $J = 7.3$  Hz, 7.6 Hz, 2H), 2.24 (t,  $J = 7.6$  Hz, 2H), 2.59 (t,  $J = 7.6$  Hz, 2H), 7.00 (dd,  $J = 8.6$  Hz, 9.2 Hz, 1H), 7.13 (ddd,  $J = 4.3$  Hz, 6.7 Hz, 8.6 Hz, 1H), 7.21 (d,  $J = 6.7$  Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 14.1, 14.2, 21.3 (d,  $J = 1.9$  Hz), 22.5, 24.6, 30.2 (d,  $J = 1.9$  Hz), 117.9 (d,  $J = 1.9$  Hz), 122.4 (d,  $J = 23.0$  Hz), 129.6 (d,  $J = 12.5$  Hz), 130.2 (d,  $J = 6.7$  Hz), 134.0 (d,  $J = 3.8$  Hz), 135.1 (d,  $J = 1.8$  Hz), 155.4 (d,  $J = 252.4$  Hz), 156.9 (d,  $J = 3.8$  Hz), 197.3 (d,  $J = 2.9$  Hz).

**4-Fluoro-3-methyl-2-(trimethylsilyl)-1*H*-inden-1-one (18).**<sup>8</sup> Yellow solid.  $R_f$  0.30 (hexane/AcOEt = 20/1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 0.29 (s, 9H), 2.46 (s, 3H), 7.01-7.06 (m, 1H), 7.19-7.24 (c, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : -0.2, 17.8 (d,  $J = 3.8$  Hz), 117.6 (d,  $J = 1.9$  Hz), 121.8 (d,  $J = 23.0$  Hz), 131.1 (d,  $J = 12.5$  Hz), 131.3 (d,  $J = 6.7$  Hz), 133.3 (d,  $J = 1.9$  Hz), 135.7 (d,  $J = 2.8$  Hz), 156.0 (d,  $J = 255.3$  Hz), 167.9 (d,  $J = 3.8$  Hz), 200.5 (d,  $J = 1.9$  Hz).

**4-Fluoro-3-phenyl-2-(trimethylsilyl)-1*H*-inden-1-one (19).**<sup>8</sup> Yellow solid.  $R_f$  0.28 (hexane/AcOEt = 20/1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 0.01 (s, 9H), 6.99 (t,  $J = 9.0$  Hz, 1H), 7.23-7.44 (c, 7H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : -0.4, 118.4, (d,  $J = 2.9$  Hz), 122.4 (d,  $J = 23.0$  Hz), 127.2 (d,  $J = 1.9$  Hz), 127.9, 128.9, 130.9 (d,  $J = 11.5$  Hz), 131.6 (d,  $J = 6.7$  Hz), 135.3 (d,  $J = 1.9$  Hz), 136.1 (d,  $J = 1.9$  Hz), 136.2 (d,  $J = 1.9$  Hz), 155.7 (d,  $J = 258.2$  Hz), 168.8 (d,  $J = 2.9$  Hz), 200.2 (d,  $J = 1.9$  Hz).

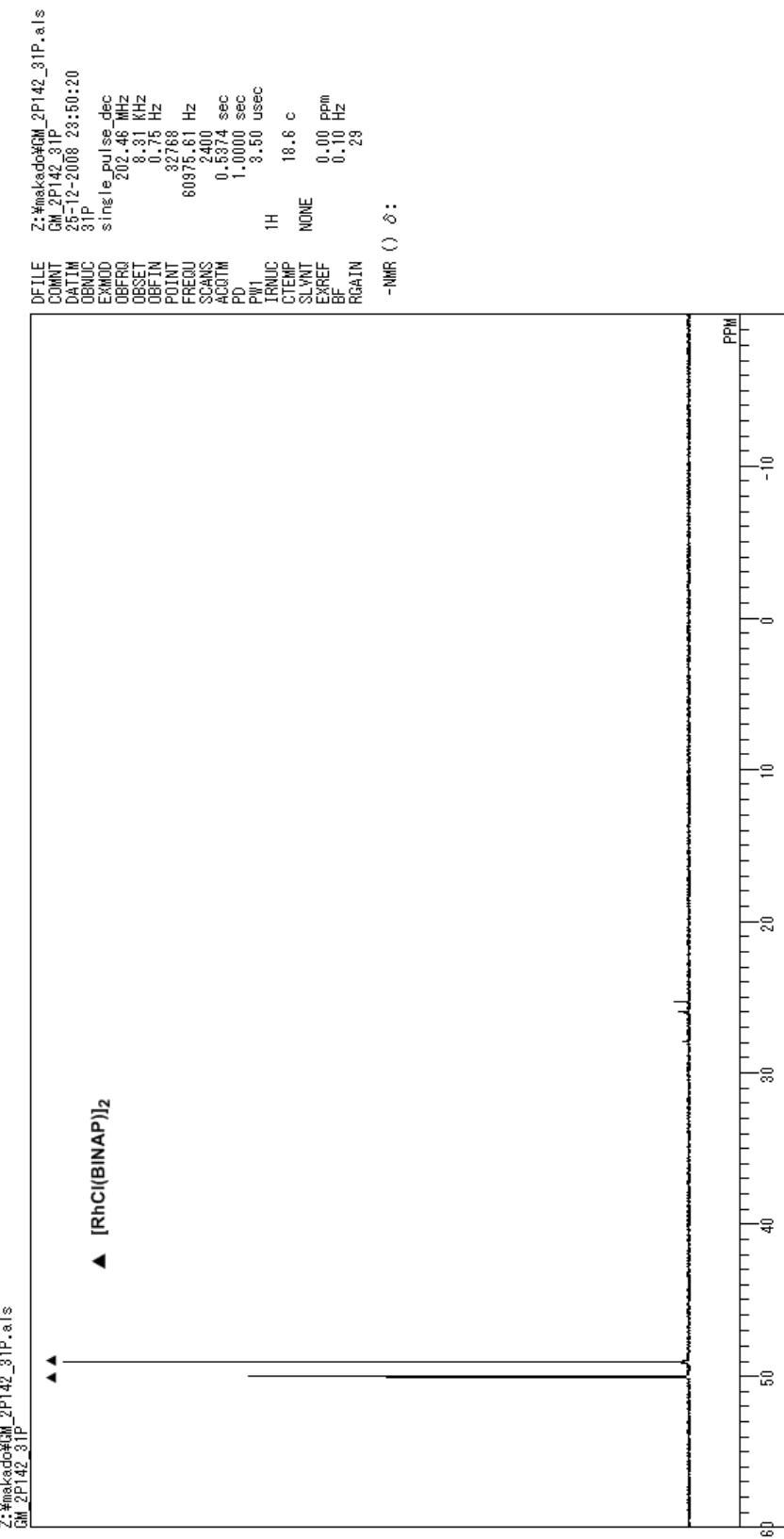
**5-Chloro-2,3-dipropyl-1*H*-inden-1-one (20).**<sup>8</sup> Yellow oil.  $R_f$  0.30 (hexane/AcOEt = 20/1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 0.94 (t,  $J = 7.3$  Hz, 3H), 1.04 (t,  $J = 7.3$  Hz, 3H), 1.49 (tq,  $J = 7.3$  Hz, 7.6 Hz, 2H), 1.63 (tq,  $J = 7.3$  Hz, 7.6 Hz, 2H), 2.24 (t,  $J = 7.6$  Hz, 2H), 2.50 (t,  $J = 7.6$  Hz, 2H), 7.00 (d,  $J = 1.8$  Hz,

1H), 7.14 (dd,  $J$  = 1.8 Hz, 7.9 Hz, 1H), 7.29 (d,  $J$  = 7.9 Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 14.1, 14.2, 21.1, 22.3, 24.9, 28.0, 119.8, 122.5, 127.3, 129.3, 136.4, 139.1, 147.5, 156.3, 197.3.

## References

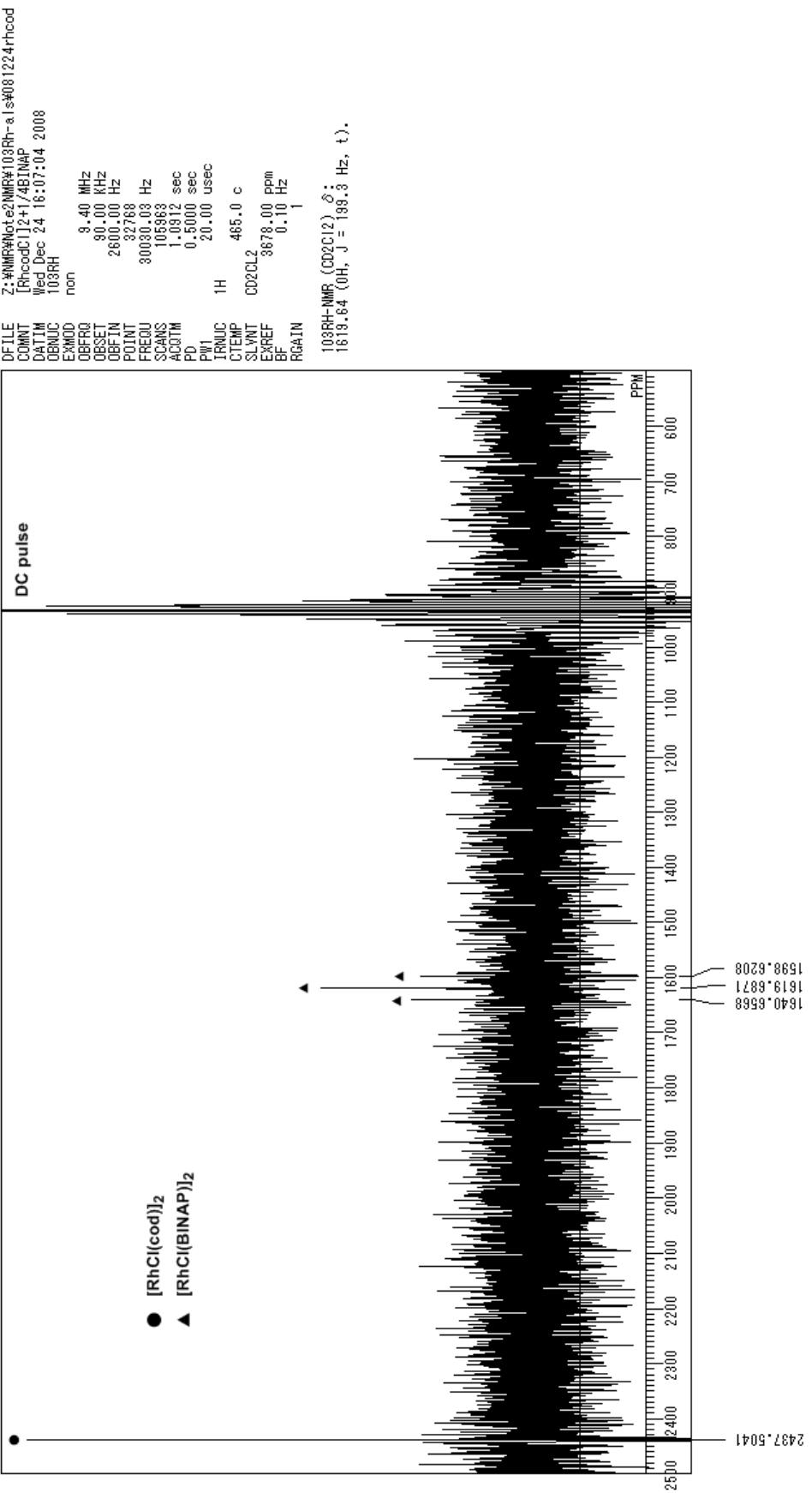
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2.5 [RhCl(cod)]<sub>2</sub> + 1 BINAP  $\xrightarrow{\text{toluene-d}_6 \text{ rt}}$  2 [RhCl(BINAP)]<sub>2</sub> + 0.5 [RhCl(BINAP)]<sub>2</sub>





$\text{Z: } ^{103}\text{Rh-NMR} \text{ Oct-e2NMR#103Rh-a | s\#081224rhcoodBINAP}$   
 $\text{[Rh(cod)]}_2 + /4\text{BINAP}$



**[RhCl(cod)]<sub>2</sub>**

Z:\#NMR\Note2NMR\103Rh-a\s\4081220\rhcod-f.in.s

