

Supplementary information

Atomically Precise Copper Clusters with Dual Sites for Highly Chemoselective and Efficient Hydroboration

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Supplementary Information (SI) for

Atomically Precise Copper Clusters with Dual Sites for Highly Chemoselective and Efficient Hydroboration

Teng Jia¹, Jie Ai¹, Xiaoguang Li², Miao-Miao Zhang^{1,3}, Yue Hua¹, Yi-Xin Li¹, Cai-Fang Sun¹, Feng Liu⁴, Ren-Wu Huang^{1*}, Zheng Wang^{2*} & Shuang-Quan Zang^{1*}

¹Henan Key Laboratory of Crystalline Molecular Functional Materials and College of Chemistry, Zhengzhou University, Zhengzhou, 450001, China.

²Institute for Advanced Study, Shenzhen University, Shenzhen, 518060, China.

³School of Chemistry and Chemical Engineering, Henan University of Technology, Zhengzhou, 450001, China.

⁴Yunnan Precious Metals Lab Co., LTD, Kunming, 650106, China.

Correspondence to: zangsqzg@zzu.edu.cn, renwuhuang@zzu.edu.cn, chzwang@szu.edu.cn

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General Methods and Materials

All the reactions were carried out under ambient atmosphere (air) conditions unless otherwise noted. All commercial reagents and solvents were obtained from the commercial provider and used without further purification. ^1H NMR, $^{13}\text{C}\{^1\text{H}\}$ NMR, ^{19}F NMR and $^{11}\text{B}\{^1\text{H}\}$ NMR spectra were recorded on Bruker 600 MHz spectrometers. Chemical shifts were reported relative to internal tetramethylsilane (δ 0.00 ppm), CDCl_3 (δ 7.26 ppm) for ^1H NMR and CDCl_3 (δ 77.0 ppm) for ^{13}C NMR. The nuclear magnetic spectra were analyzed using MestReNova software. Flash column chromatography was performed on 300–400 mesh silica gel. Electrospray ionization mass spectrometry (ESI–MS) of the clusters was recorded using an AB Sciex X500R Q-TOF spectrometer. Powder X-ray diffraction (PXRD) patterns of Cu_4NC and Cu_8NC were obtained using a Rigaku B/Max-RB X-ray diffractometer with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) in air at room temperature. UV–vis absorption spectra were obtained by means of a Hitachi UH4150 UV–visible spectrophotometer. Energy dispersive spectroscopy (EDS) and elemental mapping measurements were carried out via Zeiss Sigma 500. The *in situ* IR spectra of all reactions were recorded on ReactIR 701 C230516193 spectrometer. Inductively coupled plasma mass spectrometer (ICP–MS) was performed on IRIS Advantage (Thermo). Elemental analyses (EA) were carried out with a Perkin-Elmer 240 elemental analyser.

The *in situ* Raman spectra of hydroboration catalyzed by microcrystalline Cu_4NC were recorded on a labRAM HR Evolution-HORIBA Raman system equipped with a CCD detector using a 532 nm He–Cd laser as the excitation source. The microscope attachment of the spectrometer is a $\times 50_{\text{VIS_LWD}}$ objective. The laser spot on the sample is approximately 500 nm in diameter, and the spectral resolution is approximately $\leq 0.35 \text{ cm}^{-1}$. Low laser power (3.2%) and exposure time (1 s) were used during the experiment to minimize the impact of laser irradiation during spectral recording. The temperature was held constant at 25 °C. The spectra of the microcrystalline Cu_4NC were collected at different time (Supplementary Figure 82).

Single crystal analysis: Single-crystal X-ray diffraction measurements of Cu_4NC and Cu_8NC were performed on a Rigaku XtaLAB Pro diffractometer with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) at 200 K. Data collection and reduction were performed by the program CrysAlisPro⁽¹⁾. The crystal structures were solved with direct methods (*SHELXS*)⁽²⁾ and refined by full-matrix least squares on F^2 using *OLEX2*⁽³⁾, which utilizes the *SHELXL*-2015 module⁽⁴⁾. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions refined using idealized geometries and assigned fixed isotropic displacement parameters. Structure refinement was handled with different strategies according to the electron density distribution. The imposed restraints in least-squares refinement of each structure were noted in the corresponding CIF files. Detailed information about the X-ray crystal data, intensity collection procedure and refinement results for all cluster compounds is summarized in Supplementary Table 4.

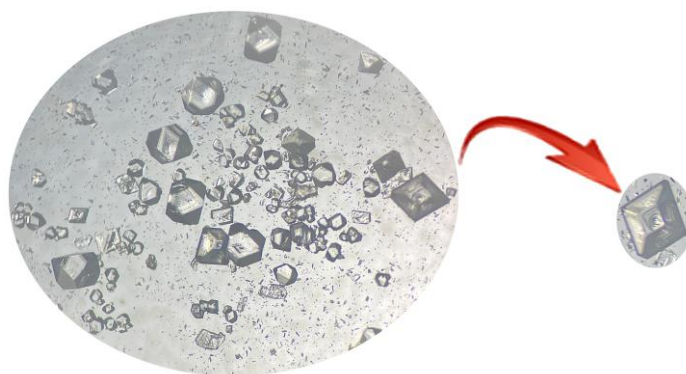
Materials

Hydroboration of alkynes was carried out under ambient atmosphere unless otherwise noted. Cu_4NC and Cu_8NC were synthesized under air atmosphere. The synthesis of deuterated phenylacetylene and 1-ethynyl-4-vinylbenzene substrates were carried out under a dry and oxygen-free N_2 atmosphere using standard Schlenk techniques. THF (HPLC grade) was dried over sodium/benzophenone and distilled under nitrogen prior to use. Methimazole (99%), B_2Pin_2 (99%), $(\text{Ph}_3\text{P})_2\text{PdCl}_2$ (98%), 4-bromostyrene (98%), 2-methyl-2-propanethiol (99%), alkynes (97%-98%), $n\text{BuLi}$ (1.6mol/l in hexane), methanol- d_4 (99.8%), various solvents (HPLC grade) and various copper salts (97%-98%) were directly purchased from companies of Energy Chemical, Bidepharm and Heowns without further purification.

The $n\text{BuSCu}$ was prepared according to the reported literature⁽⁵⁾.

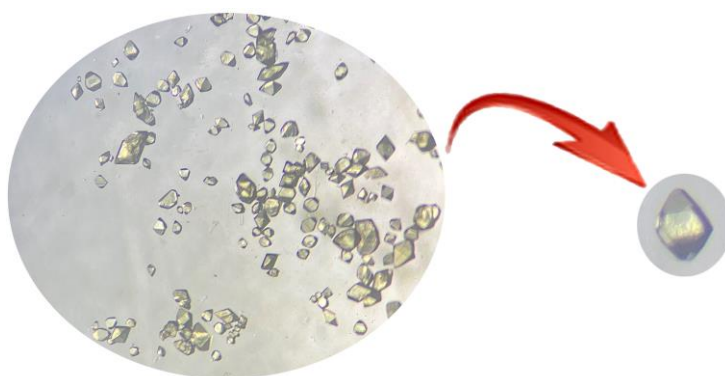
Synthetic Procedures

General Procedure for the Synthesis of Cu_4NC and Cu_8NC



Supplementary Figure 1. Photograph of the Cu_4NC single crystals. The Cu_4NC single crystals were prepared in DCM /MeCN solution.

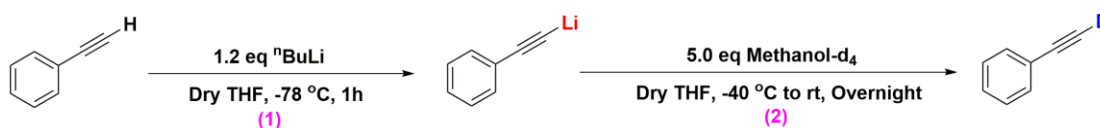
Synthesis of Cu_4NC : Under air atmosphere, the copper salt $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$ (1490.9 mg, 4.0 mmol) was dissolved in 100 mL of MeCN, to which 100 mL of methanol solution containing methimazole (456.7 mg, 4.0 mmol) was added under vigorous stirring at room temperature. After the solution turned blue, the reaction was stirred for another 10 minutes. Then excess triethylamine (2.0 ml) was added to the stirring reaction, resulting in immediate formation of microcrystalline. The suspension was centrifuged, and the microcrystalline was collected. The microcrystalline was dissolved in DCM, and the resulting solution was diffused with MeCN to obtain colorless crystals of Cu_4NC after 2 days at room temperature (Yield: 75 %, calculated based on methimazole ligand). ^1H NMR (600 MHz, CDCl_3) δ 6.55 (d, J = 20.6 Hz, 8H), 3.57 (s, 12H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 151.1, 125.7, 119.9, 34.2. HRMS(ESI) m/z : $[\text{M}+\text{Cs}]^+$ calcd for $\text{C}_{16}\text{H}_{20}\text{Cu}_4\text{N}_8\text{S}_4^+$ 838.6913. found: 838.7003. Anal. Calc. for Cu_4NC ($\text{C}_{16}\text{H}_{20}\text{Cu}_4\text{N}_8\text{S}_4$): C, 27.19; H, 2.85; N, 15.85; S, 18.14. Found: C, 27.23; H, 2.76; N, 15.75; S, 18.21.



Supplementary Figure 2. Photograph of the Cu₈NC single crystals. The Cu₈NC single crystals were prepared in DCM /MeOH solution.

Synthesis of Cu₈NC: Under air atmosphere, ^tBuSCu (305.5 mg, 2.0 mmol) was dissolved in 100 mL of DCM. After sonication, the DCM solution of ^tBuSCu became clear, to which 100 mL of methanol solution containing methimazole (114.2 mg, 1.0 mmol) was added under stirring at room temperature. Then excess triethylamine (500.0 μ L) was added to the stirring reaction, and the reaction stirred for another 10 minutes. The resulting pale-yellow solution was allowed to evaporate slowly at room temperature. After 3 days, yellow block crystals of Cu₈NC were obtained in a yield of 91.0% (calculated based on ^tBuSCu). ¹H NMR (600 MHz, CDCl₃) δ 6.46 (dd, J = 18.9, 1.4 Hz, 8H), 3.58 (s, 12H), 1.36 (s, 36H). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 150.6, 124.8, 119.5, 100.0, 48.0, 35.5, 34.0. HRMS(ESI) m/z : [M+Cs]⁺ calcd for C₃₂H₅₆CsCu₈N₈S₈⁺ 1450.5766. found: 1450.5869. Anal. Calc. for Cu₈NC (C₃₂H₅₆Cu₈N₈S₈): C, 29.17; H, 4.28; N, 8.50; S, 19.46. Found: C, 29.22; H, 4.24; N, 8.42; S, 19.52.

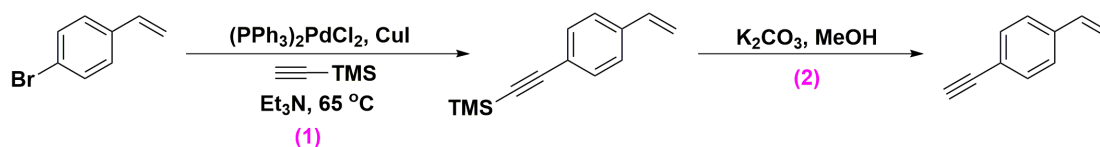
General Procedure for the Synthesis of Deuterated Phenylacetylene



Supplementary Figure 3. The Synthetic route for deuterated substrate. The synthetic route for deuterated phenylacetylene.

Under nitrogen atmosphere, ⁿBuLi (1.60 M in hexane, 3.75 mL, 6.0 mmol) was added dropwise to a solution of phenylacetylene (510.5 mg, 5.00 mmol) in 60 mL dry THF at -78 °C. The mixture was stirred for 1 hour to obtain lithium acetylide solution then allowed to warm to -40 °C and stirred for another 3 h before the addition of methanol-d₄ (900.0 mg, 25.0 mmol) in one portion. The resulting mixture was allowed to warm to room temperature gradually and stirred overnight. Removal of the volatiles under reduced pressure gave a pale-yellow residue that was then purified by column chromatography to give a pale-yellow oil with an overall isolated yield: 92%.

General Procedure for the Synthesis of 1-Ethynyl-4-vinylbenzene⁽⁶⁾

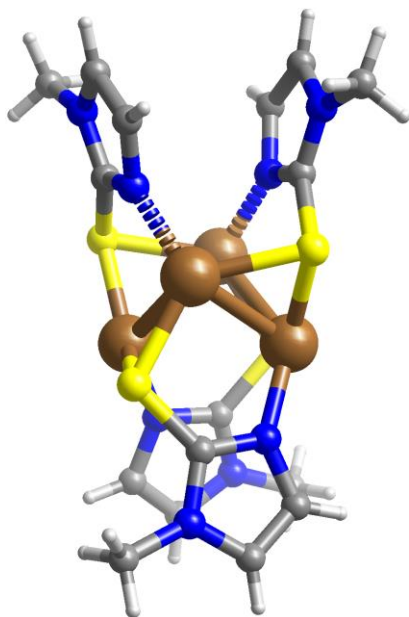


Supplementary Figure 4. The Synthetic route for substrate. The synthetic route for 1-ethynyl-4-vinylbenzene.

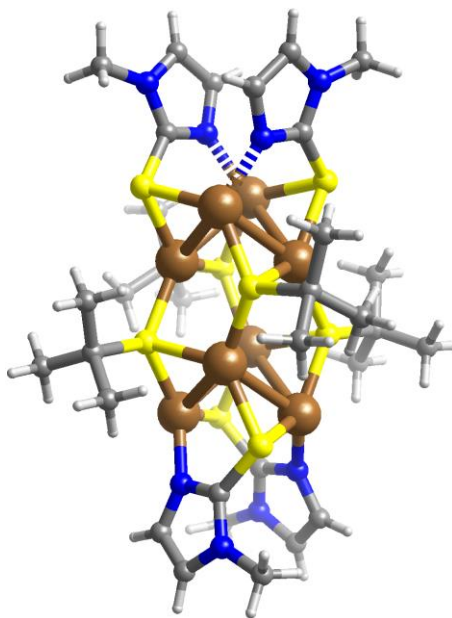
Under N_2 atmosphere, a mixture of 4-bromostyrene (1830.5 mg, 10.0 mmol), $(\text{Ph}_3\text{P})_2\text{PdCl}_2$ (140.4 mg, 0.2 mmol) and CuI (19.1 mg, 0.1 mmol) in a flask was degassed, then Et_3N (0.2 M for substrate, 50 ml) was added. To this solution ethynyl trimethylsilane (4911.0 mg, 50 mmol) was added by syringe. The mixture was heated to $65\text{ }^\circ\text{C}$ for 12 h, and TLC showed the starting 4-bromostyrene was completely consumed. After cooling to room temperature, the reaction mixture was filtrated through celite. The filtrate was concentrated and the crude product was purified by chromatography (PE-EA, v/v 1/0) to give a yellow oil with an overall isolated yield: 80%. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.43 (d, $J = 8.3\text{ Hz}$, 2H), 7.34 (d, $J = 8.2\text{ Hz}$, 2H), 6.69 (dd, $J = 17.6$, 10.9 Hz , 1H), 5.76 (d, $J = 17.6\text{ Hz}$, 1H), 5.29 (d, $J = 10.9\text{ Hz}$, 1H), 0.26 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 137.6, 136.2, 132.1, 126.0, 122.4, 114.8, 105.1, 94.8, 0.0.

Under air atmosphere, the product was dissolved in MeOH (0.2 M for substrate), and then K_2CO_3 (138.2 mg, 1.0 mmol) was added. Desilylation was conducted at room temperature for 2 hours and concentrated. The product was purified by chromatography to give a yellow solid with an overall isolated yield: 95%. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.45 (d, $J = 8.1\text{ Hz}$, 2H), 7.36 (d, $J = 8.1\text{ Hz}$, 2H), 6.70 (dd, $J = 17.6$, 10.9 Hz , 1H), 5.77 (d, $J = 17.6\text{ Hz}$, 1H), 5.30 (d, $J = 10.9\text{ Hz}$, 1H), 3.11 (s, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 138.0, 136.1, 132.3, 126.1, 121.3, 115.1, 83.6, 77.7.

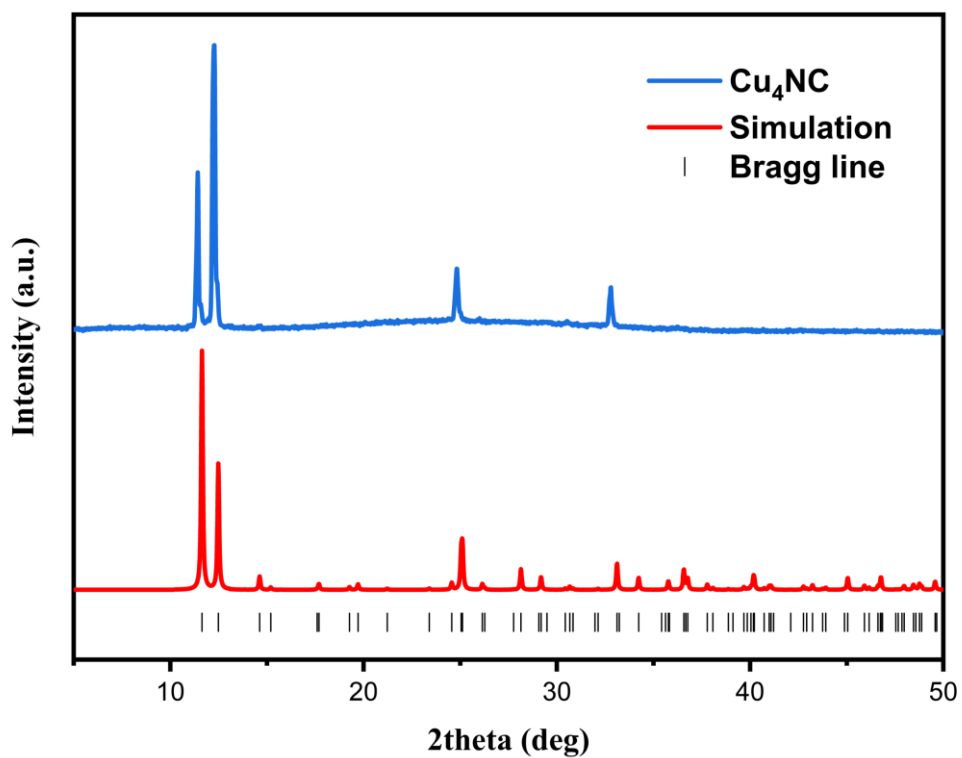
Characterizations of Cu₄NC and Cu₈NC



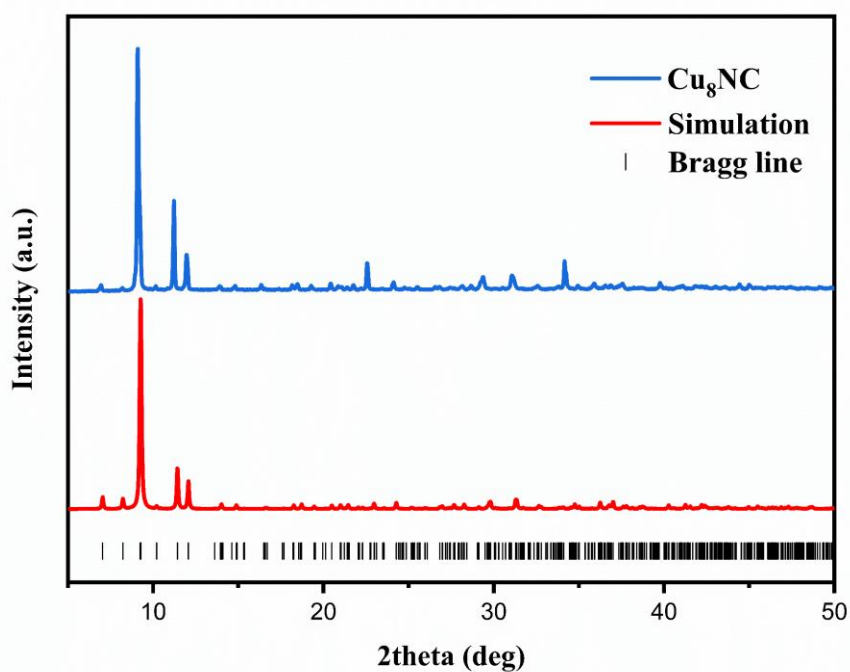
Supplementary Figure 5. Characterization of Cu₄NC. Crystal structure of Cu₄NC (CCDC: 2330281).



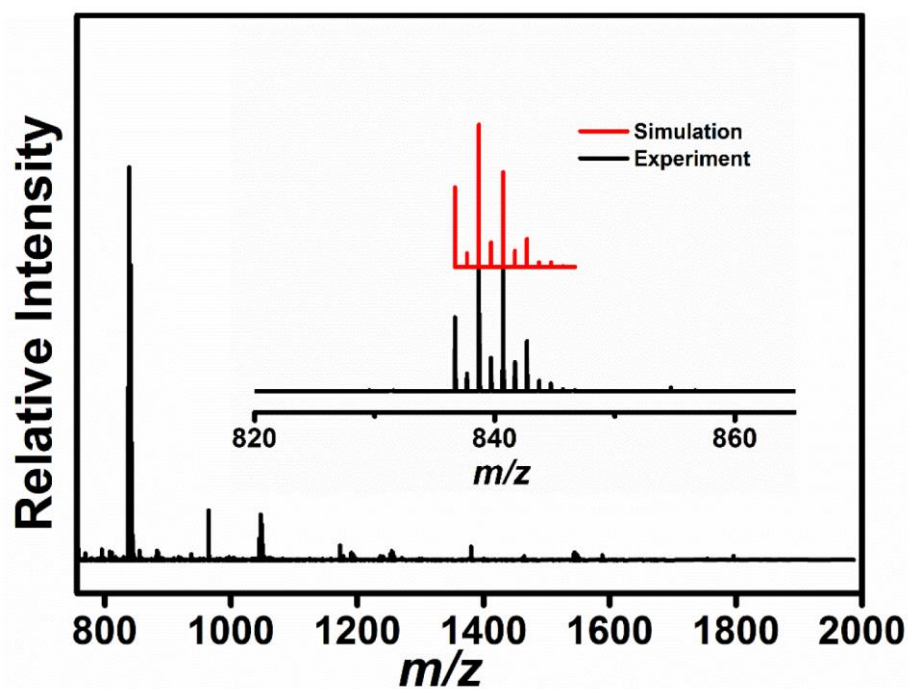
Supplementary Figure 6. Characterization of Cu₈NC. Crystal structure of Cu₈NC (CCDC: 2330282).



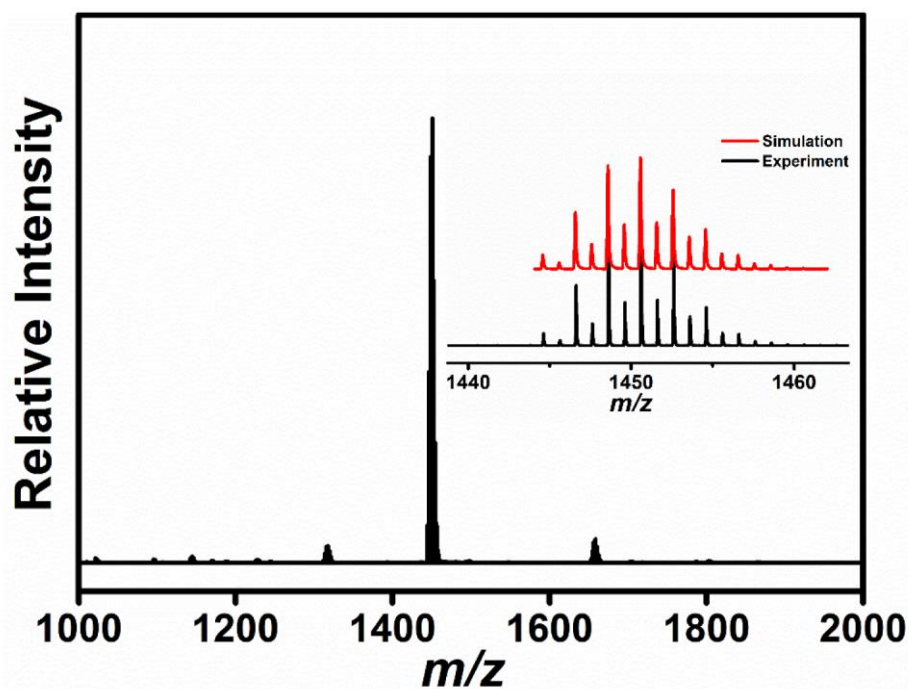
Supplementary Figure 7. Characterization of Cu_4NC . PXRD pattern of microcrystalline Cu_4NC .



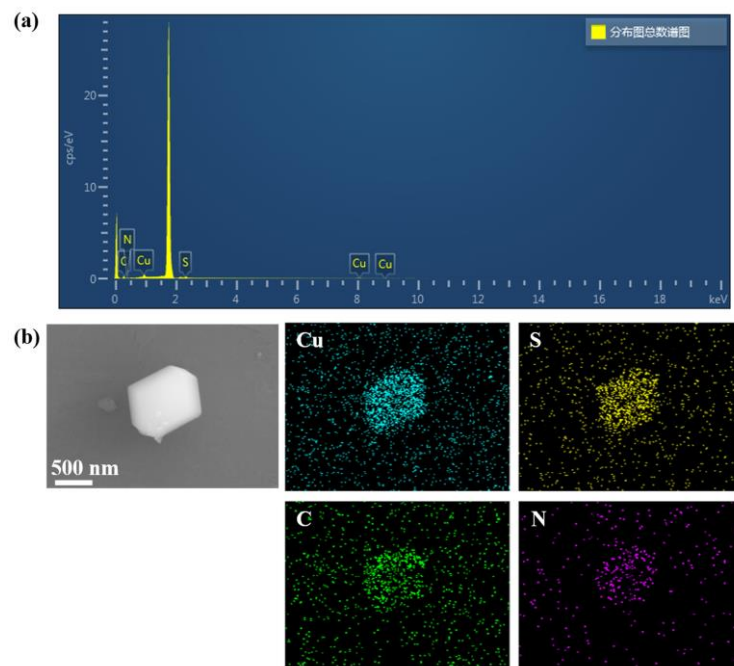
Supplementary Figure 8. Characterization of Cu_8NC . PXRD pattern of microcrystalline Cu_8NC .



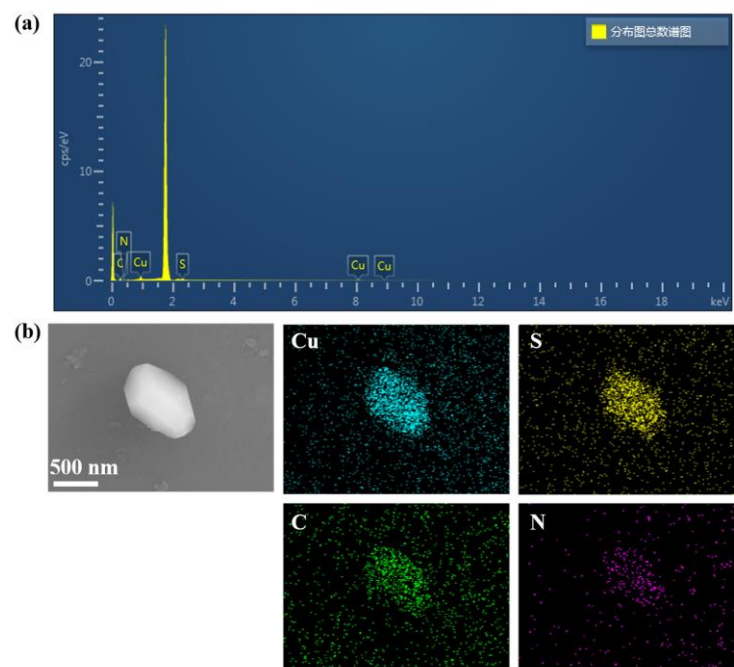
Supplementary Figure 9. ESI-MS spectrum of Cu_4NC . ESI-MS spectrum of Cu_4NC in DMSO solution.



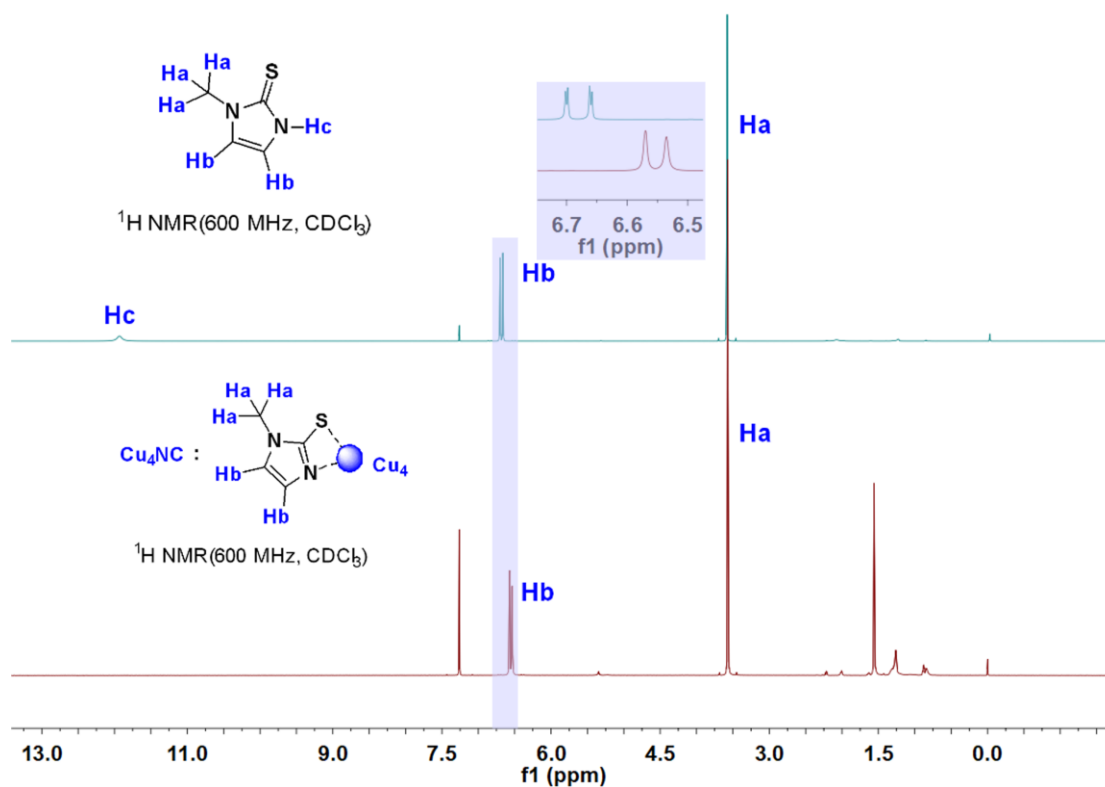
Supplementary Figure 10. ESI-MS spectrum of Cu_8NC . ESI-MS spectrum of Cu_8NC in DMSO solution.



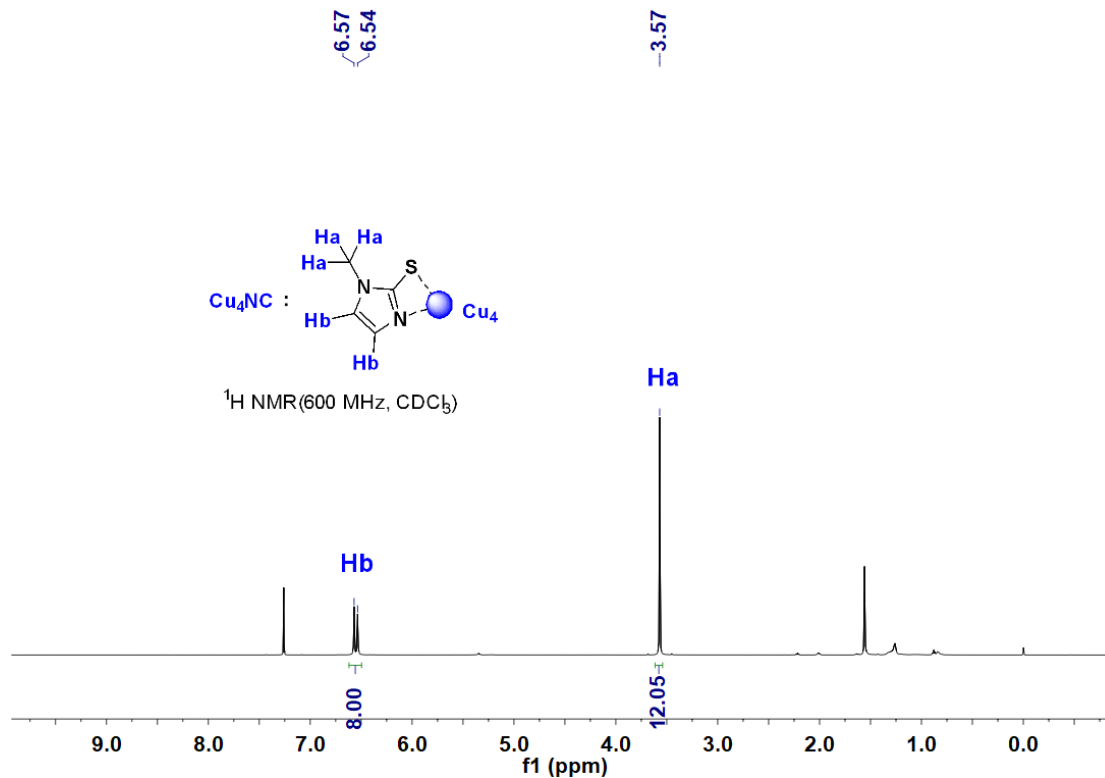
Supplementary Figure 11. Morphology and energy dispersive spectroscopy (EDS) mapping results of microcrystalline Cu_4NC . **a.** Energy dispersive spectroscopy (EDS) mapping of Cu_4NC . **b.** Mapping test of microcrystalline Cu_4NC .



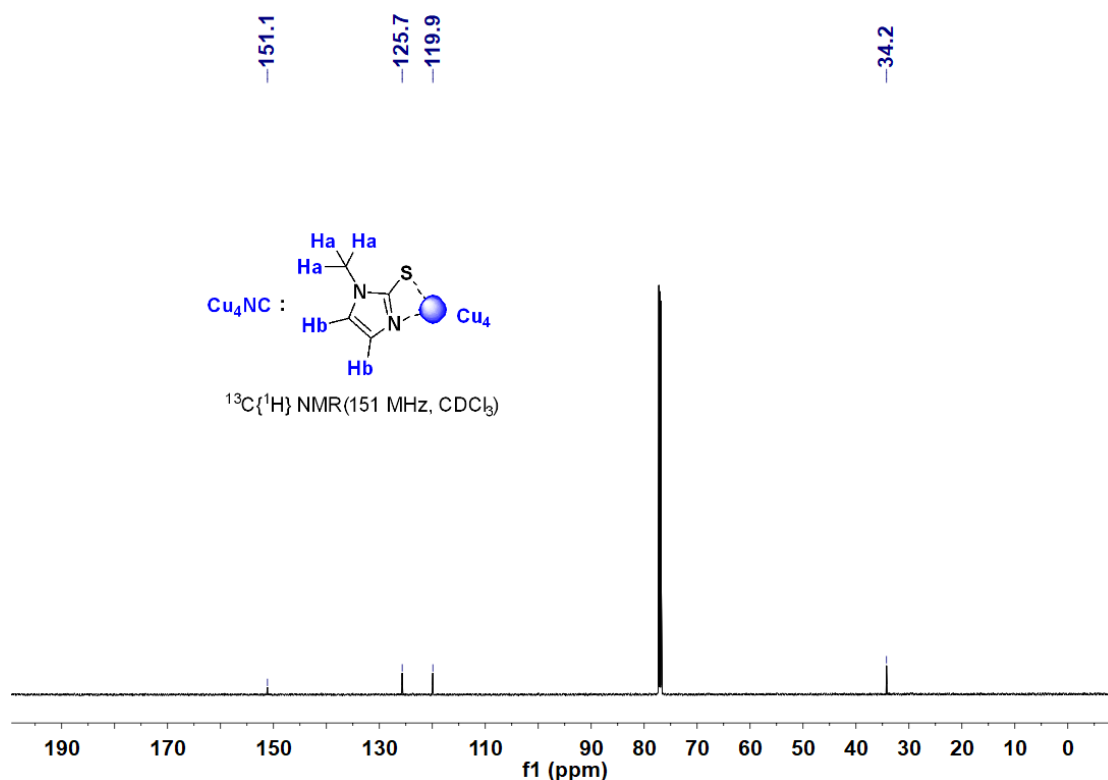
Supplementary Figure 12. Morphology and energy dispersive spectroscopy (EDS) mapping results of microcrystalline Cu_8NC . **a.** Energy dispersive spectroscopy (EDS) mapping of Cu_8NC . **b.** Mapping test of microcrystalline Cu_8NC .



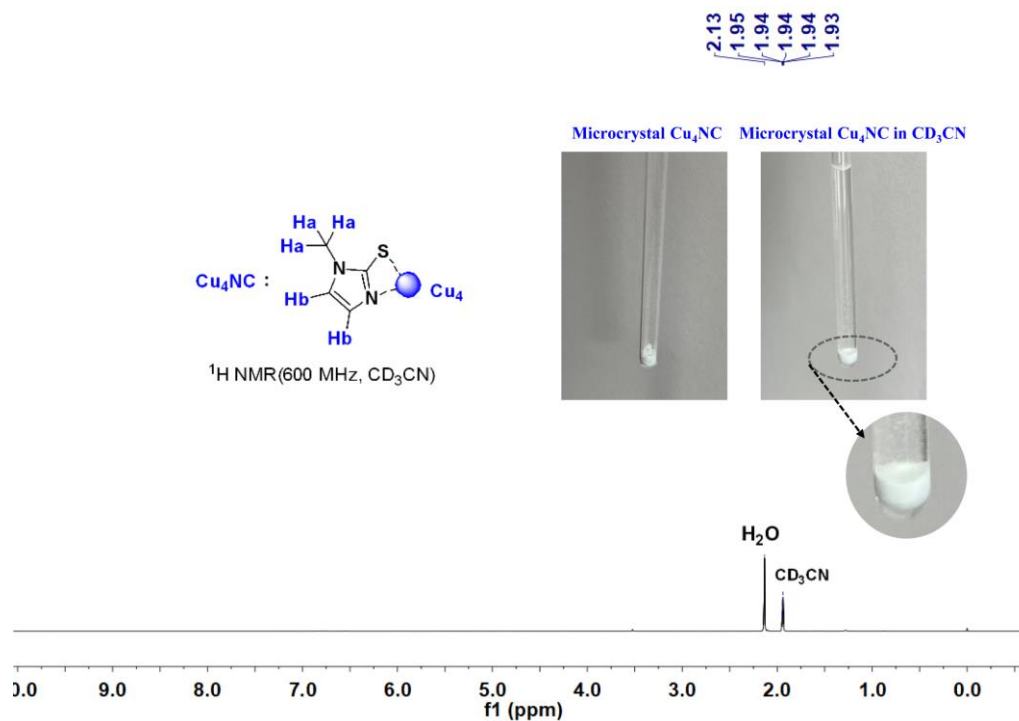
Supplementary Figure 13. ^1H NMR spectra of Cu_4NC and ligand. ^1H NMR spectra of Cu_4NC and methimazole ligand in CDCl_3 .



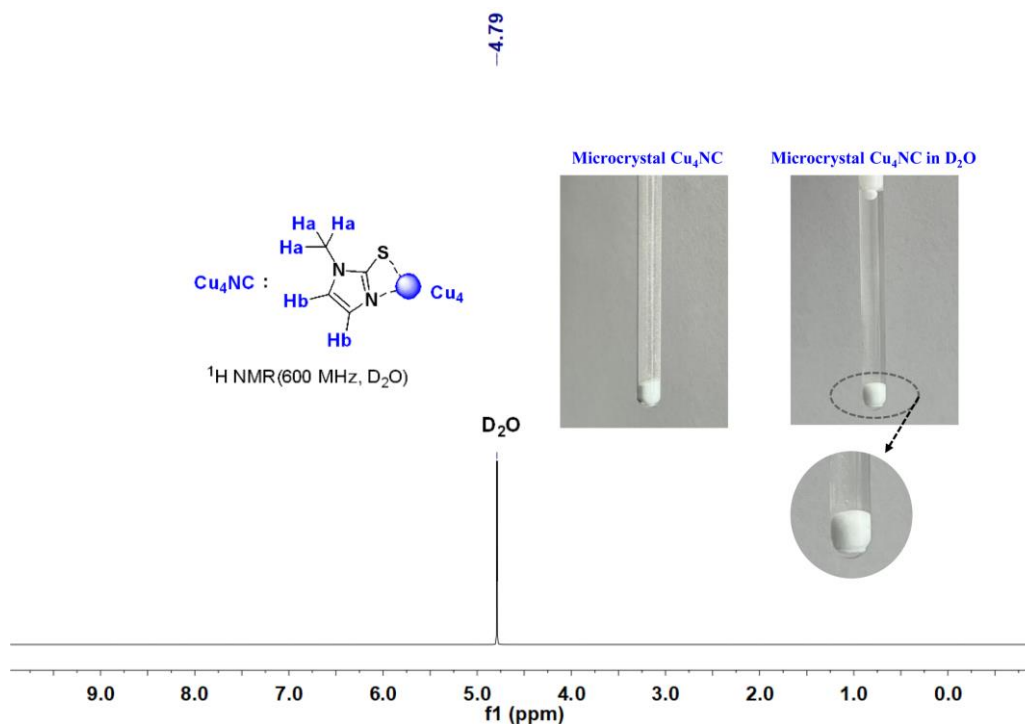
Supplementary Figure 14. ^1H NMR spectra of Cu_4NC . ^1H NMR spectrum of Cu_4NC in CDCl_3 .



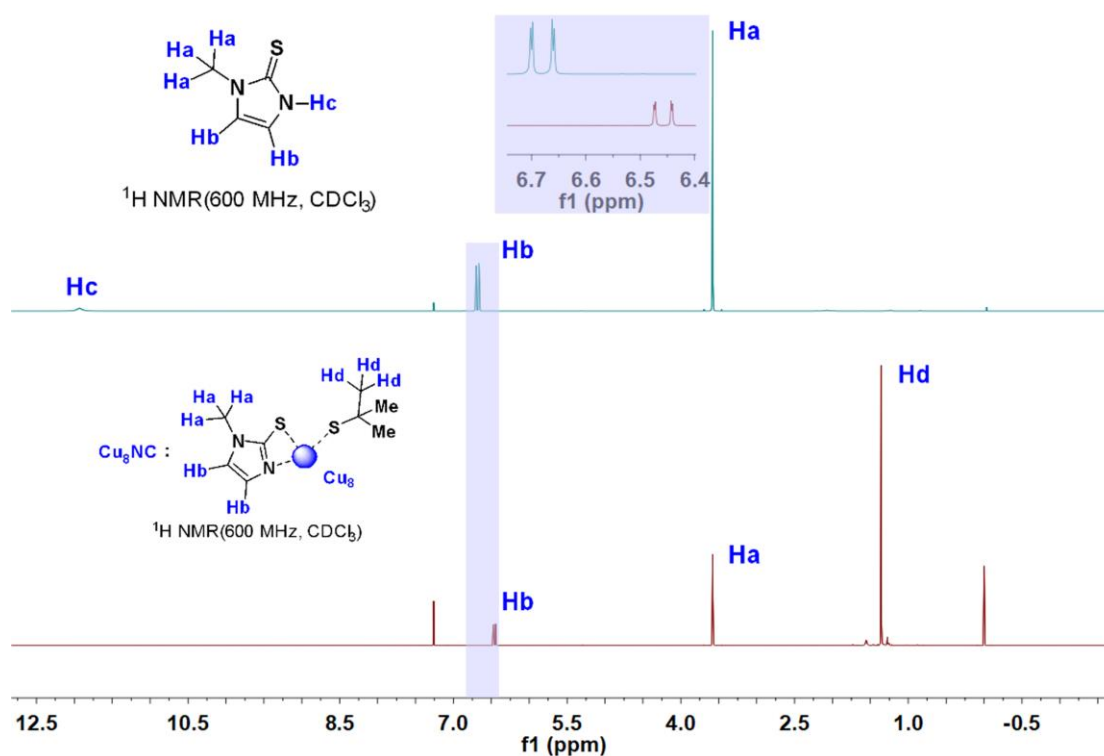
Supplementary Figure 15. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of Cu_4NC . $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of Cu_4NC in CDCl_3 .



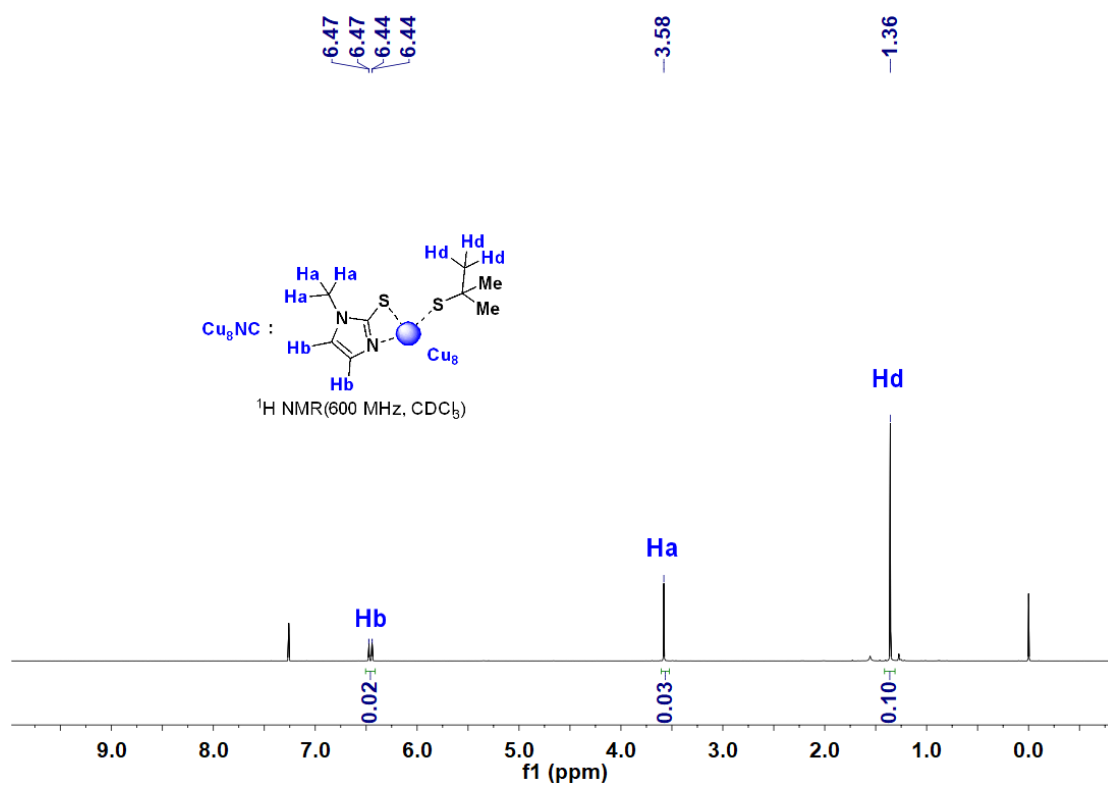
Supplementary Figure 16. ^1H NMR spectrum of microcrystalline Cu_4NC in CD_3CN . No characteristic peaks of Cu_4NC are found in ^1H NMR spectrum, proving that microcrystalline Cu_4NC is completely insoluble in MeCN solution.



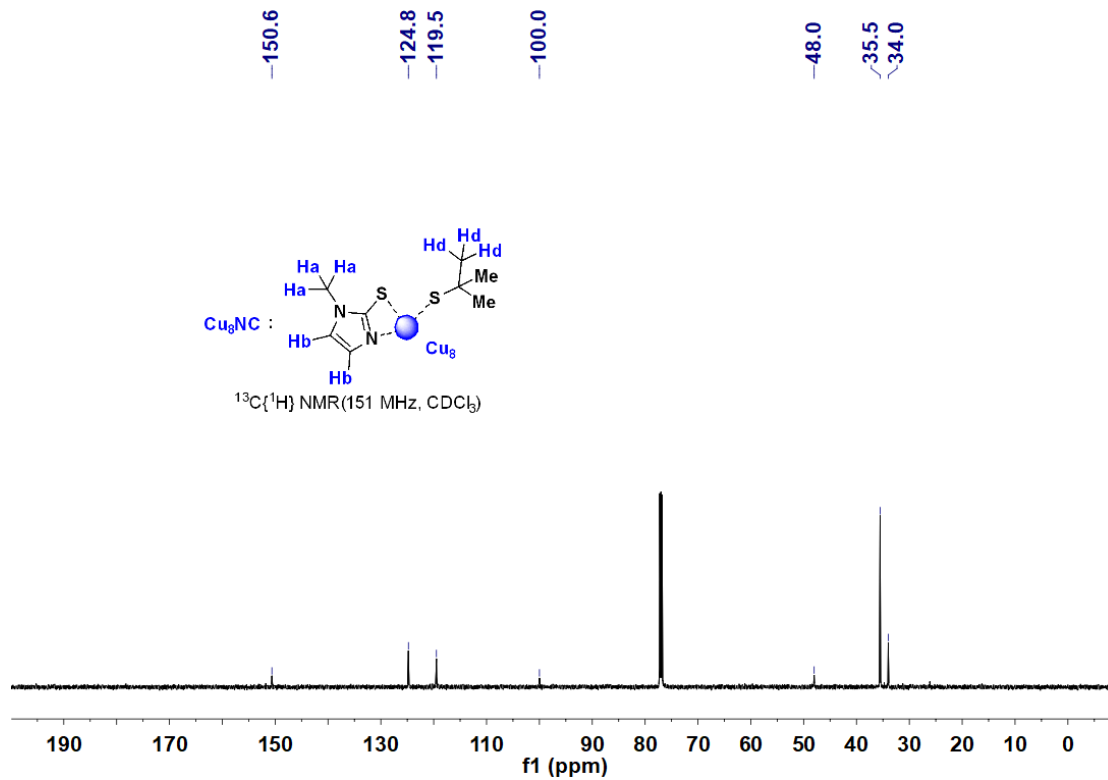
Supplementary Figure 17. $^1\text{H NMR}$ spectrum of microcrystalline Cu_4NC in D_2O . No characteristic peaks of Cu_4NC are found in $^1\text{H NMR}$ spectrum, proving that microcrystalline Cu_4NC is completely insoluble in H_2O solution.



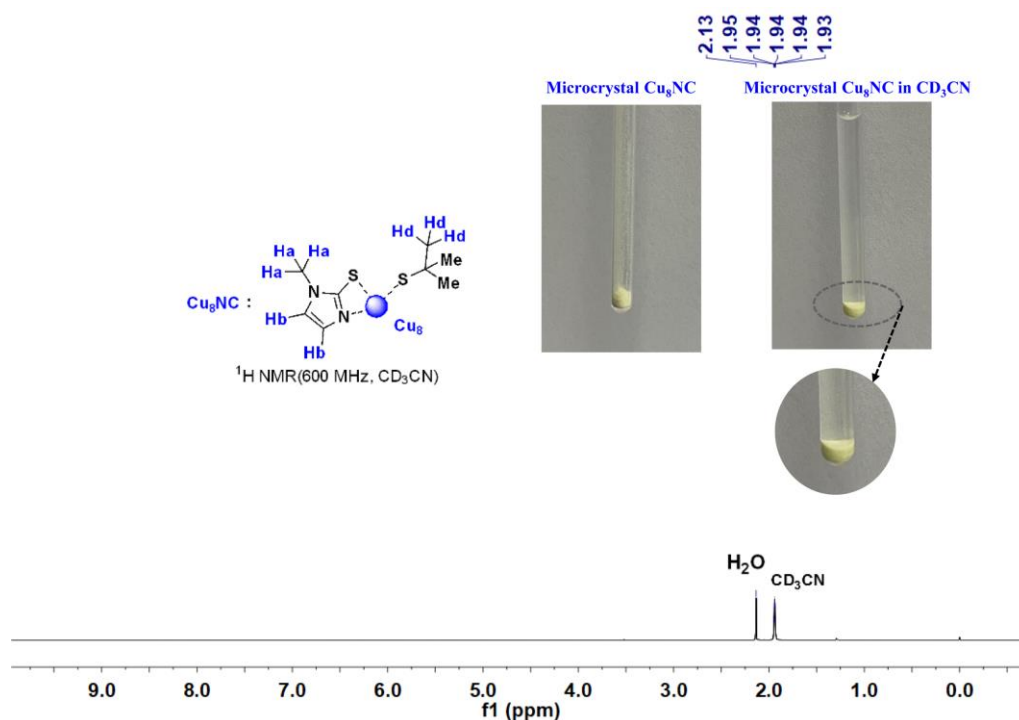
Supplementary Figure 18. $^1\text{H NMR}$ spectra of Cu_8NC and ligand. $^1\text{H NMR}$ spectra of Cu_8NC and methimazole ligand in CDCl_3 .



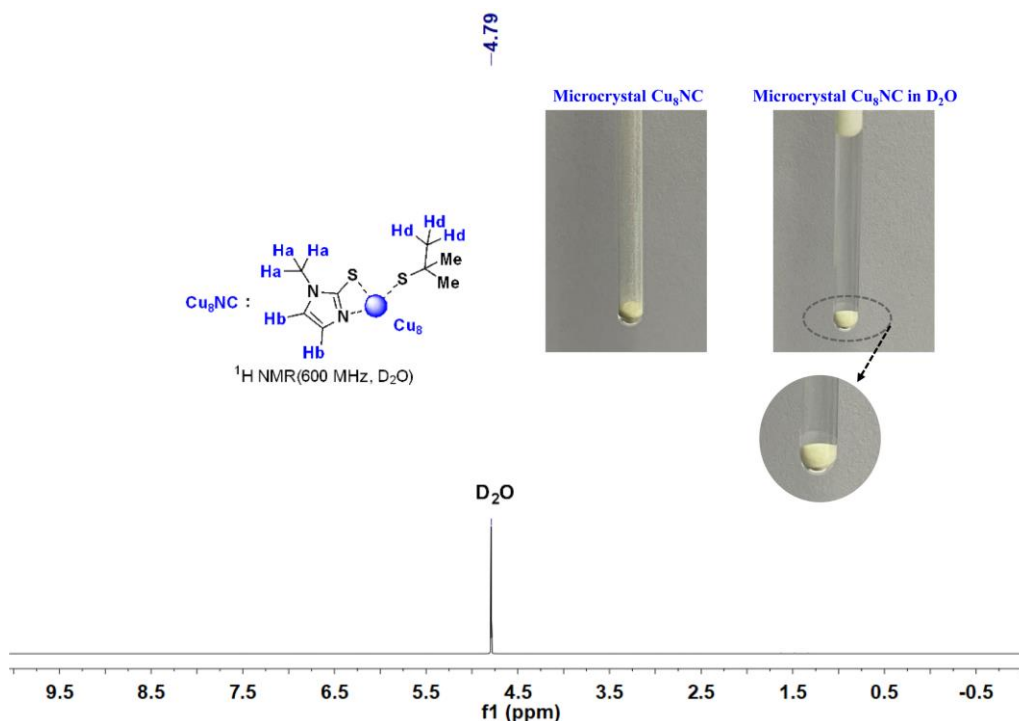
Supplementary Figure 19. ¹H NMR spectrum of Cu₈NC. ¹H NMR spectrum of Cu₈NC in CDCl₃.



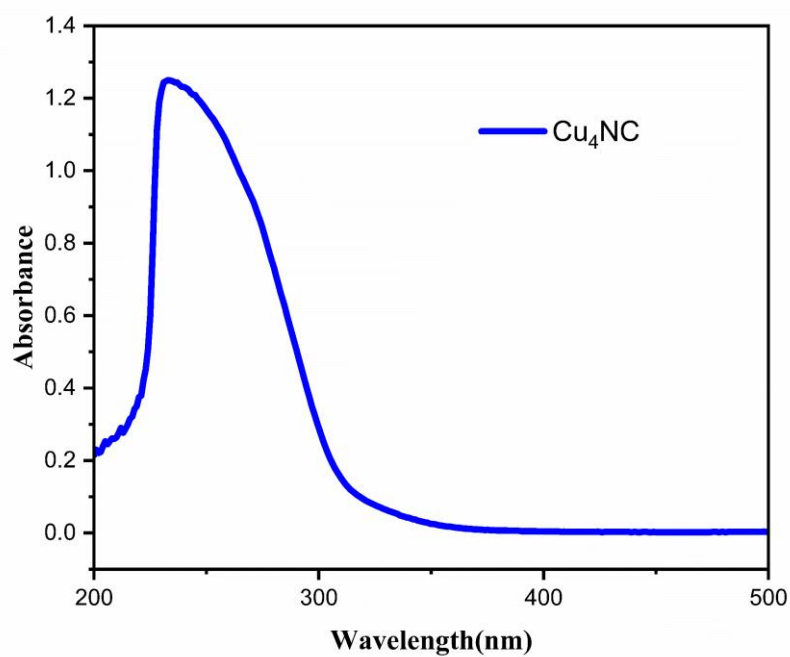
Supplementary Figure 20. ¹³C{¹H} NMR spectrum of Cu₈NC. ¹³C{¹H} NMR spectrum of Cu₈NC in CDCl₃.



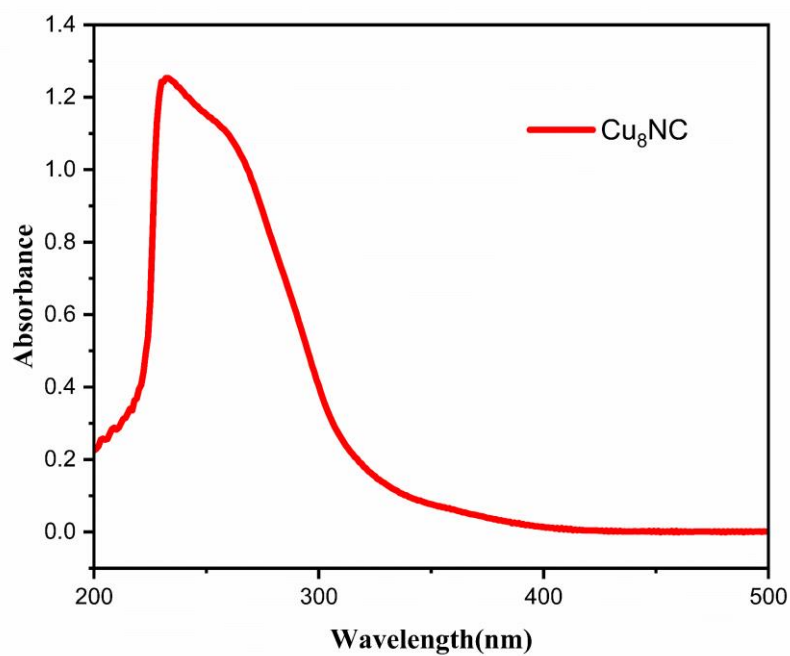
Supplementary Figure 21. ^1H NMR spectrum of microcrystalline Cu_8NC in CD_3CN . No characteristic peaks of Cu_8NC are found in ^1H NMR spectrum, proving that microcrystalline Cu_8NC is completely insoluble in MeCN solution.



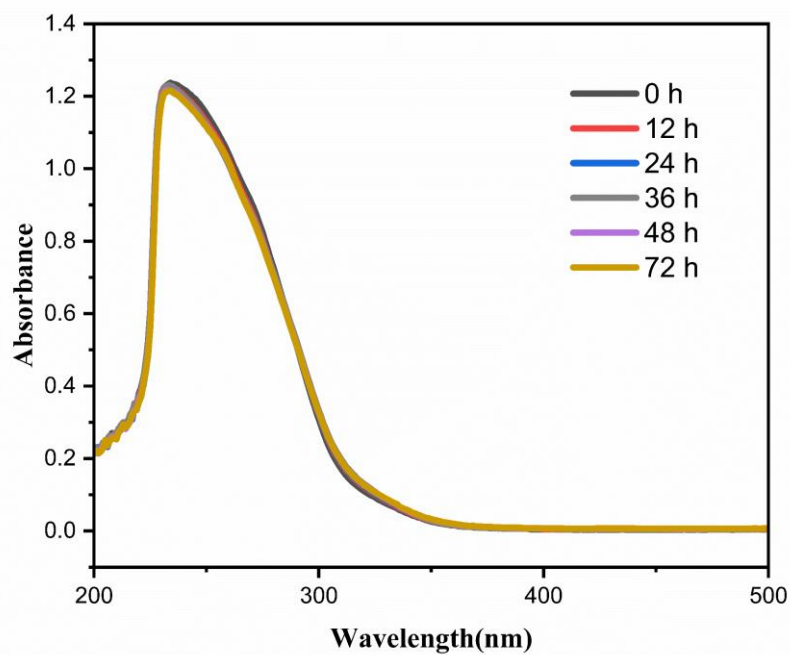
Supplementary Figure 22. ^1H NMR spectrum of microcrystalline Cu_8NC in D_2O . No characteristic peaks of Cu_8NC are found in ^1H NMR spectrum, proving that microcrystalline Cu_8NC is completely insoluble in H_2O solution.



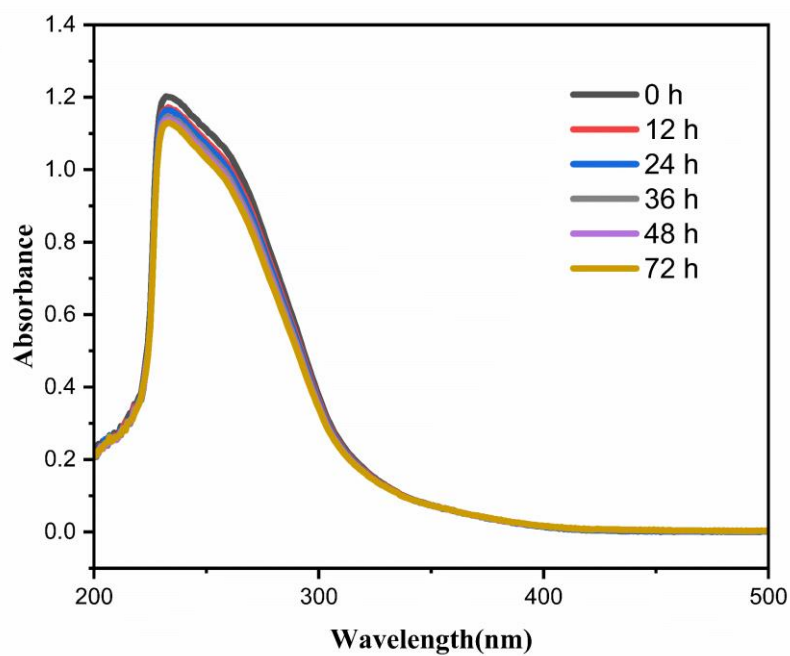
Supplementary Figure 23. Characterization of Cu_4NC . UV-vis spectrum of Cu_4NC in DCM.



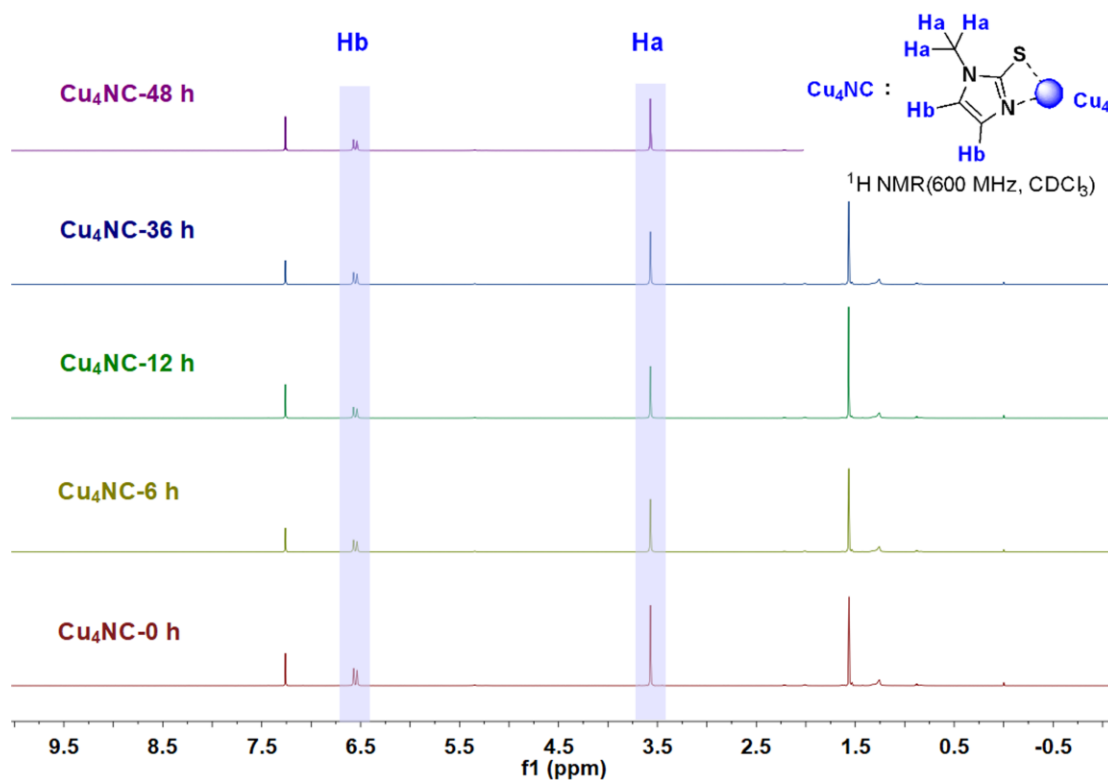
Supplementary Figure 24. Characterization of Cu_8NC . UV-vis spectrum of Cu_8NC in DCM.



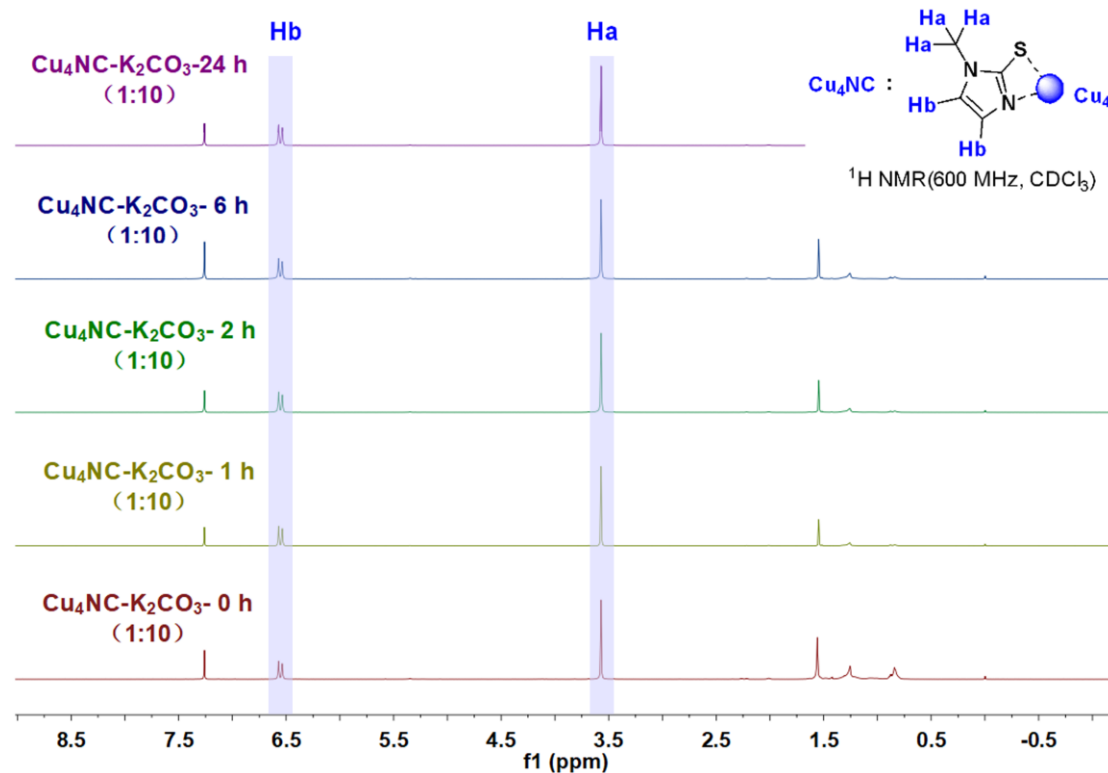
Supplementary Figure 25. Time-dependent UV-vis spectra of Cu_4NC . Time-dependent UV-vis spectra of Cu_4NC in DCM (0-72 h).



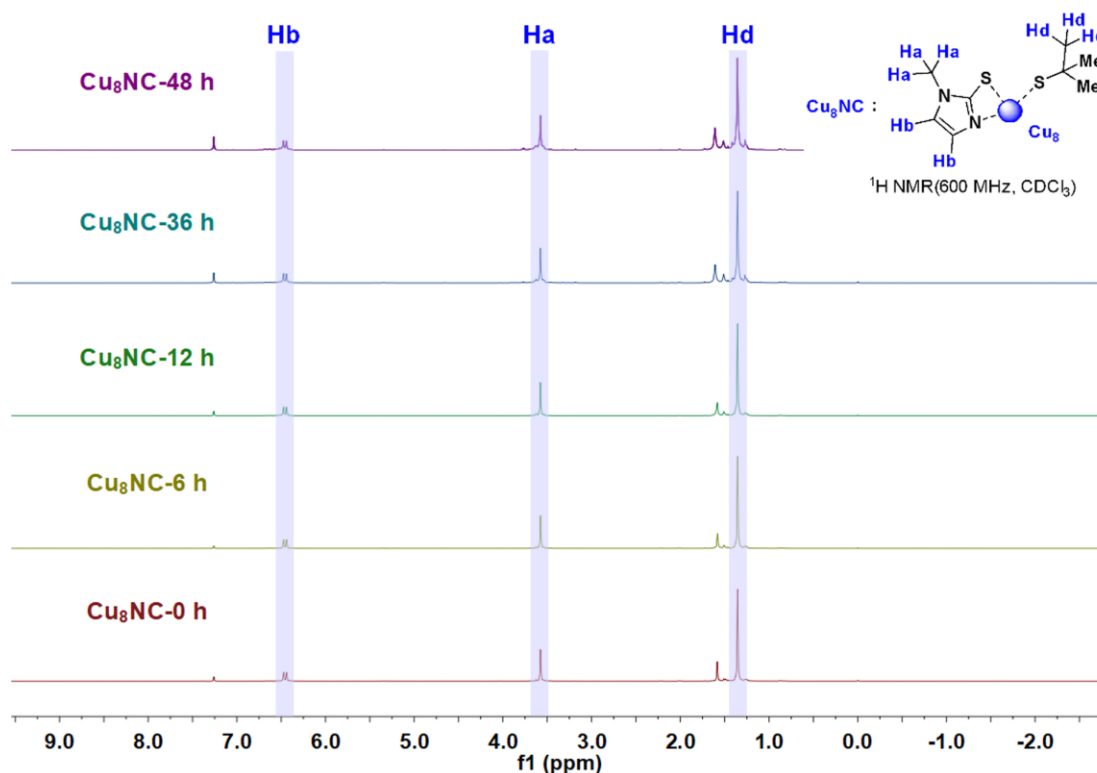
Supplementary Figure 26. Time-dependent UV-vis spectra of Cu_8NC . Time-dependent UV-vis spectra of Cu_8NC in DCM (0-72 h).



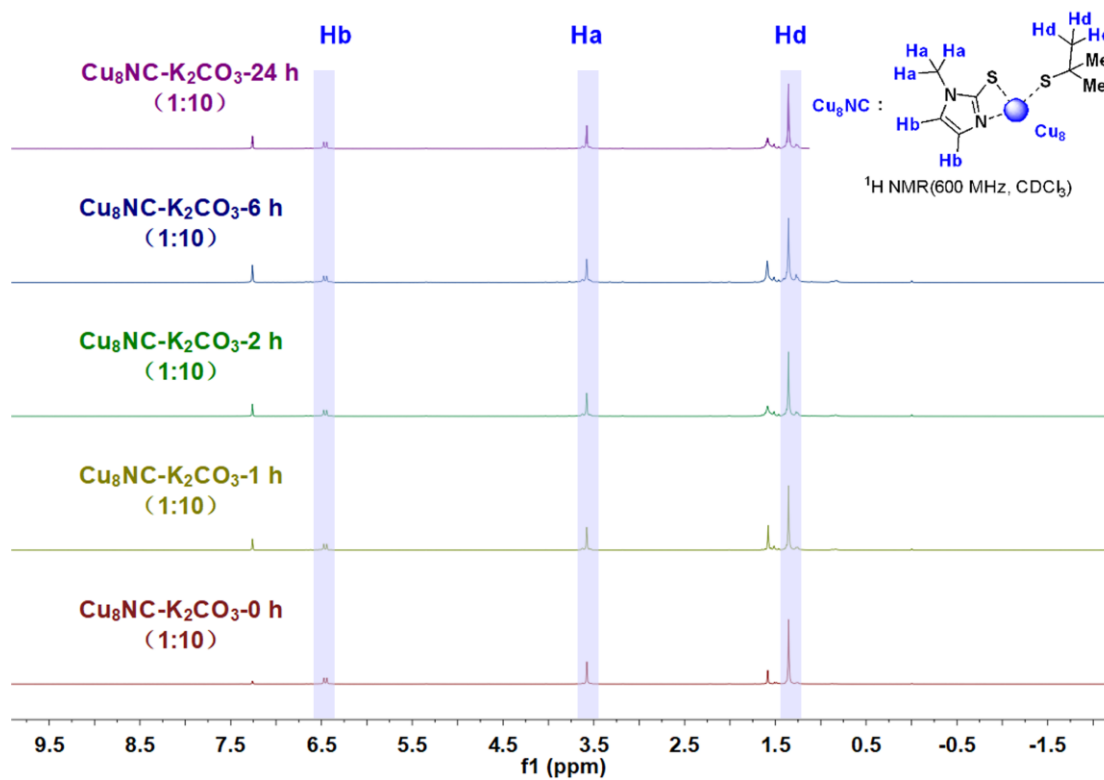
Supplementary Figure 27. ¹H NMR spectra tracking of Cu₄NC. ¹H NMR spectra tracking of Cu₄NC in CDCl₃ (0-48 h).



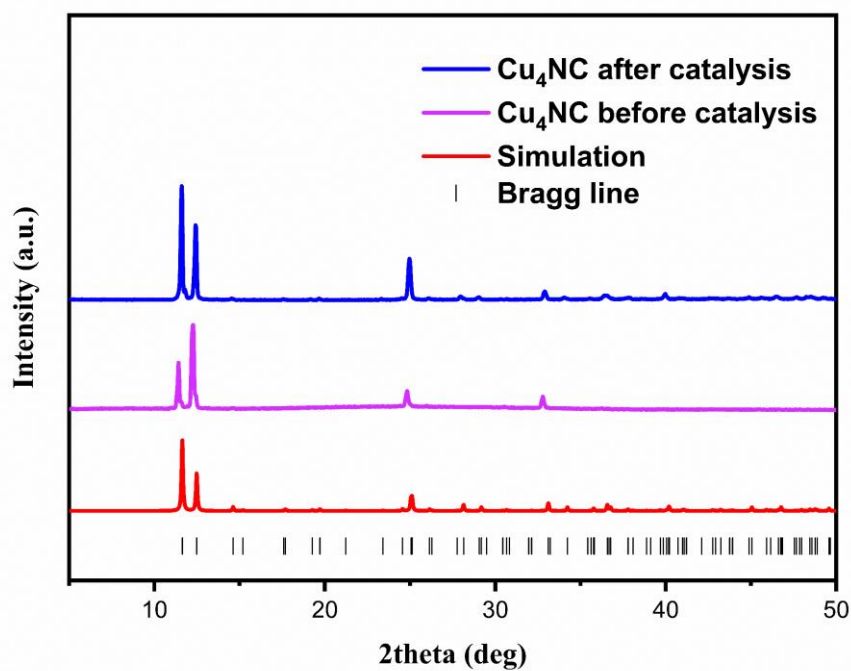
Supplementary Figure 28. ¹H NMR spectra tracking of Cu₄NC-K₂CO₃. ¹H NMR spectra tracking of Cu₄NC-K₂CO₃ (1:10) in CDCl₃ (0-24 h).



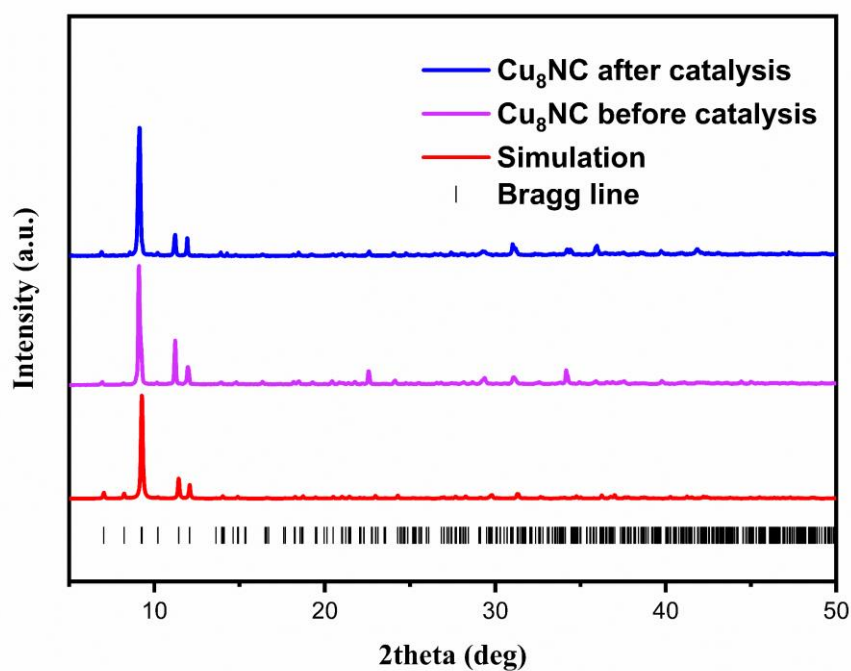
Supplementary Figure 29. ¹H NMR spectra tracking of Cu₈NC. ¹H NMR spectra tracking of Cu₈NC in CDCl₃ (0-48 h).



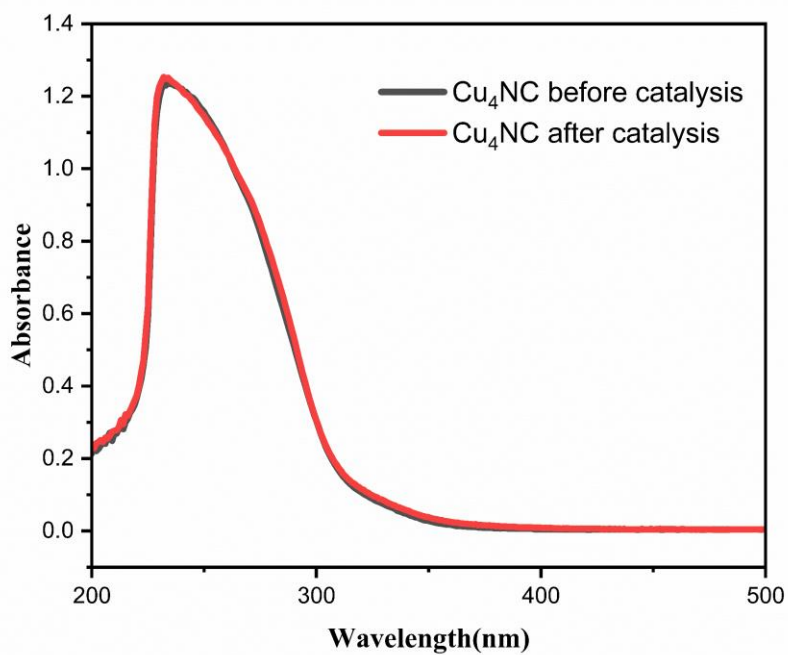
Supplementary Figure 30. ¹H NMR spectra tracking of Cu₈NC-K₂CO₃. ¹H NMR spectra tracking of Cu₈NC-K₂CO₃ (1:10) in CDCl₃ (0-24 h).



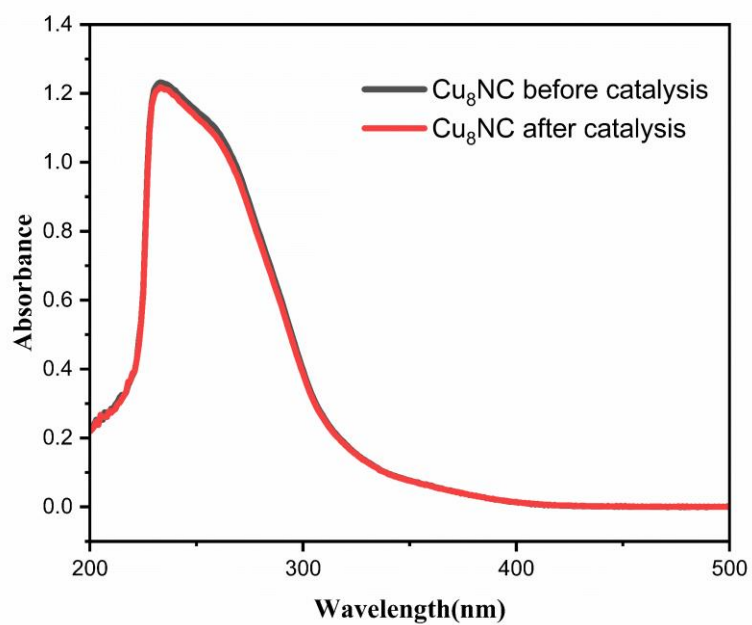
Supplementary Figure 31. PXRD pattern of Cu_4NC . PXRD patterns of microcrystalline Cu_4NC before and after catalysis.



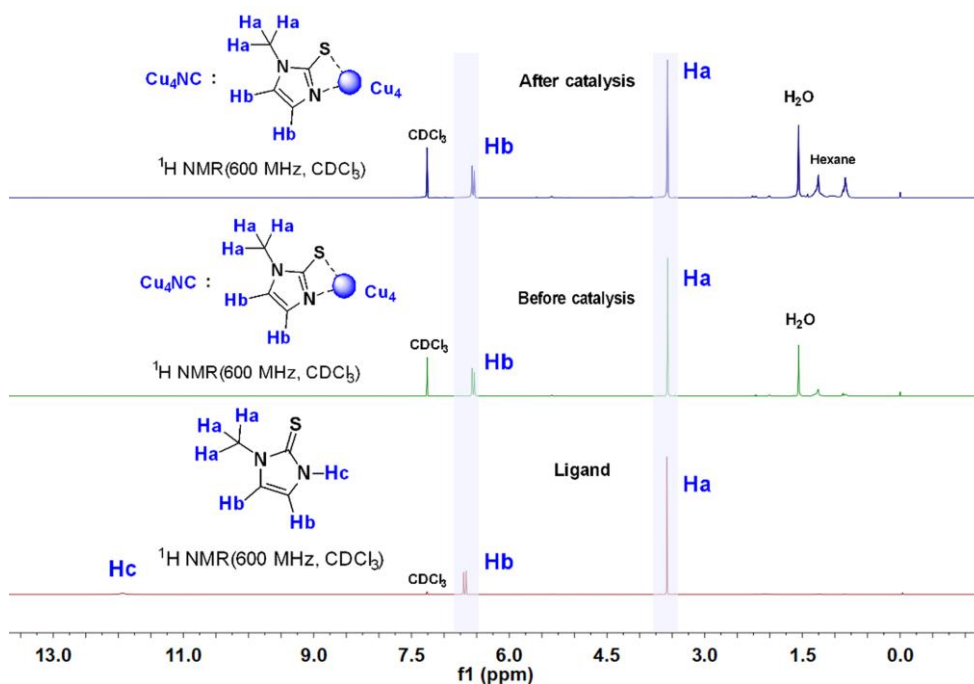
Supplementary Figure 32. PXRD pattern of Cu_8NC . PXRD patterns of microcrystalline Cu_8NC before and after catalysis.



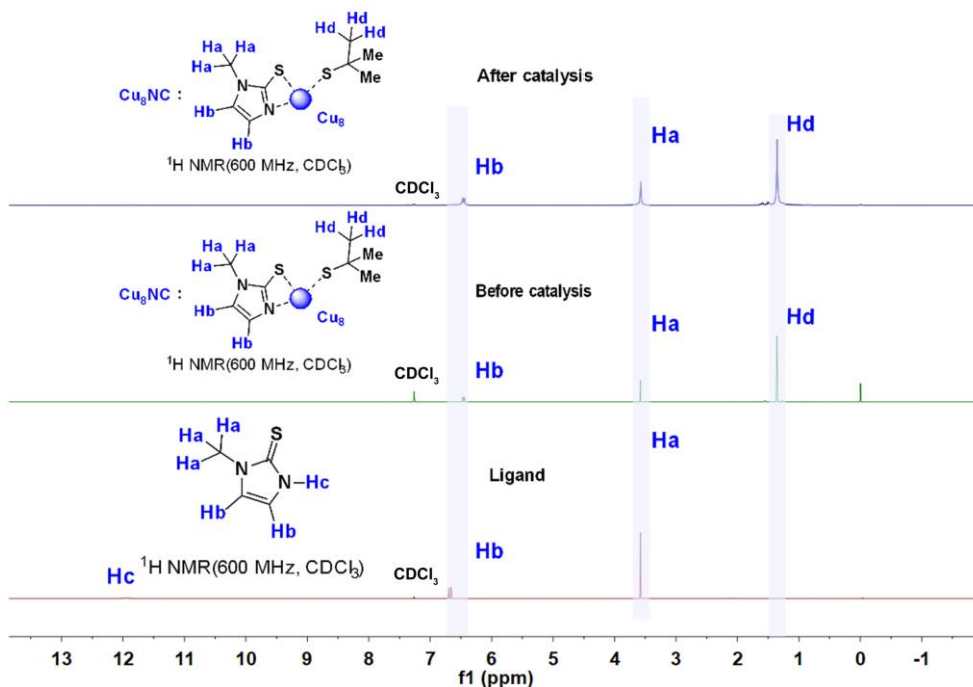
Supplementary Figure 33. Characterization of Cu_4NC before and after catalysis.
UV-vis spectra of Cu_4NC before and after catalysis in DCM.



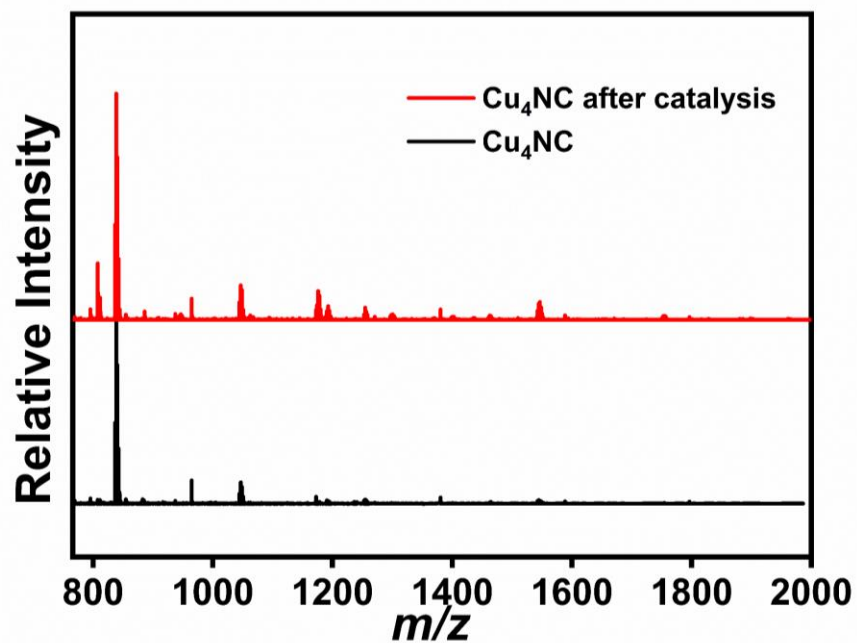
Supplementary Figure 34. Characterization of Cu_8NC before and after catalysis.
UV-vis spectra of Cu_8NC before and after catalysis in DCM.



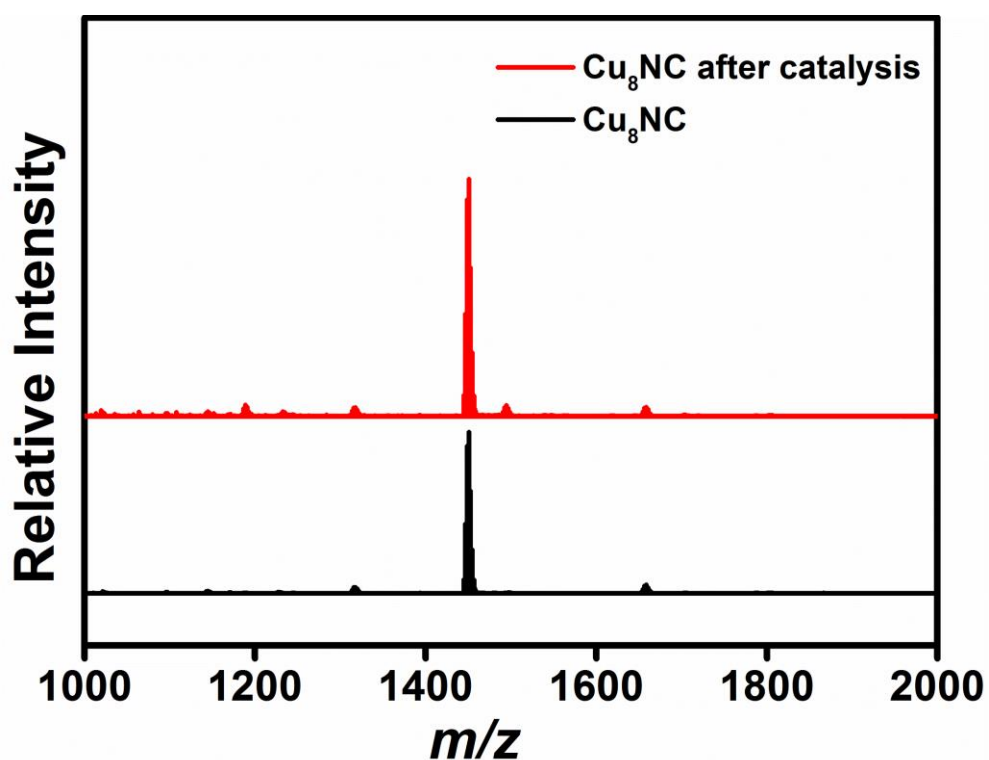
Supplementary Figure 35. ^1H NMR spectra of Cu_4NC and methimazole ligand. ^1H NMR spectra of Cu_4NC after catalysis (top: recycled microcrystalline Cu_4NC), Cu_4NC before catalysis (middle: new microcrystalline Cu_4NC) and methimazole ligand (bottom) in CDCl_3 .



Supplementary Figure 36. ^1H NMR spectra of Cu_8NC and methimazole ligand. ^1H NMR spectra of Cu_8NC after catalysis (top: recycled microcrystalline Cu_8NC), Cu_8NC before catalysis (middle: new microcrystalline Cu_8NC) and methimazole ligand (bottom) in CDCl_3 .



Supplementary Figure 37. ESI-MS spectra of the Cu_4NC . ESI-MS spectra of the Cu_4NC after catalysis (red) and the Cu_4NC before catalysis (black) in the positive mode (DMSO).



Supplementary Figure 38. ESI-MS spectra of the Cu_8NC . ESI-MS spectra of the Cu_8NC after catalysis (red) and the Cu_8NC before catalysis (black) in the positive mode (DMSO).

General Procedure for Cu₄NC-Catalyzed the Hydroboration Reaction

General Procedure for Cu Catalysts-Catalyzed Hydroboration Reaction (Method A).

Under air atmosphere, alkynes 1 (0.2 mmol, 1.0 eq), B₂Pin₂ 2 (0.44 mmol, 2.2 equiv.), Cu catalysts (0 mol%-4.0 mol%), K₂CO₃ (0.44 mmol, 2.2 equiv.) and the mixture solvent (2.0 mL, MeCN-H₂O, v/v 4/1) were added into a tube. The reaction mixture was stirred at room temperature for 1 h. The reactions were monitored by TLC. When alkynes were consumed, the reactions were quenched and concentrated. The crude products were then purified by column chromatography to give the target products.

General Procedure for Cu₄NC-Catalyzed Hydroboration Reaction (Method B).

Under air atmosphere, alkynes 1 (0.2 mmol, 1.0 eq), B₂Pin₂ 2 (0.44 mmol, 2.2 equiv.), microcrystalline Cu₄NC catalysts (2.0 mol%), K₂CO₃ (0.44 mmol, 2.2 equiv.) and the mixture solvent (2.0 mL, MeCN-H₂O, v/v 4/1) were added into a tube. The reaction mixture was stirred at room temperature for 1 h or 2 h. The reactions were monitored by TLC. When alkynes were consumed, the reactions were quenched and concentrated. The crude products were then purified by column chromatography to give the target products.

General Procedure for Cu₄NC-Catalyzed Hydroboration Reaction in Dark (Method C).

In dark, alkynes 1 (0.2 mmol, 1.0 eq), B₂Pin₂ 2 (0.44 mmol, 2.2 equiv.), microcrystalline Cu₄NC catalysts (2.0 mol%), K₂CO₃ (0.44 mmol, 2.2 equiv.) and the mixture solvent (2.0 mL, MeCN-H₂O, v/v 4/1) were added into a tube under air atmosphere. The reaction mixture was stirred at room temperature for 1 h. The reactions were monitored by TLC. When alkynes were consumed, the reactions were quenched and concentrated. The crude products were then purified by column chromatography to give the target products.

General Procedure for Cu₄NC-Catalyzed Hydroboration Reaction (Method D).

Under N₂ atmosphere, alkynes 1 (0.2 mmol, 1.0 eq), B₂Pin₂ 2 (0.44 mmol, 2.2 equiv.), microcrystalline Cu₄NC catalysts (2.0 mol%), K₂CO₃ (0.44 mmol, 2.2 equiv.) and the mixture solvent (2.0 mL, MeCN-H₂O, v/v 4/1) were added into a tube. The reaction mixture was stirred at room temperature for 1 h. The reactions were monitored by TLC. When alkynes were consumed, the reactions were quenched and concentrated. The crude products were then purified by column chromatography to give the target products.

General Procedure for Cu₄NC-Catalyzed Hydroboration Reaction (Method E).

Under air atmosphere, alkynes 1 (0.2 mmol, 1.0 eq), B₂Pin₂ 2 (0.44 mmol, 2.2 equiv.), microcrystalline Cu₄NC catalysts (2.0 mol%), base (0 mmol-0.44 mmol, 0 equiv.-2.2 equiv.) and the mixture solvent (2.0 mL, MeCN-H₂O, v/v 4/1) were added into a tube.

The reaction mixture was stirred at room temperature for 1 h. The reactions were monitored by TLC. When alkynes were consumed, the reactions were quenched and concentrated. The crude products were then purified by column chromatography to give the target products.

General Procedure for Cu₄NC-Catalyzed Hydroboration Reaction (Method F).

Under air atmosphere, alkynes **1** (0.2 mmol, 1.0 eq), B₂Pin₂ **2** (0.44 mmol, 2.2 equiv.), microcrystalline Cu₄NC catalysts (2.0 mol%), K₂CO₃ (0.44 mmol, 2.2 equiv.) and kinds of solvent (2.0 mL) were added into a tube. The reaction mixture was stirred at room temperature for 1 h. The reactions were monitored by TLC. When alkynes were consumed, the reactions were quenched and concentrated. The crude products were then purified by column chromatography to give the target products.

General Procedure for Cu₄NC-Catalyzed Hydroboration Reaction (Method G).

Under air atmosphere, alkynes **1** (0.1 mmol, 1.0 eq), B₂Pin₂ **2** (0.44 mmol, 4.4 equiv.), microcrystalline Cu₄NC catalysts (2.0 mol%), K₂CO₃ (0.44 mmol, 4.4 equiv.) and the mixture solvent (2.0 mL, MeCN-H₂O, v/v 4/1) were added into a tube. The reaction mixture was stirred at room temperature for 1 h. The reactions were monitored by TLC. When alkynes were consumed, the reactions were quenched and concentrated. The crude products were then purified by column chromatography to give products.

General Procedure for Cu₄NC-Catalyzed Hydroboration Reaction (Method H).

Under air atmosphere, alkynes **1** (0.2 mmol, 1.0 eq), alkenes (0.2 mmol, 1.0 eq), B₂Pin₂ **2** (0.44 mmol, 2.2 equiv.), microcrystalline Cu₄NC catalysts (2.0 mol%), K₂CO₃ (0.44 mmol, 2.2 equiv.) and the mixture solvent (2.0 mL, MeCN-H₂O, v/v 4/1) were added into a tube. The reaction mixture was stirred at room temperature for 1 h. The reactions were monitored by TLC. When alkynes or alkenes were consumed, the reactions were quenched and concentrated. The crude products were then purified by column chromatography to give the target products.

General Procedure for Cu₄NC-Catalyzed Hydroboration Reaction in 55 mmol Scale.

Under air atmosphere, phenylacetylene **1** (5615.5 mg, 55.0 mmol, 1.0 eq), B₂Pin₂ **2** (30721.9 mg, 121.0 mmol, 2.2 equiv.), microcrystalline Cu₄NC catalysts (0.5 mg, 7×10⁻⁴ mmol, 1.3×10⁻³ mol%), K₂CO₃ (8361.7 mg, 60.5 mmol, 1.1 equiv.) and the mixture solvent (55.0 mL, MeCN-H₂O, v/v 4/1) were added into a 100mL flask. The reaction mixture was stirred at room temperature for 12.5 h. The reactions were monitored by TLC. When alkynes were consumed, the reactions were quenched and concentrated. The crude products were then purified by column chromatography to give the (E)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (**E-4a**) products as colorless oil with an overall isolated yield: 98% (12396.8 mg).

Investigation on the Lowest Load of Cu₄NC Catalyst for the Hydroboration Transformation

Supplementary Table 1. Investigation on the lowest load of microcrystalline Cu₄NC catalyst for the hydroboration of phenylacetylene under the different conditions.

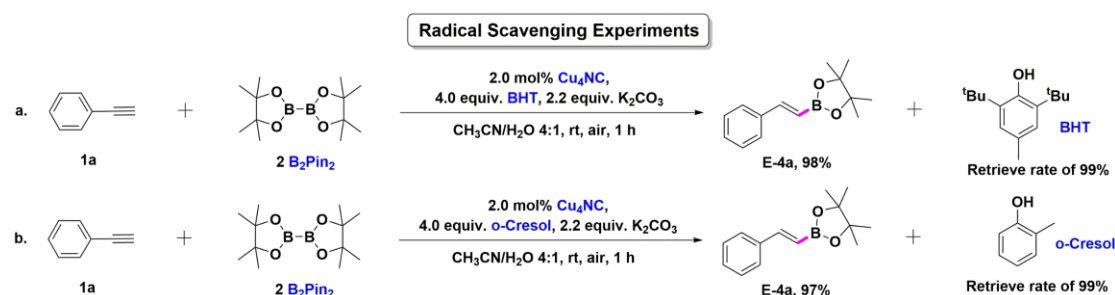
Hydroboration of alkyne

Entry	Time	Phenylacetylene	Cat.: Cu ₄ NC	Yield ^k	TON ^l	TOF (h ⁻¹) ^m
1 ^a	1 h	10 mmol	7×10 ⁻⁴ mmol	76%	10857	10857
2 ^a	2 h	10 mmol	7×10 ⁻⁴ mmol	100%	14286	7143
3 ^b	1 h	15 mmol	7×10 ⁻⁴ mmol	62%	13286	13286
4 ^b	2 h	15 mmol	7×10 ⁻⁴ mmol	88%	18857	9429
5 ^b	3 h	15 mmol	7×10 ⁻⁴ mmol	100%	21429	7143
6 ^c	1 h	20 mmol	7×10 ⁻⁴ mmol	57%	16286	16286
7 ^c	3 h	20 mmol	7×10 ⁻⁴ mmol	90%	25714	8571
8 ^c	4 h	20 mmol	7×10 ⁻⁴ mmol	100%	28571	7143
9 ^d	1 h	25 mmol	7×10 ⁻⁴ mmol	44%	15714	15714
10 ^d	3 h	25 mmol	7×10 ⁻⁴ mmol	87%	31071	10357
11 ^d	4 h	25 mmol	7×10 ⁻⁴ mmol	100%	35714	8929
10 ^e	1 h	30 mmol	7×10 ⁻⁴ mmol	35%	15000	15000
10 ^e	2 h	30 mmol	7×10 ⁻⁴ mmol	51%	21857	10929
11 ^e	4 h	30 mmol	7×10 ⁻⁴ mmol	78%	33429	8357
12 ^e	7 h	30 mmol	7×10 ⁻⁴ mmol	100%	42857	6122
13 ^f	4 h	35 mmol	7×10 ⁻⁴ mmol	75%	37500	9375
14 ^f	8 h	35 mmol	7×10 ⁻⁴ mmol	100%	50000	6250
15 ^g	9.2 h	40 mmol	7×10 ⁻⁴ mmol	100%	57143	6211
16 ^h	10.3 h	45 mmol	7×10 ⁻⁴ mmol	100%	64286	6241
17 ⁱ	11.5 h	50 mmol	7×10 ⁻⁴ mmol	100%	71429	6211
18 ^j	12.5 h	55 mmol	7×10 ⁻⁴ mmol	99%	77786	6223

^aGeneral reaction conditions: Under air atmosphere, alkynes **1** (10 mmol, 1.0 eq), B₂Pin₂ **2** (22.0 mmol, 2.2 equiv.), microcrystalline Cu₄NC catalysts (7×10⁻⁴ mmol), K₂CO₃ (22.0 mmol, 2.2 equiv.) and the mixture solvent (10.0 mL, MeCN-H₂O, v/v 4/1) were added into a 30 mL vial. The reaction mixture was stirred at room temperature. ^bGeneral reaction conditions: Under air atmosphere, alkynes **1** (15 mmol, 1.0 eq), B₂Pin₂ **2** (33.0 mmol, 2.2 equiv.), microcrystalline Cu₄NC catalysts (7×10⁻⁴ mmol), K₂CO₃ (33.0 mmol, 2.2 equiv.) and the mixture solvent (30.0 mL, MeCN-H₂O, v/v 4/1) were added into a 50 mL flask. The reaction mixture was stirred at room temperature. ^cGeneral reaction conditions: Under air atmosphere, alkynes **1** (20 mmol, 1.0 eq), B₂Pin₂ **2** (44.0 mmol, 2.2 equiv.), microcrystalline Cu₄NC catalysts (7×10⁻⁴ mmol), K₂CO₃ (33.0 mmol, 1.65 equiv.) and the mixture solvent (40.0 mL, MeCN-H₂O, v/v 4/1) were added into a 50 mL flask. The reaction mixture was stirred at room temperature. ^dGeneral reaction conditions: Under air atmosphere, alkynes **1** (25 mmol, 1.0 eq), B₂Pin₂ **2** (55.0 mmol, 2.2 equiv.), microcrystalline Cu₄NC catalysts (7×10⁻⁴ mmol), K₂CO₃ (33.0 mmol, 1.32 equiv.) and the mixture solvent (30.0 mL, MeCN-H₂O, v/v 4/1) were added into a 50 mL flask. The reaction mixture was stirred at room temperature. ^eGeneral reaction conditions: Under air atmosphere, alkynes **1** (30 mmol, 1.0 eq), B₂Pin₂ **2** (66.0 mmol, 2.2 equiv.), microcrystalline Cu₄NC catalysts (7×10⁻⁴ mmol), K₂CO₃ (33.0 mmol, 1.1 equiv.) and the mixture solvent (30.0 mL, MeCN-H₂O, v/v 4/1) were added into a 50 mL flask. The reaction mixture was stirred at room temperature. ^fGeneral reaction conditions: Under air atmosphere, alkynes **1** (35 mmol, 1.0 eq), B₂Pin₂ **2** (77.0 mmol, 2.2 equiv.),

microcrystalline Cu₄NC catalysts (7×10⁻⁴ mmol), K₂CO₃ (38.5 mmol, 1.1 equiv.) and the mixture solvent (40.0 mL, MeCN-H₂O, v/v 4/1) were added into a 100 mL flask. The reaction mixture was stirred at room temperature. ^gYield was determined by ¹H NMR using 1,3,5-trimethoxybenzene as an internal standard. ^gGeneral reaction conditions: Under air atmosphere, alkynes **1** (40 mmol, 1.0 eq), B₂Pin₂ **2** (88.0 mmol, 2.2 equiv.), microcrystalline Cu₄NC catalysts (7×10⁻⁴ mmol), K₂CO₃ (44.0 mmol, 1.1 equiv.) and the mixture solvent (40.0 mL, MeCN-H₂O, v/v 4/1) were added into a 100 mL flask. The reaction mixture was stirred at room temperature. ^hGeneral reaction conditions: Under air atmosphere, alkynes **1** (45 mmol, 1.0 eq), B₂Pin₂ **2** (99.0 mmol, 2.2 equiv.), microcrystalline Cu₄NC catalysts (7×10⁻⁴ mmol), K₂CO₃ (49.5 mmol, 1.1 equiv.) and the mixture solvent (45.0 mL, MeCN-H₂O, v/v 4/1) were added into a 100 mL flask. The reaction mixture was stirred at room temperature. ⁱGeneral reaction conditions: Under air atmosphere, alkynes **1** (50 mmol, 1.0 eq), B₂Pin₂ **2** (110.0 mmol, 2.2 equiv.), microcrystalline Cu₄NC catalysts (7×10⁻⁴ mmol), K₂CO₃ (55.0 mmol, 1.1 equiv.) and the mixture solvent (50.0 mL, MeCN-H₂O, v/v 4/1) were added into a 100 mL flask. The reaction mixture was stirred at room temperature. ^jGeneral reaction conditions: Under air atmosphere, alkynes **1** (55 mmol, 1.0 eq), B₂Pin₂ **2** (121.0 mmol, 2.2 equiv.), microcrystalline Cu₄NC catalysts (7×10⁻⁴ mmol), K₂CO₃ (60.5 mmol, 1.1 equiv.) and the mixture solvent (55.0 mL, MeCN-H₂O, v/v 4/1) were added into a 100 mL flask. The reaction mixture was stirred at room temperature. ^kYield was determined by ¹H NMR using 1,3,5-trimethoxybenzene as an internal standard. ^lTON = (Moles of reactants) × (Yield %) / (Moles of catalysts). ^mTOF = TON / Time (h).

Catalytic Mechanism Studies by a Series of Control Experiments

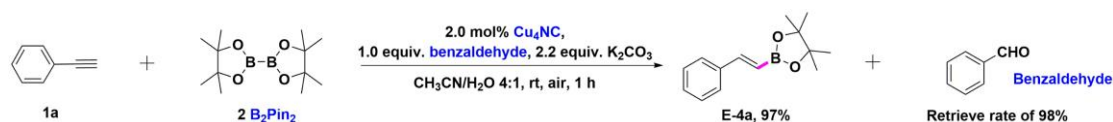


Supplementary Figure 39. Radical scavenging experiments of microcrystalline Cu₄NC-catalyzed hydroboration reaction. **a.** The BHT as radical scavenger in radical scavenging experiment. **b.** The *o*-cresol as radical scavenger in radical scavenging experiment.

Radical scavenging experiment a. Under air atmosphere, phenylacetylene **1a** (20.4 mg, 0.2 mmol, 1.0 eq), BHT (176.3 mg, 0.8 mmol, 4.0 eq), B₂Pin₂ **2** (111.8 mg, 0.44 mmol, 2.2 equiv.), microcrystalline Cu₄NC catalysts (2.8 mg, 2.0 mol%), K₂CO₃ (60.7 mg, 0.44 mmol, 2.2 equiv.) and the mixture solvent (2.0 mL, CD₃CN-H₂O, v/v 4/1) were added into a tube. The reaction mixture was stirred at room temperature for 1 h. The reactions were monitored by TLC. When alkynes were consumed, the reactions were quenched and concentrated. Conversion and yield were determined by ¹H NMR using 1,3,5-trimethoxybenzene as an internal standard. The crude products were then purified by column chromatography (PE-EA, v/v 20/1) to give the target product **E-4a** as a colorless oil with an overall isolated yield: 98%. The retrieve rate of BHT is 99%.

Radical scavenging experiment b. Under air atmosphere, phenylacetylene **1a** (20.4 mg, 0.2 mmol, 1.0 eq), *o*-cresol (86.5 mg, 0.8 mmol, 4.0 eq), B₂Pin₂ **2** (111.8 mg, 0.44 mmol, 2.2 equiv.), microcrystalline Cu₄NC catalysts (2.8 mg, 2.0 mol%), K₂CO₃ (60.7

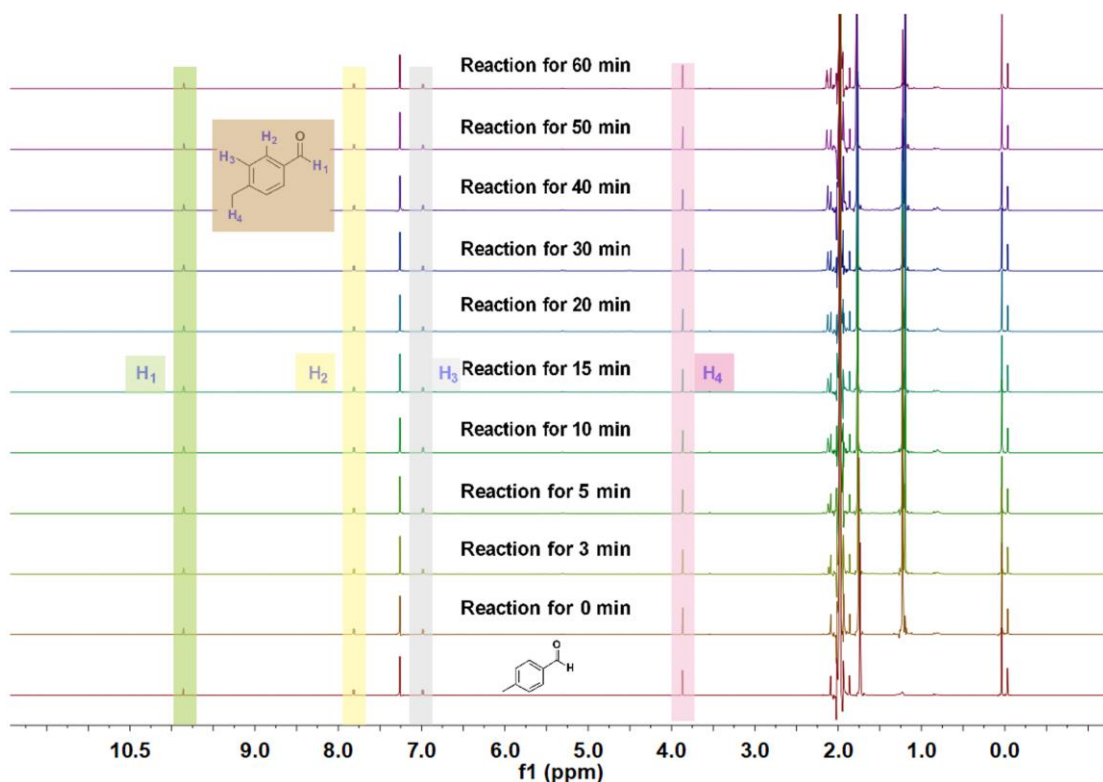
mg, 0.44 mmol, 2.2 equiv.) and the mixture solvent (2.0 mL, CD₃CN-H₂O, v/v 4/1) were added into a tube. The reaction mixture was stirred at room temperature for 1 h. The reactions were monitored by TLC. When alkynes were consumed, the reactions were quenched and concentrated. Conversion and yield were determined by ¹H NMR using 1,3,5-trimethoxybenzene as an internal standard. The crude products were then purified by column chromatography (PE-EA, v/v 20/1) to give the target product **E-4a** as a colorless oil with an overall isolated yield: 97%. The retrieve rate of o-cresol is 99%.



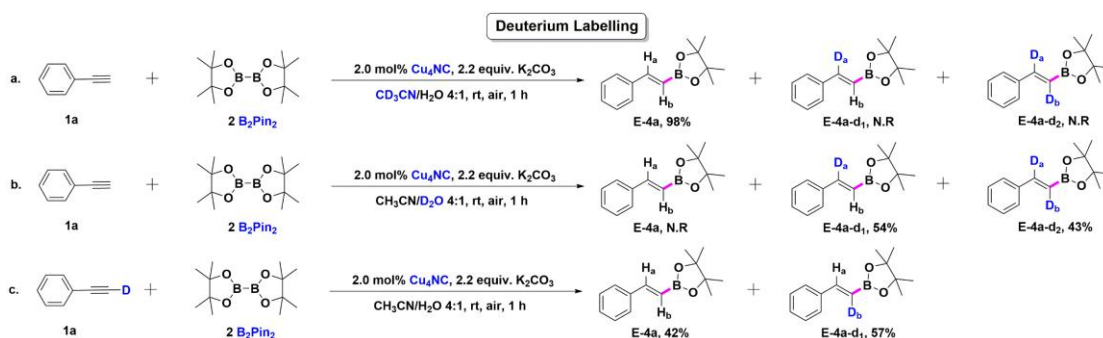
Supplementary Figure 40. The control experiment. The control experiment of microcrystalline Cu₄NC-catalyzed the hydroboration reaction.

Under air atmosphere, phenylacetylene **1a** (20.4 mg, 0.2 mmol, 1.0 eq), benzaldehyde (21.2 mg, 0.2 mmol, 1.0 eq), B₂Pin₂ **2** (111.8 mg, 0.44 mmol, 2.2 equiv.), microcrystalline Cu₄NC catalysts (2.8 mg, 2.0 mol%), K₂CO₃ (60.7 mg, 0.44 mmol, 2.2 equiv.) and the mixture solvent (2.0 mL, CD₃CN-H₂O, v/v 4/1) were added into a tube. The reaction mixture was stirred at room temperature for 1 h. The reactions were monitored by TLC. When alkynes were consumed, the reactions were quenched and concentrated. Conversion and yield were determined by ¹H NMR using 1,3,5-trimethoxybenzene as an internal standard. The crude products were then purified by column chromatography (PE-EA, v/v 20/1) to give the target product **E-4a** as a colorless oil with an overall isolated yield: 97%. The retrieve rate of benzaldehyde is 98%.

To prove that the carbonyl of benzaldehyde remains intact in our catalytic system, we carried out the NMR experiment. As reviewer suggested, 2.0 mol% microcrystalline Cu₄NC, 1.0 eq. *p*-tolualdehyde, 2.2 eq. B₂Pin₂ and 2.2 eq. K₂CO₃ were added into the mixture solvent (CH₃CN-H₂O). The *in situ* ¹H NMR was monitored at the 0 minute, the 3rd minute, 5th minute, the 10th minute, 15th minute, the 20th minute, 30th minute, the 40th minute, 50th minute and the 60th minute, showing that characteristic peaks of *p*-tolualdehyde have no change (Supplementary Figure 41). The result illustrated that *p*-tolualdehyde is inert substrate to our catalytic system, indicating that the carbonyl remains intact our catalytic system.



Supplementary Figure 41. Time-dependent *in situ* ^1H NMR spectra of the reaction catalyzed by microcrystalline Cu_4NC catalyst. Reaction conditions: *p*-tolualdehyde (0.2 mmol, 1.0 equiv.), B_2Pin_2 **2** (0.44 mmol, 2.2 equiv.), Cu_4NC catal. (0.004 mmol, 2.0 mol%) and K_2CO_3 (0.44 mmol, 2.2 equiv.) were added to the mixture solvent (2.0 mL, $\text{MeCN}/\text{H}_2\text{O}$ 4:1) under air atmosphere at room temperature and allowed to react for 1 h.

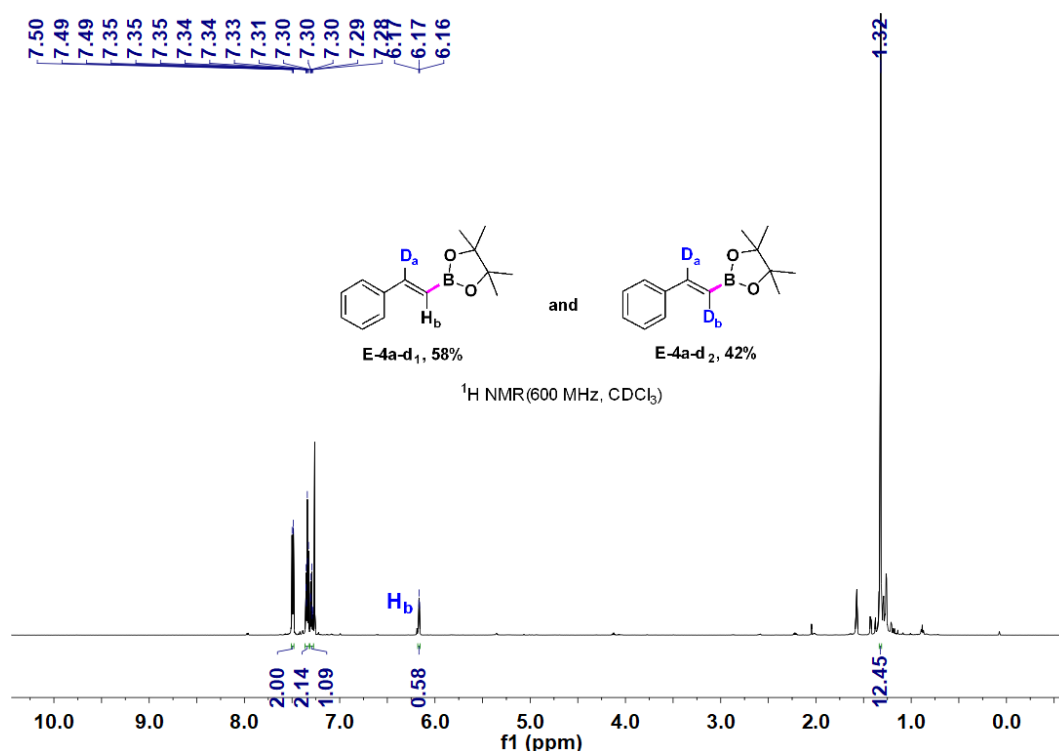


Supplementary Figure 42. Deuterium experiments of microcrystalline Cu_4NC -catalyzed hydroboration reaction. **a.** The CD_3CN as deuterium source in deuterium experiment. **b.** The D_2O as deuterium source in deuterium experiment. **c.** The phenylacetylene-d₁ as deuterium source in deuterium experiment.

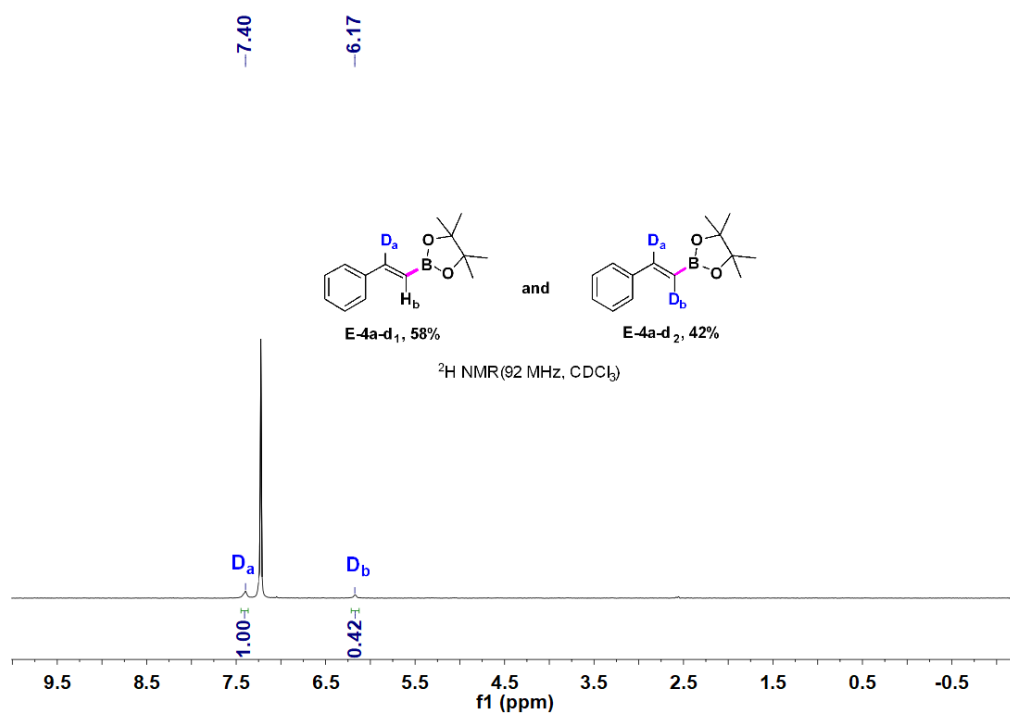
General Procedure for deuterium experiment a. Under air atmosphere, phenylacetylene **1a** (20.4 mg, 0.2 mmol, 1.0 eq), B_2Pin_2 **2** (111.8 mg, 0.44 mmol, 2.2 equiv.), microcrystalline Cu_4NC catalysts (2.8 mg, 2.0 mol%), K_2CO_3 (60.7 mg, 0.44 mmol, 2.2 equiv.) and the mixture solvent (2.0 mL, $\text{CD}_3\text{CN}-\text{H}_2\text{O}$, v/v 4/1) were added

into a tube. The reaction mixture was stirred at room temperature for 1 h. The reactions were monitored by TLC. When alkynes were consumed, the reactions were quenched and concentrated. Conversion and yield were determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard. The crude products were then purified by column chromatography (PE-EA, v/v 20/1) to give the target product **E-4a** as a colorless oil. ^1H NMR (600 MHz, CDCl_3) δ 7.49 (d, $J = 7.2$ Hz, 2H), 7.40 (d, $J = 18.4$ Hz, 1H), 7.34 (t, $J = 7.4$ Hz, 2H), 7.29 (ddd, $J = 7.3, 3.6, 1.2$ Hz, 1H), 6.17 (d, $J = 18.4$ Hz, 1H), 1.32 (s, 12H).

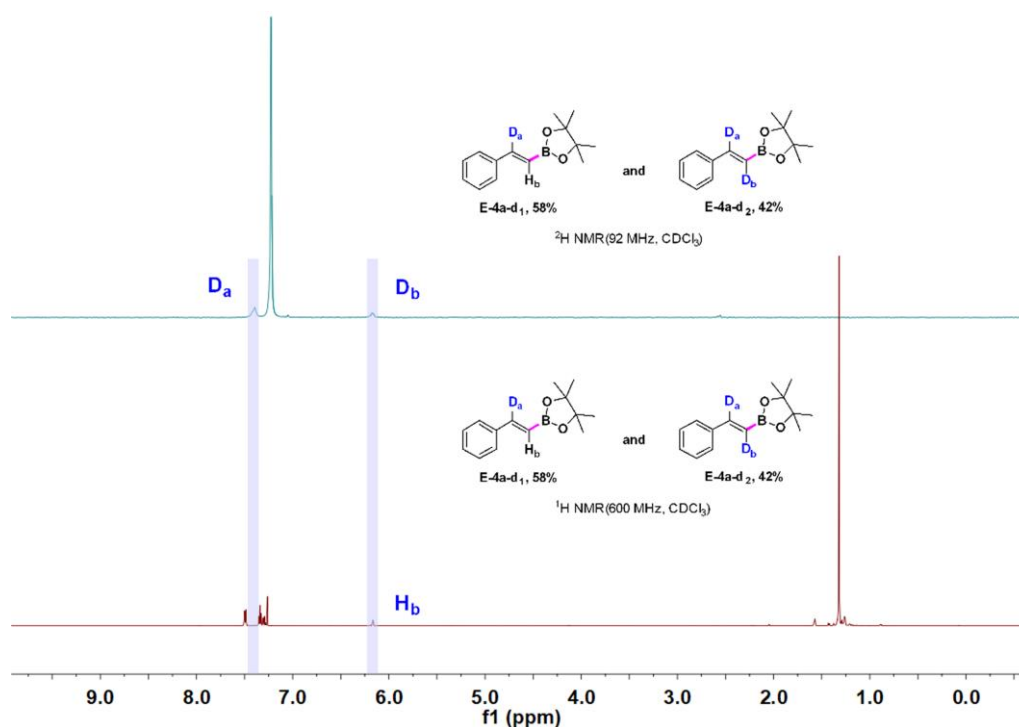
General Procedure for deuterium experiment b. Under air atmosphere, phenylacetylene **1a** (20.4 mg, 0.2 mmol, 1.0 eq), B_2Pin_2 **2** (111.8 mg, 0.44 mmol, 2.2 equiv.), microcrystalline Cu_4NC catalysts (2.8 mg, 2.0 mol%), K_2CO_3 (60.7 mg, 0.44 mmol, 2.2 equiv.) and the mixture solvent (2.0 mL, $\text{CH}_3\text{CN}-\text{D}_2\text{O}$, v/v 4/1) were added into a tube. The reaction mixture was stirred at room temperature for 1 h. The reactions were monitored by TLC. When alkynes were consumed, the reactions were quenched and concentrated. Conversion and yield were determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard. The crude products were then purified by column chromatography to give the target products **E-4a-d₁** and **E-4a-d₂** as colorless oils, which are inseparable mixture of products with an isolated ratio of **E-4a-d₁** to **E-4a-d₂** of 58:42, compared to the original ratio of 54:43. ^1H NMR (600 MHz, CDCl_3) δ 7.51 – 7.48 (m, 2H), 7.36 – 7.32 (m, 2H), 7.31 – 7.28 (m, 1H), 6.18 – 6.16 (m, 0.58H), 1.32 (s, 12H). ^2H NMR (92 MHz, CDCl_3) δ 7.40 (s, 1H), 6.17 (s, 0.42H).



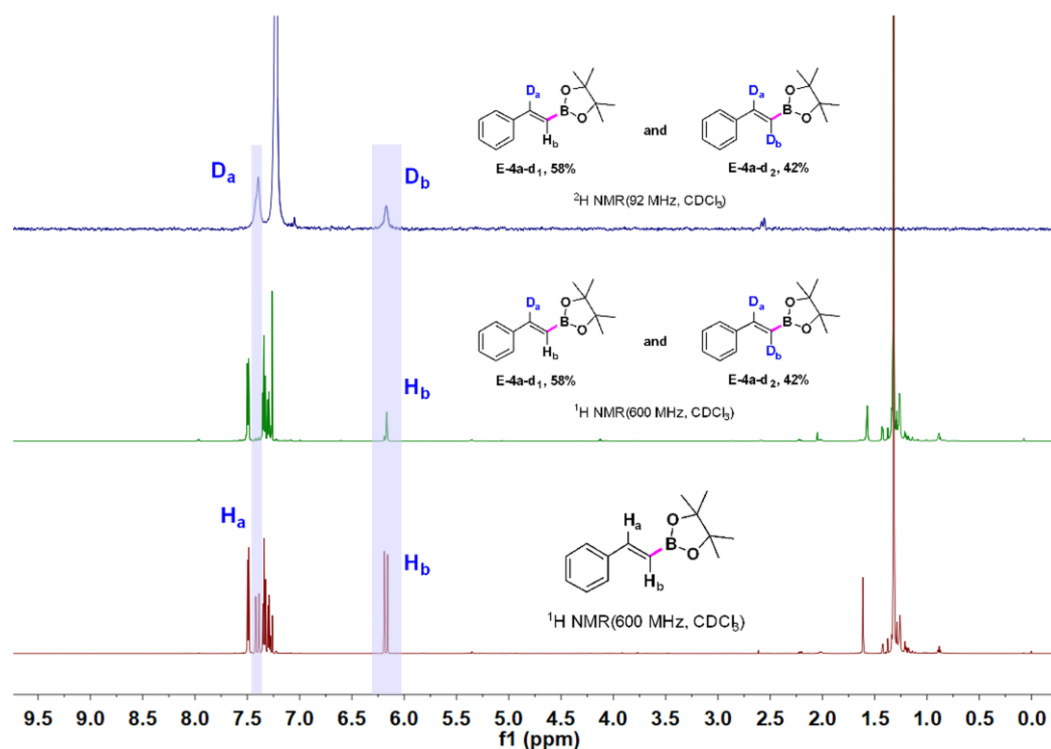
Supplementary Figure 43. ^1H NMR spectrum of inseparable compounds **E-4a-d₁** and **E-4a-d₂** in CDCl_3 . The control experiment was catalyzed by microcrystalline Cu_4NC in the mixture solvent of $\text{CH}_3\text{CN}-\text{D}_2\text{O}$.



Supplementary Figure 44. ²H NMR spectrum of inseparable compounds **E-4a-d₁** and **E-4a-d₂** in CDCl₃-DCM. The control experiment was catalyzed by microcrystalline Cu₄NC in the mixture solvent of CH₃CN-D₂O.

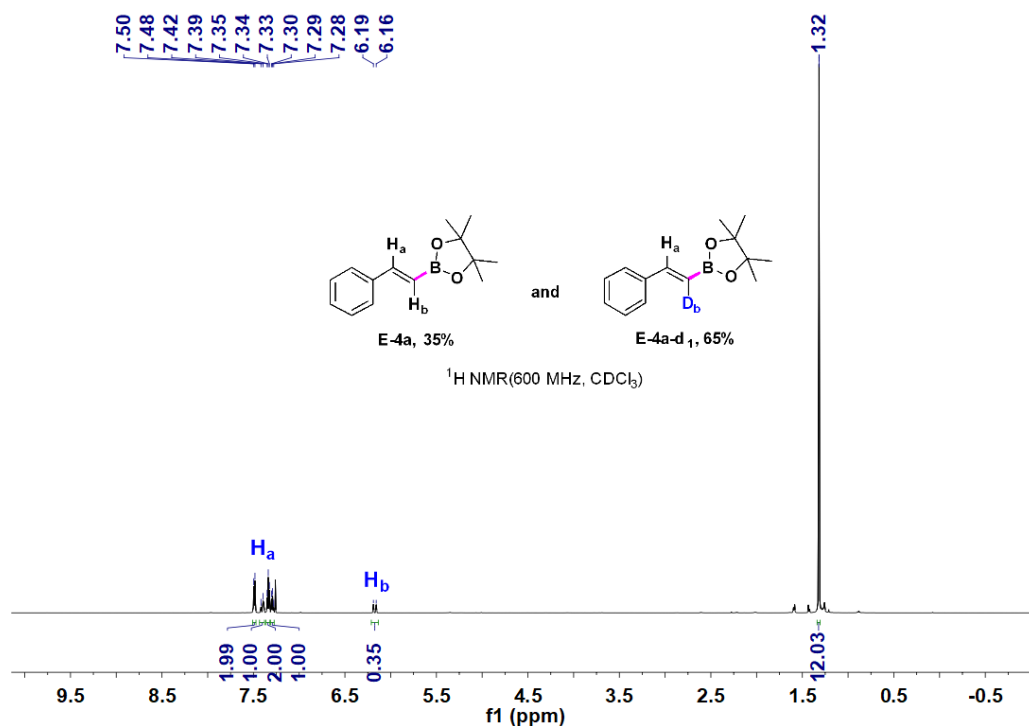


Supplementary Figure 45. ²H NMR spectrum of inseparable compounds **E-4a-d₁** and **E-4a-d₂** in CDCl₃-DCM (top) and ¹H NMR spectrum of inseparable compounds **E-4a-d₁** and **E-4a-d₂** in CDCl₃ (bottom). The control experiment was catalyzed by microcrystalline Cu₄NC in the mixture solvent of CH₃CN-D₂O.

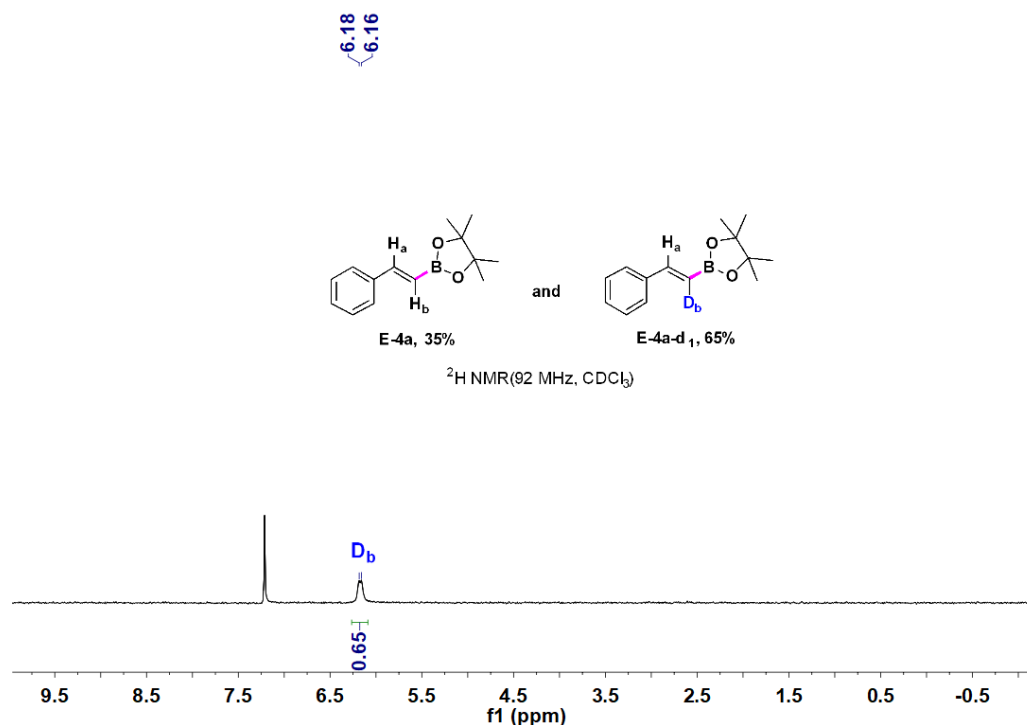


Supplementary Figure 46. ^1H NMR spectra and ^2H NMR spectra of compounds **E-4a, **E-4a-d₁** and **E-4a-d₂**.** ^2H NMR spectrum of inseparable compounds **E-4a-d₁** and **E-4a-d₂** (top) in $\text{CDCl}_3\text{-DCM}$, ^1H NMR spectra of inseparable compounds **E-4a-d₁** and **E-4a-d₂** (middle) and compound **E-4a** (bottom) in CDCl_3 . The control experiment was catalyzed by microcrystalline Cu_4NC in the mixture solvent of $\text{CH}_3\text{CN-D}_2\text{O}$.

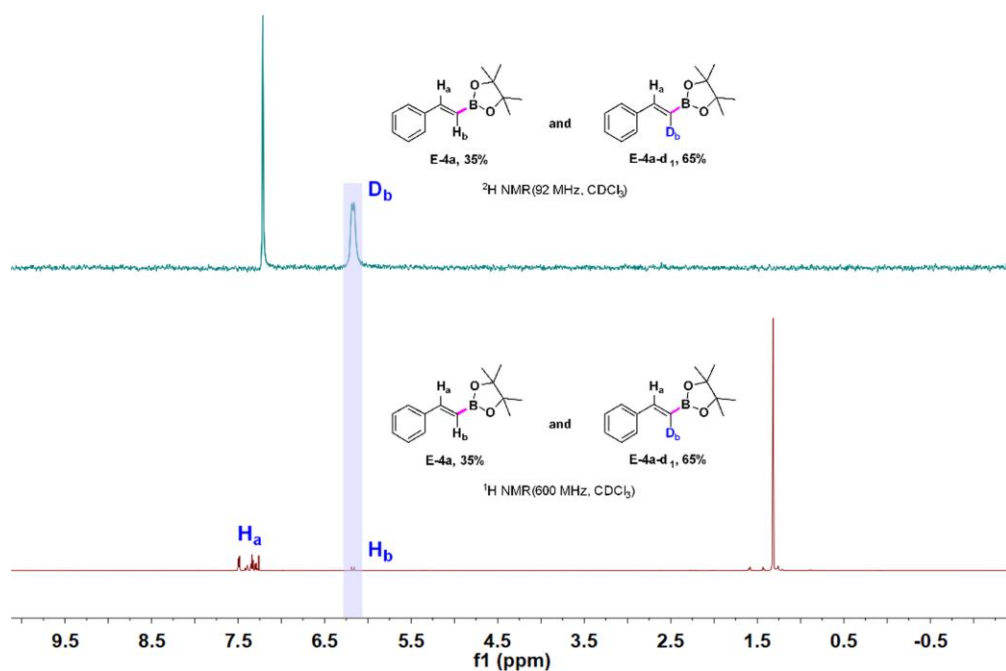
General Procedure for deuterium experiment c. Under air atmosphere, phenylacetylene- d_1 **1a** (20.6 mg, 0.2 mmol, 1.0 eq), B_2Pin_2 **2** (111.8 mg, 0.44 mmol, 2.2 equiv.), microcrystalline Cu_4NC catalysts (2.8 mg, 2.0 mol%), K_2CO_3 (60.7 mg, 0.44 mmol, 2.2 equiv.) and the mixture solvent (2.0 mL, $\text{CH}_3\text{CN-H}_2\text{O}$, v/v 4/1) were added into a tube. The reaction mixture was stirred at room temperature for 1 h. The reactions were monitored by TLC. When alkynes were consumed, the reactions were quenched and concentrated. Conversion and yield were determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard. The crude products were then purified by column chromatography to give the target products **E-4a** and **E-4a-d₁** as colorless oils, which are inseparable mixture of products with an isolated ratio of **E-4a** to **E-4a-d₁** of 35:65, compared to the original ratio of 42:57. ^1H NMR (600 MHz, CDCl_3) δ 7.49 (d, $J = 7.9$ Hz, 2H), 7.41 (d, $J = 14.2$ Hz, 1H), 7.34 (t, $J = 7.4$ Hz, 2H), 7.29 (t, $J = 7.2$ Hz, 1H), 6.17 (d, $J = 18.4$ Hz, 0.35H), 1.32 (s, 12H). ^2H NMR (92 MHz, CDCl_3) δ 6.17 (d, $J = 2.2$ Hz, 0.65H).



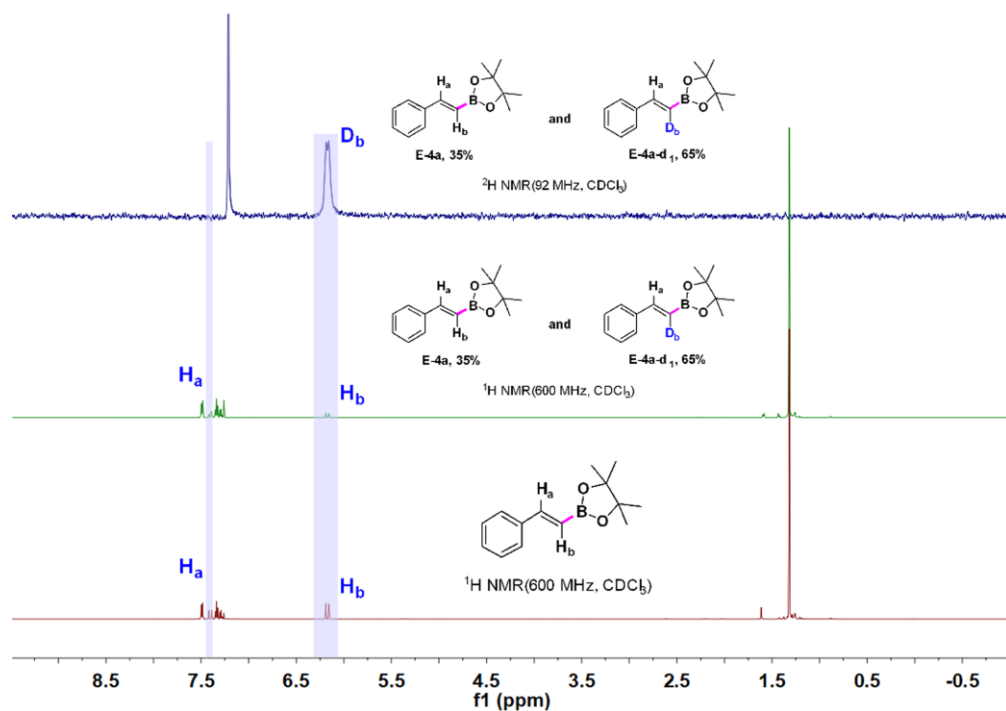
Supplementary Figure 47. ¹H NMR spectrum of inseparable compounds E-4a and E-4a-d₁ in CDCl₃. The phenylacetylene-d₁ was used in control experiment catalyzed by microcrystalline Cu₄NC.



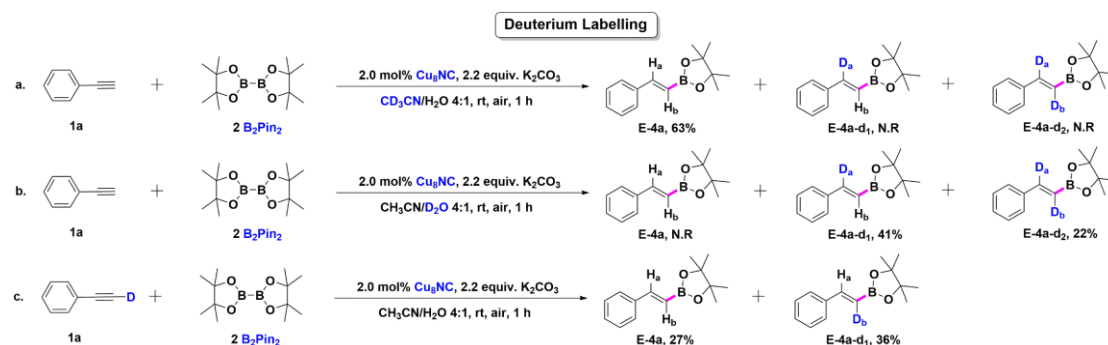
Supplementary Figure 48. ²H NMR spectrum of inseparable compounds E-4a and E-4a-d₁ in CDCl₃-DCM. The phenylacetylene-d₁ was used in control experiment catalyzed by microcrystalline Cu₄NC.



Supplementary Figure 49. ²H NMR spectrum of inseparable compounds E-4a and E-4a-d₁ in CDCl₃-DCM (top) and ¹H NMR spectrum of inseparable compounds E-4a and E-4a-d₁ in CDCl₃ (bottom). The phenylacetylene-d₁ was used in control experiment catalyzed by microcrystalline Cu₄NC.



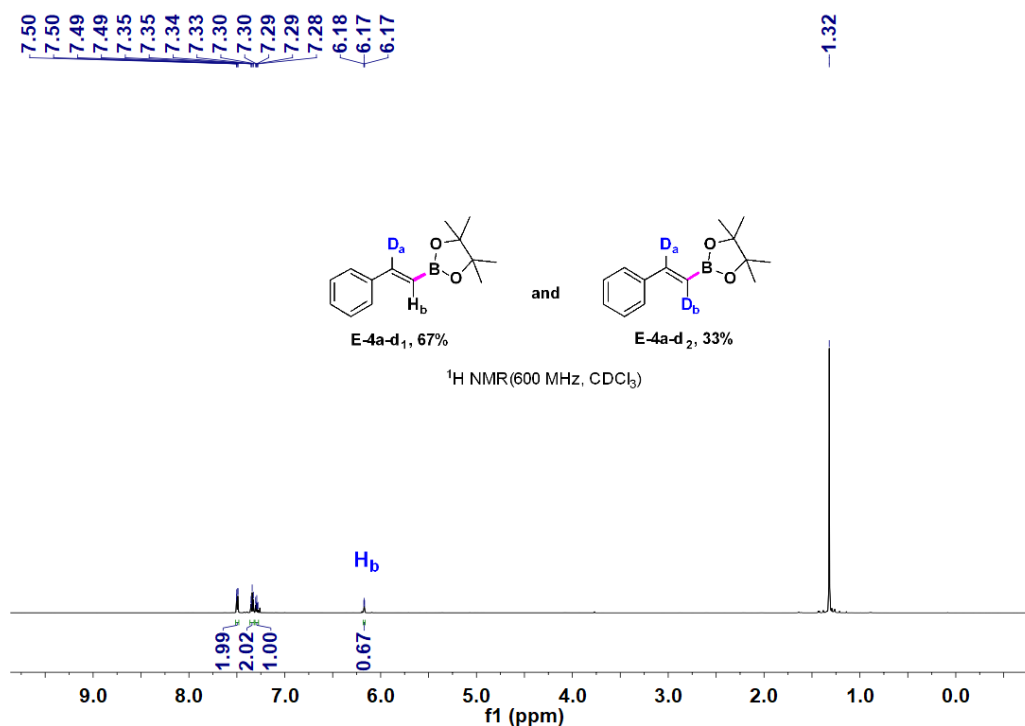
Supplementary Figure 50. ¹H NMR spectra and ²H NMR spectra of compounds E-4a and E-4a-d₁. ²H NMR spectrum of inseparable compounds E-4a and E-4a-d₁ (top) in CDCl₃-DCM, ¹H NMR spectra of inseparable compounds E-4a and E-4a-d₁ (middle) and compound E-4a (bottom) in CDCl₃. The phenylacetylene-d₁ was used in control experiment catalyzed by microcrystalline Cu₄NC.



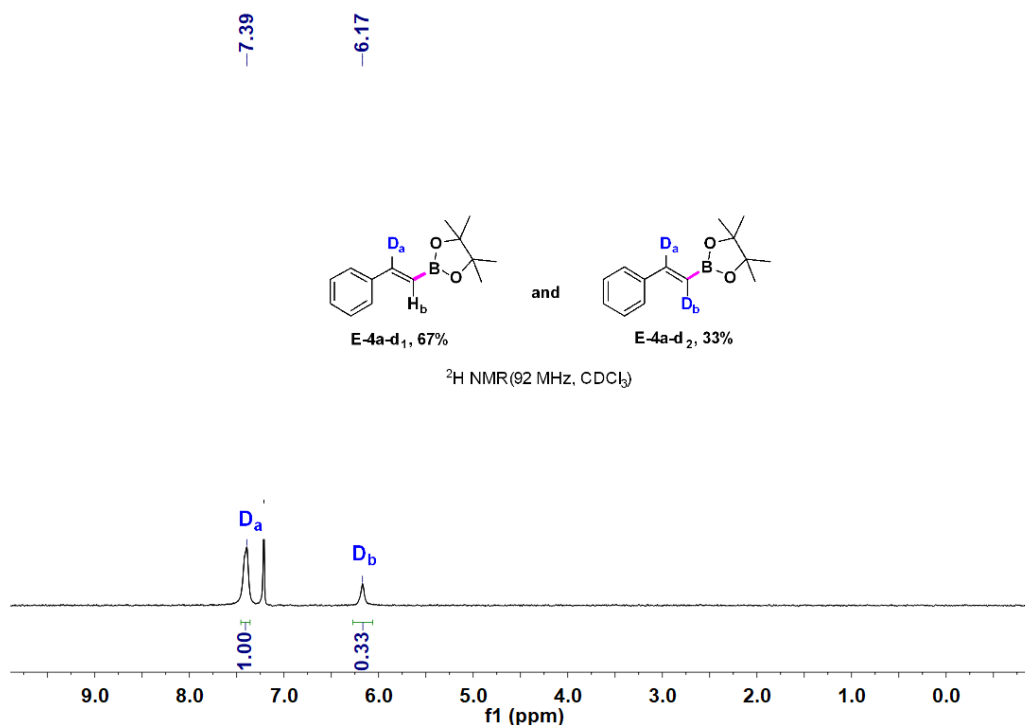
Supplementary Figure 51. Deuterium experiments of microcrystalline Cu_8NC -catalyzed hydroboration reaction. **a.** The CD_3CN as deuterium source in deuterium experiment. **b.** The D_2O as deuterium source in deuterium experiment. **c.** The phenylacetylene- d_1 as deuterium source in deuterium experiment.

General Procedure for deuterium experiment a. Under air atmosphere, phenylacetylene **1a** (20.4 mg, 0.2 mmol, 1.0 eq), B_2Pin_2 **2** (111.8 mg, 0.44 mmol, 2.2 equiv.), microcrystalline Cu_8NC catalysts (5.3 mg, 2.0 mol%), K_2CO_3 (60.7 mg, 0.44 mmol, 2.2 equiv.) and the mixture solvent (2.0 mL, CD_3CN - H_2O , v/v 4/1) were added into a tube. The reaction mixture was stirred at room temperature for 1 h. The reactions were monitored by TLC. When alkynes were consumed, the reactions were quenched and concentrated. Conversion and yield were determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard. The crude products were then purified by column chromatography to give the target product **E-4a** as a colorless oil. ^1H NMR (600 MHz, CDCl_3) δ 7.49 (d, $J = 7.2$ Hz, 2H), 7.40 (d, $J = 18.4$ Hz, 1H), 7.34 (t, $J = 7.4$ Hz, 2H), 7.29 (ddd, $J = 7.3, 3.6, 1.2$ Hz, 1H), 6.17 (d, $J = 18.4$ Hz, 1H), 1.32 (s, 12H).

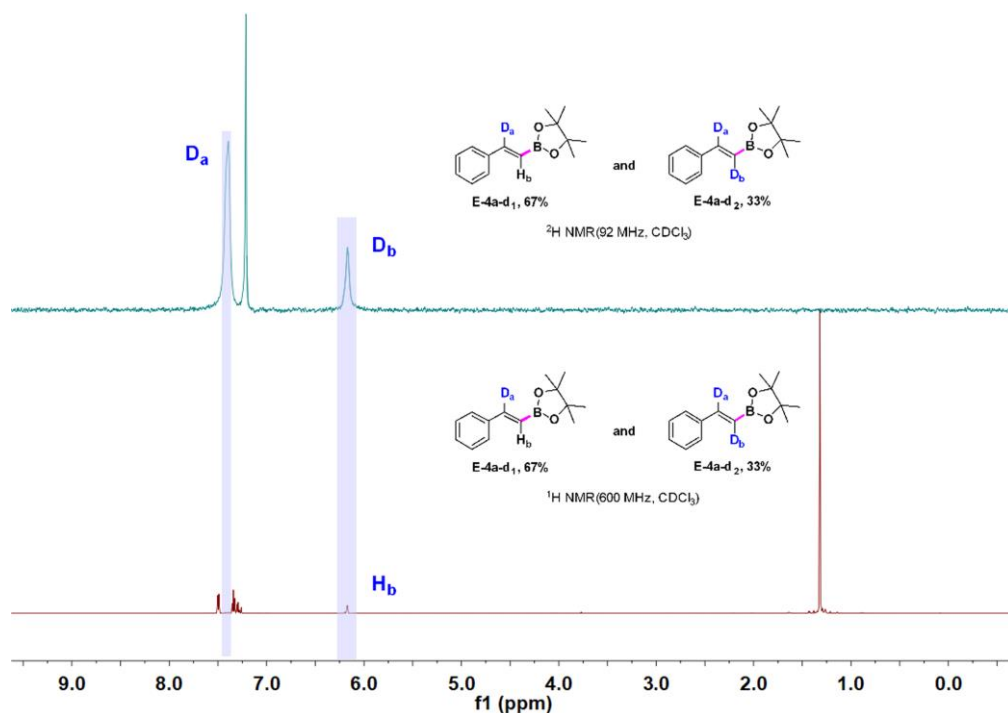
General Procedure for deuterium experiment b. Under air atmosphere, phenylacetylene **1a** (20.4 mg, 0.2 mmol, 1.0 eq), B_2Pin_2 **2** (111.8 mg, 0.44 mmol, 2.2 equiv.), microcrystalline Cu_8NC catalysts (5.3 mg, 2.0 mol%), K_2CO_3 (60.7 mg, 0.44 mmol, 2.2 equiv.) and the mixture solvent (2.0 mL, CH_3CN - D_2O , v/v 4/1) were added into a tube. The reaction mixture was stirred at room temperature for 1 h. The reactions were monitored by TLC. When alkynes were consumed, the reactions were quenched and concentrated. Conversion and yield were determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard. The crude products were then purified by column chromatography to give the target products **E-4a-d₁** and **E-4a-d₂** as colorless oils, which are inseparable mixture of products with an isolated ratio of **E-4a-d₁** to **E-4a-d₂** of 67:33, compared to the original ratio of 41:22. ^1H NMR (600 MHz, CDCl_3) δ 7.50 (dd, $J = 8.2, 1.0$ Hz, 2H), 7.34 (dd, $J = 10.1, 4.6$ Hz, 2H), 7.32 – 7.27 (m, 1H), 6.18 – 6.16 (m, 0.67H), 1.32 (s, 12H). ^2H NMR (92 MHz, CDCl_3) δ 7.39 (s, 1H), 6.17 (s, 0.33H).



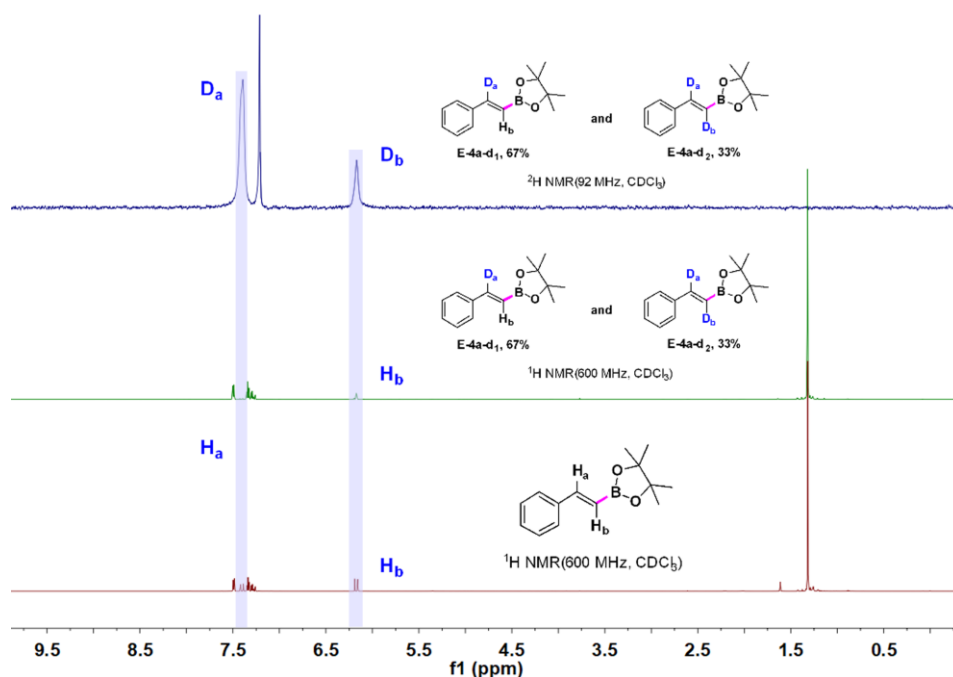
Supplementary Figure 52. ¹H NMR spectrum of inseparable compounds **E-4a-d₁** and **E-4a-d₂** in CDCl₃. The control experiment was catalyzed by microcrystalline Cu₈NC in the mixture solvent of CH₃CN-D₂O.



Supplementary Figure 53. ²H NMR spectrum of inseparable compounds **E-4a-d₁** and **E-4a-d₂** in CDCl₃-DCM. The control experiment was catalyzed by microcrystalline Cu₈NC in the mixture solvent of CH₃CN-D₂O.

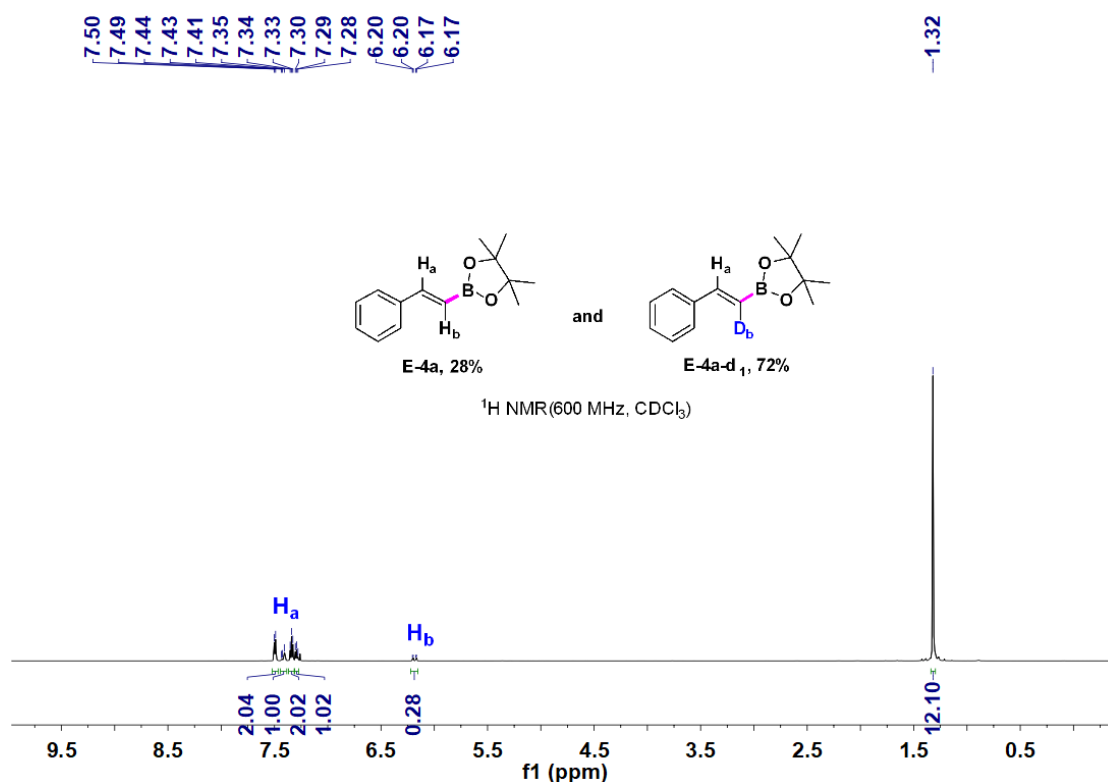


Supplementary Figure 54. ²H NMR spectrum of inseparable compounds E-4a-d₁ and E-4a-d₂ in CDCl₃-DCM (top) and ¹H NMR spectrum of inseparable compounds E-4a-d₁ and E-4a-d₂ in CDCl₃ (bottom). The control experiment was catalyzed by microcrystalline Cu₈NC in the mixture solvent of CH₃CN-D₂O.

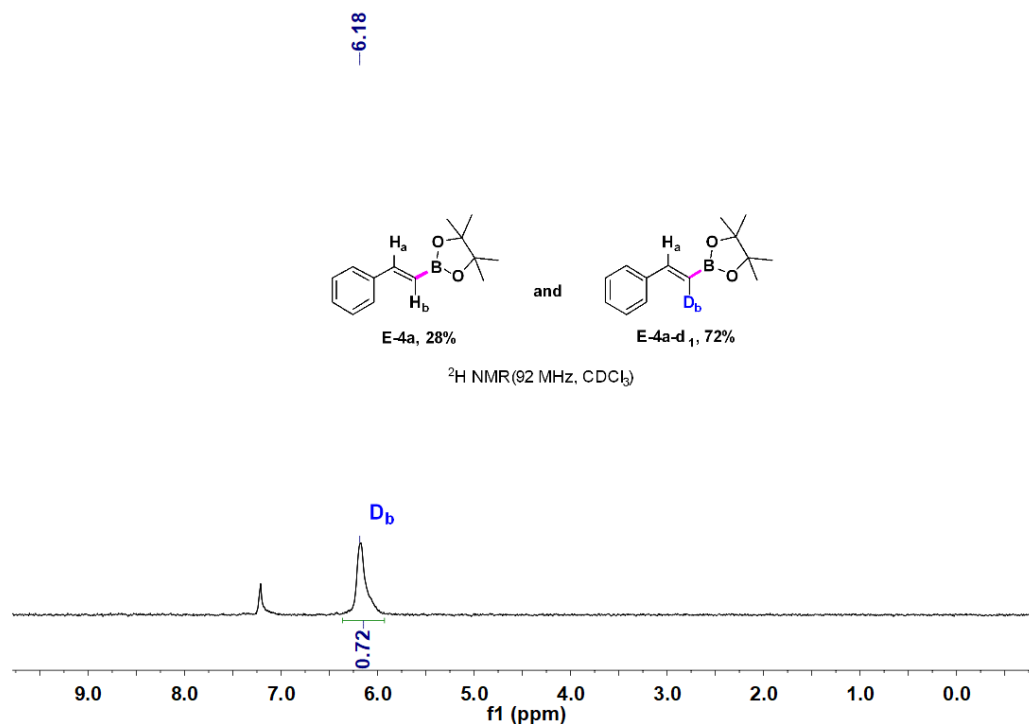


Supplementary Figure 55. ¹H NMR spectra and ²H NMR spectra of compounds E-4a, E-4a-d₁ and E-4a-d₂. ²H NMR spectrum of inseparable compounds E-4a-d₁ and E-4a-d₂ (top) in CDCl₃-DCM, ¹H NMR spectra of inseparable compounds E-4a-d₁ and E-4a-d₂ (middle) and compound E-4a (bottom) in CDCl₃. The control experiment was catalyzed by microcrystalline Cu₈NC in the mixture solvent of CH₃CN-D₂O.

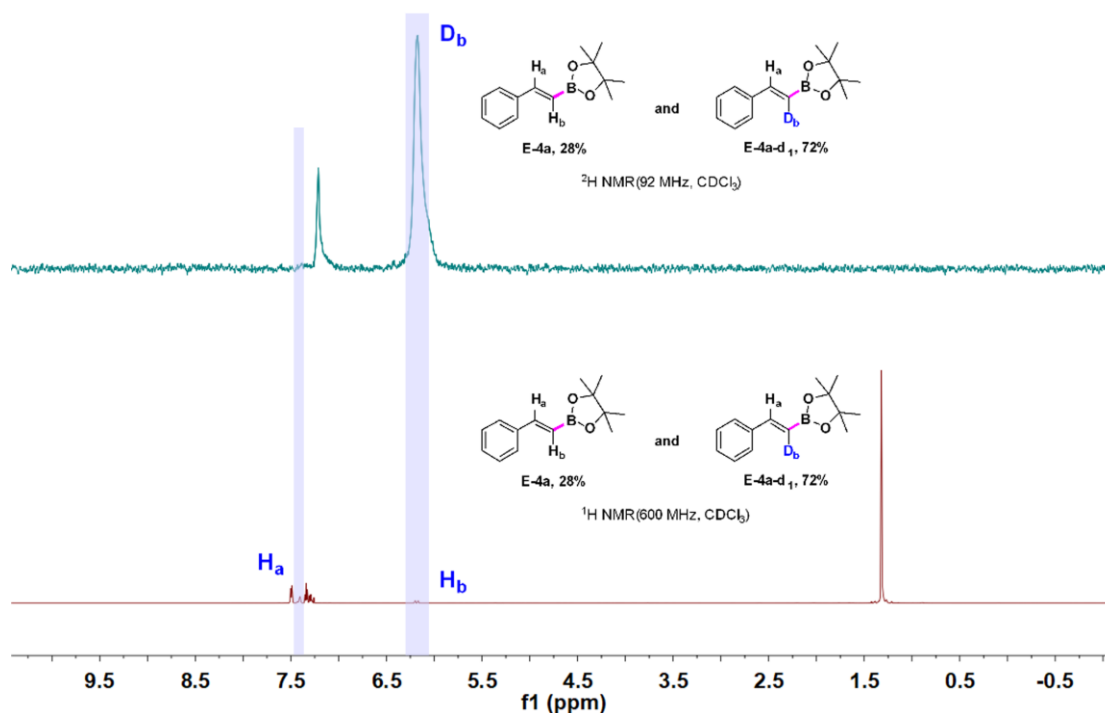
General Procedure for deuterium experiment c. Under air atmosphere, phenylacetylene- d_1 **1a** (20.6 mg, 0.2 mmol, 1.0 eq), B_2Pin_2 **2** (111.8 mg, 0.44 mmol, 2.2 equiv.), microcrystalline Cu_8NC catalysts (5.3 mg, 2.0 mol%), K_2CO_3 (60.7 mg, 0.44 mmol, 2.2 equiv.) and the mixture solvent (2.0 mL, CH_3CN-H_2O , v/v 4/1) were added into a tube. The reaction mixture was stirred at room temperature for 1 h. The reactions were monitored by TLC. When alkynes were consumed, the reactions were quenched and concentrated. Conversion and yield were determined by 1H NMR using 1,3,5-trimethoxybenzene as an internal standard. The crude products were then purified by column chromatography to give the target products **E-4a** and **E-4a- d_1** as colorless oils, which are inseparable mixture of products with an isolated ratio of **E-4a** to **E-4a- d_1** of 28:72, compared to the original ratio of 27:36. 1H NMR (600 MHz, $CDCl_3$) δ 7.50 (d, $J = 7.4$ Hz, 2H), 7.44 – 7.38 (m, 1H), 7.34 (t, $J = 7.4$ Hz, 2H), 7.29 (t, $J = 7.2$ Hz, 1H), 6.19 (dd, $J = 18.4, 5.0$ Hz, 0.28H), 1.32 (s, 12H). 2H NMR (92 MHz, $CDCl_3$) δ 6.18 (s, 0.72H).



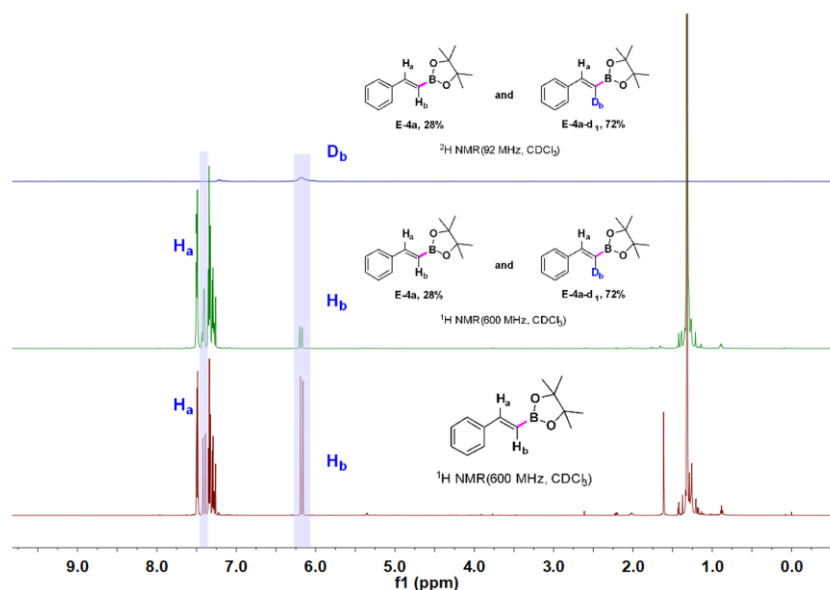
Supplementary Figure 56. 1H NMR spectrum of inseparable compounds **E-4a** and **E-4a- d_1** in $CDCl_3$. The phenylacetylene- d_1 was used in control experiment catalyzed by microcrystalline Cu_8NC .



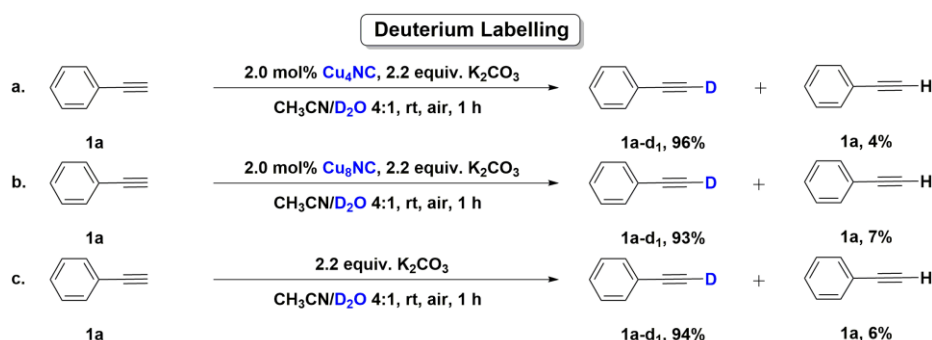
Supplementary Figure 57. ²H NMR spectrum of inseparable compounds E-4a and E-4a-d₁ in CDCl₃-DCM. The phenylacetylene-d₁ was used in control experiment catalyzed by microcrystalline Cu₈NC.



Supplementary Figure 58. ²H NMR spectrum of inseparable compounds E-4a and E-4a-d₁ in CDCl₃-DCM (top) and ¹H NMR spectrum of inseparable compounds E-4a and E-4a-d₁ in CDCl₃ (bottom). The phenylacetylene-d₁ was used in control experiment catalyzed by microcrystalline Cu₈NC.

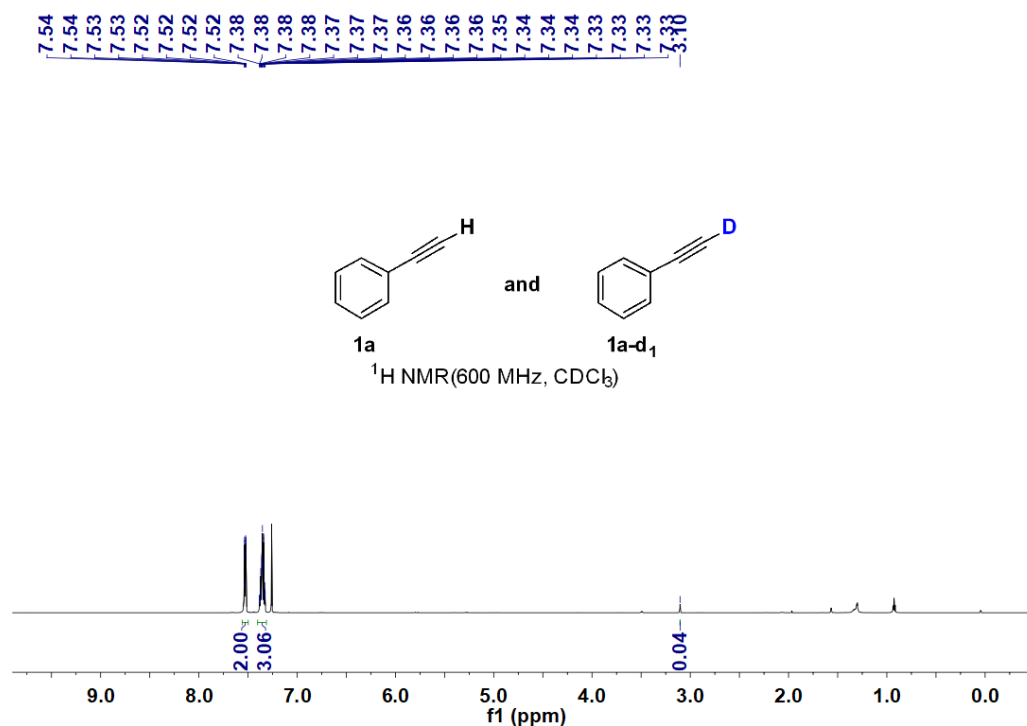


Supplementary Figure 59. ^1H NMR spectra and ^2H NMR spectra of compounds **E-4a** and **E-4a-d₁**. ^2H NMR spectrum of inseparable compounds **E-4a** and **E-4a-d₁** (top) in CDCl_3 -DCM, ^1H NMR spectra of inseparable compounds **E-4a** and **E-4a-d₁** (middle) and compound **E-4a** (bottom) in CDCl_3 . The phenylacetylene- d_1 was used in control experiment catalyzed by microcrystalline Cu_8NC .

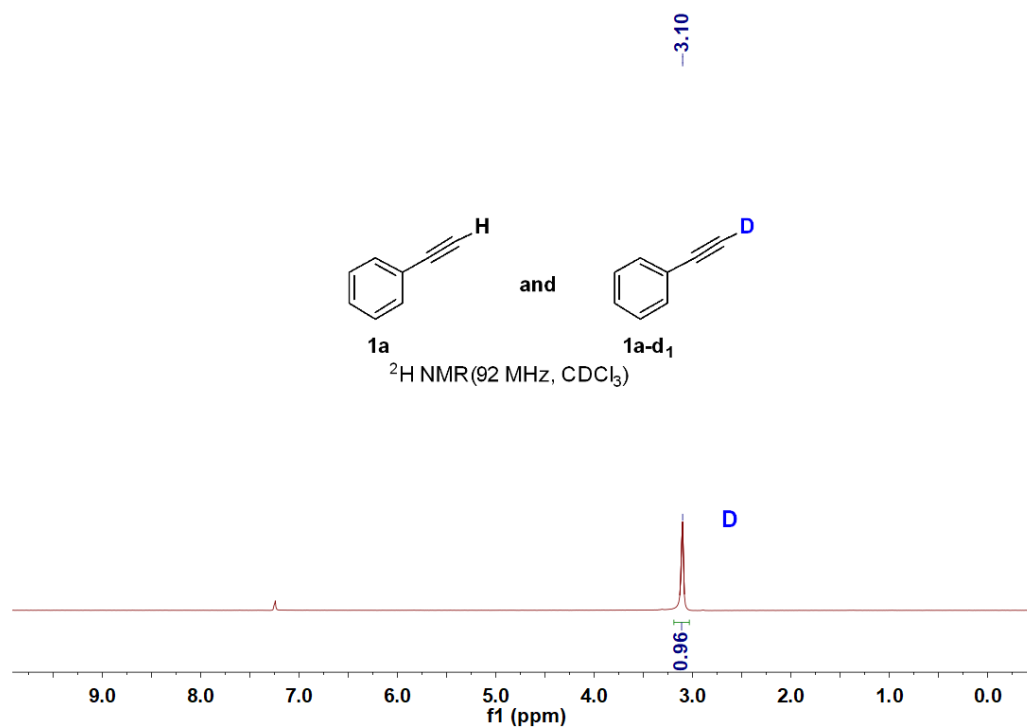


Supplementary Figure 60. Deuterium experiments of the deuteration method of phenylacetylene. **a.** The Cu_4NC as catalyst in deuterium experiment. **b.** The Cu_8NC as catalyst in deuterium experiment. **c.** No catalyst in deuterium experiment.

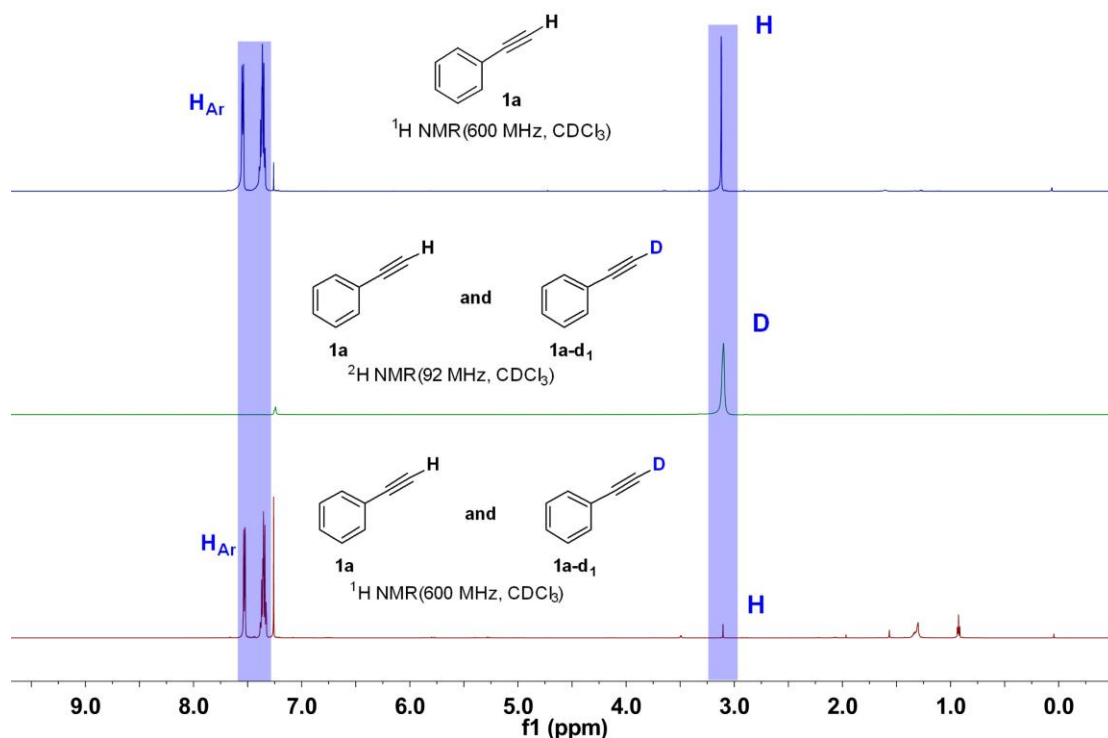
General Procedure for deuterium experiment a. Under air atmosphere, phenylacetylene **1a** (20.4 mg, 0.2 mmol, 1.0 eq), microcrystalline Cu_4NC catalysts (2.8 mg, 2.0 mol%), K_2CO_3 (60.7 mg, 0.44 mmol, 2.2 equiv.) and the mixture solvent (2.0 mL, $\text{CH}_3\text{CN}/\text{D}_2\text{O}$, v/v 4/1) were added into a tube. The reaction mixture was stirred at room temperature for 1 h. The reactions were monitored by TLC. Conversion and yield were determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard. The reaction solution was filtrated through celite and concentrated to give the target products **1a** and **1a-d₁** as a colorless oil, which are inseparable mixture of products with a ratio of **1a** to **1a-d₁** of 96:4. ^1H NMR (600 MHz, CDCl_3) δ 7.53 (ddd, $J = 2.2, 1.8, 0.9$ Hz, 2H), 7.40 – 7.31 (m, 3H), 3.10 (s, 0.4H). ^2H NMR (92 MHz, CDCl_3) δ 3.10 (s, 0.96H).



Supplementary Figure 61. ^1H NMR spectrum of inseparable compounds **1a** and **1a-d₁** in CDCl_3 . The phenylacetylene was deuterated in control experiment catalyzed by microcrystalline Cu_4NC .

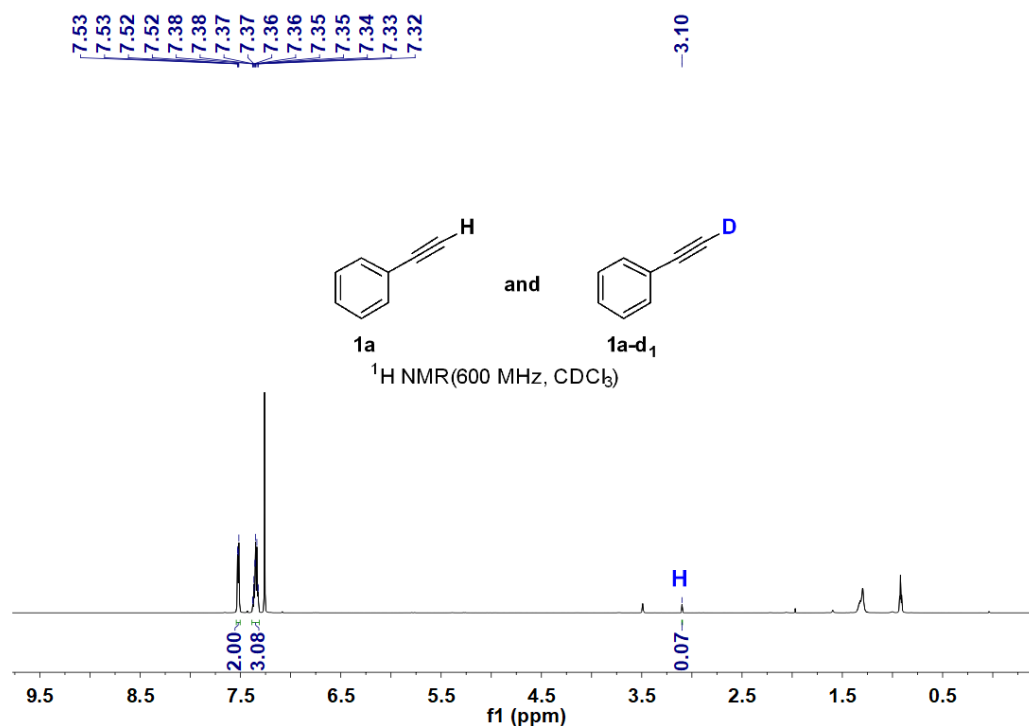


Supplementary Figure 62. ^2H NMR spectrum of inseparable compounds **1a** and **1a-d₁** in $\text{CDCl}_3\text{-DCM}$. The phenylacetylene was deuterated in control experiment catalyzed by microcrystalline Cu_4NC .

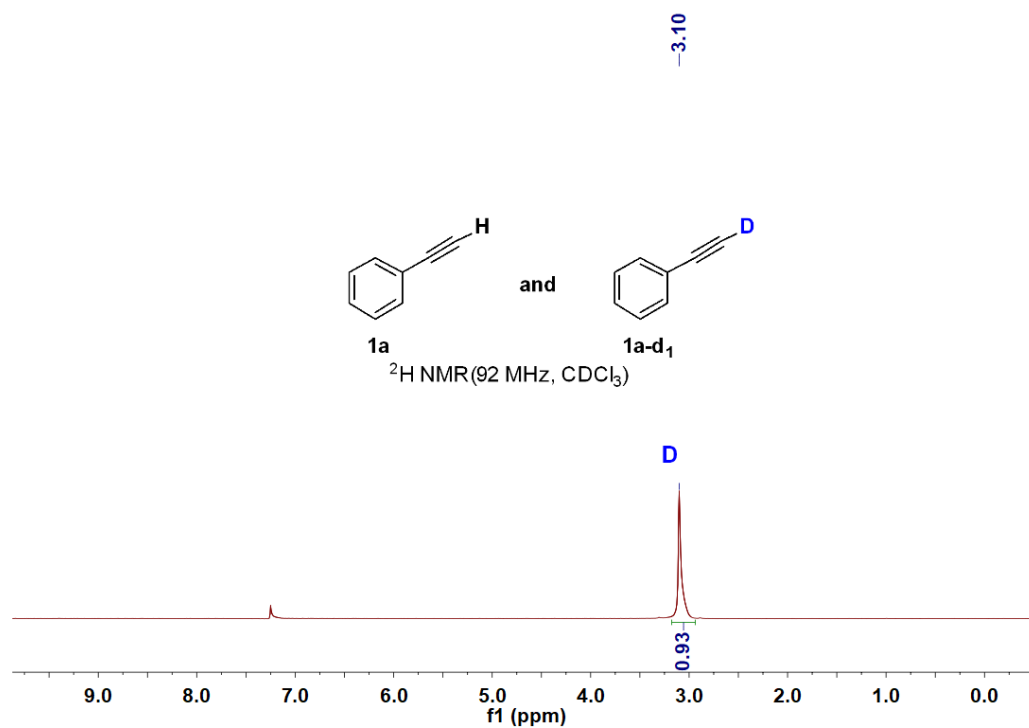


Supplementary Figure 63. ^1H NMR spectra and ^2H NMR spectra of compounds **1a and **1a-d₁**.** ^1H NMR spectrum of compounds **1a** (top), ^2H NMR spectrum of inseparable compounds **1a** and **1a-d₁** in CDCl_3 -DCM (middle) and ^1H NMR spectrum of inseparable compounds **1a** and **1a-d₁** in CDCl_3 (bottom). The phenylacetylene was deuterated in control experiment catalyzed by microcrystalline Cu_4NC .

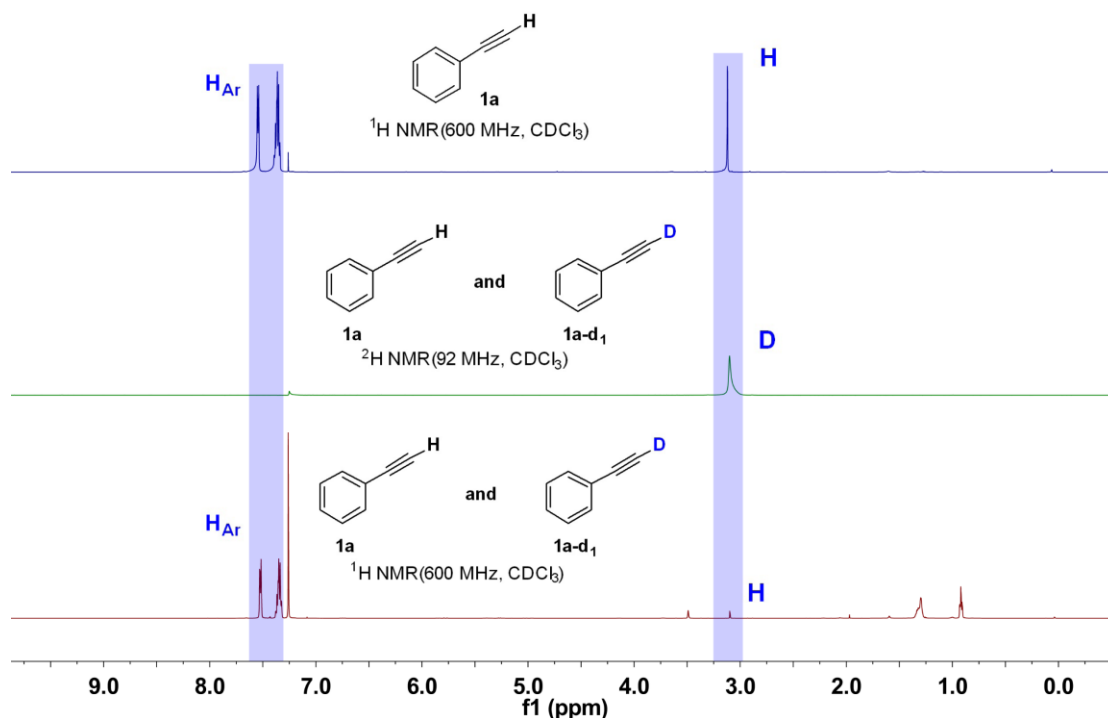
General Procedure for deuterium experiment b. Under air atmosphere, phenylacetylene **1a** (20.4 mg, 0.2 mmol, 1.0 eq), microcrystalline Cu_8NC catalysts (5.3 mg, 2.0 mol%), K_2CO_3 (60.7 mg, 0.44 mmol, 2.2 equiv.) and the mixture solvent (2.0 mL, CH_3CN - D_2O , v/v 4/1) were added into a tube. The reaction mixture was stirred at room temperature for 1 h. The reactions were monitored by TLC. Conversion and yield were determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard. The reaction solution was filtrated through celite and concentrated to give the target products **1a** and **1a-d₁** as colorless oils, which are inseparable mixture of products with a ratio of **1a** to **1a-d₁** of 93:7. ^1H NMR (600 MHz, CDCl_3) δ 7.52 (dd, J = 6.6, 1.5 Hz, 2H), 7.40 – 7.31 (m, 3H), 3.10 (s, 0.07H). ^2H NMR (92 MHz, CDCl_3) δ 3.10 (s, 0.93H).



Supplementary Figure 64. ¹H NMR spectrum of inseparable compounds **1a** and **1a-d₁** in CDCl₃. The phenylacetylene was deuterated in control experiment catalyzed by microcrystalline Cu₈NC.

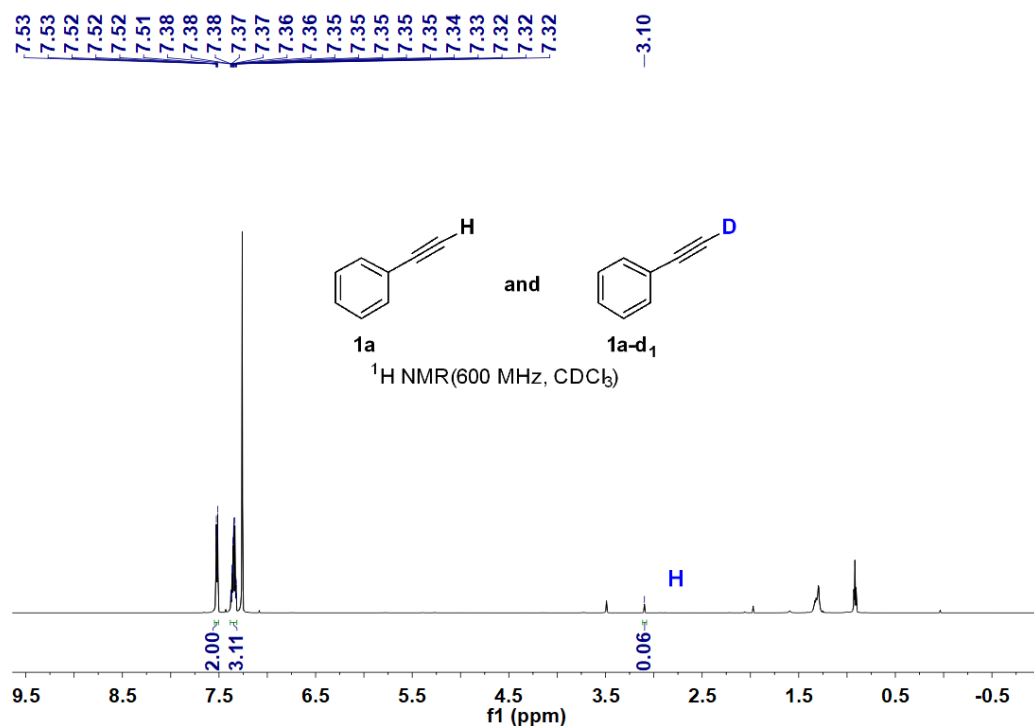


Supplementary Figure 65. ²H NMR spectrum of inseparable compounds **1a** and **1a-d₁** in CDCl₃-DCM. The phenylacetylene was deuterated in control experiment catalyzed by microcrystalline Cu₈NC.

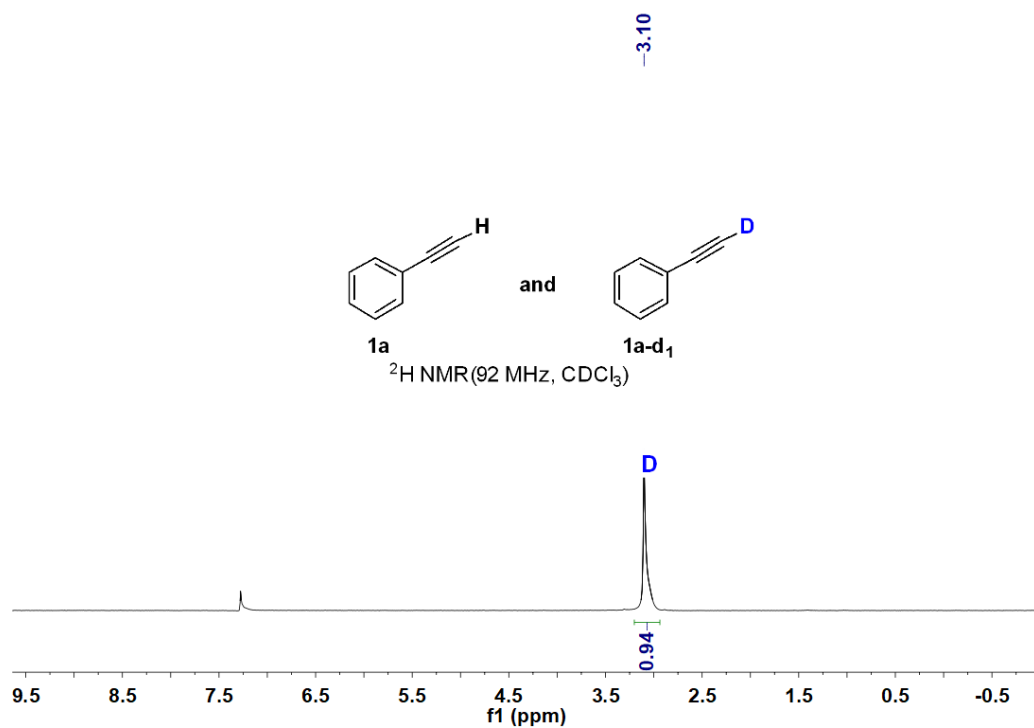


Supplementary Figure 66. ^1H NMR spectra and ^2H NMR spectra of compounds **1a and **1a-d₁**.** ^1H NMR spectrum of compound **1a** (top), ^2H NMR spectrum of inseparable compounds **1a** and **1a-d₁** in CDCl_3 -DCM (middle), ^1H NMR spectrum of inseparable compounds **1a** and **1a-d₁** in CDCl_3 (bottom). The phenylacetylene was deuterated in control experiment catalyzed by microcrystalline Cu_8NC .

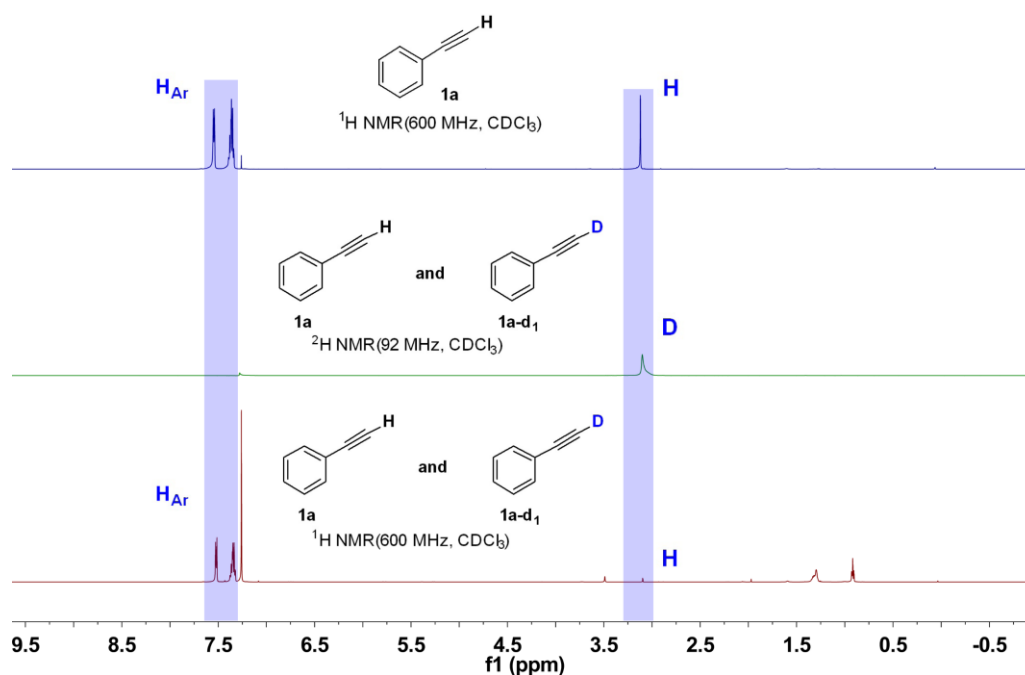
General Procedure for deuterium experiment c. Under air atmosphere, phenylacetylene **1a** (20.4 mg, 0.2 mmol, 1.0 eq), K_2CO_3 (60.7 mg, 0.44 mmol, 2.2 equiv.) and the mixture solvent (2.0 mL, CH_3CN - D_2O , v/v 4/1) were added into a tube. The reaction mixture was stirred at room temperature for 1 h. The reactions were monitored by TLC. Conversion and yield were determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard. The reaction solution was filtrated through celite and concentrated to give the target products **1a** and **1a-d₁** as colorless oils, which are inseparable mixture of products with a ratio of **1a** to **1a-d₁** of 94:6. ^1H NMR (600 MHz, CDCl_3) δ 7.56 – 7.50 (m, 2H), 7.42 – 7.31 (m, 3H), 3.10 (s, 0.06H). ^2H NMR (92 MHz, CDCl_3) δ 3.10 (s, 0.94H).



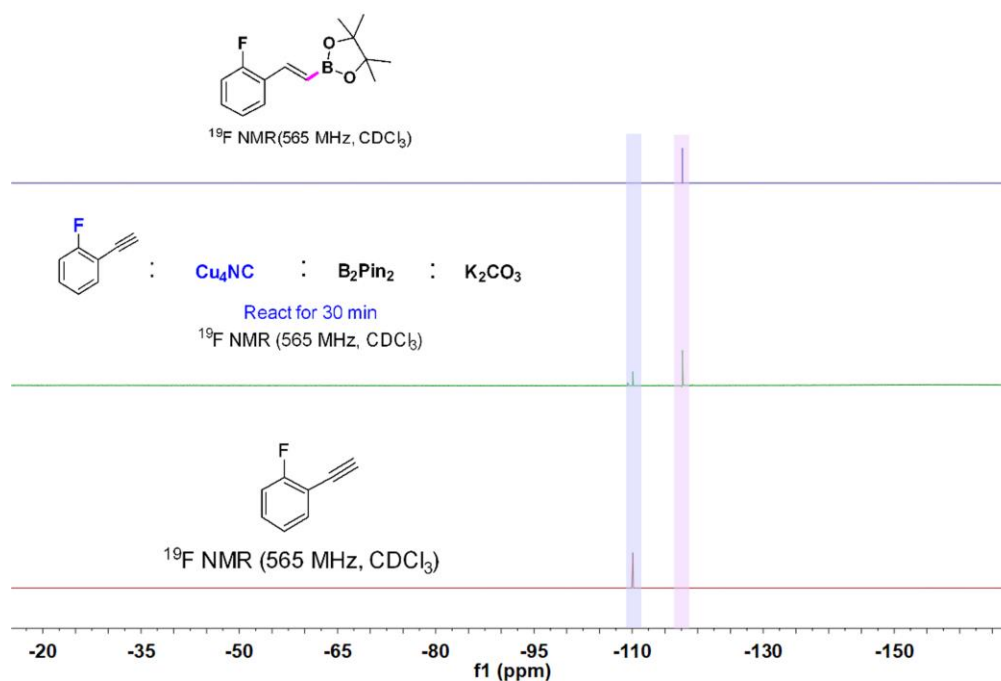
Supplementary Figure 67. ¹H NMR spectrum of inseparable compounds **1a** and **1a-d₁** in CDCl₃. The phenylacetylene was deuterated in control experiment without copper catalyst.



Supplementary Figure 68. ²H NMR spectrum of inseparable compounds **1a** and **1a-d₁** in CDCl₃-DCM. The phenylacetylene was deuterated in control experiment without copper catalyst.



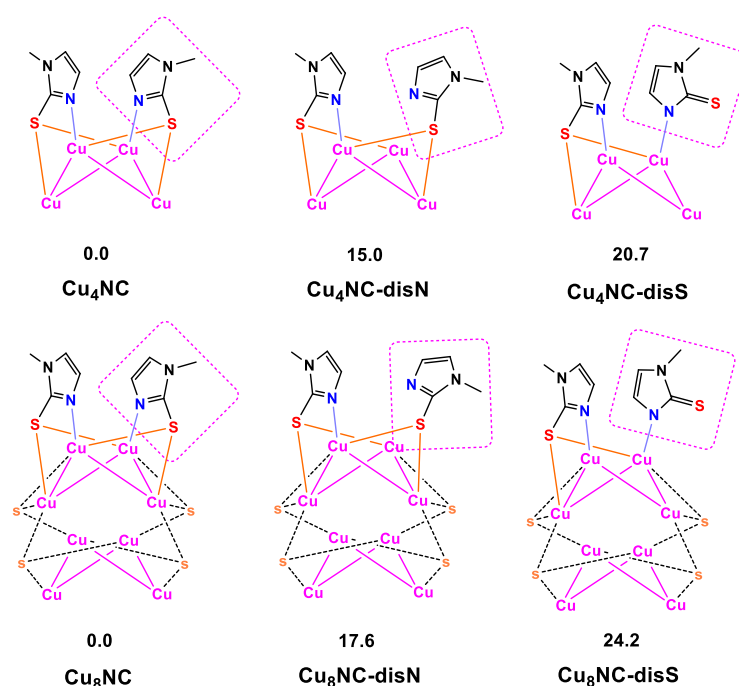
Supplementary Figure 69. ^1H NMR spectra and ^2H NMR spectra of compounds 1a and 1a-d₁. ^1H NMR spectrum of compound 1a (top), ^2H NMR spectrum of inseparable compounds 1a and 1a-d₁ in CDCl_3 -DCM (middle), ^1H NMR spectrum of inseparable compounds 1a and 1a-d₁ in CDCl_3 (bottom). The phenylacetylene was deuterated in control experiment without copper catalyst.



Supplementary Figure 70. ^{19}F NMR spectra tracking of hydroboration. ^{19}F NMR spectra of (E)-2-(2-fluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (E-4g) (top), the Cu_4NC catalyzed hydroboration for 30 min (middle) and 2-fluorophenylacetylene (bottom) in CDCl_3 .

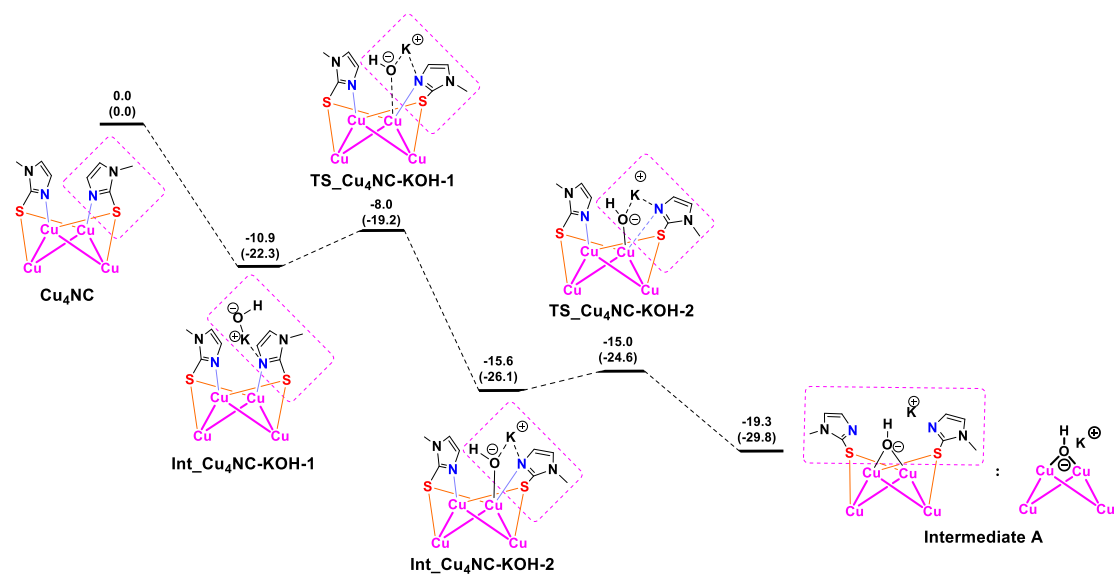
Catalytic Mechanism Studies by Density Functional Theory (DFT) Calculations

Density functional theory (DFT) calculations at the PBE0 level of theory were performed to understand the reaction mechanism^(7,8). The def2svp basis set was employed for C, O, H, B, N, S, and Cu atoms⁽⁹⁻¹²⁾. Solvation effects were modeled using the Solvation Model based on Density (SMD) with acetonitrile as the solvent⁽¹³⁾. Additional dispersion corrections were applied using the Grimme's D3 method^(14,15). Vibrational frequency calculations were performed to ensure that a transition state has only one imaginary frequency and a local minimum has no imaginary frequency. Transition states connecting relevant minima were further examined by carrying out intrinsic reaction coordinate (IRC) calculations⁽¹⁶⁻¹⁸⁾. All the calculations were performed using Gaussian 16 software⁽¹⁹⁾.

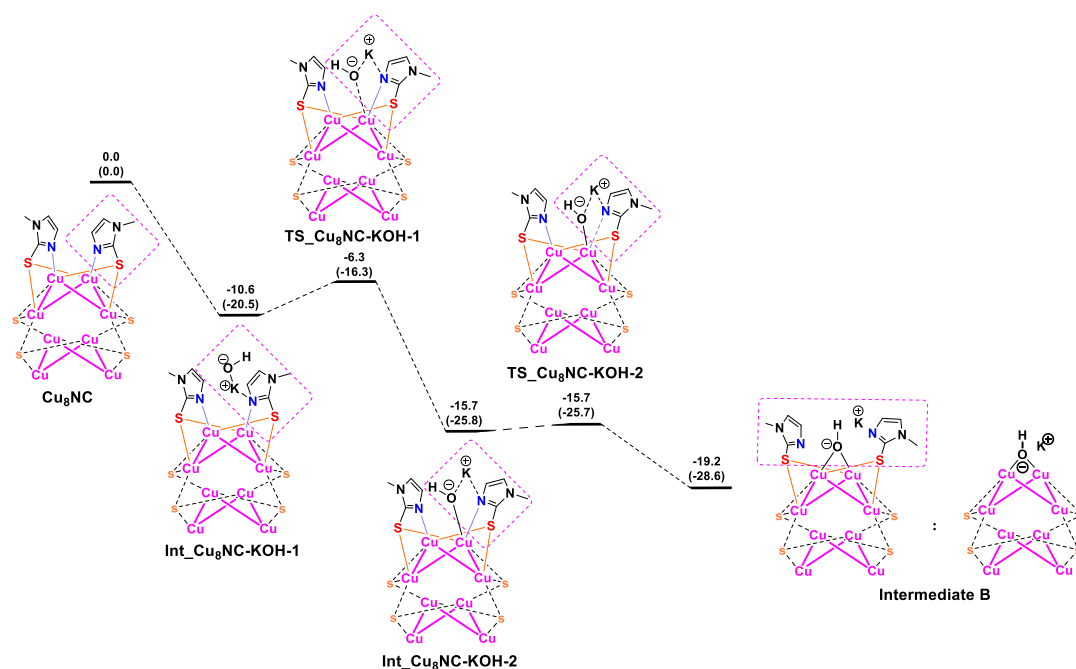


Supplementary Figure 71. DFT-calculated the binding energies of Cu-S bonds and Cu-N bonds. DFT-calculated the binding energies of Cu-S bonds and Cu-N bonds in Cu₄NC and Cu₈NC (ΔG in kcal/mol).

In our experiment, we used K₂CO₃ as the base. Since K₂CO₃ can react with water to form KOH, we simplified our calculations by using KOH as the base. In the Cu₄NC, KOH undergoes a ligand substitution reaction to form intermediate A via an association mechanism. As shown in Supplementary Figure 72, the energy barrier leading to intermediate A is only 2.9 kcal/mol and the energy of intermediate A is -19.3 kcal/mol, indicating that this process is both kinetically and thermodynamically favorable. This suggests that the formation of intermediate A from the Cu₄NC is feasible and that intermediate A serves as a suitable starting point for this reaction. Similarly, formation of Cu₈NC-OH intermediate B from Cu₈NC is also kinetically and thermodynamically favorable, suggesting intermediate B is a suitable starting point (Supplementary Figure 73).

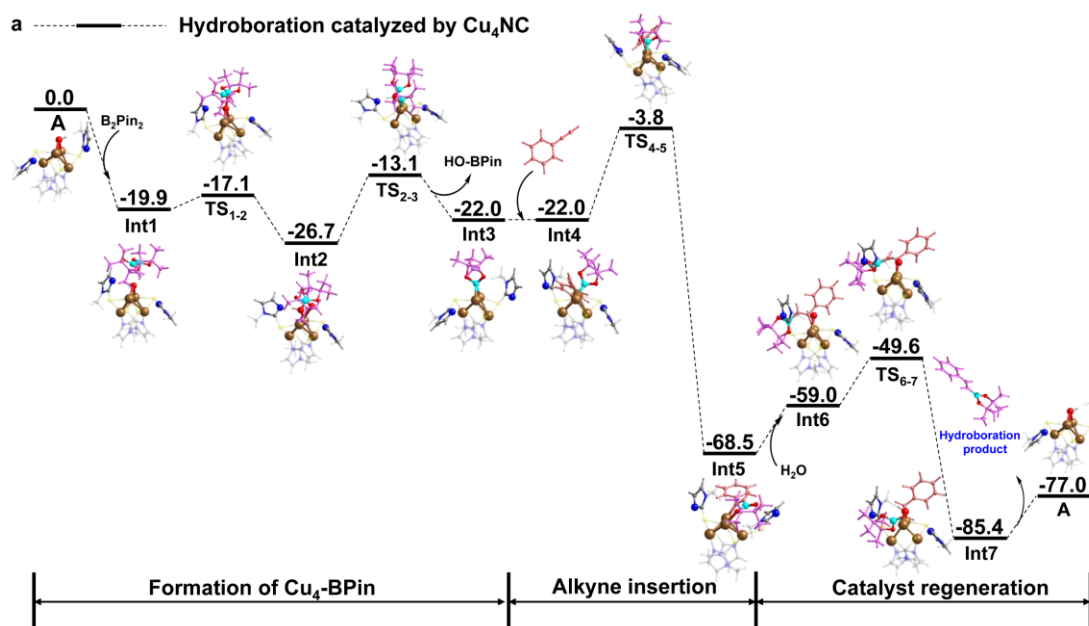


Supplementary Figure 72. DFT-computed Gibbs free energy profile for formation of Intermediate A. The relative Gibbs energies and electronic energies (in parentheses) are given in kcal/mol.

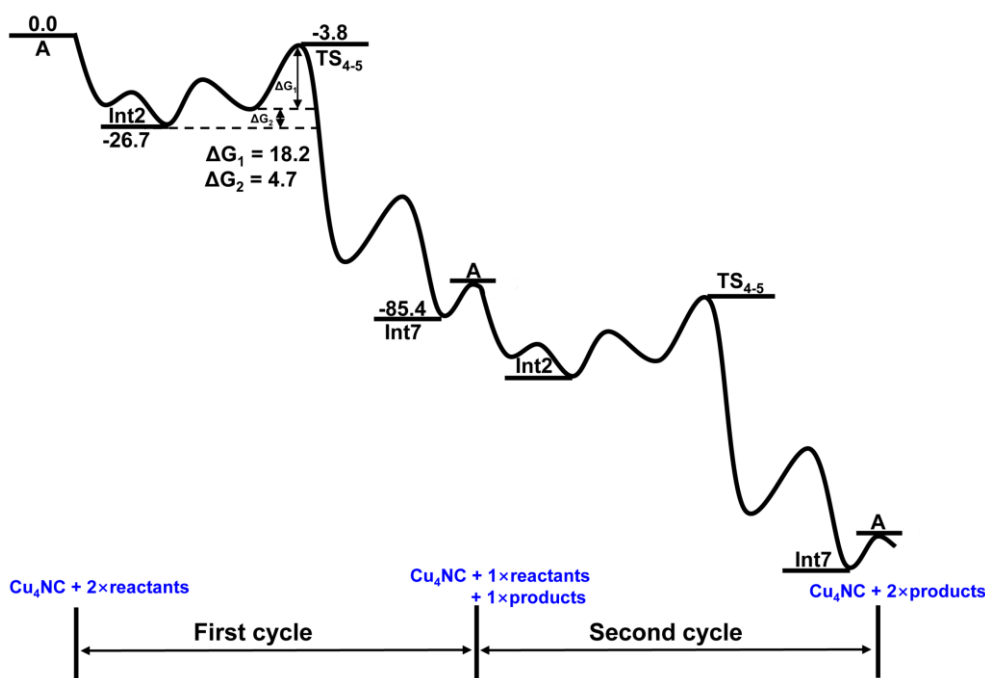


Supplementary Figure 73. DFT-computed Gibbs free energy profile for formation of Intermediate B. The relative Gibbs energies and electronic energies (in parentheses) are given in kcal/mol.

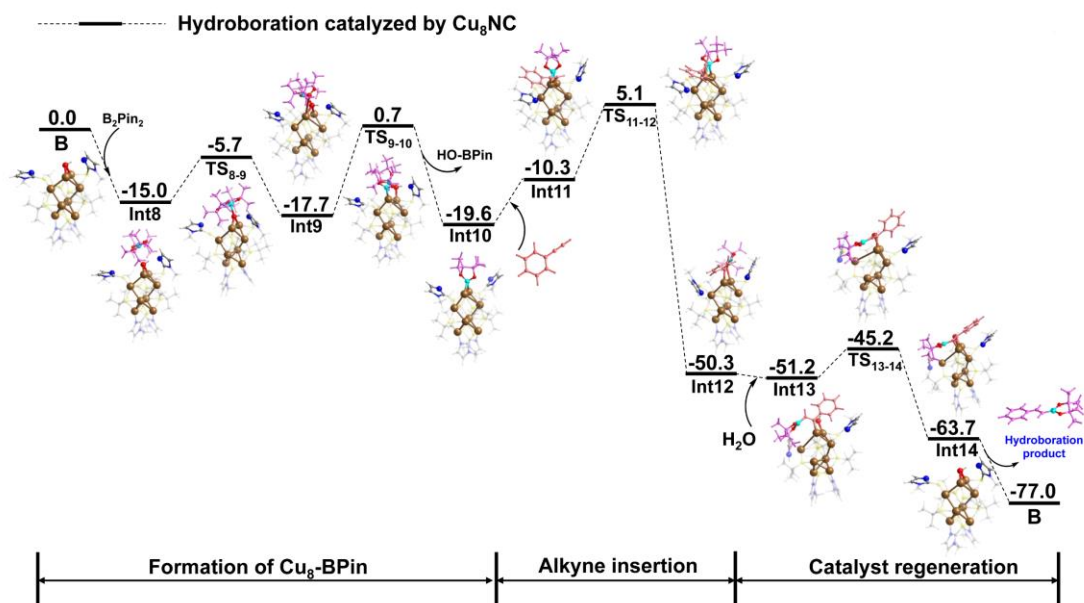
The schematic illustration of the energy profile of the microcrystalline Cu_4NC -catalyzed hydroboration reaction is depicted in Figure 5, Supplementary Figure 74 and Supplementary Figure 75. The TS_{4-5} represent rate-determining transition state. The Int_2 represent rate-determining intermediate. So the overall barrier could be calculated by $\Delta G_1 + \Delta G_2$. And we got $\Delta G_1 = 18.2 \text{ kcal mol}^{-1}$ and $\Delta G_2 = 4.7 \text{ kcal mol}^{-1}$ from the Figure 5 and Supplementary Figure 74.



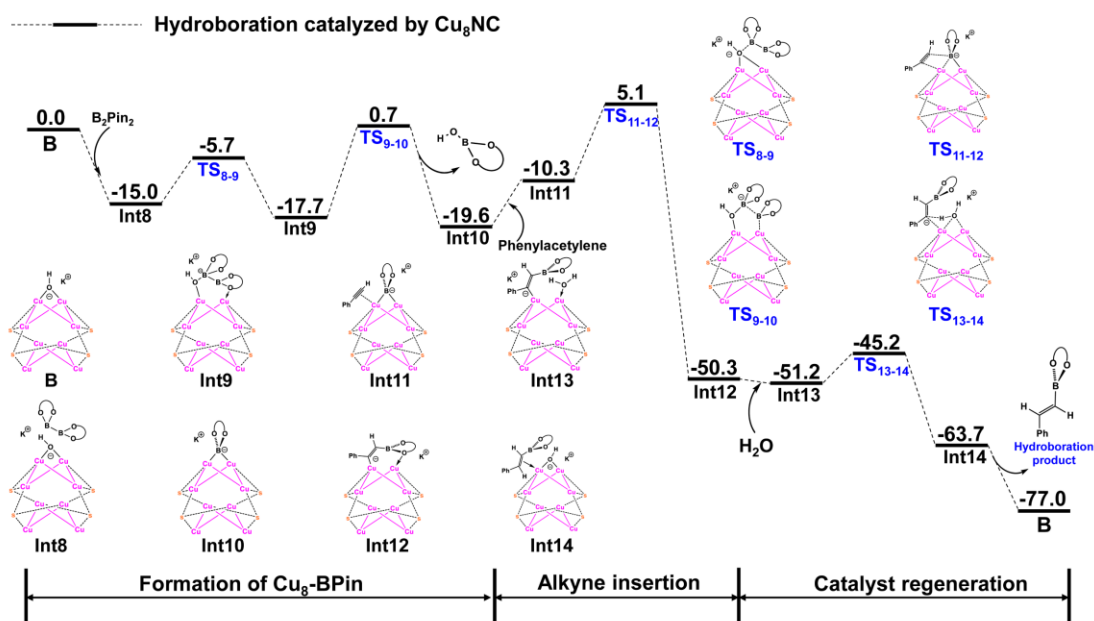
Supplementary Figure 74. DFT-computed Gibbs free energy profile. DFT-computed Gibbs free energy profile (ΔG in kcal/mol) for the hydroboration catalyzed by microcrystalline Cu_4NC .



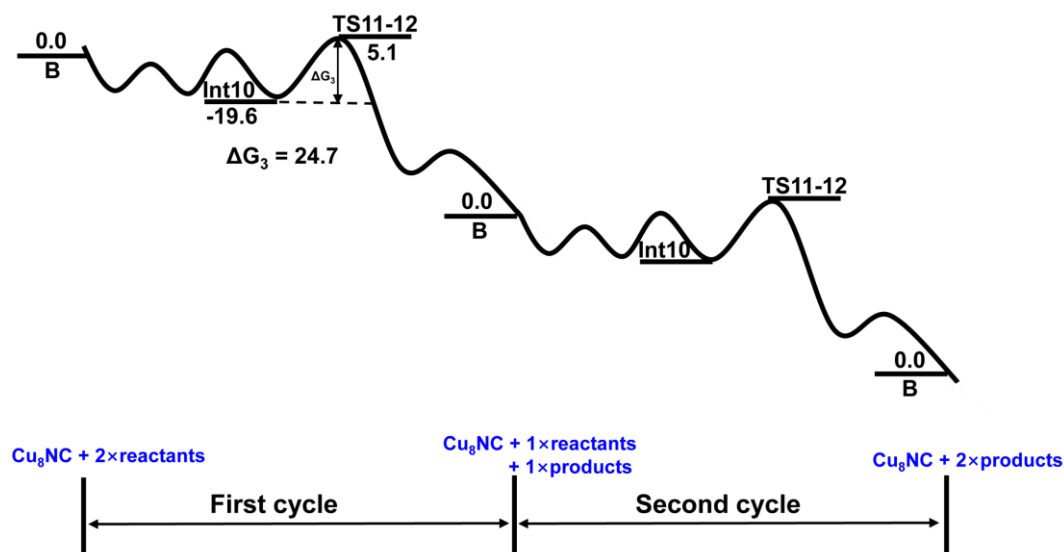
Supplementary Figure 75. Schematic illustration of the energy profile. Schematic illustration of the energy profile for an additional catalytic cycle (phenylacetylene as the alkyne substrate), which includes energy profile given the microcrystalline Cu_4NC catalyzed hydroboration reaction in Figure 5. The relative Gibbs energies (in black) are given in kcal/mol.



Supplementary Figure 77. DFT-computed Gibbs free energy profile. DFT-computed Gibbs free energy profile (ΔG in kcal/mol) for the hydroboration catalyzed by microcrystalline Cu_8NC .



Supplementary Figure 78. Energy profile calculated for the microcrystalline Cu_8NC catalyzed hydroboration reaction. The relative free energies are given in kcal/mol.



Supplementary Figure 79. Schematic illustration of the energy profile. Schematic illustration of the energy profile for an additional catalytic cycle (phenylacetylene as the alkyne substrate), which includes energy profile given the microcrystalline Cu_8NC catalyzed hydroboration reaction in Supplementary Figure 78. The relative Gibbs energies (in black) are given in kcal/mol.

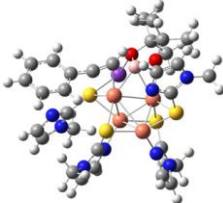
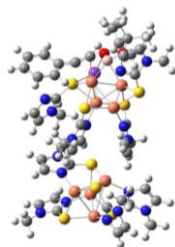
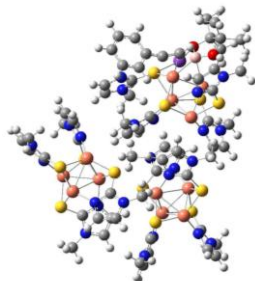
Energy difference between the barrier of Cu_4NC and Cu_8NC

As shown in Supplementary Table 2, we tested some popular functionals in Supplementary Table 2, the golden standard M06 functional enlarge the energy difference to 12.8 kcal/mol, (7.9 for dispersion corrected M06). B3LYP functional gives similar energy difference with PBE0 functional. In terms of basis set, 6-311+G** functional gives a larger difference of barrier difference. The above method can well fit our experiment (Supplementary Table 2).

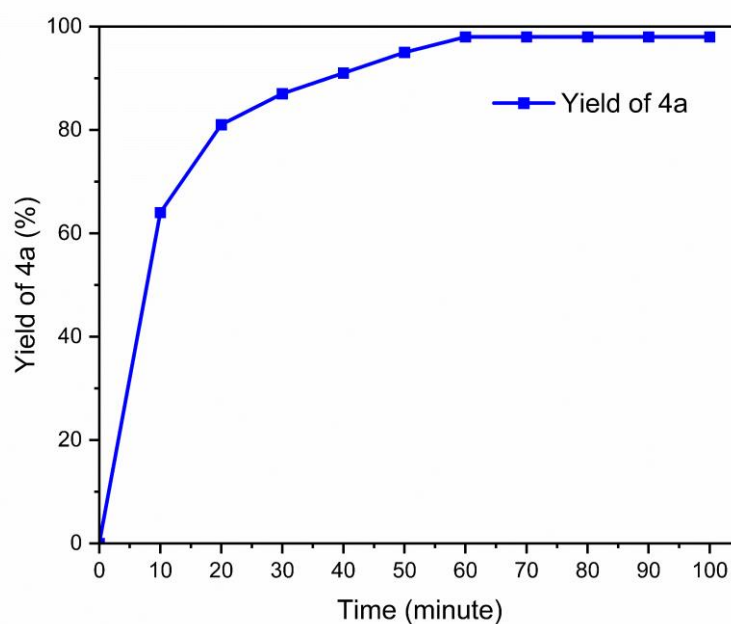
Supplementary Table 2. Energy difference between the barrier of Cu_4NC and Cu_8NC tested for different functionals and basis set.

Method	Energy difference of barrier
PBE0-D3/def2svp	1.8 kcal/mol
M06-D3/def2svp	7.9 kcal/mol
M06/def2svp	12.8 kcal/mol
B3LYP-D3/def2svp	1.6 kcal/mol
PBE0/6-311+G**	8.4 kcal/mol

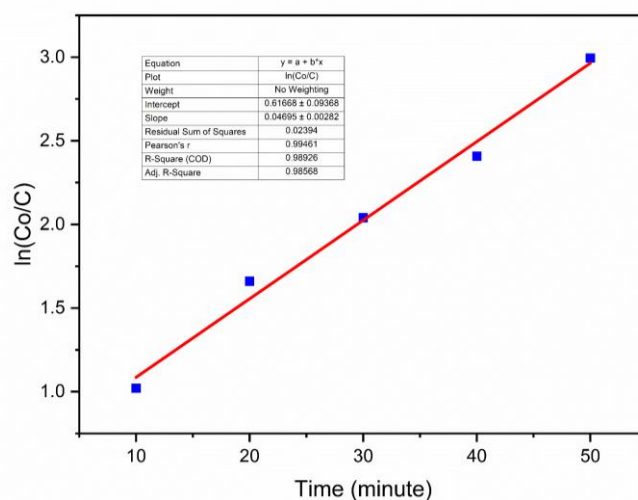
Supplementary Table 3. Theoretical calculations regarding rate-determining intermediates and the rate-determining transition states for the hydroboration catalyzed by Cu₄NC monomer, dimer and trimer.

States	The barrier (kcal/mol)	Structures of TS ₄₋₅
Cu ₄ NC monomer	22.9 kcal/mol	 Cu₄NC monomer C-B:1.88 Å Cu-C:2.05 Å Cu1-B:2.20 Å Cu2-B:2.23 Å
Cu ₄ NC dimer	20.6 kcal/mol	 Cu₄NC dimer C-B:1.91 Å Cu-C:2.05 Å Cu1-B:2.21 Å Cu2-B:2.21 Å
Cu ₄ NC trimer	22.0 kcal/mol	 Cu₄NC trimer C-B:1.89 Å Cu-C:2.04 Å Cu1-B:2.24 Å Cu2-B:2.26 Å

The Preliminary Kinetic Studies of the Hydroboration Reaction

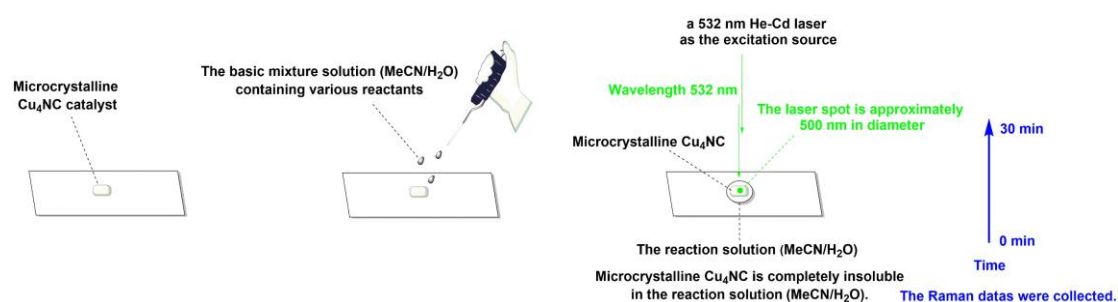


Supplementary Figure 80. Time-rate curve of hydroboration. Catalytic performances of 2.0 mol% Cu_4NC in hydroboration reaction of phenylacetylene at room temperature under air atmosphere.

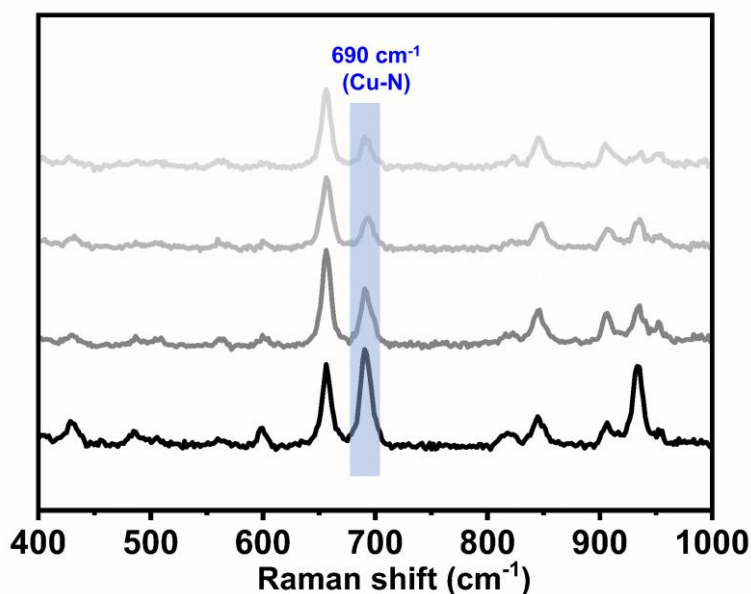


Supplementary Figure 81. Kinetic curve of hydroboration. Kinetic curve ($\ln(C_0/C)$ vs. t) of hydroboration reaction of phenylacetylene by using 2.0 mol% Cu_4NC as catalyst. C_0 and C are the phenylacetylene concentrations before the reaction and at a reaction time of t , respectively.

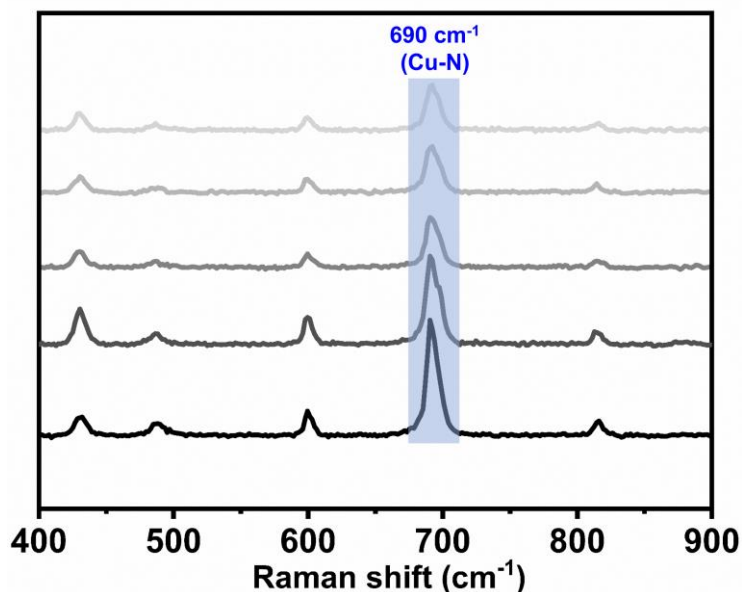
The *in situ* Raman Experiment



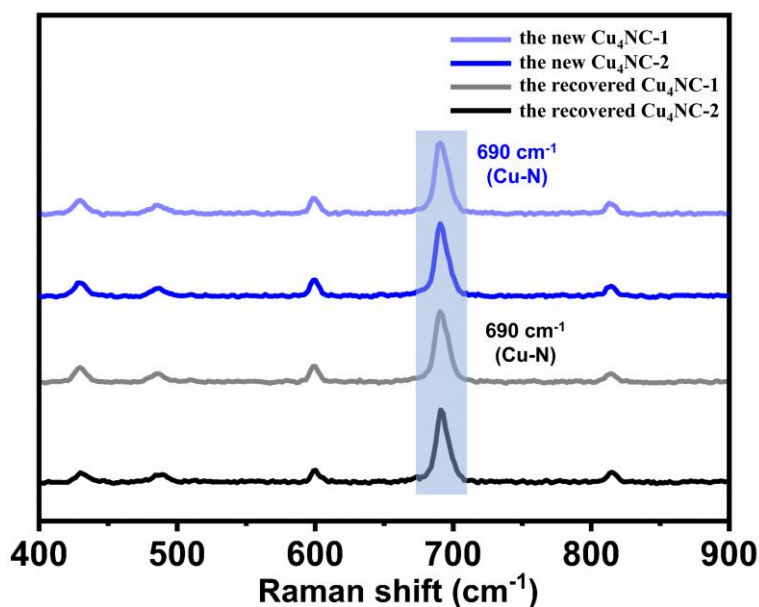
Supplementary Figure 82. The test method. The test method of the Raman spectra.



Supplementary Figure 83. Time-dependent *in situ* Raman spectra of the hydroboration reaction catalyzed by microcrystalline Cu_4NC catalyst (from bottom to top: 1min, 10min, 15min, 20min). Reaction conditions: the basic mixture solution (MeCN/ H_2O) containing various reactants was dropped onto microcrystalline Cu_4NC catalyst to react under air atmosphere at room temperature.

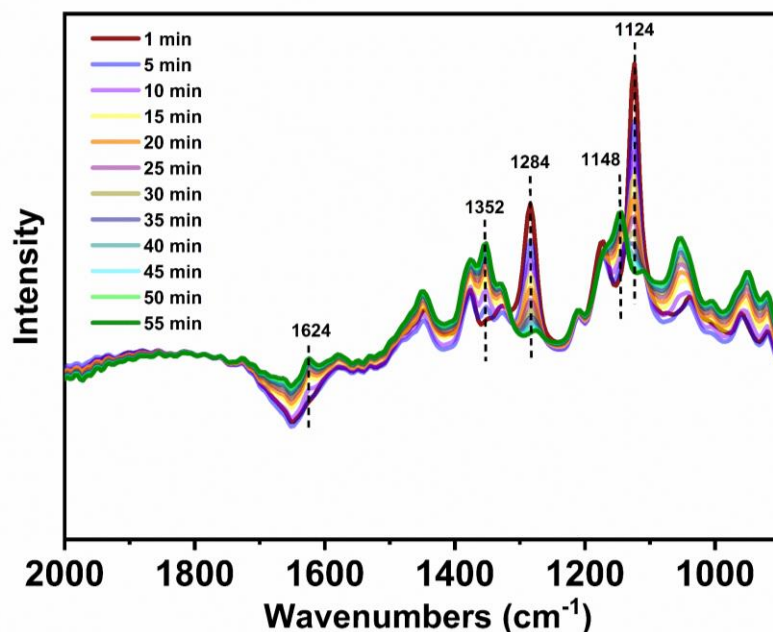


Supplementary Figure 84. Time-dependent *in situ* Raman spectra of the $\text{Cu}_4\text{NC} + \text{K}_2\text{CO}_3$ (from bottom to top: 1 min, 10 min, 15 min, 20 min, 30 min). Reaction conditions: the mixture solution ($\text{MeCN}/\text{H}_2\text{O}$) of K_2CO_3 was dropped onto microcrystalline Cu_4NC catalyst to react under air atmosphere at room temperature.

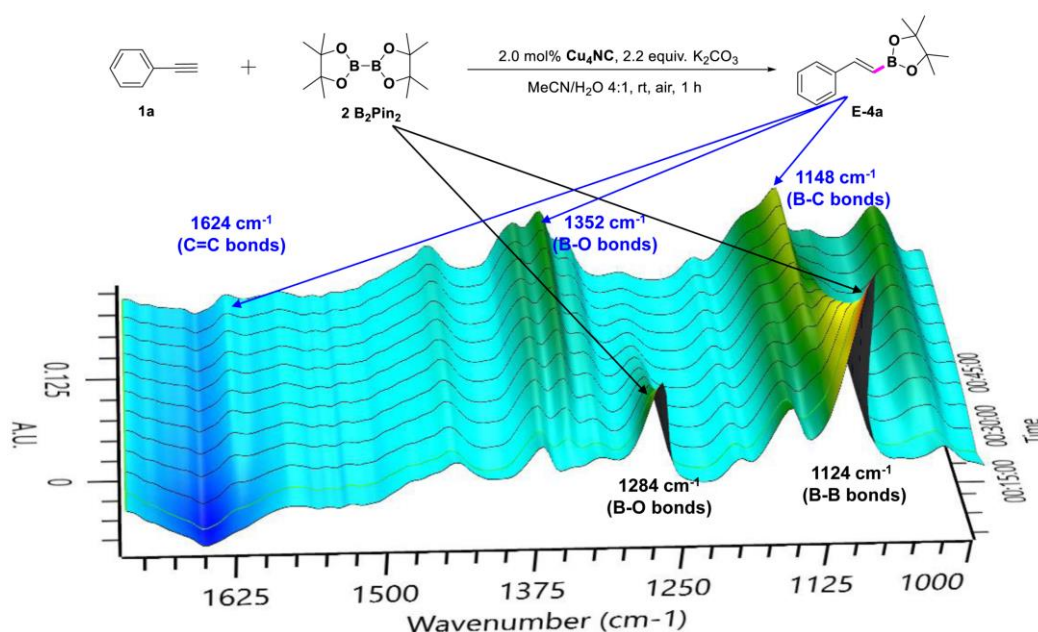


Supplementary Figure 85. The Raman spectra of the microcrystalline Cu_4NC before and after catalysis. The new Cu_4NC -1 and the new Cu_4NC -2 represent the Raman spectra of microcrystalline Cu_4NC catalysts prepared from different batches. The recovered Cu_4NC -1 and the recovered Cu_4NC -2 represent the Raman spectra of microcrystalline Cu_4NC catalysts recovered from different batches.

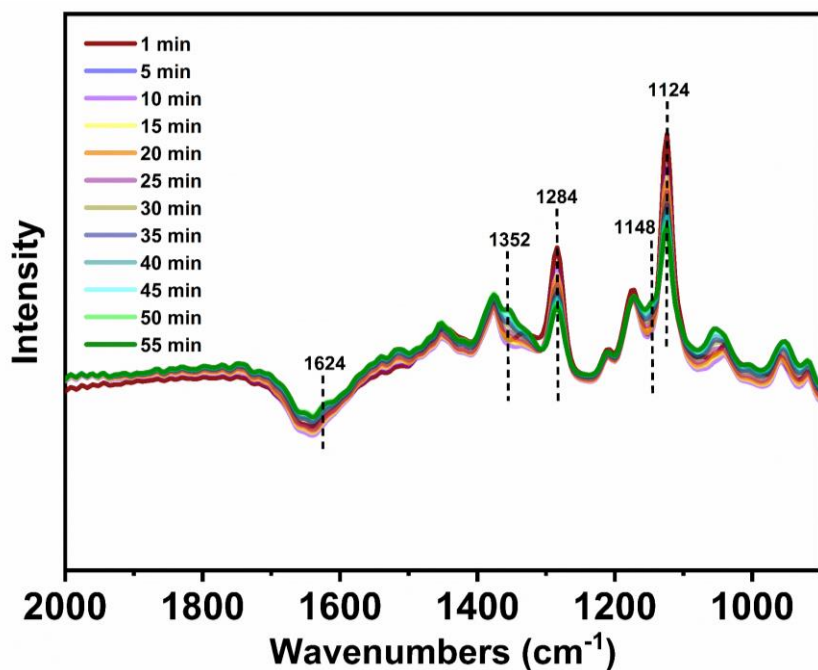
The *in situ* Fourier Transform Infrared (FT-IR) Experiment



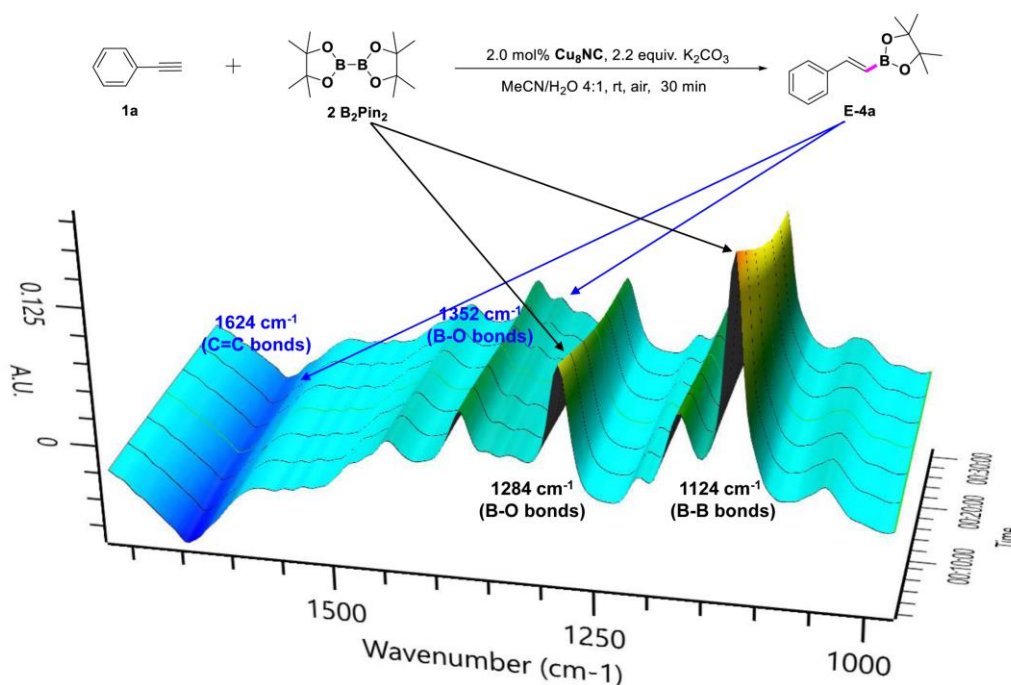
Supplementary Figure 86. Time-dependent *in situ* FT-IR spectra of the hydroboration reaction catalyzed by microcrystalline Cu_4NC catalyst. Reaction conditions: Phenylacetylene **1** (0.2 mmol, 1.0 equiv.), B_2Pin_2 **2** (0.44 mmol, 2.2 equiv.), Cu_4NC catal. (0.004 mmol, 2.0 mol%) and K_2CO_3 (0.44 mmol, 2.2 equiv.) were added to the mixture solvent (2.0 mL, MeCN/ H_2O 4:1) under air atmosphere at room temperature and allowed to react for 1 h.



Supplementary Figure 87. The *in situ* FTIR spectra for hydroboration. The top view of the three-dimensional surface of the *in situ* FTIR spectra for hydroboration process catalyzed by microcrystalline Cu_4NC catalyst.



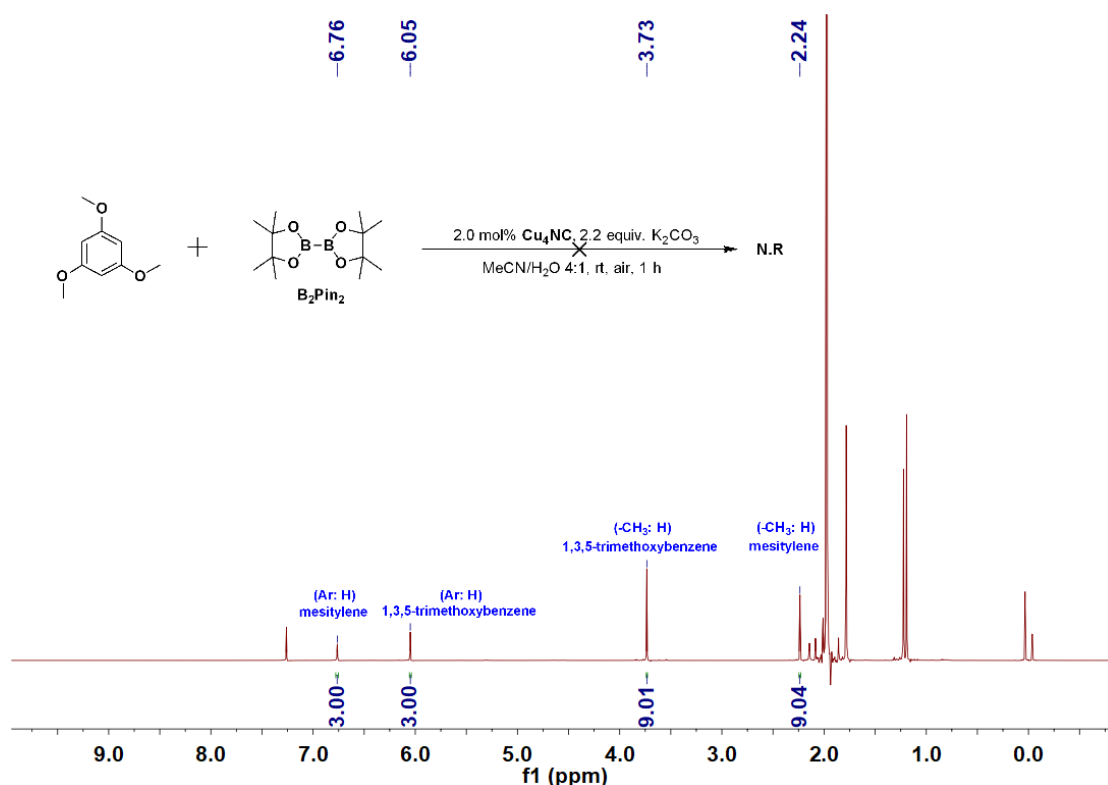
Supplementary Figure 88. Time-dependent *in situ* FT-IR spectra of the hydroboration reaction catalyzed by microcrystalline Cu_8NC catalyst. Reaction conditions: Phenylacetylene **1** (0.2 mmol, 1.0 equiv.), B_2Pin_2 **2** (0.44 mmol, 2.2 equiv.), Cu_8NC catal. (0.004 mmol, 2.0 mol%) and K_2CO_3 (0.44 mmol, 2.2 equiv.) were added to the mixture solvent (2.0 mL, MeCN/ H_2O 4:1) under air atmosphere at room temperature and allowed to react for 1 h.



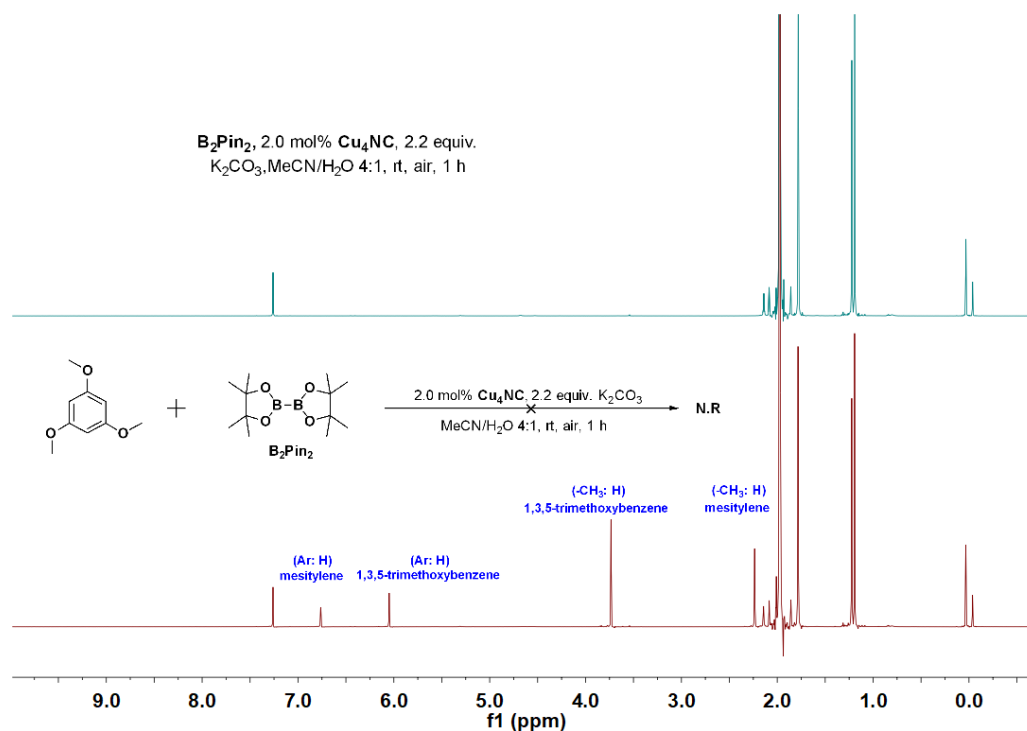
Supplementary Figure 89. The *in situ* FTIR spectra for hydroboration. The top view of the three-dimensional surface of the *in situ* FTIR spectra for hydroboration process catalyzed by microcrystalline Cu_8NC catalyst.

Deprotection of 1,3,5-Trimethoxybenzene Catalyzed by Microcrystalline Cu Clusters

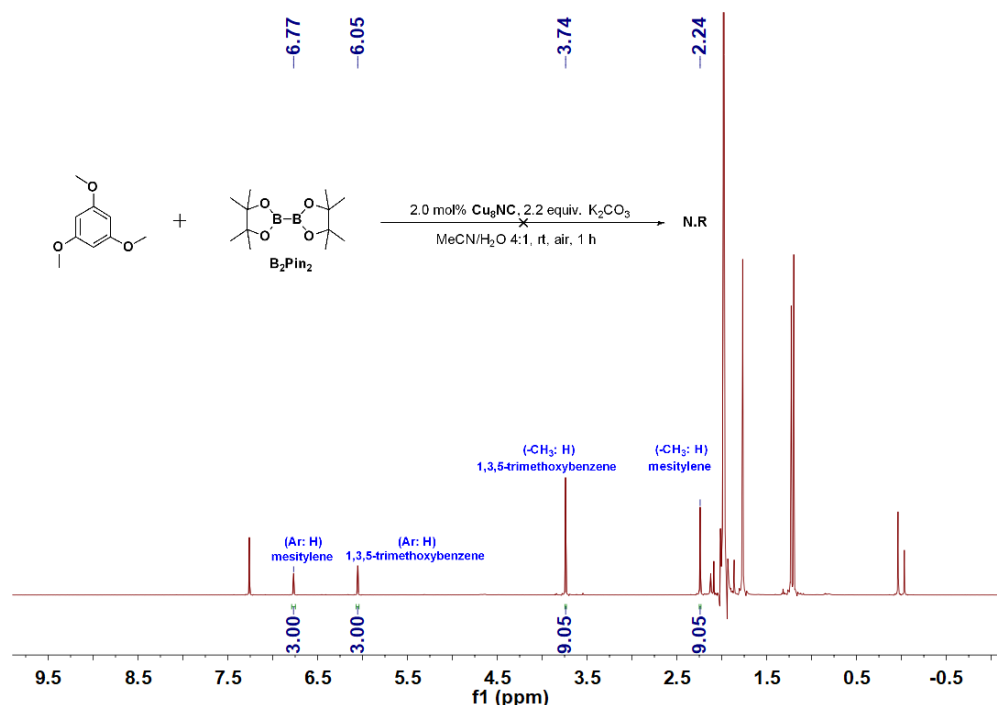
To further prove that 1,3,5-trimethoxybenzene can be utilized as an internal standard, a control experiments was carried out that the 1,3,5-trimethoxybenzene, which replaced phenylacetylene as substrate, was been added into our copper cluster catalytic system. When the reaction time reaches 1 hour, the mesitylene as the standard was added into the reaction system. The reaction result was monitored by the ^1H NMR spectrum, showing that the content of 1,3,5-trimethoxybenzene has not decreased (Supplementary Figures 87–90). It further illustrated that 1,3,5-trimethoxybenzene is an inert substrate in our catalytic system. The experiment shows that 1,3,5-trimethoxybenzene can be utilized as an internal standard in our catalytic system.



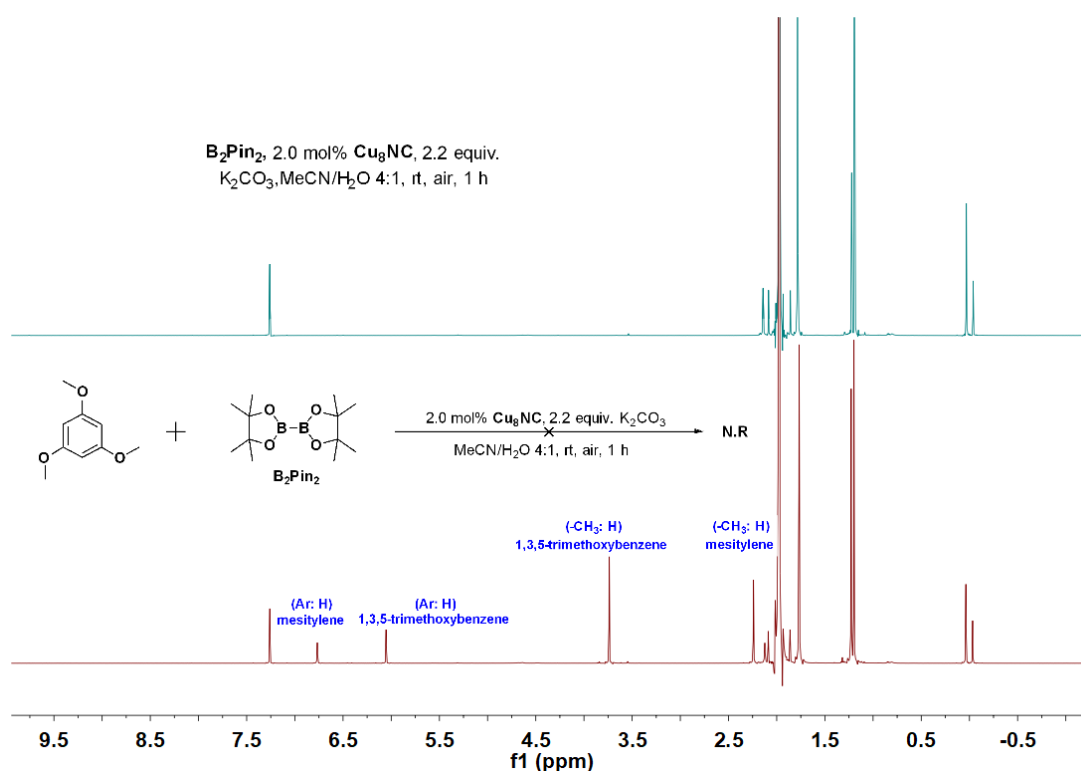
Supplementary Figure 90. The *in situ* ^1H NMR spectrum of deprotection of 1,3,5-trimethoxybenzene. The *in situ* ^1H NMR spectrum of deprotection of 1,3,5-trimethoxybenzene catalyzed by microcrystalline Cu_4NC catalyst.



Supplementary Figure 91. The *in situ* 1H NMR spectra of deprotection of 1,3,5-trimethoxybenzene. The *in situ* 1H NMR spectra of deprotection of 1,3,5-trimethoxybenzene catalyzed by microcrystalline Cu_4NC catalyst. Top: the control group. Bottom: the experimental group.



Supplementary Figure 92. The *in situ* 1H NMR spectrum of deprotection of 1,3,5-trimethoxybenzene. The *in situ* 1H NMR spectrum of deprotection of 1,3,5-trimethoxybenzene catalyzed by microcrystalline Cu_8NC catalyst.

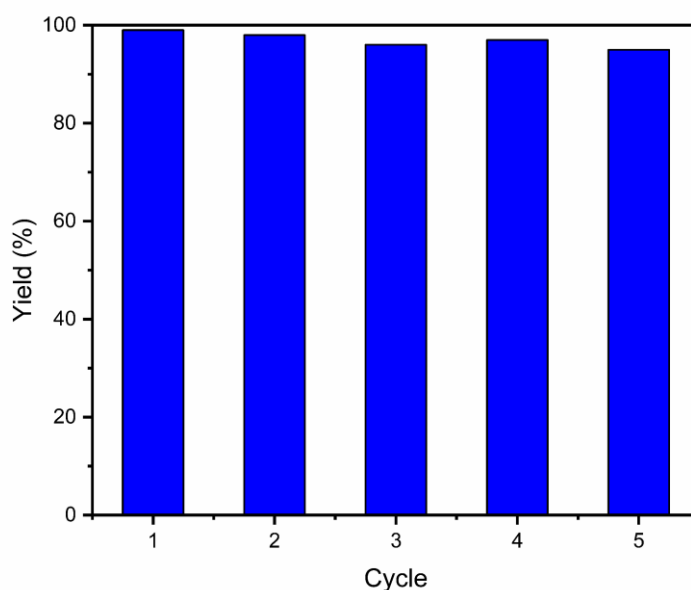


Supplementary Figure 93. The *in situ* ¹H NMR spectra of deprotection of 1,3,5-trimethoxybenzene. The *in situ* ¹H NMR spectra of deprotection of 1,3,5-trimethoxybenzene catalyzed by microcrystalline Cu₈NC catalyst. Top: the control group. Bottom: the experimental group.

Recyclability of the Cu₄NC Catalyzed Hydroboration Reaction

Recycling Procedure for Cu₄NC-Catalyzed the Hydroboration Reaction.

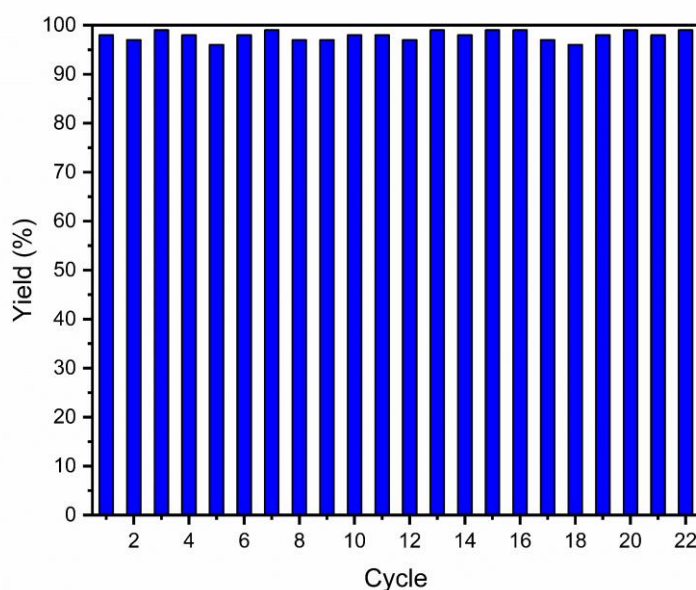
Under air atmosphere, phenylacetylene **1** (20.4 mg, 0.2 mmol, 1.0 eq), B₂Pin₂ **2** (111.8 mg, 0.44 mmol, 2.2 equiv.), Cu₄NC catalysts (2.8 mg, 2.0 mol%), K₂CO₃ (60.7 mg, 0.44 mmol, 2.2 equiv.) and the mixture solvent (2.0 mL, MeCN-H₂O, v/v 4/1) were added into a 10 mL flask. The reaction mixture was stirred at room temperature for 1 h. Conversions and yields were determined by ¹H NMR using 1,3,5-trimethoxybenzene as an internal standard. After the reaction is completed, the reaction mixture was centrifuged at 8000 rpm for 5 minutes. The microcrystalline Cu₄NC catalyst was filtered, washed with hexane and then dried in vacuum to recycle the microcrystalline Cu₄NC. The recycled microcrystalline Cu₄NC catalyst was used again in the next recycle. In this way, the hydroboration reaction of alkynes was conducted for 5 cycles with the microcrystalline Cu₄NC catalyst (Supplementary Figure 94).



Supplementary Figure 94. Cyclic experiment. Recyclability of the microcrystalline Cu_4NC catalyzed hydroboration reaction in term of yield (1 h).

When we studied the recovery experiments, we found that the weak interaction between recycled microcrystalline Cu_4NC catalyst and filter paper can lead to unnecessary loss of microcrystalline Cu_4NC catalyst, thereby limiting the number of cycles of catalysis. To eliminate the influence of the weak interaction, the repeated dosing projects were carried out. In this way, the hydroboration reaction of alkynes was conducted for more than 20 cycles (Supplementary Figure 95). The repeated dosing experiments were conducted to further demonstrate that microcrystalline Cu_4NC has excellent catalytic activity and stability.

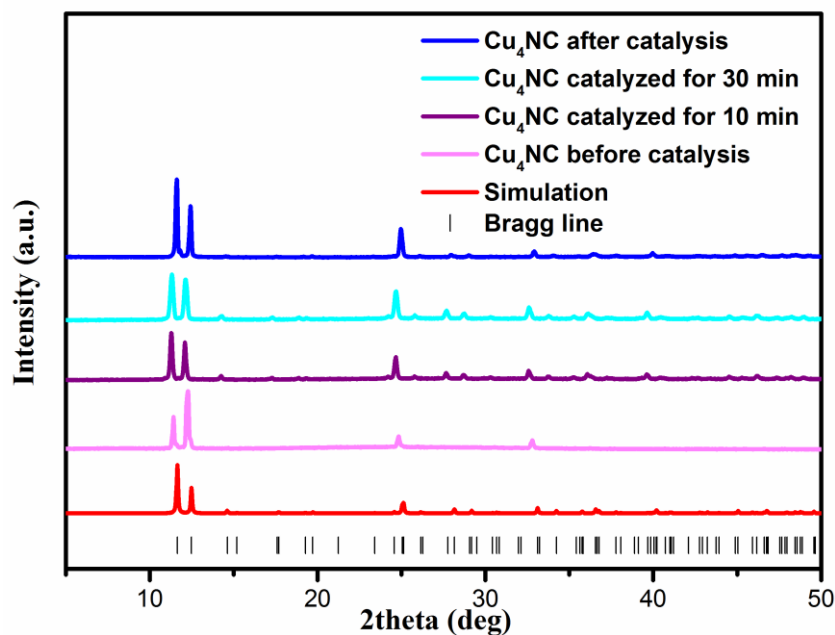
Under air atmosphere, phenylacetylene **1** (20.4 mg, 0.2 mmol, 1.0 eq), B_2Pin_2 **2** (111.8 mg, 0.44 mmol, 2.2 equiv.), Cu_4NC catalysts (2.8 mg, 2.0 mol%), K_2CO_3 (60.7 mg, 0.44 mmol, 2.2 equiv.) and the mixture solvent (2.0 mL, MeCN- H_2O , v/v 4/1) were added into a 50 mL flask. The reaction mixture was stirred at room temperature for 1 h. Conversions and yields were determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard. Then the reactants [phenylacetylene **1** (20.4 mg, 0.2 mmol, 1.0 eq), B_2Pin_2 **2** (111.8 mg, 0.44 mmol, 2.2 equiv.), K_2CO_3 (60.7 mg, 0.44 mmol, 2.2 equiv.) and the mixture solvent (1.0 mL, MeCN- H_2O , v/v 4/1)] were injected to the reaction system twenty-one consecutive times. The conversion and yield were determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard.



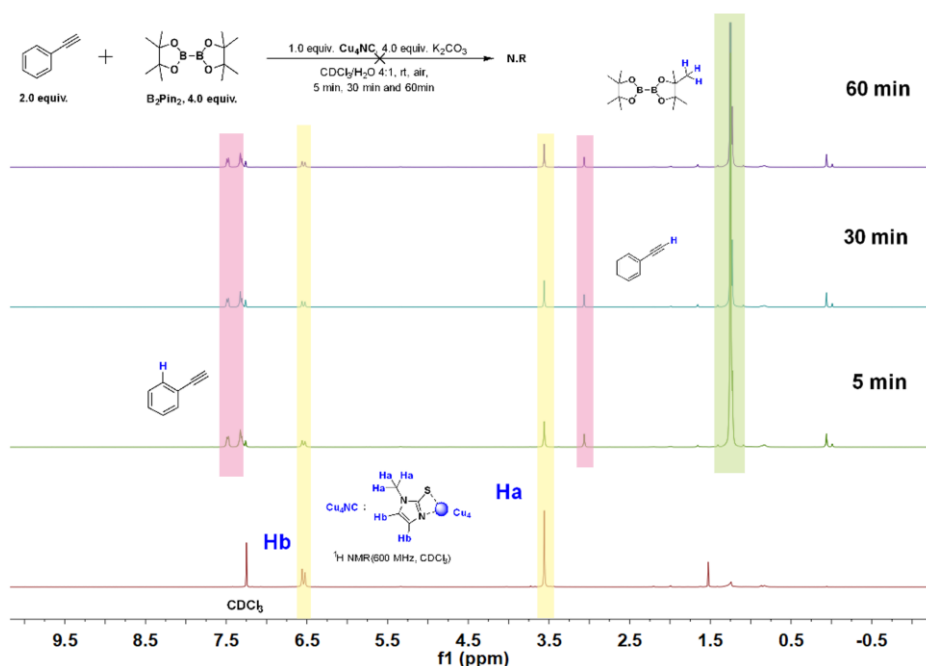
Supplementary Figure 95. The repeated dosing experiment. The repeated dosing of the microcrystalline Cu_4NC catalyzed hydroboration reaction in term of yield (1 h).

Monitor the State of the Microcrystalline Cu_4NC during the Catalytic Process Using PXRD

To verify the stability of the catalyst and to verify that the crystal state of microcrystalline Cu_4NC has been maintained in hydroboration, three parallel experiments of hydroboration catalyzed by microcrystalline Cu_4NC also were carried out. The parallel experiments will be stopped at the 10th minute, the 30th minute and the 60th minute. The reaction mixture was centrifuged at 8000 rpm for 5 minutes. The microcrystalline Cu_4NC catalyst was filtered, washed with hexane and then dried in vacuum to recycle the microcrystalline Cu_4NC . Recycled microcrystalline Cu_4NC catalyst was further characterized by PXRD (Supplementary Figure 96). It showed that the characteristic peaks of the catalyzed microcrystalline Cu_4NC at different time (the 10th minute, the 30th minute and the 60th minute) matched well with the characteristic peaks of the new microcrystalline Cu_4NC . In a word, the results illustrated that the hydroboration happens on the surface of microcrystalline Cu_4NC , and microcrystalline Cu_4NC is very stable in hydroboration process.



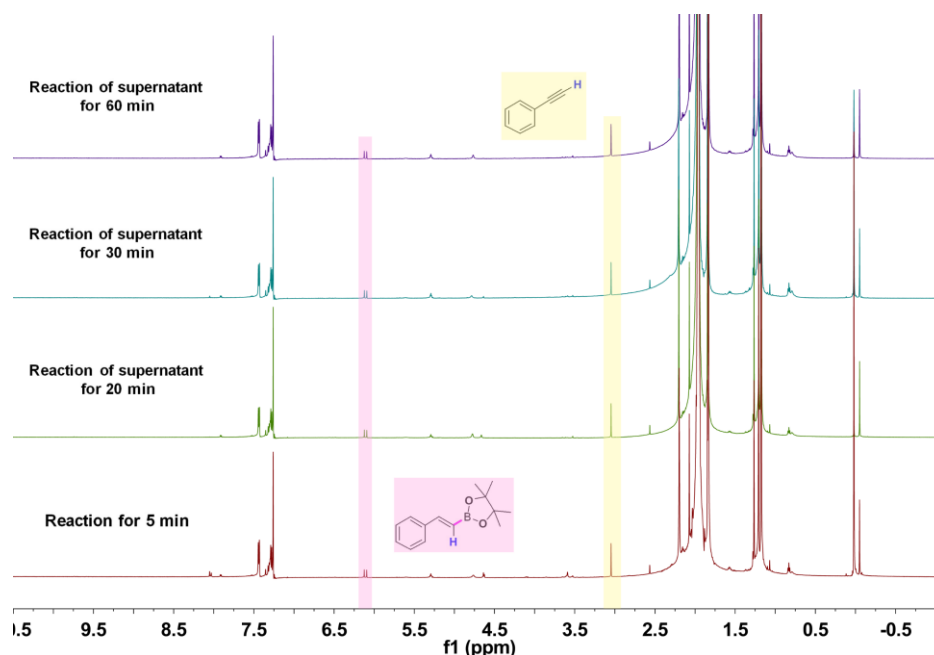
Supplementary Figure 96. PXRD patterns of Cu₄NC before catalysis and after catalysis. PXRD patterns of Cu₄NC before catalysis and after the 10th minute, the 30th minute and the 60th minute catalysis.



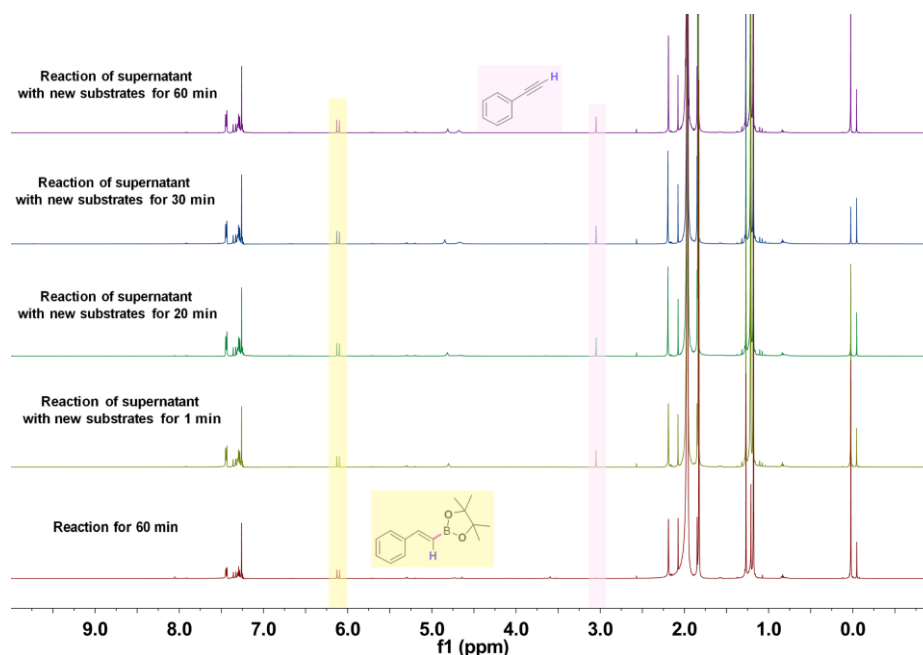
Supplementary Figure 97. Time-dependent *in situ* ¹H NMR spectra of the hydroboration reaction. Time-dependent *in situ* ¹H NMR spectra of the hydroboration reaction catalyzed by microcrystalline Cu₄NC catalyst in the mixture solvent (CDCl₃-H₂O). Reaction conditions: Phenylacetylene 1 (2.0 equiv.), B₂Pin₂ 2 (4.0 equiv.), Cu₄NC catal. (1.0 equiv.) and K₂CO₃ (4.0 equiv.) were added to the mixture solvent (2.0 mL, CDCl₃-H₂O) under air atmosphere at room temperature and allowed to react for 1 h. No product was found.

Monitor the Catalytic Ability of the Supernatant Using *in situ* ^1H NMR

To verify that the supernatant lacks any catalytic ability, corresponding experiments and characterization tests were carried out. First, the hydroboration reaction catalyzed by microcrystalline Cu_4NC was conducted. After 5 minutes, the microcrystalline Cu_4NC was removed from the catalytic system. Continuous stirring of supernatant was further monitored by the *in situ* ^1H NMR at the 5th minute, 20th minute, 30th minute and 60th minute (Supplementary Figure 98), showing that no further conversion was observed within this solution. Second, the other control experiment was carried out. When the reaction was completed, the microcrystalline Cu_4NC was removed from the catalytic system. The additional aliquot of the substrates was added to the supernatant, which was further monitored by the *in situ* ^1H NMR at the 1th minute, 20th minute, 30th minute and 60th minute (Supplementary Figure 99). The result showed that no conversion of the added material was observed. All of these observations and experimental results suggested that the supernatant lacks any catalytic ability. The possibility of forming a soluble, catalytically competent, and copper-free species under reaction conditions has been precluded. At the same time, the supernatants were characterized by inductively coupled plasma mass spectrometric (ICP-MS) measurement, showing that no Cu^+ ions were found in the reaction supernatant, suggesting that Cu^+ ions were not leached from the metal cluster catalyst into solution over the course of the reaction. These results also suggested that key intermediate A is completely insoluble in the reaction solvent system ($\text{MeCN-H}_2\text{O}$).



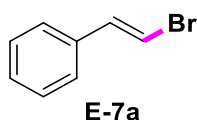
Supplementary Figure 98. Time-dependent *in situ* ^1H NMR spectra of the hydroboration reaction. Reaction conditions: Phenylacetylene 1 (1.0 equiv.), B_2Pin_2 2 (2.2 equiv.), Cu_4NC catal. (10% mol) and K_2CO_3 (2.2 equiv.) were added to the mixture solvent (2.0 mL, $\text{CD}_3\text{CN-H}_2\text{O}$) under air atmosphere at room temperature and allowed to react for 5 min. The catalyst was separated from the supernatant of the reaction system by filtration. The supernatant was stirred for 1 h.



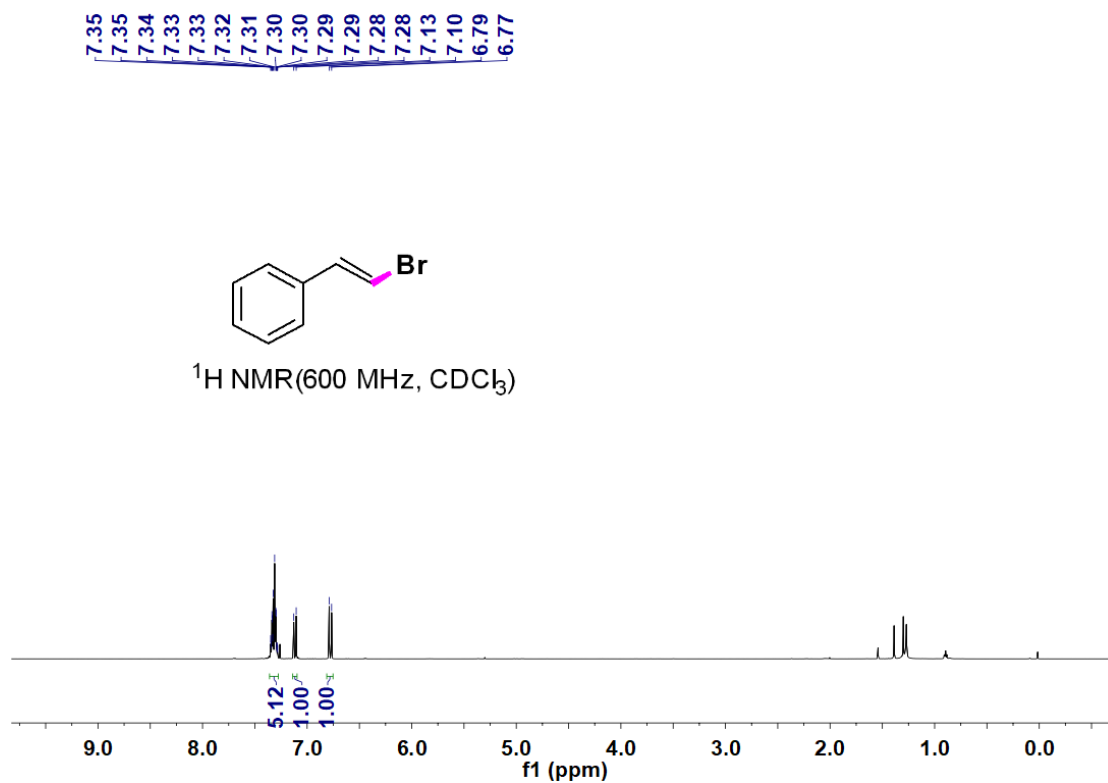
Supplementary Figure 99. Time-dependent *in situ* ^1H NMR spectra of the hydroboration reaction. Reaction conditions: Phenylacetylene **1** (1.0 equiv.), B_2Pin_2 **2** (2.2 equiv.), Cu_4NC catal. (10% mol) and K_2CO_3 (2.2 equiv.) were added to the mixture solvent (2.0 mL, $\text{CD}_3\text{CN-H}_2\text{O}$) under air atmosphere at room temperature and allowed to react for 1 h. The catalyst was separated from the supernatant of the reaction system by filtration. Phenylacetylene **1** (1.0 equiv.), B_2Pin_2 **2** (2.2 equiv.) and K_2CO_3 (2.2 equiv.) were added to the supernatant. The reaction was stirred for 1 h.

Derivatization of the Products from Hydroboration of Alkynes

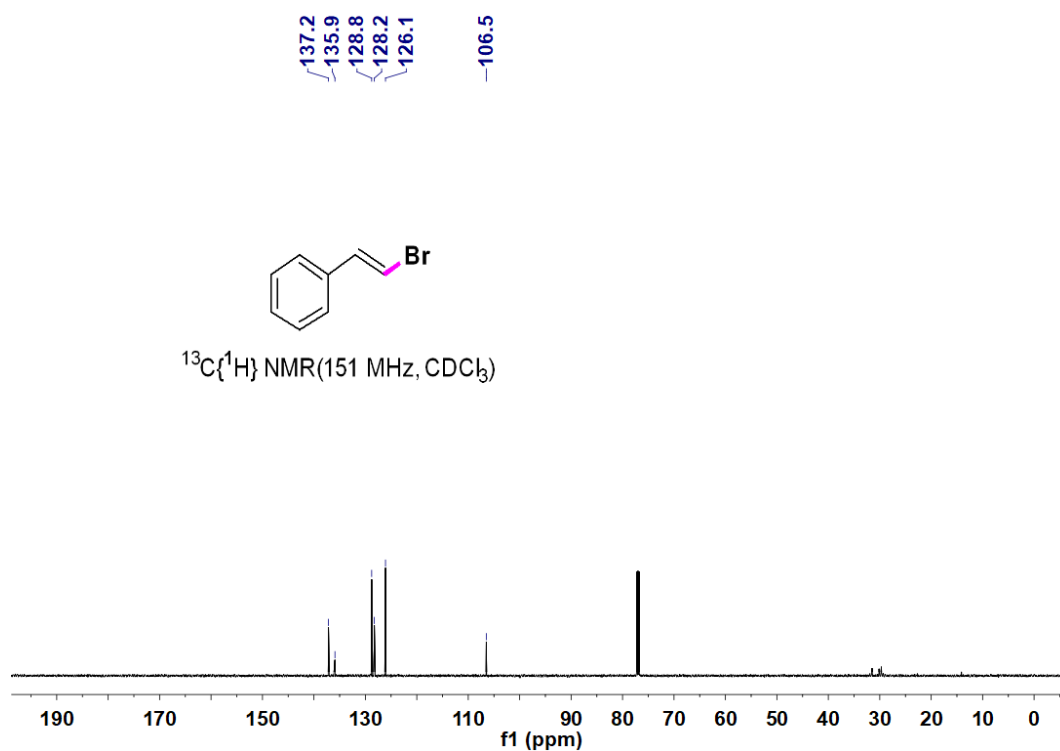
(*E*)-(2-bromovinyl) benzene (**7a**)



Under air atmosphere, the copper salt CuBr_2 (134.0 mg, 0.6 mmol), **E-4a** compound (46.0 mg, 0.2 mmol) and the mixture solvent (3.0 mL, $\text{EtOH-H}_2\text{O}$, v/v 1/1) were added into 25 mL Schlenk tube to react at $100\text{ }^\circ\text{C}$ for 24 h. The reactions were monitored by TLC. When **E-4a** compound was consumed, the reaction was cooled to room temperature, then quenched and concentrated. The crude products were then purified by column chromatography (PE-EA, v/v 1/0) to give the target products as a colorless oil with an overall isolated yield: 81% (29.4 mg). ^1H NMR (600 MHz, CDCl_3) δ 7.36 – 7.28 (m, 5H), 7.12 (d, $J = 14.0$ Hz, 1H), 6.78 (d, $J = 14.0$ Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 137.2, 135.9, 128.8, 128.3, 126.1, 106.5.

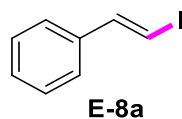


Supplementary Figure 100. Characterization of compound 7a. ^1H NMR spectrum of compound 7a in CDCl_3 .

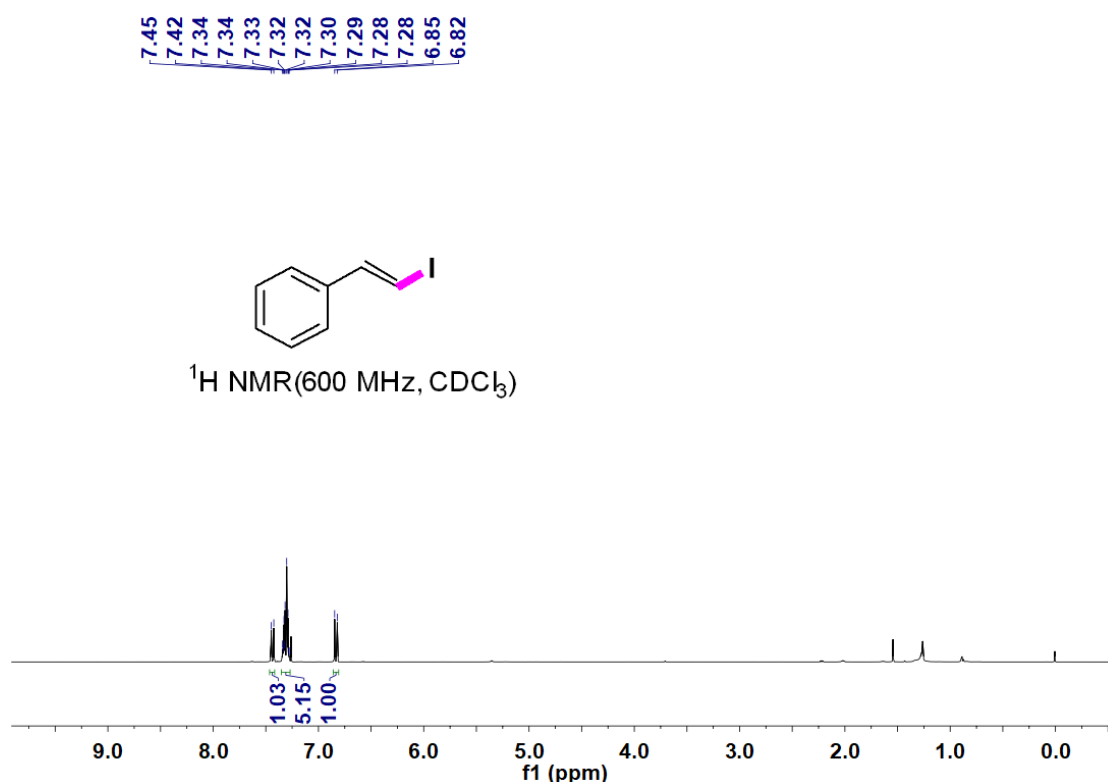


Supplementary Figure 101. Characterization of compound 7a. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound 7a in CDCl_3 .

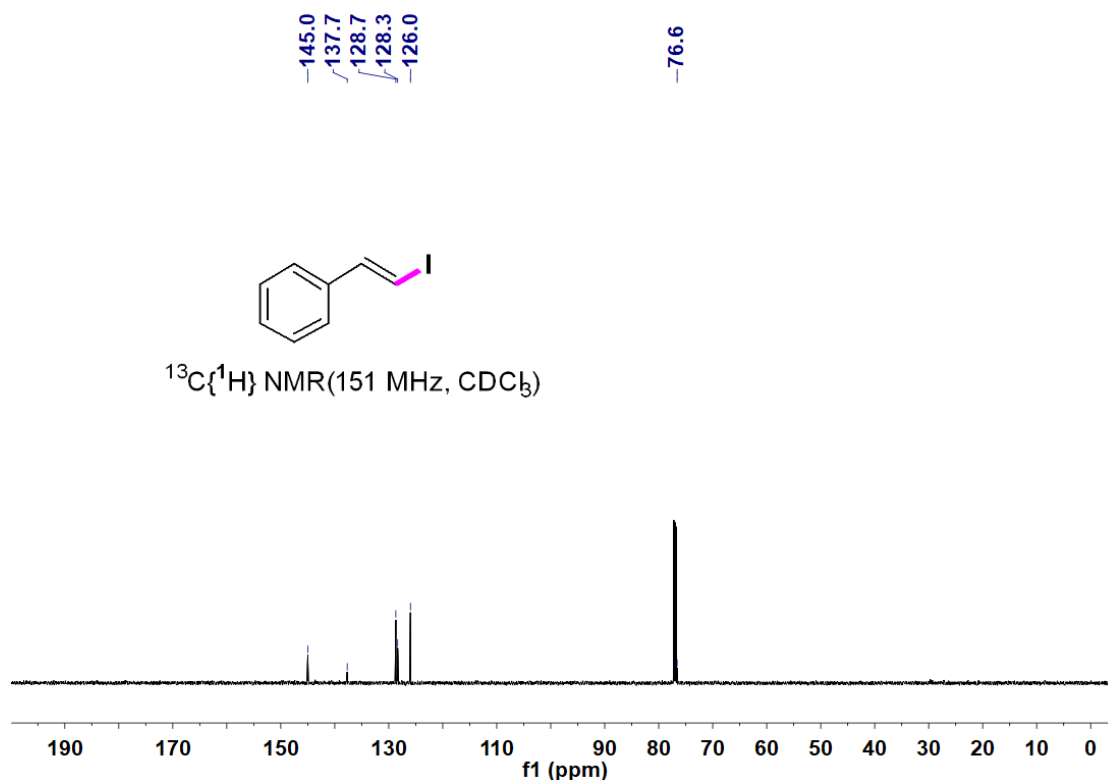
(E)-(2-iodovinyl) benzene (8a)



Under air atmosphere, the copper salts CuI (3.8 mg, 0.02 mmol), o-phenanthroline (7.2 mg, 0.04 mmol) and the mixture solvent (2.0 mL, MeOH-H₂O, v/v 4/1) were added into 25 mL Schlenk tube to react at room temperature for 30 min. Then KI (49.8 mg, 0.3 mmol) and **E-4a** compound (46.0 mg, 0.2 mmol) were added in the reaction system to react at 80 °C for 12 h. The reactions were monitored by TLC. When **E-4a** compound was consumed, the reaction was cooled to room temperature, then quenched and concentrated. The crude products were then purified by column chromatography (PE-EA, v/v 1/0) to give the target products as a colorless oil with an overall isolated yield: 51% (23.5 mg). ¹H NMR (600 MHz, CDCl₃) δ 7.44 (d, *J* = 14.9 Hz, 1H), 7.35 – 7.27 (m, 5H), 6.83 (d, *J* = 14.9 Hz, 1H). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 145.0, 137.7, 128.7, 128.4, 126.0, 76.6.

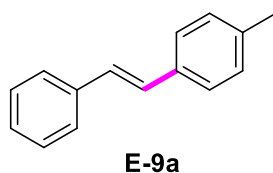


Supplementary Figure 102. Characterization of compound 8a. ¹H NMR spectrum of compound **8a** in CDCl₃

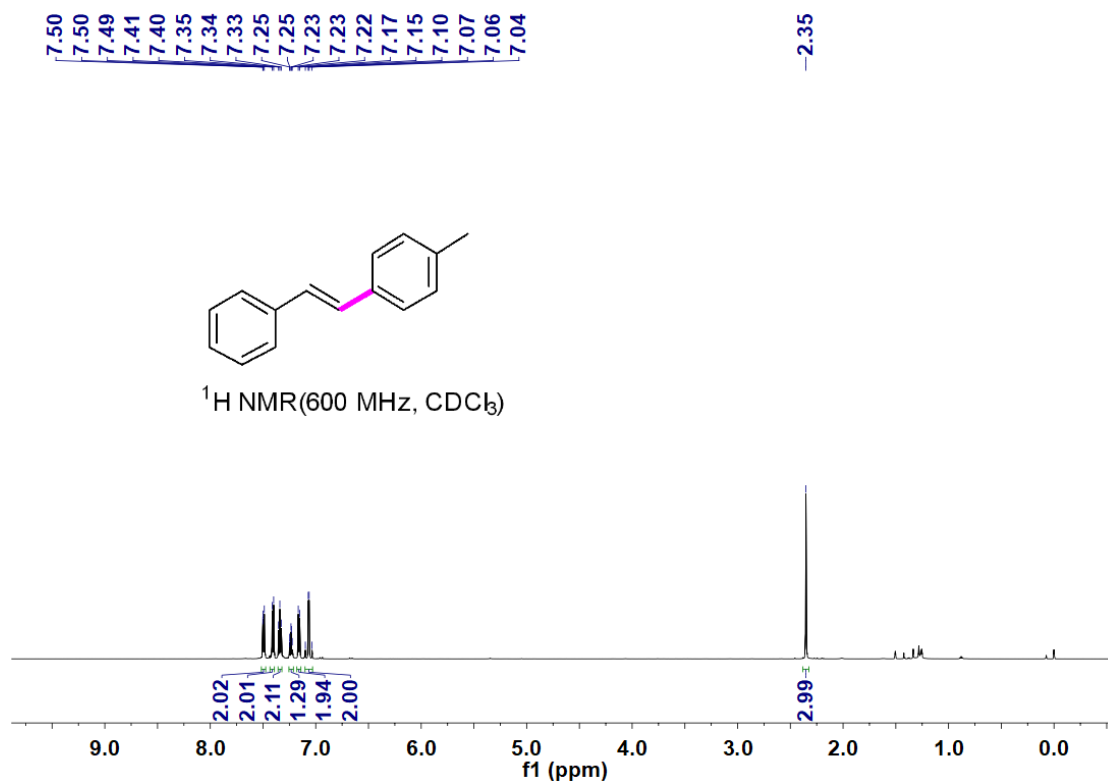


Supplementary Figure 103. Characterization of compound 8a. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound 8a in CDCl_3 .

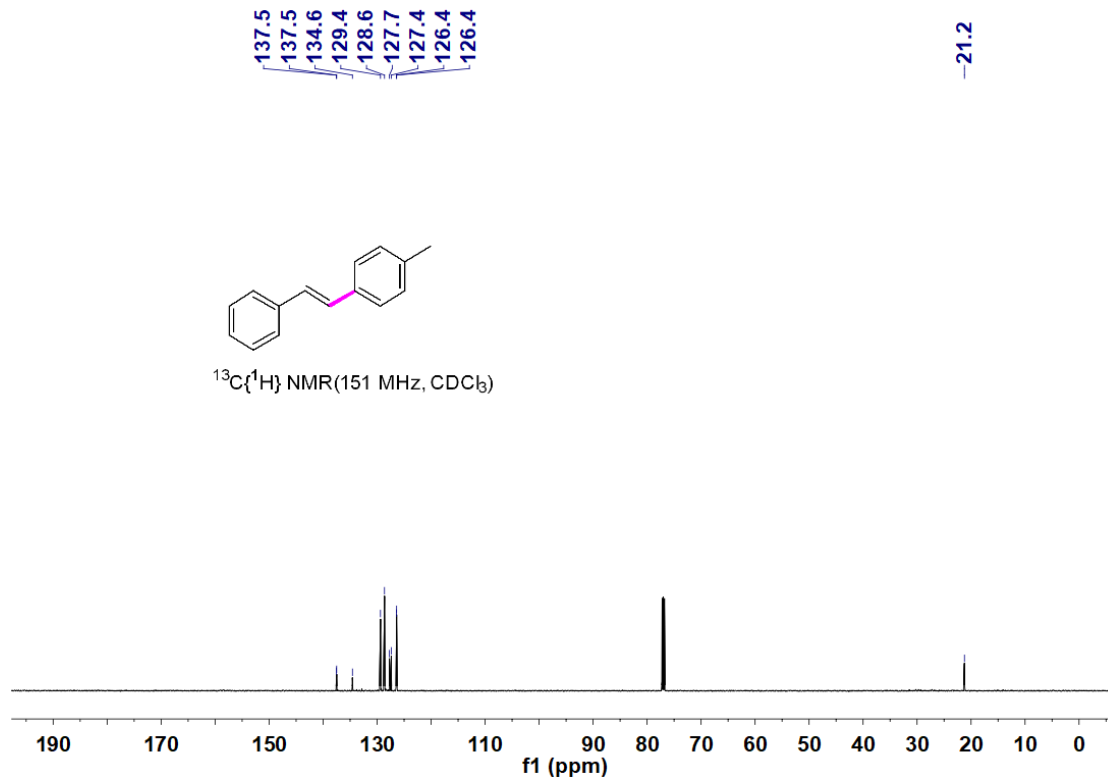
(E)-1-methyl-4-styrylbenzene (9a)



Under N_2 atmosphere, the $\text{Pd}(\text{PPh}_3)_4$ (11.6 mg, 5.0 mol%), **E-4a** compound (46.0 mg, 0.2 mmol), Cs_2CO_3 (391.0 mg, 1.2 mmol), 4-iodotoluene (43.6 mg, 0.2 mmol) and the 4.0 mL THF solvent were added into 25 mL Schlenk tube to react at 60 °C overnight. The reactions were monitored by TLC. When **E-4a** compound was consumed, the reaction was cooled to room temperature, then quenched and concentrated. The crude products were then purified by column chromatography (PE-EA, v/v 40/1) to give the target products as a white solid with an overall isolated yield: 95% (36.9 mg). ^1H NMR (600 MHz, CDCl_3) δ 7.51 – 7.47 (m, 2H), 7.41 (d, J = 8.1 Hz, 2H), 7.34 (t, J = 7.7 Hz, 2H), 7.26 – 7.22 (m, 1H), 7.16 (d, J = 7.9 Hz, 2H), 7.10 – 7.03 (m, 2H), 2.35 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 137.5, 137.5, 134.6, 129.4, 128.6, 127.7, 127.4, 126.4, 126.4, 21.2.

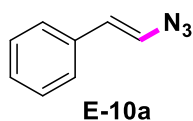


Supplementary Figure 104. Characterization of compound 9a. ¹H NMR spectrum of compound 9a in CDCl₃.

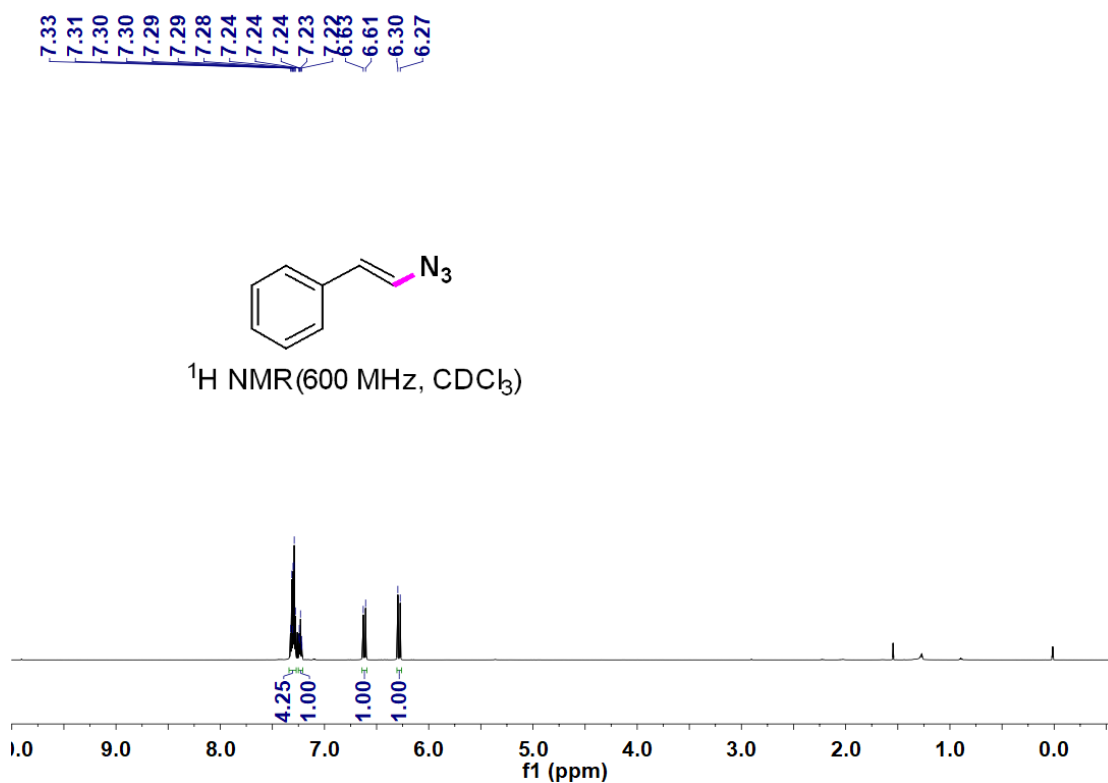


Supplementary Figure 105. Characterization of compound 9a. ¹³C{¹H} NMR spectrum of compound 9a in CDCl₃.

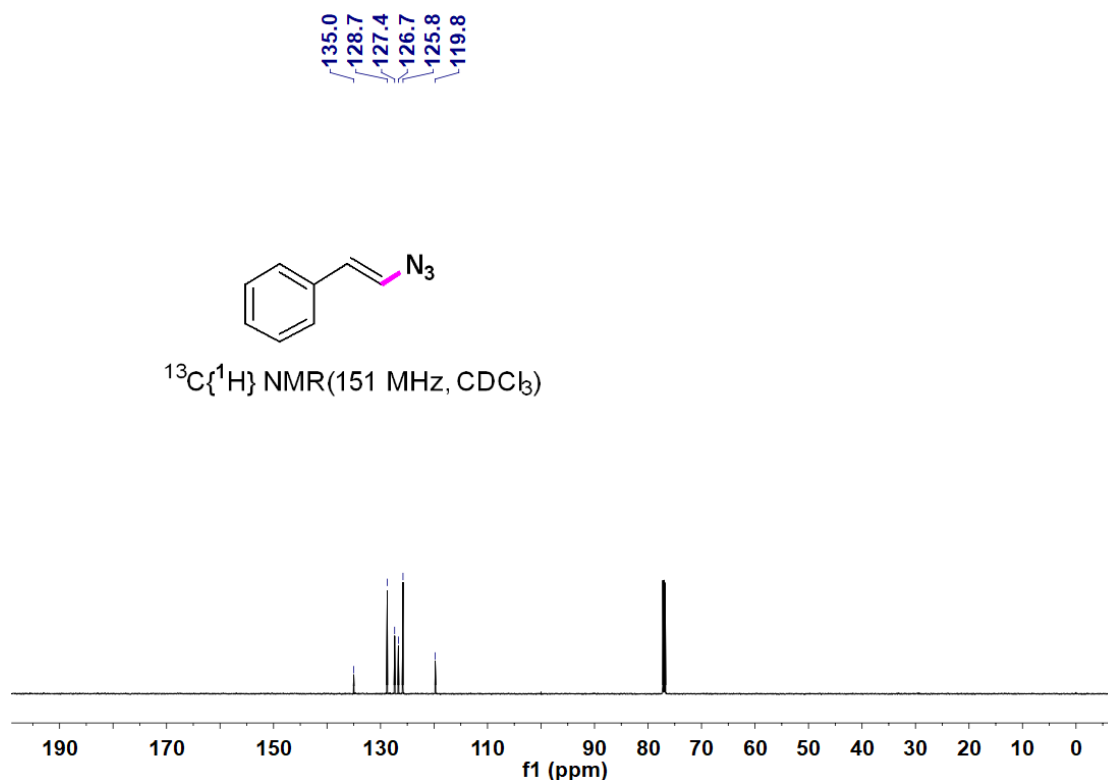
(E)-(2-azidovinyl)benzene (10a)



Under air atmosphere, the copper salts $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (30.0 mg, 0.12 mmol), **E-4a** compound (46.0 mg, 0.2 mmol), NaN_3 (19.5 mg, 0.3 mmol) and the 0.8 mL MeOH solvent were added into 25 mL round-bottom flask to react at room temperature overnight. The reactions were monitored by TLC. When **E-4a** compound was consumed, the reaction was quenched and concentrated. The crude products were then purified by column chromatography (PE-EA, v/v 1/0) to give the target products as a yellow oil with an overall isolated yield: 92% (26.7 mg). ^1H NMR (600 MHz, CDCl_3) δ 7.34 – 7.27 (m, 4H), 7.25 – 7.21 (m, 1H), 6.62 (d, $J = 13.8$ Hz, 1H), 6.28 (d, $J = 13.8$ Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 135.0, 128.7, 127.4, 126.7, 125.8, 119.8.

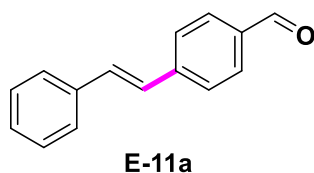


Supplementary Figure 106. Characterization of compound 10a. ^1H NMR spectrum of compound **10a** in CDCl_3 .

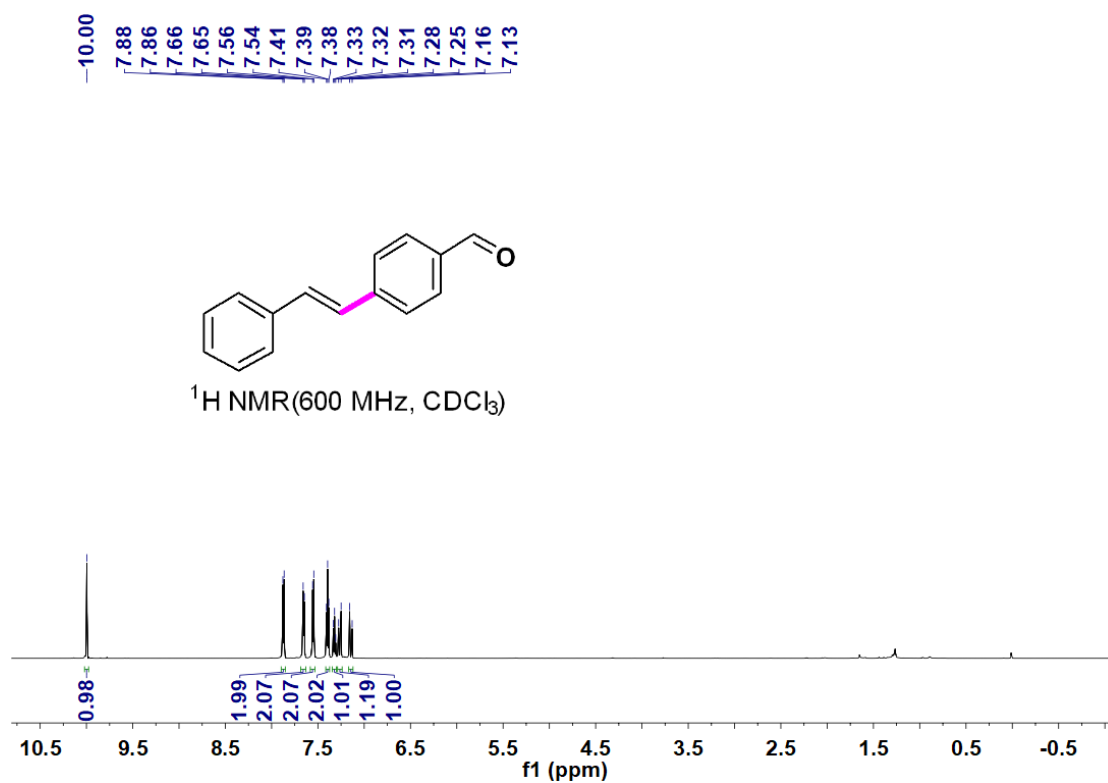


Supplementary Figure 107. Characterization of compound 10a. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound 10a in CDCl_3 .

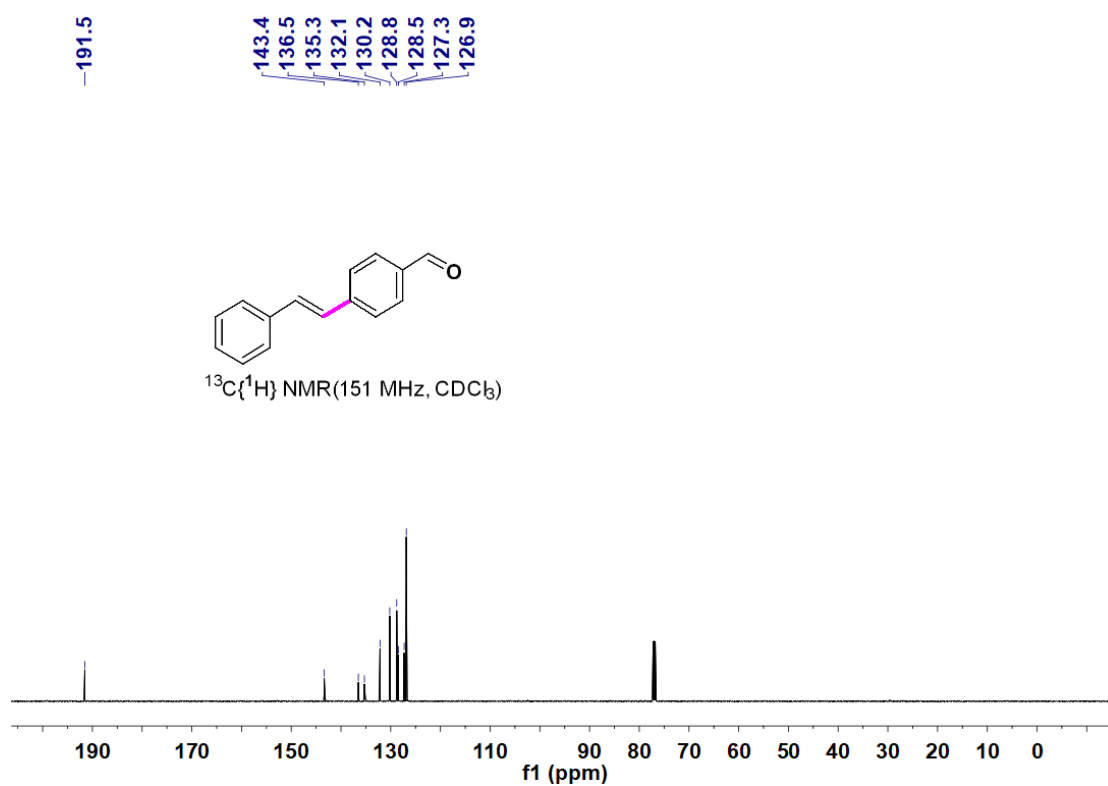
(E)-4-styrylbenzaldehyde (11a)



Under N_2 atmosphere, the $\text{Pd}(\text{PPh}_3)_4$ (11.6 mg, 5.0 mol%), **E-4a** compound (46.0 mg, 0.2 mmol), Cs_2CO_3 (391.0 mg, 1.2 mmol), 4-bromobenzaldehyde (37.0 mg, 0.2 mmol) and the 4.0 mL THF solvent were added into 25 mL Schlenk tube to react at 60 °C overnight. The reactions were monitored by TLC. When **E-4a** compound was consumed, the reaction was cooled to room temperature, then quenched and concentrated. The crude products were then purified by column chromatography (PE-EA, v/v 20/1) to give the target products as a white solid with an overall isolated yield: 93% (38.7 mg). ^1H NMR (600 MHz, CDCl_3) δ 10.00 (s, 1H), 7.87 (d, J = 8.1 Hz, 2H), 7.65 (d, J = 7.9 Hz, 2H), 7.55 (d, J = 7.5 Hz, 2H), 7.39 (t, J = 7.6 Hz, 2H), 7.32 (t, J = 7.3 Hz, 1H), 7.26 (d, J = 16.3 Hz, 1H), 7.14 (d, J = 16.3 Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 191.5, 143.4, 136.5, 135.3, 132.2, 130.2, 128.8, 128.5, 127.3, 126.9.



Supplementary Figure 108. Characterization of compound 11a. ^1H NMR spectrum of compound 11a in CDCl_3 .



Supplementary Figure 109. Characterization of compound 11a. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound 11a in CDCl_3 .

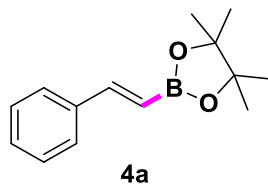
Tables of Crystal Data and Structure Refinements

Supplementary Table 4. Crystal datum and structure refinements for **Cu₄NC** and **Cu₈NC**.

	Cu₄NC	Cu₈NC
Empirical formula	C ₁₆ H ₂₀ Cu ₄ N ₈ S ₄	C ₃₂ H ₅₆ Cu ₈ N ₈ S ₈
Formula weight	706.80	3717.21
Temperature/K	200	200
Crystal system	tetragonal	monoclinic
Space group	<i>P</i> 4 ₂ /n	<i>C</i> 2/c
<i>a</i>/Å	10.01930(10)	15.47190(10)
<i>b</i>/Å	10.01930(10)	21.4708(2)
<i>c</i>/Å	11.6512(2)	14.65210(10)
<i>α</i>/°	90	90
<i>β</i>/°	90	90.3710(10)
<i>γ</i>/°	90	90
Volume/Å³	1169.62(3)	4867.24(6)
<i>Z</i>	2	4
<i>ρ</i>_{calc}/cm³	2.007	1.798
<i>μ</i>/mm⁻¹	7.626	7.217
<i>F</i>(000)	704.0	2656.0
Crystal size/mm³	0.13 × 0.12 × 0.1	0.08 × 0.07 × 0.06
Radiation	CuKα (<i>λ</i> = 1.54184 Å)	CuKα (<i>λ</i> = 1.54184 Å)
2θ range for data collection/°	11.648 to 147.848	7.042 to 147.194
Index ranges	-6 ≤ <i>h</i> ≤ 11, -11 ≤ <i>k</i> ≤ 12, -7 ≤ <i>l</i> ≤ 14	-18 ≤ <i>h</i> ≤ 17, -22 ≤ <i>k</i> ≤ 26, -17 ≤ <i>l</i> ≤ 18
Reflections collected	2629	12406
Independent reflections	1144 [<i>R</i> _{int} = 0.0166, <i>R</i> _{sigma} = 0.0218]	4687 [<i>R</i> _{int} = 0.0228, <i>R</i> _{sigma} = 0.0237]
Data/restraints/parameters	1144/0/74	4687/63/292
Goodness-of-fit on <i>F</i>²	1.070	1.041
Final <i>R</i> indexes [<i>I</i> ≥ 2σ(<i>I</i>)]	<i>R</i> _I = 0.0331, <i>wR</i> ₂ = 0.0946	<i>R</i> _I = 0.0293, <i>wR</i> ₂ = 0.0800
CCDC number	2330281	2330282

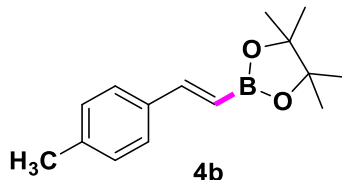
Compounds Characterization

(E)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (**4a**)⁽²⁸⁾



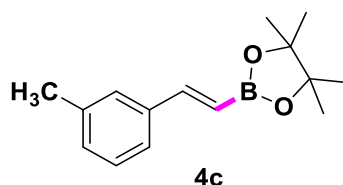
Prepared according to general procedure (B), under air atmosphere, phenylacetylene **1a** (21.0 mg, 0.2 mmol, 1.0 eq), B₂Pin₂ **2** (111.8 mg, 0.44 mmol, 2.2 equiv.), microcrystalline Cu₄NC catalysts (2.8 mg, 2.0 mol%), K₂CO₃ (60.7 mg, 0.44 mmol, 2.2 equiv.) and the mixture solvent (2.0 mL, MeCN-H₂O, v/v 4/1) were added into a tube. The reaction mixture was stirred at room temperature for 1 h. The reactions were monitored by TLC (PE-EA, v/v 10/1). When alkynes were consumed, the reactions were quenched and concentrated. The crude product was then purified by column chromatography (PE-EA, v/v 20/1) to give the target product **4a** as a colorless oil with an overall isolated yield: 97% (44.6 mg). ¹H NMR (600 MHz, CDCl₃) δ 7.49 (d, *J* = 7.2 Hz, 2H), 7.40 (d, *J* = 18.4 Hz, 1H), 7.34 (t, *J* = 7.4 Hz, 2H), 7.29 (ddd, *J* = 7.3, 3.6, 1.2 Hz, 1H), 6.17 (d, *J* = 18.4 Hz, 1H), 1.32 (s, 12H). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 149.5, 137.5, 128.9, 128.5, 127.0, 83.3, 24.8. The carbon signal attached to B was not observed due to low intensity.

(E)-4,4,5,5-tetramethyl-2-(4-methylstyryl)-1,3,2-dioxaborolane (**4b**)⁽²⁸⁾



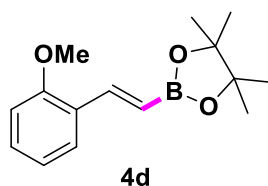
Prepared according to general procedure (B), under air atmosphere, 4-ethynyltoluene **1b** (23.2 mg, 0.2 mmol, 1.0 eq), B₂Pin₂ **2** (111.8 mg, 0.44 mmol, 2.2 equiv.), microcrystalline Cu₄NC catalysts (2.8 mg, 2.0 mol%), K₂CO₃ (60.7 mg, 0.44 mmol, 2.2 equiv.) and the mixture solvent (2.0 mL, MeCN-H₂O, v/v 4/1) were added into a tube. The reaction mixture was stirred at room temperature for 1 h. The reactions were monitored by TLC (PE-EA, v/v 10/1). When alkynes were consumed, the reactions were quenched and concentrated. The crude product was then purified by column chromatography (PE-EA, v/v 20/1) to give the target product **4b** as a colorless oil with an overall isolated yield: 92% (44.8 mg). ¹H NMR (600 MHz, CDCl₃) δ 7.38 (dd, *J* = 13.3, 7.1 Hz, 3H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.11 (d, *J* = 18.4 Hz, 1H), 2.34 (s, 3H), 1.31 (s, 12H). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 149.5, 138.9, 134.8, 129.3, 127.0, 83.3, 24.8, 21.3. The carbon signal attached to B was not observed due to low intensity.

(E)-4,4,5,5-tetramethyl-2-(3-methylstyryl)-1,3,2-dioxaborolane (4c)⁽²⁸⁾



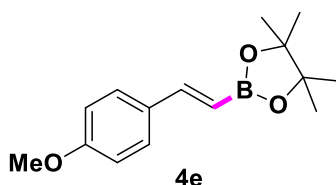
Prepared according to general procedure (B), under air atmosphere, 3-ethynyltoluene **1c** (23.2 mg, 0.2 mmol, 1.0 eq), B₂Pin₂ **2** (111.8 mg, 0.44 mmol, 2.2 equiv.), microcrystalline Cu₄NC catalysts (2.8 mg, 2.0 mol%), K₂CO₃ (60.7 mg, 0.44 mmol, 2.2 equiv.) and the mixture solvent (2.0 mL, MeCN-H₂O, v/v 4/1) were added into a tube. The reaction mixture was stirred at room temperature for 1 h. The reactions were monitored by TLC (PE-EA, v/v 10/1). When alkynes were consumed, the reactions were quenched and concentrated. The crude product was then purified by column chromatography (PE-EA, v/v 20/1) to give the target product **4c** as a colorless oil with an overall isolated yield: 93% (45.3 mg). ¹H NMR (600 MHz, CDCl₃) δ 7.37 (d, *J* = 18.4 Hz, 1H), 7.29 (d, *J* = 6.9 Hz, 2H), 7.22 (t, *J* = 7.9 Hz, 1H), 7.11 (d, *J* = 7.5 Hz, 1H), 6.15 (d, *J* = 18.4 Hz, 1H), 2.35 (s, 3H), 1.31 (s, 12H). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 149.7, 138.1, 137.5, 129.7, 128.4, 127.8, 124.2, 83.3, 24.8, 21.4. The carbon signal attached to B was not observed due to low intensity.

(E)-2-(2-methoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4d)⁽²⁶⁾



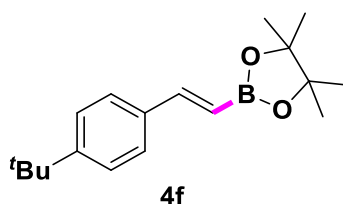
Prepared according to general procedure (B), under air atmosphere, 1-ethynyl-2-methoxybenzene **1d** (26.4 mg, 0.2 mmol, 1.0 eq), B₂Pin₂ **2** (111.8 mg, 0.44 mmol, 2.2 equiv.), microcrystalline Cu₄NC catalysts (2.8 mg, 2.0 mol%), K₂CO₃ (60.7 mg, 0.44 mmol, 2.2 equiv.) and the mixture solvent (2.0 mL, MeCN-H₂O, v/v 4/1) were added into a tube. The reaction mixture was stirred at room temperature for 2 h. The reactions were monitored by TLC (PE-EA, v/v 20/1). When alkynes were consumed, the reactions were quenched and concentrated. The crude product was then purified by column chromatography (PE-EA, v/v 40/1) to give the target product **4d** as a colorless oil with an overall isolated yield: 90% (46.7 mg). ¹H NMR (600 MHz, CDCl₃) δ 7.77 (d, *J* = 18.6 Hz, 1H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.29 – 7.24 (m, 1H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 8.3 Hz, 1H), 6.18 (d, *J* = 18.6 Hz, 1H), 3.85 (s, 3H), 1.31 (s, 12H). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 157.3, 144.1, 129.9, 127.1, 126.6, 120.6, 110.9, 83.2, 55.4, 24.8. The carbon signal attached to B was not observed due to low intensity.

(E)-2-(4-methoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4e)⁽²²⁾



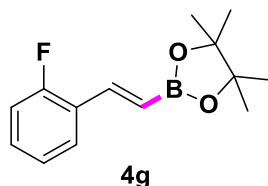
Prepared according to general procedure (B), under air atmosphere, 1-ethynyl-4-methoxybenzene **1e** (26.4 mg, 0.2 mmol, 1.0 eq), B₂Pin₂ **2** (111.8 mg, 0.44 mmol, 2.2 equiv.), microcrystalline Cu₄NC catalysts (2.8 mg, 2.0 mol%), K₂CO₃ (60.7 mg, 0.44 mmol, 2.2 equiv.) and the mixture solvent (2.0 mL, MeCN-H₂O, v/v 4/1) were added into a tube. The reaction mixture was stirred at room temperature for 2 h. The reactions were monitored by TLC (PE-EA, v/v 20/1). When alkynes were consumed, the reactions were quenched and concentrated. The crude product was then purified by column chromatography (PE-EA, v/v 40/1) to give the target product **4e** as a colorless oil with an overall isolated yield: 93% (48.3 mg). ¹H NMR (600 MHz, CDCl₃) δ 7.43 (d, *J* = 8.6 Hz, 2H), 7.35 (d, *J* = 18.4 Hz, 1H), 6.86 (d, *J* = 8.6 Hz, 2H), 6.01 (d, *J* = 18.4 Hz, 1H), 3.81 (s, 3H), 1.31 (s, 12H). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 160.3, 149.1, 130.4, 128.5, 114.0, 83.2, 55.3, 24.8. The carbon signal attached to B was not observed due to low intensity.

(E)-2-(4-(tert-butyl)styryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4f)⁽²⁴⁾



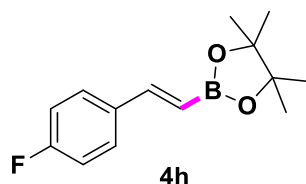
Prepared according to general procedure (B), under air atmosphere, 1-(*tert*-butyl)-4-ethynylbenzene **1f** (31.6 mg, 0.2 mmol, 1.0 eq), B₂Pin₂ **2** (111.8 mg, 0.44 mmol, 2.2 equiv.), microcrystalline Cu₄NC catalysts (2.8 mg, 2.0 mol%), K₂CO₃ (60.7 mg, 0.44 mmol, 2.2 equiv.) and the mixture solvent (2.0 mL, MeCN-H₂O, v/v 4/1) were added into a tube. The reaction mixture was stirred at room temperature for 1 h. The reactions were monitored by TLC (PE-EA, v/v 20/1). When alkynes were consumed, the reactions were quenched and concentrated. The crude product was then purified by column chromatography (PE-EA, v/v 40/1) to give the target product **4f** as a white solid with an overall isolated yield: 92% (52.5 mg). ¹H NMR (600 MHz, CDCl₃) δ 7.45 – 7.34 (m, 5H), 6.12 (d, *J* = 18.4 Hz, 1H), 1.31 (s, 21H). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 152.1, 149.4, 134.8, 126.8, 125.5, 83.3, 34.7, 31.2, 24.8. The carbon signal attached to B was not observed due to low intensity.

(E)-2-(2-fluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4g)⁽²⁶⁾



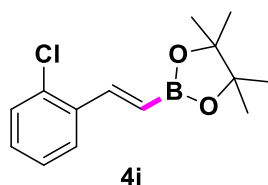
Prepared according to general procedure (B), under air atmosphere, 1-ethynyl-2-fluorobenzene **1g** (24.0 mg, 0.2 mmol, 1.0 eq), B₂Pin₂ **2** (111.8 mg, 0.44 mmol, 2.2 equiv.), microcrystalline Cu₄NC catalysts (2.8 mg, 2.0 mol%), K₂CO₃ (60.7 mg, 0.44 mmol, 2.2 equiv.) and the mixture solvent (2.0 mL, MeCN-H₂O, v/v 4/1) were added into a tube. The reaction mixture was stirred at room temperature for 1 h. The reactions were monitored by TLC (PE-EA, v/v 10/1). When alkynes were consumed, the reactions were quenched and concentrated. The crude product was then purified by column chromatography (PE-EA, v/v 20/1) to give the target product **4g** as a colorless oil with an overall isolated yield: 93% (46.0 mg). ¹H NMR (600 MHz, CDCl₃) δ 7.61 – 7.54 (m, 2H), 7.28 – 7.23 (m, 1H), 7.11 (t, *J* = 7.3 Hz, 1H), 7.03 (ddd, *J* = 10.5, 8.3, 0.9 Hz, 1H), 6.24 (d, *J* = 18.6 Hz, 1H), 1.31 (s, 12H). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 160.7 (d, *J* = 251.6 Hz), 141.3 (d, *J* = 4.0 Hz), 130.2 (d, *J* = 8.5 Hz), 127.4 (d, *J* = 3.4 Hz), 125.4, 124.1 (d, *J* = 3.5 Hz), 115.8 (d, *J* = 22.1 Hz), 83.5, 24.8. ¹⁹F NMR (565 MHz, CDCl₃) δ -117.65. The carbon signal attached to B was not observed due to low intensity.

(E)-2-(4-fluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4h)⁽²⁷⁾



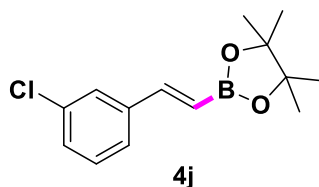
Prepared according to general procedure (B), under air atmosphere, 1-ethynyl-4-fluorobenzene **1h** (24.0 mg, 0.2 mmol, 1.0 eq), B₂Pin₂ **2** (111.8 mg, 0.44 mmol, 2.2 equiv.), microcrystalline Cu₄NC catalysts (2.8 mg, 2.0 mol%), K₂CO₃ (60.7 mg, 0.44 mmol, 2.2 equiv.) and the mixture solvent (2.0 mL, MeCN-H₂O, v/v 4/1) were added into a tube. The reaction mixture was stirred at room temperature for 1 h. The reactions were monitored by TLC (PE-EA, v/v 10/1). When alkynes were consumed, the reactions were quenched and concentrated. The crude product was then purified by column chromatography (PE-EA, v/v 20/1) to give the target product **4h** as a colorless oil with an overall isolated yield: 92% (45.5 mg). ¹H NMR (600 MHz, CDCl₃) δ 7.49 – 7.43 (m, 2H), 7.35 (d, *J* = 18.4 Hz, 1H), 7.02 (dd, *J* = 12.1, 5.3 Hz, 2H), 6.07 (d, *J* = 18.4 Hz, 1H), 1.31 (s, 12H). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 163.1 (d, *J* = 248.6 Hz), 148.2, 133.7 (d, *J* = 3.1 Hz), 128.7 (d, *J* = 8.3 Hz), 115.5 (d, *J* = 21.8 Hz), 83.4, 24.8. ¹⁹F NMR (565 MHz, CDCl₃) δ -112.40. The carbon signal attached to B was not observed due to low intensity.

(E)-2-(2-chlorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4i)⁽²⁸⁾



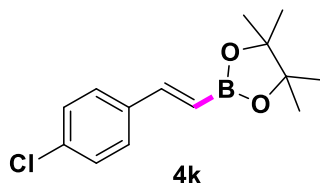
Prepared according to general procedure (B), under air atmosphere, 1-chloro-2-ethynylbenzene **1i** (27.3 mg, 0.2 mmol, 1.0 eq), B₂Pin₂ **2** (111.8 mg, 0.44 mmol, 2.2 equiv.), microcrystalline Cu₄NC catalysts (2.8 mg, 2.0 mol%), K₂CO₃ (60.7 mg, 0.44 mmol, 2.2 equiv.) and the mixture solvent (2.0 mL, MeCN-H₂O, v/v 4/1) were added into a tube. The reaction mixture was stirred at room temperature for 1 h. The reactions were monitored by TLC (PE-EA, v/v 10/1). When alkynes were consumed, the reactions were quenched and concentrated. The crude product was then purified by column chromatography (PE-EA, v/v 20/1) to give the target product **4i** as a colorless oil with an overall isolated yield: 95% (50.0 mg). ¹H NMR (600 MHz, CDCl₃) δ 7.78 (d, *J* = 18.3 Hz, 1H), 7.63 (dd, *J* = 7.4, 2.0 Hz, 1H), 7.35 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.23 (pd, *J* = 7.3, 1.7 Hz, 2H), 6.17 (d, *J* = 18.3 Hz, 1H), 1.32 (s, 12H). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 145.0, 135.6, 133.9, 129.8, 129.6, 127.0, 126.8, 83.5, 24.8. The carbon signal attached to B was not observed due to low intensity.

(E)-2-(3-chlorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4j)⁽²⁸⁾



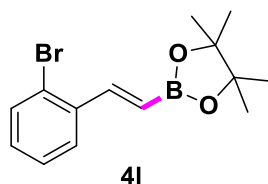
Prepared according to general procedure (B), under air atmosphere, 3-chloro-2-ethynylbenzene **1j** (27.3 mg, 0.2 mmol, 1.0 eq), B₂Pin₂ **2** (111.8 mg, 0.44 mmol, 2.2 equiv.), microcrystalline Cu₄NC catalysts (2.8 mg, 2.0 mol%), K₂CO₃ (60.7 mg, 0.44 mmol, 2.2 equiv.) and the mixture solvent (2.0 mL, MeCN-H₂O, v/v 4/1) were added into a tube. The reaction mixture was stirred at room temperature for 1 h. The reactions were monitored by TLC (PE-EA, v/v 10/1). When alkynes were consumed, the reactions were quenched and concentrated. The crude product was then purified by column chromatography (PE-EA, v/v 20/1) to give the target product **4j** as a colorless oil with an overall isolated yield: 98% (51.5 mg). ¹H NMR (600 MHz, CDCl₃) δ 7.45 (s, 1H), 7.37 – 7.29 (m, 2H), 7.28 – 7.25 (m, 2H), 6.17 (d, *J* = 18.4 Hz, 1H), 1.31 (s, 12H). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 147.8, 139.4, 134.6, 129.8, 128.7, 126.9, 125.2, 83.5, 24.8. The carbon signal attached to B was not observed due to low intensity.

(E)-2-(4-chlorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4k)⁽²⁸⁾



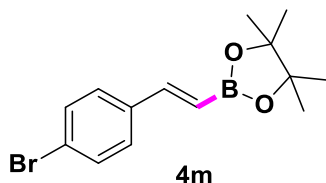
Prepared according to general procedure (B), under air atmosphere, 4-chloro-2-ethynylbenzene **1k** (27.3 mg, 0.2 mmol, 1.0 eq), B₂Pin₂ **2** (111.8 mg, 0.44 mmol, 2.2 equiv.), microcrystalline Cu₄NC catalysts (2.8 mg, 2.0 mol%), K₂CO₃ (60.7 mg, 0.44 mmol, 2.2 equiv.) and the mixture solvent (2.0 mL, MeCN-H₂O, v/v 4/1) were added into a tube. The reaction mixture was stirred at room temperature for 1 h. The reactions were monitored by TLC (PE-EA, v/v 20/1). When alkynes were consumed, the reactions were quenched and concentrated. The crude product was then purified by column chromatography (PE-EA, v/v 40/1) to give the target product **4k** as a white solid with an overall isolated yield: 99% (52.1 mg). ¹H NMR (600 MHz, CDCl₃) δ 7.41 (d, *J* = 8.5 Hz, 2H), 7.32 (dd, *J* = 19.5, 13.5 Hz, 3H), 6.13 (d, *J* = 18.4 Hz, 1H), 1.31 (s, 12H). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 148.0, 136.0, 134.6, 128.8, 128.2, 83.4, 24.8. The carbon signal attached to B was not observed due to low intensity.

(E)-2-(2-bromostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4l)⁽²³⁾



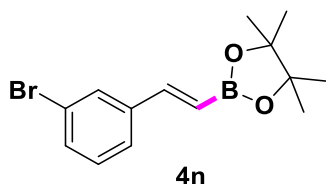
Prepared according to general procedure (B), under air atmosphere, 1-bromo-2-ethynylbenzene **1l** (36.2 mg, 0.2 mmol, 1.0 eq), B₂Pin₂ **2** (111.8 mg, 0.44 mmol, 2.2 equiv.), microcrystalline Cu₄NC catalysts (2.8 mg, 2.0 mol%), K₂CO₃ (60.7 mg, 0.44 mmol, 2.2 equiv.) and the mixture solvent (2.0 mL, MeCN-H₂O, v/v 4/1) were added into a tube. The reaction mixture was stirred at room temperature for 1 h. The reactions were monitored by TLC (PE-EA, v/v 20/1). When alkynes were consumed, the reactions were quenched and concentrated. The crude product was then purified by column chromatography (PE-EA, v/v 40/1) to give the target product **4l** as a pale-yellow oil with an overall isolated yield: 95% (58.6 mg). ¹H NMR (600 MHz, CDCl₃) δ 7.71 (d, *J* = 18.3 Hz, 1H), 7.61 (s, 1H), 7.55 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.29 (dd, *J* = 11.3, 3.9 Hz, 1H), 7.14 (td, *J* = 7.9, 1.6 Hz, 1H), 6.12 (d, *J* = 18.2 Hz, 1H), 1.32 (s, 12H). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 147.5, 137.4, 133.0, 129.9, 127.5, 127.3, 124.3, 83.5, 24.8. The carbon signal attached to B was not observed due to low intensity.

(E)-2-(4-bromostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4m)⁽²⁸⁾



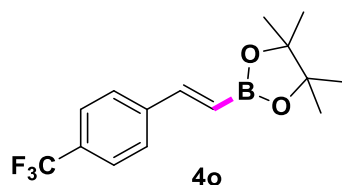
Prepared according to general procedure (B), under air atmosphere, 4-bromo-2-ethynylbenzene **1m** (36.2 mg, 0.2 mmol, 1.0 eq), B₂Pin₂ **2** (111.8 mg, 0.44 mmol, 2.2 equiv.), microcrystalline Cu₄NC catalysts (2.8 mg, 2.0 mol%), K₂CO₃ (60.7 mg, 0.44 mmol, 2.2 equiv.) and the mixture solvent (2.0 mL, MeCN-H₂O, v/v 4/1) were added into a tube. The reaction mixture was stirred at room temperature for 1 h. The reactions were monitored by TLC (PE-EA, v/v 20/1). When alkynes were consumed, the reactions were quenched and concentrated. The crude product was then purified by column chromatography (PE-EA, v/v 40/1) to give the target product **4m** as a white solid with an overall isolated yield: 96% (59.0 mg). ¹H NMR (600 MHz, CDCl₃) δ 7.46 (d, *J* = 8.4 Hz, 2H), 7.33 (t, *J* = 13.8 Hz, 3H), 6.15 (d, *J* = 18.4 Hz, 1H), 1.31 (s, 12H). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 148.1, 136.4, 131.7, 128.5, 122.9, 83.5, 24.8. The carbon signal attached to B was not observed due to low intensity.

(E)-2-(3-bromostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4n)⁽²³⁾



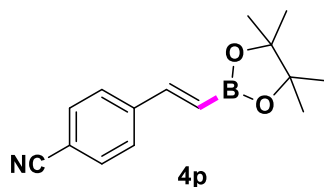
Prepared according to general procedure (B), under air atmosphere, 3-bromo-2-ethynylbenzene **1n** (36.2 mg, 0.2 mmol, 1.0 eq), B₂Pin₂ **2** (111.8 mg, 0.44 mmol, 2.2 equiv.), microcrystalline Cu₄NC catalysts (2.8 mg, 2.0 mol%), K₂CO₃ (60.7 mg, 0.44 mmol, 2.2 equiv.) and the mixture solvent (2.0 mL, MeCN-H₂O, v/v 4/1) were added into a tube. The reaction mixture was stirred at room temperature for 1 h. The reactions were monitored by TLC (PE-EA, v/v 10/1). When alkynes were consumed, the reactions were quenched and concentrated. The crude product was then purified by column chromatography (PE-EA, v/v 20/1) to give the target product **4n** as a colorless oil with an overall isolated yield: 94% (57.7 mg). ¹H NMR (600 MHz, CDCl₃) δ 7.61 (t, *J* = 1.7 Hz, 1H), 7.43 – 7.37 (m, 2H), 7.30 (d, *J* = 18.4 Hz, 1H), 7.20 (t, *J* = 7.8 Hz, 1H), 6.15 (d, *J* = 18.4 Hz, 1H), 1.31 (s, 12H). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 147.7, 139.6, 131.6, 130.1, 129.9, 125.6, 122.8, 83.5, 24.8. The carbon signal attached to B was not observed due to low intensity.

(E)-4,4,5,5-tetramethyl-2-(4-(trifluoromethyl)styryl)-1,3,2-dioxaborolane (4o)⁽²²⁾



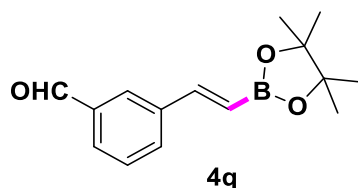
Prepared according to general procedure (B), under air atmosphere, 1-ethynyl-4-(trifluoromethyl) benzene **1o** (34.0 mg, 0.2 mmol, 1.0 eq), B₂Pin₂ **2** (111.8 mg, 0.44 mmol, 2.2 equiv.), microcrystalline Cu₄NC catalysts (2.8 mg, 2.0 mol%), K₂CO₃ (60.7 mg, 0.44 mmol, 2.2 equiv.) and the mixture solvent (2.0 mL, MeCN-H₂O, v/v 4/1) were added into a tube. The reaction mixture was stirred at room temperature for 1 h. The reactions were monitored by TLC (PE-EA, v/v 10/1). When alkynes were consumed, the reactions were quenched and concentrated. The crude product was then purified by column chromatography (PE-EA, v/v 20/1) to give the target product **4o** as a colorless oil with an overall isolated yield: 96% (57.3 mg). ¹H NMR (600 MHz, CDCl₃) δ 7.58 (q, *J* = 8.6 Hz, 4H), 7.40 (d, *J* = 18.4 Hz, 1H), 6.26 (d, *J* = 18.4 Hz, 1H), 1.32 (s, 12H). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 147.7, 140.8, 130.5 (d, *J* = 32.3 Hz), 127.1, 125.6 (q, *J* = 3.8 Hz), 83.6, 24.8. ¹⁹F NMR (565 MHz, CDCl₃) δ -62.64. The carbon signal attached to B was not observed due to low intensity.

(E)-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzonitrile (4p)⁽²³⁾



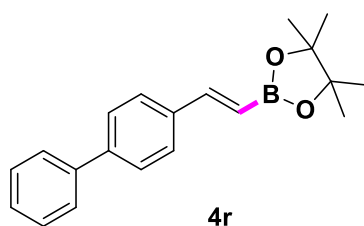
Prepared according to general procedure (B), under air atmosphere, 4-ethynylbenzonitrile **1p** (25.4 mg, 0.2 mmol, 1.0 eq), B₂Pin₂ **2** (111.8 mg, 0.44 mmol, 2.2 equiv.), microcrystalline Cu₄NC catalysts (2.8 mg, 2.0 mol%), K₂CO₃ (60.7 mg, 0.44 mmol, 2.2 equiv.) and the mixture solvent (2.0 mL, MeCN-H₂O, v/v 4/1) were added into a tube. The reaction mixture was stirred at room temperature for 1 h. The reactions were monitored by TLC (PE-EA, v/v 10/1). When alkynes were consumed, the reactions were quenched and concentrated. The crude product was then purified by column chromatography (PE-EA, v/v 1/0) to give the target product **4p** as a white solid with an overall isolated yield: 92% (46.7 mg). ¹H NMR (600 MHz, CDCl₃) δ 7.61 (d, *J* = 8.1 Hz, 2H), 7.54 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 18.4 Hz, 1H), 6.27 (d, *J* = 18.4 Hz, 1H), 1.31 (s, 12H). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 147.1, 141.6, 132.4, 127.4, 118.7, 112.0, 83.7, 24.8. The carbon signal attached to B was not observed due to low intensity.

(E)-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzaldehyde (4q)



Prepared according to general procedure (B), under air atmosphere, 3-ethynylbenzaldehyde **1q** (26.0 mg, 0.2 mmol, 1.0 eq), B₂Pin₂ **2** (111.8 mg, 0.44 mmol, 2.2 equiv.), microcrystalline Cu₄NC catalysts (2.8 mg, 2.0 mol%), K₂CO₃ (60.7 mg, 0.44 mmol, 2.2 equiv.) and the mixture solvent (2.0 mL, MeCN-H₂O, v/v 4/1) were added into a tube. The reaction mixture was stirred at room temperature for 1 h. The reactions were monitored by TLC (PE-EA, v/v 20/1). When alkynes were consumed, the reactions were quenched and concentrated. The crude product was then purified by column chromatography (PE-EA, v/v 40/1) to give the target product **4q** was purified by flash chromatography (PE-EA, v/v 40/1) as a colorless oil with an overall isolated yield: 90% (46.5 mg). ¹H NMR (600 MHz, CDCl₃) δ 10.02 (s, 1H), 7.97 (s, 1H), 7.81 (d, *J* = 7.5 Hz, 1H), 7.73 (d, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.43 (d, *J* = 18.4 Hz, 1H), 6.26 (d, *J* = 18.4 Hz, 1H), 1.31 (d, *J* = 7.2 Hz, 12H). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 192.1, 147.7, 138.5, 136.8, 132.6, 129.6, 129.3, 128.3, 83.6, 24.8. ¹¹B{¹H} NMR (193 MHz, CDCl₃) δ 30.64. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₁₅H₂₀BO₃⁺ 259.1500; found 259.1471. The carbon signal attached to B was not observed due to low intensity.

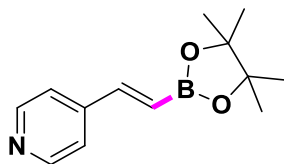
(E)-2-(2-([1,1'-biphenyl]-4-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4r)⁽²²⁾



Prepared according to general procedure (B), under air atmosphere, 4-ethynyl-1,1'-biphenyl **1r** (35.6 mg, 0.2 mmol, 1.0 eq), B₂Pin₂ **2** (111.8 mg, 0.44 mmol, 2.2 equiv.), microcrystalline Cu₄NC catalysts (2.8 mg, 2.0 mol%), K₂CO₃ (60.7 mg, 0.44 mmol, 2.2 equiv.) and the mixture solvent (2.0 mL, MeCN-H₂O, v/v 4/1) were added into a tube. The reaction mixture was stirred at room temperature for 1 h. The reactions were monitored by TLC (PE-EA, v/v 20/1). When alkynes were consumed, the reactions were quenched and concentrated. The crude product was then purified by column chromatography (PE-EA, v/v 40/1) to give the target product **4r** as a pale-yellow solid with an overall isolated yield: 99% (60.4 mg). ¹H NMR (600 MHz, CDCl₃) δ 7.59 (dt, *J* = 12.9, 7.9 Hz, 6H), 7.47 – 7.42 (m, 3H), 7.35 (t, *J* = 7.4 Hz, 1H), 6.21 (dd, *J* = 18.4, 1.2 Hz, 1H), 1.33 (s, 12H). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 149.0, 141.6, 140.6,

136.5, 128.8, 127.5, 127.4, 127.3, 127.0, 83.4, 24.8. The carbon signal attached to B was not observed due to low intensity.

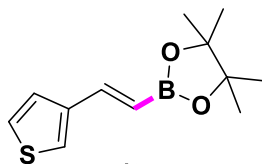
(E)-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)pyridine (4s)⁽²¹⁾



4s

Prepared according to general procedure (B), under air atmosphere, 4-ethynylpyridine **1s** (20.6 mg, 0.2 mmol, 1.0 eq), B₂Pin₂ **2** (111.8 mg, 0.44 mmol, 2.2 equiv.), microcrystalline Cu₄NC catalysts (2.8 mg, 2.0 mol%), K₂CO₃ (60.7 mg, 0.44 mmol, 2.2 equiv.) and the mixture solvent (2.0 mL, MeCN-H₂O, v/v 4/1) were added into a tube. The reaction mixture was stirred at room temperature for 1 h. The reactions were monitored by TLC (DCM-EA, v/v 3/1). When alkynes were consumed, the reactions were quenched and concentrated. The crude product was then purified by column chromatography (DCM-EA, v/v 5/1) to give the target product **4s** as a pale-yellow solid with an overall isolated yield: 86% (39.8 mg). ¹H NMR (600 MHz, CDCl₃) δ 8.59 (d, *J* = 4.4 Hz, 2H), 7.36 – 7.27 (m, 3H), 6.38 (d, *J* = 18.4 Hz, 1H), 1.32 (s, 12H). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 150.0, 146.5, 144.8, 121.2, 83.8, 24.8. The carbon signal attached to B was not observed due to low intensity.

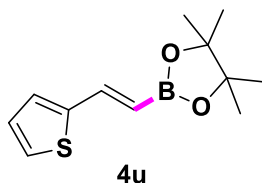
(E)-4,4,5,5-tetramethyl-2-(2-(thiophen-3-yl)vinyl)-1,3,2-dioxaborolane (4t)⁽²⁴⁾



4t

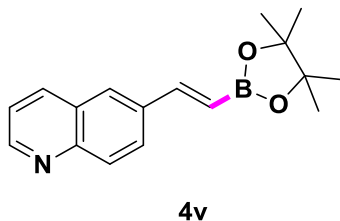
Prepared according to general procedure (B), under air atmosphere, 3-ethynylthiophene **1t** (21.6 mg, 0.2 mmol, 1.0 eq), B₂Pin₂ **2** (111.8 mg, 0.44 mmol, 2.2 equiv.), microcrystalline Cu₄NC catalysts (2.8 mg, 2.0 mol%), K₂CO₃ (60.7 mg, 0.44 mmol, 2.2 equiv.) and the mixture solvent (2.0 mL, MeCN-H₂O, v/v 4/1) were added into a tube. The reaction mixture was stirred at room temperature for 1 h. The reactions were monitored by TLC (PE-EA, v/v 20/1). When alkynes were consumed, the reactions were quenched and concentrated. The crude product was then purified by column chromatography (PE-EA, v/v 40/1) to give the target product **4t** as a colorless oil with an overall isolated yield: 95% (44.7 mg). ¹H NMR (600 MHz, CDCl₃) δ 7.38 (d, *J* = 18.4 Hz, 1H), 7.32 – 7.25 (m, 3H), 5.94 (d, *J* = 18.3 Hz, 1H), 1.30 (s, 12H). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 143.1, 141.2, 126.1, 125.0, 124.8, 83.3, 24.8. The carbon signal attached to B was not observed due to low intensity.

(E)-4,4,5,5-tetramethyl-2-(2-(thiophen-2-yl)vinyl)-1,3,2-dioxaborolane (4u)⁽²³⁾



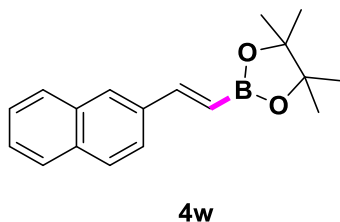
Prepared according to general procedure (B), under air atmosphere, 2-ethynylthiophene **1u** (21.6 mg, 0.2 mmol, 1.0 eq), B₂Pin₂ **2** (111.8 mg, 0.44 mmol, 2.2 equiv.), microcrystalline Cu₄NC catalysts (2.8 mg, 2.0 mol%), K₂CO₃ (60.7 mg, 0.44 mmol, 2.2 equiv.) and the mixture solvent (2.0 mL, MeCN-H₂O, v/v 4/1) were added into a tube. The reaction mixture was stirred at room temperature for 1 h. The reactions were monitored by TLC (PE-EA, v/v 20/1). When alkynes were consumed, the reactions were quenched and concentrated. The crude product was then purified by column chromatography (PE-EA, v/v 40/1) to give the target product **4u** as a yellow oil with an overall isolated yield: 97% (45.8 mg). ¹H NMR (600 MHz, CDCl₃) δ 7.47 (d, *J* = 18.0 Hz, 1H), 7.24 (d, *J* = 5.0 Hz, 1H), 7.08 (d, *J* = 3.4 Hz, 1H), 6.99 (dd, *J* = 5.0, 3.6 Hz, 1H), 5.91 (d, *J* = 18.1 Hz, 1H), 1.30 (s, 12H). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 143.9, 141.8, 127.7, 127.6, 126.3, 83.4, 24.8. The carbon signal attached to B was not observed due to low intensity.

(E)-6-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)quinoline (4v)



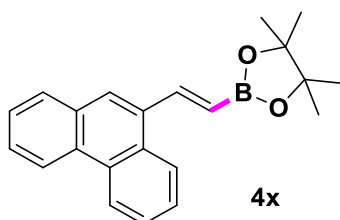
Prepared according to general procedure (B), under air atmosphere, 6-ethynylquinoline **1v** (30.6 mg, 0.2 mmol, 1.0 eq), B₂Pin₂ **2** (111.8 mg, 0.44 mmol, 2.2 equiv.), microcrystalline Cu₄NC catalysts (2.8 mg, 2.0 mol%), K₂CO₃ (60.7 mg, 0.44 mmol, 2.2 equiv.) and the mixture solvent (2.0 mL, MeCN-H₂O, v/v 4/1) were added into a tube. The reaction mixture was stirred at room temperature for 1 h. The reactions were monitored by TLC (PE-EA, v/v 1/1). When alkynes were consumed, the reactions were quenched and concentrated. The crude product was then purified by column chromatography (PE-EA, v/v 2/1) to give the target product **4v** as a colorless oil with an overall isolated yield: 96% (53.8 mg). ¹H NMR (600 MHz, CDCl₃) δ 8.89 – 8.84 (m, 1H), 8.12 (d, *J* = 7.9 Hz, 1H), 8.05 (d, *J* = 8.8 Hz, 1H), 7.91 (d, *J* = 8.8 Hz, 1H), 7.79 (s, 1H), 7.55 (d, *J* = 18.4 Hz, 1H), 7.37 (dd, *J* = 8.1, 4.2 Hz, 1H), 6.31 (d, *J* = 18.4 Hz, 1H), 1.32 (s, 12H). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 150.6, 148.6, 148.4, 136.3, 135.6, 129.8, 128.3, 127.2, 127.1, 121.4, 83.5, 24.8. ¹¹B{¹H} NMR (193 MHz, CDCl₃) δ 31.04. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₁₇H₂₁BNO₂⁺ 282.1660; found 282.1662. The carbon signal attached to B was not observed due to low intensity.

(E)-4,4,5,5-tetramethyl-2-(2-(naphthalen-2-yl)vinyl)-1,3,2-dioxaborolane (4w)⁽²³⁾



Prepared according to general procedure (B), under air atmosphere, 2-ethynynaphthalene **1w** (30.4 mg, 0.2 mmol, 1.0 eq), B₂Pin₂ **2** (111.8 mg, 0.44 mmol, 2.2 equiv.), microcrystalline Cu₄NC catalysts (2.8 mg, 2.0 mol%), K₂CO₃ (60.7 mg, 0.44 mmol, 2.2 equiv.) and the mixture solvent (2.0 mL, MeCN-H₂O, v/v 4/1) were added into a tube. The reaction mixture was stirred at room temperature for 1 h. The reactions were monitored by TLC (PE-EA, v/v 20/1). When alkynes were consumed, the reactions were quenched and concentrated. The crude product was then purified by column chromatography (PE-EA, v/v 40/1) to give the target product **4w** as a colorless oil with an overall isolated yield: 95% (53.3 mg). ¹H NMR (600 MHz, CDCl₃) δ 7.86 – 7.77 (m, 4H), 7.70 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.57 (d, *J* = 18.4 Hz, 1H), 7.50 – 7.43 (m, 2H), 6.29 (d, *J* = 18.4 Hz, 1H), 1.34 (s, 12H). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 149.5, 135.0, 133.7, 133.4, 128.4, 128.2, 128.0, 127.7, 126.4, 126.3, 123.4, 83.4, 24.8. The carbon signal attached to B was not observed due to low intensity.

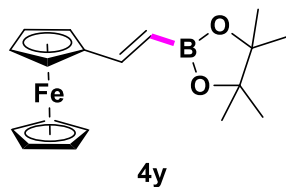
(E)-4,4,5,5-tetramethyl-2-(2-(phenanthren-9-yl)vinyl)-1,3,2-dioxaborolane (4x)⁽²⁶⁾



Prepared according to general procedure (B), under air atmosphere, 9-ethynylphenanthrene **1x** (40.4 mg, 0.2 mmol, 1.0 eq), B₂Pin₂ **2** (111.8 mg, 0.44 mmol, 2.2 equiv.), microcrystalline Cu₄NC catalysts (2.8 mg, 2.0 mol%), K₂CO₃ (60.7 mg, 0.44 mmol, 2.2 equiv.) and the mixture solvent (2.0 mL, MeCN-H₂O, v/v 4/1) were added into a tube. The reaction mixture was stirred at room temperature for 1 h. The reactions were monitored by TLC (PE-EA, v/v 20/1). When alkynes were consumed, the reactions were quenched and concentrated. The crude product was then purified by column chromatography (PE-EA, v/v 1/0) to give the target product **4x** as a yellow solid with an overall isolated yield: 80% (52.7 mg). ¹H NMR (600 MHz, CDCl₃) δ 8.72 (d, *J* = 7.9 Hz, 1H), 8.66 (d, *J* = 8.2 Hz, 1H), 8.31 – 8.28 (m, 1H), 8.21 (d, *J* = 17.9 Hz, 1H), 7.96 (s, 1H), 7.90 (d, *J* = 7.2 Hz, 1H), 7.65 (dddd, *J* = 9.5, 7.0, 3.2, 1.4 Hz, 3H), 7.61 – 7.57 (m, 1H), 6.35 (d, *J* = 18.0 Hz, 1H), 1.38 (s, 12H). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 147.2, 134.6, 131.6, 130.6, 130.3, 130.3, 129.0, 126.9, 126.7, 126.6, 126.5,

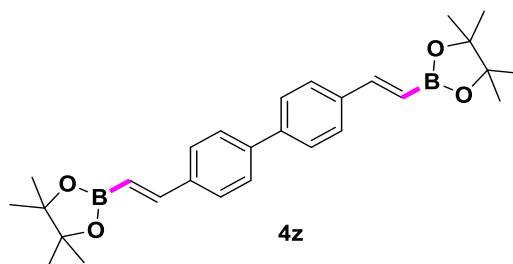
125.3, 124.7, 123.0, 122.5, 83.5, 24.9. The carbon signal attached to B was not observed due to low intensity.

(E)-4,4,5,5-tetramethyl-2-vinylferrocene-1,3,2-dioxaborolane (4y)



Prepared according to general procedure (B), under air atmosphere, ethynylferrocene **1y** (42.0 mg, 0.2 mmol, 1.0 eq), B₂Pin₂ **2** (111.8 mg, 0.44 mmol, 2.2 equiv.), microcrystalline Cu₄NC catalysts (2.8 mg, 2.0 mol%), K₂CO₃ (60.7 mg, 0.44 mmol, 2.2 equiv.) and the mixture solvent (2.0 mL, MeCN-H₂O, v/v 4/1) were added into a tube. The reaction mixture was stirred at room temperature for 2 h. The reactions were monitored by TLC (PE-EA, v/v 20/1). When alkynes were consumed, the reactions were quenched and concentrated. The crude product was then purified by column chromatography (PE-EA, v/v 1/0) to give the target product **4y** as an orange solid with an overall isolated yield: 95% (64.1 mg). ¹H NMR (600 MHz, CDCl₃) δ 7.14 (d, *J* = 18.2 Hz, 1H), 5.65 (d, *J* = 18.2 Hz, 1H), 4.38 – 4.34 (m, 2H), 4.23 – 4.19 (m, 2H), 4.03 (s, 5H), 1.23 (s, 12H). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 149.4, 83.1, 82.8, 69.6, 69.4, 67.6, 24.8. ¹¹B{¹H} NMR (193 MHz, CDCl₃) δ 30.82. HRMS(ESI) *m/z*: [M+H]⁺ calcd for C₁₈H₂₄BFeO₂⁺ 339.1213. found: 339.1229. The carbon signal attached to B was not observed due to low intensity.

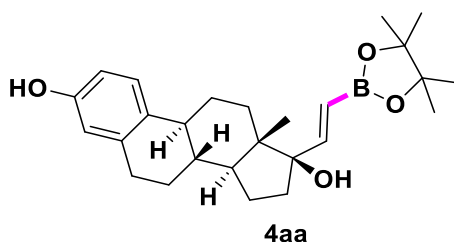
4,4'-bis((E)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)-1,1'-biphenyl (4z)



Prepared according to general procedure (G), under air atmosphere, 4,4'-diethynyl-1,1'-biphenyl **1z** (20.2 mg, 0.1 mmol, 1.0 eq), B₂Pin₂ **2** (111.8 mg, 0.44 mmol, 2.2 equiv.), microcrystalline Cu₄NC catalysts (2.8 mg, 2.0 mol%), K₂CO₃ (60.7 mg, 0.44 mmol, 2.2 equiv.) and the mixture solvent (2.0 mL, MeCN-H₂O, v/v 4/1) were added into a tube. The reaction mixture was stirred at room temperature for 1 h. The reactions were monitored by TLC (PE-EA, v/v 20/1). When alkynes were consumed, the reaction was quenched and concentrated. The crude products were then purified by column chromatography to give product **4z** as a yellow solid with an overall isolated yield: 93% (42.7 mg). ¹H NMR (600 MHz, CDCl₃) δ 7.57 (dd, *J* = 20.5, 8.3 Hz, 8H), 7.43 (d, *J* =

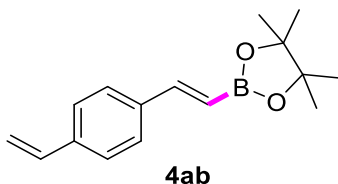
18.4 Hz, 2H), 6.21 (d, J = 18.4 Hz, 2H), 1.32 (s, 24H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 148.9, 140.9, 136.7, 127.6, 127.1, 83.4, 24.8. $^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ 31.23. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{28}\text{H}_{37}\text{B}_2\text{O}_4^+$ 459.2872; found 459.2875. The carbon signal attached to B was not observed due to low intensity.

(8R,9S,13S,14S,17R)-13-methyl-17-((E)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[*a*]phenanthrene-3,17-diol (4aa)⁽²⁵⁾



Prepared according to general procedure (B), under air atmosphere, (8R,9S,13S,14S,17R)-17-ethynyl-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[*a*]phenanthrene-3,17-diol **1aa** (59.3 mg, 0.2 mmol, 1.0 eq), B_2Pin_2 **2** (111.8 mg, 0.44 mmol, 2.2 equiv.), microcrystalline Cu_4NC catalysts (2.8 mg, 2.0 mol%), K_2CO_3 (60.7 mg, 0.44 mmol, 2.2 equiv.) and the mixture solvent (2.0 mL, $\text{MeCN-H}_2\text{O}$, v/v 4/1) were added into a tube. The reaction mixture was stirred at room temperature for 1 h. The reactions were monitored by TLC (PE-EA, v/v 2/1). When alkynes were consumed, the reactions were quenched and concentrated. The crude product was then purified by column chromatography (PE-EA, v/v 7/3) to give the target product **4aa** as a white solid with an overall isolated yield: 85% (71.9 mg). ^1H NMR (600 MHz, CDCl_3) δ 7.39 (s, 1H), 6.95 (dd, J = 17.6, 13.5 Hz, 2H), 6.63 – 6.55 (m, 2H), 5.68 (d, J = 18.2 Hz, 1H), 2.80 – 2.65 (m, 2H), 2.00 – 1.62 (m, 6H), 1.36 (d, J = 22.0 Hz, 12H), 1.21 (ddd, J = 37.8, 26.9, 16.5 Hz, 8H), 0.95 – 0.85 (m, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 158.7, 154.1, 138.3, 132.3, 125.8, 115.4, 112.0, 84.9, 84.0, 49.1, 47.1, 42.1, 38.8, 37.1, 32.2, 29.6, 27.1, 25.7, 24.8, 24.6, 23.3, 14.1. The carbon signal attached to B was not observed due to low intensity.

(E)-4,4,5,5-tetramethyl-2-(4-vinylstyryl)-1,3,2-dioxaborolane (4ab)⁽²⁰⁾



Prepared according to general procedure (B), under air atmosphere, 1-ethynyl-4-vinylbenzene **1ab** (25.6 mg, 0.2 mmol, 1.0 eq), B_2Pin_2 **2** (111.8 mg, 0.44 mmol, 2.2 equiv.), microcrystalline Cu_4NC catalysts (2.8 mg, 2.0 mol%), K_2CO_3 (60.7 mg, 0.44 mmol, 2.2 equiv.) and the mixture solvent (2.0 mL, $\text{MeCN-H}_2\text{O}$, v/v 4/1) were added into a tube. The reaction mixture was stirred at room temperature for 1 h. The reactions

were monitored by TLC (PE-EA, v/v 5/1). When alkynes were consumed, the reactions were quenched and concentrated. The crude product was then purified by column chromatography (PE-EA, v/v 10/0) to give the target product **4ab** as a yellow oil with an overall isolated yield: 95% (48.7 mg). ¹H NMR (600 MHz, CDCl₃) δ 7.45 (d, *J* = 8.2 Hz, 2H), 7.38 (dd, *J* = 13.3, 5.1 Hz, 3H), 6.70 (dd, *J* = 17.6, 10.9 Hz, 1H), 6.16 (d, *J* = 18.4 Hz, 1H), 5.76 (d, *J* = 17.6 Hz, 1H), 5.26 (d, *J* = 10.9 Hz, 1H), 1.32 (s, 12H). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 149.0, 138.1, 137.0, 136.4, 127.3, 126.4, 114.3, 83.4, 24.8.

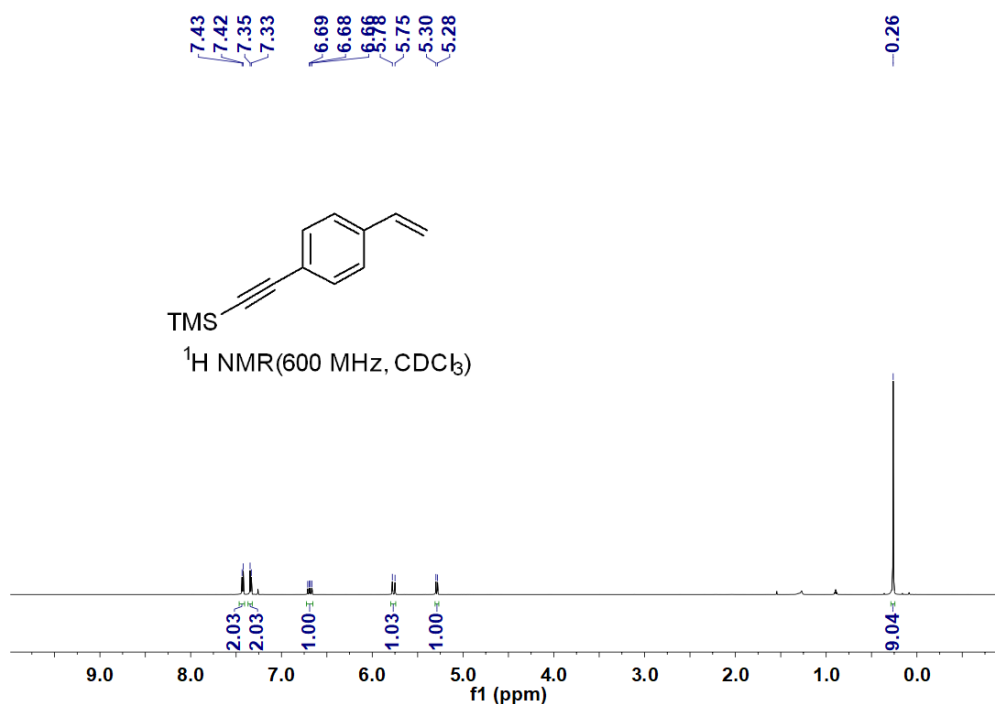
Comparison of TON and TOF

Supplementary Table 5. Comparison of TON and TOF for **microcrystalline Cu₄NC** with previous reports for the hydroboration of alkynes.

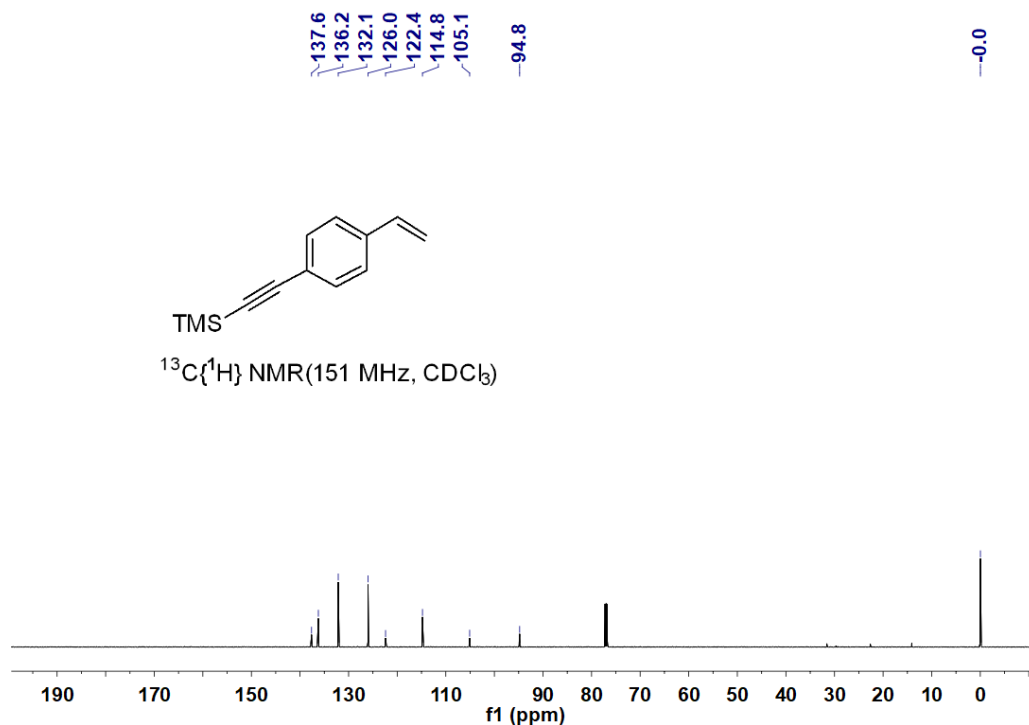
Entry	Catalyst	TON	TOF/ h ⁻¹	Condition	Reference
1	Vanadium(III) catalys	4000	----	Homogeneous, rt, N ₂ , 16h	24
2	JNM-4-Ns	41734 ^a	41734	Heterogeneous, rt, air, 20 min	29
3	Cu ₁ -O(I)/CeO ₂	198	198	Heterogeneous, 90 °C, dried, N ₂ , 1h	30
4	Co(OAc) ₂ -ligand	18.2	0.76	Homogeneous, rt, dried, N ₂ , 24h	31
5	Cu-PC-1	37.2	5.3	Homogeneous, rt, 405 nm, Ar, 7h	32
6	Cu-CuFe ₂ O ₄	190	23.75	Heterogeneous, rt, air, 8 h	33
7	MgBu ₂	12.14	0.67	Homogeneous, 80 °C, dried and N ₂ , 18h	34
8	micro copper powder	9.6	0.4	Heterogeneous, rt, Ar, 11h or 24h	35
9	Pd ₂ dba ₂ -ligand	46.5	----	Homogeneous, rt, 0.5h-2.5h	36
10	R ₃ Al·DABCO	8.9	4.45	Homogeneous, 110 °C, dried, N ₂ , 2h	37
11	(^c yAPDI)CoCH ₃	27.67	4.61	Homogeneous, rt, dried, N ₂ , 6h	38
12	[Pd(OAc) ₂] ₃ -ligand	18.6	1.55	Homogeneous, 80 °C, dried, Ar, 12h	39
13	LCuCl	23.5	1.96	Homogeneous, rt, dried, Ar, 12h	40
14	JNM-5	1182	394	Heterogeneous, rt, N ₂ , 3 h	41
15	Cu ₄₅ NC	3680	736	Heterogeneous, rt, air, 5 h	42
16	Co(acac) ₂ -ligand	198	16.5	Homogeneous, rt, N ₂ , 12h	43
17	dom-NENU-3_2	99.5	24.88	Heterogeneous, 50 °C, N ₂ , 4h	44
18	FeO/MgO	34	1.7	Heterogeneous, 160 °C, Ar, 20 h	45
19	microcrystalline Cu₄NC	77786	16286	Heterogeneous, rt, air, 1h	This work

^a represents the absence of the definitive values in the article.

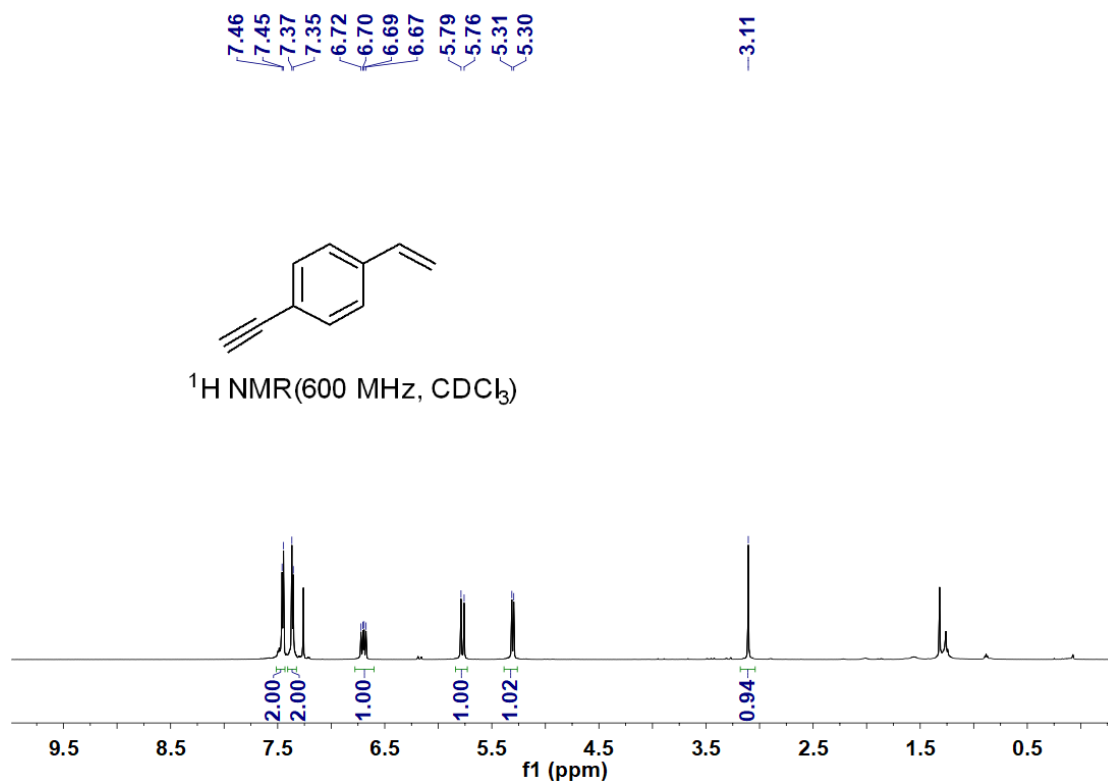
^1H , ^{13}C and ^{19}F NMR Spectra of Compounds



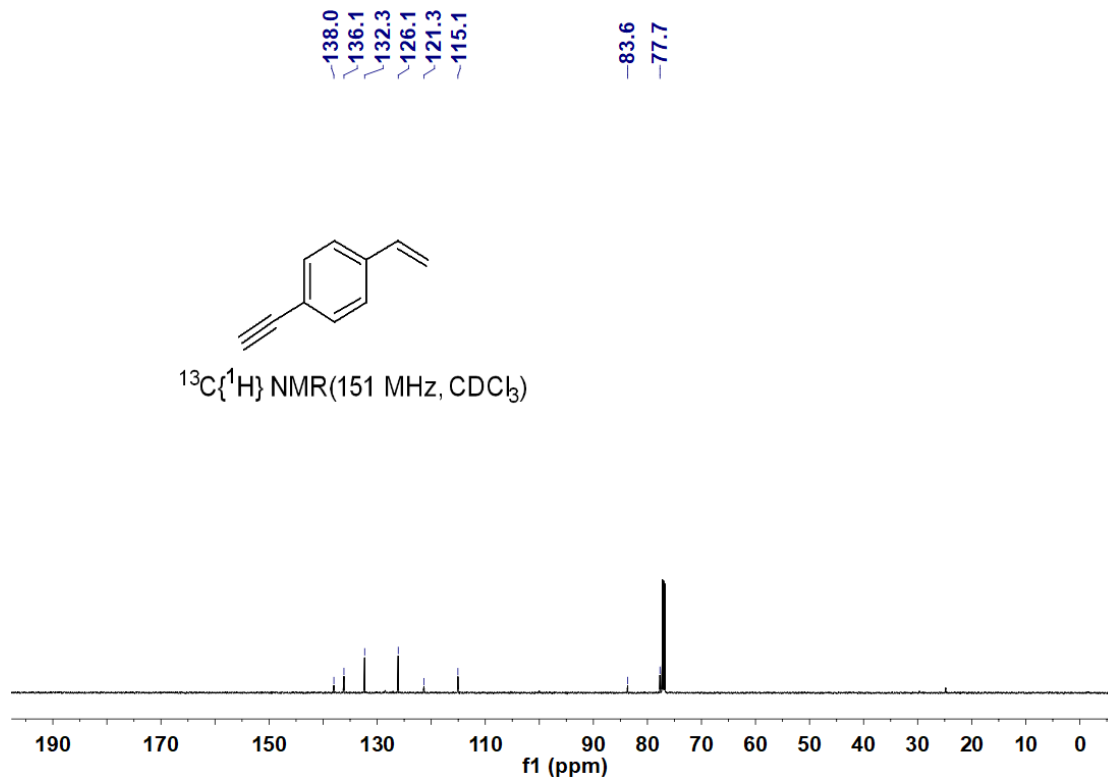
Supplementary Figure 110. Characterization of compound trimethyl((4-vinylphenyl) ethynyl) silane. ^1H NMR spectrum of trimethyl((4-vinylphenyl) ethynyl) silane in CDCl_3 .



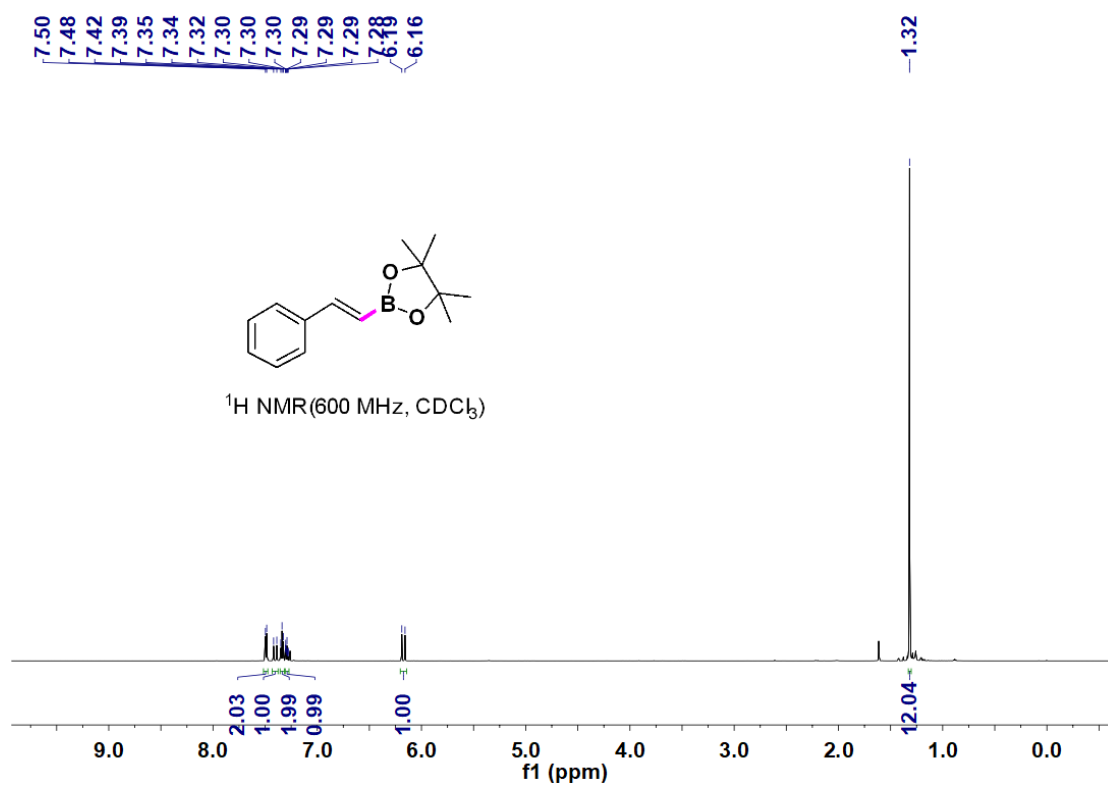
Supplementary Figure 111. Characterization of compound trimethyl((4-vinylphenyl) ethynyl) silane. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of trimethyl((4-vinylphenyl) ethynyl) silane in CDCl_3 .



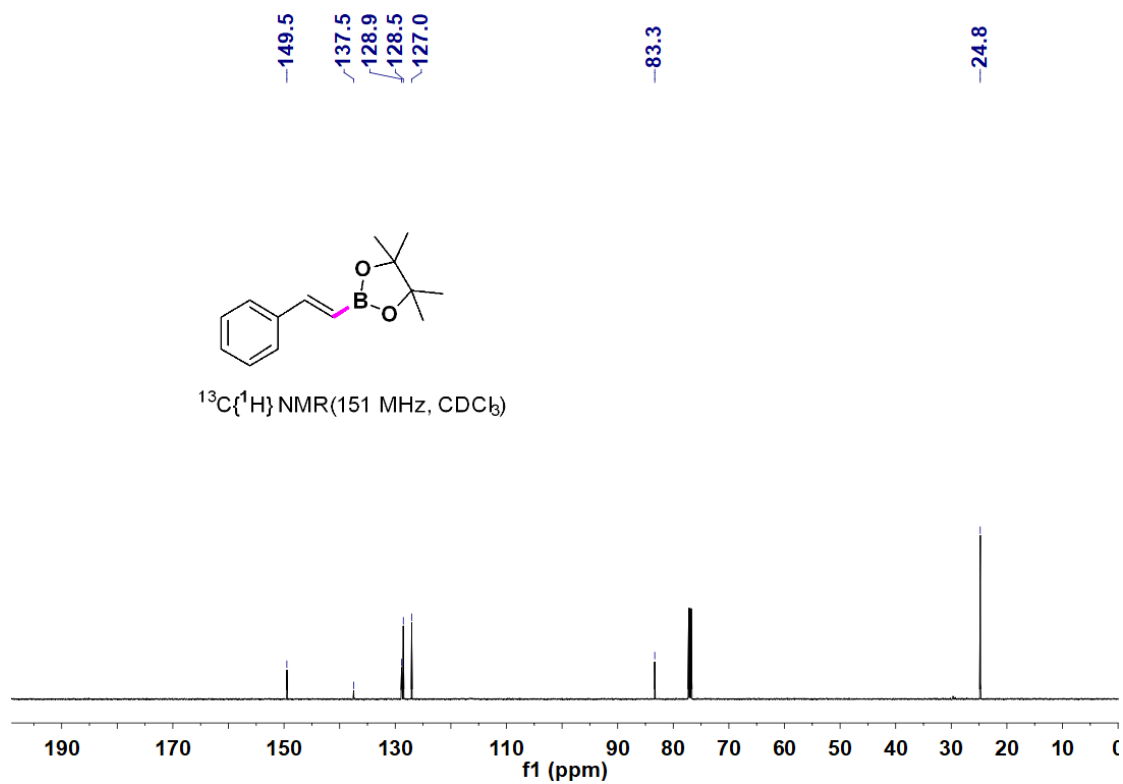
Supplementary Figure 112. Characterization of compound **1ab.** ^1H NMR spectrum of compound **1ab** in CDCl_3 .



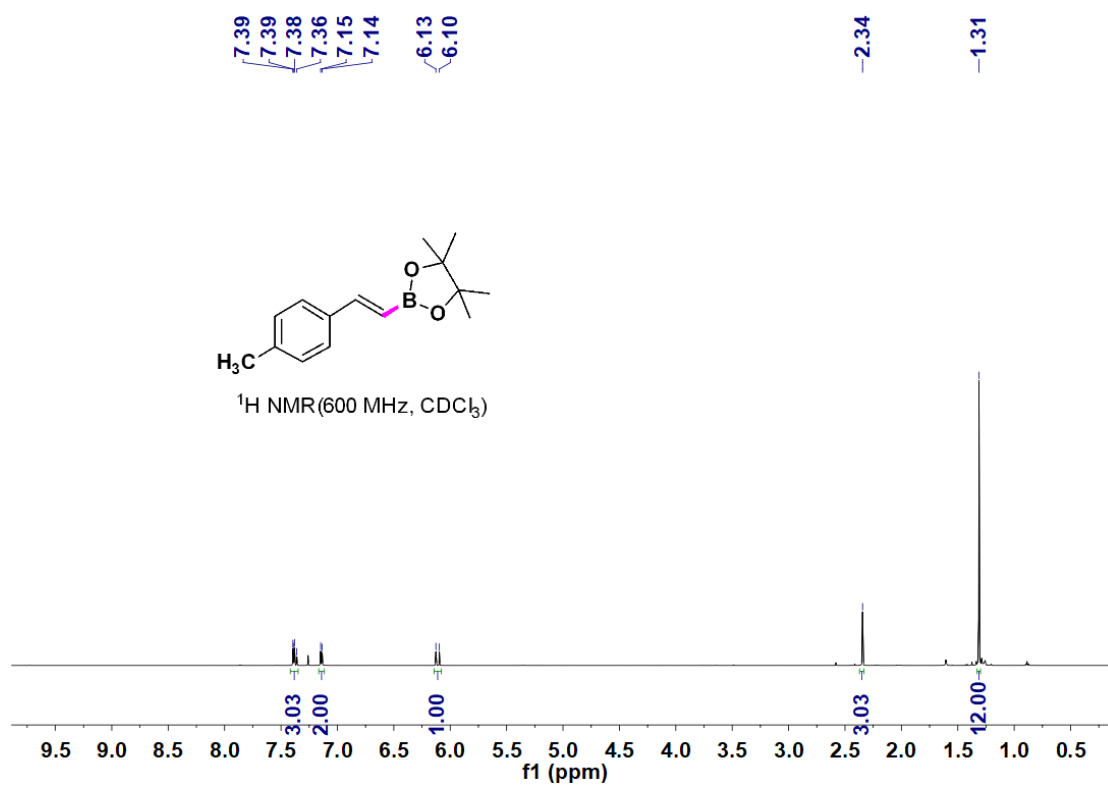
Supplementary Figure 113. Characterization of compound **1ab.** $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **1ab** in CDCl_3 .



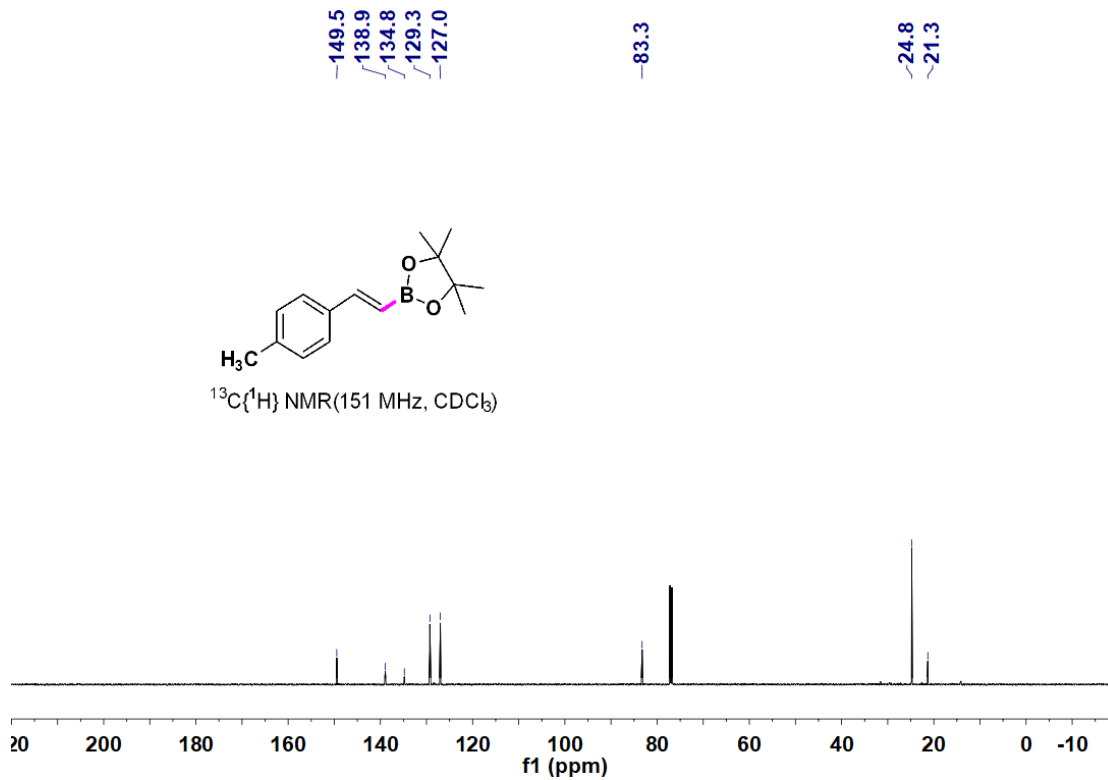
Supplementary Figure 114. Characterization of compound 4a. ^1H NMR spectrum of compound 4a in CDCl_3 .



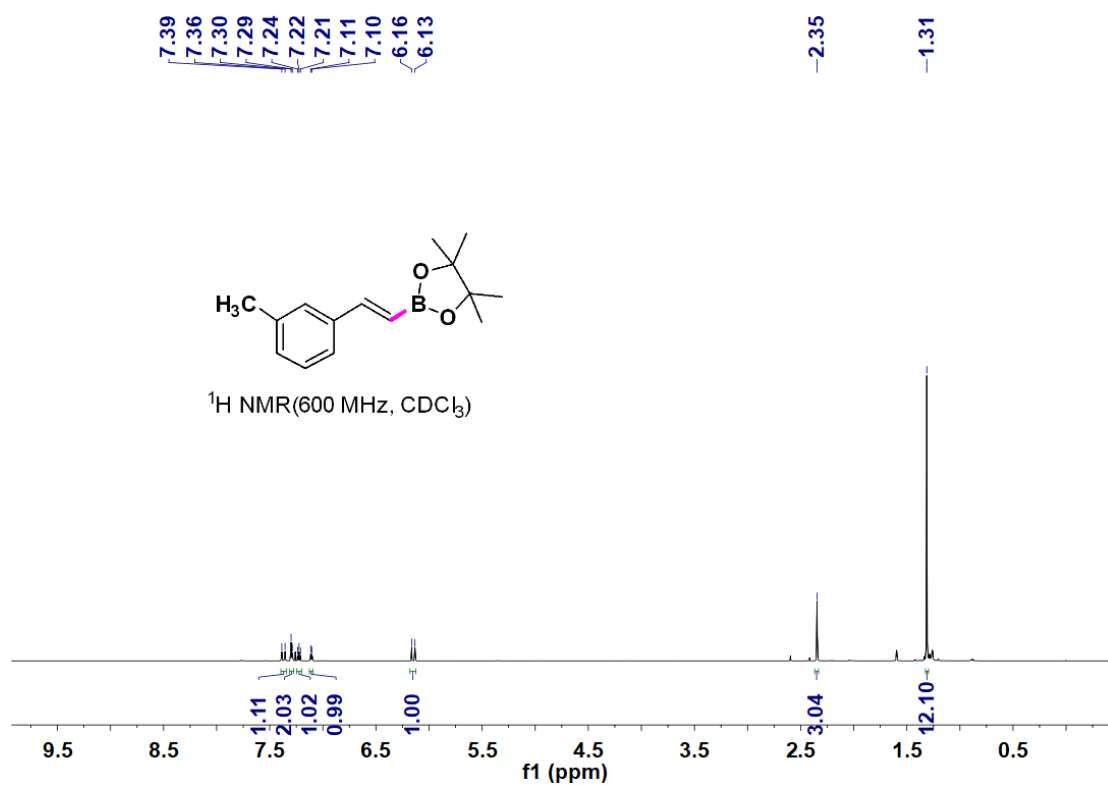
Supplementary Figure 115. Characterization of compound 4a. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound 4a in CDCl_3 .



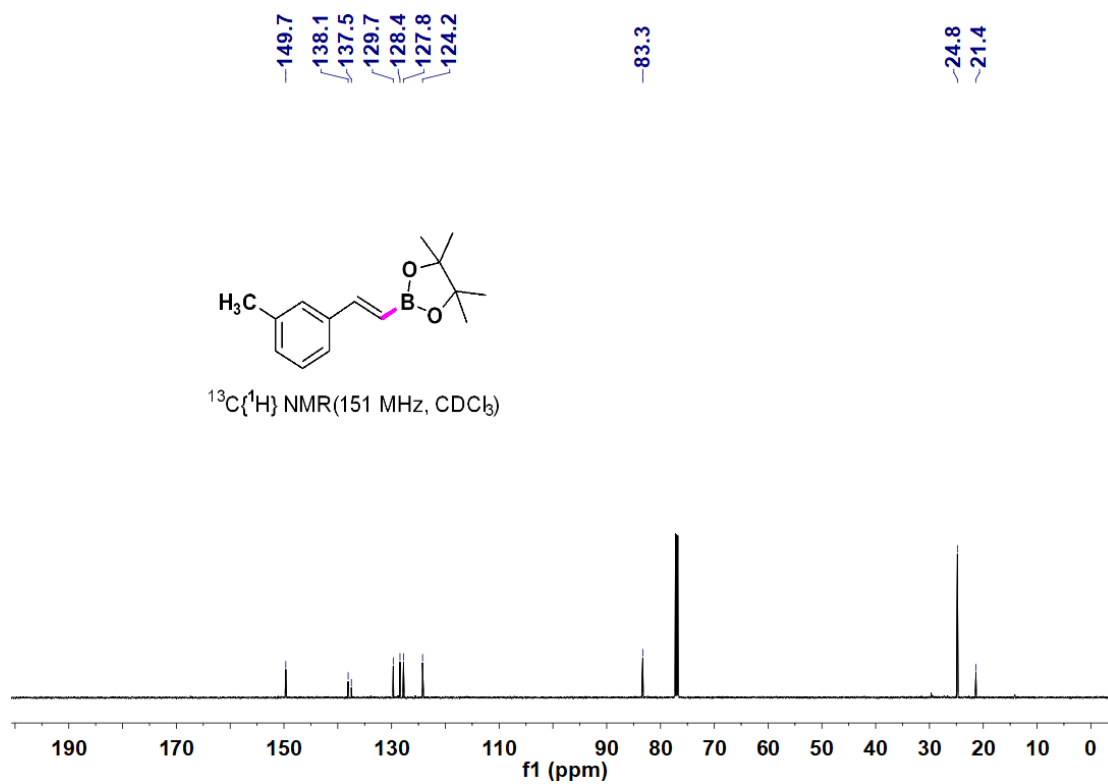
Supplementary Figure 116. Characterization of compound 4b. ^1H NMR spectrum of compound **4b** in CDCl_3 .



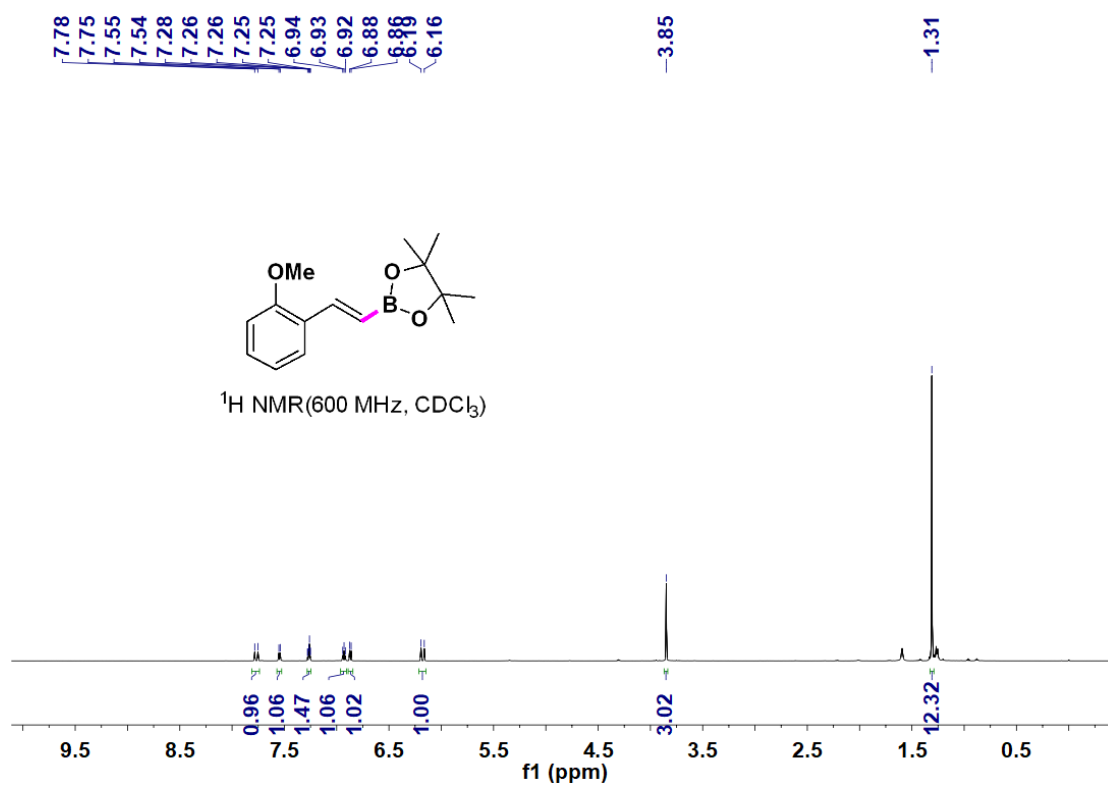
Supplementary Figure 117. Characterization of compound 4b. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **4b** in CDCl_3 .



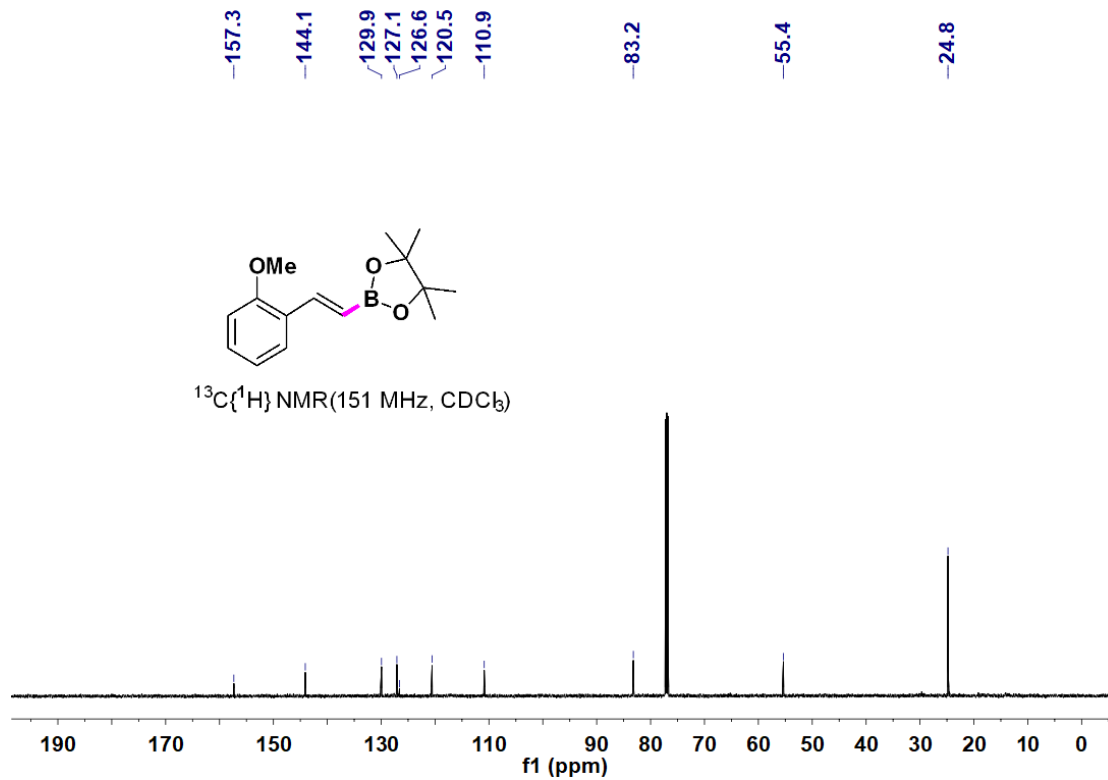
Supplementary Figure 118. Characterization of compound **4c.** ^1H NMR spectrum of compound **4c** in CDCl_3 .



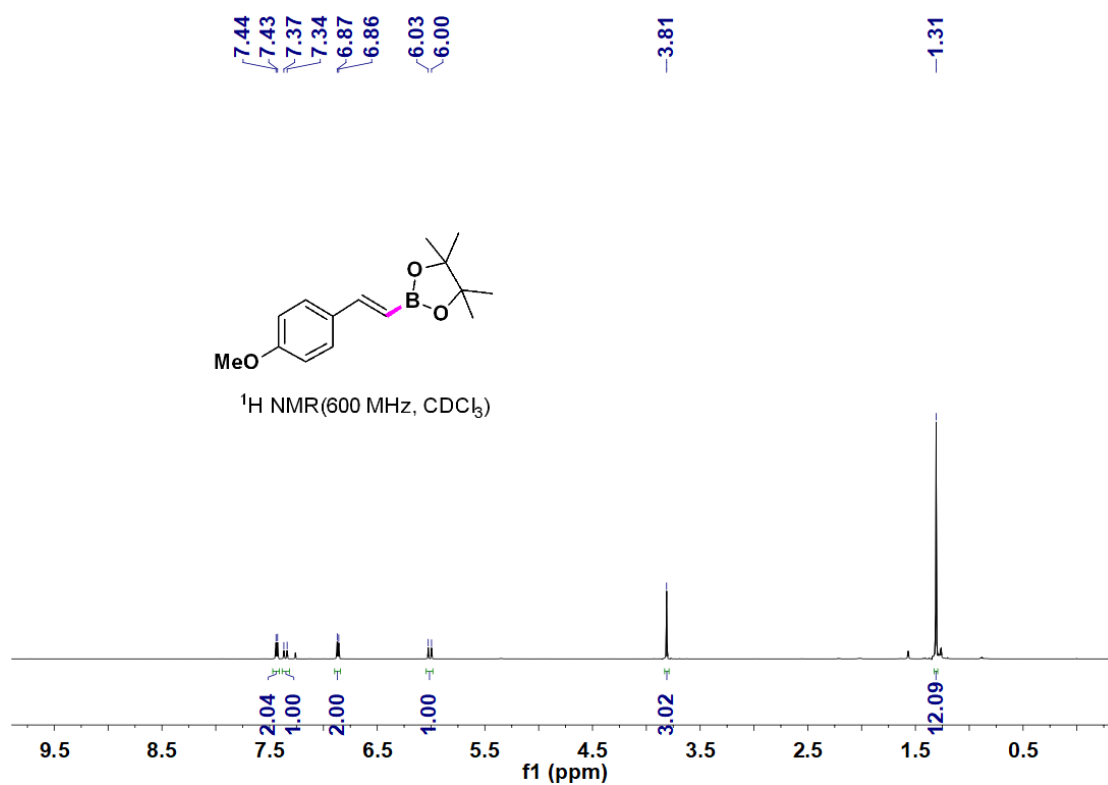
Supplementary Figure 119. Characterization of compound **4c.** $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **4c** in CDCl_3 .



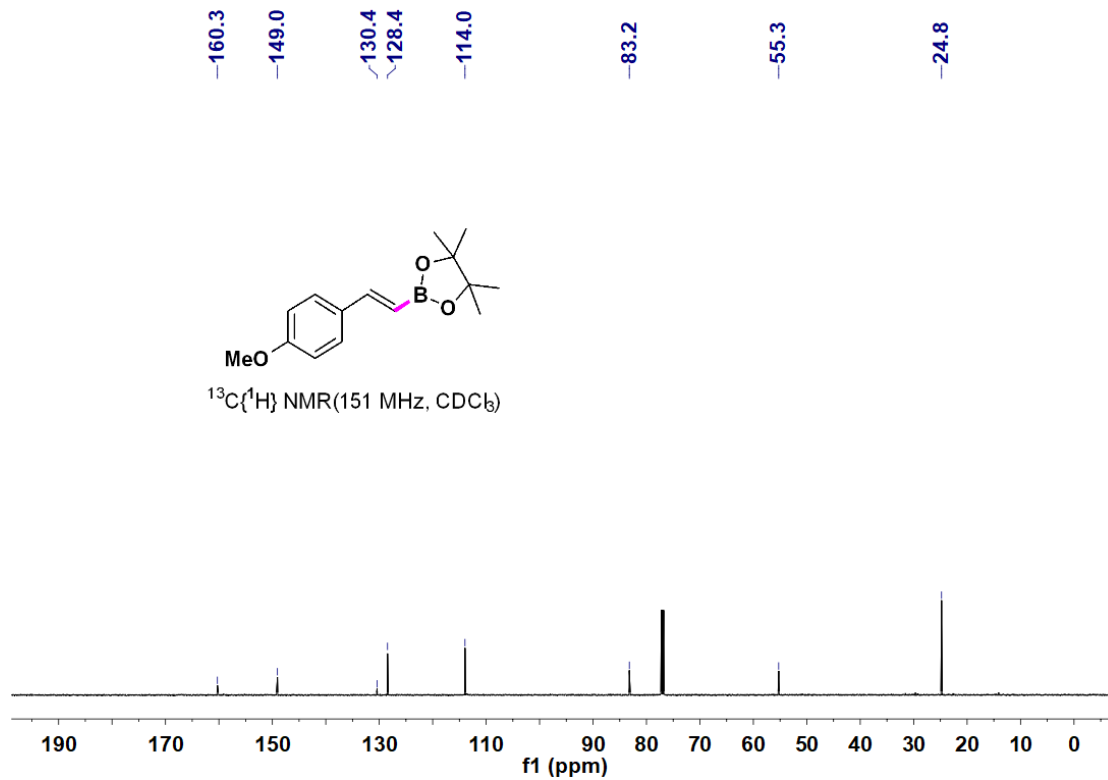
Supplementary Figure 120. Characterization of compound 4d. ¹H NMR spectrum of compound 4d in CDCl₃.



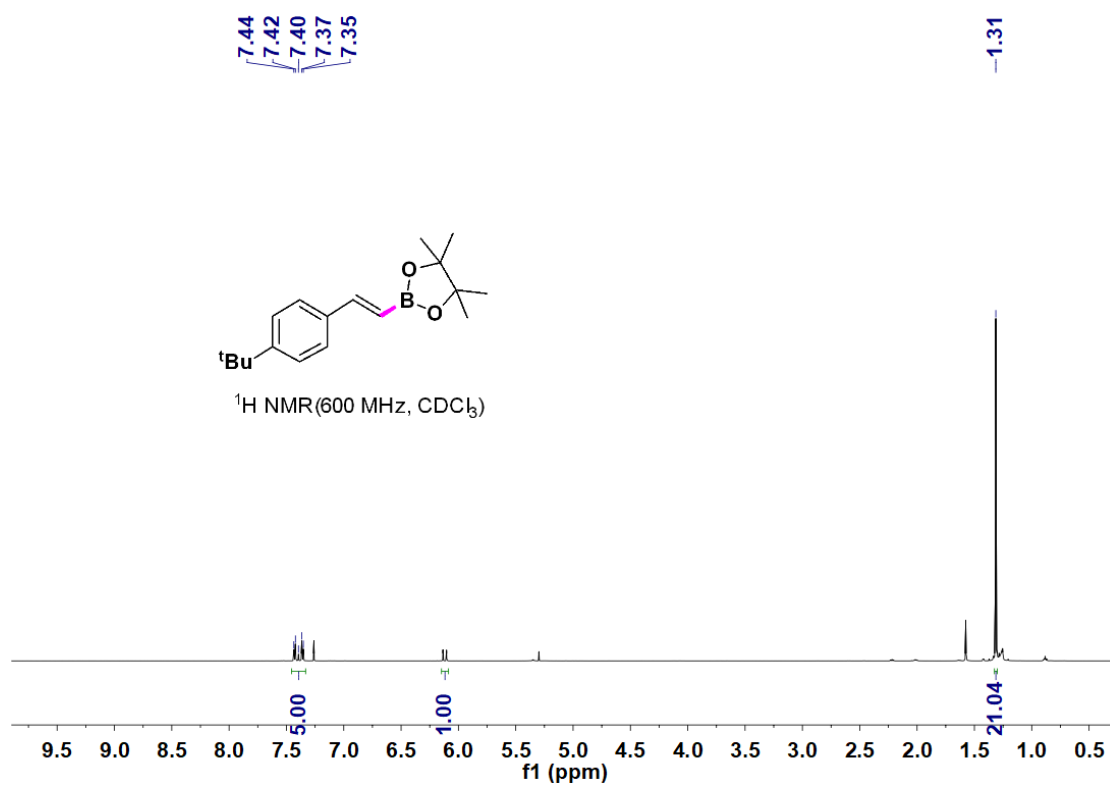
Supplementary Figure 121. Characterization of compound 4d. ¹³C{¹H} NMR spectrum of compound 4d in CDCl₃.



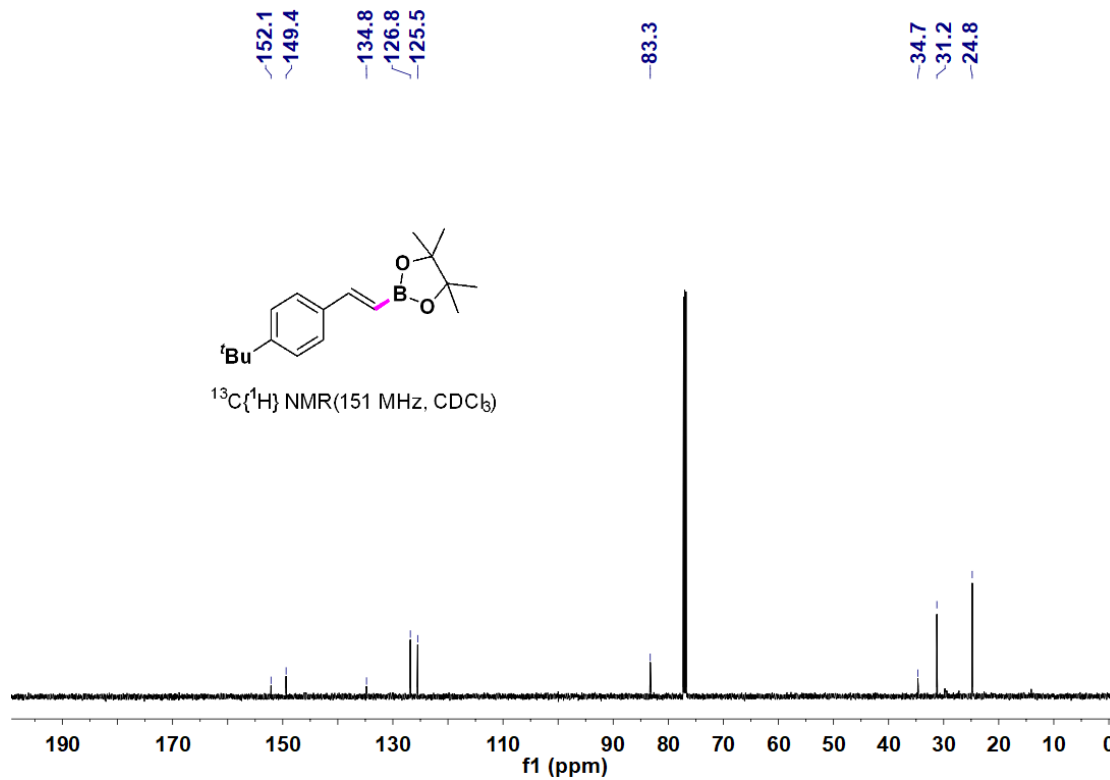
Supplementary Figure 122. Characterization of compound 4e. ^1H NMR spectrum of compound 4e in CDCl_3 .



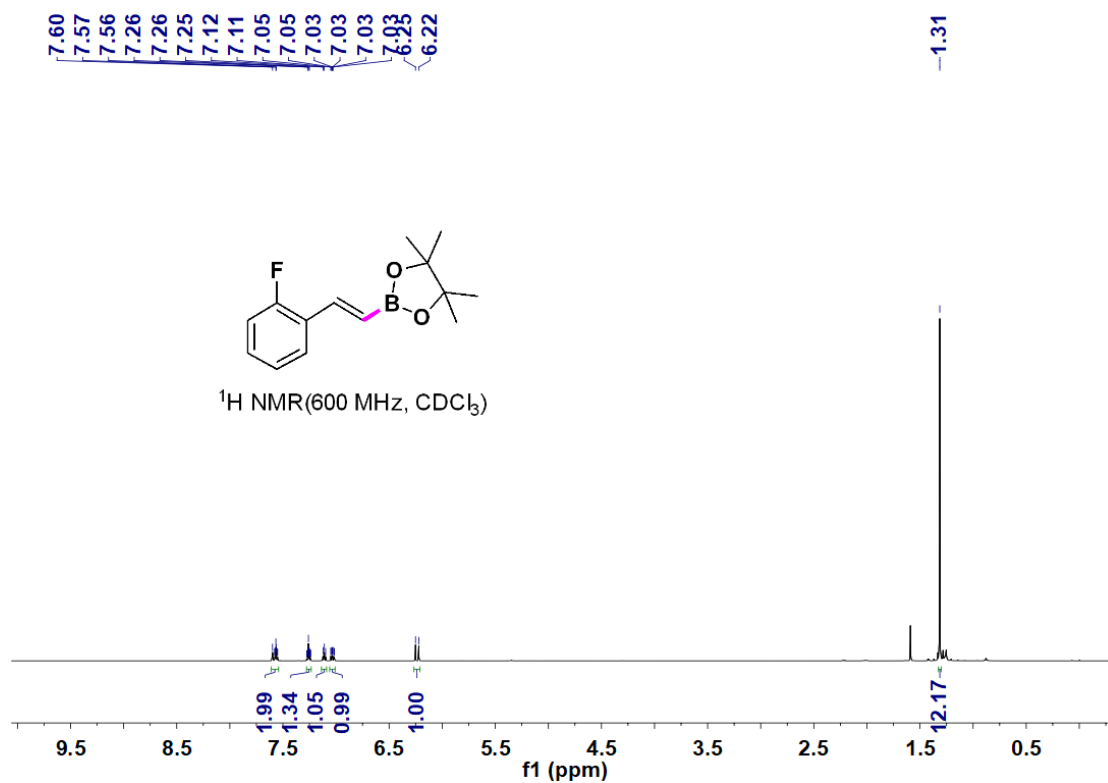
Supplementary Figure 123. Characterization of compound 4e. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound 4e in CDCl_3 .



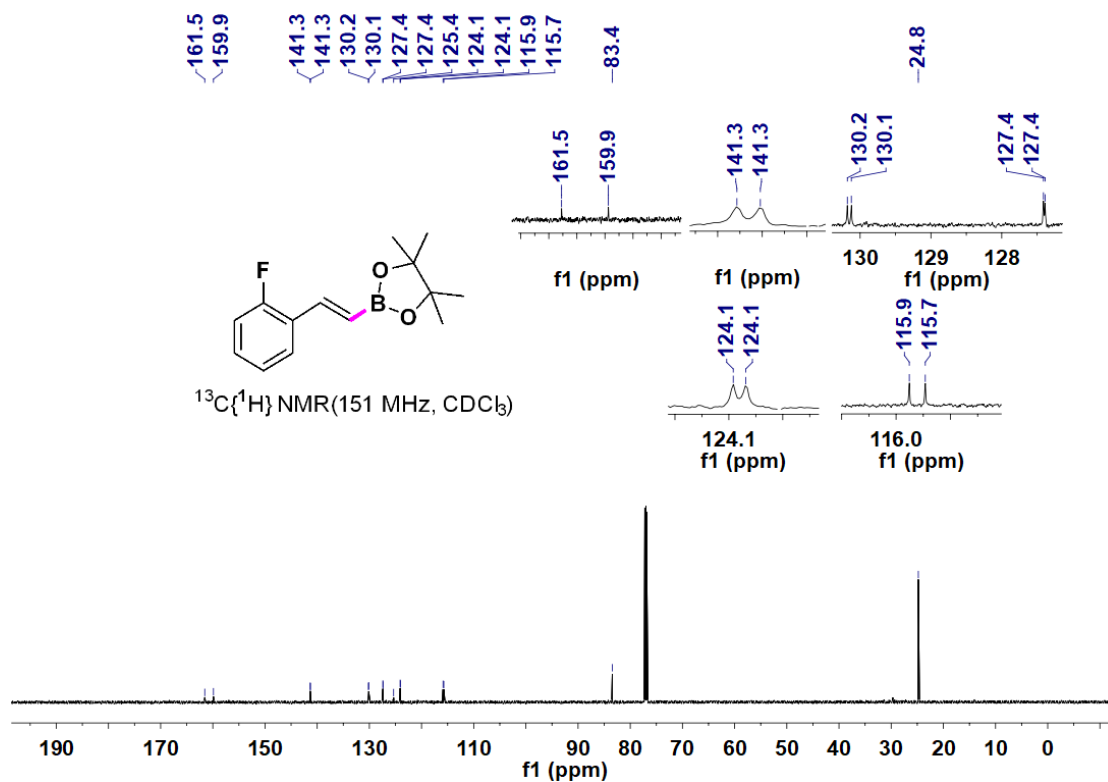
Supplementary Figure 124. Characterization of compound 4f. ^1H NMR spectrum of compound **4f** in CDCl_3 .



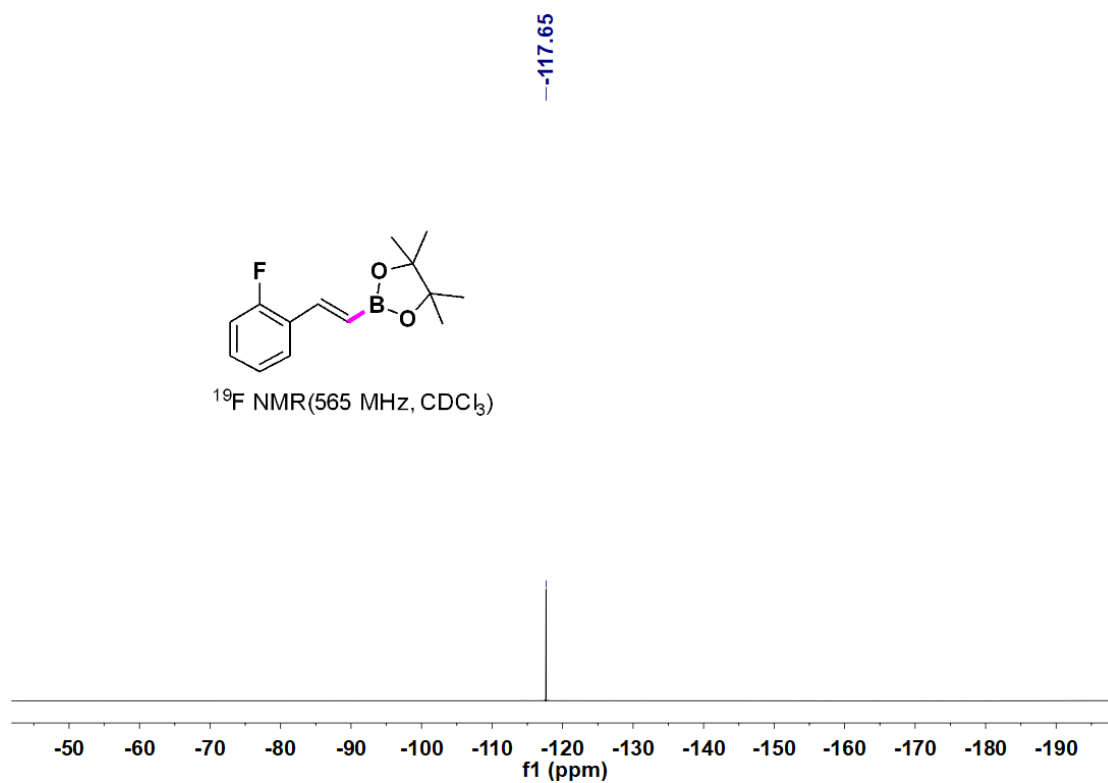
Supplementary Figure 125. Characterization of compound 4f. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **4f** in CDCl_3 .



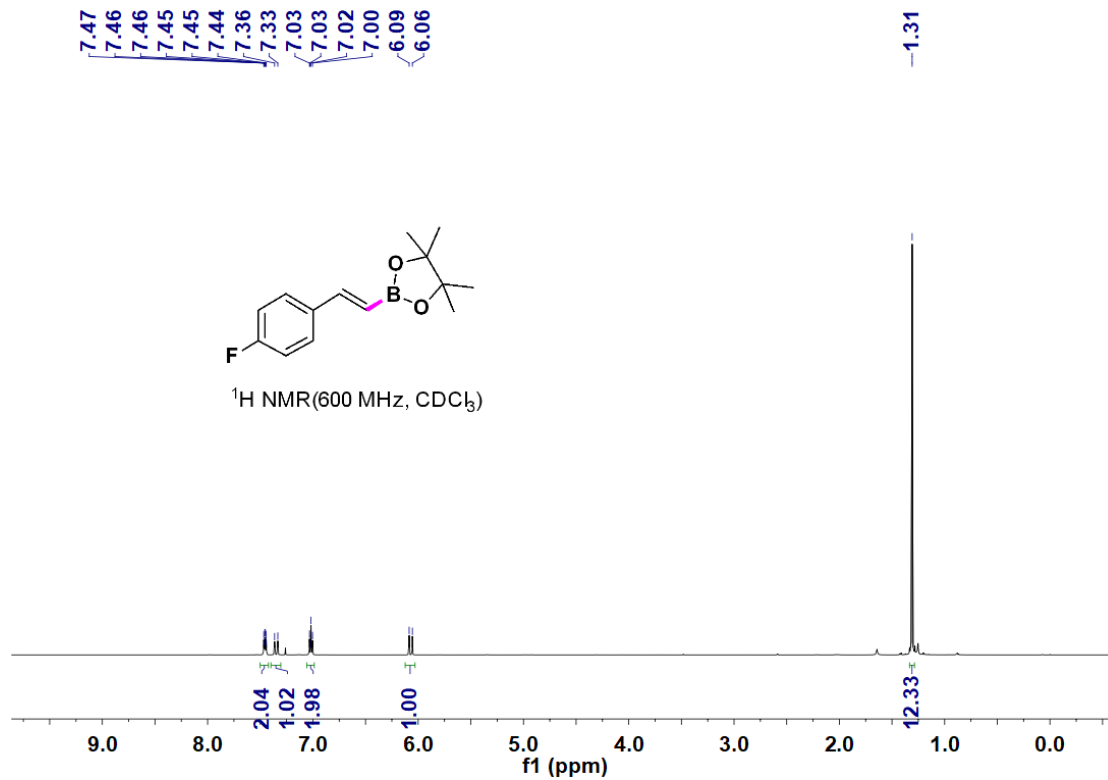
Supplementary Figure 126. Characterization of compound 4g. ¹H NMR spectrum of compound 4g in CDCl₃.



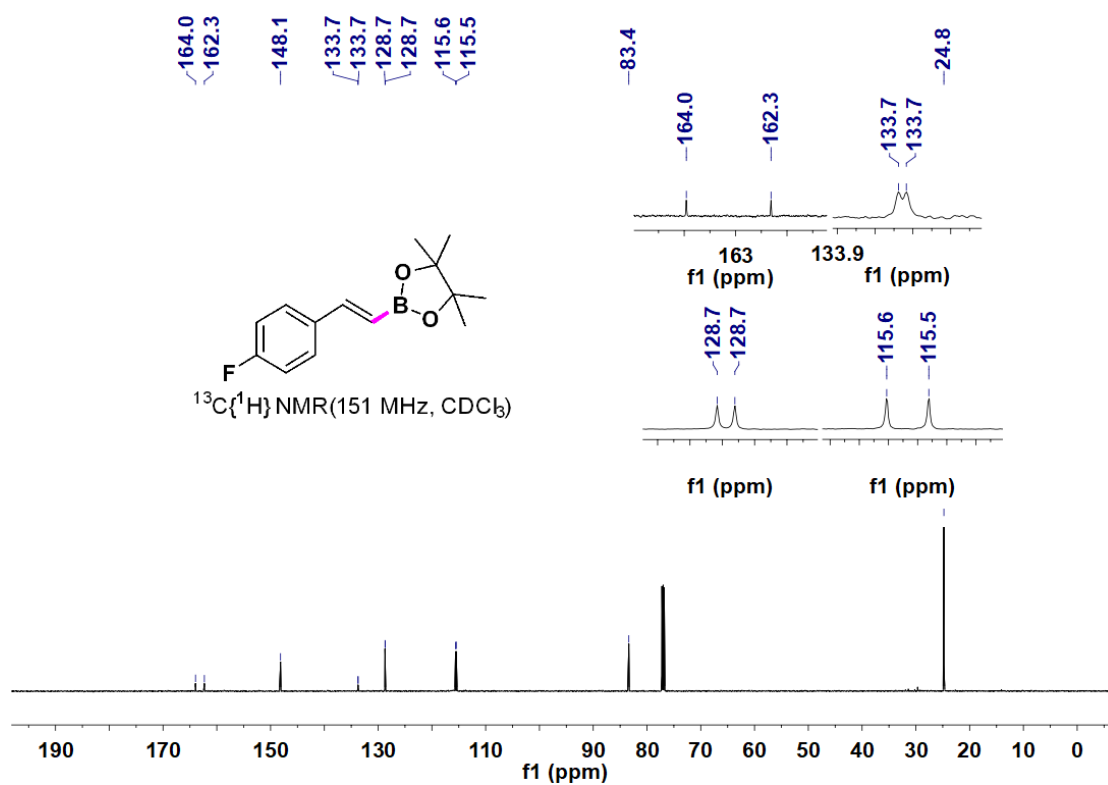
Supplementary Figure 127. Characterization of compound 4g. ¹³C{¹H} NMR spectrum of compound 4g in CDCl₃.



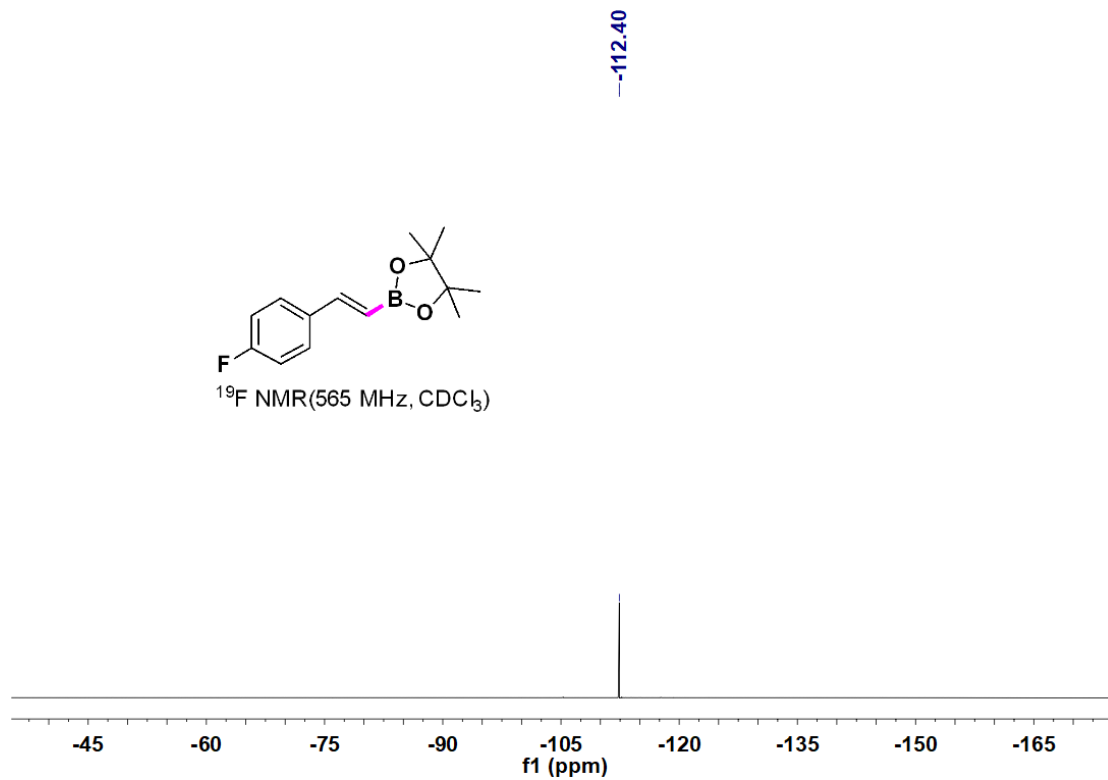
Supplementary Figure 128. Characterization of compound 4g. ¹⁹F NMR spectrum of compound **4g** in CDCl₃.



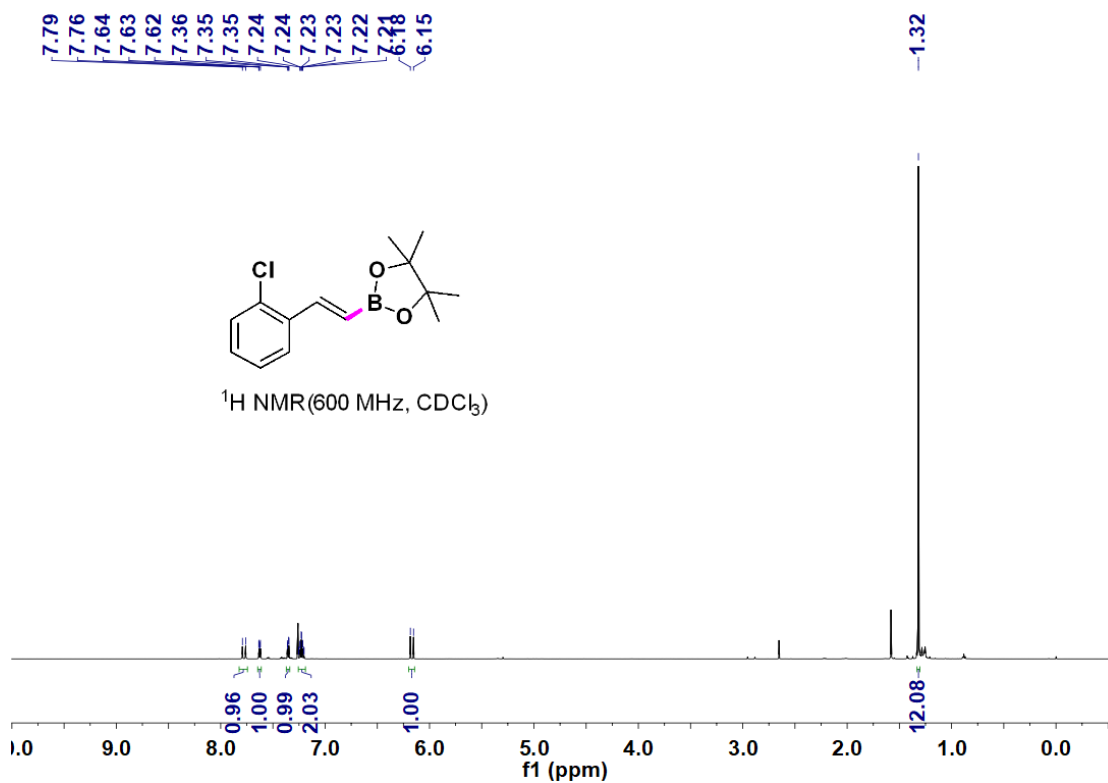
Supplementary Figure 129. Characterization of compound 4h. ¹H NMR spectrum of compound **4h** in CDCl₃.



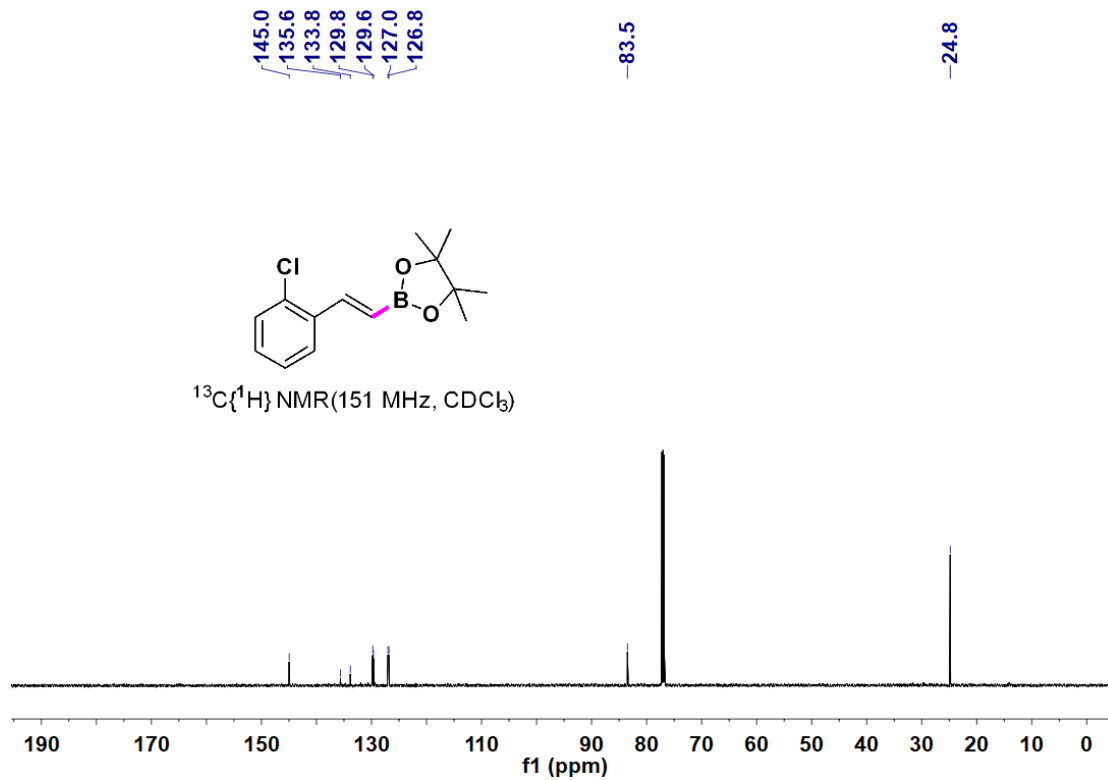
Supplementary Figure 130. Characterization of compound 4h. ¹³C{¹H} NMR spectrum of compound 4h in CDCl₃.



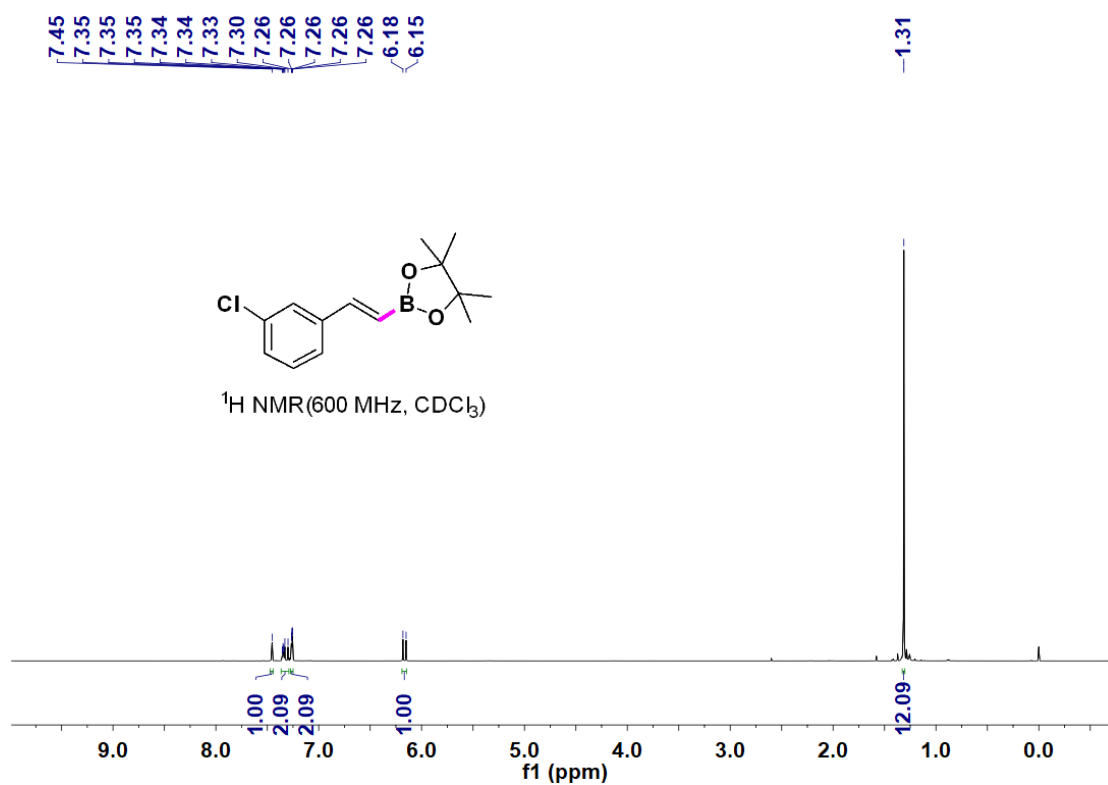
Supplementary Figure 131. Characterization of compound 4h. ¹⁹F NMR spectrum of compound 4h in CDCl₃.



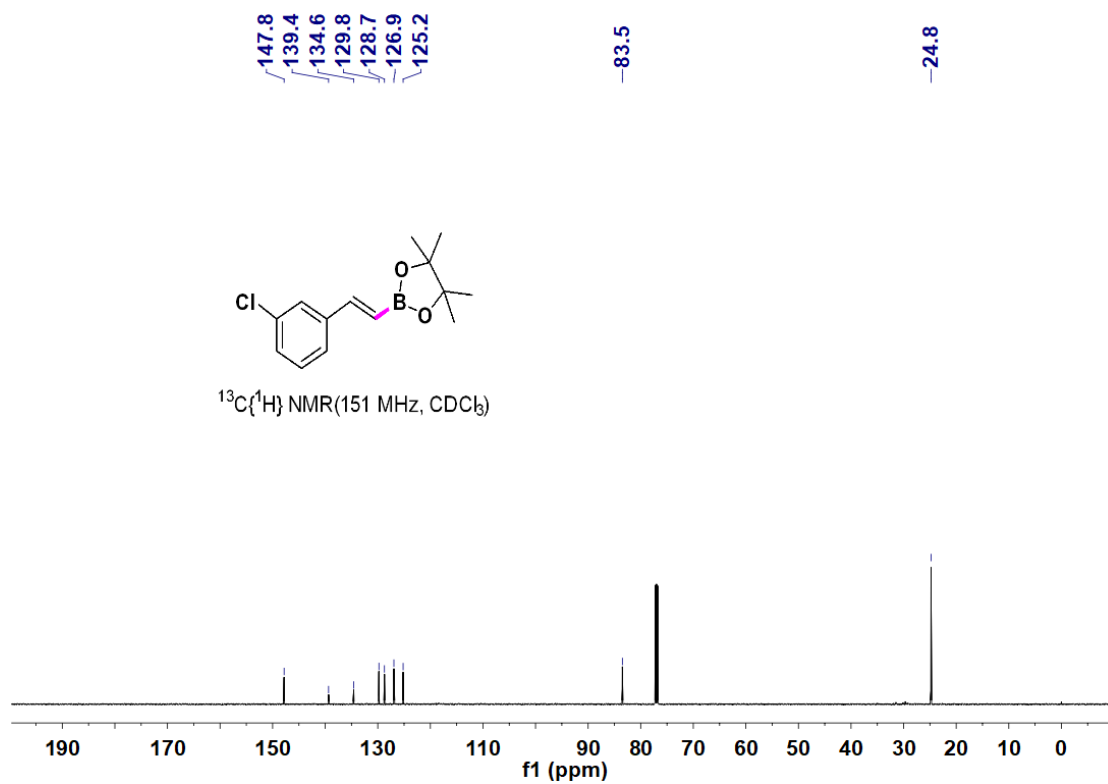
Supplementary Figure 132. Characterization of compound 4i. ¹H NMR spectrum of compound 4i in CDCl₃.



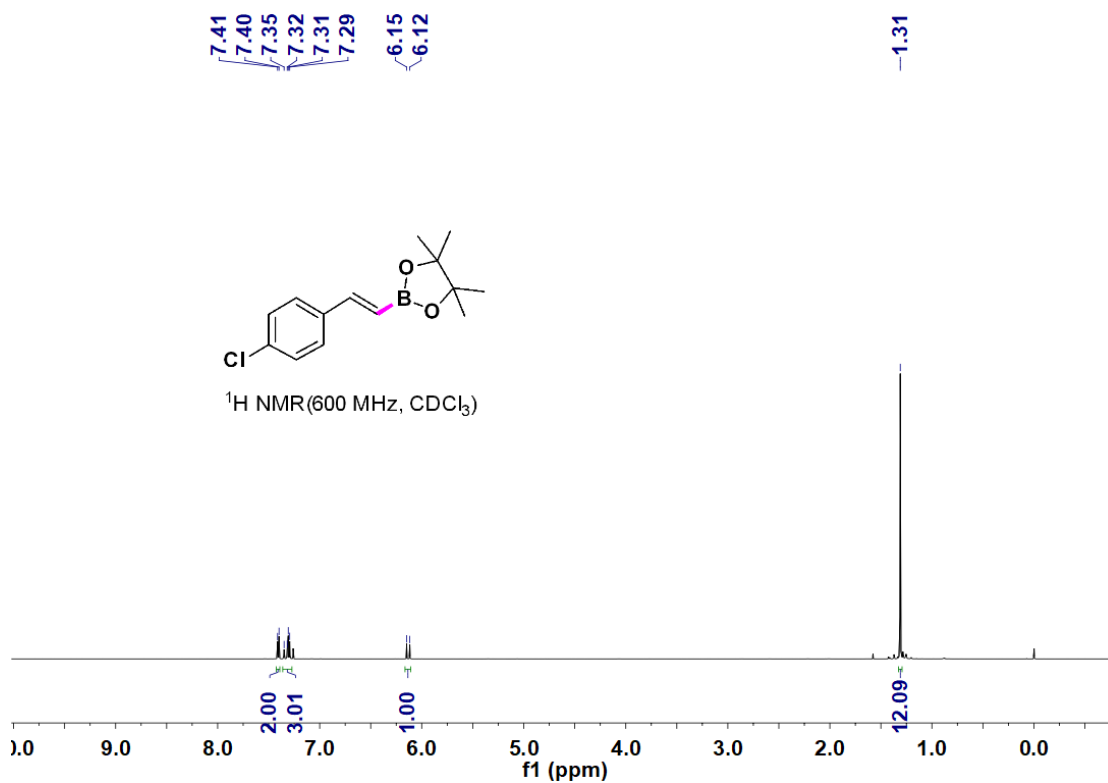
Supplementary Figure 133. Characterization of compound 4i. ¹³C{¹H} NMR spectrum of compound 4i in CDCl₃.



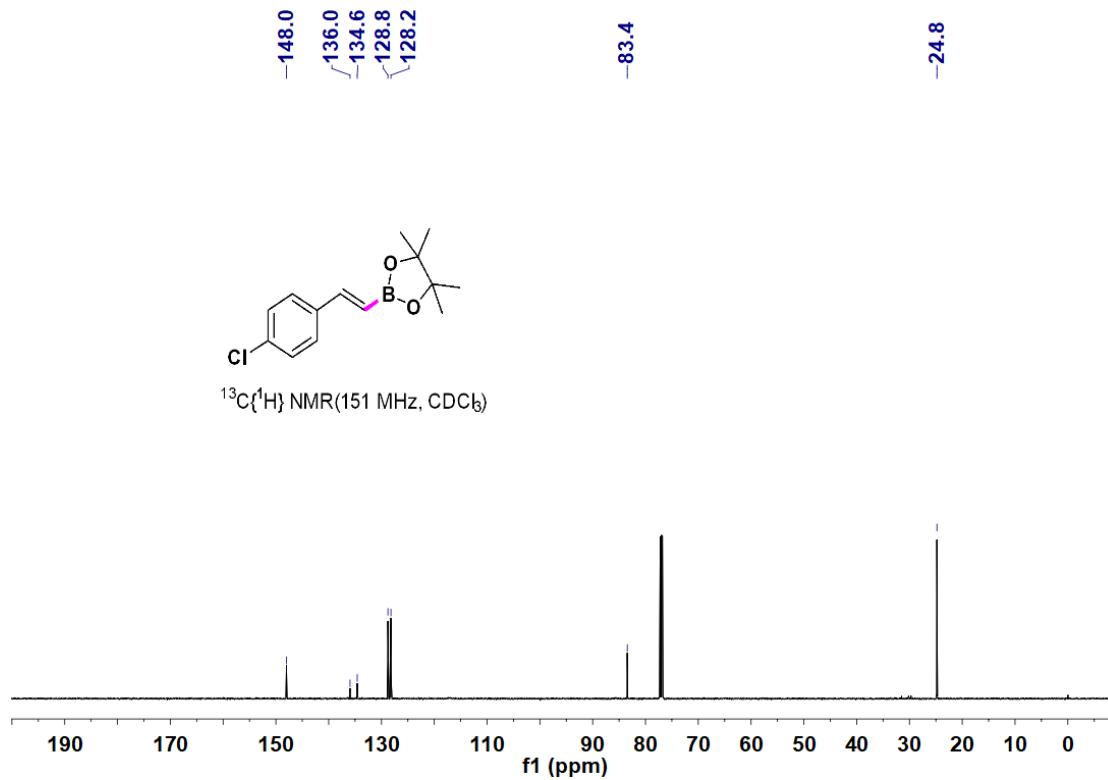
Supplementary Figure 134. Characterization of compound 4j. ^1H NMR spectrum of compound **4j** in CDCl_3 .



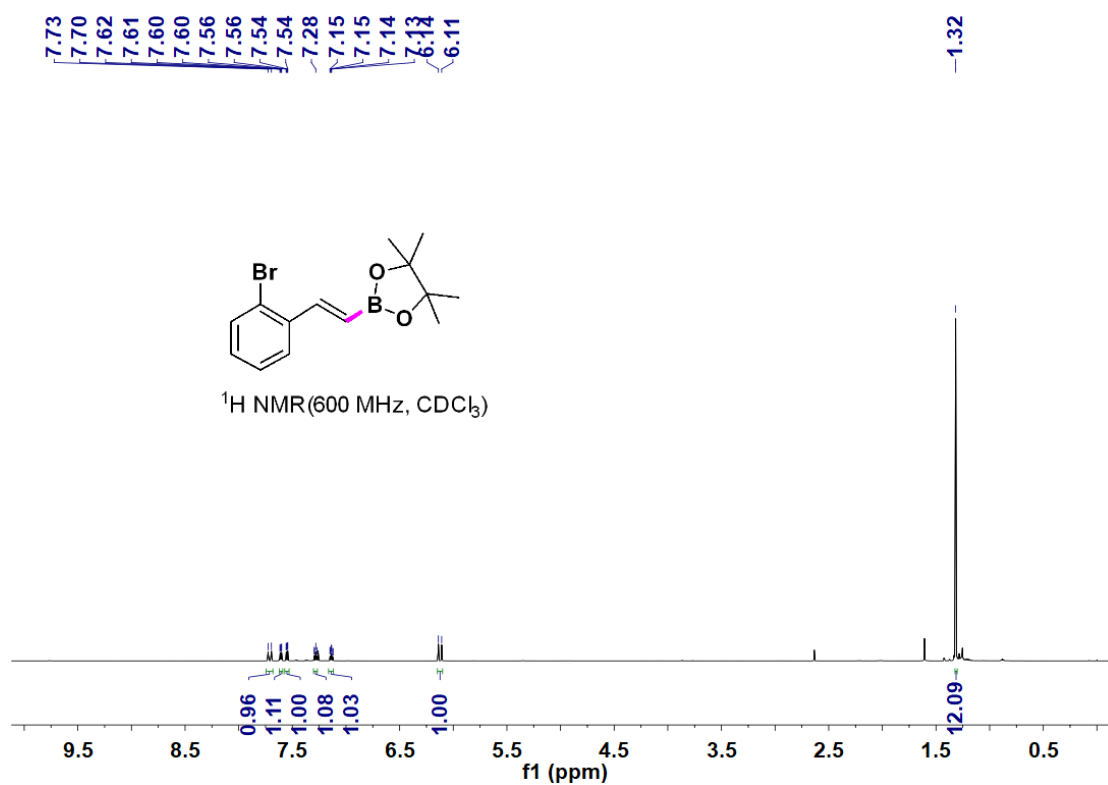
Supplementary Figure 135. Characterization of compound 4j. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **4j** in CDCl_3 .



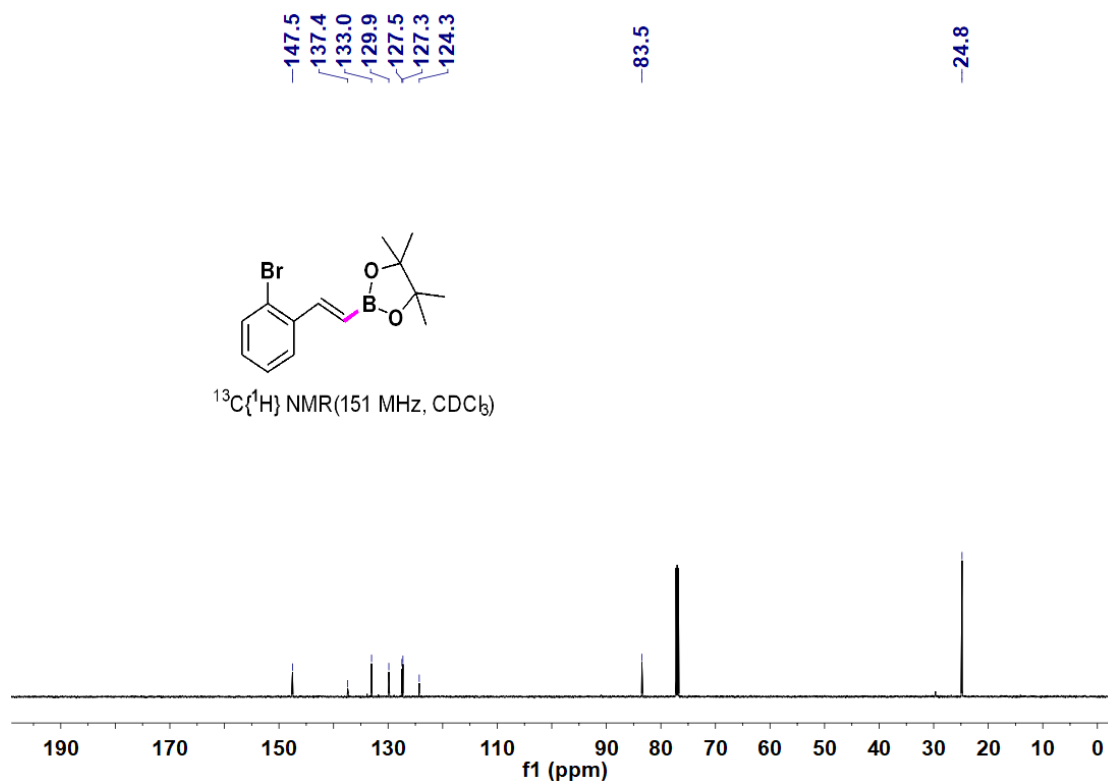
Supplementary Figure 136. Characterization of compound **4k.** ^1H NMR spectrum of compound **4k** in CDCl_3 .



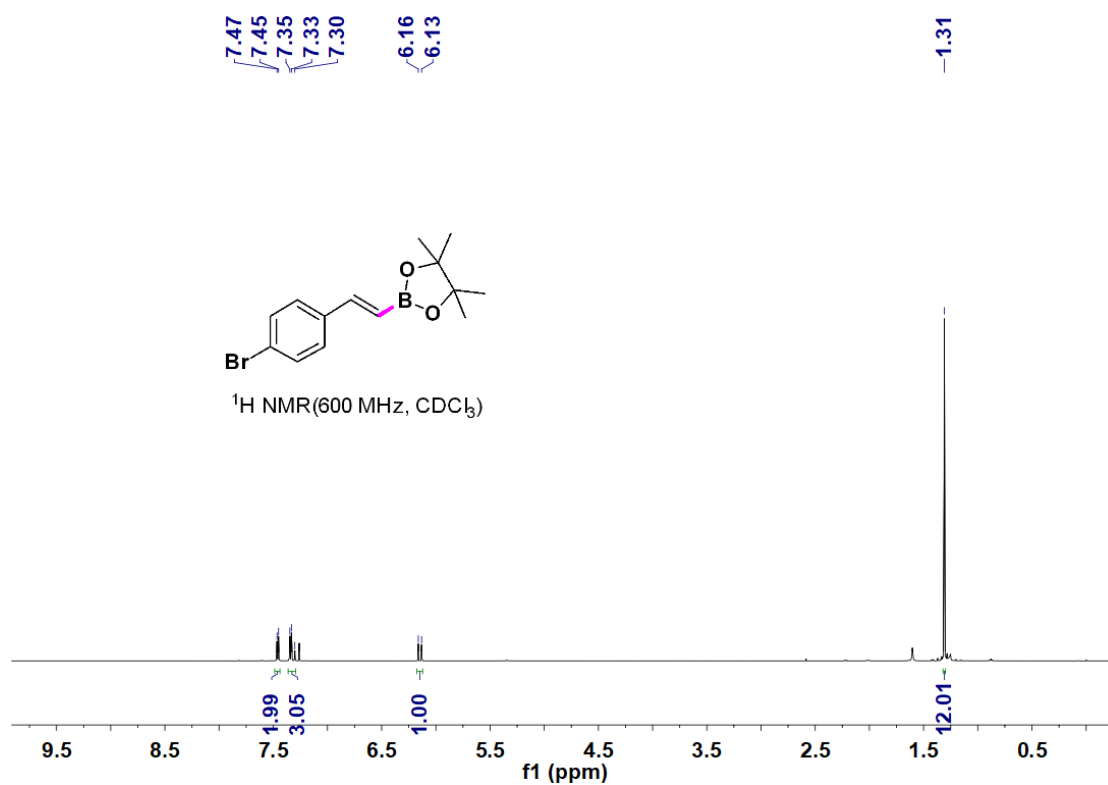
Supplementary Figure 137. Characterization of compound **4k.** $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **4k** in CDCl_3 .



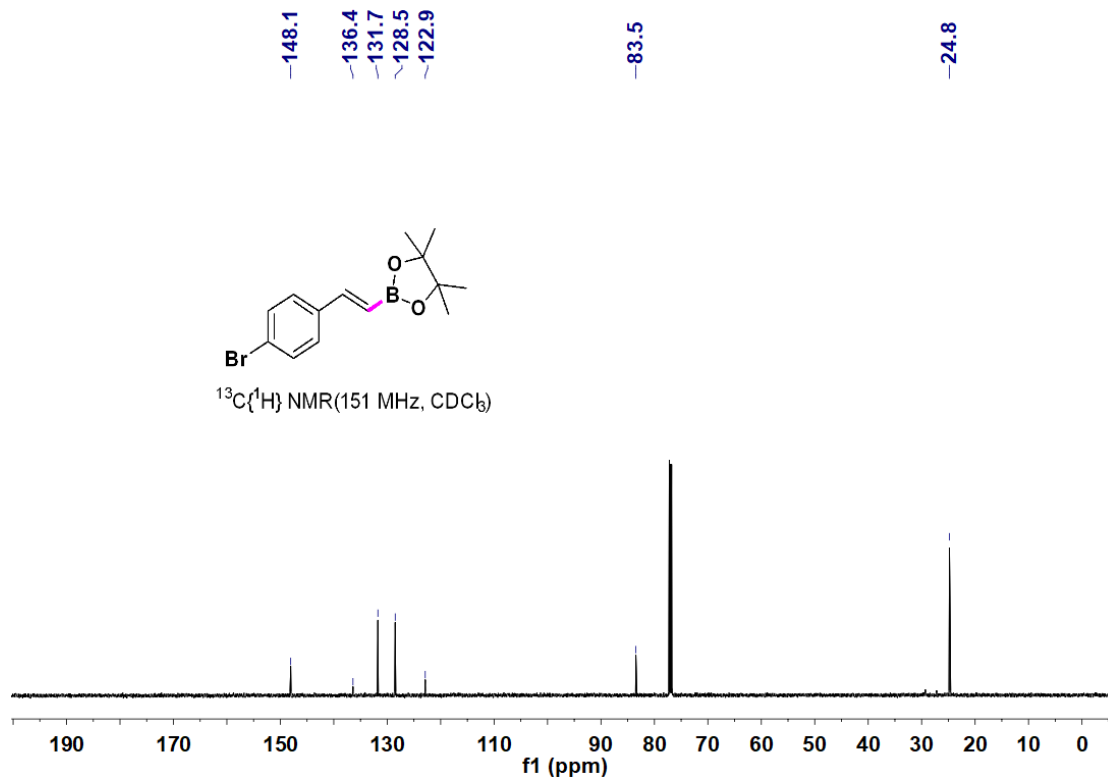
Supplementary Figure 138. Characterization of compound 4l. ¹H NMR spectrum of compound 4l in CDCl₃.



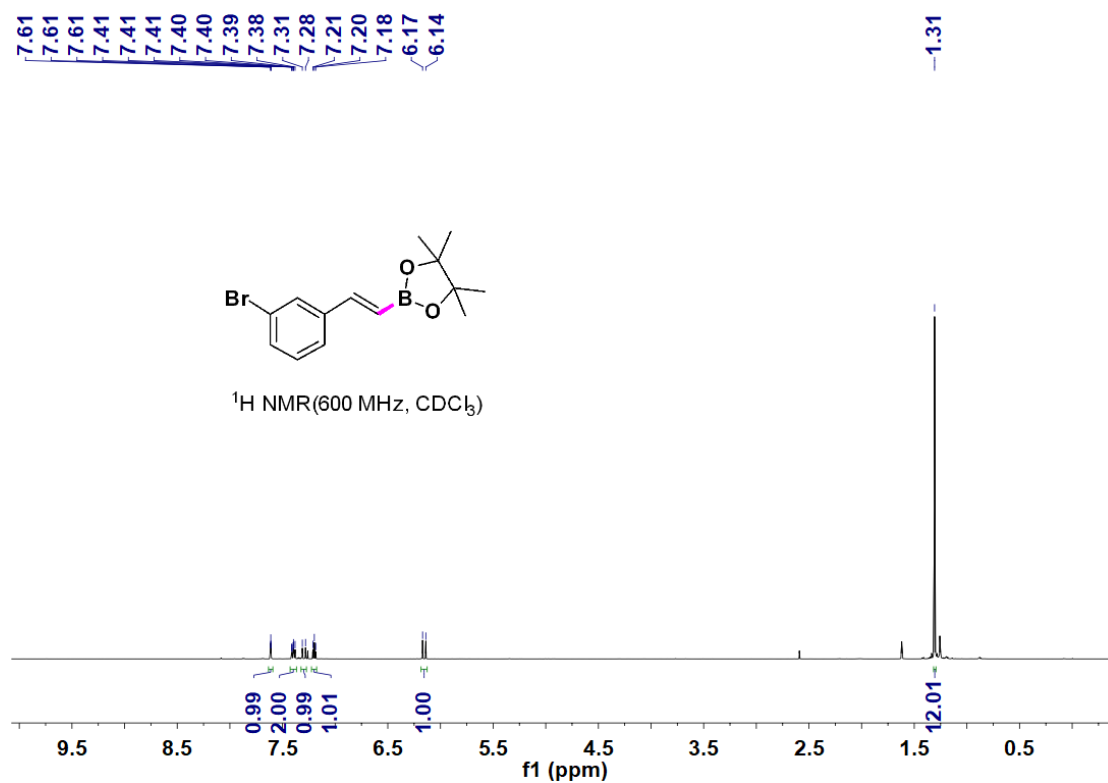
Supplementary Figure 139. Characterization of compound 4l. ¹³C{¹H} NMR spectrum of compound 4l in CDCl₃.



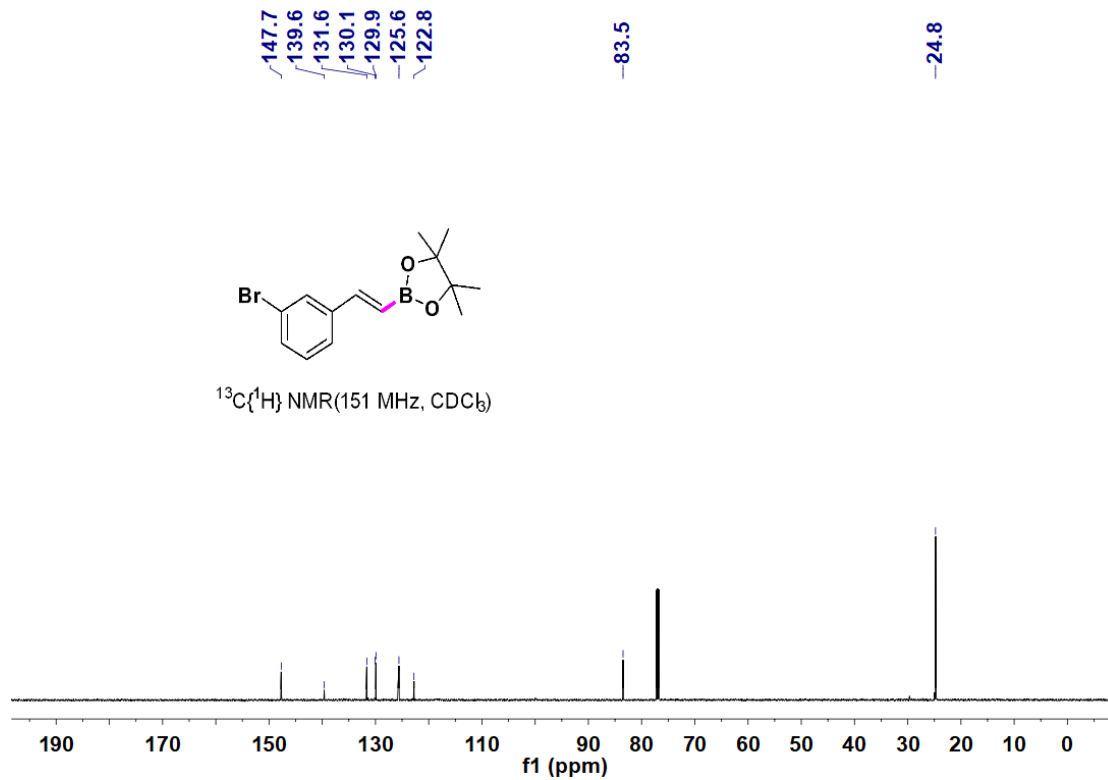
Supplementary Figure 140. Characterization of compound **4m.** ^1H NMR spectrum of compound **4m** in CDCl_3 .



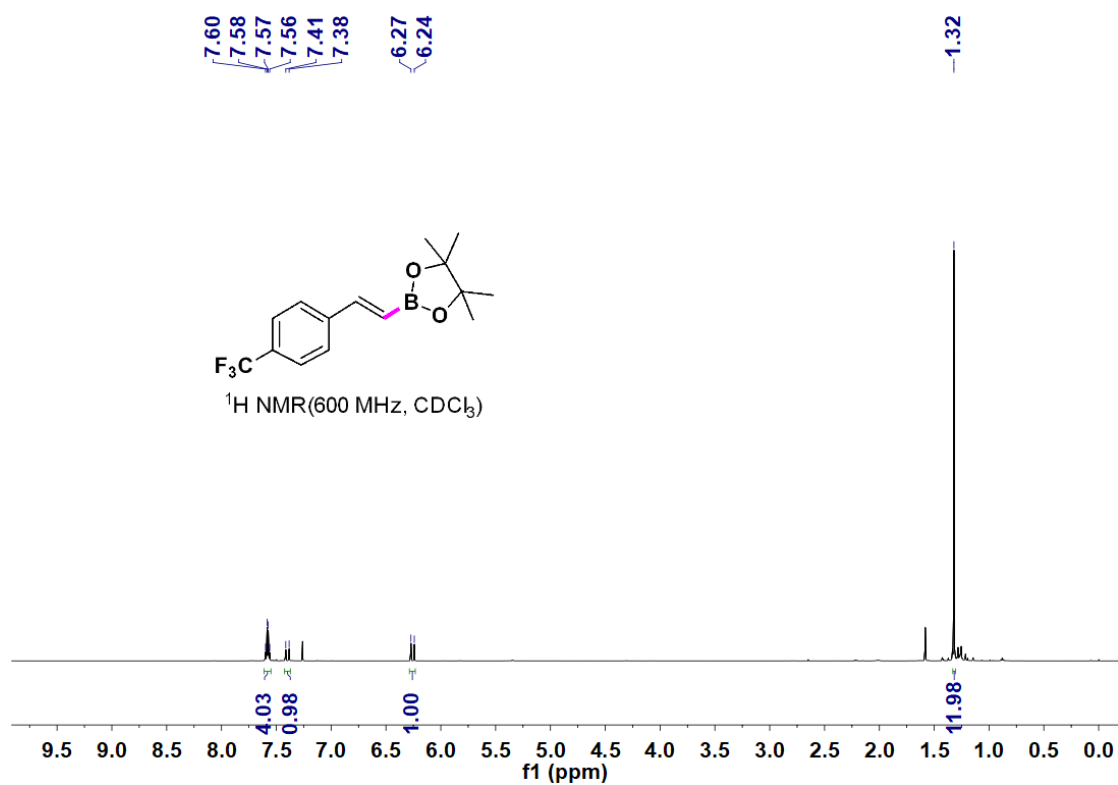
Supplementary Figure 141. Characterization of compound **4m.** $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **4m** in CDCl_3 .



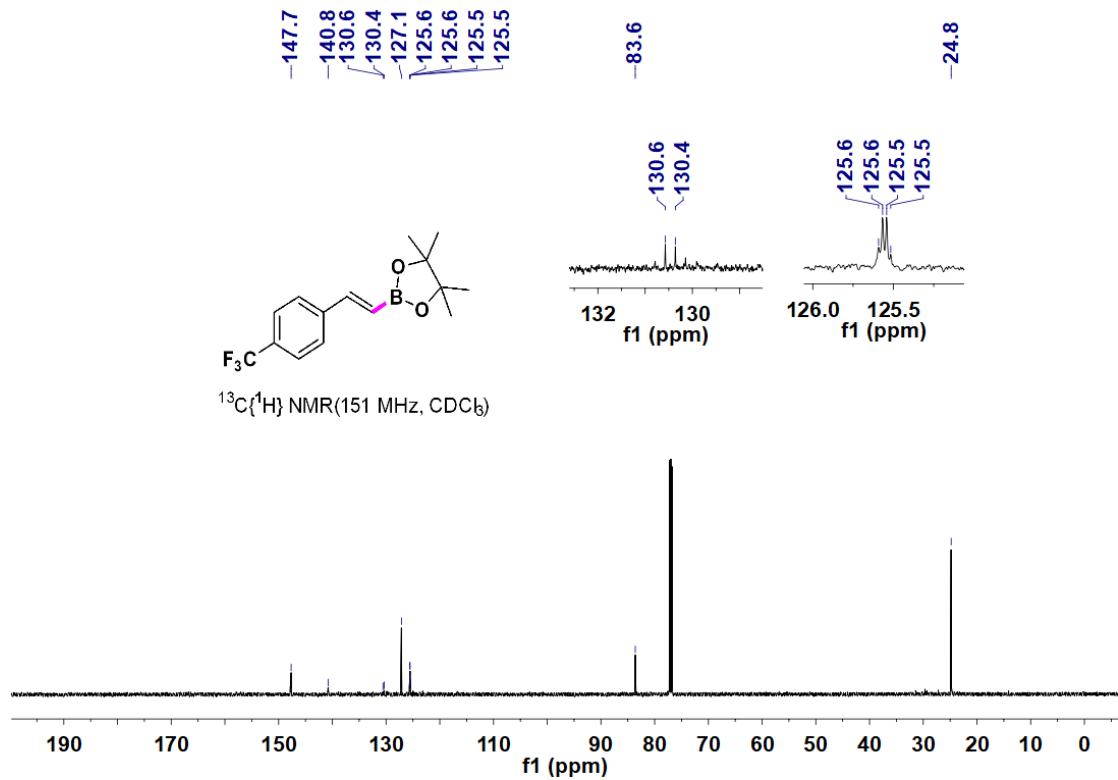
Supplementary Figure 142. Characterization of compound 4n. ¹H NMR spectrum of compound 4n in CDCl₃.



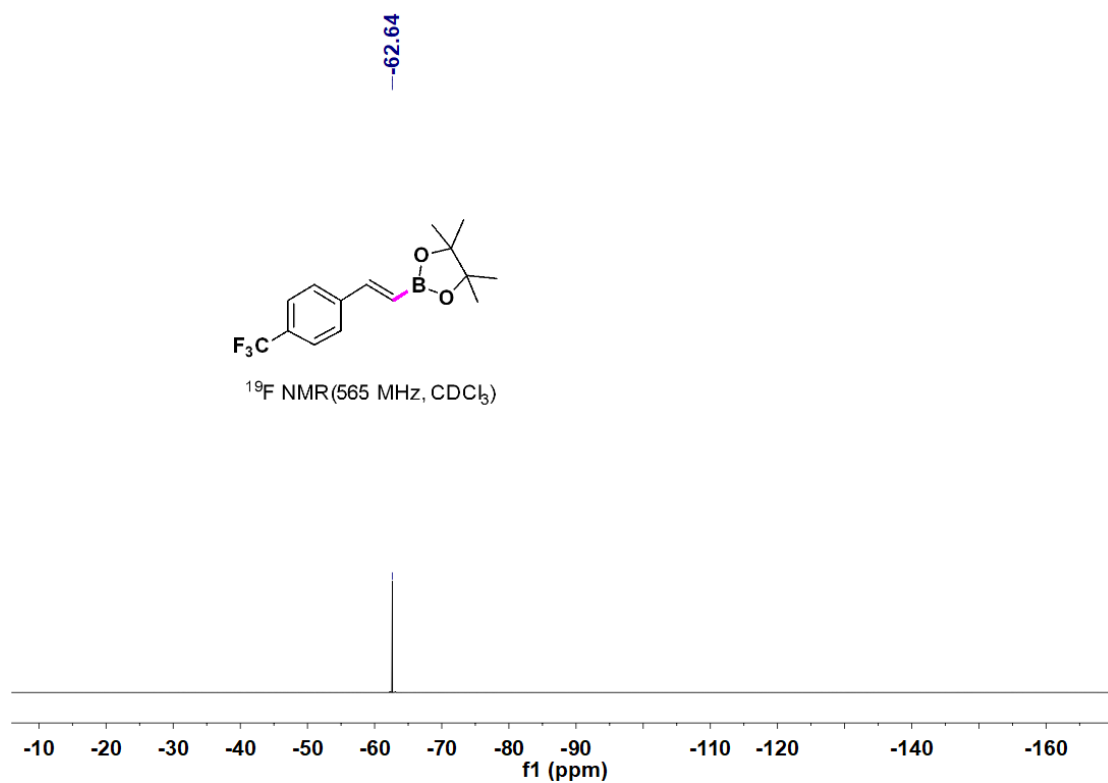
Supplementary Figure 143. Characterization of compound 4n. ¹³C{¹H} NMR spectrum of compound 4n in CDCl₃.



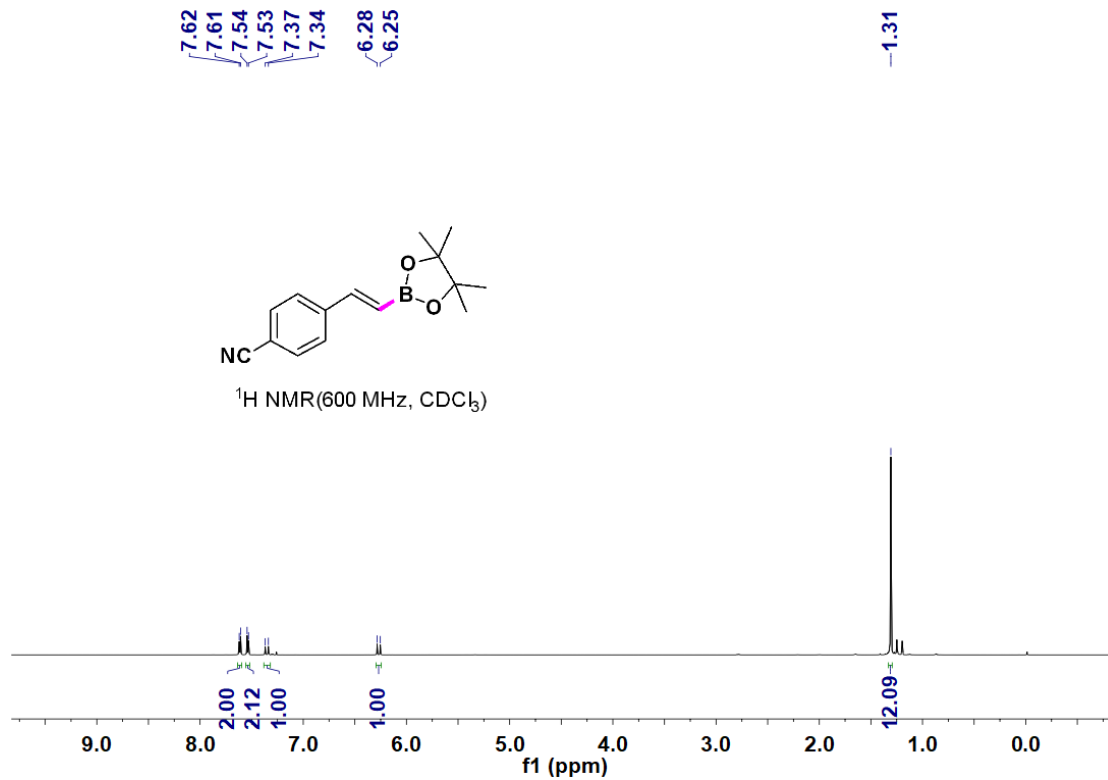
Supplementary Figure 144. Characterization of compound **4o.** ^1H NMR spectrum of compound **4o** in CDCl_3 .



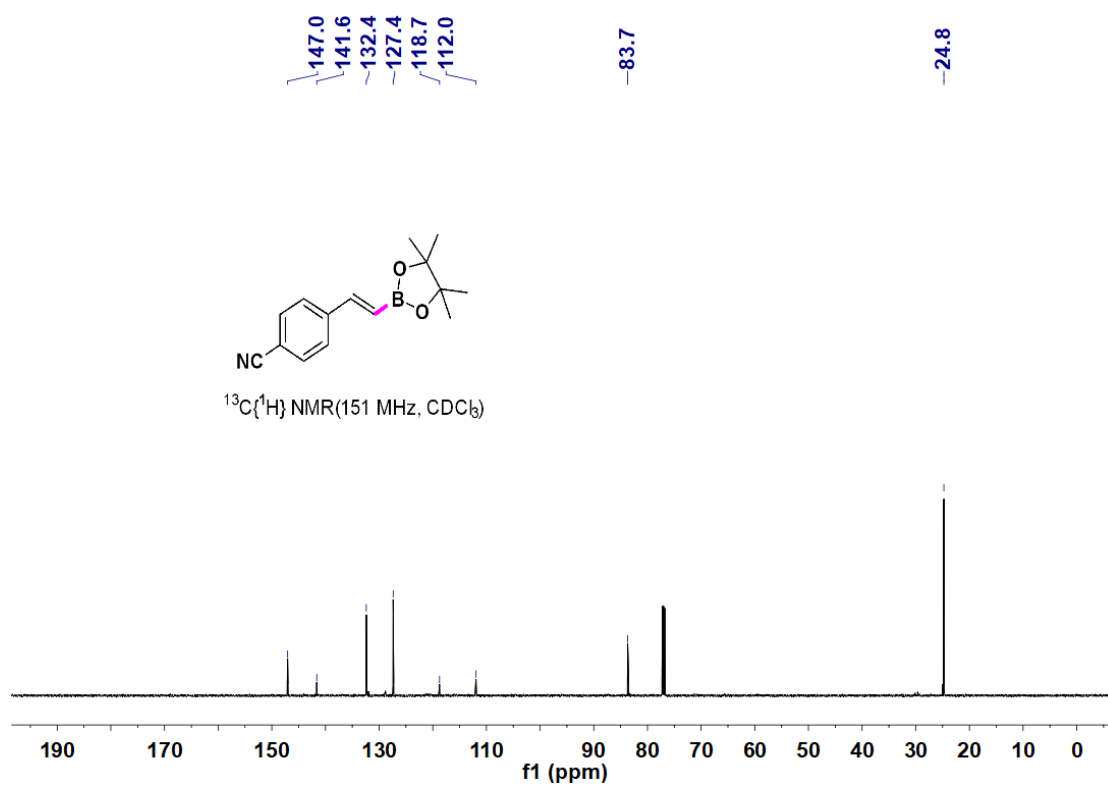
Supplementary Figure 145. Characterization of compound **4o.** $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **4o** in CDCl_3 .



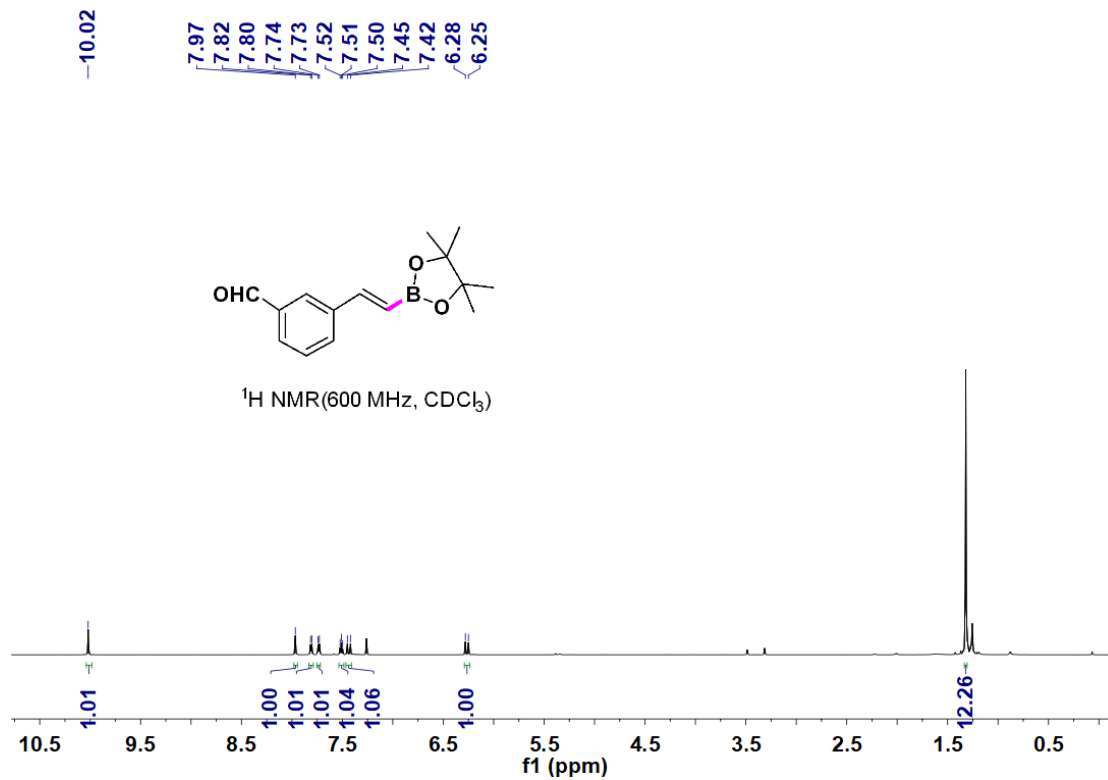
Supplementary Figure 146. Characterization of compound 4o. ^{19}F NMR spectrum of compound **4o** in CDCl_3 .



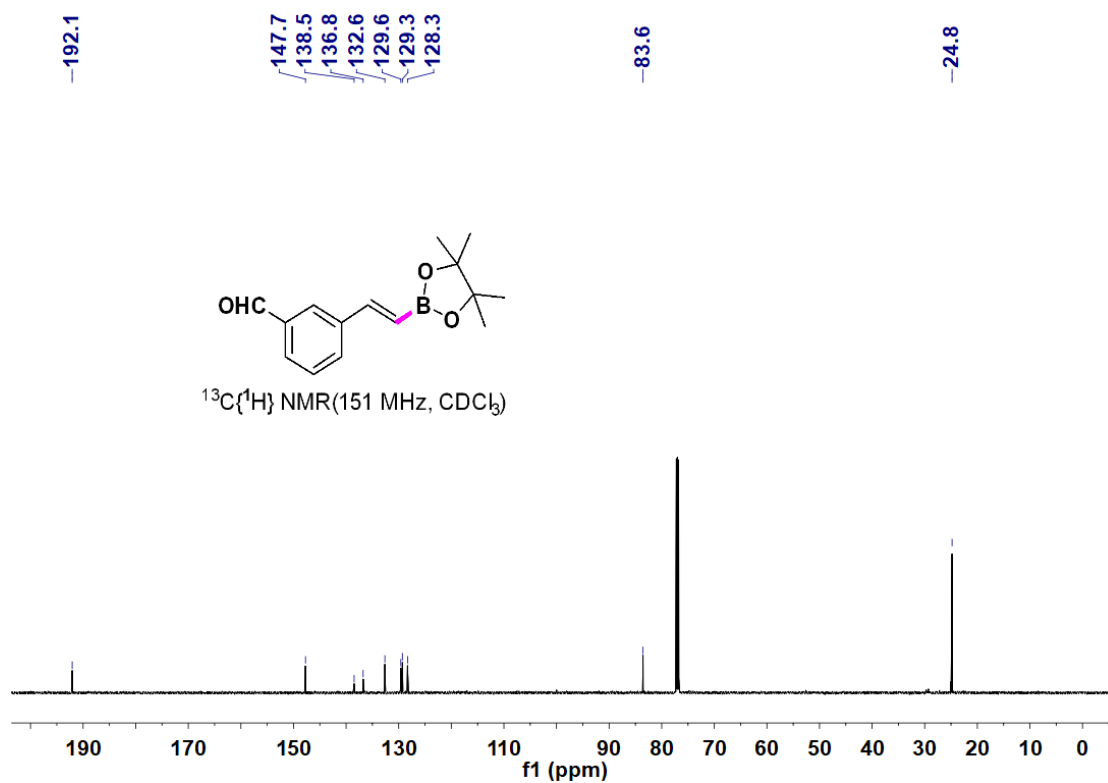
Supplementary Figure 147. Characterization of compound 4p. ^1H NMR spectrum of compound **4p** in CDCl_3 .



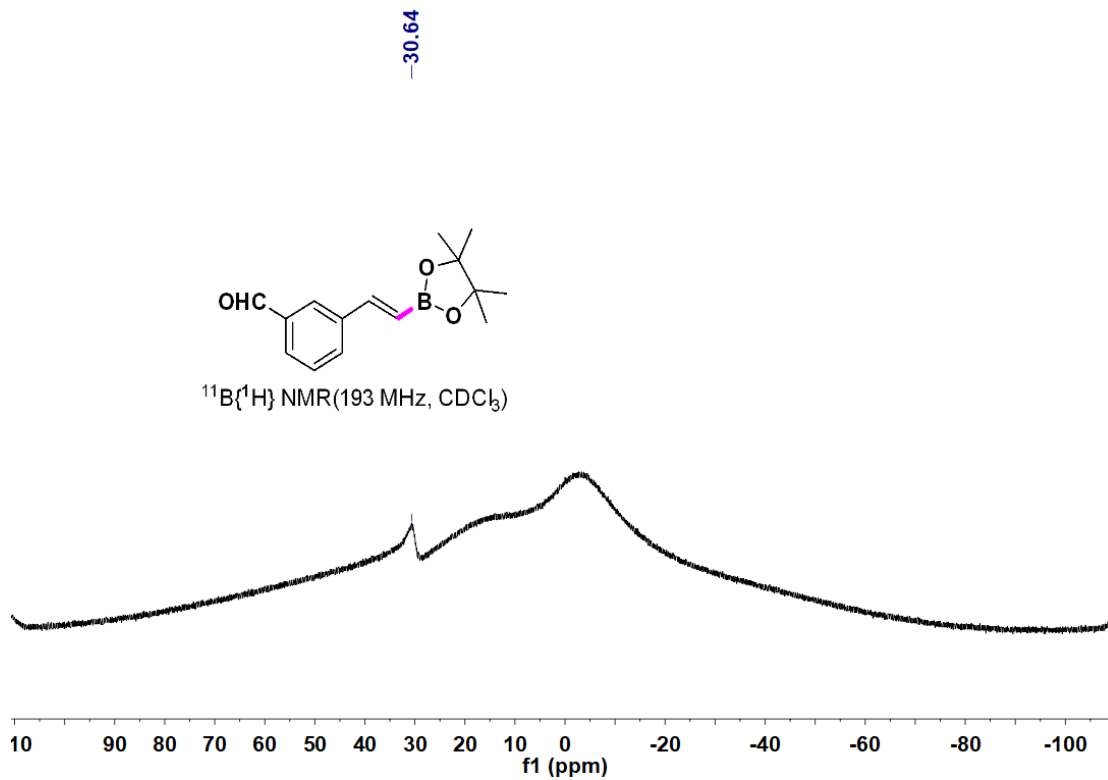
Supplementary Figure 148. Characterization of compound 4p. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **4p** in CDCl_3 .



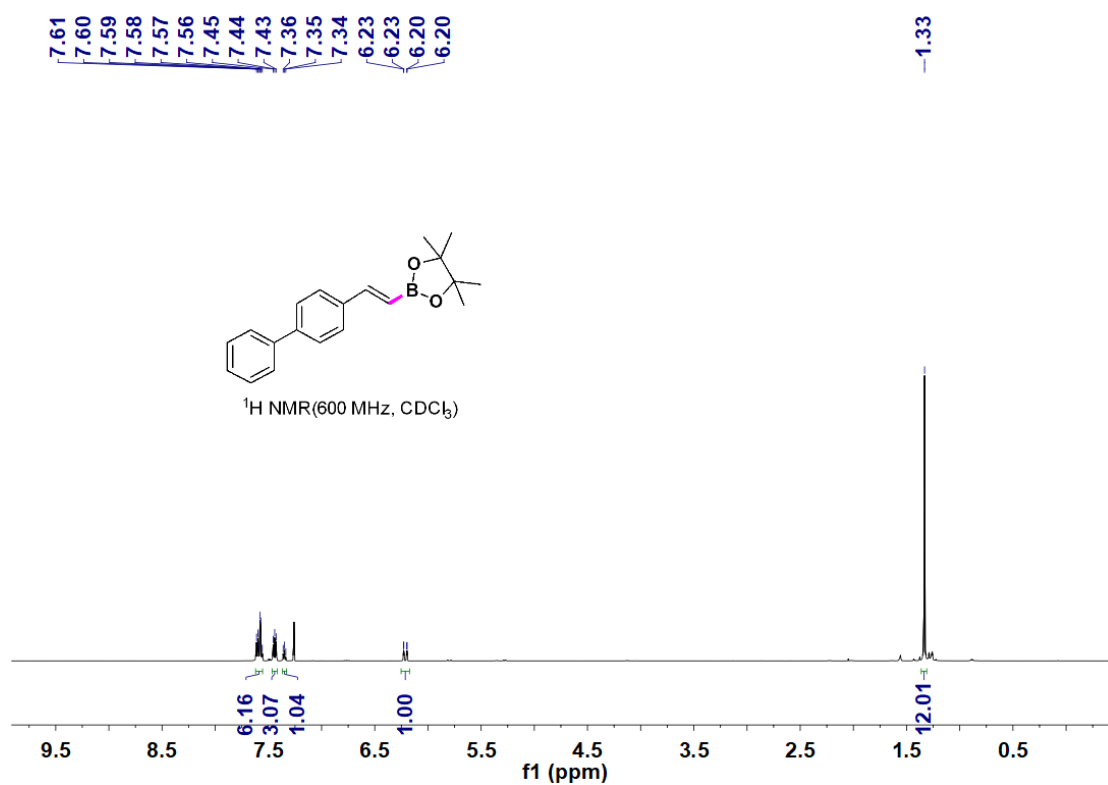
Supplementary Figure 149. Characterization of compound 4q. ^1H NMR spectrum of compound **4q** in CDCl_3 .



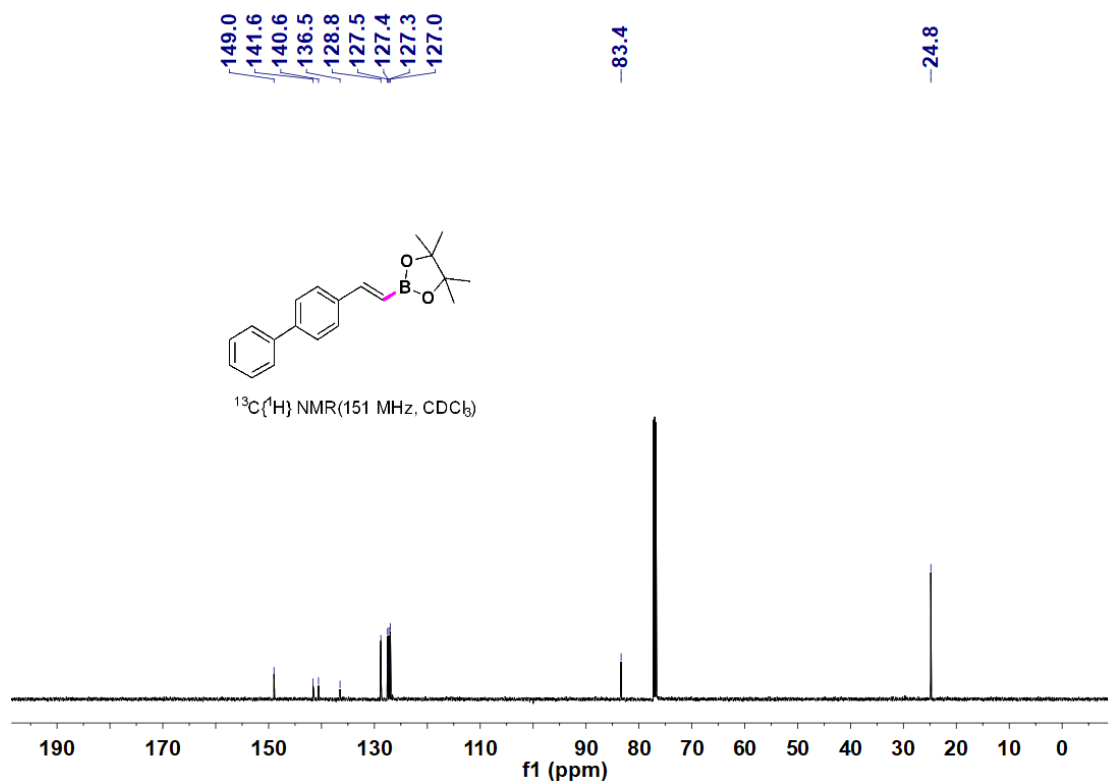
Supplementary Figure 150. Characterization of compound 4q. ¹³C{¹H} NMR spectrum of compound 4q in CDCl₃.



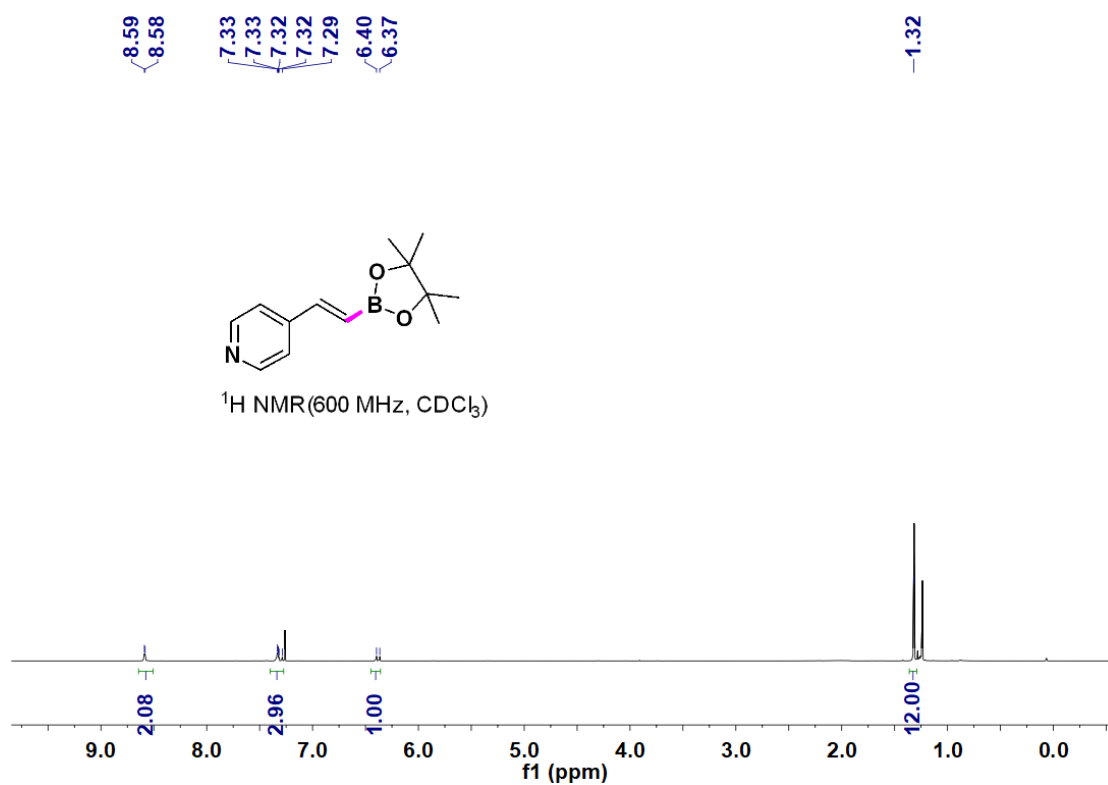
Supplementary Figure 151. Characterization of compound 4q. ¹¹B{¹H} NMR spectrum of compound 4q in CDCl₃.



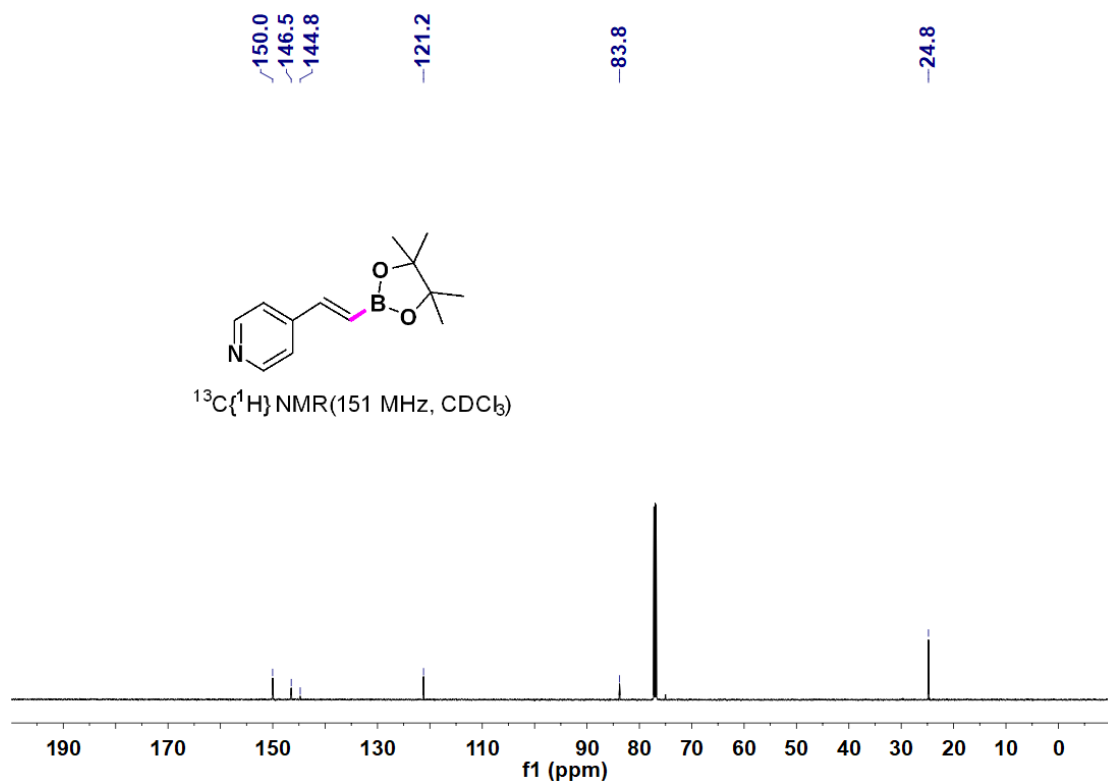
Supplementary Figure 152. Characterization of compound 4r. ¹H NMR spectrum of compound 4r in CDCl₃.



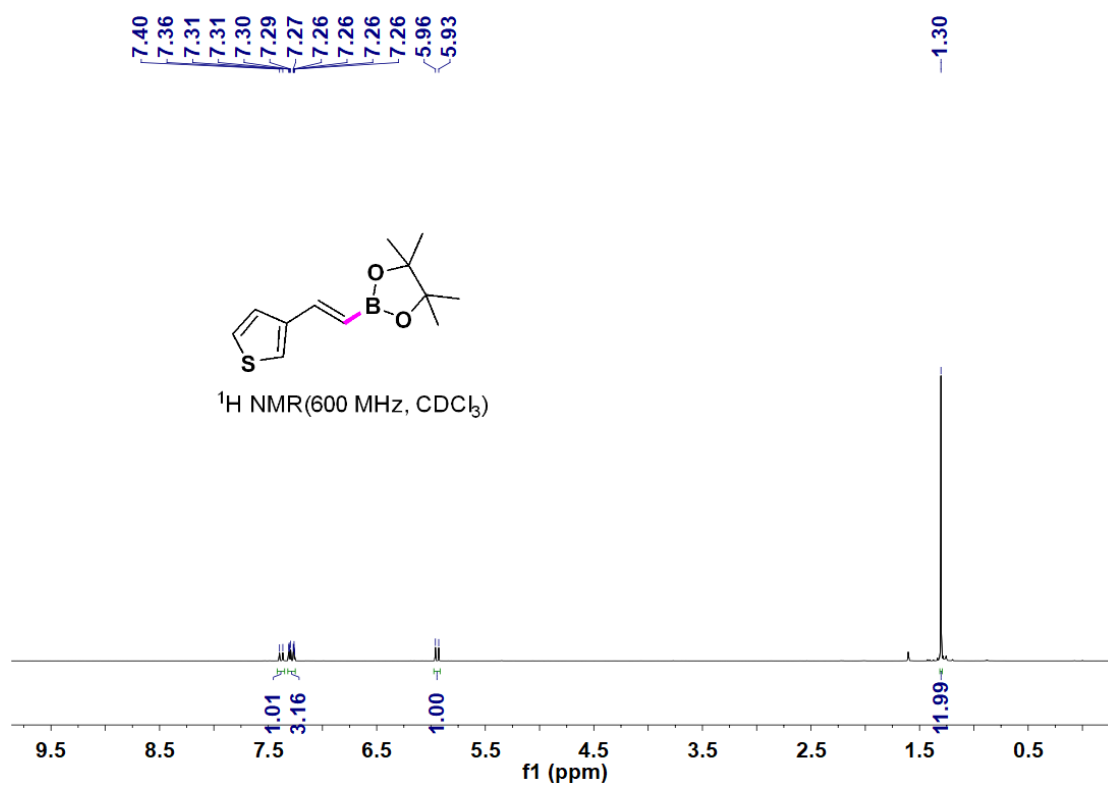
Supplementary Figure 153. Characterization of compound 4r. ¹³C{¹H} NMR spectrum of compound 4r in CDCl₃.



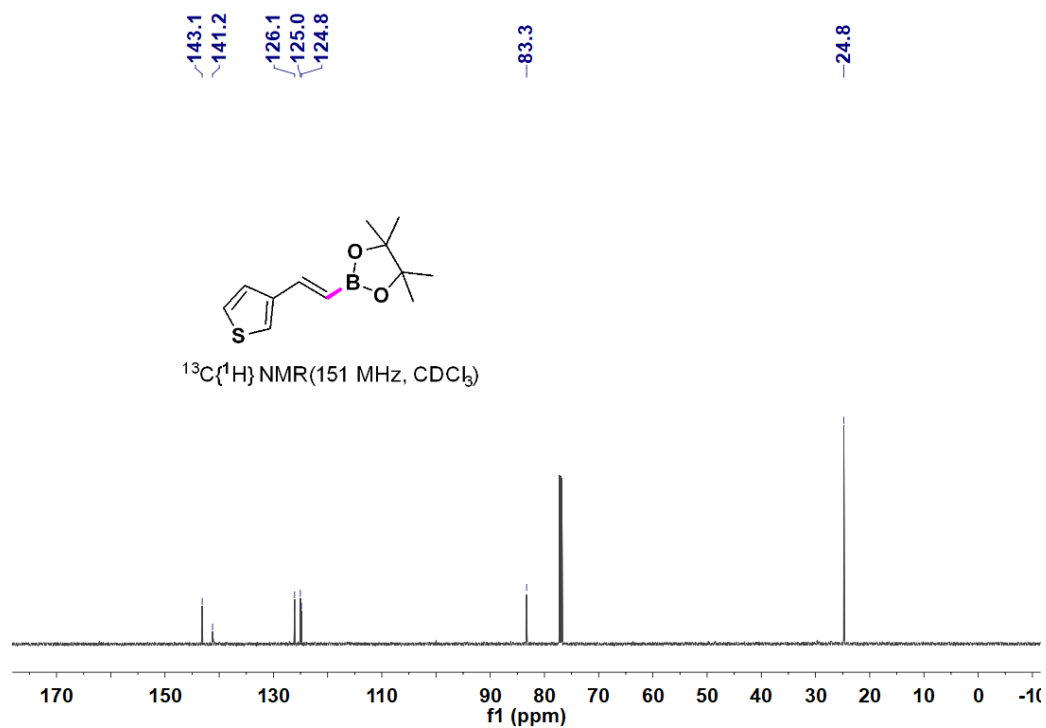
Supplementary Figure 154. Characterization of compound 4s. ^1H NMR spectrum of compound 4s in CDCl_3 .



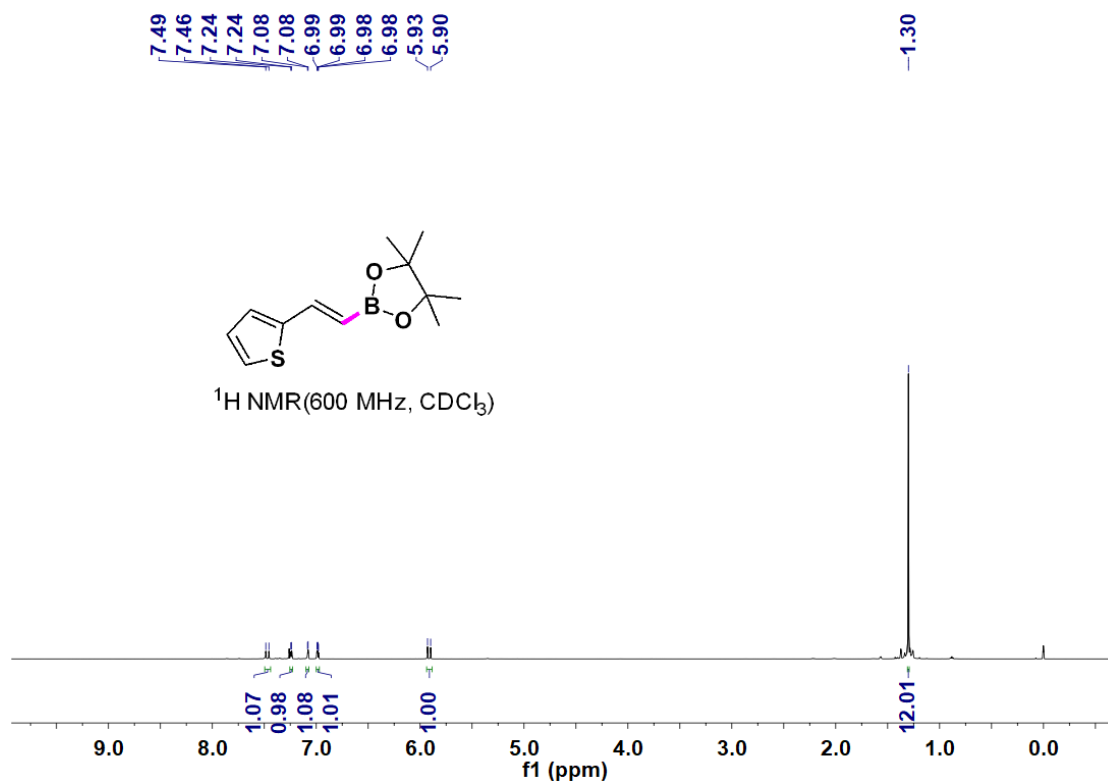
Supplementary Figure 155. Characterization of compound 4s. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound 4s in CDCl_3 .



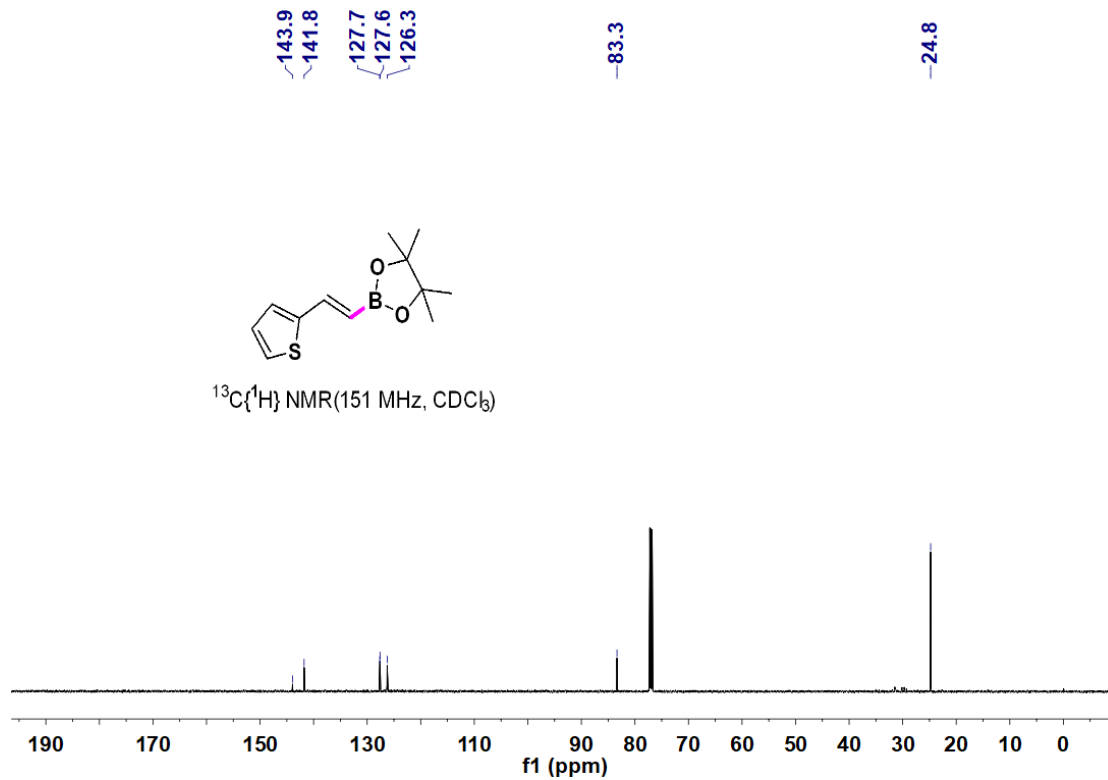
Supplementary Figure 156. Characterization of compound 4t. ¹H NMR spectrum of compound 4t in CDCl₃.



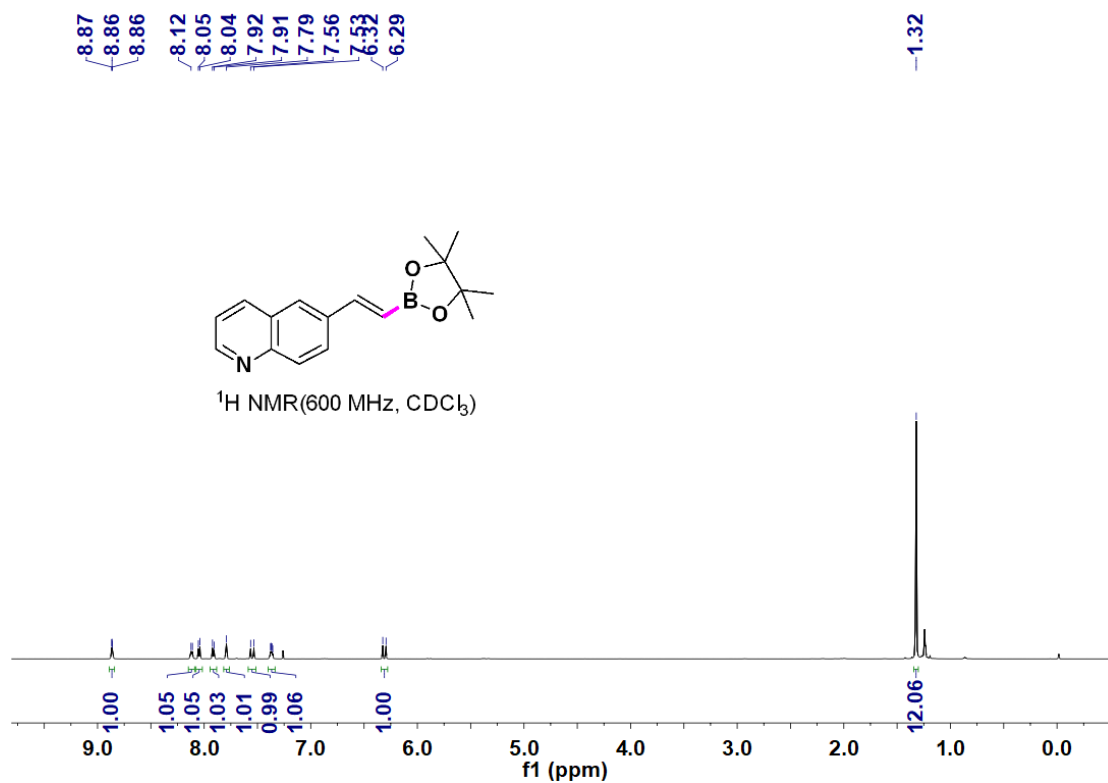
Supplementary Figure 157. Characterization of compound 4t. ¹³C{¹H} NMR spectrum of compound 4t in CDCl₃.



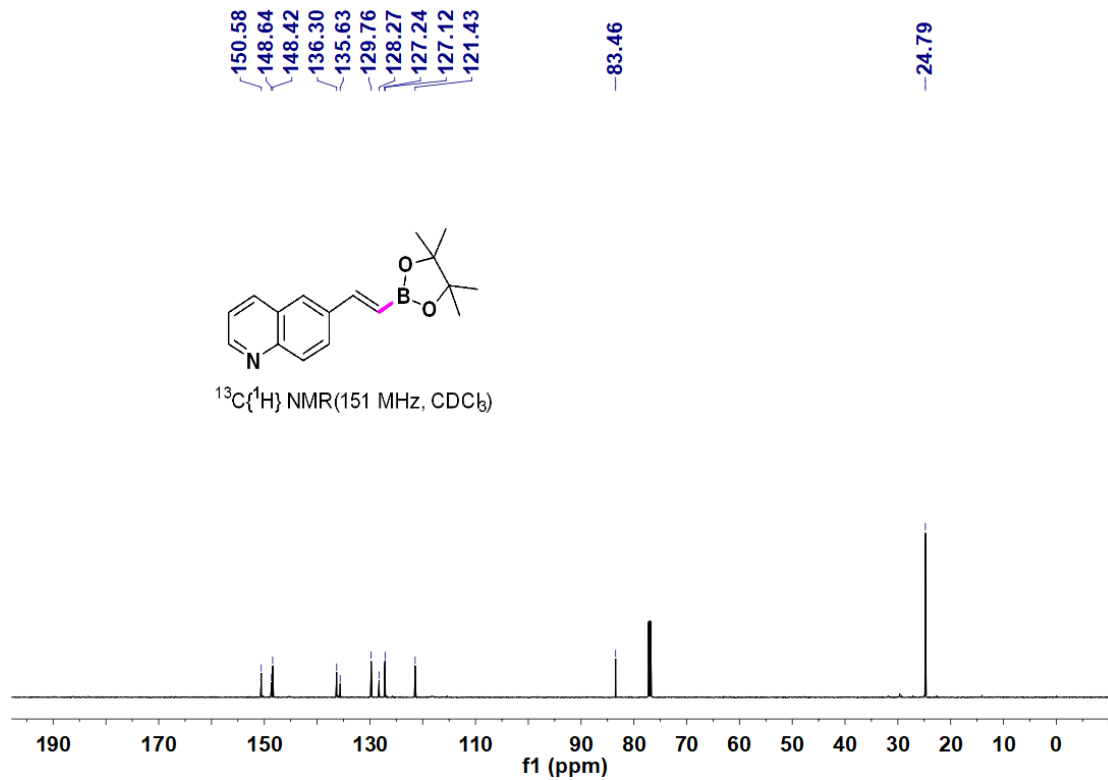
Supplementary Figure 158. Characterization of compound **4u.** ^1H NMR spectrum of compound **4u** in CDCl_3 .



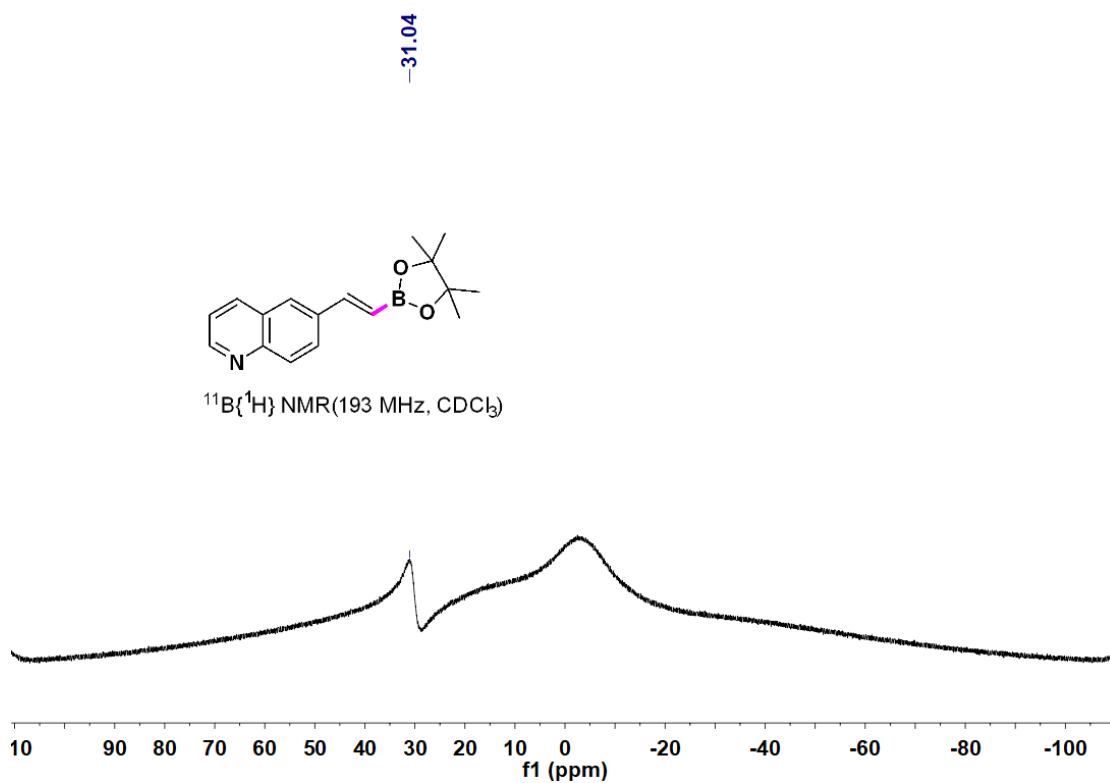
Supplementary Figure 159. Characterization of compound **4u.** $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **4u** in CDCl_3 .



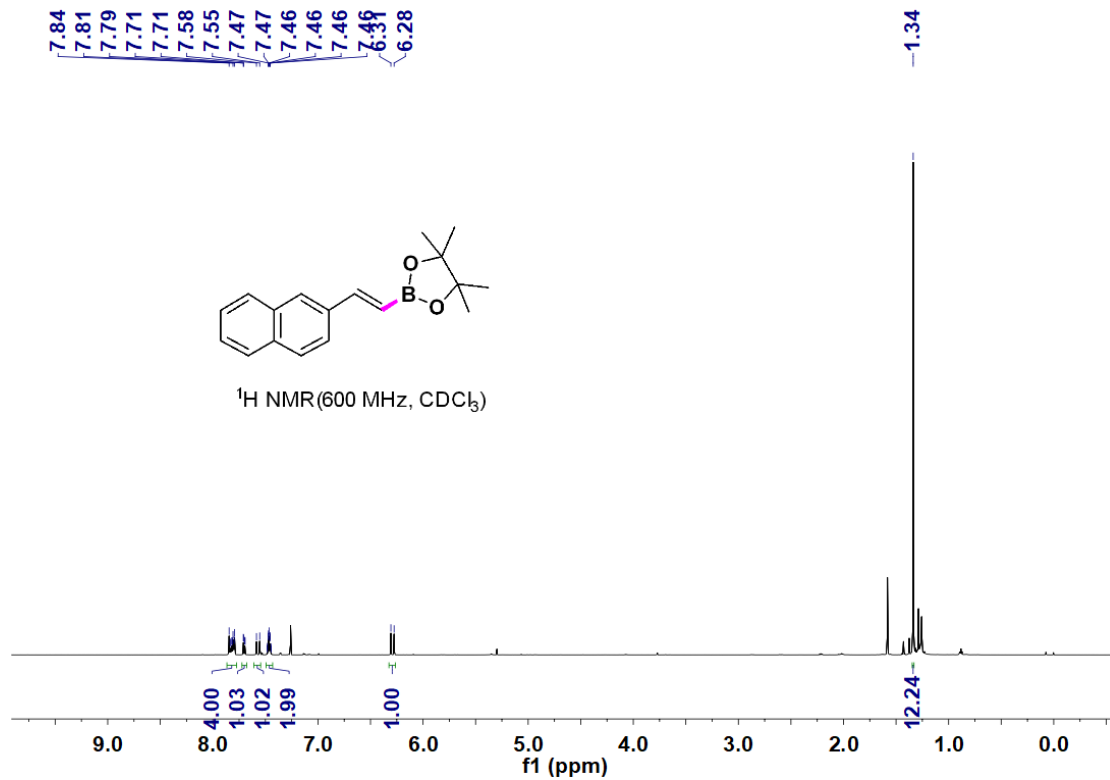
Supplementary Figure 160. Characterization of compound 4v. ¹H NMR spectrum of compound 4v in CDCl₃.



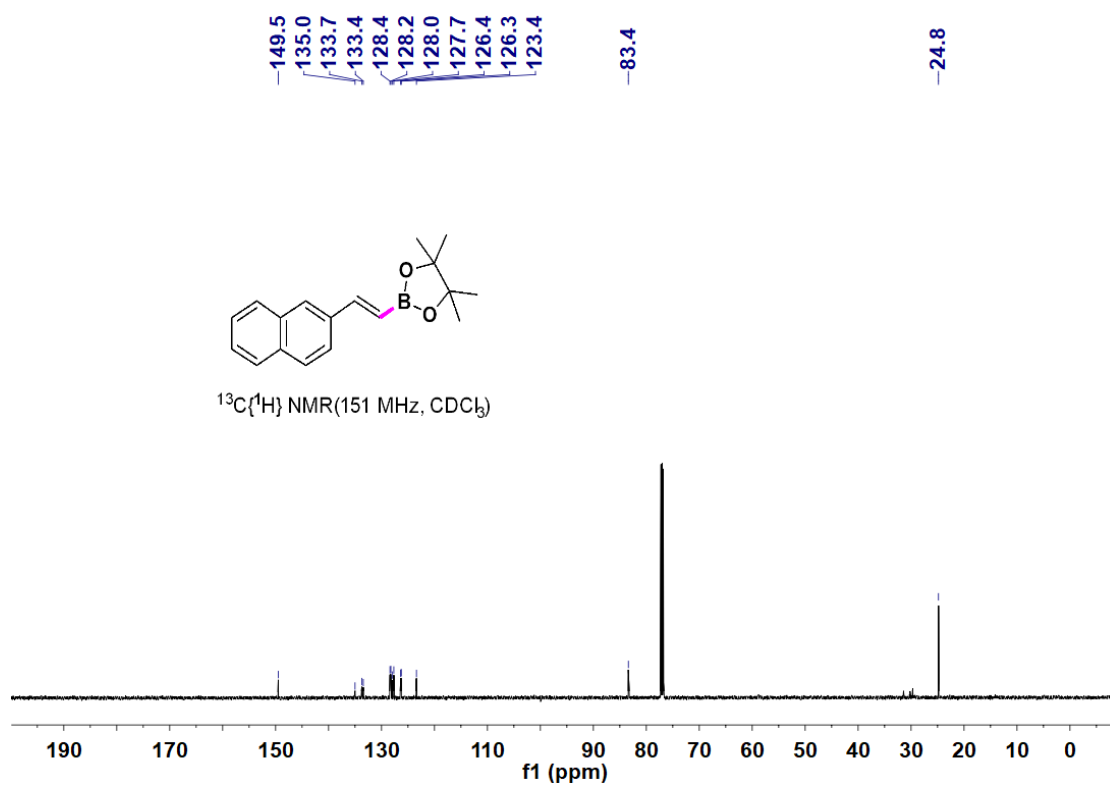
Supplementary Figure 161. Characterization of compound 4v. ¹³C{¹H} NMR spectrum of compound 4v in CDCl₃.



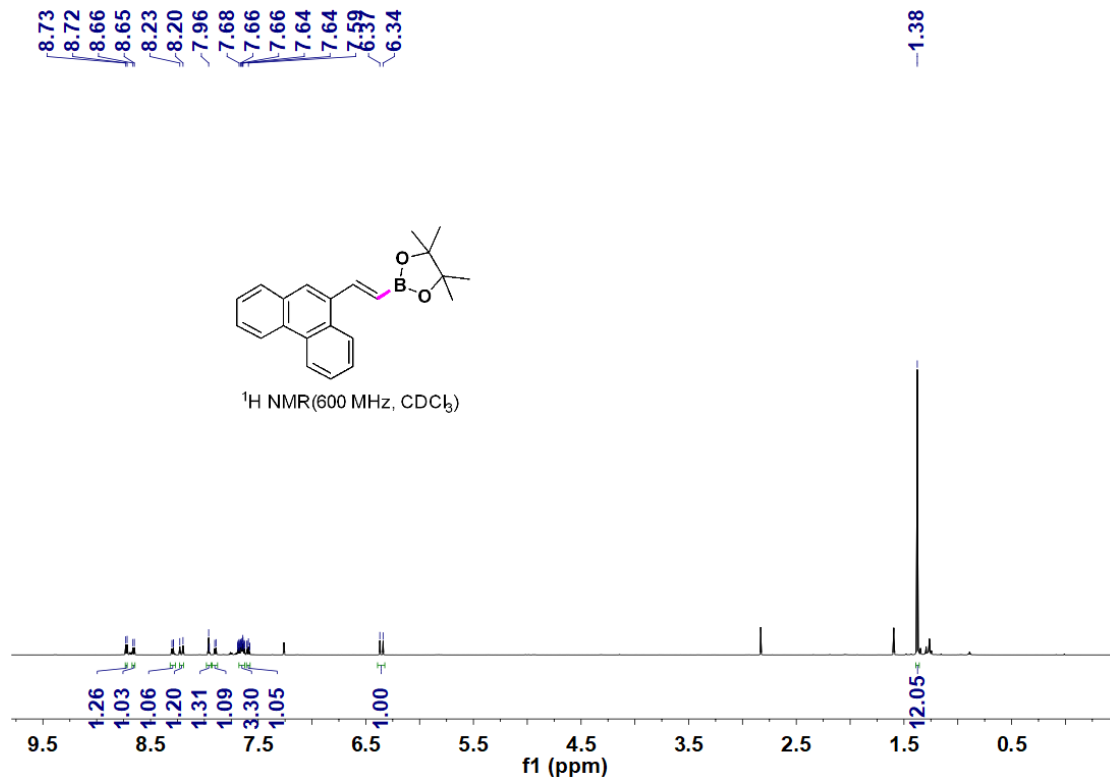
Supplementary Figure 162. Characterization of compound 4v. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of compound **4v** in CDCl_3 .



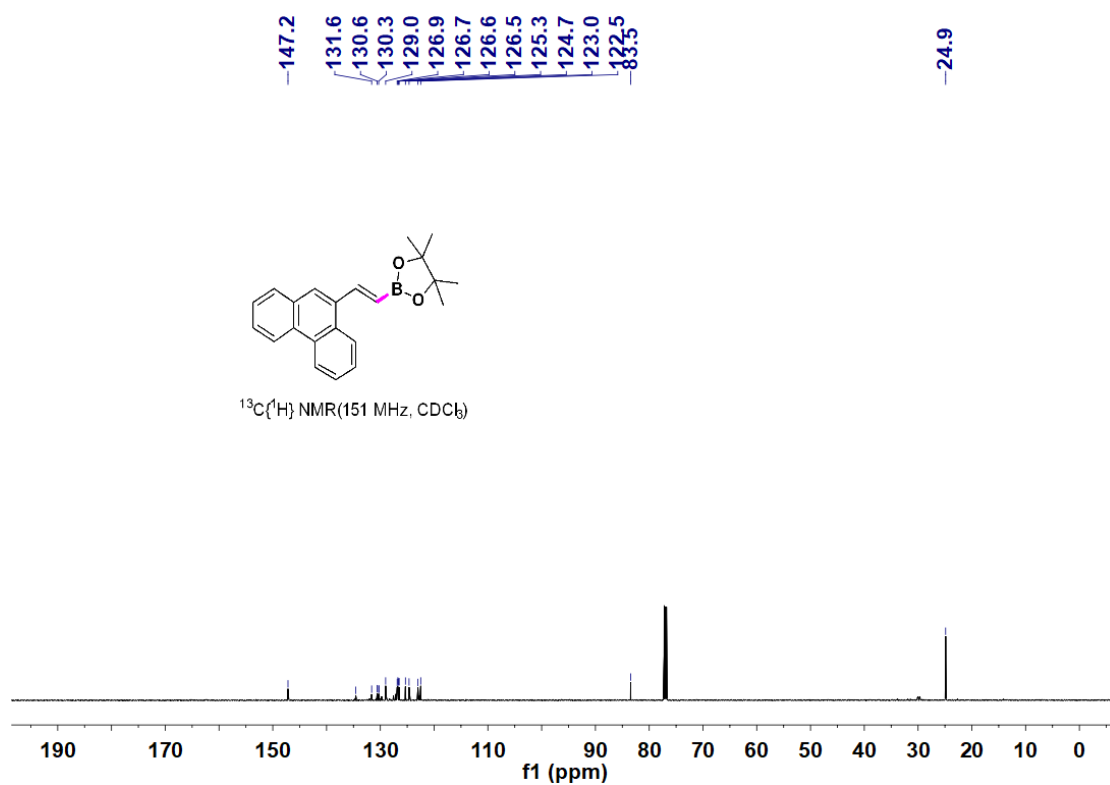
Supplementary Figure 163. Characterization of compound 4w. ^1H NMR spectrum of compound **4w** in CDCl_3 .



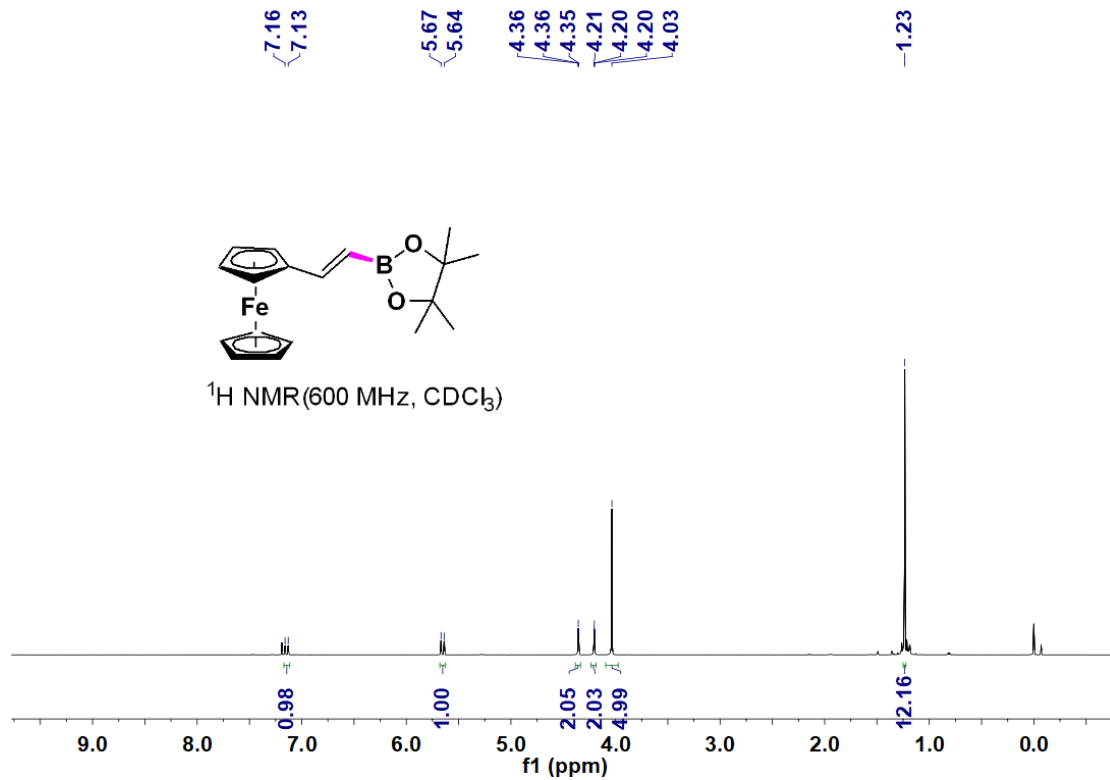
Supplementary Figure 164. Characterization of compound 4w. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **4w** in CDCl_3 .



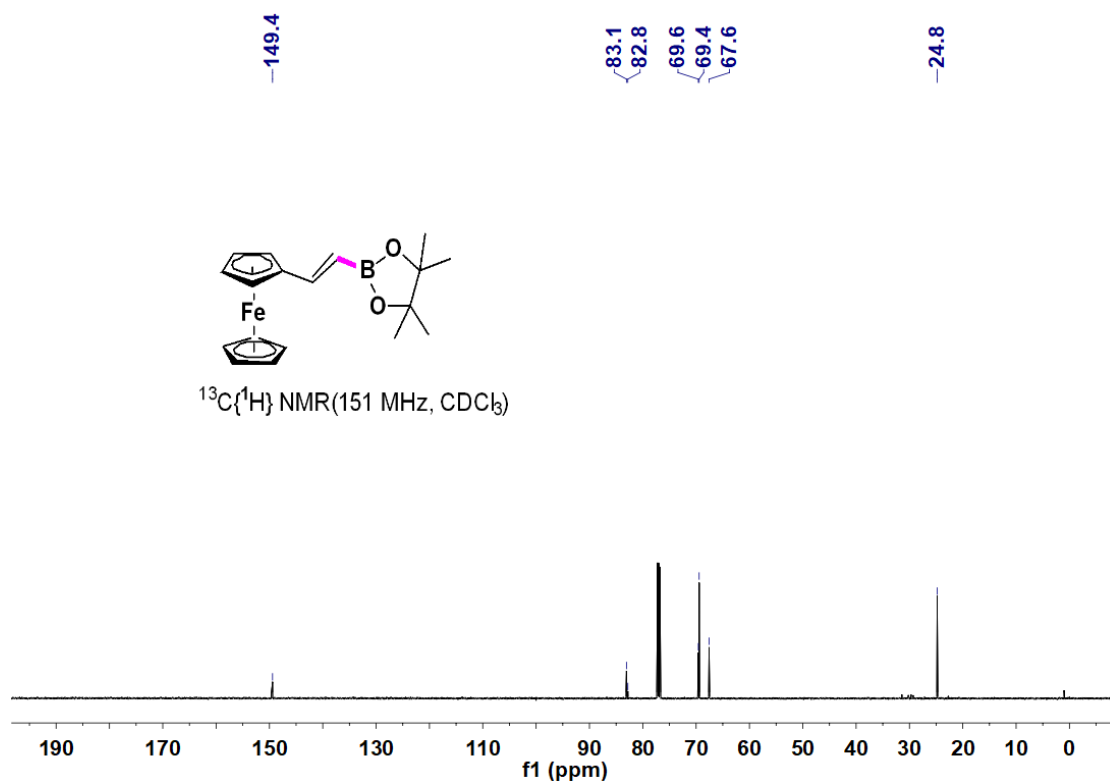
Supplementary Figure 165. Characterization of compound 4x. ^1H NMR spectrum of compound **4x** in CDCl_3 .



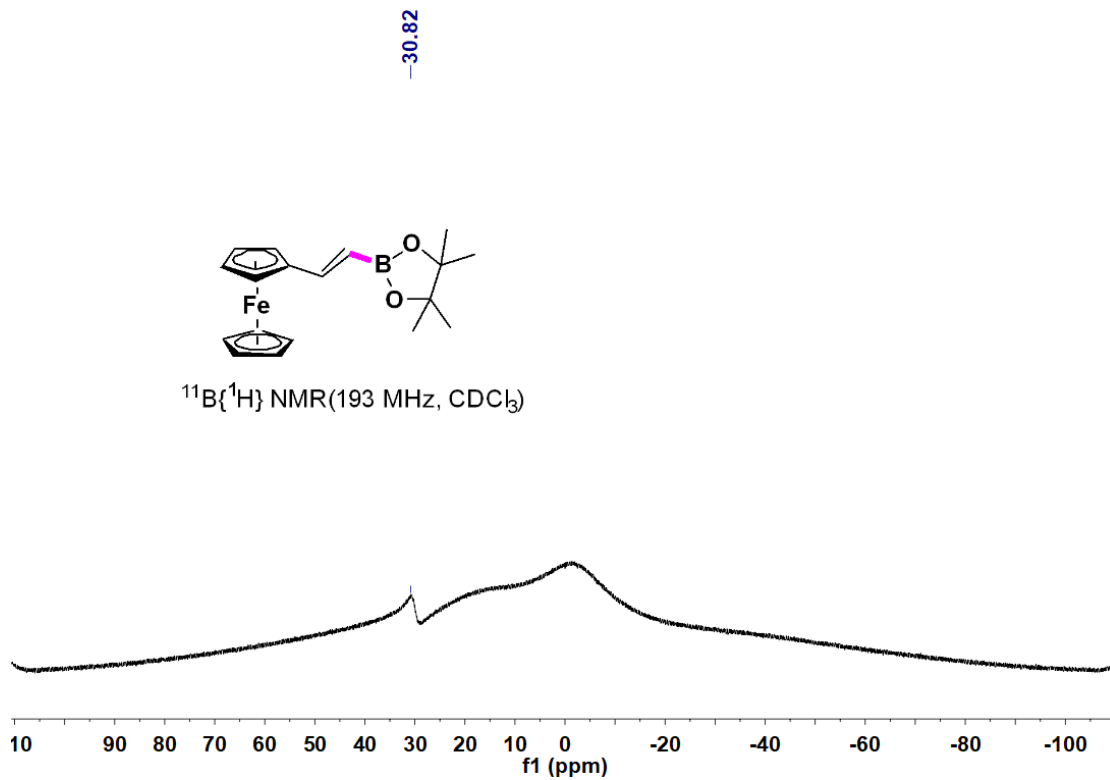
Supplementary Figure 166. Characterization of compound 4x. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound 4x in CDCl_3 .



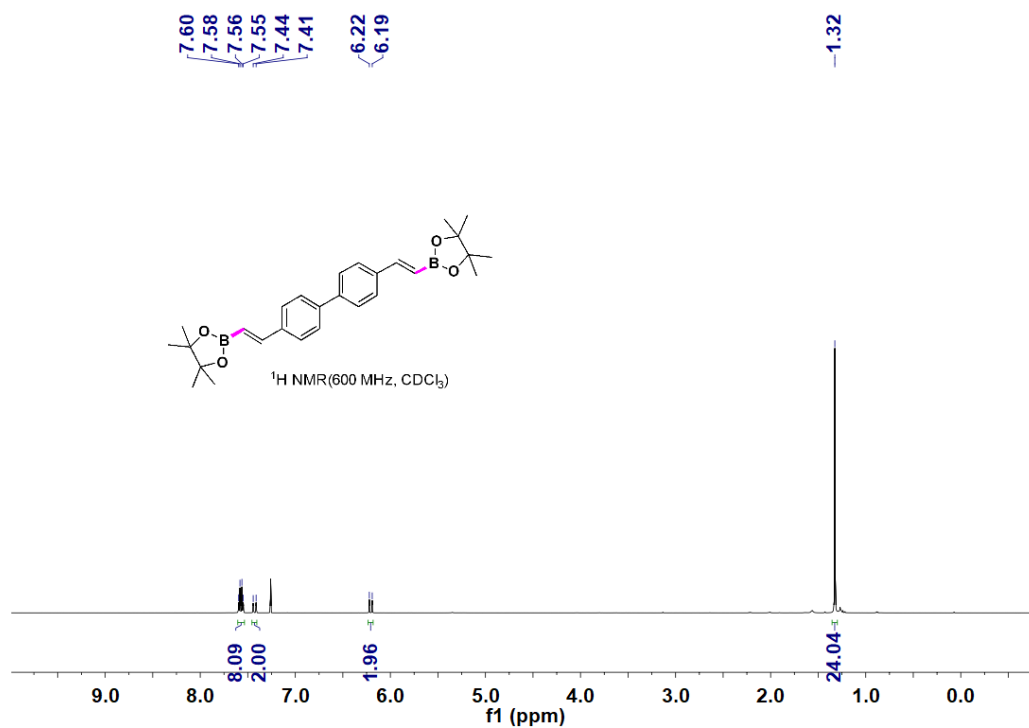
Supplementary Figure 167. Characterization of compound 4y. ^1H NMR spectrum of compound 4y in CDCl_3 .



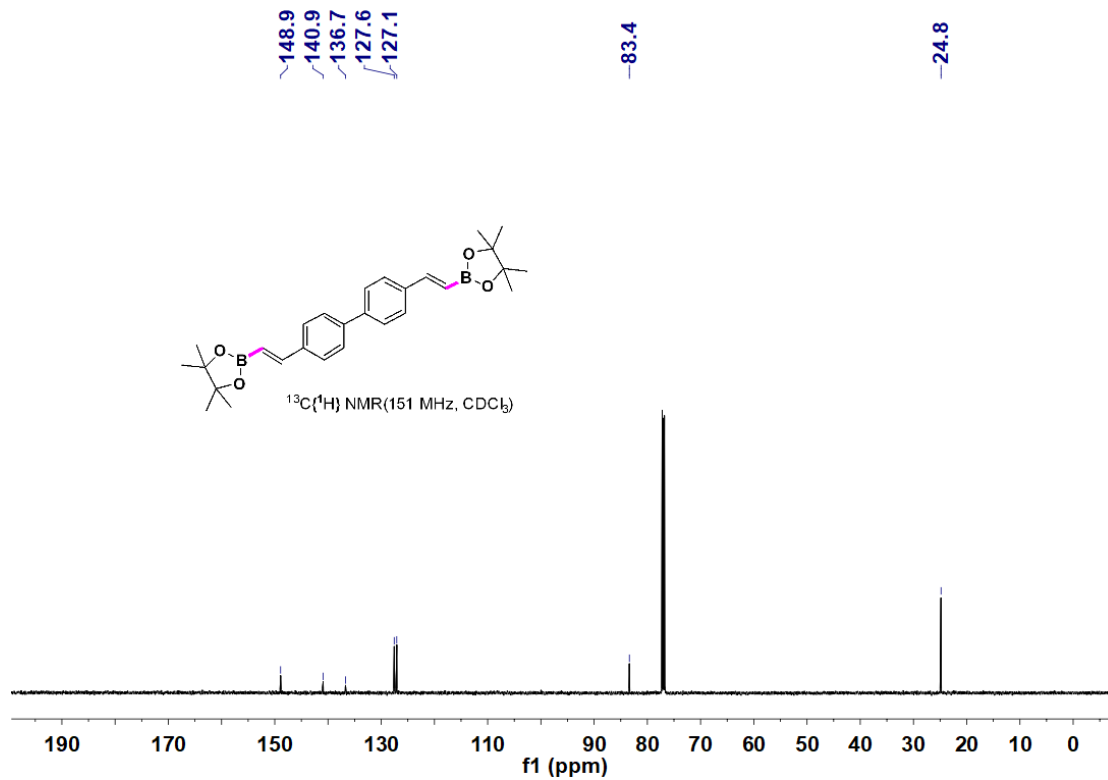
Supplementary Figure 168. Characterization of compound 4y. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **4y** in CDCl_3 .



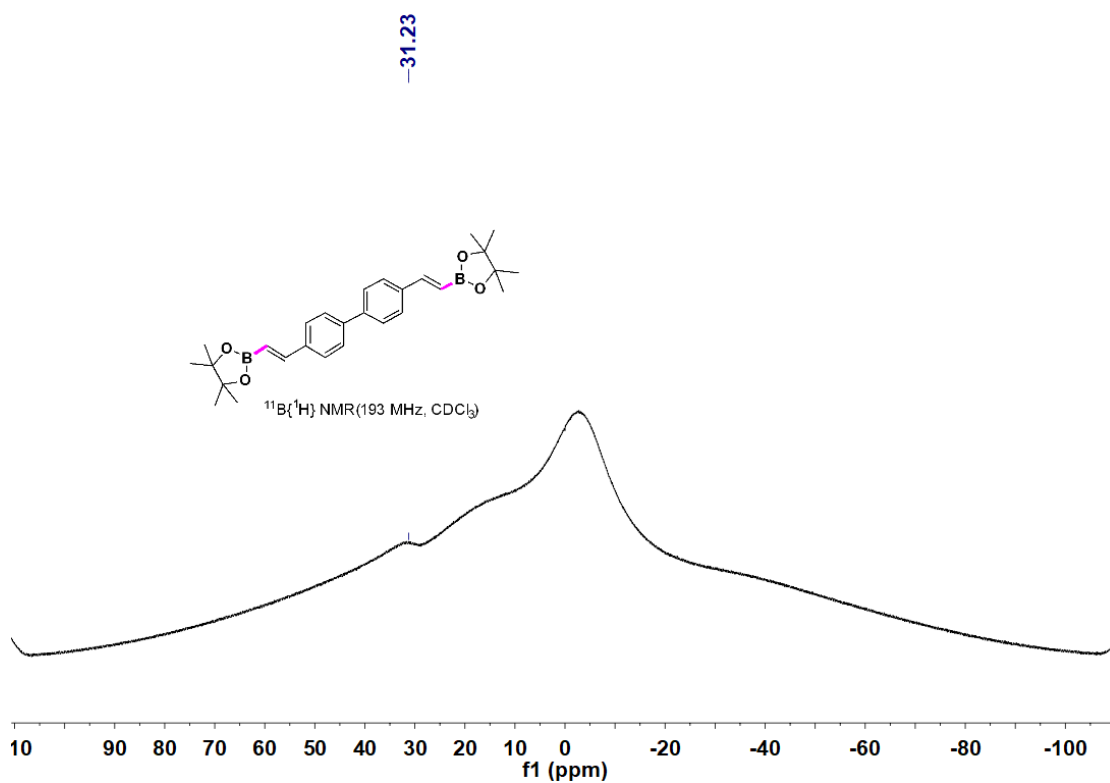
Supplementary Figure 169. Characterization of compound 4y. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of compound **4y** in CDCl_3 .



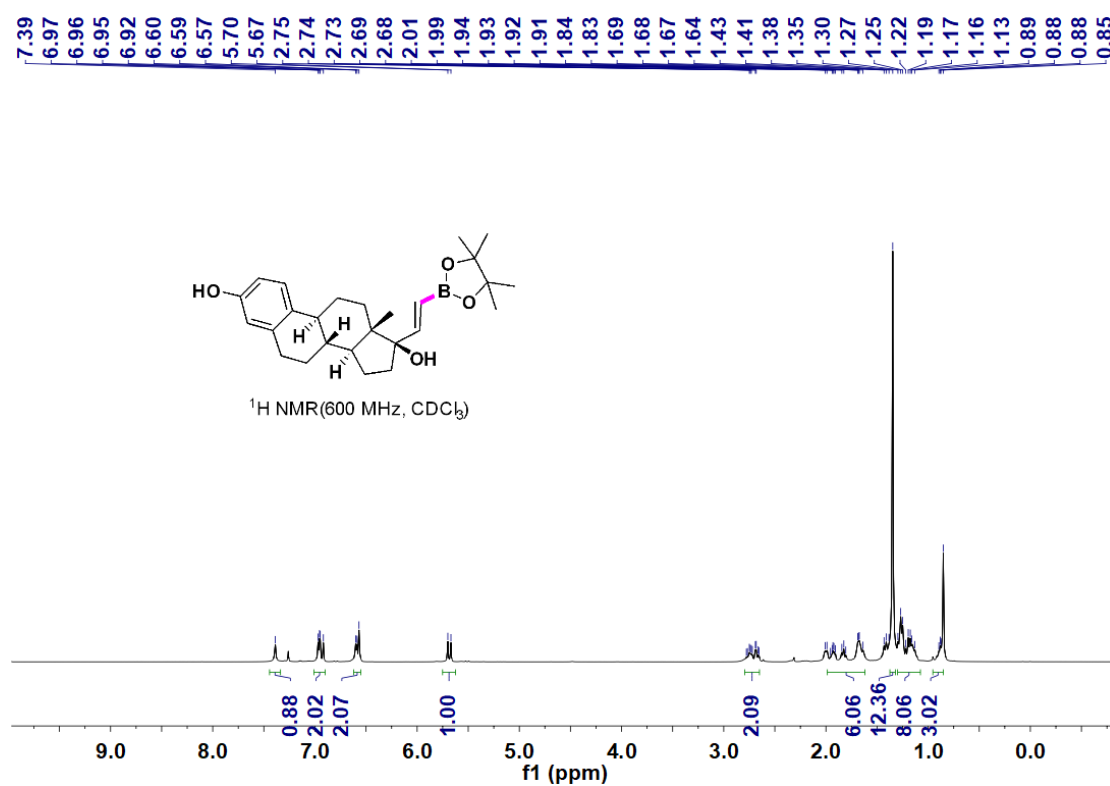
Supplementary Figure 170. Characterization of compound 4z. ¹H NMR spectrum of compound 4z in CDCl₃.



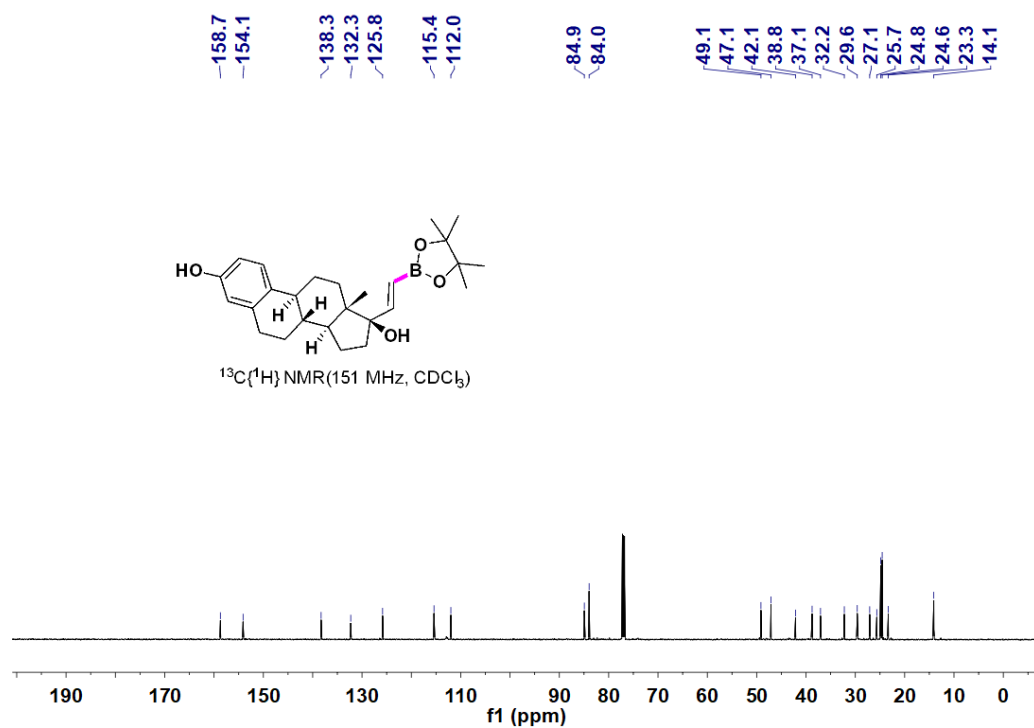
Supplementary Figure 171. Characterization of compound 4z. ¹³C{¹H} NMR spectrum of compound 4z in CDCl₃.



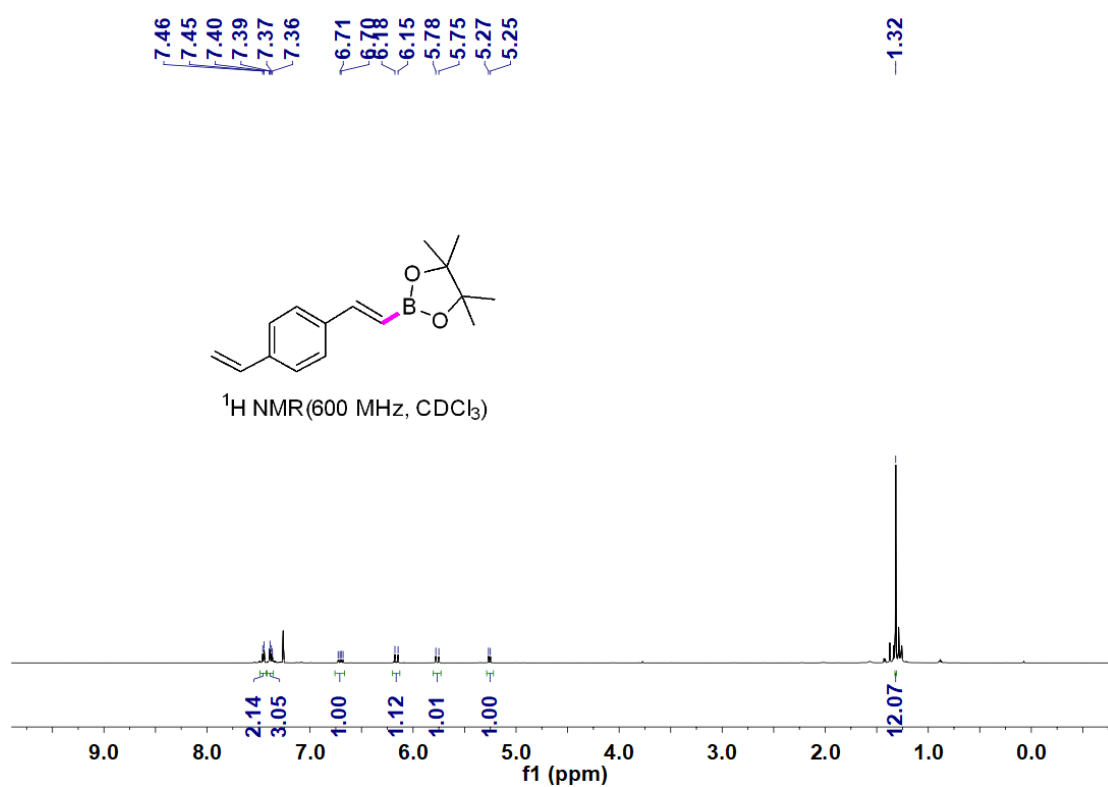
Supplementary Figure 172. Characterization of compound 4z. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of compound **4z** in CDCl_3 .



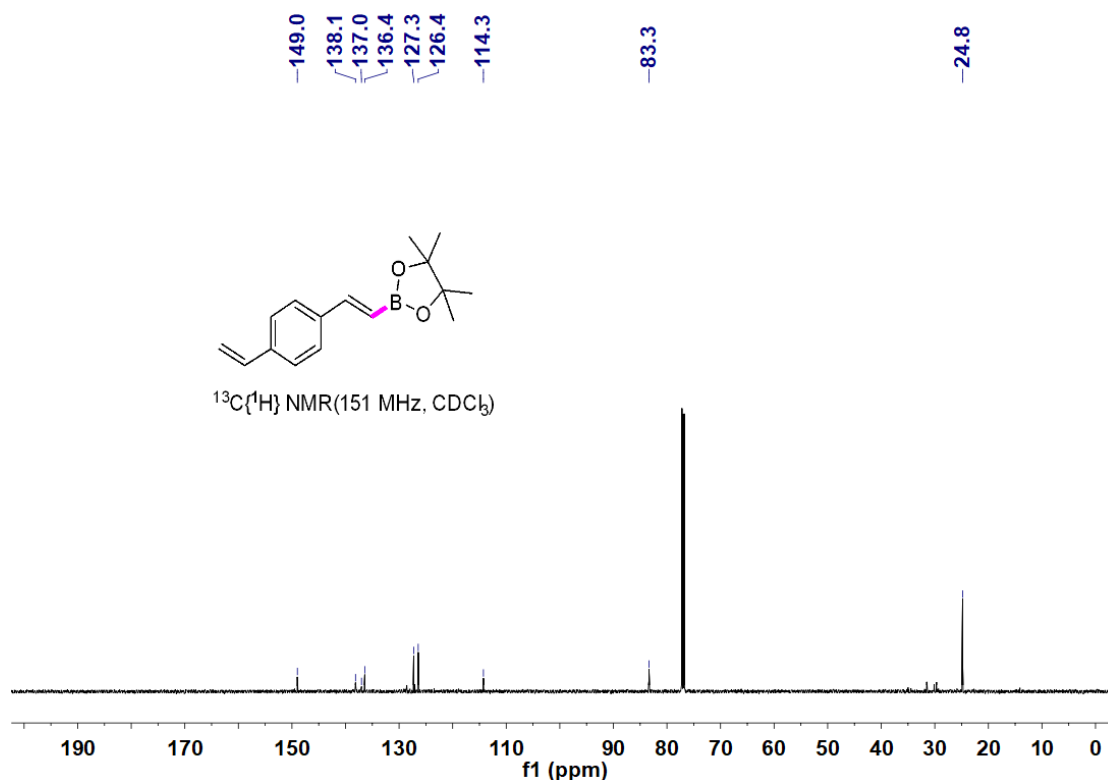
Supplementary Figure 173. Characterization of compound 4aa. ^1H NMR spectrum of compound **4aa** in CDCl_3 .



Supplementary Figure 174. Characterization of compound 4aa. ¹³C{¹H} NMR spectrum of compound 4aa in CDCl₃.



Supplementary Figure 175. Characterization of compound 4ab. ¹H NMR spectrum of compound 4ab in CDCl₃.



Supplementary Figure 176. Characterization of compound 4ab. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound 4ab in CDCl_3 .

Coordinates of the Structures

14

yne, E = -307.81480106, G = -307.734806

6	6.363200	-3.064867	2.069886
6	5.596234	-3.505268	3.144940
6	4.192504	-3.426475	3.090372
6	3.577006	-2.899275	1.940289
6	4.353218	-2.461555	0.870742
6	5.745722	-2.542728	0.931686
1	7.453097	-3.130023	2.121374
1	6.077686	-3.914202	4.036280
1	2.487293	-2.836600	1.894088
1	3.866313	-2.053362	-0.018674
1	6.351532	-2.198050	0.089595
6	3.399600	-3.878135	4.193187
6	2.727077	-4.262296	5.129564
1	2.129987	-4.602795	5.960671

3

H_2O , E = -76.283631047, G = -76.280445

8	2.310074	2.755575	5.923822
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1	2.325665	3.285407	5.117180
1	2.785837	1.958545	5.659129
42			
B ₂ pin ₂ , E = -821.03673632, G = -820.720244			
6	-3.001857	0.366375	-0.737938
6	-2.582417	0.068052	0.742536
6	0.352439	5.320638	0.668329
6	1.010730	4.848822	-0.673590
5	-1.552451	1.954670	0.000927
5	-0.558890	3.347965	-0.000730
8	-2.030746	1.360632	-1.135101
8	-1.957201	1.309954	1.137848
8	-0.343338	4.129905	1.101164
8	0.109161	3.804304	-1.104241
6	-2.908278	-0.819381	-1.677791
1	-3.572110	-1.630679	-1.342867
1	-3.222310	-0.517571	-2.688480
1	-1.883129	-1.207583	-1.742148
6	-4.372495	1.022423	-0.848655
1	-4.508533	1.392539	-1.875842
1	-5.180710	0.310044	-0.628871
1	-4.462392	1.878632	-0.163255
6	-1.517020	-1.015412	0.853737
1	-1.122662	-1.023285	1.880919
1	-1.929015	-2.011103	0.634856
1	-0.677990	-0.823570	0.168067
6	-3.733403	-0.227595	1.683840
1	-4.284838	-1.119926	1.351128
1	-3.344801	-0.424378	2.694496
1	-4.433852	0.615678	1.747259
6	1.089524	5.910954	-1.752368
1	1.697711	6.762447	-1.411617
1	1.564468	5.491460	-2.652166
1	0.094311	6.279788	-2.033922
6	2.373369	4.197367	-0.472724
1	2.675048	3.706248	-1.409976
1	3.141145	4.939091	-0.209361
1	2.338476	3.431958	0.317159
6	-0.705348	6.398659	0.467466
1	-1.266181	6.526229	1.405486
1	-0.252519	7.364888	0.202140
1	-1.419448	6.116646	-0.320845
6	1.333073	5.740202	1.745586
1	1.942175	6.590341	1.403086

1	0.783592	6.055605	2.645457
1	2.003757	4.917831	2.027767
36			
pdt, E = -719.01388375, G = -718.751496			
5	2.344927	-5.731097	5.844576
8	1.008355	-5.760143	5.547592
8	2.651421	-6.411914	6.990829
6	0.326356	-6.304966	6.696620
6	1.465393	-7.129085	7.395490
6	-0.856528	-7.128296	6.227291
6	-0.148233	-5.122411	7.531831
6	1.596217	-8.544008	6.846154
6	1.393314	-7.155374	8.909231
1	-1.337020	-7.633927	7.078386
1	-1.602701	-6.470706	5.756090
1	-0.557123	-7.885719	5.490745
1	-0.779285	-4.474964	6.904698
1	-0.742213	-5.449826	8.397206
1	0.700377	-4.522938	7.894860
1	2.532423	-8.985603	7.219221
1	0.761138	-9.182106	7.169172
1	1.633346	-8.544118	5.746272
1	0.448865	-7.611449	9.242257
1	2.222640	-7.757606	9.310186
1	1.467353	-6.146733	9.336981
6	6.126910	-2.803670	2.232703
6	5.333691	-3.518517	3.124070
6	3.934002	-3.544692	2.979637
6	3.362521	-2.831303	1.911623
6	4.157035	-2.114723	1.018389
6	5.542917	-2.098213	1.175995
1	7.212650	-2.795171	2.361048
1	5.806931	-4.065385	3.943401
1	2.275806	-2.843052	1.785876
1	3.691322	-1.566812	0.194924
1	6.169793	-1.537669	0.477402
6	3.051879	-4.280411	3.892013
6	3.401176	-5.002428	4.976797
1	4.459241	-5.077648	5.256405
1	1.985479	-4.218280	3.639121
55			
1A, E = -9885.6424861, G = -9885.337297			
29	3.779606	3.687606	9.638277
16	2.205070	0.670088	10.276902

7	3.982184	2.520573	11.315770
7	3.698692	0.730527	12.567905
6	3.361073	1.348866	11.405577
6	4.734461	2.659010	12.452585
1	5.348979	3.539933	12.630411
6	4.569351	1.553874	13.244511
1	4.985312	1.276729	14.210655
6	3.208054	-0.550792	13.018331
1	2.114204	-0.525413	13.132091
1	3.665138	-0.784191	13.987626
1	3.469993	-1.339032	12.297882
29	0.843163	2.512311	10.259378
16	2.435399	5.559803	9.644097
7	1.103819	4.080638	11.567069
7	1.751023	6.074554	12.246322
6	1.707675	5.206255	11.202107
6	0.750110	4.230419	12.881758
1	0.232988	3.443644	13.429032
6	1.147030	5.465680	13.322025
1	1.054376	5.965308	14.283907
6	2.363585	7.382684	12.237039
1	1.970495	7.983128	11.404731
1	3.455391	7.298820	12.127020
1	2.135682	7.888547	13.183149
29	1.360468	4.030823	8.312803
16	5.001345	2.562462	7.994880
7	6.030862	0.227380	9.011035
7	6.935291	2.065270	9.862711
6	6.025619	1.549371	8.981002
6	6.969595	-0.121171	9.944034
1	7.187333	-1.163061	10.182813
6	7.542719	1.003493	10.486492
1	8.309955	1.146835	11.244821
6	7.203850	3.461741	10.096451
1	6.262690	3.999957	10.285724
1	7.858522	3.559945	10.971160
1	7.694501	3.920323	9.224377
29	2.635882	1.822873	8.339699
16	-0.866804	3.297899	8.893561
7	-1.047824	0.761835	7.808600
7	-1.176849	2.407071	6.328473
6	-1.041301	2.075496	7.652268
6	-1.191012	0.231145	6.554868
1	-1.225898	-0.845832	6.384907

6	-1.274996	1.231731	5.618702
1	-1.392759	1.223322	4.536873
6	-1.210188	3.742344	5.782531
1	-0.333356	4.308703	6.131178
1	-1.189873	3.681381	4.687240
1	-2.118893	4.276491	6.097715
19	3.803802	4.175801	5.709448
8	1.930088	2.866883	6.741220
1	1.144966	2.425269	6.396535

97

Int1, E = -10706.738221, G = 10706.089262

29	4.076256	3.107105	9.334542
16	1.712045	0.636517	9.317447
7	3.977546	1.516472	10.633454
7	3.310871	-0.495548	11.236780
6	3.072710	0.564625	10.421790
6	4.815095	1.054493	11.614560
1	5.654962	1.644441	11.977482
6	4.415159	-0.196880	12.002203
1	4.807945	-0.895747	12.737380
6	2.548070	-1.721423	11.274972
1	1.490372	-1.509288	11.487541
1	2.951241	-2.366000	12.065449
1	2.616850	-2.248135	10.311745
29	1.128948	2.797326	9.860262
16	3.439495	5.293649	9.701603
7	1.752751	3.951855	11.423284
7	2.815673	5.643313	12.352697
6	2.609785	4.944224	11.207060
6	1.398998	4.015454	12.745424
1	0.697873	3.309009	13.187309
6	2.053379	5.061984	13.340084
1	2.047298	5.445199	14.358161
6	3.701835	6.773216	12.509550
1	3.586006	7.176893	13.522708
1	3.455143	7.557556	11.780113
1	4.748637	6.468606	12.361093
29	2.000828	4.424368	8.137015
16	5.010301	2.139280	7.408826
7	5.546968	-0.526995	7.785862
7	6.853869	0.835397	8.950626
6	5.818767	0.739241	8.061554
6	6.432976	-1.268392	8.520732
1	6.437609	-2.358795	8.490723

6	7.254204	-0.443869	9.250473
1	8.067051	-0.641923	9.946361
6	7.411149	2.053949	9.481052
1	6.605346	2.702657	9.857904
1	8.093736	1.809095	10.304155
1	7.963821	2.606456	8.705668
29	2.555400	1.967475	7.629267
16	-0.359910	4.158011	8.676331
7	-0.514802	3.136445	6.123744
7	-1.565417	1.922325	7.643939
6	-0.826638	3.047551	7.409947
6	-1.060901	2.037960	5.515137
1	-0.939936	1.858035	4.447078
6	-1.719203	1.269889	6.441976
1	-2.275442	0.337806	6.364327
6	-2.041871	1.473043	8.928370
1	-2.750198	2.195755	9.359391
1	-2.543760	0.505282	8.805249
1	-1.194238	1.359132	9.622057
5	1.758826	5.207175	3.815583
8	2.516210	6.158437	4.465665
8	0.508887	5.658488	3.523544
6	1.632691	7.234869	4.867232
6	0.430181	7.059521	3.870837
6	2.378123	8.548623	4.744724
6	1.243132	6.980815	6.315911
6	0.603999	7.842753	2.577083
6	-0.934216	7.326954	4.476424
1	1.704683	9.393813	4.951389
1	3.195772	8.579576	5.481251
1	2.812434	8.680507	3.744920
1	2.148757	6.940809	6.941359
1	0.603491	7.785534	6.705911
1	0.715558	6.023816	6.436005
1	-0.166474	7.522183	1.860066
1	0.492107	8.923891	2.742828
1	1.589529	7.655758	2.125071
1	-0.999825	8.360493	4.847987
1	-1.711847	7.189103	3.710120
1	-1.146417	6.637426	5.304381
19	4.455213	4.680036	5.730997
5	2.393129	3.668210	3.422286
8	1.678795	2.571514	3.041134
8	3.751523	3.430666	3.423134

6	2.582713	1.440433	3.006053
6	3.976757	2.133060	2.817760
6	2.172961	0.523701	1.871075
6	2.456041	0.726037	4.344532
6	4.326035	2.391918	1.358627
6	5.126735	1.446816	3.527305
1	2.896813	-0.297592	1.759538
1	1.188826	0.082645	2.090254
1	2.100687	1.061693	0.916379
1	1.406662	0.435113	4.500888
1	3.074544	-0.182460	4.375681
1	2.749658	1.389190	5.171775
1	5.201785	3.056693	1.313339
1	4.574742	1.458974	0.832758
1	3.496099	2.883783	0.829367
1	5.256850	0.424140	3.142216
1	6.061168	1.998663	3.340914
1	4.967333	1.396418	4.613363
8	2.239200	3.520836	6.362465
1	1.304668	3.458395	6.074037

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TS1-2, E = -10706.735961, G = 10706.084819

29	4.034307	3.066128	9.212935
16	1.712463	0.597079	9.166117
7	3.954197	1.478171	10.517143
7	3.298572	-0.545538	11.093009
6	3.061040	0.519433	10.285346
6	4.783037	1.015315	11.505461
1	5.612017	1.609626	11.885569
6	4.389797	-0.243224	11.876041
1	4.779302	-0.945011	12.610149
6	2.548077	-1.779627	11.108202
1	1.482618	-1.578119	11.289741
1	2.934278	-2.420363	11.910160
1	2.650944	-2.304999	10.147214
29	1.164944	2.757196	9.730618
16	3.398054	5.272117	9.436624
7	1.726294	4.017499	11.232336
7	2.646158	5.862141	12.011705
6	2.534393	5.032087	10.944093
6	1.306544	4.201627	12.523400
1	0.625401	3.505935	13.011109
6	1.871794	5.344742	13.024851
1	1.796011	5.834311	13.993313

6	3.455373	7.057338	12.075193
1	3.263683	7.565936	13.027778
1	3.200034	7.734812	11.248177
1	4.524395	6.805677	12.009807
29	1.910870	4.352068	7.903328
16	5.023478	2.087566	7.302511
7	5.496131	-0.588596	7.686704
7	6.816042	0.745402	8.869737
6	5.789101	0.670764	7.970159
6	6.360100	-1.348882	8.428445
1	6.343859	-2.439024	8.395351
6	7.189380	-0.541989	9.168983
1	7.990933	-0.757497	9.872697
6	7.390798	1.952691	9.407635
1	6.590391	2.626880	9.748321
1	8.036094	1.697177	10.257179
1	7.986760	2.480492	8.647116
29	2.597079	1.909415	7.478191
16	-0.392333	4.031026	8.520480
7	-0.516916	2.676006	6.127659
7	-1.599318	1.685601	7.780429
6	-0.853331	2.766451	7.405576
6	-1.052329	1.503351	5.666368
1	-0.917331	1.180241	4.634453
6	-1.730671	0.872022	6.678028
1	-2.289789	-0.060619	6.718998
6	-2.076607	1.408270	9.112167
1	-2.739129	2.211484	9.465517
1	-2.630477	0.461367	9.104126
1	-1.224082	1.326740	9.805134
5	1.796640	5.191675	4.187715
8	2.590037	6.187684	4.739739
8	0.558775	5.672171	3.864312
6	1.745549	7.322164	5.039675
6	0.554260	7.104279	4.045261
6	2.538011	8.595779	4.824355
6	1.324470	7.198261	6.496623
6	0.802333	7.723160	2.675836
6	-0.801060	7.524694	4.579702
1	1.890716	9.477855	4.942064
1	3.341683	8.663692	5.573884
1	2.996743	8.626262	3.827080
1	2.218222	7.142623	7.136767
1	0.729124	8.064198	6.820637

1	0.733371	6.285629	6.666681
1	0.035040	7.359526	1.976107
1	0.744776	8.820730	2.710804
1	1.788134	7.434532	2.281119
1	-0.807381	8.598064	4.822280
1	-1.572551	7.342809	3.816287
1	-1.073158	6.957054	5.479649
19	4.560809	4.765701	5.877266
5	2.399287	3.607868	3.968883
8	1.689345	2.535814	3.463622
8	3.777783	3.402396	3.791969
6	2.608627	1.459023	3.220727
6	3.958866	2.220941	2.992034
6	2.117187	0.666598	2.023380
6	2.649102	0.566867	4.455603
6	4.138064	2.687300	1.551510
6	5.194249	1.476788	3.461931
1	2.852841	-0.098547	1.732162
1	1.177890	0.153374	2.281261
1	1.922081	1.315778	1.159078
1	1.624657	0.266610	4.721113
1	3.242640	-0.342063	4.277958
1	3.083376	1.105158	5.309841
1	4.984678	3.389283	1.506903
1	4.351811	1.847927	0.873693
1	3.241012	3.212069	1.189679
1	5.292601	0.516905	2.932134
1	6.094116	2.074348	3.246697
1	5.161219	1.287598	4.543272
8	2.149628	3.383748	6.117068
1	1.194656	3.194002	5.946377

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Int2, E = -10706.747339, G = 10706.100031

29	4.124124	2.756982	9.176832
16	2.013169	0.063821	9.409911
7	4.181320	1.289442	10.607156
7	3.649264	-0.654538	11.495983
6	3.351468	0.252885	10.531442
6	5.032485	1.040281	11.651045
1	5.822325	1.736922	11.927037
6	4.715751	-0.166512	12.216359
1	5.144938	-0.719270	13.048974
6	2.969102	-1.909070	11.719218
1	1.896568	-1.738562	11.891231

1	3.401743	-2.393475	12.602813
1	3.087589	-2.573154	10.850578
29	1.222356	2.167593	9.813898
16	3.295539	4.879759	9.425694
7	1.778660	3.508342	11.275833
7	2.634394	5.391131	12.038234
6	2.517798	4.567279	10.966074
6	1.409009	3.656017	12.586273
1	0.789182	2.918904	13.094538
6	1.934809	4.822203	13.077633
1	1.877178	5.296519	14.054915
6	3.375013	6.631040	12.077712
1	3.232314	7.098587	13.059393
1	3.014966	7.316539	11.297244
1	4.447782	6.445720	11.919658
29	1.833390	3.768413	8.000248
16	5.120863	1.708760	7.285211
7	6.041156	-0.721442	8.185621
7	7.128218	1.022372	9.019292
6	6.115106	0.599294	8.203352
6	7.032355	-1.163543	9.020349
1	7.203945	-2.225419	9.201387
6	7.720863	-0.098620	9.547597
1	8.557775	-0.032250	10.239984
6	7.481438	2.390317	9.303979
1	6.602448	2.943402	9.673024
1	8.263894	2.405759	10.072916
1	7.854088	2.897693	8.401235
29	2.801439	1.322056	7.626075
16	-0.421324	3.543163	8.837691
7	-0.689732	1.976251	6.581394
7	-2.578667	2.359905	7.648132
6	-1.234090	2.581344	7.628176
6	-1.703967	1.352293	5.907630
1	-1.522419	0.783784	4.995972
6	-2.889367	1.578043	6.557697
1	-3.910385	1.263210	6.352464
6	-3.504486	2.853756	8.639218
1	-3.513236	3.953641	8.648505
1	-4.510764	2.489368	8.398921
1	-3.222157	2.498147	9.641099
5	1.635101	4.723373	4.835321
8	2.516182	5.748599	5.196004
8	0.392285	5.247459	4.574940

6	1.752663	6.952469	5.426572
6	0.472429	6.685234	4.567469
6	2.575569	8.151341	4.997815
6	1.459125	7.014680	6.919042
6	0.632472	7.115192	3.114204
6	-0.810075	7.249734	5.147889
1	1.980590	9.074884	5.064967
1	3.446601	8.262756	5.662453
1	2.942794	8.044660	3.968270
1	2.405059	7.020054	7.480252
1	0.897875	7.921710	7.186849
1	0.885842	6.132503	7.247918
1	-0.206945	6.710078	2.529305
1	0.629591	8.210028	3.009252
1	1.566681	6.722742	2.684560
1	-0.746003	8.343735	5.250390
1	-1.652347	7.018780	4.478070
1	-1.031218	6.814862	6.132048
19	4.822908	4.641885	6.070011
5	2.144379	3.061742	4.861391
8	1.527043	2.172481	3.891553
8	3.600429	2.913517	4.641836
6	2.512875	1.282218	3.408187
6	3.802687	2.165836	3.456618
6	2.117035	0.813840	2.016602
6	2.625379	0.071977	4.340216
6	3.870617	3.139017	2.277596
6	5.102274	1.384170	3.555774
1	2.919008	0.221538	1.548259
1	1.219666	0.177612	2.079339
1	1.878309	1.663849	1.362240
1	1.619102	-0.344484	4.503412
1	3.263729	-0.720697	3.919660
1	3.035843	0.367647	5.317300
1	4.661747	3.881415	2.470654
1	4.105977	2.633610	1.328290
1	2.917657	3.677572	2.162171
1	5.212040	0.691938	2.705899
1	5.961857	2.074369	3.538785
1	5.150405	0.818229	4.494975
8	1.840688	2.568922	6.296355
1	0.863070	2.285531	6.306962

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TS2-3, E = -10706.726267, G = 10706.078402

29	4.032954	2.608881	9.279786
16	2.177525	-0.201067	9.868753
7	4.201151	1.360346	10.917780
7	3.786615	-0.468258	12.074992
6	3.455322	0.261216	10.978747
6	5.030136	1.336892	12.008391
1	5.753567	2.128591	12.196606
6	4.785735	0.205312	12.740704
1	5.225576	-0.182452	13.656833
6	3.190823	-1.724037	12.467304
1	2.113225	-1.599831	12.649419
1	3.672813	-2.073011	13.388482
1	3.331913	-2.479006	11.680317
29	1.293679	1.921449	9.749771
16	3.095906	4.673223	9.312103
7	1.633104	3.344944	11.213856
7	2.357836	5.314696	11.885415
6	2.325967	4.421759	10.862099
6	1.211238	3.547432	12.500568
1	0.617241	2.806978	13.034632
6	1.653058	4.769786	12.935730
1	1.534132	5.297489	13.879636
6	3.021766	6.596877	11.867566
1	2.908140	7.070354	12.850307
1	2.580802	7.250996	11.100942
1	4.092471	6.470688	11.649833
29	1.801955	3.430376	7.610701
16	5.154021	1.388759	7.572584
7	6.249683	-0.813323	8.804414
7	7.168063	1.113494	9.407747
6	6.214603	0.498488	8.643421
6	7.251439	-1.052878	9.706013
1	7.505819	-2.062216	10.032011
6	7.836102	0.128338	10.092330
1	8.646770	0.358454	10.780823
6	7.402763	2.531973	9.514525
1	6.493569	3.051308	9.858627
1	8.207943	2.706289	10.238881
1	7.698978	2.955272	8.542936
29	2.887876	0.850931	7.940313
16	-0.389469	2.984975	8.631041
7	-0.616475	1.059858	6.660820
7	-2.534570	1.795795	7.441958
6	-1.178623	1.894914	7.527965

6	-1.627082	0.415813	5.998684
1	-1.428568	-0.323007	5.223120
6	-2.830898	0.861142	6.474351
1	-3.857595	0.604779	6.222180
6	-3.488261	2.545229	8.224368
1	-3.420835	3.619403	7.996433
1	-4.498700	2.190350	7.987368
1	-3.297637	2.403133	9.298022
5	1.762777	4.698877	5.997385
8	2.803755	5.510647	5.503964
8	0.565358	5.356414	5.763451
6	2.299932	6.833318	5.235995
6	0.780683	6.552861	4.997833
6	3.037939	7.424786	4.049869
6	2.565717	7.665909	6.486054
6	0.451477	6.229094	3.546153
6	-0.150288	7.636823	5.510591
1	2.624968	8.411949	3.791114
1	4.101544	7.559929	4.301666
1	2.977989	6.780392	3.163241
1	3.647256	7.666230	6.693606
1	2.243227	8.709803	6.359503
1	2.056373	7.237913	7.362074
1	-0.574853	5.835514	3.493983
1	0.514598	7.118440	2.901817
1	1.126630	5.457932	3.150962
1	0.052378	8.597574	5.012591
1	-1.194051	7.358323	5.298995
1	-0.051182	7.774642	6.595714
19	4.910422	4.141960	6.185828
5	2.175622	2.165175	5.220665
8	1.297013	2.349614	4.149613
8	3.506988	2.261452	4.780736
6	2.023644	1.950890	2.981735
6	3.506284	2.342751	3.343876
6	1.455977	2.661670	1.768840
6	1.838332	0.441760	2.828699
6	3.857132	3.762911	2.921007
6	4.556383	1.379856	2.816256
1	2.035233	2.416938	0.865677
1	0.416906	2.337153	1.605817
1	1.453542	3.750972	1.900499
1	0.760333	0.226283	2.775063
1	2.314485	0.055877	1.915542

1	2.246264	-0.101353	3.694348
1	4.867848	4.021669	3.278058
1	3.878382	3.859900	1.826240
1	3.146001	4.486588	3.335578
1	4.522398	1.326589	1.717300
1	5.558968	1.730139	3.107533
1	4.420898	0.369840	3.224684
8	1.869150	1.286555	6.249198
1	0.829025	1.157235	6.384160

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Int3, E = -10528.286356, G = 10527.720693

29	3.526897	3.273342	9.795311
16	1.655504	0.598876	9.856626
7	3.861815	1.697600	11.061123
7	3.587912	-0.444641	11.501987
6	3.093021	0.634802	10.842464
6	4.872033	1.291185	11.893820
1	5.648867	1.974001	12.233338
6	4.719245	-0.040572	12.176454
1	5.299451	-0.729919	12.785845
6	3.037081	-1.778984	11.469641
1	1.967360	-1.754298	11.721294
1	3.565332	-2.400526	12.202874
1	3.153225	-2.223236	10.469284
29	0.802448	2.573817	10.543912
16	2.728923	5.400158	10.415221
7	1.349418	3.769426	12.136915
7	2.146012	5.589901	13.091710
6	2.036266	4.888664	11.933736
6	1.007131	3.752316	13.462731
1	0.432415	2.935203	13.896313
6	1.496226	4.877560	14.073484
1	1.444995	5.234303	15.099914
6	2.840131	6.845268	13.258366
1	3.912472	6.724429	13.044481
1	2.715720	7.184613	14.293667
1	2.427899	7.605091	12.579025
29	1.295000	4.320012	8.780445
16	4.733994	2.693150	7.831646
7	6.261919	0.441589	8.217033
7	6.899337	2.166891	9.451268
6	6.003276	1.704664	8.521454
6	7.347929	0.080643	8.967178
1	7.776848	-0.921041	8.917649

6	7.762688	1.136856	9.738387
1	8.569803	1.250710	10.459442
6	6.952680	3.486313	10.025179
1	5.950756	3.794049	10.363240
1	7.626430	3.475877	10.891097
1	7.336418	4.221573	9.299015
29	2.085015	2.194258	7.935269
16	-0.882756	3.985952	9.724086
7	-1.917191	1.909250	8.215416
7	-1.916140	3.878472	7.198243
6	-1.596038	3.188761	8.334822
6	-2.453871	1.771919	6.963455
1	-2.802317	0.808938	6.587556
6	-2.460742	2.981429	6.312504
1	-2.791420	3.283602	5.320676
6	-1.693043	5.282503	6.966388
1	-0.645790	5.529263	7.191001
1	-1.897865	5.509701	5.913227
1	-2.347815	5.896057	7.603793
5	1.814246	4.104714	6.761759
8	2.853871	4.953574	6.342549
8	0.933851	3.958040	5.698903
6	2.532096	5.513347	5.048656
6	1.536229	4.452832	4.491601
6	3.807275	5.673714	4.242807
6	1.879726	6.868157	5.296457
6	2.239366	3.275952	3.822761
6	0.453642	5.004784	3.585726
1	3.573170	5.958897	3.205867
1	4.434163	6.475488	4.665798
1	4.395442	4.746488	4.226692
1	2.565517	7.507770	5.874273
1	1.654911	7.386646	4.353021
1	0.948308	6.759481	5.871642
1	1.505066	2.478179	3.636289
1	2.684626	3.562941	2.859079
1	3.028123	2.864506	4.470471
1	0.894738	5.460573	2.686190
1	-0.209161	4.187040	3.264118
1	-0.160360	5.757993	4.096484
19	4.758813	5.813556	7.907580
6	2.090276	-3.522987	7.229922
6	1.447652	-2.328895	6.913680
6	2.166225	-1.119648	6.919918

6	3.532217	-1.127463	7.248380
6	4.164207	-2.326703	7.560946
6	3.448846	-3.526403	7.554452
1	1.524411	-4.458240	7.226274
1	0.383476	-2.322149	6.666541
1	4.098213	-0.193372	7.286456
1	5.225449	-2.314980	7.821911
1	3.949126	-4.465502	7.805603
6	1.499410	0.107167	6.618144
6	0.869691	1.123060	6.349467
1	0.276770	1.938527	5.958450

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Int4, E = -10528.286356, G = 10527.720693

29	3.526897	3.273342	9.795311
16	1.655504	0.598876	9.856626
7	3.861815	1.697600	11.061123
7	3.587912	-0.444641	11.501987
6	3.093021	0.634802	10.842464
6	4.872033	1.291185	11.893820
1	5.648867	1.974001	12.233338
6	4.719245	-0.040572	12.176454
1	5.299451	-0.729919	12.785845
6	3.037081	-1.778984	11.469641
1	1.967360	-1.754298	11.721294
1	3.565332	-2.400526	12.202874
1	3.153225	-2.223236	10.469284
29	0.802448	2.573817	10.543912
16	2.728923	5.400158	10.415221
7	1.349418	3.769426	12.136915
7	2.146012	5.589901	13.091710
6	2.036266	4.888664	11.933736
6	1.007131	3.752316	13.462731
1	0.432415	2.935203	13.896313
6	1.496226	4.877560	14.073484
1	1.444995	5.234303	15.099914
6	2.840131	6.845268	13.258366
1	3.912472	6.724429	13.044481
1	2.715720	7.184613	14.293667
1	2.427899	7.605091	12.579025
29	1.295000	4.320012	8.780445
16	4.733994	2.693150	7.831646
7	6.261919	0.441589	8.217033
7	6.899337	2.166891	9.451268
6	6.003276	1.704664	8.521454

6	7.347929	0.080643	8.967178
1	7.776848	-0.921041	8.917649
6	7.762688	1.136856	9.738387
1	8.569803	1.250710	10.459442
6	6.952680	3.486313	10.025179
1	5.950756	3.794049	10.363240
1	7.626430	3.475877	10.891097
1	7.336418	4.221573	9.299015
29	2.085015	2.194258	7.935269
16	-0.882756	3.985952	9.724086
7	-1.917191	1.909250	8.215416
7	-1.916140	3.878472	7.198243
6	-1.596038	3.188761	8.334822
6	-2.453871	1.771919	6.963455
1	-2.802317	0.808938	6.587556
6	-2.460742	2.981429	6.312504
1	-2.791420	3.283602	5.320676
6	-1.693043	5.282503	6.966388
1	-0.645790	5.529263	7.191001
1	-1.897865	5.509701	5.913227
1	-2.347815	5.896057	7.603793
5	1.814246	4.104714	6.761759
8	2.853871	4.953574	6.342549
8	0.933851	3.958040	5.698903
6	2.532096	5.513347	5.048656
6	1.536229	4.452832	4.491601
6	3.807275	5.673714	4.242807
6	1.879726	6.868157	5.296457
6	2.239366	3.275952	3.822761
6	0.453642	5.004784	3.585726
1	3.573170	5.958897	3.205867
1	4.434163	6.475488	4.665798
1	4.395442	4.746488	4.226692
1	2.565517	7.507770	5.874273
1	1.654911	7.386646	4.353021
1	0.948308	6.759481	5.871642
1	1.505066	2.478179	3.636289
1	2.684626	3.562941	2.859079
1	3.028123	2.864506	4.470471
1	0.894738	5.460573	2.686190
1	-0.209161	4.187040	3.264118
1	-0.160360	5.757993	4.096484
19	4.758813	5.813556	7.907580
6	2.090276	-3.522987	7.229922

6	1.447652	-2.328895	6.913680
6	2.166225	-1.119648	6.919918
6	3.532217	-1.127463	7.248380
6	4.164207	-2.326703	7.560946
6	3.448846	-3.526403	7.554452
1	1.524411	-4.458240	7.226274
1	0.383476	-2.322149	6.666541
1	4.098213	-0.193372	7.286456
1	5.225449	-2.314980	7.821911
1	3.949126	-4.465502	7.805603
6	1.499410	0.107167	6.618144
6	0.869691	1.123060	6.349467
1	0.276770	1.938527	5.958450

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TS4-5, E = -10528.260662, G = 10527.691720

29	3.685828	3.437704	9.689259
16	1.892901	0.674387	10.032358
7	3.813734	2.170264	11.314822
7	3.511961	0.166782	12.182571
6	3.137062	1.032149	11.204501
6	4.631405	2.040007	12.406910
1	5.300264	2.839035	12.722677
6	4.457516	0.798672	12.959793
1	4.915847	0.307564	13.815262
6	3.019466	-1.179765	12.348440
1	1.930505	-1.177056	12.502981
1	3.505633	-1.632001	13.221249
1	3.248105	-1.781291	11.456061
29	0.886790	2.698290	10.206499
16	2.867828	5.598640	9.958510
7	1.331451	4.097501	11.694711
7	2.209947	5.905789	12.600380
6	2.081957	5.169384	11.465025
6	0.967128	4.147344	13.013307
1	0.341847	3.378357	13.464829
6	1.506243	5.265489	13.594214
1	1.454736	5.662947	14.605576
6	2.976099	7.122076	12.739886
1	2.628769	7.880126	12.023402
1	4.043942	6.928271	12.559065
1	2.848482	7.506827	13.758929
29	1.561625	4.267376	8.439224
16	4.910690	2.243970	8.087465
7	5.606594	-0.225700	9.082131

7	6.754614	1.464044	9.945077
6	5.770278	1.086055	9.071893
6	6.511652	-0.710277	9.985866
1	6.597035	-1.776427	10.199857
6	7.237198	0.320936	10.532299
1	8.031470	0.350216	11.275592
6	7.185739	2.811992	10.216209
1	6.307640	3.455594	10.377967
1	7.808167	2.815989	11.119627
1	7.772737	3.218958	9.377551
29	2.452913	1.956764	8.029066
16	-0.749560	3.984637	9.178766
7	-1.194279	1.772426	7.575384
7	-2.296819	3.596911	6.973799
6	-1.419694	3.043861	7.864277
6	-1.934570	1.503032	6.456596
1	-1.933656	0.517767	5.988129
6	-2.630591	2.621171	6.065316
1	-3.324939	2.810150	5.248725
6	-2.808583	4.944182	7.003670
1	-1.985097	5.660863	7.122748
1	-3.332133	5.151024	6.061787
1	-3.511900	5.081195	7.839948
5	2.057226	3.417696	6.433516
8	3.100743	4.121864	5.782941
8	0.840418	3.995923	6.059996
6	2.532028	5.245375	5.062924
6	1.042270	4.809149	4.894245
6	3.288535	5.430736	3.761287
6	2.658719	6.497339	5.928462
6	0.822480	3.926056	3.671288
6	0.034130	5.940147	4.904793
1	2.804036	6.203137	3.144986
1	4.320354	5.764663	3.955525
1	3.337086	4.498185	3.184606
1	3.712505	6.793792	6.054279
1	2.175315	7.359510	5.449486
1	2.205343	6.350099	6.921659
1	-0.171128	3.458871	3.746169
1	0.857386	4.514734	2.743251
1	1.573704	3.126299	3.598046
1	0.249025	6.661978	4.102467
1	-0.973948	5.534533	4.737152
1	0.032642	6.467471	5.867956

19	5.322985	5.002080	7.118357
6	3.278024	-3.027883	7.397172
6	2.664711	-1.784155	7.324225
6	3.164023	-0.783095	6.450123
6	4.306023	-1.093674	5.665163
6	4.916215	-2.337472	5.767103
6	4.412088	-3.317033	6.629443
1	2.872401	-3.783323	8.076719
1	1.802850	-1.554434	7.953897
1	4.712474	-0.332653	4.994509
1	5.801623	-2.549034	5.160286
1	4.896571	-4.293893	6.702385
6	2.596123	0.500181	6.412060
6	1.988634	1.574825	6.065226
1	1.179903	1.727432	5.341667

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Int5, E = -10528.368702, G = 10527.794785

29	3.635944	3.369321	9.484841
16	1.508139	0.761914	10.940299
7	3.581704	2.529832	11.366240
7	2.848031	1.535263	13.191722
6	2.709904	1.649955	11.843742
6	4.301650	2.992702	12.438820
1	5.092271	3.732317	12.320725
6	3.857376	2.384498	13.582836
1	4.158993	2.474147	14.624040
6	2.041465	0.704811	14.054073
1	0.978067	0.964693	13.945781
1	2.347627	0.868819	15.094427
1	2.171042	-0.358414	13.804278
29	0.225212	2.646162	10.504381
16	2.278275	5.281291	9.645937
7	0.784226	4.186482	11.701580
7	2.100886	5.844122	12.308985
6	1.673527	5.076548	11.270816
6	0.639620	4.388127	13.050495
1	-0.035697	3.781611	13.651968
6	1.451094	5.418439	13.444511
1	1.625102	5.883748	14.412251
6	3.090155	6.892253	12.231273
1	2.762289	7.684760	11.543151
1	4.048160	6.488587	11.871064
1	3.232921	7.319983	13.230950
29	1.013313	3.802234	8.404889

16	5.554508	3.520711	8.226526
7	7.117381	1.865971	6.736409
7	6.273719	0.846311	8.509902
6	6.331991	2.015075	7.806304
6	7.584601	0.578810	6.775144
1	8.255671	0.184194	6.011743
6	7.072981	-0.070470	7.867308
1	7.184967	-1.087663	8.236692
6	5.490651	0.594709	9.691034
1	5.860185	1.180863	10.544707
1	4.441801	0.879698	9.516946
1	5.542085	-0.474306	9.931930
29	1.954893	1.430799	8.785517
16	-1.187991	3.045454	8.744429
7	-1.632390	0.329701	8.738817
7	-1.258070	1.174570	6.724478
6	-1.345741	1.431719	8.064145
6	-1.739502	-0.665091	7.805444
1	-1.963002	-1.696015	8.083179
6	-1.512377	-0.162750	6.547314
1	-1.488930	-0.624314	5.562098
6	-0.974777	2.132492	5.684686
1	-0.239480	2.855991	6.054209
1	-0.557340	1.611057	4.813843
1	-1.886314	2.671108	5.380948
5	2.567853	3.569134	5.779854
8	3.330642	4.401968	4.985217
8	1.529023	4.276909	6.361773
6	2.885417	5.767627	5.199447
6	1.410849	5.547260	5.656943
6	3.040486	6.543017	3.908684
6	3.748325	6.362196	6.303796
6	0.457854	5.313337	4.493266
6	0.855242	6.598647	6.589632
1	2.598624	7.545392	4.011324
1	4.108315	6.667770	3.671350
1	2.558808	6.029005	3.066485
1	4.802934	6.381625	5.988139
1	3.457385	7.399667	6.519458
1	3.676109	5.769224	7.227967
1	-0.511335	4.972793	4.884462
1	0.291151	6.242334	3.930105
1	0.841583	4.547501	3.802424
1	0.834895	7.574782	6.082691

1	-0.176115	6.333808	6.867971
1	1.441217	6.684112	7.512521
19	5.942079	3.658592	5.081598
6	2.269258	-2.553098	7.066600
6	1.963461	-1.201327	7.197830
6	2.865570	-0.201072	6.782362
6	4.106432	-0.618972	6.263937
6	4.424361	-1.973325	6.155667
6	3.506247	-2.948355	6.548238
1	1.540397	-3.305119	7.382480
1	1.003793	-0.895772	7.625967
1	4.843606	0.133689	5.972253
1	5.403809	-2.267407	5.767104
1	3.756106	-4.009391	6.462833
6	2.515483	1.233556	6.922942
6	2.801401	2.053487	5.875565
1	3.255009	1.599699	4.971244

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Int6, E = -10604.650239, G = 10604.060187

29	3.897685	3.225169	9.903403
16	3.163769	0.089107	10.720259
7	4.535801	2.308988	11.606893
7	4.845132	0.512343	12.840881
6	4.223031	1.025094	11.745628
6	5.374316	2.631760	12.642112
1	5.781320	3.634493	12.762093
6	5.580008	1.522802	13.419469
1	6.170677	1.358347	14.318081
6	4.748527	-0.851617	13.304209
1	3.704263	-1.106622	13.537385
1	5.356543	-0.963555	14.210016
1	5.117259	-1.546790	12.535753
29	1.563150	1.660240	10.145596
16	2.496737	5.067473	10.141348
7	1.213409	3.127089	11.632369
7	1.189732	5.130883	12.550534
6	1.585329	4.393119	11.479693
6	0.560742	3.049448	12.833574
1	0.148128	2.110925	13.201830
6	0.537267	4.287362	13.420713
1	0.124204	4.644856	14.361509
6	1.433411	6.540902	12.745756
1	1.025681	7.120958	11.905391
1	2.512601	6.740745	12.822144

1	0.942921	6.861110	13.672965
29	1.795727	3.610799	8.498001
16	5.149861	2.560766	8.130929
7	6.789242	0.456504	8.781895
7	7.392255	2.384131	9.695737
6	6.499250	1.743662	8.884405
6	7.903544	0.260090	9.551438
1	8.367719	-0.721204	9.655352
6	8.294841	1.443746	10.128494
1	9.114846	1.701933	10.795660
6	7.400667	3.789383	10.020018
1	6.386949	4.113172	10.295761
1	8.078049	3.958422	10.866008
1	7.737846	4.390310	9.161333
29	3.447758	0.794473	8.515998
16	-0.267437	2.563900	8.926236
7	-0.841949	0.688070	6.978754
7	-0.798720	2.780548	6.250738
6	-0.649741	1.944325	7.335887
6	-1.123127	0.702578	5.640371
1	-1.317170	-0.215615	5.084732
6	-1.108361	1.989927	5.164928
1	-1.286591	2.415767	4.179442
6	-0.773251	4.225178	6.265833
1	0.157143	4.590241	6.726816
1	-0.830433	4.592295	5.233626
1	-1.619993	4.627223	6.841940
5	1.026015	-1.620342	7.873611
8	0.150545	-2.665515	7.679488
8	1.022445	-1.187024	9.171950
6	-0.642755	-2.816235	8.869941
6	0.240984	-2.096587	9.956974
6	-0.871801	-4.296138	9.119775
6	-1.973141	-2.117570	8.621527
6	1.218230	-3.040657	10.648632
6	-0.529849	-1.297760	10.991826
1	-1.405607	-4.453546	10.069330
1	-1.488371	-4.715793	8.310103
1	0.072272	-4.856325	9.150555
1	-2.458604	-2.580680	7.748210
1	-2.650403	-2.217646	9.482446
1	-1.815150	-1.054228	8.392757
1	1.926152	-2.438876	11.236891
1	0.703375	-3.741751	11.321609

1	1.797623	-3.619796	9.913620
1	-1.185334	-1.950347	11.588327
1	0.185016	-0.807405	11.670399
1	-1.138161	-0.512876	10.524041
19	4.509515	3.365069	5.242234
6	5.862246	0.432284	4.506241
6	5.106460	0.158816	5.647246
6	3.696694	0.115154	5.595633
6	3.081093	0.385479	4.354488
6	3.836831	0.690986	3.219449
6	5.233943	0.712658	3.286132
1	6.954210	0.445162	4.573357
1	5.604911	-0.009137	6.607002
1	1.988507	0.380405	4.293624
1	3.330627	0.911377	2.274957
1	5.827090	0.947045	2.398224
6	2.900261	-0.139033	6.816123
6	1.981529	-1.143867	6.749220
1	1.910364	-1.724428	5.807794
8	2.232381	2.763460	6.517704
1	1.397180	2.644833	6.036457
1	2.442179	1.845094	6.851644

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TS6-7, E = -10604.637526, G = 10604.045184

29	3.755753	3.361881	9.678743
16	2.839013	0.289853	10.687586
7	4.191268	2.548865	11.508684
7	4.290482	0.869312	12.930198
6	3.817811	1.295101	11.729302
6	4.915057	2.946281	12.602132
1	5.341374	3.945155	12.677744
6	4.989132	1.911038	13.496654
1	5.467053	1.817160	14.469317
6	4.086207	-0.440040	13.504491
1	3.014885	-0.626380	13.670508
1	4.612722	-0.491672	14.465032
1	4.480899	-1.218565	12.835691
29	1.243508	1.849296	10.159452
16	2.350934	5.174358	9.623466
7	1.101645	3.525169	11.455799
7	1.196738	5.641394	12.065127
6	1.500529	4.739147	11.095528
6	0.524023	3.650803	12.690964
1	0.106874	2.794047	13.218695

6	0.575702	4.961468	13.087725
1	0.233803	5.469386	13.987002
6	1.492233	7.054680	12.031797
1	1.032827	7.523239	11.149551
1	2.578894	7.222278	11.995629
1	1.087160	7.522852	12.936920
29	1.552457	3.484874	8.255249
16	5.162727	2.458640	8.146539
7	6.487093	0.255419	9.098465
7	7.183805	2.170797	9.972990
6	6.324251	1.568174	9.099363
6	7.483216	0.001892	10.001705
1	7.827395	-1.011310	10.211675
6	7.930471	1.176783	10.556106
1	8.694358	1.396129	11.299433
6	7.311093	3.587181	10.213606
1	6.311901	4.041778	10.260497
1	7.826847	3.745529	11.168664
1	7.881989	4.075263	9.408339
29	3.218590	0.985468	8.499724
16	-0.595066	2.762080	8.988319
7	-1.641779	0.753920	7.414236
7	-1.290801	2.658117	6.332254
6	-1.198539	1.991283	7.535459
6	-2.021789	0.605467	6.109012
1	-2.415334	-0.337741	5.727816
6	-1.821110	1.773747	5.418705
1	-2.003444	2.061044	4.384913
6	-1.094679	4.070623	6.094944
1	-0.259954	4.442677	6.704440
1	-0.865497	4.231605	5.033229
1	-1.996455	4.644720	6.359737
5	1.835567	-1.854030	8.097249
8	0.483110	-1.677746	8.062434
8	2.227397	-2.718284	9.084518
6	-0.109149	-2.351087	9.185556
6	1.052612	-3.310088	9.668167
6	-1.360650	-3.065433	8.704098
6	-0.494701	-1.286768	10.202992
6	0.949265	-4.720290	9.100697
6	1.236230	-3.363108	11.173640
1	-1.814439	-3.653219	9.516064
1	-2.096150	-2.318549	8.369179
1	-1.149567	-3.735287	7.859830

1	-1.159064	-0.563823	9.708790
1	-1.013898	-1.723631	11.068582
1	0.384501	-0.733472	10.561281
1	1.870178	-5.270908	9.345635
1	0.096151	-5.269581	9.524503
1	0.847105	-4.703588	8.005388
1	0.331615	-3.749475	11.666591
1	2.073148	-4.034516	11.419825
1	1.467917	-2.369247	11.578828
19	4.151291	3.501577	5.463017
6	6.097531	0.591246	4.541291
6	5.288419	0.256360	5.628746
6	3.882847	0.299823	5.528900
6	3.326833	0.665147	4.285411
6	4.137031	0.993690	3.195614
6	5.530016	0.972277	3.321144
1	7.185672	0.558496	4.649924
1	5.739948	-0.018940	6.585914
1	2.238169	0.696910	4.178710
1	3.676041	1.270884	2.243086
1	6.166074	1.240276	2.473495
6	3.004853	0.026503	6.688249
6	2.799908	-1.276896	7.018463
1	3.343944	-2.055404	6.441934
8	1.803342	2.555471	6.362618
1	0.937736	2.410907	5.948879
1	2.121764	1.609851	6.635977

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Int7, E = -10604.696706, G = 10604.102168

29	3.593757	3.514897	9.842760
16	1.781662	0.853471	10.461411
7	3.805139	2.370587	11.532692
7	3.654411	0.353572	12.407397
6	3.138300	1.220720	11.498685
6	4.763986	2.243398	12.502502
1	5.458721	3.048647	12.734834
6	4.683102	0.993282	13.059057
1	5.256070	0.503962	13.843614
6	3.190717	-0.993583	12.647692
1	2.224445	-0.984721	13.174681
1	3.930361	-1.518285	13.264840
1	3.070451	-1.520827	11.691541
29	0.746725	2.857568	10.494956
16	2.650567	5.606819	9.663966

7	1.040101	4.527182	11.632936
7	1.652250	6.609230	12.013218
6	1.726715	5.559990	11.153674
6	0.509301	4.926077	12.831322
1	-0.105731	4.261430	13.436181
6	0.881721	6.219805	13.084850
1	0.674511	6.891876	13.914817
6	2.284395	7.895574	11.835503
1	1.946817	8.364270	10.899858
1	3.378505	7.786887	11.801075
1	2.014464	8.543186	12.678329
29	1.493674	4.057516	8.395839
16	4.828269	2.375007	8.264690
7	6.140501	0.113020	9.096925
7	6.936832	1.991331	9.964170
6	6.002903	1.430506	9.137530
6	7.191272	-0.182376	9.923039
1	7.526226	-1.207451	10.085495
6	7.701638	0.968507	10.470968
1	8.517130	1.153872	11.167218
6	7.105399	3.397822	10.231458
1	6.123714	3.861528	10.408962
1	7.734393	3.523416	11.121472
1	7.579952	3.908455	9.378882
29	2.606260	1.178455	8.185351
16	-0.830785	3.723393	8.993110
7	-1.424402	1.221650	7.974250
7	-1.162080	2.801396	6.441802
6	-1.165244	2.505634	7.782585
6	-1.587093	0.674545	6.729868
1	-1.801346	-0.385707	6.590202
6	-1.431049	1.634780	5.761557
1	-1.487264	1.603949	4.675163
6	-0.942631	4.098850	5.849782
1	-0.032683	4.552467	6.270469
1	-0.819494	3.980756	4.765762
1	-1.789645	4.773449	6.046365
5	2.118545	-1.763663	8.579439
8	0.832051	-1.979110	8.165500
8	2.467611	-2.548654	9.648291
6	0.190677	-2.832441	9.133238
6	1.420325	-3.527578	9.822402
6	-0.744219	-3.778825	8.404526
6	-0.598919	-1.939050	10.080379

6	1.878041	-4.785367	9.093769
6	1.236557	-3.816667	11.299099
1	-1.168727	-4.516899	9.101651
1	-1.577094	-3.208998	7.964986
1	-0.232194	-4.313531	7.593388
1	-1.278482	-1.305001	9.491729
1	-1.197460	-2.532963	10.786431
1	0.068205	-1.272504	10.645137
1	2.849880	-5.099527	9.503208
1	1.165272	-5.612487	9.222852
1	2.007250	-4.597673	8.017087
1	0.407785	-4.525223	11.448083
1	2.151719	-4.273155	11.705930
1	1.023697	-2.905959	11.872545
19	3.879196	3.720669	5.707105
6	5.754404	0.833347	4.619890
6	4.985663	0.277979	5.640834
6	3.582628	0.232194	5.535971
6	2.981699	0.751170	4.373682
6	3.751725	1.308897	3.352209
6	5.144617	1.355452	3.473048
1	6.842682	0.864924	4.720712
1	5.473217	-0.105920	6.540542
1	1.891924	0.721958	4.282169
1	3.264119	1.707726	2.458417
1	5.752646	1.790119	2.675265
6	2.722788	-0.321694	6.587377
6	3.111613	-0.861396	7.795621
1	4.172472	-0.857677	8.080192
8	1.919030	2.710792	6.994418
1	1.106182	2.400514	6.577960
1	1.671829	-0.439247	6.292986

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B, E = -18668.283339, G = 18667.522546

29	-7.103979	25.368845	12.331213
29	-6.715627	23.518280	10.347112
29	-8.773742	21.496640	11.045243
29	-6.961665	19.673339	11.339166
16	-6.207151	23.399100	12.657389
16	-6.724169	21.303123	9.776530
16	-7.044157	25.134668	8.646541
16	-10.291237	19.637984	11.080573
7	-6.053298	27.490318	9.721044
7	-4.508479	26.054427	9.049913

7	-8.059539	18.072205	10.699551
7	-9.914689	17.183695	9.911950
6	-5.846426	26.302513	9.170587
6	-4.360172	23.388863	12.869467
6	-9.367372	18.252750	10.548615
6	-4.813456	28.021458	9.961871
6	-3.840249	27.147031	9.549284
6	-7.365394	21.069008	8.037433
6	-7.759495	16.852495	10.155003
6	-8.903505	16.284992	9.657508
6	-3.796820	22.347343	11.912721
6	-11.309893	17.023459	9.576042
6	-3.910872	24.849211	8.527523
6	-3.843025	24.779615	12.536142
6	-4.080729	23.012156	14.318139
6	-6.335057	21.720454	7.121067
6	-8.712810	21.770165	7.914852
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29	-8.617699	25.229780	10.321220
29	-8.914406	23.760403	13.782419
29	-7.247494	21.468580	13.358369
29	-9.220135	19.827326	13.126951
16	-9.629689	23.598543	11.545770
16	-9.321801	21.611375	14.535126
16	-8.384497	25.529536	15.187792
16	-5.888342	19.509759	13.382787
7	-11.078891	26.091231	15.341634
7	-10.126093	25.730132	17.307776
7	-8.252060	18.178687	13.850898
7	-6.483110	17.169807	14.690251
6	-9.935207	25.792564	15.955474
6	-11.482948	23.529899	11.366125
6	-6.932867	18.247507	13.995228
6	-12.022816	26.215754	16.326733
6	-11.452726	25.999261	17.554157
6	-8.808540	21.378477	16.316767
6	-8.659905	17.022013	14.459503
6	-7.570842	16.380843	14.989478
6	-12.025193	22.597890	12.438203
6	-5.106714	16.900281	15.034870
6	-9.118657	25.487892	18.311075
6	-12.040188	24.935048	11.546722
6	-11.780076	23.008253	9.967239
6	-9.841192	22.144490	17.136295

6	-7.419725	21.970356	16.519292
6	-8.824364	19.900758	16.671883
1	-2.993098	22.981949	14.500327
1	-4.529320	23.740237	15.011749
1	-4.497359	22.017808	14.544194
1	-2.743163	24.808890	12.619149
1	-4.119886	25.059561	11.508639
1	-4.263418	25.533854	13.219958
1	-2.708182	22.243500	12.057930
1	-4.269360	21.366999	12.076346
1	-3.989984	22.632484	10.867660
1	-2.753365	27.195310	9.565843
1	-4.685479	29.001387	10.422113
1	-4.012636	24.796723	7.432930
1	-2.846851	24.831856	8.793275
1	-4.410132	23.971594	8.965173
1	-9.556223	24.923302	19.145032
1	-8.302185	24.906457	17.863910
1	-8.707997	26.435167	18.695190
1	-11.857314	26.007044	18.564254
1	-13.063239	26.451784	16.101409
1	-11.568310	25.637765	10.839451
1	-13.126863	24.941533	11.358549
1	-11.888226	25.276389	12.583123
1	-11.366557	21.996803	9.837223
1	-12.869710	22.964311	9.799533
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1	-11.840070	23.008516	13.442138
1	-13.111022	22.454063	12.306777
1	-11.527297	21.618197	12.395618
1	-6.743395	16.460821	10.146660
1	-9.092634	15.338146	9.156302
1	-11.929087	17.032124	10.485066
1	-11.641961	17.837860	8.915818
1	-11.443147	16.065408	9.059273
1	-7.466791	15.449504	15.541905
1	-9.707376	16.725590	14.487558
1	-4.685924	17.736695	15.611298
1	-5.065130	15.988780	15.643277
1	-4.501116	16.756384	14.127853
1	-9.867206	23.199263	16.828844
1	-10.849591	21.723026	17.000856
1	-9.590080	22.098849	18.209857
1	-7.397758	23.020002	16.187255

1	-7.136352	21.929012	17.585557
1	-6.667729	21.407329	15.942496
1	-8.600683	19.771579	17.744910
1	-9.807780	19.448330	16.470526
1	-8.070611	19.348836	16.094983
1	-9.053593	21.778440	6.865120
1	-9.473492	21.252697	8.521006
1	-8.647258	22.808033	8.277139
1	-5.349488	21.239817	7.224983
1	-6.652813	21.627126	6.068182
1	-6.228626	22.789935	7.358246
1	-6.540913	19.059886	7.862983
1	-8.242078	19.113256	8.386548
1	-7.824138	19.447543	6.685243
19	-10.051418	27.231220	13.038273
8	-8.068946	26.849321	11.555373
1	-7.440826	27.290238	10.946090

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Int8, E = -19489.370017, G = 19488.266682

29	-7.111691	25.305964	12.279340
29	-6.563780	23.407707	10.354001
29	-8.717823	21.337402	11.010731
29	-6.879949	19.557037	11.354947
16	-6.224173	23.334172	12.681914
16	-6.609266	21.183603	9.802787
16	-6.829386	24.974293	8.633843
16	-10.208231	19.465830	11.029412
7	-6.066819	27.426991	9.661245
7	-4.385968	26.074607	9.174135
7	-7.942767	17.934982	10.717010
7	-9.770158	16.987876	9.932862
6	-5.743122	26.234222	9.185069
6	-4.392998	23.347636	13.013576
6	-9.252040	18.084986	10.545709
6	-4.888860	28.056033	9.964918
6	-3.831335	27.232683	9.668320
6	-7.222574	20.945343	8.053551
6	-7.611821	16.707419	10.209135
6	-8.738234	16.103309	9.714695
6	-3.758656	22.302161	12.106686
6	-11.158313	16.788164	9.588973
6	-3.671618	24.895868	8.747599
6	-3.866532	24.739292	12.698629
6	-4.200658	22.990886	14.481233

6	-6.163506	21.562129	7.146220
6	-8.553300	21.673175	7.901107
6	-7.385153	19.462284	7.761293
29	-8.537054	25.061751	10.205102
29	-8.899688	23.648714	13.727674
29	-7.251602	21.377914	13.347198
29	-9.184342	19.698114	13.096015
16	-9.536235	23.451242	11.472725
16	-9.352949	21.483594	14.485745
16	-8.509196	25.316401	15.290760
16	-5.858898	19.448688	13.431697
7	-11.203637	25.891002	15.208475
7	-10.396575	25.647057	17.257289
7	-8.202747	18.065114	13.840690
7	-6.426978	17.072529	14.685186
6	-10.109583	25.623968	15.919410
6	-11.386525	23.440370	11.276952
6	-6.887963	18.157440	14.008929
6	-12.213184	26.082100	16.115035
6	-11.734294	25.939729	17.391313
6	-8.877638	21.237733	16.276463
6	-8.596318	16.885966	14.414723
6	-7.502825	16.254597	14.947450
6	-11.974047	22.531157	12.344513
6	-5.050629	16.822480	15.044158
6	-9.465632	25.464842	18.343126
6	-11.882015	24.869314	11.444503
6	-11.688159	22.919643	9.878646
6	-9.876427	22.065601	17.077345
6	-7.461336	21.753292	16.496873
6	-8.980294	19.765725	16.641870
1	-3.126085	22.969470	14.729969
1	-4.693762	23.725802	15.136469
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1	-2.772948	24.774374	12.840400
1	-4.088998	25.013473	11.656276
1	-4.324610	25.494523	13.355006
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1	-4.225508	21.316879	12.254509
1	-3.890027	22.572090	11.047842
1	-2.754245	27.356834	9.760202
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1	-9.953723	24.922638	19.164211
1	-8.606797	24.885156	17.981134
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1	-13.232701	26.309541	15.801764
1	-11.361912	25.540366	10.742661
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1	-6.734308	21.150990	15.928062
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1	-9.984797	19.367275	16.429721
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1	-8.870620	21.689300	6.844147
1	-9.337812	21.169694	8.489181
1	-8.477385	22.708460	8.269050
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19	-9.892527	27.268933	13.133481

8	-8.119446	26.714632	11.401541
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6	-9.960256	29.631654	9.089603
6	-11.023148	29.647377	10.238820
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6	-5.815283	30.349730	13.454360
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5	-7.677448	29.771657	12.284995
8	-8.763621	30.065645	9.779472
8	-10.201549	29.383043	11.402949
8	-7.855841	29.210580	13.526371
8	-6.442269	30.339431	12.148120
6	-9.675582	28.230029	8.563020
1	-10.510459	27.848363	7.957551
1	-8.775254	28.263859	7.931743
1	-9.475054	27.526504	9.386147
6	-10.245290	30.585083	7.947612
1	-9.450299	30.504174	7.191108
1	-11.201588	30.332236	7.465453
1	-10.287595	31.628208	8.288347
6	-12.091406	28.579131	10.130471
1	-12.777637	28.645339	10.988772
1	-12.681795	28.720738	9.212779
1	-11.660298	27.570594	10.110353
6	-11.656748	31.015069	10.452015
1	-12.351292	31.267459	9.637998
1	-12.222125	31.003441	11.395964
1	-10.892658	31.803874	10.520186
6	-6.096247	31.715657	14.066357
1	-5.593497	31.831869	15.037287
1	-5.720928	32.496176	13.387786
1	-7.175709	31.875705	14.208381
6	-4.323530	30.139454	13.291392
1	-3.884017	30.996524	12.759119
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6	-6.773023	29.384829	15.672861
1	-7.293743	28.509133	16.089707
1	-5.805261	29.481791	16.187559
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6	-5.939109	27.825934	13.914056
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1	-5.775931	27.665337	12.838447

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Int9, E = -19489.376401, G = 19488.271001

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29	-7.070407	19.398362	11.183871
16	-6.492297	23.436871	12.204999
16	-6.870512	20.877989	9.477668
16	-6.875573	24.723878	8.318289
16	-10.375914	19.249156	10.972223
7	-5.709746	26.868199	9.616015
7	-4.275495	25.495434	8.653650
7	-8.108403	17.719267	10.680314
7	-9.940998	16.736869	9.953987
6	-5.590658	25.755027	8.905785
6	-4.726773	23.555049	12.781574
6	-9.421217	17.854882	10.525491
6	-4.442982	27.346547	9.816929
6	-3.536020	26.507654	9.221634
6	-7.584640	20.608341	7.772673
6	-7.776058	16.479986	10.202040
6	-8.906013	15.853606	9.744875
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1	-11.270168	22.023215	16.934860
1	-10.042606	21.852949	18.220787
1	-7.562963	21.985707	16.358896
1	-7.780926	20.809842	17.691551
1	-7.434984	20.236818	16.032936
1	-9.882694	19.298612	17.661569
1	-11.122903	19.545669	16.402078
1	-9.554790	18.819449	15.969930
1	-8.300298	20.957163	6.801136
1	-8.762499	20.465334	8.457970
1	-8.313397	22.159499	8.125715
1	-4.655553	21.523435	7.607625
1	-5.876579	21.586538	6.305760
1	-5.928426	22.775670	7.641906
1	-5.257279	19.109747	8.113742
1	-6.939026	18.673611	8.504076
1	-6.495100	19.110025	6.828161
19	-10.183702	26.910478	13.404866
6	-7.399743	29.425961	12.683510
6	-6.061267	29.127260	11.938500
5	-7.239027	27.160685	12.214794
8	-8.143152	28.214460	12.435122
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6	-6.121803	29.466591	10.453954
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1	-5.246966	29.028162	9.951778
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6	-4.829075	29.743324	12.571564
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1	-4.912552	30.840490	12.601379
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6	-8.181822	30.609602	12.150474
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1	-7.590124	31.533954	12.234347
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6	-7.228653	29.537340	14.195216
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1	-8.220410	29.547286	14.673458
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16	-6.351074	20.989984	10.056229
16	-6.993381	24.969555	9.732212
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7	-4.728117	25.817642	11.078990
7	-5.511203	27.244374	9.577726
7	-7.799750	17.653255	10.111243
7	-9.340946	16.865870	8.749288
6	-5.678597	26.029716	10.180328
6	-5.051992	22.367403	13.954659
6	-9.024207	17.849391	9.632913
6	-3.934564	26.933524	11.061490
6	-4.401748	27.833712	10.136373
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6	-7.320585	16.510938	9.527189
6	-8.267707	16.006761	8.674889
6	-5.206619	21.664806	15.296838
6	-10.588994	16.743426	8.033664
6	-6.334506	27.791341	8.528997
6	-4.371997	21.474326	12.928936
6	-4.266476	23.659538	14.117730
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6	-7.799788	21.663493	7.784292
6	-6.371043	19.606887	7.658602

29	-8.319200	24.880442	11.727708
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29	-7.920183	20.736268	13.357904
29	-9.670234	19.098649	12.339701
16	-9.596112	22.943411	11.449131
16	-10.309468	20.614478	13.892467
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16	-6.578298	18.730329	13.461361
7	-8.145354	22.873860	17.286297
7	-10.028929	23.755248	18.051611
7	-8.912400	17.336108	13.058768
7	-7.318575	16.141435	13.999095
6	-9.185406	23.630173	16.981199
6	-11.238741	23.398448	10.721035
6	-7.666440	17.363504	13.516280
6	-8.325186	22.489903	18.586381
6	-9.489545	23.023670	19.081923
6	-10.467328	19.866644	15.593492
6	-9.375878	16.059891	13.240943
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6	-12.116070	22.156546	10.685934
6	-6.035793	15.787673	14.559866
6	-11.280798	24.470832	18.076417
6	-11.847083	24.475028	11.609720
6	-10.989664	23.938195	9.318087
6	-11.272098	20.860324	16.423151
6	-9.082941	19.660889	16.190434
6	-11.210554	18.543329	15.469544
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1	-5.765078	20.722738	15.185453
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1	-7.607335	21.851869	19.102629
1	-11.159276	25.336159	11.663259
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1	-12.012286	24.062601	12.620047
1	-10.504735	23.176441	8.687982
1	-11.942360	24.226249	8.841280
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1	-12.220021	21.719486	11.691187
1	-13.119483	22.407476	10.301366
1	-11.676589	21.392298	10.027154
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1	-8.280972	15.129358	8.031872
1	-10.534067	15.872203	7.369834
1	-11.425832	16.610492	8.735271
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1	-8.363475	14.259092	14.134399
1	-10.382250	15.765791	12.946311
1	-5.797490	16.437890	15.413757
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1	-10.783798	21.844345	16.419678
1	-12.288796	20.985393	16.017929
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1	-8.538008	20.615482	16.247200
1	-9.160813	19.246929	17.211162
1	-8.492872	18.966968	15.575024
1	-11.341202	18.084455	16.465013
1	-12.208797	18.687103	15.026498
1	-10.651353	17.841881	14.834582
1	-7.853754	21.765009	6.686234
1	-8.653159	21.048548	8.114405
1	-7.897363	22.663483	8.232974
1	-4.346334	21.455626	8.017411
1	-5.325830	21.968664	6.614911
1	-5.390757	22.900697	8.141380
1	-5.432028	19.127609	7.976934
1	-7.205849	18.989786	8.018126
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8	-9.557320	27.371986	12.919750
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6	-10.347368	29.637055	13.235878
6	-9.966121	28.667596	10.965108
6	-7.528723	29.498265	13.895631
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1	-10.990130	28.263236	10.951969
1	-9.985565	29.665237	10.502942
1	-9.332760	28.004432	10.356461
1	-6.431983	29.461248	13.973968
1	-7.852011	30.535942	14.064156
1	-7.943779	28.863199	14.690672
1	-7.857195	30.904189	11.500884
1	-6.302879	30.038332	11.590357
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6	-7.163950	25.826331	19.435371
6	-6.596312	25.730070	18.167867
6	-7.174291	26.412675	17.082915
6	-8.334105	27.183133	17.292384
6	-8.891952	27.275810	18.563675
6	-8.310781	26.597234	19.637400
1	-6.710432	25.289495	20.272249
1	-5.704896	25.120665	18.004150
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1	-9.790519	27.878859	18.717507
1	-8.754762	26.666521	20.633860
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29	-6.942179	19.339998	11.368441
16	-7.080548	23.025309	13.432452
16	-6.322746	21.175552	10.188305
16	-7.274040	25.154002	9.892538
16	-10.010697	19.251582	10.023458
7	-4.717635	25.642489	10.801714
7	-5.326836	26.902095	9.084777

7	-7.650684	17.840394	10.167189
7	-9.048650	17.083222	8.642664
6	-5.703714	25.918853	9.961041
6	-5.350438	22.866601	14.124858
6	-8.842139	18.020584	9.605102
6	-3.684131	26.473915	10.466264
6	-4.037927	27.263320	9.401072
6	-6.421910	21.245837	8.322257
6	-7.081951	16.754011	9.557305
6	-7.938824	16.269286	8.604058
6	-5.487785	22.274704	15.519602
6	-10.233108	16.959716	7.826184
6	-6.079320	27.417972	7.967547
6	-4.568088	21.951056	13.196343
6	-4.722142	24.251286	14.152570
6	-5.313201	22.198397	7.887455
6	-7.775620	21.798217	7.896185
6	-6.201018	19.849738	7.761438
29	-8.352019	24.966500	12.017351
29	-9.900087	22.846802	13.767224
29	-8.076866	20.883752	13.504817
29	-9.656925	19.127068	12.307949
16	-9.704686	23.087506	11.461828
16	-10.474988	20.614535	13.805318
16	-10.331076	24.392039	15.369796
16	-6.601925	19.014790	13.624619
7	-8.937670	22.862109	17.197347
7	-10.739728	23.849648	18.024150
7	-8.807327	17.447469	13.114713
7	-7.208424	16.403226	14.213289
6	-9.952338	23.662474	16.918263
6	-11.360118	23.519761	10.746266
6	-7.602318	17.578774	13.657720
6	-9.067417	22.526265	18.516218
6	-10.178433	23.128687	19.051924
6	-10.785897	19.787281	15.449750
6	-9.193626	16.148580	13.314883
6	-8.209581	15.483658	13.998850
6	-12.179472	22.242169	10.639156
6	-5.950365	16.162654	14.880533
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6	-11.122116	24.137526	9.373978
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6	-9.461952	19.556350	16.163472
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1	-11.112559	16.741450	8.450041
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1	-7.948399	22.781630	8.359895
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1	-5.310217	22.302873	6.788716
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8	-7.295096	27.555182	12.577917
6	-9.408381	28.521488	12.276763
6	-7.873236	28.811026	12.181315
6	-10.253723	29.703388	12.714419
6	-9.983228	27.908982	11.006478
6	-7.402294	29.865389	13.175049
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1	-11.314009	29.408810	12.765351
1	-9.948742	30.096207	13.695046
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1	-10.013234	28.637514	10.183669
1	-9.388570	27.037323	10.691237
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1	-7.731249	30.872029	12.878824
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1	-7.887830	30.049116	10.403841
1	-6.303916	29.333478	10.804967
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6	-6.950264	25.721741	17.485963
6	-7.864582	25.984913	18.530681
6	-7.517770	25.757540	19.859199
6	-6.251537	25.269661	20.191303
1	-4.337967	24.632705	19.410523
1	-4.951929	25.007525	17.047099

1	-8.864871	26.354173	18.290477
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29	-7.209880	19.283922	11.170947
16	-6.992043	22.281040	13.974602
16	-6.464390	21.317232	10.536648
16	-5.922879	25.144841	10.797340
16	-10.308863	19.749383	10.022317
7	-4.185934	25.443855	12.912495
7	-4.364438	27.239995	11.627755
7	-8.109524	18.113154	9.771622
7	-9.733905	17.640206	8.361877
6	-4.800510	25.965868	11.862648
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6	-3.434945	27.537283	12.595544
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6	-7.724580	17.042656	9.009970
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6	-5.921755	20.930035	16.103001
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6	-4.784035	28.128752	10.569103
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6	-4.964259	23.199614	15.614520
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6	-7.620520	22.800453	8.513457
6	-6.777919	20.531878	7.894756
29	-8.130512	24.943527	11.626473
29	-9.575881	22.531801	14.353483
29	-8.122017	20.298883	13.540108
29	-9.965979	19.114407	12.231788
16	-9.586857	23.245730	12.081076
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16	-10.615821	23.831402	15.961034
16	-6.849016	18.326395	13.255348

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7	-9.262988	17.209886	12.536446
7	-7.764091	15.740528	13.204566
6	-9.849768	23.477803	17.483254
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6	-8.026743	17.058107	12.998899
6	-8.727523	22.578646	19.089382
6	-9.346907	23.676315	19.631112
6	-10.648822	19.314060	15.624906
6	-9.806297	15.956082	12.433732
6	-8.886081	15.028404	12.845857
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