

Supporting Information

Regio- and Chemoselective Hydroboration of Terminal Alkynes with Pinacolborane Catalyzed by Organo Rare Earth Metal Complexes

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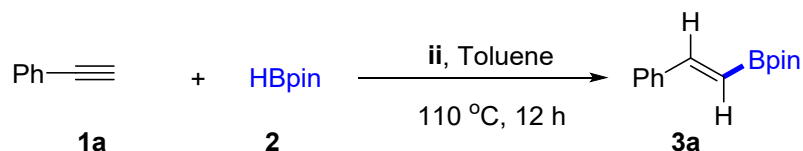
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1. General Remarks

All reactions were carried out under a nitrogen atmosphere using oven-dried glassware and standard Schlenk techniques in glove boxes. All of the solvents were dried and distilled over sodium. HBpin and part of alkynes were obtained commercially from Energy Chemical, Mayar, Acros, Alfa Aesar, or TCI without further purification. (η^3 -Flu-SiMe₂-N(^tBu)Y(CH₂SiMe₃)(THF)₂) was synthesized according to the corresponding literatures.^[1] TLC has been performed on Merck silica gel 60 F₂₅₄ TLC aluminum plates and visualized with UV light (254 nm). ¹H-NMR spectra were recorded on a 400 MHz NMR spectrometer in CDCl₃ (all signals are reported in ppm with the internal chloroform signal at 7.26 ppm). ¹³C NMR spectra were recorded with ¹H-decoupling on a Bruker Advance 101 or 176 MHz spectrometer in CDCl₃ (all signals are reported in ppm with the internal chloroform signal at 77.16 ppm). Melting points were measured on a melting point with a thermometer and are uncorrected.

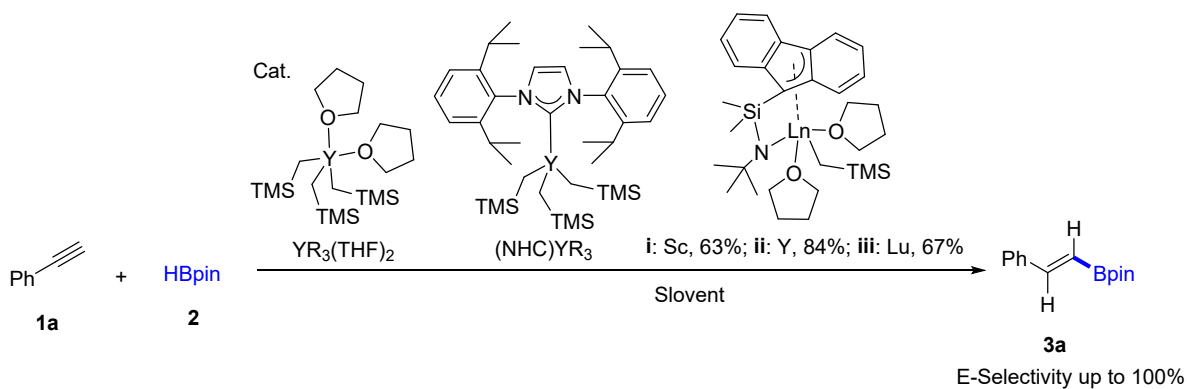
2. General procedure for the Yttrium(IV)-catalyzed hydroboration of alkynes



In an oven-dried Schlenk flask, a mixture of ethynylbenzene (**1a**) (0.30 mmol, 36.6 mg), 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2**) (1.2 mmol, 153.5 mg), η^3 -Flu-SiMe₂N(^tBu)Y(CH₂SiMe₃)-(THF)₂ (5 mol%), the mixture was well stirred for 12 h in toluene (2 mL) at 110 °C. After cooling, the reaction was quenched with saturated NH₄Cl aqueous solution (4 mL). The resulting mixture was extracted by Ethyl acetate (EA) (3×15 mL), and the combined extracts were washed with

brine, dried over sodium sulfate, and concentrated under reduced pressure. Purification by column chromatography (eluent: Petroleum ether: Ethyl acetate = 10:1) to give the product (E)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane **3a** (66 mg, 96%).

3. Reaction conditions screening for hydroboration of terminal alkyne **3a**

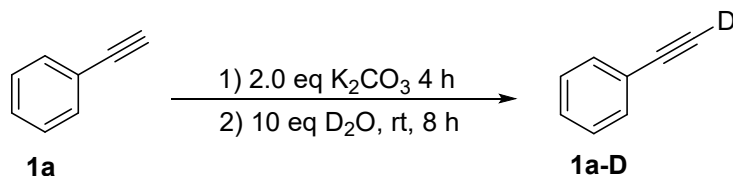


Entry	Cat. (mol%)	[HBpin]/[1a]	Base	Solvent	T (°C)	Time (h)	Yield (%) ^e
1	-	1.2	-	C ₆ D ₆	70	36	-
2	YR₃(THF)₂ (10)	1.2	-	C ₆ D ₆	70	36	-
3	(NHC)YR₃ (10)	1.2	-	C ₆ D ₆	70	36	-
4	ii (10)	1.2	-	C ₆ D ₆	70	36	34
5	ii (10)	1.2	-	C ₆ D ₆	110	36	62
^b 6	ii (10)	1.2	^t BuONa	C ₆ D ₆	110	36	62
^c 7	ii (10)	1.2	Na ₂ CO ₃	C ₆ D ₆	110	36	42
^d 8	ii (10)	1.2	Et ₃ N	C ₆ D ₆	110	36	52
9	ii (10)	1.5	-	C ₆ D ₆	110	36	59
10	ii (10)	2.0	-	C ₆ D ₆	110	36	63
11	ii (10)	3.0	-	C ₆ D ₆	110	36	86
12	ii (10)	4.0	-	C ₆ D ₆	110	12	99
13	ii (10)	5.0	-	C ₆ D ₆	110	12	99
14	ii (10)	4.0	-	C ₆ D ₆	110	12	70
15	ii (10)	4.0	-	C ₆ D ₆	90	12	66
16	ii (10)	4.0	-	C ₄ D ₈ O	110	12	70
17	ii (10)	4.0	-	C ₇ D ₈	110	12	99
18	ii (5)	4.0	-	C ₇ D ₈	110	12	99
19	ii (2)	4.0	-	C ₇ D ₈	110	12	72
20	ii (1)	4.0	-	C ₇ D ₈	110	12	61
21	ii (5)	4.0	-	C ₇ D ₈	100	6	55
22	ii (5)	4.0	-	C ₇ D ₈	100	12	84
23	i (5)	4.0	-	C ₇ D ₈	110	12	98
24	iii (5)	4.0	-	C ₇ D ₈	110	12	92
25	ii (10)	4.0	-	-	110	12	99

^a Reaction conditions: **1a** (0.15 mmol), 0.7 mL of solvent in a Schlenk NMR tube under N₂, unless otherwise indicated. ^b Added 0.1 equiv. of ^tBuONa; ^c Added 0.1 equiv. of Na₂CO₃; ^d Added 0.1 equiv. of Et₃N, ^e Yield determined by GC and ¹H NMR spectroscopy.

4. General method for the synthesis of deuterium phenylacetylene and DBpin

4.1 The synthesis of deuterium phenylacetylene^[2]



An oven-dried 10 mL 2-neck round-bottom flask was charged with phenylacetylene (1.02g, 10.0 mmol), potassium carbonate (2.76 g, 2.0 equiv.), and dry MeCN (10 mL). The reaction mixture was stirred under an N₂ atmosphere for 4 h. To this mixture, D₂O (2.0 mL, 10.0 equiv.) was added and left to stir for an additional 8 h. The resulting crude reaction mixture was diluted with CH₂Cl₂ (10.0 mL) and transferred to an oven-dried separating funnel. The organic layer was separated and dried over MgSO₄, filtered, and the solvent removed under reduced pressure. The crude product was separated through column chromatography using distilled hexane to afford 989.4 mg (97%) deuterated phenylacetylene as a colorless liquid. Spectral data are in accordance with the reported data.^[3]

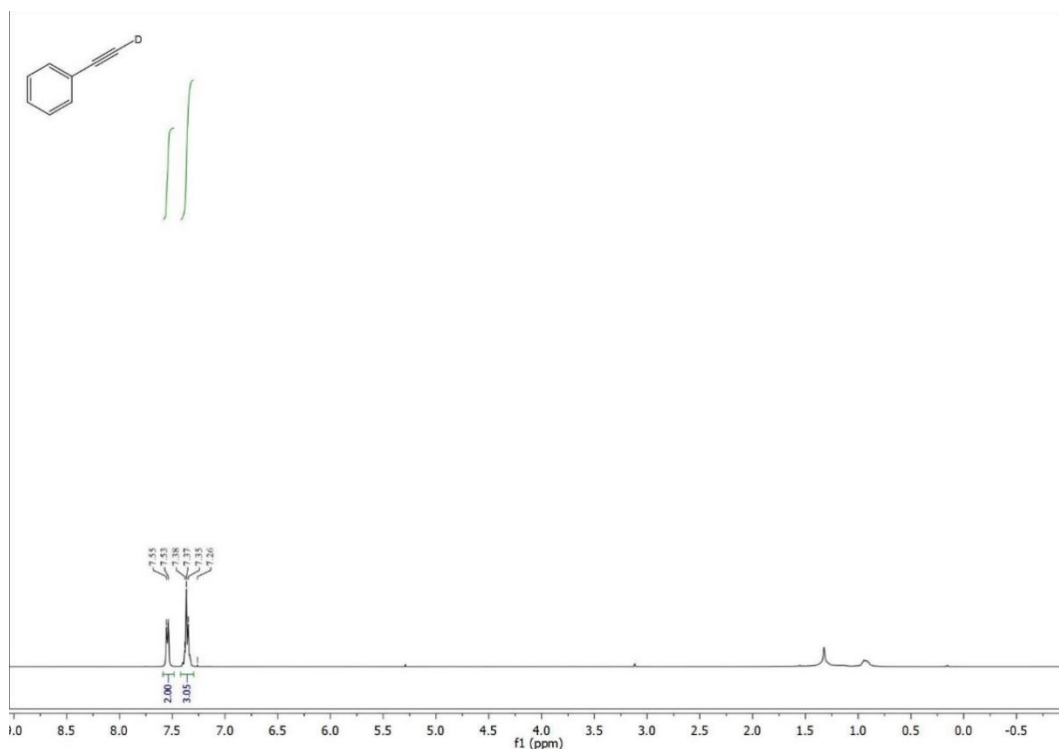
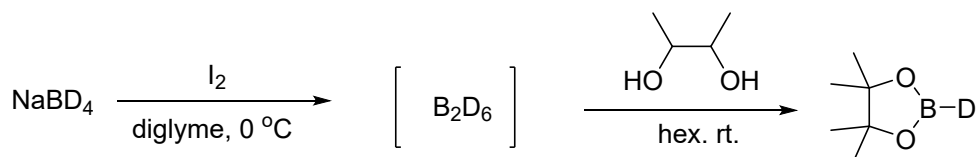


Figure S1: ^1H NMR (CDCl_3 , 400 MHz) spectra of 1a-D

4.2 The synthesis of deuterium DBpin^[4]



A Schlenk was charged with NaBD_4 (0.5 g, 12.2 mmol) and was suspended in diglyme (25 mL). To a second Schlenk pinacol (0.48 g, 4.08 mmol) was dissolved in hexane (25 mL). A cannula was fitted between the two Schlenks with the cannula submersed in the hexane solution. An exit needle was fitted to this flask. Iodine (1.55 g, 6.11 mmol) was dissolved in diglyme (25 mL) and this was added dropwise over 1h to the NaBD_4 suspension. On completion of the addition, a gentle stream of nitrogen was passed through the hexane for 1 hour to remove unreacted B_2D_6 , the hexane solution of DBpin (b.p. = 110 °C) was distilled to give pure DBpin. The product was then analyzed by NMR. Spectral data are in accordance with the reported data^[5].

5. Mechanistic Investigation:

5.1. Deuterium labelling Experiments

In a glove box, a sealed Schlenk tube equipped with a magnetic stirring bar was charged with (η^3 -Flu-SiMe₂-N(^tBu)Y(CH₂SiMe₃)(THF)₂ (**ii**) (5 mol%), pinacol borane (4 equiv.), phenyl acetylene-d1 (0.30 mmol) and 2 mL of toluene. The reaction mixture was heated at 110 °C for 12 hours. ¹H NMR of vinyl borate shows that the hydrogen has been deuterated, which indicates a cis orientation of deuterium and phenyl group in **3a-D**.

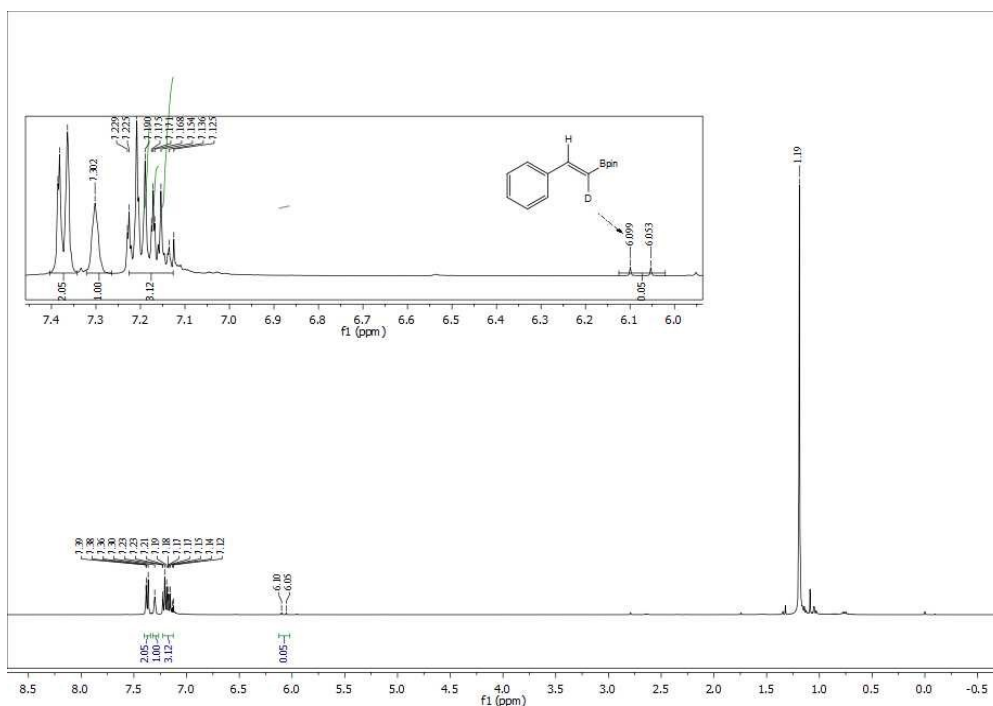
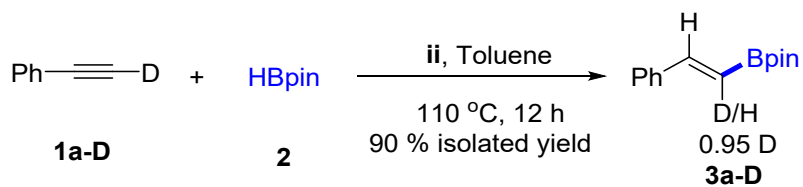


Figure S2: ¹H NMR (CDCl₃, 400 MHz) spectra of **3a-D**

In a glove box, a sealed Schlenk tube equipped with a magnetic stirring bar was charged

with (η^3 -Flu-SiMe₂-N(^tBu)Y(CH₂SiMe₃)(THF)₂ (**ii**) (5 mol%), pinacol borane-d₁ (4 equiv.), **1a** (0.30 mmol) and 2 mL of toluene. The reaction mixture was heated at 110 °C for 12 h. ¹H NMR of vinyl borate shows that the hydrogen has been deuterated, which indicates a cis orientation of deuterium and Bpin unit in **3a-D***

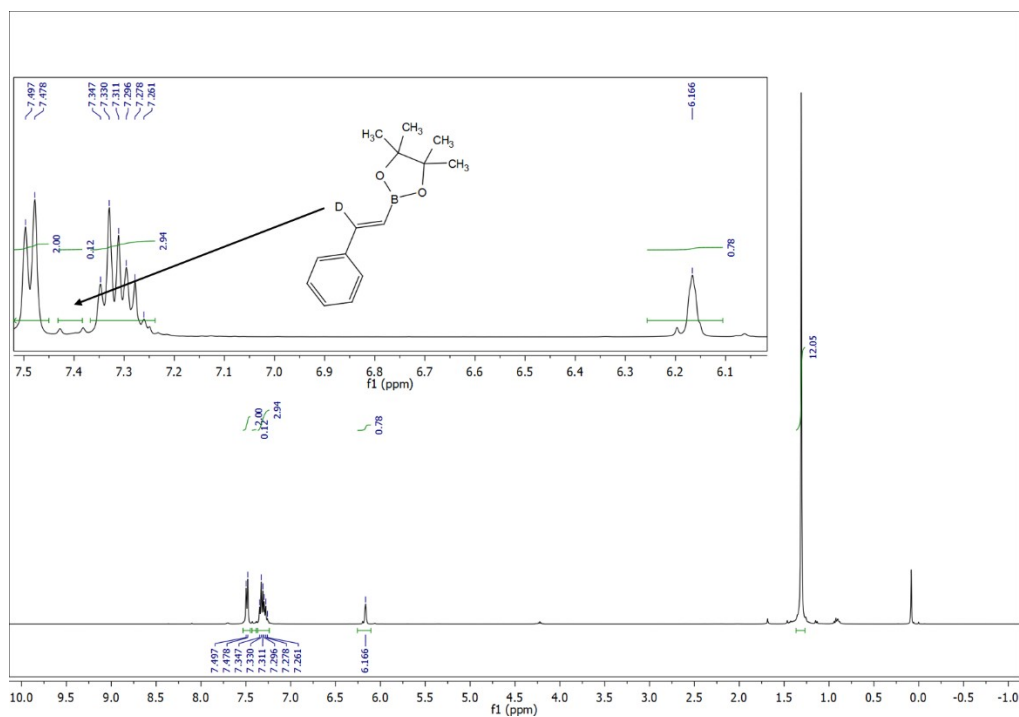
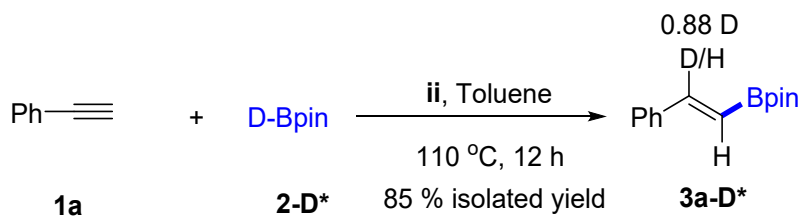


Figure S3: ¹H NMR (CDCl₃, 400 MHz) spectra of **3a-D***

5.2 NMR of (3-1) after I₂ quenching^[6]

In order to confirm the existence of a Y-alkenyl intermediate, an I₂ quenching experiment was carried out. In a NMR tube I₂ solution in CDCl₃ was added to the reaction mixture of **ii**

(0.1mmol) + **2**(0.1 mmol) + **1a**(0.1 mmol). NMR analysis of the reaction mixture further confirmed the formation of (2-iodovinyl)benzene.

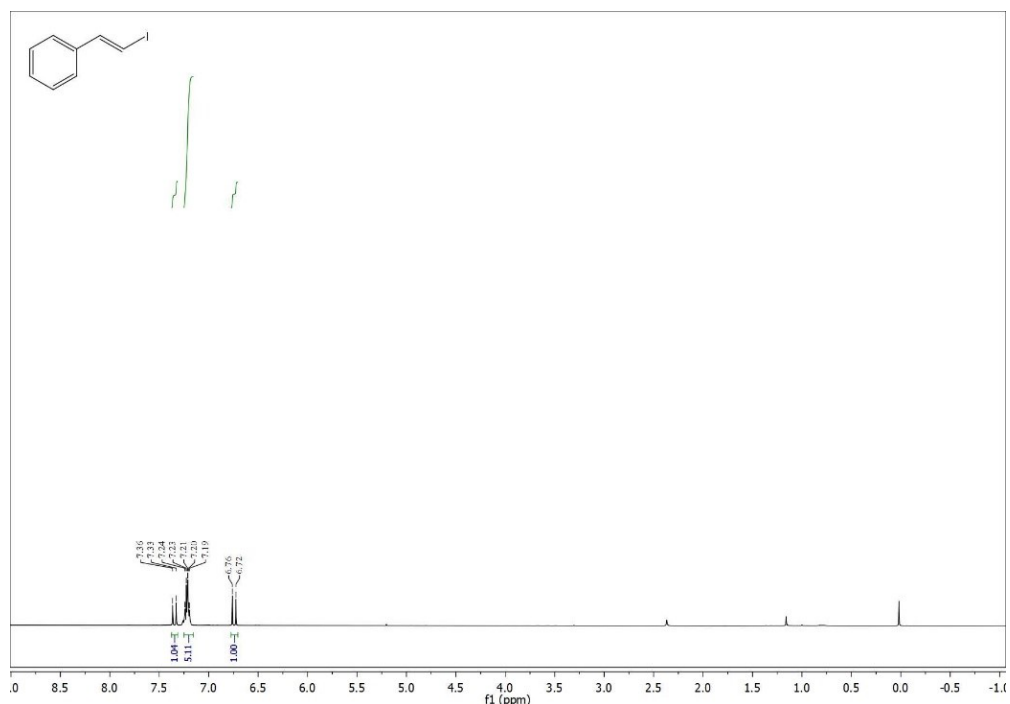
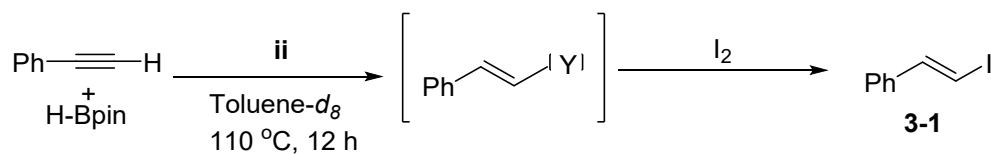


Figure S4: ^1H NMR (CDCl_3 , 400 MHz) spectra of **3-1**

5.3 ESI-Mass spectra of byproduct

In order to confirm the existence of a boronate compound $\text{TMSCH}_2\text{B}(\text{OCMe}_2\text{CMe}_2\text{O})$, which should generate from σ -bond metathesis reaction of **ii** and HBpin Y-alkenyl intermediate, The reaction mixture of **ii** (0.1mmol) + **2**(0.1 mmol) + **1a**(0.1 mmol). ESI-Mass analysis of the reaction mixture further confirmed the formation of boronate compound $\text{TMSCH}_2\text{B}(\text{OCMe}_2\text{CMe}_2\text{O})$.

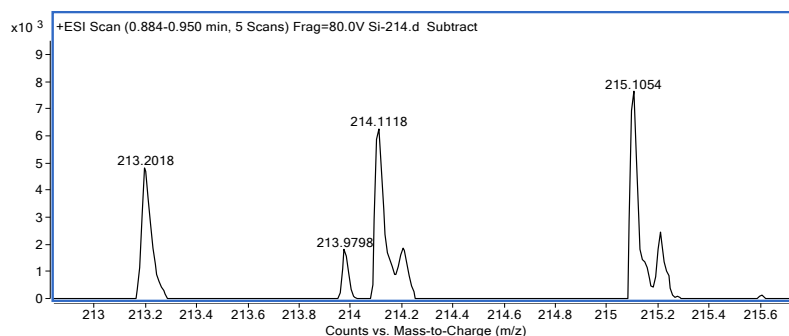


Figure S5: ESI-Mass spectra of TMSCH₂B(OCMe₂CMe₂O).

5.4 ¹H NMR-monitoring the model reaction

In a glovebox, (*η*³-Flu-SiMe₂-N(*t*Bu)Y(CH₂SiMe₃)(THF)₂ (**ii**) (5 mol%) in toluene-*d*₈ and pinacolborane (0.0384 mg, 4 equiv.) were weighed into an NMR tube equipped with a Teflon valve (J-Young). Then, to which a mixture of **1a** (10.2 mg, 0.1 mmol) in toluene-*d*₈ (0.5 mL) was added via a syringe. The ensuing catalytic reaction was monitored by ¹H NMR spectroscopy. After 3 h, 8 h and 12 h at 110 °C in an oil bath, the catalytic reaction reaches > 99% completion

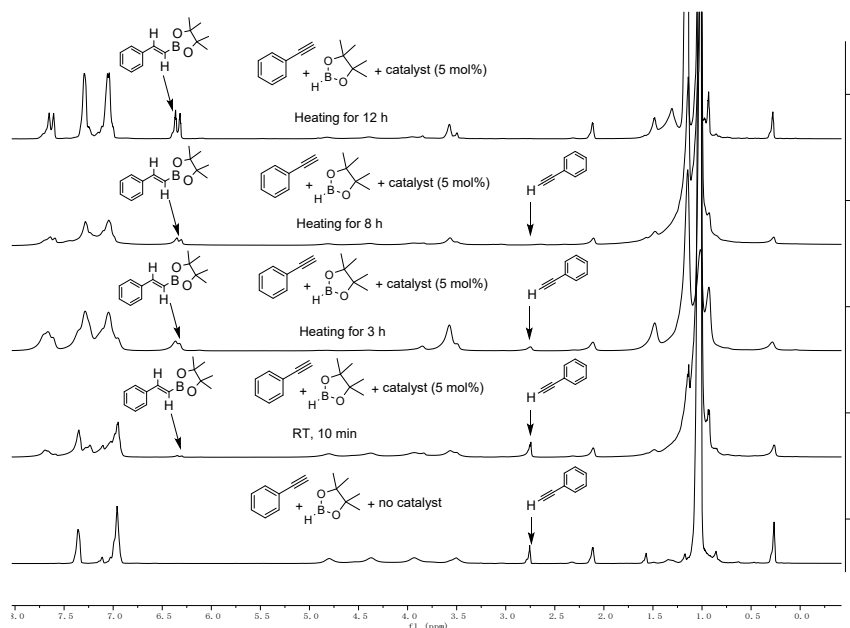


Figure S6: *in-situ* ¹H NMR spectra for the reaction of **1a** and HBpin catalyzed by **ii** in toluene-*d*₈ at 110 °C.

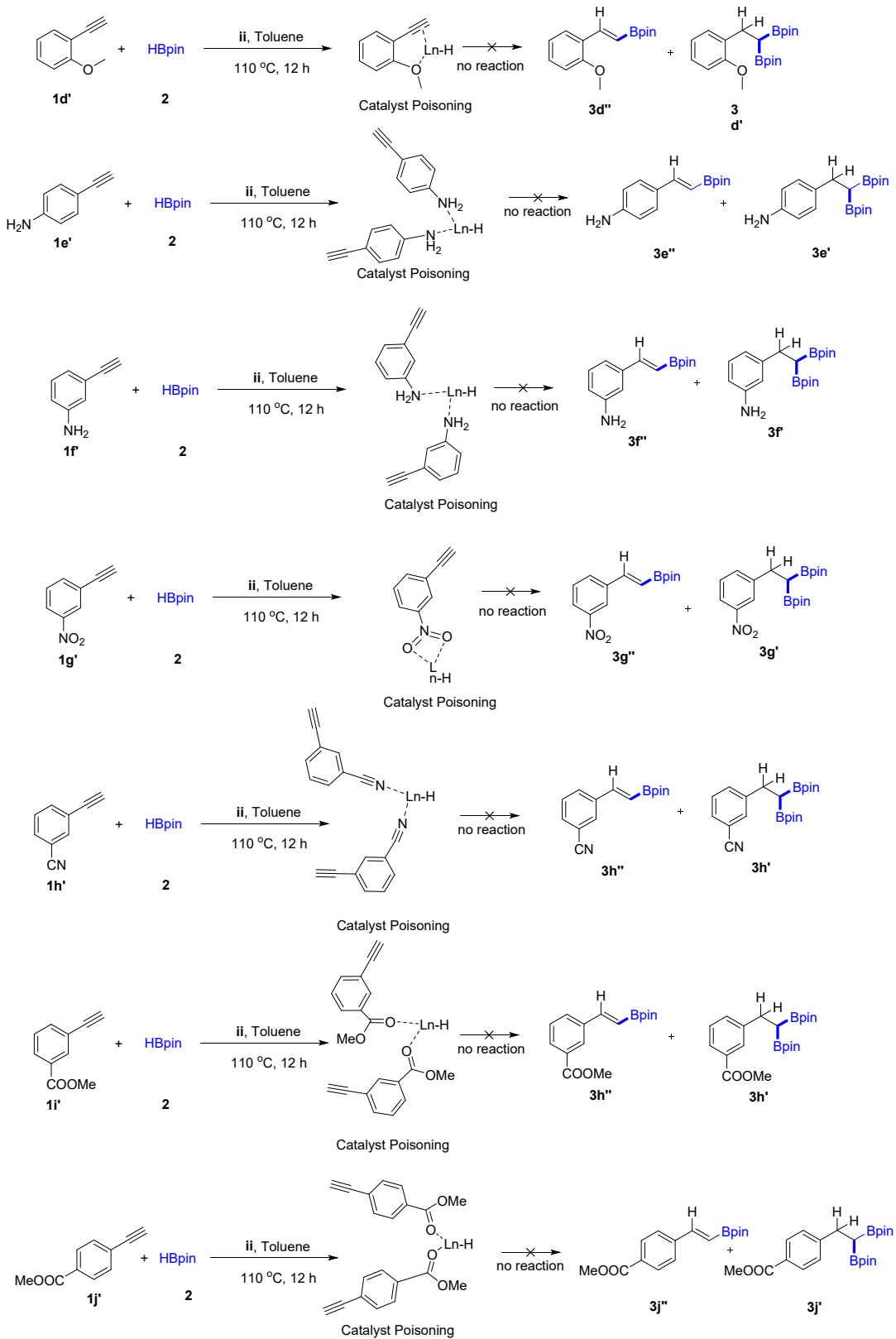


Figure S7. The further investigation of rare-earth catalyzed dihydroborylation of phenylacetylene

derivatives.

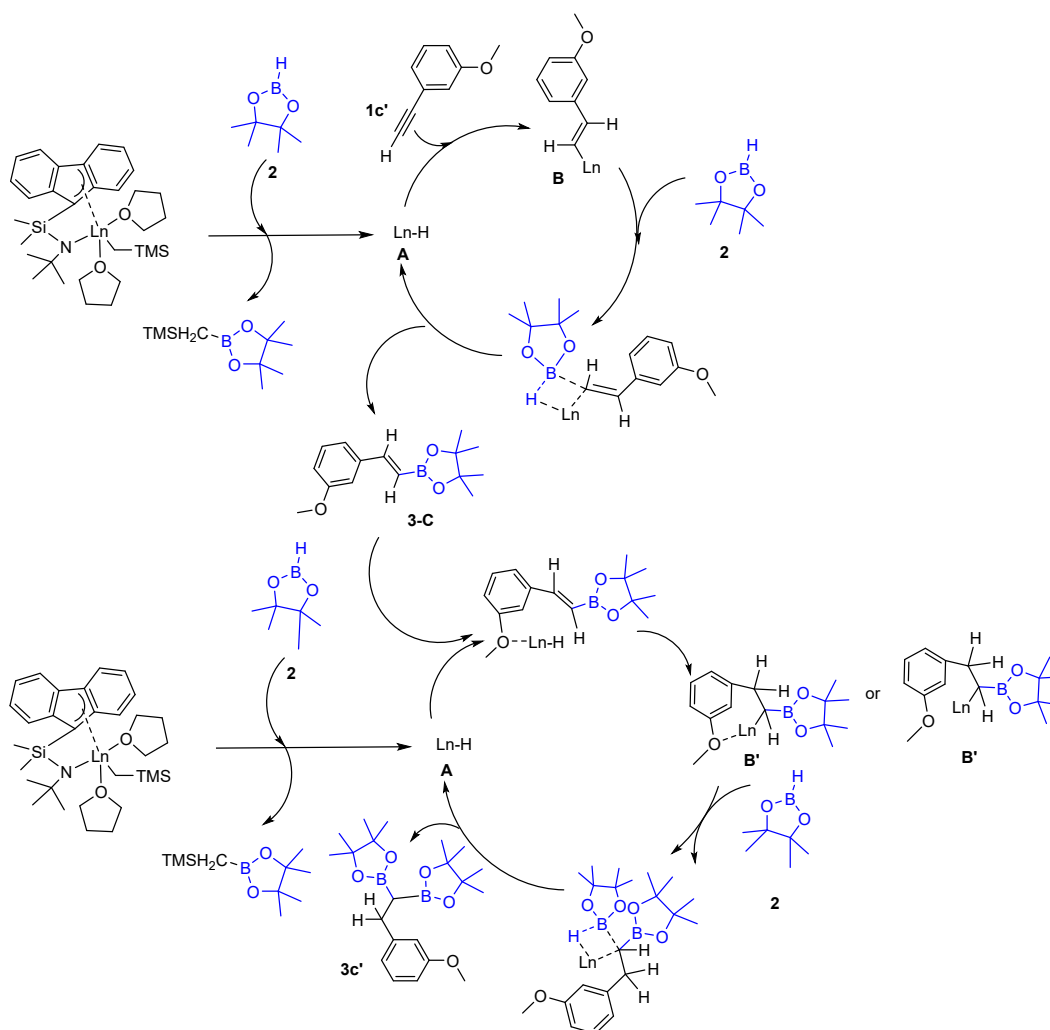


Figure S8: The proposed mechanism of the 1,1-diborylation of the substrate 1c'.

6 Product Transformation

Procedure for the synthesis of (3a) with 1.02 g of 1a.

In an oven-dried Schlenk flask, a mixture of ethynylbenzene (**1a**) (10 mmol, 1.02 g), 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2**) (40 mmol, 5.08 g), η^3 -Flu-SiMe₂N(^tBu)Y(CH₂SiMe₃)-(THF)₂ (5 mol%, 30.6 mg), the mixture was well stirred for 12 h in toluene (80 mL) at 110 °C. After cooling, the reaction was quenched with saturated NH₄Cl aqueous solution (120 mL). The resulting mixture was extracted by Ethyl acetate (EA) (3×250 mL), and the combined extracts were washed with brine, dried over sodium sulfate, and concentrated under reduced pressure. Purification by column chromatography (eluent: Petroleum ether: Ethyl acetate = 10:1) to give the product (E)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane **3a** (2.2 g, 99%).

Procedure for the synthesis of (E)-(2-iodovinyl)benzene (3-1) from 3a^[7]

The substrate **3a** (0.5 mmol, 115 mg) was dissolved in 1.25 mL THF in a 25 mL round bottom flask, then an aqueous solution of NaOH (1.5 mmol, 3 M) was added dropwise at room temperature. Subsequently, a solution of I₂ (1.0 mmol, 254 mg, 0.2 M in THF) was added slowly and stirred for 2 h before quenching with a saturated solution of sodium thiosulfate. The organic solution was separated, and the aqueous solution was washed with Et₂O. The combined organic layers were dried with MgSO₄, the solvent was evaporated and the crude product was isolated on silica gel using flash chromatography (PE as eluent) .

Procedure for the synthesis of 2-phenylacetaldehyde (3-2) from 3a^[7]

The substrate **3a** (0.23 g, 1 mmol) was dissolved in acetone (10 mL) and cooled to 0 °C, Oxone solution (0.3 g, 1.5 mmol in 15 mL H₂O) was then added dropwisely and further stirred for 1 h. Upon completion the reaction was quenched with 1M HCl (5 mL) and extracted with DCM,

the combined organics were washed with water, and brine and dried with MgSO₄. The solvent was evaporated under reduced pressure, and the crude product was isolated on silica gel using flash chromatography (PE: EA = 10:1).

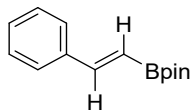
Procedure for the synthesis of 2,5-diphenyl-1*H*-imidazole (3-3) from 3a^[8]

A sealed Schlenk tube equipped with a magnetic stirring bar was charged with the substrate **3a** (0.5 mmol, 115 mg), benzimidamide (1.0 equiv), N-Bromosuccinimide (2.5 equiv), and 2.5 mL of DMSO. The reaction mixture was heated at 110 °C for 24 h under N₂. Upon completion, the reaction was quenched with H₂O and extracted with ethyl acetate, the combined organic layer wash with water, and brine and dried with MgSO₄. The solvent was evaporated under reduced pressure, and the crude product was isolated on silica gel using flash chromatography (PE: EA = 10:2).

Procedure for the synthesis of (*E*)-prop-1-ene-1,3-diyl dibenzene (3-4) from 3a^[9]

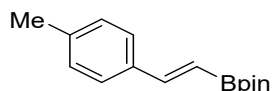
A sealed Schlenk tube equipped with a magnetic stirring bar was charged with the substrate **3a** (0.5 mmol, 115 mg), (bromomethyl)benzene (1.2 equiv), Pd(acac)₂ (10 mol%), KF (3 equiv), and THF (3.0 mL). The reaction mixture was heated at 0 °C for 15 min then 4 h at 35 °C h under N₂. Upon completion of the reaction the organic solvent was evaporated under reduced pressure, and the crude product was extracted with ethyl acetate, the combined organic layer wash with water, and brine and dried with MgSO₄. The solvent was evaporated under reduced pressure, and the crude product was isolated on silica gel using flash chromatography (PE as eluent).

7 Characterization of Products:



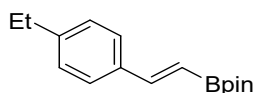
(E)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (3a)

The representative procedure was followed using Phenylacetylene (**1a**) (31 mg, 0.30 mmol). Purification by column chromatography (eluent: Petroleum ether: Ethyl acetate = 10:1) yielded **3a** (66 mg, 96%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.49 (d, *J* = 6.8 Hz, 2H), 7.40 (d, *J* = 18.4 Hz, 1H), 7.28-7.36 (m, 3H), 6.17 (d, *J* = 18.4 Hz, 1H), 1.32 (s, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 149.7, 137.6, 129.0, 128.7, 127.2, 83.5, 77.36, 25.0. The spectra data are in accordance with those reported in the literature.^[7]



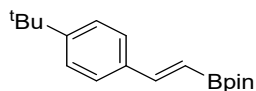
(E)-4,4,5,5-tetramethyl-2-(4-methylstyryl)-1,3,2-dioxaborolane (3b)

The representative procedure was followed using 4-Ethynyltoluene (**1b**) (35 mg, 0.30 mmol). Purification by column chromatography (eluent: Petroleum ether: Ethyl acetate = 10:1) yielded **3b** (66 mg, 93%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.33-7.43 (m, 3H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.11 (d, *J* = 18.4 Hz, 1H), 2.35 (s, 3H), 1.31 (s, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 149.6, 139.1, 134.9, 129.4, 127.2, 83.4, 77.4, 25.0, 21.5. The spectra data are in accordance with those reported in the literature.^[7]



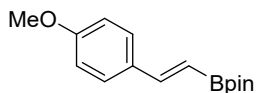
(E)-2-(4-ethylstyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3c)

The representative procedure was followed using 4-Ethylphenylacetylene (**1c**) (39 mg, 0.30 mmol). Purification by column chromatography (eluent: Petroleum ether: Ethyl acetate = 10:1) yielded **3c** (48 mg, 62%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.41 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 18.4 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.11 (d, *J* = 18.4 Hz, 1H), 2.64 (q, *J* = 7.6 Hz, 2H), 1.31 (s, 12H), 1.23 (t, *J* = 7.6 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 149.7, 145.5, 135.2, 128.2, 127.3, 83.4, 77.4, 28.8, 25.0, 15.5. The spectra data are in accordance with those reported in the literature. [10]



(E)-2-(4-(*tert*-butyl)styryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3d**)**

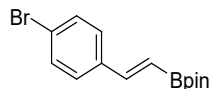
The representative procedure was followed using 4-(*tert*-butyl)phenylacetylene (**1d**) (47 mg, 0.30 mmol). Purification by column chromatography (eluent: Petroleum ether: Ethyl acetate = 10:1) yielded **3d** (74 mg, 86%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.43 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 18.4 Hz, 1H), 7.36 (d, *J* = 8.4 Hz, 2H), 6.12 (d, *J* = 18.4 Hz, 1H), 1.32 (s, 21H). ¹³C NMR (101 MHz, CDCl₃) δ 152.3, 149.5, 134.9, 127.0, 125.6, 83.4, 77.4, 34.8, 31.4, 25.0. The spectra data are in accordance with those reported in the literature. [7]



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

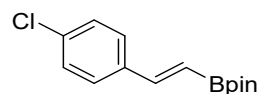
The representative procedure was followed using 4-Ethynylanisole (**1e**) (40 mg, 0.30 mmol). Purification by column chromatography (eluent: Petroleum ether: Ethyl acetate = 10:1) yielded **3e** (63 mg, 81%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.44 (d, *J* = 8.8 Hz, 2H), 7.35 (d, *J*

= 18.4 Hz, 1H), 6.86 (d, $J = 8.4$ Hz, 2H), 6.01 (d, $J = 18.4$ Hz, 1H), 3.81 (s, 3H), 1.31 (s, 12H). ^{13}C NMR (101 MHz, CDCl_3) δ 160.4, 149.2, 130.6, 128.6, 114.1, 83.4, 77.4, 55.4, 25.0. The spectra data are in accordance with those reported in the literature. ^[10]



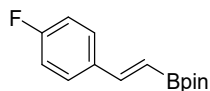
(E)-2-(4-bromostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3f)

The representative procedure was followed using 4-Bromophenylacetylene (**1f**) (54 mg, 0.30 mmol). Purification by column chromatography (eluent: Petroleum ether: Ethyl acetate = 10:1) yielded **3f** (51 mg, 55%) as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.46 (d, $J = 8.4$ Hz, 2H), 7.34 (d, $J = 8.4$ Hz, 2H), 7.31 (d, $J = 14.0$ Hz, 1H), 6.15 (d, $J = 18.4$ Hz, 1H), 1.31 (s, 12H). ^{13}C NMR (101 MHz, CDCl_3) δ 148.2, 136.5, 131.9, 128.7, 123.1, 83.6, 77.37, 25.0. The spectra data are in accordance with those reported in the literature. ^[10]



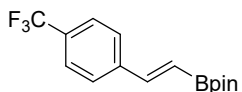
(E)-2-(4-chlorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3g)

The representative procedure was followed using 4-Chlorophenylacetylene (**1g**) (41 mg, 0.30 mmol). Purification by column chromatography (eluent: Petroleum ether: Ethyl acetate = 10:1) yielded **3g** (66 mg, 83%) as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.41 (d, $J = 8.4$ Hz, 2H), 7.33 (d, $J = 18.4$ Hz, 3H), 7.30 (s, 1H), 6.13 (d, $J = 18.4$ Hz, 1H), 1.31 (s, 12H). ^{13}C NMR (101 MHz, CDCl_3) δ 148.2, 136.1, 134.8, 128.9, 128.4, 83.6, 77.4, 25.0. The spectra data are in accordance with those reported in the literature. ^[10]



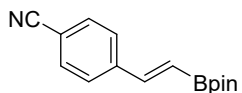
(E)-2-(4-fluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3h)

The representative procedure was followed using 4-Fluorophenylacetylene (**1h**) (36 mg, 0.30 mmol). Purification by column chromatography (eluent: Petroleum ether: Ethyl acetate = 10:1) yielded **3h** (65 mg, 88%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.46 (dd, *J* = 8.8, 5.6 Hz, 2H), 7.35 (d, *J* = 18.4 Hz, 1H), 7.02 (t, *J* = 8.8 Hz, 2H), 6.07 (d, *J* = 18.4 Hz, 1H), 1.31 (s, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 164.5, 162.1, 148.3, 133.9 (d, *J* = 3.0 Hz), 128.9 (d, *J* = 8.0 Hz), 115.7 (d, *J* = 22.2 Hz), 83.5, 77.5, 25.0. The spectra data are in accordance with those reported in the literature. ^[10]



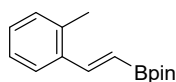
(E)-4,4,5,5-tetramethyl-2-(4-(trifluoromethyl)styryl)-1,3,2-dioxaborolane (3i)

The representative procedure was followed using 1-ethynyl-4-(trifluoromethyl)benzene (**1i**) (51.2 mg, 0.30 mmol). Purification by column chromatography (eluent: Petroleum ether: Ethyl acetate = 10:1) yielded **3i** (49.4 mg, 94%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.61 – 7.52 (m, 4H), 7.40 (d, *J* = 18.4 Hz, 1H), 6.25 (d, *J* = 18.4 Hz, 1H), 1.31 (s, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 147.7, 140.9, 130.58 (q, *J* = 32.4 Hz), 127.2, 125.67 (q, *J* = 3.8 Hz), 121.52 (q, *J* = 271.9 Hz), 83.7, 24.9. The spectra data are in accordance with those reported in the literature. ^[7]



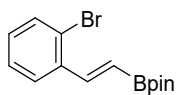
(E)-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzonitrile (3j)

The representative procedure was followed using 4-ethynylbenzonitrile (**1j**) (38.1 mg, 0.30 mmol). Purification by column chromatography (eluent: Petroleum ether: Ethyl acetate = 10:1) yielded **3j** (50.4 mg, 66%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.66 – 7.51 (m, 4H), 7.36 (d, *J* = 18.4 Hz, 1H), 6.27 (d, *J* = 18.4 Hz, 1H), 1.31 (s, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 147.2, 141.7, 132.5, 127.5, 118.9, 112.1, 83.8, 24.9. The spectra data are in accordance with those reported in the literature. [6]



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

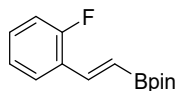
The representative procedure was followed using 1-ethynyl-2-methylbenzene (**1k**) (34.8 mg, 0.30 mmol). Purification by column chromatography (eluent: Petroleum ether: Ethyl acetate = 10:1) yielded **3k** (62.9 mg, 86%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.67 (d, *J* = 18.3 Hz, 1H), 7.60 – 7.53 (m, 1H), 7.24 – 7.10 (m, 3H), 6.10 (d, *J* = 18.3 Hz, 1H), 2.43 (s, 3H), 1.33 (s, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 147.2, 136.7, 136.3, 130.5, 128.6, 126.2, 125.8, 83.4, 24.9, 19.9. The spectra data are in accordance with those reported in the literature. [10]



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

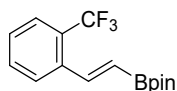
The representative procedure was followed using 1-ethynyl-2-bromobenzene (**1l**) (54.1 mg, 0.30 mmol). Purification by column chromatography (eluent: Petroleum ether: Ethyl acetate = 10:1) yielded **3l** (69.3 mg, 75%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.72 – 7.51 (m, 2H), 7.29 – 7.04 (m, 3H), 6.10 (d, *J* = 18.3 Hz, 1H), 1.33 (s, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 149.1,

137.8, 128.8, 127.4, 126.1, 83.4, 24.8. The spectra data are in accordance with those reported in the literature. [11]



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

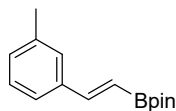
The representative procedure was followed using 1-ethynyl-2-fluorobenzene (1m) (36.2 mg, 0.30 mmol). Purification by column chromatography (eluent: Petroleum ether: Ethyl acetate = 10:1) yielded 3m (61.3 mg, 82%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.64 – 7.52 (m, 2H), 7.28 – 7.18 (m, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 7.02 (t, *J* = 8.2 Hz, 1H), 6.24 (d, *J* = 18.6 Hz, 1H), 1.30 (s, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 160.7 (d, *J* = 251.6 Hz), 141.3 (d, *J* = 4.1 Hz), 130.2 (d, *J* = 8.5 Hz), 127.4 (d, *J* = 3.3 Hz), 125.4 (d, *J* = 11.7 Hz), 124.1 (d, *J* = 3.6 Hz), 115.8 (d, *J* = 22.1 Hz), 83.4, 24.8. The spectra data are in accordance with those reported in the literature. [7]



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

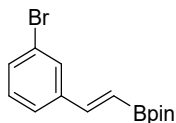
The representative procedure was followed using 1-ethynyl-2-(trifluoromethyl)benzene (1n) (51.1 mg, 0.30 mmol). Purification by column chromatography (eluent: Petroleum ether: Ethyl acetate = 10:1) yielded 3n (81.6 mg, 91%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.80 – 7.59 (m, 3H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 6.16 (d, *J* = 18.1 Hz, 1H), 1.31 (s, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 144.8 (d, *J* = 2.0 Hz), 137.0, 132.0, 128.3, 127.9(q, 30.1 Hz), 127.6,

125.8(q, 5.7 Hz), 124.8 (q, 274.0 Hz), 83.6, 24.9. The spectra data are in accordance with those reported in the literature. [6]



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

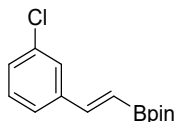
The representative procedure was followed using 1-ethynyl-3-methylbenzene (1o) (34.8 mg, 0.30 mmol). Purification by column chromatography (eluent: Petroleum ether: Ethyl acetate = 10:1) yielded 3o (65.2 mg, 89%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.35 (d, J = 18.4 Hz, 1H), 7.30 – 7.25 (m, 2H), 7.19 (t, J = 7.8 Hz, 1H), 7.08 (d, J = 7.4 Hz, 1H), 6.13 (d, J = 18.4 Hz, 1H), 2.32 (s, 3H), 1.28 (s, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 149.7, 138.1, 137.5, 129.8, 128.5, 127.8, 124.3, 83.4, 24.9, 21.4. The spectra data are in accordance with those reported in the literature. [10]



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

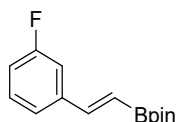
The representative procedure was followed using 1-ethynyl-3-bromobenzene (1p) (53.7 mg, 0.30 mmol). Purification by column chromatography (eluent: Petroleum ether: Ethyl acetate = 10:1) yielded 3p (74.8 mg, 81%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.61 (s, 1H), 7.43 – 7.36 (m, 2H), 7.30 (d, J = 18.4 Hz, 1H), 7.20 (t, J = 7.8 Hz, 1H), 6.16 (d, J = 18.4 Hz, 1H), 1.31

(s, 12H).. ^{13}C NMR (101 MHz, CDCl_3) δ 147.9, 139.4, 134.6, 129.9, 128.8, 127.0, 125.3, 83.6, 24.9. The spectra data are in accordance with those reported in the literature. ^[11]



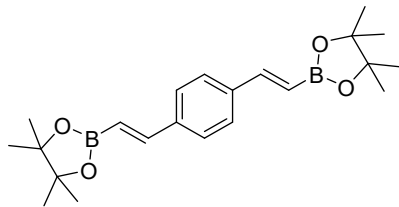
(E)-2-(3-chlorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3q)

The representative procedure was followed using 1-ethynyl-3-chlorobenzene (**1q**) (40.8 mg, 0.30 mmol). Purification by column chromatography (eluent: Petroleum ether: Ethyl acetate = 10:1) yielded **3q** (65.7 mg, 83%) as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.52 (s, 1H), 7.43 – 7.38 (m, 1H), 7.36 (s, 1H), 7.34 – 7.30 (m, 2H), 6.24 (d, $J = 18.4$ Hz, 1H), 1.38 (s, 12H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.2, 141.3, 126.2, 125.1, 124.9, 83.4, 24.9. The spectra data are in accordance with those reported in the literature. ^[7]



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

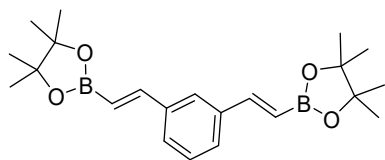
The representative procedure was followed using 1-ethynyl-3-fluorobenzene (**1r**) (36.2 mg, 0.30 mmol). Purification by column chromatography (eluent: Petroleum ether: Ethyl acetate = 10:1) yielded **3r** (65.1 mg, 87%) as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.21 (s, 1H), 7.19 – 7.02 (m, 3H), 6.89 – 6.79 (m, 2H), 6.06 (d, $J = 18.4$ Hz, 1H), 1.18 (s, 12H). ^{13}C NMR (101 MHz, CDCl_3) δ 162.9 (d, $J = 245.6$ Hz), 147.8, 139.8 (d, $J = 7.4$ Hz), 129.8 (d, $J = 8.2$ Hz), 122.8 (d, $J = 2.6$ Hz), 115.4 (d, $J = 21.5$ Hz), 113.1 (d, $J = 21.6$ Hz), 83.2, 24.6. The spectra data are in accordance with those reported in the literature. ^[12]



1,4-bis((*E*)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzene (3s)

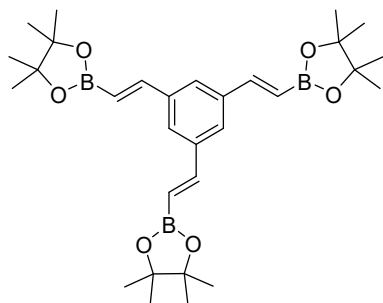
The representative procedure was followed using 1,4-diethynylbenzene (1s) (37.9 mg, 0.30 mmol). Purification by column chromatography (eluent: Petroleum ether: Ethyl acetate = 10:1) yielded 3s (104.2 mg, 91%) as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 7.44 (s, 4H), 7.36 (d, $J = 18.4$ Hz, 2H), 6.16 (d, $J = 18.4$ Hz, 2H), 1.29 (s, 24H). ^{13}C NMR (101 MHz, CDCl_3) δ .148.8, 138.0, 130.1, 127.3, 83.4, 24.8. The spectra data are in accordance with those reported in the literature.

[13]



1,3-bis((*E*)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzene (3t)

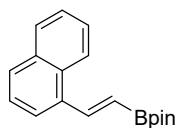
The representative procedure was followed using 1,3-diethynylbenzene (1t) (38.1 mg, 0.30 mmol). Purification by column chromatography (eluent: Petroleum ether: Ethyl acetate = 10:1) yielded 3t (104.6 mg, 92%) as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 7.55 (s, 1H), 7.44 – 7.33 (m, 4H), 7.32 – 7.26 (m, 1H), 6.15 (d, $J = 18.4$ Hz, 2H), 1.29 (s, 24H); ^{13}C NMR (101 MHz, CDCl_3) δ .149.2, 137.8, 128.9, 127.4, 126.2, 83.4, 24.9. The spectra data are in accordance with those reported in the literature. [14]



1,3,5-tris((*E*)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzene (3u)

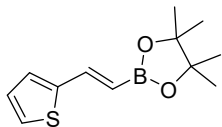
The representative procedure was followed using 1,3,5-triethynylbenzene (**1u**) (45.1 mg, 0.30 mmol). Purification by column chromatography (eluent: Petroleum ether: Ethyl acetate = 10:1) yielded **3u** (126.4 mg, 79 %) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.52 (s, 3H), 7.36 (d, *J* = 18.5 Hz, 3H), 6.16 (d, *J* = 18.5 Hz, 3H), 1.30 (s, 36H). ¹³C NMR (101 MHz, CDCl₃) δ 148.9, 138.1, 126.2, 83.5, 24.9. The spectra data are in accordance with those reported in the literature.

[15]



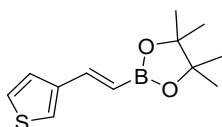
(*E*)-4,4,5,5-tetramethyl-2-(2-(naphthalen-1-yl)vinyl)-1,3,2-dioxaborolane (3v)

The representative procedure was followed using 1-ethynyl-naphthalene (**1v**) (45.6 mg, 0.30 mmol). Purification by column chromatography (eluent: Petroleum ether: Ethyl acetate = 10:1) yielded **3v** (69.8 mg, 83%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 8.15 – 8.05 (m, 2H), 7.68 – 7.55 (m, 3H), 7.37 – 7.24 (m, 3H), 6.16 (d, *J* = 18.1 Hz, 1H), 1.18 (s, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 146.4, 135.2, 133.6, 131.1, 129.0, 128.4, 126.1, 125.7, 125.5, 124.0, 123.7, 83.4, 24.8. The spectra data are in accordance with those reported in the literature. [15]



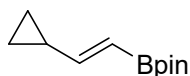
(E)-4,4,5,5-tetramethyl-2-(2-(thiophen-2-yl)vinyl)-1,3,2-dioxaborolane (3w)

The representative procedure was followed using 2-ethynylthiophene (**1w**) (32.5 mg, 0.30 mmol). Purification by column chromatography (eluent: Petroleum ether: Ethyl acetate = 10:1) yielded **3w** (55.9 mg, 79%) as a brown oil. ¹H NMR (400 MHz, CDCl₃) δ 7.47 (d, *J* = 18.1 Hz, 1H), 7.24 (d, *J* = 5.0 Hz, 1H), 7.08 (d, *J* = 3.3 Hz, 1H), 7.01 – 6.95 (m, 1H), 5.91 (d, *J* = 18.1 Hz, 1H), 1.30 (s, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 148.1, 144.0, 141.9, 127.8, 127.7, 126.4, 83.5, 24.9. The spectra data are in accordance with those reported in the literature. [7]



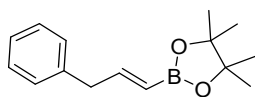
(E)-4,4,5,5-tetramethyl-2-(2-(thiophen-3-yl)vinyl)-1,3,2-dioxaborolane (3x)

The representative procedure was followed using 3-ethynylthiophene (**1x**) (32.6 mg, 0.30 mmol). Purification by column chromatography (eluent: Petroleum ether: Ethyl acetate = 10:1) yielded **3x** (58.7 mg, 84 %) as a brown oil. ¹H NMR (400 MHz, CDCl₃) δ 7.40 (d, *J* = 18.4 Hz, 1H), 7.33 – 7.30 (m, 2H), 7.28 – 7.25 (m, 1H), 5.96 (d, *J* = 18.3 Hz, 1H), 1.32 (s, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 143.2, 141.3, 126.2, 125.1, 124.9, 83.4, 24.9. The spectra data are in accordance with those reported in the literature. [15]



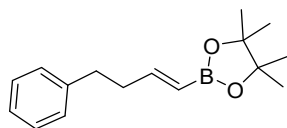
(E)-2-(2-cyclopropylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3y)

The representative procedure was followed using Cyclopropyl acetylene (**1y**) (20 mg, 0.30 mmol). Purification by column chromatography (eluent: Petroleum ether: Ethyl acetate = 10:1) yielded **5-3y** (52 mg, 89%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 6.08 (dd, *J* = 18.0, 9.2 Hz, 1H), 5.49 (d, *J* = 18.0 Hz, 1H), 1.46-1.55 (m, 1H), 1.25 (s, 12H), 0.84-0.75 (m, 2H), 0.60-0.48 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 158.7, 83.1, 77.4, 24.9, 17.2, 8.0. The spectra data are in accordance with those reported in the literature. [6]



(E)-4,4,5,5-tetramethyl-2-(3-phenylprop-1-en-1-yl)-1,3,2-dioxaborolane (3z)

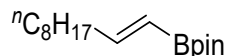
The representative procedure was followed using prop-2-yn-1-ylbenzene (**1z**) (34.9 mg, 0.30 mmol). Purification by column chromatography (eluent: Petroleum ether: Ethyl acetate = 10:1) yielded **3z** (60.8 mg, 87%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.38 – 7.13 (m, 5H), 6.86 – 6.71 (m, 1H), 5.47 (d, *J* = 17.8 Hz, 1H), 3.49 (d, *J* = 6.3 Hz, 2H), 1.27 (s, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 152.5, 139.1, 129.0, 128.5, 126.2, 83.2, 42.4, 24.9. The spectra data are in accordance with those reported in the literature. [16]



(E)-4,4,5,5-tetramethyl-2-(4-phenylbut-1-en-1-yl)-1,3,2-dioxaborolane (3a')

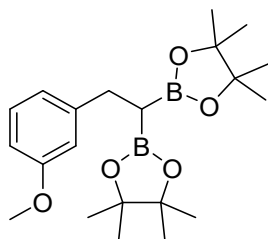
The representative procedure was followed using but-3-yn-1-ylbenzene (**1a'**) (39.1 mg, 0.30 mmol). Purification by column chromatography (eluent: Petroleum ether: Ethyl acetate = 10:1) yielded **3a'** (64.6 mg, 83%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.34 – 7.25 (m, 2H), 7.21 (d, *J* = 7.2 Hz, 3H), 6.82 – 6.65 (m, 1H), 5.54 (d, *J* = 18.0 Hz, 1H), 2.77 (d, *J* = 8.5 Hz, 2H),

2.50 (q, $J = 7.1, 6.5$ Hz, 2H), 1.29 (s, 12H). ^{13}C NMR (101 MHz, CDCl_3) δ .153.4, 141.7, 128.3, 125.9, 83.1, 37.5, 34.6, 24.8. The spectra data are in accordance with those reported in the literature. ^[11]



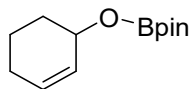
(E)-2-(dec-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3b')

The representative procedure was followed using 1-Decyne (**1b'**) (41 mg, 0.30 mmol). Purification by column chromatography (eluent: Petroleum ether: Ethyl acetate = 10:1) yielded **3b'** (69 mg, 86%) as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 6.63 (dt, $J = 18.0, 6.4$ Hz, 1H), 5.42 (dt, $J = 18.0, 6.4$ Hz, 1H), 2.10-2.18 (m, 2H), 1.37-1.44 (m, 2H), 1.26 (s, 20H), 0.87 (t, $J = 7.2$ Hz, 3H), 0.10-0.04 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 155.0, 83.1, 77.4, 36.0, 32.0, 29.6, 29.4, 28.4, 24.9, 22.8, 14.3, 1.2. The spectra data are in accordance with those reported in the literature. ^[17]



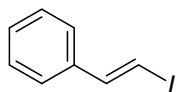
2,2'-(2-(3-methoxyphenyl)ethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3c')

The representative procedure was followed using 1-ethynyl-3-methoxybenzene (**1c'**) (39.6 mg, 0.30 mmol). Purification by column chromatography (eluent: Petroleum ether: Ethyl acetate = 10:1) yielded **3c'** (110.3 mg, 95 %) as a brown oil. ^1H NMR (400 MHz, CDCl_3) δ 7.12 (t, $J = 7.9$ Hz, 1H), 6.85 – 6.76 (m, 2H), 6.70 – 6.59 (m, 1H), 3.75 (s, 3H), 2.85 (d, $J = 8.3$ Hz, 2H), 1.24 – 0.98 (m, 24H). ^{13}C NMR (101 MHz, CDCl_3) δ 159.4, 146.1, 128.9, 120.7, 113.7, 111.1, 83.1, 55.0, 31.4, 24.8, 24.5. The spectra data are in accordance with those reported in the literature. ^[18]



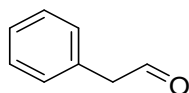
2-(cyclohex-2-en-1-yloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5)

The representative procedure was followed using cyclohex-2-en-1-one (4) (28.8 mg, 0.30 mmol). Purification by column chromatography (eluent: Petroleum ether: Ethyl acetate = 10:1) yielded **5** (34.28 mg, 51 %) as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 6.03 – 5.56 (m, 2H), 4.17 (s, 1H), 2.07 – 1.42 (m, 6H), 1.23 (s, 12H). ^{13}C NMR (101 MHz, CDCl_3) δ 130.5, 130.0, 83.4, 65.5, 32.0, 25.1, 24.8, 19. The spectra data are in accordance with those reported in the literature. [19]



(E)-(2-iodovinyl)benzene (3-1)

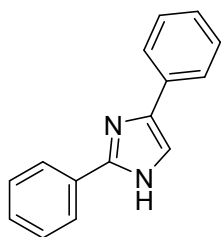
The representative procedure was followed using (*E*)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (**3a**) (69 mg, 0.30 mmol). Purification by column chromatography (eluent: Petroleum ether: Ethyl acetate = 10:1) yielded **3-1** (59.3 mg, 86%) as a yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.33 (d, J = 14.9 Hz, 1H), 7.25 – 7.14 (m, 5H), 6.72 (d, J = 14.9 Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 144.9, 137.6, 128.7, 128.3, 126.0, 76.7. The spectra data are in accordance with those reported in the literature. [7]



2-phenylacetaldehyde (3-2)

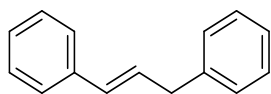
The representative procedure was followed using (*E*)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (**3a**) (69 mg, 0.30 mmol). Purification by column chromatography (eluent:

Petroleum ether: Ethyl acetate = 10:1) yielded **3-2** (34.6 mg, 96%) as a yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 9.66 (s, 1H), 7.48 – 7.41 (m, 2H), 7.37 – 7.30 (m, 1H), 7.25 – 7.12 (m, 2H), 3.70 (d, *J* = 7.6 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 193.6, 129.6, 129.0, 128.6, 128.5, 35.9. The spectra data are in accordance with those reported in the literature. [7]



2,5-diphenyl-1*H*-imidazole (**3-3**)

The representative procedure was followed using (*E*)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (**3a**) (69 mg, 0.30 mmol). Purification by column chromatography (eluent: Petroleum ether: Ethyl acetate = 10:1) yielded **3-3** (51.3 mg, 51%) as a white solid. ¹H NMR (400 MHz, DMSO-*d*₆) δ 12.64 (s, 1H), 8.04 (d, *J* = 7.5 Hz, 2H), 7.87 (d, *J* = 7.5 Hz, 2H), 7.72 (s, 1H), 7.51 – 7.43 (m, 2H), 7.43 – 7.32 (m, 3H), 7.22 (t, *J* = 7.3 Hz, 1H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 146.6, 131.2, 129.2, 129.0, 128.6, 126.8, 125.5, 124.9. The spectra data are in accordance with those reported in the literature. [8]



(*E*)-prop-1-ene-1,3-diylidibenzene (**3-4**)

The representative procedure was followed using (*E*)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (**3a**) (69 mg, 0.30 mmol). Purification by column chromatography (eluent: Petroleum ether: Ethyl acetate = 10:1) yielded **3-4** (26.19 mg, 45%) as a color oil. ¹H NMR (400

MHz, CDCl₃) δ 7.65 – 7.38 (m, 10H), 6.76 – 6.44 (m, 2H), 3.78 (d, J = 6.5 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 140.2, 131.1, 129.2, 128.7, 128.5, 127.1, 126.2(2C), 39.4. The spectra data are in accordance with those reported in the literature. [9]

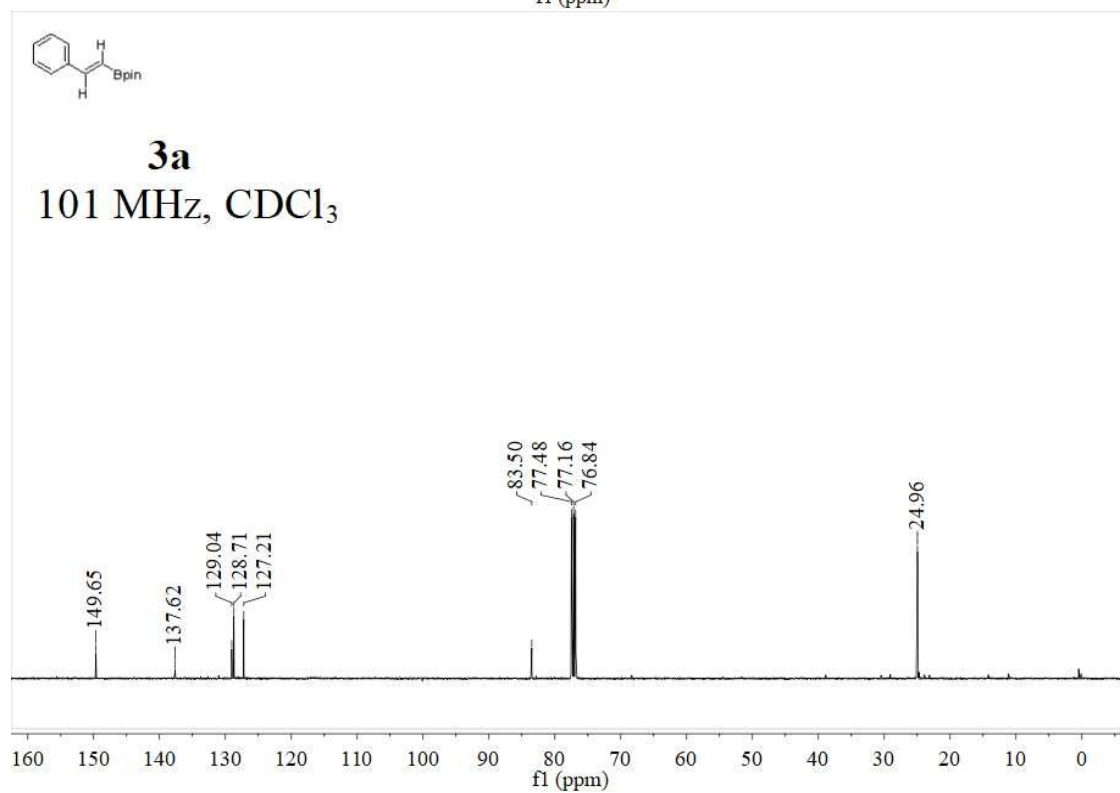
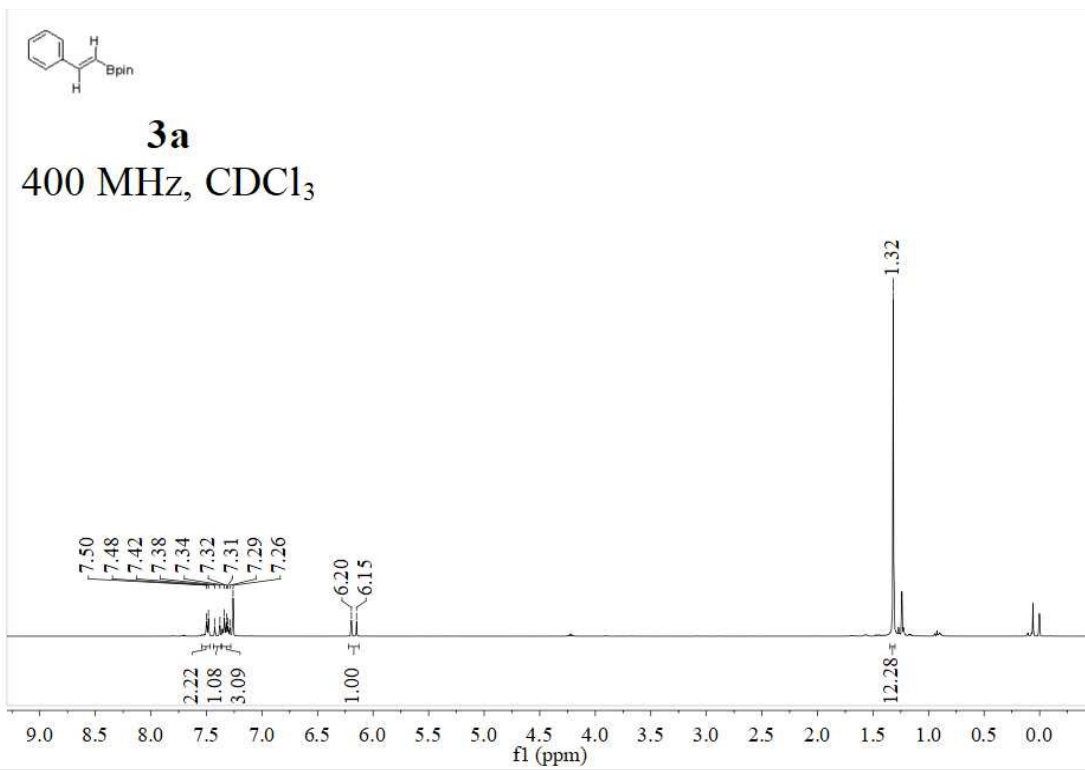
8 References

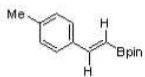
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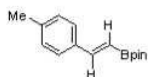
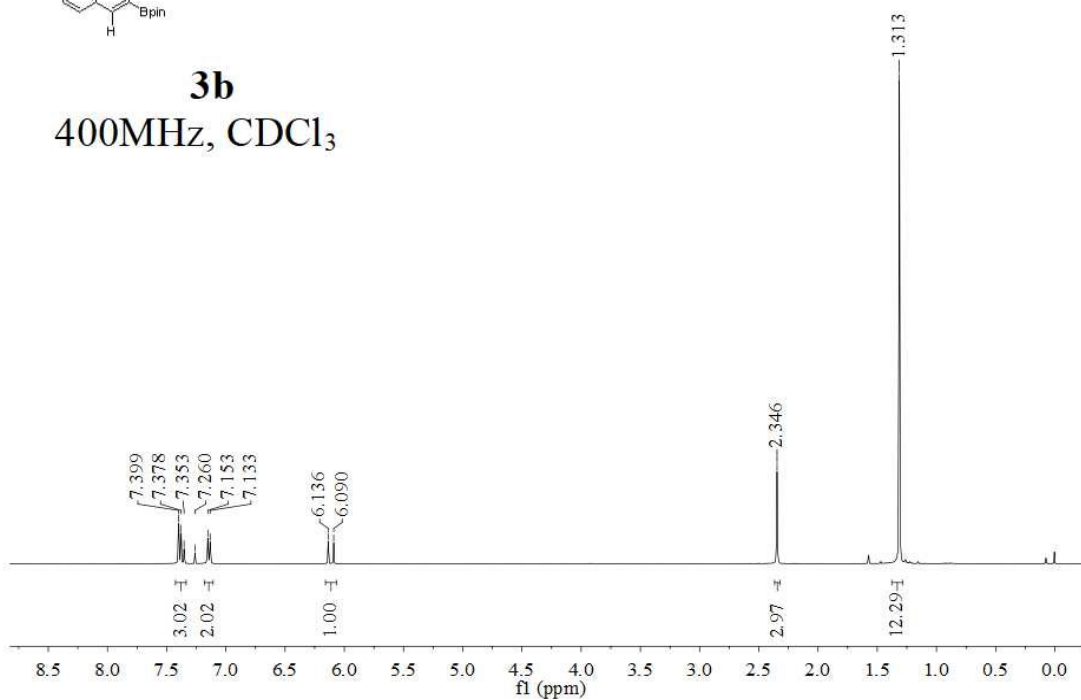
18. X. Wang, X. Cui, S. Li, Y. Wang, C. Xia, H. Jiao, L. Wu, Zirconium-Catalyzed Atom-Economical Synthesis of 1, 1-Diborylalkanes from Terminal and Internal Alkenes, *Angew. Chem., Int. Ed.*, 2020, **59**, 13608-13612.
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9 ¹H-, and ¹³C- NMR Spectra:

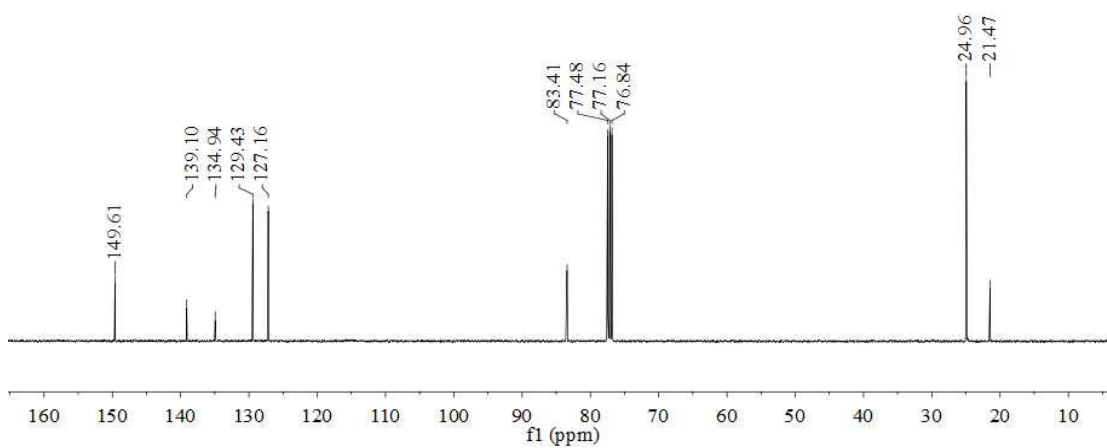


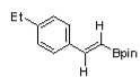


3b
400MHz, CDCl₃



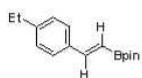
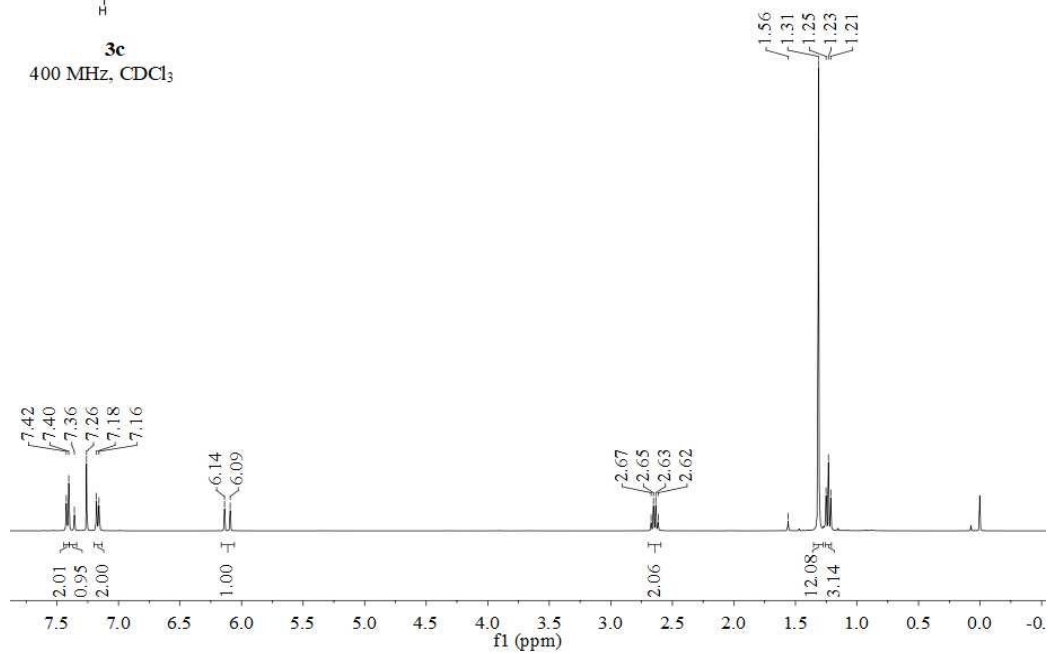
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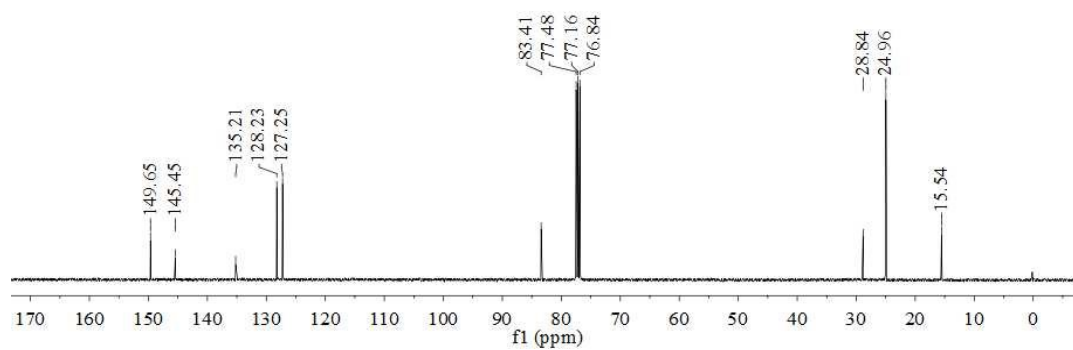
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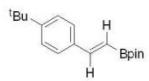
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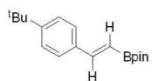
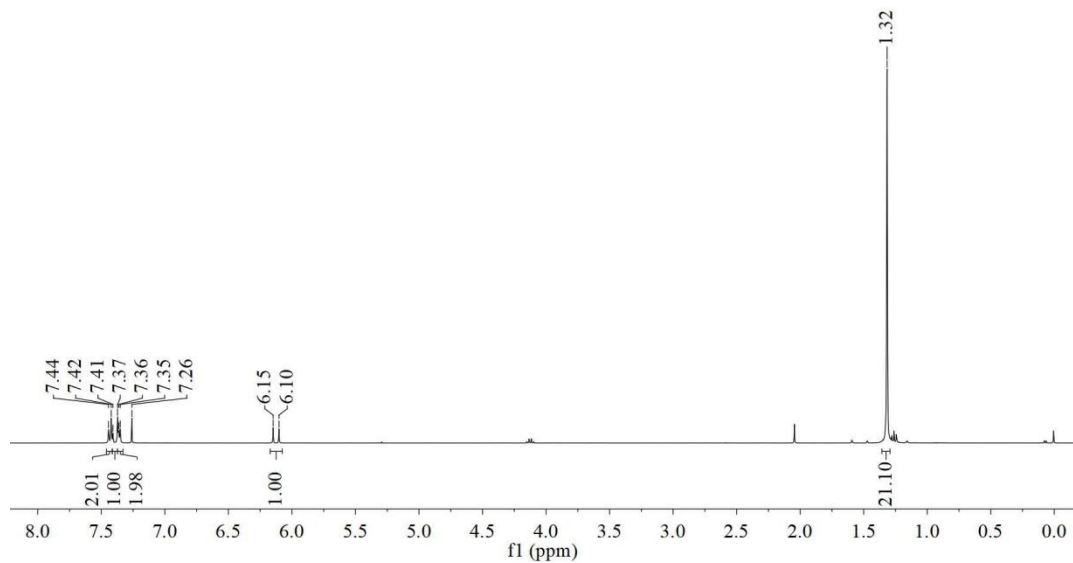
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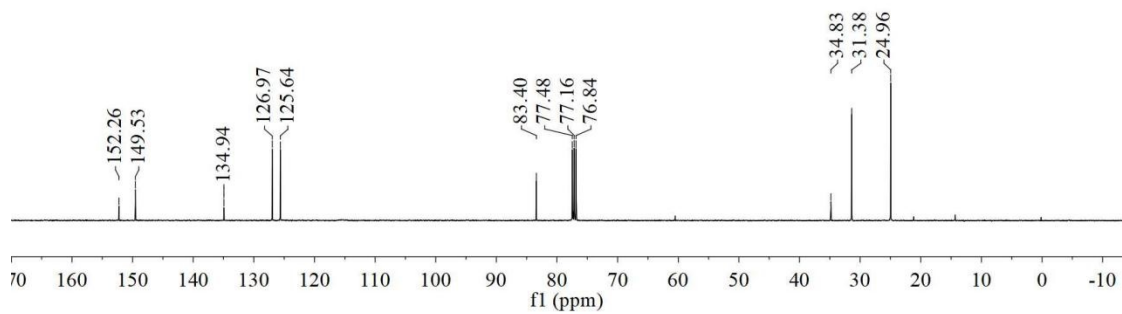
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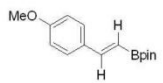
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3d

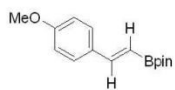
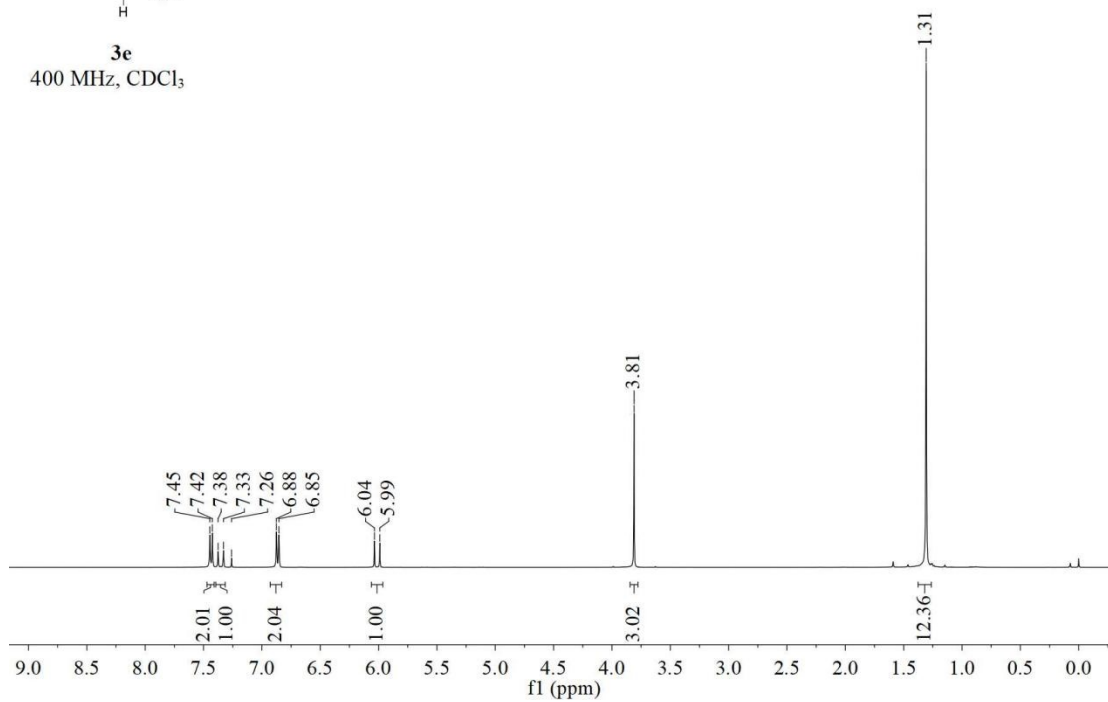
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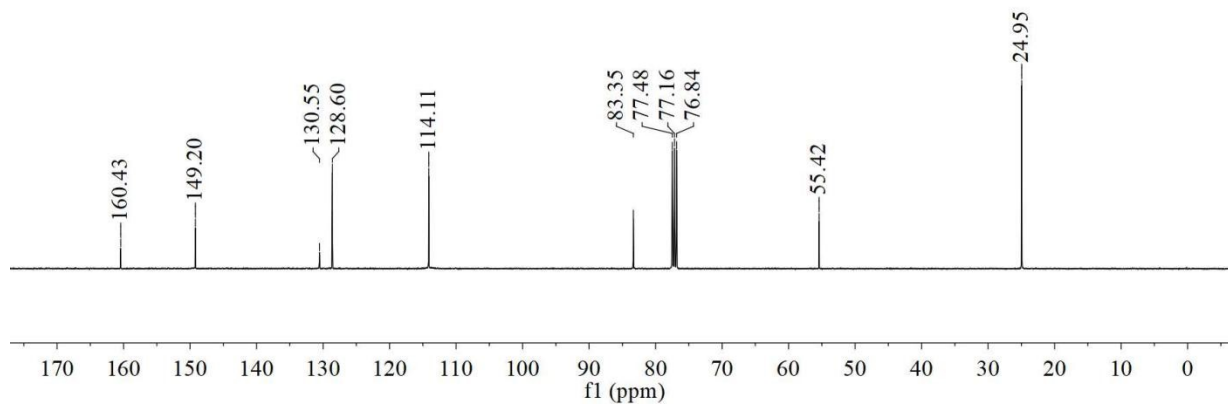
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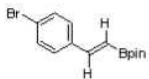
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3e

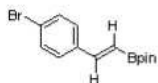
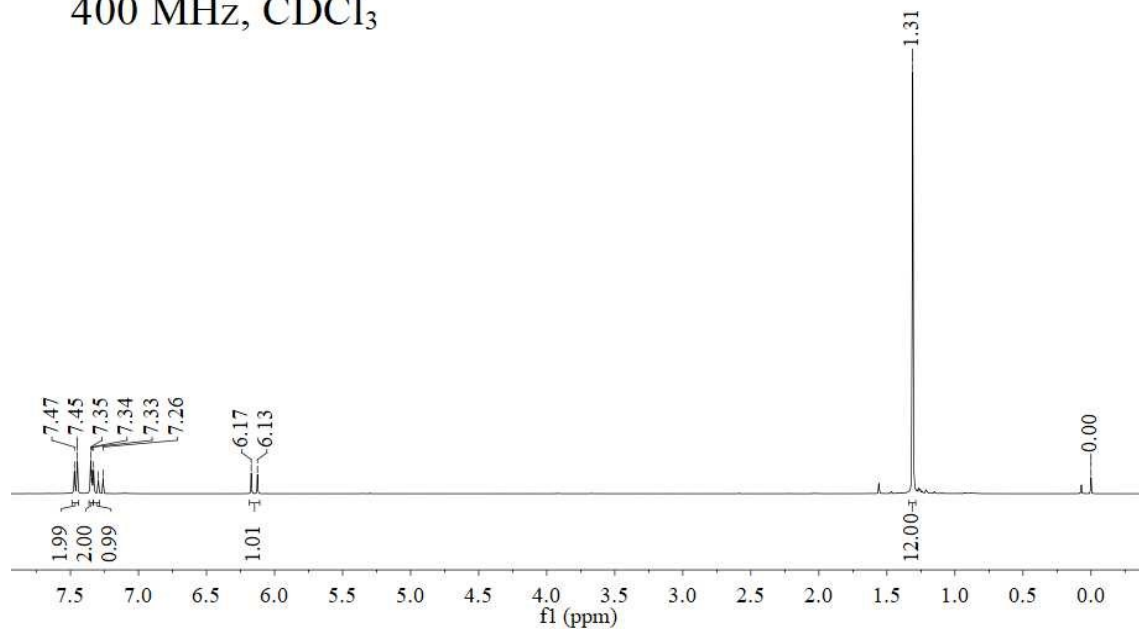
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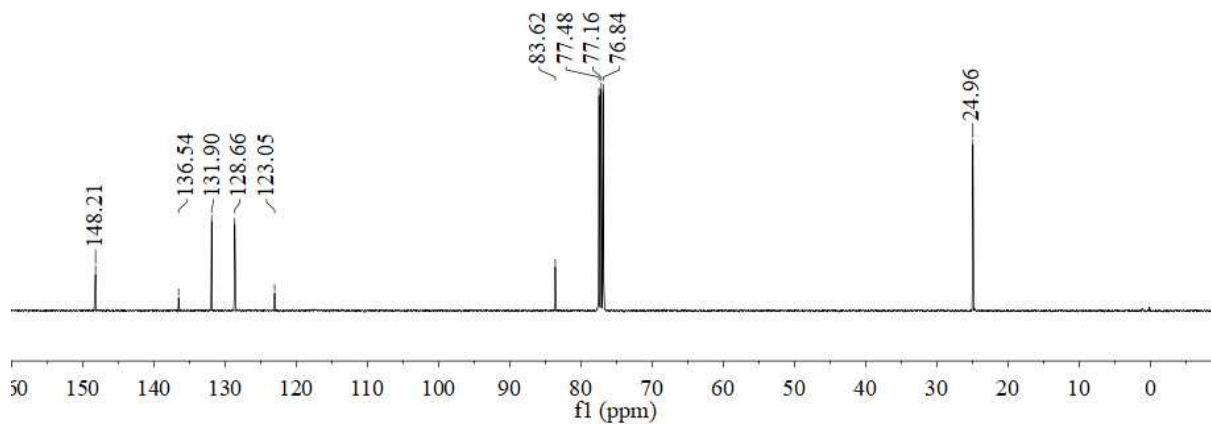
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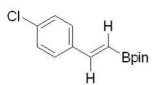
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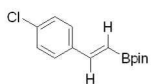
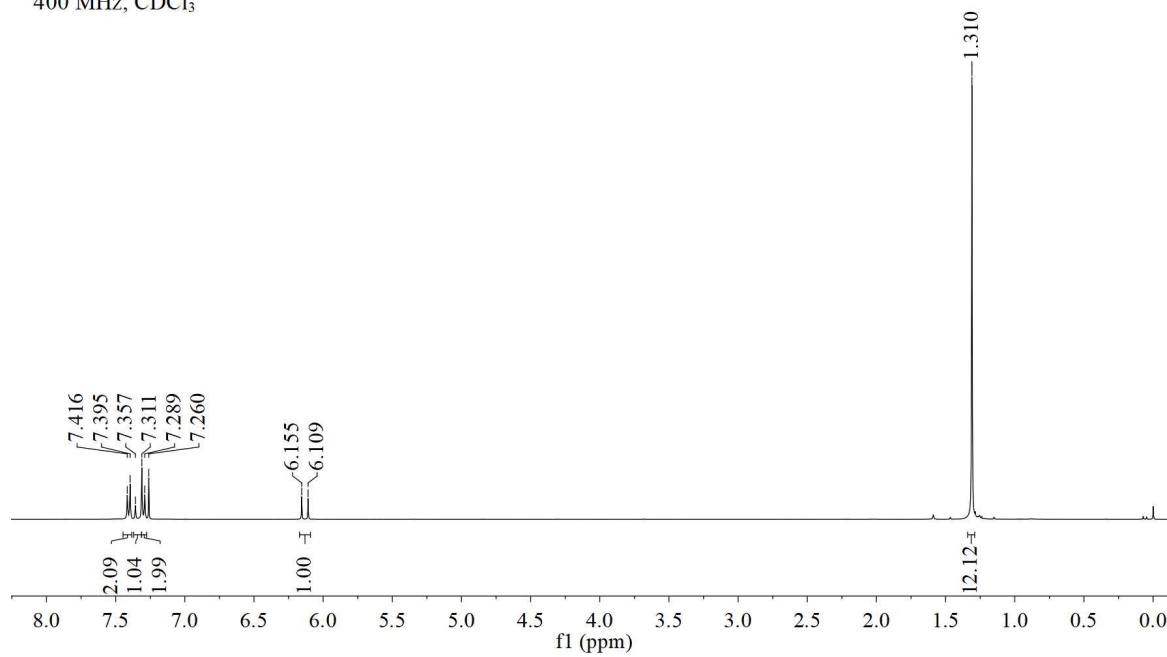
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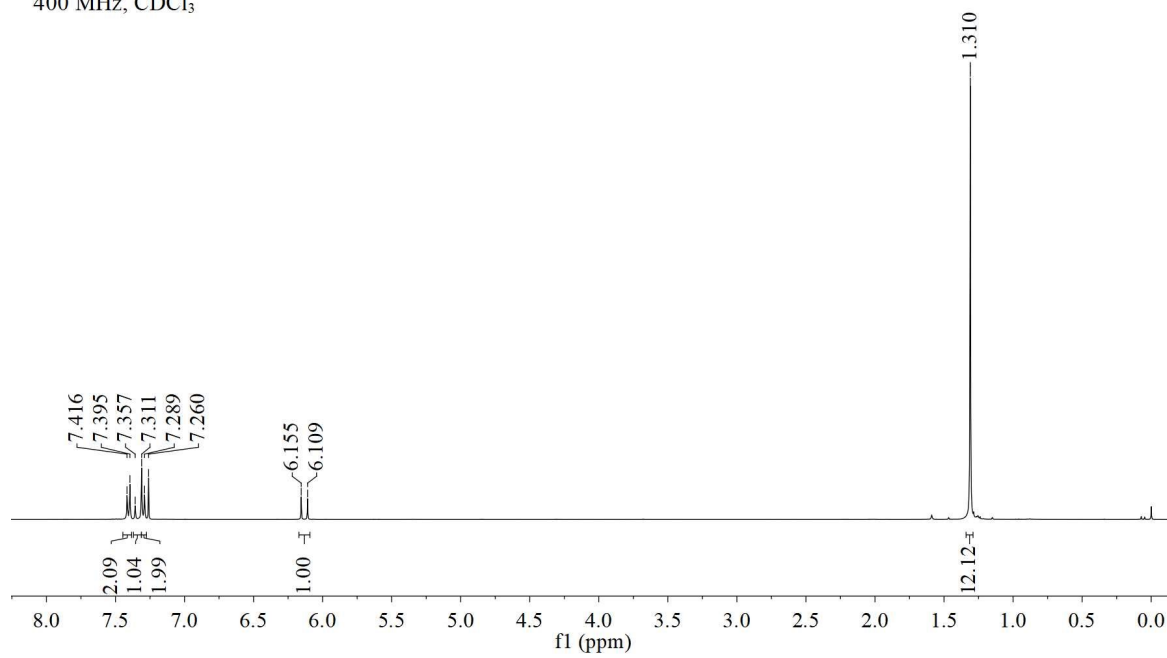


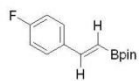


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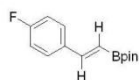
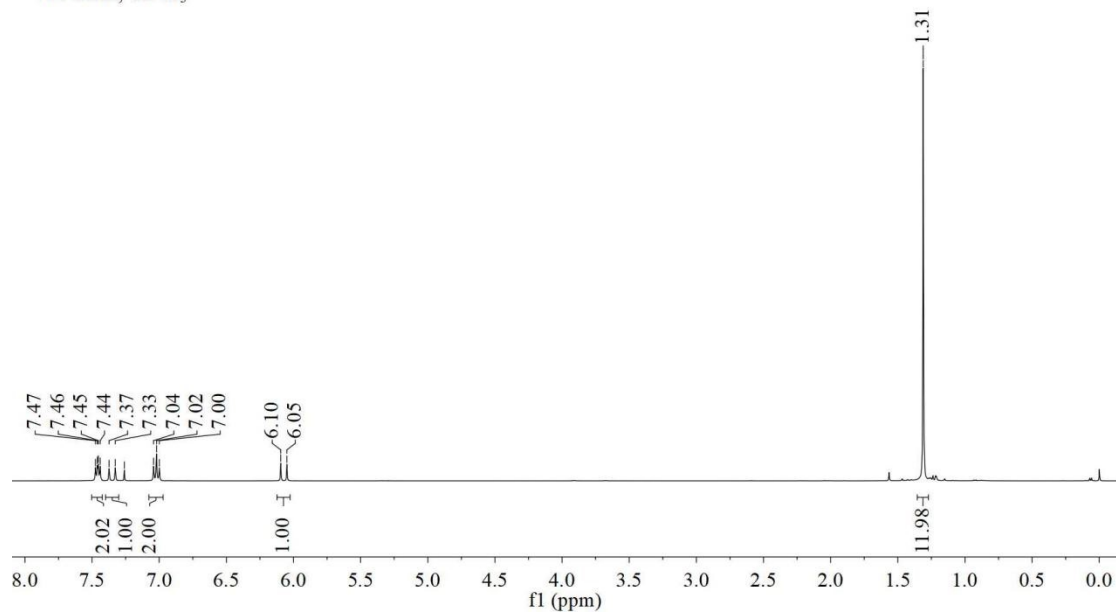


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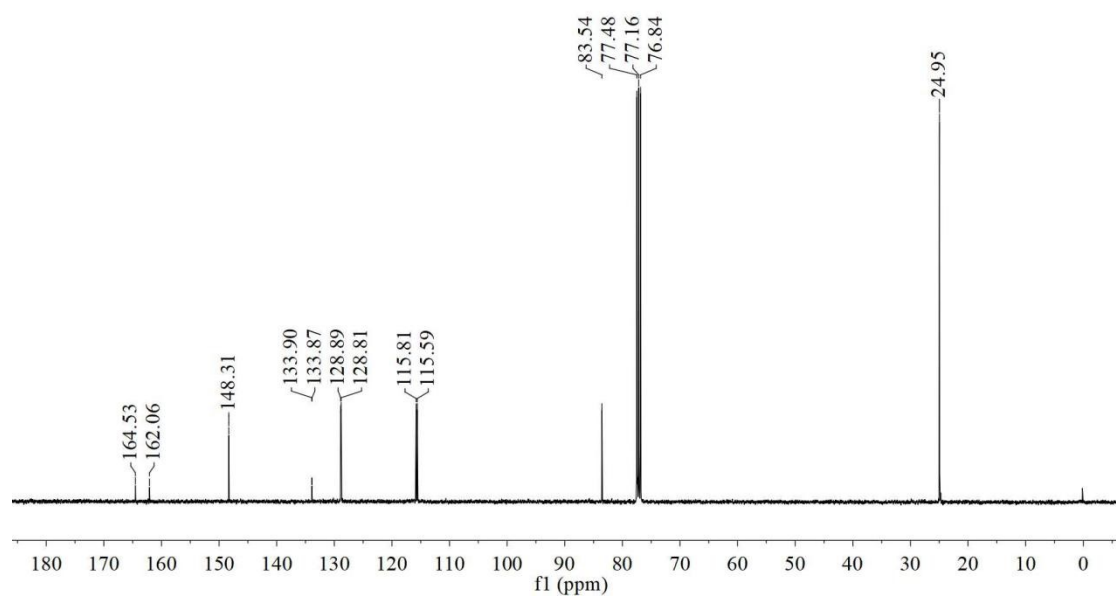


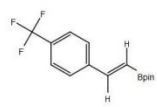


3h
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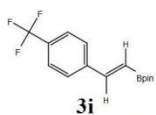
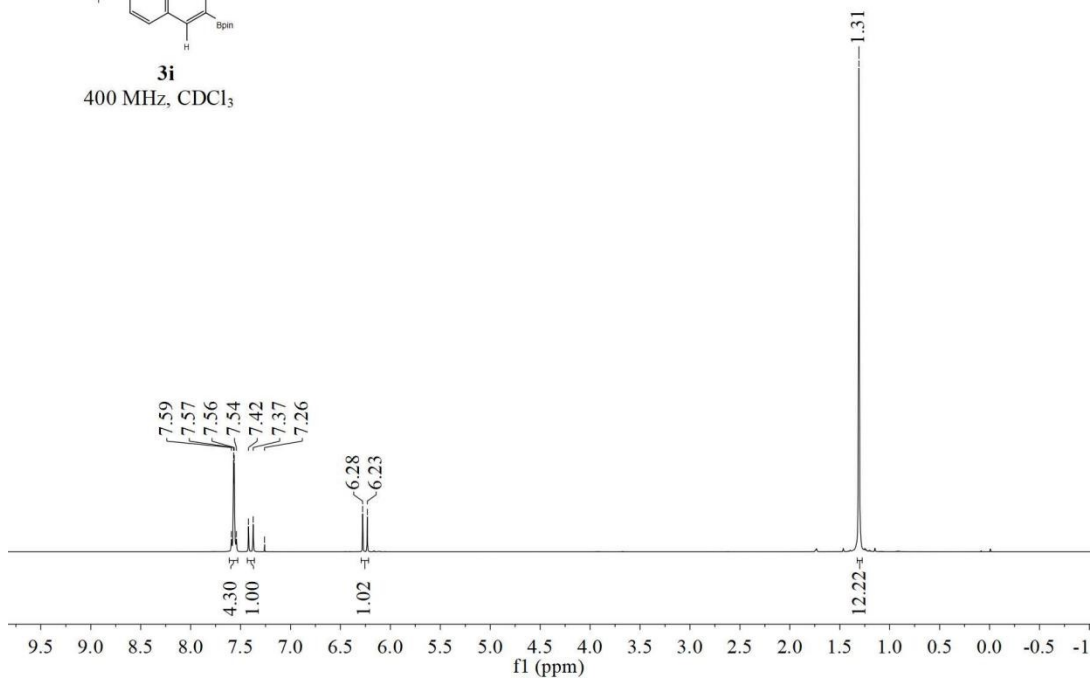
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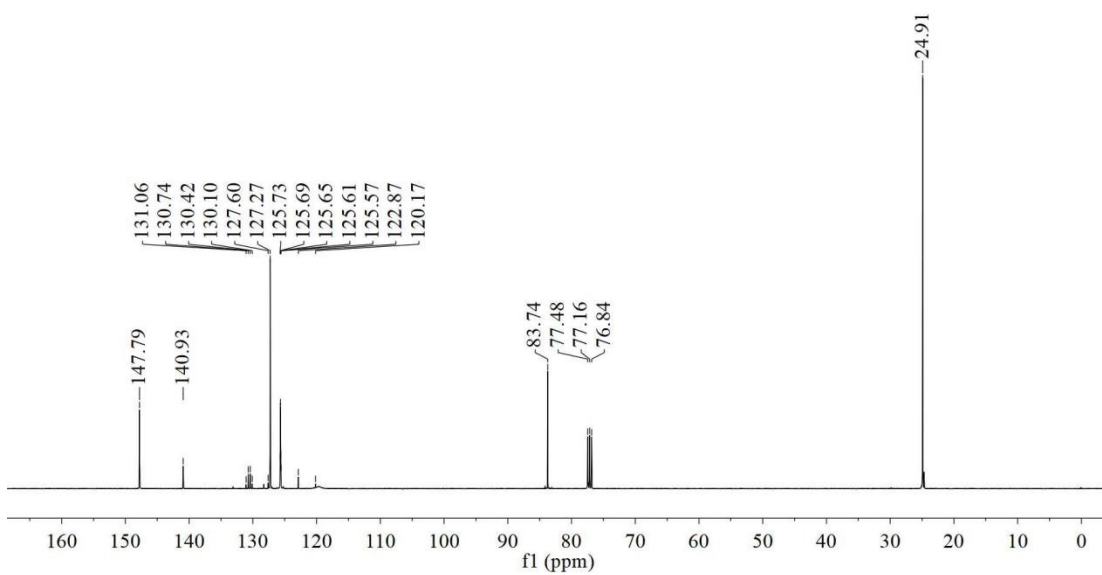
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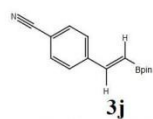
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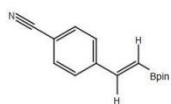
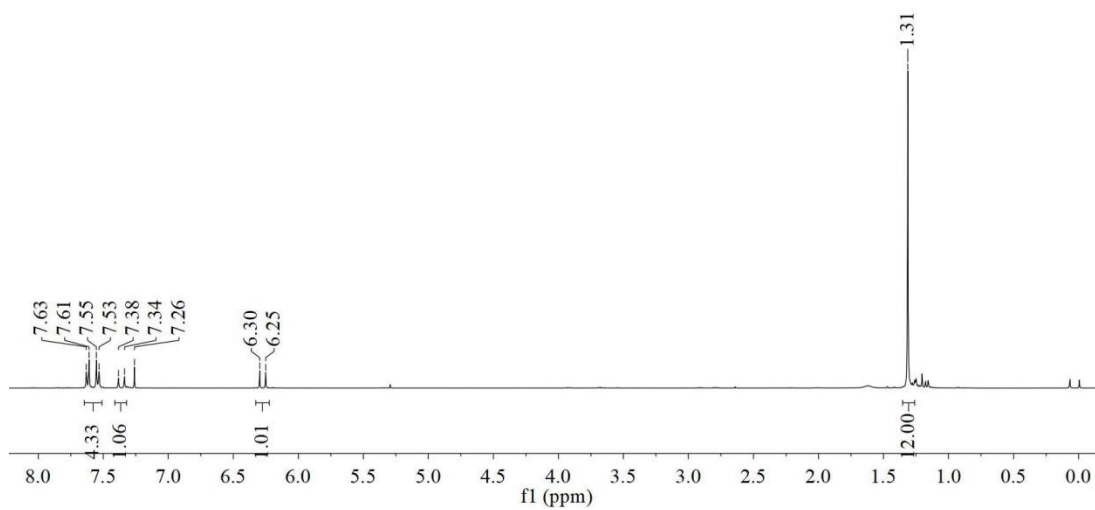
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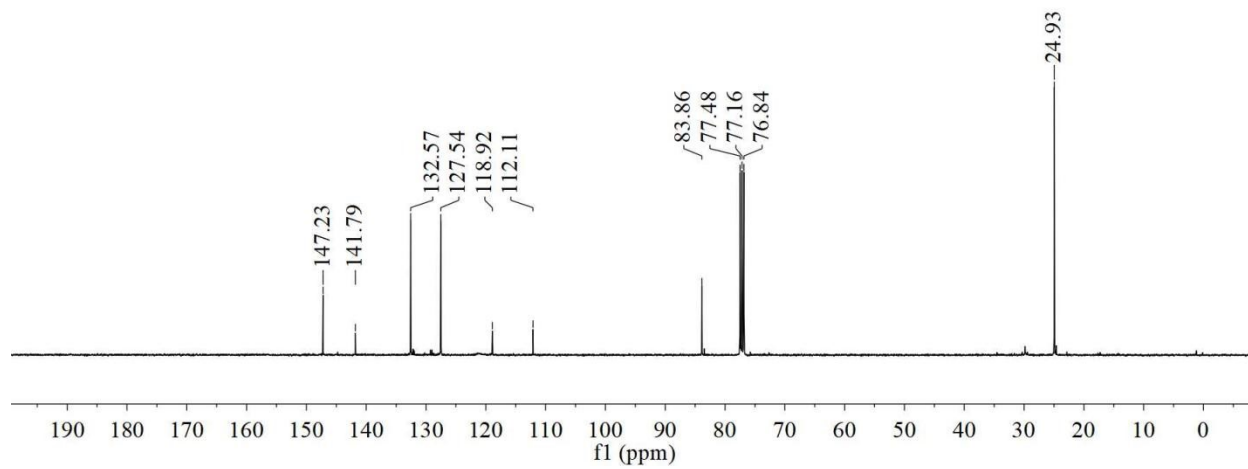


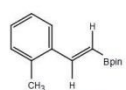


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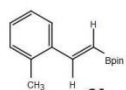
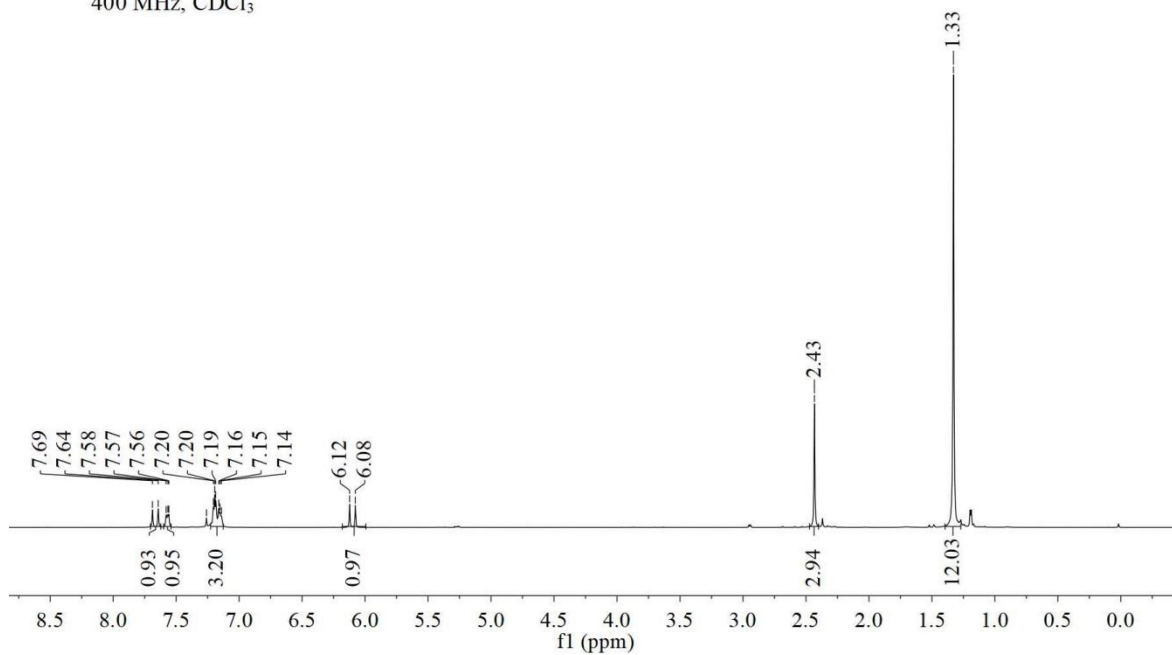
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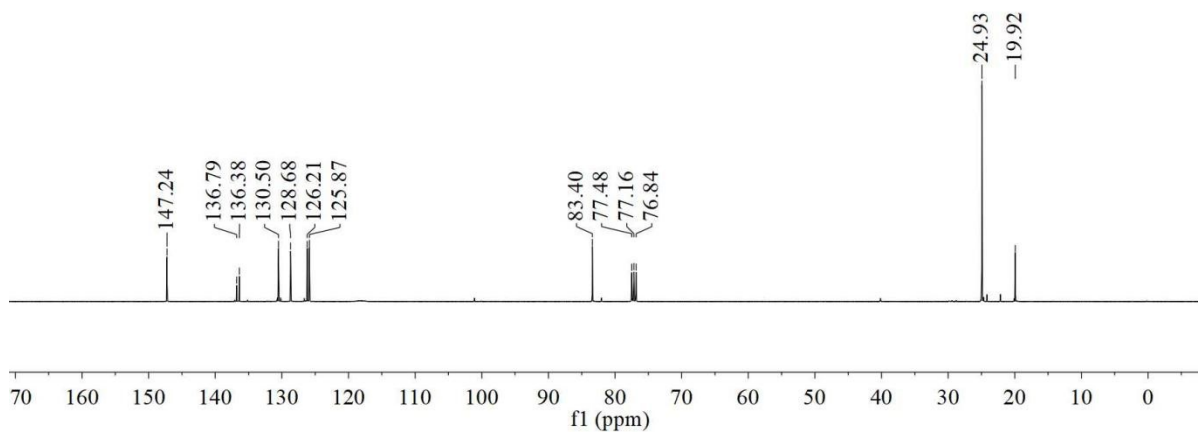
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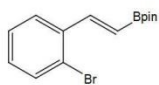
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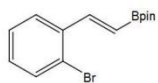
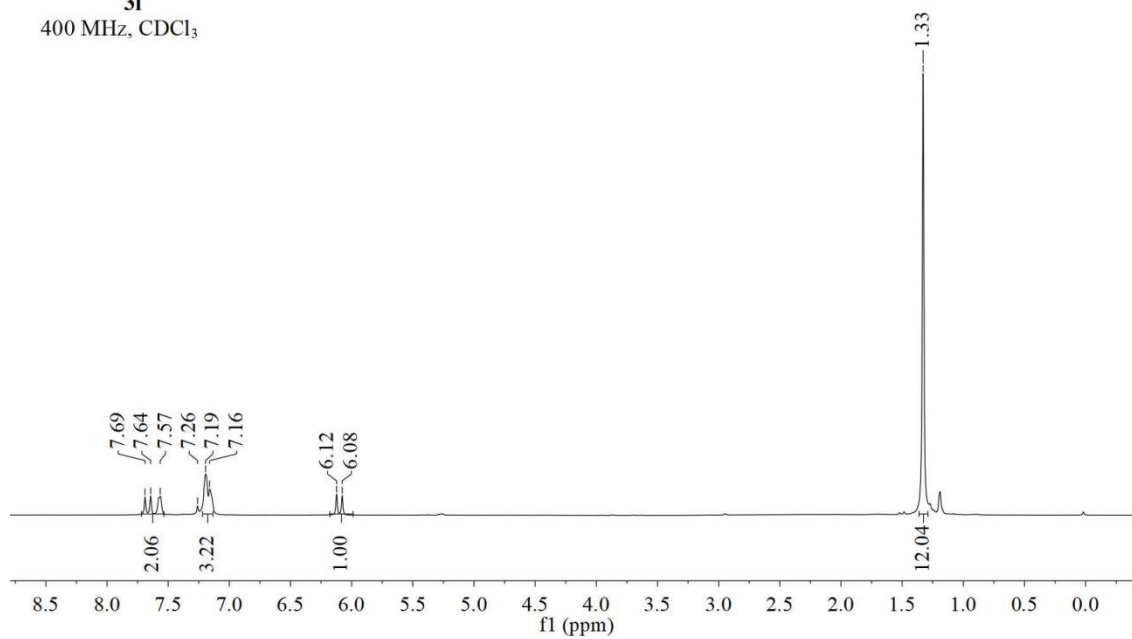
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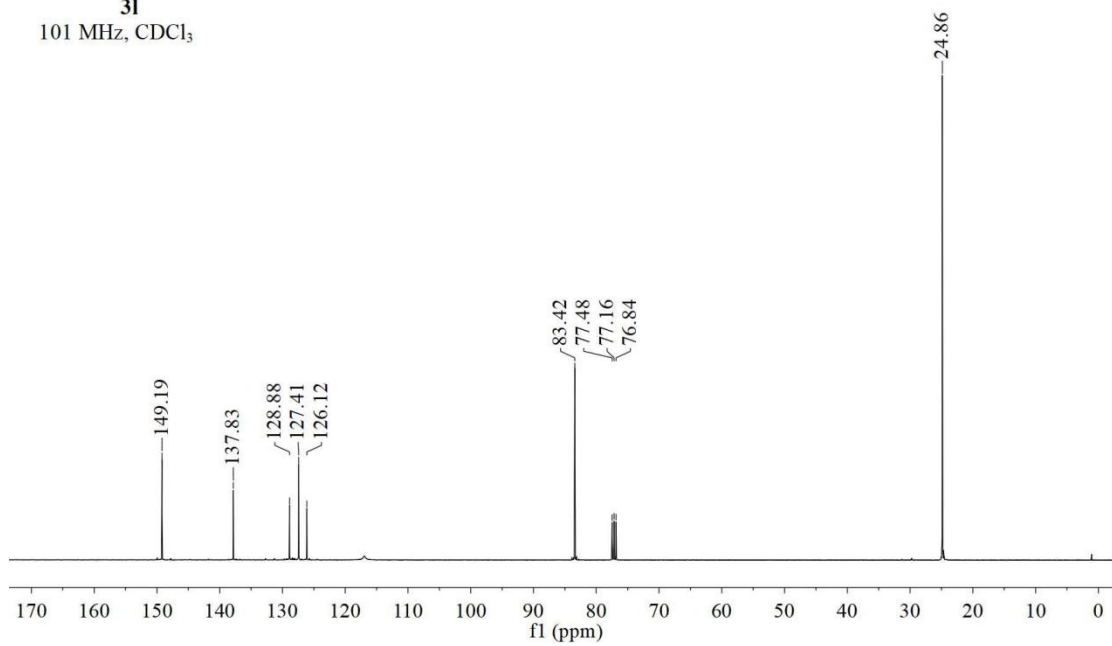


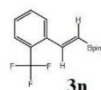


31
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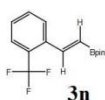
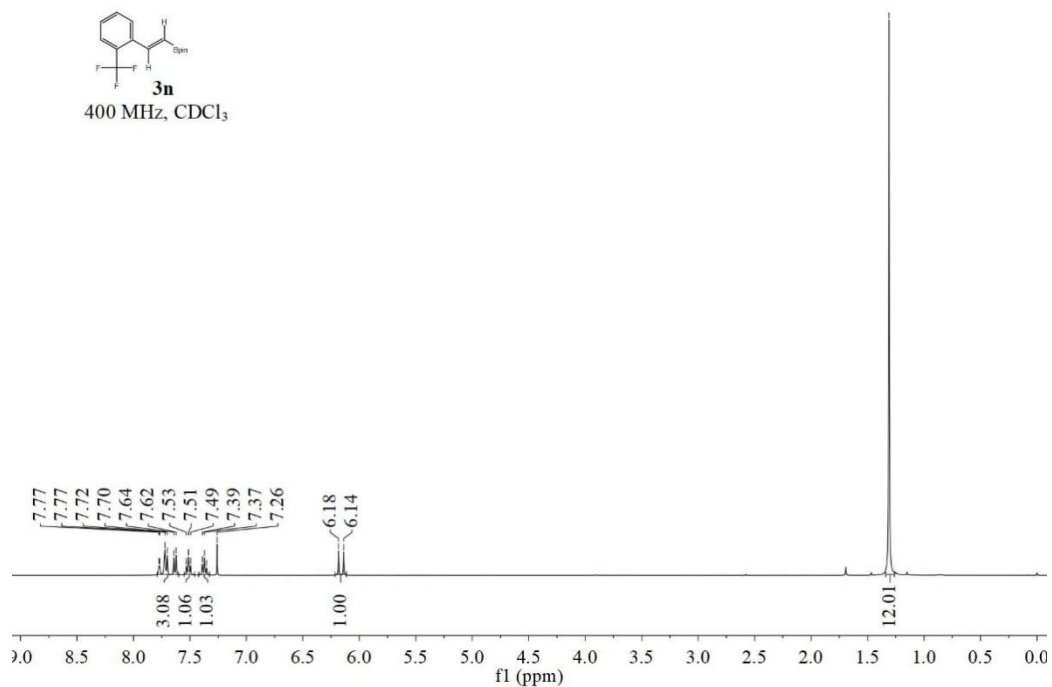


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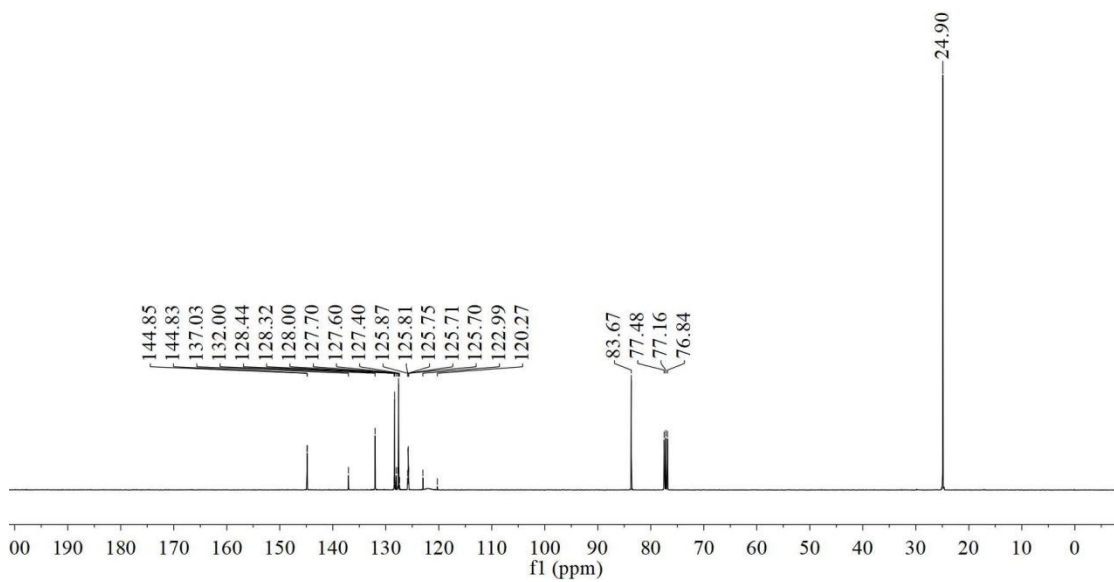




400 MHz, CDCl₃

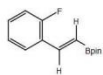
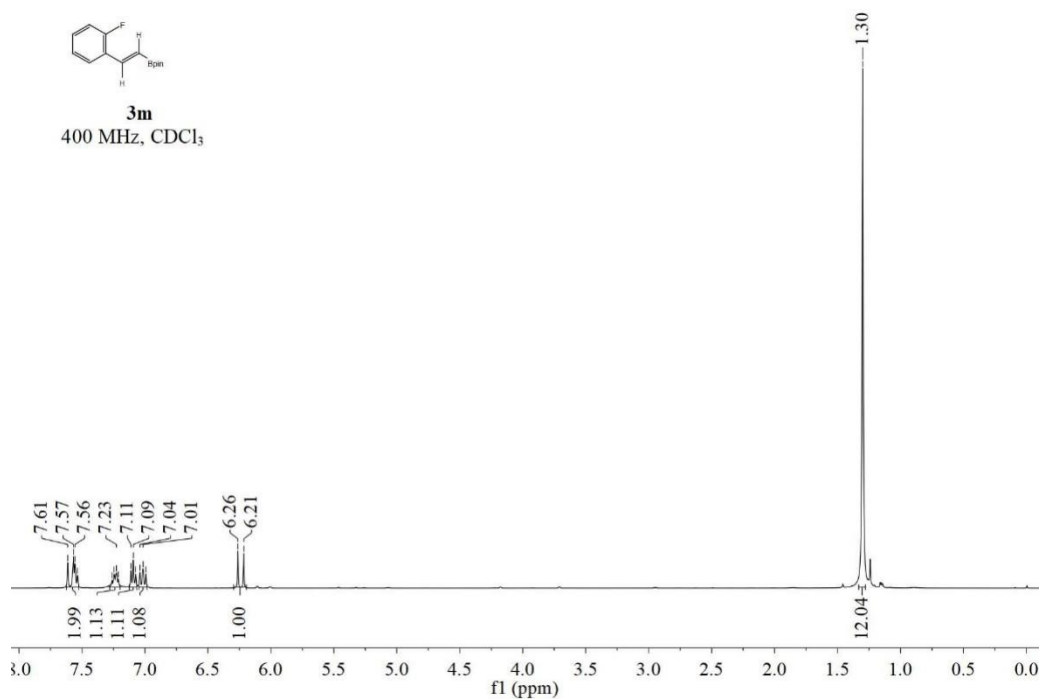


101 MHz, CDCl₃

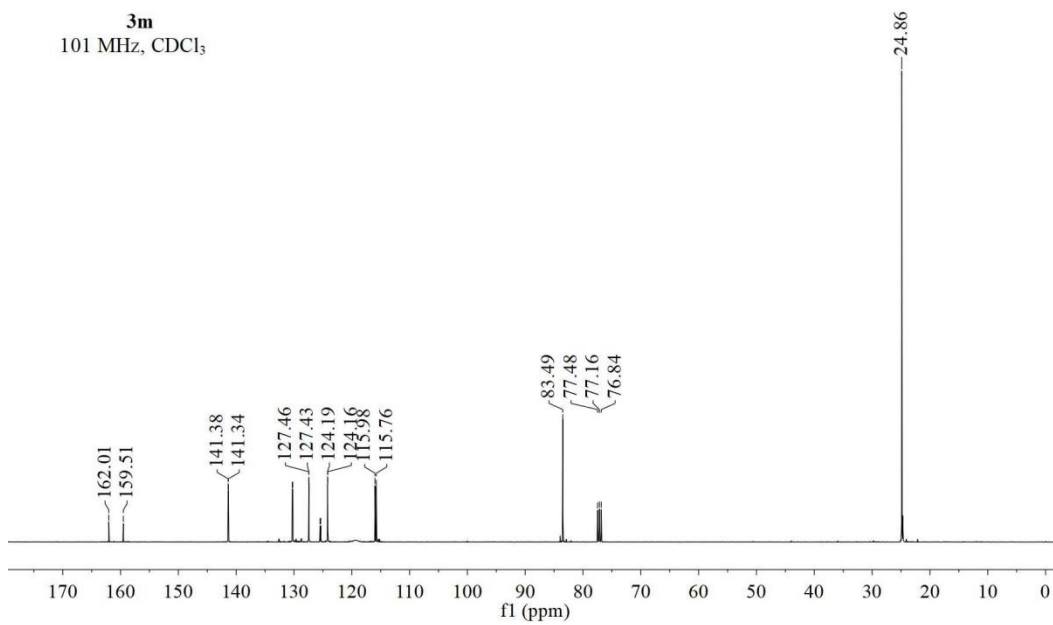


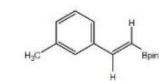


3m
400 MHz, CDCl₃

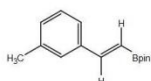
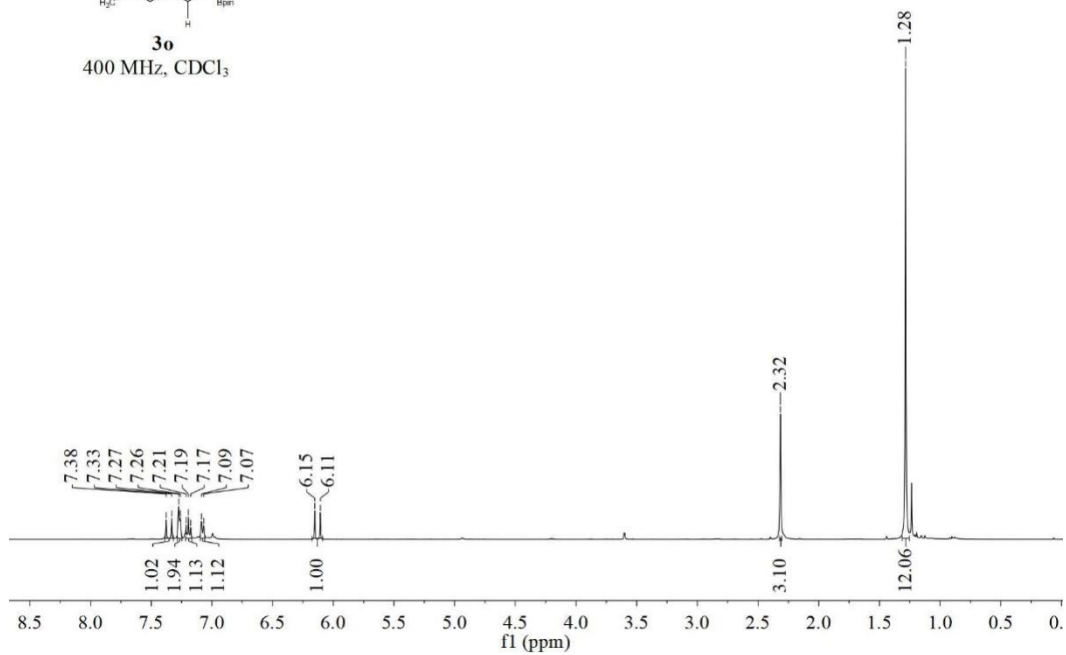


3m
101 MHz, CDCl₃

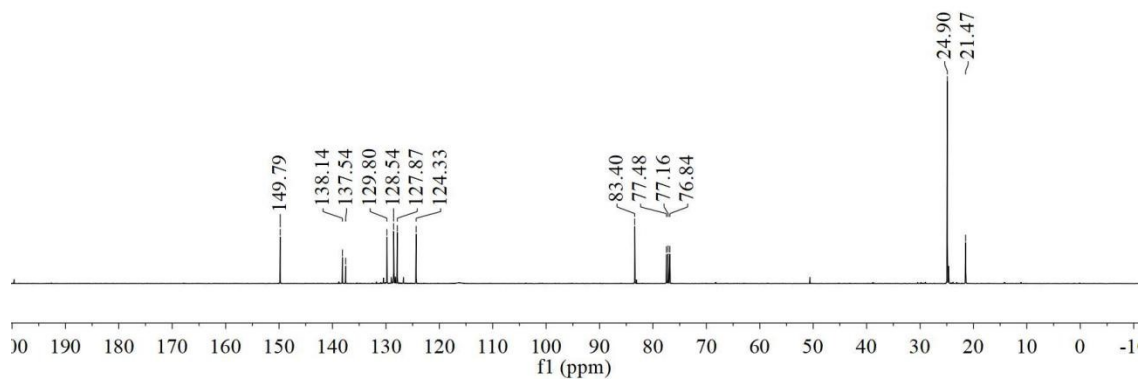


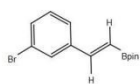


3o
400 MHz, CDCl₃



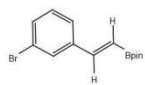
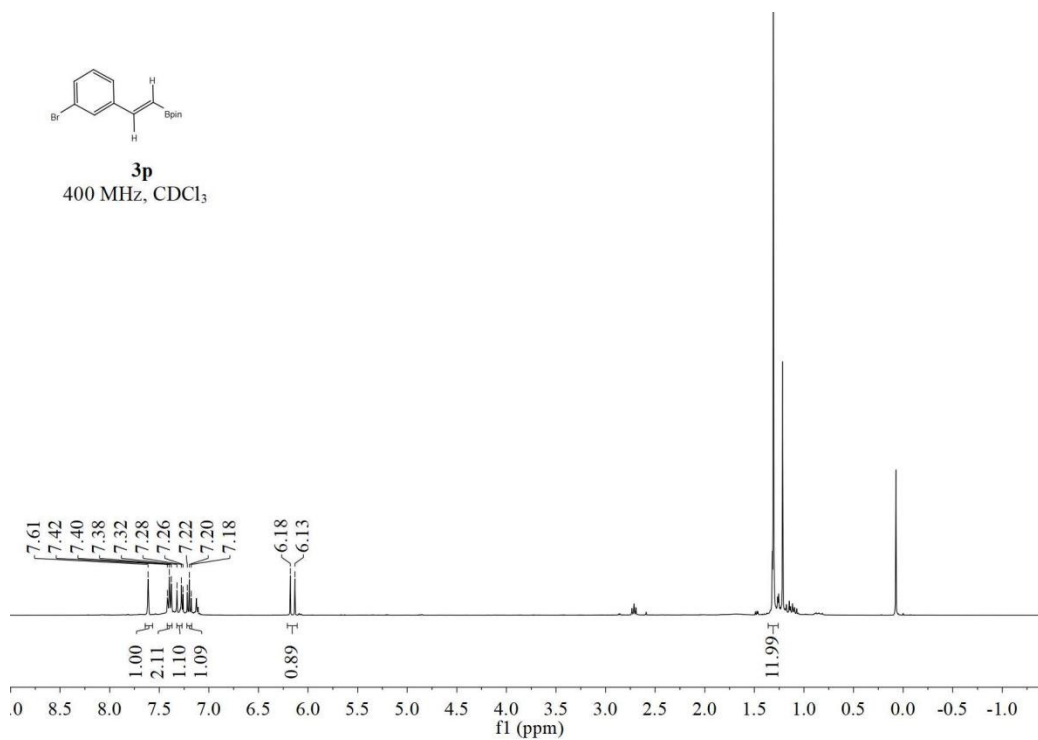
3o
101 MHz, CDCl₃





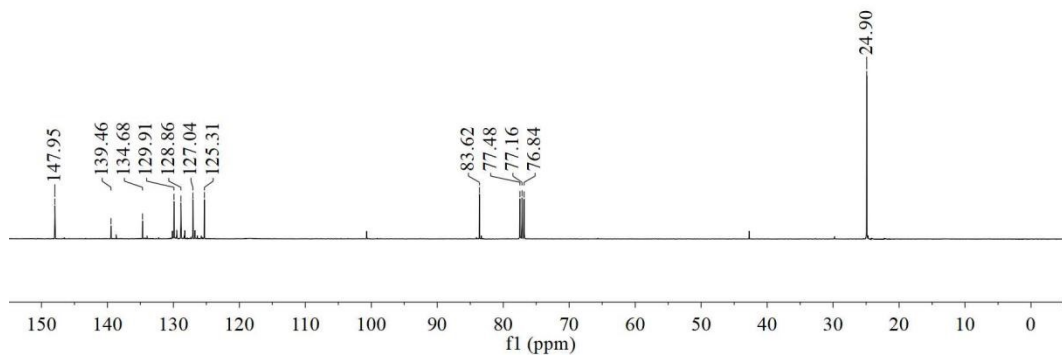
3p

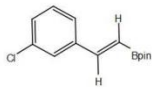
400 MHz, CDCl₃



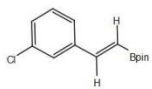
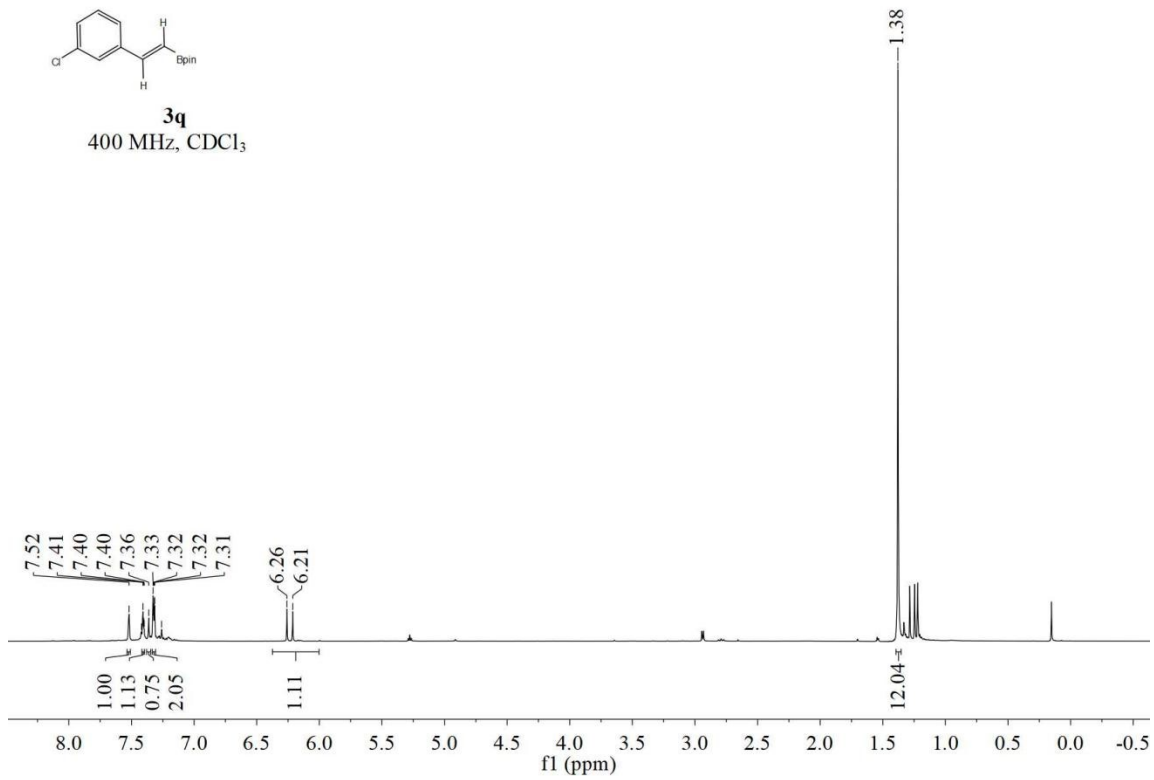
3p

101 MHz, CDCl₃

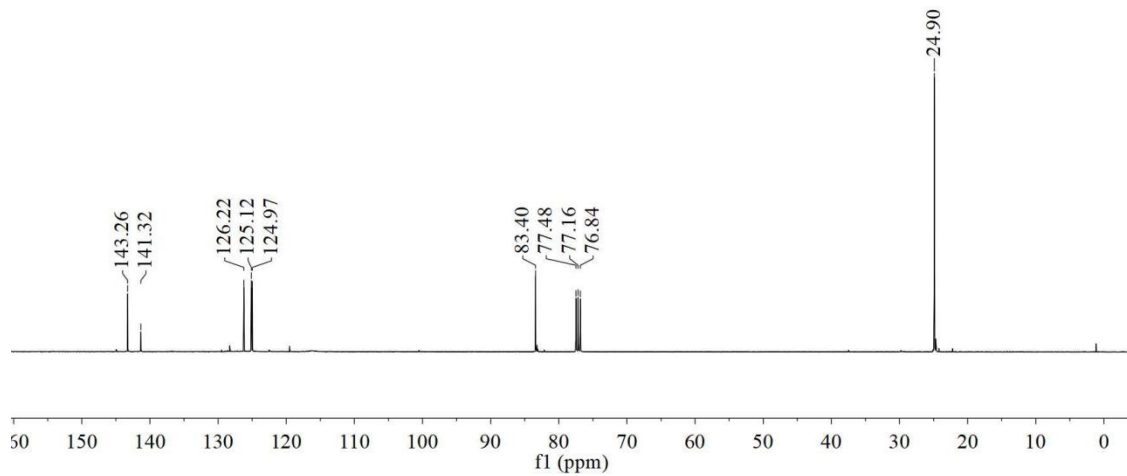


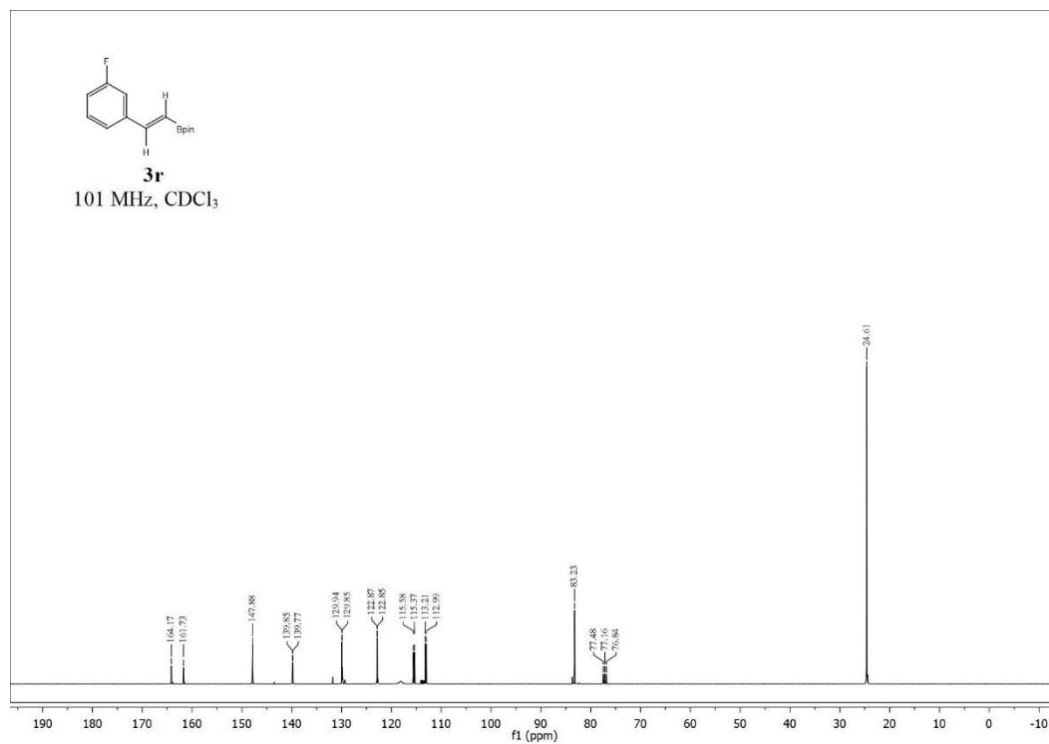
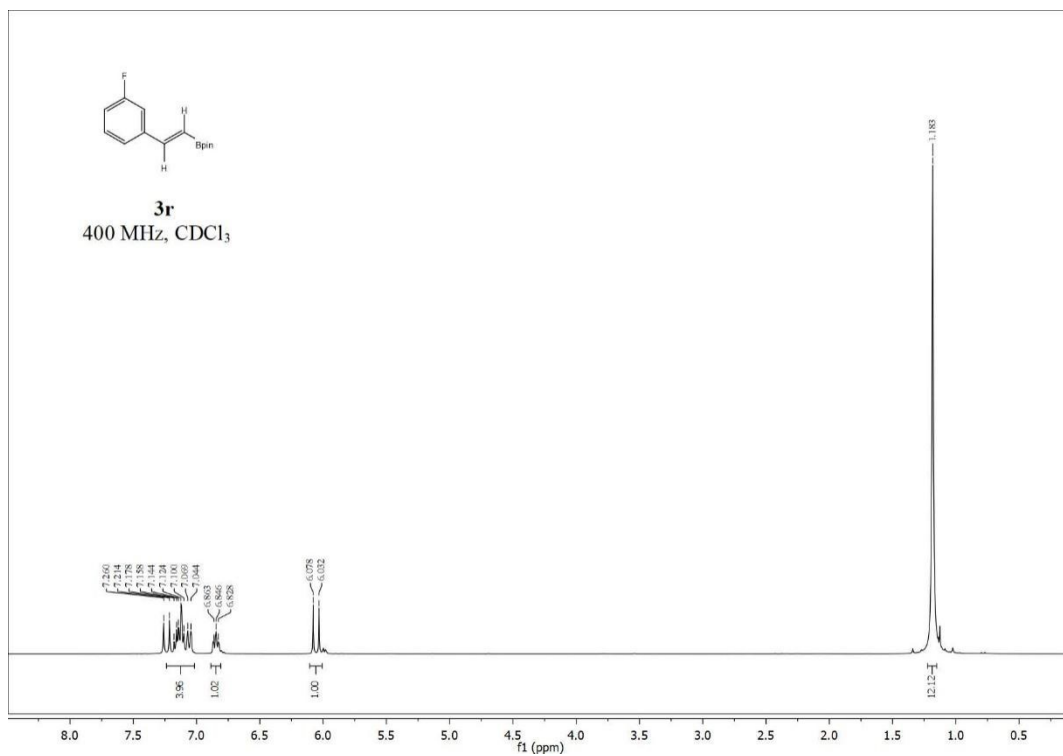


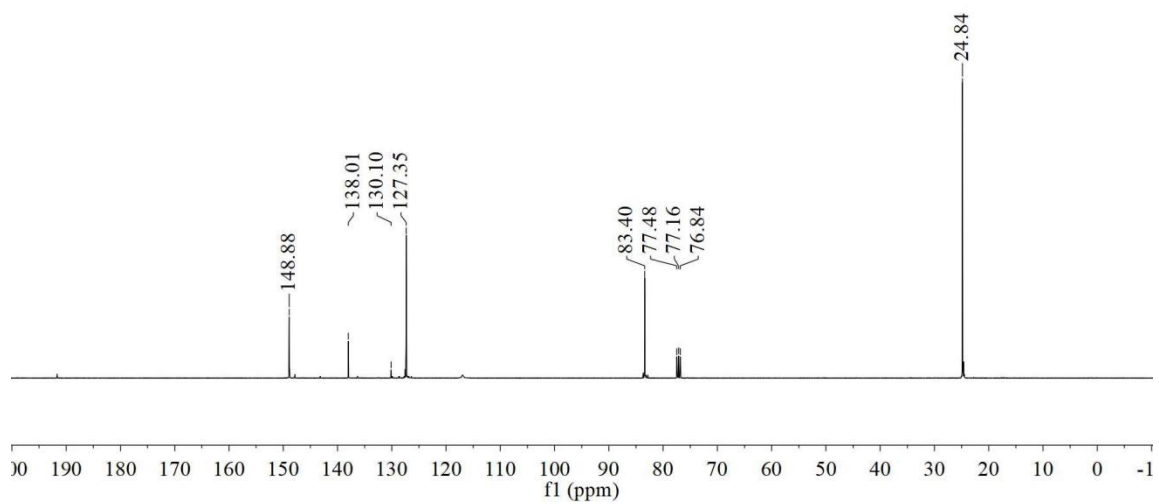
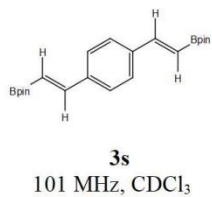
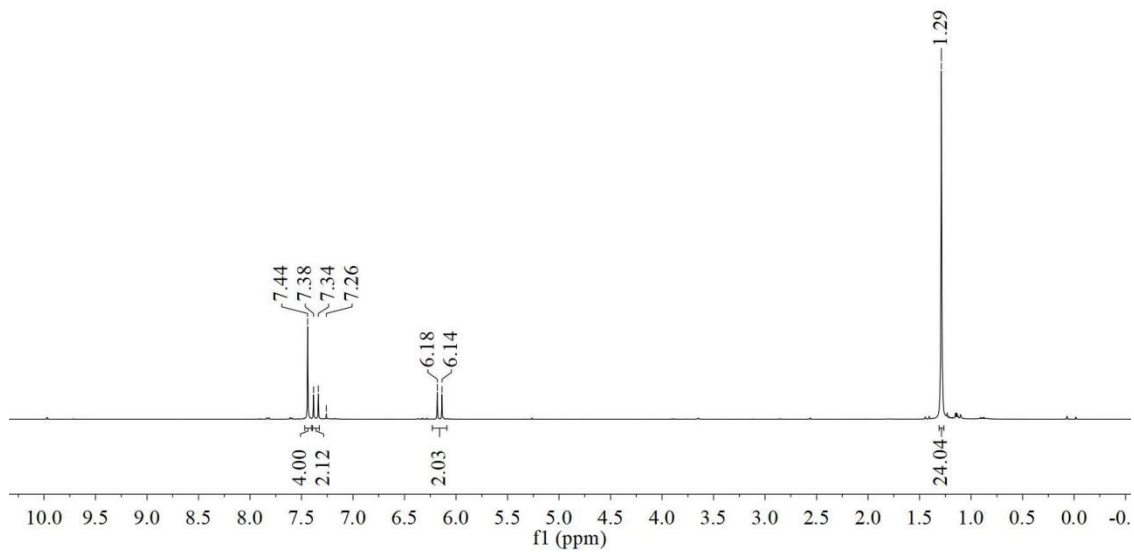
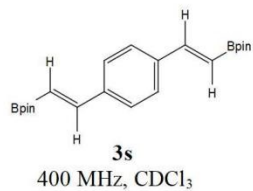
3q
400 MHz, CDCl₃

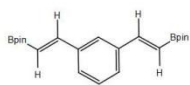


3q
101 MHz, CDCl₃



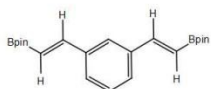
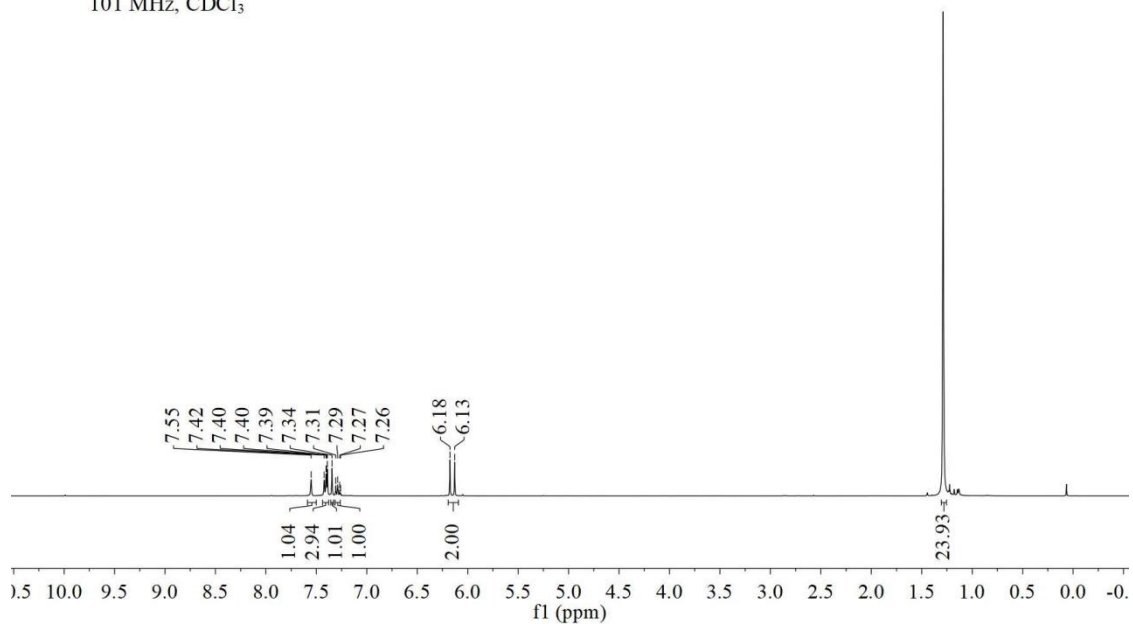






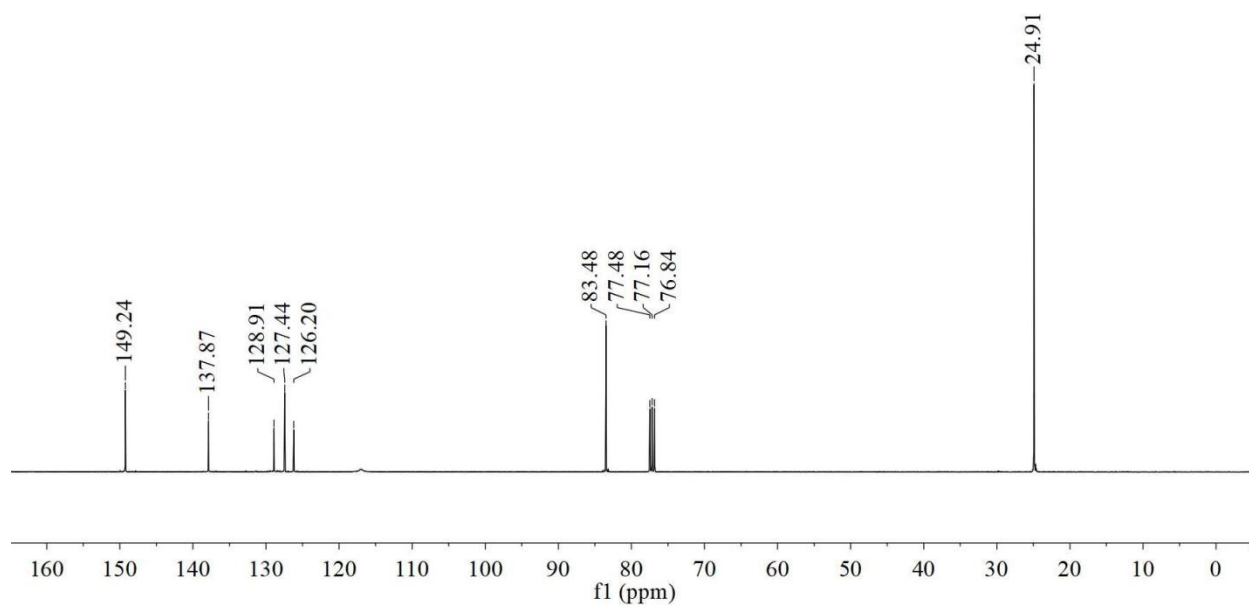
3t

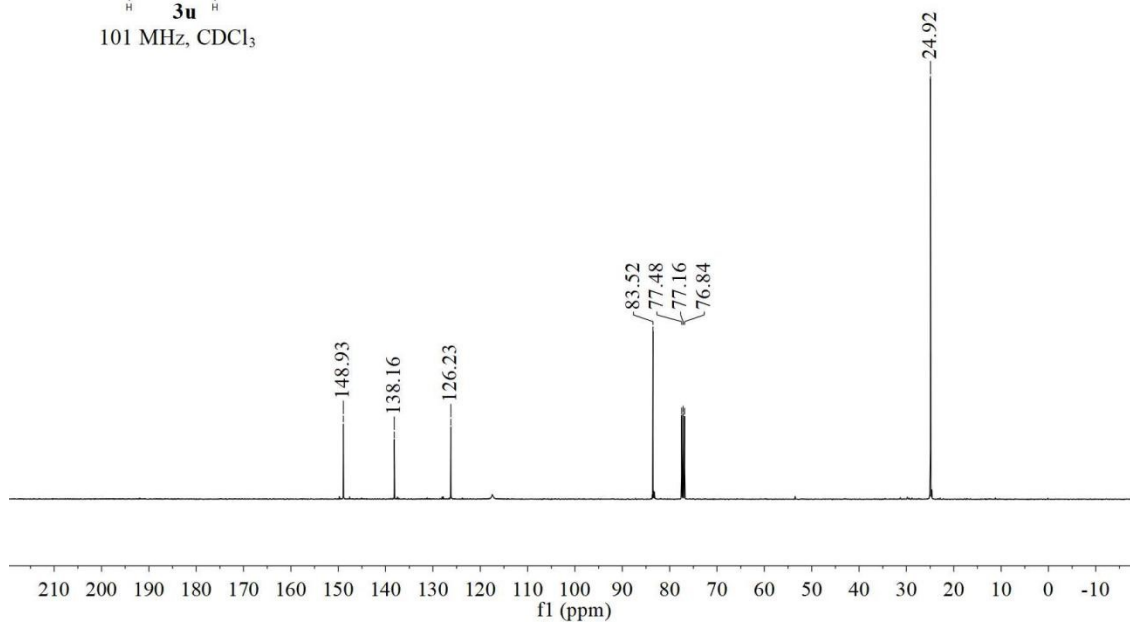
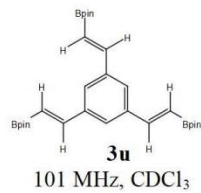
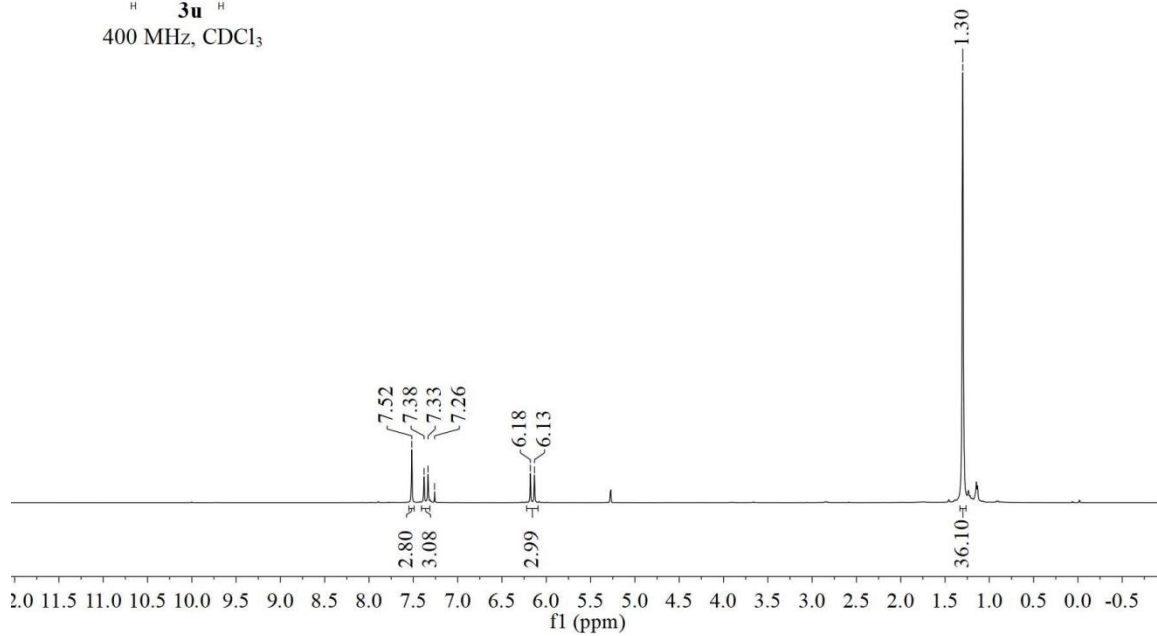
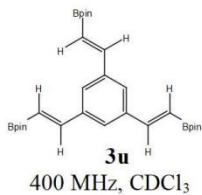
101 MHz, CDCl₃

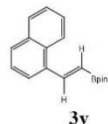


3t

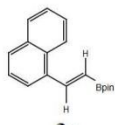
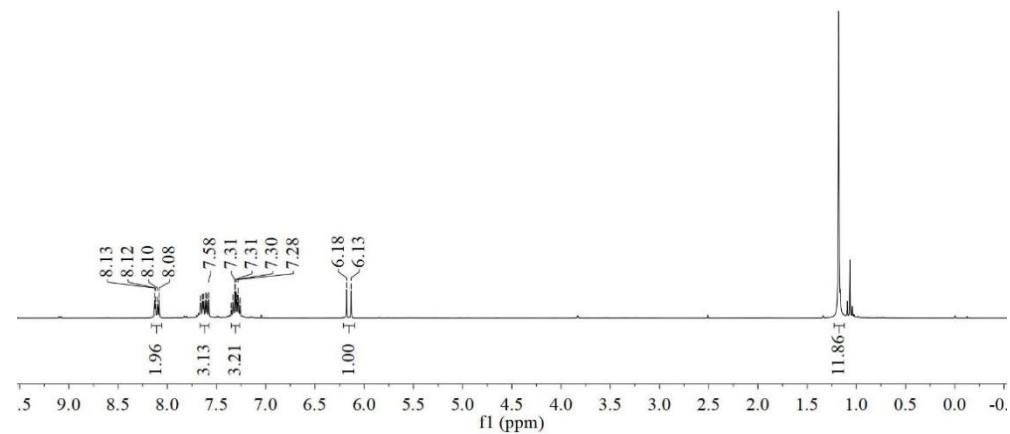
400 MHz, CDCl₃



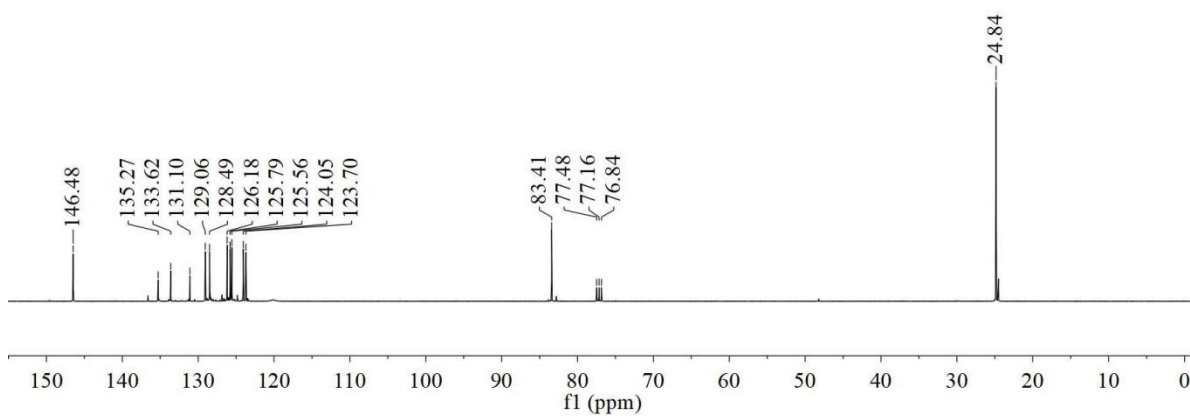


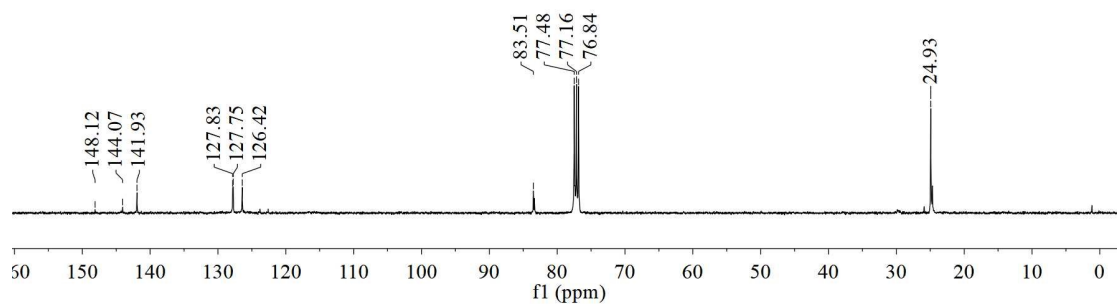
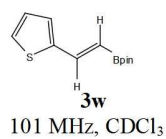
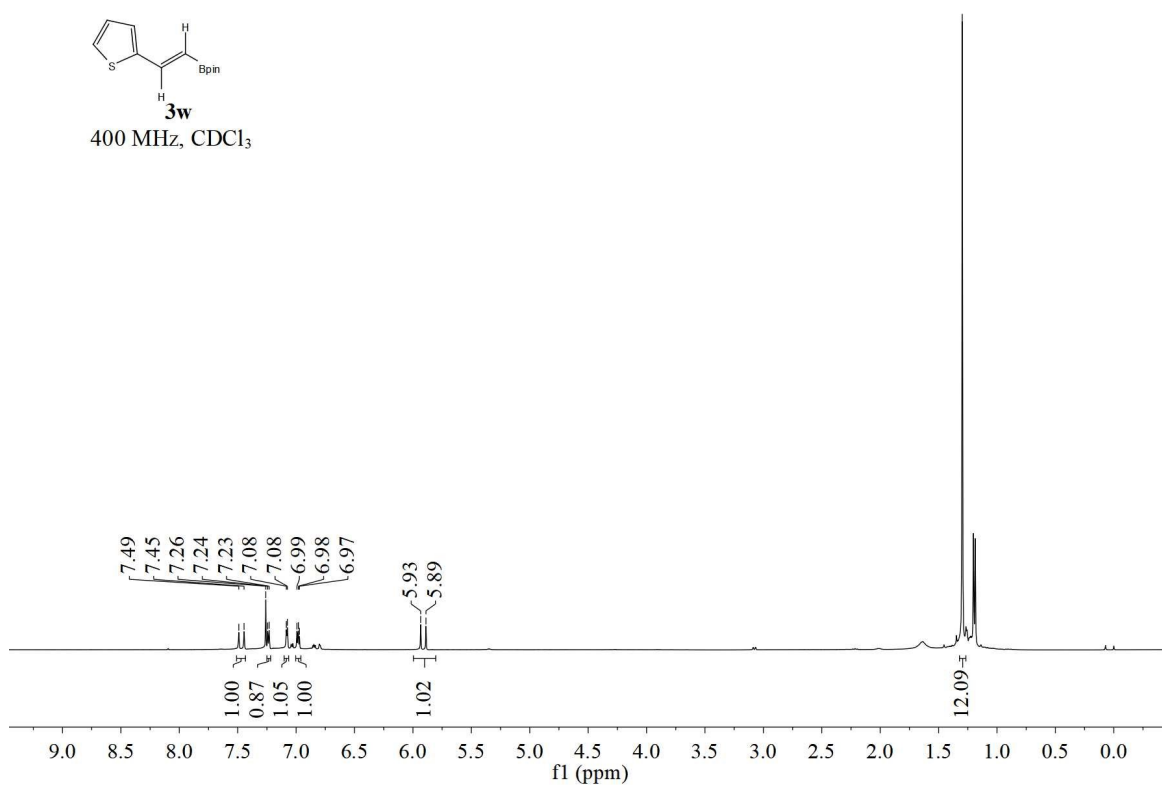
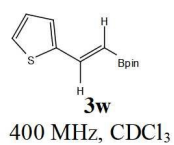


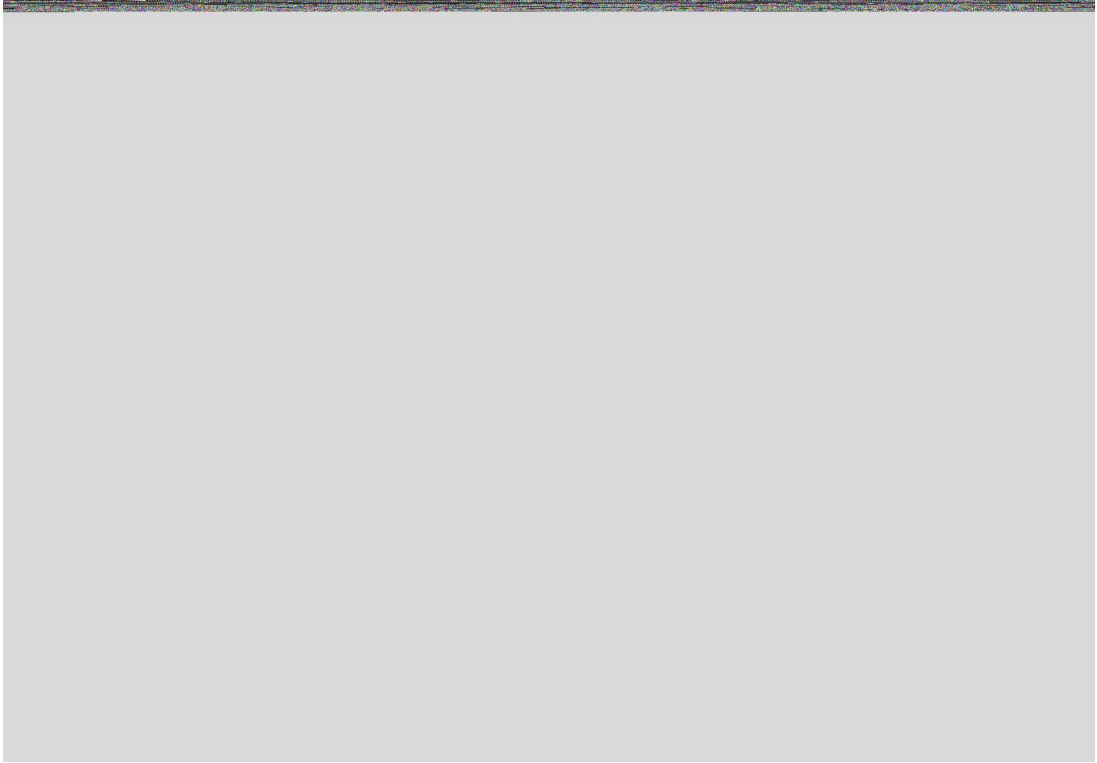
101 MHz, CDCl₃

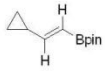


101 MHz, CDCl₃

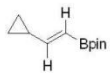
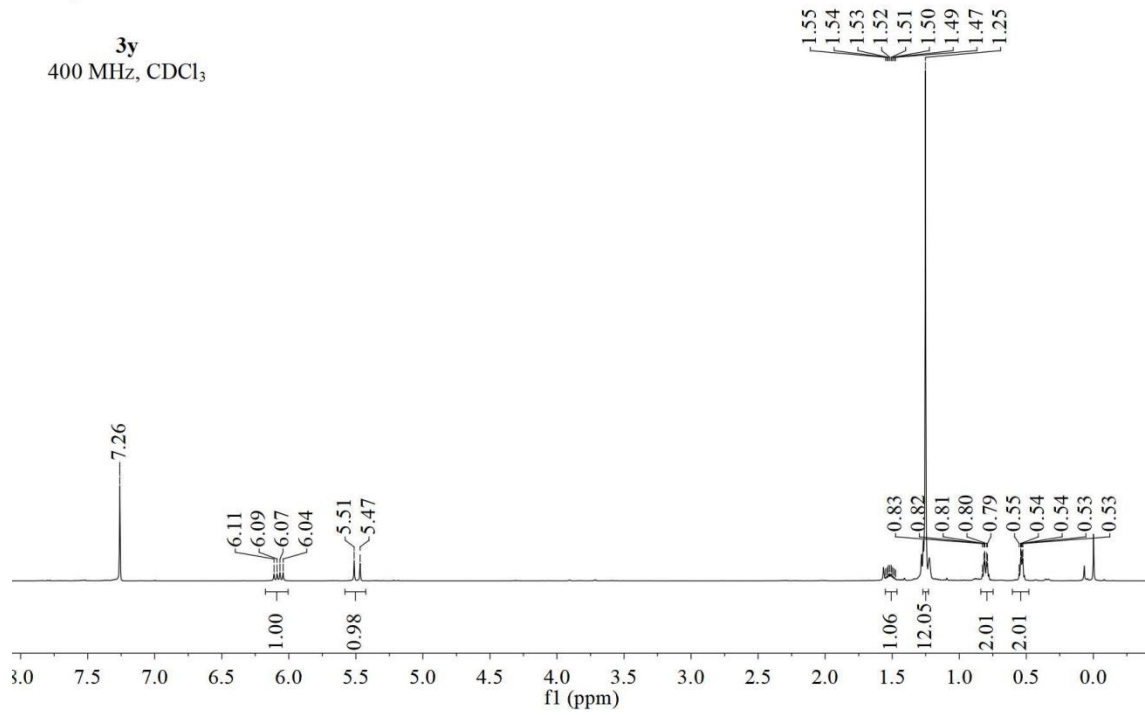




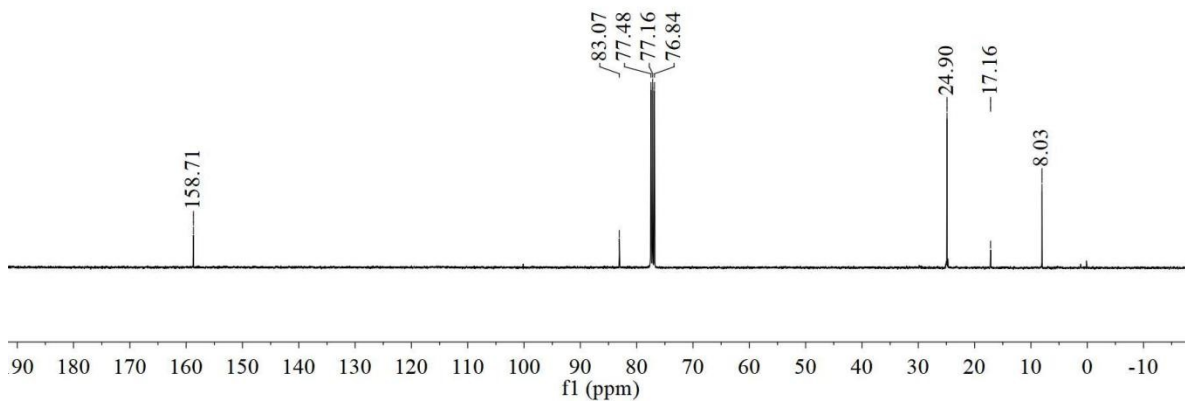


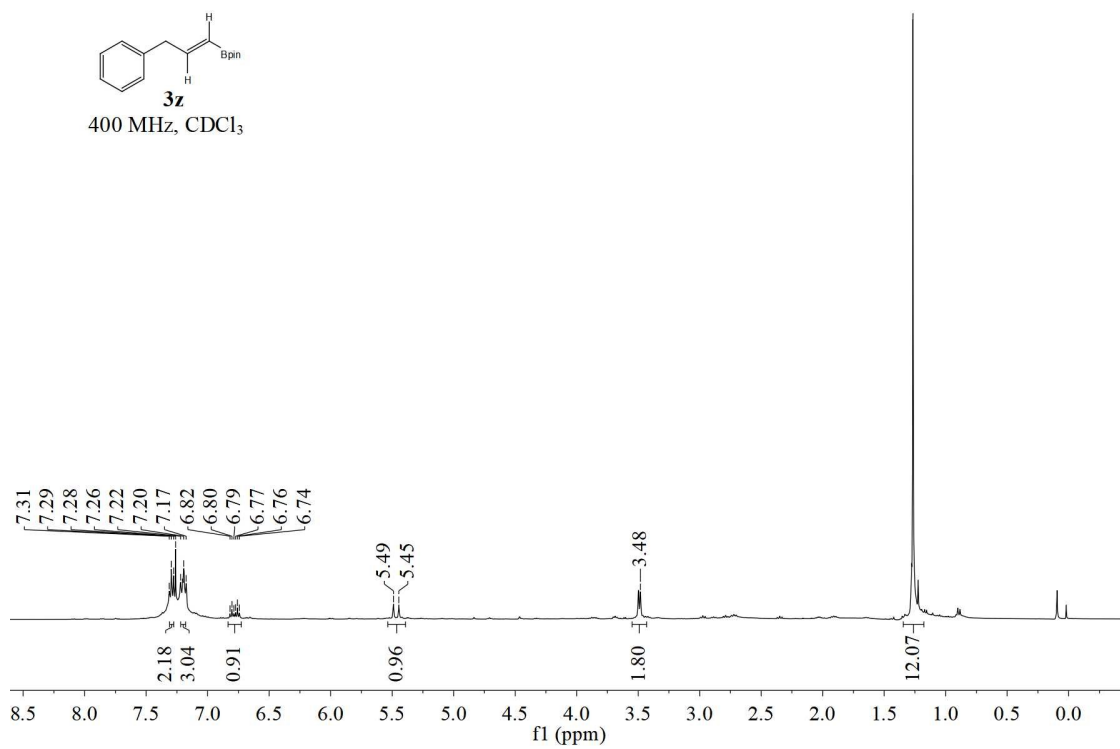
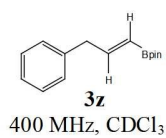
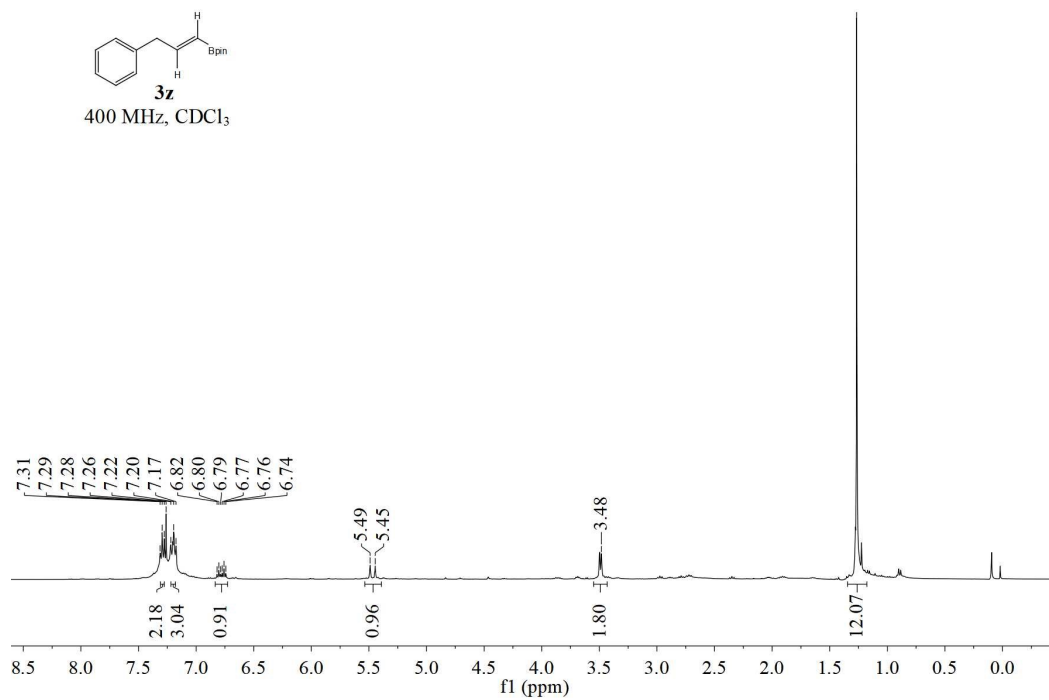
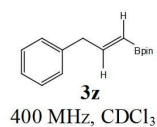


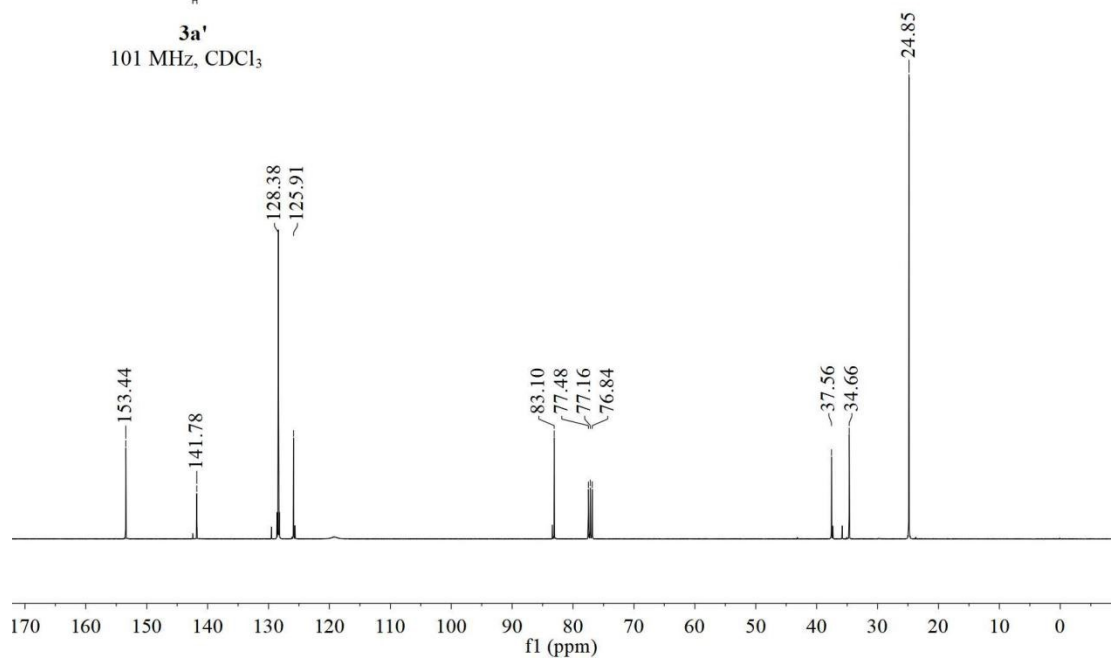
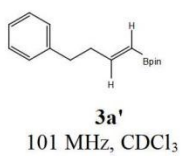
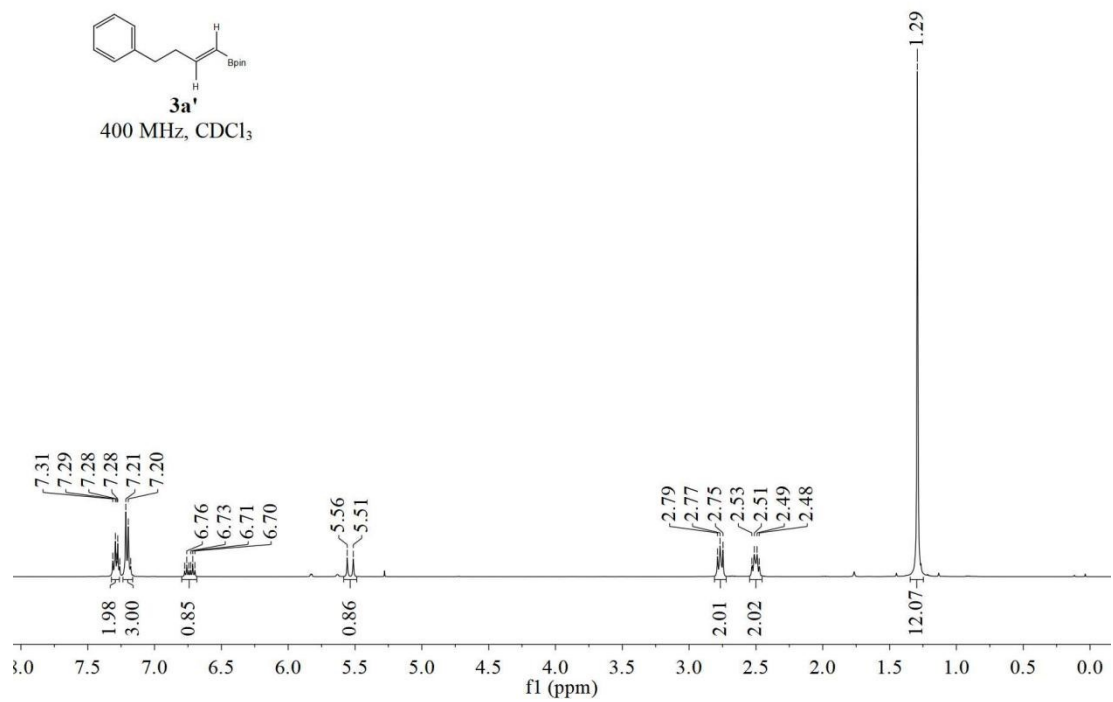
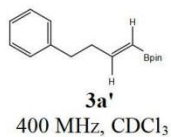
3y
400 MHz, CDCl₃

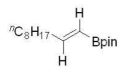


3y
101 MHz, CDCl₃

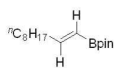
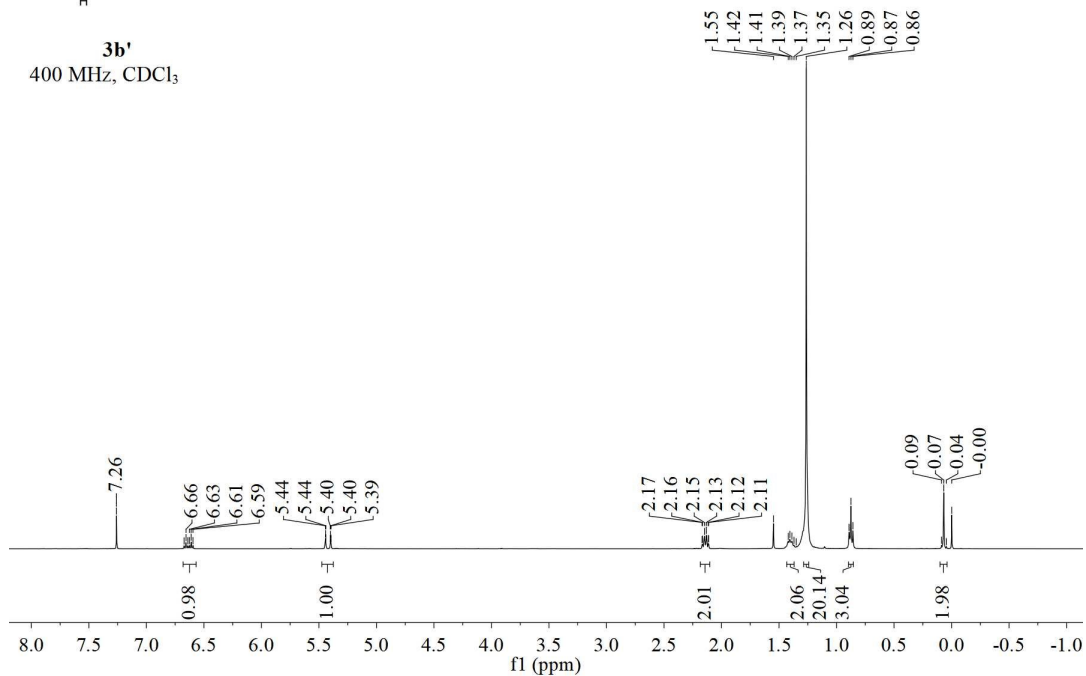




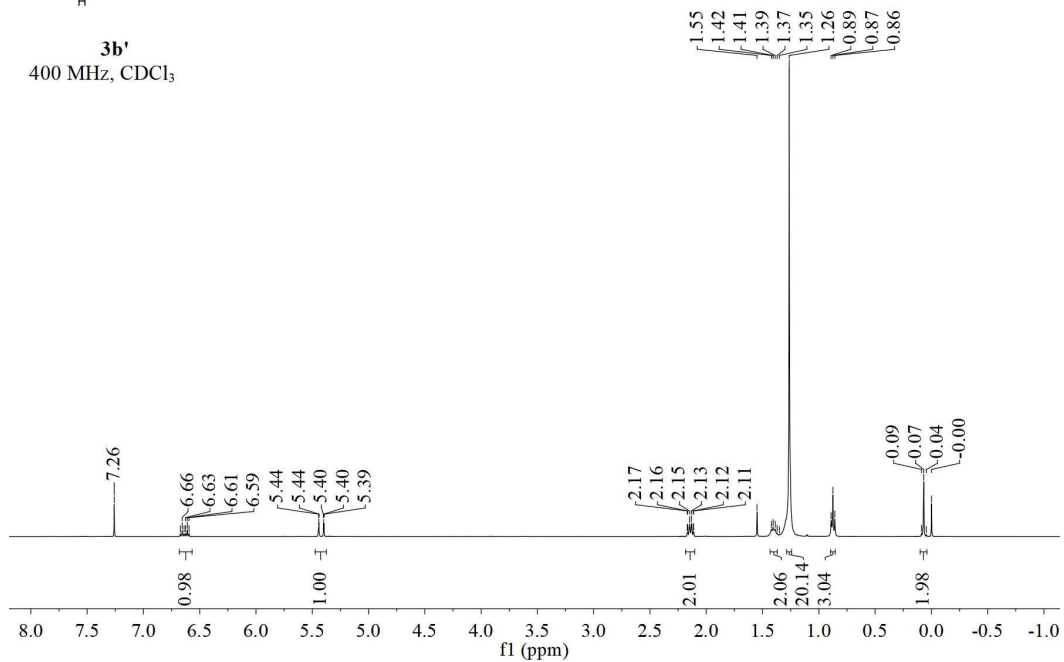


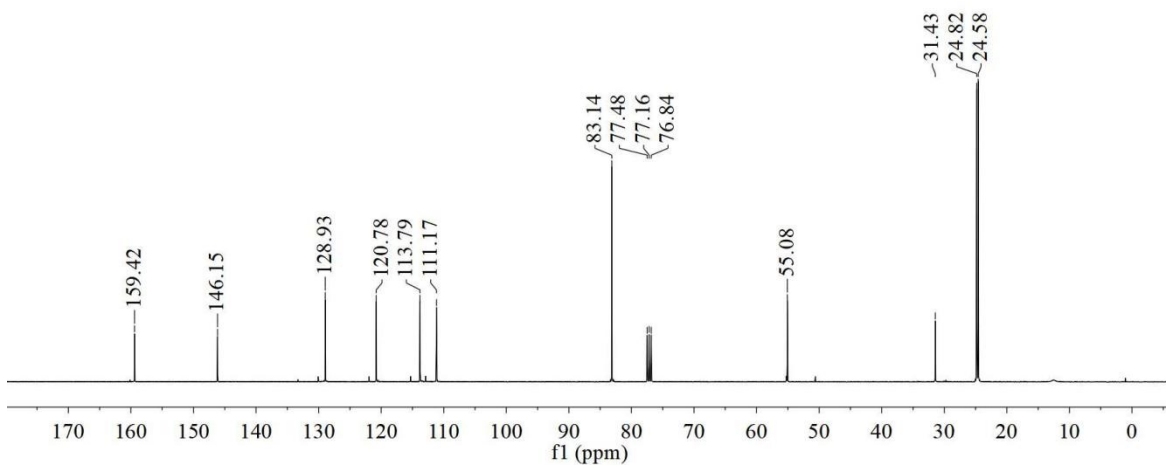
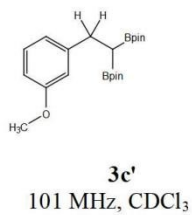
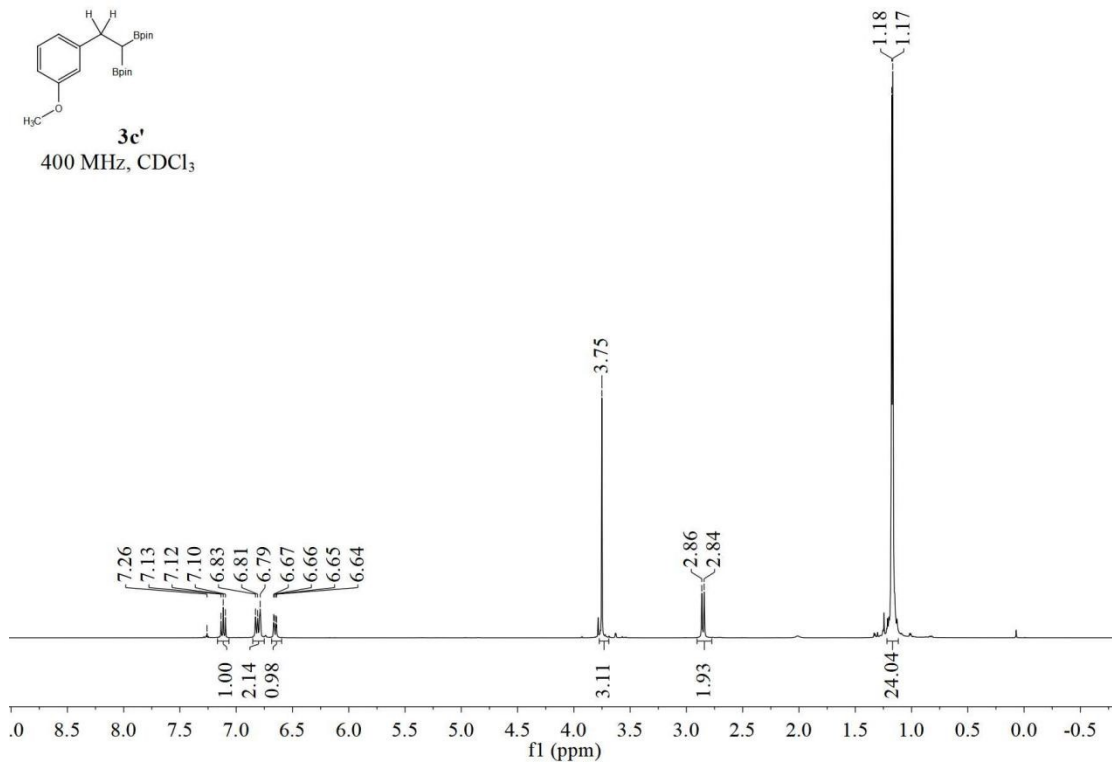
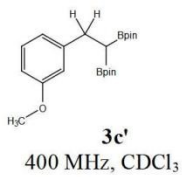


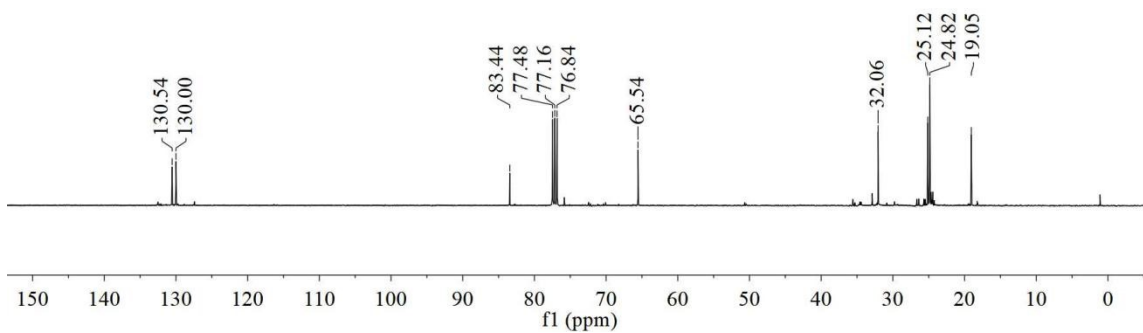
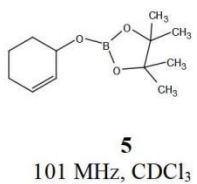
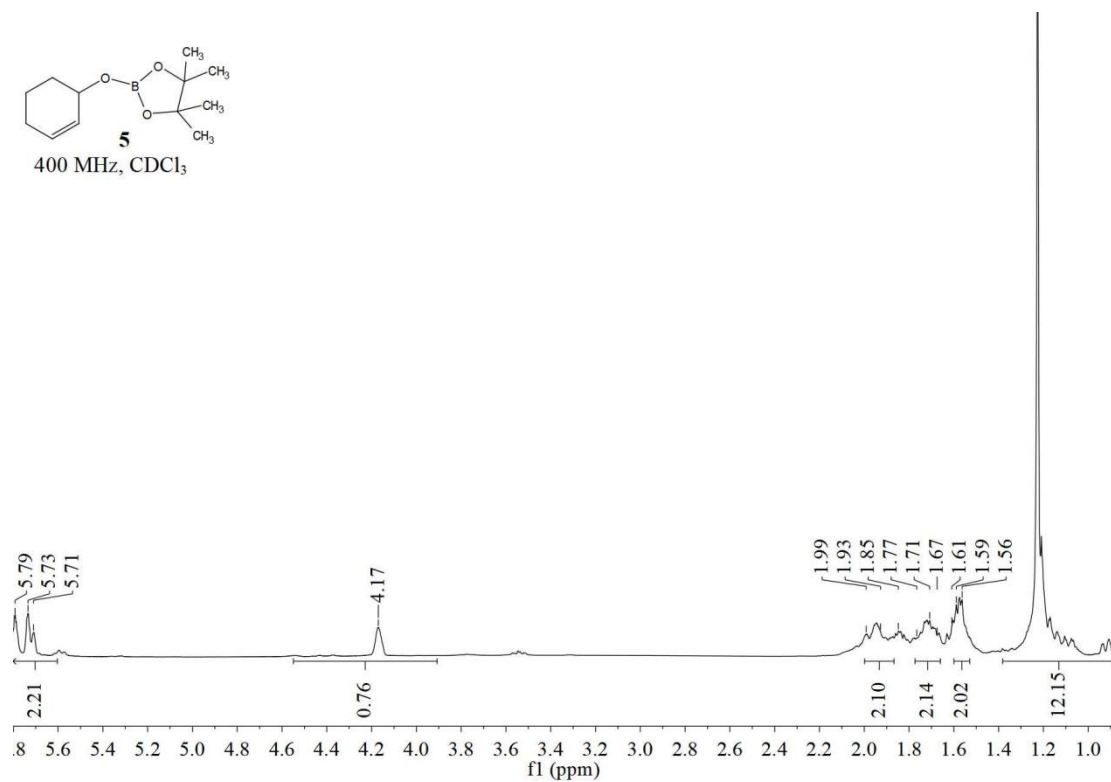
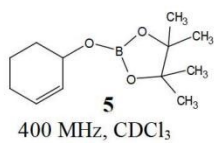
3b'
400 MHz, CDCl₃

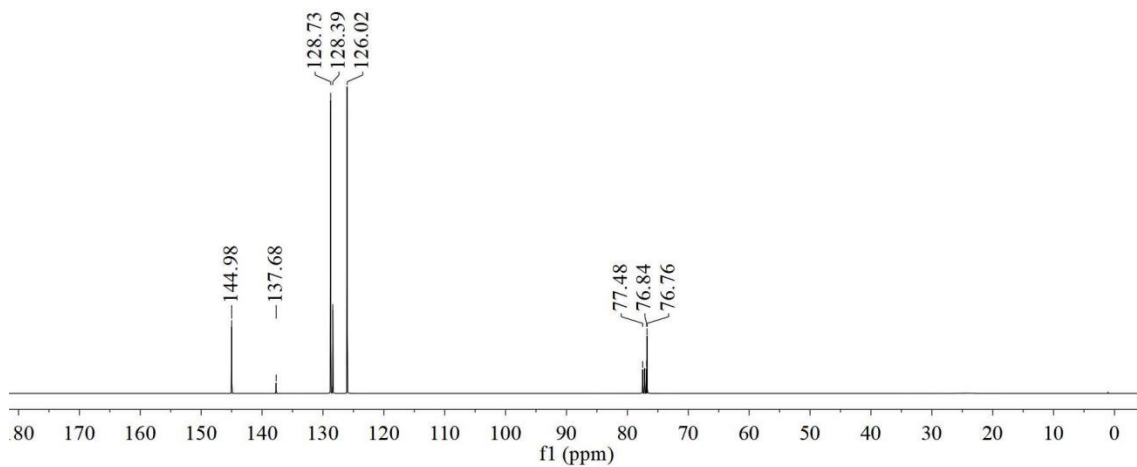
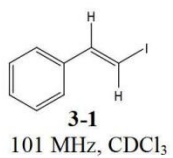
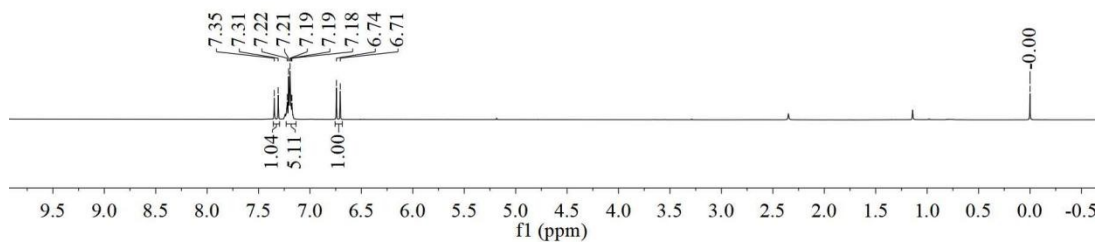
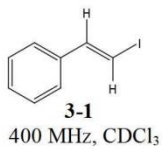


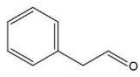
3b'
400 MHz, CDCl₃





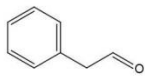
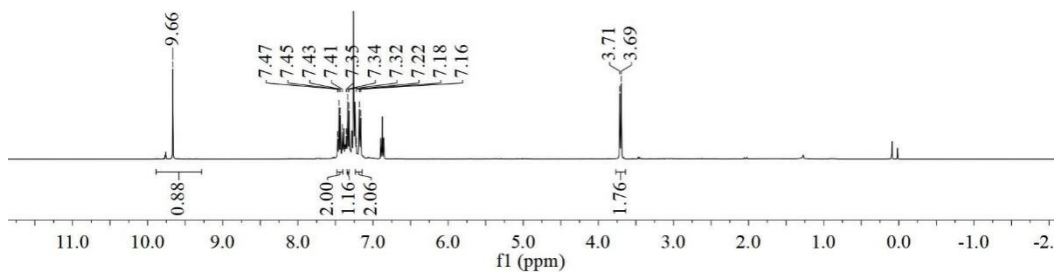






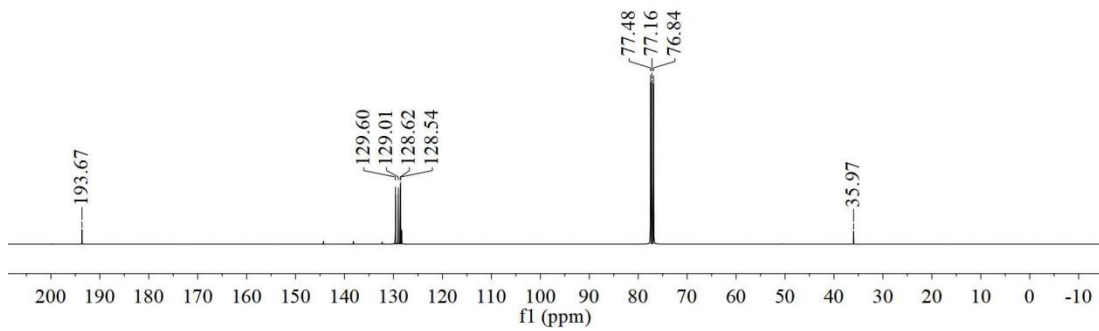
3-2

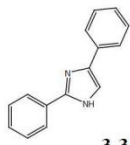
400 MHz, CDCl₃



3-2

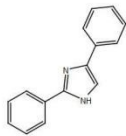
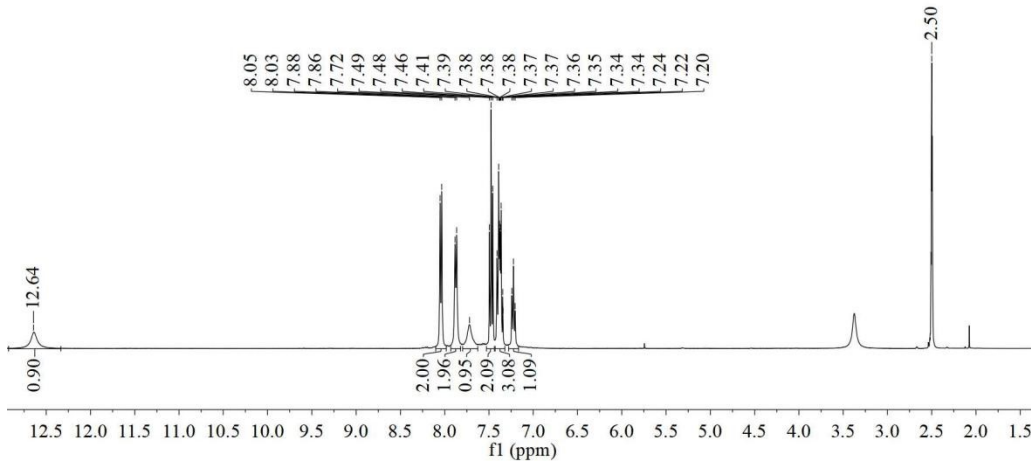
101 MHz, CDCl₃





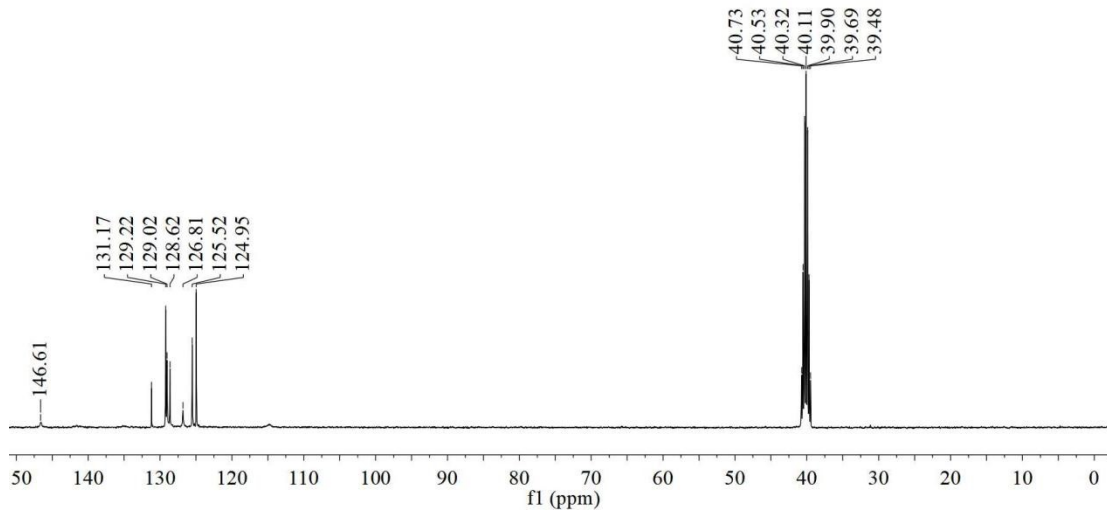
3-3

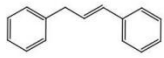
101 MHz, CDCl₃



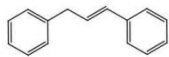
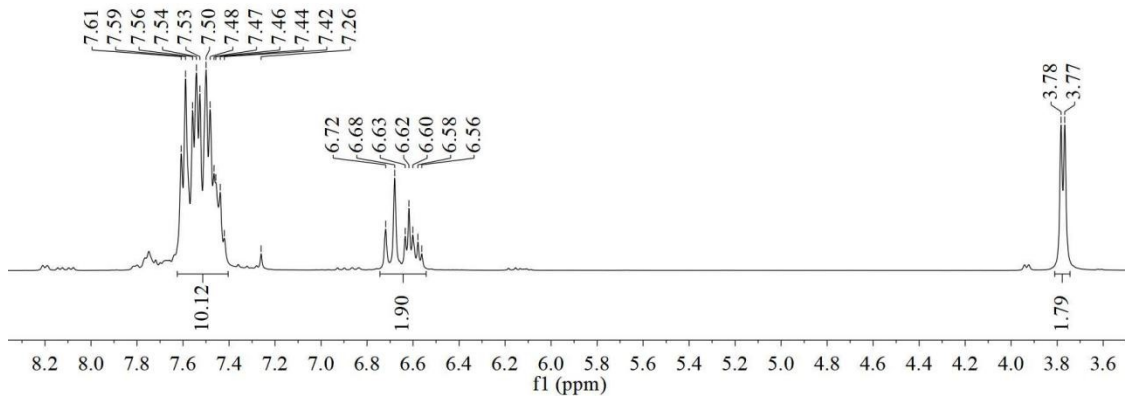
3-3

400 MHz, CDCl₃





3-4
400 MHz, CDCl₃



3-4
101 MHz, CDCl₃

