

Supplementary Information for

**Facile access to boryltetralins and borylnaphthalenes via a cycloaddition
using *o*-quinodimethanes**

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Contents

General Remarks	S2
Materials	S2
Experimental Procedures and Characterization Data of Products	S3
References	S16
¹H and ¹³C NMR Spectra of New Compounds	

General remarks.

All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under a purified argon atmosphere. Nuclear magnetic resonance spectra were taken on a JEOL EX-270 (^1H , 270 MHz; ^{13}C , 67.8 MHz) spectrometer or a JEOL Lambda-400 (^1H , 400 MHz; ^{13}C , 99.5 MHz) spectrometer using residual chloroform (^1H , $\delta = 7.26$), or CDCl_3 (^{13}C , $\delta = 77.0$) as an internal standard. ^1H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, quint = quintet, sext = sextet, br = broad, m = multiplet), coupling constants (Hz), integration. High-resolution mass spectra were obtained with a JEOL JMS-SX102A spectrometer. Preparative recycling gel permeation chromatography was performed with GL Science PU 614 equipped with Shodex GPC H-2001L and -2002L columns (chloroform or toluene as an eluent). Unless otherwise noted, commercially available reagents were used without purification. 18-Crown-6 was recrystallized from distilled MeCN. KF (spray-dried) was vacuum dried at 100 °C for 12 h. Dioxane was distilled from sodium/benzophenone ketyl. MeCN was distilled from phosphorus pentoxide.

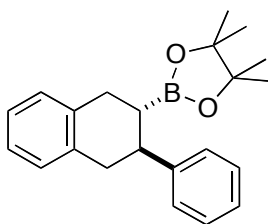
Materials.

o-Quinodimethane precursors (**1a–1e**)¹ and borylalkenes (**2a–2l**)² were prepared according to literature procedures. Other borylalkenes (**2m** and **2n**) were purchased from Aldrich.

[4+2] Cycloaddition between *o*-QDMs and borylalkenes: a general procedure.

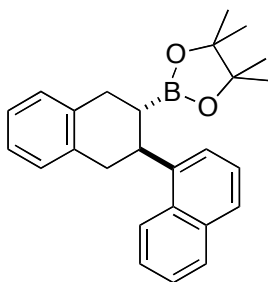
A dioxane solution (1 mL) of **1** (0.30 mmol), **2** (0.20 mmol), 18-crown-6 (0.33 mmol) and KF (0.33 mmol) was stirred at 100 °C for the period as specified in Table 1, Scheme 4 and eqn. 1. The mixture was diluted with ethyl acetate and washed with cold brine. The organic layer was dried over MgSO₄ and concentrated in vacuo. Preparative recycling gel permeation chromatography (chloroform as an eluent) gave the corresponding product.

4,4,5,5-Tetramethyl-2-(3-phenyl-1,2,3,4-tetrahydro-naphthalen-2-yl)-[1,3,2]dioxaborolane (3aa)



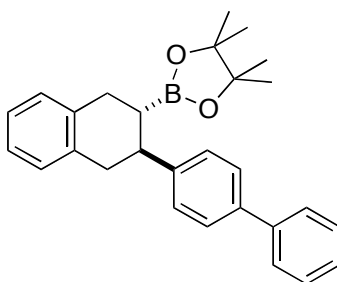
A pale yellow solid: ¹H NMR (CDCl₃): δ 0.97 (s, 6H, CH₃), 0.99 (s, 6H, CH₃), 1.74 (td, *J* = 10.9, 6.3 Hz, 1H, BCH), 2.88-3.06 (m, 5H, ArCH₂ and ArCH), 7.06-7.13 (m, 4H, ArH), 7.16-7.24 (m, 1H, ArH), 7.29-7.31 (m, 4H, ArH); ¹³C NMR (CDCl₃): δ 24.35, 24.43, 31.6, 39.1, 42.9, 76.5, 125.4, 125.6, 126.2, 127.6, 128.2, 128.6, 128.9, 136.4, 136.8, 146.4.

4,4,5,5-Tetramethyl-2-[3-(1-naphthyl)-1,2,3,4-tetrahydro-naphthalen-2-yl]-[1,3,2]dioxaborolane (3ab)



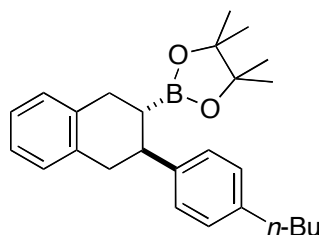
A yellow solid: ¹H NMR (CDCl₃): δ 0.74 (s, 6H, CH₃), 0.86 (s, 6H, CH₃), 1.97 (td, *J* = 11.5, 5.3 Hz, 1H, BCH), 1.91-2.02 (m, 4H, ArCH₂), 3.93 (td, *J* = 11.2, 4.6 Hz, 1H, ArCH), 7.03-7.17 (m, 4H, ArH), 7.41-7.52 (m, 4H, ArH), 7.70 (dd, *J* = 6.9, 2.3 Hz, 1H, ArH), 7.84 (dd, *J* = 6.3, 2.6 Hz, 1H, ArH), 8.23 (dd, *J* = 8.2, 2.0 Hz, 1H, ArH); ¹³C NMR (CDCl₃): δ 24.19, 24.21, 29.7, 31.8, 39.0, 82.9, 123.6, 125.3, 125.5, 125.56, 125.59, 125.7, 126.5, 128.65, 128.70, 128.9, 131.7, 133.8, 136.5, 136.9, 143.0.

4,4,5,5-Tetramethyl-2-[3-(biphenyl-4-yl)-1,2,3,4-tetrahydro-naphthalen-2-yl]-[1,3,2]dioxaborolane (3ac)



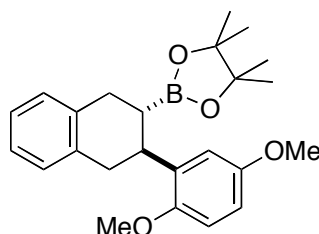
A white solid: ^1H NMR (CDCl_3): δ 0.98 (s, 6H, CH_3), 1.02 (s, 6H, CH_3), 1.76 (td, $J = 10.9$, 6.3 Hz, 1H, BCh), 2.94-3.12 (m, 5H, ArCH_2 and ArCH), 7.12-7.16 (m 4H, ArH), 7.33-7.57 (m, 9H, ArH); ^{13}C NMR (CDCl_3): δ 24.3, 24.4, 31.6, 39.0, 42.5, 83.0, 125.5, 125.6, 127.0, 128.1, 128.6, 128.7, 129.0, 136.4, 136.7, 139.2, 141.2, 145.6.

4,4,5,5-Tetramethyl-2-[3-(4-*n*-butylphenyl)-1,2,3,4-tetrahydro-naphthalen-2-yl]-[1,3,2]dioxaborolane (3ad)



A pale yellow oil: ^1H NMR (CDCl_3): δ 0.93 (t, $J = 6.8$ Hz, 3H, CH_3CH_2), 0.96 (s, 6H, CH_3), 1.00 (s, 6H, CH_3), 1.35 (sext, $J = 7.8$ Hz, 2H, CH_2), 1.57 (quint, $J = 7.7$ Hz, 2H, CH_2), 1.71 (td, $J = 11.6$, 5.8 Hz, 1H, BCh), 2.59 (t, $J = 7.7$ Hz, 2H, ArCH_2CH_2), 2.90-3.03 (m, 5H, ArCH_2 and ArCH), 7.06-7.13 (m, 6H, ArH), 7.21 (d, $J = 8.7$ Hz, 2H, ArH); ^{13}C NMR (CDCl_3): δ 13.9, 22.2, 24.3, 24.4, 31.7, 33.8, 35.2, 39.1, 42.5, 82.9, 125.4, 125.5, 127.5, 128.3, 128.6, 129.0, 136.4, 136.9, 140.7, 143.5.

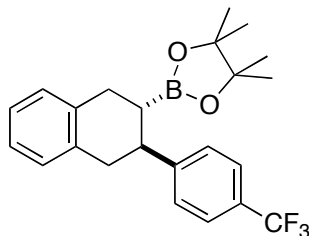
4,4,5,5-Tetramethyl-2-[3-(2,5-dimethoxyphenyl)-1,2,3,4-tetrahydro-naphthalen-2-yl]-[1,3,2]dioxaborolane (3ae)



A yellow oil: ^1H NMR (CDCl_3): δ 0.99 (s, 6H, CH_3), 1.02 (s, 6H, CH_3), 1.83 (td, $J = 11.2$, 5.6 Hz, 1H, BCh), 2.77-3.06 (m, 4H, ArCH_2), 3.46 (td, $J = 11.5$, 4.9 Hz, 1H, ArCH), 3.77 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3), 6.68-6.84 (m, 3H, ArH), 7.07-7.11 (m 4H, ArH); ^{13}C

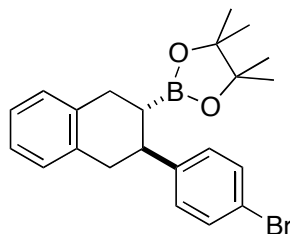
NMR (CDCl₃): δ 24.3, 24.4, 31.7, 36.0, 53.5, 55.7, 56.4, 82.8, 111.5, 112.1, 114.0, 125.3, 125.4, 128.6, 128.9, 136.1, 136.5, 137.1, 151.6, 153.7.

4,4,5,5-Tetramethyl-2-[3-(4-trifluoromethylphenyl)-1,2,3,4-tetrahydro-naphthalen-2-yl]-[1,3,2]dioxaborolane (3af)



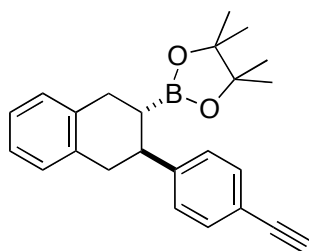
A white solid: ¹H NMR (CDCl₃): δ 0.98 (s, 6H, CH₃), 1.00 (s, 6H, CH₃), 1.73 (td, J = 10.9, 6.6 Hz, 1H, BCH), 2.83-3.15 (m, 5H, ArCH₂ and ArCH), 7.05-7.14 (m, 4H, ArH), 7.41 (d, J = 8.4 Hz, 2H, ArH), 7.57 (d, J = 8.4 Hz, 2H, ArH); ¹³C NMR (CDCl₃): δ 24.30, 24.34, 31.4, 38.7, 42.8, 83.1, 125.06, 125.11, 125.17, 125.22, 125.6, 125.8, 128.0, 128.3, 128.6, 128.9, 136.1, 136.2, 150.66, 150.68.

4,4,5,5-Tetramethyl-2-[3-(4-bromophenyl)-1,2,3,4-tetrahydro-naphthalen-2-yl]-[1,3,2]dioxaborolane (3ag)



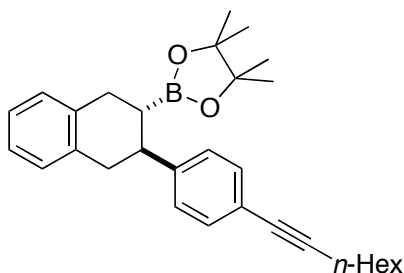
A white solid: ¹H NMR (CDCl₃): δ 1.01 (s, 6H, CH₃), 1.02 (s, 6H, CH₃), 1.65-1.72 (m, 1H, BCH), 2.79-3.01 (m, 5H, ArCH₂ and ArCH), 7.06-7.13 (m, 4H, ArH), 7.18 (d, J = 8.7 Hz, 2H, ArH), 7.43 (d, J = 7.7 Hz, 2H, ArH); ¹³C NMR (CDCl₃): δ 24.39, 24.41, 31.4, 38.9, 42.3, 83.0, 119.8, 125.5, 125.7, 128.6, 128.9, 129.4, 131.2, 136.2, 136.3.

4,4,5,5-Tetramethyl-2-[3-(4-ethynylphenyl)-1,2,3,4-tetrahydro-naphthalen-2-yl]-[1,3,2]dioxaborolane (3ah)



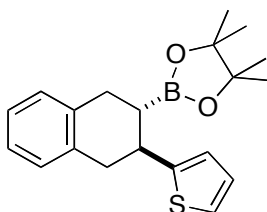
A white solid: ^1H NMR (CDCl_3): δ 1.00 (s, 6H, CH_3), 1.01 (s, 6H, CH_3), 1.71 (td, $J = 11.6$, 6.8 Hz, 1H, B CH), 2.85-3.06 (m, 6H, CH , ArCH_2 and ArCH), 7.07-7.13 (m, 4H, ArH), 7.26 (d, $J = 7.8$ Hz, 2H, ArH), 7.45 (d, $J = 7.8$ Hz, 2H, ArH); ^{13}C NMR (CDCl_3): δ 24.39, 24.40, 31.4, 38.8, 42.7, 76.5, 83.0, 83.9, 119.8, 125.5, 125.7, 127.6, 128.6, 128.9, 132.0, 136.2, 136.4, 147.5.

4,4,5,5-Tetramethyl-2-[3-(1-octynylphenyl)-1,2,3,4-tetrahydro-naphthalen-2-yl]-[1,3,2]dioxaborolane (3ai)



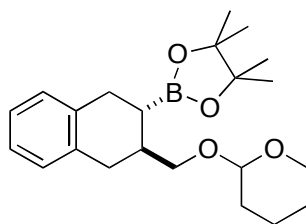
A pale yellow oil: ^1H NMR (CDCl_3): δ 0.92 (t, $J = 6.7$ Hz, 3H, CH_3CH_2), 1.00 (s, 6H, CH_3), 1.01 (s, 6H, CH_3), 1.34-1.71 (m, 9H, B CH and CH_2), 2.41 (t, $J = 6.7$ Hz, 2H, $\text{C}\equiv\text{CCH}_2$), 2.80-3.00 (m, 5H, ArCH_2 and ArCH), 7.06-7.12 (m, 4H, ArH), 7.21 (d, $J = 7.7$ Hz, 2H, ArH), 7.34 (d, $J = 7.7$ Hz, 2H, ArH); ^{13}C NMR (CDCl_3): δ 14.0, 19.4, 22.5, 24.4, 25.1, 28.6, 28.8, 31.3, 31.5, 38.9, 42.6, 80.7, 83.0, 89.6, 121.8, 125.5, 125.6, 127.5, 128.5, 128.9, 131.4, 136.3, 136.5, 146.0.

4,4,5,5-Tetramethyl-2-[3-(2-thienyl)-1,2,3,4-tetrahydro-naphthalen-2-yl]-[1,3,2]dioxaborolane (3aj)



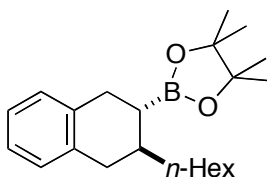
A colorless oil: ^1H NMR (CDCl_3): δ 1.07 (s, 6H, CH_3), 1.09 (s, 6H, CH_3), 1.70 (td, $J = 11.1$, 6.1 Hz, 1H, B CH), 2.89-3.02 (m, 3H, ArCH_2), 3.14 (dd, $J = 16.4$, 5.1 Hz, 1H, ArCH_2), 3.38 (td, $J = 11.1$, 5.1 Hz, 1H, (thiophene) CH), 6.91-6.93 (m, 2H, ArH), 7.06-7.14 (m, 5H, ArH); ^{13}C NMR (CDCl_3): δ 24.4, 24.5, 31.2, 37.7, 39.5, 83.1, 122.6, 123.4, 125.5, 125.7, 126.3, 128.5, 128.8, 136.0, 136.1, 150.3.

4,4,5,5-Tetramethyl-2-[3-((tetrahydro-2H-pyran-2-yloxy)methyl)-1,2,3,4-tetrahydro-naphthalen-2-yl]-[1,3,2]dioxaborolane (3ak)



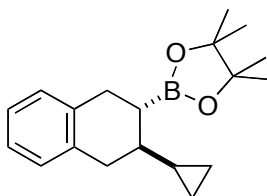
A pale yellow oil: ^1H NMR (CDCl_3): δ 1.20-1.29 (m, 2H, CH_2), 1.24 (s, 12H, CH_3), 1.52-1.85 (m, 6H, BCH and CH_2), 2.15-2.27 (m, 1H, CHCH_2O), 2.62-2.68 (m, 1H, ArCH_2), 2.80-2.83 (m, 2H, ArCH_2), 2.98 (td, $J = 16.4, 5.8$ Hz, 1H, ArCH_2), 3.31 (dd, $J = 9.8, 7.2$ Hz, 1H, OCH_2), 3.49 (dd, $J = 9.7, 4.9$ Hz, 1H, OCH_2), 3.62 (t, $J = 9.7$ Hz, 1H, OCH_2), 3.81-3.89 (m, 1H, OCH_2), 4.61 (dt, $J = 10.6, 3.8$ Hz, 1H, OCHO), 7.07 (brs, 4H, ArH); ^{13}C NMR (CDCl_3): δ 19.4, 20.8, 24.6, 24.71, 24.74, 24.8, 25.5, 30.20, 30.24, 30.3, 30.6, 30.65, 32.70, 32.9, 33.1, 33.2, 35.1, 35.2, 35.4, 35.5, 61.5, 61.8, 71.6, 71.9, 83.08, 83.12, 97.7, 98.25, 98.33, 99.1, 99.7, 124.5, 125.2, 125.5, 128.0, 128.1, 128.3, 128.8, 129.1, 136.5, 136.6, 137.0, 137.1.

4,4,5,5-Tetramethyl-2-(3-*n*-hexyl-1,2,3,4-tetrahydro-naphthalen-2-yl)-[1,3,2]dioxaborolane (3al)



A colorless oil: ^1H NMR (CDCl_3): δ 0.89 (t, $J = 6.8$, 3H, CH_3CH_2), 1.13-1.51 (m, 23H, CH_3 , CH_2 and CH), 1.83-1.92 (m, 1H, BCH), 2.39 (dd, $J = 16.4, 9.7$ Hz, 1H, ArCH_2), 2.79-2.82 (m, 2H, ArCH_2), 2.90 (dd, $J = 16.4, 4.8$ Hz, 1H, ArCH_2), 7.06 (brs, 4H, ArH); ^{13}C NMR (CDCl_3): δ 14.1, 22.7, 24.7, 24.8, 26.5, 29.5, 30.8, 31.8, 34.9, 35.0, 36.4, 83.0, 125.2, 125.3, 128.2, 128.9, 136.9, 137.1.

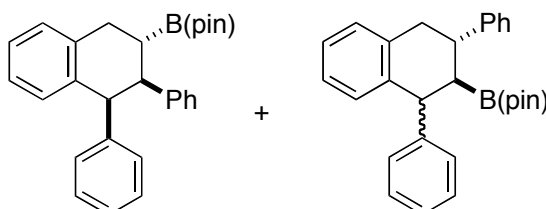
4,4,5,5-Tetramethyl-2-(3-cyclopropyl-1,2,3,4-tetrahydro-naphthalen-2-yl)-[1,3,2]dioxaborolane (3am)



A pale yellow oil: ^1H NMR (CDCl_3): δ 0.13-0.18 (m, 1H), 0.29-0.38 (m, 1H), 0.42-0.50 (m, 2H), 0.65-0.74 (m, 1H), 1.01-1.23 (m 1H), 1.24-1.38 (m, 1H, BCH), 1.29 (s, 12H, CH_3), 2.60 (dd, $J = 16.4, 10.6$ Hz, 1H, ArCH_2), 2.82 (d, 7.7 Hz, 2H, ArCH_2), 2.90 (dd, $J =$

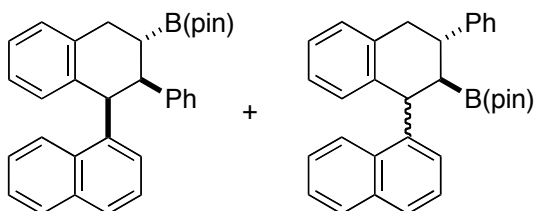
16.4, 4.8 Hz, 1H, ArCH₂), 7.07 (brs, 4H, ArH); ¹³C NMR (CDCl₃): δ 3.4, 5.3, 17.3, 24.8, 25.1, 31.2, 36.2, 40.9, 83.0, 125.3, 128.3, 128.9, 136.8, 136.9.

A mixture of 2-(3,4-diphenyl-1,2,3,4-tetrahydronaphthalen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3ba) and 2-(1,3-diphenyl-1,2,3,4-tetrahydronaphthalen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3'ba) (3ba:3'ba = 93:7)



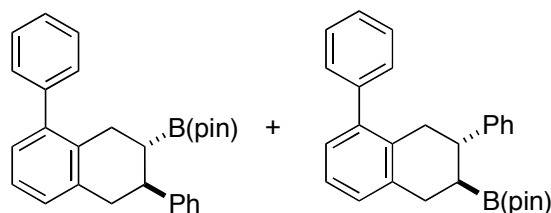
A yellow solid: ¹H NMR (CDCl₃): δ 0.67-0.97 (m, CH₃), 1.99-2.11 (m, BCH), 3.00-3.09 (m, ArCH₂), 3.47 (dd, *J* = 12.5, 4.8 Hz, PhCH), 4.07-4.27 (m, ArCHPh), 6.47 (d, *J* = 6.8 Hz, ArH), 6.71-7.36 (m, ArH); ¹³C NMR (CDCl₃): δ 24.08, 24.11, 24.15, 24.23, 24.3, 31.4, 32.3, 40.2, 43.9, 47.0, 51.3, 51.9, 55.0, 82.8, 82.88, 82.92, 125.6, 125.7, 125.9, 126.0, 126.1, 126.5, 126.9, 127.3, 127.71, 127.73, 128.2, 128.3, 128.4, 129.0, 129.4, 129.5, 130.3, 130.7, 130.8, 136.4, 136.8, 137.1, 139.6, 140.3, 140.4, 142.5, 143.5, 144.2, 145.4, 145.5.

A mixture of 4,4,5,5-tetramethyl-2-(2-phenyl-1,2,3,4-tetrahydro-1,1'-binaphthyl-3-yl)-1,3,2-dioxaborolane (3ca) and 4,4,5,5-tetramethyl-2-(3-phenyl-1,2,3,4-tetrahydro-1,1'-binaphthyl-2-yl)-1,3,2-dioxaborolane (3'ca) (3ca:3'ca = 89:11)



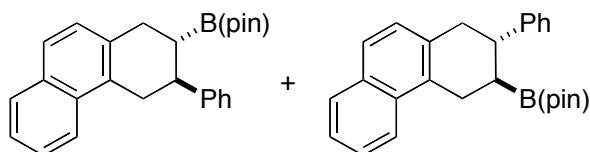
A pale yellow oil: ¹H NMR (CDCl₃): δ 0.84-0.97 (m, CH₃), 2.13-2.33 (m, BCH), 3.21 (d, *J* = 8.77 Hz, ArCH₂), 3.64 (dd, *J* = 12.6, 5.8 Hz, PhCH), 5.33 (d, *J* = 5.8 Hz, ArCHAr), 6.57-7.78 (m, ArH); ¹³C NMR (CDCl₃): δ 17.6, 24.0, 24.07, 24.14, 24.2, 24.26, 24.33, 24.4, 31.4, 32.3, 44.0, 44.1, 44.3, 47.3, 82.7, 82.8, 82.9, 123.5, 124.3, 124.56, 124.61, 124.63, 125.1, 125.5, 125.8, 125.9, 126.0, 126.4, 126.5, 127.0, 127.6, 127.7, 127.8, 127.9, 128.3, 128.5, 128.9, 129.5, 129.6, 130.8, 132.7, 133.2, 136.6, 139.6, 140.7, 143.0, 145.5.

A mixture of 2-(3,8-diphenyl-1,2,3,4-tetrahydronaphthalen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3da) and 2-(3,5-diphenyl-1,2,3,4-tetrahydronaphthalen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3'da) (3da:3'da = 68:32)



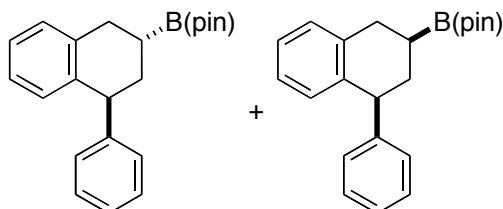
A yellow oil: ^1H NMR (CDCl_3): δ 0.92-0.94 (m, CH_3), 0.98-1.01 (m, CH_3), 1.64 (td, J = 11.6, 3.8 Hz, BCH), 1.78 (td, J = 10.6, 6.7 Hz, BCH), 2.71-3.18 (m, ArCH_2 and PhCH), 7.07-7.46 (m, ArH); ^{13}C NMR (CDCl_3): δ 24.31, 24.34, 24.4, 30.2, 32.3, 37.7, 39.7, 42.7, 43.3, 77.2, 82.88, 82.89, 125.28, 125.33, 126.1, 126.2, 126.6, 126.7, 127.3, 127.4, 127.6, 127.7, 127.8, 127.88, 127.94, 128.0, 128.1, 128.2, 128.3, 129.1, 129.2, 134.0, 134.3, 136.7, 137.2, 141.7, 141.8, 141.9, 142.1, 146.4.

A mixture of 4,4,5,5-tetramethyl-2-(3-phenyl-1,2,3,4-tetrahydrophenanthren-2-yl)-1,3,2-dioxaborolane (3ea) and 4,4,5,5-tetramethyl-2-(2-phenyl-1,2,3,4-tetrahydrophenanthren-3-yl)-1,3,2-dioxaborolane (3'ea) (3ea:3'ea = 50:50)



A yellow oil: ^1H NMR (CDCl_3): δ 0.98-1.02 (m, CH_3), 1.82 (td, J = 11.6, 4.8 Hz, BCH), 3.01-3.20 (m), 3.43 (dd, J = 17.4, 4.8 Hz), 3.54 (dd, J = 15.5, 2.9 Hz), 7.18-7.51 (m, ArH), 7.63 (d, J = 3.9 Hz, ArH), 7.65 (d, J = 2.9 Hz, ArH), 7.79-7.82 (m, ArH), 7.89 (d, J = 7.7 Hz, ArH), 8.01 (d, J = 8.7 Hz, ArH); ^{13}C NMR (CDCl_3): δ 24.37, 24.43, 24.5, 28.0, 32.6, 35.7, 40.0, 42.5, 43.0, 82.99, 83.03, 122.7, 123.0, 124.7, 125.7, 125.79, 125.82, 126.27, 126.32, 127.66, 127.71, 127.8, 128.0, 128.25, 128.33, 128.36, 128.38, 130.9, 131.2, 132.0, 132.1, 132.2, 132.3, 133.8, 134.1, 146.3, 146.6.

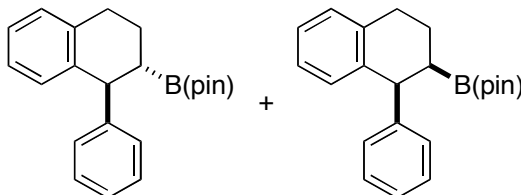
A mixture of *anti*- and *syn*-4,4,5,5-tetramethyl-2-(4-phenyl-1,2,3,4-tetrahydronaphthalen-2-yl)-1,3,2-dioxaborolane (3bo) (*anti*:*syn* = 62:38)



A colorless oil: ^1H NMR (CDCl_3): δ 1.21 (s, CH_3), 1.22 (s, CH_3), 1.43-1.58 (m), 1.70-2.31 (m), 2.80-3.00 (m, ArCH_2), 4.05 (dd, J = 11.9, 4.0 Hz, ArCHPh), 4.25 (dd, J = 5.8, 2.9 Hz, ArCHPh), 6.77-7.31 (m, ArH); ^{13}C NMR (CDCl_3): δ 24.67, 24.74, 24.8, 30.6, 31.4, 33.2,

36.1, 44.0, 47.6, 83.1, 83.2, 125.48, 125.54, 125.6, 125.9, 126.0, 128.0, 128.3, 128.6, 128.76, 128.83, 129.0, 129.8, 130.6, 137.8, 138.0, 138.4, 140.0, 147.4, 147.7.

A mixture of *anti*- and *syn*-4,4,5,5-tetramethyl-2-(1-phenyl-1,2,3,4-tetrahydronaphthalen-2-yl)-1,3,2-dioxaborolane (3'bo) (*anti*:*syn* = 84:16)



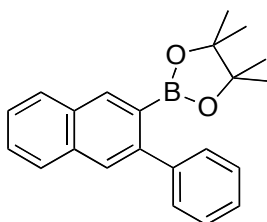
A colorless oil: ^1H NMR (CDCl_3): δ 1.02-1.12 (m, CH_3), 1.58 (td, $J = 10.6, 2.9$ Hz, BCH), 1.79-1.87 (m, CH_2), 1.96-2.02 (m, CH_2), 2.88-2.95 (m, ArCH_2), 4.16 (d, $J = 10.6$ Hz, ArCHPh), 4.41 (d, $J = 4.0$ Hz, ArCHPh), 6.75 (d, $J = 7.8$ Hz, ArH), 6.93-7.27 (m, ArH); ^{13}C NMR (CDCl_3): δ 14.1, 19.1, 23.0, 23.5, 24.0, 24.5, 24.6, 24.7, 25.1, 25.8, 29.6, 30.0, 37.7, 45.1, 47.3, 83.0, 83.1, 121.3, 125.4, 125.5, 125.6, 125.7, 125.86, 125.91, 127.6, 128.1, 128.8, 129.0, 129.3, 129.7, 129.9, 137.15, 137.19, 140.5, 147.0.

Aromatization of boryltetralins: a general procedure.

Method A: A benzene (6 mL) solution of **3** (0.10 mmol), NBS (0.50 mmol), sodium methoxide (0.30 mmol) and AIBN (5.0 μmol) was stirred at reflux temperature in the dark for the period as specified in Schemes 3 and 4. The mixture was diluted with hexane before filtration with Celite pad. Preparative recycling gel permeation chromatography (chloroform as an eluent) gave the corresponding product.

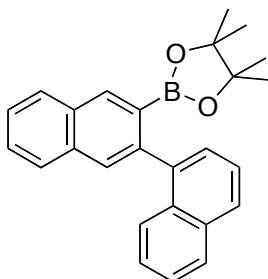
Method B: A toluene (0.5 mL) solution of **3** (0.10 mmol) and DDQ (0.25 mmol) was stirred at 100 $^\circ\text{C}$ for the period as specified in Scheme 3. The mixture was diluted with benzene before filtration with Celite pad. Preparative recycling gel permeation chromatography (chloroform as an eluent) gave the corresponding product.

4,4,5,5-Tetramethyl-2-(3-phenyl-naphthalen-2-yl)-[1,3,2]dioxaborolane (4aa)



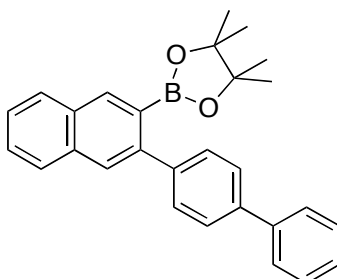
A yellow oil: ^1H NMR (CDCl_3): δ 1.26 (s, 12H, CH_3), 7.37-7.53 (m, 7H, ArH), 7.83-7.92 (m, 3H, ArH), 8.29 (s, 1H, ArH); ^{13}C NMR (CDCl_3): δ 23.7, 83.8, 125.8, 126.8, 127.1, 127.5, 127.8, 128.1, 129.3, 131.6, 134.2, 135.8, 143.1, 143.6; HRMS Calcd for $\text{C}_{22}\text{H}_{23}\text{BO}_2$: M^+ , 330.1791. Found: m/z 330.1776.

4,4,5,5-Tetramethyl-2-[3-(1-naphthyl)-naphthalen-2-yl]-[1,3,2]dioxaborolane (4ab)



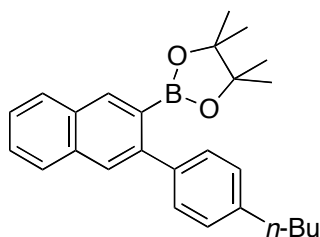
A pale yellow oil: ^1H NMR (CDCl_3): δ 0.69 (s, 6H, CH_3), 0.97 (s, 6H, CH_3), 7.34 (t, $J = 6.8$ Hz, 1H, ArH), 7.44 (t, $J = 6.8$ Hz, 1H, ArH), 7.51-7.61 (m, 5H, ArH), 7.79-7.90 (m, 4H, ArH), 7.97 (d, $J = 7.7$ Hz, 1H, ArH), 8.37 (s, 1H, ArH); ^{13}C NMR (CDCl_3): δ 24.0, 24.4, 83.3, 84.1, 124.9, 125.2, 125.3, 125.7, 125.8, 125.9, 126.3, 126.7, 127.0, 127.09, 127.14, 127.4, 127.7, 127.76, 127.79, 128.0, 128.2, 128.3, 128.4, 131.9, 133.2, 133.4, 134.5, 135.3, 141.5, 142.3; HRMS Calcd for $\text{C}_{26}\text{H}_{25}\text{BO}_2$: M^+ , 380.1948. Found: m/z 380.1942.

4,4,5,5-Tetramethyl-2-[3-(biphenyl-4-yl)-naphthalen-2-yl]-[1,3,2]dioxaborolane (4ac)



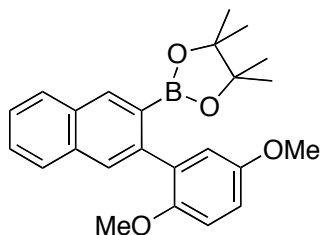
A white solid: ^1H NMR (CDCl_3): δ 1.28 (s, 12H, CH_3), 7.38 (t, $J = 8.7$ Hz, 1H, ArH), 7.47-7.70 (m, 10H, ArH), 7.85-7.92 (m, 3H, ArH), 8.31 (s, 1H, ArH); ^{13}C NMR (CDCl_3): δ 24.6, 83.9, 125.9, 126.6, 127.10, 127.12, 127.2, 127.5, 127.8, 128.1, 128.8, 129.75, 129.83, 131.7, 134.3, 136.0, 139.6, 141.1, 142.2, 143.2; HRMS Calcd for $\text{C}_{28}\text{H}_{27}\text{BO}_2$: M^+ , 406.2104. Found: m/z 406.2089.

4,4,5,5-Tetramethyl-2-[3-(4-*n*-butylphenyl)-naphthalen-2-yl]-[1,3,2]dioxaborolane (4ad)



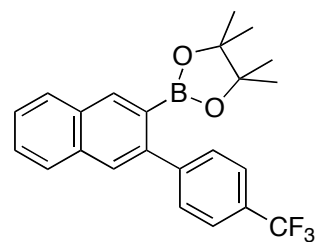
A yellow oil: ^1H NMR (CDCl_3): δ 0.96 (t, $J = 7.7$ Hz, 3H, CH_3CH_2), 1.26 (s, 12H, CH_3), 1.40 (sext, $J = 7.7$ Hz, 2H, CH_2), 1.66 (quint, $J = 7.7$ Hz, 2H, CH_2), 2.69 (t, $J = 7.7$ Hz, 2H, ArCH_2), 7.23 (d, $J = 7.7$ Hz, 2H, ArH), 7.41 (d, $J = 7.7$ Hz, 2H, ArH), 7.47 (t, $J = 7.7$ Hz, 3H, ArH), 7.51 (t, $J = 6.8$ Hz, 1H, ArH), 7.82 (s, 1H, ArH), 7.83 (d, $J = 8.7$ Hz, 1H, ArH), 7.89 (d, $J = 6.8$ Hz, 1H, ArH), 8.26 (s, 1H, ArH); ^{13}C NMR (CDCl_3): δ 14.0, 22.2, 24.6, 33.8, 35.3, 83.8, 127.2, 127.3, 127.8, 127.9, 128.1, 129.0, 129.2, 131.6, 134.2, 135.6, 135.7, 140.5, 141.4, 143.6; HRMS Calcd for $\text{C}_{26}\text{H}_{31}\text{BO}_2$: M^+ , 386.2417. Found: m/z 386.2415.

4,4,5,5-Tetramethyl-2-[3-(2,5-dimethoxyphenyl)-naphthalen-2-yl]-[1,3,2]dioxaborolane (4ae)



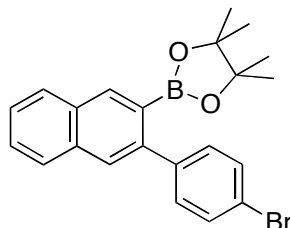
A pale yellow oil: ^1H NMR (CDCl_3): δ 1.23 (s, 12H, CH_3), 3.62 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 6.82-6.97 (m, 3H, ArH), 7.45-7.51 (m, 2H, ArH), 7.76 (s, 1H, ArH), 7.82 (d, $J = 7.7$ Hz, 1H, ArH), 7.89 (d, $J = 8.7$ Hz, 1H, ArH), 8.39 (s, 1H, ArH); ^{13}C NMR (CDCl_3): δ 24.7, 55.7, 56.5, 83.4, 112.6, 113.0, 116.6, 125.7, 126.3, 126.7, 127.8, 128.0, 128.1, 131.8, 133.7, 134.4, 135.0, 140.0, 151.4, 153.7; HRMS Calcd for $\text{C}_{24}\text{H}_{27}\text{BO}_4$: M^+ , 390.2002. Found: m/z 390.2000.

4,4,5,5-Tetramethyl-2-[3-(4-trifluoromethylphenyl)-naphthalen-2-yl]-[1,3,2]dioxaborolane (4af)



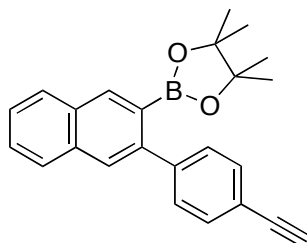
A yellow oil: ^1H NMR (CDCl_3): δ 1.27 (s, 12H, CH_3), 7.50-7.68 (m, 6H, ArH), 7.79-7.93 (m, 3H, ArH), 8.34 (s, 1H, ArH); ^{13}C NMR (CDCl_3): δ 24.6, 84.0, 124.5, 124.6, 126.3, 126.9, 127.4, 127.7, 127.9, 128.3, 129.1, 129.7, 130.2, 131.4, 131.9, 134.1, 136.5, 136.9, 142.4, 146.8; HRMS Calcd for $\text{C}_{23}\text{H}_{22}\text{BF}_3\text{O}_2$: M^+ , 398.1665. Found: m/z 398.1654.

4,4,5,5-Tetramethyl-2-[3-(4-bromophenyl)-naphthalen-2-yl]-[1,3,2]dioxaborolane (4ag)



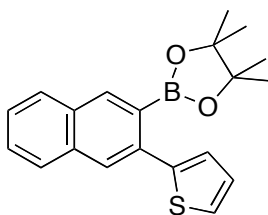
A pale yellow oil: ^1H NMR (CDCl_3): δ 1.27 (s, 12H, CH_3), 7.36 (d, $J = 8.7$ Hz, 2H, ArH), 7.47-7.57 (m, 4H, ArH), 7.77 (s, 1H, ArH), 7.83 (d, $J = 7.7$ Hz, 1H, ArH), 7.90 (d, $J = 7.7$ Hz, 1H, ArH), 8.31 (s, 1H, ArH); ^{13}C NMR (CDCl_3): δ 24.6, 83.9, 121.0, 126.1, 127.3, 127.5, 127.8, 128.1, 130.7, 131.0, 131.8, 134.2, 136.4, 142.1, 142.5; HRMS Calcd for $\text{C}_{22}\text{H}_{22}\text{BBrO}_2$: M^+ , 408.0896. Found: m/z 408.0901.

4,4,5,5-Tetramethyl-2-[3-(4-ethynylphenyl)-naphthalen-2-yl]-[1,3,2]dioxaborolane (4ah)



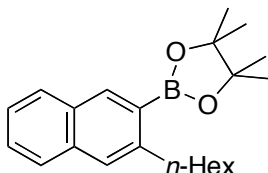
A pale yellow oil: ^1H NMR (CDCl_3): δ 1.26 (s, 12H, CH_3), 3.14 (s, 1H, CH), 7.45-7.55 (m, 6H, ArH), 7.79 (s, 1H, ArH), 7.84 (d, $J = 7.7$ Hz, 1H, ArH), 7.90 (d, $J = 8.7$ Hz, 1H, ArH), 8.30 (s, 1H, ArH); ^{13}C NMR (CDCl_3): δ 24.6, 77.2, 84.0, 120.4, 126.1, 127.28, 127.31, 127.6, 127.8, 128.1, 129.4, 131.6, 131.8, 132.5, 134.2, 136.3, 142.8, 143.8; HRMS Calcd for $\text{C}_{24}\text{H}_{23}\text{BO}_2$: M^+ , 354.1791. Found: m/z 354.1798.

4,4,5,5-Tetramethyl-2-[3-(2-thienyl)-naphthalen-2-yl]-[1,3,2]dioxaborolane (4aj)



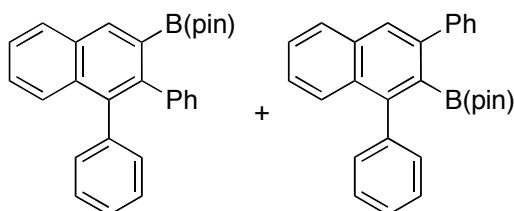
A yellow oil: ^1H NMR (CDCl_3): δ 1.31 (s, 12H, CH_3), 7.08 (t, $J = 3.9$ Hz, 1H, ArH-thiophene), 7.18 (d, $J = 4.8$ Hz, 1H, ArH-thiophene), 7.33 (d, $J = 3.9$ Hz, 1H, ArH-thiophene), 7.46-7.53 (m, 2H, ArH), 7.84 (dd, $J = 18.3, 7.7$ Hz, 2H, ArH), 7.91 (s, 1H, ArH), 8.21 (s, 1H, ArH); ^{13}C NMR (CDCl_3): δ 24.7, 84.0, 125.1, 126.1, 126.4, 127.0, 127.2, 127.8, 128.07, 128.14, 132.0, 134.1, 135.6, 135.8, 145.0; HRMS Calcd for $\text{C}_{20}\text{H}_{21}\text{BO}_2\text{S}$: M^+ , 336.1355. Found: m/z 336.1353.

4,4,5,5-Tetramethyl-2-(3-*n*-hexyl-naphthalen-2-yl)-[1,3,2]dioxaborolane (4al)



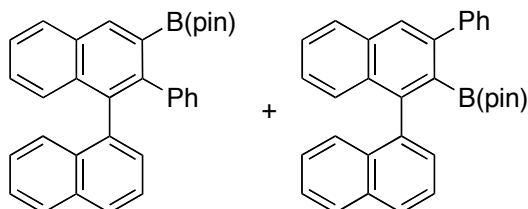
A pale yellow oil: ^1H NMR (CDCl_3): δ 0.89 (t, $J = 7.7$ Hz, 3H, CH_3CH_2), 1.27-1.39 (m, 18H, CH_3 and CH_2), 1.61 (quint, $J = 7.8$ Hz, 2H, CH_2), 3.00 (t, $J = 7.8$ Hz, 2H, Ar CH_2), 7.38 (t, $J = 7.7$ Hz, 1H, ArH), 7.46 (t, $J = 7.7$ Hz, 1H, ArH), 7.58 (s, 1H, ArH), 7.74 (d, $J = 7.7$ Hz, 1H, ArH), 7.83 (d, $J = 7.7$ Hz, 1H, ArH), 8.32 (s, 1H, ArH); ^{13}C NMR (CDCl_3): δ 14.1, 22.7, 24.9, 29.5, 31.9, 33.4, 36.1, 83.5, 124.8, 126.7, 126.9, 127.0, 128.2, 131.1, 134.9, 137.5, 145.6; HRMS Calcd for $\text{C}_{22}\text{H}_{31}\text{BO}_2$: M^+ , 338.2417. Found: m/z 338.2415.

A mixture of 2-(3,4-diphenylnaphthalen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4ba) and 2-(1,3-diphenylnaphthalen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4'ba) (4ba:4'ba = 93:7)



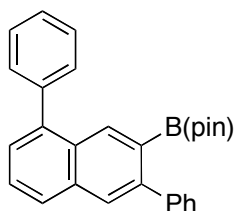
A yellow solid: ^1H NMR (CDCl_3): δ 1.14 (s, CH_3), 7.11-7.28 (m, ArH), 7.37-7.55 (m, ArH), 7.68 (d, $J = 8.6$ Hz, ArH), 7.94 (d, $J = 7.6$ Hz, ArH), 8.19 (s, ArH), 8.26 (s, ArH); ^{13}C NMR (CDCl_3): δ 24.5, 24.9, 83.6, 83.8, 125.5, 125.8, 126.3, 126.7, 126.9, 127.5, 127.7, 128.2, 130.1, 130.5, 131.2, 131.9, 133.4, 134.3, 137.6, 139.1, 141.9, 142.5; HRMS Calcd for $\text{C}_{28}\text{H}_{27}\text{BO}_2$: M^+ , 406.2104. Found: m/z 406.2107.

A mixture of **4,4,5,5-tetramethyl-2-(2-phenyl-1,1'-binaphthyl-3-yl)-1,3,2-dioxaborolane (4ca)** and **4,4,5,5-tetramethyl-2-(3-phenyl-1,1'-binaphthyl-2-yl)-1,3,2-dioxaborolane (4'ca)** (**4ca:4'ca** = **89:11**)



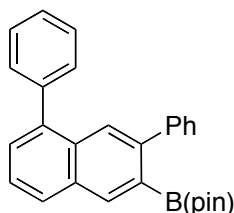
A pale yellow oil: ^1H NMR (CDCl_3): δ 1.07-1.17 (m, CH_3), 6.96-7.48 (m, ArH), 7.71-7.86 (m, ArH), 7.99 (d, $J = 7.8$ Hz, ArH), 8.27 (s, ArH), 8.35 (s, ArH), 8.40 (d, $J = 7.8$ Hz, ArH); ^{13}C NMR (CDCl_3): δ 24.3, 24.4, 24.5, 24.7, 83.7, 83.9, 125.0, 125.4, 125.56, 125.62, 125.8, 126.7, 126.8, 126.9, 127.0, 127.2, 127.9, 128.2, 128.3, 129.0, 131.7, 133.0, 133.4, 133.9, 134.6, 134.7, 135.6, 136.9, 142.4, 142.9; HRMS Calcd for $\text{C}_{32}\text{H}_{29}\text{BO}_2$: M^+ , 456.2261. Found: m/z 456.2247.

2-(3,8-Diphenylnaphthalen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4da)



A yellow oil: ^1H NMR (CDCl_3): δ 1.27 (s, 12H, CH_3), 7.32-7.54 (m, 12H, ArH), 7.92 (s, 1H, ArH), 7.93 (d, $J = 8.7$ Hz, 1H, ArH), 8.36 (s, 1H, ArH); ^{13}C NMR (CDCl_3): δ 24.6, 83.8, 125.3, 125.5, 126.7, 127.2, 127.7, 127.8, 128.2, 128.3, 129.3, 130.0, 132.0, 132.3, 136.3, 140.2, 140.5, 143.3, 143.8; HRMS Calcd for $\text{C}_{28}\text{H}_{27}\text{BO}_2$: M^+ , 406.2104. Found: m/z 406.2095.

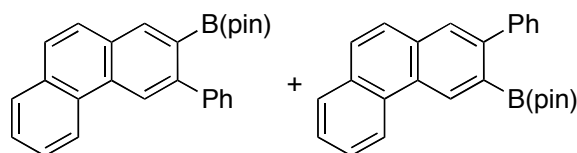
2-(3,5-Diphenylnaphthalen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4'da)



A yellow oil: ^1H NMR (CDCl_3): δ 1.17 (s, 12H, CH_3), 7.37-7.57 (m, 12H, ArH), 7.86 (d, $J = 7.7$ Hz, 1H, ArH), 7.89 (s, 1H, ArH), 8.32 (s, 1H, ArH); ^{13}C NMR (CDCl_3): δ 24.5, 83.8, 126.5, 126.8, 127.1, 127.2, 127.6, 127.7, 127.9, 128.2, 129.2, 129.7, 130.2, 133.3, 134.6,

140.5, 140.6, 143.0, 143.3; HRMS Calcd for $C_{28}H_{27}BO_2$: M^+ , 406.2104. Found: m/z 406.2119.

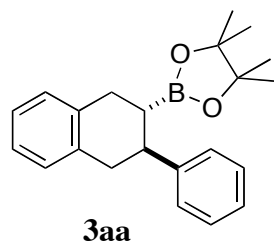
A mixture of 4,4,5,5-tetramethyl-2-(3-phenylphenanthren-2-yl)-1,3,2-dioxaborolane (4ea) and 4,4,5,5-tetramethyl-2-(2-phenylphenanthren-3-yl)-1,3,2-dioxaborolane (4'ea) (4ea:4'ea = 50:50)



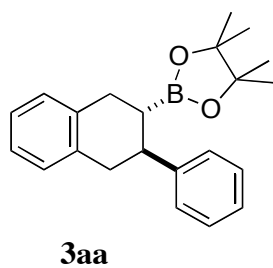
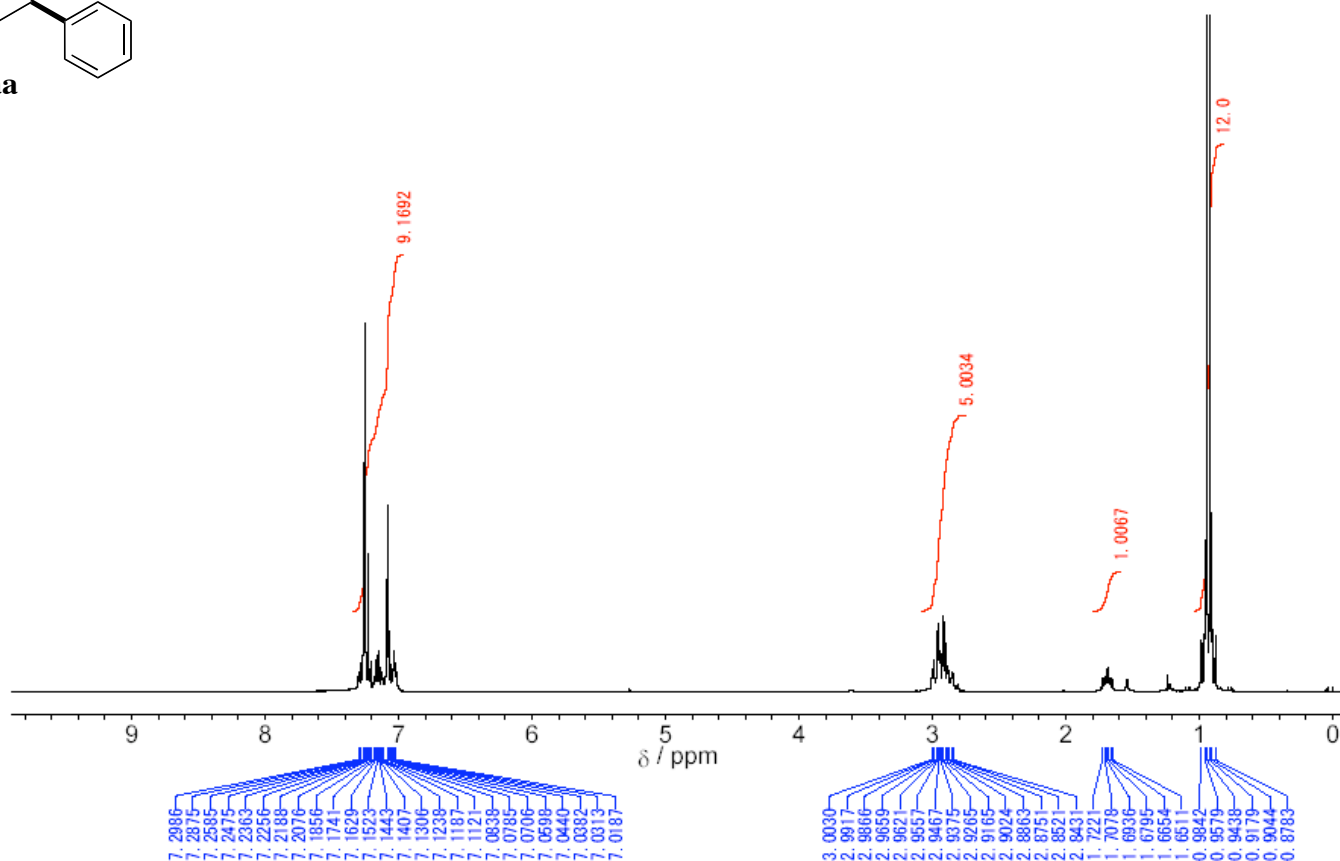
A yellow oil: 1H NMR ($CDCl_3$): δ 1.27 (s, CH_3), 1.29 (s, CH_3), 7.38-7.91 (m, ArH), 8.30 (s, ArH), 8.65 (s, ArH), 8.72 (d, $J = 6.7$ Hz, ArH), 8.82 (d, $J = 7.8$ Hz, ArH), 9.09 (s, ArH); ^{13}C NMR ($CDCl_3$): δ 24.6, 24.7, 83.91, 83.92, 122.90, 122.91, 126.46, 126.50, 126.7, 126.82, 126.84, 126.88, 126.89, 126.93, 127.8, 127.9, 128.16, 128.22, 128.3, 128.4, 128.5, 128.6, 129.4, 129.5, 130.0, 130.1, 130.2, 131.4, 132.0, 132.7, 133.2, 136.0, 143.0, 143.5, 144.97, 145.01; HRMS Calcd for $C_{26}H_{25}BO_2$: M^+ , 380.1948. Found: m/z 380.1950.

References

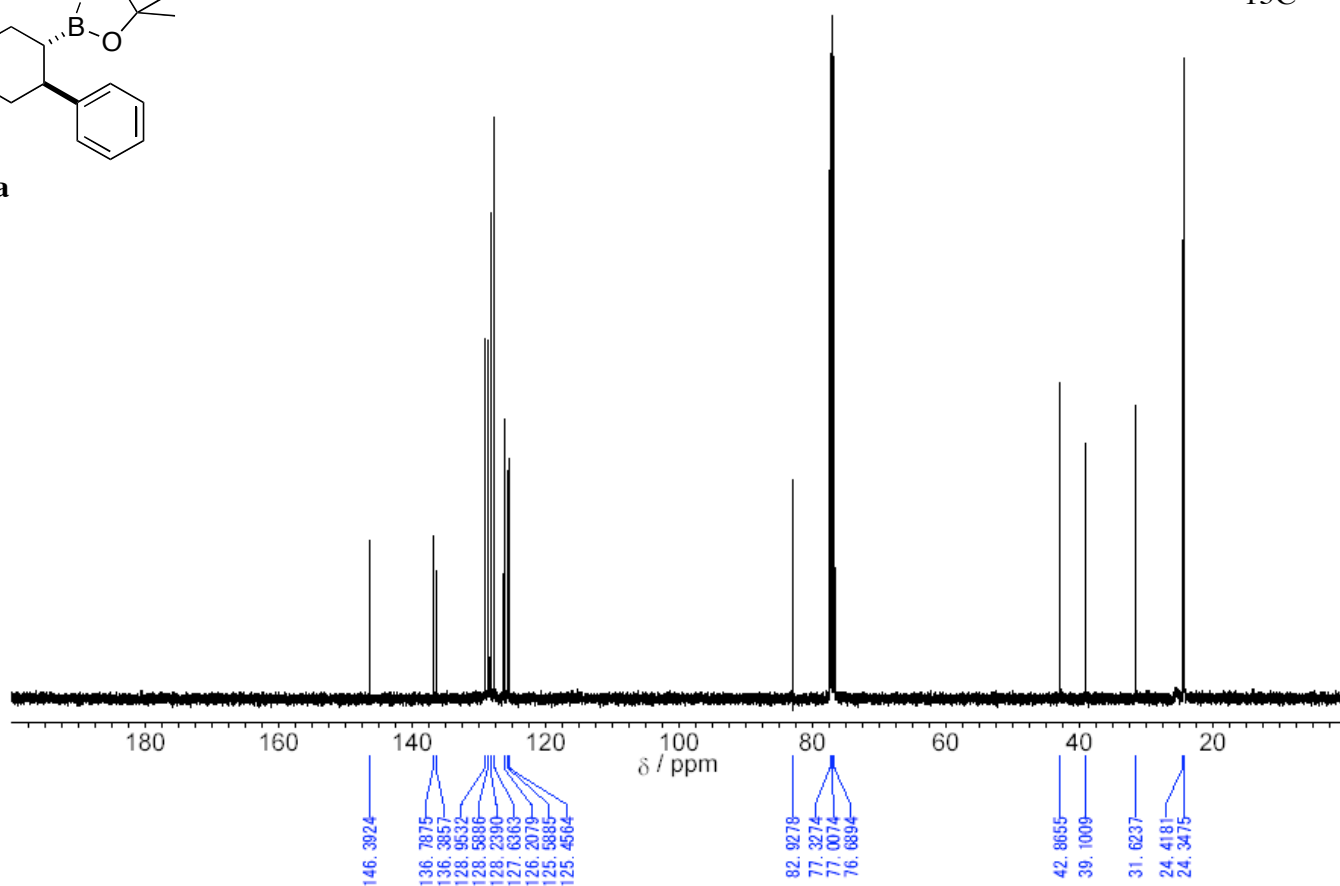
- 1 H. Yoshida, S. Nakano, Y. Yamaryo, J. Ohshita and A. Kunai, *Org. Lett.*, 2006, **8**, 4157.
- 2 S. Pereira and M. Srebnik, *Organometallics*, 1995, **14**, 3127.

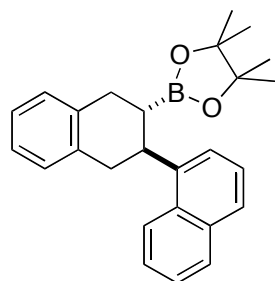


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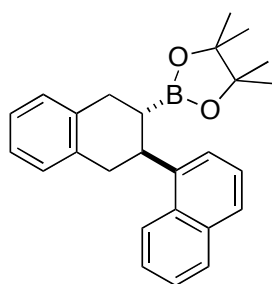
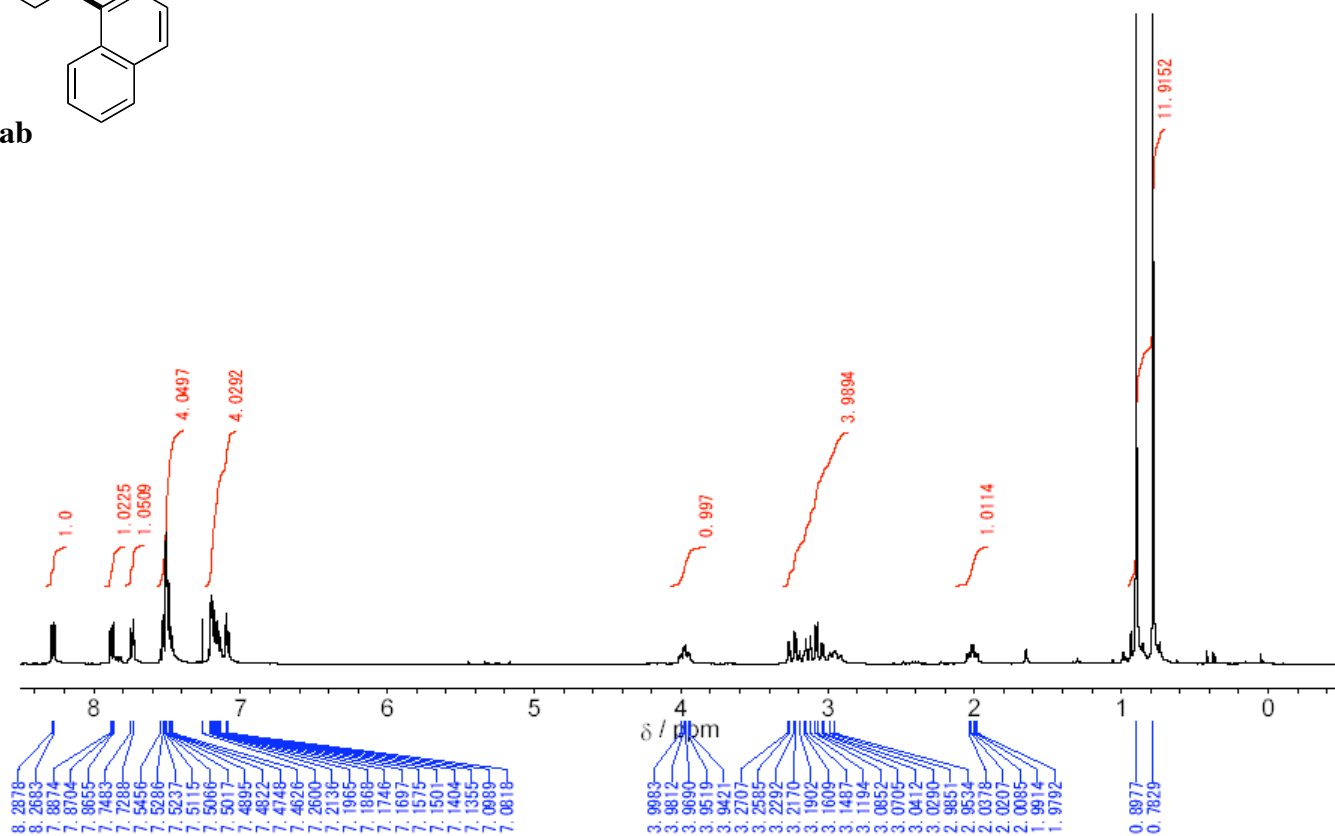
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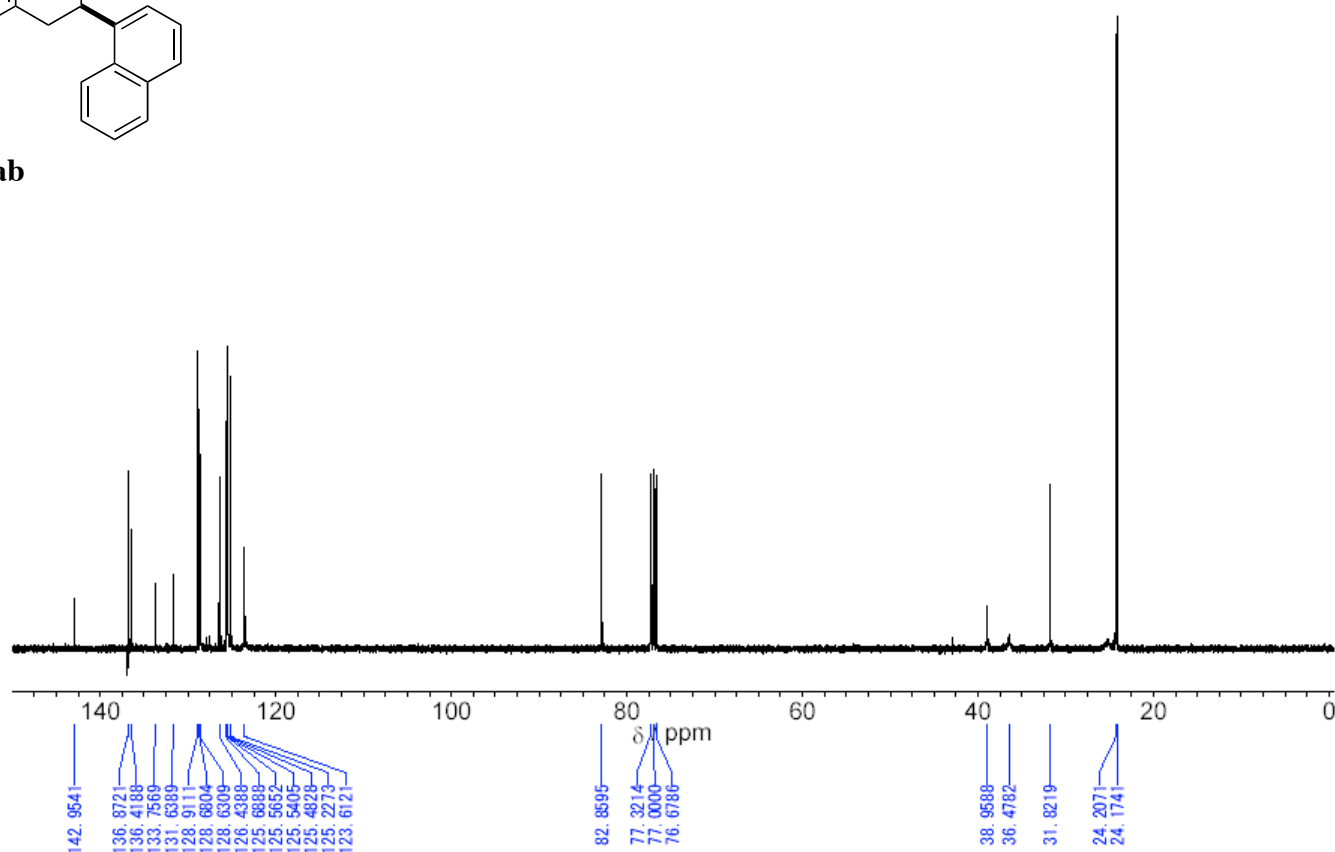
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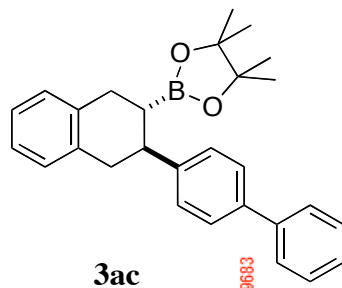
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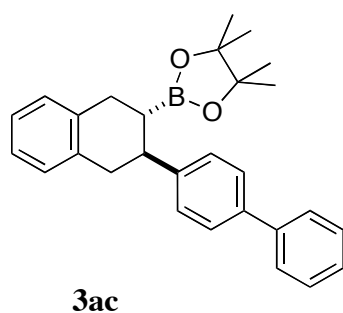
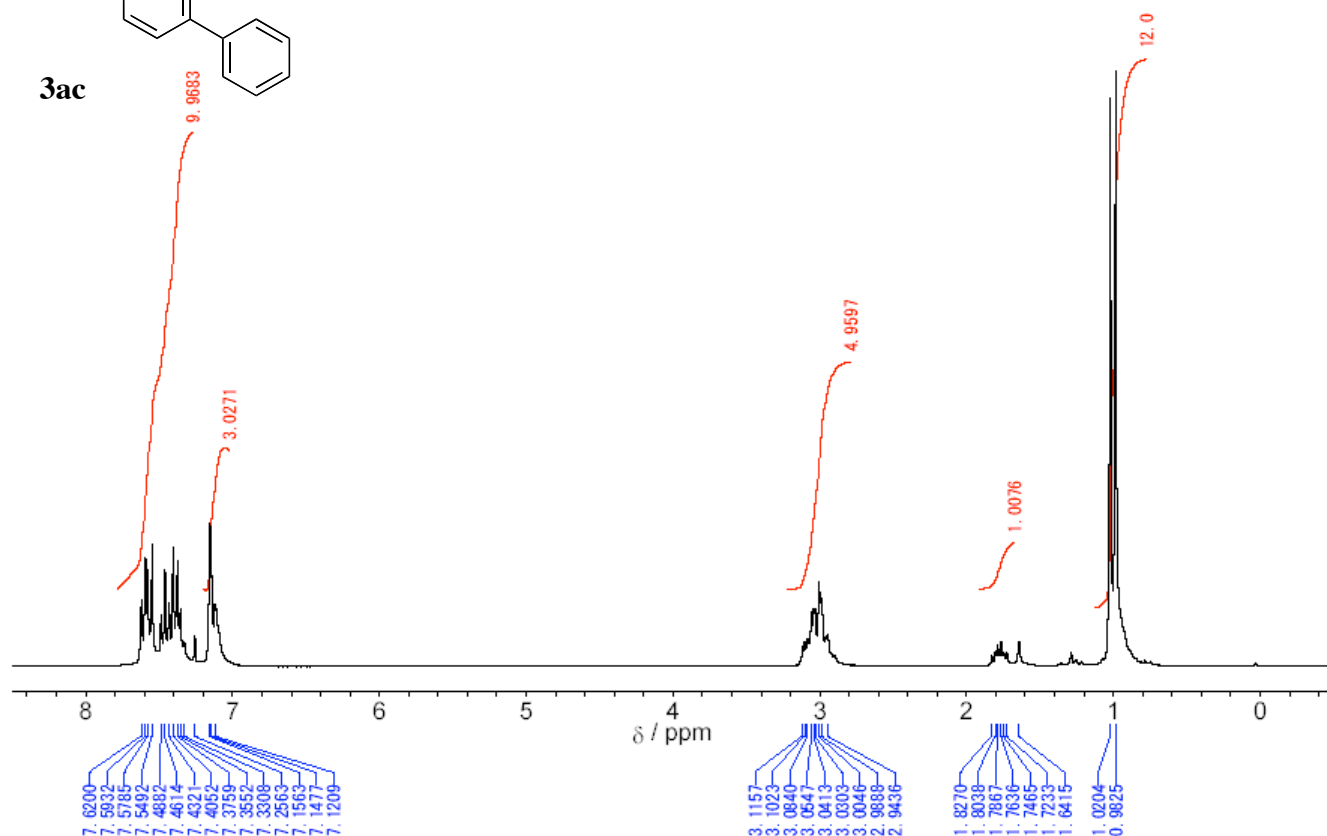
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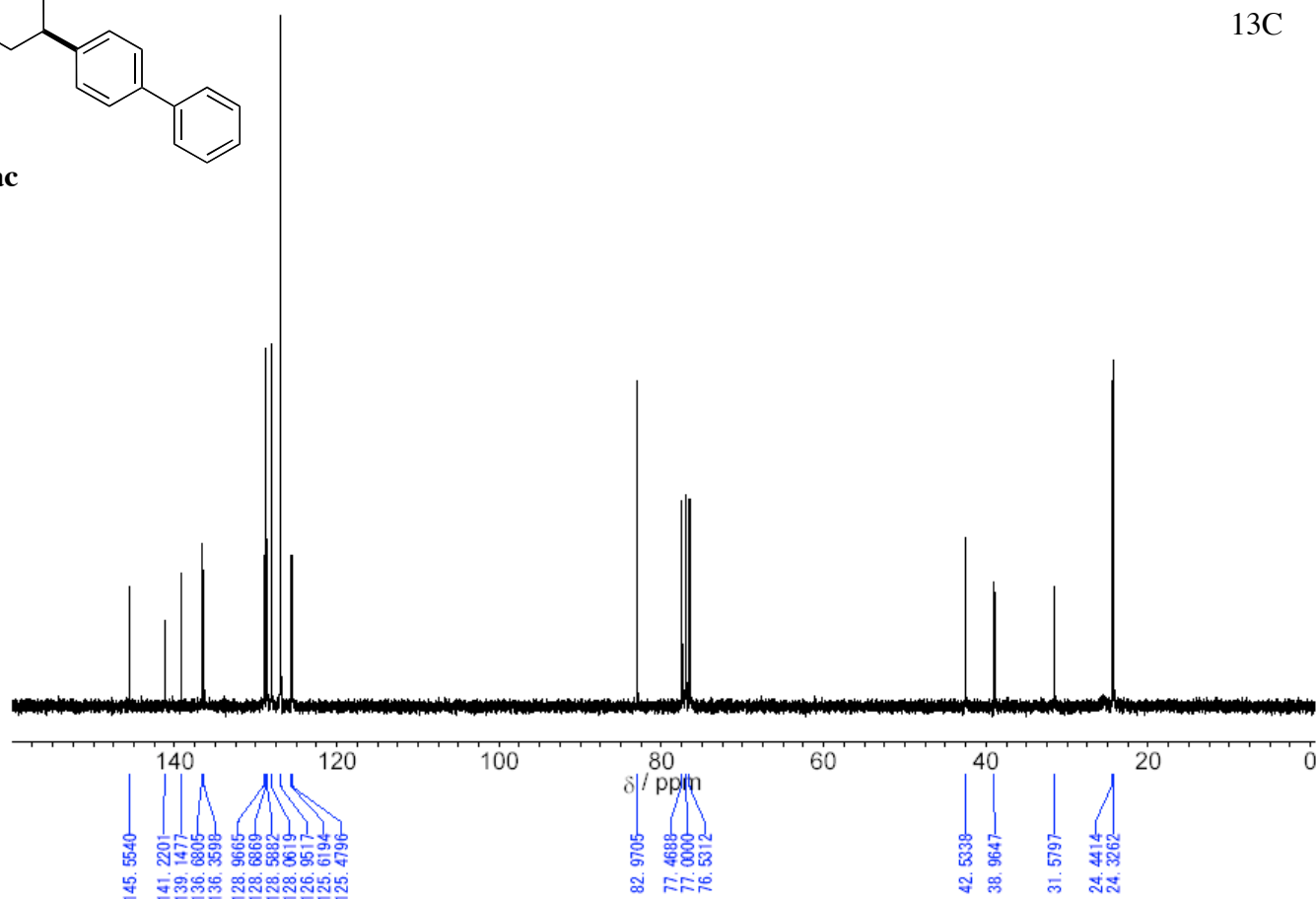


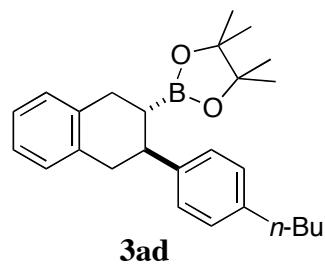


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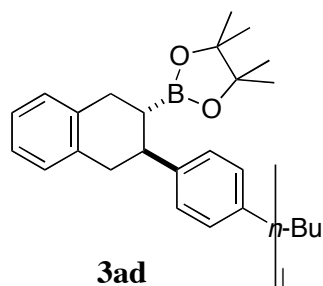
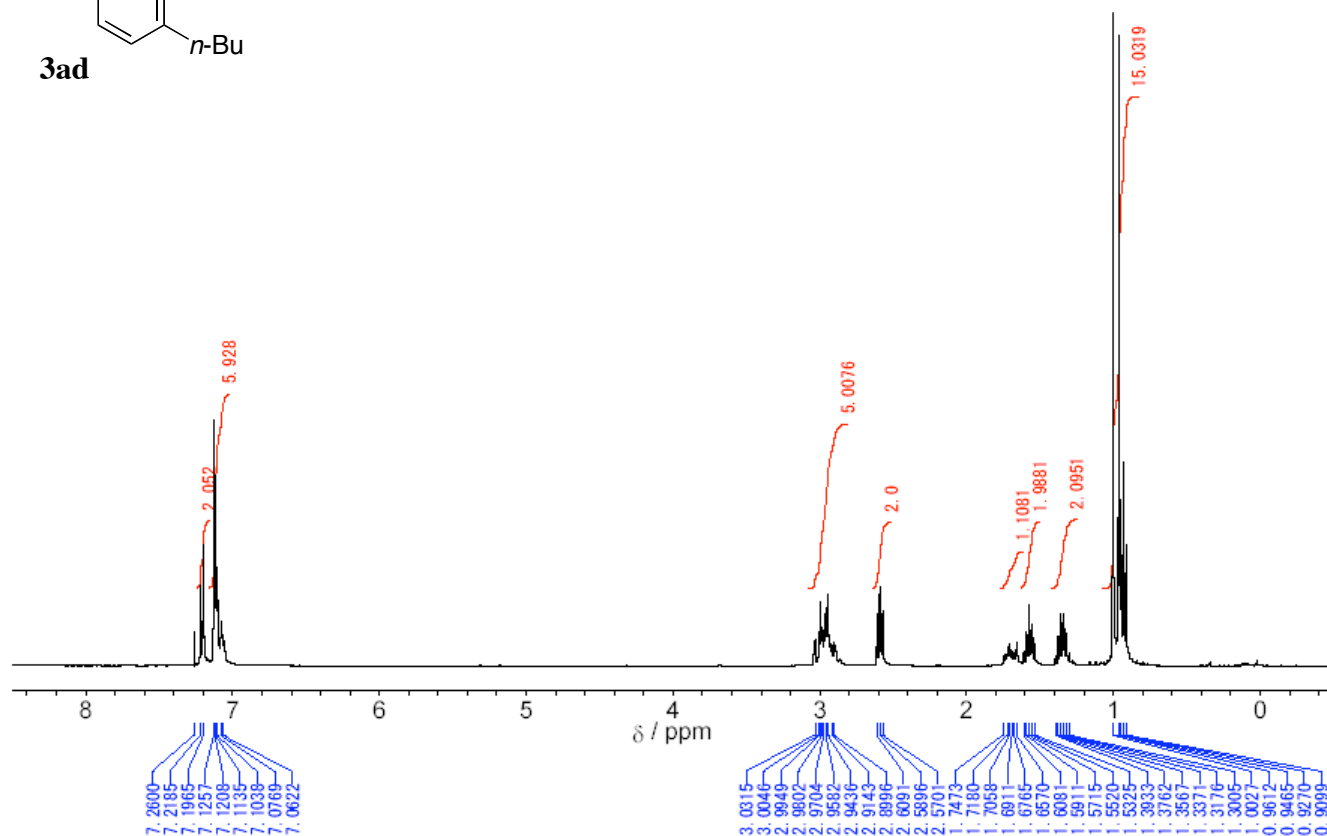


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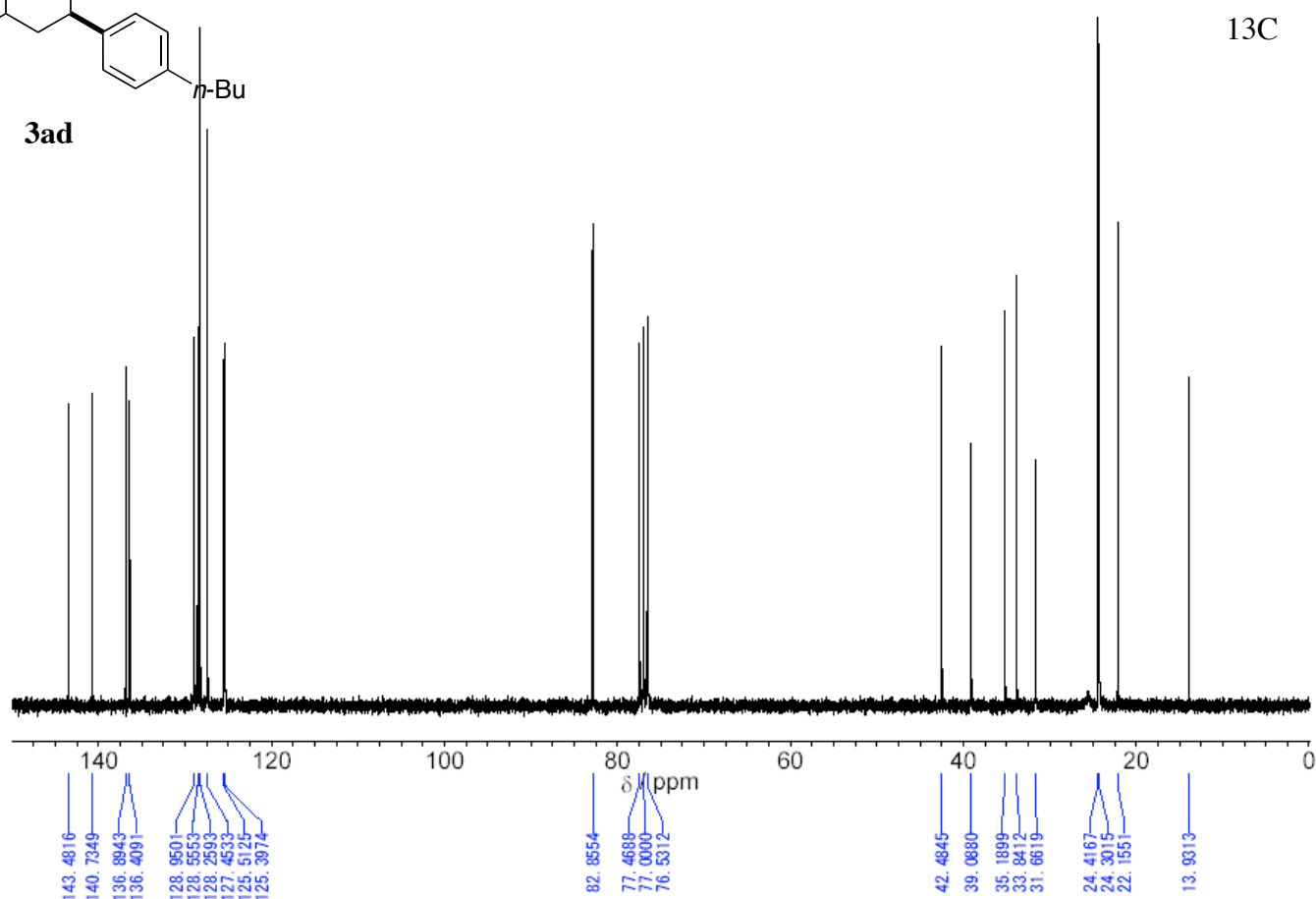


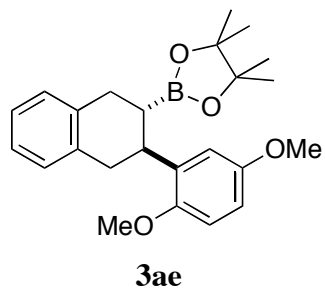


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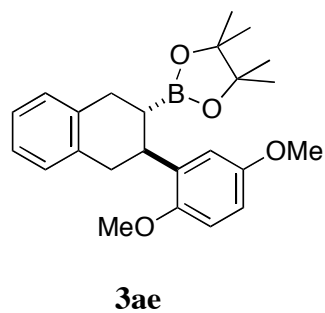
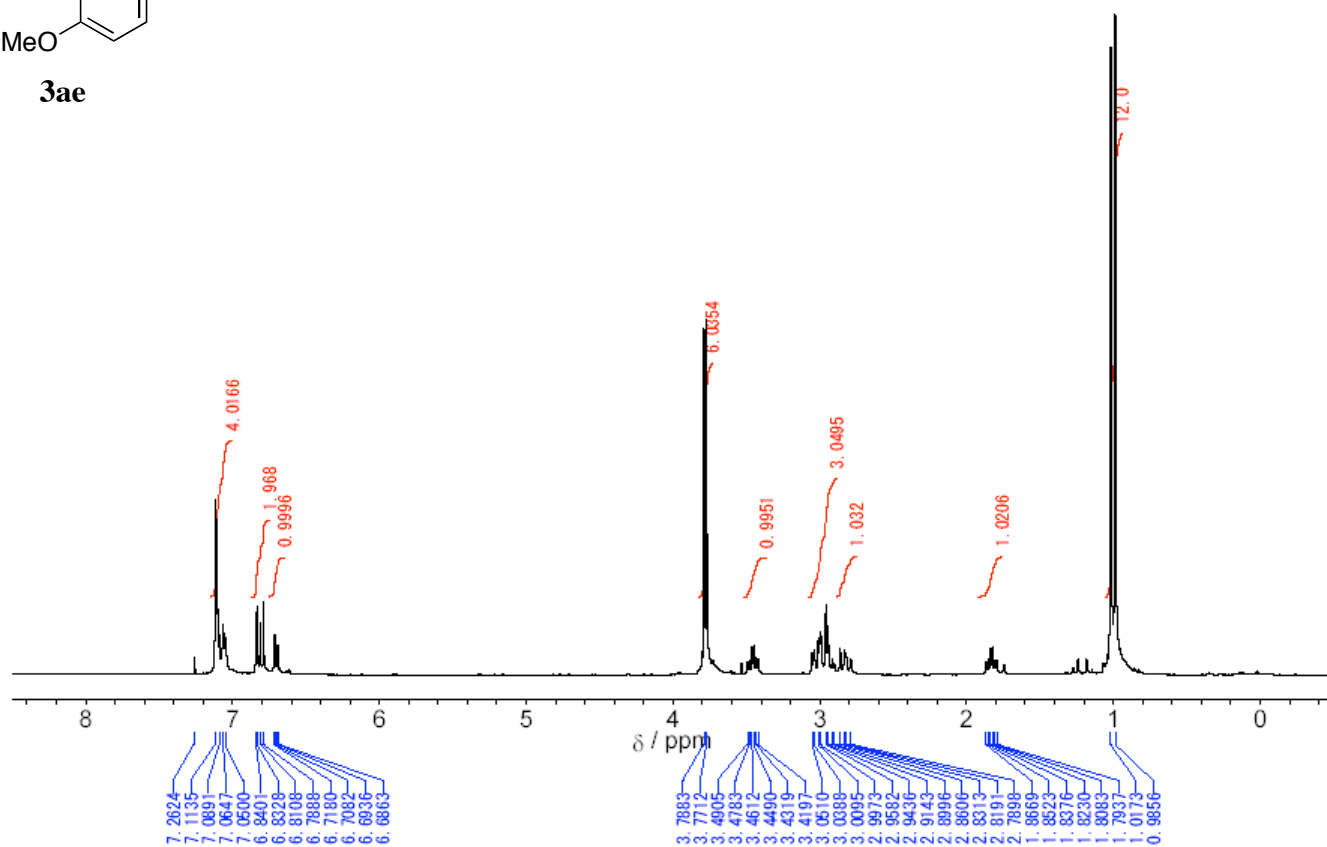


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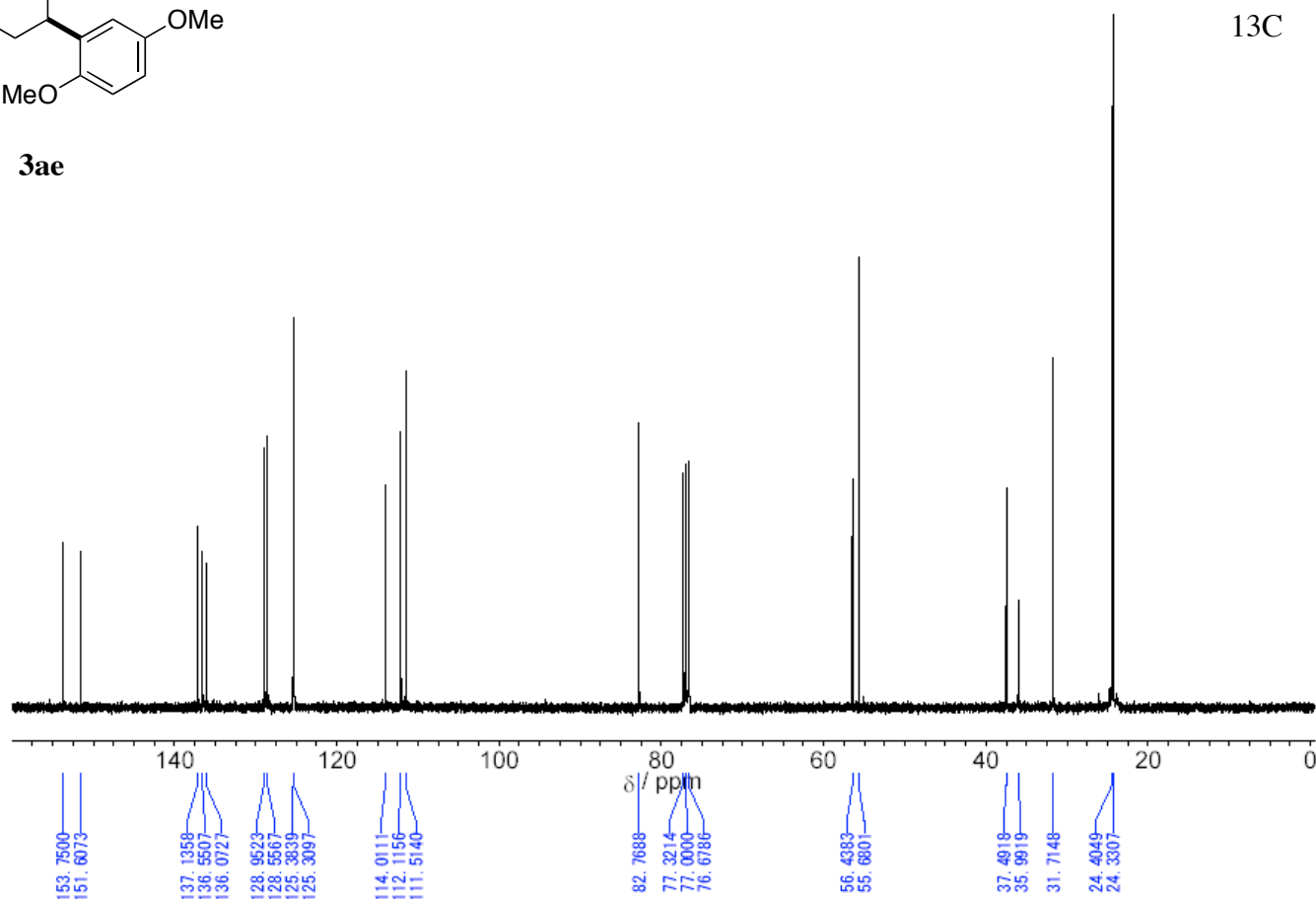


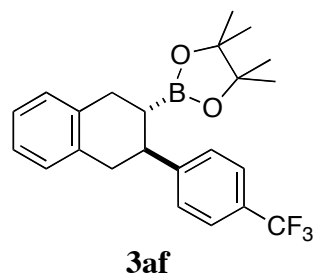


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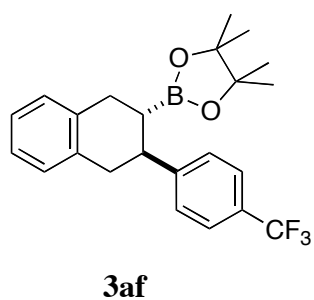
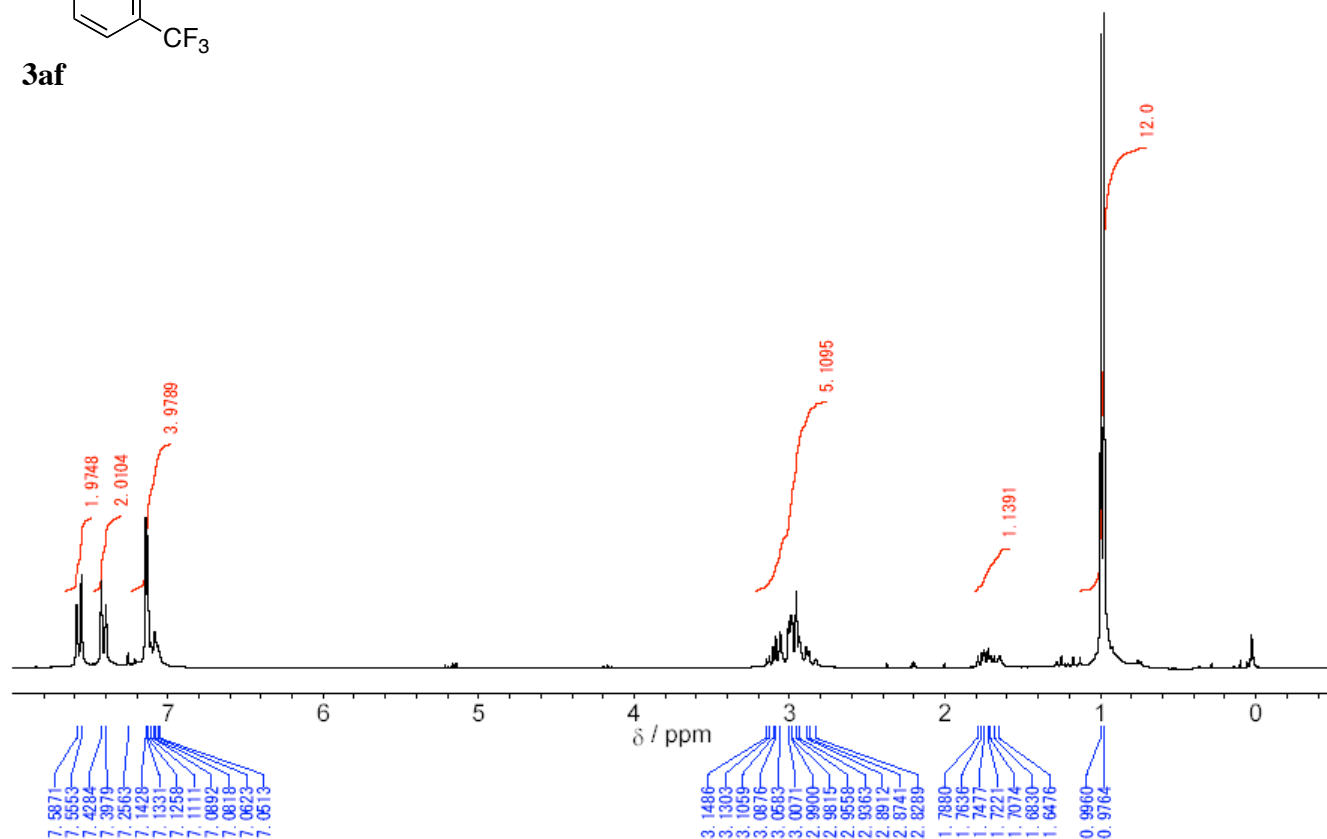


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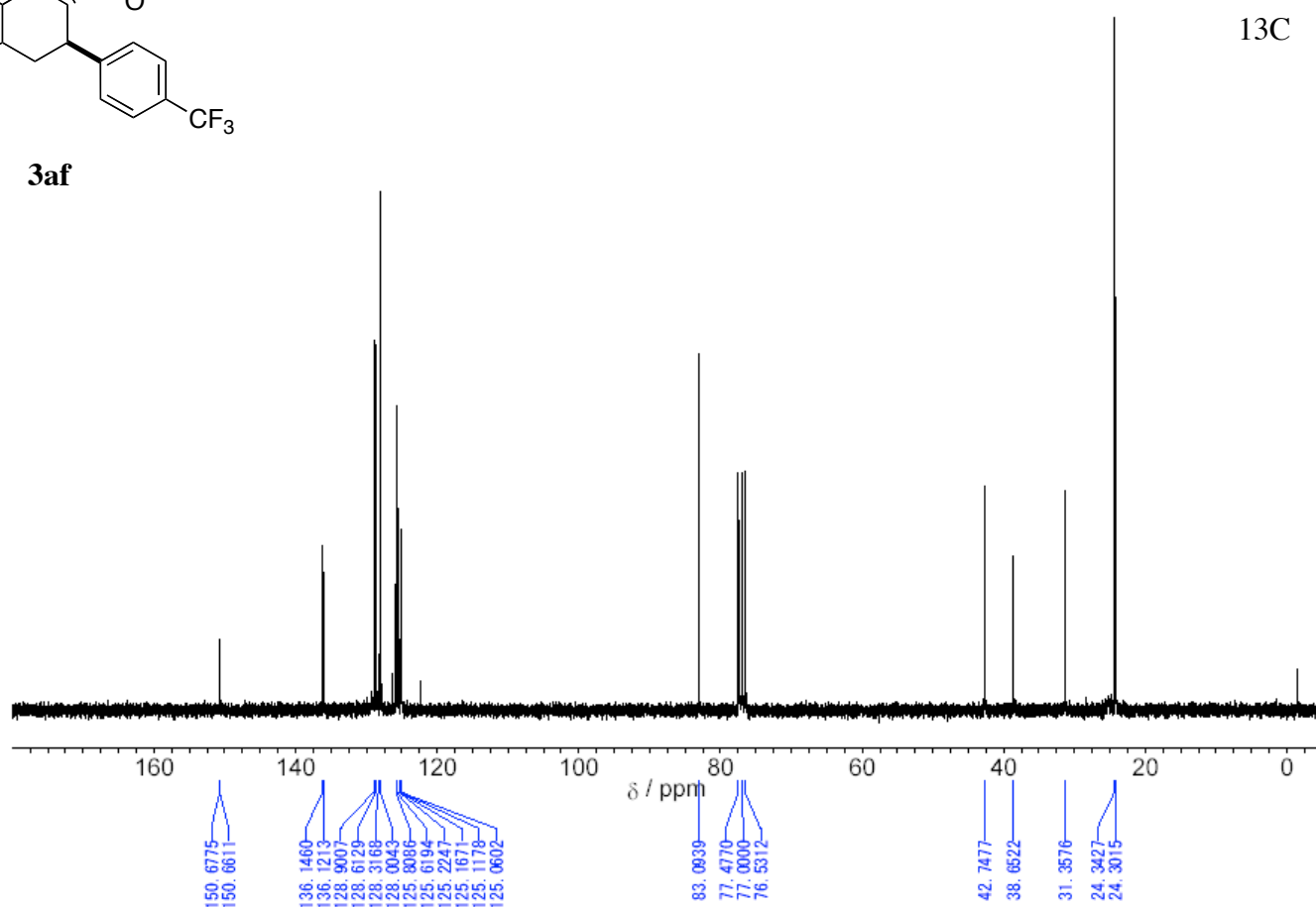


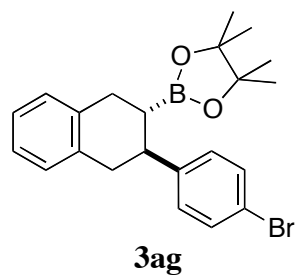


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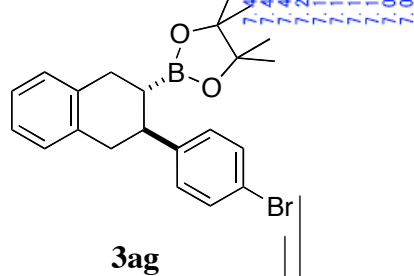
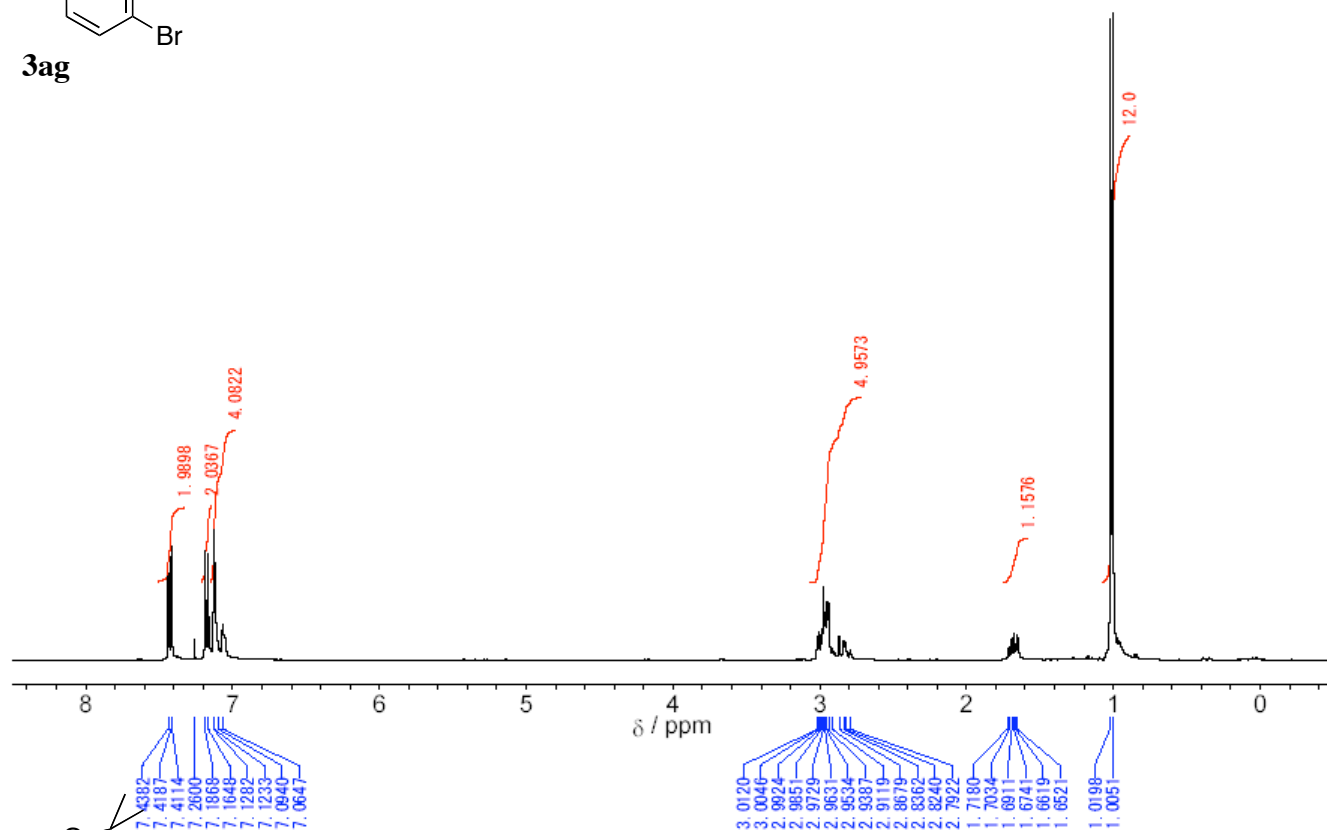


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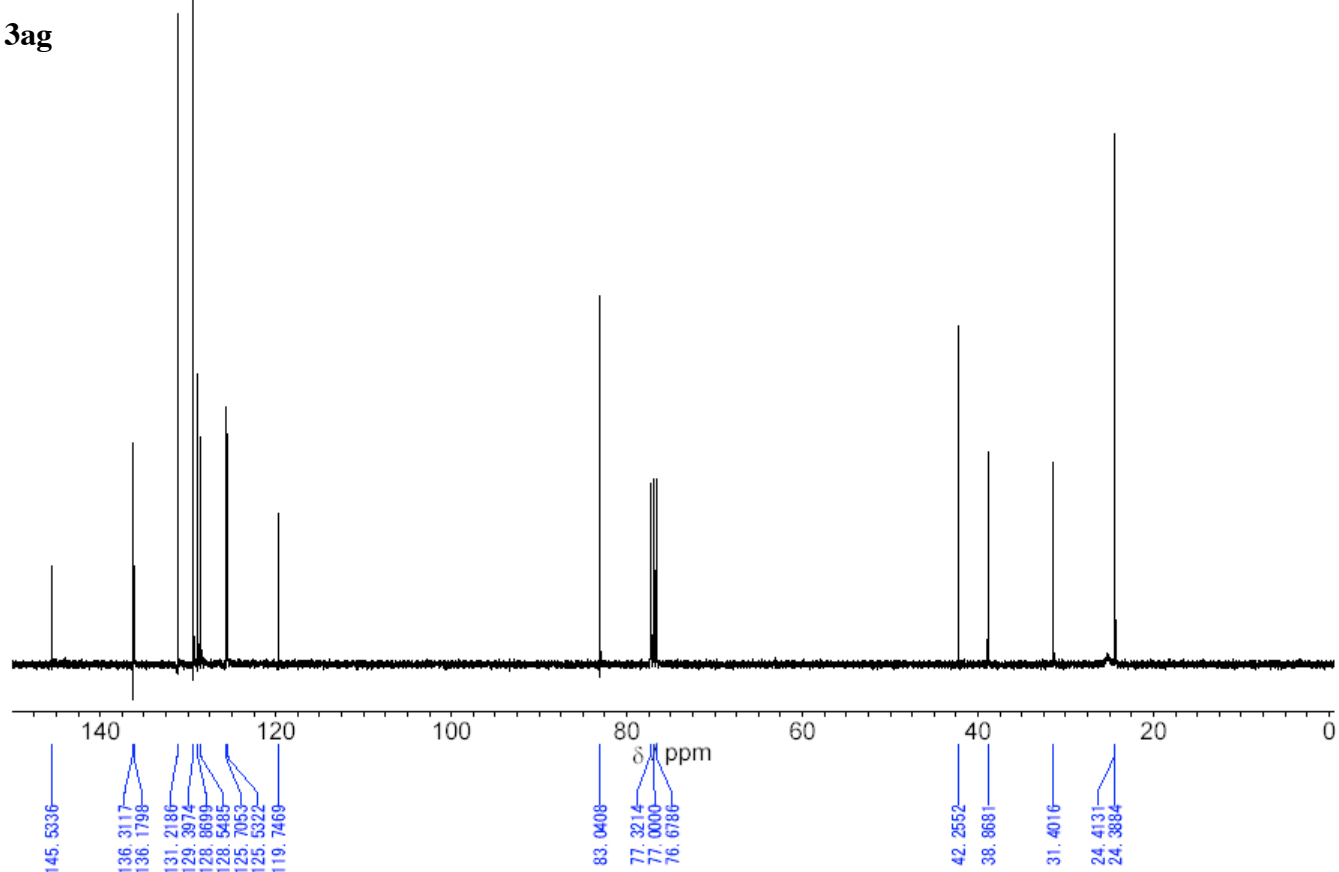


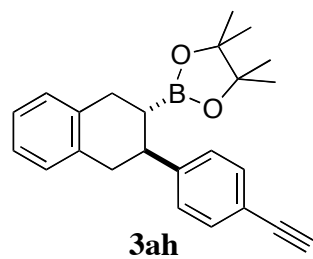


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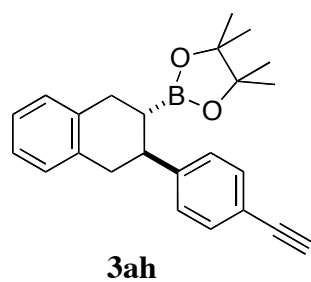
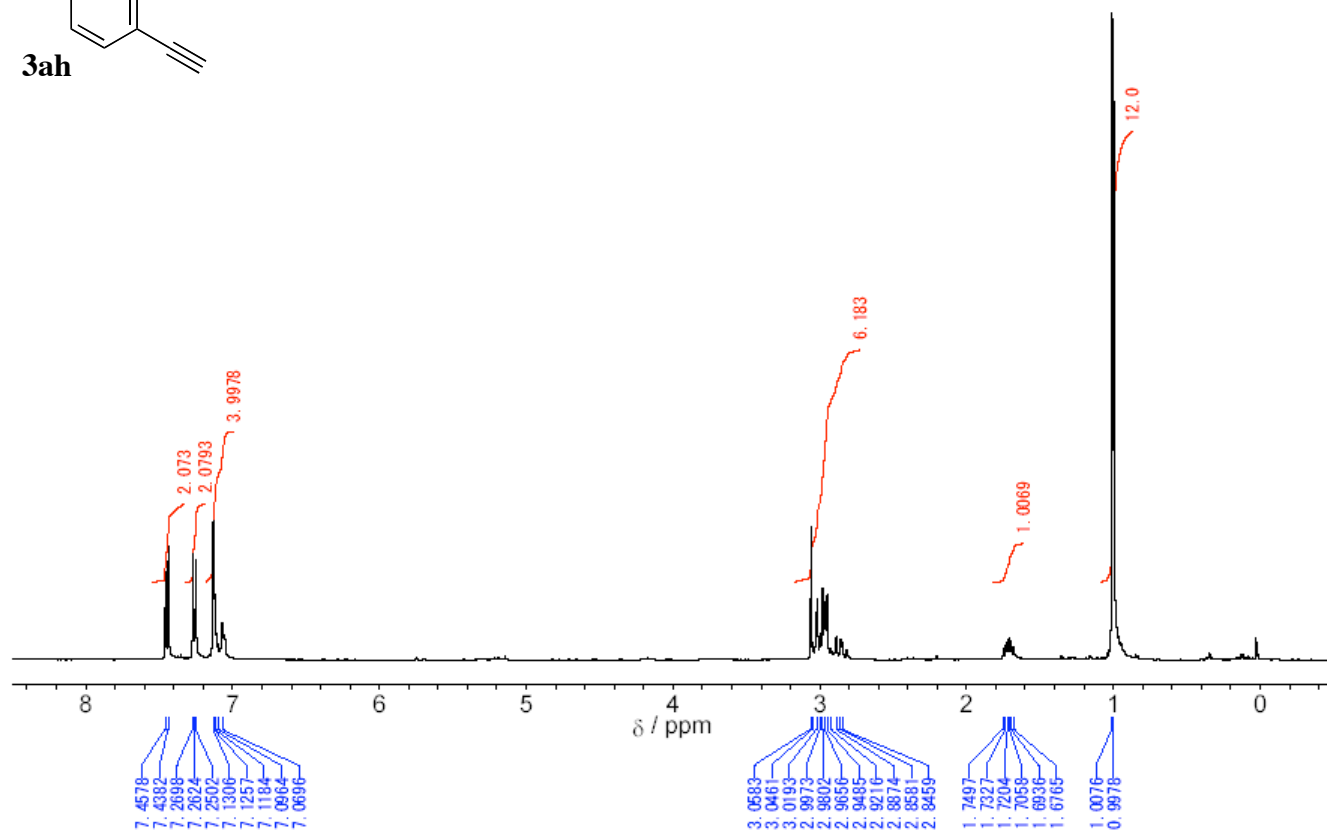


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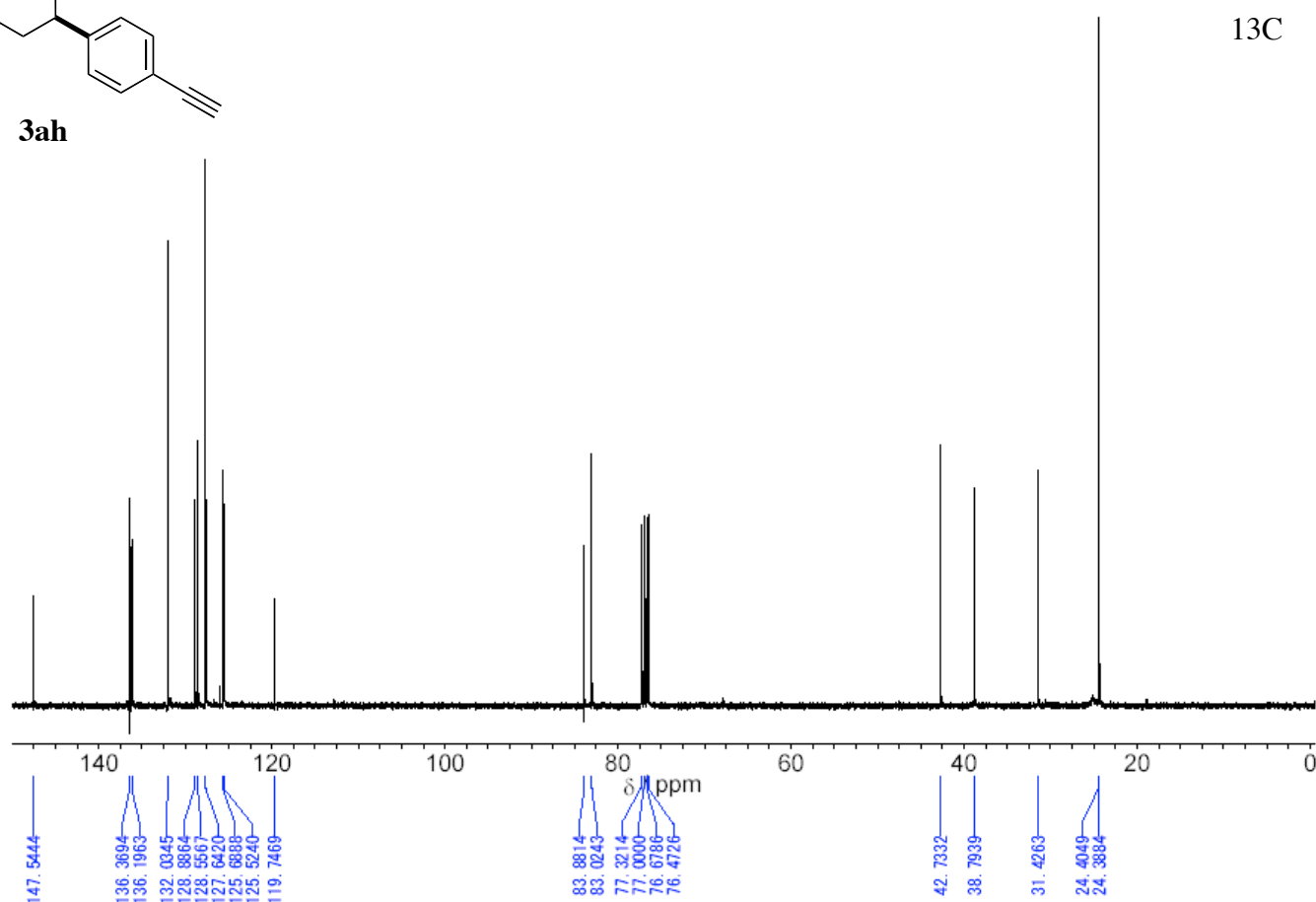


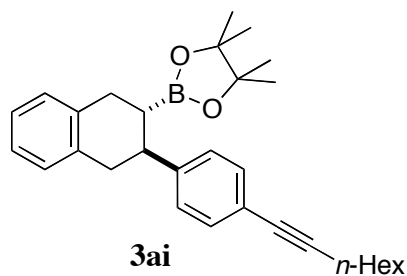


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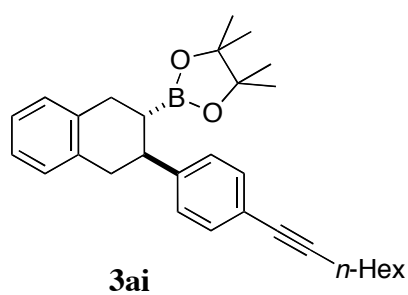
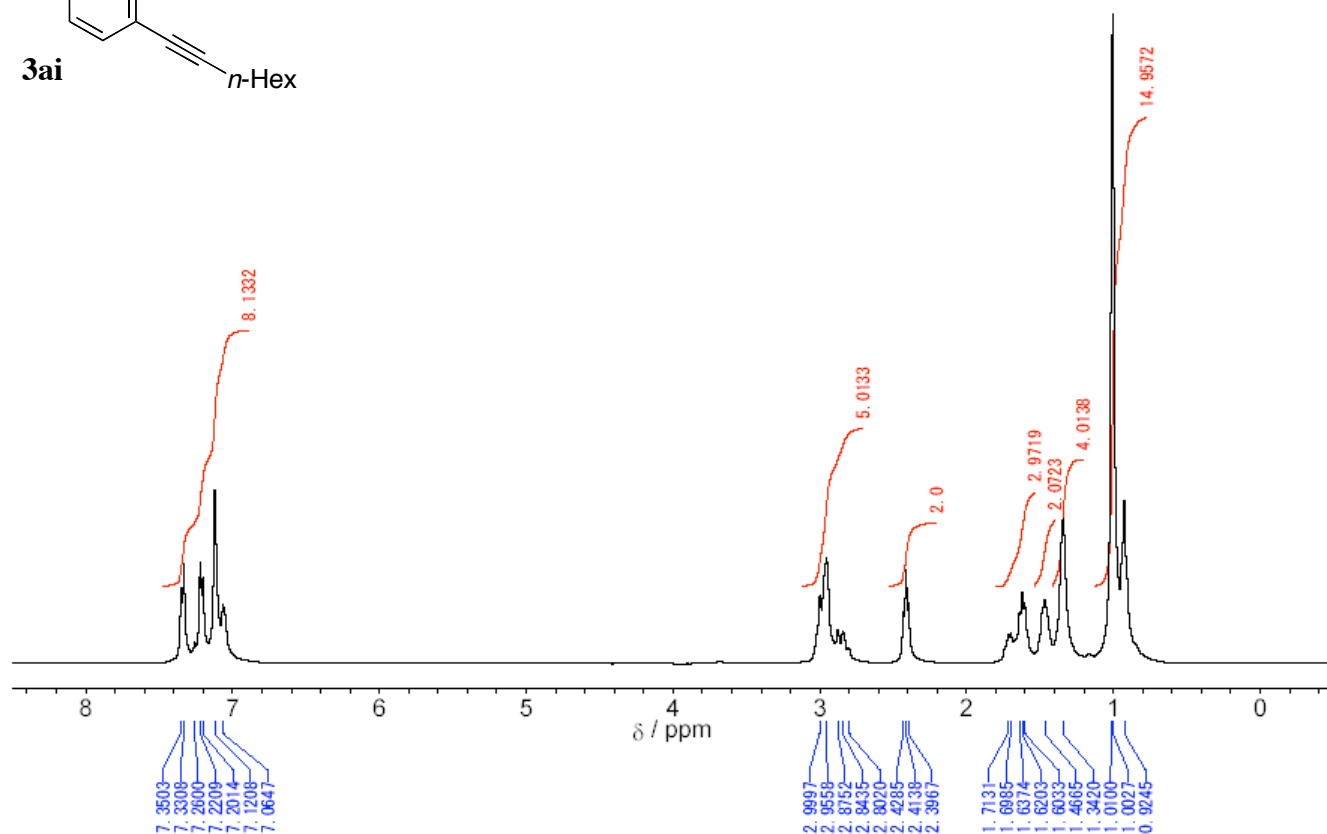


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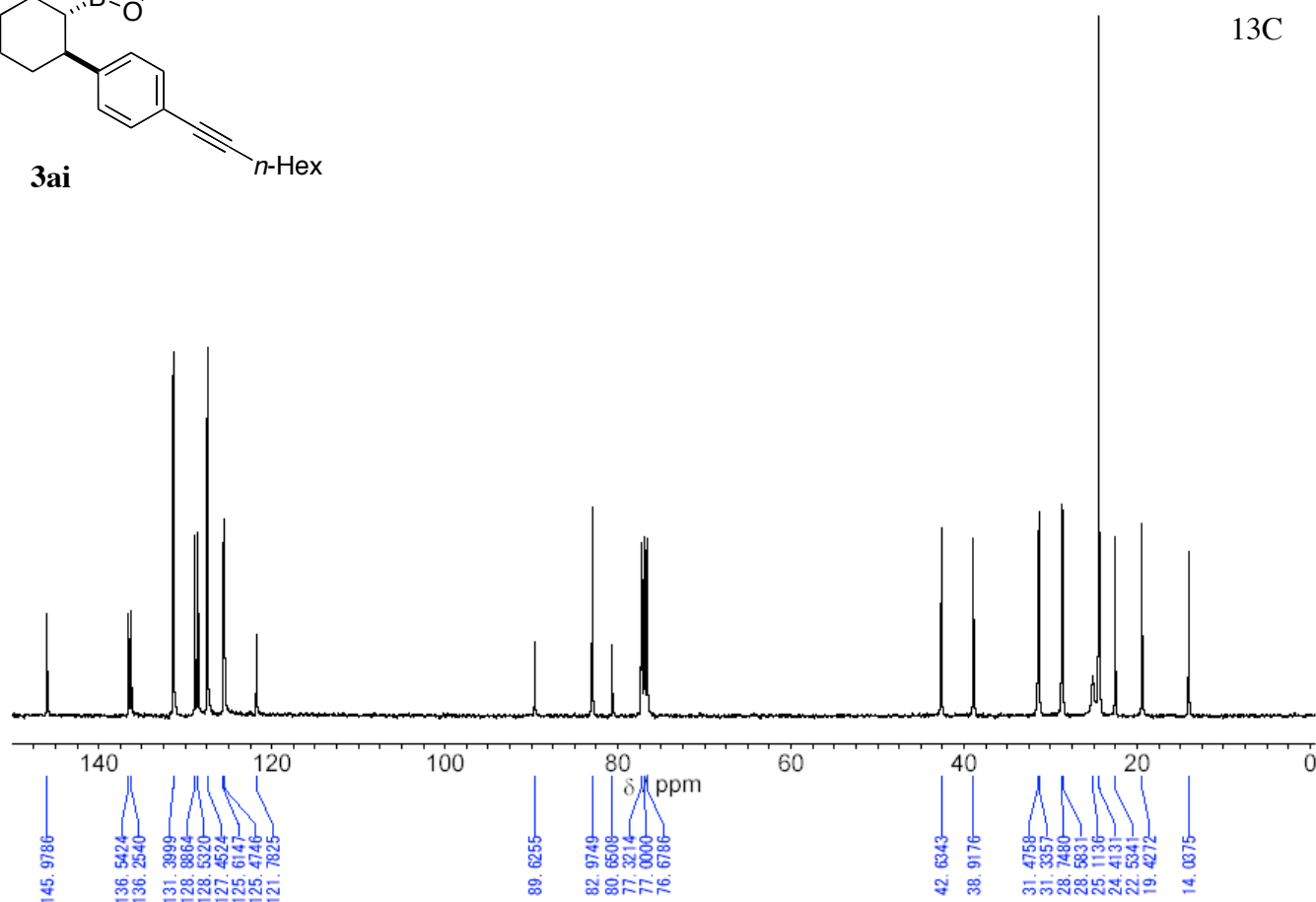


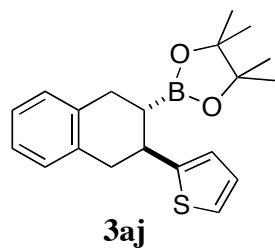


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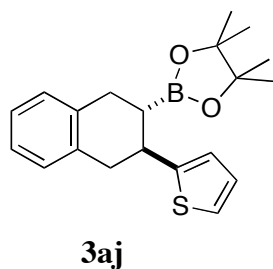
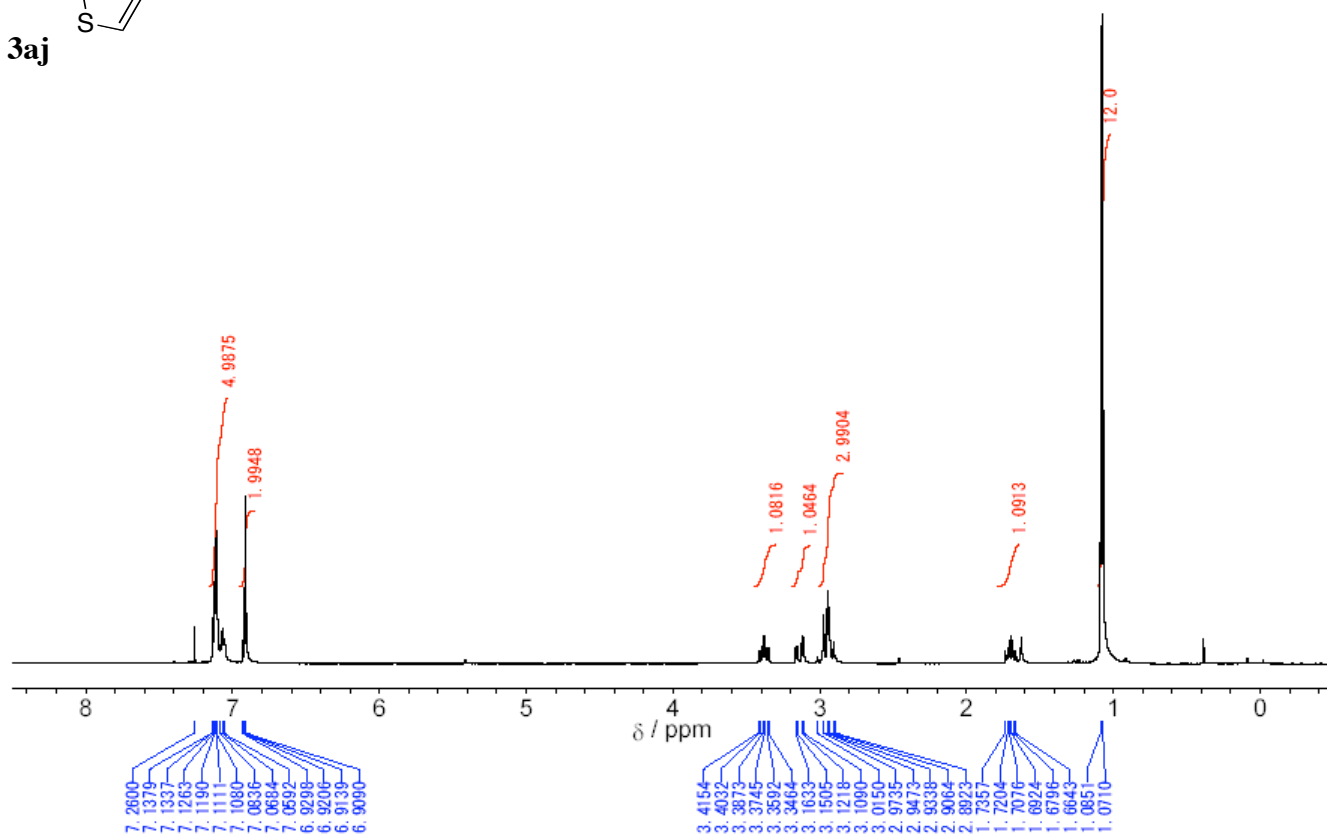


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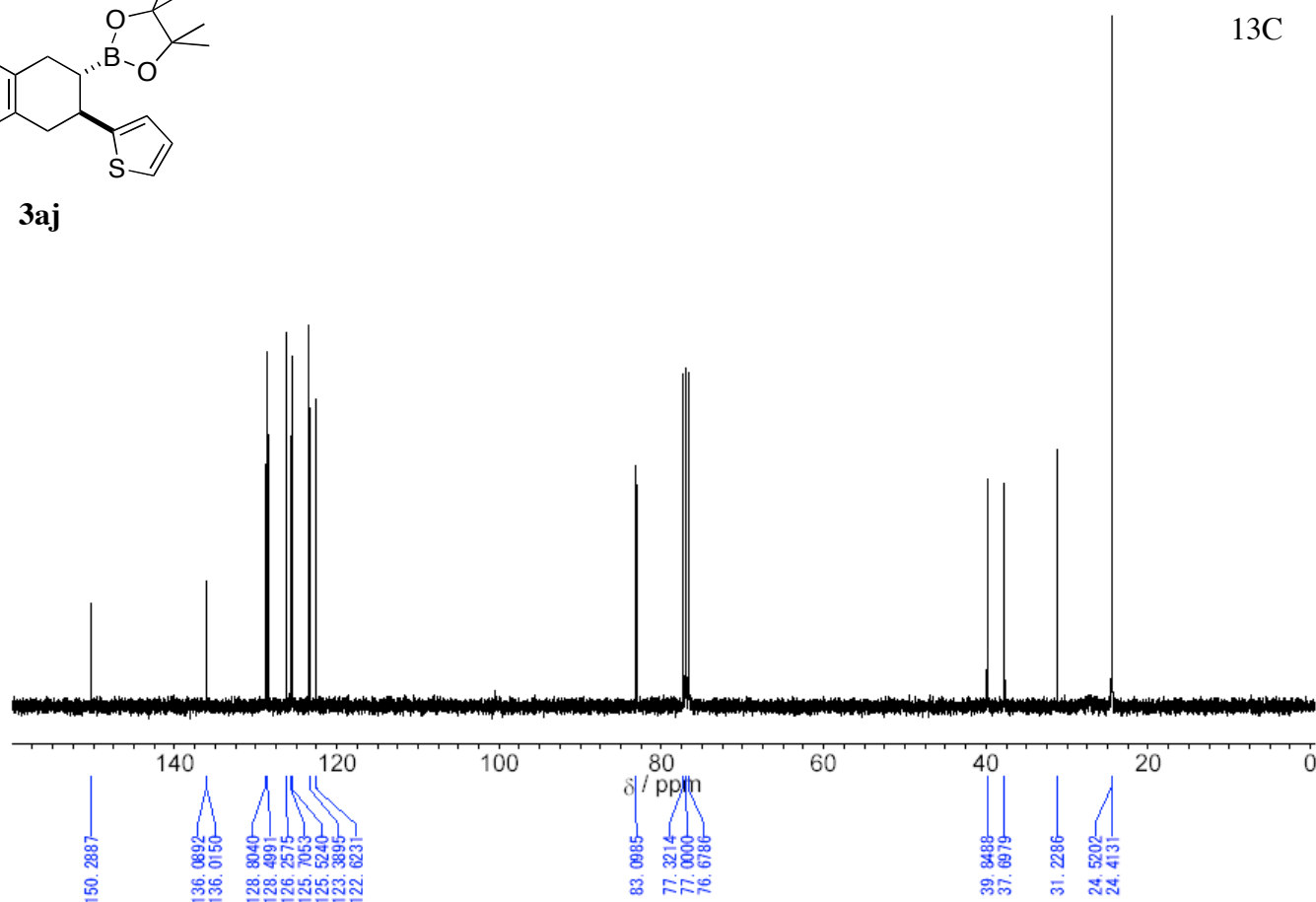


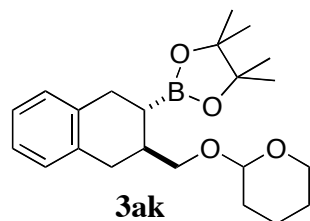


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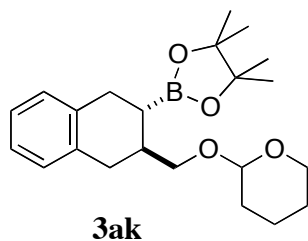
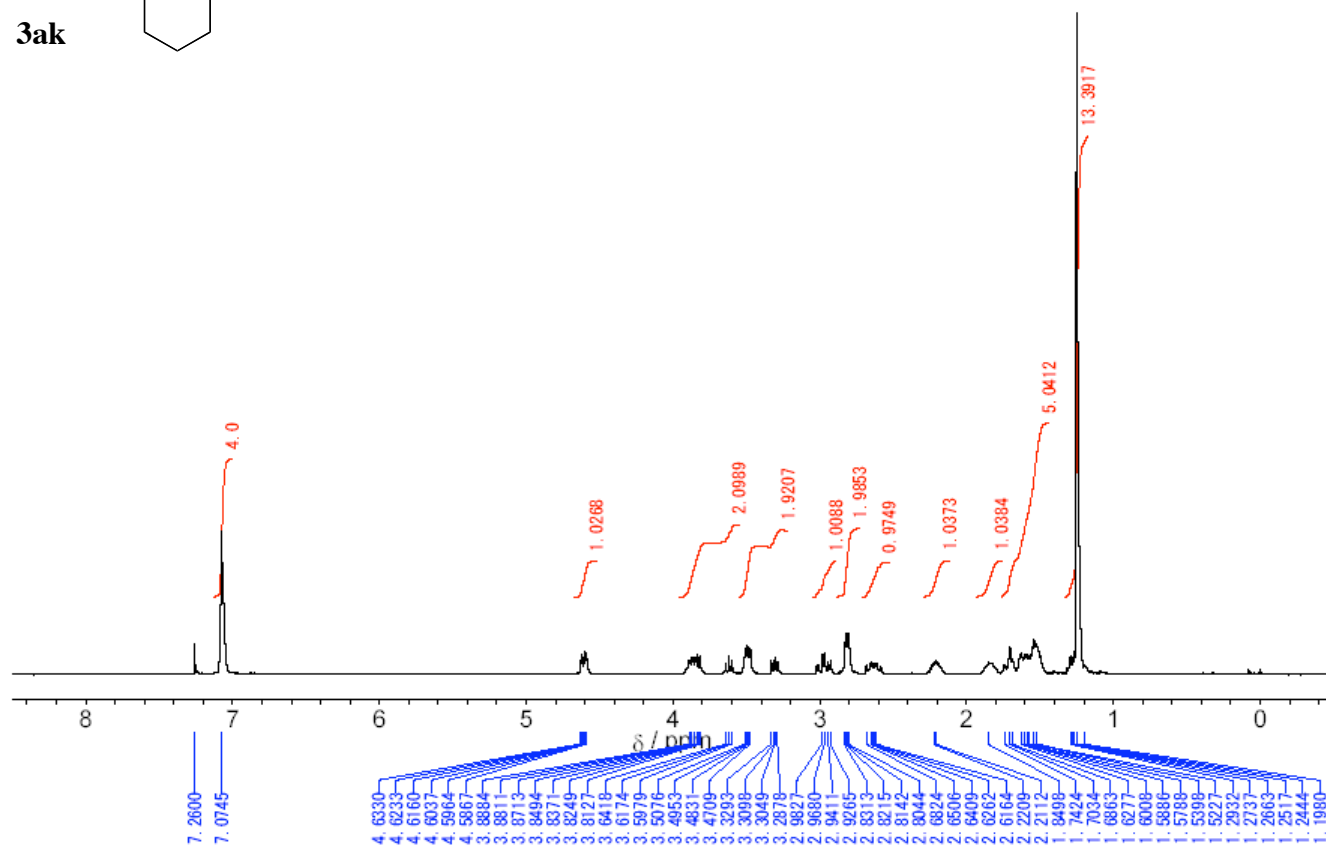


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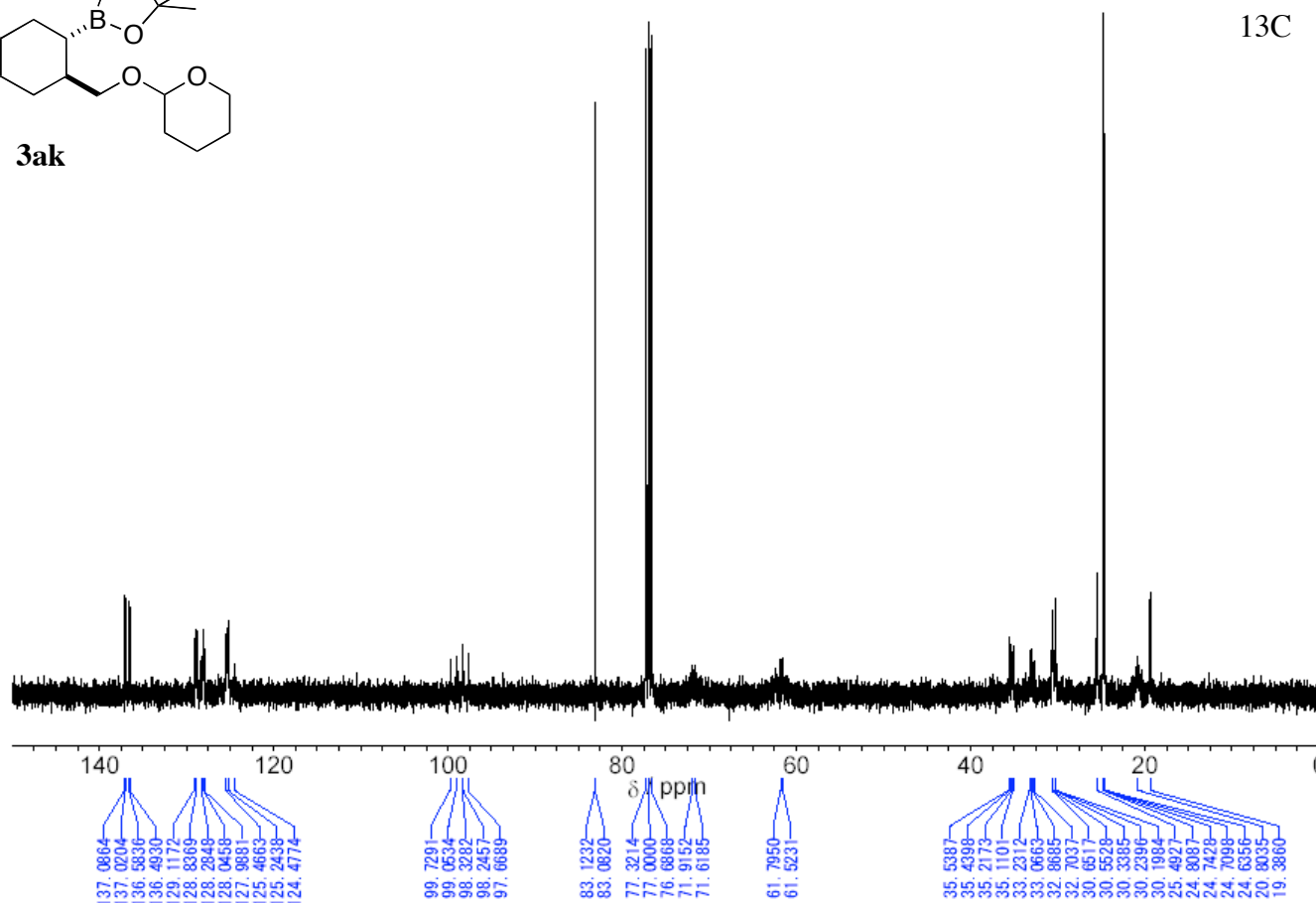


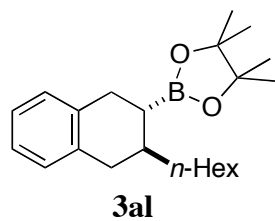


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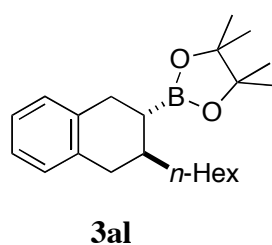
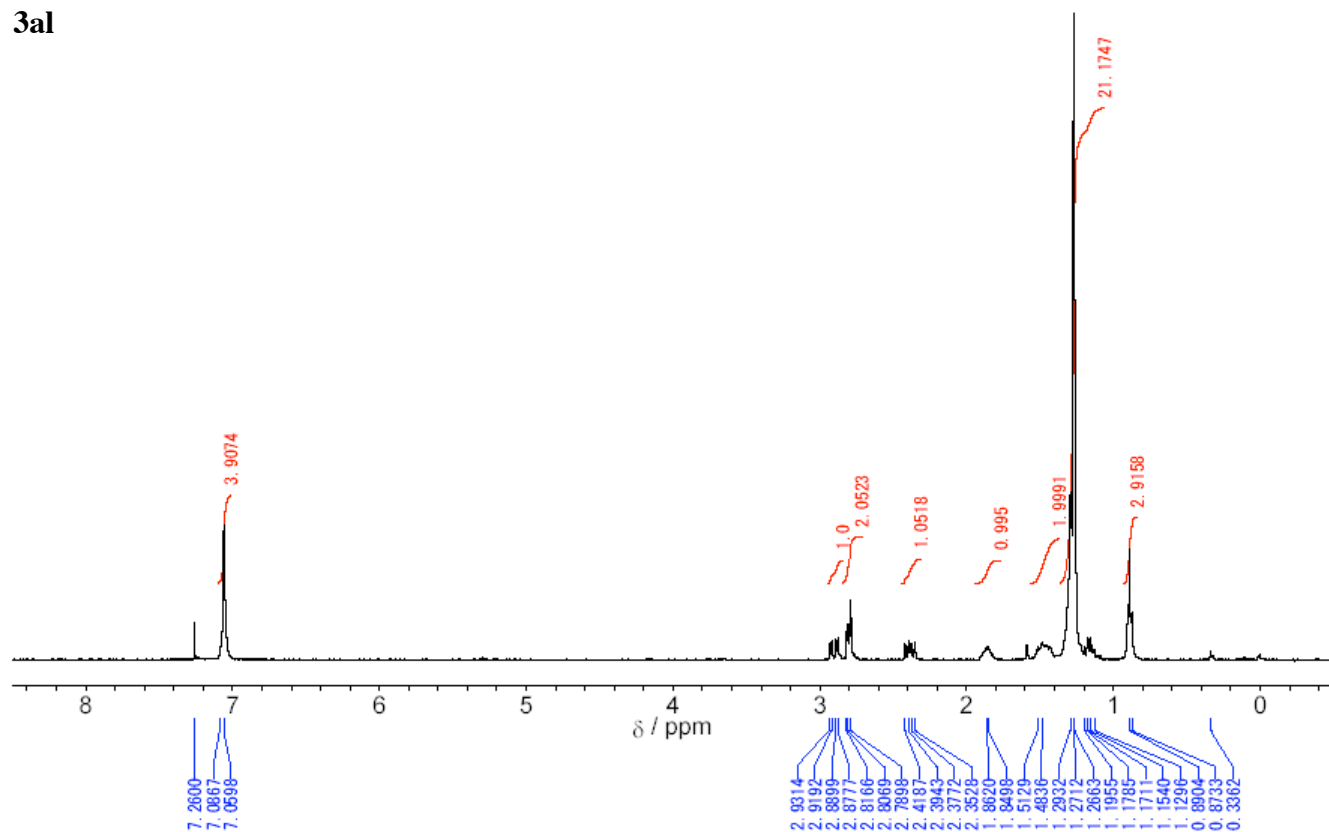


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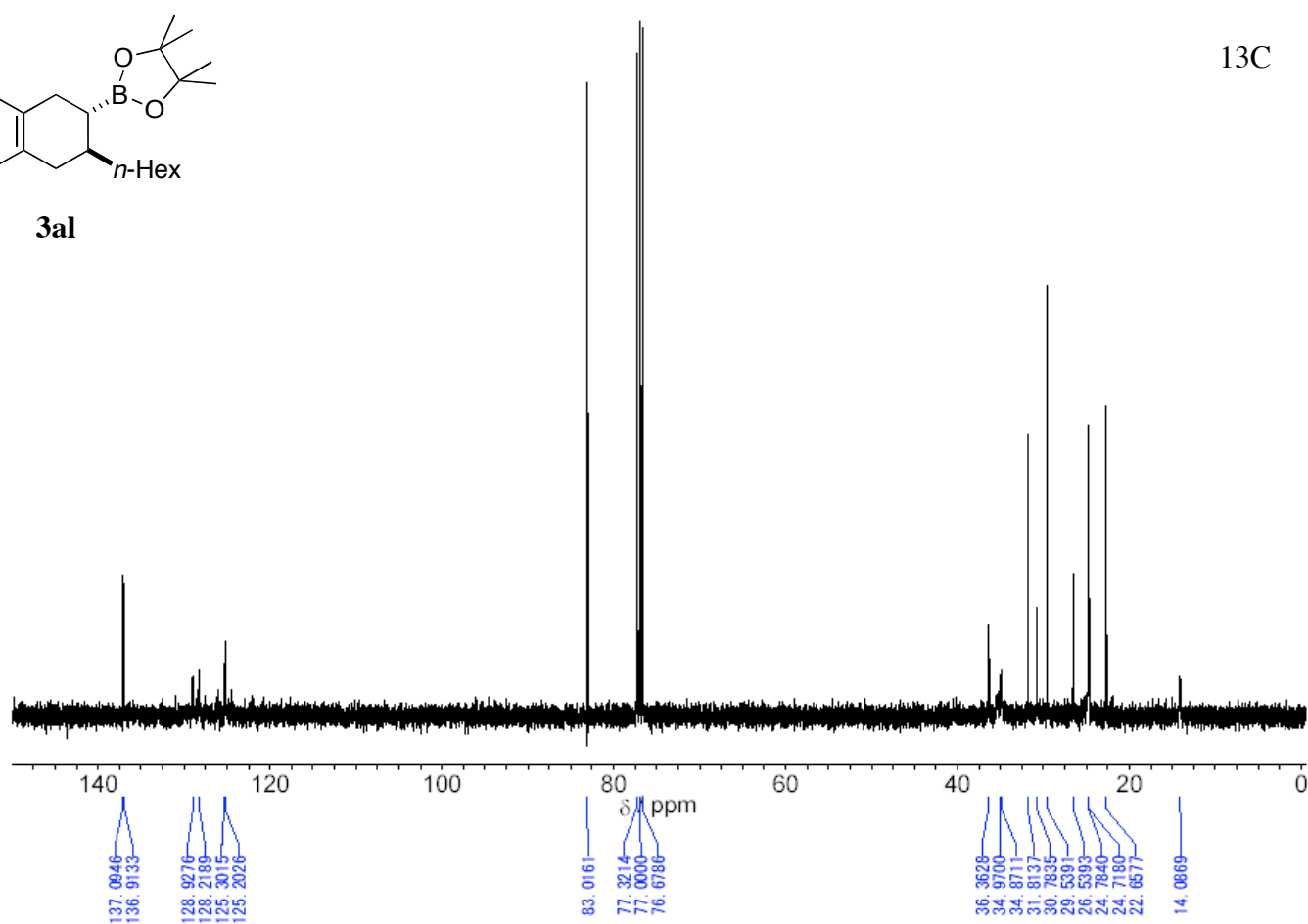


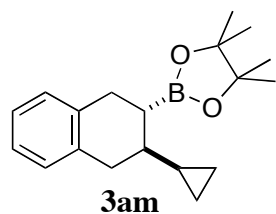


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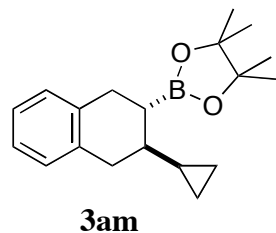
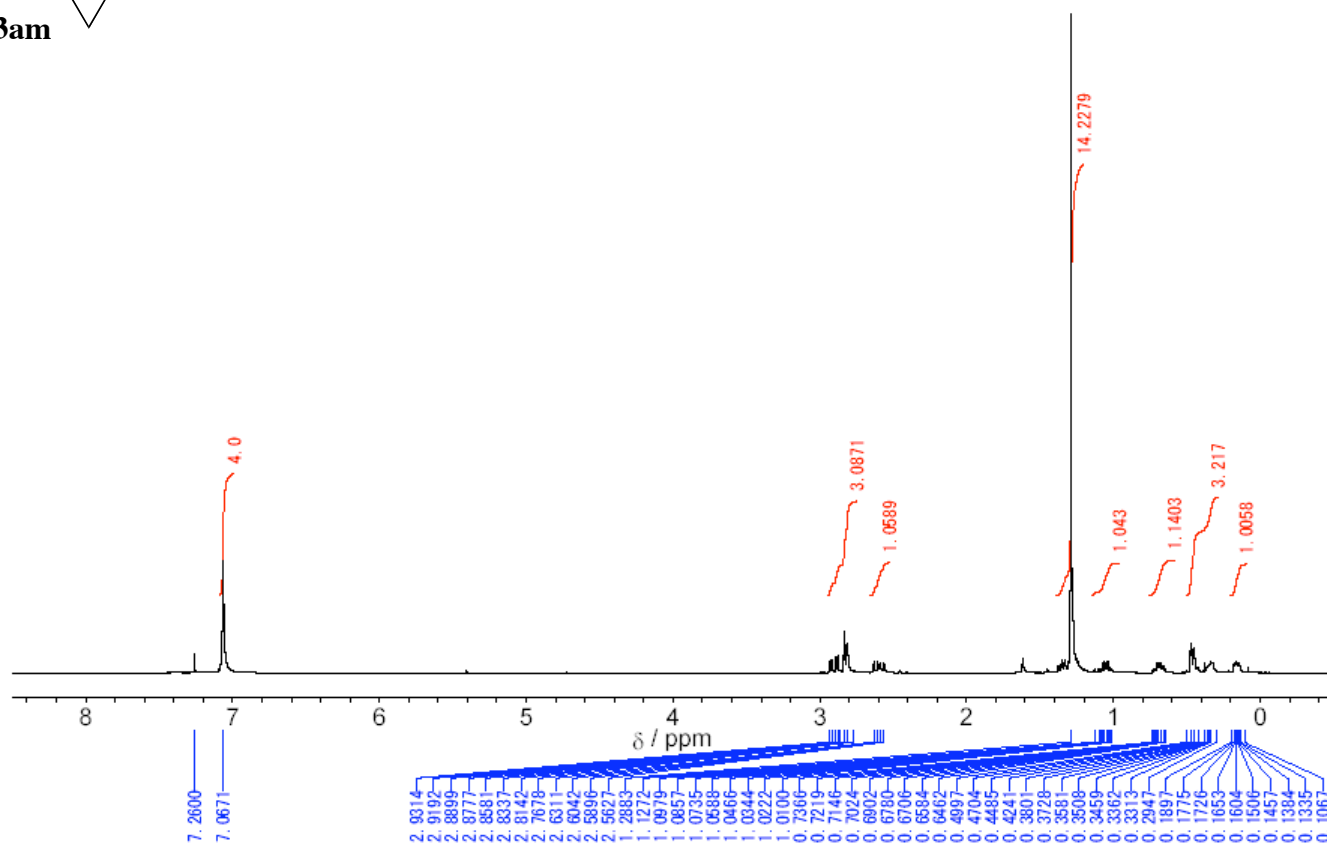


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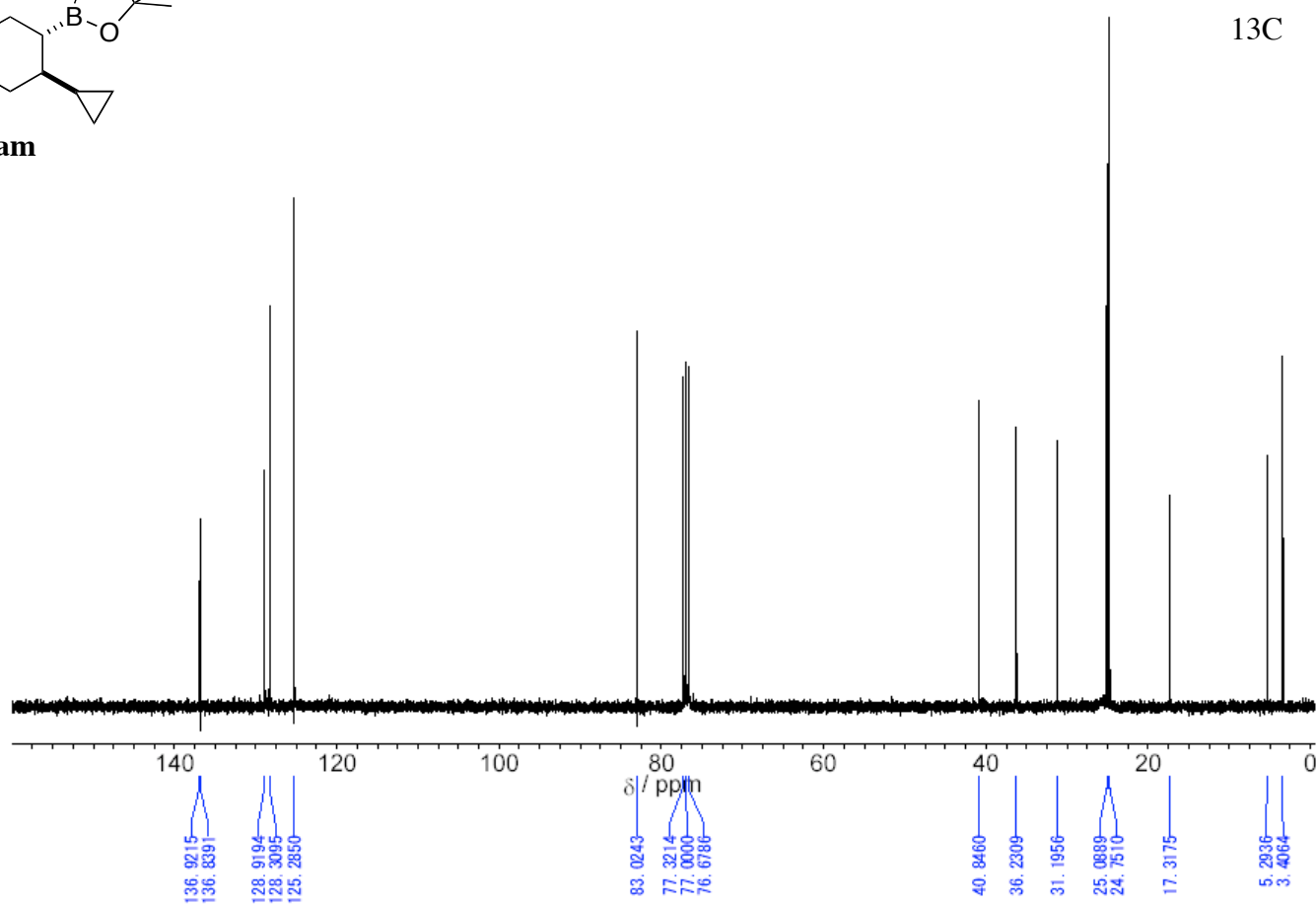


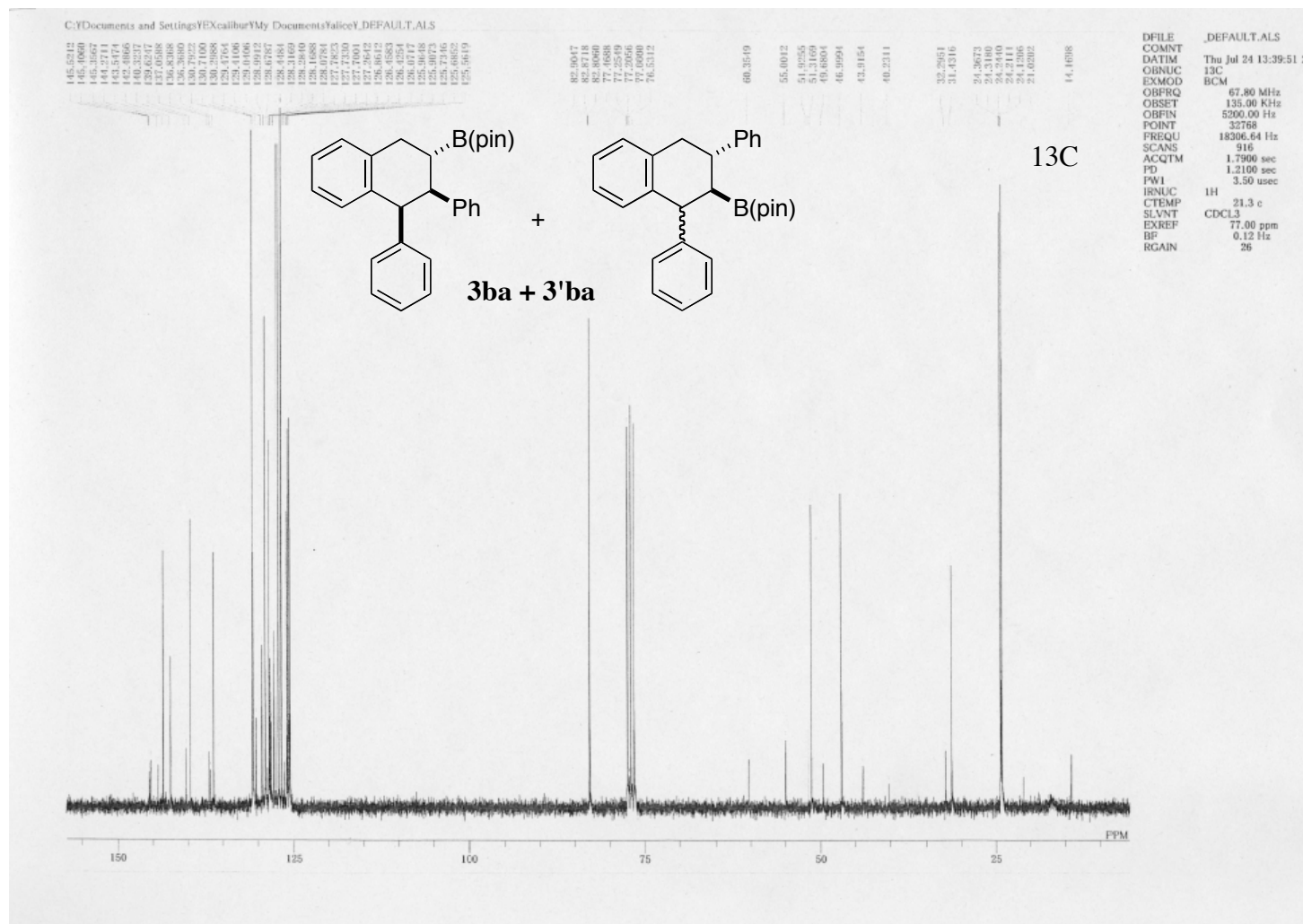


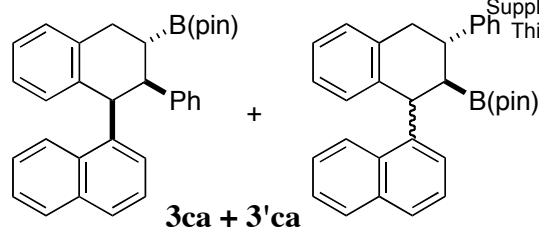
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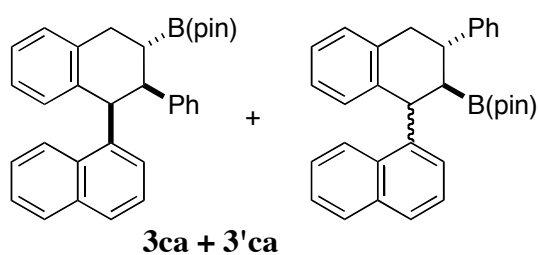
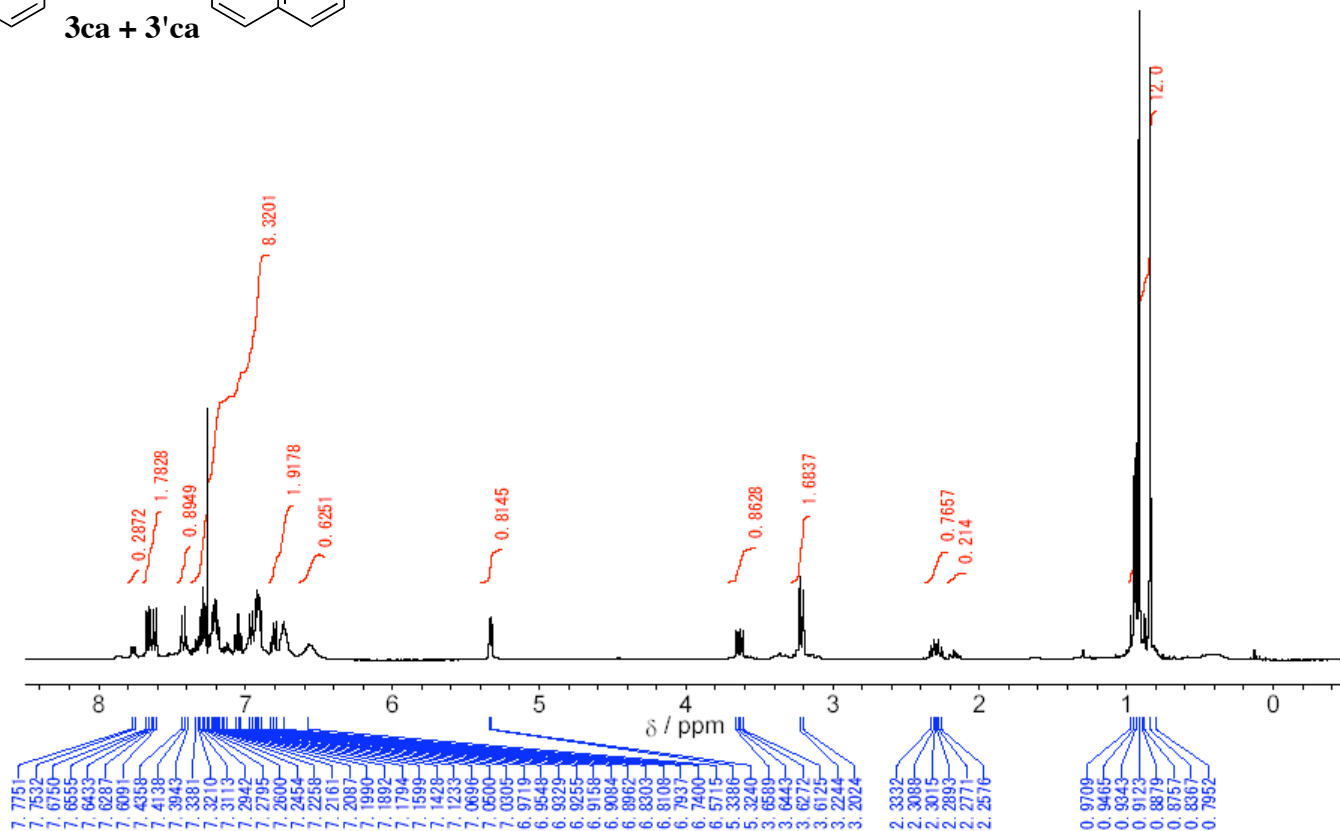
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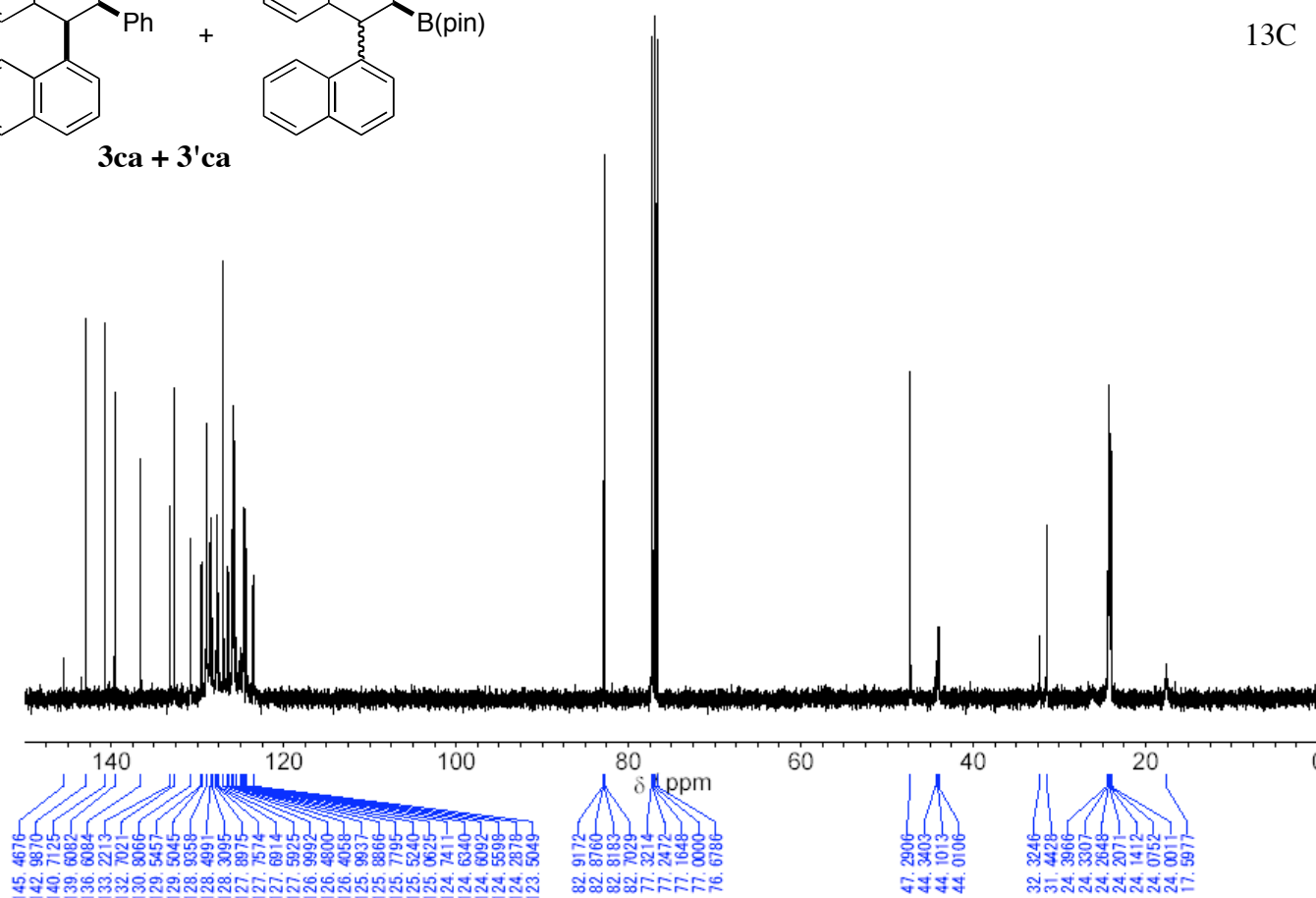




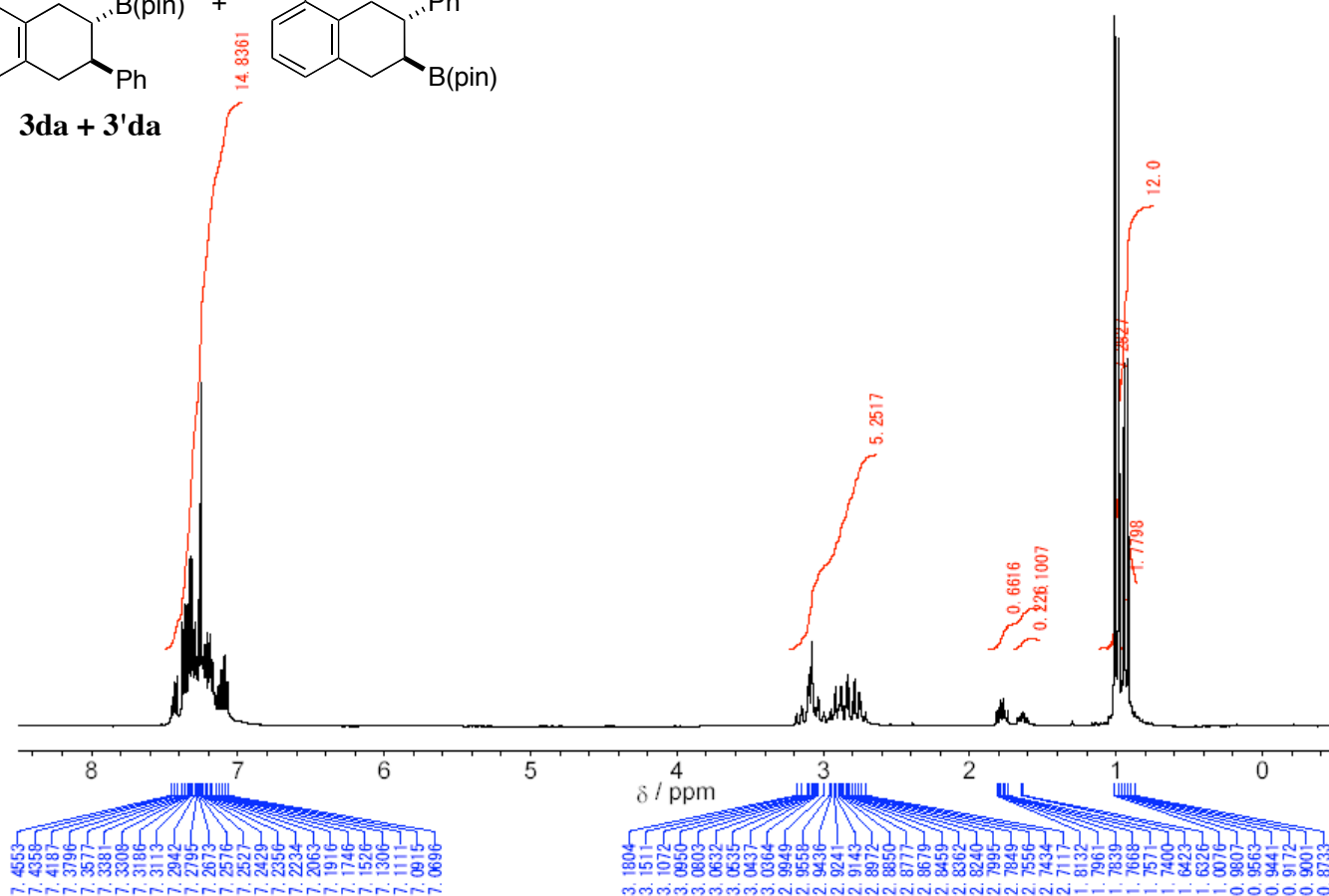
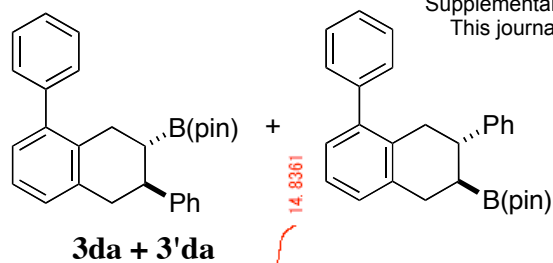
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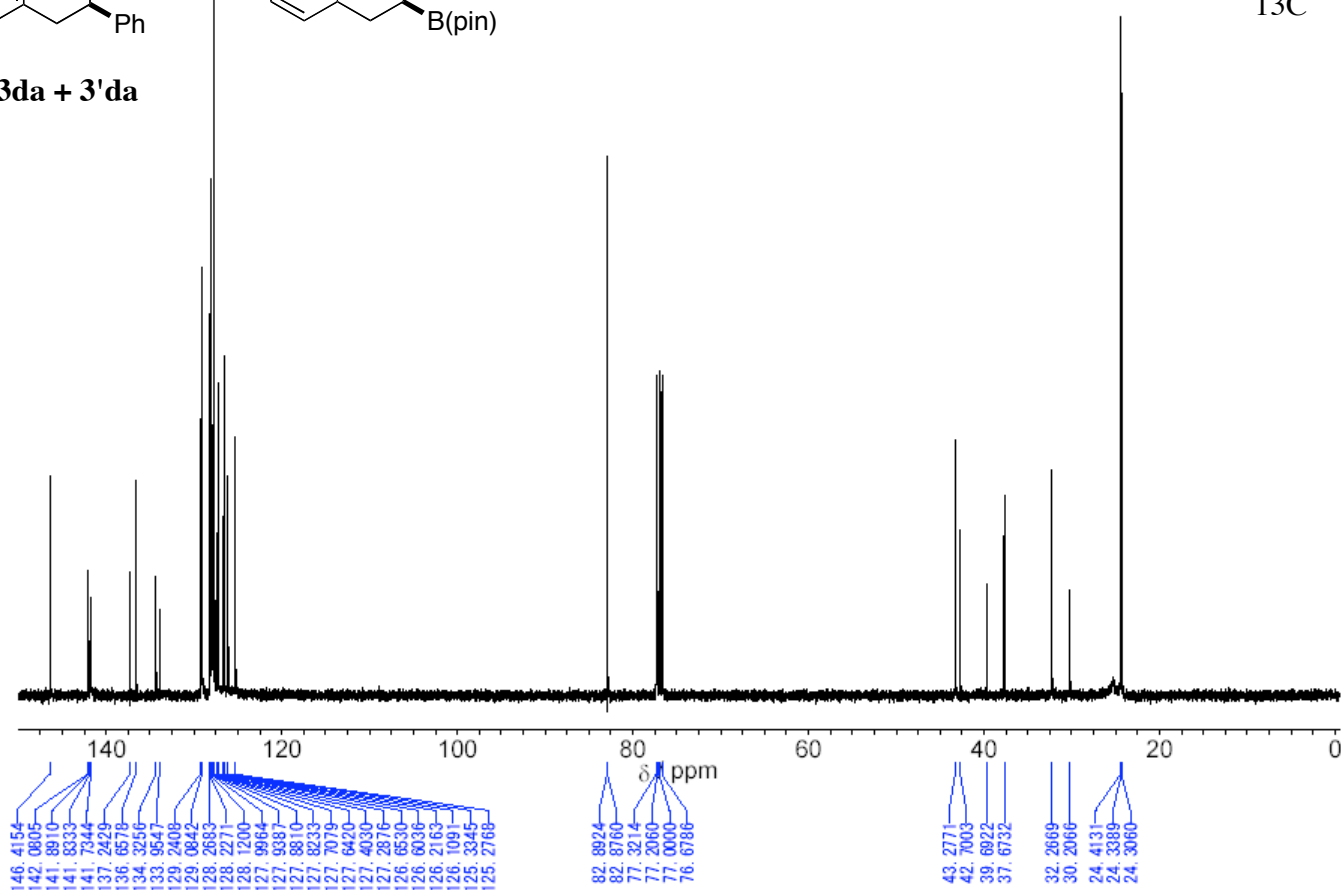
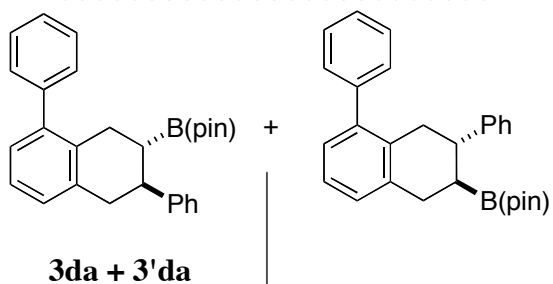
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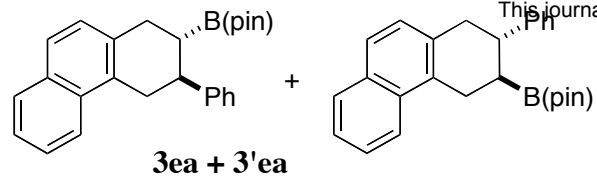


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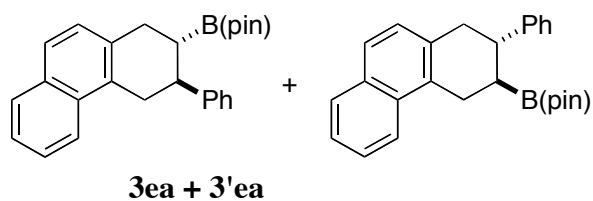
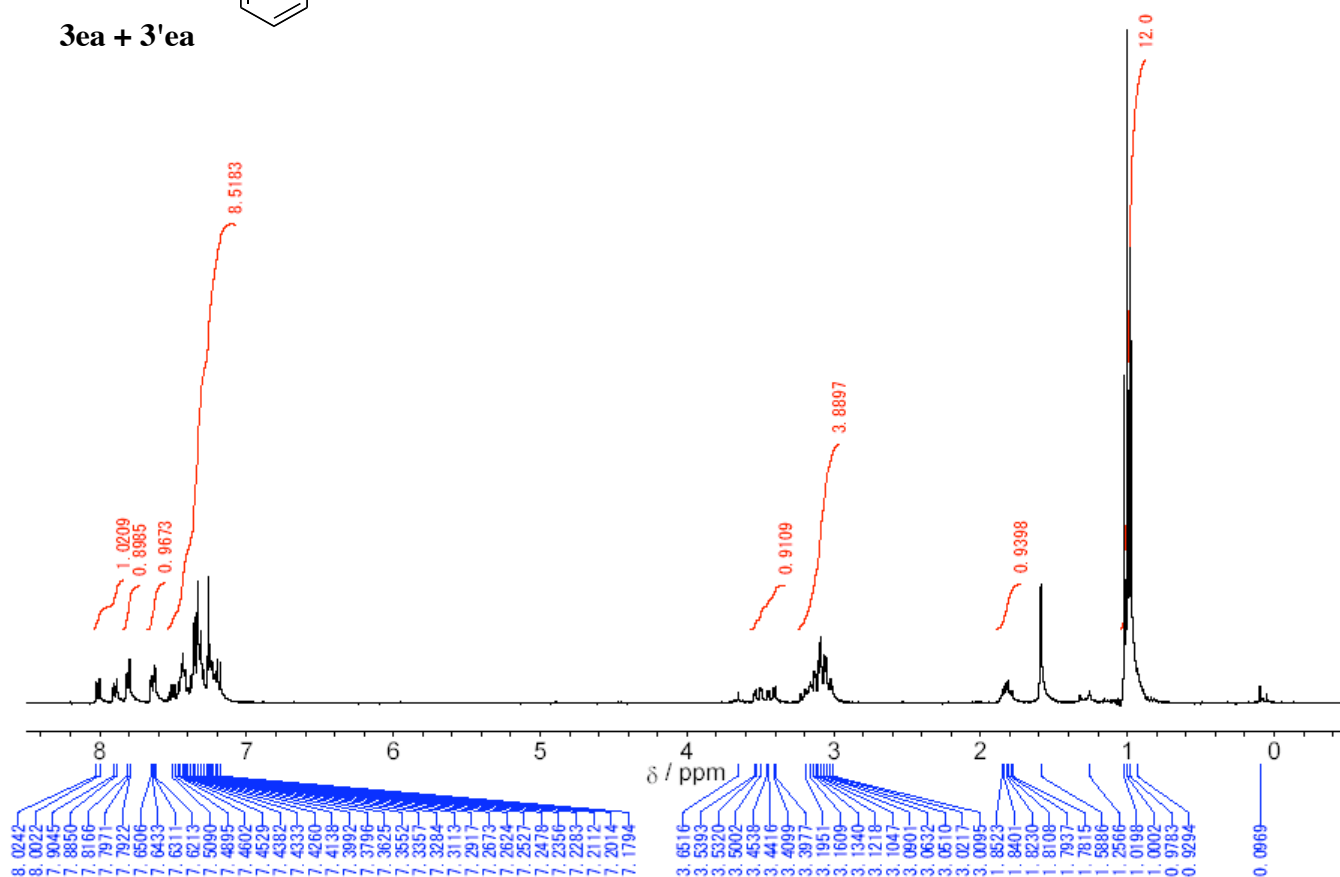


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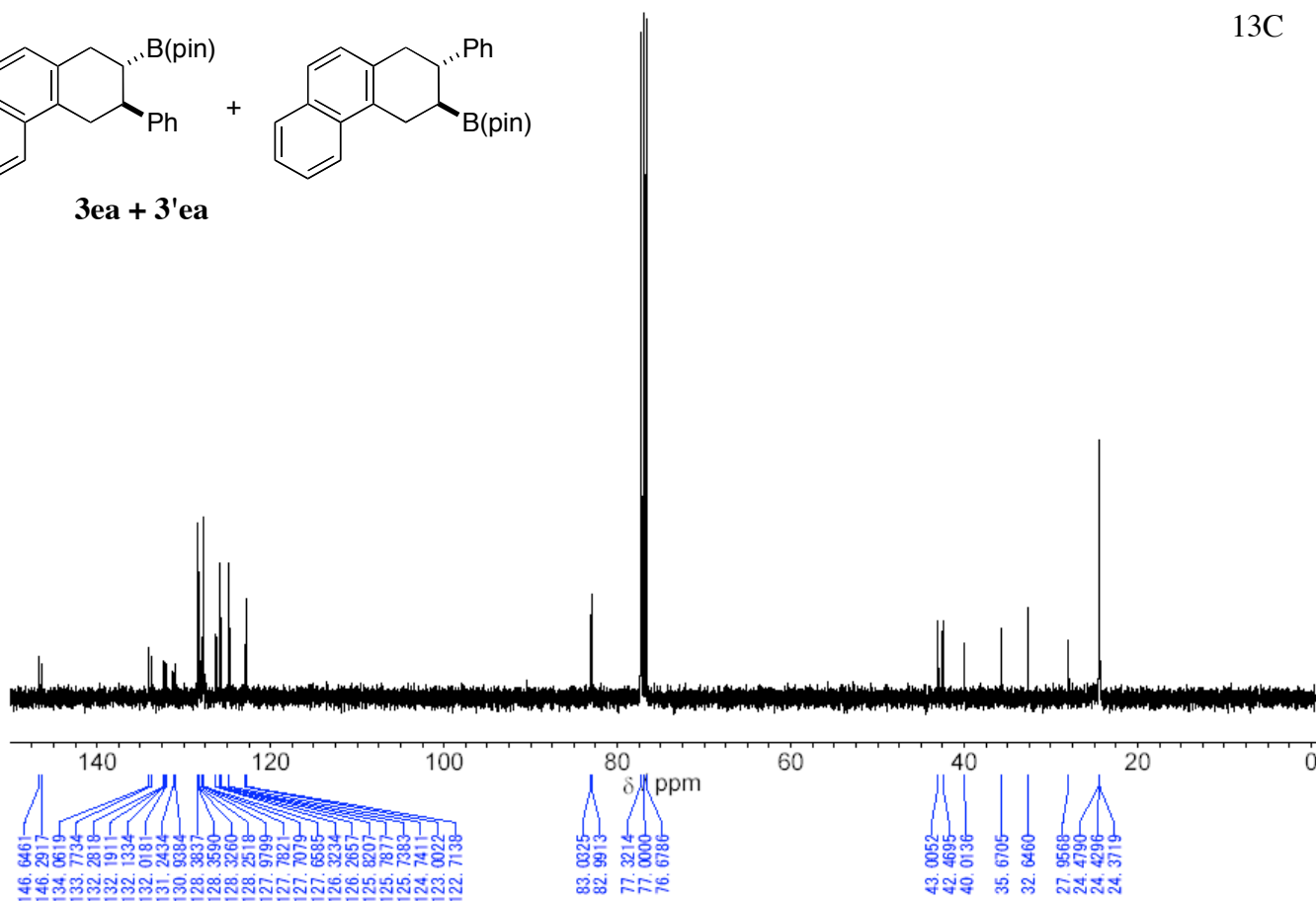




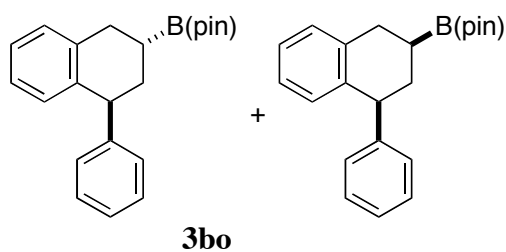
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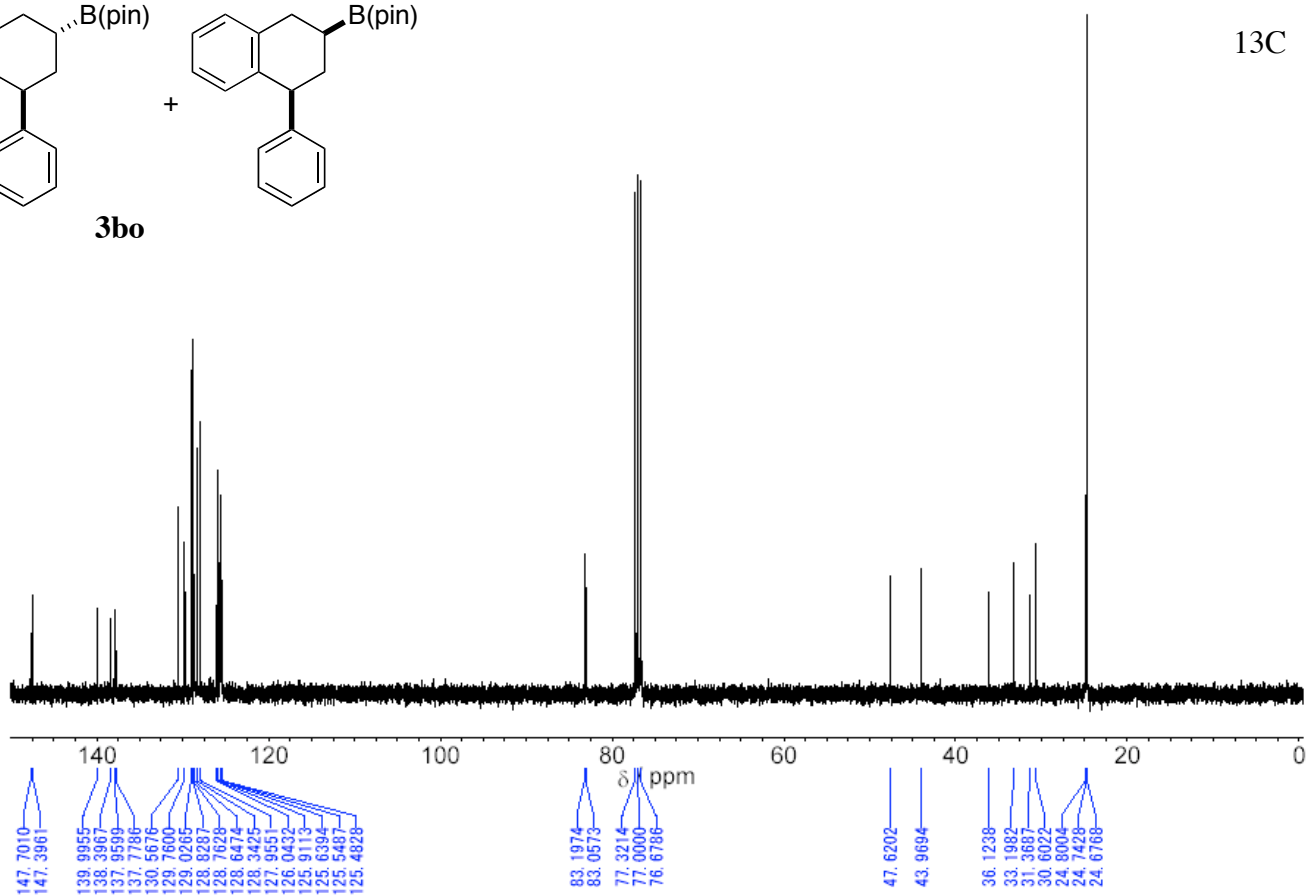
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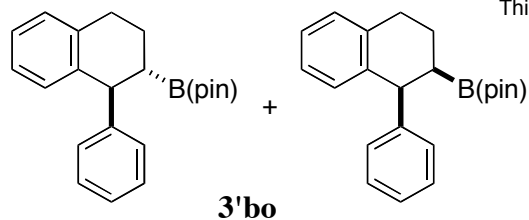


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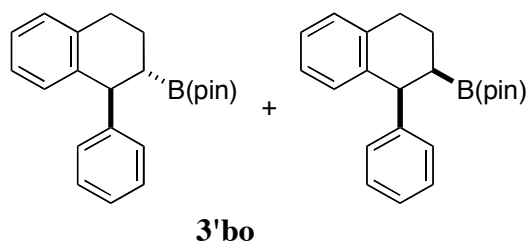
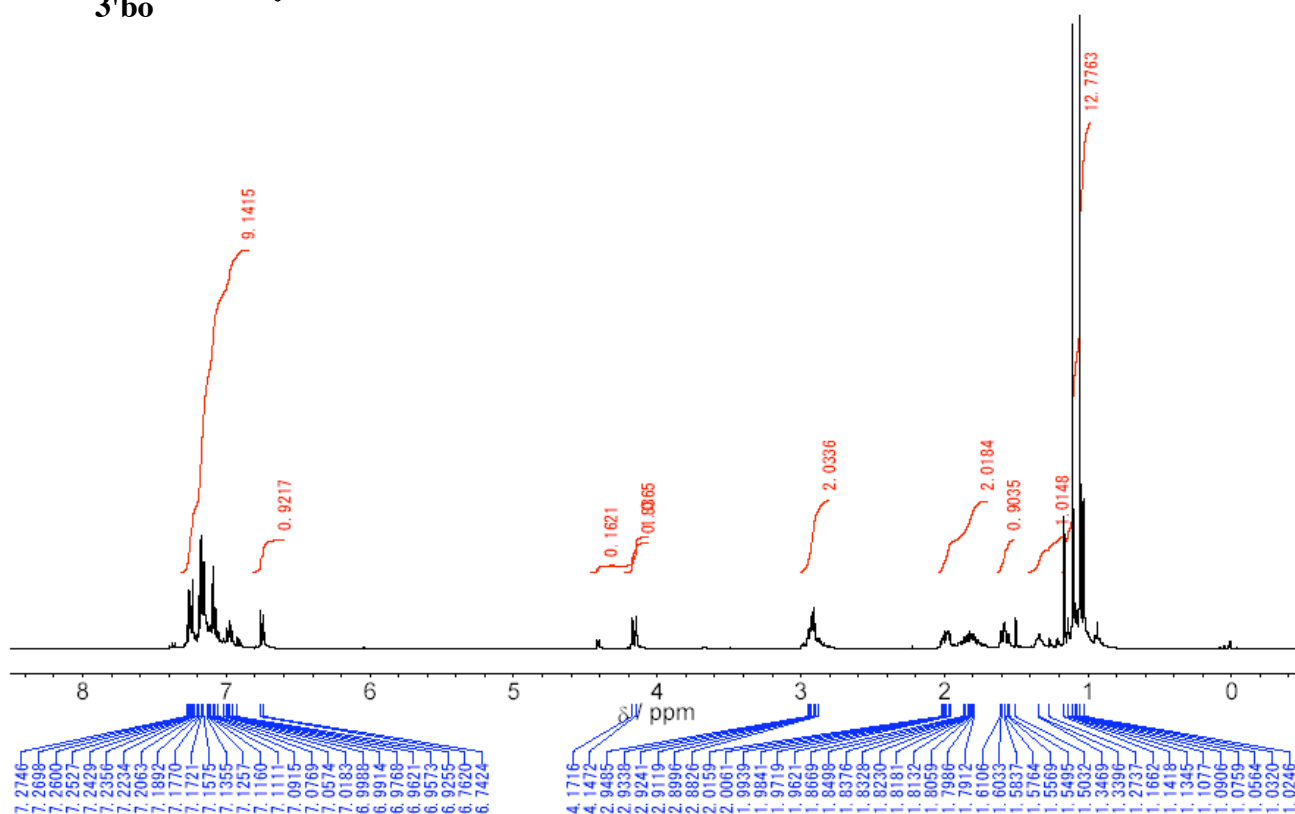


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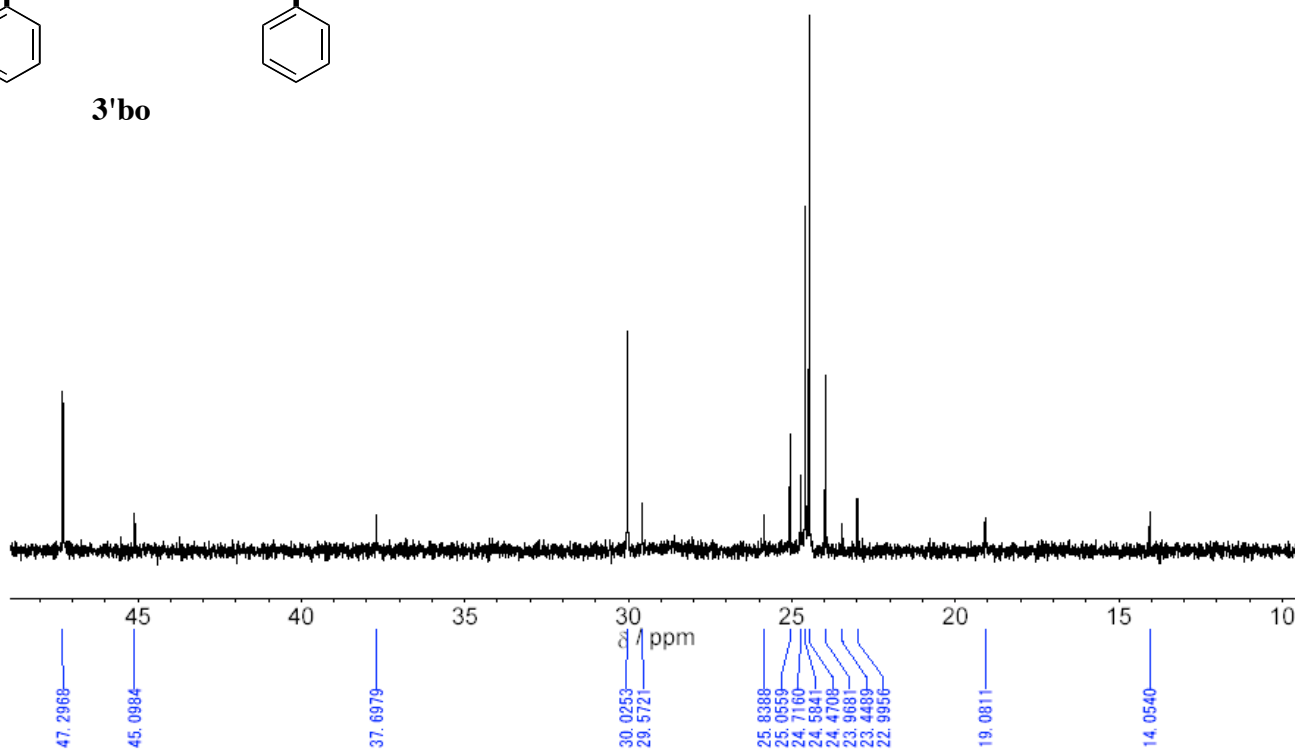


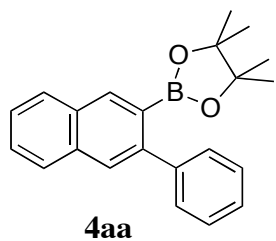


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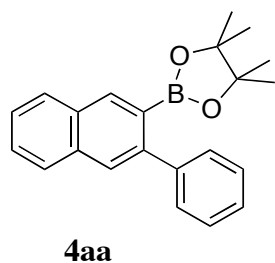
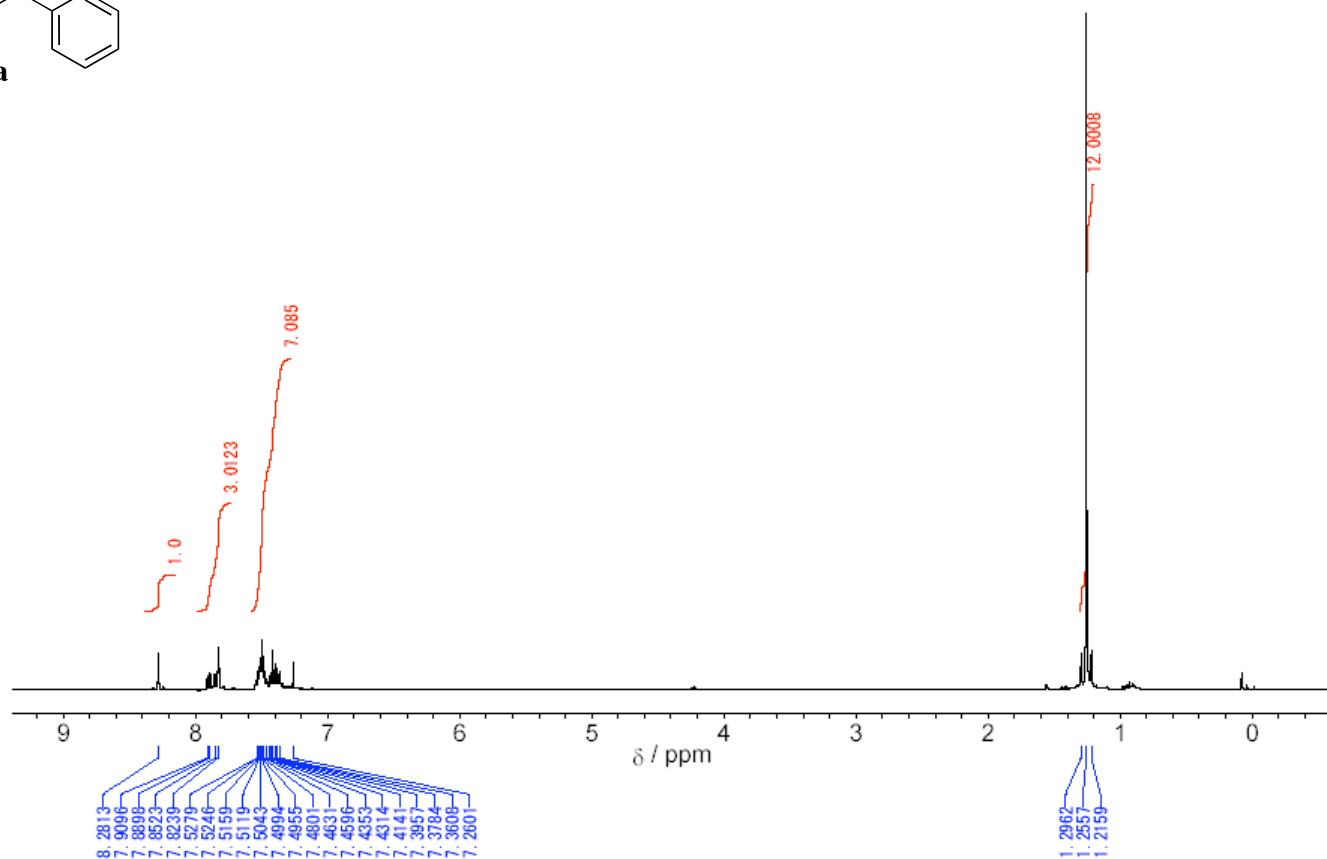


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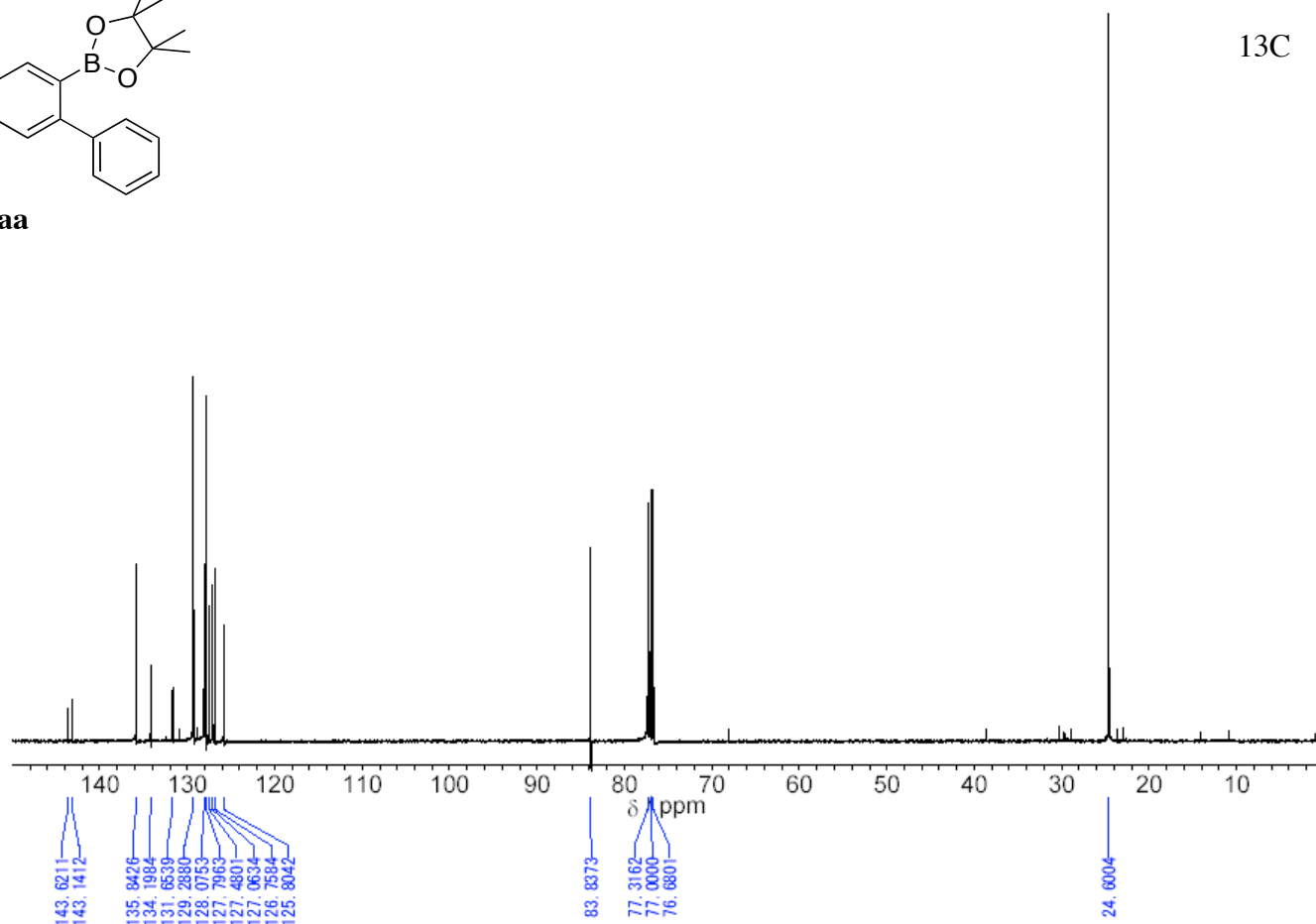


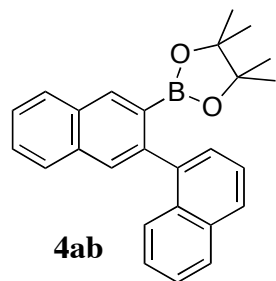


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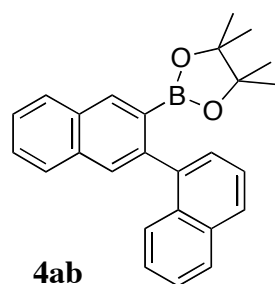
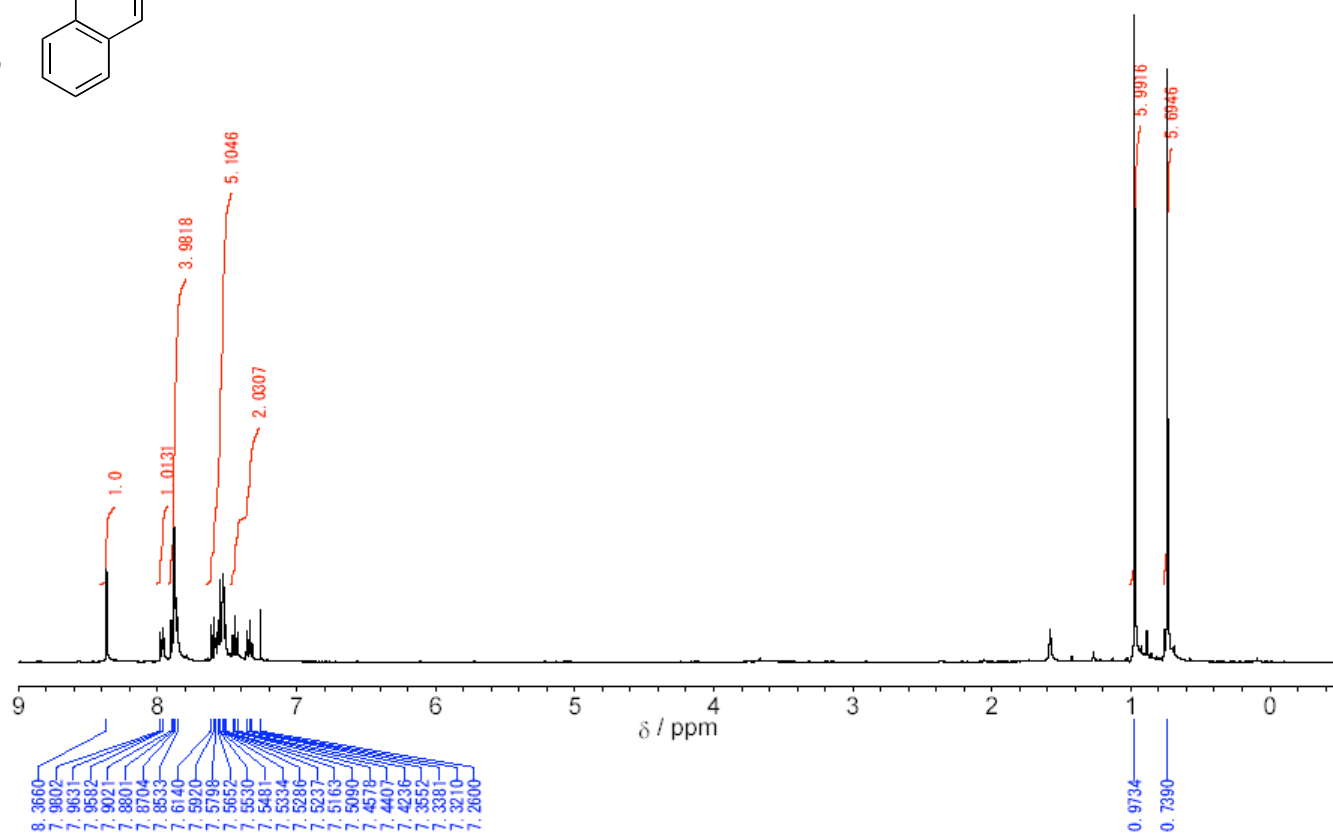


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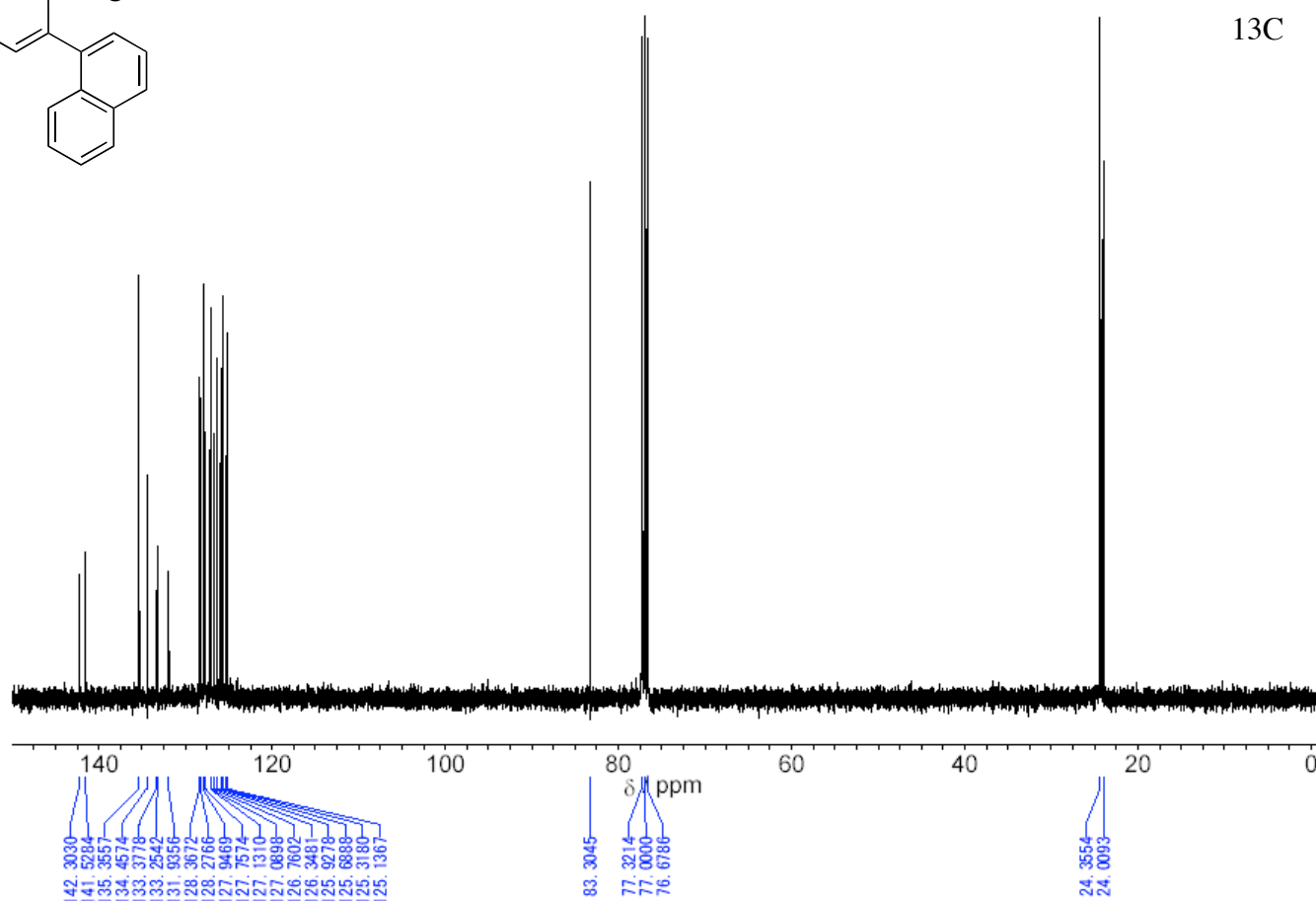


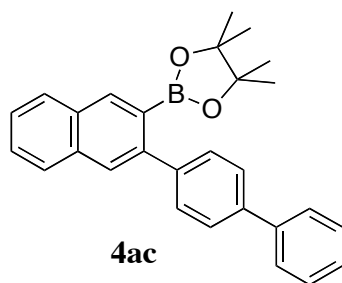


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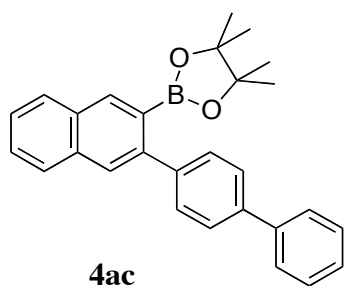
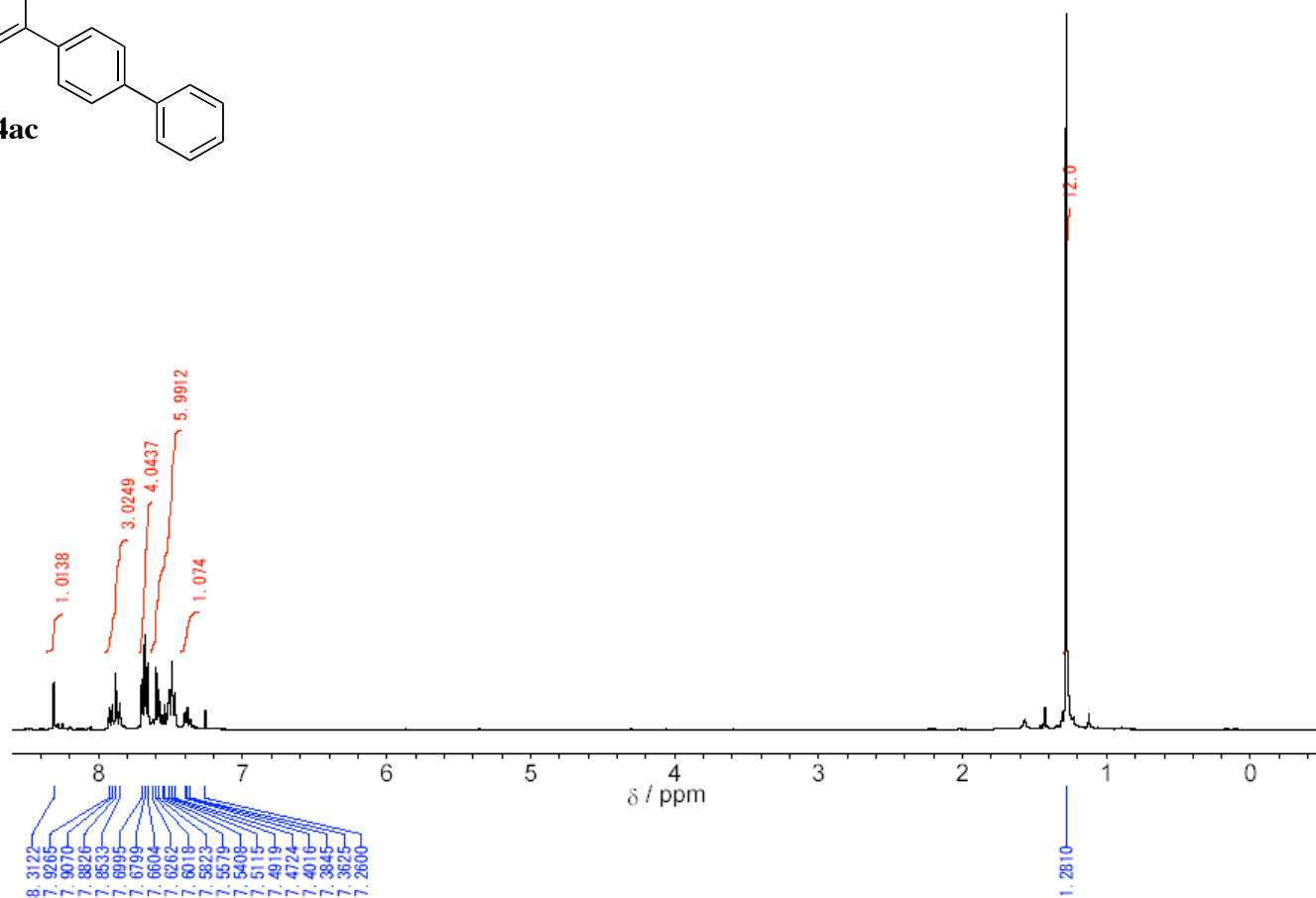


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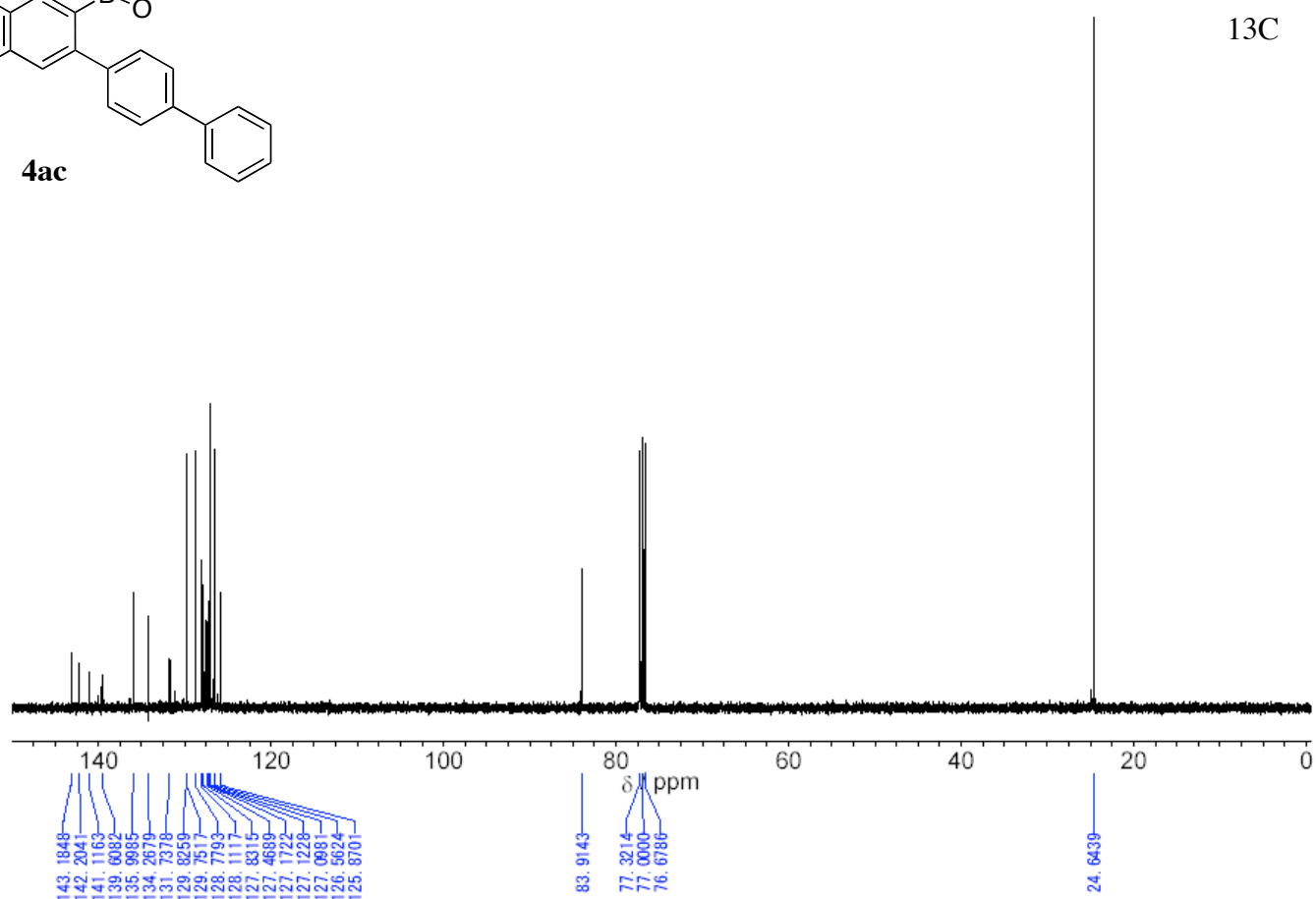


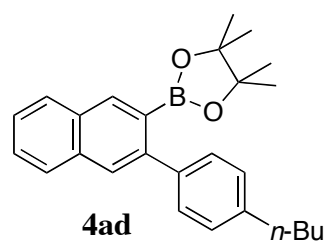


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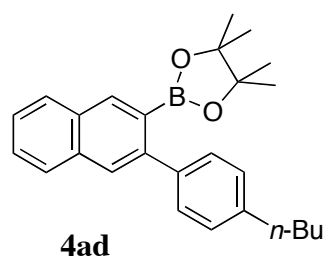
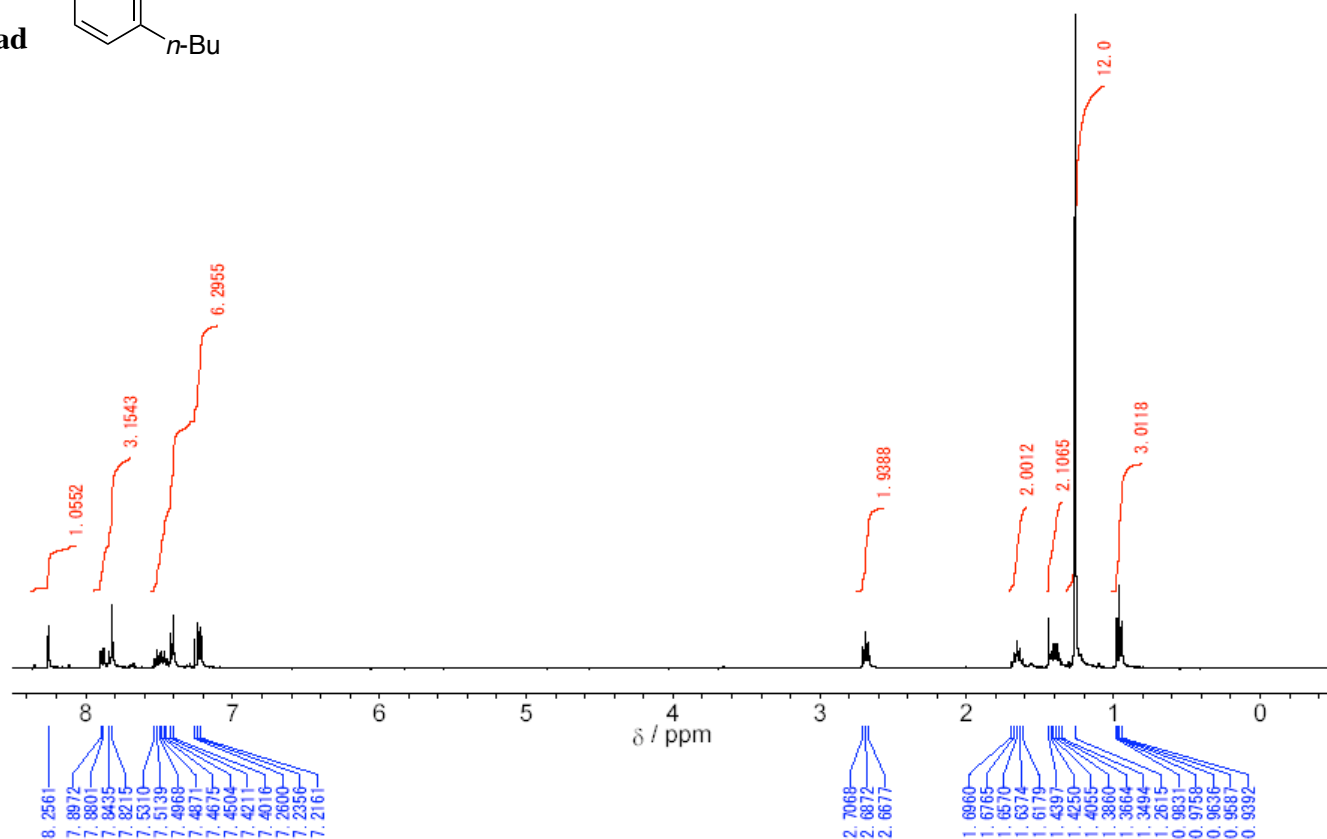


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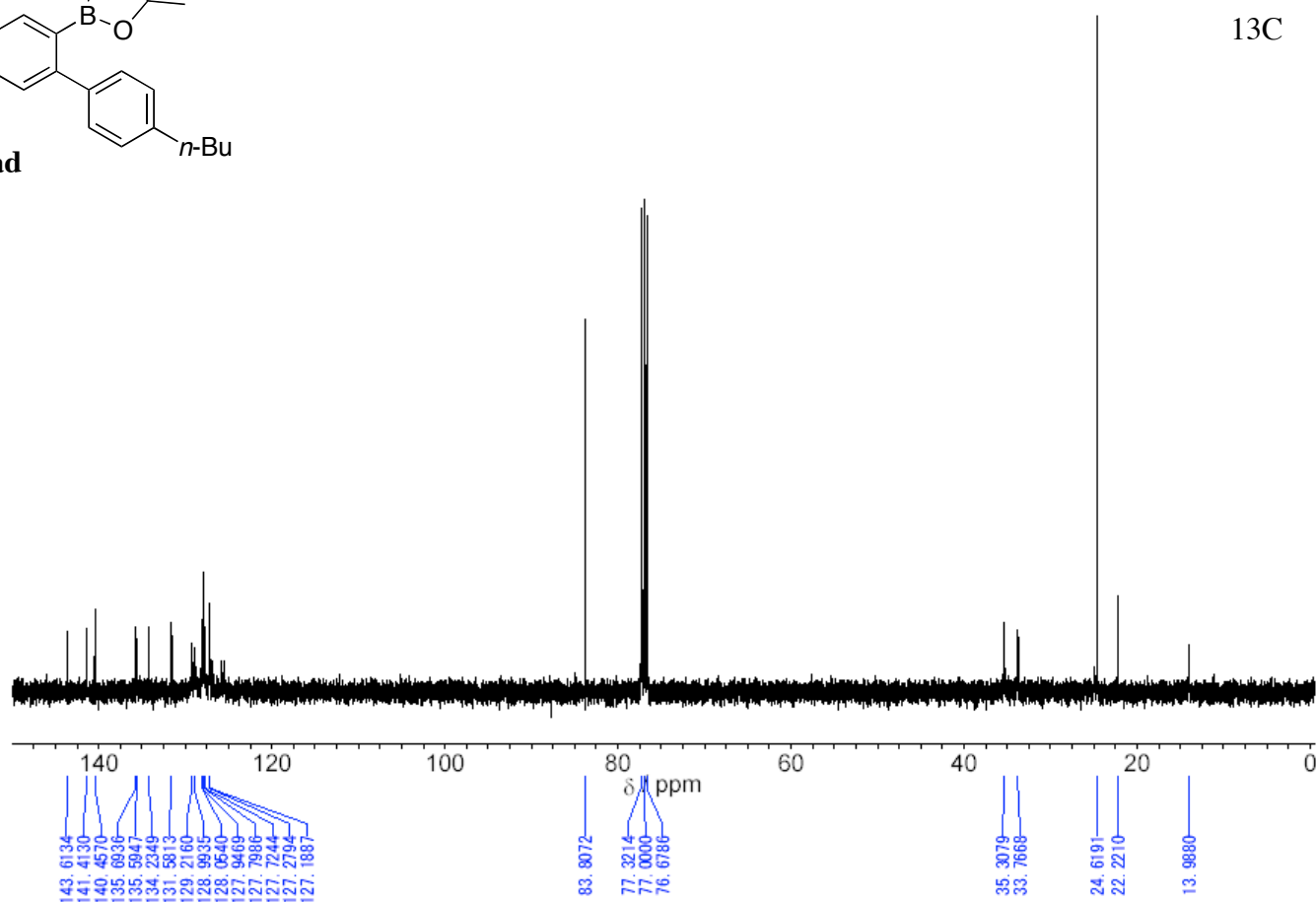


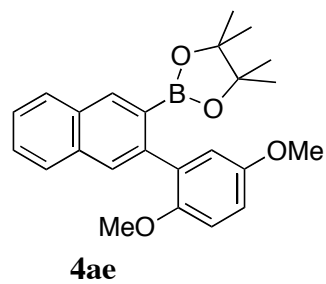


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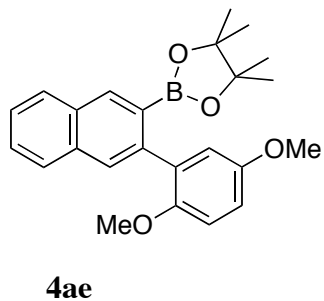
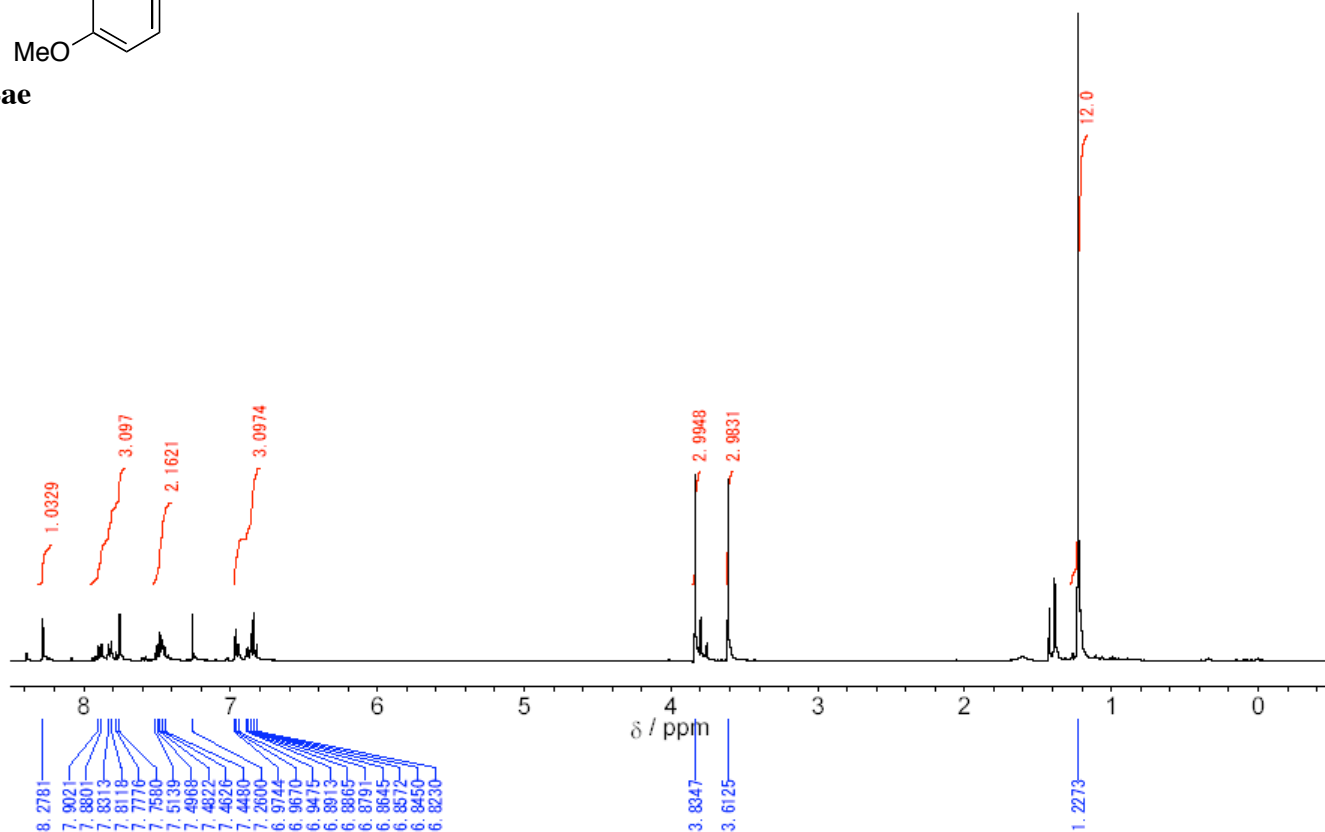


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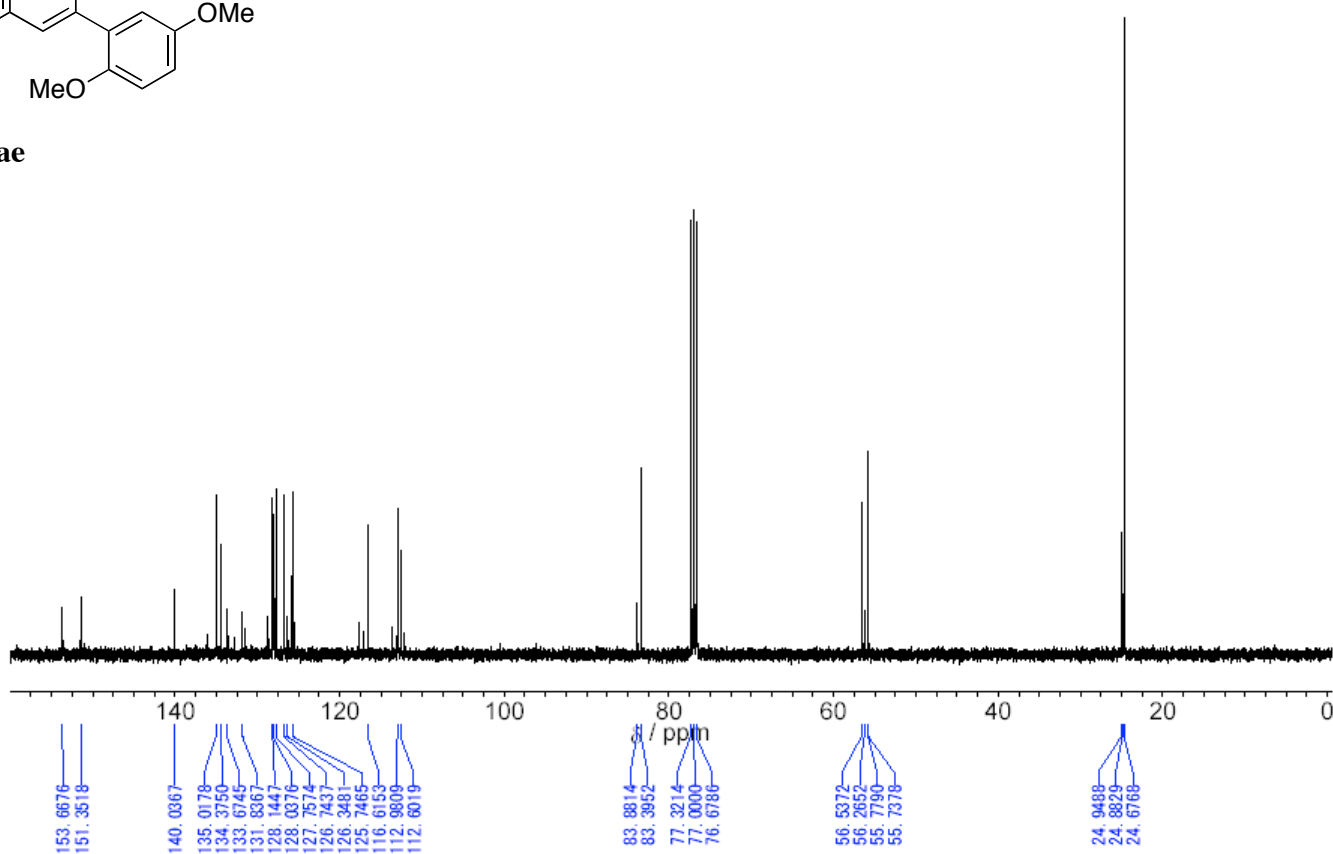


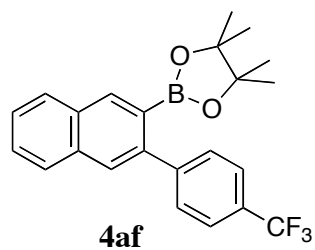


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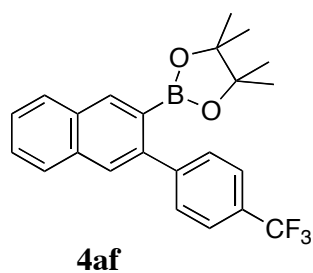
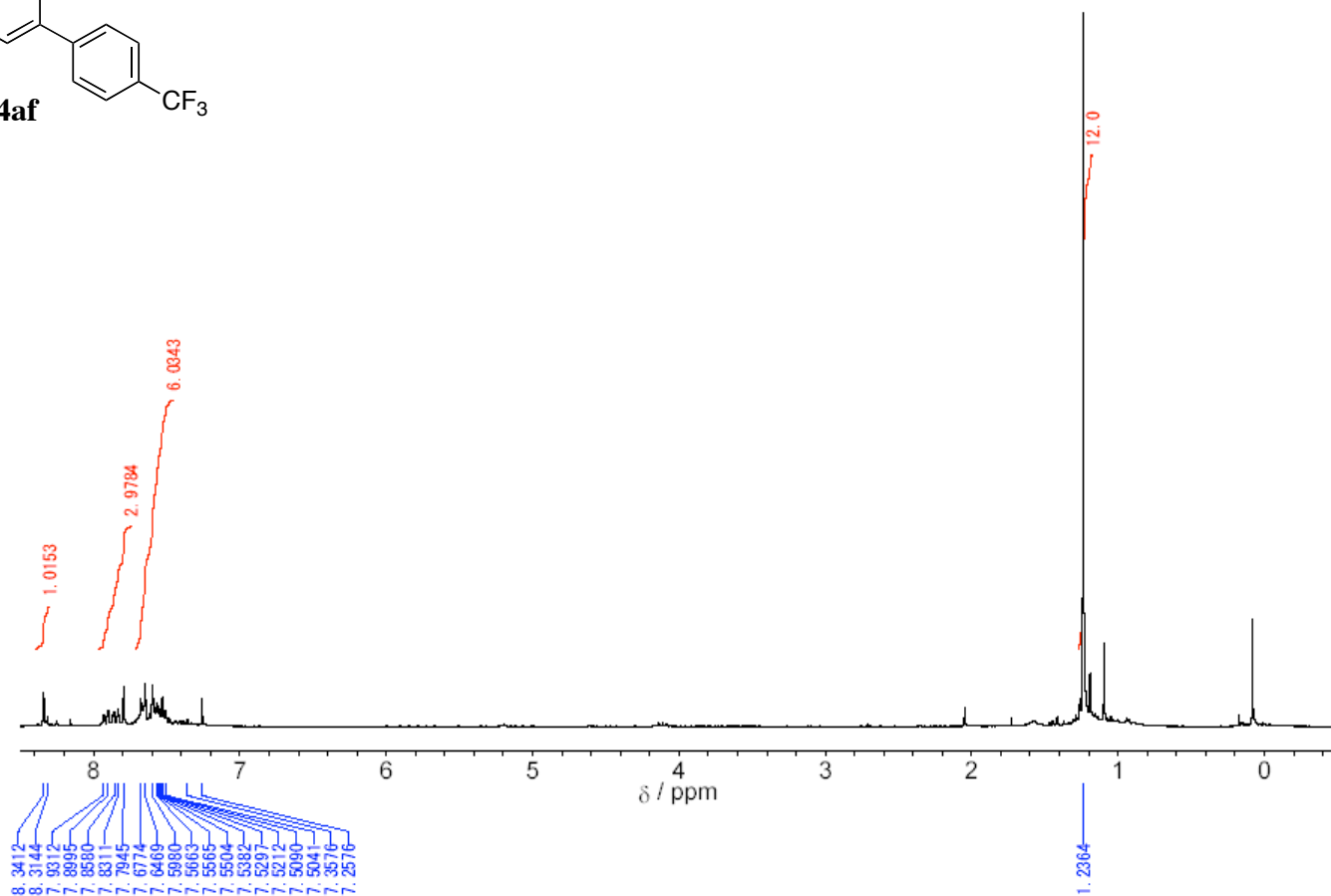


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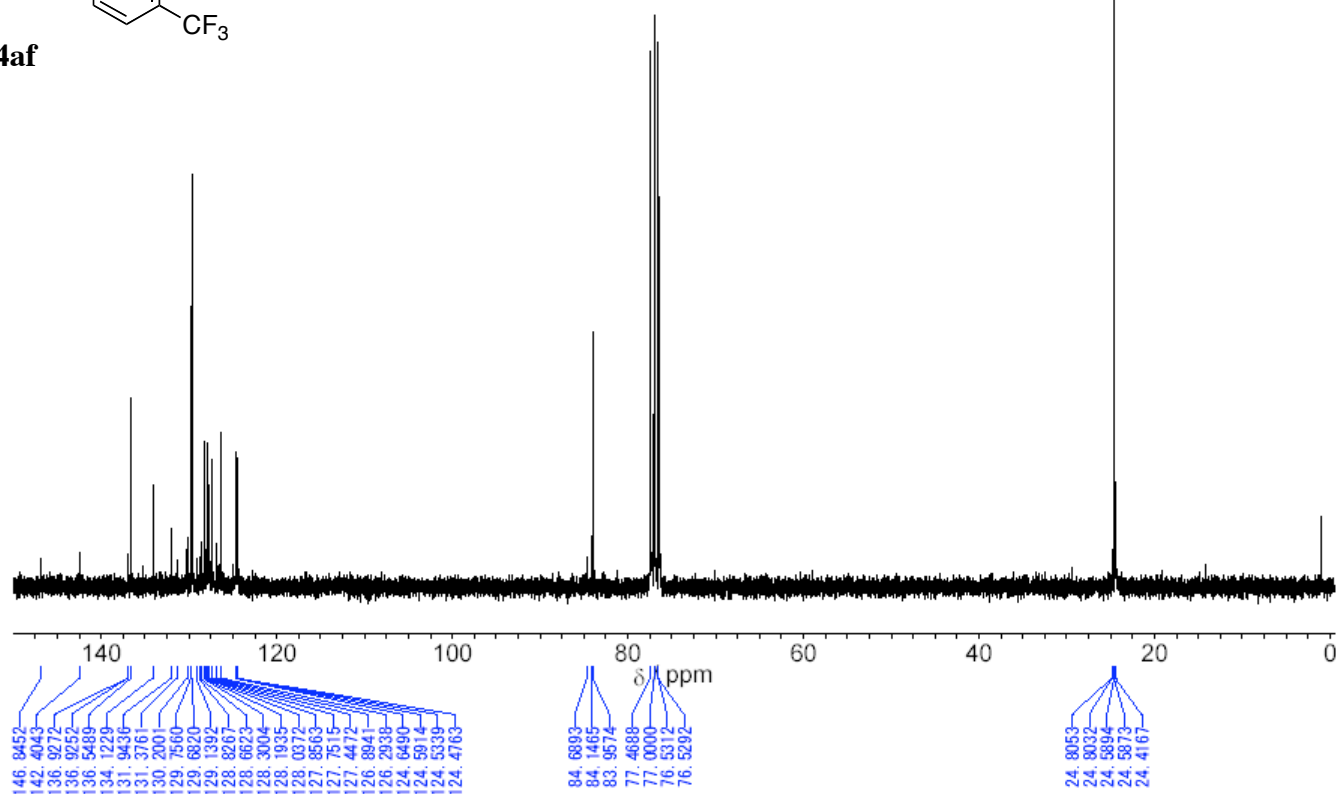


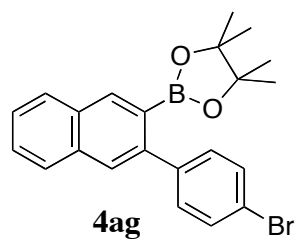


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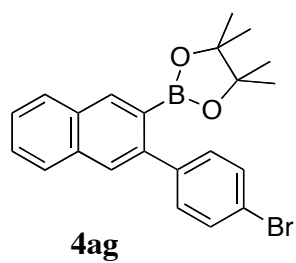
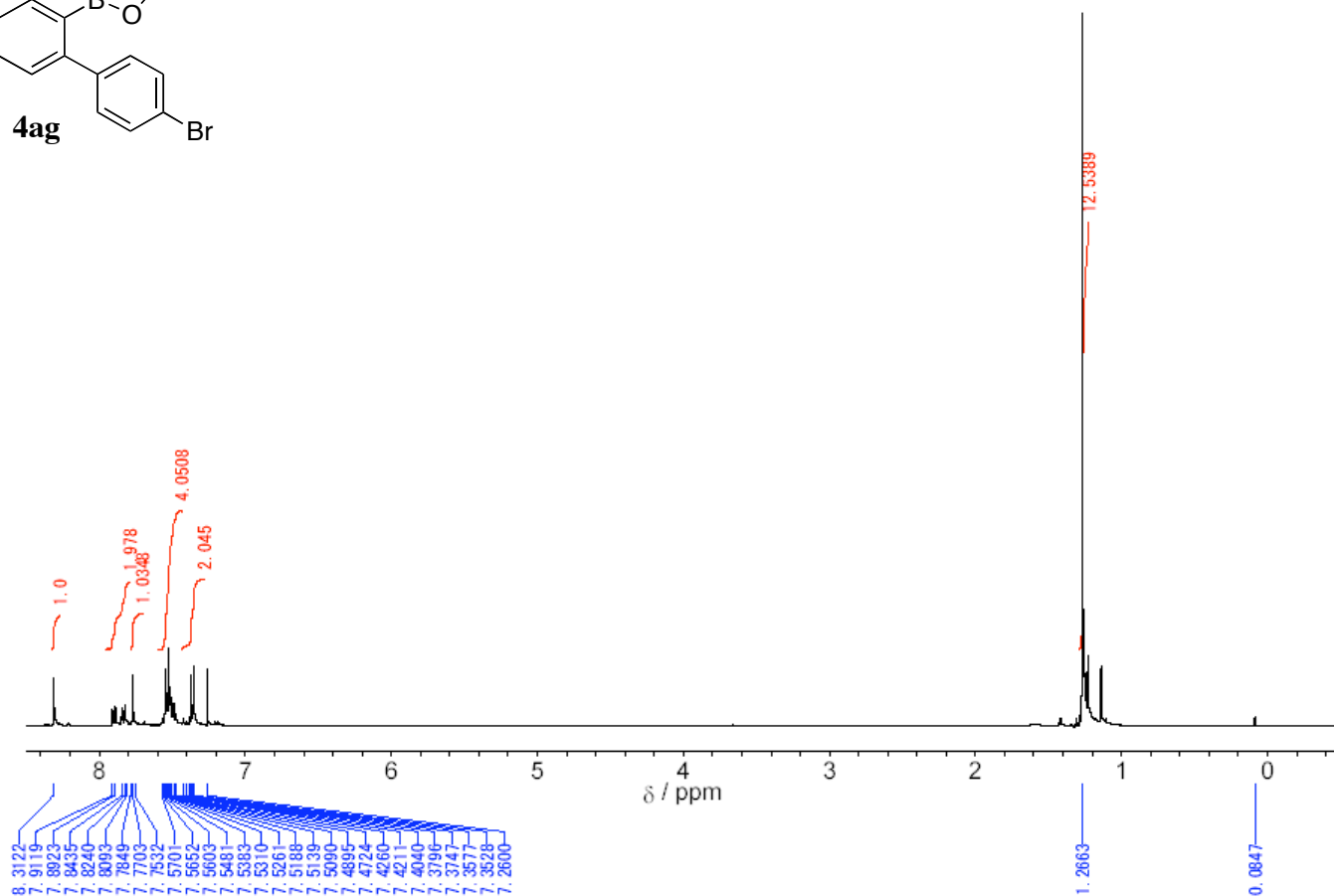


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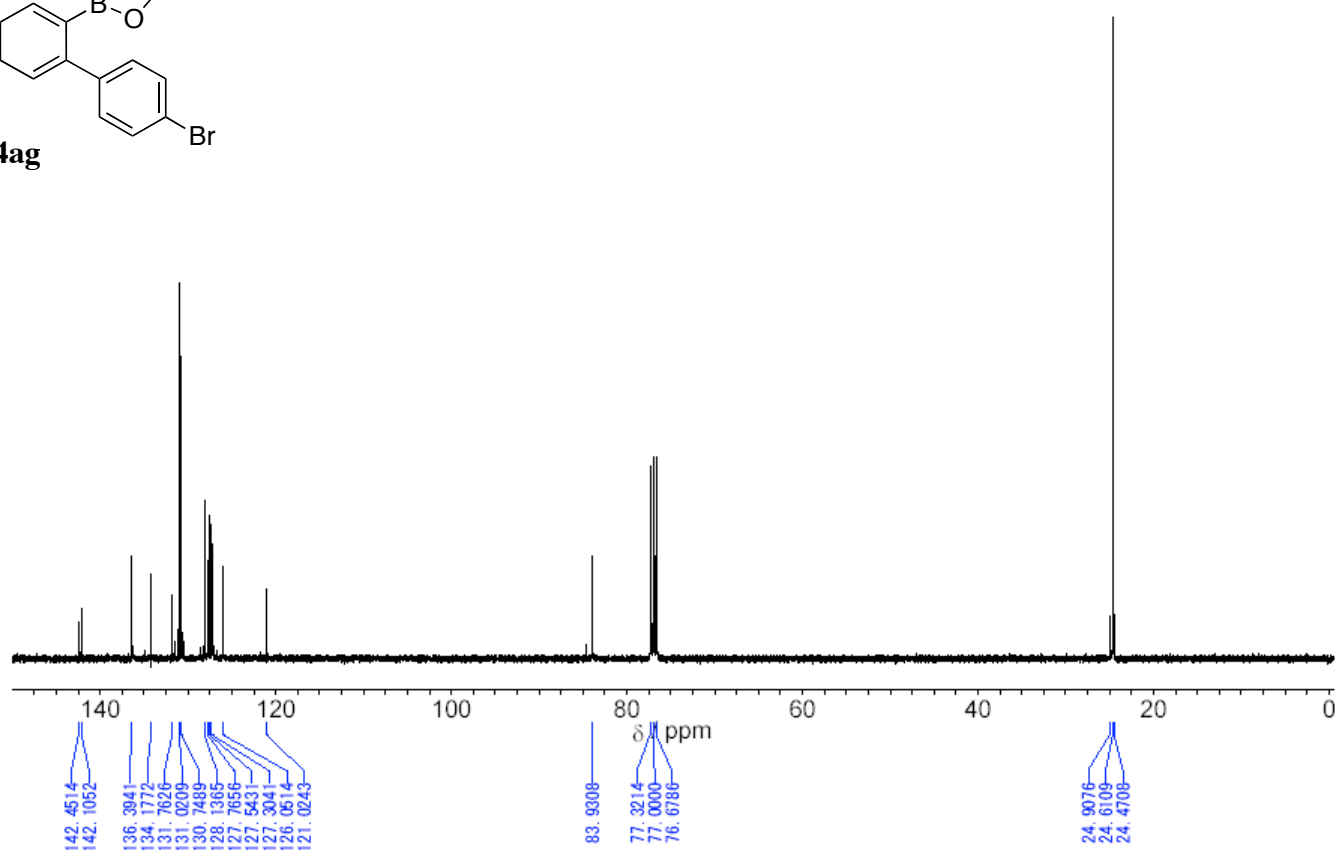


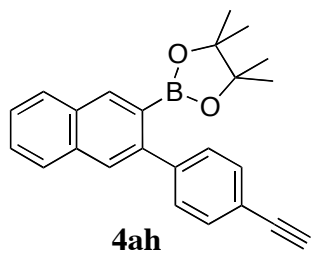


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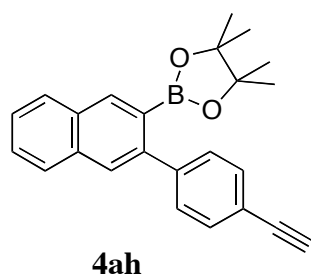
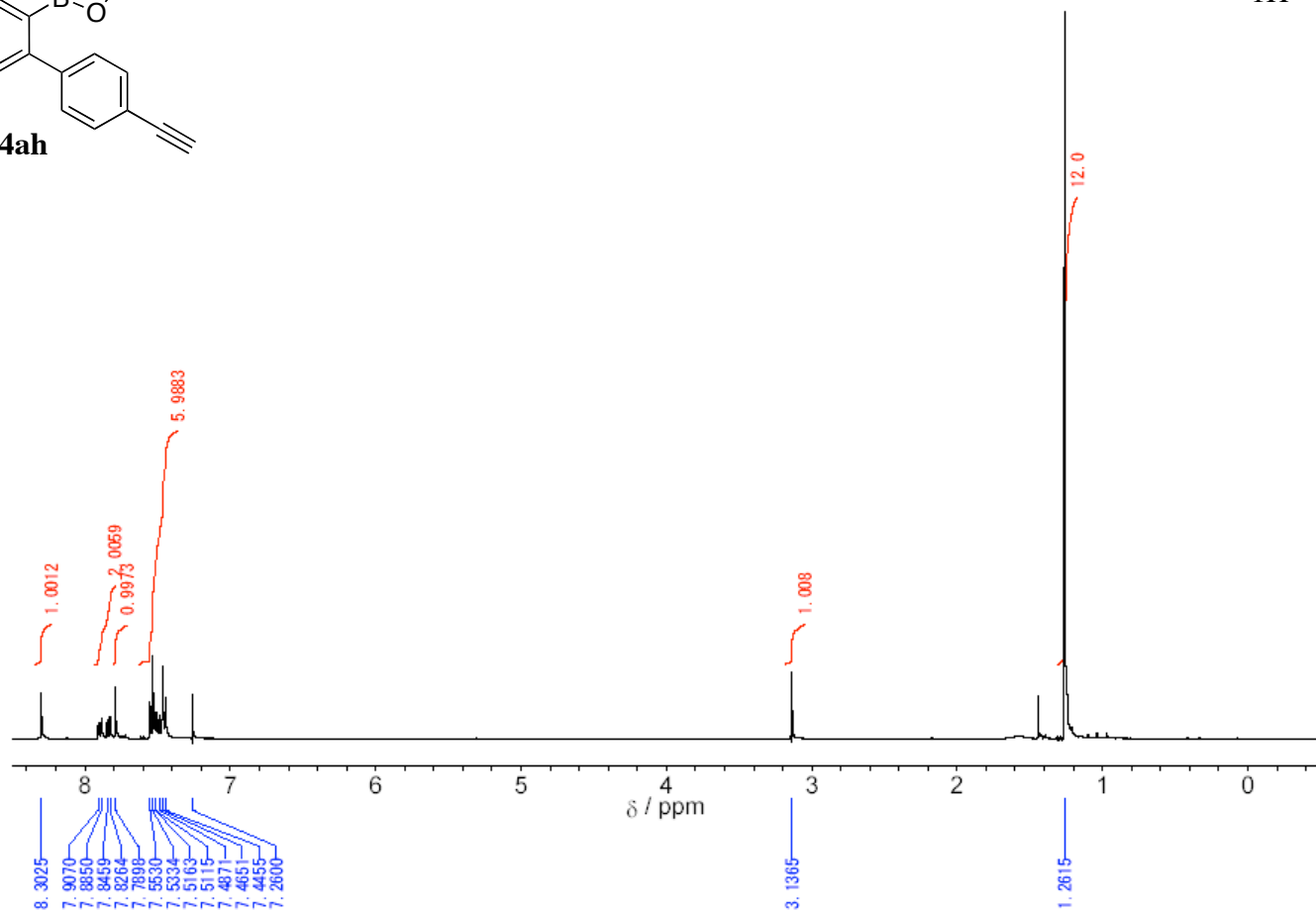


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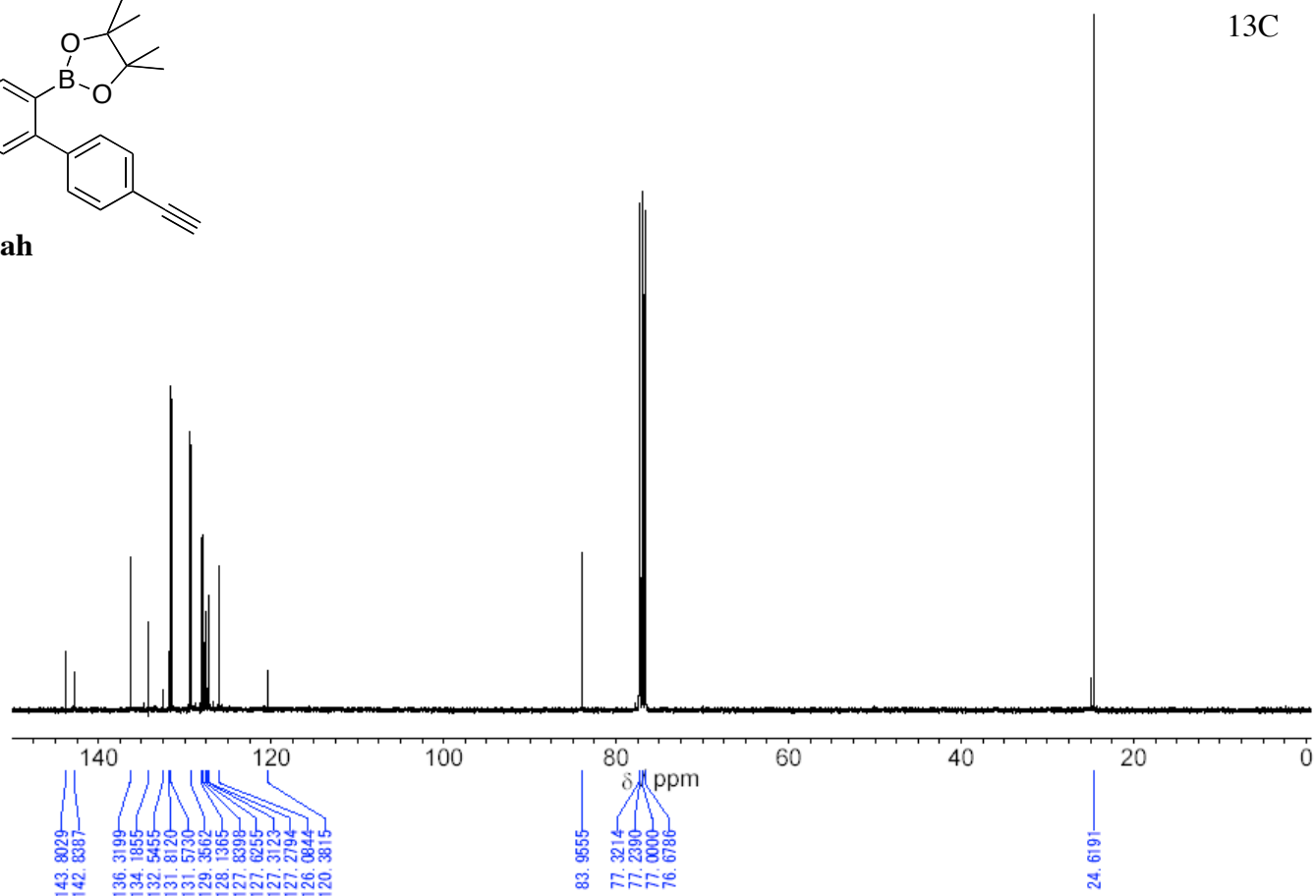


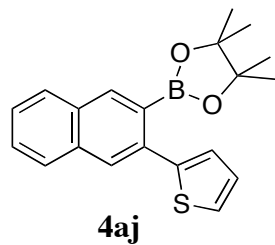


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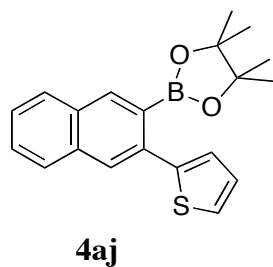
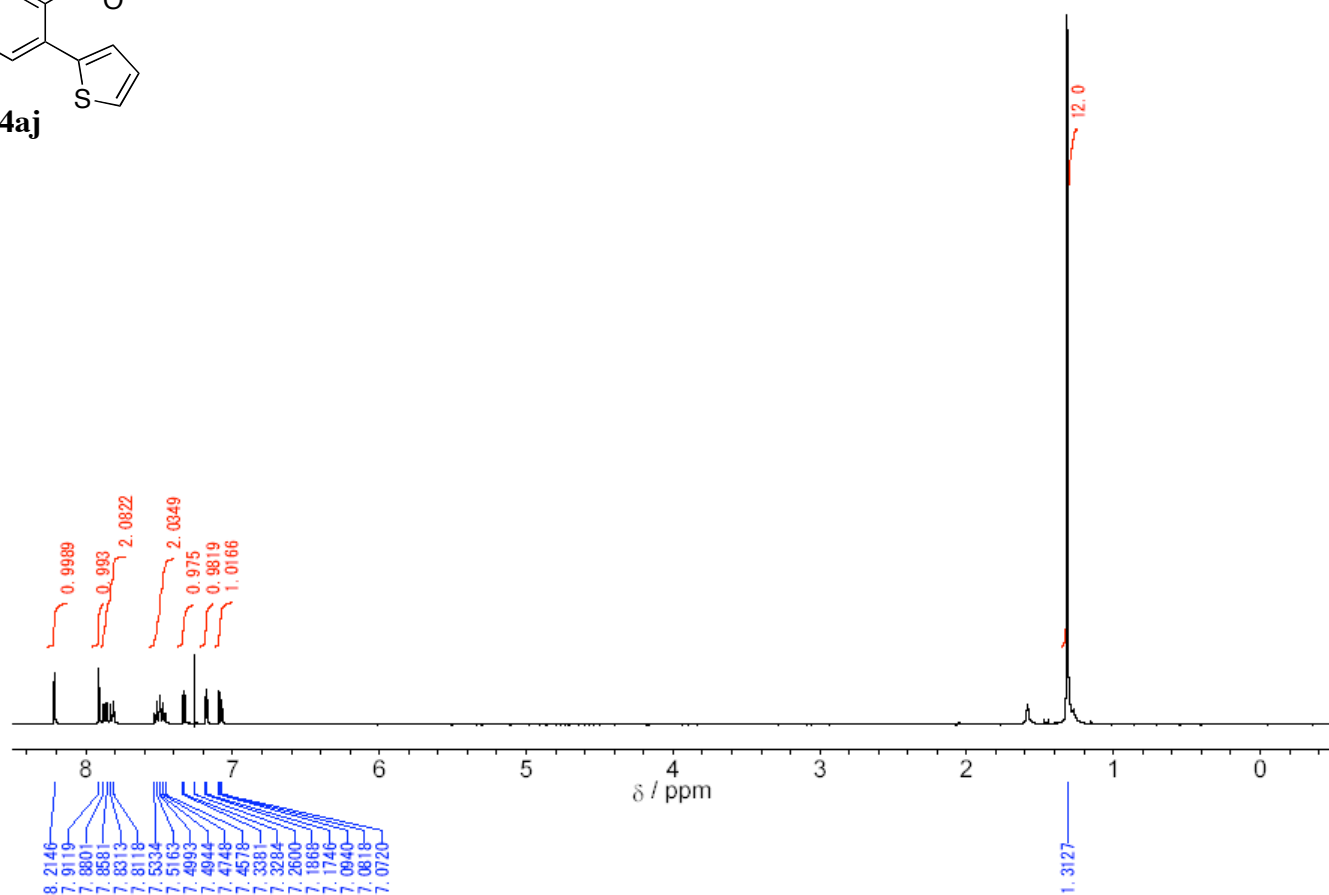


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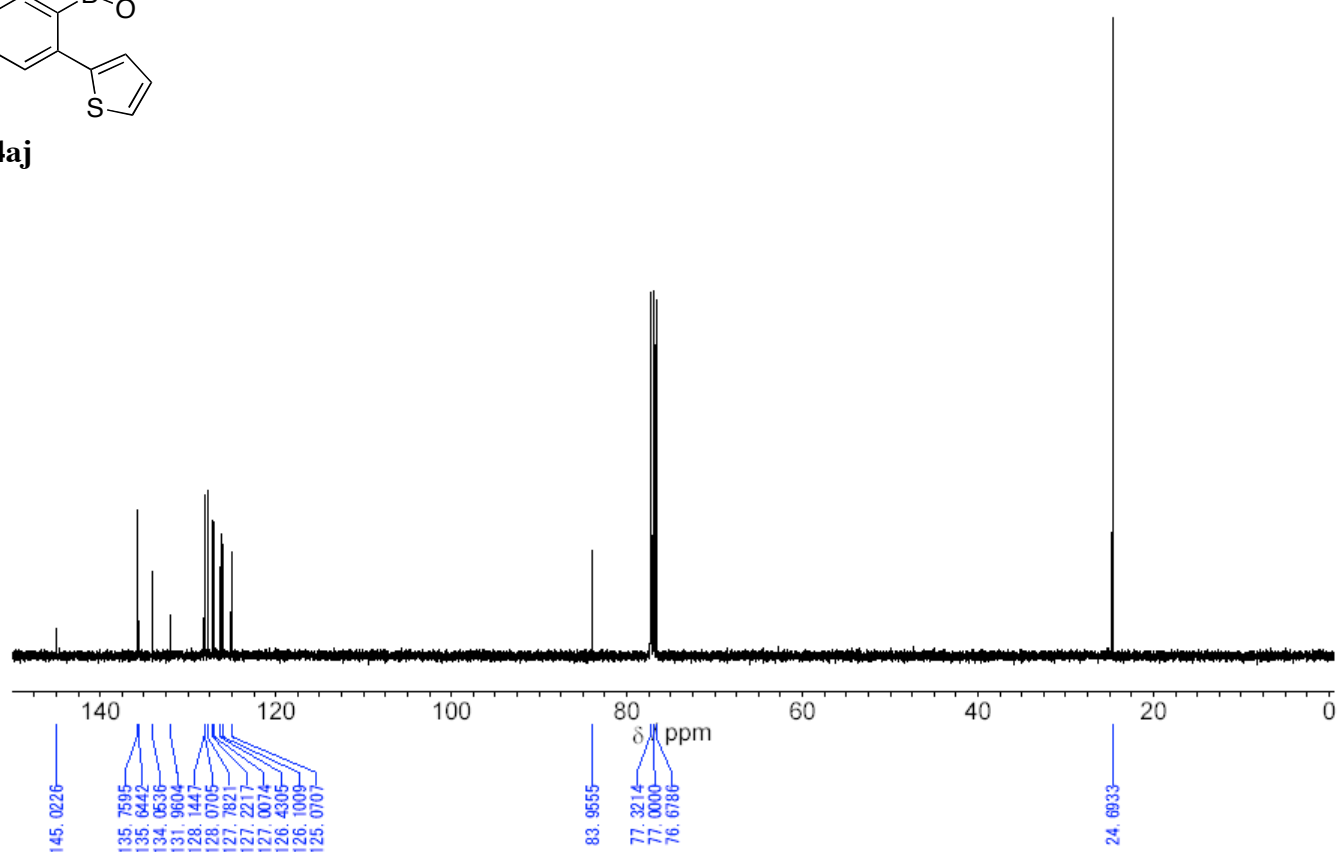


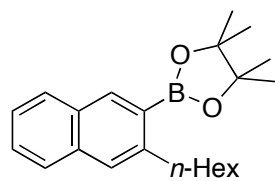


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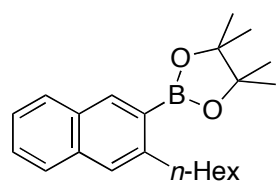
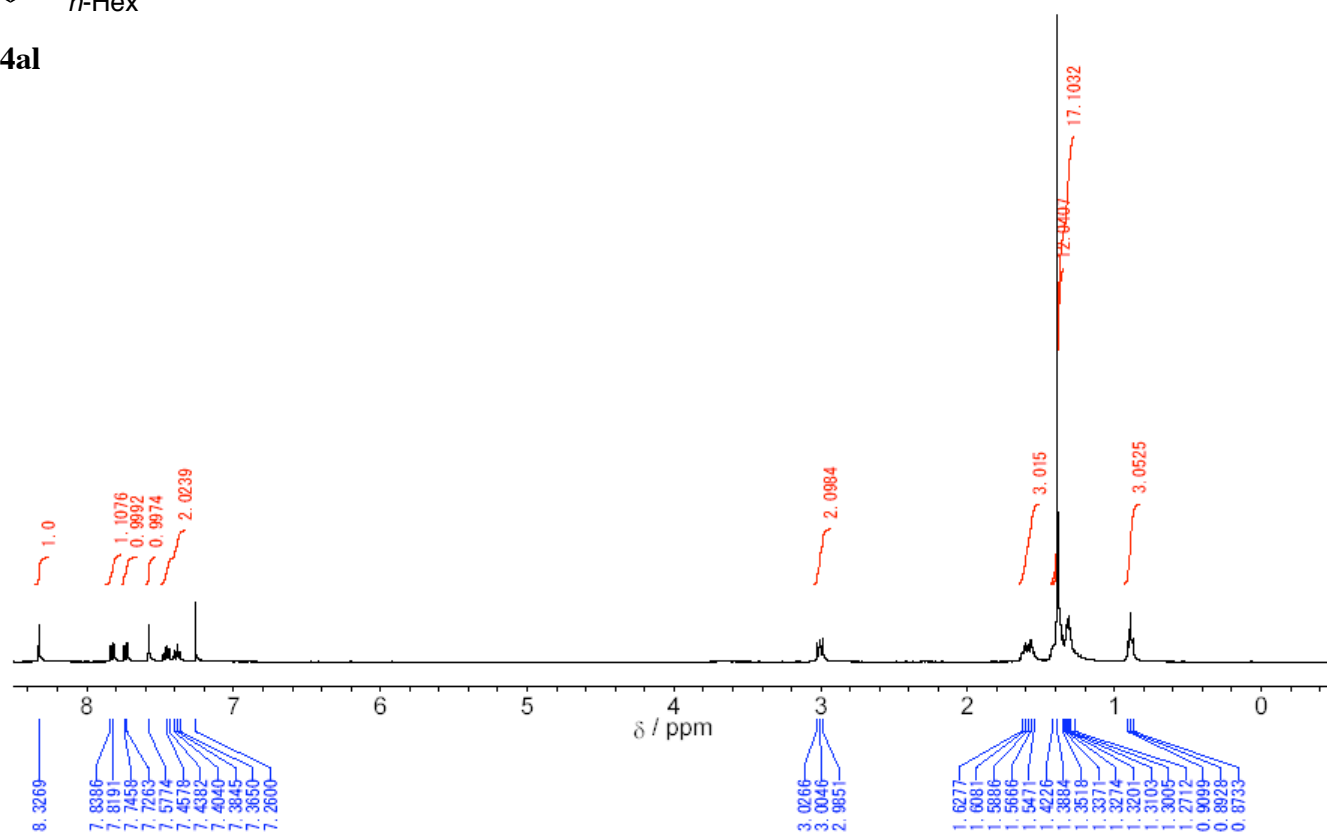


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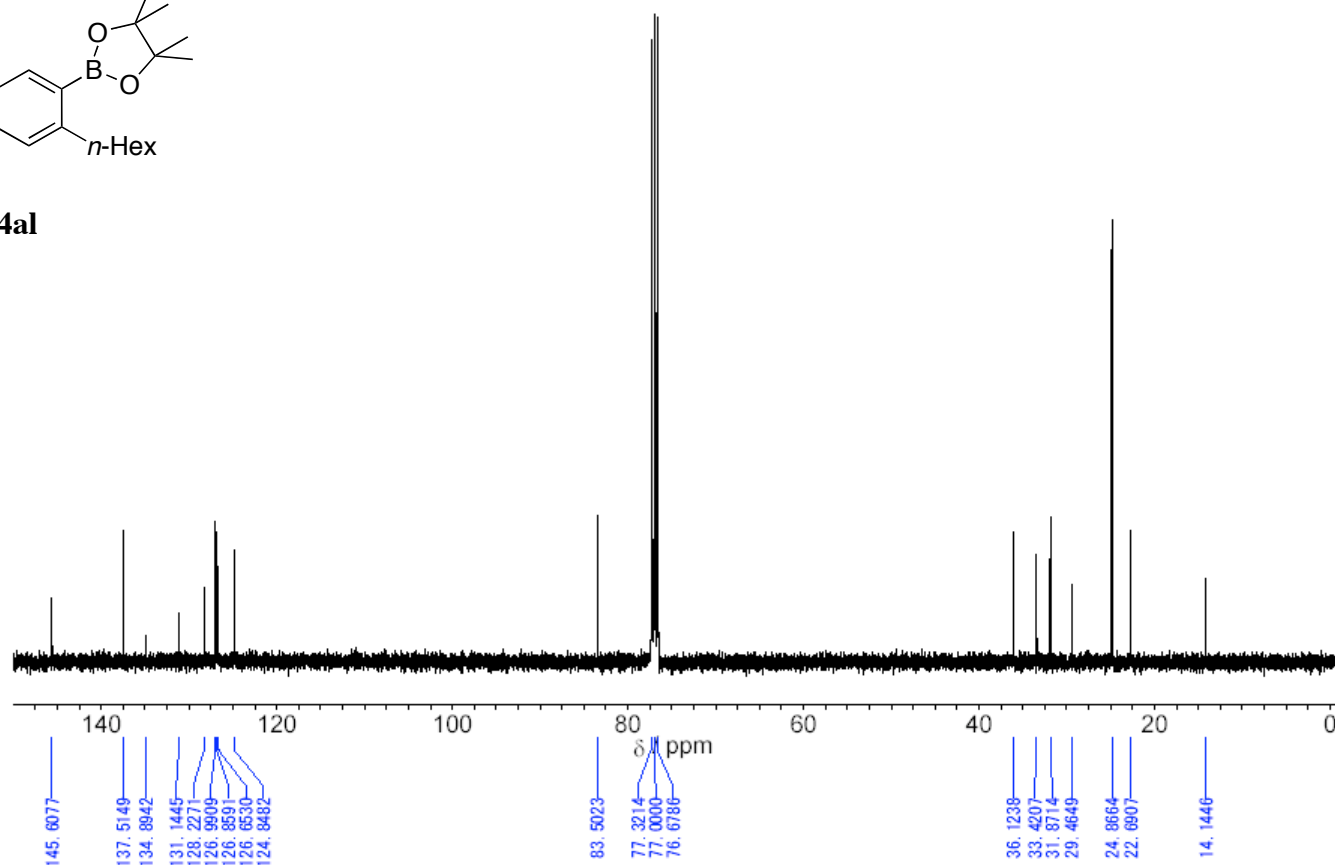


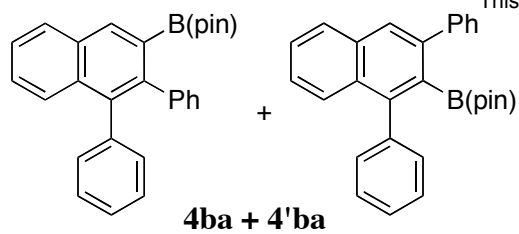


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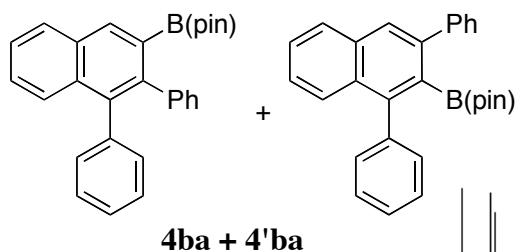
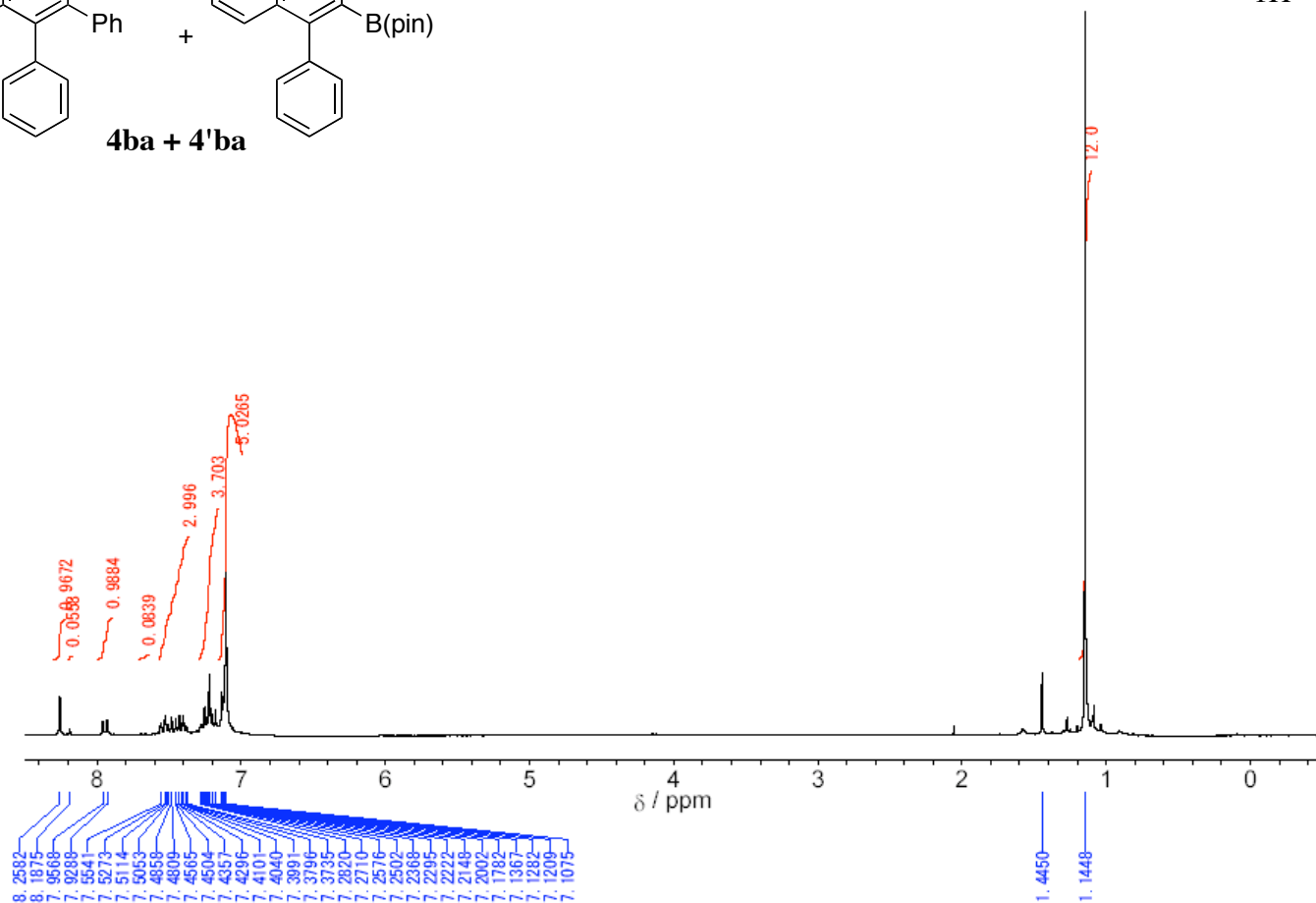


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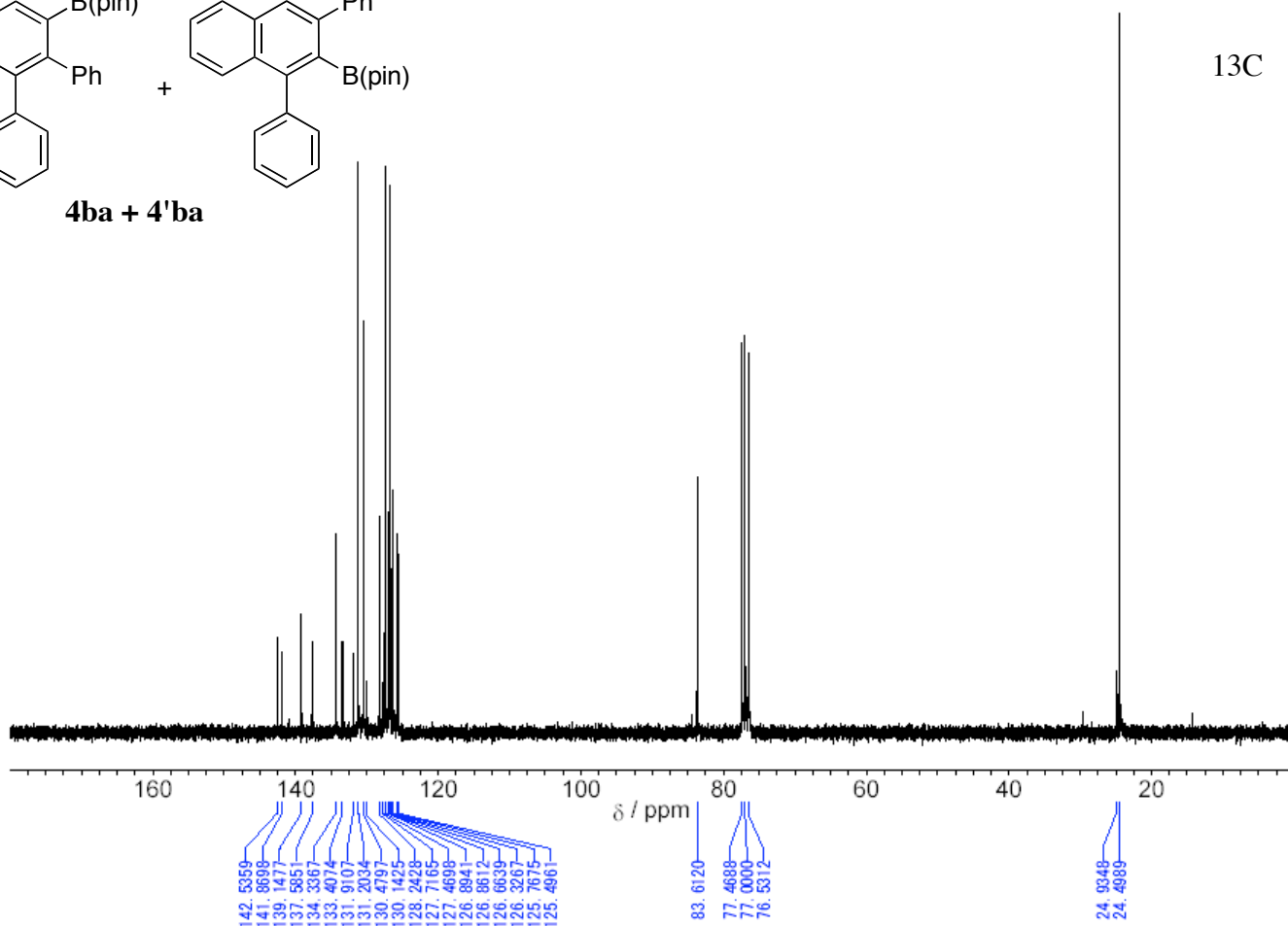


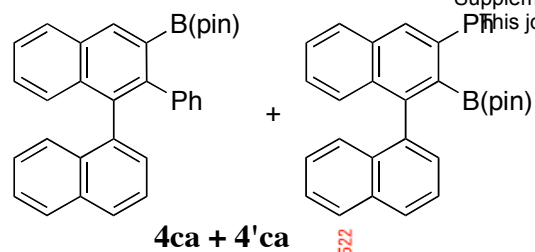


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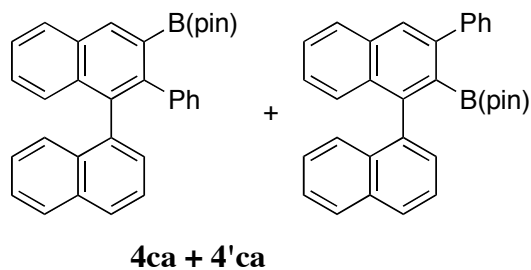
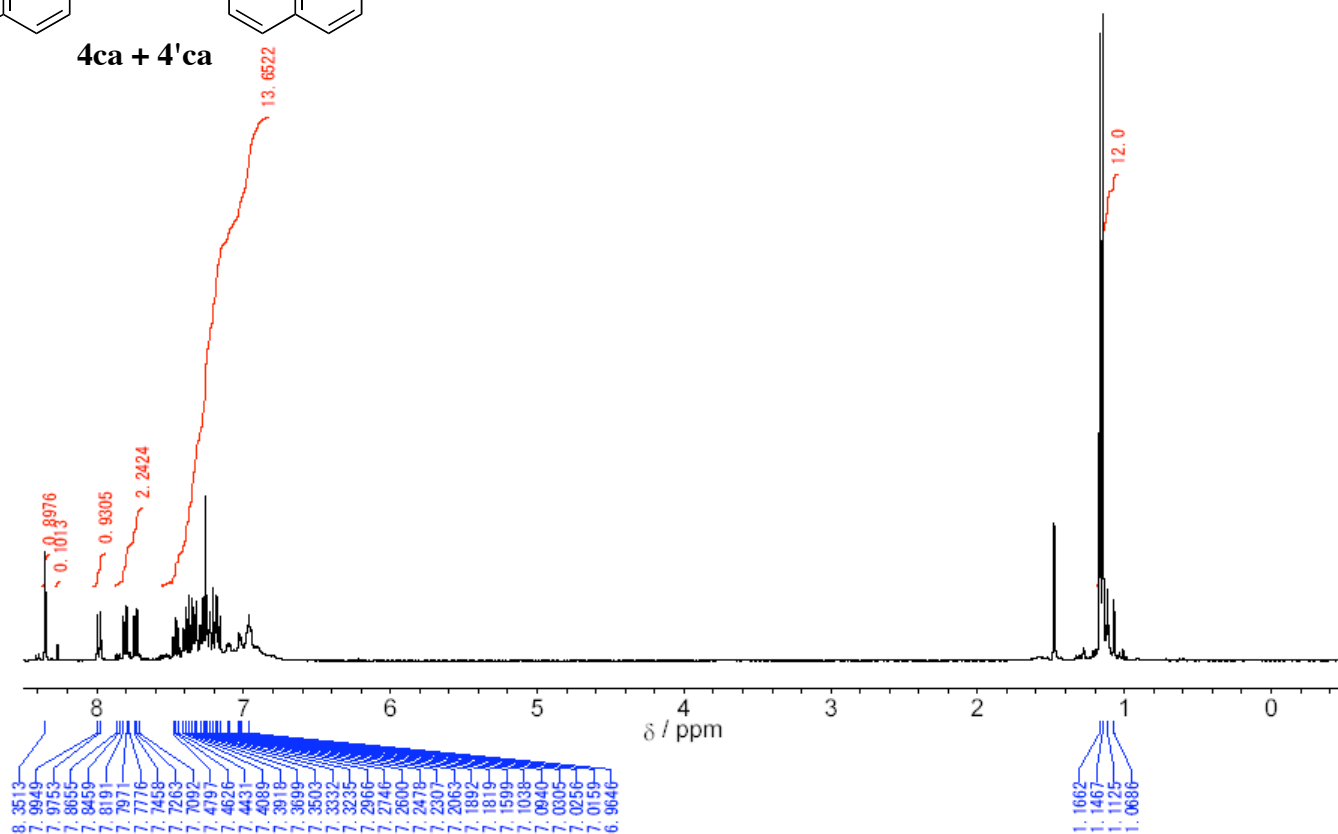


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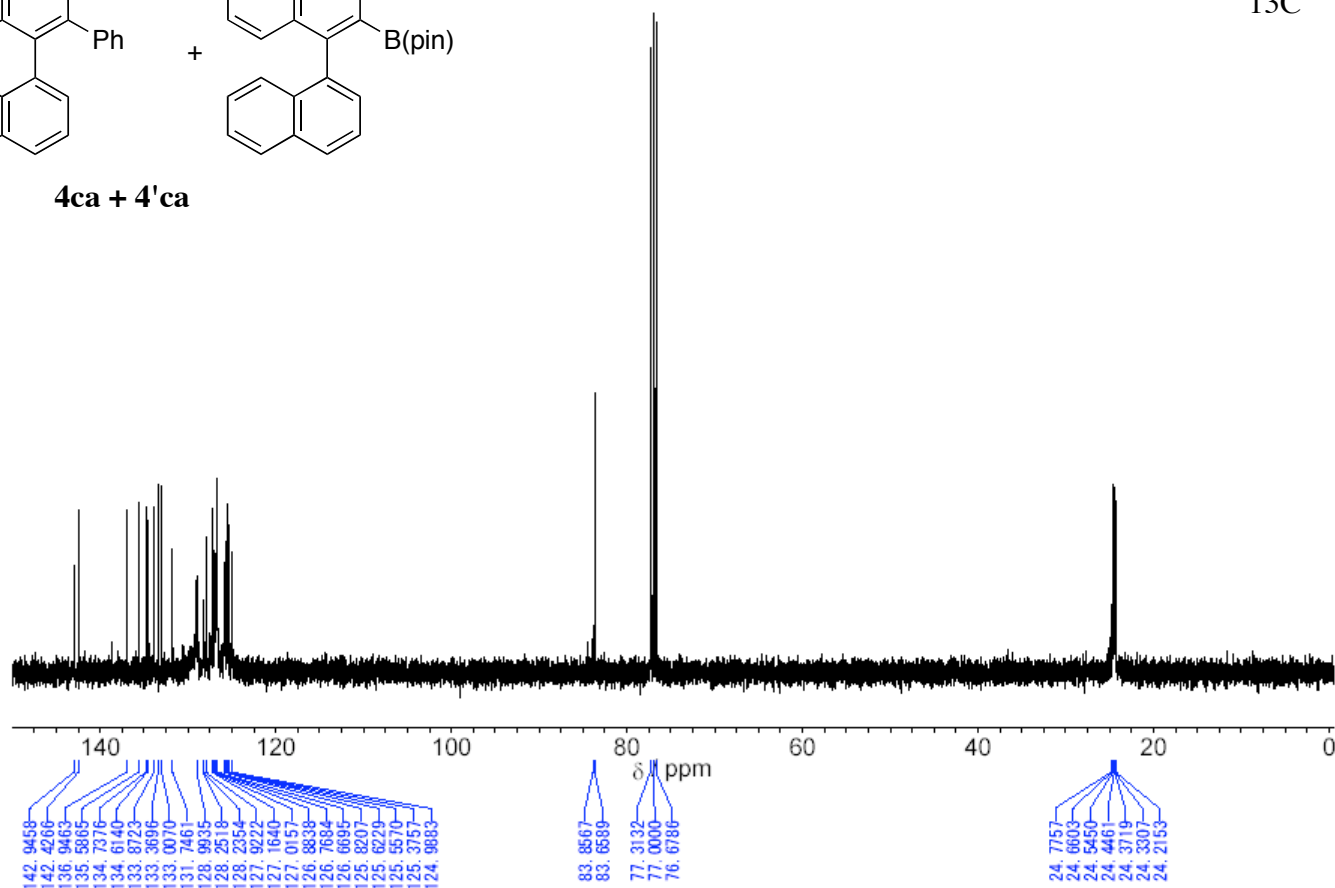


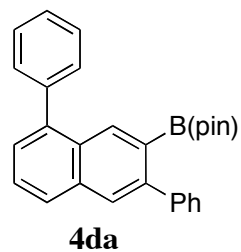


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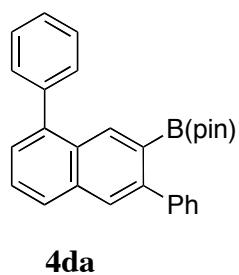
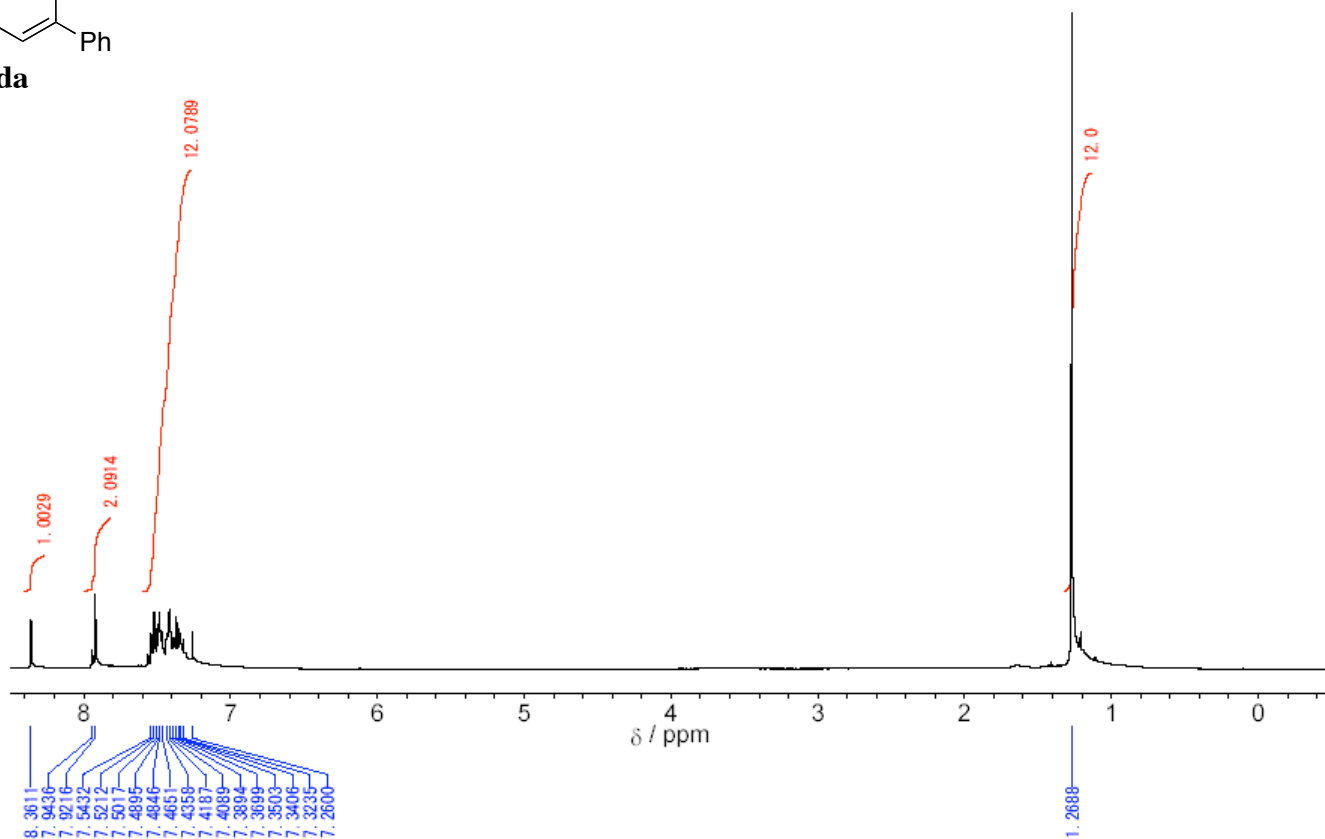


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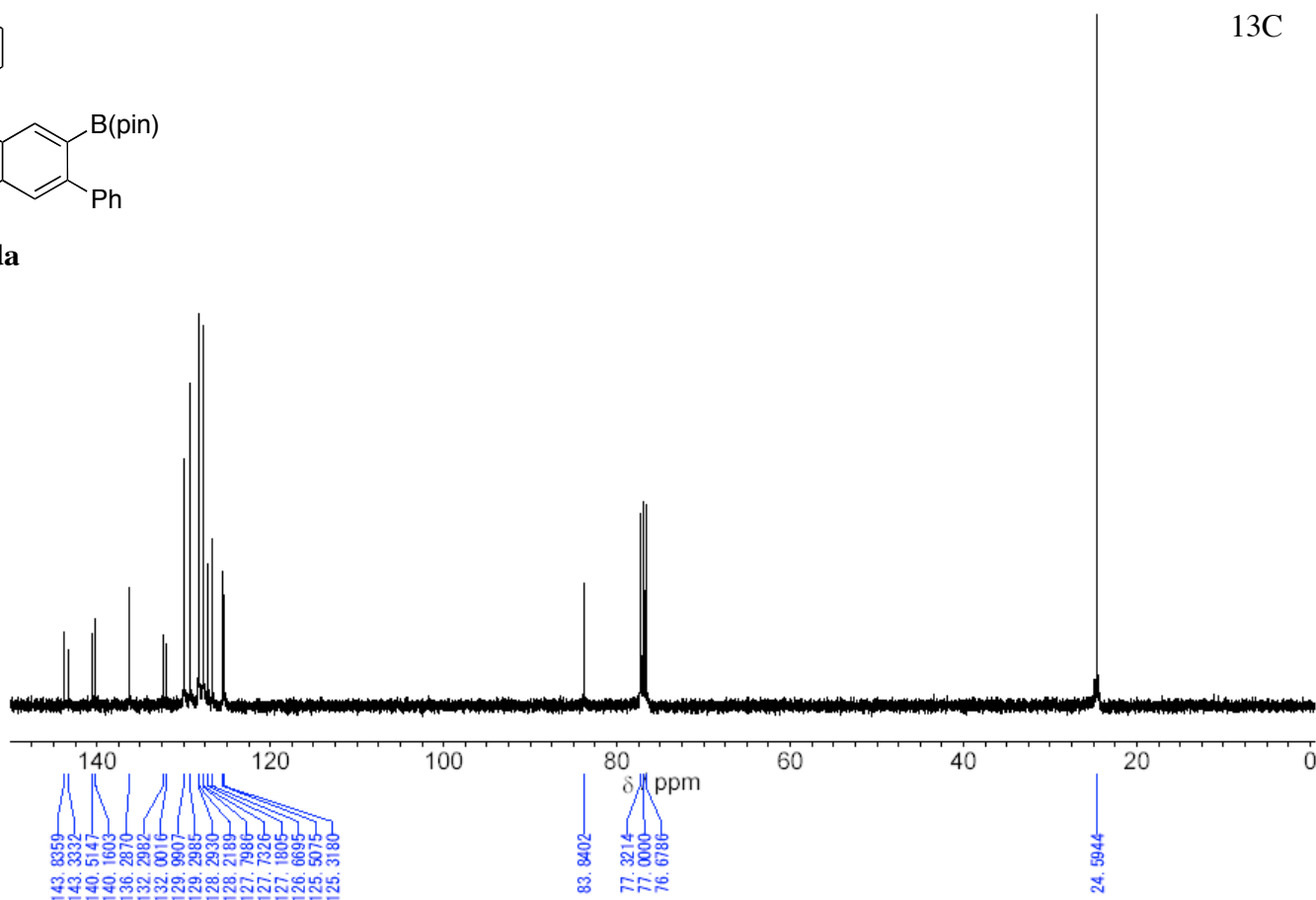


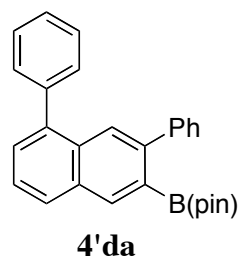


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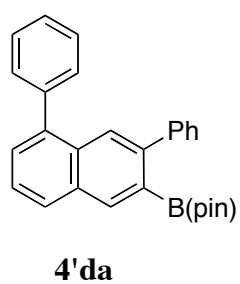
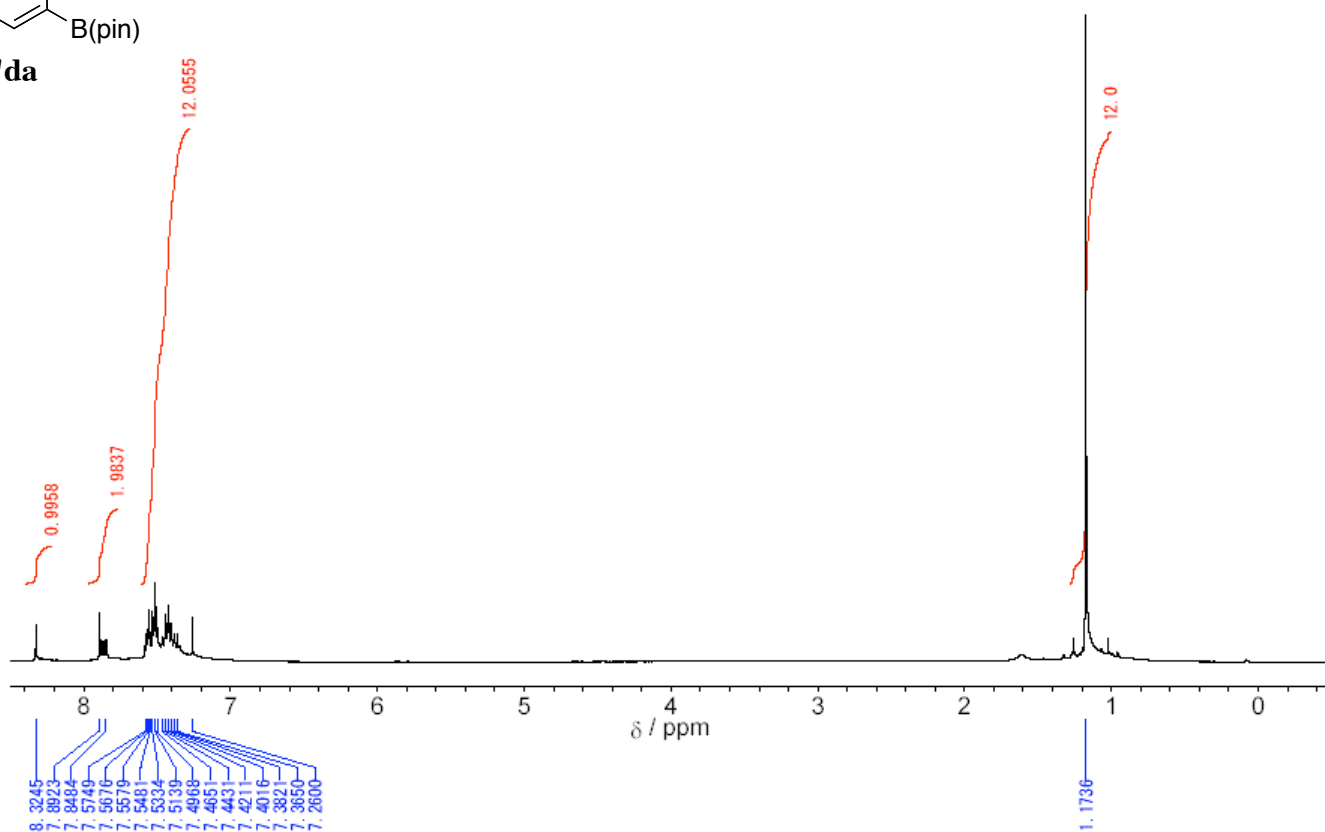


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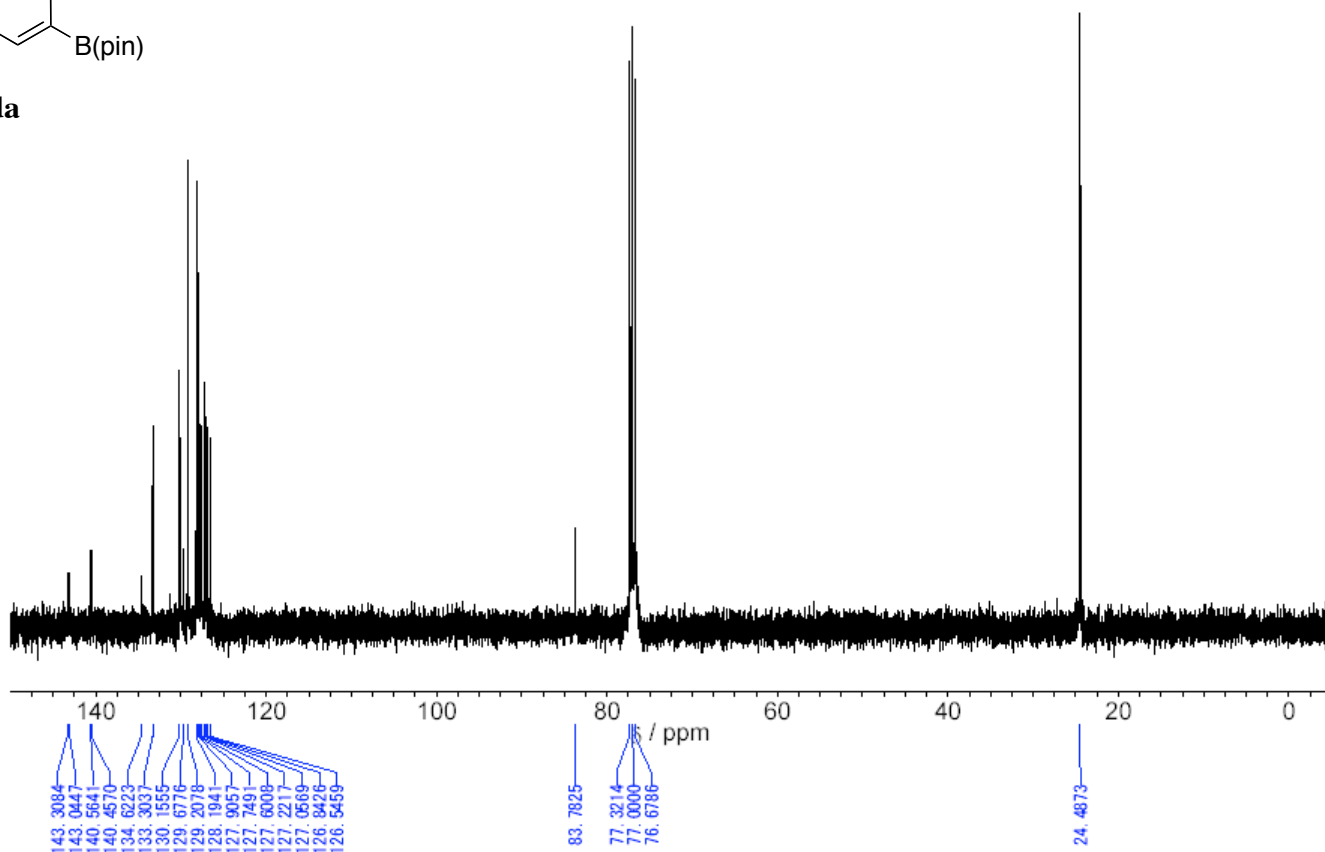


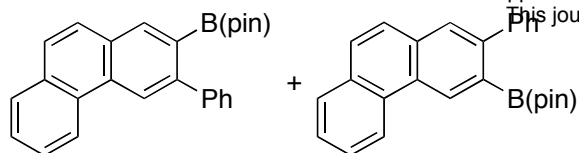


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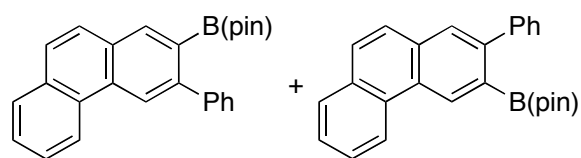
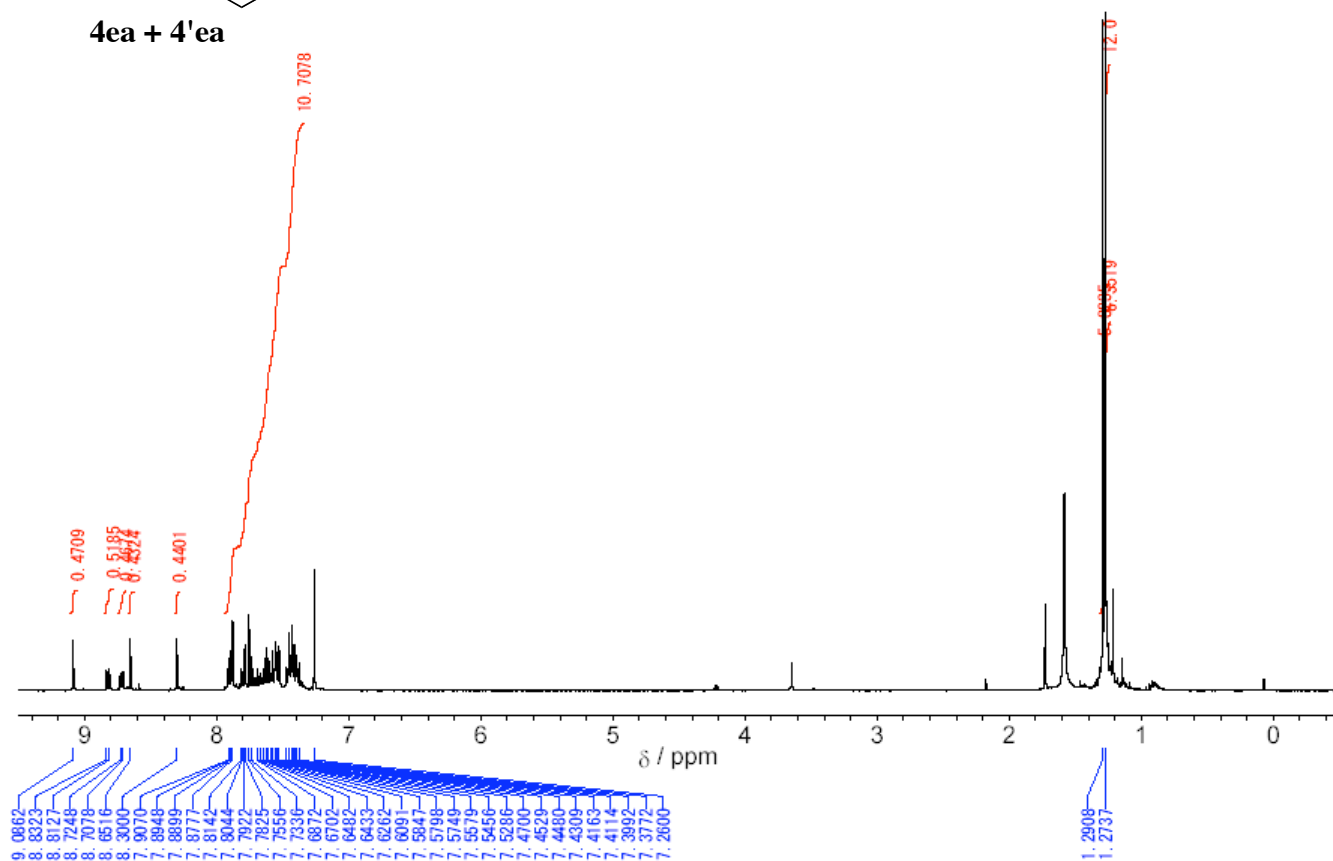
¹³C





4ea + 4'ea

¹H



4ea + 4'ea

¹³C

