Supporting Information

Remarkable Catalytic Property of Nanoporous Gold on Activation of Diborons for Direct Diboration of Alkynes

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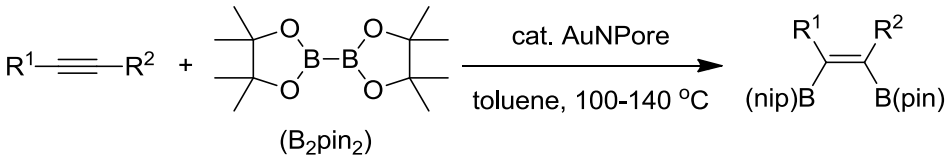


Content

General Information: GC-MS analysis was performed on an Agilent 6890N GC interfaced to an Agilent 5973 mass-selective detector (30 m × 0.25 mm capillary column, HP-5MS). Scanning electron microscope (SEM) observation was carried out using a JEOL JSM-6500F instrument operated at an accelerating voltage of 30 kV. TEM characterization was performed using a JEM-2100F TEM (JEOL, 200 kV) equipped with double spherical aberration (Cs) correctors for both the probe-forming and image-forming lenses. ^{1}H NMR and ^{13}C NMR spectra were recorded on JEOL JNM AL 400 (400, 700 MHz) spectrometers. ^{11}B NMR spectra were recorded on JEOL JNM AL 700 (225 MHz) spectrometers. ^{1}H NMR spectra are reported as follows: chemical shift in ppm (δ) relative to the chemical shift of $CDCl_3$ at 7.26 ppm, integration, multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and br = broadened), and coupling constants (Hz). ^{13}C NMR spectra were recorded on JEOL JNM AL 400 (100.5 MHz) spectrometers with complete proton decoupling, and chemical shift reported in ppm (δ) relative to the central line of triplet for $CDCl_3$ at 77 ppm. High-resolution mass spectra were obtained on a BRUKER APEXIII spectrometer and JEOL JMS-700 MStation operator. Column chromatography was carried out employing Merck silica (spherical, neutral, MercK Chemical Co.) and the florisil (particle size 150 -250 μm, Kanto Chemical Co.). Analytical thin-layer chromatography (TLC) was performed on 0.2 mm precoated plate Kieselgel 60 F254 (Merck).

Materials. The bis(pinacolato)diboron and alkynes are commercially available (Aldrich), which were used as received. Au (99.99%) and Ag (99.99%) are purchased from Tanaka Kikinzoku Hanbai K. K. and Mitsuwa's Pure Chemical, respectively. Alkyne **1o** was prepared following the reported literature.[1] Structure of **3a**[2], **3b**[3], **3d**[4], **3f**[3], **3i**[5], **3j**[2], **3k**[6], **3m**[2] and **3n**[6] were the reported compounds. Products **3c**, **3e**, **3g**, **3h**, **3l**, **3o**, **3p**, and **3bb** were determined by ^{1}H NMR, ^{13}C NMR, ^{11}B NMR and HRMS. Tran-adduct **3d'** and **3p'** were determined by using NOE.

References

1. Araki, H.; Naka, K. *J. Polym. Sci. Part A: Polym Chem*. **2012**, *50*, 4170.
2. Ishiyama, T.; Matsuda, N.; Murata, M.; Ozawa, F.; Suzuki, A.; Miyaura, N. *Organometallics*, **1996**, *15*, 713-720.
3. Morgan, J, B.; Morken, J, P. *J. Am. Chem. Soc.* **2004**, *126*, 15338-15339.
4. Thomas, R, L.; Souza, E, S.; Marder, T, B. *J. Chem. Soc., Dalton Trans.* **2001**, 1650-1656.
5. Ishiyama, T.; Matsuda, N.; Miyaura, N.; Suzuki, A. *J. Am. Chem. Soc.* **1993**, *115*, 11018-11019.
6. Yoshida, H.; Kawashima, S.; Takemoto, Y.; Okada, K.; Ohshita, J.; Takaki, K. *Angew. Chem. Int. Ed.* **2012**, *51*, 235-238.

TEM and SEM images of nanoporous metal catalysts

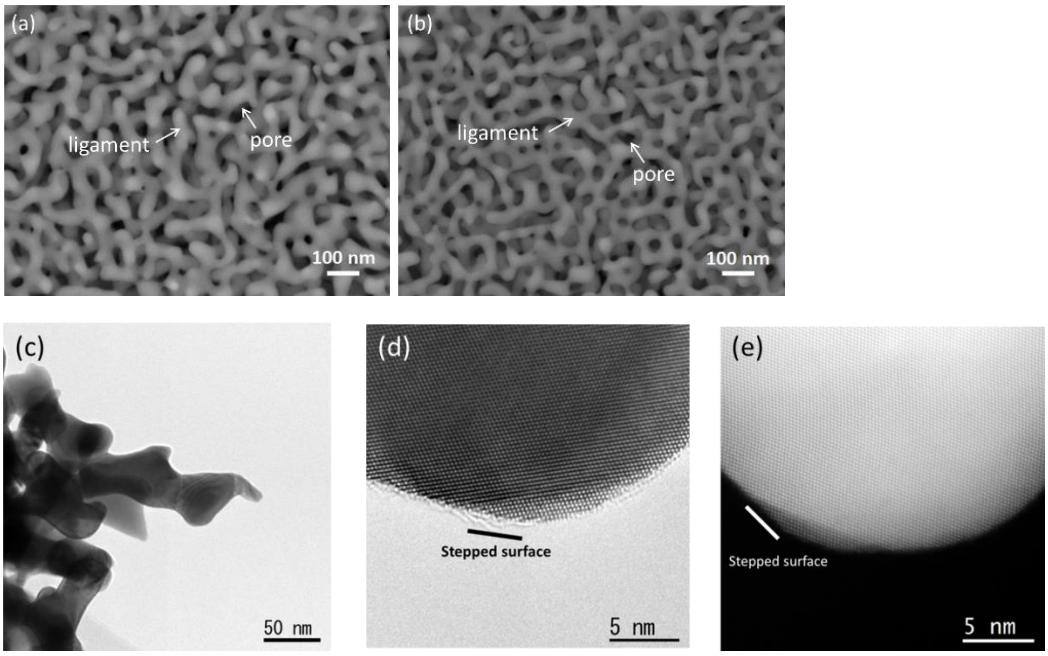


Figure S1. (a) SEM image of the fresh AuNPore (before reaction). (b) SEM image of AuNPore after third run. (c) TEM image of AuNPore. (d) HRTEM image of AuNPore. (e) HADDF-STEM image of AuNPore.

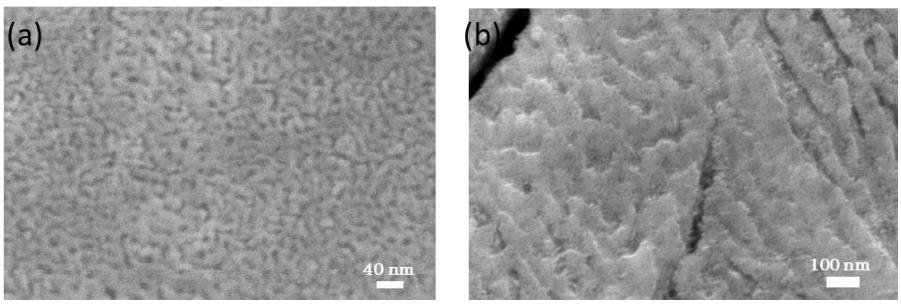
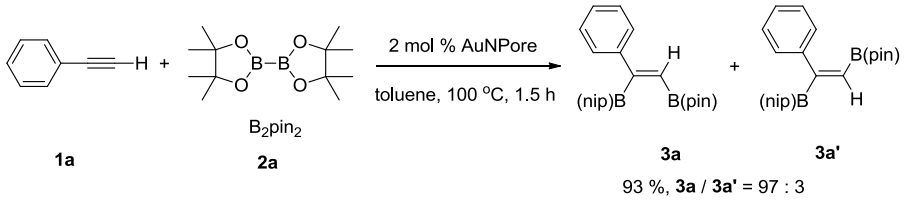


Figure S2. SEM images of PtNPore (a) and PdNPore (b).

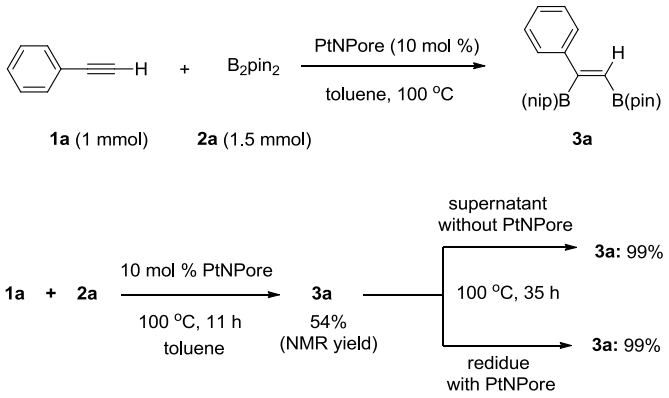
Representative procedure for the AuNPore-catalyzed diboration of 1a (Table 1, entry 2)



To a toluene solution (0.5 M, 2 ml) of AuNPore (2 mol%, 4.0 mg) were added **2a** (382 mg, 1.5 mmol) and **1a** (110 μL, 1 mmol) subsequently at room temperature. The reaction mixture was stirred

at 100 °C for 1.5 h and was monitored by GC-MS analysis. The AuNPore catalyst was recovered by filtration. The recovered AuNPore catalyst was washed with acetone and water then acetone, and dried under vacuum. After concentration of the filtrate, the remaining B_2pin_2 **2a** was removed by Kugelrohr distillation, and the residue was further purified through a pad of florisil to afford **3a** and **3a'** (332 mg, 93%, 97:3) as a light yellow liquid.

Leaching experiment of PtNPore catalyst

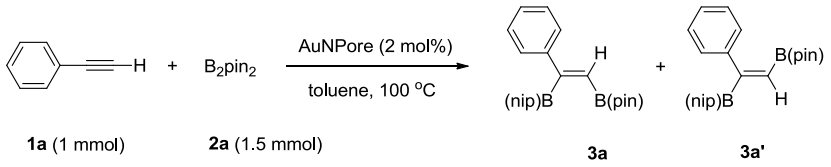


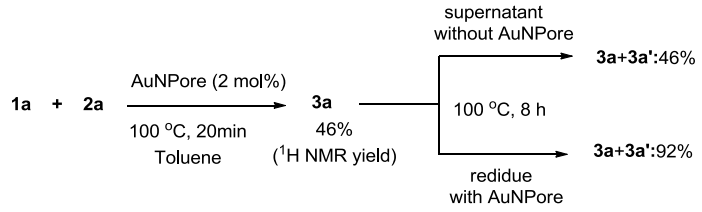
Scheme S1. Leaching experiments for the reaction using PtNPore as catalyst.

The toluene solution of phenyl acetylene (**1a**) and B_2pin_2 (**2a**) in the presence of PtNPore catalyst (10 mol%) was stirred at 100 °C for 11 h. At this time the yield of **3a** was 54% which determined by ^{1}H NMR using anisole as an internal standard. A part of the supernatant was transferred to the other reaction vessel. The supernatant without PtNPore catalyst was continuously stirred at 100 °C for 35 h, affording the corresponding product **3a** in 99% ^{1}H NMR yield, and the residual containing the PtNPore catalyst gave **3a** in 99% ^{1}H NMR yield after stirring at 100 °C for 35 h.

The ICP-MS analysis of the reaction in entry 1 of Table 1 showed that 280 ppm of Pt was leached to the toluene solution after reaction. These results clearly indicated that the PtNPore catalyst was leached in the present reaction conditions and the leached Pt species indeed acted as a homogeneous catalyst for promoting the present boration.

Leaching experiment of AuNPore catalyst



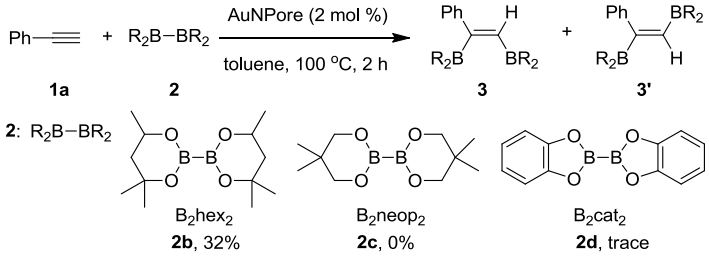


Scheme S2. Leaching experiment of the reaction using AuNPore as catalyst.

The toluene solution of phenyl acetylene (**1a**) and B_2pin_2 (**2a**) in the presence of AuNPore catalyst (2 mol%) was stirred at 100 °C for 20 min. At this time the yield of **3a** was 46% which determined by ^{1}H NMR using anisole as an internal standard. A part of the supernatant was transferred to the other reaction vessel. The supernatant without AuNPore catalyst was continuously heated at 100 °C for 8 h, affording **3a** in 46% ^{1}H NMR yield. In contrast, the residual containing the AuNPore catalyst gave **3a** in 92% ^{1}H NMR yield after heating at 100 °C for 8 h.

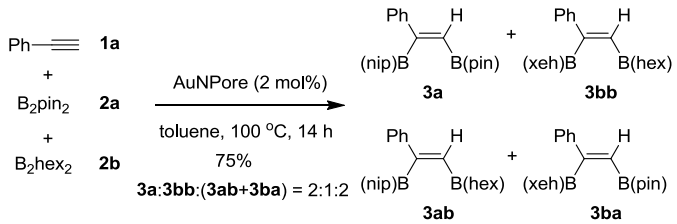
The ICP-MS analysis did not show any detectable leached Au atoms as well as Pt and Pd atoms at ppb levels. These results clearly indicated that the present boration was occurred on the solid state of AuNPore catalyst and was not catalysed by the adventitious Pt or Pd catalyst which sometimes exists in the used glassware and chemicals.

Screening of other diborons



Scheme S3. Examination of other diborons instead of using $B_2(pin)_2$.

Cross-addition Experiment for Diboration of 1a with 2a and 2b



Scheme S4. Cross-addition experiment for diboration of **1a** with **2a** and **2b**. *cis*-Adducts are major products. The corresponding *trans*-adducts were not shown for clarification.

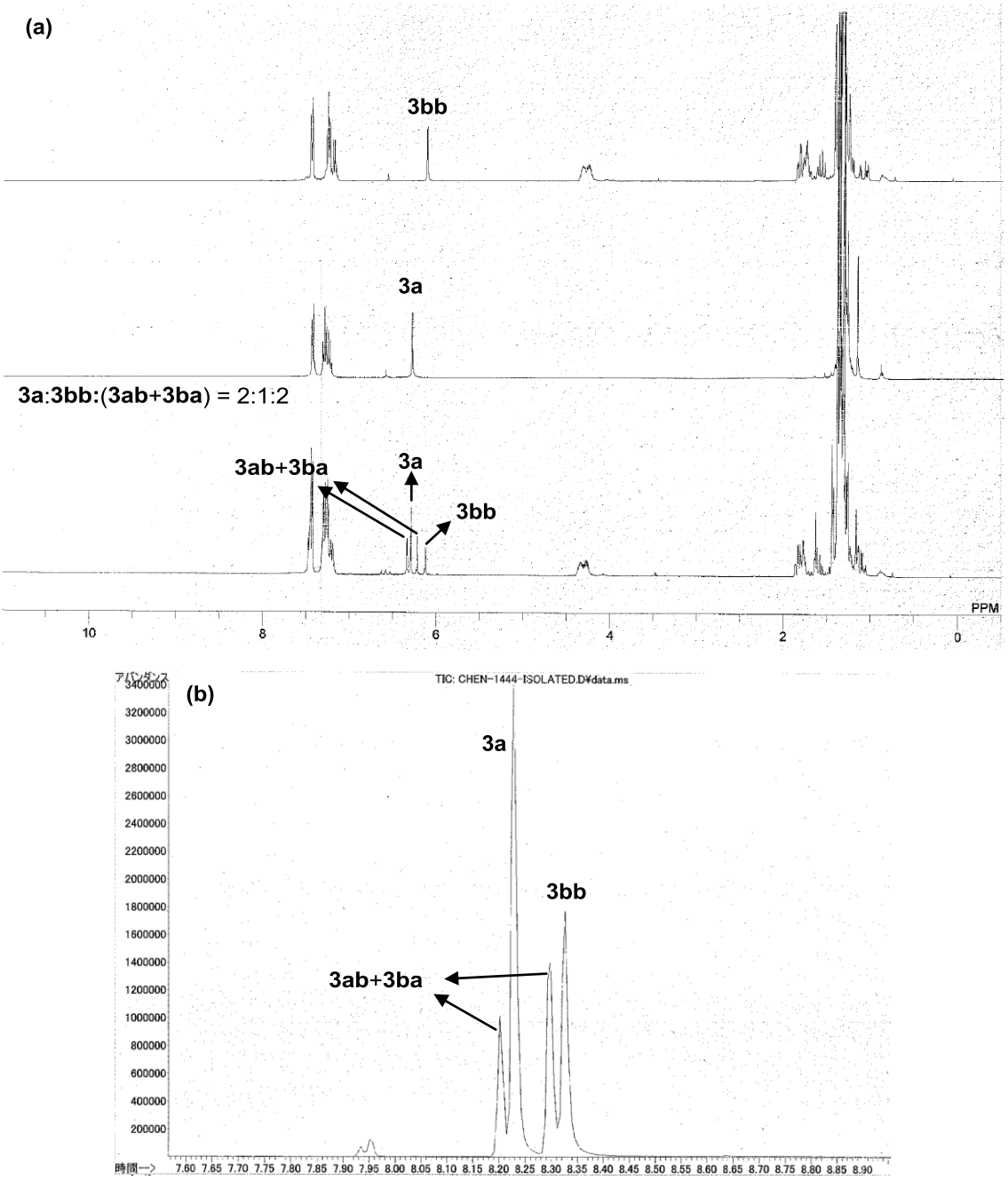
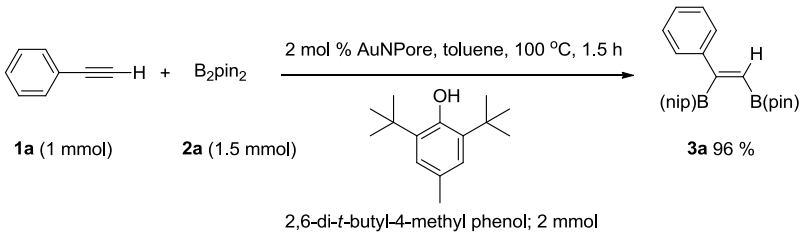


Figure S3. ^{1}H NMR spectra (a) and GC-MS spectrum (b) of cross-addition reaction.

Radical inhibitor-mediated reaction:

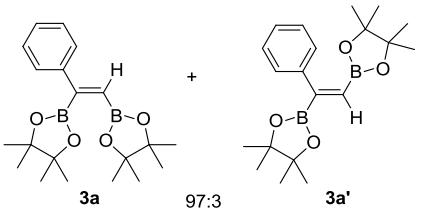


Scheme S5. Radical examination using BHT as radical inhibitor.

To a toluene solution (0.5 M, 2 ml) of AuNPore (2 mol%, 4.0 mg) were added **2a** (382 mg, 1.5 mmol), **1a** (110 μL, 1 mmol), and 2,6-di-*tert*-butyl-4-methyl phenol (BHT) (2 mmol) subsequently at room temperature. The reaction mixture was stirred at 100 ^{o}C for 1.5 h. The AuNPore catalyst was recovered by filtration. The recovered AuNPore catalyst was washed with acetone and water then acetone and dried under vacuum. After concentration of filtration, the residue showed that **3a** was formed in 96% ^{1}H NMR yield by using CH_2Br_2 as an internal standard, indicating the radical inhibitor BHT did not decrease the rate and yield of **3a**.

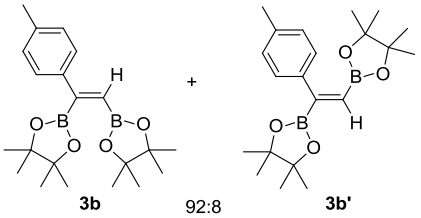
Analytical data

(*E*)-2,2'-(1-Phenylethene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3a)



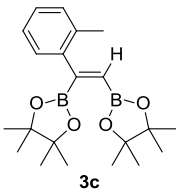
E:*Z* = 97:3; light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.36 (m, 2H), 7.32-7.16 (m, 3H), 6.25 (s, 1H), 1.34 (s, 12H), 1.27 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8, 128.1, 127.4, 126.4, 84.0, 83.5, 25.0, 24.8; ^{11}B NMR (225 MHz, $CDCl_3$) δ 30.59; HRMS (ESI positive) calcd for $C_{20}H_{30}B_2O_4$ $[M + Na]^+$: 379.2222, found: 379.2222.

(*E*)-2,2'-(1-(*p*-Tolyl)ethene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3b)



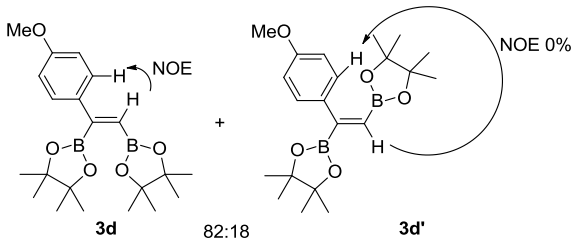
E:*Z* = 92:8; light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.29 (m, 2H), 7.16-7.07 (m, 2H), 6.26 (s, 1H), 2.33 (s, 3H), 1.39 (s, 12H), 1.31 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.0, 137.2, 128.9, 126.3, 84.0, 83.4, 25.1, 24.8, 21.1; ^{11}B NMR (225MHz, $CDCl_3$) δ 30.33; HRMS (ESI positive) calcd for $C_{21}H_{32}B_2O_4$ $[M + Na]^+$: 393.2378, found: 393.2378.

(*E*)-2,2'-(1-(*o*-Tolyl)ethene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3c)



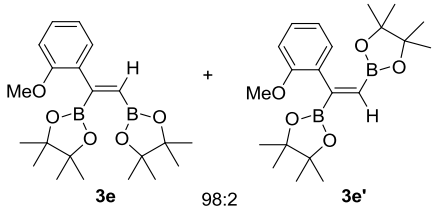
E:*Z* = 100:0; white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16-7.09 (m, 4H), 6.03 (s, 1H), 2.32 (s, 3H), 1.33 (s, 12H), 1.30 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 134.3, 129.7, 127.8, 126.5, 125.4, 83.8, 83.5, 24.9, 24.8, 20.4; ^{11}B NMR (225MHz, $CDCl_3$) δ 30.05; HRMS (ESI positive) calcd for $C_{21}H_{32}B_2O_4$ $[M + Na]^+$: 393.2378, found 393.2378.

(*E*)-2,2'-(1-(4-Methoxyphenyl)ethene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3d)



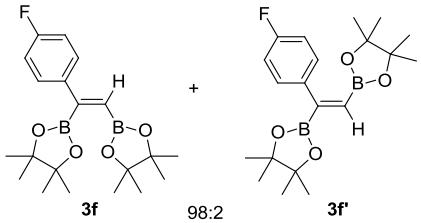
E:*Z* = 82:18; light yellow liquid; ^{1}H NMR (700 MHz, $CDCl_3$) δ **3d**: 7.40-7.38 (m, 2H), 6.84-6.82 (m, 2H), 6.21 (s, 1H), 3.78 (s, 3H), 1.38 (s, 12H), 1.29 (s, 12H); **3d'**: 7.29-7.27 (m, 2H), 6.82-6.80 (m, 2H), 6.48 (s, 1H), 3.79 (s, 3H), 1.27 (s, 12H), 1.18 (s, 12H); ^{13}C NMR (176 MHz, $CDCl_3$) δ **3d**: 159.4, 135.4, 127.7, 113.7, 84.0, 83.4, 55.1, 25.1, 24.8; **3d'**: 158.8, 134.8, 129.6, 112.9, 83.8, 83.3, 55.1, 24.7, 24.6; ^{11}B NMR (225 MHz, $CDCl_3$) δ 29.87; HRMS (ESI positive) calcd for $C_{21}H_{32}B_2O_5$ $[M + Na]^+$: 409.2328, found 409.2328.

(*E*)-2,2'-(1-(2-Methoxyphenyl)ethene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3e)



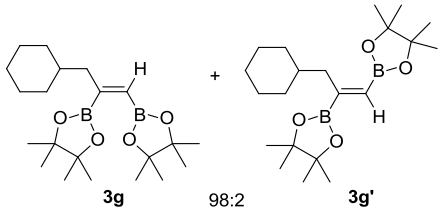
E:*Z* = 98:2; light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.16 (m, 2H), 6.93-6.87 (m, 1H), 6.81-6.76 (m, 1H), 6.20 (s, 1H), 3.77 (s, 3H), 1.34 (s, 12H), 1.29 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 133.9, 128.8, 128.7, 121.0, 110.0, 83.5, 83.3, 55.2, 25.1, 24.9; ^{11}B NMR (225 MHz, $CDCl_3$) δ 30.04; HRMS (ESI positive) calcd for $C_{21}H_{32}B_2O_5$ $[M + Na]^+$: 409.2328, found 409.2328.

(*E*)-2,2'-(1-(4-Fluorophenyl)ethene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3f)



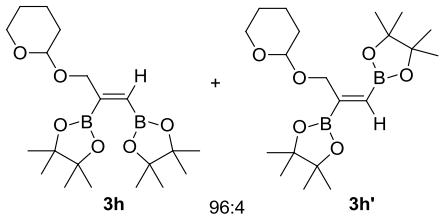
E:*Z* = 98:2; colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.32 (m, 2H), 7.02-6.89 (m, 2H), 6.23 (s, 1H), 1.36 (s, 12H), 1.30 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3 (d, J^1 = 245.0 Hz), 138.9 (d, J^4 = 3.3 Hz), 128.0 (d, J^3 = 8.2 Hz), 115.0 (d, J^2 = 21.4 Hz), 84.1, 83.5, 25.0, 24.8; ^{11}B NMR (225 MHz, $CDCl_3$) δ 30.31; HRMS (ESI positive) calcd for $C_{20}H_{29}B_2FO_4$ $[M + Na]^+$: 397.2128, found 397.2128.

(*E*)-2,2'-(3-Cyclohexylprop-1-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3g)



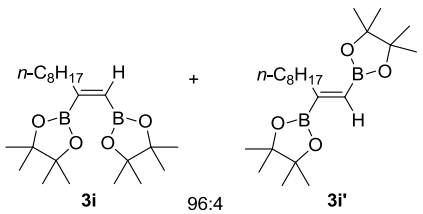
E:*Z* = 98:2; colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.76 (s, 1H), 2.09 (d, *J* = 7.2 Hz, 2H), 1.70-1.57 (m, 5H), 1.41-1.32 (m, 1H), 1.28 (s, 12H), 1.23 (s, 12H), 1.17-1.07 (m, 3H), 0.88-0.76 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 83,4, 83.1, 48.3, 37.0, 33.3, 26.5, 26.3, 24.8(8), 24.8(7); ^{11}B NMR (225 MHz, $CDCl_3$) δ 30.16; HRMS (ESI positive) calcd for $C_{21}H_{38}B_2O_4$ $[M + Na]^+$: 399.2848, found: 399.2848.

(*E*)-2,2'-(3-((Tetrahydro-2H-pyran-2-yl)oxy)prop-1-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3h)



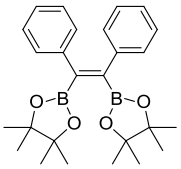
E:*Z* = 96:4; white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.11 (s, 1H), 4.62 (dd, *J* = 3.2, 3.2 Hz, 1H), 4.36 (dd, *J* = 14.4, 2.0 Hz, 1H), 4.09 (dd, *J* = 14.4 Hz, 1.6 Hz, 1H), 3.86-3.79 (m, 1H), 3.48-3.44 (m, 1H), 1.88-1.76 (m, 1H), 1.72-1.41 (m, 5H), 1.28 (s, 12H), 1.25 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 97.4, 83.6, 83.3, 71.5, 61.4, 30.4, 25.5, 24.9, 24.8, 19.0; ^{11}B NMR (225 MHz, $CDCl_3$) δ 30.17; HRMS (ESI positive) calcd for $C_{20}H_{36}B_2O_6$ $[M + Na]^+$: 417.2590, found: 417.2589.

(*E*)-2,2'-(Dec-1-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3i)



E:*Z* = 96:4; light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.82 (s, 1H), 2.19 (t, *J* = 7.2 Hz, 2H), 1.46-1.36 (m, 2H), 1.30 (s, 12H), 1.25 (s, 12H), 1.3-1.2 (m, 10H), 0.86 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 83.5, 83.1, 39.9, 31.9, 29.4(7), 29.4(1), 29.2, 28.6, 24.9, 24.8, 22.7, 14.1; ^{11}B NMR (225 MHz, $CDCl_3$) δ 30.33; HRMS (ESI positive) calcd for $C_{22}H_{42}B_2O_4$ $[M + Na]^+$: 415.3161, found 415.3161.

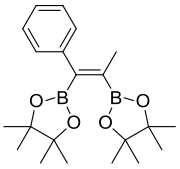
(*Z*)-1,2-Diphenyl-1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethane (3j)



3j

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13-7.01 (m, 6H), 7.00-6.93 (m, 4H), 1.34 (s, 24H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0, 129.1, 127.2, 125.6, 83.9, 24.8; ^{11}B NMR (225 MHz, $CDCl_3$) δ 30.54; HRMS (ESI positive) calcd for $C_{26}H_{34}B_2O_4$ $[M + Na]^+$: 455.2535, found 455.2535.

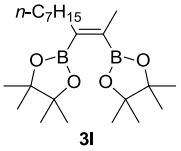
(*Z*)-2,2'-(1-Phenylprop-1-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3k)



3k

Pale liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.22 (m, 2H), 7.21-7.05 (m, 3H), 1.69 (s, 3H), 1.30 (s, 12H), 1.23 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.3, 128.1, 127.6, 125.7, 83.6, 83.5, 24.8(9), 24.8(0), 18.1; ^{11}B NMR (225 MHz, $CDCl_3$) δ 30.39; HRMS (ESI positive) calcd for $C_{21}H_{32}B_2O_4$ $[M + Na]^+$: 393.2378, found 393.2378.

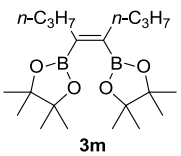
(*Z*)-2,2'-(Dec-2-ene-2,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3l)



3l

Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.169 (t, *J* = 7.2 Hz, 2H), 1.73 (s, 3H), 1.44-1.17 (m, 10H), 1.27 (s, 12H), 1.26 (s, 12H), 0.85 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 83.2, 83.1, 31.8, 31.2, 29.9, 29.2, 28.8, 24.9, 24.8, 22.6, 15.9, 14.1; ^{11}B NMR (225 MHz, $CDCl_3$) δ 30.53, 22.27; HRMS (ESI positive) calcd for $C_{22}H_{42}B_2O_4$ $[M + Na]^+$: 415.3161, found 415.3161.

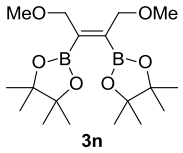
(*Z*)-2,2'-(Oct-4-ene-4,5-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3m)



3m

Light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.20-2.11 (m, 4H), 1.44-1.31 (m, 4H), 1.27 (s, 24H), 0.89 (t, *J* = 7.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 83.2, 33.0, 24.9, 23.0, 14.6; ^{11}B NMR (225 MHz, $CDCl_3$) δ 30.59; HRMS (ESI positive) calcd for $C_{20}H_{38}B_2O_4$ $[M + Na]^+$: 387.2848, found 387.2847.

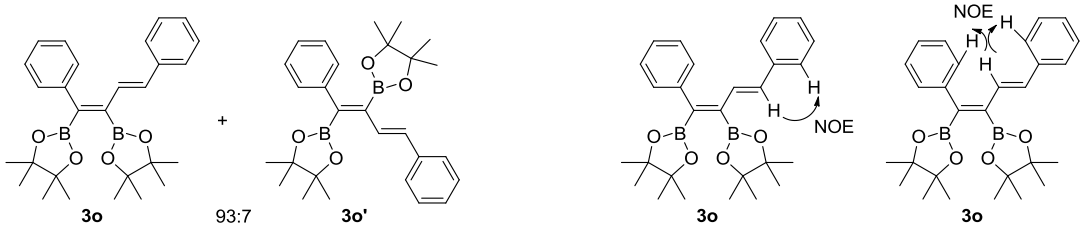
(*Z*)-2,2'-(1,4-Dimethoxybut-2-ene-2,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3n)



3n

Light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.13 (s, 4H), 3.25 (s, 6H), 1.26 (s, 24H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 83.6, 71.4, 57.9, 24.8; ^{11}B NMR (225 MHz, $CDCl_3$) δ 30.13; HRMS (ESI positive) calcd for $C_{18}H_{34}B_2O_6$ $[M + Na]^+$: 391.2433, found 391.2433.

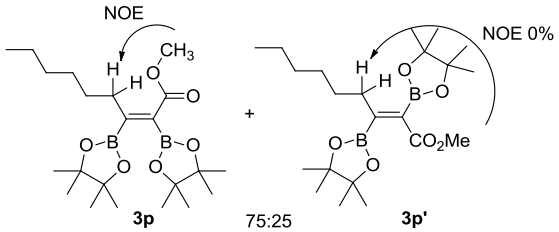
2,2'-((1*Z*,3*E*)-1,4-Diphenylbuta-1,3-diene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3o)



3o 93:7 **3o'** **3o** **3o**

Z:*E* = 93:7; white solid; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.34-7.32 (m, 2H), 7.26-7.16 (m, 8H), 6.97 (d, *J* = 16.8 Hz, 1H), 6.89 (d, *J* = 16.8 Hz, 1H), 1.46 (s, 12H), 1.28 (s, 12H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 141.4, 137.8, 133.3, 130.5, 129.4, 128.4, 127.5, 127.4, 126.6, 126.2, 84.0, 83.9, 25.3, 24.8; ^{11}B NMR (225 MHz, $CDCl_3$) δ 30.72; HRMS (ESI positive) calcd for $C_{28}H_{36}B_2O_4$ $[M + Na]^+$: 481.2691, found 481.2691.

(*Z*)-Methyl 2,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)non-2-enoate (3p)

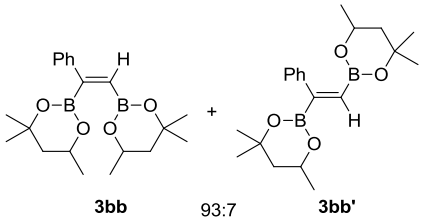


3p 75:25 **3p'**

3p:**3p'** = 75:25; light yellow liquid; ^{1}H NMR (700 MHz, $CDCl_3$) δ 3.73 (**3p'**: s, 3H), 3.70 (**3p**: s, 3H), 2.37 (**3p'**: t, *J* = 7.7 Hz, 2H), 2.35 (**3p**: t, *J* = 8.4 Hz, 2H), 1.42-1.22 (**3p**: m, 32H), 0.86 (**3p'**: t, *J* = 7.0 Hz, 3H), 0.85 (**3p**: t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ **3p**: 169.6, 84.0, 83.9,

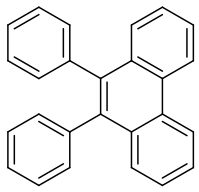
51.1, 34.4, 31.6, 29.5, 29.1, 24.8, 24.7, 22.5, 14.1; **3p'**:171.7, 83.4, 83.2, 52.3, 35.1, 31.5, 29.4, 28.7, 24.9, 24.6, 22.5, 14.1; ^{11}B NMR (225 MHz, $CDCl_3$) δ 29.84; HRMS (ESI positive) calcd for $C_{22}H_{40}B_2O_6$ $[M + Na]^+$: 445.2903, found 445.2903.

(*E*)-2,2'-(1-Phenylethene-1,2-diyl)bis(4,4,6-trimethyl-1,3,2-dioxaborinane) (3bb)



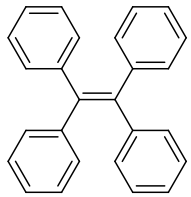
E:*Z* = 93:7; light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.44 (m, 2H), 7.27-7.20 (m, 3H), 6.12 (s, 1H), 4.38-4.22 (s, 2H), 1.86-1.54 (m, 4H), 1.48-1.25 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.47, 143.42, 127.89, 126.82, 126.35, 71.39, 71.34, 70.86, 70.78, 64.93, 64.67, 64.61, 45.90, 45.84, 45.75, 31.45, 31.35, 31.33, 28.34, 28.31, 28.27, 28.18, 23.42, 23.17, 23.13; ^{11}B NMR (225 MHz, $CDCl_3$) δ 26.59; HRMS (ESI positive) calcd for $C_{20}H_{30}B_2O_4$ $[M + Na]^+$: 379.2222, found: 379.2221.

9,10-Diphenylphenanthrene



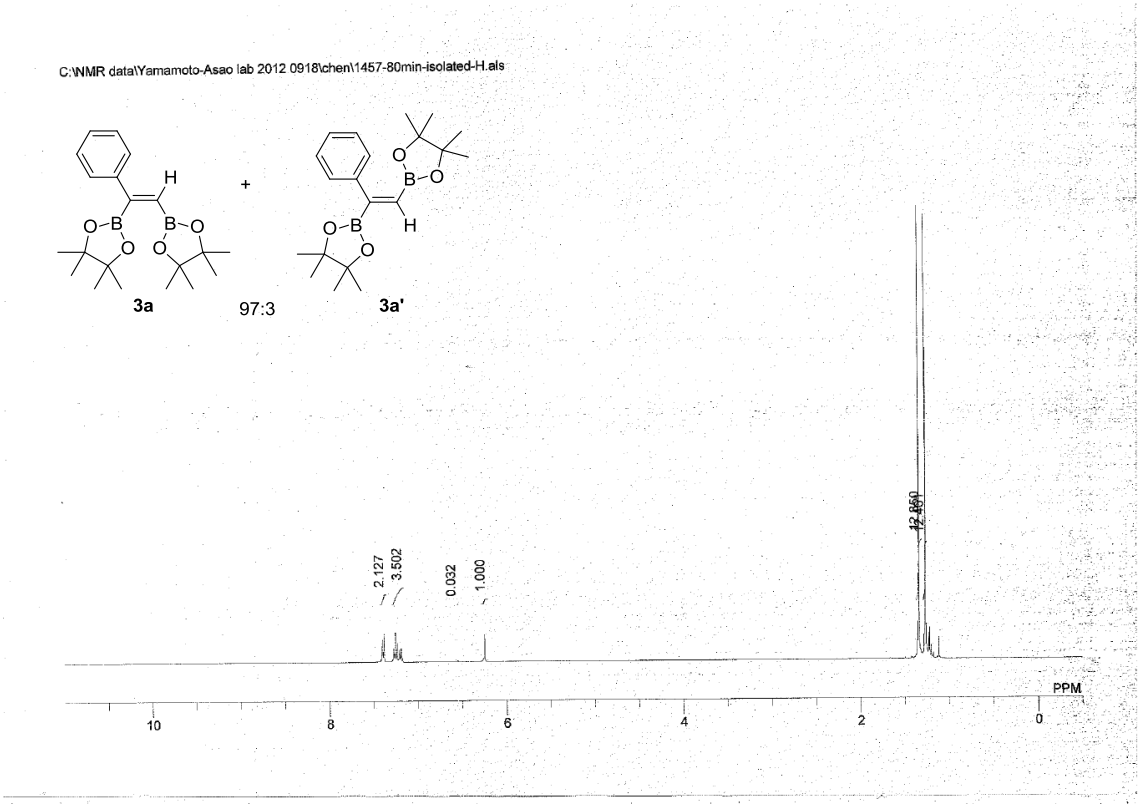
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (d, *J* = 8.4 Hz, 2H), 7.73-7.67 (m, 2H), 7.62-7.58 (m, 2H), 7.55-7.50 (m, 2H), 7.31-7.16 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.4, 137.1, 131.7, 130.9, 129.9, 127.7(5), 127.7(4), 126.5, 126.3(9), 126.3(0), 122.4; HRMS (ESI positive) calcd for $C_{26}H_{18}$: 330.1403, found 330.1402.

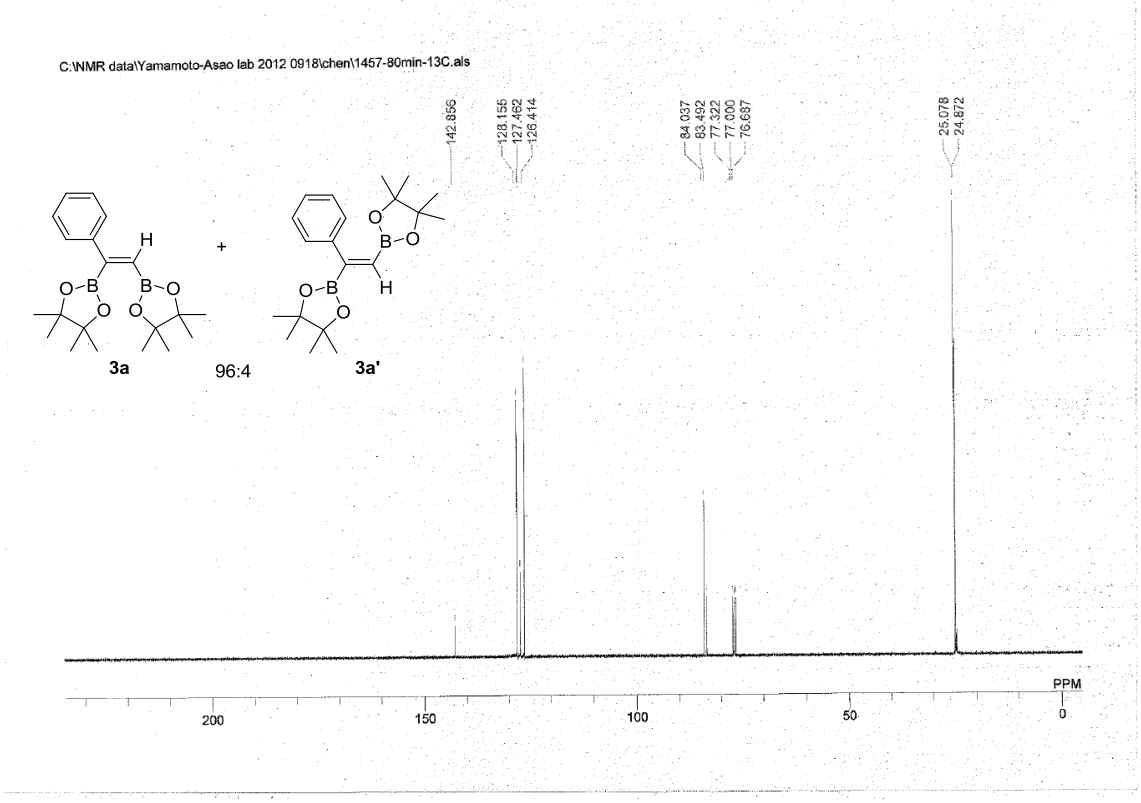
1,1,2,2-Tetraphenylethene



White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13-7.08 (m, 12H), 7.06-7.01 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 140.8, 131.2, 127.5, 126.3; HRMS (ESI positive) calcd for $C_{26}H_{20}$: 332.1559, found 332.1559.

NMR spectra


C:\NMR data\Yamamoto-Asao lab 2012 0918\chen\1457-80min-isolated-H.als
3a
97:3
3a'
2.127
3.502
0.032
1.000
12.860
PPM
10
8
6
4
2
0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3a
96:4
3a'
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128.155
127.462
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83.492
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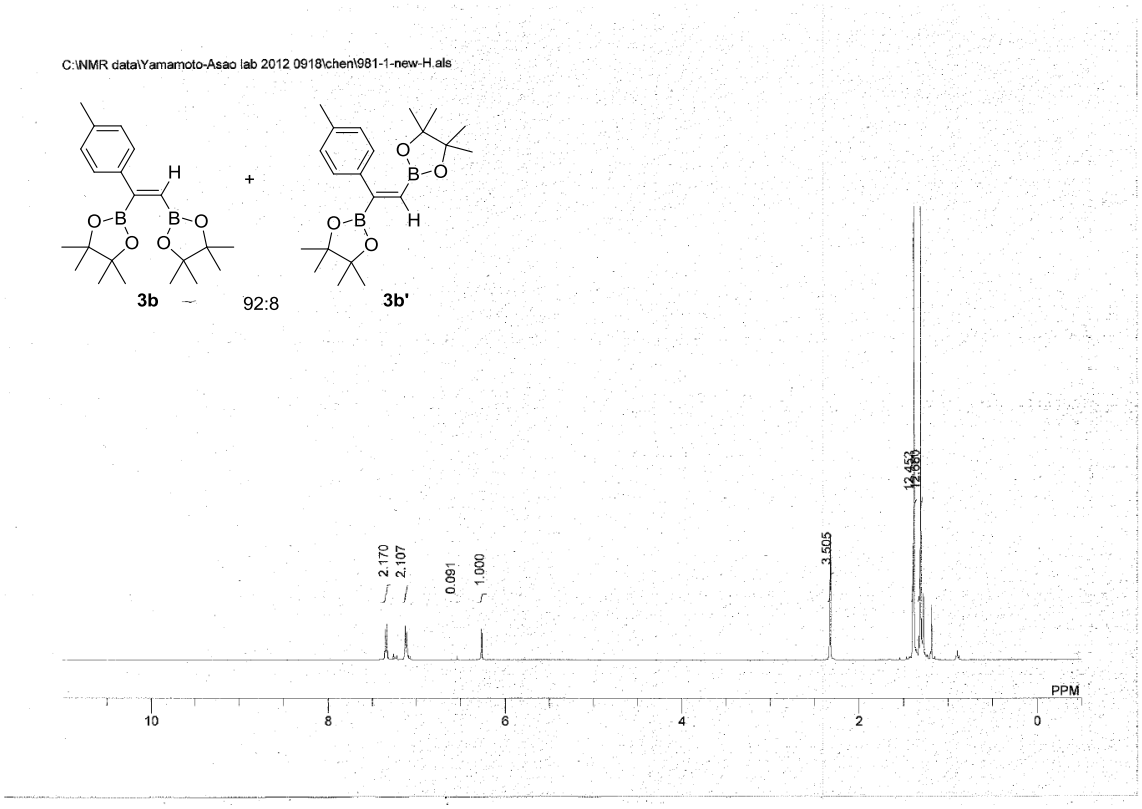
25.078
24.872
PPM
200
150
100
50
0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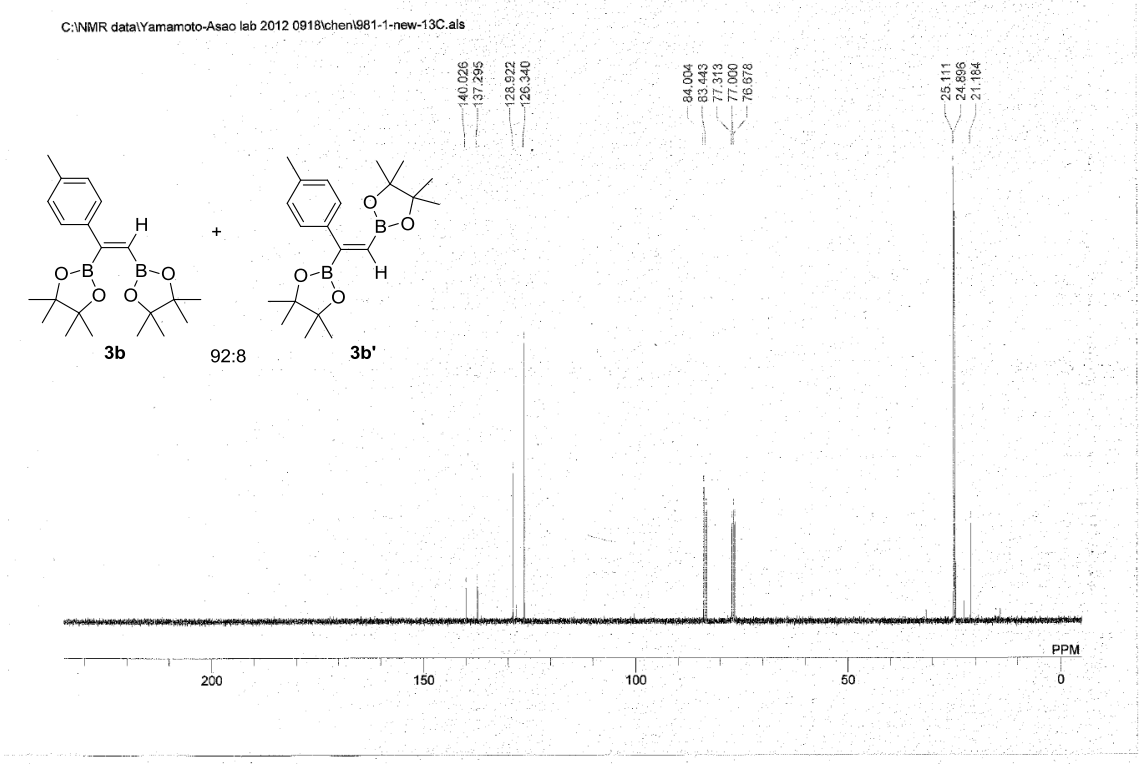
3b
92:8
3b'
2.170
2.107
0.091
1.000
3.505
12.452
12.580
PPM
10
8
6
4
2
0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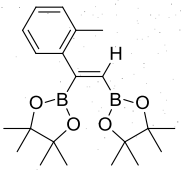
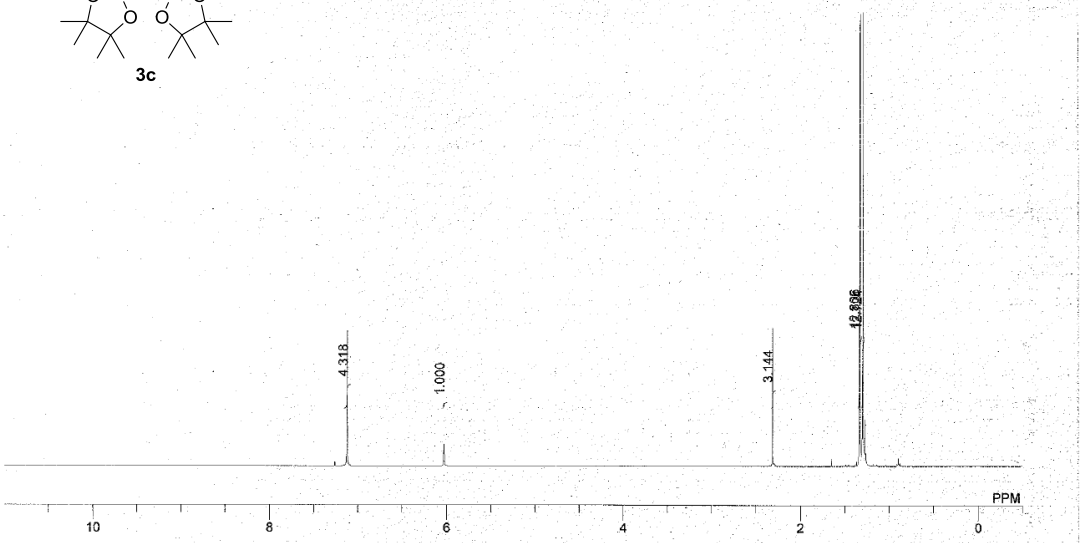
140.026
137.295
128.922
126.340
84.004
83.443
77.313
77.000
76.678
25.111
24.896
21.184
3b
92:8
3b'
PPM
200
150
100
50
0

C:\NMR data\Yamamoto-Asao lab 2012 0918\chen\1016-H.als



3c



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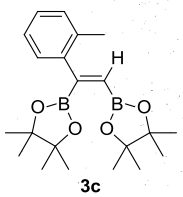
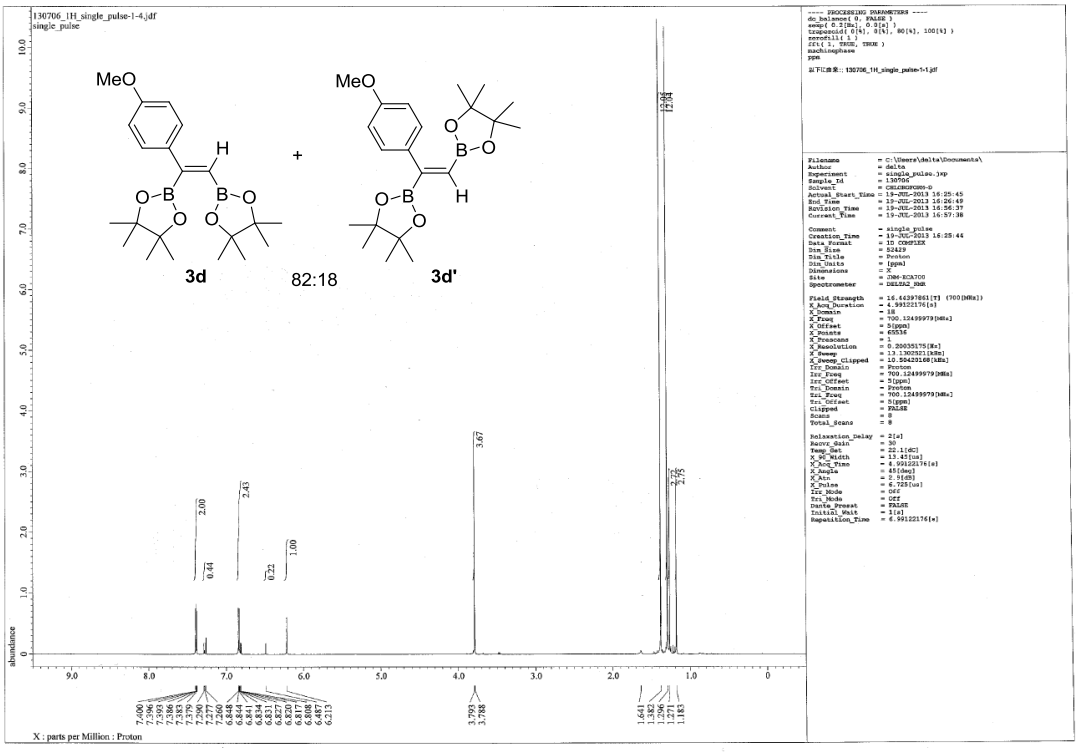


3c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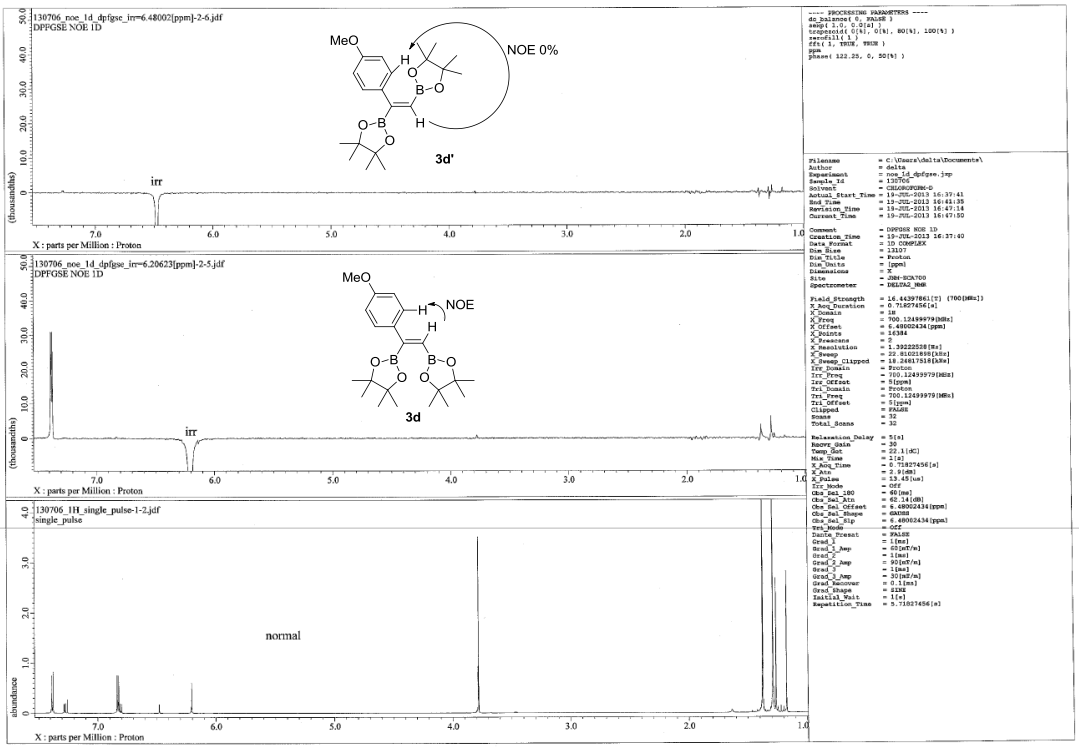
single_pulse
MeO
3d
82:18
3d'
abundance
X : parts per Million : Proton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irr
3d'
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DPFGSE NOE 1D
NOE
irr
3d
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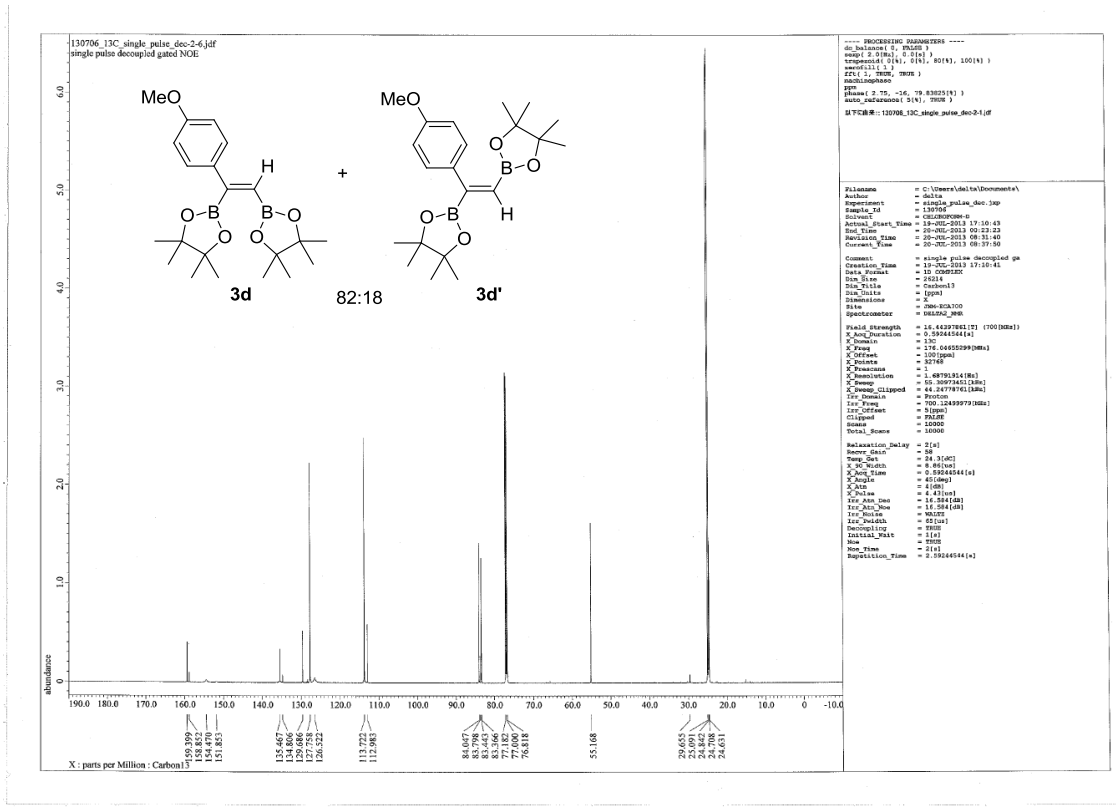
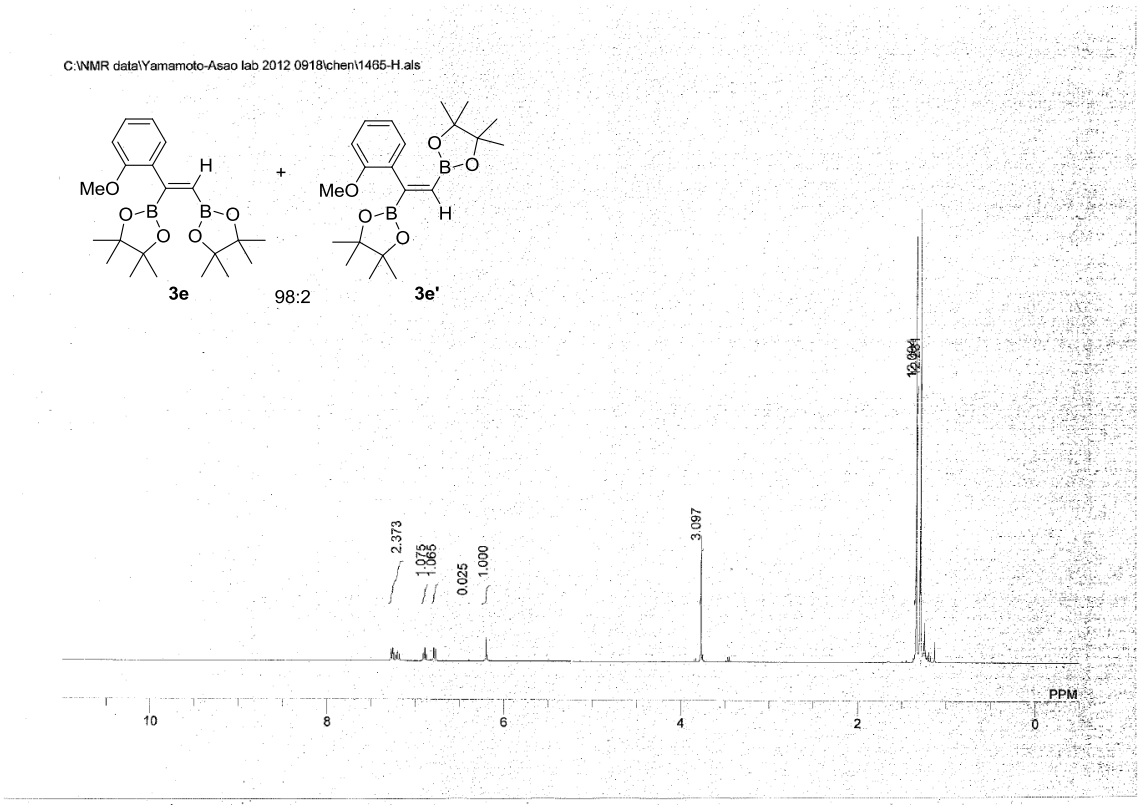
single_pulse
normal
(thousandths)
abundance
X : parts per Million : Proton


130706_13C_single_pulse_dec-2-6.jdf
single pulse decoupled gated NOE
MeO
H
3d
82:18
3d'
abundance
X : parts per Million : Carbon13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MeO
H
B-O
O-B
O
3e
98:2
3e'
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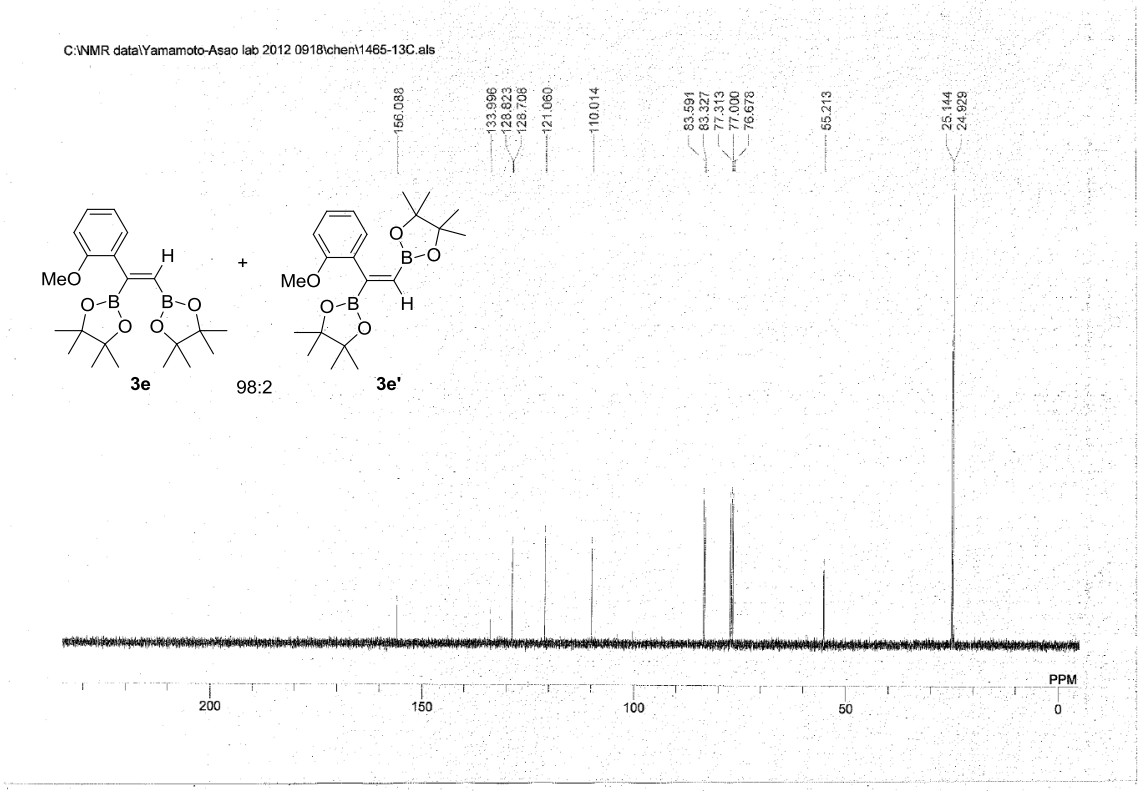
1.065
0.025
1.000
3.097
12.000
PPM
10
8
6
4
2
0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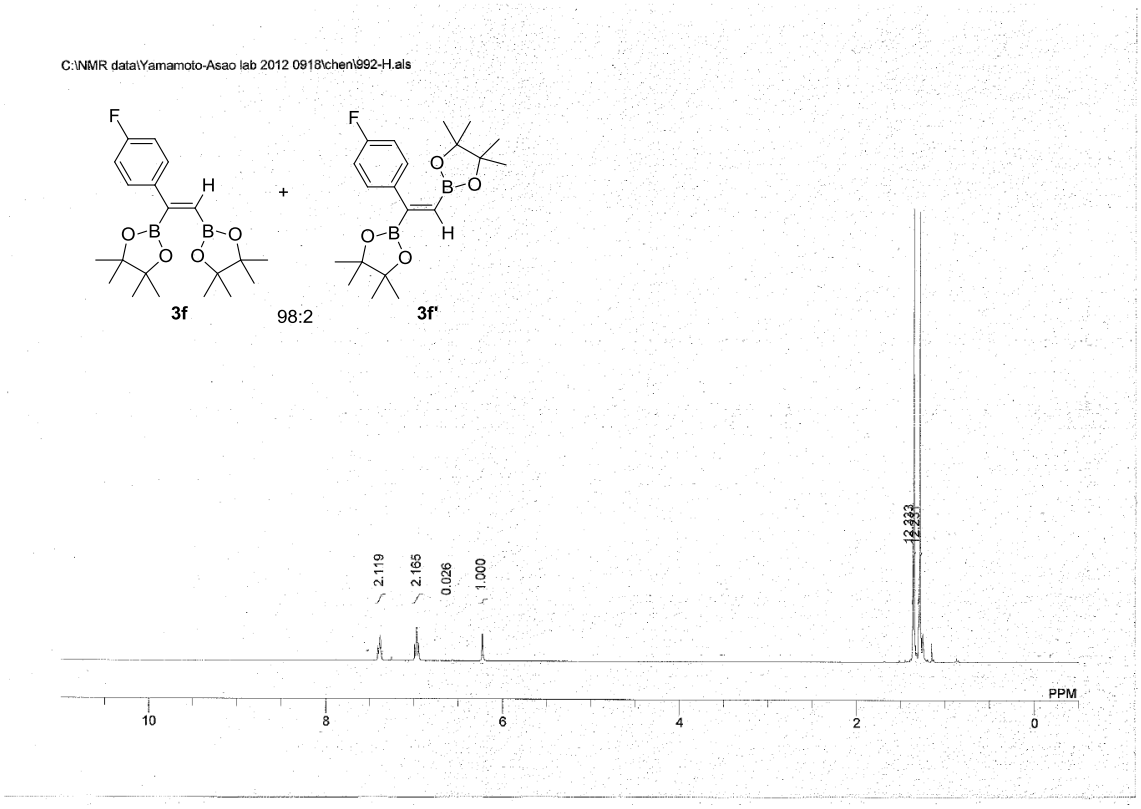
156.088
133.996
128.823
128.706
121.060
110.014
83.591
83.327
77.313
77.000
76.678
55.213
25.144
24.929
MeO
H
B-O
O-B
O
3e
98:2
3e'
PPM
200
150
100
50
0


C:\NMR data\Yamamoto-Asao lab 2012 0918\chen\992-H.als
F
H
O-B
B-O
O
3f
+
98:2
3f'
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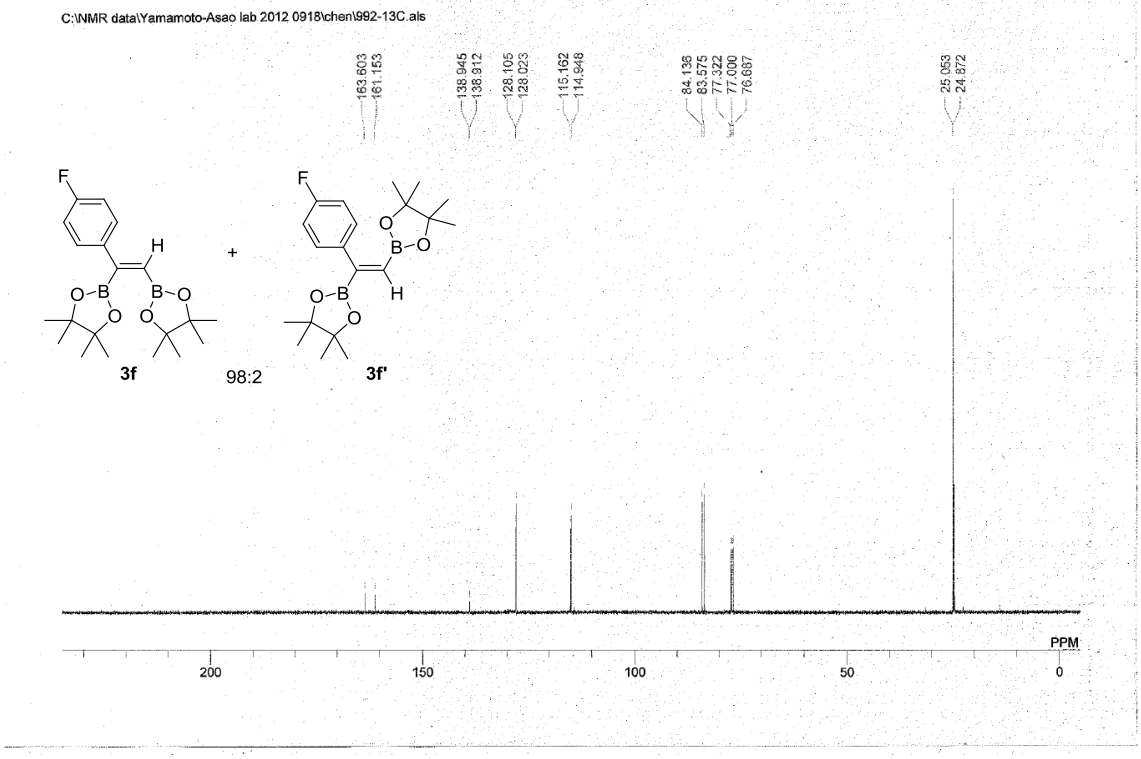
12.233
PPM
10
8
6
4
2
0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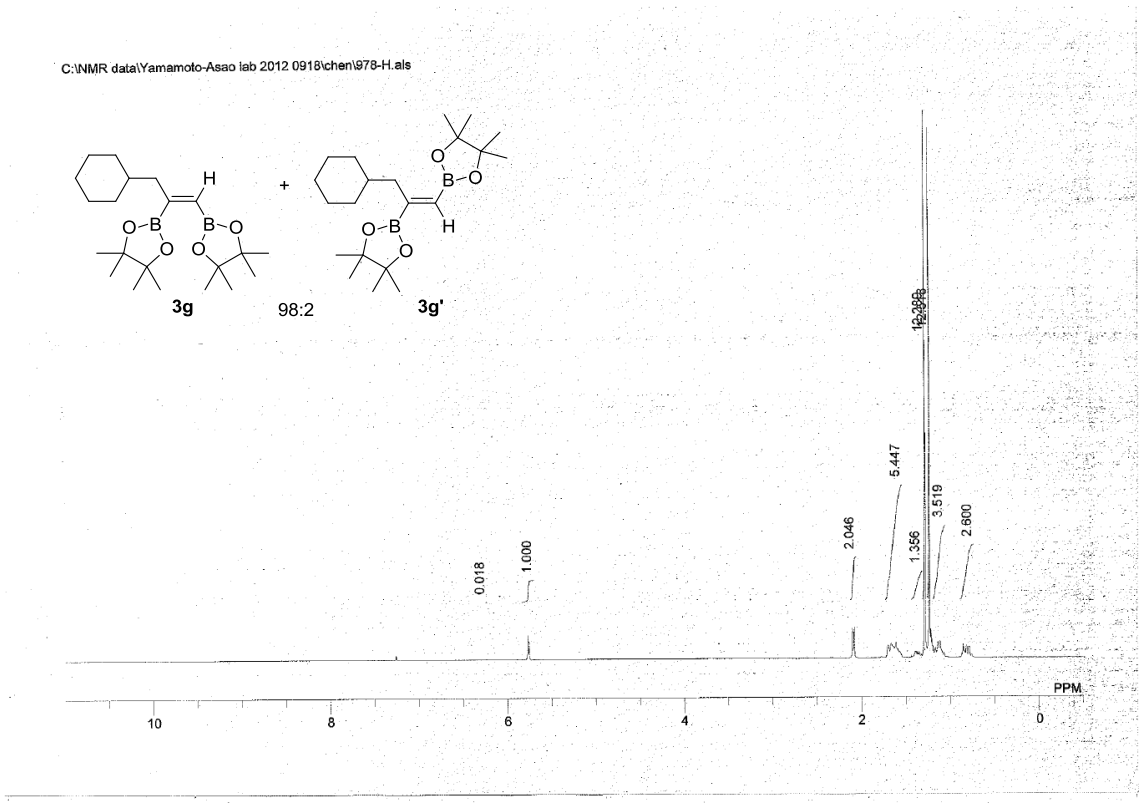
163.603
161.153
138.945
138.812
128.105
128.023
115.162
114.948
84.138
83.575
77.322
77.000
76.687
25.053
24.872
F
H
3f
+
98:2
3f'
PPM
200
150
100
50
0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3g
98:2
3g'
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1.000
2.046
5.447
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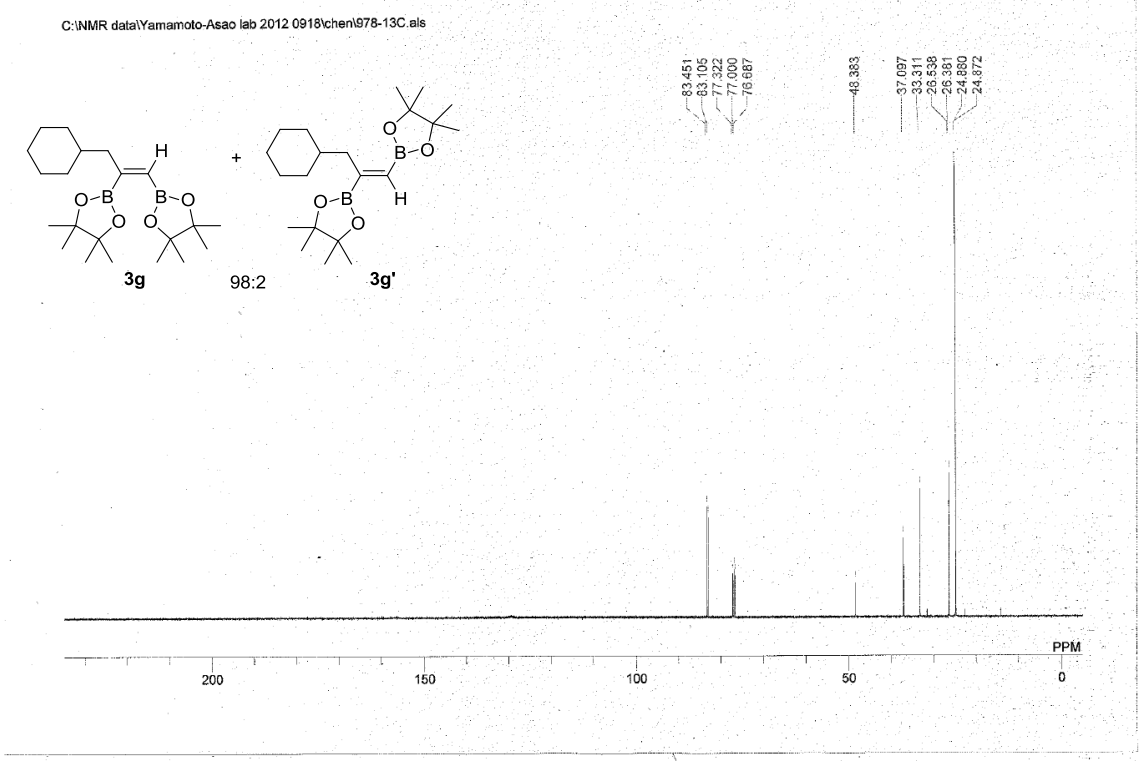
2.600
PPM
10
8
6
4
2
0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3g
98:2
3g'
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83.105
77.322
77.000
76.687
48.383
37.097
33.311
26.538
26.381
24.880
24.872
PPM
200
150
100
50
0

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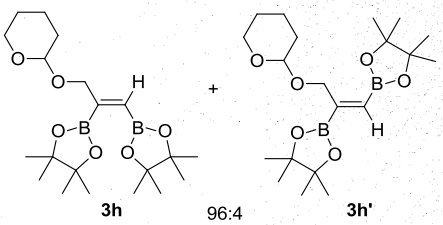

3h 96:4 **3h'**

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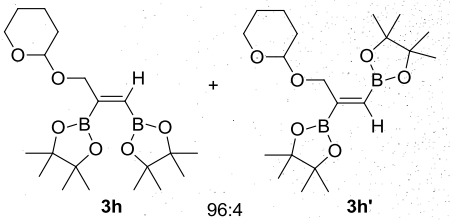
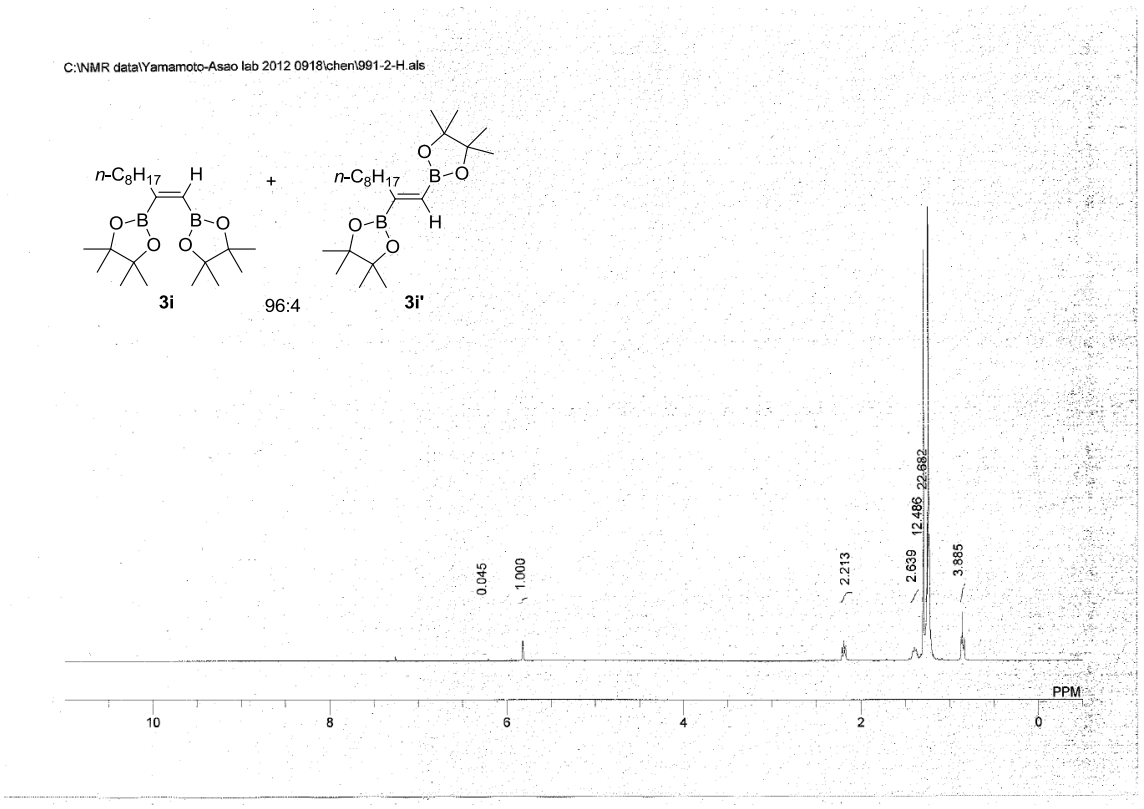


3h 96:4 **3h'**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n-C8H17
H
B
O
3i
96:4
3i'
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2.213
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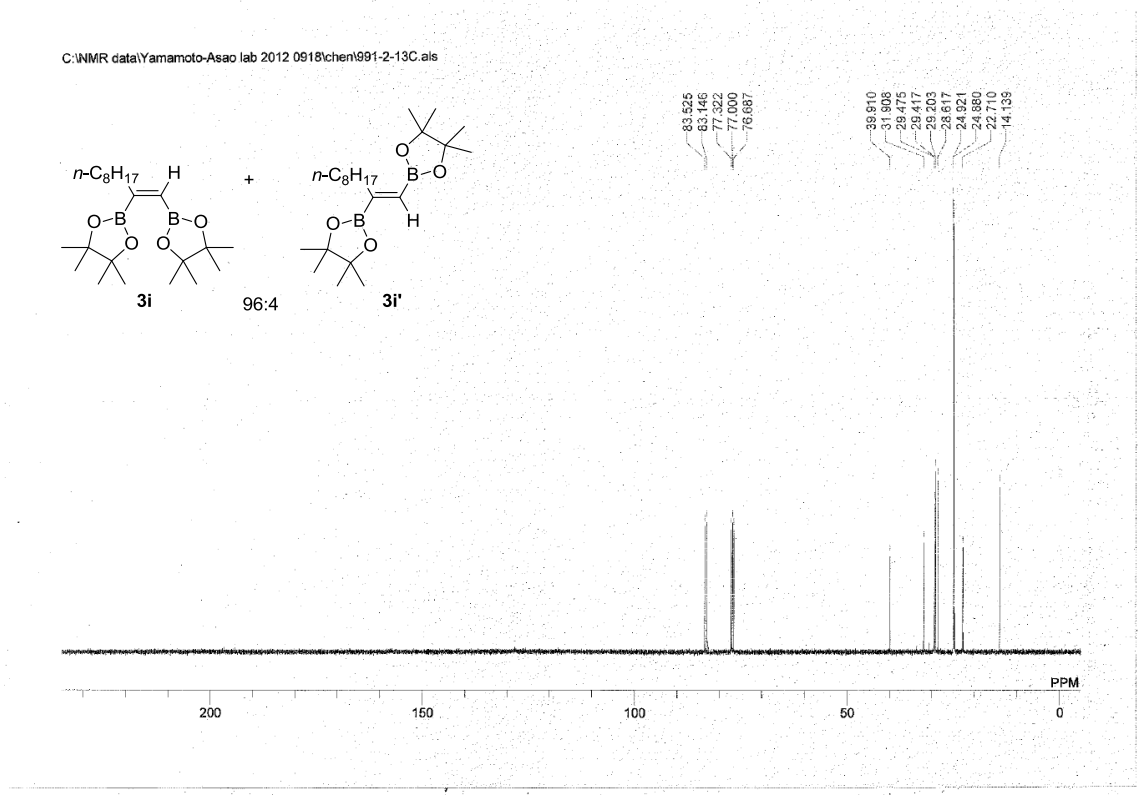
12.486
22.682
3.885
PPM
10
8
6
4
2
0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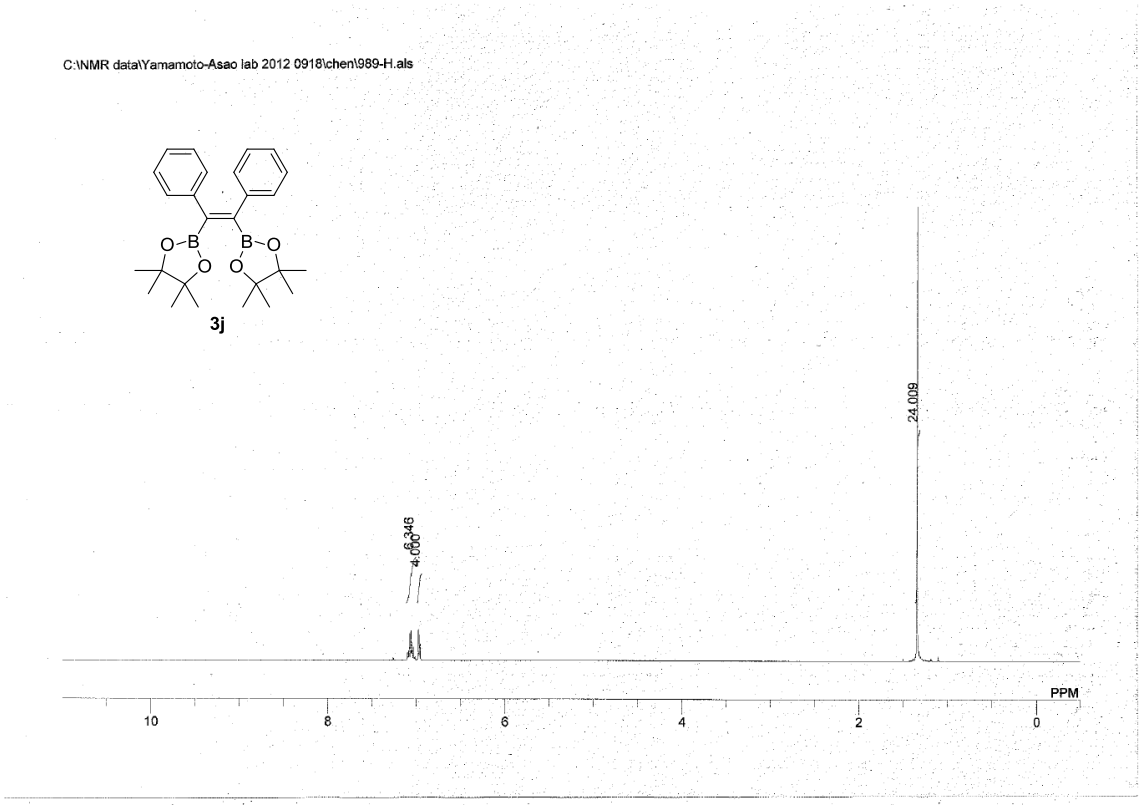
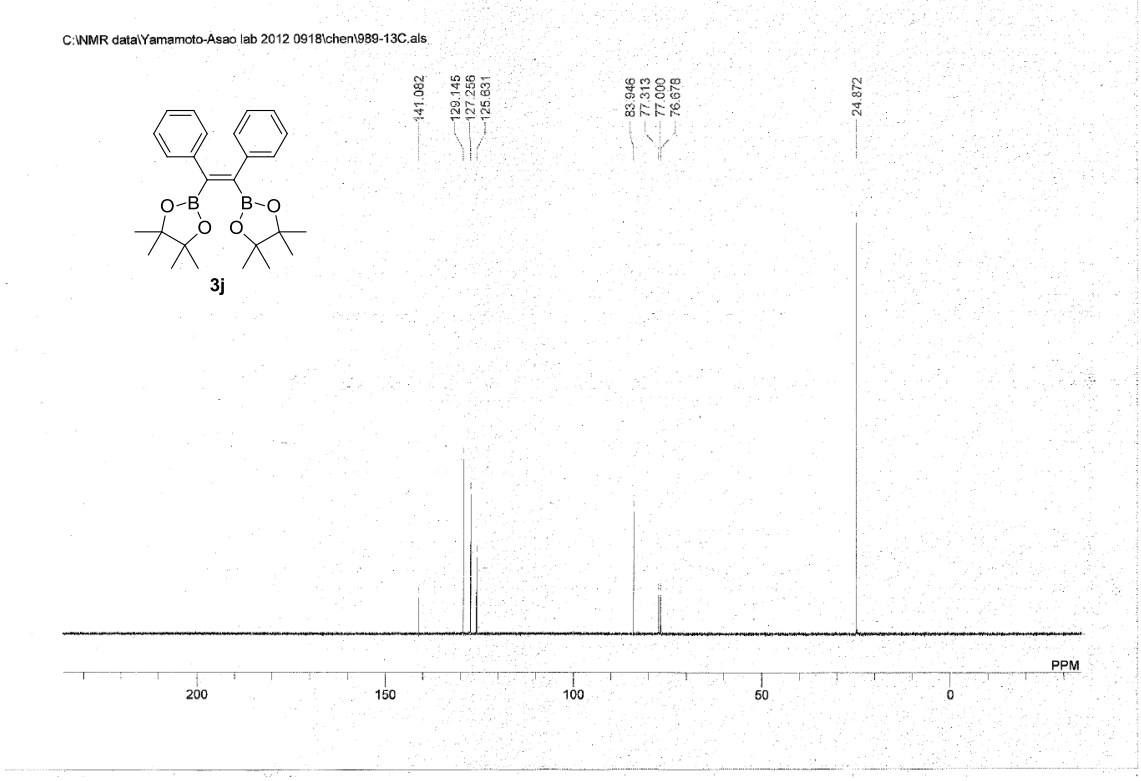
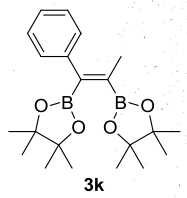
n-C8H17
H
B
O
3i
96:4
3i'
83.525
83.146
77.322
77.000
76.687
39.910
31.908
29.475
29.417
29.203
28.617
24.921
24.880
22.710
14.139
PPM
200
150
100
50
0

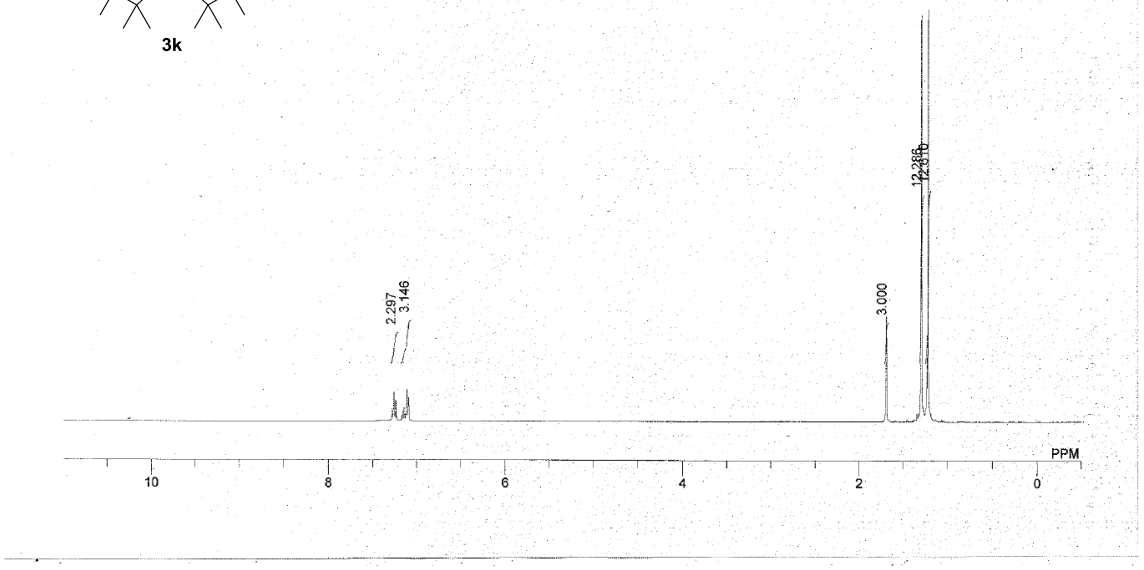

C:\NMR data\Yamamoto-Asao lab 2012 0918\chen\989-H.als
3j
6.948
4.000
24.009
PPM
10
8
6
4
2
0


C:\NMR data\Yamamoto-Asao lab 2012 0918\chen\989-13C.als
3j
141.082
129.145
127.256
125.831
83.946
77.313
77.000
76.678
24.872
PPM
200
150
100
50
0

C:\NMR data\Yamamoto-Asao lab 2012 0918\chen\1342-isolated-H.als



3k



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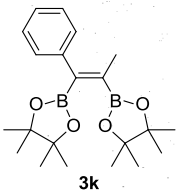
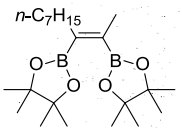


3k

C:\NMR data\Yamamoto-Asao lab 2012 0918\chen\1006-H.als



3l

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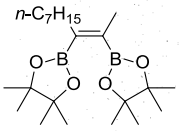
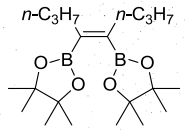
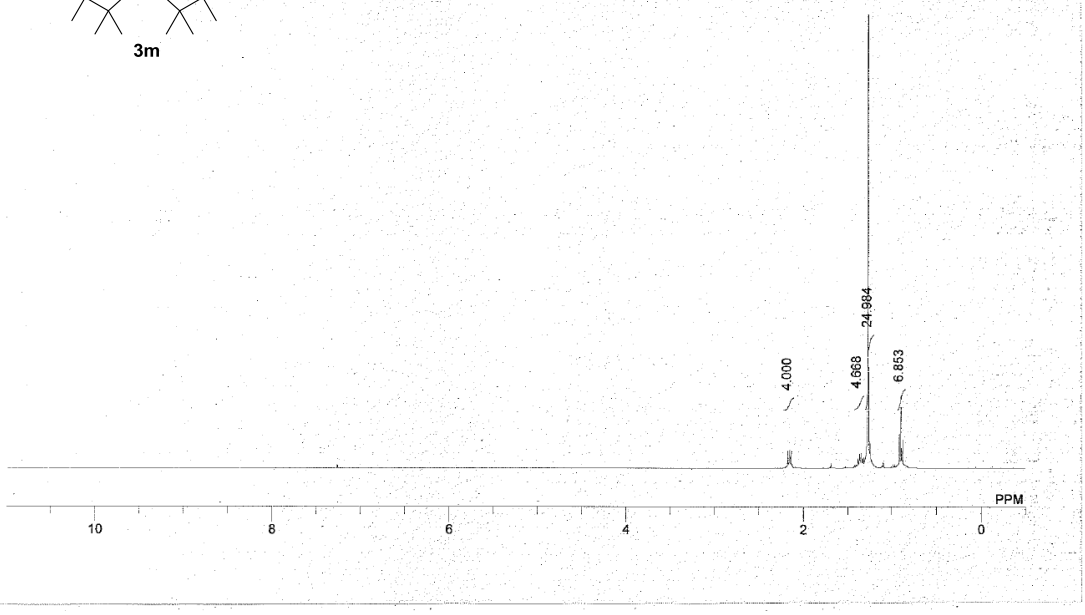


3l

C:\NMR data\Yamamoto-Asao lab 2012 0918\chen\1366-H.als



3m



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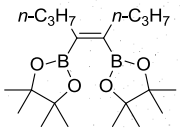
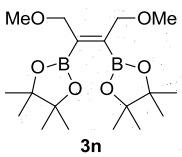
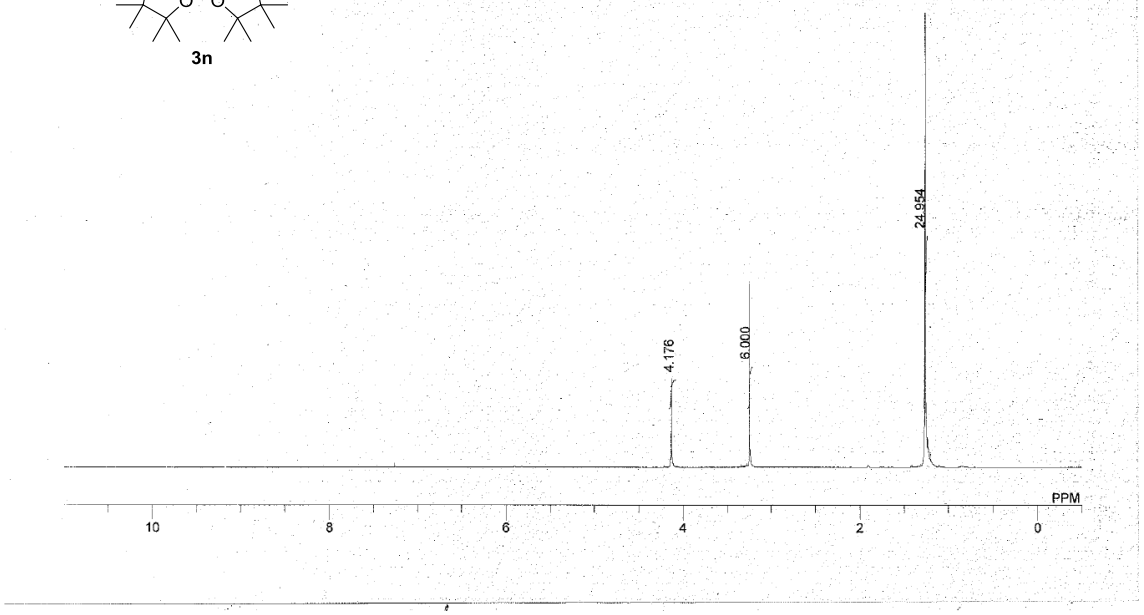


3m

C:\NMR data\Yamamoto-Asao lab 2012 0918\chen\1367-H.als



3n



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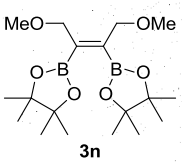
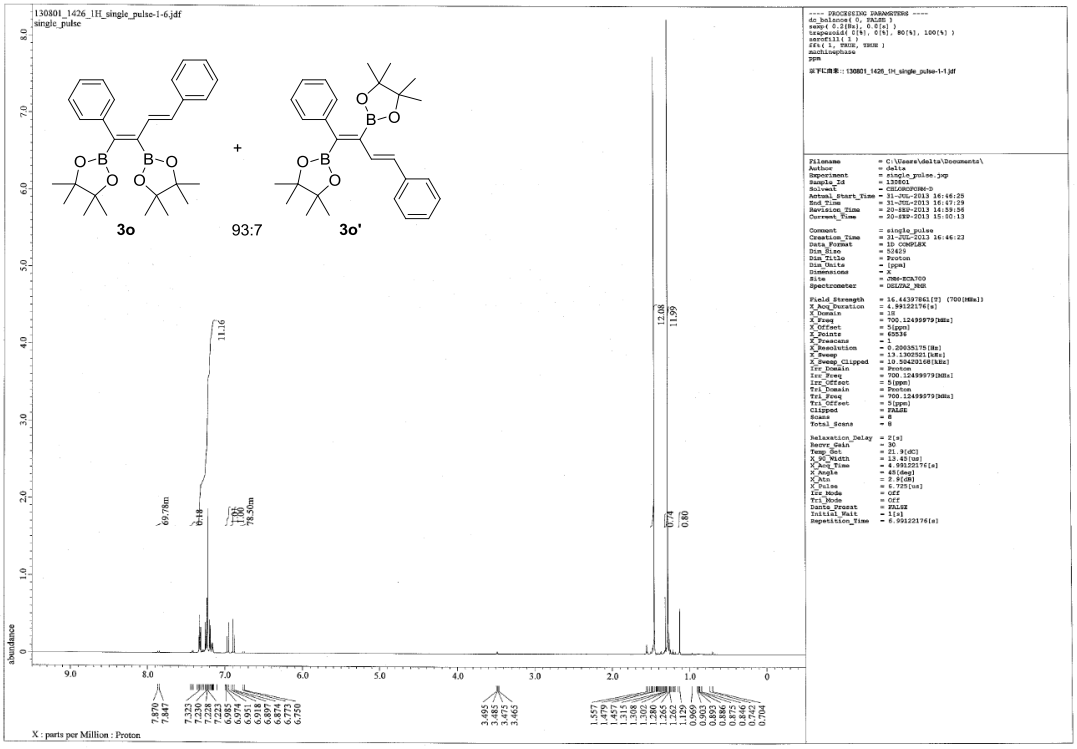
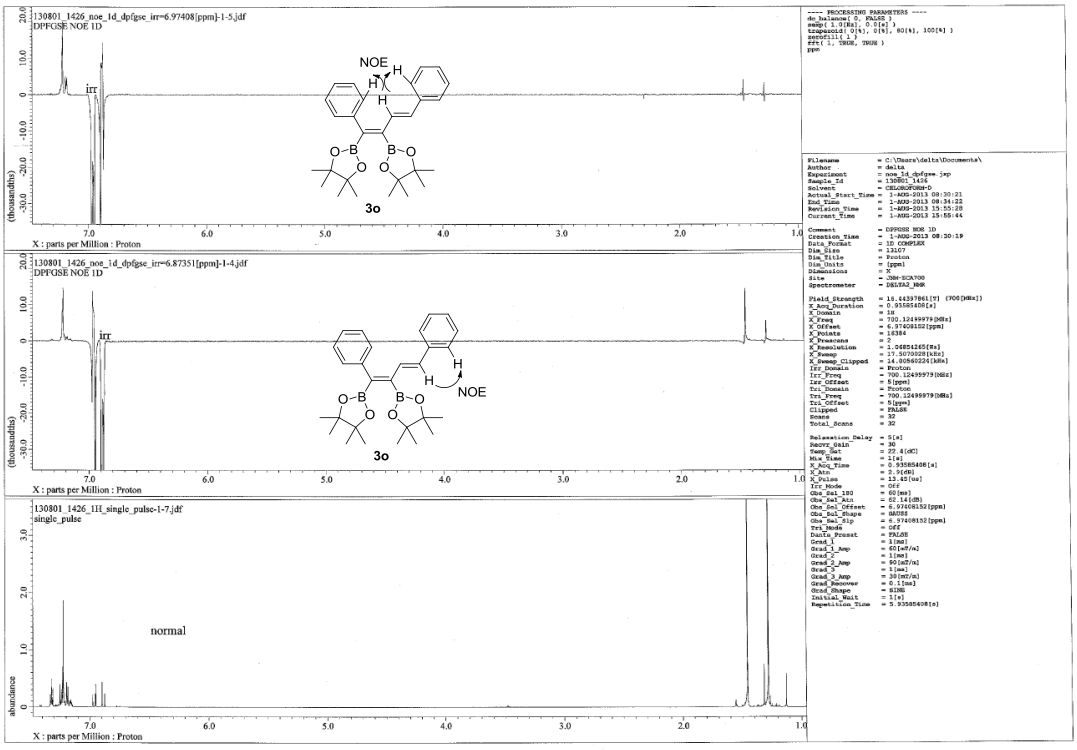
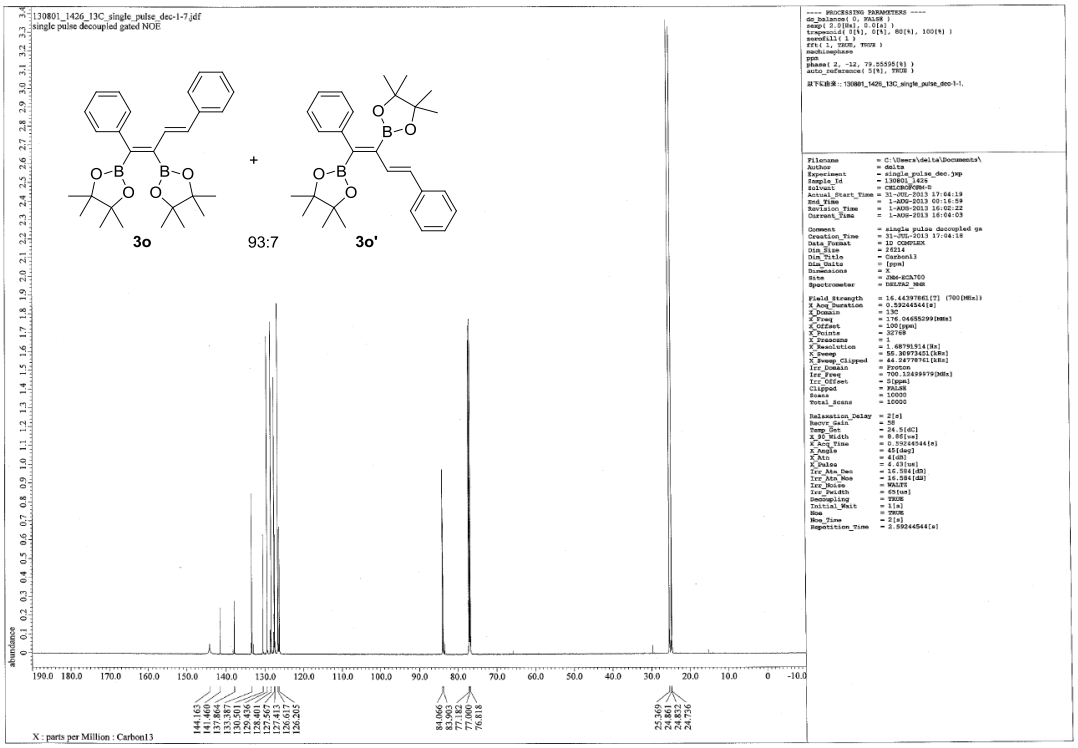
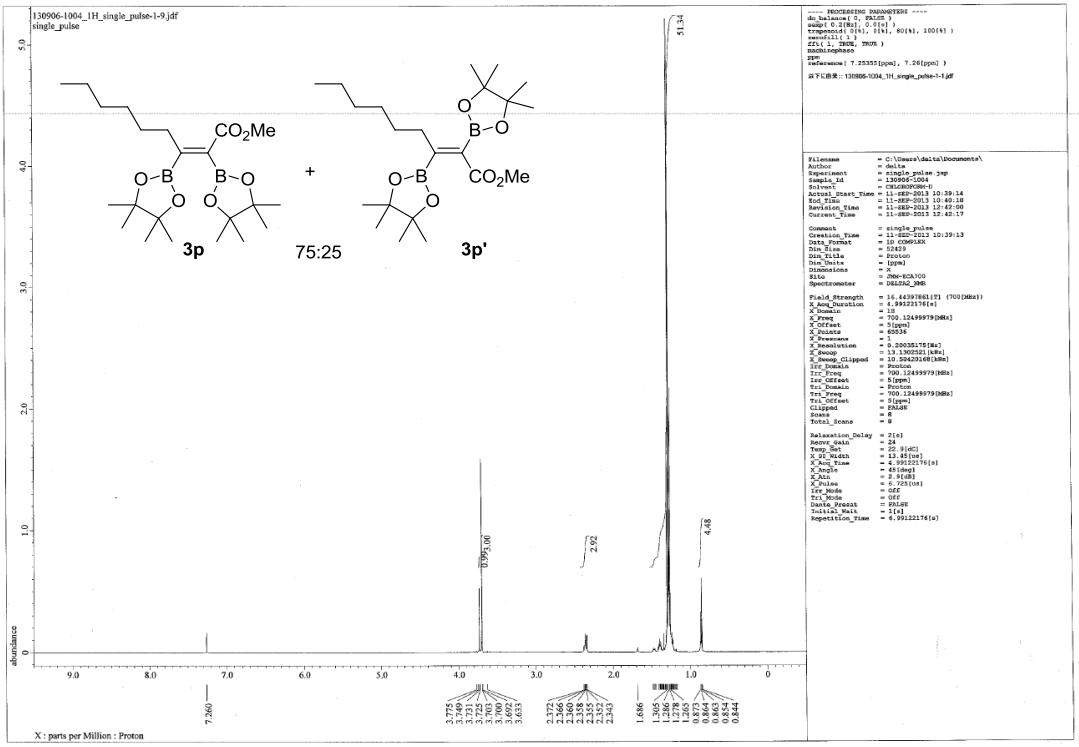


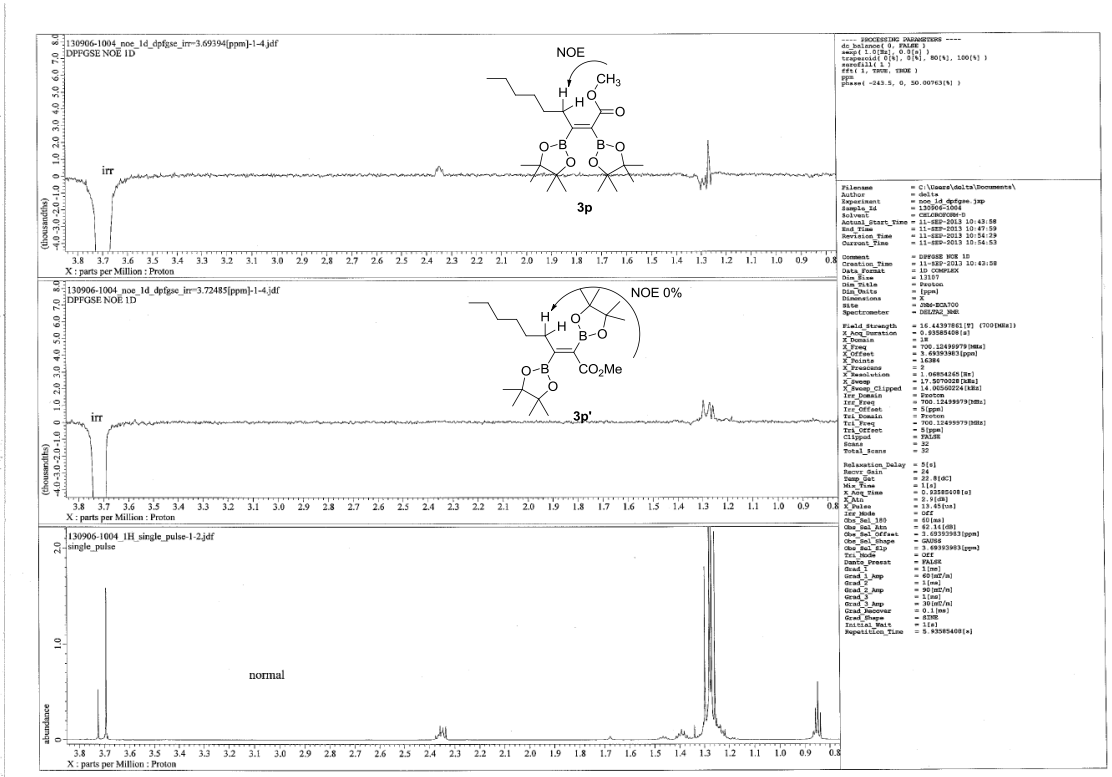
3n

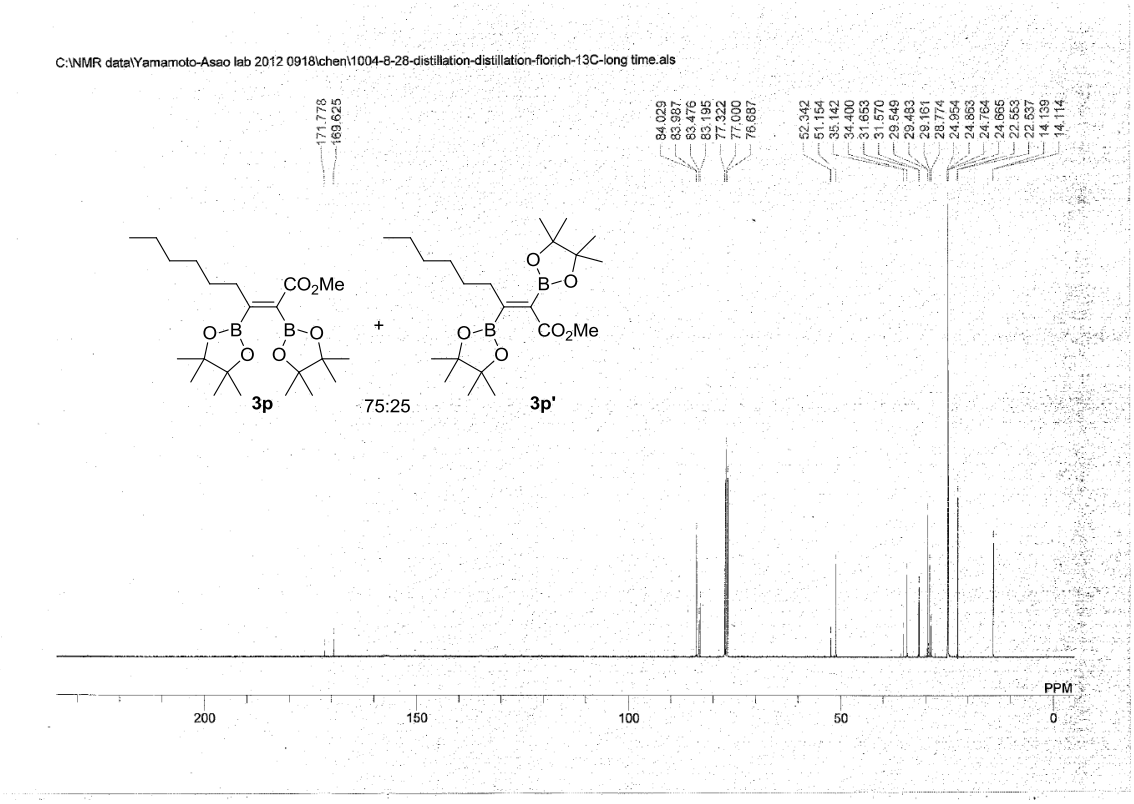

130801_1426_1H_single_pulse-1-6.jdf
single_pulse
3o
93:7
3o'
X : parts per Million : Proton

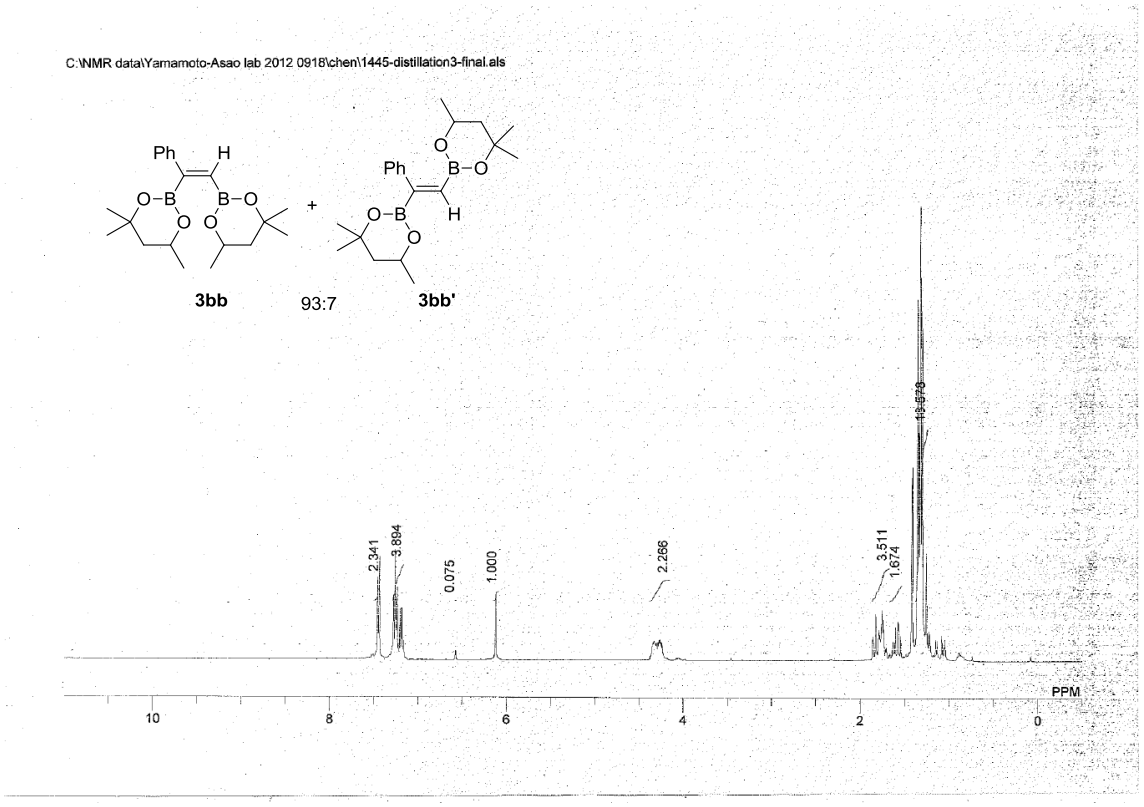

130801_1426_noe_1d_dpfgse_irr=6.97408[ppm]-1-5.jdf
DPFGSE NOE 1D
irr
NOE
3o
X : parts per Million : Proton
130801_1426_noe_1d_dpfgse_irr=6.87351[ppm]-1-4.jdf
DPFGSE NOE 1D
irr
NOE
3o
X : parts per Million : Proton
130801_1426_1H_single_pulse-1-7.jdf
single_pulse
normal
X : parts per Million : Proton

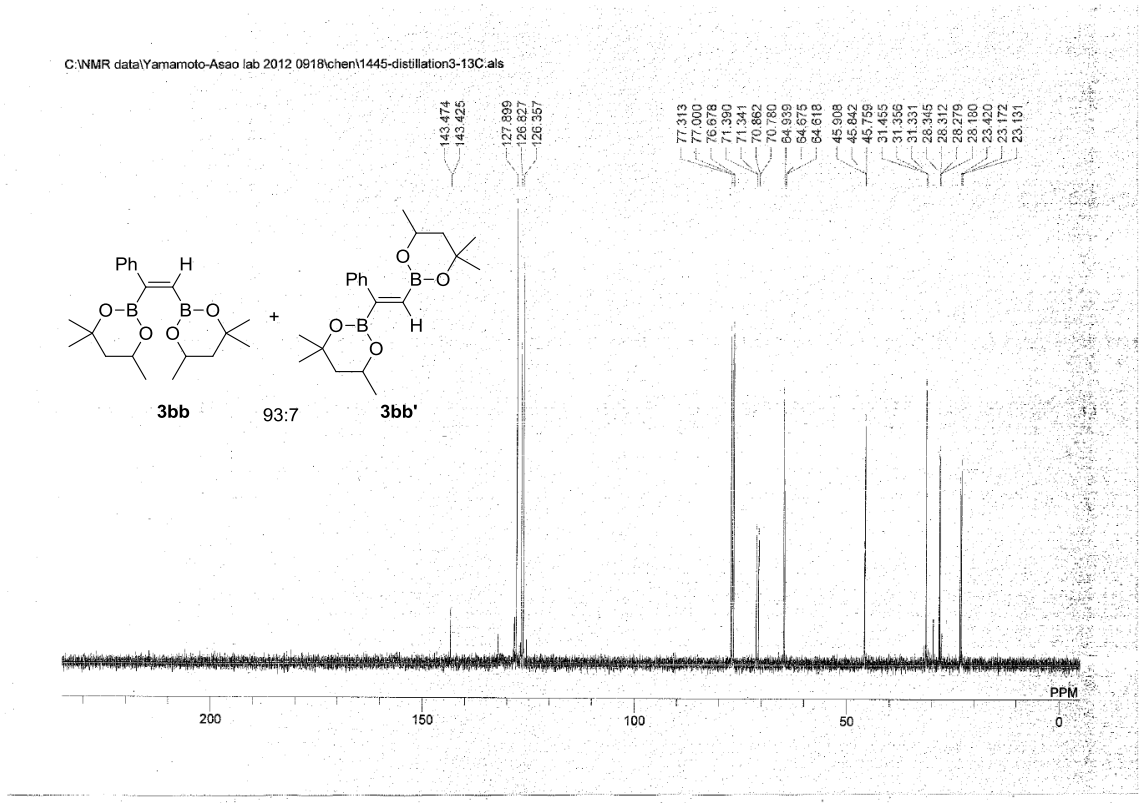

130801_1426_13C_single_pulse_dec-1-7.jdf
single pulse decoupled gated NOE
3o
93:7
3o'
X : parts per Million : Carbon13

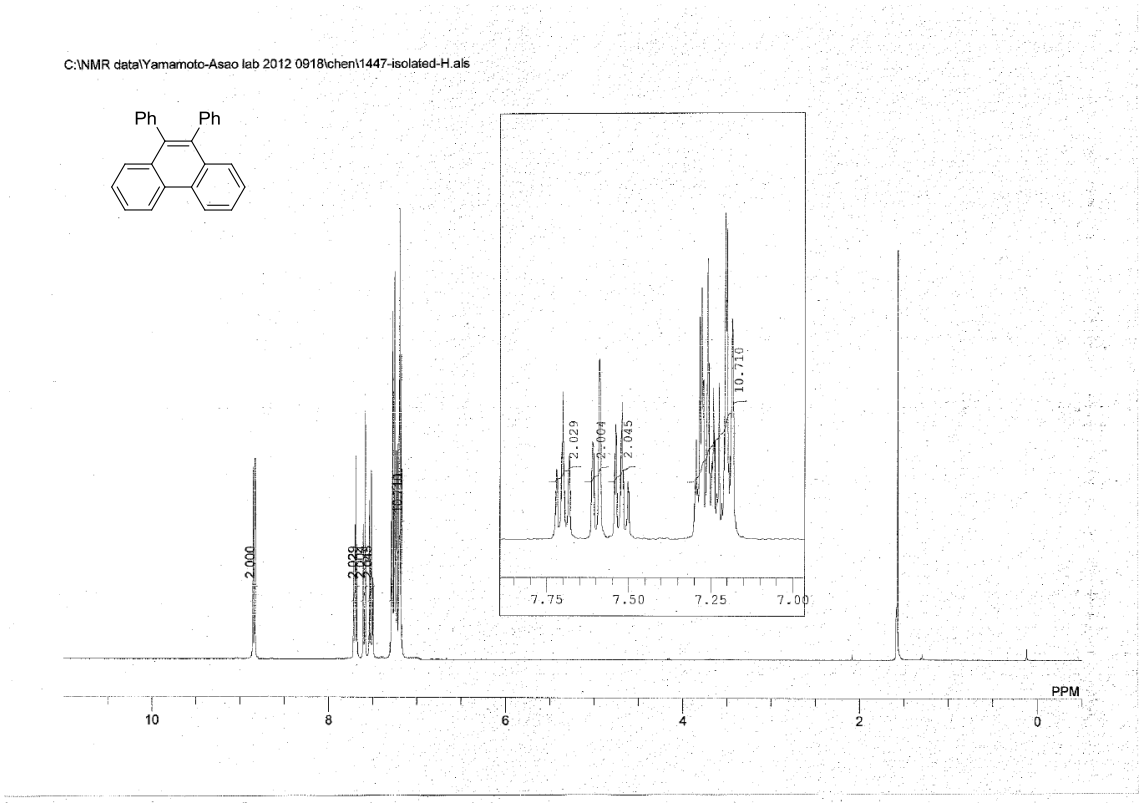

130906-1004_1H_single_pulse-1-9.jdf
single_pulse
3p
75:25
3p'
X : parts per Million : Proton

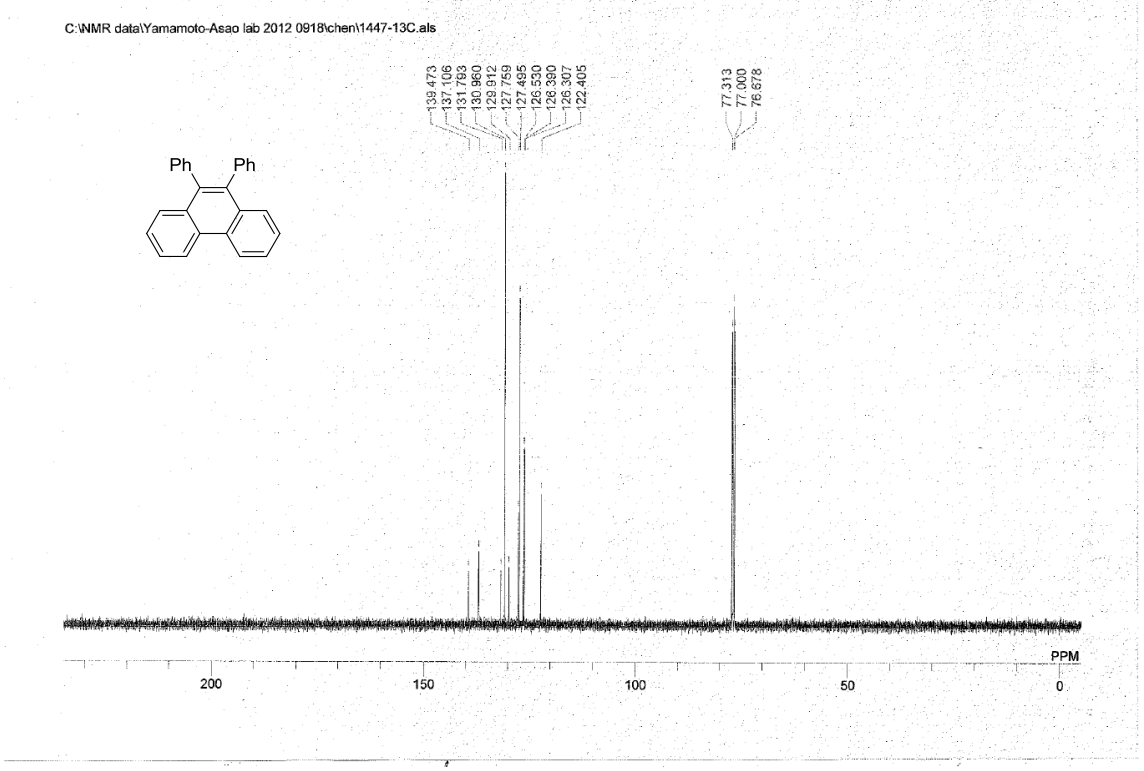

130906-1004_noe_1d_dpfgse_irr=3.69394[ppm]-1-4.jdf
DPFGSE NOE 1D
NOE
irr
3p
X : parts per Million : Proton
130906-1004_noe_1d_dpfgse_irr=3.72485[ppm]-1-4.jdf
DPFGSE NOE 1D
NOE 0%
irr
3p'
X : parts per Million : Proton
130906-1004_1H_single_pulse-1-2.jdf
single_pulse
normal
abundance
X : parts per Million : Proton

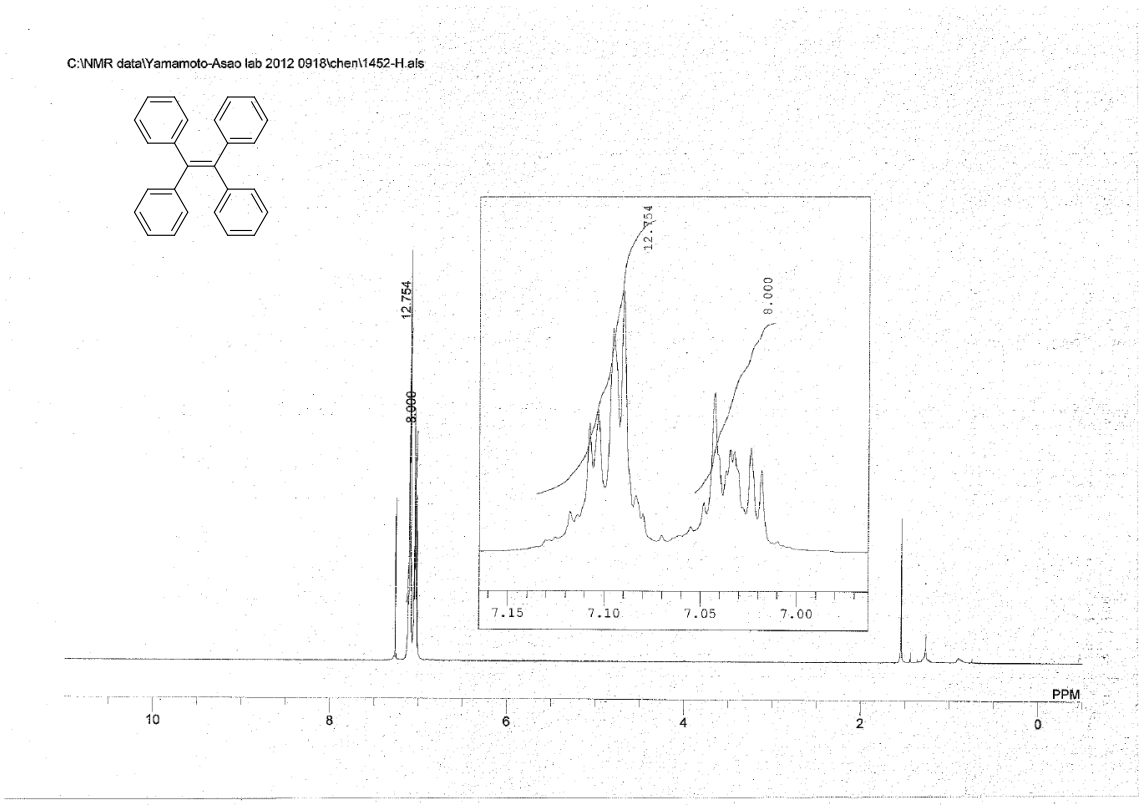

C:\NMR data\Yamamoto-Asao lab 2012 0918\chen\1004-8-28-distillation-distillation-florich-13C-long time.als
171.778
169.625
84.029
83.987
83.476
83.195
77.322
77.000
76.687
62.342
61.164
35.142
34.400
31.653
31.570
29.549
29.483
28.161
28.774
24.954
24.853
24.764
24.656
22.553
22.537
14.139
14.114
3p
75:25
3p'
PPM
200
150
100
50
0

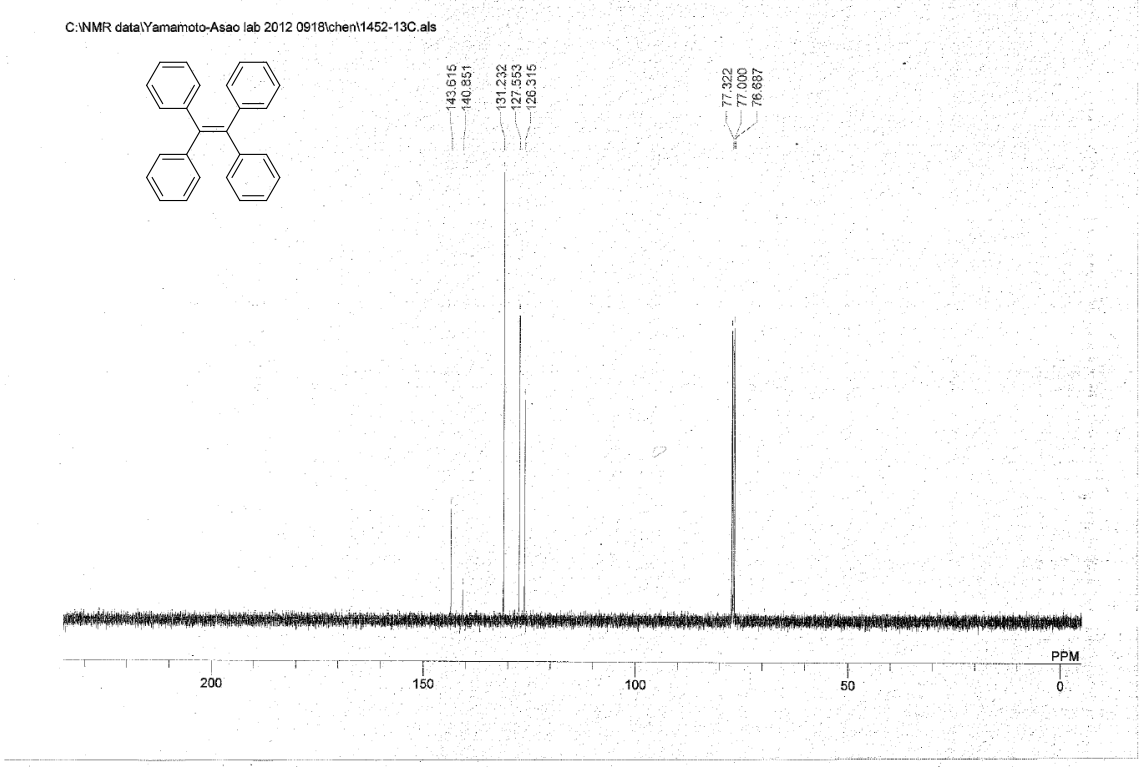

C:\NMR data\Yamamoto-Asao lab 2012 0918\chen\1445-distillation3-final.als
Ph
H
O–B
B–O
O
O
+
Ph
B–O
O–B
H
O
O
3bb
93:7
3bb'
2.341
3.894
0.075
1.000
2.266
3.511
1.674
18.573
PPM
10
8
6
4
2
0


C:\NMR data\Yamamoto-Asao lab 2012 0918\chen\1445-distillation3-13C.als
143.474
143.425
127.899
126.827
126.357
77.313
77.000
76.678
71.390
71.341
70.862
70.780
64.939
64.675
64.618
45.908
45.842
45.756
31.455
31.396
31.331
28.345
28.312
28.279
28.180
23.420
23.172
23.131
Ph
H
O–B
B–O
O
O
+
Ph
B–O
O–B
H
O
O
3bb
93:7
3bb'
PPM
200
150
100
50
0


C:\NMR data\Yamamoto-Asao lab 2012 0918\chen\1447-isolated-H.als
Ph
Ph
2.000
2.029
2.004
2.045
10.710
7.75
7.50
7.25
7.00
PPM
10
8
6
4
2
0


C:\NMR data\Yamamoto-Asao lab 2012 0918\chen\1447-13C.als
139.473
137.106
131.783
130.960
129.912
127.759
127.485
126.530
126.380
126.307
122.405
77.313
77.000
76.678
Ph
Ph
PPM
200
150
100
50
0


C:\NMR data\Yamamoto-Asao lab 2012 0918\chen\1452-H.als
12.754
8.000
7.15
7.10
7.05
7.00
PPM
10
8
6
4
2
0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143.615
140.851
131.232
127.553
126.315
77.322
77.000
76.687
PPM
200
150
100
50
0