

Supporting Information

Transition metal- and photo-free radical borylation of alkyl bromides and iodides by silane

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Contents

1. General information	2
2. Preparation of substrates.....	3
2.1 Preparation of alkyl bromides (1p,1q,1r,1s,1u).....	3
2.2 Preparation of other alkyl bromides	5
2.3 Preparation of alkyl iodides	7
3. Reaction optimization.....	9
4. Experimental procedures and characterization data.....	10
4.1 General procedure for alkyl bromides	10
4.2 General procedure for alkyl iodides	11
4.3 Compound data	12
5. Mechanistic studies.....	22
5.1 Radical clock reaction.....	22
5.2 Reaction with TEMPO	24
6. DFT computational data.....	25
6.1 Table of energies and lowest frequencies	26
6.2 Cartesian coordinates of the structures	28
6.3 IRC analysis for TS1 and TS2	40
7. X-Ray crystallographic data	42
8. NMR charts	44
9. References.....	72

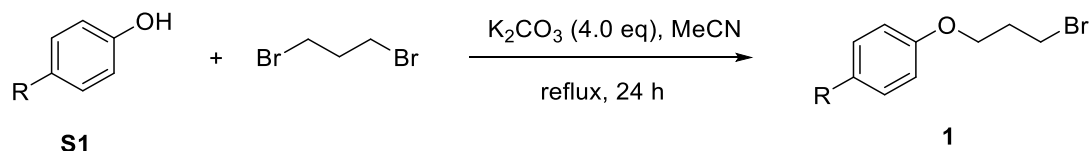
1. General information

Unless otherwise noted, all experiments were carried out under an inert atmosphere in a nitrogen-filled glovebox or by standard Schlenk techniques. All solvents were purchased from J&K Scientific and stored in a nitrogen-filled glovebox over 4Å molecular sieves. Tris(trimethylsilyl)silane (TTMSS) was purchased from J&K Scientific and stored at -20 °C in glovebox for long-term storage. Bis(catecholato)diboron (B_2cat_2) was purchased from Beijing Innochem Science & Technology co., LTD (Innochem) and stored in glovebox. Azobisisobutyronitrile (AIBN) was purchased from Tokyo Chemical Industry Co. (TCI) and stored in glovebox. (Bromomethyl)cyclopropane was purchased from Sigma-Aldrich and stored at -20 °C. Purification of the products was conducted by column chromatography on silica gel (200 - 300 mesh, in some cases 300-400 mesh were used, from Qingdao, China). Thin-layer chromatography (TLC) was performed on silica gel plates (10 - 40 µm) purchased from WISH CHEMICAL, using UV light (254/ 366 nm) or phosphomolybdic acid (PMA) in ethanol (5%) for detection. The substrates were purchased from commercial sources unless otherwise noted.

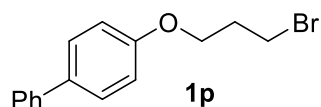
NMR spectra were measured on a Bruker ARX400 (1H at 400 MHz, ^{13}C at 101 MHz, ^{31}P at 162 MHz) magnetic resonance spectrometer. The chemical shifts are reported as parts per million (ppm) referenced to residual protium or carbon of the solvents; $CHCl_3$, δH (7.26 ppm) and δC (77.00 ppm); Coupling constants are reported in Hertz (Hz). Data for 1H NMR spectra are reported as follows: chemical shift (ppm, referenced to protium; s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, ddd = doublet of doublet of doublets, m = multiplet, coupling constant (Hz), and integration). XRD data were collected by XtaLAB PRO 007HF(Cu) Single crystal X-ray diffractometer. Infrared spectra were recorded on a Thermal Fisher Nicolet iS50 Fourier transform spectrometer (FT-IR) and were reported in wave numbers (cm^{-1}). HRMS data were obtained on a VG ZAB-HS mass spectrometer, Bruker Apex IV FTMS spectrometer. GC-MS or FID data were measured using the Agilent Technologies 7890B GC and the Agilent Technologies 5977B MSD. The FID yields were all based on standard curves with 5 points and minimum 0.996 R^2 value (or 4 points and minimum 0.997 R^2 value).

2. Preparation of substrates

2.1 Preparation of alkyl bromides (1p,1q,1r,1s,1u)



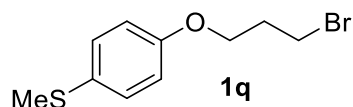
General procedure: The alkyl bromide **1** were prepared according to literature procedure¹. A solution of phenol **S1** (10 mmol) and 1,3-dibromopropane (80 mmol, 8 equiv, 8 mL) in MeCN (30 mL) was added anhydrous potassium carbonate (40 mmol, 4 equiv, 5.5 g). The reaction mixture was stirred at reflux for 24 h, and then potassium carbonate was removed by suction filtration and the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel) using PE/ EtOAc as eluent to obtain compound **1**.



4-(3-bromopropoxy)-1,1'-biphenyl (**1p**)

0.76 g, 26% yield, white solid.

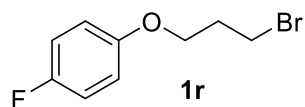
¹H NMR (400 MHz, CDCl₃) δ 7.54 (t, *J* = 9.2 Hz, 4H), 7.42 (t, *J* = 7.2 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 2H), 4.15 (t, *J* = 5.6 Hz, 2H), 3.63 (t, *J* = 6.4 Hz, 2H), 2.38-2.32 (m, 2H)².



(4-(3-bromopropoxy)phenyl)(methyl)sulfane (**1q**)

0.73 g, 28% yield, colorless liquid.

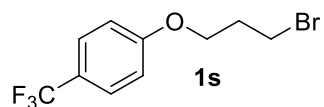
¹H NMR (400 MHz, CDCl₃) δ 7.27 (d, *J* = 7.2 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 4.08 (t, *J* = 6.0 Hz, 2H), 3.60 (t, *J* = 6.4 Hz, 2H), 2.44 (s, 3H), 2.34-2.27 (m, 2H)³.



1-(3-bromopropoxy)-4-fluorobenzene (**1r**)

2.10 g, 90% yield, colorless liquid.

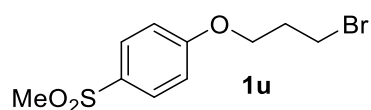
¹H NMR (400 MHz, CDCl₃) δ 6.99-6.95 (m, 2H), 6.84 (q, *J* = 4.4 Hz, 2H), 4.06 (t, *J* = 6.0 Hz, 2H), 3.60 (t, *J* = 6.4 Hz, 2H), 2.33-2.27 (m, 2H)⁴.



1-(3-bromopropoxy)-4-(trifluoromethyl)benzene (1s)

1.56 g, 55% yield, colorless liquid.

¹H NMR (400 MHz, CDCl₃) δ 7.55 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 4.15 (t, *J* = 6.0 Hz, 2H), 3.61 (t, *J* = 6.4 Hz, 2H), 2.37-2.31 (m, 2H)⁵.



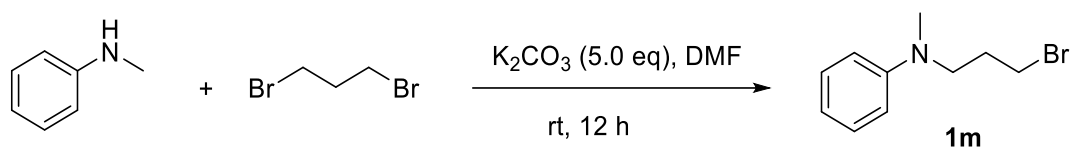
1-(3-bromopropoxy)-4-(methylsulfonyl)benzene (1u)

2.49 g, 85% yield, white solid.

¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, *J* = 8.8 Hz, 2H), 7.04 (d, *J* = 8.8 Hz, 2H), 4.20 (t, *J* = 6.0 Hz, 2H), 3.61 (t, *J* = 6.0 Hz, 2H), 3.04 (s, 3H), 2.39-2.33 (m, 2H)¹.

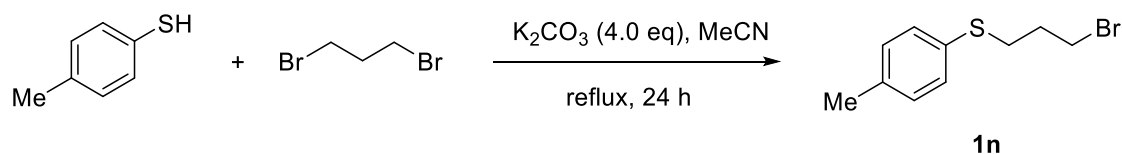
2.2 Preparation of other alkyl bromides

Preparation of N-(3-bromopropyl)-N-methylaniline (1m)



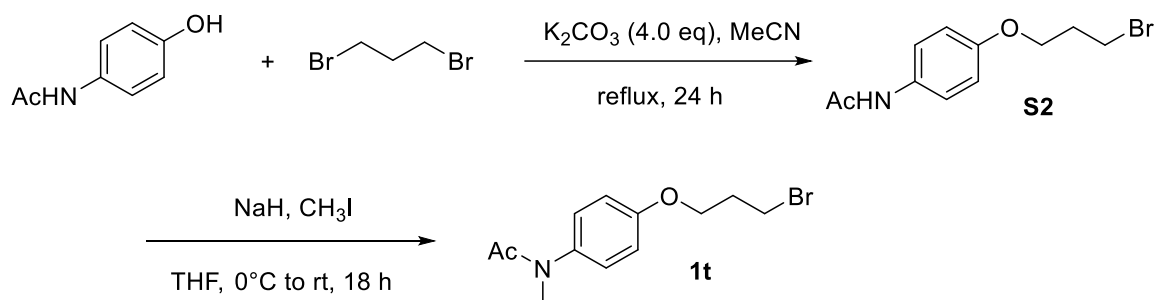
The alkyl bromide **1m** were prepared according to literature procedure⁶. To a solution of N-methylaniline (1.1 g, 10 mmol) in dry DMF (10 mL), potassium carbonate (6.9 g, 50 mmol) was added and allowed to stir for 10 min. To this reaction mixture, 1,3 dibromopropane (80 mmol, 8 equiv, 8 mL) was added slowly and then reaction mixture was allowed to stir for 12 h at room temperature under argon atmosphere. After the completion of reaction, reaction mixture was filtered and the compound was extracted with diethyl ether. Organic layer was washed with brine and solvent removed under reduced pressure. The residue was subjected to column purification on silica gel, eluting with hexane to give **1m** as a yellow liquid (1.03 g, 45%). ¹H NMR (400 MHz, CDCl₃) δ 7.25-7.22 (m, 2H), 6.74-6.69 (m, 3H), 3.51-3.44 (m, 4H), 2.96 (s, 3H), 2.17-2.10 (m, 2H).

Preparation of (3-bromopropyl)(p-tolyl)sulfane (1n)



The substrate 4-methyl thiophenol (1.24 g, 10 mmol) followed the same procedure in **section 2.1** to obtain compound **1n** as a colorless liquid (1.64 g, 67%). ¹H NMR (400 MHz, CDCl₃) δ 7.28 (s, 1H), 7.25 (s, 1H), 7.11 (d, J = 8.0 Hz, 2H), 3.51 (t, J = 6.4 Hz, 2H), 3.17 (t, J = 6.8 Hz, 2H), 2.32 (s, 3H), 2.15-2.08 (m, 2H).

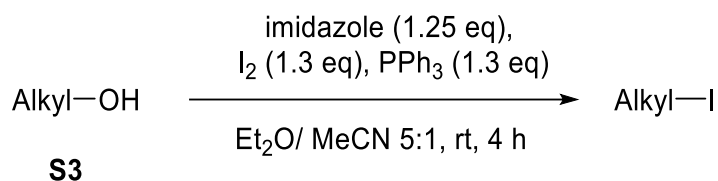
Preparation of N-(4-(3-bromopropoxy)phenyl)-N-methylacetamide (1t)



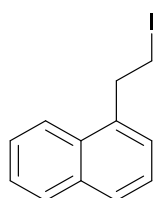
Intermediate **S2** was prepared according to procedure in **section 2.1**, affording **S2** as a white solid (1.10 g, 80%). 1H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 8.8 Hz, 2H), 6.86 (d, J = 9.2 Hz, 2H), 4.08 (t, J = 5.6 Hz, 2H), 3.60 (t, J = 6.4 Hz, 2H), 2.34-2.16 (m, 2H), 2.16 (s, 3H)¹.

In inert atmosphere, NaH (0.25g, 10.5 mmol, 3 equiv) was added to 30 mL anhydrous THF at 0°C, then added **S2** (3.5 mmol, 0.95 g, resolved in 10 mL anhydrous THF) dropwise. The reaction mixture was stirred for 30 min at 0°C, followed by CH_3I (10.7 mL, 10.5 mmol, 3 equiv, resolved in 10 mL anhydrous THF) dropwise. The reaction mixture was allowed to warm to room temperature, and stirred for 18 hours. After the reaction finished, added 20 mL water to quench the reaction, extracted by EtOAc (3×50 mL) and purified by column chromatography using PE/ EtOAc 1:1 as eluent, affording **1t** as a yellow oil (1.10 g, 96%). 1H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, J = 8.8 Hz, 2H), 6.92 (d, J = 8.4 Hz, 2H), 4.12 (t, J = 6.0 Hz, 0.74H), 4.06 (t, J = 5.6 Hz, 1.23H), 3.62 (t, J = 6.4 Hz, 0.75H), 3.38 (t, J = 6.4 Hz, 1.27H), 3.23 (s, 3H), 2.37-2.26 (m, 2H), 1.86 (s, 3H).

2.3 Preparation of alkyl iodides



The alkyl iodides **1** were prepared according to literature procedure¹. A 100 mL round-bottom flask was charged with alcohol (**S3**, 10 mmol), imidazole (12.5 mmol, 1.25 equiv, 851 mg), I₂ (13 mmol, 1.30 equiv, 3.30 g), PPh₃ (13 mmol, 1.30 equiv, 3.41 g), and Et₂O/ MeCN (5:1, 60 mL). The resulting solution was stirred for 4 h at room temperature. The reaction mixture was then quenched by 100 mL of sodium bicarbonate (sat.) and extracted with 3×100 mL of ethyl acetate. The combined organic phases were dried over Na₂SO₄ and concentrated under vacuum. The residue was purified by column chromatography (silica gel) using petroleum ether (PE) as eluent to give the desired alkyl iodide **1**.

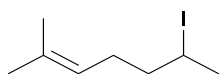


1x

1-(2-iodoethyl)naphthalene (**1x**)

yellow oil, 2.11 g, 75% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.97 (d, *J* = 8.3 Hz, 1H), 7.87 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.52 (dddd, *J* = 21.6, 8.1, 6.8, 1.4 Hz, 2H), 7.42 (dd, *J* = 8.1, 7.0 Hz, 1H), 7.35 (dd, *J* = 7.1, 1.3 Hz, 1H), 3.65 (dd, *J* = 9.0, 7.2 Hz, 2H), 3.47 (dd, *J* = 9.0, 7.1 Hz, 2H)⁷.

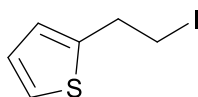


1y

6-iodo-2-methylhept-2-ene (**1y**)

yellow oil, 1.60 g, 67% yield.

¹H NMR (400 MHz, CDCl₃) δ 5.07 (t, *J* = 7.3 Hz, 1H), 4.18 (h, *J* = 6.7, 6.0 Hz, 1H), 2.11 (dh, *J* = 29.4, 7.3 Hz, 2H), 1.99 – 1.83 (m, 4H), 1.67 (d, *J* = 17.4 Hz, 6H), 1.59 (dd, *J* = 10.7, 4.4 Hz, 1H)⁸.

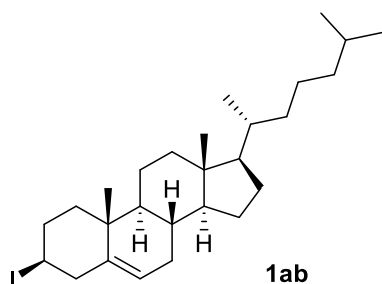


1aa

2-(2-iodoethyl)thiophene (1aa)

colorless oil, 2.10 g, 88% yield.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.19 (d, $J = 5.2$ Hz, 1H), 6.95 (t, $J = 4.2$ Hz, 1H), 6.87 (d, $J = 3.5$ Hz, 1H), 3.38 (d, $J = 4.2$ Hz, 4H)⁹.



1ab

cholesteryl iodide (1ab)

recrystallization in acetone to give a white needle, 1.45 g, 79% yield.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 5.33 (dt, $J = 5.6, 1.9$ Hz, 1H), 4.04 (tt, $J = 12.5, 4.4$ Hz, 1H), 2.93 (ddt, $J = 15.9, 13.1, 2.6$ Hz, 1H), 2.67 (ddd, $J = 13.7, 4.5, 2.1$ Hz, 1H), 2.33 – 2.13 (m, 2H), 1.98 (ddt, $J = 20.5, 15.2, 3.2$ Hz, 2H), 1.83 (dtd, $J = 13.2, 9.4, 5.8$ Hz, 1H), 1.73 (dt, $J = 13.5, 3.5$ Hz, 1H), 1.63 – 0.93 (m, 23H), 0.91 (d, $J = 6.5$ Hz, 3H), 0.86 (dd, $J = 6.6, 1.8$ Hz, 6H), 0.67 (s, 3H)¹⁰.

3. Reaction optimization

The optimization of the reaction was carried out using 1-bromooctane (0.30 mmol) as the test system. In a glovebox under a nitrogen atmosphere, sequentially add B₂cat₂, radical initiator and 2 mL solvent to a 10 mL Schlenk tube with a stir bar, followed by silane and 1-bromooctane (0.3 mmol). The capped Schlenk tube was removed from the glovebox, and the reaction mixture was stirred at a given temperature for given time. After cooling to room temperature, pinacol (4.0 equiv) and 1.0 mL triethylamine were added, and the mixture was stirred at room temperature for 1 hour. After that, the reaction mixture was washed with H₂O (5 mL), extracted using ethyl acetate (5 mL), then n-decane (~25 mg) was added as internal standard, the conversion of 1-bromooctane and the yield were measured by GC (FID). The results are shown in **Table 1**.

Table 1 Optimization of reaction conditions of alkyl bromide.

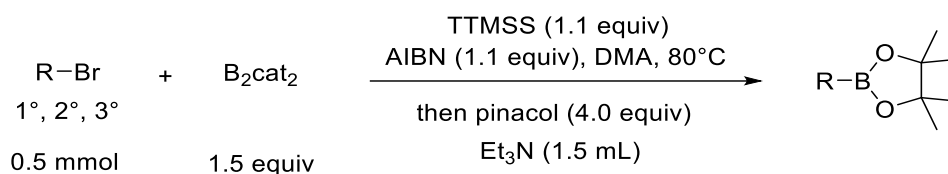
CCCCCCCCBr (1a) + B₂cat₂ $\xrightarrow[\text{then pinacol, Et}_3\text{N}]{\text{TTMSS, AIBN, DMA, 80 }^\circ\text{C}}$ CCCCCCCCBpin (2a)

1a				2a	
Entry	TTMSS (equiv)	AIBN (equiv)	B ₂ cat ₂ (equiv)	Time(h)	yield (%)
1 ^b	1.15	1.0	4.0	21	59%
2	2.0	2.0	4.0	15	87%
3	2.0	2.0	4.0	21	89% (81%)
4	2.0	2.0	4.0	21	90%
5 ^c	2.0	2.0	4.0	21	89%
6	2.0	1.1	4.0	12	87%
7	2.0	1.1	2.0	6	89%
8	2.0	1.1	1.5	6	73%
9	1.1	1.1	2.0	6	79%
10	1.1	1.1	1.5	6	84% (81%)
11	1.1	1.1	1.2	6	70%
12	1.0	1.1	1.2	6	72%
13	1.1	1.1	2.5	6	81%
14	1.1	1.1	3.0	6	75%
15 ^d	1.15	0	4.0	48	trace
16 ^e	1.1	1.1	1.5	6	76%

a: Reaction Condition: **1a** (0.3 mmol), B₂cat₂ (Bis(catecholato)diboron), AIBN (Azobisisobutyronitrile), TTMSS (Tris(trimethylsilyl)silane), DMA (Dimethylacetamide) (2 mL), 80 °C. Then pinacol (4.0 equiv), Et₃N (1 mL). Decane is used as an internal standard. GC-fid yield, the yield in bracket is isolated yield. b: The temperature is 70 °C. c: Using ACCN (1,1'-Azobis(cyclohexanecarbonitrile)) instead of AIBN. d 10W blue LED (10 cm distance), room temperature. e: in air.

4. Experimental procedures and characterization data

4.1 General procedure for alkyl bromides

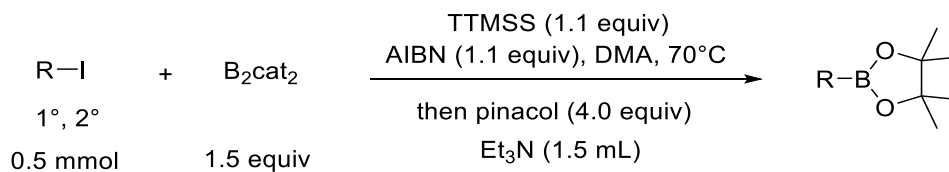


In a glovebox under a nitrogen atmosphere, sequentially added B_2cat_2 (0.75 mmol, 1.5 equiv, 178 mg), AIBN (0.55 mmol, 1.1 equiv, 90 mg), and 3 mL DMA to a 10mL Schlenk tube with a stir bar, followed by TTMSS (0.55 mol, 1.1 equiv, 170 μL) and alkyl bromide (0.5 mmol). The capped Schlenk tube was stirred at 80 $^\circ\text{C}$ for 6 hours. After cooling to room temperature, pinacol (236 mg, 4.0 equiv) and 1.5 mL triethylamine were added, and the mixture was stirred at room temperature for 1 hour.

Water was added to the reaction mixture and the aqueous layer was extracted with EtOAc (3x). If phase separation was slow, brine was added. The organic phases were combined and washed with 100 mL of saturated brine, the organic phase was dried over anhydrous sodium sulfate and filtered, and then concentrated under reduced pressure, and purified by column chromatography to give the product. The product was monitored by thin layer chromatography with phosphomolybdic acid (PMA) stain.

In some cases, after the removal of the solvent, added 5 mL diethyl ether, and then added TBAF (1mol / L in THF) (depending on the condition of different substrates) dropwise under an ice bath at 0 $^\circ\text{C}$ for 5 min, then isolated the product by column chromatography quickly. It is to remove the silyl by-products produced in reaction¹¹.

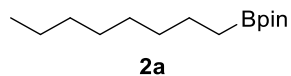
4.2 General procedure for alkyl iodides



In a glovebox under a nitrogen atmosphere, sequentially added B_2cat_2 (0.75 mmol, 1.5 equiv, 178 mg), AIBN (0.55 mmol, 1.1 equiv, 90 mg), and 3 mL DMA to a 10mL Schlenk tube with a stir bar, followed by TTMSS (0.55 mol, 1.1 equiv, 170 μL) and alkyl iodide (0.5 mmol). The capped Schlenk tube was stirred at 70 $^\circ\text{C}$ for 2 hours. After cooling to room temperature, pinacol (236 mg, 4.0 equiv) and 1.5 mL triethylamine were added, and the mixture was stirred at room temperature for 1 hour.

Water was added to the reaction mixture and the aqueous layer was extracted with EtOAc (3x). If phase separation was slow, brine was added. The organic phases were combined and washed with 100 mL of saturated brine, the organic phase was dried over anhydrous sodium sulfate and filtered, and then concentrated under reduced pressure, and purified by column chromatography to give the product. The product was monitored by thin layer chromatography with phosphomolybdic acid (PMA) stain.

4.3 Compound data



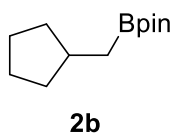
4,4,5,5-tetramethyl-2-octyl-1,3,2-dioxaborolane (2a)

97.3 mg, 81% isolated yield, colorless oil. 4.0 equiv TBAF (1M in THF) was added. Rf = 0.4 (PE), using PE/ EtOAc = 50:1-30:1 as eluent.

¹H NMR (400 MHz, CDCl₃) δ 1.39 (d, J = 7.9 Hz, 2H), 1.25 (d, J = 4.8 Hz, 22H), 0.87 (t, J = 6.6 Hz, 3H), 0.77 (t, J = 7.8 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 82.8, 32.5, 31.9, 29.4, 29.3, 24.8, 24.0, 22.7, 14.2. The signal of the α-B-carbon was not observed.

All data matched that reported in the literature¹.



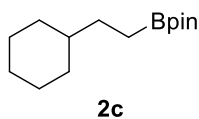
2-(cyclopentylmethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2b)

47.8 mg, 46% isolated yield, colorless oil. 4.0 equiv TBAF (1M in THF) was added. Rf = 0.6 (PE/ EtOAc = 20:1), using PE/ EtOAc = 50:1-30:1 as eluent.

¹H NMR (400 MHz, CDCl₃) δ 1.96 (p, J = 8.1 Hz, 1H), 1.83 – 1.73 (m, 2H), 1.61 (m, 2H), 1.50 (m, 2H), 1.24 (s, 12H), 1.06 (m, 2H), 0.84 (d, J = 7.4 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 82.8, 36.1, 35.1, 25.1, 24.8. The signal of the α-B-carbon was not observed.

All data matched that reported in the literature¹².



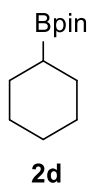
2-(2-cyclohexylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2c)

96.6 mg, 81% isolated yield, colorless oil. 6.0 equiv TBAF (1M in THF) was added. Rf = 0.6 (PE/ EtOAc = 20:1), using PE/ EtOAc = 50:1 as eluent.

¹H NMR (400 MHz, CDCl₃) δ 1.68 (m, 5H), 1.31 (m, 2H), 1.24 (s, 12H), 1.22 – 1.09 (m, 4H), 0.85 (m, 2H), 0.79 – 0.71 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 82.8, 40.0, 33.0, 31.4, 26.8, 26.5, 24.8. The signal of the α-B-carbon was not observed.

All data matched that reported in the literature¹.



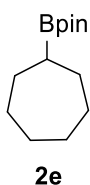
2-cyclohexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2d)

75.8 mg, 72% isolated yield, colorless oil. 3.0 equiv TBAF (1M in THF) was added. Rf = 0.6 (PE/ EtOAc = 20:1), using PE/ EtOAc = 50:1-30:1 as eluent.

¹H NMR (400 MHz, CDCl₃) δ 1.59 (m, 5H), 1.30 (m, 6H), 1.23 (s, 12H).

¹³C NMR (101 MHz, CDCl₃) δ 82.7, 28.0, 27.2, 26.8, 24.8. The signal of the α-B-carbon was not observed.

All data matched that reported in the literature¹.



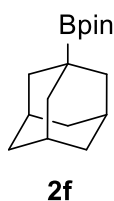
2-cycloheptyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2e)

73.6 mg, 66% isolated yield, colorless oil. 9.0 equiv TBAF (1M in THF) was added. Rf = 0.45 (PE), using PE/ EtOAc = 50:1-30:1 as eluent.

¹H NMR (400 MHz, CDCl₃) δ 1.70 (m, 4H), 1.62 – 1.36 (m, 8H), 1.24 (s, 12H), 1.13 – 1.02 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 82.8, 29.6, 29.0, 28.3, 24.7. The signal of the α-B-carbon was not observed.

All data matched that reported in the literature¹².



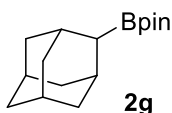
2-(adamantan-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2f)

80.8 mg, 62% isolated yield, white solid. 3.0 equiv TBAF (1M in THF) was added. Rf = 0.5 (PE/ EtOAc = 20:1), using PE/ EtOAc = 40:1-30:1 as eluent.

¹H NMR (400 MHz, CDCl₃) δ 1.85 (s, 3H), 1.75 (m, 12H), 1.21 (s, 12H).

¹³C NMR (101 MHz, CDCl₃) δ 82.6, 38.0, 37.5, 27.6, 24.7. The signal of the α-B-carbon was not observed.

All data matched that reported in the literature¹³.



2-(adamantan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2g)

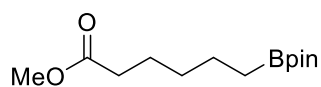
71.8 mg, 55% isolated yield, white solid. 3.0 equiv TBAF (1M in THF) was added. Rf = 0.5 (PE/EtOAc = 20:1), using PE/ EtOAc = 1-99:1 as eluent.

¹H NMR (400 MHz, CDCl₃) δ 2.05 (s, 2H), 1.90 – 1.66 (m, 12H), 1.37 (s, 1H), 1.25 (s, 12H).

¹³C NMR (101 MHz, CDCl₃) δ 82.8, 64.4, 53.4, 39.3, 37.7, 36.3, 29.3, 28.2, 28.1, 25.4, 24.8.

The signal of the α-B-carbon was not observed.

All data matched that reported in the literature¹².



2h

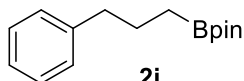
methyl 6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanoate (2h)

55.2 mg, 43% isolated yield, white solid. 4.0 equiv TBAF (1M in THF) was added. Rf = 0.4 (PE), using PE/ EtOAc = 50:1-30:1 as eluent.

¹H NMR (400 MHz, CDCl₃) δ 3.66 (s, 3H), 2.30 (t, J = 7.6 Hz, 2H), 1.67 – 1.58 (m, 2H), 1.47 – 1.38 (m, 2H), 1.35 – 1.29 (m, 2H), 1.24 (s, 12H), 0.77 (t, J = 7.7 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 172.6, 81.2, 49.7, 32.3, 30.1, 23.1, 23.0, 21.9. The signal of the α-B-carbon was not observed.

All data matched that reported in the literature¹⁴.



2i

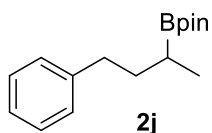
4,4,5,5-tetramethyl-2-(3-phenylpropyl)-1,3,2-dioxaborolane (2i)

53.0 mg, 43% isolated yield, colorless oil. 0.5 equiv TBAF (1M in THF) was added. Rf = 0.5 (PE/ EtOAc = 20:1), using PE/ EtOAc = 50:1-30:1 as eluent.

¹H NMR (400 MHz, CDCl₃) δ 7.24 (m, 2H), 7.17 (d, J = 7.6 Hz, 3H), 2.64 – 2.57 (m, 2H), 1.73 (p, J = 7.9 Hz, 2H), 1.24 (s, 12H), 0.83 (t, J = 7.9 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 142.7, 128.6, 128.2, 125.6, 83.0, 38.6, 26.1, 24.9. The signal of the α-B-carbon was not observed.

All data matched that reported in the literature¹.



4,4,5,5-tetramethyl-2-(4-phenylbutan-2-yl)-1,3,2-dioxaborolane (2j)

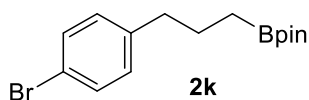
113 mg, 87 % isolated yield, colorless oil. R_f = 0.6 (PE/ EtOAc = 20:1), using toluene as eluent.

¹H NMR (400 MHz, CDCl₃) δ 7.31 – 7.11 (m, 5H), 2.78 – 2.46 (m, 2H), 1.89 – 1.56 (m, 2H), 1.25 (s, 12H), 1.15 – 0.94 (m, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 143.1, 128.5, 128.2, 125.5, 82.9, 35.4, 35.3, 24.8, 24.8, 15.5.

The signal of the α-B-carbon was not observed.

All data matched that reported in the literature¹⁵.



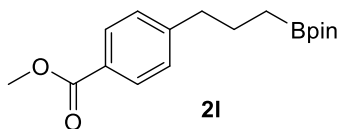
2-(3-(4-bromophenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2k)

50.2 mg, 31% isolated yield, colorless oil. R_f = 0.6 (PE/ EtOAc = 10:1), using PE/ EtOAc = 50:1-30:1 as eluent.

¹H NMR (400 MHz, CDCl₃) δ 7.41 – 7.32 (m, 2H), 7.08 – 6.99 (m, 2H), 2.59 – 2.49 (m, 2H), 1.75 – 1.64 (m, 2H), 1.24 (s, 12H), 0.80 (t, *J* = 7.9 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 141.6, 131.2, 130.4, 119.97, 84.6, 37.5, 25.9, 24.1. The signal of the α-B-carbon was not observed.

All data matched that reported in the literature¹.



methyl 4-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)benzoate (2l)

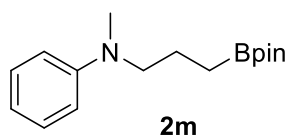
90.1 mg, 59% isolated yield, colorless oil. R_f = 0.3 (PE/ EtOAc = 10:1), using PE/ EtOAc = 30:1-20:1 as eluent.

¹H NMR (400 MHz, CDCl₃) δ 7.87 – 7.72 (m, 2H), 7.16 – 7.03 (m, 2H), 3.77 (s, 3H), 2.53 (dd, *J* = 8.8, 6.7 Hz, 2H), 1.61 (p, *J* = 7.7 Hz, 2H), 1.12 (s, 12H), 0.69 (t, *J* = 7.9 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 167.3, 148.3, 129.6, 128.6, 83.0, 52.0, 38.6, 25.7, 24.8. The signal of the α-B-carbon was not observed.

IR: ν = 3480, 2978, 2935, 2866, 1931, 1723, 1610, 1574, 1510, 1435, 1413, 1372, 1317, 1278, 1229, 1144, 1110, 1004, 968, 848, 762, 705, 674, 610, 525, 486 cm⁻¹.

HRMS (ESI) (*m/z*): Calcd. C₁₇H₂₆BO₄⁺ [M+H]⁺: 305.1919. Found: 305.1912.



N-methyl-N-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)aniline (2m)

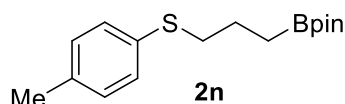
47.6 mg, 50% isolated yield, yellow oil. R_f = 0.6 (PE/ EtOAc = 20:1), using PE/ EtOAc = 100:1-30:1 as eluent.

¹H NMR (400 MHz, CDCl₃) δ 7.24 – 7.17 (m, 2H), 6.74 – 6.68 (m, 2H), 6.65 (tt, *J* = 7.2, 1.1 Hz, 1H), 3.32 – 3.24 (m, 2H), 2.97 – 2.90 (m, 3H), 1.71 – 1.64 (m, 2H), 1.25 (s, 12H), 0.78 (t, *J* = 7.8 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 149.4, 129.1, 115.7, 112.0, 83.1, 54.9, 38.3, 24.9, 21.1. The signal of the α-B-carbon was not observed.

IR: ν = 2975, 2933, 2880, 1600, 1506, 1462, 1410, 1369, 1321, 1291, 1273, 1258, 1242, 1217, 1188, 1169, 1163, 1143, 1098, 1082, 1065, 1034, 990, 963, 842, 747, 691 cm⁻¹.

HRMS (ESI) (m/z): Calcd. C₁₆H₂₇BNO₂⁺ [M+H]⁺: 276.2129. Found: 276.2129.



4,4,5,5-tetramethyl-2-(3-(p-tolylthio)propyl)-1,3,2-dioxaborolane (2n)

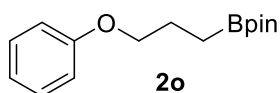
109.6 mg, 75% isolated yield, yellow oil. 5.0 equiv TBAF (1M in THF) was added. R_f = 0.4 (PE/ EtOAc = 20:1), using PE/ EtOAc = 100:1-50:1 as eluent.

¹H NMR (400 MHz, CDCl₃) δ 7.26 – 7.22 (m, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 2.92 – 2.85 (m, 2H), 2.31 (s, 3H), 1.79 – 1.70 (m, 2H), 1.24 (s, 12H), 0.90 (t, *J* = 7.8 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 135.6, 133.2, 129.6, 129.5, 83.1, 36.3, 24.8, 24.0, 21.0. The signal of the α-B-carbon was not observed.

IR: ν = 2978, 2934, 2924, 2857, 2852, 1728, 1493, 1454, 1407, 1372, 1320, 1273, 1222, 1172, 1164, 1143, 1105, 969, 845, 804 cm⁻¹.

HRMS (ESI) (m/z): Calcd. C₁₆H₂₆BO₂S⁺ [M+H]⁺: 293.1741. Found: 293.1740.



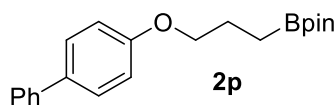
4,4,5,5-tetramethyl-2-(3-phenoxypropyl)-1,3,2-dioxaborolane (2o)

79.5 mg, 61 % isolated yield, colorless oil. 3.0 equiv TBAF (1M in THF) was added. R_f = 0.5 (PE/ EtOAc = 20:1), using PE/ EtOAc = 50:1-30:1 as eluent.

¹H NMR (400 MHz, CDCl₃) δ 7.30 – 7.26 (m, 2H), 7.04 – 6.78 (m, 3H), 3.96 (t, *J* = 6.7 Hz, 2H), 2.05 – 1.80 (m, 2H), 1.28 (s, 12H), 0.95 (t, *J* = 7.9 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 159.2, 129.4, 120.4, 114.6, 83.1, 69.5, 24.9, 23.8. The signal of the α-B-carbon was not observed.

All data matched that reported in the literature⁸.



2-(3-([1,1'-biphenyl]-4-yloxy)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2p)

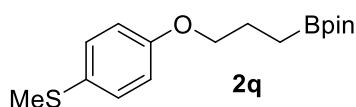
91.0 mg, 87 % isolated yield, colorless oil. R_f = 0.5 (PE/ EtOAc = 10:1), using PE/ EtOAc = 50:1 as eluent.

¹H NMR (400 MHz, CDCl₃) δ 7.58 – 7.46 (m, 4H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.30 (d, *J* = 7.3 Hz, 1H), 6.97 (d, *J* = 8.5 Hz, 2H), 3.98 (t, *J* = 6.7 Hz, 2H), 1.92 (p, *J* = 7.2 Hz, 2H), 1.26 (s, 12H), 0.94 (t, *J* = 7.8 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 157.3, 139.4, 132.0, 127.2, 126.6, 125.2, 125.0, 113.4, 81.6, 68.2, 23.3, 22.3. The signal of the α-B-carbon was not observed.

IR: ν = 2978, 2943, 1609, 1519, 1466, 1373, 1320, 1287, 1269, 1243, 1176, 1142, 1077, 1049, 846, 836, 760, 730, 696, 655, 628, 595, 593, 464, 348 cm⁻¹.

HRMS (ESI) (m/z): Calcd. C₂₁H₂₆BO₃⁺ [M+H]⁺: 339.2126. Found: 339.2118.



4,4,5,5-tetramethyl-2-(3-(4-(methylthio)phenoxy)propyl)-1,3,2-dioxaborolane (2q)

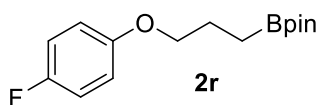
101.4 mg, 66 % isolated yield, colorless oil. R_f = 0.5 (PE/ EtOAc = 10:1), using PE/ EtOAc = 50:1-40:1 as eluent.

¹H NMR (400 MHz, CDCl₃) δ 7.33 – 7.17 (m, 2H), 6.89 – 6.74 (m, 2H), 3.91 (t, *J* = 6.7 Hz, 2H), 2.43 (s, 3H), 1.88 (ddd, *J* = 14.6, 7.9, 6.7 Hz, 2H), 1.25 (s, 12H), 0.91 (t, *J* = 7.8 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 157.8, 130.3, 128.3, 115.3, 83.1, 69.8, 24.9, 23.7, 18.2. The signal of the α-B-carbon was not observed.

IR: ν = 2980, 2945, 2923, 1493, 1429, 1372, 1319, 1277, 1239, 1159, 1143, 1052, 1015, 967, 967, 853, 835 cm⁻¹.

HRMS (ESI) (m/z): Calcd. C₁₆H₂₆BO₃S⁺ [M+H]⁺: 309.1690. Found: 309.1685.



2-(3-(4-fluorophenoxy)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2r)

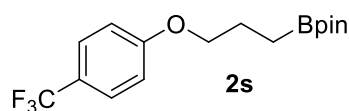
84.2 mg, 60% isolated yield, colorless oil. R_f = 0.3 (PE/ EtOAc = 20:1), using PE/ EtOAc = 50:1-40:1 as eluent.

¹H NMR (400 MHz, CDCl₃) δ 7.00 – 6.90 (m, 2H), 6.86 – 6.77 (m, 2H), 3.89 (t, *J* = 6.7 Hz, 2H), 1.88 (p, *J* = 6.9 Hz, 2H), 1.25 (s, 12H), 0.91 (t, *J* = 7.8 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 158.3, 155.3, 115.8, 115.6, 115.5, 83.1, 70.3, 24.8, 23.8. The signal of the α-B-carbon was not observed.

IR: $\nu = 2948, 1505, 1373, 1321, 1248, 1210, 1143, 1096, 1088, 1042, 837, 825, 755 \text{ cm}^{-1}$.

HRMS (ESI) (m/z): Calcd. $\text{C}_{15}\text{H}_{23}\text{BF}_3\text{O}_3^+$ [M+H]⁺: 281.1719. Found: 281.1725.



4,4,5,5-tetramethyl-2-(3-(4-(trifluoromethyl)phenoxy)propyl)-1,3,2-dioxaborolane (2s)

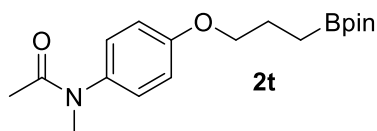
115.1 mg, 70% isolated yield, yellow oil. R_f = 0.6 (PE/ EtOAc = 10:1), using PE/ EtOAc = 40:1-30:1 as eluent.

¹H NMR (400 MHz, CDCl₃) δ 7.52 (d, J = 8.5 Hz, 2H), 6.95 (d, J = 8.4 Hz, 2H), 3.98 (t, J = 6.7 Hz, 2H), 1.91 (p, J = 7.2 Hz, 2H), 1.25 (s, 12H), 0.92 (t, J = 7.8 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 161.6, 126.8, 126.8, 114.5, 83.2, 69.8, 24.9, 23.6. The signal of the α -B-carbon was not observed.

IR: $\nu = 2958, 2924, 2915, 2854, 2115, 1616, 1374, 1327, 1303, 1252, 1168, 1158, 1143, 1105, 1065, 1044, 1024, 1008, 966, 841, 807, 753, 746 \text{ cm}^{-1}$.

HRMS (ESI) (m/z): Calcd. $\text{C}_{16}\text{H}_{23}\text{BF}_3\text{O}_3^+$ [M+H]⁺: 331.1687. Found: 331.1679.



N-methyl-N-(4-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propoxy)phenyl)acetamide (2t)

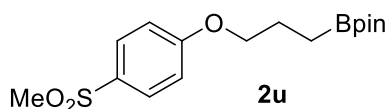
145.7 mg, 87% isolated yield, yellow oil. R_f = 0.3 (PE/ EtOAc = 10:1), using PE/ EtOAc = 30:1 as eluent.

¹H NMR (400 MHz, CDCl₃) δ 7.17 – 6.97 (m, 2H), 6.94 – 6.75 (m, 2H), 3.92 (t, J = 6.7 Hz, 2H), 3.20 (s, 3H), 1.94 – 1.85 (m, 2H), 1.82 (s, 3H), 1.22 (s, 12H), 0.90 (t, J = 7.8 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 171.1, 158.5, 137.2, 128.0, 115.4, 83.2, 69.9, 37.3, 24.8, 23.7, 22.3. The signal of the α -B-carbon was not observed.

IR: $\nu = 2980, 2934, 1643, 1595, 1568, 1511, 1488, 1470, 1434, 1432, 1424, 1372, 1342, 1319, 1297, 1277, 1241, 1193, 1165, 1141, 1107, 1079, 1057, 1030, 1011, 971, 949 \text{ cm}^{-1}$.

HRMS (ESI) (m/z): Calcd. $\text{C}_{18}\text{H}_{29}\text{BNO}_4^+$ [M+H]⁺: 334.2184. Found: 334.2190.



4,4,5,5-tetramethyl-2-(3-(4-(methylsulfonyl)phenoxy)propyl)-1,3,2-dioxaborolane (2u)

118.7 mg, 70% isolated yield, colorless oil. R_f = 0.5 (PE/ EtOAc = 3:2), using PE/ EtOAc = 5:1 as eluent.

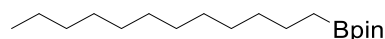
¹H NMR (400 MHz, CDCl₃) δ 7.91 – 7.79 (m, 2H), 7.06 – 6.90 (m, 2H), 4.02 (t, J = 6.7 Hz, 2H), 3.03 (s, 3H), 1.94 – 1.88 (m, 2H), 1.24 (s, 12H), 0.93 (t, J = 7.8 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 163.4, 131.8, 129.5, 115.0, 83.2, 70.1, 44.9, 24.9, 23.4. The

signal of the α -B-carbon was not observed.

IR: $\nu = 2957, 1594, 1373, 1314, 1294, 1255, 1140, 796, 724, 690, 658, 611, 570, 489, 473, 436, 428, 403 \text{ cm}^{-1}$.

HRMS (ESI) (m/z): Calcd. $\text{C}_{16}\text{H}_{29}\text{BNO}_5\text{S}^+ [\text{M}+\text{NH}_4]^+$: 358.1854. Found: 358.1844. Calcd. $\text{C}_{16}\text{H}_{25}\text{BNaO}_5\text{S}^+ [\text{M}+\text{Na}]^+$: 363.1407. Found: 363.1406.



2v

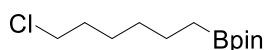
2-dodecyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2v)

99.9 mg, 67% isolated yield, colorless oil. $R_f = 0.5$ (PE/ EtOAc = 20:1), using PE/ EtOAc = 50:1-30:1 as eluent.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 1.40 (t, $J = 7.5 \text{ Hz}$, 2H), 1.25 – 1.24 (m, 30H), 0.88 (t, $J = 6.8 \text{ Hz}$, 3H), 0.76 (t, $J = 7.7 \text{ Hz}$, 2H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 82.8, 32.4, 31.9, 29.7, 29.7, 29.6, 29.4, 29.4, 24.8, 24.0, 22.7, 14.1. The signal of the α -B-carbon was not observed.

All data matched that reported in the literature¹.



2w

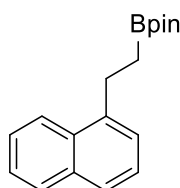
2-(6-chlorohexyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2w)

76.1 mg, 65% isolated yield, colorless oil. $R_f = 0.5$ (PE/ EtOAc = 20:1), using PE/ EtOAc = 50:1-30:1 as eluent.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 3.52 (t, $J = 6.8 \text{ Hz}$, 2H), 1.81 – 1.71 (m, 2H), 1.46 – 1.38 (m, 4H), 1.33 (dd, $J = 8.7, 5.3 \text{ Hz}$, 2H), 1.24 (s, 12H), 0.77 (t, $J = 7.7 \text{ Hz}$, 2H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 82.9, 45.2, 32.6, 31.6, 26.7, 24.8, 23.8. The signal of the α -B-carbon was not observed.

All data matched that reported in the literature¹.



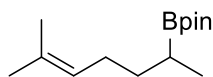
2x

4,4,5,5-tetramethyl-2-(2-(naphthalen-1-yl)ethyl)-1,3,2-dioxaborolane (2x)

93.8 mg, 66% isolated yield, colorless oil. $R_f = 0.5$ (PE/ EtOAc = 20:1), the product is not stable in silica gel, purified by using PE/ EtOAc = 50:1 (with 5% Et_3N) as eluent quickly.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.13 – 8.06 (m, 1H), 7.84 (dd, $J = 8.1, 1.5 \text{ Hz}$, 1H), 7.69 (dt, $J = 6.5, 3.5 \text{ Hz}$, 1H), 7.53 – 7.43 (m, 2H), 7.41 – 7.35 (m, 2H), 3.28 – 3.11 (m, 2H), 1.32 – 1.27 (m, 2H), 1.25 (s, 12H).

¹³C NMR (101 MHz, CDCl₃) δ 140.5, 133.8, 131.8, 128.7, 126.3, 125.6, 125.6, 125.3, 125.0, 124.0, 83.2, 27.0, 24.9. The signal of the α-B-carbon was not observed.
All data matched that reported in the literature¹⁶.



2y

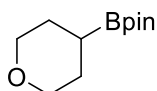
4,4,5,5-tetramethyl-2-(6-methylhept-5-en-2-yl)-1,3,2-dioxaborolane (2y)

90.7 mg, 76% isolated yield, colorless oil. R_f = 0.6 (PE/ EtOAc = 10:1), using PE/ EtOAc = 40:1-30:1 as eluent.

¹H NMR (400 MHz, CDCl₃) δ 5.12 (tdd, J = 7.2, 2.7, 1.3 Hz, 1H), 1.98 (q, J = 7.7 Hz, 2H), 1.67 (d, J = 1.4 Hz, 3H), 1.49 (dt, J = 13.0, 7.6 Hz, 1H), 1.34 – 1.28 (m, 1H), 1.23 (s, 12H), 1.09 – 0.92 (m, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 131.1, 125.0, 82.8, 33.4, 27.5, 25.7, 24.8, 24.7, 17.6, 15.5. The signal of the α-B-carbon was not observed.

All data matched that reported in the literature¹⁵.



2z

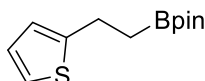
4,4,5,5-tetramethyl-2-(tetrahydro-2H-pyran-4-yl)-1,3,2-dioxaborolane (2z)

68.0 mg, 32% isolated yield, colorless oil. R_f = 0.5 (PE/ EtOAc = 10:1), using PE/ EtOAc = 40:1-30:1 as eluent.

¹H NMR (400 MHz, CDCl₃) δ 3.83 (dt, J = 11.2, 4.0 Hz, 2H), 3.47 (ddd, J = 11.2, 7.1, 5.5 Hz, 2H), 1.67 – 1.52 (m, 4H), 1.24 (s, 13H).

¹³C NMR (101 MHz, CDCl₃) δ 83.1, 68.8, 27.6, 24.8. The signal of the α-B-carbon was not observed.

All data matched that reported in the literature¹.



2aa

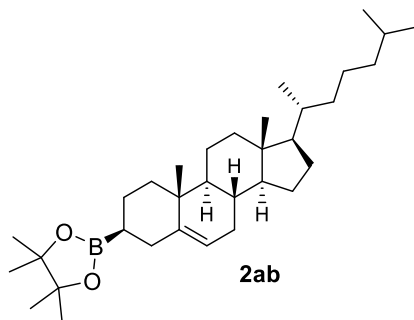
4,4,5,5-tetramethyl-2-(2-(thiophen-2-yl)ethyl)-1,3,2-dioxaborolane (2aa)

90.3 mg, 76% isolated yield, colorless oil. 0.4 equiv TBAF (1M in THF) was added. R_f = 0.6 (PE/ EtOAc = 20:1), using PE/ EtOAc = 10:1 as eluent.

¹H NMR (400 MHz, CDCl₃) δ 7.08 (d, J = 5.2 Hz, 1H), 6.89 (dd, J = 5.1, 3.3 Hz, 1H), 6.80 (d, J = 3.5 Hz, 1H), 2.96 (t, J = 8.0 Hz, 2H), 1.23 (d, J = 1.5 Hz, 15H).

¹³C NMR (101 MHz, CDCl₃) δ 147.8, 126.6, 123.4, 122.6, 83.2, 24.8, 24.4. The signal of the α-B-carbon was not observed.

All data matched that reported in the literature¹⁶.



2-((3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2ab)

146.2 mg, 59% isolated yield, white solid. R_f = 0.6 (PE/ EtOAc = 20:1), using PE/ EtOAc = 50:1 as eluent.

¹H NMR (400 MHz, CDCl₃) δ 5.40 – 5.22 (m, 1H), 2.20 (t, J = 14.3 Hz, 1H), 2.12 – 0.76 (m, 52H), 0.67 (s, 3H).

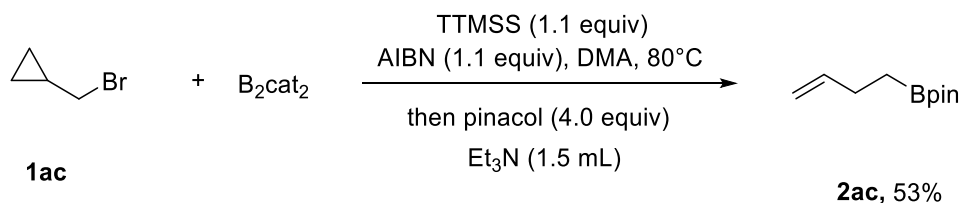
¹³C NMR (101 MHz, CDCl₃) δ 118.7, 83.0, 57.0, 56.3, 50.7, 42.5, 41.1, 40.0, 39.7, 37.5, 36.4, 36.0, 34.0, 32.1, 32.0, 28.4, 28.2, 24.9, 24.9, 24.5, 24.2, 24.0, 23.0, 22.7, 20.9, 19.7, 18.9, 12.0. The signal of the α-B-carbon was not observed.

All data matched that reported in the literature¹¹.

5. Mechanistic studies

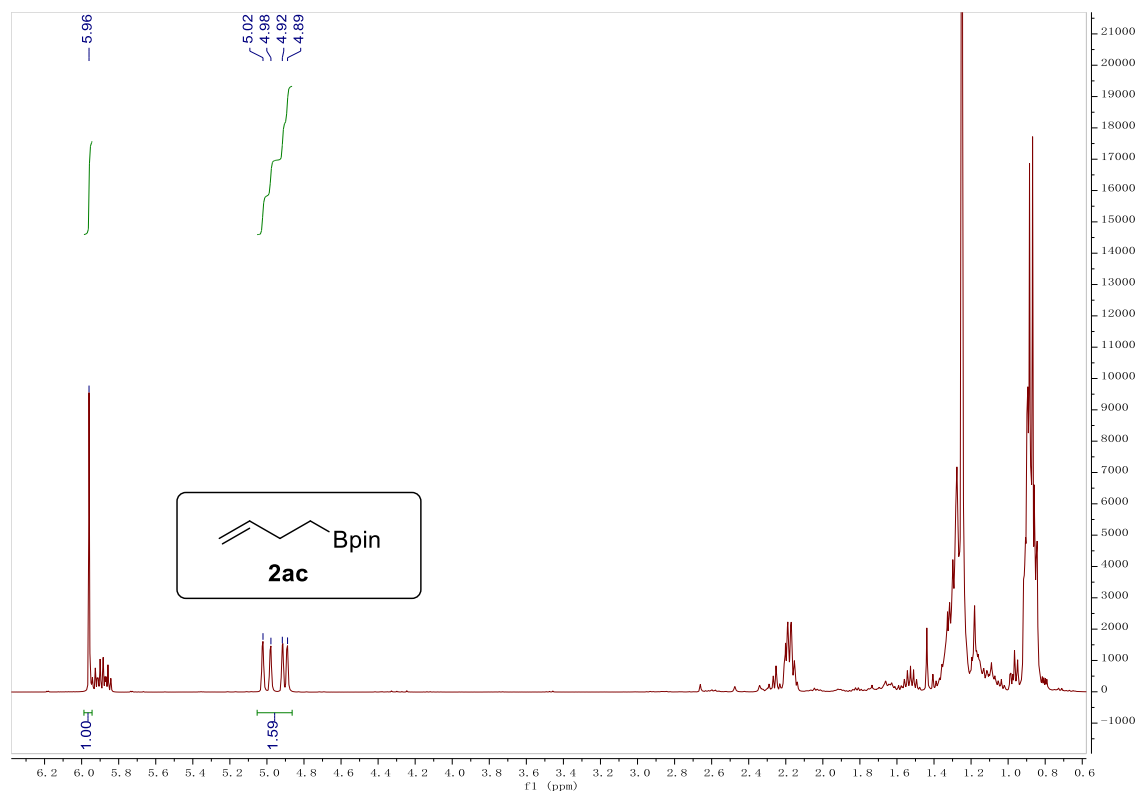
5.1 Radical clock reaction

(1)

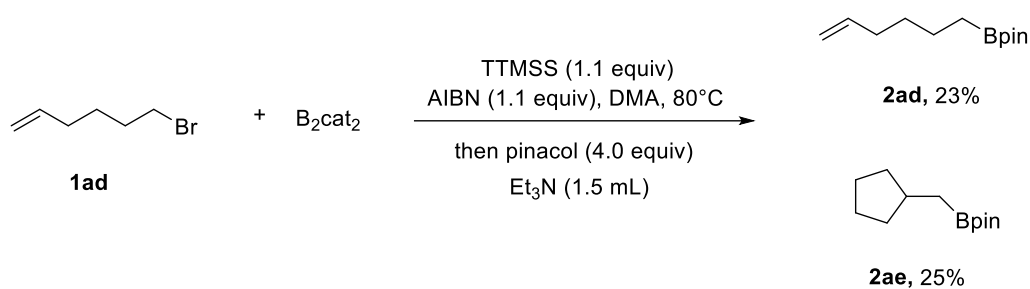


The reaction was carried out according to **General procedure for alkyl bromides** using (bromomethyl)cyclopropane **1ac** (0.5 mmol) as substrate. Water was added to the reaction mixture and the aqueous layer was extracted with EtOAc (3x). If phase separation was slow, brine was added. The organic phases were combined and washed with 100 mL of saturated brine, the organic phase was dried over anhydrous sodium sulfate and filtered, and then concentrated under reduced pressure, then added 1,1,2,2-tetrachloroethane (28.0 mg) as an internal standard, and $CDCl_3$ (5 mL) was added to the mixture, the yield of compound was tested by 1H NMR (400 MHz) according to the ratio of the area of the signals δ 4.89 (d, 1H, terminal) and δ 4.98 (d, 1H, terminal)¹⁷ with the signal of $C_2H_2Cl_4$ (28.0 mg added, signal in δ 5.96, 2H).

2ac: $1.59 \times 28.0 / 167.84 / 0.5 = 53\%$ (NMR yield).



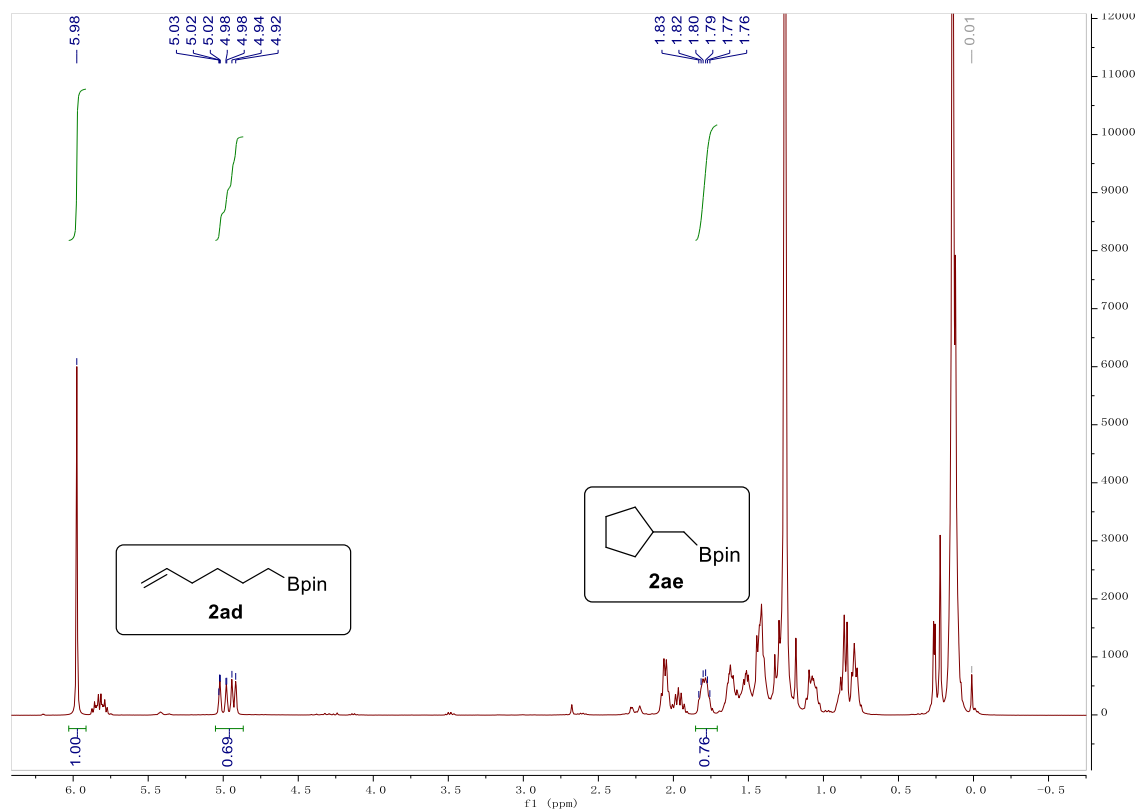
(2)



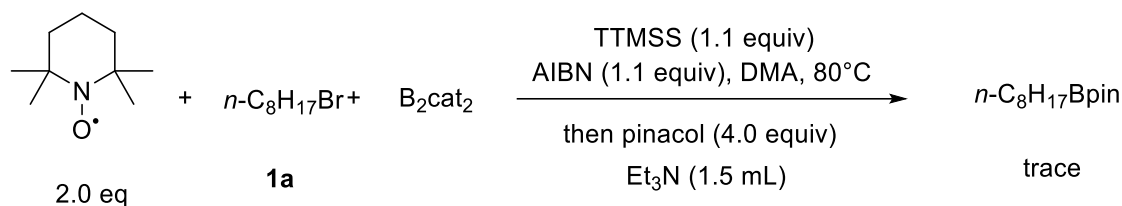
The reaction was carried out according to **General procedure for alkyl bromides** using 6-bromo-1-hexene **1ad** (0.5 mmol) as substrate. Water was added to the reaction mixture and the aqueous layer was extracted with EtOAc (3x). If phase separation was slow, brine was added. The organic phases were combined and washed with 100 mL of saturated brine, the organic phase was dried over anhydrous sodium sulfate and filtered, and then concentrated under reduced pressure, added 1,1,2,2-tetrachloroethane (27.5 mg) as an internal standard, and $CDCl_3$ (5 mL) was added to the mixture, then the yield of compound was tested by 1H NMR (400 MHz) according to the ratio of the area of the signals δ 4.92-5.03 (m, 2H, terminal) and δ 1.76-2.03 (tt, 2H, CH_2 connect to Boron atom)¹⁵ with the signal of $C_2H_2Cl_4$ (27.5 mg added, signal in δ 5.96, 2H).

2ad: $0.69 \times 27.5 / 167.84 / 0.5 = 23\%$ (NMR yield);

2ae: $0.76 \times 27.5 / 167.84 / 0.5 = 25\%$ (NMR yield).



5.2 Reaction with TEMPO



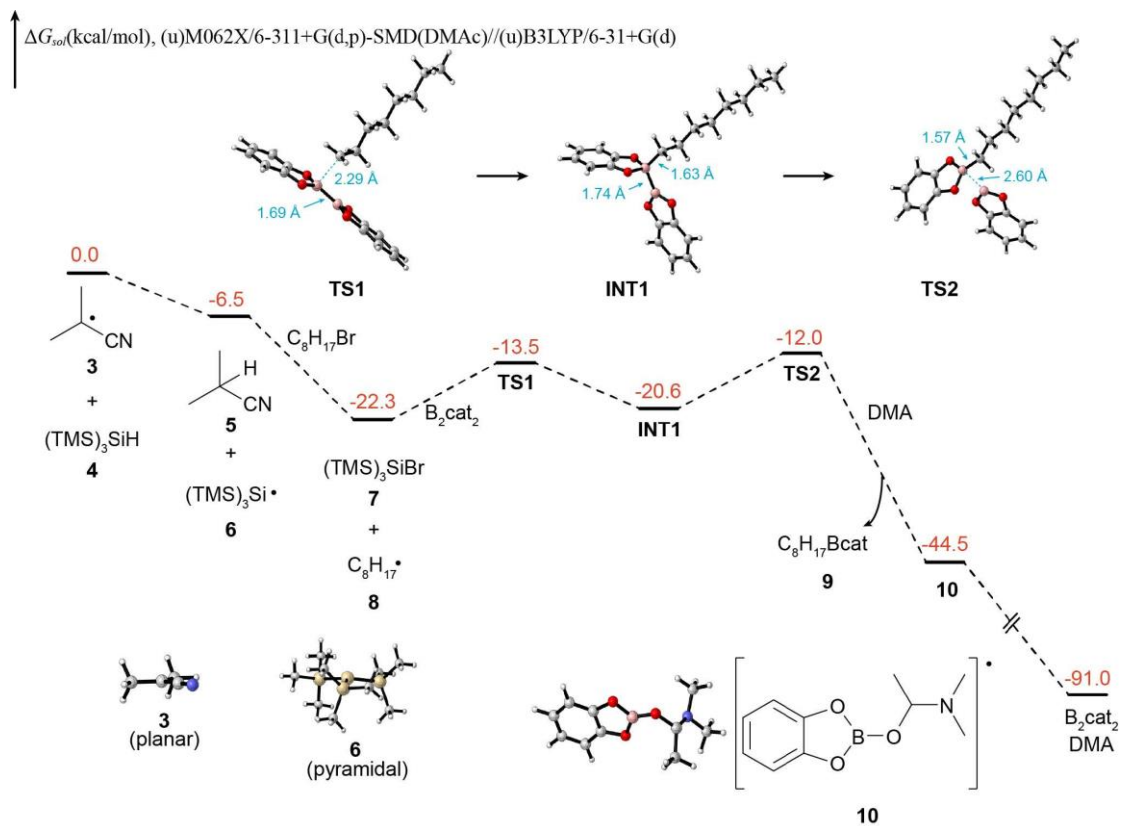
In a glovebox under nitrogen atmosphere, sequentially added B_2cat_2 (0.75 mmol, 1.5 equiv, 178 mg), AIBN (0.55 mmol, 1.1 equiv, 90 mg), 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, 1.0 mmol, 2.0 equiv, 156 mg) and 3 mL DMA to a 10 mL Schlenk tube with a stir bar, followed by TTMSS (0.55 mmol, 1.1 equiv, 170 μL) and alkyl bromide (0.5 mmol). The capped Schlenk tube was removed from the glovebox, and the reaction mixture was stirred at 80°C for 6 hours. After cooling to room temperature, pinacol (236 mg, 4.0 equiv) and 1.5 mL triethylamine were added, and the mixture was stirred at room temperature for 1 hour. Then the reaction mixture was tested by GC-MS using ethyl acetate as solvent, it showed that only trace product was formed.

6. DFT computational data

All density functional theory (DFT) calculations were performed with Gaussian 09w and supported by National Supercomputing Center in Shenzhen. All geometry optimizations and vibrational frequency analysis were computed at the B3LYP (or uB3LYP for open shell systems) level of theory with 6-31+G(d) basis set. Based on the gas phase optimized structures, the single point (SP) energies were calculated with the M062X (or uM062X for open shell systems) functional and a basis set of 6-311+G(d,p), and solvent energy corrections were calculated using the SMD model with DMA as the solvent.


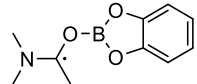
6.1 Table of energies and lowest frequencies

Figure 1 Gibbs free energy profiles for C-B bond formation via radical pathway

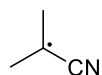


In **Table 2**, the energies are in unit of Hartree (1 Hartree = 627.5 kcal/mol = 2625 kJ/mol), and the lowest frequencies are in unit of cm^{-1} . A 'negative frequency' means imaginary frequency, e.g. -173.53 means $173.53i \text{ cm}^{-1}$.

Table 2 Energies and lowest frequencies

Structures	SP energy	TCG	G	G in kcal/mol	Lowest frequency
	-210.6992963	0.057569	-210.6417273	-132179.7903	75.56
(TMS) ₃ SiH	-1517.75729	0.289596	-1517.467694	-952226.1528	14.47
iPrCN	-211.350263	0.074116	-211.276147	-132577.895	187.40
(TMS) ₃ Si [•]	-1517.1248	0.281236	-1516.843564	-951834.5046	23.76
C ₈ H ₁₇ Br	-2889.204582	0.199184	-2889.005398	-1812879.777	44.03
(TMS) ₃ Br	-4091.397098	0.282362	-4091.114736	-2567215.408	36.78
C ₈ H ₁₇ [•]	-314.9527579	0.193362	-314.7593959	-197514.6685	53.42
B ₂ cat ₂	-812.8026806	0.146077	-812.6566036	-509950.1453	22.80
INT1	-1127.775414	0.362219	-1127.413195	-707463.0542	11.55
DMA	-287.7914783	0.097299	-287.6941793	-180530.9744	17.56
C ₈ H ₁₇ Bcat	-721.4421258	0.282104	-721.1600218	-452535.1253	17.19
	-694.1673684	0.181922	-693.9854464	-435482.8075	15.54
TS1	-1127.763086	0.361173	-1127.401913	-707455.9743	-150.38
TS2	-1127.760349	0.360827	-1127.399522	-707454.4739	-92.72

6.2 Cartesian coordinates of the structures



0 2

C	0.30954400	-0.00001500	-0.00003100
C	1.06586900	-1.29782300	0.00000300
H	0.39961200	-2.16410700	-0.00038400
H	1.72041300	-1.36367200	-0.88182200
H	1.71982800	-1.36400500	0.88223400
C	1.06546600	1.29803900	-0.00000100
H	1.72021600	1.36397400	-0.88166400
H	0.39893600	2.16411400	-0.00067100
H	1.71918600	1.36457000	0.88238600
C	-1.08320100	-0.00025700	0.00002300
N	-2.26060900	-0.00007800	-0.00000600

(TMS)₃SiH

0 1

Si	-0.00041500	0.00055200	0.66846300
H	-0.00122300	0.00086500	2.17289600
Si	1.03062800	2.04426300	0.02824200
Si	-2.28681400	-0.12938500	0.02863500
Si	1.25515500	-1.91425300	0.02841000
C	-0.13738700	3.52079300	0.30977400
H	0.37530100	4.46073400	0.06320700
H	-1.03505400	3.46018800	-0.31758600
H	-0.46382100	3.58516700	1.35491900
C	2.59860000	2.33308500	1.06678600
H	3.33565300	1.53307100	0.92948900
H	3.07704000	3.28027000	0.78203100
H	2.36304700	2.38781200	2.13679500
C	1.51486800	2.01283700	-1.81282000
H	0.64635600	1.84237600	-2.46082400
H	1.96323200	2.97191500	-2.10561500
H	2.24931900	1.22688900	-2.02781600
C	-3.31821300	1.08064600	1.07278100
H	-2.98757800	2.11780500	0.94211500
H	-4.37751400	1.02825700	0.78606800
H	-3.25007900	0.84265800	2.14144400
C	-2.50694000	0.30813700	-1.81133100
H	-3.56065500	0.20447500	-2.10388200
H	-2.20718000	1.34153900	-2.02532700
H	-1.91741100	-0.35042200	-2.46117700

C	-2.97676200	-1.88174600	0.30758300
H	-2.86400800	-2.19970100	1.35126300
H	-4.04814800	-1.90982000	0.06591700
H	-2.47642500	-2.62573100	-0.32425800
C	0.99642800	-2.31127600	-1.81547700
H	1.59482300	-3.18624300	-2.10342900
H	-0.05262500	-2.54073200	-2.03982900
H	1.29948200	-1.47697800	-2.46013000
C	0.71435000	-3.41954600	1.05846300
H	1.30198700	-4.30485100	0.77892900
H	0.86632800	-3.24409300	2.13055800
H	-0.34439100	-3.66137900	0.90833000
C	3.11677300	-1.64441200	0.32221600
H	3.51852600	-0.83674200	-0.30147200
H	3.33060500	-1.39582000	1.36895000
H	3.67437100	-2.55910000	0.07808100

iPrCN

0 1

C	-0.35740100	-0.00002200	0.39993400
H	-0.44534900	-0.00002600	1.49526500
C	-1.02347100	-1.28061800	-0.14401500
H	-0.55342800	-2.17976900	0.26649200
H	-2.08376000	-1.28698500	0.13166300
H	-0.95069400	-1.32284300	-1.23613900
C	-1.02258600	1.28111000	-0.14392800
H	-2.08289400	1.28826100	0.13166900
H	-0.55192500	2.17990000	0.26666300
H	-0.94971900	1.32337400	-1.23604400
C	1.08422800	-0.00062100	0.09679300
N	2.21902100	-0.00014400	-0.15318200

(TMS)₃Si[•]

0 2

Si	0.00000000	0.00000000	0.31169600
Si	0.00000000	2.34475400	0.01882400
Si	-2.03061700	-1.17237700	0.01882400
Si	2.03061700	-1.17237700	0.01882400
C	-1.74694400	3.04594800	0.29332000
H	-1.73488800	4.13814800	0.17490200
H	-2.46871700	2.64419900	-0.42796400
H	-2.11947800	2.82547300	1.30075000

C	1.17381000	3.17181200	1.26739300
H	2.20933900	2.83553600	1.13929000
H	1.15973100	4.26277700	1.13661000
H	0.87827800	2.95494200	2.30103600
C	0.56462300	2.83000300	-1.73509400
H	-0.09918000	2.41515000	-2.50317500
H	0.56392600	3.92349100	-1.84607900
H	1.58068900	2.47588600	-1.94719100
C	-3.33377500	-0.56935600	1.26739300
H	-3.56031600	0.49557500	1.13929000
H	-4.27153900	-1.12703200	1.13661000
H	-2.99819400	-0.71686000	2.30103600
C	-2.73316600	-0.92602400	-1.73509400
H	-3.67980600	-1.47337200	-1.84607900
H	-2.93452500	0.13097400	-1.94719100
H	-2.04199100	-1.29346800	-2.50317500
C	-1.76439700	-3.03587200	0.29332000
H	-1.38719300	-3.24825800	1.30075000
H	-2.71629700	-3.57153100	0.17490200
H	-1.05558500	-3.46007100	-0.42796400
C	2.16854300	-1.90397900	-1.73509400
H	3.11588000	-2.45012000	-1.84607900
H	1.35383600	-2.60686000	-1.94719100
H	2.14117200	-1.12168200	-2.50317500
C	2.15996400	-2.60245500	1.26739300
H	3.11180800	-3.13574500	1.13661000
H	2.11991600	-2.23808300	2.30103600
H	1.35097700	-3.33111200	1.13929000
C	3.51134100	-0.01007600	0.29332000
H	3.52430200	0.81587200	-0.42796400
H	3.50667100	0.42278500	1.30075000
H	4.45118500	-0.56661700	0.17490200

C₈H₁₇Br

0 1

C	6.54608300	-0.52897000	-0.00000300
H	6.55630000	-1.17774200	0.88541000
H	7.47813600	0.04898800	0.00000200
H	6.55629900	-1.17772600	-0.88542800
C	5.31748300	0.38858200	0.00000600
H	5.35372500	1.04884100	0.87896900
H	5.35372500	1.04885600	-0.87894700
C	3.98914500	-0.37974700	-0.00000200

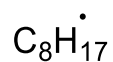
H	3.95461200	-1.04118500	0.87929500
H	3.95461700	-1.04117800	-0.87930400
C	2.75087000	0.52698500	-0.00000200
H	2.78366300	1.18765900	-0.87974600
H	2.78366600	1.18765800	0.87974200
C	1.43027400	-0.25369600	0.00000200
H	1.39971800	-0.91469700	0.87915700
H	1.39969400	-0.91466100	-0.87918000
C	0.18397200	0.64079500	0.00003700
H	0.20796700	1.30003400	-0.88040700
H	0.20794400	1.29994200	0.88055100
C	-1.12462000	-0.16913400	-0.00002900
H	-1.16016500	-0.82260800	0.88095800
H	-1.16011400	-0.82255700	-0.88105700
C	-2.32883500	0.75354100	-0.00003800
H	-2.36085400	1.38625100	-0.88894200
H	-2.36083600	1.38628400	0.88884500
Br	-4.04383800	-0.22435100	0.00000700

(TMS)₃SiBr

0 1

Si	0.00000000	0.00000000	0.04234400
Si	-0.86606000	2.13769000	-0.56114400
Si	-1.41826400	-1.81887500	-0.56114400
Si	2.28432400	-0.31881500	-0.56114400
C	-2.72640700	2.22246100	-0.21717300
H	-3.10397300	3.23095500	-0.41957500
H	-3.29633700	1.53092400	-0.84427600
H	-2.95634500	1.99091000	0.82646200
C	0.00000000	3.49030700	0.43834300
H	1.07409800	3.52989900	0.23872300
H	-0.41757100	4.47267700	0.19099500
H	-0.12809300	3.33763200	1.51314200
C	-0.56787000	2.43657700	-2.41133000
H	-1.02796100	1.66678800	-3.03750600
H	-0.99533600	3.39880400	-2.71429900
H	0.49792100	2.46606400	-2.65590600
C	-3.02269500	-1.74515300	0.43834300
H	-3.59403100	-0.83475300	0.23872300
H	-3.66466600	-2.59796600	0.19099500
H	-2.82642800	-1.77974800	1.51314200
C	-1.82620300	-1.71007800	-2.41133000
H	-2.44578300	-2.56138800	-2.71429900

H	-2.38463500	-0.80182000	-2.65590600
H	-0.92950000	-1.72363400	-3.03750600
C	-0.56150400	-3.47236800	-0.21717300
H	-0.24600600	-3.55572500	0.82646200
H	-1.24610300	-4.30359700	-0.41957500
H	0.32234900	-3.62017400	-0.84427600
C	2.39407300	-0.72649900	-2.41133000
H	3.44111900	-0.83741600	-2.71429900
H	1.88671400	-1.66424400	-2.65590600
H	1.95746100	0.05684600	-3.03750600
C	3.02269400	-1.74515400	0.43834300
H	4.08223700	-1.87471100	0.19099500
H	2.95452100	-1.55788400	1.51314200
H	2.51993300	-2.69514600	0.23872300
C	3.28791100	1.24990700	-0.21717300
H	2.97398800	2.08925000	-0.84427600
H	3.20235100	1.56481500	0.82646200
H	4.35007600	1.07264200	-0.41957500
Br	0.00000000	0.00000000	2.37442400



02

C	-4.42789900	0.26576700	-0.00000700
H	-4.49625100	0.91115100	0.88552400
H	-5.30484700	-0.39315500	-0.00001000
H	-4.49624500	0.91115300	-0.88553700
C	-3.12233000	-0.53857800	-0.00000200
H	-3.10020000	-1.19961300	0.87903400
H	-3.10019300	-1.19961000	-0.87903900
C	-1.86599700	0.34338800	0.00000500
H	-1.88902100	1.00536500	0.87955900
H	-1.88901400	1.00536800	-0.87954600
C	-0.55404100	-0.45365400	0.00000600
H	-0.53208000	-1.11536800	-0.87949200
H	-0.53208100	-1.11536600	0.87950700
C	0.70175700	0.42932500	0.00000500
H	0.68070100	1.09092700	0.87966300
H	0.68069700	1.09092900	-0.87965100
C	2.01137700	-0.37116600	0.00000100
H	2.04269200	-1.02981200	-0.87975400
H	2.04269700	-1.02981300	0.87975500
C	3.27428900	0.53209600	-0.00000200

H	3.22695800	1.18737800	0.88242000
H	3.22695300	1.18737900	-0.88242300
C	4.55719200	-0.23023500	-0.00000600
H	4.99657500	-0.58428800	-0.92861800
H	4.99657900	-0.58429000	0.92860400

B₂cat₂

0 1

C	4.11596800	-1.43399800	0.00023800
C	2.94197100	-0.69772200	0.00003500
C	2.94125800	0.69737100	-0.00001800
C	4.11448800	1.43487400	0.00012500
C	5.31137300	0.70260800	0.00031100
C	5.31209100	-0.70049100	0.00036100
H	4.10428900	-2.51923400	0.00026600
H	4.10171300	2.52009800	0.00006600
H	6.25777100	1.23599000	0.00042100
H	6.25904300	-1.23288900	0.00050000
O	1.63526800	1.14376300	-0.00026400
O	1.63644700	-1.14549300	-0.00013900
B	0.84350700	-0.00125700	-0.00029700
B	-0.84352200	-0.00126600	-0.00055400
C	-4.11454500	1.43484300	0.00028000
C	-5.31142800	0.70257600	0.00055200
C	-5.31202700	-0.70053000	0.00048300
C	-4.11591400	-1.43399900	0.00007600
C	-2.94181300	-0.69779700	-0.00025300
C	-2.94136100	0.69732800	-0.00008700
H	-4.10160600	2.52006300	0.00030100
H	-6.25789200	1.23583600	0.00084400
H	-6.25895000	-1.23299000	0.00076100
H	-4.10437100	-2.51924700	0.00005100
O	-1.63641700	-1.14531800	-0.00050100
O	-1.63533500	1.14387500	-0.00054100

INT 1

0 2

C	-2.89003600	-3.39902900	1.56780800
C	-2.35758100	-2.48242700	0.64787100
C	-2.86844700	-2.38868800	-0.68480700
C	-3.92117600	-3.20891800	-1.11953600
C	-4.43770000	-4.11234300	-0.19978900

C	-3.92966300	-4.20589400	1.12418400
H	-2.49682400	-3.46080000	2.57725300
H	-4.30272000	-3.12888200	-2.13221900
H	-5.25299400	-4.76679600	-0.49507700
H	-4.37112400	-4.92901000	1.80420500
O	-2.21921600	-1.46609900	-1.36711400
O	-1.37789600	-1.62090000	0.83126600
B	-1.17489300	-0.84220100	-0.45157600
B	-1.60637500	0.82628600	-0.21076200
C	-1.62689600	4.33316100	-0.92563900
C	-2.37772300	5.29305400	-0.22805800
C	-3.20805100	4.93399500	0.84312600
C	-3.32416400	3.59936100	1.26388000
C	-2.57872100	2.66340400	0.56562900
C	-1.75204300	3.02090600	-0.49976300
H	-0.98037700	4.59971100	-1.75583800
H	-2.31188200	6.33572600	-0.52628000
H	-3.77434200	5.70339200	1.36064700
H	-3.96314100	3.31049500	2.09246700
O	-2.49626500	1.29856900	0.75700400
O	-1.13907800	1.88555500	-0.99073400
C	1.46114700	-0.55582500	-0.15112200
H	1.34407100	0.52384700	0.02277800
H	1.38909300	-1.03586800	0.83543100
C	0.32526000	-1.05884900	-1.05421100
H	0.37198100	-0.55587600	-2.03037100
H	0.45409000	-2.13620100	-1.24789900
C	2.85949100	-0.81547400	-0.73398000
H	2.98408500	-1.89530100	-0.90785900
H	2.93325100	-0.33664300	-1.72224900
C	4.00018700	-0.31160000	0.16157800
H	3.87702100	0.76890800	0.33164300
H	3.92047900	-0.78662100	1.15149500
C	5.39796100	-0.57698500	-0.41478800
H	5.52016800	-1.65750300	-0.58644100
H	5.47880600	-0.10069800	-1.40392900
C	6.53877100	-0.07630300	0.48192700
H	6.41836300	1.00454300	0.65313600
H	6.45806800	-0.55167200	1.47172600
C	7.93710600	-0.34294000	-0.09213200
H	8.05833100	-1.42287300	-0.26236900
H	8.01922200	0.13241800	-1.08064900
C	9.06982600	0.16029200	0.81086700
H	9.03569200	-0.32277400	1.79609400

H	10.05404000	-0.04618000	0.37287100
H	8.99733800	1.24384300	0.97146900

DMA

0 1

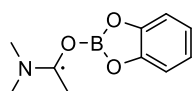
C	-0.72853200	0.29184900	0.00012300
O	-1.06870300	1.47529500	-0.00037600
C	-1.78139700	-0.81075100	0.00006200
H	-1.70643300	-1.45145700	-0.88650500
H	-1.70705900	-1.45095900	0.88704300
H	-2.75778000	-0.32435500	-0.00040400
N	0.59511200	-0.08203800	0.00100000
C	1.08118700	-1.45235100	-0.00038700
H	1.69691800	-1.64052400	-0.89137500
H	1.70341700	-1.63943500	0.88623000
H	0.25869400	-2.16582500	0.00319200
C	1.63045700	0.94326000	-0.00002100
H	2.26409000	0.84539000	-0.89208300
H	1.15459700	1.92325500	0.00158400
H	2.26710400	0.84377500	0.88966700

C₈H₁₇Bcat

0 1

C	-3.66045700	0.69533900	-0.05058900
C	-4.16007400	-0.60394100	0.04794400
C	-5.51796900	-0.86480900	0.12547400
C	-6.37306300	0.24915700	0.09946400
C	-5.87090300	1.55390900	0.00015000
C	-4.49077800	1.80311900	-0.07726100
H	-5.89610400	-1.87937300	0.20196400
H	-7.44669900	0.09336500	0.15729400
H	-6.56181700	2.39212000	-0.01765800
H	-4.09063000	2.80916100	-0.15435600
O	-2.28131700	0.64198300	-0.11052800
O	-3.10318500	-1.49221700	0.05193200
B	-1.94950800	-0.71144000	-0.04941500
C	-0.49702300	-1.29033900	-0.10337300
H	-0.39615700	-2.05835800	0.67907900
H	-0.39008500	-1.84678700	-1.04953000
C	0.63813900	-0.25654500	0.01792300
H	0.54494700	0.27896900	0.97350800
H	0.52425100	0.50660200	-0.76437300

C	2.03772700	-0.87888300	-0.07919600
H	2.14854700	-1.64654500	0.70213300
H	2.13221800	-1.40768400	-1.04027800
C	3.17431400	0.14432300	0.05011300
H	3.08229000	0.66808100	1.01388100
H	3.05828900	0.91501300	-0.72716200
C	4.57484000	-0.47480800	-0.05743500
H	4.66710400	-0.99716600	-1.02201200
H	4.69104400	-1.24646800	0.71896100
C	5.71118000	0.54868800	0.07307500
H	5.62111500	1.07019500	1.03843900
H	5.59453200	1.32163900	-0.70212600
C	7.11238600	-0.06810300	-0.03768000
H	7.20291200	-0.58980400	-1.00176900
H	7.23093800	-0.83869600	0.73816500
C	8.24035200	0.96276700	0.09104700
H	8.19789100	1.47838200	1.05923300
H	9.22670100	0.49027000	0.00847000
H	8.17025100	1.72690800	-0.69394500



0 2

C	-2.40231000	1.17847200	1.54003300
H	-1.95440800	0.91771700	2.50415100
H	-1.79267800	1.98613600	1.09715500
H	-3.40178400	1.57696800	1.74041100
C	-2.46543400	-0.05163900	0.68710700
N	-3.03025000	-0.01651600	-0.59531400
C	-3.32806600	-1.31772600	-1.20121500
H	-4.25341900	-1.75502700	-0.78774100
H	-3.44945500	-1.19018000	-2.28170500
H	-2.50587700	-2.00982000	-1.01777500
C	-4.08322600	0.96445000	-0.82844100
H	-3.74108900	1.96697200	-0.56305300
H	-4.32891600	0.96321200	-1.89469600
H	-5.00530900	0.73862700	-0.26273300
O	-1.34831200	-0.90318900	0.75574900
B	-0.07900500	-0.54650700	0.46126300
O	0.97281800	-1.46260300	0.52785500
O	0.36959100	0.72215000	0.08135100
C	2.09658800	-0.74237600	0.17703900

C	1.73403300	0.57972800	-0.09395200
C	3.40755800	-1.17558200	0.08175600
C	2.66169500	1.53321000	-0.47414400
C	4.36154700	-0.21786000	-0.30333100
H	3.67878600	-2.20468000	0.29504100
C	3.99724300	1.10658900	-0.57533400
H	2.36747100	2.55689800	-0.68322700
H	5.40296700	-0.51468200	-0.39075800
H	4.75994800	1.82153600	-0.87093500

TS1

02

C	-3.07070900	-3.47865700	1.50068700
C	-2.87622300	-2.31294800	0.77309300
C	-3.48620500	-2.10685800	-0.47055300
C	-4.31968500	-3.05677500	-1.04444300
C	-4.52421600	-4.23810000	-0.31631500
C	-3.91274200	-4.44460300	0.93006600
H	-2.59504400	-3.62678100	2.46514400
H	-4.78903400	-2.88532900	-2.00810300
H	-5.17072300	-5.00857800	-0.72716900
H	-4.09484800	-5.37191300	1.46614300
O	-3.12543500	-0.87768400	-0.95463500
O	-2.12004900	-1.21697000	1.09456500
B	-2.22326800	-0.33570900	-0.00826900
B	-1.80703200	1.29656000	0.05434000
C	-1.43232900	4.63235500	-1.18149000
C	-0.87478700	5.69909600	-0.45889900
C	-0.40433100	5.52883300	0.85125600
C	-0.47082000	4.28402500	1.49690800
C	-1.02238800	3.24021900	0.77156700
C	-1.48996100	3.40946500	-0.53251200
H	-1.80151400	4.75343500	-2.19499400
H	-0.80862100	6.67749200	-0.92656000
H	0.01972800	6.37763900	1.38041300
H	-0.11234700	4.14077100	2.51137100
O	-1.21299800	1.92715600	1.14898000
O	-1.97939000	2.20490500	-0.99274100
C	0.95162400	-0.48853300	-0.24864600
H	1.08605900	0.59739300	-0.16041200
H	0.81469500	-0.87625700	0.76949700
C	-0.25349600	-0.80291000	-1.08168400
H	-0.41453400	-0.23824000	-1.99895900

H	-0.56741600	-1.84558800	-1.13554500
C	2.24672300	-1.09874300	-0.84454400
H	2.13172800	-2.18957600	-0.91765900
H	2.38267800	-0.73084900	-1.87146400
C	3.49274600	-0.76618700	-0.01060500
H	3.34635800	-1.12571400	1.01891300
H	3.59995000	0.32667600	0.05900400
C	4.78499000	-1.36766000	-0.58039700
H	4.68009700	-2.46150900	-0.64286200
H	4.92512000	-1.01477700	-1.61347800
C	6.03362700	-1.02516100	0.24441200
H	5.89394900	-1.37629400	1.27832500
H	6.13877900	0.06890700	0.30603000
C	7.32841500	-1.62491400	-0.32107900
H	7.22513800	-2.71836800	-0.38004700
H	7.46790500	-1.27538500	-1.35458900
C	8.57017900	-1.27428900	0.50749600
H	8.47597800	-1.64075300	1.53795300
H	9.47668800	-1.71780900	0.07810800
H	8.72123600	-0.18804600	0.55533200

TS2

02

C	-3.06723500	-3.27142400	1.52701400
C	-2.34544400	-2.62837500	0.53409500
C	-2.92181900	-2.27690300	-0.68931800
C	-4.24870600	-2.54976600	-0.98169800
C	-4.98984400	-3.20493200	0.01428600
C	-4.41148000	-3.55804700	1.24189400
H	-2.61019000	-3.53764900	2.47488200
H	-4.68607700	-2.27020400	-1.93505400
H	-6.03354800	-3.44246900	-0.17198600
H	-5.01514500	-4.06392800	1.99031500
O	-1.97640900	-1.65353700	-1.47180500
O	-1.02719400	-2.23556600	0.54315400
B	-0.79970700	-1.60967200	-0.69468600
B	-1.40800800	0.82109200	-0.01772100
C	-1.73044700	4.28460500	-0.73035900
C	-2.73677600	5.11588900	-0.21264000
C	-3.72131200	4.62108300	0.65428800
C	-3.74524600	3.27233700	1.04395100
C	-2.74735600	2.46603600	0.52478600
C	-1.76779300	2.95823600	-0.33682800

H	-0.96365600	4.65619400	-1.40242100
H	-2.75085500	6.16546900	-0.49229500
H	-4.48430900	5.29437900	1.03447900
H	-4.50247900	2.87785000	1.71371700
O	-2.52383300	1.10788200	0.73471300
O	-0.91016500	1.91779500	-0.68661400
C	1.72594800	-1.01423100	-0.23691000
H	1.45475600	-0.13339400	0.36312600
H	1.77810900	-1.85503800	0.46847600
C	0.62347400	-1.28508600	-1.27663400
H	0.55911300	-0.45281000	-1.99071700
H	0.91048500	-2.16159600	-1.88463400
C	3.10900800	-0.78762600	-0.86273700
H	3.38054600	-1.66584900	-1.46869700
H	3.05554100	0.06071400	-1.56204400
C	4.21243100	-0.52544200	0.17146600
H	3.93949800	0.35139700	0.77837800
H	4.26291500	-1.37493800	0.86965600
C	5.59789400	-0.29869000	-0.44939600
H	5.86826700	-1.17230000	-1.06217900
H	5.55006200	0.55582500	-1.14166600
C	6.70165100	-0.04823300	0.58751600
H	6.43107600	0.82392200	1.20250000
H	6.75106500	-0.90386300	1.27844900
C	8.08797700	0.18160800	-0.03007100
H	8.35898100	-0.68894800	-0.64533200
H	8.03999200	1.03821400	-0.71841600
C	9.18311900	0.42799700	1.01480800
H	9.28015300	-0.42722400	1.69611000
H	10.15962800	0.58980500	0.54225800
H	8.95718300	1.31250600	1.62446900

6.3 IRC analysis for TS1 and TS2

To further identify the reasonability of the reaction pathway, the IRC analysis of **TS1** and **TS2** were conducted. These IRC analyses were taken using the local quadratic approximation (LQA) method under uB3LYP/6-31+G(d), the same basis set with the structure optimization and frequency analysis. For each transition state, 50 points were examined in each direction with step size of 10 (in unit of 0.01 Bohr).

Figure 2 IRC analysis for **TS1** (10 points SG smooth)

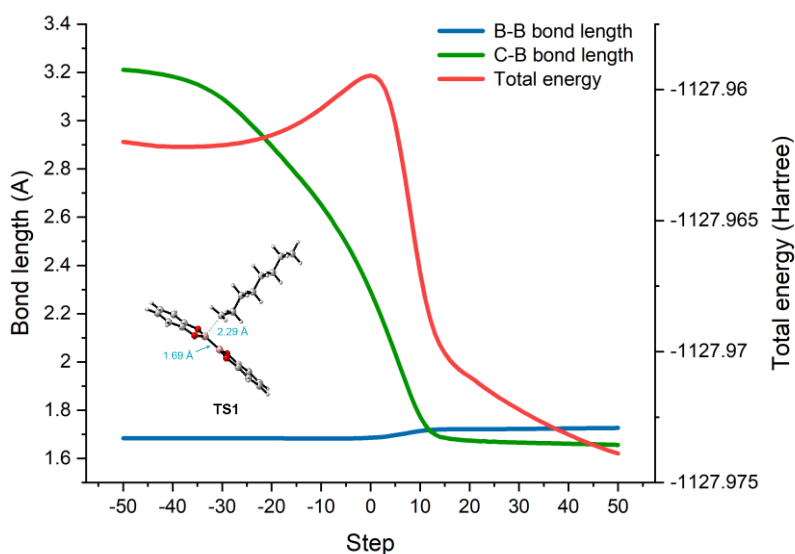
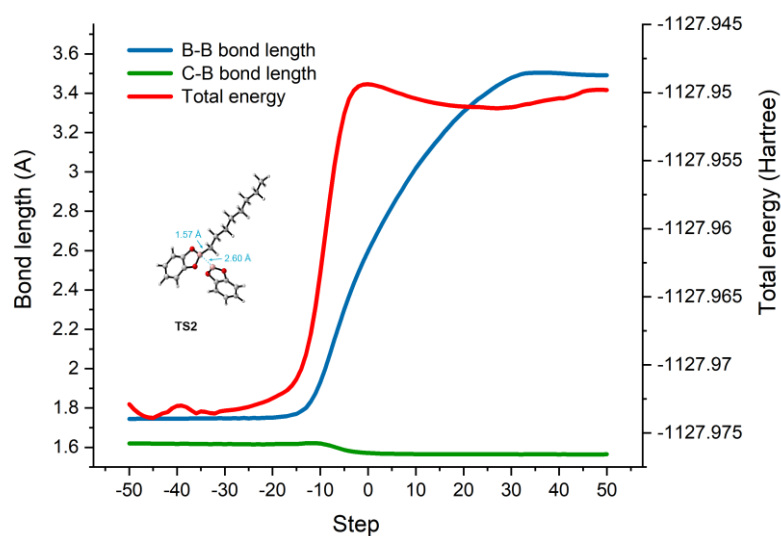


Figure 3 IRC analysis for **TS2** (10 points SG smooth)



In **Figure 2**, IRC analysis clearly gives us the information of the reaction pathway. Along with the formation of C-B bond, the total energy decreases after a small energy barrier, and B-B bond remains almost unchanged, which leads to **INT1**. In **Figure 3**, when C-B bond is established, the bond length remains almost unchanged, then the cleavage of B-B bond happened, gave the C₈H₁₇Bcat product, and Bcat radical, which is then stabilized by DMA.

These results strongly identified the reasonability of the reaction pathway and the structure of **TS1** and **TS2**.

The energies, length of the C-B bond formed in the reaction and the length of B-B bond broken in the reaction are shown in **Table 3**.

Table 3 Comparison of bond length

Structure	B-B bond length (A)	C-B bond length (A)
•C ₈ H ₁₇ + B ₂ cat ₂	1.687	none
Step -50 of TS1	1.684	3.212
Step -40 of TS1	1.684	3.182
Step -30 of TS1	1.684	3.092
Step -20 of TS1	1.684	2.896
Step -10 of TS1	1.683	2.654
TS1	1.686	2.291
Step 10 of TS1	1.715	1.767
Step 20 of TS1	1.723	1.661
Step 30 of TS1	1.722	1.666
Step 40 of TS1	1.725	1.661
Step 50 of TS1	1.727	1.657
INT1	1.740	1.650
Step -50 of TS2	1.745	1.620
Step -40 of TS2	1.745	1.618
Step -30 of TS2	1.748	1.616
Step -20 of TS2	1.773	1.613
Step -10 of TS2	1.923	1.623
TS2	2.596	1.571
Step 10 of TS2	3.024	1.566
Step 20 of TS2	3.310	1.565
Step 30 of TS2	3.481	1.565
Step 40 of TS2	3.501	1.565
Step 50 of TS2	3.491	1.564
C ₈ H ₁₇ Bcat	none	1.565

7. X-Ray crystallographic data

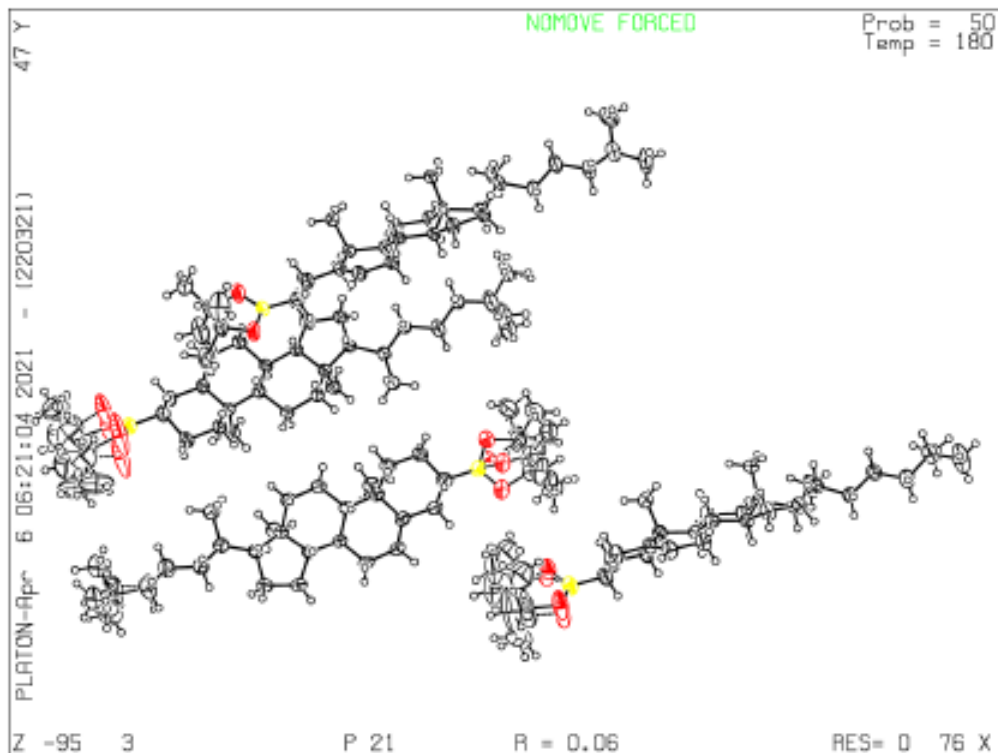
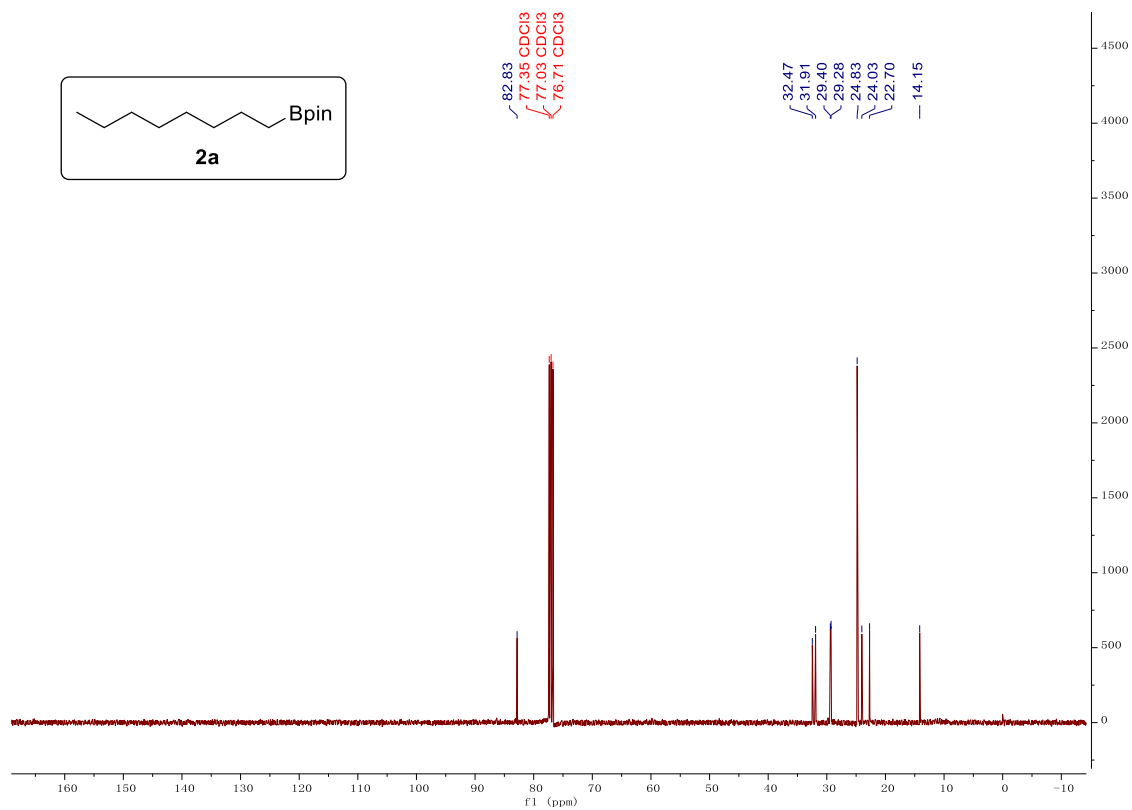
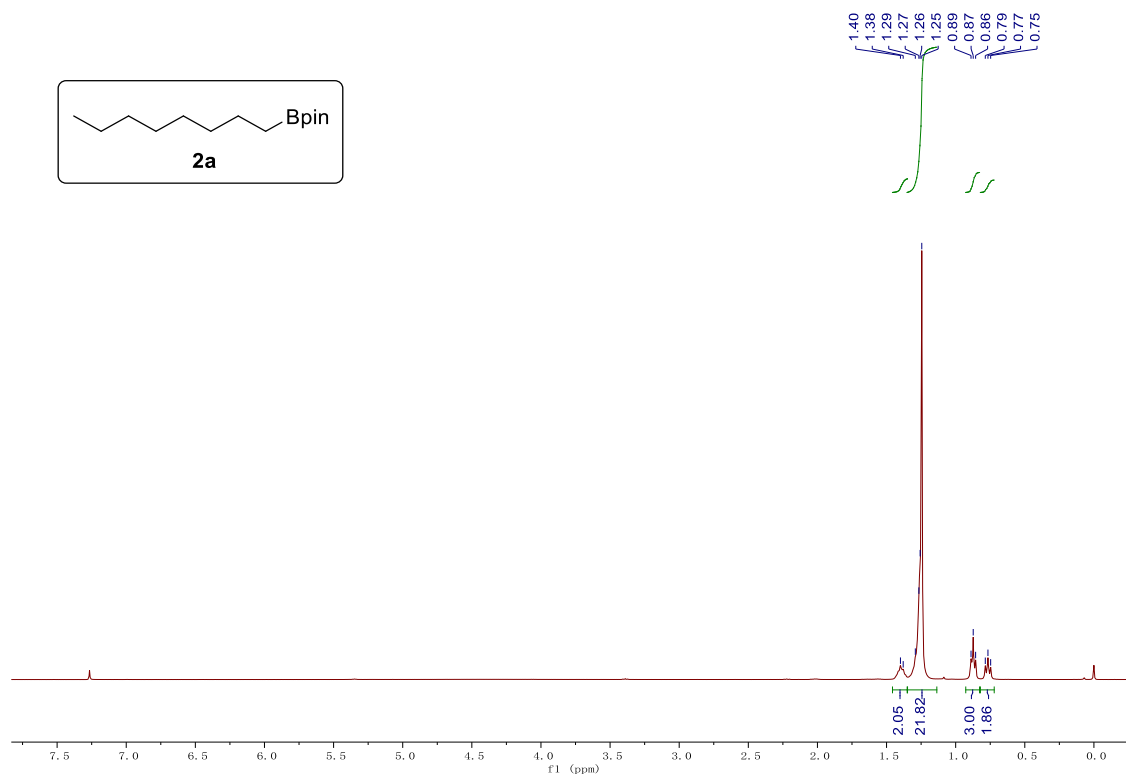


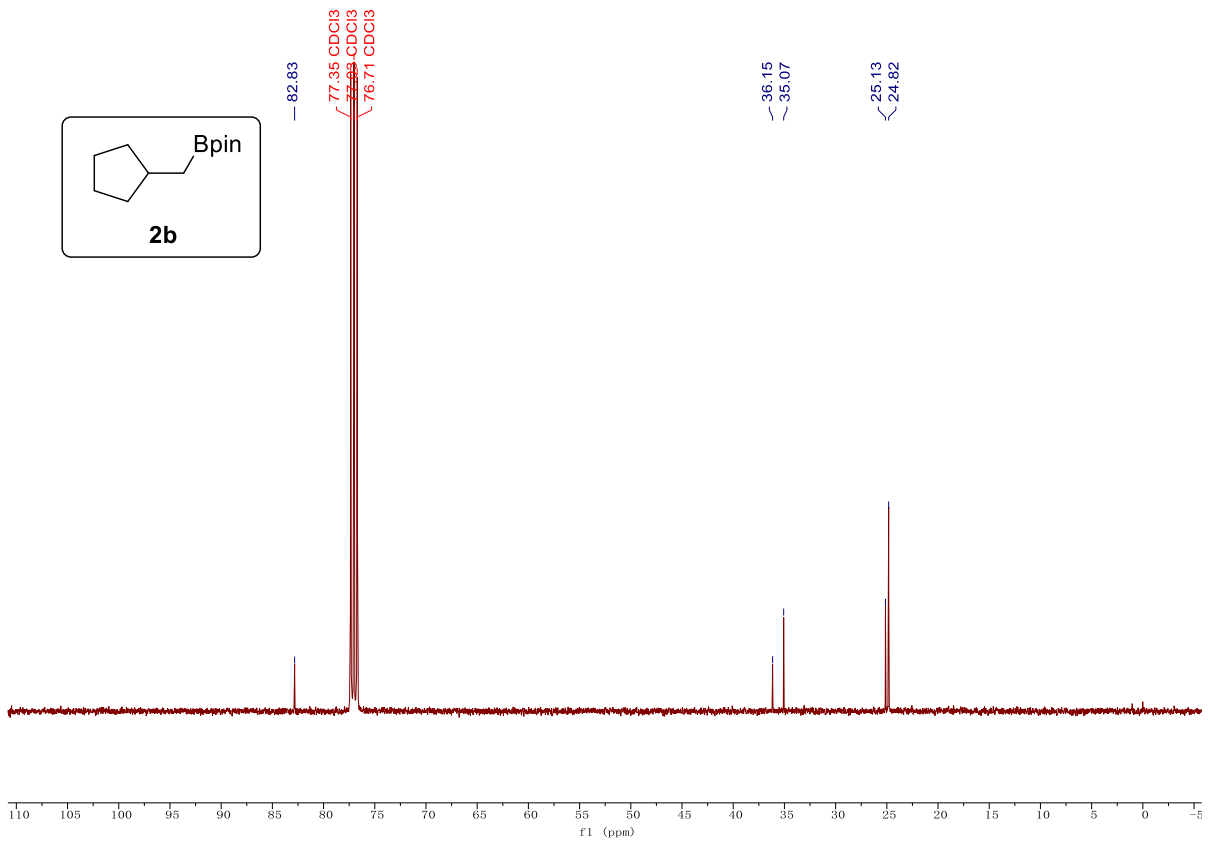
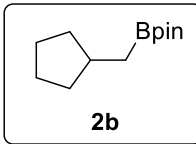
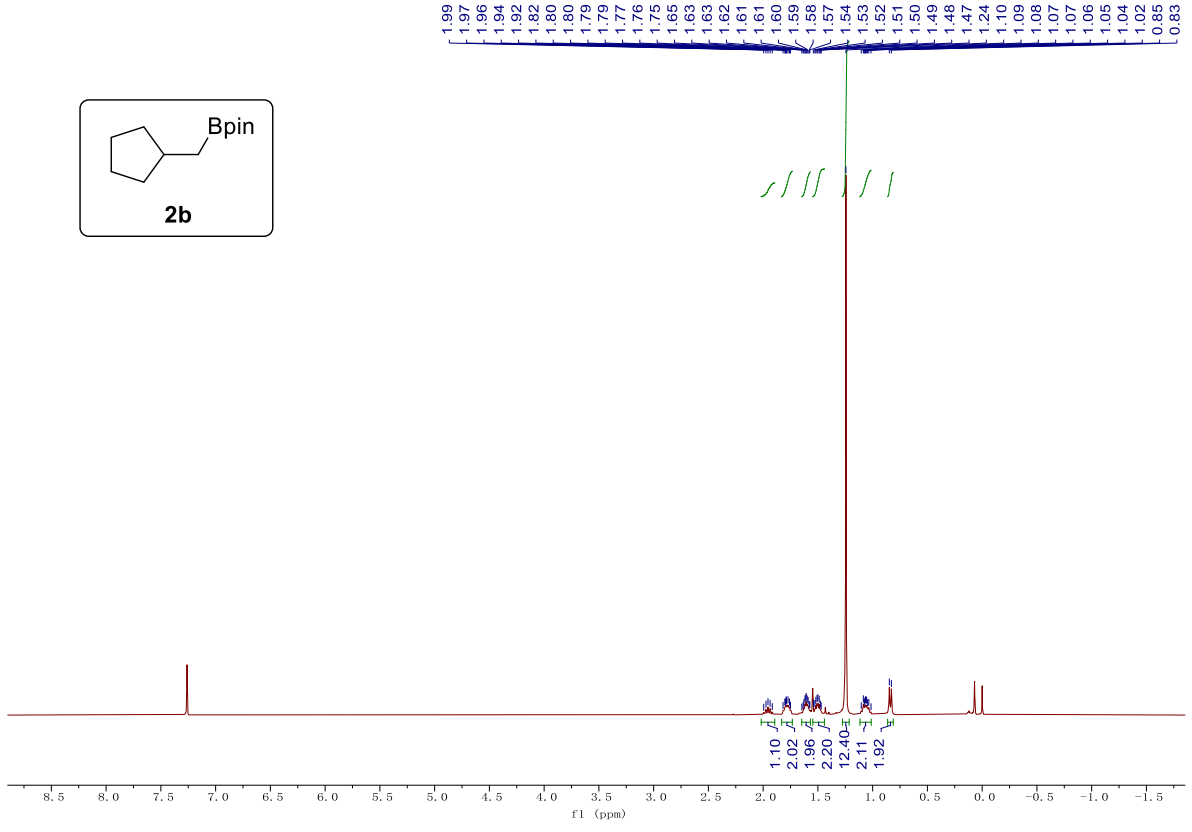
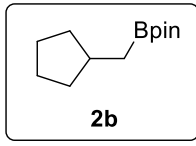
Figure 4 X-Ray crystallographic data for **2ab**. Compound **2ab** crystallizes with four formula units in the asymmetric unit, both formula units exhibit similar bond metrics.

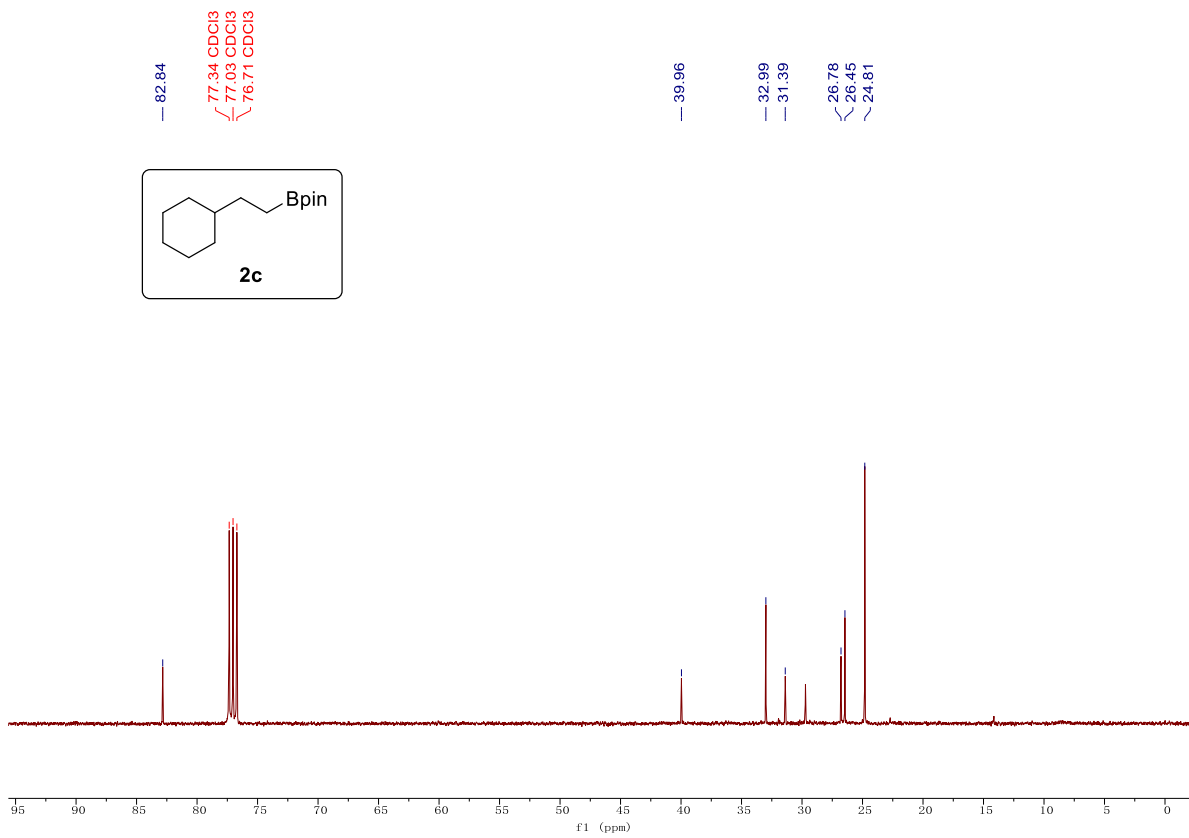
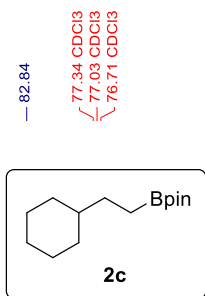
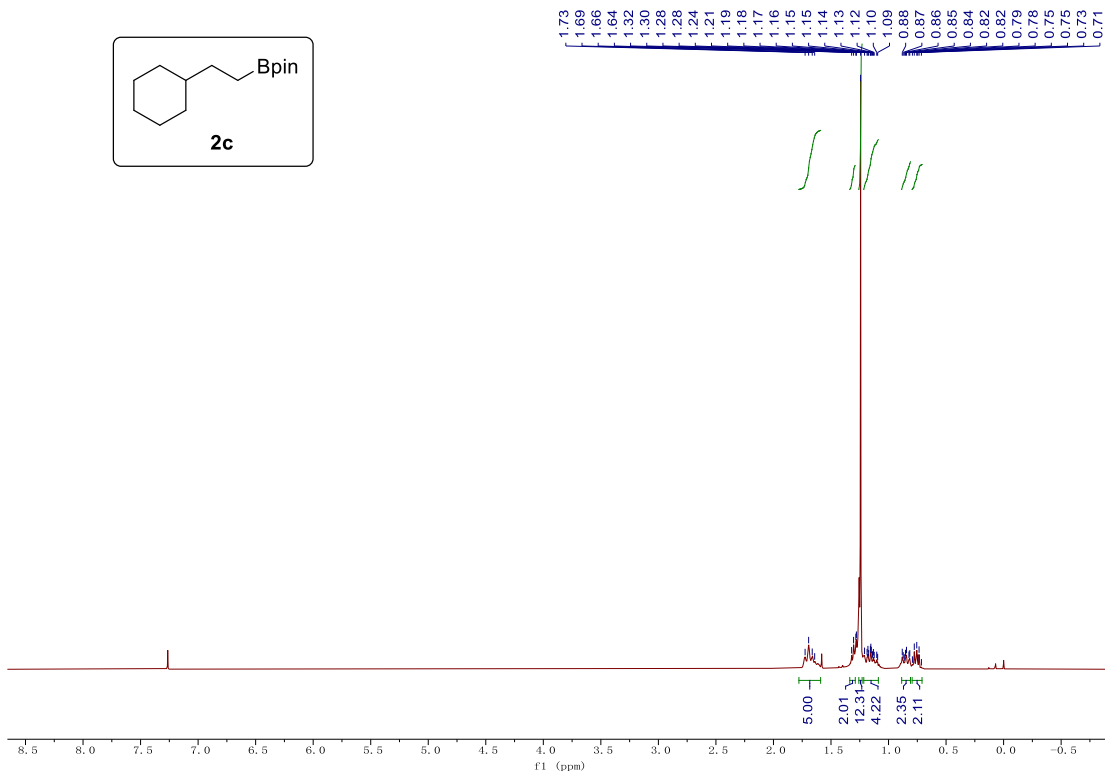
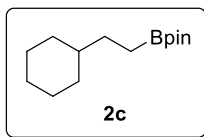
Table 4 Crystal data and structure refinement for **2ab**

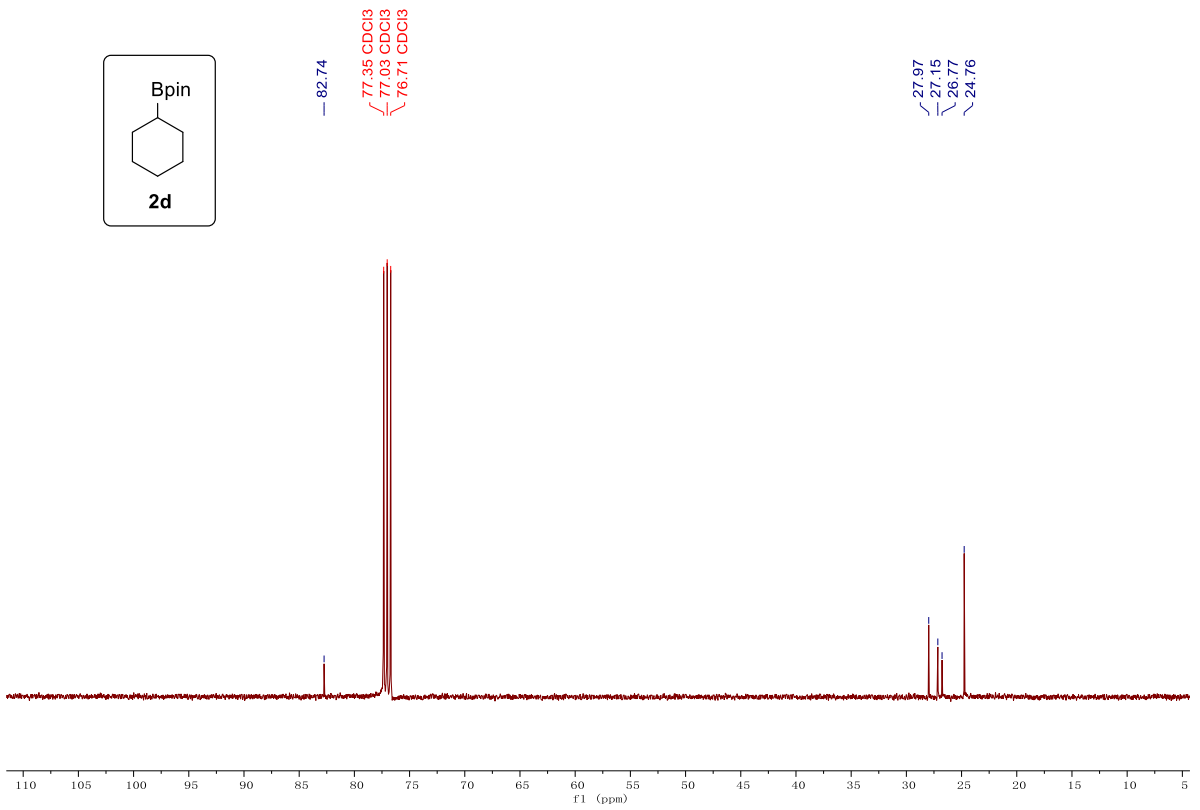
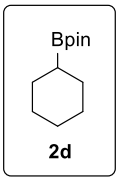
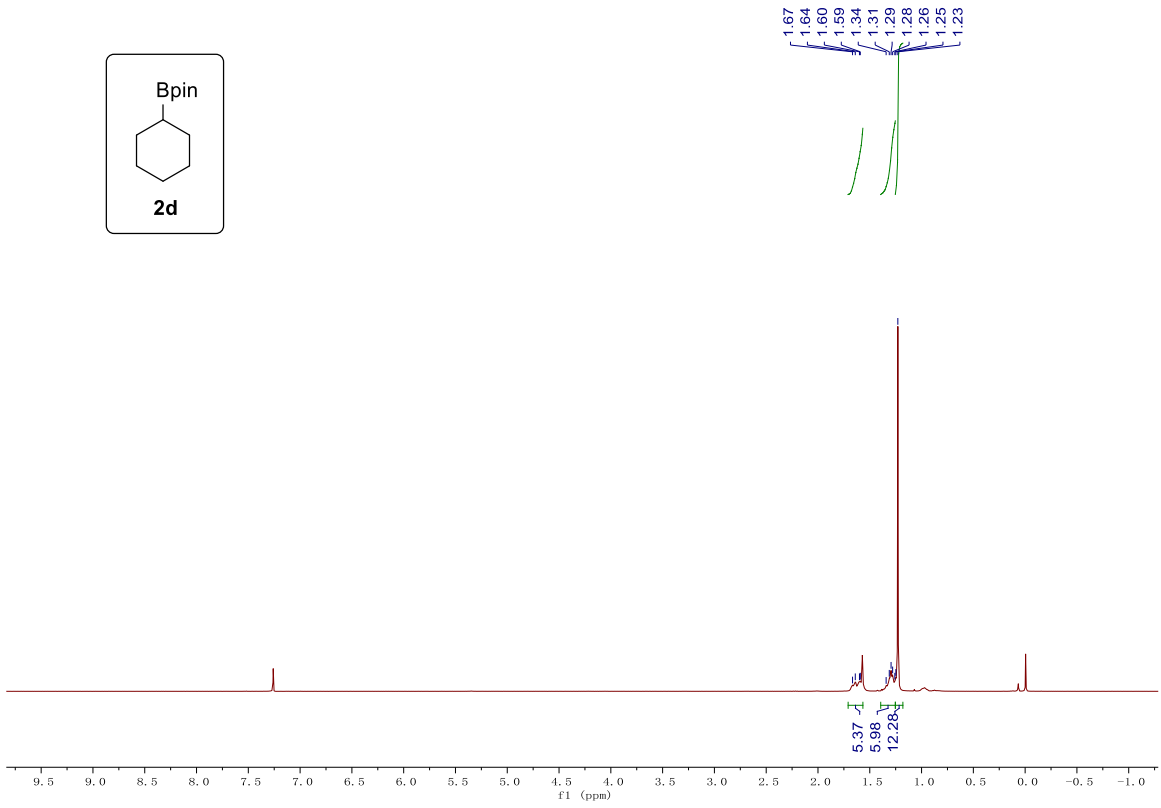
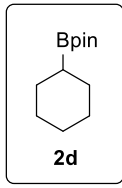
Bond precision:	C-C = 0.0045 A	Wavelength=1.54184	
Cell:	a=23.1307(1) alpha=90	b=11.0429(1) beta=97.165(1)	c=24.4853(1) gamma=90
Temperature:	180 K		
	Calculated	Reported	
Volume	6205.44(7)	6205.44(7)	
Space group	P 21	P 21	
Hall group	P 2yb	P 2yb	
Moiety formula	C33 H57 B O2	?	
Sum formula	C33 H57 B O2	C33 H57 B O2	
Mr	496.60	496.59	
Dx,g cm-3	1.063	1.063	
Z	8	8	
Mu (mm-1)	0.471	0.471	
F000	2208.0	2208.0	
F000'	2213.39		
h,k,lmax	28,13,30	28,13,30	
Nref	25379[13378]	24021	
Tmin,Tmax	0.889,0.906	0.849,1.000	
Tmin'	0.889		
Correction method= # Reported T Limits: Tmin=0.849 Tmax=1.000			
AbsCorr = MULTI-SCAN			
Data completeness=	1.80/0.95	Theta(max)= 74.580	
R(reflections)=	0.0588(22973)	wR2(reflections)= 0.1681(24021)	
S =	1.045	Npar= 1435	

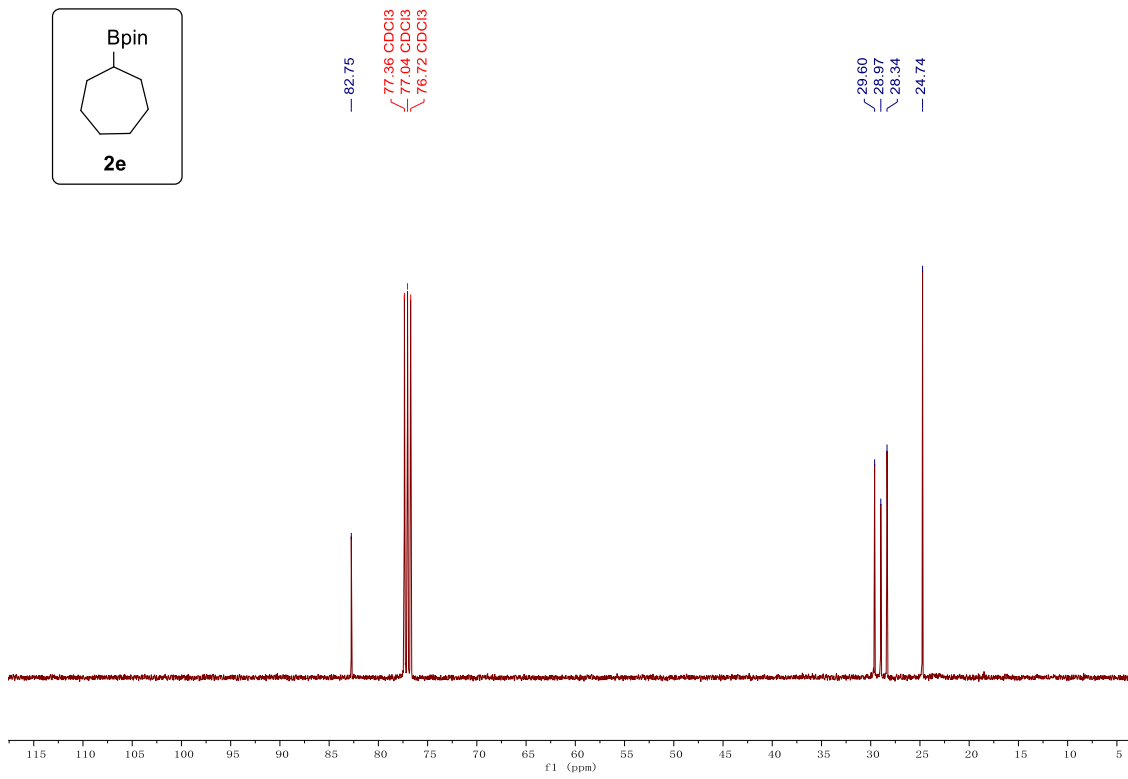
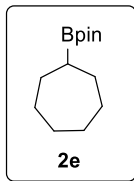
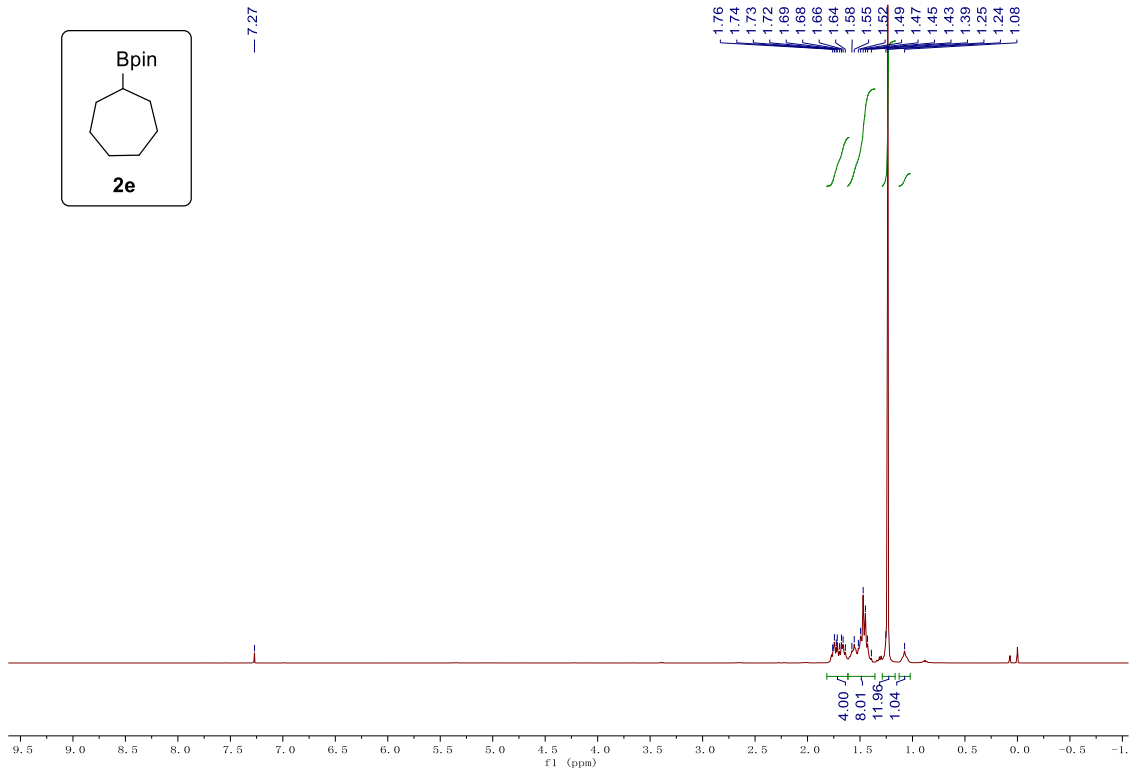
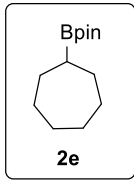
8. NMR charts

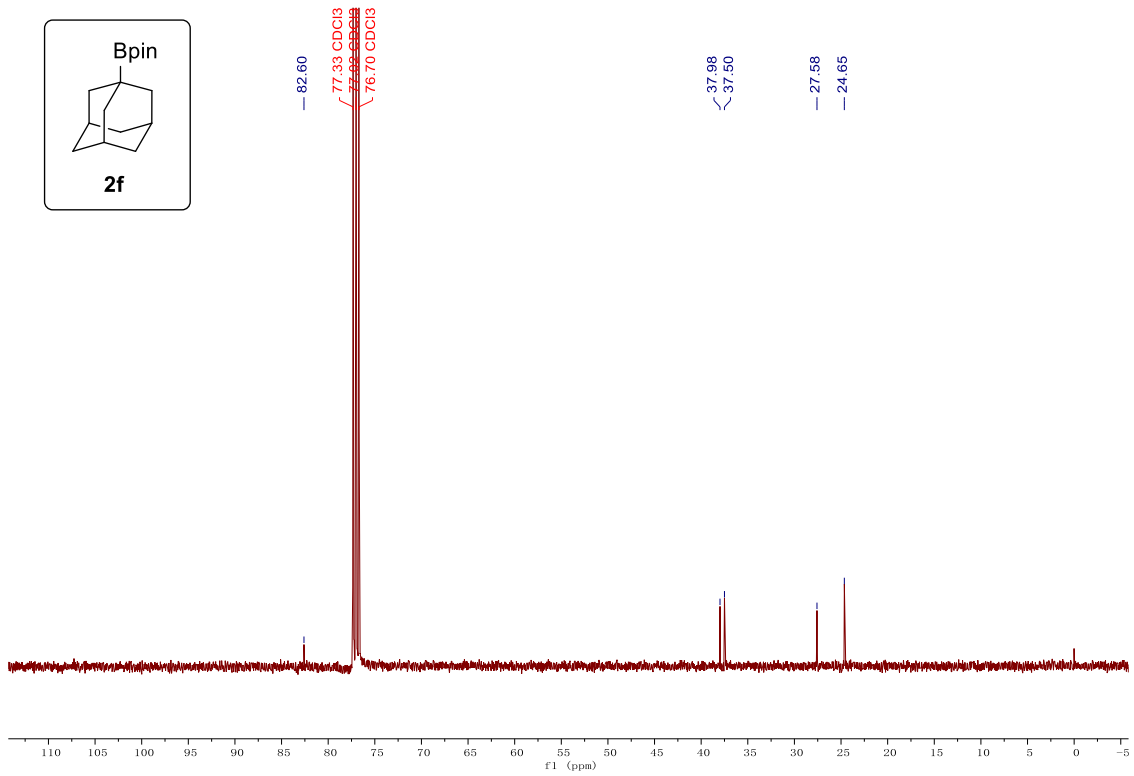
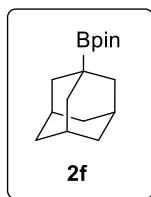
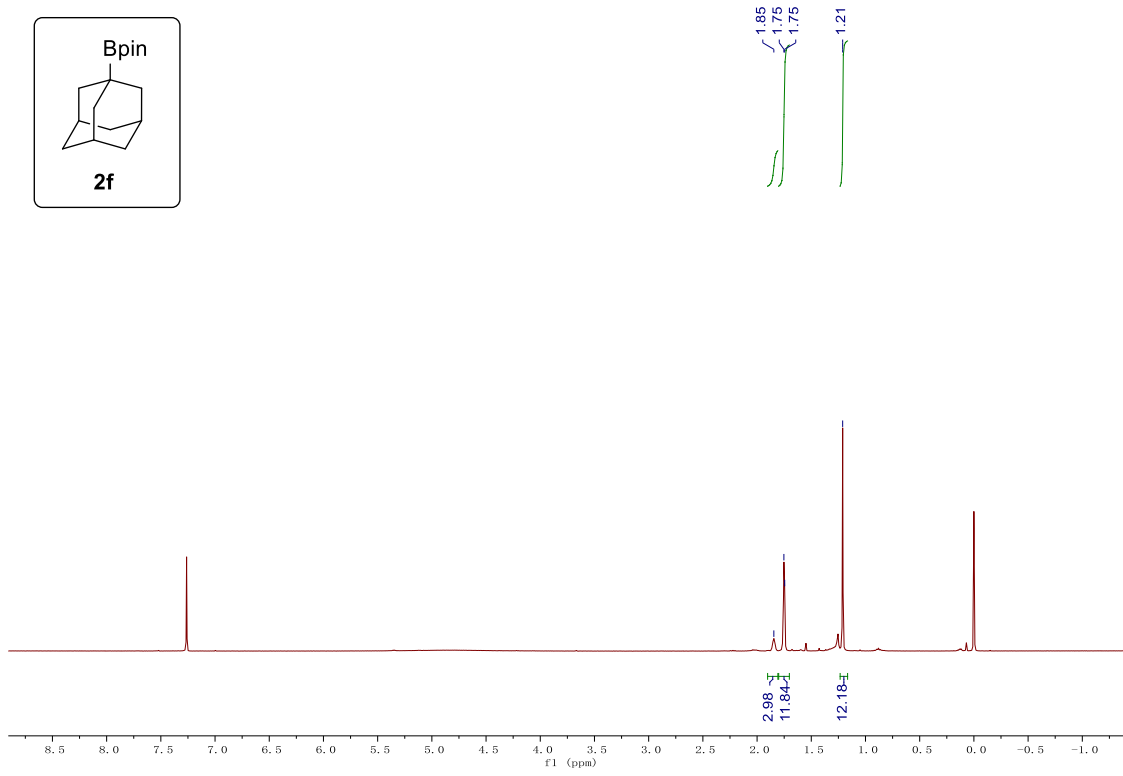
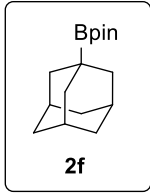


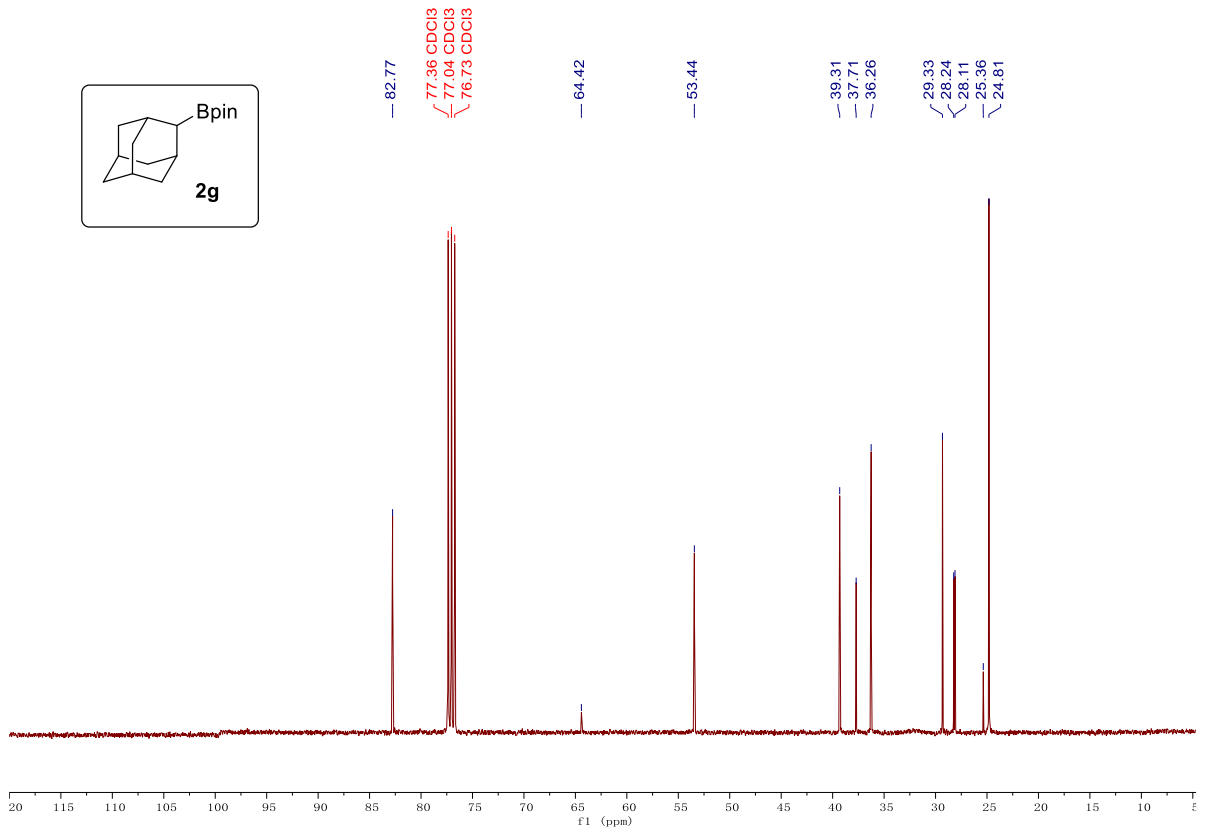
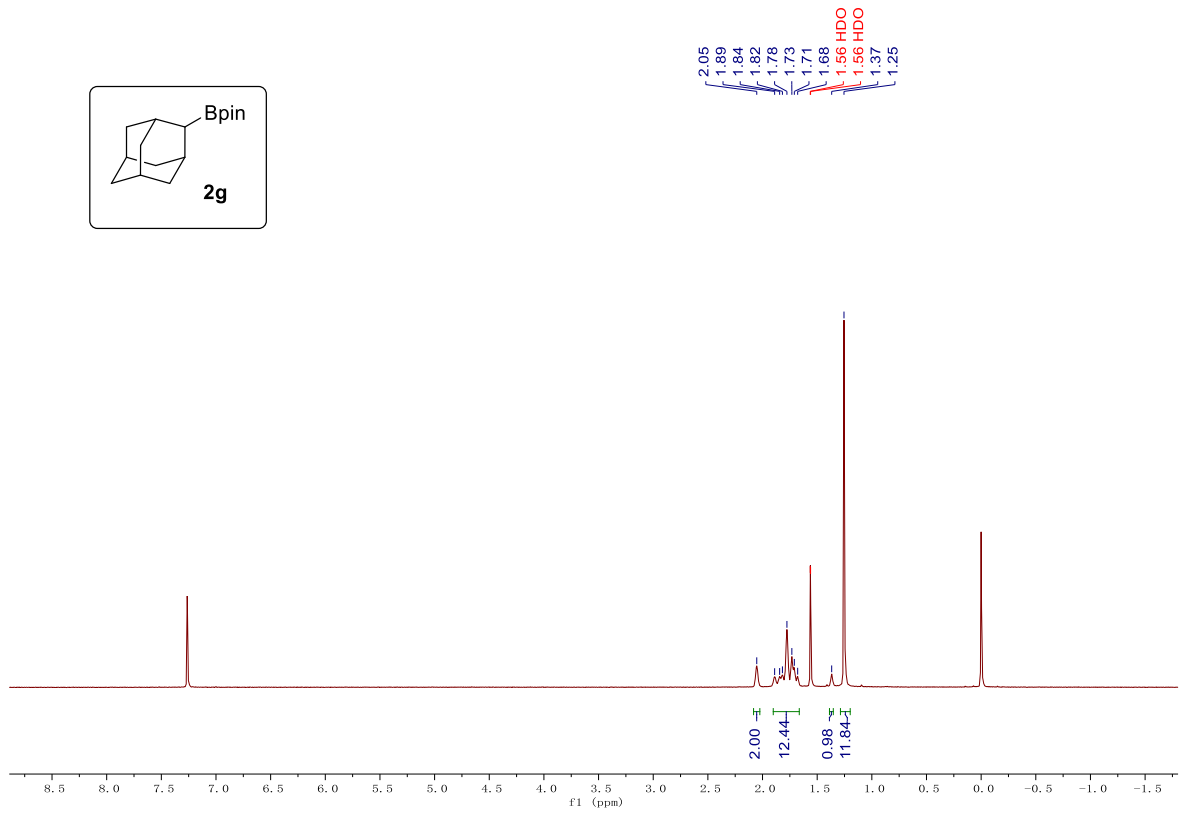
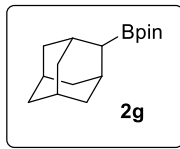


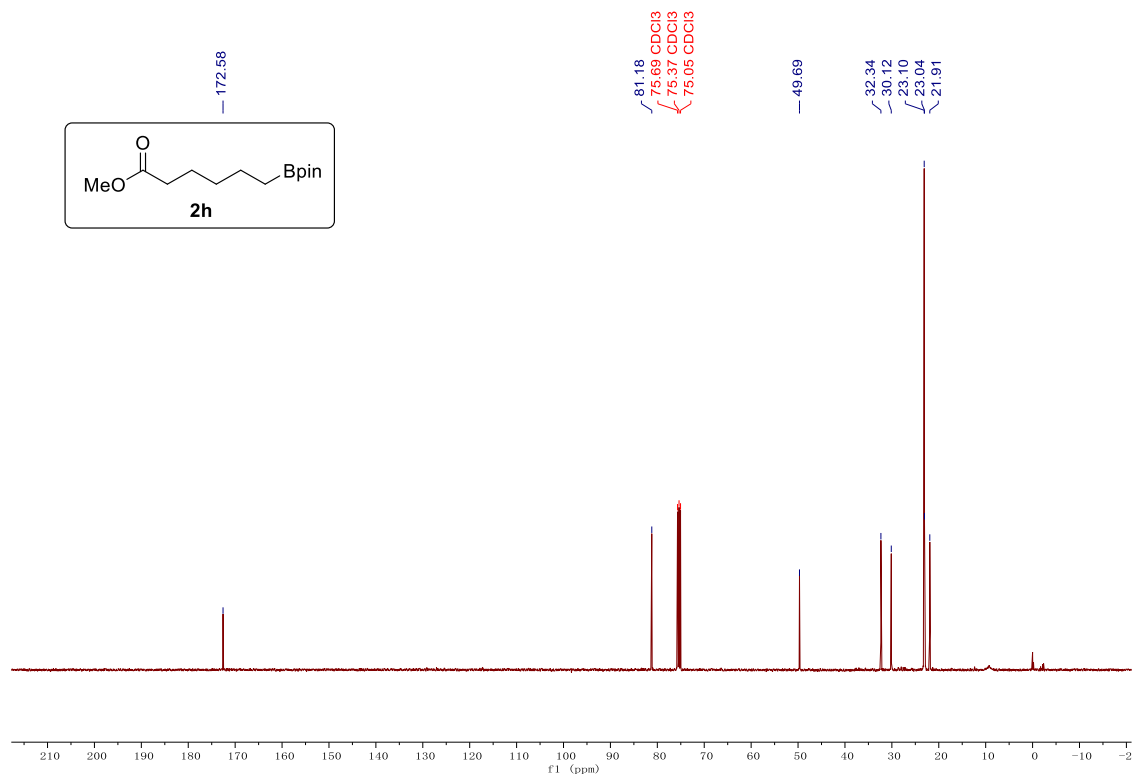
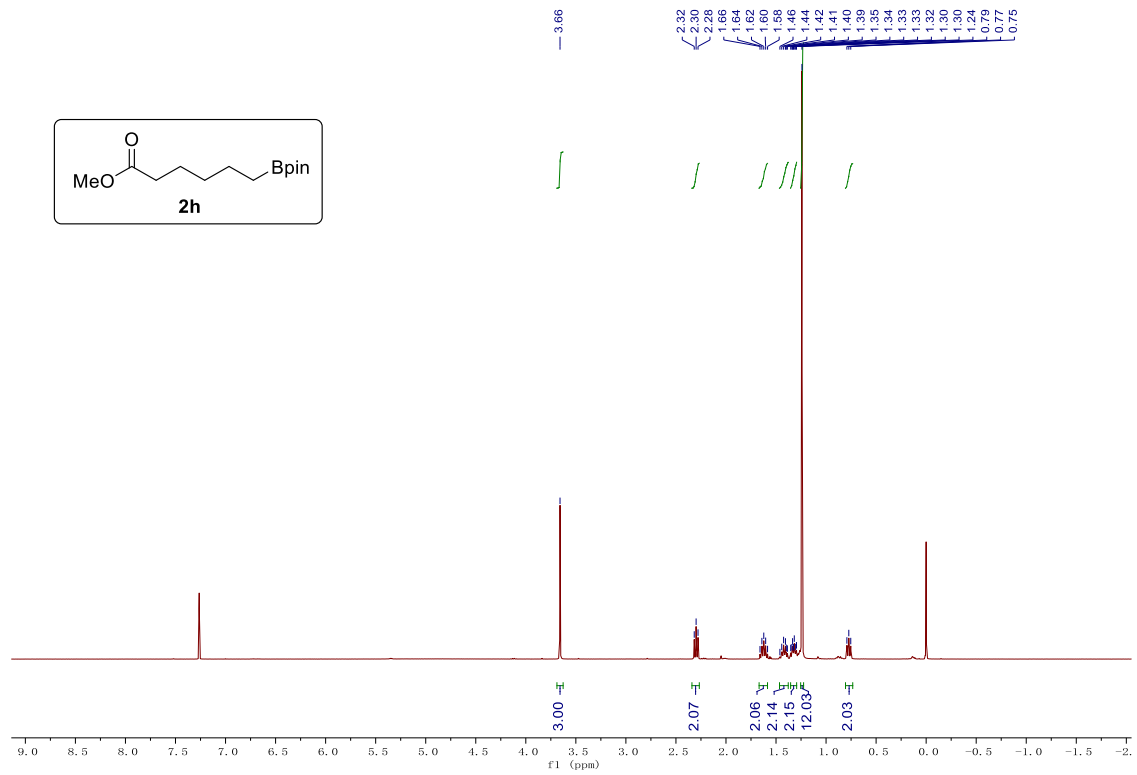


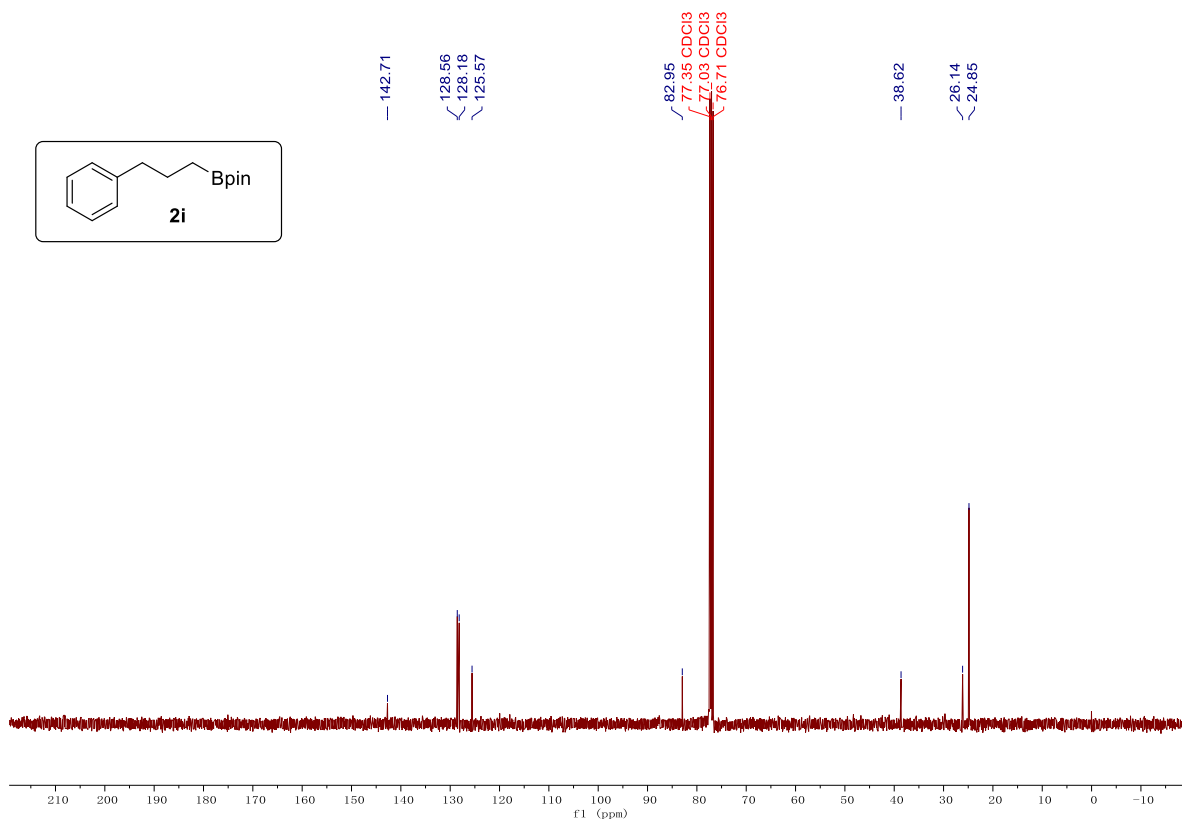
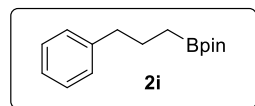
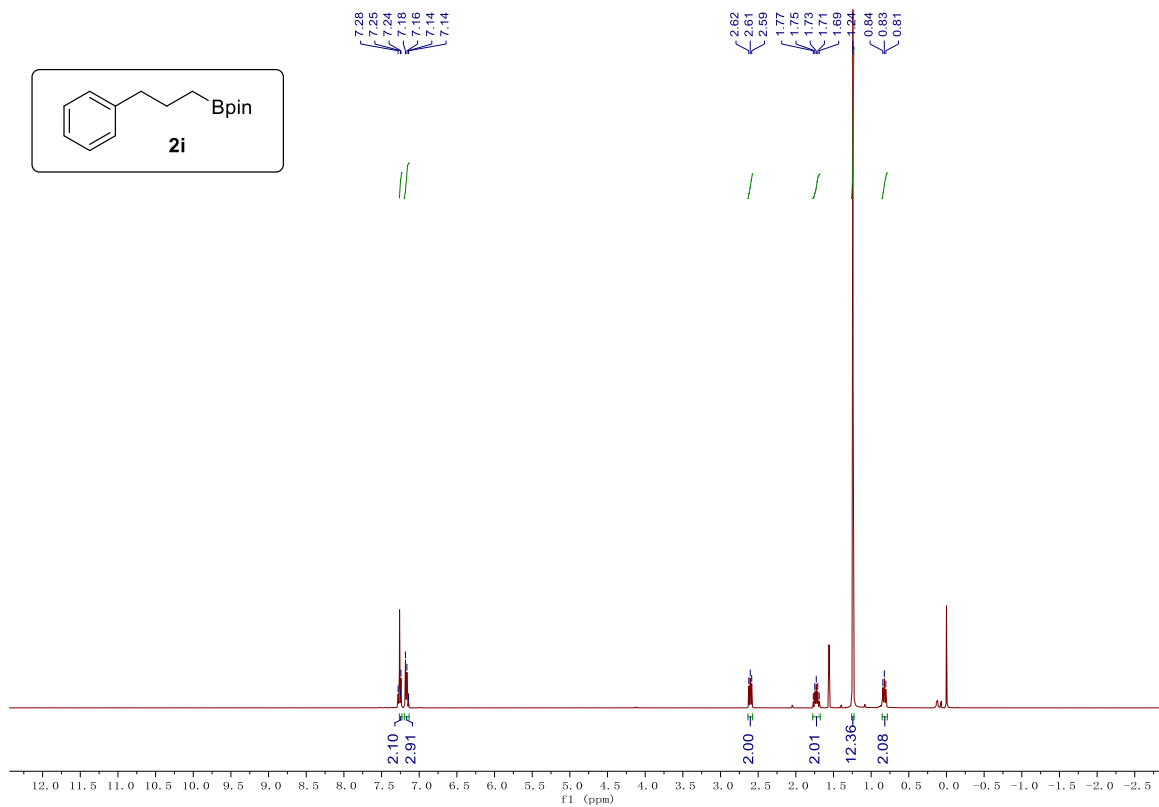
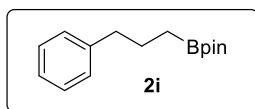


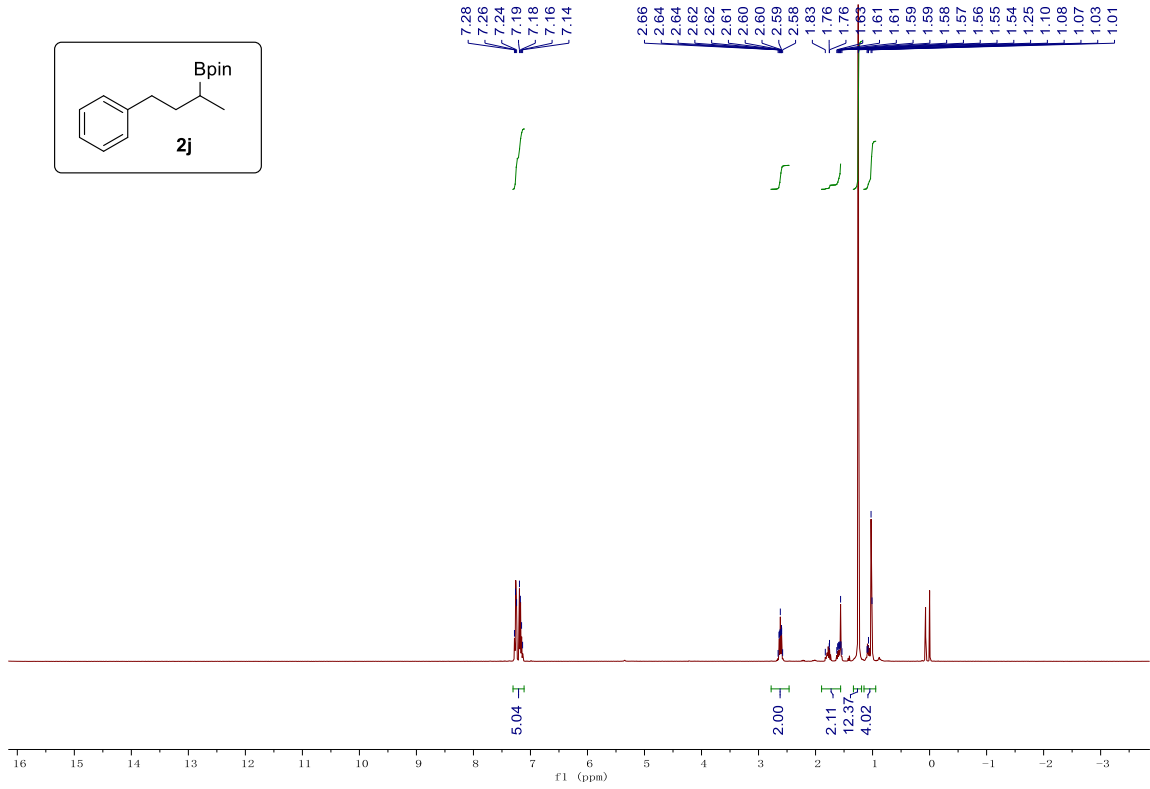
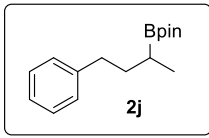












— 143.10

< 128.46
 < 128.21
 < 125.52

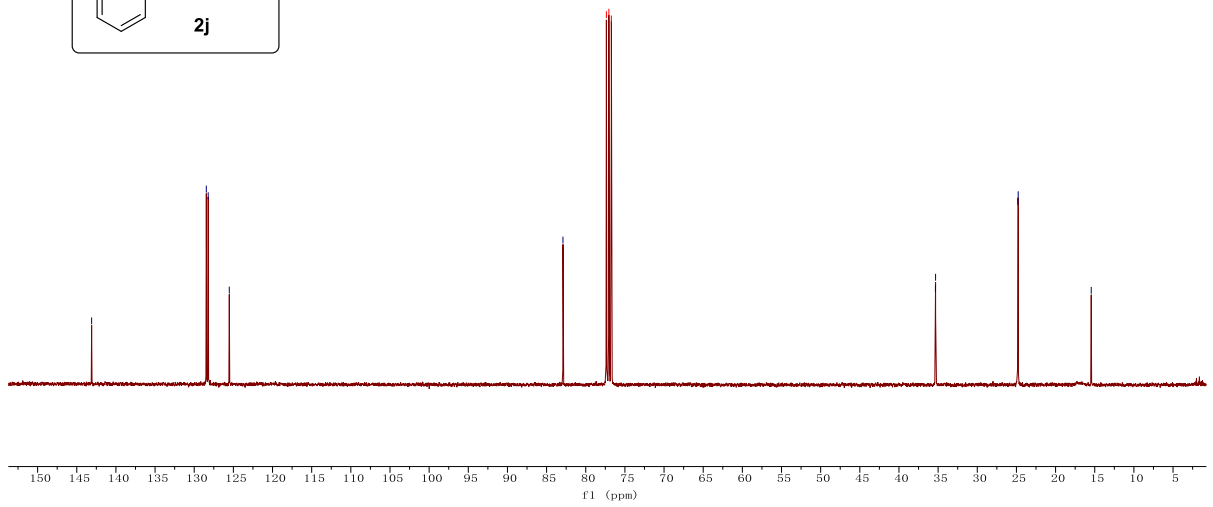
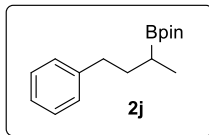
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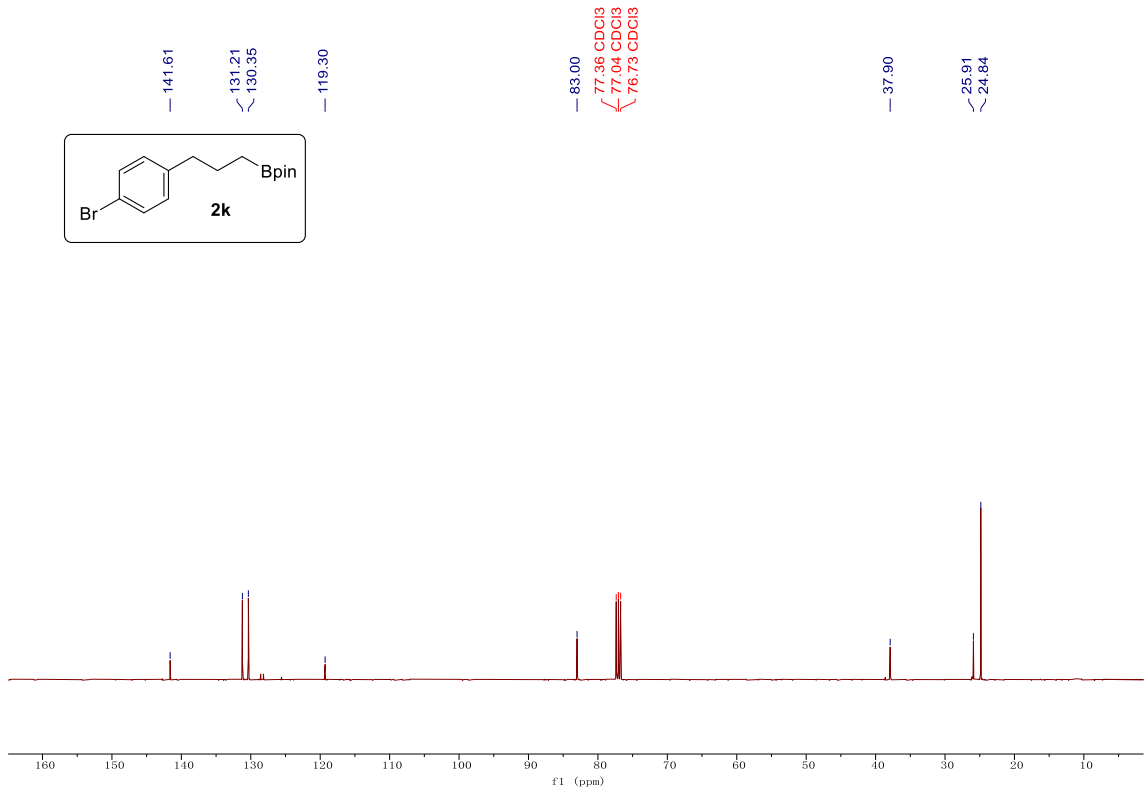
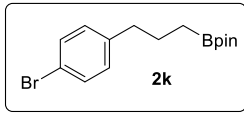
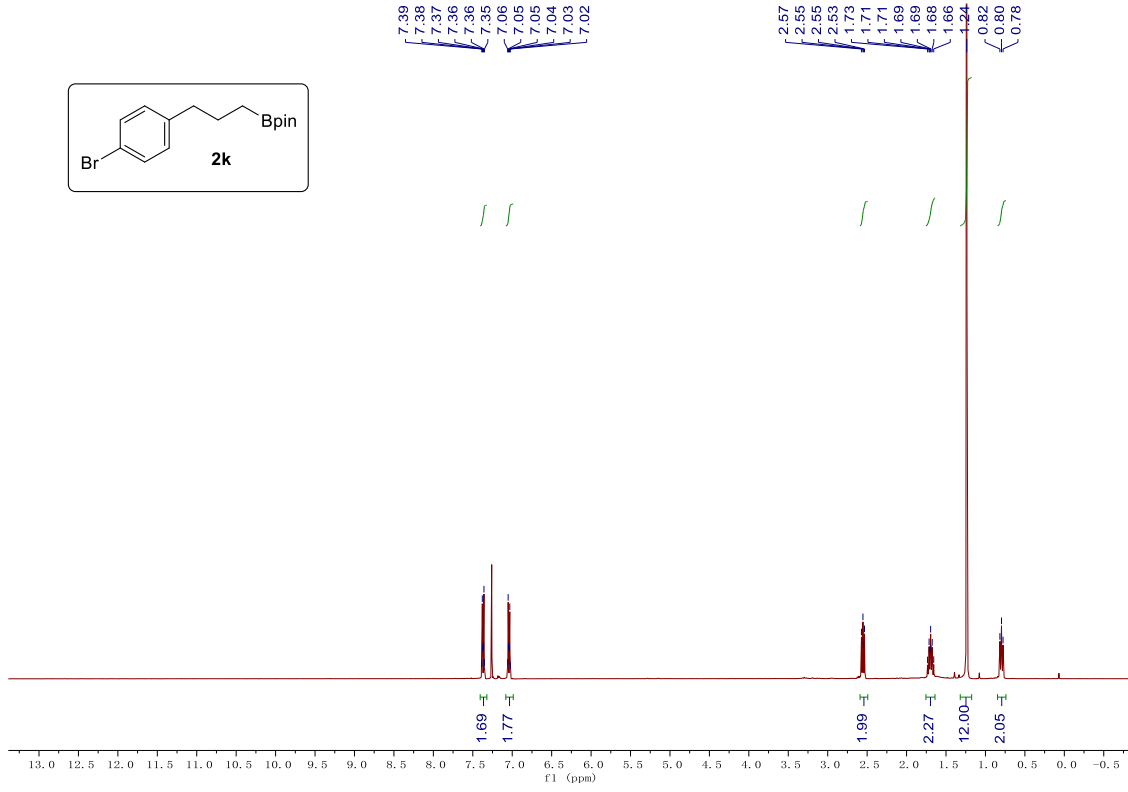
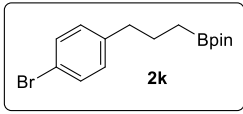
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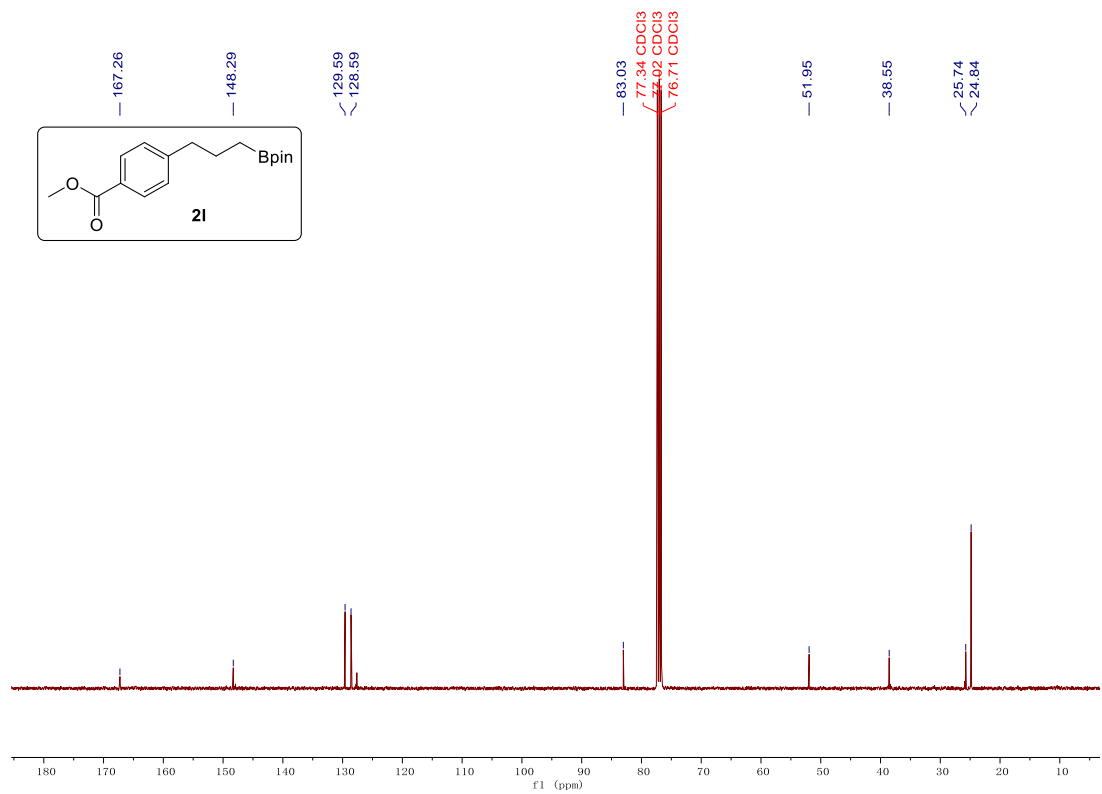
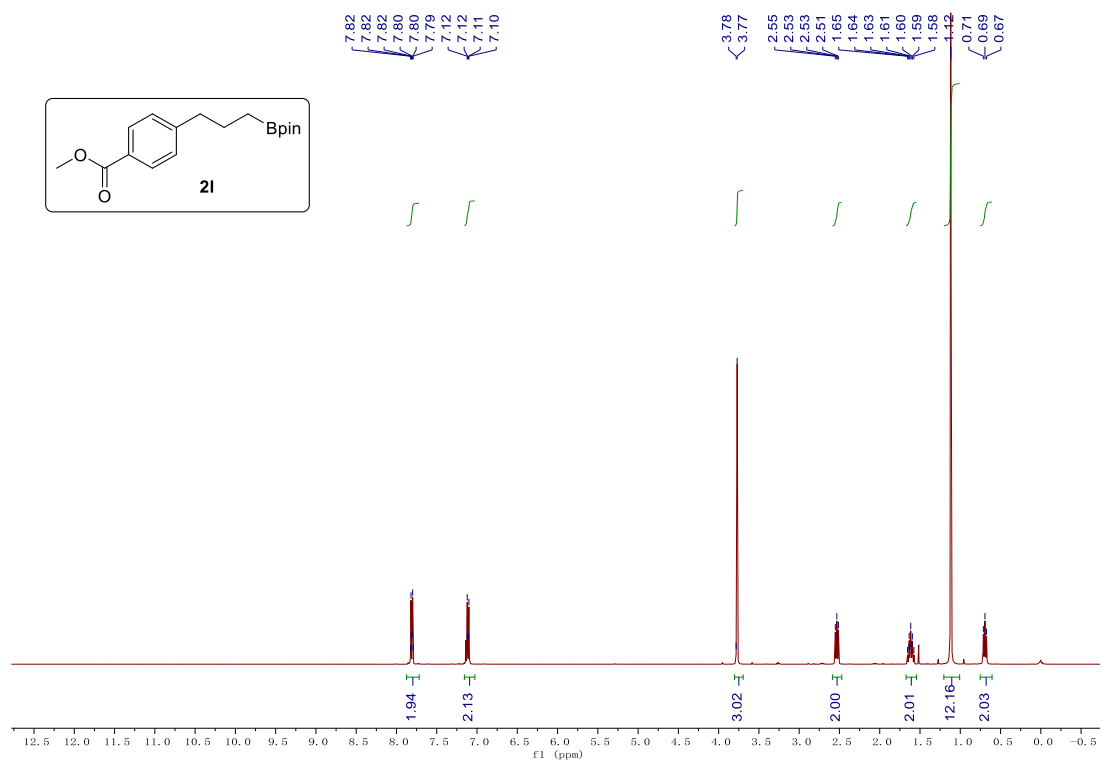
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 < 35.33

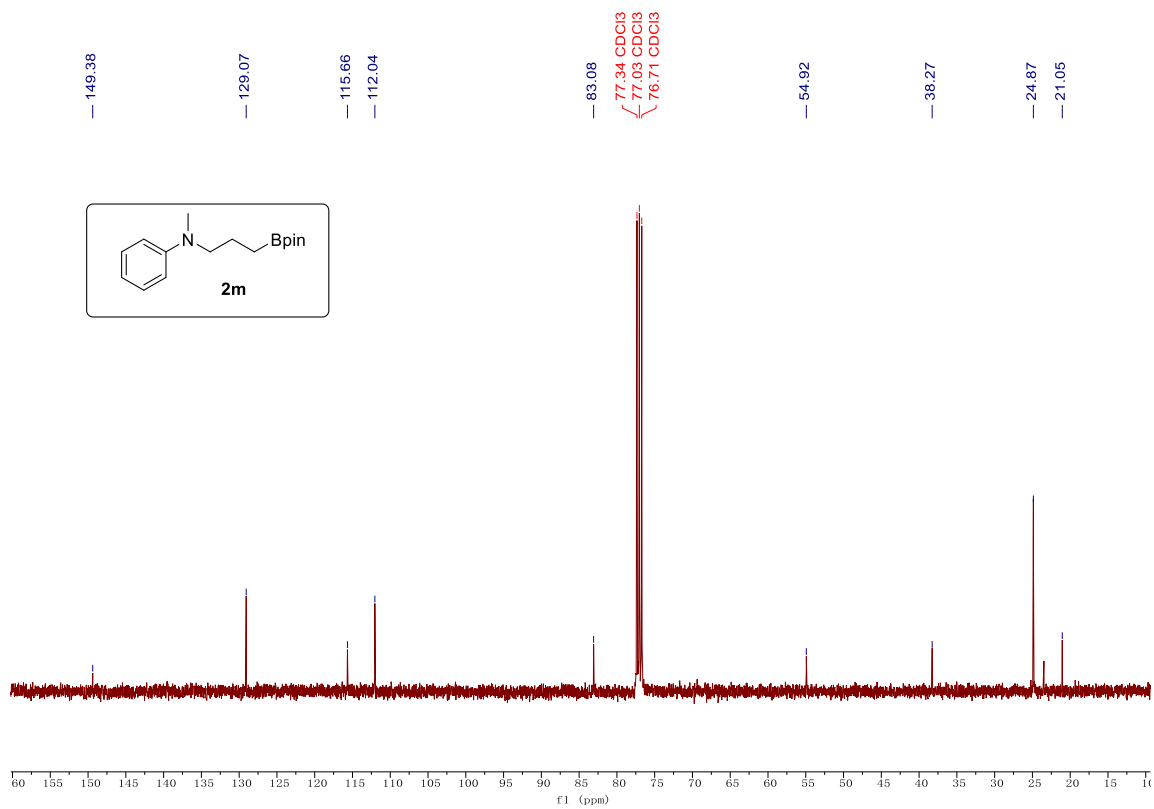
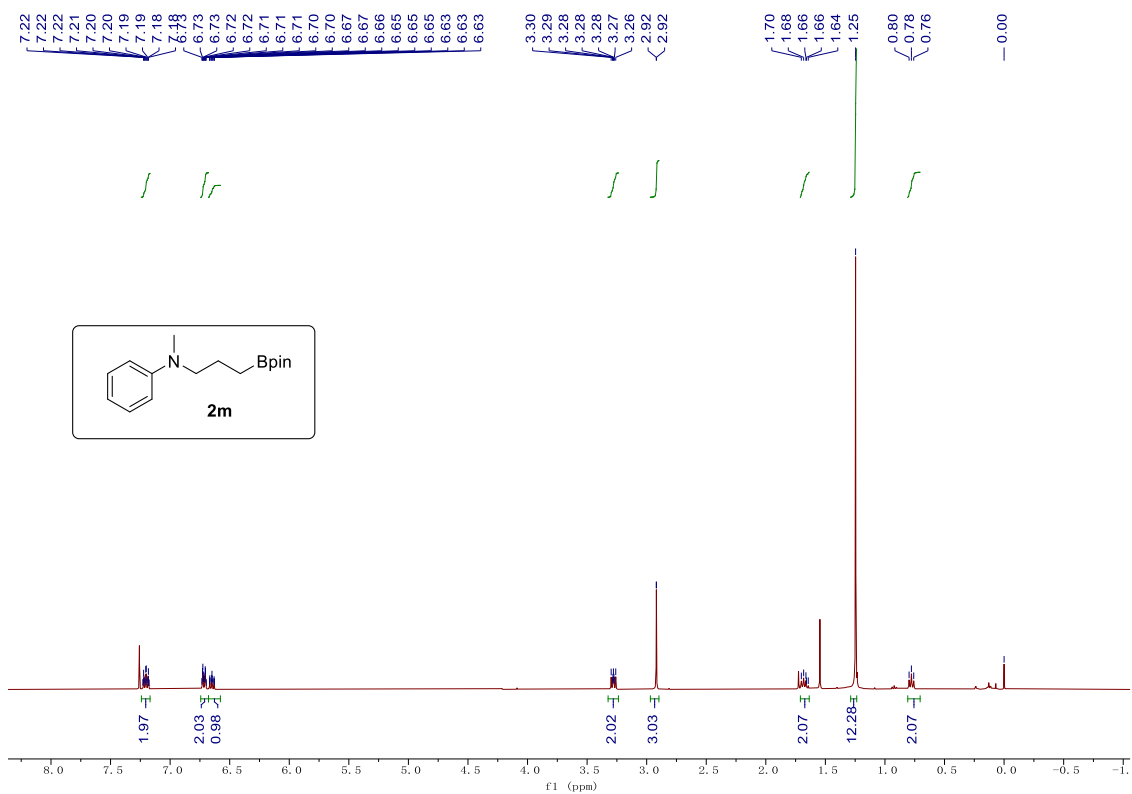
< 24.83
 < 24.77

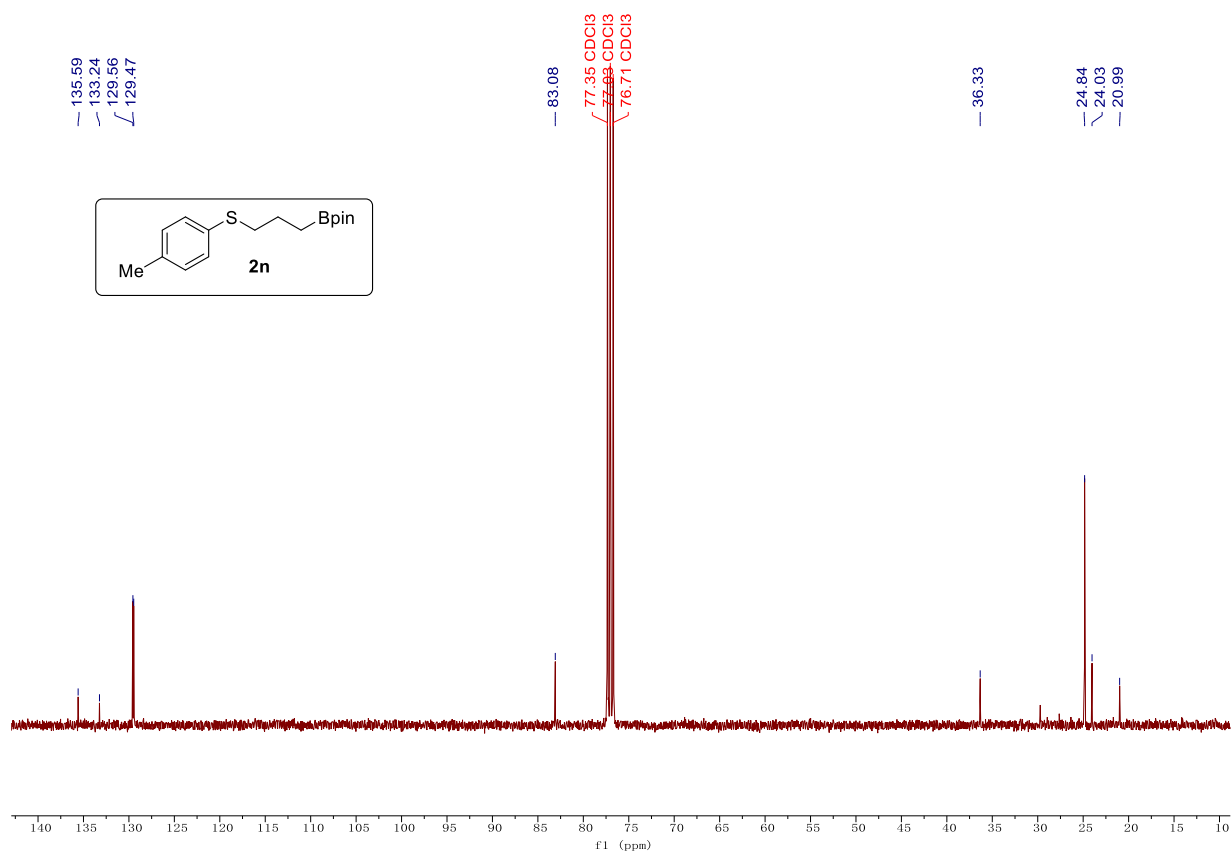
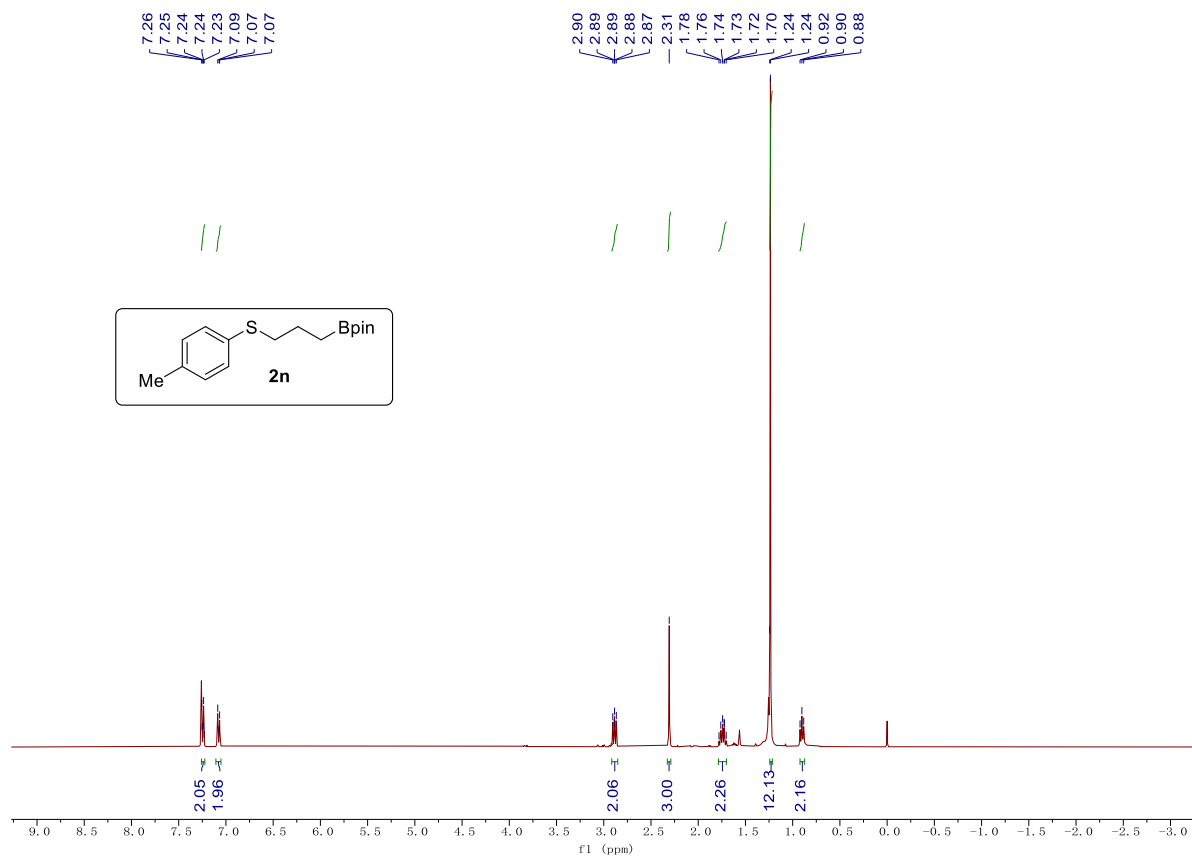
— 15.45

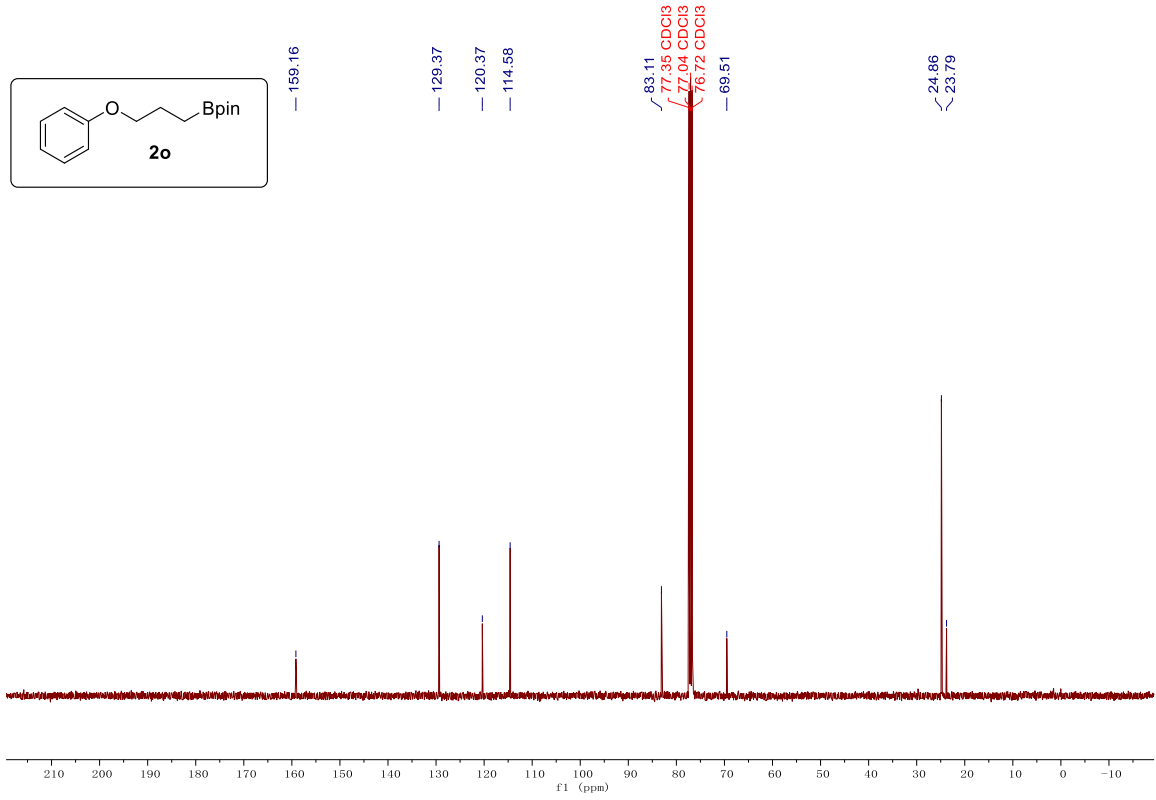
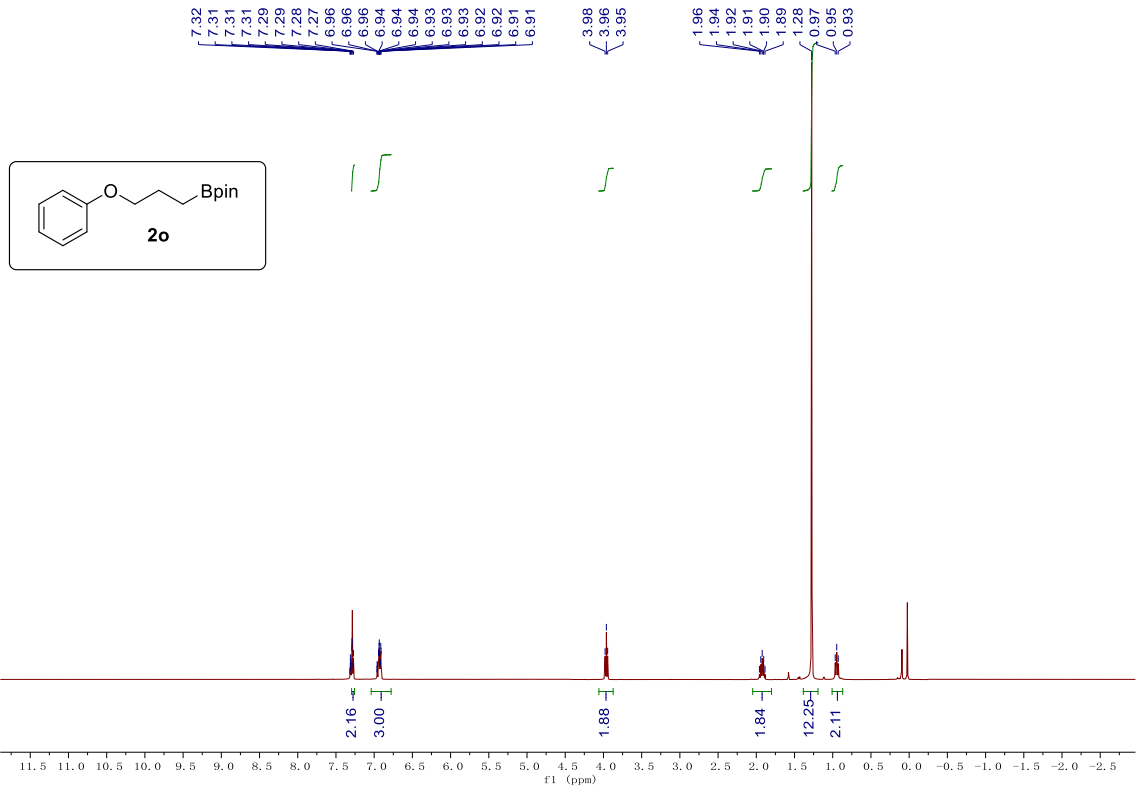


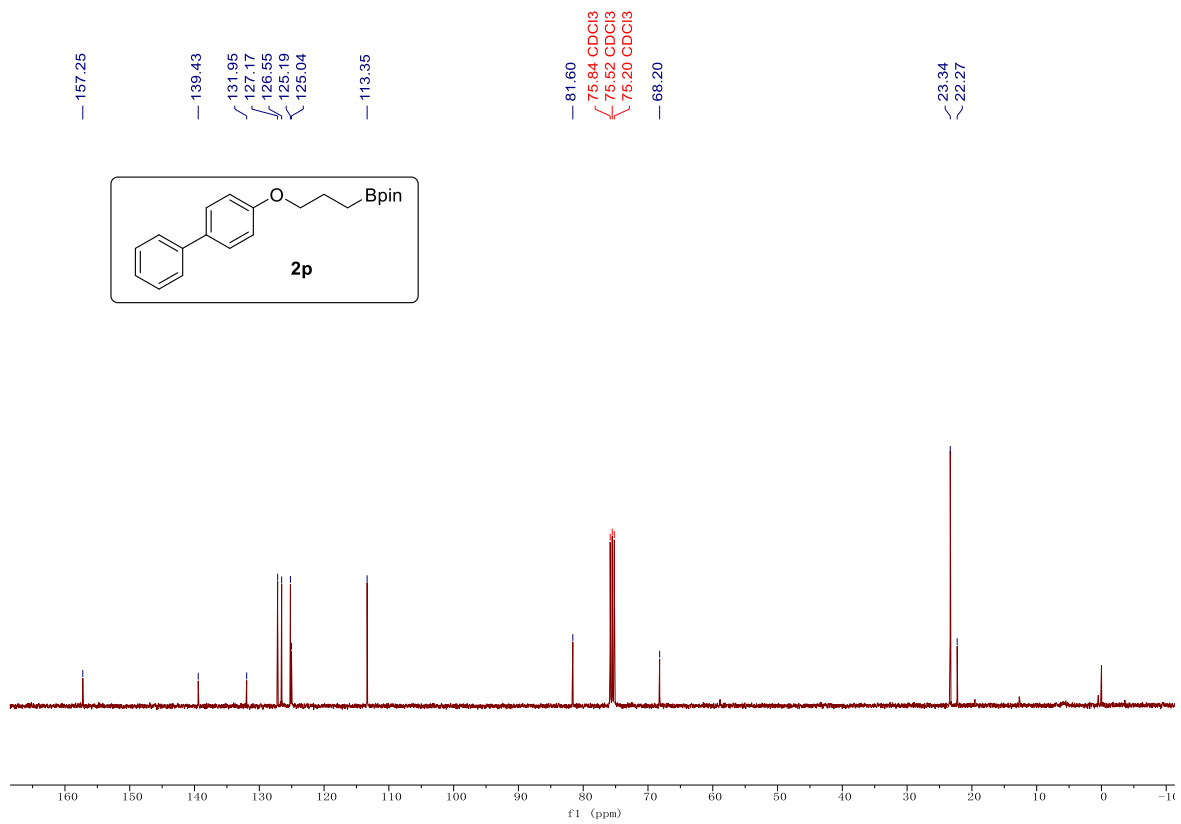
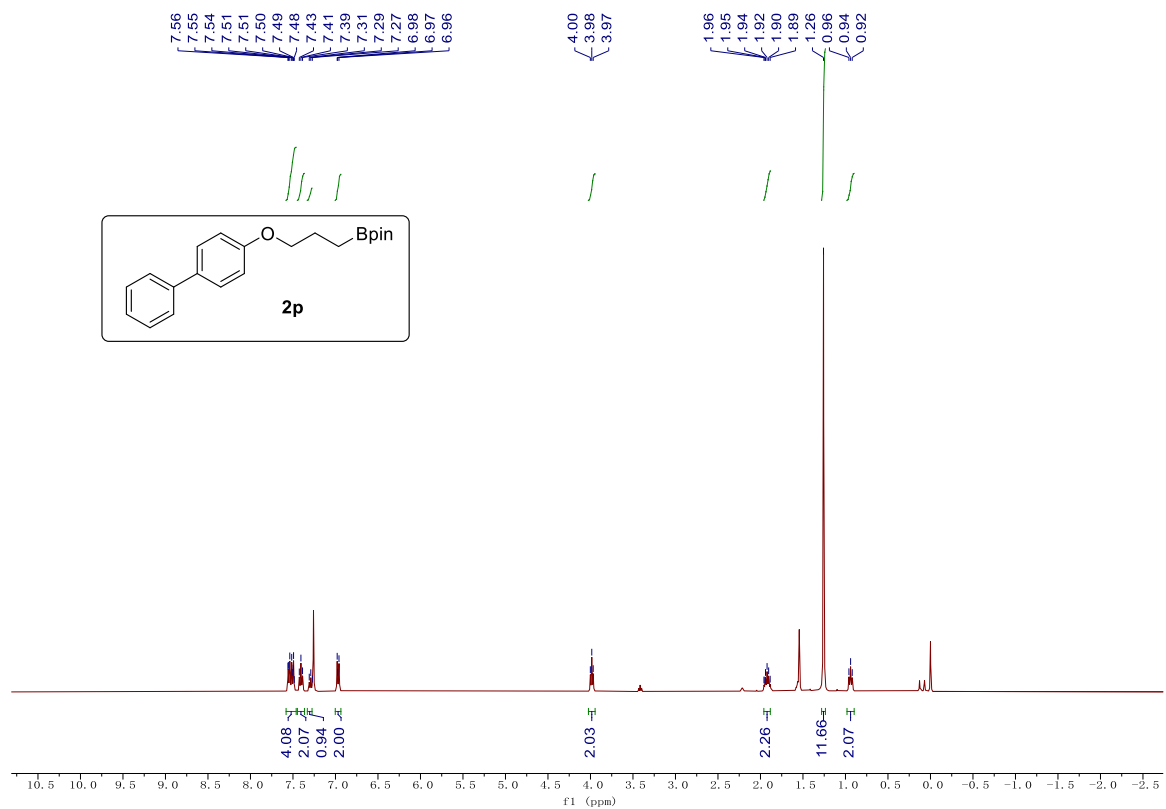


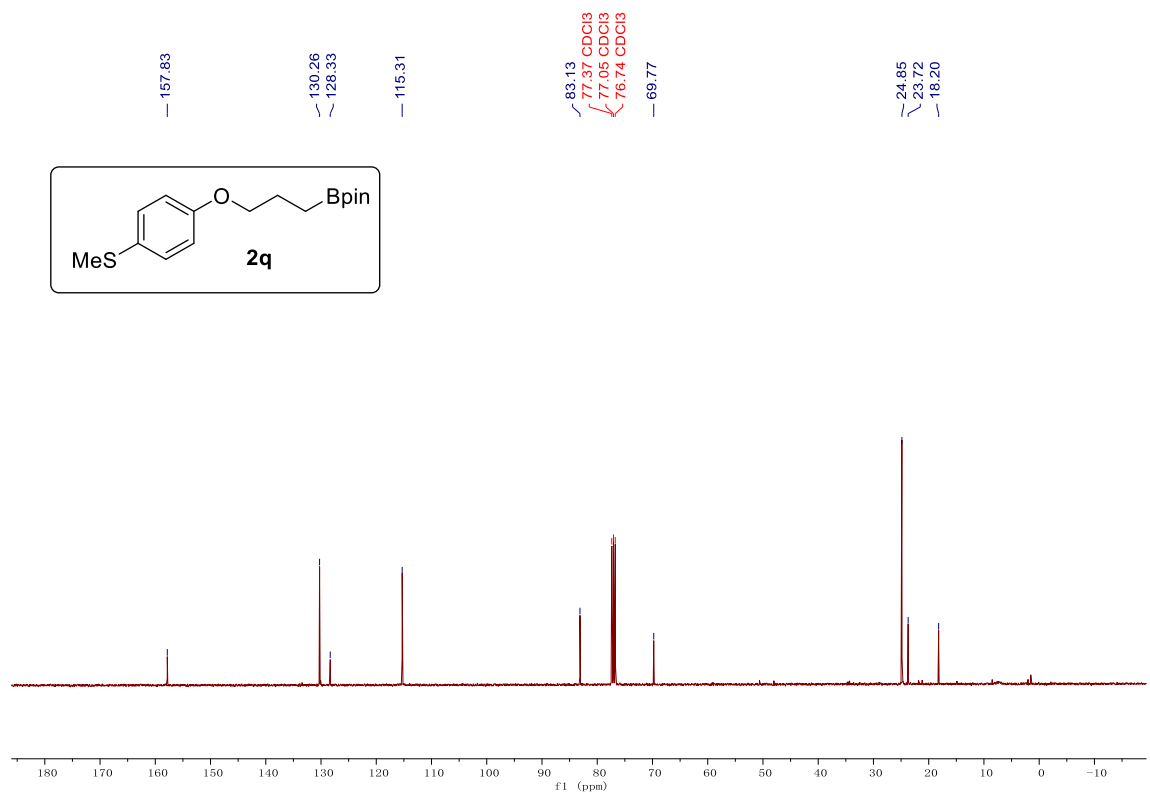
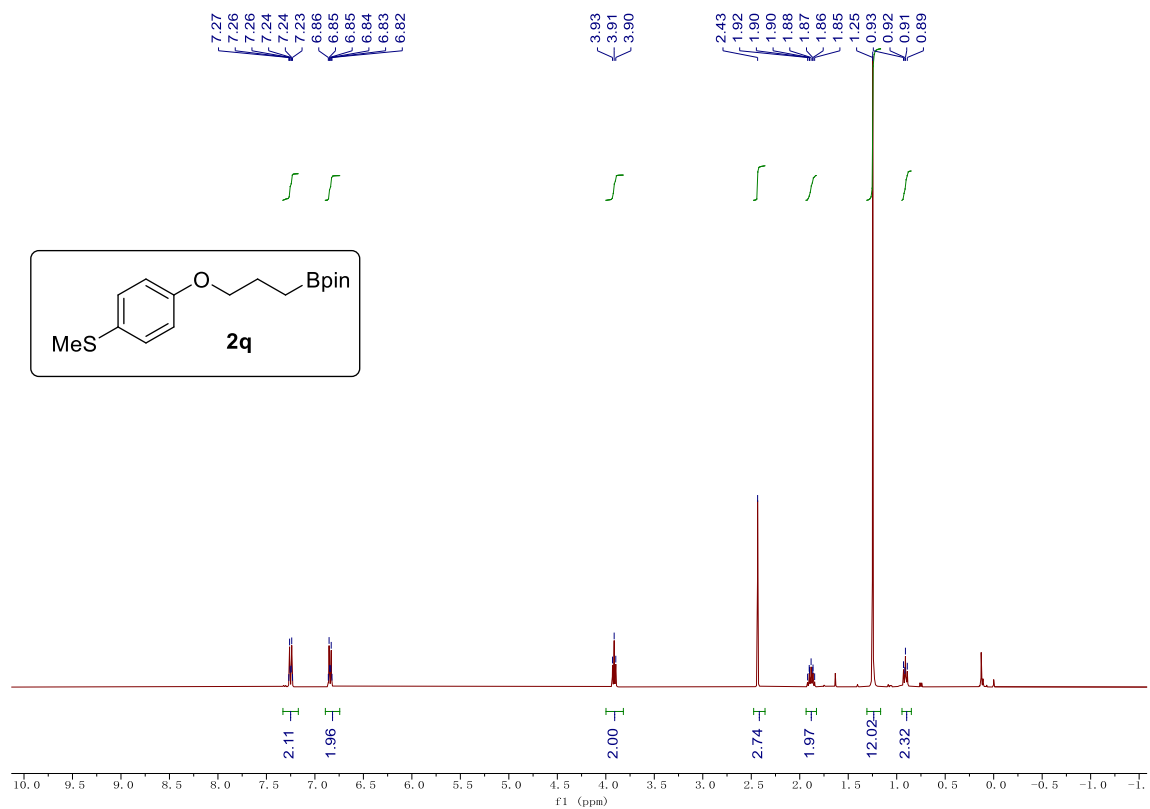


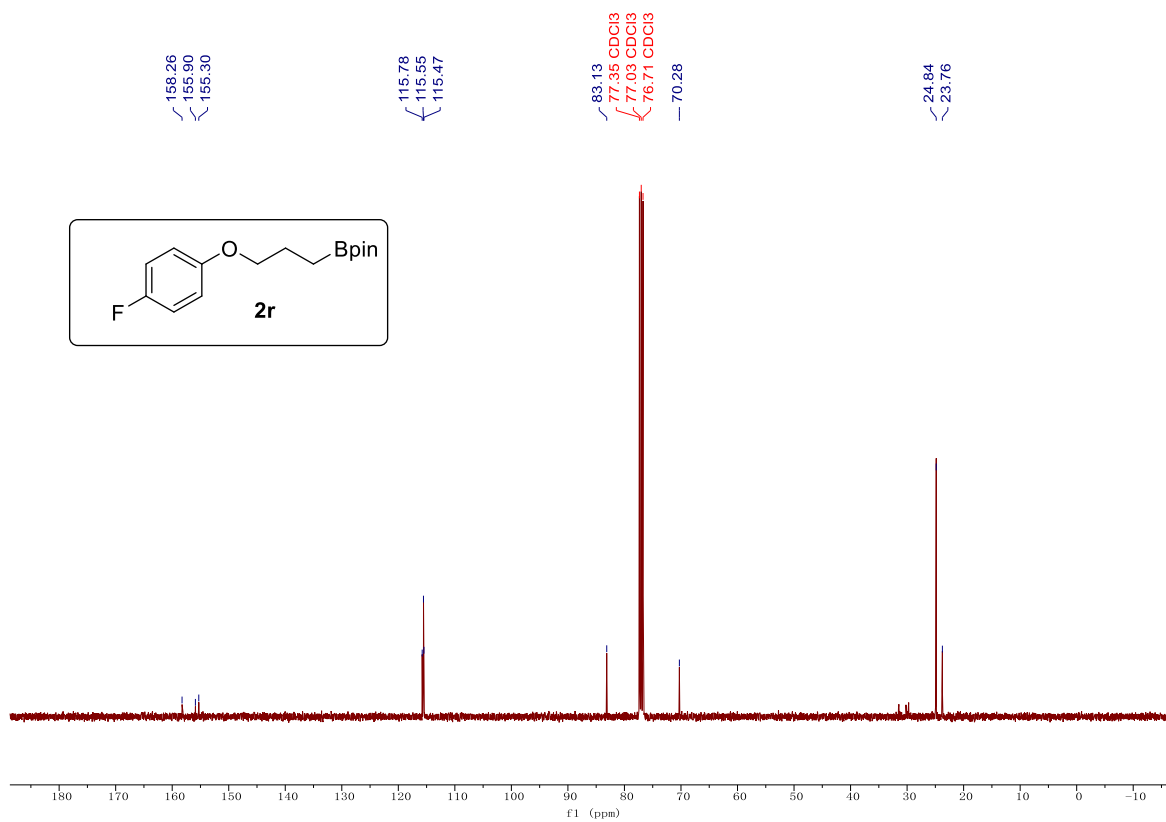
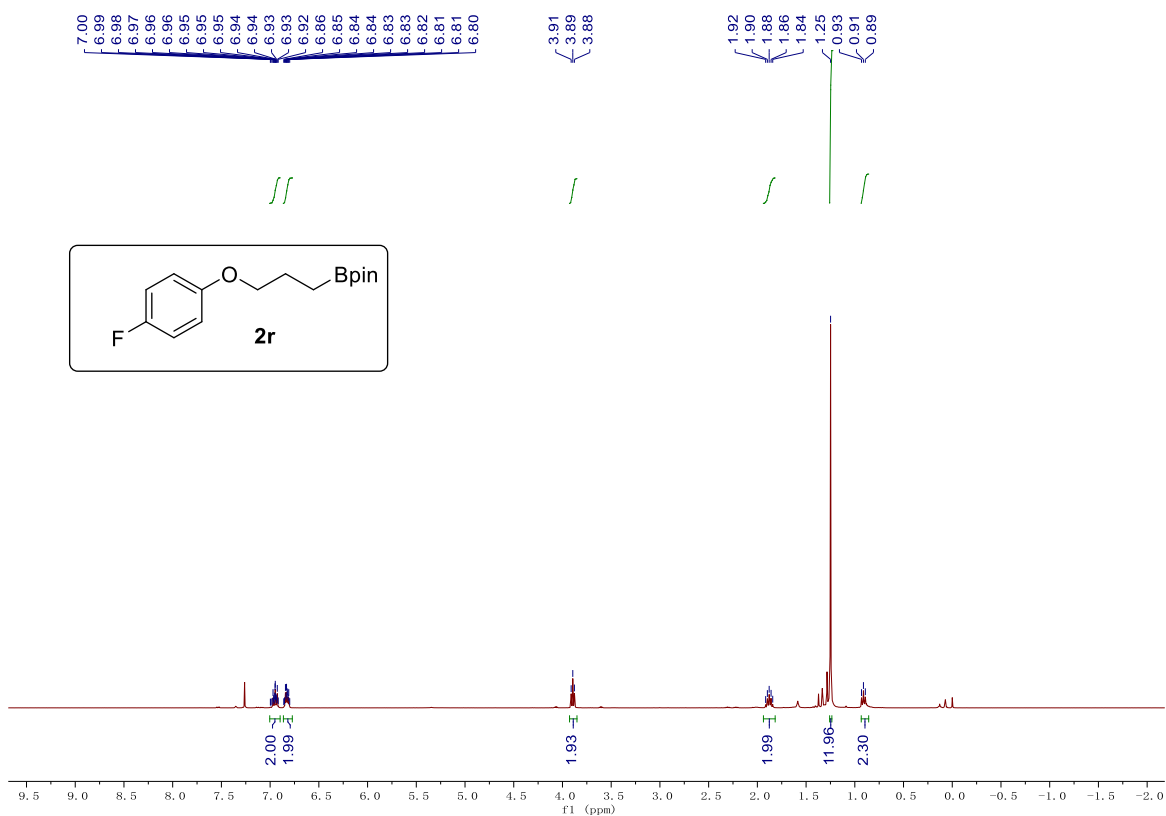


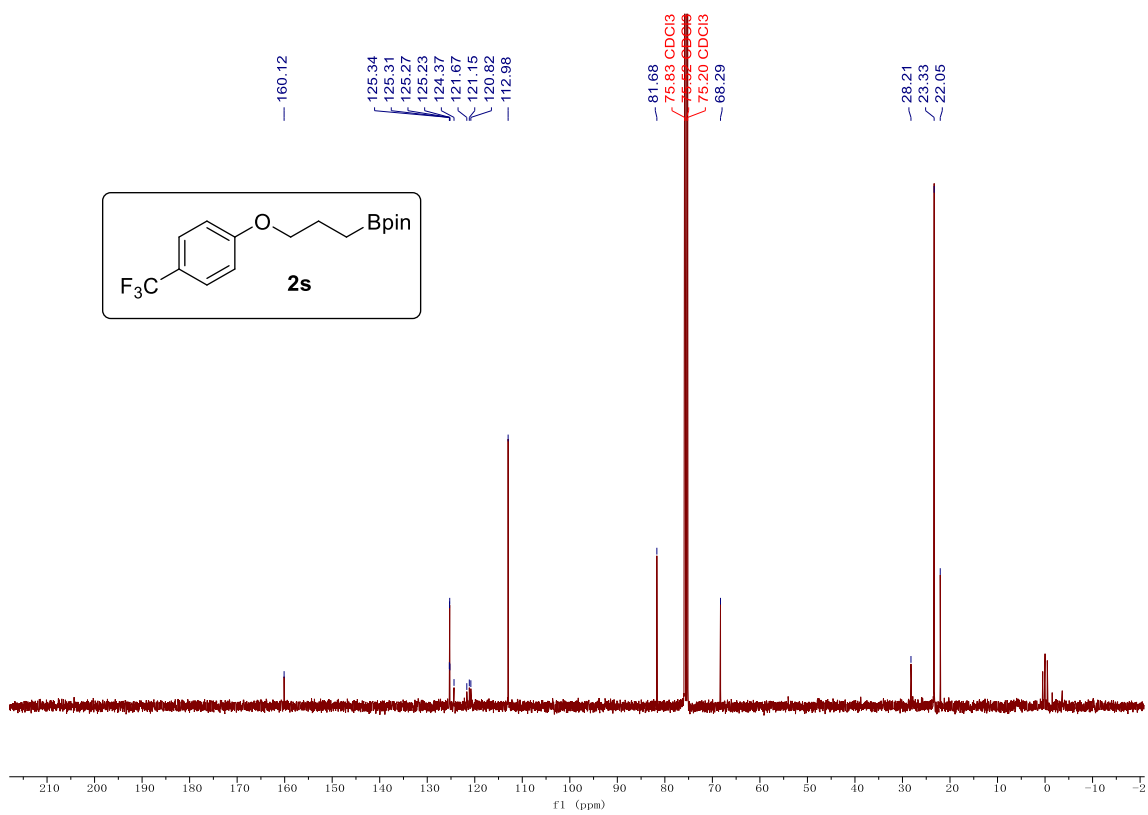
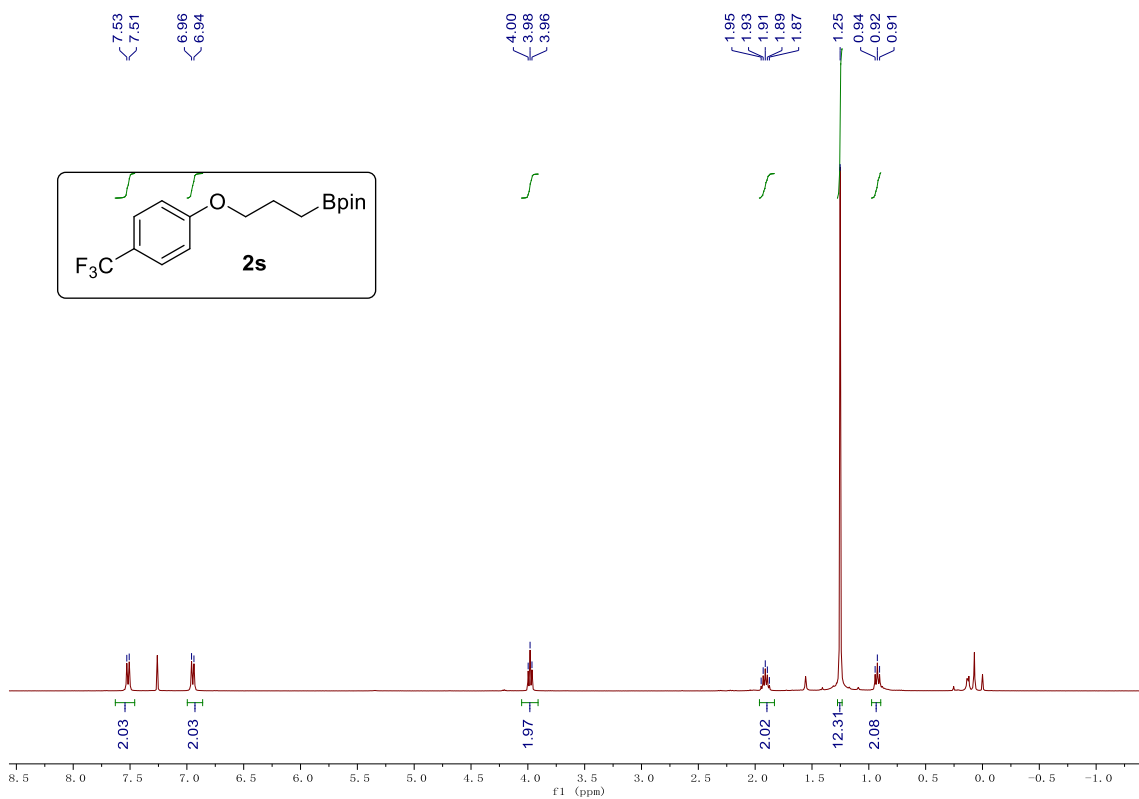


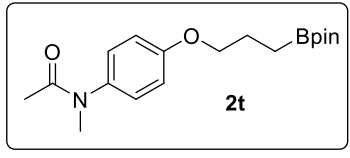
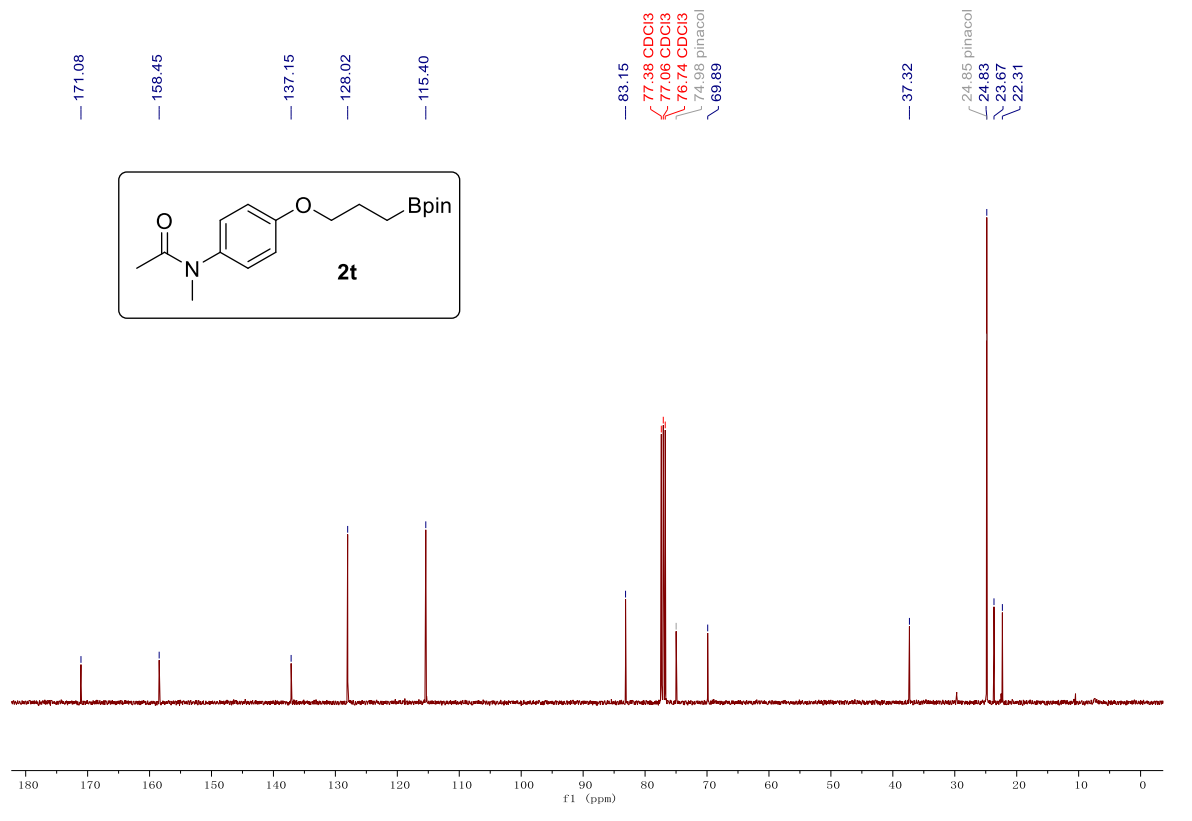
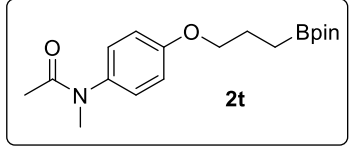
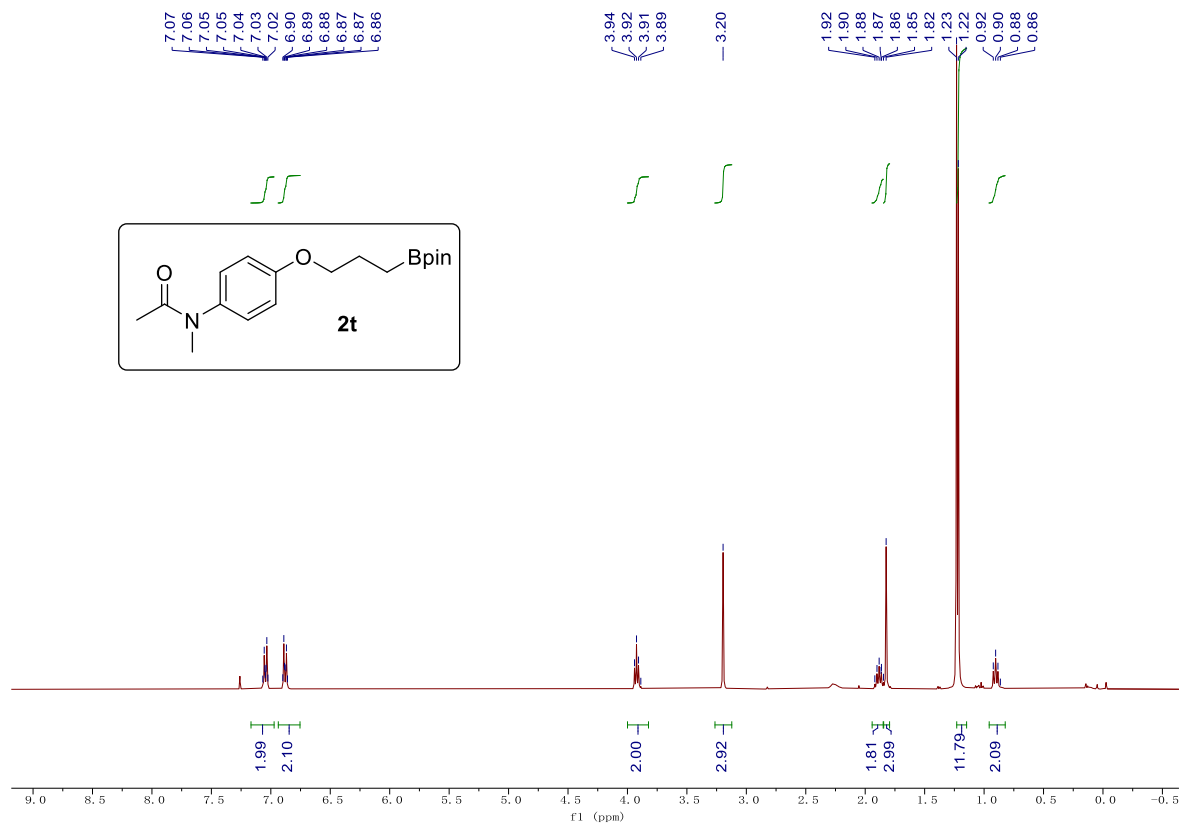


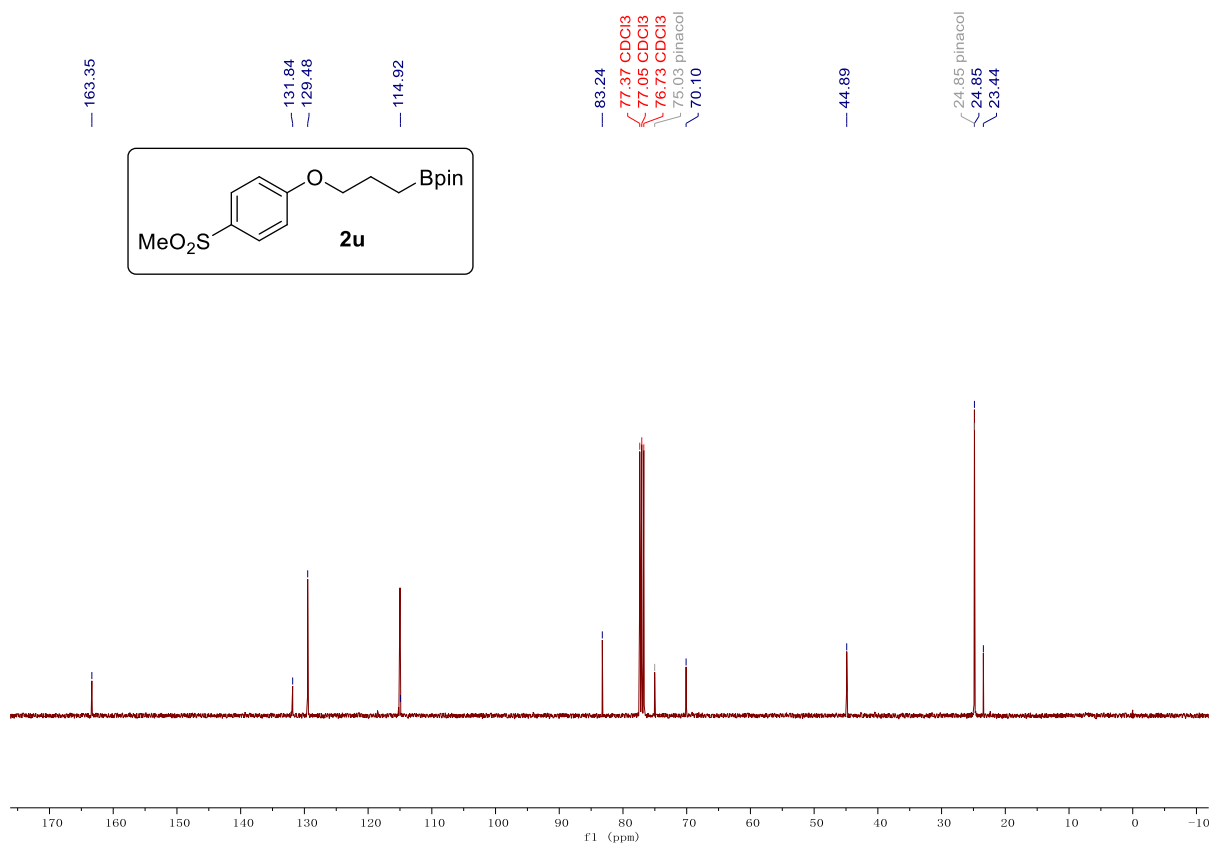
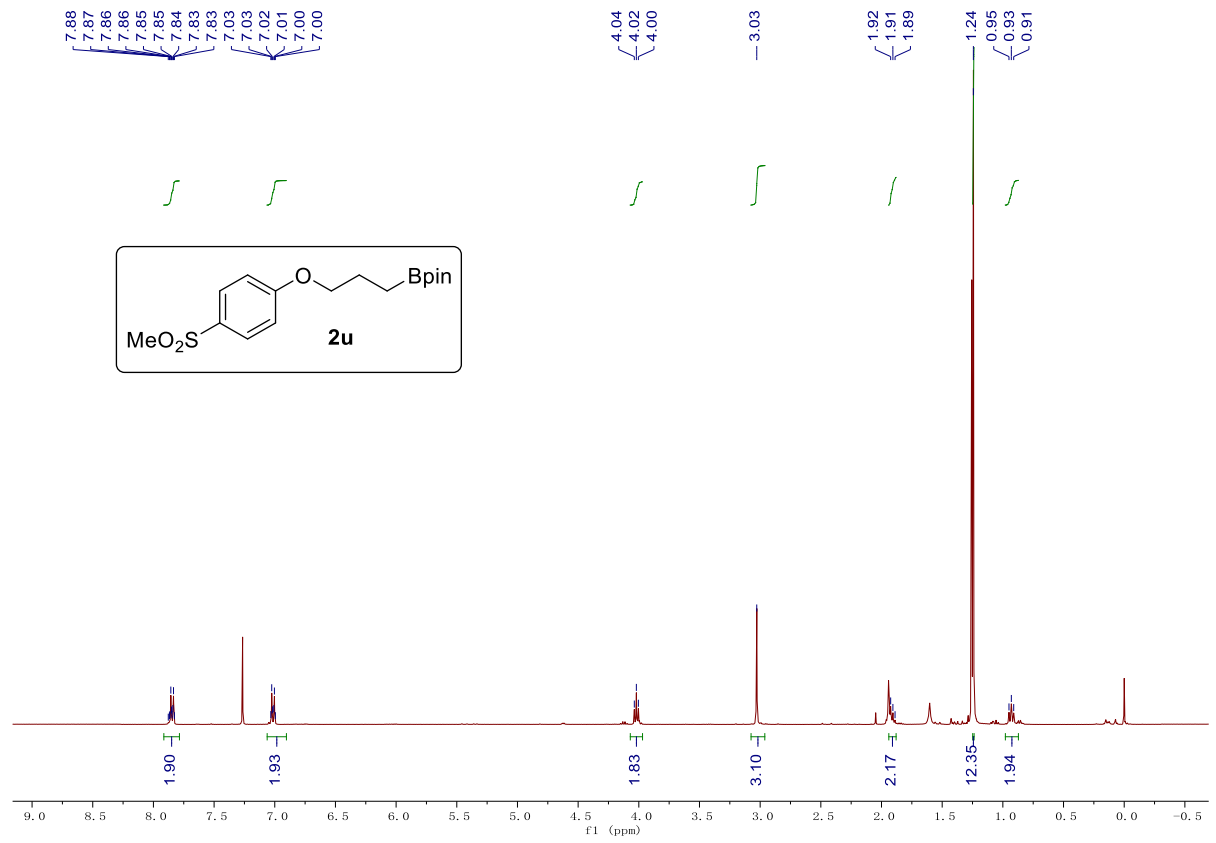


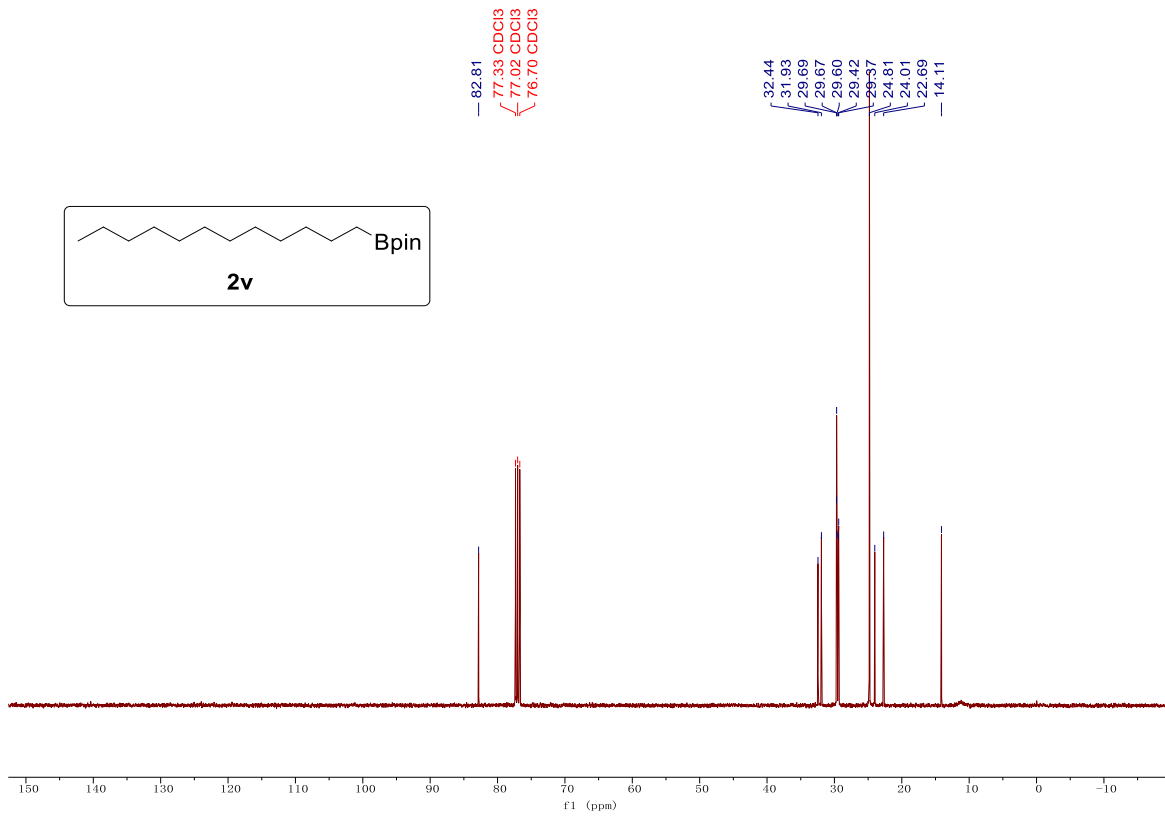
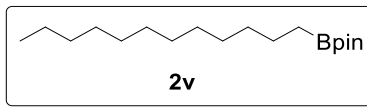
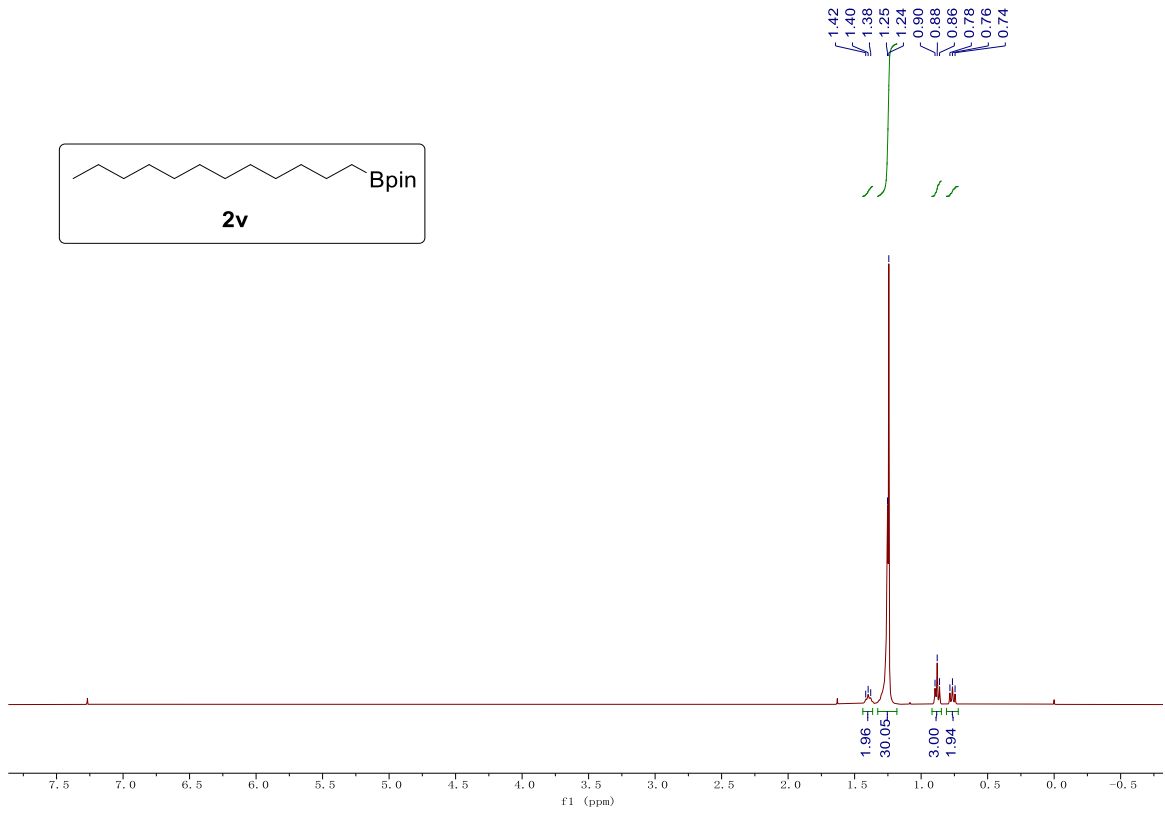
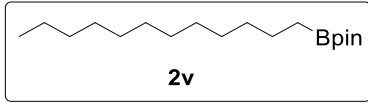


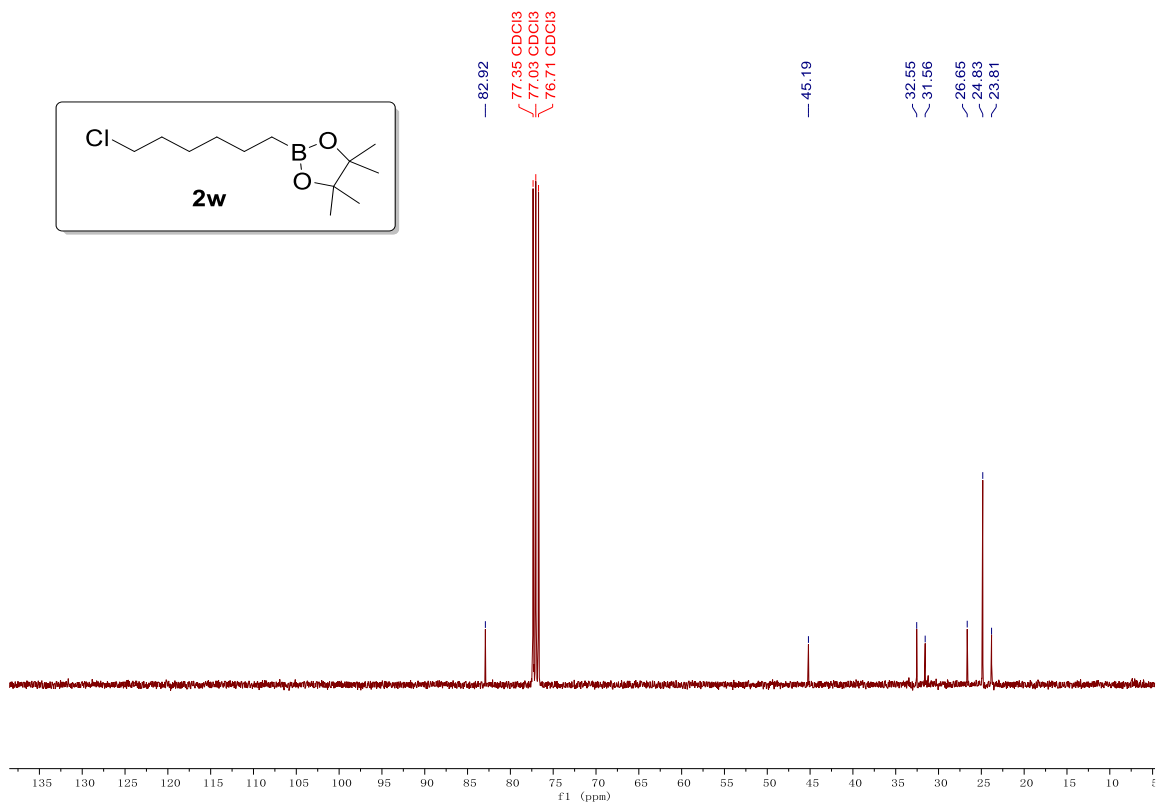
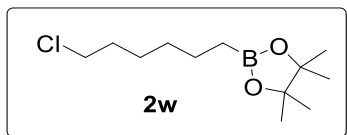
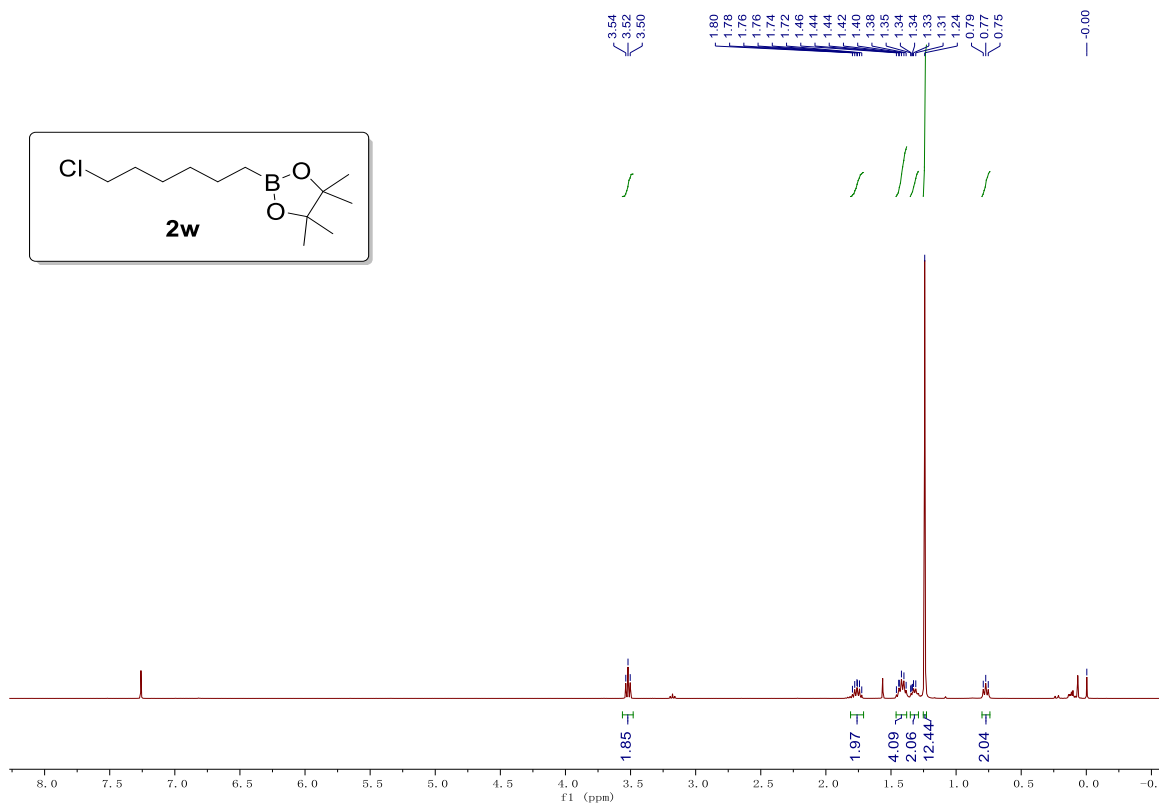
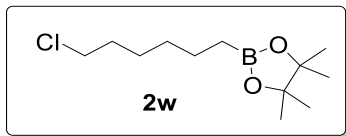


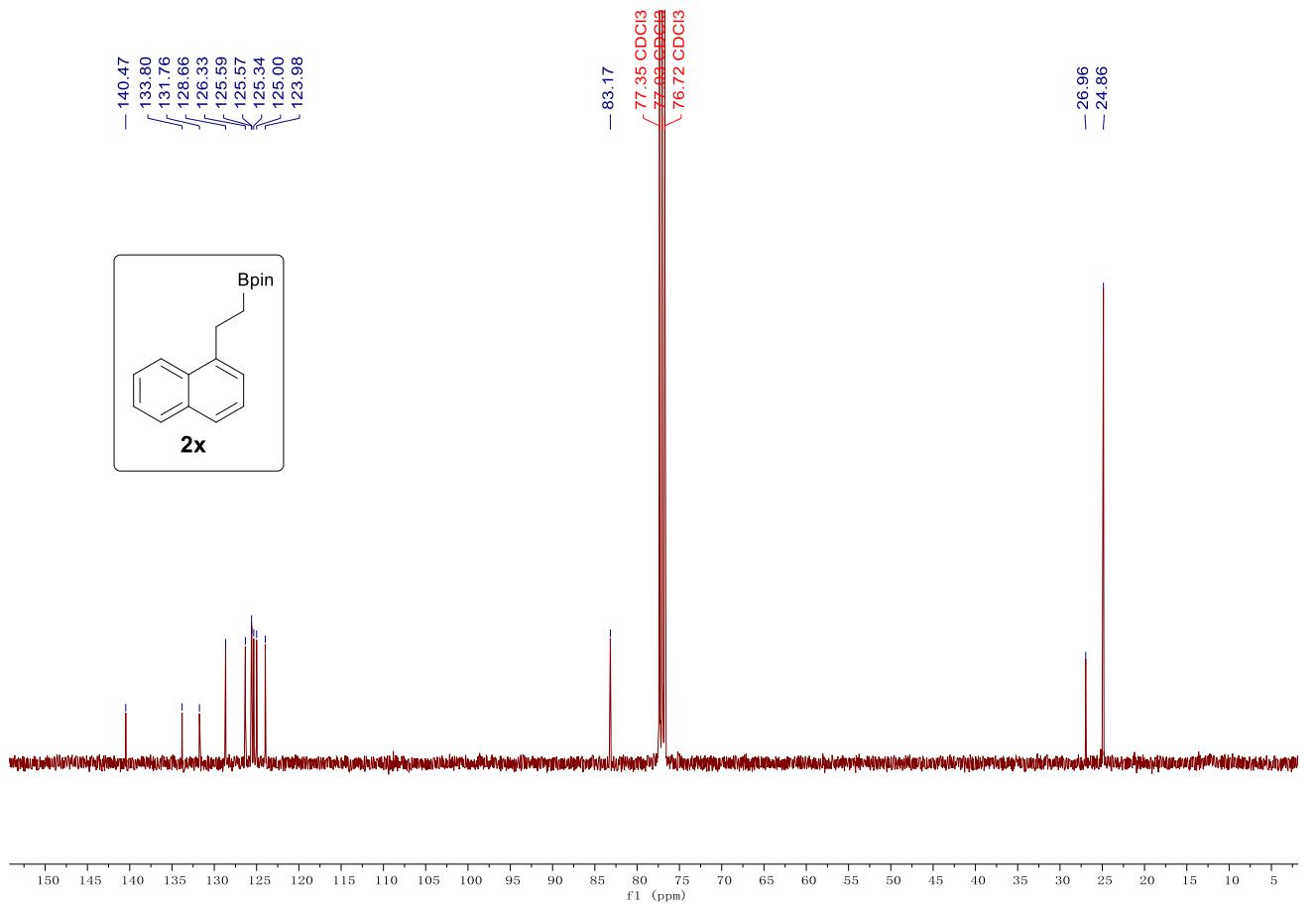
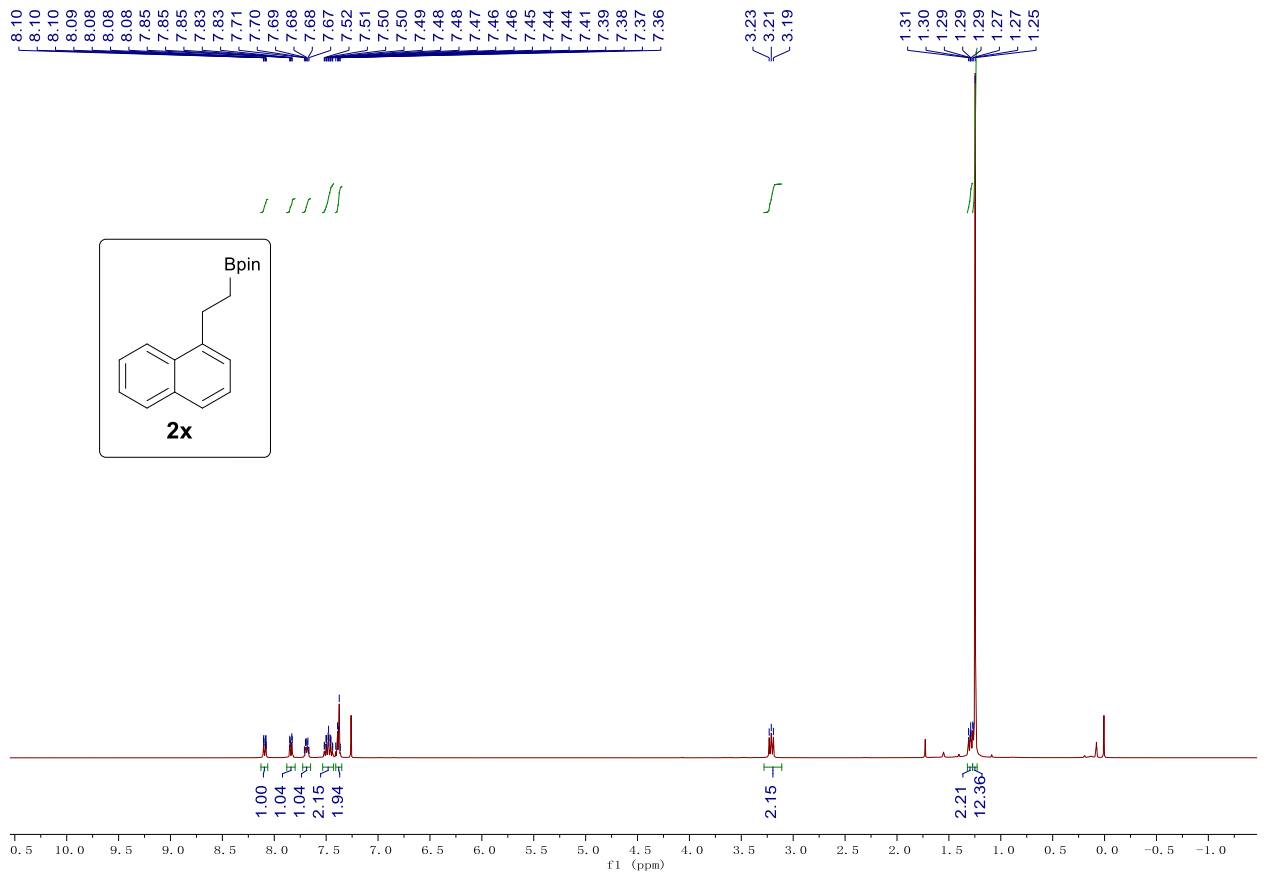


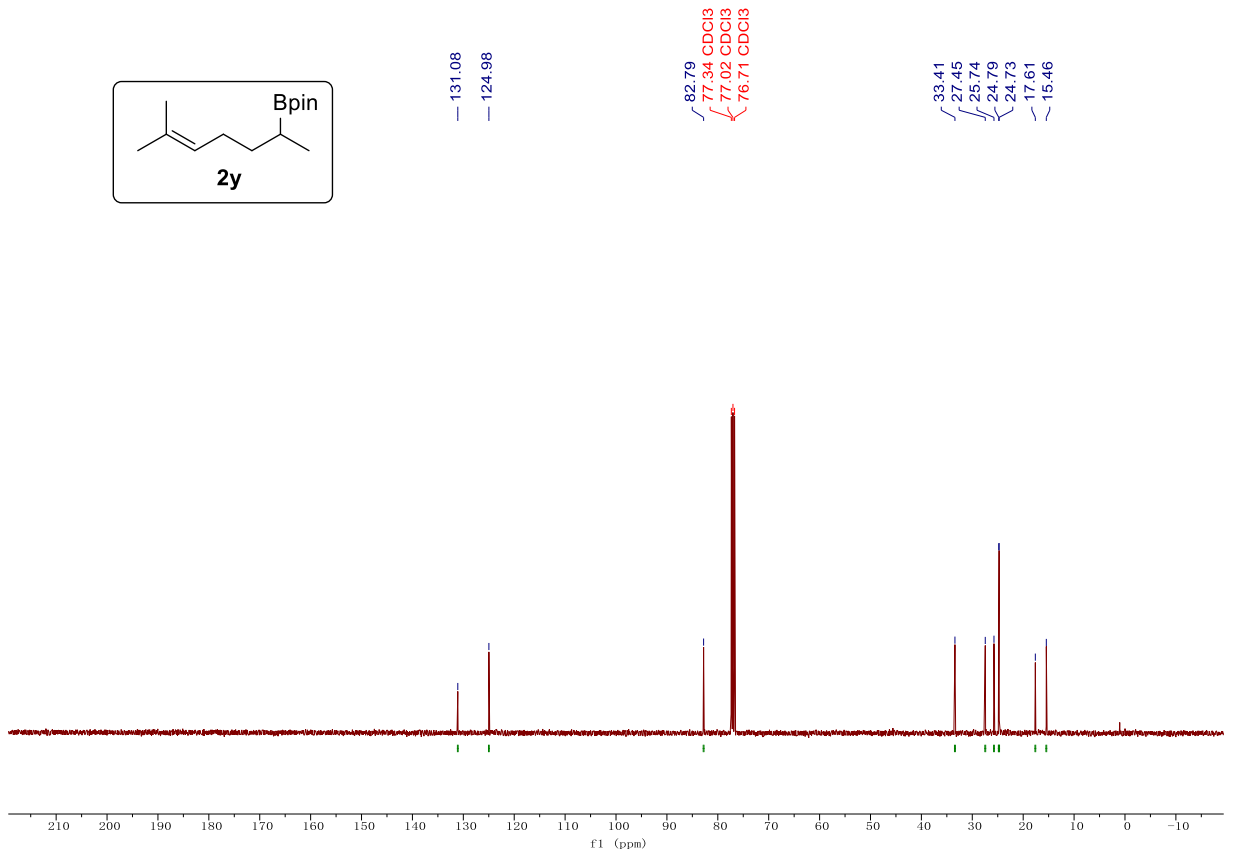
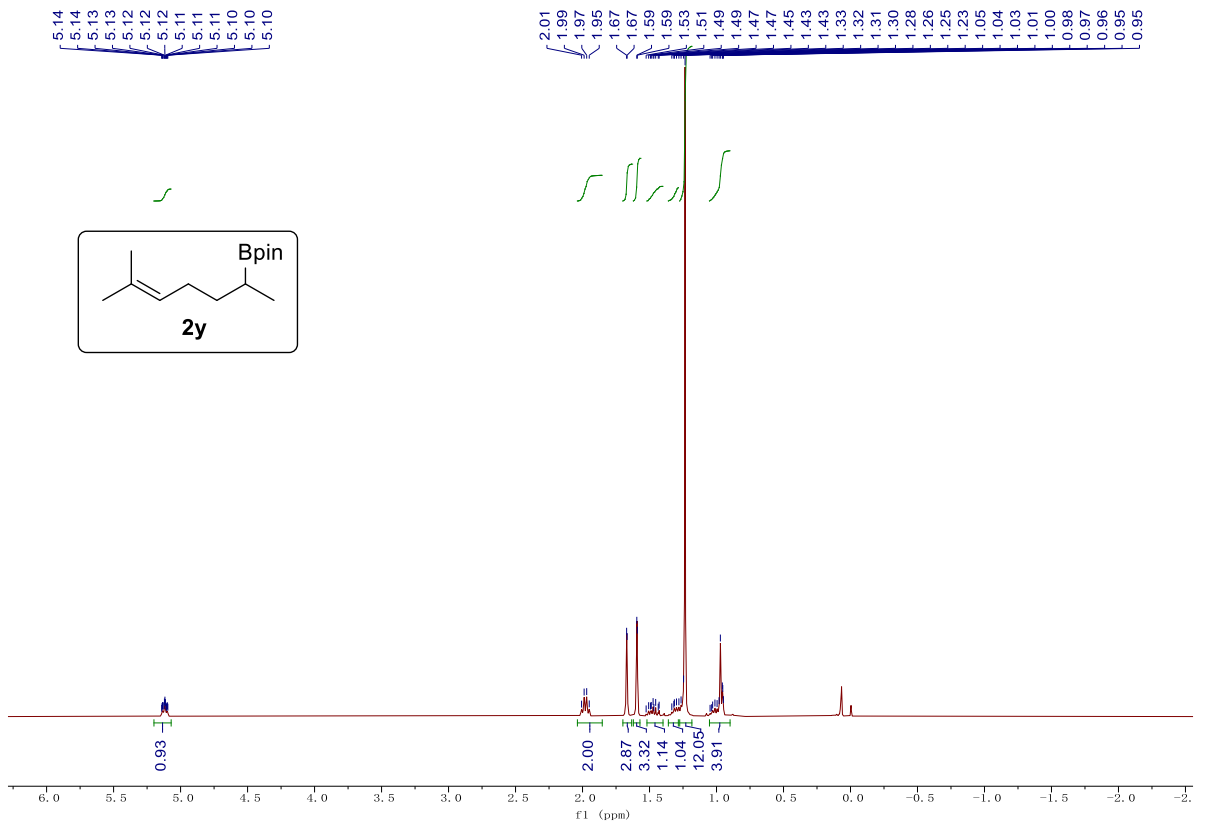


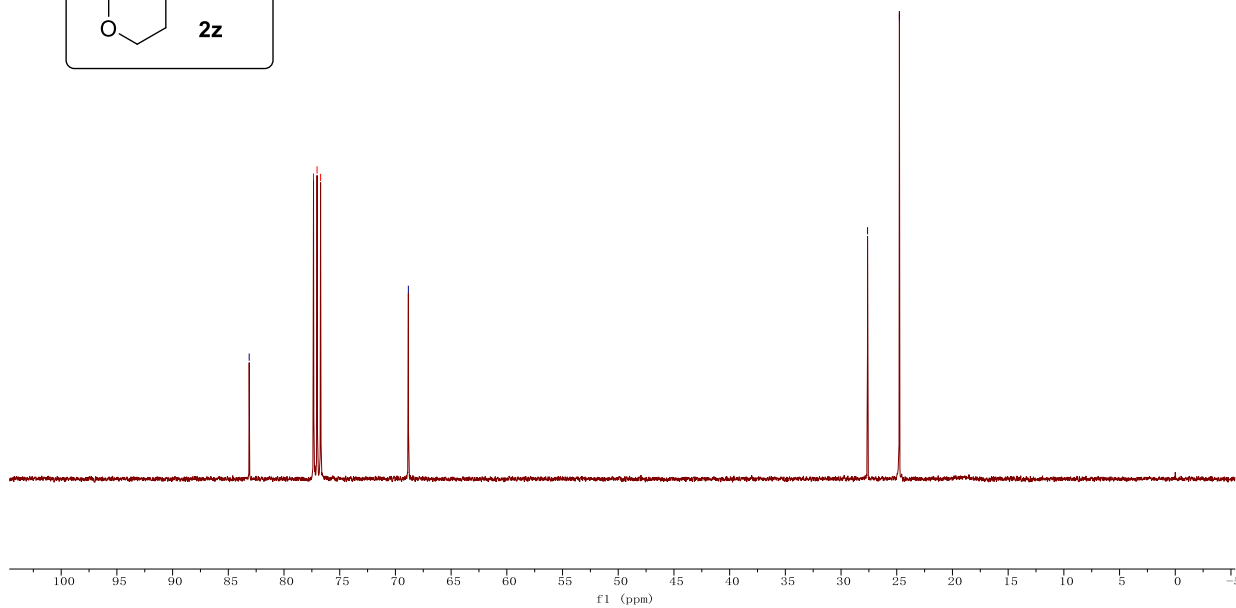
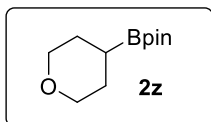
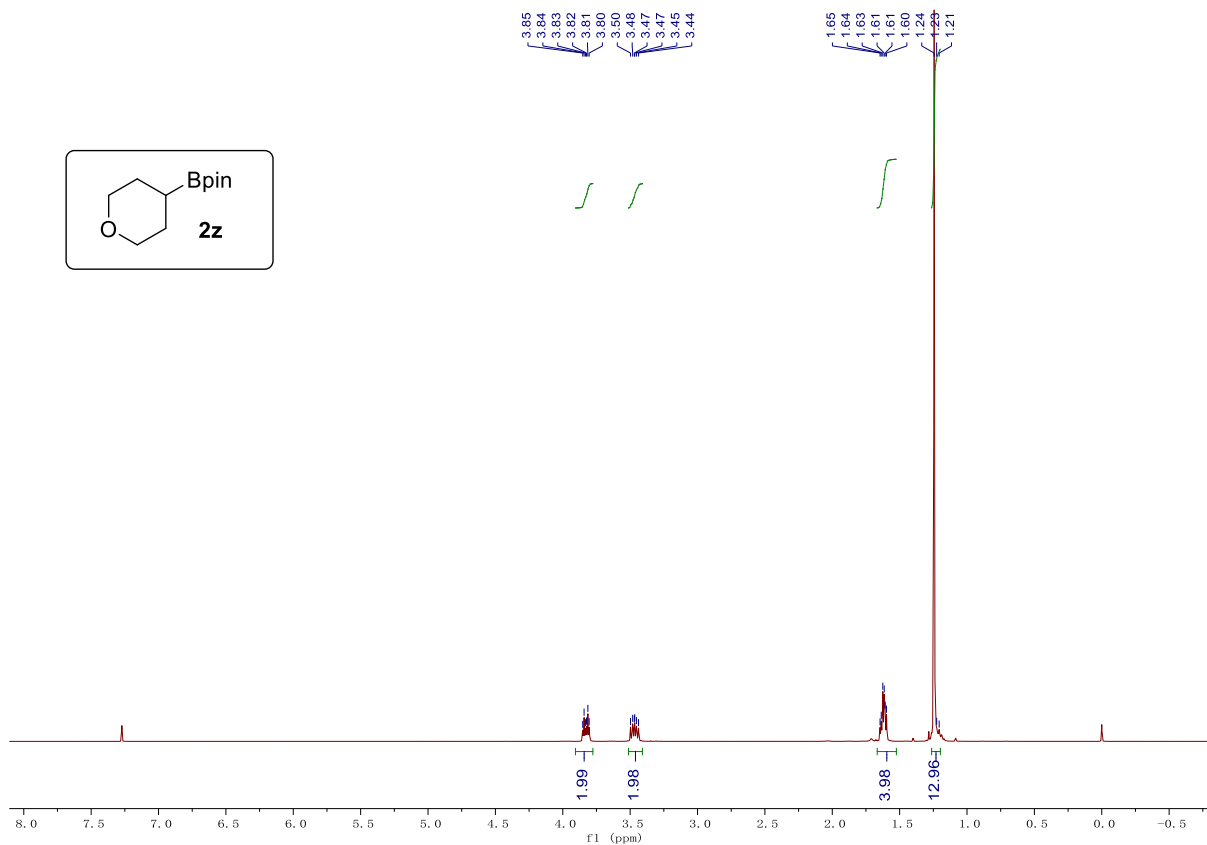
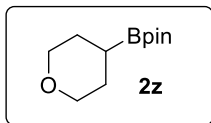


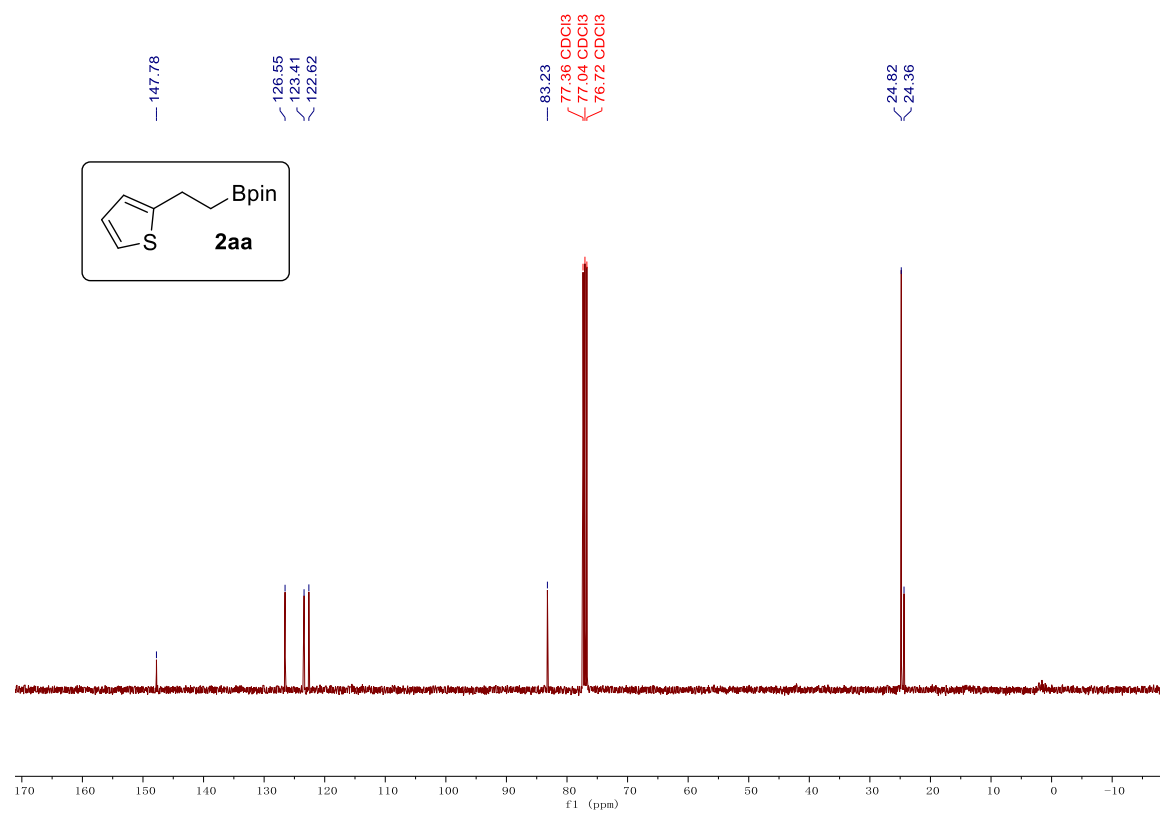
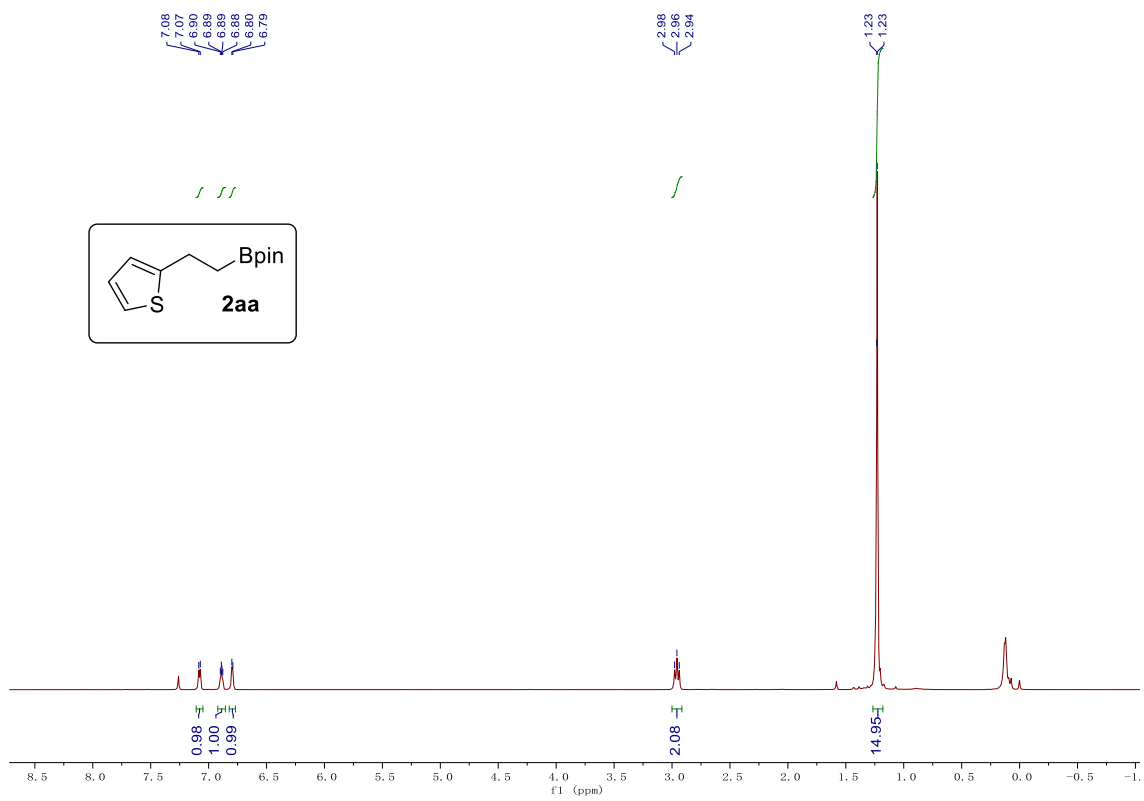


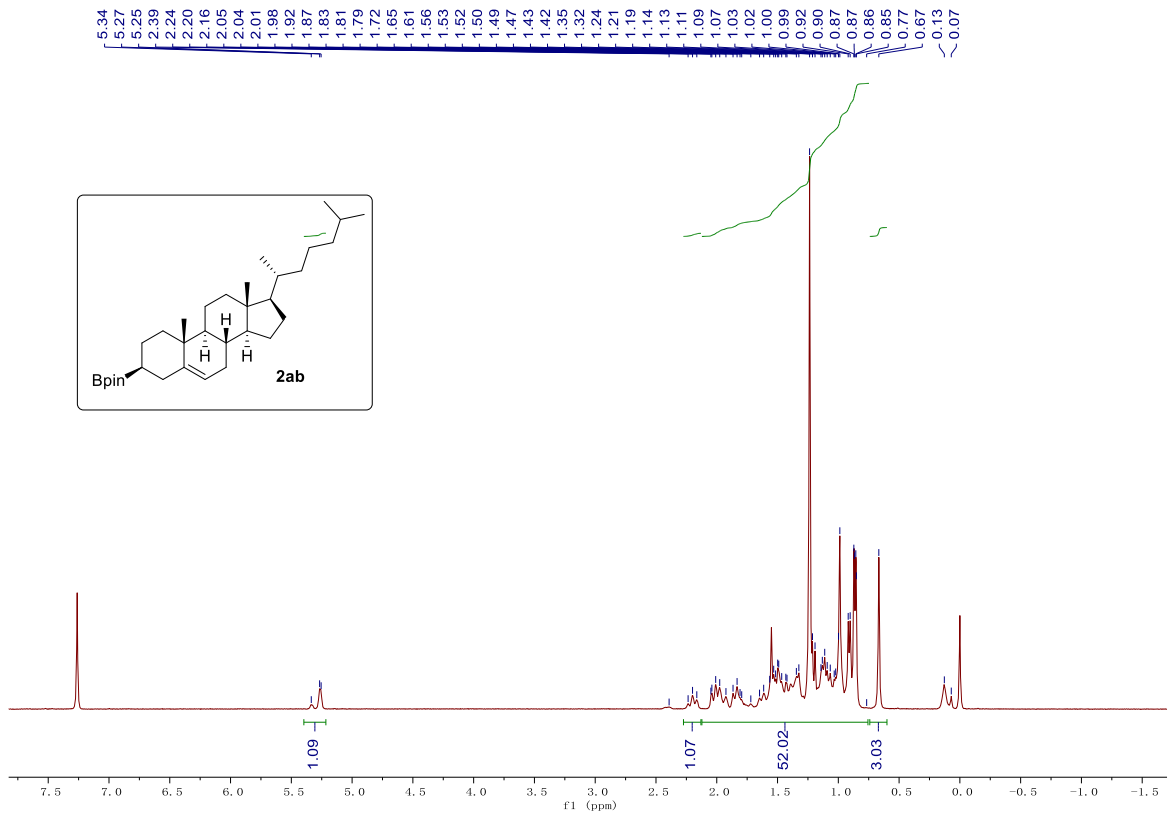












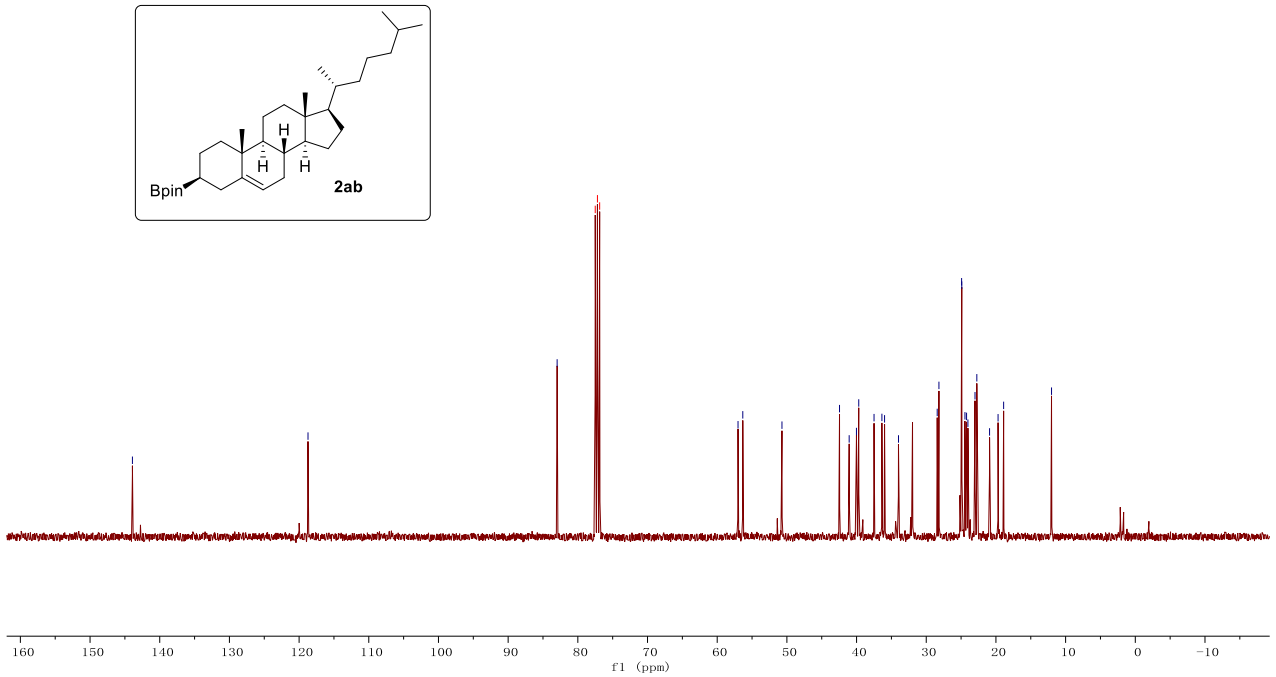
143.92

118.72

82.97

77.50 CDCl₃
77.19 CDCl₃
76.87 CDCl₃

57.01
56.33
50.71
42.45
41.06
40.02
39.69
37.49
36.36
35.98
33.98
28.43
28.18
24.92
24.90
24.45
24.21
24.02
23.00
22.74
20.91
19.69
18.89
12.02



9. References

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