Supplementary Information (SI) for Catalysis Science & Technology.

Supplementary Information

A swift and efficient approach to boron-functionalized scaffolds: Borylation of alkenes and alkynes using a carbon nanotube-copper ferrite catalyst

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1. General Remarks

Unless otherwise stated, all reactions were carried out under air. Starting materials, when not synthesized, were purchased from commercial suppliers (Merck, Sigma Aldrich) and used as received unless otherwise stated. Multi-wall carbon nanotubes were synthesized by catalytic decomposition of methane on Ni-Mg-O catalyst[1] and purified by acidic treatment. Reaction concentrations are expressed in molar (M), calculated by the ratio of the amount of the main reactant (limiting agent) in mmol and the volume of solvent applied, in mL. Yields refer to isolated compounds estimated to be > 95% pure as determined by ^{1}H-NMR. Thin layer chromatography analyses (TLC) were performed on Merck TLC Silica Gel 60 F_{254} revealed under UV light or by treatment with a solution of potassium permanganate in ethanol followed by heating. Chromatographic separations were carried out on Aldrich brand silica gel 60 (230-240 mesh). Organic solutions were concentrated by rotary evaporation at 40 °C. Centrifugations were carried out on PowerSpin™ BX C885 Centrifuge for 5 minutes at 5000 rpm. NMR spectra were recorded on a Bruker Avance DRX 400 spectrometer at 400 MHz (^{1}H) and at 100 MHz (^{13}C) and Avance NEO 600 spectrometer at 600 MHz (^{1}H) and at 150 MHz (^{13}C), employing $CDCl_3$. For the ^{1}H NMR, tetramethylsilane (TMS) was used as a reference while for the ^{13}C spectra the residual non-deuterated solvent signal was used. Chemical shifts (δ) are reported in ppm and coupling constants (J) in Hertz (Hz). The following abbreviations were used to note signal multiplicities: s - singlet; sl - singlet large; d - doublet; t - triplet; q - quartet; dd - doublet of doublets; ddd - doublet of doublet of doublets; dt - doublet of triplets; ddt - doublet of doublet of triplets; dq - doublet of quartets; m - multiplet; p - pentet; sept - septet; td - triplet of doublets; tt - triplet of triplets. Unless otherwise specified, ultrasonic mixing was achieved using a Branson sonifier 550 equipped with a 3 mm tapered microtip (300 ms/s pulses, Output power 40%). Photo-polymerization were carried out using a 40 W low-pressure mercury UV lamp (Heraeus) emitting at a wavelength of 254 nm. Mass spectra were obtained using a high-resolution mass spectrometry (HRMS) and were recorded using an Xevo G2-XS QTOF mass spectrometer with electrospray ionization (ESI) source. ChemDraw Professional 22.2 was used to generate the IUPAC names of the compounds.

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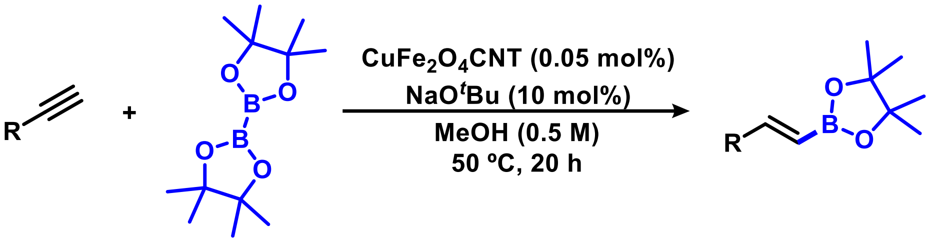
[1] **1**. Chen, P.; Zhang, H. B.; Lin, G. D.; Hong, Q.; Tsai K. R. Growth of carbon nanotubes by catalytic decomposition of CH_4 or CO on a Ni-MgO catalyst. *Carbon*, **1997**, *35*, 1495.

2. $CuFe_2O_4$ nanoparticles Synthesis and Assembly on Carbon Nanotubes

$Cu(acac)_2$ (34.0 mg, 0.13 mmol) and $Fe(acac)_3$ (91.4 mg, 0.26 mmol) were mixed in oleylamine (5 mL) under nitrogen atmosphere. The reaction mixture was heated to 220 °C to afford a dark brown solution. After 1.5 h, the solution was cooled down to room temperature, ethanol (20 mL) was added, and the precipitate was separated by centrifugation (8000 ×*g*, 10 min). The obtained nanoparticles were re-dispersed in hexane (15 mL) to obtain a stable yellow-brown dispersion.[2] The assembly of $CuFe_2O_4$ nanoparticles at the surface of carbon nanotubes to afford $CuFe_2O_4$CNT was achieved according to our previously reported procedure.[3]

3. General Procedure – Borylation Reaction



$CuFe_2O_4$CNT (208 µL of an aqueous solution, [Cu] = 1.2 mM, 0.05 mol%) was taken in a small Eppendorf tube. Methanol (1 mL) was added, and the mixture was centrifuged (5 000 ×*g*, 5 min). After discarding the supernatant, methanol (1 mL) was added and transferred to a reaction tube. Alkyne (0.5 mmol), sodium *tert*-butoxide (10 mol%, 4.8 mg) and bis(pinacolato)diboron (1.1 equiv., 0.55 mmol, 139.7 mg) were added. The reaction was stirred for 20 h at 50 °C. After completion of the reaction, the suspension was centrifuged. The supernatant (containing the product) was concentrated under vacuum and purified *via* silica gel column chromatography.

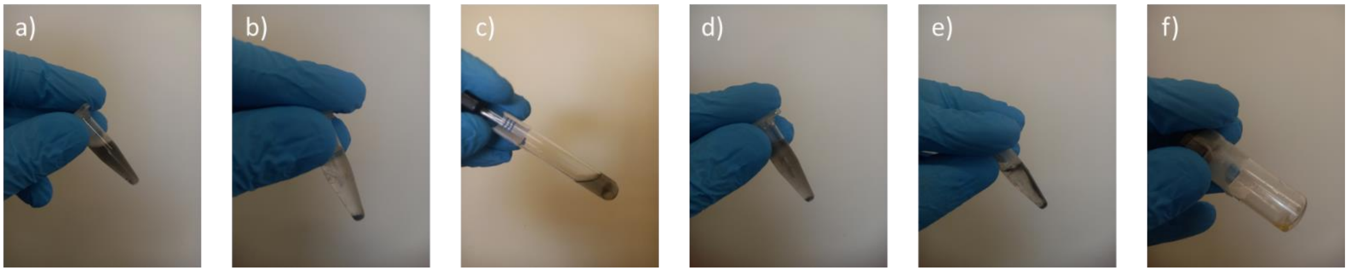


Figure S1. a) Catalyst before centrifugation; b) Catalyst after centrifugation; c) Catalyst in a reaction tube; d) Reaction crude before centrifugation; e) Reaction crude after centrifugation; f) Final product.

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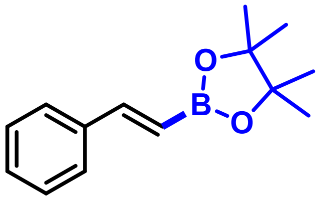
[2] Prakash, P.; Kumar, R. A.; Miserque, F.; Geertsen, V.; Gravel, E.; Doris, E. Carbon nanotube–copper ferrite-catalyzed aqueous 1,3-dipolar cycloaddition of in situ-generated organic azides with alkynes. *Chem. Commun.*, **2018**, *54*, 3644.

[3] John, J.; Gravel, E.; Hagège, A.; Li, H.; Gacoin, T.; Doris, E. Catalytic Oxidation of Silanes by Carbon Nanotube–Gold Nanohybrids. *Angew. Chem. Int. Ed.*, **2011**, *50*, 7533.

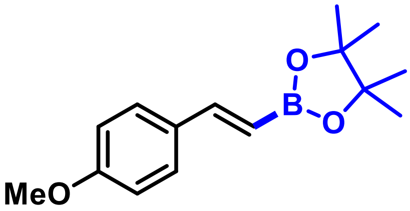
4. Synthesized Compounds

(*E*)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (2a):



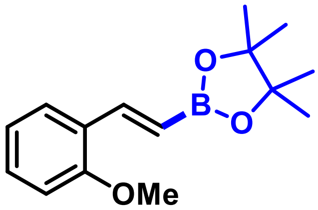
The general procedure was followed by using phenylacetylene (**1a**, 0.5 mmol, 51.1 mg). Purification by column chromatography on silica gel (*n*-hexane/ethyl acetate 95:5) afforded **2a** (92.1 mg, 80% yield) as a colorless oil. **^{1}H NMR (600 MHz, CDCl$_3$) *δ*:** 7.42 (d, *J* = 6.9 Hz, 2H), 7.33 (d, *J* = 18.4 Hz, 1H), 7.26 (t, *J* = 8.0 Hz, 2H), 7.21 (t, *J* = 7.3 Hz, 1H), 6.10 (d, *J* = 18.4 Hz, 1H), 1.24 ppm (s, 12H). **^{13}C NMR (150 MHz, CDCl$_3$) *δ*:** 149.5, 137.5, 128.9, 128.6, 127.1, 83.4, 24.8 ppm. Data consistent with the literature.[4]

(*E*)-2-(4-methoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2b):



The general procedure was followed by using 1-ethynyl-4-methoxybenzene (**1b**, 0.5 mmol, 66.1 mg). Purification by column chromatography on silica gel (*n*-hexane/ethyl acetate 95:5) afforded **2b** (96.3 mg, 74% yield) as a colorless oil. **^{1}H NMR (400 MHz, CDCl$_3$) *δ*:** 7.36 (d, *J* = 8.8 Hz, 2H), 7.28 (d, *J* = 18.3 Hz, 1H), 6.79 (d, *J* = 8.9 Hz, 2H), 5.94 (d, *J* = 18.3 Hz, 1H), 3.73 (s, 3H), 1.23 ppm (s, 12H). **^{13}C NMR (100 MHz, CDCl$_3$) *δ*:** 160.3, 149.1, 132.0, 130.4, 128.5, 114.0, 83.2, 55.3, 24.8 ppm. Data consistent with the literature.[5]

(*E*)-2-(2-methoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2c):



The general procedure was followed by using 1-ethynyl-2-methoxybenzene (**1c**, 0.5 mmol, 66.1 mg). Purification by column chromatography on silica gel (*n*-hexane/ethyl acetate 95:5) afforded **2c** (65.0 mg, 50% yield) as a colorless oil. **^{1}H NMR (400 MHz, CDCl$_3$) *δ*:** 7.80 (d, *J* = 18.7 Hz, 1H), 7.57 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.31–7.26 (m, 1H), 6.95 (t, *J* = 7.4 Hz, 1H), 6.89 (d, *J* = 9.3 Hz, 1H), 6.20 (d, *J* = 18.6 Hz, 1H), 3.87 (s, 3H), 1.33 ppm (s, 12H). **^{13}C NMR (100 MHz, CDCl$_3$) *δ*:** 157.4, 144.1, 130.0, 127.1, 120.6, 110.9, 83.2, 55.4, 24.8 ppm. Data consistent with the literature.[5]

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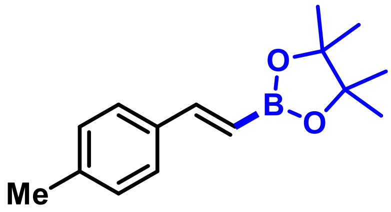
[4] Harinath, A.; Banerjee, I.; Bhattacharjee, J.; Panda, T. Aluminium complex-catalysed hydroboration of alkenes and alkynes. *New J. Chem*., **2019**, *43*, 10531.

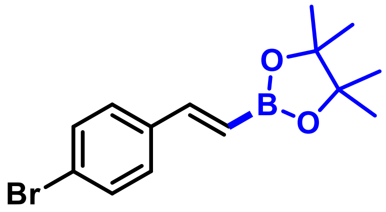
[5] Aelterman, M.; Sayes, M.; Jubault, P.; Poisson, T. Electrochemical Hydroboration of Alkynes. *Chem. Eur. J.*, **2021**, *27*, 8277.

(*E*)-4,4,5,5-tetramethyl-2-(4-methylstyryl)-1,3,2-dioxaborolane (2d):



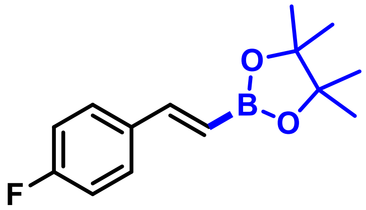
The general procedure was followed by using 1-ethynyl-4-methylbenzene (**1d**, 0.5 mmol, 58.1 mg). Purification by column chromatography on silica gel (*n*-hexane/ethyl acetate 95:5) afforded **2d** (80.6 mg, 66% yield) as a colorless oil. **^{1}H NMR (400 MHz, CDCl$_3$) *δ*:** 7.34–7.27 (m, 3H), 7.07 (d, *J* = 7.8 Hz, 2H), 6.04 (d, *J* = 18.4 Hz, 1H), 2.27 (s, 3H), 1.24 ppm (s, 12H). **^{13}C NMR (100 MHz, CDCl$_3$) *δ*:** 148.4, 138.0, 133.8, 128.3, 126.0, 82.3, 23.8, 20.3 ppm. Data consistent with the literature.[5]

(*E*)-2-(4-bromostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2e):



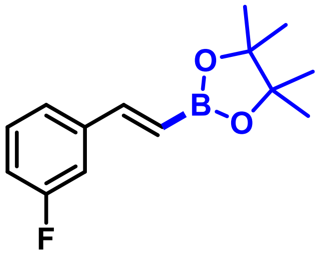
The general procedure was followed by using 1-bromo-4-ethynylbenzene (**1e**, 0.5 mmol, 90.5 mg). Purification by column chromatography on silica gel (*n*-hexane/ethyl acetate 95:5) afforded **2e** (51.0 mg, 33% yield) as a white solid. **^{1}H NMR (400 MHz, CDCl$_3$) *δ*:** 7.38 (d, *J* = 8.6 Hz, 2H), 7.30–7.20 (m, 3H), 6.07 (d, *J* = 18.3 Hz, 1H), 1.24 ppm (s, 12H). **^{13}C NMR (100 MHz, CDCl$_3$) *δ*:** 148.1, 136.4, 131.8, 128.5, 122.9, 83.5, 29.7, 24.8 ppm. Data consistent with the literature.[5]

(*E*)-2-(4-fluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2f):



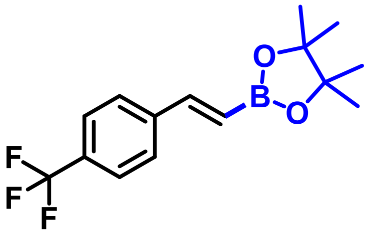
The general procedure was followed by using 1-ethynyl-4-fluorobenzene (**1f**, 0.5 mmol, 60.1 mg). Purification by column chromatography on silica gel (*n*-hexane/ethyl acetate 95:5) afforded **2f** (69.5 mg, 56% yield) as a colorless oil. **^{1}H NMR (400 MHz, CDCl$_3$) *δ*:** 7.41–7.36 (m, 2H), 7.28 (d, *J* = 18.4 Hz, 1H), 6.95 (t, *J* = 8.7 Hz, 2H), 6.00 (d, *J* = 18.4 Hz, 1H), 1.24 ppm (s, 12H). **^{13}C NMR (100 MHz, CDCl$_3$) *δ*:** 162.2 (d, $J_{C\text{-}F}$ = 247 Hz), 147.2, 132.7 (d, $J_{C\text{-}F}$ = 3 Hz), 127.7 (d, $J_{C\text{-}F}$ = 8 Hz), 114.5 (d, $J_{C\text{-}F}$ = 22 Hz), 82.4, 23.8 ppm. Data consistent with the literature.[5]

(*E*)-2-(3-fluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2g):



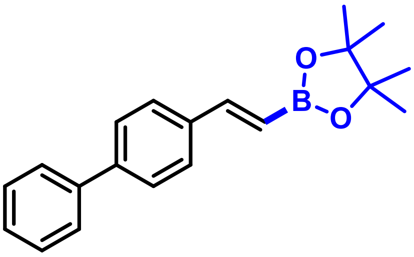
The general procedure was followed by using 1-ethynyl-3-fluorobenzene 1g, 0.5 mmol, 60.1 mg). Purification by column chromatography on silica gel (*n*-hexane/ethyl acetate 95:5) afforded **2g** (75.7 mg, 61% yield) as a colorless oil. **^{1}H NMR (400 MHz, CDCl$_3$) *δ*:** 7.31–7.14 (m, 3H), 7.13–7.07 (m, 1H), 6.95–6.85 (m, 1H), 6.09 (d, *J* = 18.5 Hz, 1H), 1.24 ppm (s, 12H). **^{13}C NMR (100 MHz, CDCl$_3$) *δ*:** 162.1 (d, *J* = 244 Hz), 147.1 (d, *J* = 2 Hz), 138.9 (d, *J* = 7 Hz), 129.0 (d, *J* = 8 Hz), 122.0 (d, *J* = 2 Hz), 114.7 (d, *J* = 22 Hz), 112.3 (d, *J* = 21 Hz), 82.5, 23.8 ppm. Data consistent with the literature.[5]

(*E*)-4,4,5,5-tetramethyl-2-(4-(trifluoromethyl)styryl)-1,3,2-dioxaborolane (2h):



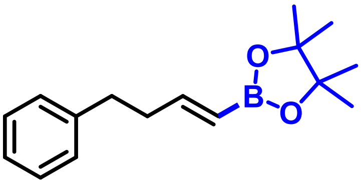
The general procedure was followed by using 1-ethynyl-4-(trifluoromethyl)benzene (**1h**, 0.5 mmol, 85.1 mg). Purification by column chromatography on silica gel (*n*-hexane/ethyl acetate 95:5) afforded **2h** (100.0 mg, 67% yield) as a white solid. **^{1}H NMR (400 MHz, CDCl$_3$) δ:** 7.51 (dd, J = 11.5, 9.0 Hz, 4H), 7.33 (d, J = 18.4 Hz, 1H), 6.18 (d, J = 18.4 Hz, 1H), 1.25 ppm (s, 12H). **^{13}C NMR (100 MHz, CDCl$_3$) δ:** 147.8, 140.9, 130.7 (q, $J_{C\text{-}F}$ = 32 Hz), 127.3, 125.7 (q, $J_{C\text{-}F}$ = 4 Hz), 124.3 (q, $J_{C\text{-}F}$ = 270 Hz), 83.8, 24.9 ppm. Data consistent with the literature.[5]

(*E*)-2-(2-([1,1'-biphenyl]-4-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2i):



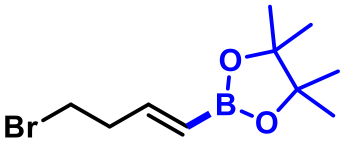
The general procedure was followed by using 4-ethynylbiphenyl (**1i**, 0.5 mmol, 89.1 mg). Purification by column chromatography on silica gel (*n*-hexane/ethyl acetate 95:5) afforded **2i** (101.3 mg, 66% yield) as a pale yellow solid. **^{1}H NMR (400 MHz, CDCl$_3$) δ:** 7.55–7.48 (m, 6H), 7.40–7.33 (m, 3H), 7.30–7.24 (m, 1H), 6.14 (d, J = 18.4 Hz, 1H), 1.25 ppm (s, 12H). **^{13}C NMR (100 MHz, CDCl$_3$) δ:** 148.0, 140.6, 139.5, 135.4, 127.8, 126.5, 126.4, 126.2, 126.0, 82.4, 23.8 ppm. Data consistent with the literature.[5]

(*E*)-4,4,5,5-tetramethyl-2-(4-phenylbut-1-en-1-yl)-1,3,2-dioxaborolane (2k):



The general procedure was followed by using 4-phenyl-1-butyne (**1k**, 0.5 mmol, 65.1 mg). Purification by column chromatography on silica gel (*n*-hexane/ethyl acetate 95:5) afforded **2k** (97.8 mg, 76% yield) as a colorless oil. **^{1}H NMR (400 MHz, CDCl$_3$) δ:** 7.23–7.17 (m, 2H), 7.14–7.08 (m, 3H), 6.63 (dt, J = 18.0 Hz, 6.2 Hz, 1H), 5.43 (dt, J = 18.0 Hz, 1.6 Hz, 1H), 2.70–2.64 (m, 2H), 2.44–2.36 (m, 2H), 1.19 ppm (s, 12H). **^{13}C NMR (100 MHz, CDCl$_3$) δ:** 153.5, 141.9, 128.5, 126.0, 83.2, 37.6, 34.7, 24.9 ppm. Data consistent with the literature.[6]

(*E*)-2-(4-bromobut-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2l):



The general procedure was followed by using 4-bromo-1-butyne (**1l**, 0.5 mmol, 66.5 mg). Purification by column chromatography on silica gel (*n*-hexane/ethyl acetate 95:5) afforded **2l** (65.2 mg, 50% yield) as a brown oil. **^{1}H NMR (600 MHz, CDCl$_3$) δ:** 6.48 (dt, J = 18.0, 6.4 Hz, 1H), 5.47 (dt, J = 18.0, 1.6 Hz, 1H), 3.35 (t, J =

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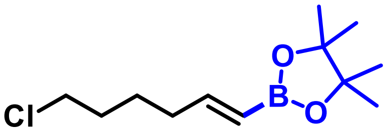
[6] **6.** Ben-Daat, H.; Rock, C. L.; Flores, M.; Groy, T. L.; Bowmanb, A. C.; Trovitch, R. J. Hydroboration of alkynes and nitriles using an α-diimine cobalt hydride catalyst. *Chem. Commun.*, **2017**, *53*, 7333.

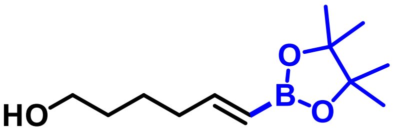
7.2 Hz, 2H), 2.65 (q, *J* = 7.2 Hz, 2H), 1.20 ppm (s, 12H). **^{13}C NMR (150 MHz, CDCl$_3$) *δ*:** 149.7, 83.4, 38.9, 30.9, 24.9 ppm. Data consistent with the literature.[5]

(*E*)-2-(6-chlorohex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2m):



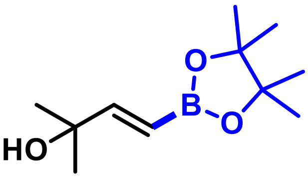
The general procedure was followed by using 6-chloro-1-hexyne (**1m**, 0.5 mmol, 58.3 mg). Purification by column chromatography on silica gel (*n*-hexane/ethyl acetate 9.5:0.5) afforded **2m** (67.2 mg, 55% yield) as a colorless oil. **^{1}H NMR (400 MHz, CDCl$_3$) *δ*:** 6.54 (dt, *J* = 18.0, 6.4 Hz 1H), 5.38 (dt, *J* = 18.0, 1.6 Hz, 1H), 3.46 (t, *J* = 6.6 Hz, 2H), 2.16 – 2.08 (m, 2H), 1.76–1.67 (m, 2H), 1.55–1.46 (m, 2H), 1.20 ppm (s, 12H). **^{13}C NMR (100 MHz, CDCl$_3$) *δ*:** 153.6, 83.2, 45.0, 35.0, 32.1, 25.5. 24.9 ppm. Data consistent with the literature.[7]

(*E*)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-en-1-ol (2n):



The general procedure was followed by using 5-hexyn-1-ol (**1n**, 0.5 mmol, 49.1 mg). Purification by column chromatography on silica gel (*n*-hexane/ethyl acetate 8:2) afforded **2n** (77.0 mg, 68% yield) as a colorless oil. **^{1}H NMR (400 MHz, CDCl$_3$) *δ*:** 6.55 (dt, *J* = 17.9, 6.4 Hz, 1H), 5.37 (dt, *J* = 17.9, 1.6 Hz, 1H), 3.57 (t, *J* = 6.4 Hz, 2H), 2.16–2.07 (m, 2H), 1.56–1.48 (m, 2H), 1.47–1.40 (m, 2H), 1.19 ppm (s, 12H). **^{13}C NMR (100 MHz, CDCl$_3$) *δ*:** 154.2, 83.2, 62.9, 35.5, 32.3, 24.9, 24.4 ppm. Data consistent with the literature.[8]

(*E*)-2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-2-ol (2o):



The general procedure was followed by using 2-methyl-3-butyn-2-ol (**1o**, 0.5 mmol, 42.1 mg). Purification by column chromatography on silica gel (*n*-hexane/ethyl acetate 8:2) afforded **2o** (93.3 mg, 88% yield) as a colorless oil. **^{1}H NMR (400 MHz, CDCl$_3$) *δ*:** 6.65 (d, *J* = 18.2 Hz, 1H), 5.54 (d, *J* = 18.2 Hz, 1H), 1.24 (s, 6H), 1.21 ppm (s, 12H). **^{13}C NMR (100 MHz, CDCl$_3$) *δ*:** 159.9, 83.4, 75.2, 71.9, 29.2, 24.9 ppm. Data consistent with the literature.[9]

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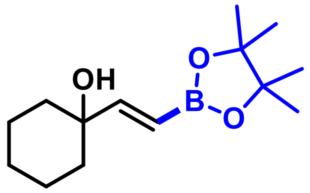
7. Liu, J.; Xie, Y.; Wu, C.; Shao, Y.; Zhang, F.; Shi, Y.; Liua, Q.; Chen, J. Samarium(iii) catalyzed synthesis of alkenylboron compounds via hydroboration of alkynes. *Org. Chem. Front.*, **2021**, *8*, 3802.

8. Xu, L. and Xu, B. Encapsulation of nano-catalysts in permeable silicone elastomers. *Tetrahedron Lett.*, **2017**, *58*, 2542.

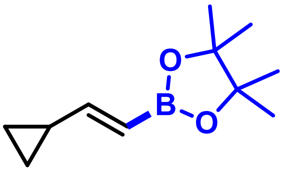
9. Zeng, X.; Gong, C.; Guo, H.; Xu, H.; Zhang, J.; Xie, J. Efficient heterogeneous hydroboration of alkynes: enhancing the catalytic activity by Cu(0) incorporated CuFe2O4 nanoparticles. *New J. Chem.*, **2018**, *42*, 17346.

(*E*)-1-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)cyclohexan-1-ol (2p):



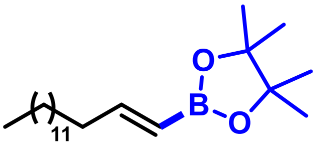
The general procedure was followed by using 1-ethynyl-1-cyclohexanol (**1p**, 0.5 mmol, 62.1 mg). Purification by column chromatography on silica gel (*n*-hexane/ethyl acetate 8:2) afforded **2p** (97.1 mg, 77% yield) as a white solid. **^{1}H NMR (400 MHz, CDCl$_3$) *δ*:** 6.63 (d, *J* = 18.2 Hz, 1H), 5.59 (d, *J* = 18.2 Hz, 1H), 1.61–1.52 (m, 4H), 1.50–1.43 (m, 6H), 1.21 ppm (s, 12H). **^{13}C NMR (100 MHz, CDCl$_3$) *δ*:** 160.1, 83.4, 72.6, 37.2, 25.6, 24.9, 22.0 ppm. Data consistent with the literature.[10]

(*E*)-2-(2-cyclopropylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2q):



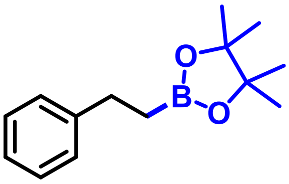
The general procedure was followed by using cyclopropylacetylene (**1q**, 0.5 mmol, 33.1 mg). Purification by column chromatography on silica gel (*n*-hexane/ethyl acetate 95:5) afforded **2q** (69.9 mg, 72% yield) as a colorless oil. **^{1}H NMR (400 MHz, CDCl$_3$) *δ*:** 6.08 (dd, *J* = 17.7, 9.3 Hz, 1H), 5.49 (d, *J* = 17.9 Hz, 1H), 1.52 (tt, *J* = 12.5, 4.7 Hz, 1H), 1.26 (s, 12H), 0.85–0.74 (m, 2H), 0.57–0.50 ppm (m, 2H). **^{13}C NMR (100 MHz, CDCl$_3$) *δ*:** 158.7, 83.1, 24.9, 17.2, 8.0 ppm. Data are according to literature.[5]

(*E*)-4,4,5,5-tetramethyl-2-(pentadec-1-en-1-yl)-1,3,2-dioxaborolane (2r):



The general procedure was followed by using 1-pentadecyne (**1r**, 0.5 mmol, 104.2 mg). Purification by column chromatography on silica gel (*n*-hexane/ethyl acetate 95:05) afforded **2r** (131.3 mg, 78% yield) as a colorless oil. **^{1}H NMR (400 MHz, CDCl$_3$) *δ*:** 6.56 (dt, *J* = 17.8, 6.5 Hz, 1H), 5.35 (dt, *J* = 17.8, 1.4 Hz, 1H), 2.1–2.03 (m, 2H), 1.36–1.30 (m, 2H), 1.22–1.16 (m, 32H), 0.81 ppm (t, *J* = 6.8 Hz, 3H). **^{13}C NMR (100 MHz, CDCl$_3$) *δ*:** 155.0, 83.1, 36.0, 32.1, 29.8 (2×), 29.7 (2×), 29.5, 29.4, 28.4, 24.9, 22.8, 14.3 ppm. **HRMS (ESI-TOF)** *m*/*z* calcd for $C_{21}H_{41}BO_2Na$ $[M + Na]^+$ 359.3101; found 359.3100.

4,4,5,5-tetramethyl-2-phenethyl-1,3,2-dioxaborolane (2s):



The general procedure was followed by using styrene (**1s**, 0.5 mmol, 52.1 mg). Purification by column chromatography on silica gel (*n*-hexane/ethyl acetate 95:5) afforded **2s** (65.0 mg, 56% yield) as a colorless oil. **^{1}H NMR (400 MHz, CDCl$_3$) *δ*:** 7.22–7.12 (m, 4H), 7.11–7.06 (m, 1H), 2.68 (t, *J* = 8.2 Hz, 2H), 1.15 (s, 12H), 1.07 ppm (t, *J* = 8.2 Hz, 2H). **^{13}C NMR (100 MHz, CDCl$_3$) *δ*:** 144.6, 128.3, 128.1, 125.6, 83.2, 30.1, 24.9 ppm. Data are according to literature.[11]

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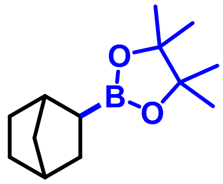
[10] **10**. Miralles, N.; Alam, R.: Szabó, K.; Fernández, E. Transition-Metal-Free Borylation of Allylic and Propargylic Alcohols. *Angew. Chem. Int. Ed.*, **2016**, *55*, 4303.

[11] **11.** Shegavi, M. L.; Saini, S.; Bhawar, R.; Vishwantha, M. D.; Bose, S. K. Recyclable Copper Nanoparticles-Catalyzed Hydroboration of Alkenes and β-Borylation of α,β-Unsaturated Carbonyl Compounds with Bis(Pinacolato)Diboron. *Adv. Synth. Catal*. **2021**, *363*, 2408.

2-((2S)-bicyclo[2.2.1]heptan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2t):



The general procedure was followed by using bicyclo[2.2.1]hept-2-ene (**1t**, 0.5 mmol, 47.1 mg). Purification by column chromatography on silica gel (*n*-hexane/ethyl acetate 95:5) afforded **2t** (86.1 mg, 77% yield) as a colorless oil. **^{1}H NMR (400 MHz, CDCl$_3$) δ:** 2.23–2.20 (m, 1H), 2.16–2.14 (m, 1H), 1.50–1.36 (m, 3H), 1.31–1.24 (m, 1H), 1.17–1.14 (m, 14H), 1.13–1.06 (m, 2H), 0.84–0.78 ppm (m, 1H). **^{13}C NMR (100 MHz, CDCl$_3$) δ:** 82.9, 38.9, 38.3, 36.8, 32.4, 32.3, 29.4, 24.8 ppm. Data consistent with the literature.[12]

5. Recycling Experiments

Step 1: CuFe$_2$O$_4$CNT (208 µL of an aqueous solution, [Cu] = 1.2 mM, 0.05 mol%) was added in an Eppendorf tube with methanol (1 mL) and the mixture was centrifuged (5 000 ×*g*, 5 min). The supernatant was discarded, and methanol (1 mL) was added and transferred to a reaction tube.

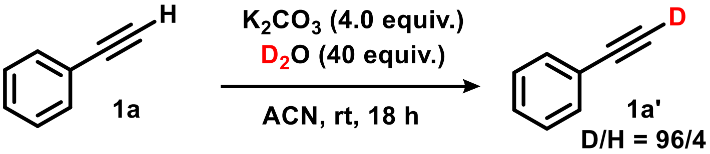
***Step 2*:** Phenylacetylene (**1a**, 0.5 mmol, 51.1 mg), sodium *tert*-butoxide (10 mol%, 4.8 mg) and bis(pinacolato)diboron (1.1 equiv., 139.7 mg) were added and the mixture was stirred for 20 h at 50 °C.

Step 3: After completion of the reaction, the mixture was transferred to an Eppendorf tube and centrifuged (5 000 ×*g*, 5 min). The supernatant was collected, and the catalyst was washed twice with methanol (2 × 2 mL) by centrifugation/resuspension. All the organic phases were collected, concentrated under vacuum and purified *via* silica gel column chromatography to obtain the product **2a** as a colorless oil.

Step 4: Methanol (1 mL) was added to the pelleted catalyst, transferred to a reaction tube and steps 2 and 3 were repeated.

6. Deuterium-Labeling Experiments

Synthesis of 1a'



An oven-dried 10 mL round-bottom flask was charged with phenylacetylene (1 equiv., 5 mmol, 1.02 g), potassium carbonate (4 equiv., 20 mmol, 5.52 g) and ACN (10 mL). The reaction mixture was stirred under an N$_2$ atmosphere for 1 h. To this mixture, D$_2$O (40 equiv., 200 mmol, 4 mL) was added and left to stir for

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12. Li, J.-F; Wei, Z.-Z.; Wang, Y.-Q.; Ye, M. Base-free nickel-catalyzed hydroboration of simple alkenes with bis(pinacolato)diboron in an alcoholic solvent. *Green Chem.*, **2017**, *19*, 4498.

18 h. The resulting crude reaction mixture was transferred to an oven-dried separating funnel. The organic layer was separated, dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The residue was purified by column chromatography on silica gel using *n*-pentane as eluent. **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.43–7.39 (m, 2H), 7.28–7.20 ppm (m, 3H). Data consistent with the literature.[13]

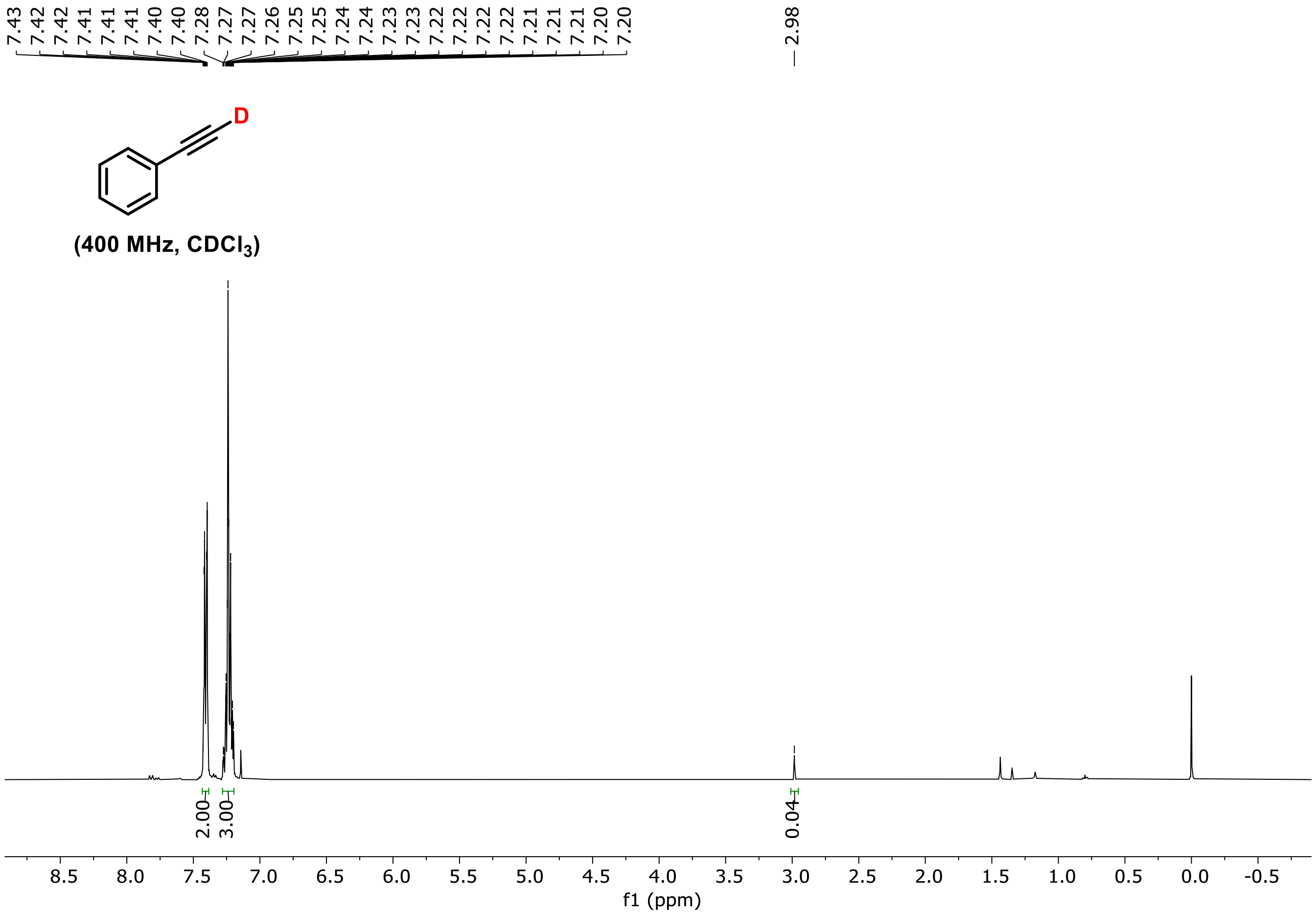
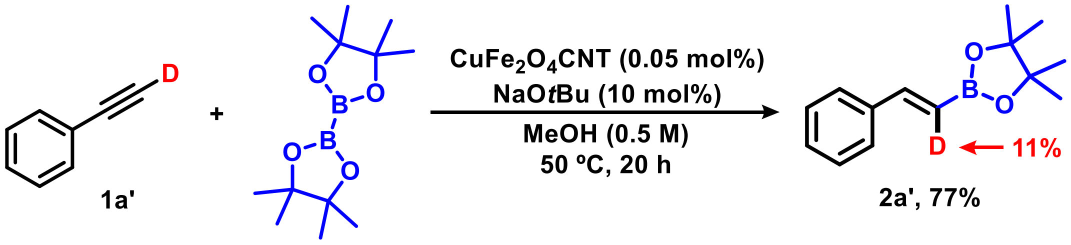


Figure S2. ^{1}H NMR spectrum of compound **1a’** in $CDCl_3$.

Synthesis of 2a’



The general procedure for borylation reaction was followed by using phenylacetylene-*d* (**1a’**, 0.5 mmol, 51.6 mg). Purification by column chromatography on silica gel (*n*-hexane/ethyl acetate 95:5) afforded **2a’** (88.9 mg, 77% yield) as a colorless oil.

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13. Virant, M.; Mihelač, M.; Gazvoda, M.; Cotman, A. E.; Frantar, A.; Pinter, B.; Košmrlj, J. Pyridine Wingtip in [Pd(Py-tzNHC)2]2+ Complex Is a Proton Shuttle in the Catalytic Hydroamination of Alkynes. *Org. Lett*., **2020**, *22*, 2157.

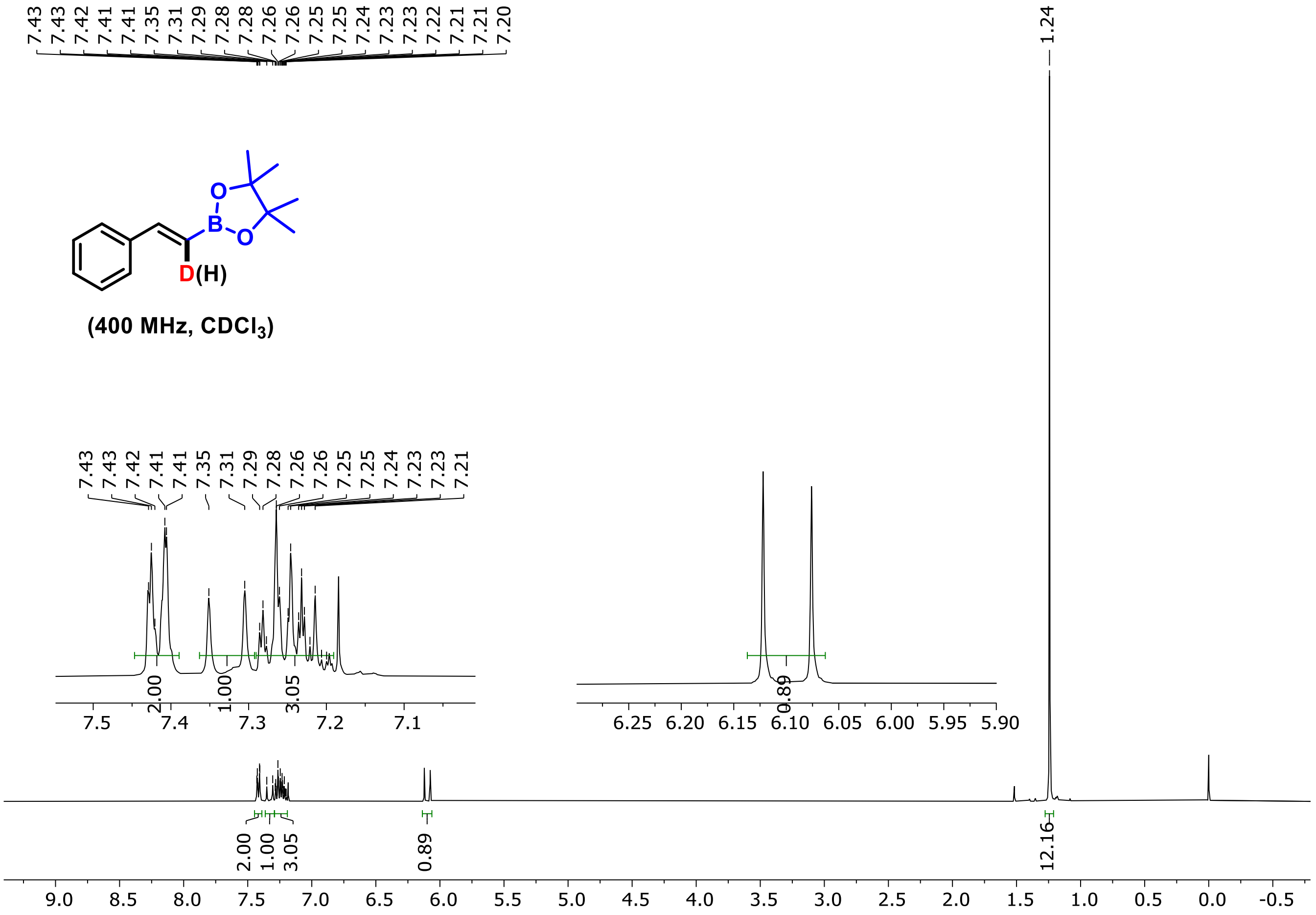
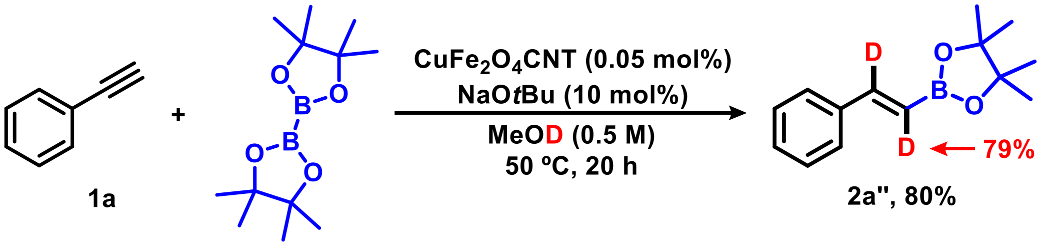


Figure S3. ^{1}H NMR spectrum of the reaction of phenylacetylene-*d* (**1a'**) with methanol in $CDCl_3$.

Synthesis of 2a''



The general procedure for borylation reaction was followed by using phenylacetylene (**1a**, 0.5 mmol, 51.1 mg). Purification by column chromatography on silica gel (*n*-hexane/ethyl acetate 95:5) afforded **2a''** (92.3 mg, 80% yield) as a colorless oil.

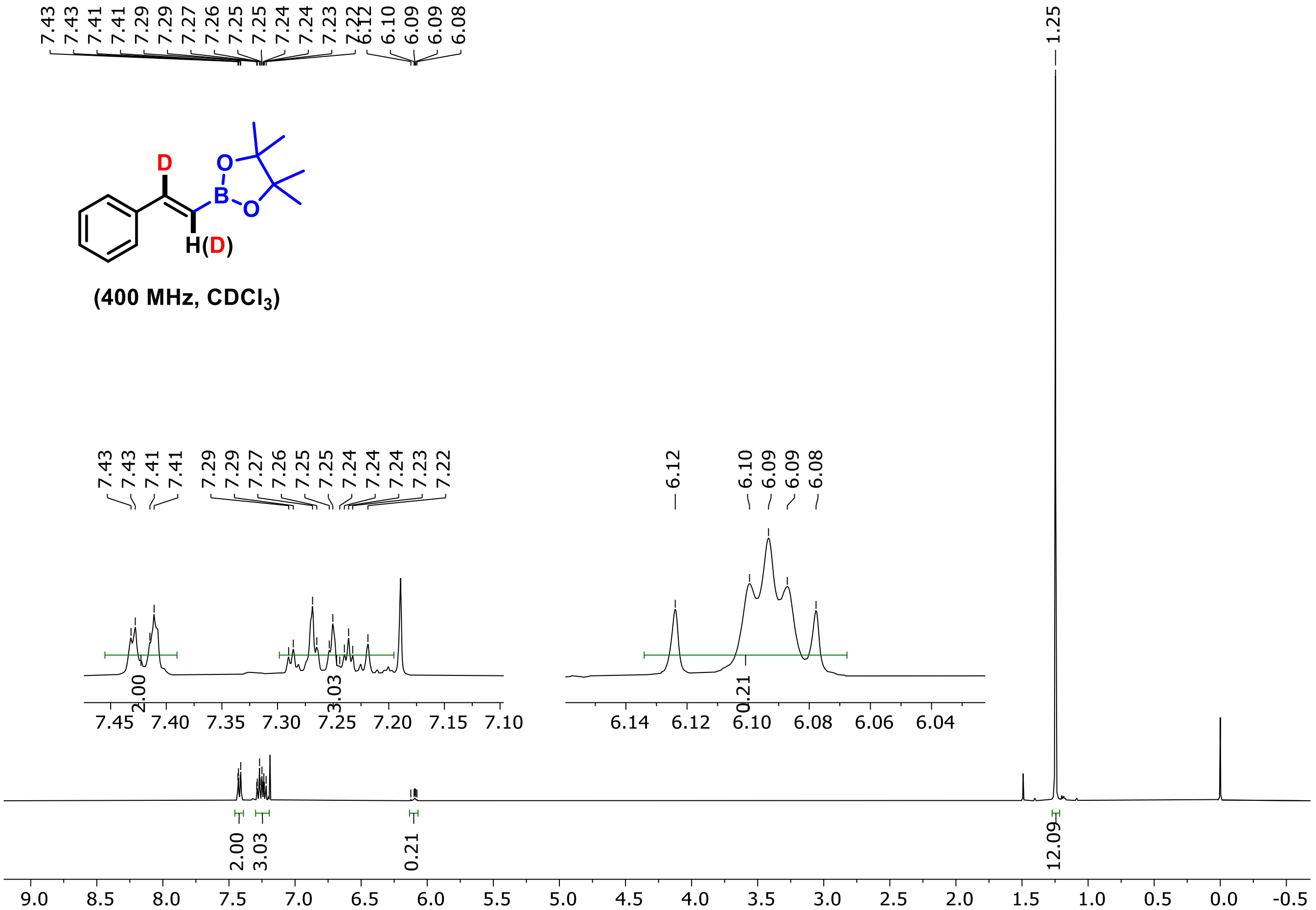
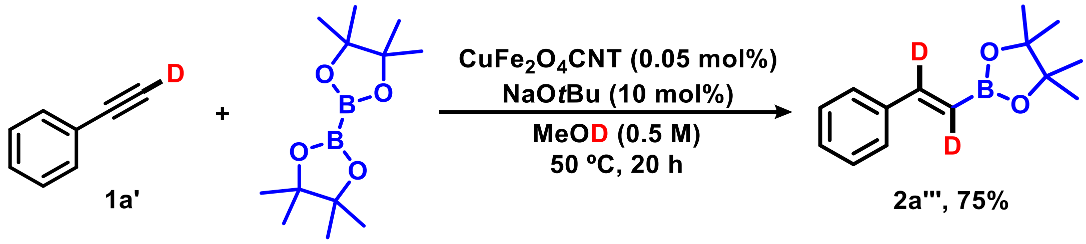


Figure S4. ^{1}H NMR spectrum of the reaction of phenylacetylene (**1a**) with methanol-*d4* in CDCl$_3$.

Synthesis of 2a'''



The general procedure for borylation reaction was followed by using phenylacetylene-*d* (**1a'**, 0.5 mmol, 51.6 mg). Purification by column chromatography on silica gel (*n*-hexane/ethyl acetate 95:5) afforded **2a'''** (86.8 mg, 75% yield) as a colorless oil.

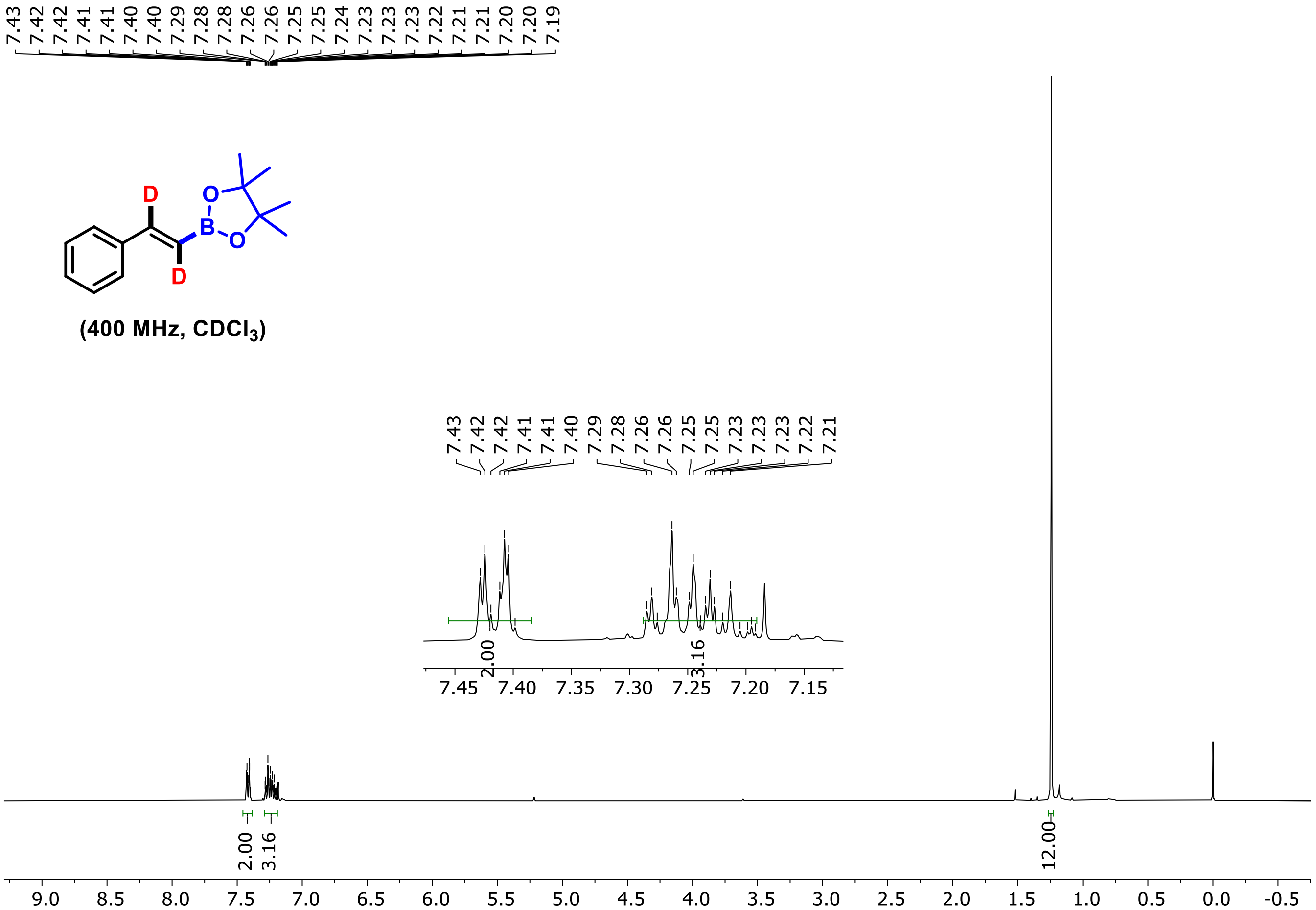
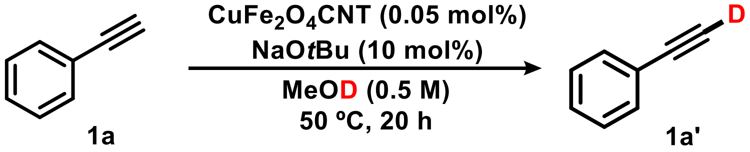


Figure S5. ^{1}H NMR spectrum of the reaction of phenylacetylene-*d* (**1a'**) with methanol-*d4* in $CDCl_3$.

Evaluation of H/D Exchange Before the Borylation Reaction



$CuFe_2O_4CNT$ (208 µL of an aqueous solution, [Cu] = 1.2 mM, 0.05 mol%) was taken in a small Eppendorf tube. Methanol-*d4* (1 mL) was added, and the mixture was centrifuged (5 000 ×*g*, 5 min). After discarding the supernatant, methanol-*d4* (1 mL) was added and transferred to a reaction tube. Phenylacetylene (**1a**, 0.5 mmol, 51.1 mg), and sodium *tert*-butoxide (10 mol%, 4.8 mg) were added. The reaction was stirred at 50 °C and monitored for 2 h. A 50 µL aliquot of the reaction mixture was collected at specific time intervals and sent for NMR analysis, as shown in the graphic in Figure S6.

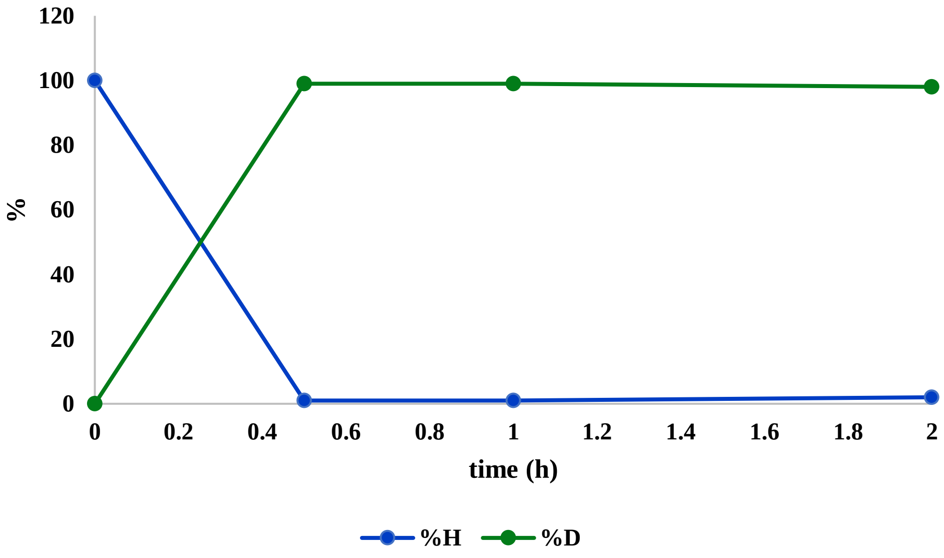
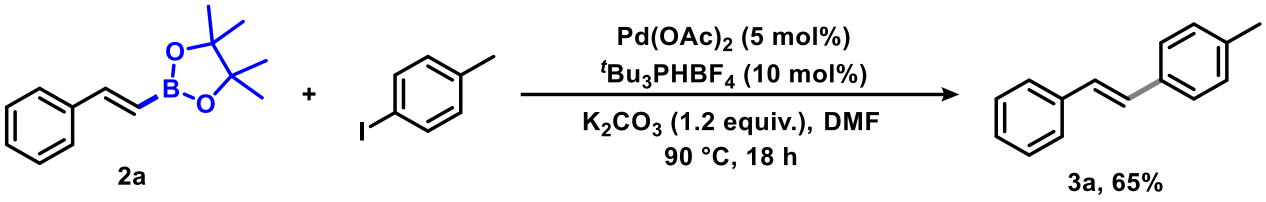


Figure S6. The percentage of hydrogen and deuterium in phenylacetylene was monitored over a 2-hour period using ^{1}H NMR in methanol-*d4*.

7. Procedure for the Valorization of 2a

Synthesis of 3a



To an oven-dried 10 mL round-bottomed flask was added Pd(OAc)$_2$ (0.05 equiv., 0.01 mmol, 2.3 mg), *t*-Bu$_3$PHBF$_4$ (0.10 equiv., 0.02 mmol, 5.8 mg), K$_2$CO$_3$ (1.2 equiv., 0.24 mmol, 33.0 mg), **2a** (1.0 equiv., 0.20 mmol, 46.0 mg) and 1-iodo-4-methylbenzene (1.0 equiv., 0.20 mmol, 43.6 mg). The flask was closed with a septum and purged with nitrogen three times. DMF (1.0 mL) was added using a syringe, the flask was sealed, and the reaction was stirred for 18 h at 90 °C. Upon reaction completion, the solution was extracted with DCM (3 × 10 mL) and the solvent was evaporated in vacuo. The residue was purified by column chromatography on silica gel (hexane) afforded **3a** (25.4 mg, 65% yield) as a white solid. **^{1}H NMR (400 MHz, CDCl$_3$) δ:** 7.45–7.41 (m, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.30–7.25 (m, 2H), 7.19–7.15 (m, 1H), 7.09 (d, *J* = 7.8 Hz, 2H), 7.00 (dd, *J* = 18.9, 16.4 Hz, 2H), 2.29 ppm (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$) δ:** 137.7, 137.6, 134.7, 129.5, 128.8, 128.7, 127.8, 127.5, 126.6, 126.5, 21.4 ppm. Data consistent with the literature.[14]

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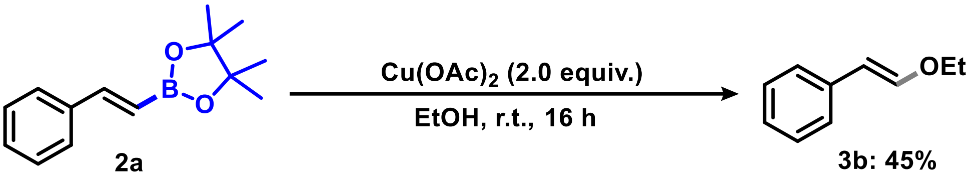
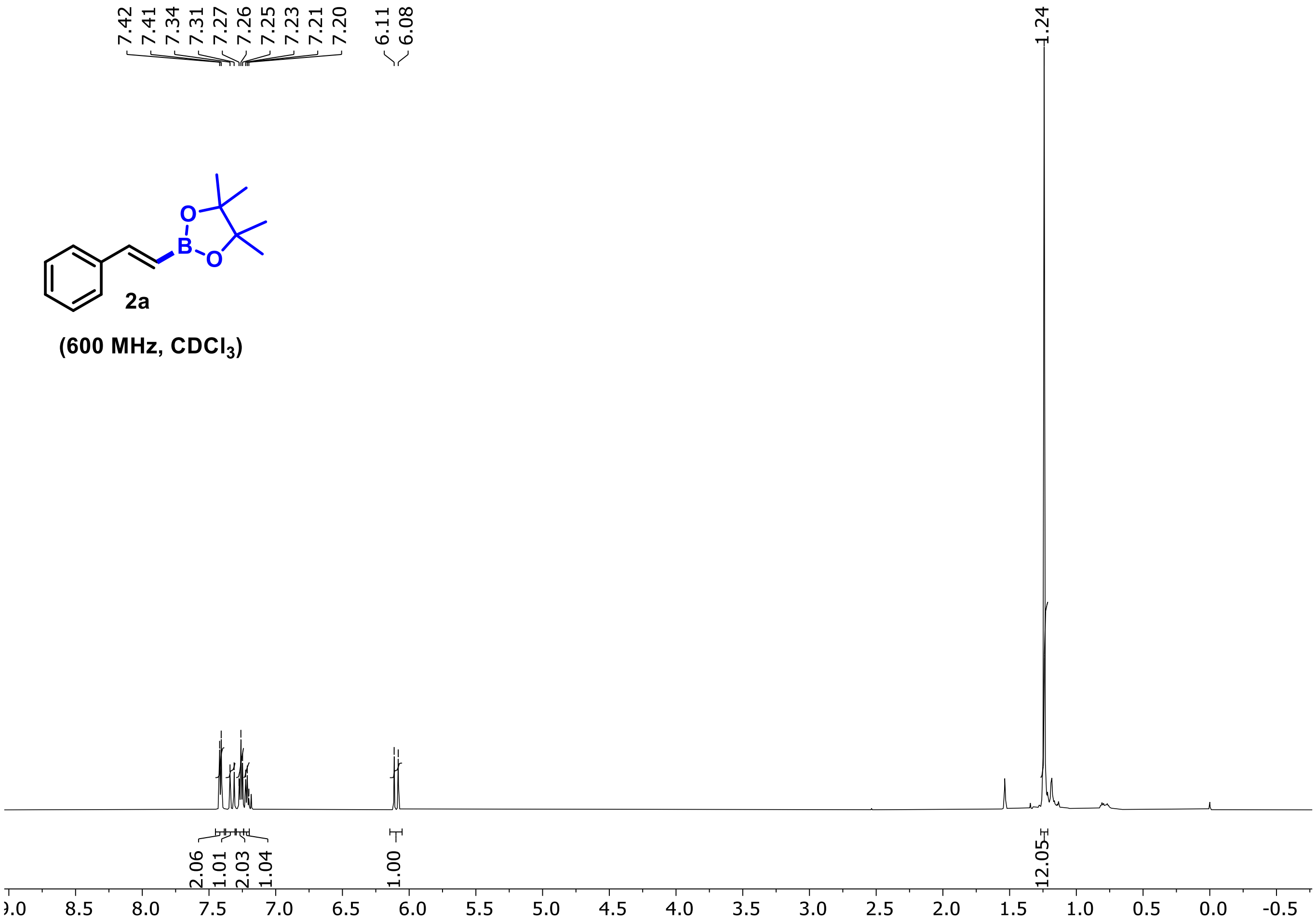
14. Rau, H. H.; Werner, N. S. Stereocontrolled synthesis of (E)-stilbene derivatives by palladium-catalyzed Suzuki-Miyaura cross-coupling reaction. *Bioorg. Med. Chem. Lett.*, **2018**, *28*, 2693.

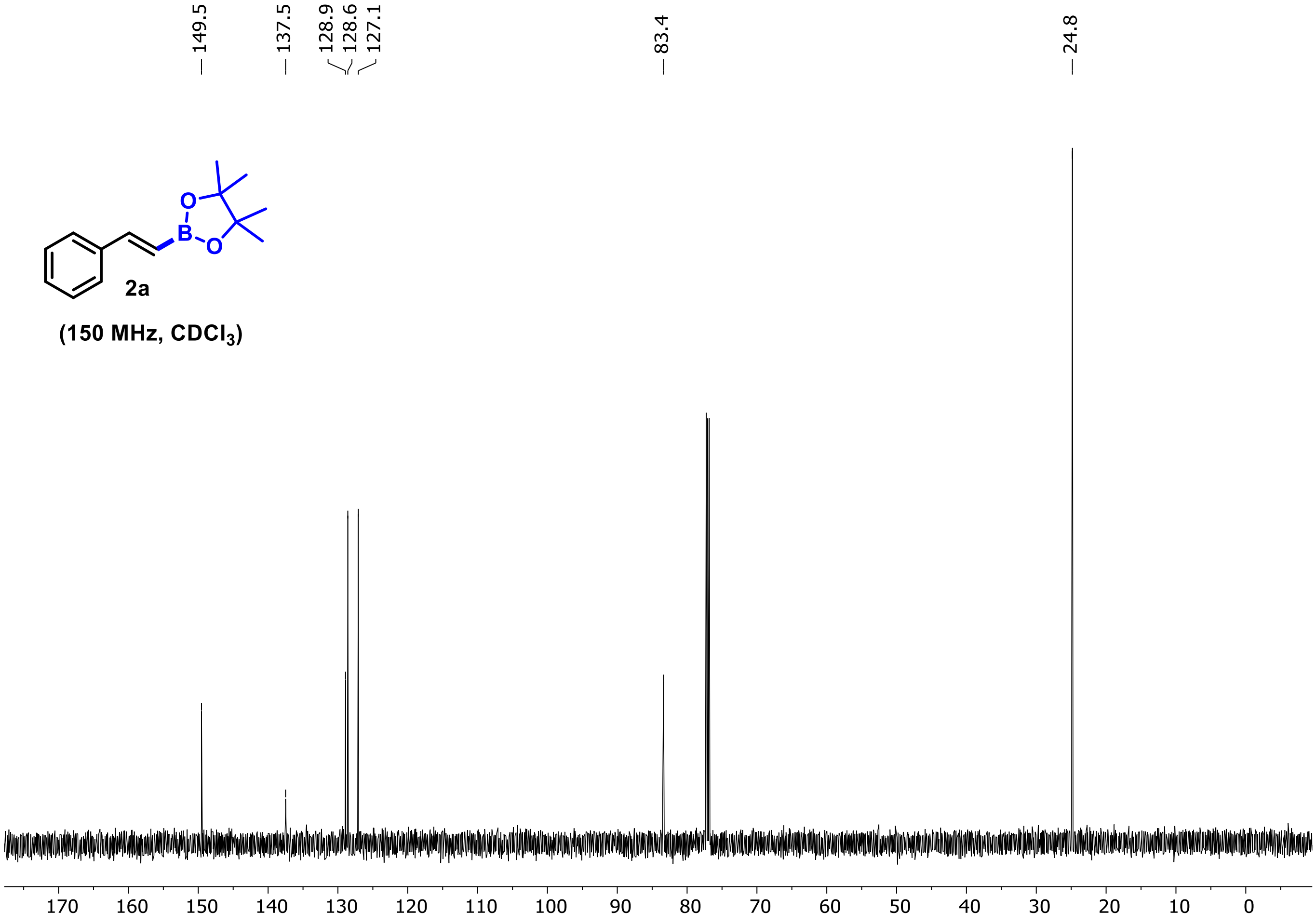
Synthesis of 3b

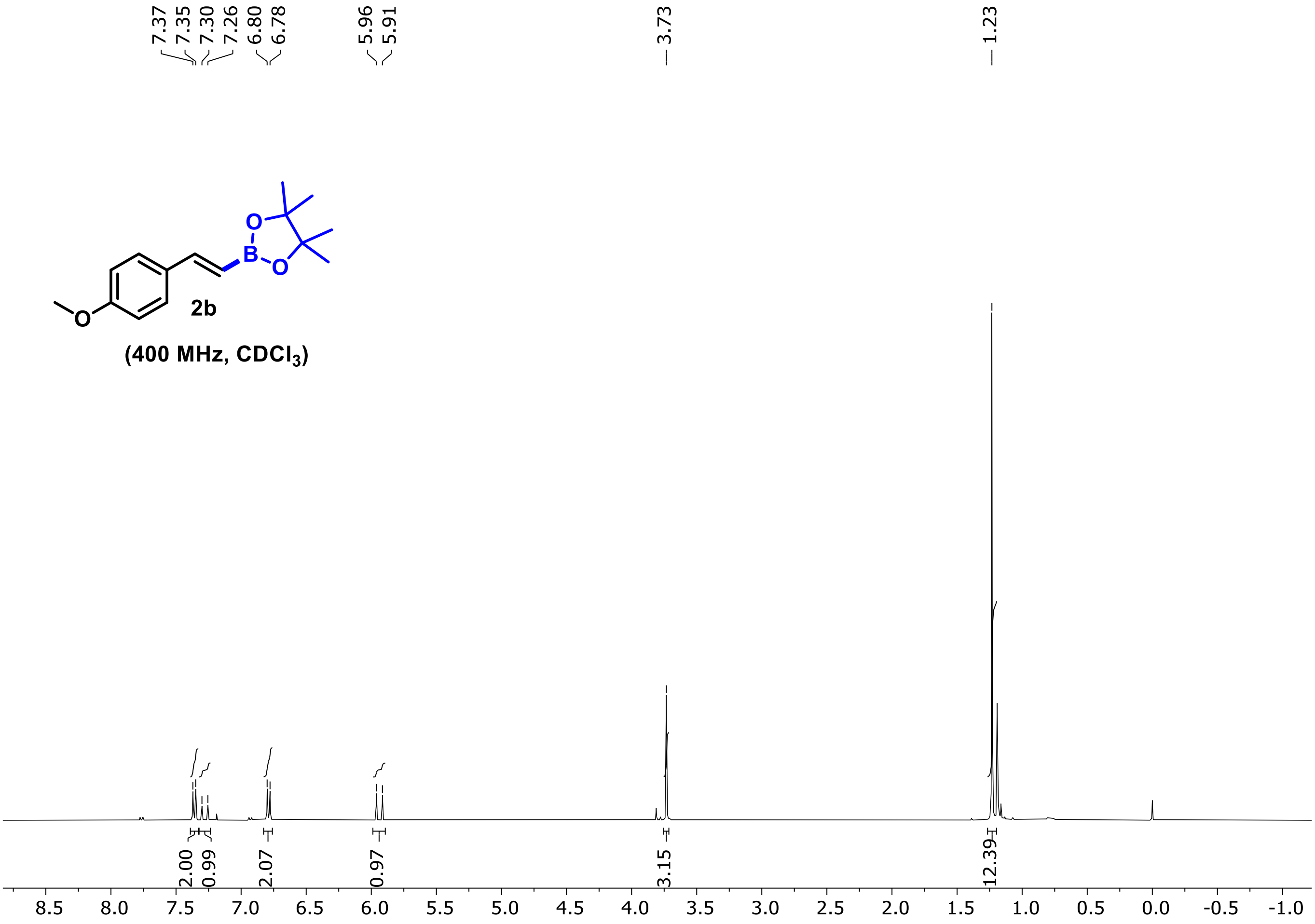


To an oven-dried 10 mL round-bottomed flask was added **2a** (1.0 equiv., 0.3 mmol, 69.0 mg), Cu(OAc)$_2$ (2.0 equiv., 0.6 mmol, 109.0 mg), EtOH (1 mL) and stirred under ambient condition for 16 h. The solvent was removed in vacuo and the residue purified by column chromatography on silica gel (hexane) afforded **3b** (20.0 mg, 45% yield) as a colorless oil. **^{1}H NMR (400 MHz, CDCl$_3$) *δ*:** 7.23–7.12 (m, 4H), 7.08–7.02 (m, 1H), 6.92 (d, *J* = 13.0 Hz, 1H), 5.77 (d, *J* = 13.0 Hz, 1H), 3.83 (q, *J* = 7.0 Hz, 2H), 1.27 ppm (t, *J* = 7.0 MHz, 3H). **^{13}C NMR (100 MHz, CDCl$_3$) *δ*:** 148.0, 136.7, 128.7, 125.7, 125.2, 106.1, 65.6, 15.0 ppm.

8. NMR Spectra



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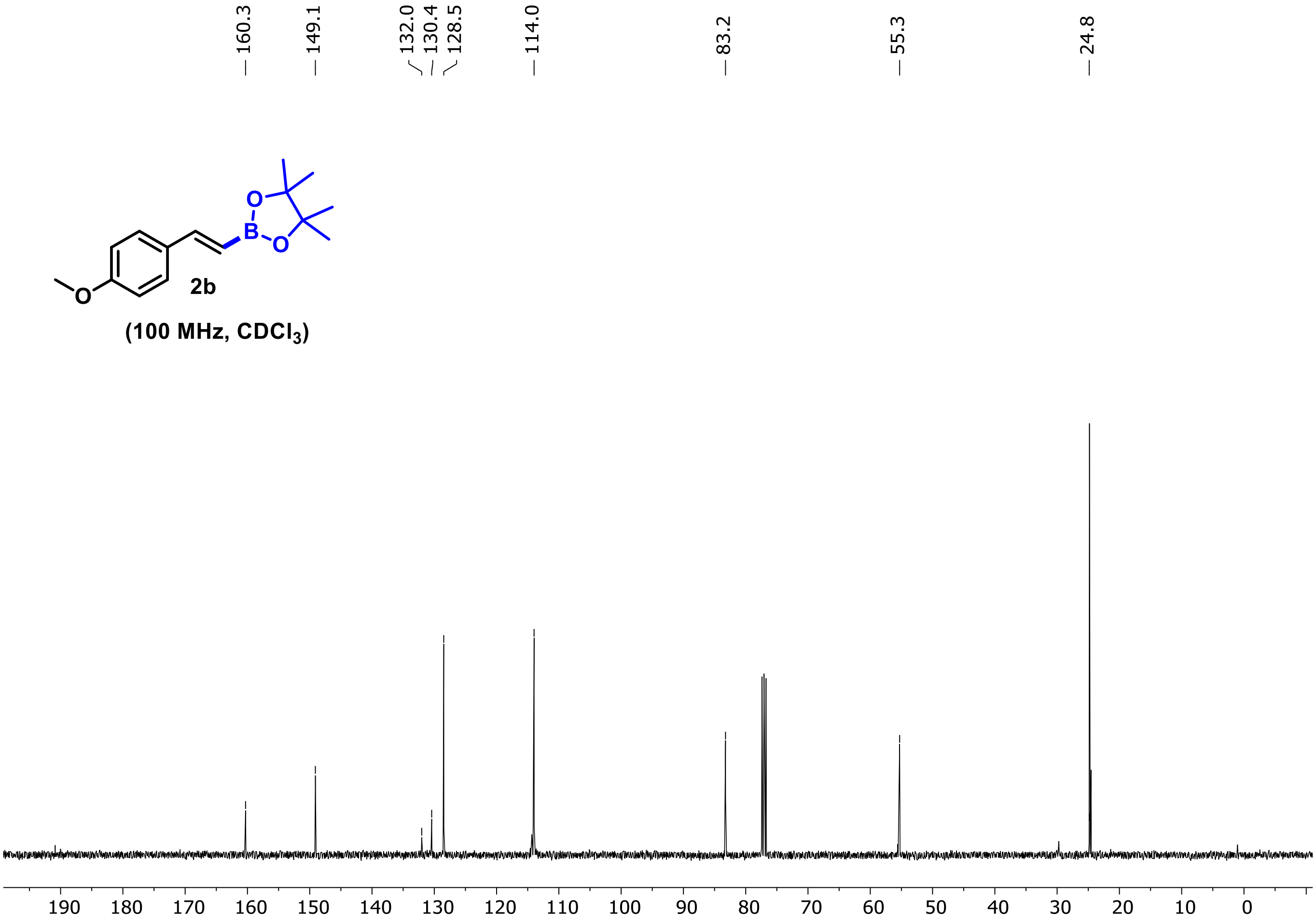
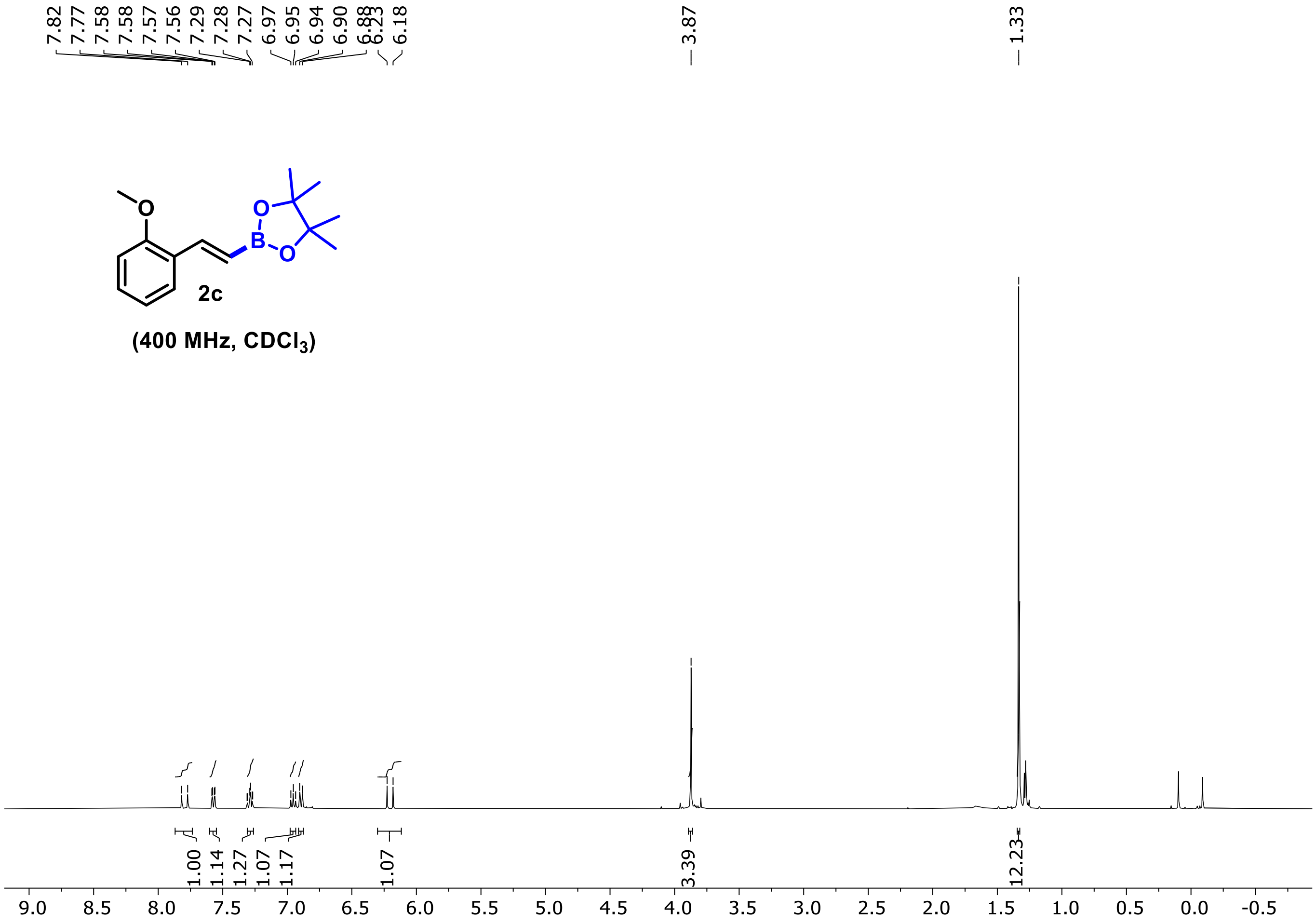
7.35
7.30
7.26
6.80
6.78
5.96
5.91
3.73
1.23
O
B
O
2b
(400 MHz, CDCl3)
2.00
0.99
2.07
0.97
3.15
12.39
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0


160.3
149.1
132.0
130.4
128.5
114.0
83.2
55.3
24.8
O
B
O
2b
(100 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0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7.58
7.57
7.56
7.29
7.28
7.27
6.97
6.95
6.94
6.90
6.88
6.23
6.18
3.87
1.33
2c
(400 MHz, CDCl3)
1.00
1.14
1.27
1.07
1.17
1.07
3.39
12.23
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.5
3.0
2.5
2.0
1.5
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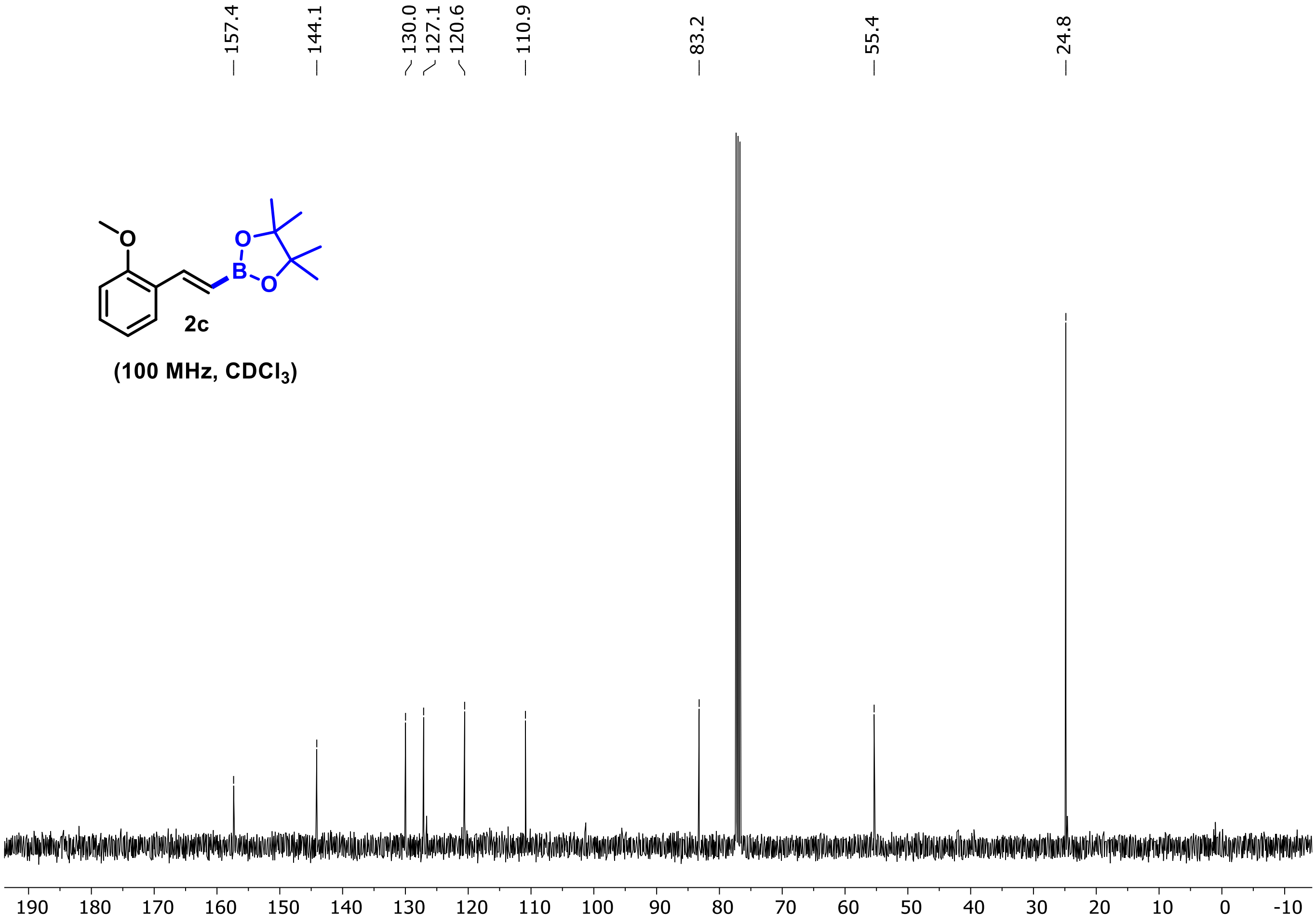
-0.5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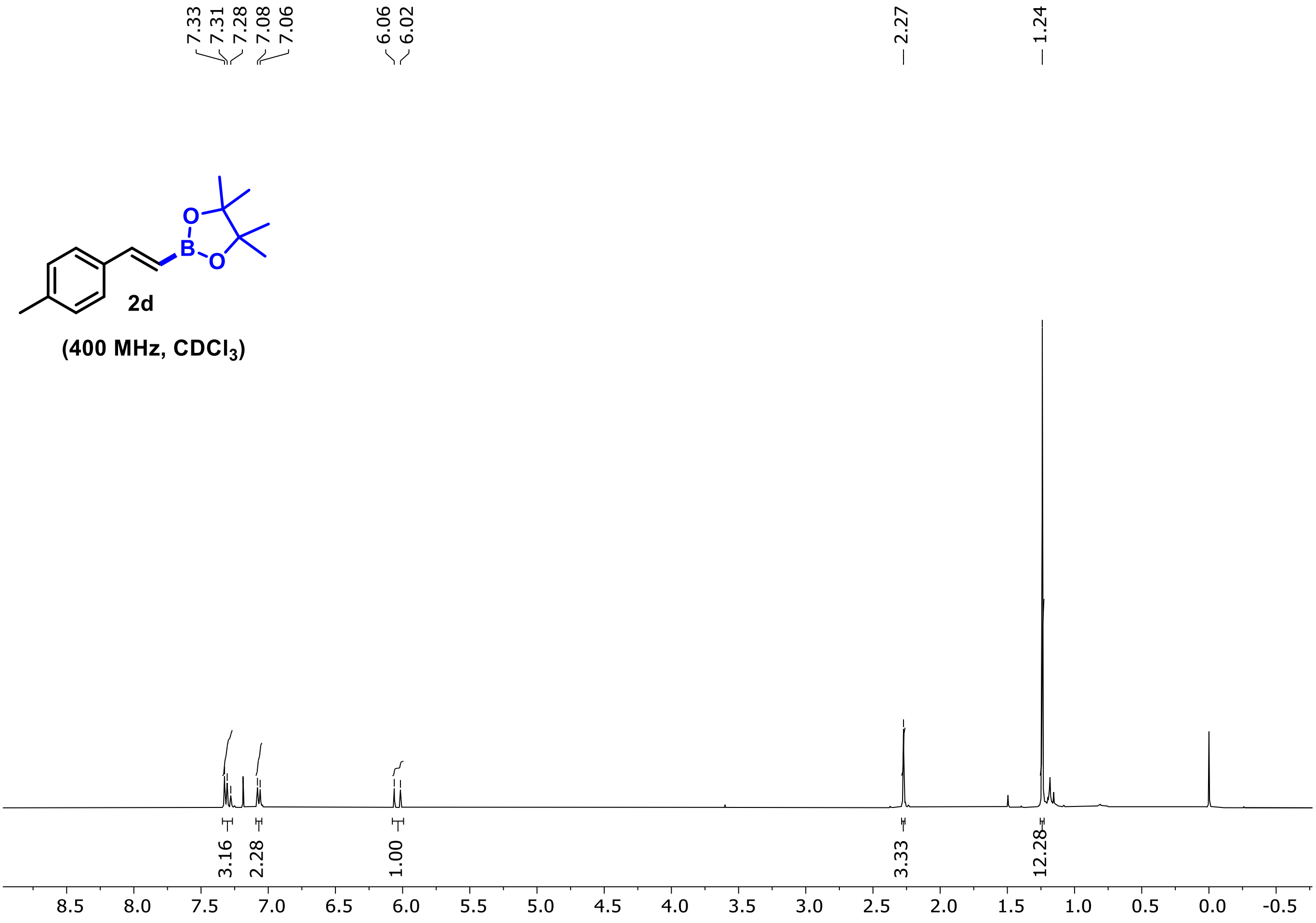
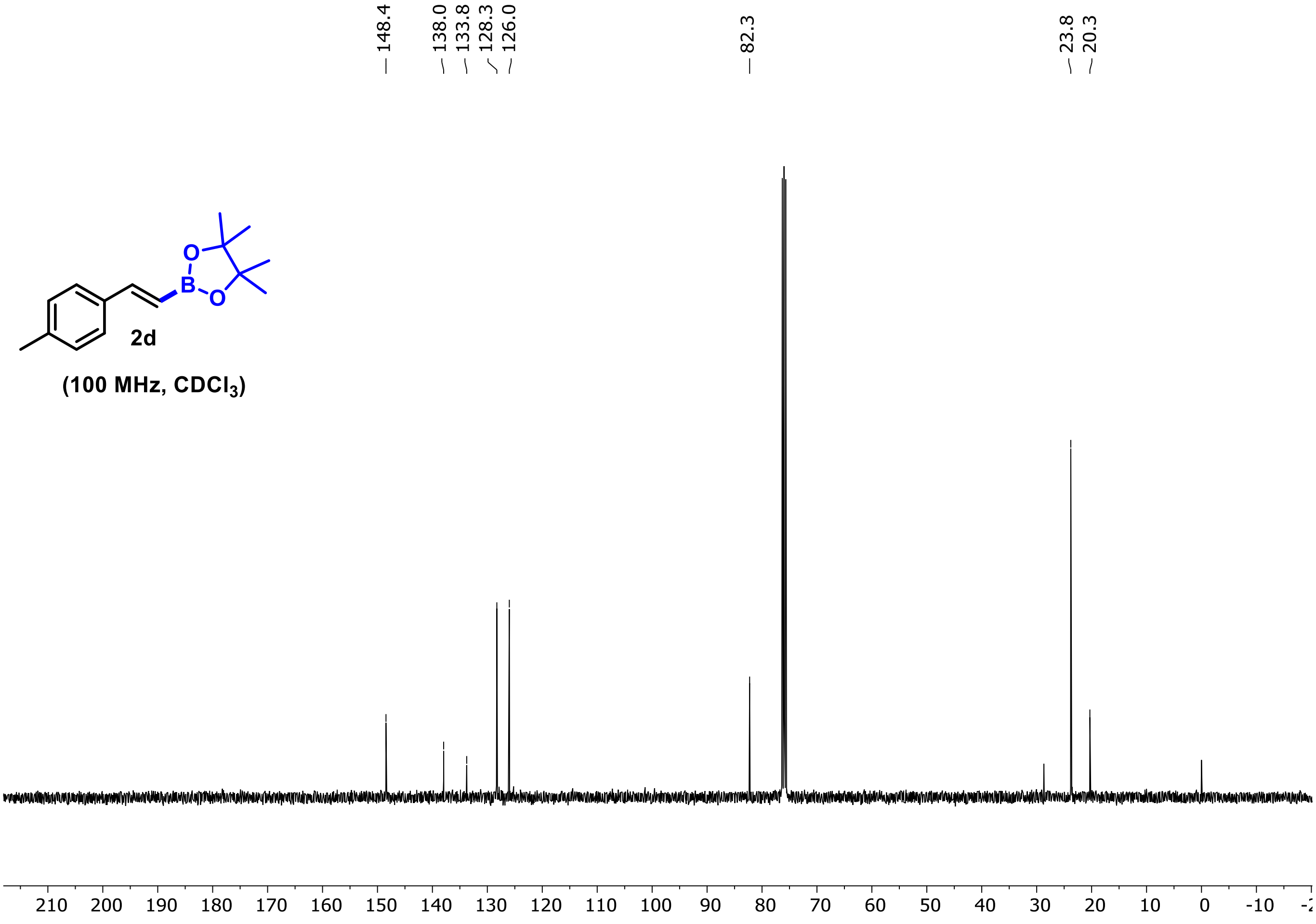
127.1
120.6
110.9
83.2
55.4
24.8
2c
(100 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10



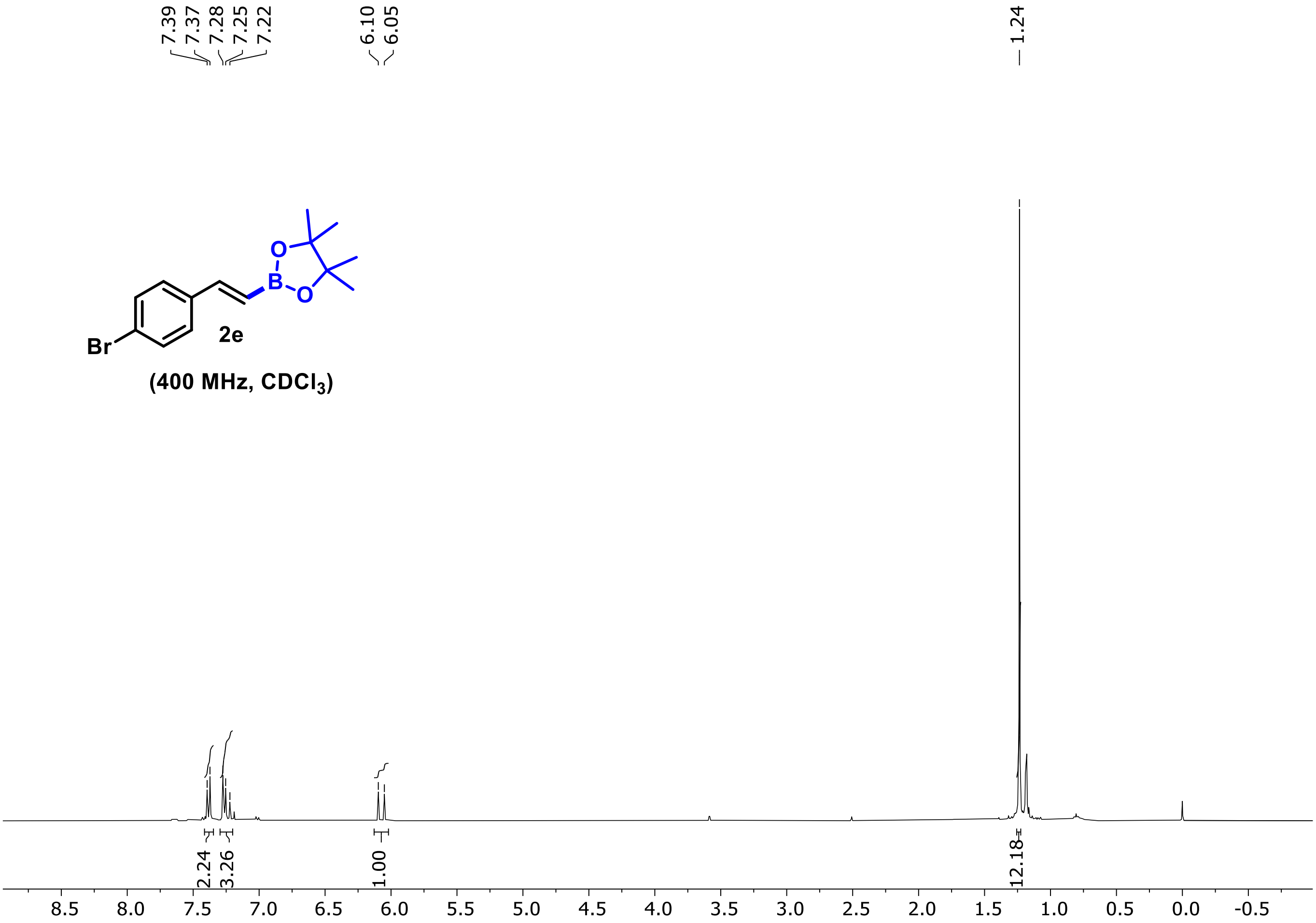
2d

(400 MHz, $CDCl_3$)



2d

(100 MHz, $CDCl_3$)


7.39
7.37
7.28
7.25
7.22
6.10
6.05
1.24
Br
O
B
O
2e
(400 MHz, CDCl$_3$)
2.24
3.26
1.00
12.18
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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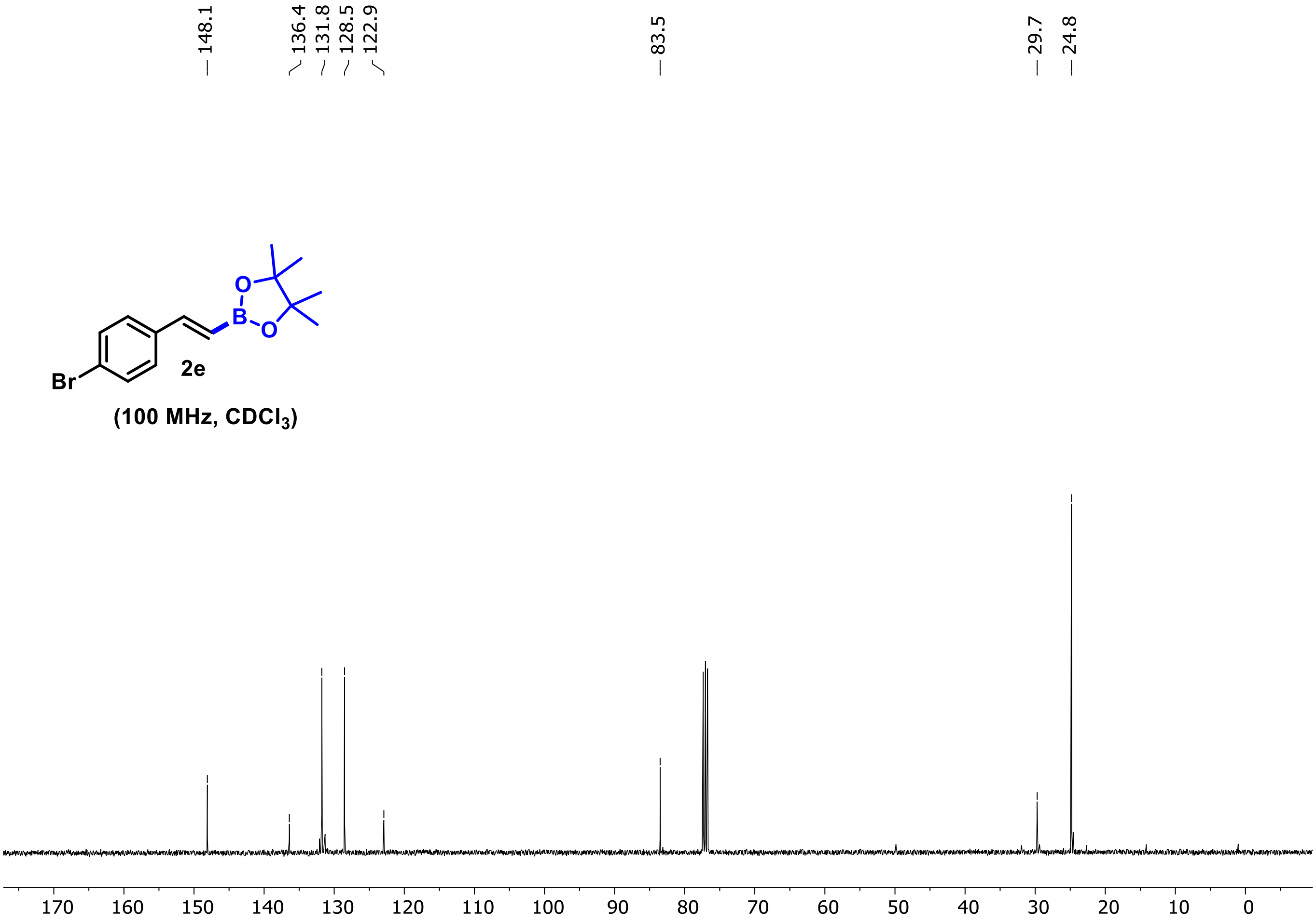
148.1
136.4
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Br
O
B
O
2e
(100 MHz, CDCl$_3$)
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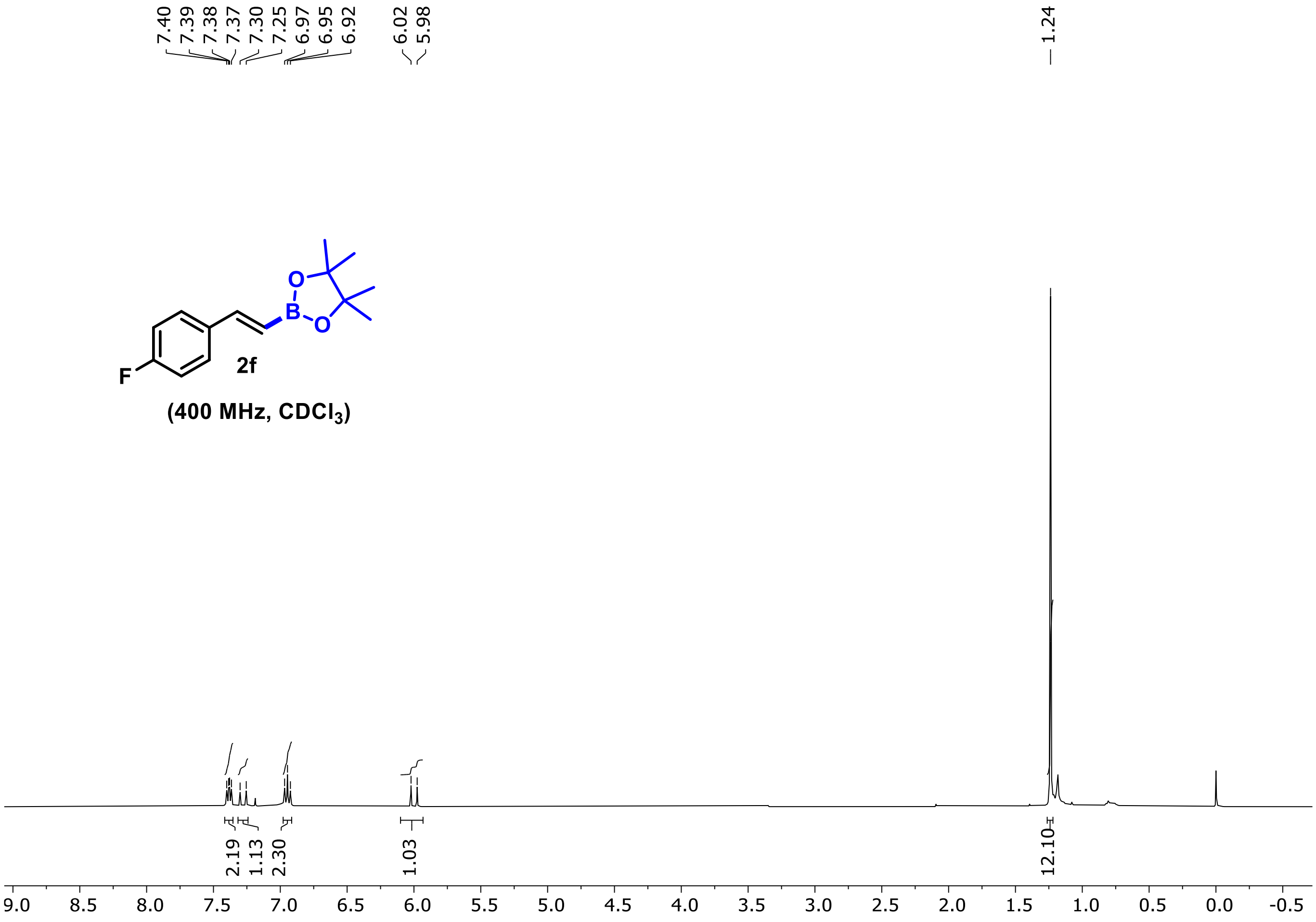
60
50
40
30
20
10
0


7.40
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7.38
7.37
7.30
7.25
6.97
6.95
6.92
6.02
5.98
1.24
F
O
B
O
2f
(400 MHz, CDCl$_3$)
2.19
1.13
2.30
1.03
12.10
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.5
3.0
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2.0
1.5
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0.0
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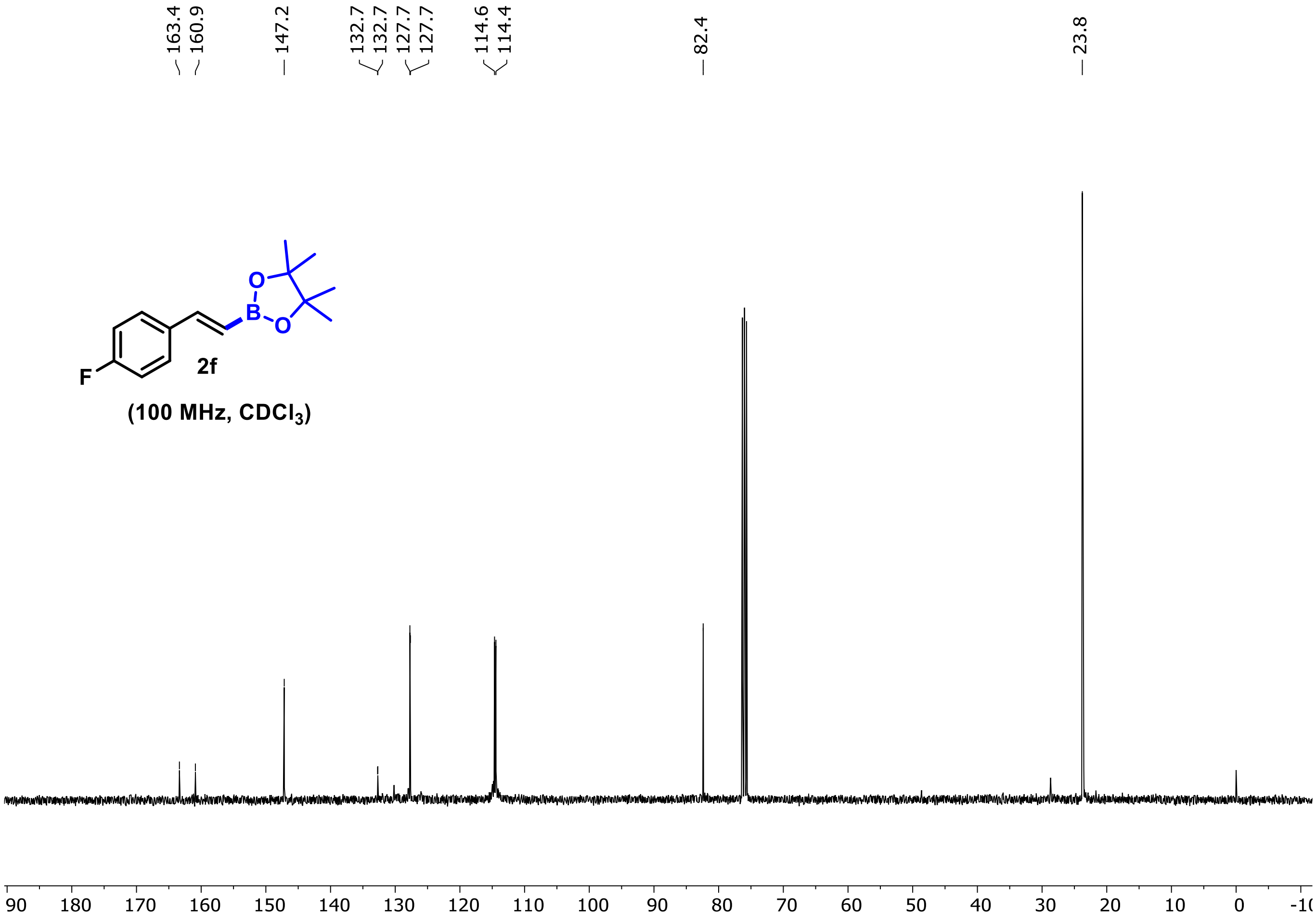
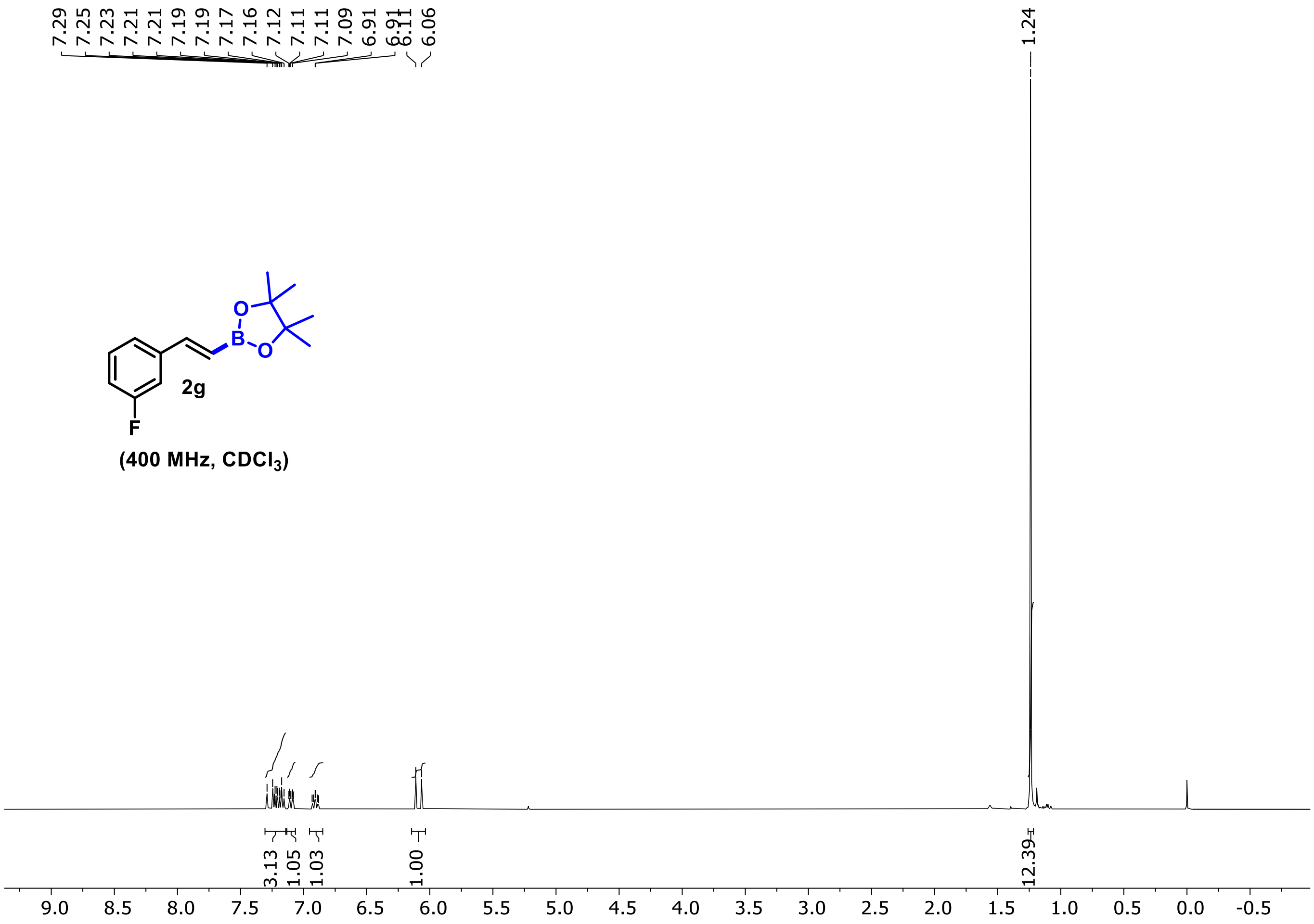
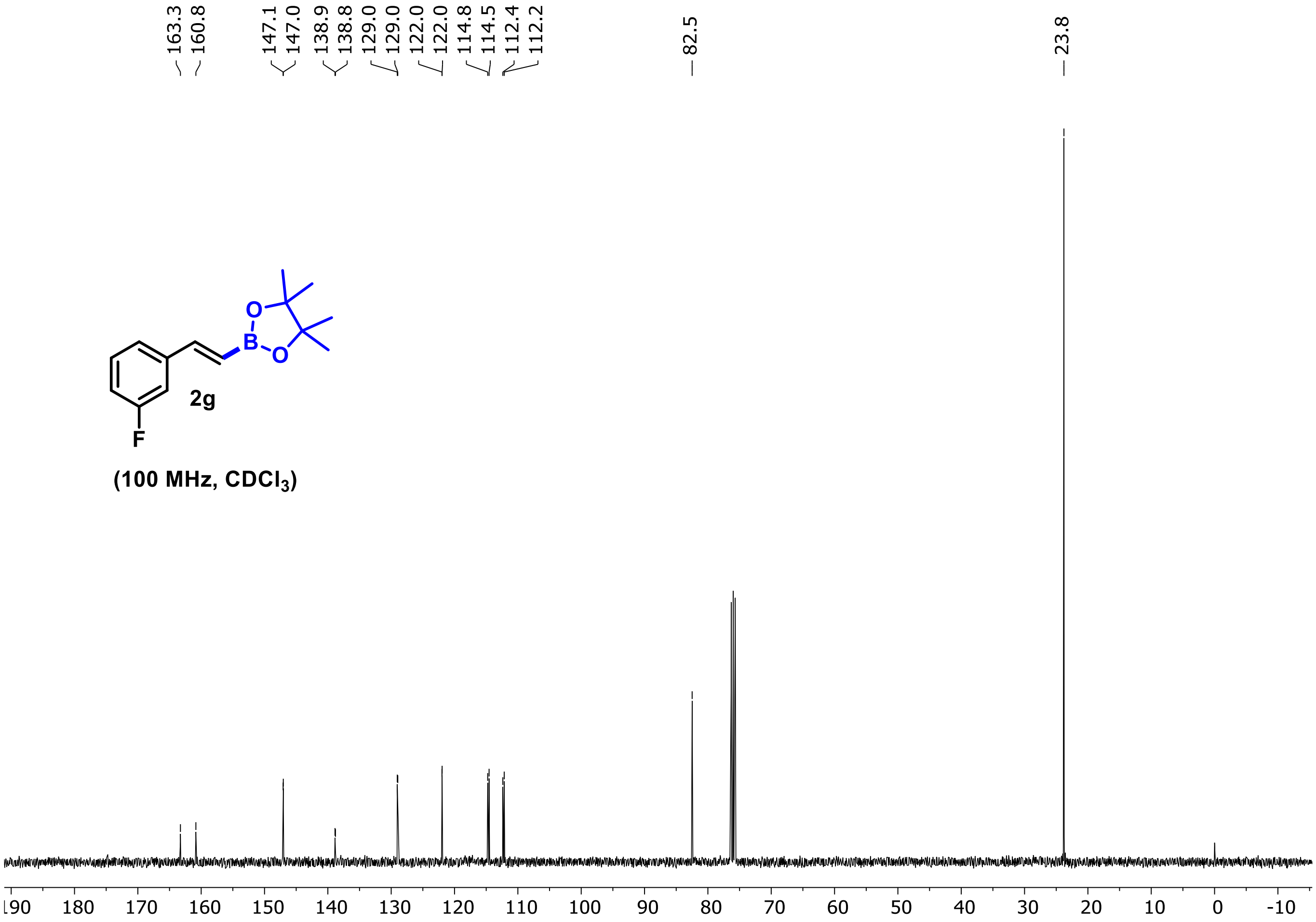
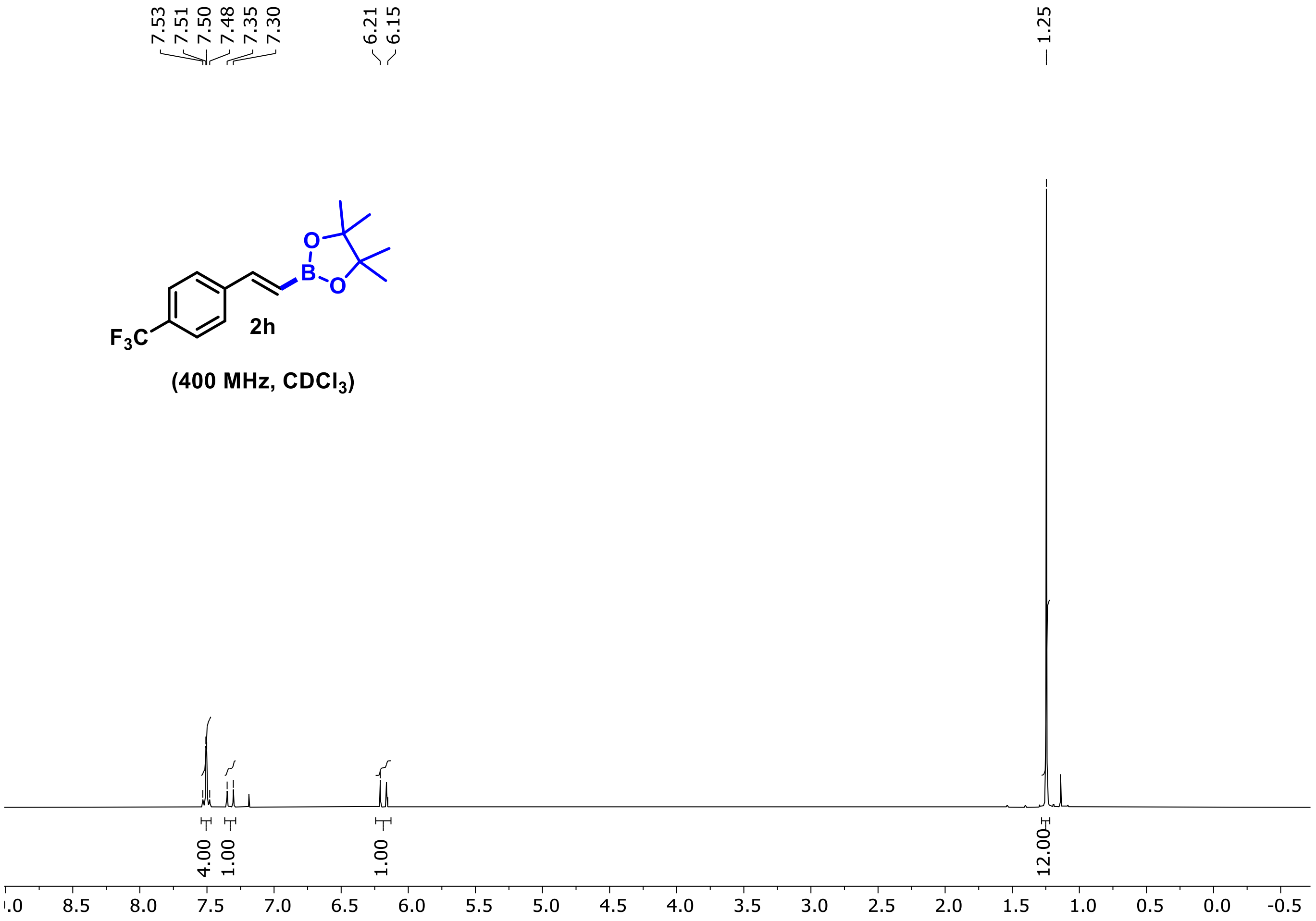
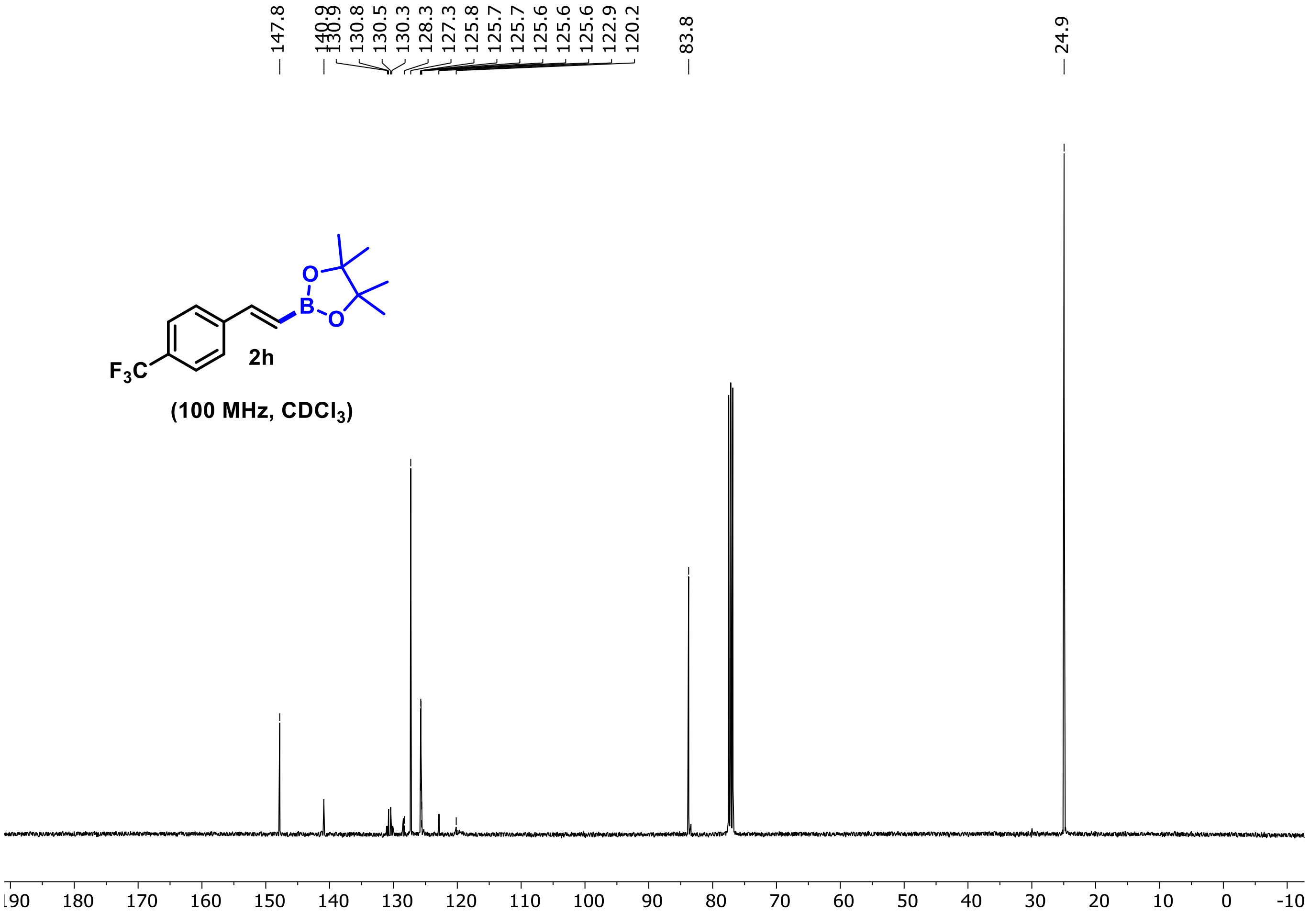
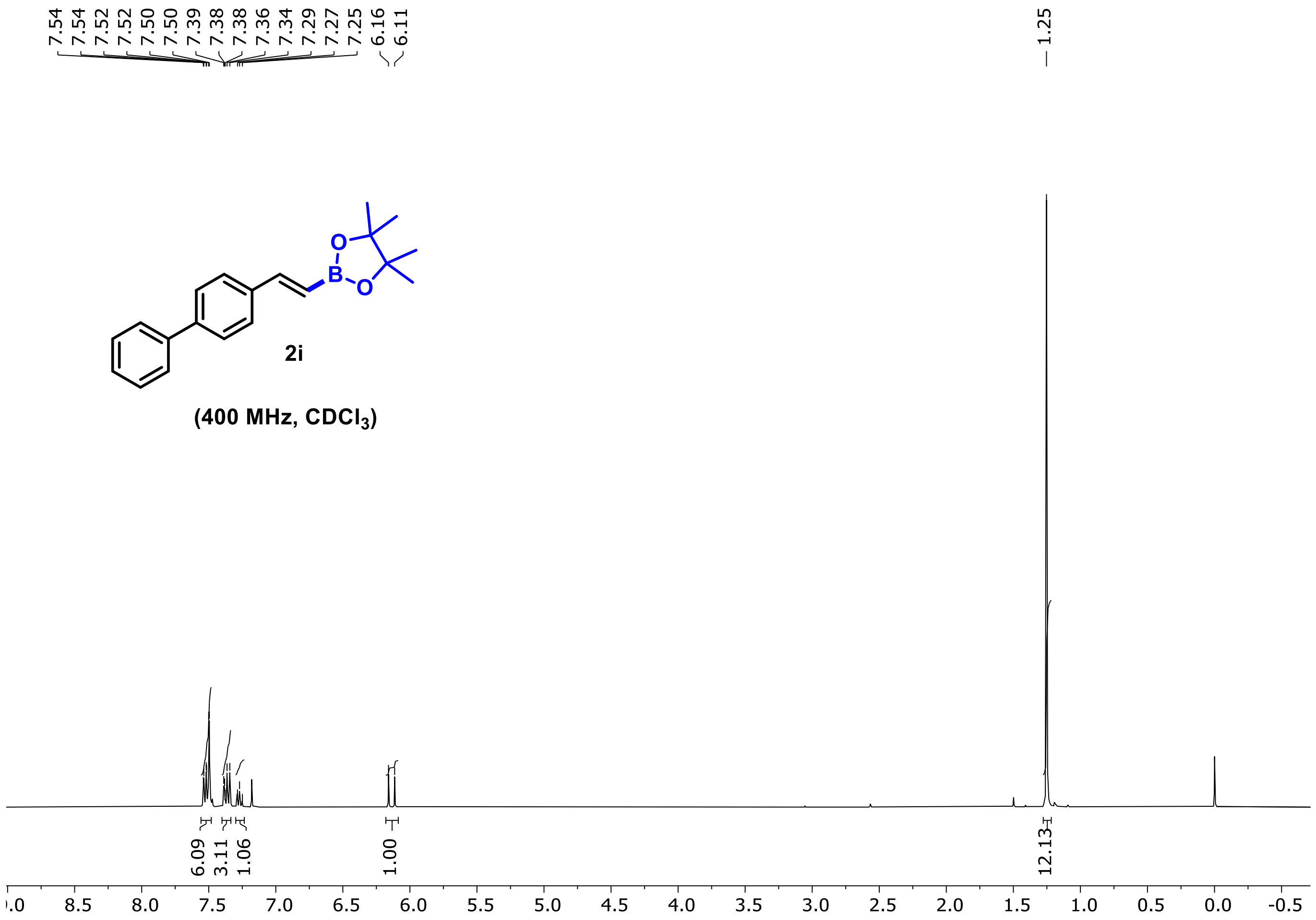

163.4
160.9
147.2
132.7
132.7
127.7
127.7
114.6
114.4
82.4
23.8
F
O
B
O
2f
(100 MHz, CDCl$_3$)
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1(

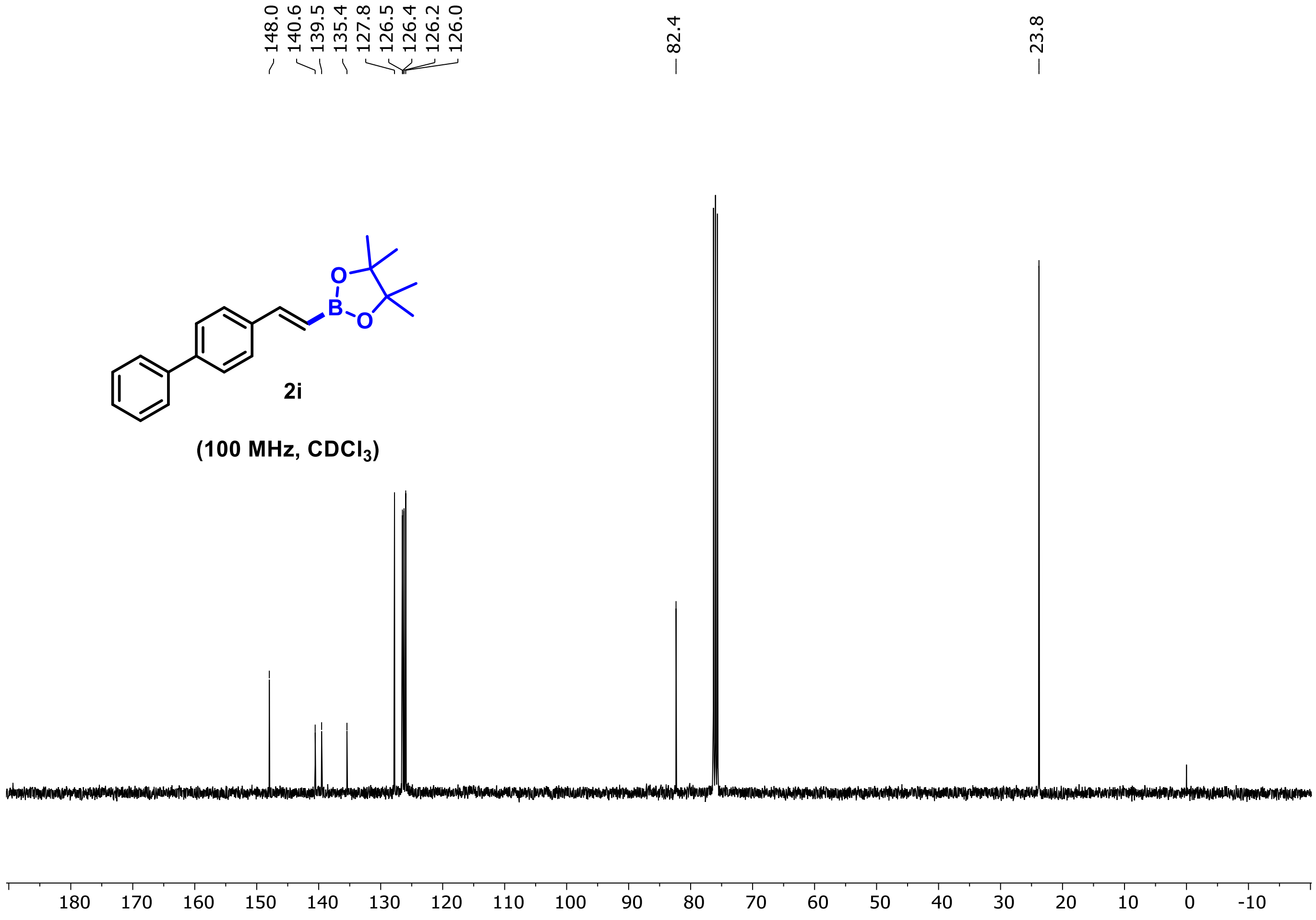

7.29
7.25
7.23
7.21
7.21
7.19
7.19
7.17
7.16
7.12
7.11
7.11
7.09
6.91
6.11
6.06
1.24
O
B
O
F
2g
(400 MHz, CDCl3)
3.13
1.05
1.03
1.00
12.39
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

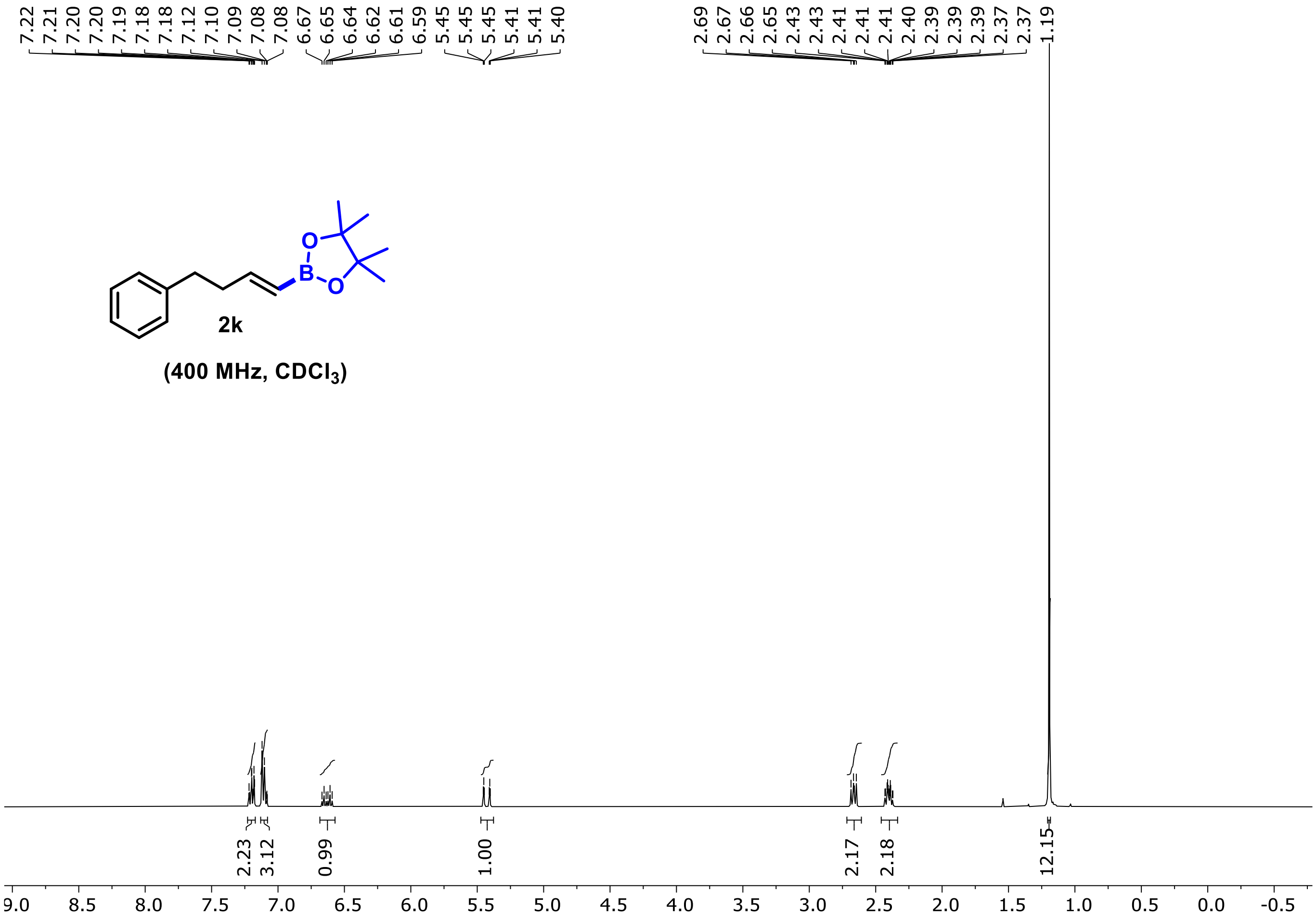

163.3
160.8
147.1
147.0
138.9
138.8
129.0
129.0
122.0
122.0
114.8
114.5
112.4
112.2
82.5
23.8
O
B
O
F
2g
(100 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


7.53
7.51
7.50
7.48
7.35
7.30
6.21
6.15
1.25
F3C
O
B
O
2h
(400 MHz, CDCl3)
4.00
1.00
1.00
12.00
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

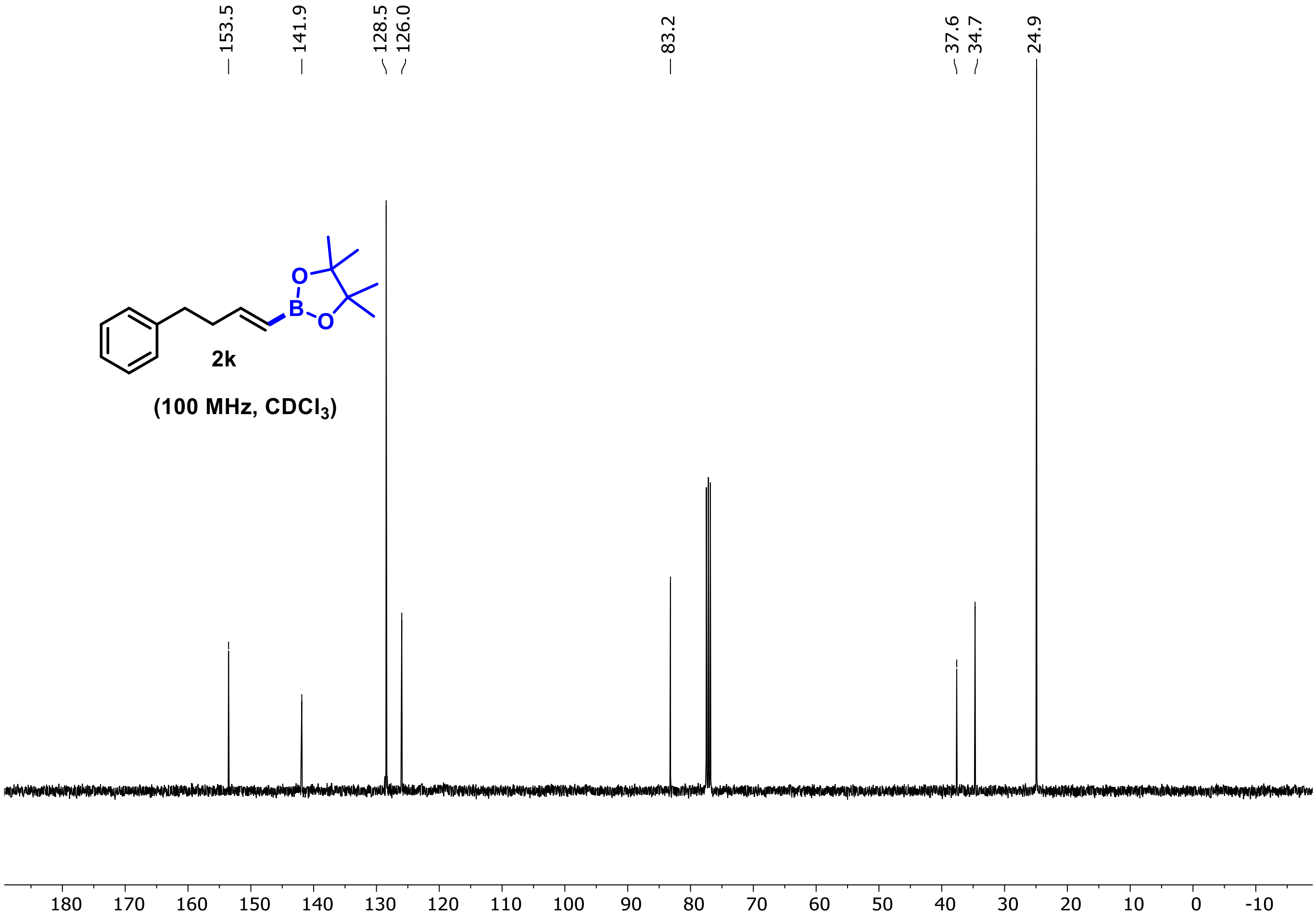

147.8
140.9
130.9
130.8
130.5
130.3
128.3
127.3
125.8
125.7
125.7
125.6
125.6
125.6
122.9
120.2
83.8
24.9
F3C
O
B
O
2h
(100 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


7.54
7.54
7.52
7.52
7.50
7.50
7.39
7.38
7.38
7.36
7.34
7.29
7.27
7.25
6.16
6.11
1.25
O
B
O
2i
(400 MHz, CDCl3)
6.09
3.11
1.06
1.00
12.13
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

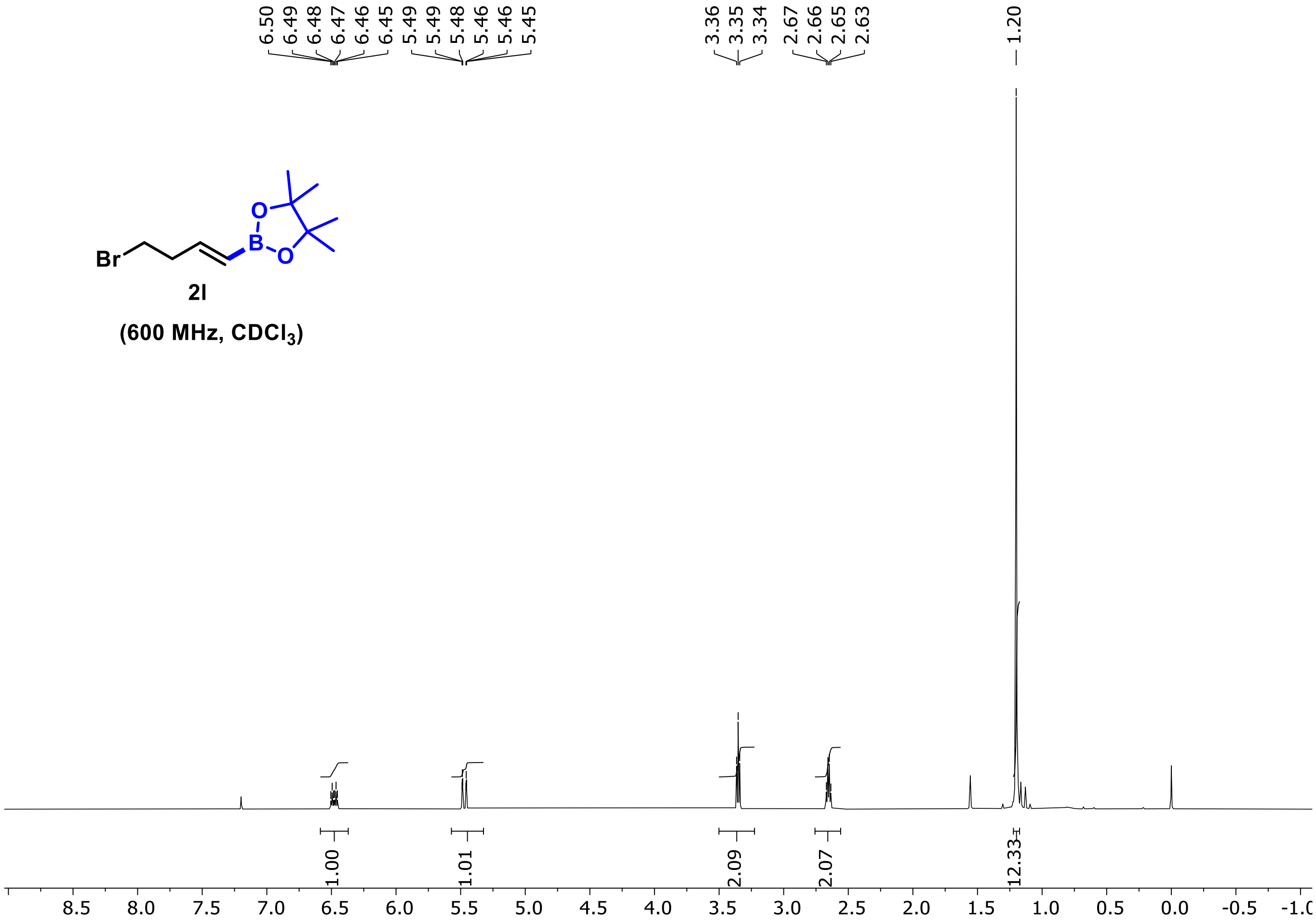

148.0
140.6
139.5
135.4
127.8
126.5
126.4
126.2
126.0
82.4
23.8
O
B
O
2i
(100 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

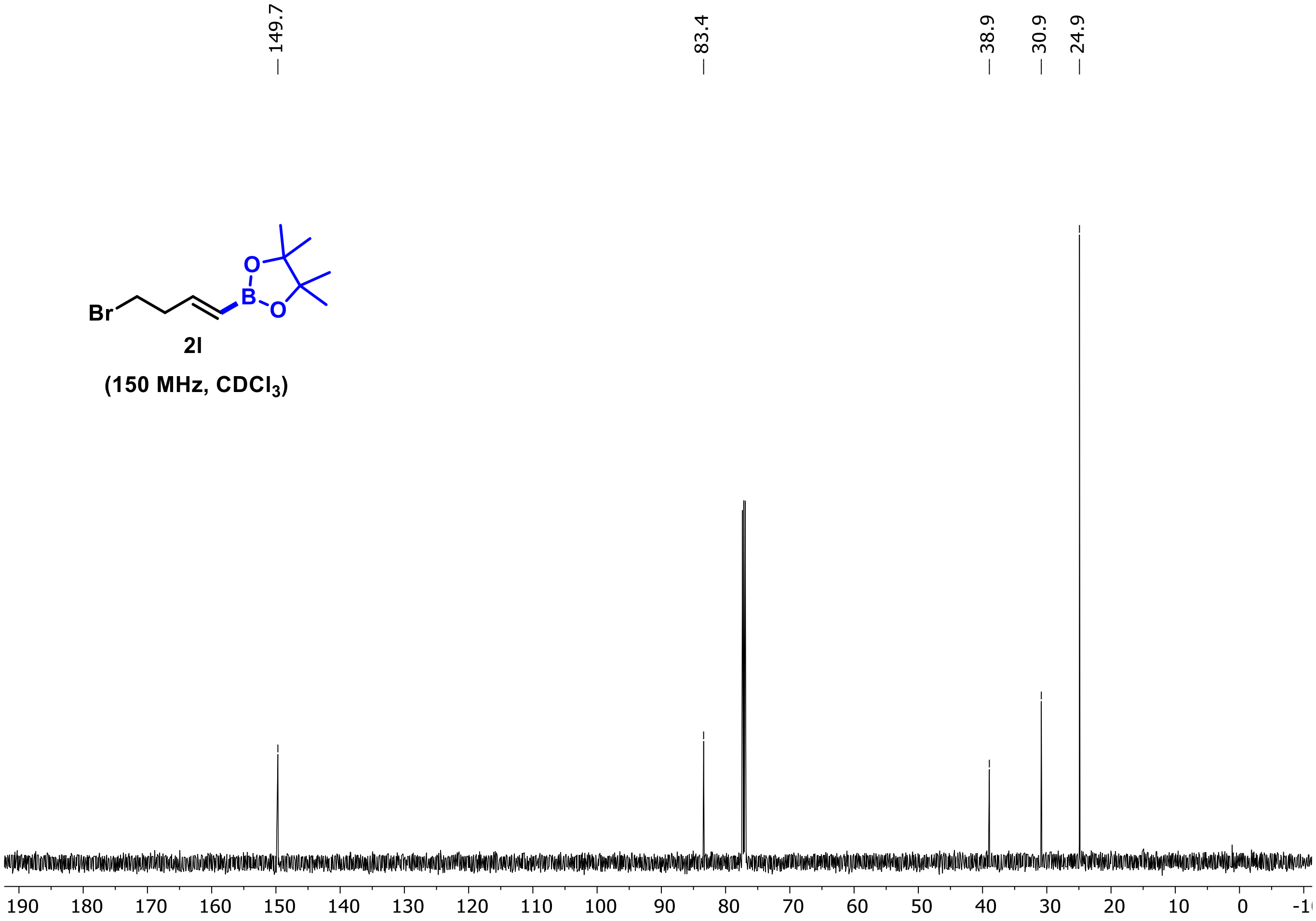

2k

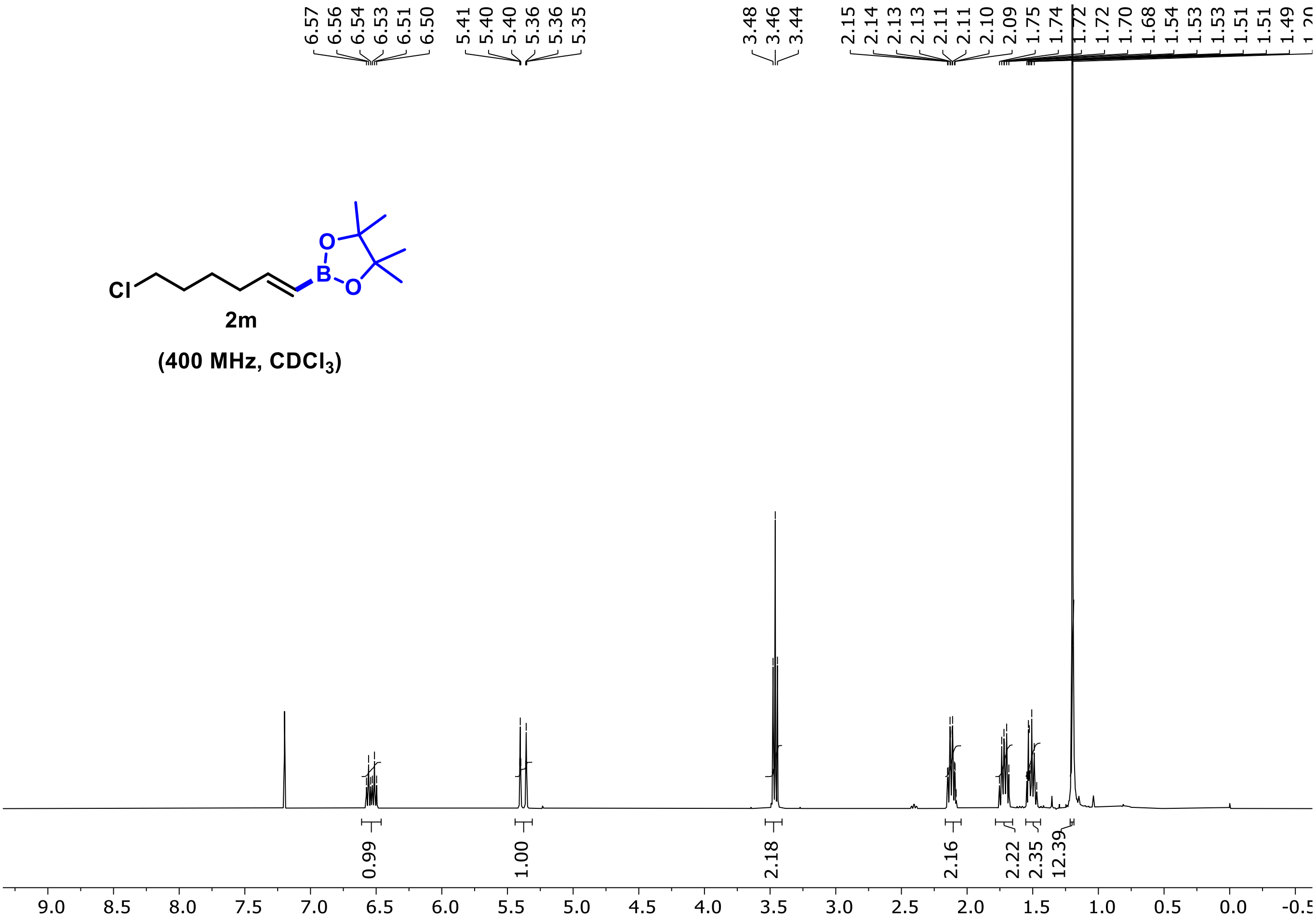
(400 MHz, $CDCl_3$)

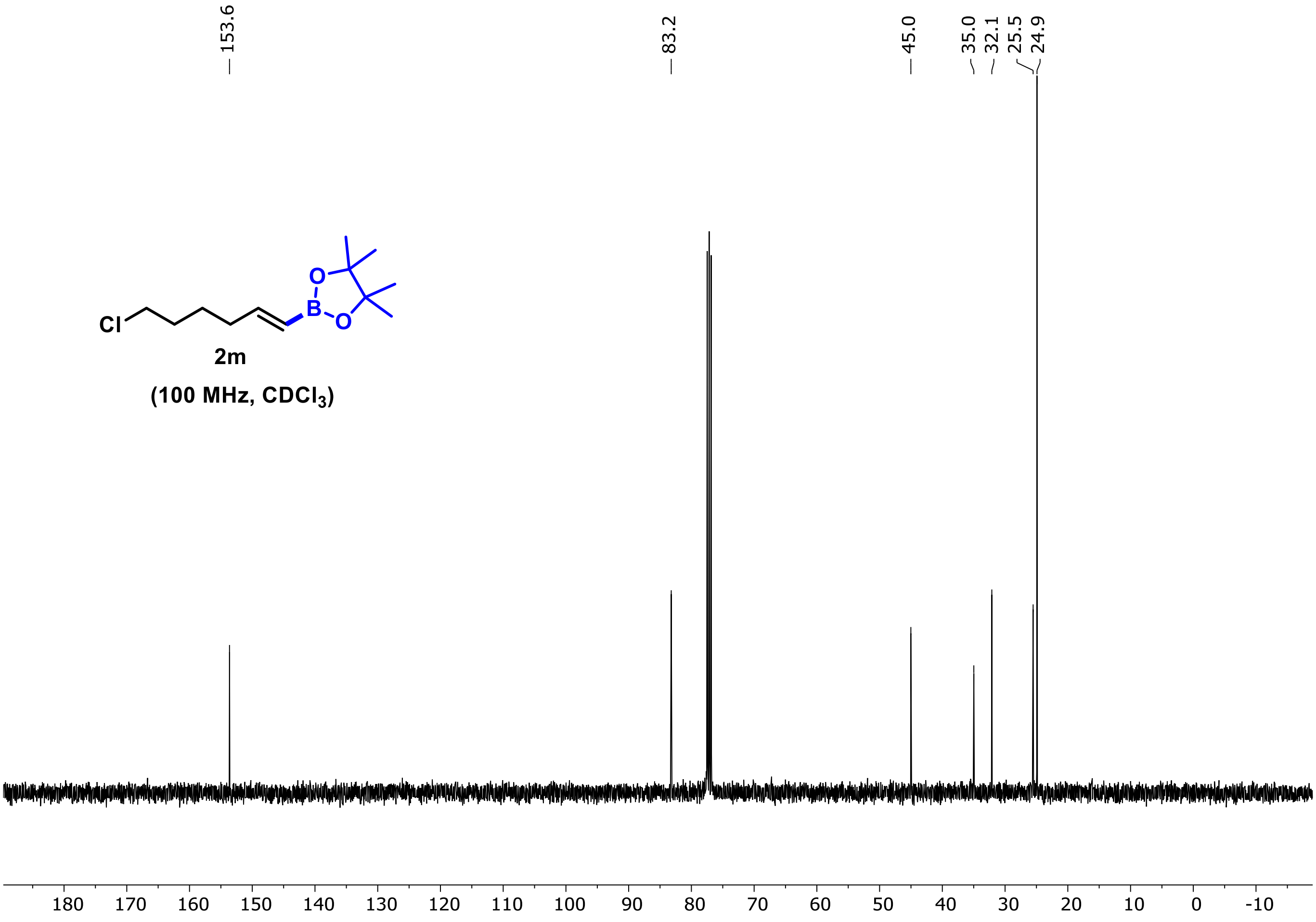

2k

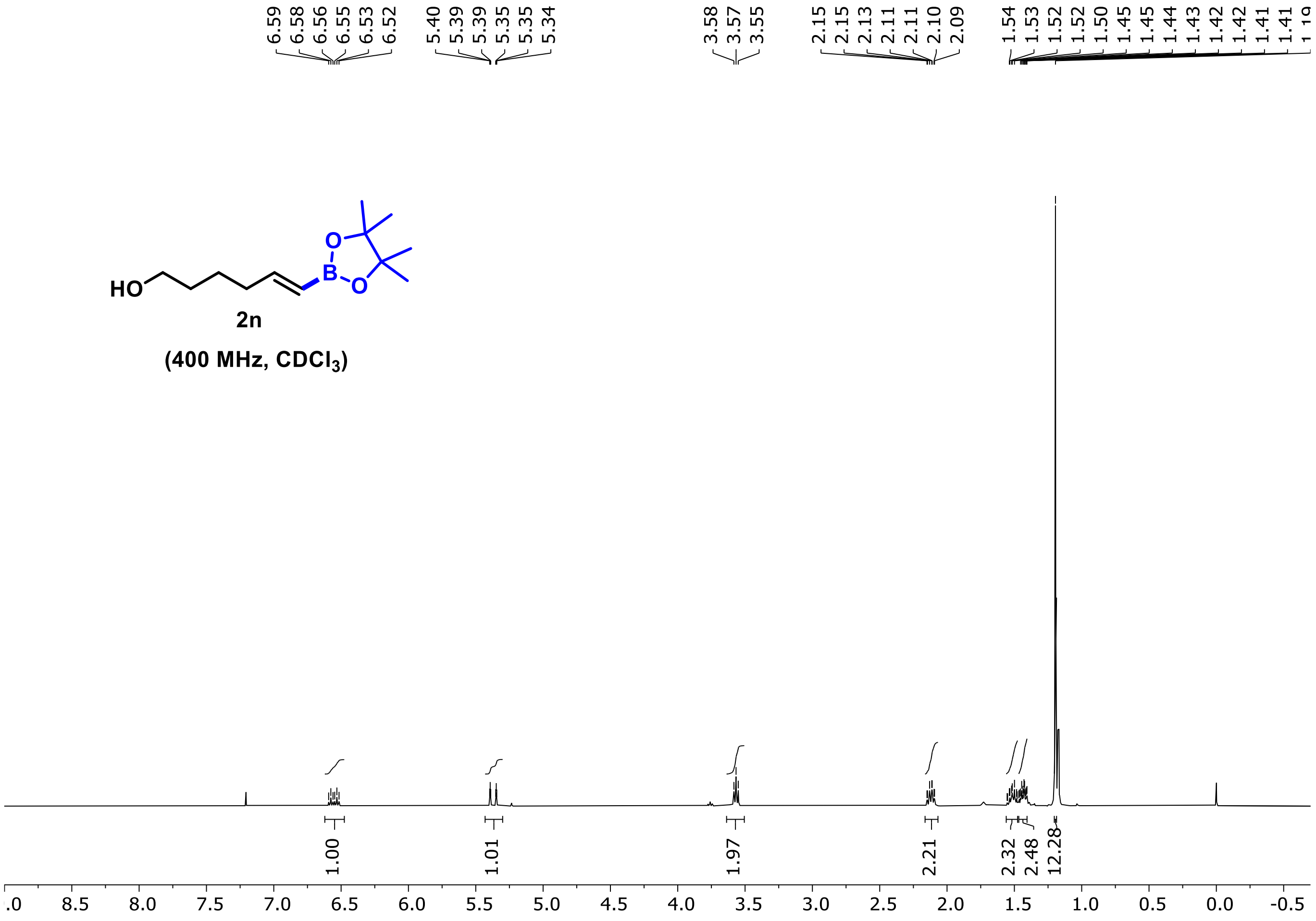
(100 MHz, $CDCl_3$)

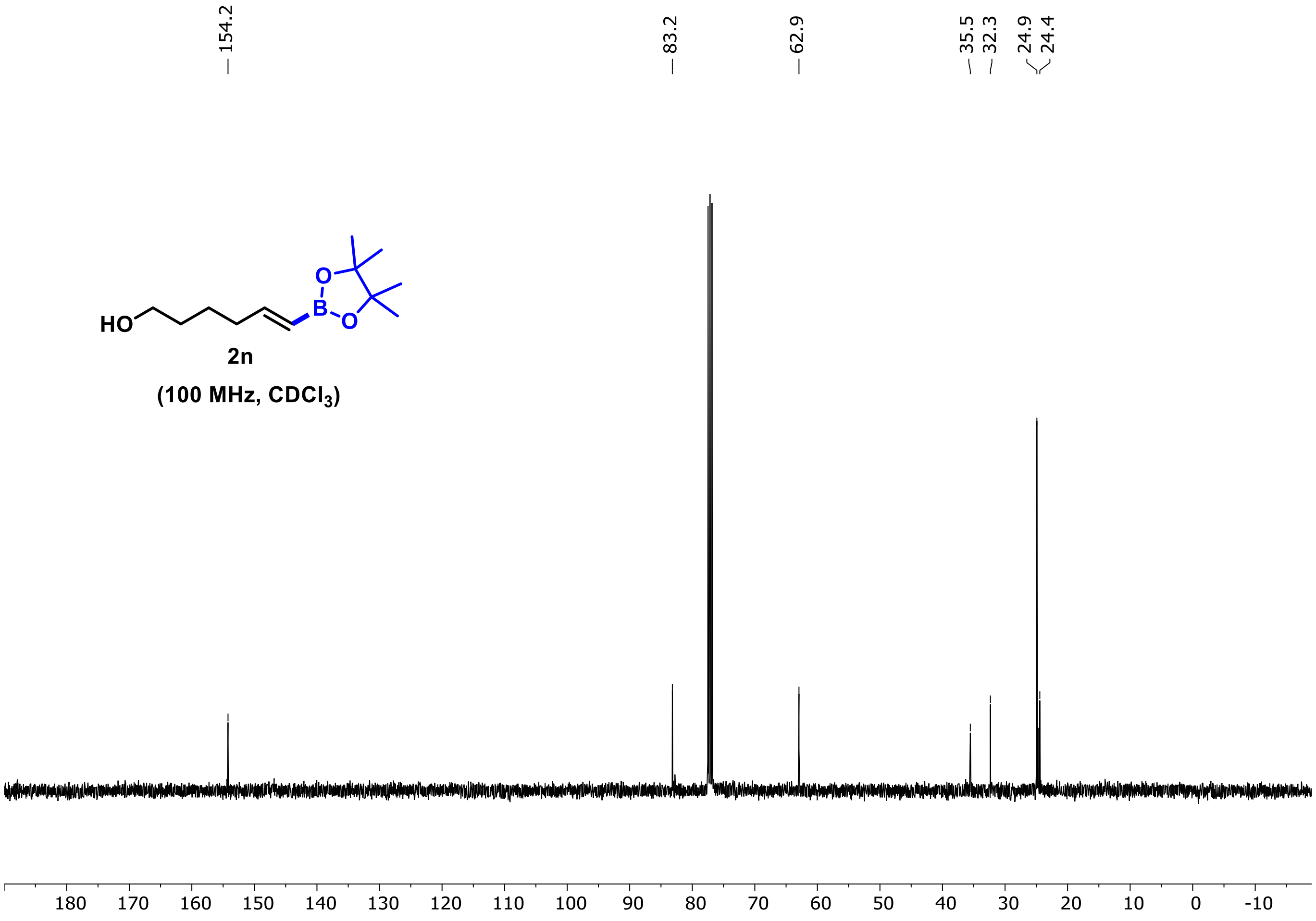

6.50 6.49 6.48 6.47 6.46 6.45 5.49 5.49 5.48 5.46 5.46 5.45
3.36 3.35 3.34 2.67 2.66 2.65 2.63
1.20
Br
O
B
O
2l
(600 MHz, CDCl$_3$)
1.00
1.01
2.09
2.07
12.33
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0

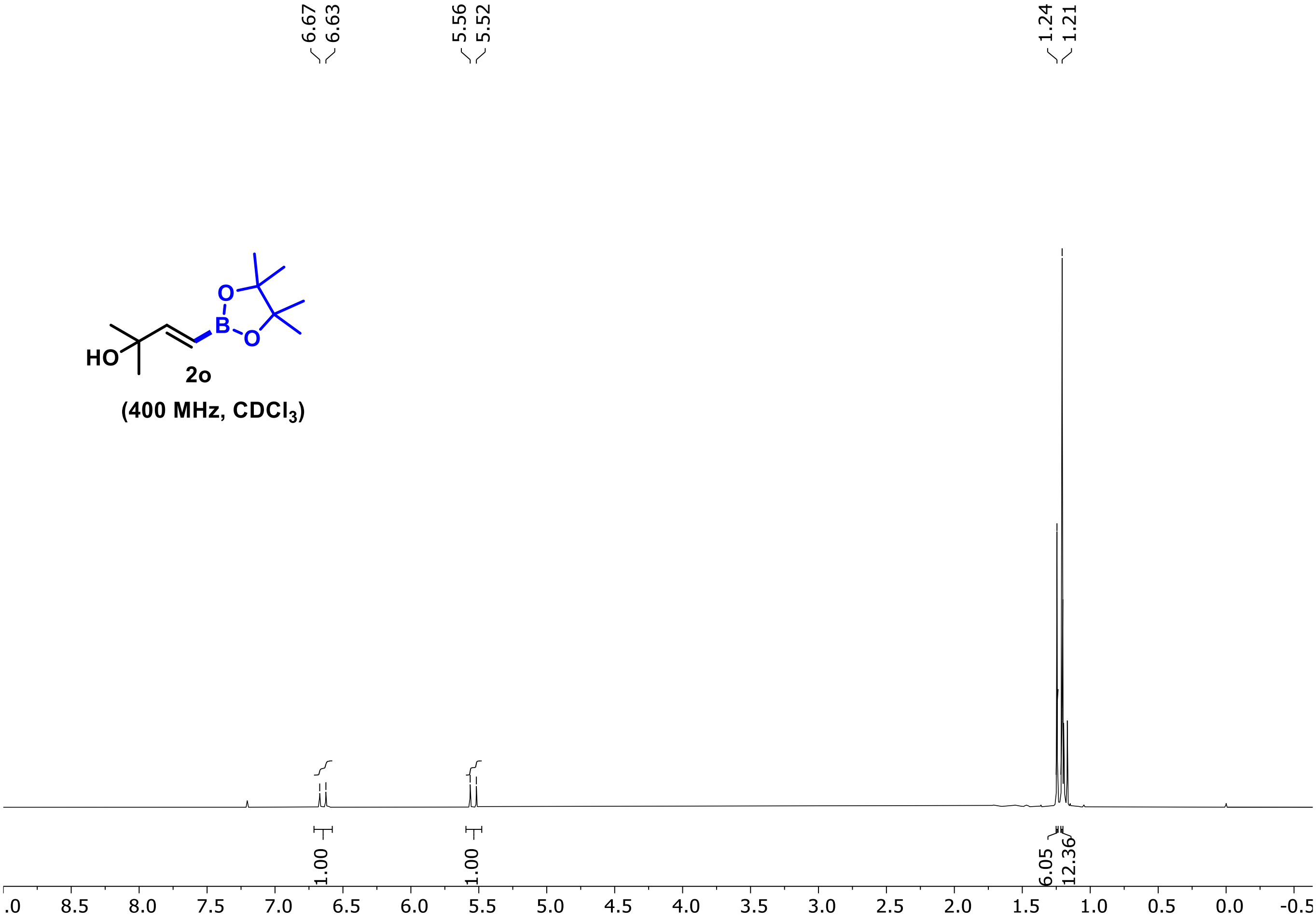

149.7
83.4
38.9
30.9
24.9
Br
O
B
O
2l
(150 MHz, CDCl$_3$)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

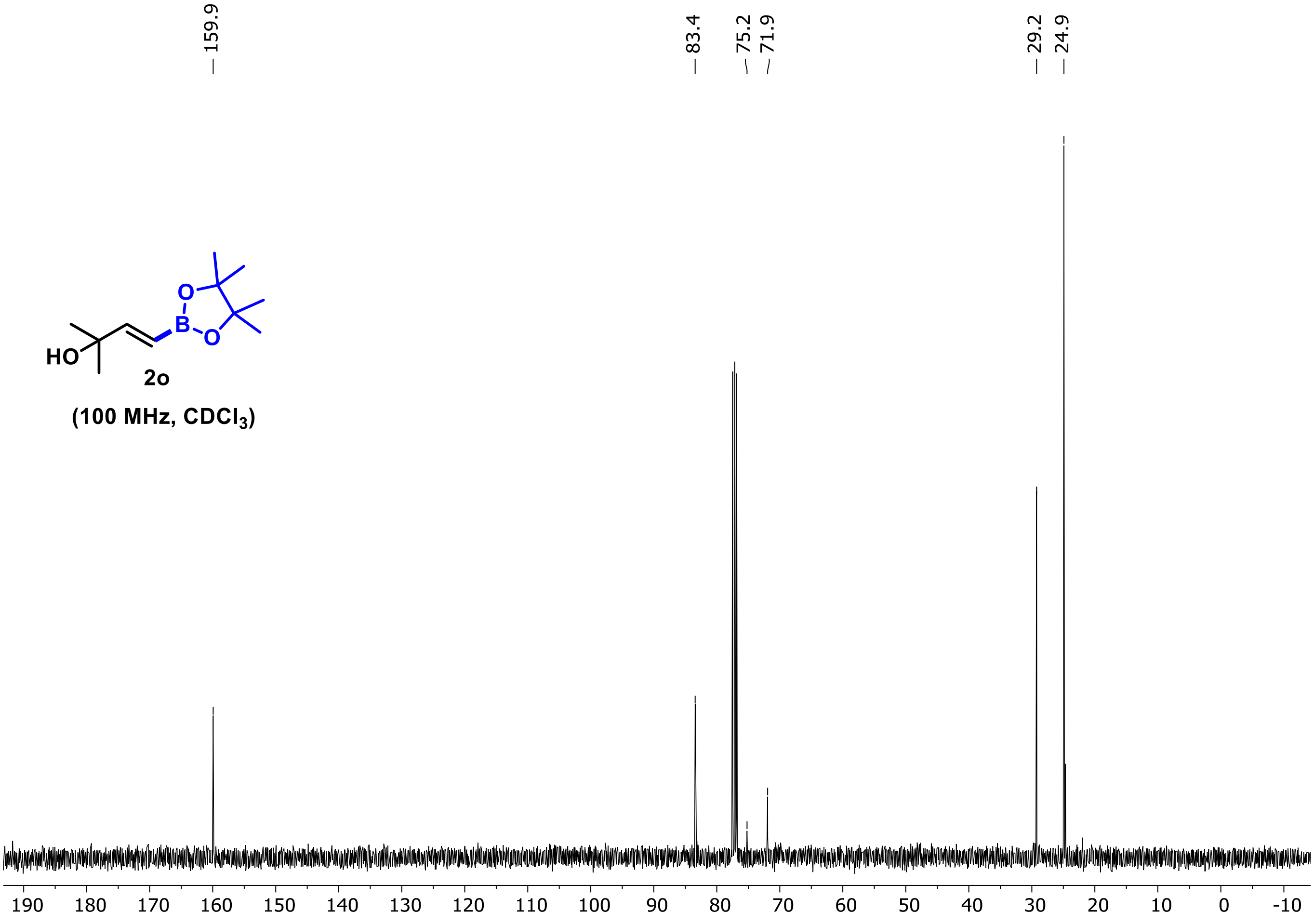

6.57
6.56
6.54
6.53
6.51
6.50
5.41
5.40
5.40
5.36
5.36
5.35
3.48
3.46
3.44
2.15
2.14
2.13
2.13
2.11
2.11
2.10
2.09
1.75
1.74
1.72
1.72
1.70
1.68
1.54
1.53
1.53
1.51
1.51
1.49
1.2
Cl
O
B
O
2m
(400 MHz, CDCl$_3$)
0.99
1.00
2.18
2.16
2.22
2.35
12.39
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.

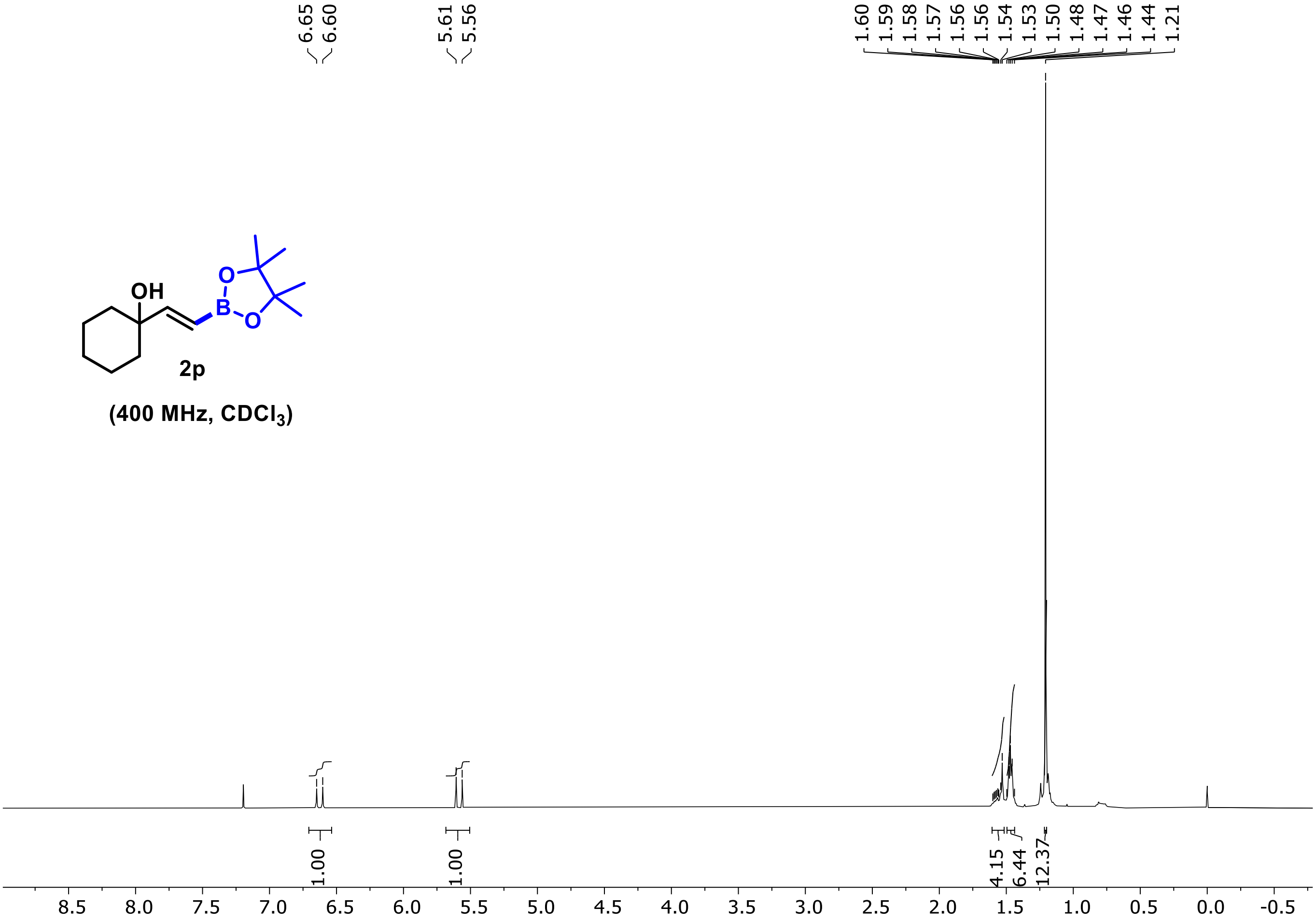

153.6
83.2
45.0
35.0
32.1
25.5
24.9
Cl
O
B
O
2m
(100 MHz, CDCl$_3$)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

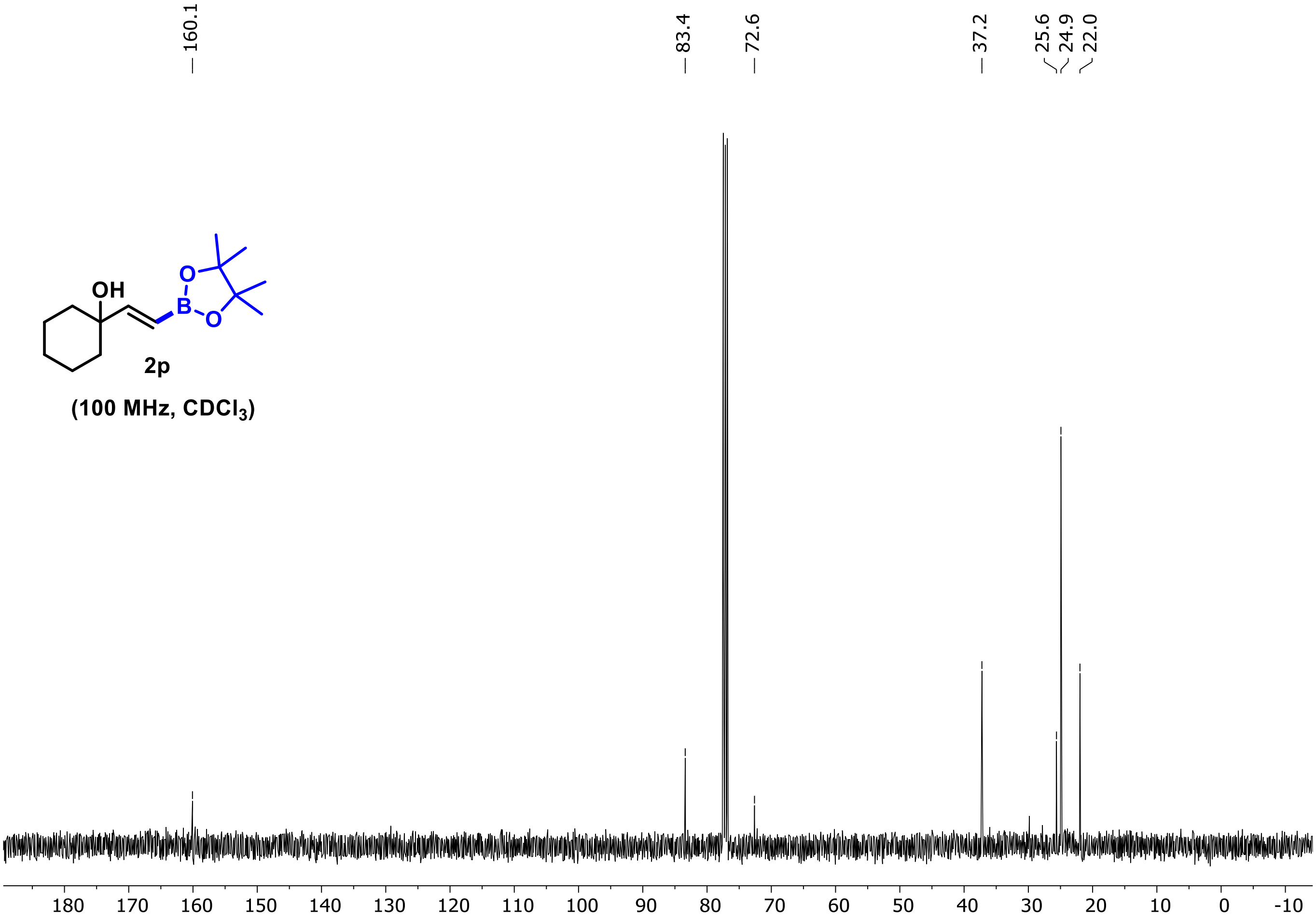

6.59
6.58
6.56
6.55
6.53
6.52
5.40
5.39
5.39
5.35
5.35
5.34
3.58
3.57
3.55
2.15
2.15
2.13
2.11
2.11
2.10
2.09
1.54
1.53
1.52
1.52
1.50
1.45
1.45
1.44
1.43
1.42
1.42
1.41
1.41
HO
O
B
O
2n
(400 MHz, CDCl3)
1.00
1.01
1.97
2.21
2.32
2.48
12.28
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

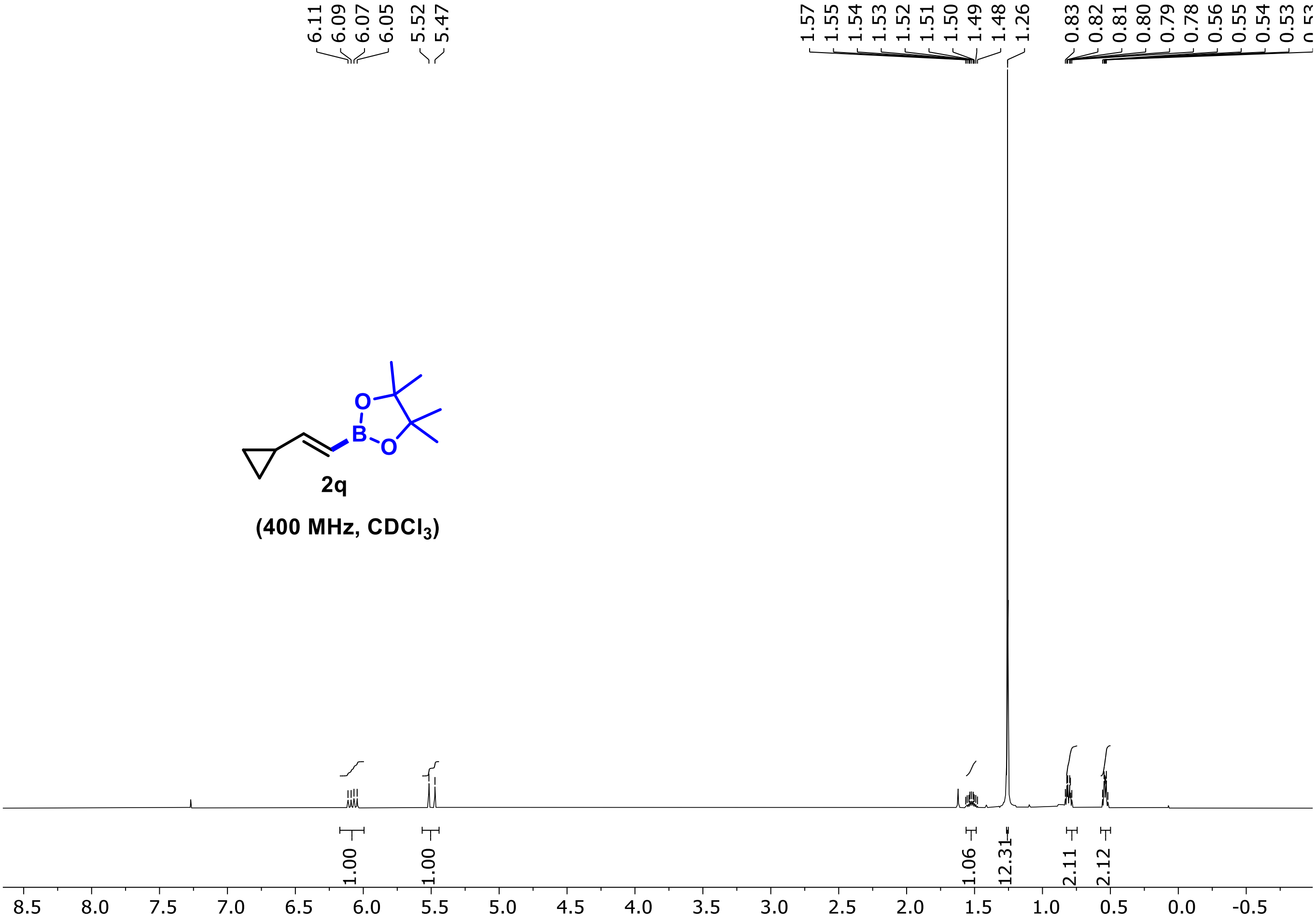

154.2
83.2
62.9
35.5
32.3
24.9
24.4
HO
O
B
O
2n
(100 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

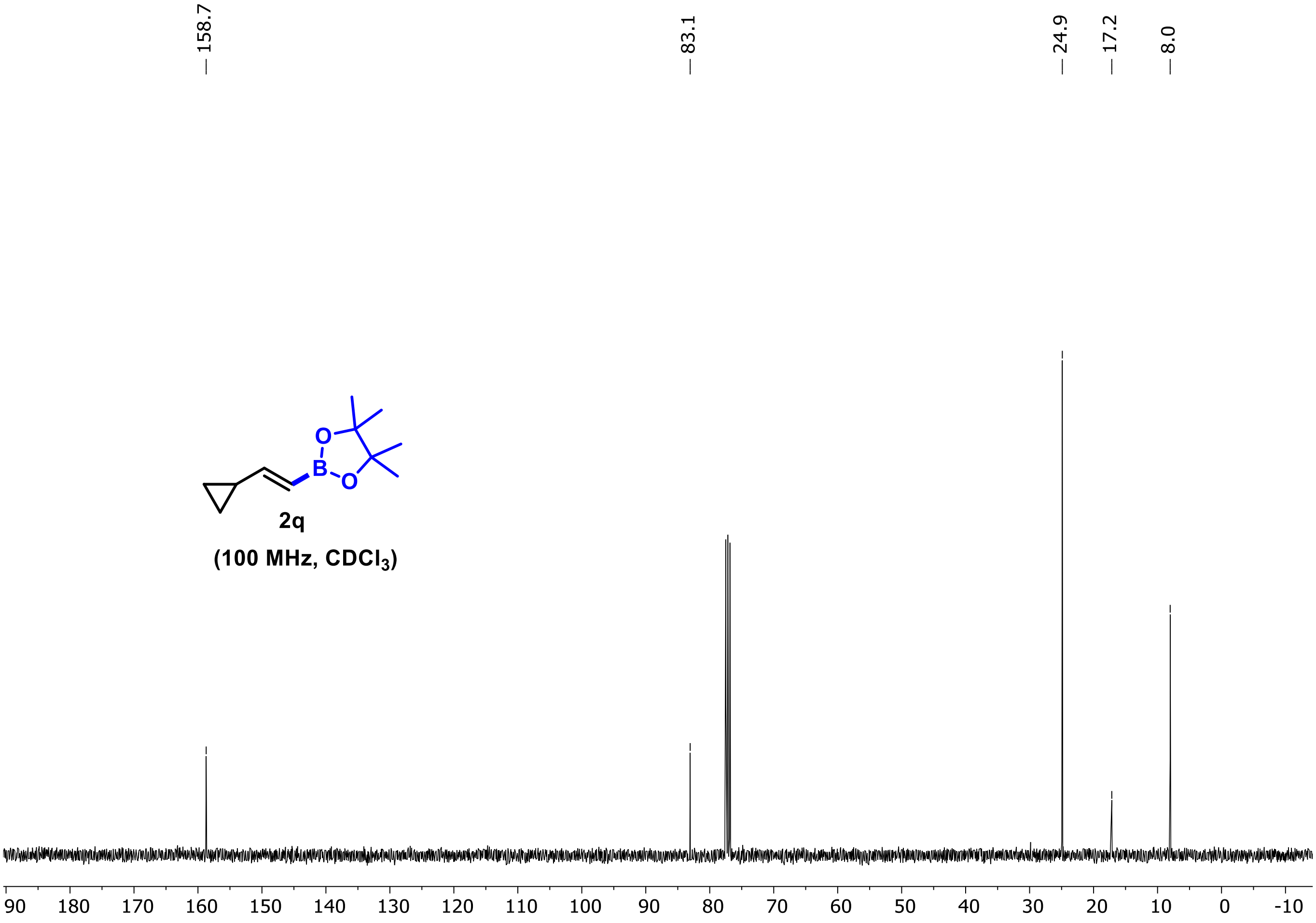

6.67
6.63
5.56
5.52
1.24
1.21
HO
O
B
O
2o
(400 MHz, CDCl$_3$)
1.00
1.00
6.05
12.36
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

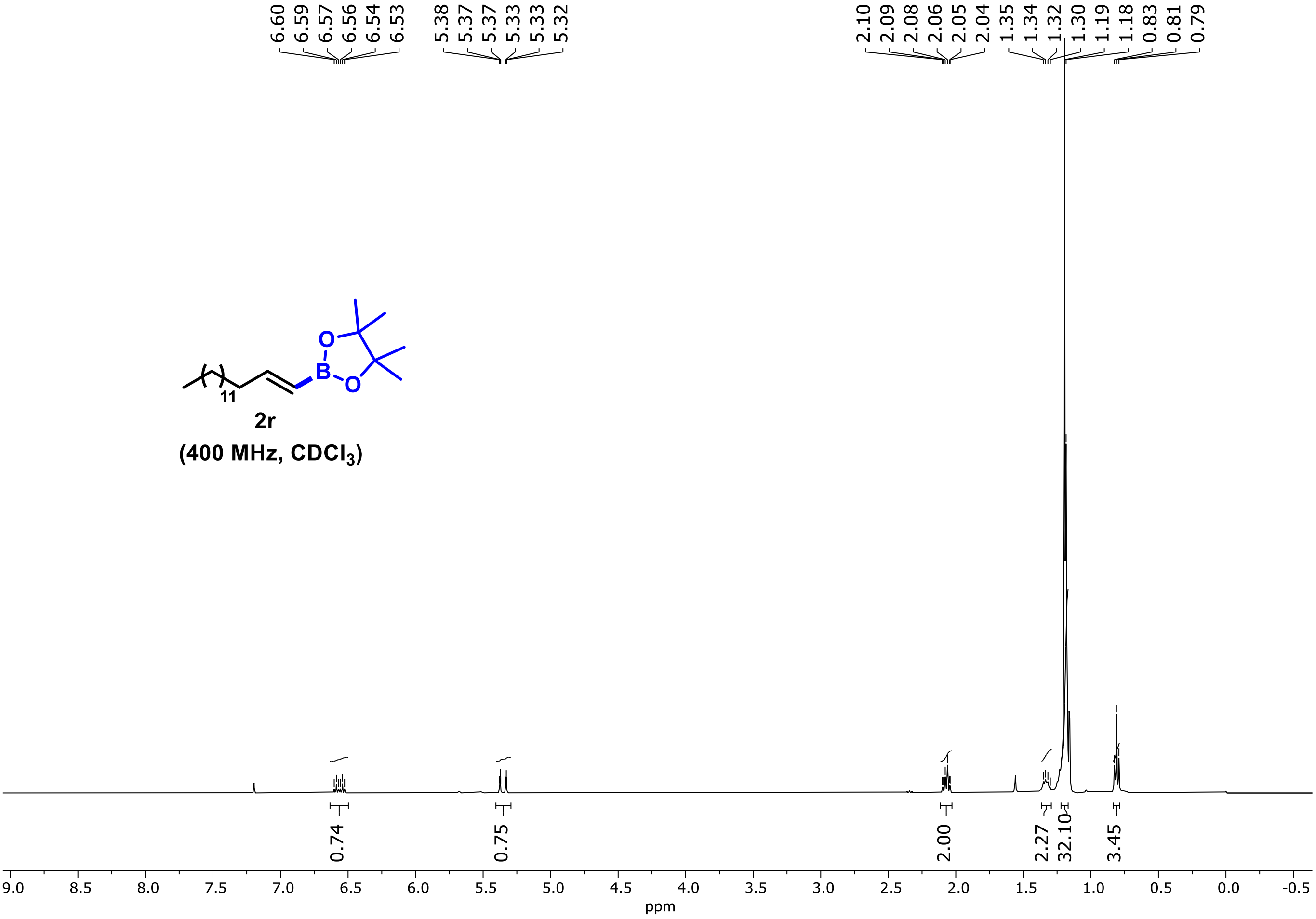

159.9
83.4
75.2
71.9
29.2
24.9
HO
O
B
O
2o
(100 MHz, CDCl$_3$)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

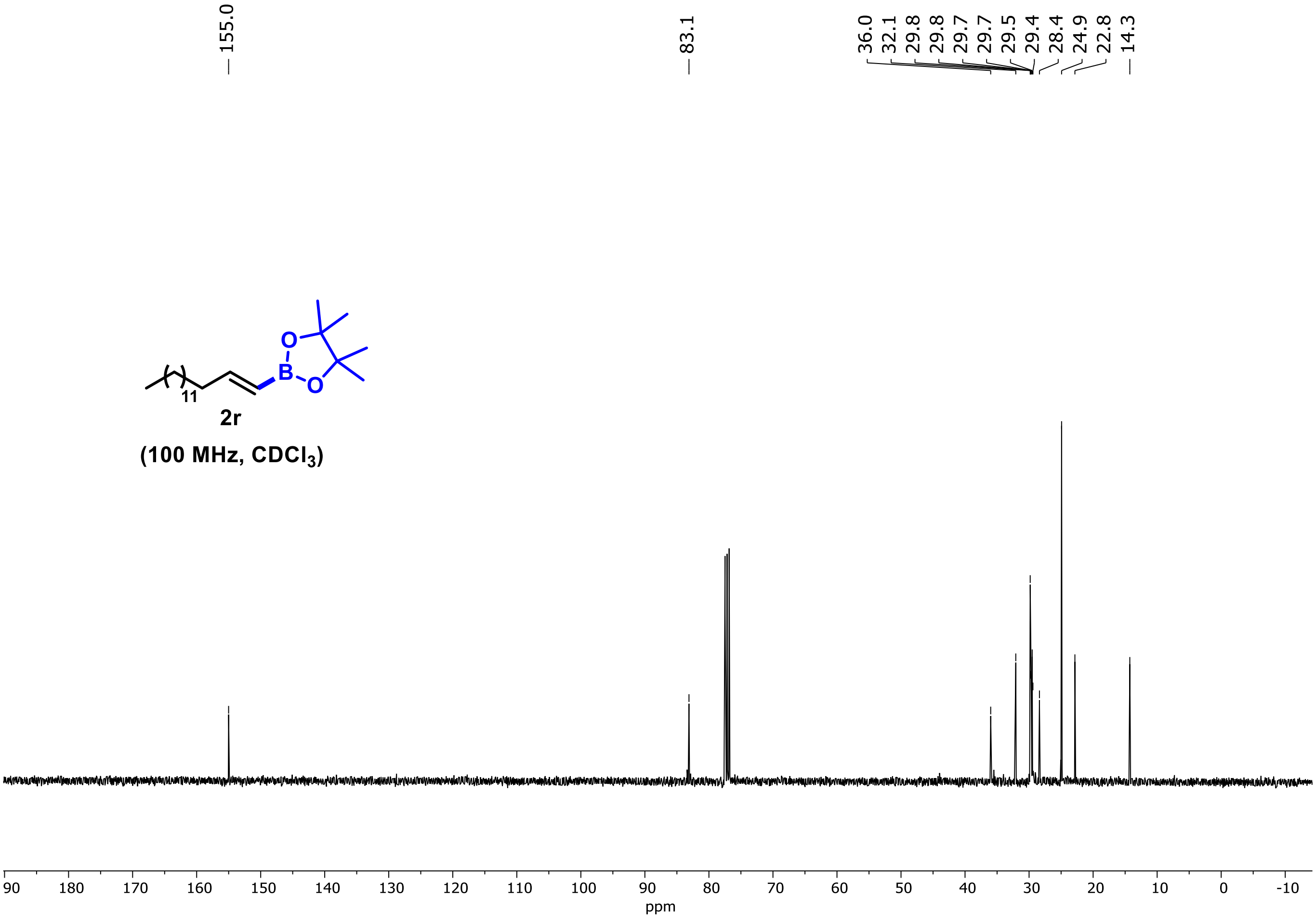

6.65
6.60
5.61
5.56
1.60
1.59
1.58
1.57
1.56
1.56
1.54
1.53
1.50
1.48
1.47
1.46
1.44
1.21
OH
O
B
O
2p
(400 MHz, CDCl$_3$)
1.00
1.00
4.15
6.44
12.37
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

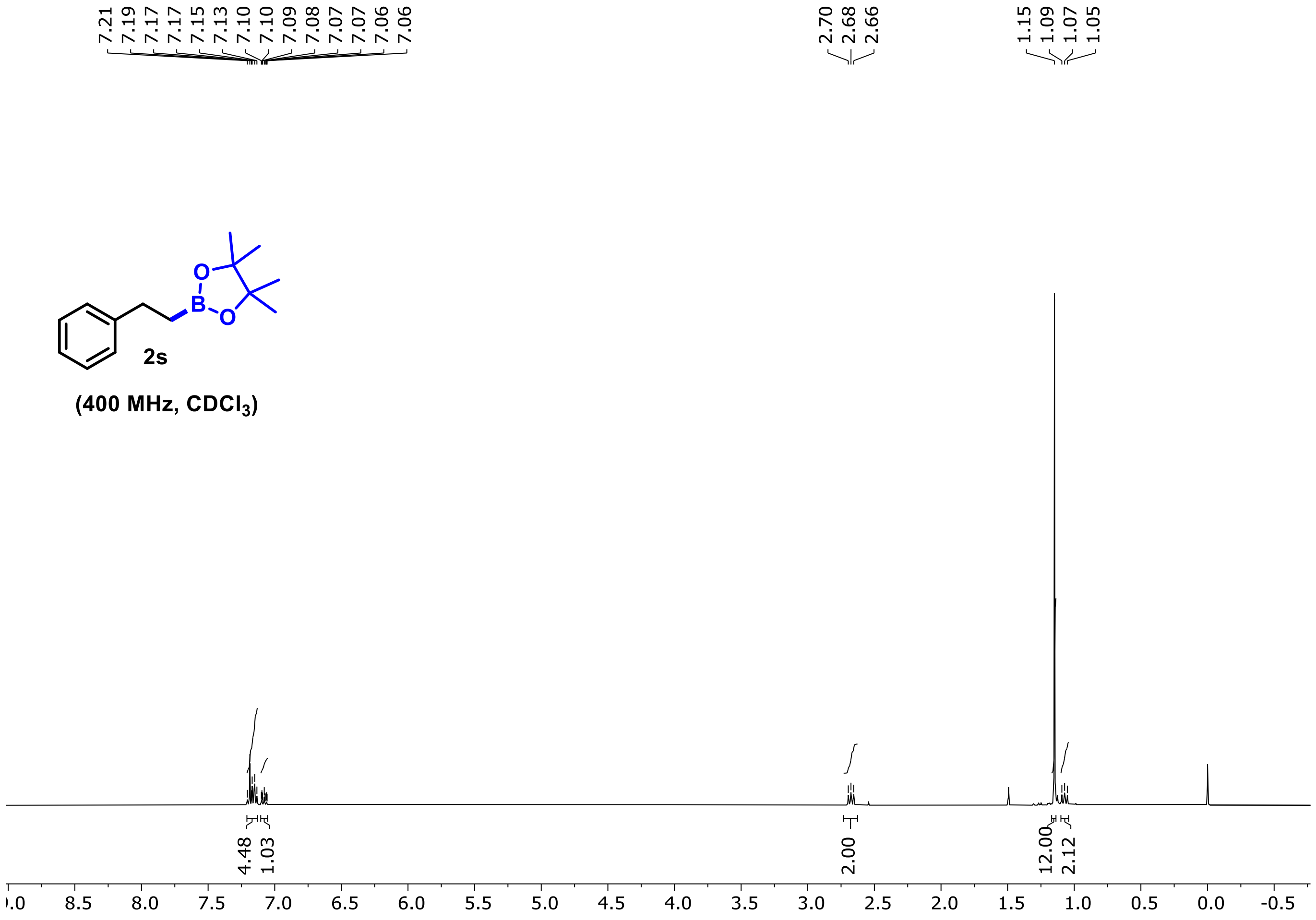

160.1
83.4
72.6
37.2
25.6
24.9
22.0
OH
O
B
O
2p
(100 MHz, CDCl$_3$)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

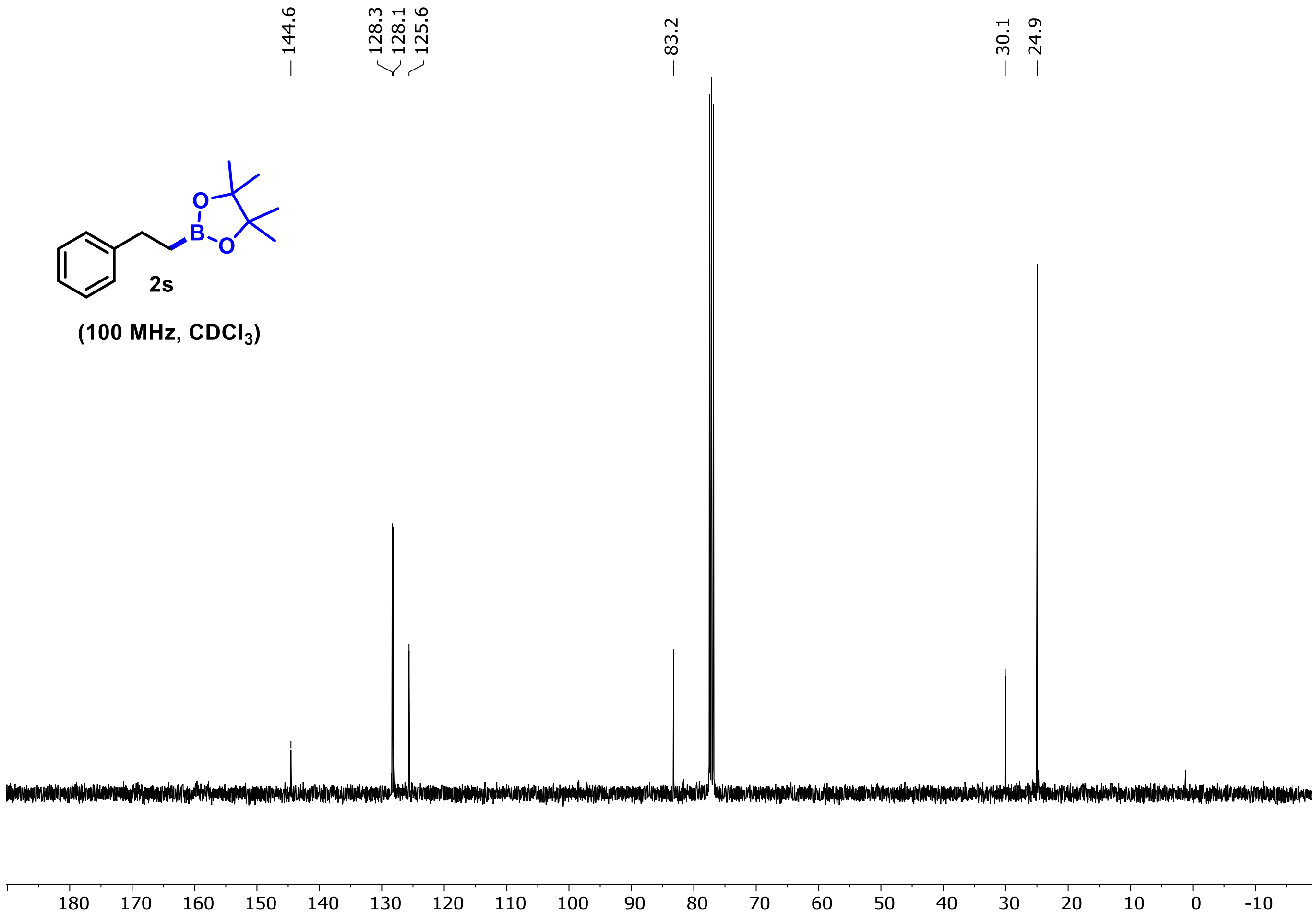

6.11
6.09
6.07
6.05
5.52
5.47
1.57
1.55
1.54
1.53
1.52
1.51
1.50
1.49
1.48
1.26
0.83
0.82
0.81
0.80
0.79
0.78
0.56
0.55
0.54
0.53
O
B
O
2q
(400 MHz, CDCl3)
1.00
1.00
1.06
12.31
2.11
2.12
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

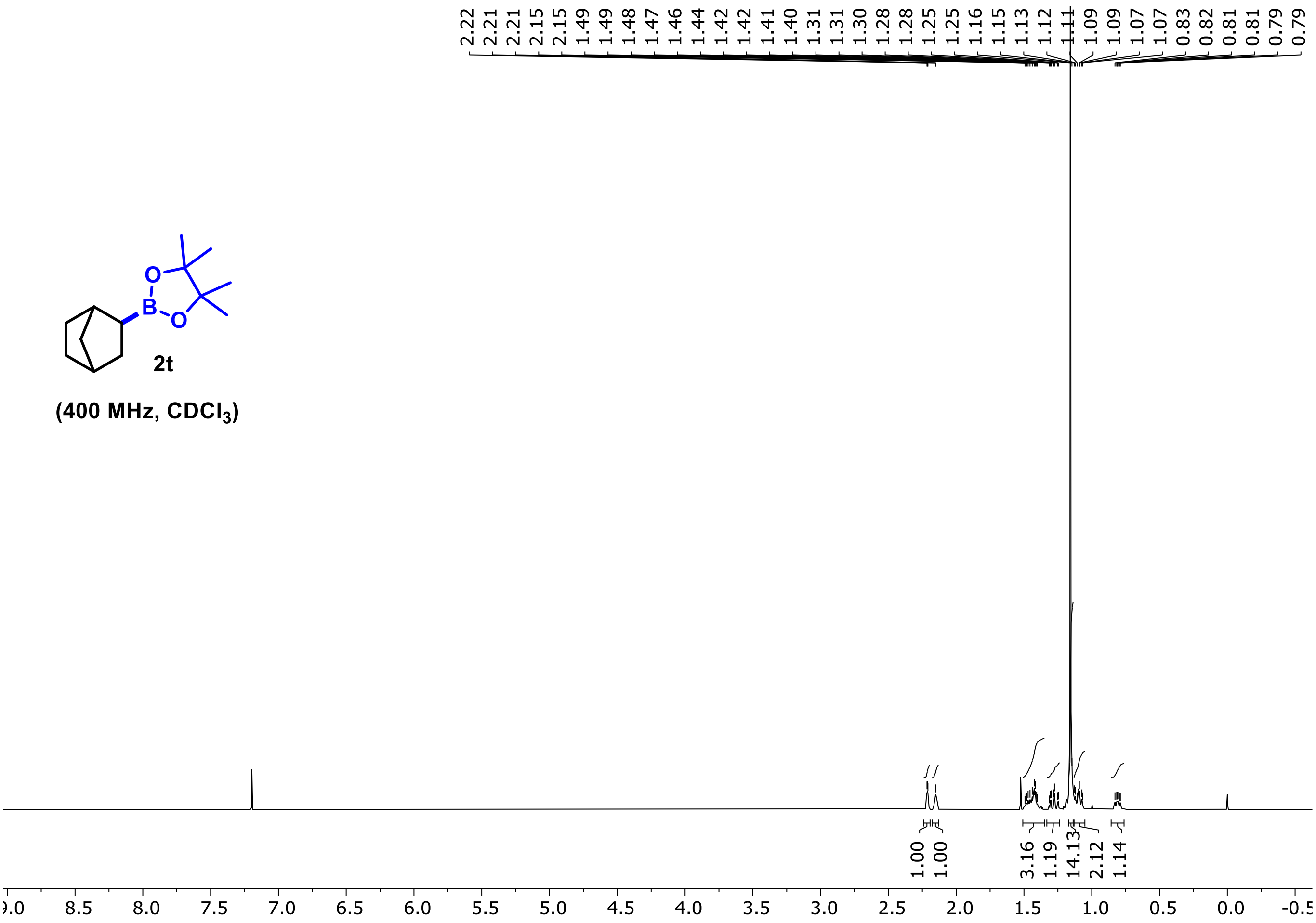

158.7
83.1
24.9
17.2
8.0
O
B
O
2q
(100 MHz, CDCl3)
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

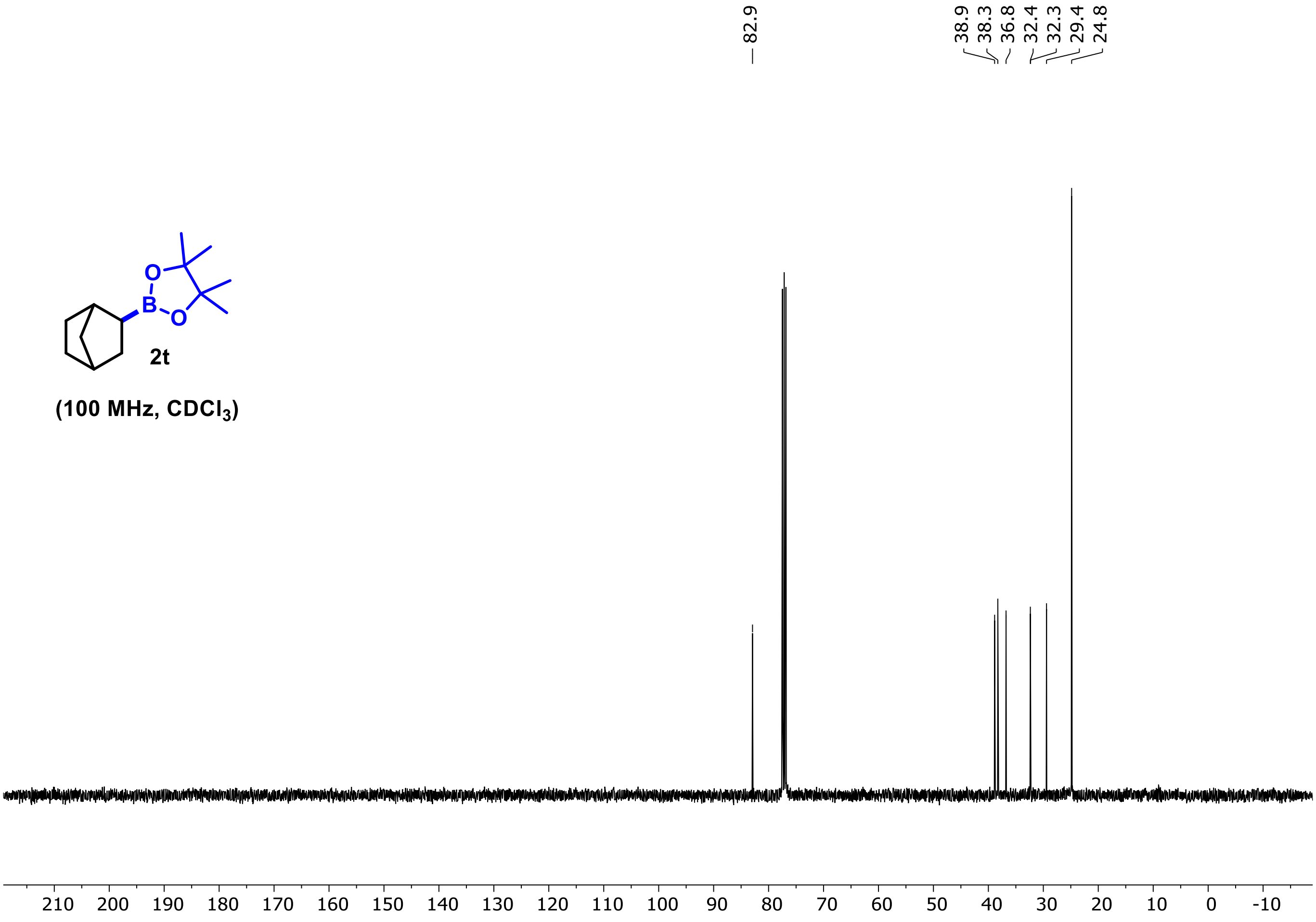

6.60
6.59
6.57
6.56
6.54
6.53
5.38
5.37
5.37
5.33
5.33
5.32
2.10
2.09
2.08
2.06
2.05
2.04
1.35
1.34
1.32
1.30
1.19
1.18
0.83
0.81
0.79
O
B
O
11
2r
(400 MHz, CDCl$_3$)
0.74
0.75
2.00
2.27
32.10
3.45
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
ppm

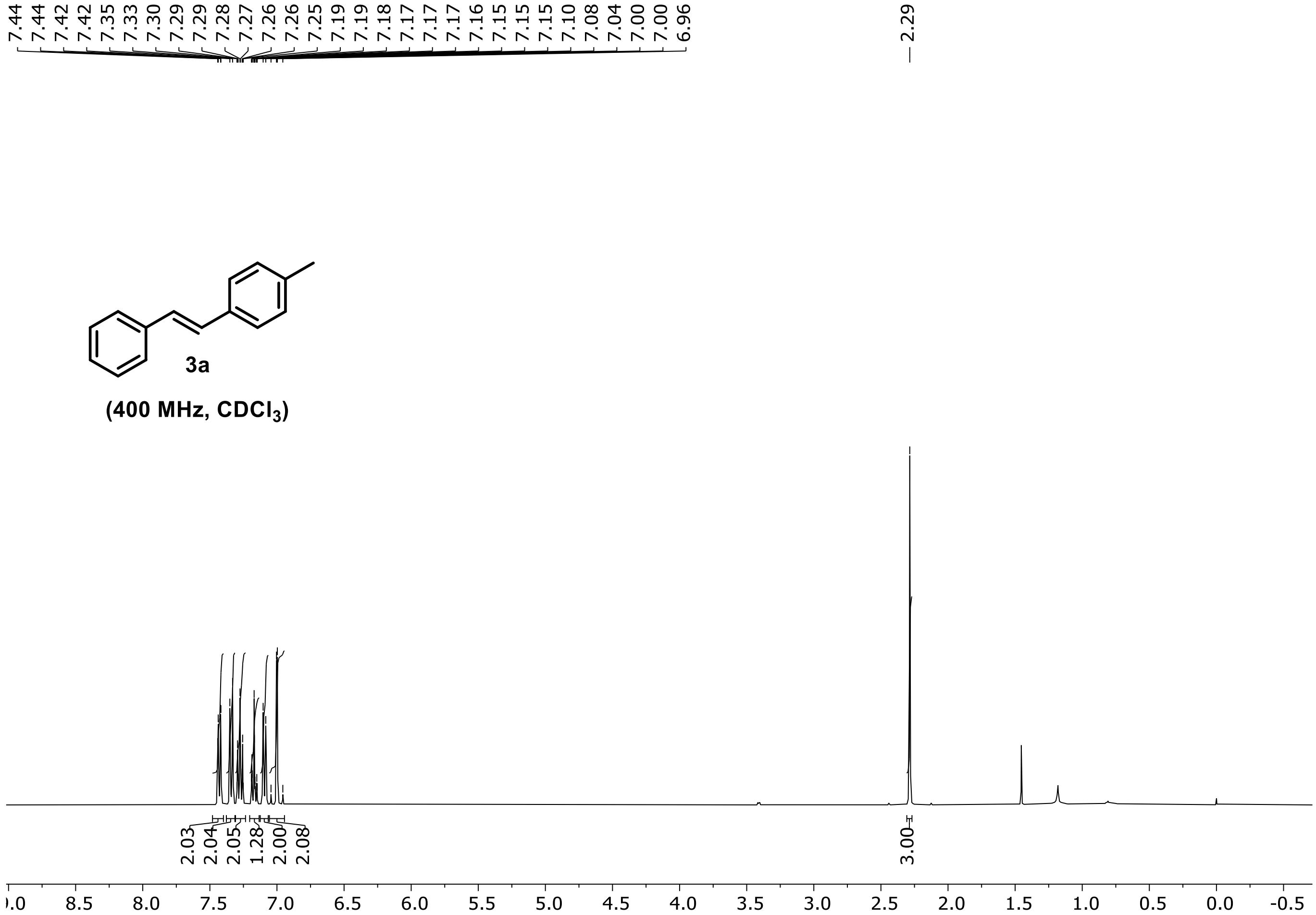

155.0
83.1
36.0
32.1
29.8
29.8
29.7
29.7
29.5
29.4
28.4
24.9
22.8
14.3
O
B
O
11
2r
(100 MHz, CDCl$_3$)
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

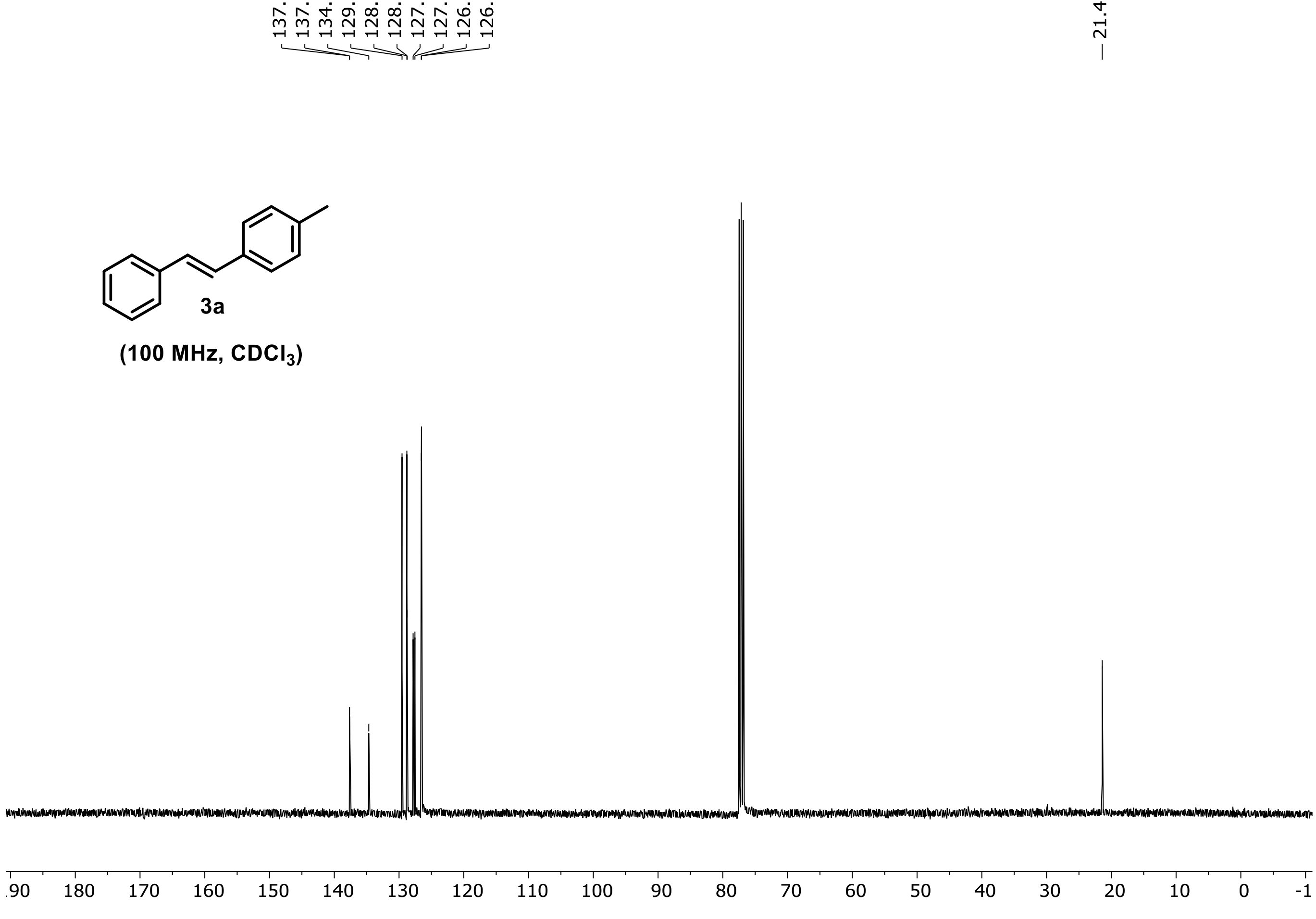

7.21
7.19
7.17
7.17
7.15
7.13
7.10
7.10
7.09
7.08
7.07
7.07
7.06
7.06
2.70
2.68
2.66
1.15
1.09
1.07
1.05
O
B
O
2s
(400 MHz, CDCl$_3$)
4.48
1.03
2.00
12.00
2.12
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

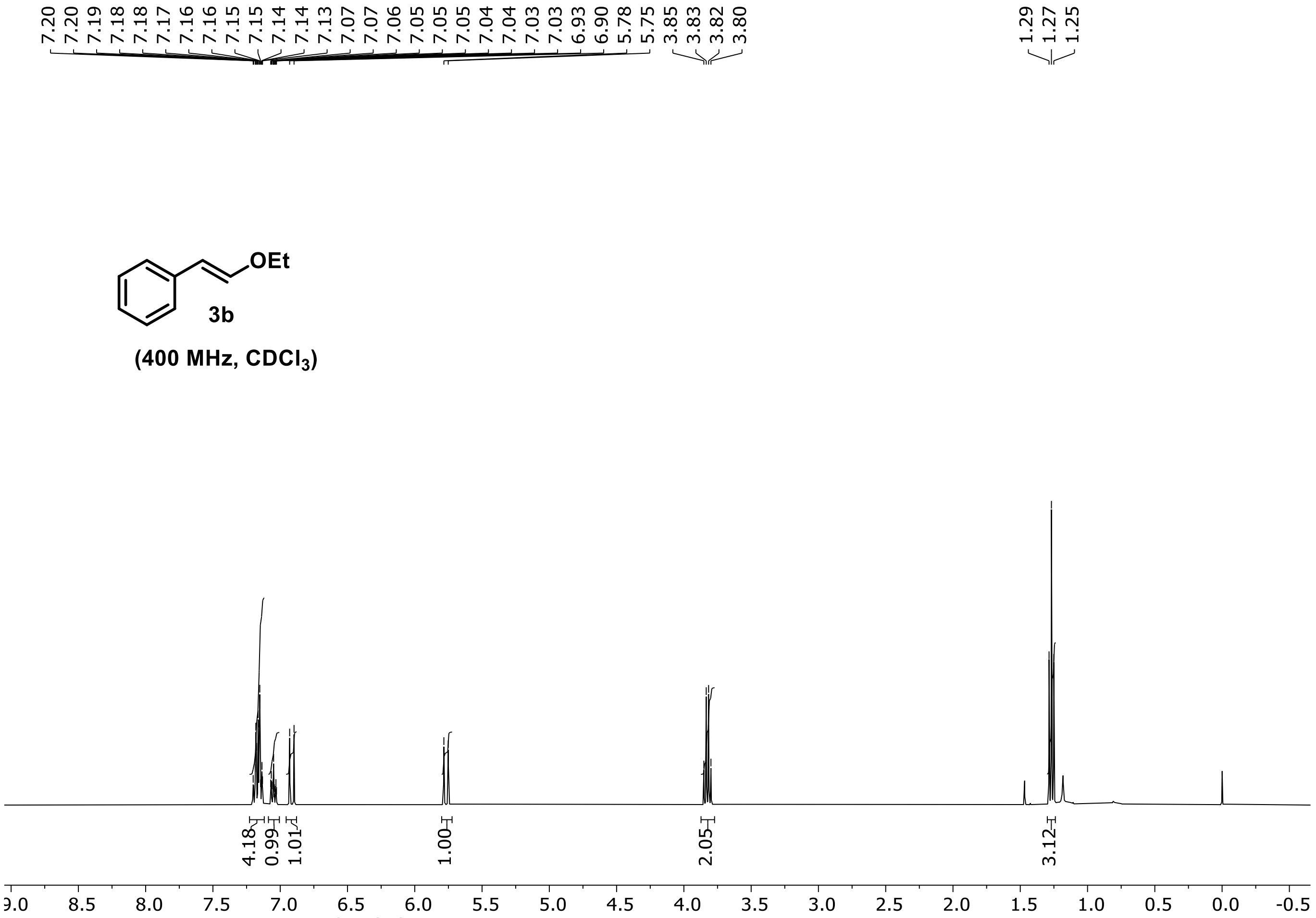

144.6
128.3
128.1
125.6
83.2
30.1
24.9
O
B
O
2s
(100 MHz, CDCl$_3$)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

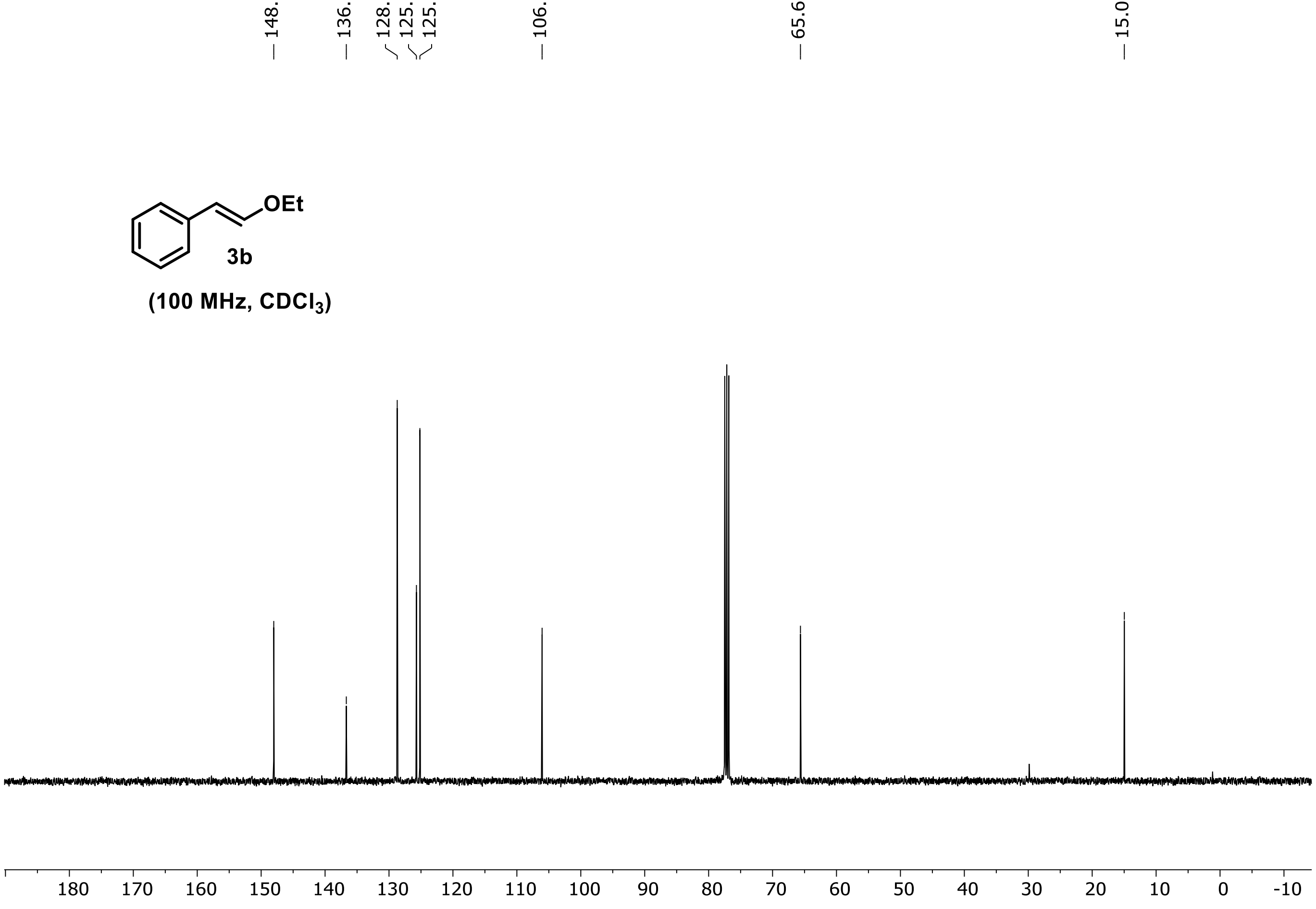

2.22
2.21
2.21
2.15
2.15
1.49
1.49
1.48
1.47
1.46
1.44
1.42
1.42
1.41
1.40
1.31
1.31
1.30
1.28
1.28
1.25
1.25
1.16
1.15
1.13
1.12
1.11
1.09
1.09
1.07
1.07
0.83
0.82
0.81
0.81
0.79
0.79
O
B
O
2t
(400 MHz, CDCl3)
1.00
1.00
3.16
1.19
14.13
2.12
1.14
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


82.9
38.9
38.3
36.8
32.4
32.3
29.4
24.8
O
B
O
2t
(100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


7.44
7.44
7.42
7.42
7.35
7.33
7.30
7.29
7.29
7.28
7.27
7.26
7.26
7.25
7.19
7.19
7.18
7.17
7.17
7.17
7.16
7.15
7.15
7.15
7.10
7.08
7.04
7.00
7.00
6.96
2.29
3a
(400 MHz, CDCl$_3$)
2.03
2.04
2.05
1.28
2.00
2.08
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5


137.7
137.6
134.7
129.5
128.8
128.7
127.8
127.5
126.6
126.5
21.4
3a
(100 MHz, CDCl$_3$)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1


7.20
7.20
7.19
7.18
7.18
7.17
7.16
7.16
7.15
7.15
7.14
7.14
7.13
7.07
7.07
7.06
7.05
7.05
7.05
7.04
7.04
7.03
7.03
6.93
6.90
5.78
5.75
3.85
3.83
3.82
3.80
1.29
1.27
1.25
OEt
3b
(400 MHz, CDCl$_3$)
4.18
0.99
1.01
1.00
2.05
3.12
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5


148.0
136.7
128.7
125.7
125.2
106.1
65.6
15.0
OEt
3b
(100 MHz, CDCl$_3$)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

9. Comparison with other catalytic systems

Table S1. Comparison of the performances of the $CuFe_2O_4$CNT with other systems.

Catalyst (mol%)	Additive(s)	Solvent	T (°C)	t (h)	Recycling	Atmosphere	Yield (%)[a]	Ref.
$CuFe_2O_4$CNT (0.05)	NaO*t*Bu (10 mol%)	MeOH	50	20	6 cycles (stable)	Air	80	This work
$CuFe_2O_4$ (0.5)	KO*t*Bu (10 mol%)	MeOH	50	12	4 cycles (-13%)	Air	90	15
CuI (10)	Cy_2NH (1.5 equiv)	H_2O	45	20	7 cycles (-44%)	Nitrogen	72	16
$PhI(OAc)_2$ (15)	NaO*t*Bu (1.8 equiv)	EtOH	rt	12	none	Air	90	17
Cu-$CuFe_2O_4$ (0.5)	NaOMe (10 mol%)	EtOH	22	8	6 cycles (stable)	Air	95	9
$Fe[(CO)H(NO)(PPh_3)_2]$ (0.5)	NaOMe (5 mol%)	THF/MeOH	80	9	none	Nitrogen	92	18
Cu-TiC (0.28)	H_2O (1 equiv)	Toluene	80	10	8 cycles (stable)	Air	89	19
Cu-organic Framework (0.3)	NaOMe (10 mol%)	EtOH	rt	1	5 cycles (stable)	Argon	93	20
Cu(I)-NHC (2.5)	NaOMe (30 mol%) MeOH (2 equiv)	CPME	25	16	none	Argon	98	21
CeO_2 nanorods (10)	KOMe (1.3 equiv) MeOH (1.5 equiv)	Toluene	50	16	6 cycles (-9%)	Nitrogen	85	22
Tetracopper(I) complex (0.5)	none	THF/H_2O	rt	8	none	Argon	90	23
dom-NENU-3_2 (1)	none	EtOH	50	12	5 cycles (stable)	Nitrogen	99	24

a. Phenylacetylene as substrate.

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