

*Supporting Information*

# Copper-Catalyzed Regioselective *trans*-Silaboration of Internal Arylalkynes with Stereochemical Switch to *cis*-Addition Mode

Toshimichi Ohmura,\* Yuta Takaoka, Michinori Suginome\*

Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University,  
Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

ohmura@sbchem.kyoto-u.ac.jp; suginome@sbchem.kyoto-u.ac.jp

## Contents

1. General ----- S2
2. Materials ----- S2
3. Initial Findings (Scheme 2) ----- S2
4. Optimization of Reaction Conditions (Table 1) ----- S4
5. Copper-Catalyzed *trans*-Silaboration of Internal Arylalkynes (Scheme 3) ----- S4
6. Solvent-Dependent Switch of Stereoselectivity in Silaboration of Internal Alkynes with **2c** (Scheme 4) ----- S16
7. Solvent Effect in Silaboration with **2c** ----- S21
8. Requirement of Additional NaO*t*-Bu (Scheme 5) ----- S21
9. *Trans*-Silaboration Mediated by NaO*t*-Bu (Scheme 6) ----- S22
10. Confirmation of No *Z/E* Isomerization of the Product (Scheme 7a) ----- S23
11. Reaction of **1a** with **2a** in the Presence of MeOH (Scheme 7b) (Table 2) ----- S24
12. References ----- S25
13. <sup>1</sup>H and <sup>13</sup>C NMR Spectra of Products ----- S25

## 1. General

Materials were weighted by an electric balance, Sartorius CPA225D or Shimadzu AP225WD (readability: 0.01 mg). Column chromatography was performed with SiliaFlash (SILICYCLE, pH 7.0, 40-63  $\mu\text{m}$ , 60  $\text{\AA}$ ).  $^1\text{H}$  NMR spectra were recorded on Varian 400-MR (399.89 MHz), JEOL JNM-ECZ500R (500.16 MHz), or JEOL JNM-ECZ600R (600.17 MHz) spectrometers.  $^{13}\text{C}$  NMR spectra were recorded on Varian 400-MR (100.55 MHz), JEOL JNM-ECZ500R (125.77 MHz), or JEOL JNM-ECZ600R (150.91 MHz) spectrometers.  $^{11}\text{B}$  NMR spectra were recorded on Varian 400-MR (128.30 MHz) or JEOL JNM-ECA600P (160.47 MHz) spectrometers.  $^1\text{H}$  NMR data were reported as follows: chemical shifts in ppm downfield from tetramethylsilane, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), coupling constant ( $J$ ), and integration. High resolution mass spectra were recorded on Thermo Scientific Exactive Plus (ESI, APCI) or JEOL JMS-SX102A (EI) spectrometers.

## 2. Materials

*Solvents:* Tetrahydrofuran (THF, dehydrated, Super plus, Kanto) and toluene (dehydrated, Super plus, Kanto) were purchased and used without further purification. Cyclohexane and methylcyclohexane were distilled over calcium hydride and degassed. 1,4-Dioxane was distilled over benzophenone ketyl.

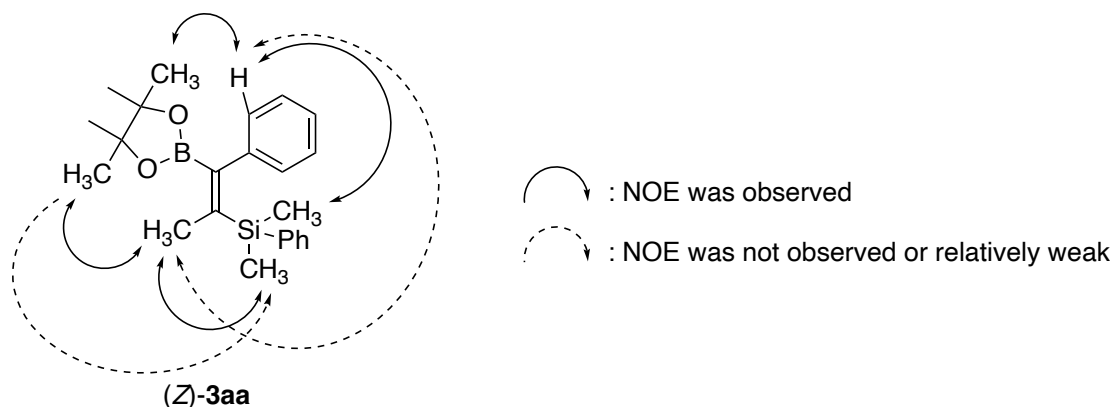
*Catalysts and Ligands:*  $(\text{CuOt-Bu})_4$  was prepared according to the procedure reported previously.<sup>1</sup> CuCl (Wako), **L1** (Aldrich), **L2** (Wako), and **L3** (TCI) were used as received from commercial source.

*Alkynes and Silylboronic Esters:* Alkynes **1c-f**, **1j**, and **1k** were prepared by Sonogashira coupling. **1b** was prepared by methylation of 4-ethynyltoluene. **1a** (TCI), **1g** (TCI), **1h** (Santa Cruz), and **1i** (Aldrich) were purchased and distilled prior to use. Silylboronic esters **2a**,<sup>2</sup> **2b**,<sup>3</sup> and **2c**<sup>4</sup> were prepared according to the procedure reported previously.

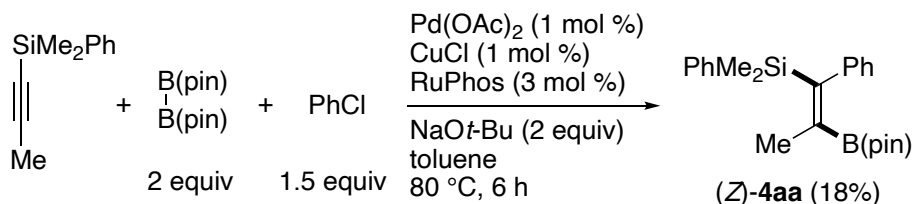
## 3. Initial Findings (Scheme 2)

In a glovebox, a glass tube (outside diameter: 20 mm, internal volume: 16 mL) having PTFE stopcock (J. Young), equipped with a magnetic stirring bar, was charged with CuCl (2.02 mg,

0.0204 mmol), **L1** (8.44 mg, 0.0232 mmol),  $\text{NaOt-Bu}$  (4.27 mg, 0.0444 mmol), **1a** (23.9 mg, 0.206 mmol), **2a** (52.4 mg, 0.200 mmol), and THF (0.6 mL). The tube was sealed by the stopcock and was taken out from the glovebox. The mixture was stirred at 110 °C by a heating magnetic stirrer with an aluminum heating block (hole size: 21 mm diameter x 33 mm depth). After 3 h, the tube was cooled to room temperature. The product (**Z-3aa**) (55.3 mg, 0.146 mmol, 73%) was obtained after purification by column chromatography on silica gel (eluent: hexane:AcOEt = 4:1) and Kugelrohr distillation (125-145 °C/0.76 Torr). The structure of the product was determined by analysis of NOE and comparison with the spectroscopic data of (*E*)-**3aa**,<sup>5</sup> (*Z*)-**4aa** (see below), and (*E*)-**4aa**.<sup>5</sup> (*Z*)-**3aa**:  $^1\text{H NMR}$  (500 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  7.47-7.52 (m, 2H), 7.29-7.33 (m, 2H), 7.15-7.19 (m, 3H), 7.04-7.09 (m, 2H), 6.99 (tt,  $J = 7.0, 1.5$  Hz, 1H), 2.35 (s, 3H), 1.02 (s, 12H), 0.05 (s, 6H).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41-7.45 (m, 2H), 7.27-7.33 (m, 3H), 7.12-7.19 (m, 3H), 7.02-7.06 (m, 2H), 2.06 (s, 3H), 1.25 (s, 12H), -0.05 (s, 6H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  150.9, 145.0, 140.3, 134.2, 129.1, 128.9, 128.10, 128.06, 126.5, 83.4, 24.8, 23.8, -1.2. Although the boron-bound carbon was not detected due to quadrupolar relaxation, it could be detected at 150.0 ppm by HMBC.  $^{11}\text{B NMR}$  (128 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  29.5. HRMS (ESI, positive)  $m/z$  calcd for  $\text{C}_{23}\text{H}_{31}\text{BNaO}_2\text{Si}^+ [\text{M} + \text{Na}]^+$ : 401.2079, found: 401.2085.

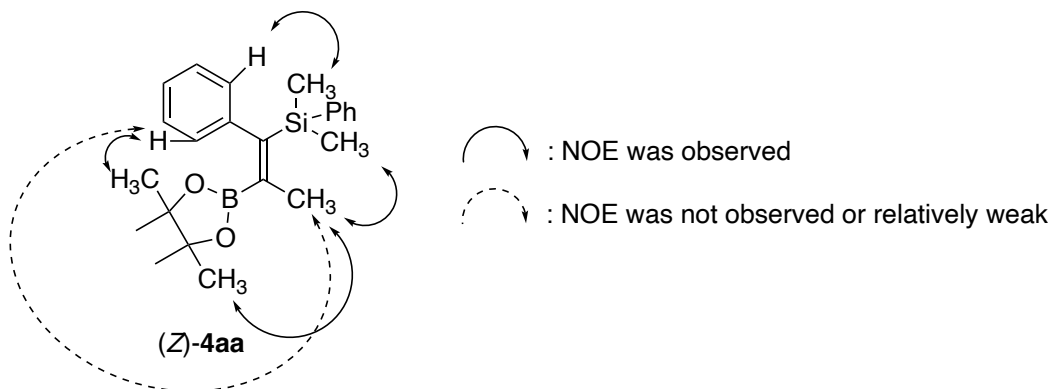


### Preparation of Authentic Sample of (*Z*)-**4aa**



(*Z*)-**4aa** was prepared by palladium/copper-catalyzed *trans*-arylboration of 1-(dimethylphenylsilyl)-1-propyne according to the literature method.<sup>6</sup> (*Z*)-**4aa**:  $^1\text{H NMR}$  (500 MHz,

CDCl<sub>3</sub>)  $\delta$  7.57-7.63 (m, 2H), 7.33-7.37 (m, 3H), 7.19-7.24 (m, 2H), 7.13 (tt,  $J = 7.5, 1.5$  Hz, 1H), 7.04-7.08 (m, 2H), 1.86 (s, 3H), 0.99 (s, 12H), 0.26 (s, 6H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  151.5, 146.5, 139.2, 133.8, 128.7, 128.1, 127.7, 127.5, 125.3, 83.1, 24.3, 21.0, -0.7. The boron-bound carbon was not detected due to quadrupolar relaxation. HRMS (EI, positive)  $m/z$  calcd for C<sub>23</sub>H<sub>31</sub>BO<sub>2</sub>Si<sup>+</sup> [M]<sup>+</sup>: 378.2181, found: 378.2183.



#### 4. Optimization of Reaction Conditions (Table 1)

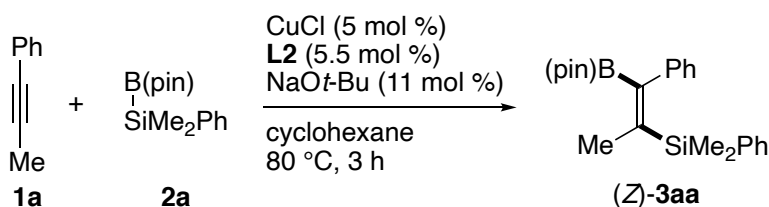
In a glovebox, a glass tube (outside diameter: 20 mm, internal volume: 16 mL) having PTFE stopcock (J. Young), equipped with a magnetic stirring bar, was charged with CuCl (0.50 mg, 0.0050 mmol, 5 mol %), a ligand (0.0055 mmol, 5.5 mol %), NaOt-Bu (1.1 mg, 0.011 mmol, 11 mol %), **1b** (13 mg, 0.10 mmol), **2a** (29 mg, 0.11 mmol), and a solvent (0.3 mL). The tube was sealed by the stopcock and was taken out from the glovebox. The mixture was stirred at 80 °C by a heating magnetic stirrer with an aluminum heating block (hole size: 21 mm diameter x 33 mm depth). After 3 h, the tube was cooled to room temperature. Dibenzyl ether (TCI, 16.8 mg, 0.10 mmol, internal standard) was added, and the resulting mixture was analyzed by <sup>1</sup>H NMR to determine the yield and *Z:E* ratio of **3ba**.

#### 5. Copper-Catalyzed *trans*-Silaboration of Internal Arylalkynes (Scheme 3)

*General procedure:* In a glovebox, a glass tube (outside diameter: 20 mm, internal volume: 16 mL) having PTFE stopcock (J. Young), equipped with a magnetic stirring bar, was charged with CuCl (1.0 mg, 0.010 mmol, 5 mol %), **L3** (3.9 mg, 0.011 mmol, 5.5 mol %), NaOt-Bu (2.1 mg, 0.022 mmol, 11 mol %), **1** (0.20 mmol), **2** (0.22 mmol), and methylcyclohexane (0.6 mL). The tube

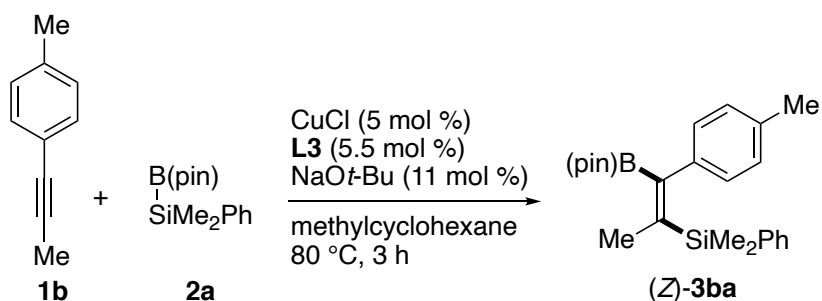
was sealed by the stopcock and was taken out from the glovebox. The mixture was stirred for 3 h at 80 °C by a heating magnetic stirrer with an aluminum heating block (hole size: 21 mm diameter x 33 mm depth). The product **3** was purified by column chromatography on silica gel and Kugelrohr distillation.

### (Z)-3aa



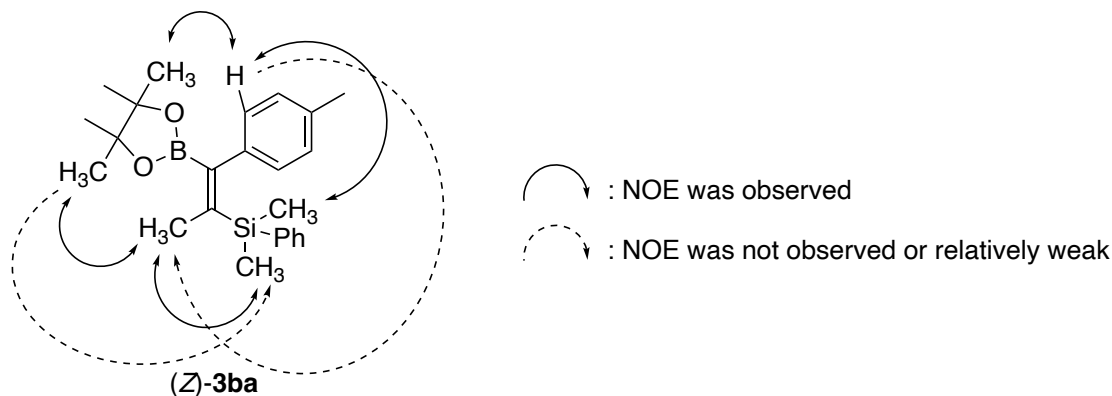
According to the *general procedure*, the reaction was carried out at 80 °C for 3 h using CuCl (0.98 mg, 0.00990 mmol), **L2** (3.08 mg, 0.0110 mmol), NaOt-Bu (2.38 mg, 0.0248 mmol), **1a** (23.2 mg, 0.200 mmol), **2a** (57.8 mg, 0.220 mmol), and cyclohexane (0.6 mL). (**Z**)-**3aa** (72.3 mg, 0.191 mmol, 96%) was obtained as a colorless oil after purification by column chromatography on silica gel (eluent: hexane:AcOEt = 4:1) and Kugelrohr distillation (105-130 °C/0.32 Torr). For characterization data of (**Z**)-**3aa**, see section 3.

### (Z)-3ba

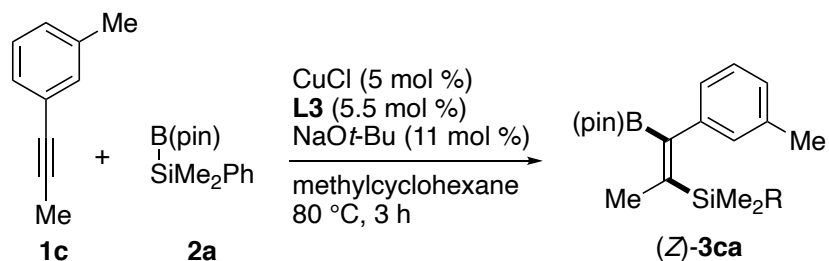


According to the *general procedure*, the reaction was carried out at 80 °C for 3 h using CuCl (1.00 mg, 0.0101 mmol), **L3** (3.97 mg, 0.0113 mmol), NaOt-Bu (2.18 mg, 0.0227 mmol), **1b** (26.0 mg, 0.200 mmol), **2a** (57.2 mg, 0.218 mmol), and methylcyclohexane (0.6 mL). (**Z**)-**3ba** (74.1 mg, 0.189 mmol, 95%) was obtained after purification by column chromatography on silica gel (eluent: hexane:AcOEt = 4:1) and Kugelrohr distillation (105-130 °C/0.45 Torr). The stereochemistry of the product was confirmed by NOE. (**Z**)-**3ba**: <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.42-7.46 (m, 2H), 7.27-7.33 (m, 3H), 6.92-6.99 (m, 4H), 2.30 (s, 3H), 2.06 (s, 3H), 1.26 (s, 12H), -0.02 (s, 6H). <sup>13</sup>C

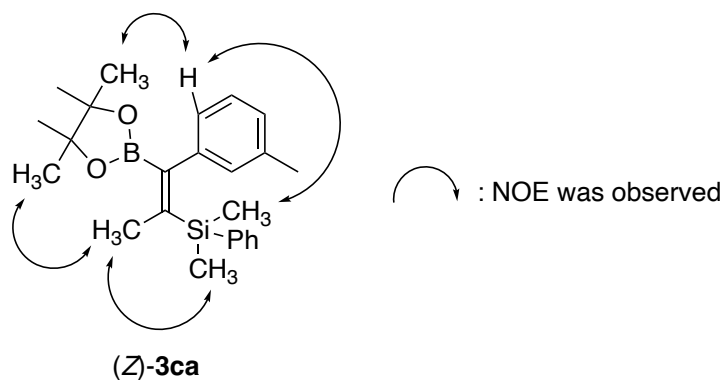
NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  148.7, 140.6, 140.0, 135.6, 133.7, 128.4, 128.3, 128.2, 127.5, 83.5, 24.7, 23.8, 21.1, -1.6. The boron-bound carbon was not detected due to quadrupolar relaxation. <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>)  $\delta$  29.3. HRMS (EI, positive)  $m/z$  calcd for C<sub>24</sub>H<sub>33</sub>BO<sub>2</sub>Si<sup>+</sup> [M]<sup>+</sup>: 392.2337, found: 392.2335.



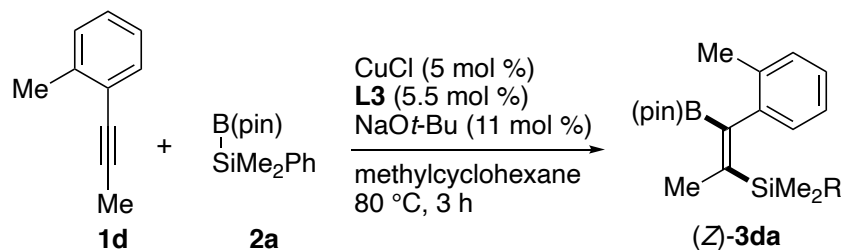
**(Z)-3ca**



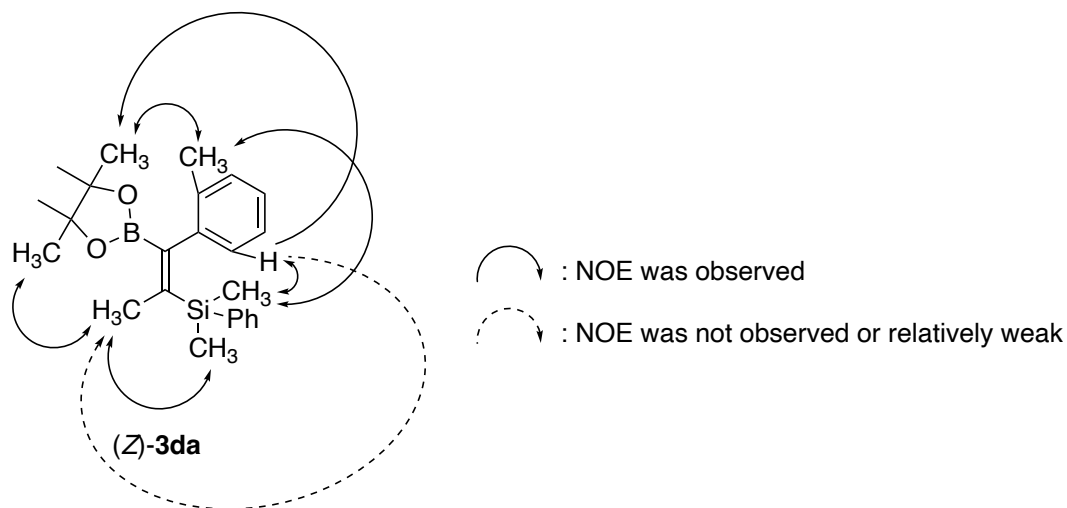
According to the *general procedure*, the reaction was carried out at 80 °C for 3 h using CuCl (1.00 mg, 0.0101 mmol), **L3** (0.110 mL from 0.1 M methylcyclohexane solution, 0.0110 mmol), NaOt-Bu (2.05 mg, 0.0213 mmol), **1c** (26.1 mg, 0.200 mmol), **2a** (56.6 mg, 0.216 mmol), and methylcyclohexane (0.5 mL). (**Z**)-**3ca** (76.8 mg, 0.196 mmol, 98%) was obtained after purification by column chromatography on silica gel (eluent: hexane:AcOEt = 4:1) and Kugelrohr distillation (110-135 °C/0.31 Torr). The stereochemistry of the product was confirmed by NOE. (**Z**)-**3ca**: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.41-7.45 (m, 2H), 7.27-7.33 (m, 3H), 7.07 (t,  $J$  = 7.5 Hz, 1H), 6.95 (d,  $J$  = 7.5 Hz, 1H), 6.87 (d,  $J$  = 7.5 Hz, 1H), 6.80 (s, 1H), 2.19 (s, 3H), 2.09 (s, 3H), 1.27 (s, 12H), -0.02 (s, 6H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  149.0, 143.6, 140.4, 137.2, 133.8, 129.6, 128.6, 127.7, 127.6, 127.0, 125.4, 83.7, 24.8, 24.0, 21.4, -1.5. The boron-bound carbon was not detected due to quadrupolar relaxation. <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>)  $\delta$  30.2. HRMS (EI, positive)  $m/z$  calcd for C<sub>24</sub>H<sub>33</sub>BO<sub>2</sub>Si<sup>+</sup> [M]<sup>+</sup>: 392.2337, found: 392.2339.



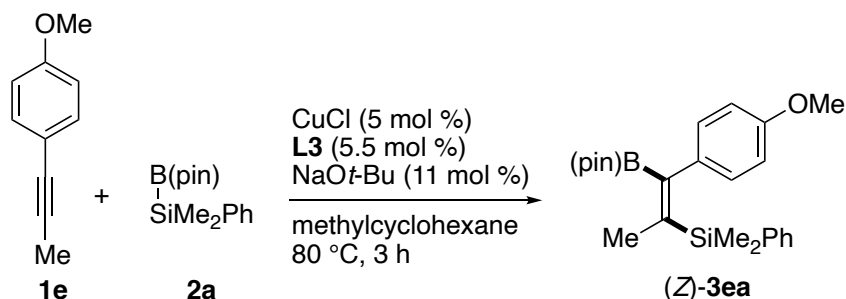
**(Z)-3da**



According to the *general procedure*, the reaction was carried out at 80 °C for 3 h using CuCl (0.97 mg, 0.00980 mmol), **L3** (0.110 mL from 0.1 M methylcyclohexane solution, 0.0110 mmol), NaOt-Bu (2.89 mg, 0.0301 mmol), NaOt-Bu (2.11 mg, 0.0220 mmol), **1d** (26.7 mg, 0.205 mmol), **2a** (58.7 mg, 0.224 mmol), and methylcyclohexane (0.2 mL). **(Z)-3da** (63.7 mg, 0.162 mmol, 79%) was obtained after purification by column chromatography on silica gel (Biotage Isolera, eluent: hexane:AcOEt = 100:0 to 90:10) and Kugelrohr distillation (115-130 °C/0.41 Torr). The stereochemistry of the product was confirmed by NOE. **(Z)-3da**: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.36-7.40 (m, 2H), 7.25-7.33 (m, 3H), 7.05-7.10 (m, 1H), 6.99-7.05 (m, 2H), 6.90-6.93 (m, 1H), 2.17 (s, 3H), 2.07 (s, 3H), 1.22 (s, 6H), 1.21 (s, 6H), -0.04 (s, 3H), -0.12 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 150.1, 143.5, 139.6, 135.9, 133.9, 129.6, 129.4, 128.6, 127.6, 126.5, 125.4, 83.5, 24.9, 24.8, 23.2, 20.3, -1.8, -2.4. The boron-bound carbon was not detected due to quadrupolar relaxation. <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) δ 29.9.

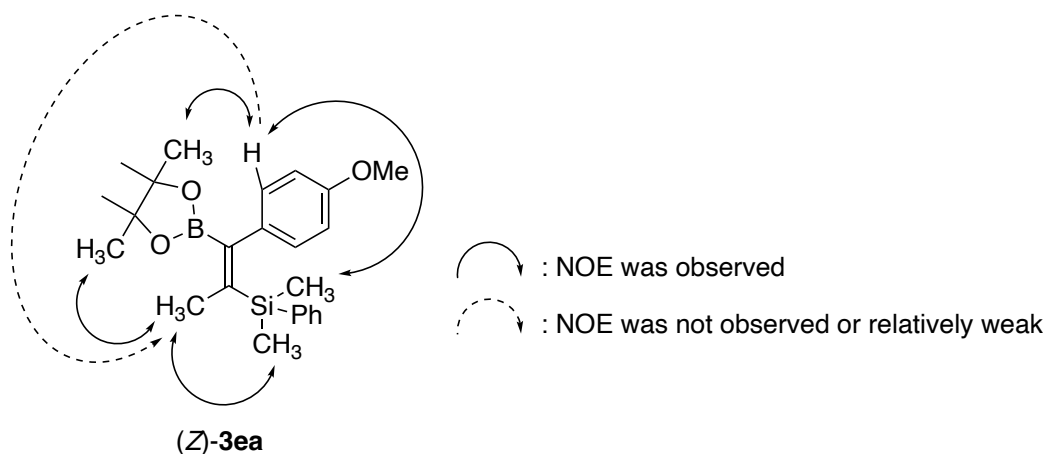


### (Z)-3ea

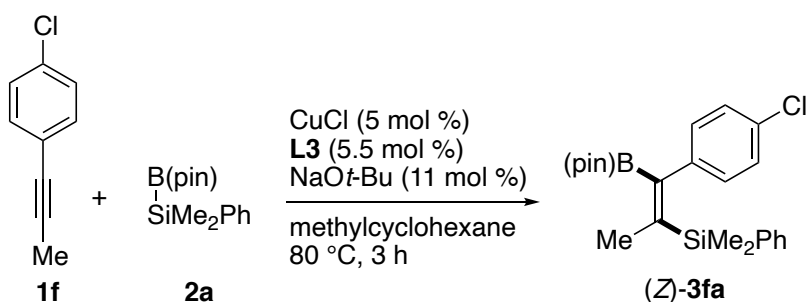


According to the *general procedure*, the reaction was carried out at 80 °C for 3 h using CuCl (1.25 mg, 0.0126 mmol), **L3** (0.130 mL from 0.1 M methylcyclohexane solution, 0.0130 mmol), NaOt-Bu (2.89 mg, 0.0301 mmol), **1e** (29.0 mg, 0.198 mmol), **2a** (57.0 mg, 0.0217 mmol), and methylcyclohexane (0.5 mL). (**Z**)-**3ea** (61.0 mg, 0.149 mmol, 75%) was obtained after purification by column chromatography on silica gel (Biotage Isolera, eluent: hexane:AcOEt = 100:0 to 90:10) and Kugelrohr distillation (125-155 °C/0.41 Torr). The stereochemistry of the product was confirmed by NOE. (**Z**)-**3ea**:  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42-7.46 (m, 2H), 7.27-7.34 (m, 3H), 6.95 (d,  $J = 8.5$  Hz, 2H), 6.70 (d,  $J = 8.5$  Hz, 2H), 3.77 (s, 3H), 2.07 (s, 3H), 1.26 (s, 12H), 0.00 (s, 6H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  158.3, 148.9, 140.2, 136.2, 133.9, 129.6, 128.6, 127.7, 113.2, 83.7, 55.2, 24.8, 23.9, -1.4. The boron-bound carbon was not detected due to quadrupolar relaxation.  $^{11}\text{B NMR}$  (160 MHz,  $\text{CDCl}_3$ )  $\delta$  30.2. HRMS (EI, positive)  $m/z$  calcd for  $\text{C}_{24}\text{H}_{33}\text{BO}_3\text{Si}^+$  [ $\text{M} + \text{H}$ ] $^+$ : 408.2287, found: 408.2287.

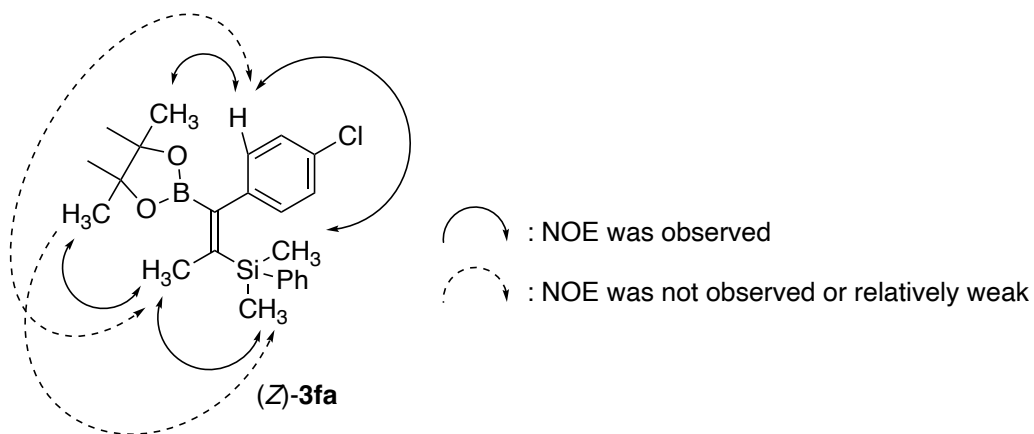




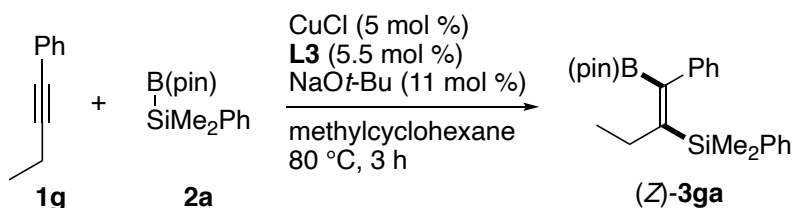
(Z)-3fa



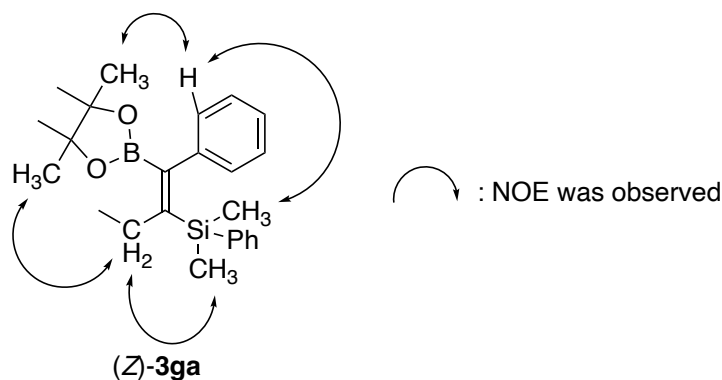
According to the *general procedure*, the reaction was carried out at 80 °C for 3 h using CuCl (1.22 mg, 0.0123 mmol), **L3** (0.135 mL from 0.1 M methylcyclohexane solution, 0.0135 mmol), NaOt-Bu (2.24 mg, 0.0233 mmol), **1f** (30.2 mg, 0.201 mmol), **2a** (57.2 mg, 0.218 mmol), and methylcyclohexane (0.5 mL). (Z)-**3fa** (73.7 mg, 0.179 mmol, 89%) was obtained after purification by column chromatography on silica gel (Biotage Isolera, eluent: hexane:AcOEt = 100:0 to 90:10) and Kugelrohr distillation (115-138 °C/0.33 Torr). The stereochemistry of the product was confirmed by NOE. (Z)-**3fa**:  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35-7.43 (m, 2H), 7.26-7.34 (m, 3H), 7.10 (d,  $J = 8.5$  Hz, 2H), 6.93 (d,  $J = 8.5$  Hz, 2H), 2.09 (s, 3H), 1.25 (s, 12H), 0.02 (s, 6H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  150.9, 142.3, 139.6, 133.8, 132.1, 130.0, 128.7, 127.9, 127.8, 83.8, 24.8, 23.9, -1.4. Although the boron-bound carbon was not detected due to quadrupolar relaxation, it could be detected at 147.4 ppm by HMBC.  $^{11}\text{B NMR}$  (160 MHz,  $\text{CDCl}_3$ )  $\delta$  29.9. HRMS (EI, positive)  $m/z$  calcd for  $\text{C}_{23}\text{H}_{30}\text{BClO}_2\text{Si}^+ [\text{M}]^+$ : 412.1791, found: 412.1793.



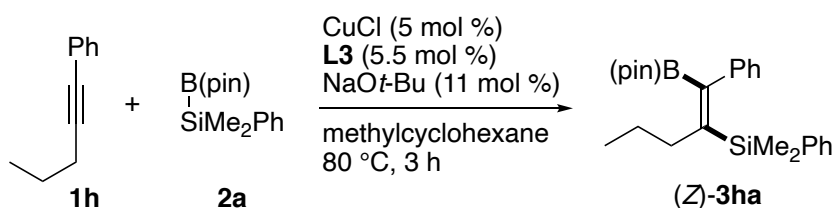
**(Z)-3ga**



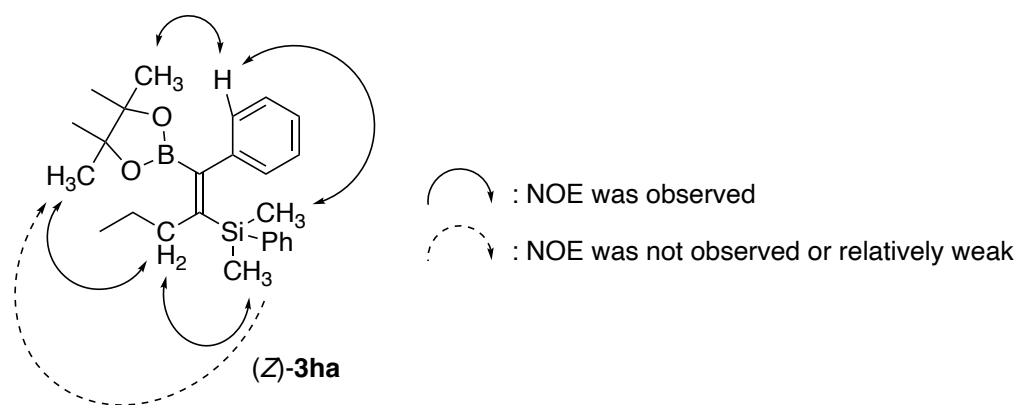
According to the *general procedure*, the reaction was carried out at 80 °C for 3 h using CuCl (1.26 mg, 0.0127 mmol), **L3** (0.135 mL from 0.1 M methylcyclohexane solution, 0.0135 mmol), NaOt-Bu (2.88 mg, 0.0300 mmol), **1g** (25.7 mg, 0.197 mmol), **2a** (57.3 mg, 0.219 mmol), and methylcyclohexane (0.5 mL). **3ga** (69.8 mg, 0.178 mmol, 90%, *Z*:*E* = 85:15) was obtained after purification by column chromatography on silica gel (Biotage Isolera, eluent: hexane:AcOEt = 100:0 to 90:10) and Kugelrohr distillation (120-140 °C/0.51 Torr). The stereochemistry of the product was confirmed by NOE. (*Z*)- and (*E*)-**3ga**: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.59-7.63 (m, *E* 2H), 7.37-7.41 (m, *Z* 2H), 7.22-7.37 (m, *Z* 3H + *E* 5H), 7.07-7.20 (m, *Z* 3H + *E* 3H), 7.00-7.05 (m, *Z* 2H), 2.39 (q, *J* = 7.5 Hz, *Z* 2H), 2.09 (q, *J* = 7.5 Hz, *E* 2H), 1.22 (s, *Z* 12H), 1.03 (t, *J* = 7.5 Hz, *Z* 3H), 0.94 (s, *E* 12H), 0.76 (t, *J* = 7.5 Hz, *E* 3H), 0.49 (s, *E* 6H), 0.00 (s, *Z* 6H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 154.9 (*Z*), 143.4 (*Z*), 140.5 (*Z*), 134.3 (*E*), 134.0 (*Z*), 128.6 (*Z*), 128.5 (*Z*), 128.2 (*E*), 127.9 (*E*), 127.75 (*Z*), 127.70 (*E*), 127.6 (*Z*), 126.2 (*Z*), 125.6 (*E*), 83.7 (*Z*), 83.5 (*E*), 31.7 (*E*), 30.6 (*Z*), 24.8 (*Z*), 16.4 (*Z*), 15.1 (*E*), 0.1 (*E*), -0.6 (*Z*). For the minor *E*-isomer, some carbons could not be detected. The boron-bound carbon was not detected due to quadrupolar relaxation. <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) δ 30.2. HRMS (APCI, positive) *m/z* calcd for C<sub>24</sub>H<sub>33</sub>BNaO<sub>2</sub>Si<sup>+</sup> [*M* + Na]<sup>+</sup>: 415.2235, found: 415.2238.



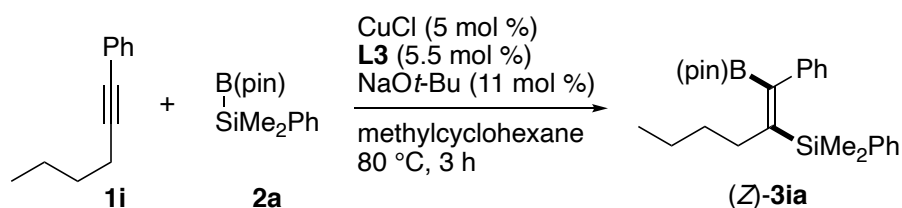
### (Z)-3ha



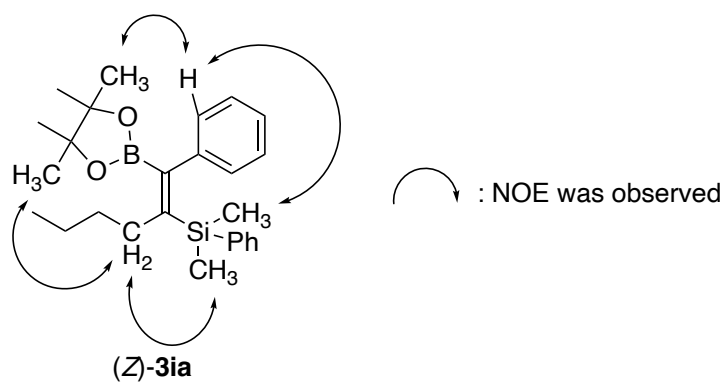
According to the *general procedure*, the reaction was carried out at 80 °C for 3 h using CuCl (1.05 mg, 0.0106 mmol), **L3** (4.03 mg, 0.0115 mmol), NaOt-Bu (2.14 mg, 0.0223 mmol), **1h** (29.0 mg, 0.201 mmol), **2a** (58.0 mg, 0.221 mmol), and methylcyclohexane (0.6 mL). (**Z**)-**3ha** (69.5 mg, 0.171 mmol, 85%, *Z*:*E* = 81:19) was obtained as a colorless oil after purification by column chromatography on silica gel (Biotage Isolera, eluent: hexane:AcOEt = 100:0 to 90:10) and Kugelrohr distillation (120-135 °C/0.50 Torr). The stereochemistry of the product was confirmed by NOE. (*Z*)- and (*E*)-**3ha**: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.61-7.64 (m, *E* 2H), 7.38-7.42 (m, *Z* 2H), 7.24-7.35 (m, *Z* 3H + *E* 5H), 7.17-7.21 (m, *E* 1H), 7.08-7.15 (m, *Z* 3H + *E* 2H), 7.01-7.06 (m, *Z* 2H), 2.32-2.37 (m, *Z* 2H), 2.03-2.09 (m, *E* 2H), 1.40-1.50 (m, *Z* 2H), 1.24 (s, *Z* 12H), 1.16-1.28 (m, *E* 2H), 0.96 (s, *E* 12H), 0.87 (t, *J* = 7.5 Hz, *Z* 3H), 0.61 (t, *J* = 7.5 Hz, *E* 3H), 0.50 (s, *E* 6H), 0.01 (s, *Z* 6H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 153.5 (*Z*), 143.8 (*E*), 143.5 (*Z*), 140.8 (*E*), 140.5 (*Z*), 134.3 (*E*), 134.0 (*Z*), 128.6 (*Z*), 128.5 (*Z*), 128.2 (*E*), 127.9 (*E*), 127.73 (*Z*), 127.67 (*E*), 127.5 (*Z*), 126.2 (*Z*), 125.6 (*E*), 83.6 (*Z*), 83.5 (*E*), 40.2 (*Z*), 36.5 (*E*), 25.1 (*Z*), 24.8 (*Z*), 23.7 (*E*), 14.43 (*Z*), 14.38 (*E*), 0.1 (*E*), -0.7 (*Z*). For the minor *E*-isomer, some carbons could not be detected. The boron-bound carbon was not detected due to quadrupolar relaxation. <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) δ 30.1. HRMS (ESI, positive) *m/z* calcd for C<sub>25</sub>H<sub>35</sub>BNaO<sub>2</sub>Si<sup>+</sup> [M + Na]<sup>+</sup>: 429.2392, found: 429.2394.



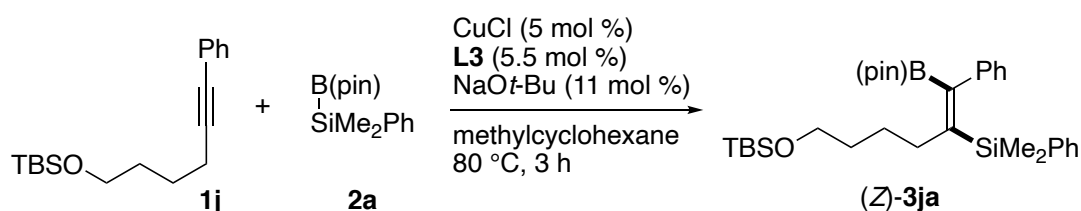
### (Z)-3ia



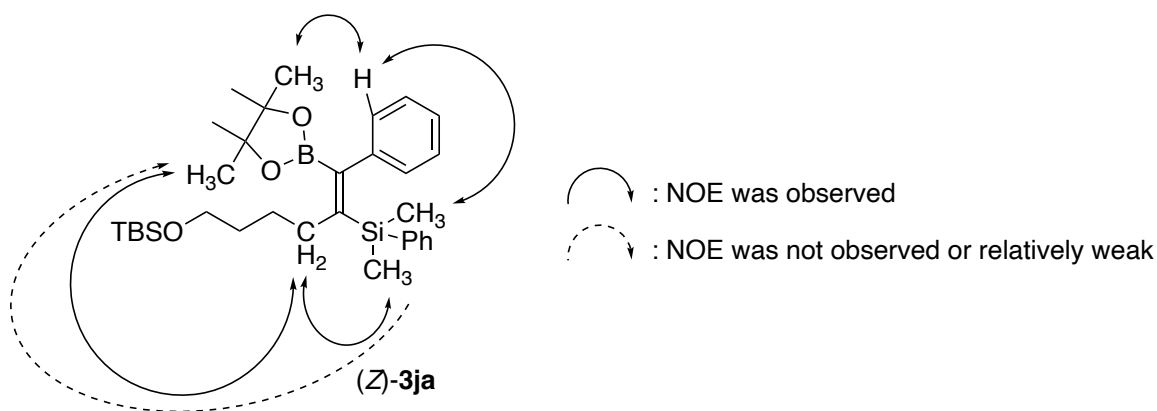
According to the *general procedure*, the reaction was carried out at 80 °C for 3 h using CuCl (1.20 mg, 0.0121 mmol), **L3** (0.130 mL from 0.1 M methylcyclohexane solution, 0.0130 mmol), NaOt-Bu (2.50 mg, 0.0260 mmol), **1i** (32.9 mg, 0.208 mmol), **2a** (57.6 mg, 0.220 mmol), and methylcyclohexane (0.5 mL). (**Z**)-**3ia** (79.1 mg, 0.188 mmol, 90%) was obtained after purification by column chromatography on silica gel (Biotage Isolera, eluent: hexane:AcOEt = 100:0 to 90:10) and Kugelrohr distillation (120-145 °C/0.40 Torr). The stereochemistry of the product was confirmed by NOE. (**Z**)-**3ia**: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.38-7.42 (m, 2H), 7.24-7.30 (m, 3H), 7.11-7.15 (m, 3H), 7.02-7.05 (m, 2H), 2.33-2.38 (m, 2H), 1.36-1.45 (m, 2H), 1.20-1.31 (m, 2H), 1.23 (s, 12H), 0.85 (t, *J* = 7.5 Hz, 3H), 0.01 (s, 6H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 153.7, 143.5, 140.5, 134.0, 128.6, 128.5, 127.7, 127.5, 126.2, 83.6, 37.8, 34.0, 24.8, 23.2, 14.1, -0.6. The boron-bound carbon was not detected due to quadrupolar relaxation. <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) δ 30.2. HRMS (APCI, positive) *m/z* calcd for C<sub>26</sub>H<sub>37</sub>BNaO<sub>2</sub>Si<sup>+</sup> [*M* + Na]<sup>+</sup>: 443.2548, found: 443.2551.



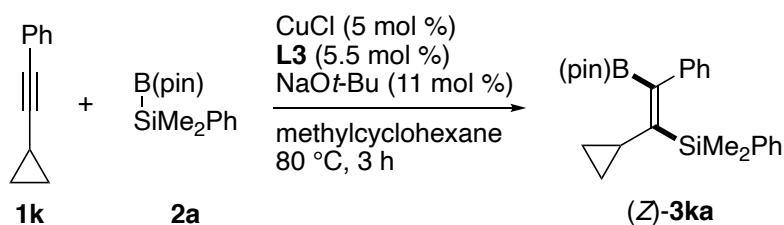
### (Z)-3ja



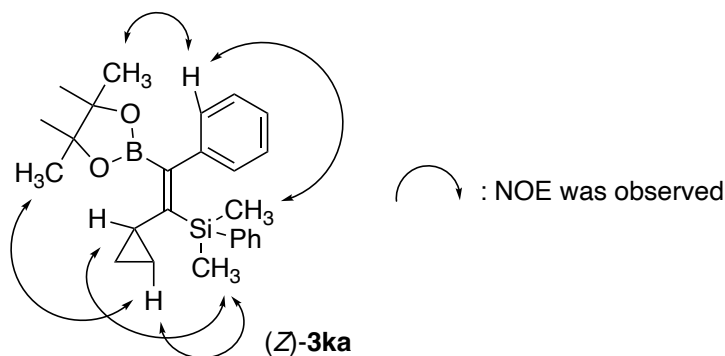
According to the *general procedure*, the reaction was carried out at 80 °C for 3 h using CuCl (1.05 mg, 0.0106 mmol), **L3** (0.115 mL from 0.1 M methylcyclohexane solution, 0.0115 mmol), NaOt-Bu (2.12 mg, 0.0221 mmol), **1j** (58.3 mg, 0.202 mmol), **2a** (57.6 mg, 0.220 mmol), and methylcyclohexane (0.5 mL). (**Z**)-**3ja** (101.9 mg, 0.185 mmol, 92%) was obtained after purification by column chromatography on silica gel (eluent: hexane:AcOEt = 4:1) and Kugelrohr distillation (140-160 °C/0.40 Torr). The stereochemistry of the product was confirmed by NOE. (**Z**)-**3ja**: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.36-7.41 (m, 2H), 7.22-7.30 (m, 3H), 7.10-7.16 (m, 3H), 7.00-7.05 (m, 2H), 3.49-3.56 (m, 2H), 2.32-2.40 (m, 2H), 1.37-1.52 (m, 4H), 1.23 (s, 12H), 0.91 (s, 9H), 0.05 (s, 6H), 0.02 (s, 6H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 153.7, 143.5, 140.4, 134.0, 128.6, 128.5, 127.7, 127.5, 126.2, 83.6, 63.4, 37.9, 33.5, 28.2, 26.2, 24.8, 18.5, -0.7, -5.1. Although the boron-bound carbon was not detected due to quadrupolar relaxation, it could be detected at 150.1 ppm by HMBC. <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) δ 30.1. HHRMS (ESI, positive) *m/z* calcd for C<sub>32</sub>H<sub>51</sub>BNaO<sub>3</sub>Si<sup>+</sup> [M + Na]<sup>+</sup>: 573.3362, found: 573.3363.



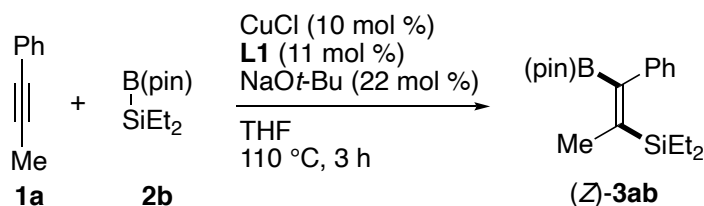
### (Z)-3ka



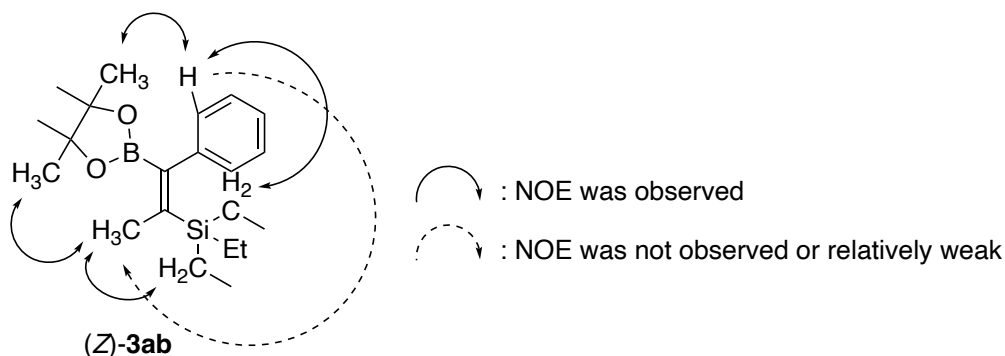
According to the *general procedure*, the reaction was carried out at 80 °C for 3 h using CuCl (1.01 mg, 0.010 mmol), **L3** (0.110 mL from 0.1 M methylcyclohexane solution, 0.0110 mmol), NaOt-Bu (2.20 mg, 0.0229 mmol), **1k** (28.0 mg, 0.197 mmol), **2a** (57.7 mg, 0.220 mmol), and methylcyclohexane (0.5 mL). (**Z**)-**3ka** (69.1 mg, 0.171 mmol, 87%) was obtained after purification by column chromatography on silica gel (Biotage Isolera, eluent: hexane:AcOEt = 100:0 to 92:8) and Kugelrohr distillation (130-150 °C/0.45 Torr). The stereochemistry of the product was confirmed by NOE. (**Z**)-**3ka**:  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41-7.44 (m, 2H), 7.23-7.30 (m, 3H), 7.12-7.17 (m, 3H), 6.98-7.02 (m, 2H), 1.62-1.69 (m, 1H), 1.26 (s, 12H), 0.61-0.66 (m, 2H), 0.53-0.58 (m, 2H), 0.05 (s, 6H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  153.0, 143.4, 140.6, 134.1, 128.4, 128.3, 127.9, 127.4, 126.4, 83.7, 24.9, 19.7, 7.1, -0.7. The boron-bound carbon was not detected due to quadrupolar relaxation.  $^{11}\text{B NMR}$  (160 MHz,  $\text{CDCl}_3$ )  $\delta$  30.3. HRMS (APCI, positive)  $m/z$  calcd for  $\text{C}_{25}\text{H}_{33}\text{BNaO}_2\text{Si}^+$  [ $\text{M} + \text{Na}$ ] $^+$ : 427.2235, found: 427.2241.



### (Z)-3ab



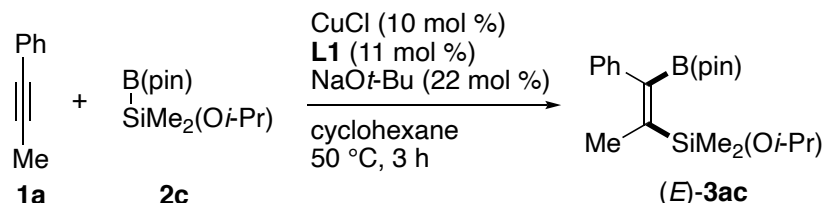
According to the *general procedure*, the reaction was carried out at 110 °C for 3 h using CuCl (2.01 mg, 0.0203 mmol), **L1** (0.220 mL from 0.1 M THF solution, 0.0220 mmol), NaOt-Bu (4.53 mg, 0.0471 mmol), **1a** (23.0 mg, 0.198 mmol), **2b** (48.4 mg, 0.200 mmol), and THF (0.38 mL). (**Z-3ab** (52.1 mg, 0.145 mmol, 73%) was obtained after purification by column chromatography on silica gel (eluent: hexane:AcOEt = 4:1) and Kugelrohr distillation (100-120 °C/0.44 Torr). The stereochemistry of the product was confirmed by NOE. (**Z-3ab**:  $^1\text{H NMR}$  (600 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  7.35-7.38 (m, 2H), 7.13-7.17 (m, 2H), 7.05 (tt,  $J = 7.2, 1.2$  Hz, 1H), 2.35 (s, 3H), 1.02 (s, 12H), 0.91 (t,  $J = 7.8$  Hz, 9H), 0.42 (q,  $J = 7.8$  Hz, 6H).  $^{13}\text{C NMR}$  (151 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  150.2, 145.1, 129.0, 128.3, 126.5, 83.3, 24.8, 24.0, 8.0, 4.3. The boron-bound carbon was not detected due to quadrupolar relaxation.  $^{11}\text{B NMR}$  (160 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  30.4. HRMS (APCI, positive)  $m/z$  calcd for  $\text{C}_{21}\text{H}_{35}\text{BNaO}_2\text{Si}^+ [\text{M} + \text{Na}]^+$ : 381.2392, found: 381.2386.



## 6. Solvent-Dependent Switch of Stereoselectivity in Silaboration of Internal Alkynes with **2c** (Scheme 4)

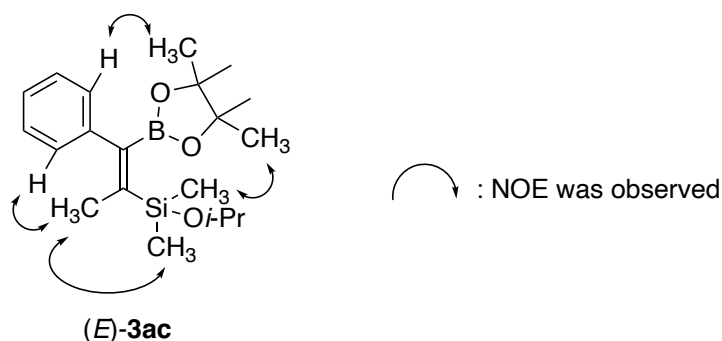
*General procedure:* In a glovebox, a glass tube (outside diameter: 20 mm, internal volume: 16 mL) having PTFE stopcock (J. Young), equipped with a magnetic stirring bar, was charged with CuCl (0.020 mmol, 10 mol %), **L1** (0.022 mmol, 11 mol %), NaO*t*-Bu (0.044 mmol, 22 mol %), **1** (0.20 mmol), **2c** (0.30 mmol), and cyclohexane (0.4 mL). The tube was sealed by the stopcock and was taken out from the glovebox. The mixture was stirred for 3 h at 50 °C by a heating magnetic stirrer with an aluminum heating block (hole size: 21 mm diameter x 33 mm depth). The product **3** was purified by column chromatography on silica gel and Kugelrohr distillation.

### (*E*)-**3ac**

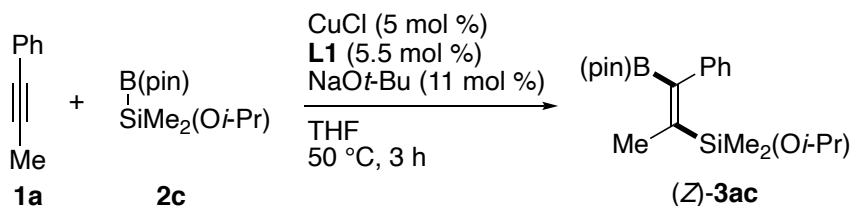


According to the *general procedure*, the reaction was carried out at 50 °C for 3 h using CuCl (1.92 mg, 0.0194 mmol), **L1** (8.0 mg, 0.0219 mmol), NaO*t*-Bu (4.00 mg, 0.0416 mmol), **1a** (22.8 mg, 0.196 mmol), **2c** (72.1 mg, 0.275 mmol), and cyclohexane (0.4 mL). **3ac** (52.1 mg, 0.145 mmol, 74%, *Z*:*E* = 20:80) was obtained after purification by column chromatography on silica gel (Biotage Isolera, eluent: hexane:AcOEt = 100:0 to 90:10) and Kugelrohr distillation (110-120 °C/0.33 Torr). The stereochemistry of the product was confirmed by NOE. (*E*)-**3ac**: <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>) δ 7.24-7.28 (m, 2H), 7.19-7.24 (m, 2H), 7.06 (tt, *J* = 7.5, 4.5 Hz, 1H), 4.09 (septet, *J* = 6.0 Hz, 1H), 1.93 (s, 3H), 1.22 (d, *J* = 6.0 Hz, 6H), 1.04 (s, 12H), 0.52 (s, 6H). <sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>) δ 150.7, 144.1, 128.7, 128.3, 126.1, 83.5, 65.5, 26.1, 25.0, 20.3, 0.6. The boron-bound carbon was not detected due to quadrupolar relaxation. <sup>11</sup>B NMR (160 MHz, C<sub>6</sub>D<sub>6</sub>) δ 30.2. HRMS (ESI, positive) *m/z* calcd for C<sub>20</sub>H<sub>33</sub>BNaO<sub>3</sub>Si<sup>+</sup> [*M* + Na]<sup>+</sup>: 383.2184, found: 383.2187.

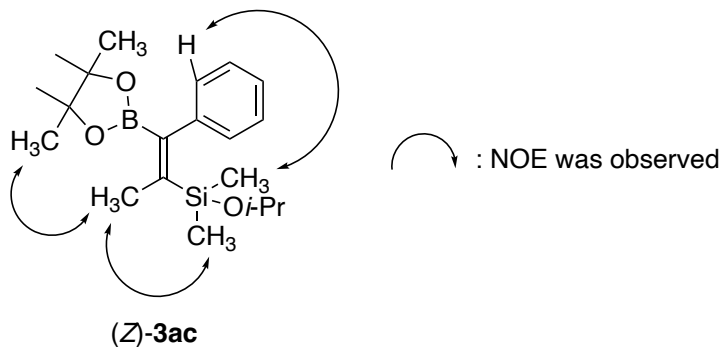


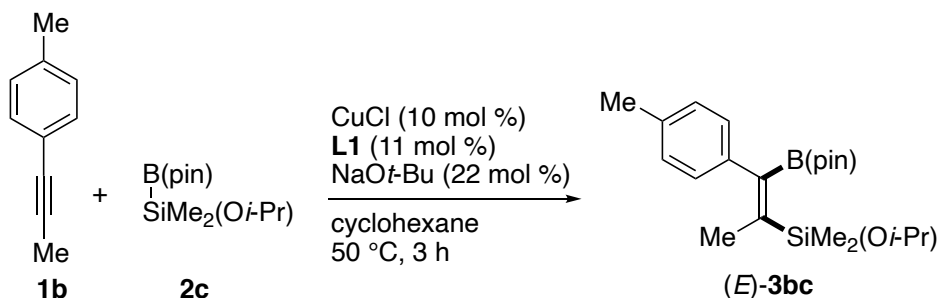


### (Z)-3ac

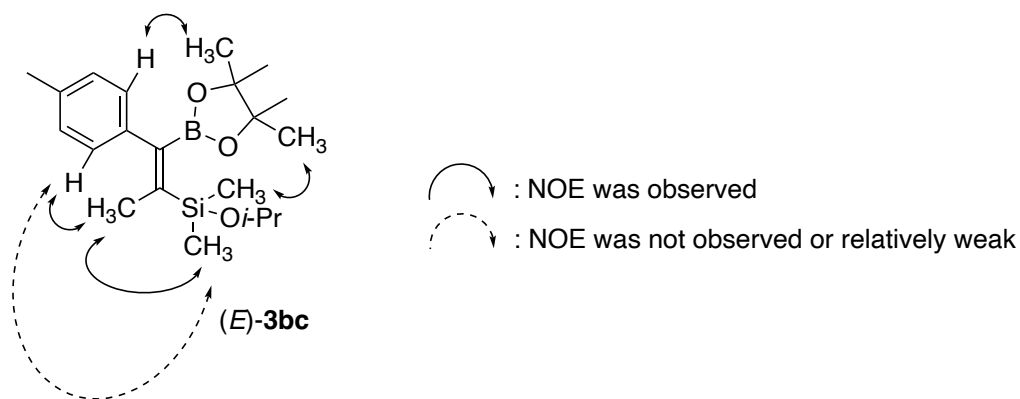


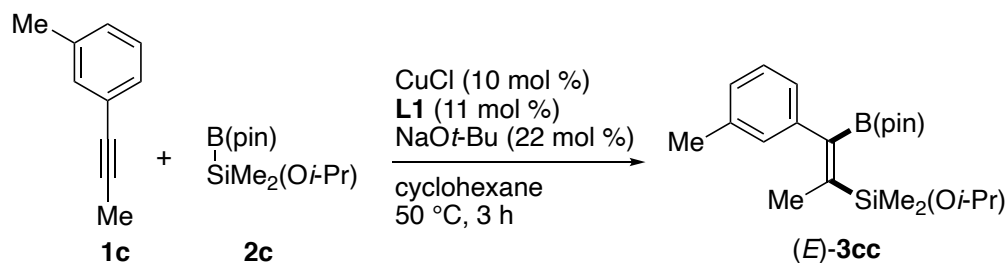
According to the *general procedure*, the reaction was carried out at 50 °C for 3 h using CuCl (0.97 mg, 0.00980 mmol), **L1** (3.97 mg, 0.0109 mmol), NaO*t*-Bu (2.23 mg, 0.0232 mmol), **1a** (23.3 mg, 0.201 mmol), **2c** (49.7 mg, 0.204 mmol), and THF (2 mL). **3ac** (51.4 mg, 0.143 mmol, 71%, *Z:E* = 95:5) was obtained after purification by column chromatography on silica gel (eluent: hexane:AcOEt = 4:1) and Kugelrohr distillation (105-120 °C/0.60 Torr). The stereochemistry of the product was confirmed by NOE. (*Z*)-**3ac**: <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>) δ 7.39-7.42 (m, 2H), 7.14-7.18 (m, 2H), 7.04 (tt, *J* = 7.5, 1.5 Hz, 1H), 3.84 (septet, *J* = 6.0 Hz, 1H), 2.47 (s, 3H), 1.08 (d, *J* = 6.0 Hz, 6H), 1.03 (s, 12H), -0.07 (s, 6H). <sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>) δ 152.3, 145.0, 129.2, 128.4, 126.6, 83.4, 65.1, 26.0, 24.8, 22.7, 0.3. Although the boron-bound carbon was not detected due to quadrupolar relaxation, it could be detected at 148.4 ppm by HMBC. <sup>11</sup>B NMR (128 MHz, C<sub>6</sub>D<sub>6</sub>) δ 30.2. HRMS (ESI, positive) *m/z* calcd for C<sub>20</sub>H<sub>33</sub>BNaO<sub>3</sub>Si<sup>+</sup> [*M* + Na]<sup>+</sup>: 383.2184, found: 383.2194.



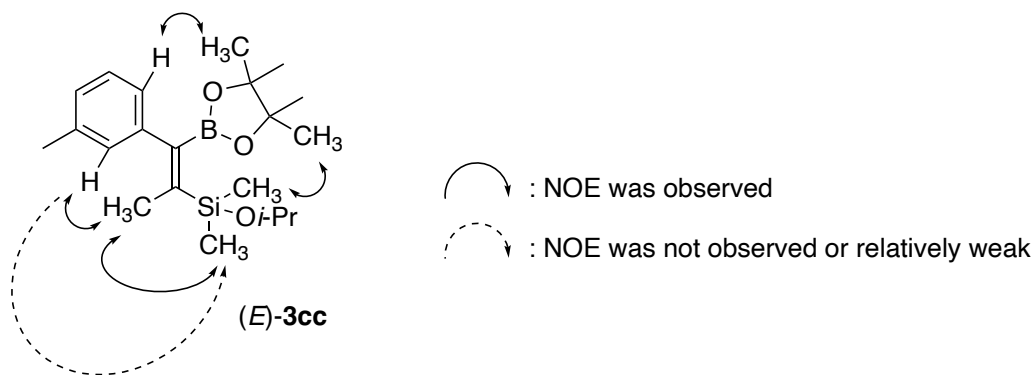
**(E)-3bc**

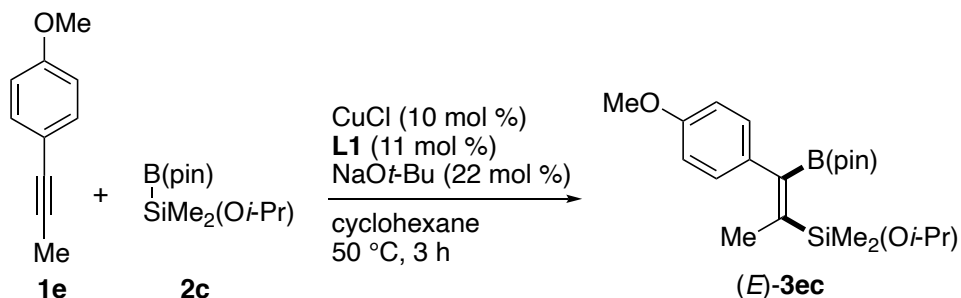
According to the *general procedure*, the reaction was carried out at 50 °C for 3 h using  $\text{CuCl}$  (2.81 mg, 0.0284 mmol), **L1** (7.91 mg, 0.0217 mmol),  $\text{NaOt-Bu}$  (4.22 mg, 0.0439 mmol), **1b** (26.4 mg, 0.203 mmol), **2c** (72.6 mg, 0.297 mmol), and cyclohexane (0.6 mL). **3bc** (55.8 mg, 0.149 mmol, 73%, *Z:E* = 9:91) was obtained after purification by column chromatography on silica gel (Biotage Isolera, eluent: hexane:AcOEt = 100:0 to 90:10) and Kugelrohr distillation (105–115 °C/0.35 Torr). The stereochemistry of the product was confirmed by NOE. (**E**)-**3bc**:  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  7.20 (d,  $J$  = 8.4 Hz, 2H), 7.04 (d,  $J$  = 8.4 Hz, 2H), 4.10 (septet,  $J$  = 6.0 Hz, 1H), 2.12 (s, 3H), 1.98 (s, 3H), 1.23 (d,  $J$  = 6.0 Hz, 6H), 1.06 (s, 12H), 0.53 (s, 6H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  150.3, 141.1, 135.2, 129.1, 128.7, 83.5, 65.5, 26.1, 25.1, 21.2, 20.4, 0.6. The boron-bound carbon was not detected due to quadrupolar relaxation.  $^{11}\text{B}$  NMR (160 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  30.3. HRMS (ESI, positive)  $m/z$  calcd for  $\text{C}_{21}\text{H}_{35}\text{BNaO}_3\text{Si}^+ [\text{M} + \text{Na}]^+$ : 397.2341, found: 397.2341.



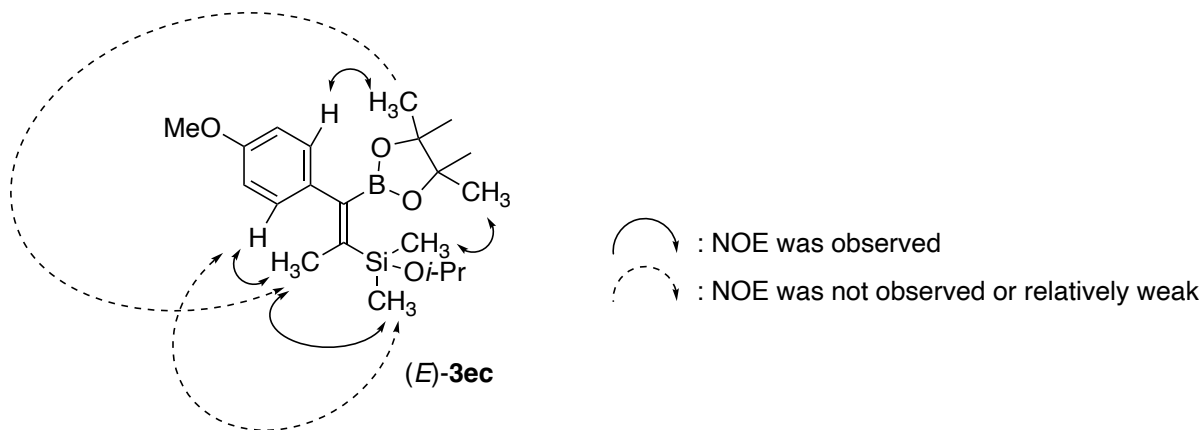
**(E)-3cc**

According to the *general procedure*, the reaction was carried out at 50 °C for 3 h using CuCl (2.01 mg, 0.0203 mmol), **L1** (8.18 mg, 0.0224 mmol), NaOt-Bu (4.16 mg, 0.0433 mmol), **1c** (25.8 mg, 0.198 mmol), **2c** (72.5 mg, 0.297 mmol), and cyclohexane (0.6 mL). **3cc** (53.1 mg, 0.142 mmol, 72%, *Z:E* = 9:91) was obtained after purification by column chromatography on silica gel (Biotage Isolera, eluent: hexane:AcOEt = 100:0 to 90:10) and Kugelrohr distillation (110-125 °C/0.32 Torr). The stereochemistry of the product was confirmed by NOE. (*E*)-**3cc**:  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  7.18 (t,  $J$  = 7.2 Hz, 1H), 7.10-7.14 (m, 2H), 6.89-6.93 (m, 1H), 4.11 (septet,  $J$  = 6.0 Hz, 1H), 2.15 (s, 3H), 1.96 (s, 3H), 1.24 (d,  $J$  = 6.0 Hz, 6H), 1.06 (s, 12H), 0.53 (s, 6H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  150.3, 141.2, 137.6, 129.4, 128.4, 126.9, 125.8, 83.5, 65.5, 26.1, 25.0, 21.6, 20.4, 0.6. The boron-bound carbon was not detected due to quadrupolar relaxation.  $^{11}\text{B}$  NMR (160 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  30.2. HRMS (ESI, positive)  $m/z$  calcd for  $\text{C}_{21}\text{H}_{35}\text{BNaO}_3\text{Si}^+$  [ $\text{M} + \text{Na}$ ] $^+$ : 397.2341, found: 397.2342.



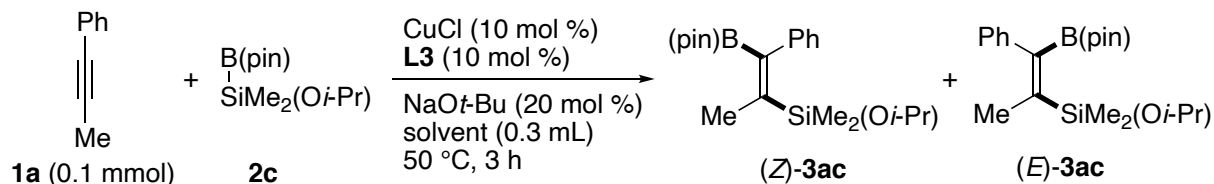
**(E)-3ec**

According to the *general procedure*, the reaction was carried out at 50 °C for 3 h using  $\text{CuCl}$  (1.92 mg, 0.0194 mmol), **L1** (8.20 mg, 0.0225 mmol),  $\text{NaOt-Bu}$  (4.28 mg, 0.0445 mmol), **1e** (29.4 mg, 0.201 mmol), **2c** (72.5 mg, 0.297 mmol), and cyclohexane (0.6 mL). **3ec** (64.6 mg, 0.165 mmol, 82%, *Z:E* = 3:97) was obtained after purification by column chromatography on silica gel (eluent: hexane:AcOEt = 100:0 to 90:10) and Kugelrohr distillation (120-135 °C/0.43 Torr). The stereochemistry of the product was confirmed by NOE. **(E)-3ec**:  $^1\text{H NMR}$  (600 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  7.18-7.22 (m, 2H), 6.82-6.85 (m, 2H), 4.11 (septet,  $J = 6.0$  Hz, 1H), 3.29 (s, 3H), 2.00 (s, 3H), 1.24 (d,  $J = 6.0$  Hz, 6H), 1.08 (s, 12H), 0.54 (s, 6H).  $^{13}\text{C NMR}$  (151 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  158.5, 150.2, 136.0, 129.9, 113.9, 83.5, 65.5, 54.7, 26.1, 25.1, 20.3, 0.6. The boron-bound carbon was not detected due to quadrupolar relaxation.  $^{11}\text{B NMR}$  (160 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  30.3. HRMS (ESI, positive)  $m/z$  calcd for  $\text{C}_{21}\text{H}_{35}\text{BNaO}_4\text{Si}^+ [\text{M} + \text{Na}]^+$ : 413.2290, found: 413.2288.



## 7. Solvent Effect in Silaboration with 2c

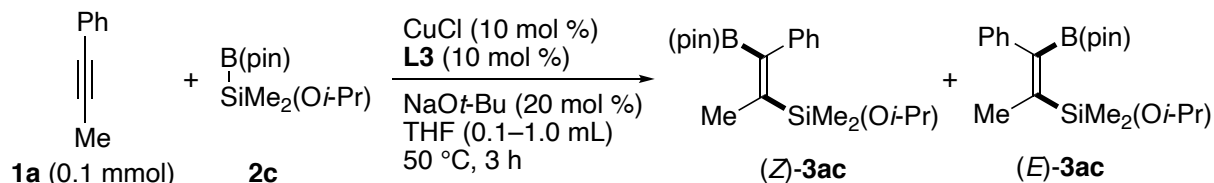
**Table S1.** Effect of Solvent on Stereoselectivity



entry	solvent	yield (%) <sup>a</sup>	<i>Z</i> : <i>E</i> <sup>a</sup>
1	THF	75	89:11
2	2-methyltetrahydrofuran	82	66:34
3	1,4-dioxane	92	50:50
4	$\text{CH}_2\text{Cl}_2$	0	–
5	toluene	78	35:65
6	cyclohexane	72	15:85
7	methylcyclohexane	79	19:81

<sup>a</sup> Determined by  $^1\text{H}$  NMR.

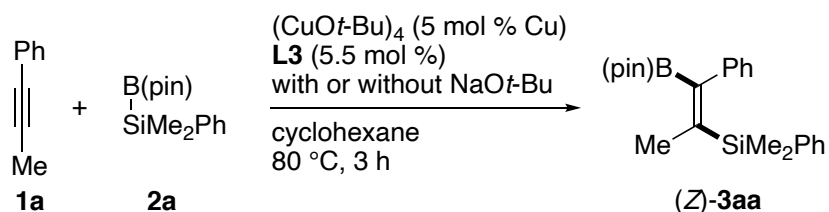
**Table S2.** Effect of Concentration on Stereoselectivity



entry	amount of THF (mL)	yield (%) <sup>a</sup>	<i>Z</i> : <i>E</i> <sup>a</sup>
1	0.1	64	66:34
2	0.3	75	89:11
3	1.0	70	97:3

<sup>a</sup> Determined by  $^1\text{H}$  NMR.

## 8. Requirement of Additional $\text{NaOt-Bu}$ (Scheme 5)

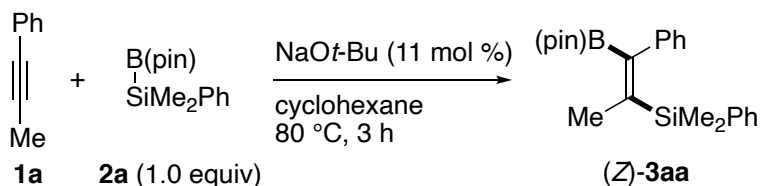


*Without NaOt-Bu:* In a glovebox, a glass tube (outside diameter: 20 mm, internal volume: 16 mL) having PTFE stopcock (J. Young), equipped with a magnetic stirring bar, was charged with  $(\text{CuOt-Bu})_4$  (0.88 mg, 0.00161 mmol), **L3** (0.070 mL from 0.1 M methylcyclohexane solution,

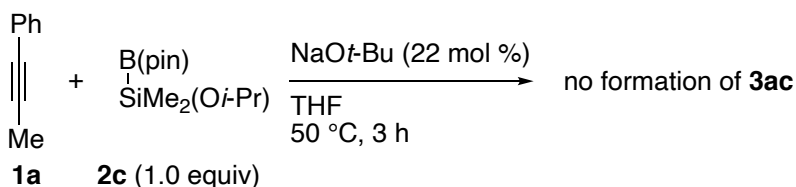
0.0070 mmol), **1a** (12.0 mg, 0.103 mmol), **2a** (29.4 mg, 0.112 mmol), and methylcyclohexane (0.25 mL). The tube was sealed by the stopcock and was taken out from the glovebox. The mixture was stirred for 3 h at 80 °C by a heating magnetic stirrer with an aluminum heating block (hole size: 21 mm diameter x 33 mm depth). <sup>1</sup>H NMR analysis (internal standard: dibenzyl ether) of the resulting mixture indicated that **3aa** was not formed.

*With NaOt-Bu (5.5 mol %)*: In a glovebox, a glass tube (outside diameter: 20 mm, internal volume: 16 mL) having PTFE stopcock (J. Young), equipped with a magnetic stirring bar, was charged with (CuOt-Bu)<sub>4</sub> (0.77 mg, 0.00141 mmol), **L3** (0.060 mL from 0.1 M methylcyclohexane solution, 0.0060 mmol), NaOt-Bu (0.59 mg, 0.00614 mmol), **1a** (12.2 mg, 0.105 mmol), **2a** (28.8 mg, 0.110 mmol), and methylcyclohexane (0.25 mL). The tube was sealed by the stopcock and was taken out from the glovebox. The mixture was stirred for 3 h at 80 °C by a heating magnetic stirrer with an aluminum heating block (hole size: 21 mm diameter x 33 mm depth). <sup>1</sup>H NMR analysis (internal standard: dibenzyl ether) of the resulting mixture indicated that (*Z*)-**3aa** was formed in 74% yield (*Z*:*E* = >99:1).

### 9. *Trans*-Silaboration Mediated by NaOt-Bu (Scheme 6)

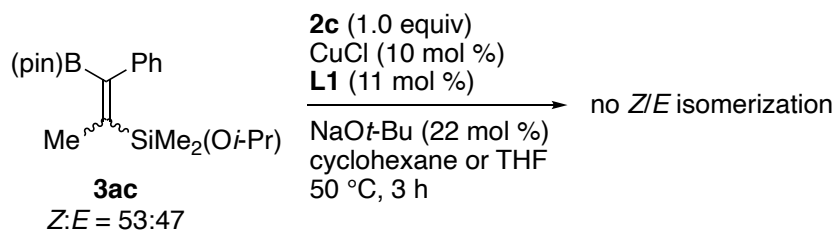


In a glovebox, a glass tube (outside diameter: 20 mm, internal volume: 16 mL) having PTFE stopcock (J. Young), equipped with a magnetic stirring bar, was charged with NaOt-Bu (1.18 mg, 0.0123 mmol), **1a** (11.8 mg, 0.102 mmol), **2a** (26.3 mg, 0.100 mmol), and cyclohexane (0.3 mL). The tube was sealed by the stopcock and was taken out from the glovebox. The mixture was stirred for 3 h at 80 °C by a heating magnetic stirrer with an aluminum heating block (hole size: 21 mm diameter x 33 mm depth). <sup>1</sup>H NMR analysis (internal standard: dibenzyl ether) of the resulting mixture indicated that **3aa** was formed in 42% yield (*Z*:*E* = 95:5).



In a glovebox, a glass tube (outside diameter: 20 mm, internal volume: 16 mL) having PTFE stopcock (J. Young), equipped with a magnetic stirring bar, was charged with NaOt-Bu (2.45 mg, 0.0255 mmol), **1a** (11.6 mg, 0.0999 mmol), **2c** (24.6 mg, 0.101 mmol), and THF (0.25 mL). The tube was sealed by the stopcock and was taken out from the glovebox. The mixture was stirred for 3 h at 50 °C by a heating magnetic stirrer with an aluminum heating block (hole size: 21 mm diameter x 33 mm depth). <sup>1</sup>H NMR analysis (internal standard: dibenzyl ether) of the resulting mixture indicated that **3ac** was not formed.

#### 10. Confirmation of No *Z/E* Isomerization of the Product (Scheme 7a)



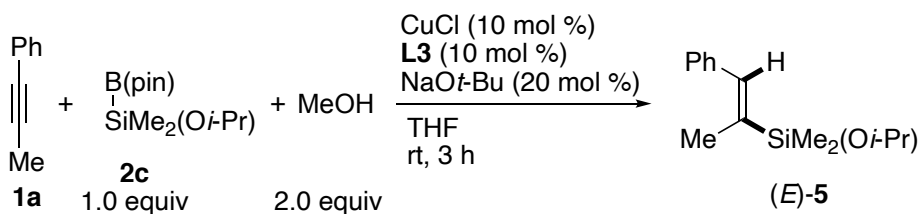
A *Z/E* mixture of **3ac** (*Z:E* = 53:47) was prepared by copper-catalyzed reaction of **1a** with **2c** in 1,4-dioxane that is found as a solvent for non-stereoselective silaboration. According to the *general procedure* described in section 5, the reaction was carried out at 50 °C for 3 h using CuCl (2.95 mg, 0.0298 mmol), **L1** (10.7 mg, 0.0294 mmol), NaOt-Bu (6.63 mg, 0.0690 mmol), **1a** (34.4 mg, 0.296 mmol), **2c** (73.1 mg, 0.299 mmol), and 1,4-dioxane (0.9 mL). **3ac** (56.5 mg, 0.157 mmol, 52%, *Z:E* = 53:47) was obtained after purification by column chromatography on silica gel (eluent: hexane:AcOEt = 100:0 to 90:10) and Kugelrohr distillation (120-140 °C/0.50 Torr).

In a glovebox, a glass tube (outside diameter: 20 mm, internal volume: 16 mL) having PTFE stopcock (J. Young), equipped with a magnetic stirring bar, was charged with CuCl (0.80 mg, 0.00808 mmol), **L1** (0.090 mL from 0.1 M cyclohexane solution, 0.0090 mmol), NaOt-Bu (1.89 mg, 0.0197 mmol), **3ac** (*Z:E* = 53:47, 26.9 mg, 0.0746 mmol), **2c** (20.4 mg, 0.0835 mmol), and cyclohexane (0.2 mL). The tube was sealed by the stopcock and was taken out from the glovebox. The mixture was stirred for 3 h at 50 °C by a heating magnetic stirrer with an aluminum heating

block (hole size: 21 mm diameter x 33 mm depth). <sup>1</sup>H NMR analysis (internal standard: dibenzyl ether) of the resulting mixture indicated that 100% of **3ac** was recovered with the *Z:E* ratio of 53:47.

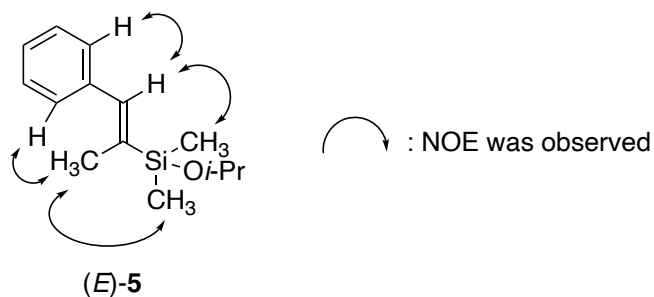
In a glovebox, a glass tube (outside diameter: 20 mm, internal volume: 16 mL) having PTFE stopcock (J. Young), equipped with a magnetic stirring bar, was charged with CuCl (0.80 mg, 0.00808 mmol), **L1** (0.090 mL from 0.1 M THF solution, 0.0090 mmol), NaO*t*-Bu (1.72 mg, 0.0179 mmol), **3ac** (*Z:E* = 53:47, 28.1 mg, 0.0780 mmol), **2c** (20.2 mg, 0.0827 mmol), and THF (0.2 mL). The tube was sealed by the stopcock and was taken out from the glovebox. The mixture was stirred for 3 h at 50 °C by a heating magnetic stirrer with an aluminum heating block (hole size: 21 mm diameter x 33 mm depth). <sup>1</sup>H NMR analysis (internal standard: dibenzyl ether) of the resulting mixture indicated that 90% of **3ac** was recovered with the *Z:E* ratio of 53:47.

### 11. Reaction of **1a** with **2a** in the Presence of MeOH (Scheme 7b)



In a glovebox, a glass tube (outside diameter: 20 mm, internal volume: 16 mL) having PTFE stopcock (J. Young), equipped with a magnetic stirring bar, was charged with CuCl (1.06 mg, 0.0107 mmol), **L3** (0.110 mL from 0.1 M THF solution, 0.0110 mmol), NaO*t*-Bu (2.20 mg, 0.0229 mmol), **1a** (11.3 mg, 0.0973 mmol), **2c** (24.5 mg, 0.100 mmol), MeOH (6.31 mg, 0.197 mmol), and THF (0.2 mL). The tube was sealed by the stopcock and the mixture was stirred for 3 h at room temperature by a magnetic stirrer. <sup>1</sup>H NMR analysis (internal standard: dibenzyl ether) of the resulting mixture indicated that (*E*)-**5** was formed in 88% yield. (*E*)-**5** was isolated in 51% yield by column chromatography on silica gel (eluent: hexane) and Kugelrohr distillation (70-120 °C/0.60 Torr). The stereochemistry of the product was confirmed by NOE. (*E*)-**5**: <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>) δ 7.28-7.32 (m, 2H), 7.16-7.22 (m, 2H), 7.07 (tt, *J* = 7.5, 1.5 Hz, 1H), 7.03-7.05 (m, 1H), 3.94 (septet, *J* = 6.0 Hz, 1H), 2.00 (d, *J* = 2.0 Hz, 3H), 1.50 (d, *J* = 6.0 Hz, 6H), 0.27 (s, 6H). <sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>) δ 139.1, 139.0, 138.7, 129.5, 128.4, 127.0, 65.3, 26.1, 16.2, -1.9. HRMS (EI, positive) *m/z* calcd for C<sub>14</sub>H<sub>22</sub>OSi<sup>+</sup> [M]<sup>+</sup>: 234.1434, found: 234.1436.





## 12. References

- (1) T. Tsuda, T. Hashimoto, T. Saegusa, *J. Am. Chem. Soc.* 1972, **94**, 658.
- (2) M. Suginome, T. Matsuda, Y. Ito, *Organometallics* 2000, **19**, 4647.
- (3) T. Boebel, J. F. Hartwig, *Organometallics* 2008, **27**, 6013.
- (4) T. Ohmura, K. Masuda, H. Furukawa, M. Suginome, *Organometallics* 2007, **26**, 1291.
- (5) M. Suginome, T. Matsuda, H. Nakamura, Y. Ito, *Tetrahedron* 1999, **55**, 8787.
- (6) K. Semba, M. Yoshizawa, Y. Ohtagaki, Y. Nakao, *Bull. Chem. Soc. Jpn.* 2017, **90**, 1340.

## 13. <sup>1</sup>H and <sup>13</sup>C NMR Spectra of Products

<sup>1</sup>H and <sup>13</sup>C NMR spectra of products are given in following pages.

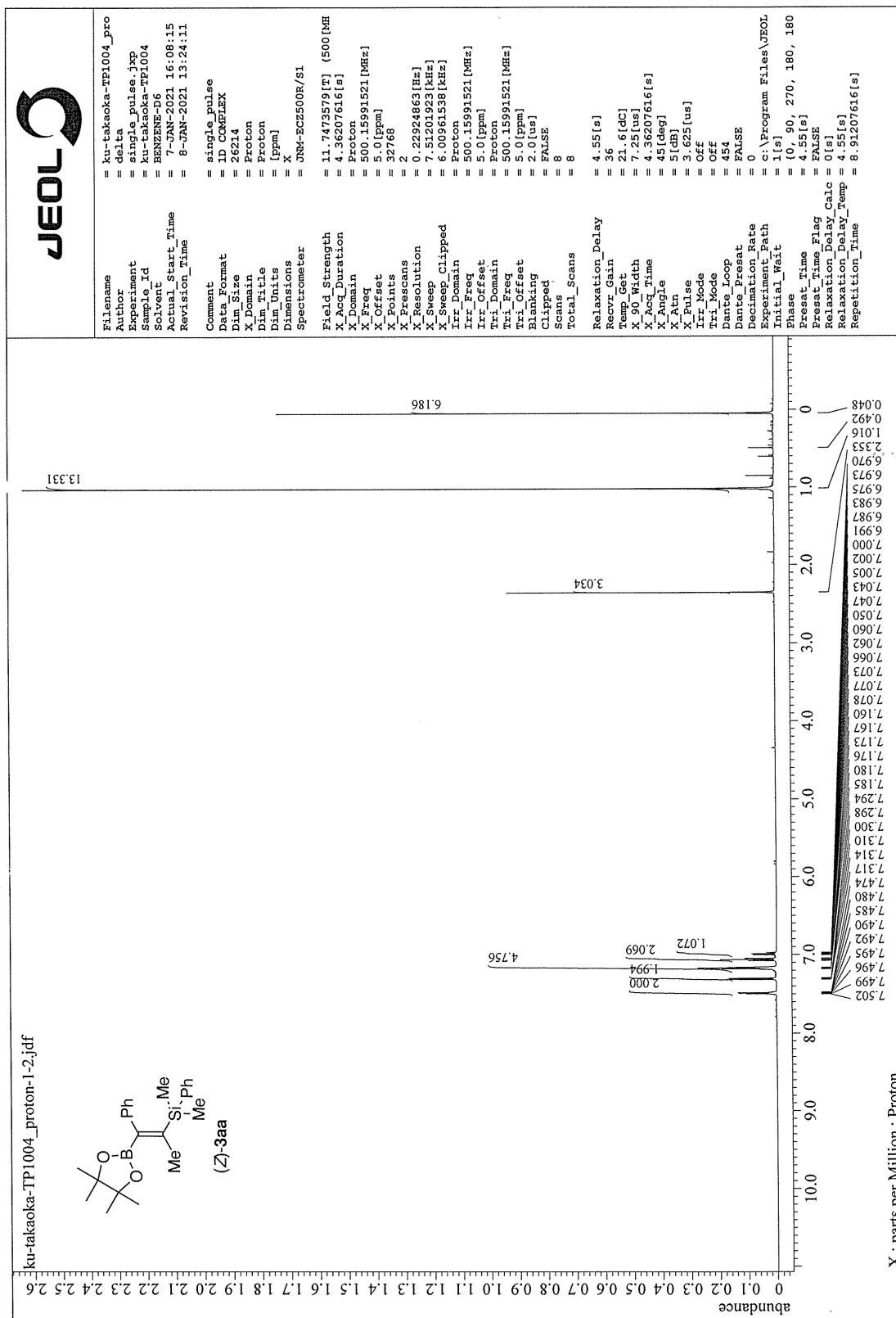


Figure S1. <sup>1</sup>H NMR Spectrum of (Z)-3aa (500 MHz, C<sub>6</sub>D<sub>6</sub>)

STANDARD PROTON PARAMETERS

Sample Name: TP1016kugel  
 Data Collected on: Agilent-NMR-vnmrs400  
 Archive directory:  
 Sample directory:  
 FidFile: TP1016kugel  
 Pulse Sequence: PROTON (s2pul)  
 Solvent: cdcl3  
 Data collected on: Jan 8 2021

Temp. 25.0 C / 298.1 K  
 Operator: vnmr1

Relax. delay 1.500 sec  
 Pulse 45.0 degrees  
 Acq. time 3.500 sec  
 Width 6410.3 Hz  
 16 repetitions  
 OBSERVE H1, 399.8841861 MHz  
 DATA PROCESSING  
 Line broadening 0.2 Hz  
 FT size 65536  
 Total time 1 min 20 sec

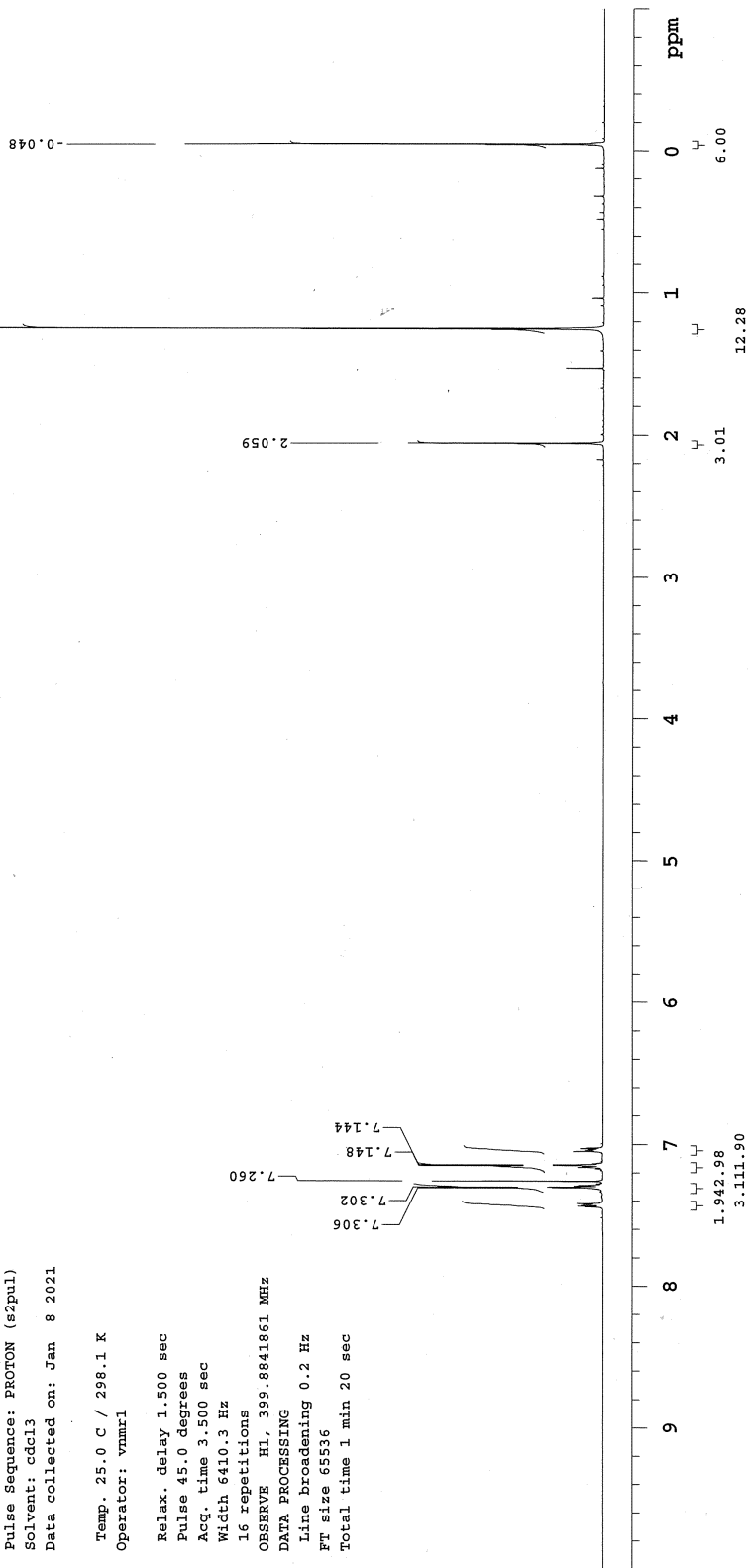
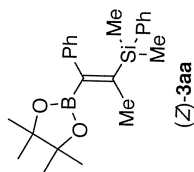


Figure S2. <sup>1</sup>H NMR Spectrum of (Z)-3aa (400 MHz, CDCl<sub>3</sub>)

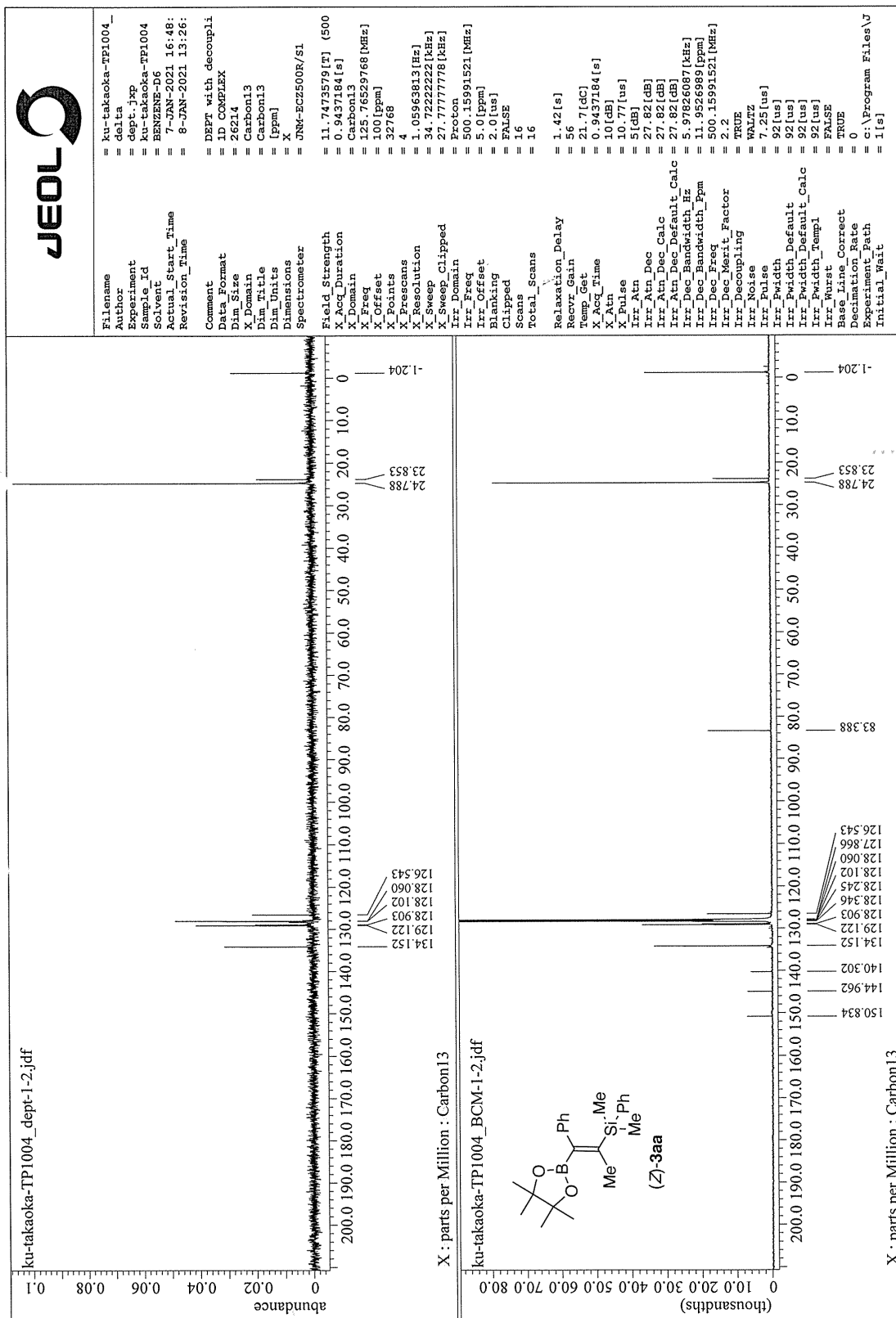


Figure S3. <sup>13</sup>C NMR Spectrum of (Z)-3aa (126 MHz, C<sub>6</sub>D<sub>6</sub>)

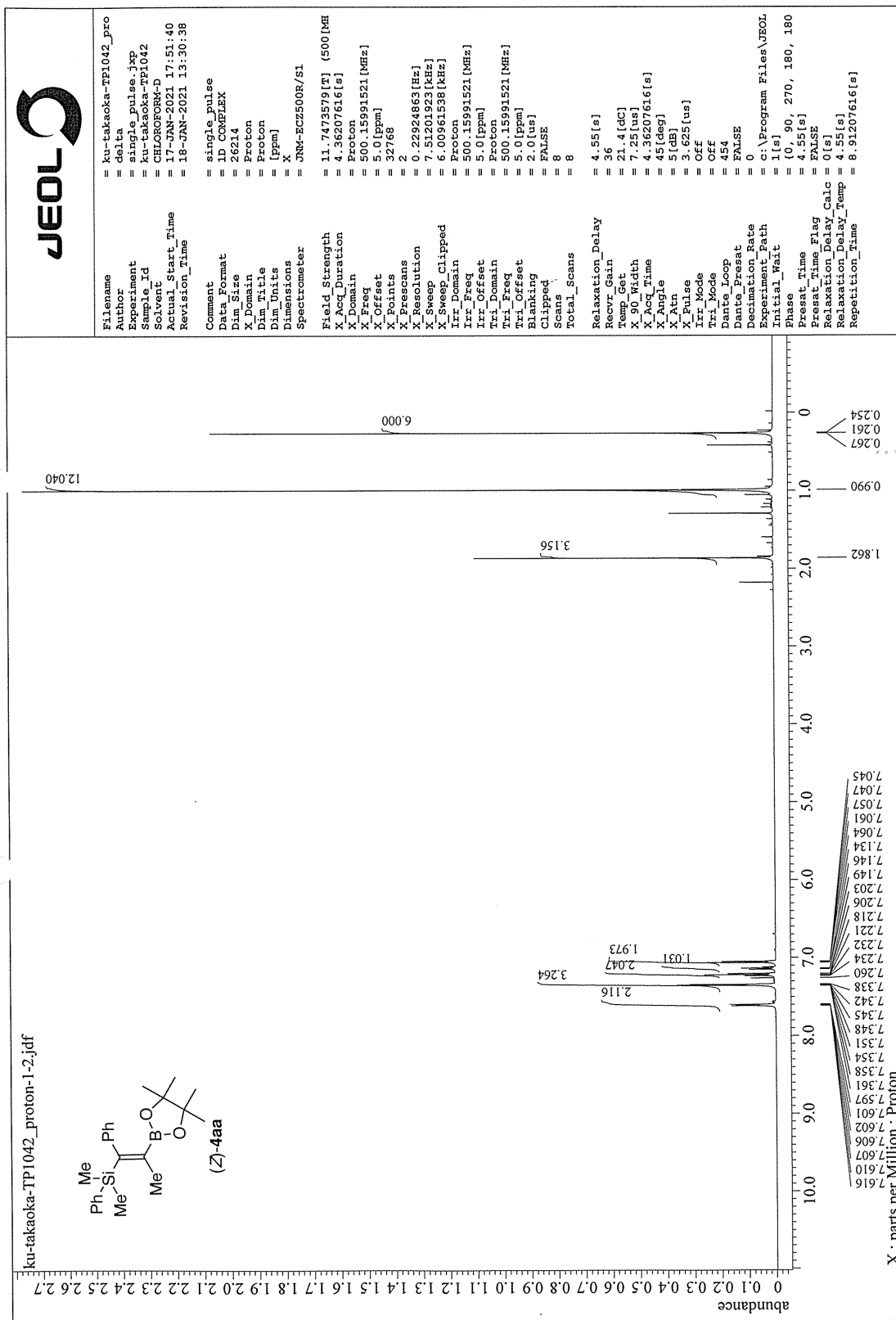


Figure S4. <sup>1</sup>H NMR Spectrum of (Z)-4aa (500 MHz, CDCl<sub>3</sub>)

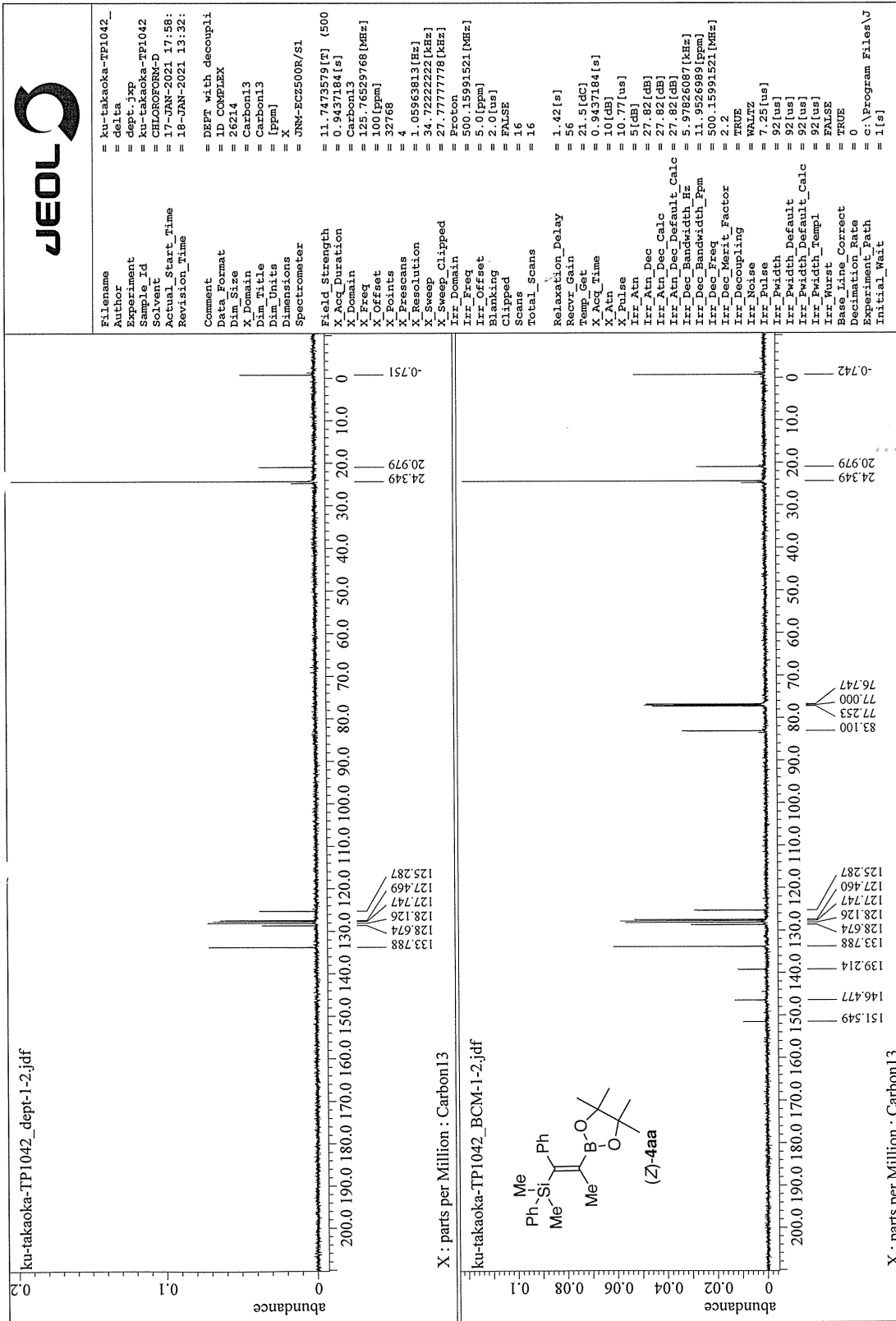


Figure S5.  $^{13}\text{C}$  NMR Spectrum of (Z)-4aa (126 MHz,  $\text{CDCl}_3$ )

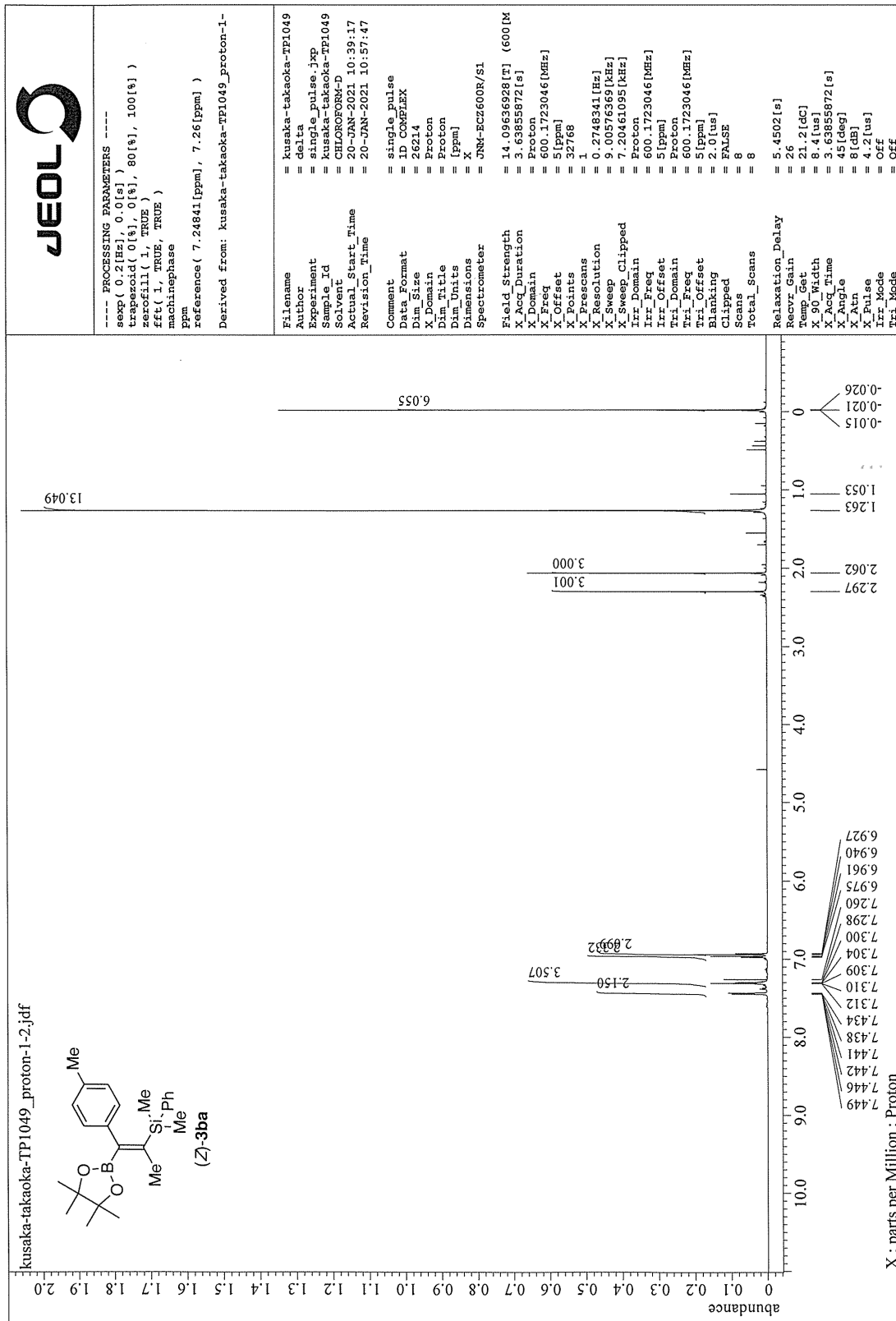


Figure S6. <sup>1</sup>H NMR Spectrum of (Z)-3ba (600 MHz, CDCl<sub>3</sub>)

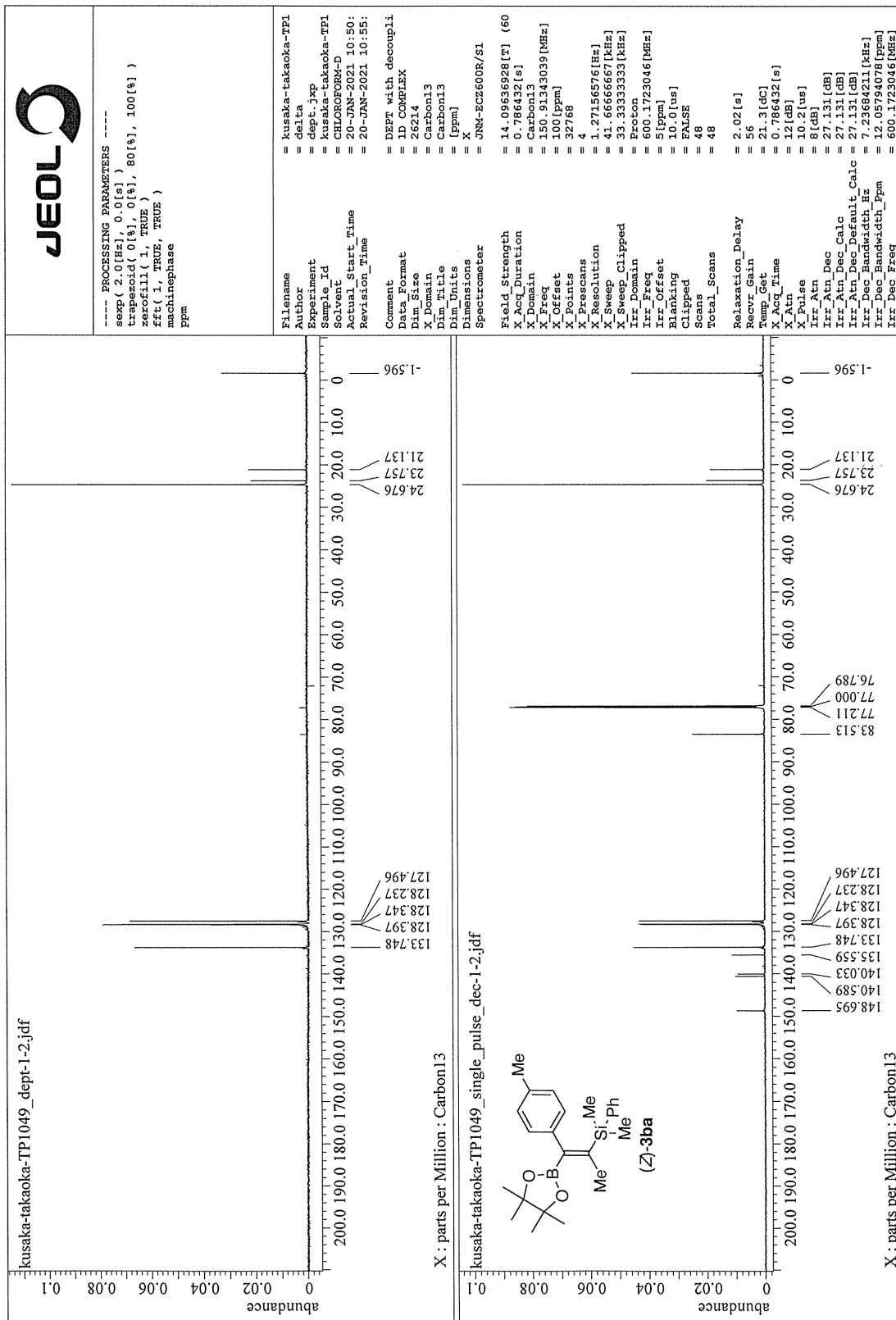


Figure S7. <sup>13</sup>C NMR Spectrum of (Z)-3ba (151 MHz, CDCl<sub>3</sub>)



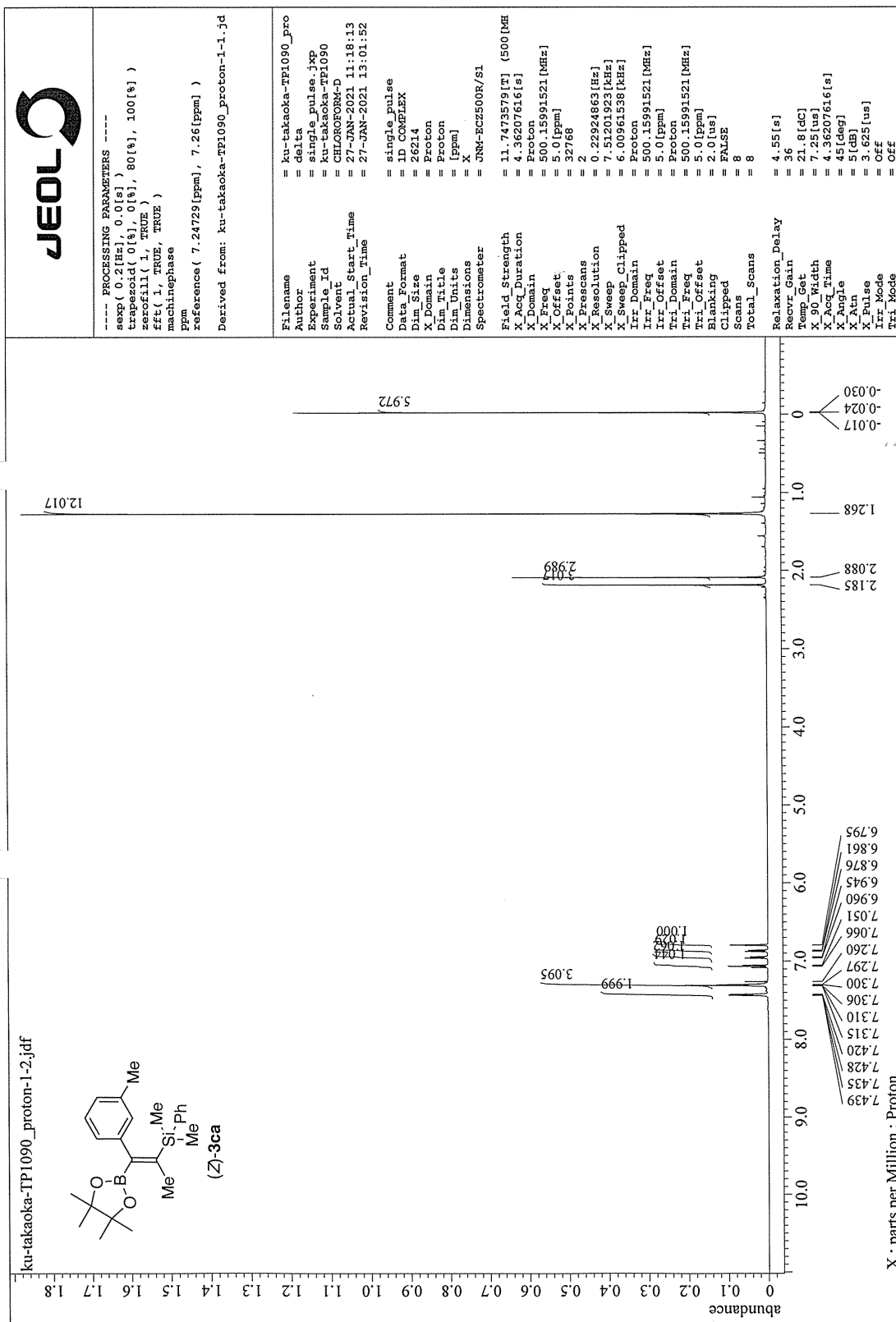


Figure S8. <sup>1</sup>H NMR Spectrum of (Z)-3ca (500 MHz, CDCl<sub>3</sub>)

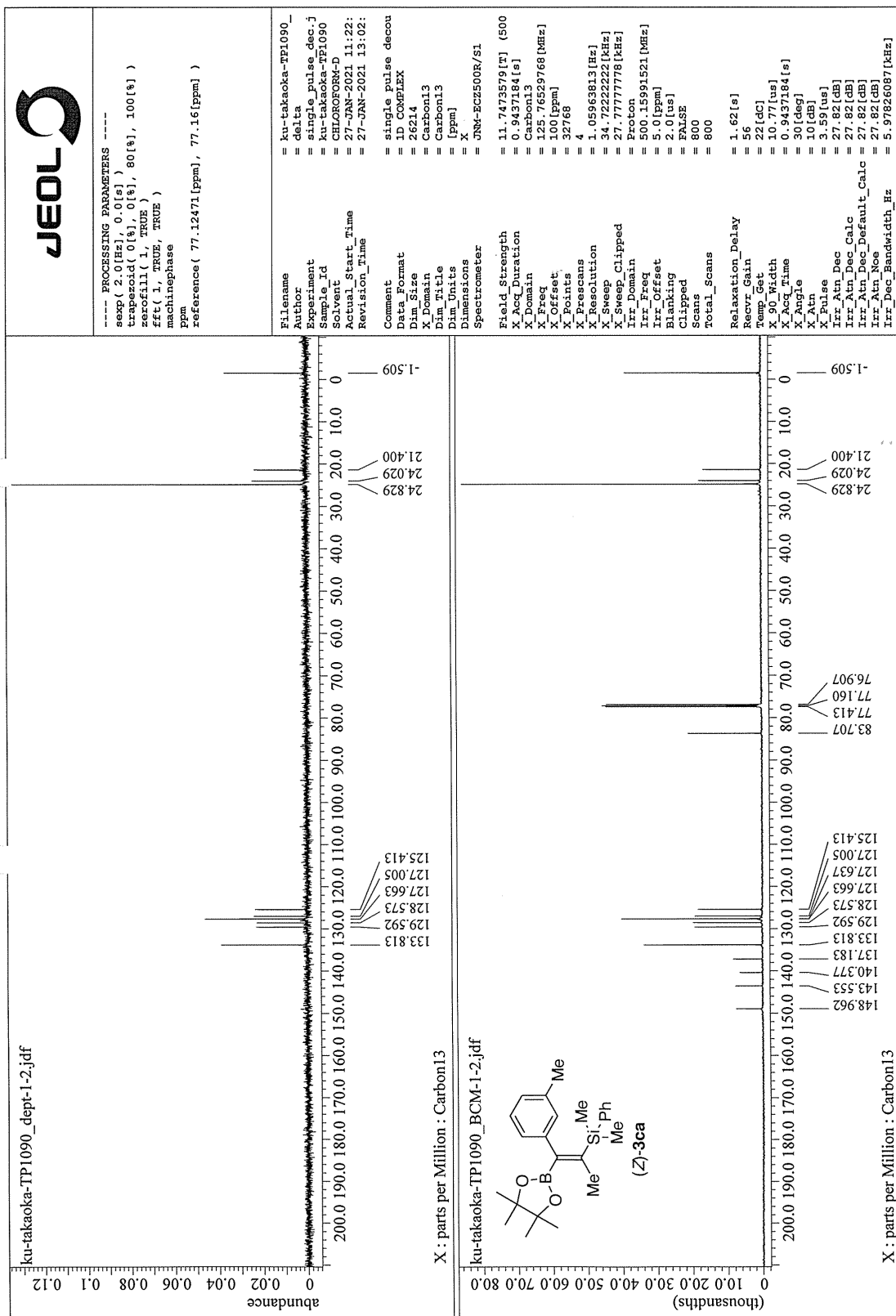


Figure S9. <sup>13</sup>C NMR Spectrum of (*Z*-3ca (126 MHz, CDCl<sub>3</sub>)

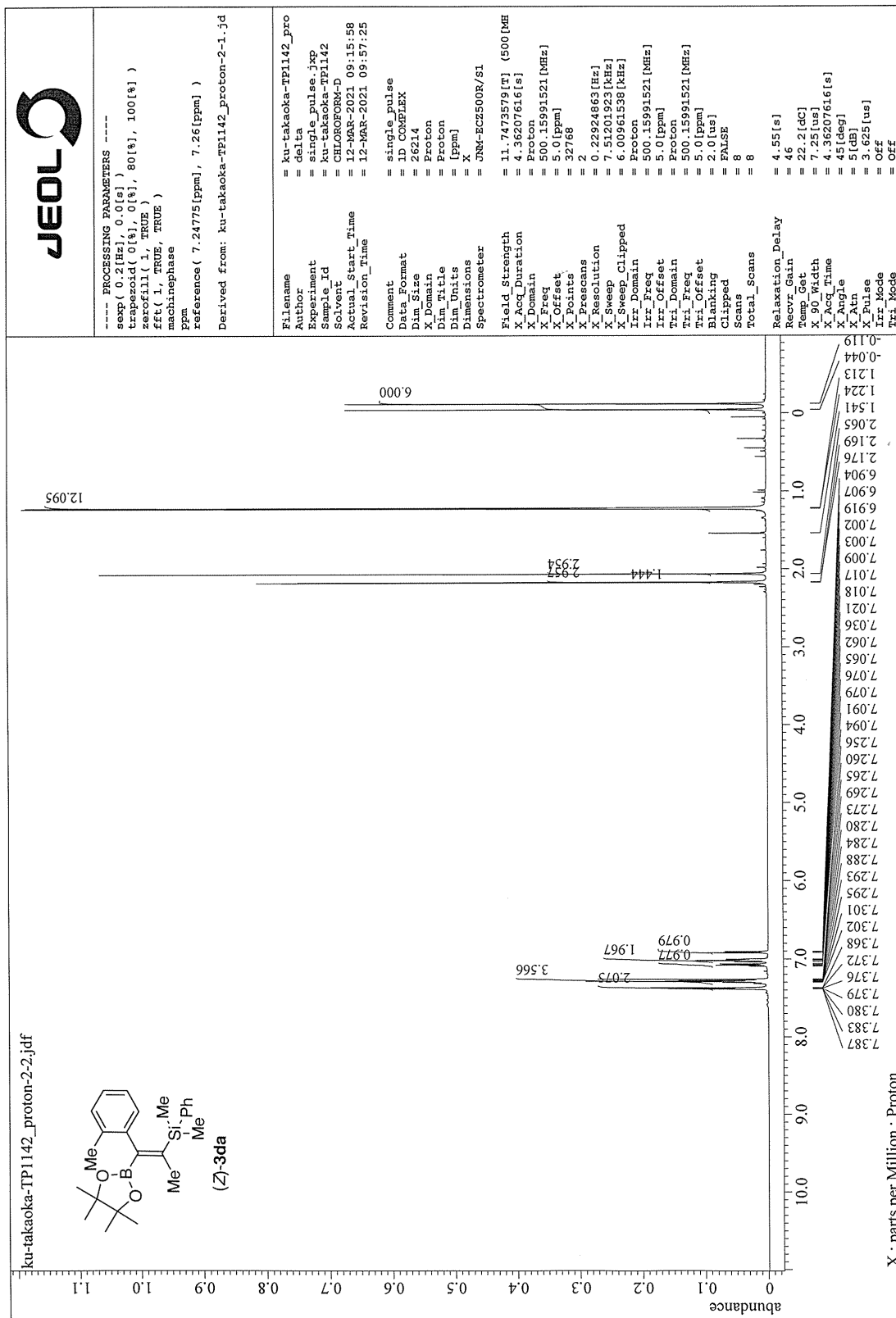


Figure S10. <sup>1</sup>H NMR Spectrum of (Z)-3da (500 MHz, CDCl<sub>3</sub>)

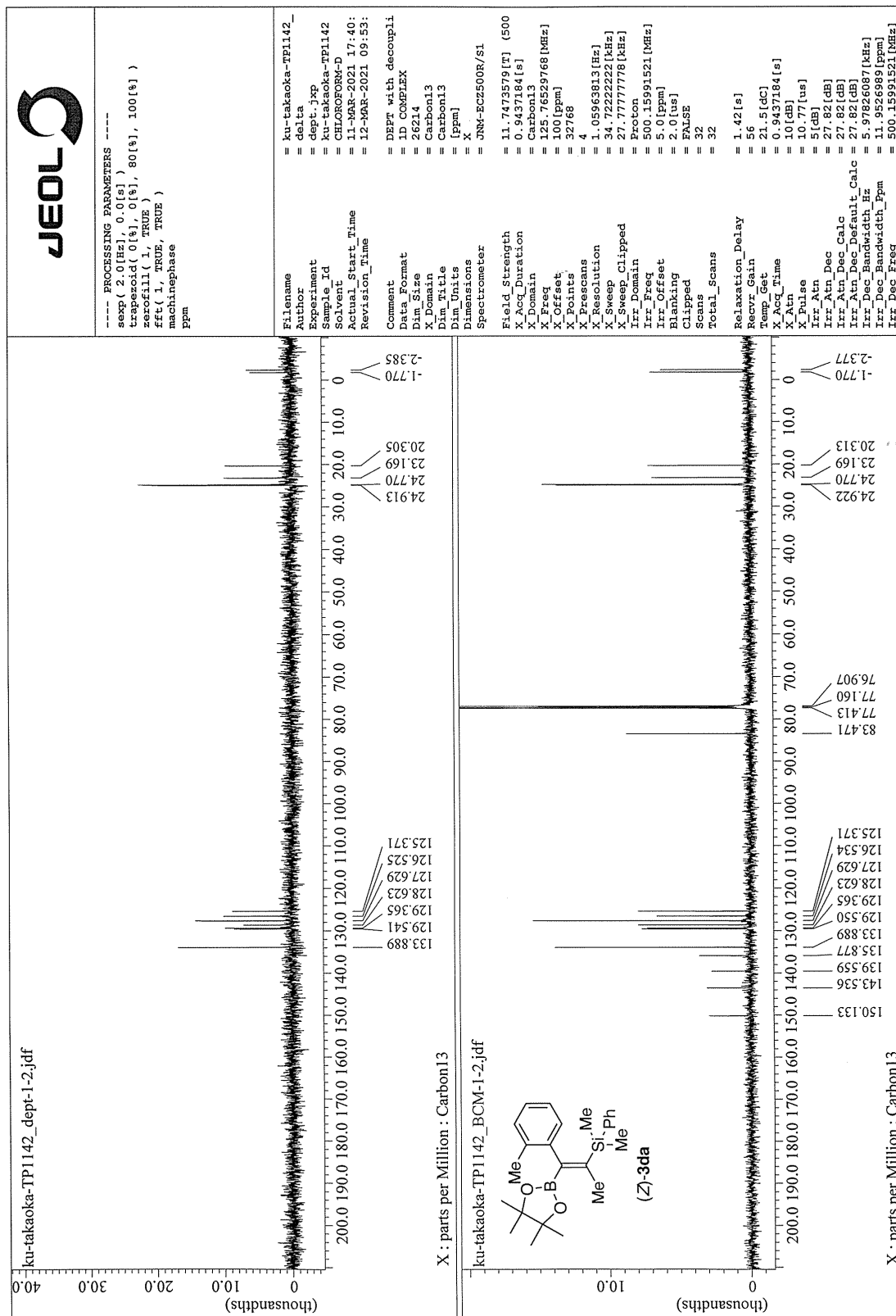


Figure S11. <sup>13</sup>C NMR Spectrum of (Z)-3da (126 MHz, CDCl<sub>3</sub>)

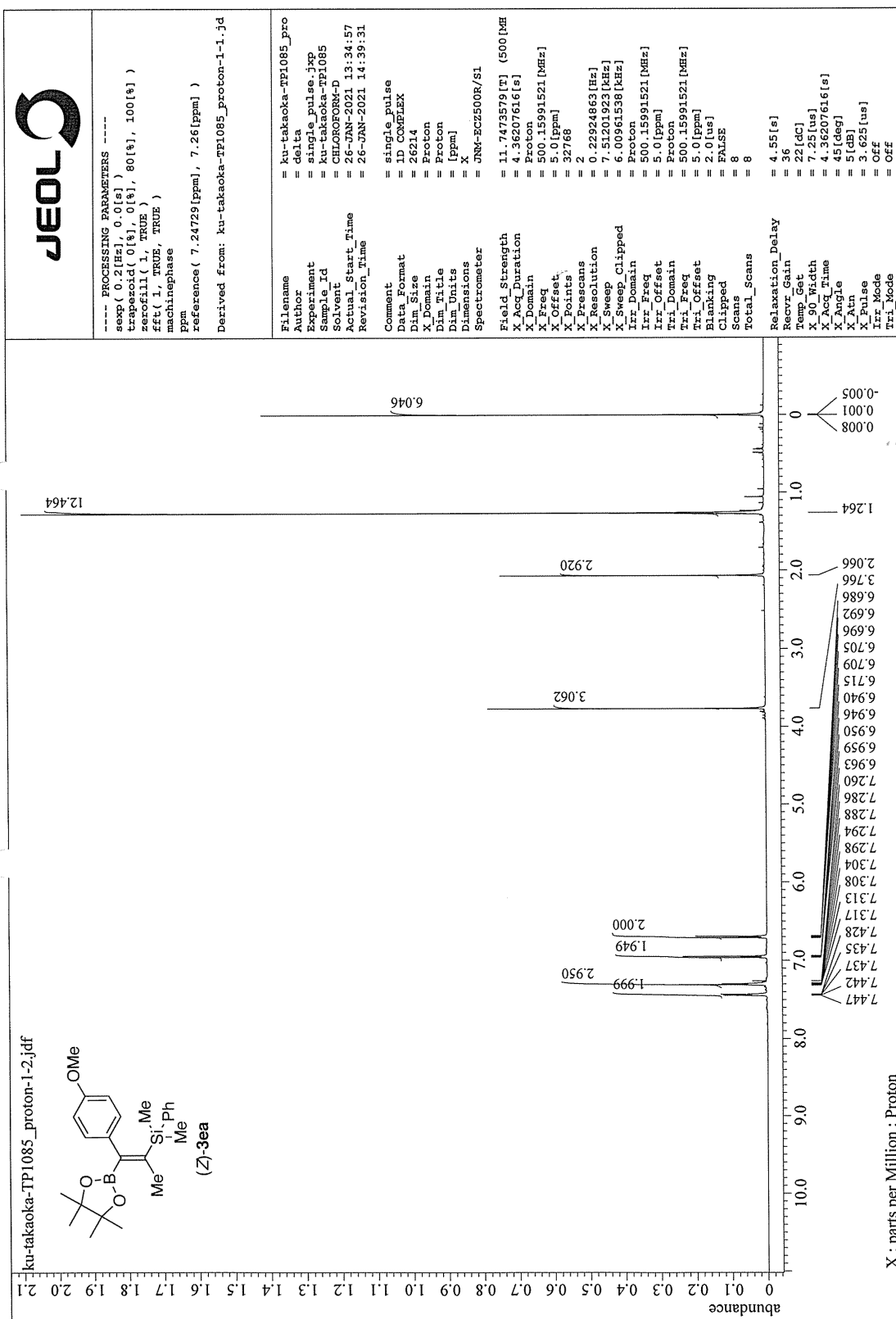


Figure S12. <sup>1</sup>H NMR Spectrum of (Z)-3ea (500 MHz, CDCl<sub>3</sub>)

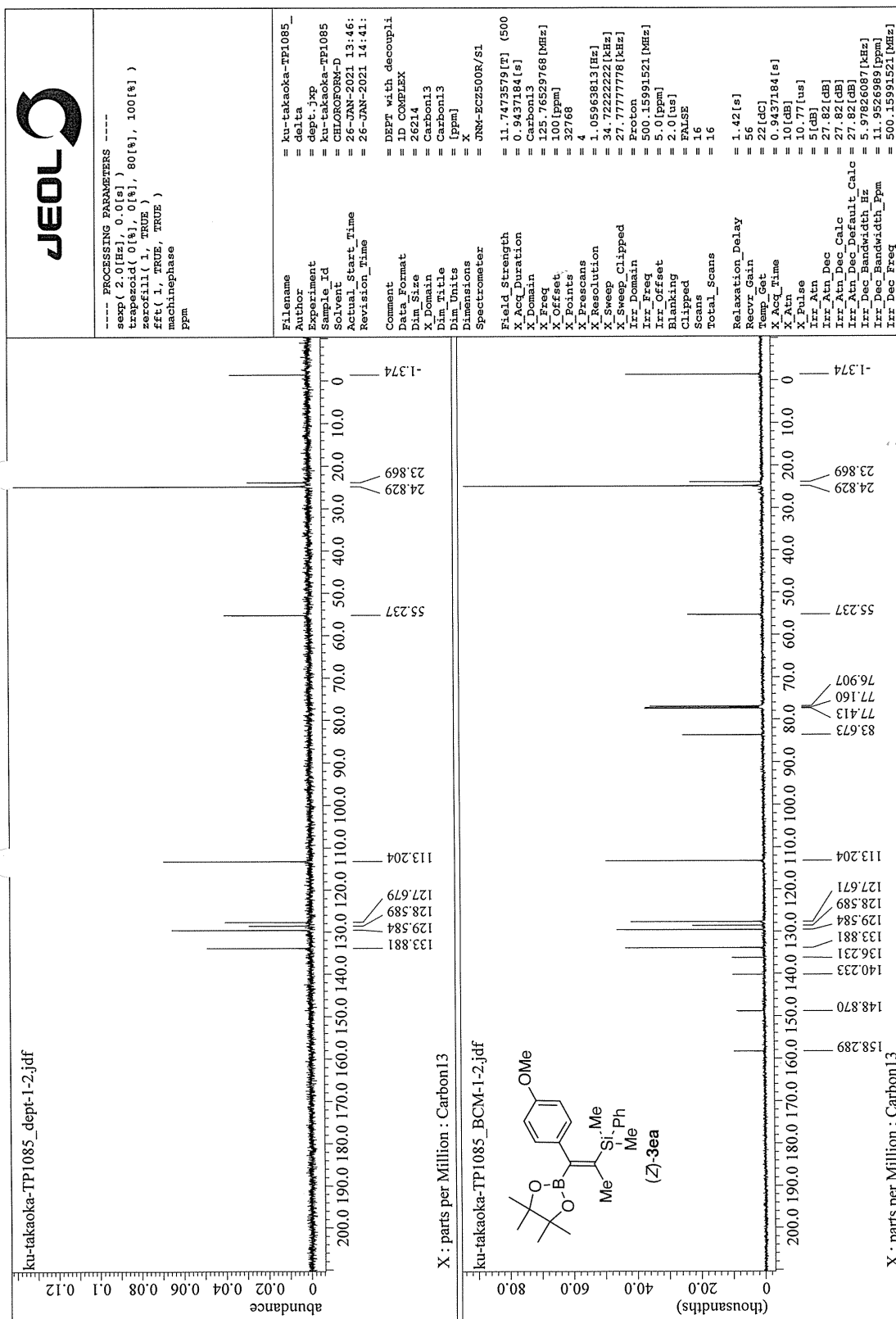


Figure S13. <sup>13</sup>C NMR Spectrum of (Z)-3ea (126 MHz, CDCl<sub>3</sub>)

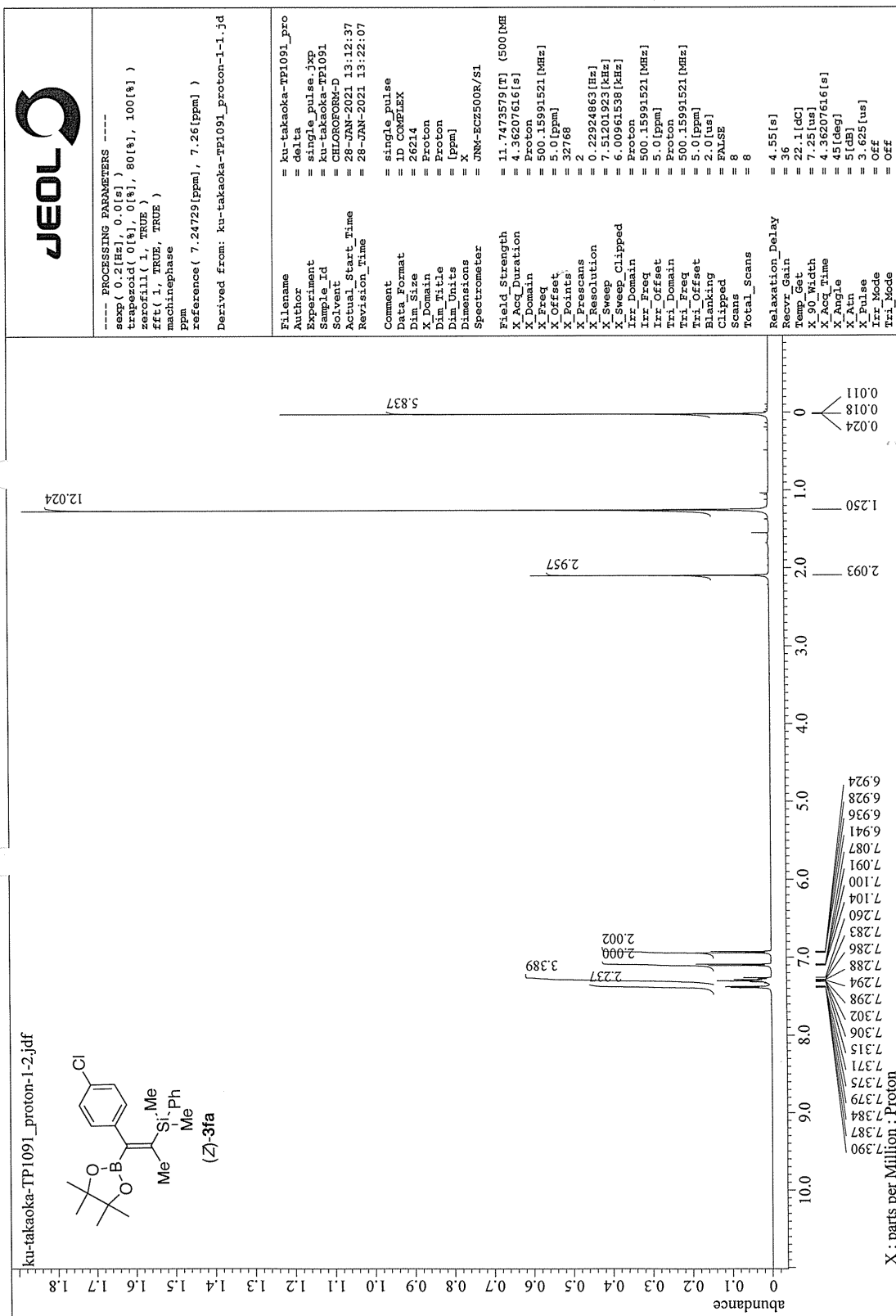


Figure S14. <sup>1</sup>H NMR Spectrum of (Z)-3fa (500 MHz, CDCl<sub>3</sub>)

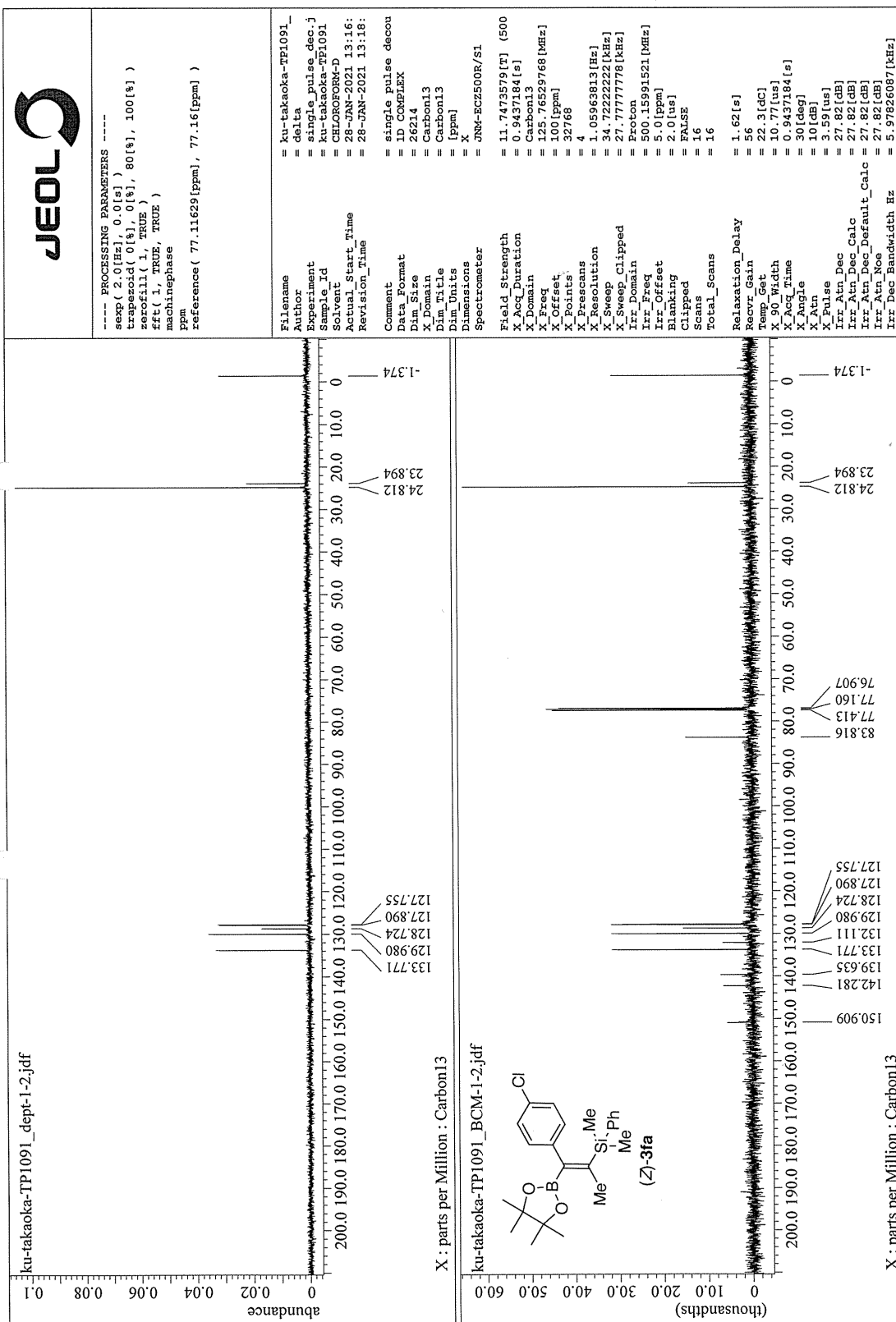


Figure S15. <sup>13</sup>C NMR Spectrum of (Z)-3fa (126 MHz, CDCl<sub>3</sub>)



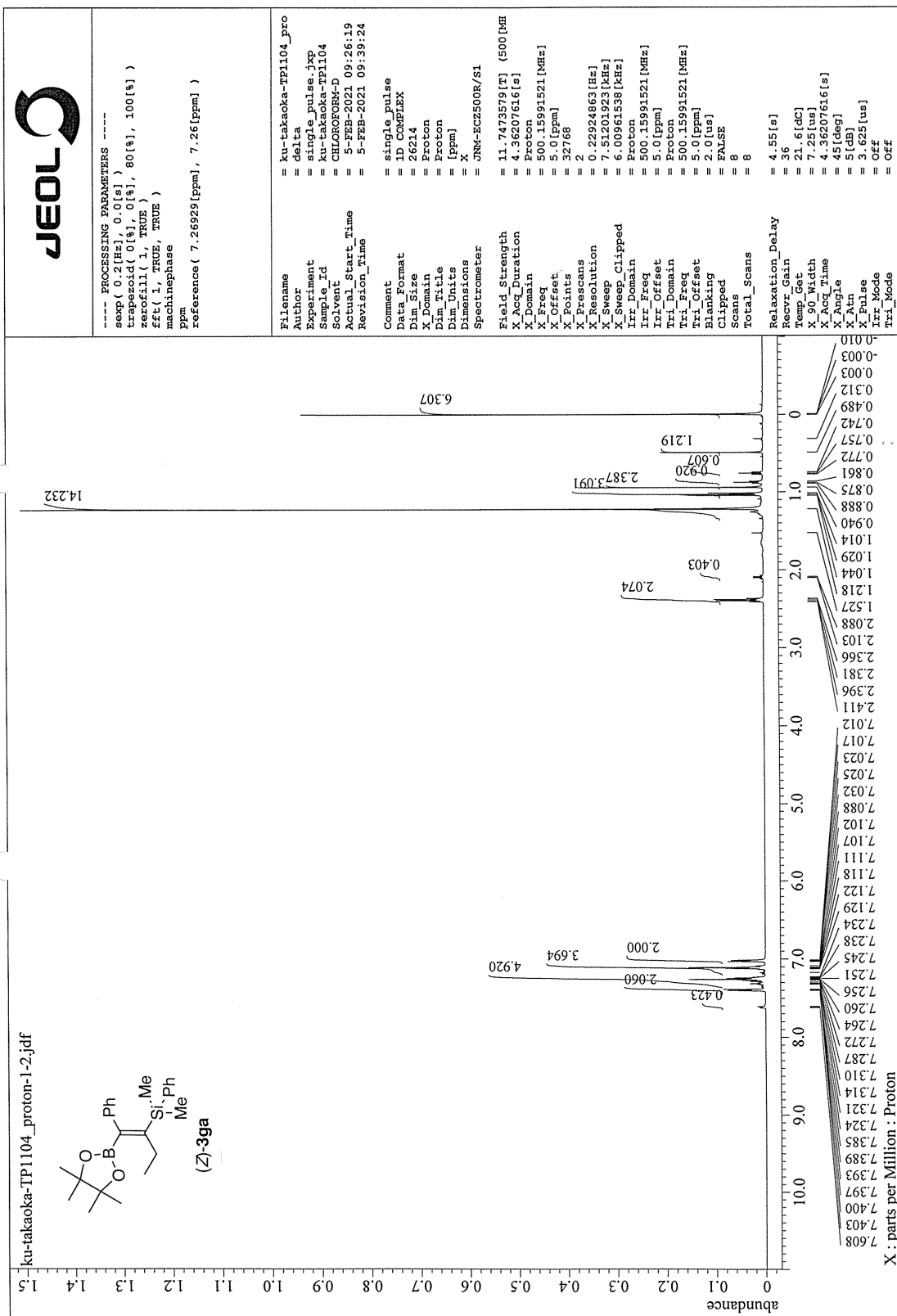


Figure S16. <sup>1</sup>H NMR Spectrum of (Z)-3ga (Z:E = 85:15) (500 MHz, CDCl<sub>3</sub>)

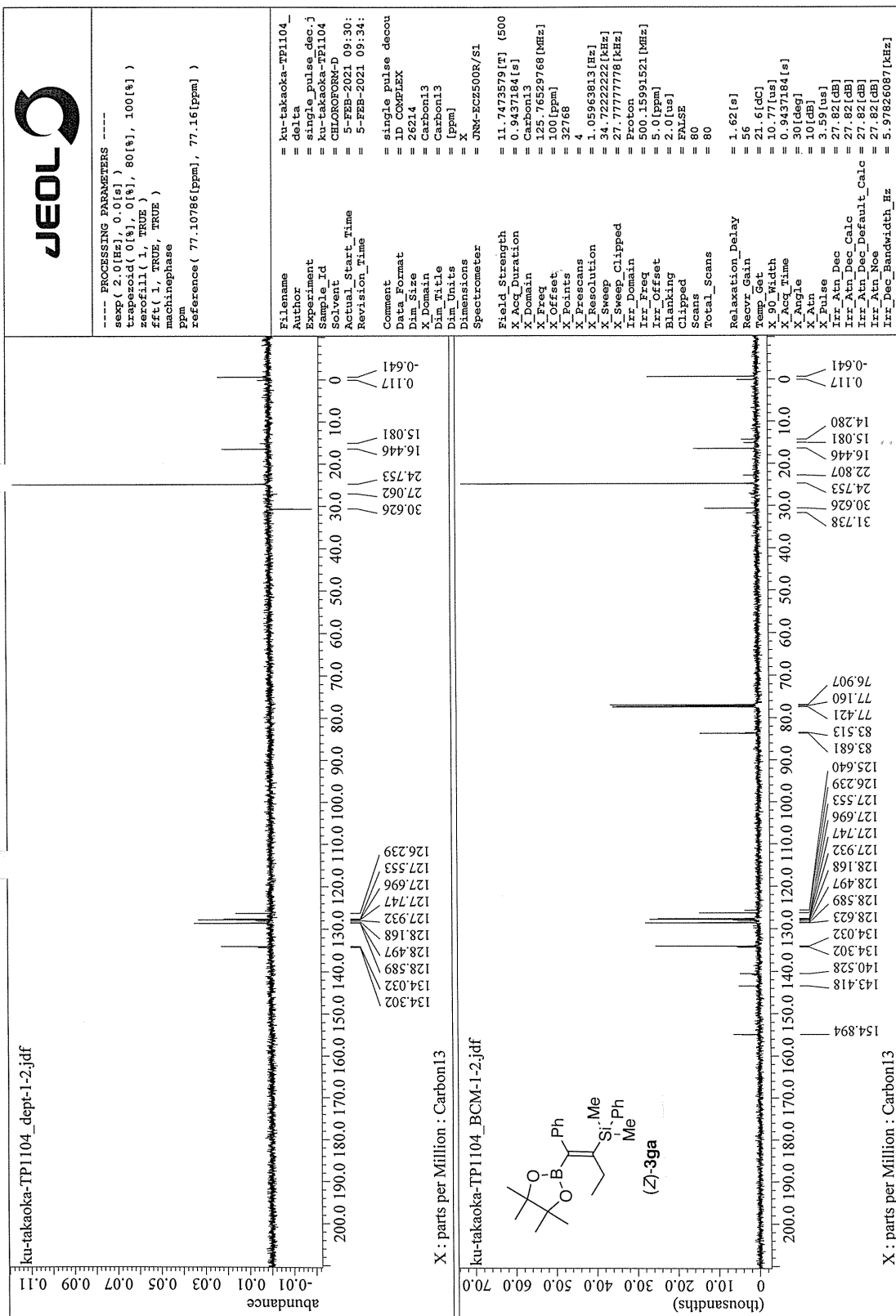


Figure S17. <sup>13</sup>C NMR Spectrum of (Z)-3ga (Z:E = 85:15) (126 MHz, CDCl<sub>3</sub>)

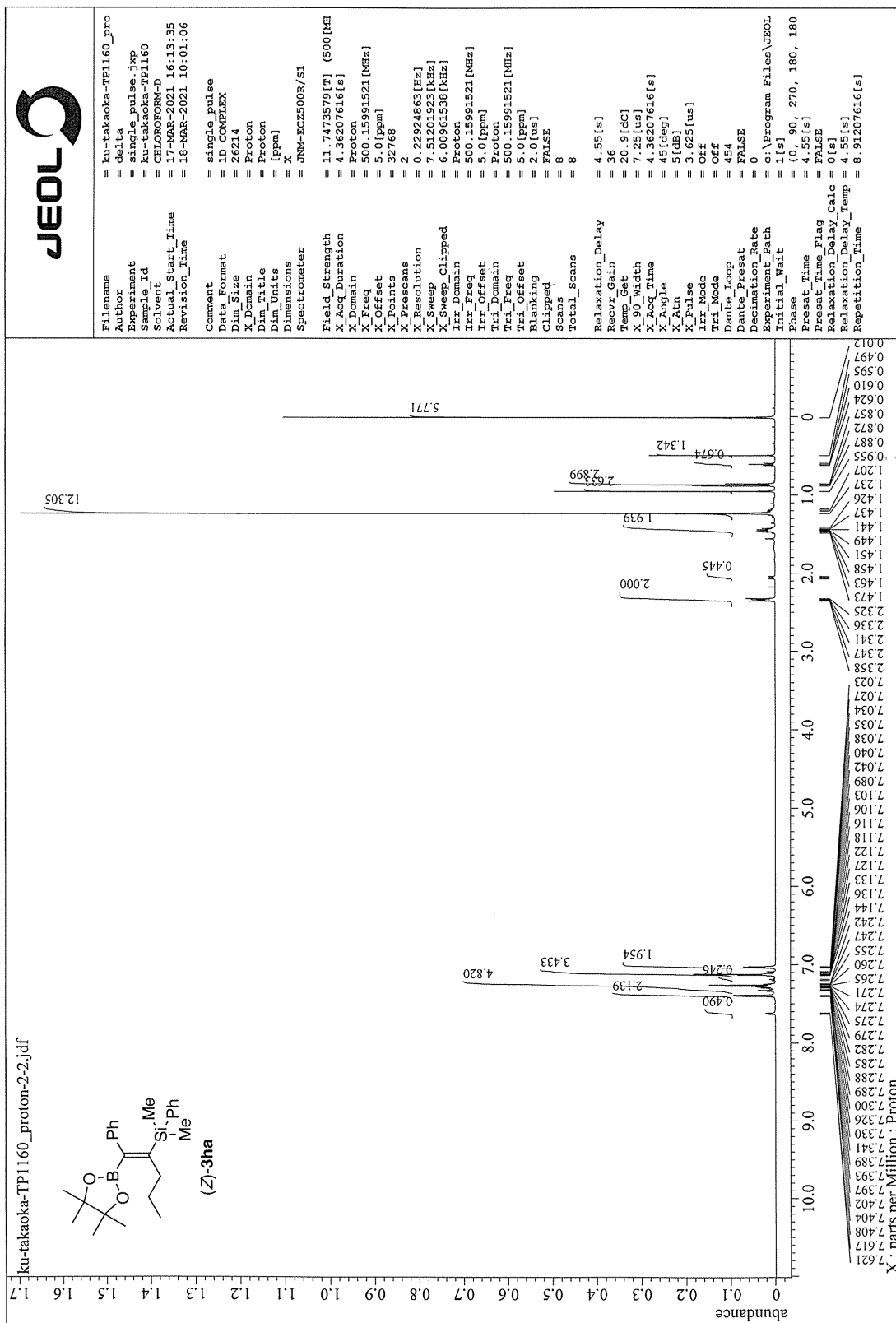


Figure S18. <sup>1</sup>H NMR Spectrum of (Z)-3ha (Z:E = 81:19) (500 MHz, CDCl<sub>3</sub>)

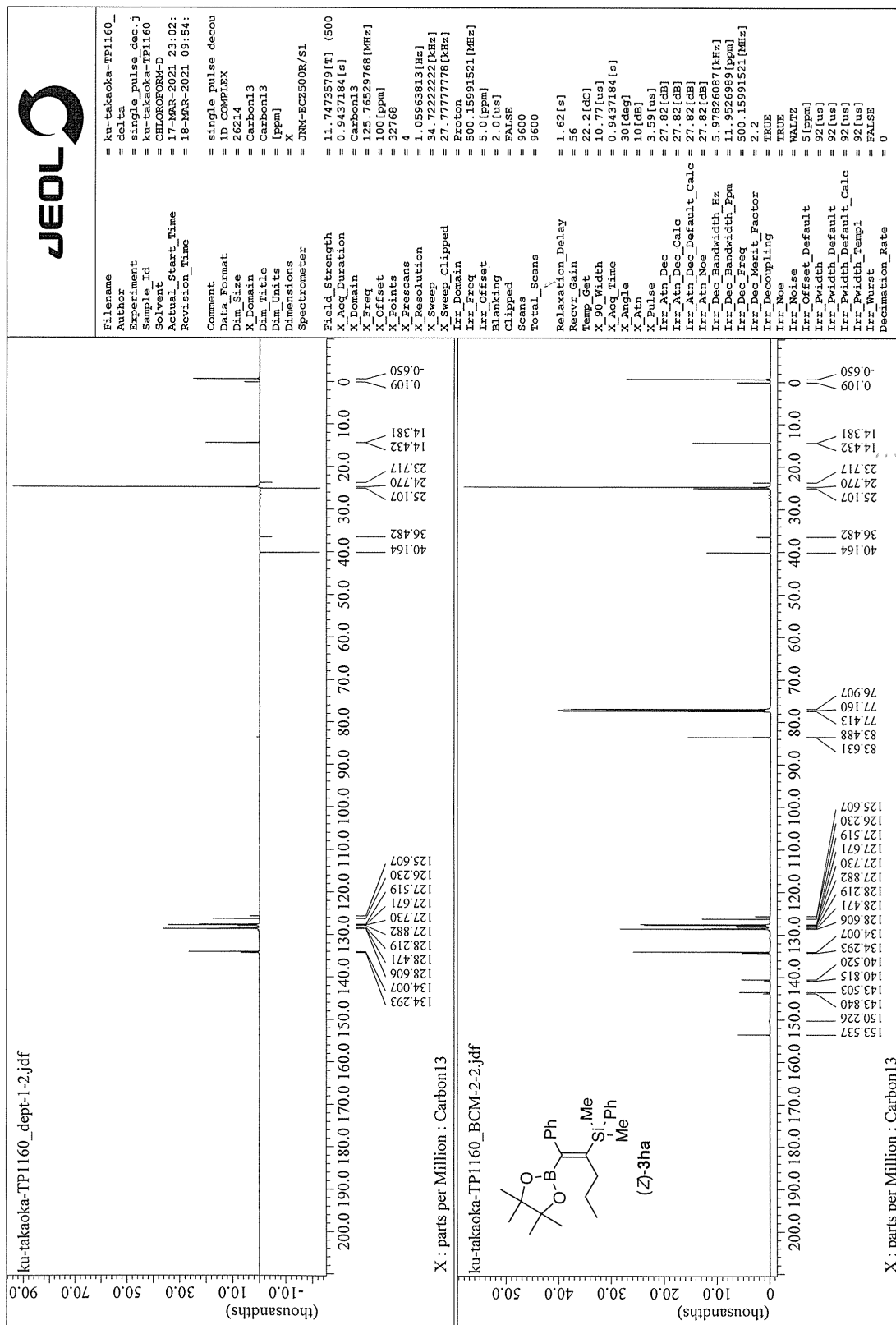


Figure S19. <sup>13</sup>C NMR Spectrum of (Z)-3ha (Z:E = 81:19) (101 MHz, CDCl<sub>3</sub>)

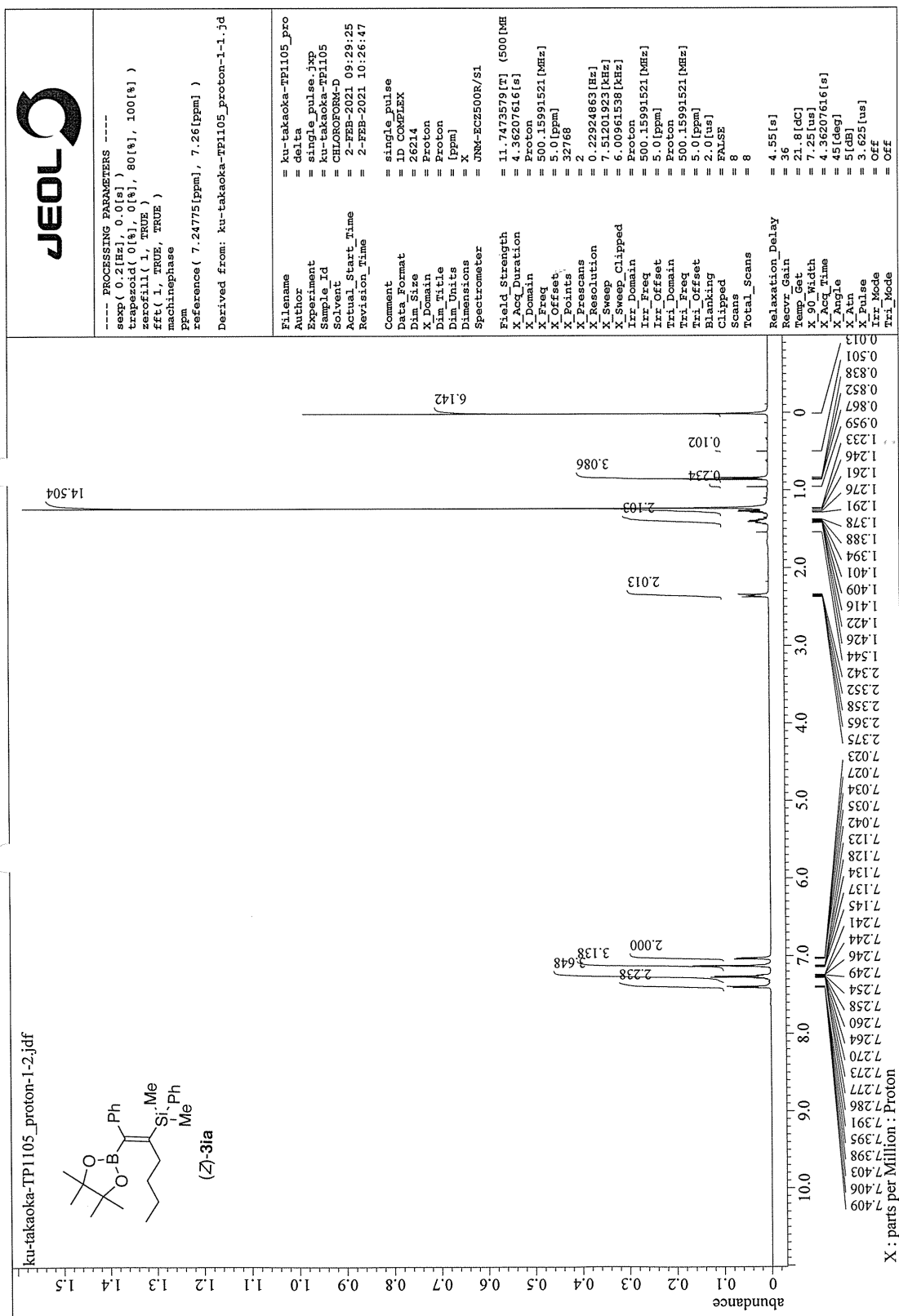


Figure S20. <sup>1</sup>H NMR Spectrum of (Z)-3ia (500 MHz, CDCl<sub>3</sub>)

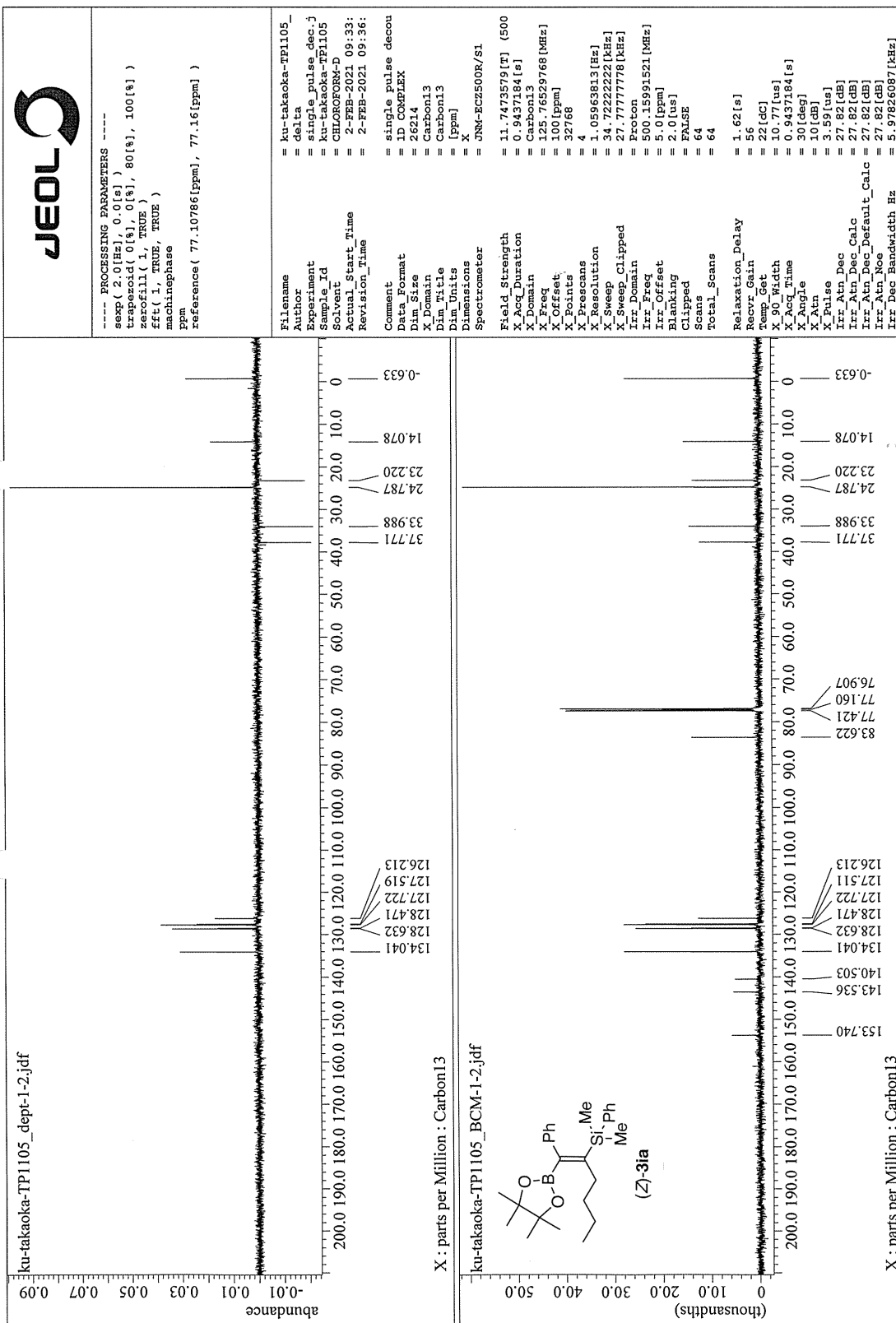


Figure S21. <sup>13</sup>C NMR Spectrum of (Z)-3ia (126 MHz, CDCl<sub>3</sub>)

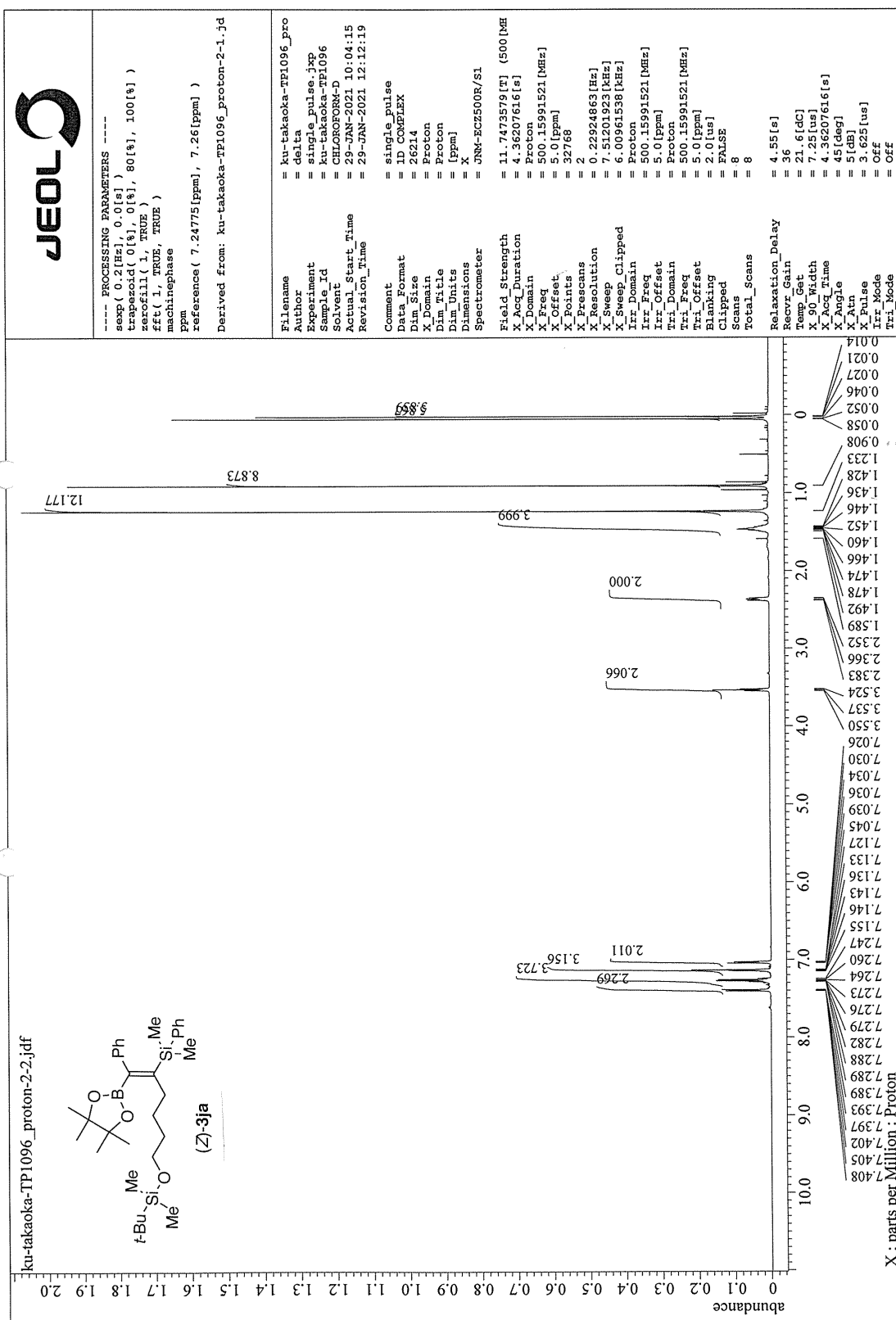


Figure S22. <sup>1</sup>H NMR Spectrum of (Z)-3ja (500 MHz, CDCl<sub>3</sub>)

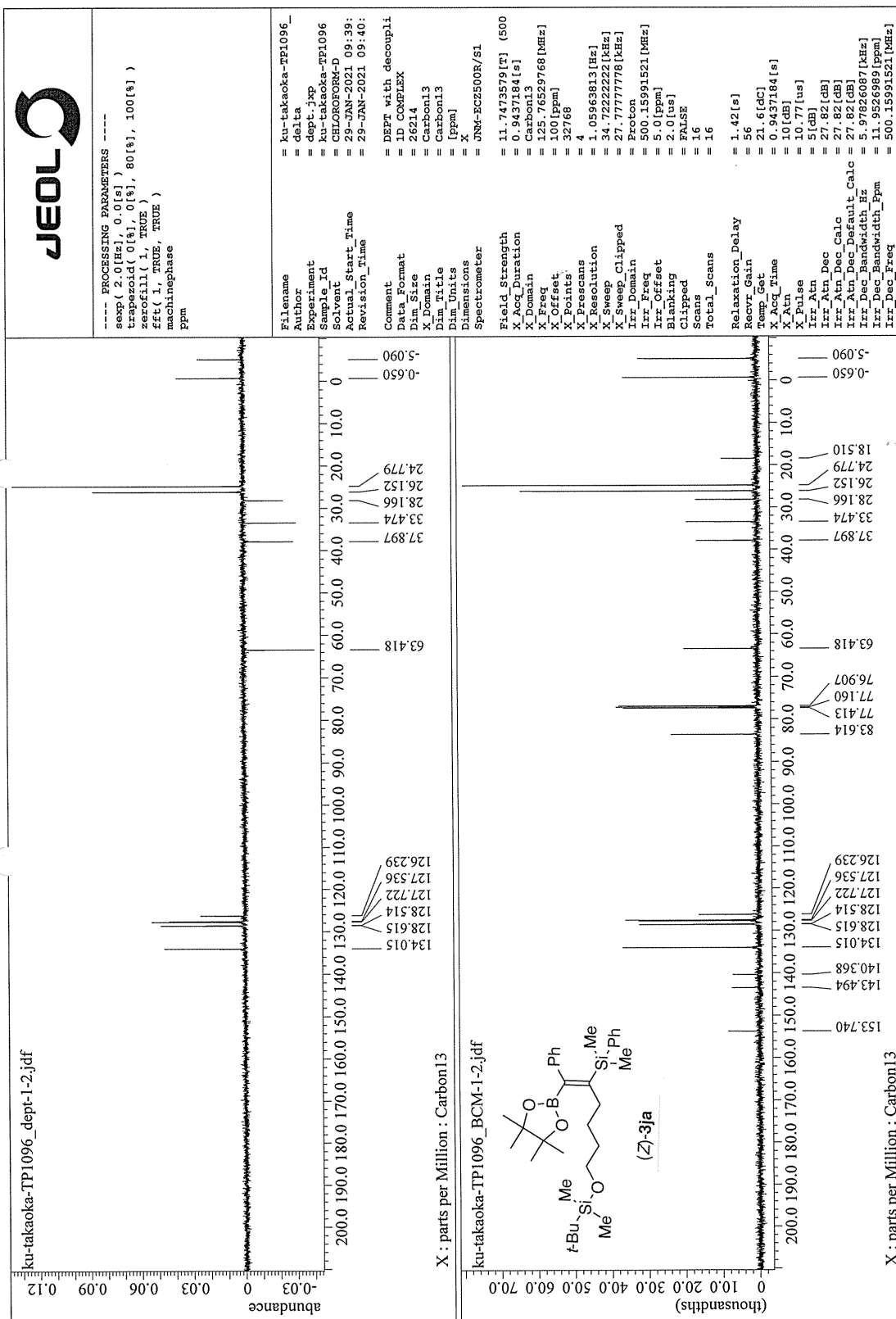


Figure S23. <sup>13</sup>C NMR Spectrum of (Z)-3ja (126 MHz, CDCl<sub>3</sub>)



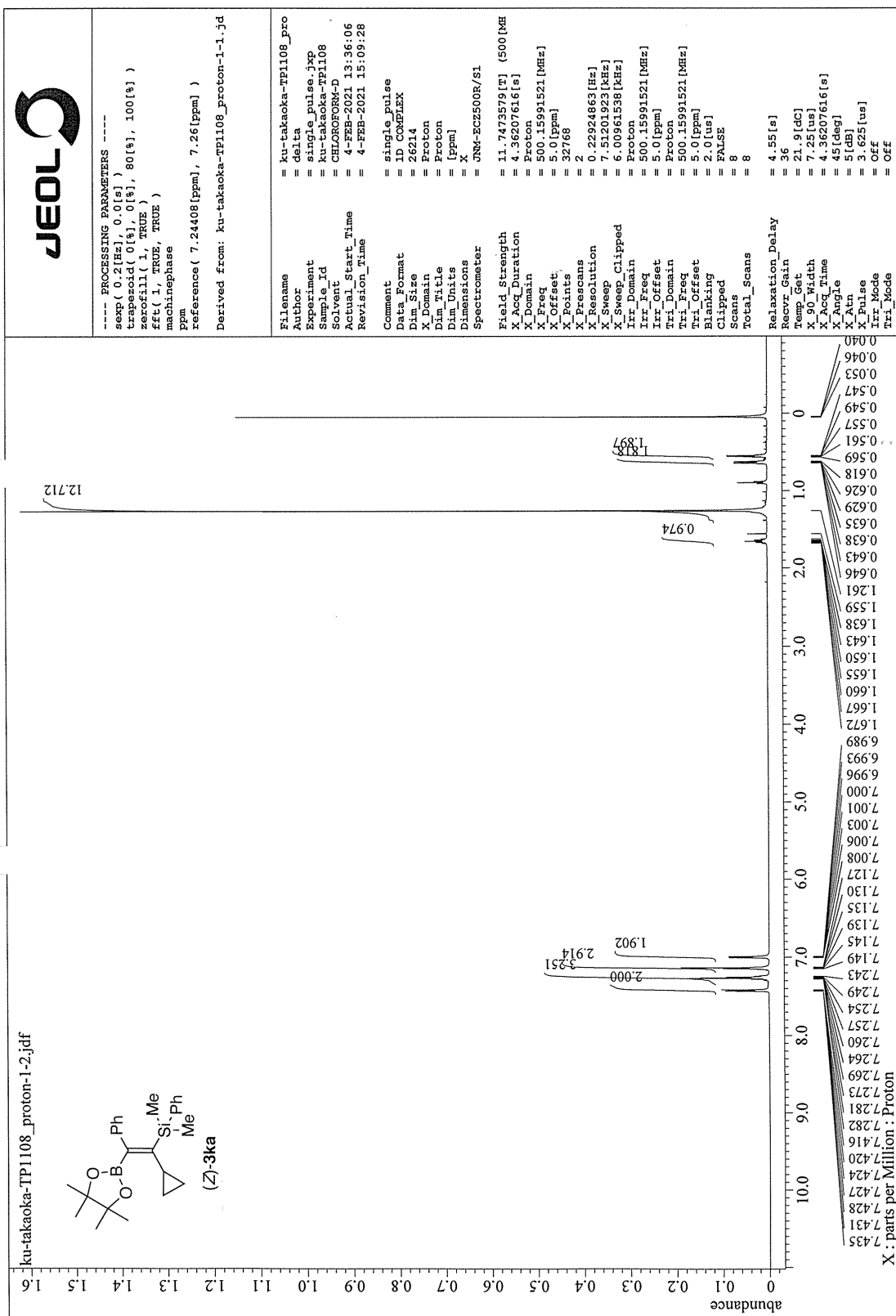


Figure S24. <sup>1</sup>H NMR Spectrum of (Z)-3ka (500 MHz, CDCl<sub>3</sub>)

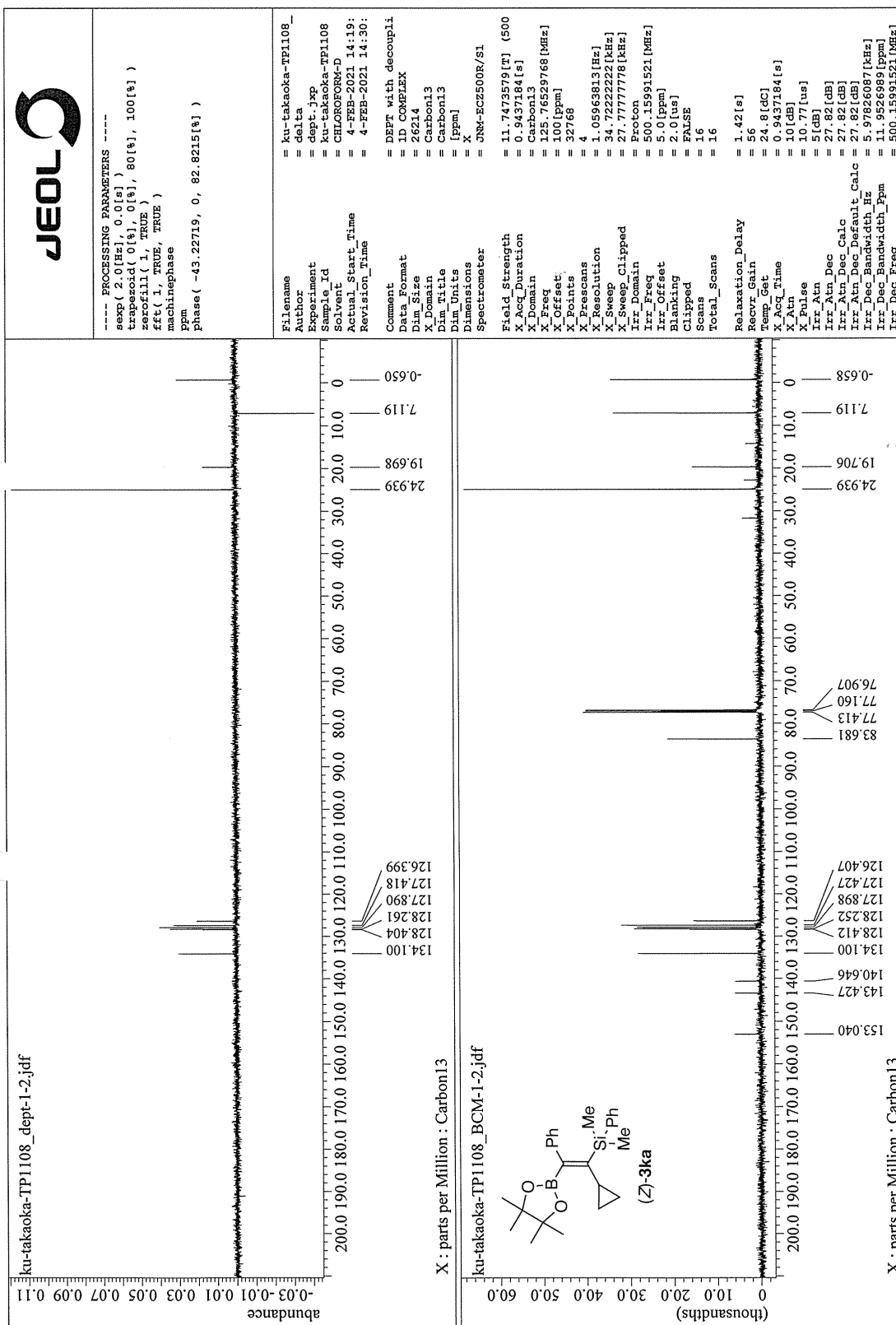


Figure S25. <sup>13</sup>C NMR Spectrum of (Z)-3ka (126 MHz, CDCl<sub>3</sub>)

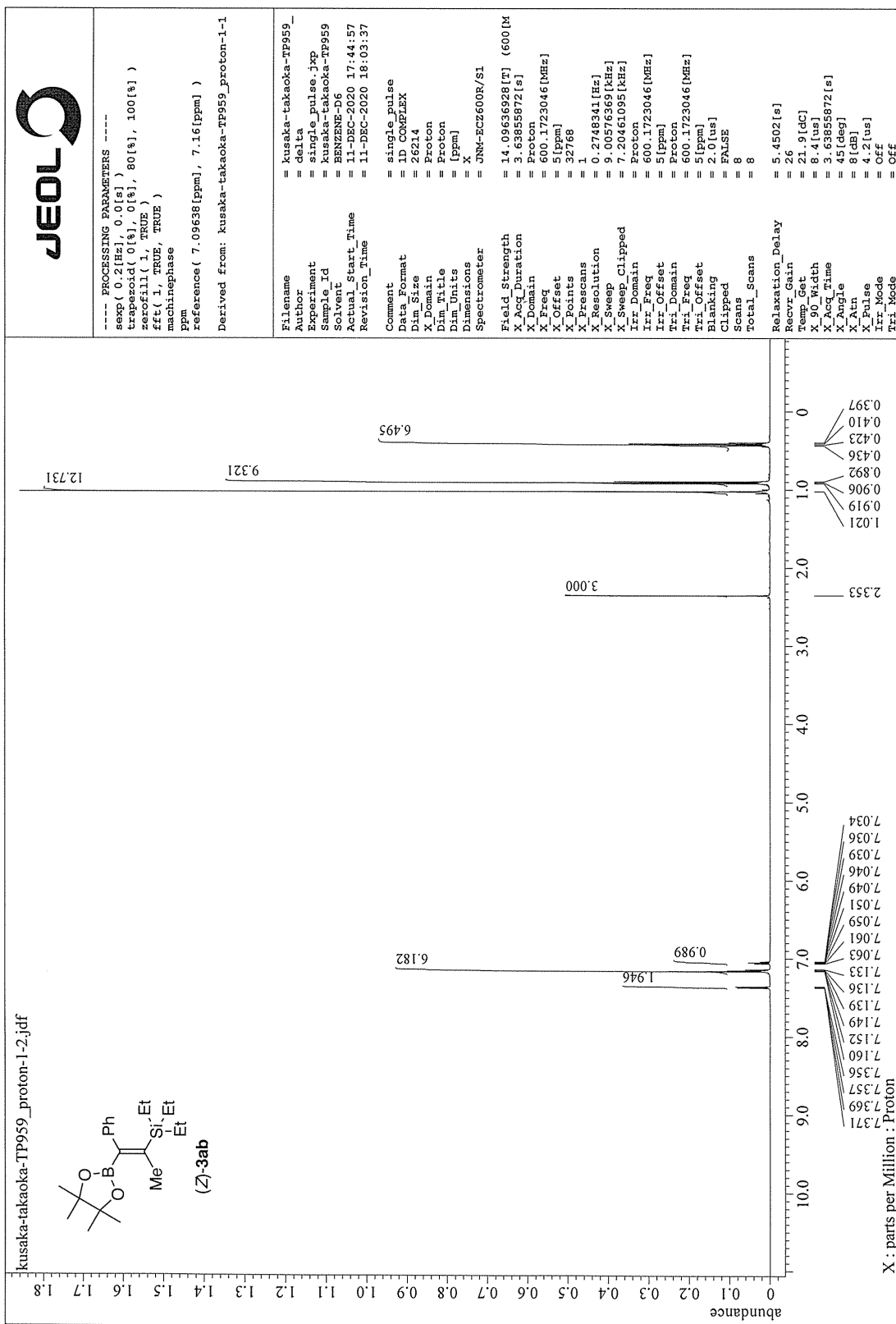


Figure S26. <sup>1</sup>H NMR Spectrum of (Z)-3ab (600 MHz, CDCl<sub>3</sub>)

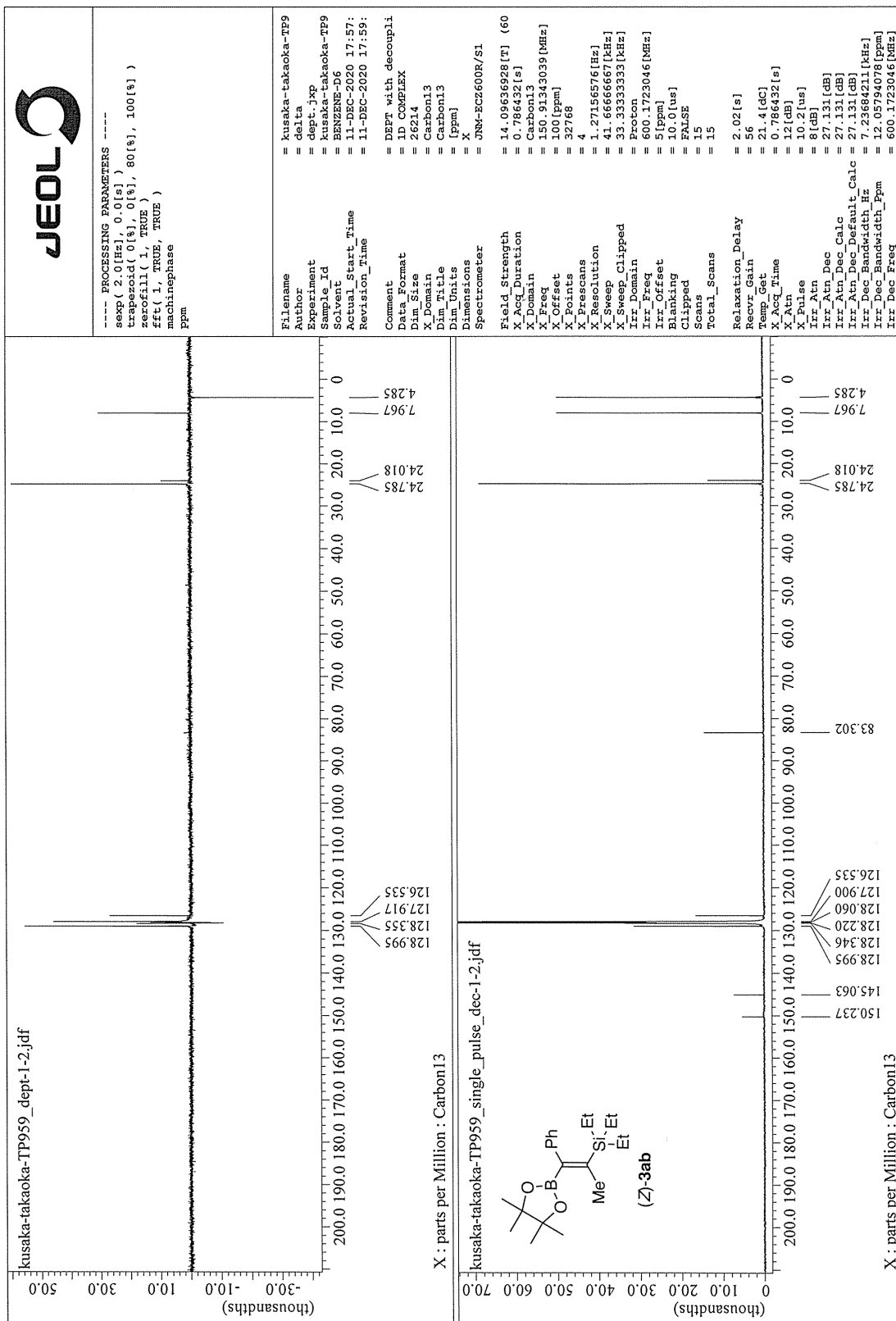


Figure S27. <sup>13</sup>C NMR Spectrum of (Z)-3ab (151 MHz, CDCl<sub>3</sub>)

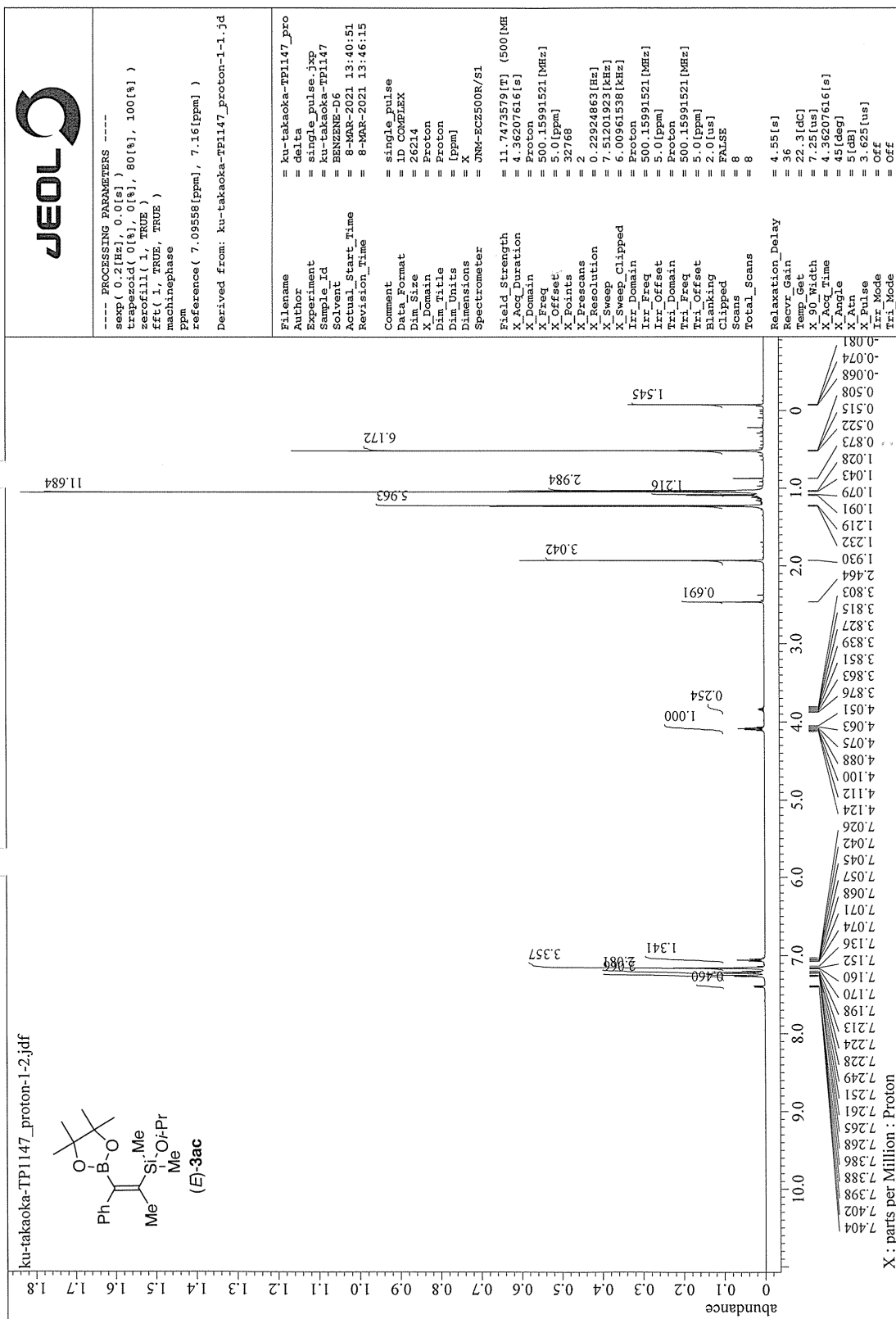


Figure S28. <sup>1</sup>H NMR Spectrum of (E)-3ac (Z:E = 20:80) (500 MHz, CDCl<sub>3</sub>)

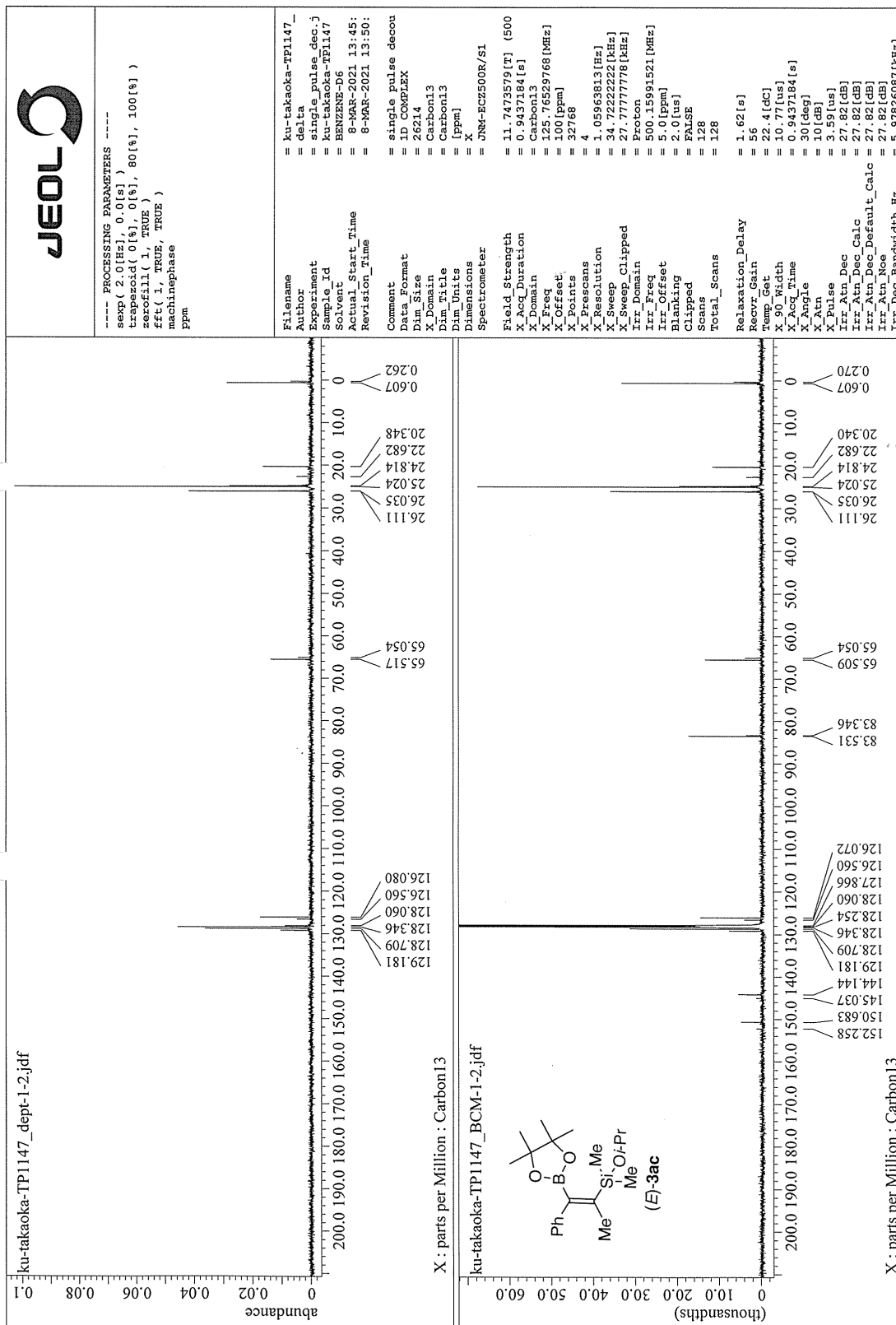


Figure S29. <sup>13</sup>C NMR Spectrum of (E)-3ac (Z:E = 20:80) (126 MHz, CDCl<sub>3</sub>)

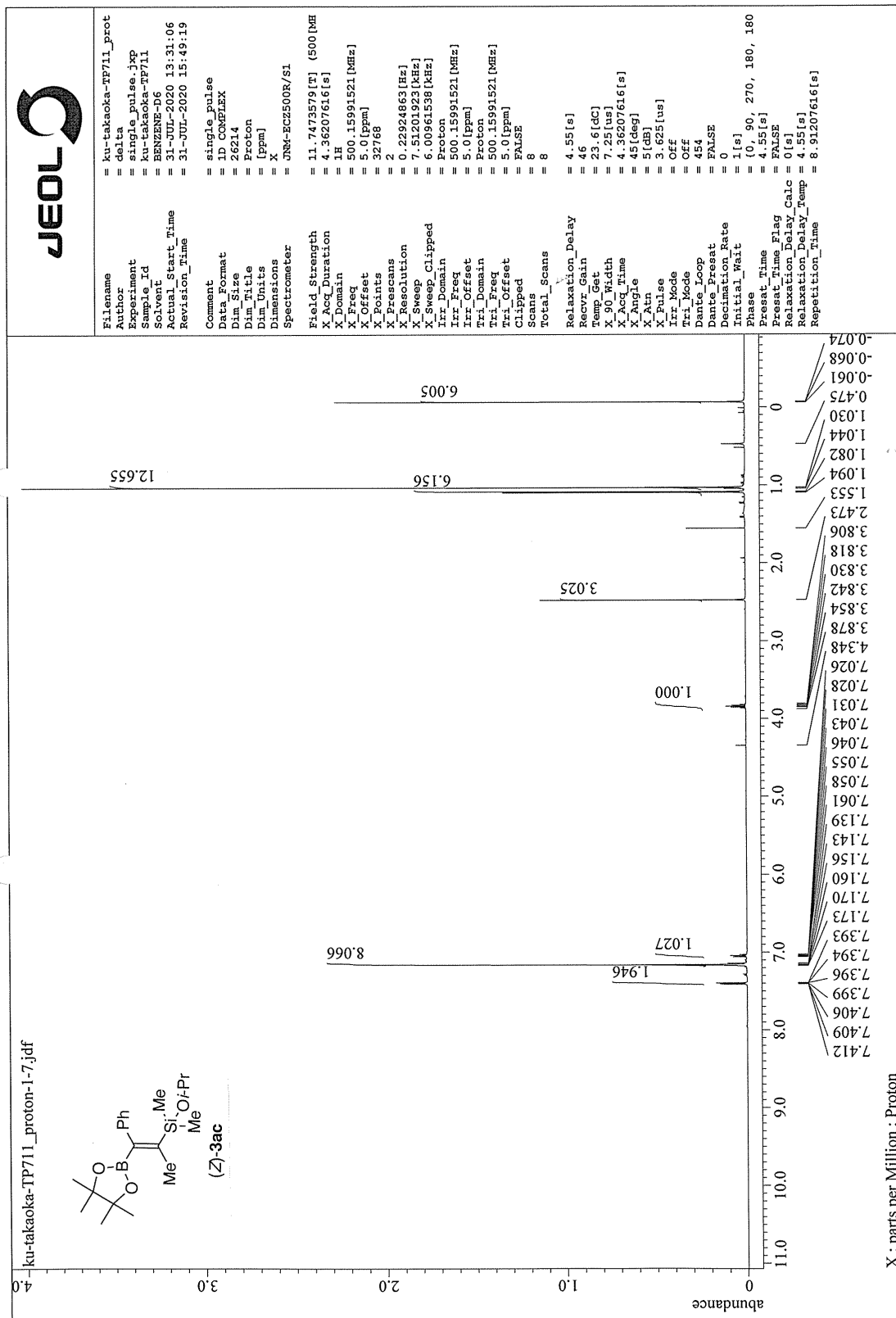


Figure S30. <sup>1</sup>H NMR Spectrum of (Z)-3ac (500 MHz, CDCl<sub>3</sub>)

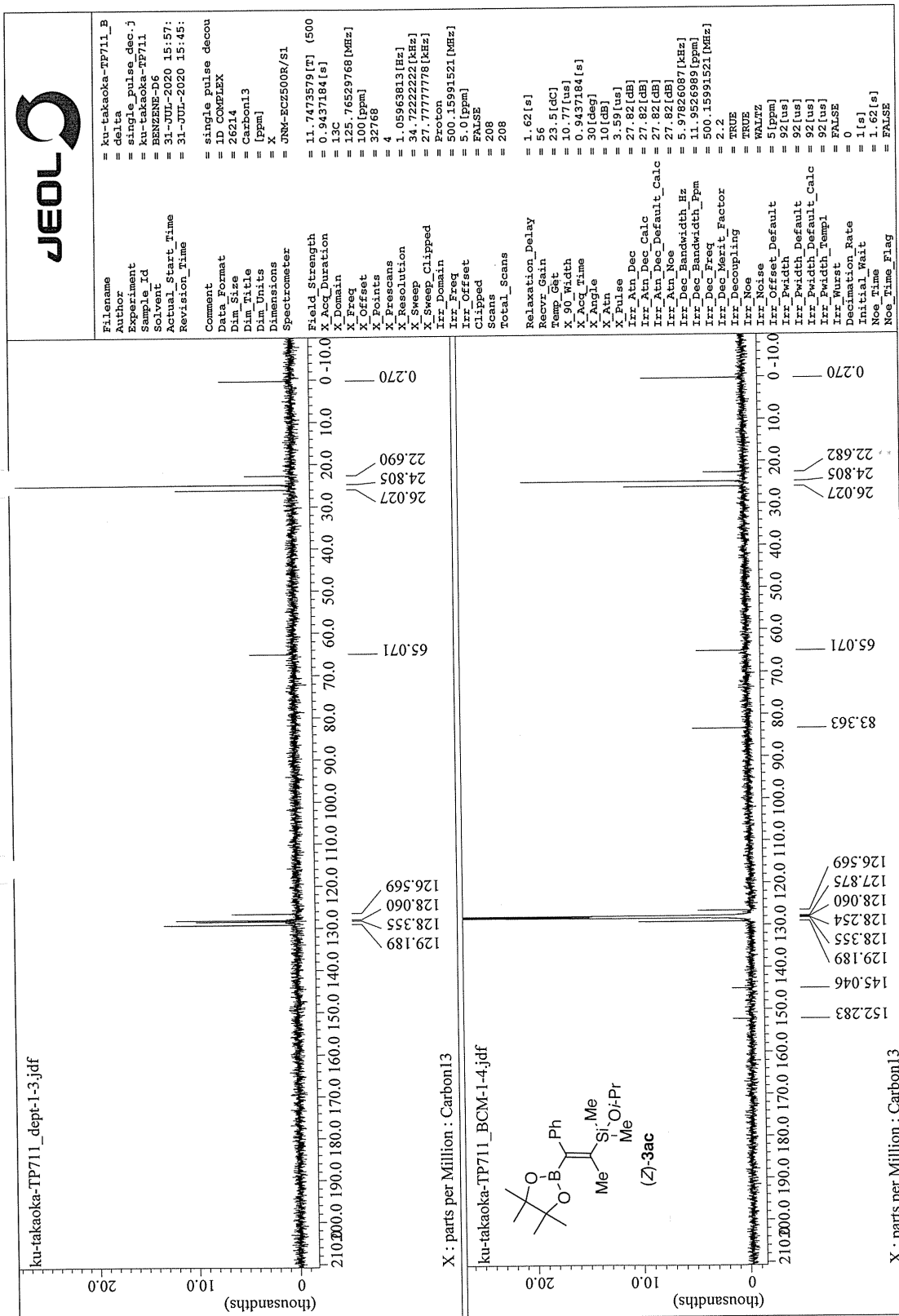


Figure S31. <sup>13</sup>C NMR Spectrum of (Z)-3ac (126 MHz, CDCl<sub>3</sub>)





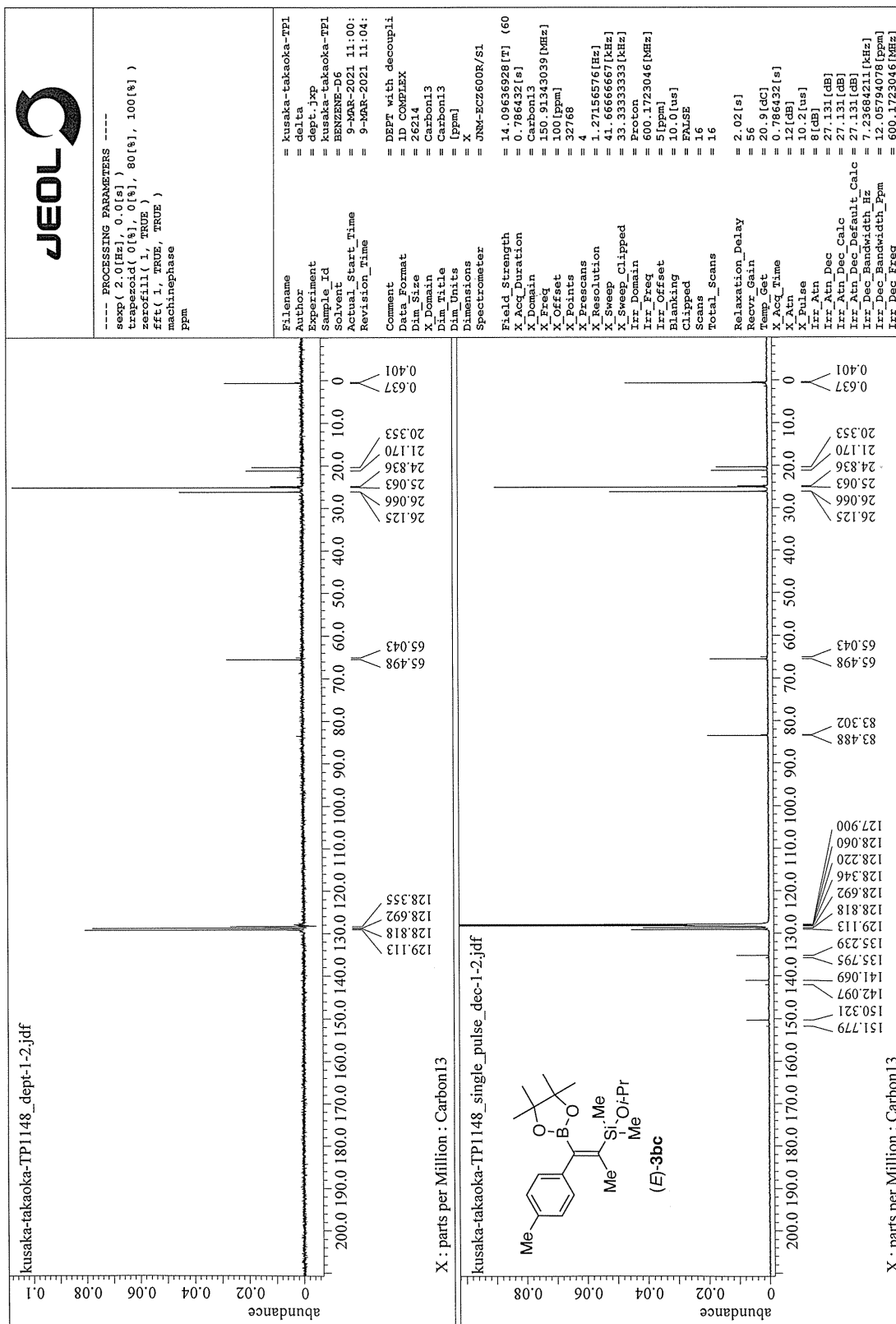


Figure S33. <sup>13</sup>C NMR Spectrum of (E)-3bc (Z:E = 9:91) (151 MHz, CDCl<sub>3</sub>)

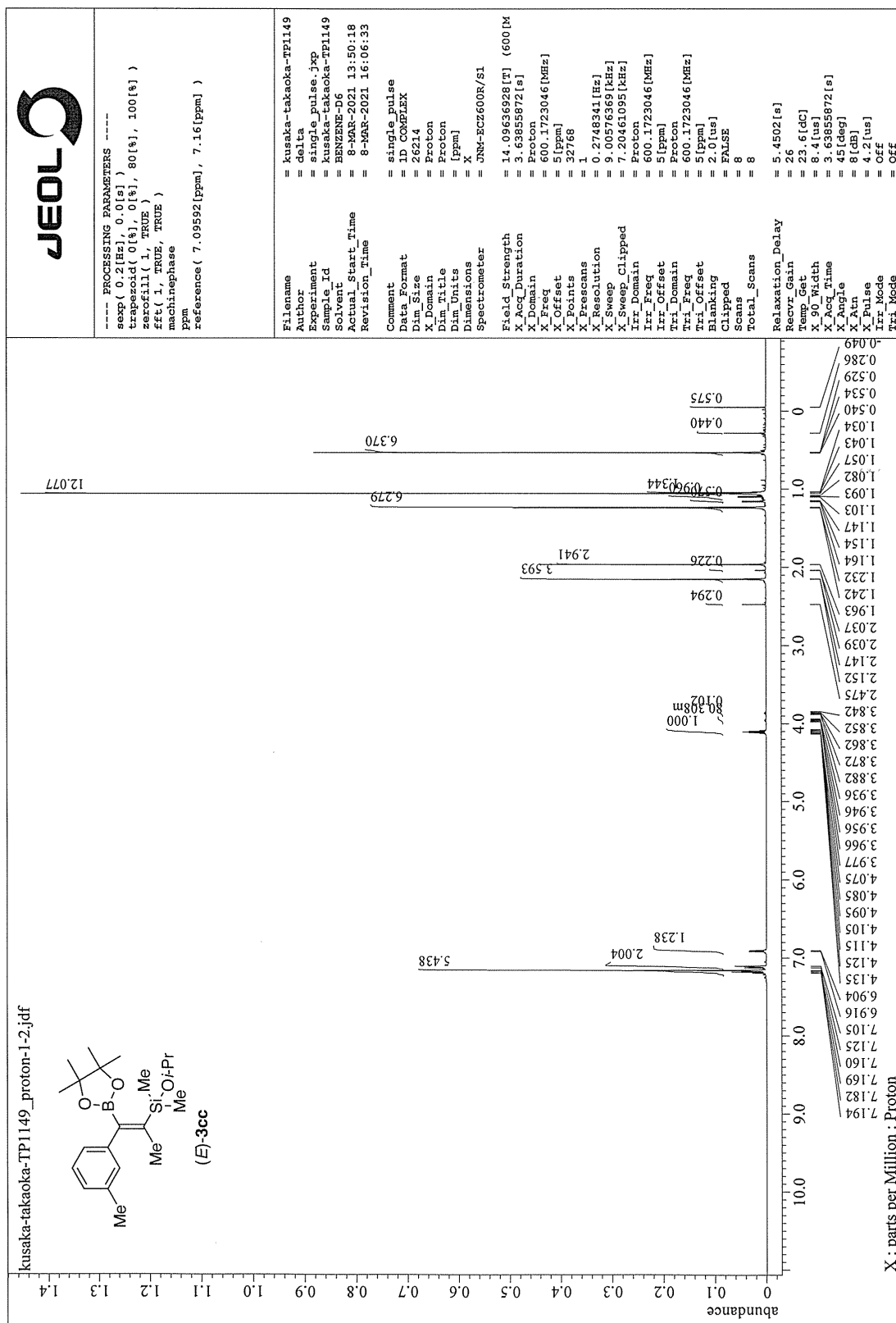


Figure S37. <sup>1</sup>H NMR Spectrum of (E)-3cc (Z:E = 9:91) (600 MHz, CDCl<sub>3</sub>)

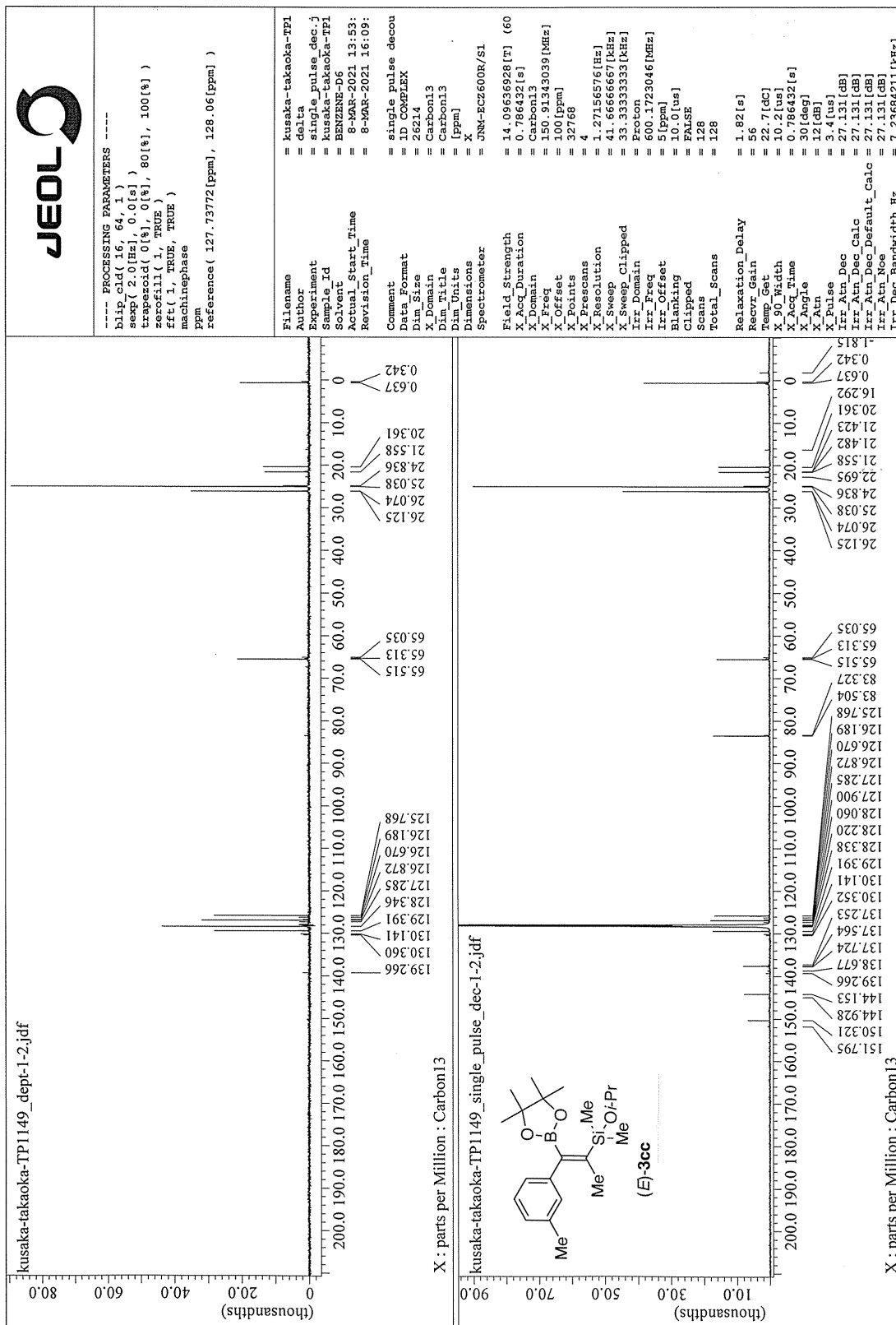


Figure S38. <sup>13</sup>C NMR Spectrum of (E)-3cc (Z:E = 9:1) (151 MHz, CDCl<sub>3</sub>)

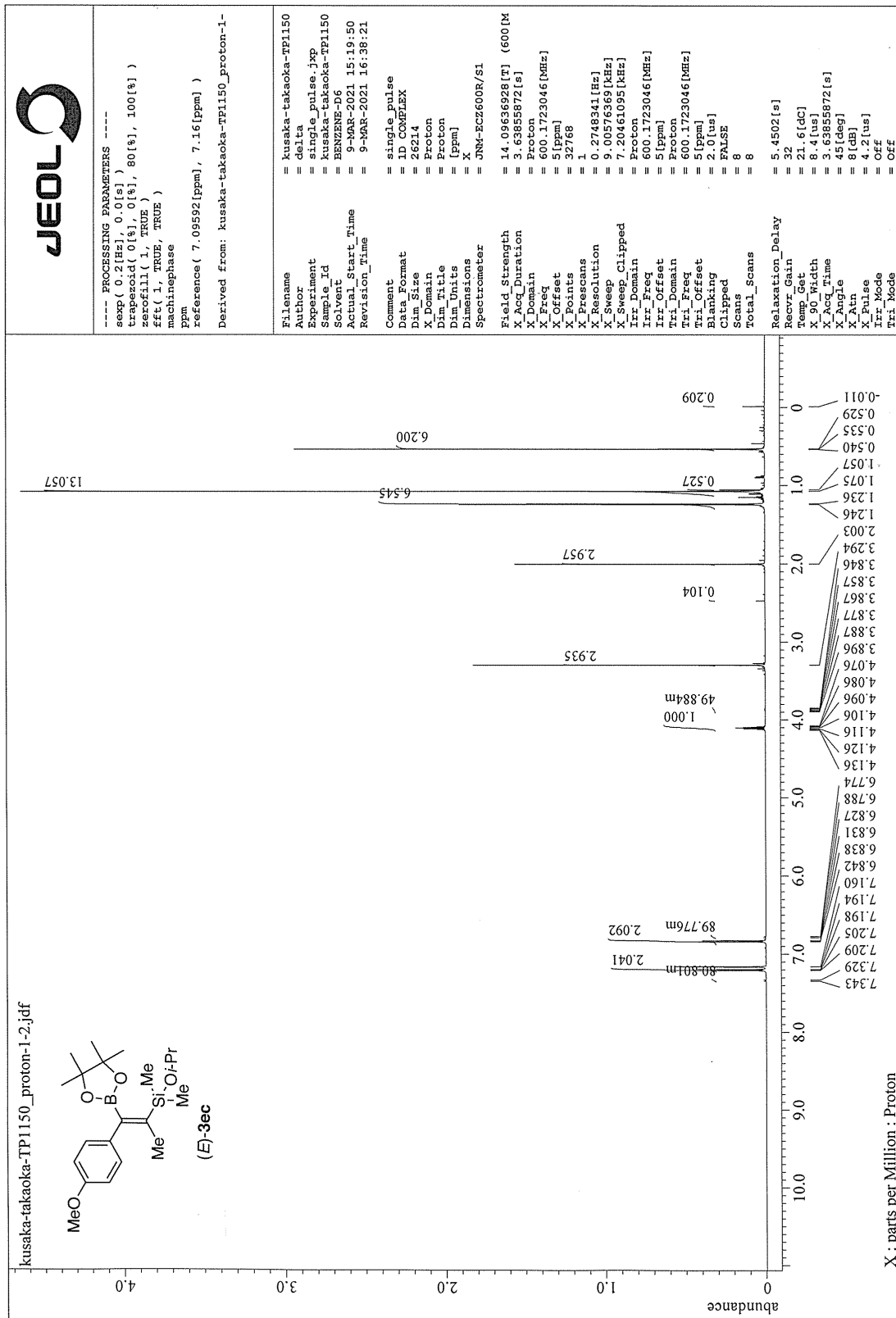


Figure S39. <sup>1</sup>H NMR Spectrum of (E)-3ec (Z:E = 3:97) (600 MHz, CDCl<sub>3</sub>)

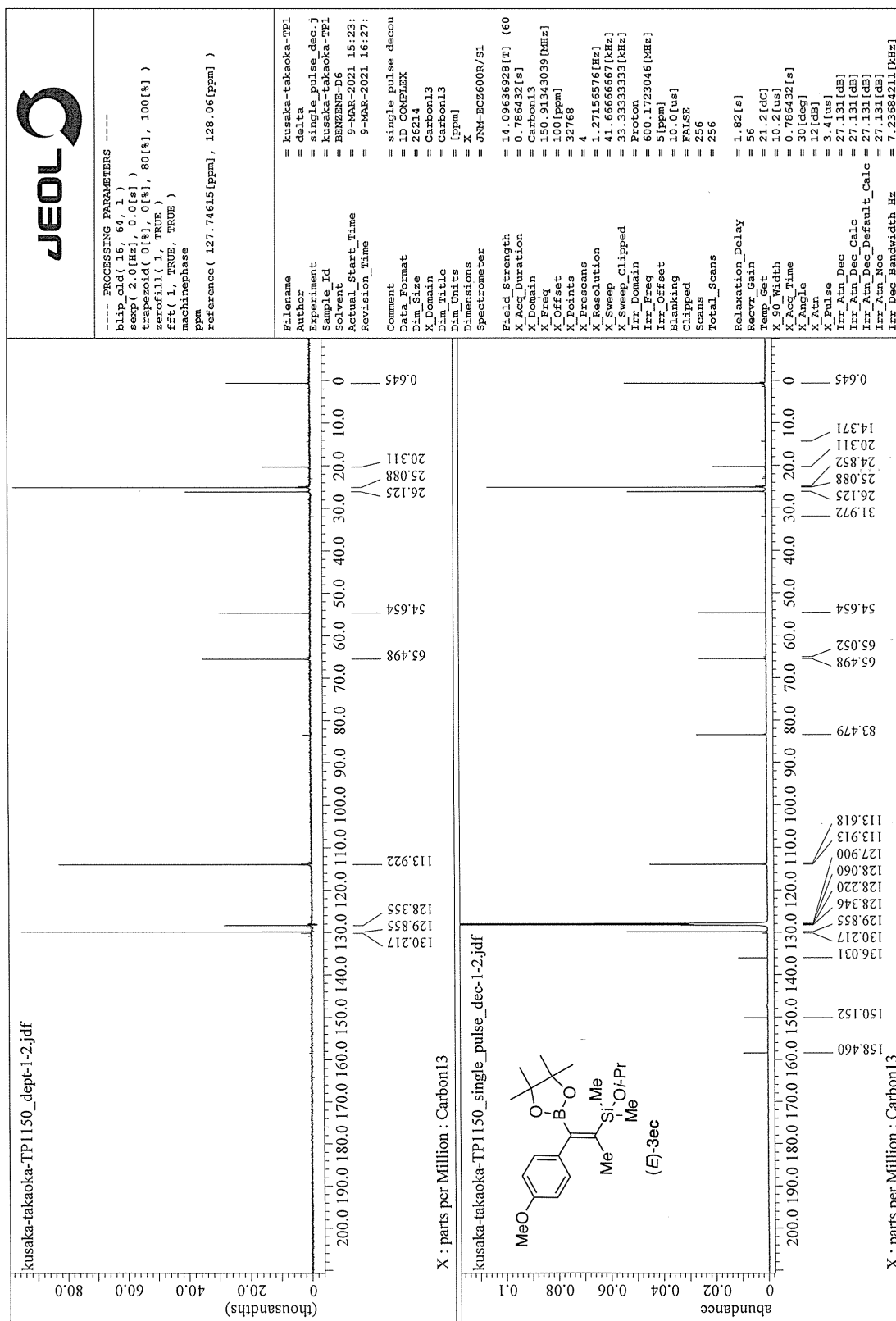


Figure S40. <sup>13</sup>C NMR Spectrum of (*E*)-**3ec** (*Z*:*E* = 3:97) (151 MHz, CDCl<sub>3</sub>)

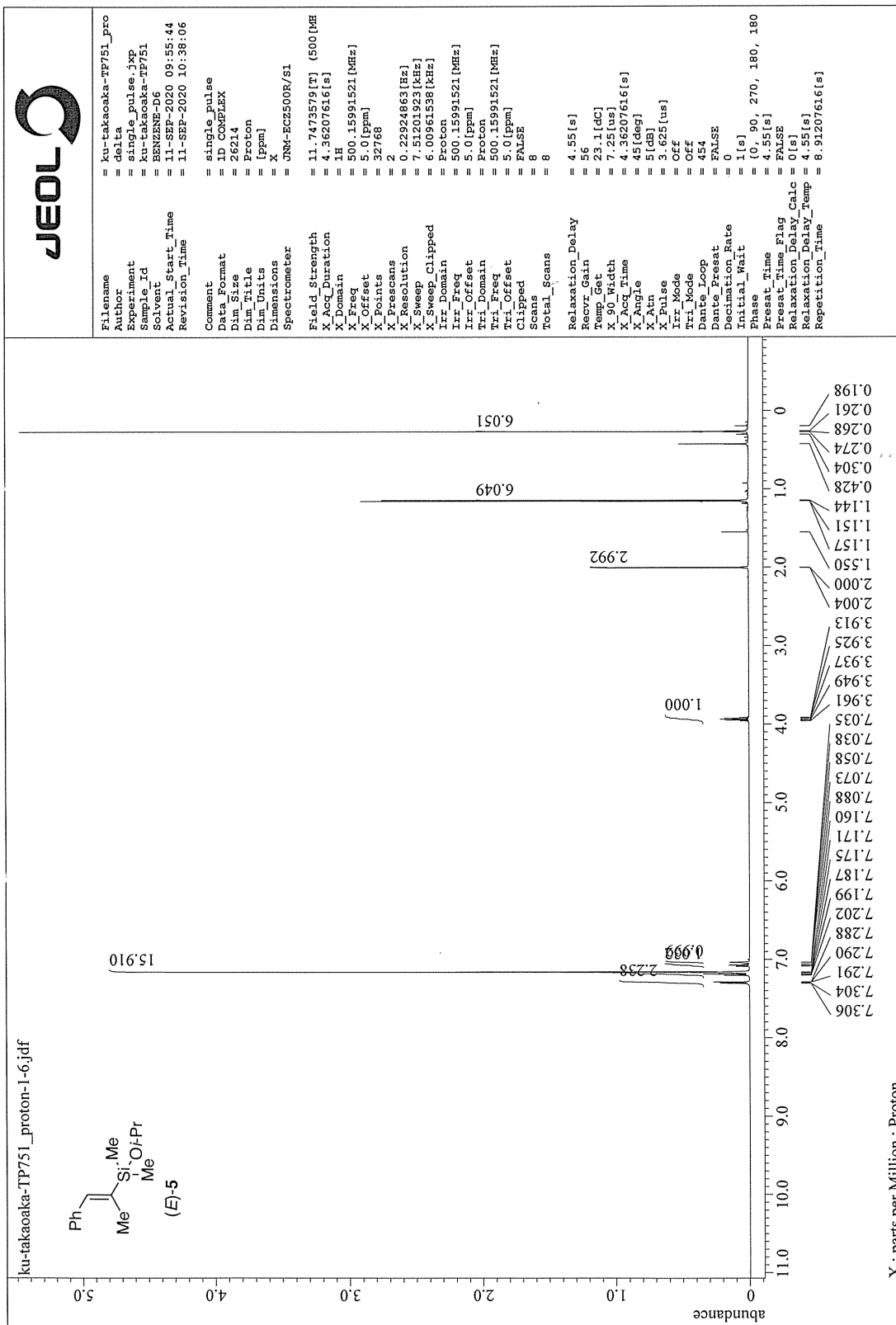


Figure S41. <sup>1</sup>H NMR Spectrum of (E)-5 (500 MHz, CDCl<sub>3</sub>)

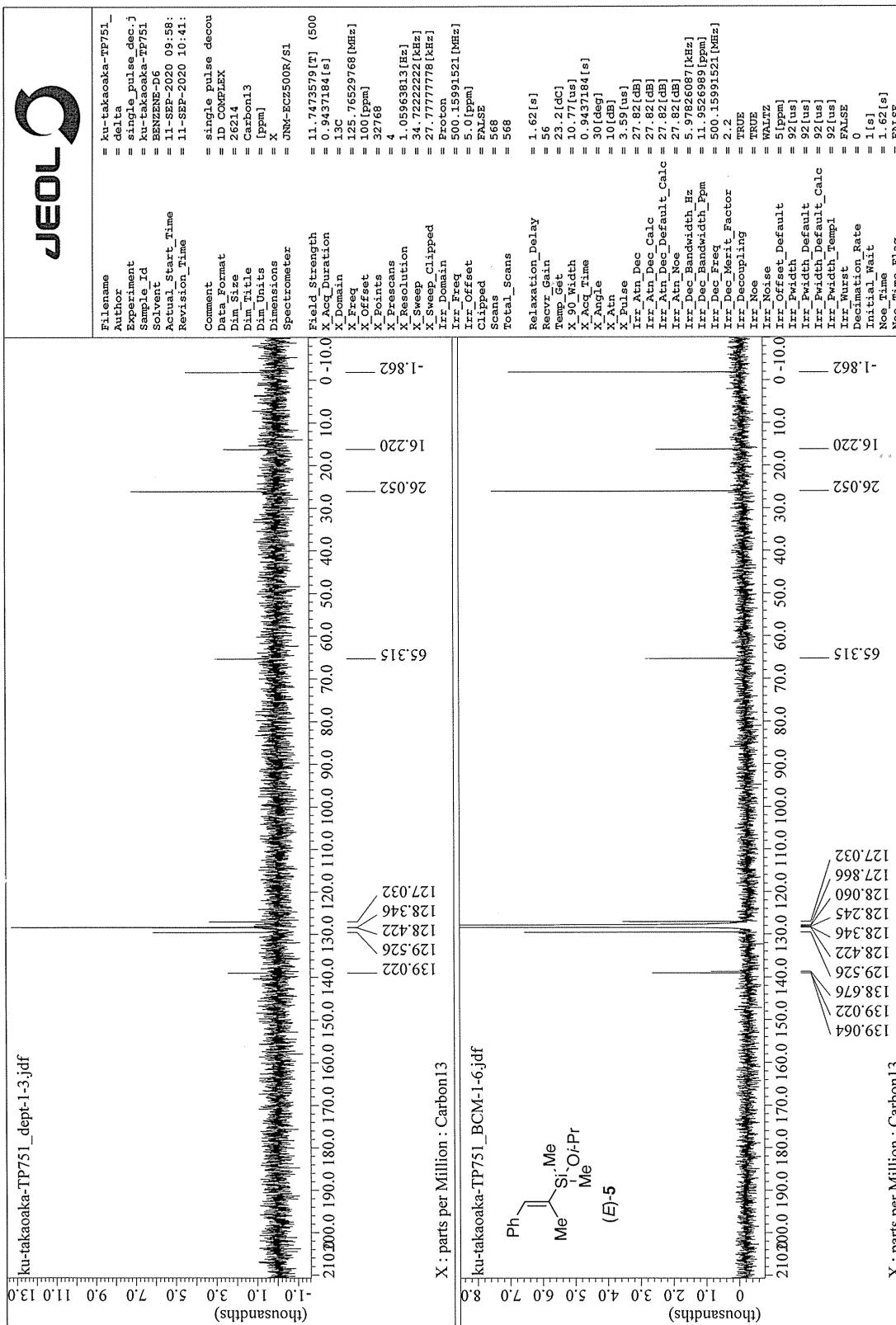


Figure S42. <sup>13</sup>C NMR Spectrum of (*E*)-5 (126 MHz, CDCl<sub>3</sub>)