Supporting Information

Low-Valent Tungsten Catalysis Enables Hydroboration of Esters and Nitriles

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1. General Procedures

All manipulations were conducted under a N_2 atmosphere on Schlenk techniques or in a glovebox, unless otherwise stated. In addition to borane purchased from Bide Pharmaceuticals, other pharmaceuticals were purchased from Energy Chemical Company, and used without further purification unless otherwise noted. Dichloromethane, *n*-hexane, tetrahydrofuran, acetonitrile were dried and degassed by Solvent Purification Systems (Innovative Technology). Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. Chromatographic purification of products was accomplished by flash chromatography on silica gel.

^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a JEOL 400M spectrometer. The chemical shifts are reported on ppm relative to either the residual solvent peak or TMS as an internal standard. Coupling constants (*J*) was reported on Hz. Attribution of peaks was performed by using the multiplicity and integrals of the peaks. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentad, sext = sextet, hept = septet, m = multiplet, brs = broad singlet), and coupling constant (Hz). Data for ^{13}C NMR are reported in terms of chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sext = sextet, hept = heptet, m = multiplet. brs = broad singlet), coupling constant (Hz) and no special nomenclature is used for equivalent carbons.

Crystal of **W-2** suitable for X-ray diffraction was obtained by slowly diffusing pentane into the concentrated CH_2Cl_2 solution of **W-2**. The solid structures are shown in **Figure S5**. Single crystals with appropriate dimensions were selected under an optical microscope and quickly coated with high vacuum grease (Dow Corning Corporation) to prevent decomposition. Crystallographic data were collected using a Bruker D8 VENTURE with Mo *Kα* radiation (λ = 0.71073 Å) or micro-focus Cu *Kα* radiation (λ = 1.5418 Å) at 297 K. Crystal data collection and refinement parameters are summarized in **Tables S4**.

2. Experimental Procedures

2.1 General Procedure for Synthesis of $W(CO)_4(NCMe)_2$

To a 100 mL Schlenk flask fitted with a stir bar was added $W(CO)_6$ (3 mmol, 1.056 g) and CH_3CN (40 mL). Slowly introduce nitrogen gas into the flask and the mixture was conducted in an oil bath at 120 °C for 48 h. After removing of the solvent under vacuum, the resulting residue was separated and purified by recrystallization to afford yellow solid (yield, 92%, 1.046 g). ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.07 (s, 1H). ^{13}C{^{1}H}NMR (101 MHz, DMSO-d_6) δ 197.6, 118.6, 1.7. HRMS [ESI-TOF] m/z: $[M+H]^+$ calcd for $C_8H_7N_2O_4W$ 378.9915; found, 378.9920.

2.2 General Method for Catalytic Hydroboration Reactions of Esters

To a 5 mL Schlenk tube fitted with a stir bar was added ester (0.4 mmol), $W(CO)_4(NCMe)_2$ (0.016 mmol, 4 mol%) and HBpin (1.2 mmol, 3.0 equiv.). The tube was sealed and the mixture was conducted in an oil bath at 80 °C for 16 h. Yields were determined by ^{1}H NMR spectroscopy of the crude reaction mixture versus tetraethylsilane as the internal standard.

2.3 General Method for Catalytic Hydroboration Reactions of Nitriles

To a 5 mL Schlenk tube fitted with a stir bar was added nitrile (0.4 mmol), $W(CO)_4(NCMe)_2$ (0.016 mmol, 4 mol%) and HBpin (1.2 mmol, 3.0 equiv.). The tube was sealed and the mixture was conducted in an oil bath at 100 °C for 8 h. Yields were determined by ^{1}H NMR spectroscopy of the crude reaction mixture versus tetraethylsilane as the internal standard.

2.4 General Procedure for Isolation of W-2

To a 10 mL Schlenk tube fitted with a stir bar was added $W(CO)_4(NCMe)_2$ (0.1 mmol, 38 mg), anisonitrile（0.3 mmol, 3.0 equiv）and THF (1 mL). The mixture was conducted in an oil bath at 25 °C for 5 h. After removing of the solvent under vacuum, the resulting residue was separated and purified by recrystallization, affording **W-2** as orange solid (yield, 37%, 14 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.73 (d, J = 9.0 Hz, 2H), 7.07 (d, J = 9.0 Hz, 2H), 3.80 (s, 3H). ^{13}C{^{1}H}NMR (101 MHz, DMSO-d_6) δ 196.7, 163.2, 134.7, 119.7, 115.7, 103.3, 56.2. HRMS [ESI-TOF] m/z: $[M+H]^+$ calcd for $C_{20}H_{15}N_2O_6W$ 563.0439; found, 563.0444. IR (THF): ν_{CO} = 1938, 1894 cm^{-1}, ν_{CN} = 2226 cm^{-1}.

2.5 Spectra of Complex $W(CO)_4(NCMe)_2$

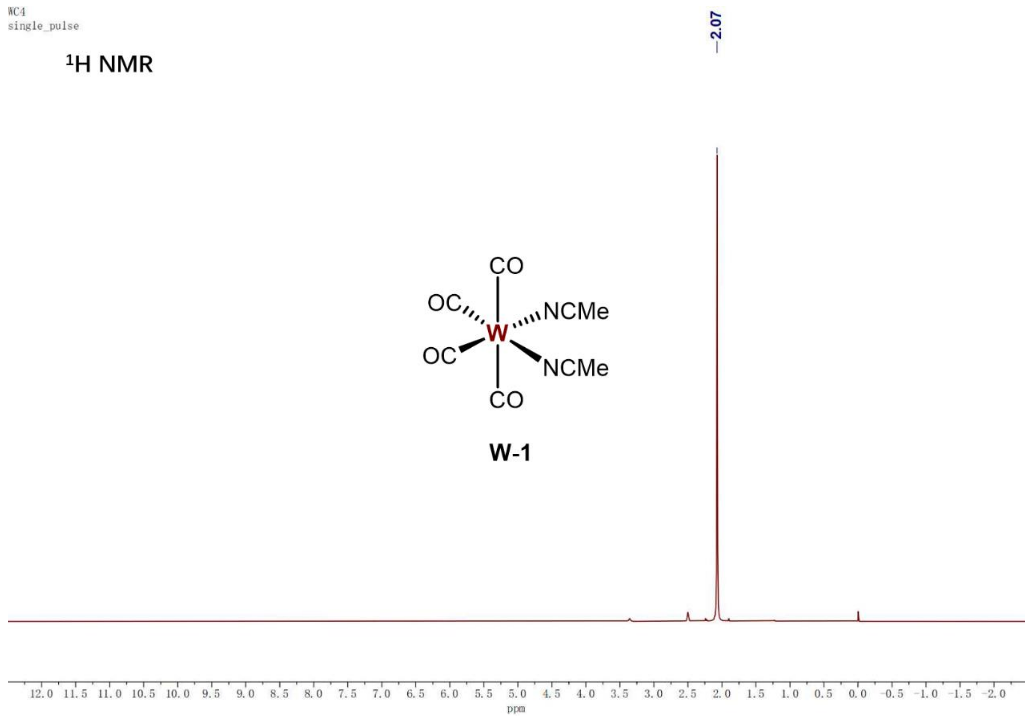


Figure S1. [1]H NMR spectrum of **$W(CO)_4(NCMe)_2$** (400 MHz, DMSO-d_6).

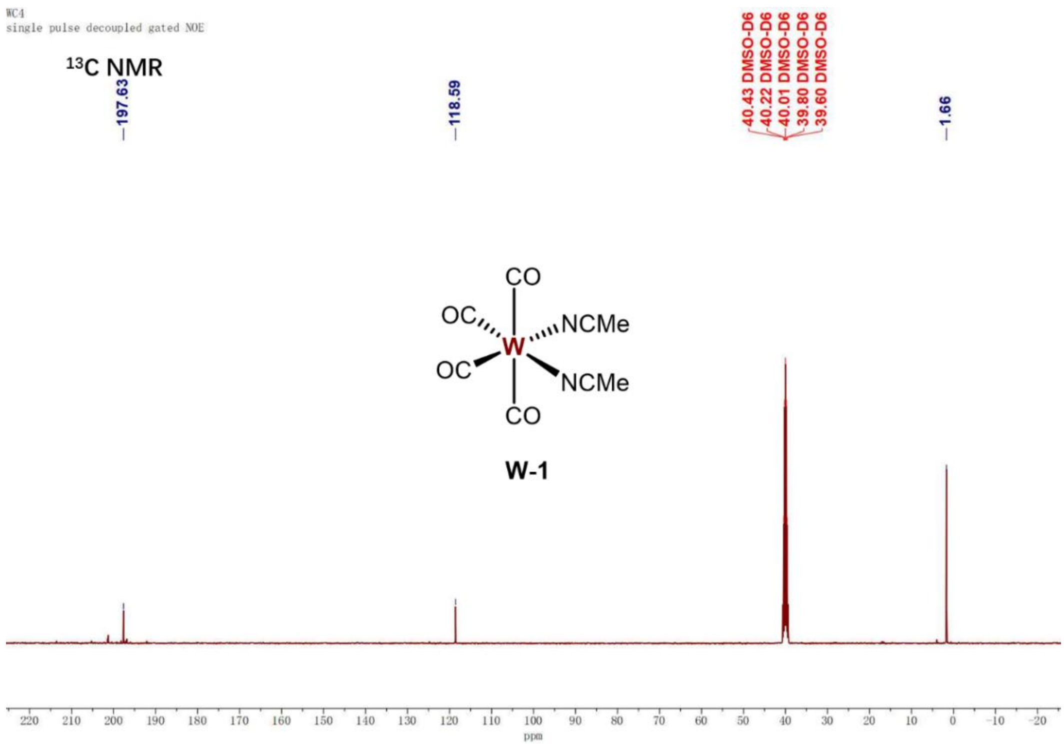


Figure S2. [13]C NMR spectrum of **$W(CO)_4(NCMe)_2$** (101 MHz, DMSO-d_6).

2.6 Spectra of Complex W-2

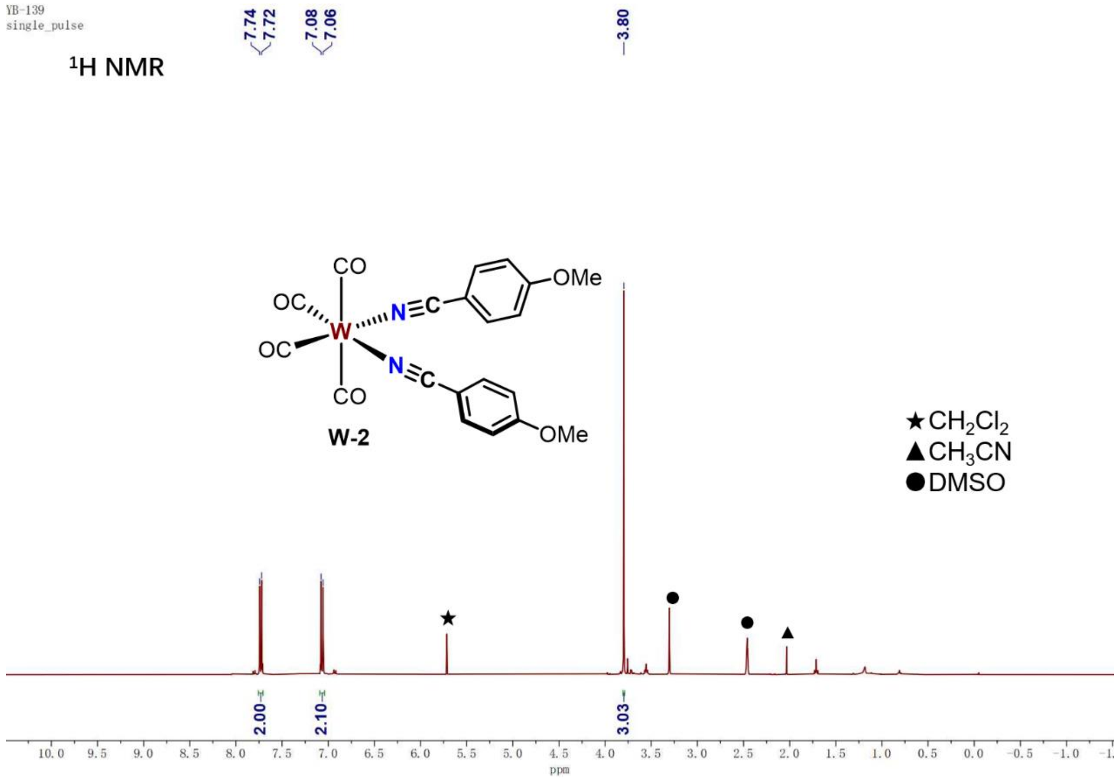


Figure S3. ^{1}H NMR spectrum of **W-2** (400 MHz, DMSO-d_6).

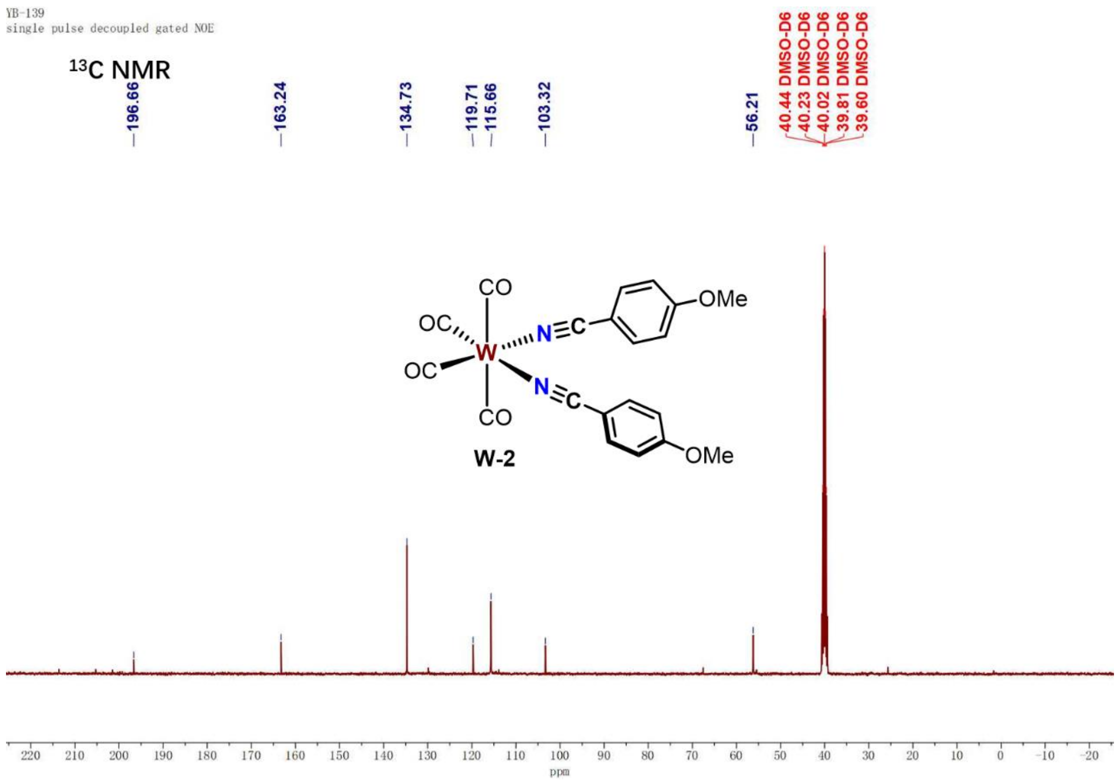


Figure S4. ^{13}C NMR spectrum of **W-2** (101 MHz, DMSO-d_6).

2.7 Solid-Sate Structure of W-2 (CCDC Deposition Number 2320446)

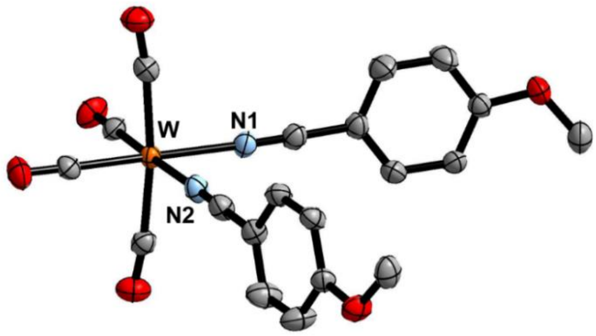
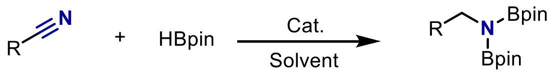


Figure S5. Molecular view of **W-2**. Hydrogen atoms are omitted for clarity.

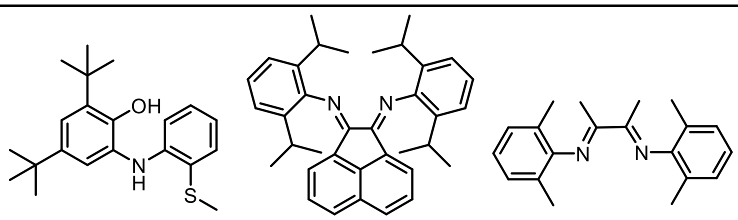
3. Optimization of Catalyzed Hydroboration Reaction of Nitrile

Table S1. Screening of Reaction Conditions.[a]



1a 3 equiv **2a**

entry	Cat. [4 mmol%]	solvent	T [°C]	time [h]	yield for **2a**[b] [%]
1	$W(CO)_4(MeCN)_2$	THF	80	16	82
2	$W(CO)_4(MeCN)_2$	CH_3CN	80	16	12
3	$W(CO)_4(MeCN)_2$	DMA	80	16	19
4	$W(CO)_4(MeCN)_2$	C_6D_6	80	16	97
5	$W(CO)_4(MeCN)_2$	Neat	60	16	32
6	$W(CO)_4(MeCN)_2$	Neat	80	16	86
7	$W(CO)_4(MeCN)_2$	Neat	100	8	>99
8	$W(CO)_4(MeCN)_2$+**1**	Neat	80	16	74
9	$W(CO)_4(MeCN)_2$+**2**	Neat	80	16	46
10	$W(CO)_4(MeCN)_2$+**3**	Neat	80	24	44
11	WCl_6+**3**	Neat	80	16	39
12	$W(CO)_6$	Neat	80	16	10
13	$W(CO)_6$	Neat	100	16	18
14	$W(CO)_6$	Neat	120	16	60
15	no catalyst	Neat	80	16	trace
16	$W(CO)_4(MeCN)_2$(2%)	Neat	80	16	78
17	$W(CO)_4(MeCN)_2$(8%)	Neat	80	16	67



1 **2** **3**

[a]Reaction conditions: benzonitrile **1a** (0.4 mmol), HBpin (3.0 equiv.) and Cat. (4 mol%); [b]Yields were determined by ^{1}H NMR spectroscopy using tetraethylsilane as the internal standard.

4. IR spectroscopy of complex W-2

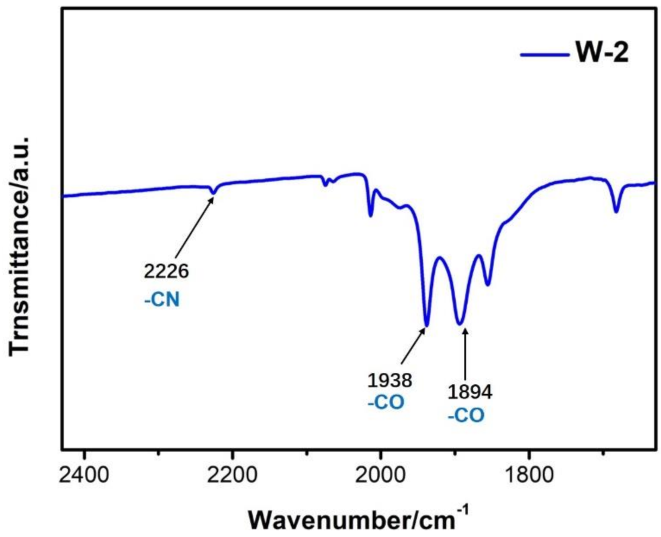
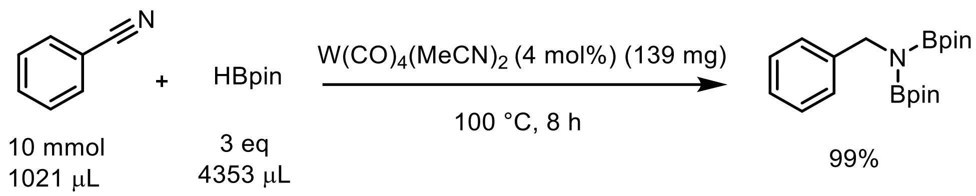
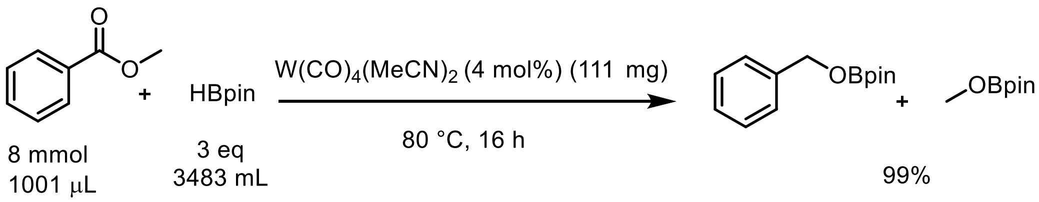


Figure S6. IR spectroscopy of complex **W-2** (in THF).

5. Gram-scale experiments

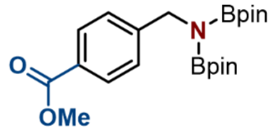


To a 10 mL Schlenk tube fitted with a stir bar was added benzonitrile (10 mmol, 1021 μL), $W(CO)_4(NCMe)_2$ (4 mol%, 139 mg) and HBpin (3.0 equiv., 4353 μL). The tube was sealed and the mixture was conducted in an oil bath at 100 °C for 8 h. Yield was determined by ^{1}H NMR spectroscopy of the crude reaction mixture versus tetraethylsilane as the internal standard.



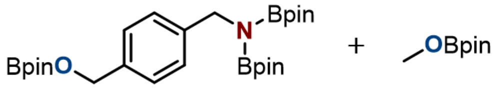
To a 10 mL Schlenk tube fitted with a stir bar was added methyl benzoate (0.4 mmol, 1001 μL), $W(CO)_4(NCMe)_2$ (4 mol%, 111 mg) and HBpin (3.0 equiv., 3483 μL). The tube was sealed and the mixture was conducted in an oil bath at 80 °C for 16 h. Yield was determined by ^{1}H NMR spectroscopy of the crude reaction mixture versus tetraethylsilane as the internal standard.

6. Chemoselective Hydroboration by W-Catalysis



7a

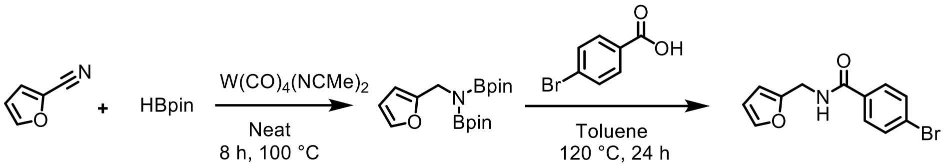
Methyl 4-((bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)amino)methyl) benzoate (7a)[1]**:** To a 100 mL Schlenk tube fitted with a stir bar was added methyl 4-cyanobenzoate (8 mmol, 1.29 g), $W(CO)_4(NCMe)_2$ (0.32 mmol, 4 mol%) and HBpin (20 mmol, 2.5 equiv.). The tube was sealed and the mixture was conducted in an oil bath at 80 °C for 16 h. Yield (90%) was determined by ^{1}H NMR spectroscopy of the crude reaction mixture versus tetraethylsilane as the internal standard. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 4.24 (s, 2H), 3.85 (s, 3H), 1.15 (s, 24H), 0.89 (t, *J* = 8.0 Hz, 13H), 0.47 (q, *J* = 7.9 Hz, 9H). ^{13}C{^{1}H}NMR (101 MHz, Chloroform-*d*) δ 167.3, 148.5, 129.5, 129.3, 128.1, 82.6, 52.0, 47.2, 24.5, 7.5, 3.0.



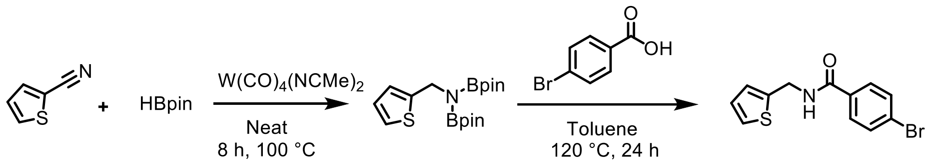
7b

4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-*N*-(4-(((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)benzyl)-1,3,2-dioxaborolan-2-amine (7b)[2]**:** To a 100 mL Schlenk tube fitted with a stir bar was added methyl 4-cyanobenzoate (8 mmol, 1.29 g), $W(CO)_4(NCMe)_2$ (0.64 mmol, 8 mol%) and HBpin (40 mmol, 5 equiv.). The tube was sealed and the mixture was conducted in an oil bath at 80 °C for 16 h. Yield (81%) was determined by ^{1}H NMR spectroscopy of the crude reaction mixture versus tetraethylsilane as the internal standard. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.21 – 7.14 (m, 4H), 4.80 (s, 2H), 4.14 (s, 2H), 3.52 (s, 3H), 1.19 (s, 12H), 1.18 (s, 12H), 1.12 (s, 24H), 0.87 (t, *J* = 8.0 Hz, 15H), 0.44 (q, *J* = 8.0 Hz, 10H). ^{13}C{^{1}H}NMR (101 MHz, Chloroform-*d*) δ 142.3, 137.0, 127.4, 126.4, 82.8, 82.3, 66.6, 52.5, 47.0, 24.6, 24.5, 7.4, 2.9.

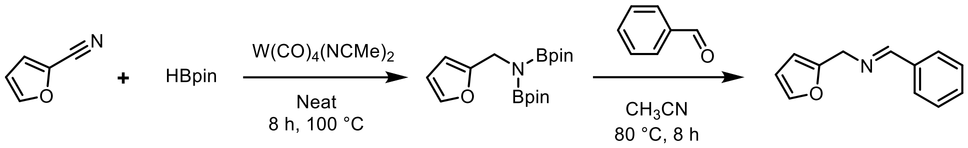
7. One-Pot Synthesis of *N*-Containing Derivatives



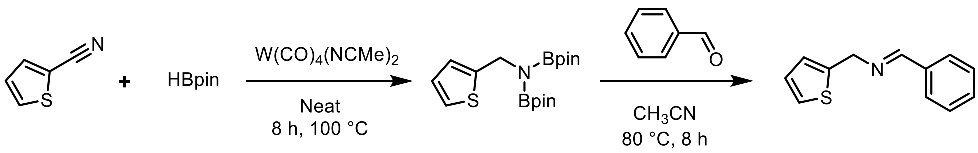
4-Bromo-*N*-(furan-2-ylmethyl) benzamide (7c)[3]: To a 5 mL Schlenk tube fitted with a stir bar was added furan-2-carbonitrile (0.4 mmol, 35 μL), $W(CO)_4(NCMe)_2$ (0.016 mmol, 4 mol%) and HBpin (1.2 mmol, 3.0 equiv.). The tube was sealed and the mixture was conducted in an oil bath at 100 °C for 8 h. Then the Schlenk tube was directly added 4-bromobenzoic acid (0.8 mmol, 161 mg, 2.0 equiv.) and toluene (1mL). The tube was sealed and the mixture was conducted in an oil bath at 120 °C for 24 h, then concentrated under reduced pressure and purified by column chromatography to give **7c**. Yield (96%) was determined by ^{1}H NMR spectroscopy of the crude reaction mixture versus tetraethylsilane as the internal standard. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 8.6 Hz, 2H), 7.51 (d, *J* = 8.6 Hz, 2H), 7.34 (m, 1H), 6.68 (s, 1H), 6.31 (m, 1H), 6.26 (d, *J* = 3.1 Hz, 1H), 4.58 (d, *J* = 5.5 Hz, 2H). ^{13}C{^{1}H}NMR (101 MHz, Chloroform-*d*) δ 166.5, 151.0, 142.5, 133.0, 131.9, 128.8, 126.4, 110.7, 108.0, 37.1.



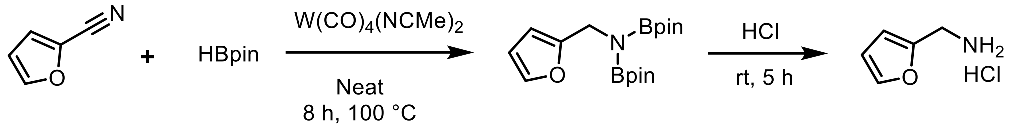
4-Bromo-*N*-(thiophen-2-ylmethyl) benzamide (7d)[3]: To a 5 mL Schlenk tube fitted with a stir bar was added thiophene-2-carbonitrile (0.4 mmol, 37 μL), $W(CO)_4(NCMe)_2$ (0.016 mmol, 4 mol%) and HBpin (1.2 mmol, 3.0 equiv.). The tube was sealed and the mixture was conducted in an oil bath at 100 °C for 8 h. Then the Schlenk tube was directly added 4-bromobenzoic acid (0.8 mmol, 161 mg, 2.0 equiv.) and toluene (1mL). The tube was sealed and the mixture was conducted in an oil bath at 120 °C for 24 h, then concentrated under reduced pressure and purified by column chromatography to give **7d**. Yield (74%) was determined by ^{1}H NMR spectroscopy of the crude reaction mixture versus tetraethylsilane as the internal standard. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 8.6 Hz, 2H), 7.55 (d, *J* = 8.6 Hz, 2H), 7.24 (d, *J* = 1.2 Hz, 1H), 7.03 (d, *J* = 2.5 Hz, 1H), 6.96 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.45 (s, 1H), 4.78 (d, J = 5.5 Hz, 2H). $^{13}C\{^1H\}$NMR (101 MHz, Chloroform-*d*) δ 166.3, 140.5, 133.0, 132.0, 128.7, 127.1, 126.5, 126.5, 125.6, 39.0.



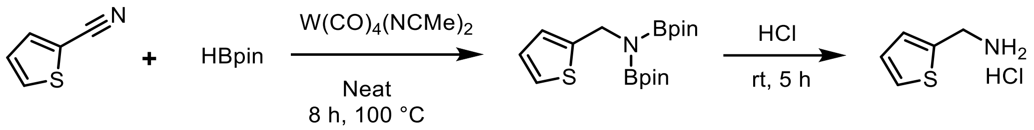
(*E*)-*N*-(furan-2-ylmethyl)-1-phenylmethanimine (7e)[3]: To a 5 mL Schlenk tube fitted with a stir bar was added furan-2-carbonitrile (0.4 mmol, 35 μL), $W(CO)_4(NCMe)_2$ (0.016 mmol, 4 mol%) and HBpin (1.2 mmol, 3.0 equiv.). The tube was sealed and the mixture was conducted in an oil bath at 100 °C for 8 h. Then the Schlenk tube was directly added benzaldehyde (0.8 mmol, 82 μL, 2.0 equiv.) and CH_3CN (0.5mL). The tube was sealed and the mixture was conducted in an oil bath at 80 °C for 8 h. Yield (80%) was determined by ^1H NMR spectroscopy of the crude reaction mixture versus tetraethylsilane as the internal standard. ^1H NMR (400 MHz, Chloroform-*d*) δ 8.32 (s, 1H), 7.73 – 7.76 (m, 2H), 7.51 (m, 4H), 6.33 (m, 1H), 6.28 – 6.24 (m, 1H), 4.77 (s, 2H). $^{13}C\{^1H\}$NMR (101 MHz, Chloroform-*d*) δ 163.4, 152.3, 142.2, 135.9, 131.1, 128.7, 128.5, 110.5, 107.6, 57.2.



(*E*)-1-phenyl-*N*-(thiophen-2-ylmethyl) methanimine (7f)[3]: To a 5 mL Schlenk tube fitted with a stir bar was added thiophene-2-carbonitrile (0.4 mmol, 37 μL), $W(CO)_4(NCMe)_2$ (0.016 mmol, 4 mol%) and HBpin (1.2 mmol, 3.0 equiv.). The tube was sealed and the mixture was conducted in an oil bath at 100 °C for 8 h. Then the Schlenk tube was directly added benzaldehyde (0.8 mmol, 82 μL 2.0 equiv.) and CH_3CN (0.5mL). The tube was sealed and the mixture was conducted in an oil bath at 80 °C for 8 h. Yield (78%) was determined by ^1H NMR spectroscopy of the crude reaction mixture versus tetraethylsilane as the internal standard. ^1H NMR (400 MHz, Chloroform-*d*) δ 8.35 (s, 1H), 7.76 – 7.79 (m, 2H), 7.41 – 7.42 (m, 3H), 7.21 – 7.24 (m, 1H), 6.98 – 6.99 (m, 2H), 4.99 (s, 2H). $^{13}C\{^1H\}$NMR (101 MHz, Chloroform-*d*) δ 162.6, 142.0, 135.9, 131.1, 128.7, 128.5, 127.0, 125.2, 124.9, 59.2.

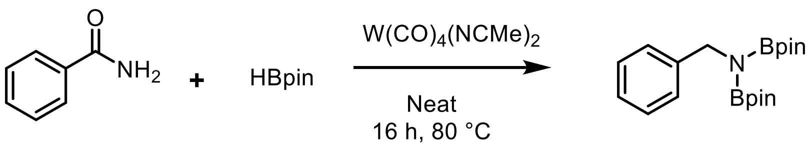


Furan-2-ylmethanamine hydrochloride (7g)[4]: To a 5 mL Schlenk tube fitted with a stir bar was added furan-2-carbonitrile (0.4 mmol, 35 μL), $W(CO)_4(NCMe)_2$ (0.016 mmol, 4 mol%) and HBpin (1.2 mmol, 3.0 equiv.). The tube was sealed and the mixture was conducted in an oil bath at 100 °C for 8 h. Then the Schlenk tube was directly added concentrated HCl (1mL). The reaction mixture was stirred at room temperature for 5 h. Yield (94%) was determined by ^{1}H NMR spectroscopy of the crude reaction mixture versus methanol as the internal standard. ^{1}H NMR (400 MHz, Deuterium Oxide) δ 7.51 (m, 1H), 6.52 – 6.47 (m, 1H), 6.42 (m, 1H), 4.16 (s, 2H). ^{13}C{^{1}H}NMR (101 MHz, Deuterium Oxide) δ 146.1, 144.4, 110.9, 35.7.



Thiophen-2-ylmethanamine hydrochloride (7h)[4]: To a 5 mL Schlenk tube fitted with a stir bar was added thiophene-2-carbonitrile (0.4 mmol, 37 μL), $W(CO)_4(NCMe)_2$ (0.016 mmol, 4 mol%) and HBpin (1.2 mmol, 3.0 equiv.). The tube was sealed and the mixture was conducted in an oil bath at 100 °C for 8 h. Then the Schlenk tube was directly added concentrated HCl (1mL). The reaction mixture was stirred at room temperature for 5 h. Yield (80%) was determined by ^{1}H NMR spectroscopy of the crude reaction mixture versus methanol as the internal standard. ^{1}H NMR (400 MHz, Deuterium Oxide) δ 7.44 (m, 1H), 7.20 – 7.15 (m, 1H), 7.03 (m, 1H), 4.33 (s, 2H). ^{13}C{^{1}H}NMR (101 MHz, Deuterium Oxide) δ 133.7, 129.6, 128.0, 127.8, 37.4.

8. Expansion of the Hydroboration Substrate Scope



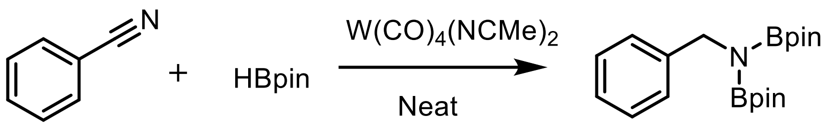
N-benzyl-4,4,5,5-tetramethyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (8b)[5]: To a 5 mL Schlenk tube fitted with a stir bar was added thiophene-2-carbonitrile (0.3 mmol, 36 mg), $W(CO)_4(NCMe)_2$ (0.012 mmol, 4 mol%) and HBpin (1.5 mmol, 5.0 equiv.). The tube was sealed and the mixture was conducted in an oil bath at 80 °C for 16 h. Yield (52%) was determined by ^{1}H NMR spectroscopy of the crude reaction mixture versus tetraethylsilane as the internal standard.

9. Reaction Profiles and Hammett Plot

9.1 Temperature Monitoring of Nitrile

To three 5 mL Schlenk tubes fitted with a stir bar, each of them was added benzonitrile (1.2 mmol, 123 μL), $W(CO)_4(NCMe)_2$ (0.048 mmol, 4 mol%) and HBpin (3.6 mmol, 3.0 equiv.), respectively. The tubes were sealed and were carried out in an oil bath at 100 °C, 80 °C, and 60 °C, respectively.

Table S2. Reaction Conditions.[a]



Entry	Time	Yield (100°C)[b]	Yield (80°C)[b]	Yield (60°C)[b]
1	0	0	0	0
2	10	15%	6%	0
3	30	44%	16%	0
4	50	63%	21%	0
5	80	83%	33%	0
6	110	91%	45%	0
7	170	96%	64%	0
8	230	100%	71%	0
9	350	100%	80%	2%

[a]Reaction conditions: benzonitrile (1.2 mmol), HBpin (3.6mmol) and Cat. (4 mol%); [b]Yield was determined by ^{1}H NMR in reference to internal standard tetraethylsilane.

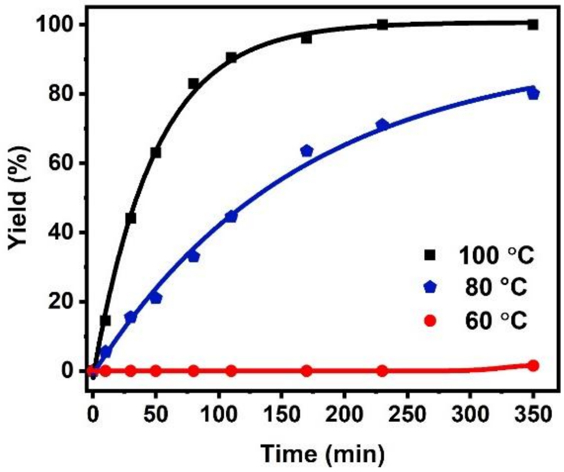
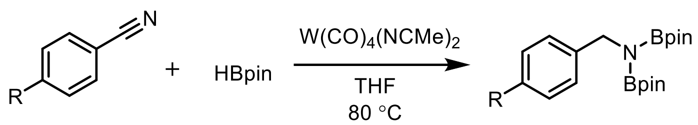


Figure S7. The reaction profiles at different temperatures.

9.2 Hammett Plot

To a 5 mL Schlenk tube fitted with a stir bar was added nitrile (0.2 mmol), $W(CO)_4(NCMe)_2$ (0.08 mmol, 4 mol%) and HBpin (0.6 mmol, 3.0 equiv.). The tube was sealed and the mixture was conducted in an oil bath at 80 °C. ^{1}H NMR spectra were collected at consistent intervals. Reaction was carried out with 6 different aryl substituted nitriles: 4-methoxybenzonitrile, *para*-tolunitrile, 4-bromobenzonitrile, 4-(trifluoromethyl)benzonitrile, 4-(dimethylamino)benzonitrile and benzonitrile.

Table S3. Reaction Conditions.[a]



R	σ^{para}	Time	k_x/k_H [b]	$\lg(k_x/k_H)$
$-OCH_3$	-0.268	10 min	0.29	-0.54
$-CH_3$	-0.17	10 min	0.69	-0.16
-H	0	-	1	0
-F	0.062	5 min	1.6	0.20
-Br	0.232	5 min	2.2	0.34
$-CF_3$	0.54	5 min	5.3	0.72

[a]Reaction conditions: substrate (0.2 mmol), HBpin (0.6 mmol) ,THF (1 mL) and Cat. (4 mol%); 80 °C; [b]Yield was determined by ^{1}H NMR in reference to internal standard tetraethylsilane.

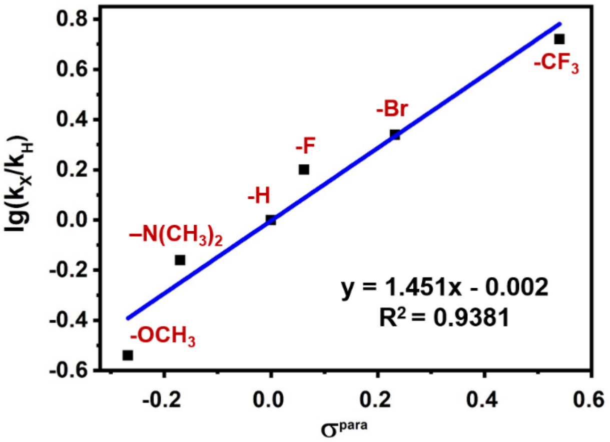


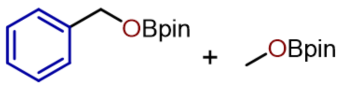
Figure S8. Hammett plot.

10. Investigation of Intermediate W-2

To a 5 mL Schlenk tube fitted with a stir bar was added **W-2** (0.05 mmol, 28 mg) and HBpin (1 mmol, 20 equiv.). The tube was sealed and the mixture was conducted in an oil bath at 80 °C for 8 h. Then, the mixture was analyzed by ^{1}H NMR and 50% of **5g** was detected using tetraethylsilane as the internal standard.

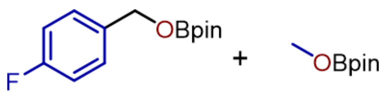
11. Characterization Data of Compounds

11.1 Characterization Data of Ester Compounds



2a **3a**

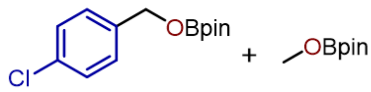
2-(Benzyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2a) + 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3a)[2]**.** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 (m, 4H), 7.25 – 7.19 (m, 1H), 4.90 (s, 2H), 3.57 (s, 3H), 1.23 (s, 12H), 1.23 (s, 12H), 0.90 (t, *J* = 7.9 Hz, 12H), 0.48 (q, *J* = 7.6 Hz, 8H). ^{13}C{^{1}H}NMR (101 MHz, Chloroform-*d*) δ 139.3, 128.3, 127.4, 126.8, 83.0, 82.8, 66.7, 52.6, 24.6, 24.6, 7.5, 3.0.



2b **3b**

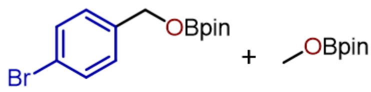
2-((4-Fluorobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2b) + 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3b)[6]**.** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 (m, 2H), 6.97 (t, *J* = 8.8 Hz, 2H), 4.84 (s, 2H), 3.56 (s, 3H), 1.23

(s, 12H), 1.22 (s, 12H), 0.89 (t, J = 7.9 Hz, 12H), 0.46 (q, J = 7.9 Hz, 8H). $^{13}C\{^1H\}$NMR (101 MHz, Chloroform-d) δ 163.5, 161.0, 135.1, 135.0, 128.7, 128.6, 115.3, 115.0, 83.1, 82.8, 66.1, 52.6, 24.6, 24.6, 7.5, 3.0. ^{19}F NMR (376 MHz, Chloroform-d) δ -115.22.



2c **3c**

2-((4-Chlorobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2c) + 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3c)[2]. ^1H NMR (400 MHz, Chloroform-d) δ 7.23 (d, J = 1.0 Hz, 4H), 4.82 (s, 2H), 3.54 (s, 3H), 1.20 (s, 12H), 1.19 (s, 12H), 0.88 (t, J = 7.9 Hz, 12H), 0.45 (q, J = 7.6 Hz, 8H). $^{13}C\{^1H\}$NMR (101 MHz, Chloroform-d) δ 137.8, 133.1, 128.4, 128.1, 83.1, 82.7, 65.9, 52.5, 24.6, 7.4, 3.0.

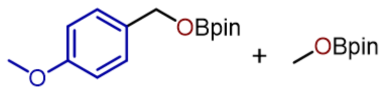


2d **3d**

2-((4-Bromobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2d) + 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3d)[7]. ^1H NMR (400 MHz, Chloroform-d) δ 7.39 (d, J = 8.4 Hz, 2H), 7.17 (d, J = 8.4 Hz, 2H), 4.81 (s, 2H), 3.55 (s, 3H), 1.21 (s, 12H), 1.20 (s, 12H), 0.88 (t, J = 8.0 Hz, 12H), 0.45 (q, J = 8.0 Hz, 8H). $^{13}C\{^1H\}$NMR (101 MHz, Chloroform-d) δ 138.3, 131.4, 128.4, 121.2, 83.1, 82.7, 66.0, 52.6, 24.6, 24.6, 7.4, 3.0.

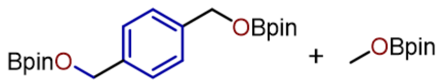
2e **3e**

4,4,5,5-Tetramethyl-2-((4-methylbenzyl)oxy)-1,3,2-dioxaborolane (2e) + 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3e)[2]. ^1H NMR (400 MHz, Chloroform-d) δ 7.21 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 7.8 Hz, 2H), 4.86 (s, 2H), 3.57 (s, 3H), 2.30 (s, 3H), 1.23 (s, 12H), 1.23 (s, 12H), 0.91 (t, J = 7.9 Hz, 12H), 0.48 (q, J = 7.7 Hz, 8H). $^{13}C\{^1H\}$NMR (101 MHz, Chloroform-d) δ 137.0, 136.3, 129.0, 126.9, 82.9, 82.8, 66.6, 52.6, 24.6, 21.1, 7.5, 3.0.



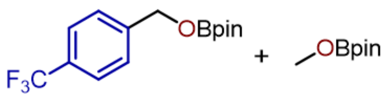
2f 3f

2-((4-Methoxybenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2f) + 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3f)[2]. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24 (d, *J* = 8.7 Hz, 2H), 6.84 – 6.80 (m, 2H), 4.81 (s, 2H), 3.74 (s, 3H), 3.56 (s, 3H), 1.22 (s, 12H), 1.22 (s, 12H), 0.89 (t, *J* = 8.0 Hz, 12H), 0.47 (q, *J* = 7.9 Hz, 8H). $^{13}C\{^{1}H\}$NMR (101 MHz, Chloroform-*d*) δ159.1, 131.5, 128.6, 113.7, 82.9, 82.8, 66.5, 55.2, 52.6, 24.6, 7.5, 3.0.



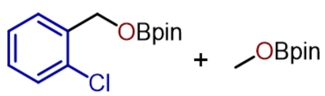
2g 3g

1,4-Bis(((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)benzene (2g) + 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3g)[8]. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.22 (d, *J* = 1.9 Hz, 4H), 4.81 (s, 4H), 3.50 (s, 6H), 1.17 (s, 24H), 1.16 (s, 12H), 0.84 (t, *J* = 7.9 Hz, 12H), 0.42 (q, *J* = 7.7 Hz, 8H). $^{13}C\{^{1}H\}$NMR (101 MHz, Chloroform-*d*) δ 138.4, 126.7, 82.9, 82.7, 66.4, 52.5, 24.6, 24.5, 7.4, 2.9.



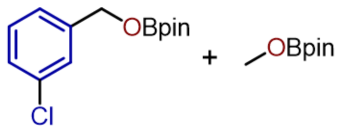
2h 3h

4,4,5,5-Tetramethyl-2-((4-(trifluoromethyl)benzyl)oxy)-1,3,2-dioxaborolane (2h) + 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3h)[2]. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 7.3 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 4.94 (s, 2H), 3.55 (s, 2H), 1.22 (s, 12H), 1.20 (s, 6H), 0.88 (t, *J* = 7.9 Hz, 12H), 0.46 (q, *J* = 7.9 Hz, 8H). $^{13}C\{^{1}H\}$NMR (101 MHz, Chloroform-*d*) δ 143.3, 129.8, 129.4, 126.6, 125.6, 125.3, 122.9, 83.2, 82.8, 65.9, 52.6, 24.6, 7.4, 3.0. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.47.



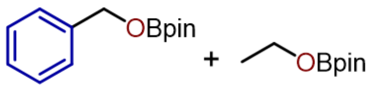
2i 3i

2-((2-Chlorobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2i) + 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3i)[9]. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 (d, *J* = 6.8 Hz, 1H), 7.27 (d, *J* = 9.1 Hz, 1H), 7.24 – 7.19 (m, 1H), 7.18 – 7.12 (m, 1H), 4.98 (s, 2H), 3.55 (s, 3H), 1.23 (s, 12H), 1.21 (s, 12H), 0.88 (t, *J* = 8.0 Hz, 12H), 0.46 (q, *J* = 8.0 Hz, 8H). ^{13}C{^{1}H}NMR (101 MHz, Chloroform-*d*) δ 136.9, 131.9, 128.9, 128.6, 127.7, 126.6, 83.1, 82.8, 64.1, 52.6, 24.6, 24.6, 7.5, 3.0.



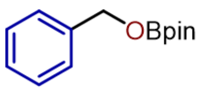
2j **3j**

2-((3-Chlorobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2j) + 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3j)[10]. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 (s, 1H), 7.22 – 7.13 (m, 3H), 4.84 (s, 2H), 3.54 (s, 3H), 1.21 (s, 12H), 1.19 (s, 12H), 0.87 (t, *J* = 8.0 Hz, 12H), 0.45 (q, *J* = 8.0 Hz, 8H). ^{13}C{^{1}H}NMR (101 MHz, Chloroform-*d*) δ 141.3, 134.3, 130.1, 129.2, 128.0, 127.2, 127.0, 126.4, 125.1, 124.2, 83.1, 82.7, 65.9, 52.8, 24.6, 24.6, 7.4, 3.0.



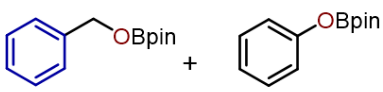
2k **3k**

2-(Benzyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2k) + 2-ethoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3k)[2]. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.24 (m, 4H), 7.20 (t, *J* = 6.7 Hz, 1H), 4.88 (s, 2H), 3.86 (q, *J* = 7.1 Hz, 2H), 1.22 (s, 12H), 1.21 (s, 11H), 1.18 – 1.15 (m, 3H)., 0.90 (t, *J* = 7.9 Hz, 12H), 0.47 (q, *J* = 8.0 Hz, 8H). ^{13}C{^{1}H}NMR (101 MHz, Chloroform-*d*) δ 139.3, 128.3, 127.4, 126.7, 82.9, 82.6, 66.7, 60.6, 24.6, 17.2, 7.4, 3.0.



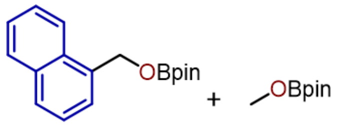
2l

2-(Benzyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2l)[8]. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.30 (m, 8H), 7.25 (t, *J* = 6.8 Hz, 2H), 4.93 (s, 4H), 1.26 (s, 24H), 0.95 (t, *J* = 7.9 Hz, 12H), 0.52 (q, *J* = 8.0 Hz, 8H). ^{13}C{^{1}H}NMR (101 MHz, Chloroform-*d*) δ 139.3, 128.4, 127.5, 126.8, 83.0, 66.7, 24.7, 7.5, 3.0.



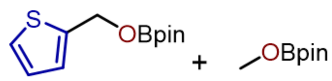
2m **3m**

2-(Benzyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2m) + 4,4,5,5-tetramethyl-2-phenoxy-1,3,2-dioxaborolane (3m)[6]. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.30 (m, 4H), 7.29 – 7.23 (m, 3H), 7.10 (d, *J* = 7.6 Hz, 2H), 7.04 (t, J = 7.4 Hz, 1H), 4.93 (s, 2H), 1.31 (s, 12H), 1.26 (s, 12H), 0.94 (t, J = 8.0 Hz, 12H), 0.51 (q, J = 8.0 Hz, 8H). $^{13}C\{^1H\}$NMR (101 MHz, Chloroform-*d*) δ 153.6, 139.3, 129.4, 128.4, 127.5, 126.8, 123.1, 119.6, 83.6, 83.0, 66.8, 24.7, 24.6, 7.5, 3.0.



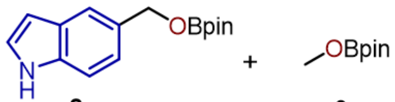
2n **3n**

4,4,5,5-Tetramethyl-2-(naphthalen-1-ylmethoxy)-1,3,2-dioxaborolane (2n) + 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3n)[11]. ^1H NMR (400 MHz, Chloroform-*d*) δ 8.03 (d, J = 7.5 Hz, 1H), 7.84 – 7.81 (m, 1H), 7.76 (d, J = 8.2 Hz, 1H), 7.57 (d, J = 7.0 Hz, 1H), 7.49 – 7.41 (m, 3H), 5.39 (s, 2H), 3.59 (s, 3H), 1.26 (s, 12H), 1.23 (s, 12H), 0.93 (t, J = 7.9 Hz, 12H), 0.51 (q, J = 7.9 Hz, 8H). $^{13}C\{^1H\}$NMR (101 MHz, Chloroform-*d*) δ 134.7, 133.7, 131.1, 128.6, 128.2, 126.1, 125.7, 125.4, 124.9, 123.5, 83.0, 82.8, 65.1, 52.6, 24.7, 24.3, 7.5, 3.0.



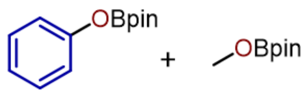
2o **3o**

4,4,5,5-Tetramethyl-2-(thiophen-2-ylmethoxy)-1,3,2-dioxaborolane (2o) + 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3o)[2]. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.17 (d, J = 6.2 Hz, 1H), 6.93 (d, J = 3.0 Hz, 1H), 6.89 – 6.85 (m, 1H), 4.96 (s, 2H), 3.52 (s, 3H), 1.19 (s, 12H), 1.18 (s, 12H), 0.86 (t, J = 8.0 Hz, 14H), 0.44 (q, J = 7.9 Hz, 9H). $^{13}C\{^1H\}$NMR (101 MHz, Chloroform-*d*) δ 142.0, 126.6, 125.9, 125.6, 83.0, 82.7, 61.6, 52.5, 24.6, 24.5, 7.4, 2.9.



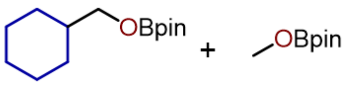
2p **3p**

5-(((4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)-1*H*-indole (2p) + 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3p). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.67 (s, 1H), 7.64 – 7.60 (m, 1H), 7.31 (d, J = 8.4 Hz, 1H), 7.18 – 7.13 (m, 2H), 6.50 – 6.45 (m, 1H), 5.01 (s, 2H), 3.60 (s, 3H), 1.26 (s, 12H), 1.24 (s, 12H), 0.93 (t, J = 8.0 Hz, 14H), 0.50 (q, J = 8.0 Hz, 10H). $^{13}C\{^1H\}$NMR (101 MHz, Chloroform-*d*) δ 135.5, 130.5, 127.9, 124.8, 121.7, 119.6, 111.2, 102.3, 83.1, 82.9, 67.8, 52.7, 24.7, 24.6, 7.5, 3.0. HRMS (TOF MS ES$^+$) calcd for $C_{15}H_{20}BNNaO_3^+$ [M+Na$^+$] m/z 296.1428, found 296.1433.



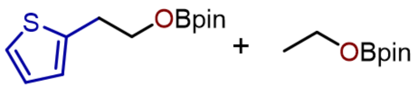
2q **3q**

4,4,5,5-Tetramethyl-2-phenoxy-1,3,2-dioxaborolane (2q) + 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3q)[12]**.** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25 – 7.21 (m, 4H), 7.05 (d, *J* = 7.8 Hz, 4H), 7.00 (t, *J* = 7.4 Hz, 2H), 3.56 (s, 3H), 1.28 (s, 12H), 1.22 (s, 12H), 0.90 (t, *J* = 8.0 Hz, 12H), 0.47 (q, *J* = 7.9 Hz, 8H). ^{13}C{^{1}H}NMR (101 MHz, Chloroform-*d*) δ 153.5, 129.3, 123.1, 119.6, 83.5, 83.1, 52.6, 24.6, 24.6, 7.5, 3.0.



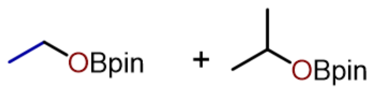
2r **3r**

2-(Cyclohexylmethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2r) + 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3r)[2]**.** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.55 (d, *J* = 6.4 Hz, 2H), 3.50 (s, 3H), 1.63 (m, 6H), 1.42 (m, 1H), 1.17 (s, 12H), 1.15 (s, 12H), 1.10 – 1.03 (m, 2H), 0.95 – 0.86 (m, 2H), 0.84 (t, *J* = 8.0 Hz, 12H), 0.41 (q, *J* = 7.9 Hz, 8H). ^{13}C{^{1}H}NMR (101 MHz, Chloroform-*d*) δ 83.0, 82.5, 70.3, 52.5, 39.3, 29.3, 26.5, 25.8, 24.6, 24.5, 7.4, 2.9.



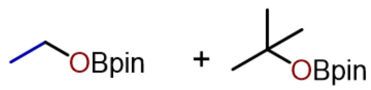
2s **3s**

4,4,5,5-Tetramethyl-2-(2-(thiophen-2-yl)ethoxy)-1,3,2-dioxaborolane (2s) + 2-ethoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3s)[12]**.** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.06 (d, *J* = 5.1 Hz, 1H), 6.87 – 6.84 (m, 1H), 6.79 (d, *J* = 3.3 Hz, 1H), 4.00 (t, *J* = 6.7 Hz, 2H), 3.86 – 3.82 (m, 2H), 3.02 (t, *J* = 6.7 Hz, 2H), 1.21 (s, 12H), 1.19 (s, 12H), 1.13 (m, 3H), 0.87 (t, *J* = 8.0 Hz, 16H), 0.45 (q, *J* = 7.7 Hz, 11H). ^{13}C{^{1}H}NMR (101 MHz, Chloroform-*d*) δ 140.5, 126.7, 125.4, 123.7, 83.1, 82.6, 65.4, 60.6, 32.1, 24.6, 24.6, 17.2, 7.4, 3.0.



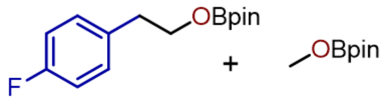
2t 3t

2-Ethoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2t) + 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3t)[10]**.** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.24 (m, 1H), 3.80 (q, *J* = 7.1 Hz, 2H), 1.18 (s, 12H), 1.16 (s, 12H), 1.14 – 1.12 (m, 3H), 1.11 (d, *J* = 6.2 Hz, 6H), 0.84 (t, *J* = 8.0 Hz, 17H), 0.42 (q, *J* = 7.7 Hz, 11H). ^{13}C{^{1}H}NMR (101 MHz, Chloroform-*d*) δ 83.0, 82.4, 67.2, 60.6, 24.8, 24.5, 24.3, 17.2, 7.4, 2.9.



2u 3u

2-Ethoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2u) + 2-(tert-butoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3u)[6]**.** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.78 (q, *J* = 7.1 Hz, 2H), 1.23 (s, 9H), 1.16 (s, 12H), 1.14 (s, 12H), 1.10 (d, *J* = 7.0 Hz, 3H), 0.82 (t, *J* = 8.0 Hz, 14H), 0.40 (q, *J* = 7.8 Hz, 9H). ^{13}C{^{1}H}NMR (101 MHz, Chloroform-*d*) δ 82.9, 81.9, 73.7, 60.5, 29.9, 24.5, 24.4, 17.1, 7.3, 2.9.



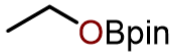
2v 3v

2-(4-Fluorophenethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2v) + 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3v)[13]**.** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.18 – 7.10 (m, 2H), 6.95 – 6.87 (m, 2H), 3.98 (t, *J* = 6.7 Hz, 2H), 3.55 (s, 3H), 2.79 (t, *J* = 6.7 Hz, 2H), 1.21 (s, 12H), 1.14 (s, 12H), 0.88 (t, *J* = 7.9 Hz, 12H), 0.45 (q, *J* = 7.9 Hz, 8H). ^{13}C{^{1}H}NMR (101 MHz, Chloroform-*d*) δ 162.9, 160.4, 134.3, 130.7, 115.1, 83.0, 82.7, 65.6, 52.6, 37.2, 24.6, 24.5, 7.5, 3.0. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -117.26.

2w

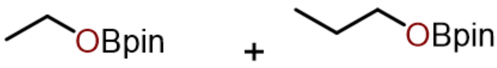
4,4,5,5-Tetramethyl-2-propoxy-1,3,2-dioxaborolane (2w)[14]**.** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.69 (t, *J* = 6.6 Hz, 4H), 1.51 – 1.44 (m, 4H), 1.17 (s, 12H), 1.15 (s, 12H), 0.83 (t, *J* = 7.3 Hz, 12H), 0.80 (d, *J* = 6.5 Hz, 6H), 0.40 (q, *J* = 8.0 Hz, 8H).

$^{13}C\{^1H\}$NMR (101 MHz, Chloroform-*d*) δ 83.0, 82.5, 66.5, 24.6, 24.5, 24.5, 10.0, 7.3, 2.9.



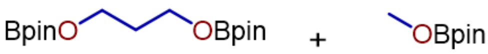
2x

2-Ethoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2x)[6]**.** ^1H NMR (400 MHz, Chloroform-*d*) δ 3.80 (q, *J* = 7.1 Hz, 4H), 1.18 (s, 12H), 1.16 (s, 12H), 1.14 – 1.12 (m, 6H), 0.84 (t, *J* = 8.0 Hz, 16H), 0.42 (q, *J* = 8.0 Hz, 11H). $^{13}C\{^1H\}$NMR (101 MHz, Chloroform-*d*) δ 83.0, 82.5, 60.6, 24.8, 24.5, 17.2, 7.4, 2.9.



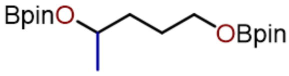
2y **3y**

2-Ethoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2y) + 4,4,5,5-tetramethyl-2-propoxy-1,3,2-dioxaborolane (3y)[14]**.** ^1H NMR (400 MHz, Chloroform-*d*) δ 3.81 (q, *J* = 7.1 Hz, 2H), 3.71 (t, *J* = 6.6 Hz, 2H), 1.53 – 1.45 (m, 2H), 1.18 (s, 12H), 1.17 (s, 12H), 1.14 – 1.13 (m, 3H), 0.84 (t, *J* = 7.3 Hz, 12H), 0.82 (d, *J* = 6.1 Hz, 3H), 0.42 (q, *J* = 7.9 Hz, 8H). $^{13}C\{^1H\}$NMR (101 MHz, Chloroform-*d*) δ 83.0, 82.5, 66.5, 60.6, 24.8, 24.5, 24.5, 17.2, 10.0, 7.4, 2.9.



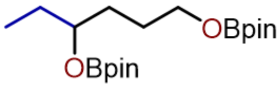
2z **3z**

1,3-Bis((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)propane (2z) + 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3z)[12]**.** ^1H NMR (400 MHz, Chloroform-*d*) δ 3.84 (t, *J* = 6.3 Hz, 4H), 3.50 (s, 3H), 1.76 – 1.71 (m, 2H), 1.16 (s, 10H), 1.15 (s, 24H), 0.83 (t, *J* = 7.9 Hz, 13H), 0.41 (q, *J* = 7.8 Hz, 9H). $^{13}C\{^1H\}$NMR (101 MHz, Chloroform-*d*) δ 82.7, 82.6, 61.5, 52.5, 33.3, 24.6, 24.6, 7.4, 2.9.



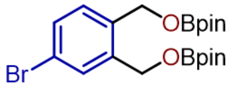
2aa

2,2'-(Pentane-1,4-diylbis(oxy))bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2aa)[15]**.** ^1H NMR (400 MHz, Chloroform-*d*) δ 4.09 (m, 1H), 3.79 – 3.71 (m, 2H), 1.62 – 1.48 (m, 2H), 1.46 – 1.42 (m, 2H), 1.18 (s, 12H), 1.16 (s, 12H), 1.10 (d, *J* = 6.2 Hz, 3H), 0.84 (t, *J* = 7.9 Hz, 16H), 0.41 (q, *J* = 7.9 Hz, 11H). $^{13}C\{^1H\}$NMR (101 MHz, Chloroform-*d*) δ 83.0, 82.4, 70.5, 64.8, 34.1, 27.5, 24.6, 24.5, 22.6, 7.4, 2.9.



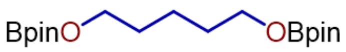
2ab

2,2'-(hexane-1,4-diylbis(oxy))bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2ab)[18]**.** ^1H NMR (400 MHz, Chloroform-*d*) δ 3.88 (s, 1H), 3.83 – 3.70 (m, 2H), 1.57 – 1.38 (m, 6H), 1.19 (s, 12H), 1.17 (s, 12H), 0.87 – 0.84 (m, 13H), 0.83 – 0.82 (m, 3H), 0.42 (m, 8H). $^{13}C\{^1H\}$NMR (101 MHz, Chloroform-*d*) δ 82.9, 82.4, 75.5, 64.8, 32.0, 29.3, 27.5, 24.6, 24.5, 9.7, 7.4, 2.9.



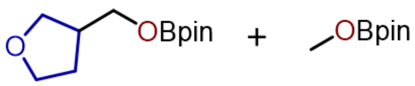
2ac

2,2'-(((4-Bromo-1,2-phenylene)bis(methylene))bis(oxy))bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2ac). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.57 (s, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.25 (d, *J* = 8.2 Hz, 1H), 4.88 (s, 2H), 4.83 (s, 2H), 1.21 (s, 12H), 1.20 (s, 12H), 0.87 (t, *J* = 8.0 Hz, 13H), 0.45 (q, *J* = 8.4, 7.9 Hz, 8H). $^{13}C\{^1H\}$NMR (101 MHz, Chloroform-*d*) δ 138.7, 135.1, 130.3, 129.9, 129.0, 121.6, 83.1, 63.6, 63.3, 24.6, 7.5, 3.0. HRMS (TOF MS ES$^+$) calcd for $C_{19}H_{29}B_2BrNaO_6^+$ [M+Na$^+$] m/z 477.1226, found 477.1230.



2ad

1,5-Bis((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)pentane (2ad)[8]**.** ^1H NMR (400 MHz, Chloroform-*d*) δ 3.77 (q, *J* = 6.5 Hz, 4H), 1.56 – 1.47 (m, 4H), 1.35 (m, 2H), 1.20 (s, 24H), 0.90 – 0.83 (m, 12H), 0.51 – 0.39 (m, 8H). $^{13}C\{^1H\}$NMR (101 MHz, Chloroform-*d*) δ 82.6, 64.8, 31.1, 24.6, 21.7, 7.4, 3.0.

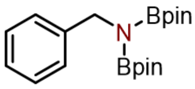


2ae **3ae**

4,4,5,5-tetramethyl-2-((tetrahydrofuran-3-yl)methoxy)-1,3,2-dioxaborolane (2ae) + 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3ae)[12]**.** ^1H NMR (400

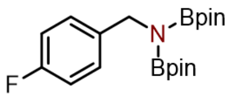
MHz, Chloroform-*d*) δ 3.83 – 3.57 (m, 6H), 3.50 (d, *J* = 4.6 Hz, 3H), 3.48 (d, *J* = 5.6 Hz, 1H), 2.40 (p, *J* = 7.4 Hz, 1H), 1.94 – 1.83 (m, 1H), 1.51 (dq, *J* = 12.1, 6.5 Hz, 1H), 1.17 (s, 12H), 1.16 (s, 12H), 0.83 (t, *J* = 8.0 Hz, 13H), 0.41 (q, *J* = 8.0 Hz, 9H). $^{13}C\{^1H\}$NMR (101 MHz, Chloroform-*d*) δ 83.0, 82.8, 70.4, 67.7, 66.6, 52.5, 40.6, 28.6, 24.6, 24.5, 7.4, 2.9. [M+Na$^+$] m/z 228.1533, found 228.1530.

11.2. Characterization Data of Nitriles Compounds



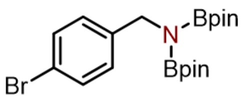
5a

***N*-benzyl-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (5a)**[2]**.** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 7.1 Hz, 2H), 7.23 (t, *J* = 7.4 Hz, 2H), 7.15 (t, *J* = 7.2 Hz, 1H), 4.22 (s, 2H), 1.19 (s, 24H), 0.92 (t, *J* = 8.0 Hz, 12H), 0.50 (q, *J* = 8.0 Hz, 8H). $^{13}C\{^1H\}$NMR (101 MHz, Chloroform-*d*) δ 143.1, 127.9, 127.6, 126.1, 82.4, 47.3, 24.6, 7.5, 3.0.



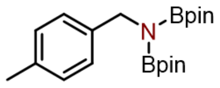
5b

***N*-(4-fluorobenzyl)-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (5b)**[2]**.** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 – 7.22 (m, 2H), 6.90 (t, *J* = 8.8 Hz, 2H), 4.16 (s, 2H), 1.18 (s, 24H), 0.91 (t, *J* = 8.0 Hz, 12H), 0.49 (q, *J* = 7.9 Hz, 8H). $^{13}C\{^1H\}$NMR (101 MHz, Chloroform-*d*) δ 162.9, 160.4, 138.9, 129.2, 114.4, 82.5, 46.6, 24.6, 7.5, 3.0. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -117.43.



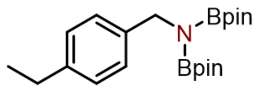
5c

***N*-(4-bromobenzyl)-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (5c)**[2]**.** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 4.15 (s, 2H), 1.18 (s, 24H), 0.91 (t, *J* = 7.9 Hz, 13H), 0.49 (q, *J* = 7.9 Hz, 8H). $^{13}C\{^1H\}$NMR (101 MHz, Chloroform-*d*) δ 142.2, 130.9, 129.4, 120.0, 82.5, 46.8, 24.6, 7.5, 3.0.



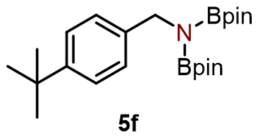
5d

4,4,5,5-Tetramethyl-*N*-(4-methylbenzyl)-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (5d)[2]**.** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.19 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 7.9 Hz, 2H), 4.18 (s, 2H), 2.29 (s, 3H), 1.19 (s, 24H), 0.92 (t, *J* = 8.0 Hz, 12H), 0.50 (q, *J* = 7.9 Hz, 8H). ^{13}C{^{1}H}NMR (101 MHz, Chloroform-*d*) δ 140.1, 135.5, 128.6, 127.5, 82.4, 47.0, 24.6, 21.1, 7.5, 3.0.



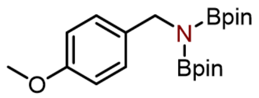
5e

***N*-(4-ethylbenzyl)-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (5e).** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24 (d, *J* = 8.1 Hz, 2H), 7.07 (d, *J* = 8.1 Hz, 2H), 4.21 (s, 2H), 2.60 (q, *J* = 7.6 Hz, 2H), 1.27 (d, *J* = 1.4 Hz, 3H), 1.20 (s, 24H), 0.95 (t, *J* = 8.0 Hz, 12H), 0.52 (q, *J* = 8.0 Hz, 8H). ^{13}C{^{1}H}NMR (101 MHz, Chloroform-*d*) δ 141.9, 140.5, 127.7, 127.3, 82.3, 47.0, 28.6, 24.6, 15.8, 7.5, 3.0. HRMS (TOF MS ES^{+}) calcd for $C_{21}H_{35}B_2NNaO_4^{+}$ [M+Na^{+}] m/z 410.2644, found 410.2638.



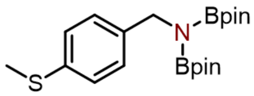
5f

***N*-(4-(tert-butyl)benzyl)-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (5f)**[10]**.** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25 (d, *J* = 1.5 Hz, 4H), 4.20 (s, 2H), 1.30 (s, 9H), 1.20 (s, 24H), 0.93 (t, *J* = 7.9 Hz, 13H), 0.51 (q, *J* = 7.9 Hz, 9H). ^{13}C{^{1}H}NMR (101 MHz, Chloroform-*d*) δ 148.9, 140.2, 127.4, 124.7, 82.4, 46.9, 34.4, 31.5, 24.6, 7.5, 3.0.



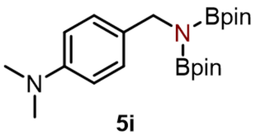
5g

***N*-(4-methoxybenzyl)-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (5g)**[2]**.** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24 (d, *J* = 8.7 Hz, 2H), 6.78 (d, *J* = 8.7 Hz, 2H), 4.15 (s, 2H), 3.77 (s, 3H), 1.20 (s, 24H), 0.93 (t, *J* = 7.9 Hz, 13H), 0.50 (q, *J* = 7.9 Hz, 9H). $^{13}C\{^1H\}$NMR (101 MHz, Chloroform-*d*) δ 158.1, 135.6, 128.9, 113.2, 82.3, 55.3, 46.7, 24.6, 7.5, 3.0.



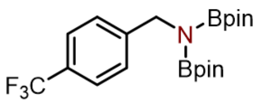
5h

4,4,5,5-Tetramethyl-*N*-(4-(methylthio)benzyl)-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (5h)[2]**.** ^1H NMR (400 MHz, Chloroform-*d*) δ 7.23 (d, *J* = 8.5 Hz, 2H), 7.15 (d, *J* = 8.5 Hz, 2H), 4.17 (s, 2H), 2.45 (s, 3H), 1.19 (s, 24H), 0.92 (t, *J* = 7.9 Hz, 15H), 0.50 (q, *J* = 8.0 Hz, 10H). $^{13}C\{^1H\}$NMR (101 MHz, Chloroform-*d*) δ 140.4, 135.5, 128.7, 128.1, 127.8, 127.2, 126.9, 126.5, 126.3, 82.4, 46.9, 24.6, 16.4, 7.5, 3.0.



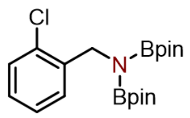
5i

***N*-(4-(dimethylamino)benzyl)-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (5i)**[2]**.** ^1H NMR (400 MHz, Chloroform-*d*) δ 7.21 (d, *J* = 8.7 Hz, 2H), 6.65 (d, *J* = 8.6 Hz, 2H), 4.13 (s, 2H), 2.90 (s, 6H), 1.21 (s, 24H), 0.93 (t, *J* = 8.0 Hz, 12H), 0.51 (q, *J* = 8.0 Hz, 8H). $^{13}C\{^1H\}$NMR (101 MHz, Chloroform-*d*) δ 149.4, 131.9, 128.7, 112.6, 82.2, 46.6, 41.0, 24.6, 7.5, 3.0.



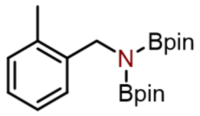
5j

4,4,5,5-Tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-*N*-(4-(trifluoromethyl)benzyl)-1,3,2-dioxaborolan-2-amine (5j)[2]**.** ^1H NMR (400 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 8.1 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 4.27 (s, 2H), 1.19 (s, 24H), 0.92 (t, *J* = 7.9 Hz, 12H), 0.50 (q, *J* = 7.7 Hz, 8H). $^{13}C\{^1H\}$NMR (101 MHz, Chloroform-*d*) δ 147.2, 132.8, 128.6, 127.7, 127.0, 124.9, 82.6, 47.0, 24.6, 24.5, 7.5, 3.0. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.25.



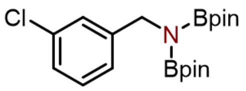
5k

***N*-(2-chlorobenzyl)-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (5k)[17].** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.22 (m, 2H), 7.20 – 7.13 (m, 1H), 7.13 – 7.06 (m, 1H), 4.33 (s, 2H), 1.17 (s, 24H), 0.92 (t, *J* = 8.0 Hz, 14H), 0.49 (q, *J* = 7.9 Hz, 9H). ^{13}C{^{1}H}NMR (101 MHz, Chloroform-*d*) δ 140.1, 132.8, 128.9, 127.3, 127.1, 126.3, 82.5, 45.2, 24.5, 7.5, 3.0.



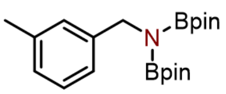
5l

4,4,5,5-Tetramethyl-*N*-(2-methylbenzyl)-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (5l)[2]. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24 (d, *J* = 7.2 Hz, 1H), 7.12 (m, 1H), 7.07 (d, *J* = 3.8 Hz, 2H), 4.23 (s, 2H), 2.31 (s, 3H), 1.18 (s, 24H), 0.94 (t, *J* = 7.9 Hz, 13H), 0.51 (q, *J* = 7.9 Hz, 9H). ^{13}C{^{1}H}NMR (101 MHz, Chloroform-*d*) δ 140.7, 135.3, 129.5, 126.2, 125.8, 125.5, 82.4, 44.9, 24.5, 19.2, 7.5, 3.0.



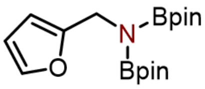
5m

***N*-(3-chlorobenzyl)-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (5m)[17].** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 (s, 1H), 7.20 – 7.08 (m, 3H), 4.17 (s, 2H), 1.19 (s, 24H), 0.91 (t, *J* = 8.0 Hz, 13H), 0.49 (q, *J* = 7.9 Hz, 8H). ^{13}C{^{1}H}NMR (101 MHz, Chloroform-*d*) δ 145.2, 133.7, 129.2, 127.9, 126.3, 125.8, 82.6, 46.9, 24.6, 7.5, 3.0.



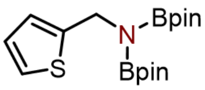
5n

4,4,5,5-Tetramethyl-*N*-(3-methylbenzyl)-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (5n)[2]. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.12 (m, 3H), 6.97 (d, *J* = 7.1 Hz, 1H), 4.20 (s, 2H), 2.30 (s, 3H), 1.21 (s, 24H), 0.93 (t, *J* = 7.9 Hz, 13H), 0.54 – 0.48 (m, 9H). $^{13}C\{^{1}H\}$NMR (101 MHz, Chloroform-*d*) δ 143.0, 137.3, 128.4, 127.8, 126.8, 124.6, 82.4, 47.2, 24.6, 21.5, 7.5, 3.0.



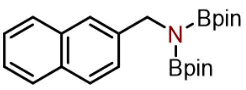
5o

***N*-(furan-2-ylmethyl)-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (5o)[2].** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.21 (m, 1H), 6.19 (m, 1H), 6.01 (m, 1H), 4.16 (s, 2H), 1.18 (s, 12H), 1.18 (s, 12H), 0.90 (t, *J* = 8.0 Hz, 12H), 0.47 (q, *J* = 7.9 Hz, 8H). $^{13}C\{^{1}H\}$NMR (101 MHz, Chloroform-*d*) δ 156.6, 140.8, 110.0, 105.2, 82.5, 40.7, 24.5, 7.5, 3.0.



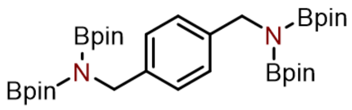
5p

4,4,5,5-Tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-*N*-(thiophen-2-ylmethyl)-1,3,2-dioxaborolan-2-amine (5p)[2]. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.09 (m, 1H), 6.91 (m, 1H), 6.86 (m, 1H), 4.37 (s, 2H), 1.22 (s, 24H), 0.93 (t, *J* = 7.9 Hz, 14H), 0.50 (q, *J* = 7.7 Hz, 10H). $^{13}C\{^{1}H\}$NMR (101 MHz, Chloroform-*d*) δ 146.9, 126.3, 124.7, 123.6, 82.6, 42.2, 24.6, 7.5, 3.0.



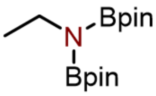
5q

4,4,5,5-Tetramethyl-*N*-(naphthalen-2-ylmethyl)-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (5q)[18]. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 – 7.73 (m, 4H), 7.48 – 7.40 (m, 3H), 4.43 (s, 2H), 1.22 (s, 24H), 0.95 (t, *J* = 7.9 Hz, 14H), 0.53 (q, *J* = 7.9 Hz, 9H). $^{13}C\{^{1}H\}$NMR (101 MHz, Chloroform-*d*) δ 140.6, 133.6, 132.4, 127.8, 127.6, 127.5, 126.5, 125.6, 125.5, 125.1, 82.5, 47.4, 24.6, 7.5, 3.0.



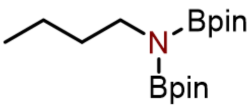
5r

***N*,*N*'-(1,4-phenylenebis(methylene))bis(4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine) (5r)[1].** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.16 – 7.10 (m, 4H), 4.16 (s, 4H), 1.17 (s, 48H),), 0.90 (t, *J* = 7.9 Hz, 14H), 0.48 (q, *J* = 7.7 Hz, 9H). ^{13}C{^{1}H}NMR (101 MHz, Chloroform-*d*) δ 140.8, 127.0, 82.3, 47.0, 24.5, 7.5, 3.0.



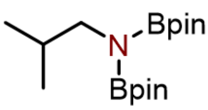
5s

***N*-ethyl-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (5s)[2].** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.03 (q, *J* = 7.0 Hz, 2H), 1.21 (s, 24H), 1.00 (t, *J* = 7.1 Hz, 3H), 0.90 (t, *J* = 7.9 Hz, 12H), 0.48 (d, *J* = 8.0 Hz, 8H). ^{13}C{^{1}H}NMR (101 MHz, Chloroform-*d*) δ 82.1, 38.7, 24.6, 18.7, 7.5, 3.0.



5t

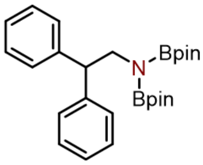
***N*-butyl-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (5t)[9].** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.00 (t, *J* = 6.8 Hz, 2H), 1.36 – 1.30 (m, 3H), 1.20 (s, 24H), 0.90 (t, *J* = 7.9 Hz, 13H), 0.85 (t, *J* = 7.2 Hz, 4H), 0.48 (q, *J* = 7.7 Hz, 9H). ^{13}C{^{1}H}NMR (101 MHz, Chloroform-*d*) δ 82.0, 43.3, 35.4, 24.5, 19.7, 14.1, 7.5, 3.0.



5u

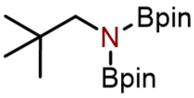
***N*-isobutyl-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (5u)[2].** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.82 (d, *J* = 7.0 Hz, 2H), 1.60 (m, 1H), 1.19 (s, 24H), 0.90 (t, *J* = 7.9 Hz, 13H), 0.80 (d, *J* = 6.7

Hz, 6H), 0.48 (q, *J* = 8.0 Hz, 8H). ^{13}C{^{1}H}NMR (101 MHz, Chloroform-*d*) δ 82.1, 51.1, 30.8, 24.5, 20.0, 7.5, 3.0.



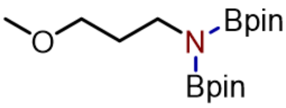
5v

***N*-(2,2-diphenylethyl)-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (5v)**[2]**.** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24 (q, *J* = 2.7 Hz, 8H), 7.13 (m, 2H), 4.20 (t, *J* = 7.9 Hz, 1H), 3.69 (d, *J* = 7.9 Hz, 2H), 1.15 (s, 24H), 0.93 (t, *J* = 8.0 Hz, 13H), 0.50 (q, *J* = 7.9 Hz, 9H). ^{13}C{^{1}H}NMR (101 MHz, Chloroform-*d*) δ 143.5, 128.8, 128.3, 126.1, 82.2, 53.6, 48.5, 24.5, 7.5, 3.0.



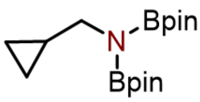
5w

4,4,5,5-Tetramethyl-*N*-neopentyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (5w)[19]**.** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.86 (s, 2H), 1.20 (s, 24H), 0.91 (t, *J* = 7.9 Hz, 13H), 0.80 (s, 9H), 0.49 (q, *J* = 7.7 Hz, 9H). ^{13}C{^{1}H}NMR (101 MHz, Chloroform-*d*) δ 82.2, 54.5, 33.2, 27.3, 24.5, 7.5, 3.0.



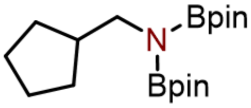
5x

***N*-(3-methoxypropyl)-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (5x)**[9]**.** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.29 (t, *J* = 7.0 Hz, 2H), 3.23 (s, 3H), 3.02 (t, *J* = 6.8 Hz, 2H), 1.62 (m, 2H), 1.15 (s, 24H), 0.85 (t, *J* = 7.9 Hz, 12H), 0.49 – 0.37 (m, 8H). ^{13}C{^{1}H}NMR (101 MHz, Chloroform-*d*) δ 82.1, 70.7, 58.4, 40.6, 32.9, 24.5, 7.4, 3.0.



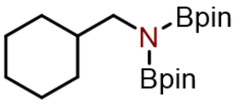
5y

***N*-(cyclopropylmethyl)-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (5y)**[2]**.** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.85 (d, *J* = 6.8 Hz, 2H), 1.18 (s, 24H), 1.02 – 0.90 (m, 1H), 0.87 (t, *J* = 7.9 Hz, 13H), 0.45 (q, *J* = 7.9 Hz, 8H), 0.26 (m, 2H), 0.18 – 0.11 (m, 2H). $^{13}C\{^1H\}$NMR (101 MHz, Chloroform-*d*) δ 82.1, 48.0, 24.5, 14.2, 7.4, 3.2, 3.0.



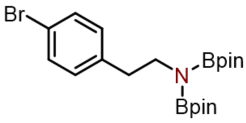
5z

***N*-(cyclopentylmethyl)-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (5z)[1].** ^1H NMR (400 MHz, Chloroform-*d*) δ 2.93 (d, *J* = 7.4 Hz, 2H), 1.89 (m, 1H), 1.67 – 1.37 (m, 8H), 1.19 (s, 24H), 0.90 (t, *J* = 7.9 Hz, 13H), 0.48 (q, *J* = 7.6 Hz, 9H). $^{13}C\{^1H\}$NMR (101 MHz, Chloroform-*d*) δ 82.1, 48.2, 42.9, 29.8, 25.0, 24.5, 7.5, 3.0.



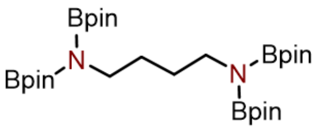
5aa

***N*-(cyclohexylmethyl)-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (5aa)[2].** ^1H NMR (400 MHz, Chloroform-*d*) δ 2.85 (d, *J* = 6.9 Hz, 2H), 1.65 (d, *J* = 10.1 Hz, 4H), 1.59 (s, 1H), 1.25 (s, 4H), 1.19 (s, 24H), 1.12 (d, *J* = 6.8 Hz, 2H), 0.90 (t, *J* = 7.9 Hz, 13H), 0.48 (q, *J* = 7.7 Hz, 9H). $^{13}C\{^1H\}$NMR (101 MHz, Chloroform-*d*) δ 82.0, 49.8, 40.6, 30.6, 26.9, 26.2, 24.5, 7.5, 3.0.



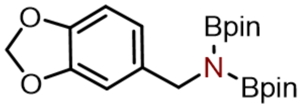
5ab

***N*-(4-bromophenethyl)-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (5ab)[20].** ^1H NMR (400 MHz, Chloroform-*d*) δ 7.31 (d, *J* = 8.3 Hz, 2H), 7.00 (d, *J* = 8.3 Hz, 2H), 3.23 (t, *J* = 6.9 Hz, 2H), 2.62 (t, *J* = 6.9 Hz, 2H), 1.13 (s, 24H), 0.89 (t, *J* = 8.0 Hz, 12H), 0.47 (q, *J* = 7.9 Hz, 8H). $^{13}C\{^1H\}$NMR (101 MHz, Chloroform-*d*) δ 139.4, 131.2, 131.1, 119.6, 82.1, 44.9, 38.7, 24.5, 7.5, 3.0.



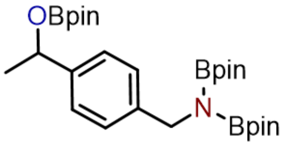
5ac

N^1,N^1,N^4,N^4-tetrakis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butane-1,4-diamine (5ac)[21]. ^1H NMR (400 MHz, Chloroform-*d*) δ 2.96 (s, 4H), 1.34 – 1.31 (m, 4H), 1.18 (s, 48H), 0.89 (t, *J* = 7.9 Hz, 13H), 0.47 (q, *J* = 7.9 Hz, 8H). $^{13}C\{^1H\}$NMR (101 MHz, Chloroform-*d*) δ 83.1, 82.0, 43.79,41.0, 30.6, 30.3, 24.6, 24.5, 7.5, 3.0.



5ad

***N*-(benzo[d][1,3]dioxol-5-ylmethyl)-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (5ad).** ^1H NMR (400 MHz, Chloroform-*d*) δ 6.83 (d, *J* = 1.6 Hz, 1H), 6.76 (m, 1H), 6.65 (d, *J* = 7.9 Hz, 1H), 5.86 (s, 2H), 4.10 (s, 2H), 1.18 (s, 24H), 0.91 (t, *J* = 8.0 Hz, 12H), 0.48 (q, *J* = 8.0 Hz, 8H). $^{13}C\{^1H\}$NMR (101 MHz, Chloroform-*d*) δ 137.3, 120.9, 108.5, 107.6, 100.7, 82.4, 47.1, 24.6, 7.5, 3.0. [M+Na$^+$] m/z 403.2337, found 403.2332.



5ae

4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-*N*-(4-(1-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)ethyl)benzyl)-1,3,2-dioxaborolan-2-amine (2ae)[22]**.** ^1H NMR (400 MHz, Chloroform-*d*) δ 7.24 – 7.17 (m, 4H), 5.18 (q, *J* = 6.4 Hz, 1H), 4.18 (s, 2H), 1.44 (d, *J* = 6.5 Hz, 3H), 1.20 (s, 12H), 1.17 (s, 24H), 0.90 (t, *J* = 8.0 Hz, 14H), 0.48 (q, *J* = 7.9 Hz, 10H). $^{13}C\{^1H\}$NMR (101 MHz, Chloroform-*d*) δ 142.4, 142.0, 127.4, 124.9, 82.6, 82.3, 72.6, 47.0, 24.9, 24.6, 24.5, 7.5, 3.0.

12. NMR Spectra (● stand for another product; ▲ stand for internal standard tetraethylsilane)

12.1. NMR Spectra for Esters

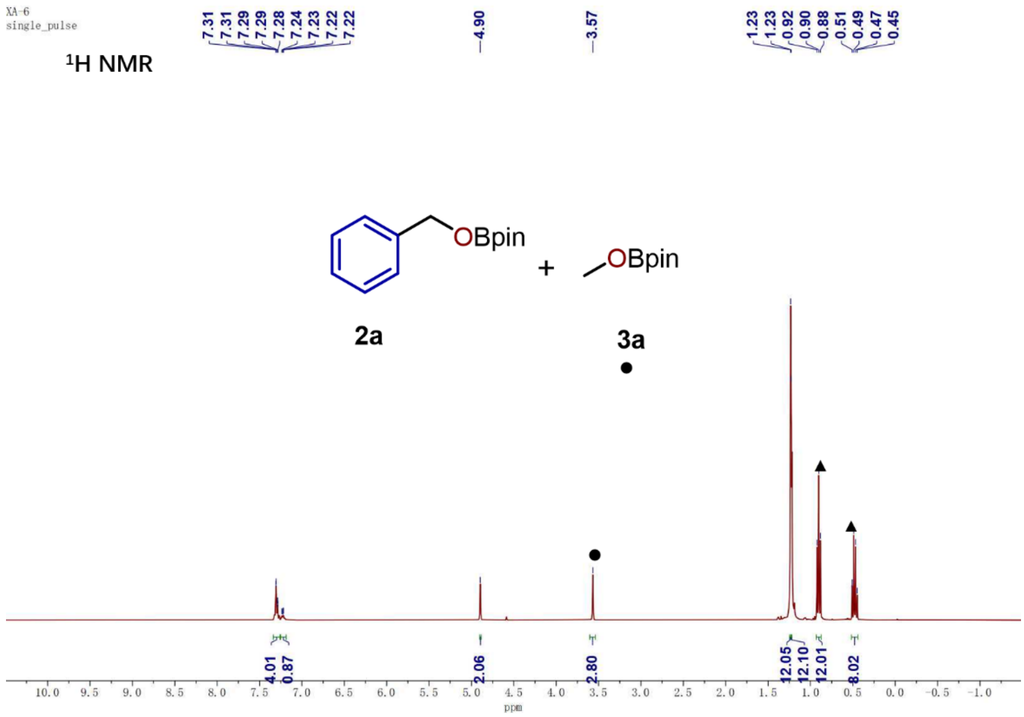


Figure S9. ^{1}H NMR spectrum of **2a** (400 MHz, Chloroform-*d*).

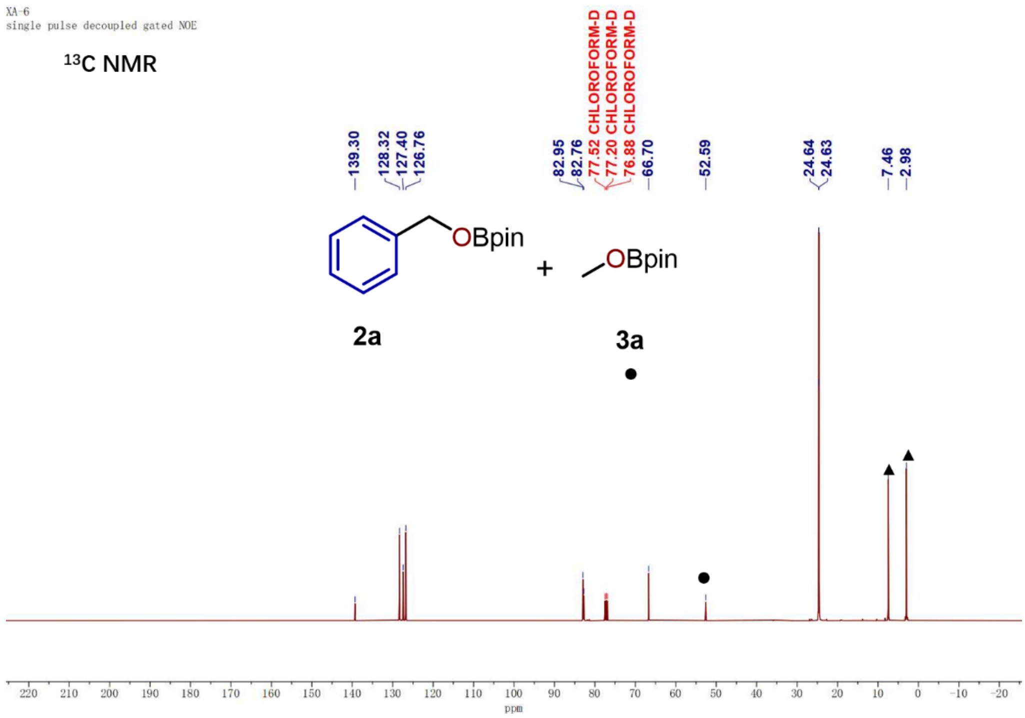


Figure S10. ^{13}C NMR spectrum of **2a** (101 MHz, Chloroform-*d*).

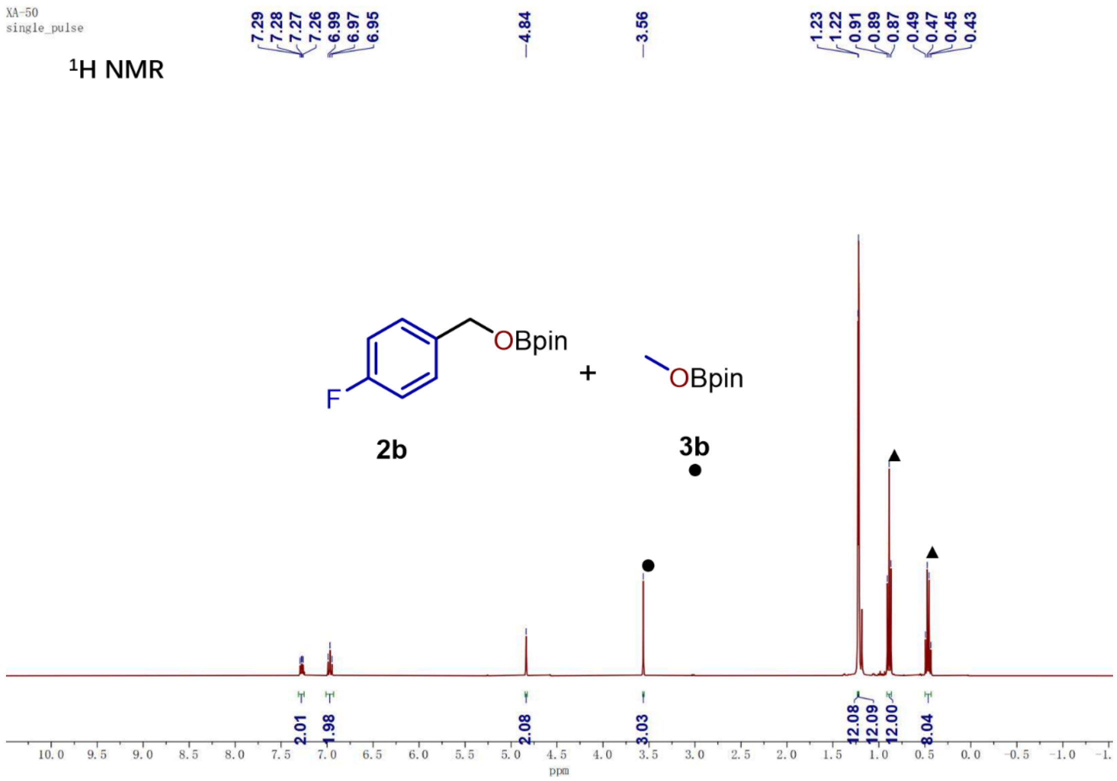


Figure S11. ^{1}H NMR spectrum of **2b** (400 MHz, Chloroform-*d*).

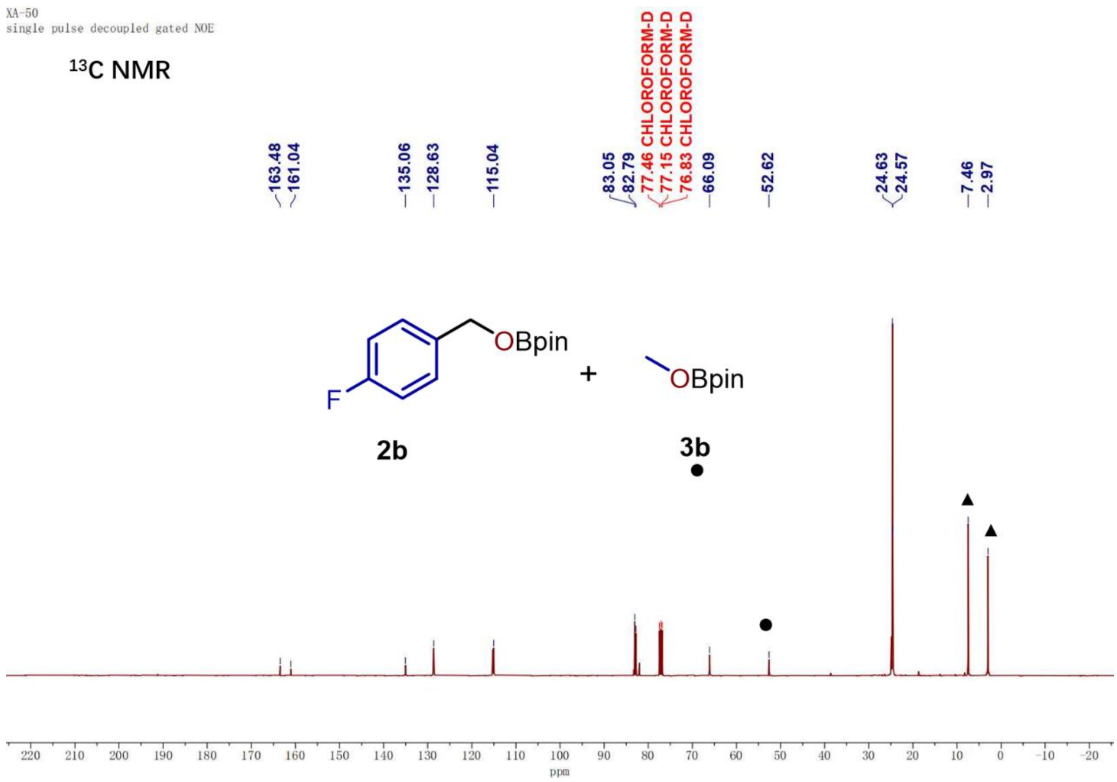


Figure S12. ^{13}C NMR spectrum of **2b** (101 MHz, Chloroform-*d*).

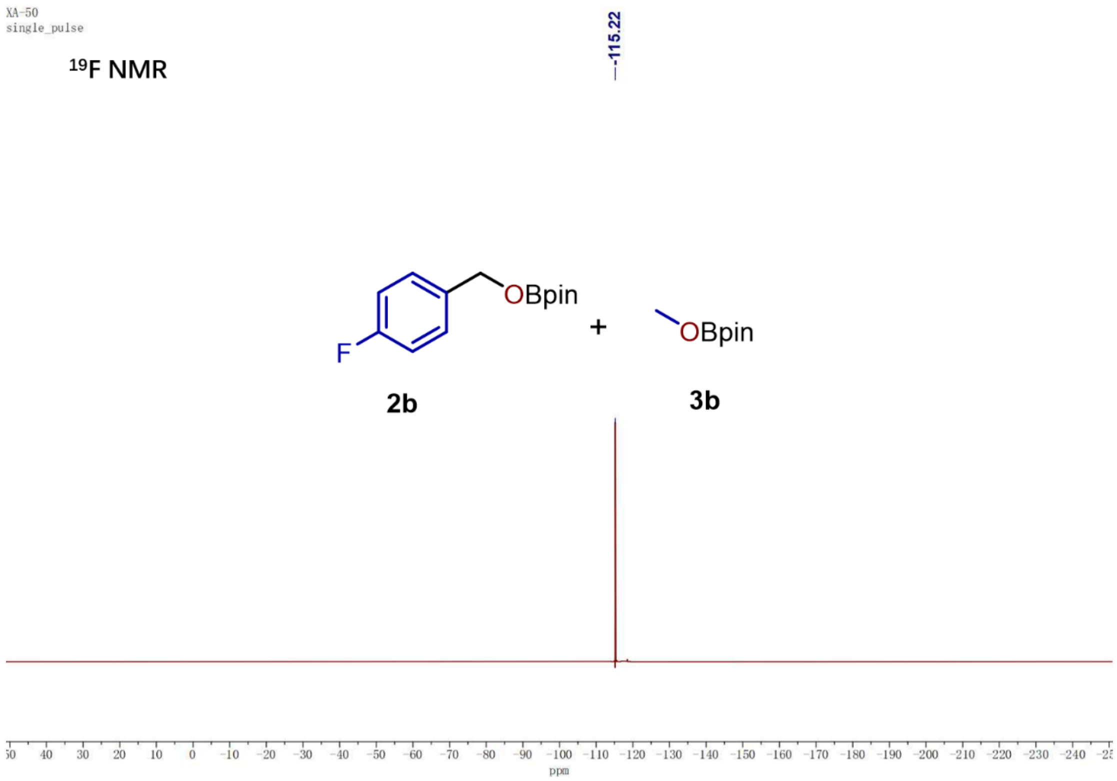


Figure S13. ^{19}F NMR spectrum of **2b** (376 MHz, Chloroform-*d*).

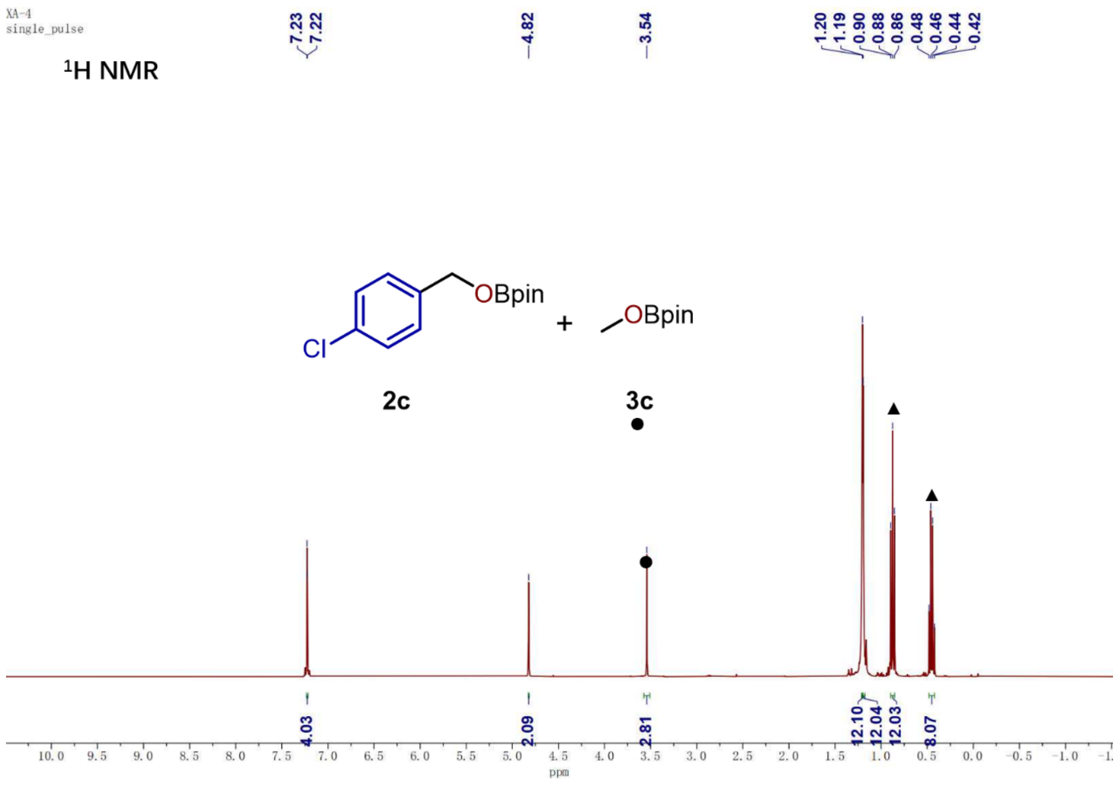


Figure S14. ^{1}H NMR spectrum of **2c** (400 MHz, Chloroform-*d*).

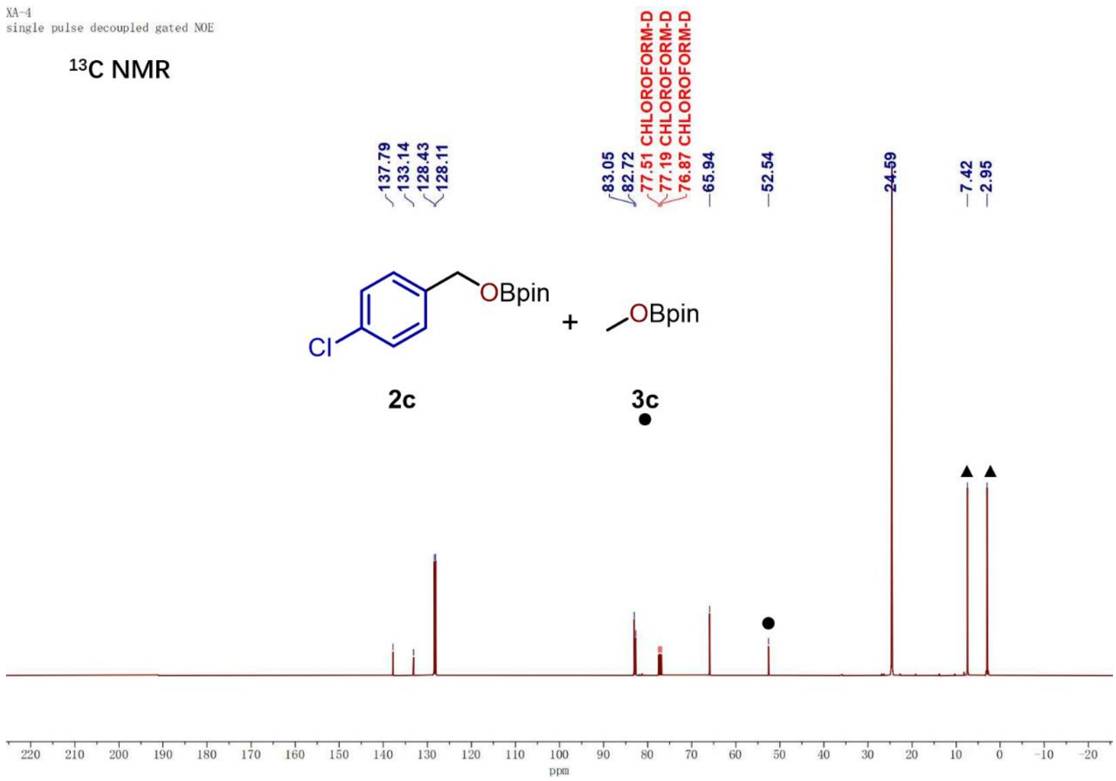


Figure S15. ^{13}C NMR spectrum of **2c** (101 MHz, Chloroform-*d*).

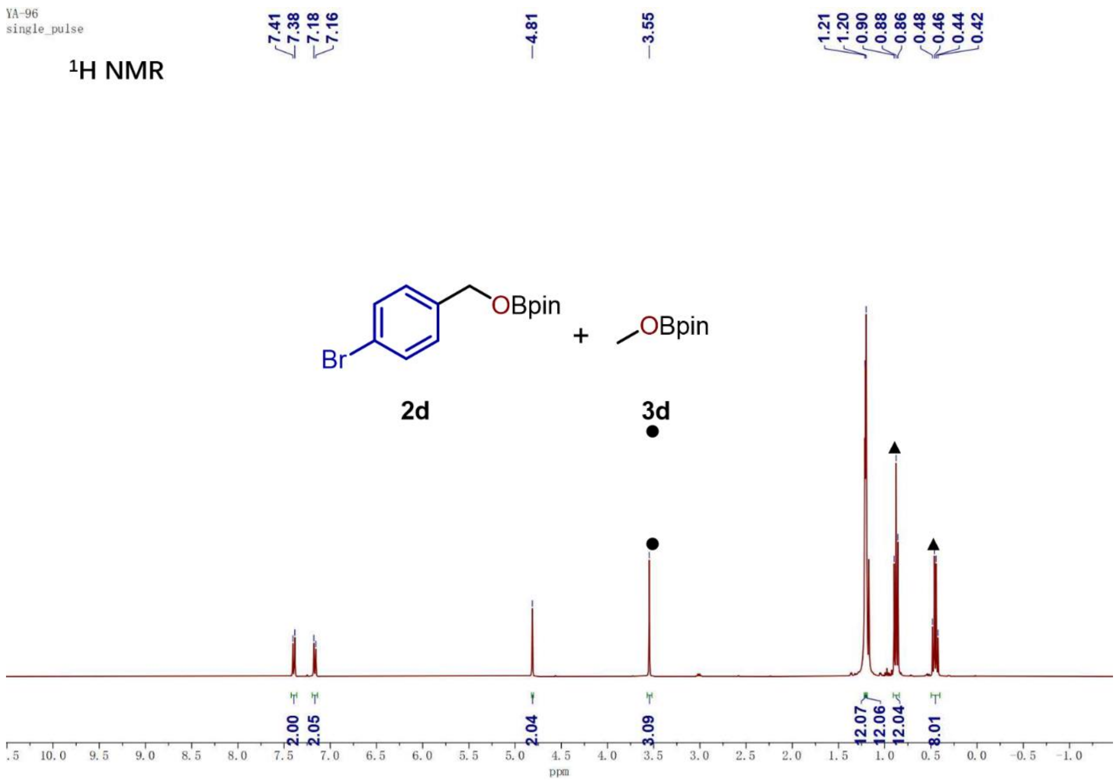


Figure S16. ^{1}H NMR spectrum of **2d** (400 MHz, Chloroform-*d*).

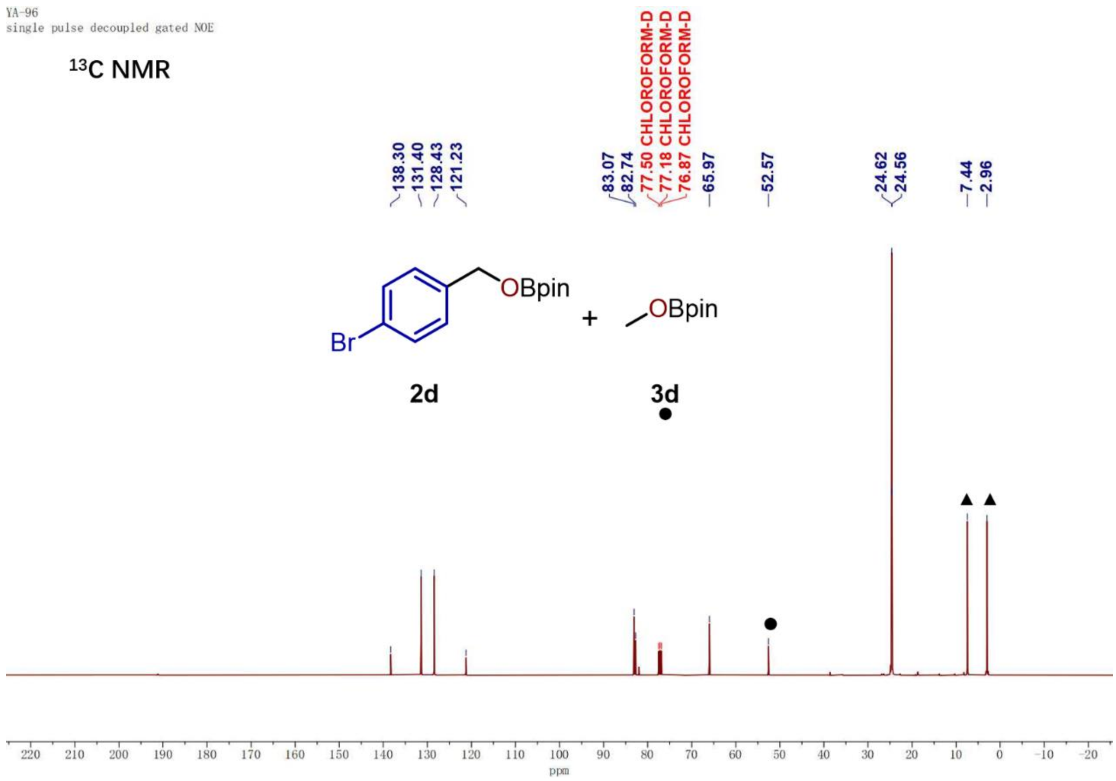


Figure S17. ^{13}C NMR spectrum of **2d** (101 MHz, Chloroform-*d*).

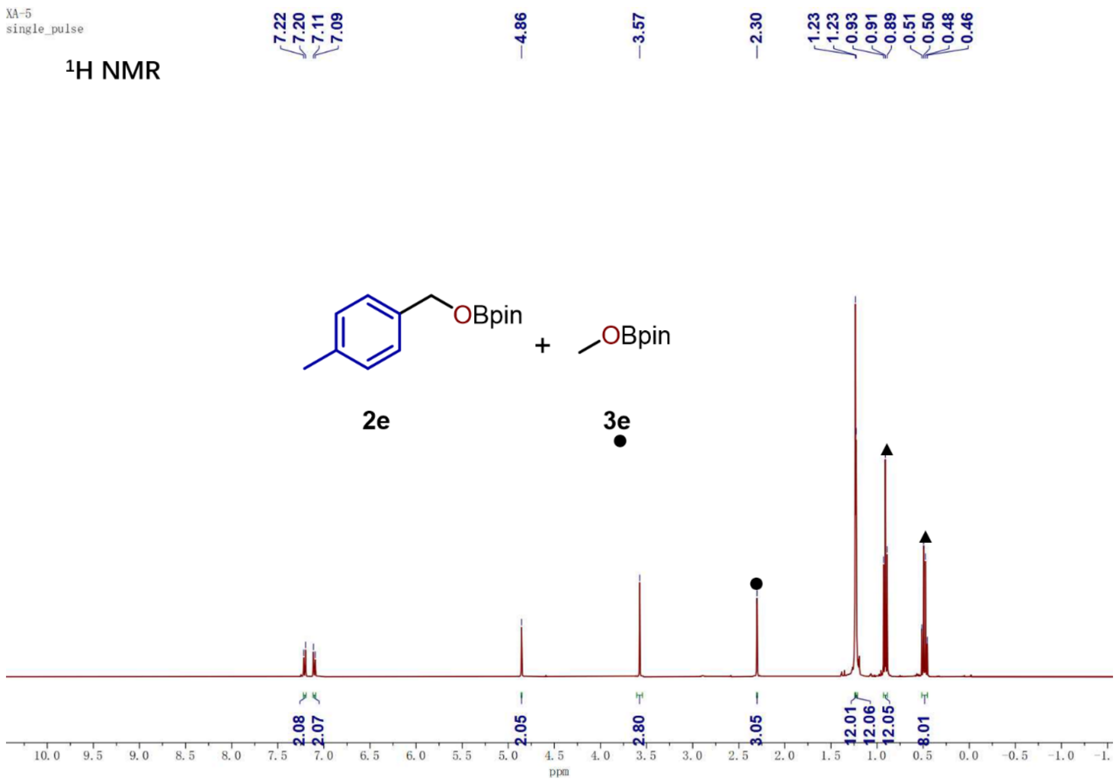


Figure S18. ^{1}H NMR spectrum of **2e** (400 MHz, Chloroform-*d*).

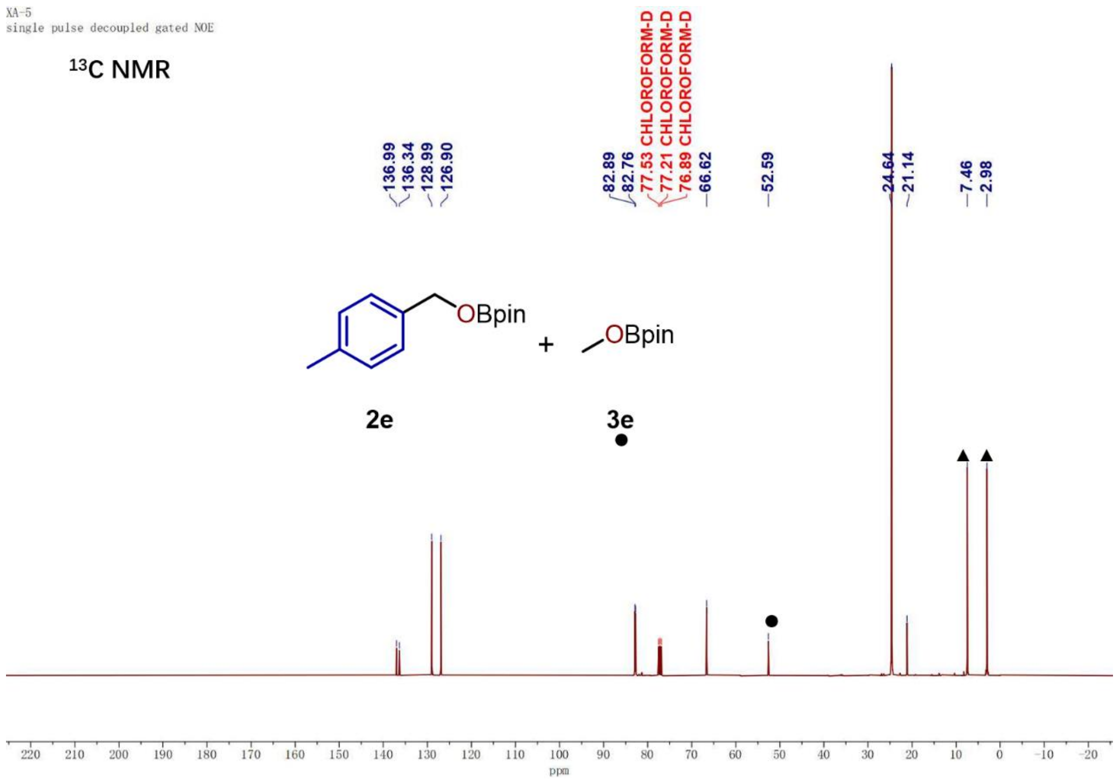


Figure S19. ^{13}C NMR spectrum of **2e** (101 MHz, Chloroform-*d*).

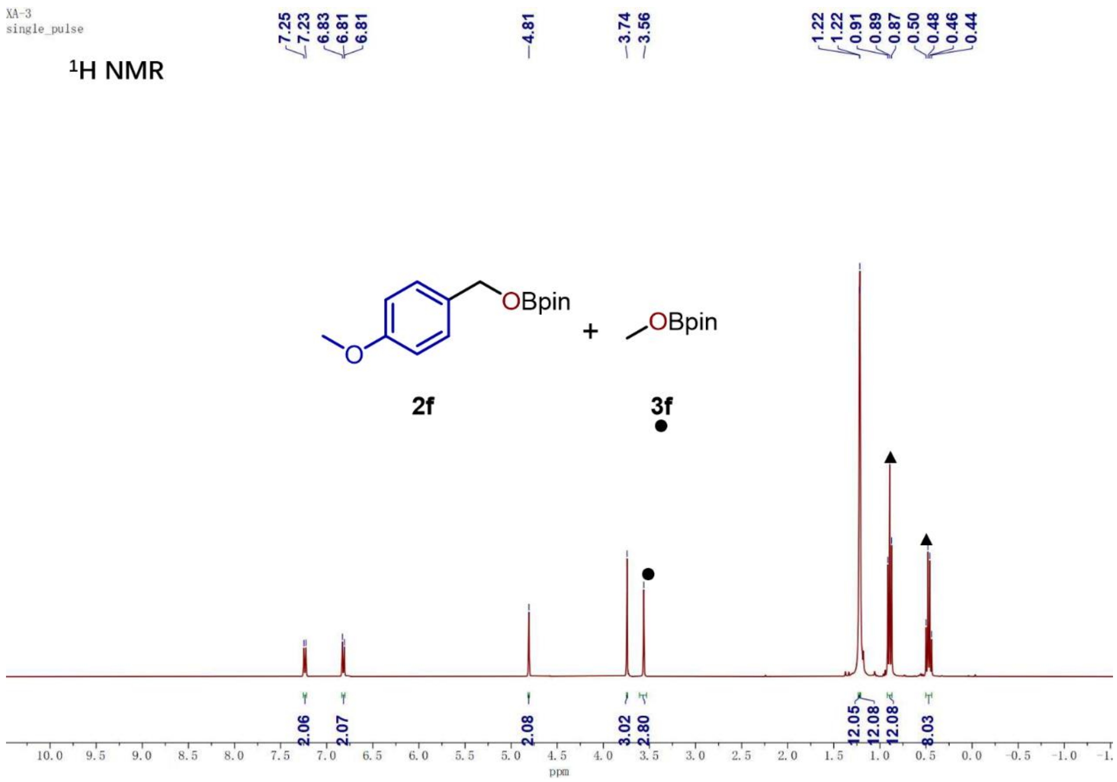


Figure S20. ^{1}H NMR spectrum of **2f** (400 MHz, Chloroform-*d*).

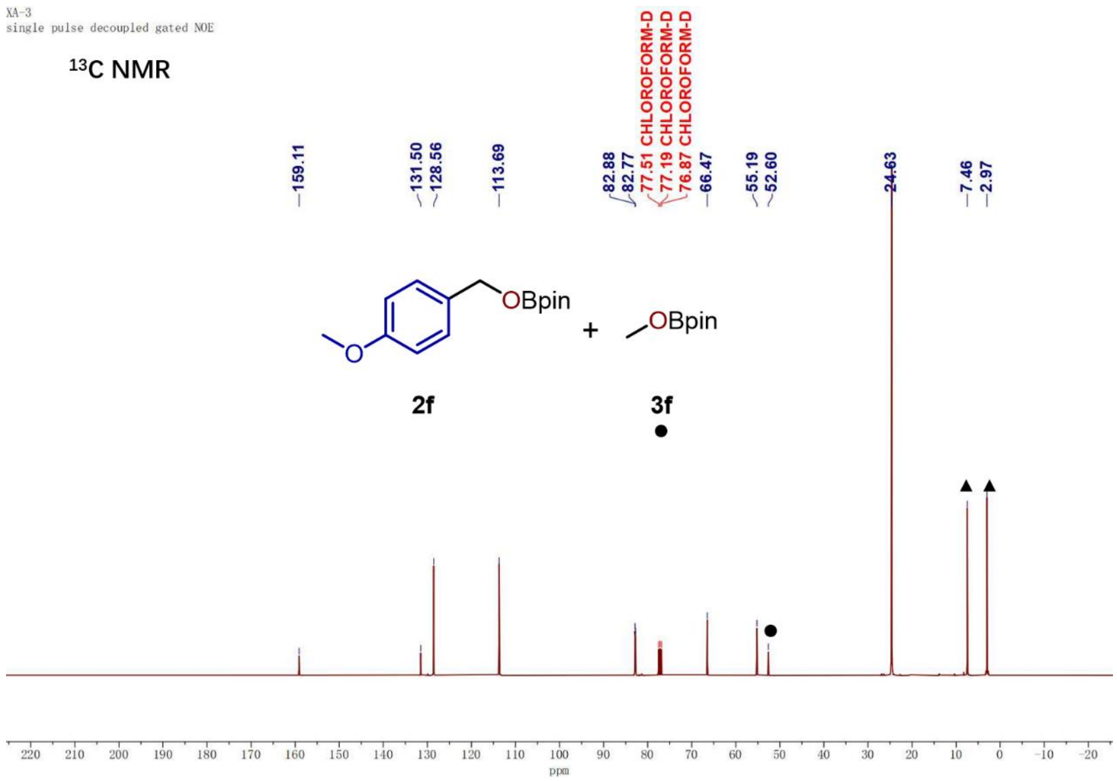


Figure S21. ^{13}C NMR spectrum of **2f** (101 MHz, Chloroform-*d*).

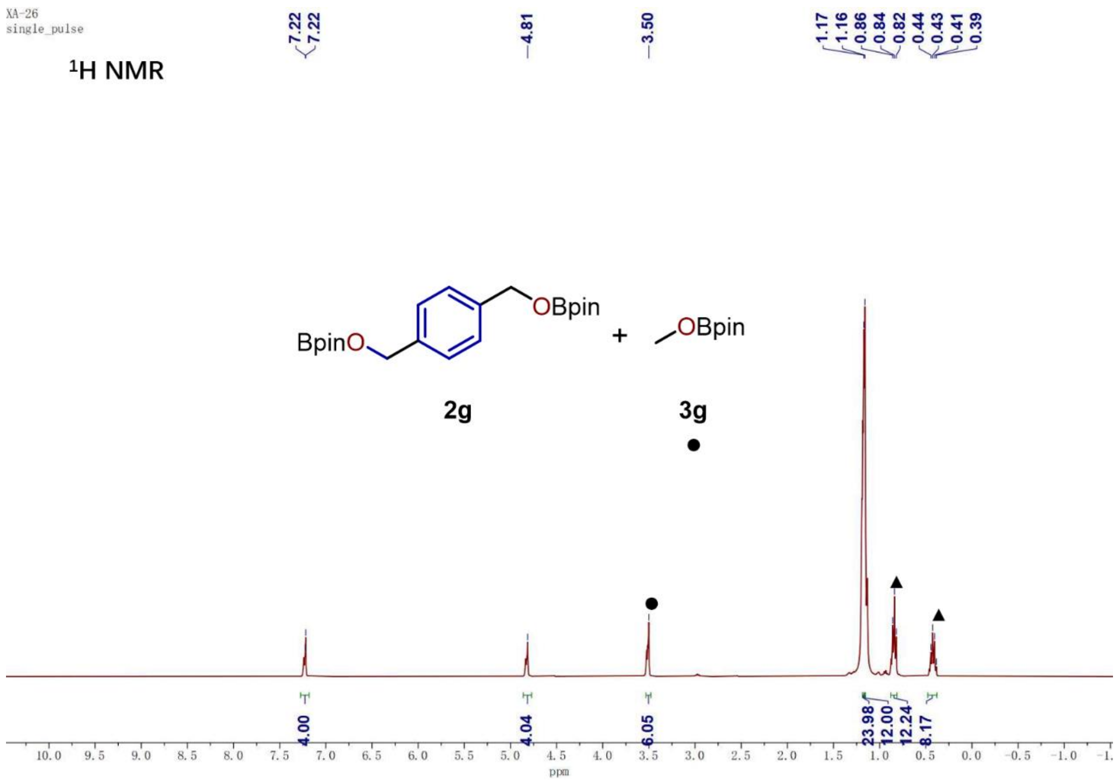


Figure S22. ^{1}H NMR spectrum of **2g** (400 MHz, Chloroform-*d*).

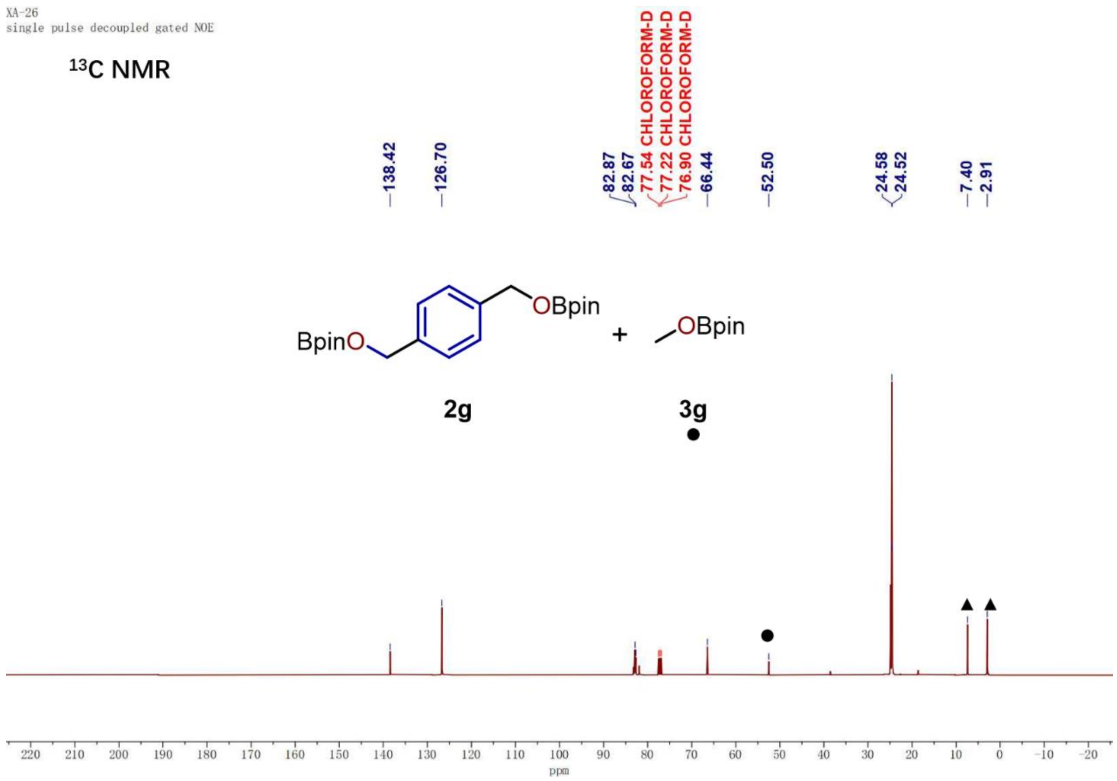


Figure S23. ^{13}C NMR spectrum of **2g** (101 MHz, Chloroform-*d*).

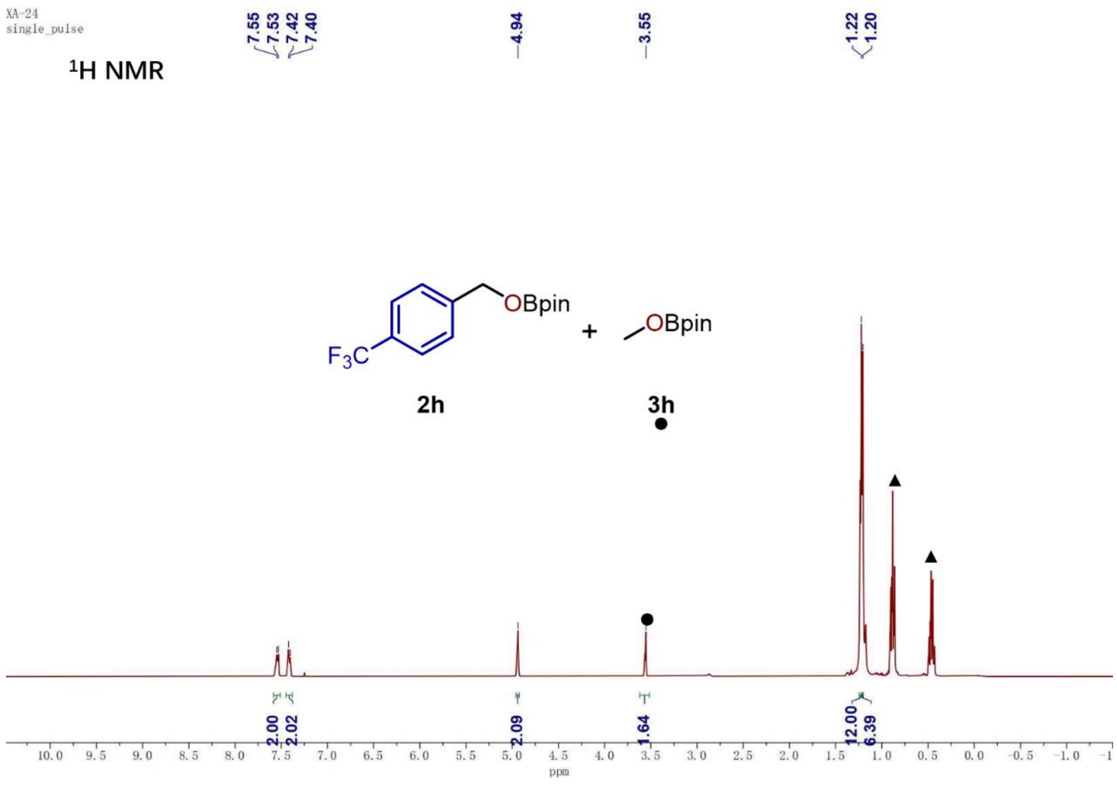


Figure S24. ^{1}H NMR spectrum of **2h** (400 MHz, Chloroform-*d*).

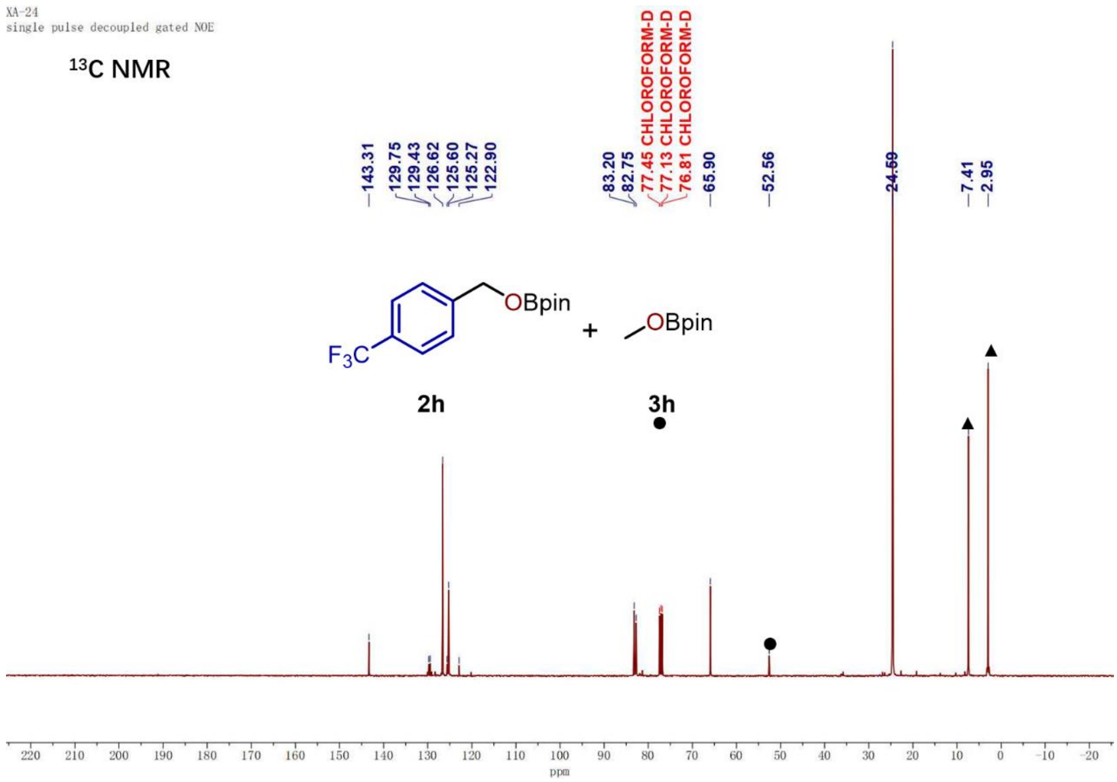


Figure S25. ^{13}C NMR spectrum of **2h** (101 MHz, Chloroform-*d*).

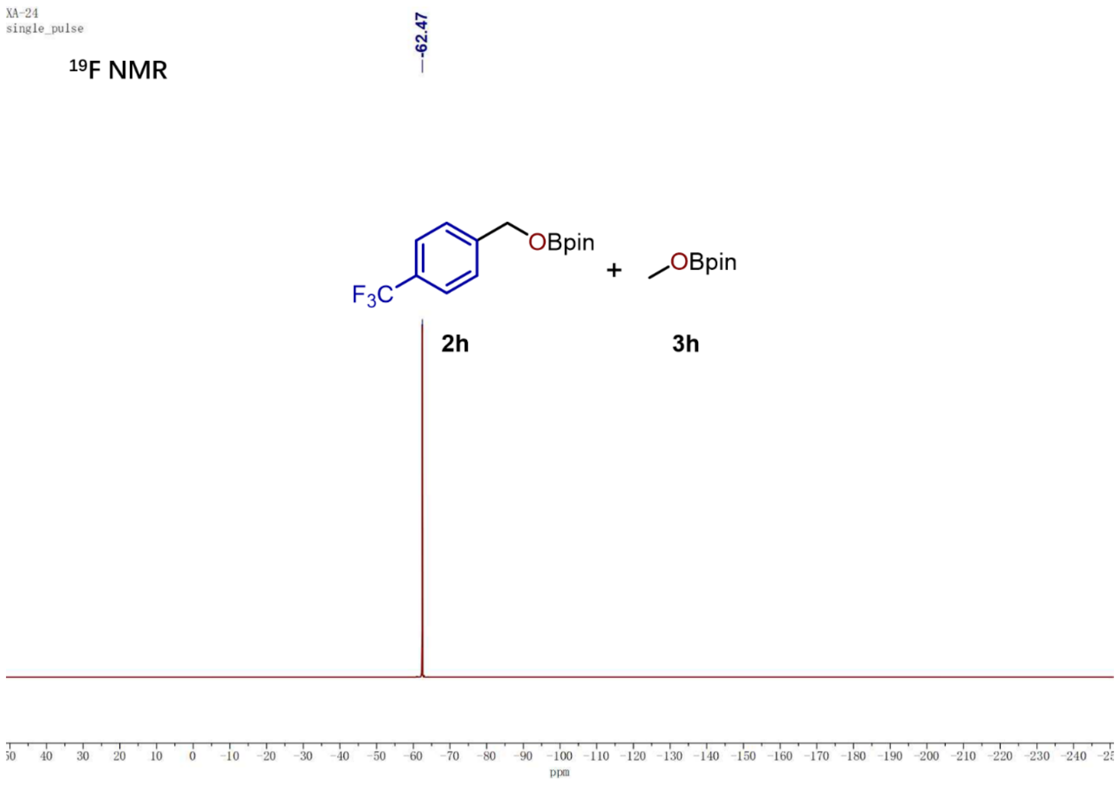


Figure S26. ^{19}F NMR spectrum of **2h** (376 MHz, Chloroform-*d*).

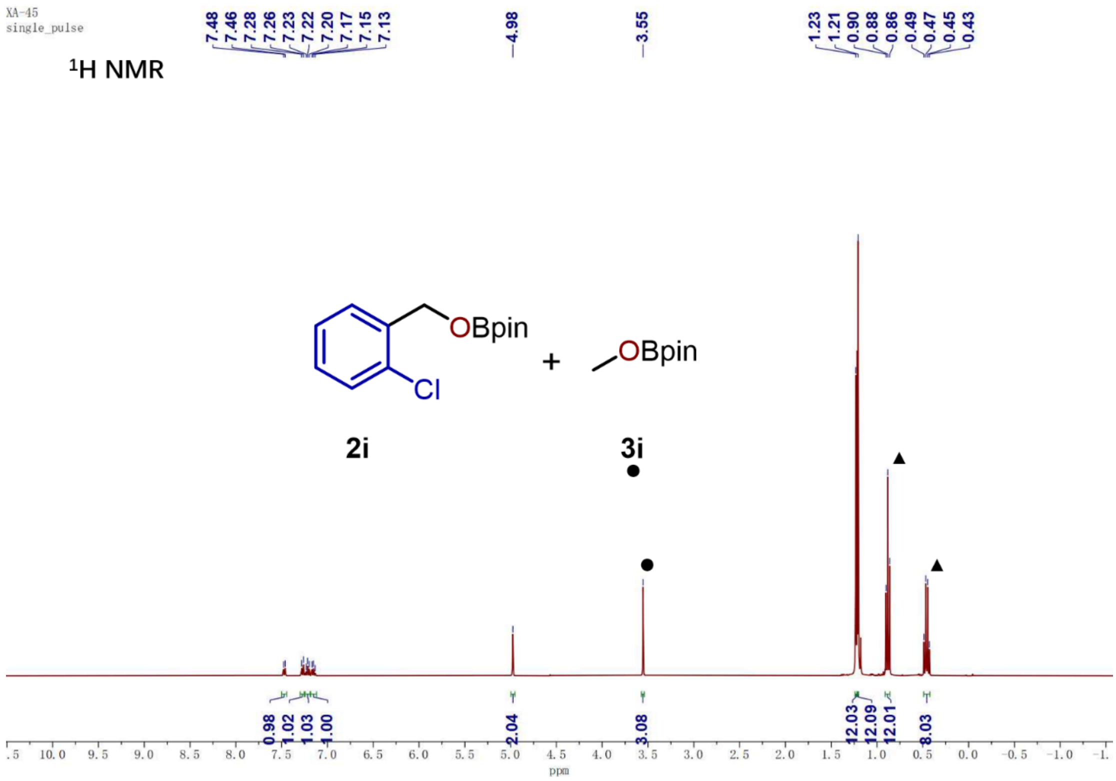


Figure S27. ^{1}H NMR spectrum of **2i** (400 MHz, Chloroform-*d*).

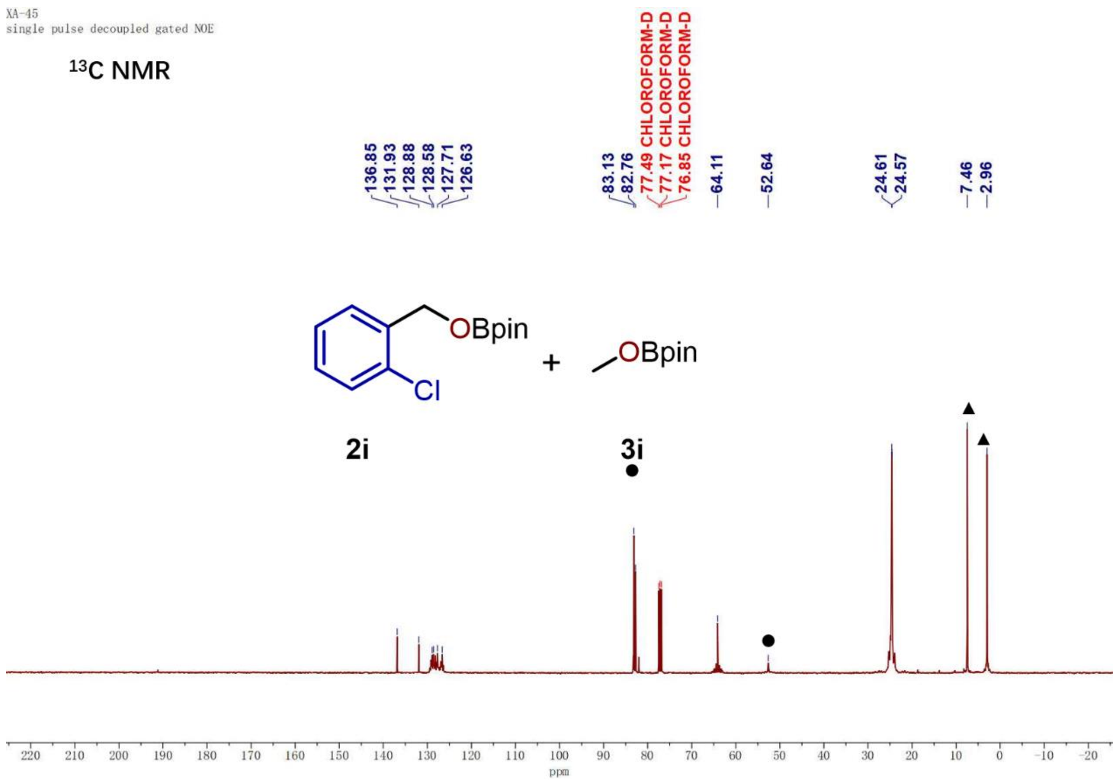


Figure S28. ^{13}C NMR spectrum of **2i** (101 MHz, Chloroform-*d*).

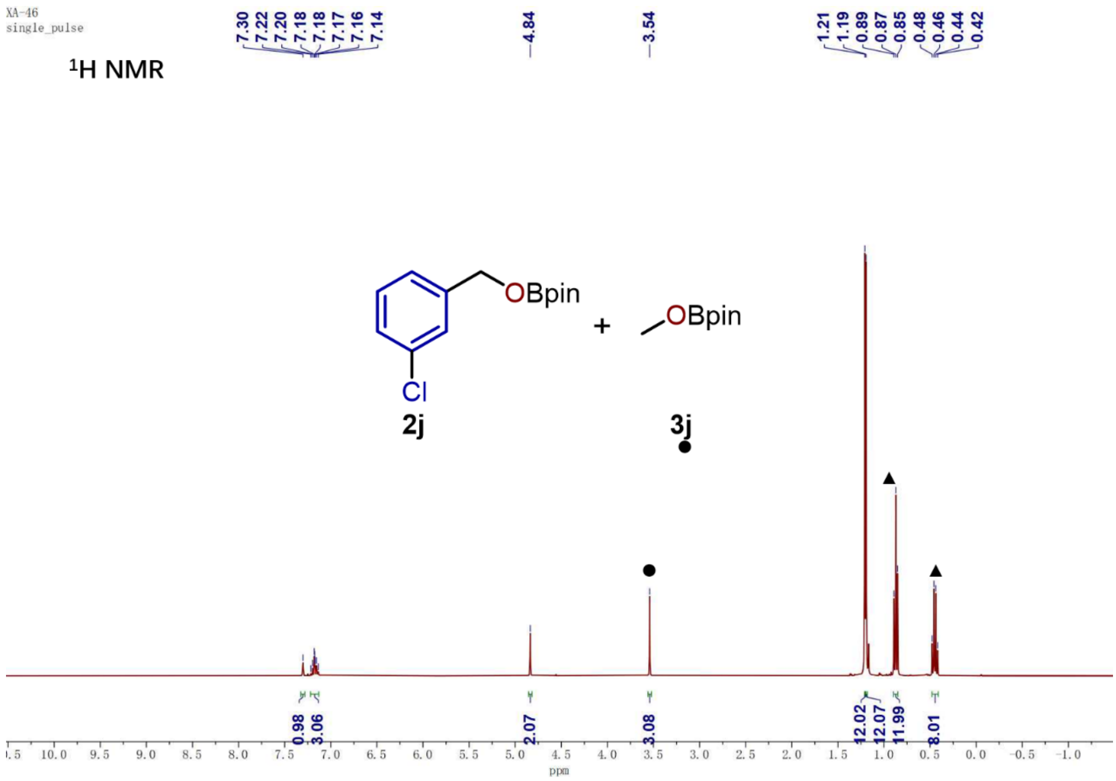


Figure S29. ^{1}H NMR spectrum of **2j** (400 MHz, Chloroform-*d*).

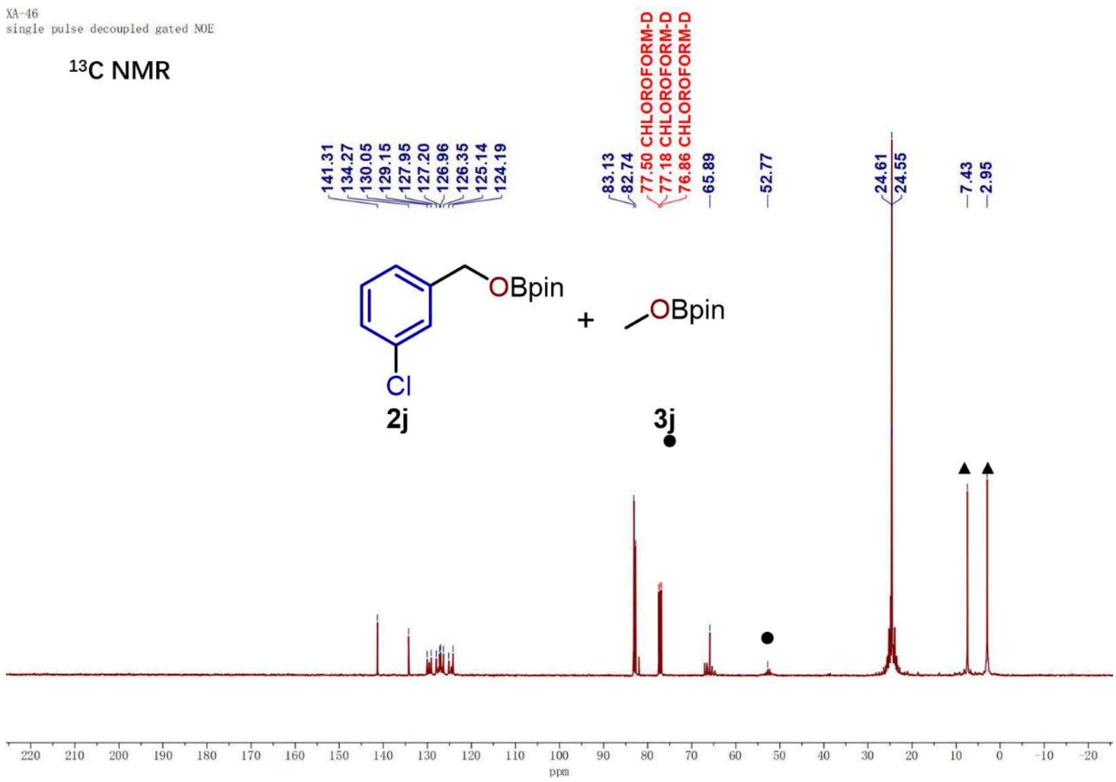


Figure S30. ^{13}C NMR spectrum of **2j** (101 MHz, Chloroform-*d*).

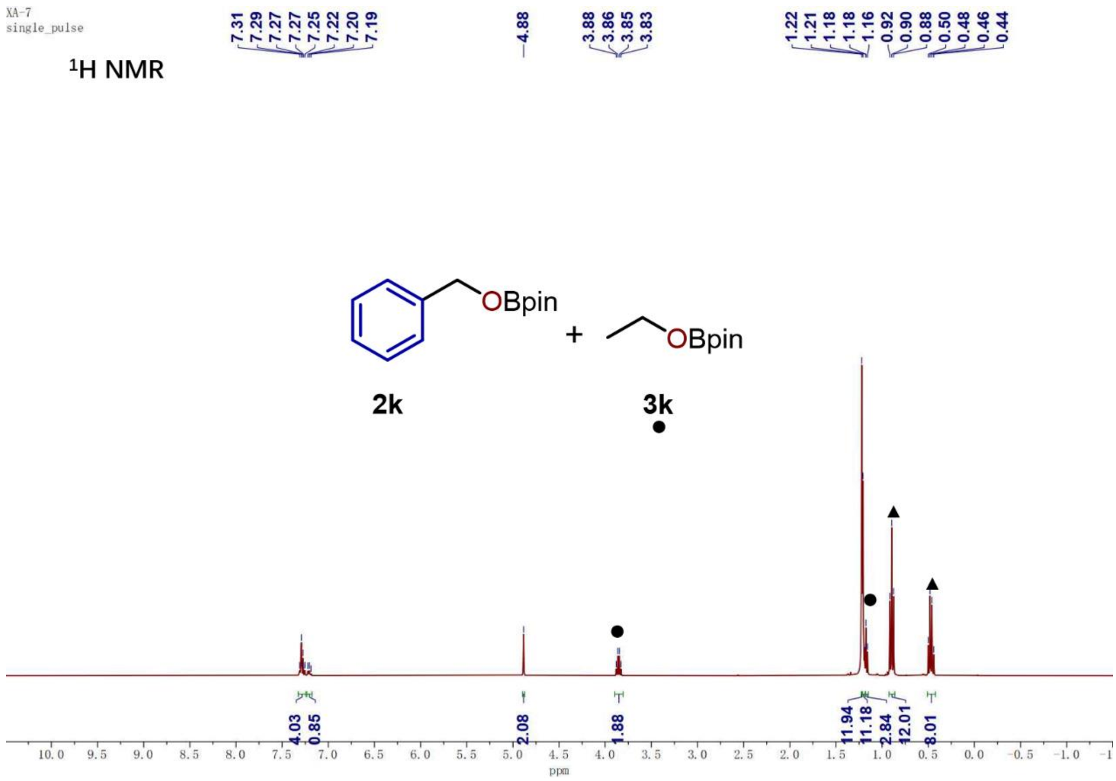


Figure S31. ^{1}H NMR spectrum of **2k** (400 MHz, Chloroform-*d*).

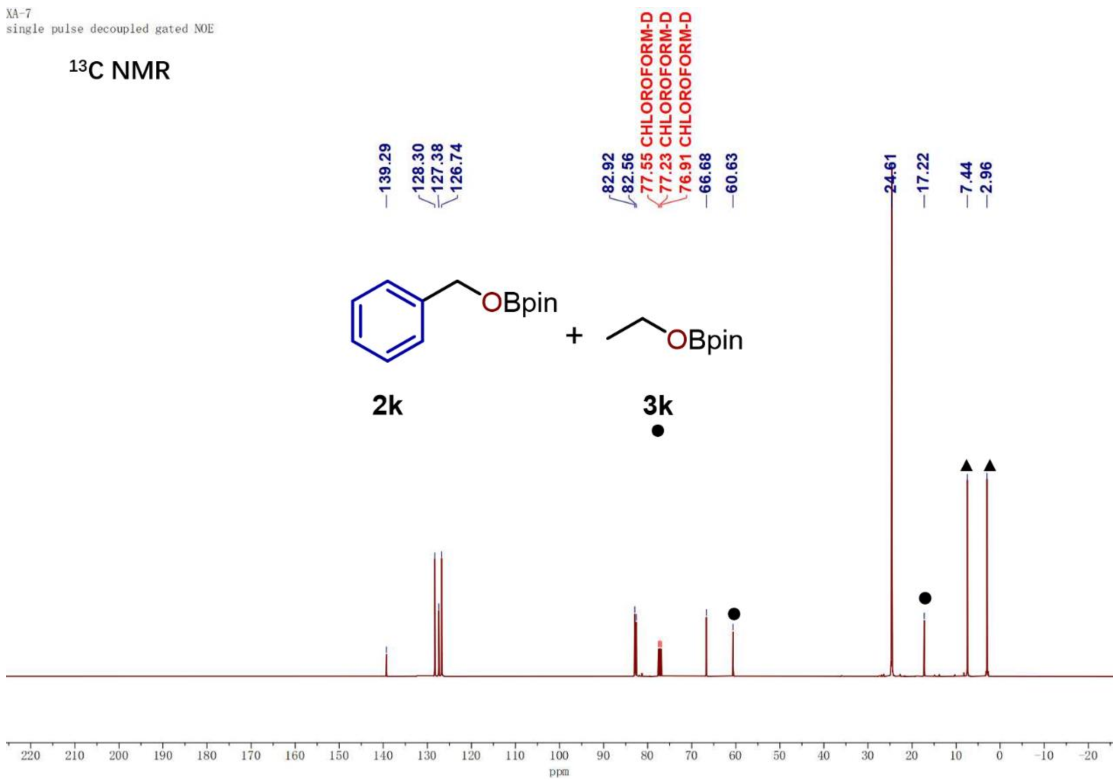


Figure S32. ^{13}C NMR spectrum of **2k** (101 MHz, Chloroform-*d*).

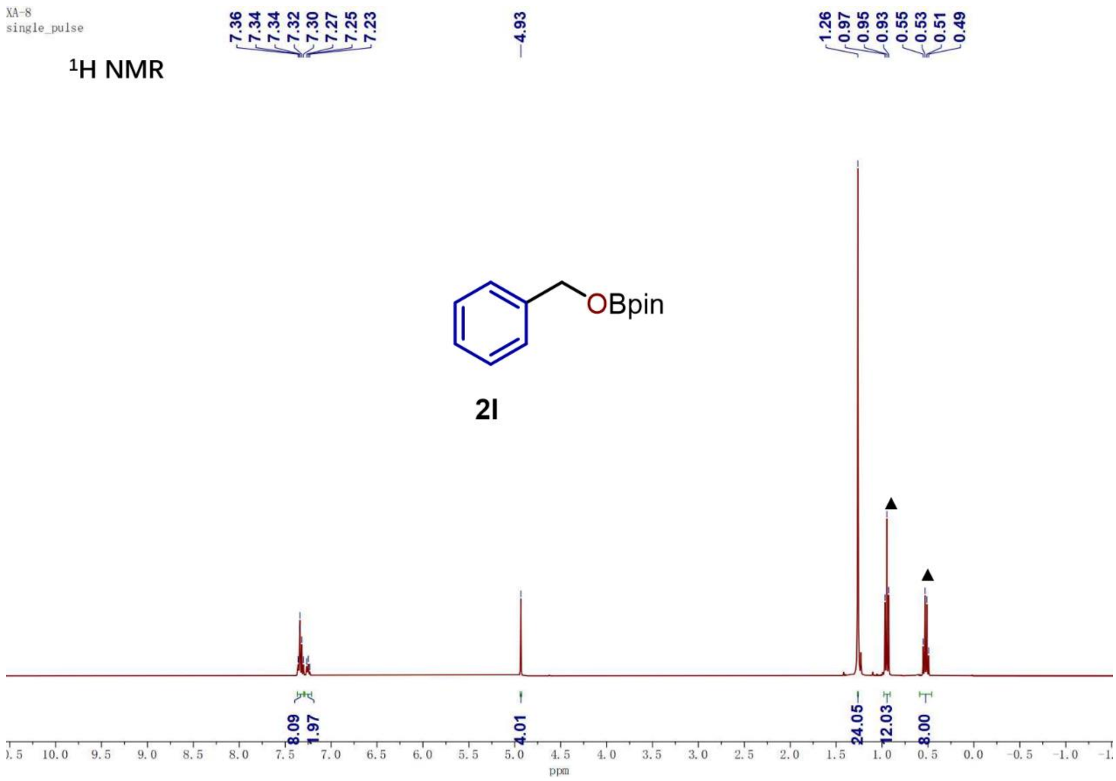


Figure S33. ^{1}H NMR spectrum of **2l** (400 MHz, Chloroform-*d*).

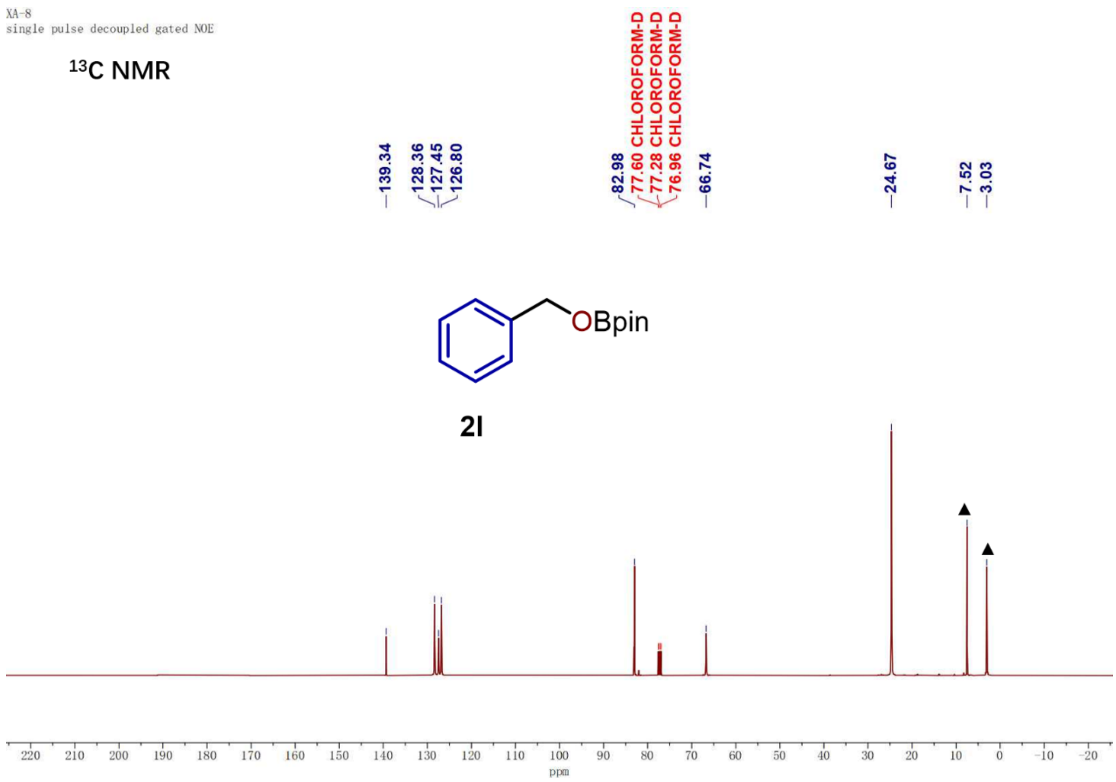


Figure S34. ^{13}C NMR spectrum of **2l** (101 MHz, Chloroform-*d*).

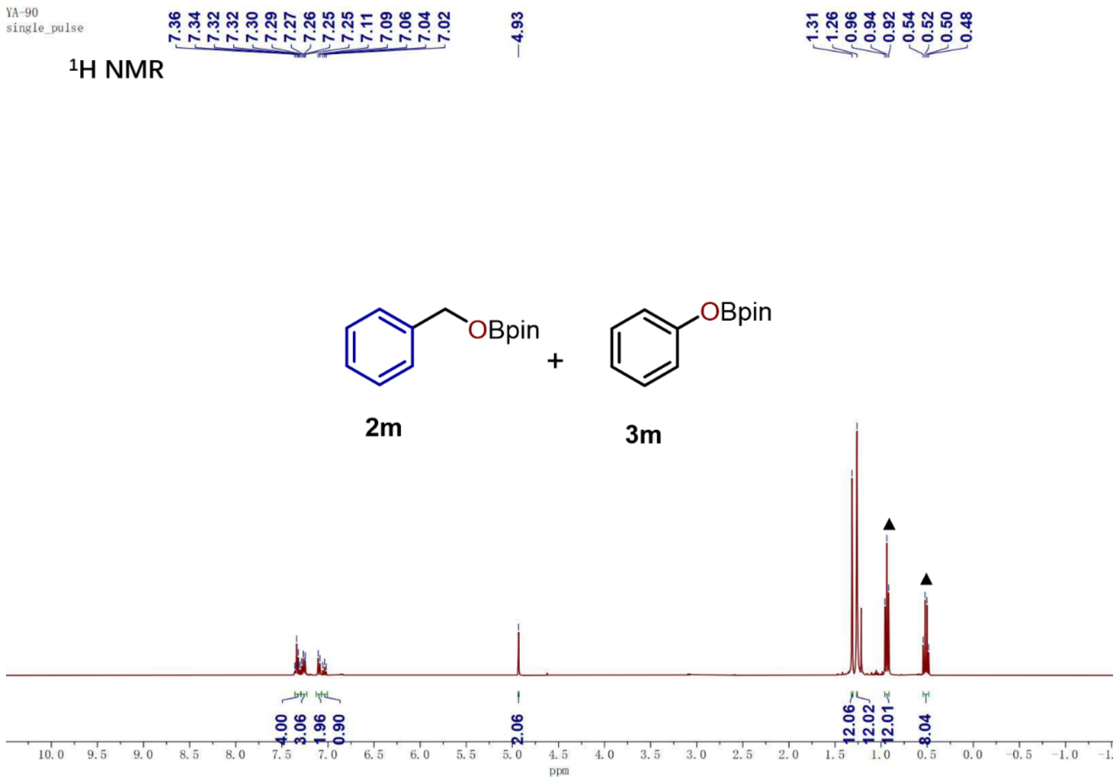


Figure S35. ^{1}H NMR spectrum of **2m** (400 MHz, Chloroform-*d*).

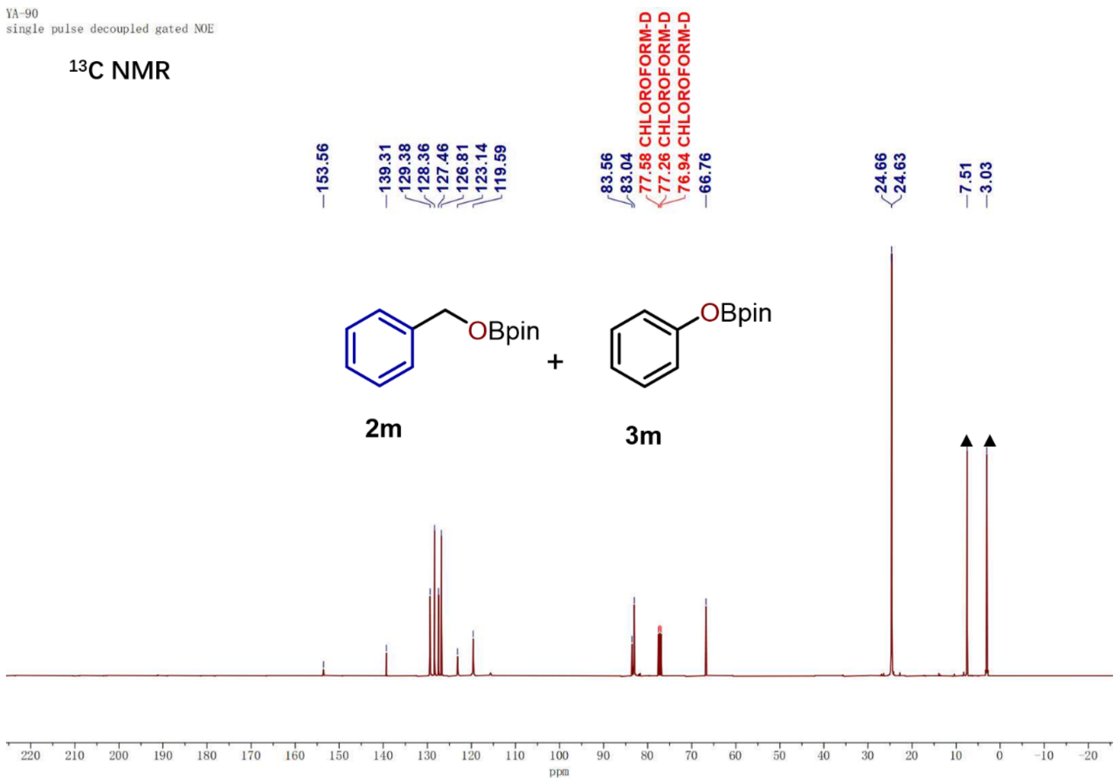


Figure S36. ^{13}C NMR spectrum of **2m** (101 MHz, Chloroform-*d*).

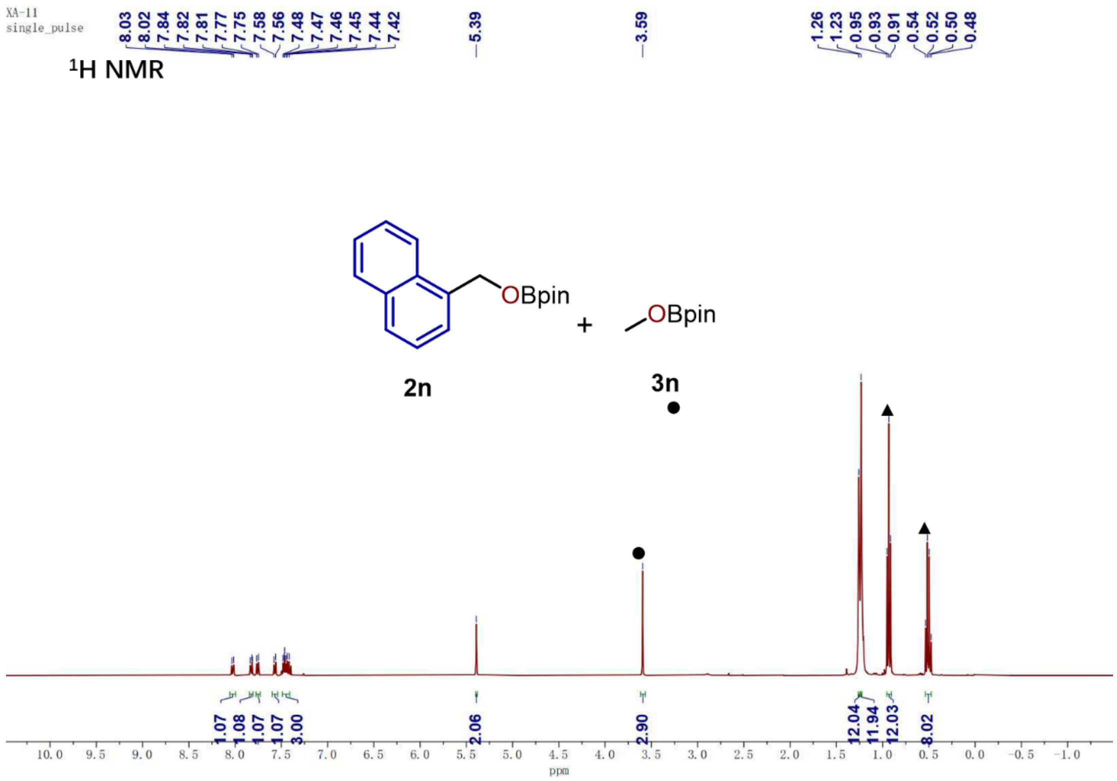


Figure S37. ^{1}H NMR spectrum of **2n** (400 MHz, Chloroform-*d*).

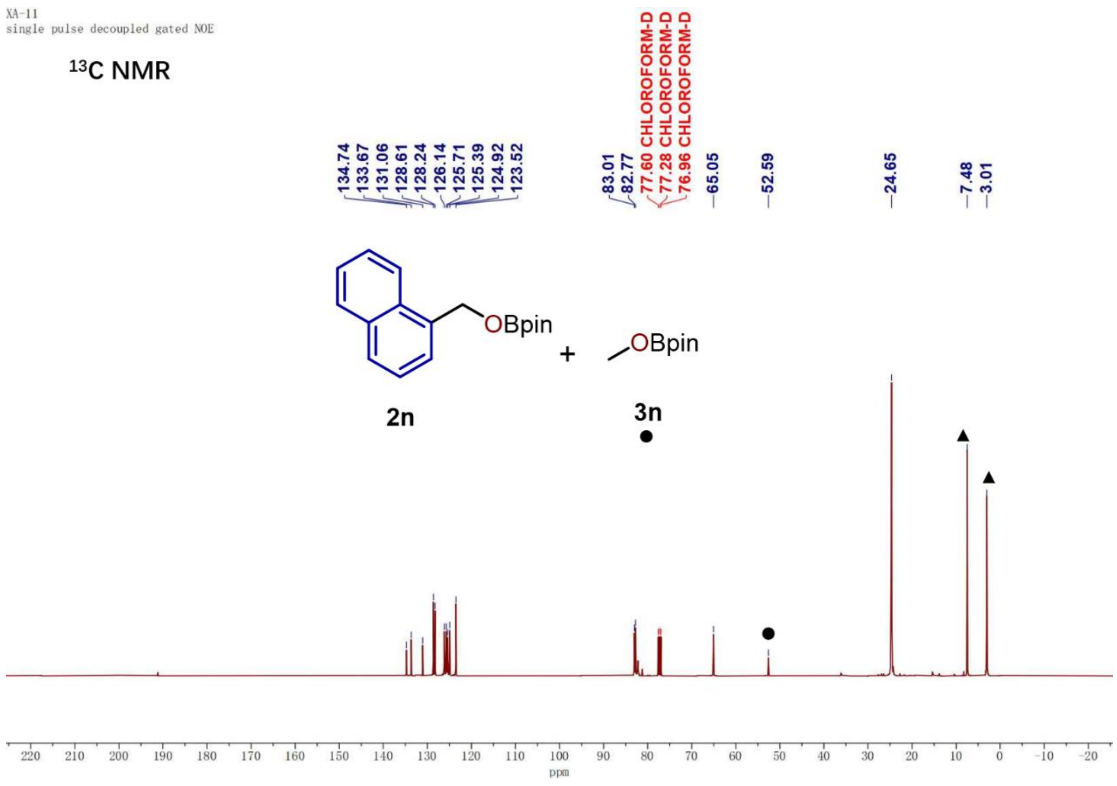


Figure S38. ^{13}C NMR spectrum of **2n** (101 MHz, Chloroform-*d*).

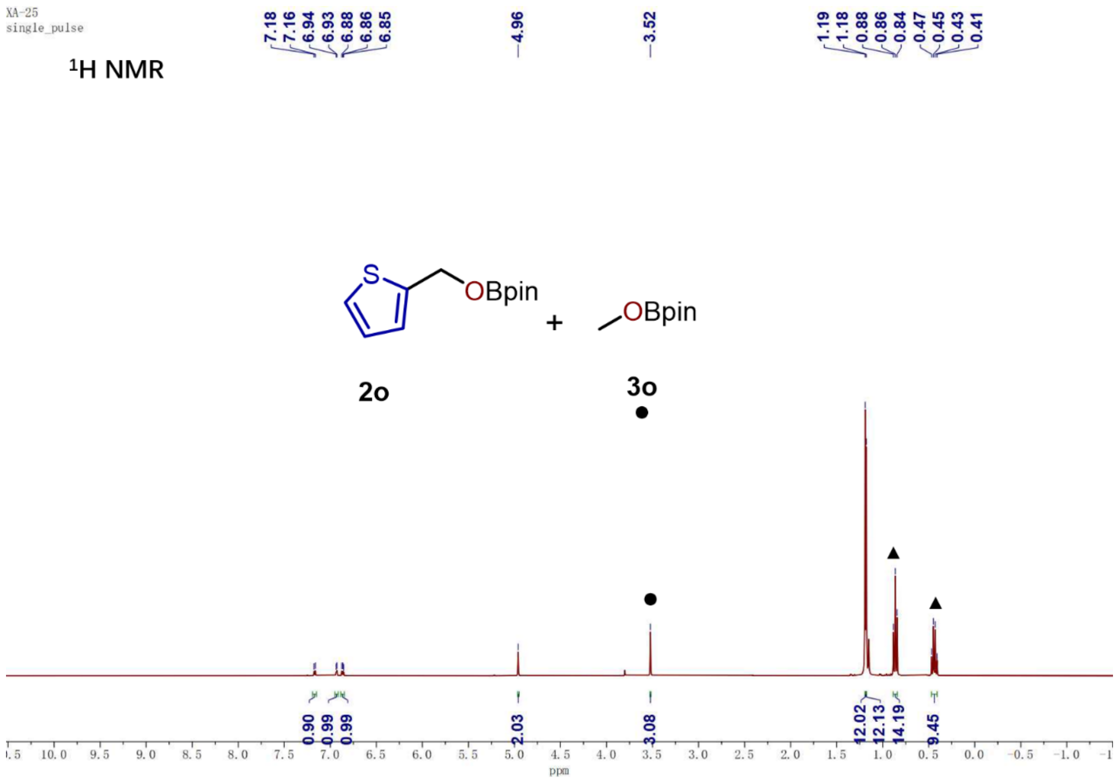


Figure S39. ^{1}H NMR spectrum of **2o** (400 MHz, Chloroform-*d*).

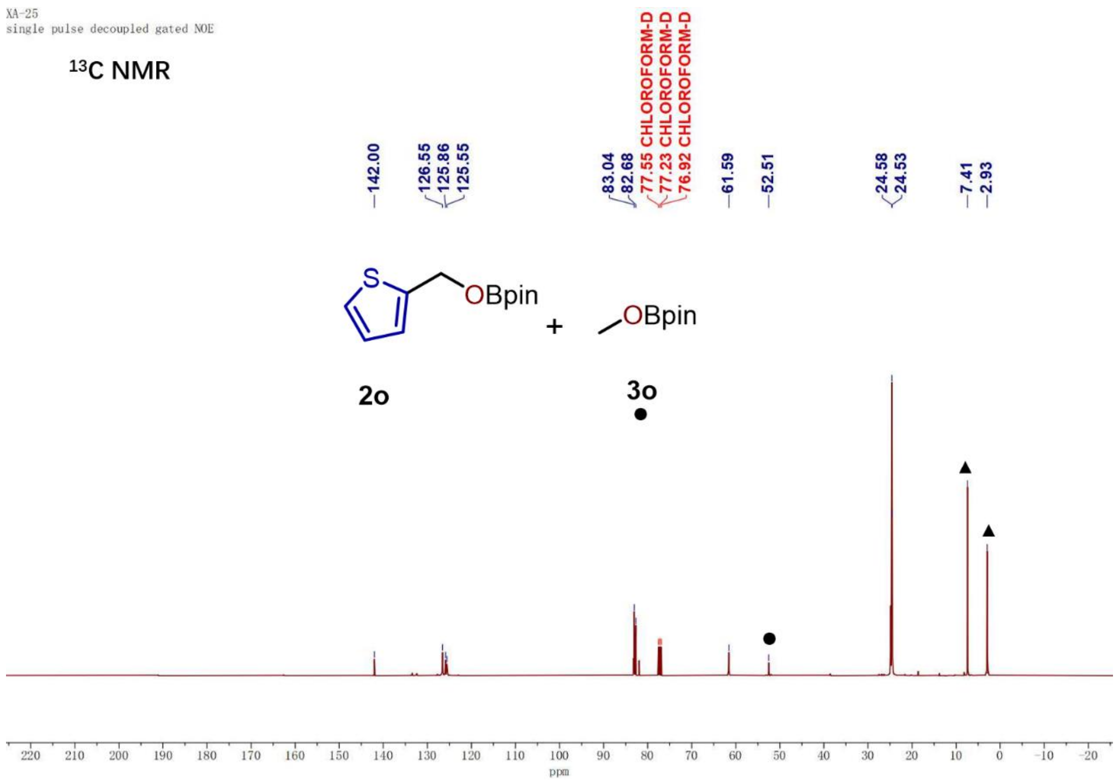


Figure S40. ^{13}C NMR spectrum of **2o** (101 MHz, Chloroform-*d*).

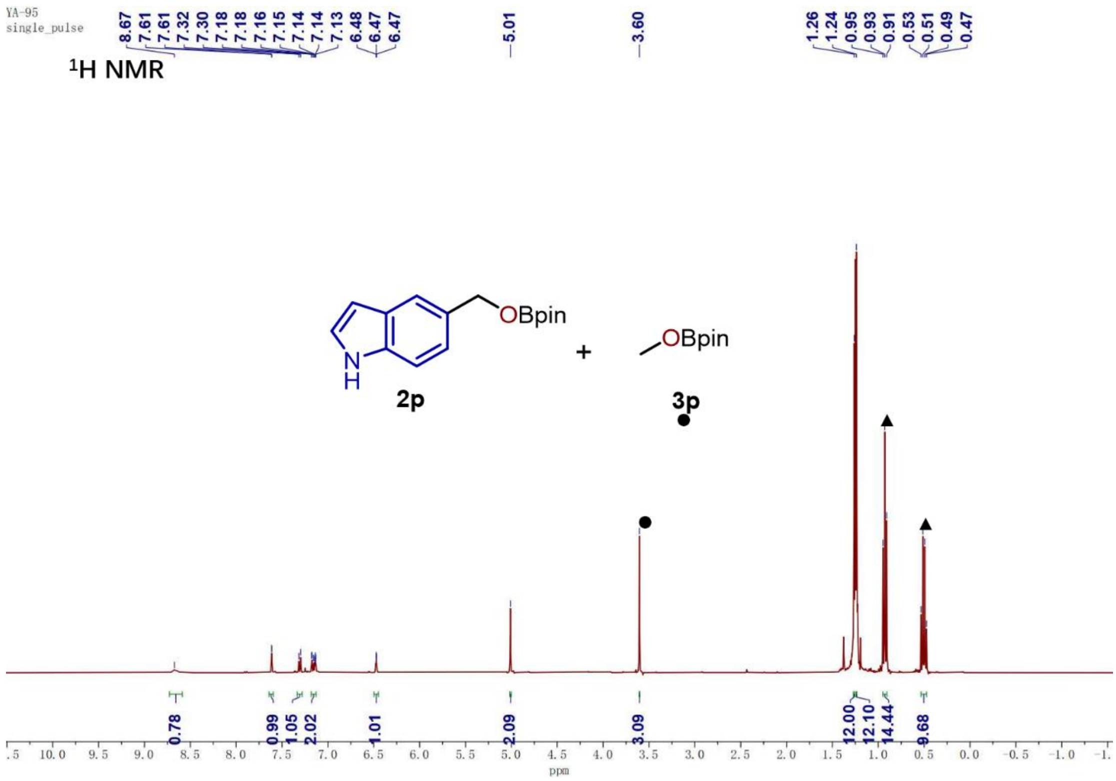


Figure S41. ^{1}H NMR spectrum of **2p** (400 MHz, Chloroform-*d*).

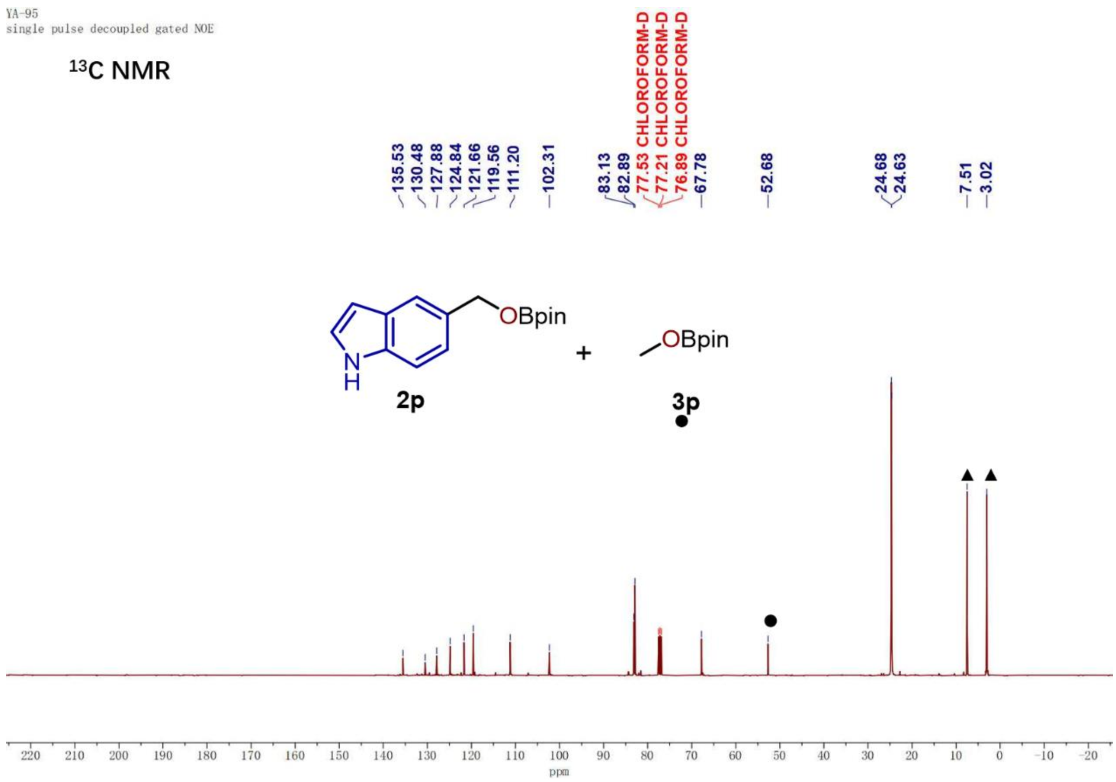


Figure S42. ^{13}C NMR spectrum of **2p** (101 MHz, Chloroform-*d*).

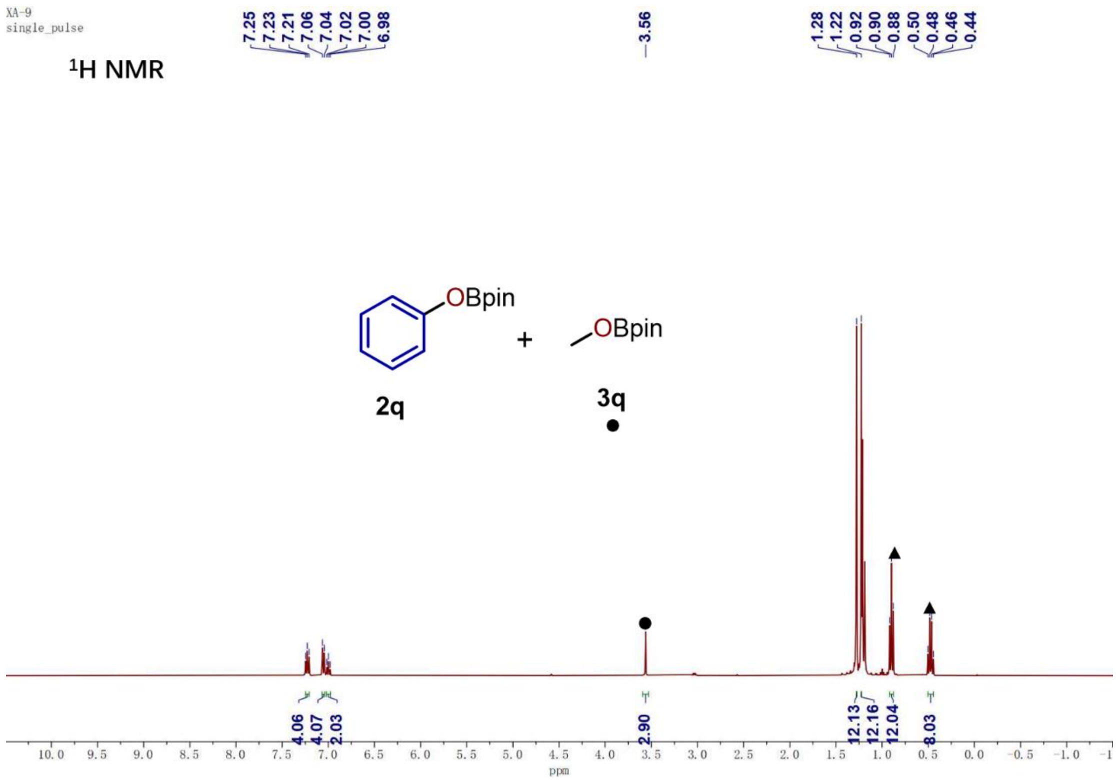


Figure S43. ^{1}H NMR spectrum of **2q** (400 MHz, Chloroform-*d*).

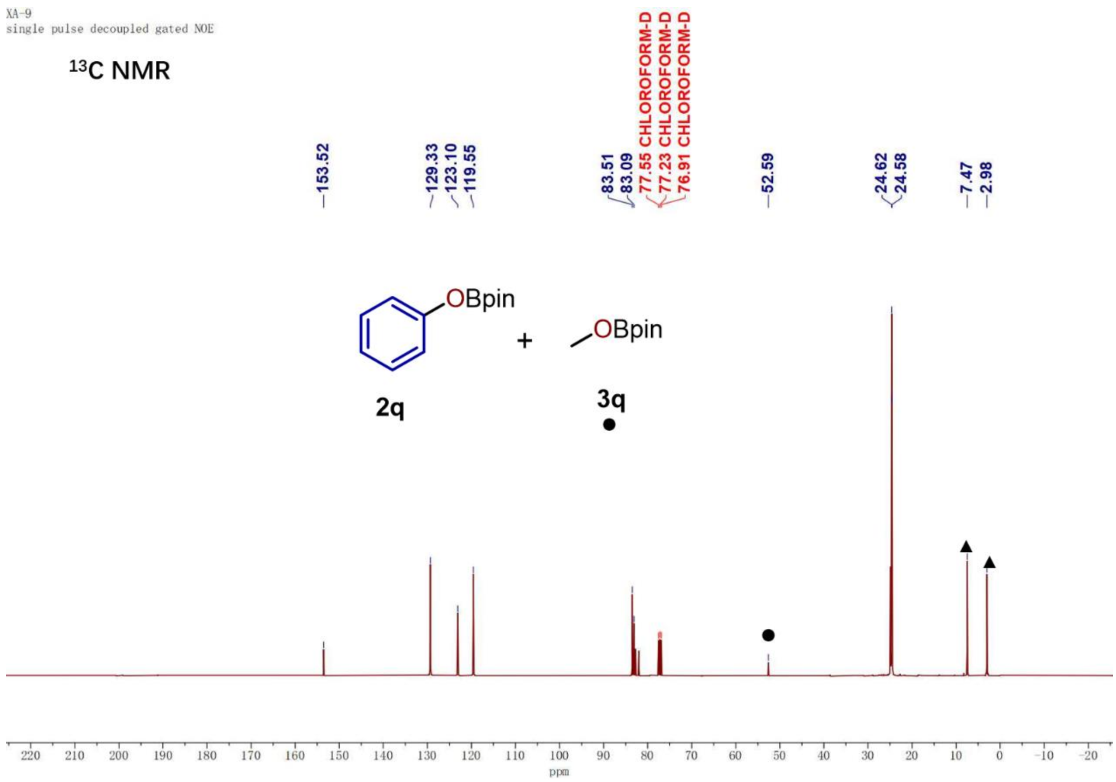


Figure S44. ^{13}C NMR spectrum of **2q** (101 MHz, Chloroform-*d*).

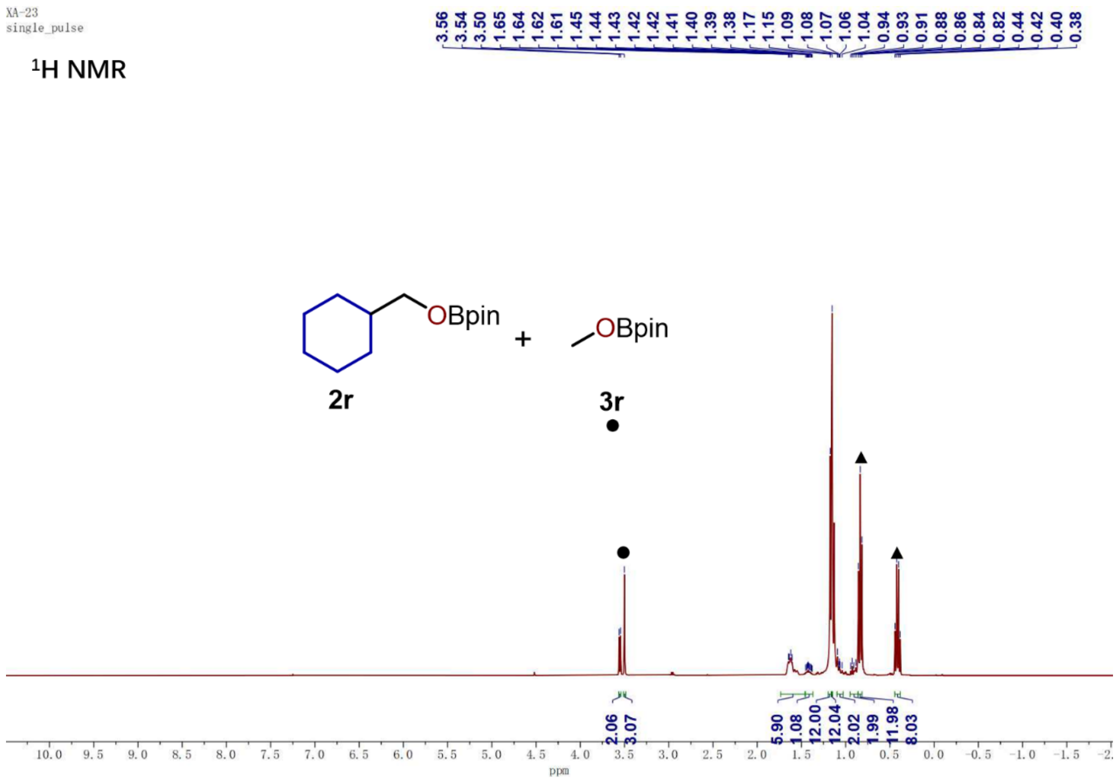


Figure S45. ^{1}H NMR spectrum of **2r** (400 MHz, Chloroform-*d*).

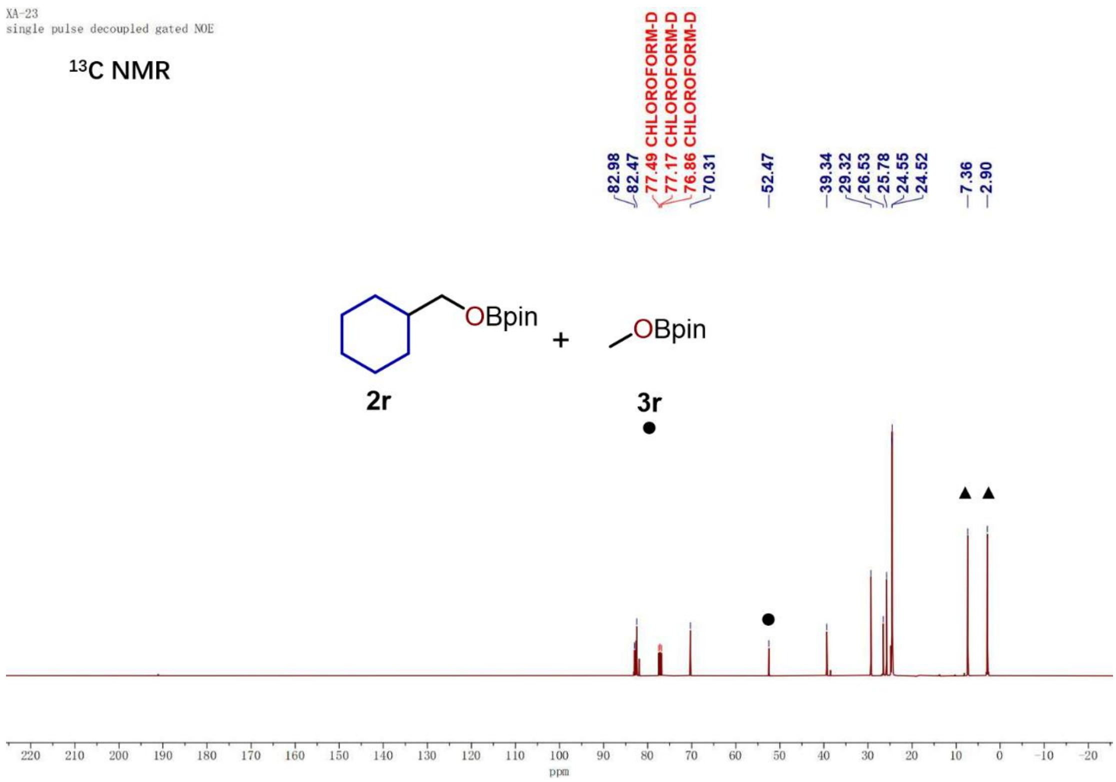


Figure S46. ^{13}C NMR spectrum of **2r** (101 MHz, Chloroform-*d*).

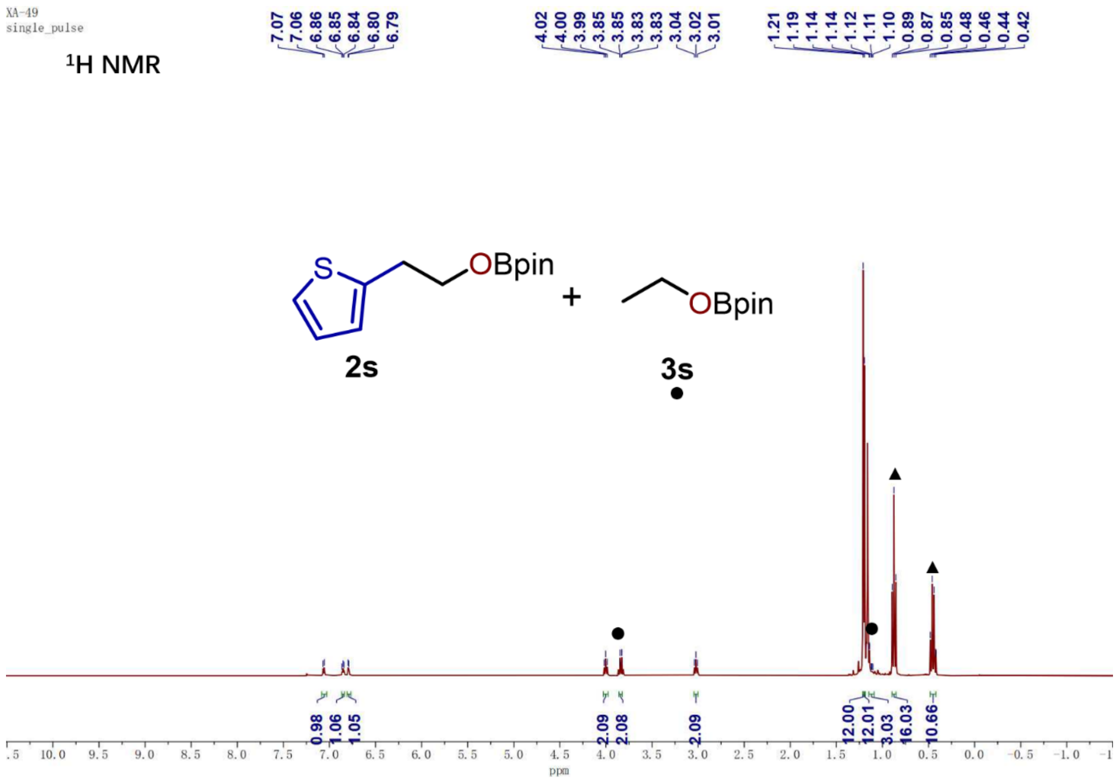


Figure S47. ^{1}H NMR spectrum of **2s** (400 MHz, Chloroform-*d*).

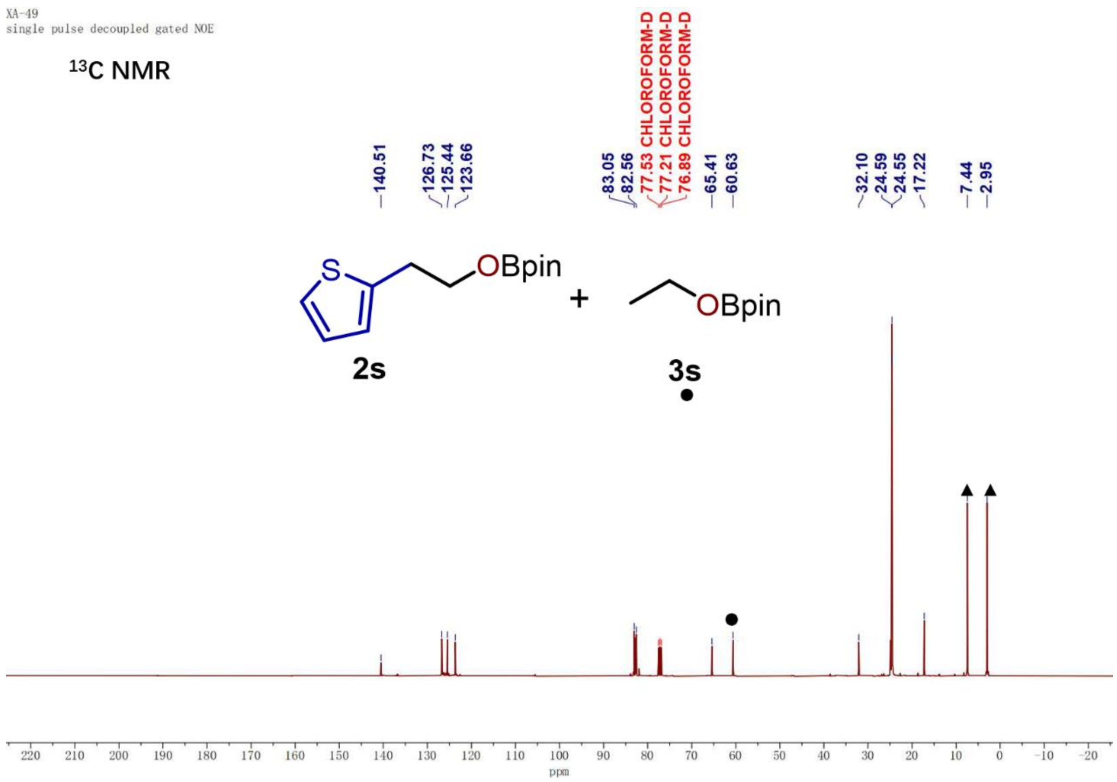


Figure S48. ^{13}C NMR spectrum of **2s** (101 MHz, Chloroform-*d*).

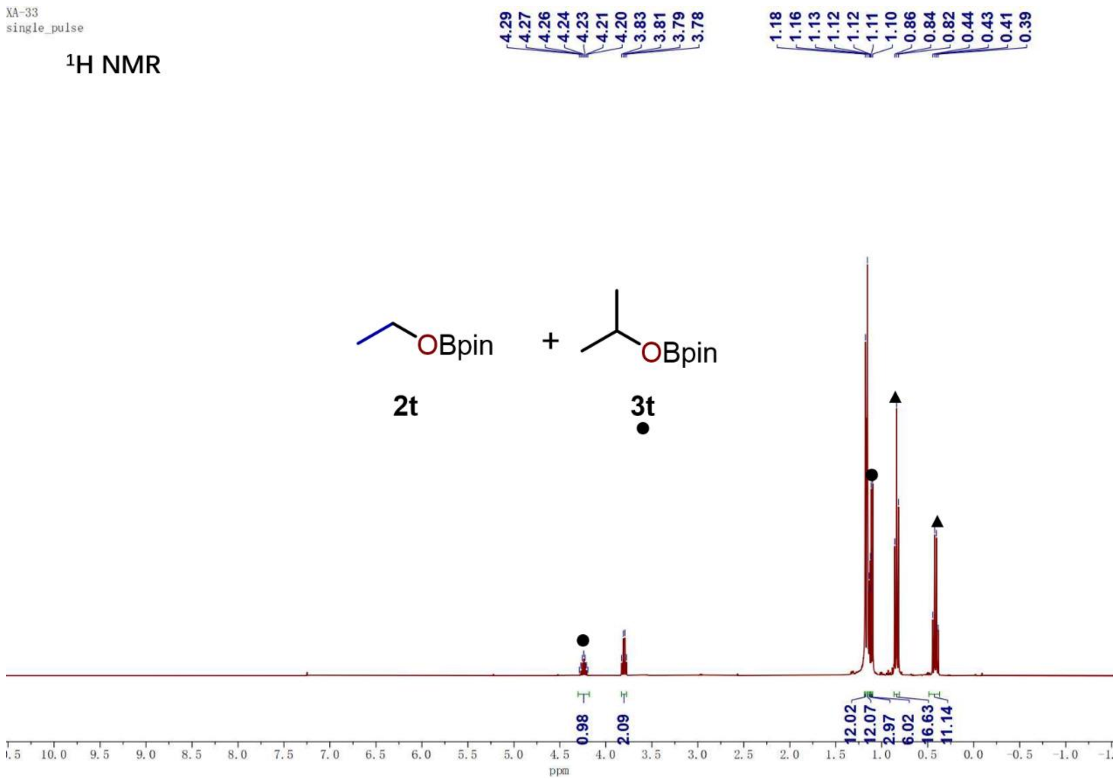


Figure S49. ^{1}H NMR spectrum of **2t** (400 MHz, Chloroform-*d*).

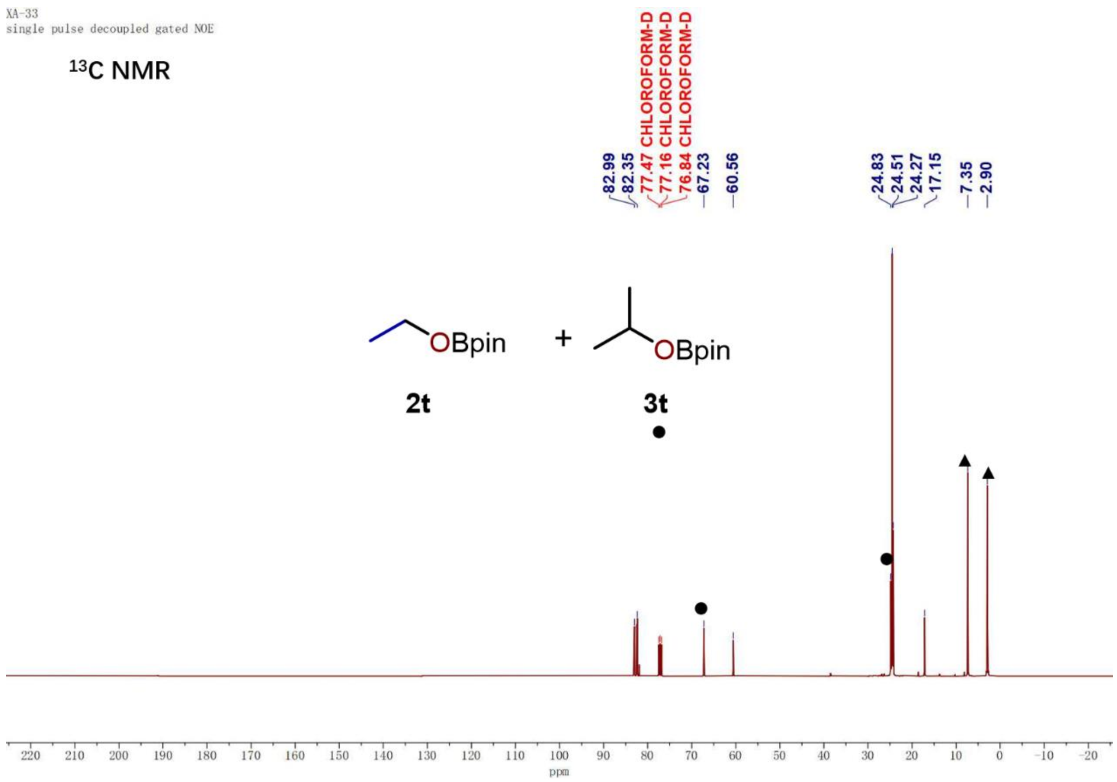


Figure S50. ^{13}C NMR spectrum of **2t** (101 MHz, Chloroform-*d*).

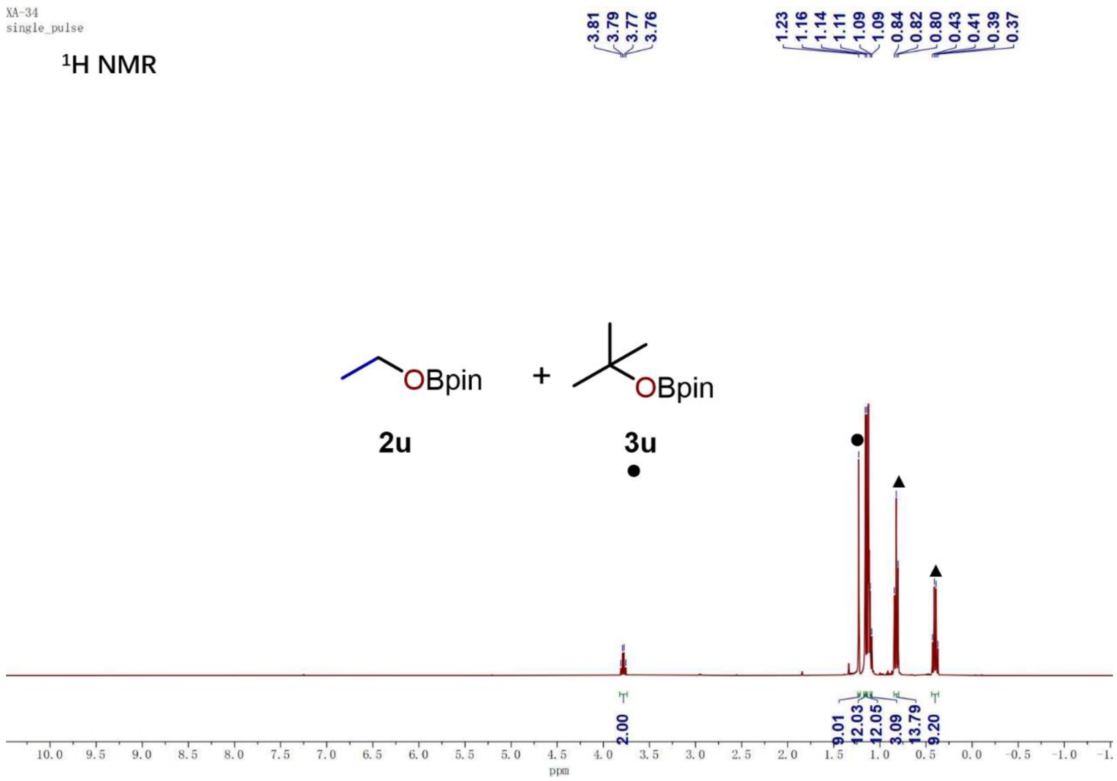


Figure S51. ^{1}H NMR spectrum of **2u** (400 MHz, Chloroform-*d*).

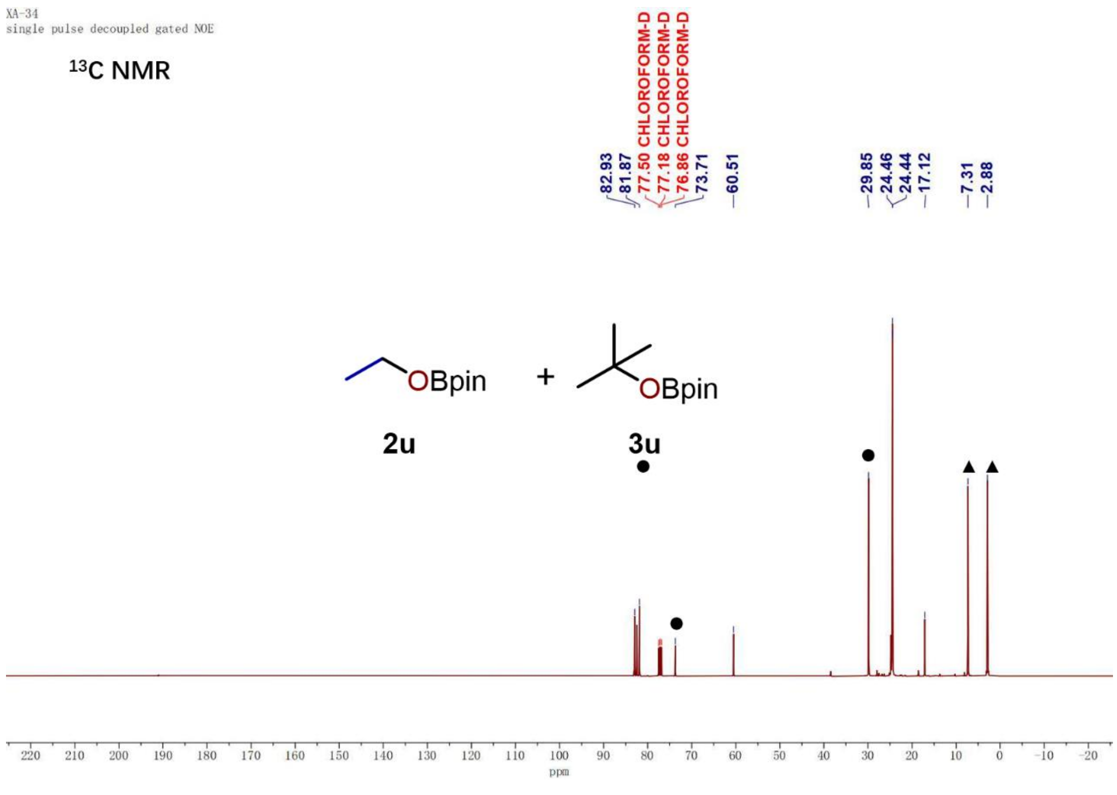


Figure S52. ^{13}C NMR spectrum of **2u** (101 MHz, Chloroform-*d*).

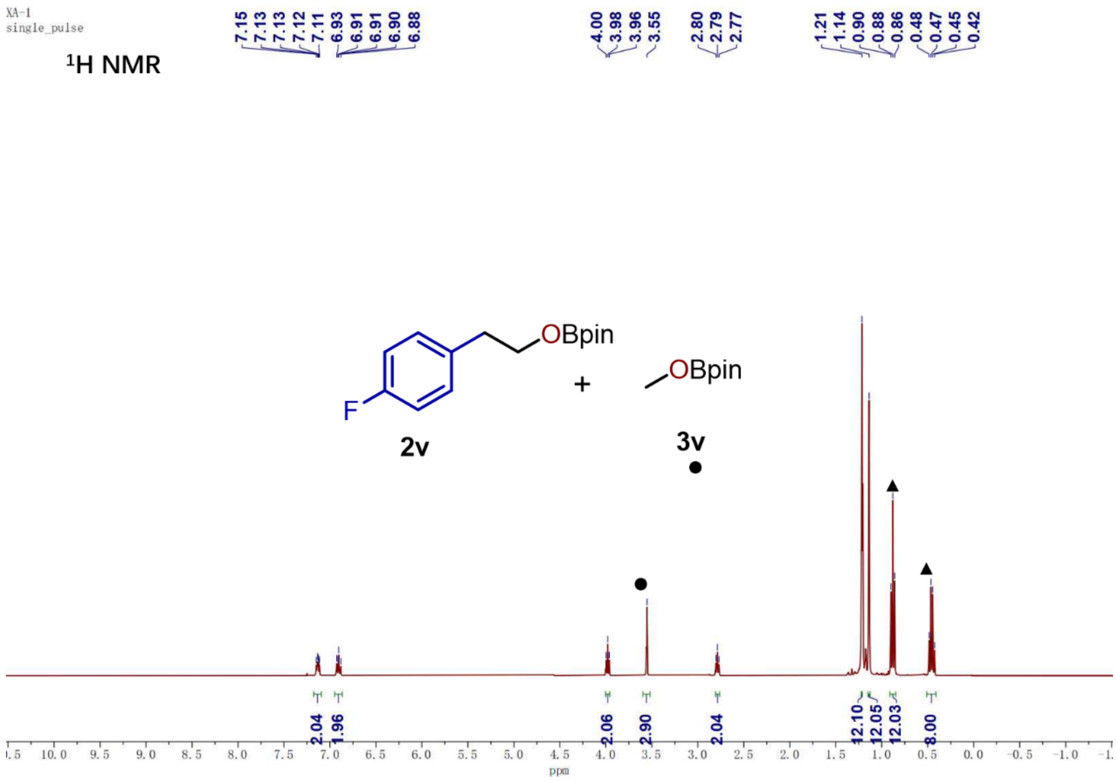


Figure S53. ^{1}H NMR spectrum of **2v** (400 MHz, Chloroform-*d*).

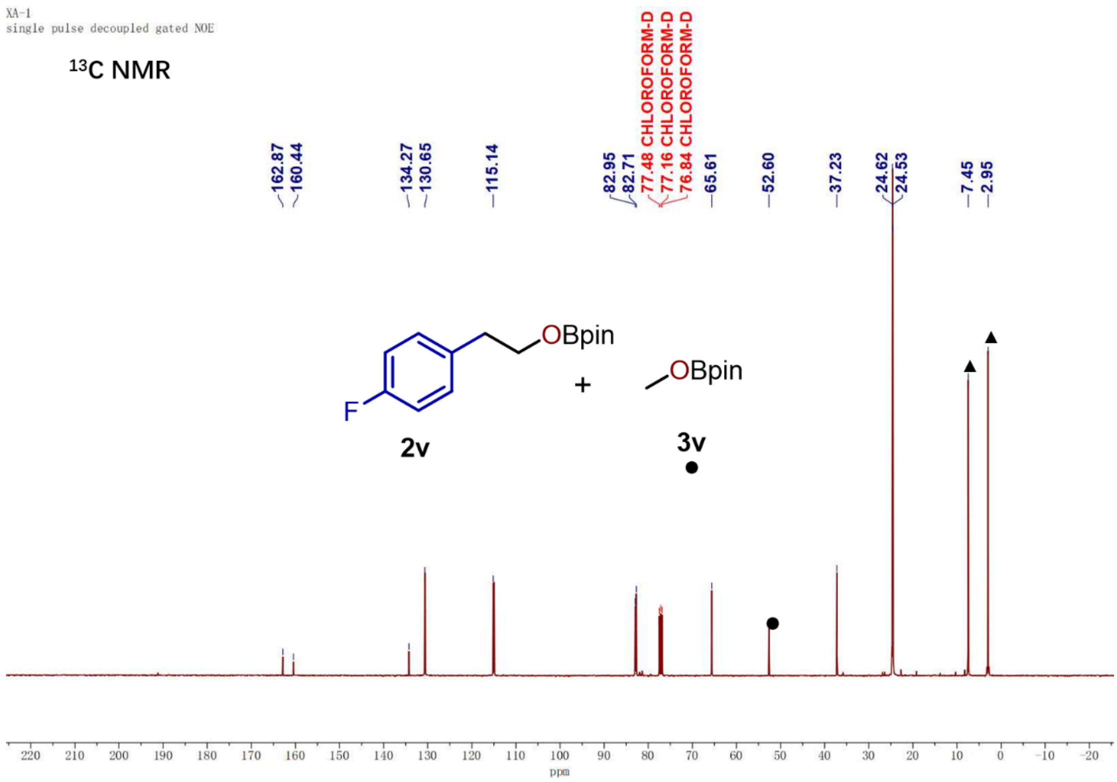


Figure S54. ^{13}C NMR spectrum of **2v** (101 MHz, Chloroform-*d*).

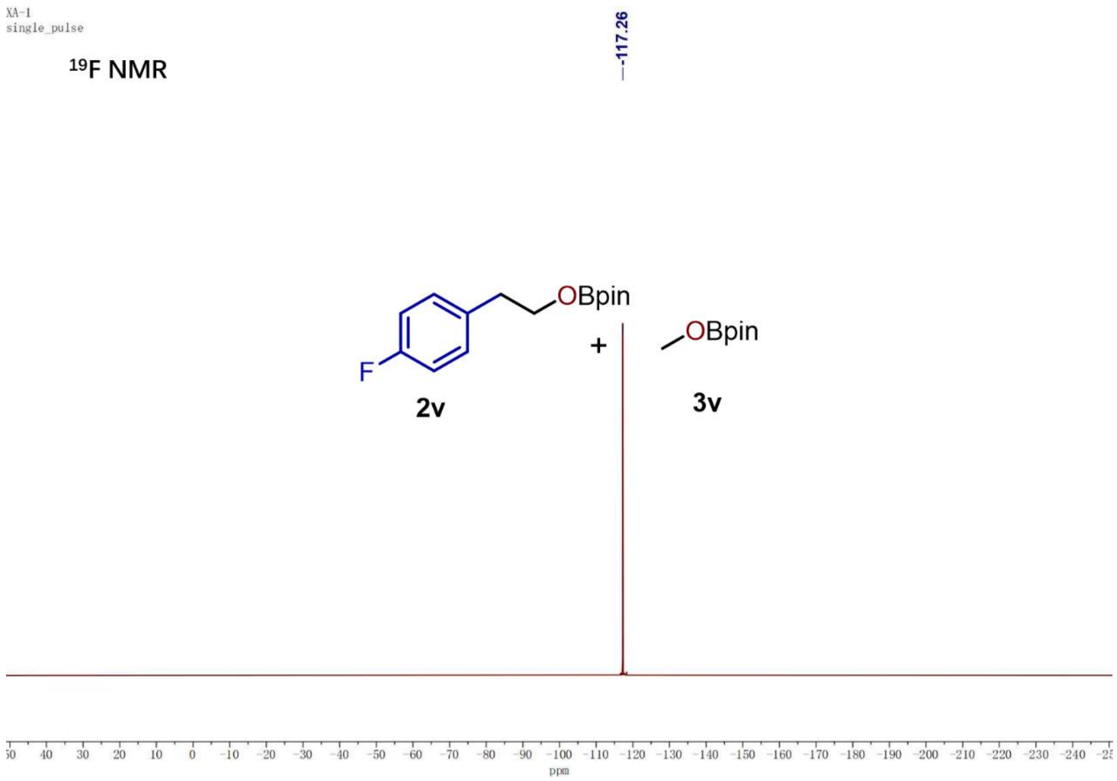


Figure S55. ^{19}F NMR spectrum of **2v** (376 MHz, Chloroform-*d*).

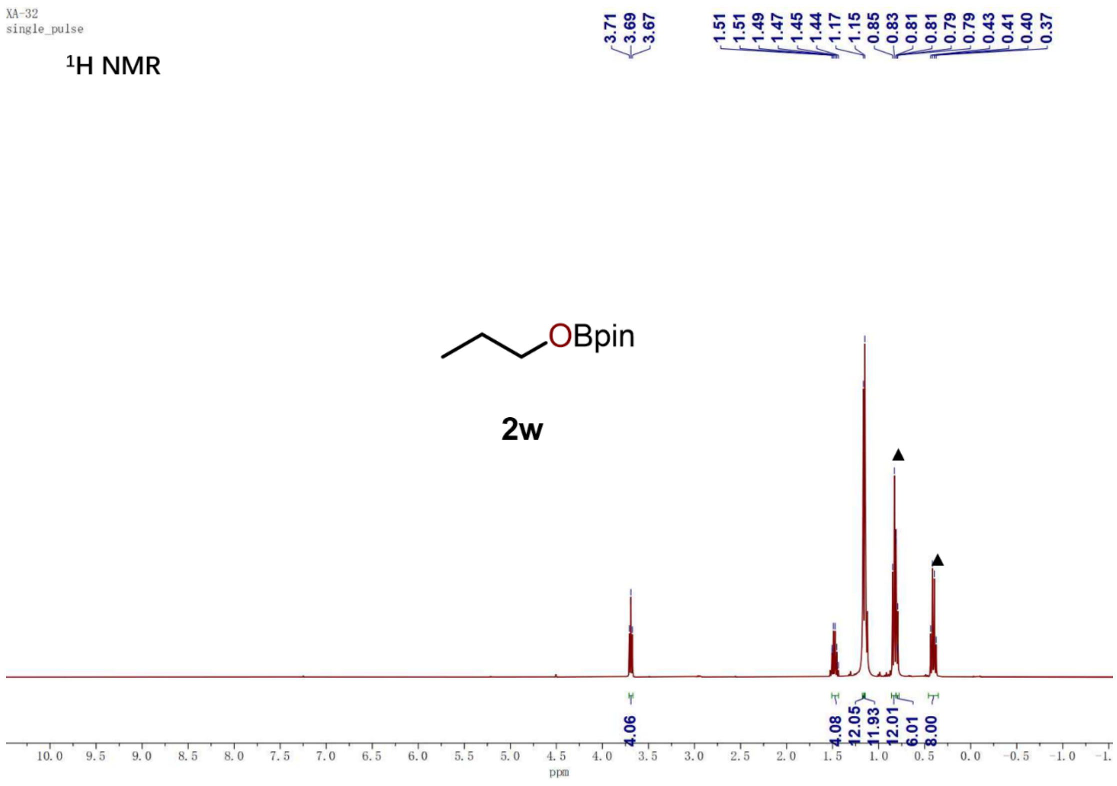


Figure S56. ^{1}H NMR spectrum of **2w** (400 MHz, Chloroform-*d*).

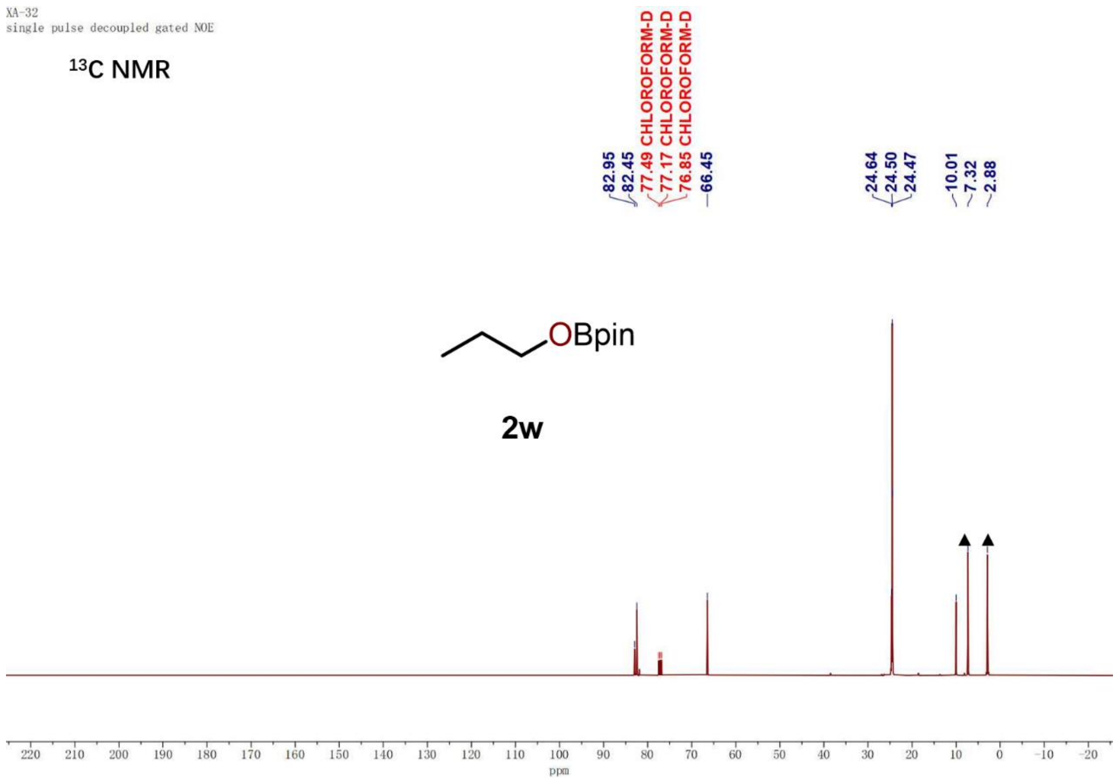


Figure S57. ^{13}C NMR spectrum of **2w** (101 MHz, Chloroform-*d*).

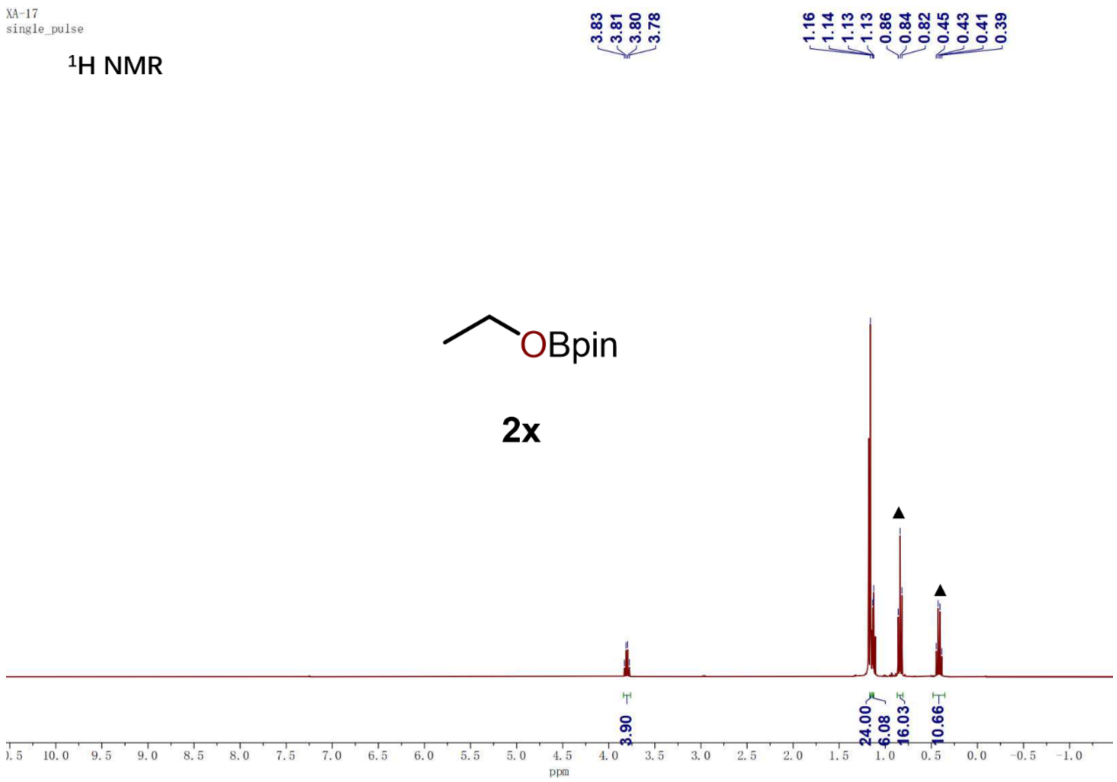


Figure S58. ^{1}H NMR spectrum of **2x** (400 MHz, Chloroform-*d*).

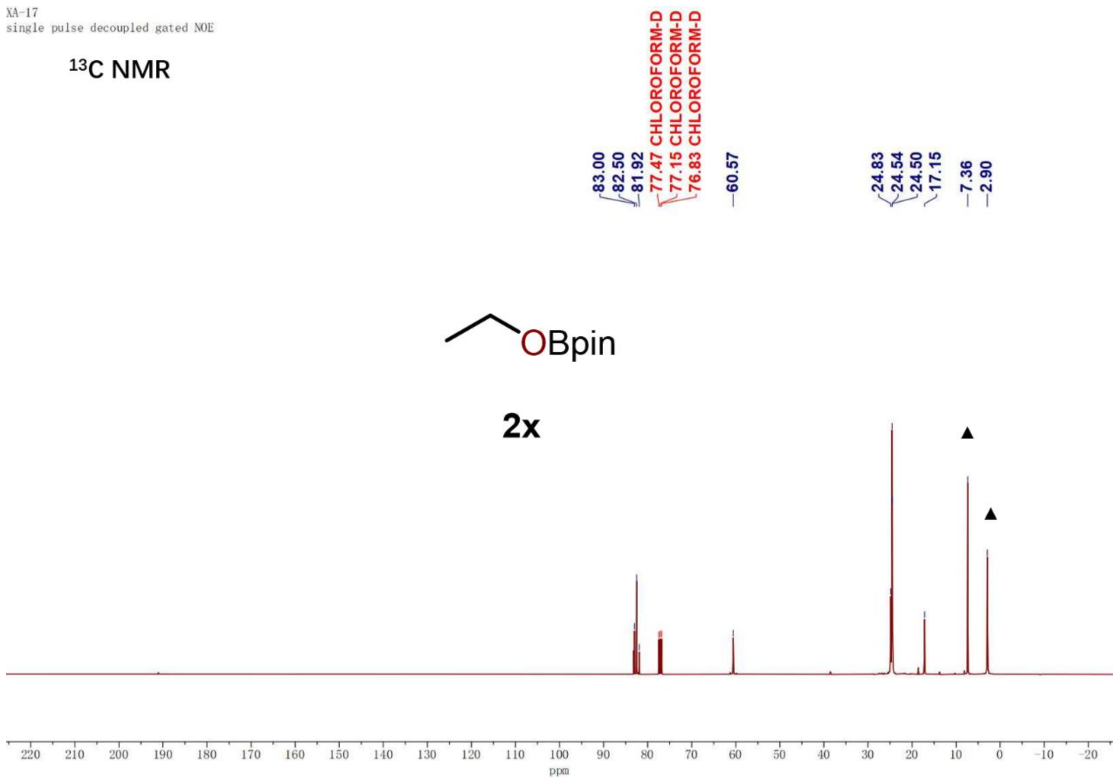


Figure S59. ^{13}C NMR spectrum of **2x** (101 MHz, Chloroform-*d*).

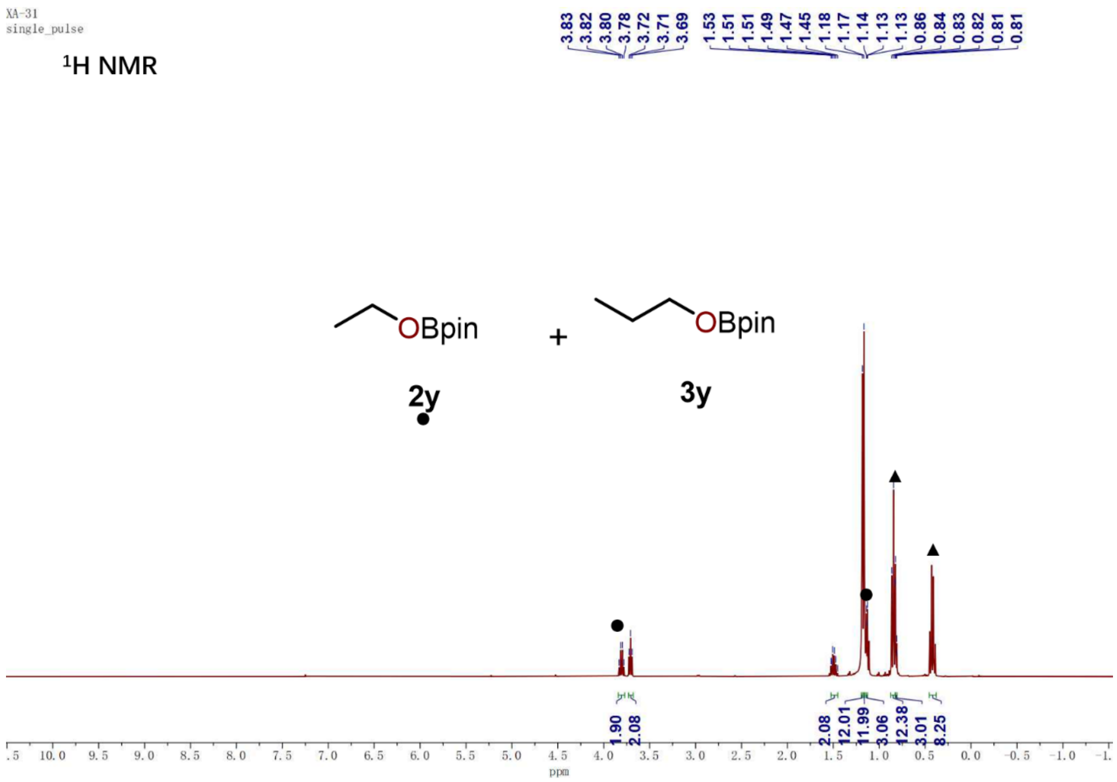


Figure S60. ^{1}H NMR spectrum of **2y** (400 MHz, Chloroform-*d*).

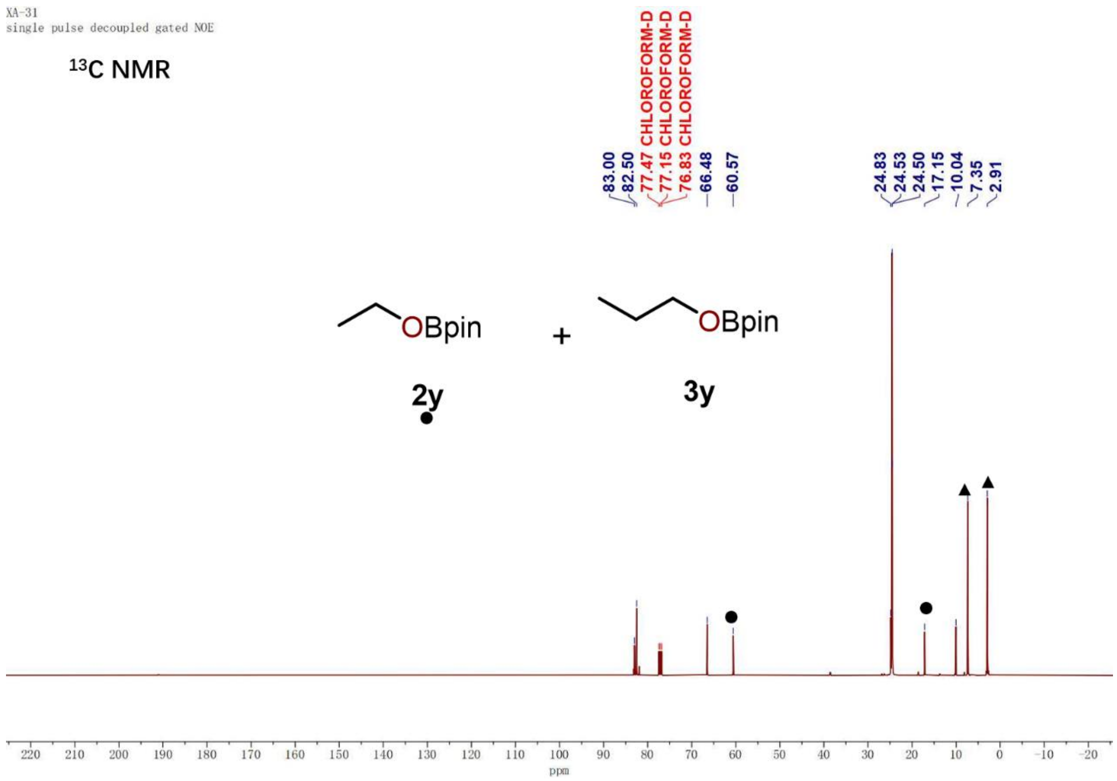


Figure S61. ^{13}C NMR spectrum of **2y** (101 MHz, Chloroform-*d*).

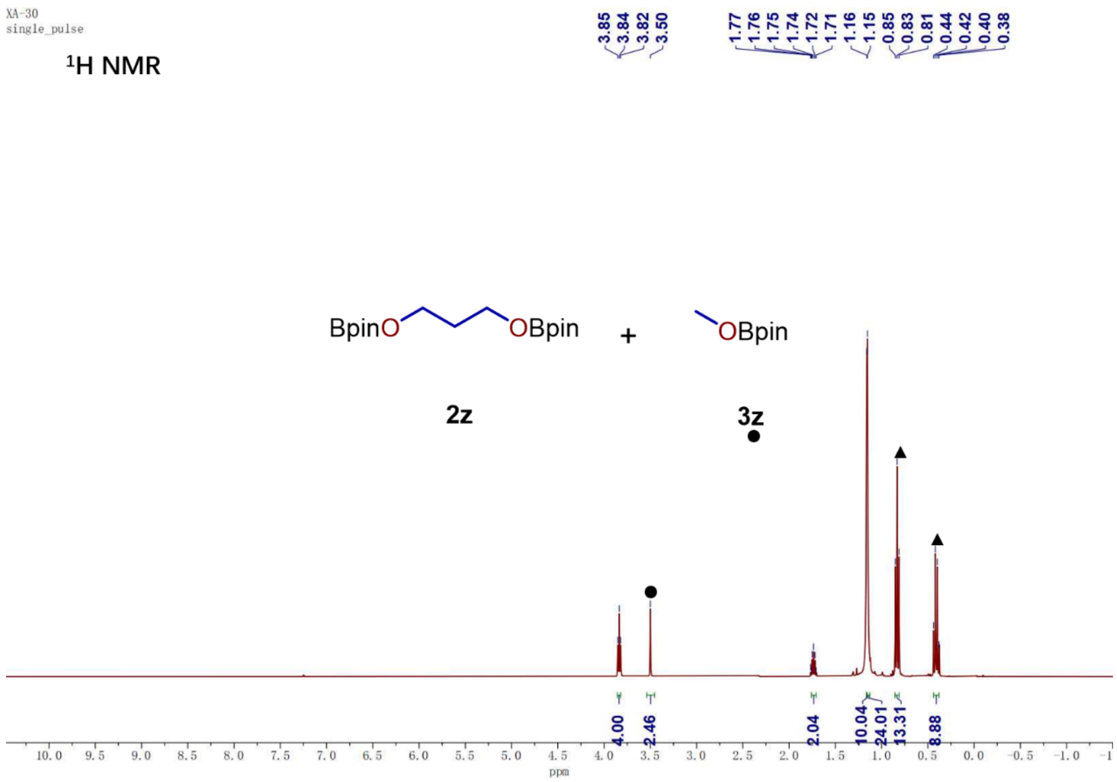


Figure S62. ^{1}H NMR spectrum of **2z** (400 MHz, Chloroform-*d*).

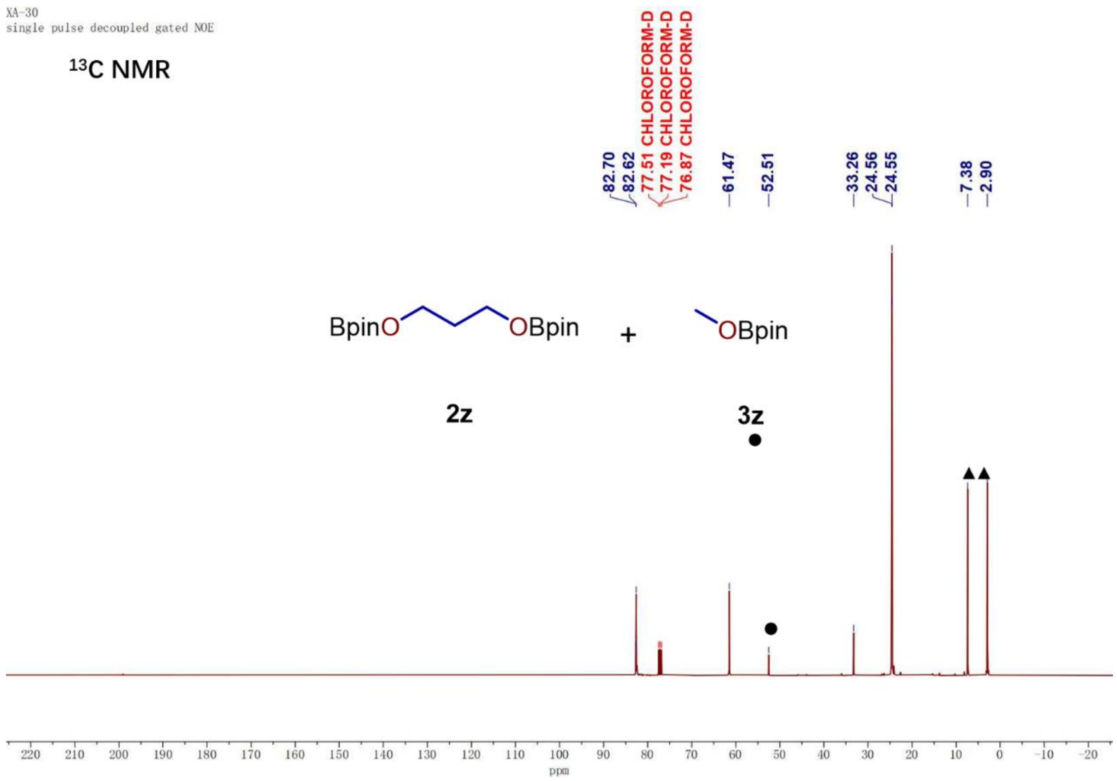


Figure S63. ^{13}C NMR spectrum of **2z** (101 MHz, Chloroform-*d*).

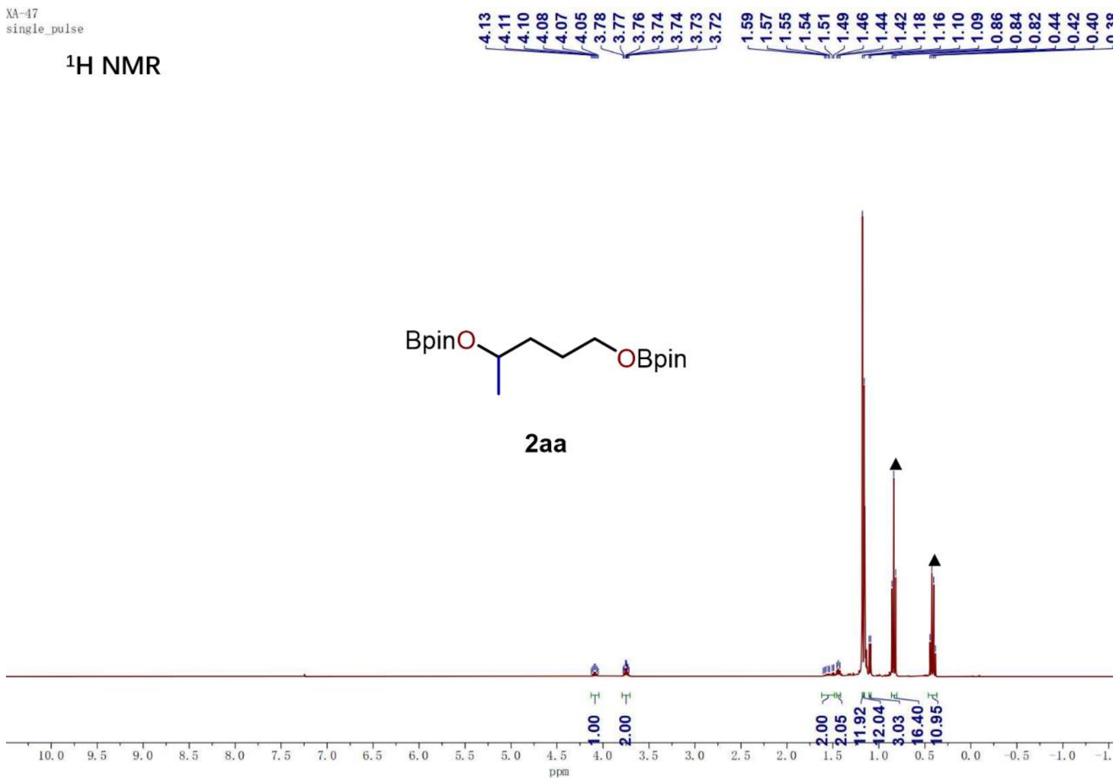


Figure S64. ^{1}H NMR spectrum of **2aa** (400 MHz, Chloroform-*d*).

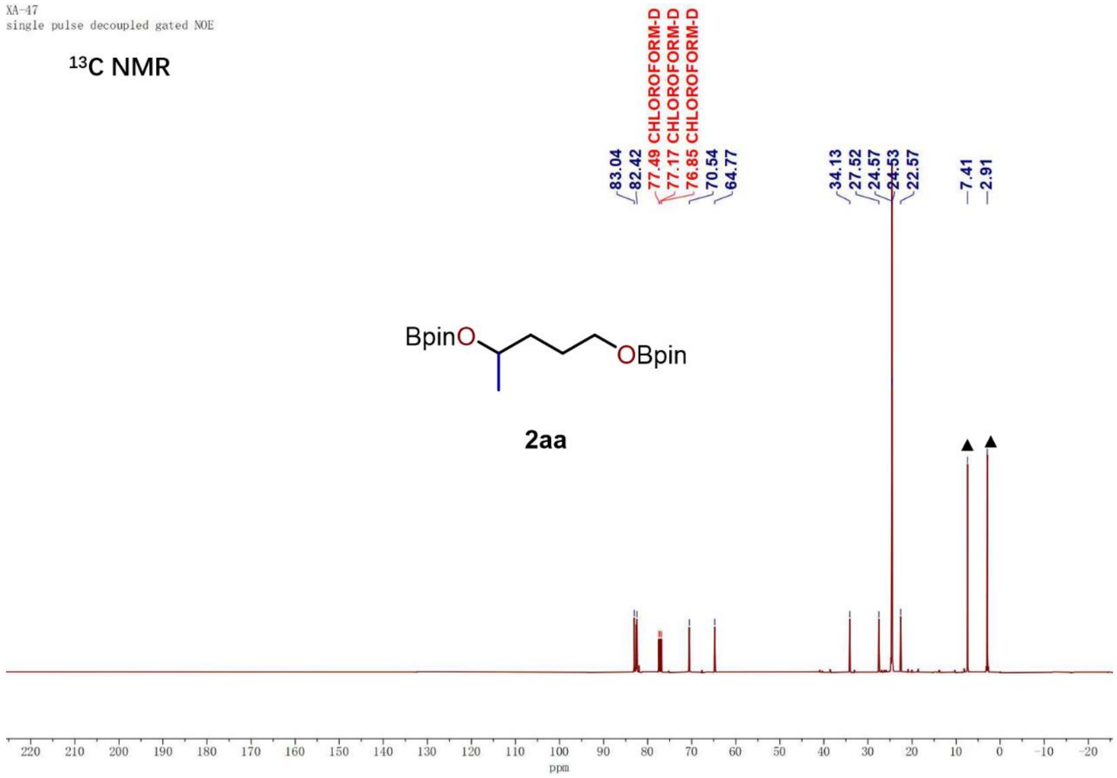


Figure S65. ^{13}C NMR spectrum of **2aa** (101 MHz, Chloroform-*d*).

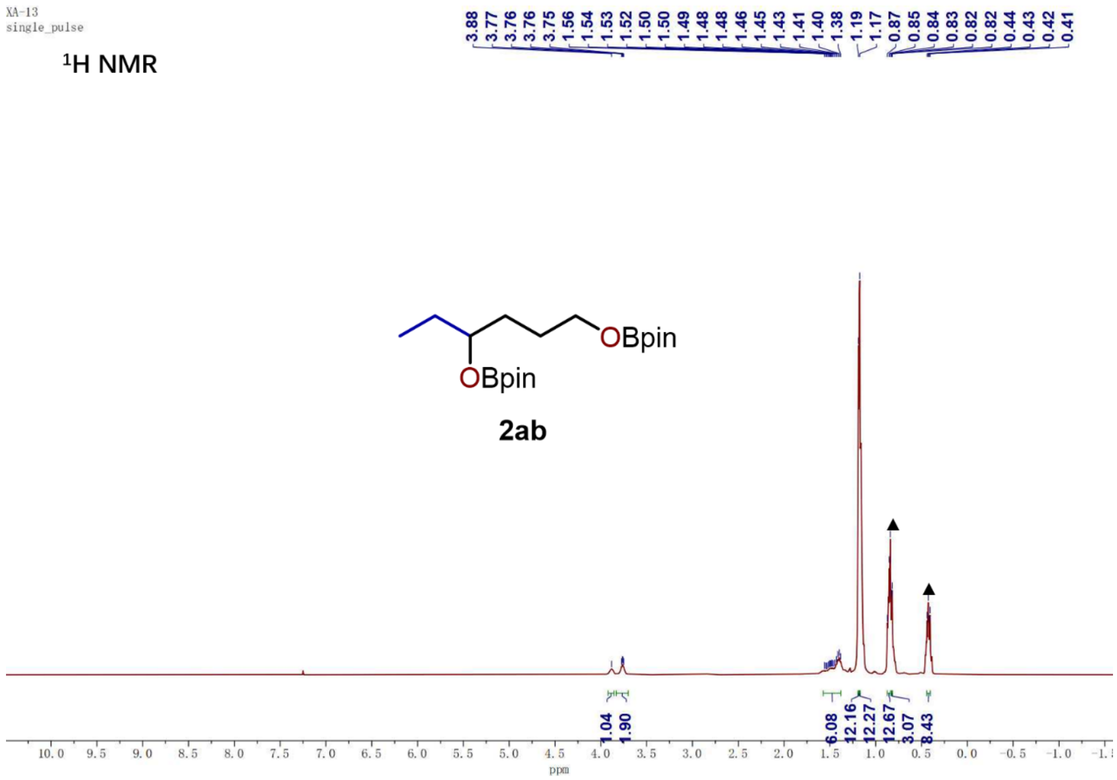


Figure S66. ^{1}H NMR spectrum of **2ab** (400 MHz, Chloroform-*d*).

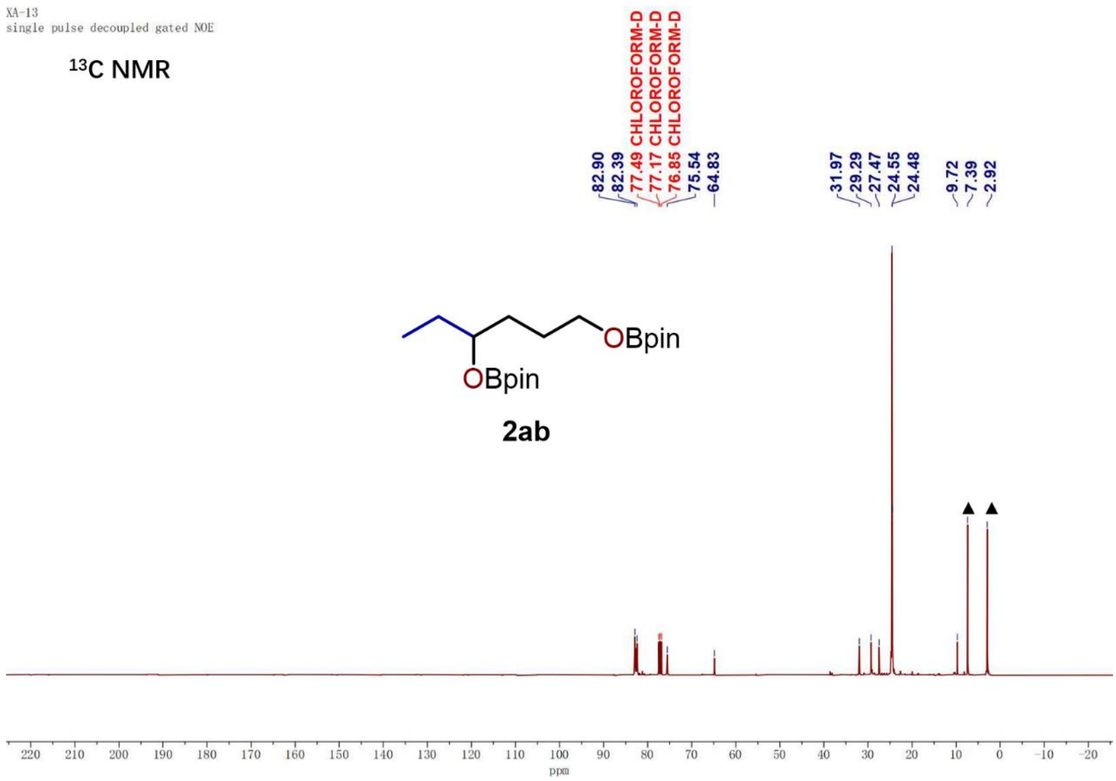


Figure S67. ^{13}C NMR spectrum of **2ab** (101 MHz, Chloroform-*d*).

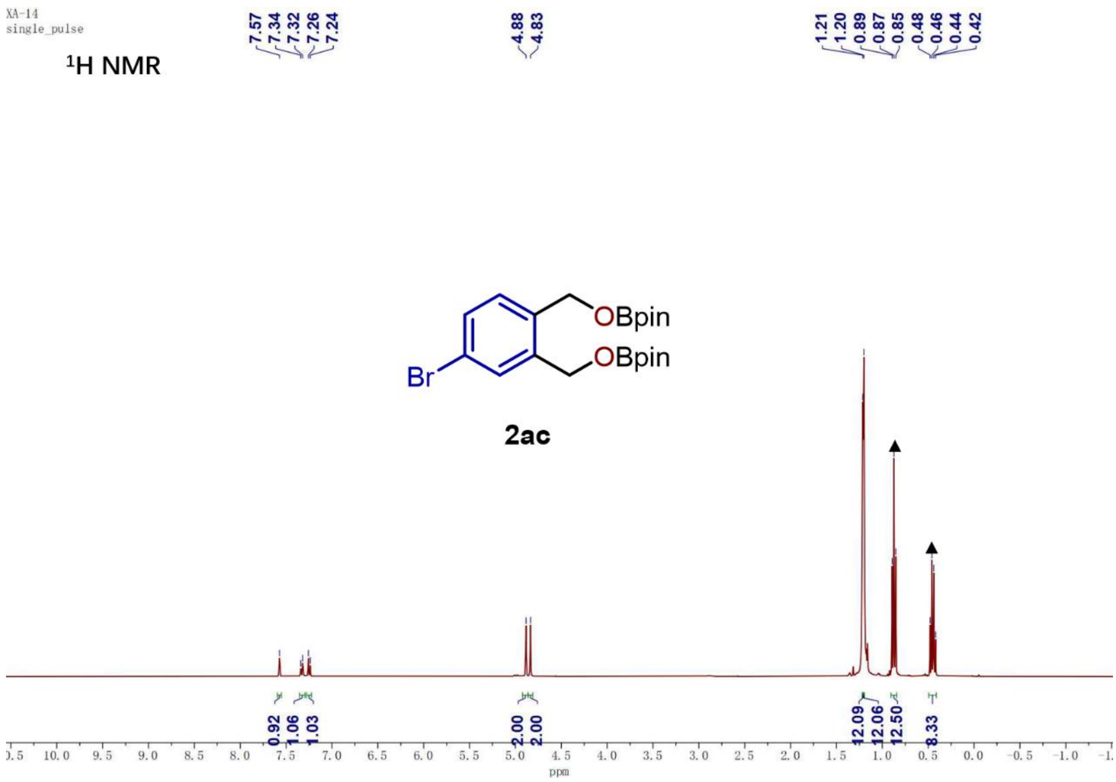


Figure S68. ^{1}H NMR spectrum of **2ac** (400 MHz, Chloroform-*d*).

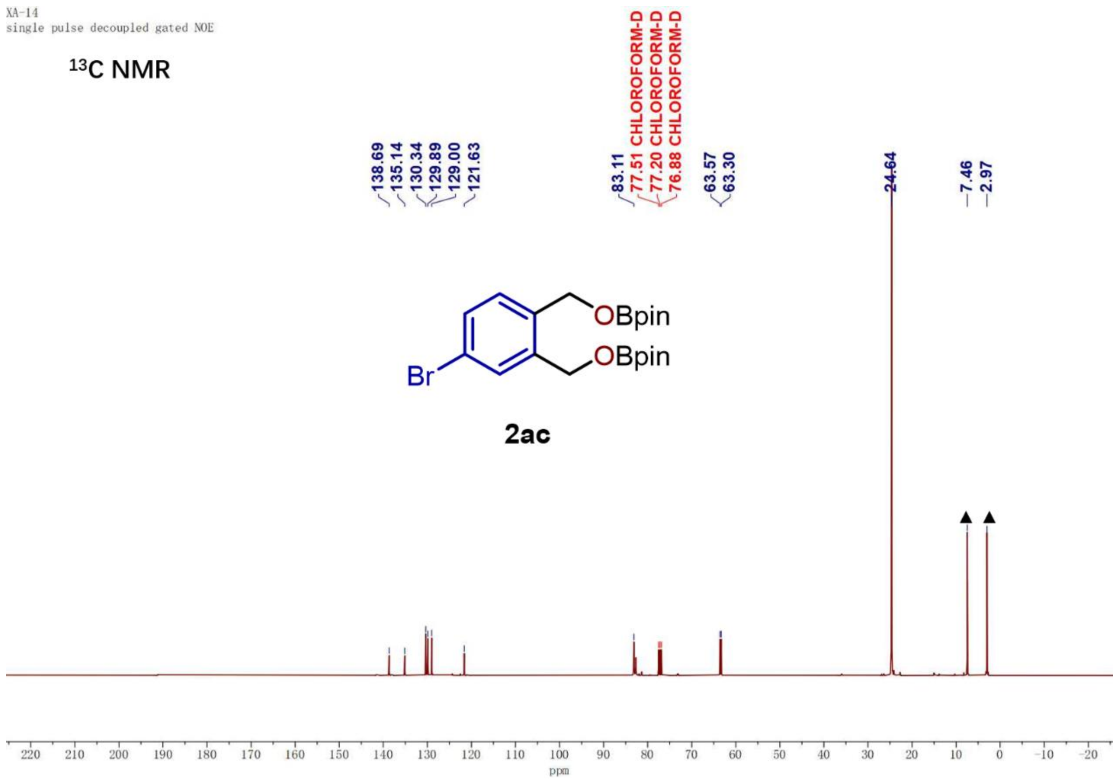


Figure S69. ^{13}C NMR spectrum of **2ac** (101 MHz, Chloroform-*d*).

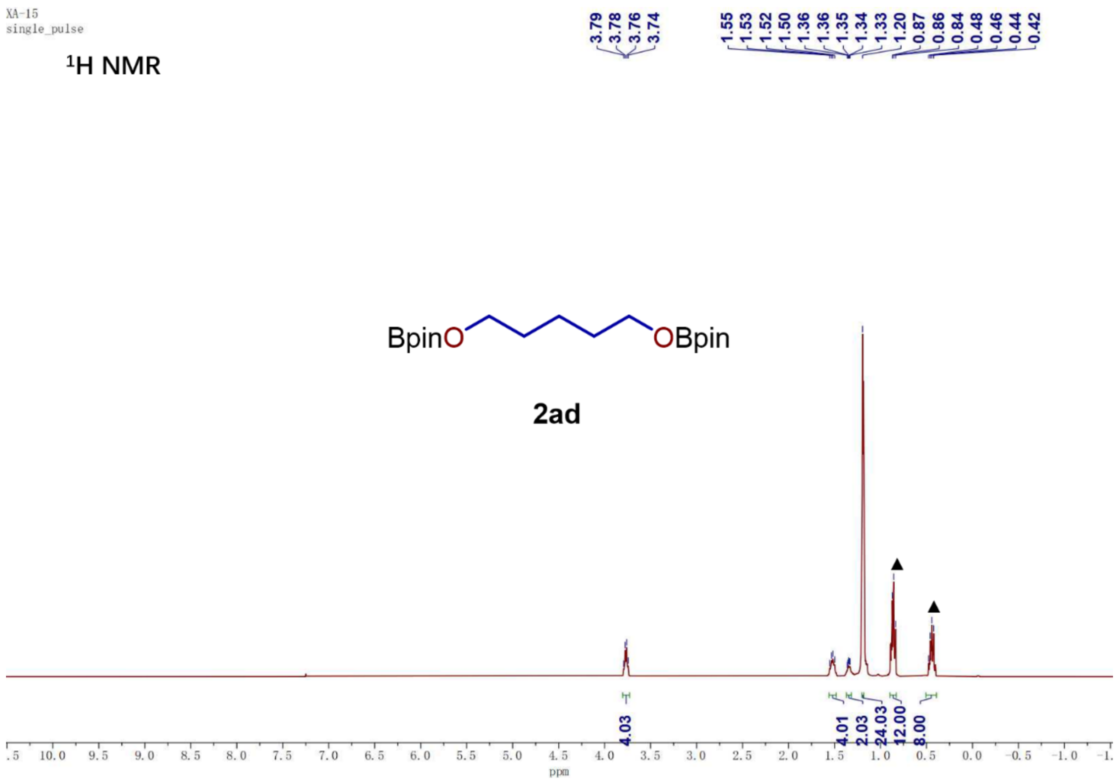


Figure S70. ^{1}H NMR spectrum of **2ad** (400 MHz, Chloroform-*d*).

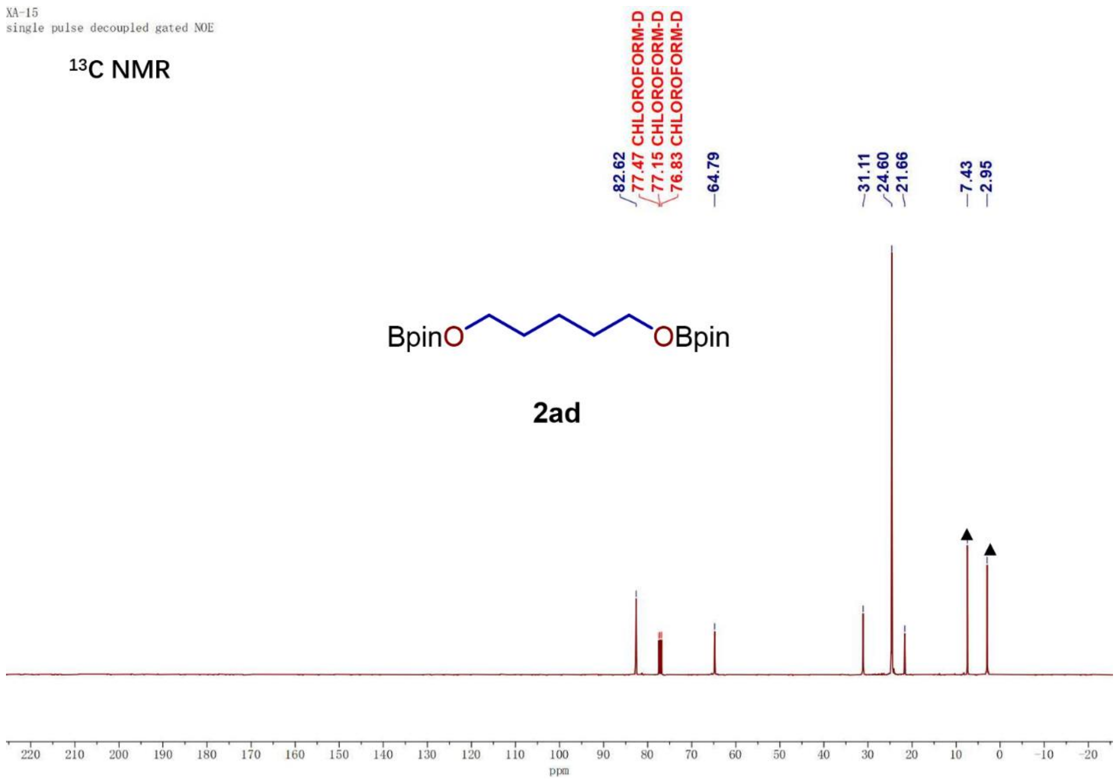


Figure S71. ^{13}C NMR spectrum of **2ad** (101 MHz, Chloroform-*d*).

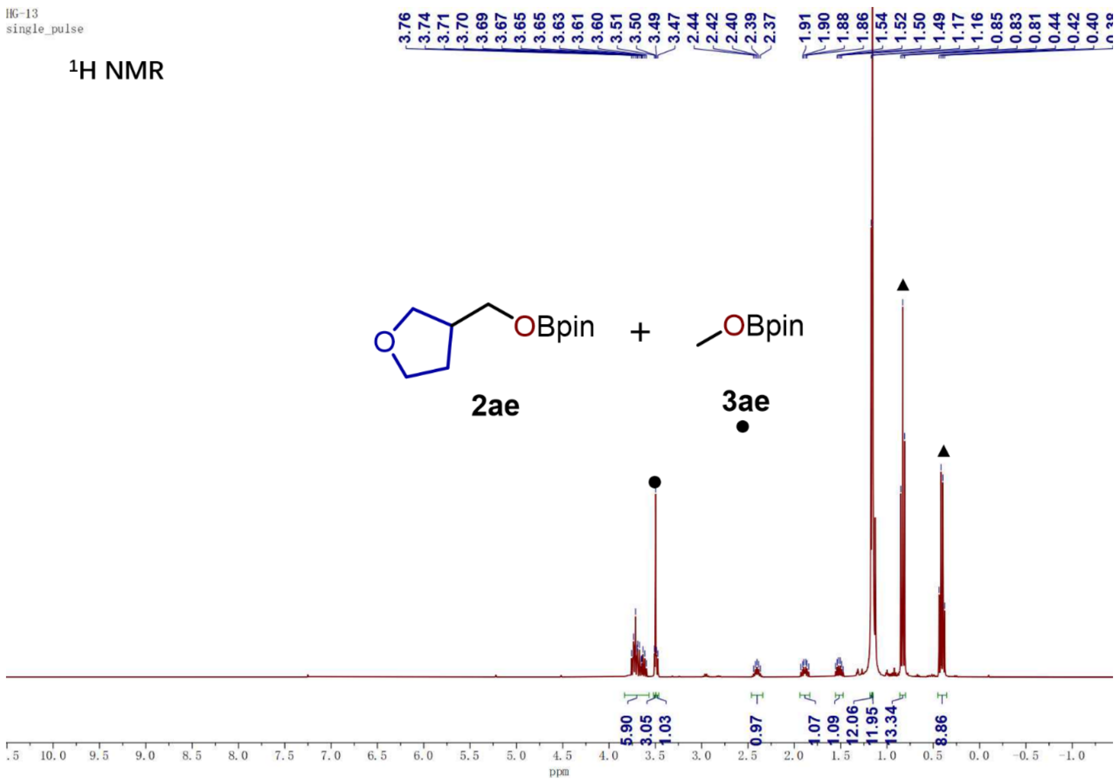


Figure S72. ^{1}H NMR spectrum of **2ae** (400 MHz, Chloroform-*d*).

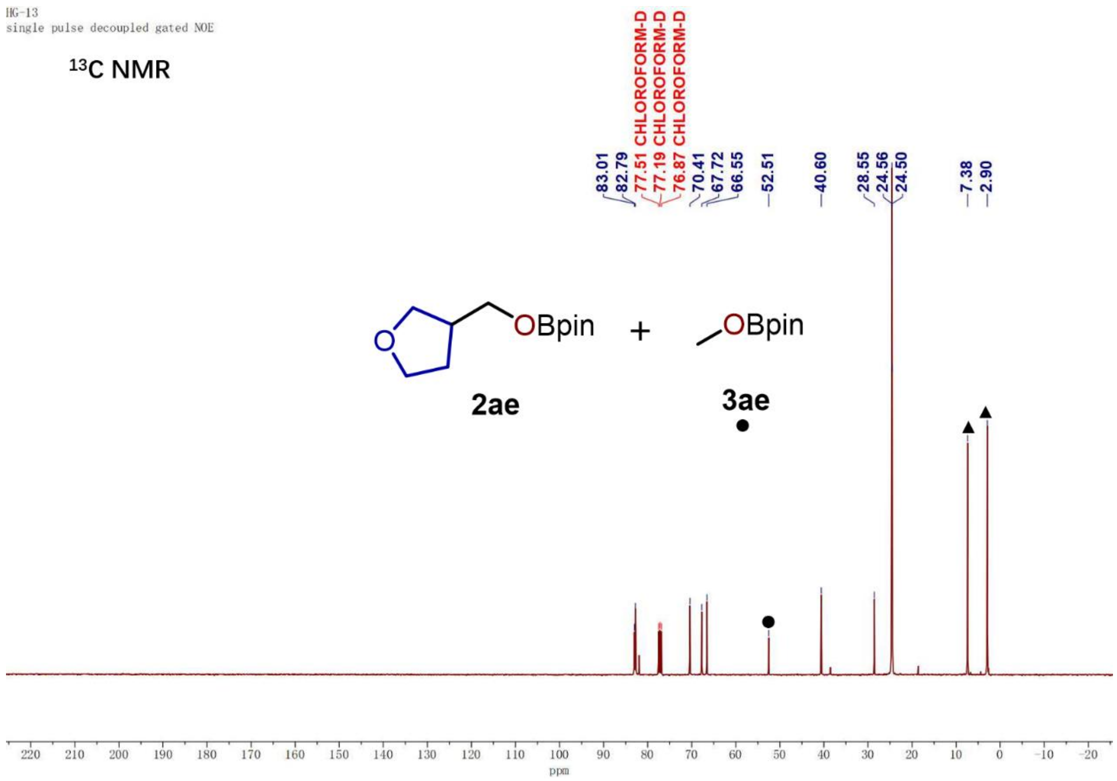


Figure S73. ^{13}C NMR spectrum of **2ae** (101 MHz, Chloroform-*d*).

12.2. NMR Spectra for Nitriles

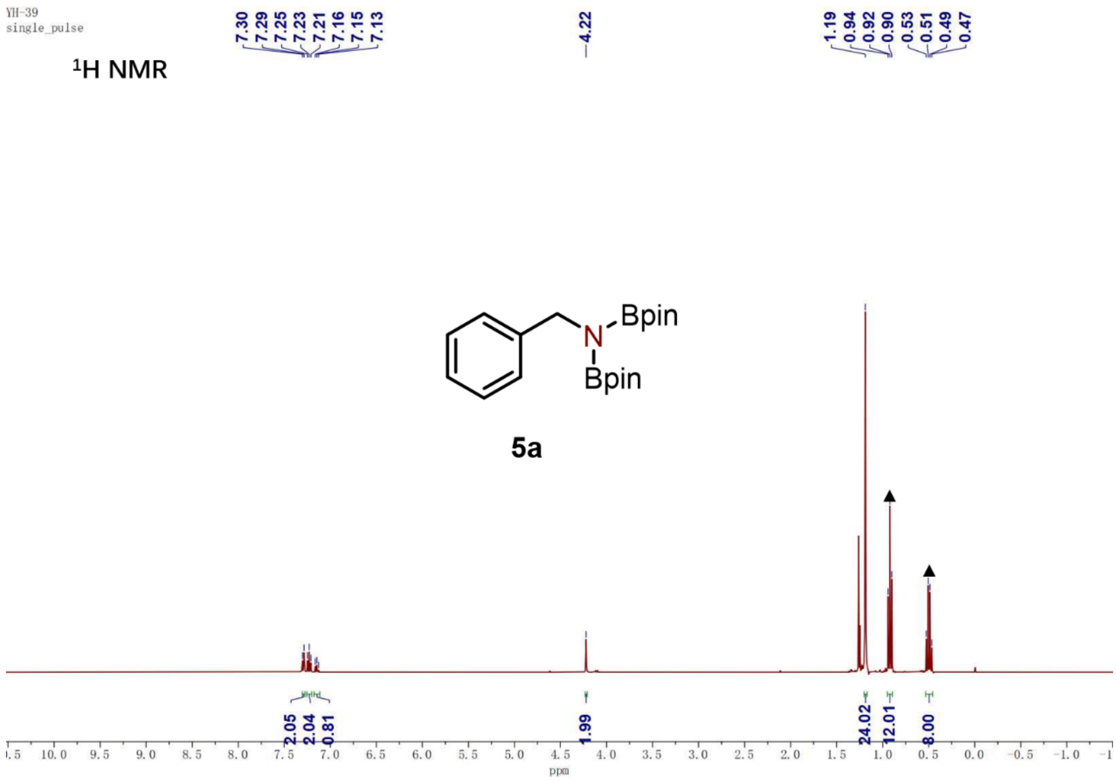


Figure S74. ^{1}H NMR spectrum of **5a** (400 MHz, Chloroform-*d*).

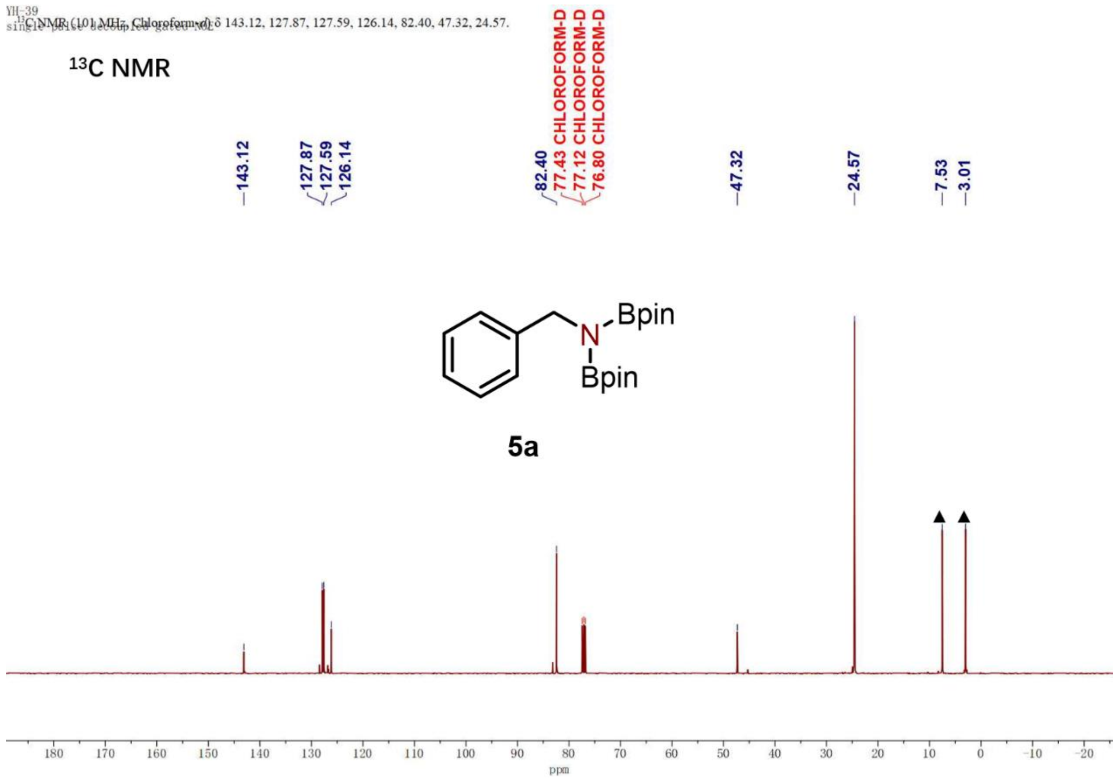


Figure S75. ^{13}C NMR spectrum of **5a** (101 MHz, Chloroform-*d*).

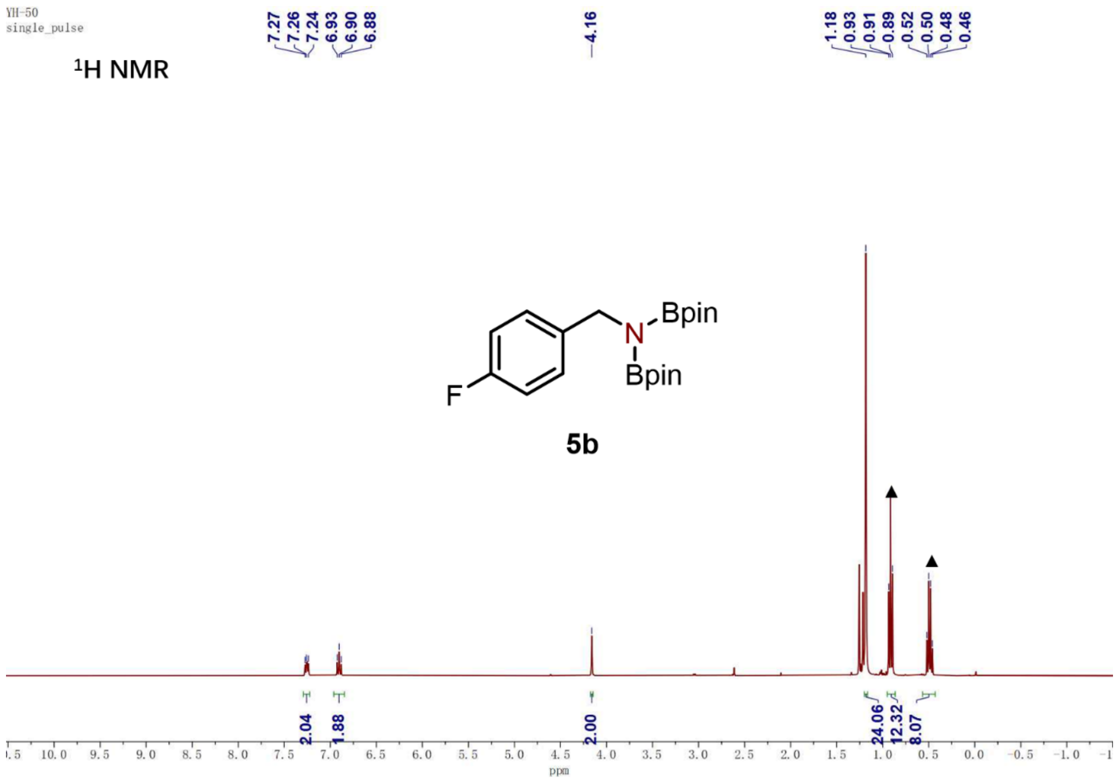


Figure S76. ^{1}H NMR spectrum of **5b** (400 MHz, Chloroform-*d*).

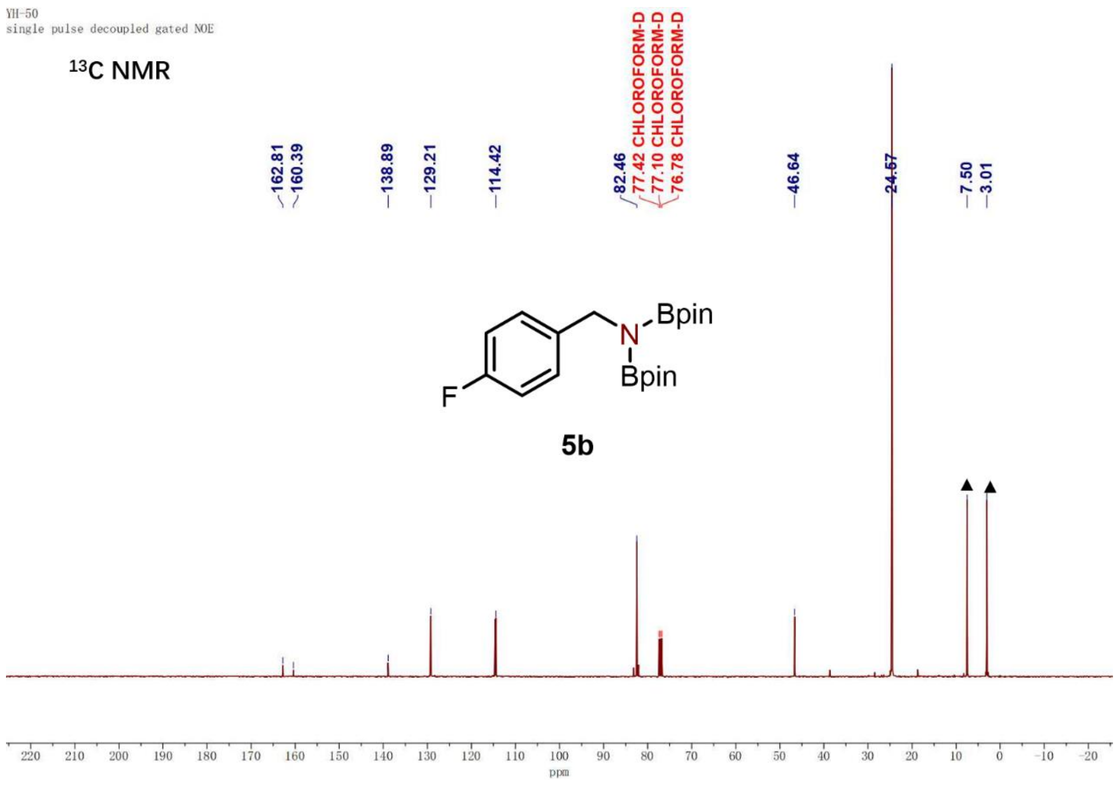


Figure S77. ^{13}C NMR spectrum of **5b** (101 MHz, Chloroform-*d*).

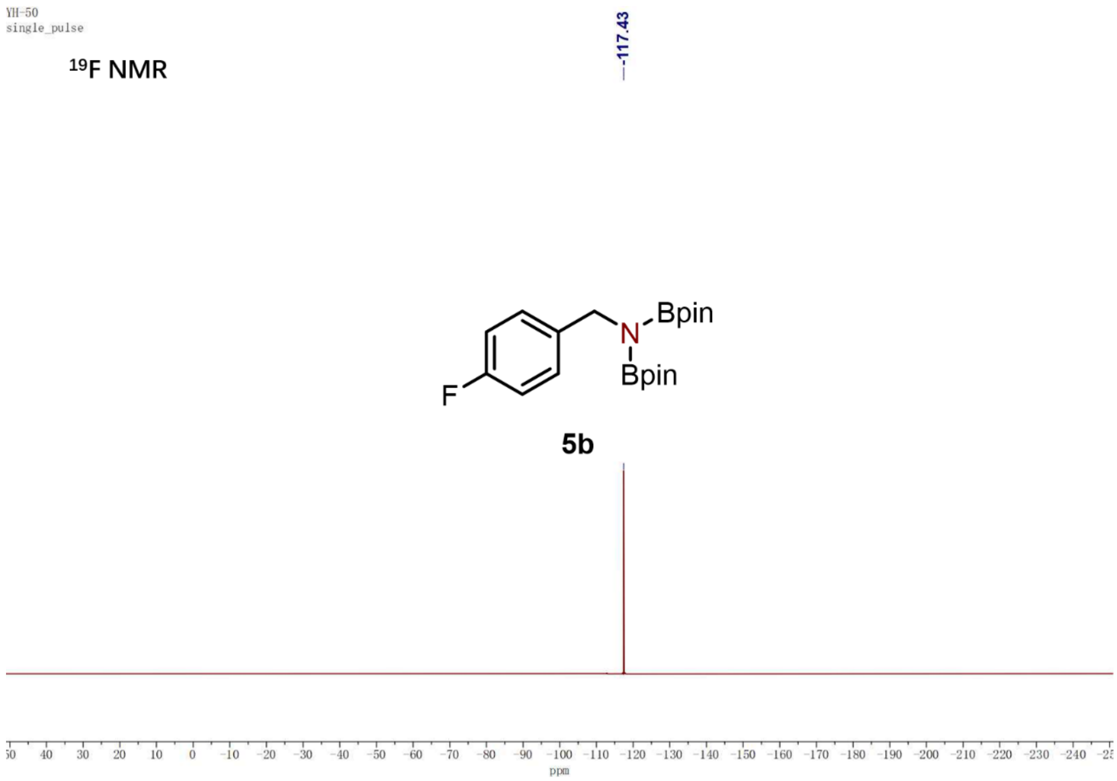


Figure S78. ^{19}F NMR spectrum of **5b** (376 MHz, Chloroform-*d*).

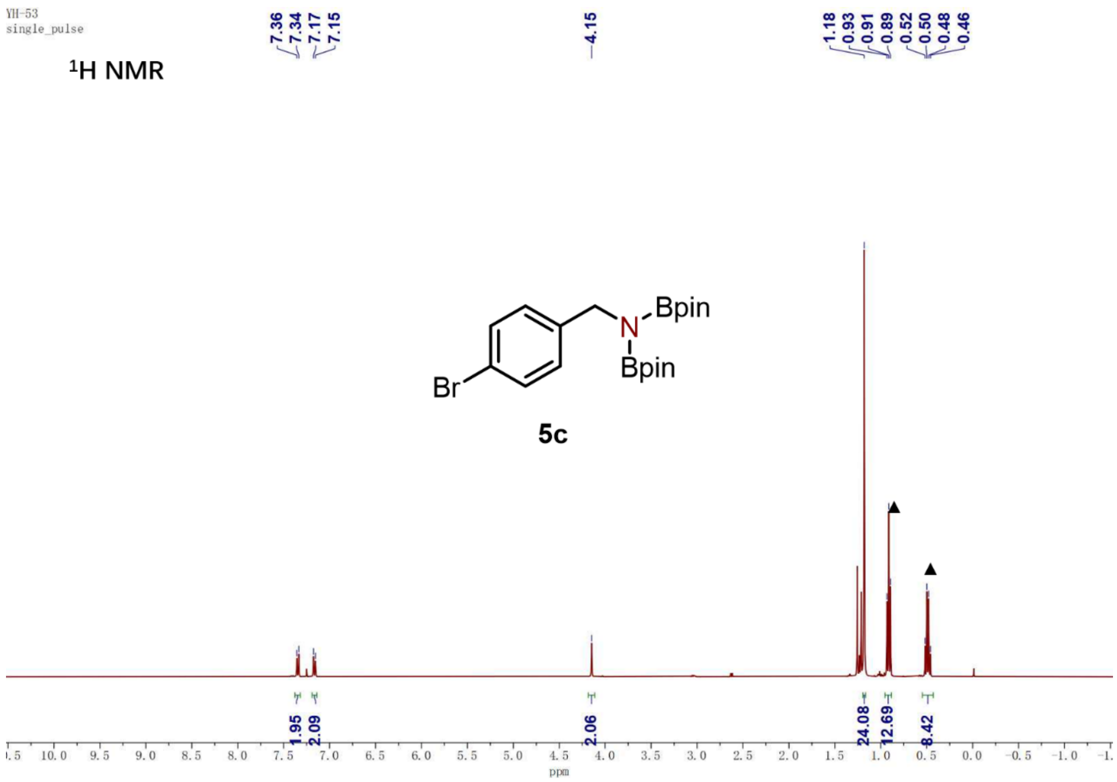


Figure S79. ^{1}H NMR spectrum of **5c** (400 MHz, Chloroform-*d*).

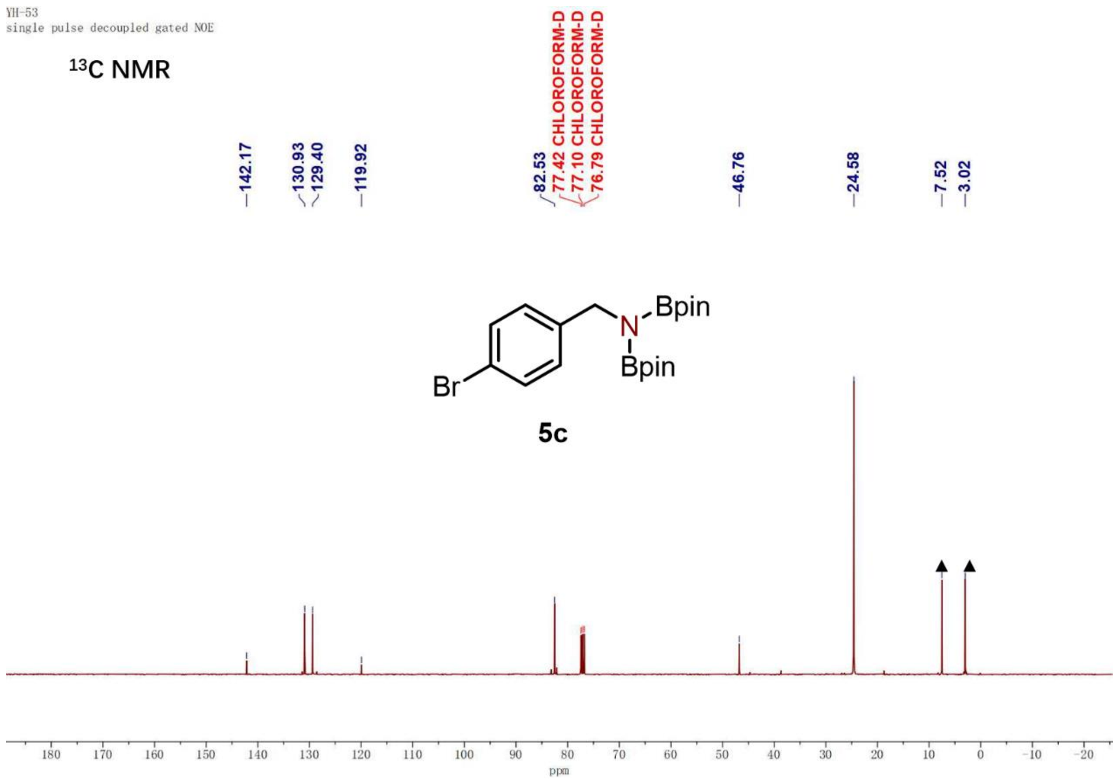


Figure S80. ^{13}C NMR spectrum of **5c** (101 MHz, Chloroform-*d*).

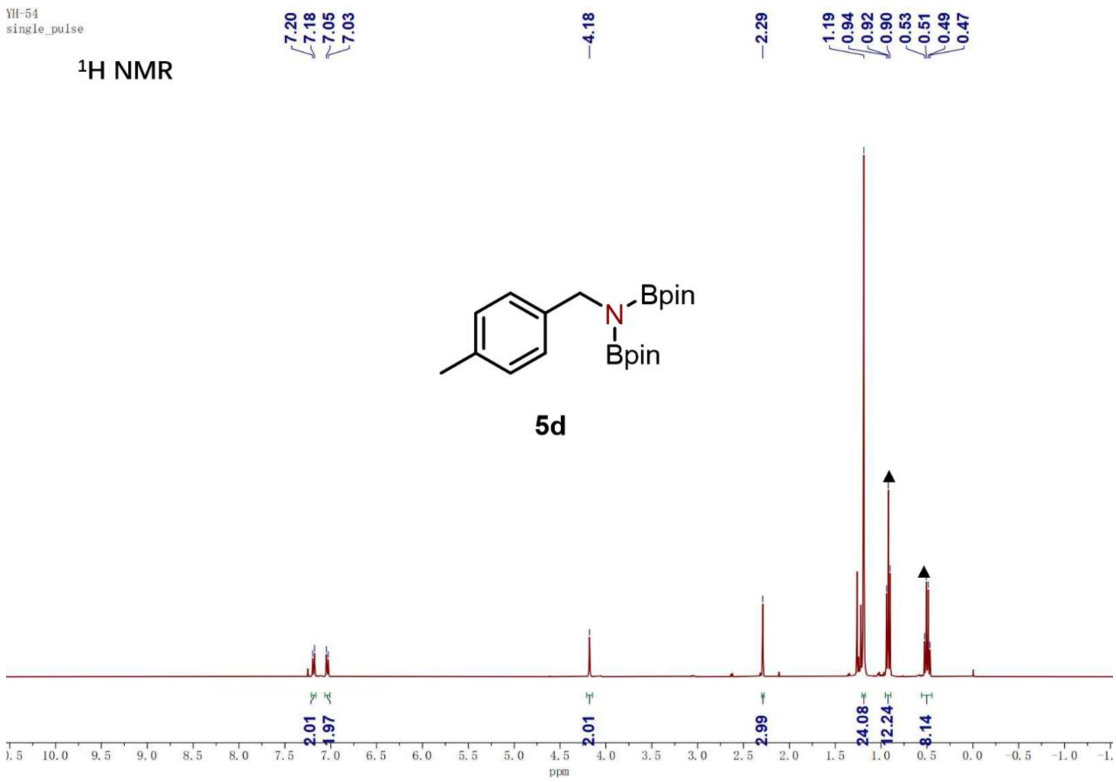


Figure S81. ^{1}H NMR spectrum of **5d** (400 MHz, Chloroform-*d*).

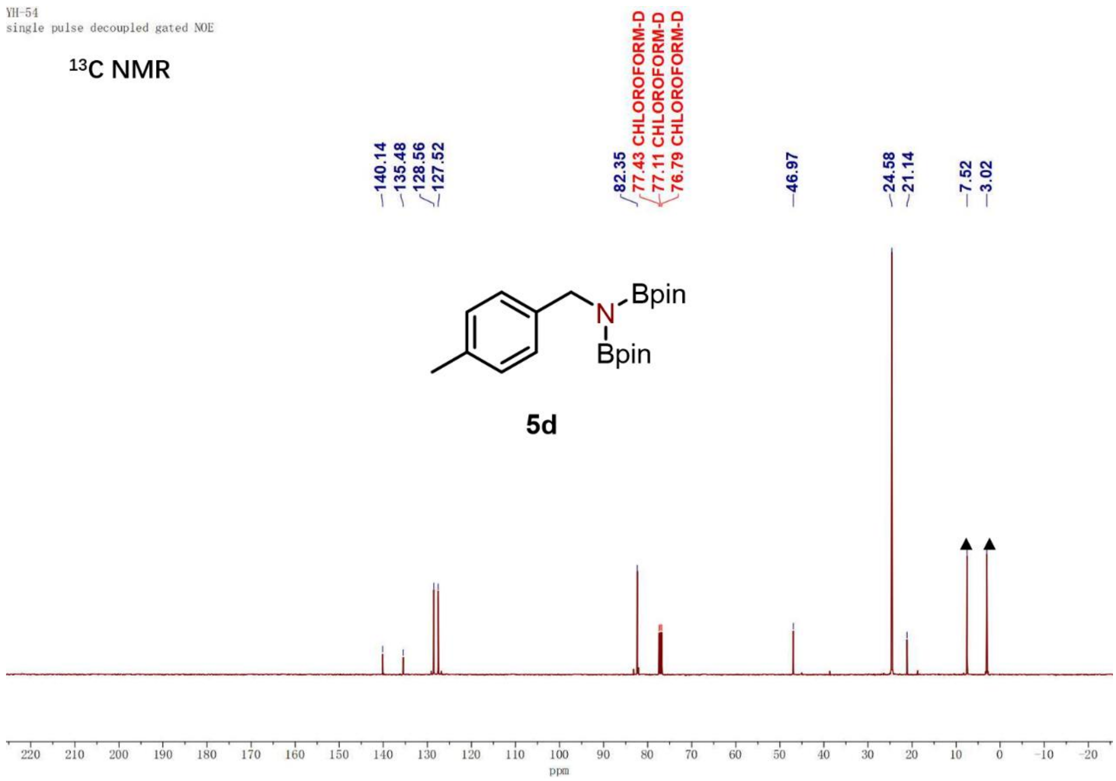


Figure S82. ^{13}C NMR spectrum of **5d** (101 MHz, Chloroform-*d*).

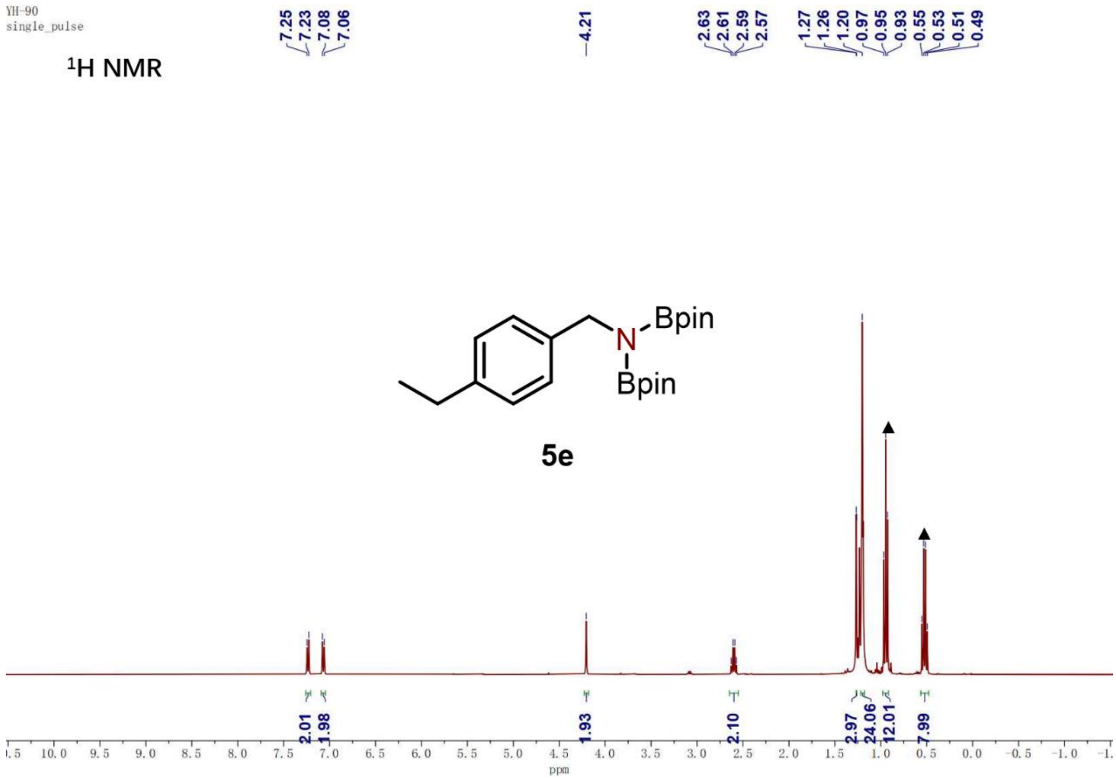


Figure S83. ^{1}H NMR spectrum of **5e** (400 MHz, Chloroform-*d*).

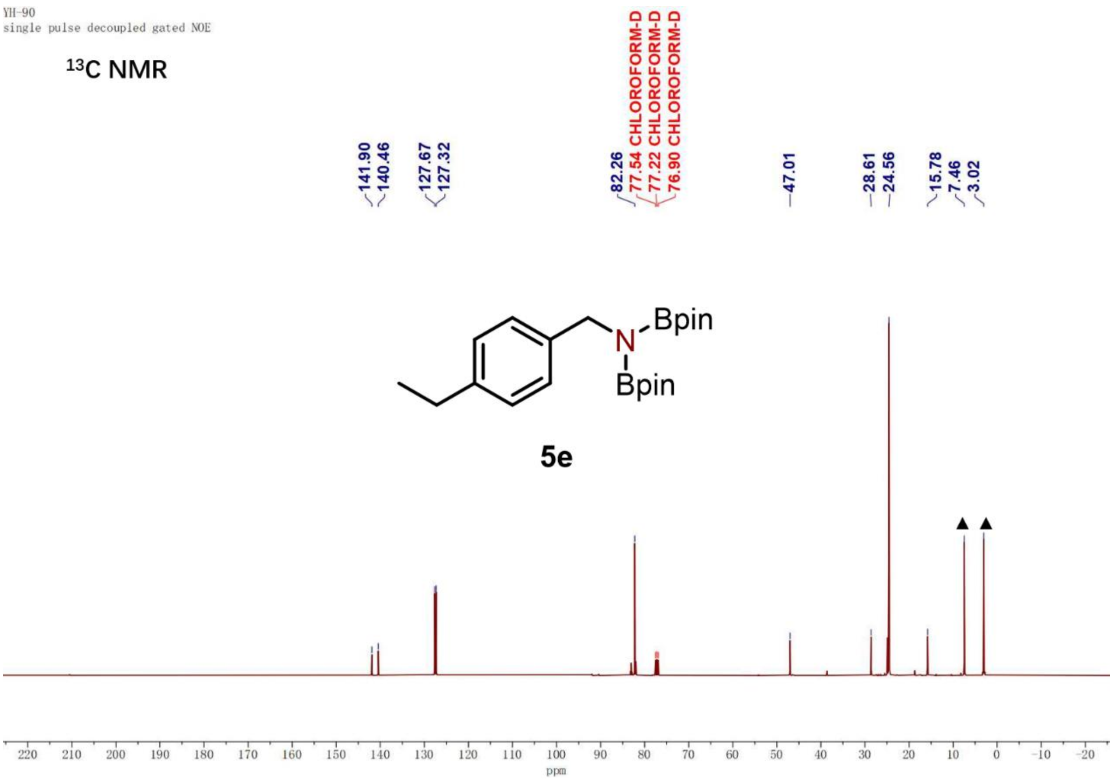


Figure S84. ^{13}C NMR spectrum of **5e** (101 MHz, Chloroform-*d*).

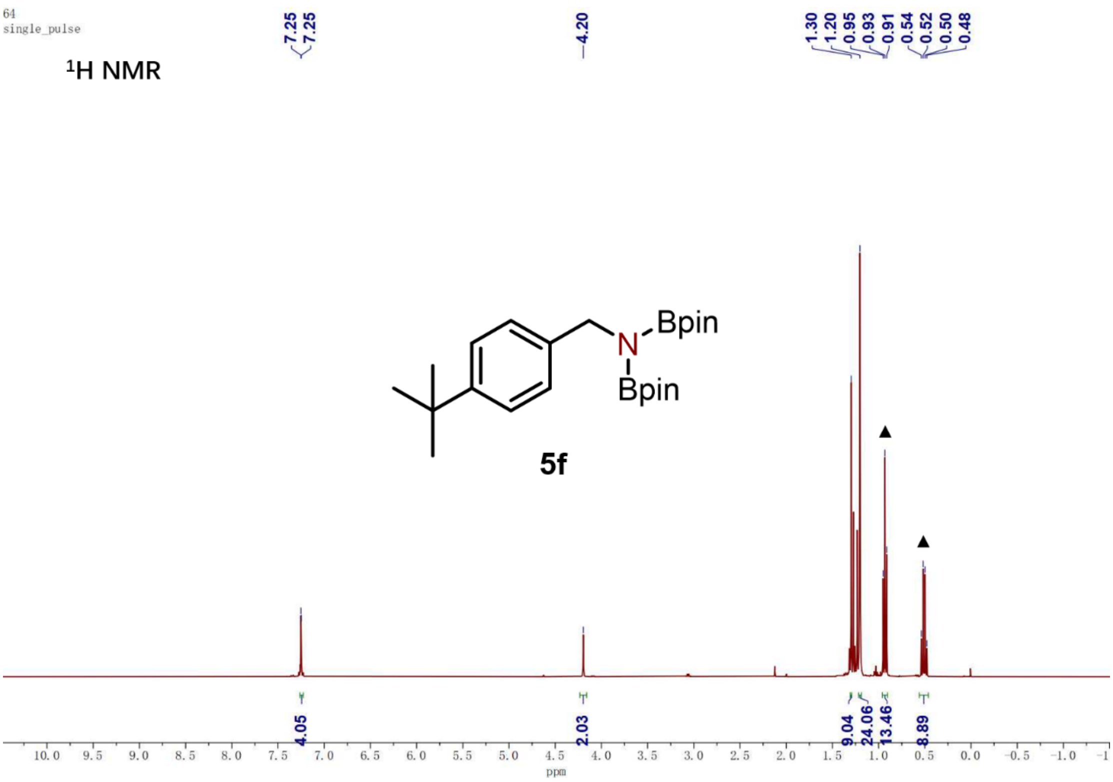


Figure S85. ^{1}H NMR spectrum of **5f** (400 MHz, Chloroform-*d*).

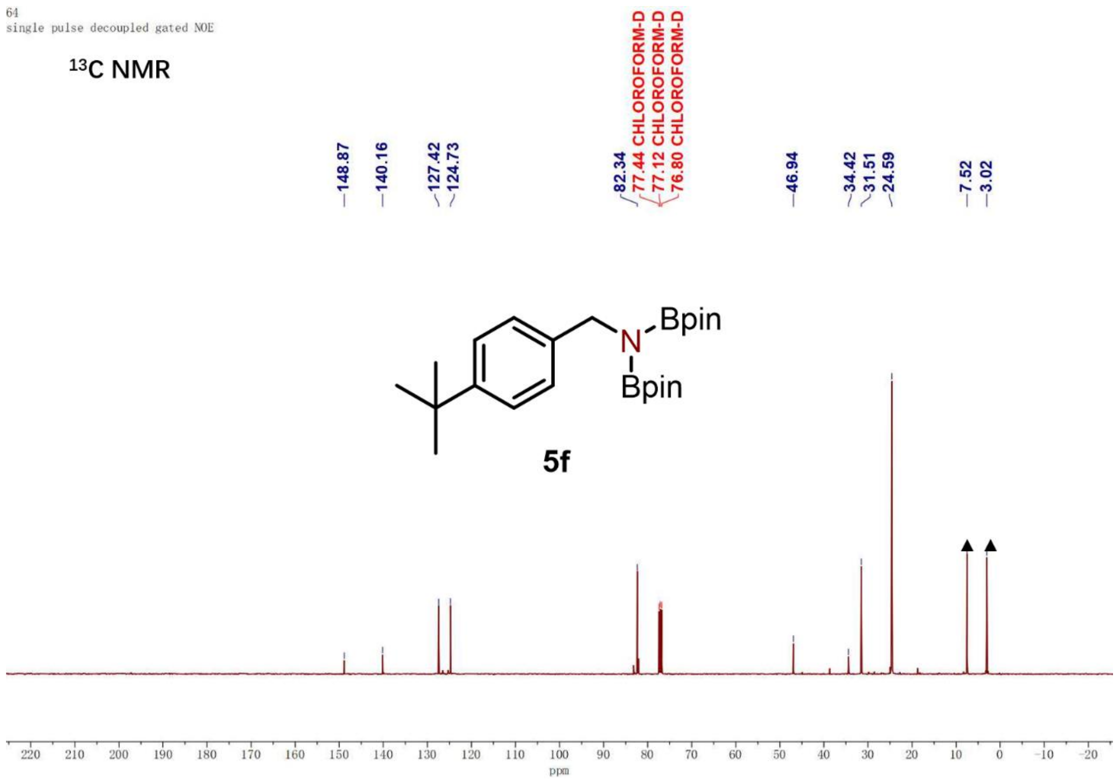


Figure S86. ^{13}C NMR spectrum of **5f** (101 MHz, Chloroform-*d*).

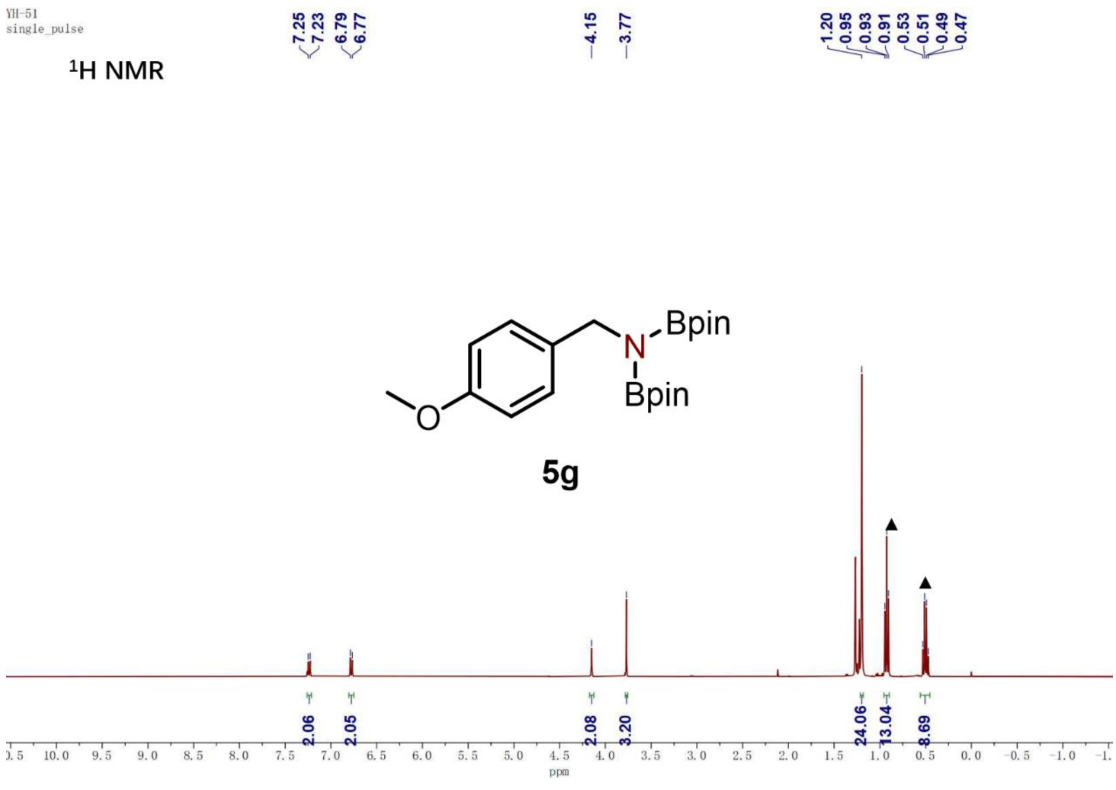


Figure S87. ^{1}H NMR spectrum of **5g** (400 MHz, Chloroform-*d*).

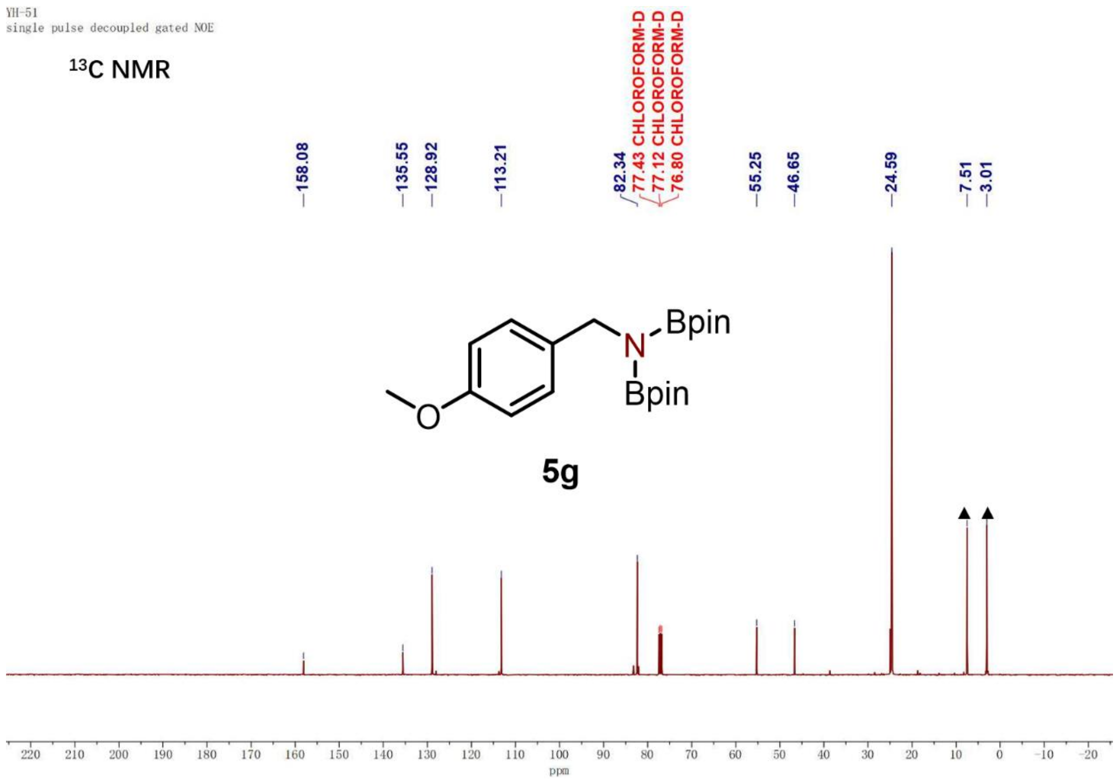


Figure S88. ^{13}C NMR spectrum of **5g** (101 MHz, Chloroform-*d*).

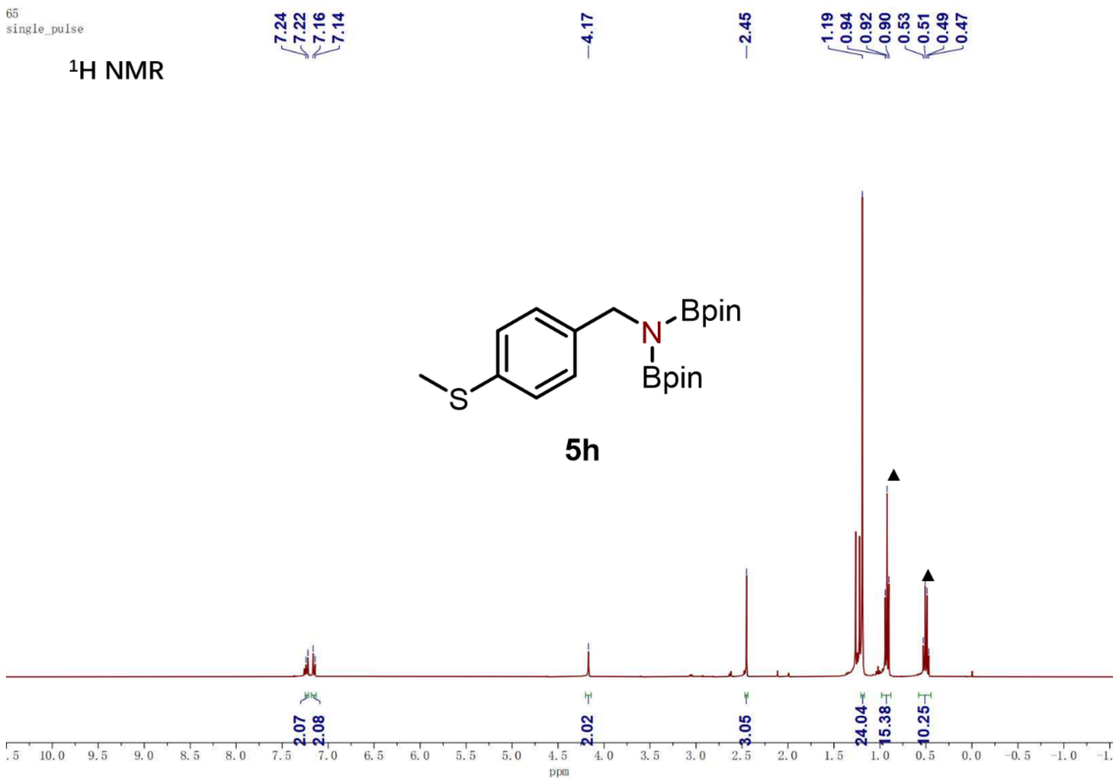


Figure S89. ^{1}H NMR spectrum of **5h** (400 MHz, Chloroform-*d*).

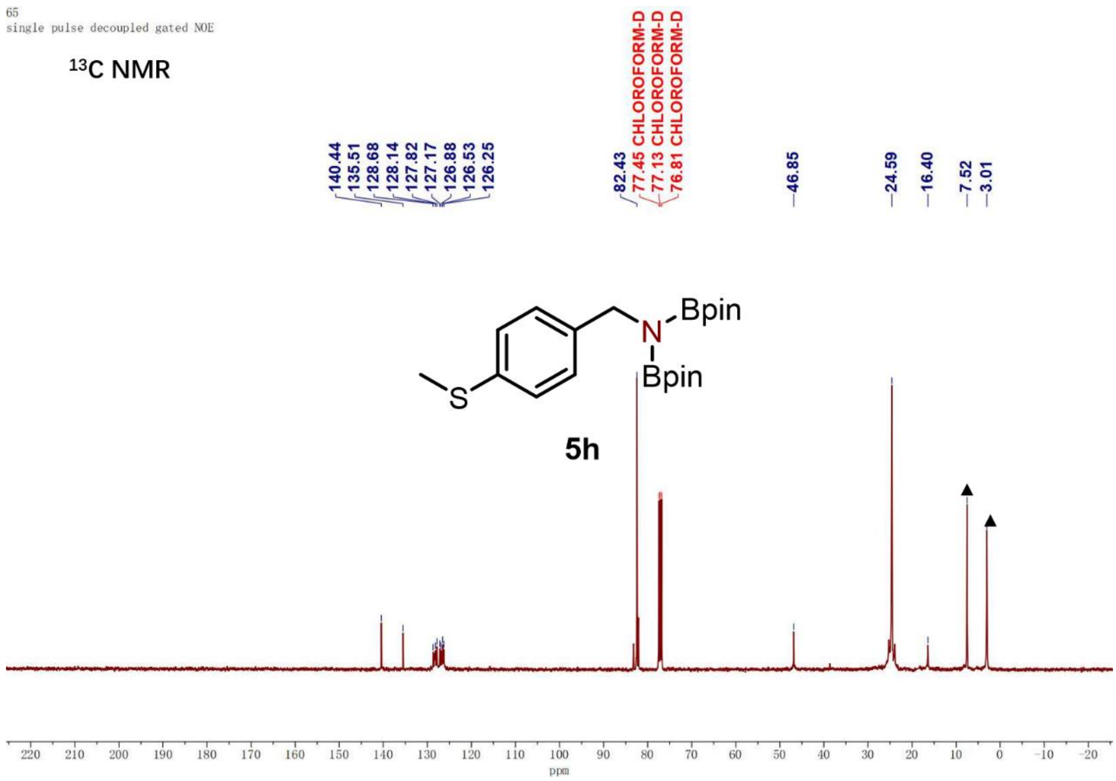


Figure S90. ^{13}C NMR spectrum of **5h** (101 MHz, Chloroform-*d*).

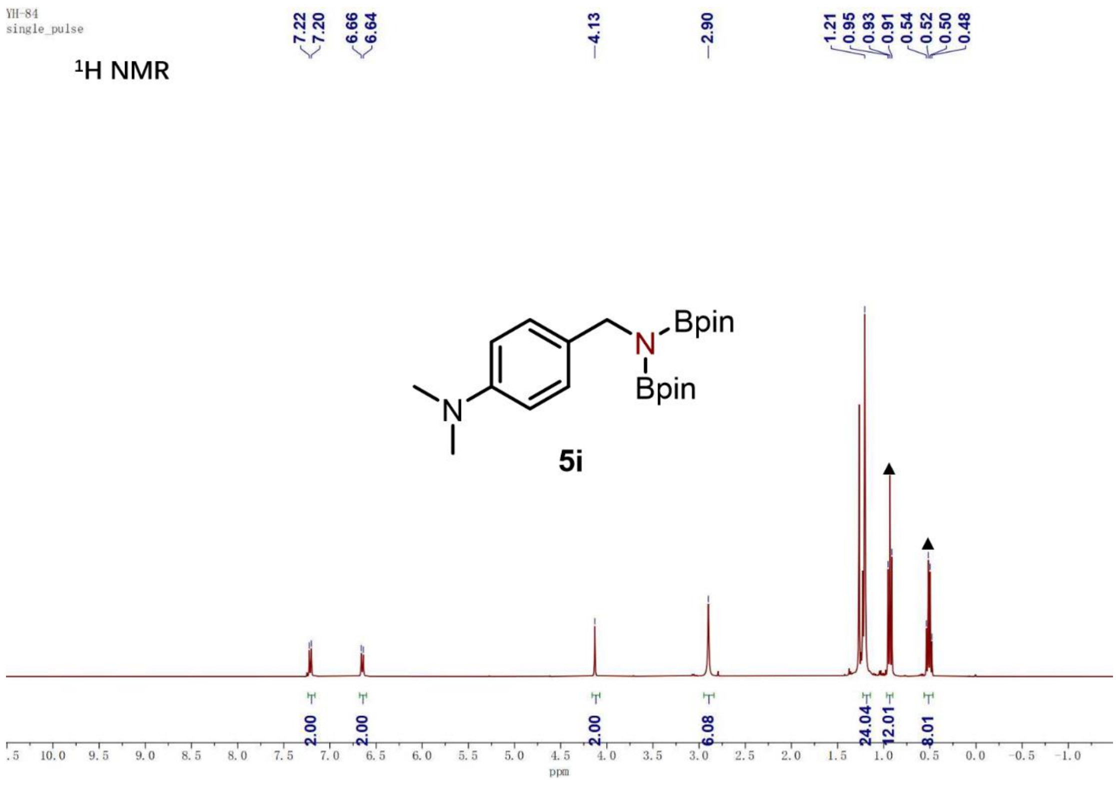


Figure S91. ^{1}H NMR spectrum of **5i** (400 MHz, Chloroform-*d*).

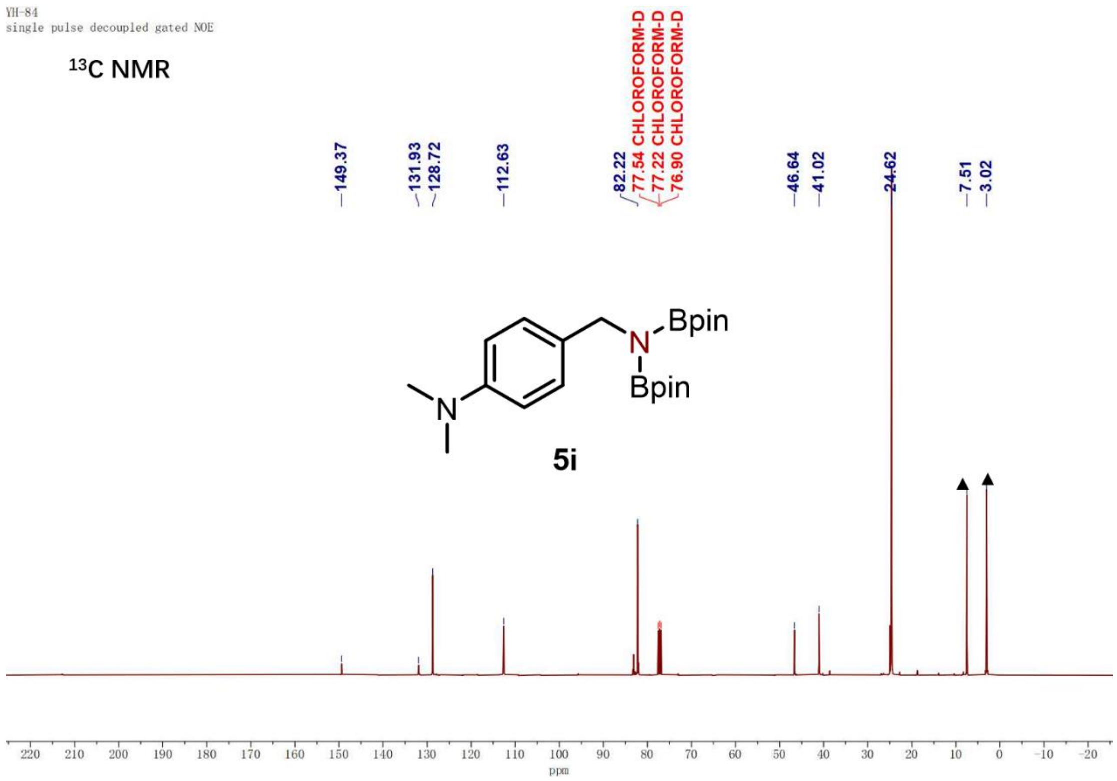


Figure S92. ^{13}C NMR spectrum of **5i** (101 MHz, Chloroform-*d*).

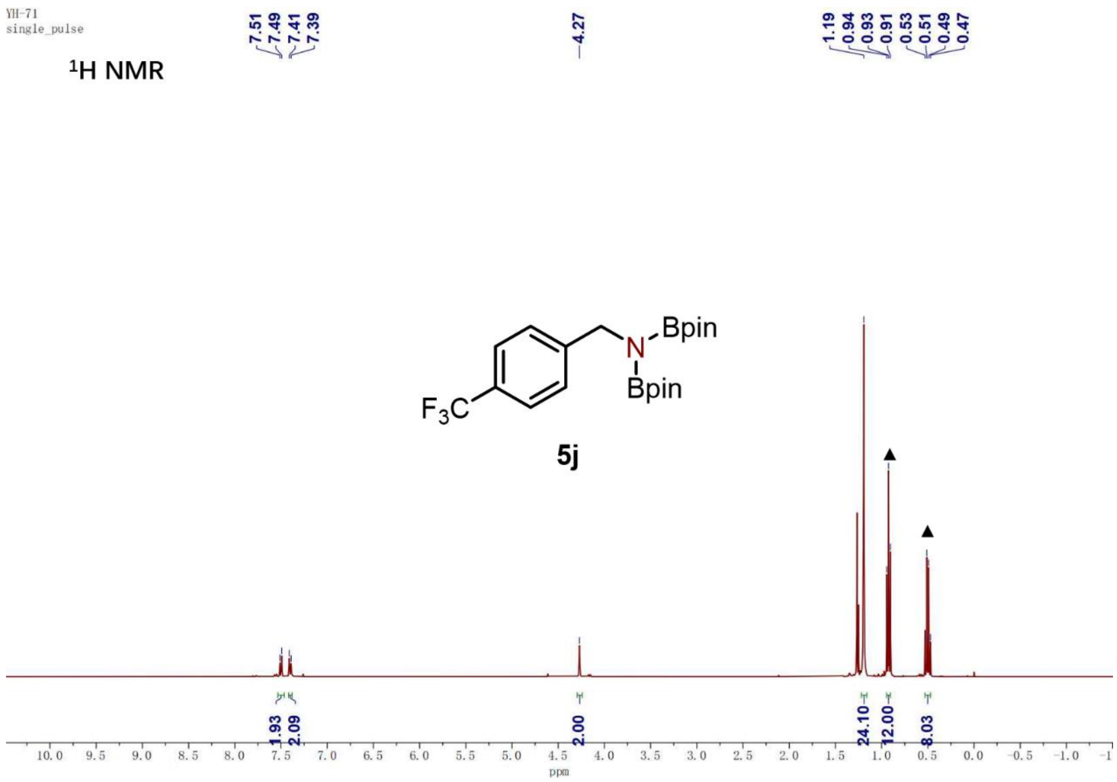


Figure S93. ^{1}H NMR spectrum of **5j** (400 MHz, Chloroform-*d*).

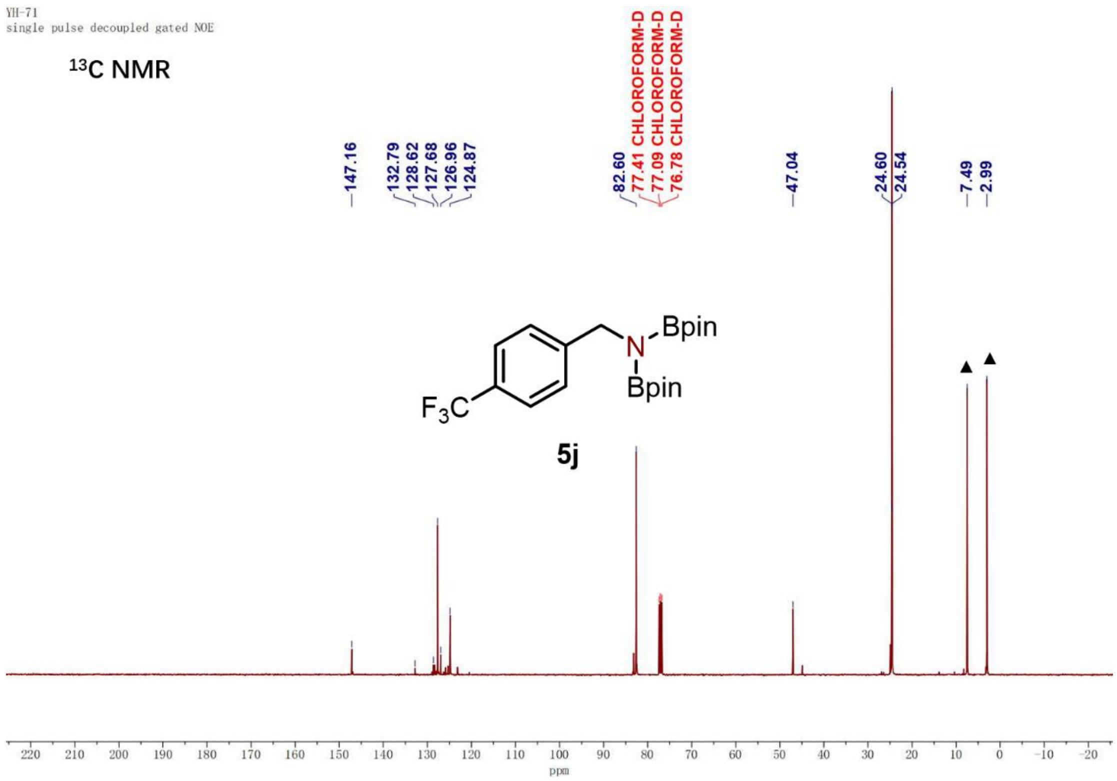


Figure S94. ^{13}C NMR spectrum of **5j** (101 MHz, Chloroform-*d*).

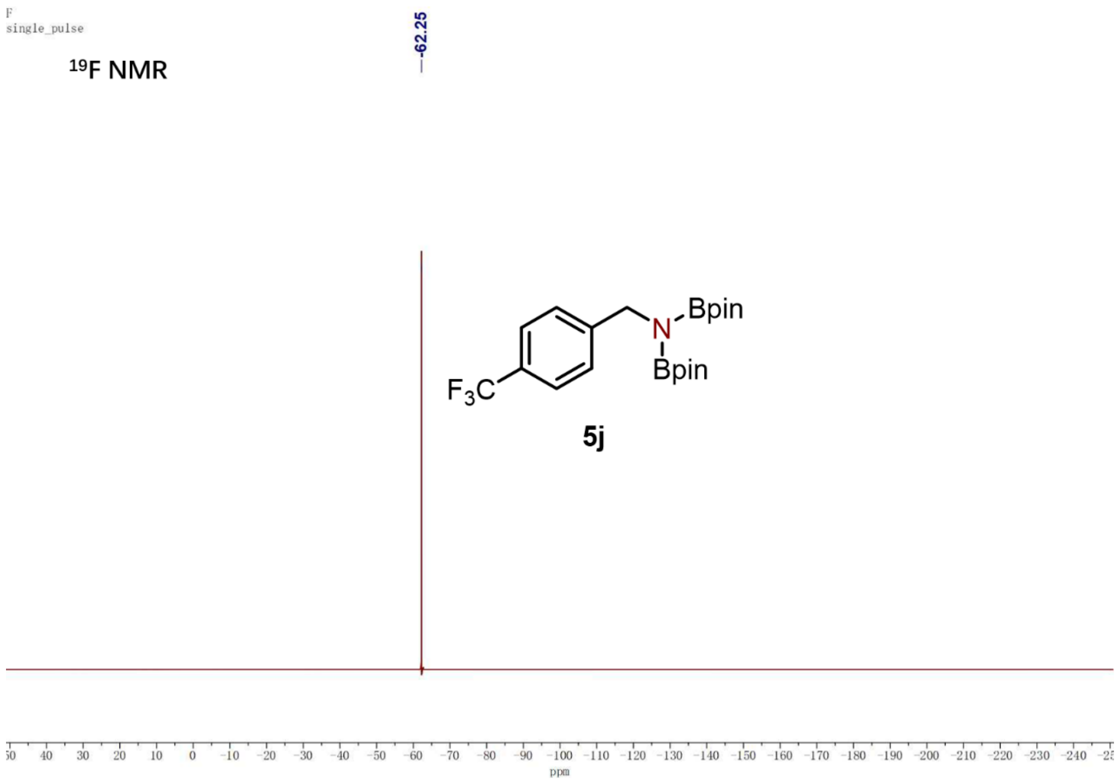


Figure S95. ^{19}F NMR spectrum of **5j** (376 MHz, Chloroform-*d*).

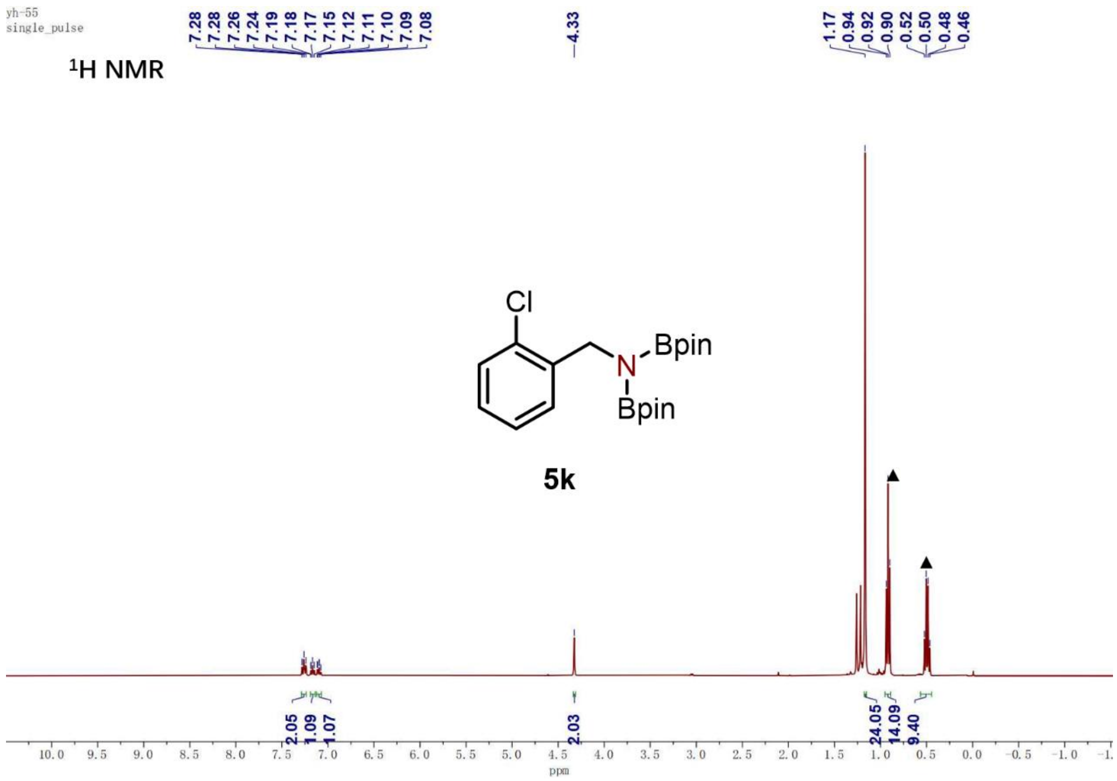


Figure S96. ^{1}H NMR spectrum of **5k** (400 MHz, Chloroform-*d*).

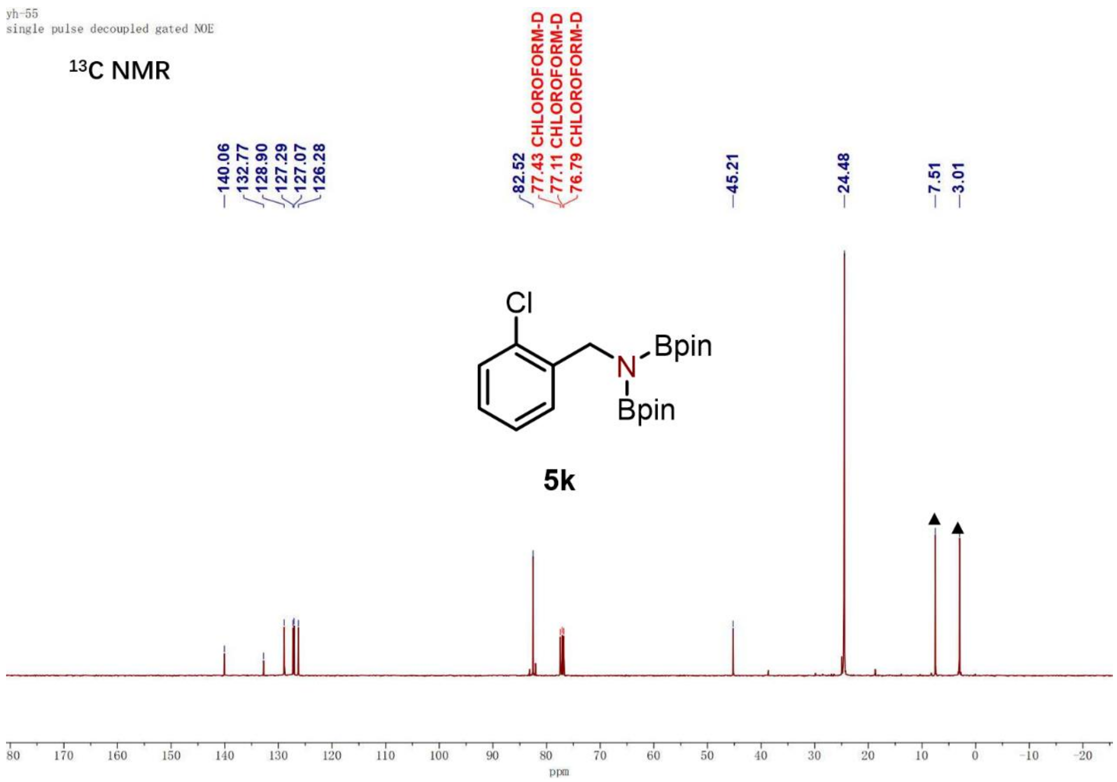


Figure S97. ^{13}C NMR spectrum of **5k** (101 MHz, Chloroform-*d*).

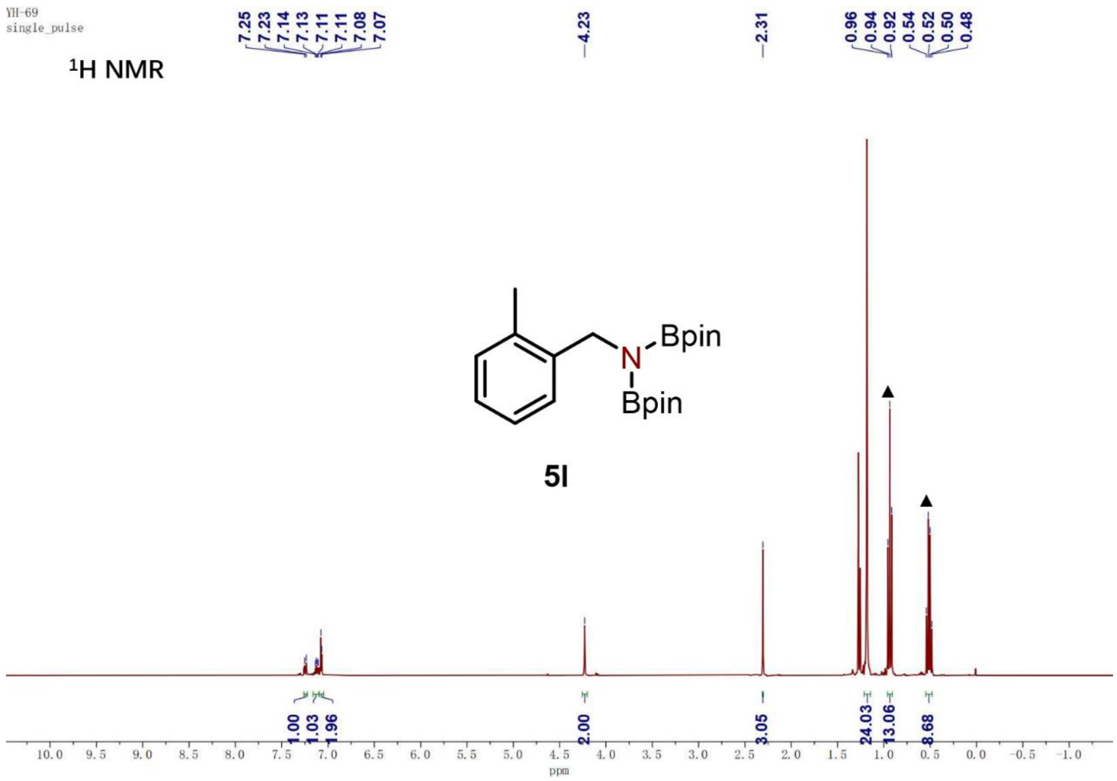


Figure S98. ^{1}H NMR spectrum of **5l** (400 MHz, Chloroform-*d*).

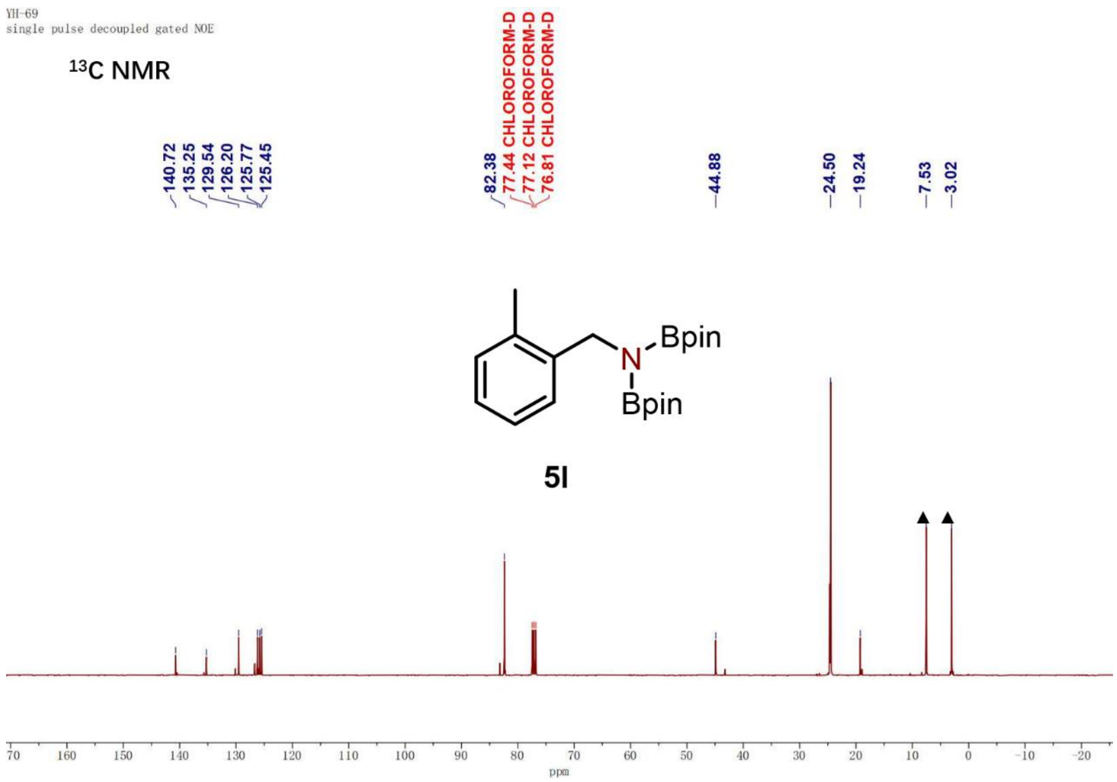


Figure S99. ^{13}C NMR spectrum of **5l** (101 MHz, Chloroform-*d*).

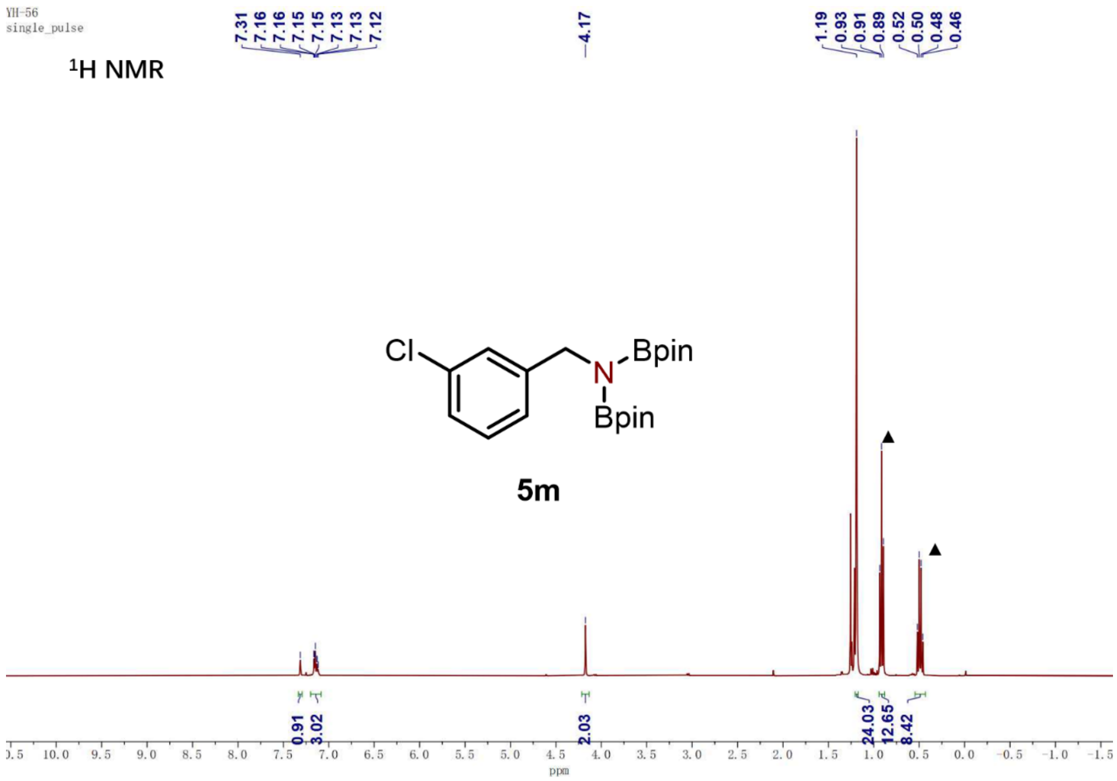


Figure S100. ^{1}H NMR spectrum of **5m** (400 MHz, Chloroform-*d*).

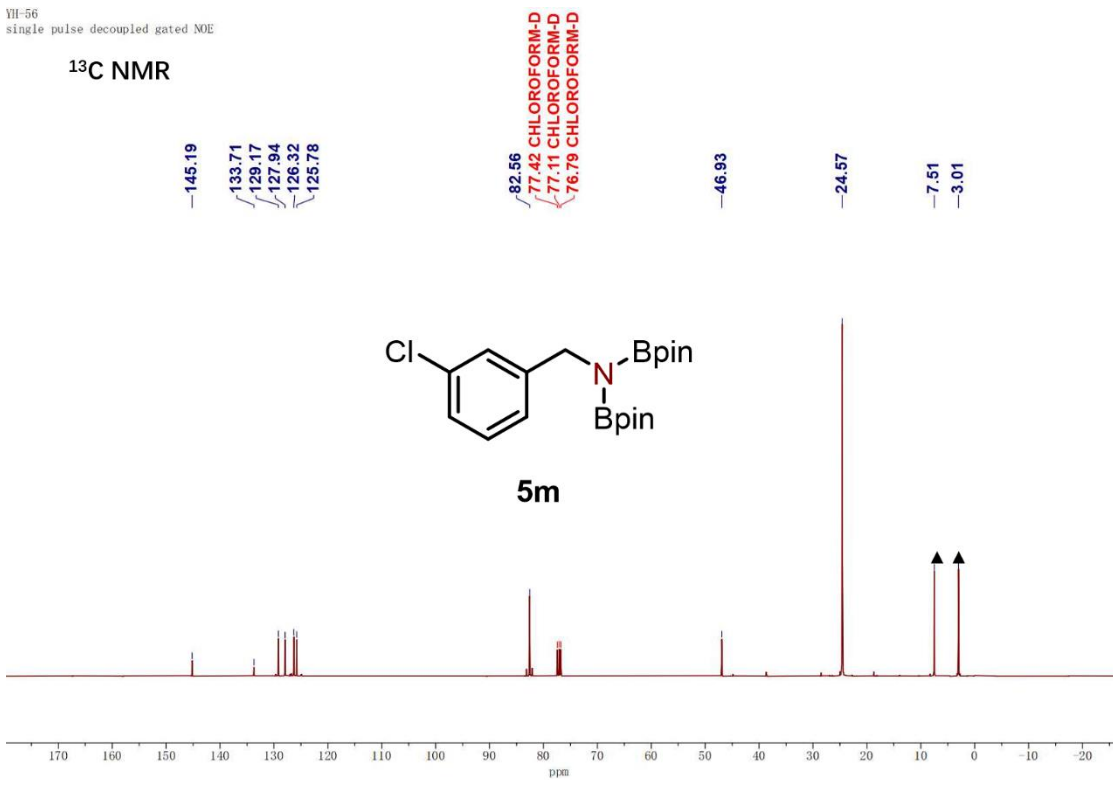


Figure S101. ^{13}C NMR spectrum of **5m** (101 MHz, Chloroform-*d*).

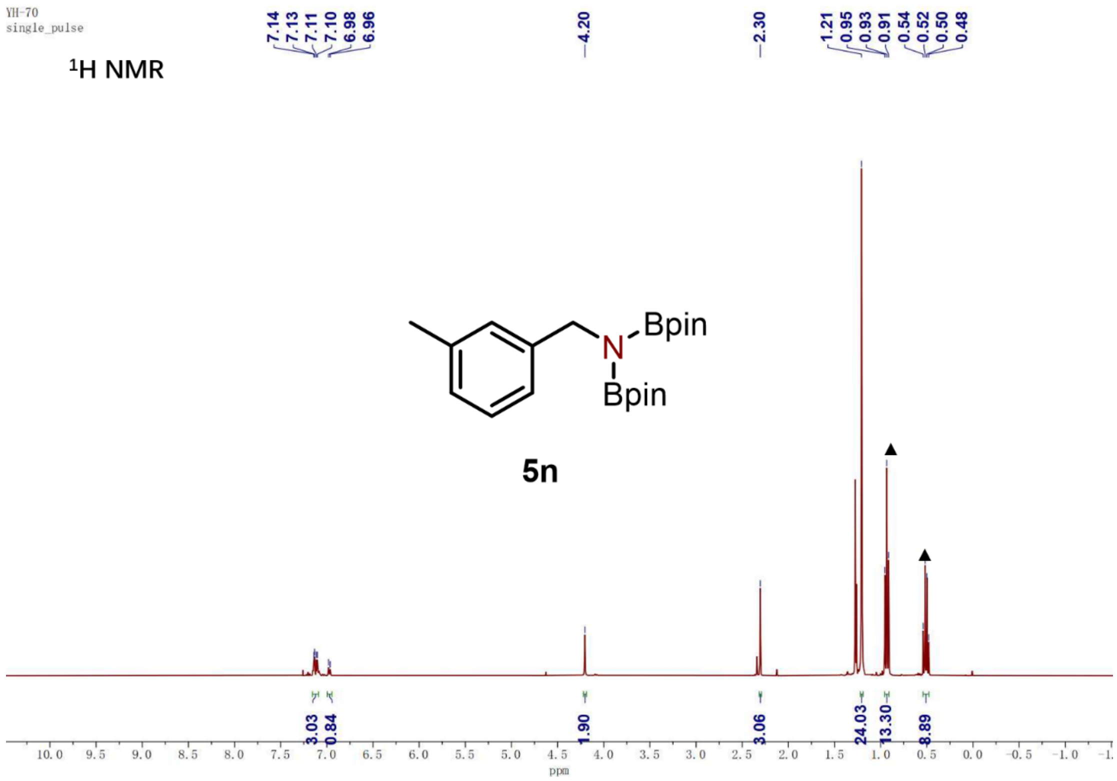


Figure S102. ^{1}H NMR spectrum of **5n** (400 MHz, Chloroform-*d*).

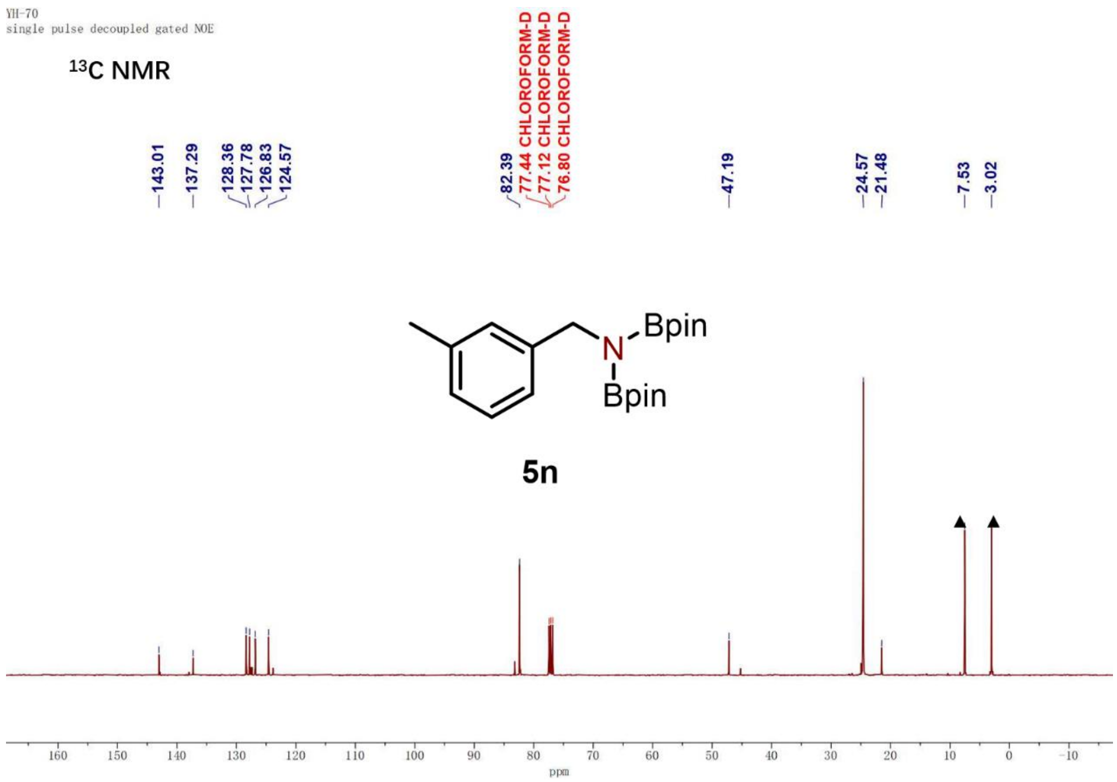


Figure S103. ^{13}C NMR spectrum of **5n** (101 MHz, Chloroform-*d*).

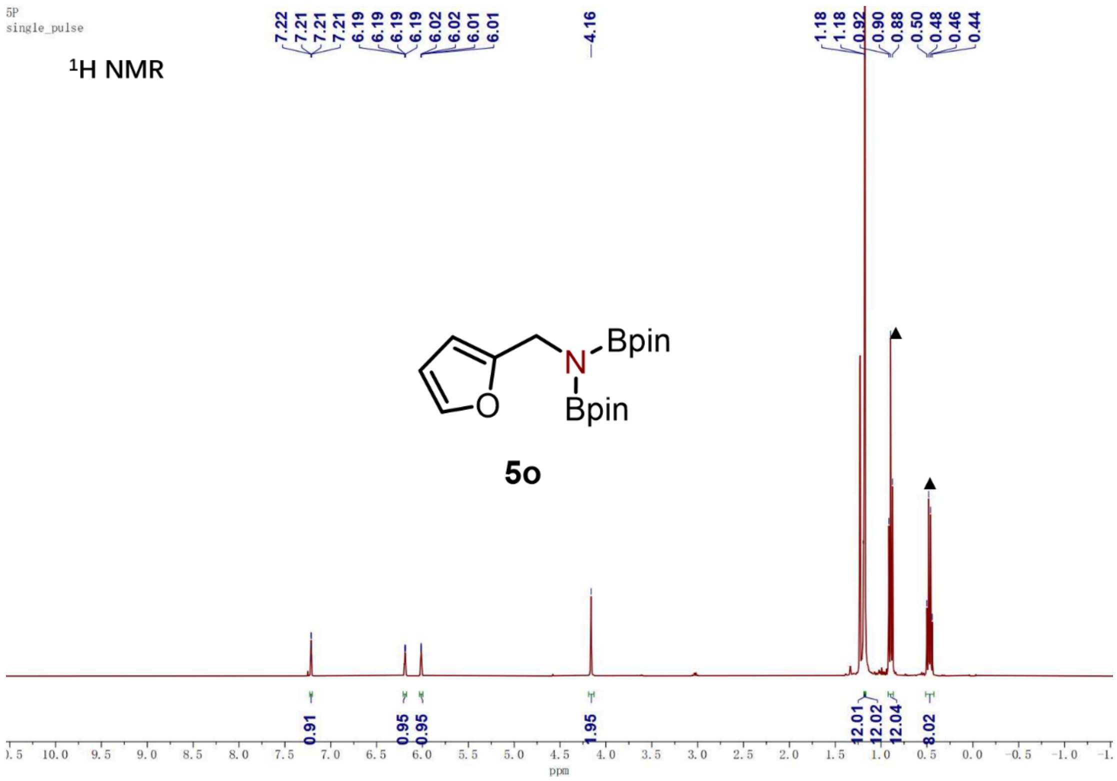


Figure S104. ^{1}H NMR spectrum of **5o** (400 MHz, Chloroform-*d*).

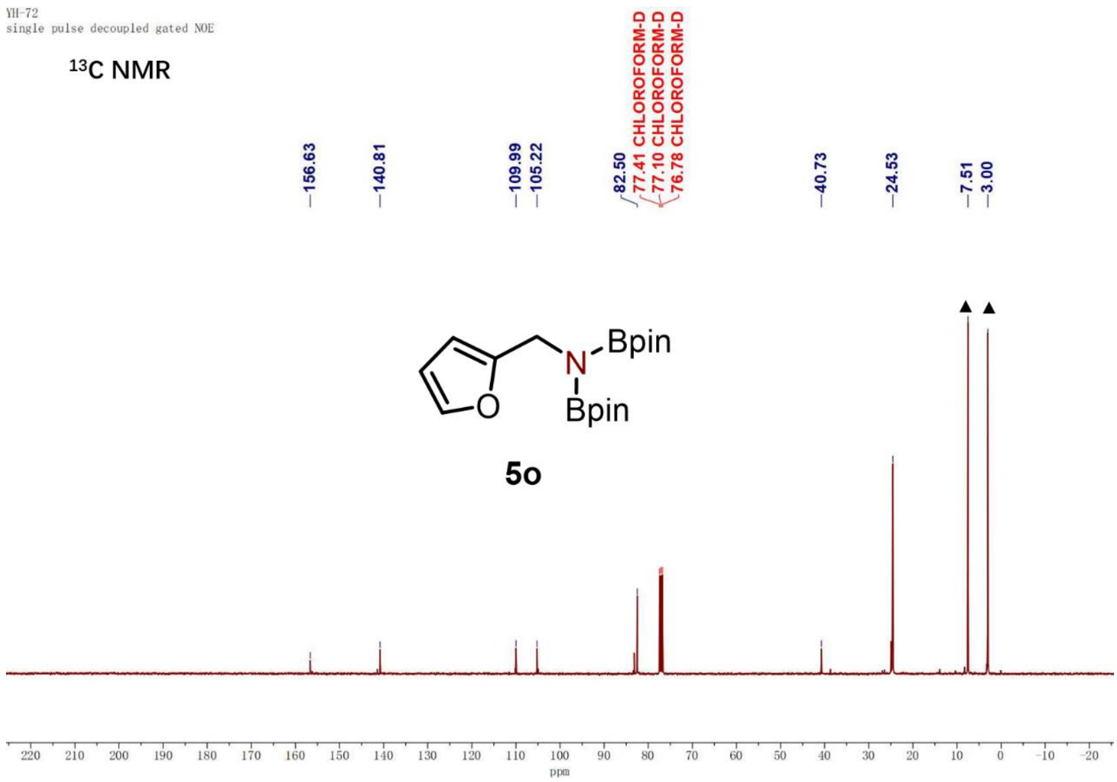


Figure S105. ^{13}C NMR spectrum of **5o** (101 MHz, Chloroform-*d*).

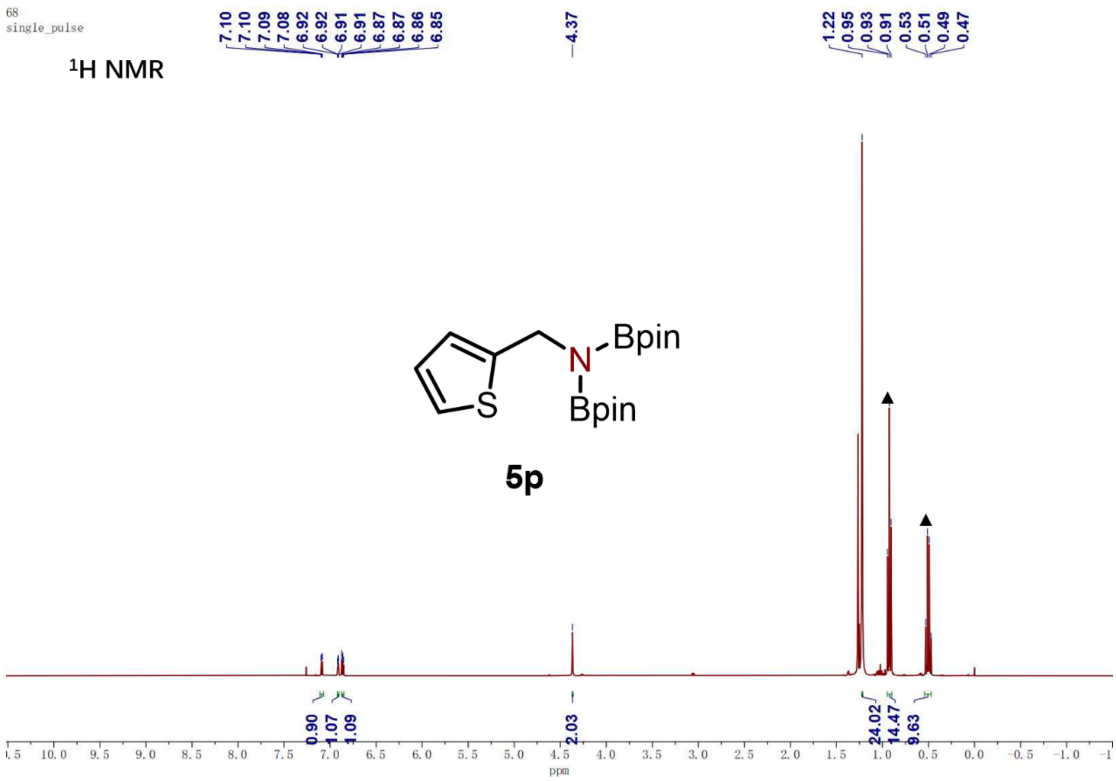


Figure S106. ^{1}H NMR spectrum of **5p** (400 MHz, Chloroform-*d*).

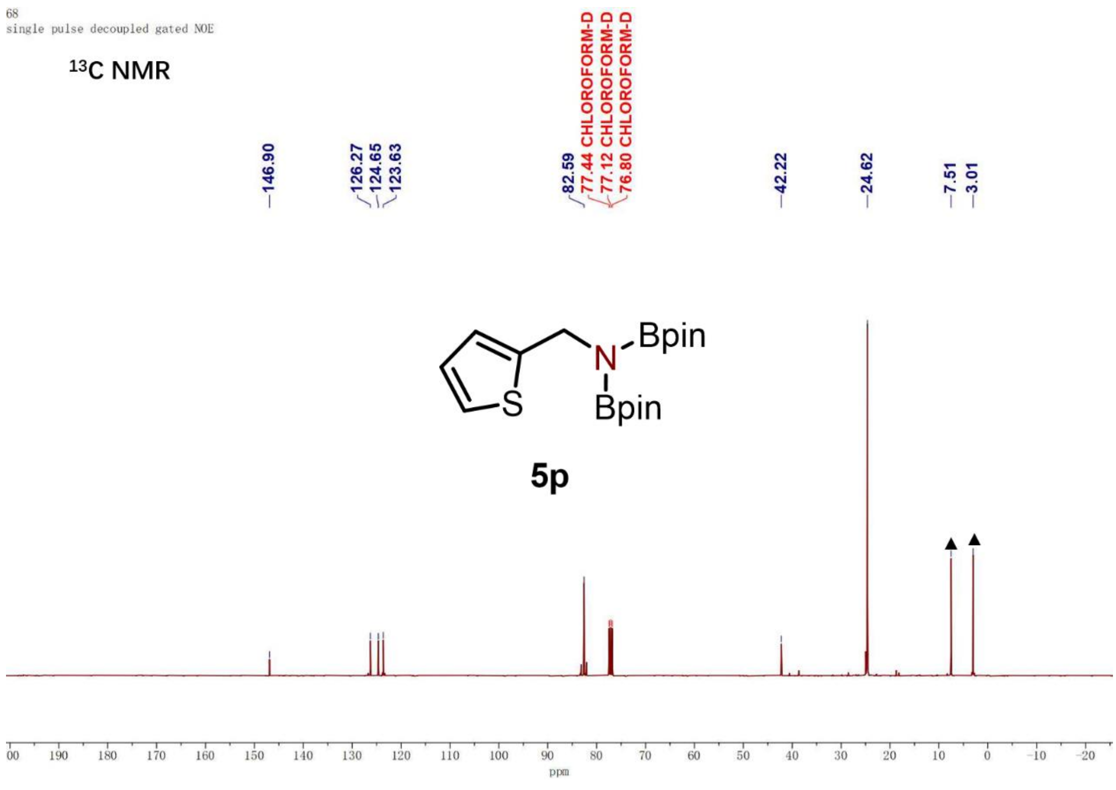


Figure S107. ^{13}C NMR spectrum of **5p** (101 MHz, Chloroform-*d*).

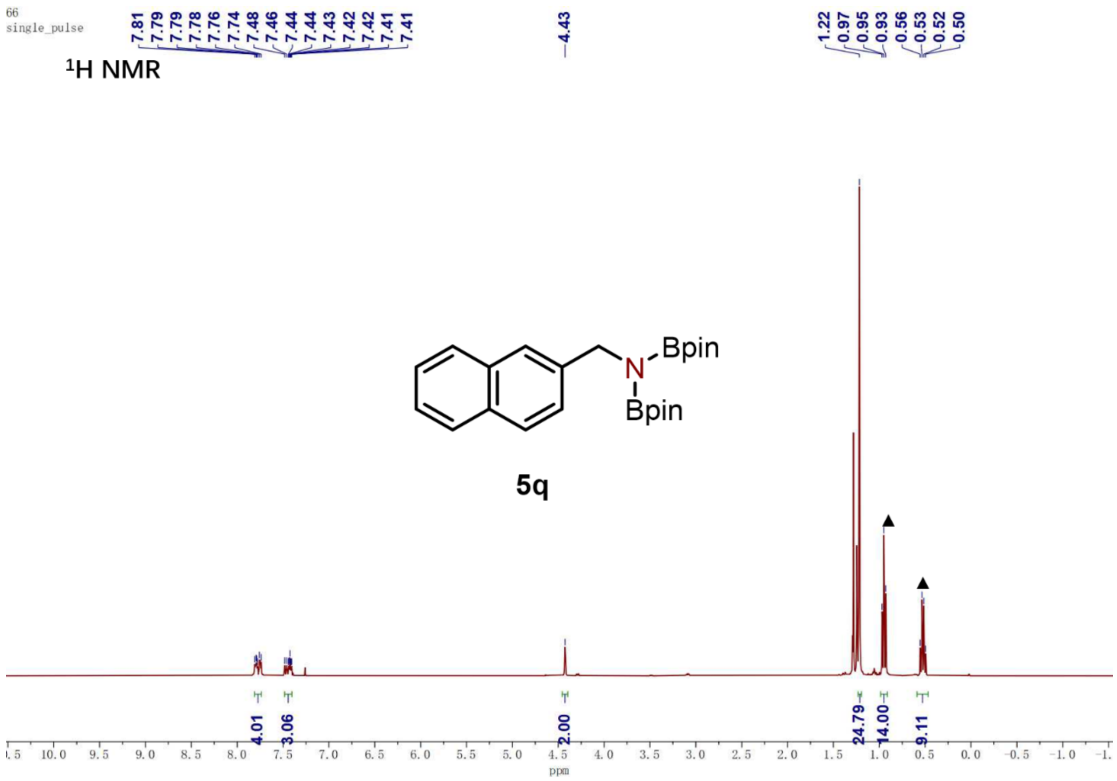


Figure S108. ^{1}H NMR spectrum of **5q** (400 MHz, Chloroform-*d*).

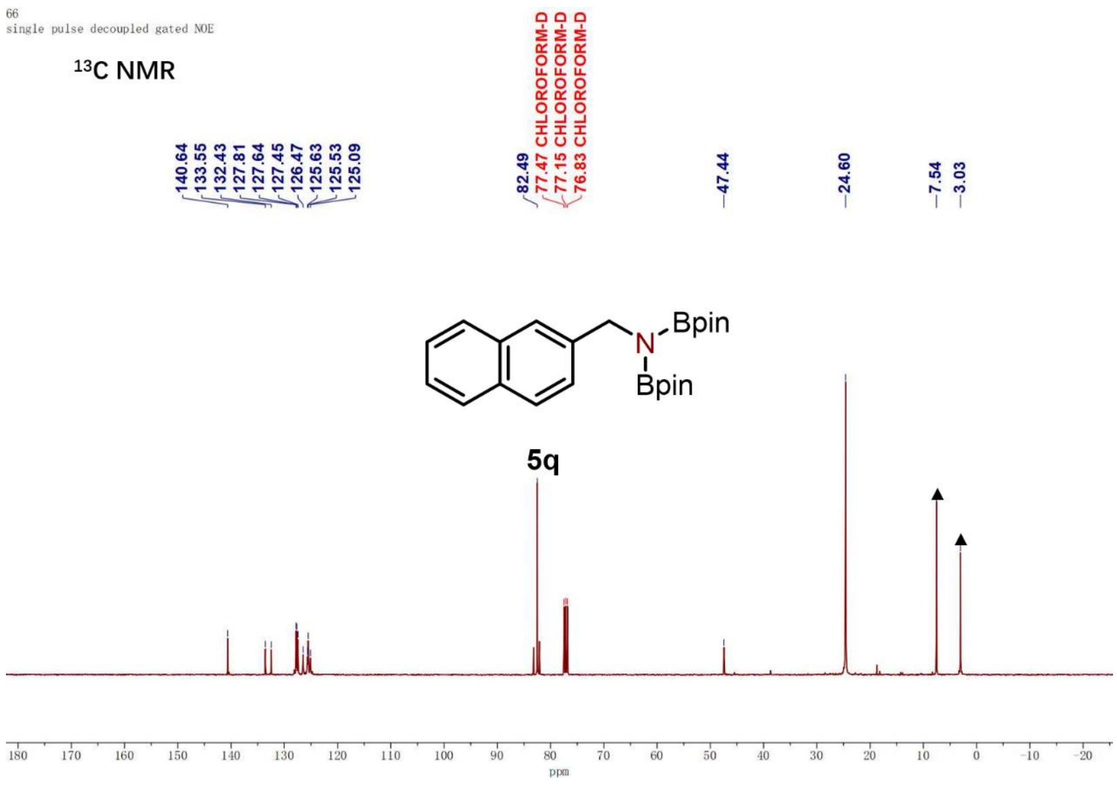


Figure S109. ^{13}C NMR spectrum of **5q** (101 MHz, Chloroform-*d*).

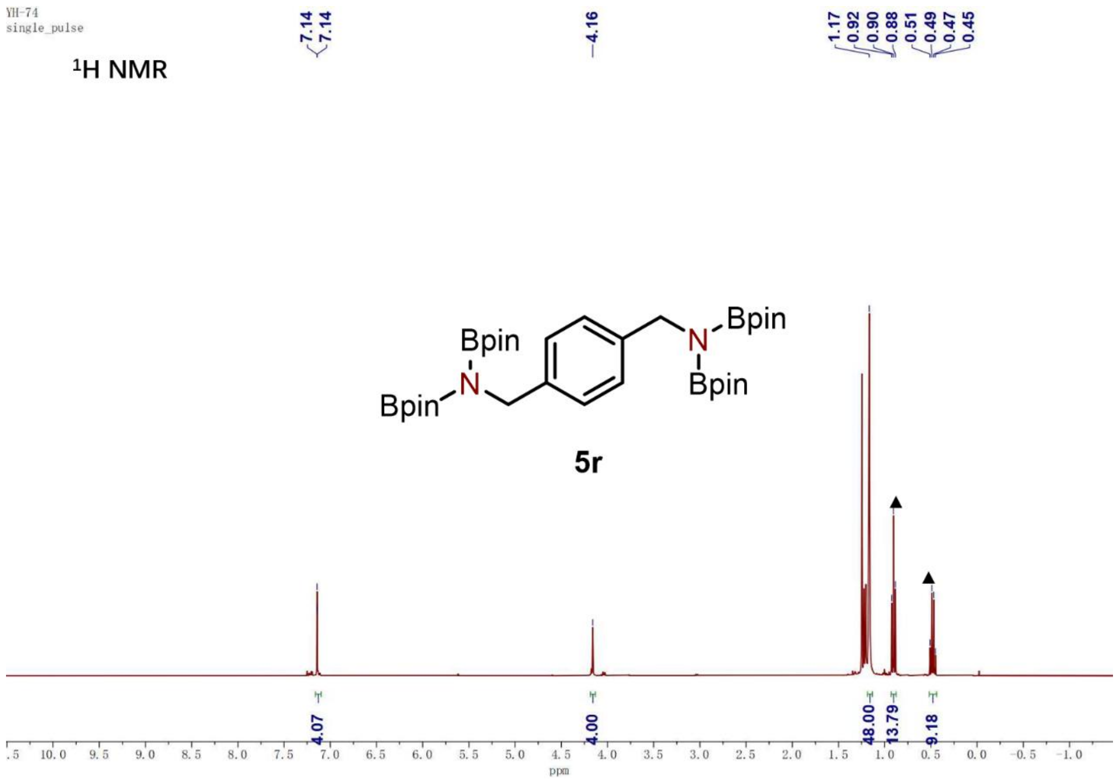


Figure S110. ^{1}H NMR spectrum of **5r** (400 MHz, Chloroform-*d*).

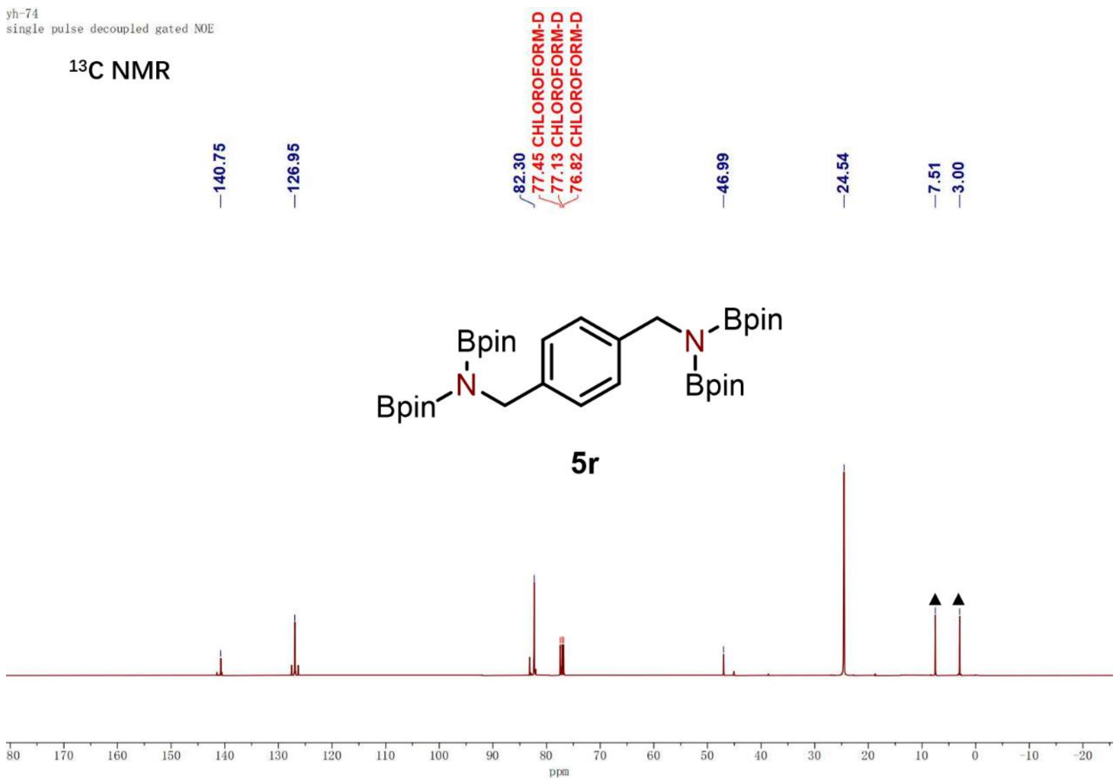


Figure S111. ^{13}C NMR spectrum of **5r** (101 MHz, Chloroform-*d*).

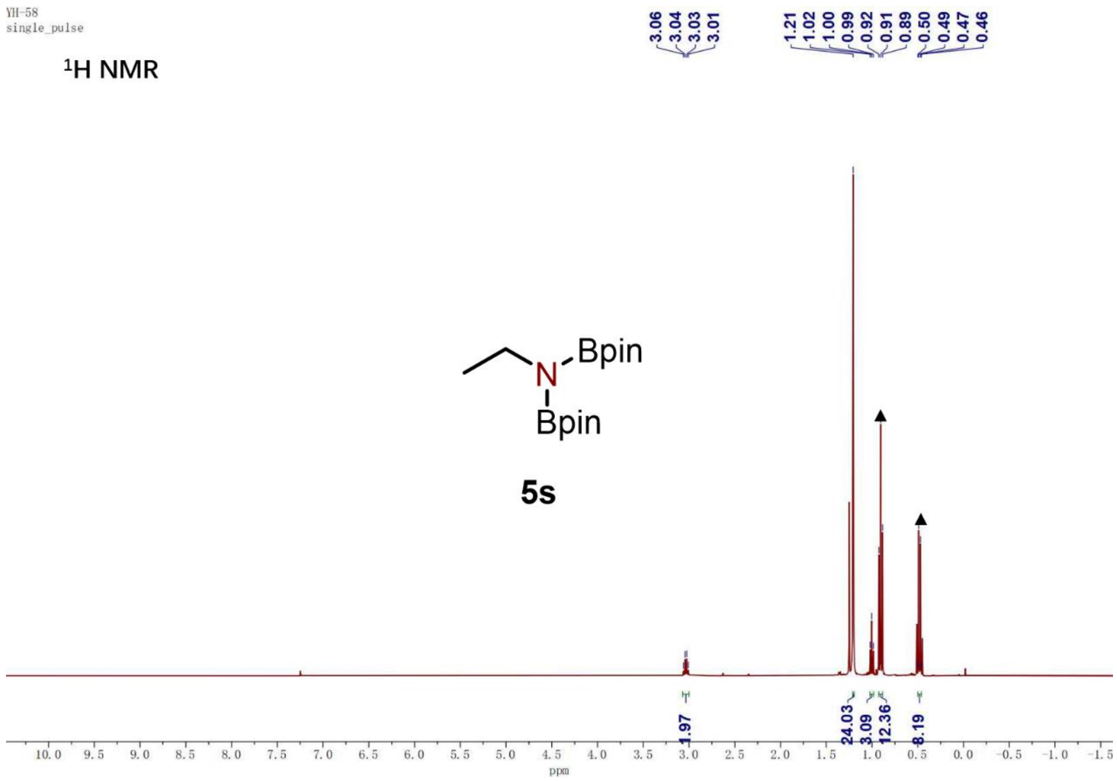


Figure S112. ^{1}H NMR spectrum of **5s** (400 MHz, Chloroform-*d*).

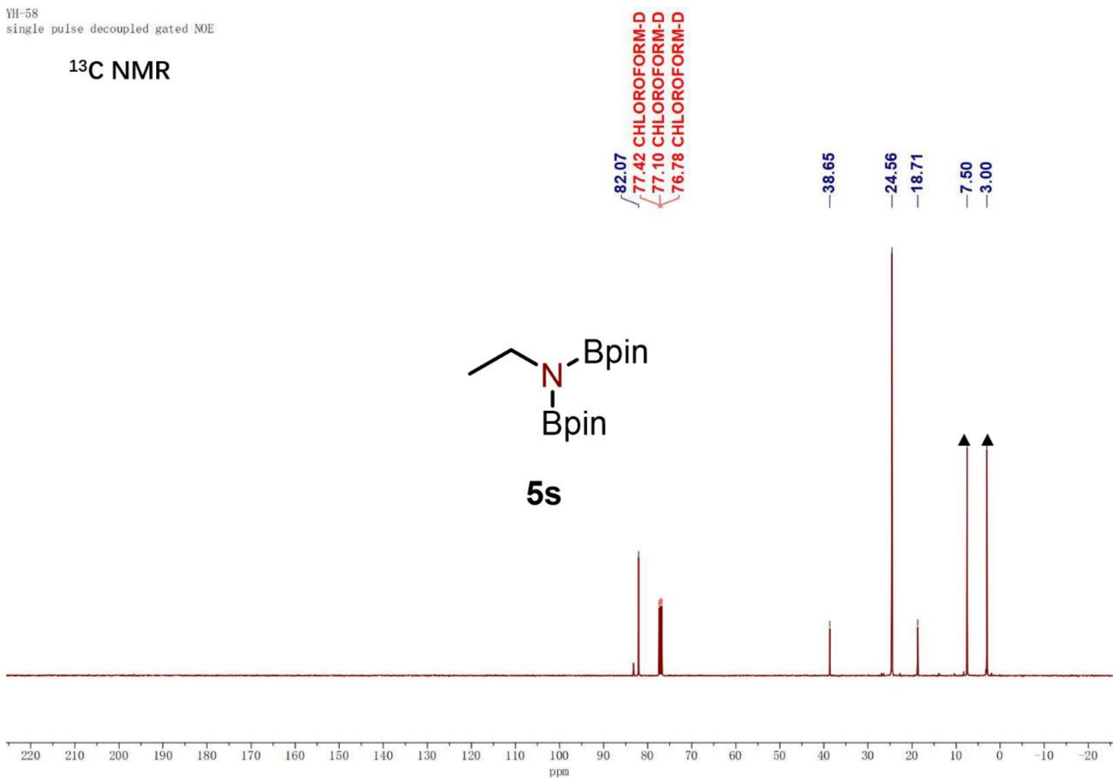


Figure S113. ^{13}C NMR spectrum of **5s** (101 MHz, Chloroform-*d*).

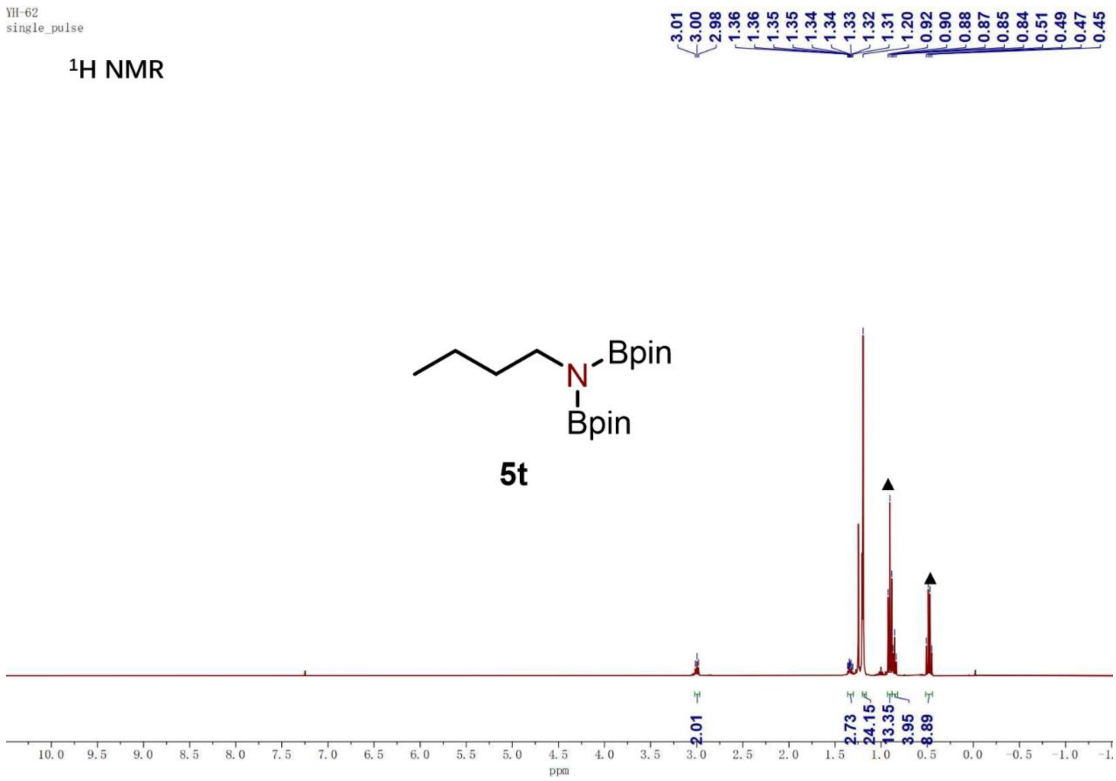


Figure S114. ^{1}H NMR spectrum of **5t** (400 MHz, Chloroform-*d*).

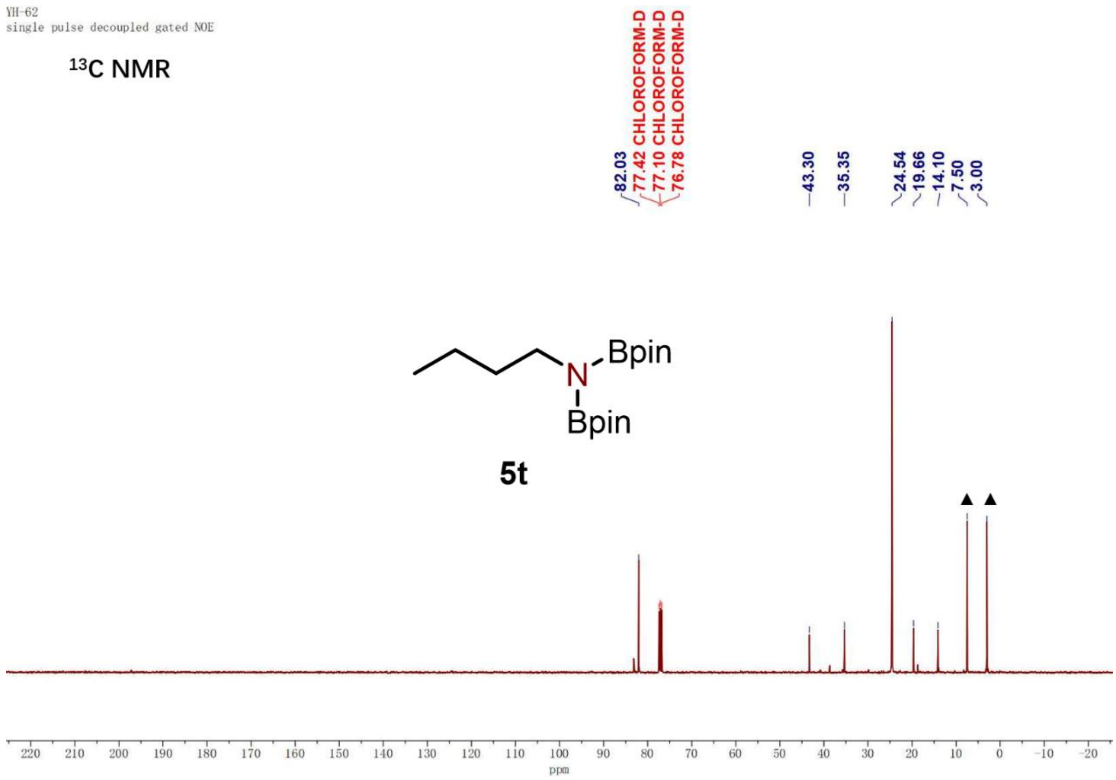


Figure S115. ^{13}C NMR spectrum of **5t** (101 MHz, Chloroform-*d*).

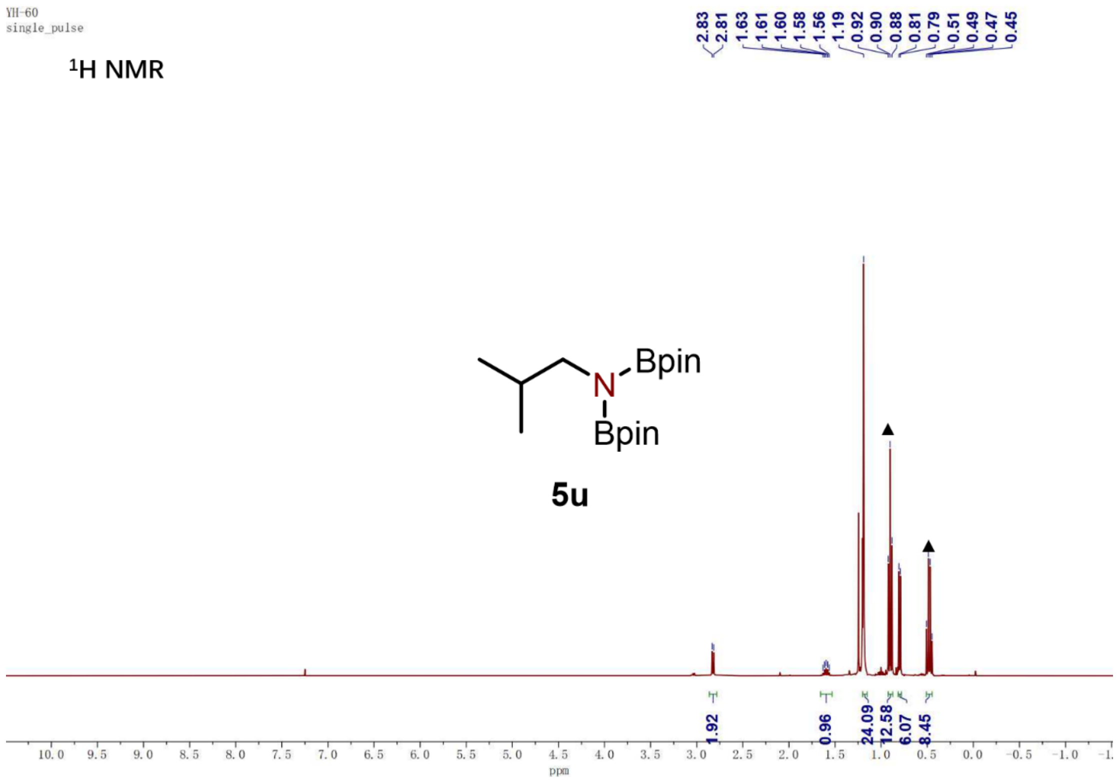


Figure S116. ^{1}H NMR spectrum of **5u** (400 MHz, Chloroform-*d*).

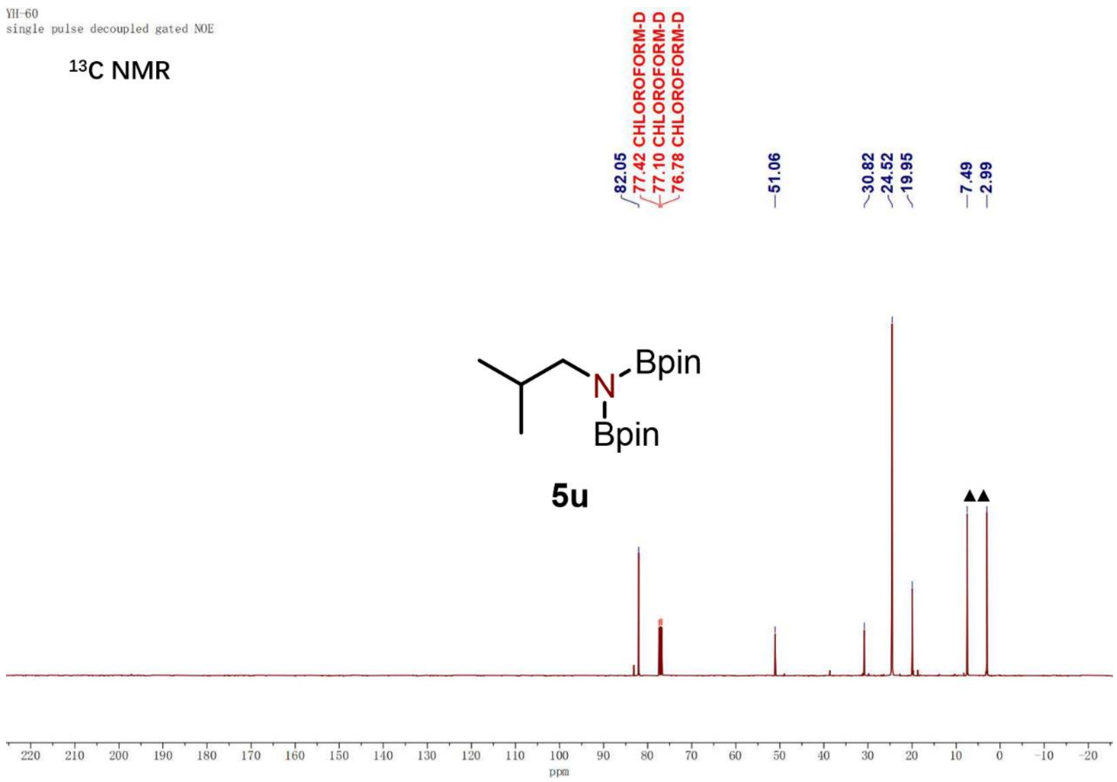


Figure S117. ^{13}C NMR spectrum of **5u** (101 MHz, Chloroform-*d*).

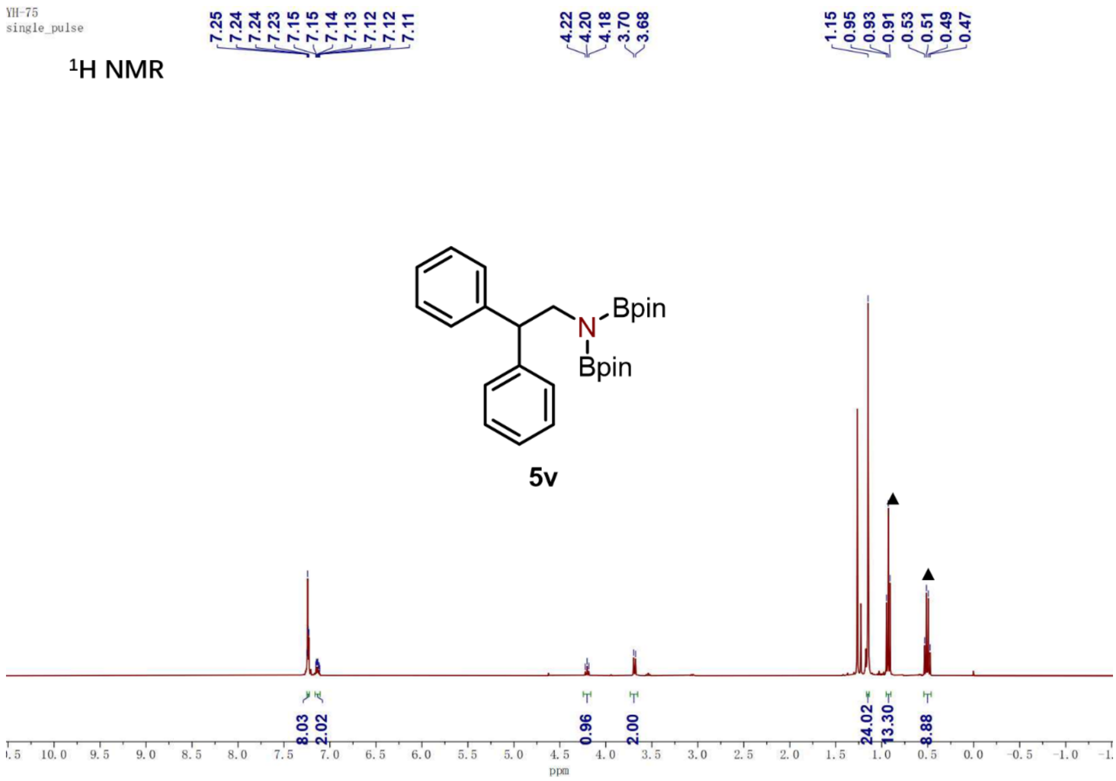


Figure S118. ^{1}H NMR spectrum of **5v** (400 MHz, Chloroform-*d*).

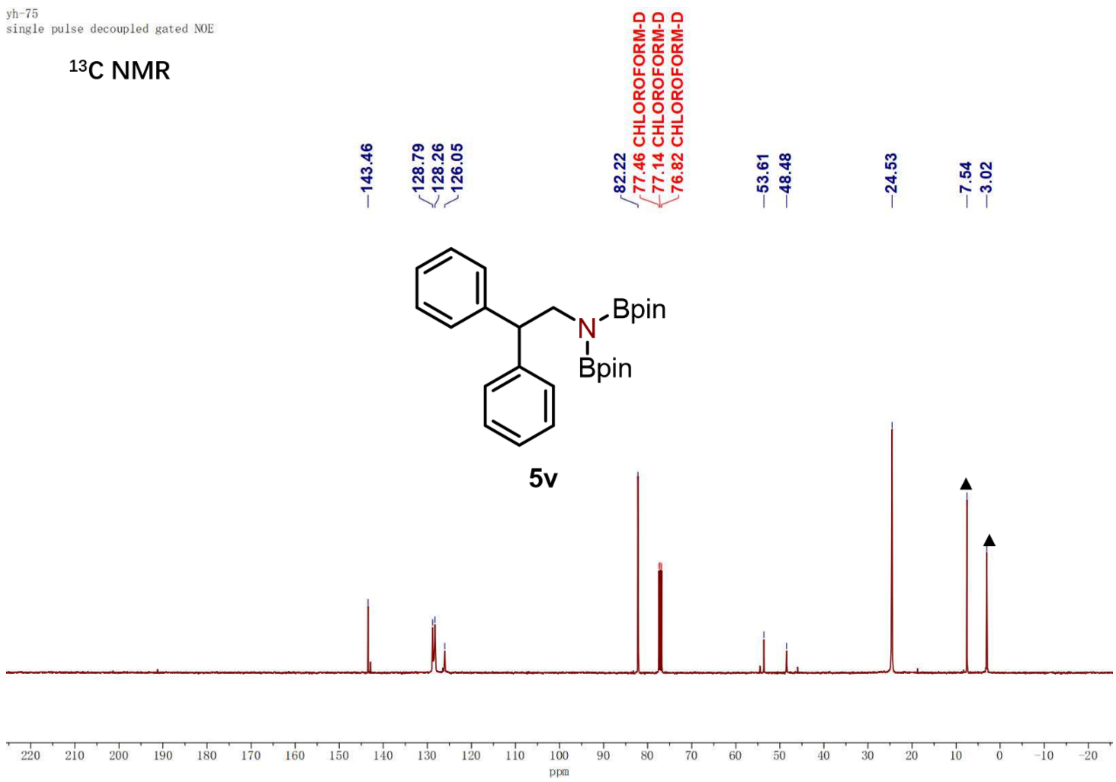


Figure S119. ^{13}C NMR spectrum of **5v** (101 MHz, Chloroform-*d*).

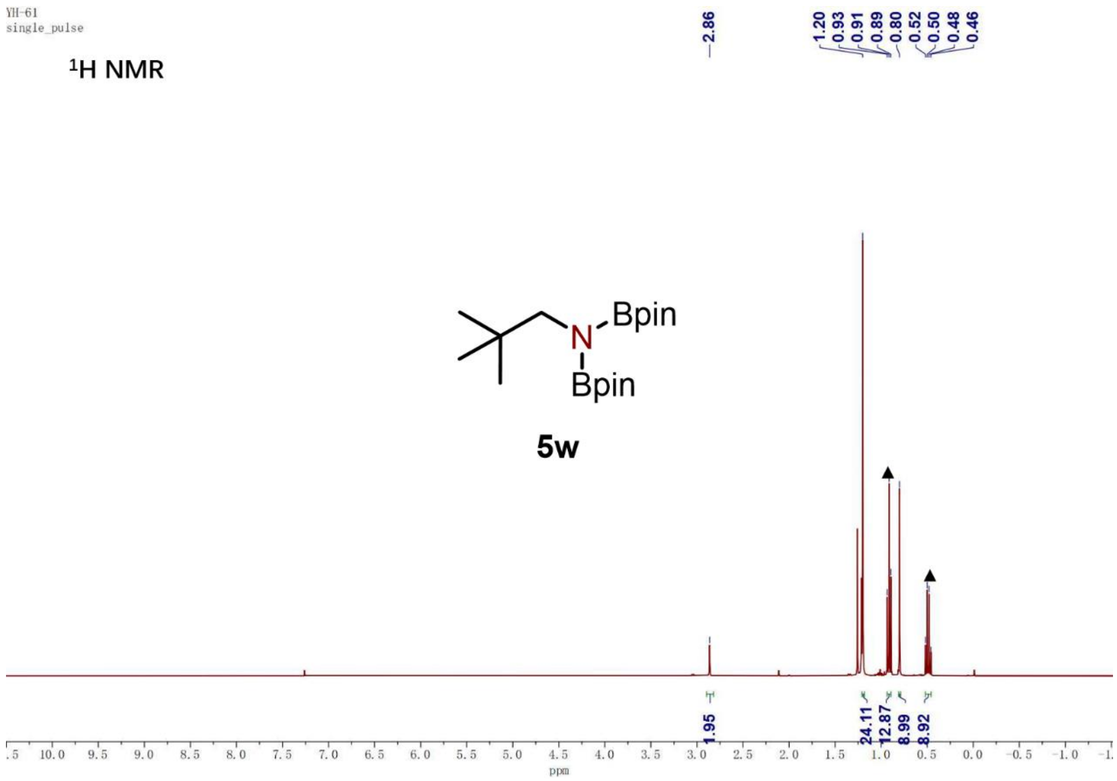


Figure S120. ^{1}H NMR spectrum of **5w** (400 MHz, Chloroform-*d*).

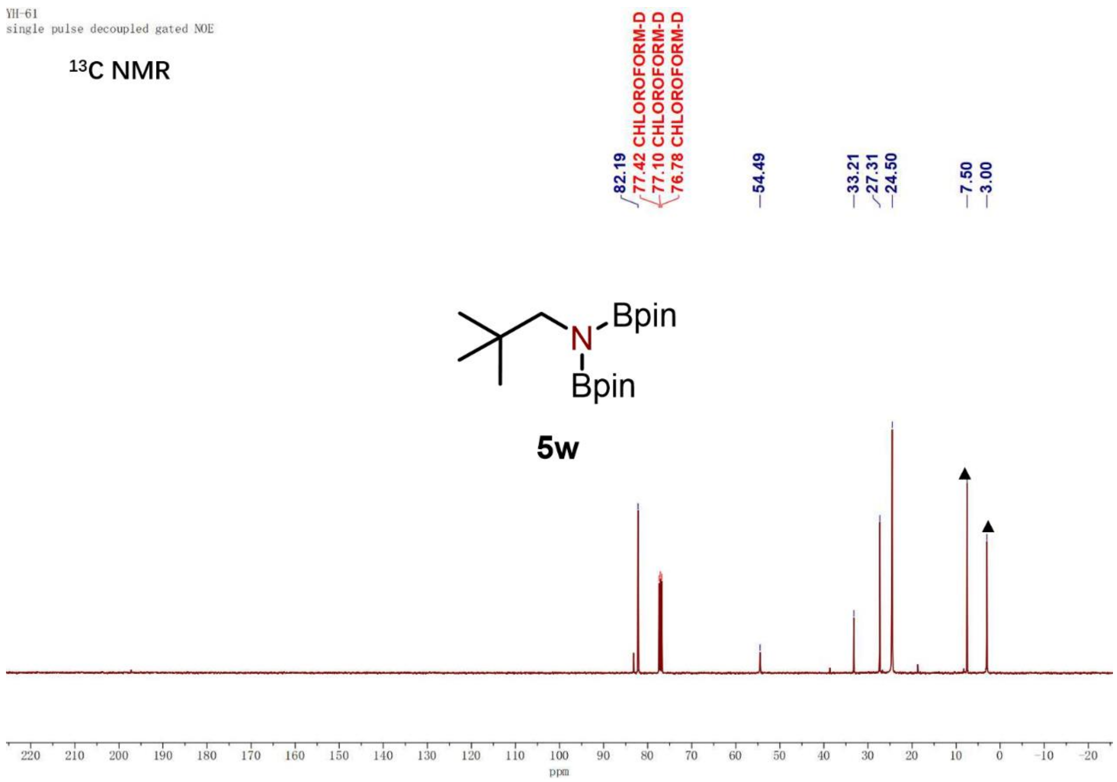


Figure S121. ^{13}C NMR spectrum of **5w** (101 MHz, Chloroform-*d*).

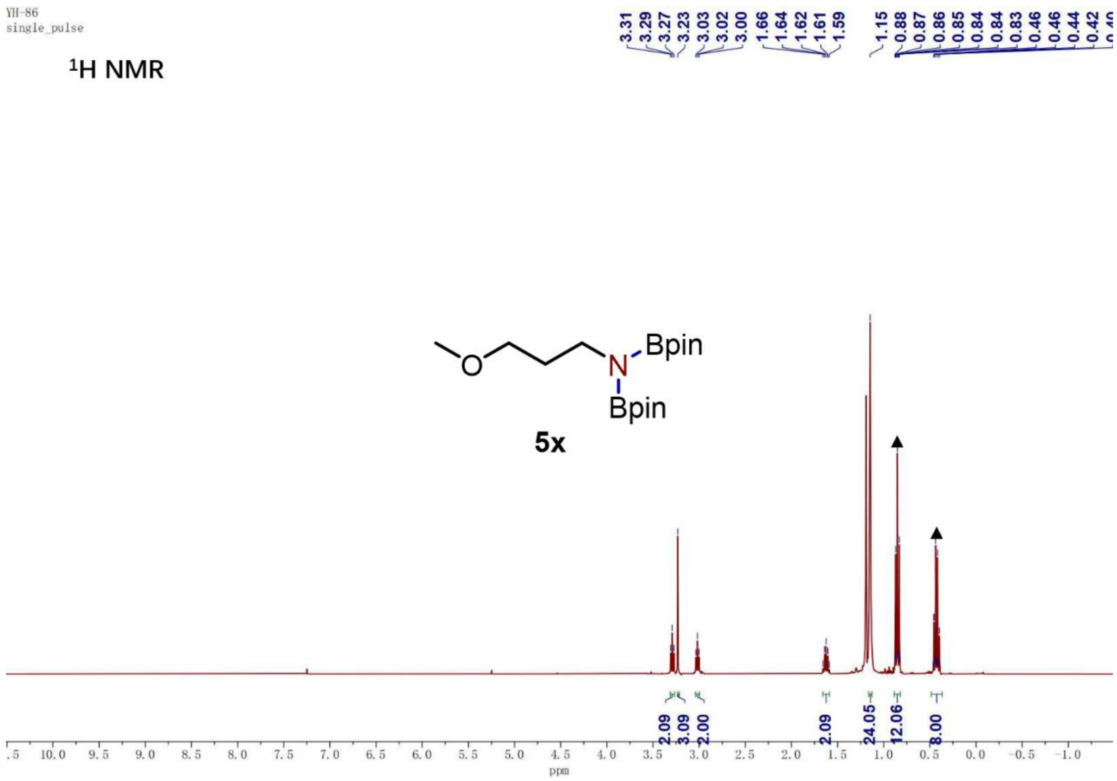


Figure S122. ^{1}H NMR spectrum of **5x** (400 MHz, Chloroform-*d*).

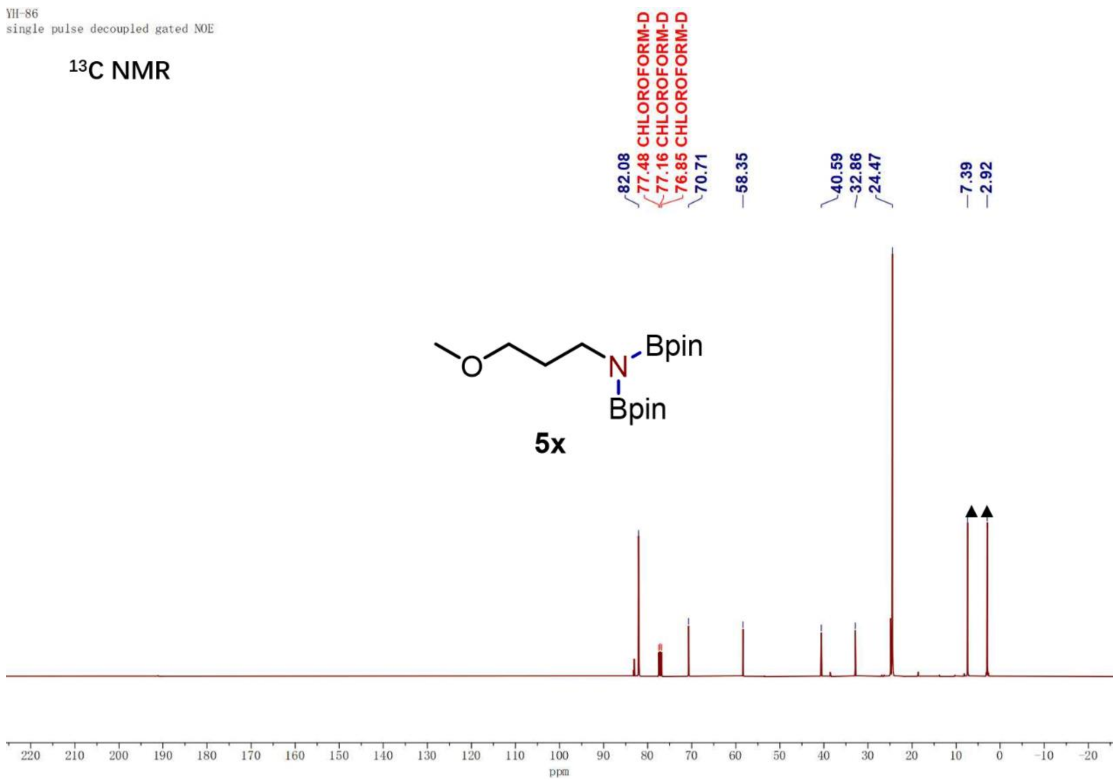


Figure S123. ^{13}C NMR spectrum of **5x** (101 MHz, Chloroform-*d*).

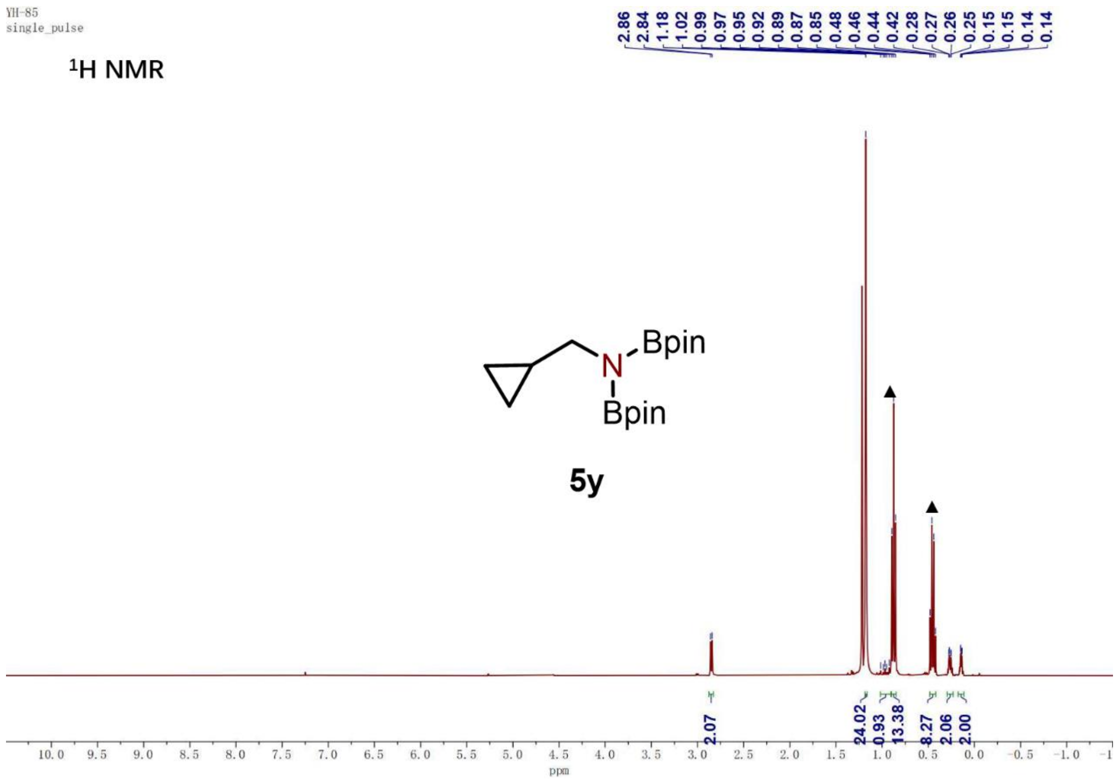


Figure S124 ^{1}H NMR spectrum of **5y** (400 MHz, Chloroform-*d*).

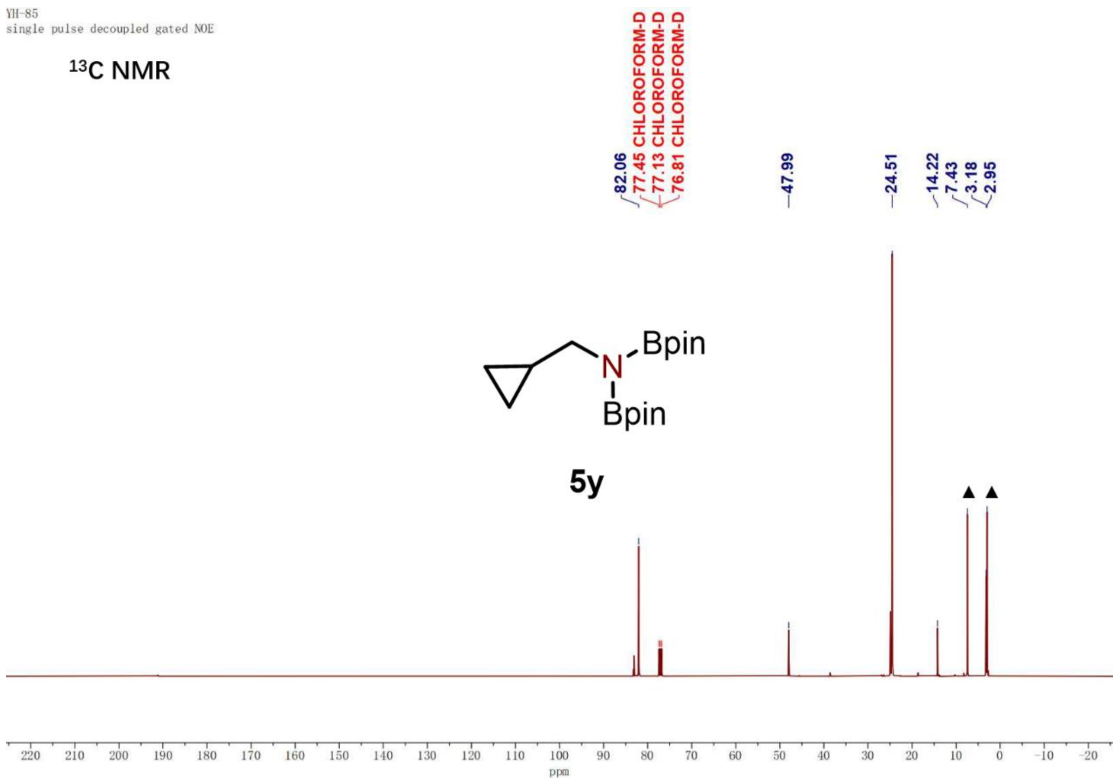


Figure S125. ^{13}C NMR spectrum of **5y** (101 MHz, Chloroform-*d*).

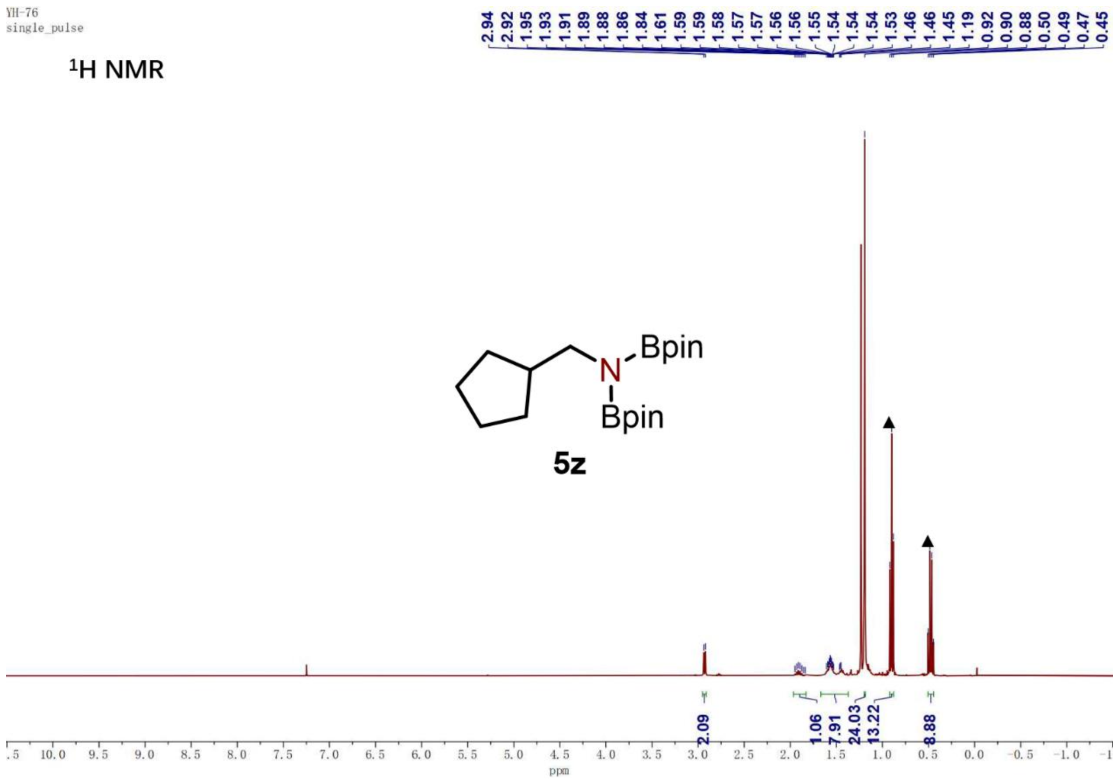


Figure S126. ^{1}H NMR spectrum of **5z** (400 MHz, Chloroform-*d*).

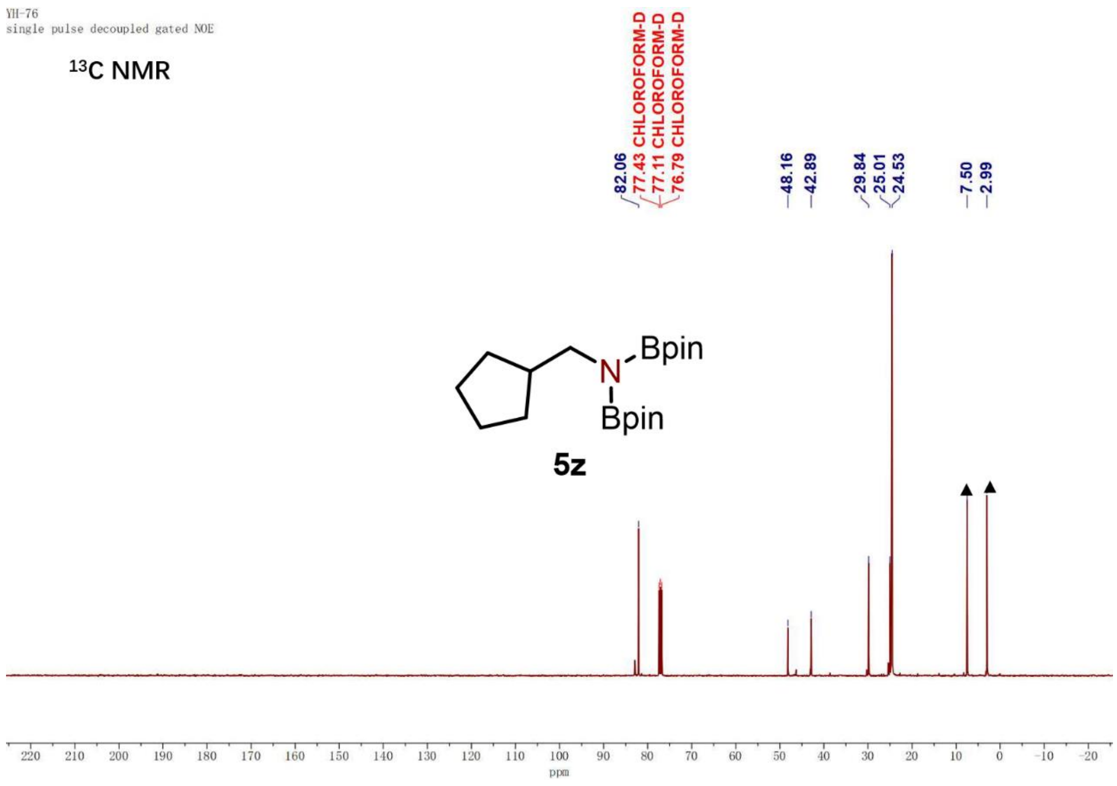


Figure S127. ^{13}C NMR spectrum of **5z** (101 MHz, Chloroform-*d*).

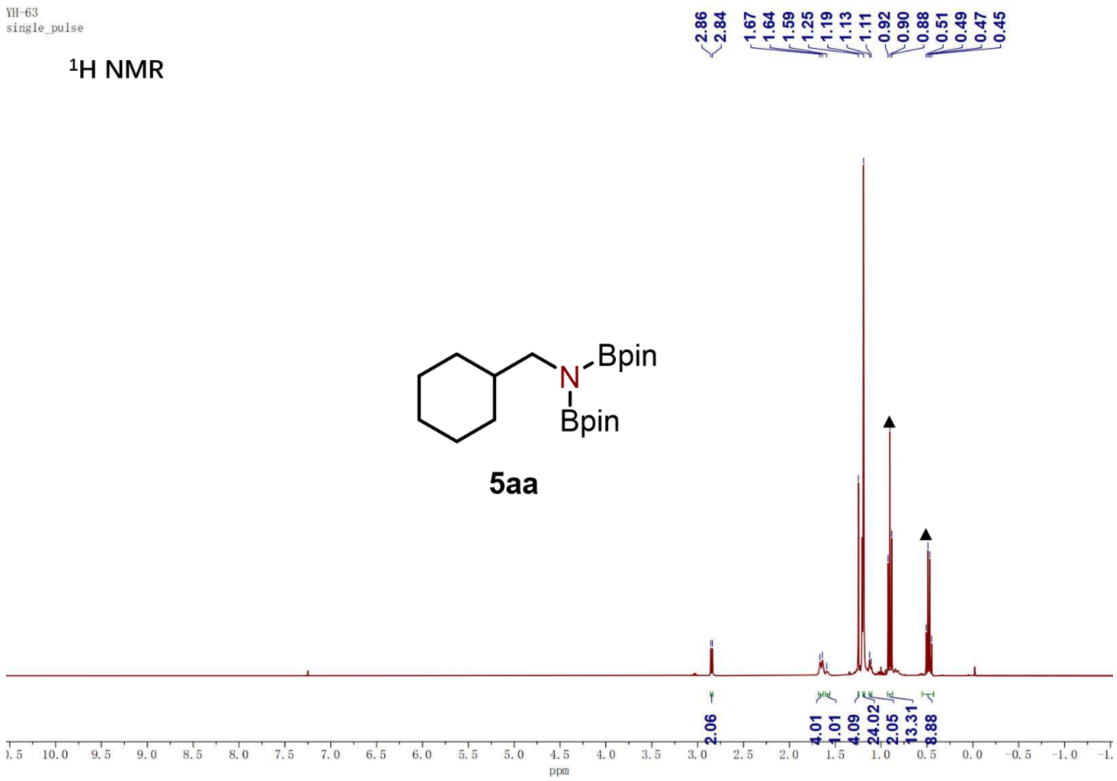


Figure S128. ^{1}H NMR spectrum of **5aa** (400 MHz, Chloroform-*d*).

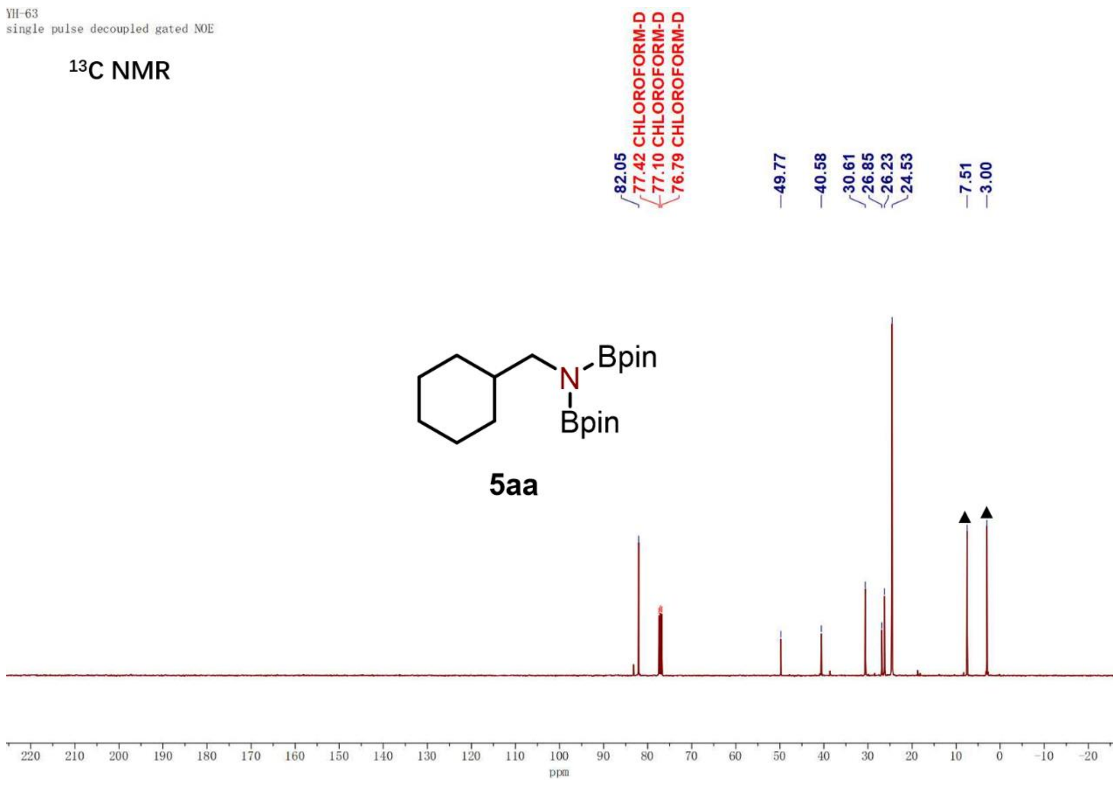


Figure S129. ^{13}C NMR spectrum of **5aa** (101 MHz, Chloroform-*d*).

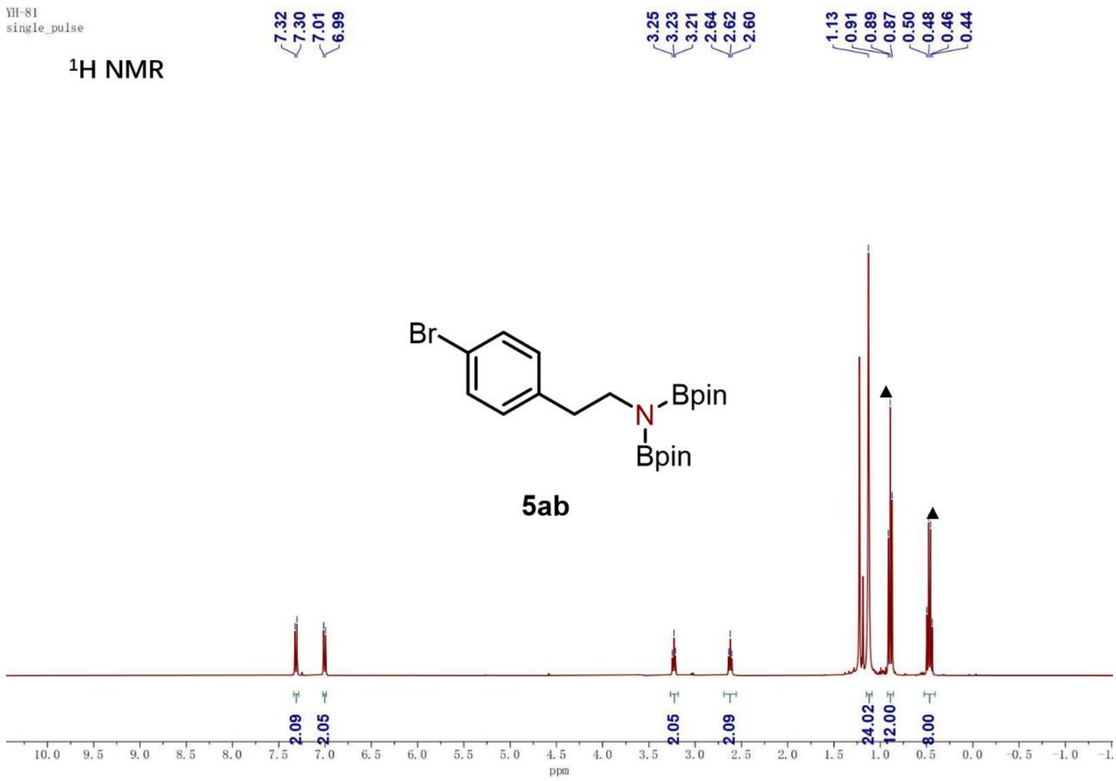


Figure S130. ^{1}H NMR spectrum of **5ab** (400 MHz, Chloroform-*d*).

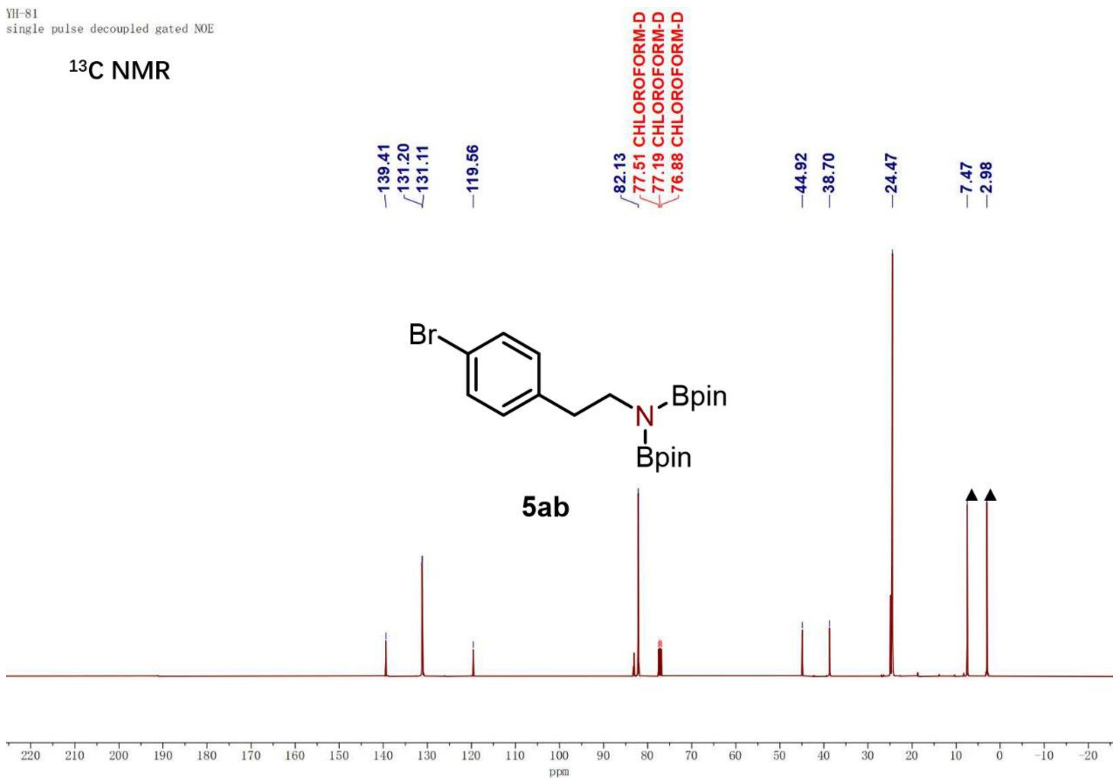


Figure S131. ^{13}C NMR spectrum of **5ab** (101 MHz, Chloroform-*d*).

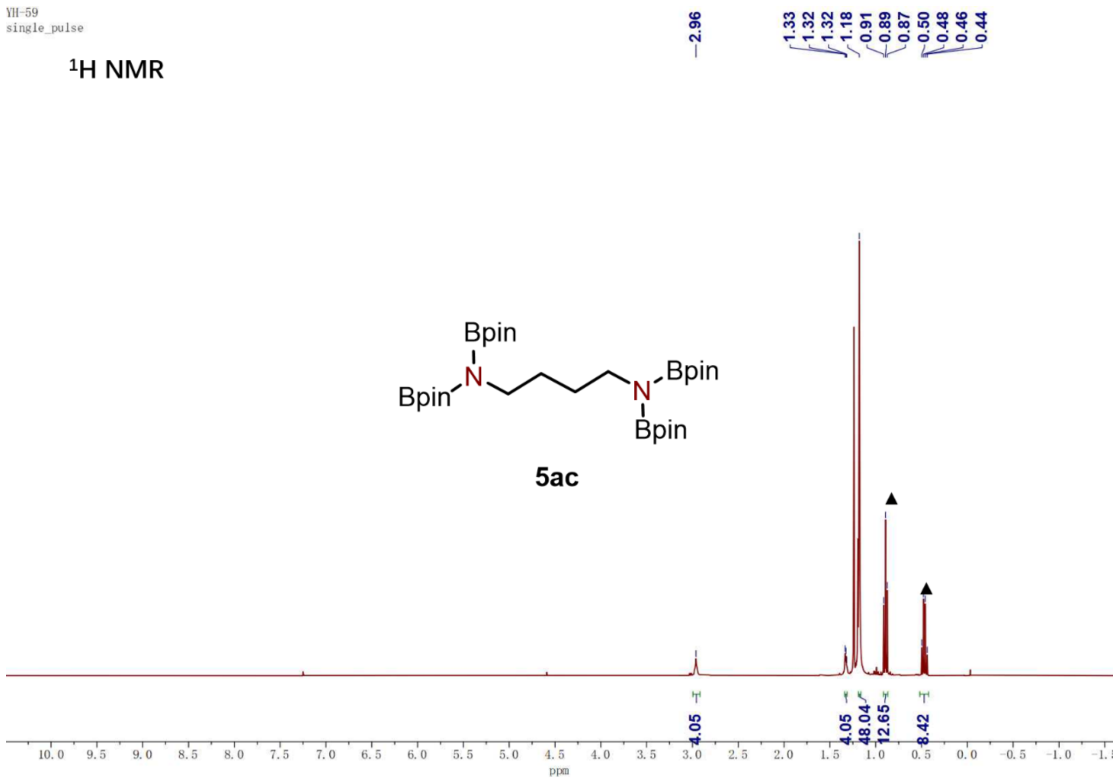


Figure S132. ^{1}H NMR spectrum of **5ac** (400 MHz, Chloroform-*d*).

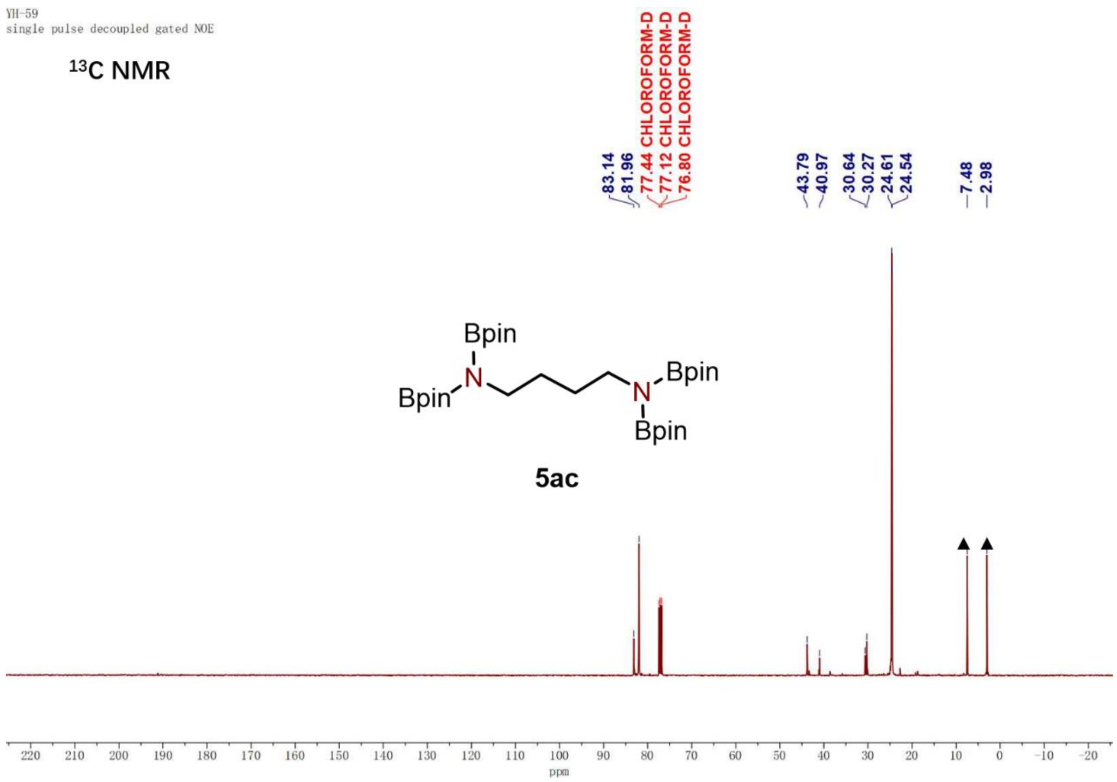


Figure S133. ^{13}C NMR spectrum of **5ac** (101 MHz, Chloroform-*d*).

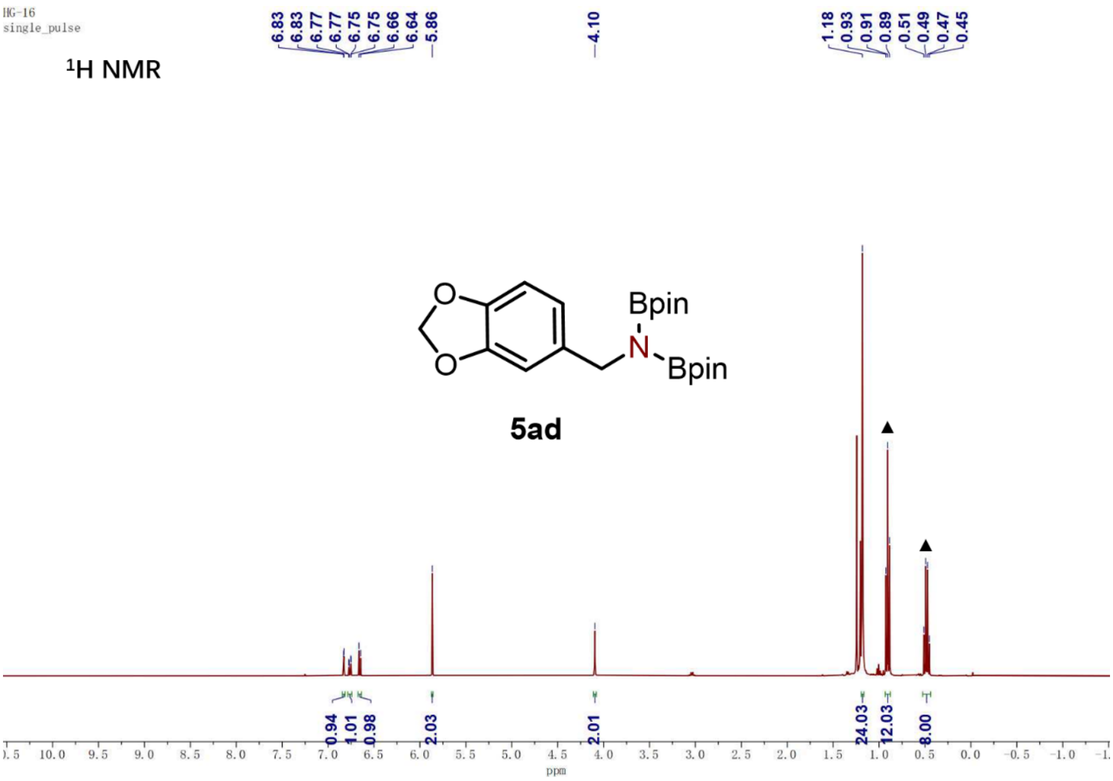


Figure S134. ^{1}H NMR spectrum of **5ad** (400 MHz, Chloroform-*d*).

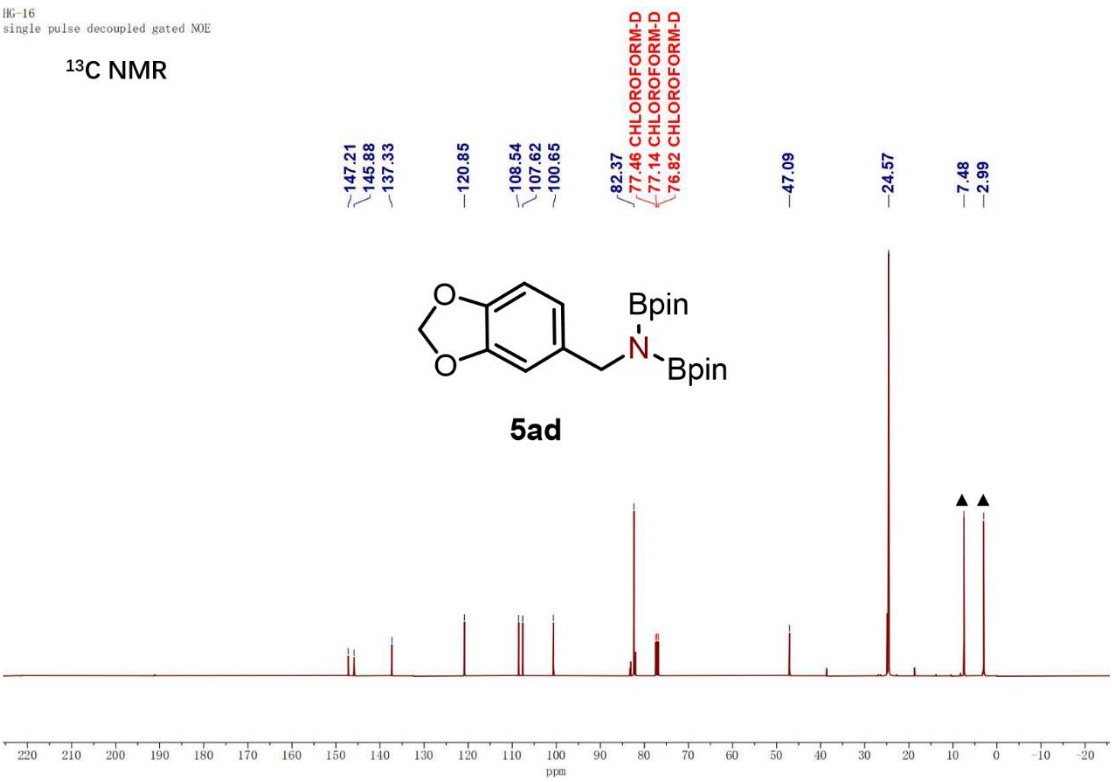


Figure S135. ^{13}C NMR spectrum of **5ad** (101 MHz, Chloroform-*d*).

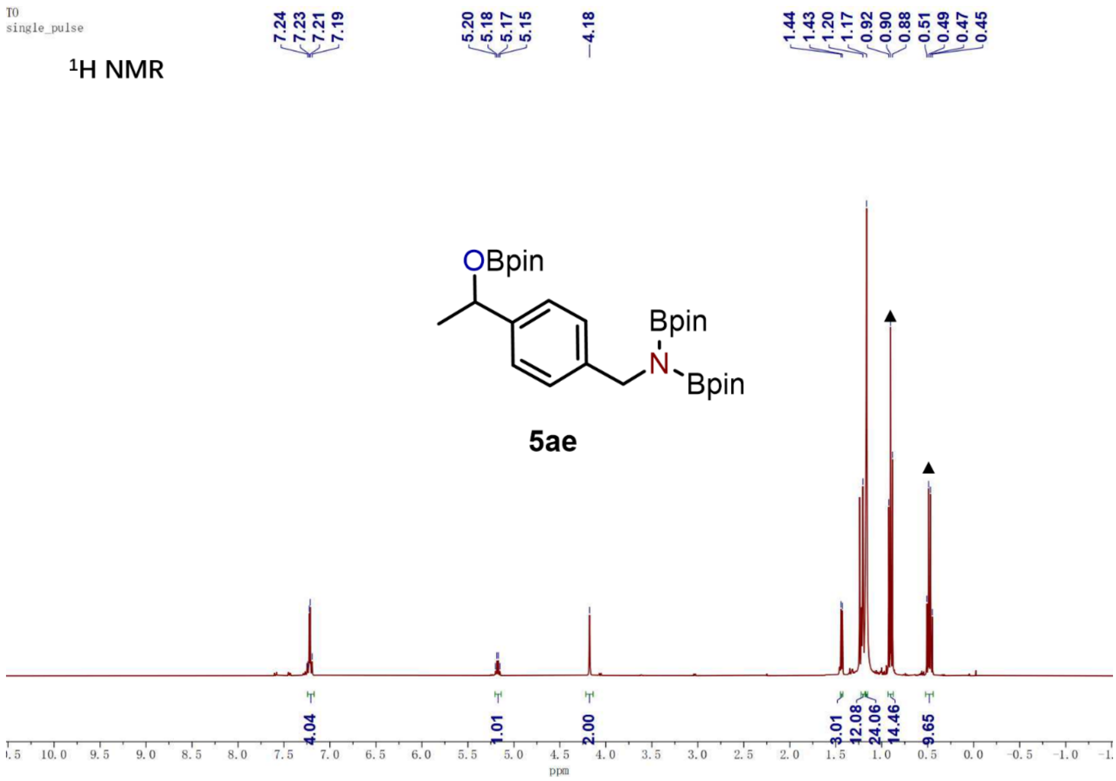


Figure S136. ^{1}H NMR spectrum of **5ae** (400 MHz, Chloroform-*d*).

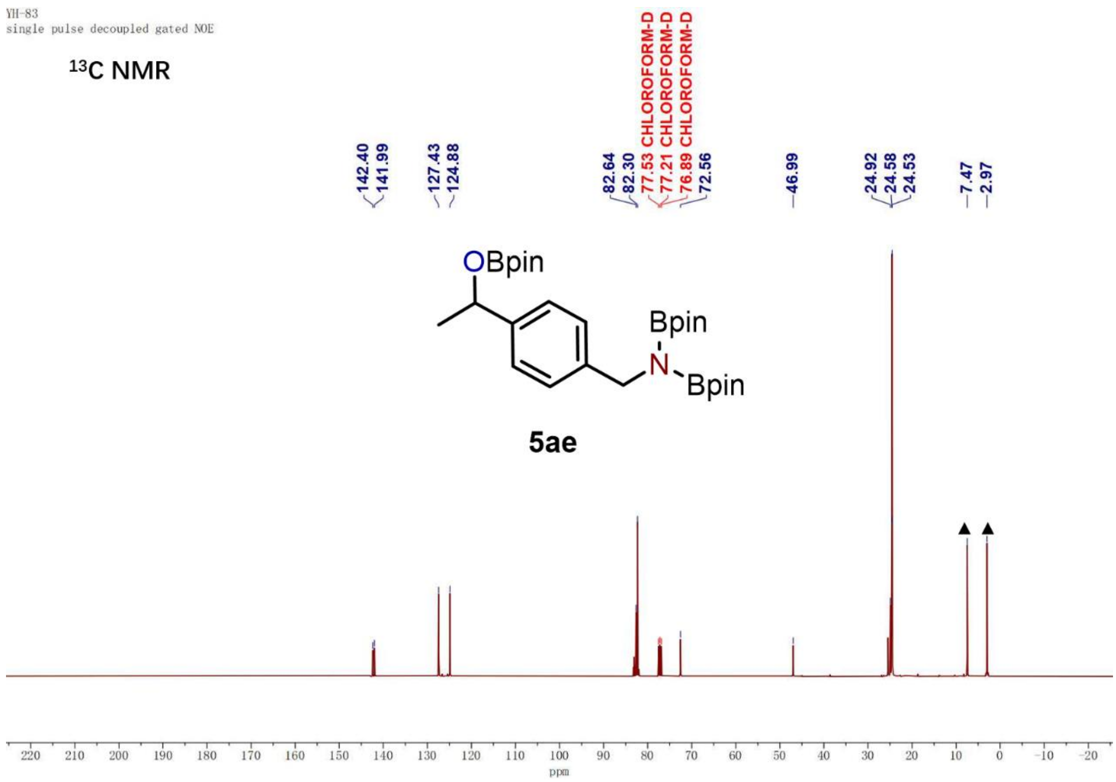


Figure S137. ^{13}C NMR spectrum of **5ae** (101 MHz, Chloroform-*d*).

12.3. NMR Spectra for 7a-7d

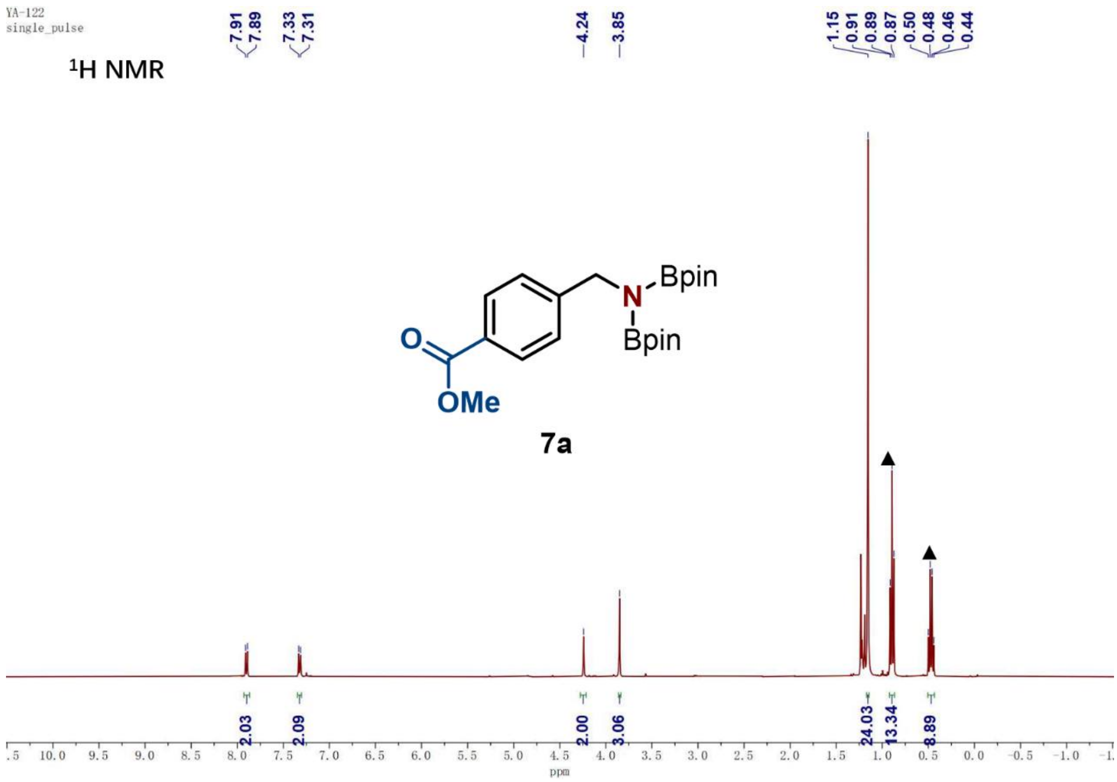


Figure S138. ^{1}H NMR spectrum of **7a** (400 MHz, Chloroform-*d*).

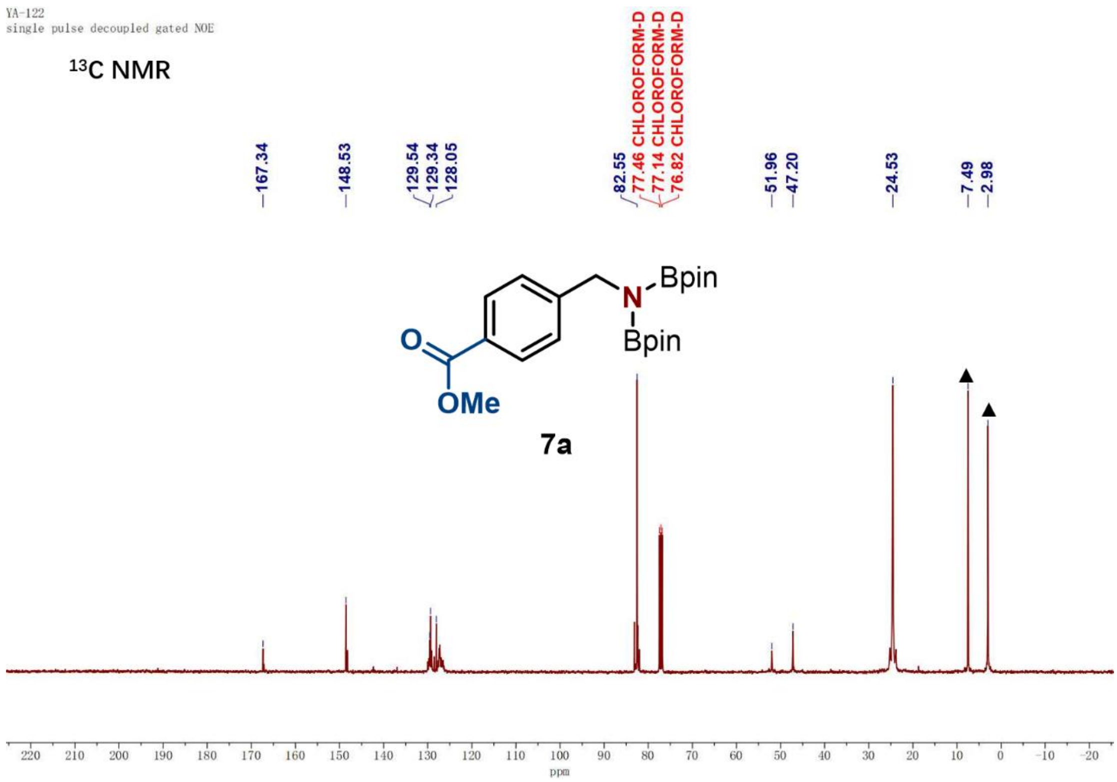


Figure S139. ^{13}C NMR spectrum of **7a** (101 MHz, Chloroform-*d*).

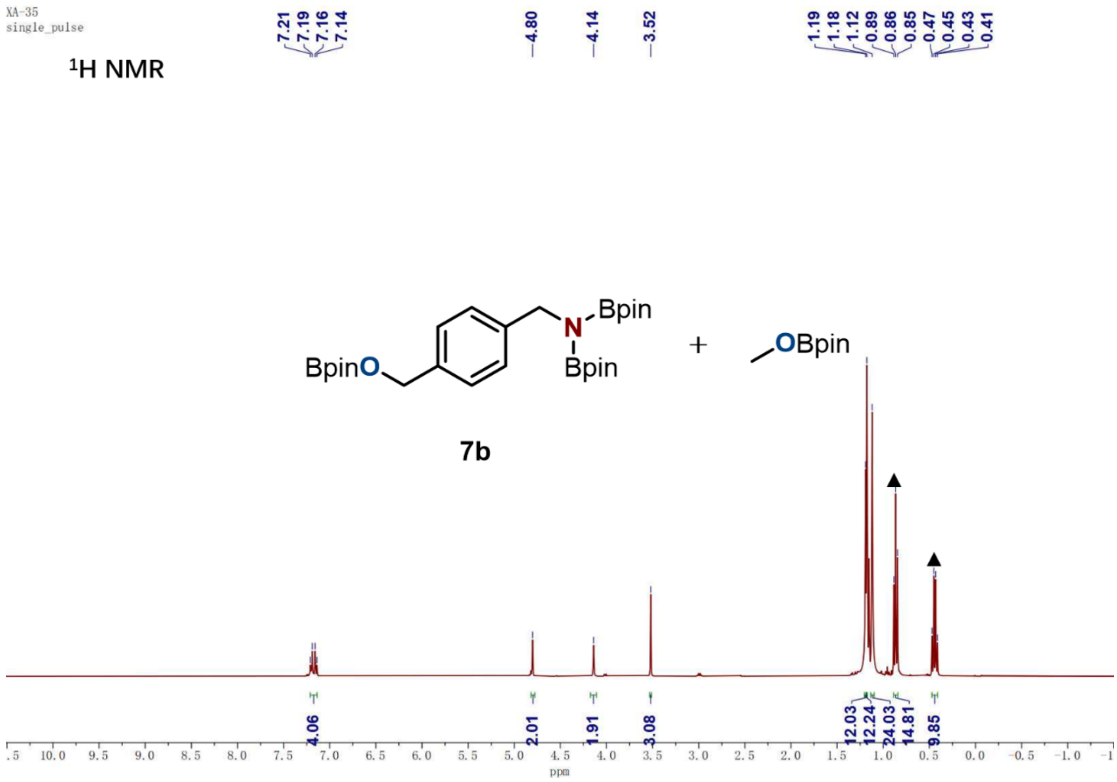


Figure S140. ^{1}H NMR spectrum of **7b** (400 MHz, Chloroform-*d*).

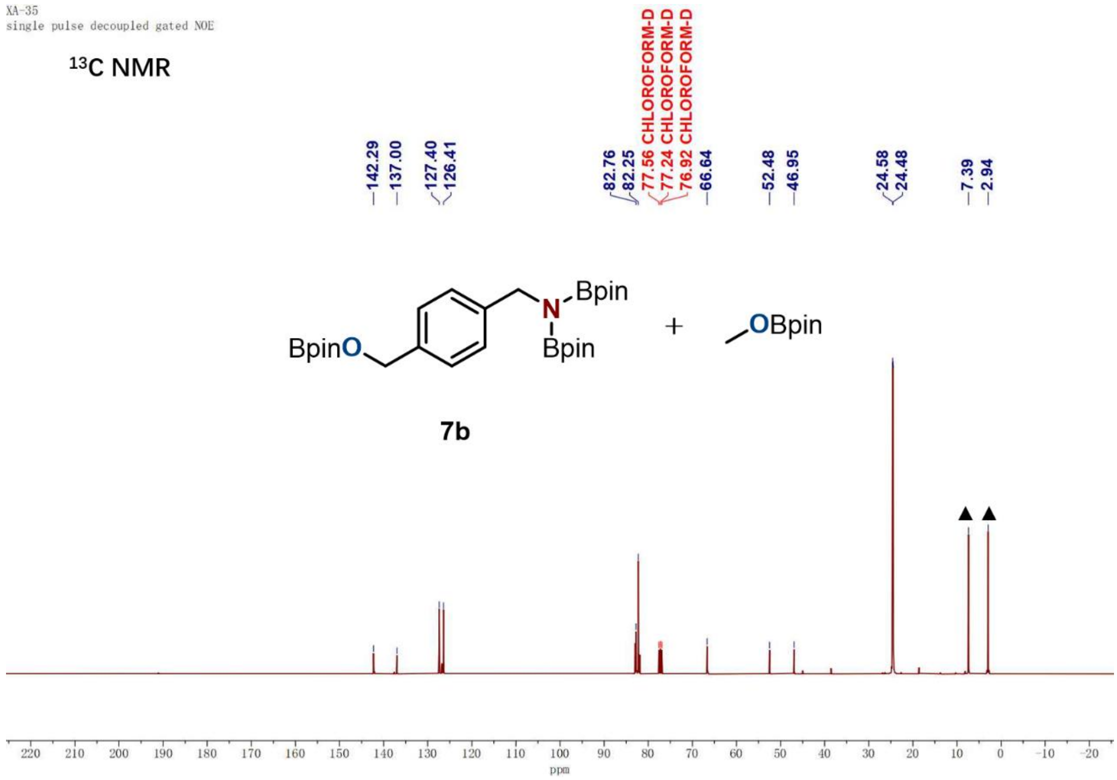


Figure S141. ^{13}C NMR spectrum of **7b** (101 MHz, Chloroform-*d*).

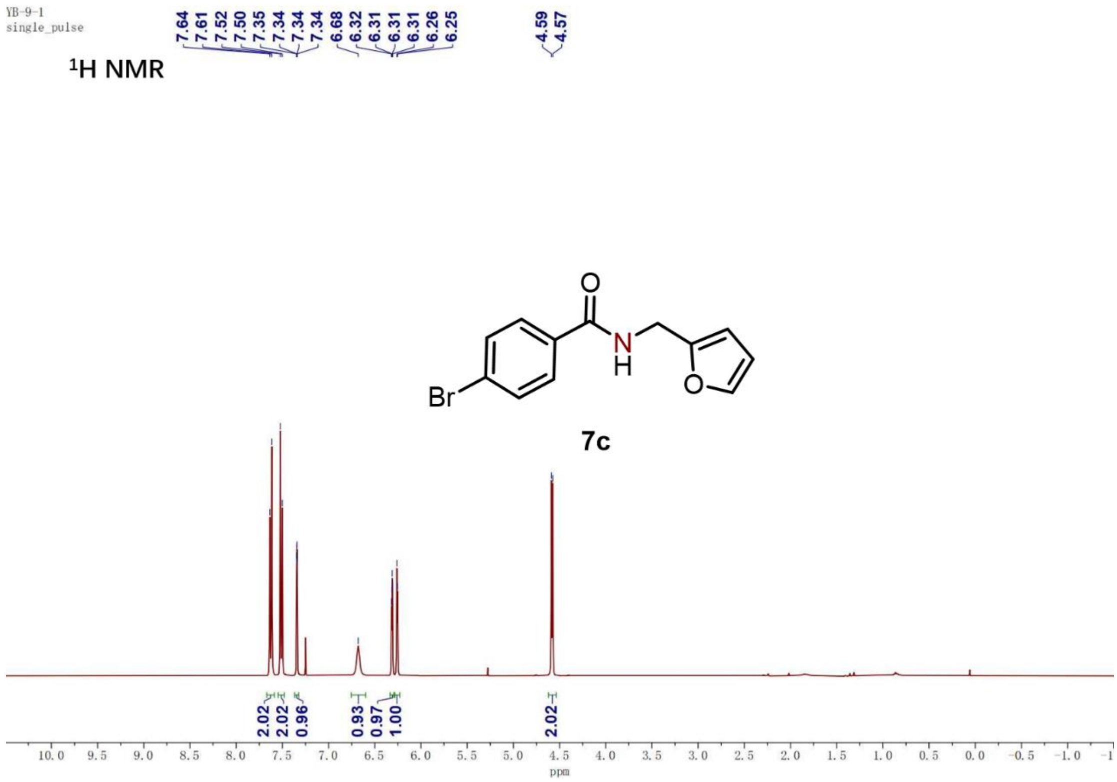


Figure S142. ^{1}H NMR spectrum of **7c** (400 MHz, Chloroform-*d*).

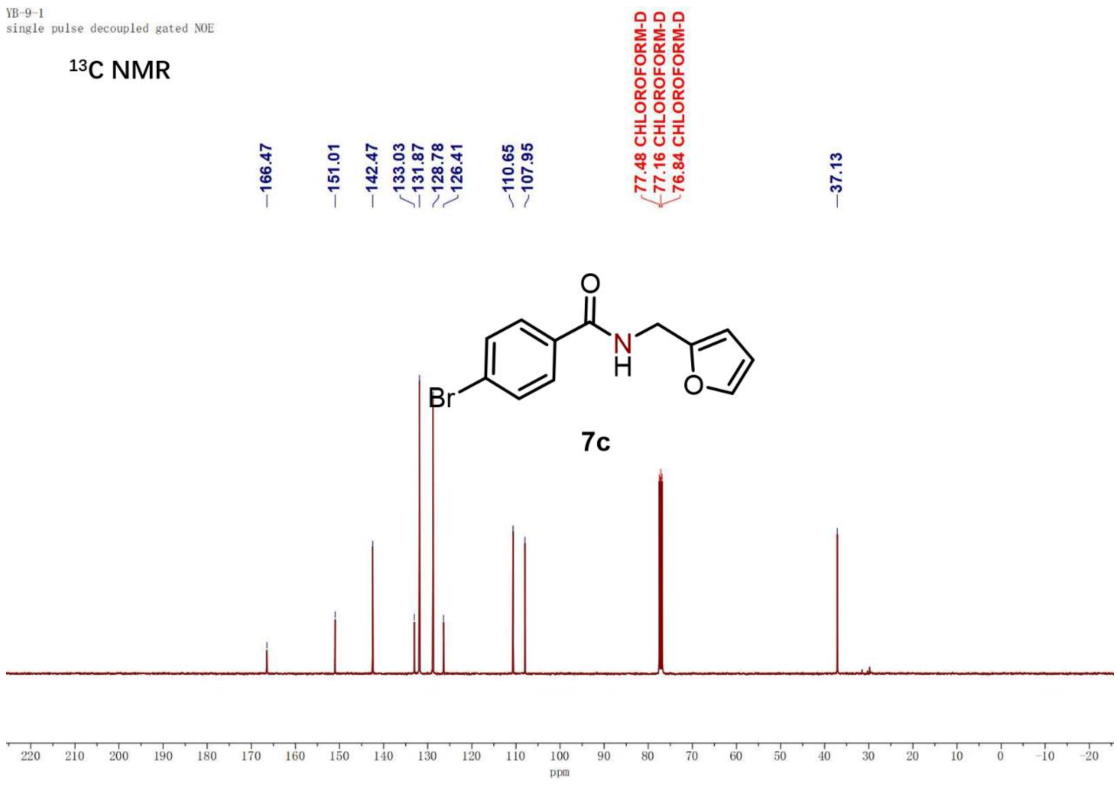


Figure S143. ^{13}C NMR spectrum of **7c** (101 MHz, Chloroform-*d*).

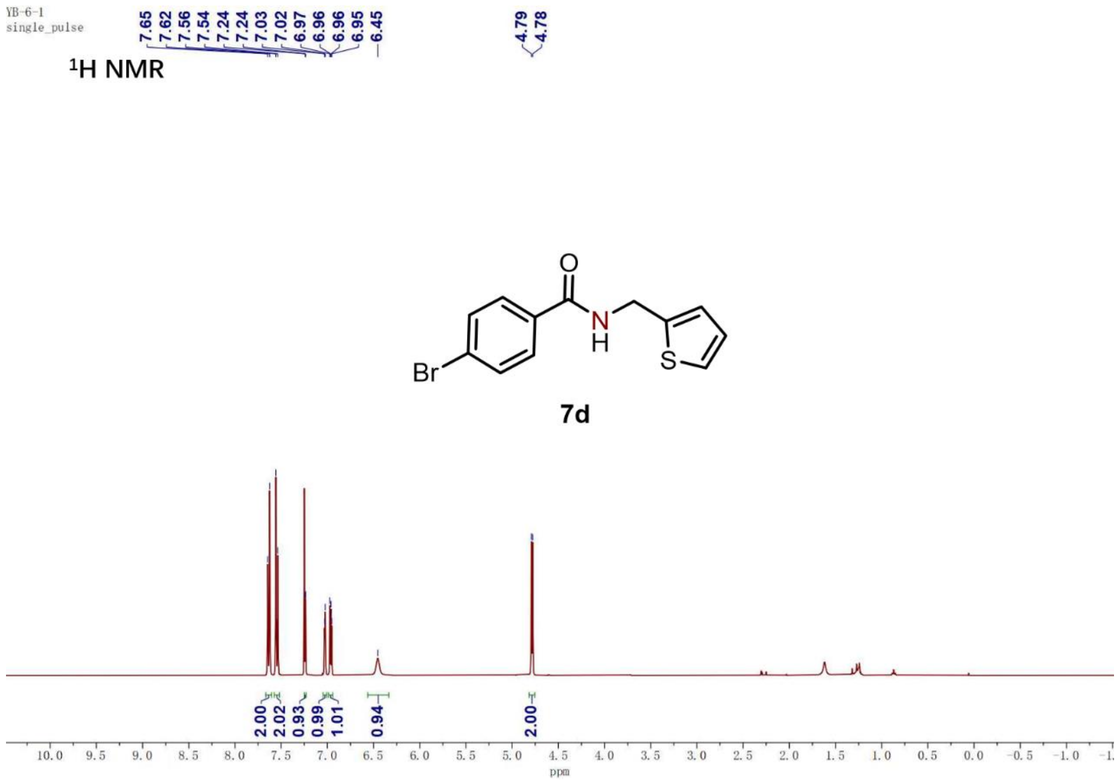


Figure S144. ^{1}H NMR spectrum of **7d** (400 MHz, Chloroform-*d*).

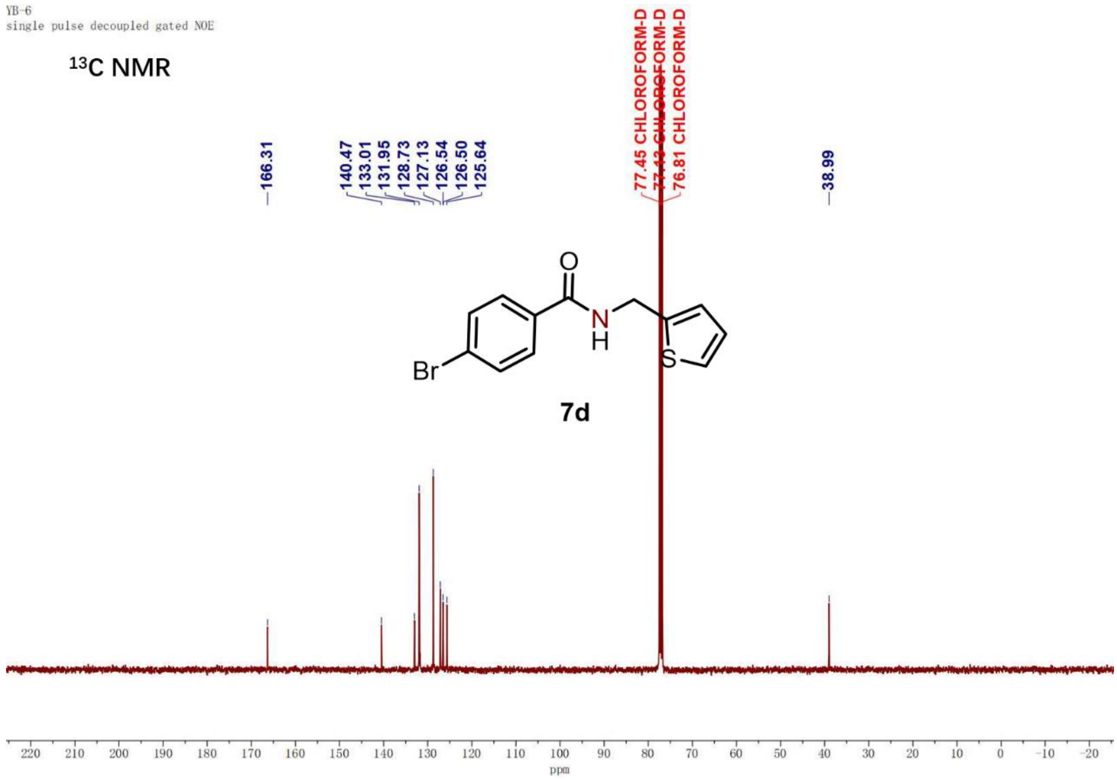


Figure S145. ^{13}C NMR spectrum of **7d** (101 MHz, Chloroform-*d*).

13. Crystal Data and Structure Refinement Parameters

Table S4. Crystal Data and Structure Refinement Parameters for W-2

	W-2
Empirical formula	$C_{20}H_{14}N_2O_6W$
Formula weight	562.18
Temperature (K)	300.00
Crystal system	monoclinic
Space group	C2/c
a (Å)	16.6532(10)
b (Å)	10.7273(6)
c (Å)	11.4809(7)
α (°)	90
β (°)	103.498(4)
γ (°)	90
Volume (Å^3)	1994.3(2)
Z	4
Density (calculated) (g/cm^3)	1.872
Absorption coefficient (mm^{-1})	5.831
F(000)	1080.0
Radiation	Mo-*K*α (λ= 0.71073)
Crystal color, morphology	orange, block
θ range (°)	5.032 to 55.03
Absorption correction	Multi-scan
Index ranges	-21 ≤ h ≤ 18, -11 ≤ k ≤ 13, -14 ≤ l ≤ 14
GOF	1.081
Reflections collected	9847
Independent reflections	2286 [R_{int} = 0.0195, R_{sigma} = 0.0230]
Final R indexes [I>=2σ (I)]	R_1 = 0.0234, wR_2 = 0.0441
Final R indexes (all data)	R_1 = 0.0281, wR_2 = 0.0455
Largest diff. peak / hole (e.Å^{-3})	0.86/-0.41

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