

Supporting Information

The Hydroboration of Deoxygenation of Primary, Secondary, Tertiary Amides and HBpin Catalyzed by NaHBET₃

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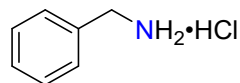
General Information.

All operations during the experiment were performed in a pure N₂ atmosphere using Schlenk techniques or inside a Mbraun MB 150-GI glove box. Commercially available chemicals were purchased from J&K chemical reagents company or Aldrich reagents company, and stored and used according to the instructions. The NMR spectra were provided using the Bruker Ascend II 400 spectrometer.

General Procedure for Hydroboration of Primary Amides.

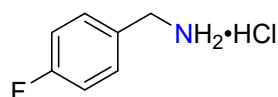
In a 10 ml Schlenk flask equipped with a magnetic stir bar in the glovebox, primary amide (0.5 mmol), pinacolborane (2.2 mmol, 4.4 eq) and NaHBEt₃ (0.025 mmol) were combined and heated in an oil bath at 60 °C for 12 h. The reaction mixture was hydrolyzed with 1 M HCl in ether (10 mL). The volatiles were removed under reduced pressure, and the residue was washed with ethyl acetate (3 × 5 mL) to give a pure desired product as an ammonium salt. The ¹H NMR and ¹³C NMR spectra of the isolated ammonium salts were recorded in D₂O.

2a



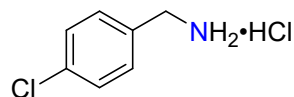
¹H NMR (400 MHz, D₂O): δ 7.31 (s, 5H, -CH₂Ph), 4.03 (s, 2H, -CH₂Ph). ¹³C NMR (101 MHz, D₂O): δ 132.62, 129.23, 128.81, 43.15.

2b



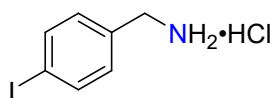
¹H NMR (400 MHz, D₂O): δ 7.42 (s, 2H, -CH₂PhF), 7.15 (s, 2H, -CH₂PhF), 4.12 (s, 2H, -CH₂PhF). ¹³C NMR (101 MHz, D₂O): δ 164.09, 161.65, 131.00, 128.81, 115.88, 42.51.

2c



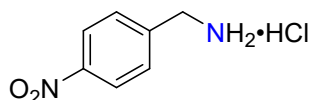
¹H NMR (400 MHz, D₂O): δ 7.44 (d, *J* = 7.8 Hz, 2H, -CH₂PhCl), 7.39 (d, *J* = 8.1 Hz, 2H, -CH₂PhCl), 4.14 (s, 2H, -CH₂PhCl). ¹³C NMR (101 MHz, D₂O): δ 134.56, 131.23, 130.49, 129.21, 42.50.

2d



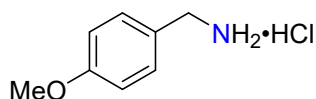
^1H NMR (400 MHz, D_2O): δ 7.79 (d, $J = 7.9$ Hz, 2H, $-\text{CH}_2\text{PhI}$), 7.17 (d, $J = 8.0$ Hz, 2H, $-\text{CH}_2\text{PhI}$), 4.09 (s, 2H, $-\text{CH}_2\text{PhI}$). ^{13}C NMR (101 MHz, D_2O): δ 138.26, 132.28, 130.72, 94.65, 42.66.

2e



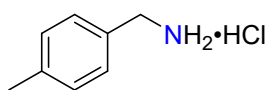
^1H NMR (400 MHz, D_2O): δ 8.25 (d, $J = 8.6$ Hz, 2H, $-\text{CH}_2\text{PhNO}_2$), 7.64 (d, $J = 8.6$ Hz, 2H, $-\text{CH}_2\text{PhNO}_2$), 4.31 (s, 2H, $-\text{CH}_2\text{PhNO}_2$). ^{13}C NMR (101 MHz, D_2O): δ 147.96, 139.89, 129.85, 124.27, 42.33.

2f



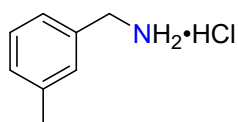
^1H NMR (400 MHz, D_2O): δ 7.35 (d, $J = 7.2$ Hz, 2H, $-\text{CH}_2\text{PhOMe}$), 6.99 (d, $J = 7.1$ Hz, 2H, $-\text{CH}_2\text{PhOMe}$), 4.07 (s, 2H, $-\text{CH}_2\text{PhOMe}$), 3.78 (s, 3H, $-\text{CH}_2\text{PhOMe}$). ^{13}C NMR (101 MHz, D_2O): δ 159.42, 130.58, 125.23, 114.60, 55.44, 42.64.

2g



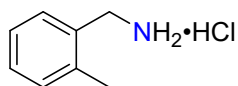
^1H NMR (400 MHz, D_2O): δ 7.28 (d, $J = 8.5$ Hz, 4H, $-\text{CH}_2\text{PhMe}$), 4.09 (s, 2H, $-\text{CH}_2\text{PhMe}$), 2.30 (s, 3H, $-\text{CH}_2\text{PhMe}$). ^{13}C NMR (101 MHz, D_2O): δ 139.63, 129.77, 128.88, 42.90, 20.27.

2h



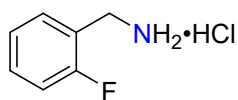
^1H NMR (400 MHz, D_2O): δ 7.34 (t, $J = 7.3$ Hz, 1H, $-\text{CH}_2\text{PhMe}$), 7.29-7.15 (m, 3H, $-\text{CH}_2\text{PhMe}$), 4.10 (s, 2H, $-\text{CH}_2\text{PhMe}$), 2.33 (s, 3H, $-\text{CH}_2\text{PhMe}$). ^{13}C NMR (101 MHz, D_2O): δ 139.50, 132.86, 129.79, 129.34, 129.18, 125.69, 43.13, 20.38.

2i



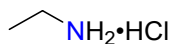
^1H NMR (400 MHz, D_2O): δ 7.68-7.09 (m, 4H, $-\text{CH}_2\text{PhMe}$), 4.18 (s, 2H, $-\text{CH}_2\text{PhMe}$), 2.33 (s, 3H, $-\text{CH}_2\text{PhMe}$). ^{13}C NMR (101 MHz, D_2O): δ 137.22, 130.97, 130.89, 129.41, 129.05, 126.66, 40.50, 18.03.

2j



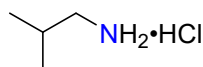
$^1\text{H NMR}$ (400 MHz, D_2O): δ 7.46 (d, $J = 5.6$ Hz, 2H, $-\text{CH}_2\text{PhF}$), 7.24 (dd, $J = 12.9, 8.3$ Hz, 2H, $-\text{CH}_2\text{PhF}$), 4.23 (s, 2H, $-\text{CH}_2\text{PhF}$). $^{13}\text{C NMR}$ (101 MHz, D_2O): δ 162.18, 159.74, 131.75, 131.25, 125.02, 119.51, 115.92, 37.28, 37.24.

2k



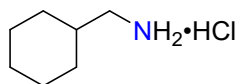
$^1\text{H NMR}$ (400 MHz, D_2O): δ 2.88 (d, $J = 7.3$ Hz, 2H, $-\text{CH}_3\text{CH}_2$), 1.11 (t, $J = 7.3$ Hz, 3H, $-\text{CH}_3\text{CH}_2$). $^{13}\text{C NMR}$ (101 MHz, D_2O): δ 34.97, 11.82.

2l



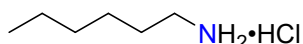
$^1\text{H NMR}$ (400 MHz, D_2O): δ 2.81 (d, $J = 7.1$ Hz, 2H, $-\text{CH}_2\text{CH}(\text{CH}_3)_2$), 1.91 (dt, $J = 13.7, 6.8$ Hz, 1H, $-\text{CH}_2\text{CH}(\text{CH}_3)_2$), 0.95 (d, $J = 6.7$ Hz, 6H, $-\text{CH}_2\text{CH}(\text{CH}_3)_2$). $^{13}\text{C NMR}$ (101 MHz, D_2O): δ 46.40, 26.30, 18.86.

2m



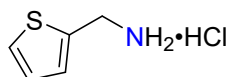
$^1\text{H NMR}$ (400 MHz, D_2O): δ 2.81 (d, $J = 7.0$ Hz, 2H, $-\text{CH}_2\text{C}_6\text{H}_{11}$), 1.70 (d, $J = 11.7$ Hz, 4H, $-\text{CH}_2\text{C}_6\text{H}_{11}$), 1.62 (d, $J = 10.5$ Hz, 2H, $-\text{CH}_2\text{C}_6\text{H}_{11}$), 1.18 (dt, $J = 24.1, 12.4$ Hz, 3H, $-\text{CH}_2\text{C}_6\text{H}_{11}$), 0.97 (t, $J = 10.7$ Hz, 2H, $-\text{CH}_2\text{C}_6\text{H}_{11}$). $^{13}\text{C NMR}$ (101 MHz, D_2O): δ 45.21, 35.40, 29.63, 25.58, 25.03.

2n



$^1\text{H NMR}$ (400 MHz, D_2O): δ 3.20-2.73 (m, 2H, $-\text{CH}_2(\text{CH}_2)_3\text{CH}_2\text{CH}_3$), 1.87-1.47 (m, 2H, $-\text{CH}_2(\text{CH}_2)_3\text{CH}_2\text{CH}_3$), 1.40-1.16 (m, 6H, $-\text{CH}_2(\text{CH}_2)_3\text{CH}_2\text{CH}_3$), 0.86 (t, $J = 6.9$ Hz, 3H, $-\text{CH}_2(\text{CH}_2)_3\text{CH}_2\text{CH}_3$). $^{13}\text{C NMR}$ (101 MHz, D_2O): δ 39.64, 30.48, 26.70, 25.26, 21.79, 13.32.

2o

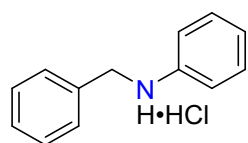


$^1\text{H NMR}$ (400 MHz, D_2O): δ 7.47 (d, $J = 5.1$ Hz, 1H, $-\text{CH}_2\text{C}_4\text{SH}_3$), 7.20 (d, $J = 3.3$ Hz, 1H, $-\text{CH}_2\text{C}_4\text{SH}_3$), 7.10-7.03 (m, 1H, $-\text{CH}_2\text{C}_4\text{SH}_3$), 4.35 (s, 2H, $-\text{CH}_2\text{C}_4\text{SH}_3$). $^{13}\text{C NMR}$ (101 MHz, D_2O): δ 134.08, 129.49, 127.95, 127.78, 37.50.

General Procedure for Hydroboration of Secondary Amides.

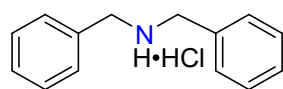
In a 10 ml Schlenk flask equipped with a magnetic stir bar in the glovebox, secondary amide (0.5 mmol), pinacolborane (1.5mmol, 3.0 eq) and NaHBET₃ (0.025 mmol) were combined and heated in an oil bath at 60 °C for 12 h. The reaction mixture was hydrolyzed with 1 M HCl in ether (10 mL). The volatiles were removed under reduced pressure, and the residue was washed with ethyl acetate (3 × 5 mL) to give a pure desired product as an ammonium salt. The ¹H NMR and ¹³C NMR spectra of the isolated ammonium salts were recorded in D₂O.

4a



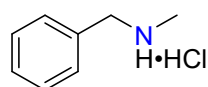
¹H NMR (400 MHz, D₂O): δ 7.51-7.45 (m, 3H, *Ph*), 7.43-7.34 (m, 3H, *Ph*), 7.31-7.24 (m, 4H, *Ph*), 4.58 (s, 2H, -CH₂). ¹³C NMR (101 MHz, D₂O): δ 133.86, 130.41, 130.22, 129.94, 129.82, 129.11, 123.00, 55.59.

4b



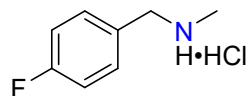
¹H NMR (400 MHz, D₂O): δ 7.55-7.26 (m, 10H, *Ph*), 4.22 (s, 4H, CH₂). ¹³C NMR (101 MHz, D₂O): δ 130.83, 129.87, 129.68, 129.32, 50.59.

4c



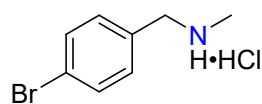
¹H NMR (400 MHz, D₂O): δ 7.42 (s, 5H, *Ph*), 4.15 (s, 2H, CH₂), 2.66 (s, 3H, CH₃). ¹³C NMR (101 MHz, D₂O): δ 130.70, 129.71, 129.68, 129.27, 52.38, 32.06.

4d



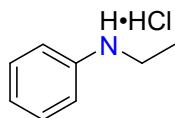
¹H NMR (400 MHz, D₂O): δ 7.45 (dd, *J* = 8.2, 5.4 Hz, 2H, *Ph*), 7.18 (t, *J* = 8.8 Hz, 2H, *Ph*), 4.16 (s, 2H, CH₂), 2.68 (s, 3H, CH₃). ¹³C NMR (101 MHz, D₂O): δ 164.41, 161.97, 132.03, 131.95, 126.82, 116.21, 115.99, 51.65, 32.06.

4e



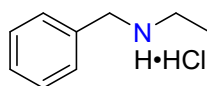
$^1\text{H NMR}$ (400 MHz, D_2O): δ 7.60 (d, $J = 8.3$ Hz, 2H, *Ph*), 7.33 (d, $J = 8.3$ Hz, 2H, *Ph*), 4.14 (s, 2H, CH_2), 2.67 (s, 3H, CH_3). $^{13}\text{C NMR}$ (101 MHz, D_2O): δ 132.28, 131.60, 130.02, 123.31, 51.74, 32.22.

4f



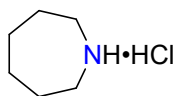
$^1\text{H NMR}$ (400 MHz, D_2O): δ 7.53 (d, $J = 7.6$ Hz, 3H, *Ph*), 7.42 (d, $J = 6.9$ Hz, 2H, *Ph*), 3.43 (q, $J = 7.3$ Hz, 2H, CH_2), 1.26 (t, $J = 7.3$ Hz, 3H, CH_3). $^{13}\text{C NMR}$ (101 MHz, D_2O): δ 134.38, 130.36, 129.92, 122.56, 47.33, 10.26.

4g



$^1\text{H NMR}$ (400 MHz, D_2O): δ 7.55 (s, 5H, *Ph*), 4.27 (s, 2H, CH_2), 3.19 (q, $J = 7.3$ Hz, 2H, CH_2), 1.36 (t, $J = 7.3$ Hz, 3H, CH_3). $^{13}\text{C NMR}$ (101 MHz, D_2O): δ 131.06, 129.70, 129.60, 129.29, 50.66, 42.49, 10.55.

4h

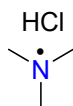


$^1\text{H NMR}$ (400 MHz, D_2O): δ 3.30-3.13 (m, 2H, $-\text{NC}_6\text{H}_{10}$), 1.81 (s, 2H, $-\text{NC}_6\text{H}_{10}$), 1.64 (s, 2H, $-\text{NC}_6\text{H}_{10}$). $^{13}\text{C NMR}$ (101 MHz, D_2O) δ 45.21, 35.40, 29.63, 25.58, 25.03.

General Procedure for Hydroboration of Tertiary Amides.

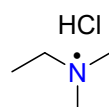
In a 10 ml Schlenk flask equipped with a magnetic stir bar in the glovebox, tertiary amide (0.5 mmol), pinacolborane (1.5 mmol, 3.0 eq) and NaHBET_3 (0.025 mmol) were combined and heated in an oil bath at 60 °C for 12 h. The reaction mixture was hydrolyzed with 1 M HCl in ether (10 mL). The volatiles were removed under reduced pressure, and the residue was washed with ethyl acetate (3×5 mL) to give a pure desired product as an ammonium salt. The $^1\text{H NMR}$ and $^{13}\text{C NMR}$ spectra of the isolated ammonium salts were recorded in D_2O .

6a



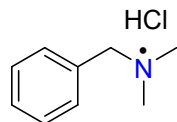
$^1\text{H NMR}$ (400 MHz, D_2O): δ 2.74 (s, 9H, CH_3). $^{13}\text{C NMR}$ (101 MHz, D_2O): δ 44.78.

6b



^1H NMR (400 MHz, D_2O): δ 2.25 (d, $J = 7.3$ Hz, 2H, CH_2), 2.06 (s, 6H, CH_3), 0.91 (t, $J = 7.3$ Hz, 3H, CH_3). ^{13}C NMR (101 MHz, D_2O): δ 52.30, 43.23, 11.36.

6c



^1H NMR (400 MHz, D_2O): δ 7.47-7.17 (m, 5H, Ph), 3.43 (s, 2H, CH_2), 2.12 (s, 6H, CH_2). ^{13}C NMR (101 MHz, D_2O): δ 137.45, 129.92, 128.47, 127.61, 62.75, 43.59.

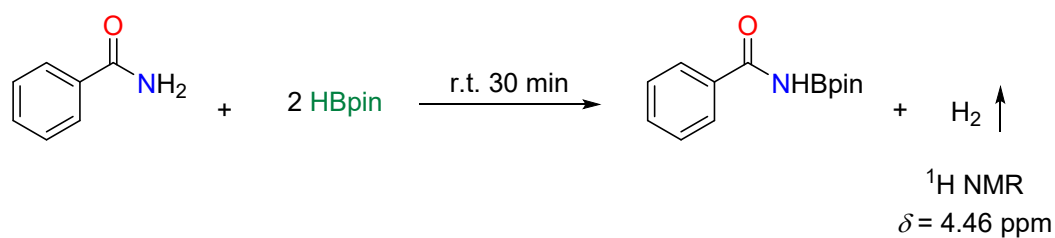
Control experiments for the mechanistic investigation.

To understand the mechanism associated with hydroboration of primary amide, we have carried out a series of experimental studies as mentioned below.

a) Detection of molecular hydrogen in hydroboration of benzamide.

In a glovebox, an oven dried screw-cap NMR tube was charged with benzamide (12.10 mg, 0.10 mmol, 1.0 equivalent), HBpin (25.56 mg, 0.20 mmol, 2.0 equivalent), and CDCl_3 (500 μL) and reacted at room temperature for 30 min. H_2 production was observed and subsequently characterized by ^1H NMR spectroscopy. A sharp resonance at δ 4.46 ppm in ^1H NMR spectrum indicates the formation of molecular hydrogen (**Scheme S1** and Figure S1).

Scheme S1. Detection of molecular hydrogen in hydroboration of benzamide.



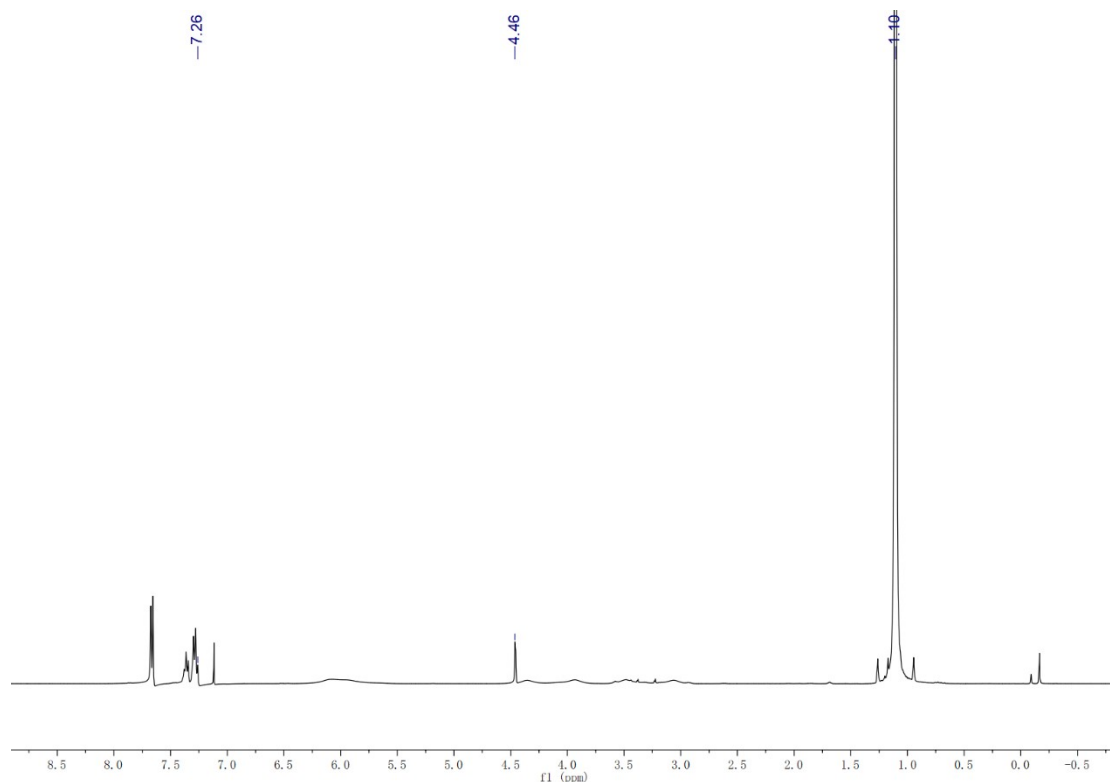
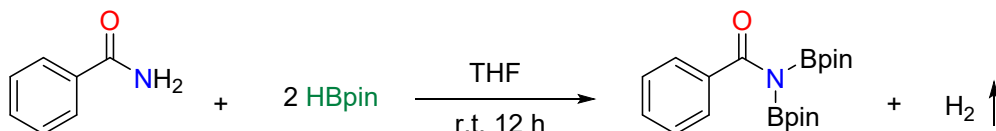


Figure S1. ^1H NMR spectrum of molecular hydrogen recorded in CDCl_3 for hydroboration of benzamide.

b) Isolation and characterization of intermediate $\text{PhCON}(\text{Bpin})_2$

In a glovebox, benzamide (0.25 mmol), HBpin (0.5 mmol, 2.0 equivalent), and THF (1 mL) were added in a Schlenk flask. The reaction mixture was stirred at ambient temperature overnight. Removal of the volatiles under reduced pressure afforded a white powder, which was washed with *n*-hexane for three times. Drying up the residue gave a white solid. The borylated-amide compound $\text{PhCON}(\text{Bpin})_2$ was isolated by recrystallization from THF/hexane, and was characterized by ^1H , ^{13}C , and ^{11}B NMR spectroscopy (Scheme S2 and Figures S2-S4)

Scheme S2. Preparation and isolation of intermediate $\text{PhCON}(\text{Bpin})_2$



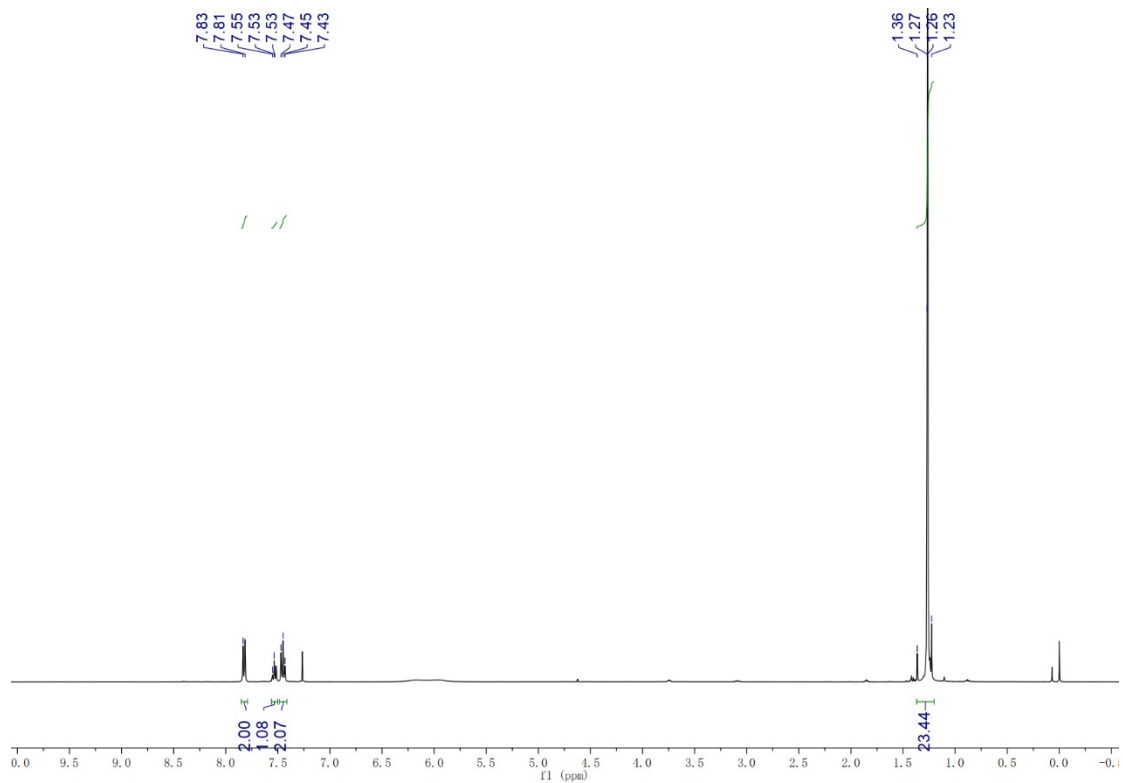


Figure S2. ^1H NMR spectrum of intermediate $\text{PhCON}(\text{Bpin})_2$

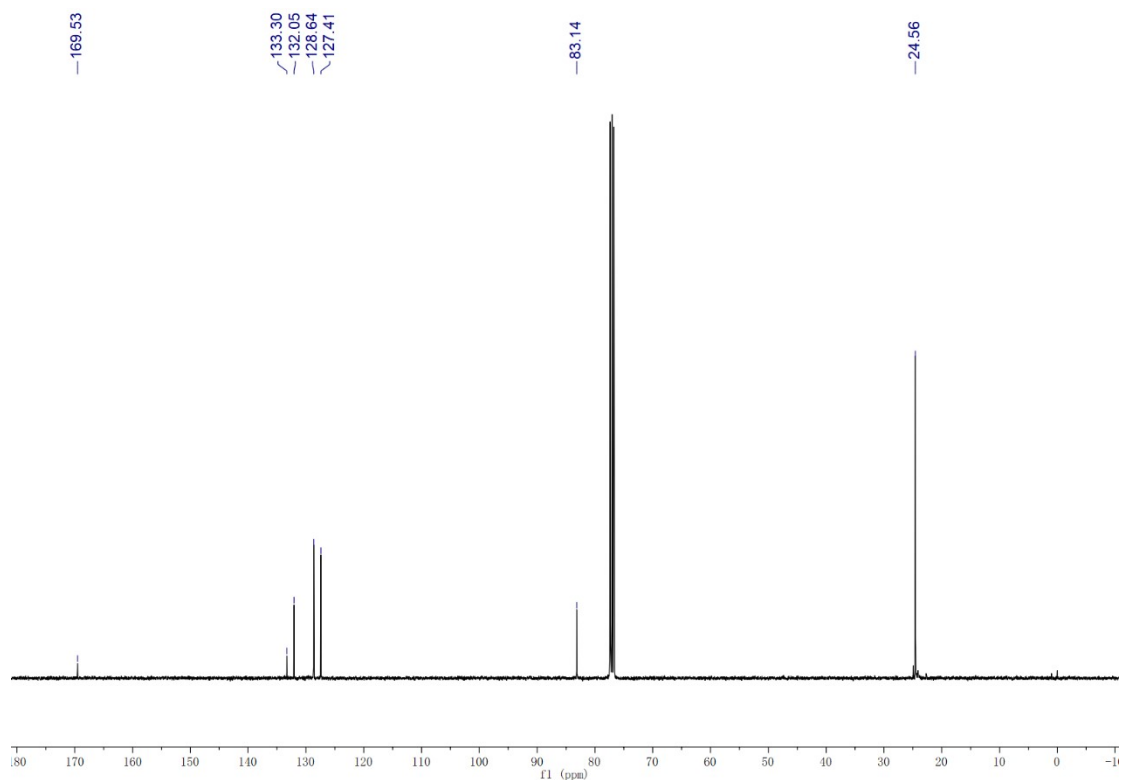


Figure S3. ^{13}C NMR spectrum of intermediate $\text{PhCON}(\text{Bpin})_2$

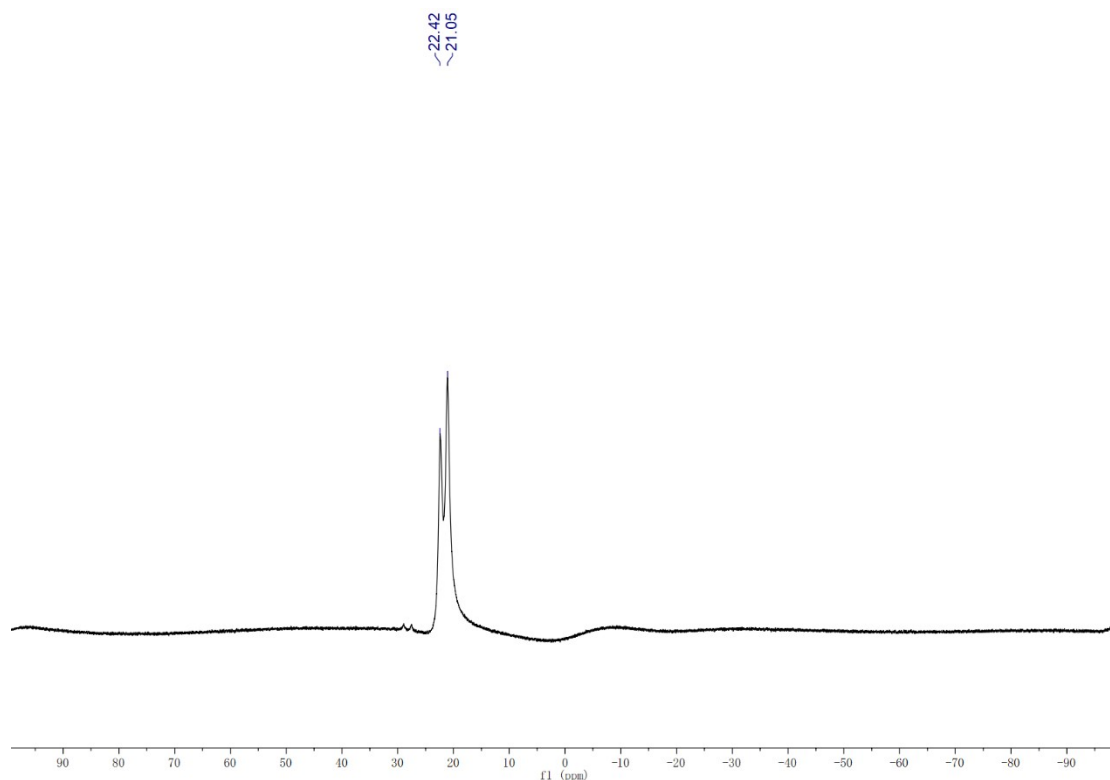
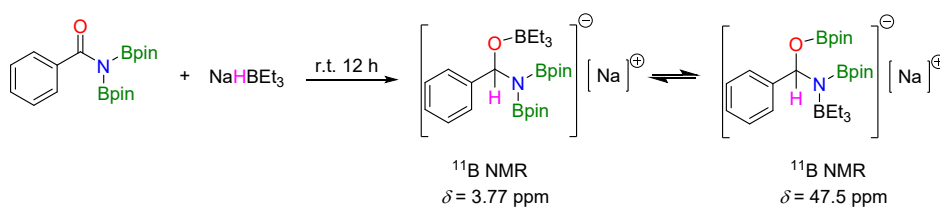


Figure S4. ^{11}B NMR spectrum of intermediate $\text{PhCON}(\text{Bpin})_2$

c) In situ NMR study to characterize the interaction between $\text{PhCON}(\text{Bpin})_2$ and NaHBEt_3 .

In a glovebox, $\text{PhCON}(\text{Bpin})_2$ (0.25 mmol), NaHBEt_3 (0.25 mmol, 1.0 equivalent), and CDCl_3 (500 μL) in a Schlenk flask and reacted at room temperature for overnight. Next, the interaction between $\text{PhCON}(\text{Bpin})_2$ and NaHBEt_3 was characterized through ^1H and ^{11}B NMR spectroscopies. In ^1H NMR spectrum, $\sim \delta$ 4.5 ppm was observed as compared to that of $\text{PhCON}(\text{Bpin})_2$. And in ^{11}B NMR spectroscopy comparison with $\text{PhCON}(\text{Bpin})_2$ shows several new peaks, 87.2 ppm (BEt_3)^[S1], 47.5 ppm, 3.77 ppm. These observations clearly suggest the interaction between two compounds which is consistent with result reported by Ramachandaran^[S2]. And there is an interconversion of two intermediates with ^{11}B NMR spectra corresponding to 47.5 ppm and 3.77 ppm, respectively (Scheme S3 and Figures S5-S6).

Scheme S3. Preparation and isolation of intermediate $\text{PhCON}(\text{Bpin})_2$



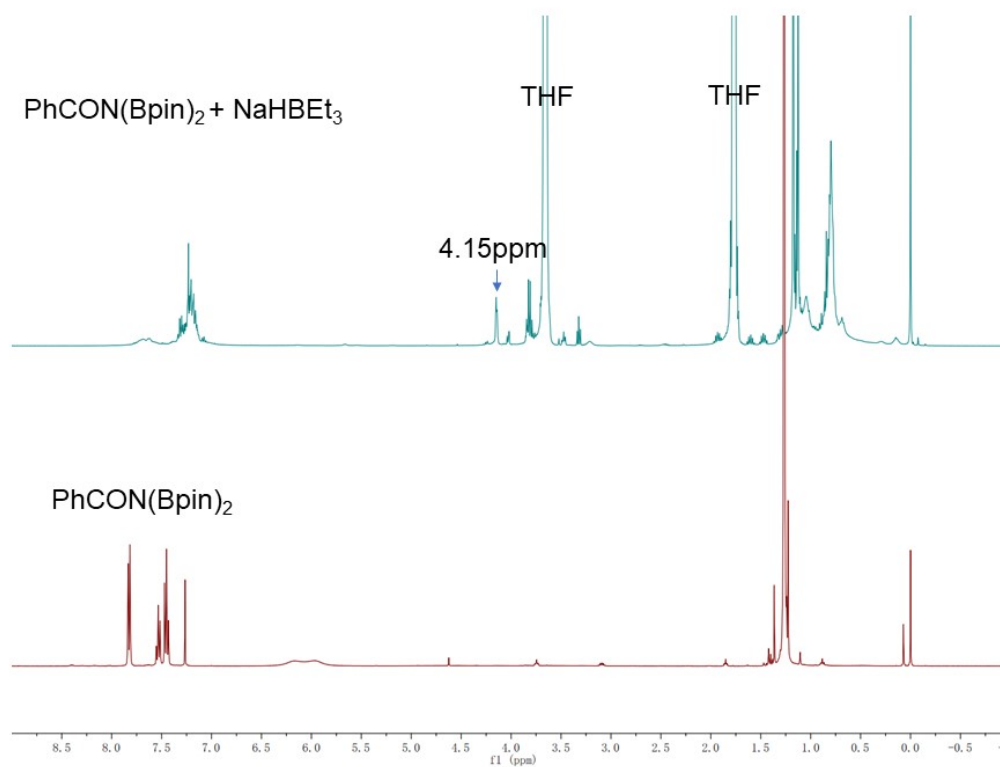


Figure S5. ¹H NMR spectrum of the reaction of PhCON(Bpin)₂ and NaHBET₃

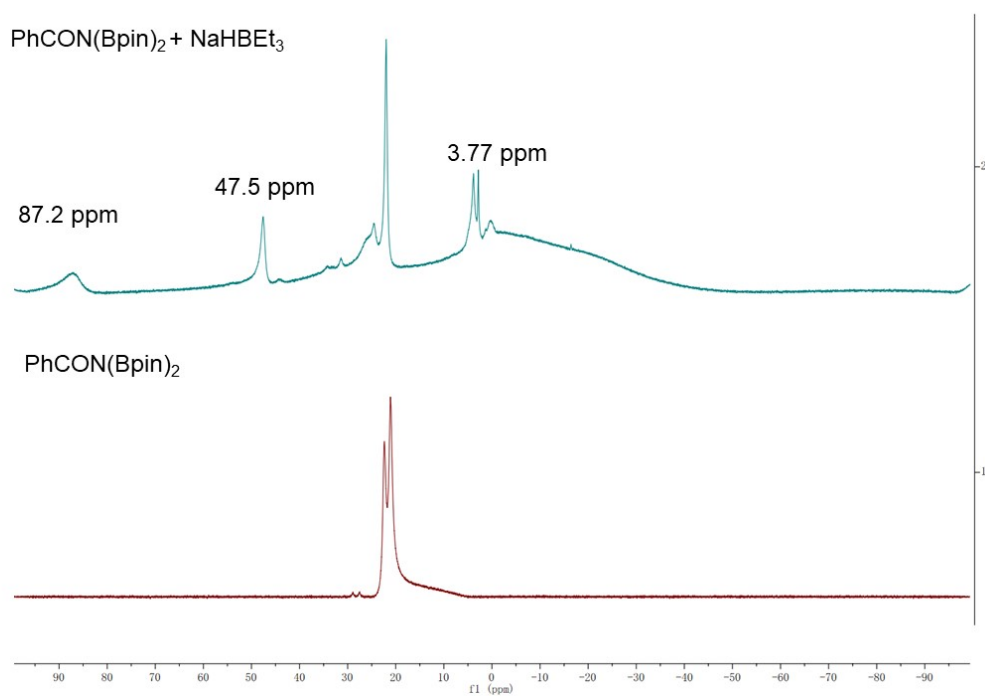


Figure S6. ¹¹B NMR spectrum of the reaction of PhCON(Bpin)₂ and NaHBET₃

d) Characterization of in situ generated intermediate imine.

In a glovebox, benzamide (0.25 mmol), HBpin (1.0 mmol, 4.0 equivalent) and NaHBEt₃ (0.0125 mmol) in a Schlenk flask and reacted at 60 °C for 4 hours. Next, all volatiles were removed using high vacuum and ¹H NMR spectroscopy of the reaction mixture was recorded in CDCl₃. A sharp resonance at δ 10.21 ppm for benzamide was observed in ¹H NMR spectrum, which clearly indicates the formation of an imine intermediate (Scheme S4 and Figure S7).

Scheme S4. Synthetic scheme for the formation of intermediate imine.

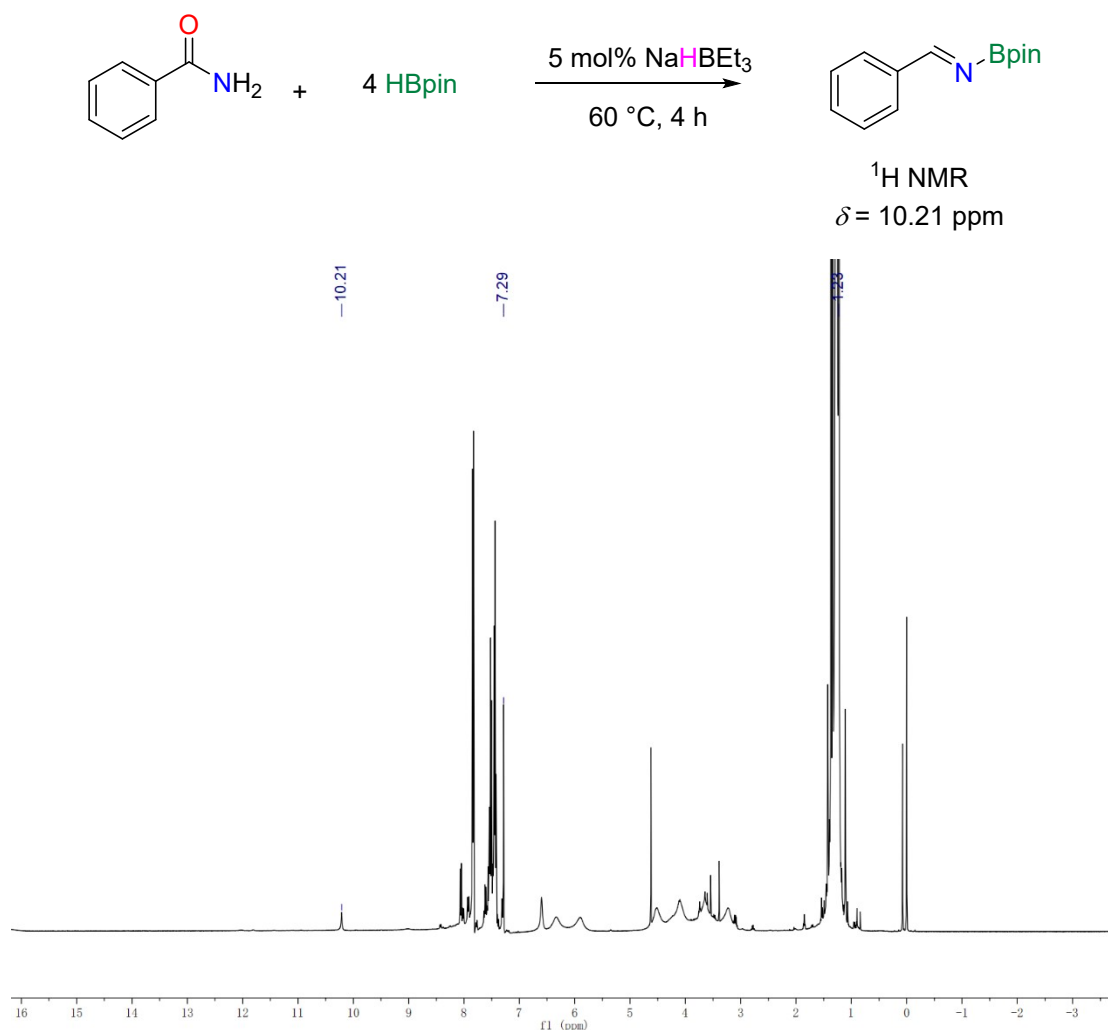


Figure S7. ¹H NMR spectrum of in situ generated *N*-borylated imine recorded in CDCl₃.

e) Preparation of *N,N*-diborylated amine upon hydroborylation of benzamide.

In a 10 ml Schlenk flask equipped with a magnetic stir bar in the glovebox, primary amide (0.5 mmol), pinacolborane (2.2 mmol, 4.4 eq) and NaHBEt₃ (0.025 mmol) were combined and heated in an oil bath at 60 °C for 12 h. After completion of the reaction ¹H NMR was recorded in CDCl₃ (Scheme S5 and Figure S8).

Scheme S5. Synthetic scheme for the formation of *N,N*-diborylated amine from benzamide.

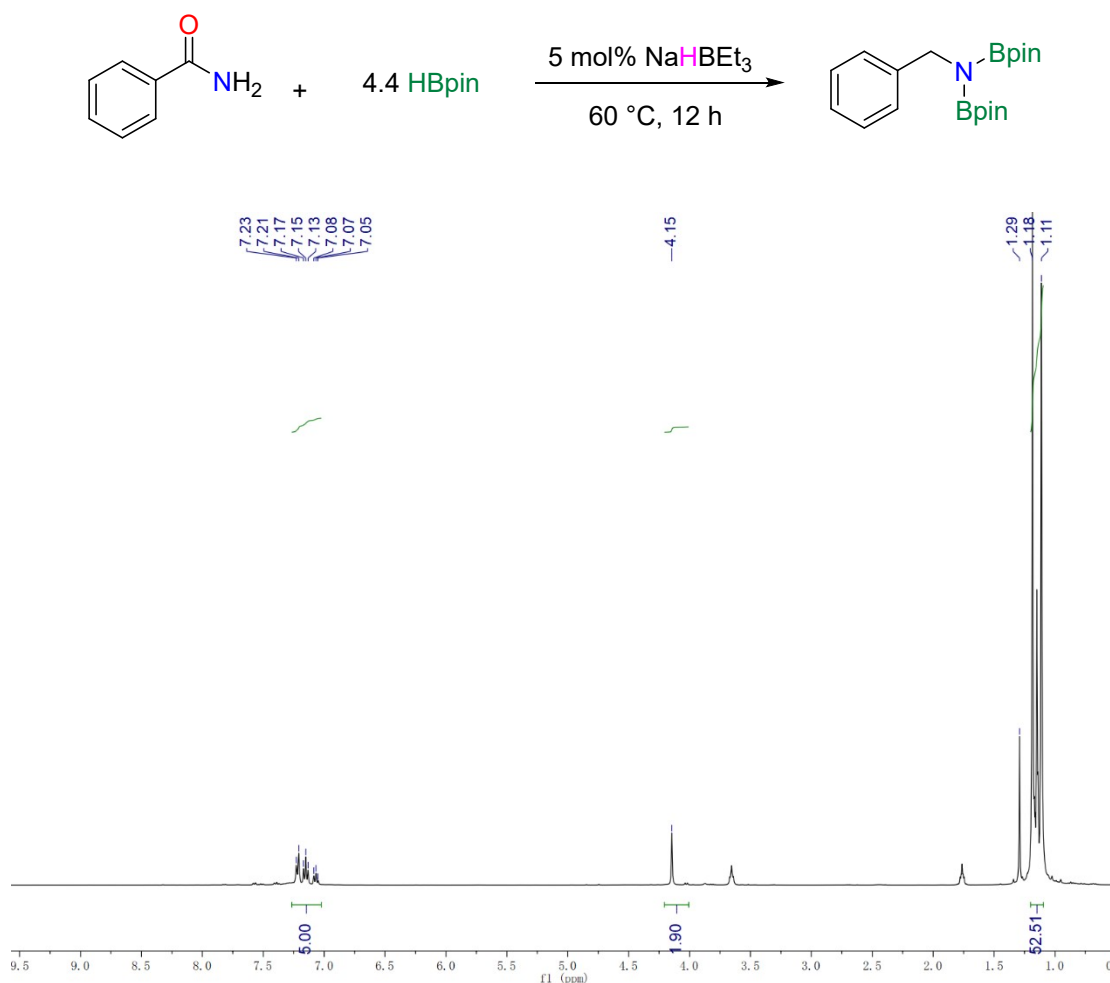
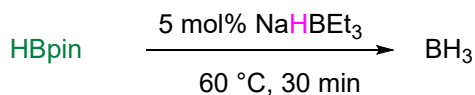


Figure S8. ^1H NMR spectrum of the reaction of benzamide with HBpin catalyzed by NaHBET_3 .

f) In situ NMR study to characterize the interaction between HBpin and NaHBET_3 .

In a 10 ml Schlenk flask equipped with a magnetic stir bar in the glovebox, pinacolborane (2.2 mmol, 4.4 eq) and NaHBET_3 (0.025 mmol) were combined and heated in an oil bath at $60\text{ }^\circ\text{C}$ for 30 min. After completion of the reaction ^{11}B NMR was recorded in CDCl_3 , we can find that a new quadruple peak around $\delta = -13$ ppm reveals the presence of BH_3 . (Scheme S6 and Figure S9).

Scheme S6. The formation of BH_3 from HBpin and NaHBET_3 .



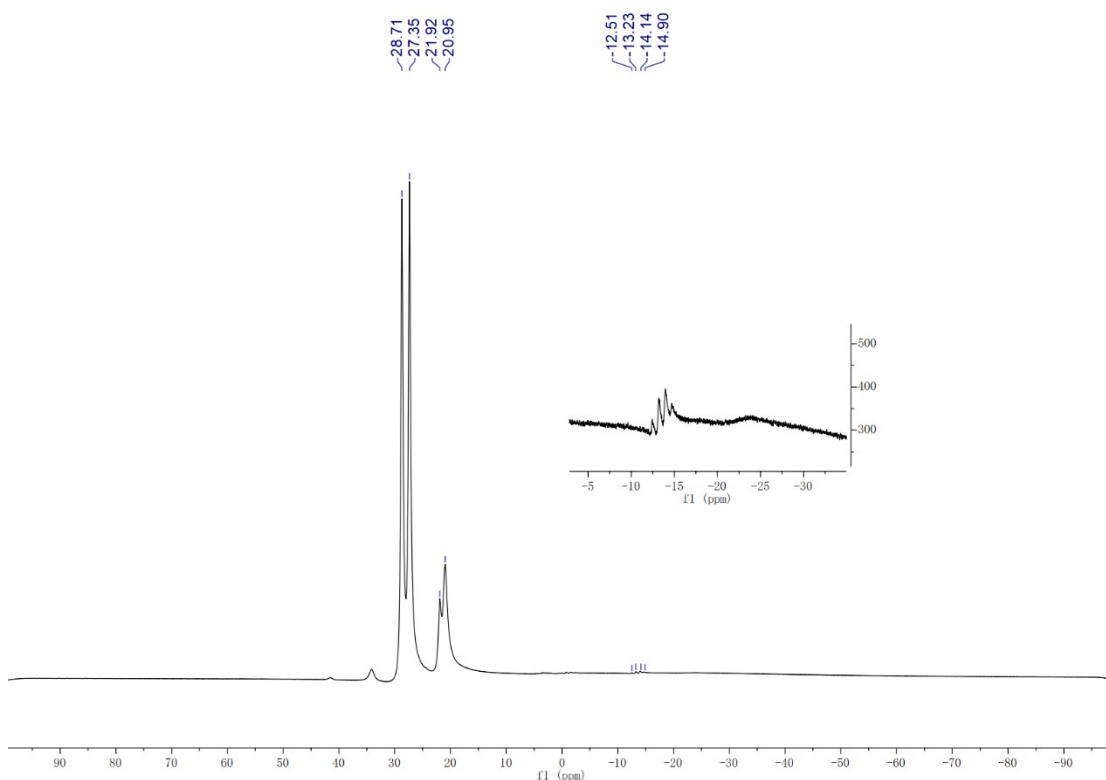


Figure S9. ^{11}B NMR spectrum of the reaction of with HBpin with NaHBET_3 .

g) The study the effect of BH_3 on the hydroboration reaction of amide

In a 10 ml Schlenk flask equipped with a magnetic stir bar in the glovebox, primary amide (0.5 mmol), pinacolborane (2.2 mmol, 4.4 eq) and catalyst **X** (5 mol%) were combined and heated in an oil bath at 60 °C for 12 h. After completion of the reaction ^1H NMR was recorded in CDCl_3 and calculated its yield (**Scheme S7**, Figure S10 and Table 1). For the mentioned reaction, the yield of product is up to 92% in the presence of TMEDA (95% for without TMEDA). When only $\text{BH}_3\cdot\text{SMe}_2$ as catalyst which is consistent with the amount of reaction of HBpin and NaHBET_3 , we cannot find any reaction. Even if the amount of $\text{BH}_3\cdot\text{SMe}_2$ is raised to 5%, only 7% product is obtained. We also investigated the effect of BEt_3 and found that BEt_3 does not act as a catalyst for this reaction. These results suggest for the noninvolvement or very less influence of BH_3 and BEt_3 as an active catalyst for the hydroboration of benzamide.

Scheme S7. Synthetic scheme for the hydroboration of benzamide in presence of catalyst X.

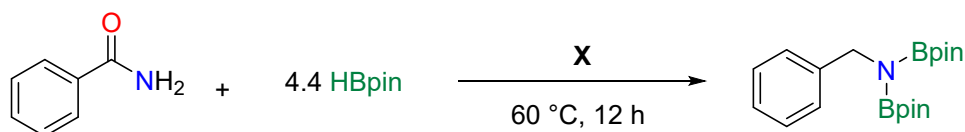


Table1. The hydroboration reaction of benzamide with HBpin in the presence of X

X (5 mol%)	Yield
NaHBET ₃	95%
NaHBET ₃ + TMEDA (1:2)	91%
BH ₃ ·SMe ₂ ^a	n.d.
BH ₃ ·SMe ₂ ^b	7%
BEt ₃	n.d.

^a 0.3 mol% BH₃·SMe₂ which quantity is consistent with BH₃ that reaction of with HBpin with NaHBET₃; ^b 5 mol% BH₃·SMe₂

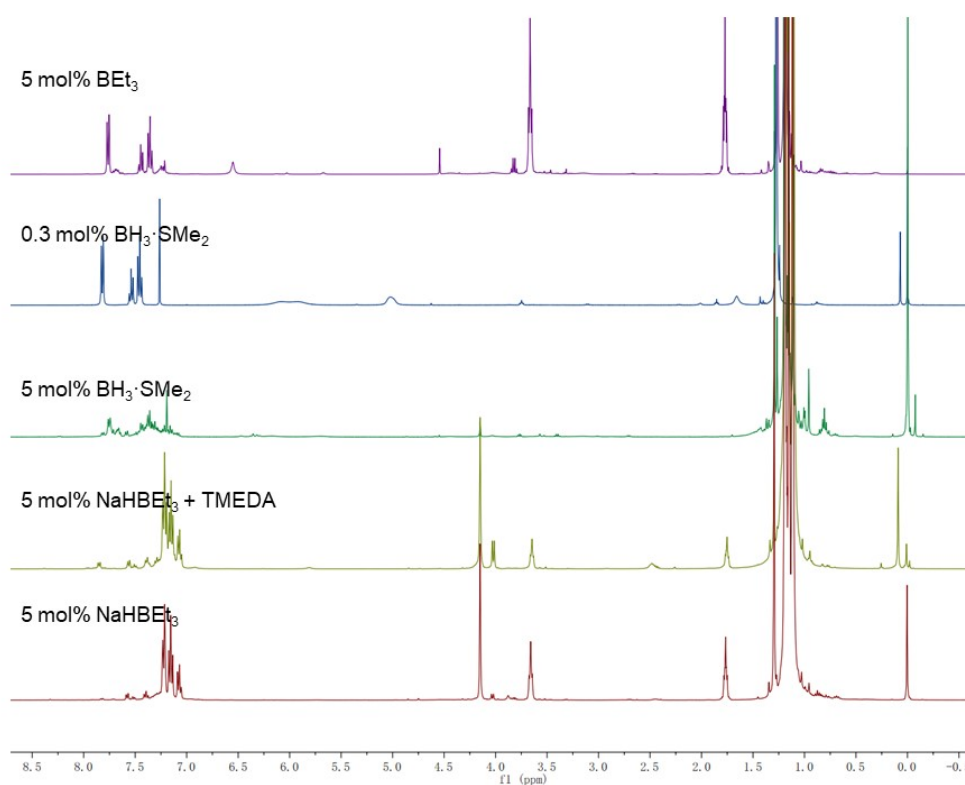


Figure S10. ¹H NMR spectrum of the reaction of PhCONH₂ and HBpin as X as a catalyst

¹H, and ¹³C Spectra of Hydroboration Products of Primary Amides

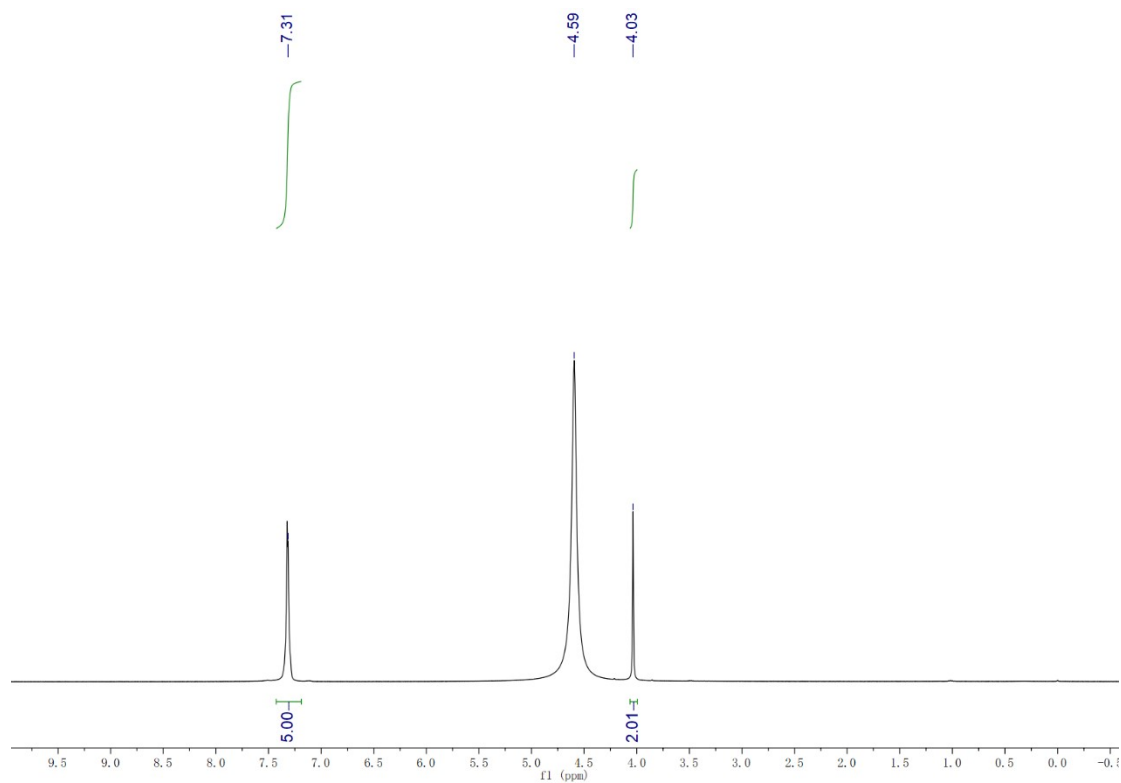


Figure S1.1.1 ^1H NMR of compound **2a** in D_2O

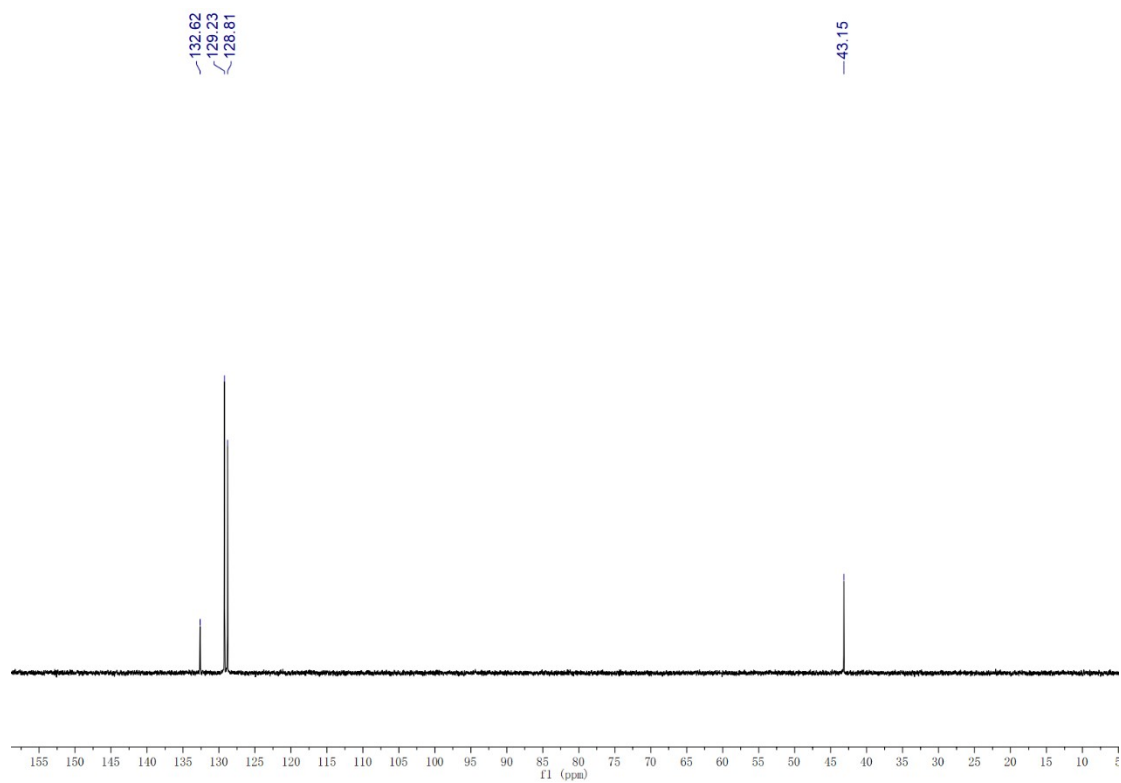


Figure S1.1.2 ^{13}C NMR of compound **2a** in D_2O

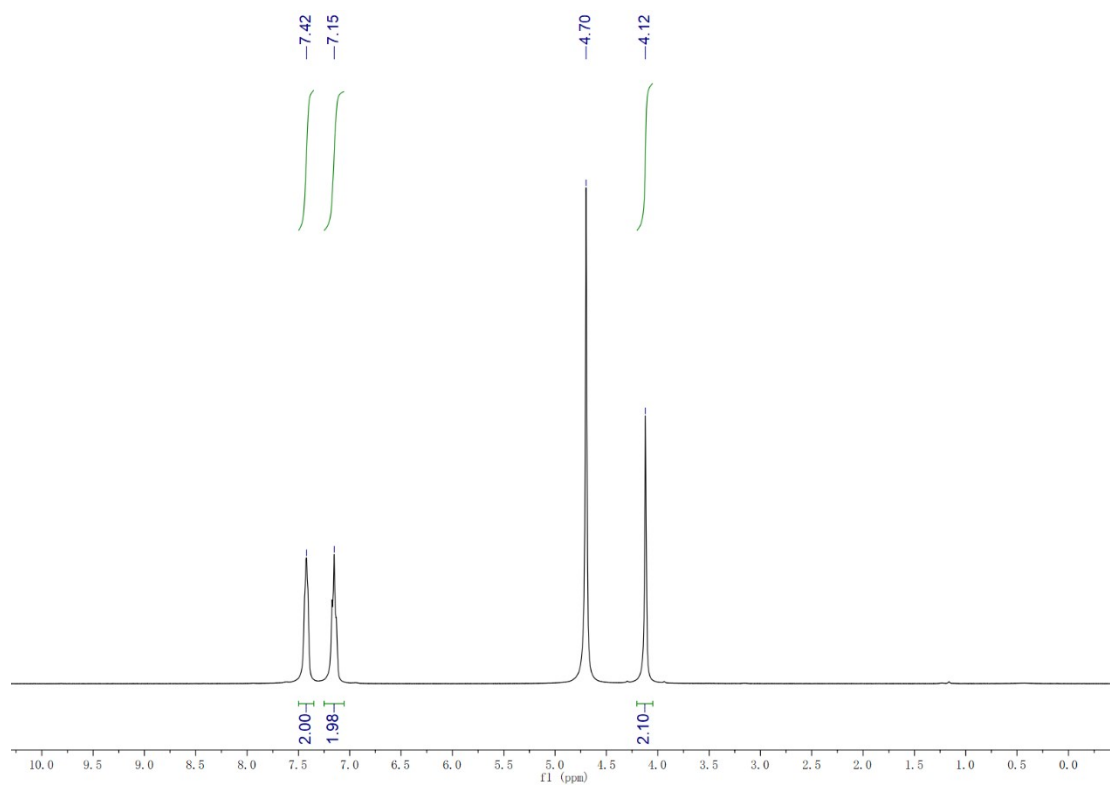


Figure S1.2.1 ¹H NMR of compound **2b** in D₂O

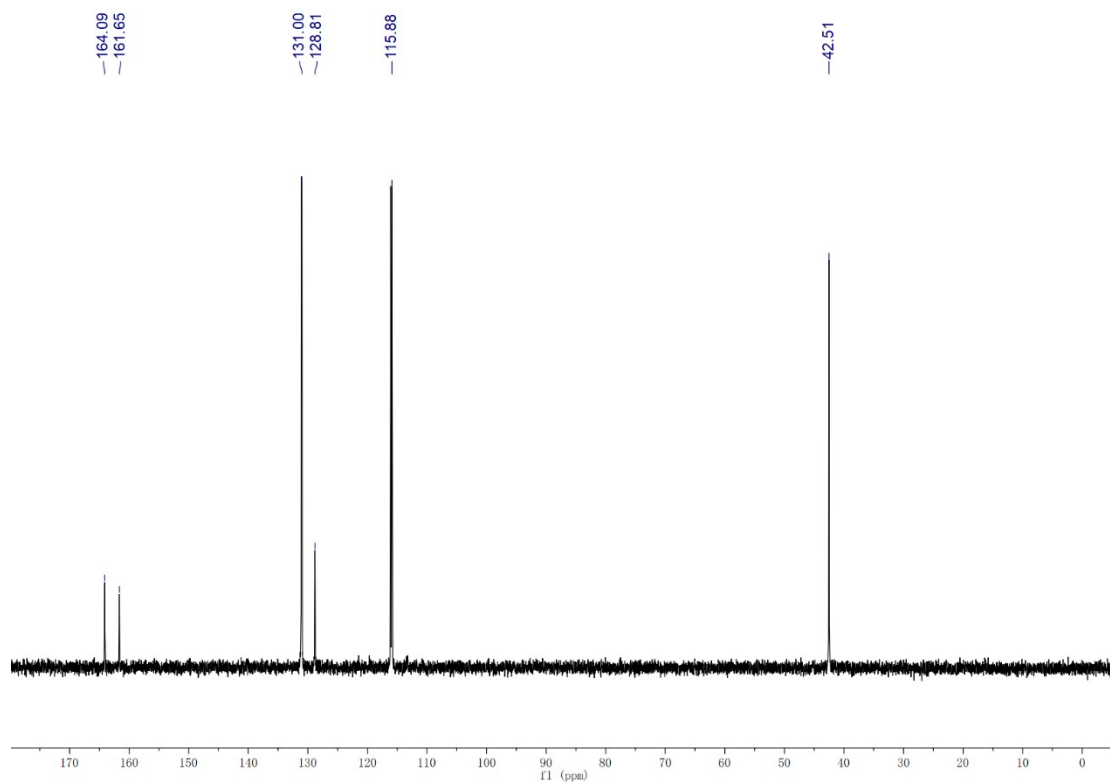


Figure S1.2.2 ¹³C NMR of compound **2b** in D₂O

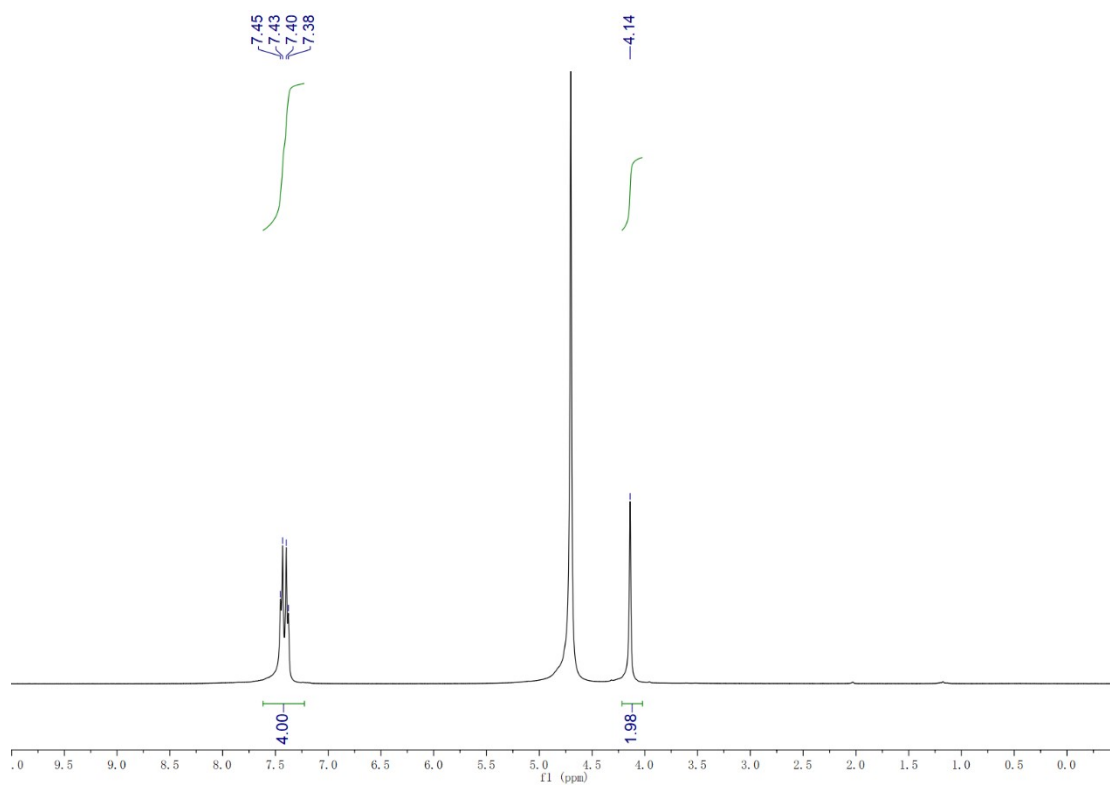


Figure S1.3.1 ^1H NMR of compound **2c** in D_2O

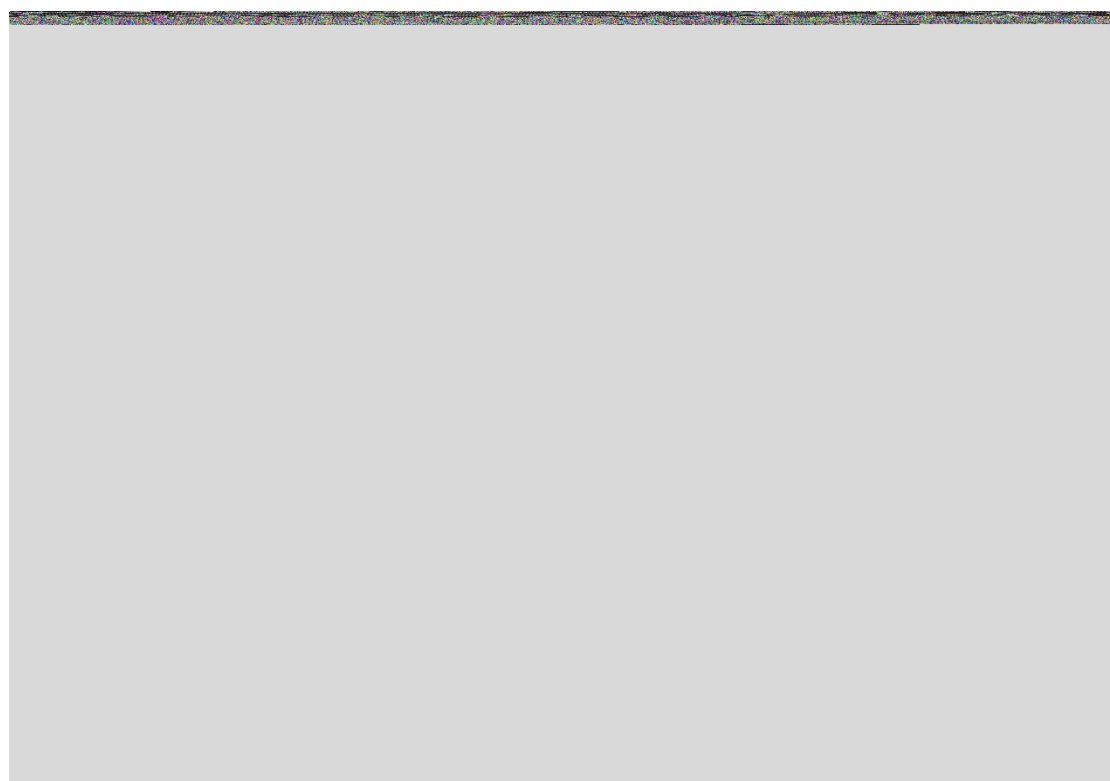


Figure S1.3.2 ^{13}C NMR of compound **2c** in D_2O

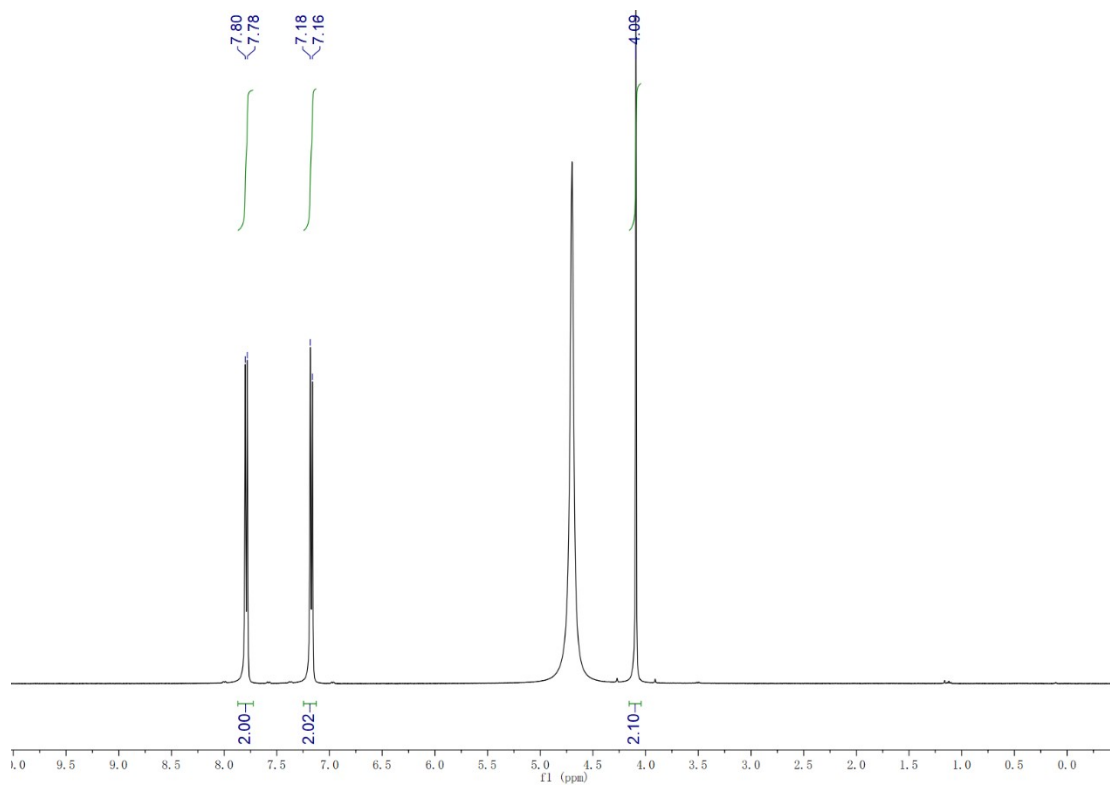


Figure S1.4.1 ^1H NMR of compound **2d** in D_2O

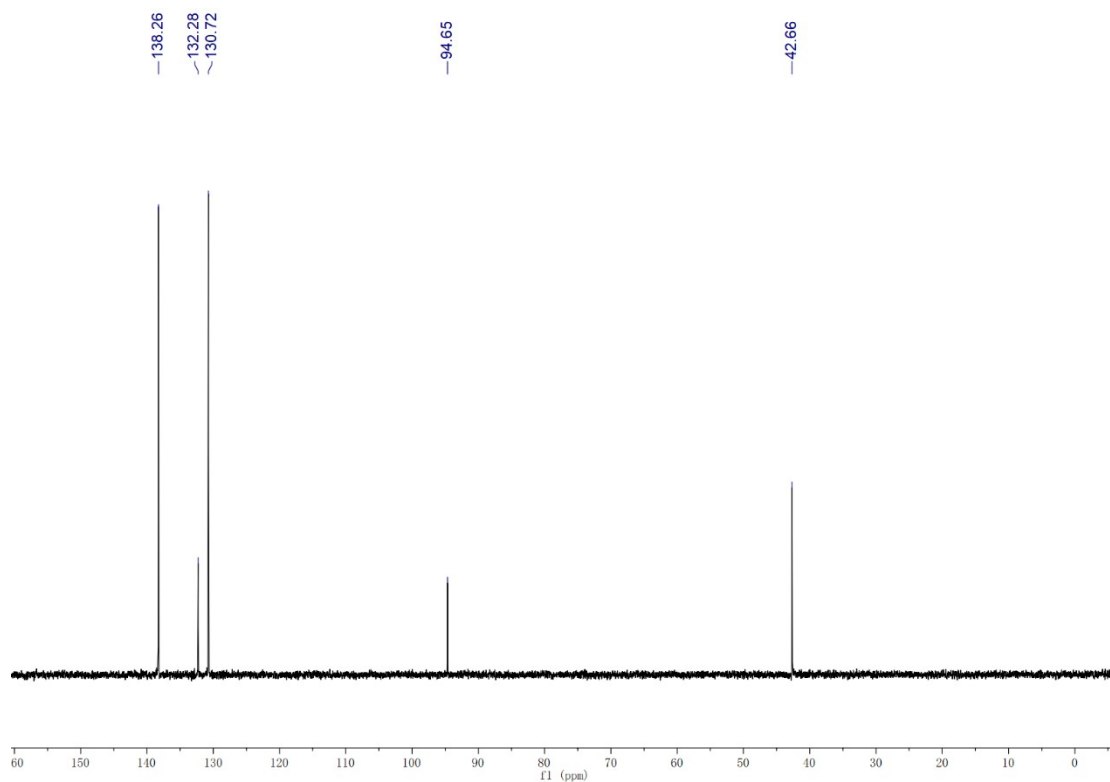


Figure S1.4.2 ^{13}C NMR of compound **2d** in D_2O

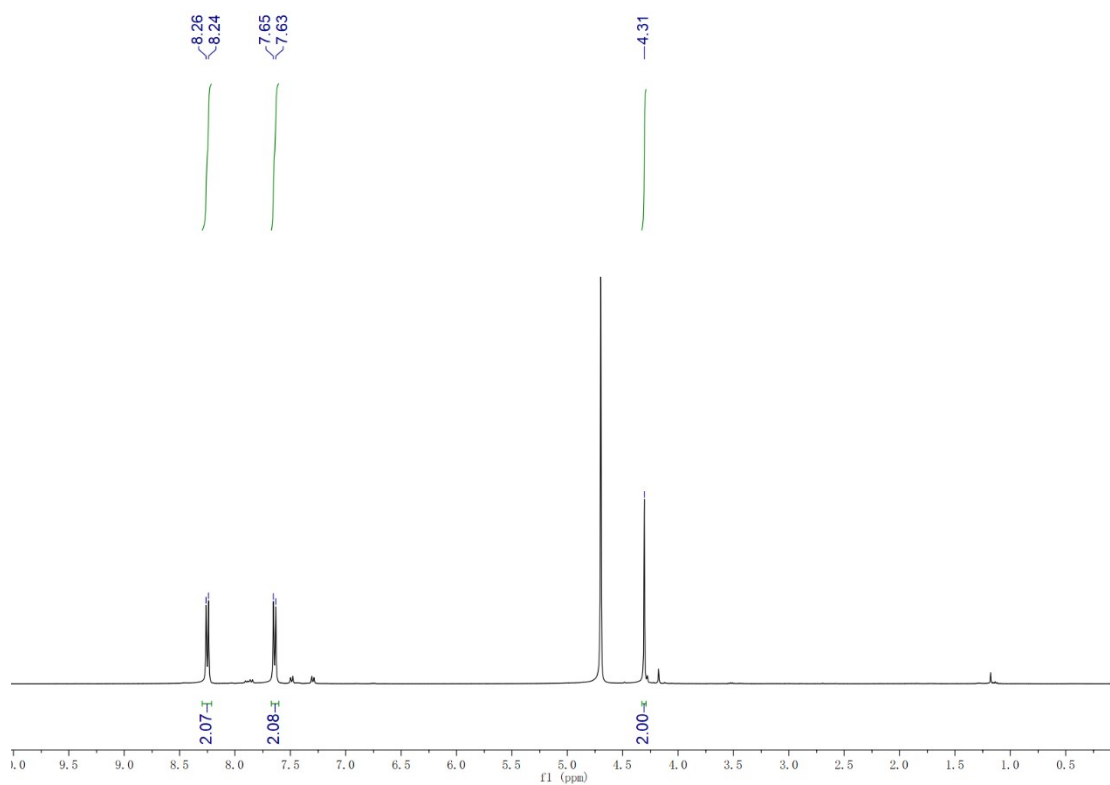


Figure S1.5.1 ^1H NMR of compound **2e** in in D_2O

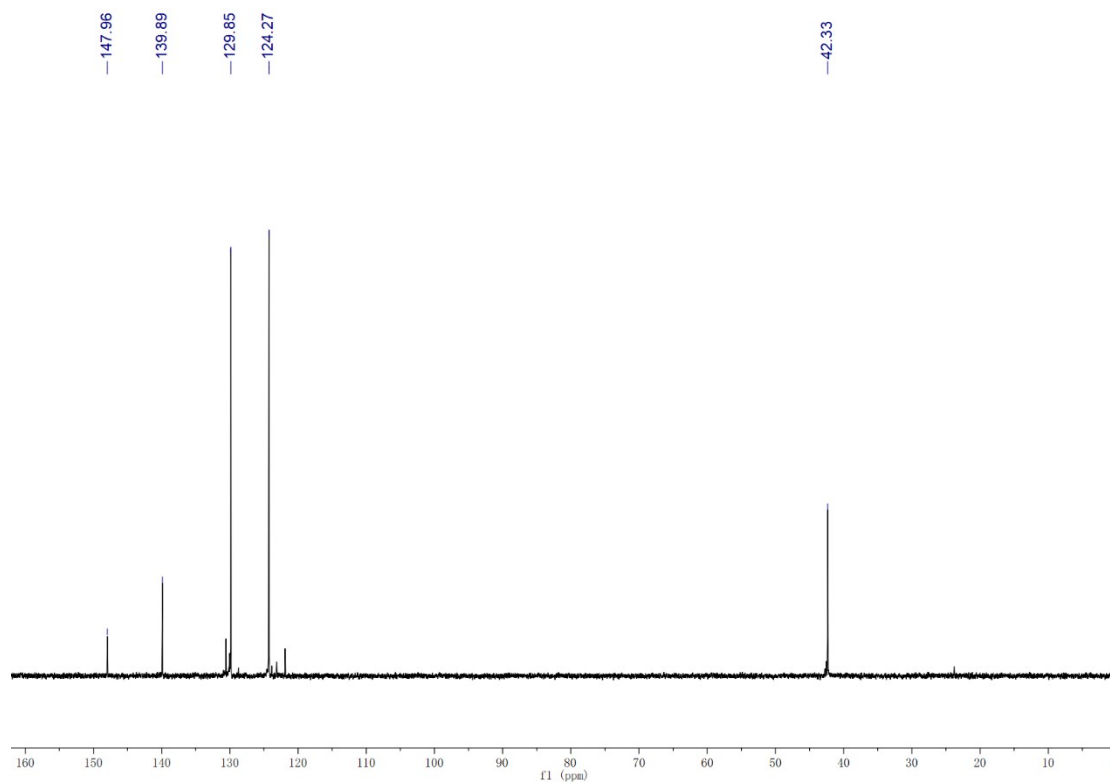


Figure S1.5.2 ^{13}C NMR of compound **2e** in in D_2O

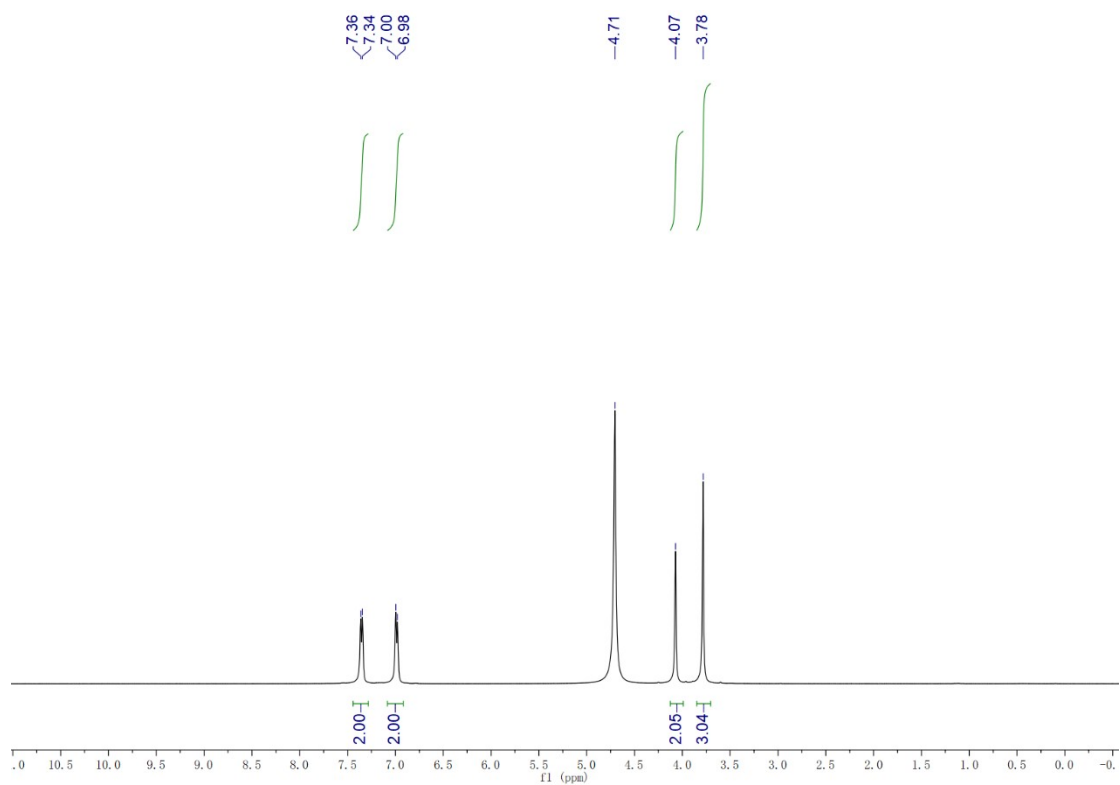


Figure S1.6.1 ^1H NMR of compound **2f** in D_2O

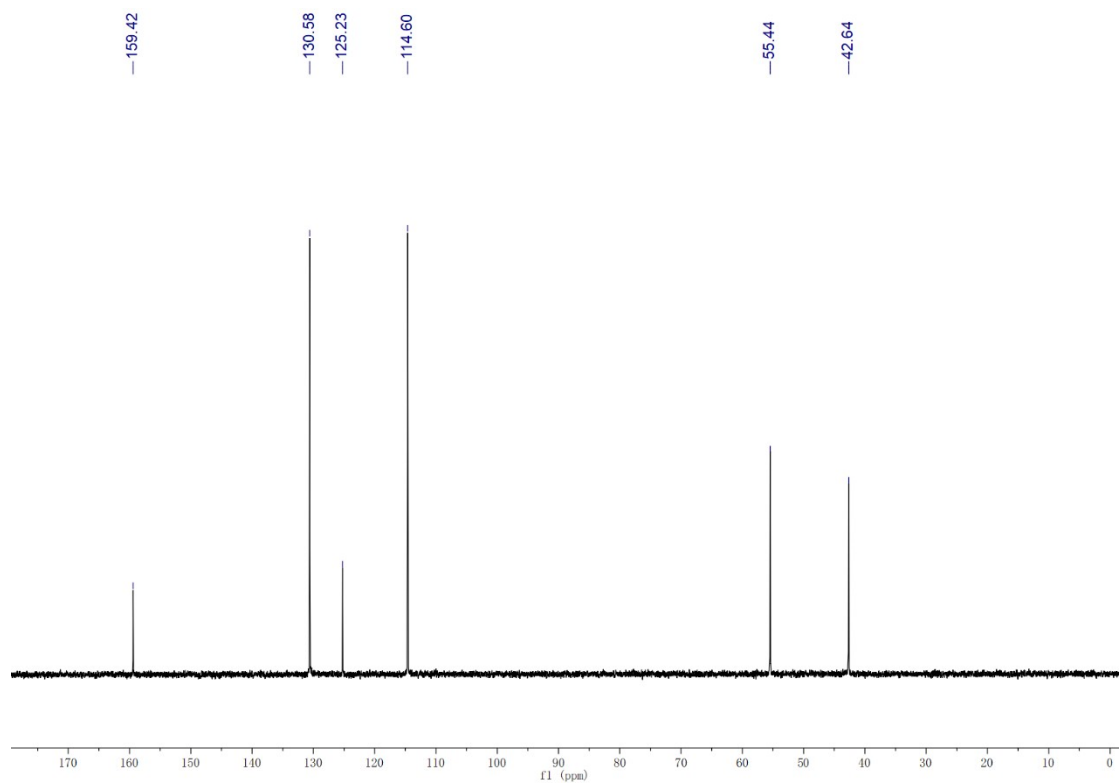


Figure S1.6.2 ^{13}C NMR of compound **2f** in D_2O

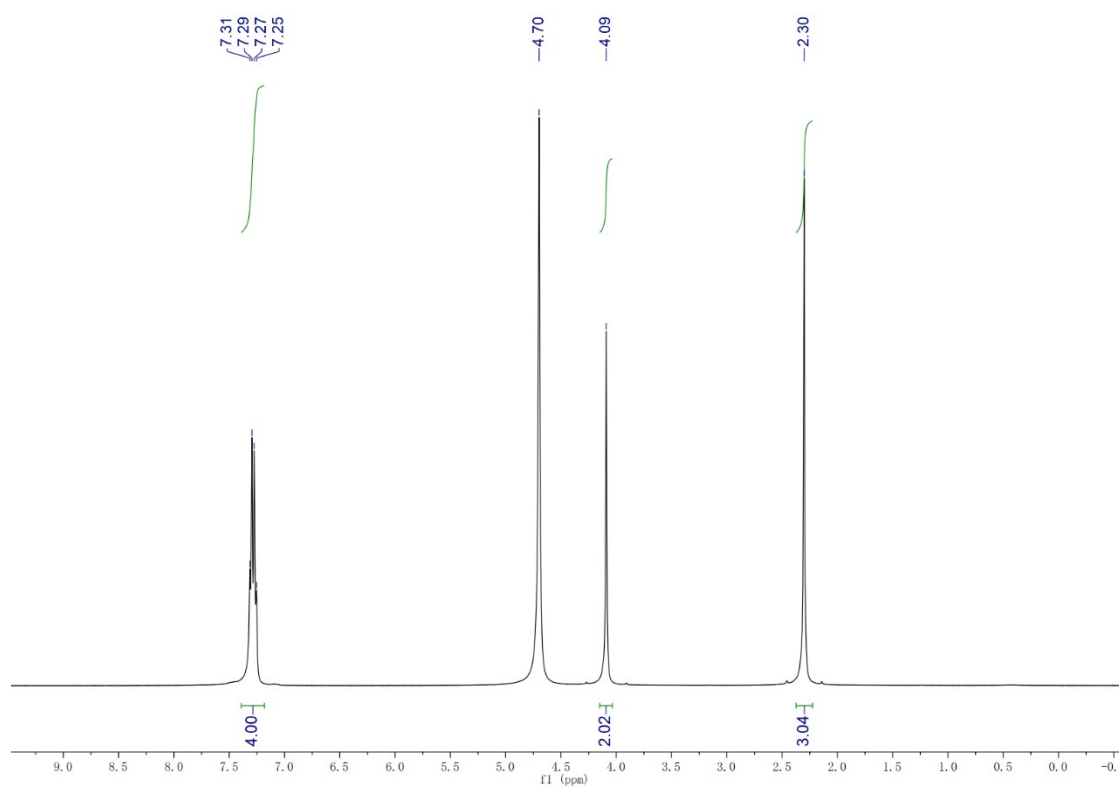


Figure S1.7.1 ^1H NMR of compound **2g** in D_2O

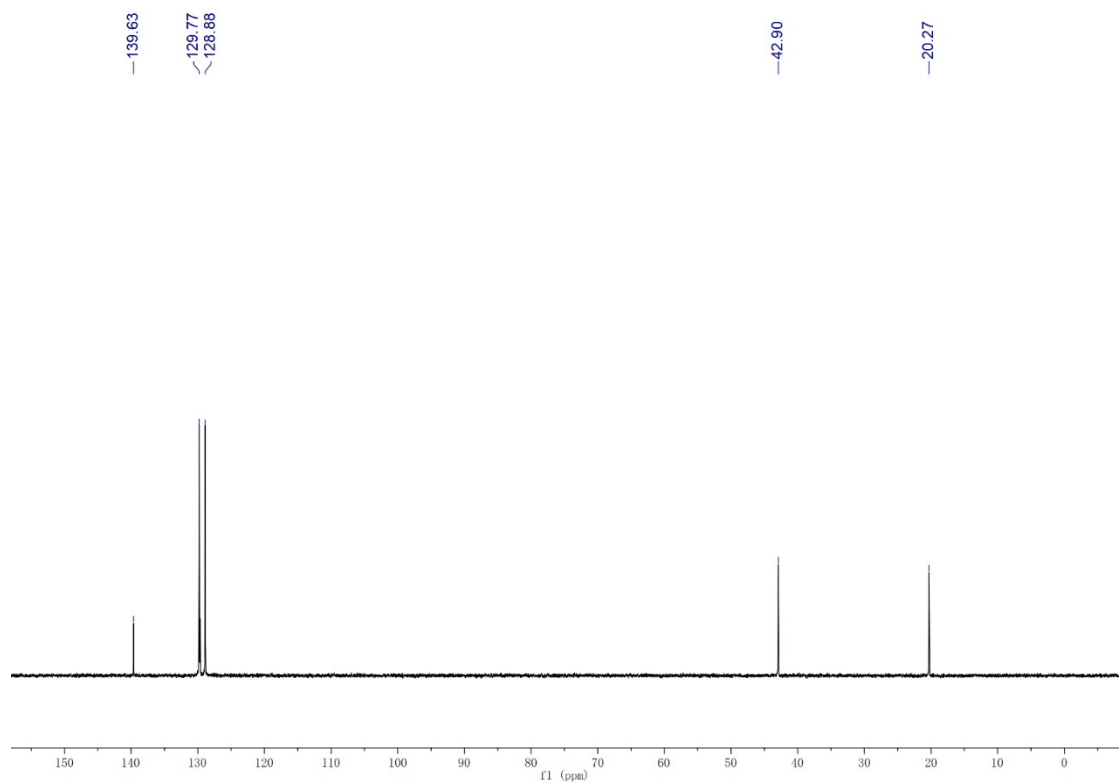


Figure S1.7.2 ^{13}C NMR of compound **2g** in D_2O

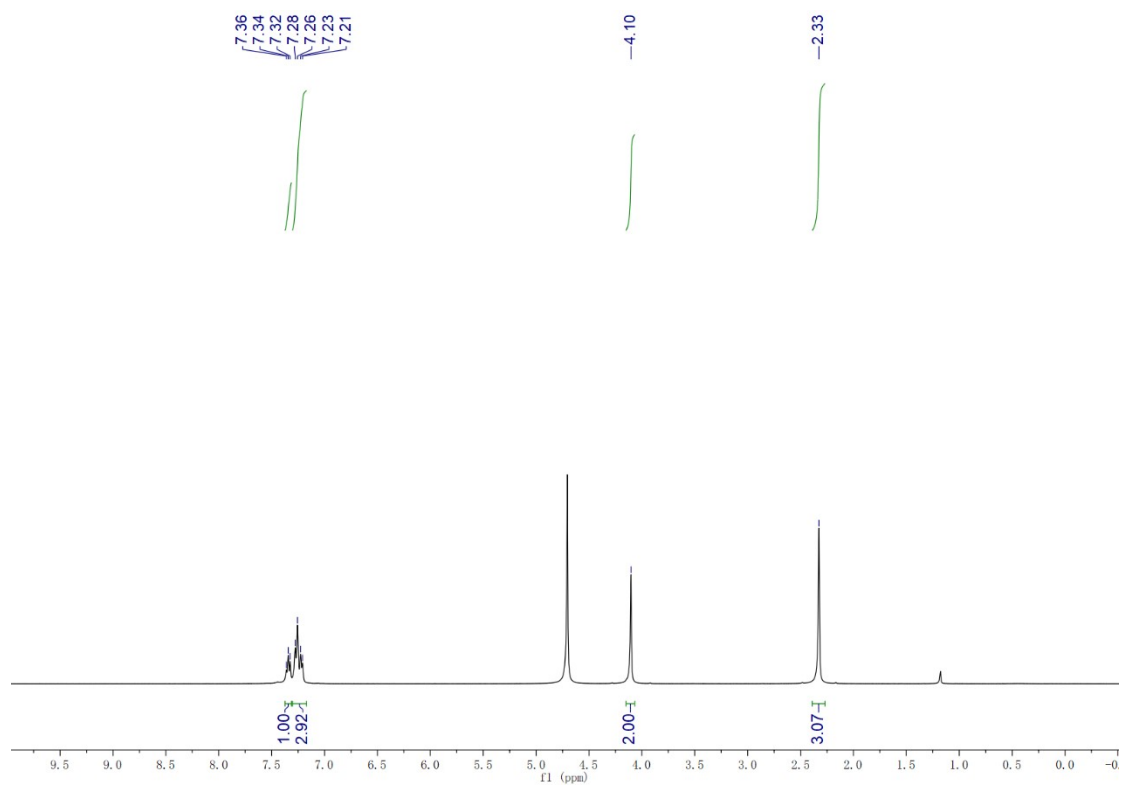


Figure S1.8.1 ^1H NMR of compound **2h** in D_2O

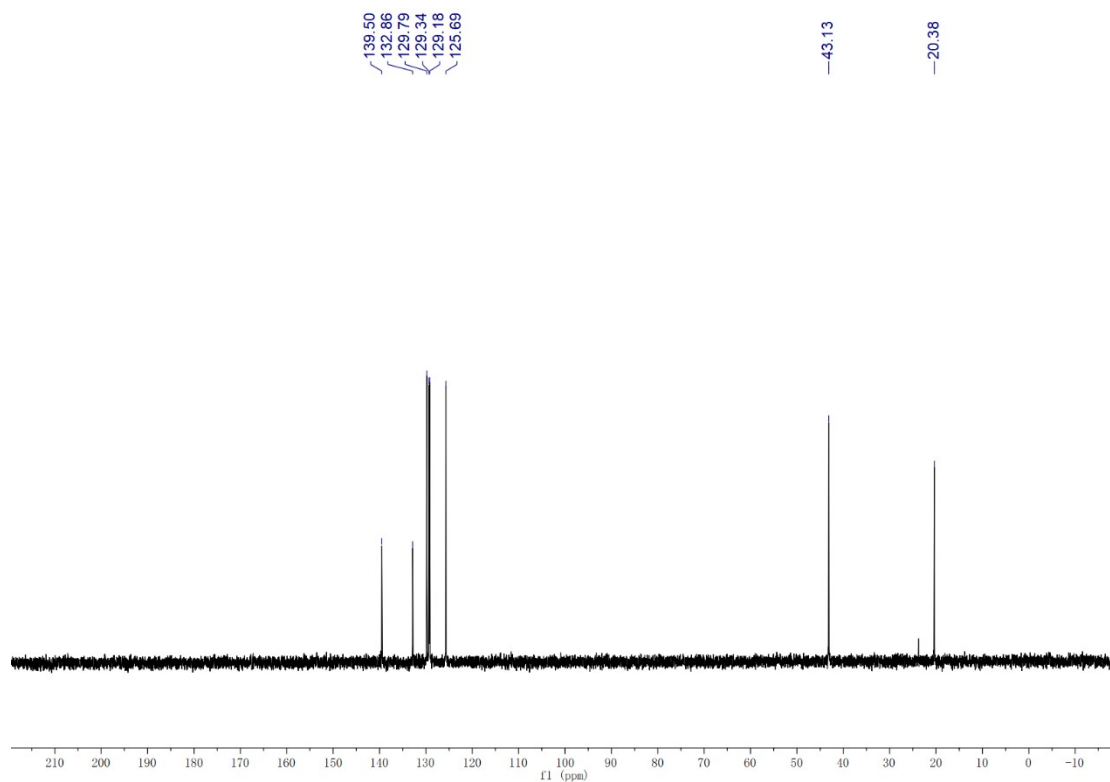


Figure S1.8.2 ^{13}C NMR of compound **2h** in D_2O

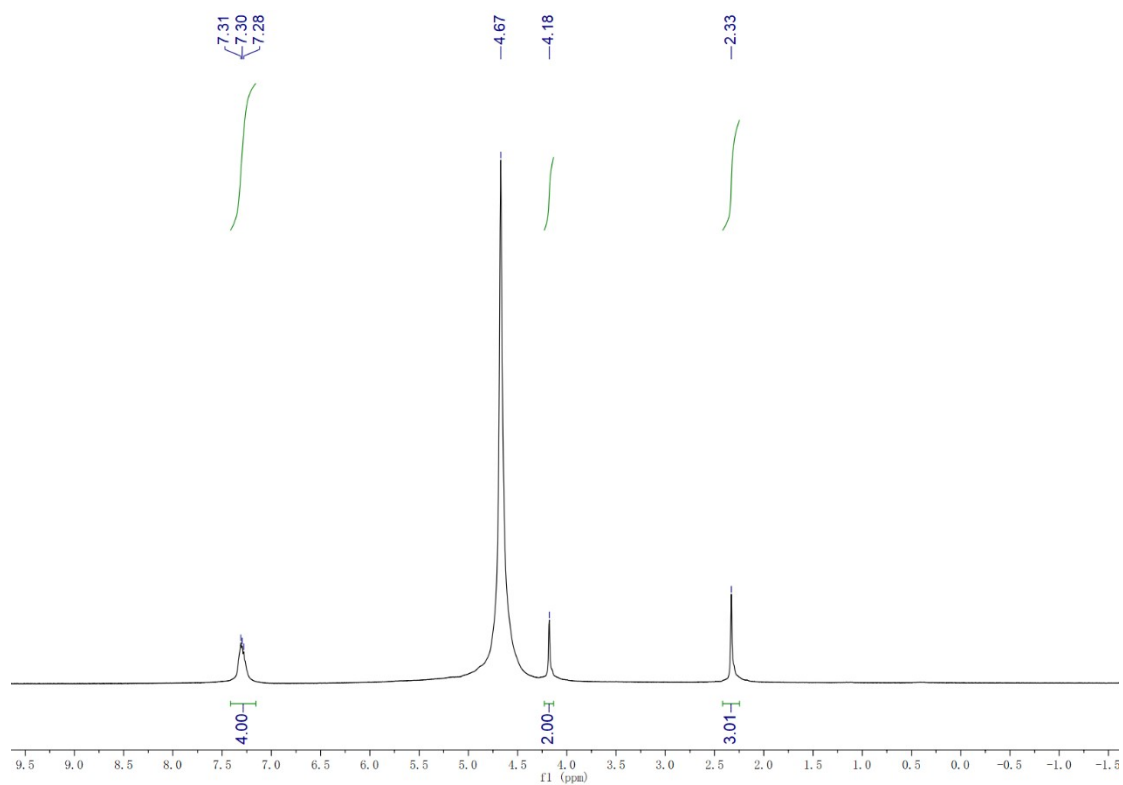


Figure S1.9.1 ^1H NMR of compound **2i** in D_2O

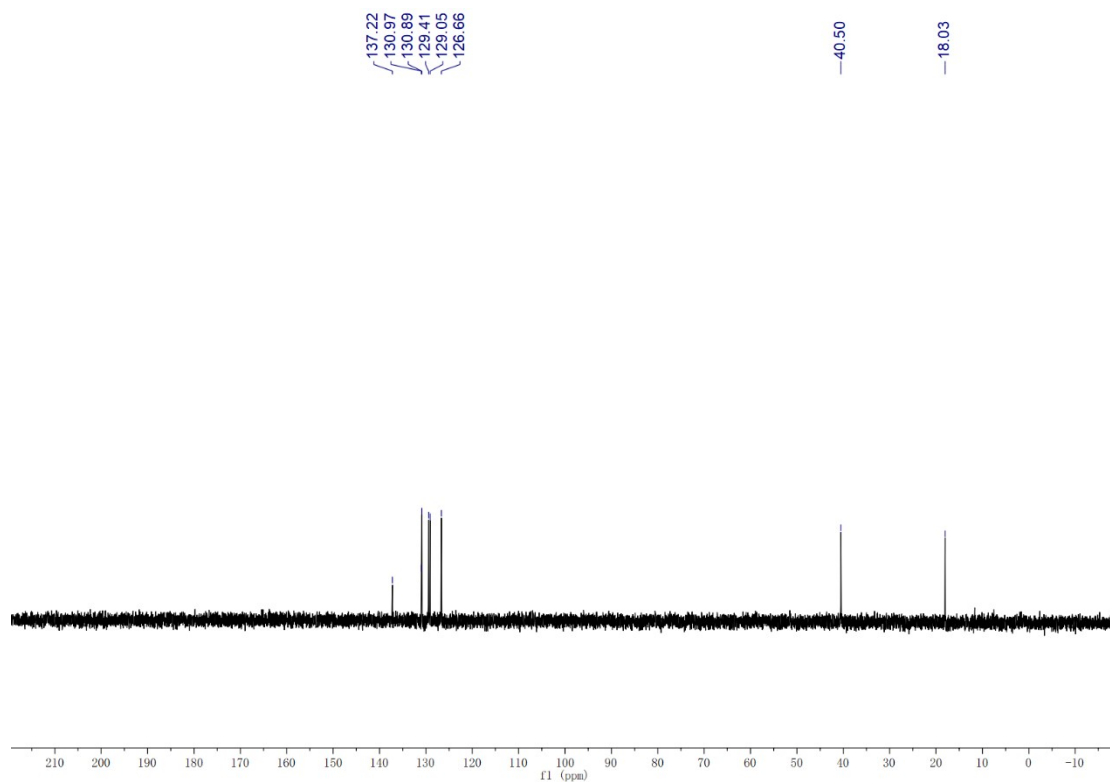


Figure S1.9.2 ^{13}C NMR of compound **2i** in D_2O

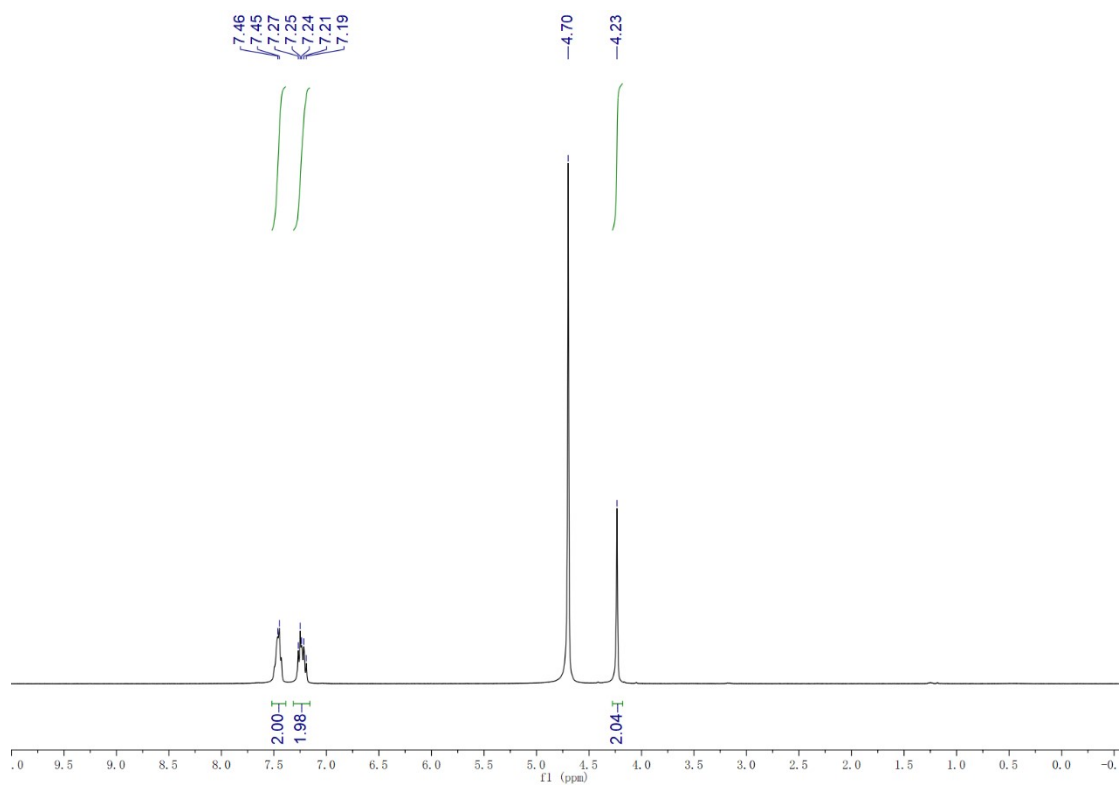


Figure S1.10.1 ^1H NMR of compound **2j** in D_2O

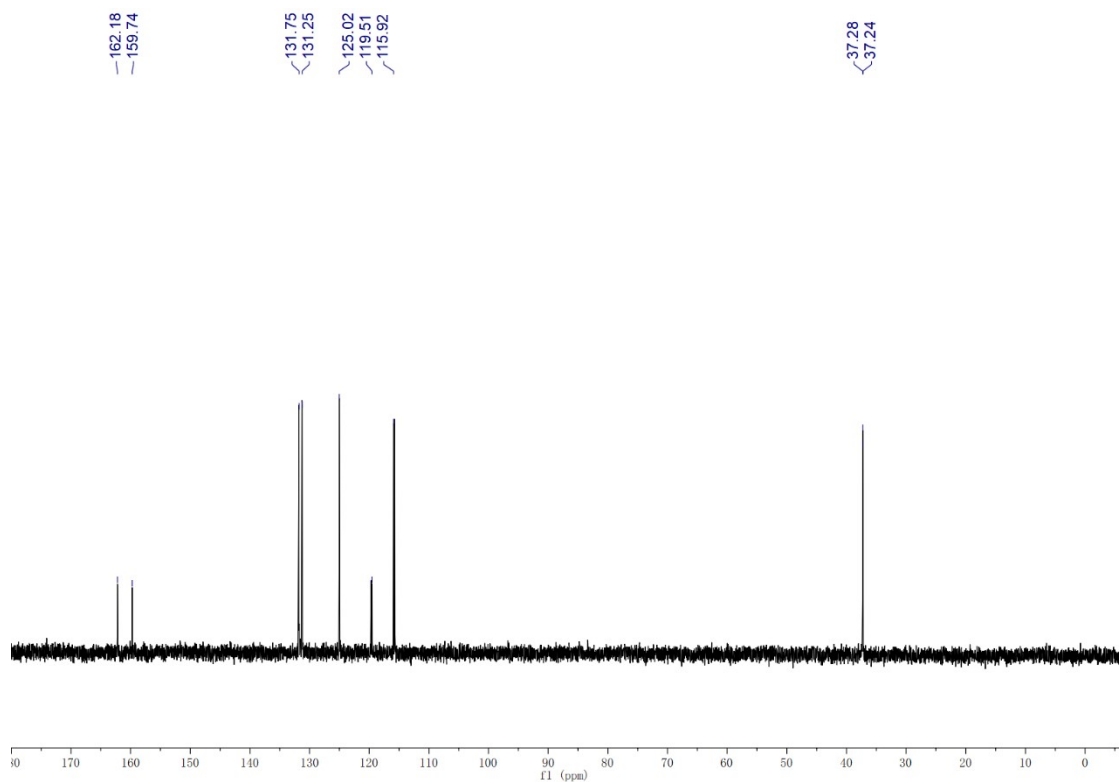


Figure S1.10.2 ^{13}C NMR of compound **2j** in D_2O

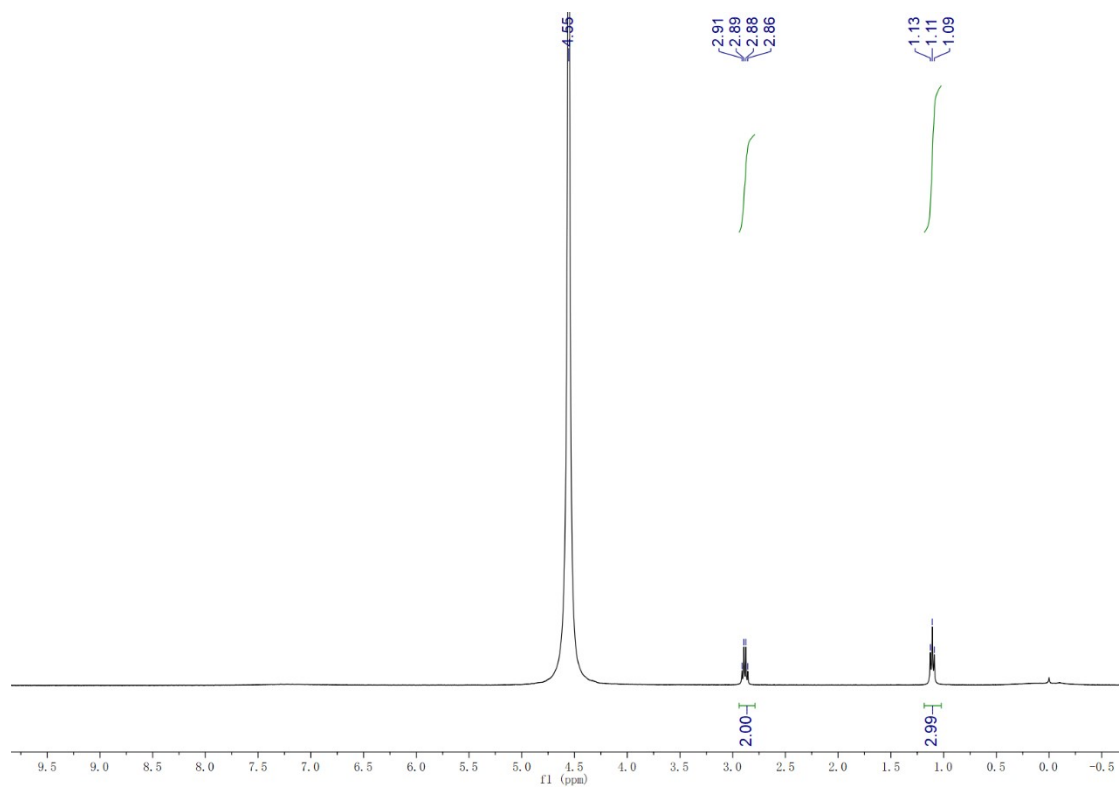


Figure S1.11.1 ^1H NMR of compound **2k** in D_2O

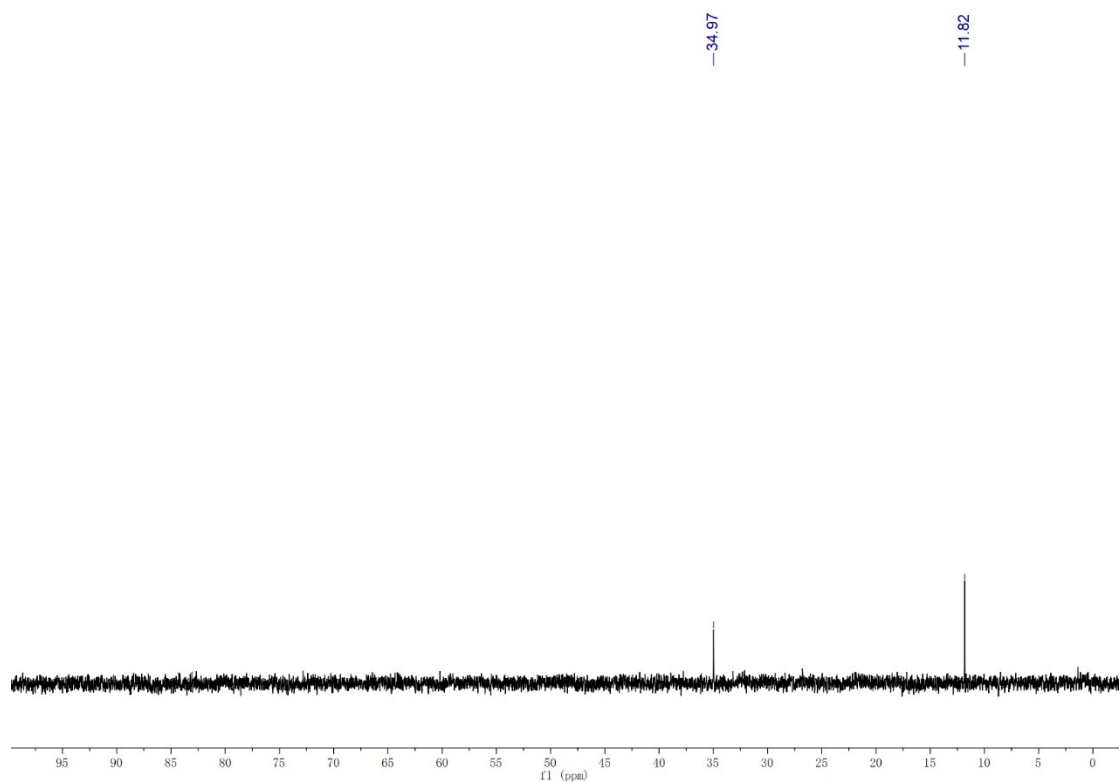


Figure S1.11.2 ^{13}C NMR of compound **2k** in D_2O

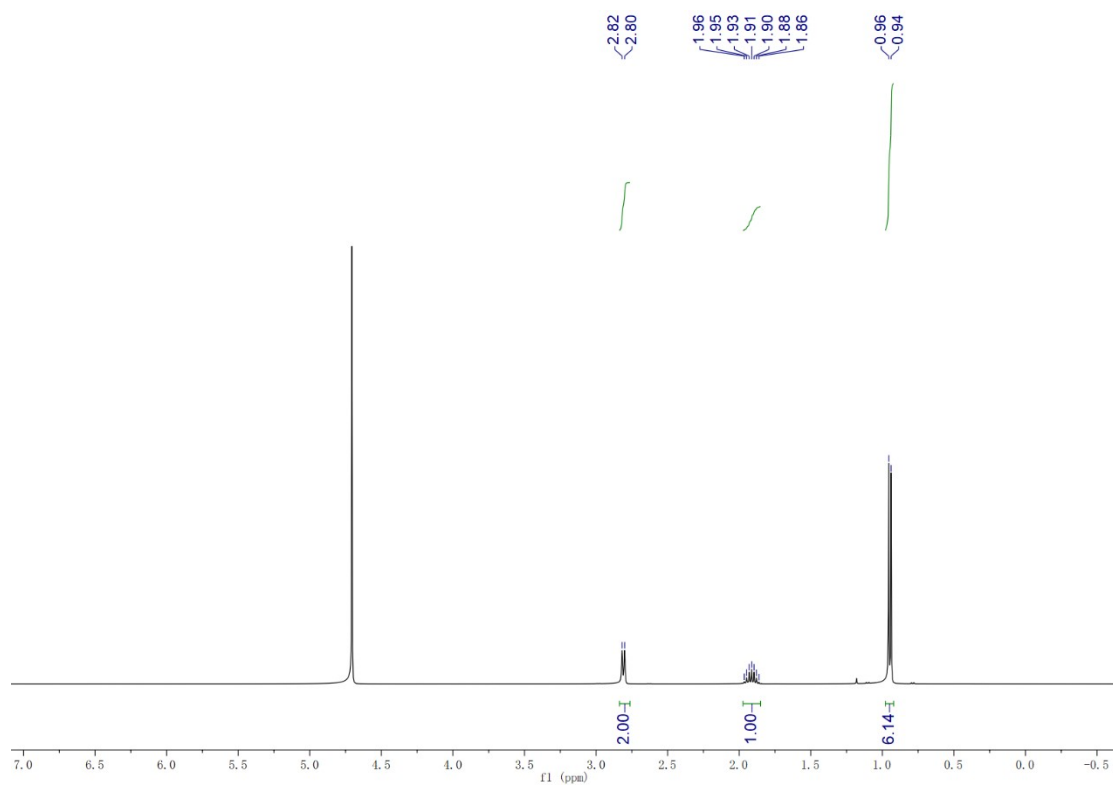


Figure S1.12.1 ¹H NMR of compound **2I** in D₂O

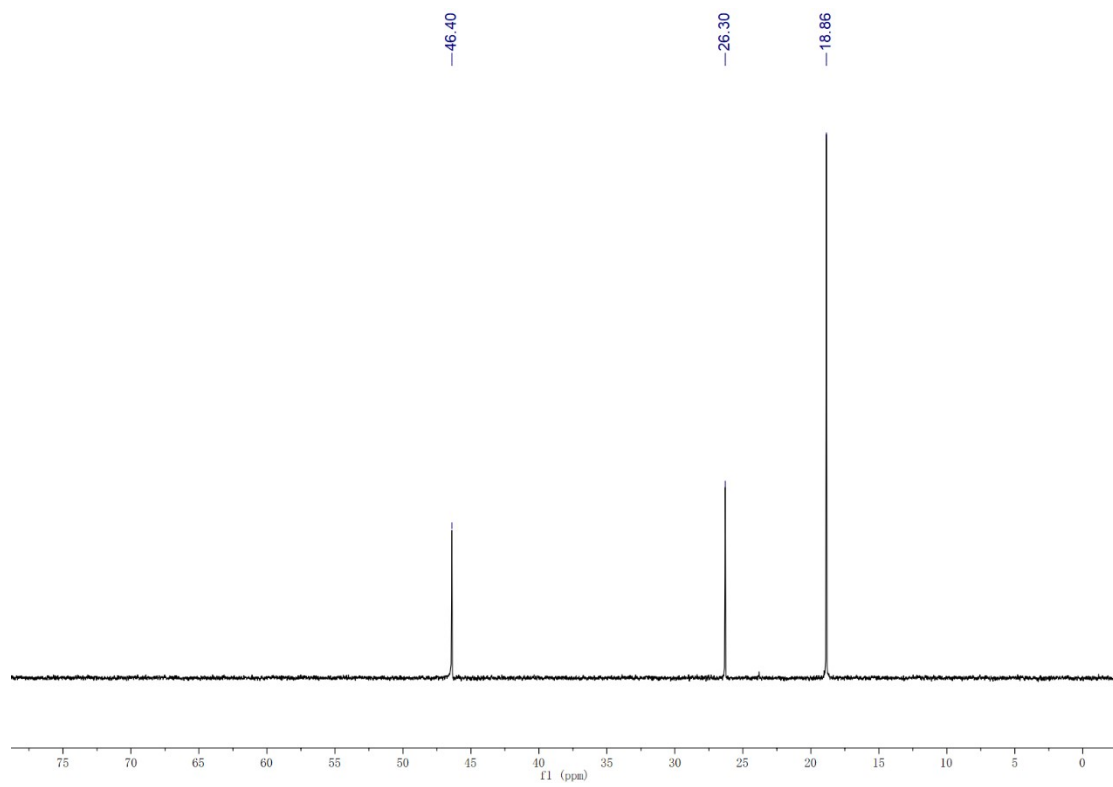


Figure S1.12.2 ¹³C NMR of compound **2I** in D₂O

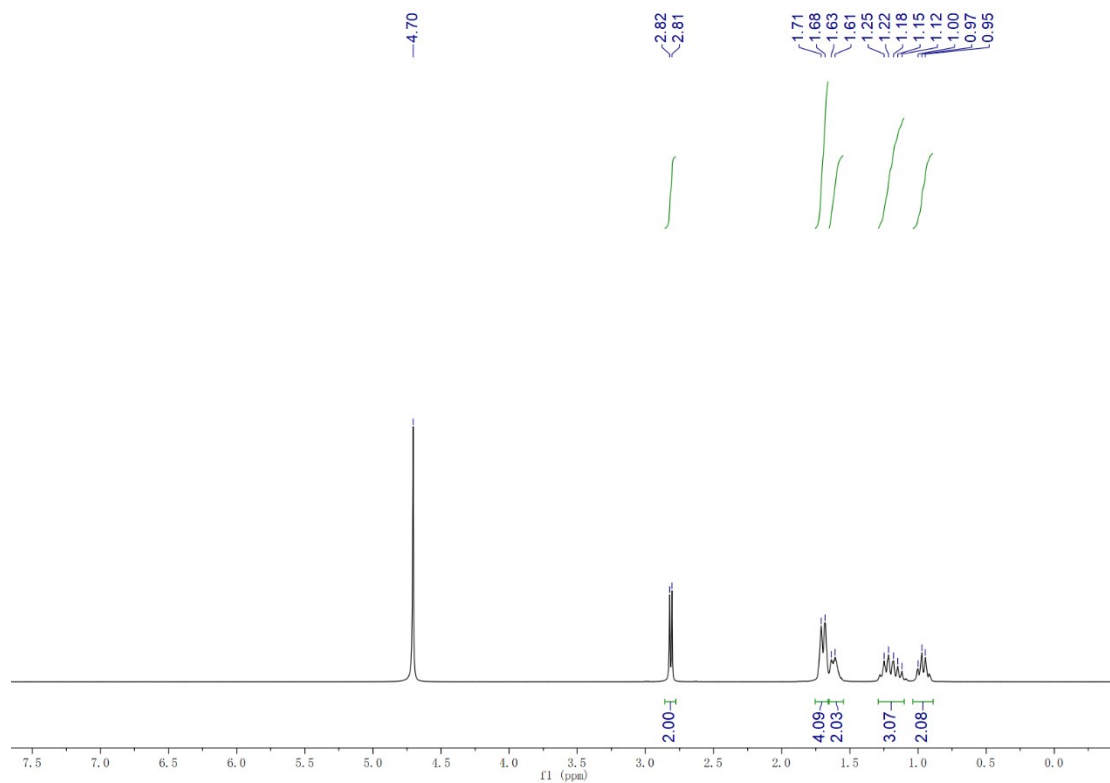


Figure S1.13.1 ^1H NMR of compound **2m** in D_2O

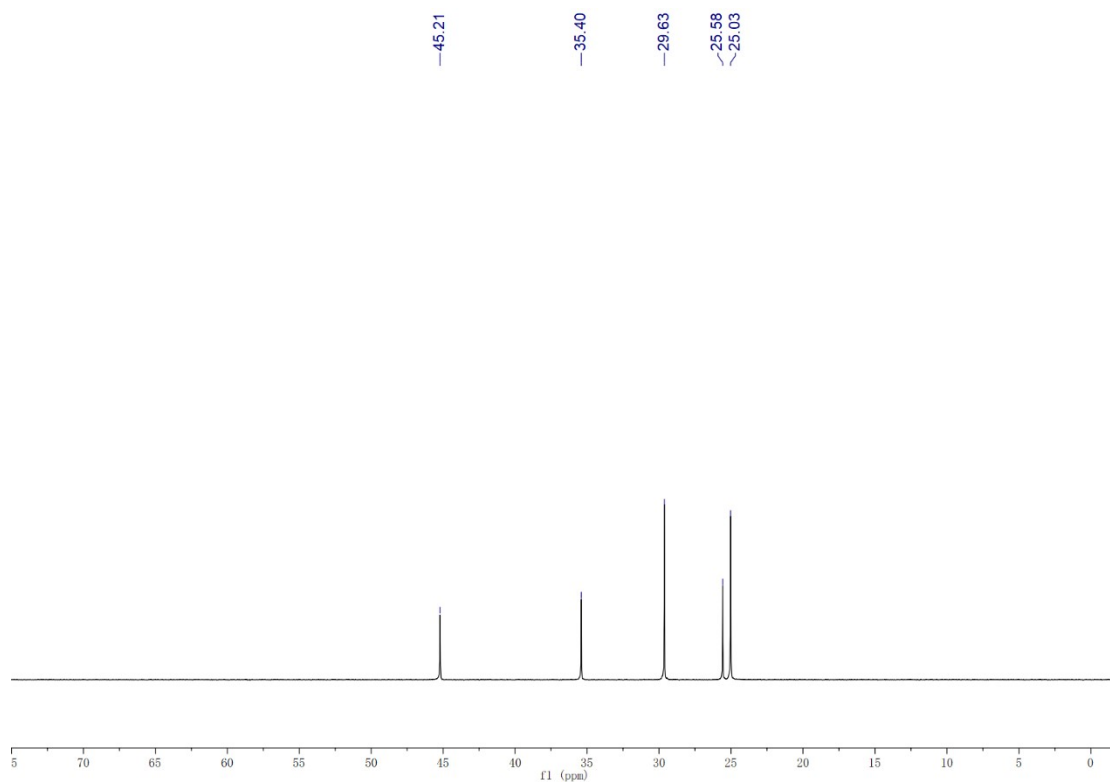


Figure S1.13.2 ^{13}C NMR of compound **2m** in D_2O

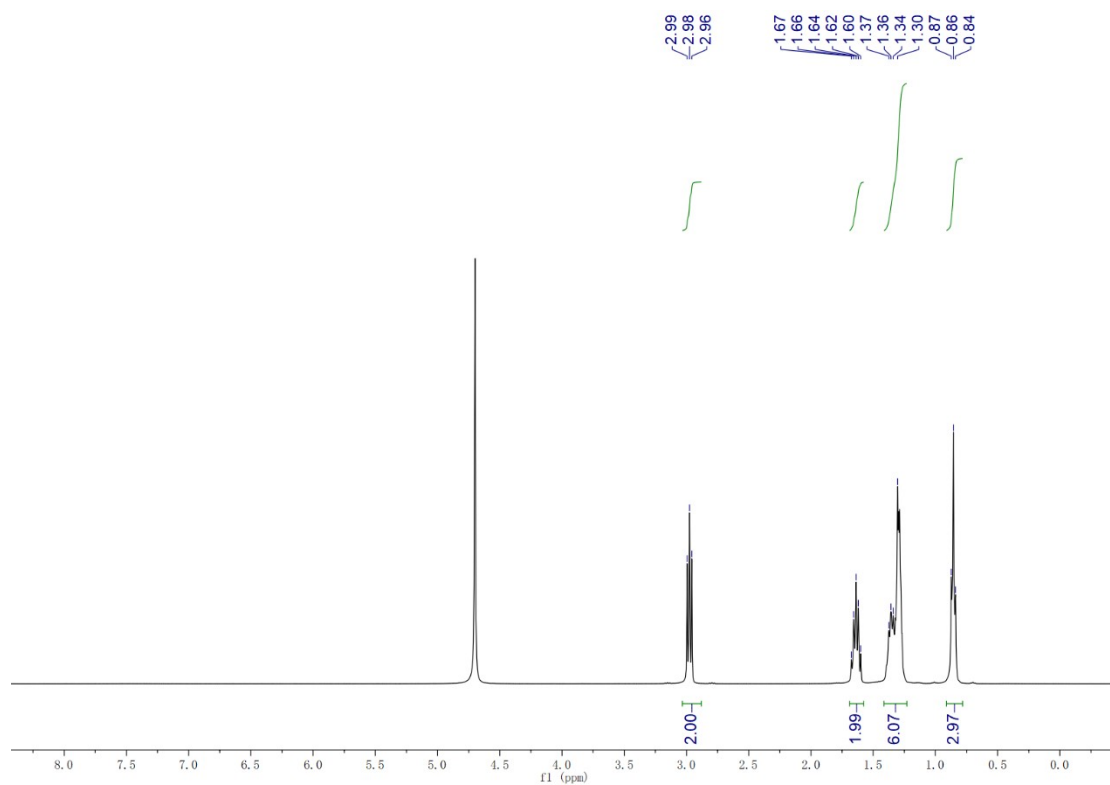


Figure S1.14.1 ^1H NMR of compound **2n** in D_2O

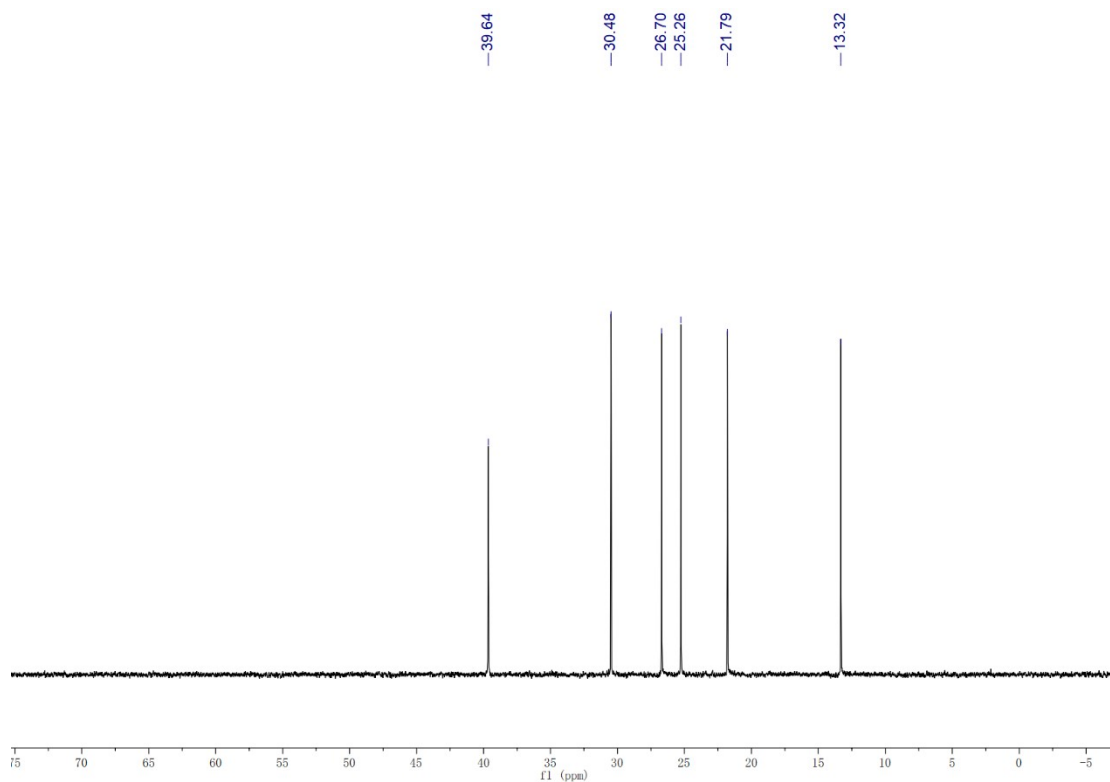


Figure S1.14.2 ^{13}C NMR of compound **2n** in D_2O

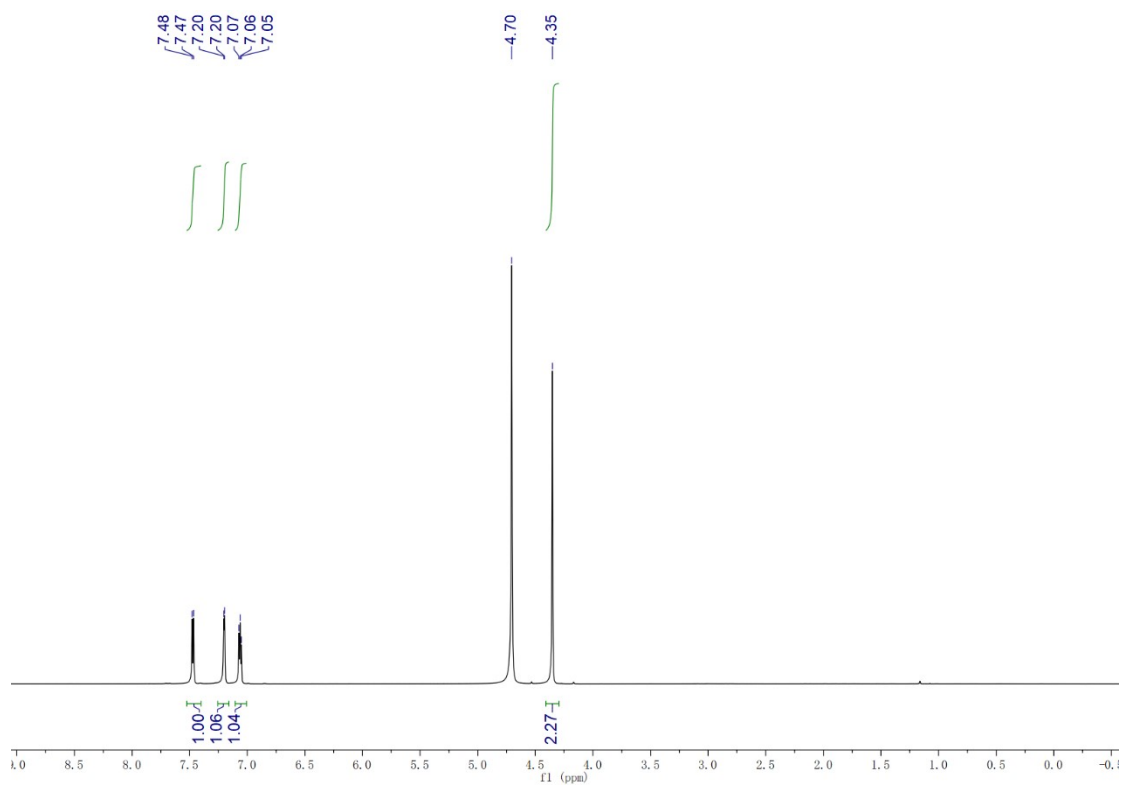


Figure S1.15.1 ^1H NMR of compound **2o** in D_2O

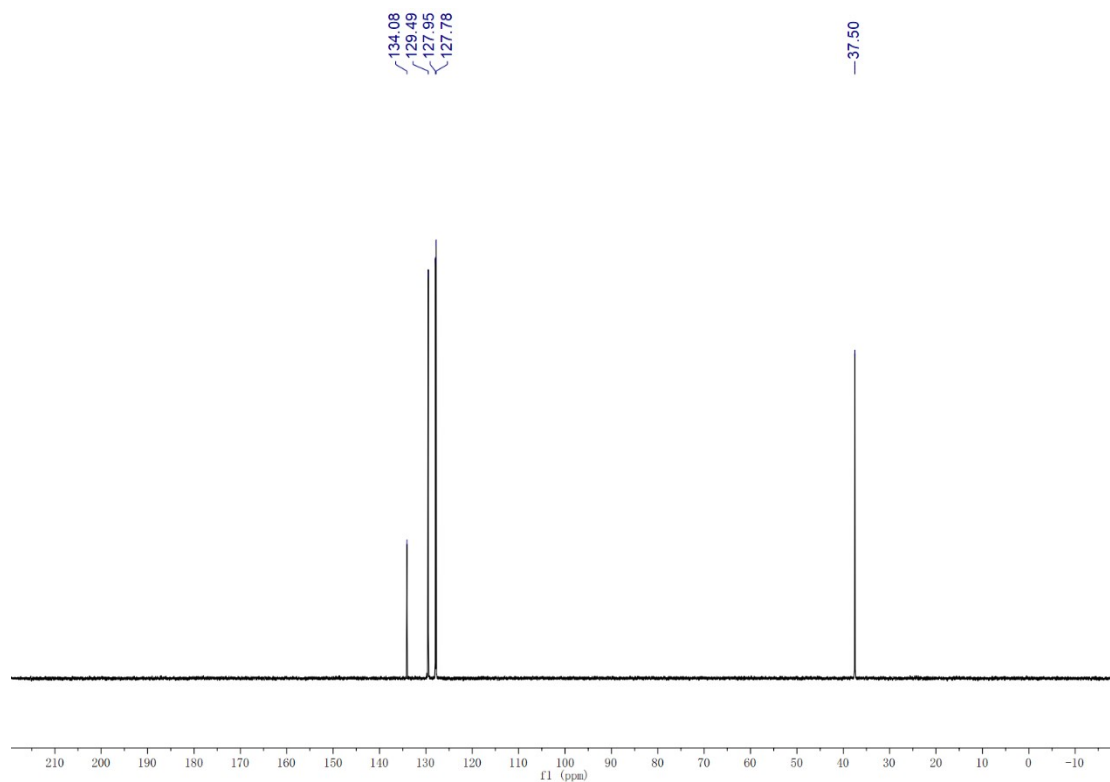


Figure S1.15.2 ^{13}C NMR of compound **2o** in D_2O

^1H , and ^{13}C Spectra of Hydroboration Products of Secondary Amides

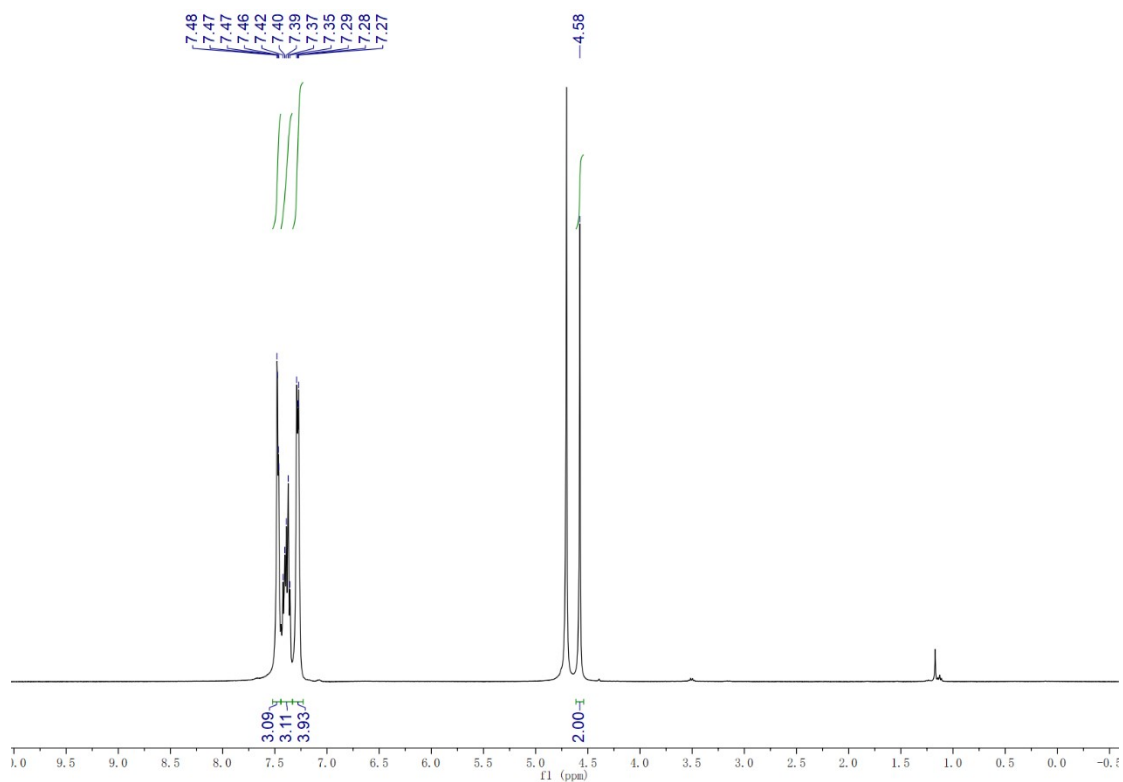


Figure S2.1.1 ^1H NMR of compound **4a** in D_2O

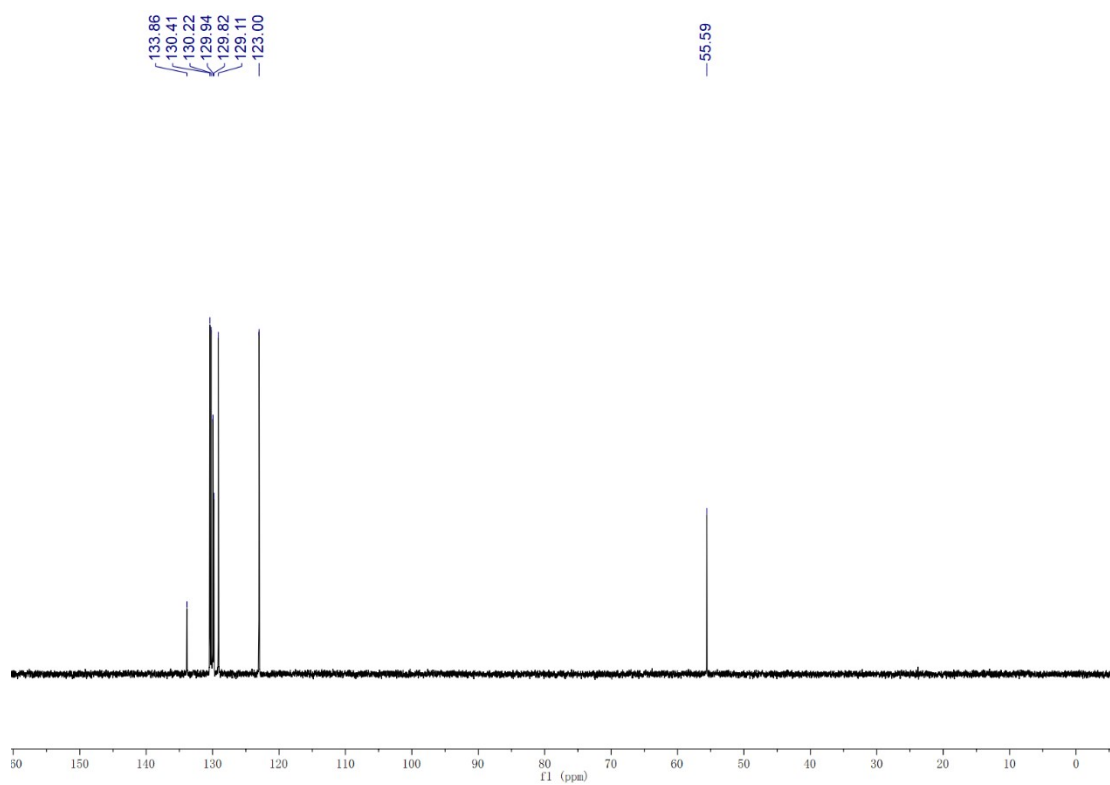


Figure S2.1.2 ^{13}C NMR of compound **4a** in D_2O

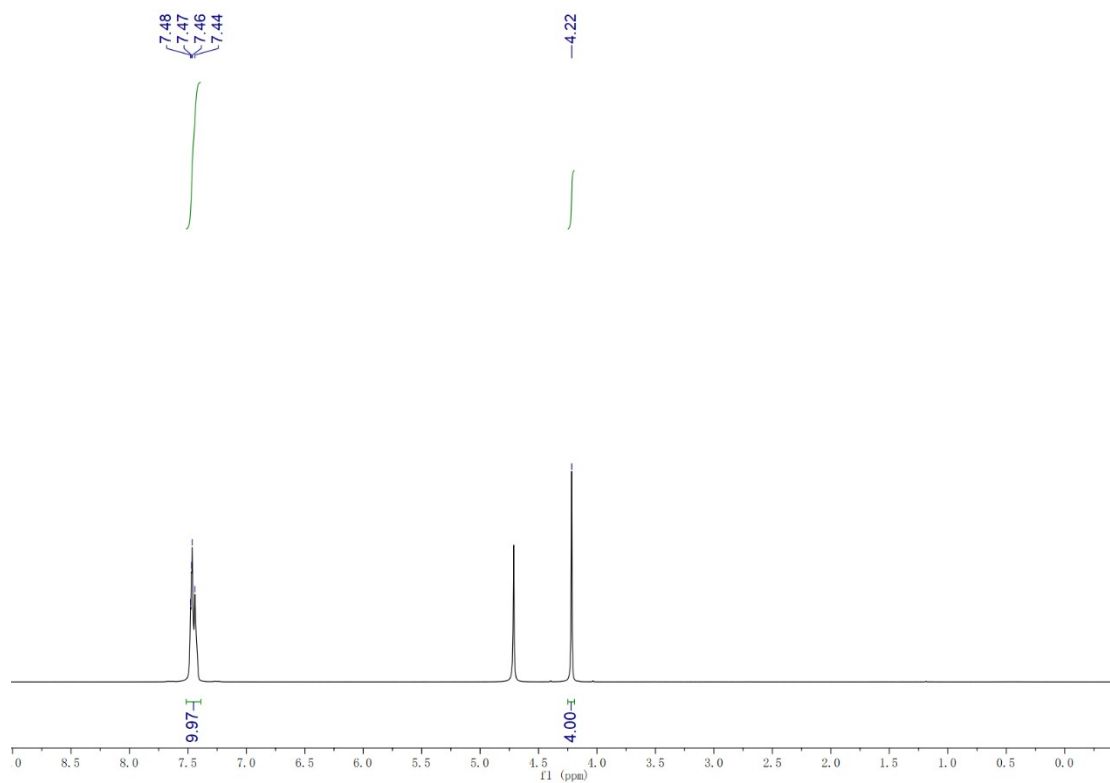


Figure S2.2.1 ^1H NMR of compound **4b** in D_2O

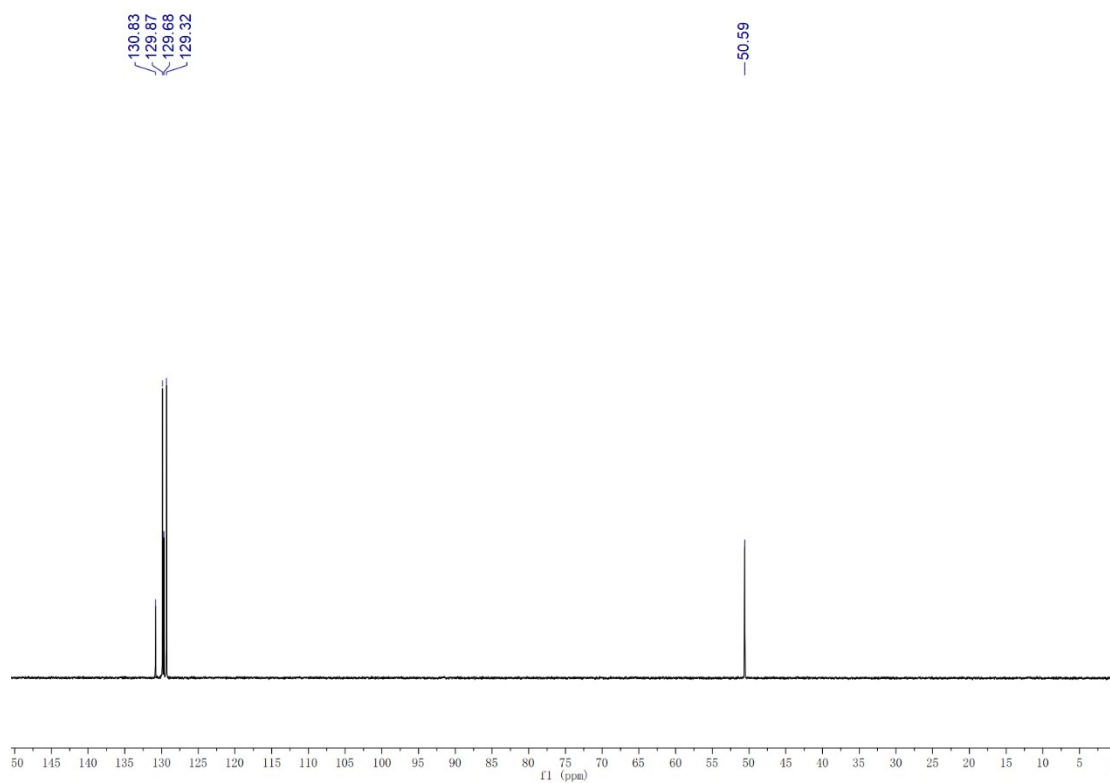


Figure S2.2.2 ^{13}C NMR of compound **4b** in D_2O

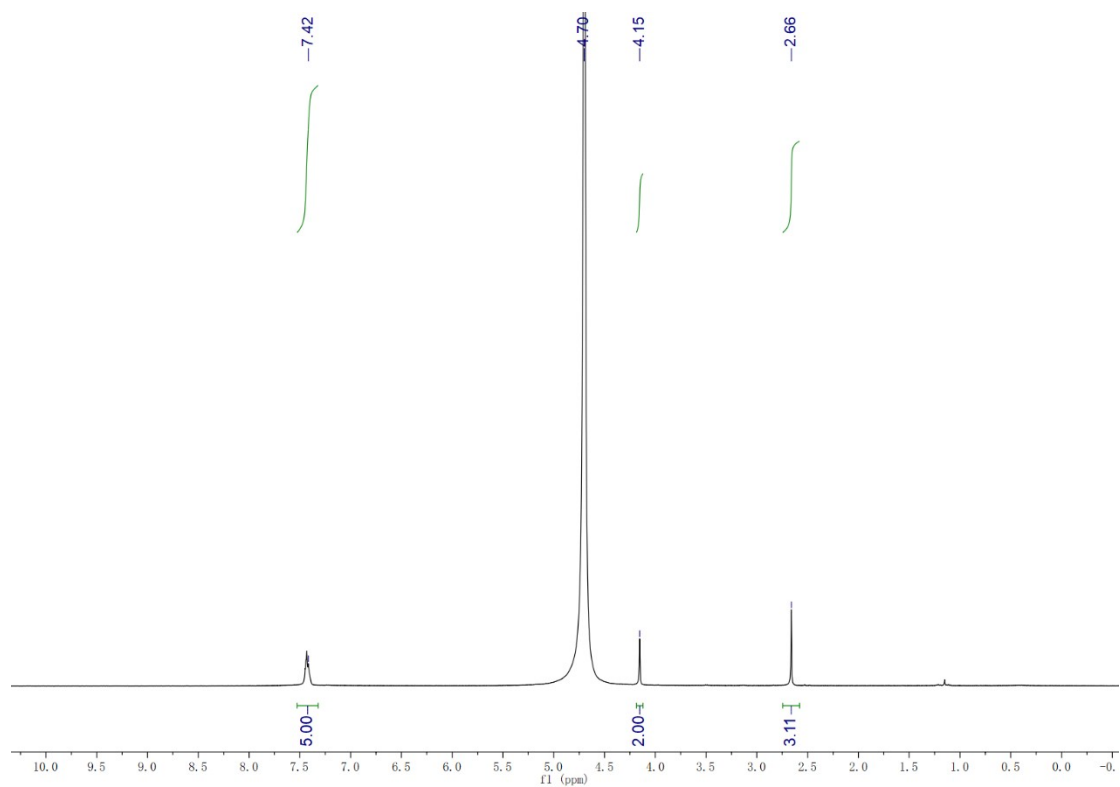


Figure S2.3.1 ^1H NMR of compound **4c** in D_2O

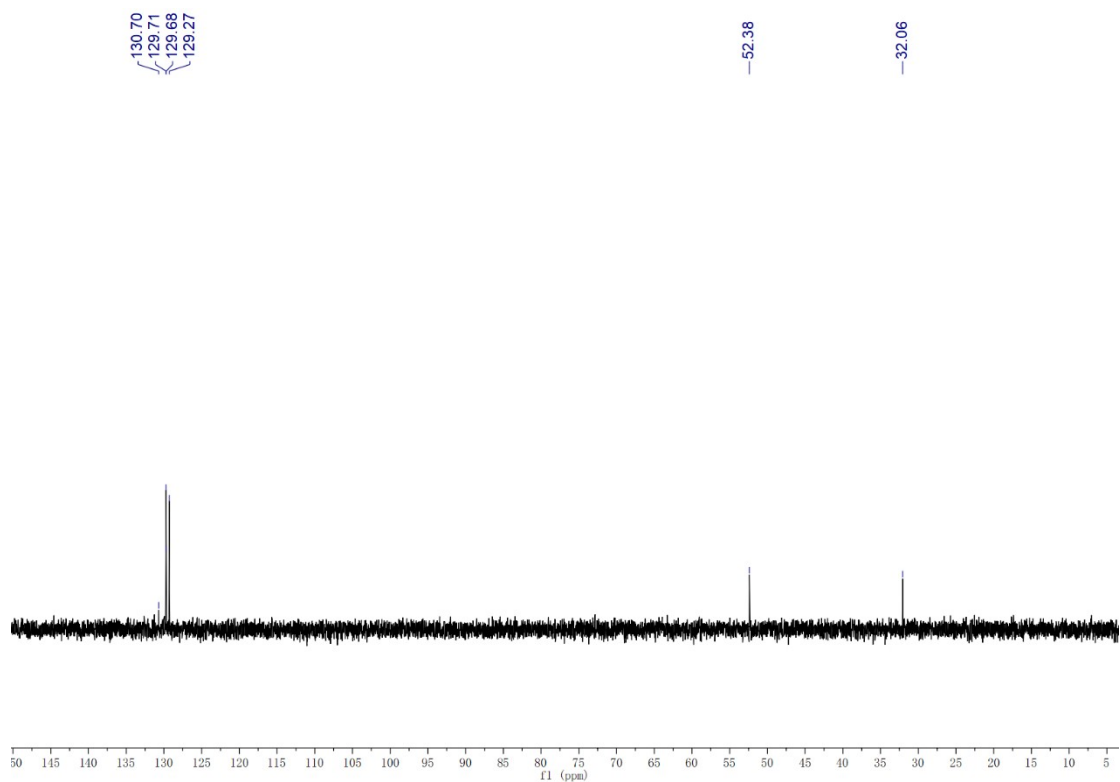


Figure S2.3.2 ^{13}C NMR of compound **4c** in D_2O

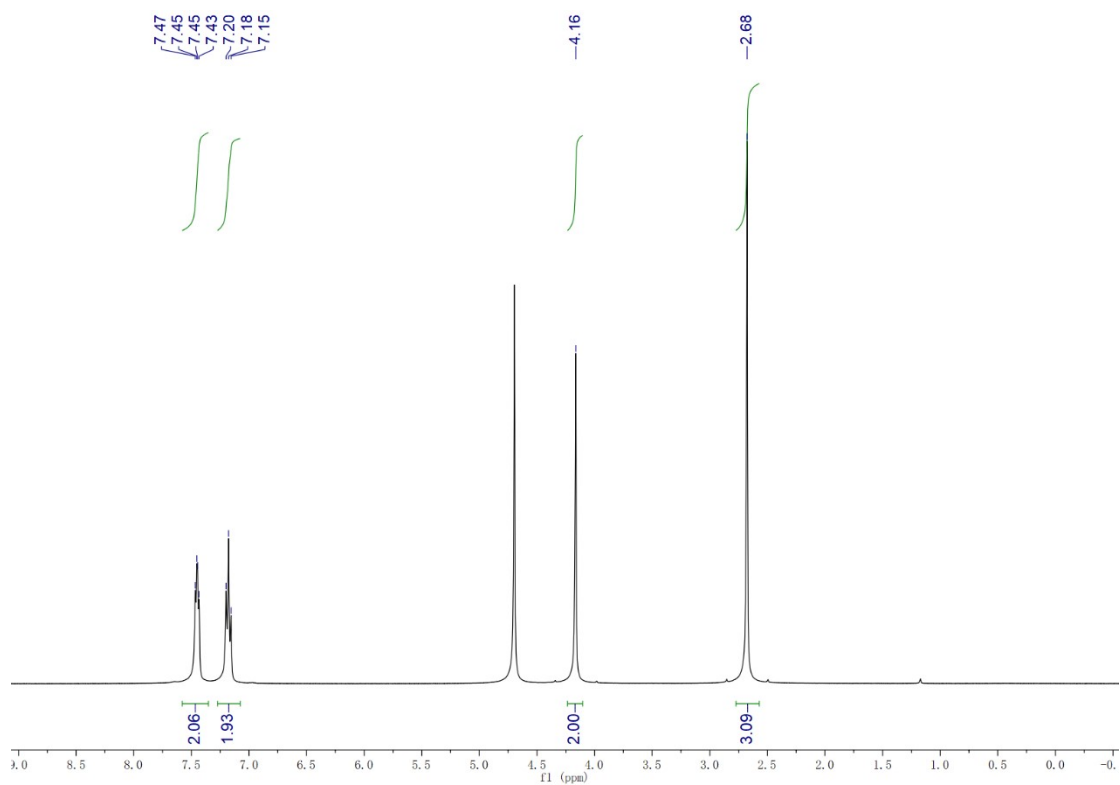


Figure S2.4.1 ^1H NMR of compound **4d** in D_2O

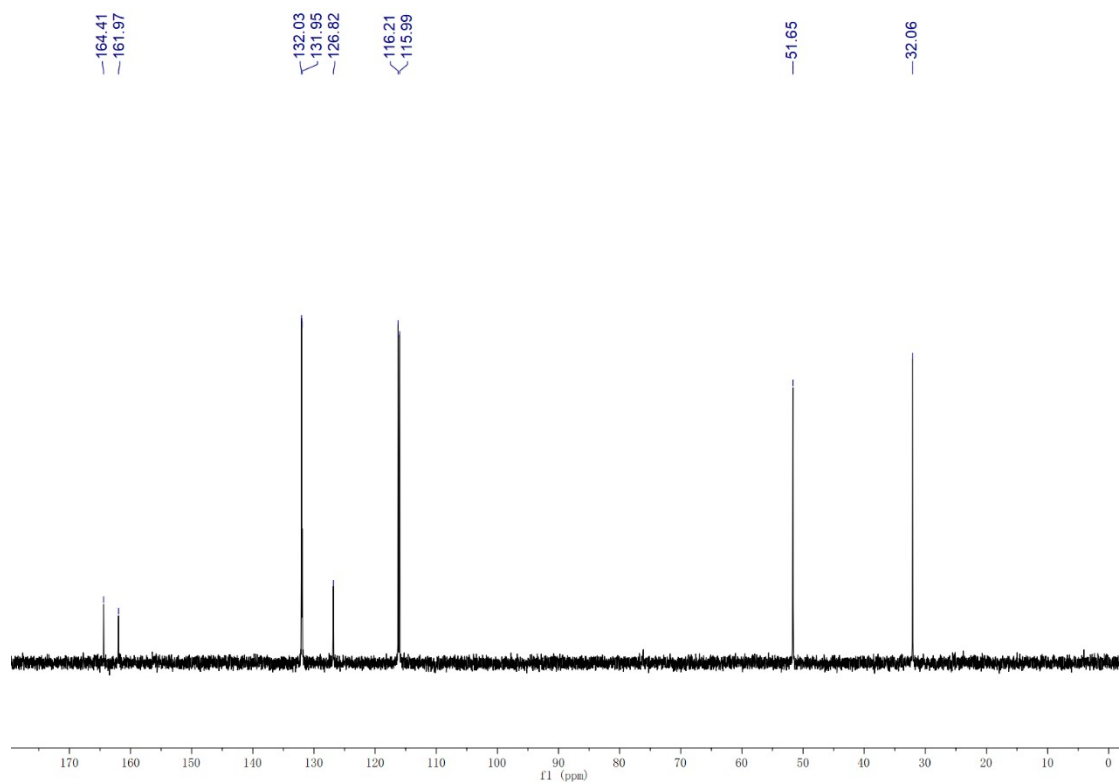


Figure S2.4.2 ^{13}C NMR of compound **4d** in D_2O

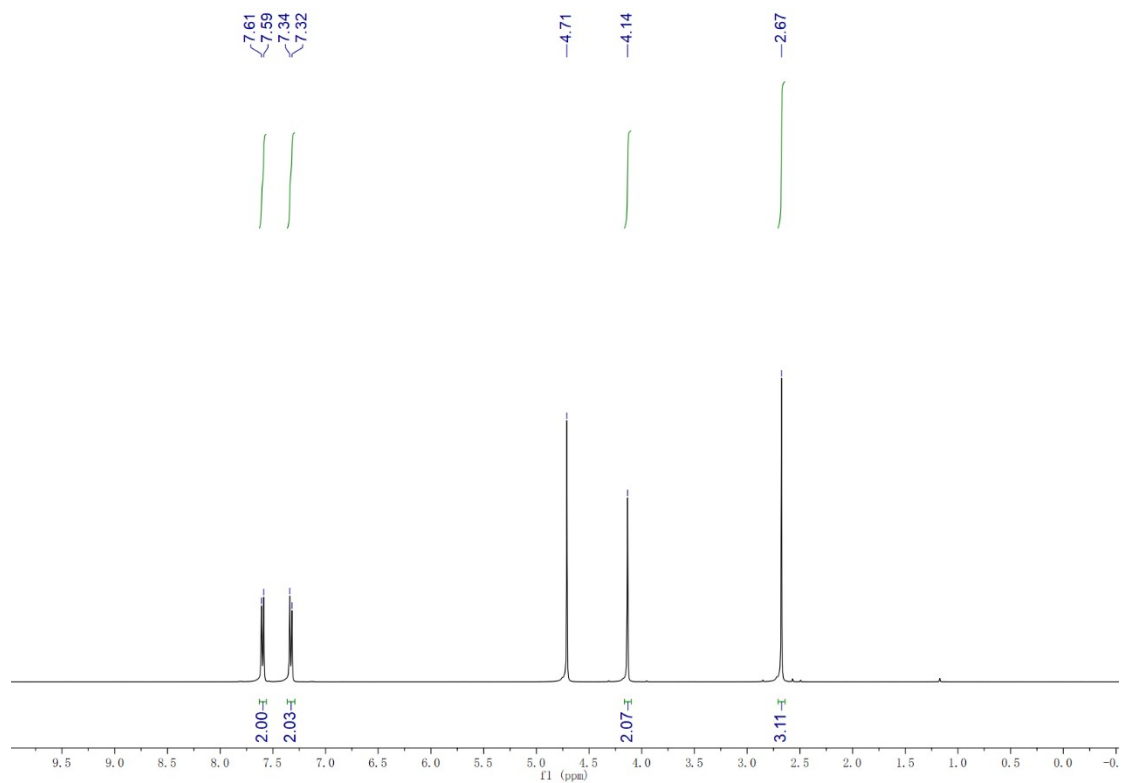


Figure S2.5.1 ^1H NMR of compound **4e** in D_2O

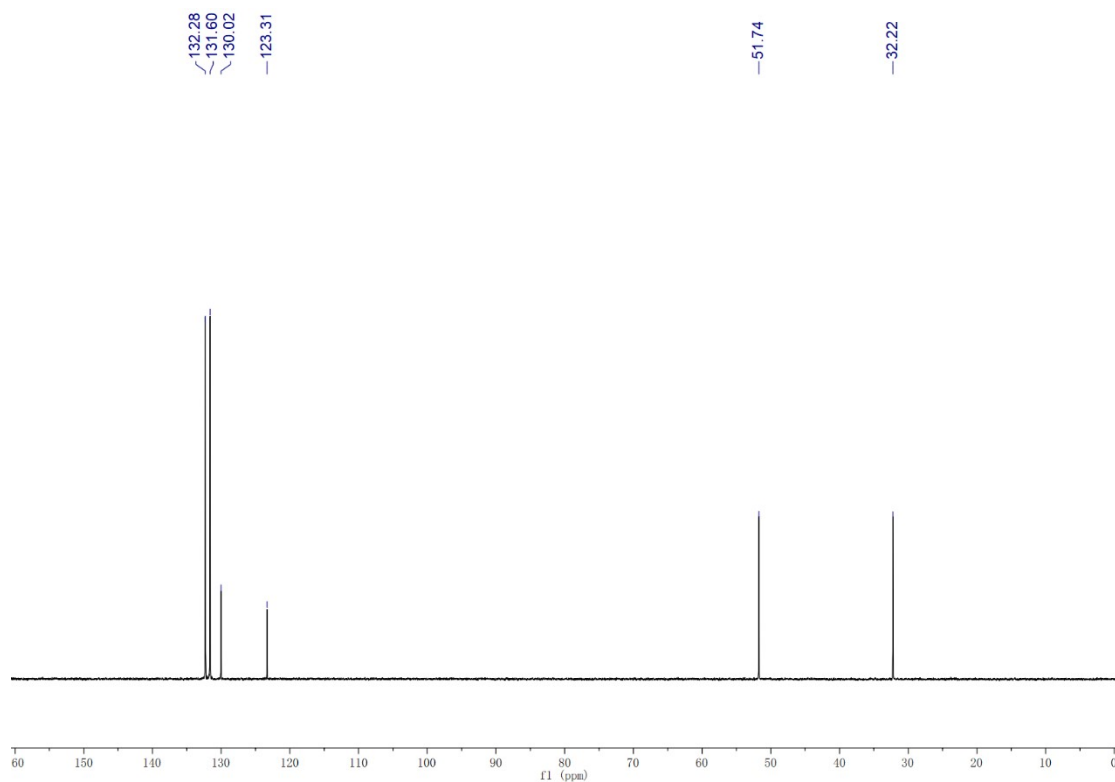


Figure S2.5.2 ^{13}C NMR of compound **4e** in D_2O

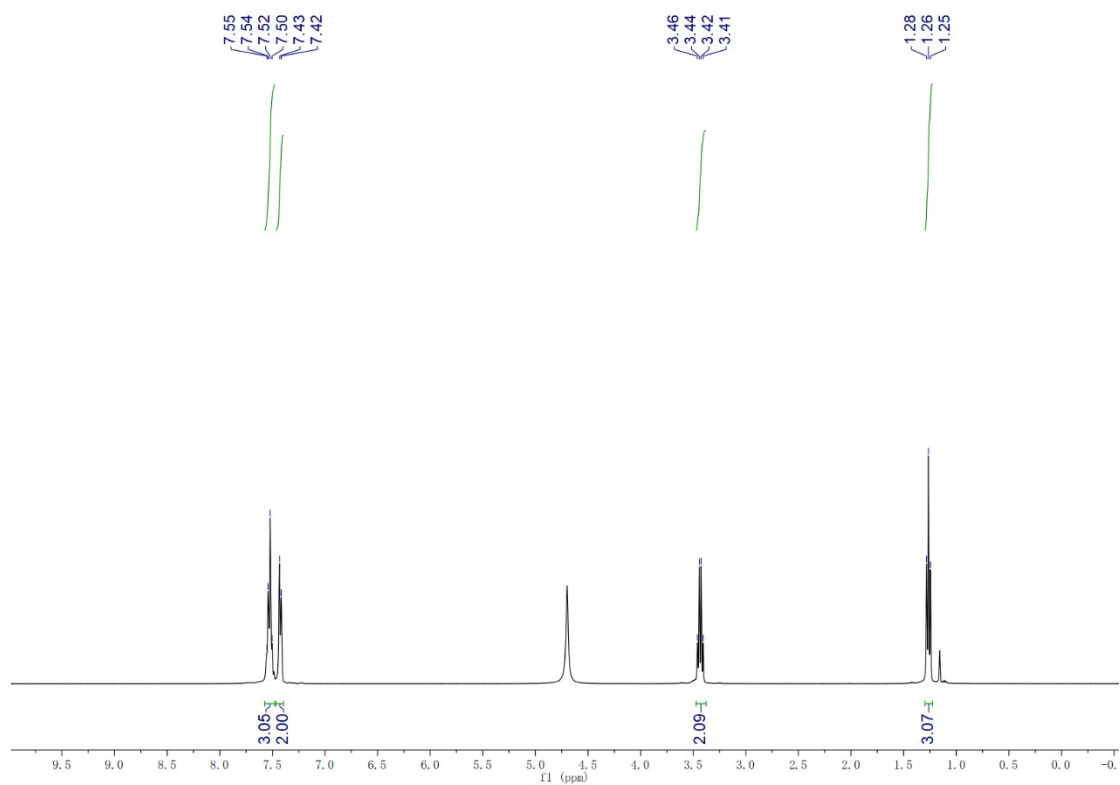


Figure S2.6.1 ^1H NMR of compound **4f** in D_2O

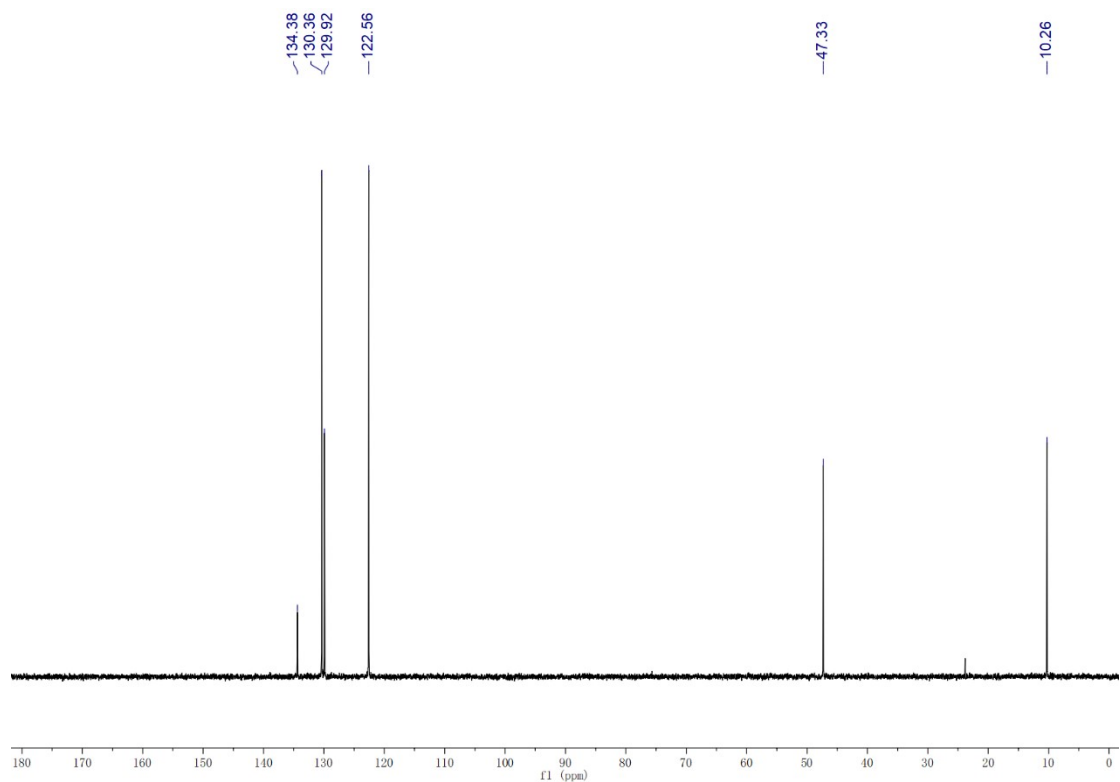


Figure S2.6.2 ^{13}C NMR of compound **4f** in D_2O

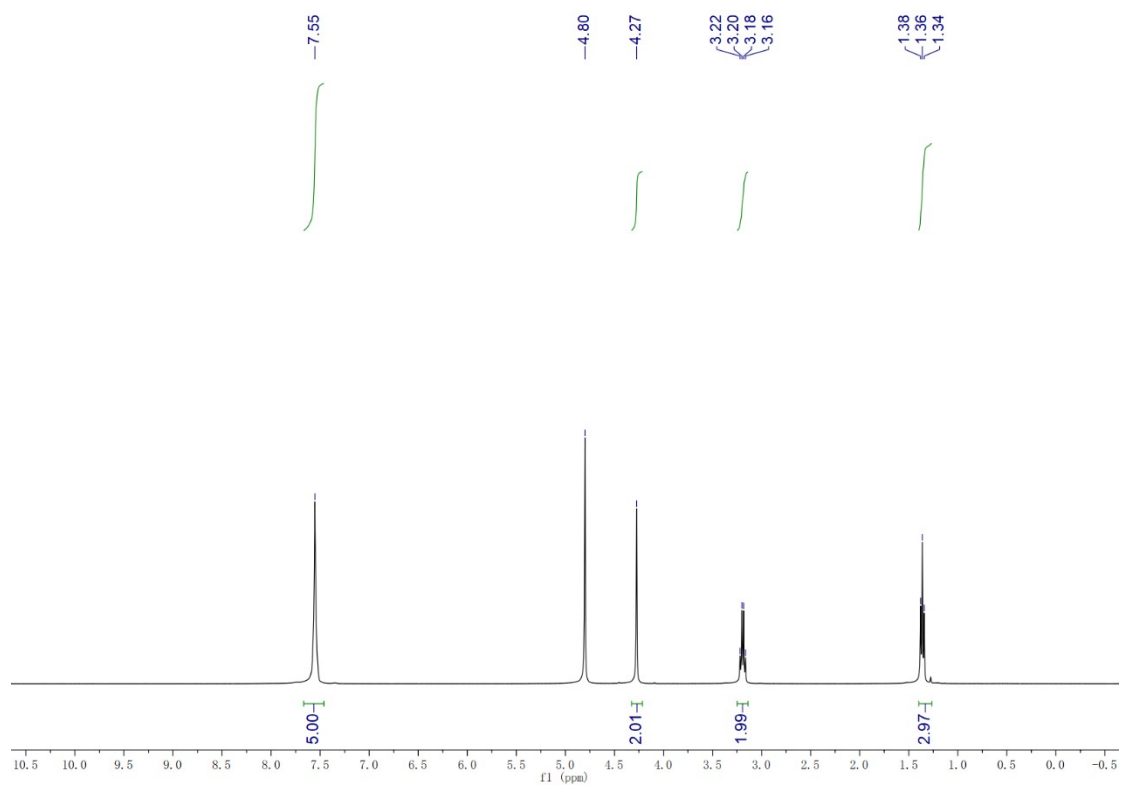


Figure S2.7.1 ^1H NMR of compound **4g** in D_2O

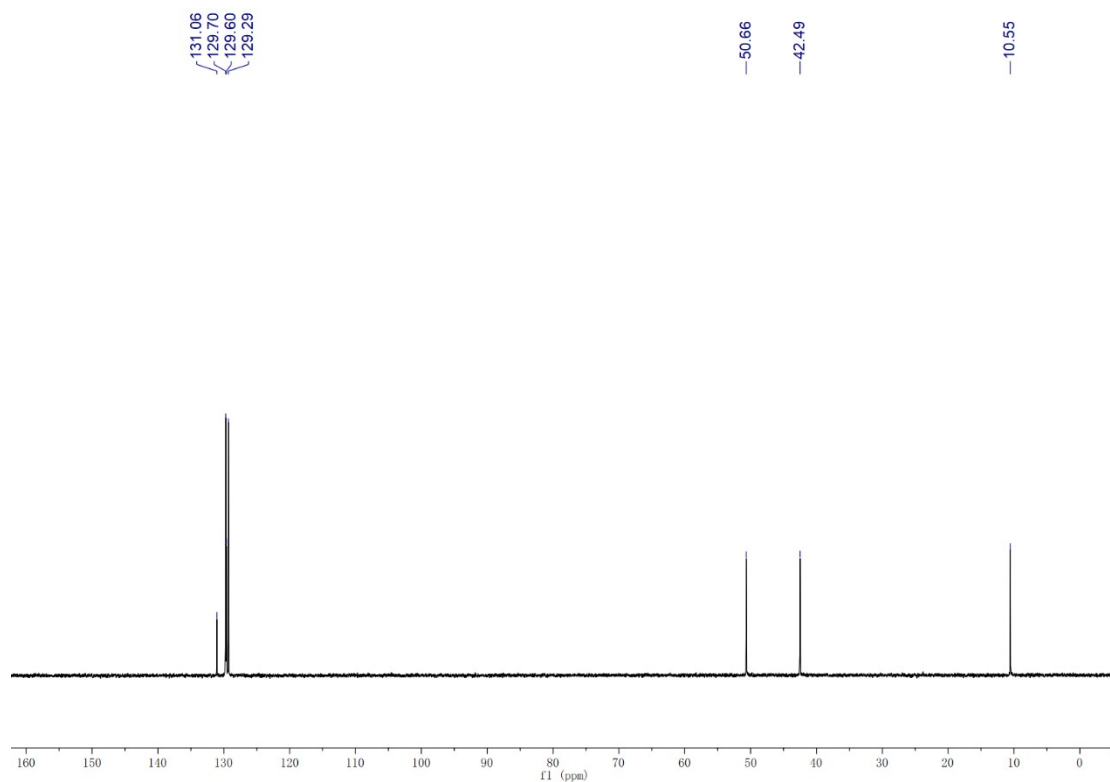


Figure S2.7.2 ^{13}C NMR of compound **4g** in D_2O

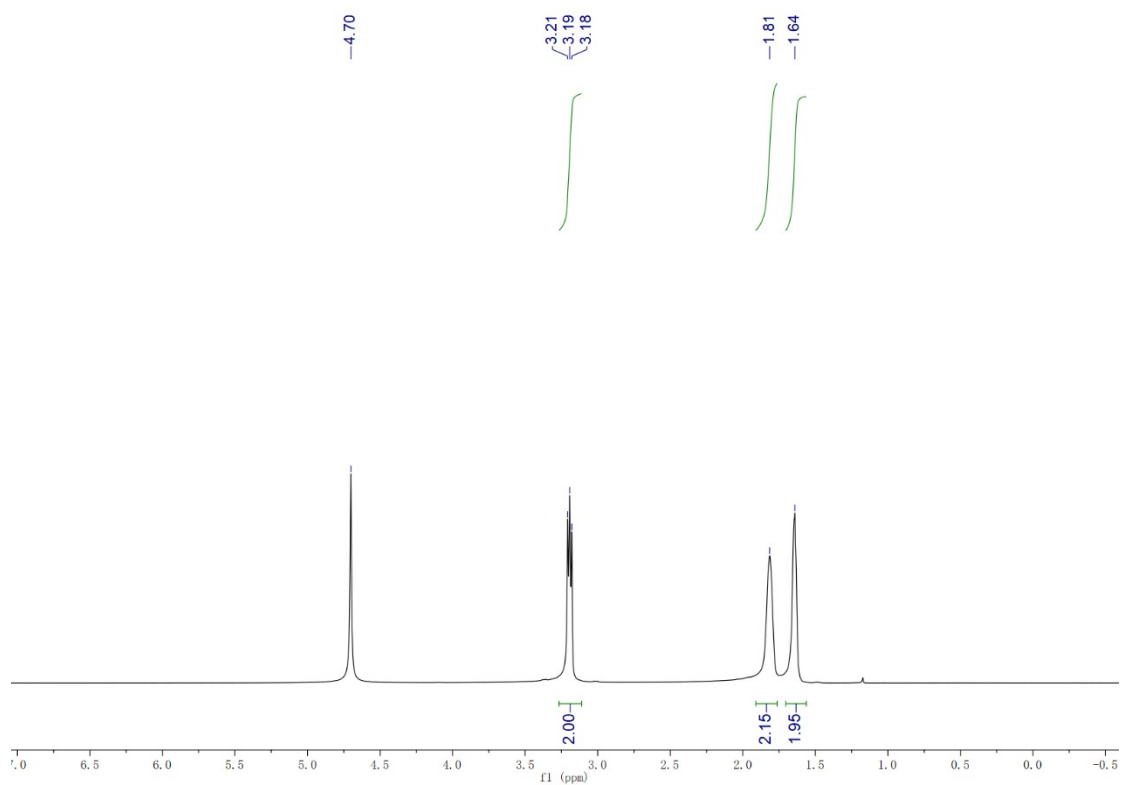


Figure S2.8.1 ^1H NMR of compound **4h** in D_2O

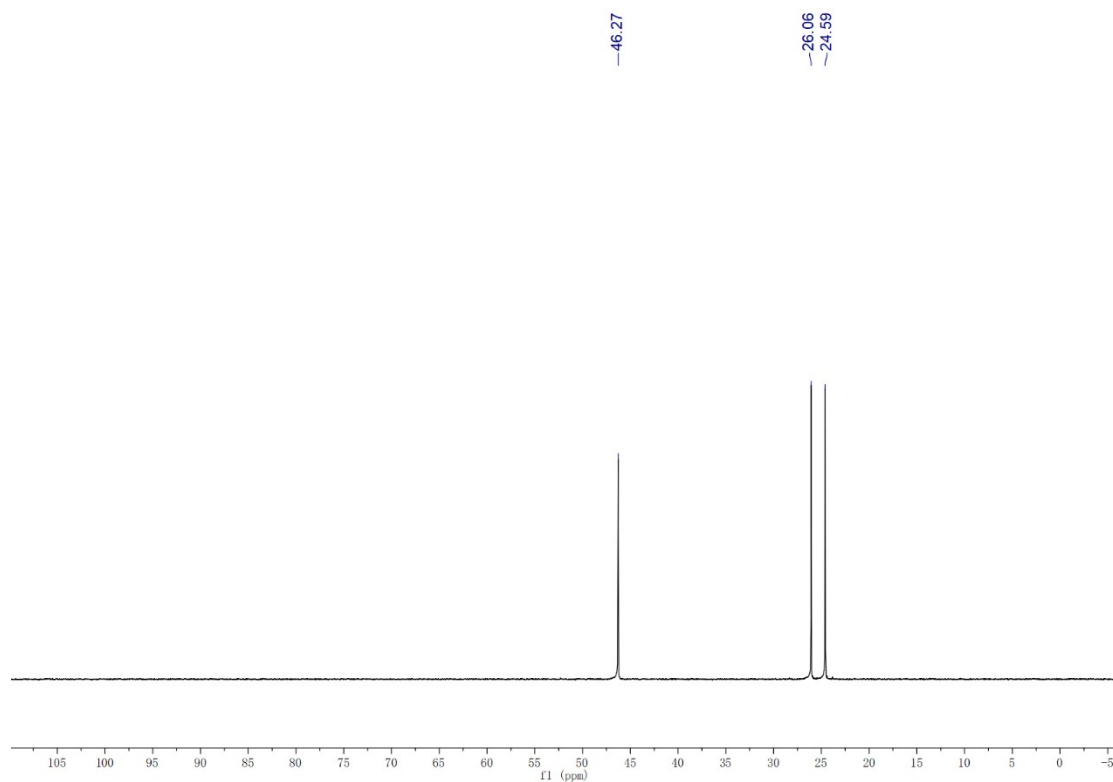


Figure S2.8.2 ^{13}C NMR of compound **4h** in D_2O

^1H , and ^{13}C Spectra of Hydroboration Products of Tertiary Amides

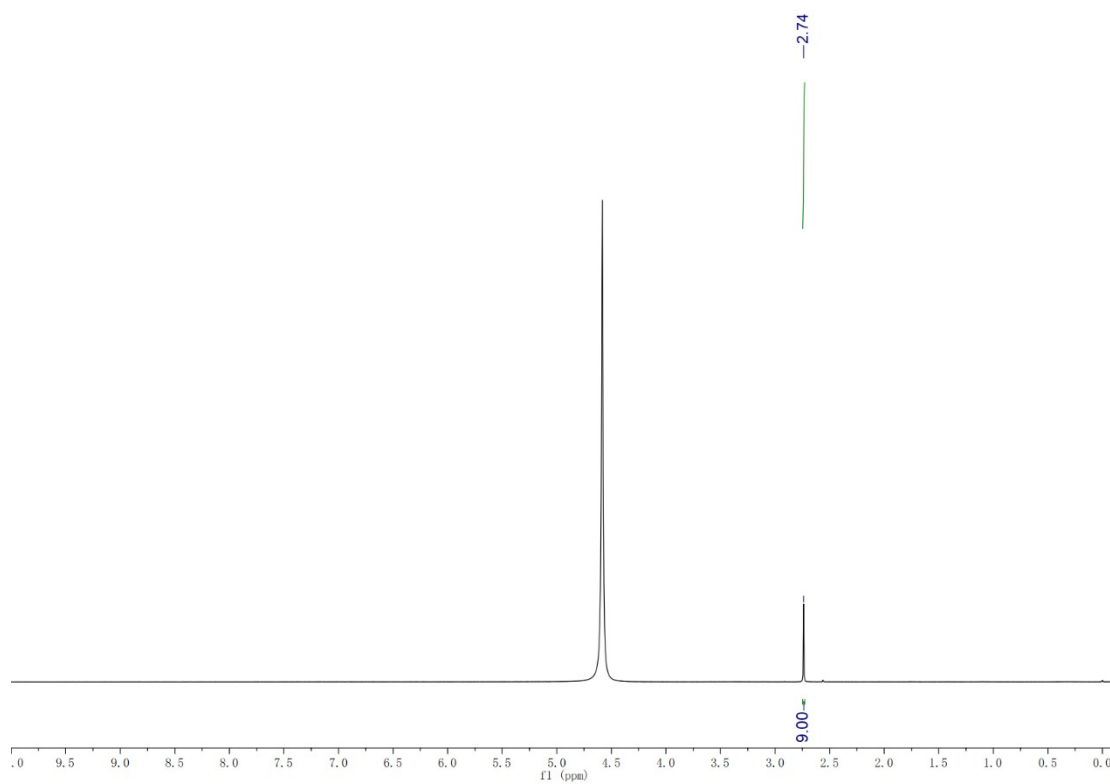


Figure S3.1.1 ^1H NMR of compound **6a** in D_2O

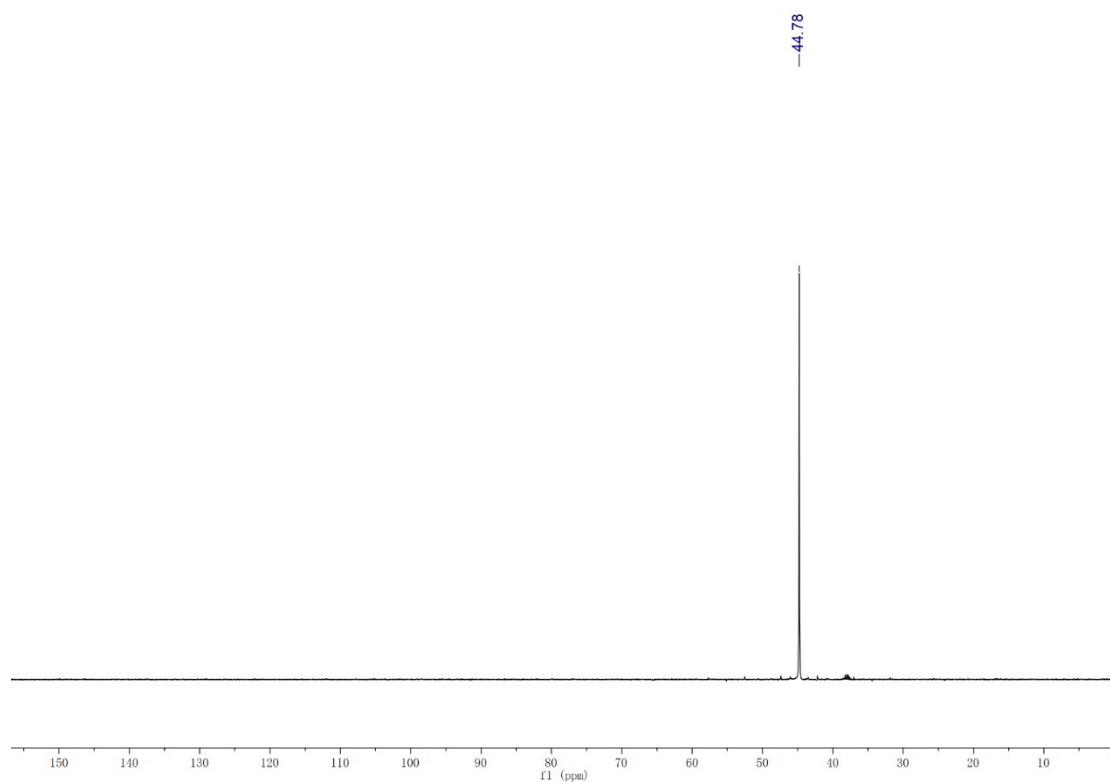


Figure S3.1.2 ^{13}C NMR of compound **6a** in D_2O

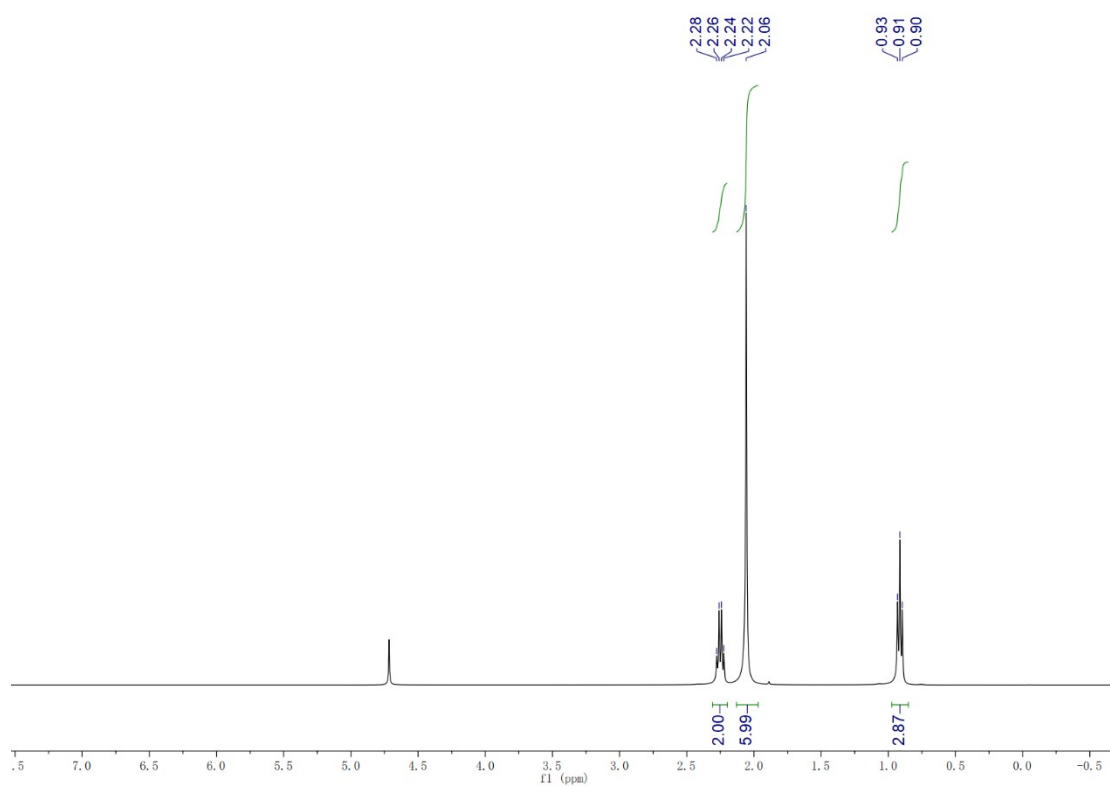


Figure S3.2.1 ^1H NMR of compound **6b** in D_2O

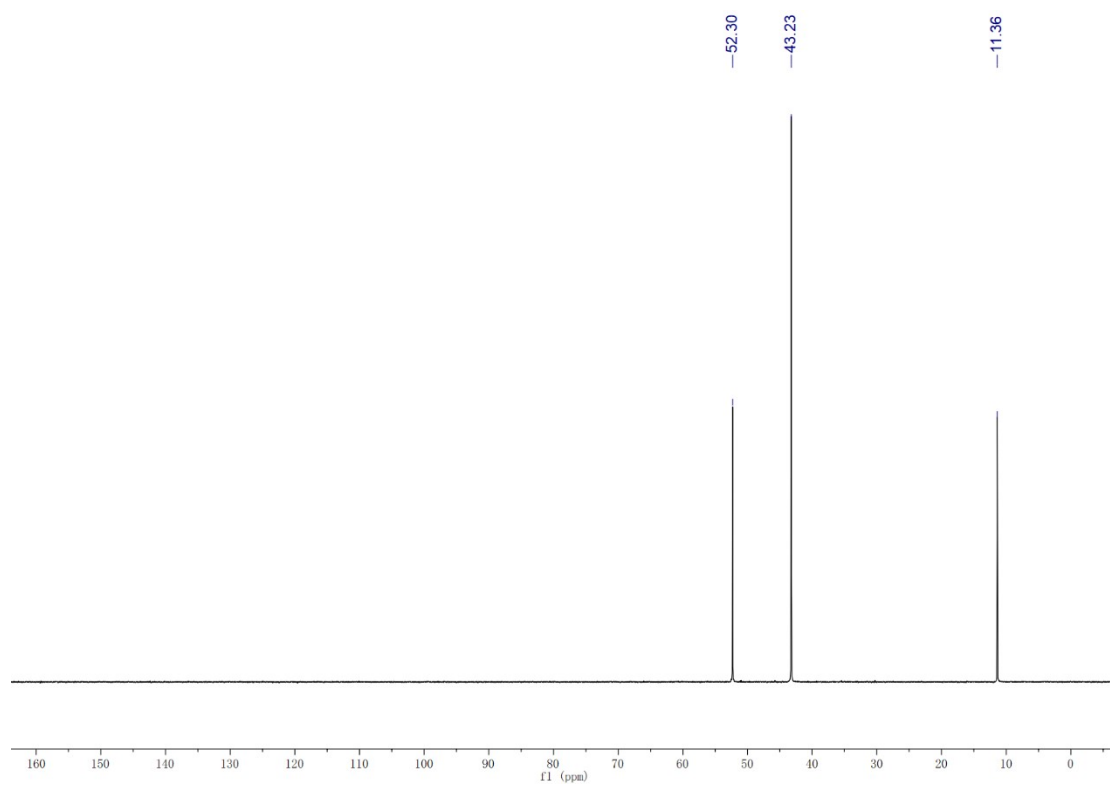


Figure S3.2.2 ^{13}C NMR of compound **6b** in D_2O

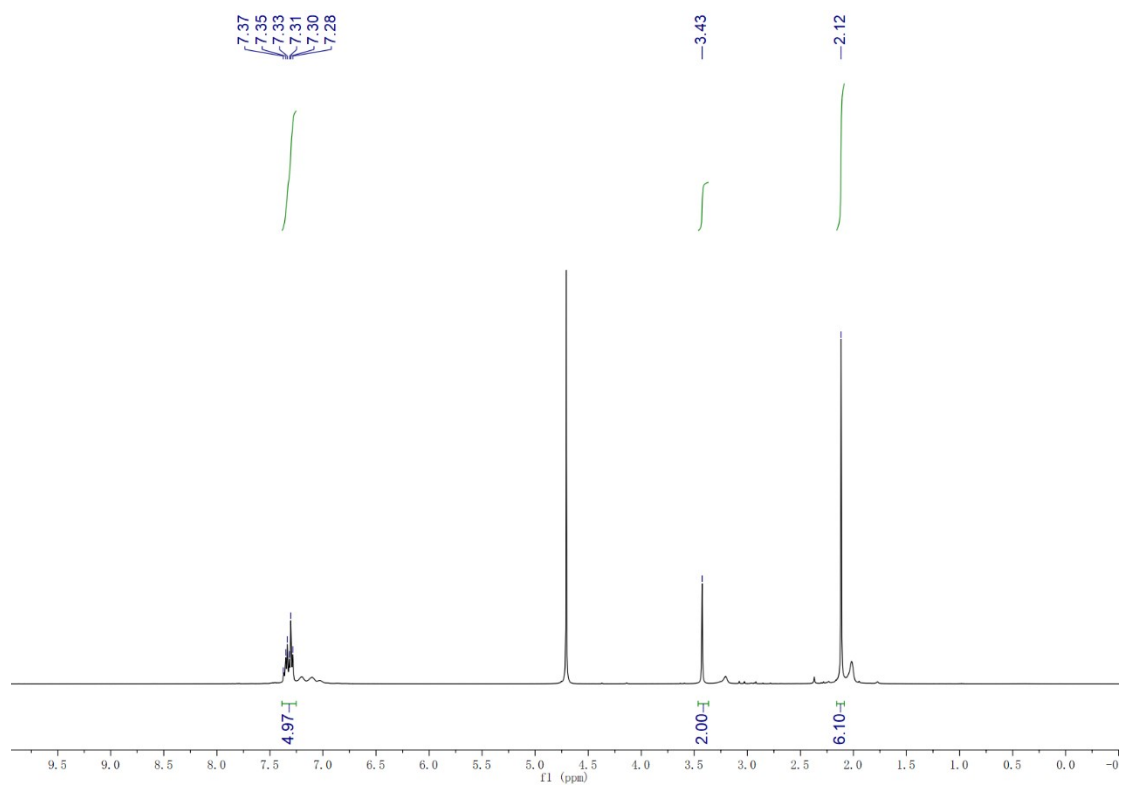


Figure S3.3.1 ^1H NMR of compound **6c** in D_2O

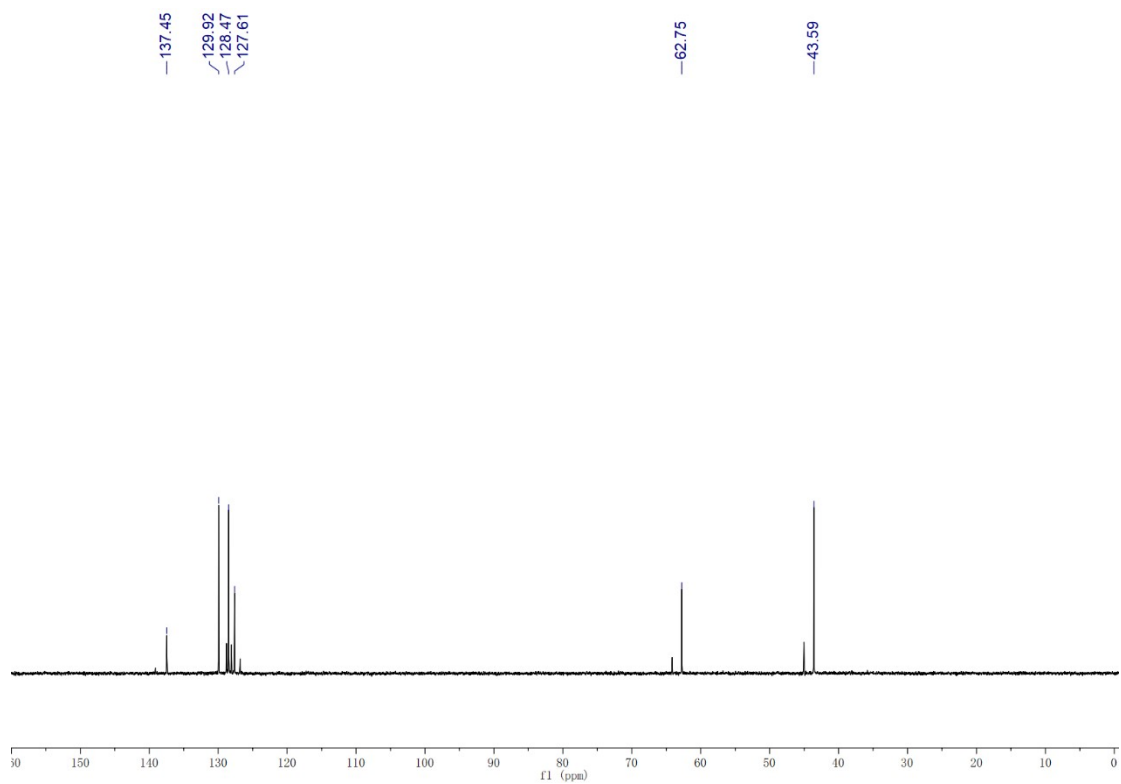


Figure S3.3.2 ^{13}C NMR of compound **6c** in D_2O

References

- [S1] D. Peng, M. Zhang, Z. Huang, *Chem. Eur. J.*, 2015, **21**(42), 14737-14741.
[S2] P. V. Ramachandran and D. Biswas, *Org. Lett.*, 2007, **9**, 3025-3027.