

## Supporting Information

### Chemoselective Luche-Type Reduction of $\alpha,\beta$ -unsaturated Ketones by Organoaluminum Catalysis

Ben Yan,<sup>a</sup> Xiaoli Ma,<sup>\*a</sup> Ziyuan Pang<sup>a</sup> and Zhi Yang<sup>\*a</sup>

<sup>a</sup> School of Chemistry and Chemical Engineering, Beijing Institute of Technology,  
Beijing 100081, P. R. China

#### Table of Contents

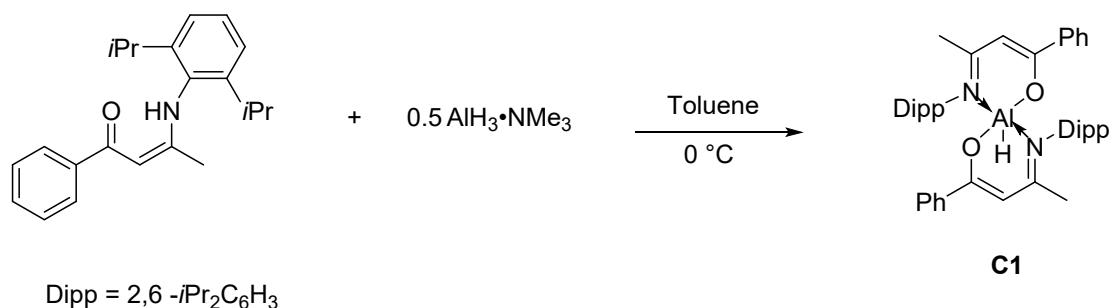
General considerations: .....	2
Synthesis of Aluminum Hydrides C1 .....	2
a) Method for preparation of C1 .....	2
b) Single Crystal X-ray Structure and Refinement .....	4
General procedure for the Al-catalyzed hydroboration of $\alpha,\beta$ -unsaturated ketones .....	5
Mechanistic control experiment .....	9
a) The study of stoichiometric reaction and 1a .....	9
b) The verification of BH <sub>3</sub> generation from the reaction of C1 and HBpin. ....	10
c) The study of the effect of BH <sub>3</sub> on the hydroboration reaction of enone .....	11
<sup>1</sup> H and <sup>13</sup> C NMR spectra of alcohols .....	13
Refences .....	29

## General considerations:

All manipulations were carried out under a purified nitrogen atmosphere using Schlenk techniques or inside a Mbraun MB 150-GI glove box. All solvents were refluxed over the appropriate drying agent and distilled prior to use. Commercially available chemicals were purchased from J&K chemical or Aldrich and used as received.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded with a Varian Mercury Plus 400 MHz or Bruker Avance III 600 MHz spectrometer. The elemental analyses were performed by the Analytical Instrumentation Center of the Beijing Institute of Technology. Melting points were measured in sealed glass tubes. Compound **C2** and **C3** were prepared according to the literature procedures.<sup>[1-2]</sup> CCDC- 2293553 (**C1**) contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

## Synthesis of Aluminum Hydrides C1

Scheme S1. Synthesis of Aluminum Hydride Complex C1



### a) Method for preparation of C1

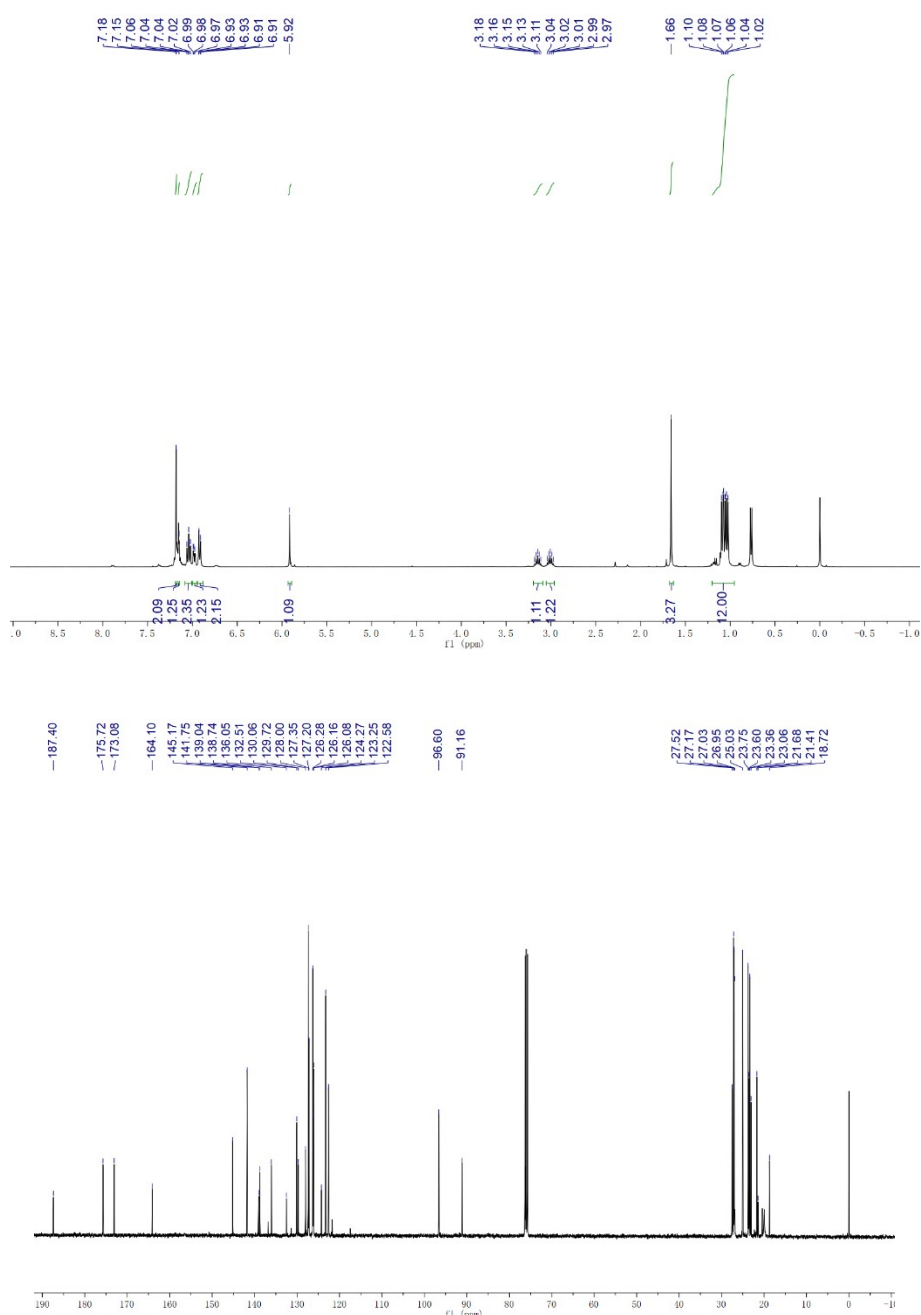
A solution of LH (L = PhCOCHC(Me)NHAr, Ar = 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) (0.321 g, 1 mmol) in toluene (10 mL) was added at ice bath to a solution of AlH<sub>3</sub>·NMe<sub>3</sub> (0.045 g, 0.5 mmol) in toluene (2 mL) under nitrogen atmosphere, and the reaction mixture was stirred for additional 24 h, concentrated to 5 mL and stored overnight at -25 °C. The crude product was crystallized from toluene to afford colorless crystals of **C1** and dried in vacuo. (0.53 g, yield 80% based on LH); m.p. 168~170 °C.

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.18 (s, 2H, Ar-*H*), 7.15 (s, 1H, Ar-*H*), 7.04 (dd,  $J = 8.5, 7.1$  Hz, 2H, Ar-*H*), 7.00 – 6.96 (m, 1H, Ar-*H*), 6.94 – 6.86 (m, 2H, Ar-*H*), 5.92 (s, 1H,  $\gamma$ -CH), 3.15 (p,  $J = 6.9$  Hz, 1H, CHMe<sub>2</sub>), 3.01 (p,  $J = 6.8$  Hz, 1H, CHMe<sub>2</sub>), 1.66 (s, 3H, CH<sub>3</sub>), 1.14 – 0.93 (m, 12H, CHMe<sub>2</sub>).

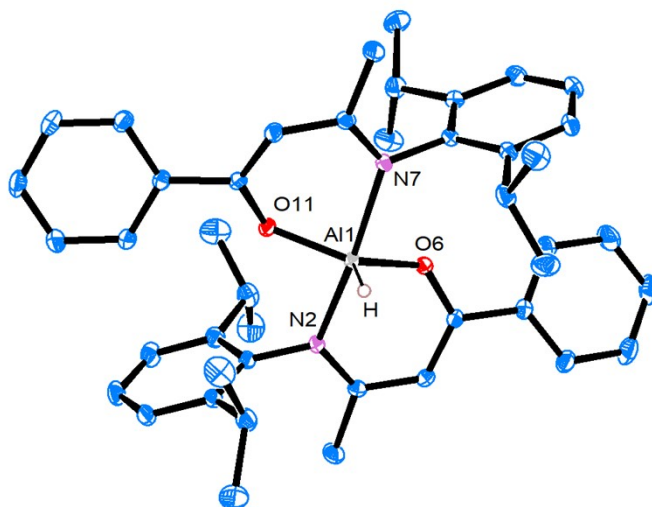
$^{13}\text{C}$  NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  187.40, 175.72 (C(Ph)OAl), 173.08, 164.10 (MeCNAI), 145.17, 141.75, 139.04, 138.74, 136.05, 132.51, 130.06, 129.72, 128.00, 127.35, 127.20, 126.28, 126.16, 126.08, 124.27, 123.25, 122.58 (Ar-C), 96.60, 91.16 ( $\gamma$ -CH), 27.52, 27.17, 27.03, 26.95 (CHMe<sub>2</sub>), 25.03, 23.75, 23.60, 23.36, 23.06, 21.68 (CHMe<sub>2</sub>), 21.41, 18.72 (N=C(CH<sub>3</sub>)).

Elemental analysis (%) for C<sub>44</sub>H<sub>52</sub>AlN<sub>2</sub>O<sub>2</sub>: Calcd C 79.13 H 7.85 N 4.19; Found C 79.18 H 7.78 N 4.13

**Scheme S2.**  $^1\text{H}$  (top) and  $^{13}\text{C}$  NMR (bottom) (CDCl<sub>3</sub>, 298 K) of Compound C1



## b) Single Crystal X-ray Structure and Refinement



**Figure S1.** Molecular structure of **C1**. Thermal ellipsoids are drawn at the 50% level and the hydrogen atoms are omitted for clarity except those at the aluminum. Selected bond distances (Å) and angles (deg): Al(1)-O(11) 1.8224(10), Al(1)-O(6) 1.8088(10), Al(1)-N(7) 2.0649(11), Al(1)-N(2)-2.0639(11), Al(1)-H 1.494(16), O(11)-Al(1)-N(7) 87.56(4), O(11)-Al(1)-N(2) 86.52(4), O(11)-Al(1)-H 111.2(6), O(6)-Al(1)-O(11) 135.98(5), O(6)-Al(1)-N(7) 85.55(4), O(6)-Al(1)-N(2) 88.09(4), O(6)-Al(1)-H 112.8(6), N(7)-Al(1)-H 97.6(6), N(2)-Al(1)-N(7) 163.55(5) N(2)-Al(1)-H 98.8(6).

The single crystal of **C1** was mounted with glue on a glass fiber and crystal data were collected on the Rigaku AFC10 Saturn724 + (2 × 2 bin mode) diffractometer equipped with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Empirical absorption correction was applied using the SADABS program.<sup>[3]</sup> The structure was solved by direct methods.<sup>[4]</sup> and refined by full-matrix least squares on  $F^2$  using the SHELXL-97 program.<sup>[5]</sup> The summary of the crystal data was given in Table S1.

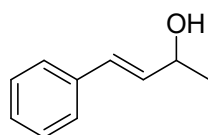
Table S1	<b>C1</b>
Empirical formula	C <sub>44</sub> H <sub>52</sub> AlN <sub>2</sub> O <sub>2</sub>
Formula weight	667.85
Temperature (K)	180.00
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	<i>P</i> 21/n
<i>a</i> (Å)	11.3973(4)
<i>b</i> (Å)	8.7653(3)
<i>c</i> (Å)	38.0302(14)
$\alpha$ (°)	90
$\beta$ (°)	90.076(3)
$\gamma$ (°)	90

V (Å <sup>3</sup> )	3799.2(2)
Z	4
$\rho$ c (g/cm <sup>3</sup> )	1.168
Absorption coefficient (mm <sup>-1</sup> )	0.092
F(000)	1.436
Crystal size(mm <sup>3</sup> )	0.15×0.1×0.1
$\theta$ range for data collection(°)	4.284 to 62.002
Index ranges	-14 ≤ h ≤ 14 -11 ≤ k ≤ 9 -45 ≤ l ≤ 49
Reflections collected	22199
R (int)	0.0296
Data / restraints / parameters	8834/0/452
Goodness-of-fit on $F^2$	1.082
$R1a, wR2b(I > 2\sigma(I))$	0.0451, 0.1210
$R1a, wR2b(\text{all data})$	0.0624, 0.1303
Largest diff. peak/hole [eÅ <sup>-3</sup> ]	0.70/-0.31

## General procedure for the Al-catalyzed hydroboration of $\alpha,\beta$ -unsaturated ketones

A nitrogen filled oven-dried 10 mL tube, equipped with a magnetic stir bar, was charged with the corresponding ketones (0.5mmol). The reaction tube was sealed with a septum and dry toluene (0.5 mL, 1M) followed by HBPIn (1.2 equiv.) were added. Then catalysis **C1** (5 mol%) was added and the reaction was left stirring at 80 °C. After the 12 hours, the reaction mixture was quenched with MeOH (1 mL) and stirred for 30 min. The solvents were removed under reduced pressure and the crude mixture was purified by flash chromatography (SiO<sub>2</sub>, DCM:hexane as eluent system, 50 to 100% DCM in hexane) to afford the pure product.

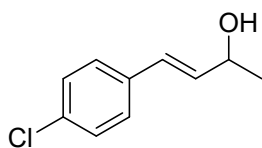
**2a**



<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.28 (d,  $J = 7.2$  Hz, 2H), 7.22 (t,  $J = 7.4$  Hz, 2H), 7.18 – 7.11 (m, 1H), 6.47 (d,  $J = 15.9$  Hz, 1H), 6.17 (dd,  $J = 15.9, 6.4$  Hz, 1H), 4.47 – 4.22 (m, 1H), 1.87 (s, 1H), 1.28 (d,  $J = 6.4$  Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  135.68, 132.55, 128.31, 127.55, 126.58, 125.42, 67.85, 22.37.

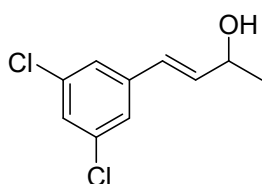
Spectroscopic data are in agreement with the reported values in the literature.<sup>[6]</sup>

2b



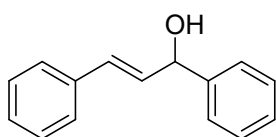
$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.18 (s, 4H), 6.41 (dd,  $J = 15.9, 1.3$  Hz, 1H), 6.13 (dd,  $J = 15.9, 6.2$  Hz, 1H), 4.38 (td,  $J = 6.4, 1.3$  Hz, 1H), 1.99 (s, 1H), 1.27 (d,  $J = 6.4$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  135.25, 134.25, 133.21, 128.74, 128.08, 127.67, 68.72, 23.42.

2c



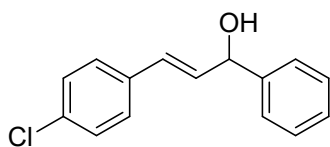
$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.22 (d,  $J = 8.0$  Hz, 2H), 7.00 (t,  $J = 8.1$  Hz, 1H), 6.48 (dd,  $J = 16.3, 1.4$  Hz, 1H), 6.21 (dd,  $J = 16.3, 5.9$  Hz, 1H), 4.47 (pd,  $J = 6.4, 1.4$  Hz, 1H), 2.09 – 1.70 (m, 1H), 1.33 (d,  $J = 6.4$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  141.21, 133.37, 133.24, 127.36, 127.09, 121.61, 67.83, 22.16.

2d



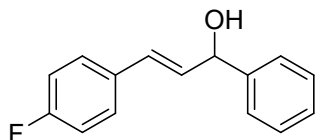
$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.37 – 7.34 (m, 2H), 7.33 – 7.27 (m, 4H), 7.23 (tt,  $J = 7.4, 2.2$  Hz, 3H), 7.18 – 7.12 (m, 1H), 6.61 (d,  $J = 15.9$  Hz, 1H), 6.31 (dd,  $J = 15.9, 6.5$  Hz, 1H), 5.31 (d,  $J = 6.5$  Hz, 1H), 2.00 (s, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  142.79, 136.55, 131.54, 130.59, 128.67, 128.60, 127.85, 127.82, 126.64, 126.38, 75.18.

2e



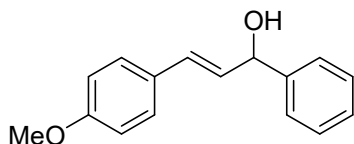
$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.29 (dq,  $J = 3.6, 2.1$  Hz, 2H), 7.26 (t,  $J = 4.4$  Hz, 4H), 7.24 – 7.20 (m, 2H), 7.19 – 7.16 (m, 1H), 6.58 (dd,  $J = 15.9, 1.2$  Hz, 1H), 6.24 (dd,  $J = 15.8, 6.6$  Hz, 1H), 5.27 (d,  $J = 6.6$  Hz, 1H), 2.07 (s, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  140.15, 135.23, 132.45, 130.03, 127.74, 127.70, 127.60, 126.96, 126.68, 125.60, 73.45.

2f



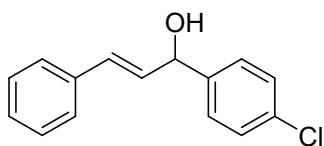
$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.35 – 7.28 (m, 4H), 7.23 (t,  $J$  = 7.4 Hz, 2H), 7.19 – 7.16 (m, 1H), 6.97 (t,  $J$  = 8.7 Hz, 2H), 6.59 (d,  $J$  = 15.8 Hz, 1H), 6.27 (dd,  $J$  = 15.8, 6.5 Hz, 1H), 5.29 (d,  $J$  = 6.5 Hz, 1H), 2.02 (s, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  163.58, 161.14, 138.54, 136.37, 131.33, 130.81, 128.64, 128.12, 127.95, 126.64, 115.56, 115.35, 74.51.

**2g**



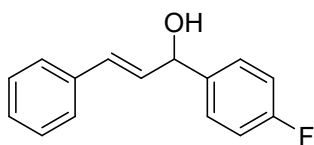
$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.34 – 7.27 (m, 2H), 7.23 (ddd,  $J$  = 7.8, 6.2, 1.4 Hz, 3H), 7.17 (d,  $J$  = 9.4 Hz, 2H), 6.85 – 6.79 (m, 2H), 6.60 (dd,  $J$  = 15.9, 1.3 Hz, 1H), 6.31 (dd,  $J$  = 15.8, 6.3 Hz, 1H), 5.28 (dd,  $J$  = 6.8, 2.7 Hz, 1H), 3.73 (d,  $J$  = 4.0 Hz, 3H), 1.49 (s, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  158.26, 135.59, 133.99, 130.67, 129.18, 127.54, 126.69, 125.57, 125.28, 113.00, 73.66, 54.30.

**2h**



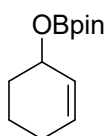
$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.36 – 7.26 (m, 4H), 7.24 – 7.15 (m, 5H), 6.55 (dd,  $J$  = 15.8, 1.3 Hz, 1H), 6.26 (dd,  $J$  = 15.8, 6.3 Hz, 1H), 5.28 (dd,  $J$  = 6.3, 1.3 Hz, 1H), 2.16 – 2.00 (m, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  162.60, 160.15, 141.70, 131.68, 130.24, 128.30, 127.64, 127.14, 127.06, 126.84, 125.29, 114.56, 114.34, 74.02.

**2i**



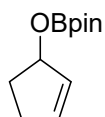
$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.35 – 7.31 (m, 2H), 7.31 – 7.27 (m, 2H), 7.27 – 7.21 (m, 3H), 6.90 (t,  $J$  = 8.7 Hz, 2H), 6.55 (dd,  $J$  = 15.9, 1.3 Hz, 1H), 6.20 (dd,  $J$  = 15.8, 6.5 Hz, 1H), 5.35 – 5.20 (m, 1H), 2.12 (s, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  141.55, 134.02, 132.35, 131.12, 128.15, 127.69, 127.67, 126.90, 126.78, 125.31, 73.95.

**2j**



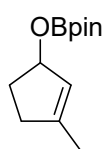
$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  5.76 – 5.67 (m, 1H), 5.65 – 5.57 (m, 1H), 4.48 (d,  $J$  = 5.0 Hz, 1H), 1.92 (dd,  $J$  = 17.2, 11.9 Hz, 1H), 1.83 – 1.64 (m, 3H), 1.64 – 1.53 (m, 1H), 1.53 – 1.41 (m, 1H), 1.18 (s, 24H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  149.54, 129.23, 127.86, 81.52, 67.08, 29.78, 23.90, 23.58, 18.00.

**2k**



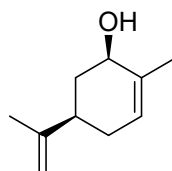
$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  5.97 – 5.85 (m, 1H), 5.73 (dd,  $J$  = 5.5, 2.3 Hz, 1H), 5.10 (dd,  $J$  = 4.3, 2.4 Hz, 1H), 2.52 – 2.33 (m, 1H), 2.24 – 2.07 (m, 2H), 1.69 (dq,  $J$  = 13.0, 3.9 Hz, 1H), 1.18 (s, 12H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  134.22, 130.92, 81.56, 78.76, 31.07, 29.99, 23.60, 23.58.

**2l**



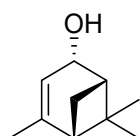
$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  5.35 (s, 1H), 5.12 – 4.92 (m, 1H), 2.35 (dq,  $J$  = 11.0, 5.9 Hz, 1H), 2.17 (d,  $J$  = 7.7 Hz, 1H), 2.07 (s, 1H), 1.68 (s, 3H), 1.18 (d,  $J$  = 8.0 Hz, 12H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  145.87, 130.66, 126.18, 82.84, 82.42, 80.29, 35.14, 33.04, 24.54, 24.49, 16.64.

**2m**



$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  5.50 – 5.32 (m, 1H), 4.67 (s, 2H), 4.20 – 4.04 (m, 1H), 2.26 – 2.15 (m, 1H), 2.09 (ddt,  $J$  = 12.2, 5.9, 2.2 Hz, 1H), 1.99 (tt,  $J$  = 3.4, 1.7 Hz, 1H), 1.93 – 1.82 (m, 1H), 1.69 (dq,  $J$  = 2.8, 1.4 Hz, 3H), 1.67 (d,  $J$  = 1.2 Hz, 2H), 1.52 (d,  $J$  = 5.5 Hz, 1H), 1.47 – 1.37 (m, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  148.99, 136.16, 123.88, 109.15, 70.93, 40.46, 38.03, 31.04, 20.63, 18.95.

**2n**



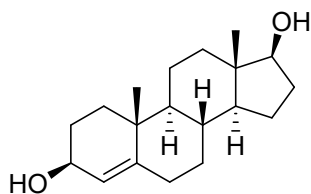
$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  5.30 (dq,  $J$  = 3.1, 1.6 Hz, 1H), 4.39 (td,  $J$  = 3.1, 1.6 Hz, 1H), 2.43 – 2.29 (m, 1H), 2.22 (dd,  $J$  = 3.5, 2.1 Hz, 1H), 1.90 (td,  $J$  = 5.5, 1.4 Hz, 1H), 1.66 (t,



$J = 1.7$  Hz, 3H), 1.64 – 1.58 (m, 1H), 1.28 (s, 3H), 1.24 (d,  $J = 9.1$  Hz, 1H), 1.01 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  147.38, 119.33, 73.56, 48.21, 47.75, 38.95, 35.58, 26.88, 22.64, 22.60.

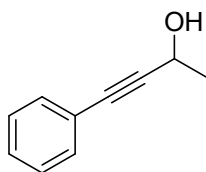
Spectroscopic data are in agreement with the reported values in the literature.<sup>[7,8]</sup>

**2o**



$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  5.28 (s, 1H), 4.14 (d,  $J = 8.0$  Hz, 1H), 3.60 (s, 1H), 2.18 (d,  $J = 13.8$  Hz, 1H), 1.99 (d,  $J = 33.8$  Hz, 6H), 1.89 – 1.68 (m, 3H), 1.65 – 1.33 (m, 4H),  $\delta$  1.64 – 1.34 (m, 10 H). 1.06 (s, 3H), 0.97 – 0.83 (m, 2H), 0.76 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  147.47, 123.53, 81.86, 67.94, 54.60, 50.74, 42.89, 37.43, 36.64, 36.01, 35.43, 32.63, 32.10, 30.52, 29.52, 23.39, 20.64, 18.97, 11.06.

**2p**



$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.49 – 7.40 (m, 2H), 7.30 (dd,  $J = 4.9, 2.1$  Hz, 3H), 4.76 (d,  $J = 6.6$  Hz, 1H), 1.56 (d,  $J = 6.6$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  131.67, 128.40, 128.30, 122.60, 90.94, 84.05, 58.90, 24.42.

## Mechanistic control experiment

### a) The study of stoichiometric reaction of **C1** and **1a**

The stoichiometric reaction of **C1** with benzylideneacetone **1a** (1:1) was performed at room temperature for 24 h under nitrogen atmosphere, solvent toluene was removed in vacuo resulting in a solid containing a mixture of products and then subjected to NMR analysis.

**Scheme S3.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K). Top spectrum, starting material of **C1**, bottom spectrum of the crude product from the reaction of **C1** with **1a**.



CDCl<sub>3</sub>, we can find that a new quadruple peak around  $\delta = -20$  ppm reveals the presence of BH<sub>3</sub>. (Scheme S4 and Figure S2)

**Scheme S4.** The formation of BH<sub>3</sub> from HBpin and C1.

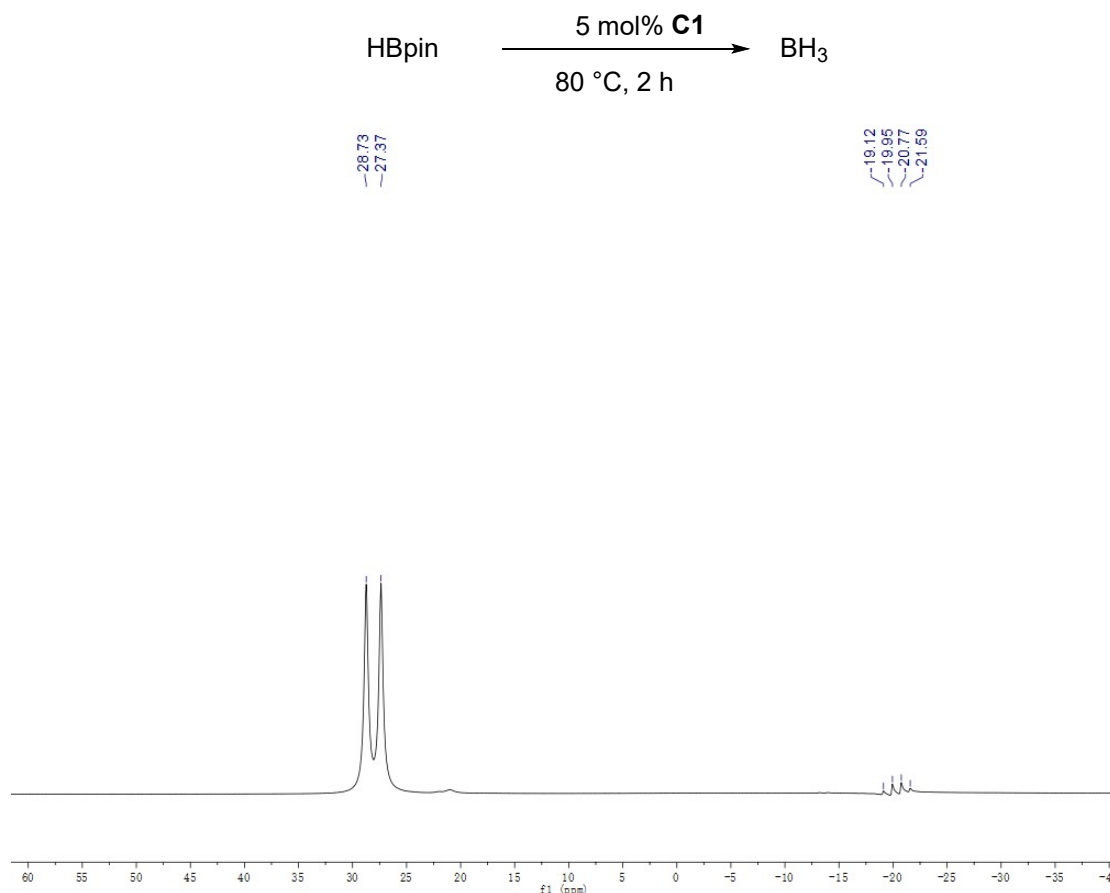
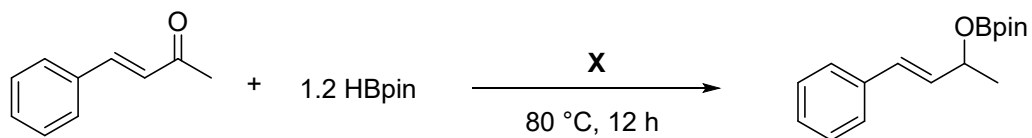


Figure S2. <sup>11</sup>B NMR spectrum of the reaction of HBpin and C1.

### c) The study of the effect of BH<sub>3</sub> on the hydroboration reaction of enone

In a 10 mL Schlenk flask equipped with a magnetic stir bar in the glovebox, enone (1.0 mmol), pinacolborane (1.2 mmol, 1.2 eq.) and catalyst X (5 mol%) were combined and heated in an oil bath at 80 °C for 12 h. After completion of the reaction, its yield was calculated by the <sup>1</sup>H NMR in CDCl<sub>3</sub> (Scheme S5, Figure S3 and Table 1). For the mentioned reaction, the yield of product is up to 97% in the presence of TMEDA (99% without TMEDA). When only BH<sub>3</sub>·SMe<sub>2</sub> acted as a catalyst which was consistent with the amount of reaction of HBpin and C1, we cannot find any product. Even if the amount of BH<sub>3</sub>·SMe<sub>2</sub> was raised to 5%, no product was obtained. These results suggest that there is no hidden catalyst such as BH<sub>3</sub> in this catalytic system.

**Scheme S5.** Synthetic scheme for the hydroboration of enone in presence of catalyst X.



**Table1.** The hydroboration reaction of enone and HBpin in the presence of X

X (5 mol%)	Yield
<b>C1</b>	99%
<b>C1</b> + TMEDA (1:2)	97%
BH <sub>3</sub> ·SMe <sub>2</sub> <sup>a</sup>	n.d.
BH <sub>3</sub> ·SMe <sub>2</sub> <sup>b</sup>	n.d.

<sup>a</sup> 0.7 mol% BH<sub>3</sub>·SMe<sub>2</sub> which quantity is consistent with BH<sub>3</sub> that reaction of HBpin with C1; <sup>b</sup> 5 mol% BH<sub>3</sub>·SMe<sub>2</sub>

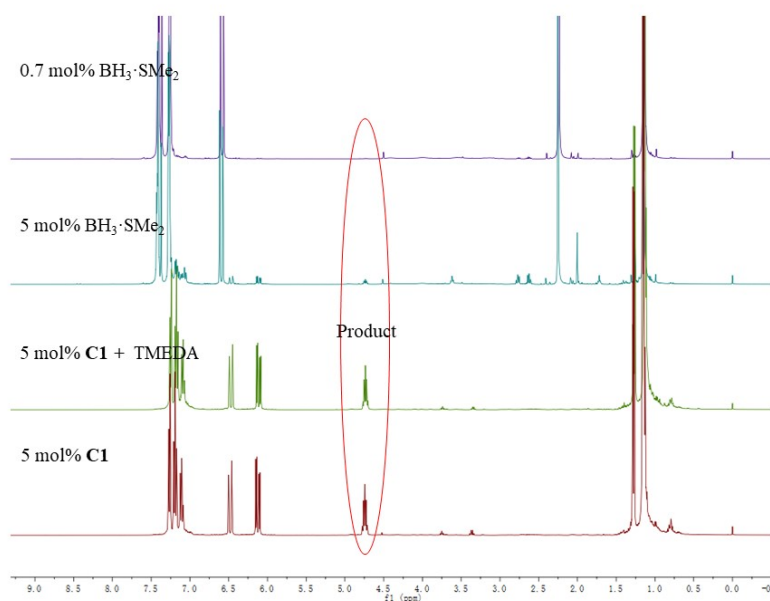


Figure S3. <sup>1</sup>H NMR spectrum of the reaction of enone and HBpin using X as a catalyst

# $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of alcohols

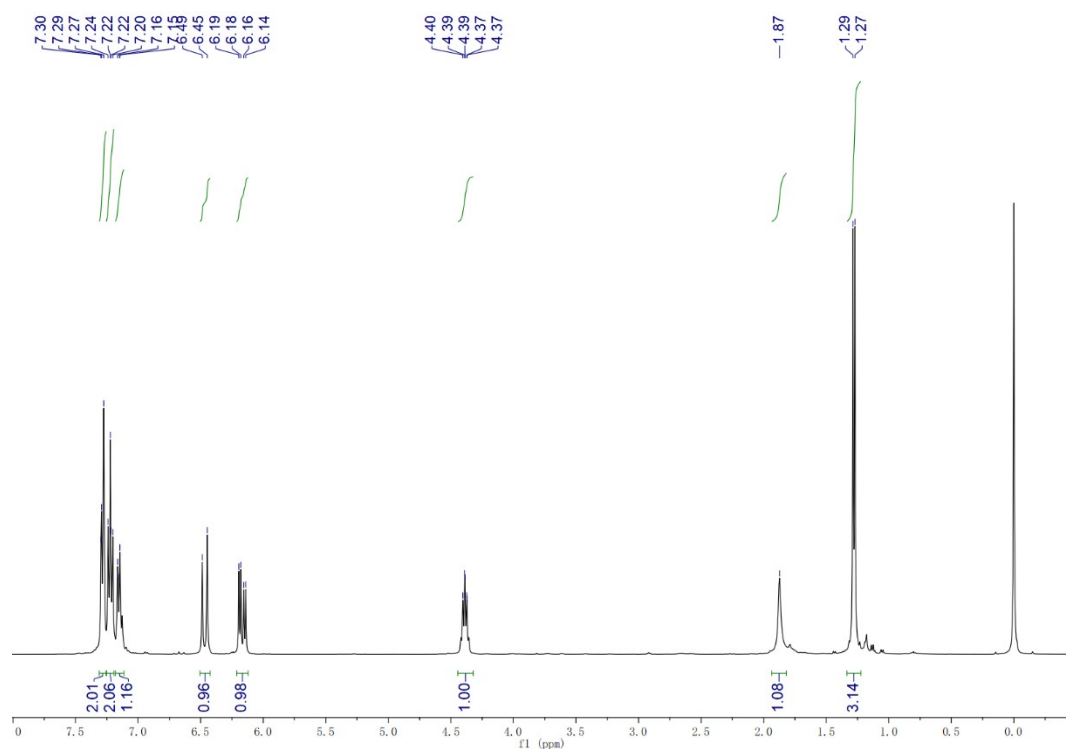


Figure S4.1  $^1\text{H}$  NMR of compound **2a** in  $\text{CDCl}_3$

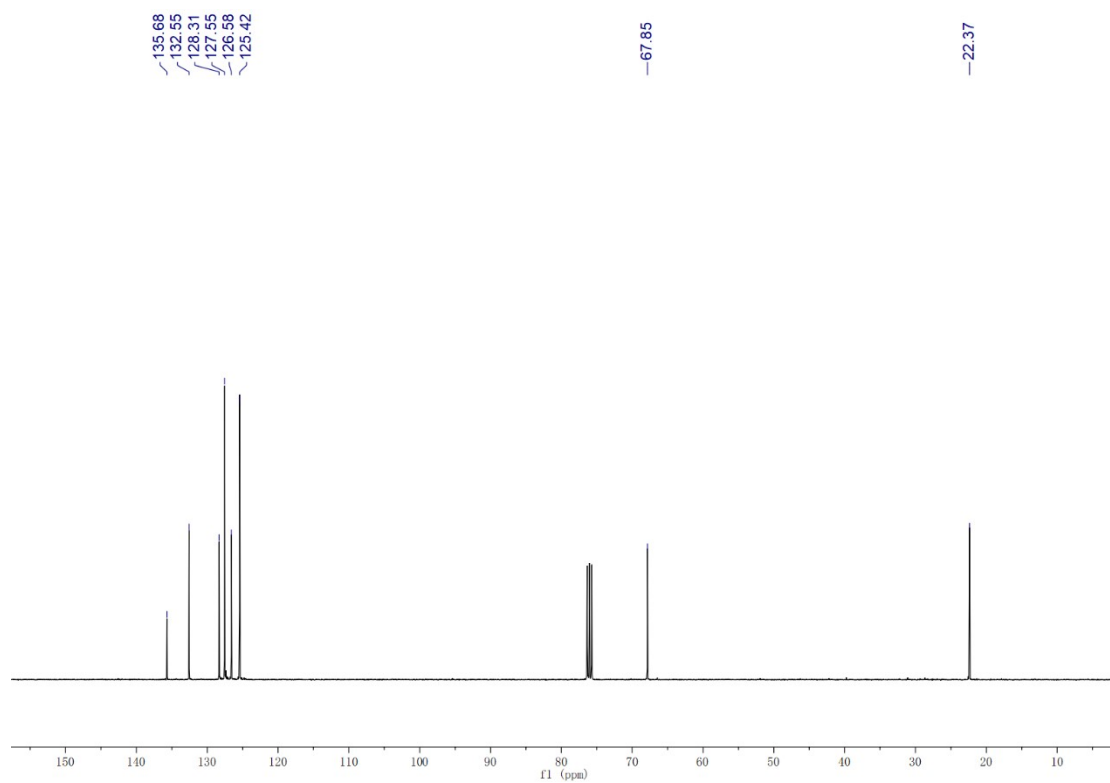


Figure S4.2  $^{13}\text{C}$  NMR of compound **2a** in  $\text{CDCl}_3$

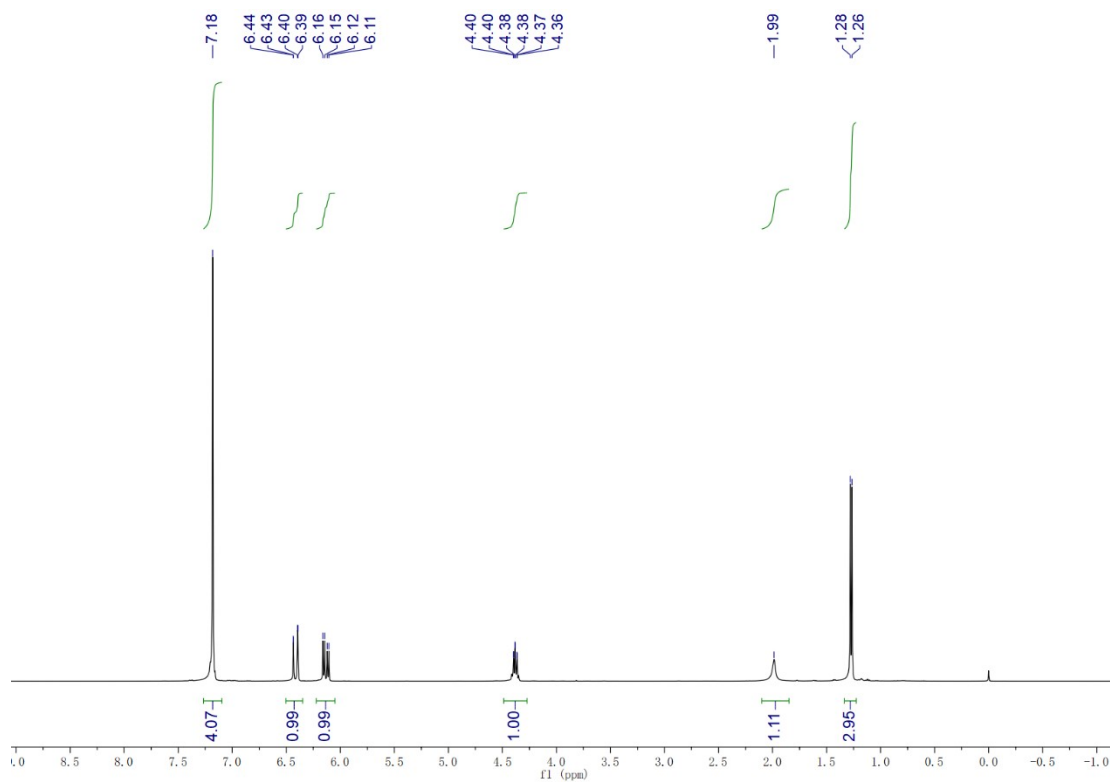


Figure S4.3  $^1\text{H}$  NMR of compound **2b** in  $\text{CDCl}_3$

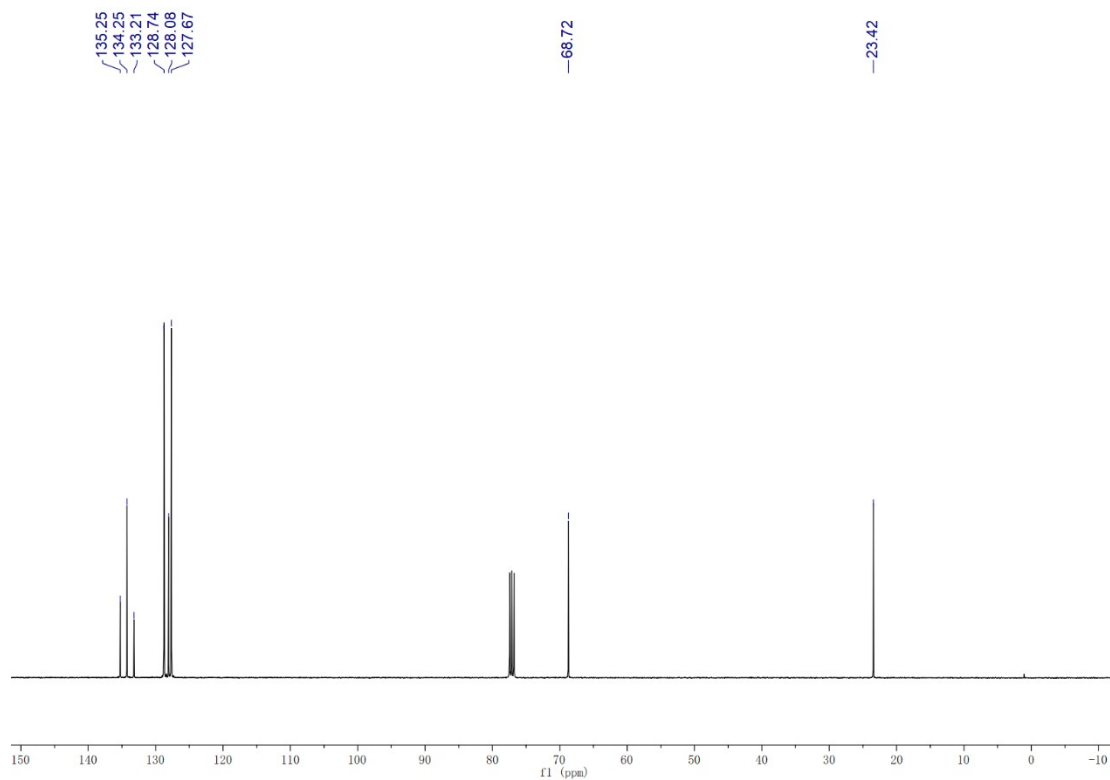


Figure S4.4  $^{13}\text{C}$  NMR of compound **2b** in  $\text{CDCl}_3$

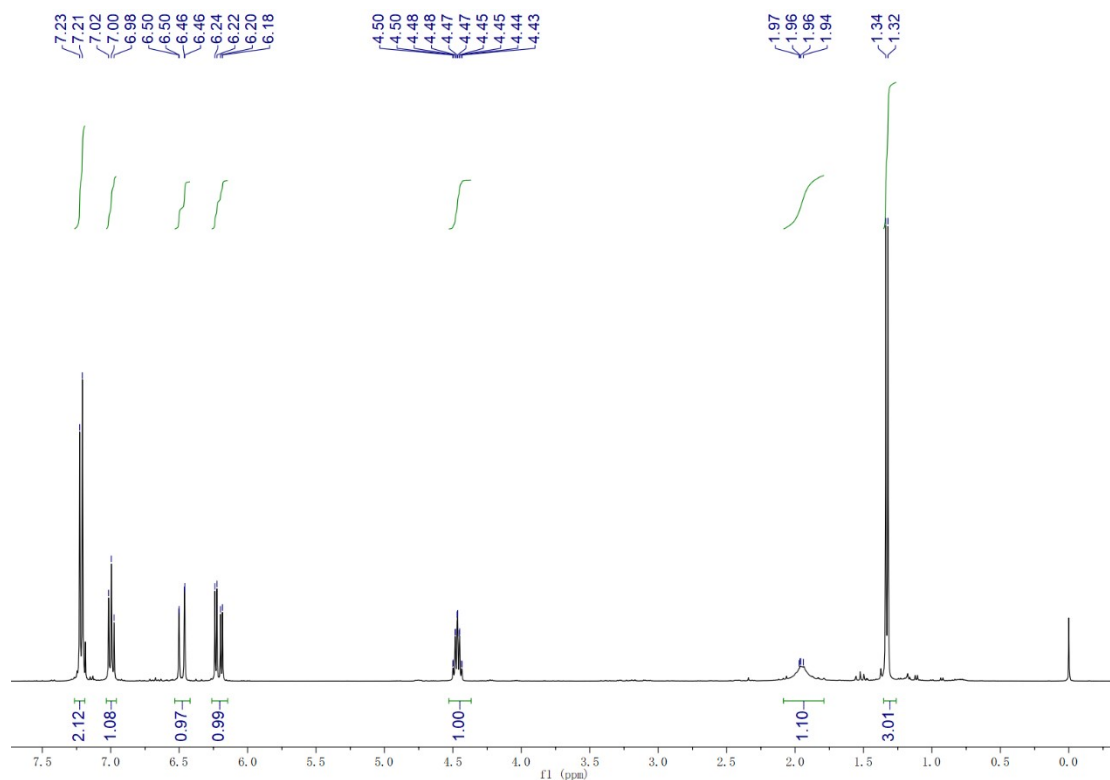


Figure S4.5  $^1\text{H}$  NMR of compound **2c** in  $\text{CDCl}_3$

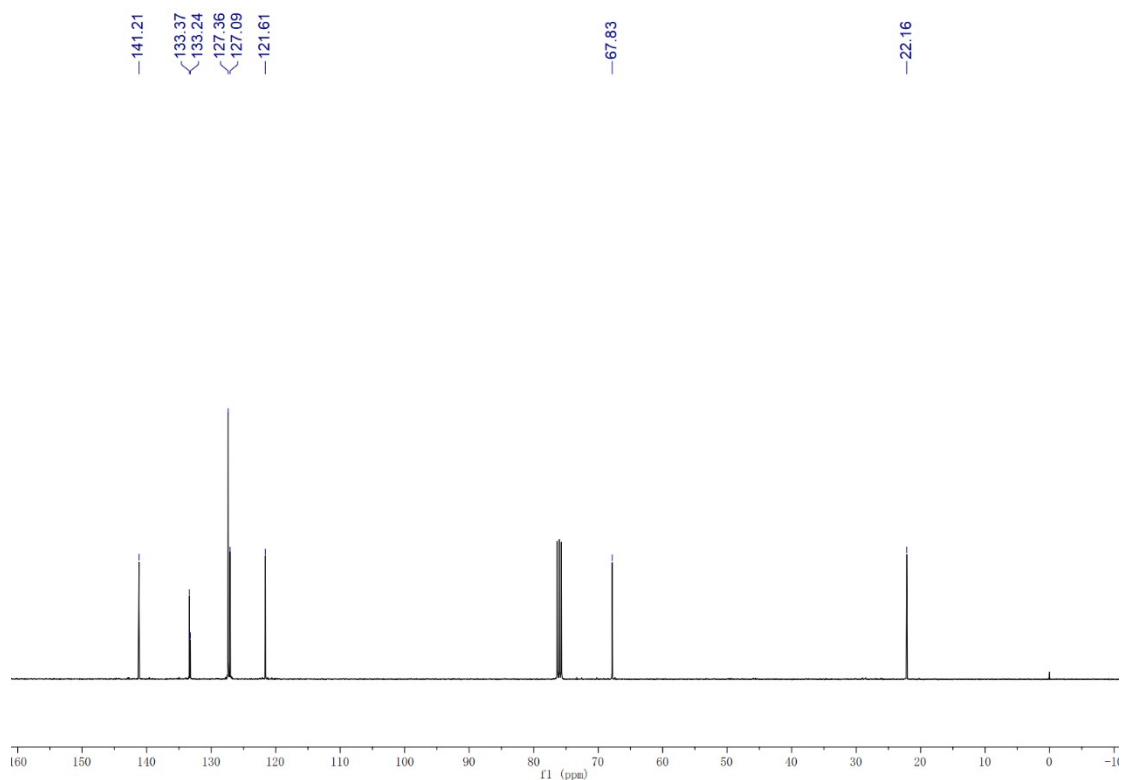


Figure S4.6  $^{13}\text{C}$  NMR of compound **2c** in  $\text{CDCl}_3$

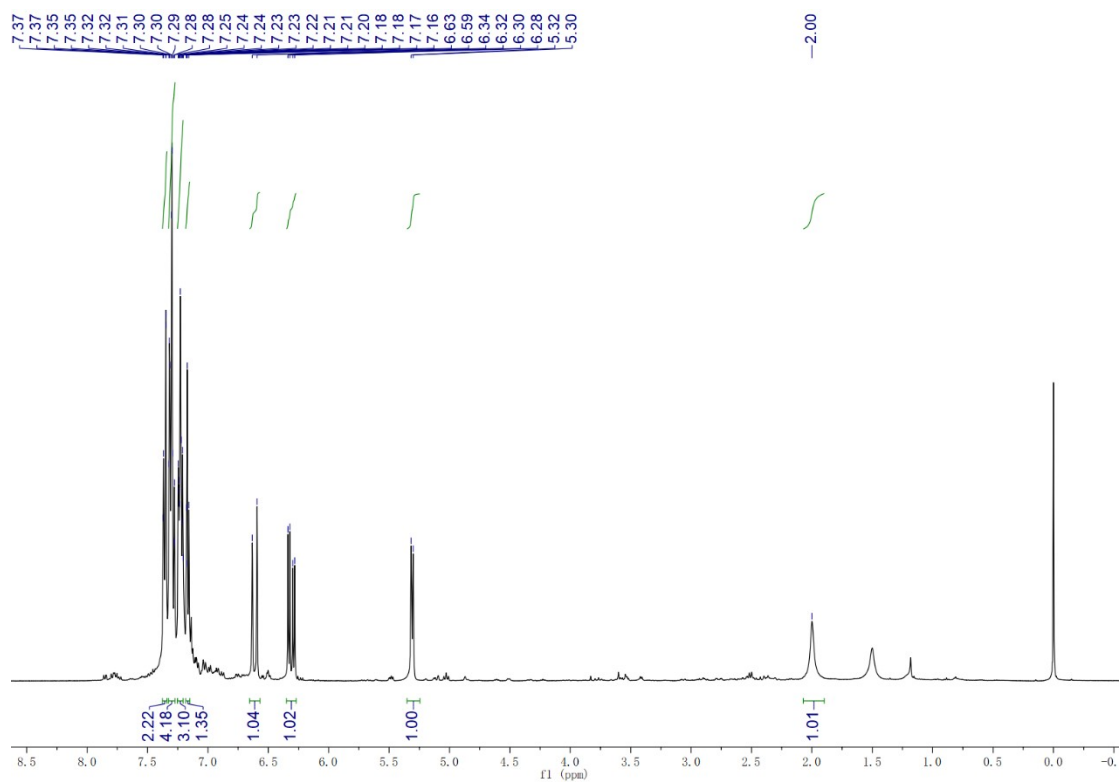


Figure S4.7  $^1\text{H}$  NMR of compound **2d** in  $\text{CDCl}_3$

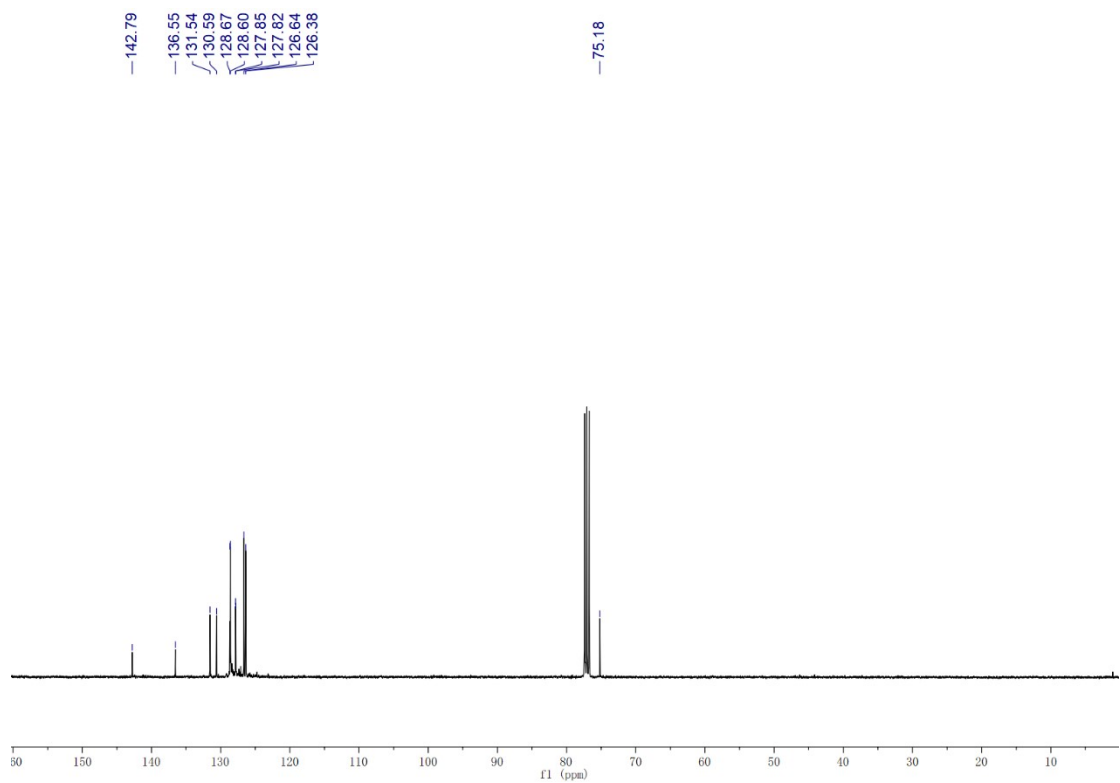


Figure S4.8  $^{13}\text{C}$  NMR of compound **2d** in  $\text{CDCl}_3$



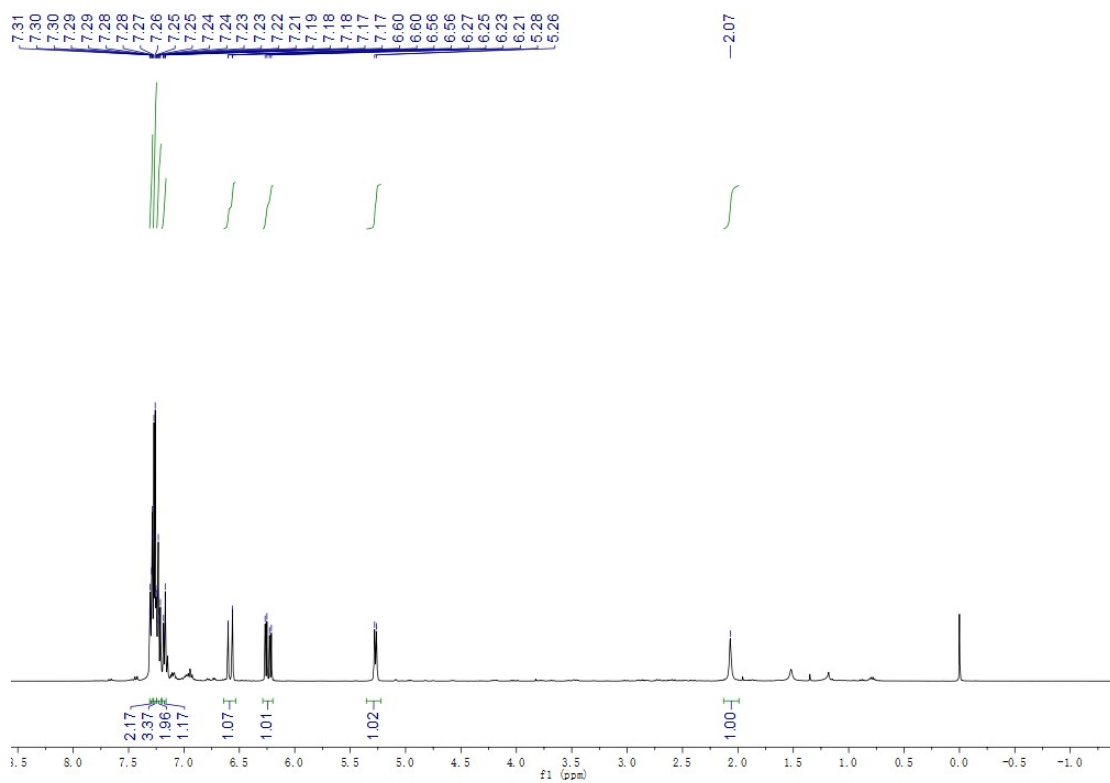


Figure S4.9  $^1\text{H}$  NMR of compound **2e** in  $\text{CDCl}_3$

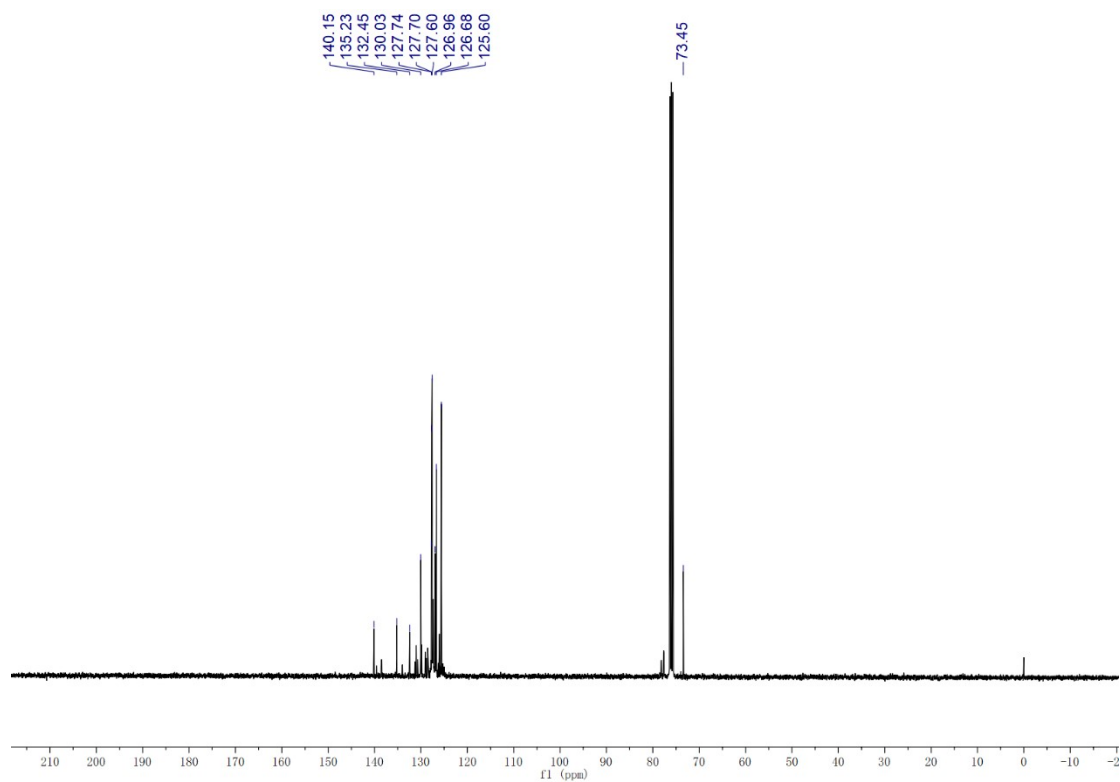


Figure S4.10  $^{13}\text{C}$  NMR of compound **2e** in  $\text{CDCl}_3$

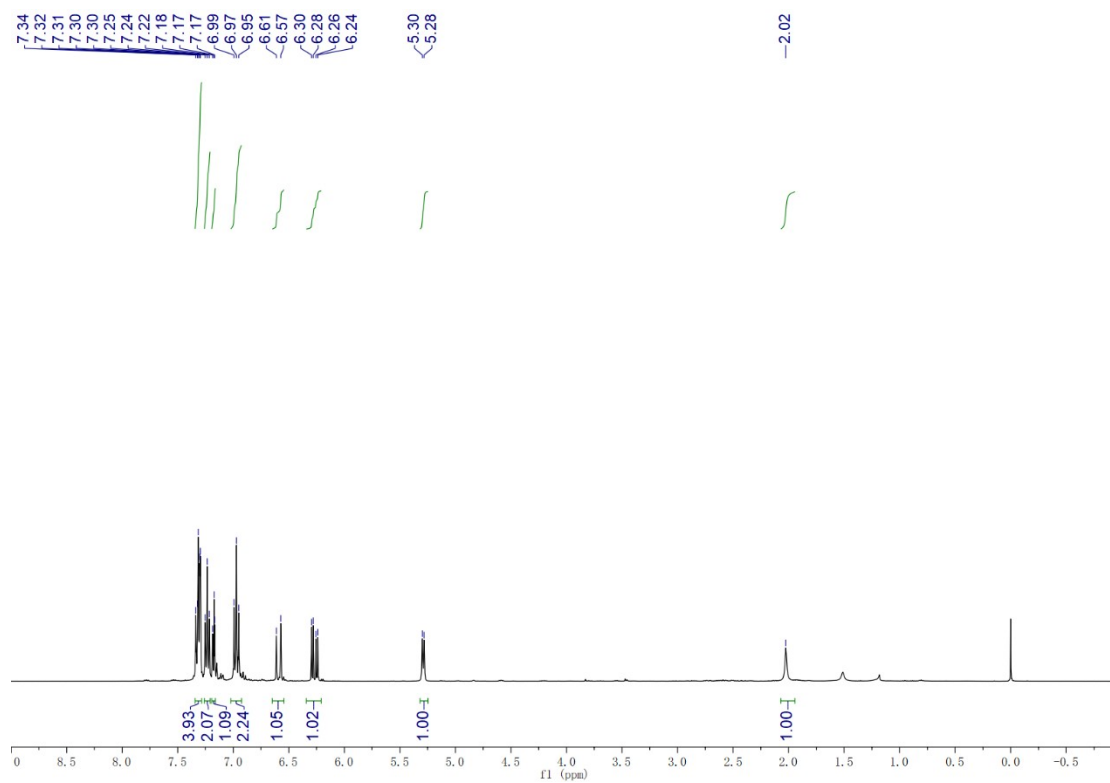


Figure S4.11  $^1\text{H}$  NMR of compound **2f** in  $\text{CDCl}_3$

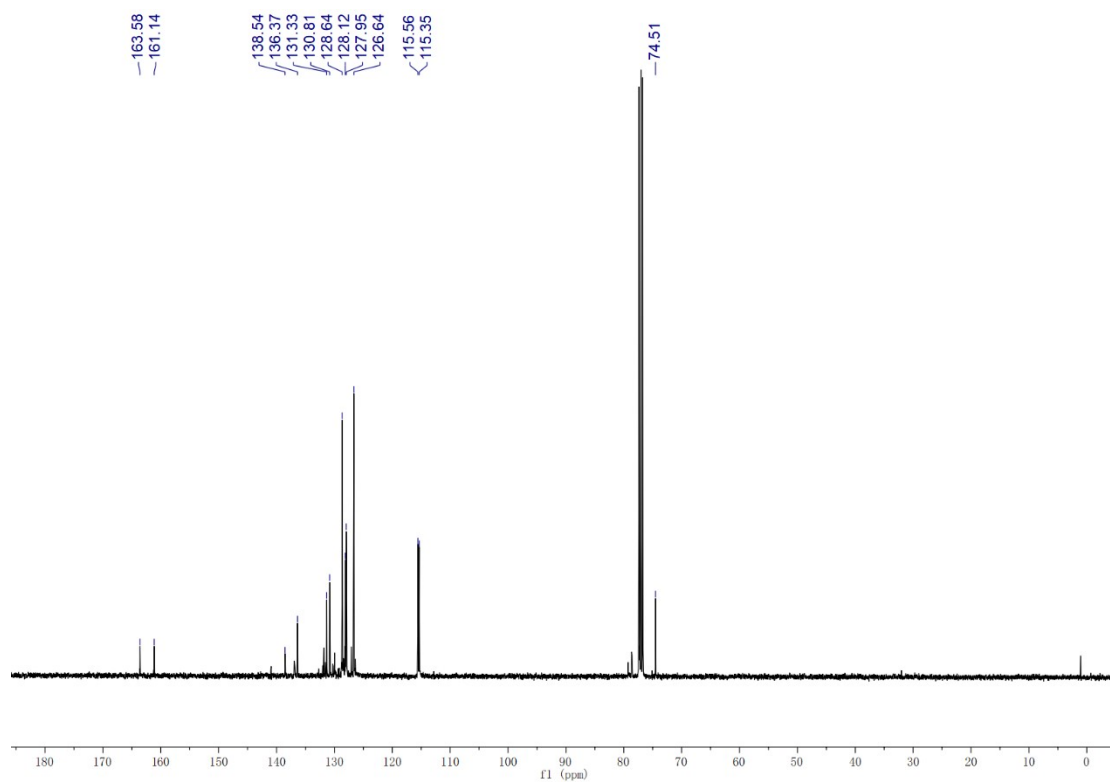


Figure S4.12  $^{13}\text{C}$  NMR of compound **2f** in  $\text{CDCl}_3$

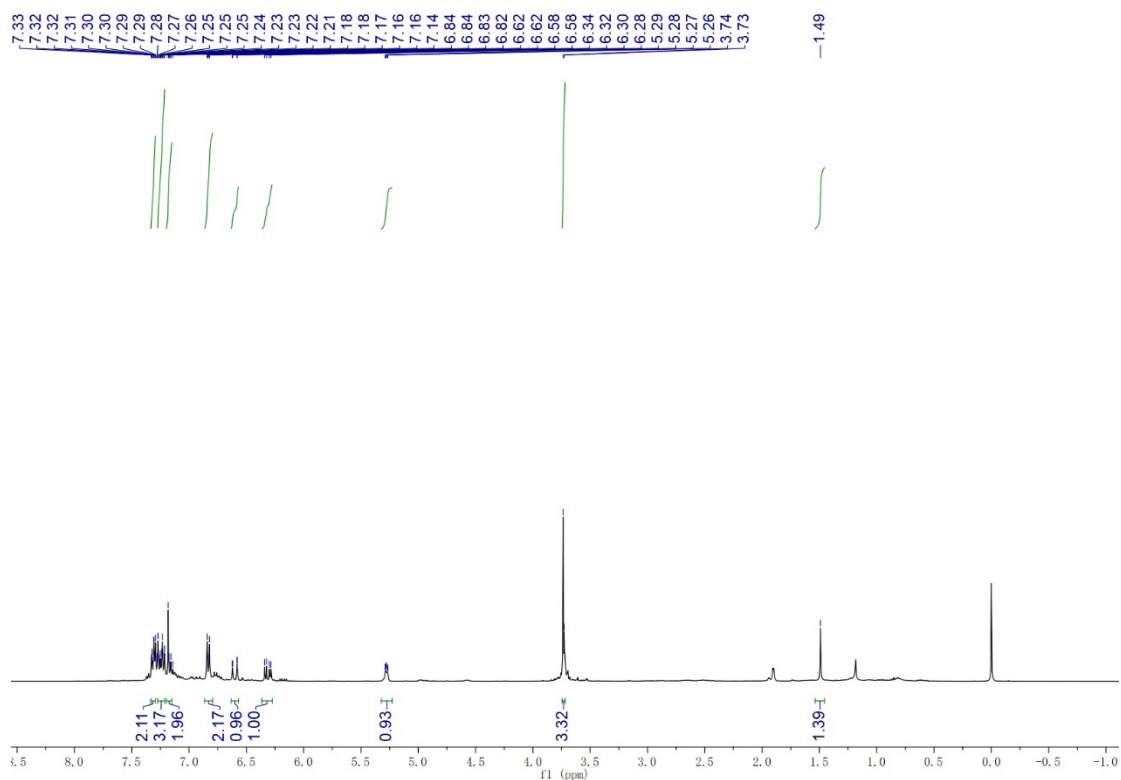


Figure S4.13  $^1\text{H}$  NMR of compound **2g** in  $\text{CDCl}_3$

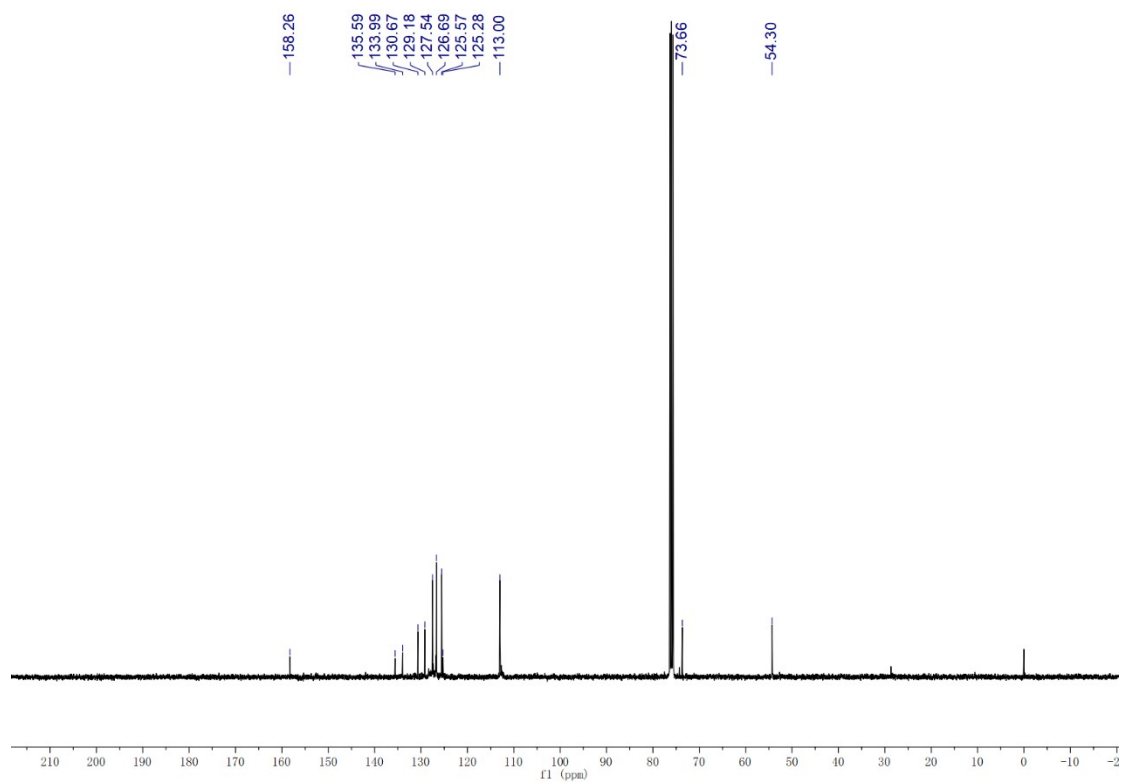


Figure S4.14  $^{13}\text{C}$  NMR of compound **2g** in  $\text{CDCl}_3$

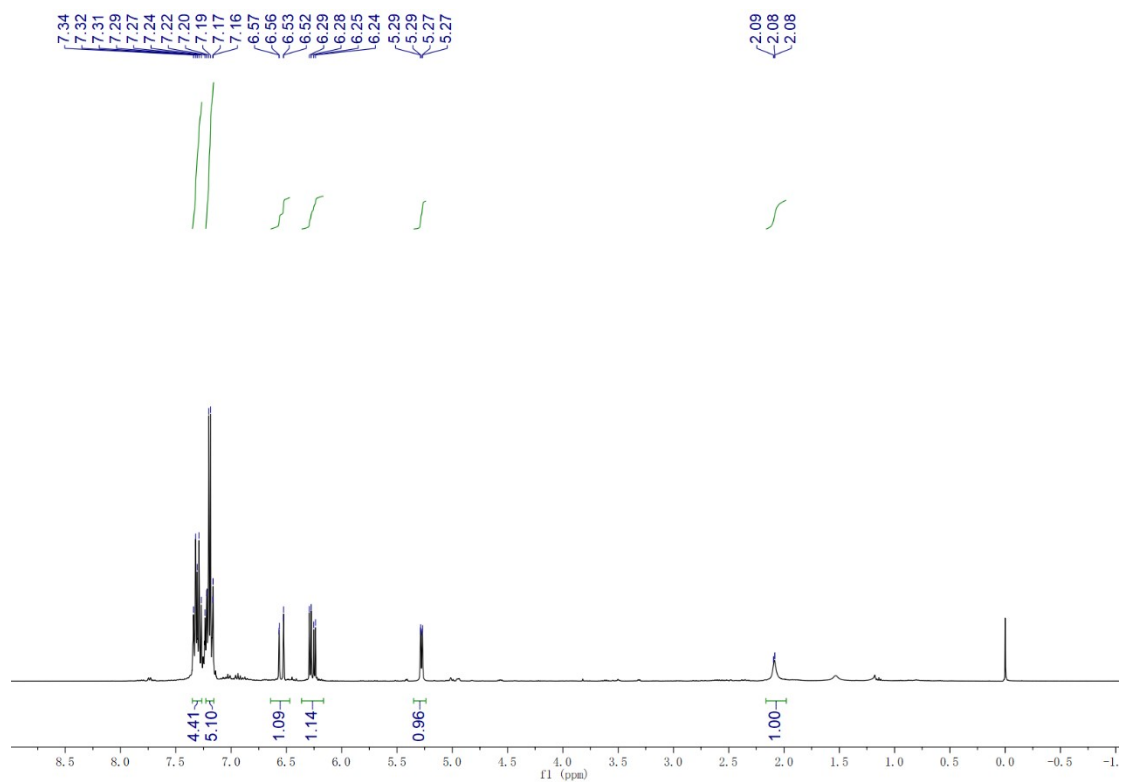


Figure S4.15  $^1\text{H}$  NMR of compound **2h** in  $\text{CDCl}_3$

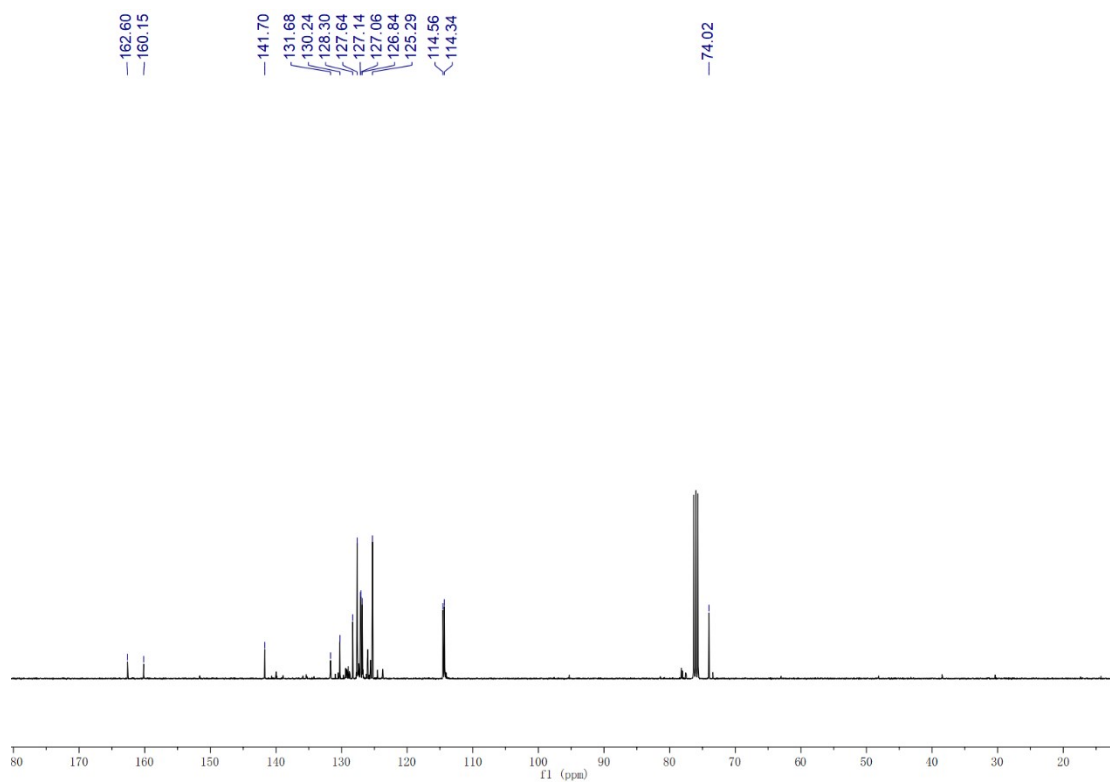


Figure S4.16  $^{13}\text{C}$  NMR of compound **2h** in  $\text{CDCl}_3$

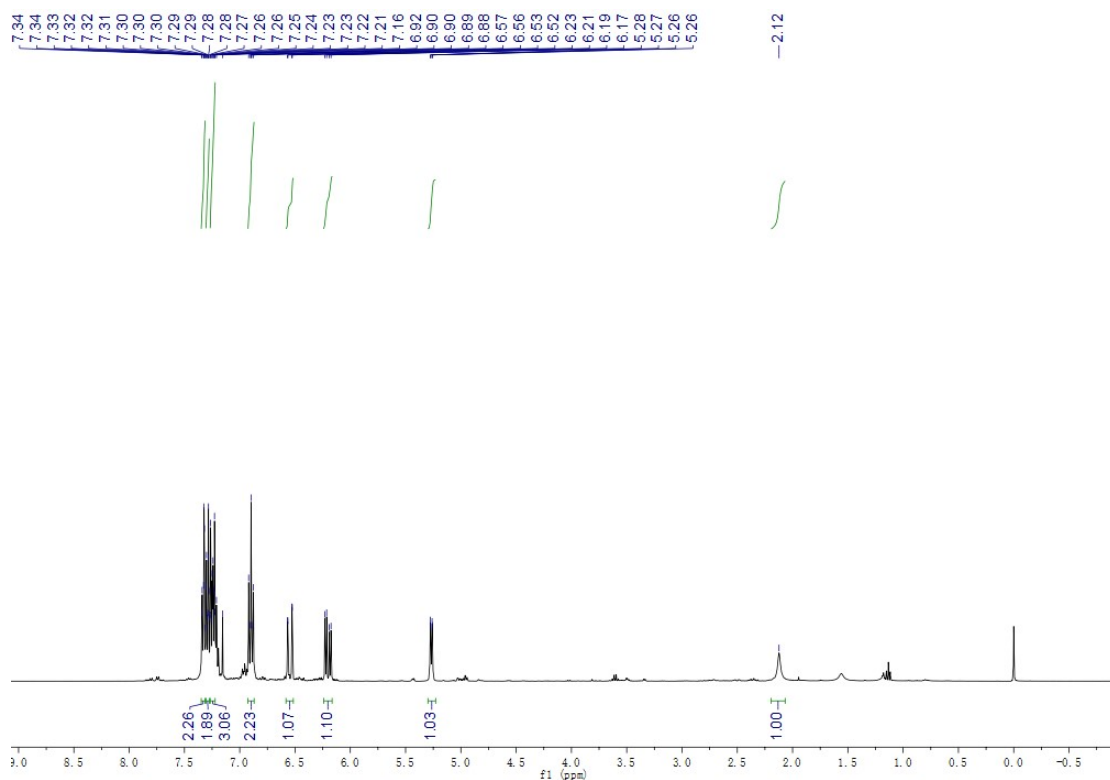


Figure S4.17  $^1\text{H}$  NMR of compound **2i** in  $\text{CDCl}_3$

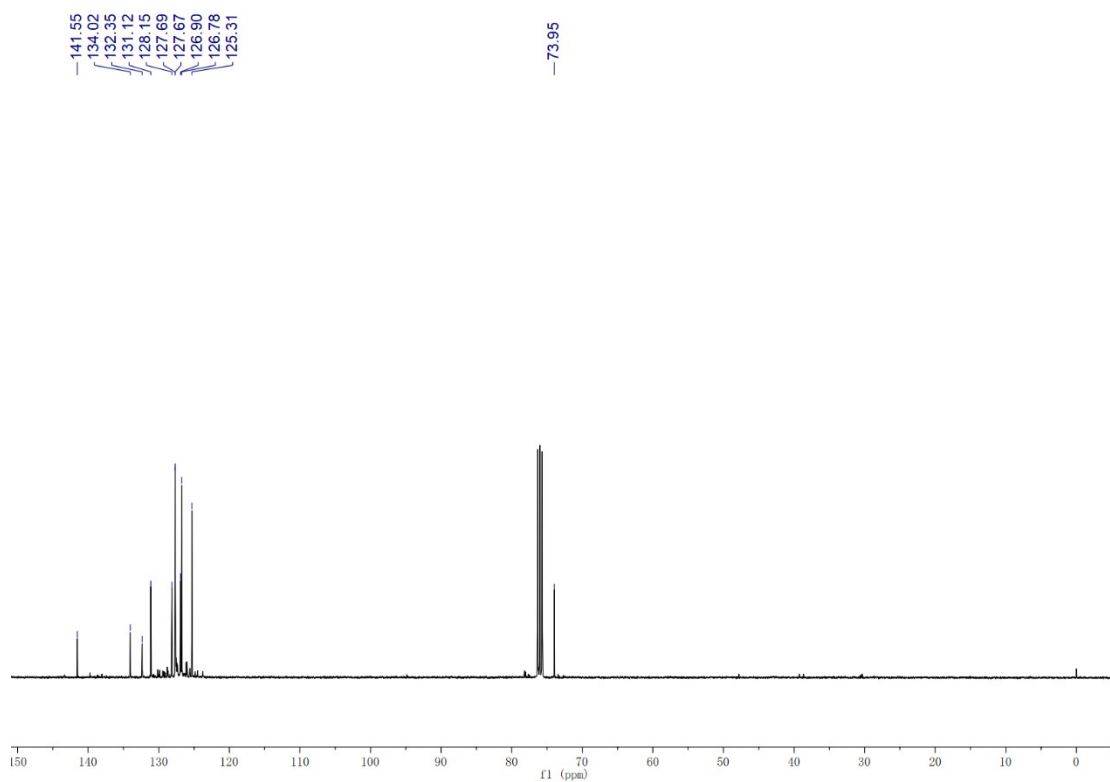


Figure S4.18  $^{13}\text{C}$  NMR of compound **2i** in  $\text{CDCl}_3$

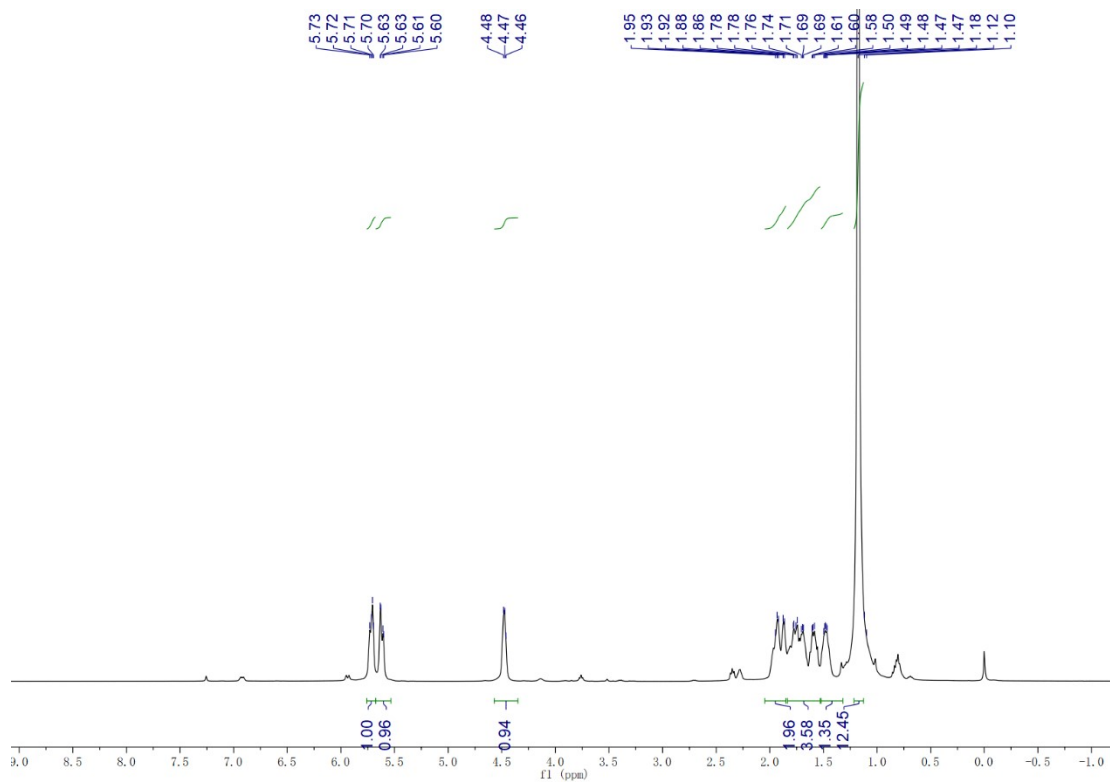


Figure S4.19  $^1\text{H}$  NMR of compound **2j** in  $\text{CDCl}_3$

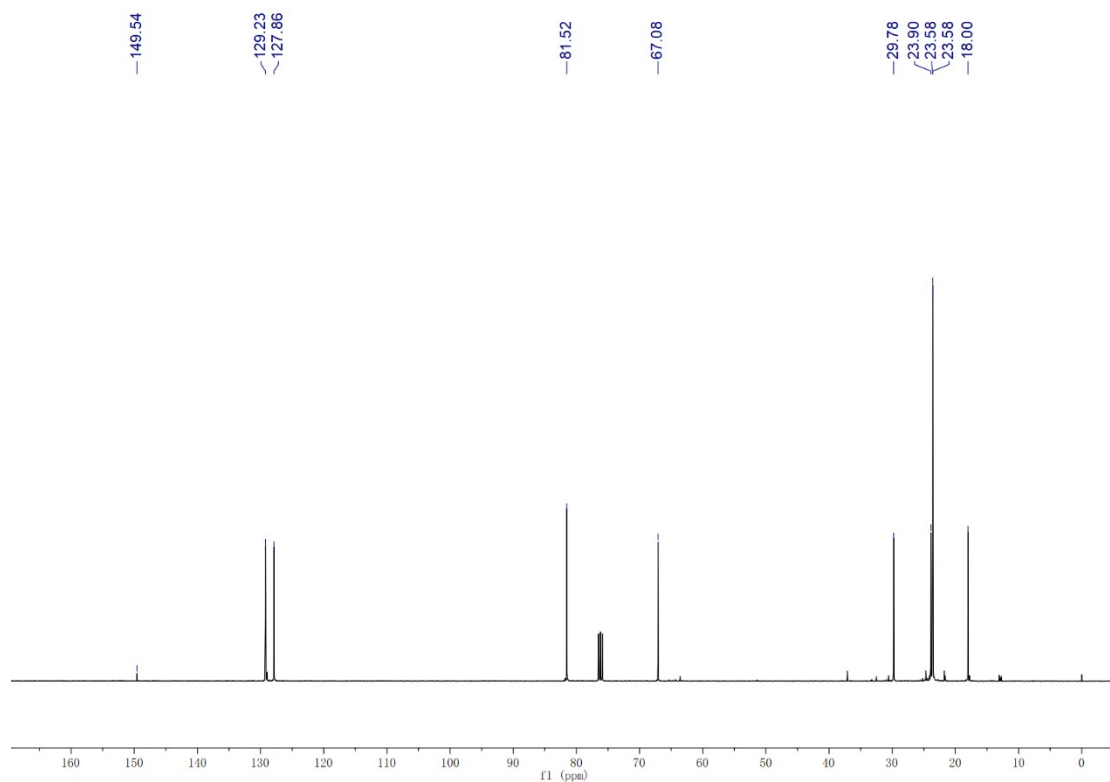


Figure S4.20  $^{13}\text{C}$  NMR of compound **2j** in  $\text{CDCl}_3$

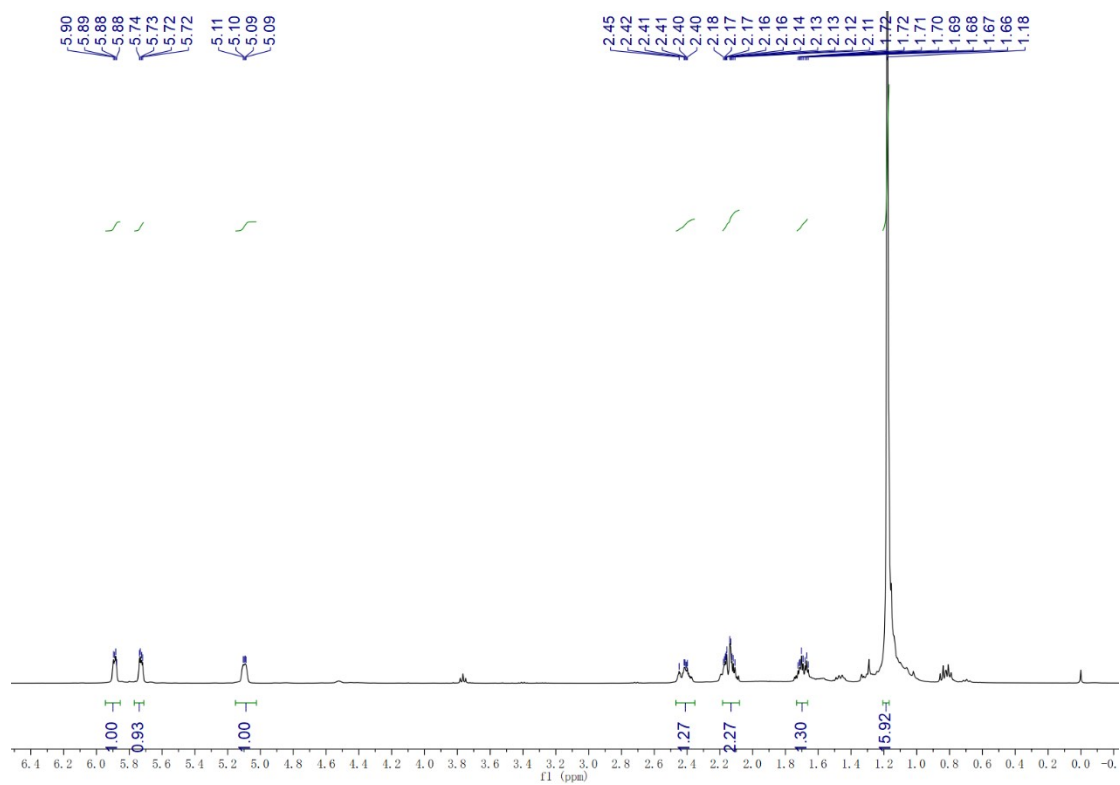


Figure S4.21  $^1\text{H}$  NMR of compound **2k** in  $\text{CDCl}_3$

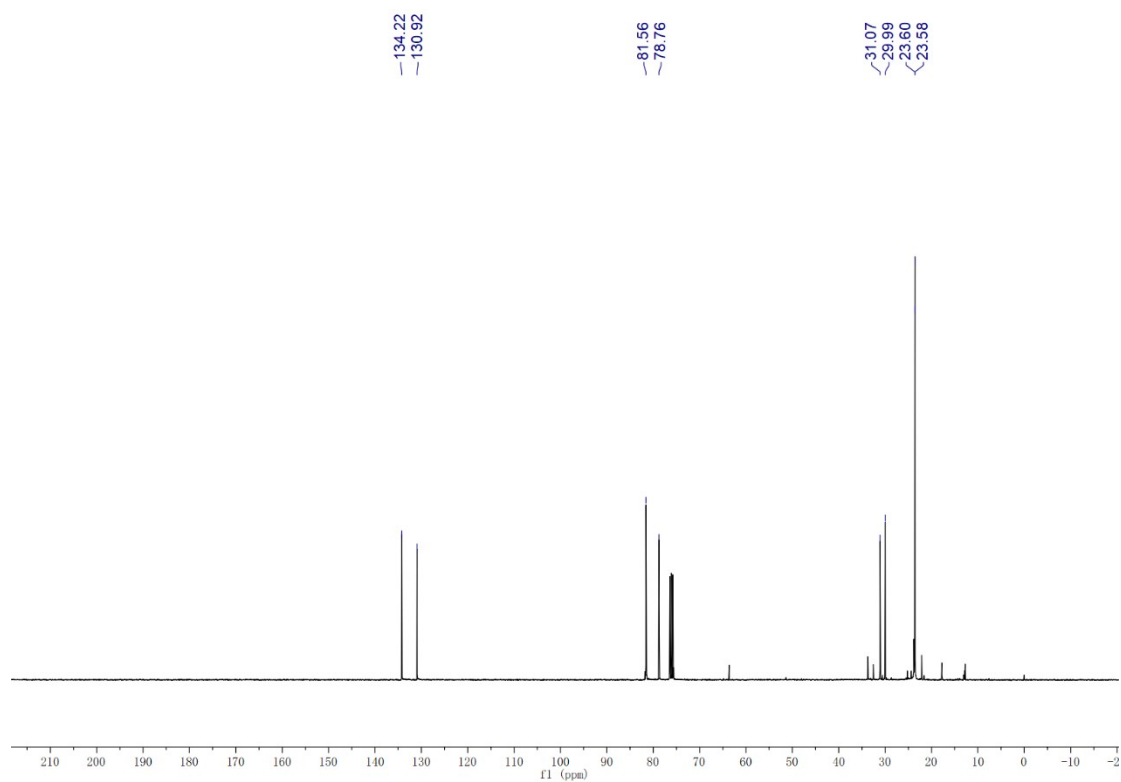


Figure S4.22  $^{13}\text{C}$  NMR of compound **2k** in  $\text{CDCl}_3$

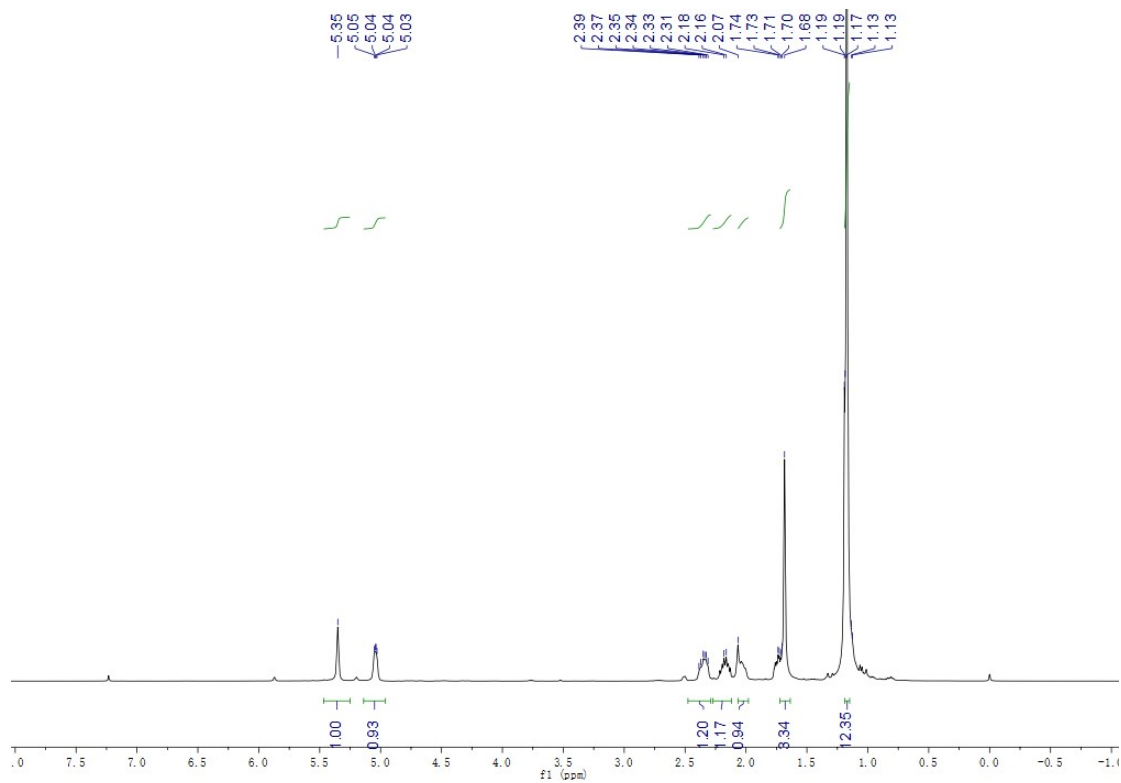


Figure S4.23  $^1\text{H}$  NMR of compound **21** in  $\text{CDCl}_3$

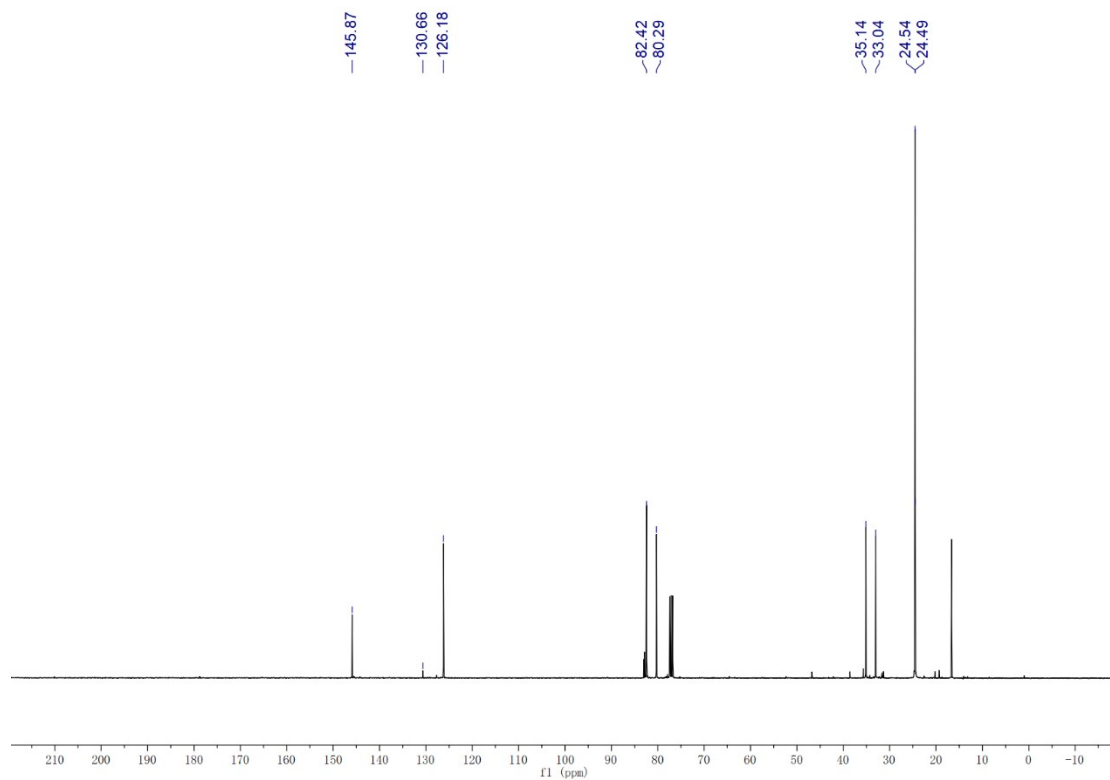


Figure S4.24  $^{13}\text{C}$  NMR of compound **21** in  $\text{CDCl}_3$



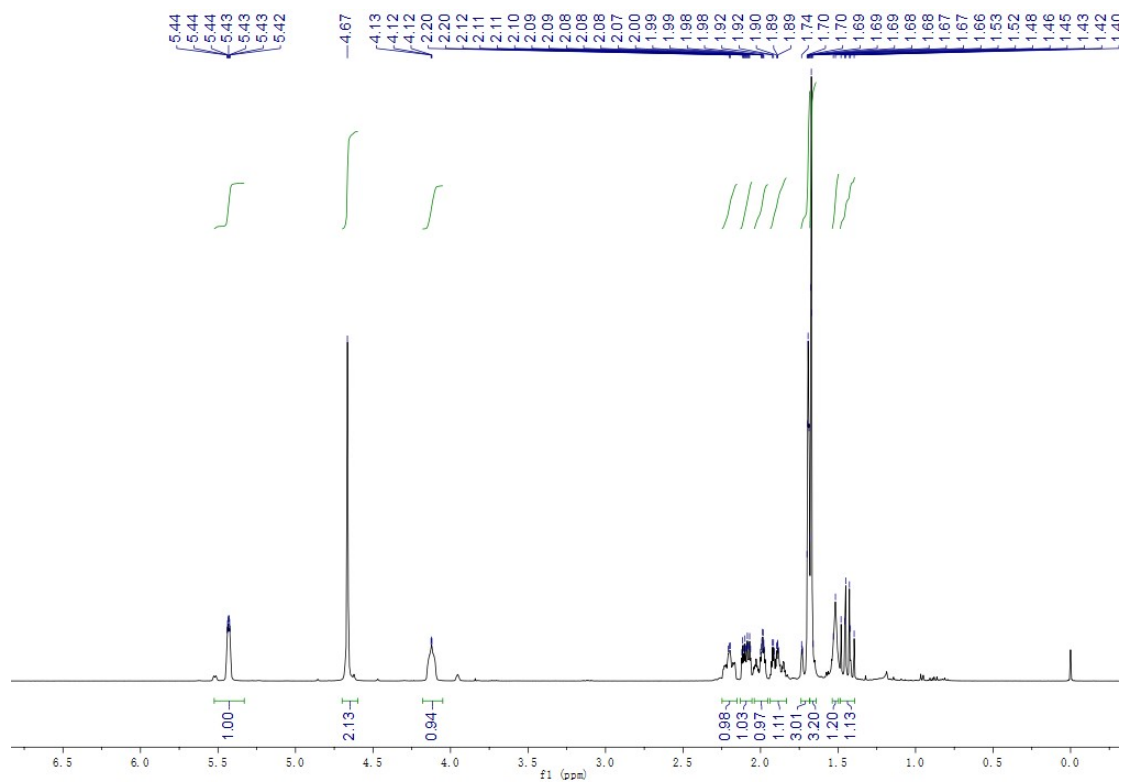


Figure S4.25  $^1\text{H}$  NMR of compound **2m** in  $\text{CDCl}_3$

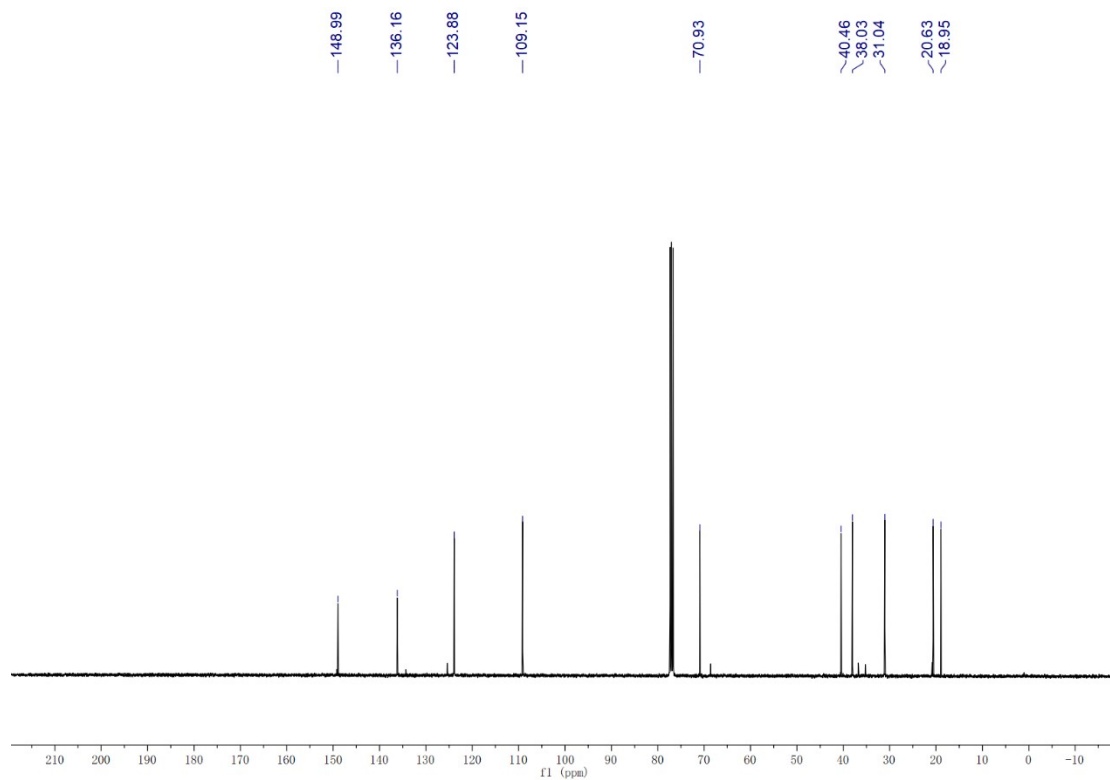


Figure S4.26  $^{13}\text{C}$  NMR of compound **2m** in  $\text{CDCl}_3$

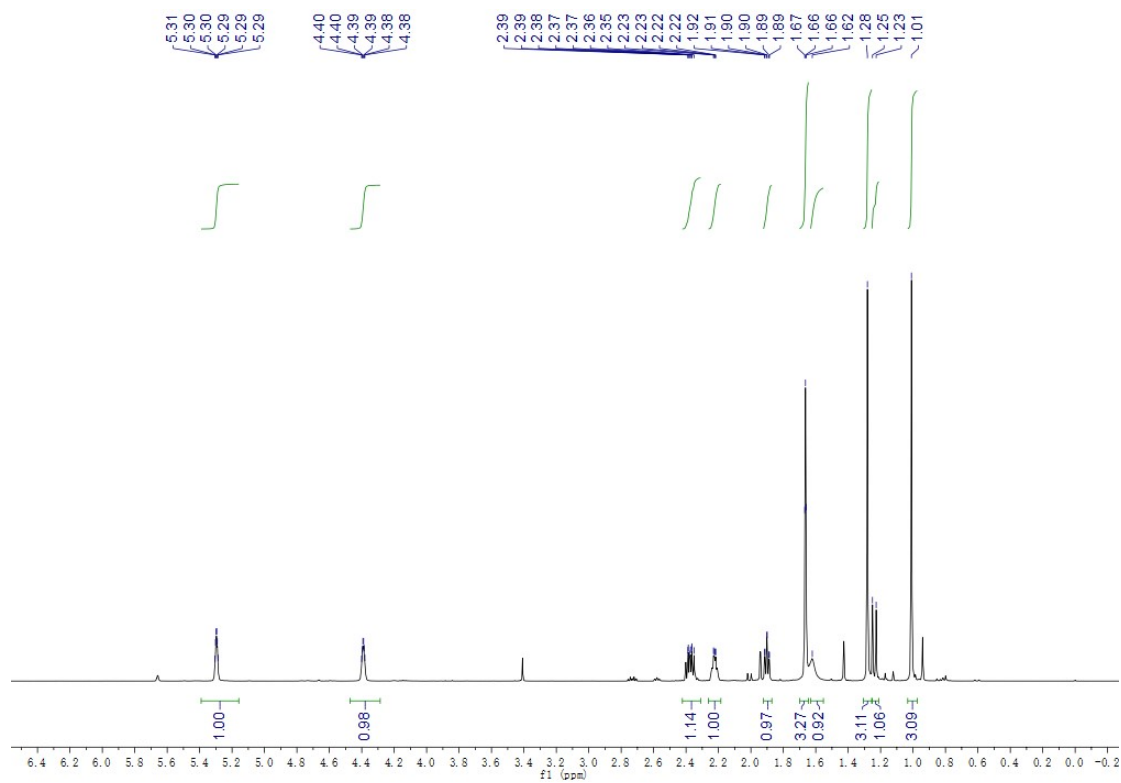


Figure S4.27  $^1\text{H}$  NMR of compound **2n** in  $\text{CDCl}_3$

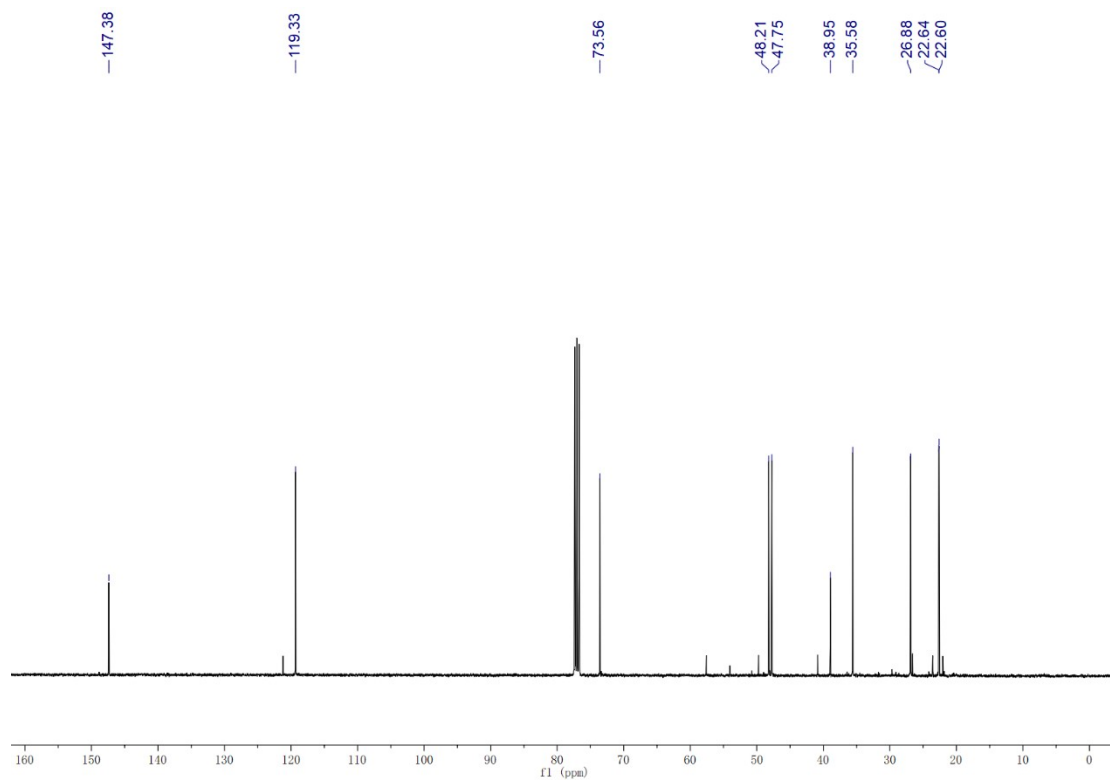


Figure S4.28  $^{13}\text{C}$  NMR of compound **2n** in  $\text{CDCl}_3$

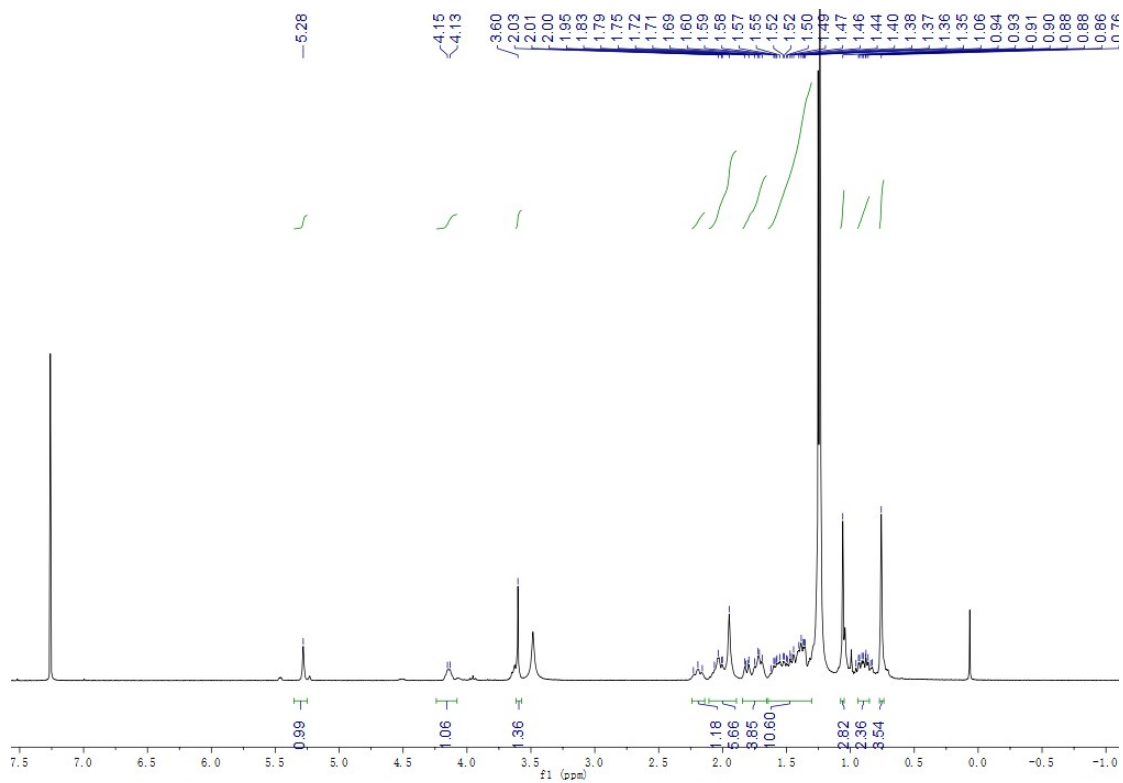


Figure S4.29  $^1\text{H}$  NMR of compound **2o** in  $\text{CDCl}_3$

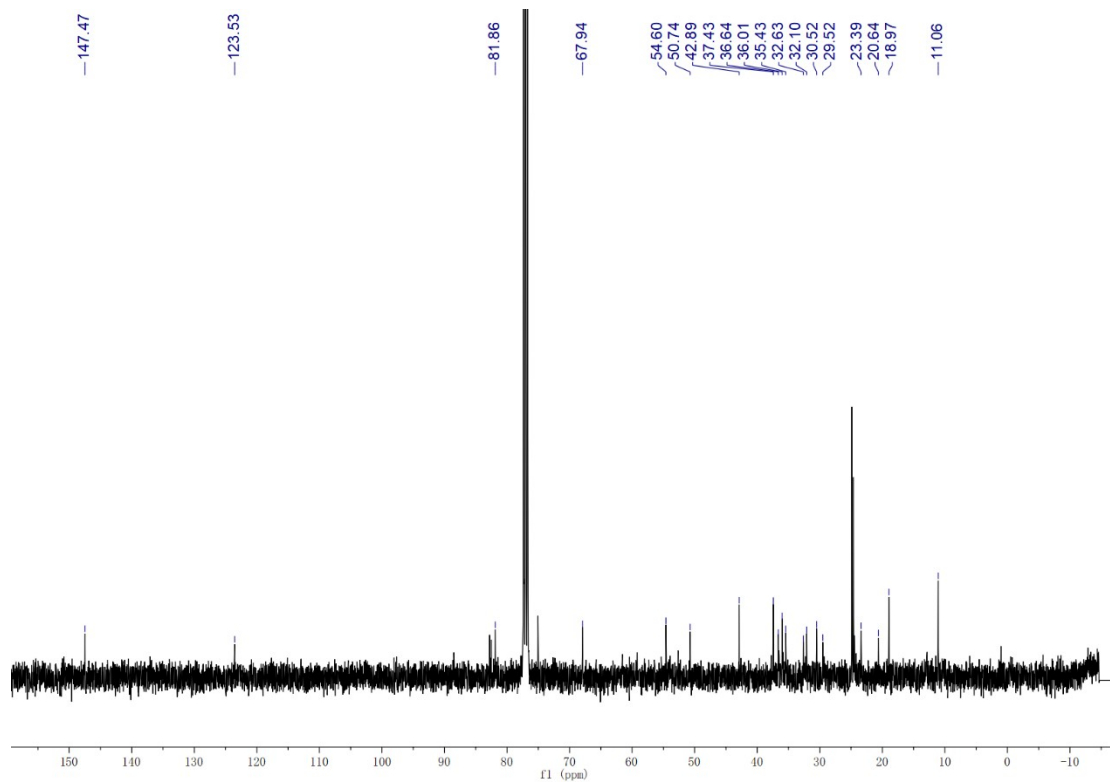


Figure S4.30  $^{13}\text{C}$  NMR of compound **2o** in  $\text{CDCl}_3$

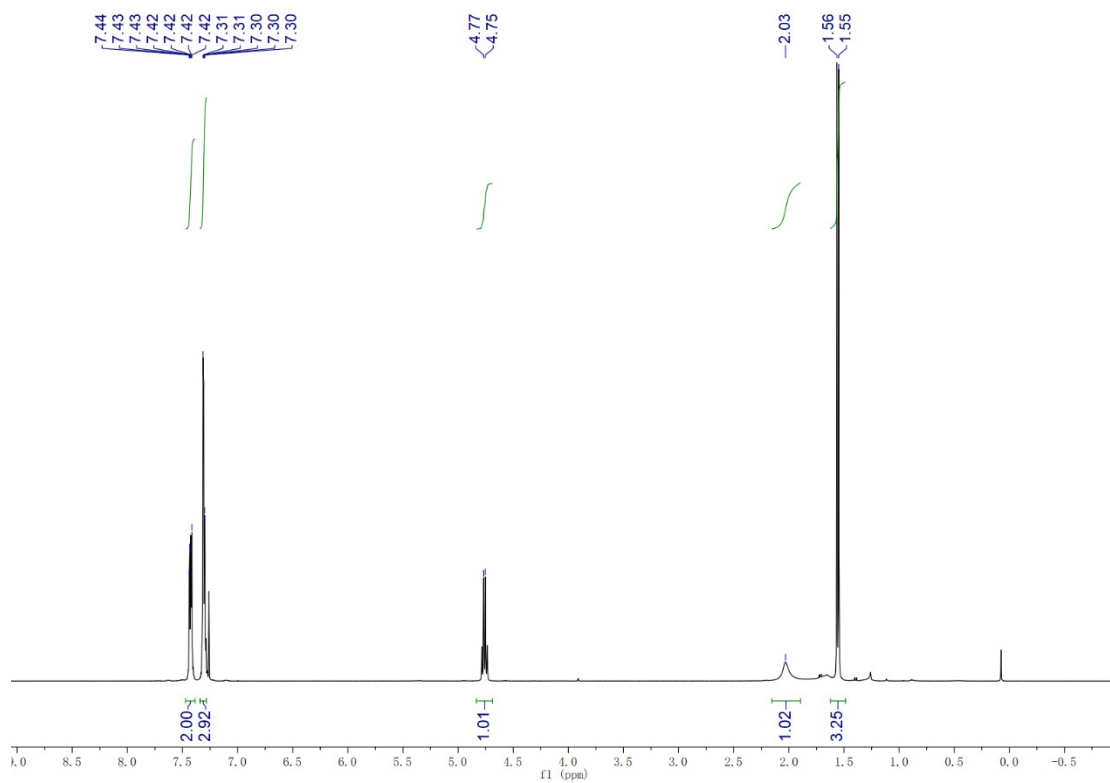


Figure S4.31  $^1\text{H}$  NMR of compound **2p** in  $\text{CDCl}_3$

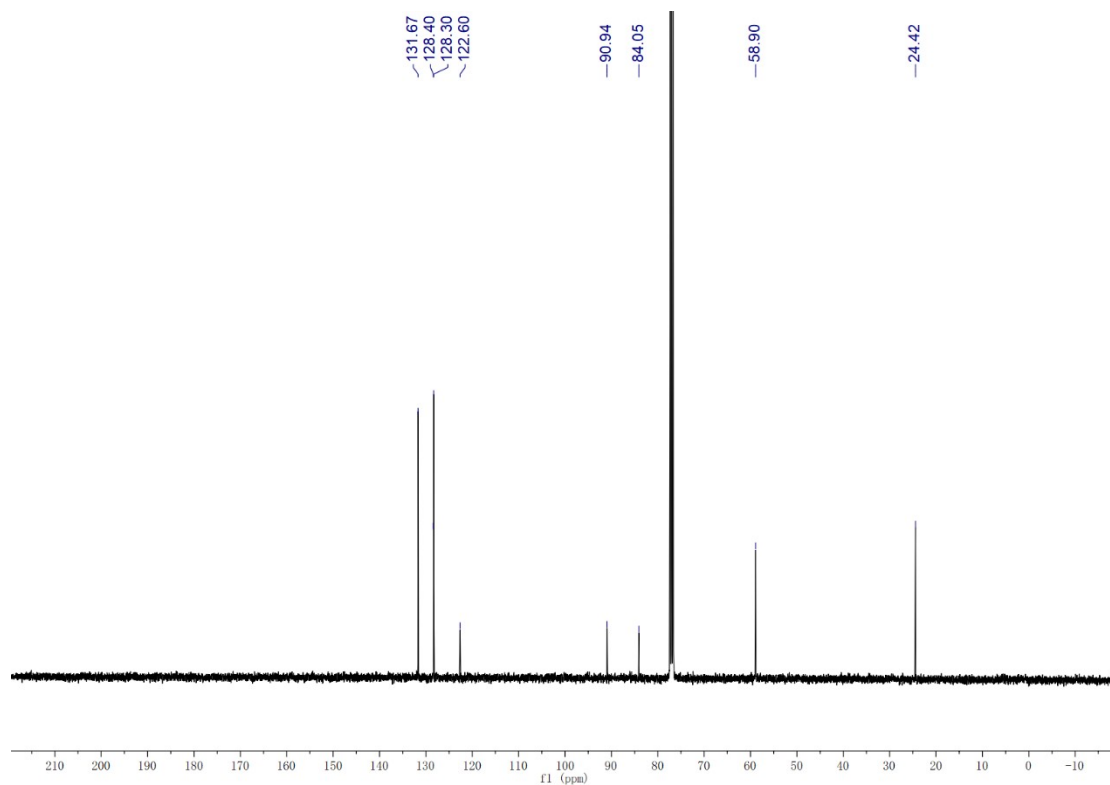


Figure S4.32  $^{13}\text{C}$  NMR of compound **2p** in  $\text{CDCl}_3$

## References

- [1] Yang Z., Zhong M. D., Roesky H. W. *J. Am. Chem. Soc.* 2016, 138, 2548-2551.
- [2] Yang Z., Zhong M., Ma X., Roesky H. W. *Angew. Chem.Int. Ed.*, **2015**, 54(35): 10225-10229.
- [3] Sheldrick, G. M. SADABS, Empirical Absorption Correction Program, University of Göttingen, Göttingen, Germany, **1997**, 28, 53-56.
- [4] Sheldrick, G. M. SHELXS-90, Program for Structure Solution. *Acta Crystallogr. Sect. A.* **1990**, 46, 467-473.
- [5] Sheldrick, G. M. SHELXL-97, Program for Crystal Structure Refinement; University of Göttingen, Germany, **1997**.
- [6] Jiang Y. K., Magre M., Rueping M. *Org. Lett.*, **2019**, 21, 8349-8352.
- [7] Forkel N. V., Henderson D.A., Fuchter M. J. *Green Chem.*, **2012**, 14, 2129-2132.
- [8] Elamparuthi E., Fellay C., Neuburger M., Gademann K. *Angew. Chem. Int. Ed.* **2012**, 51, 4071-4073.