Supporting Information

Visible-light-Driven Proton Reduction for Semi-hydrogenation of Alkynes via Organophotoredox/Manganese Dual Catalysis

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Table of Contents

General information S2

Methods for preparing [Mn-1] S3

XPS Spectra of [Mn-1] S4

Comparison of HRMS Spectra of Mn(acac)$_2$ and [Mn-1] S5

General Procedure for Synthesis of 2 and 3 .... S8

Conditional Screening S9

Characterization Data for Products S10

Mechanistic studies S16

Possible reaction mechanism S24

Spectrum S25

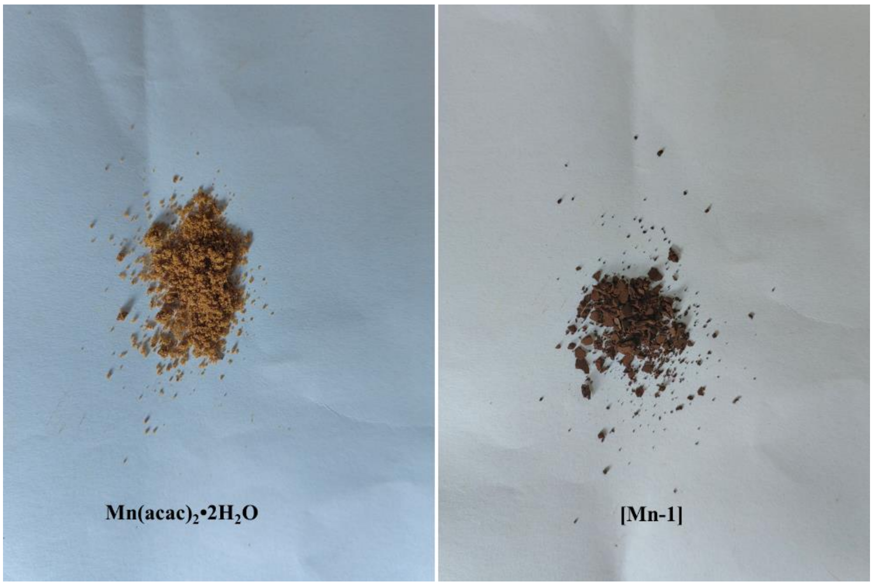
References S59

1. General Information

The alkynes were either purchased from chemical energy or synthesized according to the reported literature.[1] $Mn(acac)_2•2H_2O$ were purchased from Adamas-beta. THF were extra dry solvent also purchased from chemical energy. If no special indicated, other reagents and solvents were used as commercially available without further purification. All the reactions were carried out under argon atmosphere. Column chromatographic purification of products was accomplished using 200-300 mesh silica gel. NMR spectra were measured on a Bruker Avance-400 spectrometer in the solvents indicated; chemical shifts are reported in units (ppm) by assigning TMS resonance in the ^{1}H spectrum as 0.00 ppm or $CHCl_3$ resonance in $CDCl_3$ as 7.26 ppm, $CDCl_3$ resonance in the ^{13}C spectrum as 77.0 ppm, and DMSO-d_6 resonance in the ^{1}H spectrum as 2.50 ppm and ^{13}C spectrum as 39.52 ppm. Coupling constants are reported in Hz with multiplicities denoted as br (broad), s (singlet), bs (broad singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). HRMS were performed on Fourier Transform Ion Cyclotron Resonance Mass Spectrometer. The emission spectra were recorded using a HITACHI F-7000 FL Spectrophotometer. Cyclic voltammetry experiments were studied on a CHI660E Electrochemical Workstation equipped with the conventional three electrode system under argon atmosphere. The measurements were performed in solvent of CH_3CN containing 0.1 M n-Bu_4PF_6 using ferrocene/ferrocenium (Fc^+/Fc^0) as an internal reference. The working electrode was a glassy carbon disk electrode (d = 0.3 cm). The auxiliary and reference electrode consisted of a Pt tablets and an $Ag/AgNO_3$ (0.1 M in CH_3CN), respectively. Irradiation was carried out on Wattecs Parallel Light Reactor (Blue, 10 W, 445 nm–450 nm) equipping with a coolant circulating pump. X-ray photoelectron spectroscopic measurement was recorded by Thermo Scientific K-Alpha.

2. Methods for Preparing [Mn-1].

$$Mn(acac)_2 \bullet 2H_2O \xrightarrow[\textbf{Method 2: } H_2O,\ 80\ ^oC,\ \text{in air}]{\textbf{Method 1}:\ Et_3N\ (3.0\ \text{equiv.}),\ H_2O\ (5.0\ \text{equiv.}),\ \text{in air}} \textbf{[Mn-1]} \qquad \text{(eq S1)}$$



Method

To a 100 mL round bottom flask containing a stirring bar and $Mn(acac)_2 \bullet 2H_2O$ (yellow, 10 mmol, 2.53 g, purchased from Adamas-beta) was added Et_3N (30 mmol, 4.2 mL) and H_2O (50 mmol, 0.9 mL). This mixture quickly turned to black color within 10 min at 30 ^oC, which mixture continued stirring for another 2 h. Subsequently, the solvent was removed in vacuum and the residue was dried in a vacuum oven overnight to give the dark brown solid **[Mn-1]** 2.61 g.

Another method for forming catalytic active pre-catalyst

To a 100 ml round bottom flask containing a stirring bar and $Mn(acac)_2 \bullet 2H_2O$ (yellow, 10.0 mmol, 2.53 g) was added H_2O (6.0 mL). This mixture was vigorous stirred at 80 ^oC in air overnight and the solvent was totally evaporated. Then, the dark brown colored Mn catalyst in the flask was collected in 1.96 g.

3. XPS Spectra of [Mn-1].

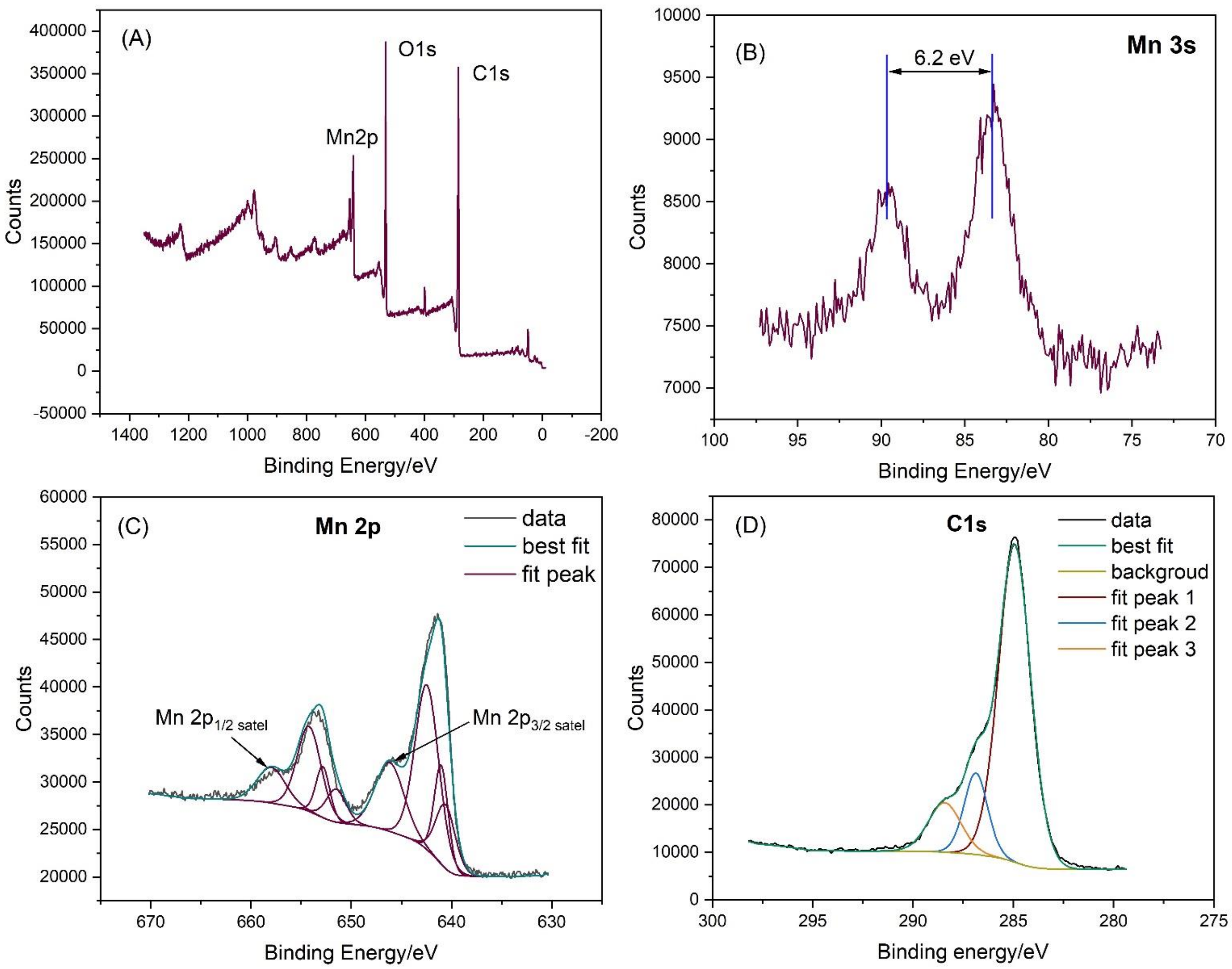


Figure S1. X-Ray photoelectron spectra of **[Mn-1]**.

Table S1. Comparison the analytical data (Atom%) for free Mn(acac)$_2$ and [Mn-1] via XPS analysis.[a]

Compounds	C	O	Mn	O/Mn ratio
Mn(acac)$_2$ *ref 2*	66.32	26.79	5.63	4.8/1
[Mn-1]	70.15	24.48	5.37	4.6/1

[a]The data of O/Mn ratio for Mn(acac)$_2$ comes from *ref 3a*.

X-ray photoelectron spectroscopic measurement was recorded by Thermo Scientific K-Alpha. Al(Kα) [1486.6 eV] radiation was used for excitation and the measured binding energies were calculated with respect to the C(1s) level, present in samples, which was assumed to have a binding energy of 284.8 eV. Spectra were analyzed using Avantage software and related literature[2].

A reliable approach to determine the oxidation state of Mn is the evaluation of the peak binding energy distance in the multiplet split Mn3s region.[3] Thus, for the sample of **[Mn-1]**, both peaks of Mn3s and Mn2p was recorded (Figure S1, A). The 3s splitting energies for reference samples were 5.8 eV for MnO, 5.3 eV for MnOOH and 4.6 eV for MnO_2.[3a] As a comparison, the 3s peak widths in the samples of **[Mn-1]** were 6.2 eV, consistent with the character of Mn(II) species, suggesting that **[Mn-1]** still exists mainly in an oxidation of II (Figure S1, B).

Besides, both Mn 2p1/2 and Mn 2p3/2 displayed shake-up satellite peaks (Fgure S1, C), which phenomenon is widely found in manganese (II/III) β-diketonato complex.[4] This phenomenon originates from the charge transfer between outer electron shell of ligand and an unfilled 3d shell of Mn during creation of core-hole in the photoelectron process, indicating the presence of diketonato-type ligand in **[Mn-1]**. This dedution is further confirmed by O/Mn atomic ratio, since **[Mn-1]** (O/Mn = 4.6/1) displayed a similar O/Mn ratio towards $Mn(acac)_2$ (O/Mn = 4.8/1, see Table 1), which is obviously higher than manganese oxide (e.g. MnO, Mn_2O_3, MnO_2, O/Mn ratio range from 1/1 to 2/1).

4. Comparison of HRMS Spectra of $Mn(acac)_2{\bullet}2H_2O$ and [Mn-1].

The high-resolution mass spectra (HRMS) of both $Mn(acac)_2{\bullet}2H_2O$ and **[Mn-1]** were recorded. As shown in Figure S2, $Mn(acac)_2{\bullet}2H_2O$ displayed a clear molecular ion peak located at 253.0291, which was well consistent with the calculated value (253.0273). From HRMS ananlysis (Figure S3), we found that none of $Mn(acac)_2{\bullet}2H_2O$ exsit in **[Mn-1]**, demonstrating the full conversion of the reaction (see eq S1). Unfortunately, we could not speculate the possible structure of **[Mn-1]** at this stage.

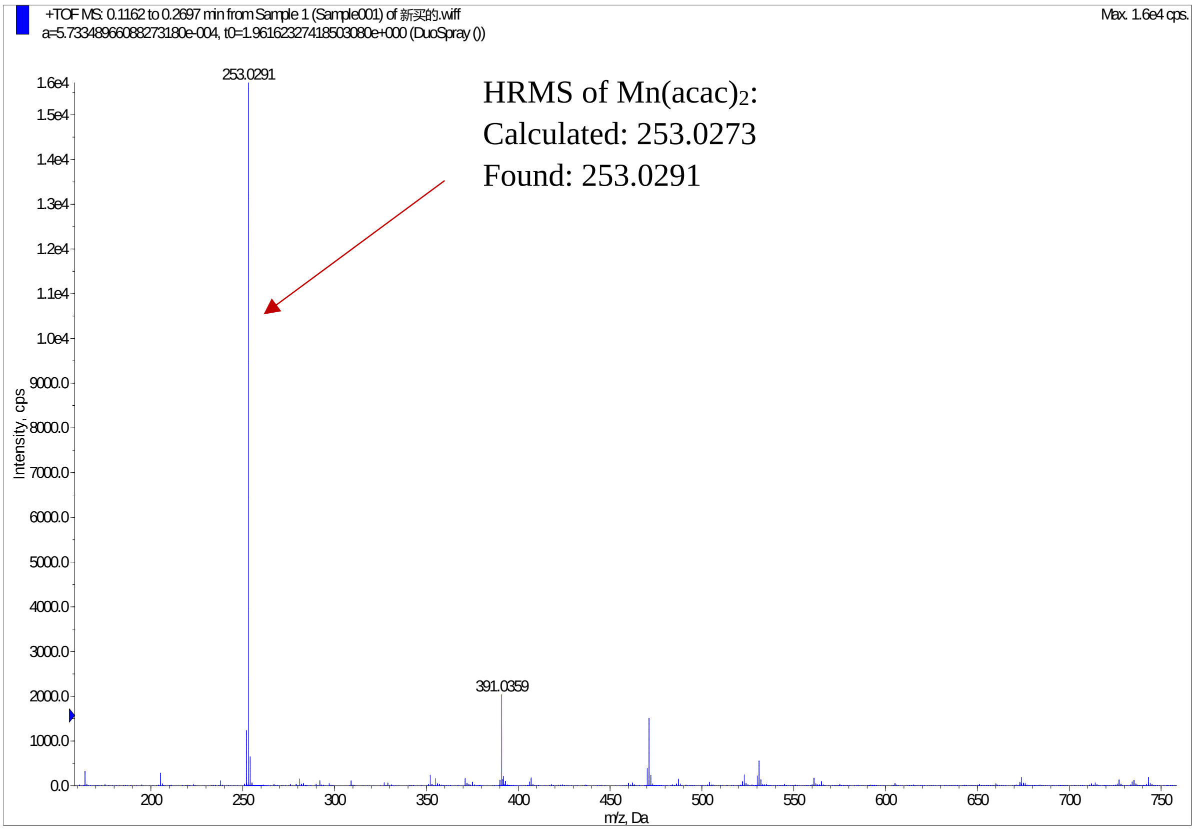


Figure S2. HRMS spectrum of Mn(acac)$_2$.

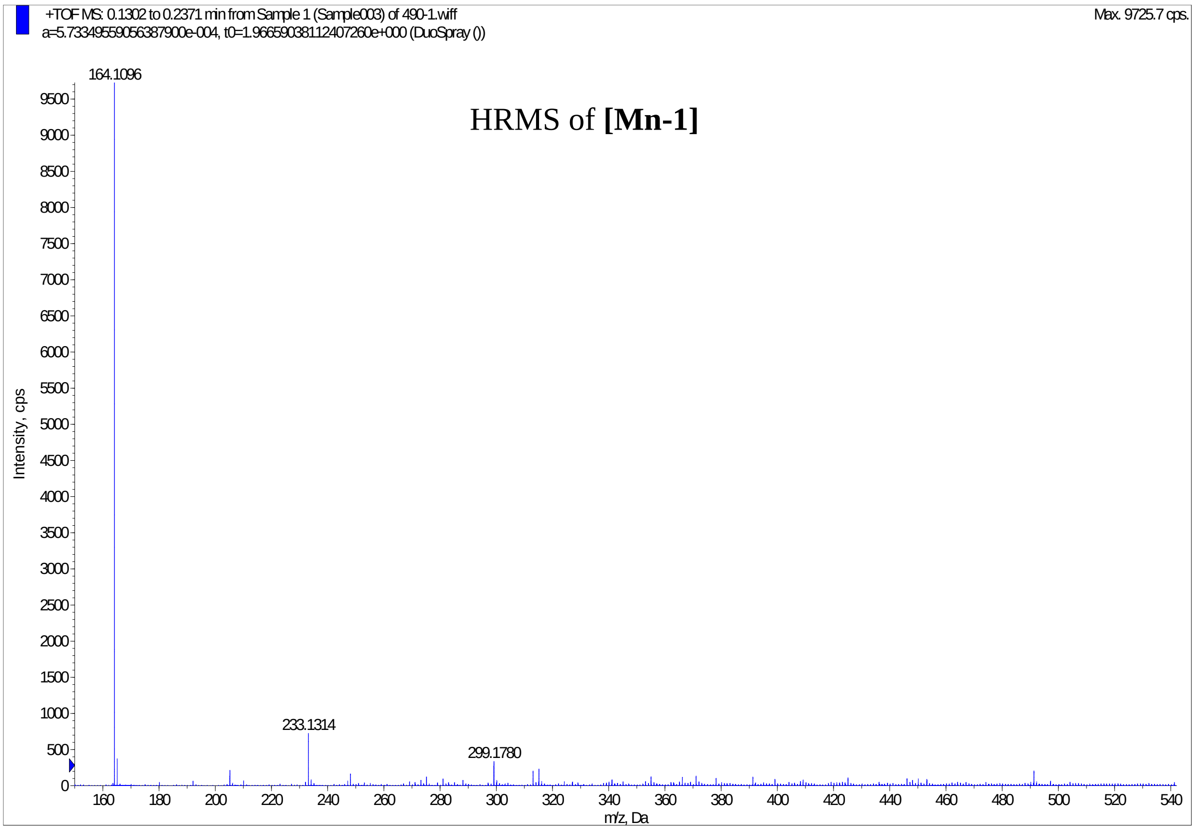


Figure S3. HRMS spectrum of **[Mn-1]**.

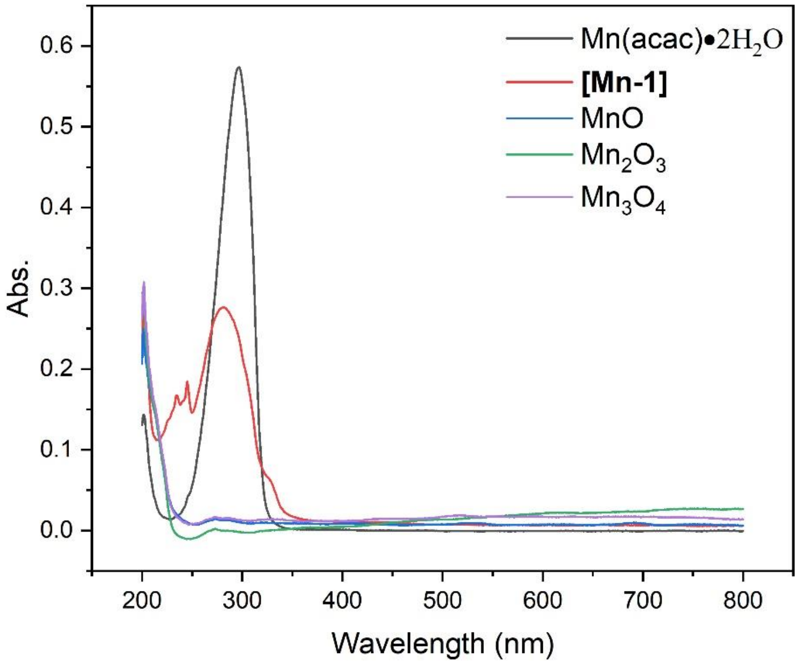


Figure S4. UV-vis spectra of Mn(acac)22H2O, [Mn-1], and Mn oxides.

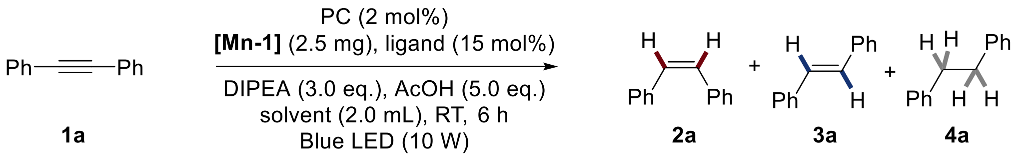
5. General Procedure for Synthesis of 2 and 3.

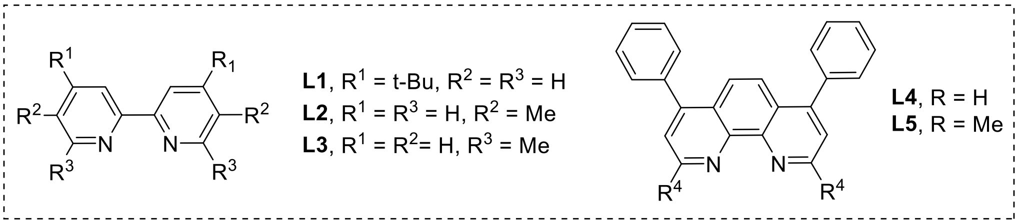
Substrate **1** (0.20 mmol, 1.0 equiv), 4CzIPN (0.004 mmol, 2 mol%), [**Mn-1**] (2.5 mg), and **L2** (0.03 mmol, 15 mol%) were added into a 20 mL reaction tube. Then, DIPEA (0.6 mmol, 3.0 equiv.), AcOH (1.0 mmol, 5.0 equiv.), and anhydrous THF (2.0 mL) were sequentially added to the reaction tube via syringe in Ar atmosphere. The reaction mixture was stirred at ambient temperature (28 ~ 30 ^{o}C) for 6 h on Wattecs Parallel Light Reactor. A coolant circulating pump is equipped with the Parallel Light Reactor to keep the temperature constant. Finally, the solvent was removed in vacuum and the residue was purified by column chromatography on silica gel to afford the compound **2** or **3.**

Wattecs Parallel Light Reactor equipped with a coolant circulating pump (Blue LED Light source, 445-450 nm, 10 W every position)

6. Conditional Screening

Table S2. Optimization of the reaction conditions.[a]



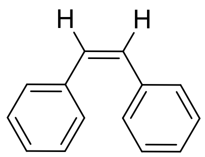


entry	photocatalyst	[Mn]	ligand	solvent	yield (%) **2a** : **3a** : **4a**
1	4CzIPN	$Mn(acac)_2$•$2H_2O$	**L1~L5**	1,4-dioxane	n.r.
2	4CzIPN	**[Mn-1]**	**L1**	1,4-dioxane	n.r.
3	4CzIPN	**[Mn-1]**	**L2**	1,4-dioxane	44 : 20 : 0
4	4CzIPN	**[Mn-1]**	**L3**	1,4-dioxane	n.r.
5	4CzIPN	**[Mn-1]**	**L4**	1,4-dioxane	n.r.
6	4CzIPN	**[Mn-1]**	**L5**	1,4-dioxane	20 : 6 : 0
7	4CzIPN	**[Mn-1]**	dppp	1,4-dioxane	n.r.
8	4CzIPN	**[Mn-1]**	**L2**	THF	85 : 15 : 0
9	4CzIPN	**[Mn-1]**	**L2**	CH_3CN or acetone	n.r.
10	4CzIPN	$Mn(acac)_3$	**L2**	THF	n.r.
11[b]	4CzIPN	**[Mn-1]**	**L2**	THF	n.r.
12	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	**[Mn-1]**	**L2**	THF	n.r.
13	$Ir(ppy)_2(bpy)PF_6$	**[Mn-1]**	**L2**	THF	38 : 16 : 0
14	-	**[Mn-1]**	**L2**	THF	n.r.
15	4CzIPN	-	-	THF	n.r.
16[c]	4CzIPN	**[Mn-1]**	**L2**	THF	n.r.
17[d]	4CzIPN	**[Mn-1]**	**L2**	THF	n.r.
18[e]	4CzIPN	**[Mn-1]**	**L2**	THF	83 : 17 : 0
19	4CzIPN	MnO, Mn_2O_3 or Mn_3O_4	**L2**	THF	n.r.

[a] **1a** (0.2 mmol), PC (2 mol%), $Mn(acac)_2$•$2H_2O$(5 mol%) or **[Mn-1]** (2.5 mg), ligand (15 mol%), DIPEA (3.0 eq.), acid (5.0 eq.), solvent (2.0 mL), irradiation with blue LED for 6 h. Yields were determined by ^1H NMR spectroscopy vs. $Cl_2CHCHCl_2$ as an internal standard. [b] H_2O instead of AcOH. [c] No DIPEA or AcOH. [d] In dark. [e] With a drop of Hg.

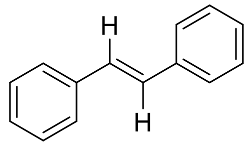
7. Characterization Data for Products

(*Z*)-1,2-Diphenylethylene **2a**[5] and (*E*)-1,2-Diphenylethylene **3a**[5]



2a

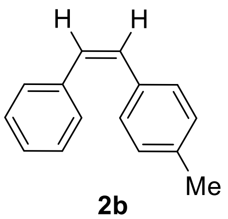
and



3a

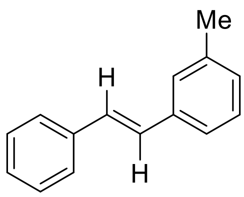
Purified by column chromatography on silica gel (petroleum ether/ethyl acetate /DCM = 200/1/1), total yield: >99% (35.8 mg), *Z:E* = 85:15. **2a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25–7.16 (m, 10H), 6.59 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.2 (2C), 130.2 (2C), 128.9 (4C), 128.2 (4C), 127.1 (2C). **3a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.6 Hz, 4H), 7.35 (t, *J* = 7.6 Hz, 4H), 7.27–7.22 (m, 2H), 7.10 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.4 (2C), 128.7 (2C), 128.7 (4C), 127.6 (2C), 126.5 (4C).

(*Z*)-1-methyl-4-styrylbenzene **2b**[5] and (*E*)-1-methyl-4-styrylbenzene **3b**[5]



2b

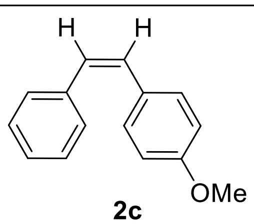
and



3b

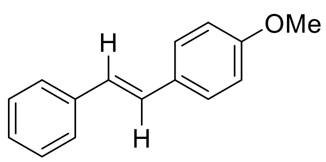
Purified by column chromatography on silica gel (petroleum ether/ethyl acetate /DCM = 200/1/1), total yield: 95% (37.0 mg), *Z:E* = 63:37. **2b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27–7.17 (m, 5H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 7.6 Hz, 2H), 6.55 (s, 2H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5, 136.8, 134.2, 130.2, 129.5, 128.9 (2C), 128.8 (2C), 128.8 (2C), 128.2 (2C), 126.9, 21.2. **3b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.6 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.26–7.23 (m, 1H), 7.17 (d, *J* = 7.6 Hz, 2H), 7.08 (d, *J* = 2.4 Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5 (2C), 134.6, 129.4 (2C), 128.6 (2C), 128.6, 127.7, 127.4, 126.4 (2C), 126.4 (2C), 21.2.

(*Z*)-1-methoxy-4-styrylbenzene **2c**[5] and (*E*)-1-methoxy-4-styrylbenzene **3c**[5]



2c

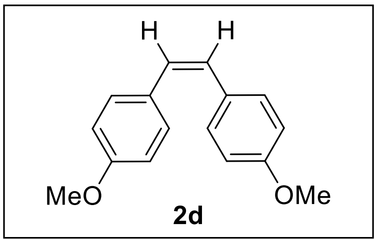
and



3c

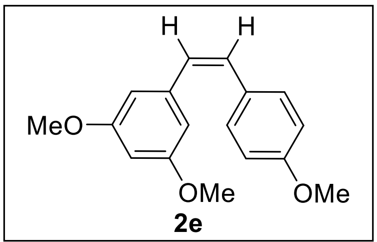
Purified by column chromatography on silica gel (petroleum ether/ethyl acetate/DCM = 200/1/1), total yield: 99% (41.5 mg), *Z:E* = 72:28. **2c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28–7.17 (m, 7H), 6.75 (d, *J* = 8.8 Hz, 2H), 6.55–6.48 (m, 2H), 3.77 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 137.6, 130.1 (2C), 129.7, 129.6, 128.8 (2C), 128.7, 128.2 (2C), 126.9, 113.5 (2C), 55.1. **3c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50–7.44 (m, 4H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.24 (d, *J* = 6.4 Hz, 1H), 7.07 (d, *J* = 16.0 Hz, 1H), 6.97 (d, *J* = 16.4 Hz, 1H), 6.90 (d, *J* = 8.8 Hz, 2H), 3.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 137.6, 130.1, 128.6 (2C), 128.2, 127.7 (2C), 127.2, 126.6, 126.2 (2C), 114.1 (2C), 55.3.

(*Z*)-1,2-Di-(4-methoxyphenyl)ethylene **2d**[6]



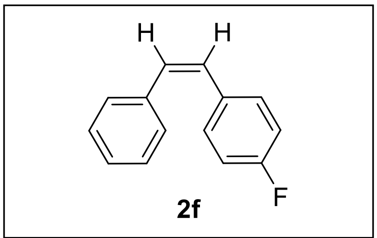
Purified by column chromatography on silica gel (petroleum ether/ethyl acetate/DCM = 200/1/1), yield: 75% (35.9 mg), *Z:E* > 95:5. **2d**: ^{1}H NMR (400 MHz, DMSO) δ 7.16 (d, *J* = 8.4 Hz, 4H), 6.82 (d, *J* = 8.8 Hz, 4H), 6.44 (s, 2H), 3.72 (s, 6H). ^{13}C NMR (100 MHz, DMSO) δ 158.3 (2C), 129.7 (4C), 129.4 (2C), 128.1 (2C), 113.8 (4C), 55.0 (2C).

(*Z*)-1,3-dimethoxy-5-(4-methoxystyryl)benzene **2e**[7]



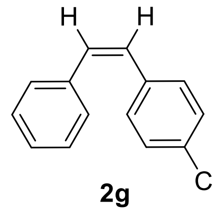
Purified by column chromatography on silica gel (petroleum ether/ethyl acetate /DCM = 100/1/1), total yield: 97% (52.3 mg), *Z:E* = 79:21. **2e**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.4 Hz, 2H), 6.76 (d, *J* = 8.4 Hz, 2H), 6.52 (d, *J* = 12.4 Hz, 1H), 6.45–6.43 (m, 3H), 6.32 (s, 1H), 3.78 (s, 3H), 3.67 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5 (2C), 158.7, 139.4, 130.2 (2C), 130.1, 129.5, 128.6, 113.5 (2C), 106.6 (2C), 99.6, 55.2 (3C).

(*Z*)-1-fluoro-4-styrylbenzene **2f**[5]



Purified by column chromatography on silica gel (petroleum ether/ethyl acetate/DCM = 200/1/1), total yield: 91% (36.0 mg), *Z:E* = 80:20. **2f**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24–7.18 (m, 7H), 6.90 (t, *J* = 8.8 Hz, 2H), 6.59 (d, *J* = 12.0 Hz, 1H), 6.53 (d, *J* = 12.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.8 (d, $^1J_{C-F}$ = 245.2 Hz), 137.0, 133.2 (d, $^4J_{C-F}$ = 3.4 Hz), 130.5 (d, $^3J_{C-F}$ = 7.8 Hz), 130.5 (d, $^3J_{C-F}$ = 7.8 Hz), 130.2, 129.0, 128.8 (2C), 128.3 (2C), 127.2, 115.2 (d, $^2J_{C-F}$ = 21.2 Hz), 115.0 (d, $^2J_{C-F}$ = 21.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ -114.7.

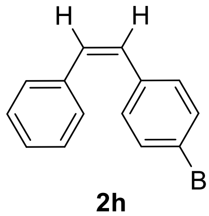
(*Z*)-1-chloro-3-styrylbenzene **2g**[5]



2g

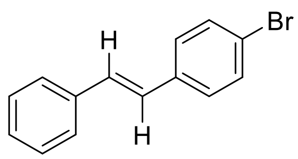
Purified by column chromatography on silica gel (petroleum ether/ethyl acetate/DCM = 200/1/1), total yield: 74% (31.5 mg), *Z:E* = 80:20. **2g**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25–7.15 (m, 9H), 6.62 (d, *J* = 12.0 Hz, 1H), 6.52 (d, *J* = 12.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 135.6, 132.7, 130.9, 130.2 (2C), 128.9, 128.8 (2C), 128.4 (2C), 128.3 (2C), 127.3.

(*Z*)-1-bromo-4-styrylbenzene **2h**[8] and (*E*)-1-bromo-4-styrylbenzene **3h**[8]



2h

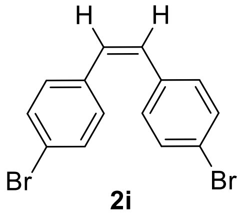
and



3h

Purified by column chromatography on silica gel (petroleum ether/ethyl acetate /DCM = 200/1/1), total yield: 82% (42.3 mg), *Z:E* = 76:24. **2h**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.4 Hz, 2H), 7.25–7.18 (m, 5H), 7.09 (d, *J* = 8.4 Hz, 2H), 6.62 (d, *J* = 12.4 Hz, 1H), 6.49 (d, *J* = 12.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 136.1, 131.3 (2C), 131.0, 130.5 (2C), 128.9, 128.8 (2C), 128.3 (2C), 127.3, 120.9. **3h**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51–7.46 (m, 4H), 7.38–7.34 (m, 4H), 7.29–7.25 (m, 1H), 7.10 (d, *J* = 16.0 Hz, 1H), 7.02 (d, *J* = 16.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.9, 136.3, 131.8 (2C), 129.4, 128.7 (2C), 128.0 (2C), 127.9, 127.4, 126.5 (2C), 121.3.

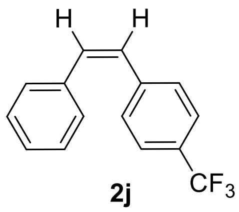
(*Z*)-1,2-bis(4-bromophenyl)ethene **2i**[9]



2i

Purified by column chromatography on silica gel (petroleum ether/ethyl acetate /DCM = 200/1/1), total yield: 70% (47.2 mg), *Z:E* = 82:18. **2i**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (m, *J* = 8.0 Hz, 4H), 7.08 (d, *J* = 8.4 Hz, 4H), 6.53 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.6 (2C), 131.5 (4C), 130.4 (4C), 129.7 (2C), 121.2 (2C).

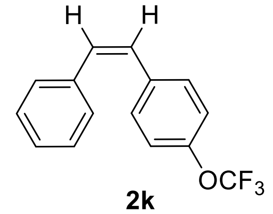
(*Z*)-1-styryl-4-(trifluoromethyl)benzene **2j**[9]



2j

Purified by column chromatography on silica gel (petroleum ether/ethyl acetate/DCM = 200/1/1), total yield: 78% (38.8 mg), *Z:E* = 80:20. **2j**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.32–7.22 (m, 5H), 6.72 (d, *J* = 12.0 Hz, 1H), 6.59 (d, *J* = 12.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.9 (q, $^{3}J_{C\text{-}F}$ = 1.2 Hz), 136.5, 132.3, 129.1 (2C), 128.8 (2C), 128.7, 128.4 (2C), 127.6 (2C), 125.1 (q, $^{3}J_{C\text{-}F}$ = 3.6 Hz, 2C), 124.2 (q, $^{1}J_{C\text{-}F}$ = 270.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.5.

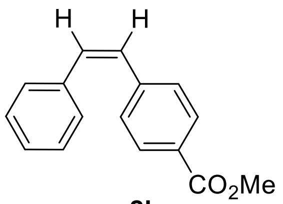
(*Z*)-1-styryl-4-(trifluoromethoxy)benzene **2k**[10]



2k

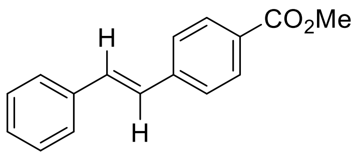
Purified by column chromatography on silica gel (petroleum ether/ethyl acetate/DCM = 200/1/1), total yield: 63% (33.2 mg), *Z:E* = 80:20. **2k**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26–7.23 (m, 7H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.65 (d, *J* = 12.0 Hz, 1H), 6.55 (d, *J* = 12.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0, 136.8, 135.8, 131.1, 130.2 (2C), 128.8 (2C), 128.7, 128.4 (2C), 127.4, 120.6 (2C), 120.4 (d, $^{1}J_{C\text{-}F}$ = 255.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ -57.8.

(*Z*)-methyl-4-styrylbenzoate **2l**[5] and (*E*)-methyl-4-styrylbenzoate **3l**[5]



2l

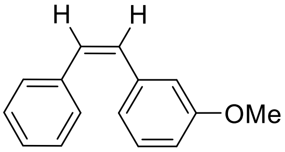
and



3l

Purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1), total yield: 91% (43.2 mg), *Z:E* = 75:25. **2l**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.21 (s, 5H), 6.70 (d, *J* = 12.4 Hz, 1H), 6.59 (d, *J* = 12.0 Hz, 1H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 142.0, 136.6, 132.2, 129.5 (2C), 129.2, 128.8 (4C), 128.5, 128.3 (2C), 127.5, 52.0. **3l**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.4 Hz, 2H), 7.58–7.53 (m, 4H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.31 (d, *J* = 7.2 Hz, 1H), 7.22 (d, *J* = 16.4 Hz, 1H), 7.13 (d, *J* = 16.0 Hz, 1H), 3.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 141.8, 136.7, 131.2, 130.0 (2C), 128.9, 128.8 (2C), 128.2, 127.5, 126.8 (2C), 126.3 (2C), 52.1.

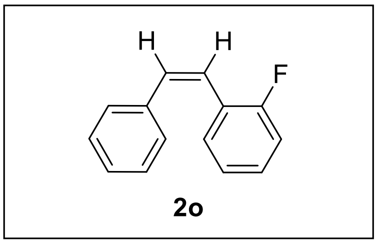
(*Z*)-1-methoxy-3-styrylbenzene **2m**[8]



2m

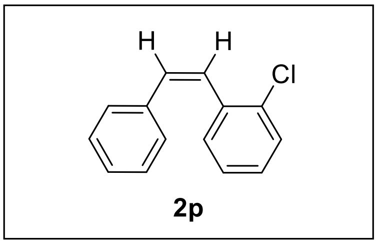
Purified by column chromatography on silica gel (petroleum ether/ethyl acetate /DCM = 200/1/1), total yield: 84% (35.4 mg), *Z:E* = 85:15. **2m**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27–7.12 (m, 6H), 6.83 (d, *J* = 7.6 Hz, 1H), 6.78 (s, 1H), 6.75–6.73 (m, 1H), 6.61 (d, *J* = 12.0 Hz, 1H), 6.56 (d, *J* = 12.4 Hz, 1H), 3.63 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 138.5, 137.3, 130.5, 130.1, 129.2, 128.9 (2C), 128.2 (2C), 127.1, 121.5, 113.7, 113.3, 55.0.

(*Z*)-1-fluoro-2-styrylbenzene **2o**[10]



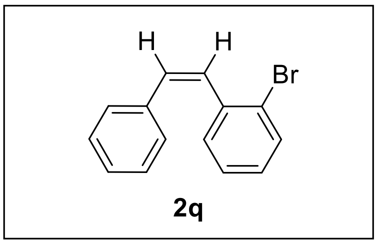
Purified by column chromatography on silica gel (petroleum ether/ethyl acetate/DCM = 200/1/1), total yield: 55% (21.6 mg), *Z:E* > 95:5. **2o**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24–7.18 (m, 7H), 7.03 (t, *J* = 8.8 Hz, 1H), 6.92 (t, *J* = 7.6 Hz, 1H), 6.71 (d, *J* = 12.4 Hz, 1H), 6.61 (d, *J* = 12.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.3 (d, $^1J_{C\text{-}F}$ = 246.1 Hz), 136.8, 132.2, 130.5 (d, $^4J_{C\text{-}F}$ = 3.5 Hz), 128.9 (d, $^3J_{C\text{-}F}$ = 7.1 Hz), 128.7 (2C), 128.2 (2C), 127.3, 125.0 (d, $^2J_{C\text{-}F}$ = 24.4 Hz), 123.6 (d, $^4J_{C\text{-}F}$ = 3.4 Hz), 122.6 (d, $^4J_{C\text{-}F}$ = 3.2 Hz), 115.6 (d, $^2J_{C\text{-}F}$ = 21.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ -114.7.

(*Z*)-1-chloro-2-styrylbenzene **2p**[11]



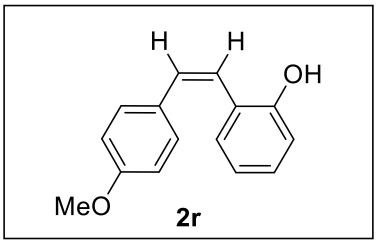
Purified by column chromatography on silica gel (petroleum ether/ethyl acetate/DCM = 200/1/1), total yield: 51% (21.7 mg), *Z:E* > 95:5. **2p**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.2 Hz, 1H), 7.20–7.12 (m, 7H), 7.03–6.99 (m, 1H), 6.70 (d, *J* = 12.0 Hz, 1H), 6.66 (d, *J* = 12.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.4, 136.0, 133.6, 131.7, 130.7, 129.5, 128.9 (2C), 128.5, 128.1 (2C), 127.3, 127.2, 126.3.

(*Z*)-1-bromo-2-styrylbenzene **2q**[12]



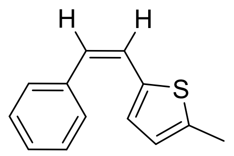
Purified by column chromatography on silica gel (petroleum ether/ethyl acetate/DCM = 200/1/1), total yield: 59% (30.6 mg), *Z:E* > 95:5. **2q**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61–7.58 (m, 1H), 7.18–7.13 (m, 6H), 7.10–7.06 (m, 2H), 6.68 (d, *J* = 12.0 Hz, 1H), 6.61 (d, *J* = 12.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 136.3, 132.7, 131.3, 130.8, 129.4, 129.0 (2C), 128.6, 128.1 (2C), 127.3, 127.0, 123.9.

(*Z*)-2-(4-methoxystyryl)phenol **2r**[13]



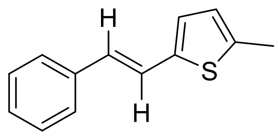
Purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1), total yield: 95% (42.8 mg), *Z:E* > 95:5. **2r**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21–7.12 (m, 4H), 6.90–6.85 (m, 2H), 6.74–6.72 (m, 2H), 6.68 (d, *J* = 12.0 Hz, 1H), 6.44 (d, *J* = 12.4 Hz, 1H), 5.20 (s, 1H), 3.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 152.3, 132.4, 130.0 (2C), 129.6, 128.8, 128.4, 124.0, 122.2, 120.6, 115.6, 113.8 (2C), 55.1.

(*Z*)-2-methyl-5-styrylthiophene **2s**[8] and (*E*)-2-methyl-5-styrylthiophene **3s**[8]



2s

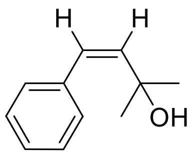
and



3s

Purified by column chromatography on silica gel (petroleum ether/ethyl acetate /DCM = 200/1/1), total yield: 92% (36.7 mg), *Z:E* = 60:40. **2s**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.25 (m, 5H), 6.77 (d, *J* = 3.2 Hz, 1H), 6.61 (d, *J* = 12.0 Hz, 1H), 6.54–6.53 (m, 1H), 6.47 (d, *J* = 12.0 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.2, 137.7, 137.5, 128.8 (2C), 128.6, 128.4 (2C), 127.4, 127.3, 124.6, 123.7, 15.3. **3s**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 1H), 7.14 (d, *J* = 16.0 Hz, 1H), 6.84 (d, *J* = 3.2 Hz, 1H), 6.79 (d, *J* = 16.0 Hz, 1H), 6.64 (d, *J* = 2.4 Hz, 1H), 2.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 139.3, 137.2, 128.6 (2C), 127.3, 127.0, 126.4, 126.1 (2C), 125.7, 122.1, 15.6.

(*Z*)-2-methyl-4-phenylbut-3-en-2-ol **2t**[14]

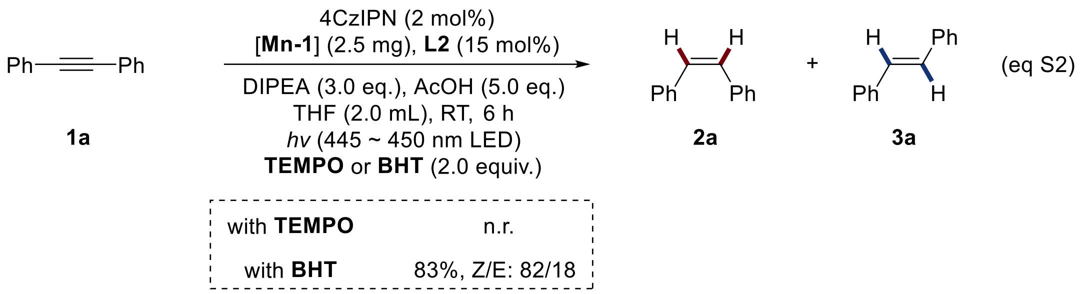


2t

Purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1), total yield: 52% (16.7 mg), *Z:E* > 95:5. **2t**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.30 (m, 4H), 7.25 (d, *J* = 8.0 Hz, 1H), 6.46 (d, *J* = 12.8 Hz, 1H), 5.76 (d, *J* = 12.8 Hz, 1H), 1.62 (s, 1H), 1.36 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3, 137.5, 129.0 (2C), 128.0 (2C), 127.8, 126.9, 72.1, 31.1 (2C).

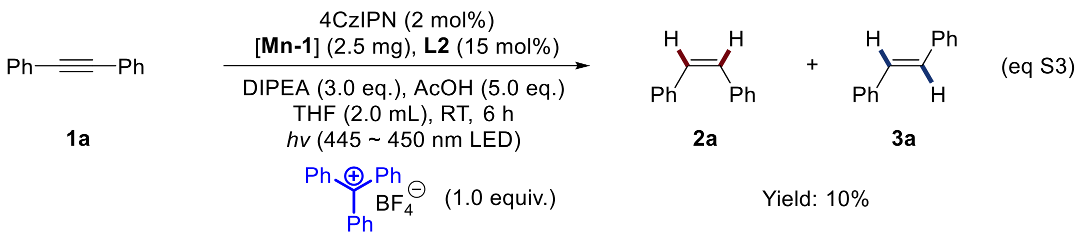
8. Mechanistic Studies.

1) Radical trap experiment



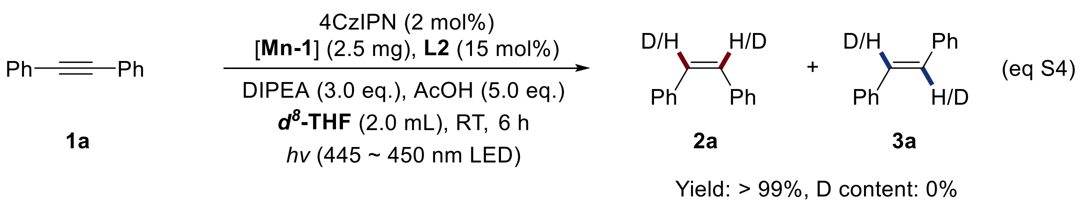
Following the general procedure, TEMPO or BHT (0.4 mmol, 2.0 equiv.) was added as the additive, and the crude ^{1}H NMR yields were recorded when the reactions were finished (eq S2). Notably, the addition of TEMPO led to the totally inhibition of the transformation. However, BHT only slightly reduced the catalyst activity, delivering alkenes in total yield of 83% with 82/18 Z/E stereoselectivity. Since radical traps might react with metal-hydride to inhibit the reaction, we thus deduced that radical species might not involve in the catalytic cycle.

2) Mn-H detection reaction



To confirm the involvement of Mn-H species, triphenylcarbenium tetrafluoroborate (0.2 mmol, 1.0 equiv) was added to the model reaction as the additive (eq S3). The reaction yield was sharply decreased to 10%, suggesting the involvement of Mn-H species in catalytic cycles.

3) Deuterium-labelling experiments



To confirm the hydrogen source of the semi-hydrogenation reaction, deuterium-labelling experiments was conducted by using d^8-THF as the solvent (eq S5). After finishing irradiation, the reaction yield was analysed by ^{1}H NMR spectroscopy immediately. The deuterium incorporation was determined by ^{1}H NMR spectroscopy of isolated product. This result shows that no deuterium incorporation was observed (see Figure S5).

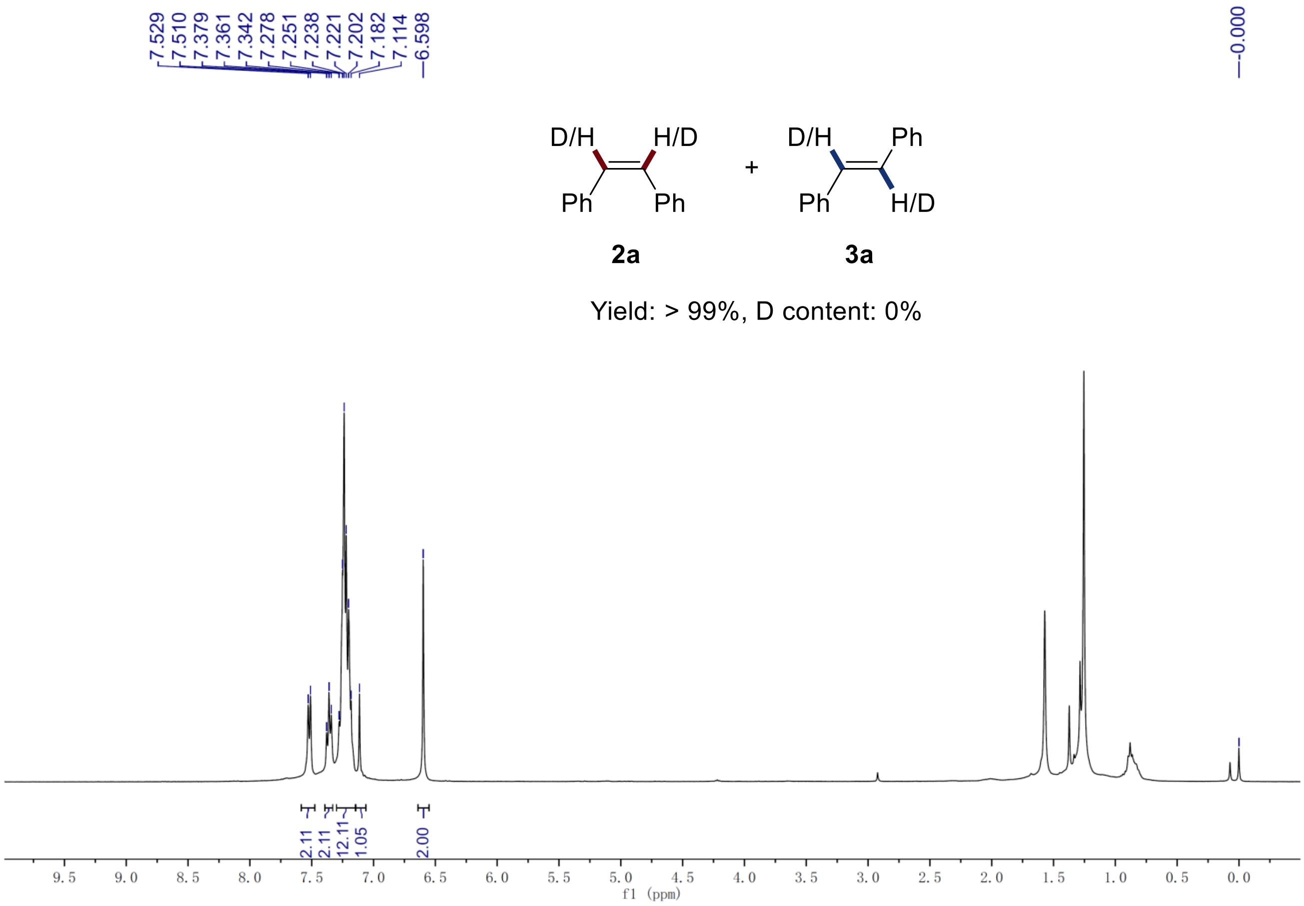
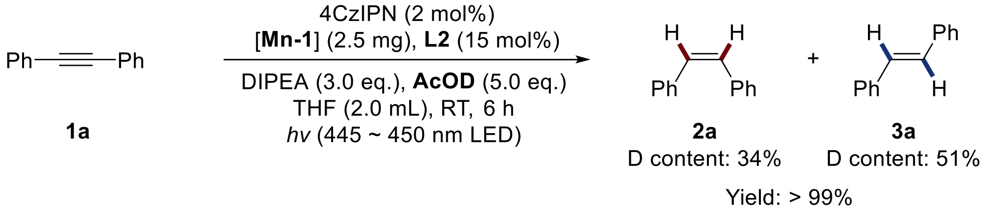


Figure S5. ^{1}H NMR spectrum of deuterium labeling reaction by using d^8-THF as the solvent.



(eq S5)

Next, another deuterium-labelling experiment was conducted by using AcOD as the proton additive (eq S5). ^{1}H NMR spectroscopy analysis showed that 34% of D was cooperated in Z-alkene **2a**, and 51% of D was cooperated in E-alkene **3a** (see Figure S6). The reason of different deuterium content may arise from the Mn-H catalyzed Z to E isomerization reaction.

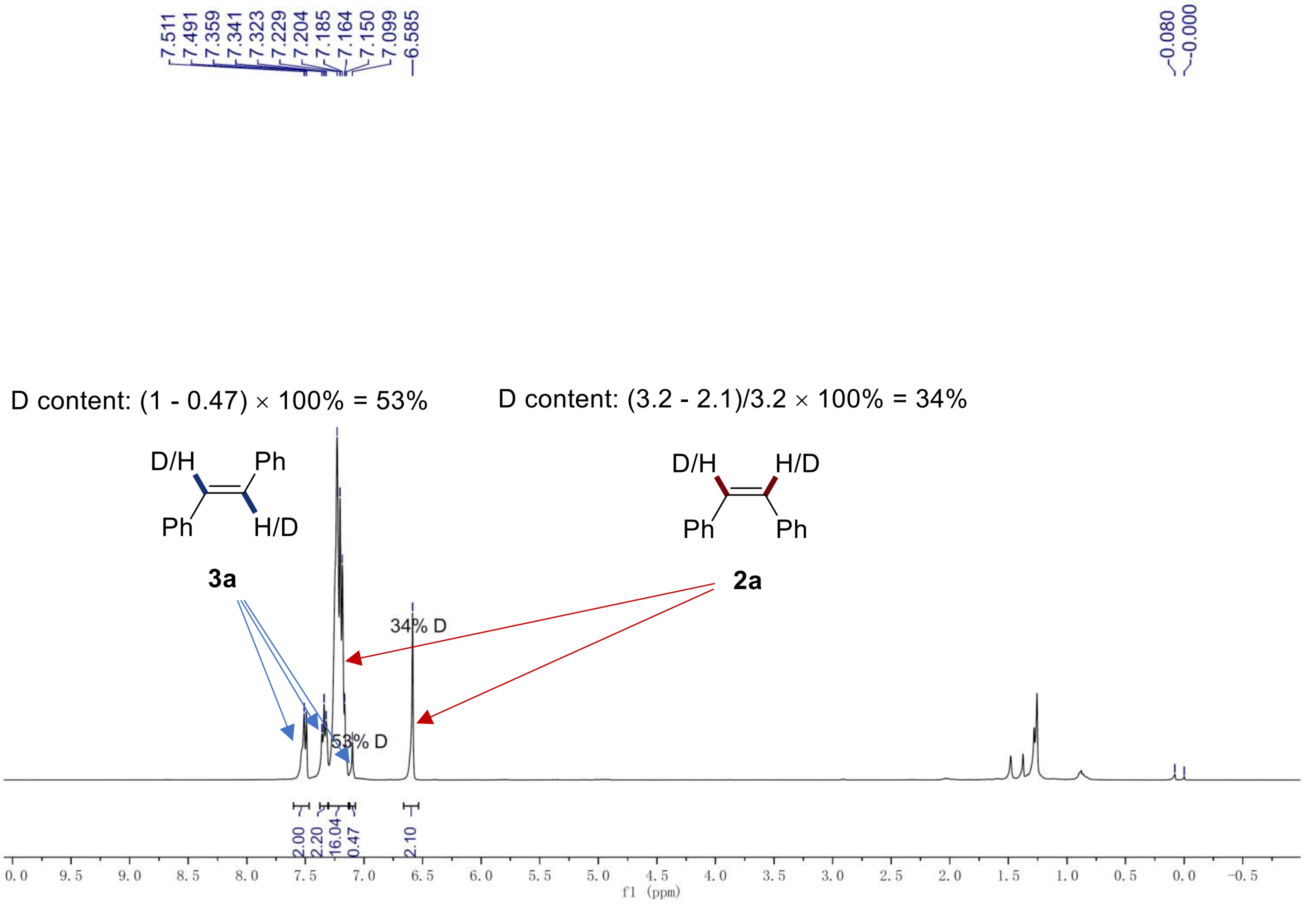
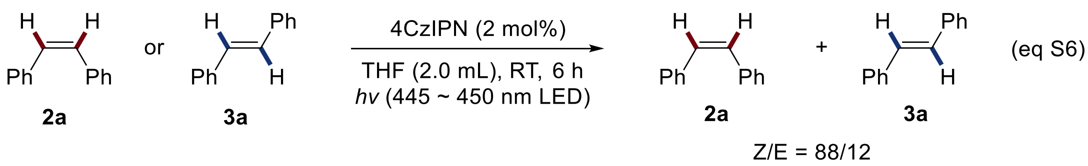
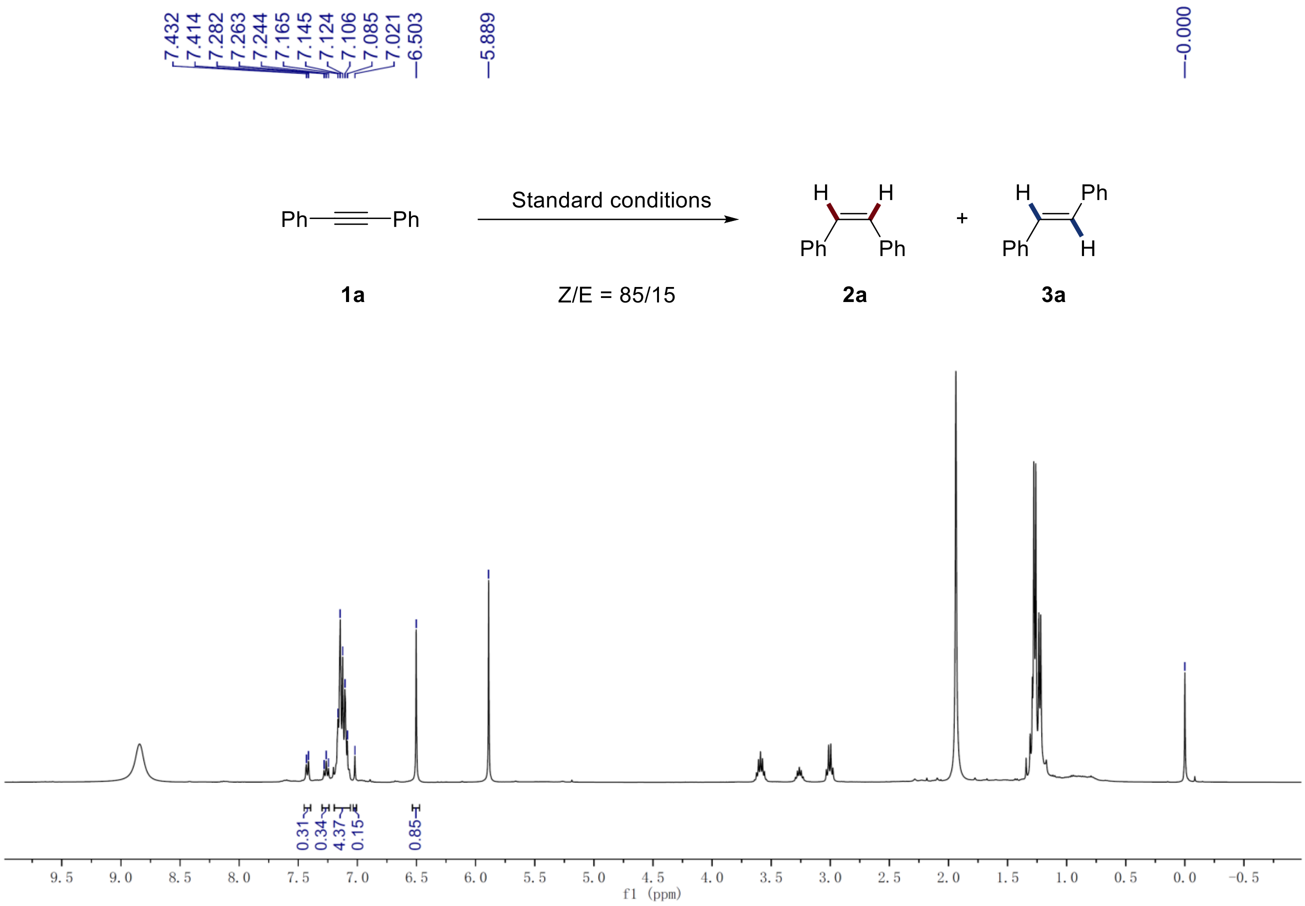


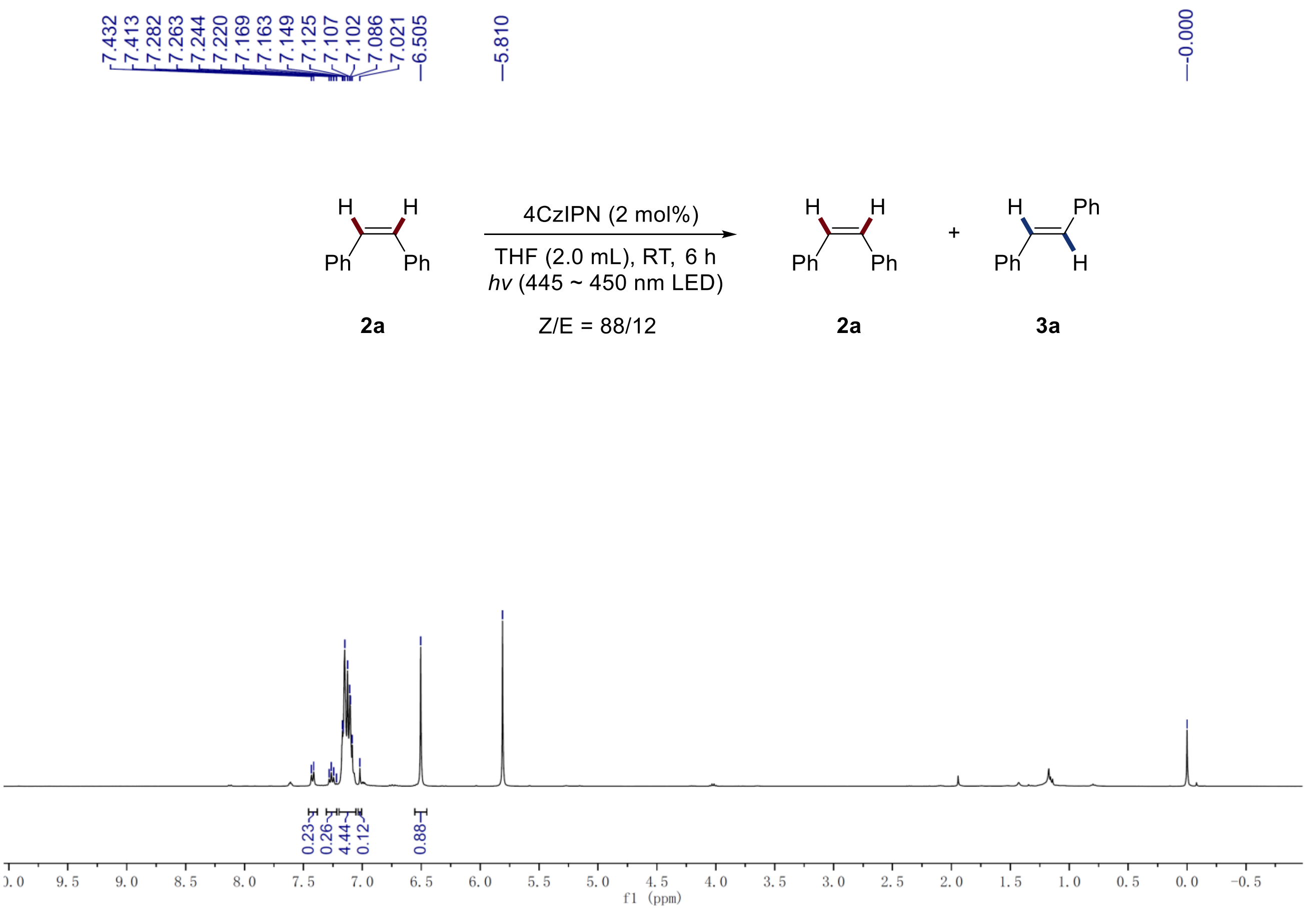
Figure S6. [1]H NMR spectrum of deuterium labeling reaction by using AcOD as proton additive.

4) Isomerization experiments



We also conducted the isomerization experiments by employing either **2a** or **3a** as substrate without the Mn complex, DIPEA and AcOH (eq S6). Both reactions gave the same Z/E value (88/12) as the standard reaction (85/15), indicating that photo-induced energy transfer process is the overwhelming factor for the stereoselectivity (Figure S7).[15]


Ph—≡—Ph
Standard conditions
1a
Z/E = 85/15
2a
3a
f1 (ppm)


4CzIPN (2 mol%)
THF (2.0 mL), RT, 6 h
hv (445 ~ 450 nm LED)
2a
Z/E = 88/12
2a
3a
f1 (ppm)

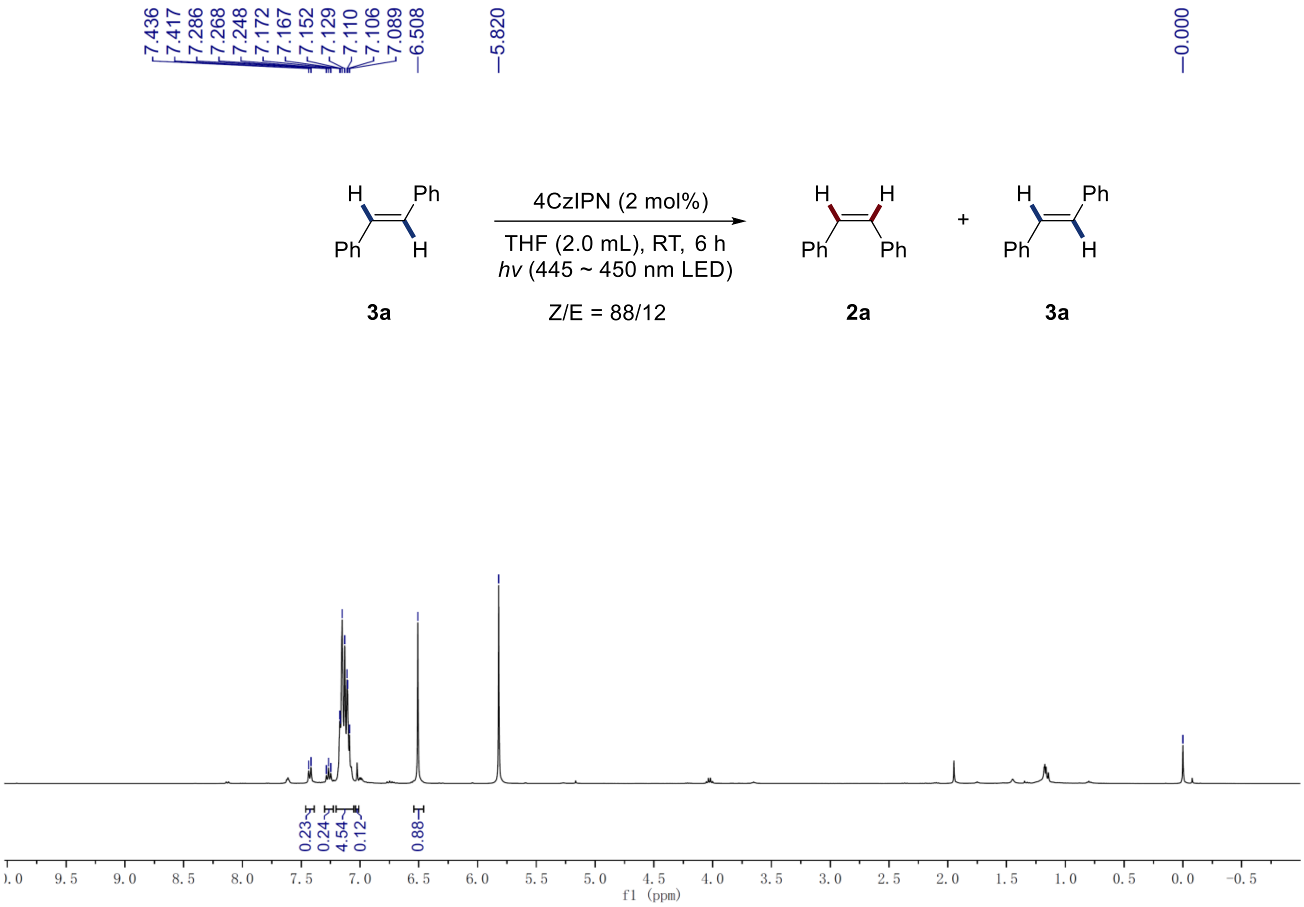


Figure S7. [1]H NMR spectra of model reaction and isomerization reactions.

5) Emission Quenching Experiments

Emission intensities were recorded using a spectrofluorimeter. All 4CzIPN solutions were excited at 400 nm and the emission intensity at 540 nm was observed. THF was selected as solvent, and the solvent was degassed with a stream of argon for 30 min. In a typical experiment, the emission spectrum of the sample was collected after the sample was degassed with a stream of argon for 15 minutes. The sample of Mn complex was prepared by stirring the mixture of **[Mn-1]** and **L2** (molar ratio of **[Mn-1]**/**L2** = 1/2) in THF under Ar armosphere for 2 h. The molecular weight of **[Mn-1]** was roughly estimated the same as that of $Mn(acac)_2•2H_2O$. Then, the mixture was diluted to the required concertration. In the emmission quenching experiments, the emission spectrum of a $5×10^{-6}$ M solution of 4CzIPN in THF was firstly collected. Then, appropriate amount of quencher was added to the measured solution and the emission spectrum of the sample was collected.

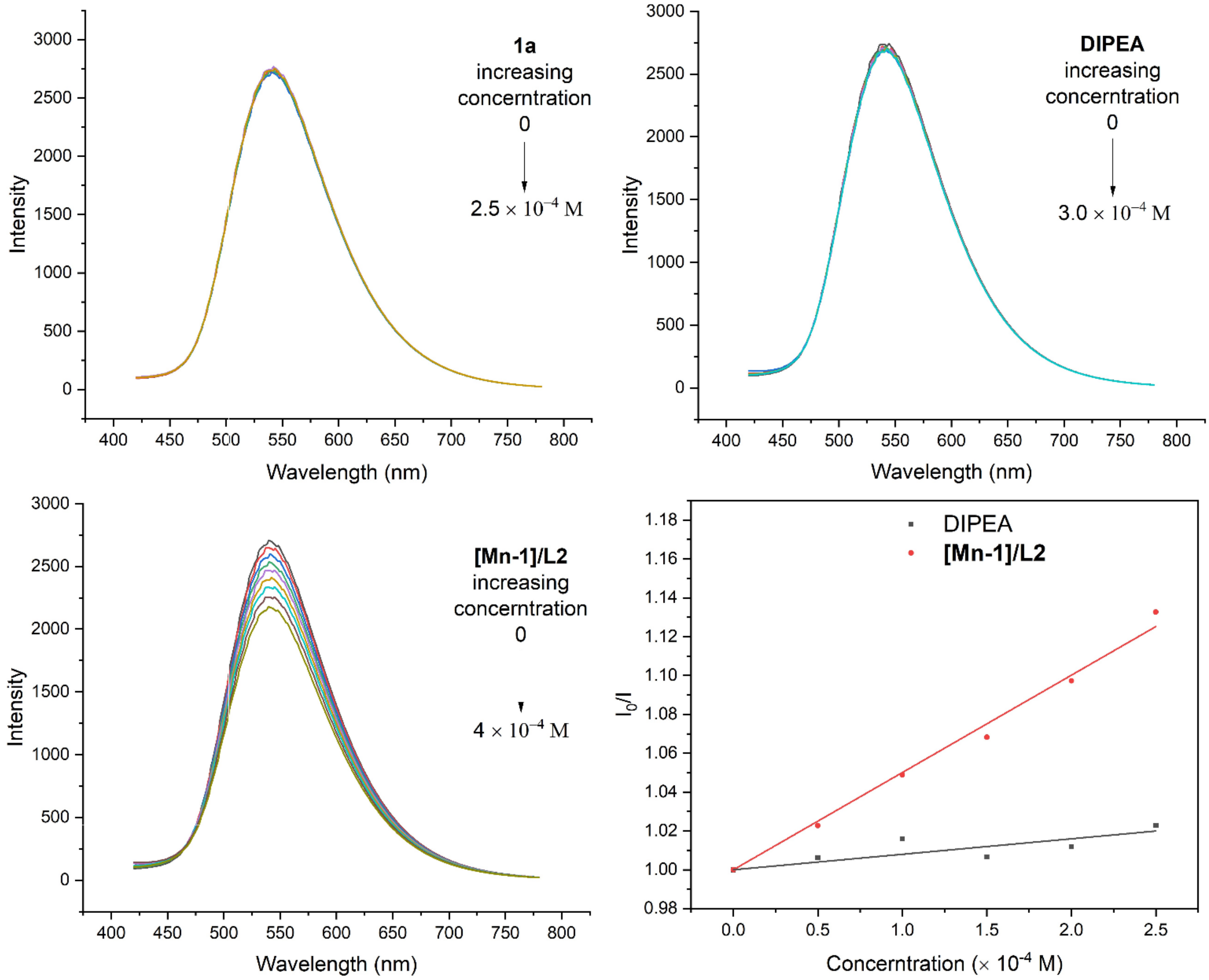
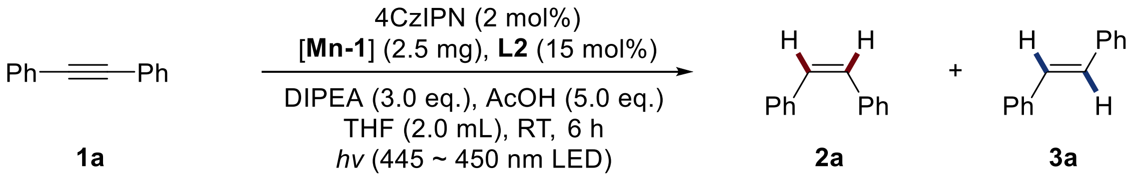


Figure S8. Emission-quenching experiments of **1a**, DIPEA, and **[Mn-1]/L2**, and the Stern-Volmer plot of DIPEA and Mn complex.

6) Light on/off Experiments

Table S3. Light on/off experiments of model reaction.



entry[a]	time (h.)	yield (%) 2a + 3a
1	0 —light→ 2	51
2	2 —dark→ 4	50
3	4 —light→ 6	80
4	6 —dark→ 8	80
5	8 —light→ 10	94
6	10 —dark→ 12	95

[a] Reaction condition: **1a** (0.2 mmol), 4CzIPN (2 mol%), **[Mn-1]** (2.5 mg), 5,5'-dimethyl-2,2'-bipyridine (**L2**, 15 mol%), DIPEA (3.0 equiv.), AcOH (5.0 equiv.) in THF (2.0 mL), irradiation with blue LEDs (445~450 nm, 10 W), ^{1}H NMR yield was reported using $Cl_2CHCHCl_2$ as an internal standard.

7) Cyclic Voltammetry (CV) Experiments

For the electrochemical measurements, a three-electrode system connected to an electrochemical station was used. The reference electrode, $Ag/AgNO_3$ in 0.1 M $AgNO_3$, was calibrated versus Fc^+/Fc^0 using the same experimental conditions as for the sample. A glassy carbon electrode was used as working electrode. And a Pt wire was used as counter electrode. All electrochemical measurements were performed in CH_3CN under dry argon atmosphere.

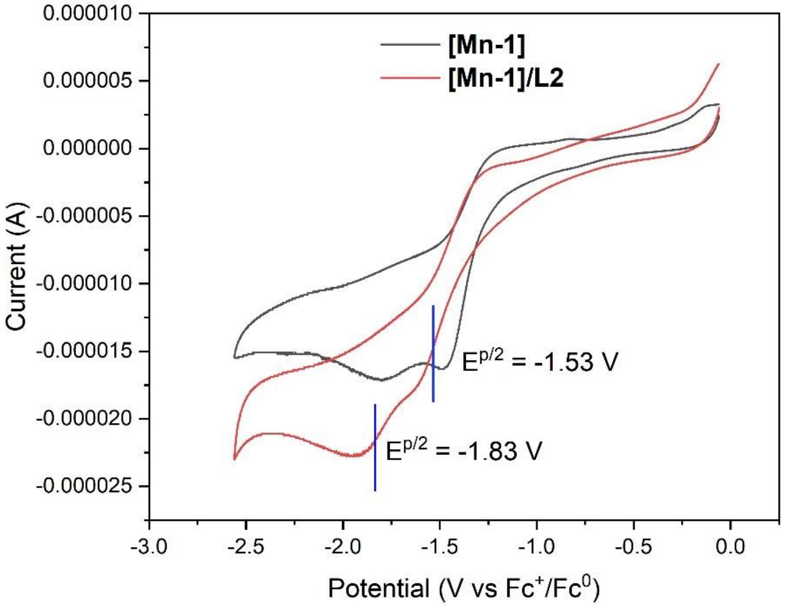


Figure S9. Cyclic voltammogram (CV) of 2 mM **[Mn-1]** and **[Mn-1]/L2** in 0.1 M *n*-Bu_4PF_6 CH_3CN solution under Ar. The relative molecular mass of **[Mn-1]** was roughly estimated the same as that of $Mn(acac)_2$•$2H_2O$. Conditions: working electrode: glassy carbon electrode; reference electrode: Ag^+/Ag; scan rate = 100 mV/s. By comparing with the CV plot of **[Mn-1]**, we located the two reduction peaks for **[Mn-1]/L2**, which were assigned as $E^{p/2}$ = -1.13 V vs. SCE; $E^{p/2}$ = -1.43 V vs. SCE.

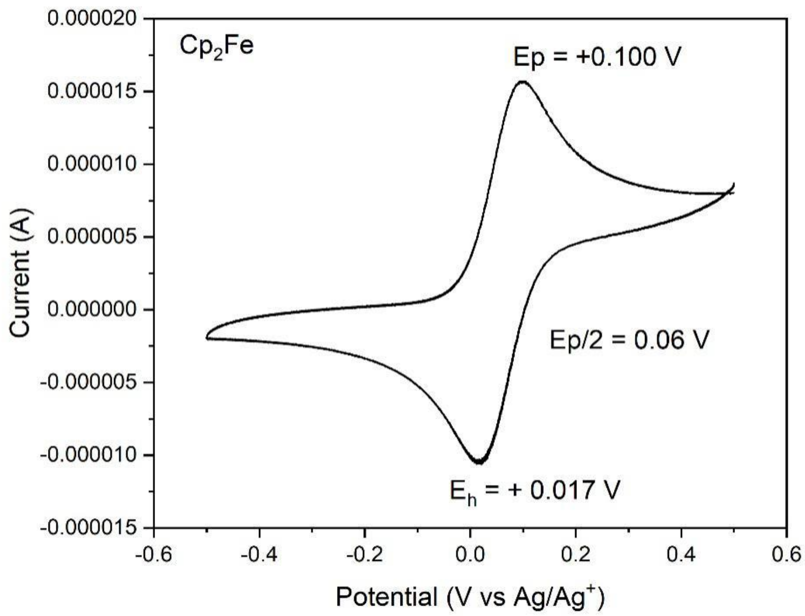
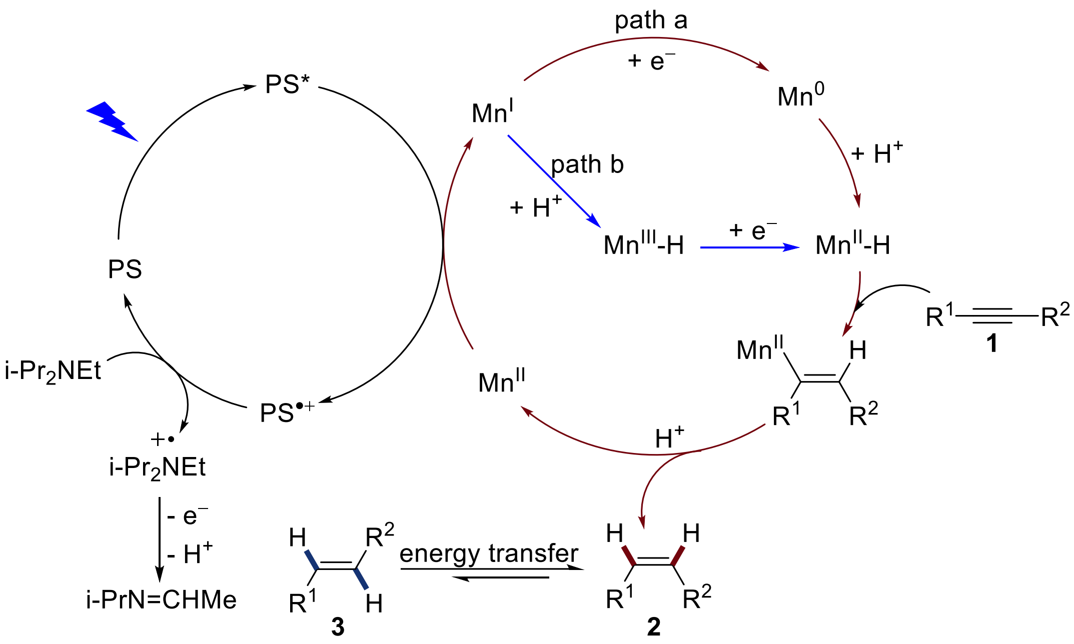


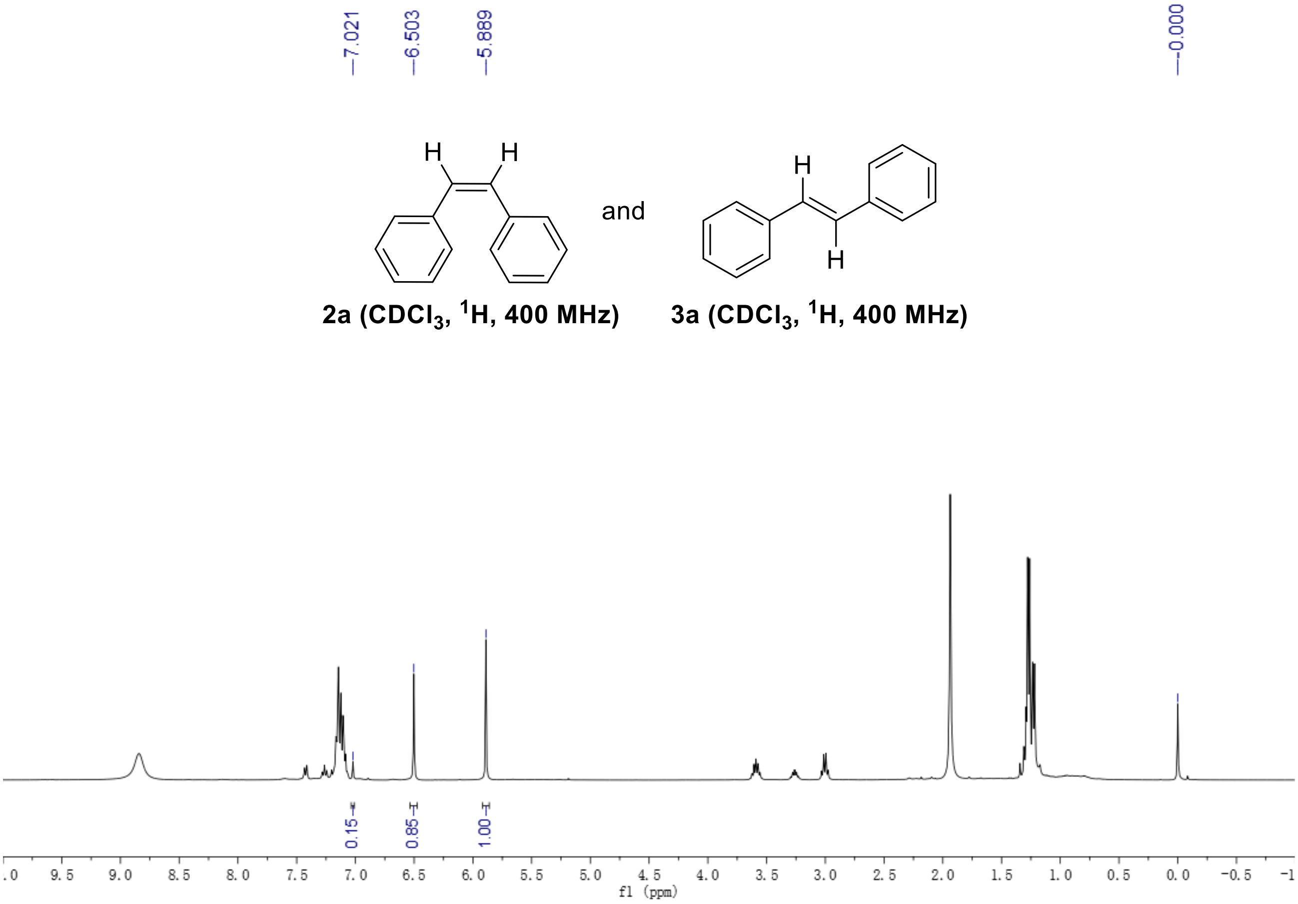
Figure S10. Cyclic voltammogram (CV) of 2 mM Cp_2Fe in 0.1 M *n*-Bu_4PF_6 CH_3CN solution under Ar with scan rate 100 mV/s.

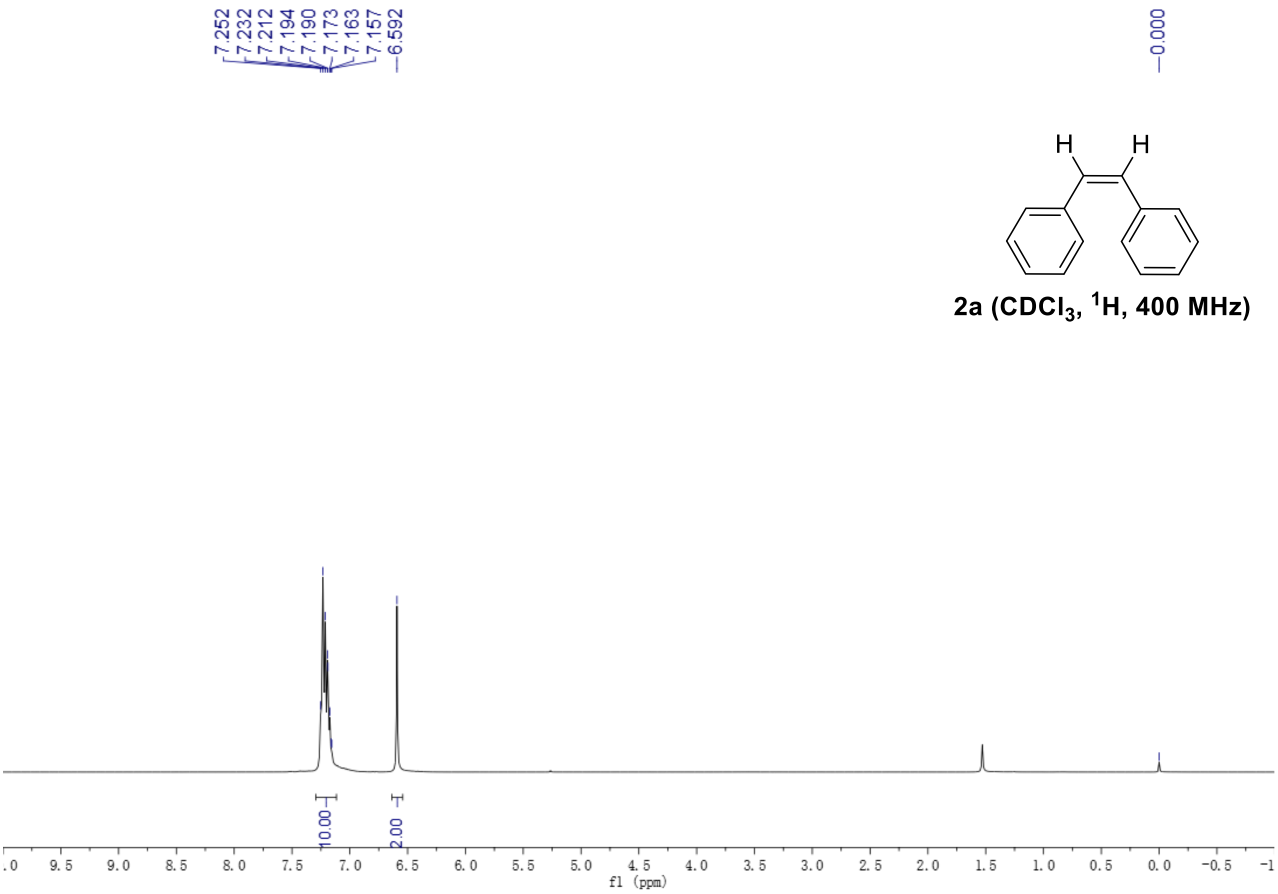
9. Possible reaction mechanism

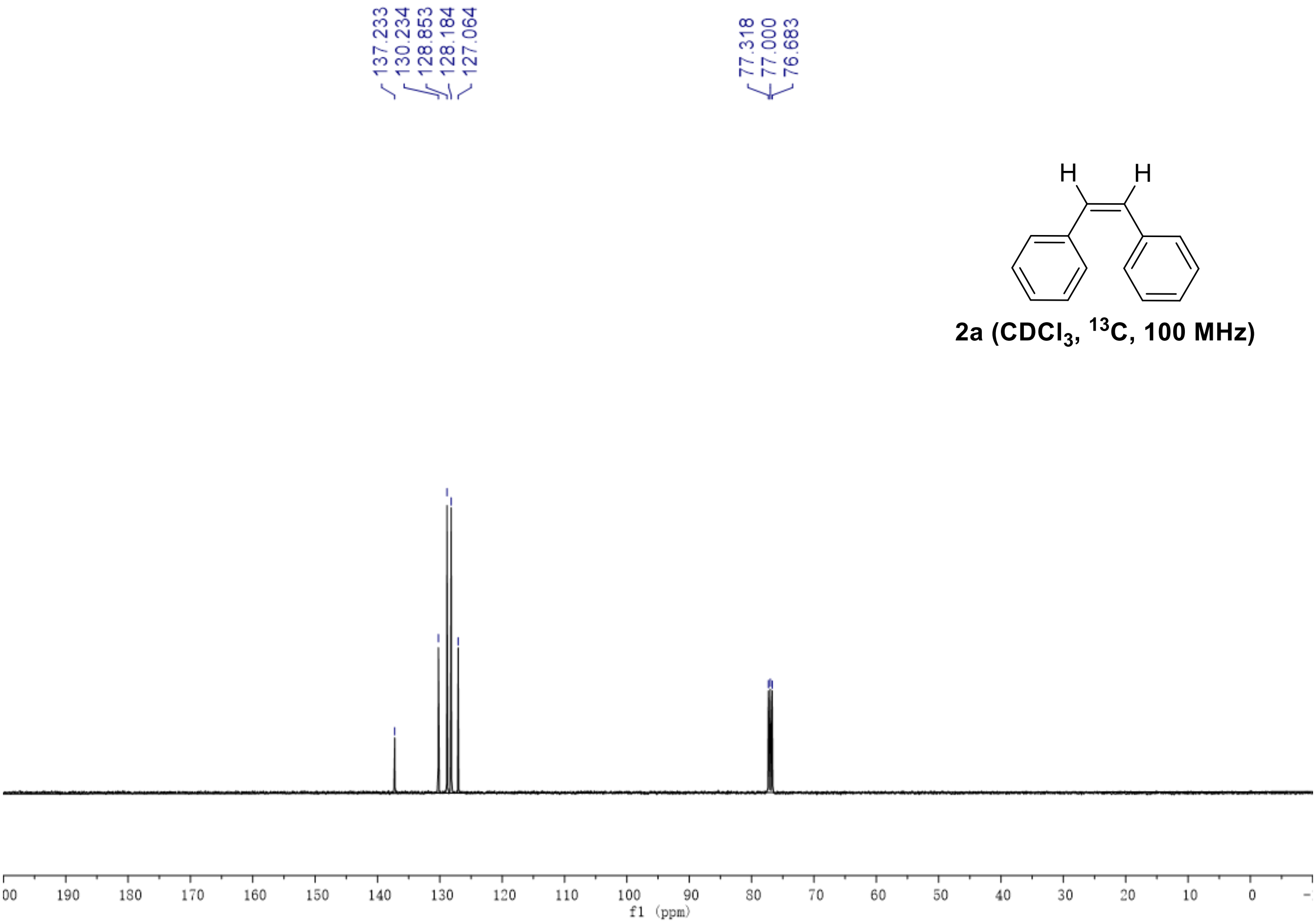


Scheme S1. Possible reaction mechanism.

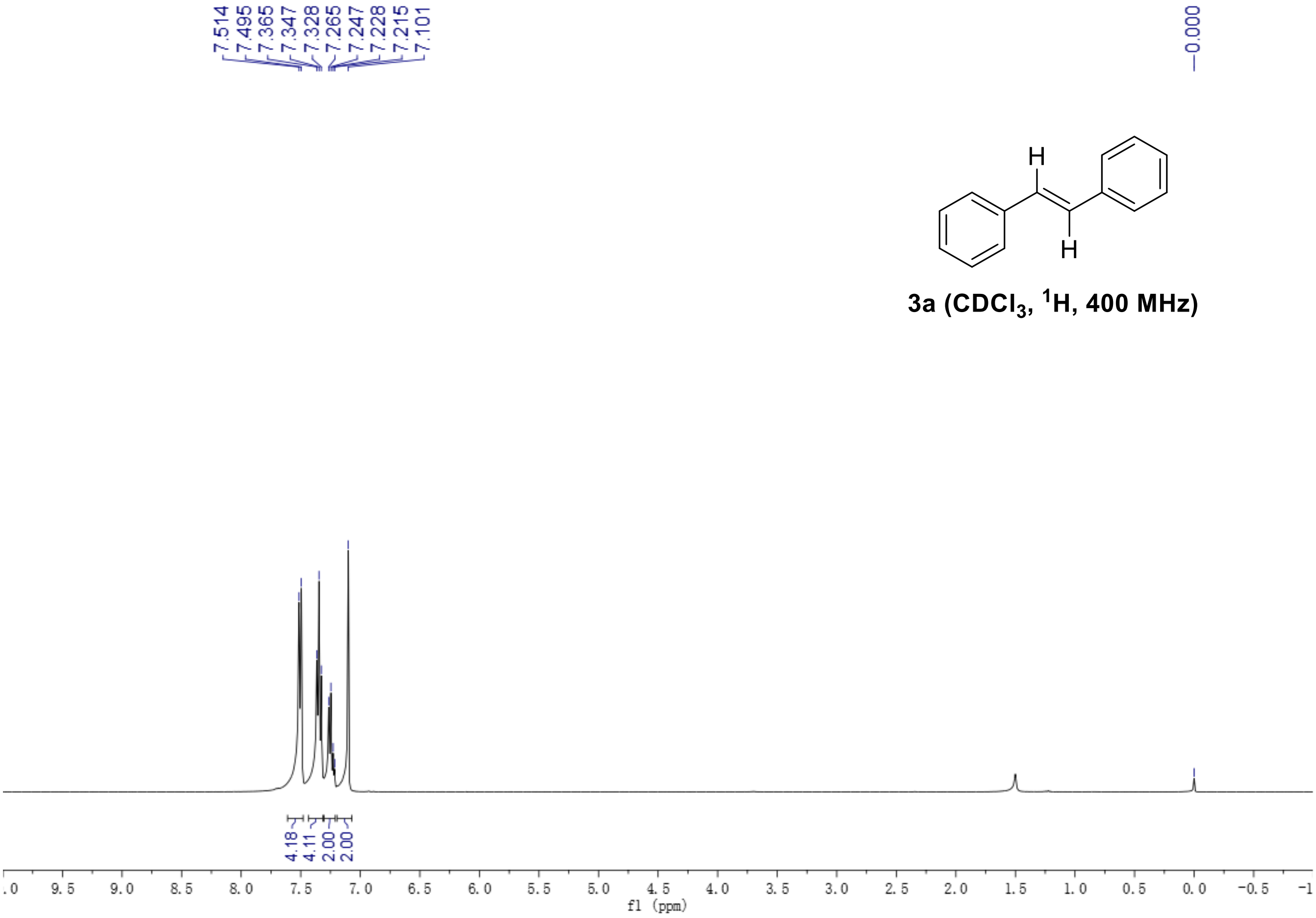
10. Spectrum


7.021
6.503
5.889
0.000
and
2a (CDCl3, 1H, 400 MHz)
3a (CDCl3, 1H, 400 MHz)
0.15
0.85
1.00
f1 (ppm)

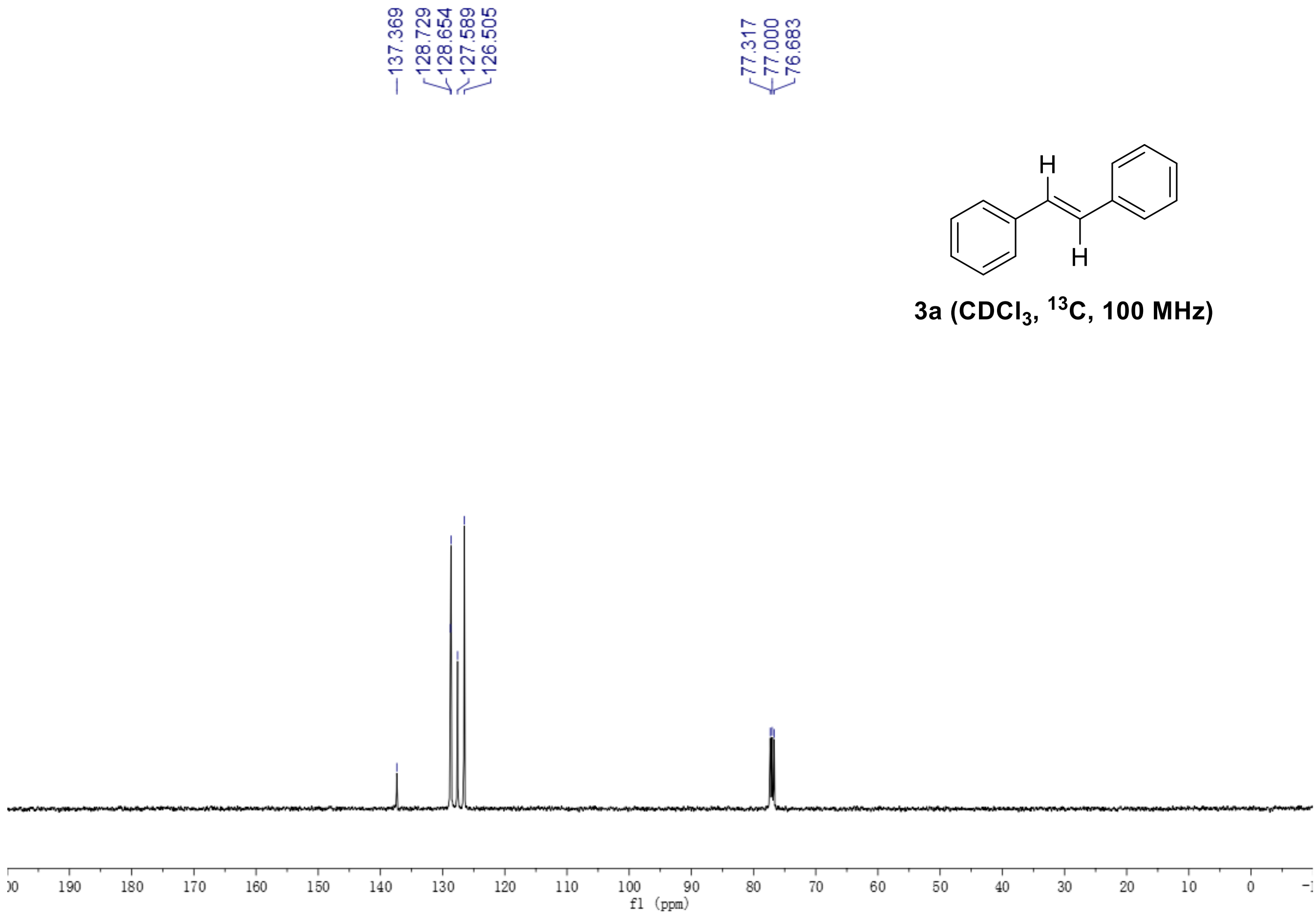

7.252
7.232
7.212
7.194
7.190
7.173
7.163
7.157
6.592
0.000
2a (CDCl3, 1H, 400 MHz)
10.00
2.00
f1 (ppm)



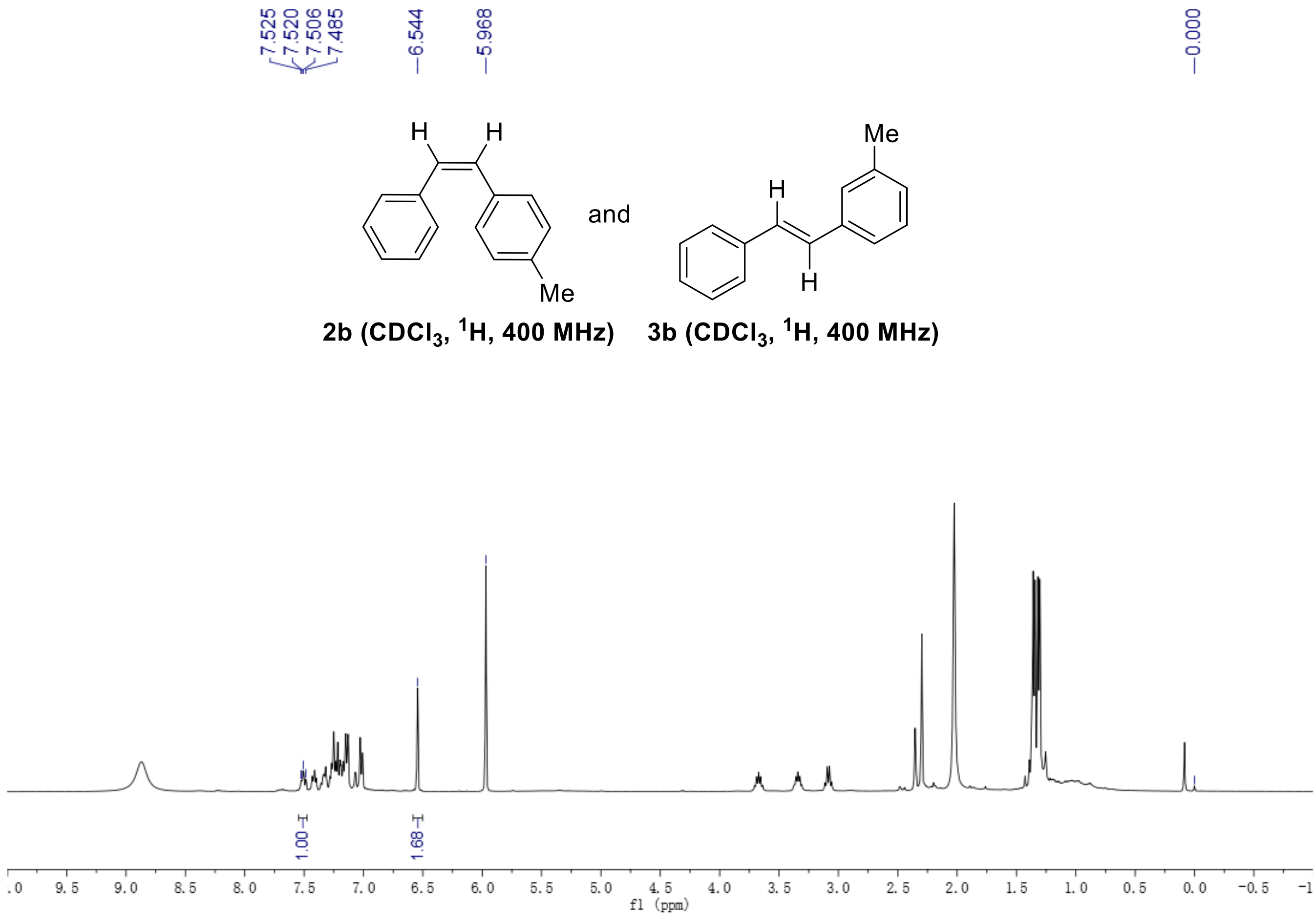
2a (CDCl$_3$, ^{13}C, 100 MHz)



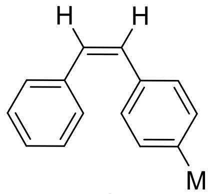
3a (CDCl$_3$, ^{1}H, 400 MHz)



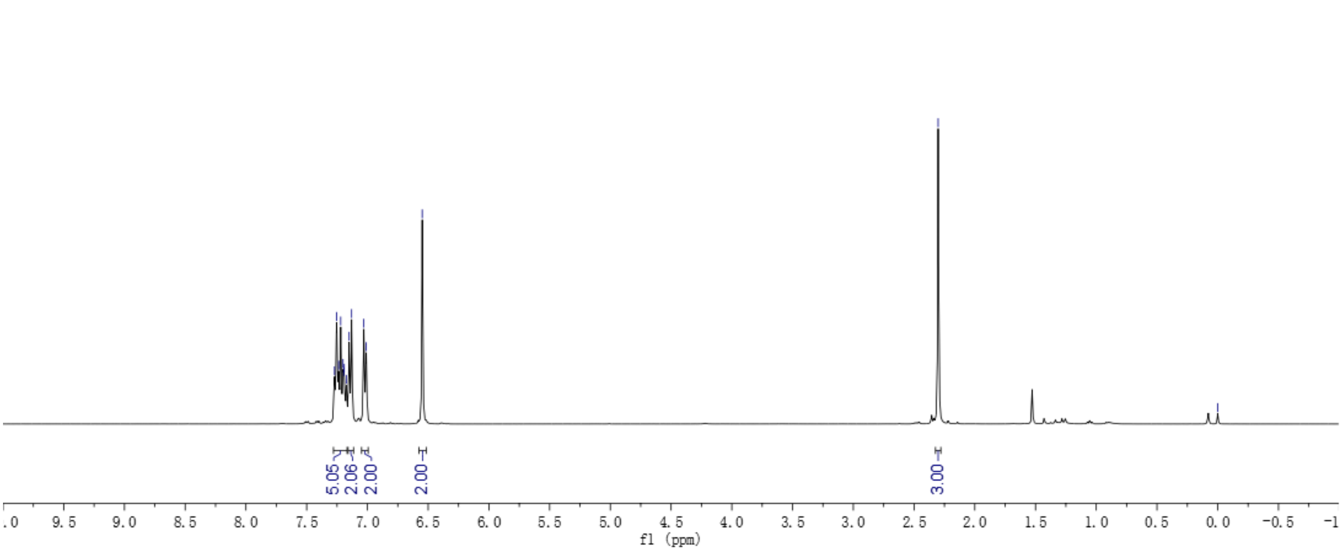
3a ($CDCl_3$, ^{13}C, 100 MHz)

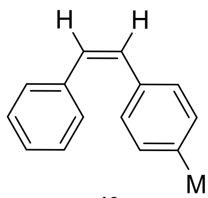


2b ($CDCl_3$, ^{1}H, 400 MHz) 3b ($CDCl_3$, ^{1}H, 400 MHz)

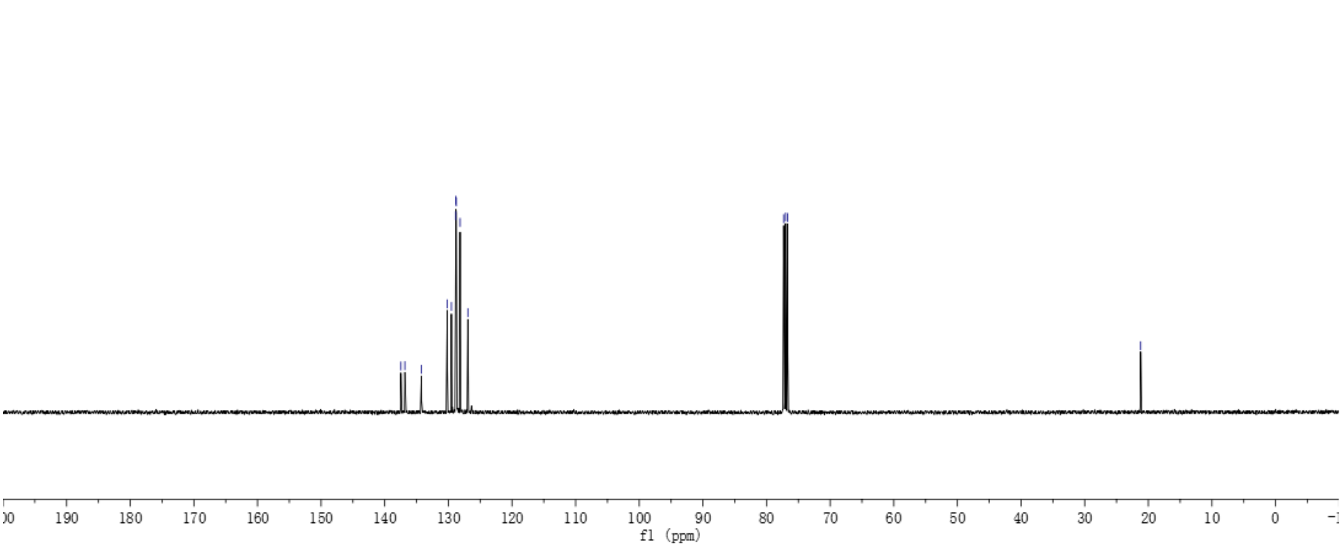


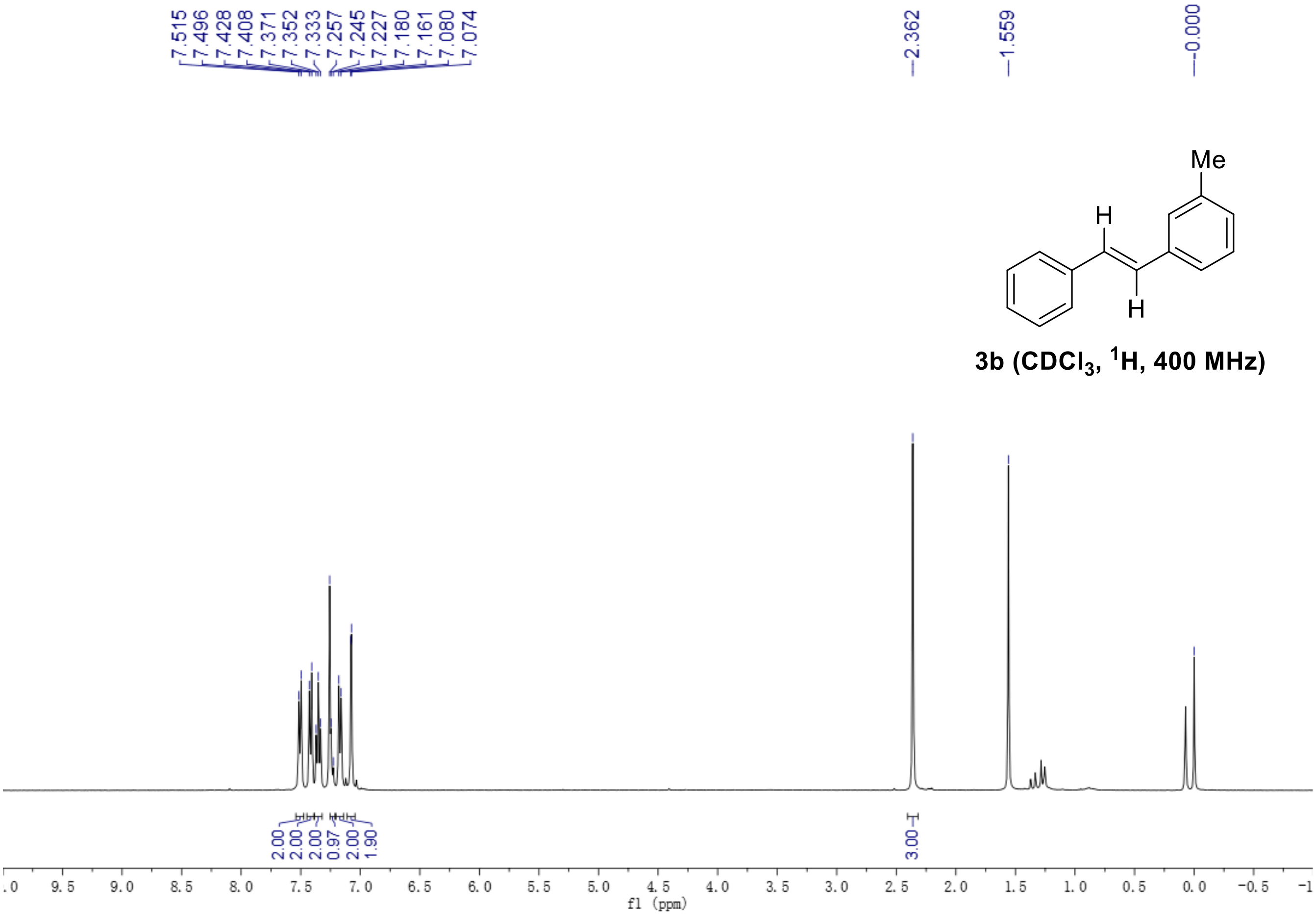
2b ($CDCl_3$, ^1H, 400 MHz)



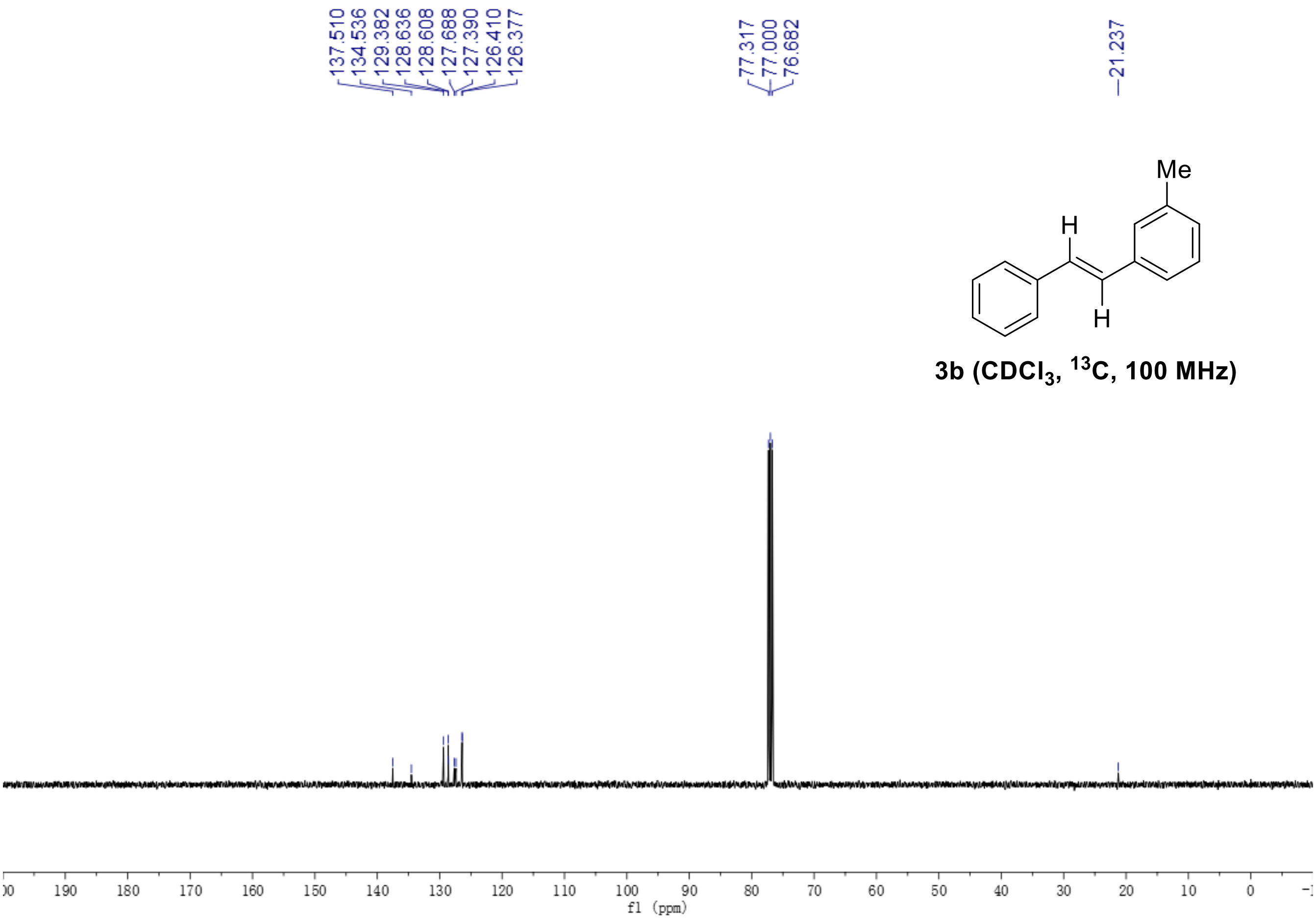


2b ($CDCl_3$, ^{13}C, 100 MHz)

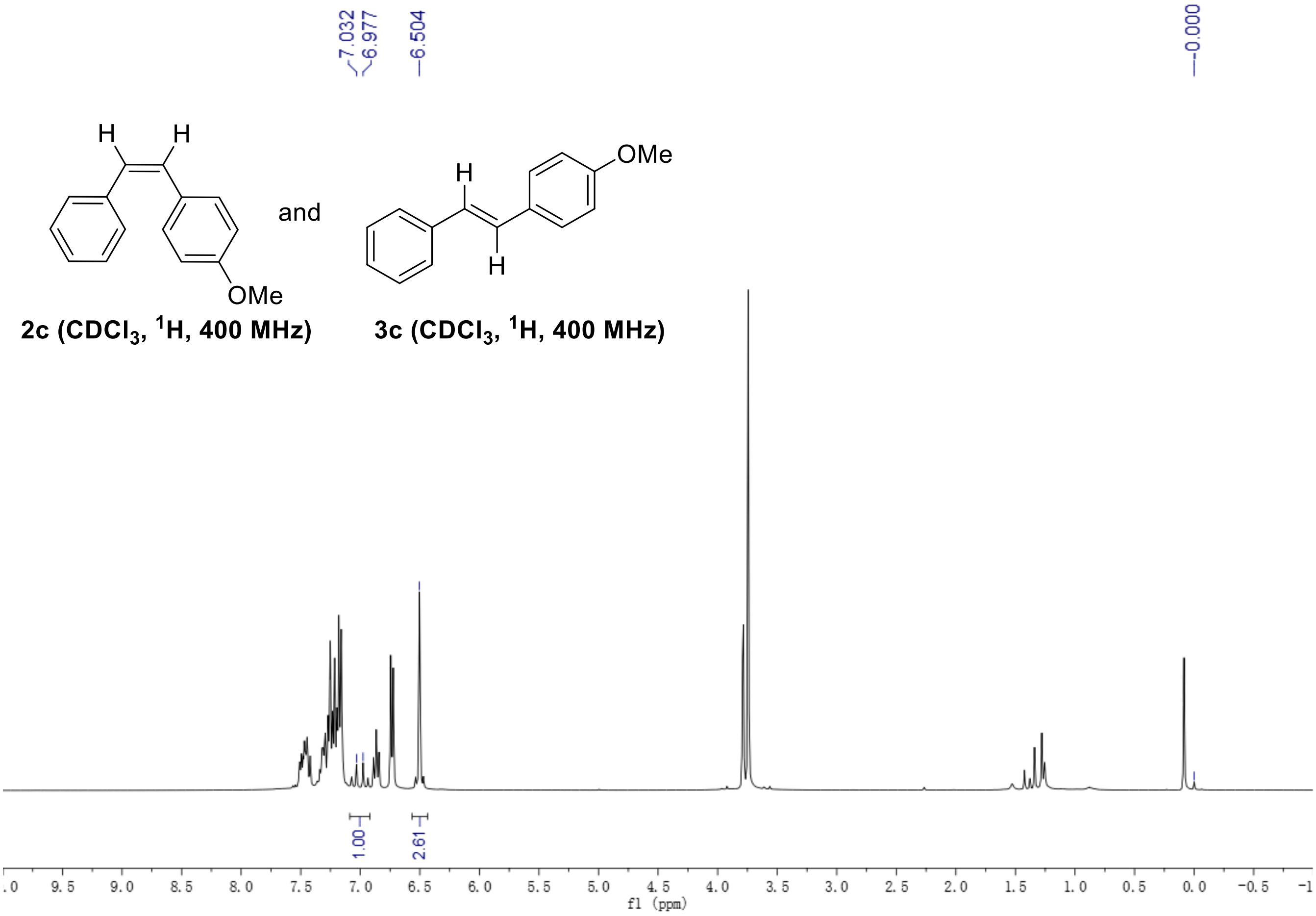


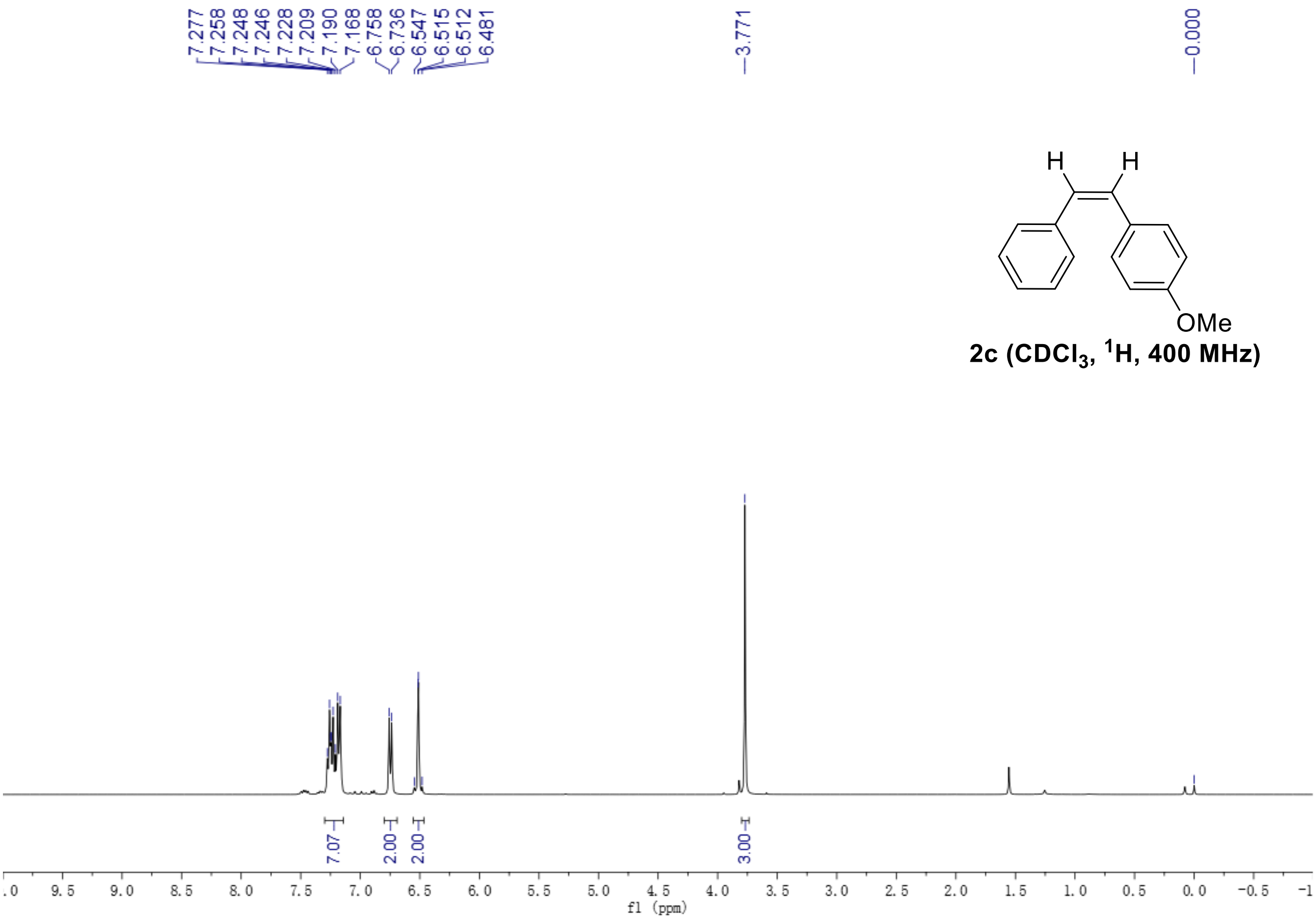


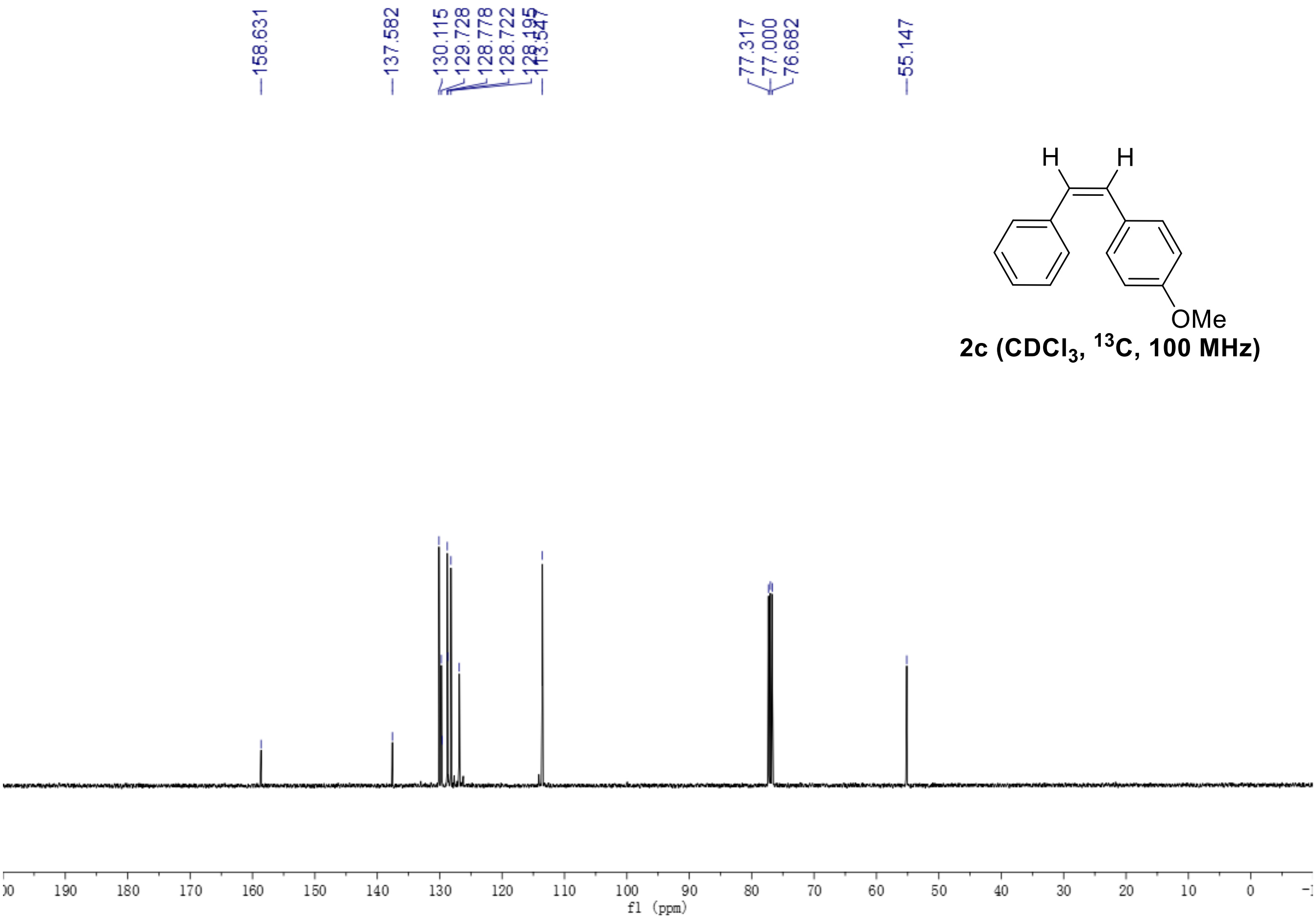
3b (CDCl$_3$, ^{1}H, 400 MHz)



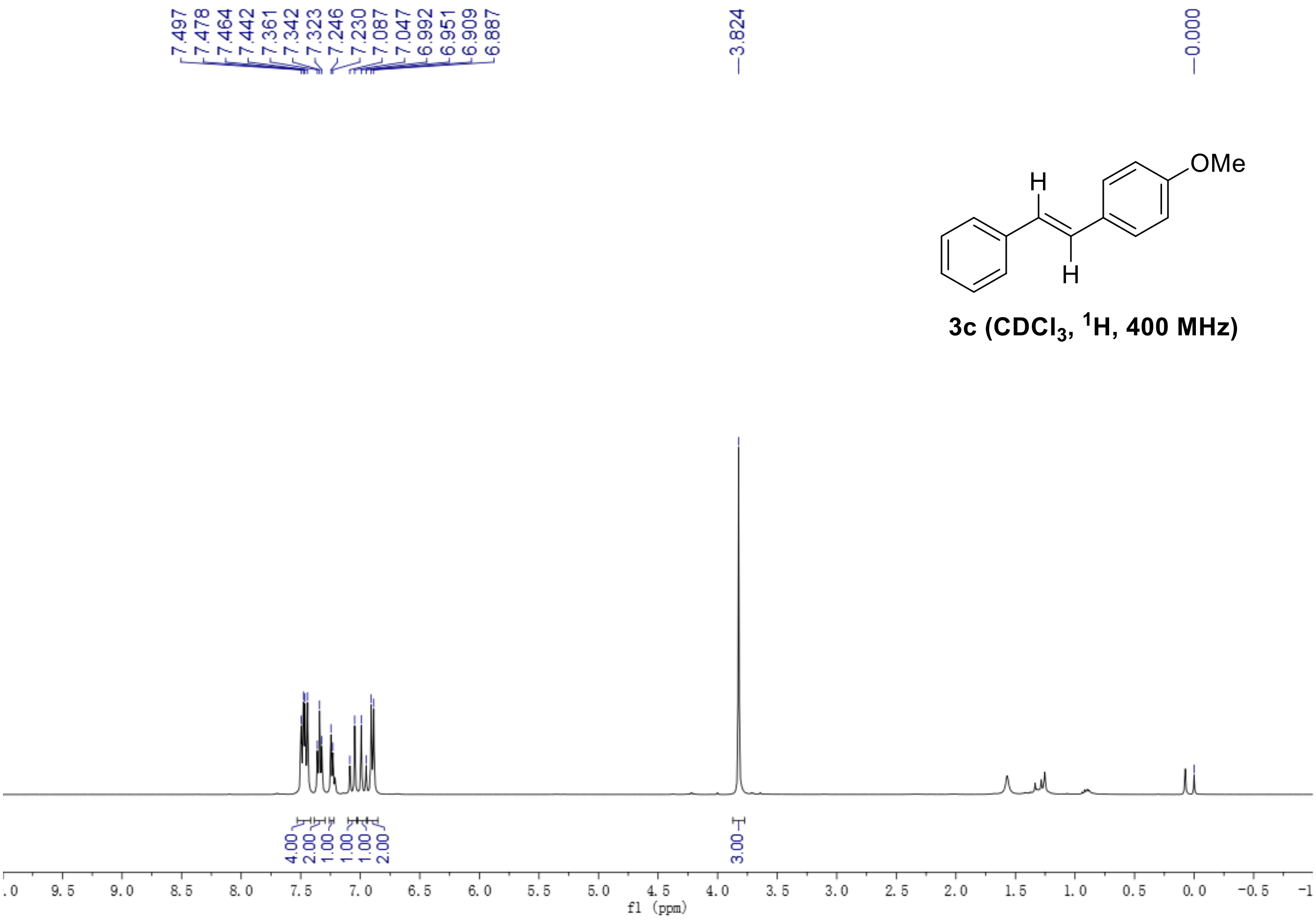
3b (CDCl$_3$, ^{13}C, 100 MHz)


7.032
6.977
6.504
0.000
H
H
OMe
and
H
OMe
H
2c (CDCl$_3$, ^{1}H, 400 MHz)
3c (CDCl$_3$, ^{1}H, 400 MHz)
1.00
2.61
fl (ppm)

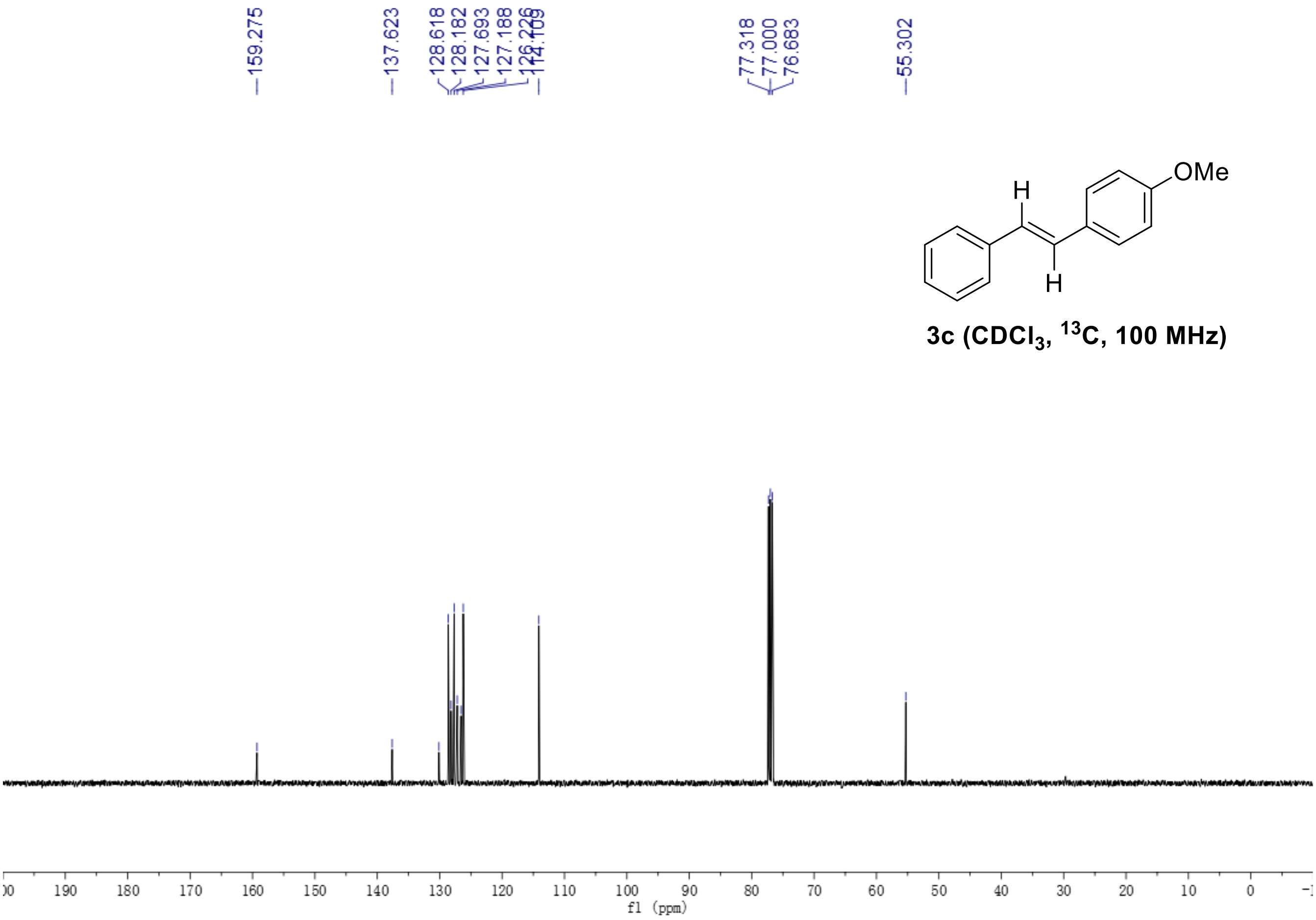

7.277
7.258
7.248
7.246
7.228
7.209
7.190
7.168
6.758
6.736
6.547
6.515
6.512
6.481
3.771
0.000
H
H
OMe
2c (CDCl$_3$, ^{1}H, 400 MHz)
7.07
2.00
2.00
3.00
fl (ppm)

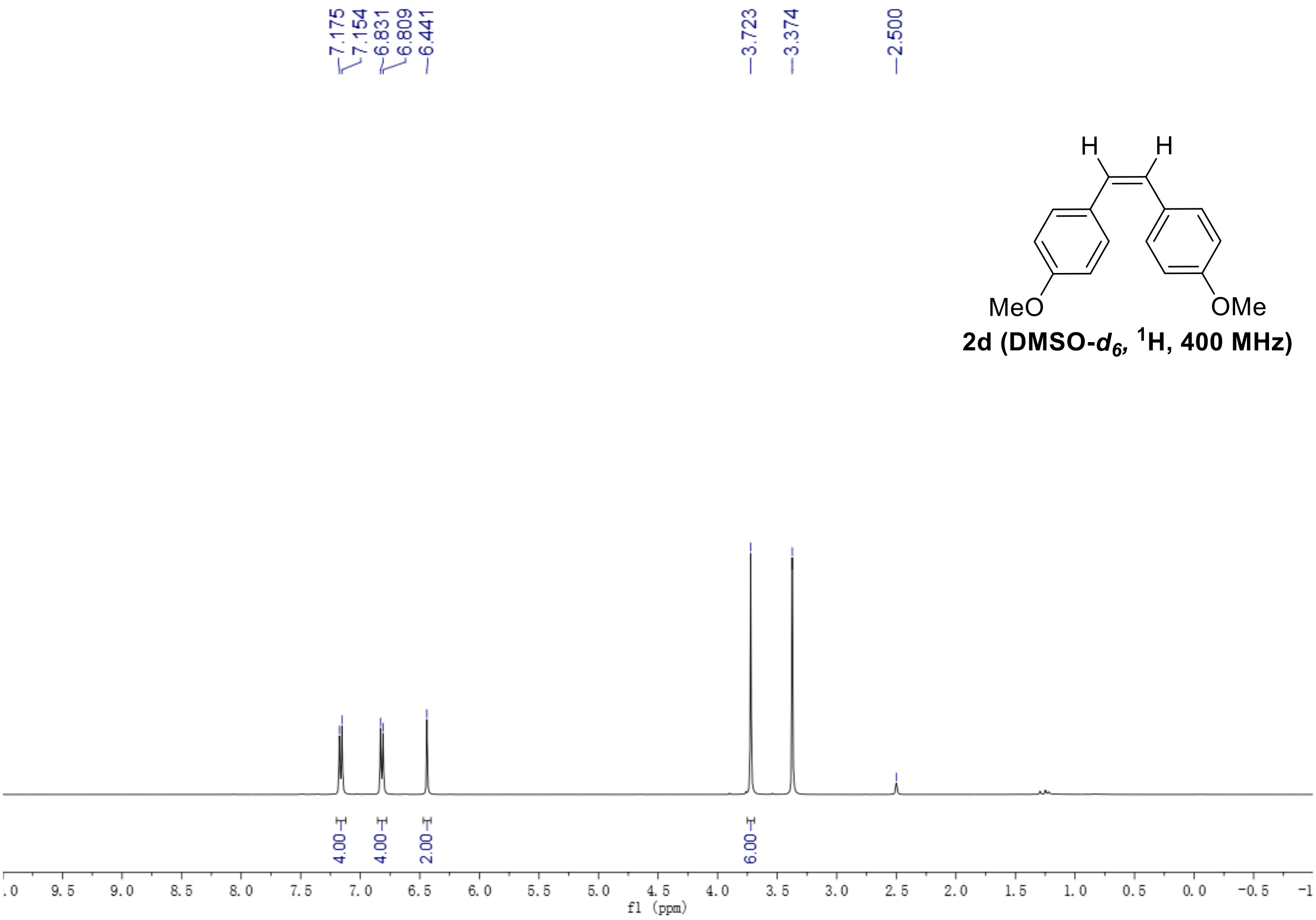


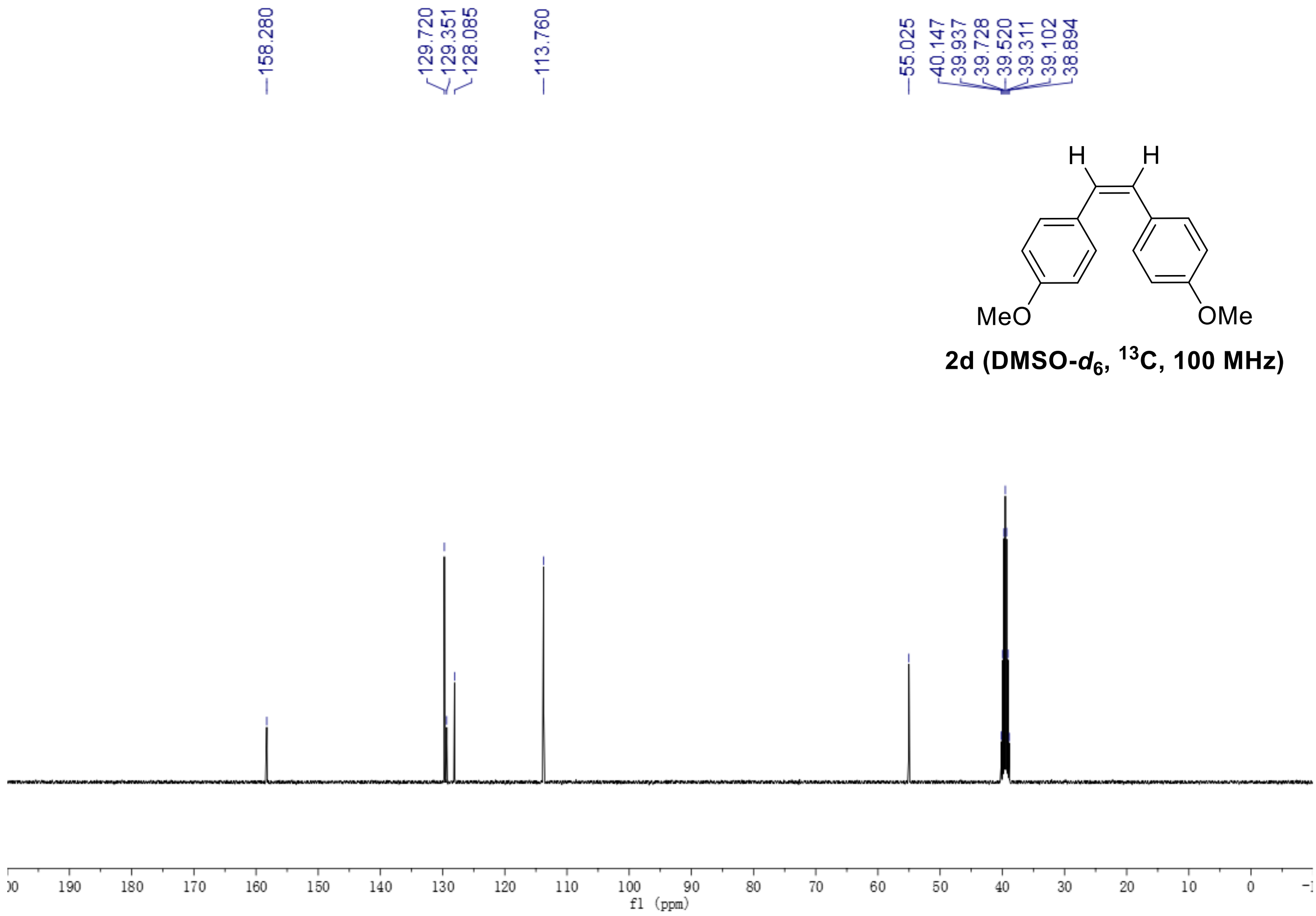
2c ($CDCl_3$, ^{13}C, 100 MHz)



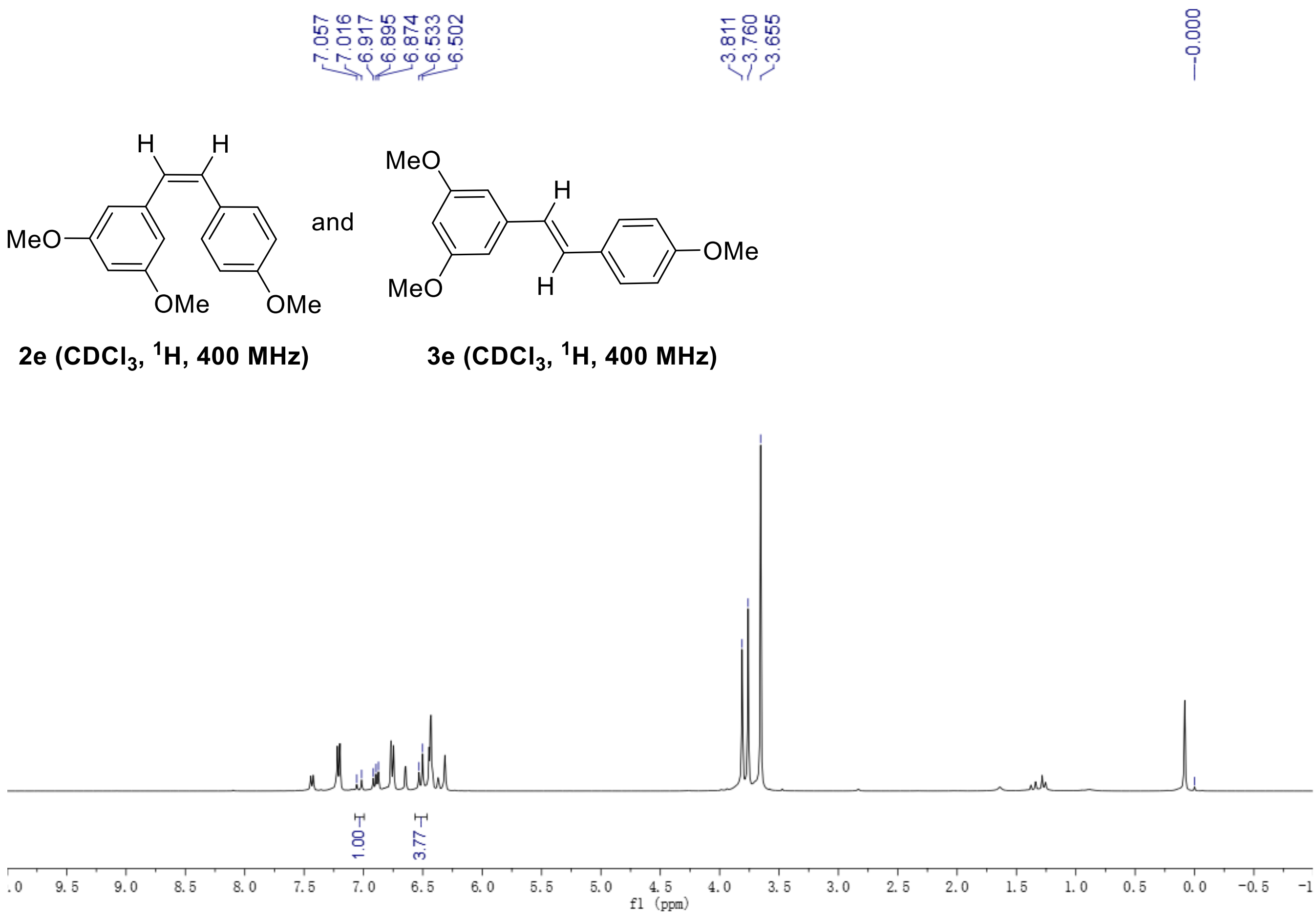
3c ($CDCl_3$, ^{1}H, 400 MHz)


159.275
137.623
128.618
128.182
127.693
127.188
126.226
114.109
77.318
77.000
76.683
55.302
OMe
H
H
3c (CDCl3, 13C, 100 MHz)
fl (ppm)

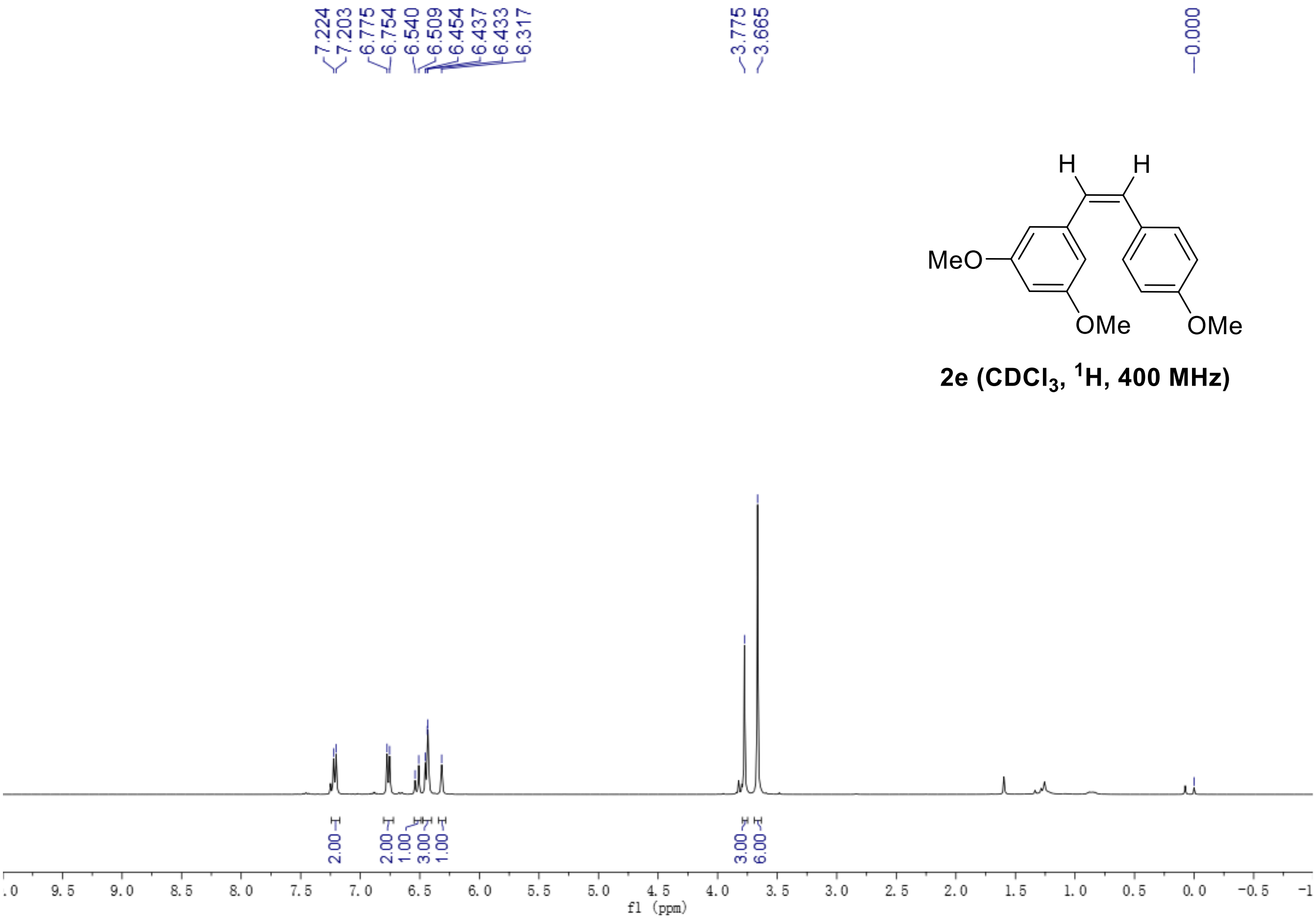

7.175
7.154
6.831
6.809
6.441
3.723
3.374
2.500
H
H
MeO
OMe
2d (DMSO-d6, 1H, 400 MHz)
4.00
4.00
2.00
6.00
fl (ppm)



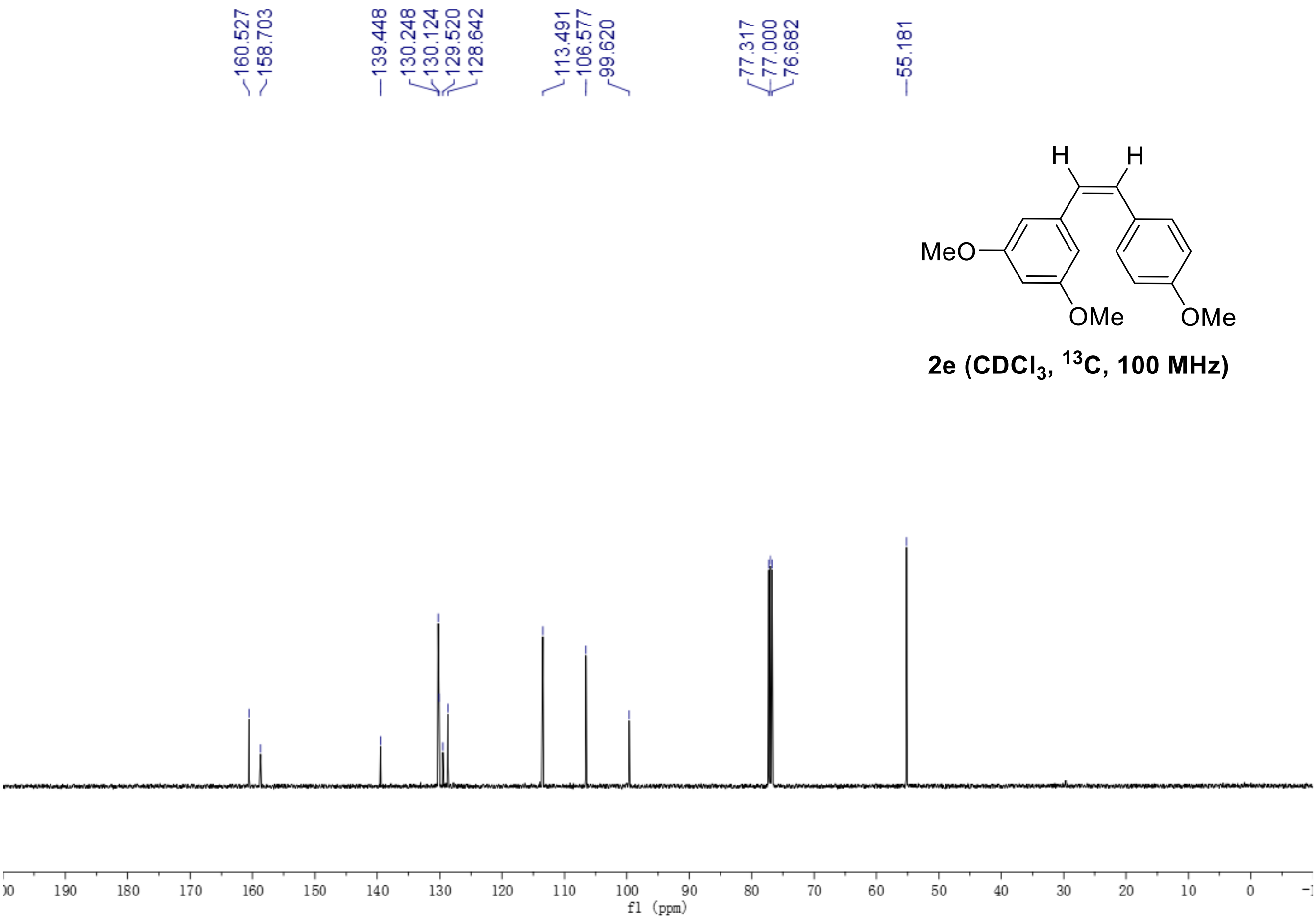
158.280
129.720
129.351
128.085
113.760
55.025
40.147
39.937
39.728
39.520
39.311
39.102
38.894
H
H
MeO
OMe
2d (DMSO-d_6, ^{13}C, 100 MHz)
f1 (ppm)



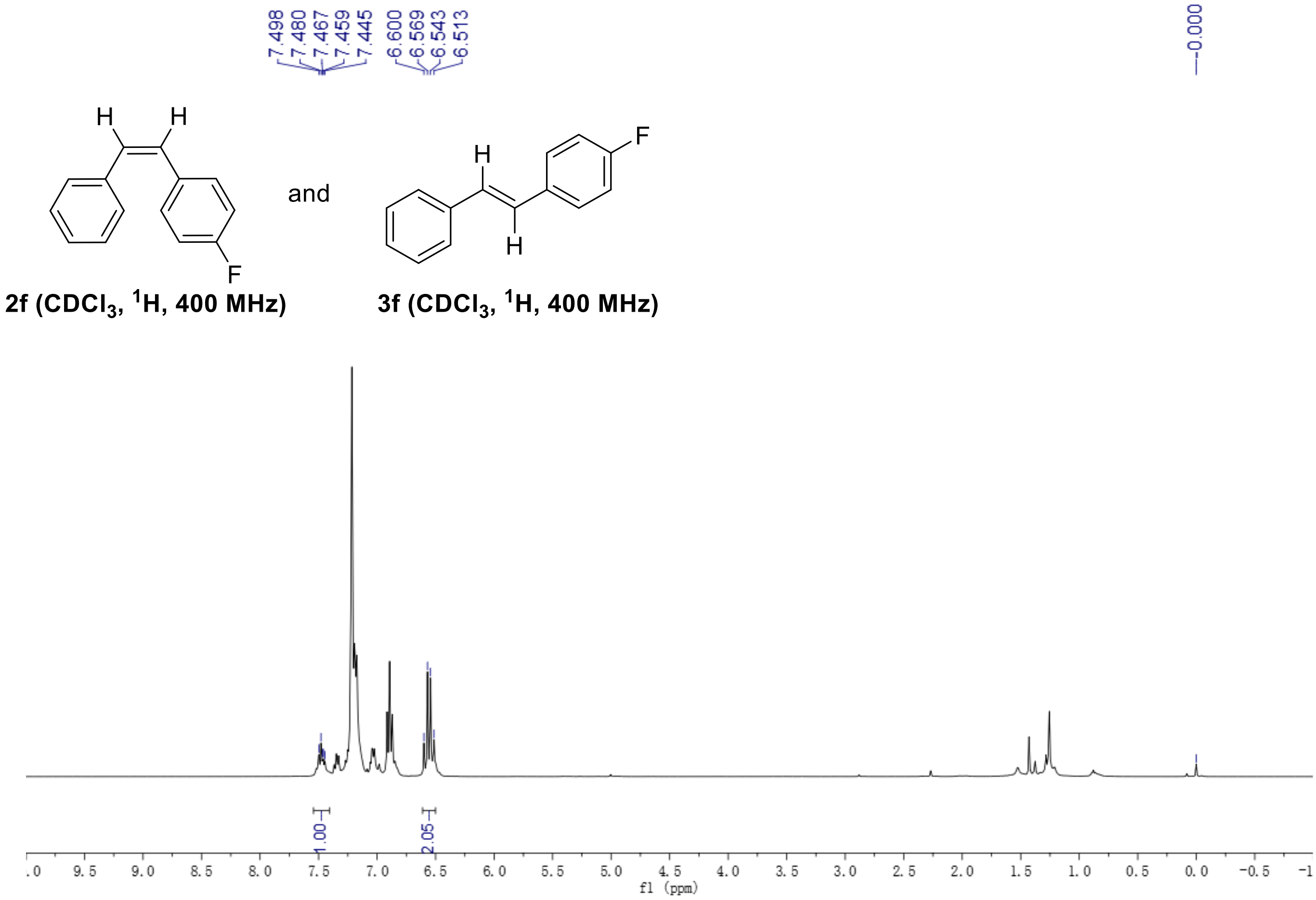
7.057
7.016
6.917
6.895
6.874
6.533
6.502
3.811
3.760
3.655
0.000
H
H
MeO
OMe
OMe
and
MeO
H
MeO
H
OMe
2e (CDCl$_3$, ^{1}H, 400 MHz)
3e (CDCl$_3$, ^{1}H, 400 MHz)
1.00
3.77
f1 (ppm)

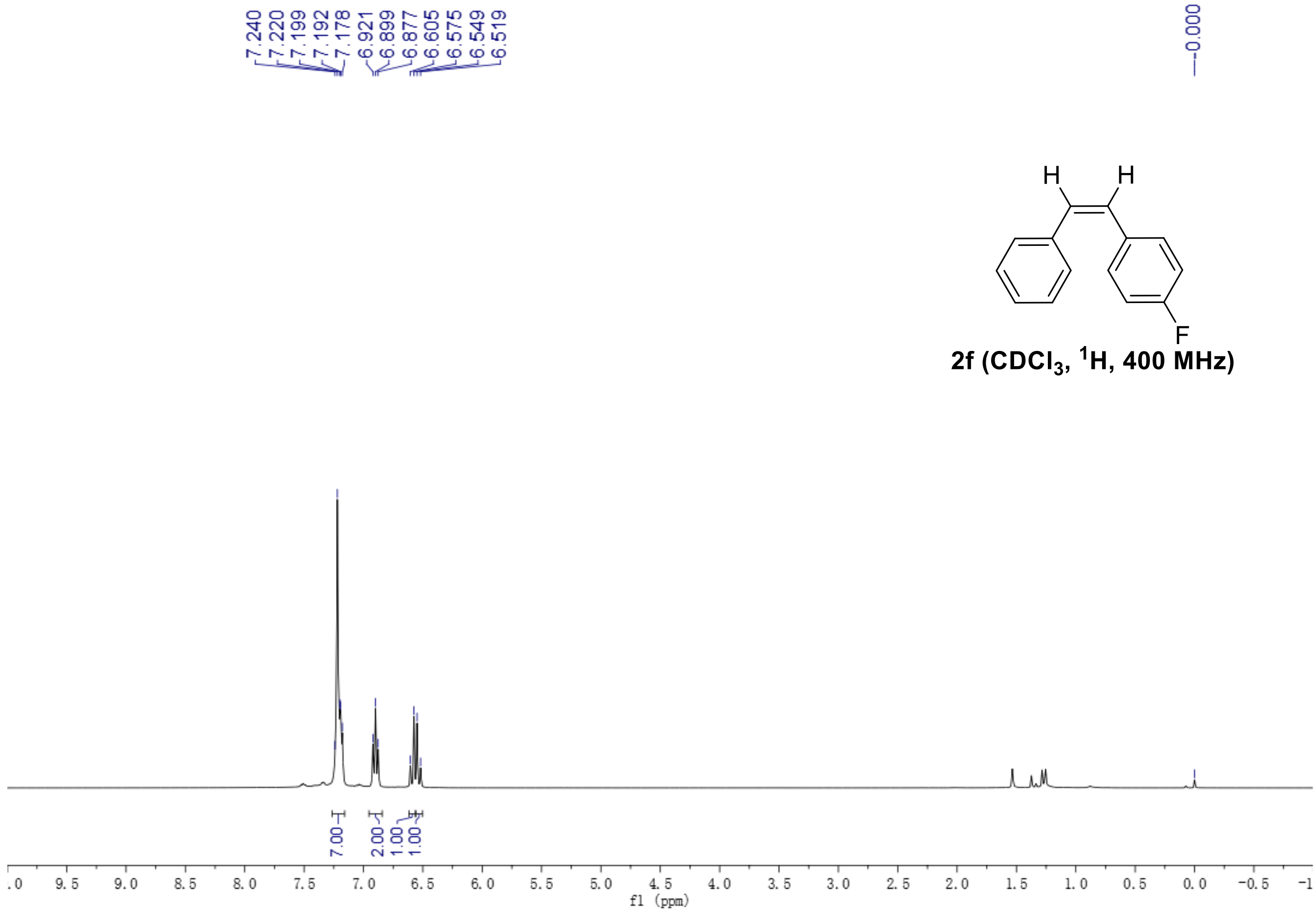


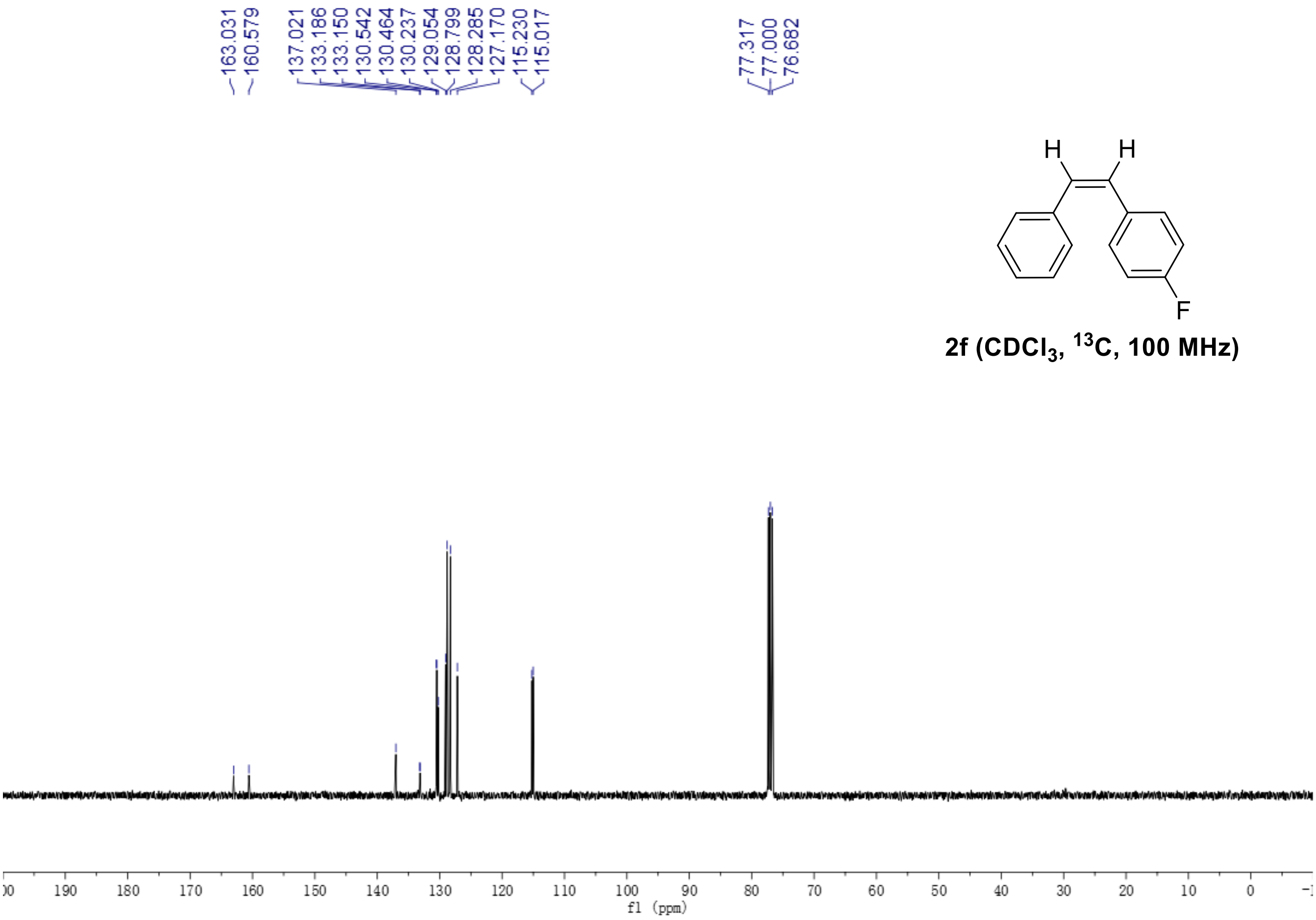
2e (CDCl$_3$, ^{1}H, 400 MHz)



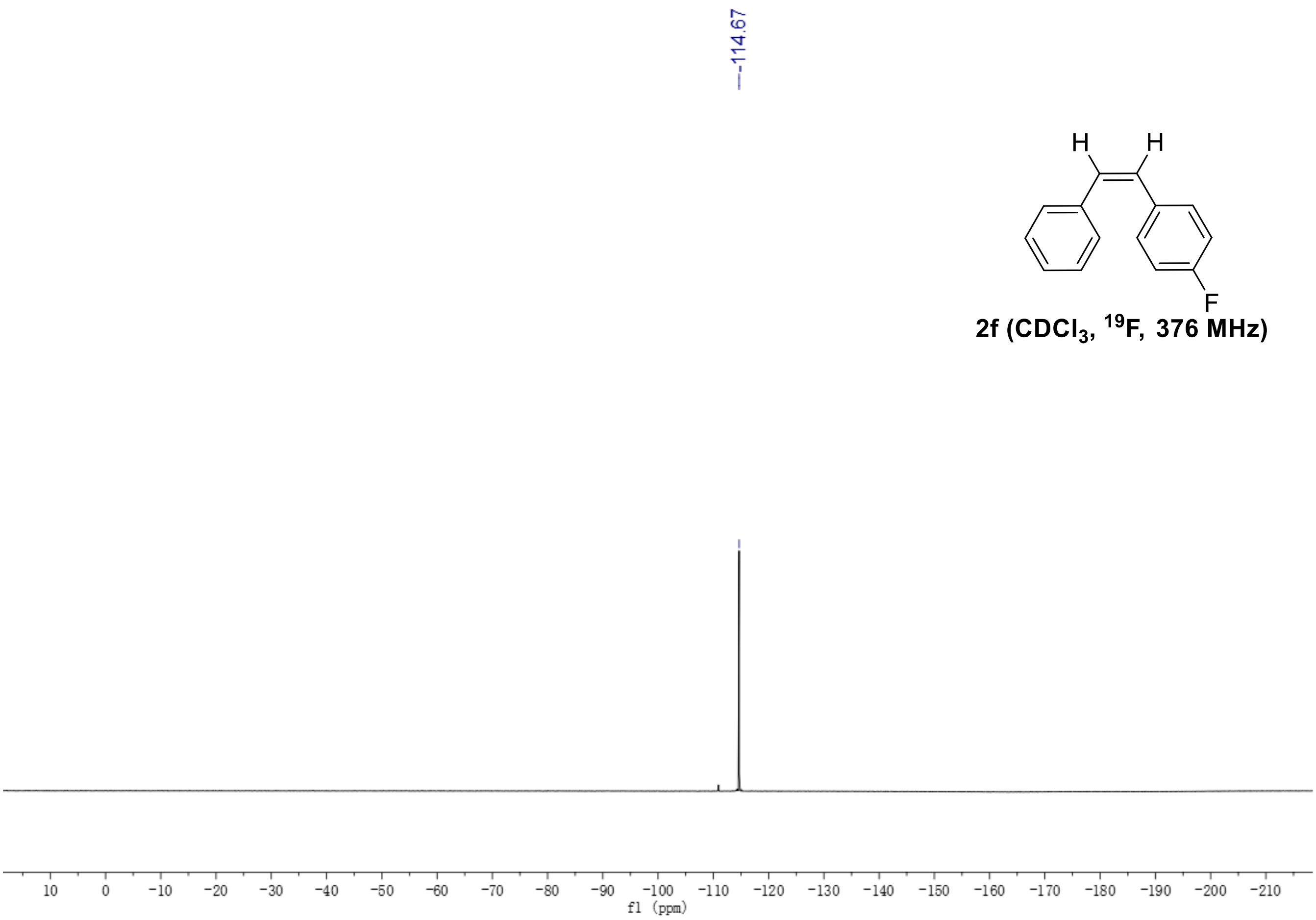
2e (CDCl$_3$, ^{13}C, 100 MHz)


7.498
7.480
7.467
7.459
7.445
6.600
6.569
6.543
6.513
0.000
and
2f (CDCl3, 1H, 400 MHz)
3f (CDCl3, 1H, 400 MHz)
1.00
2.05
fl (ppm)

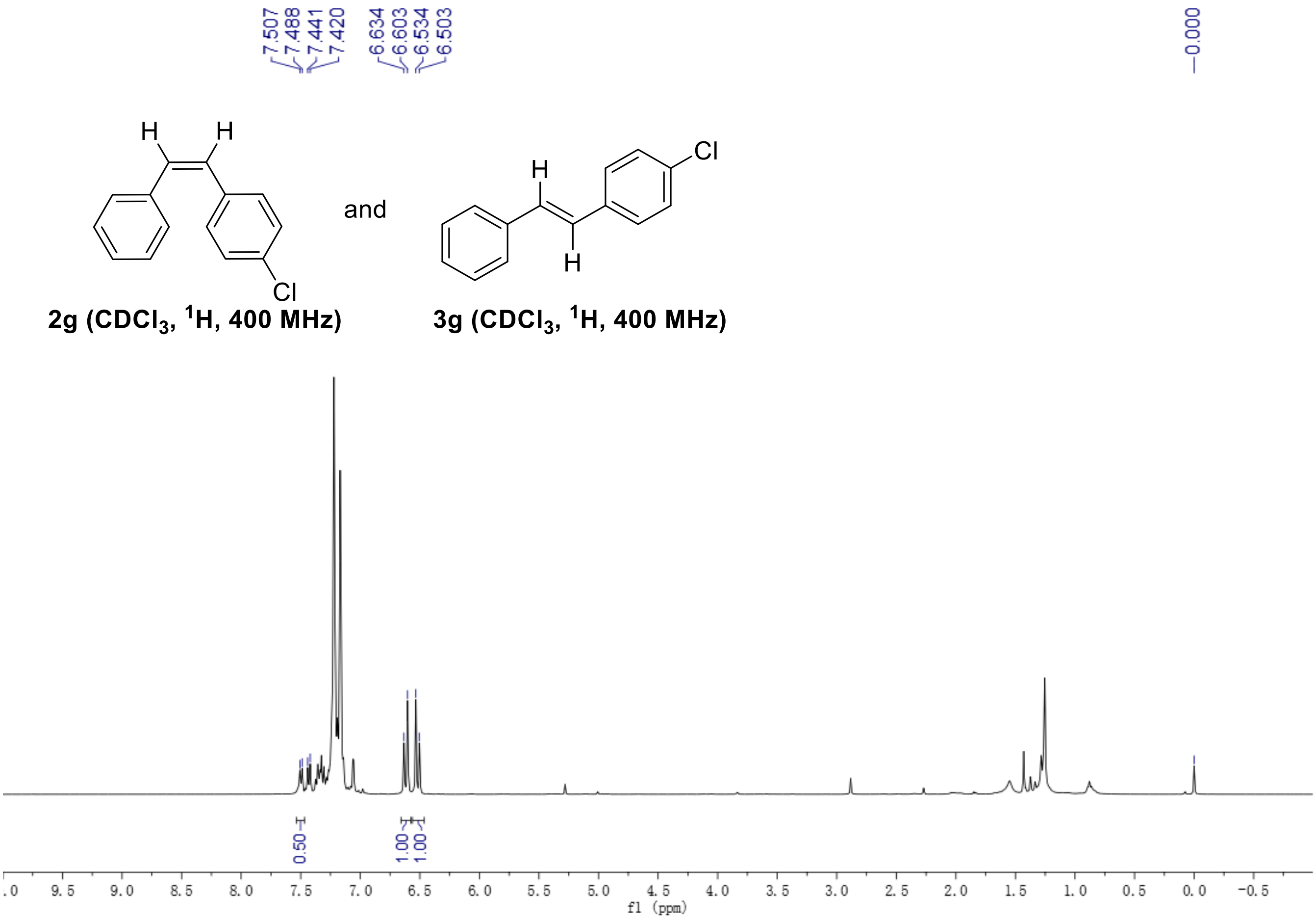

7.240
7.220
7.199
7.192
7.178
6.921
6.899
6.877
6.605
6.575
6.549
6.519
0.000
2f (CDCl3, 1H, 400 MHz)
7.00
2.00
1.00
1.00
fl (ppm)

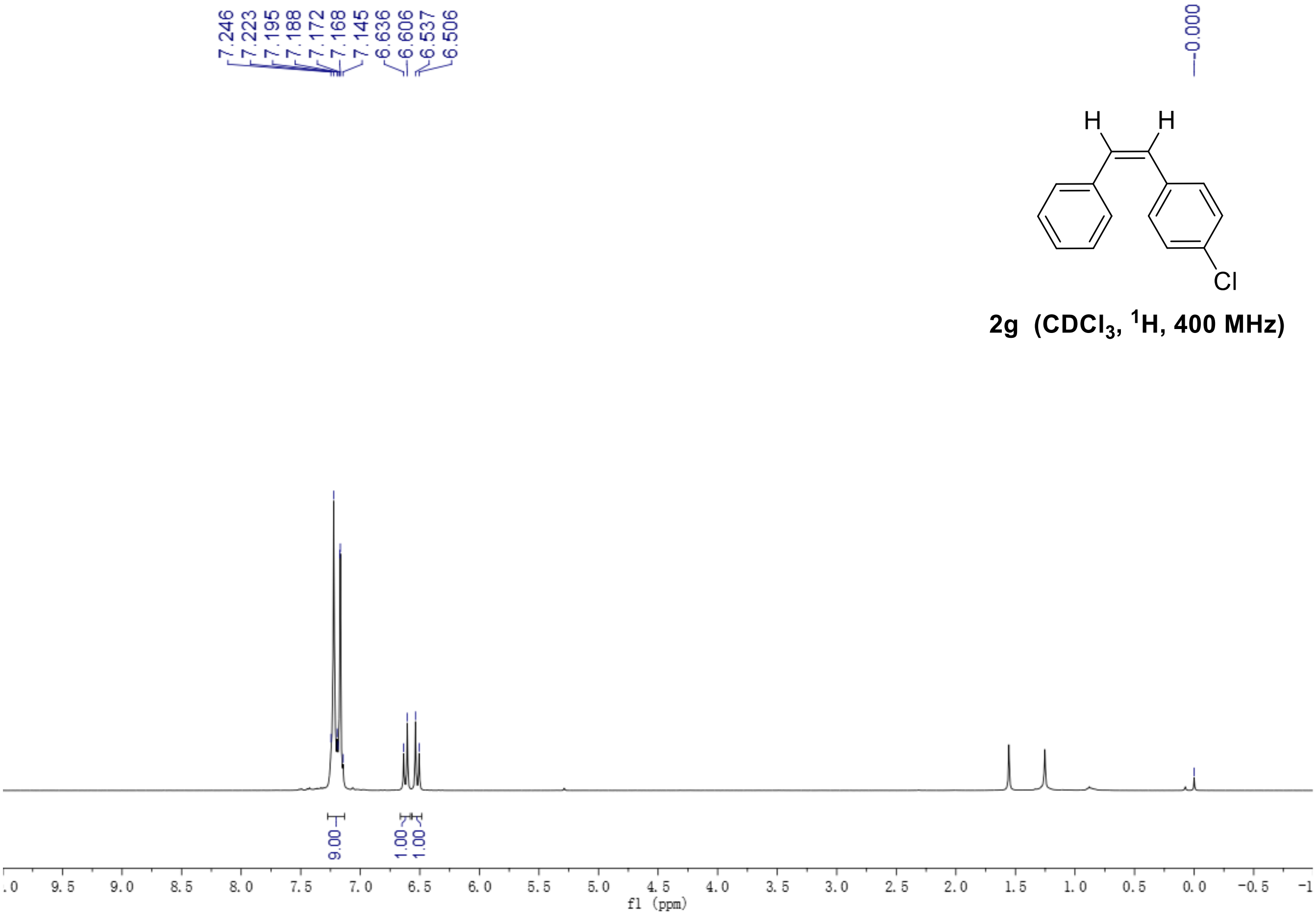


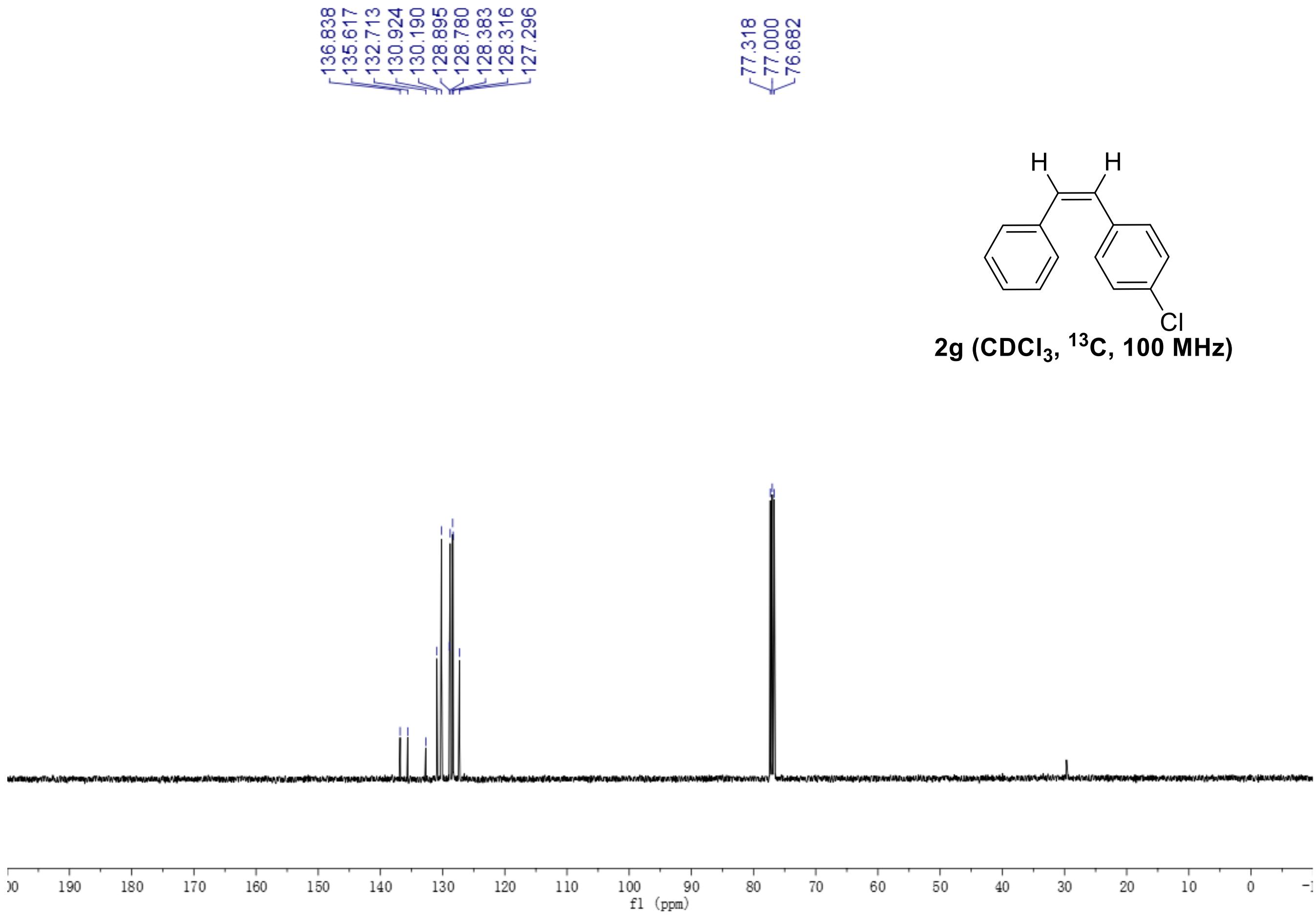
2f ($CDCl_3$, ^{13}C, 100 MHz)

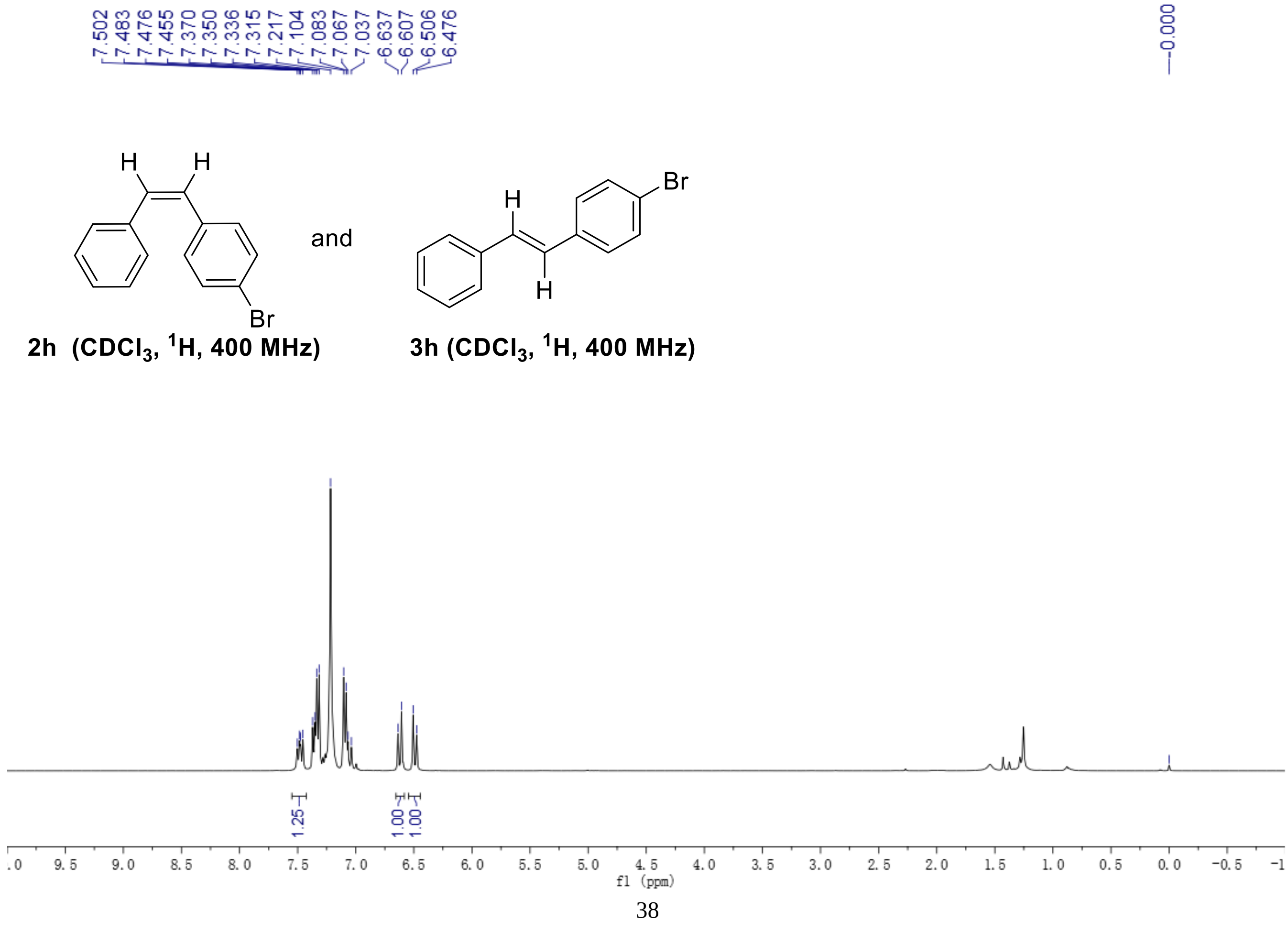


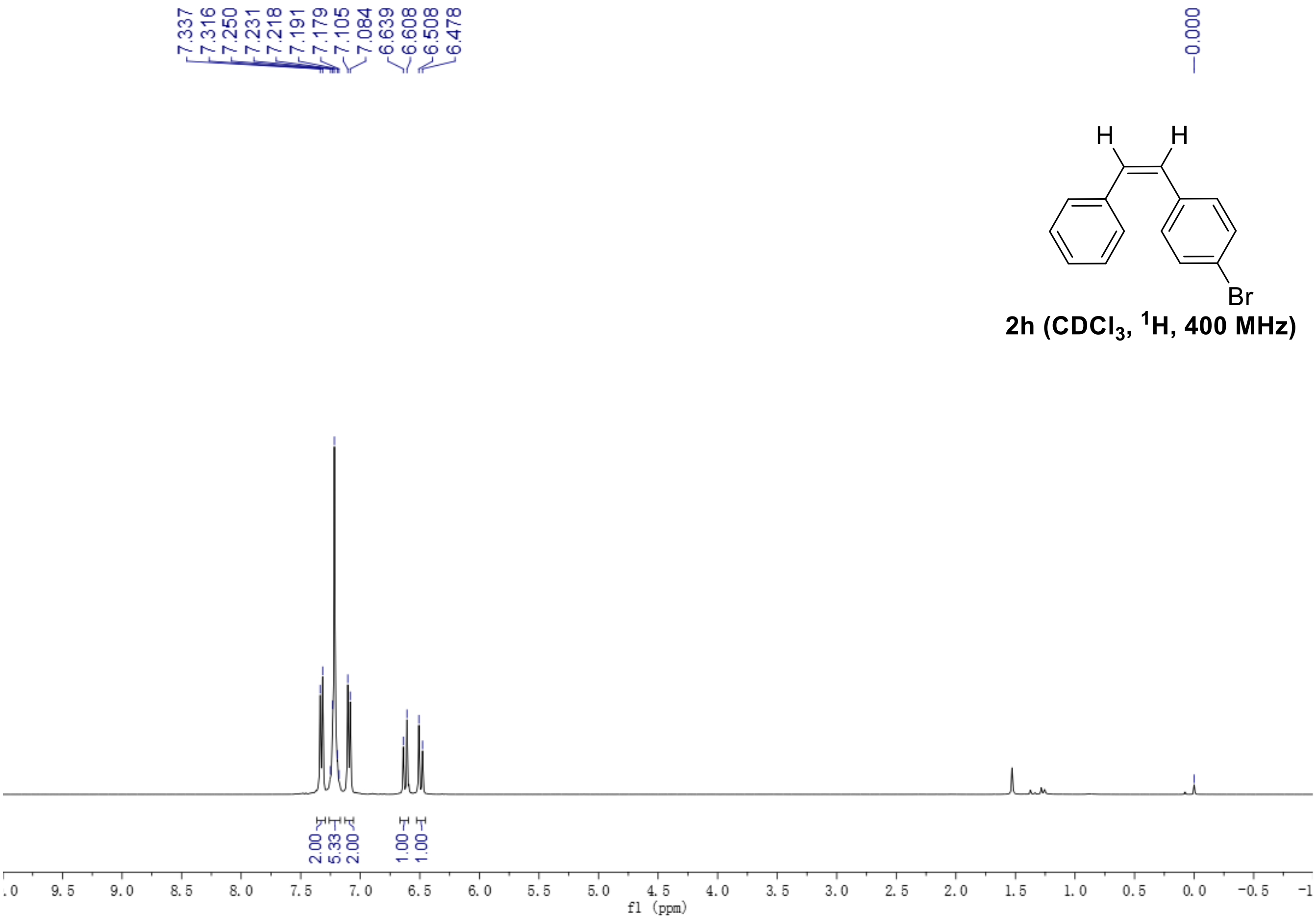
2f ($CDCl_3$, ^{19}F, 376 MHz)

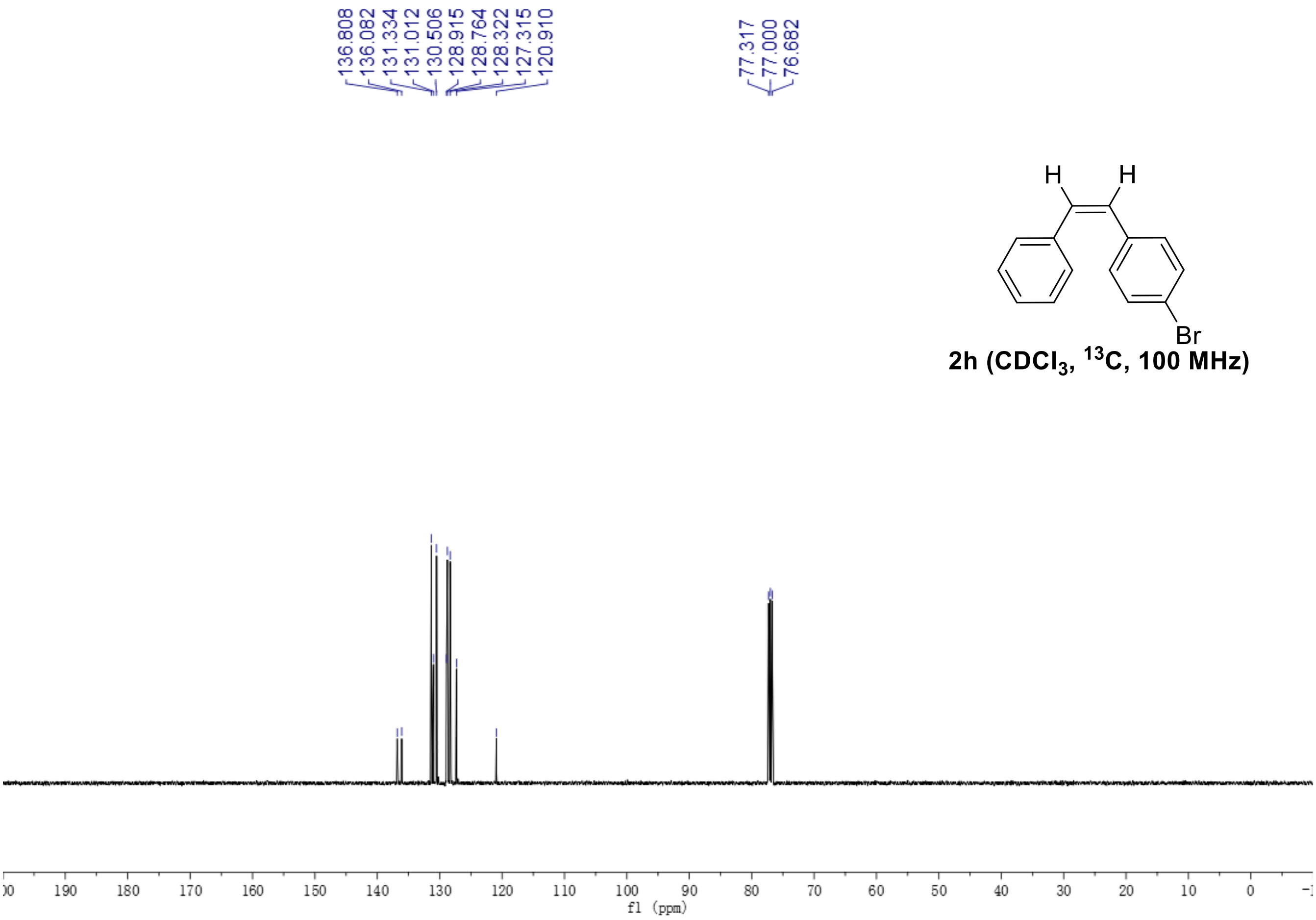

7.507
7.488
7.441
7.420
6.634
6.603
6.534
6.503
0.000
and
2g (CDCl3, 1H, 400 MHz)
3g (CDCl3, 1H, 400 MHz)
0.50
1.00
1.00
f1 (ppm)

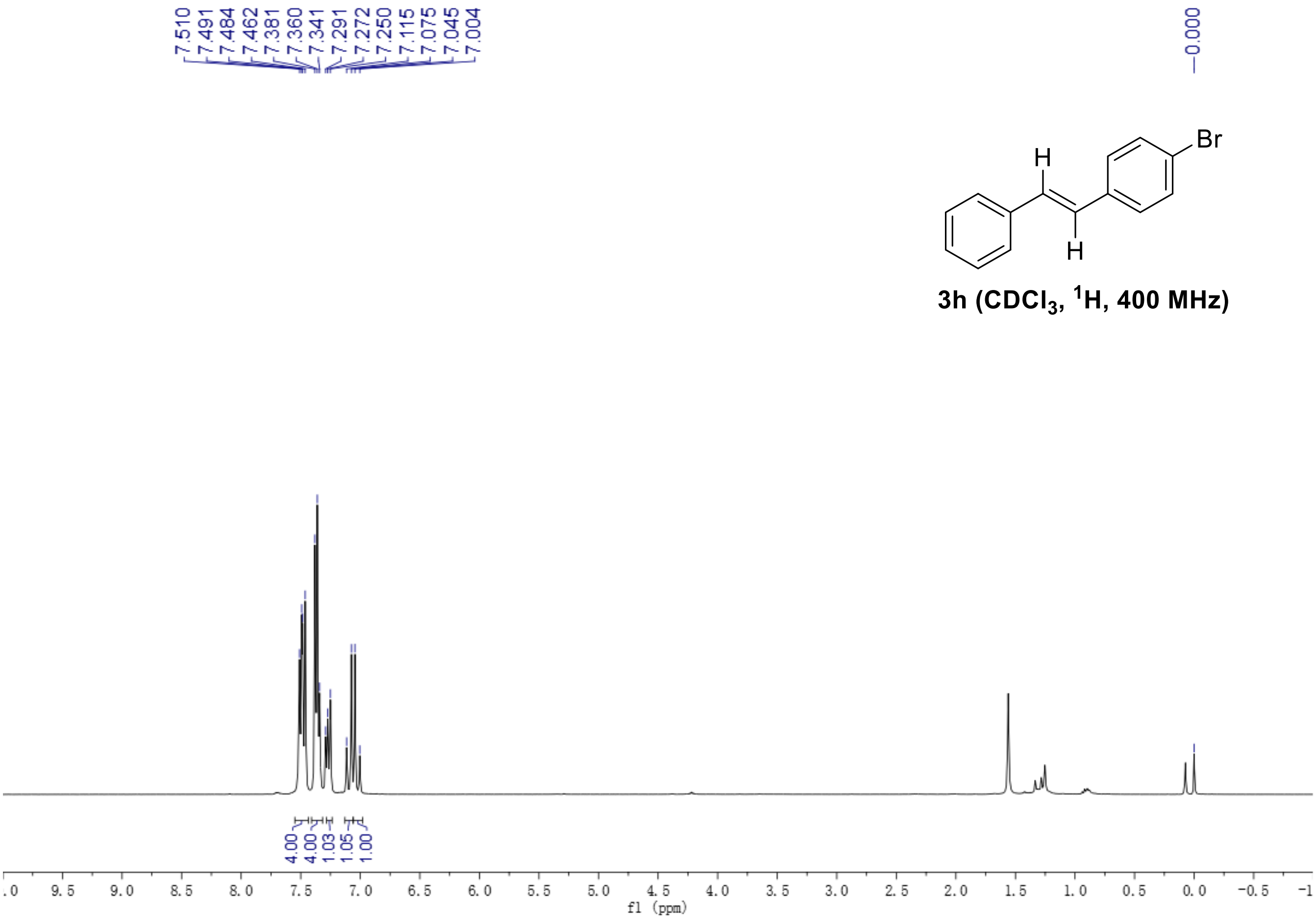

7.246
7.223
7.195
7.188
7.172
7.168
7.145
6.636
6.606
6.537
6.506
0.000
2g (CDCl3, 1H, 400 MHz)
9.00
1.00
1.00
f1 (ppm)


136.838
135.617
132.713
130.924
130.190
128.895
128.780
128.383
128.316
127.296
77.318
77.000
76.682
H
H
Cl
2g (CDCl3, 13C, 100 MHz)
f1 (ppm)

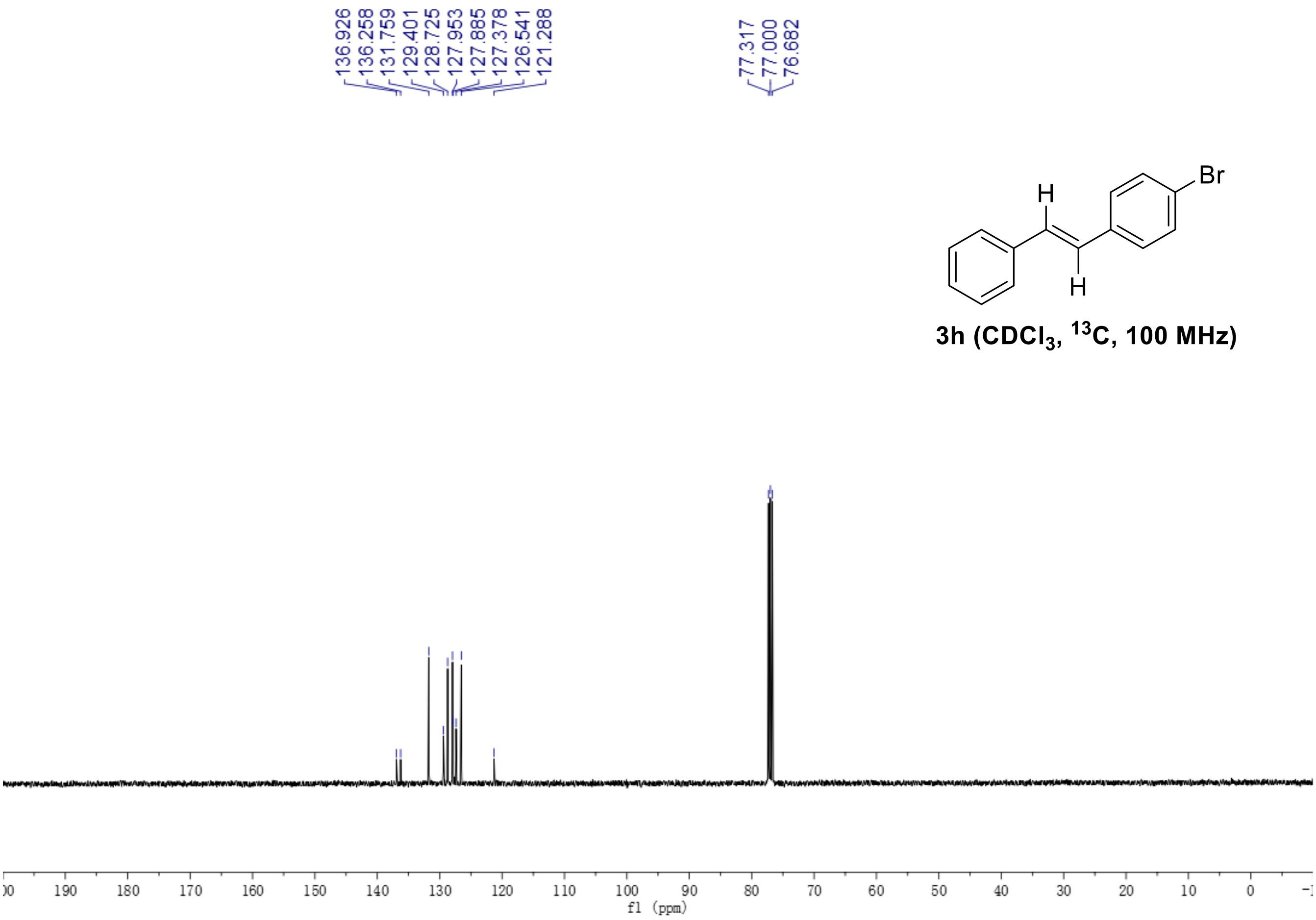

7.502
7.483
7.476
7.455
7.370
7.350
7.336
7.315
7.217
7.104
7.083
7.067
7.037
6.637
6.607
6.506
6.476
0.000
H
H
Br
and
Br
H
H
2h (CDCl3, 1H, 400 MHz)
3h (CDCl3, 1H, 400 MHz)
1.25
1.00
1.00
f1 (ppm)


7.337
7.316
7.250
7.231
7.218
7.191
7.179
7.105
7.084
6.639
6.608
6.508
6.478
0.000
H
H
Br
2h (CDCl$_3$, ^{1}H, 400 MHz)
2.00
5.33
2.00
1.00
1.00
fl (ppm)

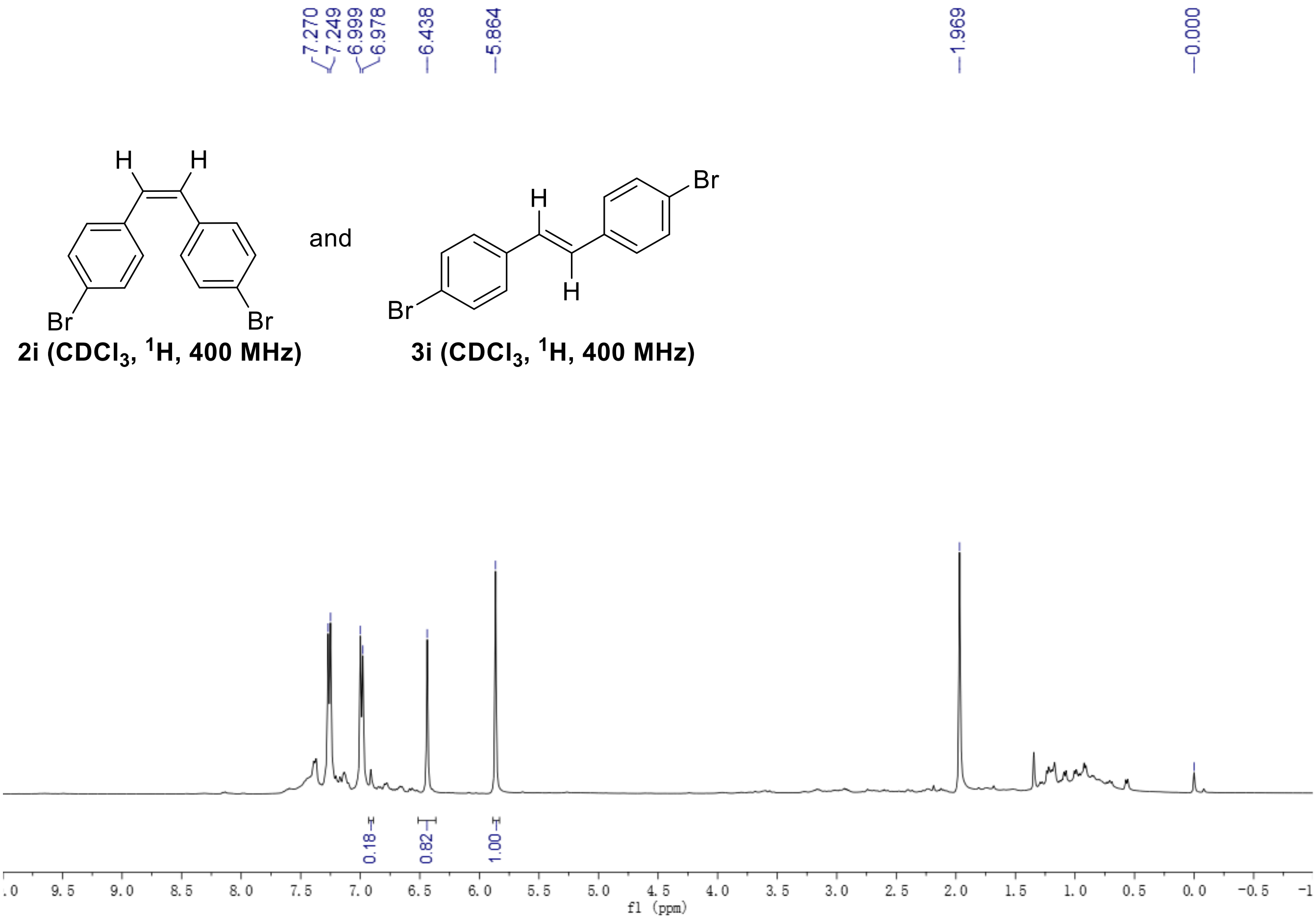

136.808
136.082
131.334
131.012
130.506
128.915
128.764
128.322
127.315
120.910
77.317
77.000
76.682
H
H
Br
2h (CDCl$_3$, ^{13}C, 100 MHz)
fl (ppm)



3h ($CDCl_3$, ^{1}H, 400 MHz)

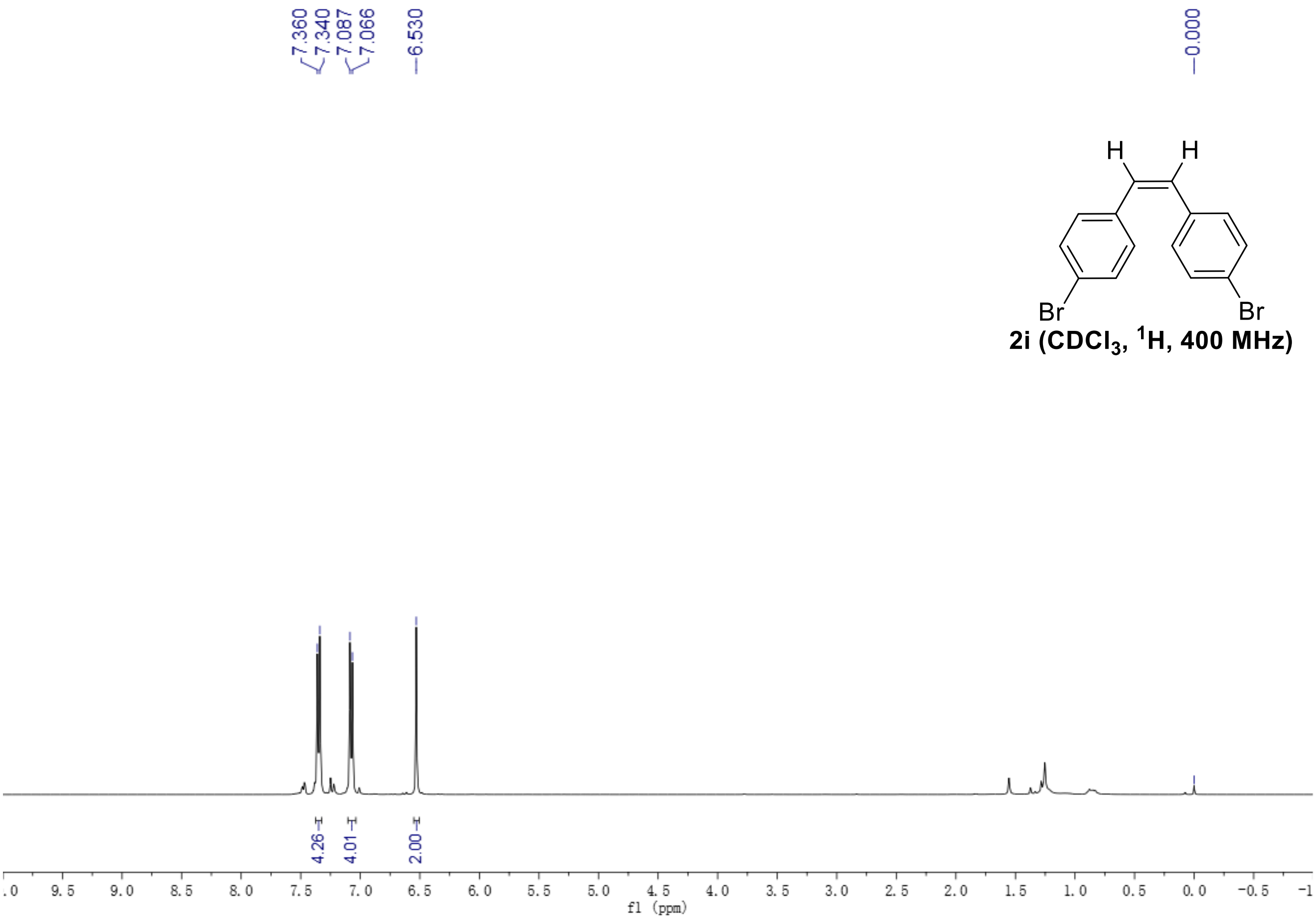


3h ($CDCl_3$, ^{13}C, 100 MHz)

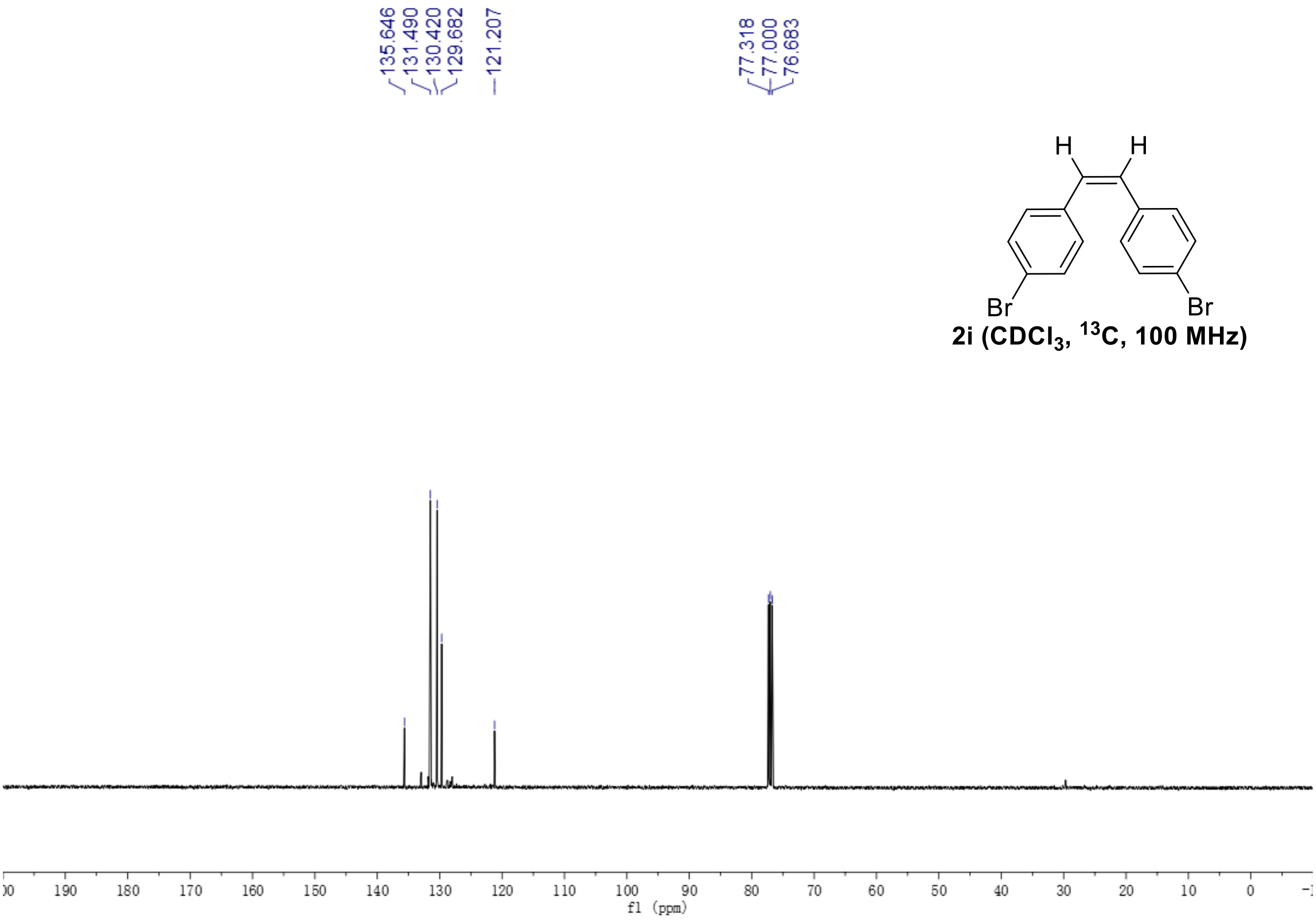


2i ($CDCl_3$, ^1H, 400 MHz)

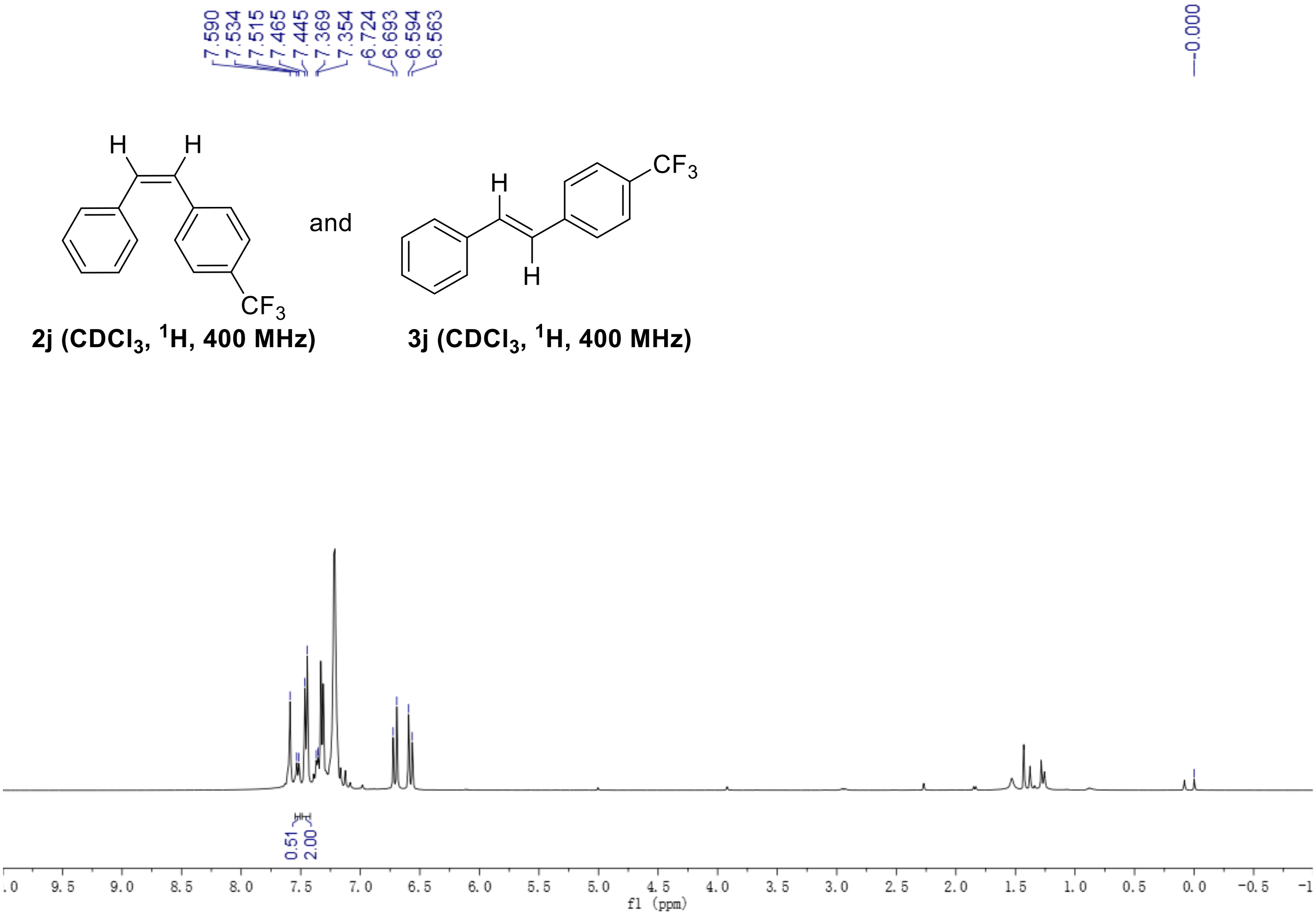
3i ($CDCl_3$, ^1H, 400 MHz)



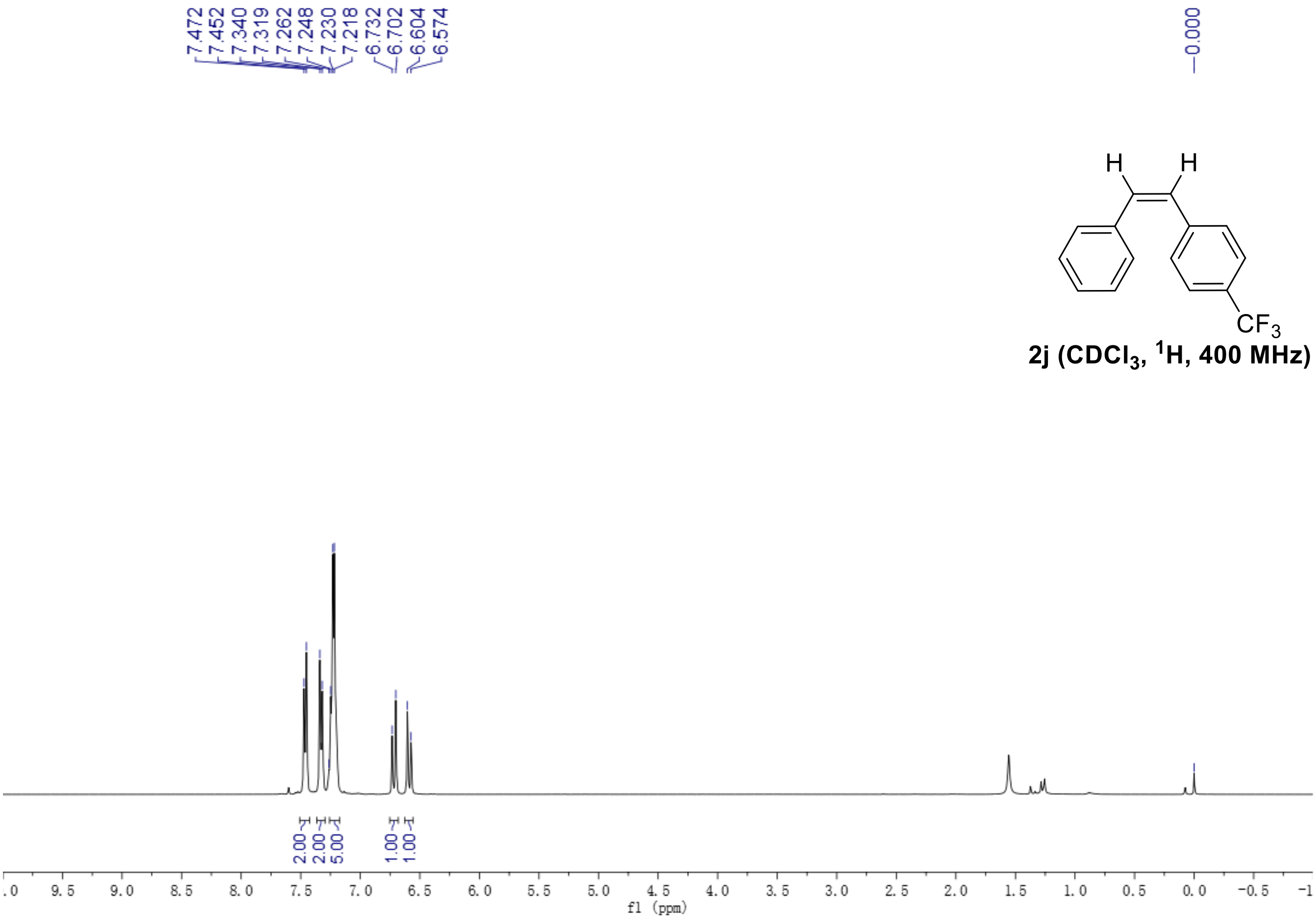
2i ($CDCl_3$, ^1H, 400 MHz)



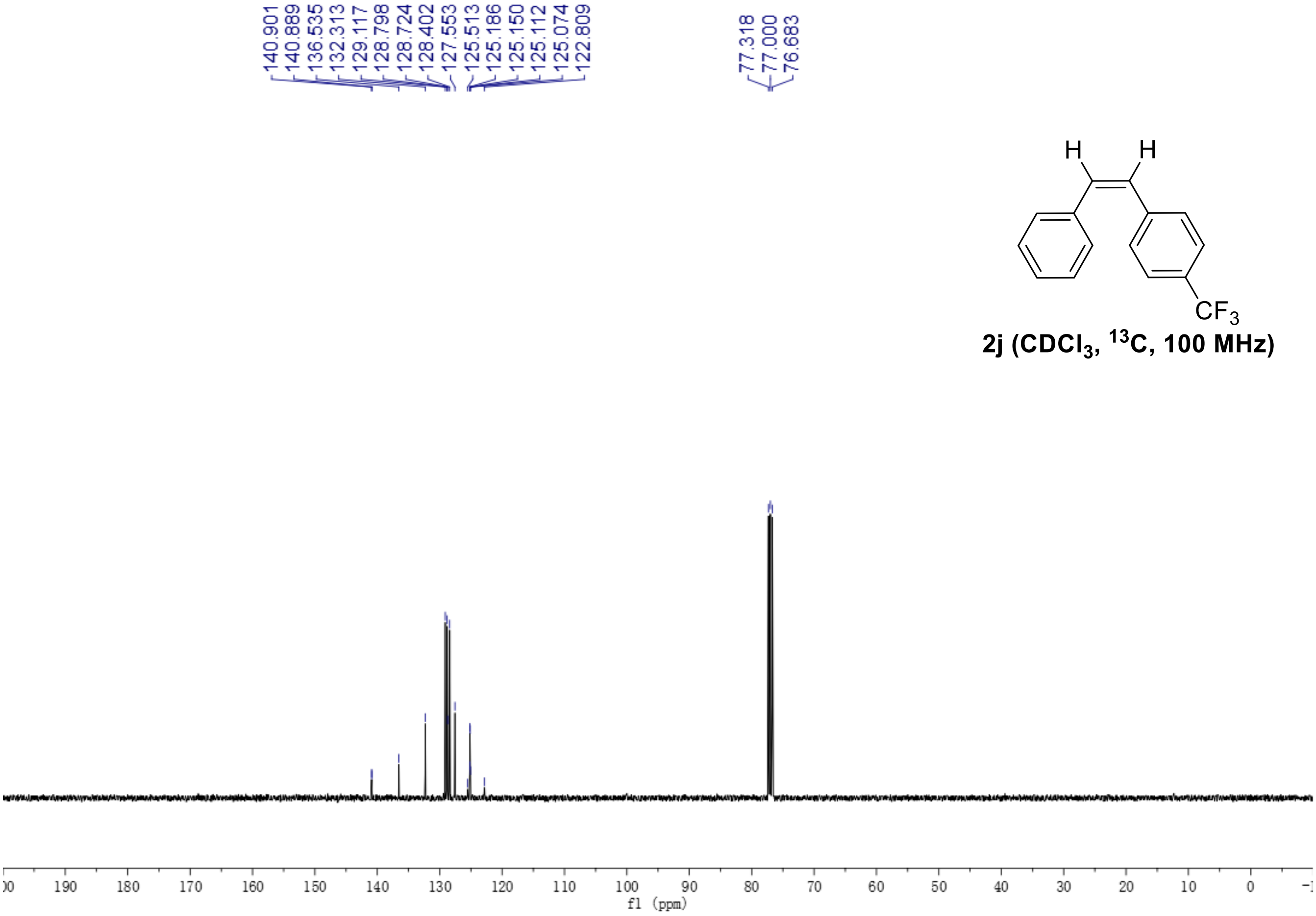
2i ($CDCl_3$, ^{13}C, 100 MHz)



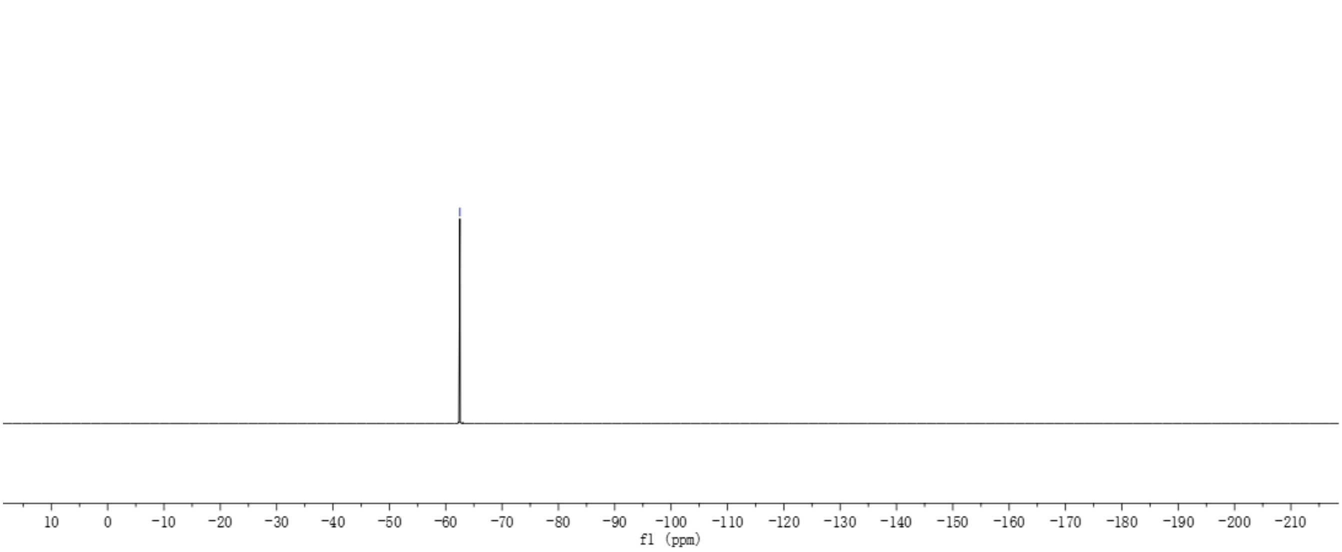
2j ($CDCl_3$, ^1H, 400 MHz) 3j ($CDCl_3$, ^1H, 400 MHz)

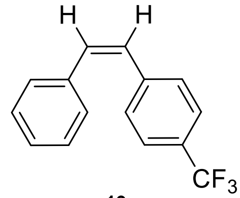


2j ($CDCl_3$, ^1H, 400 MHz)

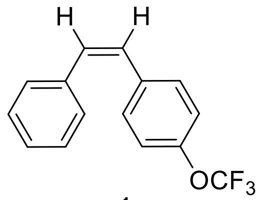


2j ($CDCl_3$, ^{13}C, 100 MHz)

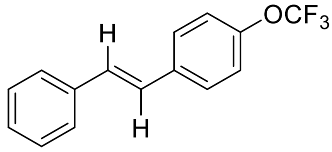




2j ($CDCl_3$, ^{19}F, 376 MHz)

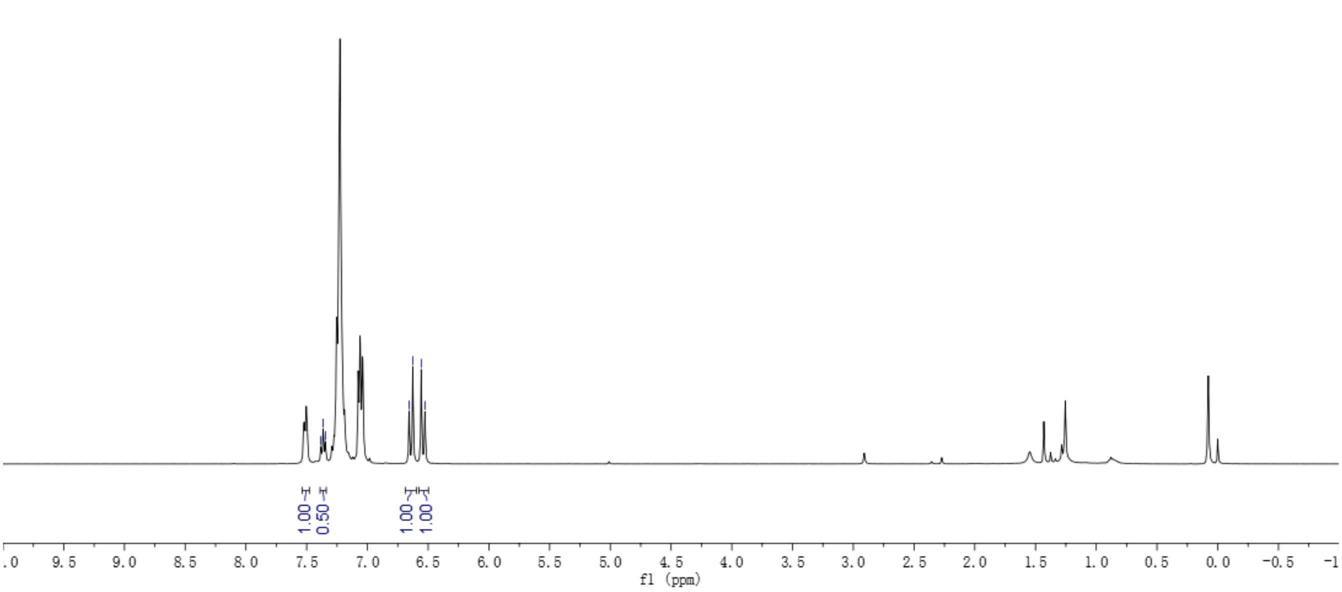


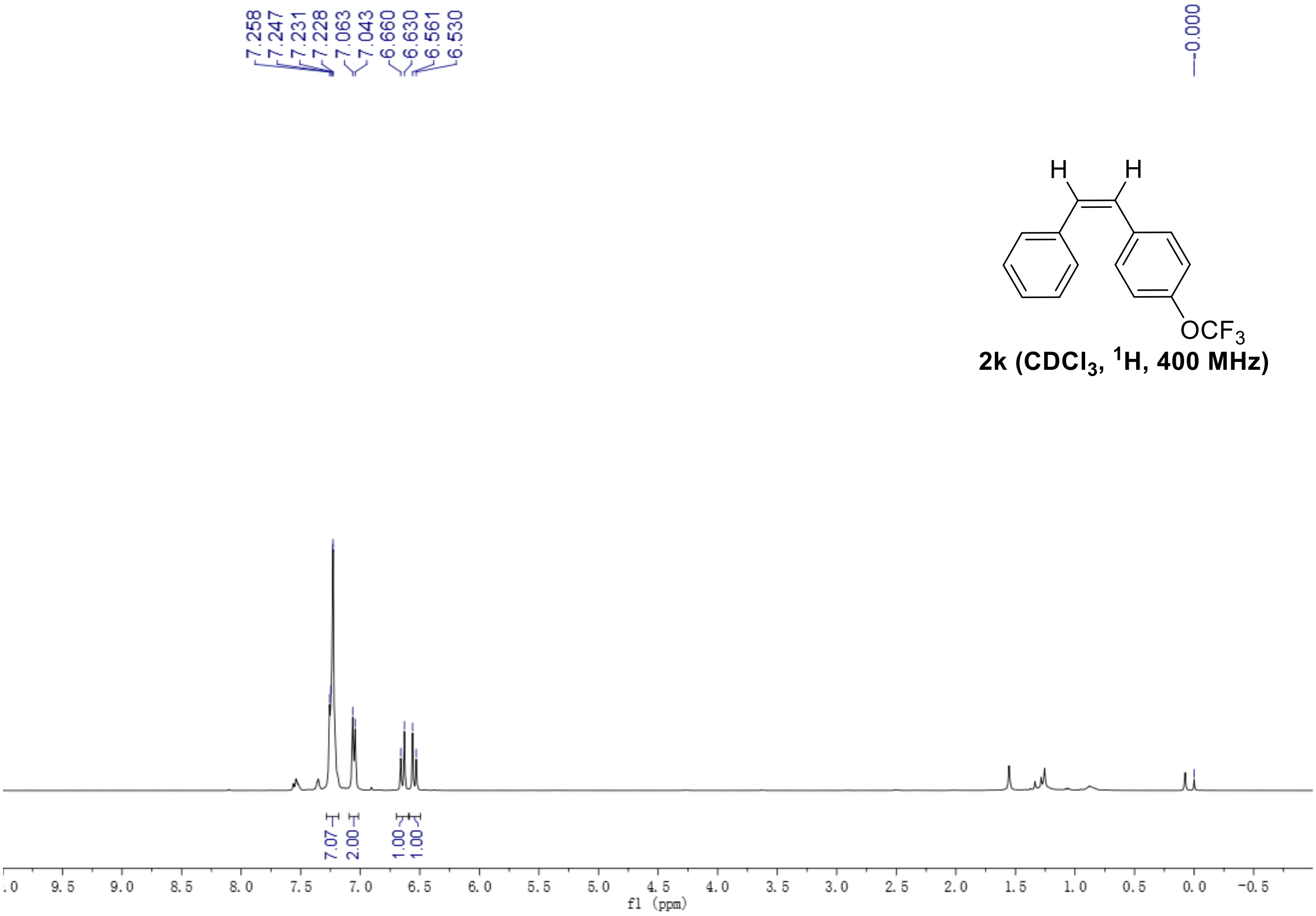
and



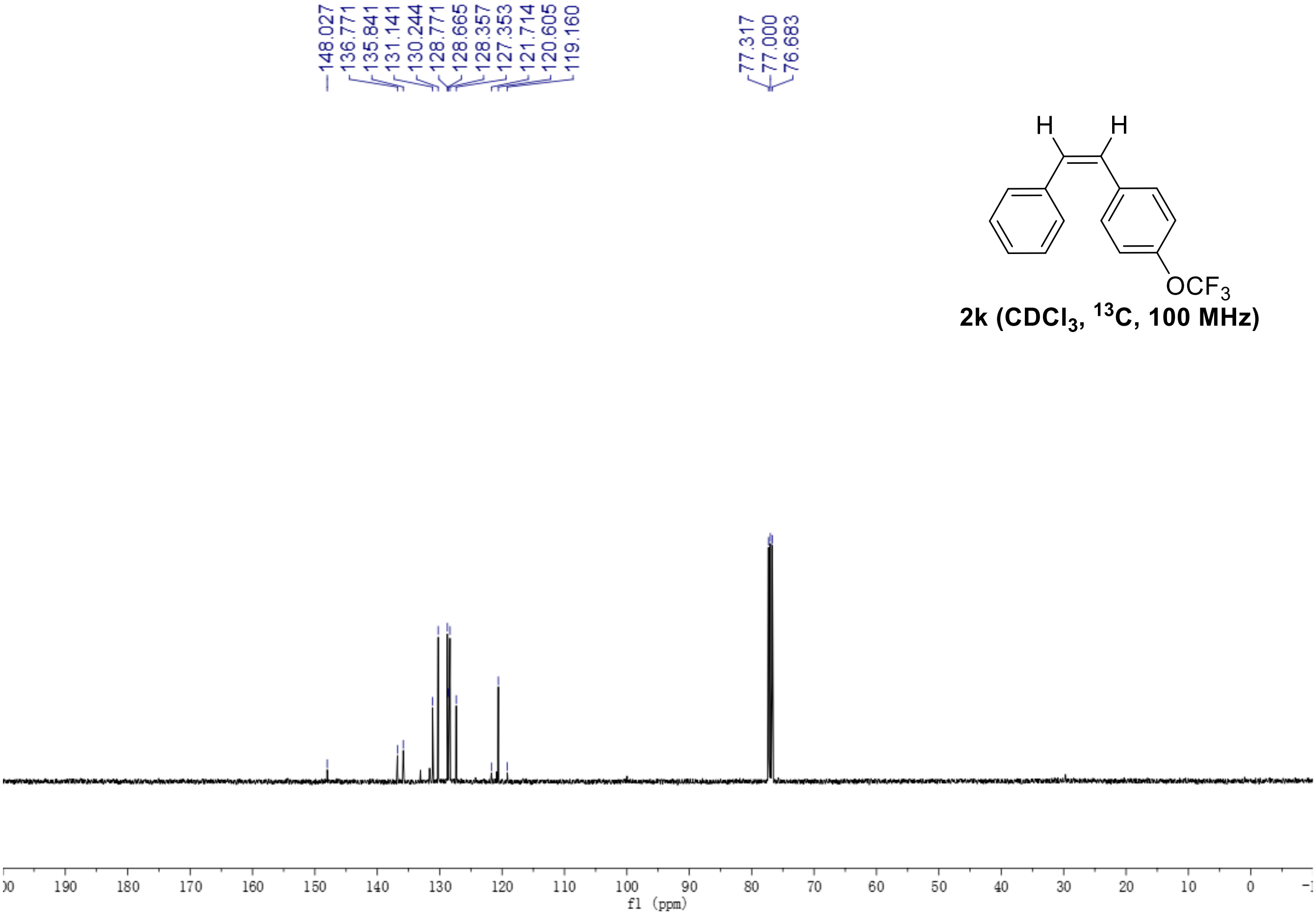
2k ($CDCl_3$, ^{1}H, 400 MHz)

3k ($CDCl_3$, ^{1}H, 400 MHz)

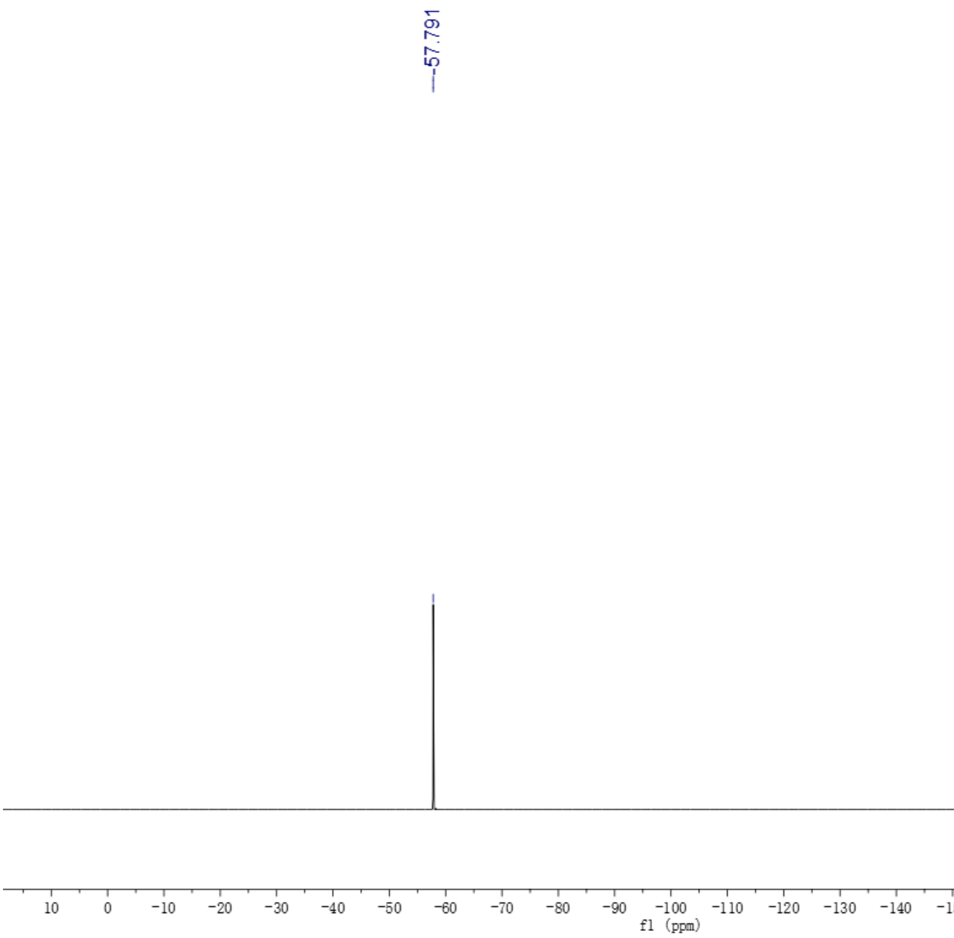


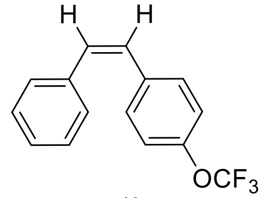


2k (CDCl$_3$, ^{1}H, 400 MHz)

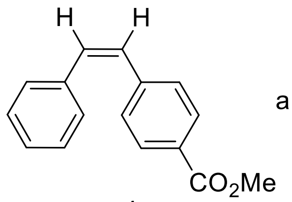


2k (CDCl$_3$, ^{13}C, 100 MHz)



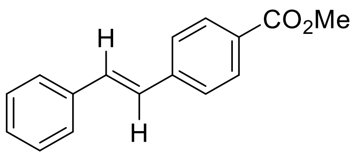


2k ($CDCl_3$, ^{19}F, 376 MHz)

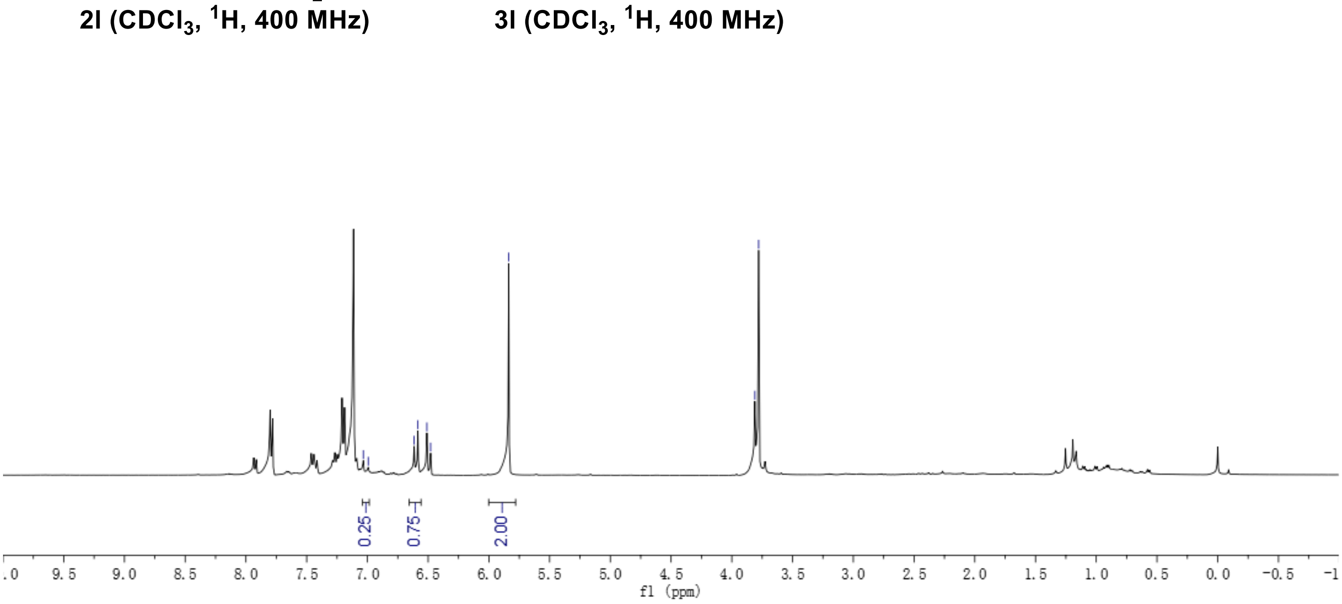


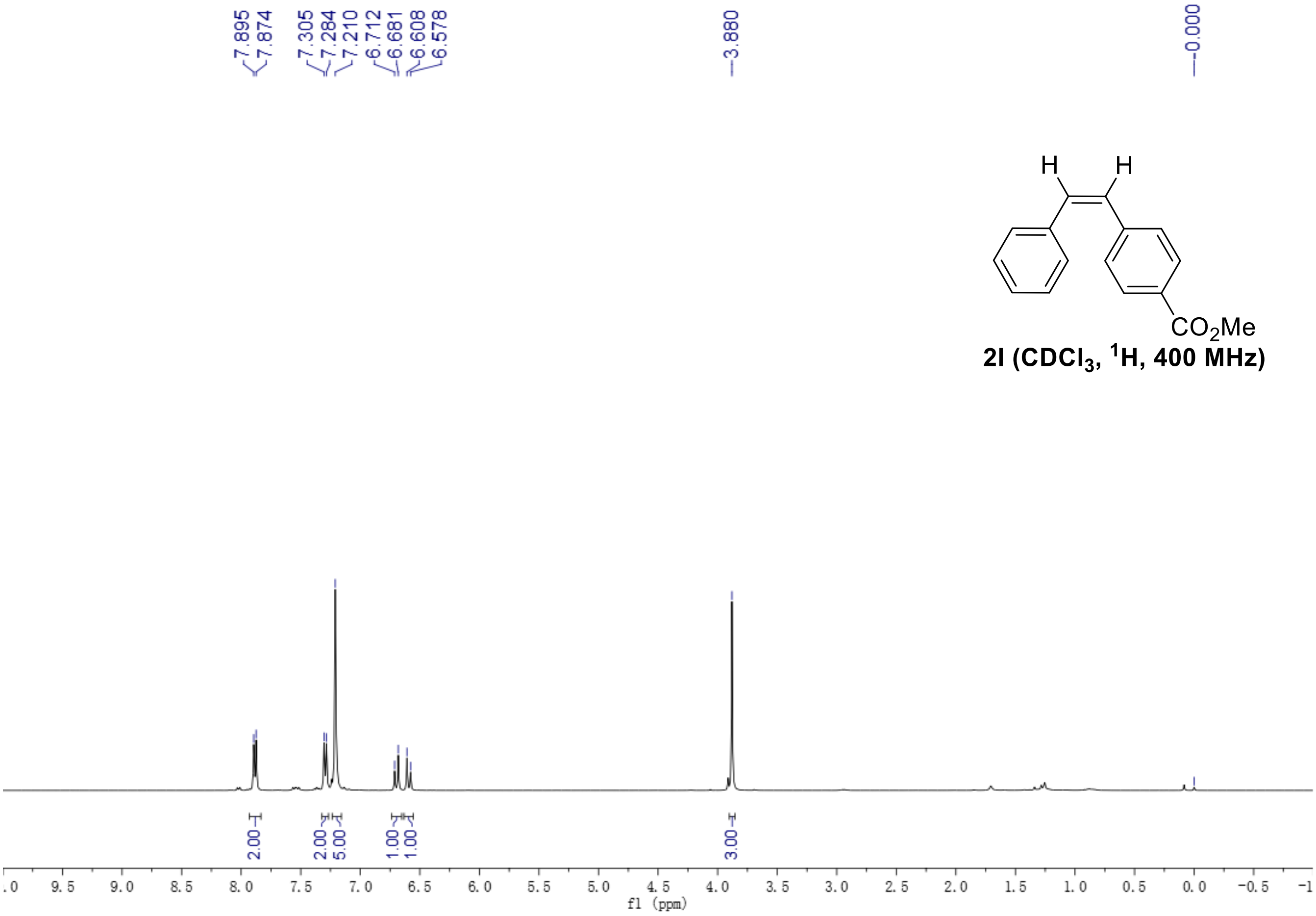
2l ($CDCl_3$, ^{1}H, 400 MHz)

and

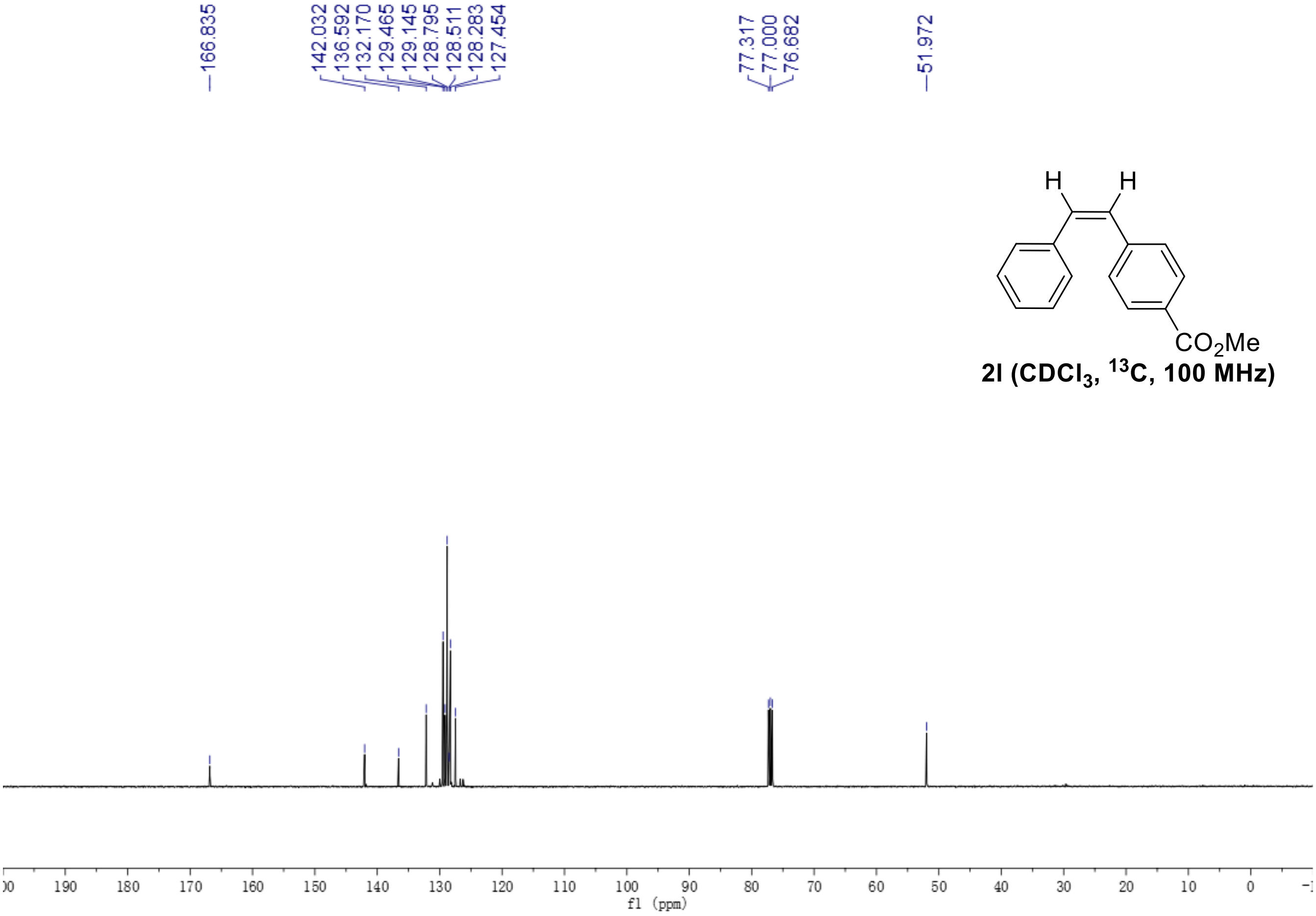


3l ($CDCl_3$, ^{1}H, 400 MHz)

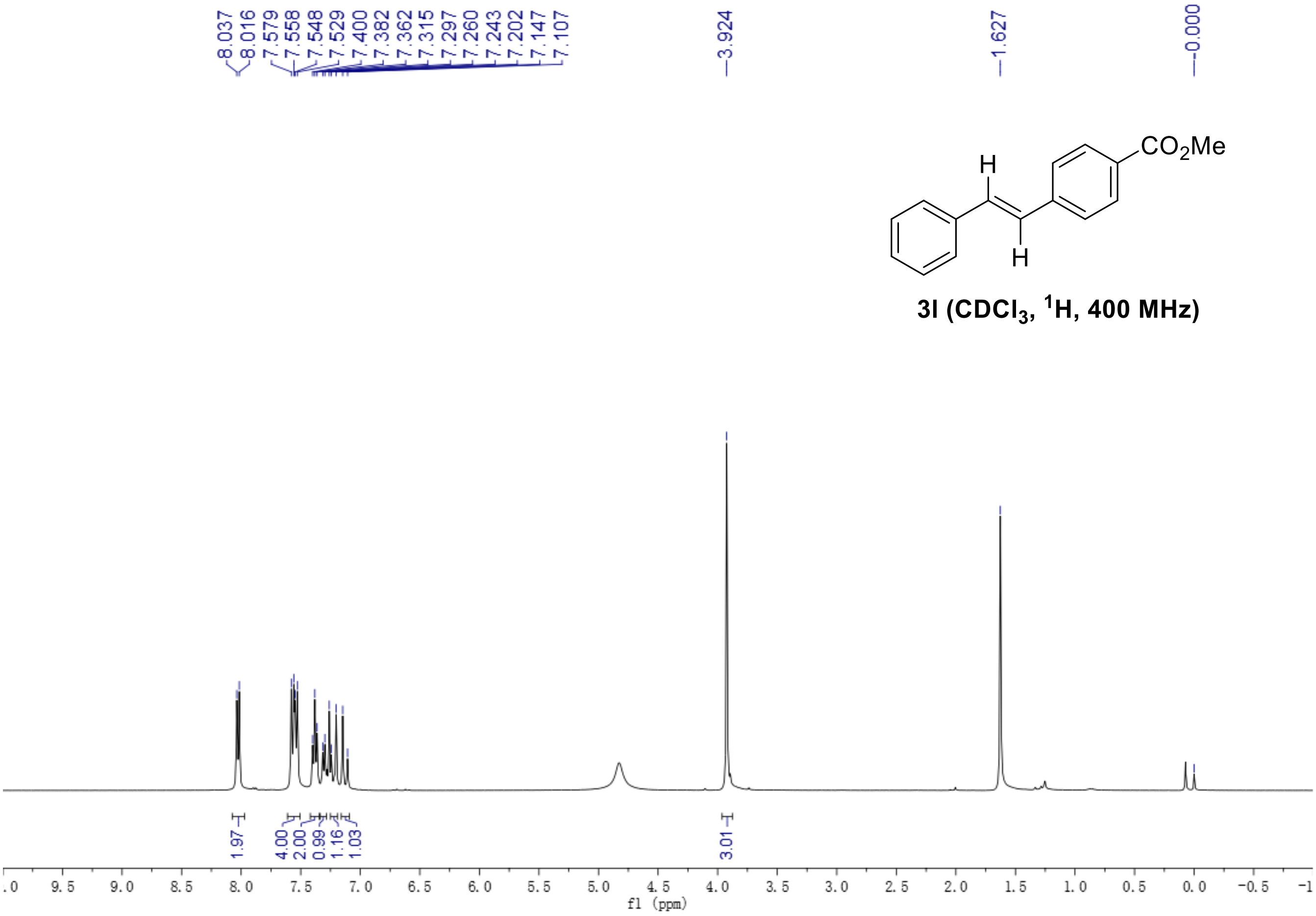


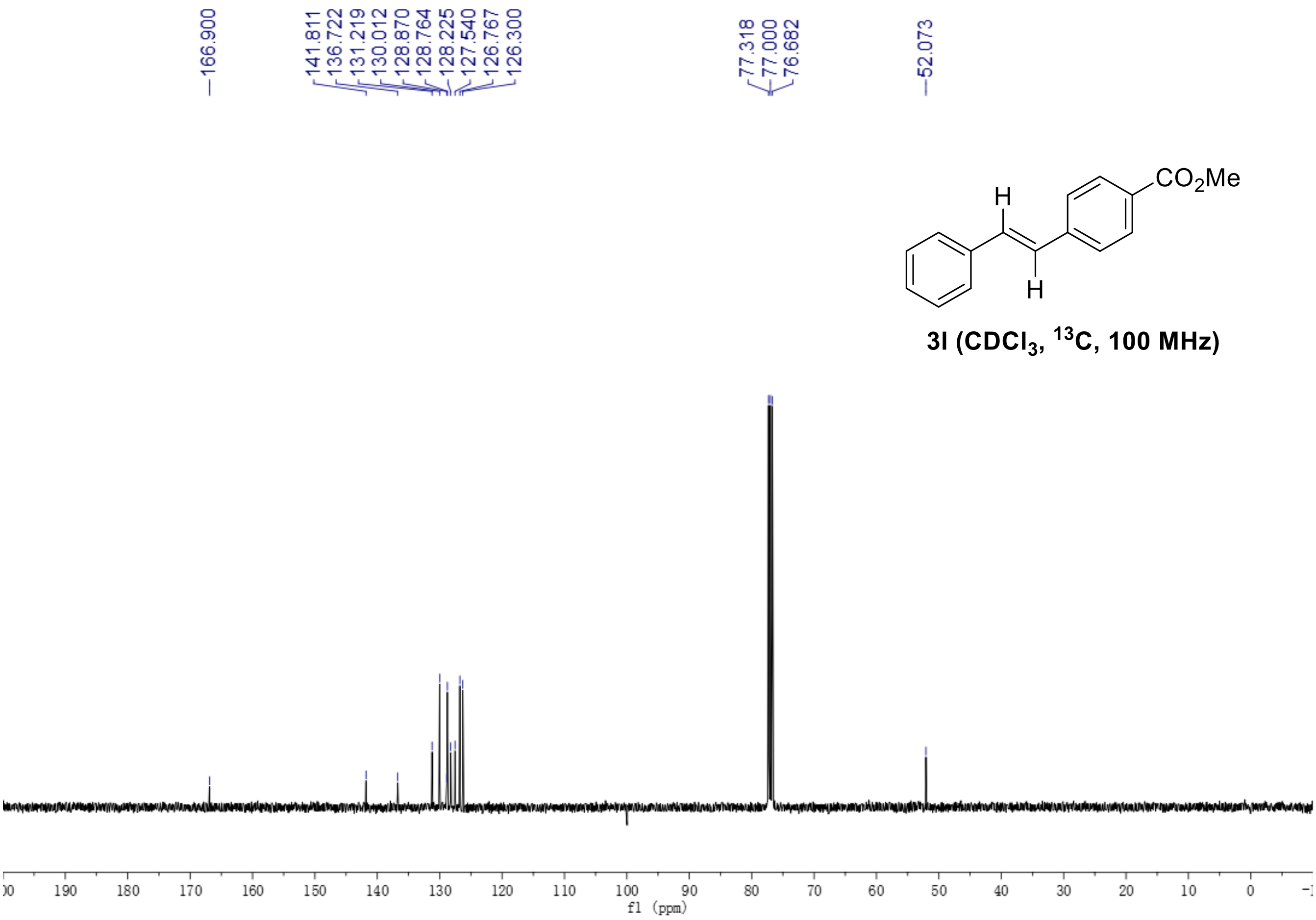


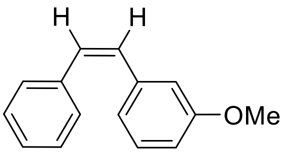
2l (CDCl$_3$, ^{1}H, 400 MHz)



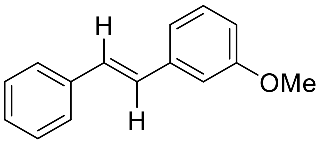
2l (CDCl$_3$, ^{13}C, 100 MHz)


8.037 8.016 7.579 7.558 7.548 7.529 7.400 7.382 7.362 7.315 7.297 7.260 7.243 7.202 7.147 7.107
3.924
1.627
0.000
CO2Me
H
H
3l (CDCl3, 1H, 400 MHz)
1.97 4.00 2.00 0.99 1.16 1.03 3.01
f1 (ppm)

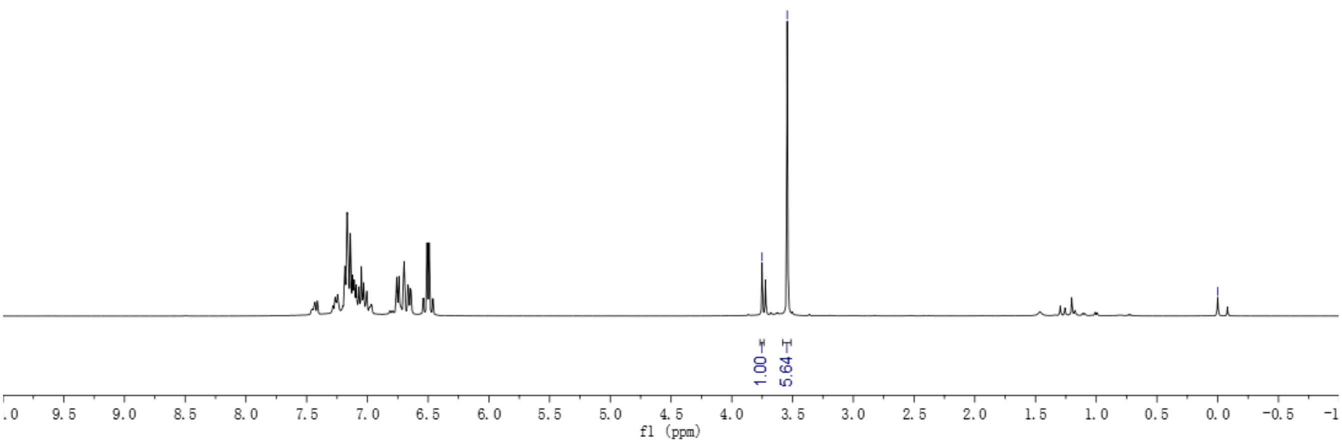

166.900
141.811 136.722 131.219 130.012 128.870 128.764 128.225 127.540 126.767 126.300
77.318 77.000 76.682
52.073
CO2Me
H
H
3l (CDCl3, 13C, 100 MHz)
f1 (ppm)

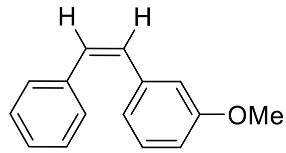


and

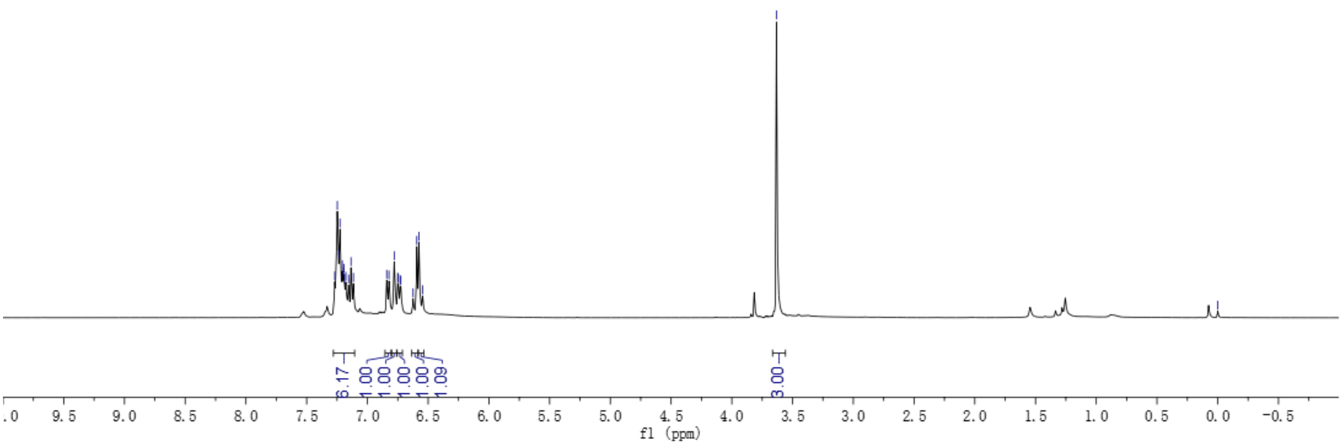


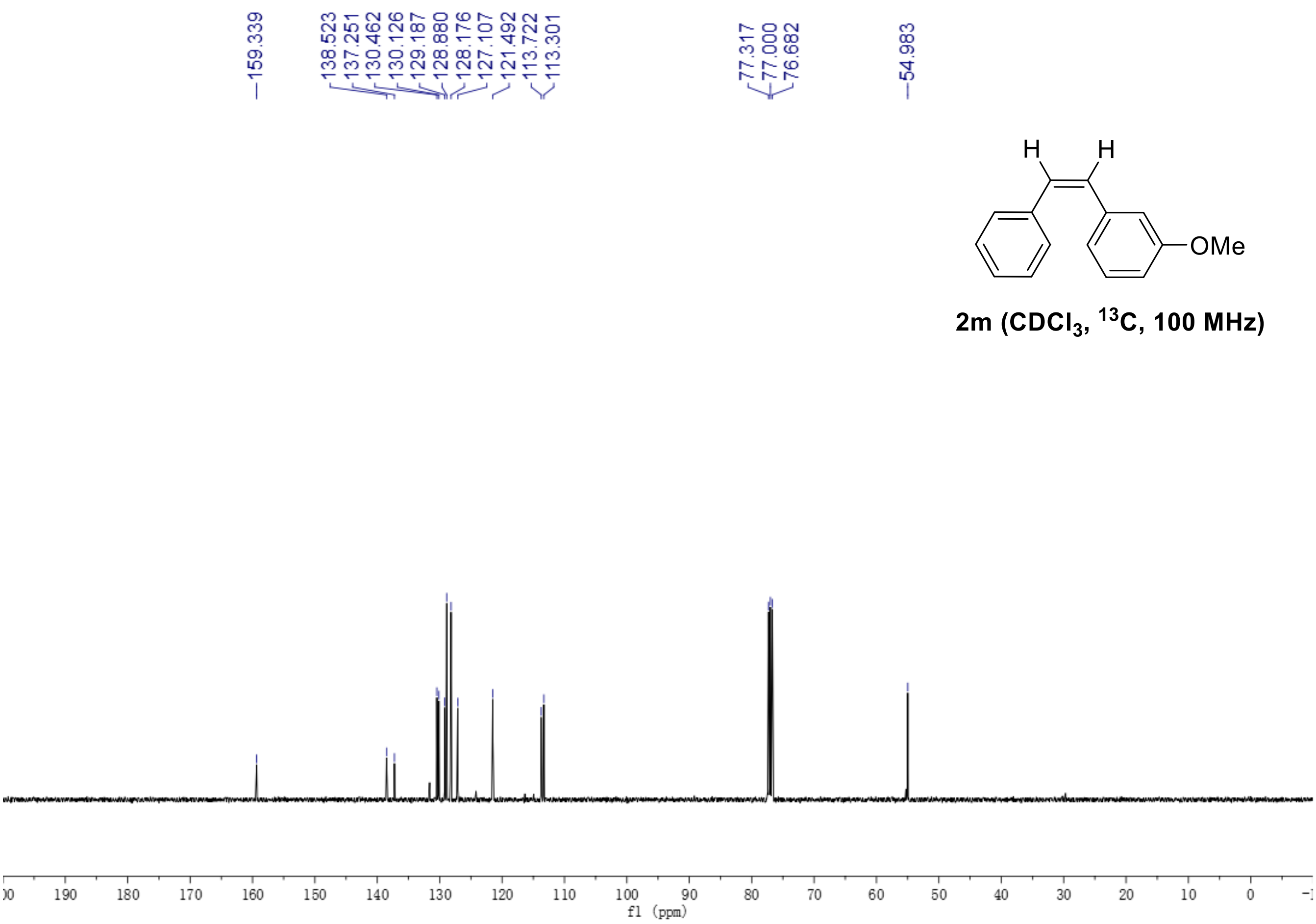
2m (CDCl$_3$, ^{1}H, 400 MHz) **3m (CDCl$_3$, ^{1}H, 400 MHz)**



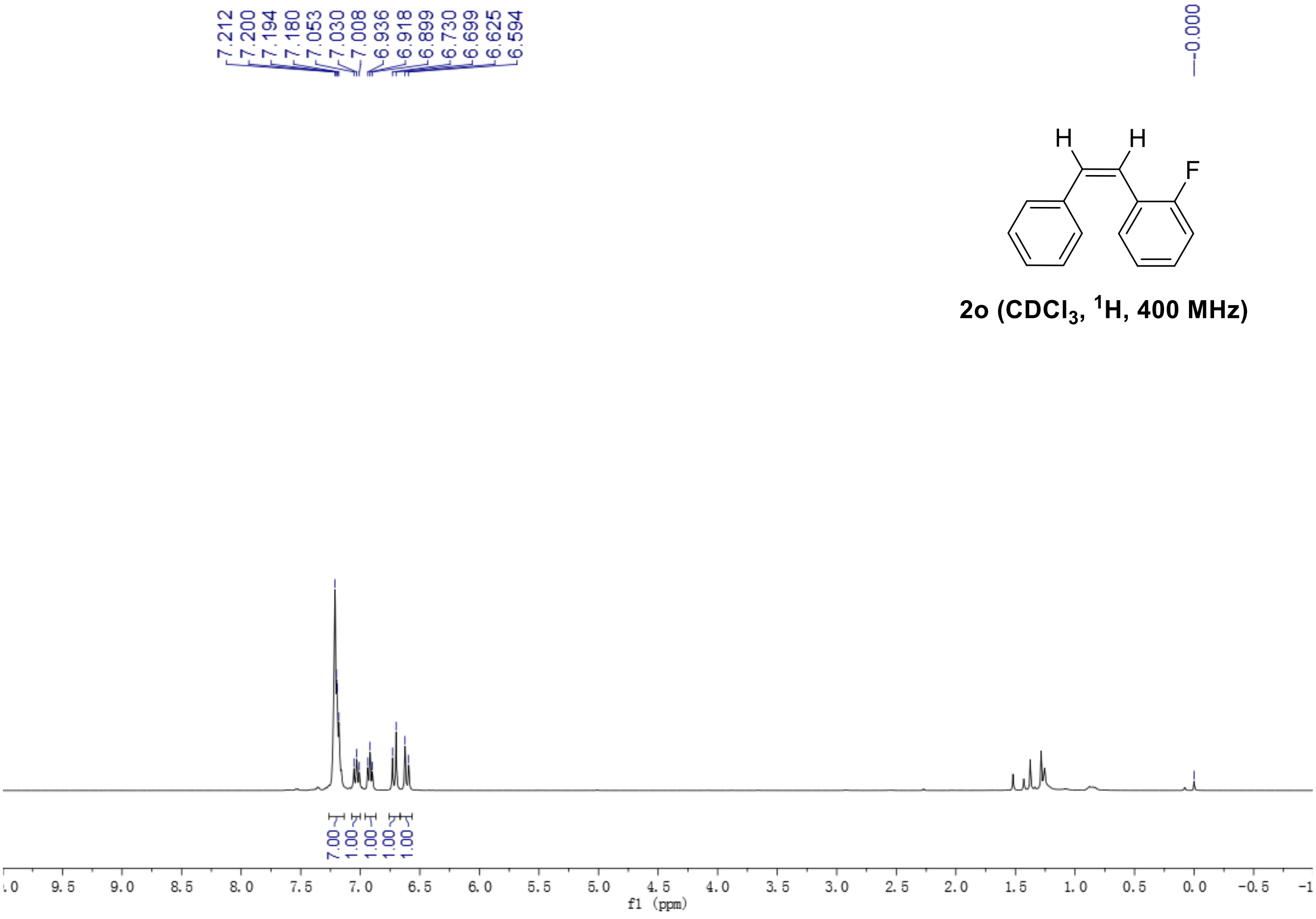


2m (CDCl$_3$, ^{1}H, 400 MHz)

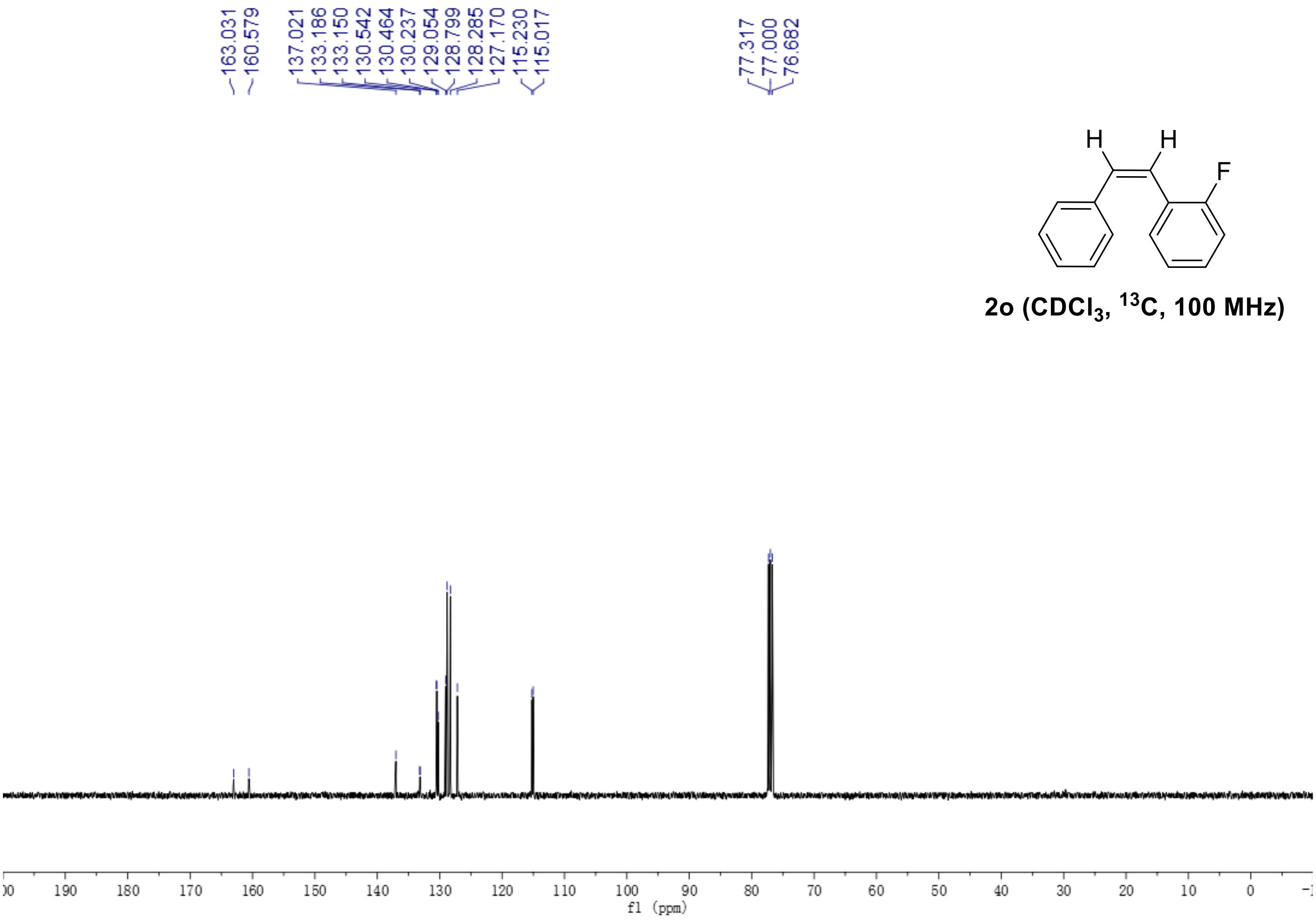




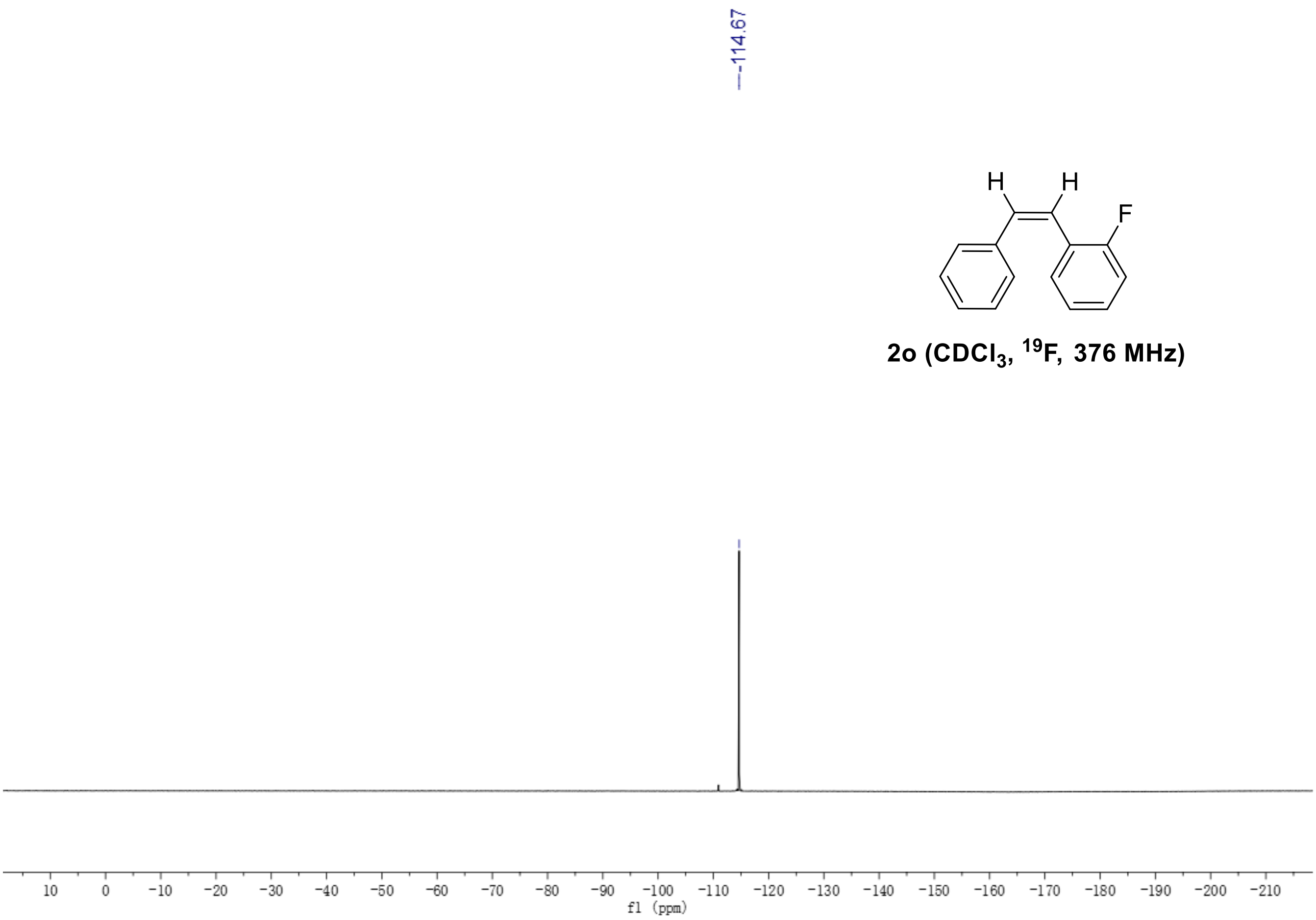
2m ($CDCl_3$, ^{13}C, 100 MHz)



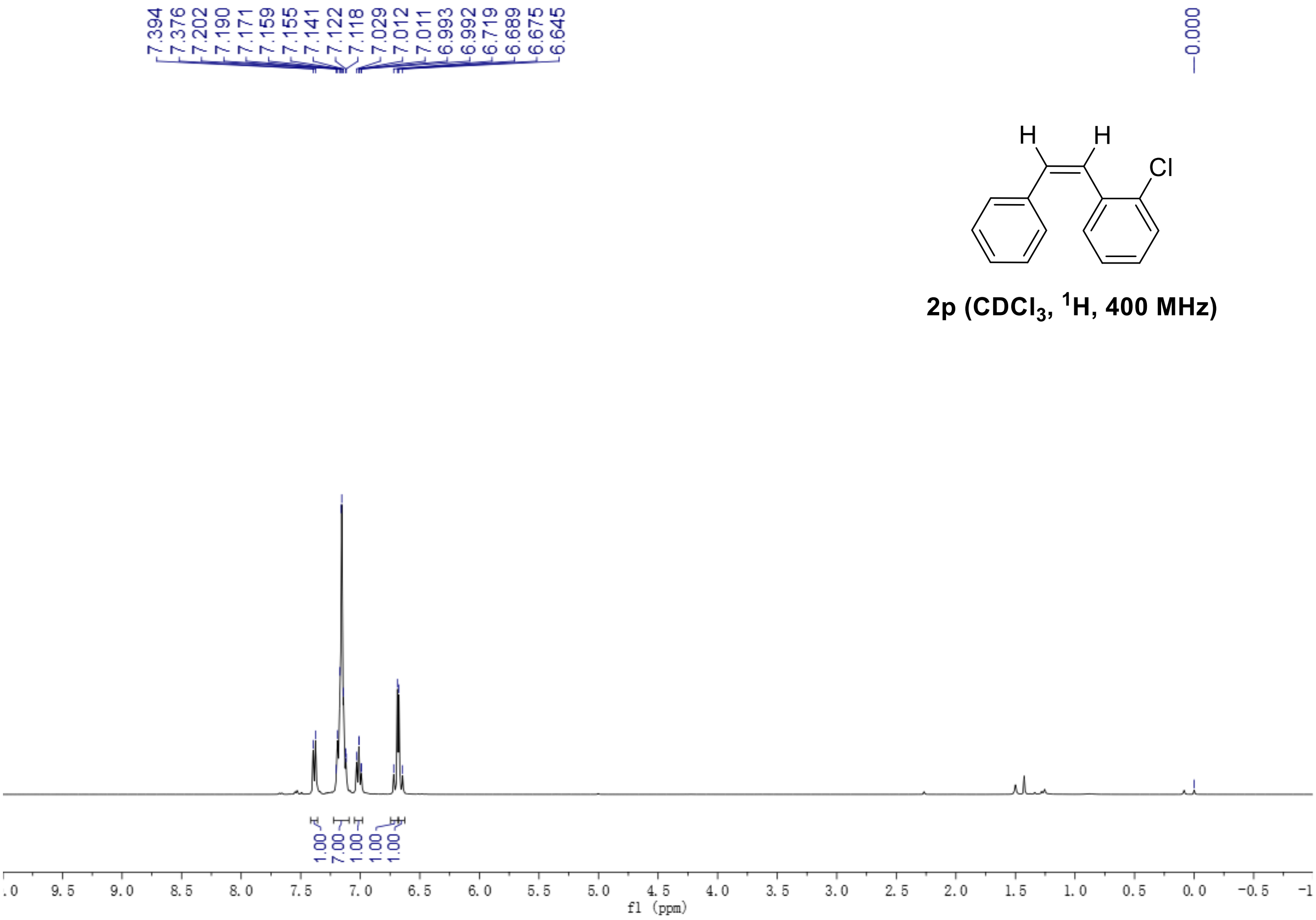
2o ($CDCl_3$, ^{1}H, 400 MHz)



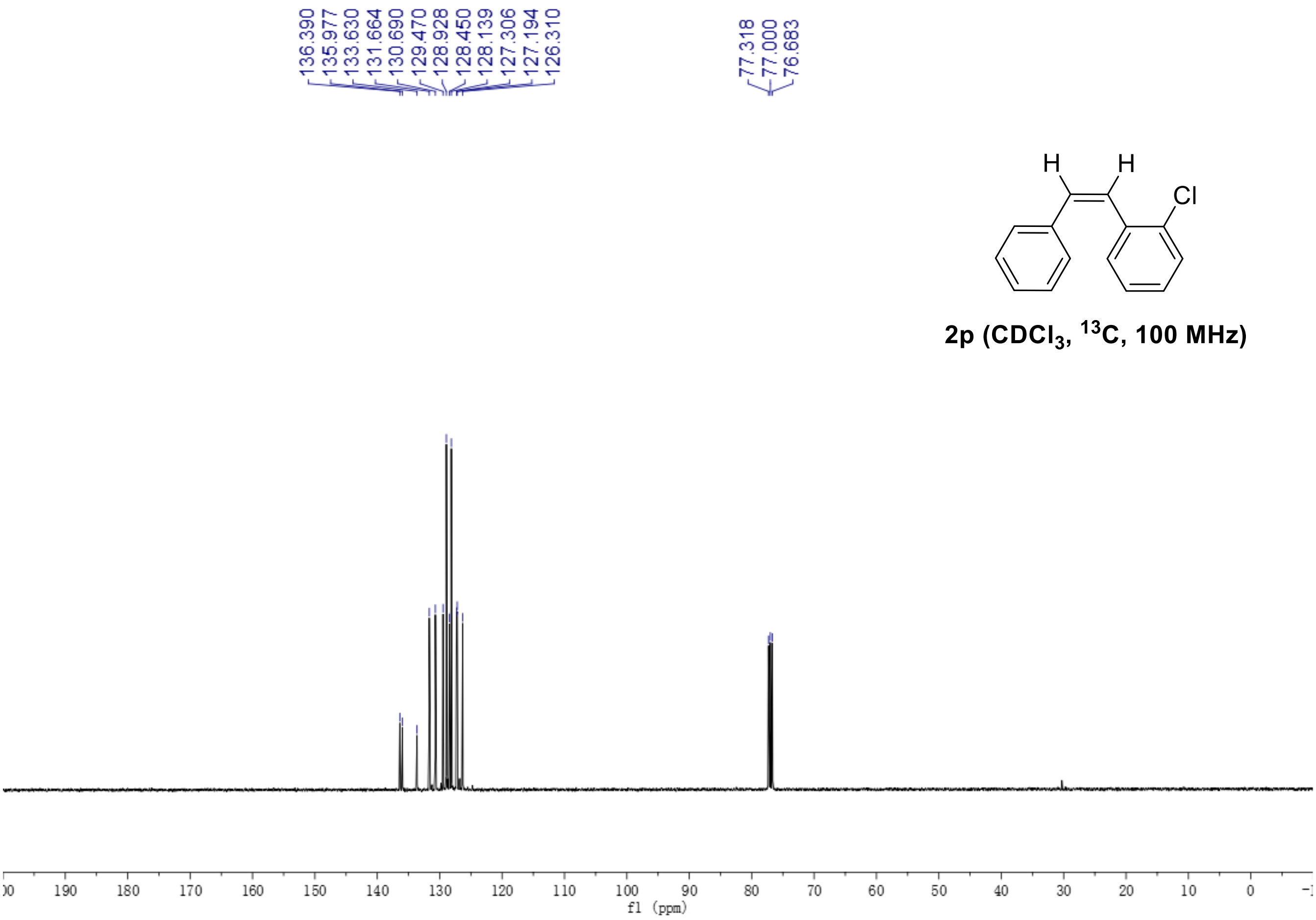
2o (CDCl$_3$, ^{13}C, 100 MHz)



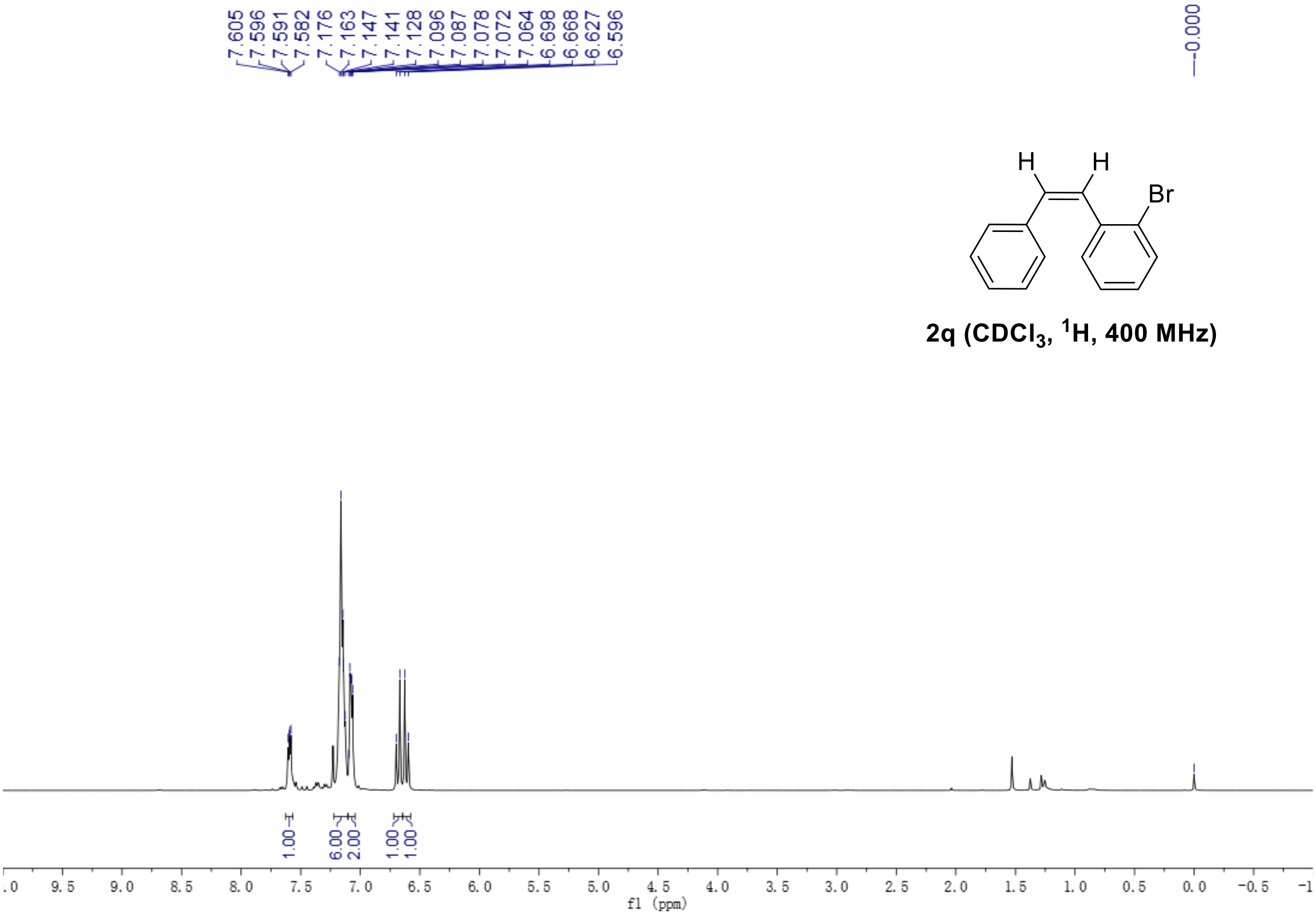
2o (CDCl$_3$, ^{19}F, 376 MHz)



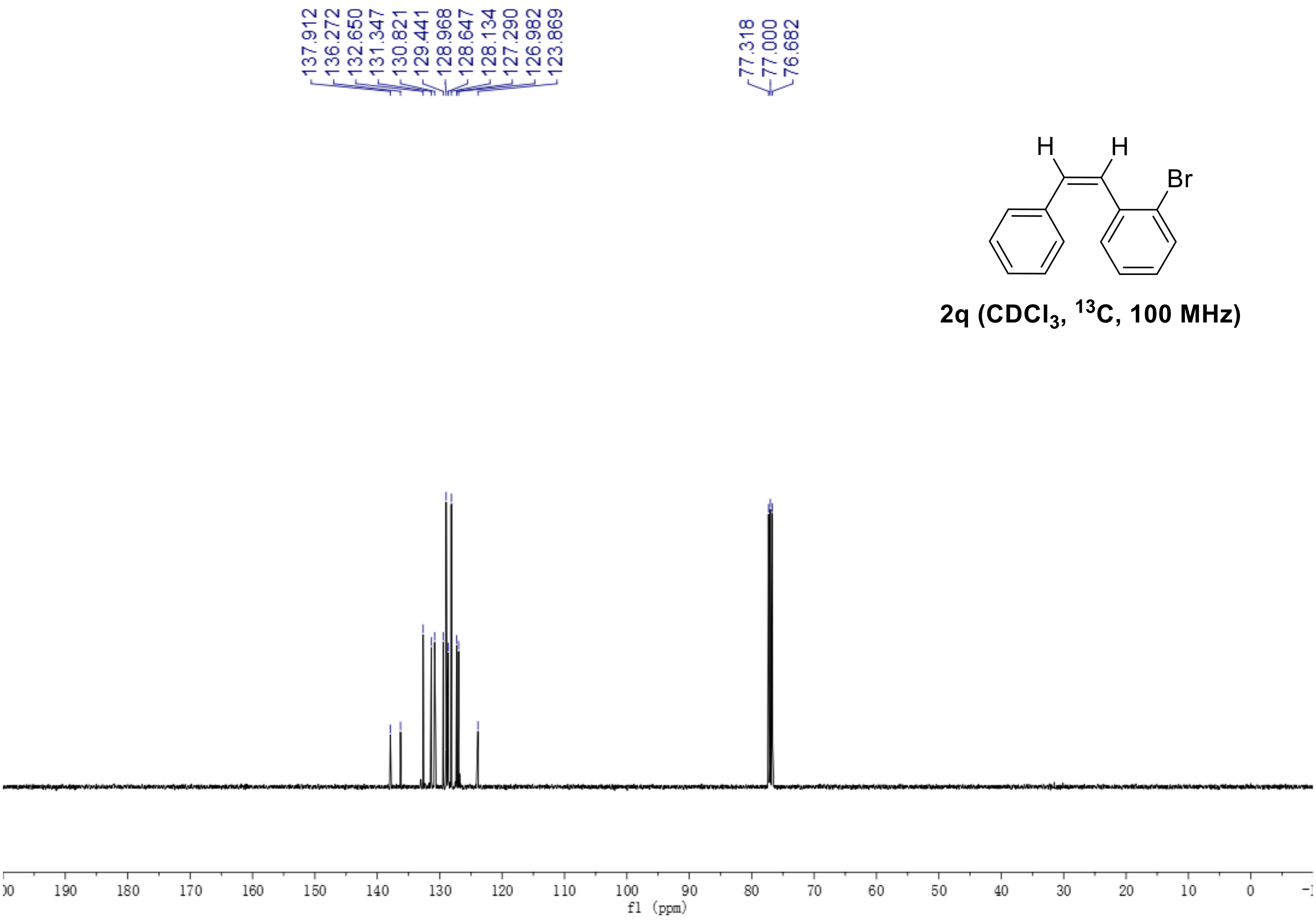
2p ($CDCl_3$, ^1H, 400 MHz)



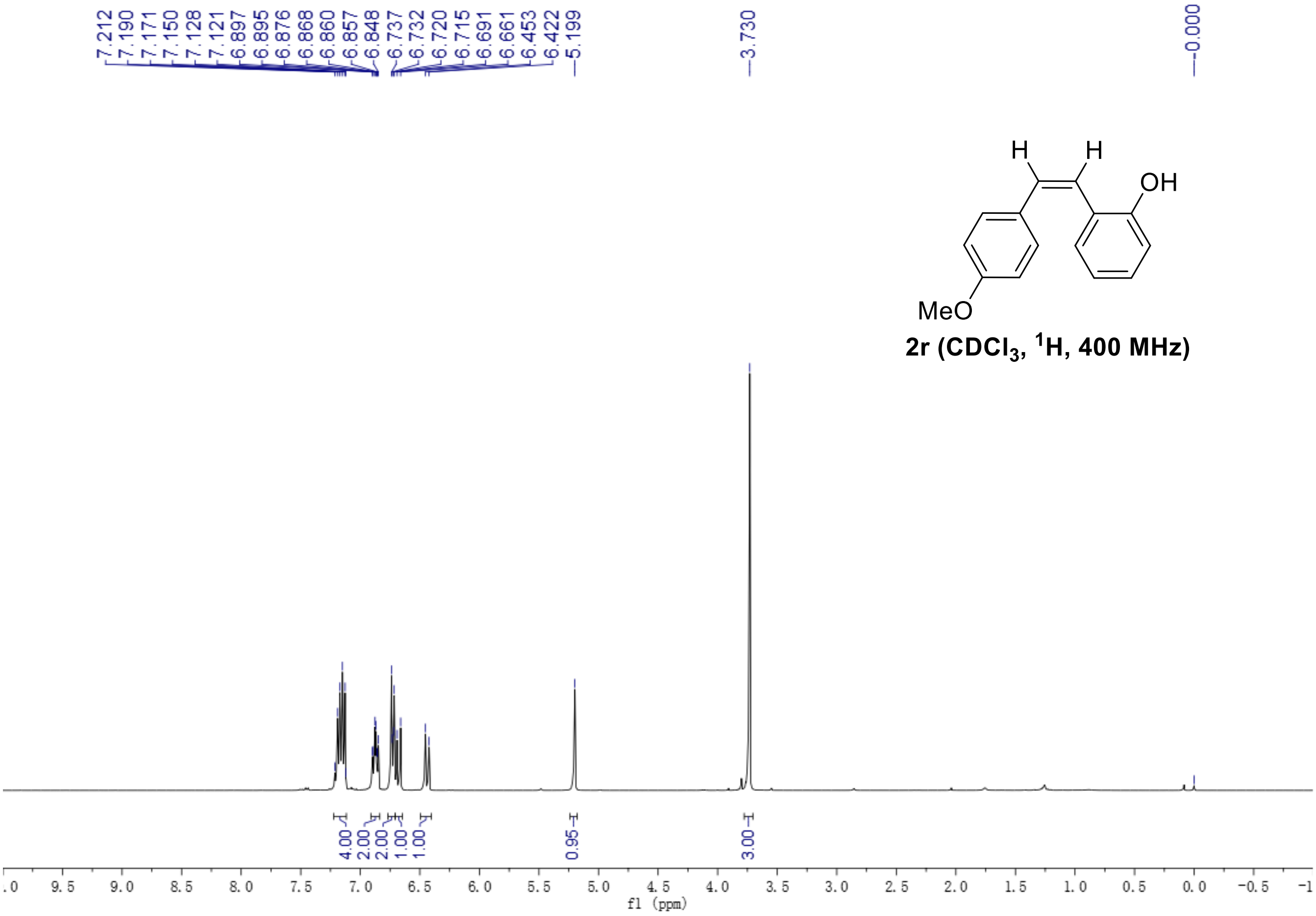
2p ($CDCl_3$, ^{13}C, 100 MHz)



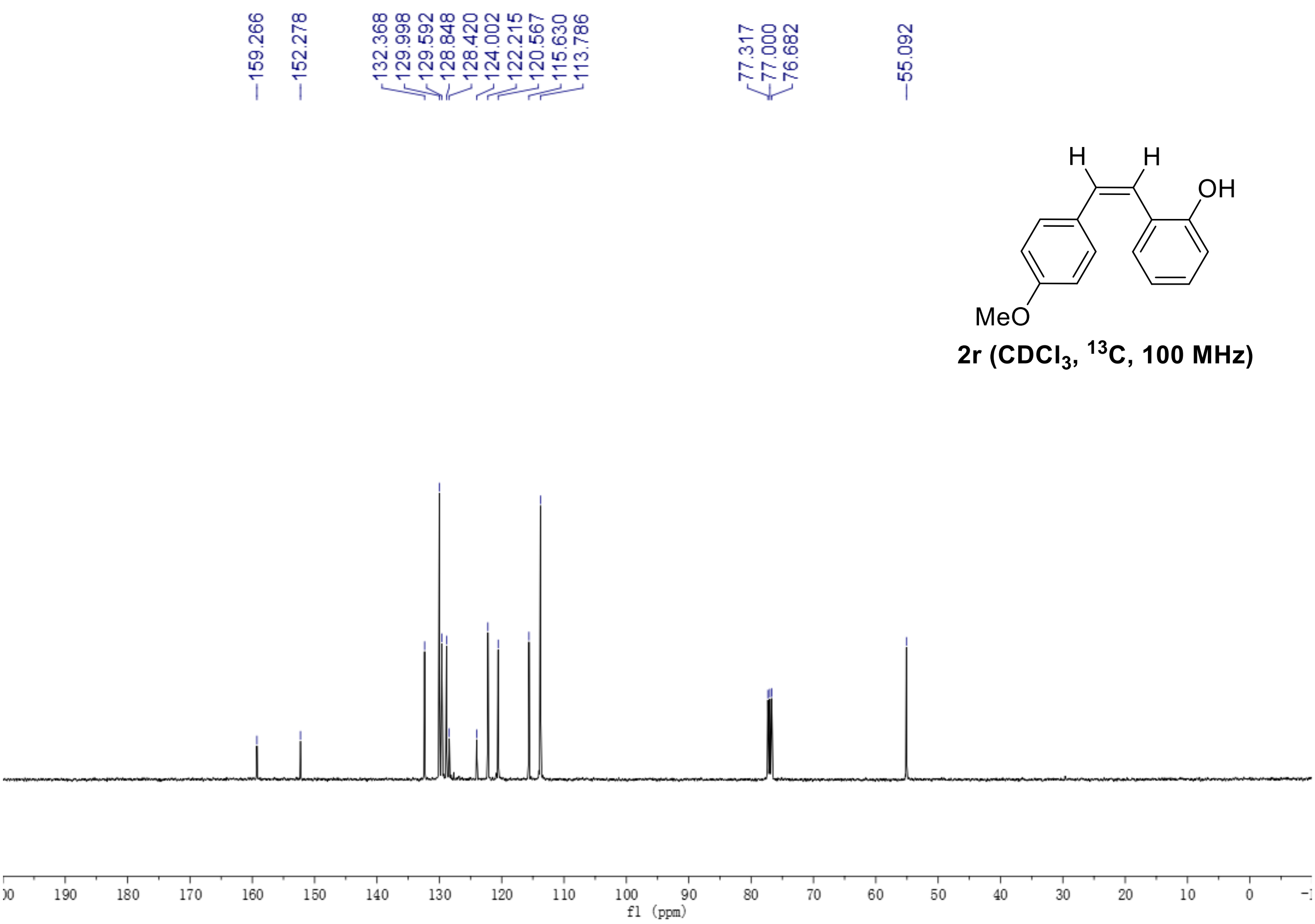
2q (CDCl$_3$, ^{1}H, 400 MHz)



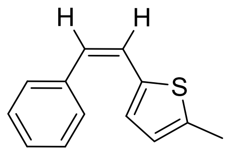
2q (CDCl$_3$, ^{13}C, 100 MHz)



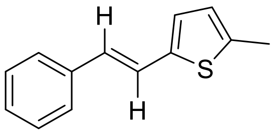
7.212
7.190
7.171
7.150
7.128
7.121
6.897
6.895
6.876
6.868
6.860
6.857
6.848
6.737
6.732
6.720
6.715
6.691
6.661
6.453
6.422
5.199
3.730
0.000
H
H
OH
MeO
2r (CDCl3, 1H, 400 MHz)
4.00
2.00
2.00
1.00
1.00
0.95
3.00
f1 (ppm)



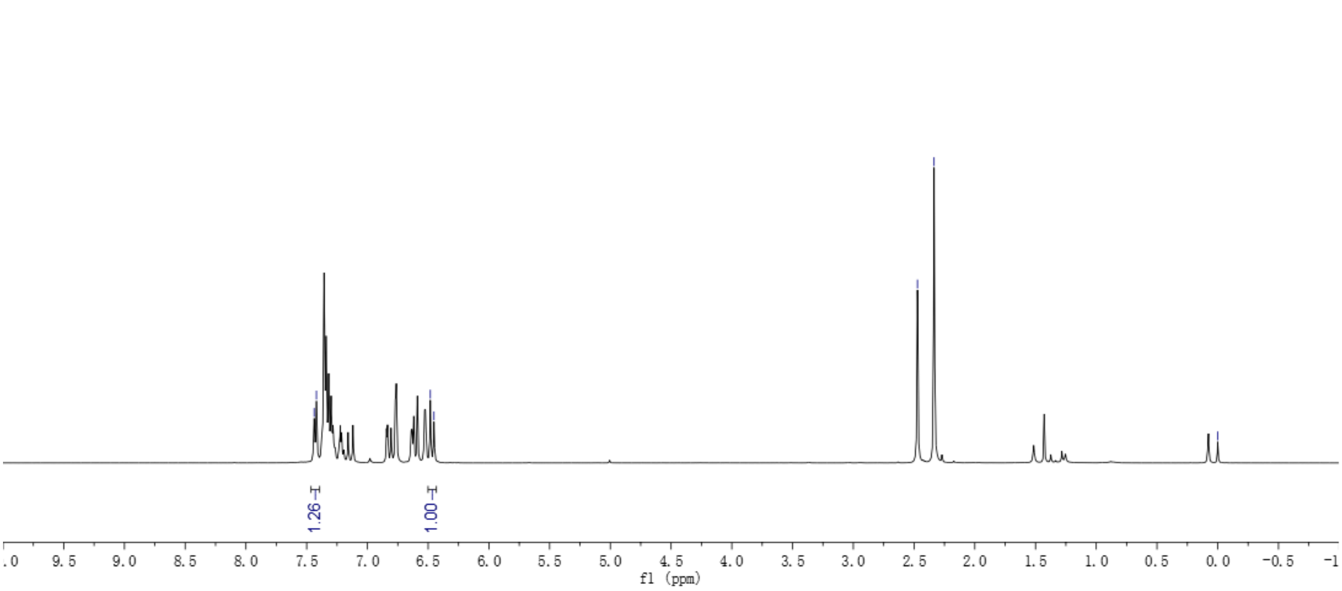
159.266
152.278
132.368
129.998
129.592
128.848
128.420
124.002
122.215
120.567
115.630
113.786
77.317
77.000
76.682
55.092
H
H
OH
MeO
2r (CDCl3, 13C, 100 MHz)
f1 (ppm)

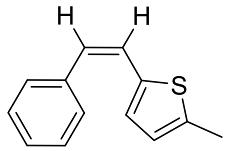


and

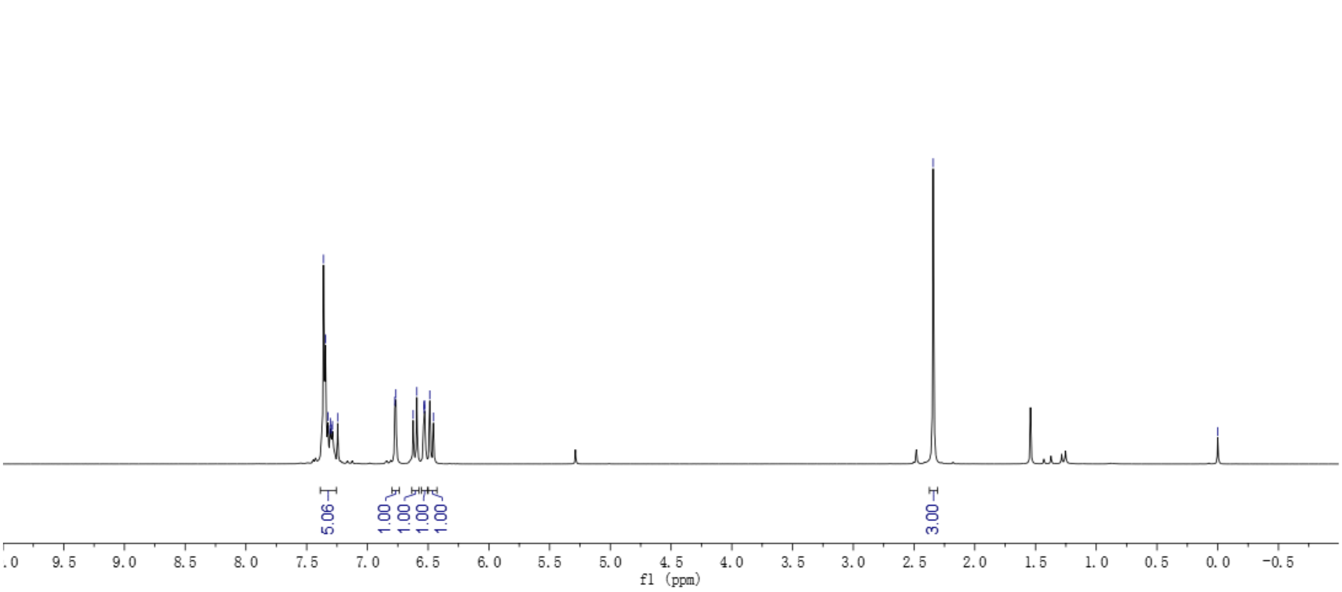


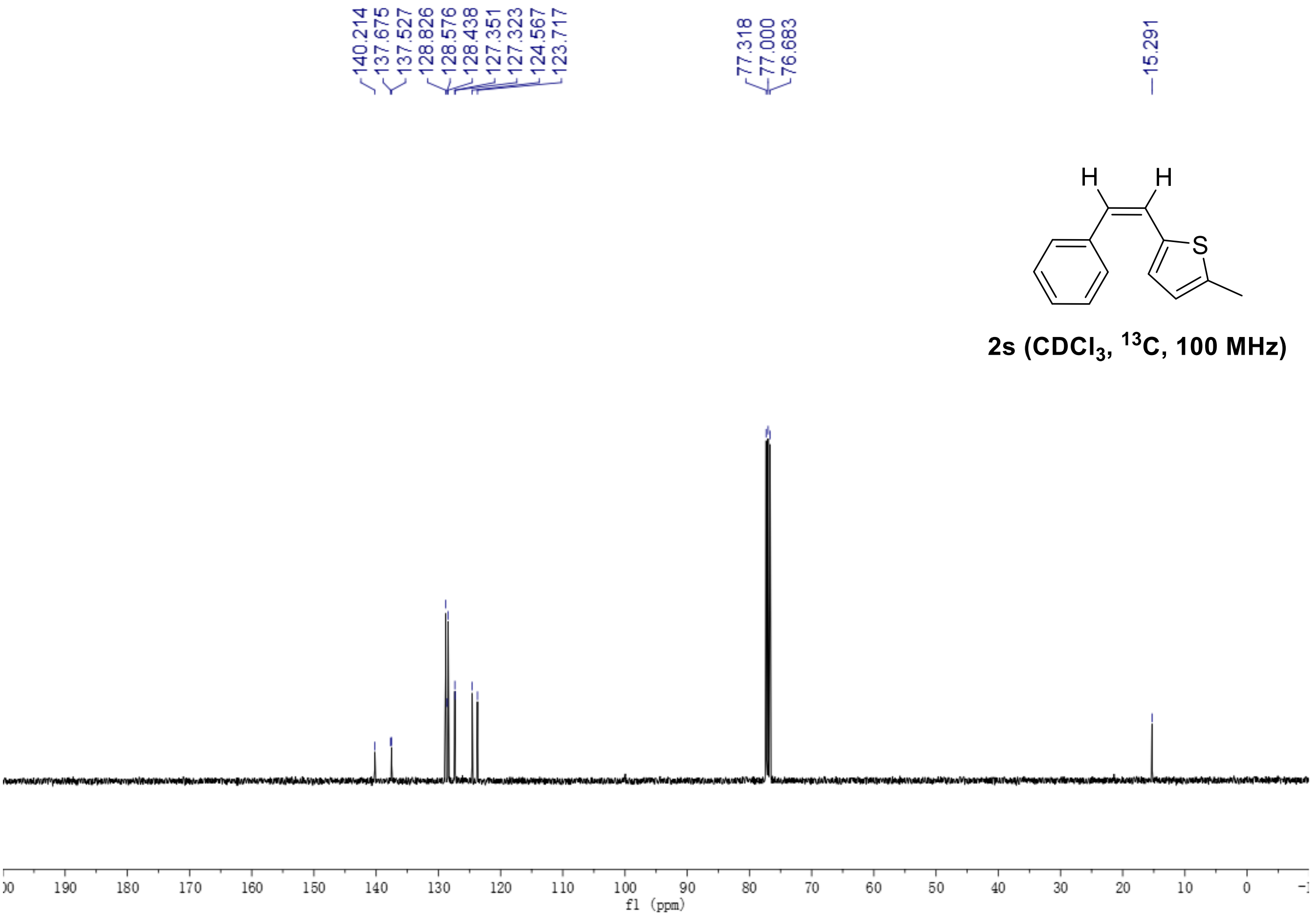
2s ($CDCl_3$, ^1H, 400 MHz) **3s ($CDCl_3$, ^1H, 400 MHz)**



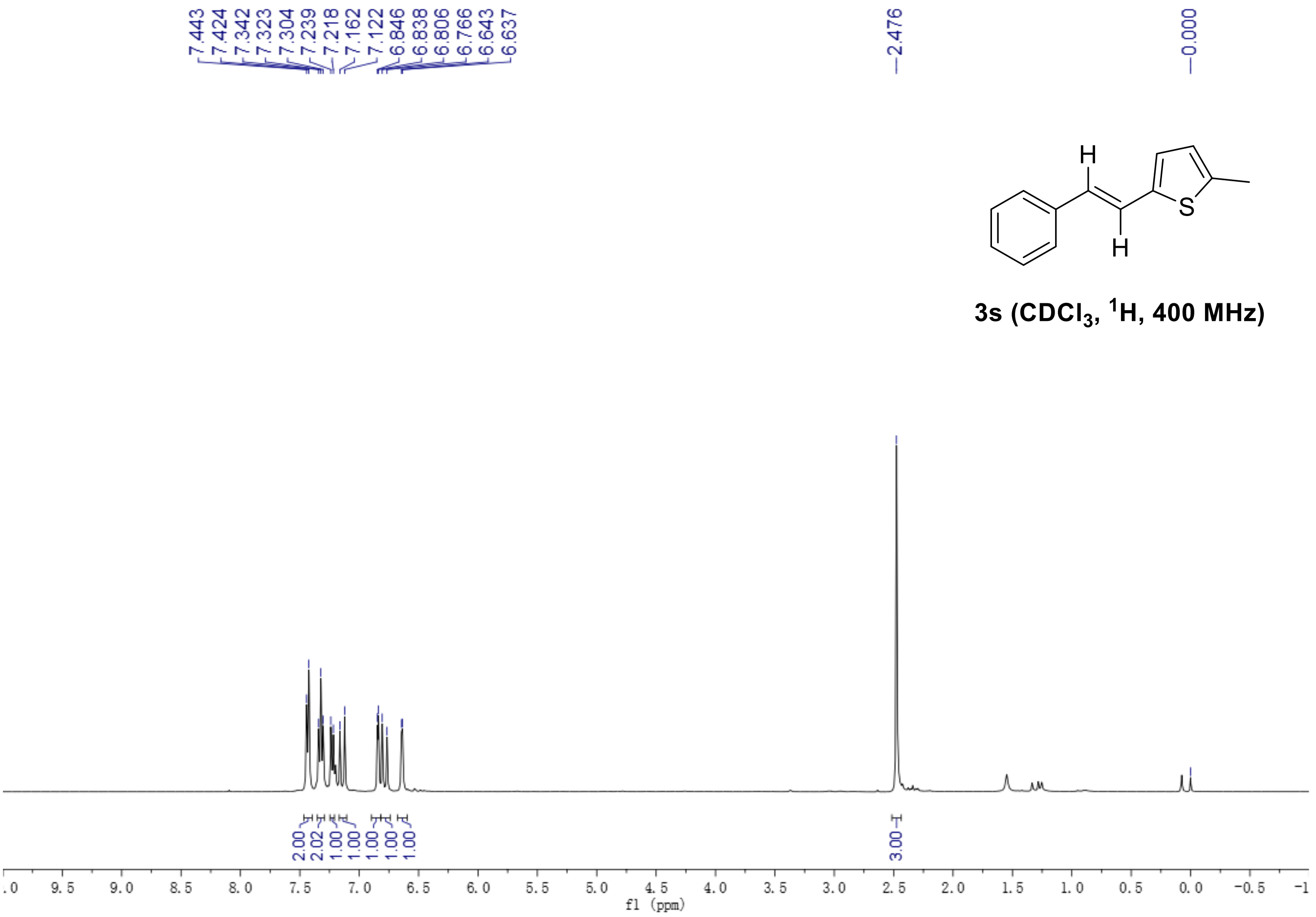


2s ($CDCl_3$, ^1H, 400 MHz)

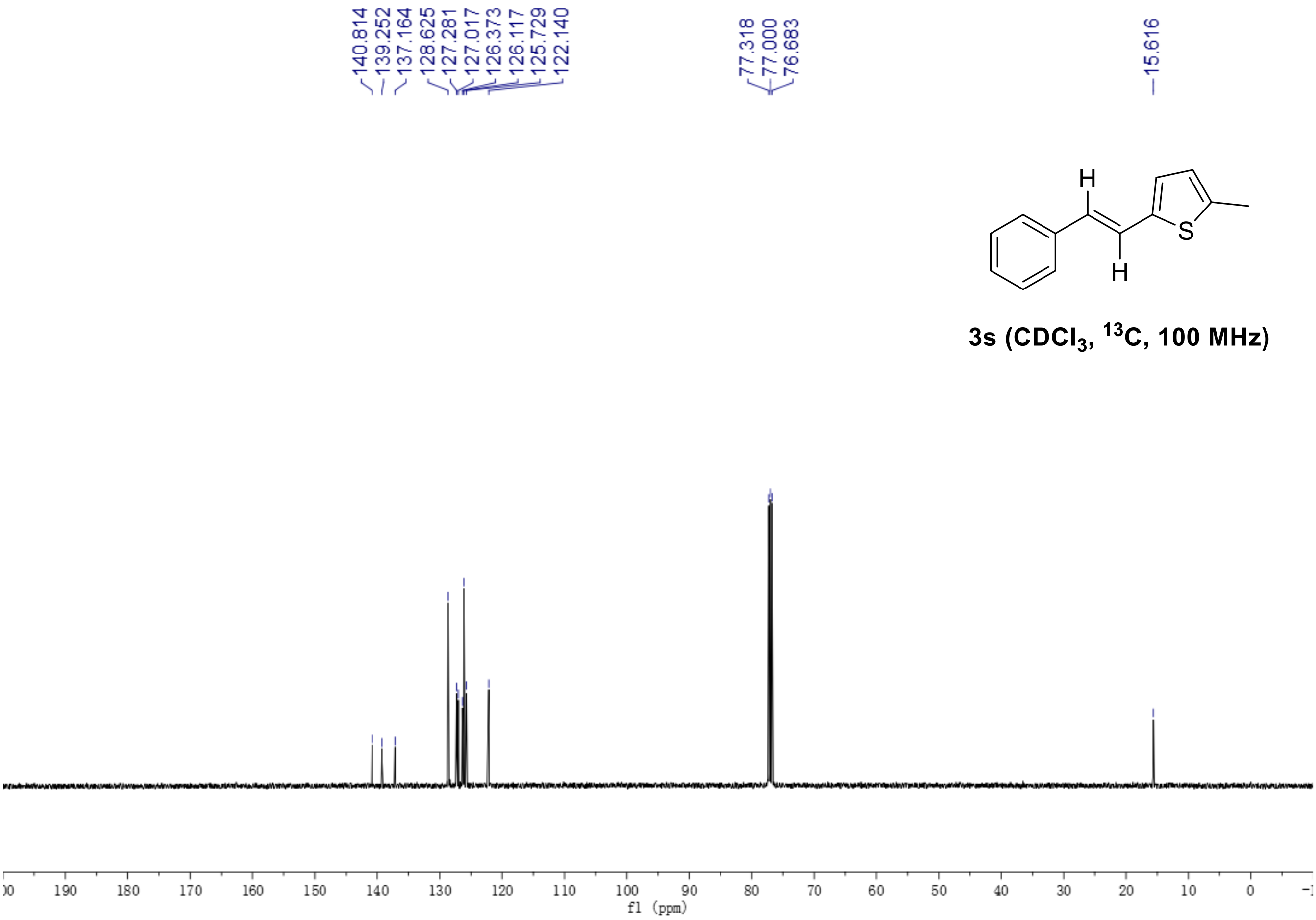




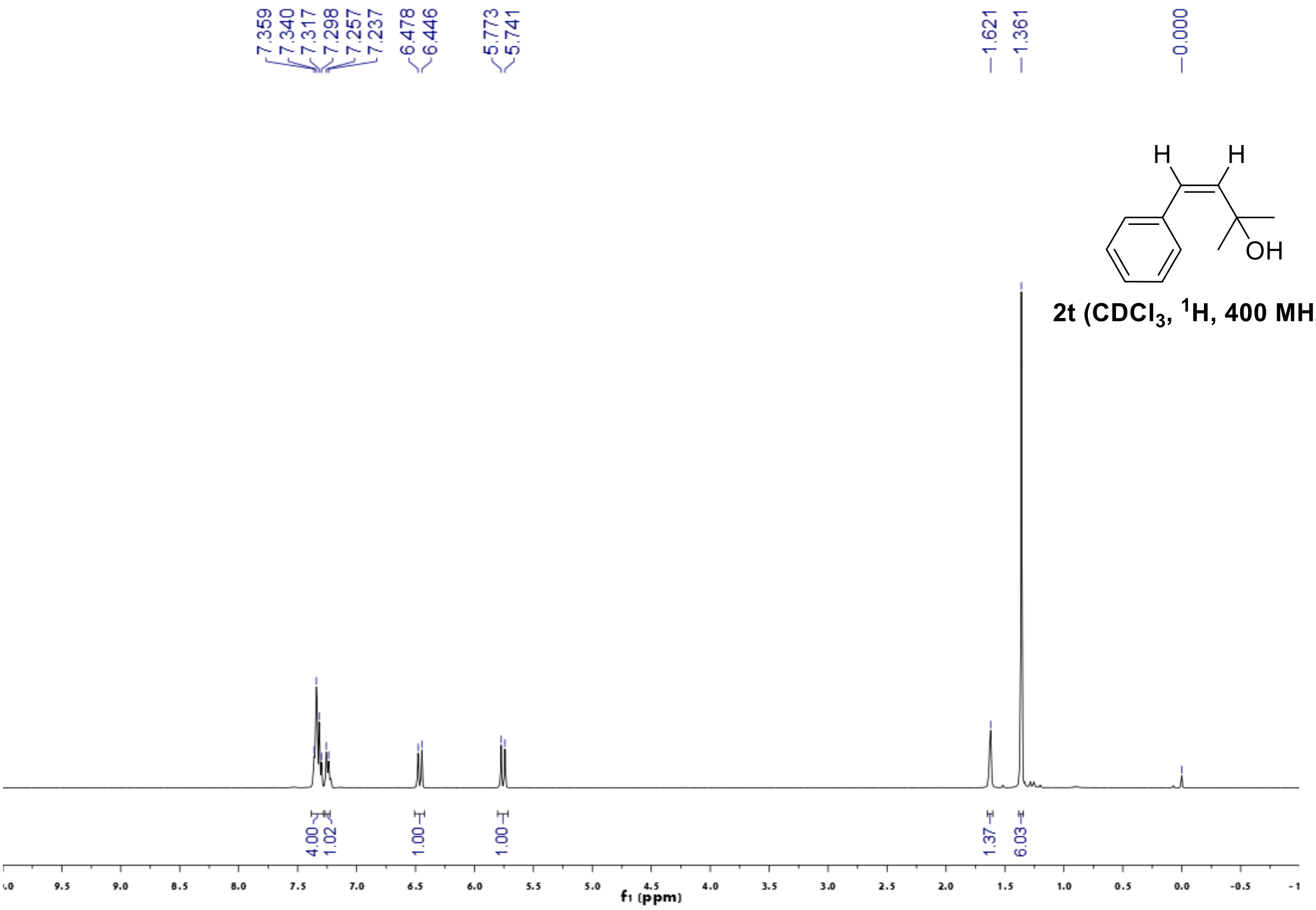
2s ($CDCl_3$, ^{13}C, 100 MHz)



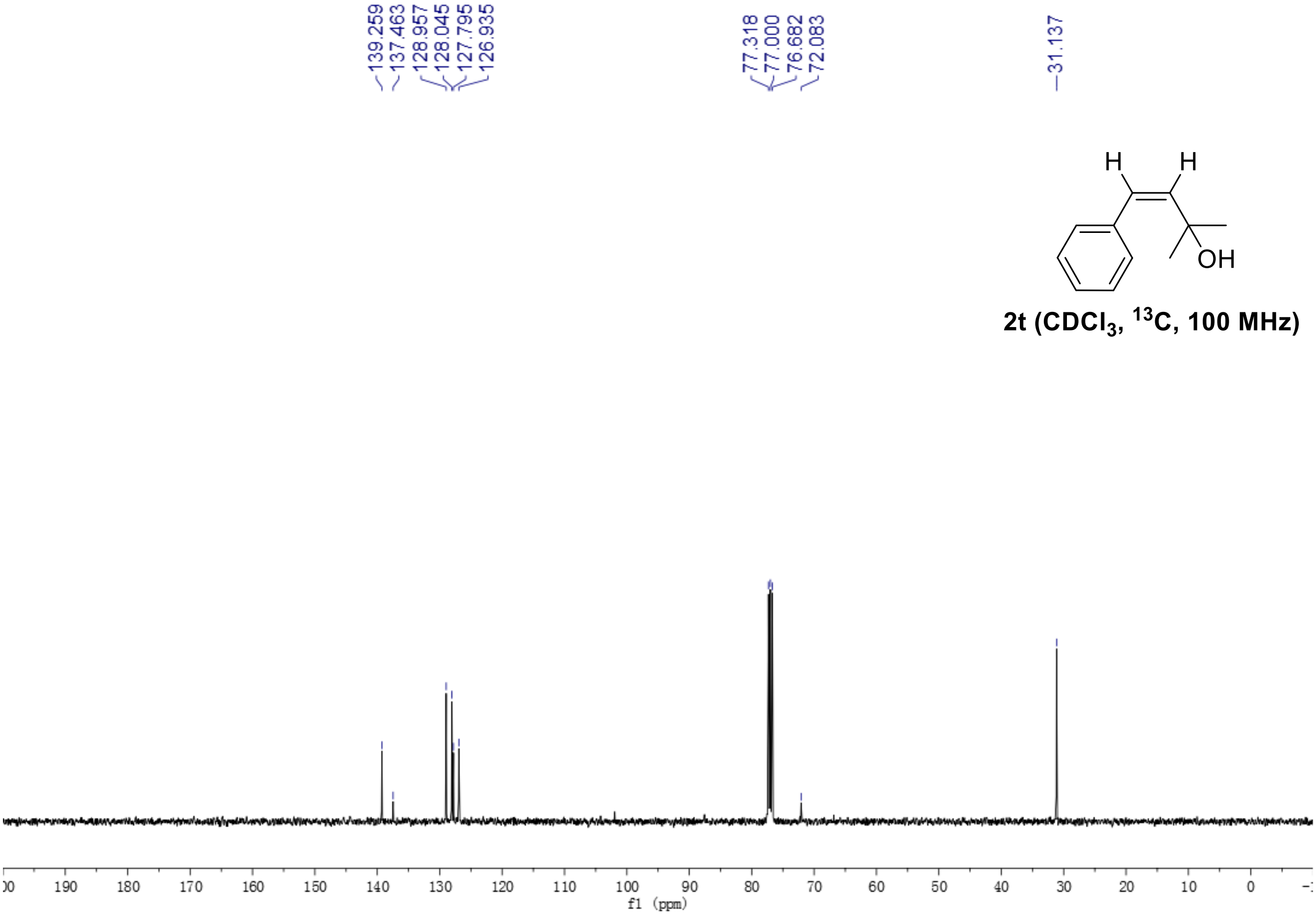
3s ($CDCl_3$, ^{1}H, 400 MHz)



3s ($CDCl_3$, ^{13}C, 100 MHz)



2t ($CDCl_3$, ^{1}H, 400 MHz)


139.259
137.463
128.957
128.045
127.795
126.935
77.318
77.000
76.682
72.083
31.137
H
H
OH
2t (CDCl3, 13C, 100 MHz)
f1 (ppm)

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