Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

An efficient catalytic method for the borohydride reaction of esters using diethylzinc as precatalyst

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General Information.

Unless otherwise stated, all reactions were performed using standard Schlenk techniques or inside an Etelux MB 200G glovebox. All solvents were refluxed over the appropriate drying agent and distilled prior to use. Commercially available chemicals are purchased from Minrell Chemical Reagent Company or Anaiji Reagent Company, and stored and used according to the instructions. The NMR spectrum was provided by the Bruker Ascend II 400 spectrometer. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = quintet, m = multiplet), integration and coupling constants (Hz). It should be noted that the boiling point of one of the reaction products, CH_3OBpin, is close to the boiling point of the catalyst solvent. Although we have tried various methods to remove the solvent, which resulted in the absence of CH_3OBpin to some extent. So in order to calculate the accuracy of the yield, our final spectrum retained solvent peaks (Figure S1). In addition, only the solvent peak at δ 0.8 ppm is marked in the ^1H NMR spectrum. Interestingly, in the subsequent experiments to explore the reaction mechanism, when zinc hydride was used to catalyze the hydroboration of dimethyl carbonate, satisfactory yield was obtained, which was the same as that of $ZnEt_2$. Furthermore, ^1H NMR showed that pure product was obtained (**Figure S7.2**, compared with **Figure S7.1**). This would also apply to other types of esters in this reaction.

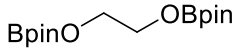
In the NMR spectra we used the following markers:

* - MeOBPin: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.53 (s, 3 H, *Me*OBPin), 1.18 (s, 12 H, BOC*Me*$_2$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 81.7, 51.6, 23.6.

▼- Hexane ($ZnEt_2$, 1.0 M in hexane): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.15(s, 4 H, C*H*$_2$CH$_2$CH$_3$), 1.17 (s, 4 H, CH$_2$C*H*$_2$CH$_3$), 0.82 (m, 6 H, C*H*$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 30.6, 21.6, 13.1.

General Procedure for Hydroboration of Carbonates.

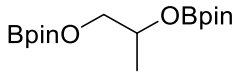
Carbonate (1.0 mmol, 1 equiv), HBpin (3.2 mmol, 3.2 equiv) and $ZnEt_2$ (0.07 mmol, 7 mol%, 1.0 M in hexane) were placed in a 10 mL Schlenk flask equipped with a magnetic stirring bar in a glove box. The reaction mixture was stirred at 80 °C for 12 h and then subjected to NMR analysis. The reaction process was monitored by ^{1}H NMR, ^{13}C NMR and the results showed the disappearance of the carbonate protons and the appearance of the new product and CH_3OBpin, indicating the completion of the reaction.



2a

NMR yield: 99%, white gum. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.87 (s, 4H, OC*H*$_2$), 1.18 (s, 24H, BOC*Me*$_2$).

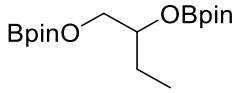
^{13}C NMR (101 MHz, $CDCl_3$) δ 81.7, 64.1, 23.6, 23.5.



2b

NMR yield: 50%, white gum. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.20 (q, J = 6.1 Hz, 1H, C*H*), 3.67 (dd, J = 5.6, 1.7 Hz, 2H, OC*H*$_2$), 1.18 (s, 24H, BOC*Me*$_2$), 1.10 (d, J = 6.4 Hz, 3H, *Me*).

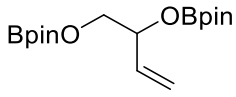
^{13}C NMR (101 MHz, $CDCl_3$) δ 81.7, 81.6, 69.3, 68.1, 23.6, 23.5, 17.5.



2c

NMR yield: 87%, white gum. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.05-3.93 (m, 1H, C*H*), 3.76-3.67 (m, 2H, OC*H*$_2$), 1.48-1.37 (m, 2H, C*H*$_2$), 1.17 (s, 24H, BOC*Me*$_2$), 0.86 (d, J = 7.4 Hz, 3H, *Me*).

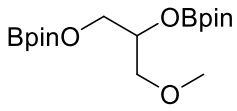
^{13}C NMR (101 MHz, $CDCl_3$) δ 81.7, 81.6, 74.4, 66.7, 24.3, 23.6, 23.5, 8.4.



2d

NMR yield: 87%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.79-5.70 (m, 1H, C*H*=CH$_2$), 5.27 (d, J = 17.2 Hz, 1H, CH=C*H*$_2$), 5.09 (d, J = 10.6 Hz, 1H, CH=C*H*$_2$), 4.60-4.54 (m, 1H, C*H*), 3.79-3.67 (m, 2H, OC*H*$_2$), 1.18 (s, 24H, BOC*Me*$_2$).

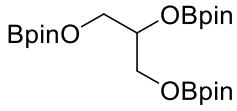
^{13}C NMR (101 MHz, $CDCl_3$) δ 134.4, 115.4, 81.7, 73.8, 66.8, 23.6, 23.5.



2e

NMR yield: 99%, white gum. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.23 (q, J = 4.1 Hz, 1H, C*H*), 3.87-3.77 (m, 2H, OCH_2), 3.39-3.34 (m, 2H, CH_2), 3.27 (s, 3H, CH_3), 1.17 (s, 24H, BOCMe_2).

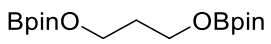
^{13}C NMR (101 MHz, $CDCl_3$) δ 81.8, 81.7, 71.9, 71.8, 64.5, 57.6, 23.6, 23.5.



2f

NMR yield: 91%, white gum. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.27-4.18 (m, 1H, C*H*), 3.93-3.87 (m, 2H, OCH_2), 3.86 -3.79 (m, 2H, CH_2), 1.22 (s, 36H, BOCMe_2).

^{13}C NMR (101 MHz, $CDCl_3$) δ 81.8, 81.7, 72.6, 64.1, 23.6, 23.5.



2g

NMR yield: 95%, white gum. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.89-3.83 (m, 4H, OCH_2), 1.76 (dd, J = 8.7, 4.1 Hz, 2H, CH_2), 1.17 (s, 24H, BOCMe_2).

^{13}C NMR (101 MHz, $CDCl_3$) δ 81.8, 81.7, 60.5, 32.3, 23.7, 23.6.

2h

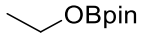
NMR yield: 56%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.56 (s, 4H, OCH_2), 1.17 (s, 24H, BOCMe_2), 0.80 (s, 6H, *Me*)

^{13}C NMR (101 MHz, $CDCl_3$) δ 81.7, 81.6, 69.3, 35.7, 23.6, 23.5, 19.8.

2i

NMR yield: 99%, white gum. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.51 (s, 3H, *Me*), 1.19 (s, 12H, BOCMe_2).

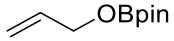
^{13}C NMR (101 MHz, $CDCl_3$) δ 81.8, 51.6, 23.6.



2j

NMR yield: 92%, white gum. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.82 (q, J = 7.1, 5.7 Hz, 2H, OCH_2), 1.18 (s, 12H, BOCMe_2), 1.15-1.09 (m, 3H, *Me*).

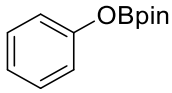
^{13}C NMR (101 MHz, $CDCl_3$) δ 81.6, 59.6, 23.6, 16.2.



2l

NMR yield: 98%, white gum. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.84 (q, J = 8.7, 7.0 Hz, 1H, C*H*=CH_2), 5.21 (d, J = 17.1 Hz, 1H, CH=C*H*$_2$), 5.05 (d, J = 10.5 Hz, 1H, CH=C*H*$_2$), 4.29 (d, J = 4.9 Hz, 2H, C*H*$_2$), 3.53 (s, 3H, OC*H*$_3$), 1.18 (s, 12H, BOC*Me*$_2$)

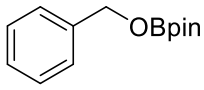
^{13}C NMR (101 MHz, $CDCl_3$) δ 134.4, 113.9, 81.8, 81.7, 64.5, 23.6, 23.5.



2m

NMR yield: 99%, white gum. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (t, J = 7.1 Hz, 2H, Ar−*H*), 7.05-6.92 (m, 3H, Ar−*H*), 1.21 (d, J = 24.9 Hz, 12H, BOC*Me*$_2$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.4, 128.3, 122.1, 118.5, 82.5, 81.8, 23.6.



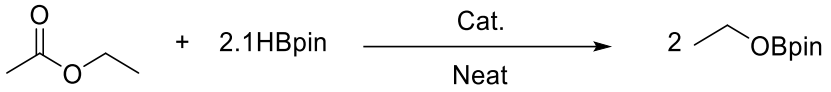
2n

NMR yield: 72%, white gum. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.16 (m, 5H, *Ph*CH_2OBpin), 4.83 (s, 2H, OC*H*$_2$), 1.17 (s, 12H, BOC*Me*$_2$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.3, 127.3, 126.3, 125.7, 81.9, 81.7, 65.7, 23.6.

Optimization of Esters Hydroboration

Table S1. Optimization of ethyl acetate hydroboration[a]



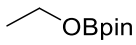
3a **4a**

Entry	Cat (mol %)	*T* (°C)	*t* (h)	Yield (%)[b]
1	None	60	8	0
2	5	25	8	32
3	5	60	8	86
4	5	60	10	92
5	**5**	**60**	**12**	**99**
6	3	60	12	90

[a]Ethyl Acetate (**3a**) (1 mmol, 1 equiv), HBpin (2.1 mmol, 2.1 equiv), catalysts (0.05 mmol, 5 mol %, 1.0 M in hexane). [b]The reaction was monitored by ^{1}H NMR spectroscopy.

General Procedure for Hydroboration of Esters.

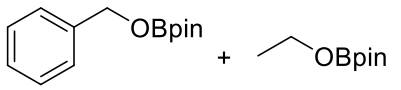
In a glove box, the catalyst $ZnEt_2$ (0.05 mmol, 5 mol%, 1.0 M in hexane) was added to a solution of esters (1.0 mmol, 1 equiv) and HBpin (2.1 mmol, 2.1 equiv) in a 10 ml Schlenk flask. The reaction mixture was stirred at 60 °C for 12 h and then subjected to NMR analysis. The progress of the reaction was monitored by ^{1}H NMR and ^{13}C NMR, which indicated the completion of the reaction by the disappearance of the ester proton and appearance of new products.



4a

NMR yield: 99%, white gum. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.83 (q, J = 7.0 Hz, 2H, MeCH_2OBpin), 1.18 (d, J = 2.5 Hz, 12H, BOCMe_2), 1.14 (s, 3H, MeCH$_2$OBpin).

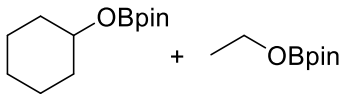
^{13}C NMR (101 MHz, $CDCl_3$) δ 81.6, 59.6, 23.6, 16.2.



4b

NMR yield: 77%, white gum. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.12 (m, 5H, Ar-H), 4.82 (s, 2H, PhCH_2OBpin), 3.79 (q, J = 7.0 Hz, 2H, MeCH_2OBpin), 1.14 (d, J = 4.4 Hz, 24H, BOCMe_2), 1.11 (s, 3H, MeCH$_2$OBpin).

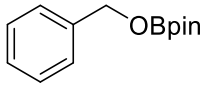
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.3, 127.2, 126.3, 125.7, 81.8, 81.5, 65.6, 59.6, 23.7, 23.6, 16.2.



4c

NMR yield: 99%, white gum. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.91 (q, J = 4.8 Hz, 1H, *Cy*OBpin), 3.82 (q, J = 7.1 Hz, 2H, MeCH_2OBpin), 1.79-1.73 (m, 2H, *Cy*OBpin), 1.64 (dt, J = 8.1, 4.4 Hz, 2H, *Cy*OBpin), 1.43 (dt, J = 11.8, 4.5 Hz, 2H, *Cy*OBpin), 1.30 (d, J = 9.0 Hz, 1H, *Cy*OBpin), 1.24 (d, J = 11.2 Hz, 3H, *Cy*OBpin), 1.18 (s, 24H, BOCMe_2), 1.14 (s, 3H, *Me*CH_2OBpin).

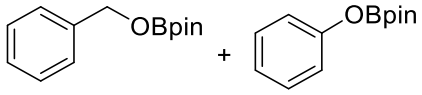
^{13}C NMR (101 MHz, $CDCl_3$) δ 81.6, 81.4, 71.6, 59.6, 33.2, 24.5, 23.6, 22.8, 16.2.



4d

NMR yield: 95%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.14 (m, 5H, Ar-*H*), 4.84 (s, 2H, PhCH_2OBpin), 1.17 (s, 12H, BOCMe_2).

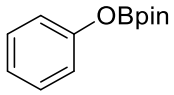
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.2, 127.2, 126.3, 125.7, 81.9, 65.6, 23.6.



4e

NMR yield: 99%, white gum. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.12 (m, 7H, Ar-*H*), 7.00 (d, J = 8.7 Hz, 2H, Ar-*H*), 6.95 (d, J = 7.4 Hz, 1H, Ar-*H*), 4.84 (s, 2H, PhCH_2OBpin), 1.20 (d, J = 20.9 Hz, 24H, BOCMe_2).

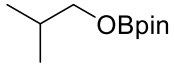
^{13}C NMR (101 MHz, $CDCl_3$) δ 152.4, 138.2, 128.3, 127.3, 126.4, 125.7, 122.1, 118.5, 82.5, 81.9, 65.7, 23.6, 23.5.



4f

NMR yield: 99%, white gum. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 7.8 Hz, 2H, Ar-*H*), 7.13-7.03 (m, 3H, Ar-*H*), 1.30 (d, J = 24.7 Hz, 12H, BOCMe_2).

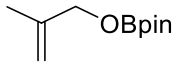
^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9, 128.3, 122.1, 118.5, 82.6, 81.9, 23.6, 23.5.



4g

NMR yield: 99%, white gum. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.54 (d, J = 6.5 Hz, 2H, CH_2OBpin), 1.74 (dt, J = 13.3, 6.7Hz, 1H, C*H*Me_2), 1.18 (d, J = 2.9 Hz, 12H, BOCMe_2), 0.82 (d, J = 6.7 Hz, 6H, CHMe_2).

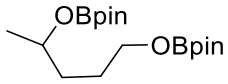
^{13}C NMR (101 MHz, $CDCl_3$) δ 81.6, 70.4, 28.8, 23.8, 23.6, 17.7.



4h

NMR yield: 99%, white gum. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.90 (s, 1H, C=CH_2), 4.75 (s, 1H, C=CH_2), 4.18 (s, 2H, CH_2OBpin), 1.65 (s, 3H, *Me*C=CH_2), 1.18 (s, 12H, BOC*Me*$_2$).

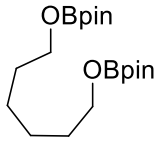
^{13}C NMR (101MHz, $CDCl_3$) δ 141.7, 108.9, 81.8, 67.3, 23.6, 23.5, 17.9.



4i

NMR yield: 99%, white gum. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.10 (q, J = 6.0 Hz, 1H, CH_3C*H*OBpin), 3.76 (td, J = 6.2, 3.4 Hz, 2H, CH_2), 1.56 (dd, J = 15.5, 8.7 Hz, 2H, C$H_2$$CH_2$OBpin), 1.48-1.42 (m, 2H, CH_2CH_2OBpin), 1.17 (d, J = 1.7 Hz, 24H, BOC*Me*$_2$), 1.11 (d, J = 6.3 Hz, 3H, CH_3CHOBpin).

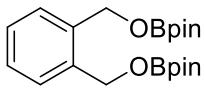
^{13}C NMR (101 MHz, $CDCl_3$) δ 81.6, 81.4, 69.6, 63.8, 33.1, 26.5, 23.6, 23.5, 21.6.



4j

NMR yield: 99%, white gum. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.76 (t, J = 6.6 Hz, 4H, pinBOC$H_2$$CH_2$$CH_2$$CH_2$$CH_2CH_2$OBpin), 1.49 (t, J = 6.8 Hz, 4H, pinBOCH_2CH_2 - $CH_2$$CH_2CH_2$$CH_2$OBpin), 1.32-1.25 (m, 4H, pinBOC$H_2$$CH_2CH_2CH_2$$CH_2$$CH_2$OBpin), 1.18 (s, 24H, BOC*Me*$_2$).

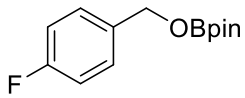
^{13}C NMR (101 MHz, $CDCl_3$) δ 81.6, 63.9, 30.4, 24.3, 23.6.



4k

NMR yield: 92%, white gum. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (dd, J = 9.3, 4.0 Hz, 2H, Ar-*H*), 7.20-7.14 (m, 2H, Ar-*H*), 4.88 (s, 4H, PhCH_2OBpin), 1.20-1.12 (m, 24H, BOC*Me*$_2$).

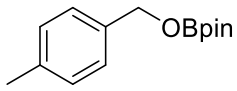
^{13}C NMR (101 MHz, $CDCl_3$) δ 136.5, 127.5, 127.3, 82.8, 64.1, 24.6.



4m

NMR yield: 99%, white gum. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (dd, J = 9.8, 4.3 Hz, 2H, Ar-*H*), 6.91 (t, J = 8.7 Hz, 2H, Ar-*H*), 4.78 (s, 2H, PhCH_2OBpin), 1.16 (s, 12H, BOCMe_2).

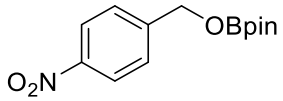
^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5, 160.1, 134.1, 114.2, 81.9, 81.7, 65.1, 23.8, 23.6.



4n

NMR yield: 98%, white gum. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, J = 4.4 Hz, 2H, Ar-*H*), 7.01 (d, J = 6.3 Hz, 2H, Ar-*H*), 4.77 (s, 2H, MePhCH_2OBpin), 2.22 (s, 3H, *Me*PhCH_2OBpin), 1.19-1.13 (m, 12H, BOCMe_2).

^{13}C NMR (101 MHz, $CDCl_3$) δ 135.9, 135.3, 127.9, 125.9, 81.9, 81.7, 65.6, 23.8, 23.6, 20.1.



4o

NMR yield: 99%, white gum. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (dt, J = 8.7, 3.0 Hz, 2H, Ar-*H*), 7.42 (d, J = 8.8 Hz, 2H, Ar-*H*), 4.94 (s, 2H, NO_2PhCH_2OBpin), 1.23-1.15 (m, 12H, BOCMe_2).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.3, 145.7, 125.9, 122.6, 82.3, 81.7, 64.6, 23.6, 23.5.

^{1}H, ^{13}C NMR Spectra of Hydroboration Products of Carbonates.

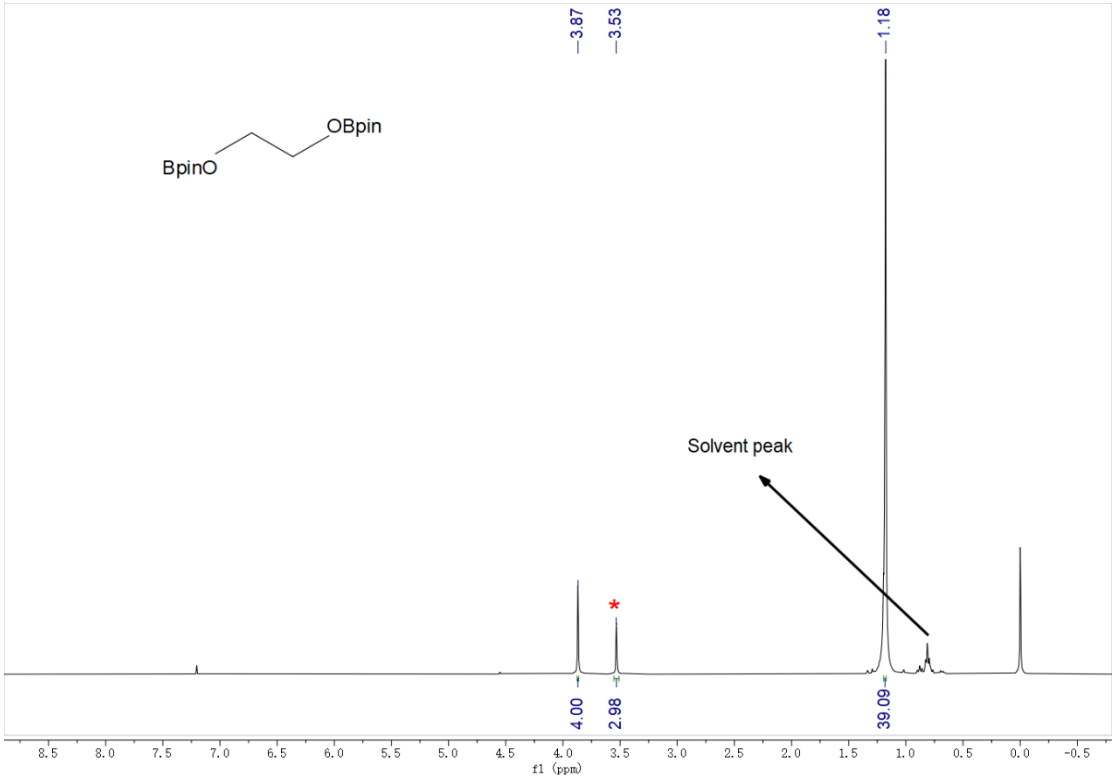


Figure S1.1.1 ^{1}H NMR (400 MHz, $CDCl_3$) of the compound without removing the solvent

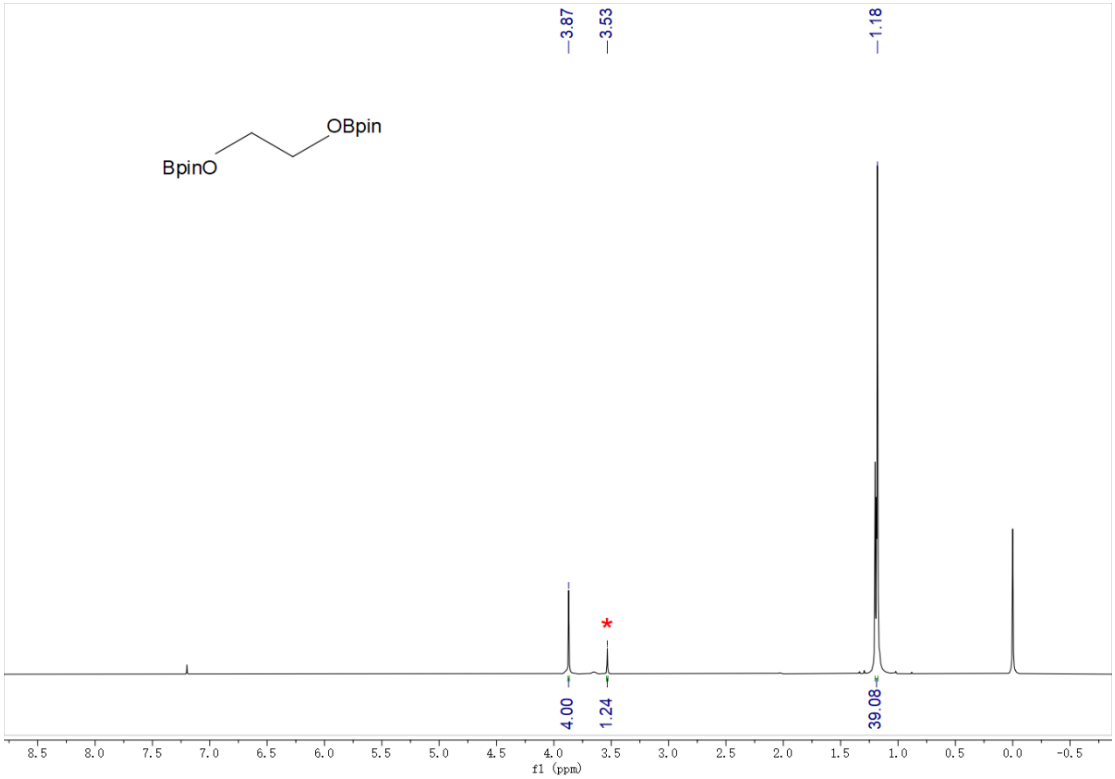


Figure S1.1.2 ^{1}H NMR (400 MHz, $CDCl_3$) of the compound with the solvent removed

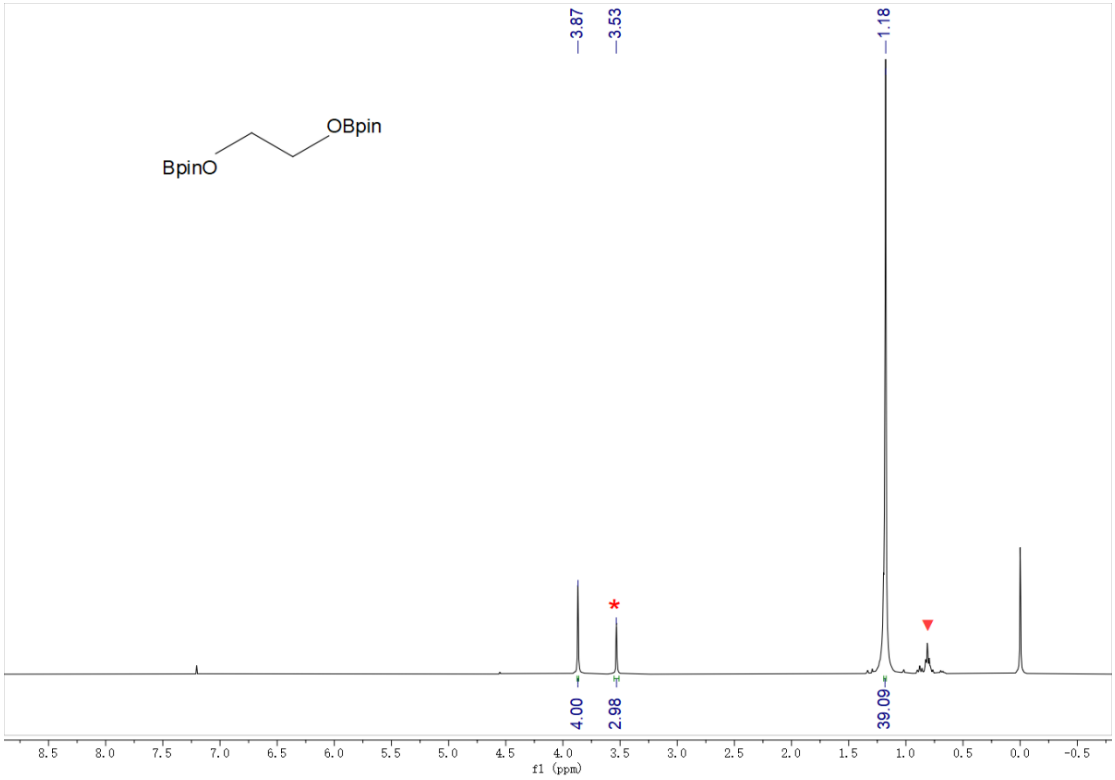


Figure S2.1.1 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **2a**

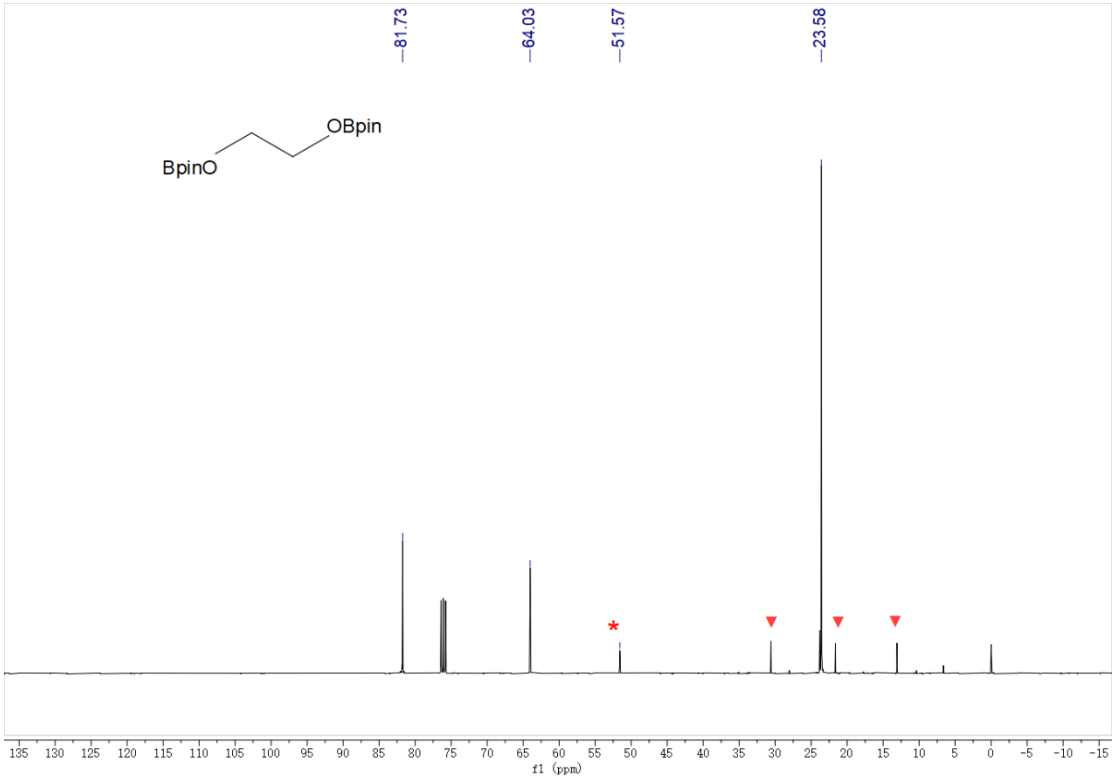


Figure S2.1.2 ^{13}C NMR (101 MHz, $CDCl_3$) of compound **2a**

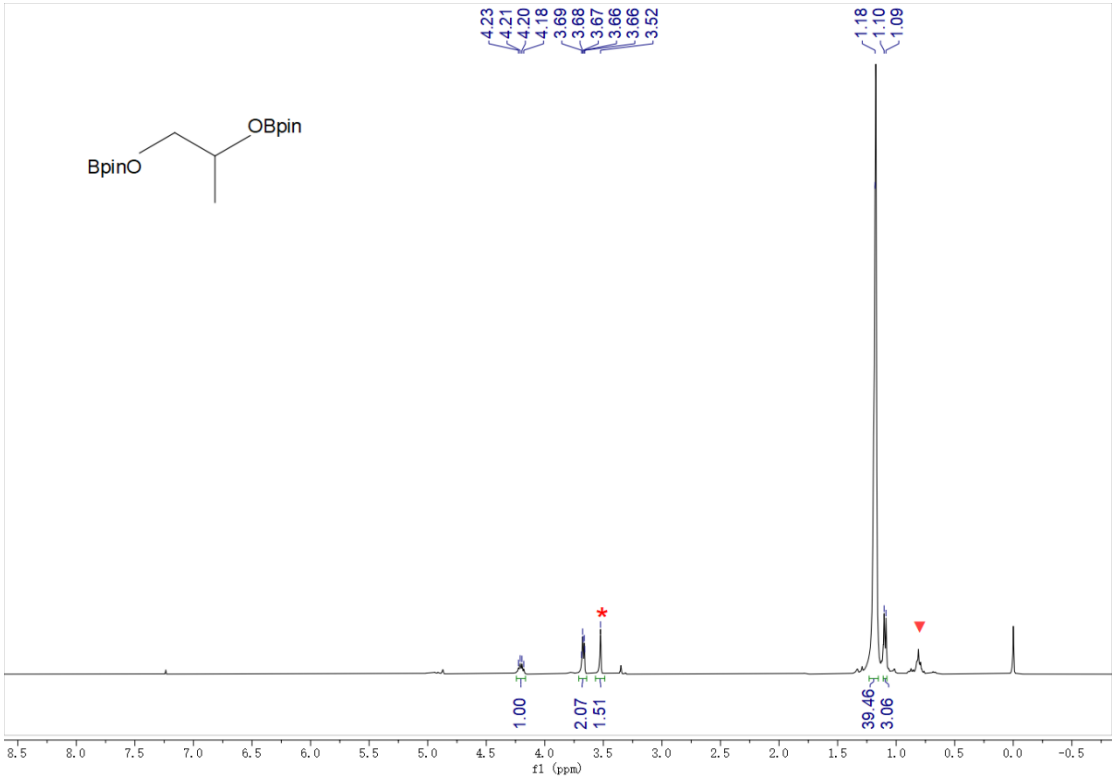


Figure S2.2.1 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **2b**

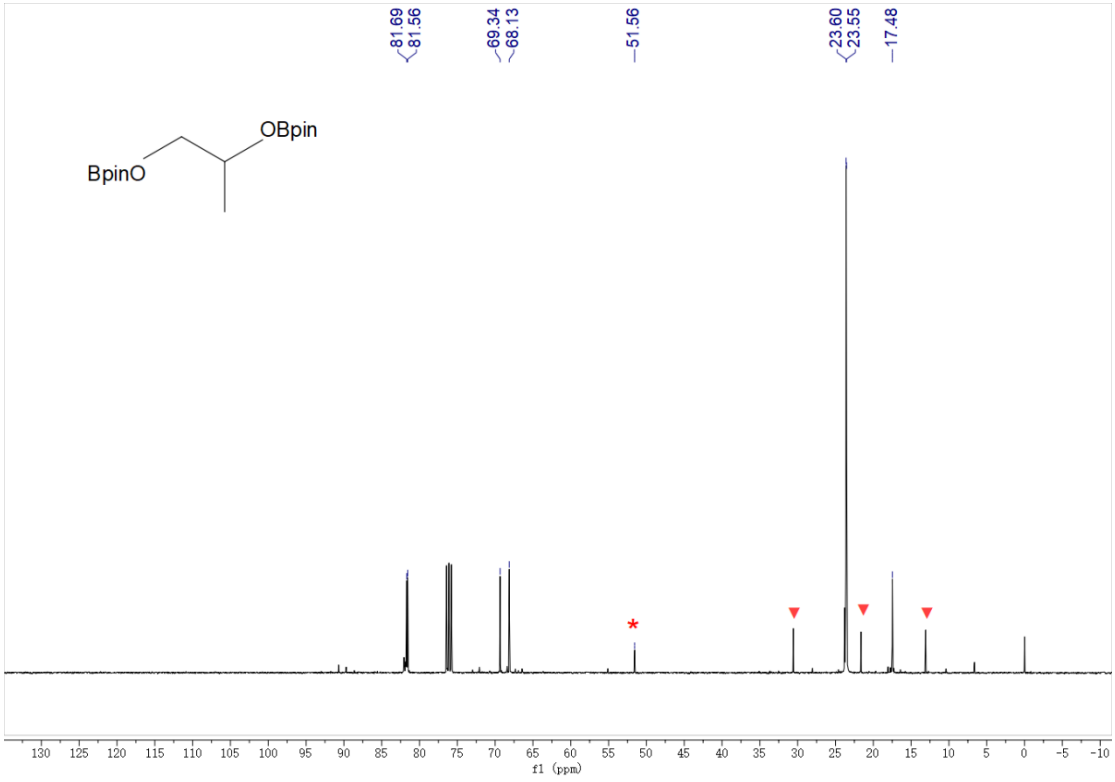


Figure S2.2.2 ^{13}C NMR (101 MHz, $CDCl_3$) of compound **2b**

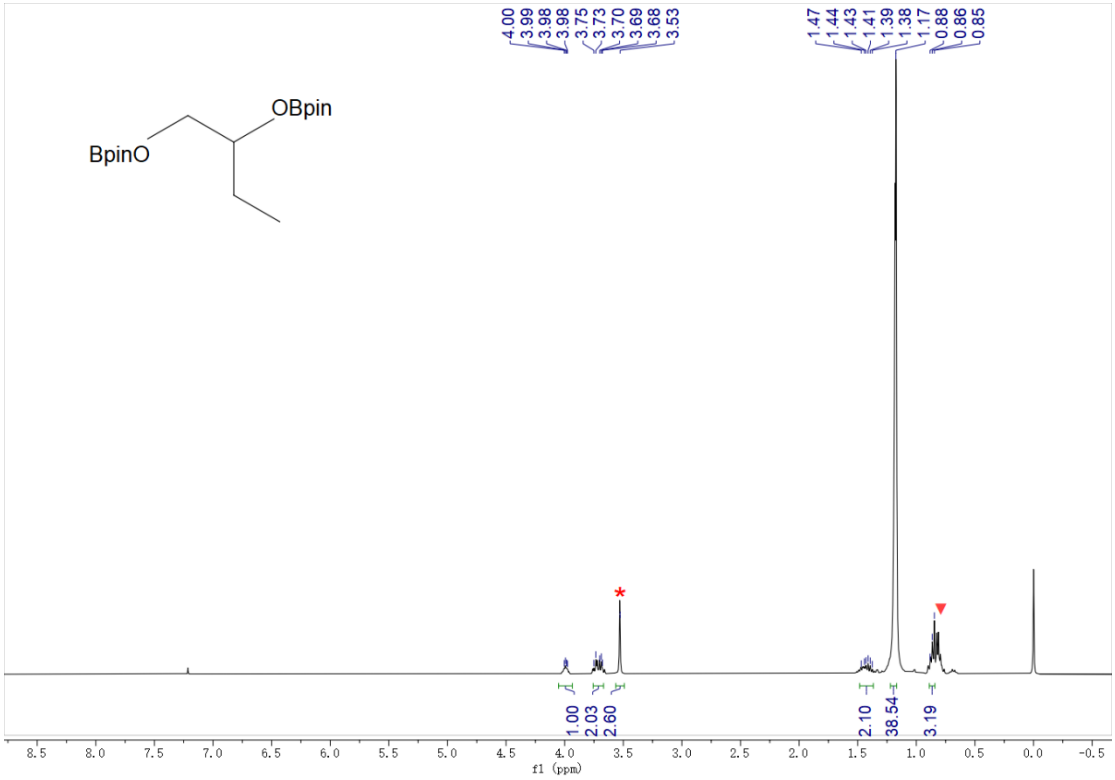


Figure S2.3.1 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **2c**

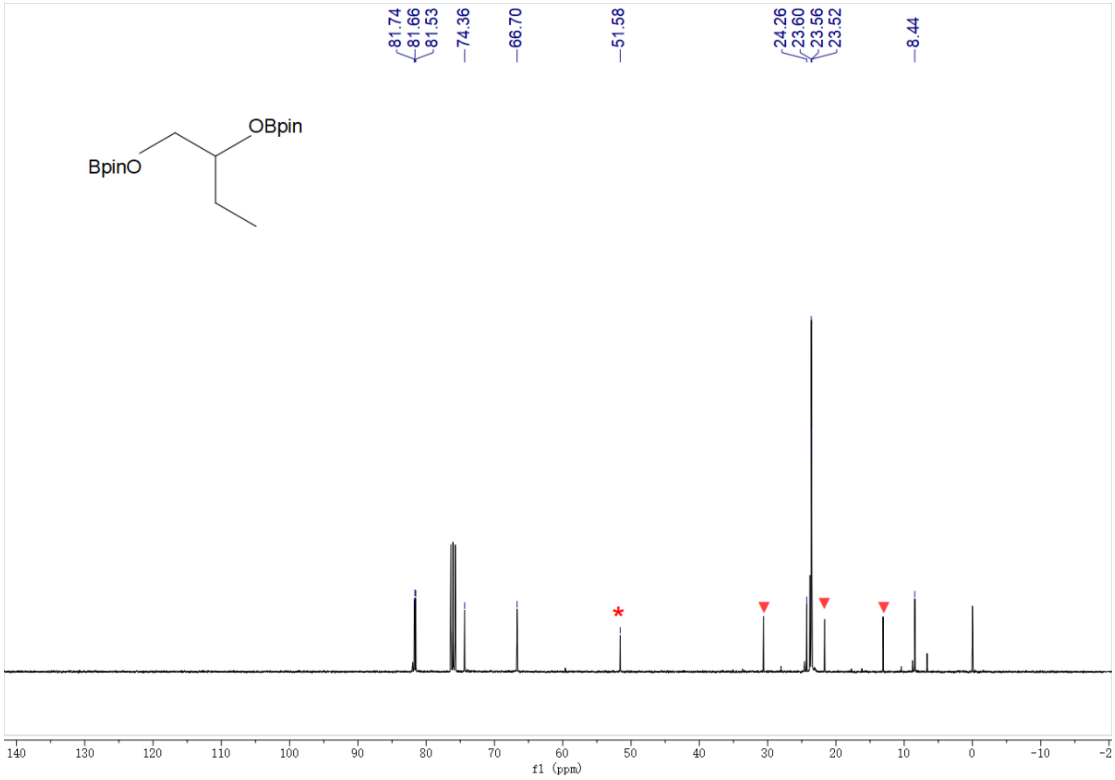


Figure S2.3.2 ^{13}C NMR (101 MHz, $CDCl_3$) of compound **2c**

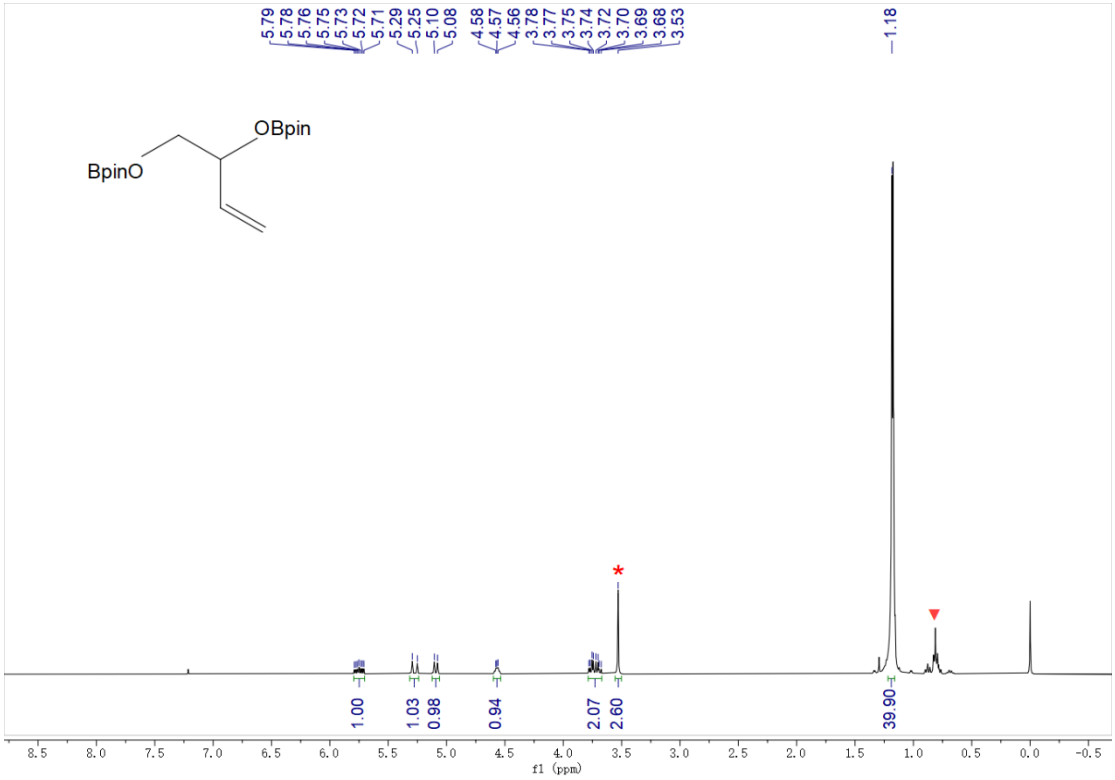


Figure S2.4.1 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **2d**

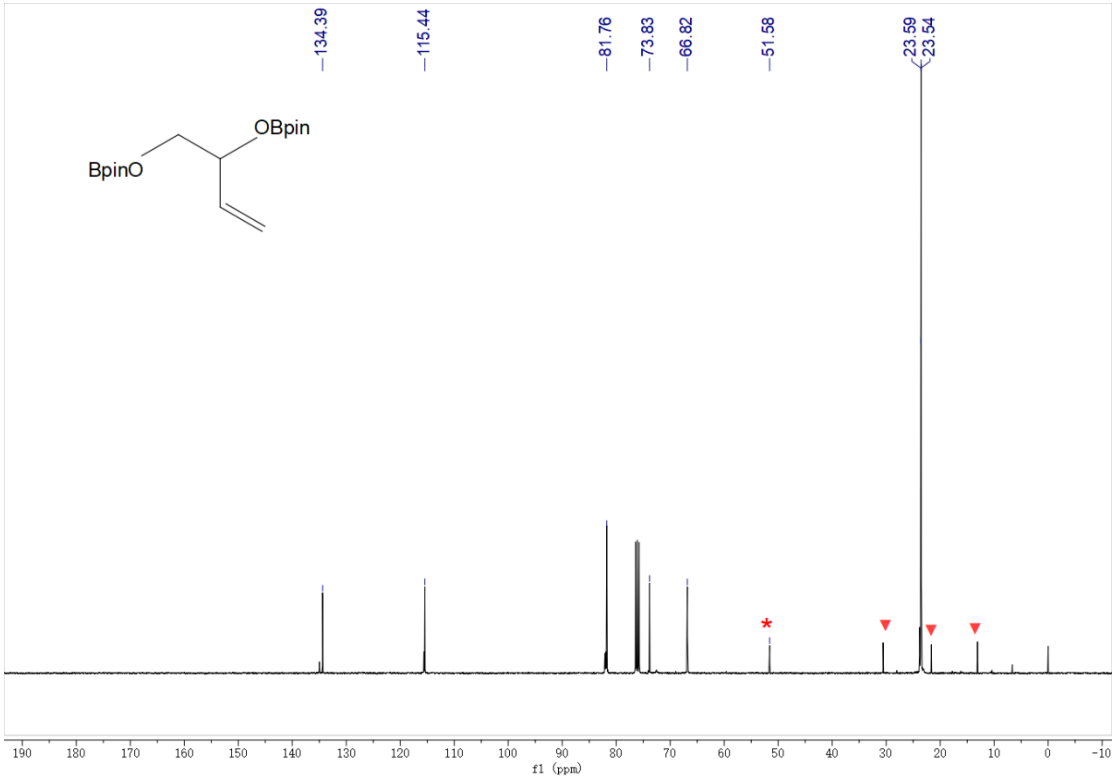


Figure S2.4.2 ^{13}C NMR (101 MHz, $CDCl_3$) of compound **2d**

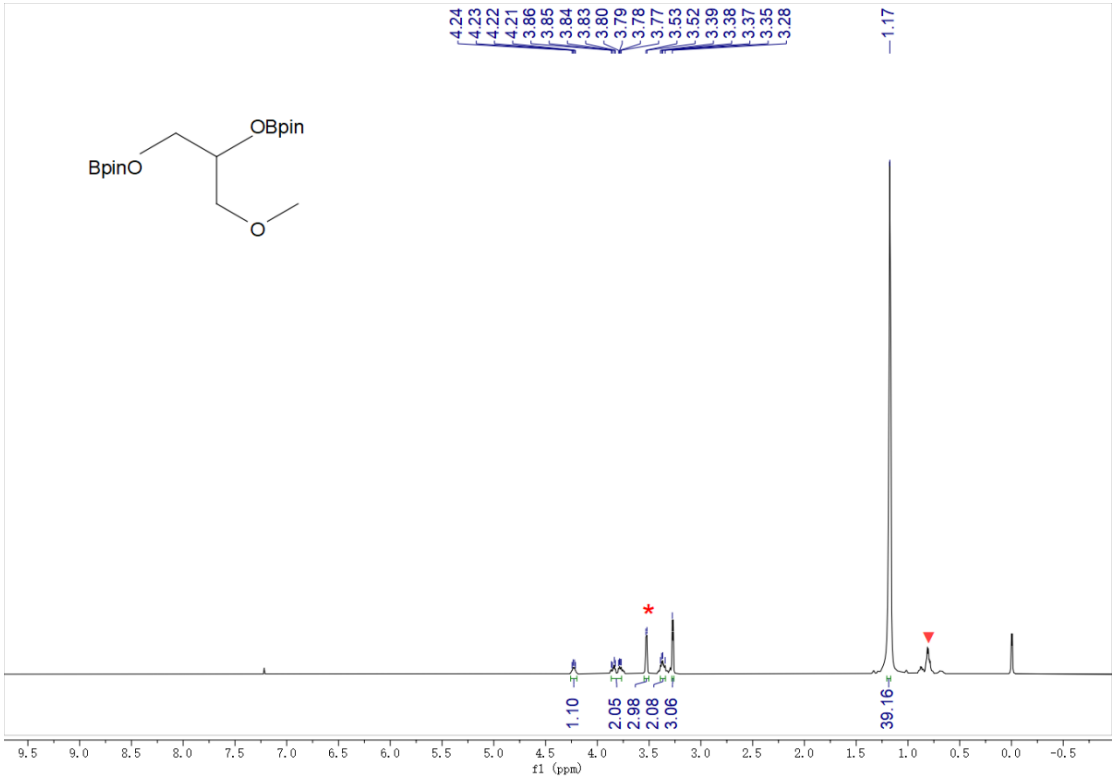


Figure S2.5.1 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **2e**

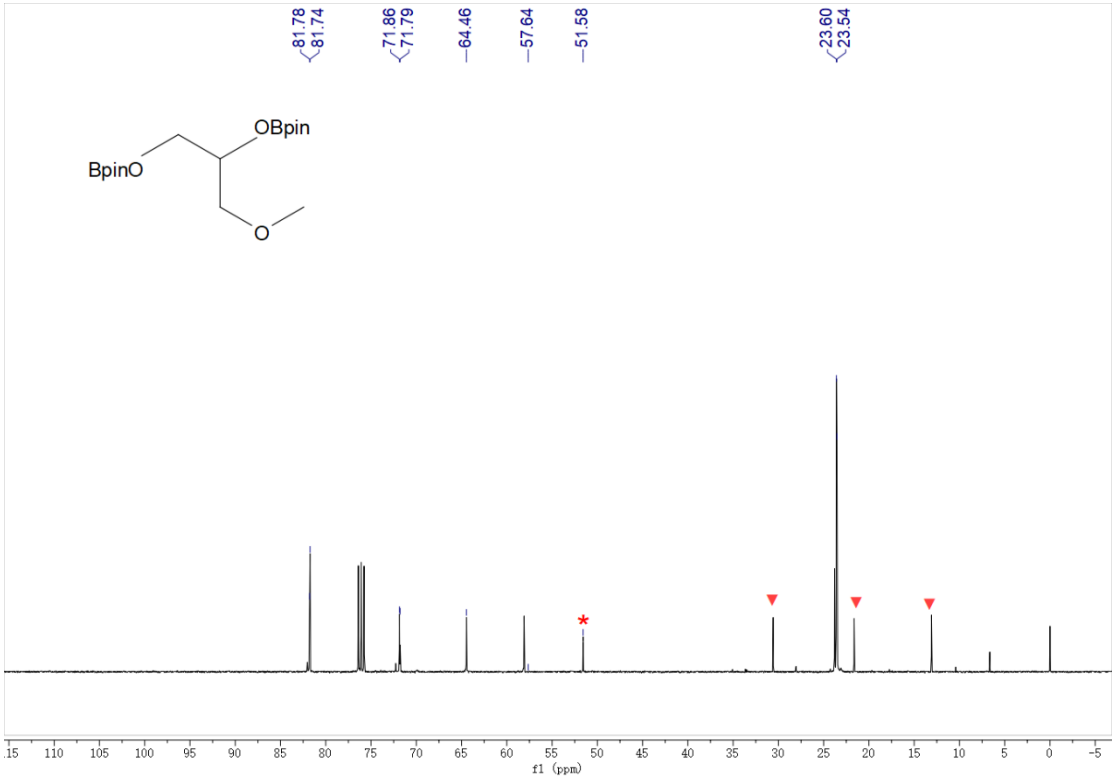


Figure S2.5.2 ^{13}C NMR (101 MHz, $CDCl_3$) of compound **2e**

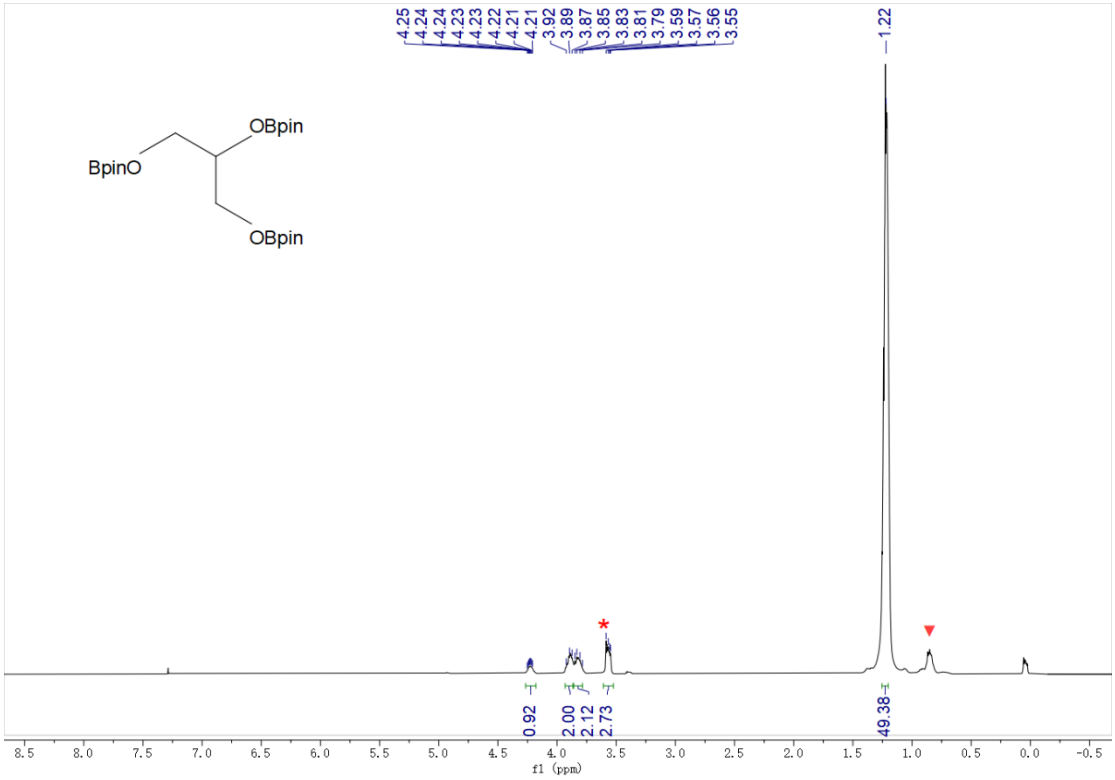


Figure S2.6.1 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **2f**

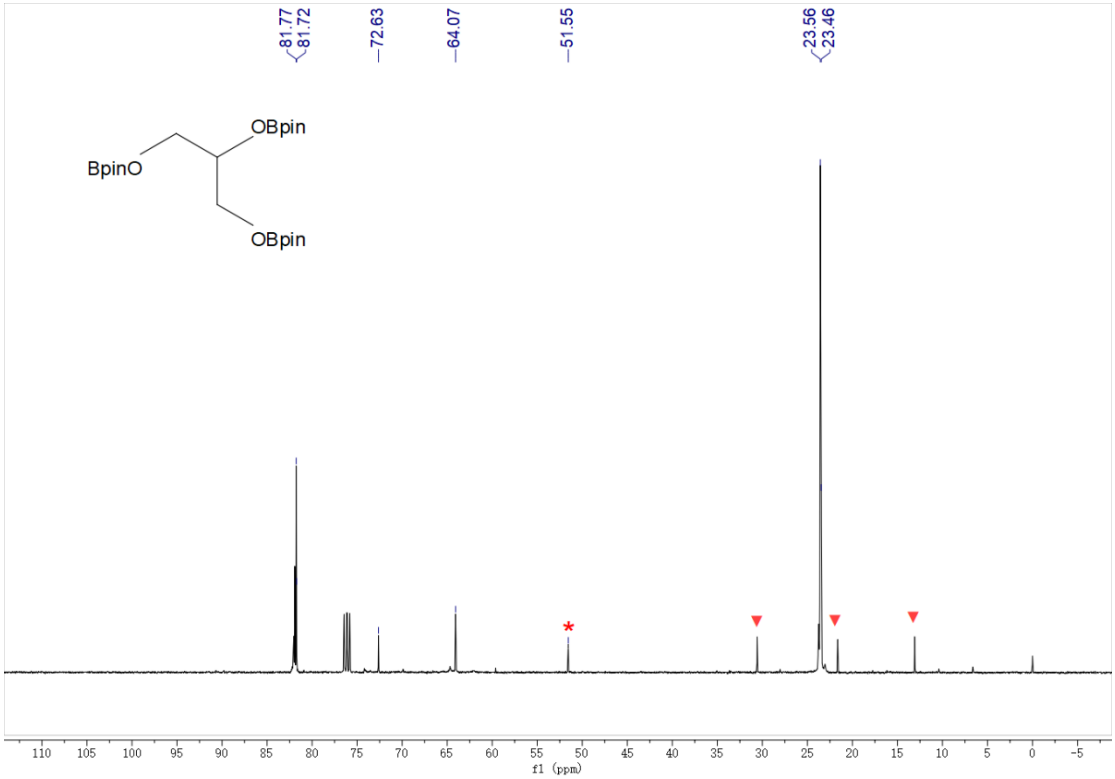


Figure S2.6.2 ^{13}C NMR (101 MHz, $CDCl_3$) of compound **2f**

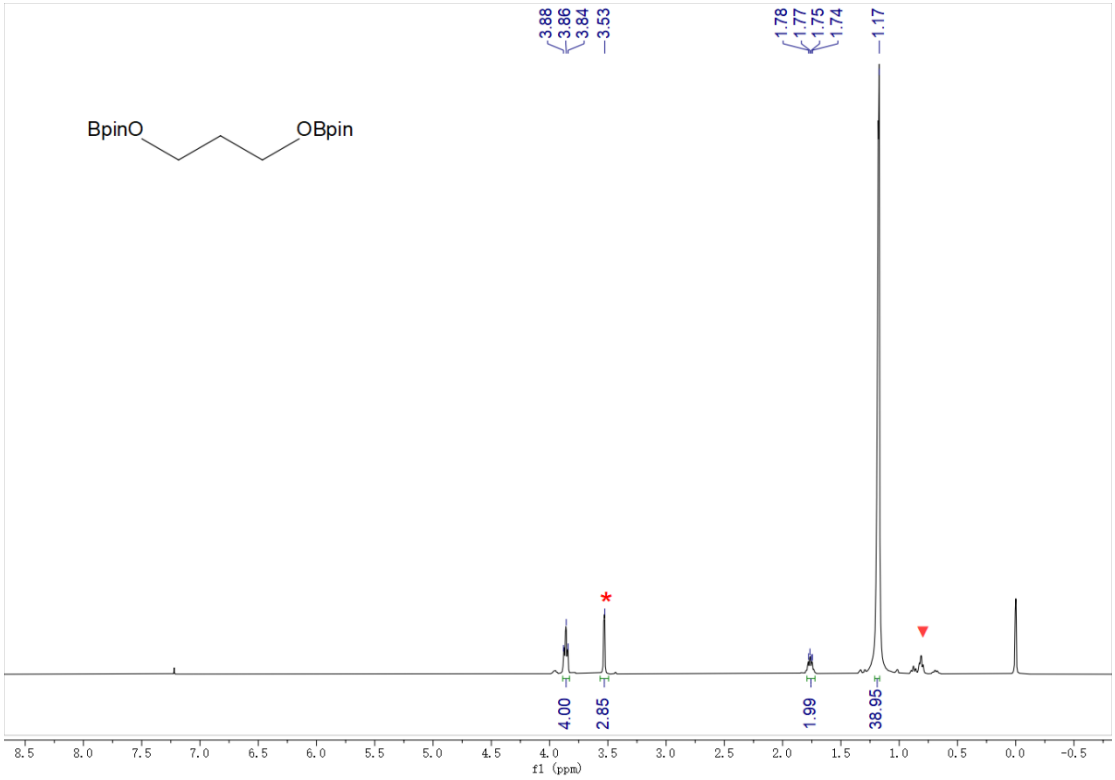


Figure S2.7.1 ^{1}H NMR (400 MHz, $CDCl_3$)of compound **2g**

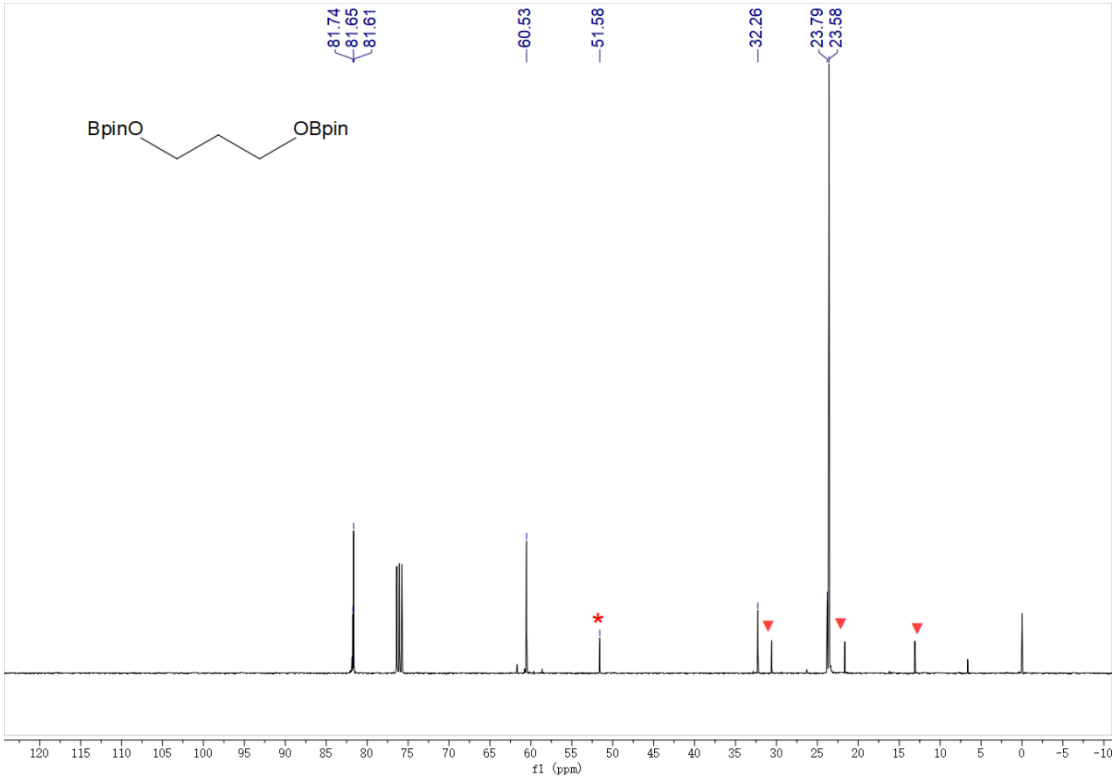


Figure S2.7.2 ^{13}C NMR (101 MHz, $CDCl_3$) of compound **2g**

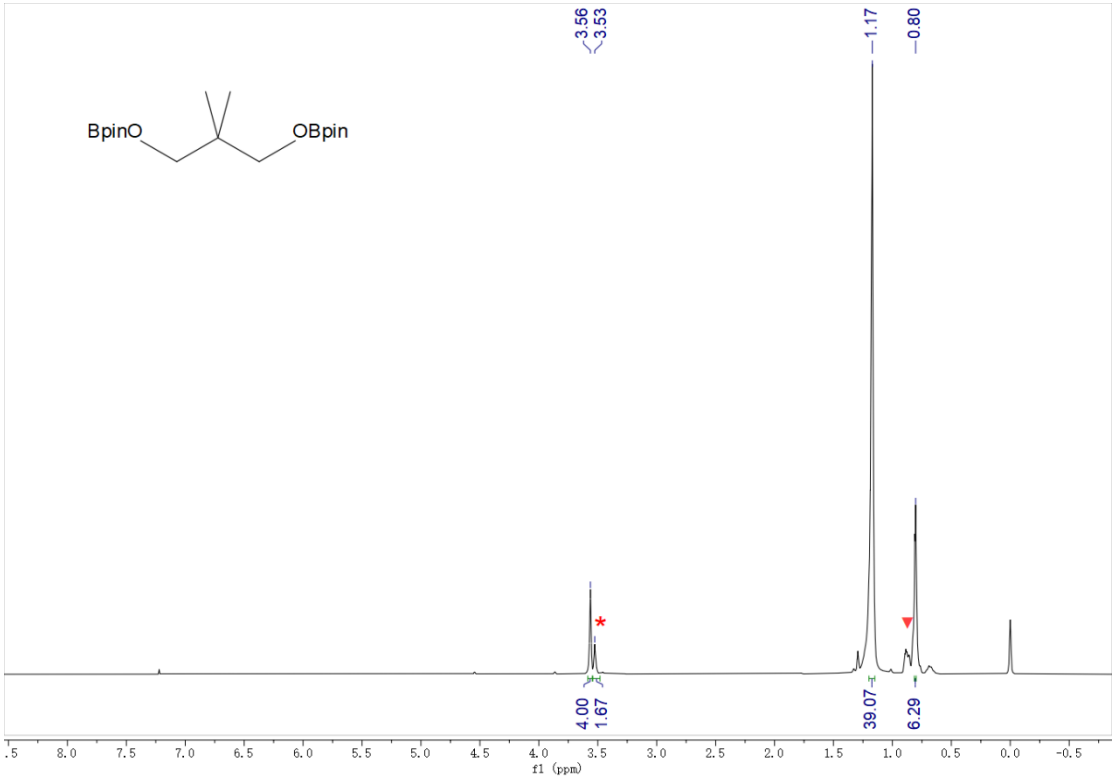


Figure S2.8.1 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **2h**

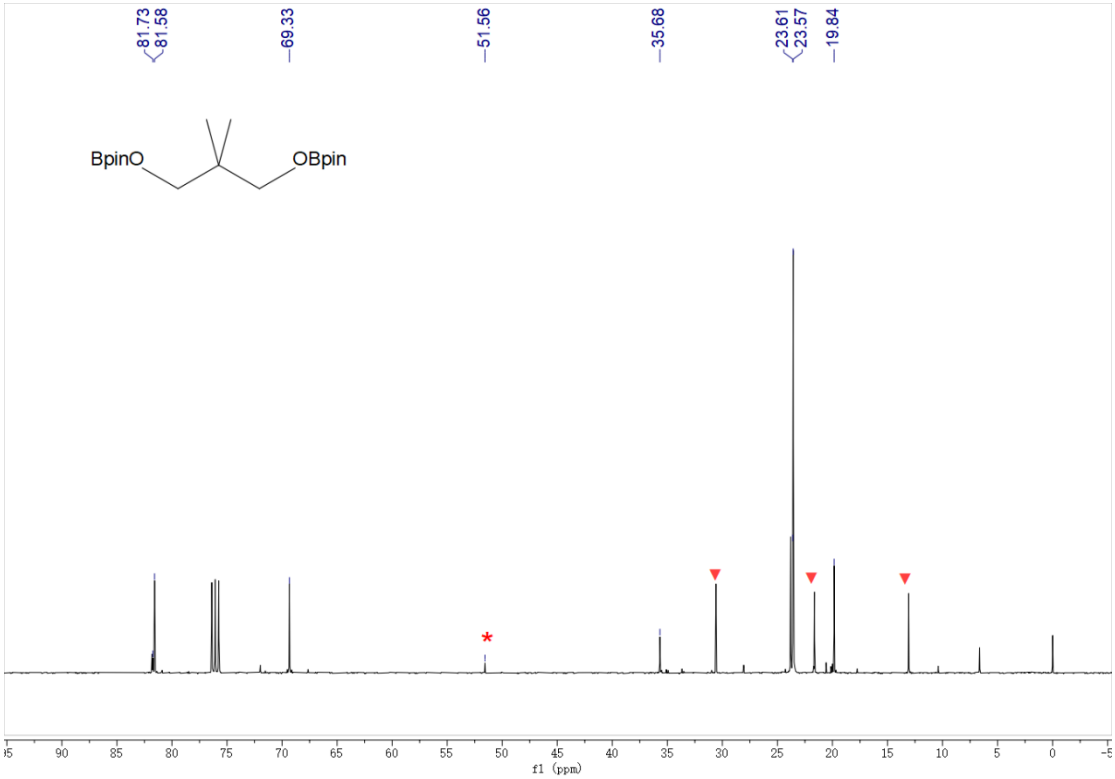


Figure S2.8.2 ^{13}C NMR (101 MHz, $CDCl_3$) of compound **2h**

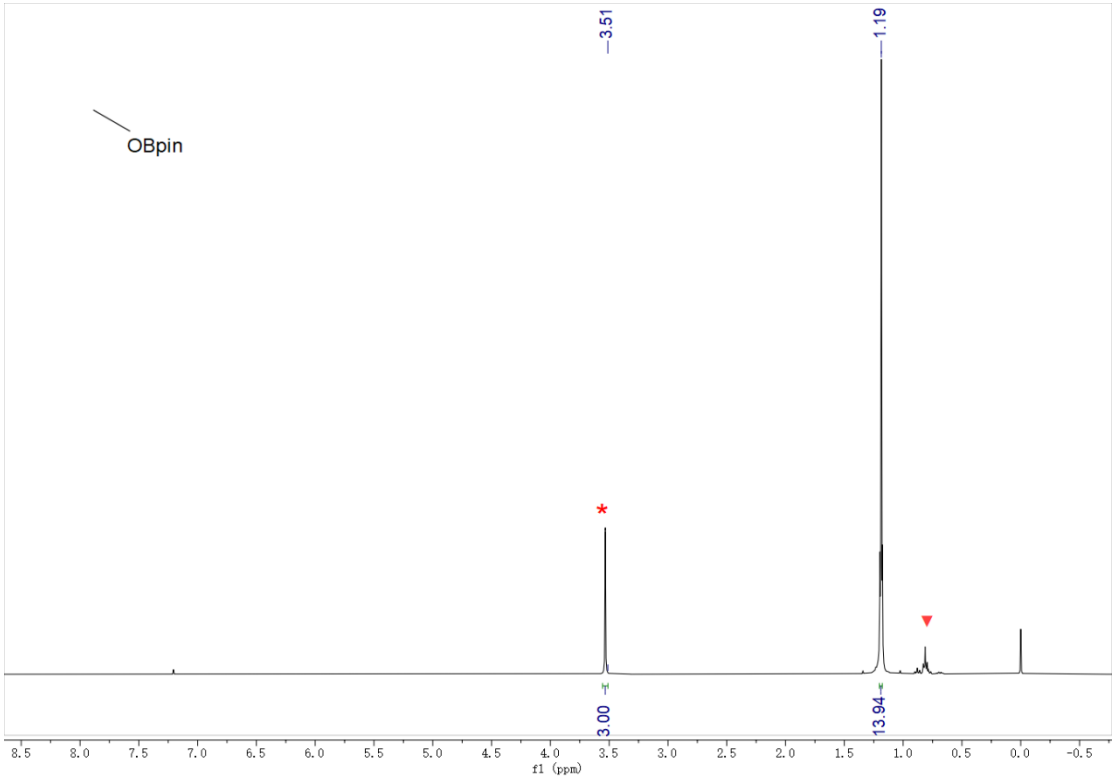


Figure S2.9.1 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **2i**

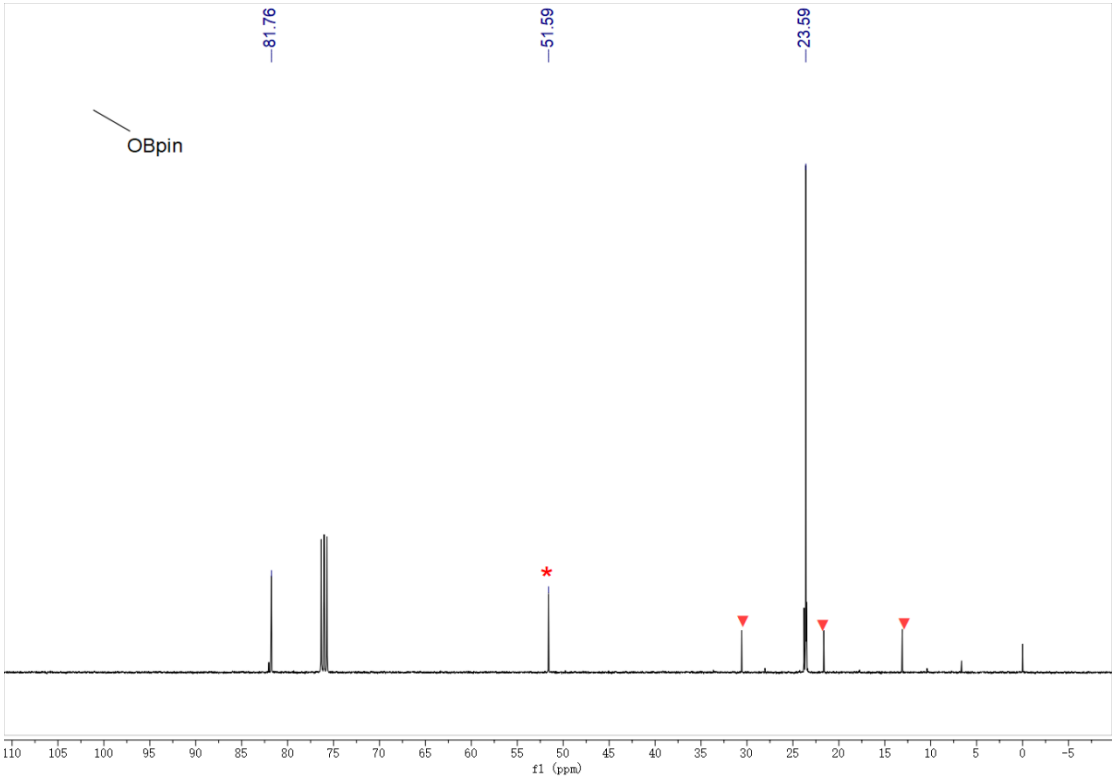


Figure S2.9.2 ^{13}C NMR (101 MHz, $CDCl_3$) of compound **2i**

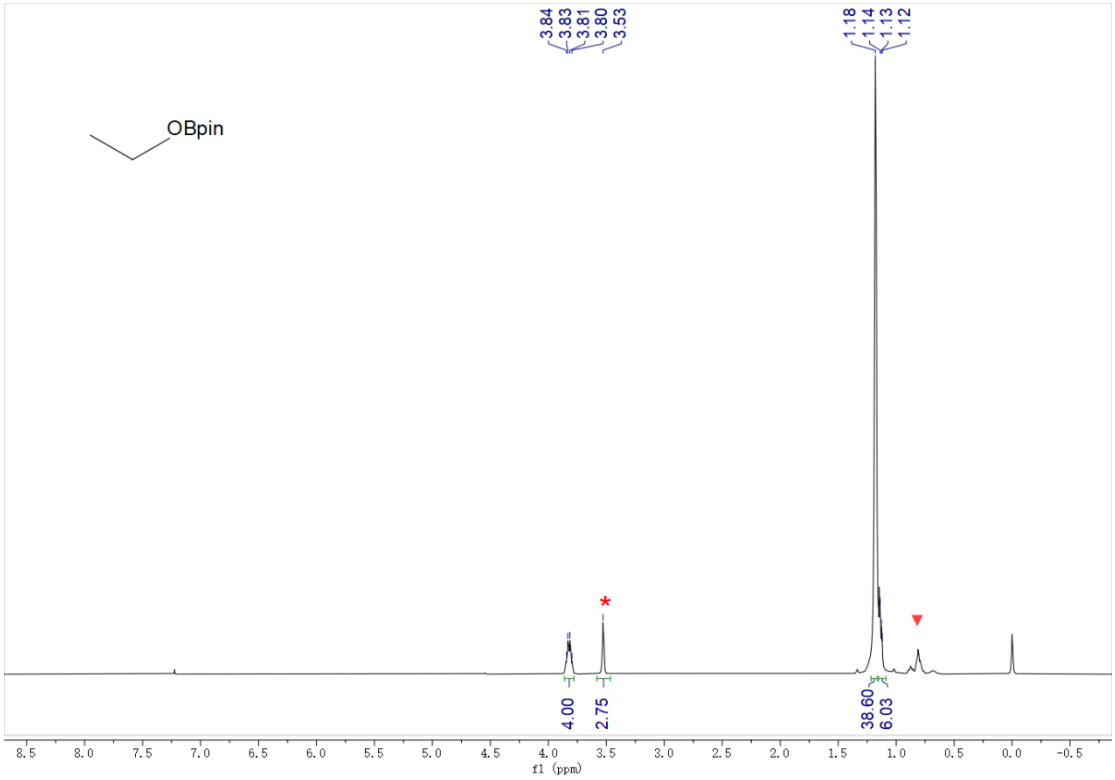


Figure S2.10.1 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **2j**

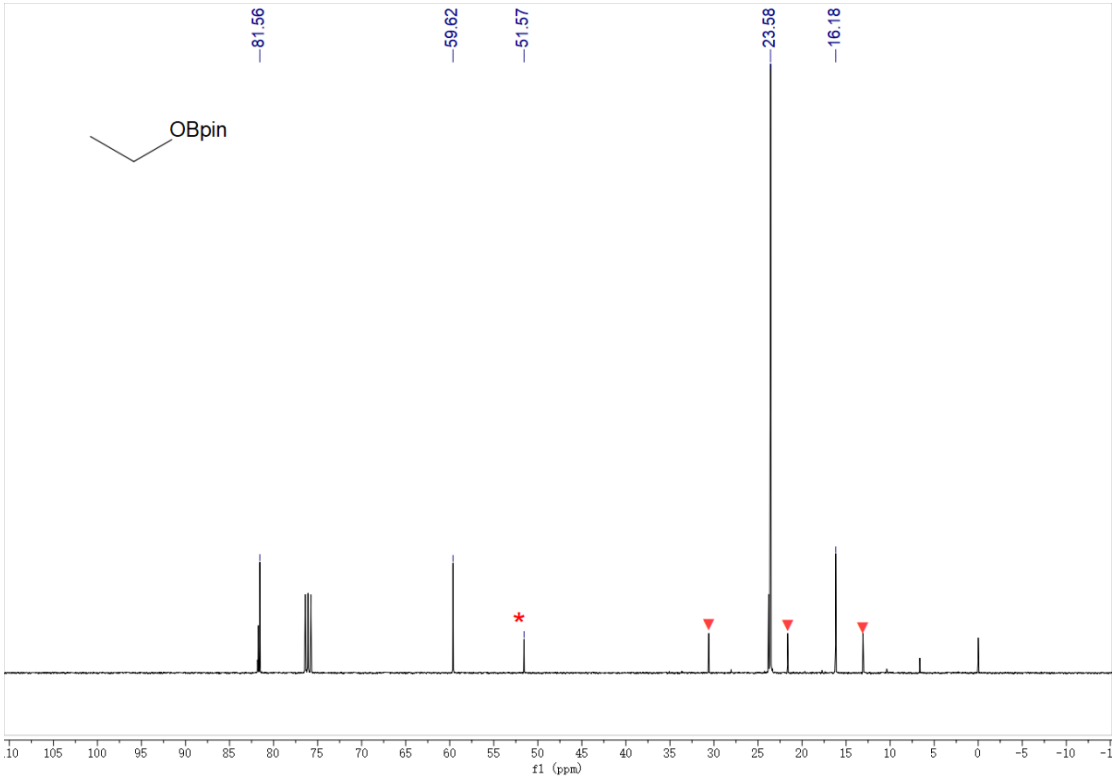


Figure S2.10.2 ^{13}C NMR (101 MHz, $CDCl_3$) of compound **2j**

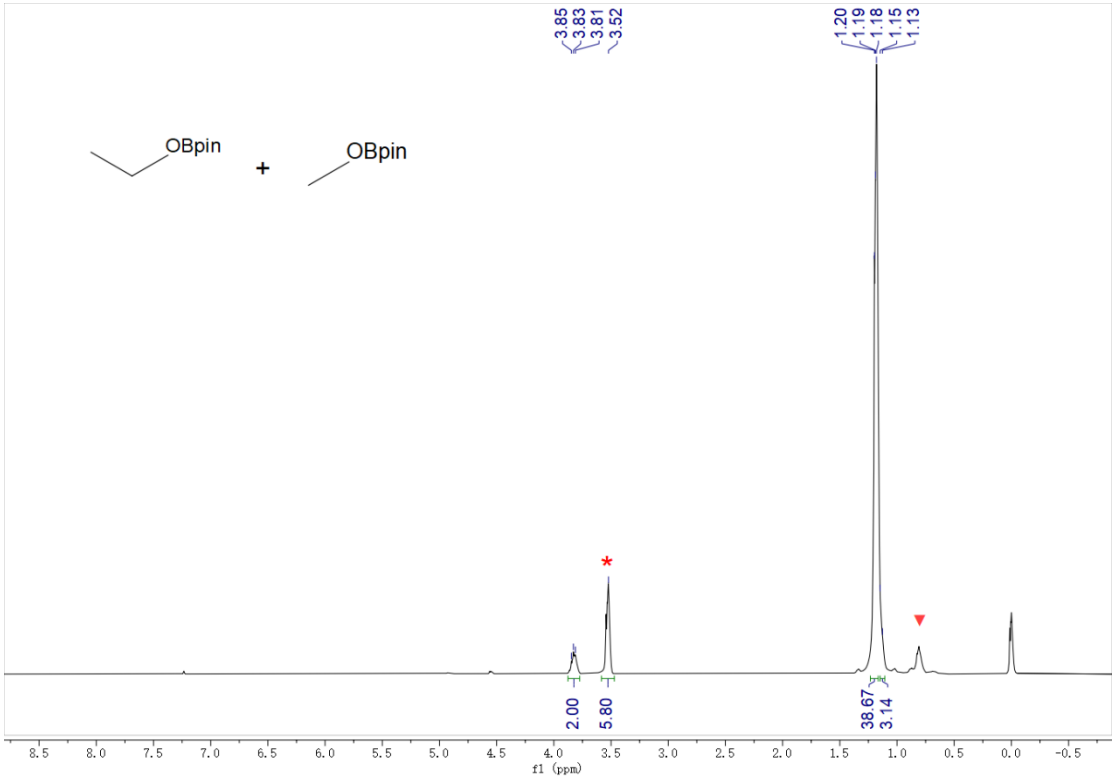


Figure S2.11.1 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **2k**

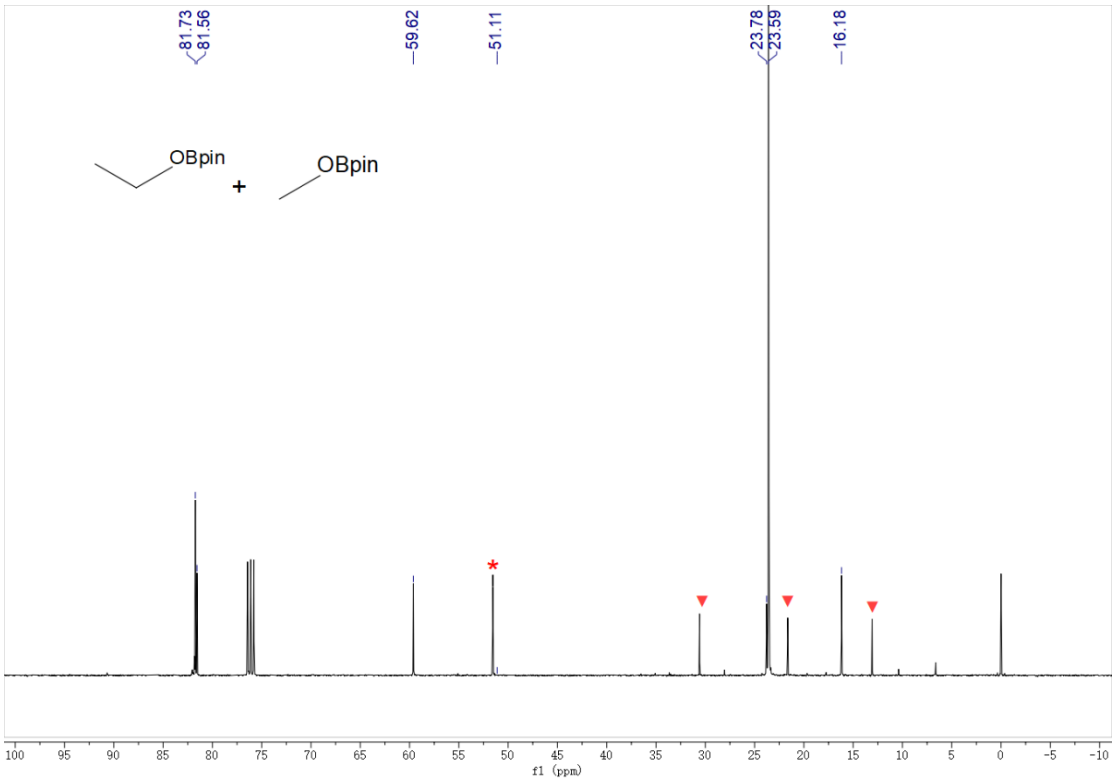


Figure S2.11.2 ^{13}C NMR (101 MHz, $CDCl_3$) of compound **2k**

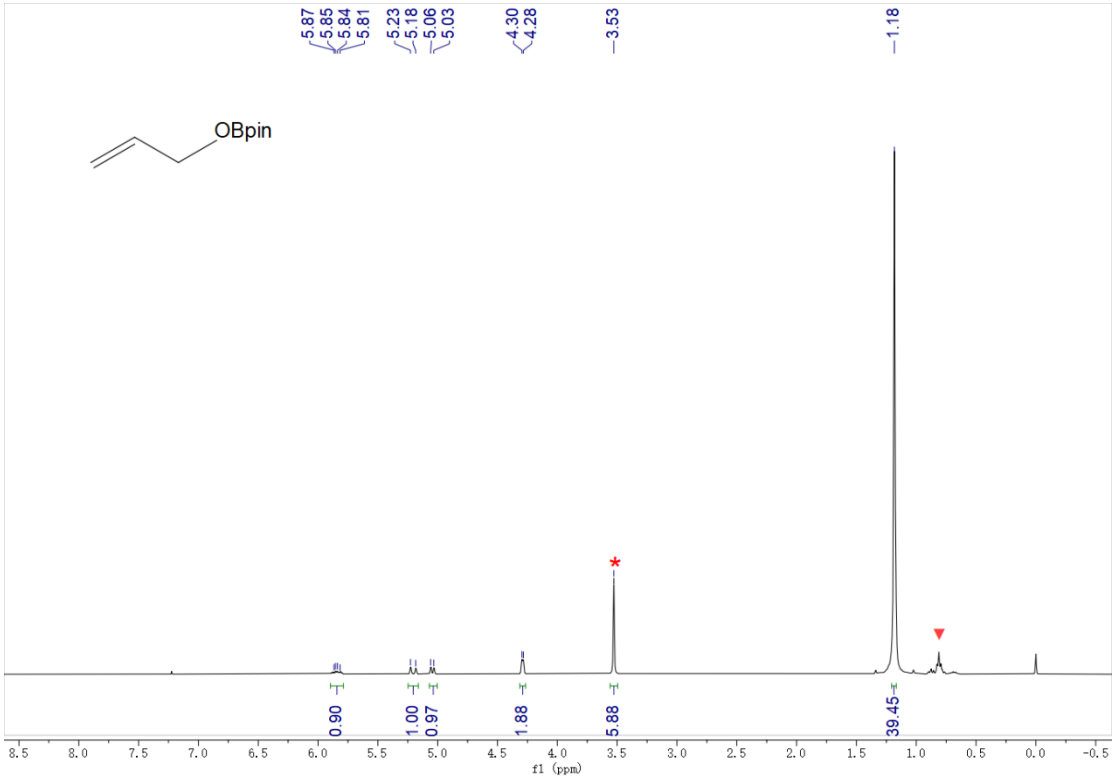


Figure S2.12.1 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **2l**

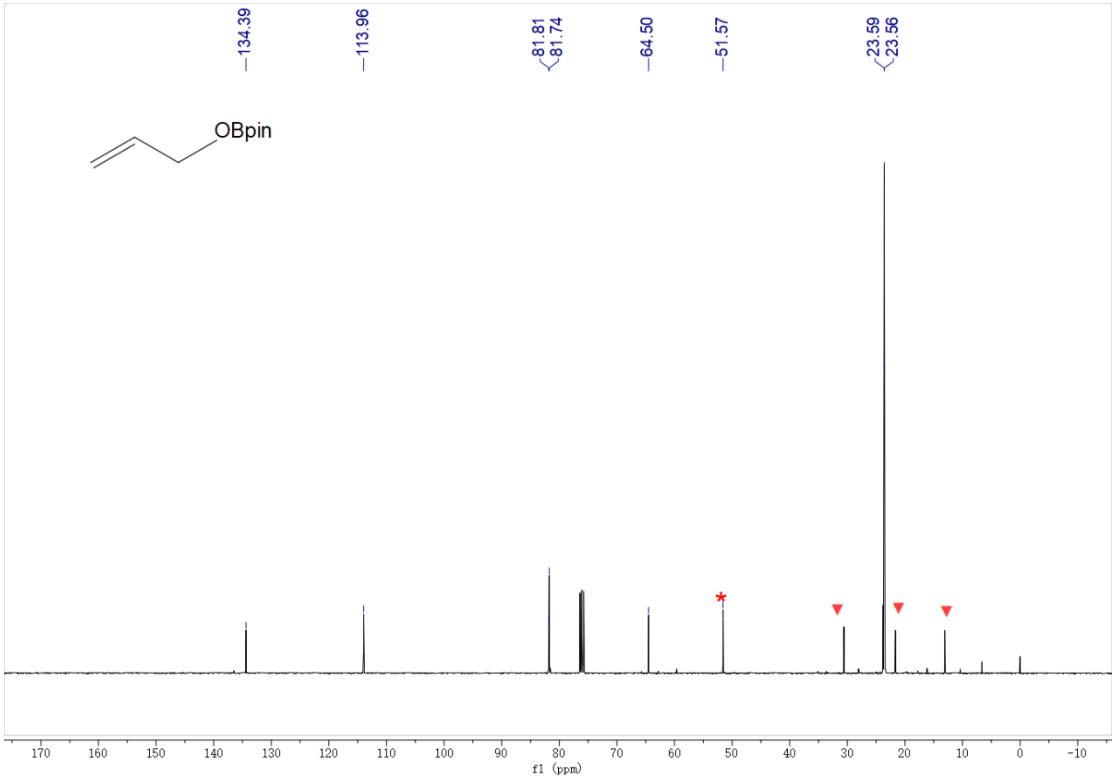


Figure S2.12.2 ^{13}C NMR (101 MHz, $CDCl_3$) of compound **2l**

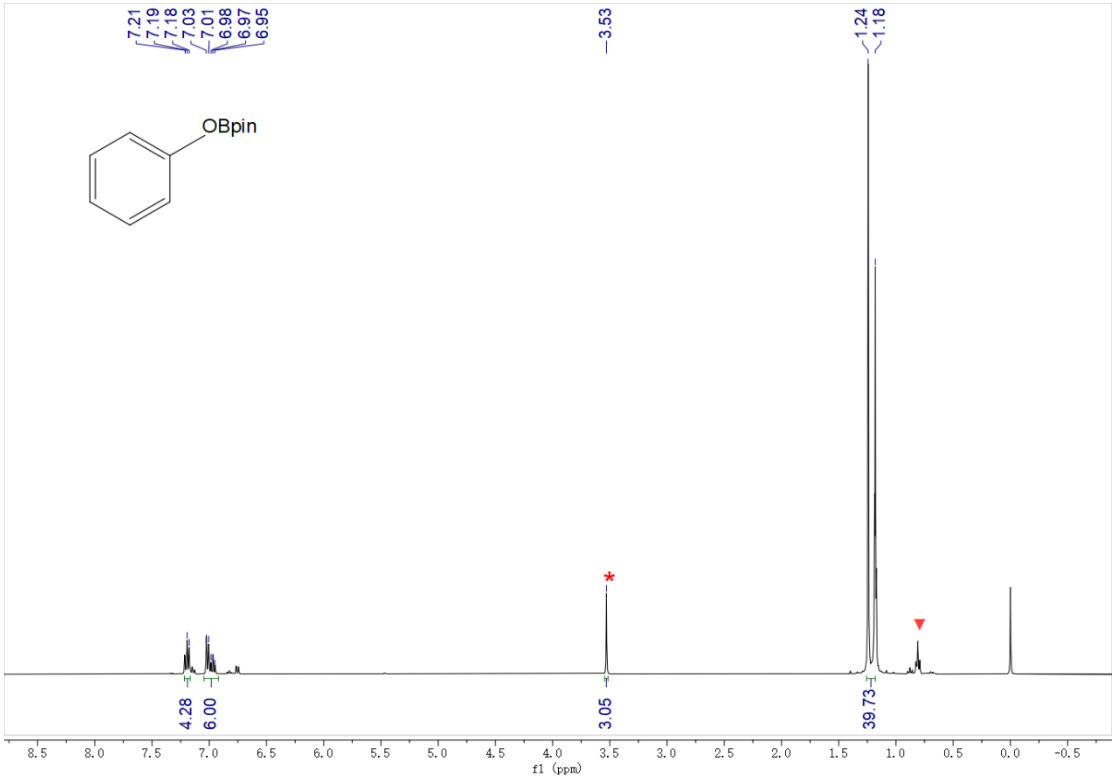


Figure S2.13.1 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **2m**

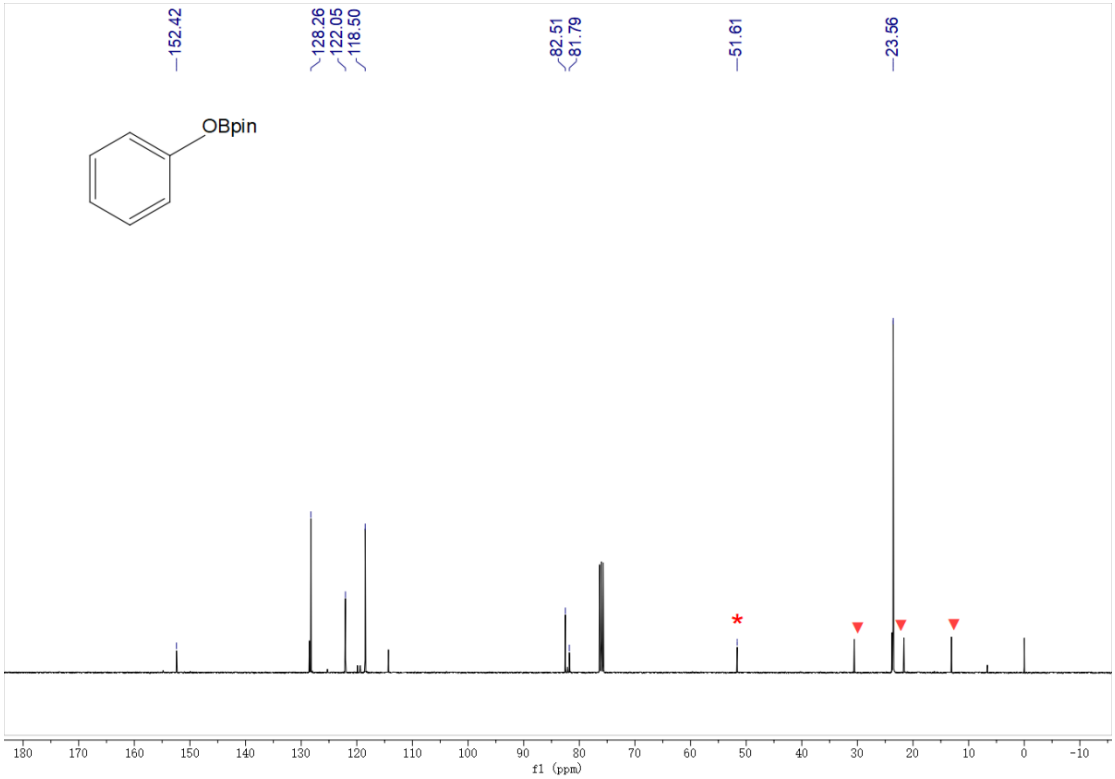


Figure S2.13.2 ^{13}C NMR (101 MHz, $CDCl_3$) of compound **2m**

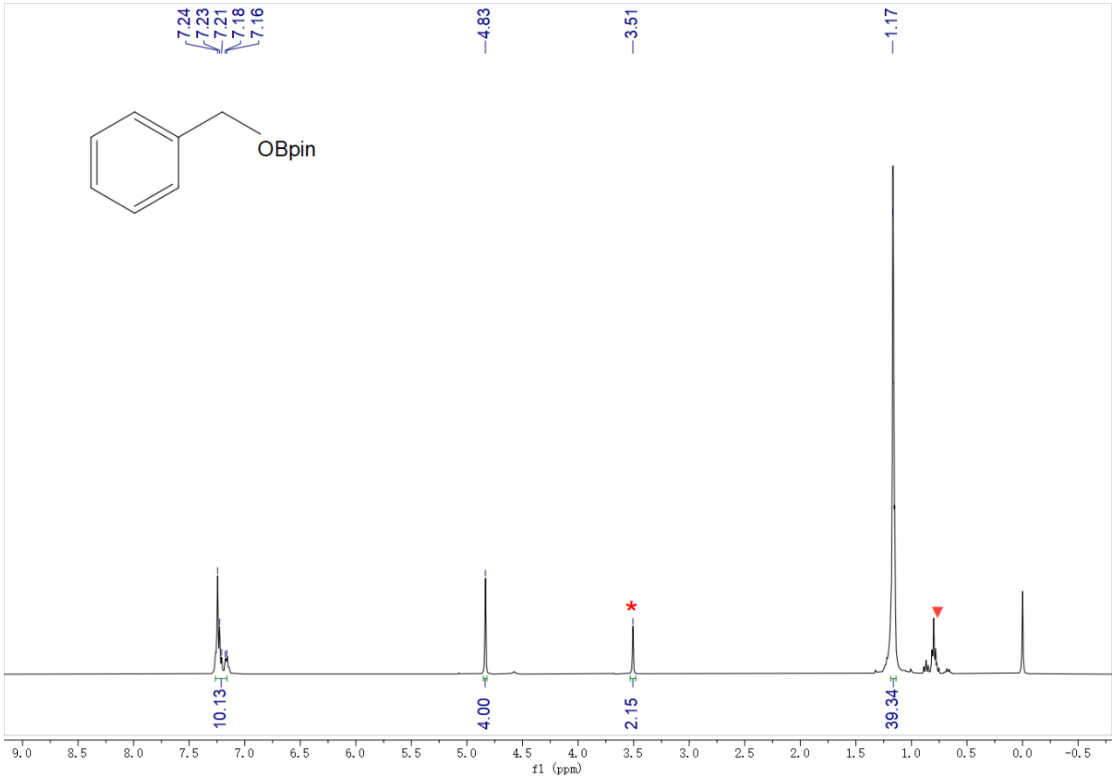


Figure S2.14.1 ^{1}H NMR (400 MHz, $CDCl_3$ of compound **2n**

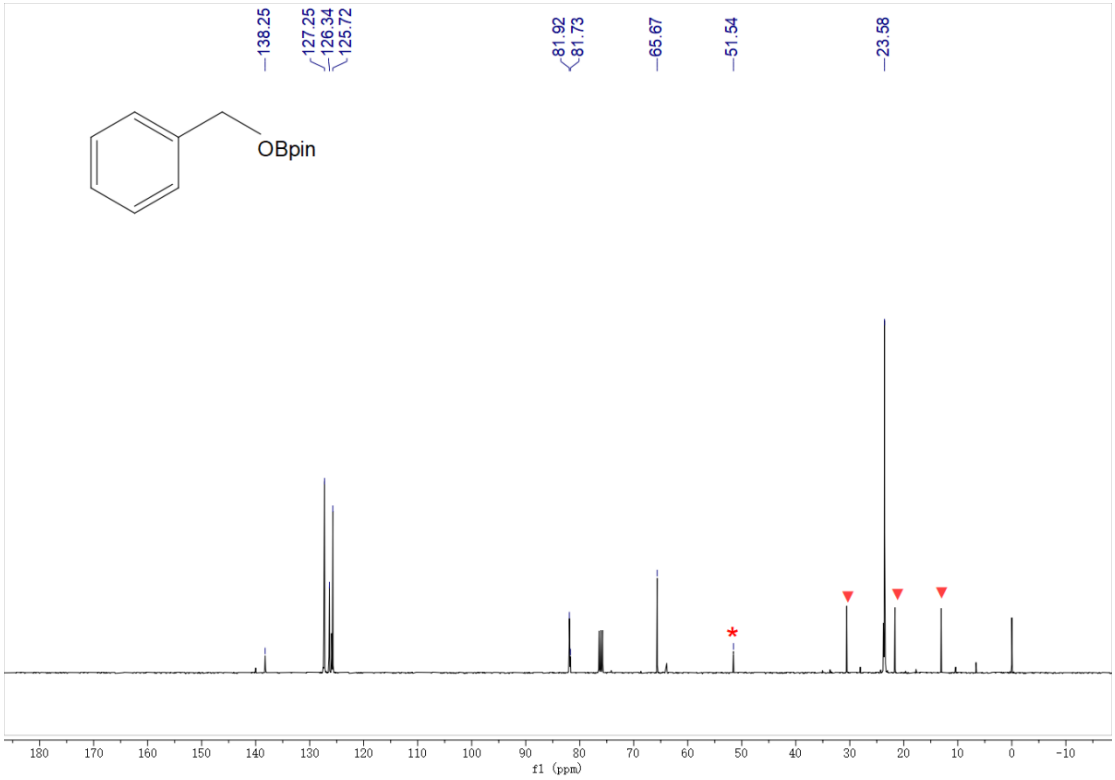


Figure S2.14.2 ^{13}C NMR (101 MHz, $CDCl_3$) of compound **2n**

^{1}H, ^{13}C NMR Spectra of Hydroboration Products of Esters.

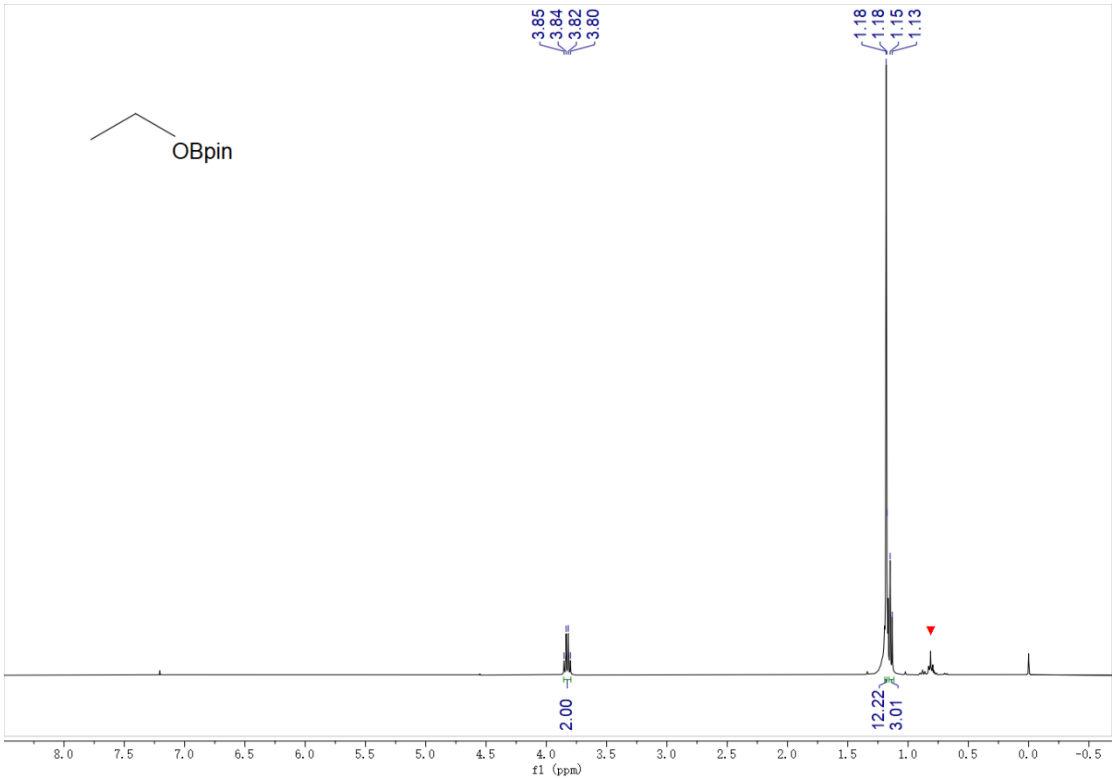


Figure S3.1.1 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **4a**

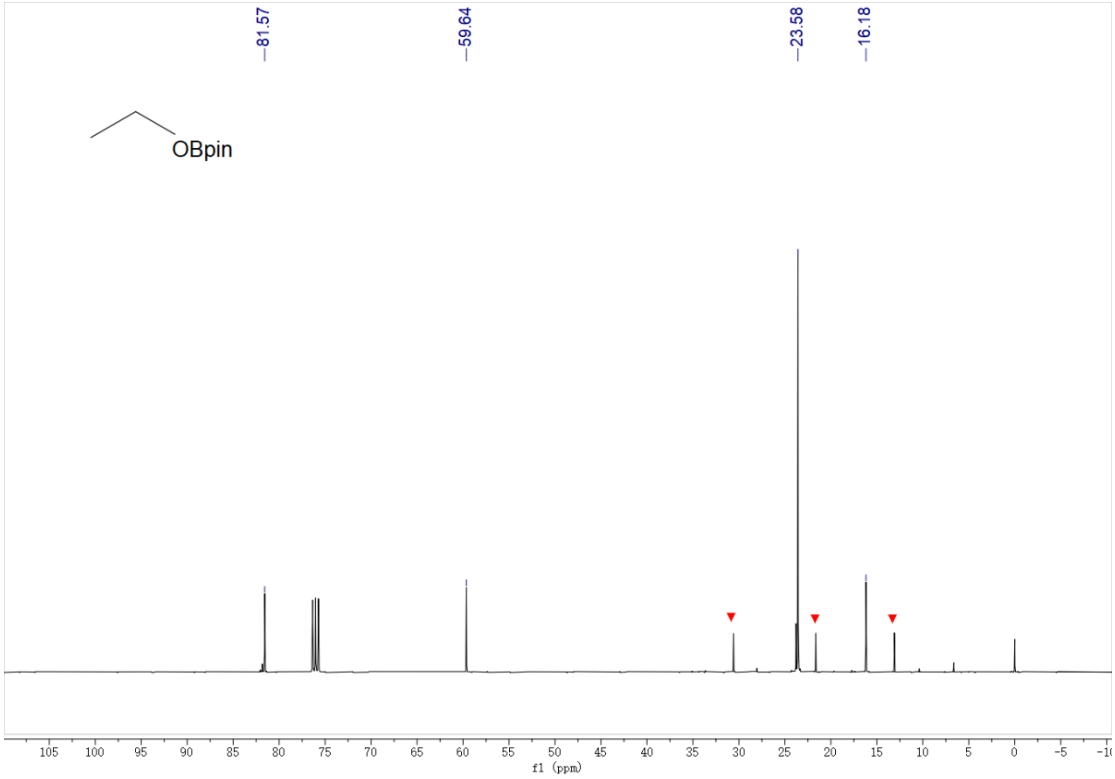


Figure S3.1.2 ^{13}C NMR (101 MHz, $CDCl_3$) of compound **4a**

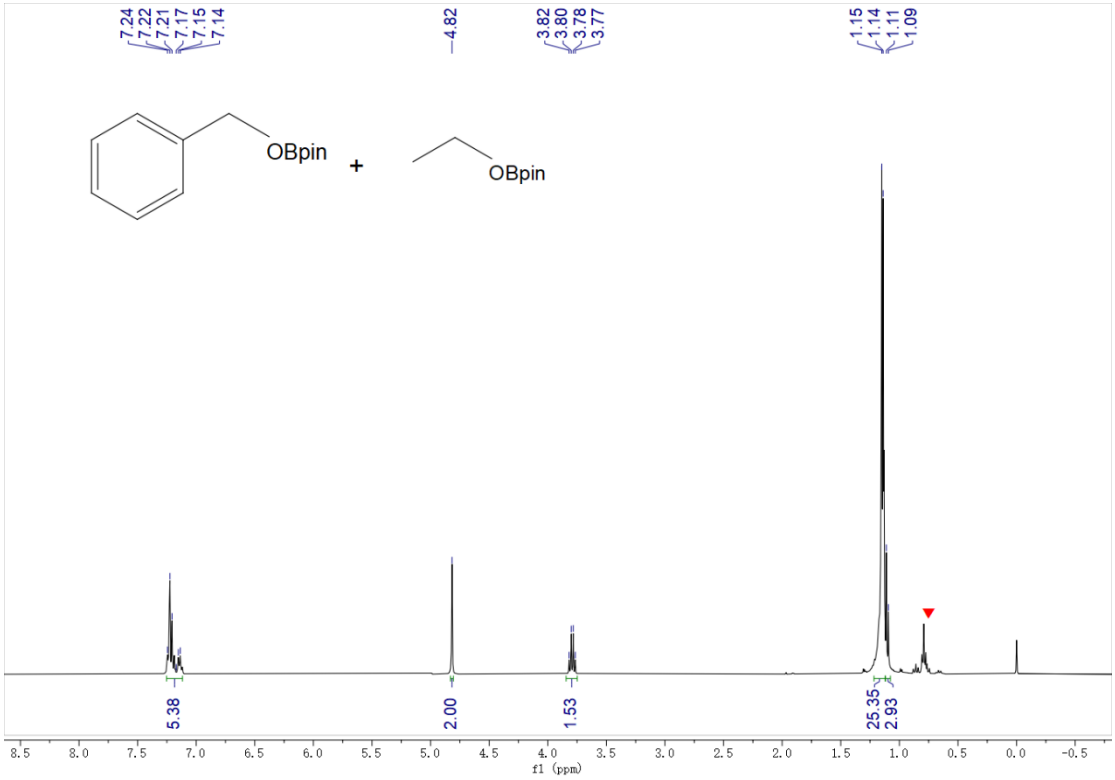


Figure S3.2.1 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **4b**

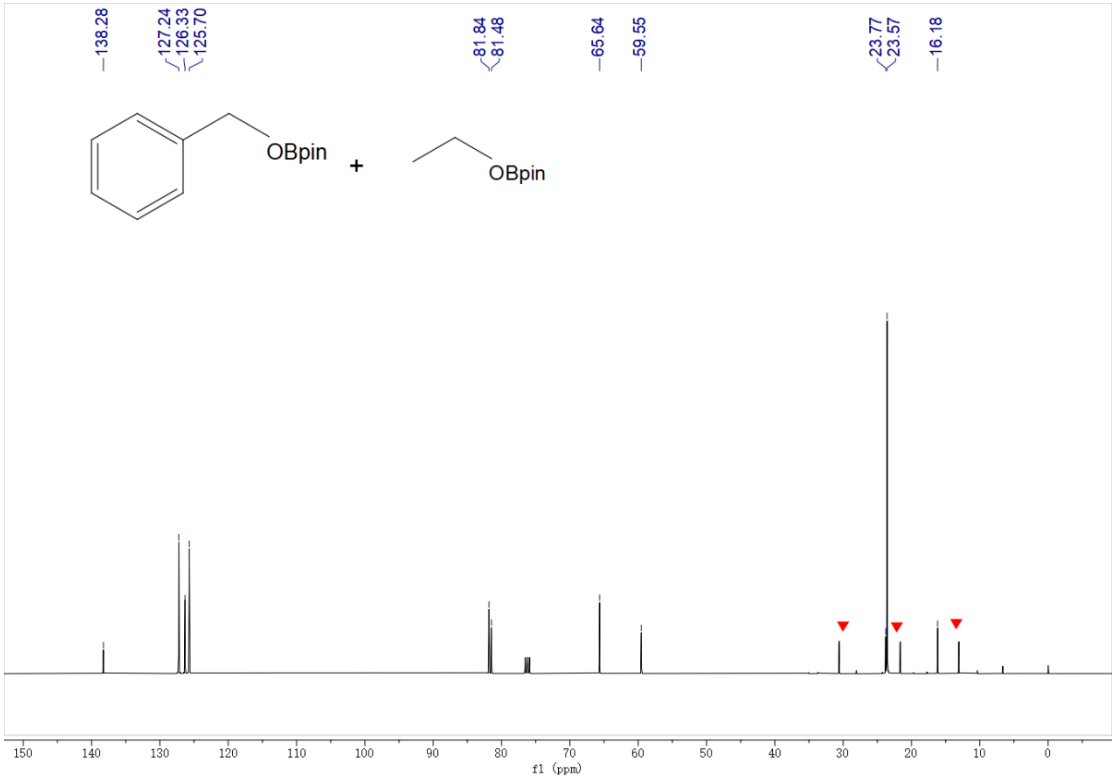


Figure S3.2.2 ^{13}C NMR (101 MHz, $CDCl_3$) of compound **4b**

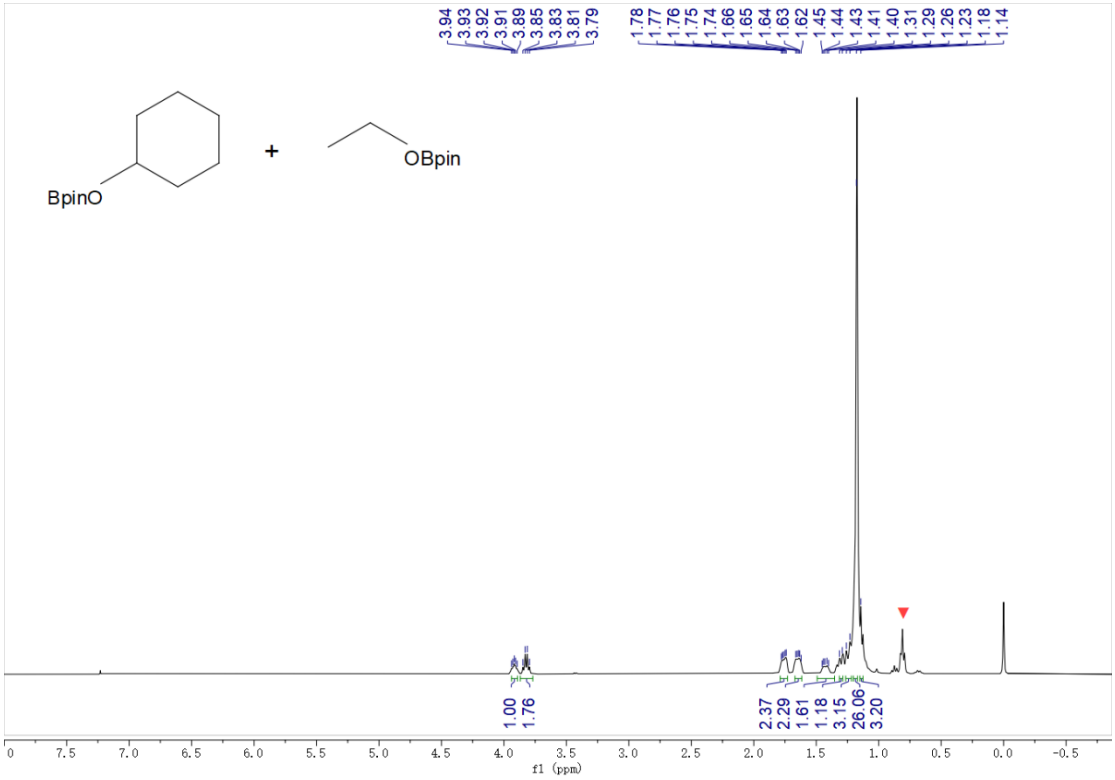


Figure S3.3.1 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **4c**

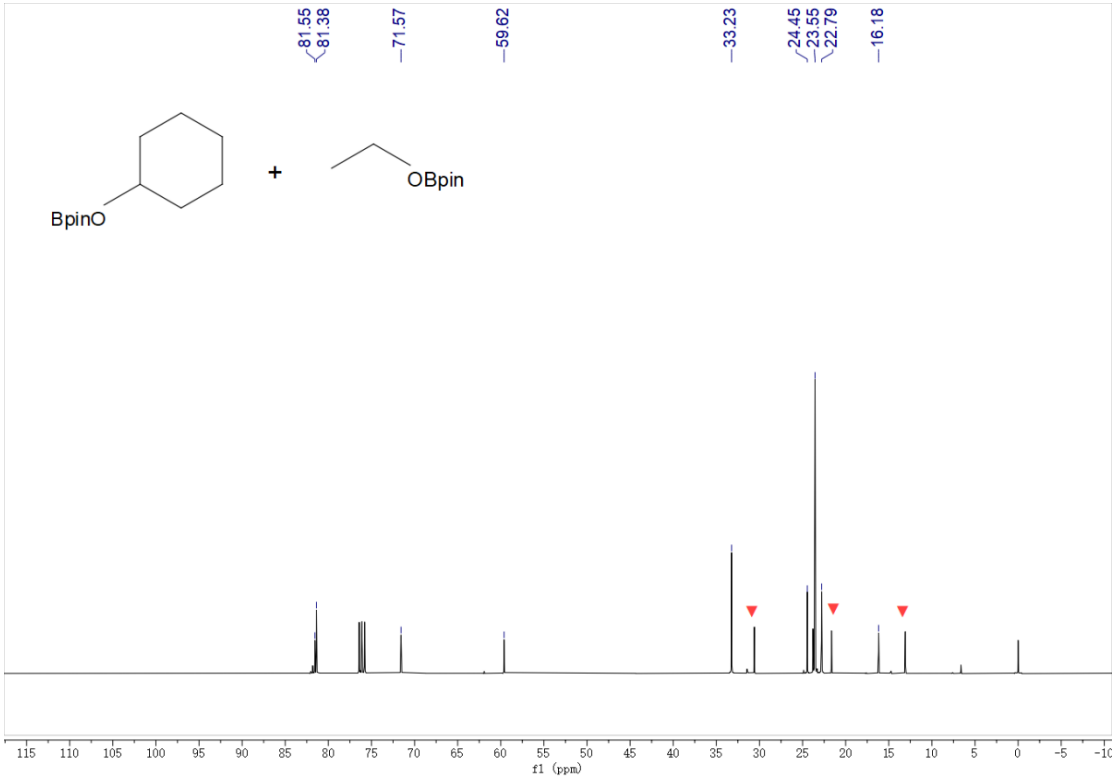


Figure S3.3.2 ^{13}C NMR (101 MHz, $CDCl_3$) of compound **4c**

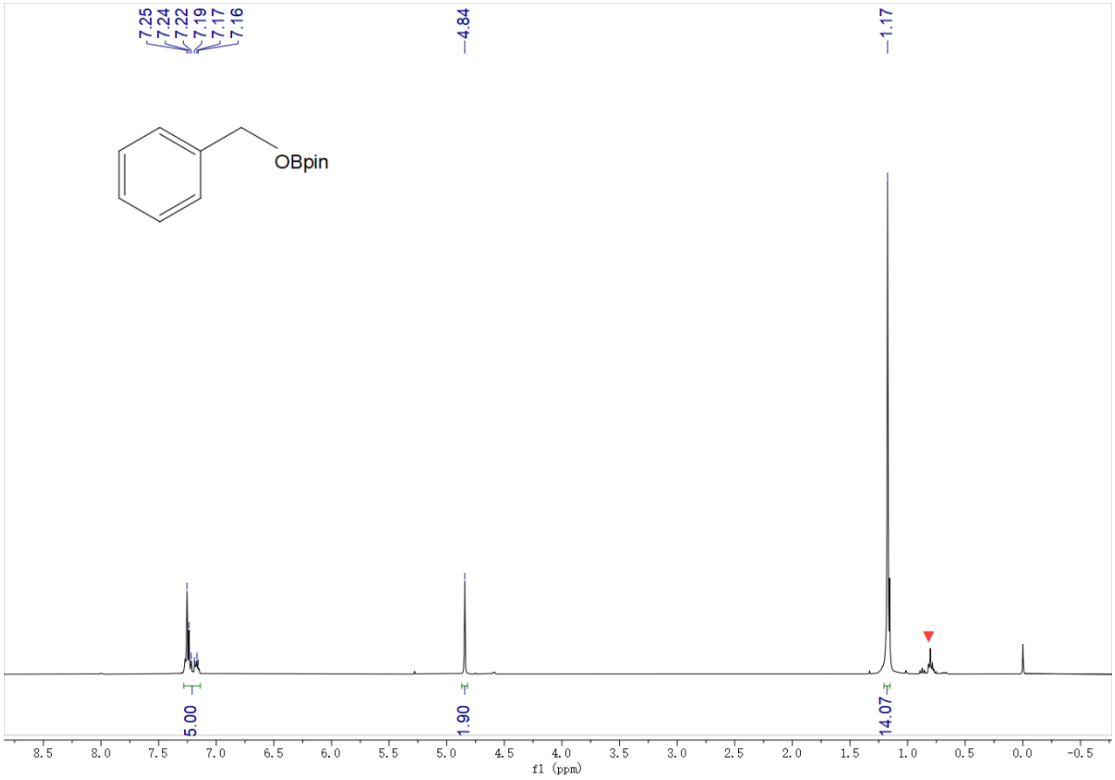


Figure S3.4.1 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **4d**

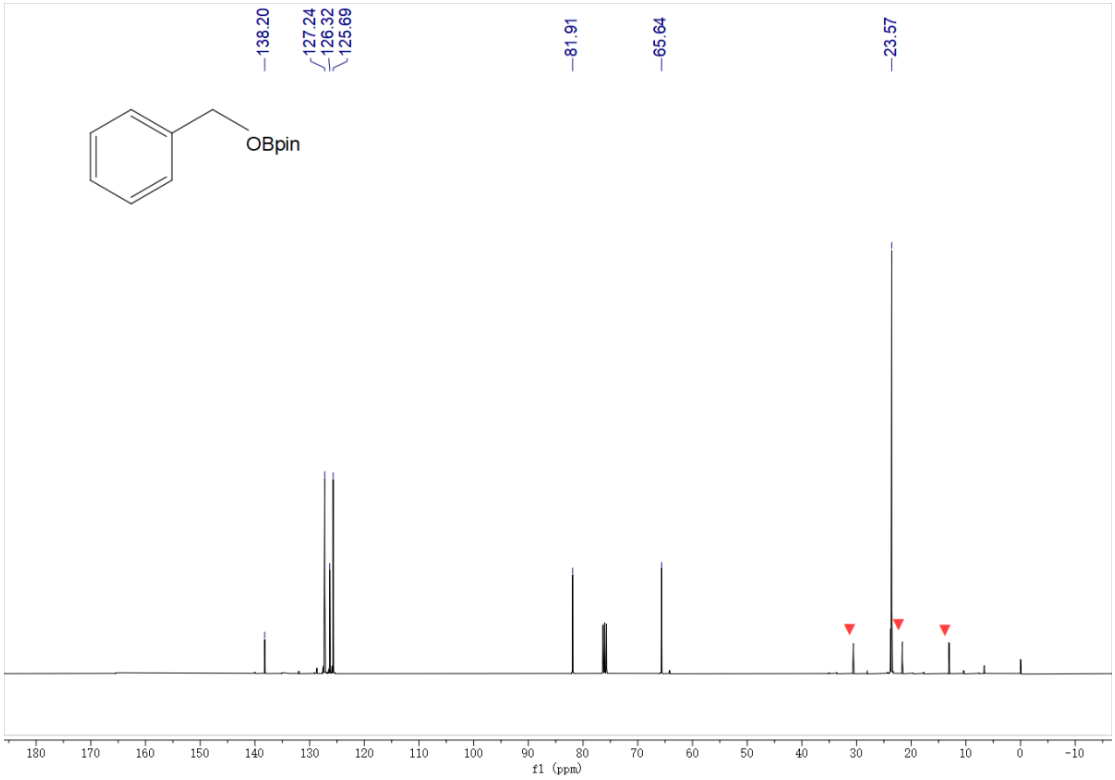


Figure S3.4.2 ^{13}C NMR (101 MHz, $CDCl_3$) of compound **4d**

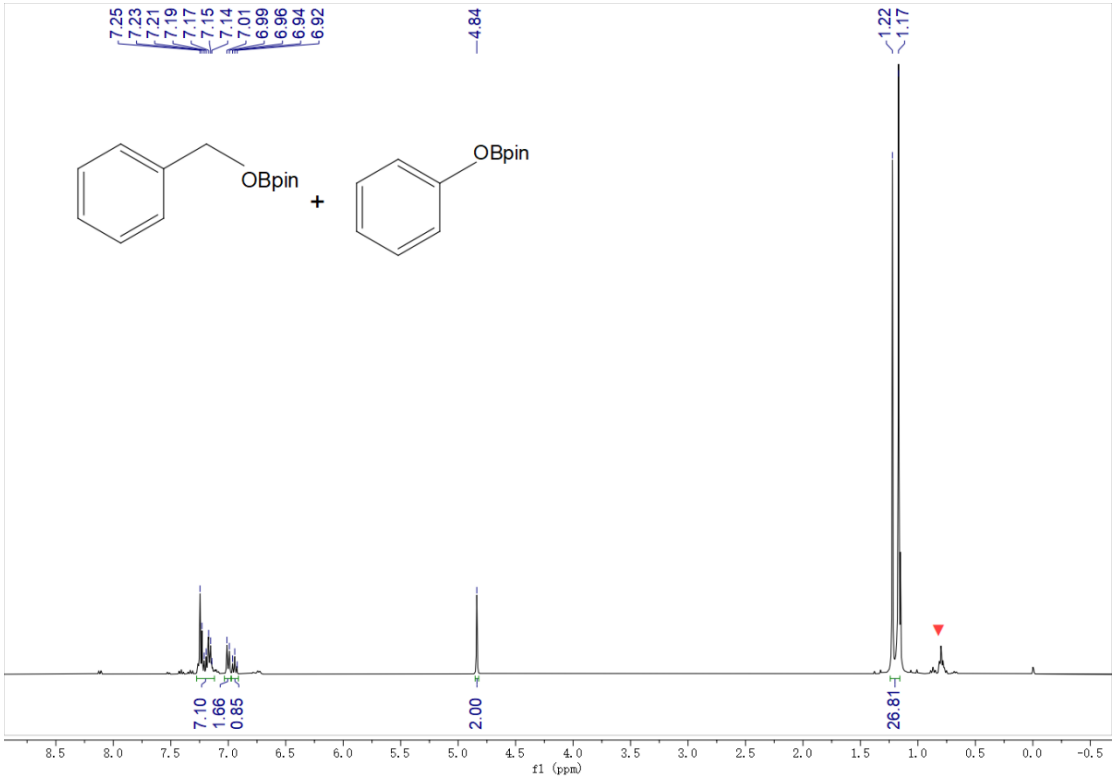


Figure S3.5.1 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **4e**

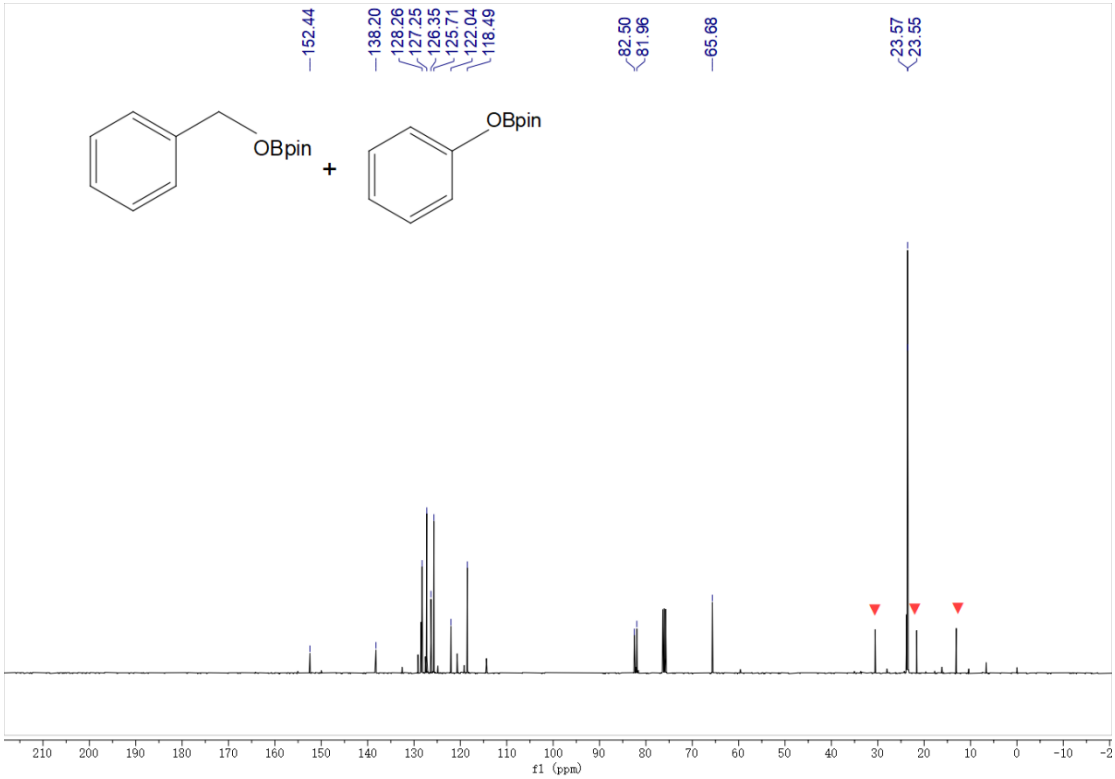


Figure S3.5.2 ^{13}C NMR (101 MHz, $CDCl_3$) of compound **4e**

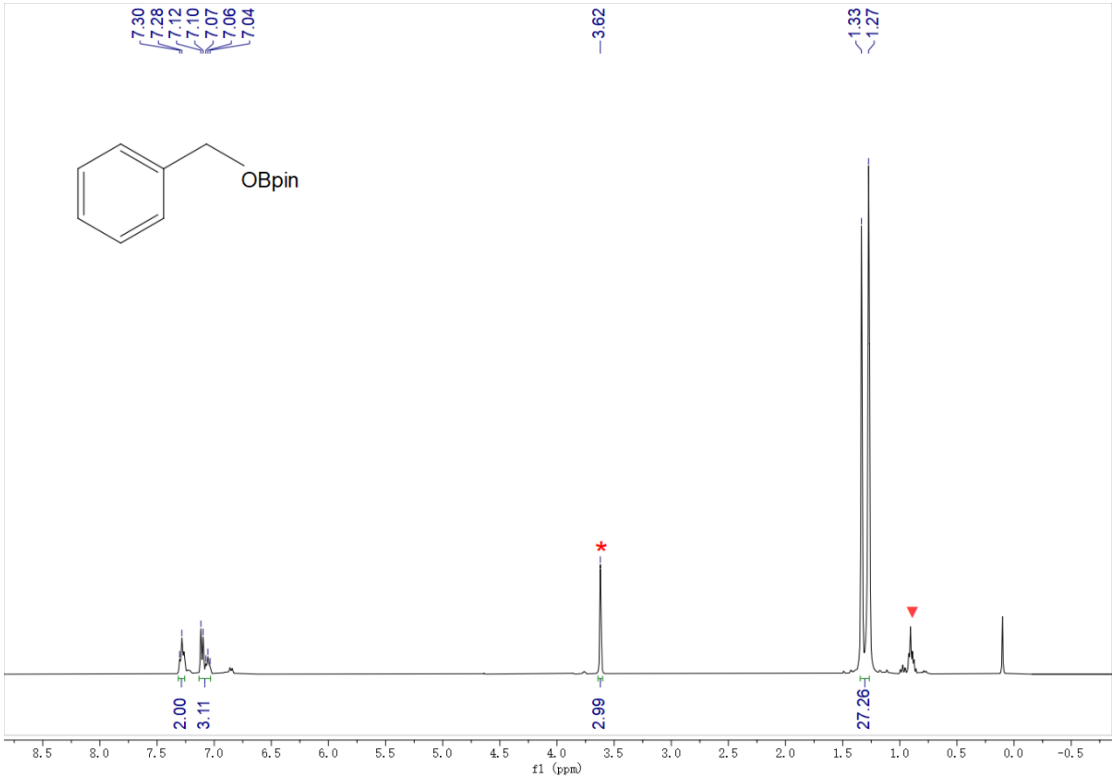


Figure S3.6.1 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **4f**

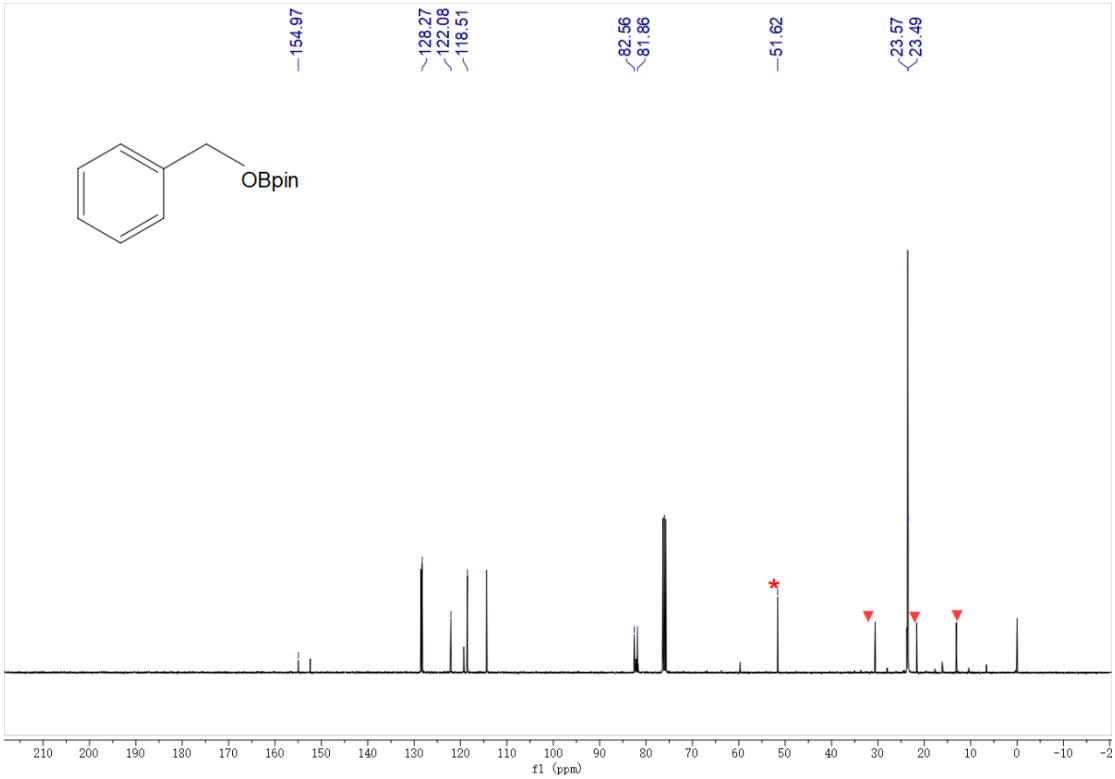


Figure S3.6.2 ^{13}C NMR (101 MHz, $CDCl_3$) of compound **4f**

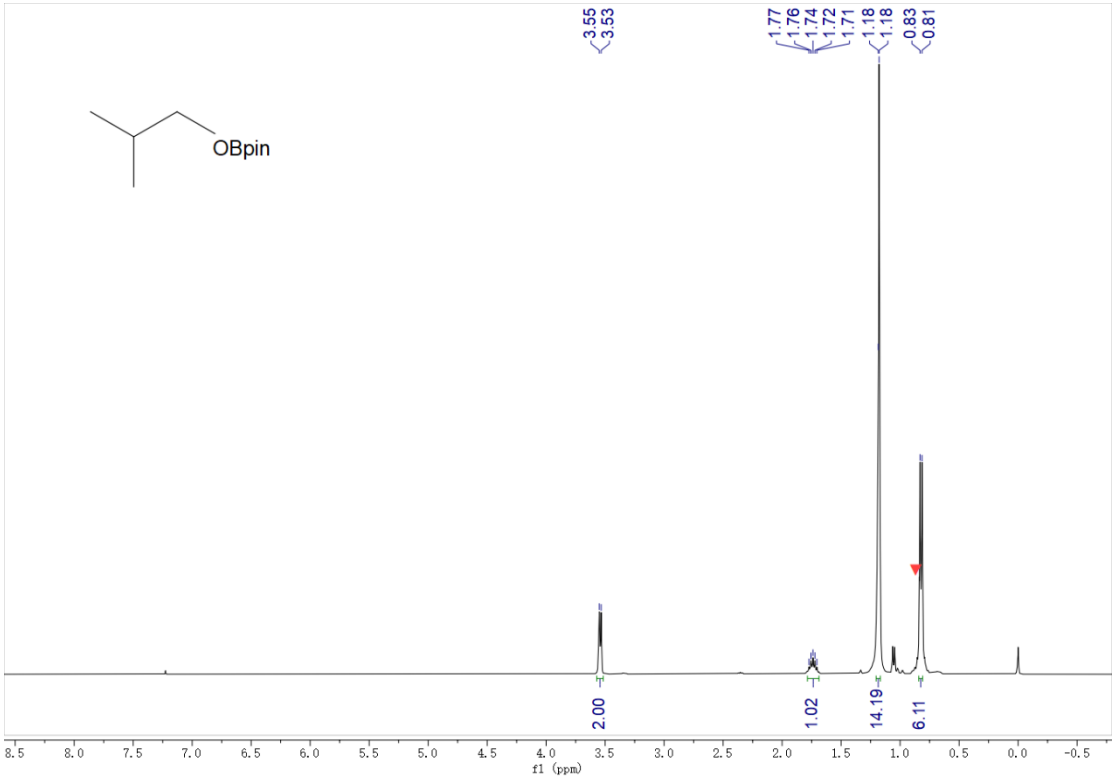


Figure S3.7.1 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **4g**

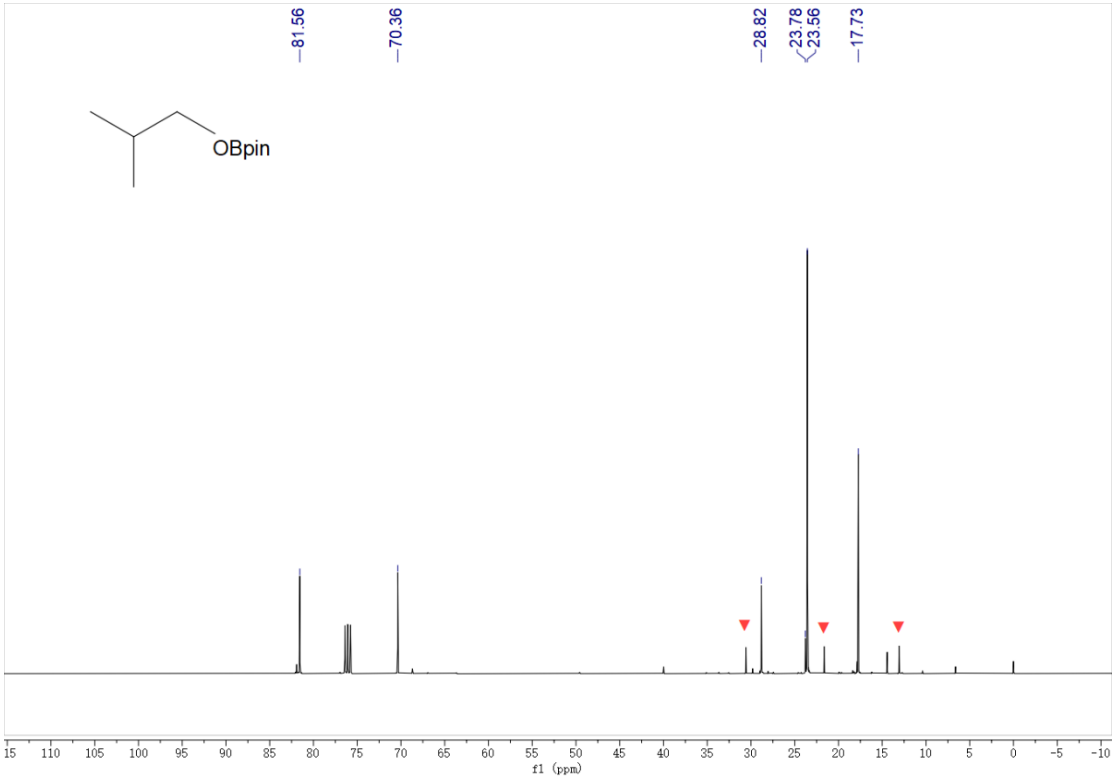


Figure S3.7.2 ^{13}C NMR (101 MHz, $CDCl_3$) of compound **4g**

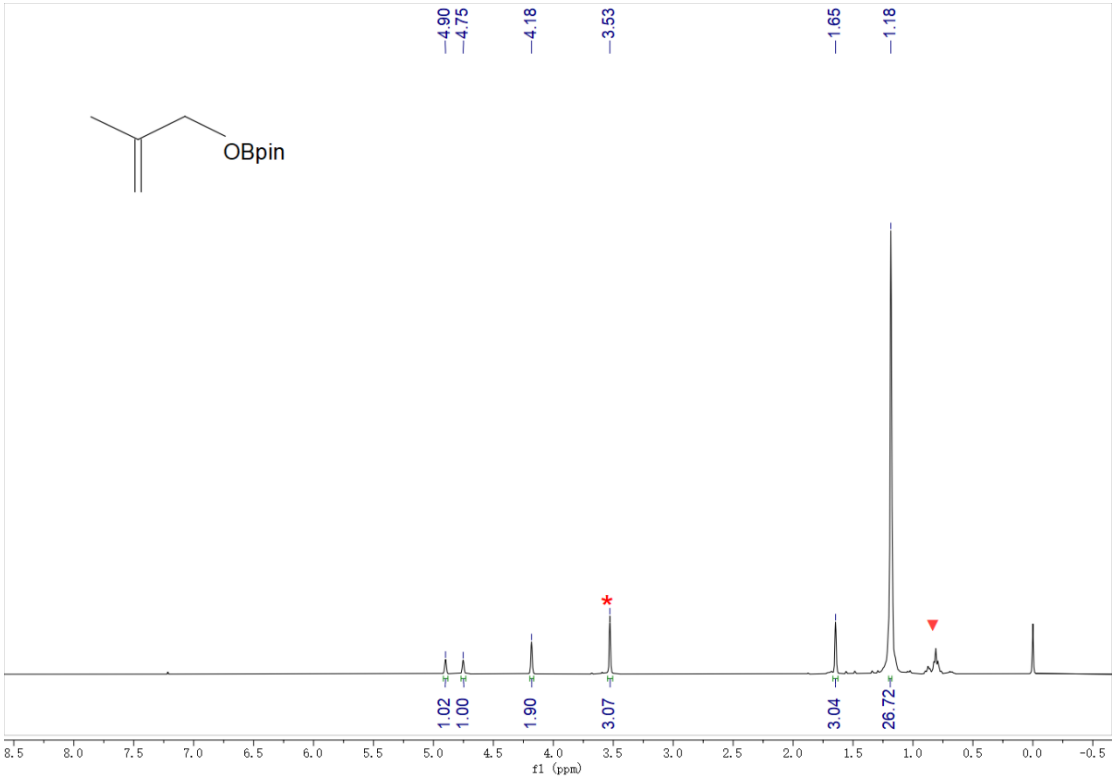


Figure S3.8.1 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **4h**

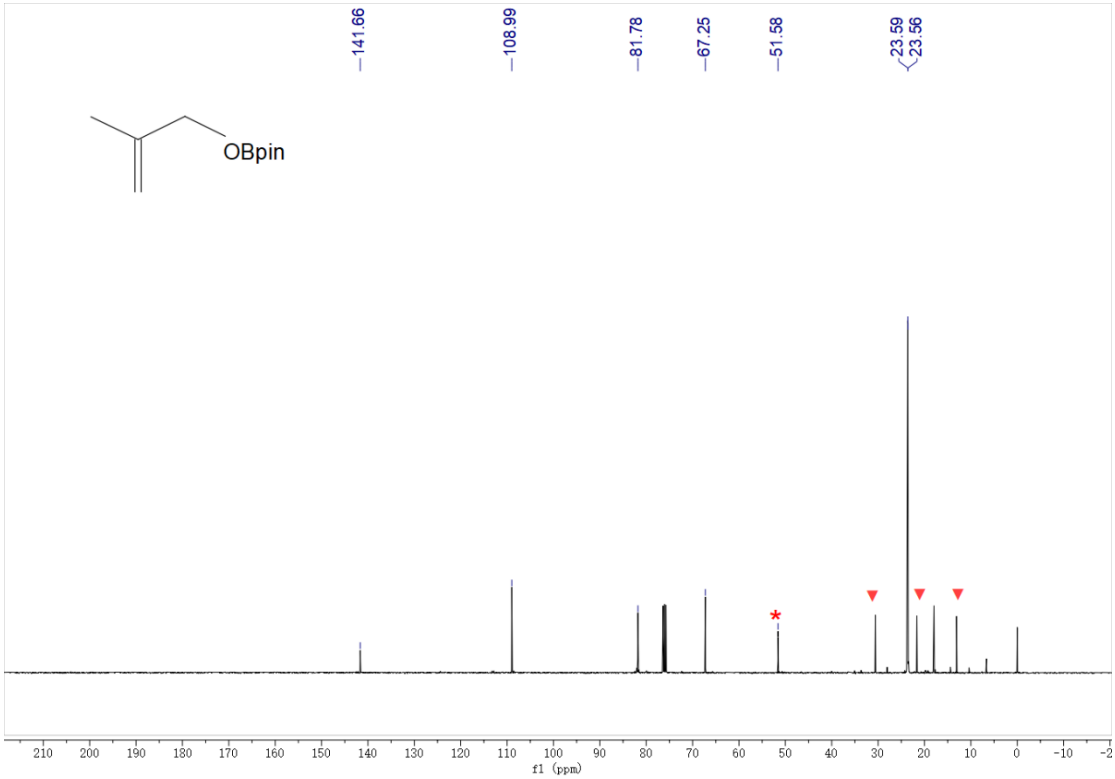


Figure S3.8.2 ^{13}C NMR (101 MHz, $CDCl_3$) of compound **4h**

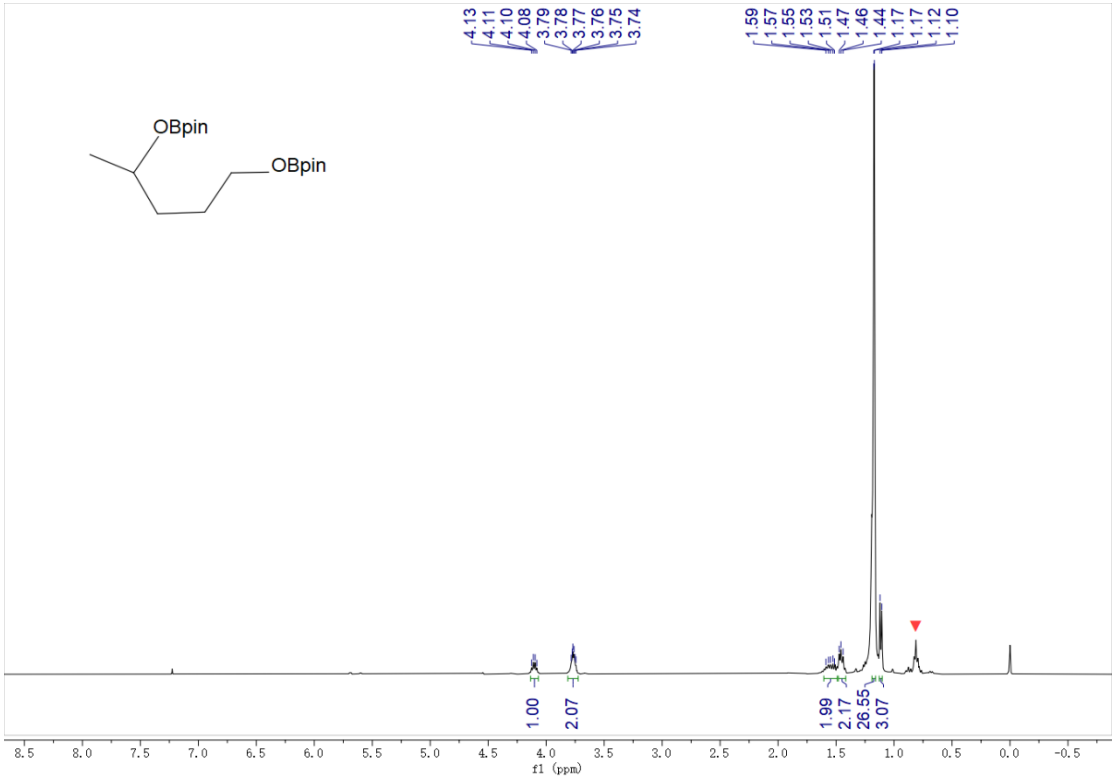


Figure S3.9.1 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **4i**

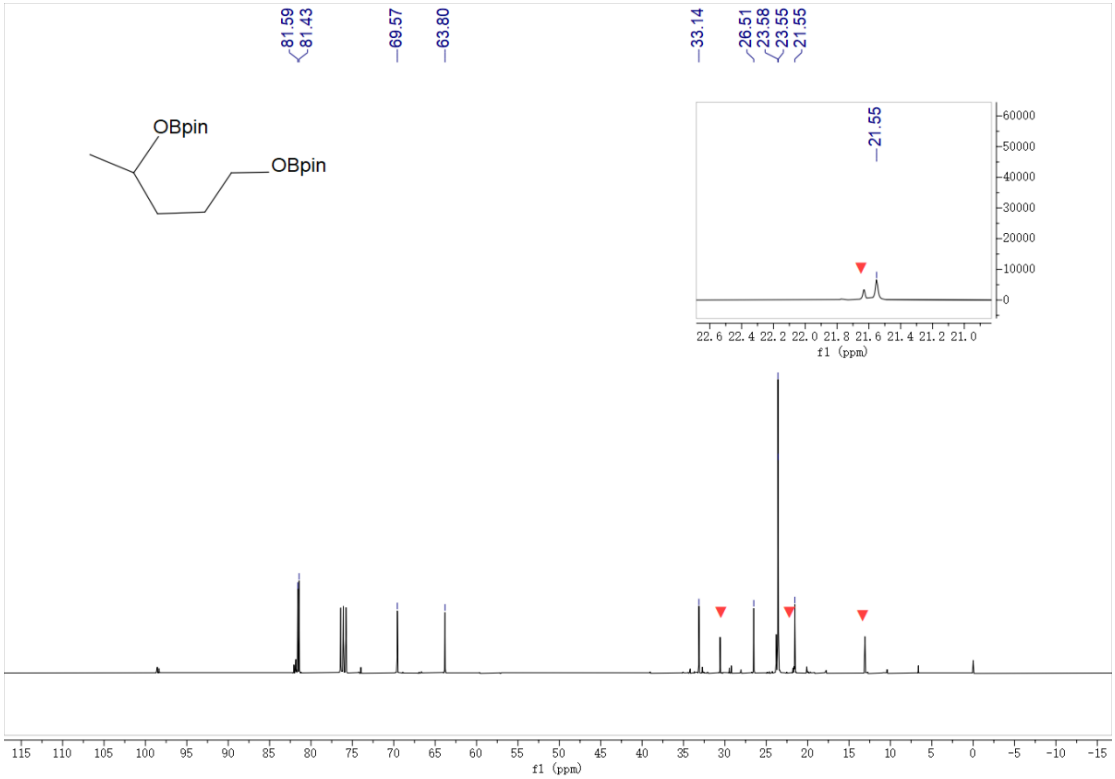


Figure S3.9.2 ^{13}C NMR (101 MHz, $CDCl_3$) of compound **4i**

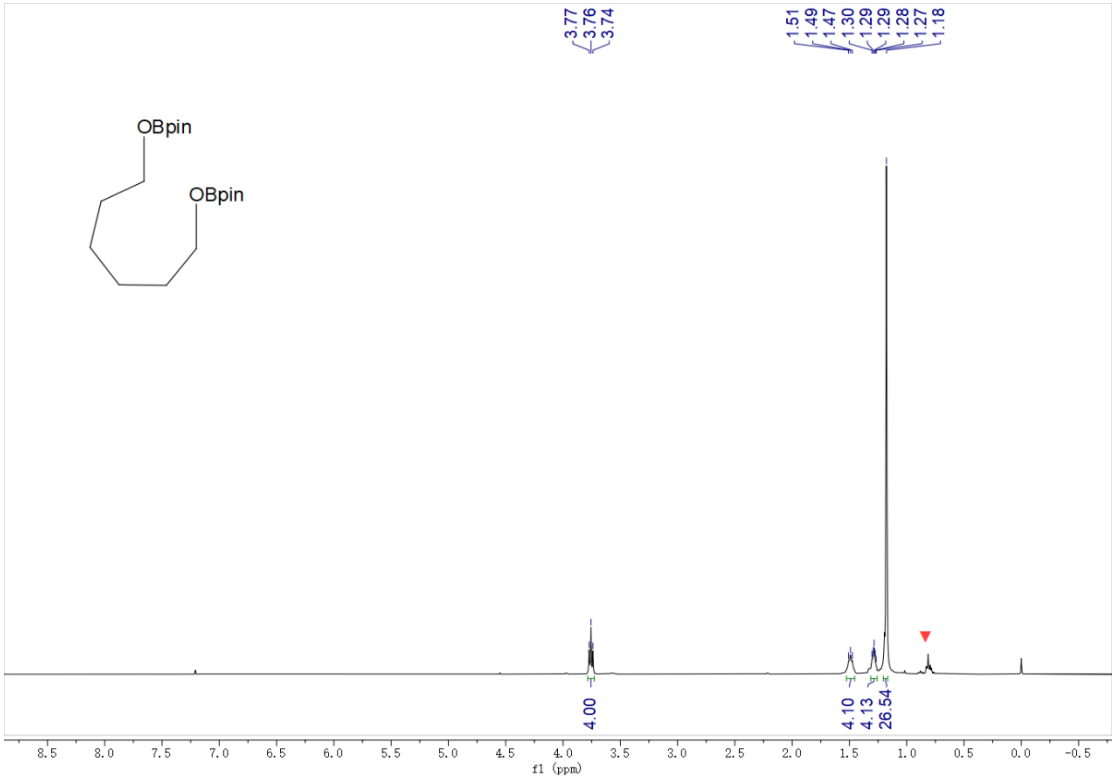


Figure S3.10.1 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **4j**

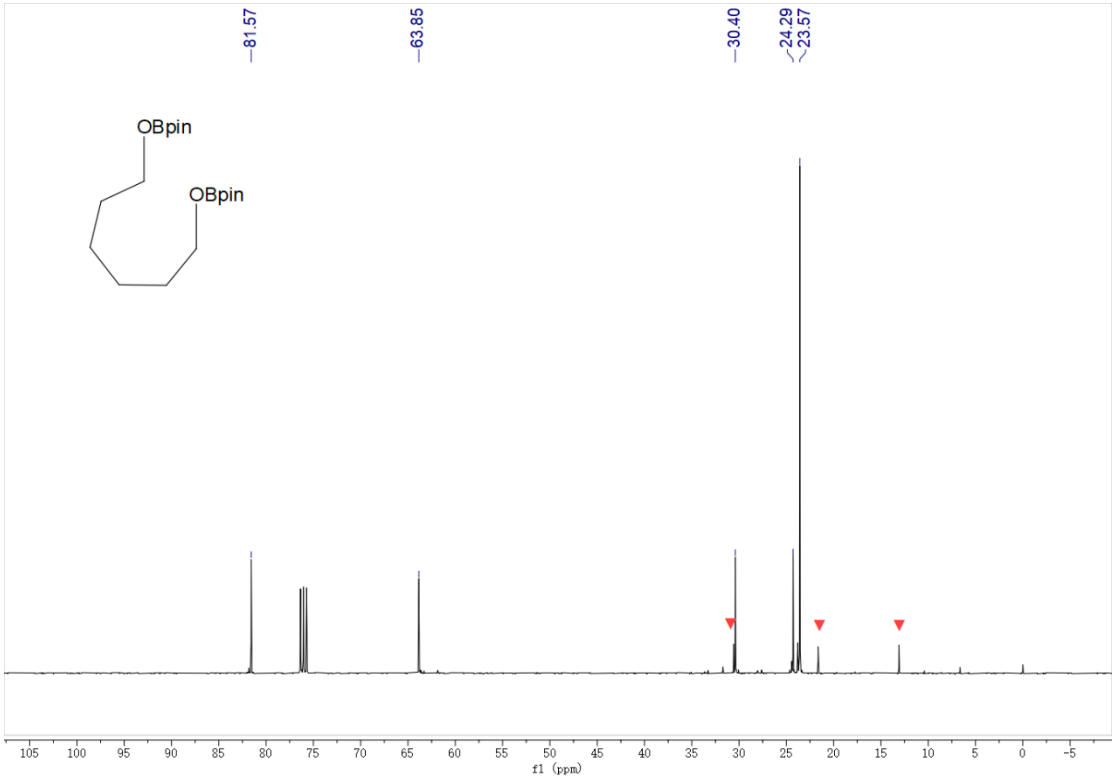


Figure S3.10.2 ^{13}C NMR (101 MHz, $CDCl_3$) of compound **4j**

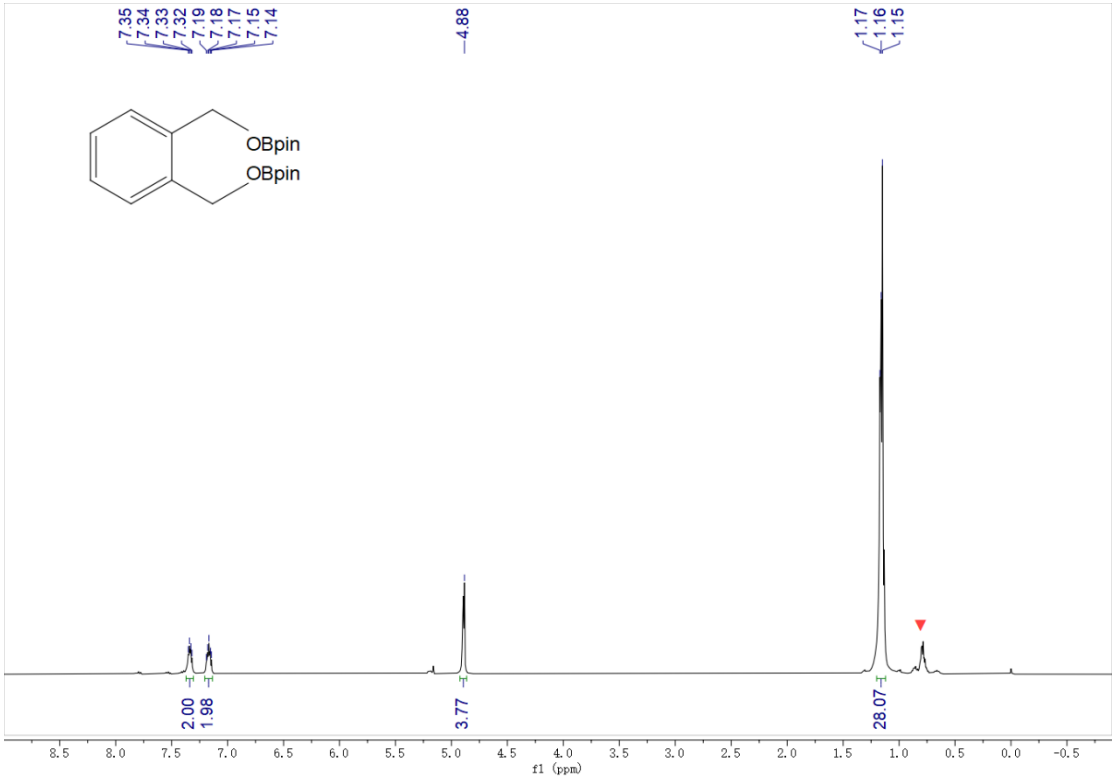


Figure S3.11.1 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **4k**

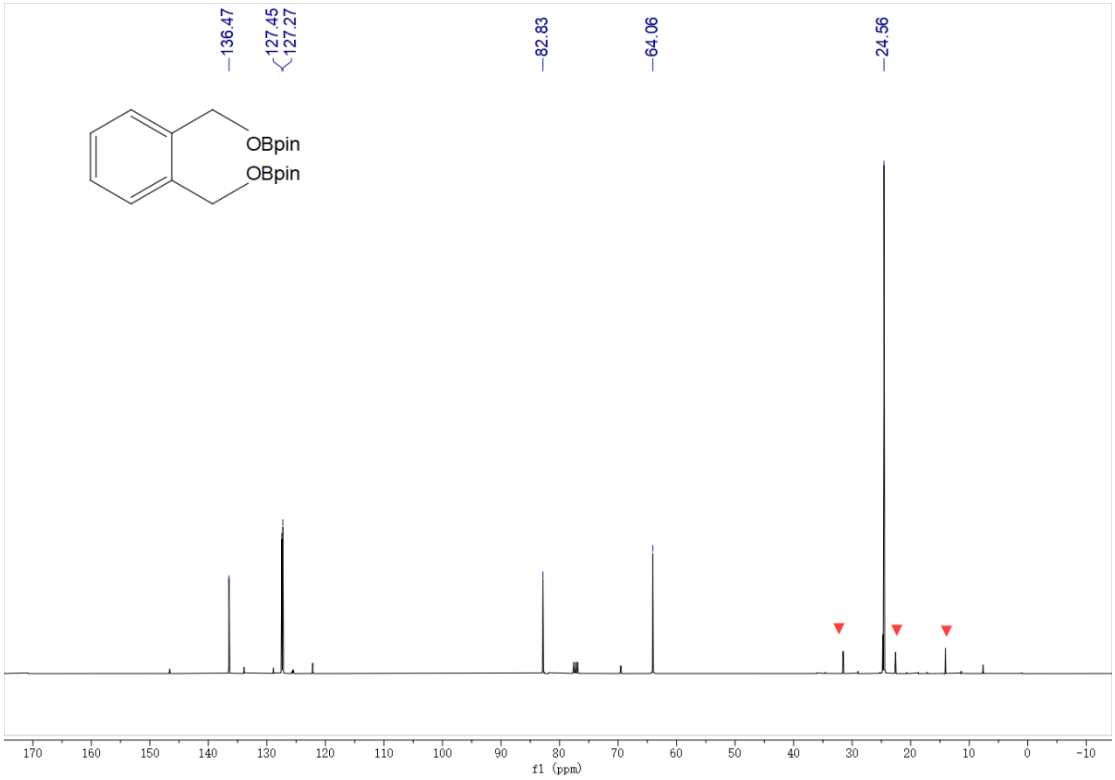


Figure S3.11.2 ^{13}C NMR (101 MHz, $CDCl_3$) of compound **4k**

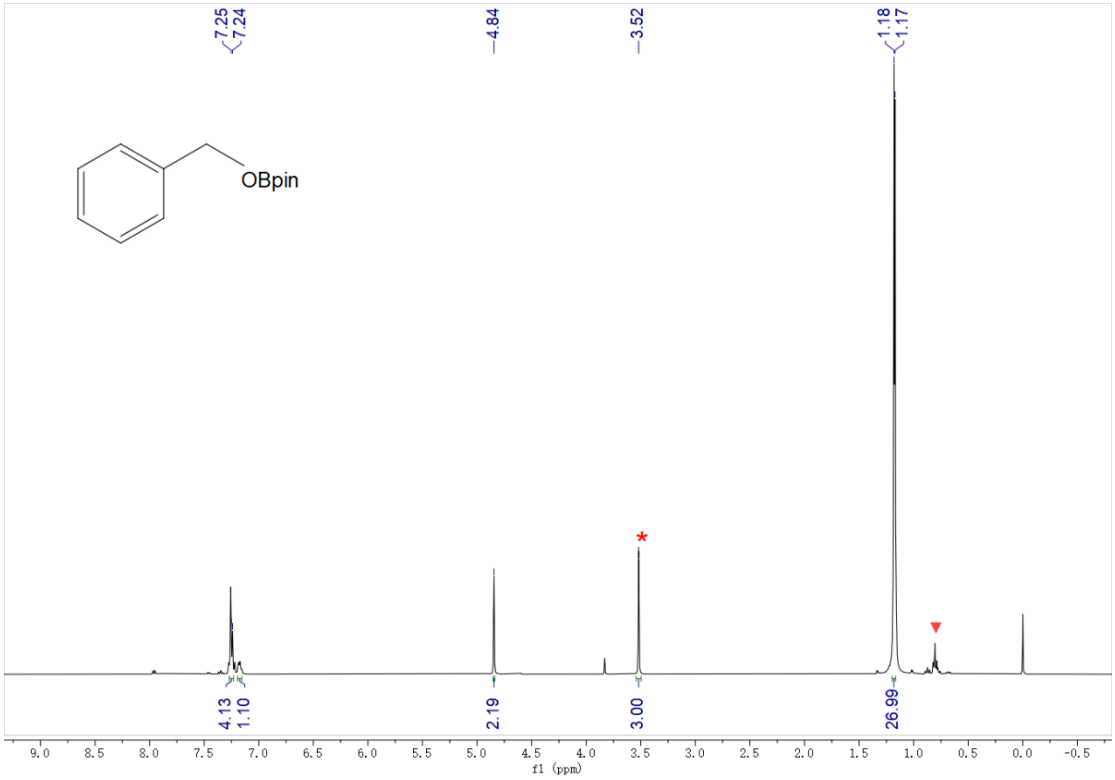


Figure S3.12.1 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **4l**

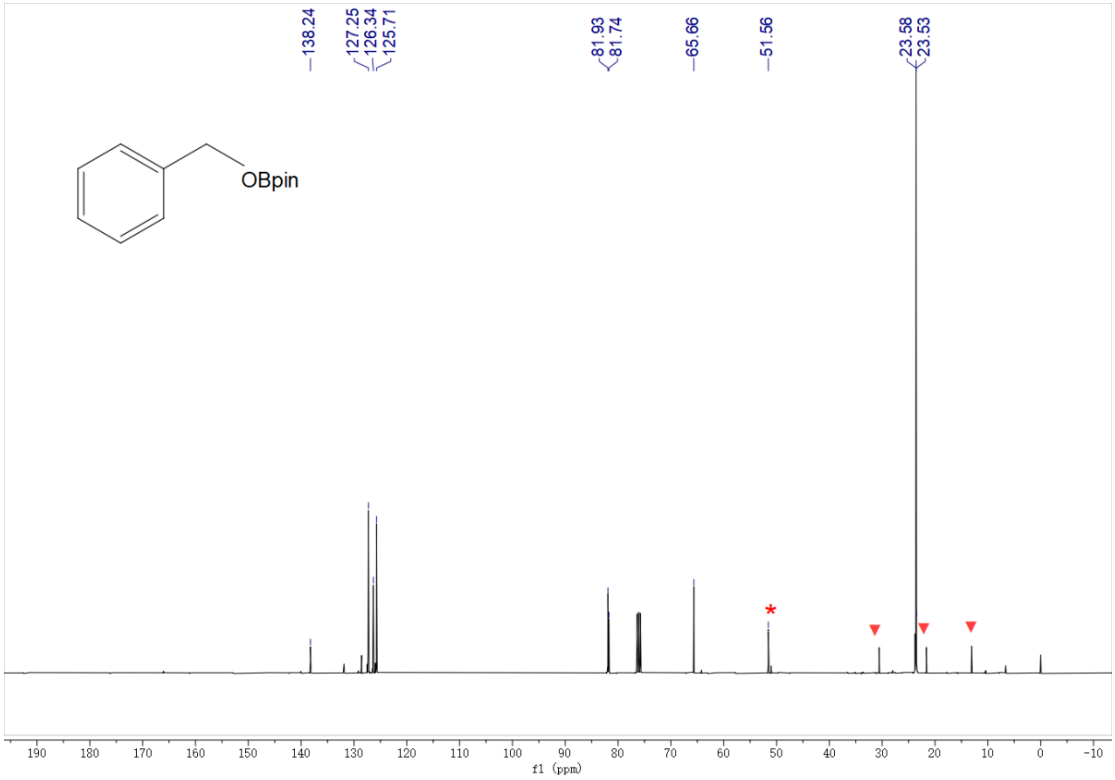


Figure S3.12.2 ^{13}C NMR (101 MHz, $CDCl_3$) of compound **4l**

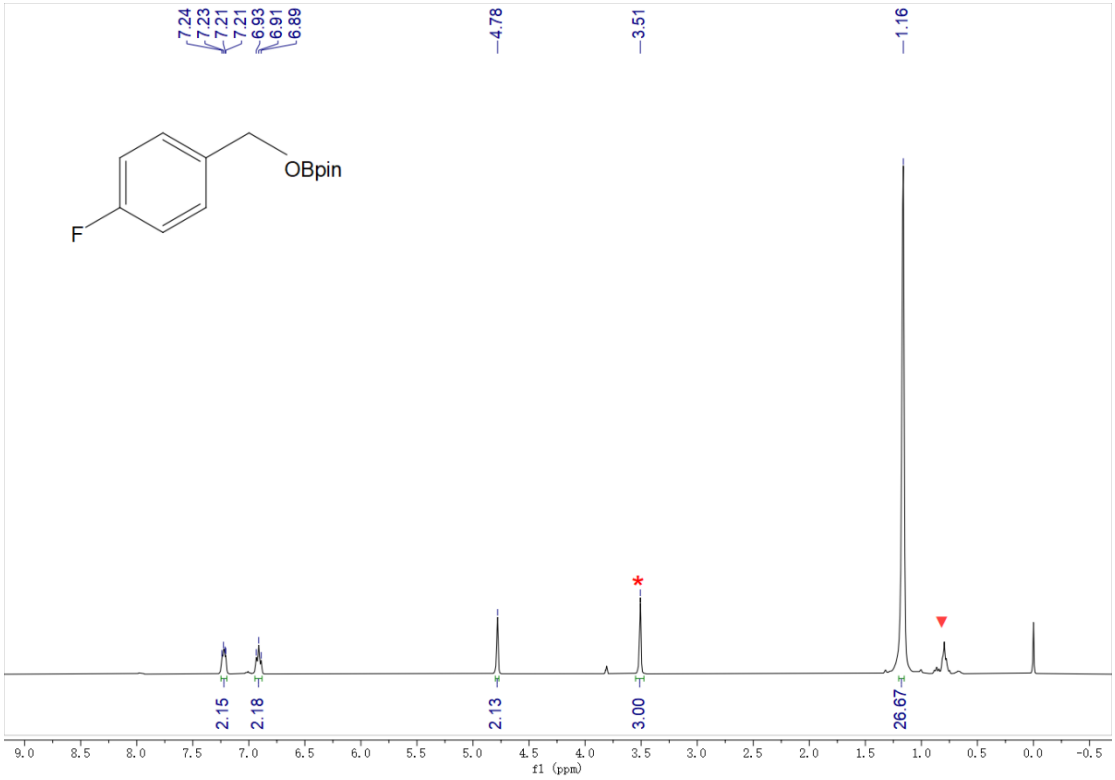


Figure S3.13.1 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **4m**

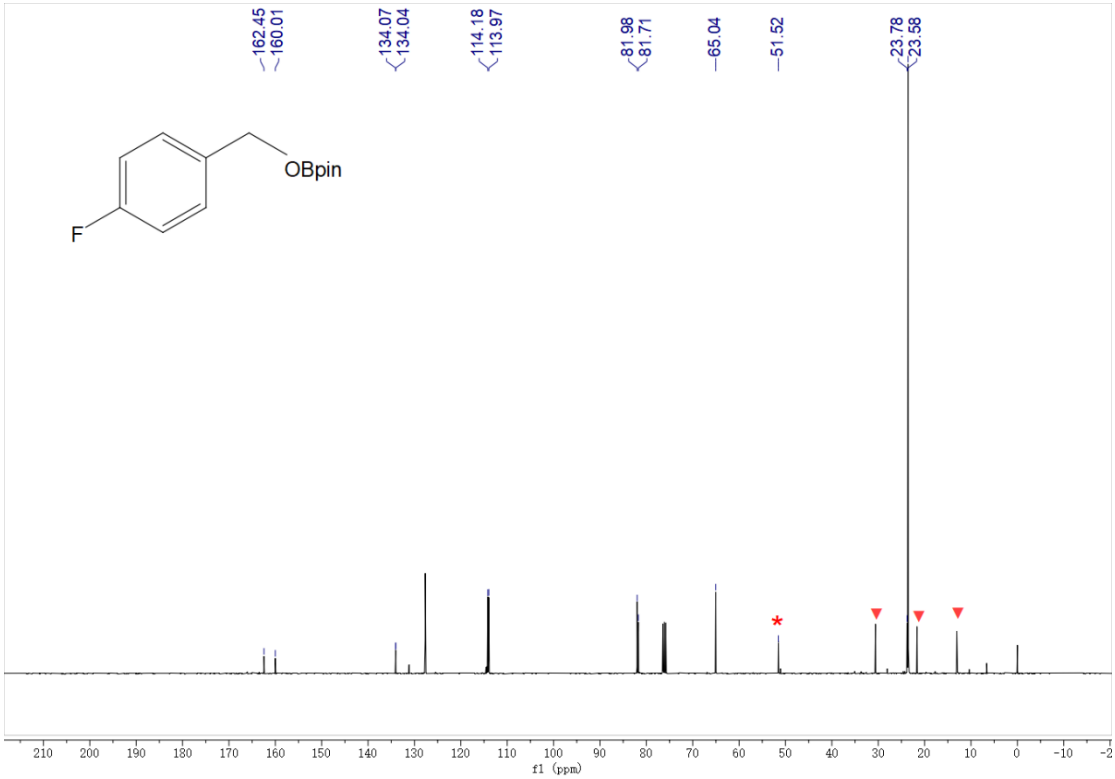


Figure S3.13.2 ^{13}C NMR (101 MHz, $CDCl_3$) of compound **4m**

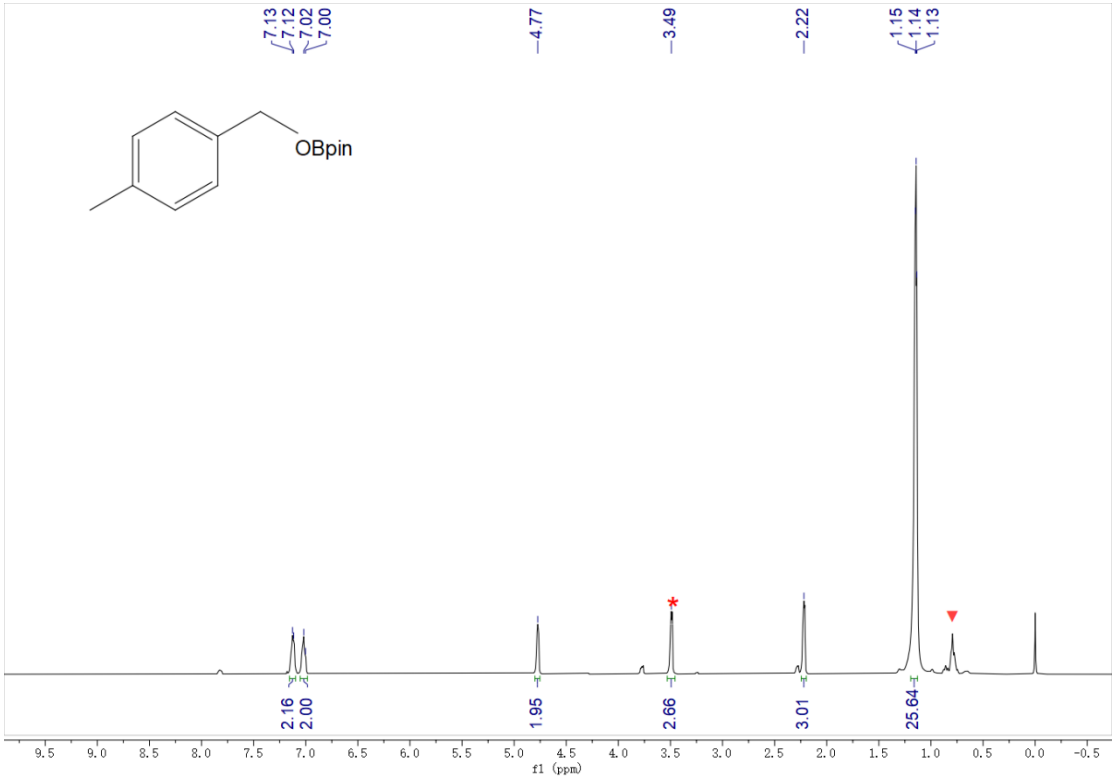


Figure S3.14.1 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **4n**

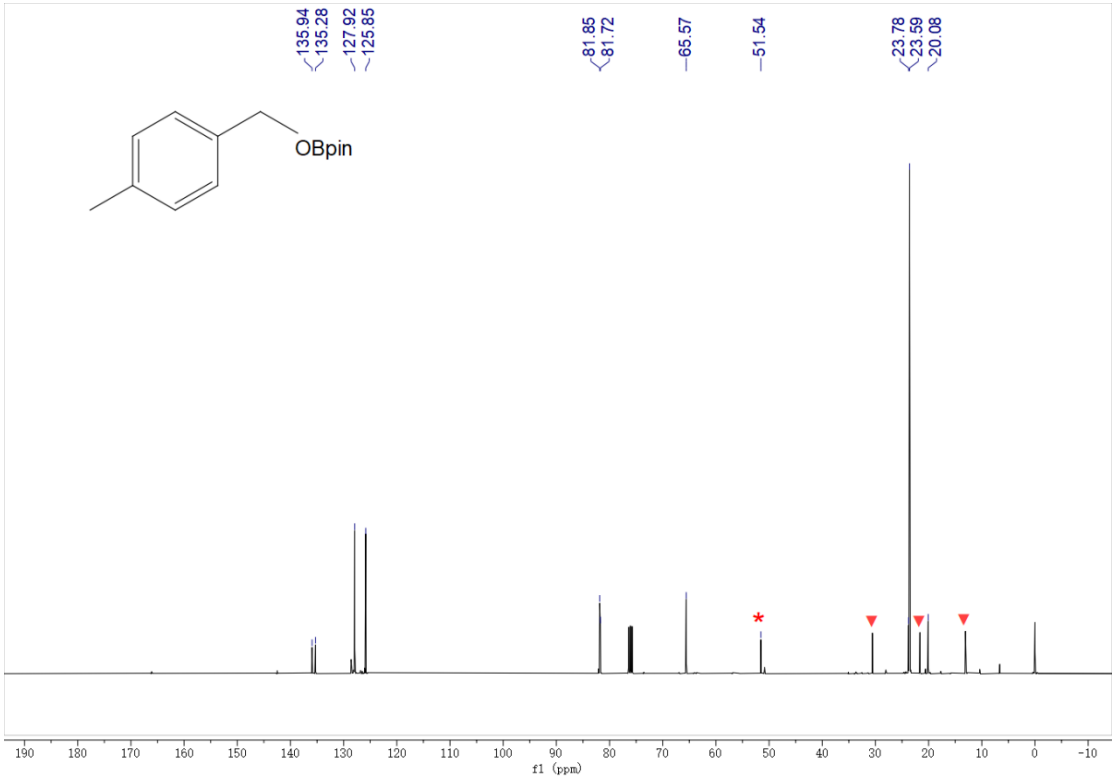


Figure S3.14.2 ^{13}C NMR (101 MHz, $CDCl_3$) of compound **4n**

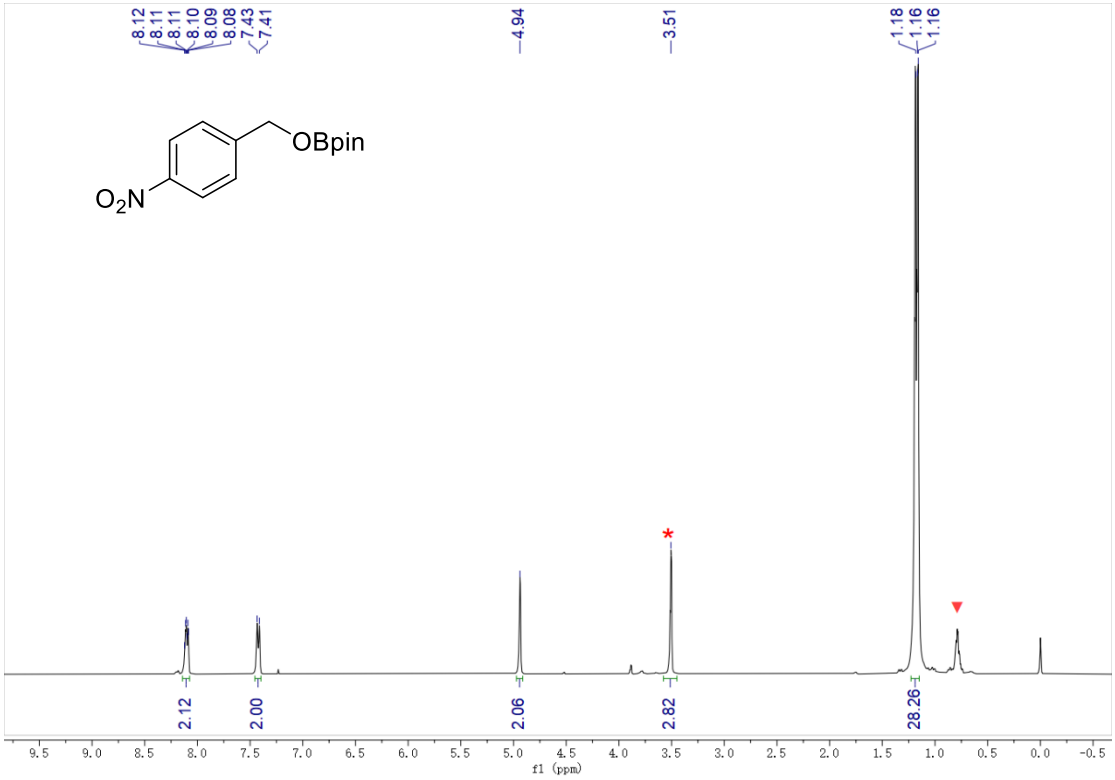


Figure S3.15.1 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **4o**

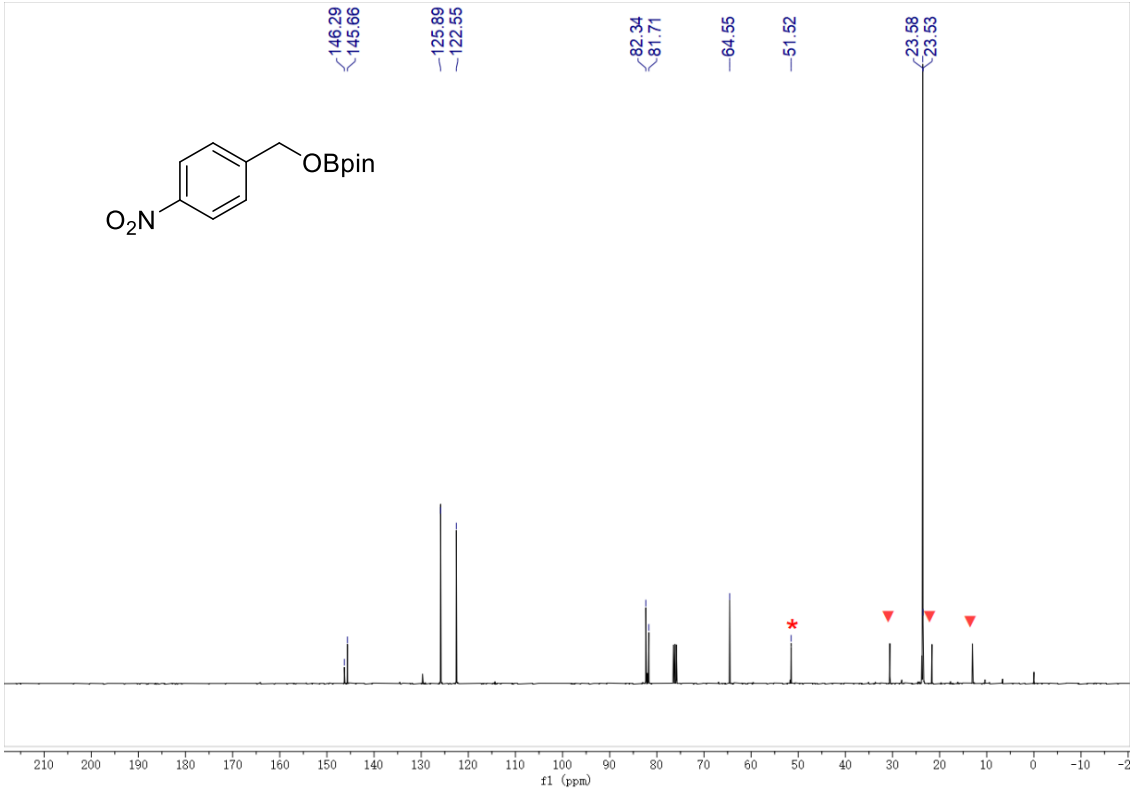
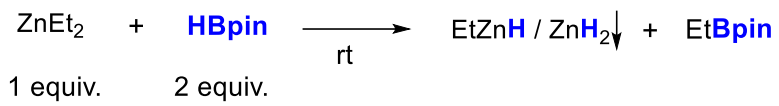


Figure S3.15.2 ^{13}C NMR (101 MHz, $CDCl_3$) of compound **4o**

Mechanism Experiment

a) Formation of zinc hydride

When $ZnEt_2$ (1 mmol, 1 equiv) and HBpin (2 mmol, 2 equiv) were mixed in a Schlenk bottle. The solution was stirred at room temperature for 4 h, forming a white suspension. Take out an aliquot of the solution and analysed by NMR spectroscopy. However, no Zn-H signal was detected in ^{1}H NMR (Figure S5.1), the formation of Et-Bpin was indeed observed [^{11}B NMR 34.3 ppm in $CDCl_3$ (Figure S5.2)]. Insoluble material was also observed to form, presumably $(ZnH_2)_\infty$. [S1, S2]



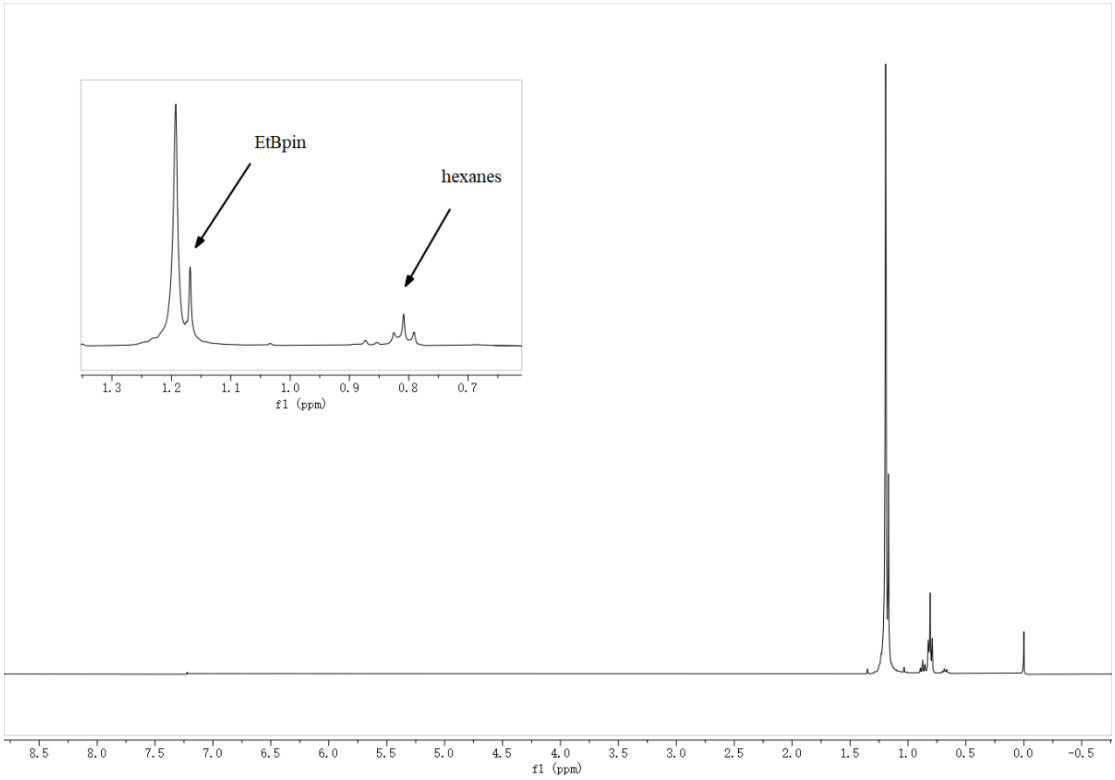


Figure S5.1 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the reaction mixture of $ZnEt_2$ and HBpin

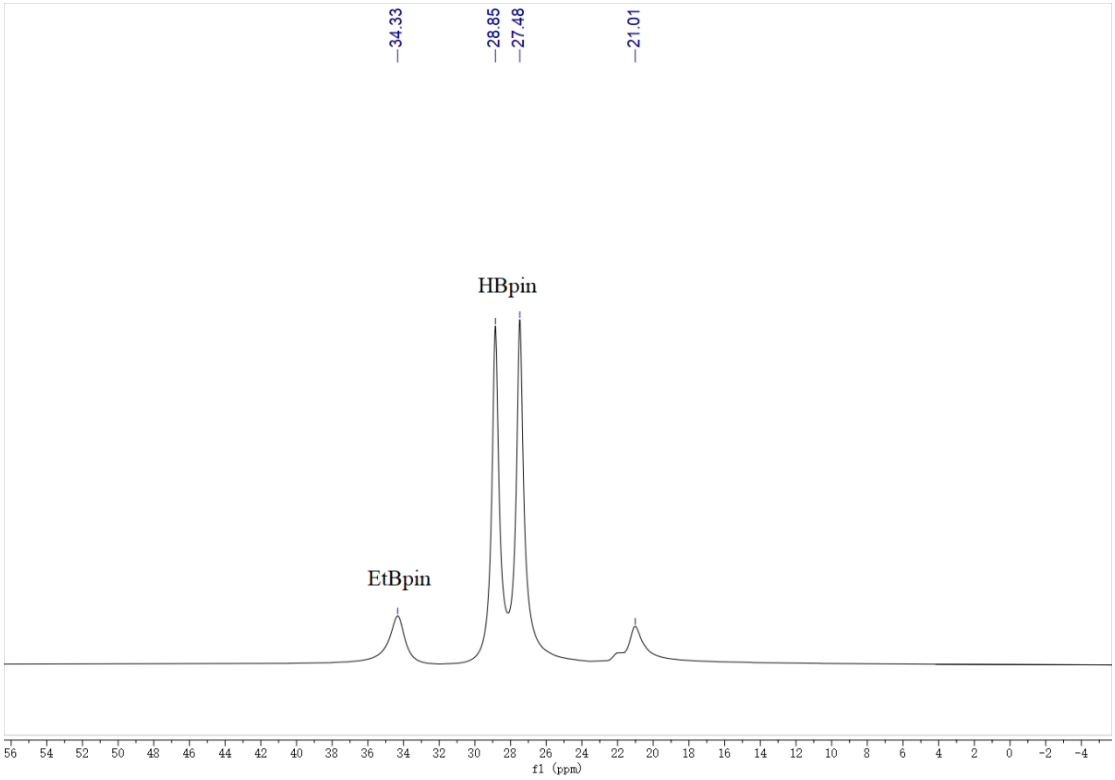


Figure S5.2 ^{11}B NMR (128 MHz, $CDCl_3$) spectrum of the reaction mixture of $ZnEt_2$ and HBpin

b) Reaction of $ZnEt_2$ and HBpin under different conditions

When $ZnEt_2$ and HBpin were reacted at different temperatures and in different ratios, the formation of Et-Bpin was observed (^{11}B NMR 34.3 ppm in $CDCl_3$), but no Zn-H signal was detected by ^{1}H NMR. Insoluble white material could still be observed to form.

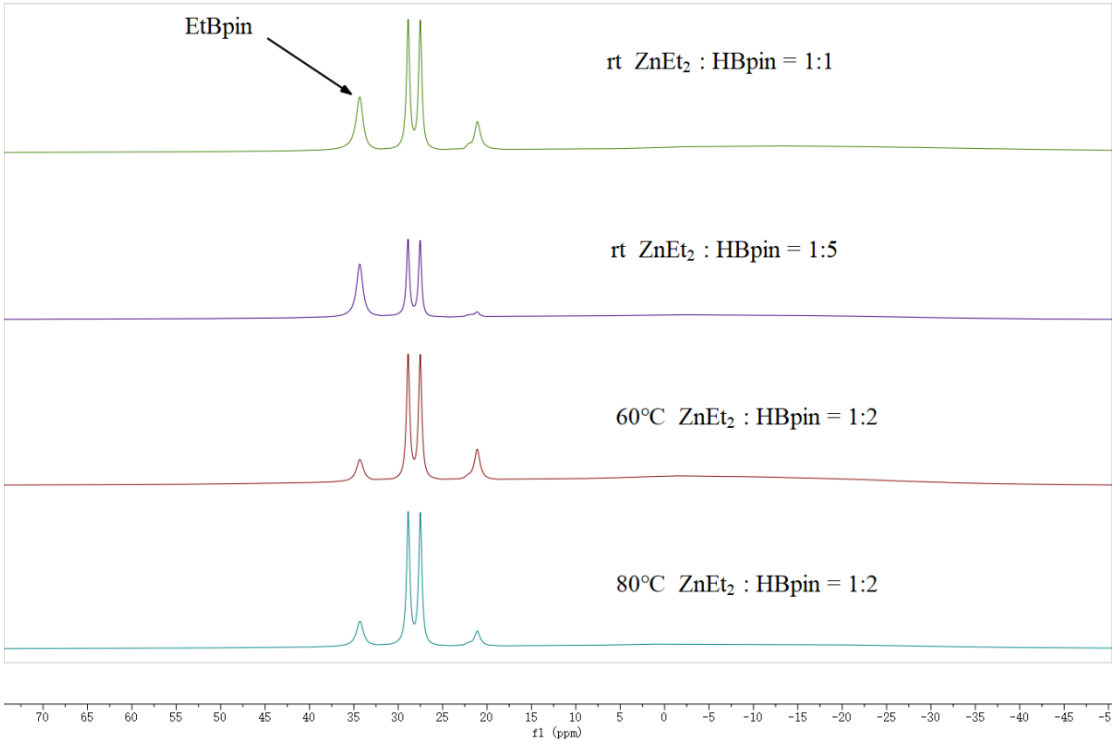


Figure S6. ^{11}B NMR (128 MHz, $CDCl_3$) of the reaction of $ZnEt_2$ and HBpin under different conditions

c) The reaction of carbonate esters catalyzed by zinc hydride

A Schlenk bottle was charged with 5 mL of THF followed by the addition of diethylzinc (1 mmol, 1 equiv) and HBpin (2 mmol, 2 equiv). The solution was stirred at room temperature for 4 h, forming a white suspension. The suspension was allowed to stand for a period of time, the supernatant was filtered off, and the solvent was removed under vacuum to obtain a white solid. Then added dimethyl carbonate (1 mmol, 1 equiv.) and HBpin (3.2 mmol 3.2 equiv.) into it, which reacted for 12 h at 80 °C. A portion of the sample was removed and analysed by NMR spectroscopy. The yield of ^1H NMR spectroscopy indicates that ZnH_2 is the real catalyst in the borohydride reaction.

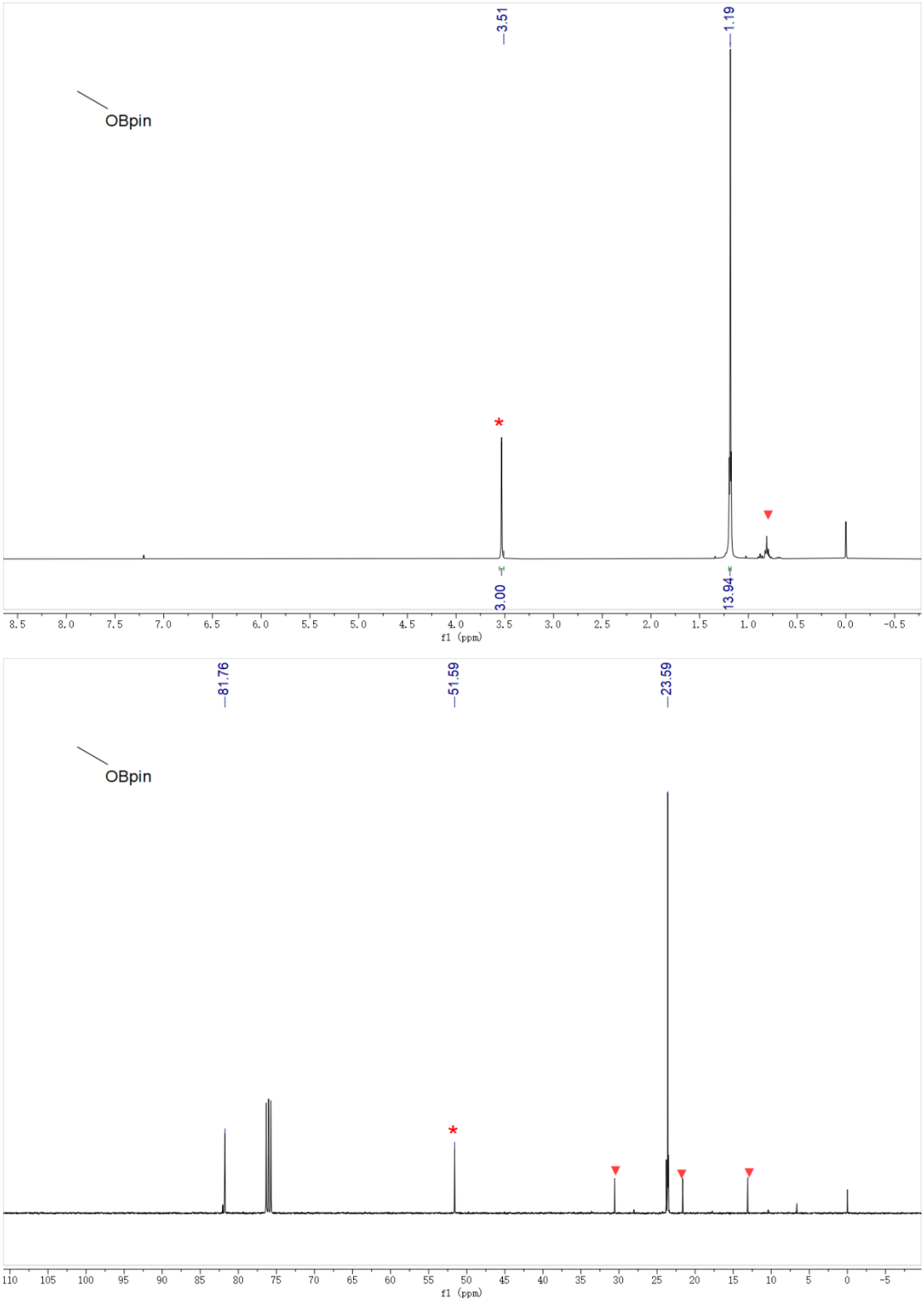


Figure S7.1. ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$) of dimethyl carbonate catalyzed by $ZnEt_2$

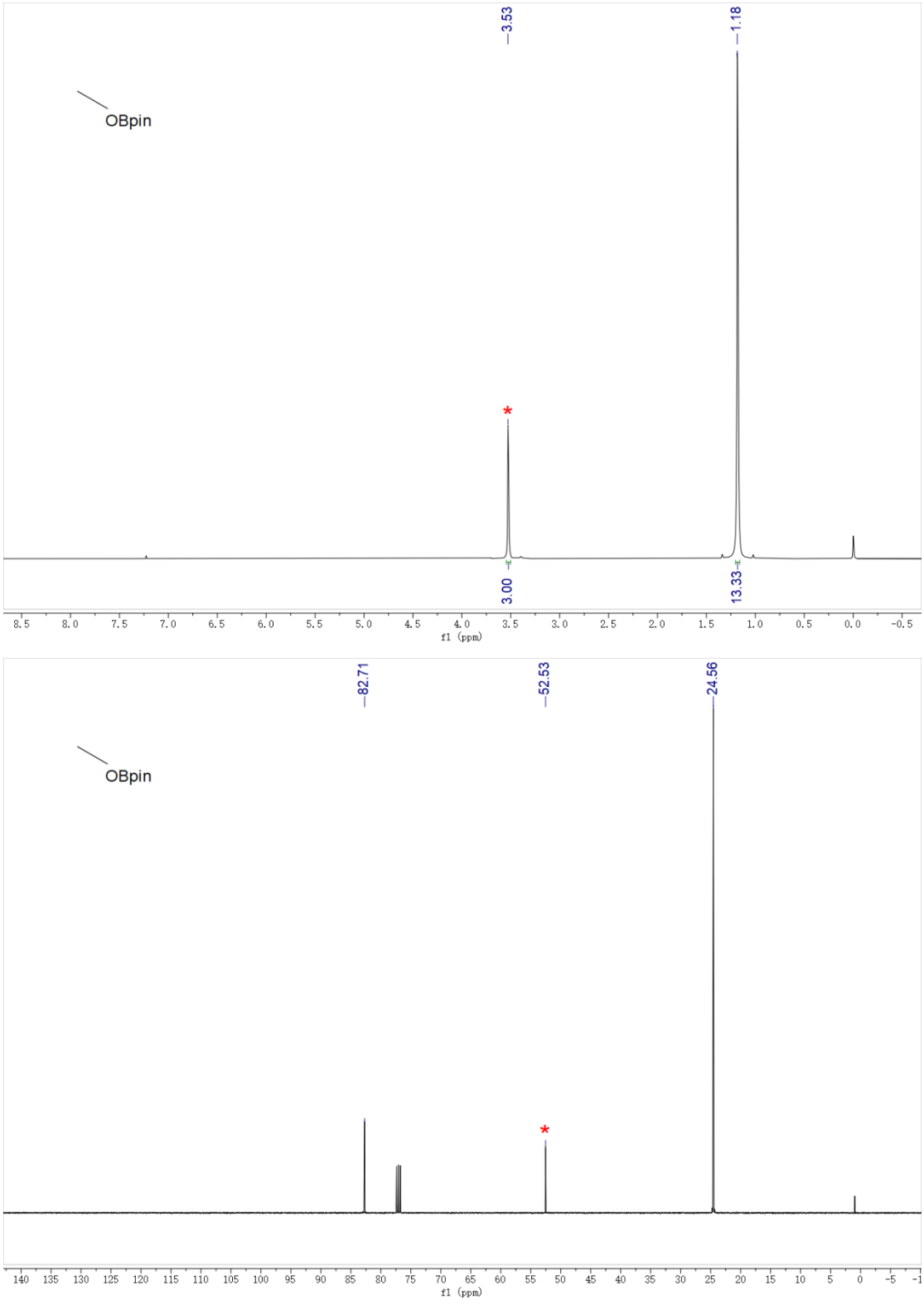


Figure S7.2. ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$) of dimethyl carbonate catalyzed by ZnH_2

Computational Details

In this study, the computations were performed by a DFT method using the Gaussian 16 suite of programs.[S3] The BP86 functional[S4,S5] and Ahlrichs' split valence plus polarization basis set (def2-SVP)[S6,S7] were chosen to optimize the geometry structures. Vibrational frequency were calculated at the same level to confirm that the stable structures possess no imaginary frequency and every transition state possesses only one imaginary frequency. Intrinsic reaction coordinate (IRC) calculations were carried out to ensure that the transition state connects the corresponding reactant and product. Single-point calculations were further performed using R-BP86 functional and the triple-ζ valence plus polarization basis set (def2-TZVP)[S6,S7] based on the optimized geometries at the BP86/def2-SVP level of theory to improve the accuracy of the energies. The Grimme's D3 empirical corrections were used to incorporate the London dispersion effects.[S8] All the energy values reported in this article were obtained at the BP86-D3/def2-TZVP//BP86/def2-SVP level.

Table S2. Absolute energies (in Hartree) of all the studied structures. E_e = Electronic energy, G = gas-phase Gibbs free energy at 80 °C, and number of imaginary vibrational frequencies (Nimg) at the BP86-D3/def2-TZVP//BP86/def2-SVP level of theory.

Species	E_e	G	Nimg
1a	-342.523443	-342.516974	0
ZnH_2	-1780.842350	-1780.838092	0
HBpin	-411.897833	-411.889382	0
2a	-1051.812509	-1051.796494	0
CH_3OBpin	-526.504428	-526.494514	0
HCHO	-114.554723	-114.549966	0
INT-1	-2123.368276	-2123.360508	0
INT-2	-2123.368276	-2123.360508	0
INT-3	-2123.379528	-2123.371460	0
INT-4	-3789.661124	-3789.652169	0
INT-5	-4201.556730	-4201.543026	0
INT-6	-2420.732184	-2420.720289	0
INT-7	-2832.634118	-2832.616920	0
INT-8	-1895.424353	-1895.418303	0
INT-9	-2307.325635	-2307.314065	0

TS-1	-2123.328924	-2123.321168	1
TS-2	-2123.361644	-2123.354089	1
TS-3	-3904.172116	-3904.162093	1
TS-5	-4201.558013	-4201.544294	1
TS-7	-2832.636129	-2832.618916	1
TS-8	-1895.373344	-1895.367209	1
TS-10	-2307.325631	-2307.314394	1

Table S3. Cartesian coordinates (Å) of the reactants, intermediates and transition states at the BP86/def2-SVP level of theory.

1a

O	2.055845	-0.000012	0.000010
C	0.857107	-0.000002	-0.000003
O	0.068221	1.118558	-0.108823
O	0.068199	-1.118557	0.108800
C	-1.301911	0.760379	0.120067
C	-1.301932	-0.760368	-0.120055
H	-1.580256	1.026739	1.163879
H	-1.948563	1.323470	-0.581068
H	-1.948583	-1.323439	0.581099
H	-1.580307	-1.026731	-1.163858

ZnH_2

Zn	0.000000	0.000000	0.000000
H	0.000000	0.000000	1.549086
H	0.000000	0.000000	-1.549086

HBpin

C	-0.794660	-0.190744	-0.045745
C	0.794660	-0.190746	0.045744
O	1.093055	1.207308	0.364533
O	-1.093052	1.207311	-0.364536
B	0.000003	1.953672	-0.000002
H	0.000005	3.162936	-0.000005
C	-1.379422	-1.075293	-1.149551
H	-1.120301	-2.141207	-0.982189
H	-2.484803	-0.988712	-1.150332
H	-1.017008	-0.776663	-2.151241
C	-1.483298	-0.490366	1.295889
H	-2.564185	-0.262516	1.203428
H	-1.375840	-1.555265	1.585315
H	-1.073420	0.138700	2.111443

C	1.379414	-1.075292	1.149555
H	1.120299	-2.141207	0.982190
H	2.484796	-0.988706	1.150343
H	1.016992	-0.776664	2.151242
C	1.483301	-0.490374	-1.295888
H	2.564189	-0.262529	-1.203427
H	1.375839	-1.555274	-1.585311
H	1.073425	0.138691	-2.111444

2a

B	-2.651997	-0.886110	-0.089537
O	-3.858699	-1.037710	-0.745324
O	-2.565034	0.271275	0.668340
C	-3.729057	1.081356	0.324716
C	-4.750307	-0.013879	-0.217072
C	-5.576259	-0.668877	0.903450
H	-6.345090	0.019269	1.309637
H	-6.089435	-1.562020	0.493959
H	-4.928140	-1.003411	1.738730
C	-5.669498	0.462842	-1.344187
H	-6.315466	1.298618	-1.004061
H	-5.093889	0.796009	-2.228391
H	-6.328524	-0.369277	-1.664868
C	-3.282086	2.074232	-0.761288
H	-2.417044	2.655565	-0.383292
H	-2.961809	1.546302	-1.682303
H	-4.089126	2.786173	-1.028267
C	-4.189376	1.832583	1.575782
H	-4.366170	1.144886	2.424276
H	-3.410018	2.558361	1.885271
H	-5.122812	2.398700	1.377082
O	-1.658349	-1.814095	-0.200915
C	-0.399879	-1.628384	0.444316
C	0.703180	-2.151714	-0.479748
H	-0.378632	-2.203046	1.397717
H	-0.227137	-0.556767	0.685592
O	1.958074	-2.147159	0.198541
H	0.742334	-1.538474	-1.406420
H	0.472720	-3.199993	-0.764921
B	2.799948	-1.078667	0.091964
O	4.033170	-1.063615	0.714472
O	2.521109	0.070695	-0.631882
C	4.548142	0.293224	0.586632
C	3.760576	0.839377	-0.685329

C	4.184164	1.038212	1.882417
C	6.068432	0.225504	0.423309
C	3.415034	2.329411	-0.642253
C	4.450142	0.488785	-2.014498
H	4.586182	0.471158	2.745884
H	4.611917	2.060948	1.907475
H	3.085145	1.114461	2.008778
H	6.494724	1.234764	0.246930
H	6.524904	-0.181014	1.348467
H	6.361180	-0.435053	-0.414577
H	4.335006	2.948496	-0.601001
H	2.855770	2.610899	-1.557622
H	2.781727	2.577801	0.230326
H	5.367746	1.089965	-2.175764
H	4.723393	-0.585092	-2.055486
H	3.749370	0.694509	-2.848607

CH_3OBPin

O	-2.502550	-0.716368	-0.192493
B	-1.183548	-0.389181	-0.105501
O	-0.190785	-1.287945	-0.449698
O	-0.702175	0.840335	0.321743
C	1.069412	-0.704150	-0.013079
C	0.727365	0.850187	0.033068
C	1.382672	-1.289455	1.374937
C	2.161807	-1.094595	-1.011627
C	1.443776	1.638864	1.131468
C	0.908297	1.544167	-1.327602
H	1.385355	-2.395679	1.303975
H	2.373223	-0.961742	1.750573
H	0.612026	-0.999184	2.117627
H	3.125438	-0.605820	-0.758598
H	2.317829	-2.192073	-0.983330
H	1.885956	-0.820842	-2.047551
H	2.544127	1.602067	0.992815
H	1.131226	2.702324	1.094186
H	1.200694	1.250728	2.138658
H	1.978404	1.665804	-1.591366
H	0.410289	0.975124	-2.138651
H	0.445382	2.550620	-1.282689
C	-3.514539	0.230854	0.124325
H	-4.305012	0.186801	-0.654225
H	-3.980199	-0.021525	1.102164

H	-3.115656	1.265904	0.178570

HCHO

C	0.000000	0.000000	-0.528216
H	-0.000000	-0.953067	-1.140344
H	0.000000	0.953067	-1.140344
O	0.000000	0.000000	0.681248

INT-1

O	-0.451619	1.359432	-0.057374
C	0.670409	0.953103	0.545079
O	1.849245	0.922727	-0.240681
O	0.443866	-0.514729	0.910716
C	1.948305	-0.363775	-0.843351
C	1.490793	-1.283036	0.295060
H	1.279767	-0.458984	-1.734521
H	2.995525	-0.525203	-1.166831
H	1.080428	-2.257794	-0.039912
H	2.309906	-1.464563	1.027103
Zn	-1.511183	-0.186775	-0.134723
H	0.917431	1.512691	1.478747
H	-2.636534	-1.180089	-0.404914

INT-2

O	0.451605	1.359437	-0.057385
C	-0.670412	0.953100	0.545079
O	-1.849267	0.922718	-0.240666
O	-0.443861	-0.514729	0.910715
C	-1.948308	-0.363776	-0.843346
C	-1.490771	-1.283046	0.295052
H	-2.995528	-0.525226	-1.166818
H	-1.279779	-0.458967	-1.734525
H	-2.309878	-1.464604	1.027093
H	-1.080390	-2.257792	-0.039939
H	-0.917434	1.512695	1.478742
Zn	1.511186	-0.186770	-0.134723
H	2.636559	-1.180068	-0.404882

INT-3

O	-0.193641	-1.617496	0.072387
C	-1.343935	-1.450438	-0.324725
O	-2.128101	-0.403508	-0.116166
O	0.351795	1.188024	-0.680228
C	-1.630510	0.711817	0.692997

C	-0.808773	1.702237	-0.136260
H	-2.548249	1.181360	1.101368
H	-1.029228	0.293996	1.531543
H	-1.476747	2.094638	-0.947574
H	-0.638411	2.578380	0.554408
H	-1.895766	-2.221747	-0.915113
Zn	1.443402	-0.077011	0.084269
H	2.745230	-0.734161	0.547277

INT-4

O	-1.526822	-1.034757	0.139909
O	1.526831	1.034796	-0.139686
C	-0.199895	-0.724548	-0.166609
C	0.199908	0.724582	0.166838
H	0.047108	-0.906201	-1.247049
H	0.482840	-1.399765	0.423228
H	-0.047080	0.906235	1.247280
H	-0.482838	1.399798	-0.422990
H	-4.188461	0.910149	-0.075282
Zn	2.905612	-0.103001	0.011963
Zn	-2.905618	0.102983	-0.012071
H	4.188449	-0.910194	0.074912

INT-5

O	-3.050949	-1.351257	0.538034
O	0.557872	-1.530189	-0.212324
C	-1.688365	-1.543883	0.823149
C	-0.852503	-1.530091	-0.466831
H	-1.561889	-2.531478	1.329077
H	-1.262687	-0.776517	1.514389
H	-1.098761	-0.611672	-1.052101
H	-1.094931	-2.405927	-1.105513
B	1.289247	-0.247655	-0.023195
O	1.280979	0.611082	-1.148363
O	1.051040	0.492894	1.165523
H	2.607099	-0.839216	0.127886
C	1.487956	1.955517	-0.659119
C	0.864809	1.881968	0.807291
C	3.003487	2.235236	-0.650984
C	0.786042	2.932364	-1.608351
C	1.567631	2.762334	1.847808
C	-0.649340	2.174175	0.831226
H	3.403351	2.057153	-1.669817

H	3.233219	3.282124	-0.366298
H	3.538639	1.559337	0.045930
H	0.841611	3.972964	-1.226549
H	1.278770	2.907123	-2.601697
H	-0.277996	2.665433	-1.755215
H	1.507331	3.836276	1.573585
H	1.080863	2.634470	2.836248
H	2.632654	2.484834	1.960685
H	-0.875950	3.240593	0.627702
H	-1.192075	1.558735	0.082288
H	-1.047942	1.921842	1.834966
Zn	-3.720845	0.101213	-0.278245
H	-4.471614	1.239731	-0.944448
Zn	2.310541	-2.500718	-0.032165
H	2.793364	-3.958345	-0.070936

INT-6

O	-3.296546	-0.693718	-0.244298
O	0.165759	-1.867174	-0.260003
C	-2.034100	-0.963242	0.317917
C	-1.096201	-1.457991	-0.791806
H	-2.095077	-1.757350	1.104774
H	-1.554603	-0.074437	0.801824
H	-0.972400	-0.655504	-1.551961
H	-1.557556	-2.338461	-1.286840
B	1.191246	-0.978488	-0.144968
O	2.431727	-1.359675	0.334100
O	1.114592	0.364881	-0.488938
C	3.196569	-0.138023	0.536590
C	2.477283	0.882935	-0.451268
C	3.043215	0.251932	2.017026
C	4.665750	-0.421193	0.213302
C	2.437393	2.333892	0.033803
C	3.025189	0.814956	-1.886822
H	3.362088	-0.602880	2.646616
H	3.664707	1.131244	2.282093
H	1.987044	0.480603	2.265840
H	5.273986	0.504557	0.280975
H	5.073468	-1.151627	0.941208
H	4.786190	-0.852108	-0.798592
H	3.462820	2.741075	0.152412
H	1.905208	2.962930	-0.708611
H	1.905926	2.428156	0.999720
H	4.035701	1.264441	-1.966438

H	3.078001	-0.232174	-2.247730
H	2.342824	1.373215	-2.559078
Zn	-4.426574	0.620284	0.176133
H	-5.472169	1.688109	0.425285

INT-7

B	-2.499361	-0.147288	0.098746
O	-2.532915	0.694713	1.232271
O	-2.023417	0.551667	-1.034249
C	-2.183256	1.963630	-0.753624
C	-2.066860	2.009793	0.837310
C	-0.614107	2.152853	1.327379
H	-0.219387	3.176034	1.158619
H	-0.586323	1.949259	2.417372
H	0.063492	1.433480	0.824830
C	-2.948095	3.067311	1.512547
H	-2.672748	4.090430	1.181400
H	-4.021050	2.902627	1.297823
H	-2.813690	3.017882	2.612518
C	-3.568860	2.398271	-1.269167
H	-3.645956	2.139901	-2.344843
H	-4.386552	1.873377	-0.735573
H	-3.728670	3.490498	-1.162663
C	-1.087385	2.732914	-1.498576
H	-0.081549	2.337394	-1.261230
H	-1.240893	2.635727	-2.592886
H	-1.115887	3.813159	-1.245260
O	-1.991726	-1.530171	0.276417
C	-0.616801	-1.796071	0.576370
C	0.232226	-1.807371	-0.700764
H	-0.557722	-2.785330	1.076852
H	-0.244427	-1.026838	1.287089
O	1.565359	-2.210457	-0.389121
H	0.203551	-0.807331	-1.180971
H	-0.190783	-2.548445	-1.412888
B	2.557404	-1.286969	-0.231524
O	3.861034	-1.667360	0.017138
O	2.376915	0.088252	-0.302238
C	4.594095	-0.454615	0.355847
C	3.713762	0.679260	-0.331946
C	4.611814	-0.351342	1.890548
C	6.020490	-0.579149	-0.184493
C	3.682612	2.013191	0.416017
C	4.072426	0.903110	-1.810420

H	5.041233	-1.284635	2.306750
H	5.226520	0.501895	2.242071
H	3.587304	-0.237125	2.299140
H	6.592620	0.356565	-0.015770
H	6.547567	-1.400966	0.341118
H	6.029735	-0.811062	-1.266242
H	4.701068	2.447937	0.487397
H	3.042882	2.736487	-0.129153
H	3.273994	1.902078	1.438059
H	5.046049	1.421092	-1.924832
H	4.119562	-0.056498	-2.364018
H	3.288826	1.530353	-2.280963
H	-3.902624	-0.542444	-0.160967
Zn	-3.873842	-2.215993	-0.026297
H	-4.525443	-3.608318	-0.043893

INT-8

O	0.875544	-0.519860	-0.000001
C	2.061604	0.229300	-0.000001
H	1.921299	1.339951	-0.000898
H	2.687699	-0.007865	0.896294
H	2.688451	-0.009223	-0.895401
Zn	-0.812638	0.036578	0.000002
H	-2.292281	0.362892	-0.000029

INT-9

O	-1.564296	0.940357	-0.301585
C	-1.427388	2.332451	-0.582995
H	-0.880251	2.482497	-1.537967
H	-2.439239	2.775233	-0.671367
H	-0.875977	2.841947	0.235882
B	-0.378712	0.088620	-0.060424
O	0.446188	-0.168981	-1.176266
O	0.397981	0.346034	1.093181
H	-1.153038	-1.148270	0.235795
C	1.745845	-0.538381	-0.657197
C	1.796659	0.257257	0.724664
C	1.770276	-2.067986	-0.469432
C	2.812685	-0.125789	-1.676535
C	2.560748	-0.454476	1.846958
C	2.324615	1.695213	0.565971
H	1.513702	-2.549444	-1.434881
H	2.769104	-2.432689	-0.154432
H	1.025831	-2.398857	0.282292

H	3.834076	-0.308173	-1.282515
H	2.693524	-0.722082	-2.604200
H	2.724021	0.942762	-1.950123
H	3.625259	-0.609171	1.572825
H	2.532664	0.162599	2.768352
H	2.110772	-1.436425	2.087076
H	3.417023	1.721464	0.374524
H	1.812562	2.222915	-0.263692
H	2.124287	2.254643	1.502401
Zn	-2.747098	-0.631506	0.180159
H	-4.267461	-0.825875	0.306133

TS-1

O	-0.514196	-0.377522	1.195675
C	0.432474	-0.121012	0.376507
O	1.241259	-1.153373	-0.064237
O	1.206966	1.007628	0.570418
C	2.521123	-0.623534	-0.442383
C	2.326287	0.903269	-0.312744
H	3.288615	-1.021827	0.256324
H	2.773764	-0.943364	-1.474403
H	3.186448	1.432835	0.139934
H	2.079597	1.374274	-1.291960
Zn	-1.829062	0.066543	-0.251645
H	-0.263436	0.271678	-0.958646
H	-3.344688	0.123905	-0.465025

TS-2

O	0.255410	1.466214	-0.202209
C	-0.754394	1.133674	0.507089
O	-1.956181	0.782090	-0.034329
O	-0.211583	-0.686595	0.891405
C	-1.840414	-0.421097	-0.808055
C	-1.198109	-1.411070	0.192142
H	-2.857061	-0.706295	-1.140448
H	-1.195898	-0.256201	-1.702330
H	-1.973674	-1.783396	0.902773
H	-0.775145	-2.292650	-0.343731
H	-0.909080	1.580336	1.516808
Zn	1.431607	-0.141537	-0.108222
H	2.818978	-0.598404	-0.572414

TS-3

C	-1.646636	1.432744	0.562578

O	2.332802	-0.757674	0.877195
O	-1.296794	-0.131037	0.607566
C	1.051053	-0.408184	1.326048
C	0.033566	-0.456958	0.177966
H	1.012059	0.611005	1.790284
H	0.732912	-1.128082	2.118082
H	0.005625	-1.476176	-0.263523
H	0.343952	0.265099	-0.616718
H	4.140443	0.550387	-1.558252
H	-3.032894	1.167362	0.071482
O	-0.976598	2.144804	-0.157655
H	-1.958600	1.669133	1.609291
Zn	-3.054197	-0.467486	-0.369737
Zn	3.231177	0.020336	-0.466862
H	-3.656088	-1.698575	-1.069070

TS-5

O	3.443199	0.583306	0.341917
O	-0.034984	1.248343	-0.719480
C	2.102978	0.970683	0.492587
C	1.310318	0.752850	-0.804085
H	2.067471	2.061000	0.738629
H	1.577027	0.434916	1.320957
H	1.293087	-0.334768	-1.052915
H	1.813584	1.284177	-1.640053
B	-1.109667	0.397431	-0.266268
O	-1.998825	-0.145970	-1.193292
O	-0.921316	-0.432388	0.843799
H	-2.033736	1.735477	0.365408
C	-2.748262	-1.177926	-0.497062
C	-1.726177	-1.628693	0.643147
C	-4.034019	-0.540249	0.060676
C	-3.108384	-2.273683	-1.505206
C	-2.377125	-2.015073	1.974480
C	-0.767263	-2.740633	0.182748
H	-4.589412	-0.069733	-0.775631
H	-4.694759	-1.293345	0.535850
H	-3.809064	0.251669	0.802001
H	-3.608680	-3.127861	-1.003614
H	-3.808042	-1.865890	-2.262712
H	-2.215617	-2.649056	-2.040322
H	-3.053776	-2.885848	1.849853
H	-1.593479	-2.294971	2.707849
H	-2.956173	-1.175867	2.403699

H	-1.281021	-3.718241	0.082112
H	-0.300506	-2.491606	-0.791882
H	0.040761	-2.852648	0.934106
Zn	4.054460	-1.040038	-0.101283
H	4.740437	-2.344633	-0.456120
Zn	-0.972198	2.936838	0.164960
H	-0.324613	4.336087	0.236557

TS-7

B	-2.325657	-0.176953	0.033755
O	-2.297289	0.585624	1.197795
O	-2.192664	0.588097	-1.121161
C	-2.472187	1.966345	-0.745040
C	-2.110975	1.977636	0.811826
C	-0.637850	2.322476	1.090343
H	-0.418502	3.390390	0.886200
H	-0.423180	2.126404	2.160587
H	0.052853	1.698920	0.487441
C	-3.026995	2.852832	1.672908
H	-2.960078	3.918344	1.369828
H	-4.083318	2.531350	1.604354
H	-2.719831	2.781071	2.736128
C	-3.961225	2.234296	-1.027345
H	-4.166630	2.015418	-2.094723
H	-4.615389	1.579513	-0.418470
H	-4.234434	3.290808	-0.830966
C	-1.603893	2.885647	-1.608941
H	-0.531825	2.621419	-1.538389
H	-1.907317	2.793583	-2.671608
H	-1.729164	3.946774	-1.309251
O	-1.878102	-1.545281	0.053221
C	-0.506651	-1.845861	0.354487
C	0.358932	-1.729752	-0.905783
H	-0.465711	-2.883148	0.746536
H	-0.138125	-1.158131	1.146942
O	1.692501	-2.145028	-0.616594
H	0.330246	-0.688888	-1.292784
H	-0.047667	-2.402062	-1.691000
B	2.667259	-1.228691	-0.346602
O	3.973133	-1.612270	-0.117861
O	2.463184	0.143107	-0.277894
C	4.679933	-0.429519	0.356423
C	3.789775	0.755468	-0.224473
C	4.673938	-0.486098	1.893610

C	6.115835	-0.474526	-0.171024
C	3.723975	2.003513	0.657446
C	4.165637	1.137514	-1.665725
H	5.113964	-1.450523	2.217478
H	5.268369	0.335756	2.341536
H	3.641915	-0.431810	2.295652
H	6.668994	0.447707	0.102589
H	6.649701	-1.337779	0.275273
H	6.144628	-0.593072	-1.270649
H	4.733541	2.443970	0.791847
H	3.080650	2.769960	0.179580
H	3.301173	1.779470	1.654931
H	5.131081	1.680849	-1.710137
H	4.238225	0.241514	-2.314890
H	3.377401	1.797081	-2.081249
H	-4.052871	-0.705718	-0.049860
Zn	-3.866539	-2.294787	0.122611
H	-4.166132	-3.801183	0.290648

TS-8

O	-1.202904	-0.818043	-0.000001
C	-1.575771	0.400008	0.000001
H	-0.138121	1.472715	-0.000006
H	-1.941429	0.899567	-0.937326
H	-1.941424	0.899566	0.937330
Zn	0.704135	0.055533	0.000000
H	1.974781	-0.793547	0.000001

TS-10

O	-1.551240	0.934517	-0.503930
C	-1.555702	2.364900	-0.534979
H	-1.005911	2.735900	-1.426744
H	-2.608195	2.704839	-0.598143
H	-1.086748	2.782740	0.380994
B	-0.328860	0.230365	-0.197458
O	0.499701	-0.214211	-1.225789
O	0.377157	0.548242	0.964450
H	-1.198194	-1.231194	0.240340
C	1.761230	-0.592724	-0.610103
C	1.789628	0.320906	0.700075
C	1.701374	-2.099090	-0.297607
C	2.887272	-0.314019	-1.610354
C	2.421876	-0.340256	1.928660
C	2.427281	1.700238	0.458340

H	1.477984	-2.648443	-1.234439
H	2.663750	-2.475473	0.104501
H	0.898257	-2.333233	0.428764
H	3.880754	-0.511118	-1.156853
H	2.776089	-0.979502	-2.490423
H	2.864109	0.730923	-1.973443
H	3.487145	-0.590338	1.743350
H	2.380359	0.355947	2.791068
H	1.886358	-1.264785	2.215639
H	3.526073	1.632442	0.324501
H	1.996102	2.193196	-0.436200
H	2.225460	2.347584	1.335796
Zn	-2.715728	-0.679498	0.209586
H	-4.249942	-0.604495	0.368954

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