Supporting Information

Transition-Metal-Free Borylation of Alkyl Iodides via a Radical Mechanism

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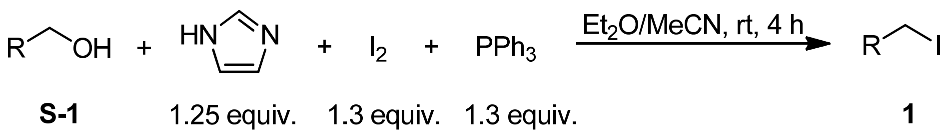
Contents

1. General information

Solvents were purchased from TONGGUANG CHEMICAL, Beijing or BEIJING CHEMICAL, in GR (or CCER). If not clarified, chemicals are purchased from ENERGY CHEMICAL. Purification of products was conducted by column chromatography on silica gel (200-300 mesh, for some cases 300-400 mesh were used, from Qingdao, China). NMR spectra were measured on a Bruker ARX400 (^{1}H at 400 MHz, ^{13}C at 101 MHz) magnetic resonance spectrometer. Chemical shifts (δ) are reported in ppm using tetramethylsilane as internal standard (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet), and coupling constants (*J*) were reported in Hertz (Hz). 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). EPR experiments were conducted using Bruker Elexsys E580 Spectrometer. The substrates were purchased from commercial sources unless otherwise noted.

2. Preparation of substrates

2.1 Preparation of alkyl iodides from alcohol (1f, 1k, 1m, 1o)



The alkyl iodides **1** were prepared according to literature procedure[1]. A 100 mL round-bottom flask was charged with alcohol (**S-1**, 10 mmol), imidazole (12.5 mmol, 1.25 equiv., 851 mg), I_2 (13 mmol, 1.30 equiv., 3.30 g), PPh_3 (13 mmol, 1.30 equiv., 3.41 g), and Et_2O/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 was dried over Na_2SO_4 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**.

(2-iodoethyl)cyclohexane (1f) 2.19 g, 92% yield. Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.21 (t, *J* = 7.5 Hz, 2H), 1.97 – 1.57 (m, 7H), 1.48 – 1.32 (m, 1H), 1.32 – 1.08 (m, 3H), 0.99 – 0.80 (m, 2H).[2]

1-bromo-4-(2-iodoethyl)benzene (1k) 3.21 g, 99% yield. Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.3 Hz, 2H), 7.07 (d, *J* = 8.3 Hz, 2H), 3.15 (t, *J* = 6.8 Hz, 2H), 2.69 (t, *J* = 7.3 Hz, 2H), 2.09 (p, *J* = 6.9 Hz, 2H).[3]

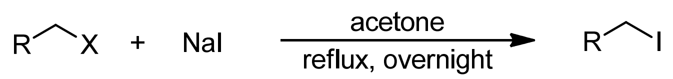
4-hydroxy-phenethyl iodide (1m) 2.25 g, 91% yield (40 mL DCM was used as solvent). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (d, *J* = 8.4 Hz, 2H), 6.78 (d, *J* = 8.5 Hz, 2H), 4.79 (s, 1H), 3.30 (t, *J* = 7.8 Hz, 2H), 3.10 (t, *J* = 7.8 Hz, 2H).[3]

1-iodo-2-(4-methoxyphenyl)ethane (1o) 1.42 g, 54% yield. Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 3.79 (s, 3H), 3.30 (t, *J* = 7.8 Hz, 2H), 3.11 (t, *J* = 7.8 Hz, 2H).[4]

3-iodooctane (1x) 3.14 g, 65% yield (from 20 mmol alcohol). Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.10 (tt, *J* = 8.7, 4.7 Hz, 1H), 1.94 – 1.61 (m, 4H), 1.58 – 1.22 (m, 6H), 1.02 (t, *J* = 7.2 Hz, 3H), 0.90 (t, *J* = 7.0 Hz, 3H).[5]

(3-iodobutyl)benzene (1y) 2.07 g, 79% yield. Pale-yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.26 (m, 2H), 7.25 – 7.17 (m, 3H), 4.22 – 3.98 (m, 1H), 2.91 – 2.79 (m, 1H), 2.76 – 2.61 (m, 1H), 2.35 – 2.07 (m, 1H), 1.95 (d, *J* = 6.8 Hz, 3H), 1.93 – 1.83 (m, 1H).[6]

2.2 Preparation of alkyl iodides from other halides (1h, 1l, 1n, 1q, 1w, 1aa)



S-2 (X = Cl or Br) 4 equiv. **1**

The alkyl iodides **1** were prepared according to literature procedure[7]. In a 100 mL round-bottom flask, alkyl-X (X = Cl, Br) (**S-2**, 10 mmol) and NaI (40 mmol, 4 equiv., 6 g) were dissolved in acetone (30 mL). The resulting solution was stirred overnight at reflux temperature. After cooling to room temperature, CH_2Cl_2 was added until the complete precipitation of salts. The mixture was filtered and the solvent was evaporated under vacuum. Then, the mixture was extracted with EtOAc and 0.1 M aqueous $Na_2S_2O_3$ solution. The combined organic phases were washed with saturated brine and dried over anhydrous Na_2SO_4, then filtered and concentrated by rotary evaporation. If necessary, the crude product was purified by column chromatography on a silica gel (PE/EtOAc) to obtain the desired alkyl iodide **1**.

(3-iodopropyl)benzene (1h) 2.11 g, 86% yield (from chloride). Orange liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.23 (m, 2H), 7.23 – 7.02 (m, 3H), 3.15 (t, *J* = 6.8 Hz, 2H), 2.71 (t, *J* = 7.3 Hz, 2H), 2.11 (p, *J* = 7.0 Hz, 2H).[8]

1-iodohexan-6-ol (1l) 2.26 g, 99% yield (from chloride). Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.77 – 3.48 (m, 2H), 3.20 (t, J = 7.0 Hz, 2H), 1.84 (p, J = 7.0 Hz, 2H), 1.59 (p, J = 6.6 Hz, 2H), 1.48 – 1.22 (m, 5H).[9]

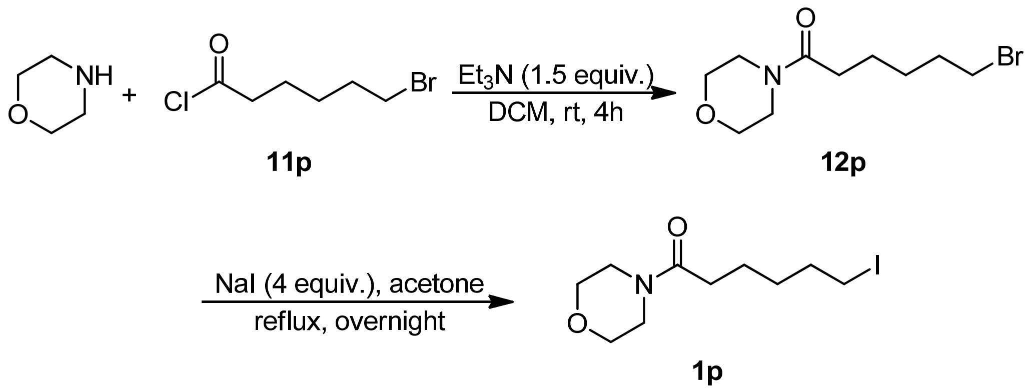
4-iodobutyl methyl ether (1n) 2.11 g, 99% yield (from chloride). Orange liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.39 (t, J = 6.2 Hz, 2H), 3.32 (s, 3H), 3.22 (t, J = 7.0 Hz, 2H), 1.97 – 1.85 (m, 2H), 1.73 – 1.61 (m, 2H).[10]

1-(3-iodopropoxy)benzene (1q) 2.57 g, 98% yield (from bromide). Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.26 (m, 2H), 7.02 – 6.93 (m, 1H), 6.93 – 6.79 (m, 2H), 4.04 (t, J = 5.8 Hz, 2H), 3.38 (t, J = 6.7 Hz, 2H), 2.38 – 2.14 (m, 2H).[11]

Iodocycloheptane (1w) 1.94 g, 87% yield (from bromide). Pale-yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.49 (tt, J = 8.8, 4.3 Hz, 1H), 2.38 – 2.23 (m, 2H), 2.23 – 2.10 (m, 2H), 1.70 – 1.55 (m, 6H), 1.52 – 1.36 (m, 2H).[6]

(Iodomethyl)cyclopropane (1aa) 2.53 g, 70% yield (from 20 mmol bromide). Colorless liquid. Purified by extraction with PE (30 ~ 60 °C) and evaporated under P >= 0.2 atm and T <= 20 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.14 (dd, J = 7.7, 1.6 Hz, 2H), 1.41 – 1.22 (m, 1H), 0.90 – 0.74 (m, 2H), 0.31 (td, J = 4.7, 2.5 Hz, 2H).[12]

2.3 Preparation of alkyl iodide (1p)

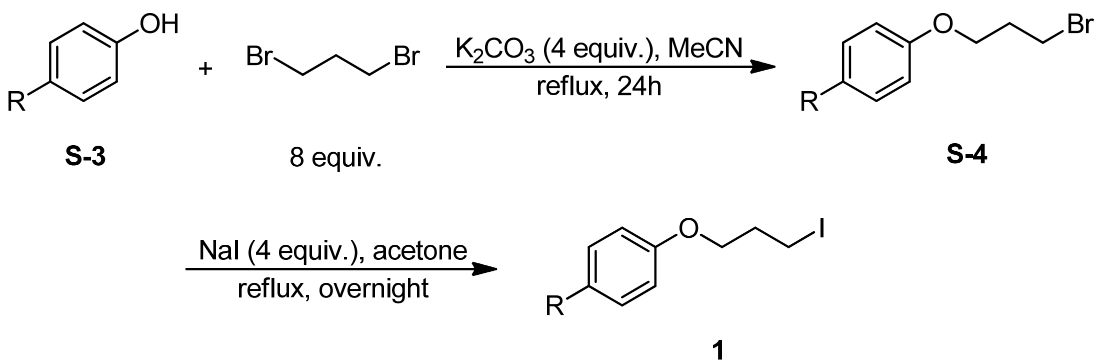


In a well-dried flask, morpholine (10 mmol, 1 equiv., 870 μL) and Et_3N (15 mmol, 1.5 equiv., 2.08 mL) were dissolved in DCM (25 mL) and cooled in an ice bath. After a solution of **11p** (10 mmol, 1.53 mL) in DCM (15 mL) was added dropwise during 30 min, the mixture was allowed to warm into room temperature and stirred for another 4 h. The reaction mixture was poured into water (100 mL) and extracted with DCM (50 mL×3). The combined organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. Compound **12p** was purified by column chromatography (silica gel) using PE/EA 5:1 ~ 3:1 as eluent. Yield: 2.40 g (91%), colorless liquid. After that, **12p** (5 mmol) was dissolved in acetone (20 mL). NaI (20 mmol, 4 equiv., 3 g) was added. Compound **1p** was then obtained according to the procedure in **Section 2.2**.

6-bromo-1-(morpholin-4-yl)-hexan-1-one (12p) 2.40 g, 91% yield. Colorless liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 3.80 – 3.53 (m, 6H), 3.53 – 3.26 (m, 4H), 2.33 (t, *J* = 7.5 Hz, 2H), 1.98 – 1.79 (m, 2H), 1.77 – 1.58 (m, 2H), 1.57 – 1.41 (m, 2H).[13]

6-iodo-1-(morpholin-4-yl)-hexan-1-one (1p) 1.55 g, 99% yield. Colorless liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 3.78 – 3.52 (m, 6H), 3.46 (t, *J* = 4.9 Hz, 2H), 3.20 (t, *J* = 6.9 Hz, 2H), 2.39 – 2.22 (m, 2H), 1.86 (p, *J* = 7.1 Hz, 2H), 1.67 (dt, *J* = 15.2, 7.5 Hz, 2H), 1.53 – 1.37 (m, 2H).

2.4 Preparation of alkyl iodides (1r, 1s, 1t)



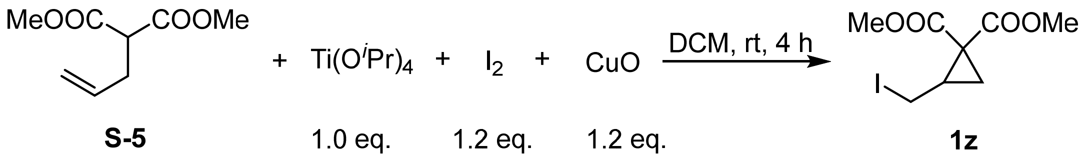
The alkyl iodide **1** were prepared according to literature procedure[14]. A solution of phenol **S-3** (10 mmol) and 1,3-dibromopropane (80 mmol, 8 equiv., 8 mL) in MeCN (30 mL) was adding anhydrous potassium carbonate (40 mmol, 4 equiv., 5.5 g). The reaction mixture was stirred at reflux for 24 h, 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 **S-4**. After that, the product **1r**/**1s**/**1t** was prepared according to the procedure in **Section 2.2**.

methyl 4-(3-iodo-propoxy)-benzoate (1r) 1.68 g, 52% yield. Pale-yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.9 Hz, 2H), 6.85 (d, J = 8.9 Hz, 2H), 4.02 (t, J = 5.8 Hz, 2H), 3.81 (s, 3H), 3.30 (t, J = 6.7 Hz, 2H), 2.22 (p, J = 6.5 Hz, 2H).[15]

acetic acid-[4-(3-iodo-propoxy)-anilide] (1s) 1.57 g, 77% yield. Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 9.0 Hz, 2H), 7.19 (s, 1H), 6.86 (d, J = 8.9 Hz, 2H), 4.01 (t, J = 5.8 Hz, 2H), 3.36 (t, J = 6.7 Hz, 2H), 2.26 (p, J = 6.3 Hz, 2H), 2.15 (s, 3H).

1-(3-iodo-propoxy)-4-(methyl-sulfonyl)-benzene (1t) 1.68 g, 86% yield. Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.9 Hz, 2H), 7.04 (d, J = 8.9 Hz, 2H), 4.20 (t, J = 5.8 Hz, 2H), 3.61 (t, J = 6.3 Hz, 2H), 3.03 (s, 3H), 2.36 (p, J = 6.1 Hz, 2H).

2.5 Preparation of alkyl iodide (1z)



The alkyl iodide **1z** was prepared according to literature procedure[16]. Under N_2 atmosphere, to a solution of dimethyl allylmalonate (10 mmol, 1.72 g) in DCM (12 mL) was added Ti(O*i*-Pr)$_4$ (10 mmol, 1.0 equiv., 3 mL) and stirred for 10 min. I_2 (12 mmol, 1.2 equiv., 3.05 g) and CuO (12 mmol, 1.2 equiv., 0.95 g) were successively added, and then the mixture was stirred for 4 h. The mixture was poured into 10 % HCl, and the product was extracted with ether. The ether extracts were washed with aqueous $Na_2S_2O_3$ solution, dried over Na_2SO_4, and evaporated. The residue was crudely purified by column chromatography (PE/EA = 9:1) and the product **1z** was purified by recrystallization using PE/EA under -18 °C.

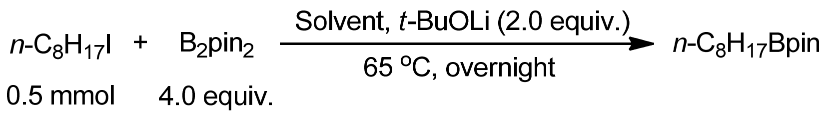
dimethyl 2-(iodomethyl)cyclopropane-1,1-dicarboxylate (1z) 1.51 g, 51% yield. White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.81 (s, 3H), 3.75 (s, 3H), 3.22 (dd, J = 10.3, 7.6 Hz, 1H), 3.13 (dd, J = 10.3, 8.4 Hz, 1H), 2.54 – 2.40 (m, 1H), 1.62 (dd, J = 9.0, 5.1 Hz, 1H), 1.54 (dd, J = 7.6, 5.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.47, 165.80, 51.05, 51.02, 36.49, 29.24, 22.38.[17]

3. Optimization of reaction conditions

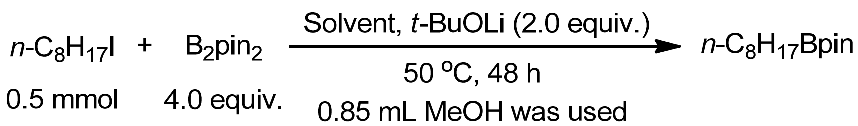
3.1 Optimization of reaction conditions for primary alkyl halides

In a glove box, a vial equipped with a stir bar was charged with base, B_2pin_2, *n*-iodooctane **1a** (0.5 mmol, 120 mg, 91 μL) or *n*-bromooctane **1a'** (0.5 mmol, 97 mg, 87 μL), other additives and the solvent. After removing the sealed vial from the glove box, the reaction mixture was stirred at given temperature for given time. Upon cooling to room temperature, *n*-decane (~ 30 mg) was added, the conversion of halide and the yield were measured by GC (FID).

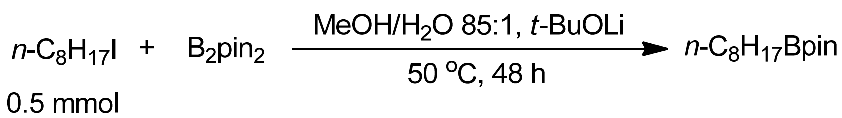
Table S1 Optimization of reaction conditions for primary alkyl halides.



Entry	Solvent and conditions	Conv. of $C_8H_{17}I$	Conv. of B_2pin_2	Yield
1	MeOH (2 mL), 9 h	90.2%	49.2%	61.3%
2	MeOH (1 mL)	95.7%	60.0%	69.5%
3	MeOH (0.5 mL)	97.4%	60.9%	72.6%
4	MeCN (1 mL)	99.6%	37.2%	64.4%
5	DMF (1 mL)	100%	31.1%	55.0%
6	DCM (1 mL)	47.4%	29.7%	14.9%
7	MeOH (1 mL), 80 °C, 6 h	100%	65.8%	64.0%



Entry	Conditions	Conv. of $C_8H_{17}I$	Conv. of B_2pin_2	Yield
8	MeOH/DMF 20:1	95.6%	60.2%	76.0%
9	MeOH/DMF 5:1	84.3%	55.3%	63.0%
10	MeOH/H_2O 85:1, with TEMPO (2 eq.)	52.6%	84.5%	14.4%
11	**MeOH/H_2O 85:1**	**98.5%**	**58.3%**	**86.7%**



Entry	B_2pin_2 equiv.	*t*-BuOLi equiv.	Conv. of $C_8H_{17}I$	Conv. of B_2pin_2	Yield
11	**4.0**	**2.0**	**98.5%**	**58.3%**	**86.7% (86.2% isolated)**
12	4.0	3.0	100%	92.3%	67.7%

13	3.5	2.0	98.1%	69.5%	76.3%
14	3.5	1.5	100%	57.5%	76.9%
15	**3.0**	**1.5**	**100%**	**61.9%**	**83.8% (82.7% isolated)**
16	2.5	1.5	100%	74.9%	71.5%
17	2.0	1.5	95.6%	78.8%	60.2%
18	2.0	1.0	85.7%	77.6%	61.9%

$$n\text{-}C_8H_{17}I + B_2pin_2 \xrightarrow[50\ ^oC,\ 48\ h]{MeOH/H_2O\ 85:1,\ base\ (2.0\ equiv.)} n\text{-}C_8H_{17}Bpin$$

0.5 mmol 4.0 equiv.

Entry	Base	Conv. of $C_8H_{17}I$	Conv. of B_2pin_2	Yield
11	***t*-BuOLi**	**98.5%**	**58.3%**	**86.7% (86.2% isolated)**
19	MeOLi	95.0%	66.1%	63.7%
20	*t*-BuONa	90.3%	90.3%	65.9%
21	MeONa	88.3%	84.6%	61.6%
22	*t*-BuOK	84.9%	96.8%	49.6%
23	MeOK	93.1%	94.4%	62.5%
24	Cs_2CO_3	100%	97.1%	14.8%
25	$LiOH{\cdot}H_2O$	96.1%	91.9%	66.5%

$$n\text{-}C_8H_{17}Br + B_2pin_2 \xrightarrow[[I],\ 50\ ^oC,\ 48\ h]{MeOH/H_2O\ 85:1,\ t\text{-}BuOLi\ (2.0\ equiv.)} n\text{-}C_8H_{17}Bpin$$

0.5 mmol 4.0 equiv.

Entry	[I]	Conv. of $C_8H_{17}Br$	Conv. of B_2pin_2	Yield
26	None	39.2%	79.5%	25.9%
27	KI (0.2 equiv.)	81.1%	73.1%	55.5%
28	I_2 (0.2 equiv.)	94.9%	72.7%	71.8%
29	I_2 (0.1 equiv.)	90.8%	70.4%	59.4%
30	**I_2 (0.4 equiv.)**	**99.8%**	**70.5%**	**76.2%**
31	KI (0.1 equiv.)	80.6%	74.8%	51.6%
32	KI (0.4 equiv.)	97.1%	74.5%	70.0%

$$n\text{-}C_8H_{17}Br + B_2pin_2 \xrightarrow[I_2\ (0.2\ equiv.),\ 50\ ^oC,\ 48\ h]{MeOH/H_2O\ 85:1,\ t\text{-}BuOLi} n\text{-}C_8H_{17}Bpin$$

0.5 mmol

Entry	B_2pin_2 equiv.	*t*-BuOLi equiv.	Conv. of $C_8H_{17}Br$	Conv. of B_2pin_2	Yield
28	4.0	2.0	94.9%	72.7%	71.8%
33	**3.0**	**1.5**	**97.1%**	**86.5%**	**65.9%**
34	2.0	1.0	79.3%	61.2%	44.3%

$$n\text{-}C_8H_{17}Br + B_2pin_2 \xrightarrow[[I],\ 50\ ^oC,\ 48\ h]{MeOH/H_2O\ 85:1,\ t\text{-}BuOLi\ (1.5\ equiv.)} n\text{-}C_8H_{17}Bpin$$

0.5 mmol 3.0 equiv.

Entry	[I]	Conv. of $C_8H_{17}Br$	Conv. of B_2pin_2	Yield
33	**I_2 (0.2 eq.)**	**97.1%**	**86.5%**	**65.9%**
35	I_2 (0.4 eq.)	92.5%	56.6%	56.4%
36	I_2 (1 eq.)	78.8%	35.7%	Trace
37	KI (0.2 eq.)	76.3%	68.4%	44.2%
38	KI (0.4 eq.)	83.4%	67.9%	43.9%
39	KI (1 eq.)	100%	70.3%	62.5%

n-$C_8H_{17}X$ (0.5 mmol) + B_2pin_2 (4.0 equiv.) → [MeOH/H_2O 85:1, *t*-BuOLi (2.0 equiv.), [I] (0.2 equiv.), 50 °C, 48 h] → *n*-$C_8H_{17}Bpin$

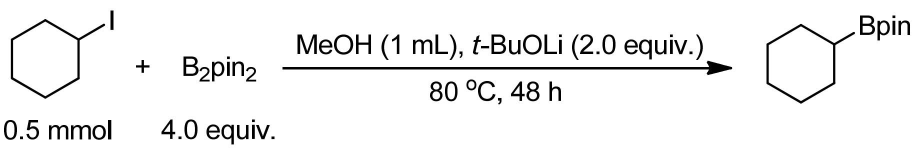
Entry	X	[I]	Conv. of $C_8H_{17}X$	Conv. of B_2pin_2	Yield
40	Cl	KI	17.6%	71.2%	6.9%
41	Cl	I_2	10.3%	57.8%	10.4%
42	OTs	None			ND
43	OTs	KI	-	65.1%	9.2%
44	OTs	I_2	-	57.0%	17.5%
45	OMs	None			ND
46	OMs	KI	-	62.1%	36.3%
47	OMs	I_2	-	53.2%	45.0%
48	OTf	None			ND
49	OTf	KI	-	48.3%	9.0%
50	OTf	I_2	-	61.3%	3.9%

3.2 Optimization of reaction conditions for secondary alkyl halides

Procedure A: using B_2pin_2 directly.

In a glove box, a vial equipped with a stir bar was charged with base, B_2pin_2, iodocyclohexane **1u** (0.5 mmol, 105 mg, 65 μL) and the solvent. After removing the sealed vial from the glove box, the reaction mixture was stirred at given temperature for given time. Upon cooling to room temperature, *n*-decane (~ 30 mg) was added, the conversion of halide and the yield were measured by GC (FID).

Table S2. Optimization of secondary alkyl halides: using B_2pin_2 as reagent.



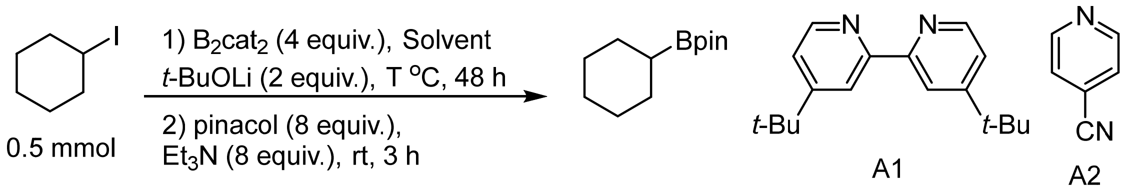
Entry	Conditions	Conv. of Substrate	Conv. of B_2pin_2	Yield
1	MeOH/H_2O 100:1, 50 °C			29.3% (Isolated)

2	MeOH/H_2O 100:1	85.4%	92.4%	17.7%
3	MeOH/DMF 5:1	91.0%	98.7%	13.1%
4	MeOH/H_2O 100:1, Cs_2CO_3 as base	99.4%	99.2%	3.1%
5	MeCN, $NaNH_2$	100%	72.9%	2.5%
6	DMF, $NaNH_2$	100%	48.1%	ND

Procedure B: using B_2cat_2.

In a glove box, a vial equipped with a stir bar was charged with base, B_2cat_2 (2 mmol, 476 mg), iodocyclohexane **1u** (0.5 mmol, 105 mg, 65 μL) and the solvent. After removing the sealed vial from the glove box, the reaction mixture was stirred at given temperature for given time. Upon cooling to room temperature, pinacol (4 mmol, 472 mg) and Et_3N (4 mmol, 405 mg, 0.56 mL) were added and the reaction mixture was stirred at room temperature for at least 3 hours. After that, *n*-decane (~ 30 mg) was added, the conversion of halide and the yield were measured by GC (FID).

Table S3. Optimization of secondary alkyl halides: using B_2cat_2 as reagent.



Entry	Solvent	Volume (mL)	Temperature	Conv. Sub	Yield
1	MeOH/DMF 10:1	0.85	50 (B_2pin_2 used)	42.6%	17.3%
2	MeOH/DMF 10:1	0.85	50	20.8%	18.1%
3	MeOH/DMF 3:1	0.85	50	24.5%	17.9%
4	MeOH/DMF 1:1	0.85	50	28.9%	20.7%
5	DMF	0.85	50	41.9%	10.7%
6	MeOH/DMF 10:1	0.85	80	88.6%	45.7%
7	MeOH/DMF 10:1	0.45	80	70.0%	29.0%
8	MeOH	0.45	80	73.9%	44.8%
9	MeOH	0.45	80 (With 0.2 equiv. A1)	75.4%	12.0%
10	MeOH	0.45	80 (With 0.2 equiv. A2)	-	Trace
11	MeOH	0.45	80 (MeOLi as the base)	-	Trace
12	MeOH	0.45	80 (LiOH as the base)	86.8%	46.1%
13	**MeOH**	**0.85**	**80**	**96.3%**	**66.2%**
14	MeOH	0.85	80 (LiOH as the base)	93.2%	51.1%

15	MeOH	1.5	80	96.3%	53.3%
16	MeOH	2	80	97.5%	36.3%

4. Experimental procedures and characterization data

4.1 Procedure for borylation of primary alkyl halides

$$\underset{\mathbf{1}}{R{-}X} + \underset{3\ \text{equiv.}}{B_2pin_2} \xrightarrow[\text{MeOH/H}_2\text{O, 50 °C, 48 h}]{t\text{-BuOLi (1.5 equiv.)}} \underset{\mathbf{2}}{R{-}Bpin}$$

In a glove box, a vial equipped with a stir bar was charged with *t*-BuOLi (0.75 mmol, 1.5 equiv., 60.1 mg), B_2pin_2 (1.5 mmol, 3 equiv., 380.9 mg), alkyl halide **1** (0.5 mmol), and a mixture of methanol (0.85 mL) and H_2O (10 μL) as solvent. After removing the sealed vial from the glove box, the reaction mixture was stirred at 50 °C for 48 h. Upon cooling to room temperature, the reaction mixture was transferred to a 100 mL flask by methanol, and then a little silica gel was added into it. After removal of the solvent *in vacuo*, the residue was poured onto a silica gel column and purified by column chromatography to give the desired product **2**.

n-C_8H_{17}-Bpin **2a**

99.3 mg, 83% isolated yield. Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.32 (q, *J* = 7.3 Hz, 2H), 1.27 – 1.04 (m, 22H), 0.80 (t, *J* = 6.8 Hz, 3H), 0.69 (t, *J* = 7.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.79, 32.43, 31.89, 29.37, 29.25, 24.79, 23.99, 22.67, 14.10. Rf = 0.65 (PE/EA 10:1), using PE/EA 50:1 ~ 30:1 as eluent.[18]

CH_3-Bpin **2b**

42% GC-FID yield. Highly volatile that couldn't be isolated. Standard curve was obtained with the authentic sample. Colorless liquid. GC-MS data: Calcd. $C_7H_{15}BO_2^+$ $[M]^+$: 142.1. Found: 142.1, 127.1 (M-CH_3).[19]

n-C_6H_{13}-Bpin **2c**

52.0 mg, 49% isolated yield. Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.39 – 1.27 (m, 2H), 1.26 – 1.09 (m, 18H), 0.86 – 0.75 (m, 3H), 0.70 (t, *J* = 7.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.79, 32.08, 31.63, 24.79, 23.95, 22.57, 14.07. Rf = 0.65 (PE/EA 10:1), using PE/EA 50:1 ~ 30:1 as eluent.[20]

n-C_9H_{19}-Bpin **2d**

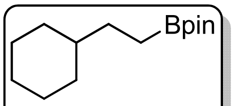
89.7 mg, 71% isolated yield. White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ

1.39 (q, J = 7.1 Hz, 2H), 1.34 – 1.16 (m, 24H), 0.87 (t, J = 6.8 Hz, 3H), 0.77 (t, J = 7.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.80, 32.43, 31.91, 29.54, 29.42, 29.33, 24.80, 24.00, 22.69, 14.11. Rf = 0.7 (PE/EA 10:1), using PE/EA 50:1 ~ 30:1 as eluent.[21]

n-$C_{12}H_{25}$-Bpin

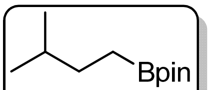
2e

100.2 mg, 68% isolated yield (118.7 mg, 80% isolated yield). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.45 – 1.35 (m, 2H), 1.34 – 1.15 (m, 30H), 0.88 (t, J = 6.8 Hz, 3H), 0.76 (t, J = 7.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.81, 32.45, 31.93, 29.70, 29.67, 29.60, 29.42, 29.37, 24.81, 24.01, 22.69, 14.12. Rf = 0.7 (PE/EA 10:1), using PE/EA 100:1 ~ 35:1 as eluent.[22]



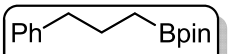
2f

73.3 mg, 62% isolated yield (101.4 mg, 85% isolated yield). Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.72 – 1.49 (m, 5H), 1.30 – 0.95 (m, 18H), 0.78 (td, J = 11.6, 2.9 Hz, 2H), 0.72 – 0.61 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.79, 39.94, 32.97, 31.36, 26.76, 26.43, 24.79. Rf = 0.4 (PE), using PE as eluent.[23]



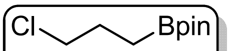
2g

62.0 mg, 63% isolated yield (29.4 mg, 30% isolated yield using bromide). Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ1.39 (dq, J = 13.3, 6.6 Hz, 1H), 1.29 – 1.19 (m, 2H), 1.17 (s, 12H), 0.79 (d, J = 6.6 Hz, 6H), 0.72 – 0.62 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.83, 32.91, 30.21, 24.81, 22.20. Rf = 0.55 (PE/EA 10:1), using PE/Et_2O 20:1 ~ 10:1 as eluent.[18]



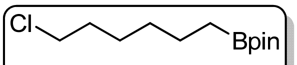
2h

65.7 mg, 53% isolated yield (75.1 mg, 61% isolated yield). Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.20 (m, 2H), 7.16 (dd, J = 7.9, 2.9 Hz, 3H), 2.71 – 2.52 (m, 2H), 1.73 (p, J = 7.8 Hz, 2H), 1.24 (s, 12H), 0.82 (t, J = 7.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.70, 128.57, 128.18, 125.58, 82.95, 38.62, 26.14, 24.86. Rf = 0.6 (PE/EA 10:1), using PE/EA 40:1 as eluent.[24]



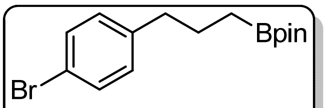
2i

41.3 mg, 41% isolated yield (76.4 mg, 75% isolated yield). Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$), δ 3.53 (t, J = 6.9 Hz, 2H), 2.00 – 1.79 (m, 2H), 1.25 (s, 12H), 0.91 (t, J = 7.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 83.16, 47.12, 27.31, 25.02, 24.80. Rf = 0.55 (PE/EA 10:1), using PE/EA 50:1 ~ 30:1 as eluent.[25]



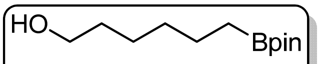
2j

84.2 mg, 68% isolated yield. Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$), δ 3.52 (t, *J* = 6.8 Hz, 2H), 1.76 (p, *J* = 7.0 Hz, 2H), 1.42 (p, *J* = 7.5 Hz, 4H), 1.36 – 1.28 (m, 2H), 1.24 (s, 12H), 0.77 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.88, 45.12, 32.53, 31.52, 26.62, 24.81, 23.78. Rf = 0.6 (PE/EA 10:1), using PE/EA 50:1 ~ 30:1 as eluent.[18]



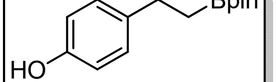
2k

69.5 mg, 43% isolated yield. Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.37 (d, *J* = 8.3 Hz, 2H), 7.04 (d, *J* = 8.4 Hz, 2H), 2.61 – 2.48 (m, 2H), 1.78 – 1.64 (m, 2H), 1.24 (s, 12H), 0.80 (t, *J* = 7.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.60, 131.20, 130.34, 119.28, 83.01, 37.90, 25.91, 24.84. ^{11}B NMR (160 MHz, $CDCl_3$) δ 34.04. IR: ν = 2977, 2930, 1488, 1459, 1404, 1371, 1318, 1269, 1226, 1165, 1143, 1109, 1072, 1011, 968, 875, 847, 814, 785, 512 cm^{-1}. HRMS: Calcd. $C_{15}H_{23}BBrO_2^+$ $[M+H]^+$: 325.0969. Found: 325.0971. Calcd. $C_{15}H_{26}BBrNO_2^+$ $[M+NH_4]^+$: 342.1234. Found: 342.1232. Rf = 0.55 (PE/EA 10:1), using PE/EA 50:1 as eluent.



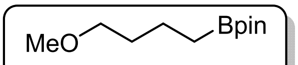
2l

82.1 mg, 72% isolated yield. Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.63 (t, *J* = 6.6 Hz, 2H), 1.56 (p, *J* = 6.9 Hz, 3H), 1.46 – 1.38 (m, 2H), 1.33 (dd, *J* = 7.3, 3.7 Hz, 4H), 1.24 (s, 12H), 0.78 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.88, 63.00, 32.67, 32.05, 25.43, 24.80, 23.90. ^{11}B NMR (160 MHz, $CDCl_3$) δ 34.01. IR: ν = 3370, 2977, 2928, 2858, 1464, 1372, 1317, 1273, 1214, 1165, 1144, 1111, 1056, 968, 882, 847, 721, 674, 579 cm^{-1}. HRMS: Calcd. $C_{12}H_{26}BO_3^+$ $[M+H]^+$: 229.1970. Found: 229.1967. Calcd. $C_{12}H_{29}BNO_3^+$ $[M+NH_4]^+$: 246.2235. Found: 246.2233. Rf = 0.2 (PE/EA 5:1), using PE/EA 15:1 ~ 5:1 as eluent.



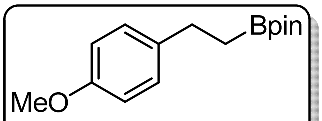
2m

50.8 mg, 41% isolated yield. Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (d, *J* = 8.2 Hz, 2H), 6.72 (d, *J* = 8.1 Hz, 2H), 5.44 – 4.83 (m, 1H), 2.67 (t, *J* = 8.1 Hz, 2H), 1.22 (s, 12H), 1.11 (t, *J* = 8.1 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.51, 136.41, 129.07, 115.01, 83.25, 29.03, 24.80. ^{11}B NMR (160 MHz, $CDCl_3$) δ 33.84. IR: ν = 3385, 2978, 2930, 1614, 1595, 1514, 1447, 1371, 1315, 1215, 1168, 1140, 1107, 1089, 966, 879, 840, 828, 777, 715, 674, 579, 552, 528, 436 cm^{-1}. HRMS: Calcd. $C_{14}H_{22}BO_3^+$ [M+H]$^+$: 249.1657. Found: 249.1663. Calcd. $C_{14}H_{25}BNO_3^+$ [M+NH$_4$]$^+$: 266.1922. Found: 266.1928. Rf = 0.4 (PE/EA 10:1). Using PE/EA 15:1 ~ 10:1 as eluent.



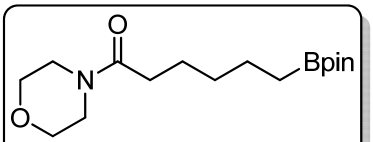
2n

43.9 mg, 41% isolated yield. 48% NMR yield. The polarity (Rf = 0.4 using PE/EA 10:1) is relatively close to B_2pin_2 that couldn't be fully purified. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.36 (t, *J* = 6.6 Hz, 2H), 3.32 (s, 3H), 1.61 – 1.53 (m, 2H), 1.51 – 1.41 (m, 2H), 1.24 (s, 12H), 0.80 (t, *J* = 7.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.92, 72.72, 58.48, 32.13, 24.82, 20.57. Rf = 0.4 (PE/EA 10:1), using PE/EA 15:1 ~ 10:1 as eluent. NMR Yield was measured by ^{1}H NMR via the ratio of the total area of the signals in δ 3.36 (2H) and 3.32 (3H), with the signal of $C_2H_2Cl_4$ (49.2 mg added, signal in δ 5.96, 2H). GC-MS data: Calcd. $C_{11}H_{23}BO_3^+$ [M]$^+$: 214.2. Found: 214.1, 199.1 (M-CH$_3$).[26]



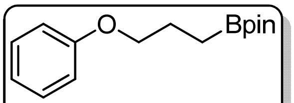
2o

76.4 mg, 58% isolated yield. White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, *J* = 8.4 Hz, 2H), 6.80 (d, *J* = 8.6 Hz, 2H), 3.77 (s, 3H), 2.76 – 2.61 (m, 2H), 1.22 (s, 12H), 1.16 – 1.06 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.54, 136.57, 128.86, 113.59, 83.07, 55.25, 29.06, 24.83. Rf = 0.6 (PE/EA 10:1), using PE/EA 30:1 as eluent.[25]



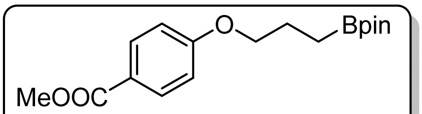
2p

121.2 mg, 78% isolated yield. Pale-yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.74 – 3.64 (m, 4H), 3.61 (d, *J* = 5.4 Hz, 2H), 3.46 (t, *J* = 4.8 Hz, 2H), 2.35 – 2.25 (m, 2H), 1.63 (p, *J* = 7.5 Hz, 2H), 1.50 – 1.32 (m, 4H), 1.24 (s, 12H), 0.78 (t, *J* = 7.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.90, 82.90, 66.96, 66.70, 46.06, 41.84, 33.10, 32.19, 25.06, 24.82, 23.74. ^{11}B NMR (160 MHz, $CDCl_3$) δ 34.15. IR: *ν* = 2975, 2926, 2856, 1645, 1427, 1371, 1319, 1272, 1247, 1226, 1166, 1145, 1115, 1069, 1029, 968, 847, 578 cm^{-1}. HRMS: Calcd. $C_{16}H_{31}BNO_4^+$ [M+H]$^+$: 312.2341. Found: 312.2348. Rf = 0.55 (DCM/MeOH 20:1), using DCM/MeOH 1:0 ~ 30:1 as eluent.



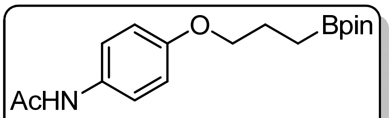
2q

67.5 mg, 52% isolated yield (85.2 mg, 65% isolated yield). Colorless liquid. ^{1}H NMR δ 7.24 – 7.11 (m, 2H), 6.89 – 6.75 (m, 3H), 3.85 (t, J = 6.7 Hz, 2H), 1.91 – 1.72 (m, 2H), 1.16 (s, 12H), 0.84 (t, J = 7.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.11, 128.29, 119.31, 113.53, 82.03, 68.44, 23.80, 22.74. Rf = 0.75 (PE/EA 5:1), using PE/EA 50:1 ~ 30:1 as eluent.[27]



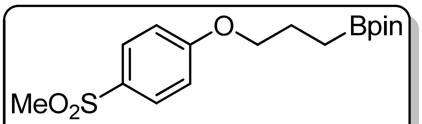
2r

41% NMR yield. The polarity (Rf = 0.5 using PE/EA 5:1) is same with B_2pin_2 that couldn't be purified. Yield was measured by ^{1}H NMR via the ratio of the average area of the signals in δ 7.97 (2H), 6.91 (2H), 3.99 (2H) with the signal of $C_2H_2Cl_4$ (65.9 mg added, signal in δ 5.96, 2H). GC-MS data: Calcd. $C_{17}H_{25}BO_5^+$ [M]$^+$: 320.2. Found: 320.2, 305.2 (M-CH_3). Standard sample was prepared according to the procedure in the end of Section 4.1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.9 Hz, 2H), 6.91 (d, J = 8.9 Hz, 2H), 3.99 (t, J = 6.7 Hz, 2H), 3.88 (s, 3H), 1.91 (p, J = 7.0 Hz, 2H), 1.25 (s, 12H), 0.93 (t, J = 7.8 Hz, 2H).



2s

110.0 mg, 69% isolated yield. White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.37 (d, J = 8.9 Hz, 2H), 6.83 (d, J = 8.9 Hz, 2H), 3.90 (t, J = 6.7 Hz, 2H), 2.12 (s, 3H), 1.88 (p, J = 7.1 Hz, 2H), 1.25 (s, 12H), 0.91 (t, J = 7.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.43, 155.97, 130.82, 121.89, 114.79, 83.12, 69.86, 24.85, 24.29, 23.73. ^{11}B NMR (160 MHz, $CDCl_3$) δ 33.94. IR: ν = 3295, 2977, 2930, 1660, 1604, 1544, 1510, 1471, 1411, 1371, 1317, 1240, 1168, 1144, 1111, 1018, 968, 912, 846, 829, 674, 578, 543, 521 cm^{-1}. HRMS: Calcd. $C_{17}H_{27}BNO_4^+$ [M+H]$^+$: 320.2028. Found: 320.2027. Calcd. $C_{17}H_{30}BN_2O_4^+$ [M+NH_4]$^+$: 337.2293. Found: 337.2291. M.p. 66-68 °C. Rf = 0.25 (PE/EA 1:1), using PE/EA 5:1 ~ 1:1 as eluent.

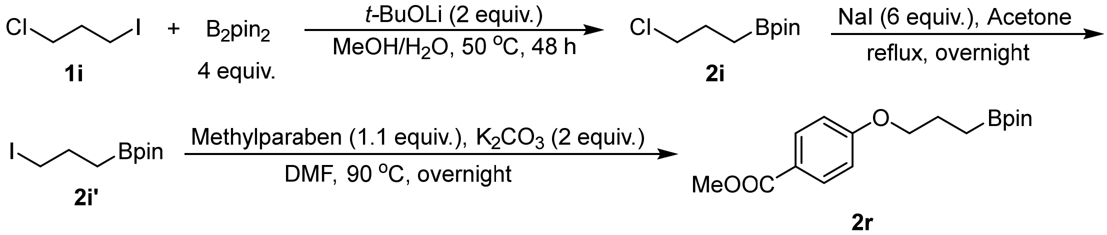


2t

71.1 mg, 42% isolated yield. Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.9 Hz, 2H), 7.01 (d, J = 9.0 Hz, 2H), 4.02 (t, J = 6.7 Hz, 2H), 3.03 (s, 3H), 1.92 (p, J = 7.0 Hz, 2H), 1.26 (s, 12H), 0.93 (t, J = 7.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.34, 131.83, 129.49, 114.98, 83.25, 70.09, 44.91, 24.86, 23.45. IR: ν = 2977, 2923, 1595, 1578, 1499, 1470, 1412, 1373, 1315, 1298, 1259, 1143, 1112, 1093, 1009, 964, 845, 765, 534, 489 cm^{-1}. HRMS: Calcd. $C_{16}H_{25}BO_5SNa^+$ [M+Na]$^+$: 363.1408. Found: 363.1402. Calcd.

$C_{16}H_{29}BNO_5S^+$ [M+NH$_4$]$^+$: 358.1854. Found: 358.1849. Rf = 0.65 (PE/EA 1:1), using PE/EA 5:1 ~ 2:1 as eluent.

Preparation for authentic sample of **2r**



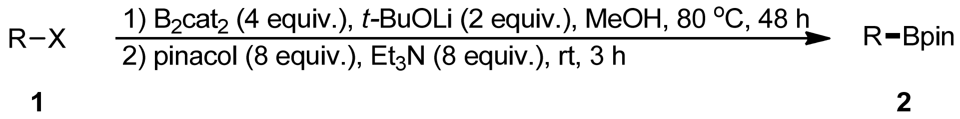
In a well-dried 50 mL flask, **1i** (5 mmol, 1.02 g), *t*-BuOLi (10 mmol, 2 equiv., 0.80 g) and B_2pin_2 (20 mmol, 4 equiv., 5.08 g) were dissolved in a mixed solvent of methanol (10 mL) and water (0.1 mL). After the flask was closed, the reaction mixture was stirred at 50 °C for 48 h. Upon cooling to room temperature, the product **2i** was isolated by column chromatography (silica gel) using PE/EA 50:1 ~ 30:1 as eluent. Yield: 0.75 g (3.67 mmol, 73%), colorless liquid.

Then, the product **2i** obtained from the former procedure was dissolved in acetone (5 mL), NaI (20 mmol, 6 equiv., 3.0 g) was added. The reaction mixture was heated at reflux overnight, following with the solvent was removed under vacuum. Water (100 mL) was added and the solvent was extracted by EtOAc (50 mL each time) 3 times. The combined organic layer was washed via brine and dried over Na_2SO_4, the solvent was removed and the product **2i'** was obtained as a yellow liquid. Yield: 0.789 g (2.66 mmol, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.22 (t, J = 7.1 Hz, 2H), 1.93 (p, J = 7.3 Hz, 2H), 1.24 (s, 12H), 0.92 – 0.84 (m, 2H).[28]

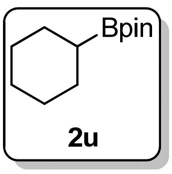
Finally, the product **2r** was prepared according to the literature procedure.[29] In a 10 mL well-dried Schlenk tube, **2i'** (1 mmol, 296 mg), methylparaben (1.1 mmol, 1.1 equiv., 167 mg) and K_2CO_3 (2 mmol, 2 equiv., 276 mg) were dissolved in DMF (3 mL). The reaction mixture was stirred at 90 °C overnight. Upon cooling to room temperature, the reaction mixture was poured into water (100 mL) and extracted via EtOAc (50 mL * 3). After the combined organic layer was washed by brine and dried over Na_2SO_4, the solvent was removed and the product **2r** was purified by column chromatography (silica gel) using

PE/EA 15:1 ~ 10:1 as eluent. 51.1 mg (16%) of the product was entirely purified as a pale-yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.9 Hz, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 3.99 (t, *J* = 6.7 Hz, 2H), 3.88 (s, 3H), 1.91 (p, *J* = 7.0 Hz, 2H), 1.25 (s, 12H), 0.93 (t, *J* = 7.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.94, 162.99, 131.52, 122.22, 114.13, 83.17, 69.75, 51.81, 24.84, 23.58. ^{11}B NMR (160 MHz, $CDCl_3$) δ 33.98. IR: *ν* = 2977, 2950, 1716, 1605, 1578, 1511, 1469, 1435, 1372, 1317, 1277, 1251, 1190, 1166, 1143, 1103, 1011, 968, 911, 846, 770, 740, 697, 673, 648, 611, 578, 516 cm^{-1}. HRMS: Calcd. $C_{17}H_{26}BO_5^+$ $[M+H]^+$: 321.1868. Found: 321.1877. Rf = 0.5 (PE/EA 5:1).

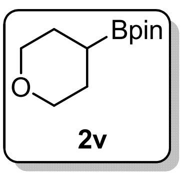
4.2 Procedure for borylation of secondary alkyl halides



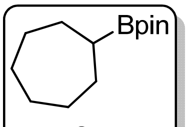
In a glove box, a vial equipped with a stir bar was charged with *t*-BuOLi (1 mmol, 2 equiv., 80.1 mg), B_2cat_2 (2 mmol, 4 equiv., 476 mg), 0.85 mL methanol as solvent, alkyl halide **1** (0.5 mmol). After removing the sealed vial from the glove box, the reaction mixture was stirred at 80 °C for 48 h. Upon cooling to room temperature, pinacol (4 mmol, 8 equiv., 472 mg) and Et_3N (4 mmol, 405 mg, 0.56 mL) were added and the reaction mixture was stirred at room temperature for at least 3 h. After that, the reaction mixture was transferred to a 100 mL flask by methanol, and then a little silica gel was added into it. After removal of the solvent *in vacuo*, the residue was poured onto a silica gel column and purified by column chromatography to give the desired product **2**.



57.7 mg, 55% isolated yield. Colorless liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.65 – 1.46 (m, 5H), 1.33 – 1.18 (m, 5H), 1.16 (s, 12H), 0.97 – 0.84 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.72, 27.96, 27.14, 26.76, 24.75. Rf = 0.7 (PE/EA 10:1), using PE/EA 50:1 ~ 30:1 as eluent.[18]

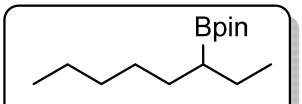


57.8 mg, 55% isolated yield. Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.89 – 3.73 (m, 2H), 3.55 – 3.36 (m, 2H), 1.73 – 1.52 (m, 4H), 1.25 – 1.19 (m, 13H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 83.13, 81.56, 68.84, 29.70, 27.62, 24.77. Rf = 0.45 (PE/EA 10:1), using PE/EA 30:1 ~ 20:1 as eluent.[18]



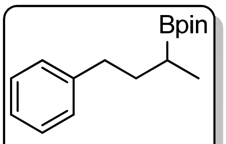
2w

57.3 mg, 51% isolated yield. Colorless liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.84 – 1.36 (m, 12H), 1.24 (s, 12H), 1.07 (dq, *J* = 9.4, 4.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.75, 29.60, 28.98, 28.34, 24.74. Rf = 0.7 (PE/EA 10:1), using PE/EA 50:1 ~ 30:1 as eluent.[30]



2x

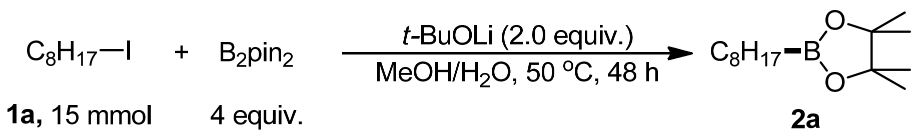
33% GC-FID yield (comparing with the purified product and decane). 10.9 mg, 9% isolated yield. Slight volatile colorless oil. GC-MS data: Calcd. $C_{14}H_{29}BO_2^+$ [M]$^+$: 240.2. Found: 240.2, 225.2 (M-CH_3). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.47 – 1.18 (m, 22H), 1.00 – 0.80 (m, 7H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.77, 32.16, 31.13, 29.71, 28.94, 24.81, 24.32, 22.63, 14.08, 13.75. ^{11}B NMR (160 MHz, $CDCl_3$) δ 34.60. IR: *ν* = 2957, 2923, 2855, 1633, 1466, 1410, 1387, 1379, 1371, 1313, 1266, 1214, 1145, 1026, 967, 859, 791, 685, 578 cm^{-1}. HRMS (gas chromatography): Calcd. $C_{14}H_{29}BO_2^+$ [M]$^+$: 240.2255. Found: 240.2256. Calcd. $C_{13}H_{26}BO_2^+$ [M-CH_3]$^+$: 225.2020. Found: 225.2025. Rf = 0.8 (PE/EA 10:1), using PE as eluent.



2y

91.9 mg, 71% isolated yield. Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 6.94 (m, 5H), 2.62 (t, *J* = 8.1 Hz, 2H), 1.68 (dt, *J* = 76.0, 8.0 Hz, 2H), 1.25 (s, 12H), 1.02 (d, *J* = 6.6 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.10, 128.46, 128.22, 125.53, 82.92, 35.35, 24.83, 24.78, 15.46. Rf = 0.6 (PE/EA 10:1), using PE/EA 50:1 ~ 30:1 as eluent.[22]

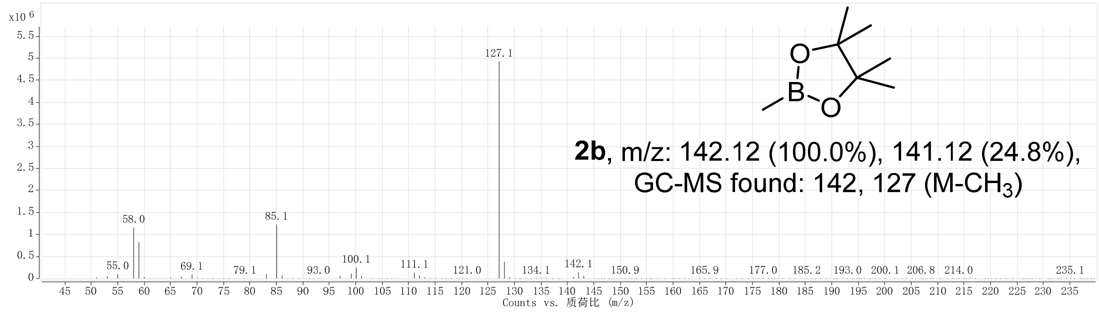
4.3 Large scale reaction

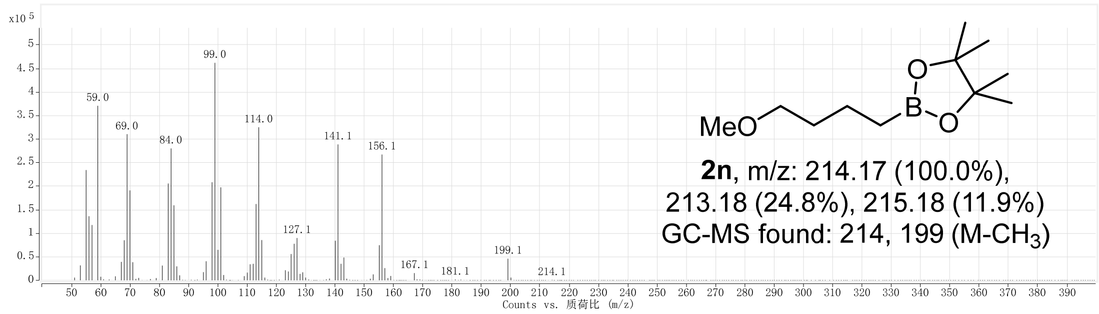


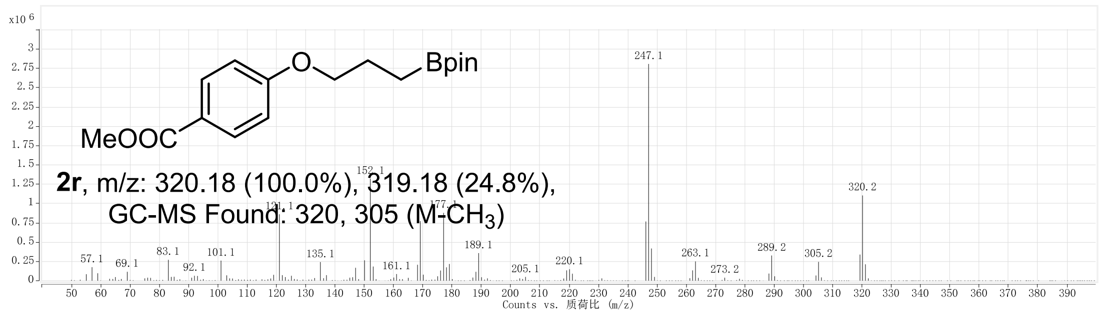
In a well-dried 100 mL flask, **1a** (15 mmol, 3.60 g, 2.71 mL), *t*-BuOLi (30 mmol, 2 equiv., 2.40 g) and B_2pin_2 (60 mmol, 4 equiv., 15.24 g) were dissolved in a mixed solvent of methanol (30 mL) and water (0.15 mL). The reaction was allowed to expose into air atmosphere. After the flask was closed, the reaction mixture was stirred at 50 °C for 48 h. Upon cooling to room temperature, the desired product **2a** was isolated by column chromatography (silica gel) using PE/EA 50:1 ~ 30:1 as eluent. Yield: 2.95 g (82%), colorless liquid. Then, the unconverted B_2pin_2 was recycled using the eluent of PE/EA 10:1 ~ 5:1. Recycled B_2pin_2 amount: 7.57 g (50%).

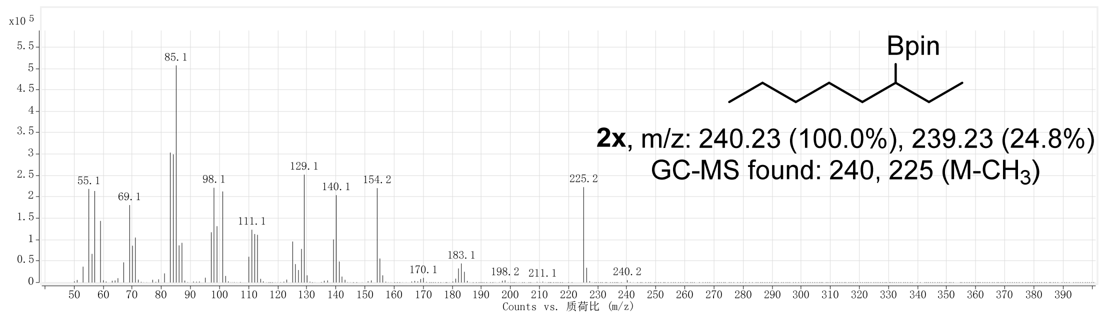
4.4 GC-MS data for products measured by GC-FID or NMR

5





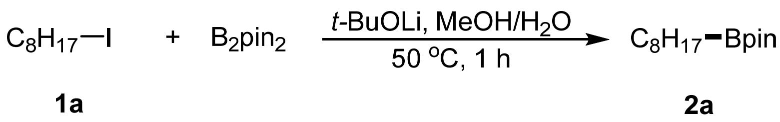




5. Mechanistic studies

5.1 Kinetic experiments

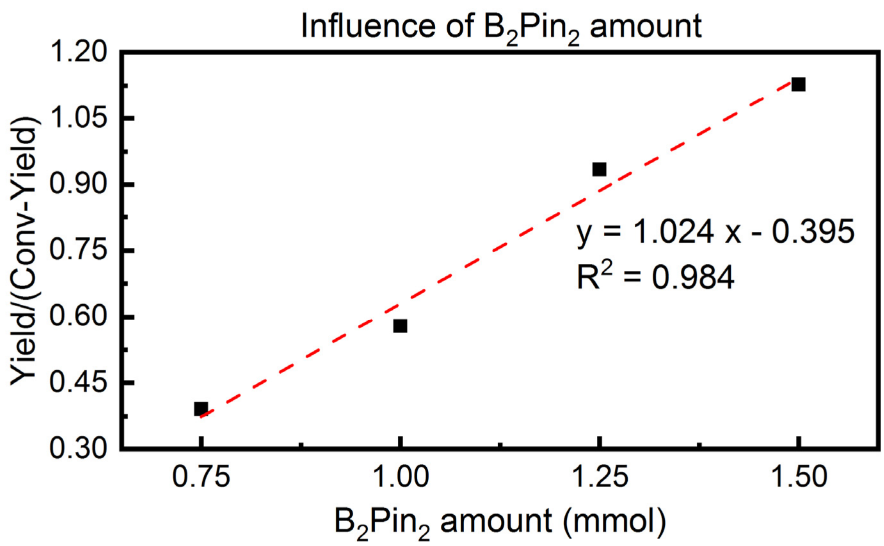
In this part, we tested the reaction rate in the first 1 hour. The iodide was added in kinetic interval. Each group of experiments ran in parallel.



General procedure: in a glove box, **1a** (about 0.1 mmol), *t*-BuOLi and B_2pin_2 were dissolved in methanol (0.85 mL) and water (10 μL). After removing the sealed vial from the glove box, the reaction mixture was stirred at 50 °C for 1 h. Upon cooling to room temperature, decane (~30 mg) was added, the conversion and yield were tested by GC (FID).

A. Influence of "free" B_2pin_2 concentration

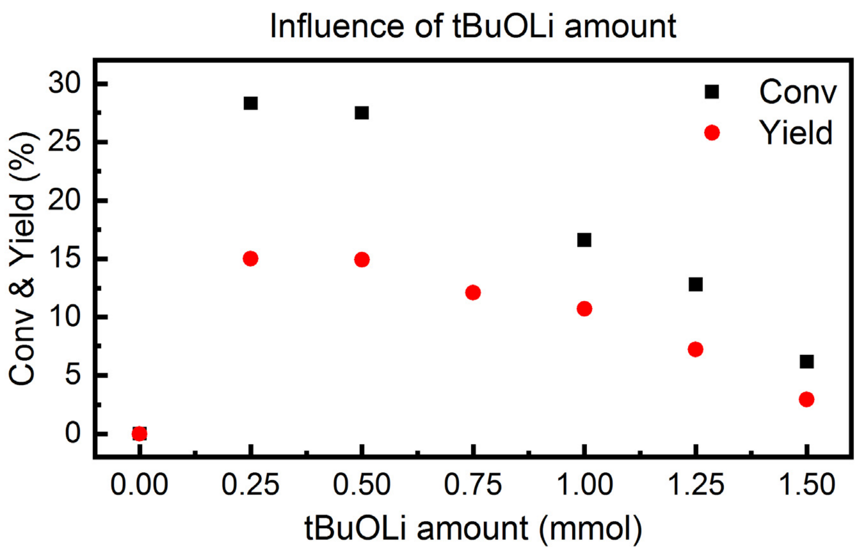
Exp No.	$C_8H_{17}I$ (mmol)	B_2pin_2 (mmol)	*t*-BuOLi (mmol)	Conv. Sub	Yield	Conv – Yield	Yield/(Conv-yield)
1	0.1	0.75	0.5	30.2%	8.5%	21.7%	0.3917
2	0.1	1	0.5	37.1%	13.6%	23.5%	0.5787
3	0.1	1.25	0.5	55.5%	26.8%	28.7%	0.9338
4	0.1	1.5	0.5	38.5%	20.4%	18.1%	1.1271



With constant concentration of substrate and base, we found that the ratio of the product and by-products (described by the difference between the conversion of substrate and the yield) showed linear relation with the amount of B_2pin_2 ($R^2 = 0.984$).

B. Influence of base concentration with the same B_2pin_2 amount

Exp No.	$C_8H_{17}I$ (mmol)	B_2pin_2 (mmol)	*t*-BuOLi (mmol)	*t*-BuOLi/ B_2pin_2	Conv. Sub	Yield	Yield/Conv
1	0.1	1.5	0	0	0	0	
2	0.1	1.5	0.25	0.167	28.3%	15.0%	0.530
3	0.1	1.5	0.5	0.333	27.5%	14.9%	0.542
4	0.1	1.5	0.75	0.5	14.9%	12.1%	(0.812)
5	0.1	1.5	1	0.667	16.6%	10.7%	0.645
6	0.1	1.5	1.25	0.833	12.8%	7.19%	0.562
7	0.1	1.5	1.5	1	6.16%	2.94%	0.477

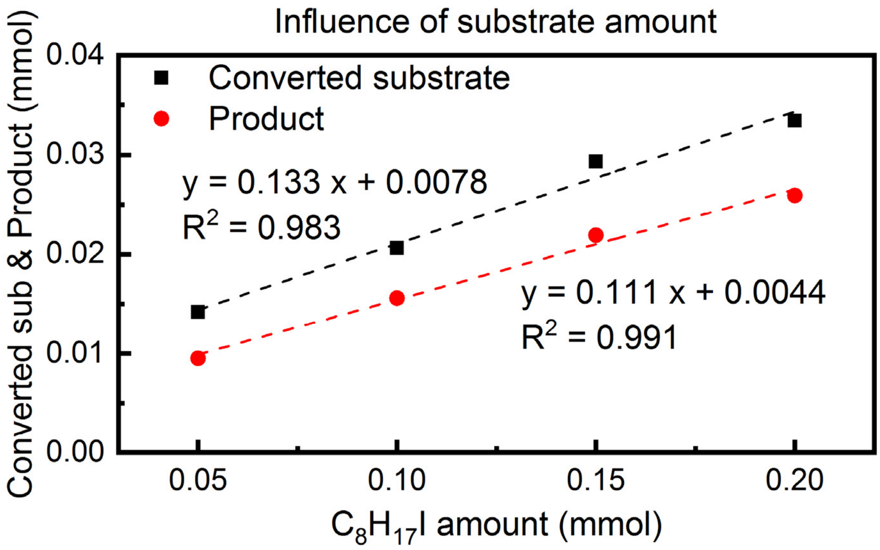


In this group, the 4th case might be a bad point (marked in red). With constant content of substrate and B_2pin_2, we changed the amount of base from 0 to 1.5 mmol. In 1.0 to 1.5 mmol interval, we found that the conversion and yield both decreased with the increasing of base content (nearly linear, with $R^2 = 0.977$ for conversion and $R^2 = 0.997$ for yield), while the yield decreased a little bit faster. However, in 0.25 to 0.5 mmol interval, the conversion and yield were both insensitive with base amount. Finally, the reaction didn't run at all without base.

C. Influence of substrate concentration

Exp. No	$C_8H_{17}I$ (mmol)	B_2pin_2 (mmol)	*t*-BuOLi (mmol)	Conv.Sub	Yield	Converted sub (mmol)	Product (mmol)

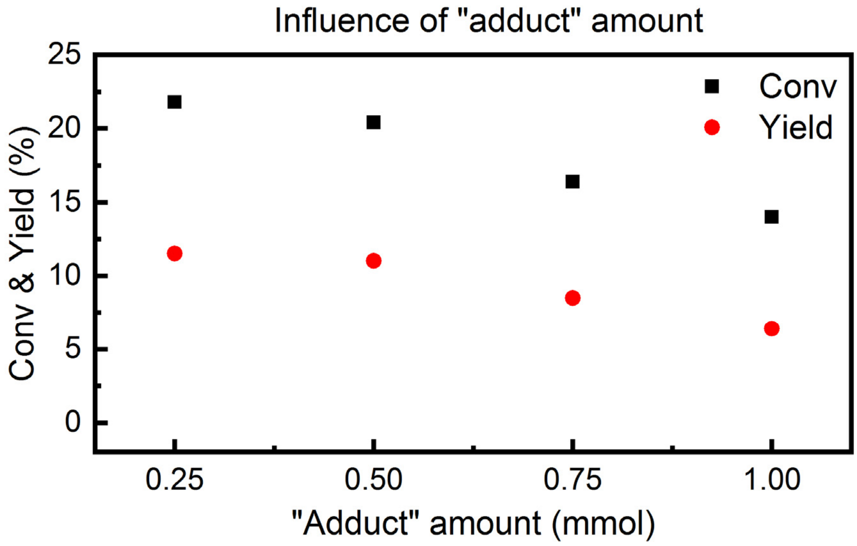
1	0.05	1.5	0.5	28.4%	19.0%	0.0142	0.0095
2	0.1	1.5	0.5	20.6%	15.6%	0.0206	0.0156
3	0.15	1.5	0.5	19.5%	14.6%	0.0293	0.0219
4	0.2	1.5	0.5	16.7%	12.9%	0.0334	0.0259



In this group, the kinetic was described by the amount of the converted substrate and the desired product, instead of the conversion and yield due to the different substrate concentration in each case. With the same concentration of B_2pin_2 and base, we found that the amount of the converted substrate and the product both showed linear relation with the concentration of substrate (with R^2 of 0.983 and 0.991, respectively), indicating that the conversion of the substrate and the formation of the desired product both mainly through a first-order reaction pathway for the substrate. Small intercepts were found might due to the other uncertain pathways. In addition, the ratio of the slopes for the product and the converted substrate was 0.835, indicating that with a high enough substrate concentration the yield would approach 83.5% after the substrate complete conversion. It showed agreement with the yield of **2a** using 3 equiv. of B_2pin_2 (83%, using 0.5 mmol of **1a** and 1.5 mmol of B_2pin_2 in same amount of solvent).

D. Influence of "adduct" concentration

Exp No	$C_8H_{17}I$ (mmol)	B_2pin_2 (mmol)	*t*-BuOLi (mmol)	Conv. Sub	Yield
1	0.1	0.75	0.25	21.8%	11.5%
2	0.1	1	0.5	20.4%	11.0%
3	0.1	1.25	0.75	16.4%	8.5%
4	0.1	1.5	1	14.0%	6.4%



The substrate concentration and the difference between B_2pin_2 and *t*-BuOLi were fixed, i.e., each case had the same "free" B_2pin_2 concentration and different "adduct" concentration. The conversion and yield were similar with 0.25 to 0.50 mmol of "adduct", but they were slowly decreased with higher "adduct" concentration. Because for the first two cases clear solutions were given but for the latter two cases precipitates were formed, we suggested that the reaction rate was independent with the concentration of "adduct" while the decreasing yields of the latter two cases was due to the inhibition of the precipitate under high reagent concentration.

We can summarize the above four groups of experiments as follows. First of all, the reaction is mainly a first-order process for the substrate. Moreover, the key species to form the borylation product is the "free" B_2pin_2, instead of the "adduct". Thus we suggest that since the alkyl radical is formed, it interacts with the "free" B_2pin_2, and somehow forms the desired product.

5.2 Metal residue experiments and reaction in the absence of light

The ICP analysis for transition metal residues was taken by *Tsinghua University Analysis Center*. We compared the transition metal residues of the chemicals provided from ENERGY CHEMICAL and SIGMA-ALDRICH.

Table S4 ICP analysis for B_2pin_2 and *t*-BuOLi (in ppm)

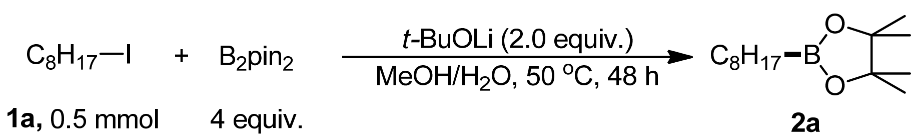
B_2pin_2 TM residue	57Fe (KED)	55Mn (KED)	60Ni (KED)	63Cu (KED)	66Zn (KED)	105Pd (KED)
ENERGY	1.77	0.06	0.09	0.16	3.13	0.18
SIGMA	3.74	0.09	0.46	1.09	1.51	0.06

t-BuOLi TM residue	63Cu (KED)	66Zn (KED)	57Fe (KED)	55Mn (KED)	60Ni (KED)	105Pd (KED)
ENERGY	2.63	22.90	67.39	5.18	1.07	1.30
SIGMA	0.32	0.84	3.56	0.06	0.16	0.13

These results showed that the chemicals from SIGMA-ALDRICH have significantly lower TM residues.

Subsequently, we compared the standard reaction using the chemicals from ENERGY CHEMICAL and SIGMA-ALDRICH.

Table S5. Control experiments using different chemical sources

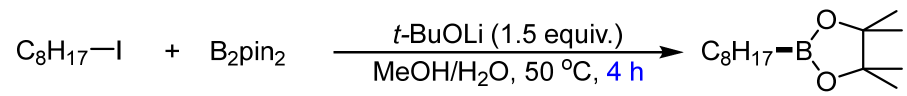


Source of reagents	Conv. of Substrate	Yield
ENERGY CHEMICAL	98.5%	86.7%
SIGMA-ALDRICH	100%	79.2%

Accordingly, the yields were close.

Furthermore, we have performed these reactions with additional transition metal salts. Those reactions were continued for 4 h. The results are depicted in **Table S6**.

Table S6. Reaction with additional TM salts

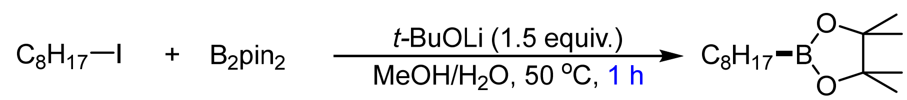


1a, 0.5 mmol (distilled) 3 equiv. **2a**

Exp. No	Additive	Conv. of **1a**	Conv. of B_2pin_2	Yield of **2a**
1	None	73.8%	66.9%	52.3%
2	CuCl (2.5 mol%)	97.9%	73.4%	85.8%
3	CuCl (5 mol%)	100%	77.0%	79.9%
4	$MnBr_2.4H_2O$ (2.5 mol%)	73.9%	71.5%	51.7%
5	$MnBr_2.4H_2O$ (5 mol%)	73.4%	71.4%	51.8%
6	$NiCl_2.6H_2O$ (2.5 mol%)	100%	82.0%	56.9%
7	$NiCl_2.6H_2O$ (5 mol%)	100%	78.6%	52.9%
8	$Zn(NO_3)_2.6H_2O$ (2.5 mol%)	100%	76.9%	37.9%
9	$Zn(NO_3)_2.6H_2O$ (5 mol%)	100%	81.4%	36.9%

These results indicate that many transition-metal salts, such as Mn(II), Ni(II) and Zn(II) show no catalytic ability on the desired borylation reaction despite the fact that Cu salts are catalytically active in catalytic amount (2.5% ~ 5%). This is consistent with other Cu-catalyzed borylation of alkyl halides works published in the past decade.[31-32] However, in our system the amount of Cu residue was only several ppm. To further examine whether the Cu residue in the reagents play an important role in this transformation, we compared the yield of the borylation product formed in 1 h using distilled n-iodooctane and chemicals from different source (**Table S7**).

Table S7. Effect of Cu residue with different concentration level



1a, 0.5 mmol (distilled) 3 equiv. **2a**

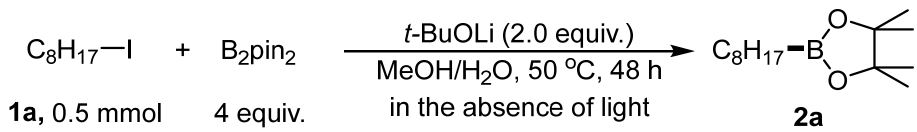
Exp. No	B_2pin_2	*t*-BuOLi	Cu equivalency	Conv. of **1a**	Conv. of B_2pin_2	Yield of **2a**

1	ENERGY	SIGMA	2.5e-6	26.1%	67.5%	12.8%
2	SIGMA	ENERGY	18.0e-6	19.1%	67.6%	6.4%
3	ENERGY	ENERGY	6.9e-6	20.2%	69.5%	10.5%
4	SIGMA	SIGMA	13.7e-6	17.7%	68.3%	6.7%

These results show that the yields are not relevant to the Cu residue concentration.

In addition, we designed a reaction in the absence of light to verify whether our reaction is photocatalytic. The standard reaction was run with packing the whole vial by aluminum foil.

Table S8. Reaction in the absence of light.

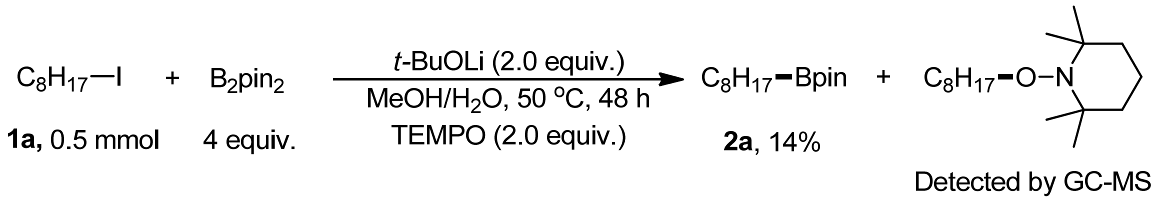


Condition	Conv. of Substrate	Yield
Non-packed (standard)	98.5%	86.7%
Aluminum foil packed	96.7%	85.4%

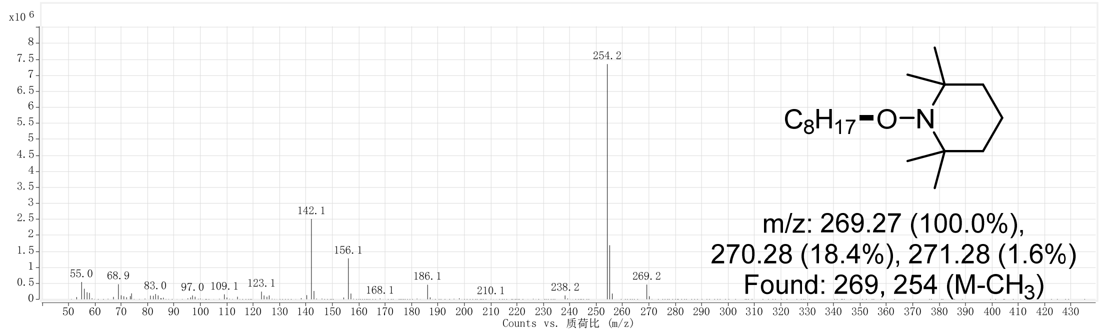
The yield of the reaction in the absence of light is closed to the standard reaction. Thus we suggested that our reaction is non-photocatalytic.

5.3 Other mechanistic experiments

Reaction with TEMPO

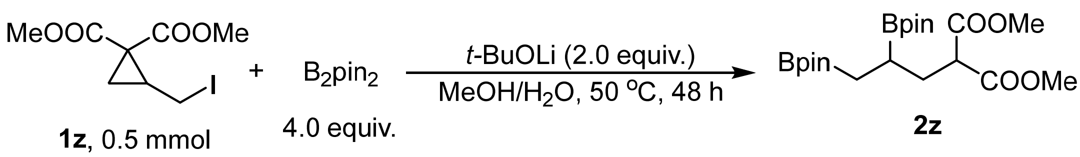


In a glove box, **1a** (0.5 mmol, 120 mg, 91 μL), *t*-BuOLi (1.0 mmol, 80.1 mg), B_2pin_2 (2.0 mmol, 508 mg) and TEMPO (1.0 mmol, 156 mg) were dissolved in methanol (0.85 mL) and water (10 μL). After removing the sealed vial from the glove box, the reaction mixture was stirred at 50 °C for 48 h. Upon cooling to room temperature, decane (~30 mg) was added, the conversion and yield were tested by GC (FID), and the reaction mixture was measured by GC-MS.



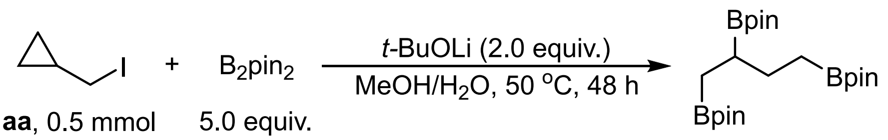
Condition	Conv. of Substrate	Yield
Without TEMPO (standard)	98.5%	86.7%
With TEMPO (this experiment)	52.6%	14.4%

"Clock" reaction



In a glove box, **1z** (0.5 mmol, 149 mg), *t*-BuOLi (1.0 mmol, 80.1 mg) and B_2pin_2 (2 mmol, 508 mg) were dissolved in methanol (0.85 mL) and water (10 μL). After removing the sealed vial from the glove box, the reaction mixture was stirred at 50 °C for 48 h. Upon cooling to room temperature, silica gel was added, the solvent was removed and the product

2z was purified by column chromatography using PE/EA 10:1 ~ 5:1 as eluent (Rf = 0.5 using PE/EA 3:1). Yield: 177.4 mg (83%), colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.72 (s, 6H), 3.60 (dd, *J* = 8.3, 6.8 Hz, 1H), 2.11 – 2.03 (m, 1H), 1.98 – 1.86 (m, 1H), 1.23 (s, 12H), 1.23 (s, 12H), 1.15 – 1.04 (m, 1H), 0.86 (d, *J* = 7.3 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.31, 170.12, 83.12, 83.01, 52.33, 52.31, 50.84, 32.25, 24.83, 24.70. IR: *ν* = 2978, 2931, 2160, 2033, 1976, 1754, 1735, 1435, 1407, 1371, 1314, 1268, 1239, 1213, 1139, 1109, 1026, 967, 923, 882, 847, 706, 671, 578, 522, 458 cm^{-1}. ^{11}B NMR (160 MHz, $CDCl_3$) δ 33.85. HRMS: Calcd. $C_{20}H_{37}B_2O_8^+$ [M+H]$^+$: 427.2669. Found: 427.2686. Calcd. $C_{20}H_{40}B_2NO_8^+$ [M+NH_4]$^+$: 444.2934. Found: 444.2931.

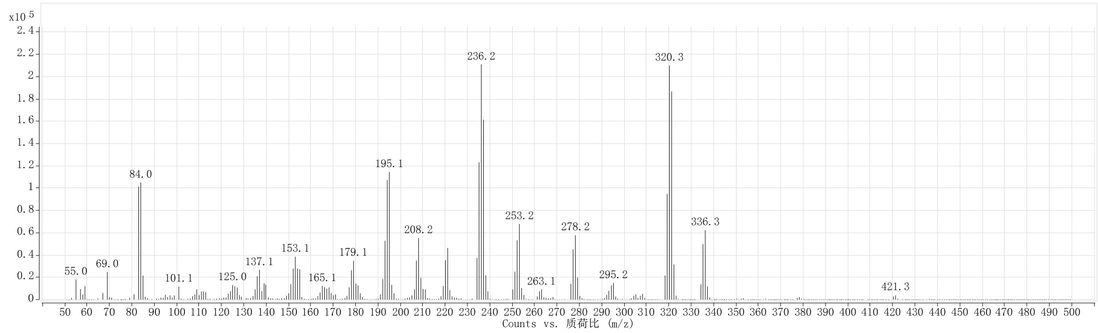


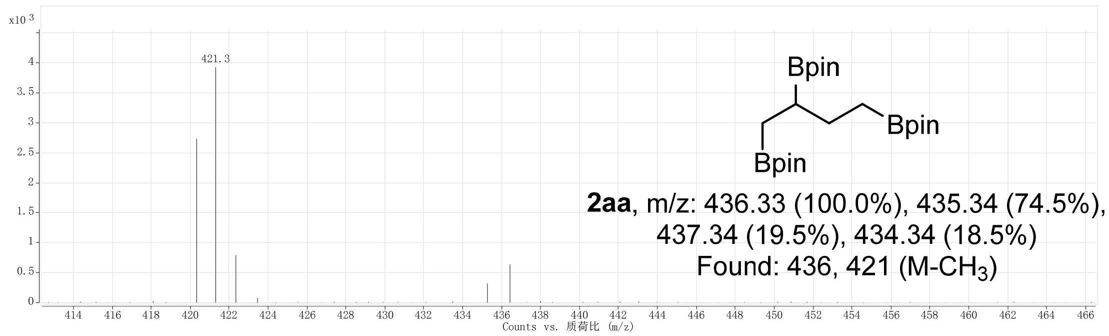
1aa, 0.5 mmol   5.0 equiv.   **2aa**, 42% (NMR)

In a glove box, (iodomethyl)cyclopropane **1aa** (0.5 mmol, 91 mg), *t*-BuOLi (1.0 mmol, 80.1 mg) and B_2pin_2 (2.5 mmol, 635 mg) were dissolved in methanol (0.85 mL) and water (10 μL). After removing the sealed vial from the glove box, the reaction mixture was stirred at 50 °C for 48 h. Upon cooling to room temperature, the reaction mixture was filtered by a small silica column (using PE/EA 3:1 as eluent). After the solvent was removed under vacuum, $C_2H_2Cl_4$ (54.8 mg) was added and the yield of compound **2aa** was tested by ^{1}H NMR (600 MHz, using $CDCl_3$ as solvent) according to the ratio of the area of the signals around δ 1.23 (36H, three Bpin groups) with the signal of $C_2H_2Cl_4$ (65.9 mg added, signal in δ 5.96, 2H). GC-MS data: Calcd. $C_{22}H_{43}B_3O_6^+$ [M]$^+$: 436.3. Found: 436.3, 421.3 (M-CH_3). (Can't separate with B_2pin_2 as the polarity closed to B_2pin_2, Rf = 0.4 using PE/EA 10:1).

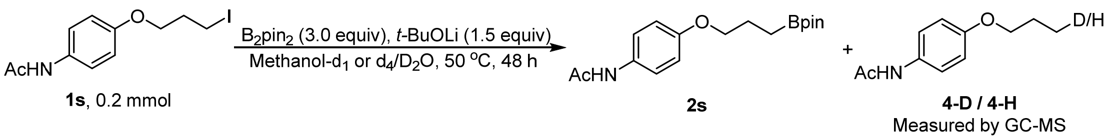
Data of standard sample: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.61 – 1.49 (m, 1H), 1.46 – 1.40 (m, 1H), 1.21 (s, 12H), 1.20 (s, 24H), 1.12 – 1.02 (m, 1H), 0.89 – 0.68 (m, 4H) according to the literature data.[25]

GC-MS data



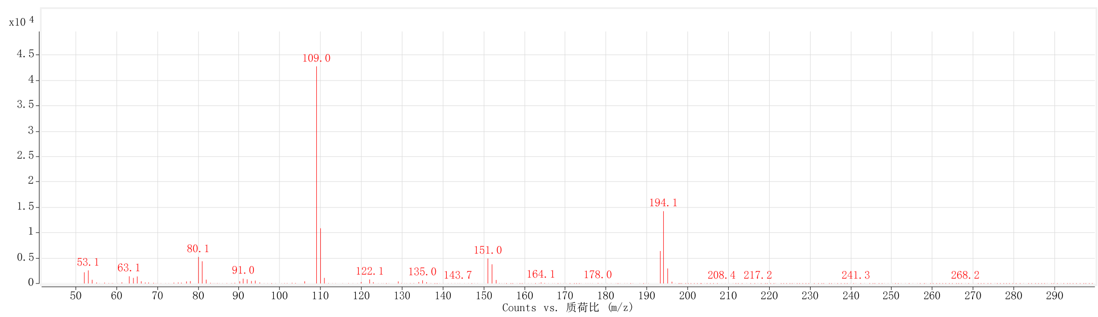


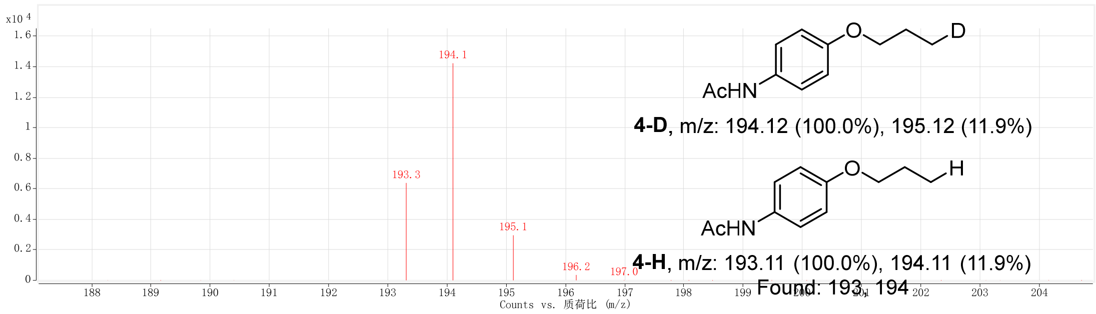
Deuteration reaction and DFT calculations



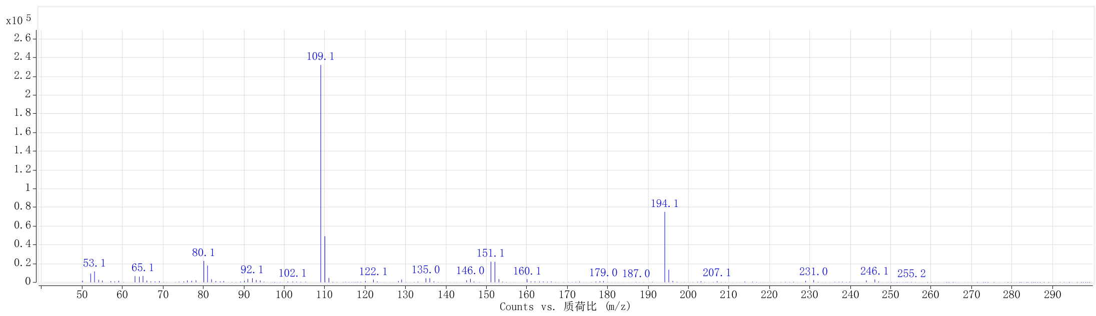
In a glove box, **1s** (0.2 mmol, 64 mg), *t*-BuOLi (0.3 mmol, 24.0 mg) and B_2pin_2 (0.6 mmol, 152 mg) were dissolved in methanol-d_1 or methanol-d_4 (1.2 mL) and D_2O (12 μL). After remove the tight vial from the glove box, the reaction mixture was stirred at 50 °C for 48 h. Upon cooling to room temperature, the reaction mixture was filtered by a small silica column (using EtOAc as eluent) and analyzed by GC-MS.

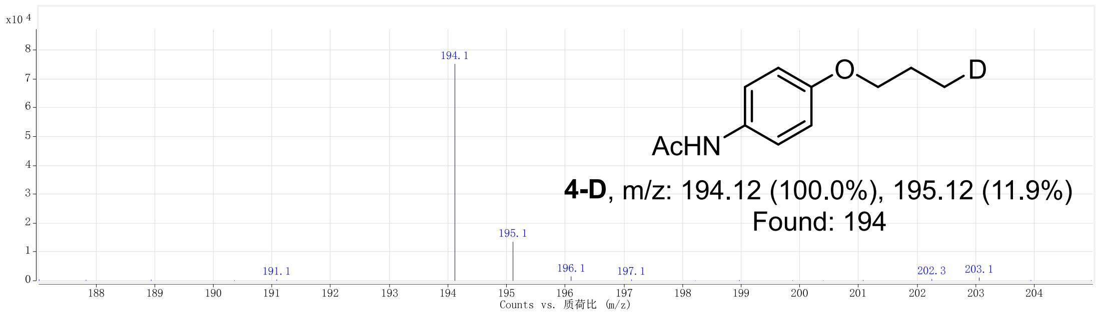
Case using methanol-d_1 as solvent: a mixture of **4-D** and **4-H** was found.





Case using methanol-d_4 as solvent: Only **4-D** was found.





According to the result using methanol-d_4, only deuterated by-product was found, indicating that the by-product was mainly obtained from the solvent. Then, according to the result using methanol-d_1 (CH_3OD), a mixture of hydrogenated and deuterated by-product was found, thus ignored the procedure from alkyl anion which could only form deuterated by-product in methanol-d_1.

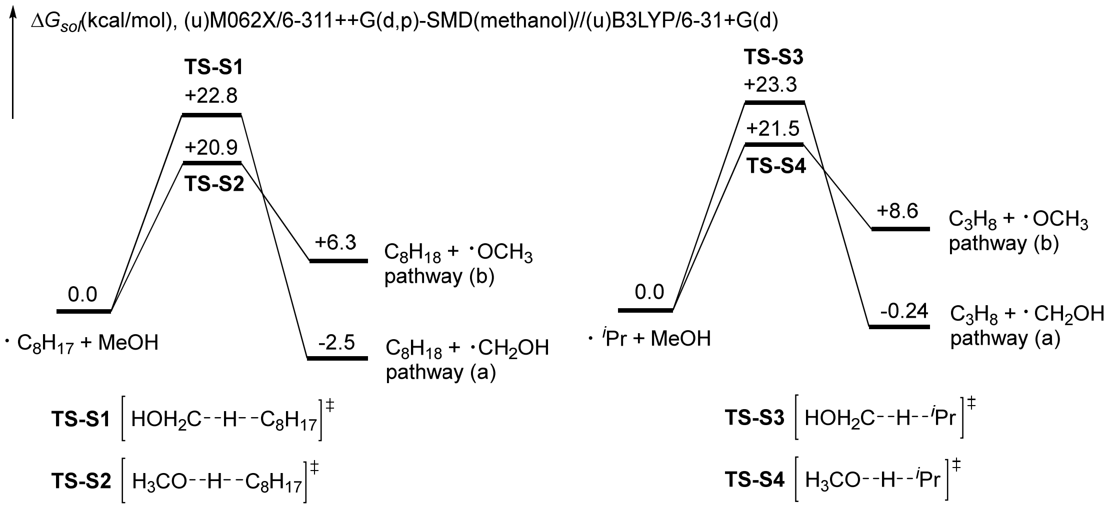
To further support the radical pathway, we conducted a DFT calculation for the hydrogenation procedure of alkyl radical and methanol. There're two possible pathways, i.e. reaction with the proton atoms of $\mathit{CH}_3\mathrm{OH}$ or $\mathrm{CH_3O}\mathit{H}$. In methanol-d_1, pathway (a) and (b) will obtain hydrogenated and deuterated by-product, respectively.

$$R\cdot + \mathit{CH}_3\mathrm{OH} \longrightarrow RH + \cdot CH_2OH \quad (a)$$

$$R\cdot + \mathrm{CH_3O}\mathit{H} \longrightarrow RH + \cdot OCH_3 \quad (b)$$

For primary and secondary alkyl radicals, $^{n}C_8H_{17}$• and ^{i}Pr• were chosen as examples. As shown in **Figure S1**, although pathway (a) is more thermodynamic favorable, as the significantly lower concentration of RH and radicals comparing with the solvent methanol, pathway (b) is also feasible, which even has lower activation energy. Thus the hydrogenation procedure would through a mixed pathway of (a) and (b), which showed agreement with our experiment using methanol-d_1. These experiments and calculation further supported the formation of alkyl radical, instead of alkyl anion.

Figure S1. DFT calculation for hydrogenation procedure of alkyl radicals



In addition, comparing with the borylation procedure, the hydrogenation procedure has higher activation energy (20.9 vs 15.1 kCal/mol), thus the borylation procedure was competitive. However, firstly, the impact of radical and solvent doesn't need to overcome the solvation, thus the hydrogenation reaction has remarkable higher pre-exponential factor *A* comparing with the borylation procedure. Secondly, as the solvent, methanol has very high concentration comparing with B_2pin_2. Thus the hydrogenation reaction could also have certain competitiveness, and forming the hydrogenated by-products. Therefore a high B_2pin_2 concentration is beneficial for the formation of the borylation product.

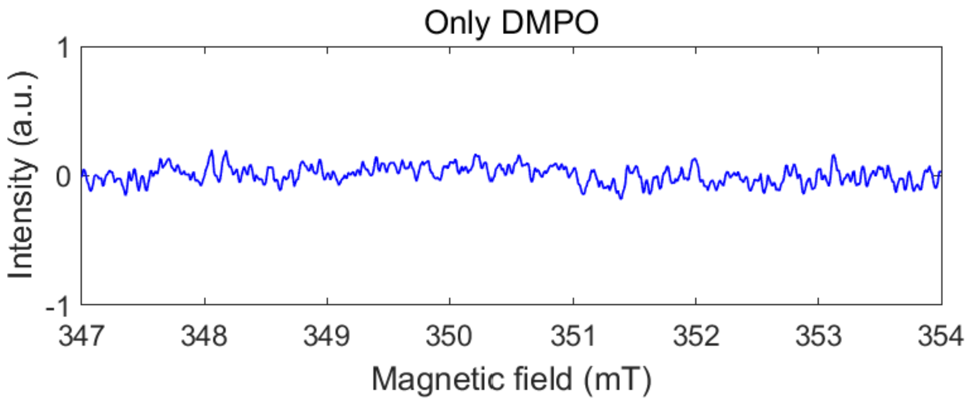
6. EPR experiments and data

For each case, in a 3 mL glassy flask, **1a-F$_{17}$** (if necessary, 273 mg, 132 μl, 0.5 mmol, 1.0 equiv.) or **1a** (if necessary, 120 mg, 91 μl, 0.5 mmol, 1.0 equiv.), B_2pin_2 (if necessary, 508 mg, 2.0 mmol, 4.0 equiv.), *t*-BuOLi (if necessary, 80 mg, 1.0 mmol, 2.0 equiv.) and DMPO (5.0 μl, 0.05 mmol, 0.1 equiv.) were dissolved in MeOH (2.5 mL), and the flask was closed. After stirred at 50 °C (using a water bath) for 10 min, small amount of the reaction mixture was encased into a capillary tube (diameter 1.0 mm) and measured the EPR signal on a Bruker A 200 EPR spectrometer at room temperature. Each case was measured for 4 scans, and each scan was measured for 20 s. The magnetic field scanning region was centered by g = 2 with 100 G (or 10 mT) width (about 3462 to 3562 G or 346.2 to 356.2 mT) and contained 1024 points. The EPR spectra were simulated using the EasySpin-5.2.14 running in Matlab (R2017a) and carefully compared with literature data.[33]

6.1 EPR profiles data

In these figures, blue lines are experiment data and red lines are simulation data.

Background: only DMPO.



DOS Format

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MAX 44536.429688

JSS 0

GST 3462.228475

GSI 99.975580

JUN G

JON Bruker BioSpin GmbH

JEX field-sweep

JNS 4

JSD 4

CCF 1

HCF 3512.228475

HSW 100.000000

EMF 3462.228475

RCT 20.000000

RTC 40.960000

RRG 8.933672e+003

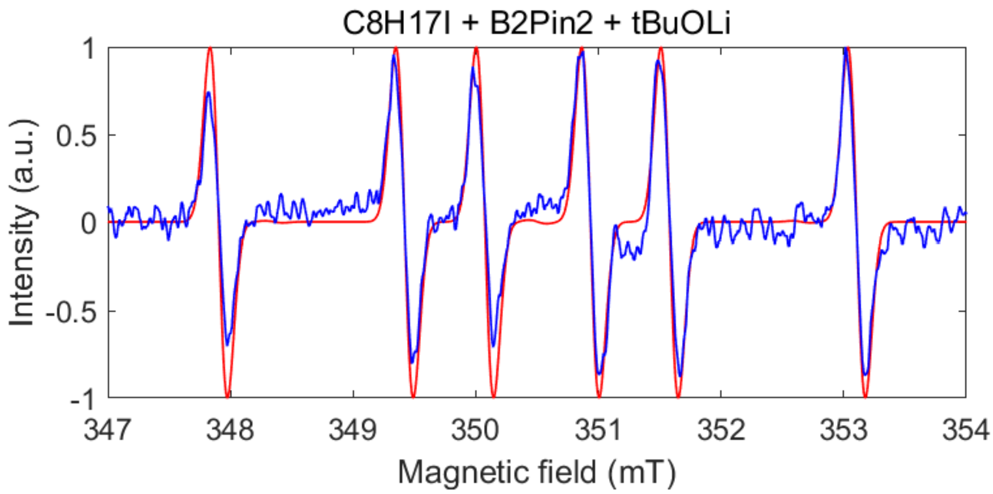
ROF 2.700000

RMA 0.500000

MF 9.842960

MP 1.904e+001

Reaction A: 1a + B_2pin_2 + *t*-BuOLi



DOS Format

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JUN G

JON Bruker BioSpin GmbH

JEX field-sweep

JNS 4

JSD 4

CCF 1

HCF 3512.228475

HSW 100.000000

EMF 3462.228475

RCT 20.000000

RTC 40.960000

RRG 8.933672e+003

ROF 2.700000

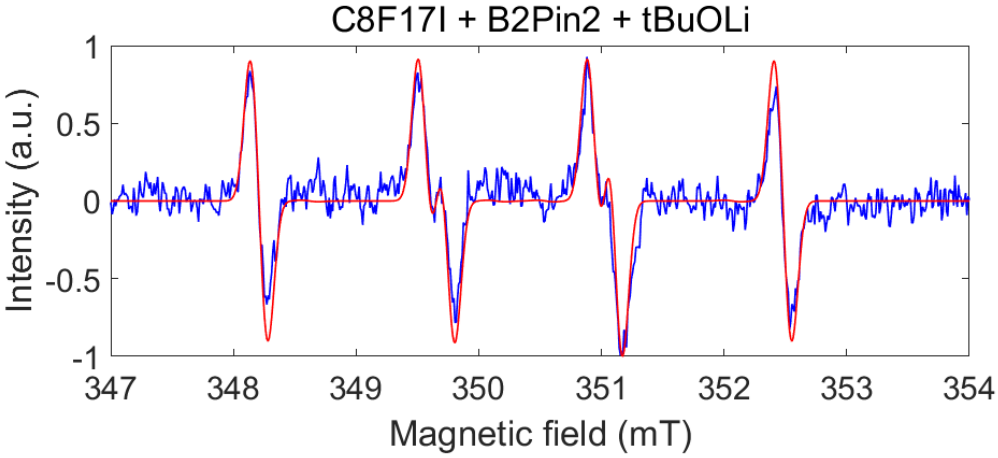
RMA 0.500000

MF 9.842752

MP 1.904e+001

Reaction B: 1a-F_{17} + B_2pin_2 + *t*-BuOLi

Note: this reaction was continued for 90 min to obtain a maximum signal-noise ratio (at 10 min smaller amount of the same signal was found, may be due to the low reactivity of **1a-F_{17}**). And each EPR scan was measured for 60 s.



DOS Format

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MAX 166050.515625

JSS 0

GST 3462.228475

GSI 99.975580

JUN G

JON Bruker BioSpin GmbH

JEX field-sweep

JNS 4

JSD 4

CCF 1

HCF 3512.228475

HSW 100.000000

EMF 3462.228475

RCT 20.000000

RTC 40.960000

RRG 8.933672e+003

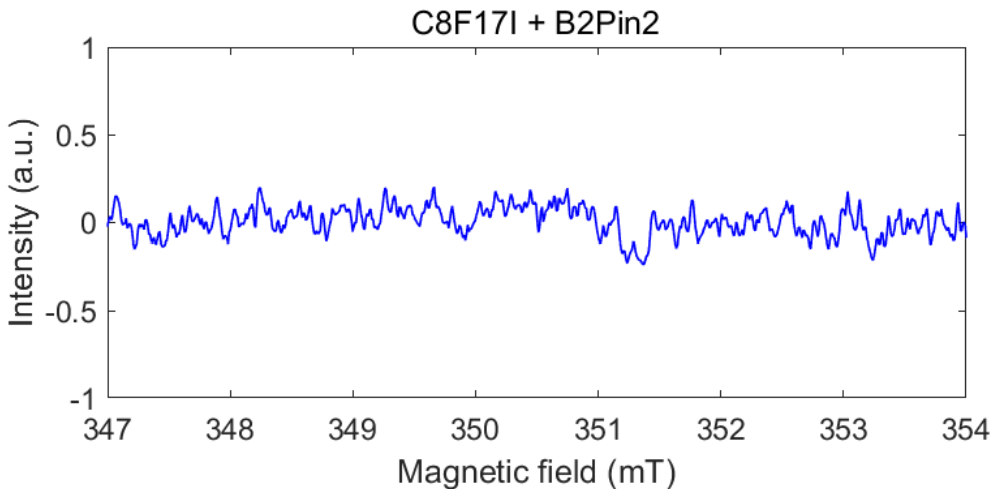
ROF 2.700000

RMA 0.500000

MF 9.842752

MP 1.904e+001

Reaction C: 1a-F_{17} + B_2pin_2



DOS Format

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MAX 53671.792969

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GST 3462.228475

GSI 99.975580

JUN G

JON Bruker BioSpin GmbH

JEX field-sweep

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JSD 4

CCF 1

HCF 3512.228475

HSW 100.000000

EMF 3462.228475

RCT 20.000000

RTC 40.960000

RRG 8.933672e+003

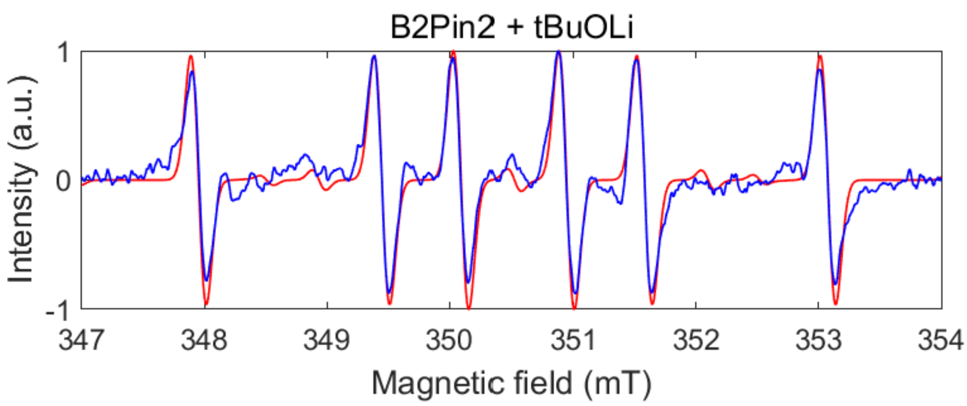
ROF 2.700000

RMA 0.500000

MF 9.843080

MP 1.907e+001

Reaction D: B_2pin_2 + *t*-BuOLi



DOS Format

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GSI 99.975580

JUN G

JON Bruker BioSpin GmbH

JEX field-sweep

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HSW 100.000000

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RCT 20.000000

RTC 40.960000

RRG 8.933672e+003

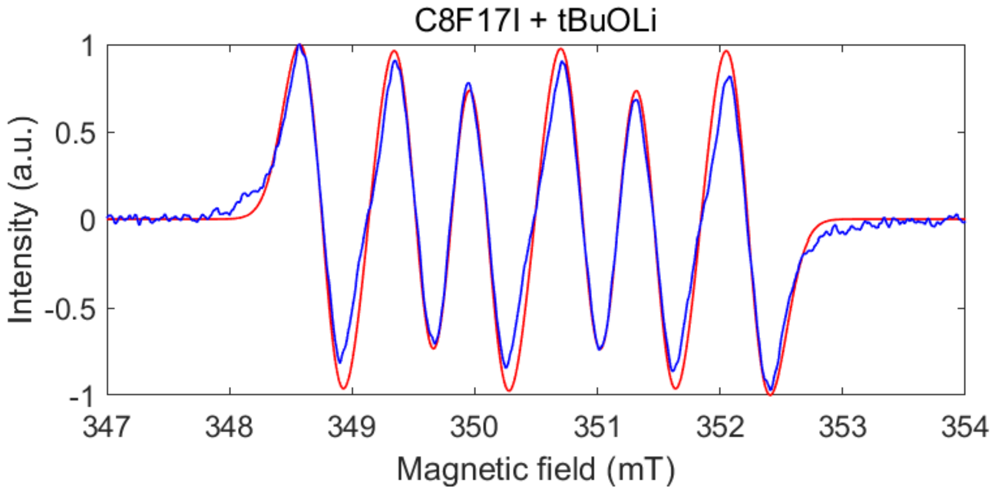
ROF 2.700000

RMA 0.500000

MF 9.843340

MP 1.909e+001

Reaction E: 1a-F_{17} + *t*-BuOLi



DOS Format

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GSI 99.975580

JUN G

JON Bruker BioSpin GmbH

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HSW 100.000000

EMF 3462.228475

RCT 20.000000

RTC 40.960000

RRG 8.933672e+003

ROF 2.700000

RMA 0.500000

MF 9.843120

MP 1.902e+001

6.2 Simulations

Reaction A: suggested DMPO·C_8H_{17}-*n*, residual = 0.0939.

React. A	*g* value	linewidth (G)	A_N (G)	A_H (G)	Comments
Exp	2.00633	1.667	15.16	21.66	
Ref			14.2	20.5	DMPO·C_2H_5, in benzene[34]
			16.3	23.5	DMPO·C_2H_5, in water[35]

Reaction B: suggested DMPO·OC_8F_{17}-*n*, residual = 0.0923.

React.B	*g* value	linewidth (G)	A_N (G)	A_H (G)	Comments
Exp	2.00692	1.343	13.74	15.30	A_F = 0.67 G
Ref			13.2	15.5	DMPO·CF_3, in benzene, with A_F = 1.01 G[34]

Reaction D: Radical 1 (suggested DMPO·CH_2OH) : Radical 2 (suggested DMPO·H) = 1 : 0.0624, residual = 0.0788.

Radical 1	*g* value	linewidth (G)	A_N (G)	A_H (G)	Comments
Exp	2.00638	1.485	14.91	21.37	
Ref	-	-	14.7	20.7	In benzene[34]
	-	-	15.9	22.6	In water[36]
Radical 2	***g* value**	**linewidth (G)**	**A_N (G)**	**A_H (G)**	**Comments**
Exp	2.00636	1.302	15.79	20.08	
Ref	-	-	14.4	18.9	In benzene[34]
	-	-	16.6	22.5	In water[37]

Reaction E: suggested DMPO·OMe or DMPO·OBu-*t*, residual = 0.0836.

React. E	*g* value	linewidth (G)	A_N (G)	A_H (G)	Comments
Exp	2.00651	4.145	13.51	7.83	
Ref	-	-	13.6	7.6	DMPO·OMe, in benzene[34]
	-	-	13.1	7.9	DMPO·OBu-*t*, in benzene[34]

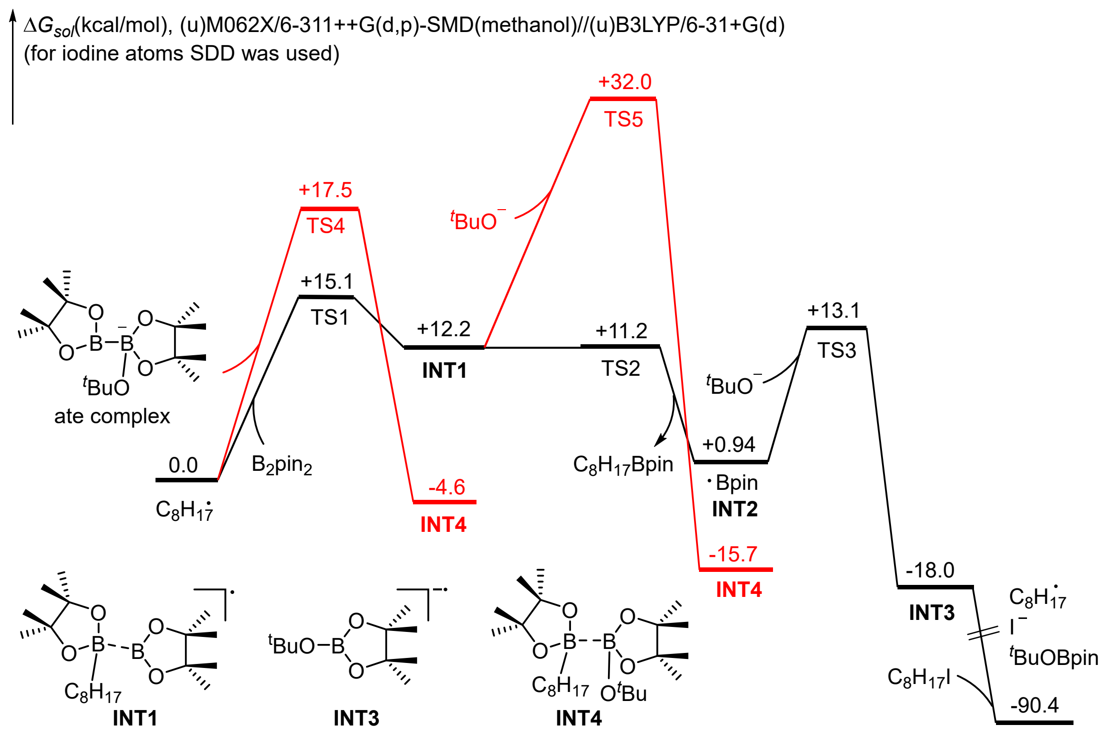
7. DFT computational data

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. On the basis of the gas phase optimized structures, the single point (SP) energies were calculated with the M062X (or uM062X for open shell systems) functional and basis set of 6-311++G(d,p), and solvent energy corrections were calculated using the SMD model with methanol as the solvent. For cases contain an iodine atom, a basis set of SDD potential function were used for iodine atom in the geometry optimization, vibrational frequency analysis and single point energy calculation.

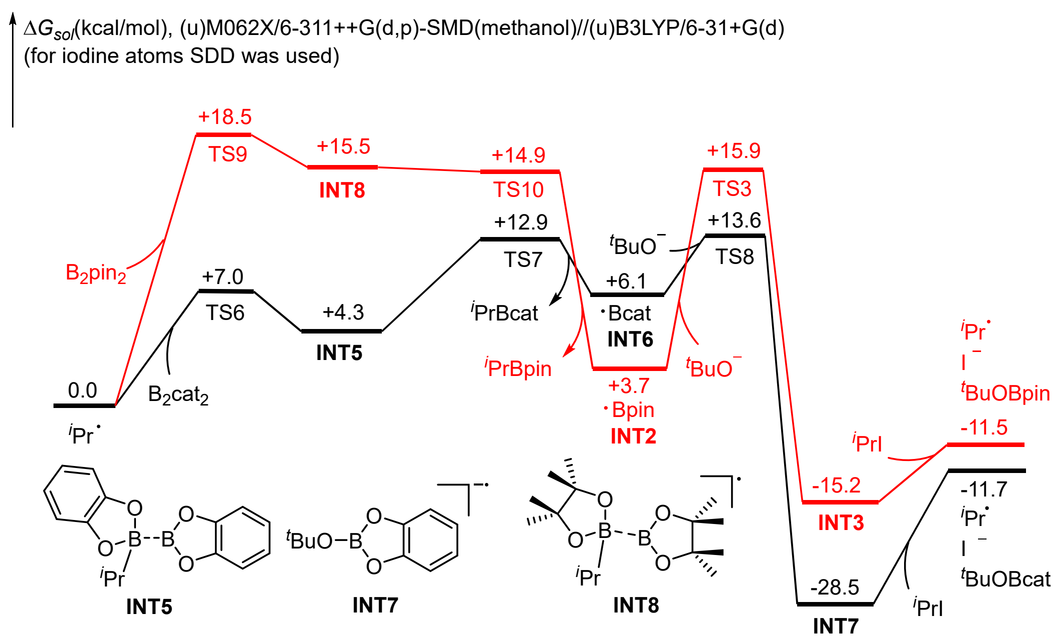
7.1 Table of energies and lowest frequencies

In **Table S9**, 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 173.53*i* cm^{-1}.

(a) Gibbs free energy profile for C−B bond formation pathways with B_2pin_2



(b) Gibbs free energy profile for C−B bond formation pathways with B_2pin_2 and B_2cat_2



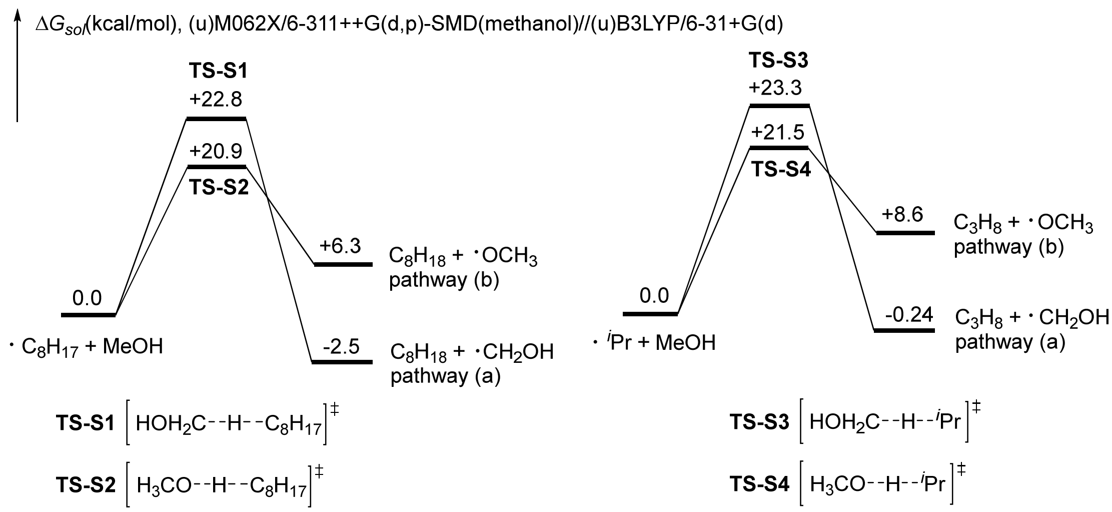


Table S9. Energies and lowest frequencies

Structure	SP energy	ZPE	TCH	TCG	G	Lowest frequency
$^{n}C_8H_{17}$•	-314.953523	0.231629	0.244096	0.193292	-314.760231	53.06
B_2pin_2	-822.449694	0.364287	0.385081	0.315828	-822.133866	5.02
TS1	-1137.402809	0.597927	0.630635	0.532745	-1136.870064	-173.53
INT1	-1137.408912	0.599248	0.632056	0.534257	-1136.874655	13.33
TS2	-1137.409139	0.598891	0.631415	0.532927	-1136.876212	-106.68
$^{n}C_8H_{17}$Bpin	-726.266339	0.419049	0.440865	0.367566	-725.898773	15.70
•Bpin (INT2)	-411.140861	0.180061	0.190437	0.147033	-410.993828	89.72
$^{t}BuO^{-}$	-233.136953	0.120550	0.127871	0.091854	-233.045099	212.71
TS3	-644.274755	0.301456	0.319298	0.255227	-644.019528	-48.45
INT3	-644.334430	0.307654	0.324729	0.265280	-644.069150	35.69
$^{n}C_8H_{17}I$	-326.396890	0.237322	0.250609	0.195797	-326.201093	36.67
I^{-}	-11.552811	0.000000	0.002360	-0.016848	-11.569659	None
^{t}BuOBpin	-644.323066	0.309339	0.326496	0.267367	-644.055699	33.93
Ate complex	-1055.628790	0.486886	0.514773	0.432267	-1055.196523	24.94
TS4	-1370.576861	0.720007	0.759940	0.648058	-1369.928803	-220.72
TS5	-1370.533153	0.720589	0.760714	0.644894	-1369.888259	-47.27
INT4	-1370.616977	0.723879	0.763623	0.652834	-1369.964143	16.63
^{i}Pr•	-118.435499	0.088224	0.094360	0.060956	-118.374543	109.68

B_2cat_2	-812.799312	0.187480	0.201201	0.146077	-812.653235	22.80
TS6	-931.245901	0.278273	0.297305	0.229254	-931.016647	-212.53
INT5	-931.252414	0.279904	0.298763	0.231431	-931.020983	14.51
TS7	-931.235912	0.279545	0.298475	0.228700	-931.007212	-83.65
•Bcat (INT6)	-406.309804	0.091700	0.098543	0.060939	-406.248865	231.64
^{i}PrBcat	-524.918909	0.187599	0.199226	0.149693	-524.769216	9.65
TS8	-639.446837	0.212303	0.227241	0.164928	-639.281909	-30.26
INT7	-639.527885	0.218183	0.231971	0.178826	-639.349059	40.31
^{i}PrI	-130.000524	0.094050	0.100573	0.063845	-129.936679	240.08
^{t}BuOBcat	-639.495907	0.220592	0.234406	0.181146	-639.314761	40.09
TS9	-940.881358	0.455736	0.481451	0.402361	-940.478997	-209.13
INT8	-940.887708	0.457072	0.482895	0.404014	-940.483694	20.64
TS10	-940.887206	0.456629	0.482236	0.402573	-940.484633	-104.22
^{i}PrBpin	-529.744564	0.276107	0.291176	0.235918	-529.508646	15.53
MeOH	-115.713801	0.051299	0.055559	0.028551	-115.685250	329.04
•CH_2OH	-115.049633	0.037294	0.041553	0.014313	-115.035320	436.50
•OCH_3	-115.034949	0.036602	0.040567	0.013660	-115.021289	723.18
$^{n}C_8H_{18}$	-315.623849	0.246582	0.258588	0.209695	-315.414154	53.34
C_3H_8	-119.102893	0.103719	0.109191	0.078045	-119.024848	218.64
TS-S1	-430.645131	0.280882	0.296615	0.235928	-430.409203	-1710.91
TS-S2	-430.646722	0.280281	0.296090	0.234590	-430.412132	-1638.06
TS-S3	-234.126995	0.138041	0.147268	0.104302	-234.022693	-1728.77
TS-S4	-234.129399	0.137672	0.146877	0.103915	-234.025484	-1502.14

7.2 Cartesian coordinates of the structures

$^{n}C_8H_{17}$•

C	4.42760400	0.26578500	0.00000000
H	5.30449500	-0.39300100	-0.00000100
H	4.49565500	0.91103900	0.88546000
H	4.49565500	0.91104000	-0.88546000
C	3.12211400	-0.53875700	-0.00000100
H	3.10000400	-1.19963200	-0.87892800
H	3.10000400	-1.19963400	0.87892400
C	1.86590700	0.34340600	0.00000000
H	1.88893200	1.00522200	0.87943900
H	1.88893200	1.00522300	-0.87943800
C	0.55402000	-0.45380700	-0.00000100
H	0.53203300	-1.11535400	-0.87939900
H	0.53203300	-1.11535600	0.87939500
C	-0.70159100	0.42950600	0.00000100
H	-0.68046900	1.09093500	-0.87955000
H	-0.68046900	1.09093200	0.87955400
C	-2.01129100	-0.37101100	0.00000000
H	-2.04270900	-1.02945400	0.87966700
H	-2.04270900	-1.02945100	-0.87967000
C	-3.27396900	0.53244800	0.00000100
H	-3.22659500	1.18756600	-0.88227700
H	-3.22659500	1.18756300	0.88228200
C	-4.55670000	-0.23081000	0.00000000
H	-4.99737700	-0.58410200	0.92836500
H	-4.99737800	-0.58409700	-0.92836600

B_2pin_2

C	-3.01075700	-0.47450500	0.62998900
C	-3.01078200	0.47449900	-0.62998100
C	3.01076100	-0.63001500	-0.47447500
C	3.01077900	0.63001000	0.47447200
B	-0.85203300	0.00003600	-0.00001200
B	0.85202500	0.00003200	-0.00000700
O	1.61779300	0.68881000	0.91270800
O	-1.61781700	0.91280300	-0.68870000
O	-1.61777600	-0.91275800	0.68869000
O	1.61777800	-0.68876900	-0.91272000
C	-3.29482600	-0.25530400	-1.95051200
H	-4.34165500	-0.57186100	-2.01858800
H	-3.08627000	0.42506300	-2.78258700
H	-2.65589600	-1.13640500	-2.06880800
C	-3.90178000	1.70987300	-0.51345100
H	-4.95425000	1.42150700	-0.40318000
H	-3.62002900	2.33500100	0.33714600
H	-3.80950400	2.31489400	-1.42164300
C	-3.29481200	0.25529100	1.95052100
H	-2.65591100	1.13641400	2.06880800
H	-4.34165100	0.57181100	2.01860900
H	-3.08622500	-0.42506700	2.78259700
C	-3.90171000	-1.70991100	0.51346600
H	-3.61994600	-2.33502400	-0.33713800
H	-3.80939800	-2.31493300	1.42165300
H	-4.95419300	-1.42158600	0.40321100
C	3.90171300	0.51351800	1.70989100
H	4.95419400	0.40320800	1.42158000
H	3.80942600	1.42174200	2.31486200
H	3.61992000	-0.33704300	2.33505000

C	3.29489500	1.95049700	-0.25538100
H	3.08633300	2.78261500	0.42493200
H	4.34174300	2.01852100	-0.57188500
H	2.65601400	2.06877400	-1.13652000
C	3.29483000	-1.95051200	0.25538000
H	4.34167300	-2.01856900	0.57189300
H	2.65593800	-2.06877000	1.13651300
H	3.08624800	-2.78262200	-0.42493700
C	3.90170900	-0.51355100	-1.70988800
H	3.61993800	0.33701300	-2.33505200
H	4.95419000	-0.40326500	-1.42157100
H	3.80940500	-1.42177500	-2.31485600

TS1

C	-1.83798200	3.17251200	-0.67619300
C	-1.56786800	3.06651700	0.87645400
C	-2.26014700	-2.80742300	0.76438200
C	-3.21310400	-2.48490500	-0.45651800
B	-1.62773900	0.96615800	-0.06631800
B	-1.69568200	-0.75635100	-0.17166300
O	-2.54704900	-1.37219400	-1.10432200
O	-1.74756000	1.63934600	1.12758100
O	-1.52636000	1.82456300	-1.13979900
O	-1.58392800	-1.54318600	0.98046400
C	-0.12716500	3.40933500	1.27999500
H	0.07261800	4.48282900	1.18637800
H	0.02527100	3.12037000	2.32497000
H	0.60391500	2.86772600	0.67165800
C	-2.54821300	3.83612600	1.76097300
H	-2.48857100	4.91372100	1.56513200

H	-3.57917200	3.50966400	1.60481500
H	-2.29872900	3.66852300	2.81410200
C	-3.31014000	3.42640800	-1.03019700
H	-3.97280800	2.71598700	-0.52575400
H	-3.62094900	4.44297400	-0.76401500
H	-3.44093500	3.29749500	-2.10953100
C	-0.94567800	4.16119800	-1.42546400
H	0.11395000	3.91828000	-1.31444900
H	-1.18691900	4.13536700	-2.49347600
H	-1.10888500	5.18440700	-1.06558900
C	-3.37440700	-3.61738900	-1.47249900
H	-3.84201300	-4.49553300	-1.01035800
H	-4.01889100	-3.28192200	-2.29205200
H	-2.41607800	-3.91886000	-1.90282800
C	-4.60046600	-1.97635200	-0.02969700
H	-5.12971100	-1.61160200	-0.91629700
H	-5.20131000	-2.77028900	0.42834700
H	-4.52053000	-1.14662200	0.67996500
C	-1.19189700	-3.87021800	0.45711100
H	-1.63549600	-4.86901000	0.37239700
H	-0.65015400	-3.65939000	-0.46906800
H	-0.46605400	-3.88753700	1.27702400
C	-2.97998600	-3.18703400	2.06124500
H	-3.64164800	-2.38846400	2.40475700
H	-3.57054900	-4.10203800	1.92943100
H	-2.24090400	-3.37057500	2.84862300
C	1.31875200	-0.47164900	-0.18426000
H	1.23883100	-1.09248000	0.71723100
H	1.26388000	0.57382800	0.14716900
C	2.69763400	-0.70848800	-0.84556300

H	2.77192000	-0.09812600	-1.75723100
H	2.76812900	-1.75694000	-1.16987600
C	3.87444600	-0.38104200	0.08548600
H	3.79476300	0.66548600	0.41645700
H	3.80034100	-0.99574000	0.99510700
C	5.24542800	-0.60228500	-0.56900200
H	5.31357200	0.00977500	-1.48132400
H	5.32563900	-1.64953300	-0.89816600
C	6.42791100	-0.26957400	0.35147100
H	6.34583000	0.77639600	0.68489500
H	6.36530400	-0.88506700	1.26200500
C	7.79777000	-0.48191100	-0.30808300
H	7.88202700	-1.52766400	-0.63835900
H	7.85858400	0.13133100	-1.21916700
C	0.18668200	-0.78330300	-1.12426800
H	0.01938000	-0.08886100	-1.94623600
H	0.09032900	-1.82666700	-1.42306400
C	8.97447700	-0.14202000	0.61442200
H	8.96178500	-0.76325500	1.51941100
H	9.93648700	-0.30395100	0.11315200
H	8.93775900	0.90768100	0.93356700

INT1

C	-1.62971600	3.03356500	-0.67456400
C	-1.91868400	2.82863500	0.86544300
C	-2.42462200	-2.67987100	0.73881100
C	-3.27020400	-2.14268600	-0.48473000
B	-1.44387100	0.82749300	-0.12633700
B	-1.23165200	-1.00428000	-0.36285700
O	-2.29228400	-1.38718900	-1.23917500

O	-2.06192800	1.36884000	0.96344300
O	-1.04391200	1.74239000	-1.05531700
O	-1.37614700	-1.69388700	0.86874800
C	-0.74371300	3.21163800	1.77332800
H	-0.59884600	4.29732800	1.80346300
H	-0.95319000	2.86370900	2.78988000
H	0.19050500	2.74517600	1.44525400
C	-3.20740700	3.46891100	1.37532300
H	-3.16713000	4.55968000	1.26800200
H	-4.08562600	3.09846800	0.84137800
H	-3.33532500	3.23806500	2.43808100
C	-2.89519000	3.20314500	-1.52424900
H	-3.62472500	2.41227100	-1.32384500
H	-3.37272100	4.17280000	-1.34412500
H	-2.62089900	3.14569300	-2.58242300
C	-0.62207400	4.13146500	-1.00604600
H	0.34552600	3.95307500	-0.53133700
H	-0.46482000	4.16934900	-2.08902800
H	-0.99566000	5.11069700	-0.68303400
C	-3.84196800	-3.22818000	-1.40079300
H	-4.54213700	-3.87142300	-0.85356300
H	-4.38712900	-2.75874500	-2.22682800
H	-3.05527000	-3.85318300	-1.83029000
C	-4.39532600	-1.17719200	-0.07522000
H	-4.79865900	-0.70420300	-0.97759700
H	-5.21320500	-1.70730100	0.42622800
H	-4.03065100	-0.39065300	0.59093600
C	-1.73386300	-4.02512400	0.45398300
H	-2.45670500	-4.84775700	0.40501800
H	-1.17448900	-3.99951300	-0.48648100

H	-1.02641400	-4.23636900	1.26267500
C	-3.18607800	-2.76471900	2.06306500
H	-3.56647200	-1.78807700	2.37157200
H	-4.02791000	-3.46412200	1.98735800
H	-2.51358400	-3.12672700	2.84838300
C	1.44858400	-0.59379800	-0.10871900
H	1.39152800	-1.18019300	0.81829700
H	1.35178900	0.46143200	0.18679100
C	2.82720600	-0.79694600	-0.75893800
H	2.87421900	-0.21691200	-1.69310400
H	2.93757200	-1.85275800	-1.04978700
C	4.00084700	-0.39678000	0.14633400
H	3.88796200	0.65769600	0.44207600
H	3.95680600	-0.98087200	1.07823500
C	5.37453900	-0.59250800	-0.51052000
H	5.41660600	-0.00672800	-1.44159900
H	5.48641500	-1.64613000	-0.80902000
C	6.55260800	-0.19532600	0.38961100
H	6.43968000	0.85698900	0.69312900
H	6.51603400	-0.78527100	1.31841000
C	7.92424900	-0.38363900	-0.27348300
H	8.03773100	-1.43461200	-0.57746100
H	7.96134400	0.20728400	-1.20046200
C	0.29448300	-0.98309300	-1.03469100
H	0.28752000	-0.36650600	-1.93971400
H	0.40526400	-2.03341800	-1.35103100
C	9.09625200	0.01421400	0.63180500
H	9.10766400	-0.58449500	1.55190200
H	10.05972800	-0.13126400	0.12813900
H	9.02992300	1.06996200	0.92540500

TS2

C	-1.22118900	3.15878000	-0.65103800
C	-1.80143800	2.95702000	0.80525100
C	-2.72104700	-2.51420600	0.83028900
C	-3.42283000	-2.06313900	-0.52363200
B	-1.37340900	0.94167100	-0.16287000
B	-1.20456400	-1.36883800	-0.50004700
O	-2.30969700	-1.59326200	-1.32589600
O	-2.12264100	1.51369300	0.81605700
O	-0.72036300	1.80793600	-0.97834200
O	-1.44956700	-1.81692000	0.79859400
C	-0.77260300	3.17565500	1.91992500
H	-0.51393500	4.23546100	2.02228300
H	-1.19849600	2.83242100	2.86809500
H	0.14586100	2.60839800	1.74005600
C	-3.08164800	3.73015700	1.10718400
H	-2.89982300	4.81087300	1.06247100
H	-3.88347200	3.48302400	0.40774500
H	-3.42608700	3.48714900	2.11774300
C	-2.28617400	3.48975000	-1.70256300
H	-3.12385300	2.78634100	-1.66538100
H	-2.67680300	4.50487100	-1.56939300
H	-1.83504900	3.42242900	-2.69753000
C	-0.05307000	4.13483200	-0.75555000
H	0.78418800	3.84014500	-0.11895100
H	0.30436900	4.16773600	-1.78991800
H	-0.36825600	5.14685100	-0.47352600
C	-4.11032200	-3.19282400	-1.29687600
H	-4.93650500	-3.62020500	-0.71592700

H	-4.52284200	-2.79333200	-2.22963800
H	-3.41311900	-3.99339300	-1.55507400
C	-4.41169200	-0.89854900	-0.36032600
H	-4.70815400	-0.55017400	-1.35603400
H	-5.31593700	-1.21533900	0.17226400
H	-3.97123900	-0.05655600	0.17826800
C	-2.38520200	-4.01348800	0.88239100
H	-3.28835000	-4.63091700	0.94884000
H	-1.81161100	-4.32857100	0.00494900
H	-1.77183700	-4.20569400	1.76894700
C	-3.46350300	-2.11171000	2.10638400
H	-3.59355200	-1.02910400	2.17296600
H	-4.44932300	-2.59016800	2.15502300
H	-2.88614500	-2.43530900	2.97927700
C	1.41261500	-0.96247900	-0.14227600
H	1.36694000	-1.64661000	0.71649800
H	1.27904500	0.04897700	0.26912700
C	2.80052800	-1.04926800	-0.79346400
H	2.82908400	-0.38329800	-1.66965700
H	2.95444400	-2.06821400	-1.18135600
C	3.95387300	-0.68802600	0.15271800
H	3.80266600	0.33390600	0.53379100
H	3.92379300	-1.34823600	1.03321400
C	5.33845300	-0.78160300	-0.50353500
H	5.36170600	-0.13227600	-1.39234600
H	5.49567100	-1.80678900	-0.87245300
C	6.49400300	-0.39806200	0.43096900
H	6.33811900	0.62792700	0.79901700
H	6.47370200	-1.04631200	1.32070200
C	7.87662600	-0.49106900	-0.22922000

H	8.03590400	-1.51707500	-0.59223000
H	7.89541500	0.15345100	-1.12046900
C	0.26615200	-1.28112200	-1.11490600
H	0.29099100	-0.59313400	-1.96966900
H	0.43423000	-2.28622800	-1.54376100
C	9.02519100	-0.09784200	0.70758000
H	9.05627500	-0.74758500	1.59194900
H	9.99713200	-0.17354400	0.20478100
H	8.91251400	0.93552500	1.06075500

$^{n}C_8H_{17}$Bpin

C	-3.72192800	0.84361200	-0.36155700
C	-3.99301300	-0.36552300	0.62010700
B	-1.93136300	-0.59413200	-0.36629000
O	-2.67519200	-0.98025600	0.72652000
O	-2.56131200	0.37921000	-1.11089700
C	-4.46087500	0.02665600	2.02055200
H	-5.42501200	0.54761300	1.97802200
H	-4.58934300	-0.87459900	2.62945800
H	-3.73744500	0.67202700	2.52478900
C	-4.92941100	-1.43244500	0.03505700
H	-4.91359500	-2.31254300	0.68634700
H	-5.96172700	-1.07113100	-0.03015600
H	-4.60789900	-1.74683400	-0.96338900
C	-3.29687800	2.13259600	0.35595900
H	-4.13022000	2.58024700	0.90882100
H	-2.47411500	1.95106800	1.05514700
H	-2.95141400	2.85556500	-0.39037100
C	-4.84847000	1.14443000	-1.34851800
H	-5.07927600	0.28100700	-1.97703200

H	-5.76052600	1.44698900	-0.81996200
H	-4.54887900	1.96819700	-2.00521200
C	-0.50591200	-1.16442700	-0.70850300
H	-0.39310400	-1.23336600	-1.80029400
H	-0.40369200	-2.18385600	-0.31135000
C	0.63854700	-0.28604700	-0.14660700
H	0.53487200	0.73875600	-0.53177500
H	0.54251400	-0.21556100	0.94694200
C	2.03854800	-0.81263100	-0.49270300
H	2.13694200	-0.88024800	-1.58694600
H	2.14176000	-1.84043200	-0.11246700
C	3.17477700	0.05381200	0.06798100
H	3.07577500	0.11734900	1.16253400
H	3.06491600	1.08272000	-0.30783600
C	4.57648200	-0.46432400	-0.28290800
H	4.68703200	-1.49368000	0.09127800
H	4.67670600	-0.52587700	-1.37739300
C	5.71111000	0.40249600	0.28048400
H	5.61266400	0.46273000	1.37537300
H	5.60010500	1.43264800	-0.09185900
C	7.11380800	-0.11161400	-0.07149700
H	7.22622200	-1.14059600	0.30065000
H	7.21365400	-0.17060300	-1.16528400
C	8.23984300	0.76094300	0.49628500
H	8.18756400	0.81274900	1.59162100
H	9.22733300	0.36560300	0.22861300
H	8.17726800	1.78788600	0.11340400

•Bpin (INT2)

C	-0.78915600	-0.15344500	0.04279100

C	0.78915600	-0.15344500	-0.04279100
B	0.00000000	1.98119200	0.00000000
O	1.08668300	1.25715600	-0.37463700
O	-1.08668300	1.25715600	0.37463700
C	1.48210100	-0.43683600	1.29456300
H	1.36071000	-1.48423600	1.59286000
H	2.55219200	-0.23096300	1.19023900
H	1.09291200	0.20048900	2.09481500
C	1.38048200	-1.03136700	-1.14196300
H	1.14002300	-2.08708800	-0.96606700
H	1.01279000	-0.74980600	-2.13149700
H	2.47056800	-0.92873800	-1.14478600
C	-1.48210100	-0.43683600	-1.29456300
H	-1.09291200	0.20048900	-2.09481500
H	-1.36071000	-1.48423600	-1.59286000
H	-2.55219200	-0.23096300	-1.19023900
C	-1.38048200	-1.03136700	1.14196300
H	-1.01279000	-0.74980600	2.13149700
H	-2.47056900	-0.92873800	1.14478600
H	-1.14002300	-2.08708800	0.96606700

$^{t}BuO^{-}$

C	0.00014800	0.00012300	-0.14922200
C	1.35992400	-0.52824300	0.43633700
H	1.53403200	-1.54747400	0.06435200
H	2.17648000	0.10637600	0.06483300
H	1.39999300	-0.54378600	1.54111900
C	-1.13776700	-0.91395500	0.43478300
H	-1.17346500	-0.94046100	1.53955600
H	-2.10712400	-0.55584300	0.06110500

H	-0.99554800	-1.93853100	0.06390600
C	-0.22311200	1.44163800	0.43615000
H	0.57356900	2.10196000	0.06631800
H	-1.17987500	1.83189800	0.06225600
H	-0.23219800	1.48323900	1.54089500
O	0.00112200	0.00065500	-1.49407900

TS3

C	1.89872600	0.80101300	0.13039500
C	1.88876700	-0.80302900	0.12866000
B	0.89370400	0.00739200	-1.76636500
O	1.28796300	-1.14693700	-1.17122700
O	1.30229900	1.15538200	-1.16862200
C	3.27799100	-1.45253900	0.13988200
H	3.80276800	-1.25502300	1.08353800
H	3.15886200	-2.53720800	0.03928500
H	3.90456200	-1.10657600	-0.68839800
C	0.99786700	-1.43019800	1.20340100
H	1.01573000	-2.52086900	1.07899500
H	1.37464100	-1.19847900	2.20919300
H	-0.03996500	-1.08196000	1.09824000
C	3.29606500	1.43299200	0.14277600
H	3.81861900	1.22673700	1.08578900
H	3.91783700	1.08077000	-0.68647800
H	3.19065700	2.51927600	0.04446800
C	1.01592100	1.43714200	1.20662200
H	-0.02627700	1.10304400	1.10146200
H	1.38976300	1.19811100	2.21177600
H	1.04803600	2.52775600	1.08477600
O	-1.61882700	0.02081900	0.34370800

C	-2.94312300	0.00277200	0.03319900
C	-3.82088700	-0.13513300	1.32020500
H	-3.55119500	-1.06221700	1.84429100
H	-3.60628400	0.70509200	1.99459800
H	-4.90517300	-0.15177100	1.11332600
C	-3.37326000	1.31640800	-0.69500500
H	-2.77803500	1.43163200	-1.61019400
H	-4.44357000	1.33926200	-0.96486100
H	-3.15793000	2.17667500	-0.04667000
C	-3.28755700	-1.19685200	-0.90623600
H	-2.68886200	-1.11821600	-1.82302000
H	-3.01222100	-2.13665500	-0.40870000
H	-4.35502000	-1.24590800	-1.18385600

INT3

C	1.62203700	0.81180300	0.06738500
C	1.98382300	-0.72202500	-0.05579400
B	-0.27437100	-0.43808400	-0.19992500
O	0.74789600	-1.29630100	-0.56193200
O	0.18134500	0.76884100	0.29269900
C	3.11111100	-1.03571600	-1.03761100
H	4.04232700	-0.53879300	-0.73514100
H	3.29469800	-2.11625500	-1.05602800
H	2.86194700	-0.71780600	-2.05507600
C	2.26816400	-1.37825700	1.30300300
H	2.30788800	-2.46528300	1.17052500
H	3.22665500	-1.04418400	1.72045500
H	1.47872100	-1.15720500	2.03264600
C	1.84930700	1.59056100	-1.23558200
H	2.91850000	1.72941000	-1.44250600

H	1.39182600	1.08445800	-2.09550000
H	1.38768100	2.58008200	-1.14430500
C	2.27207500	1.53910500	1.24221100
H	1.99645100	1.08978500	2.20218400
H	3.36718300	1.53072800	1.15196600
H	1.94336800	2.58450300	1.25476700
O	-1.57036600	-0.81997000	-0.33569300
C	-2.74089900	-0.03424200	0.00457800
C	-2.78426500	1.24321700	-0.84582000
H	-1.94869600	1.90744100	-0.60445100
H	-2.73257700	0.99245800	-1.91308700
H	-3.72144100	1.78730700	-0.66539900
C	-3.92497000	-0.94595700	-0.34029000
H	-3.86988400	-1.87608800	0.23813600
H	-4.87510400	-0.44695000	-0.11204600
H	-3.91008800	-1.20329600	-1.40643800
C	-2.73182400	0.28936600	1.50561200
H	-2.64251200	-0.63341400	2.09292500
H	-1.89611200	0.94650300	1.76615500
H	-3.66733200	0.78933600	1.79310400

ⁿ$C_8H_{17}I$

C	-7.25682500	-0.58120500	0.00000000
H	-8.19560300	-0.01413100	-0.00000300
H	-7.25943100	-1.23005700	0.88547400
H	-7.25942900	-1.23006500	-0.88546800
C	-6.03915600	0.35108000	-0.00000200
H	-6.08336200	1.01076300	-0.87903100
H	-6.08336300	1.01076900	0.87902200
C	-4.70076000	-0.40107200	0.00000100

H	-4.65741000	-1.06172400	0.87947400
H	-4.65740900	-1.06172800	-0.87947000
C	-3.47577700	0.52418800	-0.00000100
H	-3.51975200	1.18438100	-0.87962200
H	-3.51975100	1.18438300	0.87961900
C	-2.13898100	-0.23073700	0.00000000
H	-2.09343400	-0.89017100	-0.87959200
H	-2.09343400	-0.89017100	0.87959200
C	-0.91488000	0.69749900	0.00000000
H	-0.95765600	1.35577700	0.88035800
H	-0.95765600	1.35577700	-0.88035700
C	0.41908800	-0.07320900	0.00000000
H	0.46819100	-0.72579300	-0.88081100
H	0.46819100	-0.72579400	0.88081100
C	1.60229600	0.88142200	0.00000000
H	1.63760700	1.50921900	0.89128400
H	1.63760700	1.50921900	-0.89128300
I	3.55011400	-0.17544200	0.00000000

I^-

I	0.00000000	0.00000000	0.00000000

^{t}BuOBpin

C	1.62306900	0.81371800	0.06543800
C	1.99037200	-0.71924500	-0.05402200
B	-0.27464900	-0.44700200	-0.16658000
O	0.74895500	-1.29880800	-0.53451200
O	0.18845900	0.76555600	0.31875400
C	3.09794200	-1.04273000	-1.05560000
H	4.04070400	-0.56386400	-0.76450500

H	3.26161200	-2.12532200	-1.08225200
H	2.83722300	-0.71823000	-2.06587200
C	2.30042500	-1.37547100	1.29950200
H	2.34809100	-2.46065400	1.16229100
H	3.26081400	-1.03609000	1.70349800
H	1.51952200	-1.16323800	2.03742500
C	1.82142900	1.58919400	-1.24456400
H	2.88392200	1.72116500	-1.47723600
H	1.34357800	1.08127700	-2.08891600
H	1.36719800	2.58062100	-1.14412900
C	2.29401800	1.55607700	1.21956200
H	2.04975000	1.10841300	2.18604500
H	3.38411400	1.55759500	1.09986500
H	1.95416300	2.59737400	1.23414200
O	-1.56766500	-0.82818900	-0.29067800
C	-2.74918000	-0.03565600	0.00403700
C	-2.77221300	1.21543800	-0.88452800
H	-1.93030900	1.87560100	-0.65656900
H	-2.72146200	0.93220200	-1.94226700
H	-3.70172800	1.77478200	-0.72520500
C	-3.92548700	-0.95810700	-0.33353100
H	-3.88220800	-1.86960600	0.27255500
H	-4.87931200	-0.45424300	-0.13903900
H	-3.89276300	-1.24888400	-1.38920900
C	-2.76434600	0.33407100	1.49389000
H	-2.70816600	-0.57044000	2.11061800
H	-1.92212500	0.98449400	1.74815500
H	-3.69356500	0.85985900	1.74389700

Ate complex

C	-3.12921700	-0.11355800	-0.64587300
C	-2.93345800	-0.80583700	0.75284500
C	2.65186700	-1.06365300	0.62654600
C	2.11279200	-1.72251400	-0.70416000
B	-0.89102200	0.01603000	-0.01510400
B	0.83637400	0.23639500	-0.18901500
O	1.30683200	-0.70486300	-1.26567400
O	-1.49937300	-0.91449000	0.84207300
O	-1.89307000	0.61331900	-0.79936400
O	1.56238700	-0.25828000	1.03422000
C	-3.39836500	0.06442300	1.93384300
H	-4.49200900	0.14880100	1.97848500
H	-3.04654500	-0.39243600	2.86547900
H	-2.97051600	1.07029600	1.87430100
C	-3.54142400	-2.20539200	0.88136700
H	-4.63302100	-2.17905400	0.75986700
H	-3.12218200	-2.89334100	0.14249700
H	-3.31911400	-2.60818100	1.87643000
C	-3.21289100	-1.11355000	-1.81248100
H	-2.37615500	-1.81840600	-1.78546400
H	-4.15446200	-1.67817000	-1.80429400
H	-3.14796700	-0.55831300	-2.75474600
C	-4.29758800	0.87193000	-0.73103000
H	-4.19594800	1.68039800	-0.00215600
H	-4.32250400	1.32289000	-1.72989500
H	-5.25733800	0.36496400	-0.56162900
C	3.20159500	-2.10859400	-1.71815700
H	3.90547400	-2.84215700	-1.29807000
H	2.73364800	-2.55601300	-2.60494100
H	3.76243800	-1.22913200	-2.04668700

C	1.23571100	-2.96514100	-0.42324800
H	0.73463700	-3.25183800	-1.35688000
H	1.82361300	-3.82508300	-0.07093900
H	0.46600300	-2.73349800	0.31888200
C	3.89421500	-0.17646000	0.37508800
H	4.78978300	-0.76802600	0.13389900
H	3.69789600	0.53394300	-0.43195500
H	4.09875200	0.39828900	1.28751000
C	2.97955900	-2.05982400	1.74968600
H	2.08914000	-2.61672100	2.05569100
H	3.75755900	-2.77435500	1.44292300
H	3.34877200	-1.51277500	2.62713600
O	1.29954900	1.58447200	-0.62102800
C	0.99713200	2.82563900	-0.02510600
C	2.28524700	3.67384500	-0.11093900
H	2.12271700	4.69957100	0.25285700
H	3.08122400	3.21215300	0.48551600
H	2.62624700	3.71954100	-1.15252100
C	-0.11884500	3.52679500	-0.83423800
H	0.20419500	3.64792500	-1.87615800
H	-1.02657800	2.91624100	-0.83445400
H	-0.35467400	4.52104000	-0.42363900
C	0.57786900	2.72119200	1.45919000
H	0.47871700	3.72449800	1.89960800
H	-0.38420100	2.20841100	1.56743600
H	1.31983900	2.14933500	2.02468200

TS4

C	0.66428800	-2.57174700	1.27650800
C	1.66923200	-1.77035700	2.19708500

C	1.42389600	3.00210700	0.87358900
C	2.67459000	2.88589700	-0.07852700
B	1.71011700	-0.89839900	-0.03423200
B	1.47703100	0.89212200	-0.14723200
O	2.35655700	1.72898700	-0.87017300
O	2.44810000	-1.04180800	1.26520200
O	0.46218700	-1.68311900	0.18649500
O	0.94951200	1.64626800	0.92577300
C	0.94326900	-0.79170000	3.14607800
H	0.38442600	-1.31809100	3.93298500
H	1.69257700	-0.15090200	3.62717800
H	0.26335000	-0.14034500	2.59224000
C	2.61216600	-2.65131000	3.03484900
H	2.05547600	-3.29587500	3.73109500
H	3.24007300	-3.27930200	2.39661900
H	3.27600900	-2.00809300	3.62651500
C	1.27183100	-3.89641700	0.76308800
H	2.24791400	-3.71750000	0.30472800
H	1.37764700	-4.64179000	1.56416300
H	0.60667400	-4.31174500	-0.00413400
C	-0.69585600	-2.87624100	1.92134300
H	-1.21922000	-1.95681900	2.19905500
H	-1.32635700	-3.42076400	1.20640500
H	-0.58352400	-3.50113500	2.81875100
C	2.89947800	4.08065100	-1.01048500
H	3.09831200	4.99818100	-0.43973800
H	3.76763000	3.88348900	-1.65016400
H	2.03759900	4.25403000	-1.66093600
C	3.98044100	2.56800200	0.67372700
H	4.75675200	2.32971900	-0.06197600

H	4.32460300	3.41631000	1.28003400
H	3.85639700	1.69082200	1.31604100
C	0.29972300	3.88757000	0.30478900
H	0.57620100	4.95016800	0.31064800
H	0.04121600	3.60117800	-0.71818700
H	-0.59487300	3.76291700	0.92537100
C	1.73964500	3.46112500	2.30205500
H	2.42903500	2.77387400	2.79814300
H	2.17739500	4.46892100	2.30909400
H	0.81434200	3.48836300	2.88990600
C	-1.72134000	0.67889000	-0.56841300
H	-1.74204400	1.54507000	0.10643400
H	-1.54371700	-0.20723800	0.05393400
C	-3.10521800	0.54870900	-1.25074000
H	-3.09647200	-0.32443600	-1.92001500
H	-3.28491500	1.42661900	-1.89120900
C	-4.25801000	0.40776300	-0.24526500
H	-4.07401600	-0.47179700	0.38958300
H	-4.25589000	1.27672200	0.43124600
C	-5.64132500	0.28145200	-0.89902800
H	-5.64445300	-0.58652900	-1.57638200
H	-5.82573500	1.16291700	-1.53319200
C	-6.78975100	0.13772300	0.10998000
H	-6.60882300	-0.74627500	0.74066100
H	-6.78420800	1.00270200	0.79146100
C	-8.17548400	0.01812700	-0.53941500
H	-8.35824900	0.90249600	-1.16797800
H	-8.18264700	-0.84589000	-1.22033700
C	-0.58127000	0.80185600	-1.53103800
H	-0.35376300	-0.06194500	-2.14673100

H	-0.37234000	1.76613900	-1.99362100
C	-9.31407000	-0.12623800	0.47848200
H	-9.35206700	0.73848800	1.15415500
H	-10.29066100	-0.20647300	-0.01616800
H	-9.17929000	-1.02249700	1.09818600
O	2.63705800	-1.47055100	-1.03968800
C	2.52396400	-1.69310300	-2.42492800
C	1.26570600	-2.51116900	-2.79542600
H	1.22722700	-2.69151000	-3.87994900
H	1.27713800	-3.47883000	-2.28202300
H	0.35165000	-1.99481100	-2.49223700
C	3.77306200	-2.51968100	-2.80348900
H	3.78296200	-3.46262400	-2.24346800
H	3.79688900	-2.74784100	-3.87890400
H	4.67980500	-1.96174400	-2.54049300
C	2.55310500	-0.37764800	-3.23536100
H	1.68105300	0.24481100	-3.02516600
H	3.43977600	0.20577000	-2.96704600
H	2.57765900	-0.58929800	-4.31487600

TS5

C	-0.92577700	-2.38672500	-1.97799900
C	-2.46952900	-2.03983000	-1.87991700
C	-1.42482500	3.25176400	-0.84069100
C	-2.46712200	2.76426100	0.24642500
B	-1.22196400	-0.45286800	-0.73212300
B	-0.75135100	1.13255500	0.01795000
O	-1.77645500	1.71177400	0.90715800
O	-2.46000100	-0.70706400	-1.30915100
O	-0.32010700	-1.45075500	-1.05807400

O	-0.67354300	2.07842100	-1.12775500
C	-3.20222900	-1.97450700	-3.22434300
H	-3.20534800	-2.95428900	-3.72041500
H	-4.24361900	-1.67885300	-3.05252500
H	-2.75305400	-1.24143200	-3.89997500
C	-3.24835400	-2.94025900	-0.91047400
H	-3.30393000	-3.97450100	-1.27526400
H	-2.79431200	-2.91949400	0.08508900
H	-4.27114400	-2.55397300	-0.82224300
C	-0.55514200	-3.80034900	-1.52090900
H	-0.84408900	-3.96112600	-0.47965200
H	-1.03405600	-4.56218400	-2.15072500
H	0.53097700	-3.93081000	-1.59448800
C	-0.31092800	-2.10647200	-3.35962300
H	-0.50787100	-1.07851200	-3.68020800
H	0.77574100	-2.23101200	-3.29241200
H	-0.69082500	-2.79497500	-4.12543900
C	-2.84442500	3.82837900	1.28913800
H	-3.32140900	4.70007600	0.81937200
H	-3.55482700	3.39766700	2.00510400
H	-1.96957200	4.16710700	1.85121900
C	-3.76332500	2.20405200	-0.37558600
H	-4.36090200	1.74360600	0.42003200
H	-4.36654900	2.99373400	-0.84440600
H	-3.54483000	1.42816900	-1.11251200
C	-0.45202800	4.32080800	-0.29497900
H	-0.94912800	5.28559200	-0.12346600
H	0.00621500	3.99153400	0.64226800
H	0.34931800	4.47136000	-1.02812400
C	-2.04965100	3.77206600	-2.14284500

H	-2.65033500	2.99883600	-2.62936400
H	-2.68515700	4.65017800	-1.96149100
H	-1.25276000	4.06633100	-2.83741100
C	1.92791700	0.68615700	-0.04821900
H	2.02436000	1.49034500	-0.79368500
H	1.78841100	-0.24423900	-0.61349000
C	3.23734700	0.58816700	0.75321200
H	3.13266100	-0.19824400	1.51703500
H	3.40040900	1.52831400	1.30505600
C	4.47208500	0.28876300	-0.10975800
H	4.30930300	-0.65458600	-0.65376600
H	4.57510400	1.06920200	-0.88036900
C	5.78129900	0.19089500	0.68656000
H	5.67321500	-0.58010200	1.46529200
H	5.95330400	1.13889200	1.22026500
C	7.01011900	-0.13296600	-0.17477500
H	6.83934100	-1.08194400	-0.70667400
H	7.12033100	0.63619900	-0.95534000
C	8.31871200	-0.23214000	0.62164500
H	8.49369800	0.71691400	1.15006000
H	8.20873700	-0.99893900	1.40281400
C	0.68919300	0.94137900	0.81914800
H	0.57182700	0.12302700	1.54361700
H	0.84217500	1.86686500	1.40427000
C	9.53856900	-0.56309200	-0.24750600
H	9.69576700	0.20373200	-1.01774700
H	10.45639200	-0.62742300	0.35125100
H	9.40809700	-1.52427500	-0.76219100
O	-1.62405700	-2.10110900	1.87033000
C	-2.24148600	-1.69643100	3.03731200

C	-1.30791200	-0.78996200	3.87702100
H	-1.76270300	-0.52350400	4.84285900
H	-0.35847500	-1.30630100	4.06437200
H	-1.09678300	0.13202300	3.32647200
C	-2.54976100	-2.99195300	3.84597800
H	-1.61926900	-3.52779900	4.06713000
H	-3.05188800	-2.74535100	4.79252000
H	-3.20107900	-3.65361800	3.26298500
C	-3.56331300	-0.94967000	2.73563300
H	-3.34569500	-0.06962200	2.12243000
H	-4.24656200	-1.60186600	2.17739200
H	-4.06593800	-0.62331200	3.65858900

INT4

C	-0.51438600	-2.59577600	-1.31606000
C	-1.60430500	-1.78551600	-2.12402100
C	-2.06528600	2.81096800	-0.99058800
C	-2.94843900	2.47852100	0.27914100
B	-1.55361100	-1.06882300	0.11516700
B	-0.97252600	1.22363400	0.34960500
O	-2.01379200	1.82849700	1.14157700
O	-2.35274900	-1.14858600	-1.08942700
O	-0.32086400	-1.79069800	-0.14893300
O	-1.07113900	1.78389800	-0.97847000
C	-0.99146900	-0.71967500	-3.05086900
H	-0.45523400	-1.17666300	-3.89399500
H	-1.79910300	-0.09904800	-3.45437600
H	-0.32000900	-0.05421900	-2.50552500
C	-2.56766800	-2.65715600	-2.94435700
H	-2.03309900	-3.23257200	-3.71364900

H	-3.12292800	-3.35093400	-2.30722200
H	-3.29622500	-2.01187400	-3.45005600
C	-1.02003800	-3.98268200	-0.86618400
H	-1.98010100	-3.89756800	-0.34797200
H	-1.13354900	-4.67630000	-1.71075000
H	-0.29325000	-4.41218600	-0.16624000
C	0.83045500	-2.76438400	-2.03180500
H	1.28593700	-1.79712700	-2.25843000
H	1.52230700	-3.31963300	-1.38603300
H	0.71530400	-3.32689100	-2.96875300
C	-3.50189300	3.70870400	1.01278200
H	-4.16987900	4.29392500	0.36531800
H	-4.07976700	3.37881300	1.88460100
H	-2.69988300	4.36048600	1.37082400
C	-4.11212700	1.51653300	-0.02556900
H	-4.55309400	1.19353500	0.92448800
H	-4.89555400	2.00645900	-0.62082100
H	-3.76674800	0.62299200	-0.54984100
C	-1.33057500	4.16354800	-0.87265300
H	-2.01672000	5.01930800	-0.93915100
H	-0.77948800	4.22894700	0.07131100
H	-0.60517500	4.23866000	-1.69146700
C	-2.82064400	2.76837900	-2.32419600
H	-3.25488300	1.78161700	-2.50027000
H	-3.62390700	3.51789200	-2.35006200
H	-2.12676200	2.98551000	-3.14604600
C	1.68350000	0.82198500	0.16440900
H	1.68165600	1.44414800	-0.74361400
H	1.55541000	-0.21530700	-0.16686800
C	3.04368800	0.96617800	0.86583900

H	3.04512600	0.34962400	1.77910700
H	3.17359000	2.00743500	1.20354700
C	4.24193800	0.56770700	-0.00804500
H	4.11295700	-0.47263000	-0.34377100
H	4.24490400	1.18321700	-0.92152700
C	5.59876400	0.70604000	0.69740000
H	5.59504700	0.09103600	1.61093600
H	5.72854600	1.74694100	1.03330400
C	6.79752600	0.30518800	-0.17376300
H	6.66850900	-0.73482100	-0.51159500
H	6.80554300	0.92144600	-1.08649100
C	8.15228600	0.43925000	0.53559000
H	8.28239900	1.47803100	0.87407200
H	8.14616300	-0.17837000	1.44603900
C	0.48894000	1.21395000	1.04595000
H	0.49152600	0.59344800	1.95376700
H	0.64652300	2.25154200	1.40654700
C	9.34382700	0.03765800	-0.34303200
H	9.39915700	0.66247000	-1.24437100
H	10.29550800	0.14197700	0.19404400
H	9.25877400	-1.00669100	-0.67138200
O	-2.34309400	-1.38316300	1.26138100
C	-2.01429700	-1.69356300	2.60739500
C	-0.57749800	-2.21525000	2.79841900
H	-0.41471700	-2.46074400	3.85753600
H	-0.40196900	-3.11240800	2.19774200
H	0.16208100	-1.46913300	2.49826000
C	-3.00719200	-2.79881200	3.02425200
H	-2.85403700	-3.69753000	2.41465700
H	-2.88311400	-3.06830300	4.08269500

H	-4.03594300	-2.45362400	2.86796800
C	-2.24539100	-0.45060100	3.48837200
H	-1.58512800	0.36802300	3.19487200
H	-3.27461300	-0.09463200	3.36685600
H	-2.07659500	-0.68907400	4.54845200

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C	-1.30014800	-0.19837600	0.00304400
H	-1.49097100	-0.63986600	0.99946100
H	-1.31700800	-1.03790100	-0.70838500
H	-2.14955100	0.45561200	-0.22496100
C	0.00000000	0.53531400	-0.04531500
H	-0.00000100	1.61293600	0.10314000
C	1.30014800	-0.19837600	0.00304400
H	1.31701700	-1.03788700	-0.70840200
H	2.14955300	0.45561700	-0.22493900
H	1.49095900	-0.63988700	0.99945400

B_2cat_2

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

TS6

C	3.88110600	-0.51514000	1.52771300
C	2.73598800	-0.38955800	0.75245600
C	2.72407300	-0.72473400	-0.60869500
C	3.85660200	-1.20176500	-1.25499500
C	5.01740100	-1.33495800	-0.47910400
C	5.02955800	-0.99842200	0.88374200
H	3.87838400	-0.25486800	2.58162000
H	3.83587600	-1.46087100	-2.30899200
H	5.92569700	-1.70833800	-0.94394300
H	5.94693300	-1.11645700	1.45378300
O	1.47621400	-0.50711300	-1.11973900
O	1.49511100	0.04313600	1.12500300
B	0.69429200	0.02053800	-0.05243500

B	-0.98639100	-0.16886300	-0.01520100
C	-4.26249300	-0.56110500	-1.39963100
C	-5.44538600	-0.66048700	-0.64999400
C	-5.42985200	-0.60918000	0.75130000
C	-4.23062500	-0.45629900	1.46514300
C	-3.07164400	-0.35851700	0.71231100
C	-3.08706500	-0.40930300	-0.68199900
H	-4.26251900	-0.60158000	-2.48430600
H	-6.39220300	-0.78105700	-1.16896800
H	-6.36481500	-0.69072800	1.29858200
H	-4.20627500	-0.41759900	2.54960400
O	-1.76847500	-0.20476500	1.14046300
O	-1.79424300	-0.28762500	-1.14862000
C	0.56686000	2.17161300	-0.55597900
H	-0.11051100	2.04942700	-1.40322900
C	1.97319600	2.54450200	-0.93584100
H	2.67126800	2.42645800	-0.09847400
H	2.34332200	1.96610100	-1.78687600
H	2.00247500	3.60991600	-1.22436900
C	-0.01975700	2.86548500	0.64473300
H	-1.02942300	2.51911200	0.88605300
H	0.60864700	2.73010500	1.53248800
H	-0.08298600	3.95016100	0.45139800

INT5

C	-3.37588400	-1.32102800	-1.33711600
C	-2.45123500	-0.54031800	-0.62775600
C	-2.39133800	-0.57653000	0.79907900
C	-3.25228700	-1.39662400	1.54314500
C	-4.16368200	-2.16524600	0.82925400

C	-4.22454400	-2.12782100	-0.58914500
H	-3.41224400	-1.28763600	-2.42109900
H	-3.19732300	-1.41877500	2.62667500
H	-4.84959400	-2.81451700	1.36608300
H	-4.95502900	-2.74995300	-1.09861100
O	-1.45091500	0.23729600	1.24347800
O	-1.54909000	0.29434800	-1.10785600
B	-0.78282700	0.88868300	0.04730500
B	0.87226200	0.35277800	0.01231000
C	4.34393000	0.39549200	0.88032500
C	5.29172400	-0.54969100	0.45588000
C	4.93384700	-1.62206600	-0.37343200
C	3.61230300	-1.79645800	-0.81489500
C	2.68821100	-0.85728900	-0.38701000
C	3.04452400	0.21010700	0.43750200
H	4.60998300	1.22967400	1.52187800
H	6.32405300	-0.44564500	0.77822200
H	5.69364400	-2.33456900	-0.68248200
H	3.32402500	-2.62240600	-1.45753800
O	1.33701700	-0.77941500	-0.66057300
O	1.92210300	0.97311100	0.69169800
C	-0.91875100	2.53215800	0.09570100
H	-0.35699100	2.84276500	0.98900100
C	-2.37967000	2.98436300	0.25891700
H	-2.99066400	2.69075000	-0.60481600
H	-2.84291900	2.56571400	1.16002700
H	-2.43794500	4.07949200	0.33825900
C	-0.27356600	3.18986000	-1.13485300
H	0.79244900	2.94731700	-1.22010500
H	-0.76585000	2.86989100	-2.06211400

H	-0.35718600	4.28442700	-1.07900100

TS7

C	2.98365000	-1.85032500	1.29862600
C	2.45954600	-0.78595900	0.58262000
C	2.12285000	-0.89799700	-0.76876600
C	2.29122100	-2.07990100	-1.47234600
C	2.82535600	-3.16487700	-0.75950800
C	3.16402700	-3.05249500	0.59654100
H	3.24022700	-1.75268400	2.34879800
H	2.02361300	-2.15593400	-2.52160300
H	2.97831600	-4.11098600	-1.27129500
H	3.57471300	-3.91313900	1.11718700
O	1.62852600	0.30765800	-1.21238600
O	2.18577500	0.49204000	1.01266000
B	1.64954900	1.16860200	-0.09569200
B	-0.88009700	0.60442100	0.29637300
C	-4.33418700	0.85539500	-0.48638300
C	-5.26003100	-0.19251300	-0.35818200
C	-4.87401000	-1.45822600	0.10519500
C	-3.54450700	-1.73482500	0.46226100
C	-2.64423000	-0.69199100	0.32997100
C	-3.02814800	0.56672000	-0.13084900
H	-4.62122200	1.83890500	-0.84416700
H	-6.29806200	-0.01601700	-0.62529900
H	-5.61852100	-2.24462000	0.19081100
H	-3.23382100	-2.71047700	0.82166300
O	-1.27961400	-0.67537600	0.60627800
O	-1.91110800	1.39872800	-0.15485700
C	1.48692600	2.73443000	-0.19212500

H	0.64494000	2.95395200	-0.86404900
C	2.76107700	3.32440800	-0.85206000
H	3.64971100	3.14443300	-0.23323200
H	2.94516100	2.89074000	-1.84171300
H	2.65922500	4.41095600	-0.97412600
C	1.21819700	3.40607800	1.16663300
H	0.28805600	3.04672900	1.62284400
H	2.03159100	3.20642100	1.87488900
H	1.13376400	4.49468000	1.05256200

•Bcat (INT6)

C	0.84409200	-1.43452400	-0.00012800
C	-0.32725900	-0.69699500	-0.00009400
C	-0.32730000	0.69712700	-0.00025500
C	0.84425600	1.43448800	-0.00037700
C	2.04146300	0.70102900	0.00015300
C	2.04140200	-0.70116900	0.00021900
H	0.83139800	-2.51964300	-0.00009200
H	0.83191200	2.51962600	-0.00033800
H	2.98788800	1.23419800	0.00045100
H	2.98781500	-1.23433800	0.00050400
O	-1.64451100	1.14888700	0.00024700
O	-1.64456500	-1.14885500	-0.00016500
B	-2.40526700	0.00003200	0.00034200

^{i}PrBcat

C	-2.15229800	-1.43303000	0.02664800
C	-0.98137800	-0.69769100	-0.05036600
C	-0.98132100	0.69767600	-0.05013000
C	-2.15218300	1.43308400	0.02713400

C	-3.34822100	0.70087300	0.10475100
C	-3.34827800	-0.70075000	0.10451300
H	-2.14052500	-2.51839300	0.02632200
H	-2.14032800	2.51844600	0.02717700
H	-4.29233300	1.23481500	0.16663200
H	-4.29243400	-1.23463400	0.16621300
O	0.32210800	1.14591000	-0.13336200
O	0.32201500	-1.14600700	-0.13374400
B	1.11729300	-0.00006700	-0.18939300
C	2.68068200	-0.00015400	-0.33716400
H	2.87057600	-0.00062800	-1.42584500
C	3.32950800	-1.27654200	0.23731900
H	2.89458500	-2.18426700	-0.19507000
H	4.40848700	-1.28785200	0.03658700
H	3.19622100	-1.33266200	1.32543000
C	3.32959900	1.27666600	0.23622200
H	4.40858700	1.28768400	0.03552100
H	2.89477900	2.18404800	-0.19699200
H	3.19627000	1.33375900	1.32427500

TS8

C	3.51947900	-1.37938100	0.39293800
C	2.47788300	-0.73680500	-0.25818500
C	2.42873300	0.65488000	-0.37365500
C	3.41861300	1.46727400	0.15721400
C	4.48147500	0.82842800	0.81970400
C	4.53094400	-0.56731000	0.93527200
H	3.54360400	-2.46162500	0.48170600
H	3.36587200	2.54840300	0.06737700
H	5.27626600	1.43059000	1.25392200

H	5.36373800	-1.03261200	1.45756800
O	1.29188400	1.00681100	-1.06478200
O	1.37256400	-1.27649100	-0.87534100
B	0.61801700	-0.19374300	-1.37499000
O	-3.20704400	-0.04856200	1.42304700
C	-3.99852600	0.03110300	0.31922700
C	-4.16705500	1.50008400	-0.16656300
H	-4.60685300	2.10380100	0.63875400
H	-3.18020700	1.91783200	-0.40092900
H	-4.80590800	1.58931400	-1.06009300
C	-3.39898100	-0.81458400	-0.85013200
H	-3.26140100	-1.85071200	-0.51692600
H	-4.05068700	-0.81003600	-1.73906200
H	-2.41476300	-0.41638800	-1.12353200
C	-5.41200800	-0.55243700	0.64607800
H	-5.86120600	0.01901700	1.46850300
H	-6.09191100	-0.51584900	-0.21977500
H	-5.30920800	-1.59459600	0.97267000

INT7

C	-3.05368900	-1.31628600	0.00933700
C	-1.76302000	-0.80516100	-0.02351300
C	-1.51499700	0.56816000	-0.02889800
C	-2.53874700	1.50486800	0.01052700
C	-3.85351000	0.99795300	0.00614800
C	-4.10504300	-0.37726800	0.00442300
H	-3.23598700	-2.38629900	0.01585800
H	-2.32903400	2.56943200	0.01634800
H	-4.68839800	1.69562800	0.01815900
H	-5.13322000	-0.73367200	0.01291600

O	-0.15100200	0.78406500	-0.00773300
O	-0.56937100	-1.48901700	-0.00336600
B	0.42373200	-0.49478600	0.00510000
O	1.72455500	-0.82455600	-0.01890500
C	2.87171100	0.07661600	0.00332500
C	2.83486200	0.98775300	-1.23037400
H	2.76465400	0.38695900	-2.14641900
H	1.98214100	1.67423500	-1.19865300
H	3.75431500	1.58726600	-1.28185100
C	2.86476400	0.87843800	1.31017900
H	2.83649600	0.20223700	2.17407500
H	3.77429900	1.49141100	1.38148200
H	1.99854600	1.54669100	1.36687100
C	4.08499700	-0.85711700	-0.05223700
H	4.06413000	-1.45695400	-0.97056200
H	5.01512800	-0.27525900	-0.03375100
H	4.08084500	-1.53941800	0.80655700

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C	0.05102700	-1.96608500	-1.27565700
H	-0.24879600	-3.02450600	-1.28707100
H	1.14440700	-1.92430400	-1.32588500
H	-0.35495900	-1.48867200	-2.17194700
C	-0.47247500	-1.32464000	0.00000000
H	-1.56323300	-1.28353900	0.00000000
C	0.05102700	-1.96608500	1.27565700
H	1.14440700	-1.92430400	1.32588500
H	-0.35495900	-1.48867200	2.17194700
H	-0.24879600	-3.02450600	1.28707100
I	0.05102700	0.86225200	0.00000000

^{t}BuOBcat

C	-3.05526900	-1.30980600	0.00000400
C	-1.76493200	-0.80847900	-0.00002600
C	-1.50850000	0.56519000	-0.00002600
C	-2.52461700	1.50400200	0.00000500
C	-3.84004100	1.00795200	0.00003500
C	-4.09881700	-0.36810800	0.00003400
H	-3.24476700	-2.37856100	0.00000400
H	-2.31187100	2.56849300	0.00000600
H	-4.66996700	1.70901200	0.00006200
H	-5.12716900	-0.71864000	0.00006000
O	-0.14097200	0.77147600	-0.00005600
O	-0.57212000	-1.49856600	-0.00005500
B	0.42382000	-0.51404200	-0.00005100
O	1.72616000	-0.83518100	-0.00001700
C	2.86650600	0.07668000	0.00000600
C	2.83105900	0.93741100	-1.26903900
H	2.81050700	0.30195500	-2.16160100
H	1.95349500	1.59098400	-1.28311900
H	3.72657400	1.56757200	-1.31932300
C	2.83107400	0.93716200	1.26922300
H	2.81035400	0.30151600	2.16164600
H	3.72666600	1.56719500	1.31970100
H	1.95358400	1.59082900	1.28335500
C	4.09040200	-0.84337400	-0.00008200
H	4.08728300	-1.48556600	-0.88735200
H	5.01318900	-0.25247400	-0.00003900
H	4.08729700	-1.48571800	0.88707700

TS9

C	-3.09338800	-0.00034500	-0.71773600
C	-2.93251500	-0.67735200	0.69861400
C	2.77417500	-0.58042800	0.75954600
C	2.52320800	-1.01204900	-0.74801800
B	-0.90842100	0.15146700	-0.01763600
B	0.81609200	0.40725000	-0.05815600
O	1.49528200	-0.09338800	-1.19087200
O	-1.48018000	-0.76127000	0.83888800
O	-1.83553300	0.72904400	-0.85582300
O	1.55820200	0.12707900	1.10215600
C	-3.43626000	0.19145100	1.85930200
H	-4.52984300	0.26213500	1.86463900
H	-3.11502300	-0.25879500	2.80410000
H	-3.02347400	1.20427200	1.81317500
C	-3.50918000	-2.08731800	0.81722700
H	-4.59591100	-2.07911900	0.66834500
H	-3.06277200	-2.77185900	0.09192000
H	-3.30771300	-2.48008000	1.81946900
C	-3.14785900	-1.00470000	-1.87739100
H	-2.31850700	-1.71757600	-1.83117000
H	-4.08975400	-1.56482200	-1.88133100
H	-3.06772100	-0.45851100	-2.82294300
C	-4.24487800	0.99668500	-0.83586900
H	-4.15264700	1.81101200	-0.11313800
H	-4.24862500	1.43470100	-1.83965900
H	-5.20934700	0.49833300	-0.67984900
C	3.73501200	-0.87032900	-1.67220600
H	4.55099500	-1.53054800	-1.35380500
H	3.44938000	-1.15170500	-2.69154500

H	4.10953500	0.15587400	-1.69979700
C	1.93595900	-2.42712100	-0.89038000
H	1.65048500	-2.58576000	-1.93583700
H	2.66225000	-3.19900000	-0.61138700
H	1.04051900	-2.55151500	-0.27358600
C	3.95758600	0.37994600	0.94821700
H	4.91436200	-0.13371100	0.79842000
H	3.91322600	1.22735700	0.26162300
H	3.93599600	0.76990400	1.97160700
C	2.92567200	-1.74591600	1.74436700
H	2.03894800	-2.38377300	1.75708300
H	3.80001300	-2.36070300	1.49729100
H	3.06558600	-1.34873800	2.75562200
C	0.62284500	2.41968500	-0.27178000
H	-0.16221900	2.42165400	-1.02859400
C	0.18076000	2.97919100	1.06159400
H	0.07968200	4.07500800	0.98997400
H	-0.78878500	2.58302500	1.38108800
H	0.91207000	2.76494300	1.84898000
C	1.93069400	2.96597100	-0.79718200
H	2.71713700	2.95498300	-0.03559800
H	2.27907600	2.42396300	-1.68099700
H	1.78157400	4.01953100	-1.08975100

INT8

C	-2.99923800	0.03174200	-0.69816000
C	-2.78711100	-0.65017500	0.71142500
C	2.64330100	-0.66937100	0.73740400
C	2.25496700	-1.10613600	-0.73895200
B	-0.83708700	0.29224800	-0.01535000

B	0.96784400	0.74423700	-0.09774200
O	1.46539200	0.00861700	-1.21521400
O	-1.32238100	-0.65824000	0.83632100
O	-1.77705500	0.83239900	-0.84300500
O	1.63531500	0.30984900	1.07452000
C	-3.31870500	0.17855100	1.88684300
H	-4.41419100	0.19404100	1.90256800
H	-2.96664500	-0.26655200	2.82289200
H	-2.95705900	1.21088400	1.84956600
C	-3.28050600	-2.09116500	0.81888700
H	-4.36729600	-2.14153200	0.68001600
H	-2.80458800	-2.74132800	0.08104800
H	-3.04822600	-2.48294000	1.81467000
C	-3.01217800	-0.95951300	-1.86864000
H	-2.14713200	-1.62949900	-1.84130300
H	-3.92405000	-1.56715600	-1.86815900
H	-2.97174400	-0.39901600	-2.80806300
C	-4.19859000	0.97176800	-0.79110600
H	-4.13959500	1.77998200	-0.05847900
H	-4.23457800	1.42149700	-1.78877300
H	-5.13449900	0.42252900	-0.63240600
C	3.44122600	-1.28420400	-1.69233100
H	4.09951700	-2.09338800	-1.35313600
H	3.06938000	-1.54507000	-2.68909600
H	4.03210300	-0.36981200	-1.78398100
C	1.37101100	-2.36376400	-0.80068100
H	1.01777200	-2.49390600	-1.82960500
H	1.93168200	-3.26142900	-0.51580800
H	0.49913600	-2.27809500	-0.14730300
C	4.00554500	0.03825600	0.83267000

H	4.83264800	-0.65814900	0.65211800
H	4.08656900	0.86424900	0.12099400
H	4.11843500	0.45021100	1.84113700
C	2.58791400	-1.79380700	1.77605500
H	1.58885000	-2.23040900	1.84467900
H	3.30559200	-2.58812600	1.53636500
H	2.84580800	-1.39006100	2.76110200
C	0.77868900	2.40540000	-0.29779000
H	0.08430100	2.55719200	-1.13171200
C	0.23008900	3.09953200	0.95436200
H	0.20319800	4.18917700	0.81048600
H	-0.79109000	2.77954200	1.19487900
H	0.85875200	2.89299900	1.82870800
C	2.14830600	2.99096800	-0.69263200
H	2.87555200	2.89263500	0.12190600
H	2.55746000	2.50514200	-1.58441900
H	2.04165800	4.06446500	-0.91054300

TS10

C	-3.15379200	0.22258200	-0.61286300
C	-2.91550800	-0.76555600	0.59721200
C	2.66341600	-0.82378500	0.73144900
C	2.31399000	-1.09908100	-0.79694300
B	-0.97165700	0.27448200	0.02834500
B	1.30921500	0.87552100	-0.08592400
O	1.67354200	0.13493400	-1.21332900
O	-1.43941000	-0.83644900	0.65663400
O	-1.90596100	1.01298300	-0.62205500
O	1.80079200	0.28863500	1.07900200
C	-3.37360400	-0.21152800	1.95071200

H	-4.46680500	-0.18058800	2.01947700
H	-2.99704100	-0.86210400	2.74638900
H	-2.98471500	0.79597200	2.12838100
C	-3.45070000	-2.18006100	0.39494400
H	-4.54195500	-2.16726200	0.28571300
H	-3.01839800	-2.65871400	-0.48680000
H	-3.20542900	-2.79356200	1.26811000
C	-3.23266800	-0.47345000	-1.97622500
H	-2.38703500	-1.14962300	-2.13593600
H	-4.16162200	-1.04536300	-2.07934600
H	-3.20750800	0.28631600	-2.76380500
C	-4.32363400	1.18732200	-0.44278600
H	-4.21695700	1.80469900	0.45200100
H	-4.37579300	1.85416600	-1.30952500
H	-5.27145400	0.63889900	-0.37933500
C	3.52897500	-1.32008600	-1.70396500
H	4.08276300	-2.21953200	-1.40835700
H	3.18872600	-1.45611900	-2.73625400
H	4.21311700	-0.46833300	-1.68761500
C	1.31692000	-2.24659100	-1.01614000
H	1.01403900	-2.25094300	-2.06921000
H	1.77237900	-3.21749800	-0.78940000
H	0.41982000	-2.13473600	-0.40363800
C	4.10416800	-0.33903800	0.95788900
H	4.83493500	-1.12887800	0.75001700
H	4.34051200	0.52749600	0.33275100
H	4.21380400	-0.03620700	2.00453500
C	2.36035700	-1.98429900	1.68212400
H	1.30502600	-2.26488500	1.65290700
H	2.96765800	-2.86414400	1.43694100

H	2.59928300	-1.68313800	2.70791500
C	1.00179300	2.44723500	-0.18483900
H	0.24388500	2.62119200	-0.95990100
C	0.50767100	3.06574800	1.13382700
H	0.36506500	4.15028800	1.02990000
H	-0.45029300	2.63876200	1.45559700
H	1.22946200	2.89767100	1.94258800
C	2.30024800	3.15303800	-0.65112800
H	3.10766100	3.02785700	0.08281400
H	2.65134900	2.76009600	-1.61189500
H	2.13022700	4.23267900	-0.76874100

^{i}PrBpin

C	-1.26756600	-0.77024900	-0.06940600
C	-1.20234000	0.79841900	0.10795700
B	0.91082600	-0.05277200	-0.18953500
O	0.16456800	1.09951600	-0.30002200
O	0.13044900	-1.15629100	0.07899600
C	-2.15944800	1.59376700	-0.77863100
H	-3.20277600	1.35290200	-0.54134700
H	-2.01189300	2.66532300	-0.60694300
H	-1.98867300	1.39728800	-1.83995000
C	-1.33769400	1.25559800	1.56701300
H	-1.09474000	2.32147000	1.62907200
H	-2.35763800	1.11234300	1.94048400
H	-0.64826100	0.71395200	2.22292000
C	-1.69958800	-1.21095800	-1.47507800
H	-2.76200200	-1.00999600	-1.65183900
H	-1.11694800	-0.70581000	-2.25247900
H	-1.53232100	-2.28839500	-1.57533900

C	-2.08995100	-1.51066200	0.98417400
H	-1.70955800	-1.33504700	1.99339500
H	-3.14129400	-1.20069200	0.94722900
H	-2.04760400	-2.58791100	0.79116700
C	2.47668600	-0.11724000	-0.38791700
H	2.62222900	-0.40627900	-1.44471800
C	3.13249400	-1.21800100	0.47179000
H	2.66143100	-2.19345500	0.30860100
H	4.20196400	-1.31200700	0.24050100
H	3.04842900	-0.98626600	1.54203800
C	3.16775000	1.24499000	-0.18648900
H	4.23861600	1.18205000	-0.42218500
H	2.72508600	2.02175700	-0.81976500
H	3.07963800	1.58284200	0.85456600

MeOH

C	0.66901500	-0.02081700	0.00000000
H	1.08099300	0.99121400	-0.00010700
H	1.02890400	-0.54660700	0.89614200
H	1.02888900	-0.54678900	-0.89604000
O	-0.74964800	0.12298200	0.00000000
H	-1.15569400	-0.75677800	0.00000200

•CH_2OH

C	0.68781700	0.02951400	0.07105500
H	1.23111500	-0.89095100	-0.10223300
H	1.12171800	0.99091300	-0.19390600
O	-0.67089300	-0.12585100	-0.02680600
H	-1.11258500	0.72976300	0.08425700

•OCH_3

C	-0.57732900	-0.00008000	0.01316000
H	-0.87098500	0.00294200	-1.05842100
H	-1.00667100	-0.91305400	0.45701600
H	-1.00642800	0.91082400	0.46156200
O	0.79350800	-0.00002900	0.00761000

$^{n}C_8H_{18}$

C	-4.50381100	0.25677400	0.00003200
H	-4.57452400	0.90183200	0.88562500
H	-4.57449100	0.90196400	-0.88546900
H	-5.37826800	-0.40565400	-0.00003600
C	-3.19454500	-0.54171400	-0.00001000
H	-3.16972500	-1.20273200	0.87887600
H	-3.16974200	-1.20266900	-0.87894300
C	-1.94211800	0.34576900	-0.00000200
H	-1.96841300	1.00777600	-0.87936800
H	-1.96840400	1.00776300	0.87937500
C	-0.62592500	-0.44426600	-0.00001300
H	-0.60073300	-1.10615500	-0.87934800
H	-0.60070600	-1.10613200	0.87933700
C	0.62592500	0.44426700	-0.00003700
H	0.60071500	1.10617200	0.87928500
H	0.60072400	1.10611500	-0.87940000
C	1.94211800	-0.34576900	-0.00000600
H	1.96842100	-1.00778000	-0.87936900
H	1.96839600	-1.00775900	0.87937400
C	3.19454600	0.54171400	0.00000300
H	3.16972200	1.20270700	0.87890800
H	3.16974500	1.20269400	-0.87891100

C	4.50381100	-0.25677400	0.00002600
H	4.57451800	-0.90190500	-0.88551500
H	5.37826800	0.40565400	0.00003300
H	4.57449600	-0.90189200	0.88557900

C_3H_8

C	-1.27829500	-0.26007500	0.00000000
H	-1.32310500	-0.90777100	-0.88545000
H	-1.32314900	-0.90768400	0.88551200
H	-2.17804800	0.36760800	-0.00005300
C	0.00000000	0.58693500	0.00000000
H	0.00000000	1.24747600	-0.87850000
H	0.00000000	1.24750700	0.87847800
C	1.27829500	-0.26007500	0.00000100
H	2.17804800	0.36760800	-0.00019400
H	1.32321500	-0.90758200	0.88558300
H	1.32303900	-0.90787300	-0.88537900

TS-S1

C	-5.42983400	-0.51822000	-0.22758600
H	-5.74881000	0.51685200	-0.40666400
H	-5.38052300	-1.02205100	-1.20170600
H	-6.21263700	-1.01045100	0.36232400
C	-4.07491500	-0.56429400	0.48899000
H	-4.16622000	-0.08469100	1.47470400
H	-3.79991800	-1.61125700	0.68385400
C	-2.94720400	0.11504100	-0.30023500
H	-2.85602500	-0.36619200	-1.28623600
H	-3.22417000	1.16225100	-0.49737500
C	-1.58738300	0.07547600	0.41042200

H	-1.31227400	-0.97158500	0.60869800
H	-1.67933200	0.55831800	1.39556400
C	-0.45956600	0.75216600	-0.38091500
H	-0.73551300	1.79866700	-0.58308900
H	-0.36535300	0.26581000	-1.36384100
C	0.89861300	0.71444900	0.33244200
H	1.17397200	-0.33036200	0.53325000
H	0.80821800	1.20603900	1.31346200
C	2.02620000	1.38888500	-0.46383000
H	1.72748900	2.42692900	-0.69412900
H	2.13060800	0.88893500	-1.43858300
C	3.36218800	1.39364400	0.25202200
H	4.18822800	1.83728600	-0.31298900
H	3.33350800	1.77264400	1.27917400
C	4.14679500	-1.20755700	0.51812900
H	5.23873500	-1.18291700	0.63286500
H	3.64525600	-1.58949600	1.40896400
O	3.70439400	-1.94294000	-0.59089400
H	4.21978800	-1.68976100	-1.37172700
H	3.77046200	0.07101000	0.41399500

TS-S2

C	5.60860400	0.49606200	-0.23230700
H	5.92780400	-0.53181700	-0.01597200
H	5.62343800	0.62437200	-1.32241400
H	6.35887200	1.17382100	0.19280200
C	4.21332100	0.77491400	0.33929800
H	4.23938600	0.67142500	1.43406400
H	3.93820500	1.82072600	0.13853900
C	3.12846400	-0.15011700	-0.22955200

H	3.10392700	-0.04703100	-1.32530300
H	3.40454100	-1.19686500	-0.02847700
C	1.72812900	0.12315900	0.33611100
H	1.45256800	1.16922800	0.13366200
H	1.75347800	0.02128400	1.43192000
C	0.64417400	-0.80269600	-0.23305600
H	0.91644600	-1.84945200	-0.02650700
H	0.62225100	-0.70358600	-1.32896800
C	-0.75627800	-0.51998300	0.32667300
H	-1.03592500	0.52061700	0.11295500
H	-0.73757100	-0.61697500	1.42299100
C	-1.83571200	-1.45340700	-0.24139400
H	-1.56426600	-2.50109400	-0.01873200
H	-1.85527200	-1.37794100	-1.33787500
C	-3.22170100	-1.19472100	0.30629600
H	-4.01420400	-1.82418100	-0.10910600
H	-3.28607900	-1.11986900	1.39683600
H	-3.55607800	-0.00197100	-0.10004700
O	-3.88632700	1.11215300	-0.49135500
C	-5.13697400	1.43053300	0.07116000
H	-5.39392300	2.42861500	-0.31091800
H	-5.93222900	0.73469600	-0.23840000
H	-5.10692100	1.48630800	1.17041200

TS-S3

C	-1.05701700	-0.03474400	0.49096600
H	-1.36073000	-0.12519200	1.54110400
C	1.65082800	-0.34994500	0.58180900
H	2.00401300	0.18760800	1.47172000
H	1.81947800	-1.42596100	0.65060500

O	2.20065000	0.11064500	-0.62298200
H	2.15802800	1.07857700	-0.64644000
H	0.29989900	-0.20192100	0.57375000
C	-1.26736800	1.36119800	-0.06174600
H	-2.33858400	1.60521400	-0.14952300
H	-0.81422600	2.12715600	0.58123500
H	-0.83522800	1.45995800	-1.06705900
C	-1.56487600	-1.17252500	-0.37170200
H	-1.11044800	-1.14543800	-1.37096600
H	-1.33965000	-2.14975900	0.07289600
H	-2.65716400	-1.11930900	-0.50943400

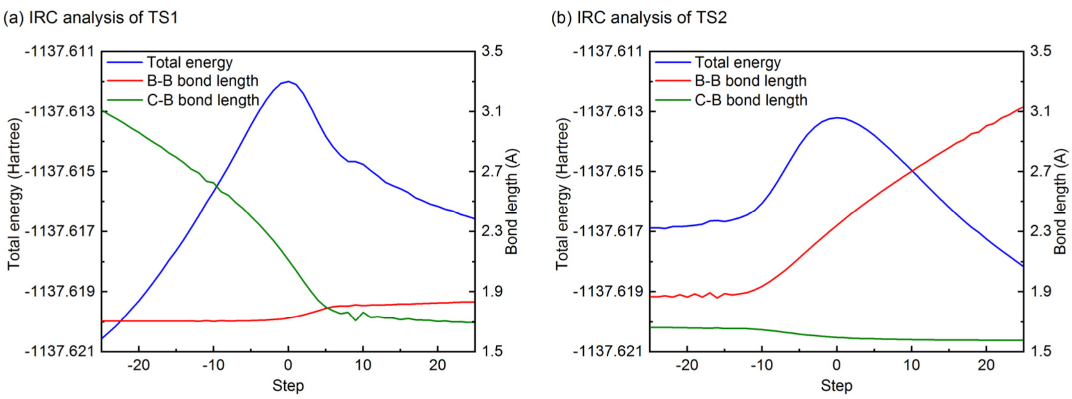
TS-S4

C	-0.88625300	0.04865400	0.41190000
H	-0.73010600	0.08898100	1.49713600
H	0.26979100	-0.29516400	-0.01032300
O	1.40561200	-0.64105700	-0.43318200
C	2.37805100	0.16018900	0.18920600
H	3.34743000	-0.17554100	-0.20758500
H	2.26920100	1.22944600	-0.05263500
H	2.40043000	0.03258500	1.28307400
C	-1.78861700	-1.09286300	-0.01180300
H	-1.81872000	-1.19027800	-1.10370200
H	-1.45378200	-2.04799800	0.40703300
H	-2.81980800	-0.91816500	0.33395800
C	-1.18479700	1.40497300	-0.19434900
H	-0.44600200	2.15810500	0.10318800
H	-1.20161400	1.35502500	-1.28971200
H	-2.17202200	1.76573900	0.13530100

7.3 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 analysis were taken using local quadratic approximation (LQA) method under uB3LYP/6-31+G(d), the same basis set with the structure optimization and the frequency analysis. For each transition state, 25 points were examined in each direction with step size of 15 (in unit of 0.01 Bohr).

Figure S2. IRC analysis for **TS1** and **TS2.**



The energies, length of the C-B bond formed in the reaction and length of B-B bond broken in the reaction were shown in **Figure S2**.

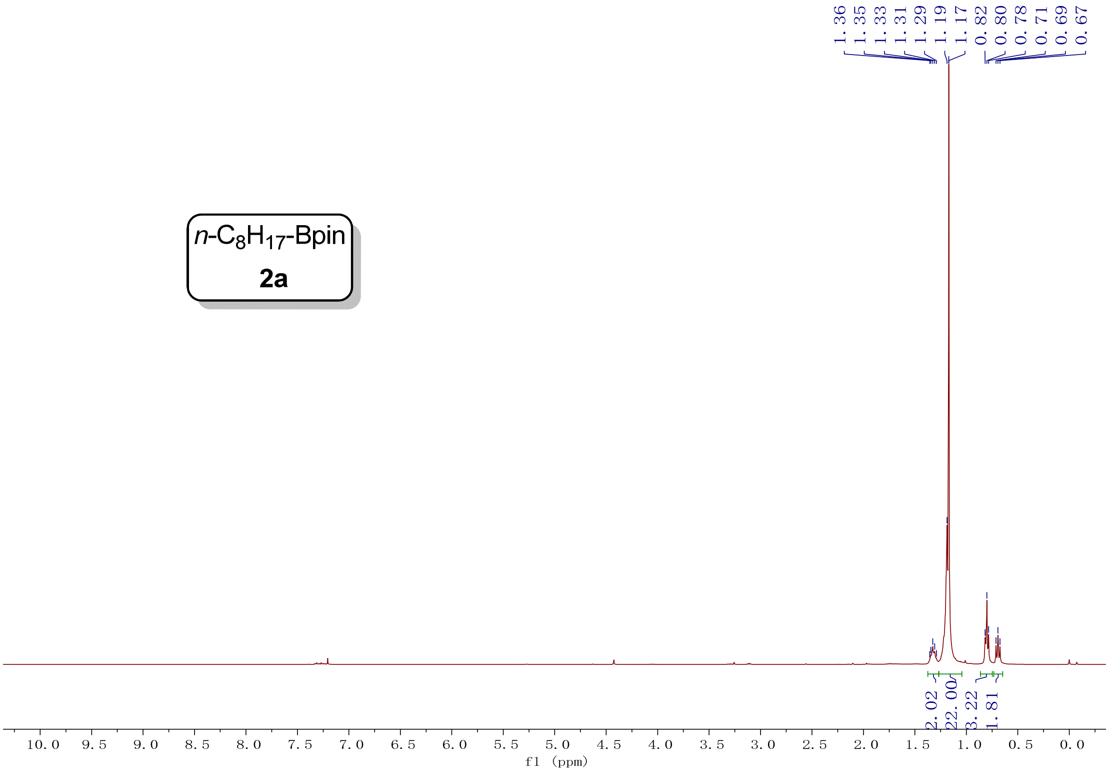
Table S10. Comparison of bond length

Structure	B-B bond length (A)	C-B bond length (A)
•C_8H_{17} + B_2pin_2	1.704	None
Step -25 of TS1	1.706	3.111
Step -10 of TS1	1.703	2.626
Step -5 of TS1	1.708	2.401
TS1	1.727	2.110
Step 5 of TS1	1.790	1.800
Step 10 of TS1	1.808	1.763
Step 25 of TS1	1.833	1.695
INT1	1.859	1.668
Step -25 of TS2	1.868	1.663
Step -10 of TS2	1.937	1.648

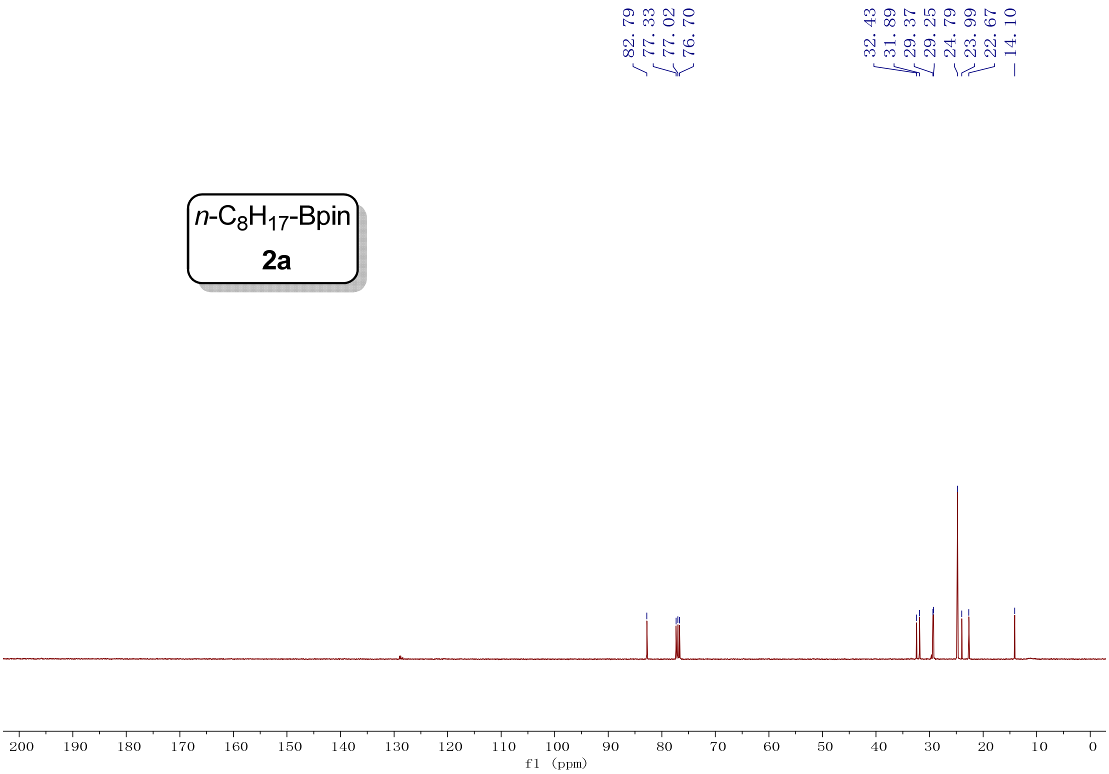
Step -5 of TS2	2.126	1.618
TS2	2.341	1.596
Step 5 of TS2	2.533	1.586
Step 10 of TS2	2.703	1.581
Step 25 of TS2	3.135	1.576
C_8H_{17}Bpin + •Bpin	None	1.573

Furthermore, the bond length were carefully compared with the reactant (B_2pin_2), the intermediate (**INT1**), the product (C_8H_{17}Bpin) and the transition states (**TS1**, **TS2**) as shown in **Table S10**. It clearly represented the formation of the C-B bond and the breakage of the B-B bond form the reactant to **INT1** through **TS1**, and further to the product through **TS2**. These results strongly identified the reasonability of the reaction pathway and the structure of **TS1** and **TS2**.

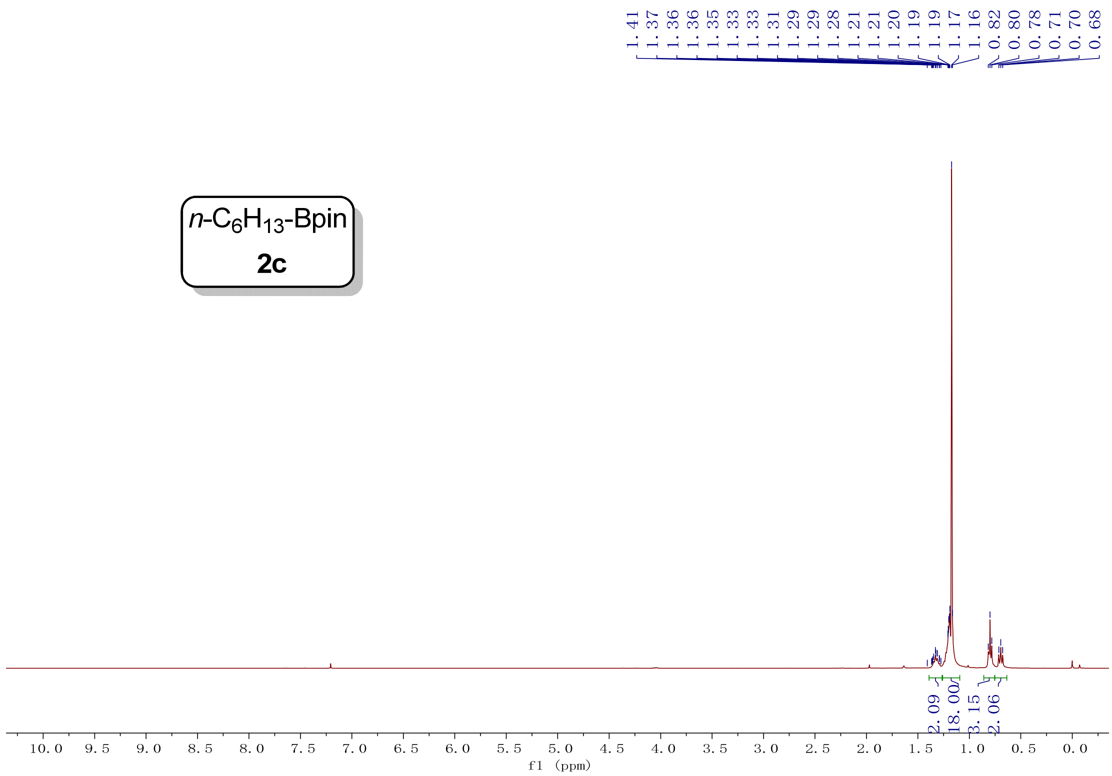
8. NMR charts

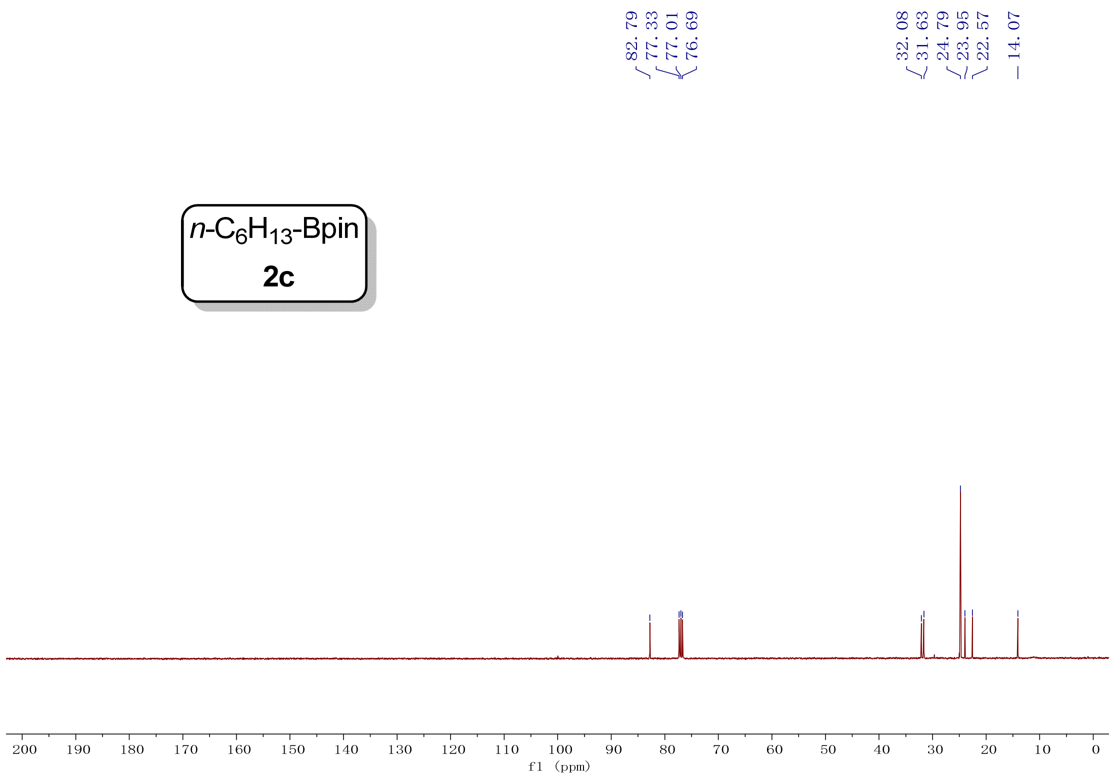


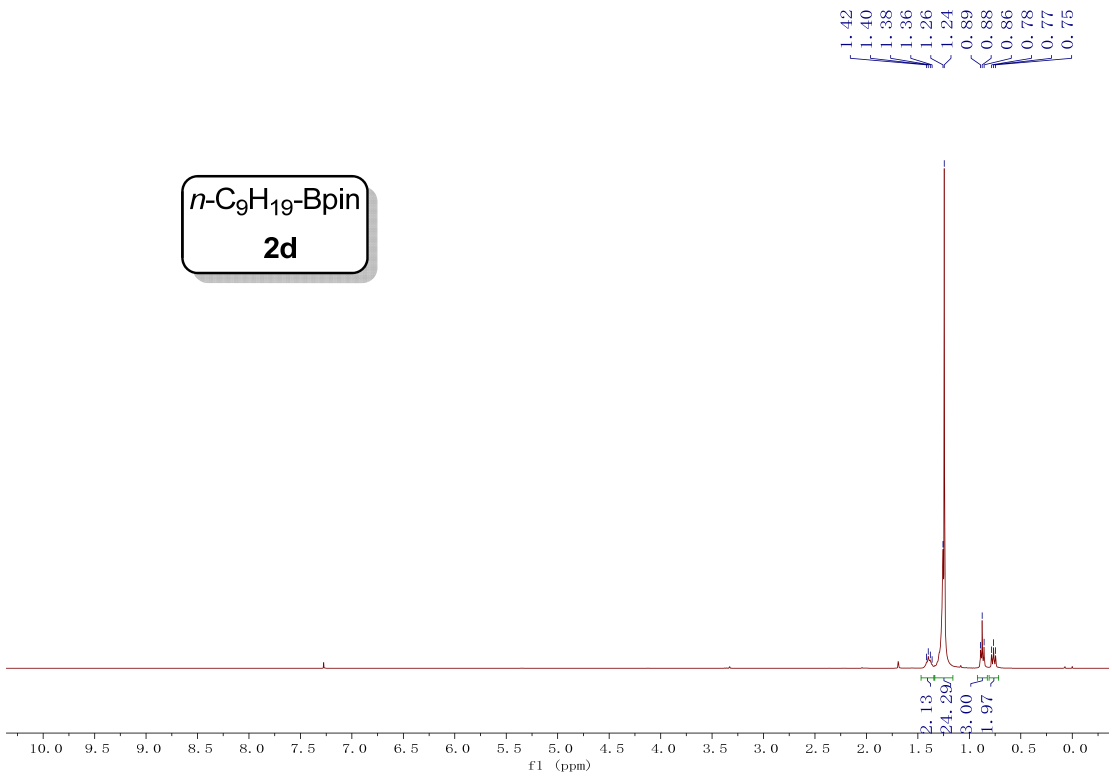
n-C8H17-Bpin
2a
1.36
1.35
1.33
1.31
1.29
1.19
1.17
0.82
0.80
0.78
0.71
0.69
0.67
2.02
22.00
3.22
1.81
f1 (ppm)

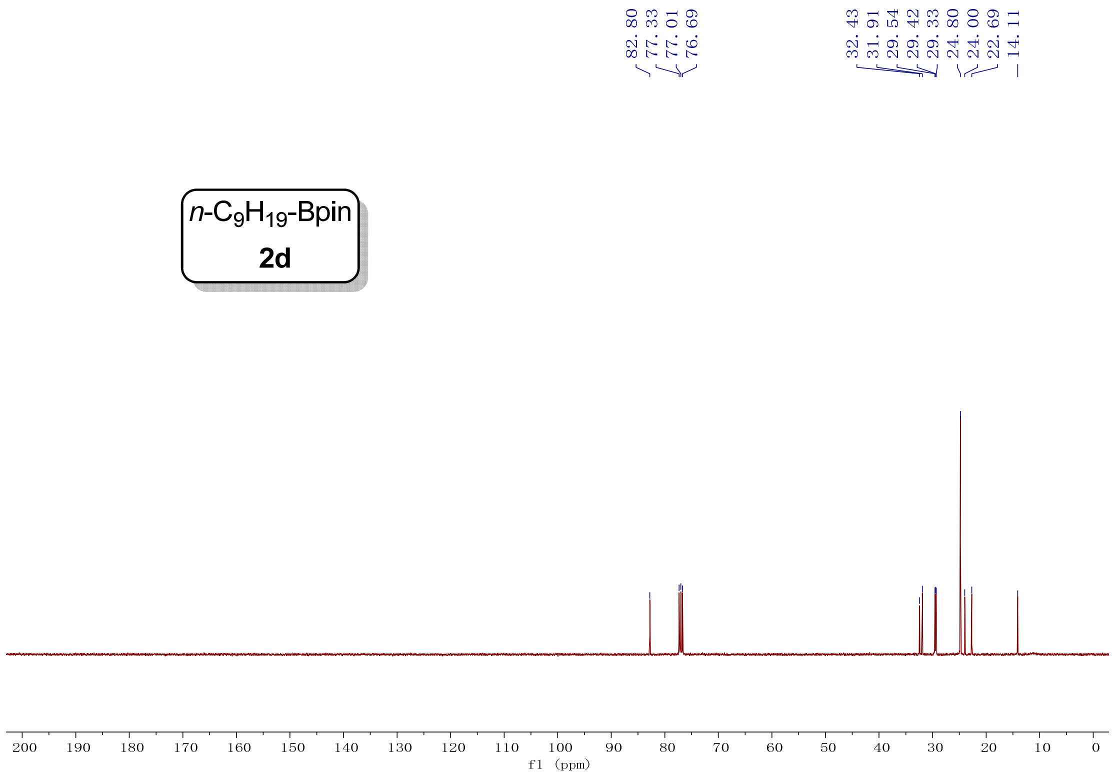


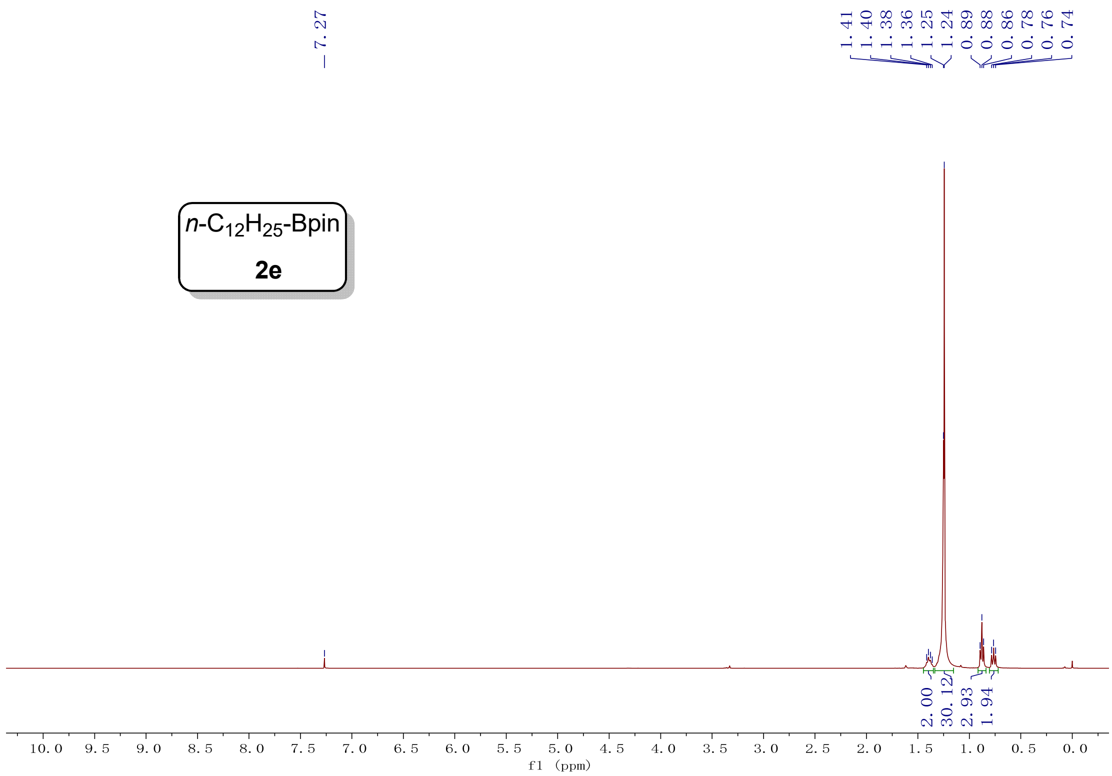
n-C8H17-Bpin
2a
82.79
77.33
77.02
76.70
32.43
31.89
29.37
29.25
24.79
23.99
22.67
14.10
f1 (ppm)

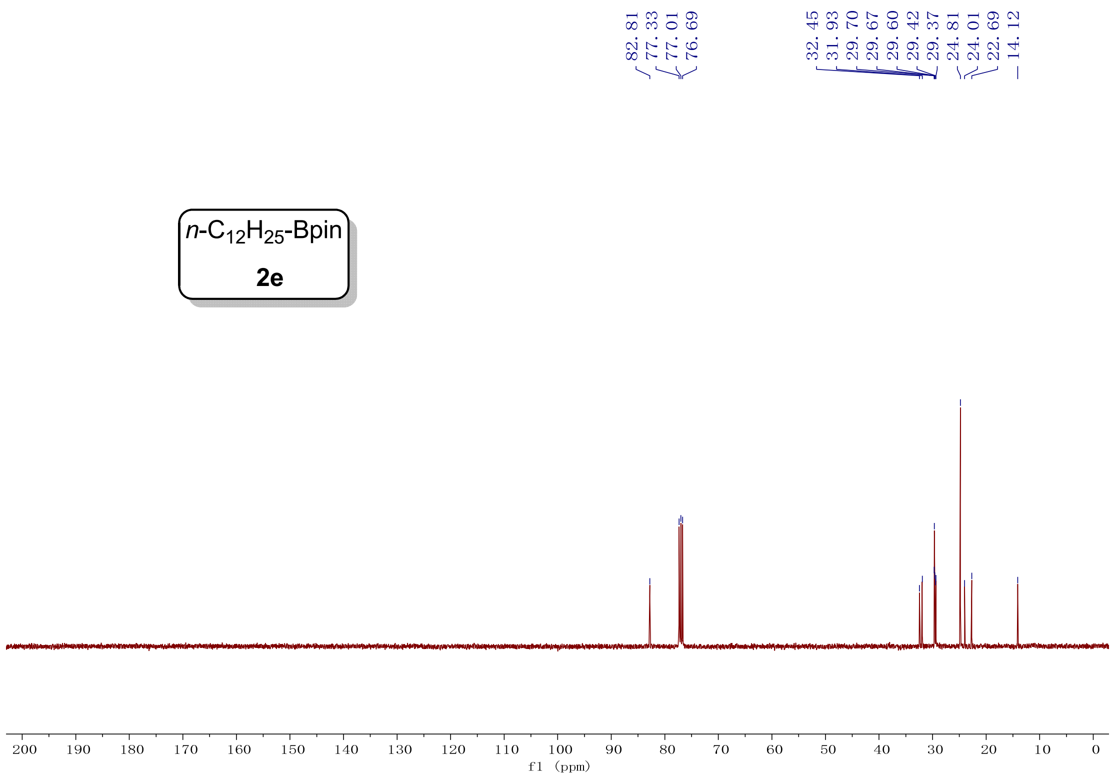

n-C6H13-Bpin
2c
f1 (ppm)

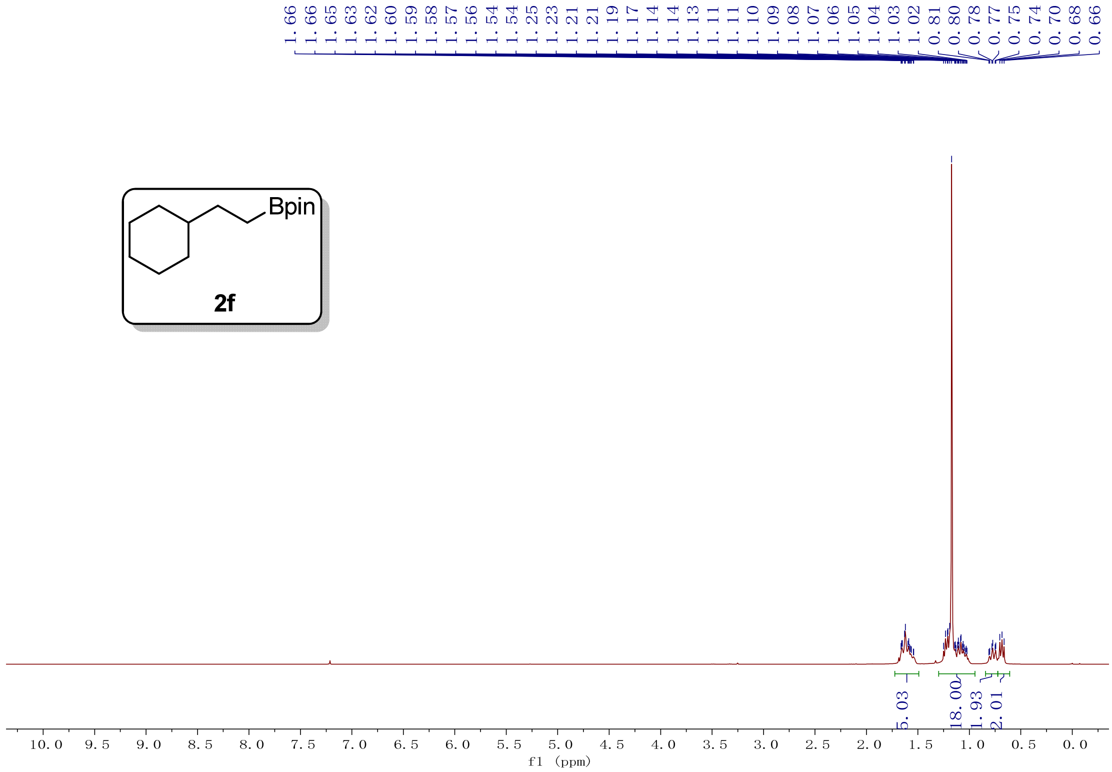

82.79
77.33
77.01
76.69
32.08
31.63
24.79
23.95
22.57
14.07
n-C6H13-Bpin
2c
f1 (ppm)

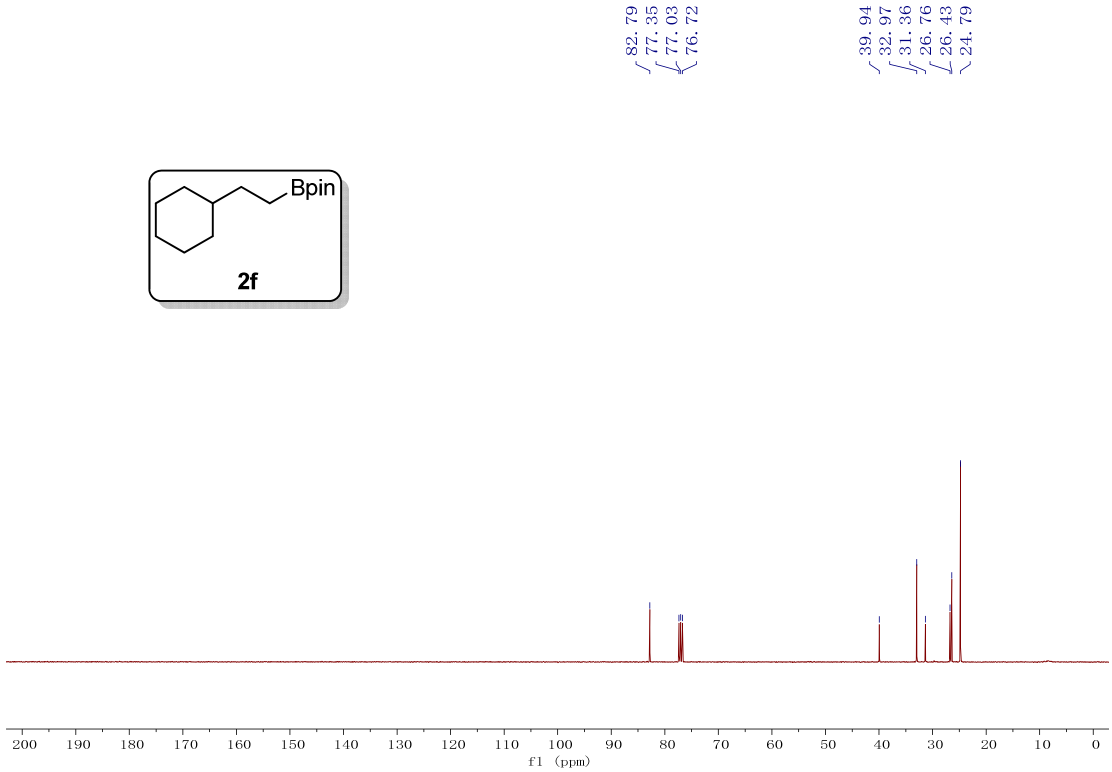

1.42
1.40
1.38
1.36
1.26
1.24
0.89
0.88
0.86
0.78
0.77
0.75
n-C9H19-Bpin
2d
2.13
24.29
3.00
1.97
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

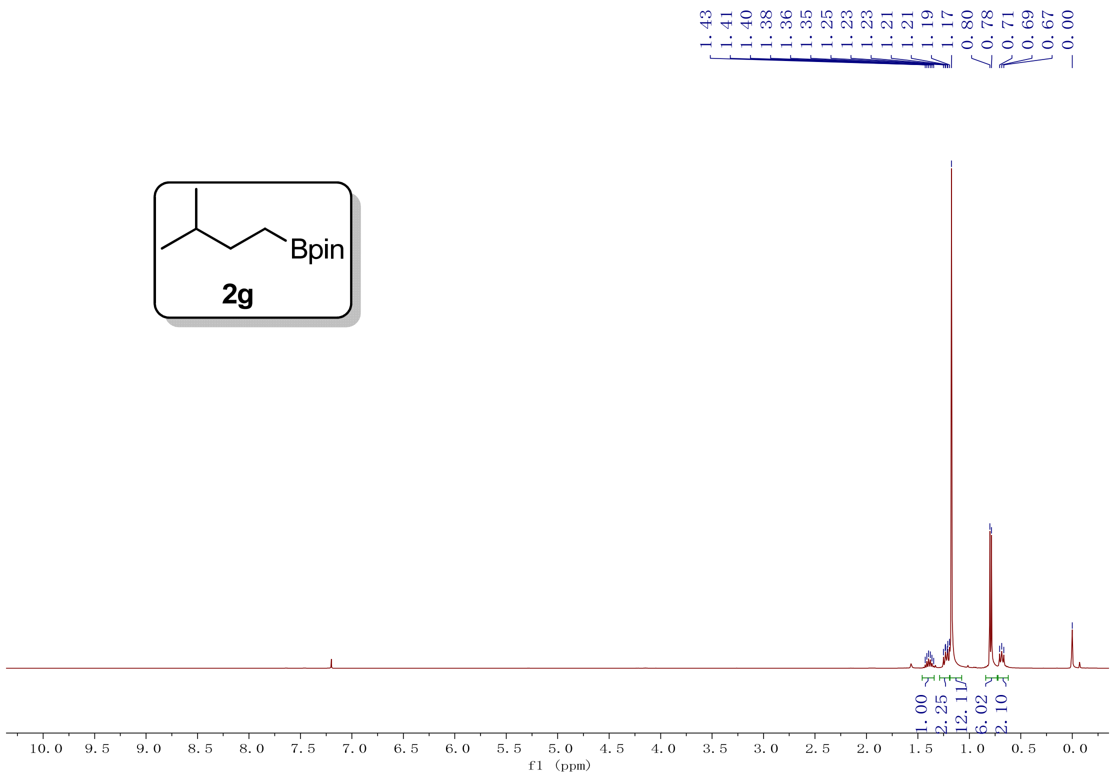

82.80
77.33
77.01
76.69
32.43
31.91
29.54
29.42
29.33
24.80
24.00
22.69
14.11
n-C9H19-Bpin
2d
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

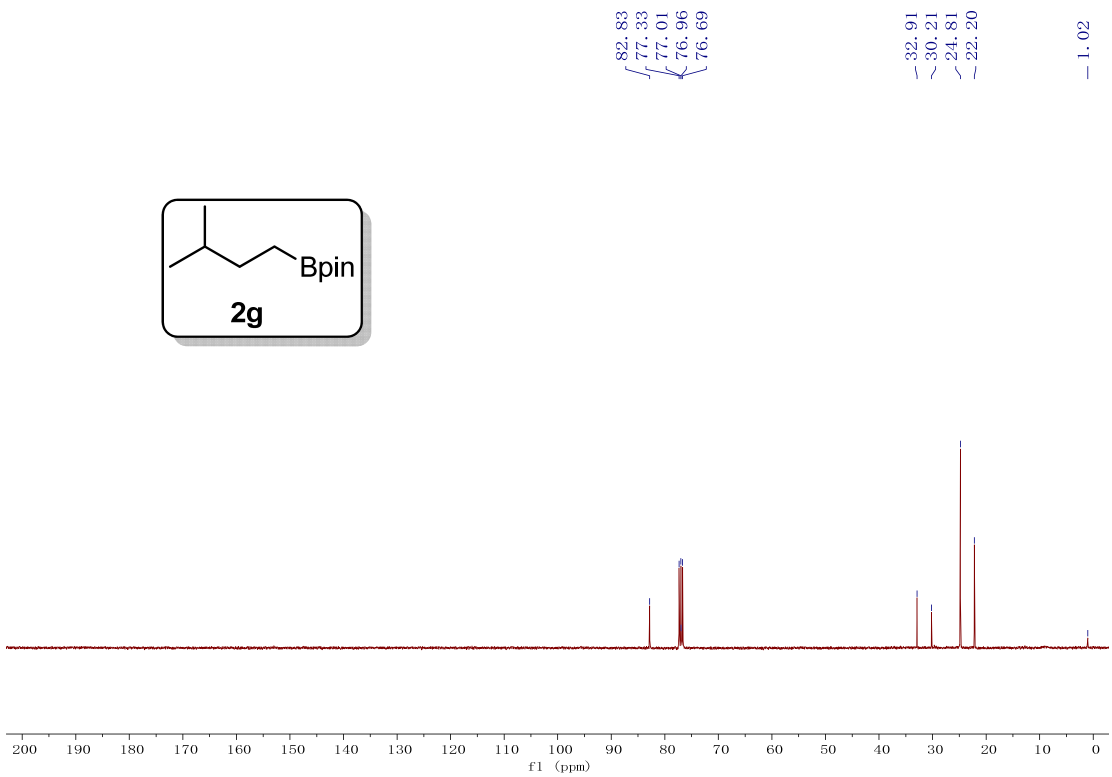

7.27
1.41
1.40
1.38
1.36
1.25
1.24
0.89
0.88
0.86
0.78
0.76
0.74
n-C12H25-Bpin
2e
2.00
30.12
2.93
1.94
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

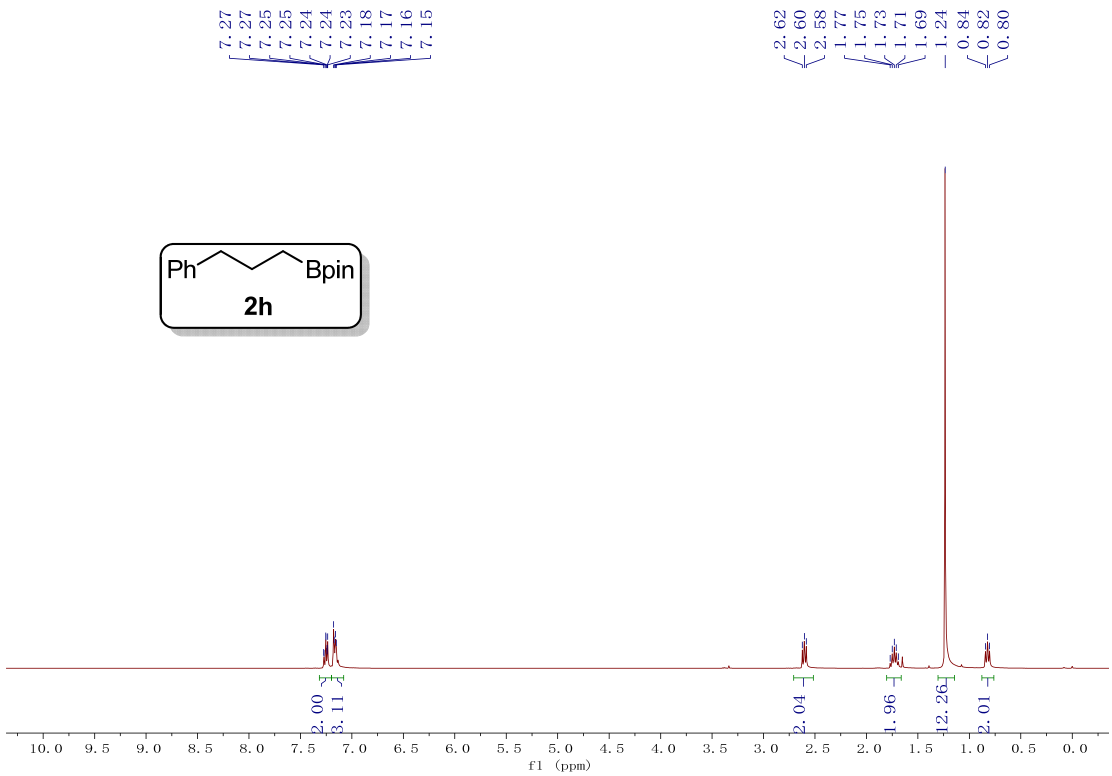

82.81
77.33
77.01
76.69
32.45
31.93
29.70
29.67
29.60
29.42
29.37
24.81
24.01
22.69
14.12
n-C12H25-Bpin
2e
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

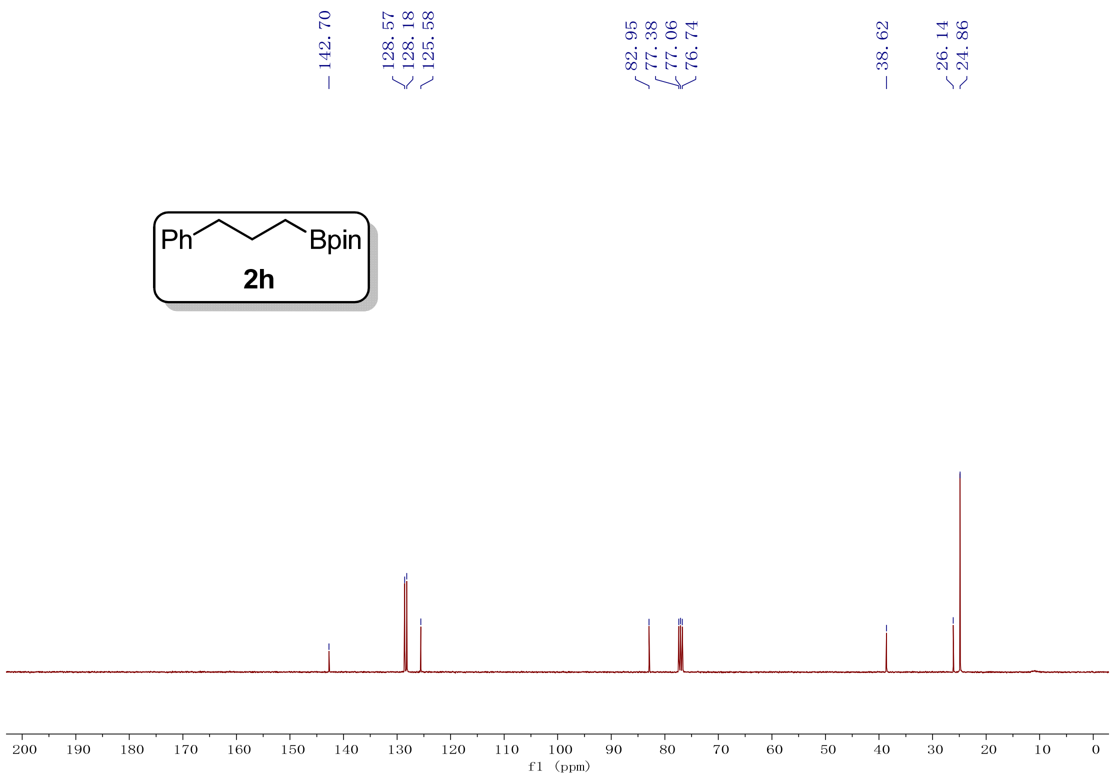

1.66 1.66 1.65 1.63 1.62 1.60 1.59 1.58 1.57 1.56 1.54 1.54 1.25 1.23 1.21 1.21 1.19 1.17 1.14 1.14 1.13 1.11 1.11 1.10 1.09 1.08 1.07 1.06 1.05 1.04 1.03 1.02 0.81 0.80 0.78 0.77 0.75 0.74 0.70 0.68 0.66
Bpin
2f
5.03
18.00
1.93
2.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

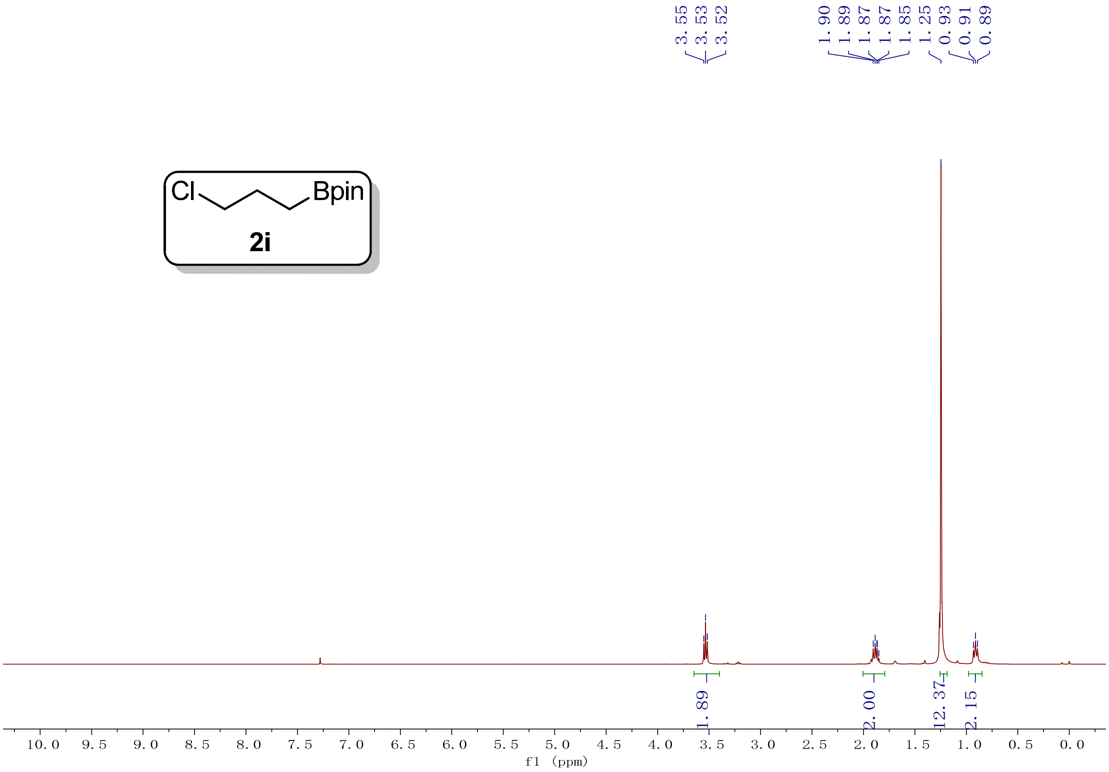

82.79 77.35 77.03 76.72
39.94 32.97 31.36 26.76 26.43 24.79
Bpin
2f
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

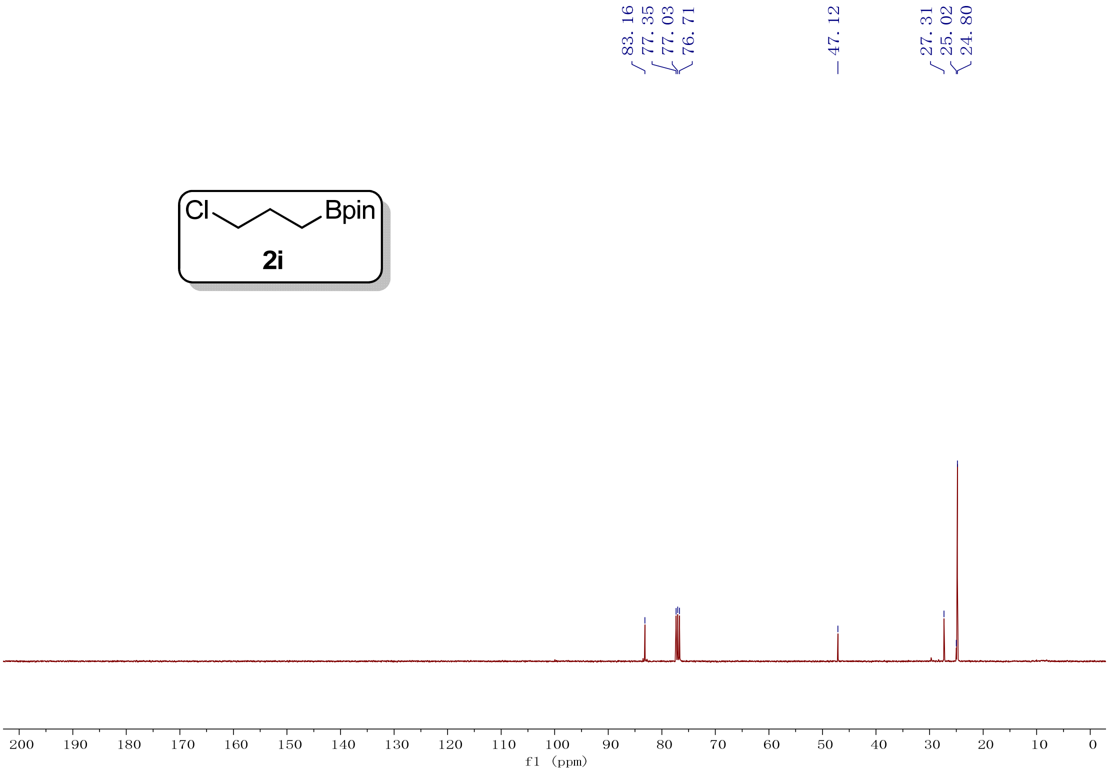

1.43 1.41 1.40 1.38 1.36 1.35 1.25 1.23 1.23 1.21 1.21 1.19 1.17 0.80 0.78 0.71 0.69 0.67 0.00
Bpin
2g
1.00 2.25 12.11 6.02 2.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

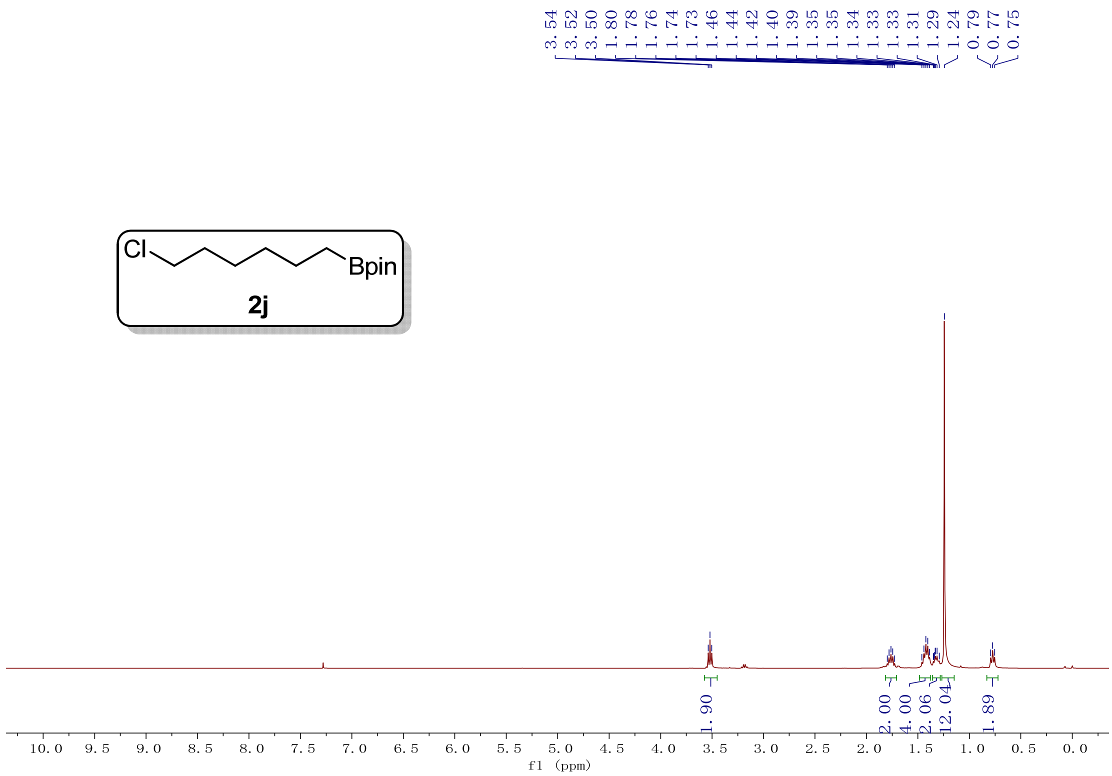

82.83 77.33 77.01 76.96 76.69
32.91 30.21 24.81 22.20
1.02
Bpin
2g
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.27 7.27 7.25 7.25 7.24 7.24 7.23 7.18 7.17 7.16 7.15
2.62 2.60 2.58 1.77 1.75 1.73 1.71 1.69 1.24 0.84 0.82 0.80
Ph Bpin
2h
2.00 3.11 2.04 1.96 12.26 2.01
f1 (ppm)

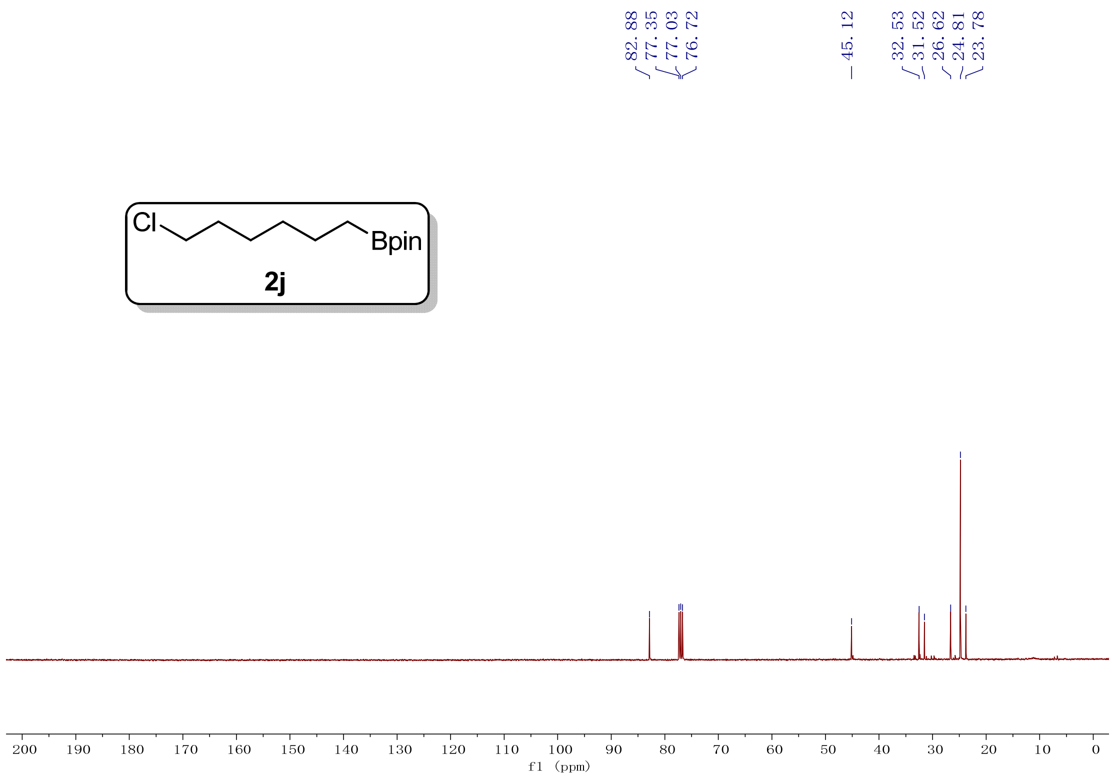

142.70 128.57 128.18 125.58 82.95 77.38 77.06 76.74 38.62 26.14 24.86
Ph Bpin
2h
f1 (ppm)


Cl
Bpin
2i
3.55
3.53
3.52
1.90
1.89
1.87
1.87
1.85
1.25
0.93
0.91
0.89
1.89
2.00
12.37
2.15
f1 (ppm)

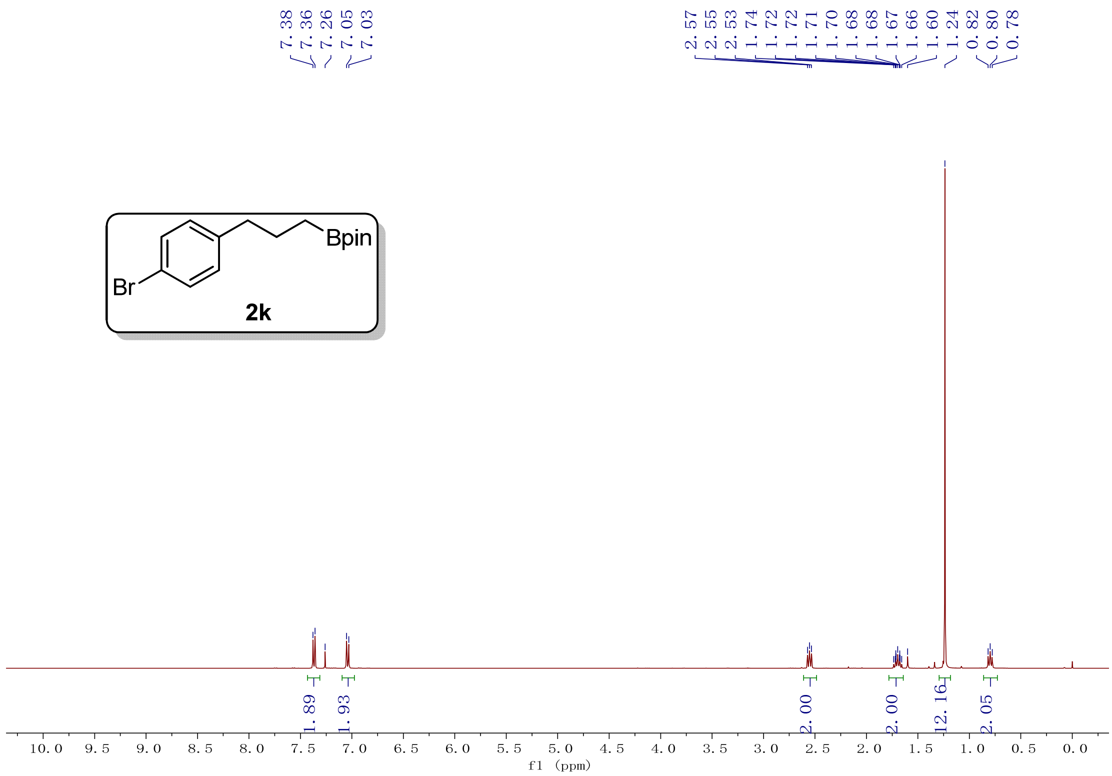

Cl
Bpin
2i
83.16
77.35
77.03
76.71
47.12
27.31
25.02
24.80
f1 (ppm)

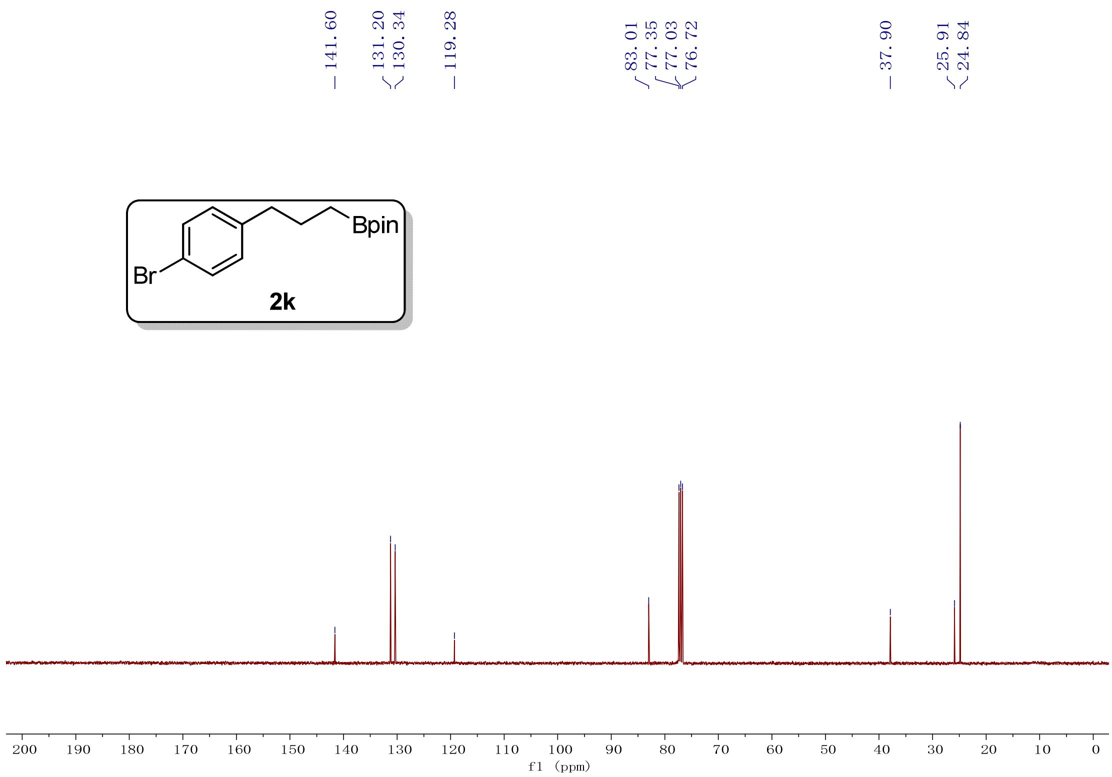


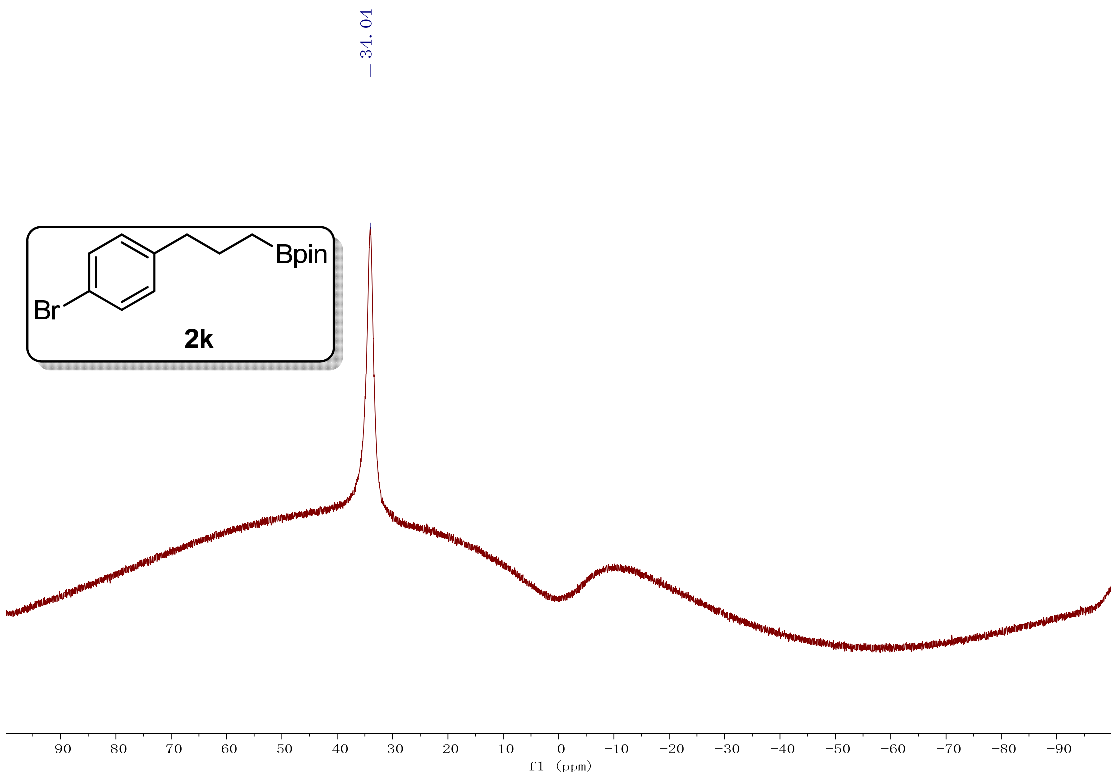
3.54 3.52 3.50 1.80 1.78 1.76 1.74 1.73 1.46 1.44 1.42 1.40 1.39 1.35 1.35 1.34 1.33 1.33 1.31 1.29 1.24 0.79 0.77 0.75
Cl
Bpin
2j
1.90
2.00
4.00
2.06
12.04
1.89
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



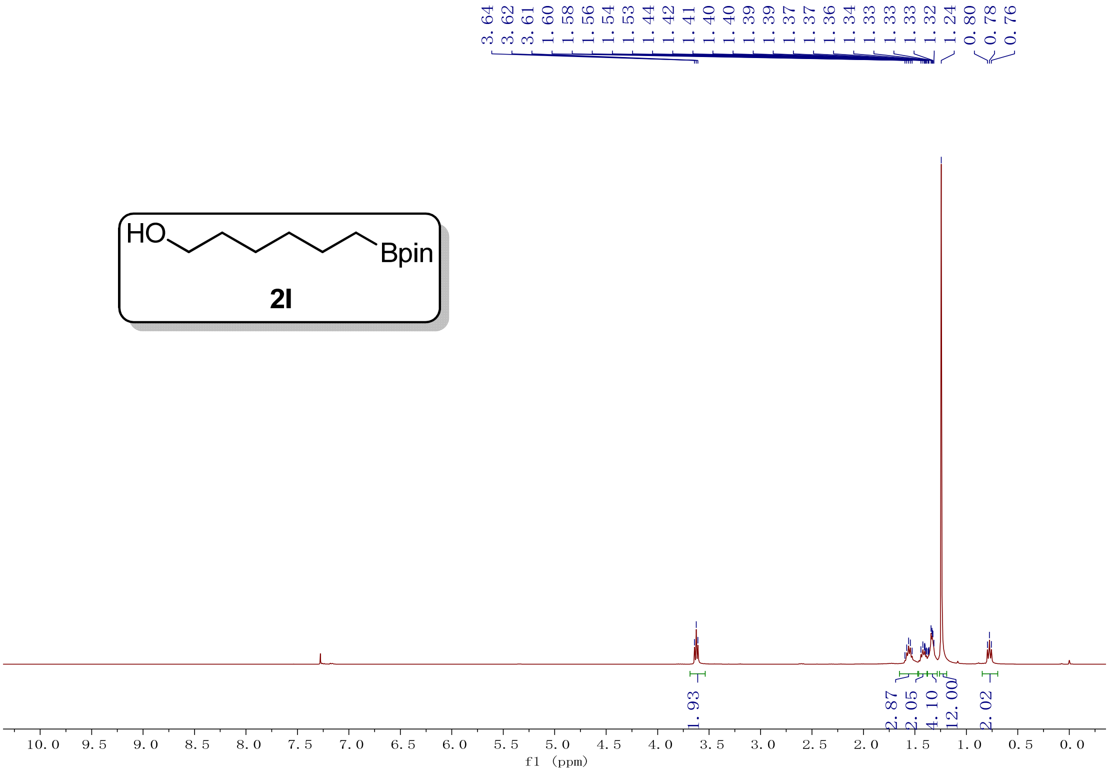
82.88 77.35 77.03 76.72
45.12
32.53 31.52 26.62 24.81 23.78
Cl
Bpin
2j
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

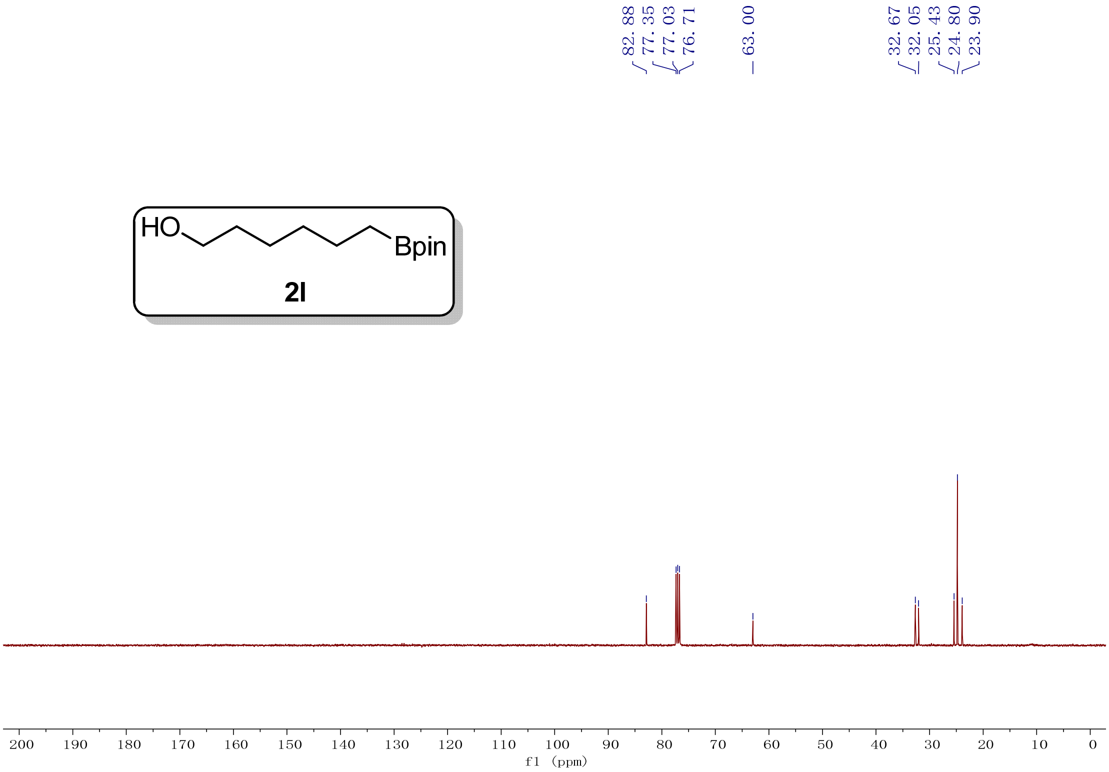

7.38
7.36
7.26
7.05
7.03
2.57
2.55
2.53
1.74
1.72
1.72
1.71
1.70
1.68
1.68
1.67
1.66
1.60
1.24
0.82
0.80
0.78
Bpin
Br
2k
1.89
1.93
2.00
2.00
12.16
2.05
f1 (ppm)

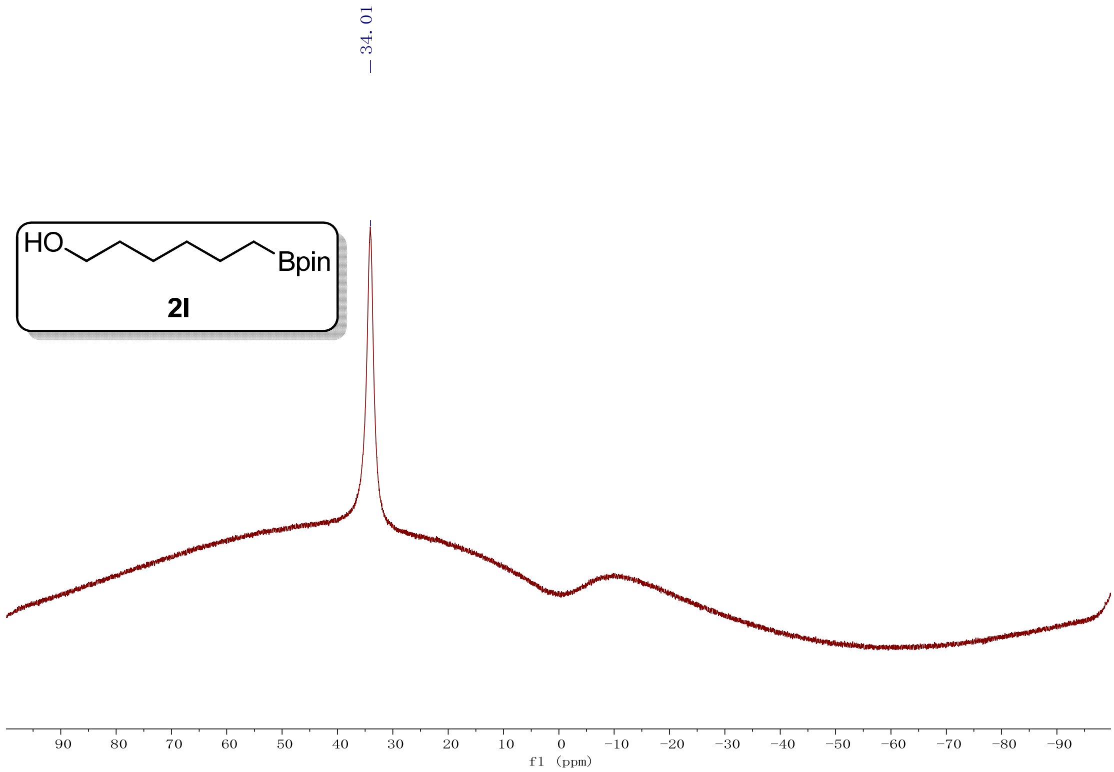

141.60
131.20
130.34
119.28
83.01
77.35
77.03
76.72
37.90
25.91
24.84
Bpin
Br
2k
f1 (ppm)

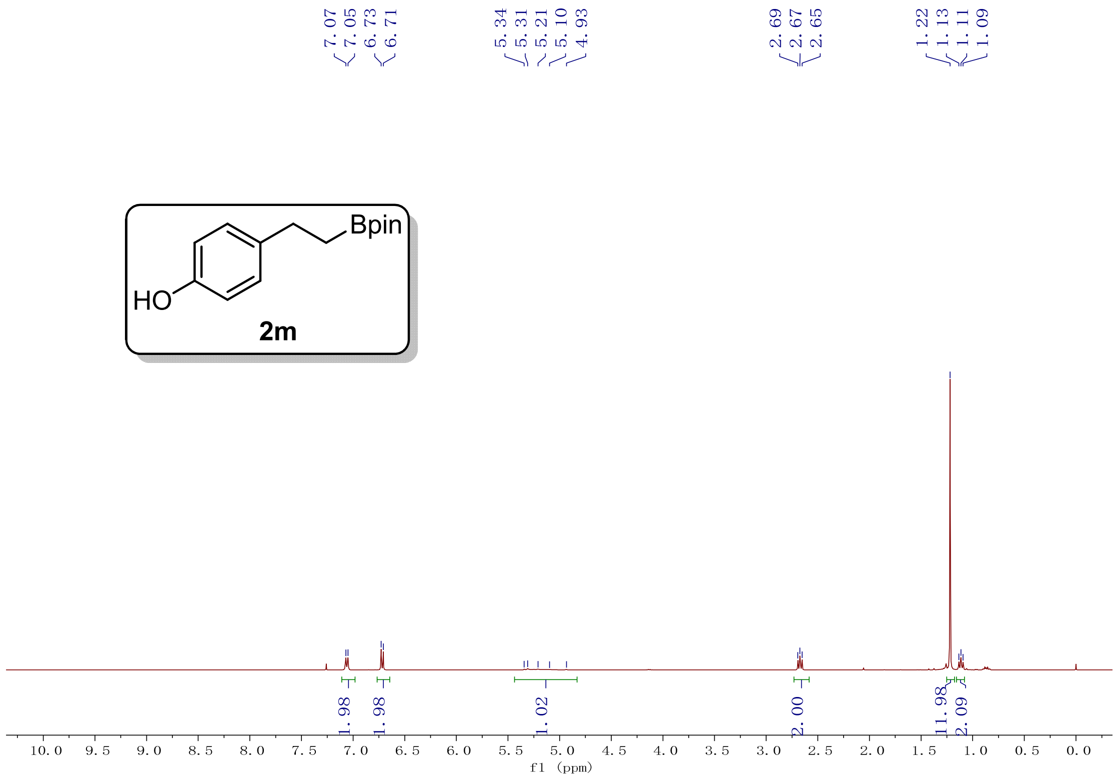


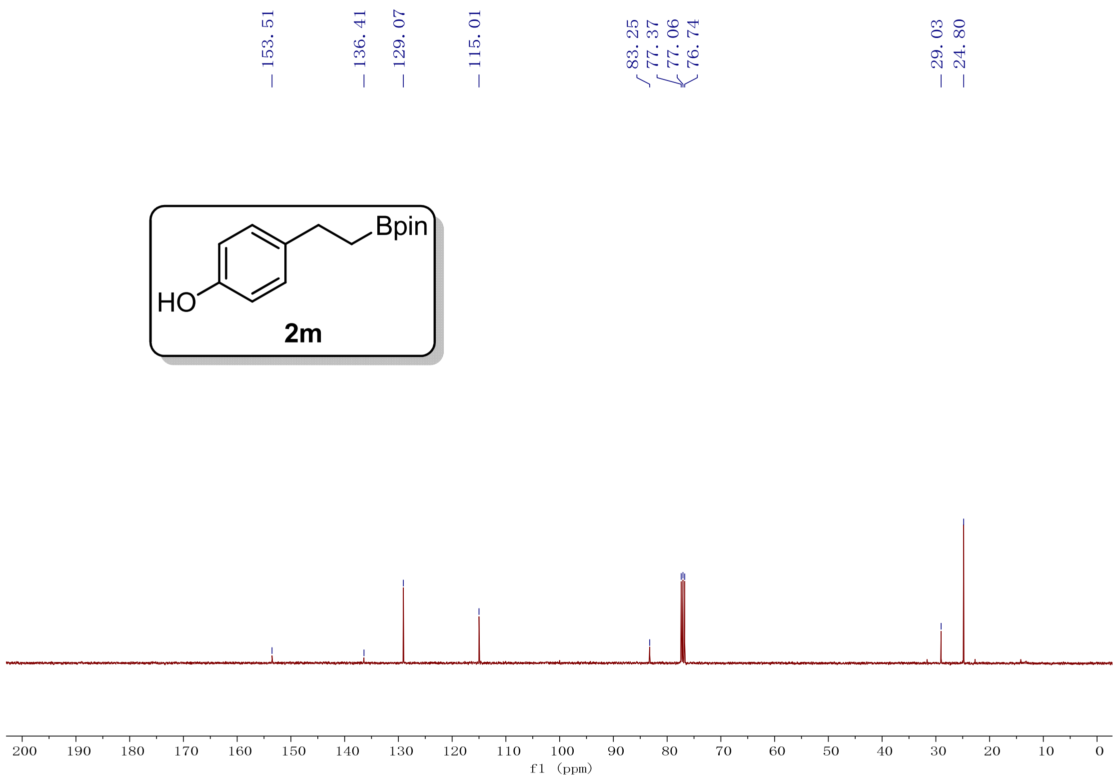
34.04
Bpin
Br
2k
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

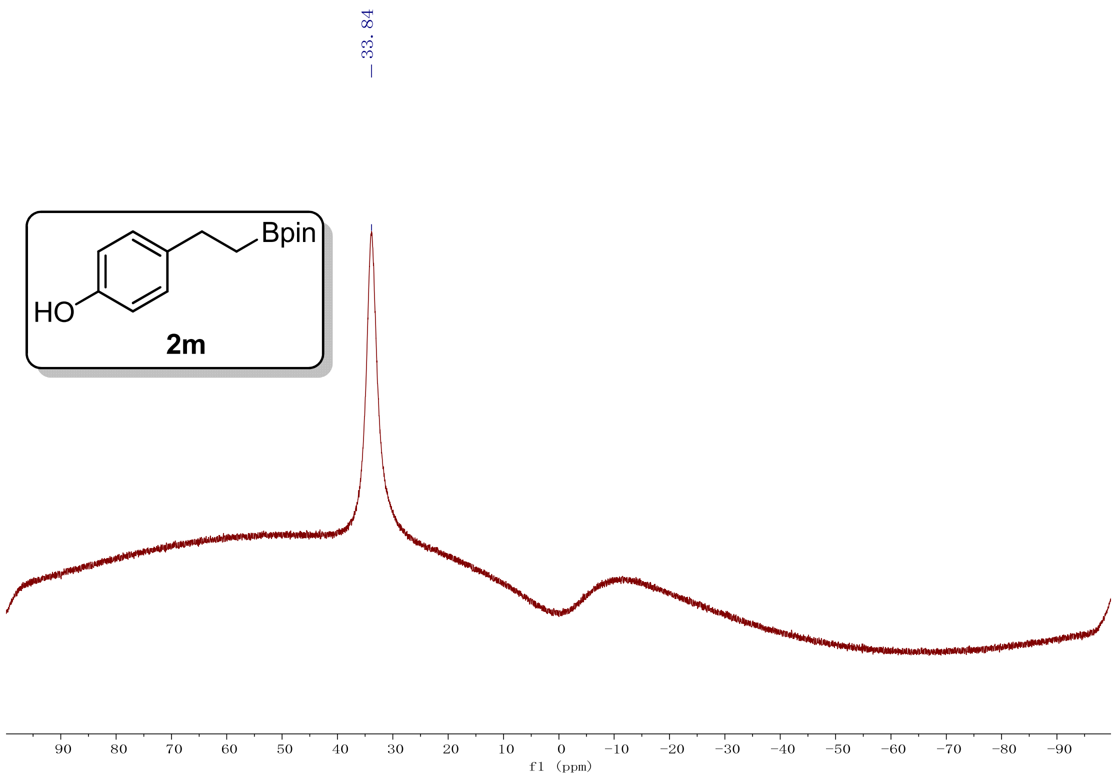

3.64
3.62
3.61
1.60
1.58
1.56
1.54
1.53
1.44
1.42
1.41
1.40
1.40
1.39
1.39
1.37
1.37
1.36
1.34
1.33
1.33
1.33
1.32
1.24
0.80
0.78
0.76
HO
Bpin
2l
1.93
2.87
2.05
4.10
12.00
2.02
f1 (ppm)

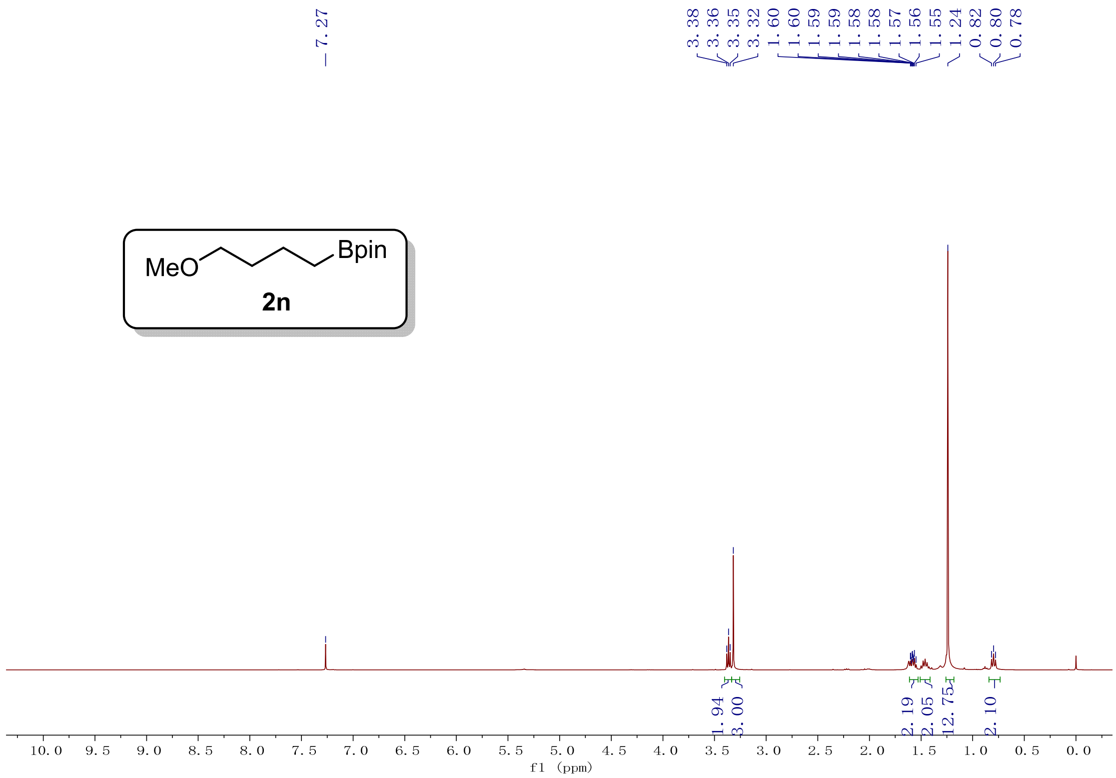

82.88
77.35
77.03
76.71
63.00
32.67
32.05
25.43
24.80
23.90
HO
Bpin
2l
f1 (ppm)

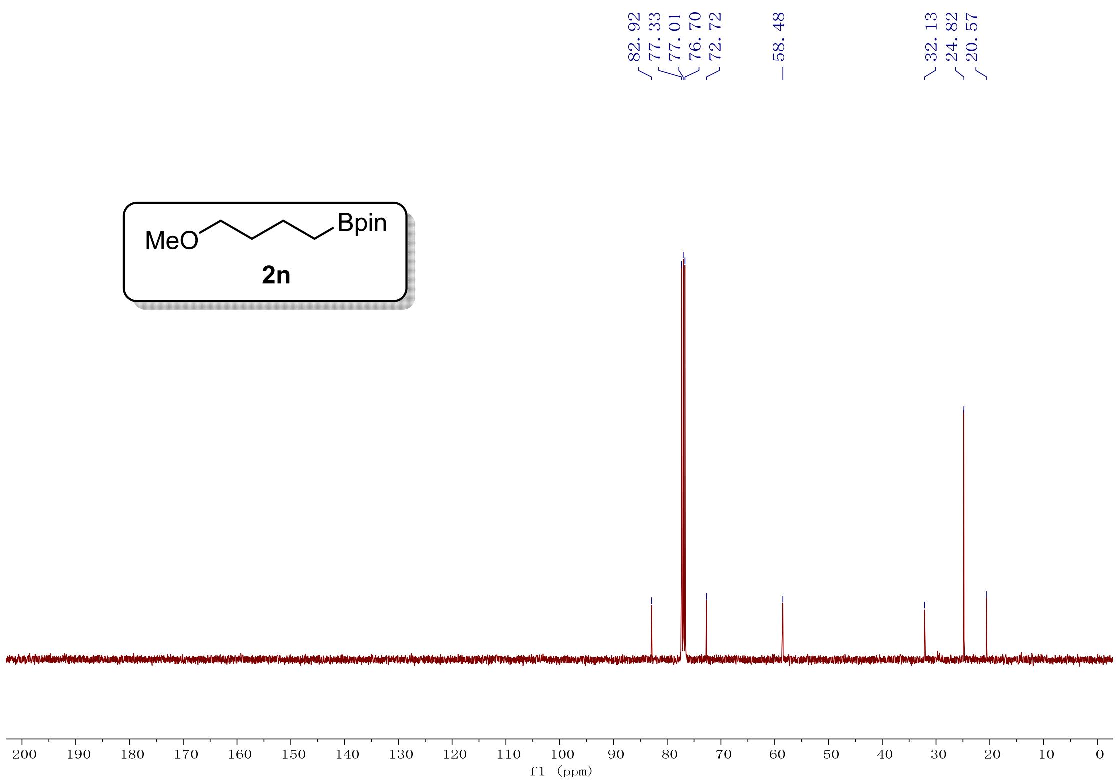

34.01
HO
Bpin
2l
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

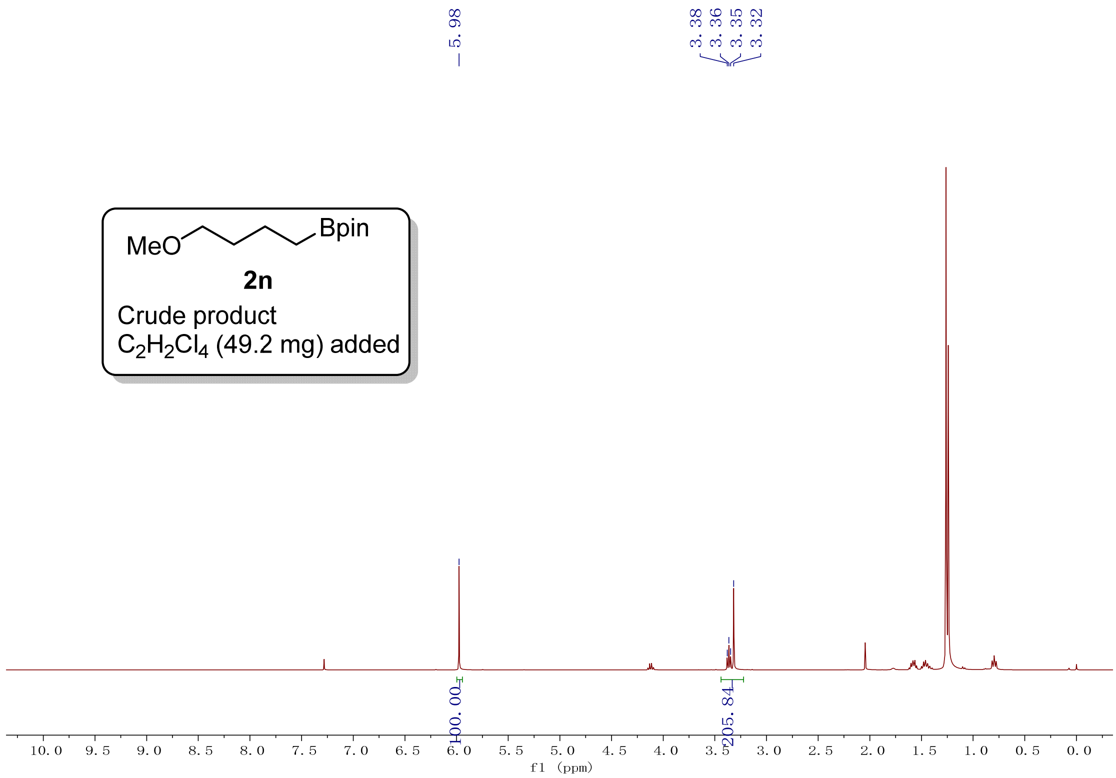

7.07
7.05
6.73
6.71
5.34
5.31
5.21
5.10
4.93
2.69
2.67
2.65
1.22
1.13
1.11
1.09
Bpin
HO
2m
1.98
1.98
1.02
2.00
11.98
2.09
f1 (ppm)

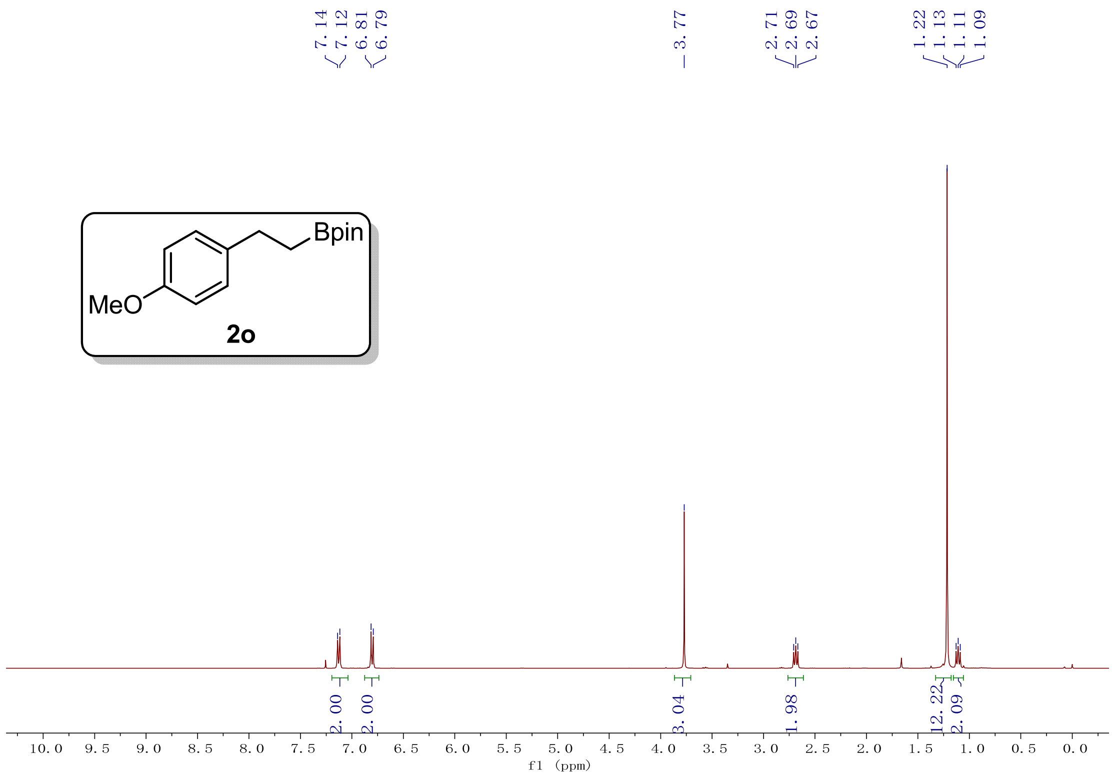

153.51
136.41
129.07
115.01
83.25
77.37
77.06
76.74
29.03
24.80
Bpin
HO
2m
f1 (ppm)

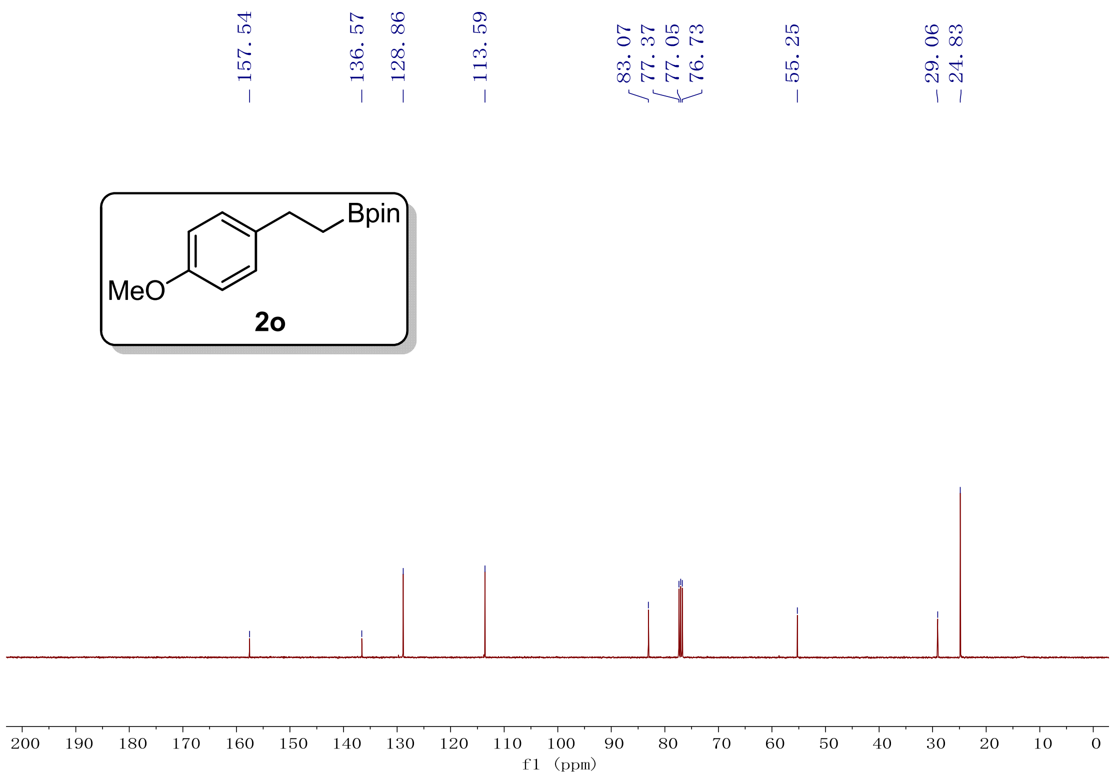

33.84
Bpin
HO
2m
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

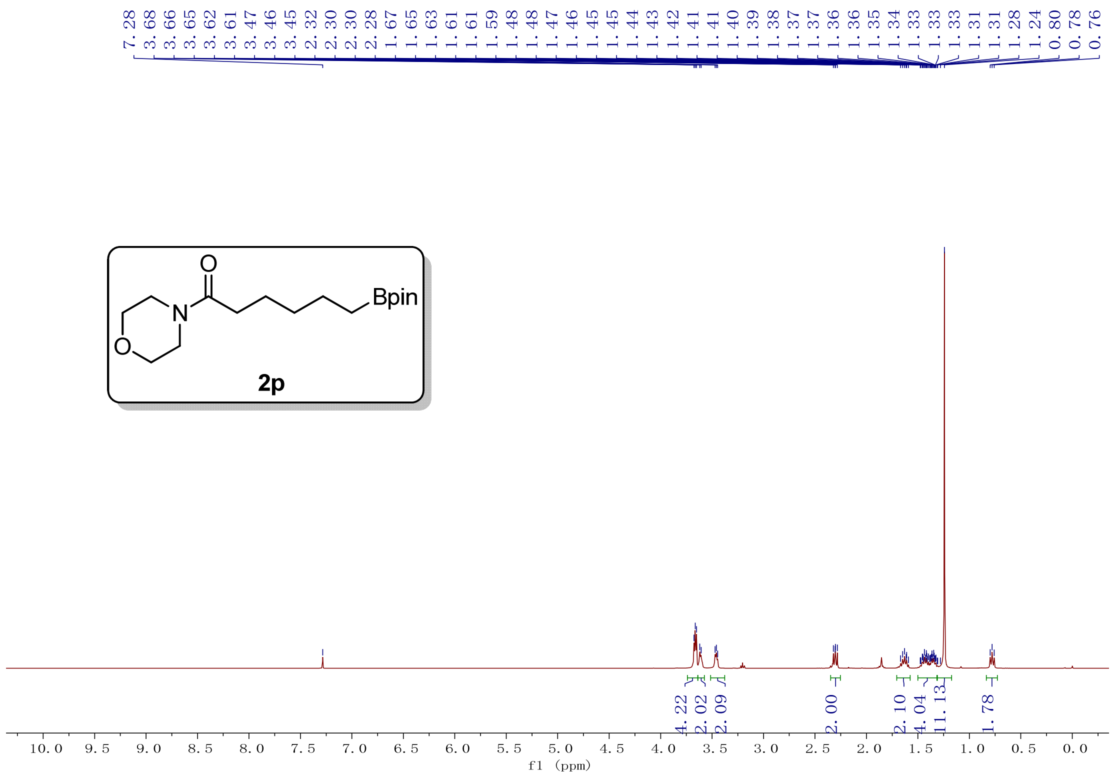

7.27
3.38
3.36
3.35
3.32
1.60
1.60
1.59
1.59
1.58
1.58
1.57
1.56
1.55
1.24
0.82
0.80
0.78
MeO
Bpin
2n
1.94
3.00
2.19
2.05
12.75
2.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

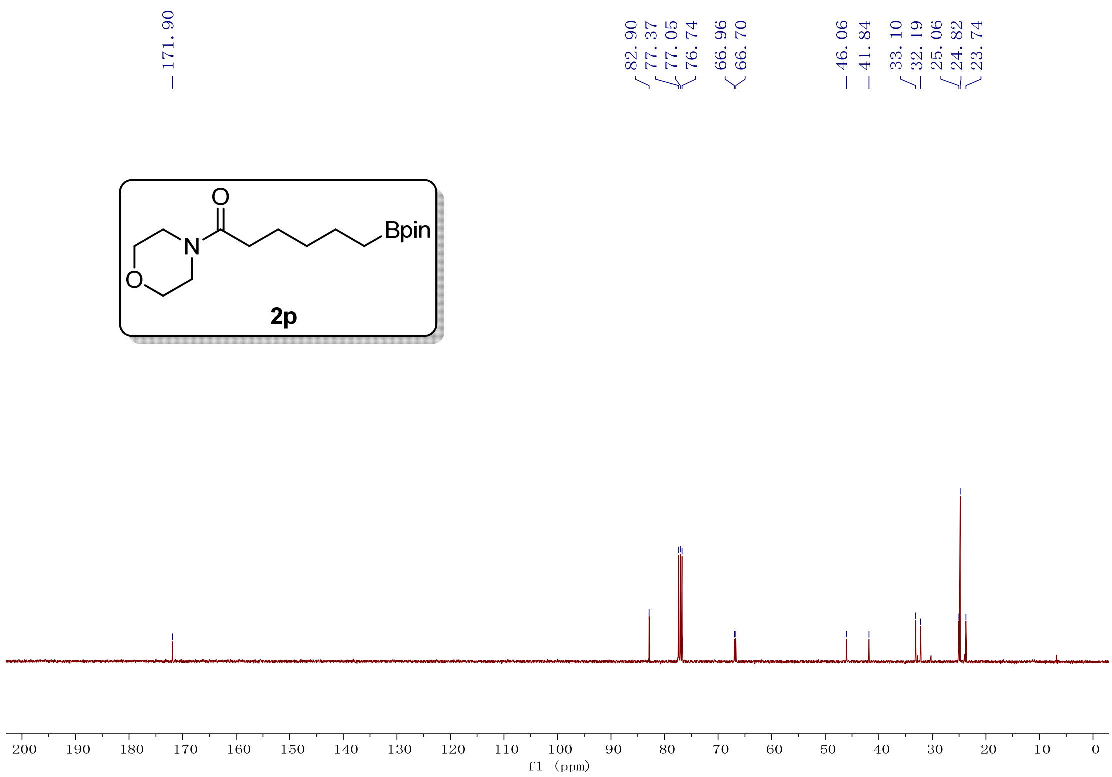

82.92
77.33
77.01
76.70
72.72
58.48
32.13
24.82
20.57
MeO
Bpin
2n
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

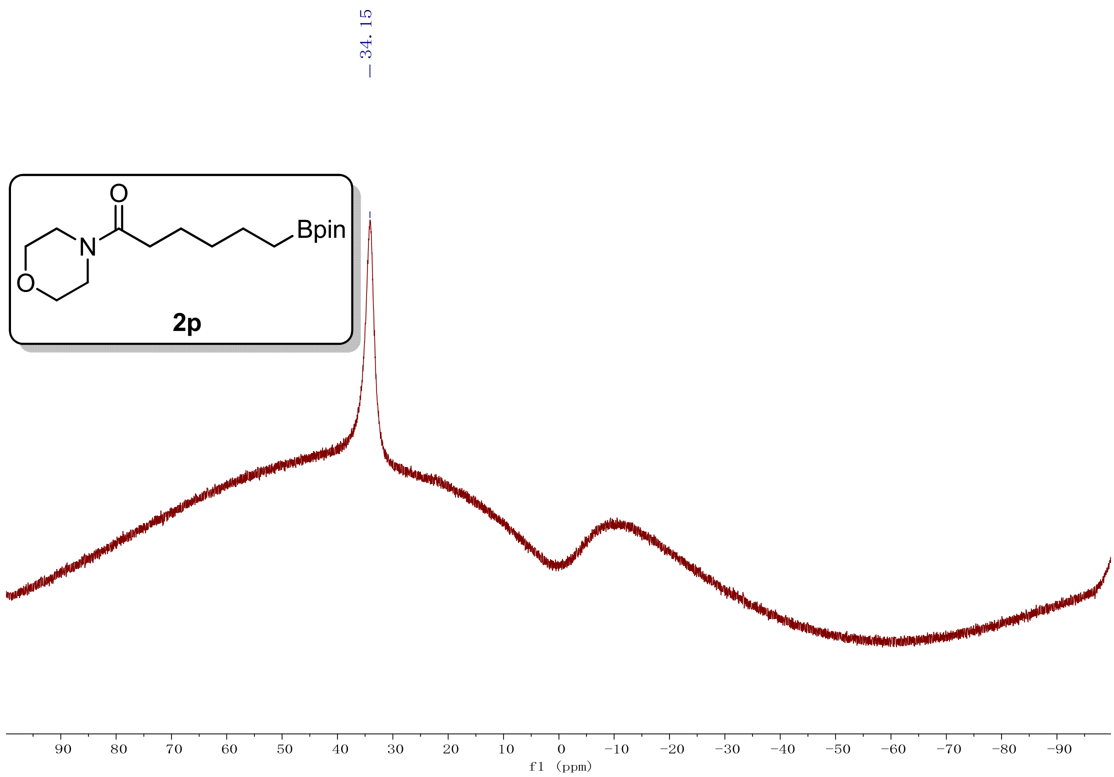

MeO
Bpin
2n
Crude product
C2H2Cl4 (49.2 mg) added
5.98
3.38
3.36
3.35
3.32
100.00
205.84
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

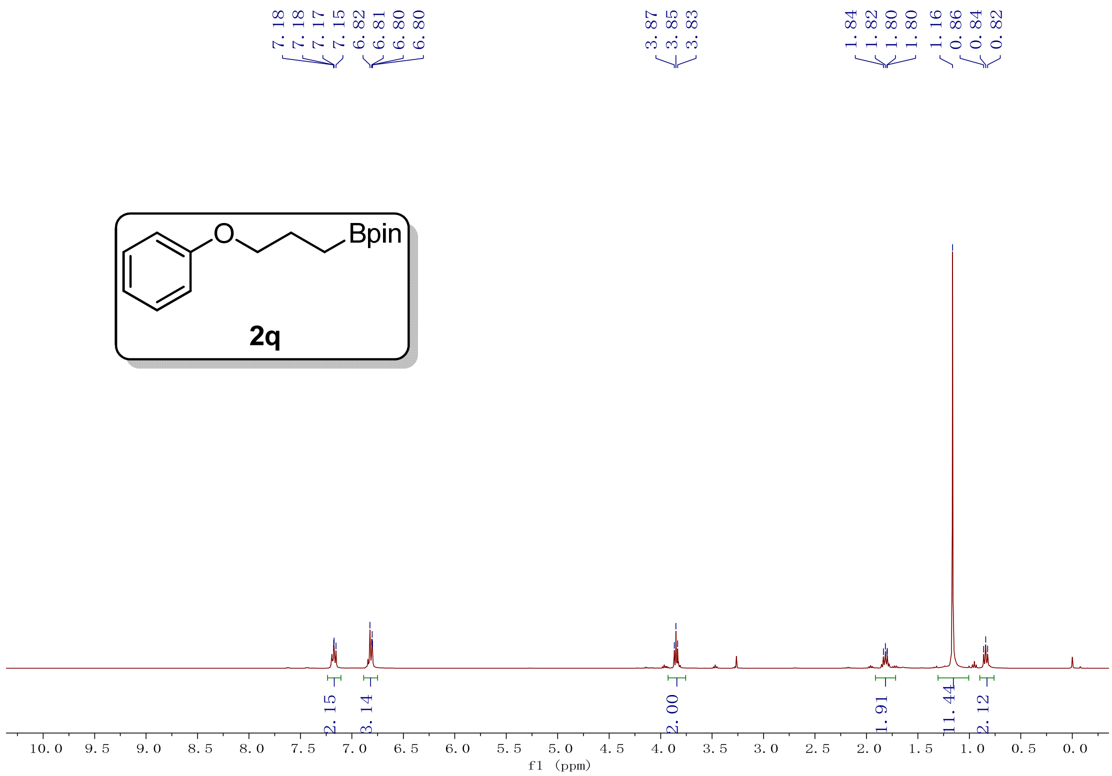

7.14
7.12
6.81
6.79
3.77
2.71
2.69
2.67
1.22
1.13
1.11
1.09
Bpin
MeO
2o
2.00
2.00
3.04
1.98
12.22
2.09
f1 (ppm)

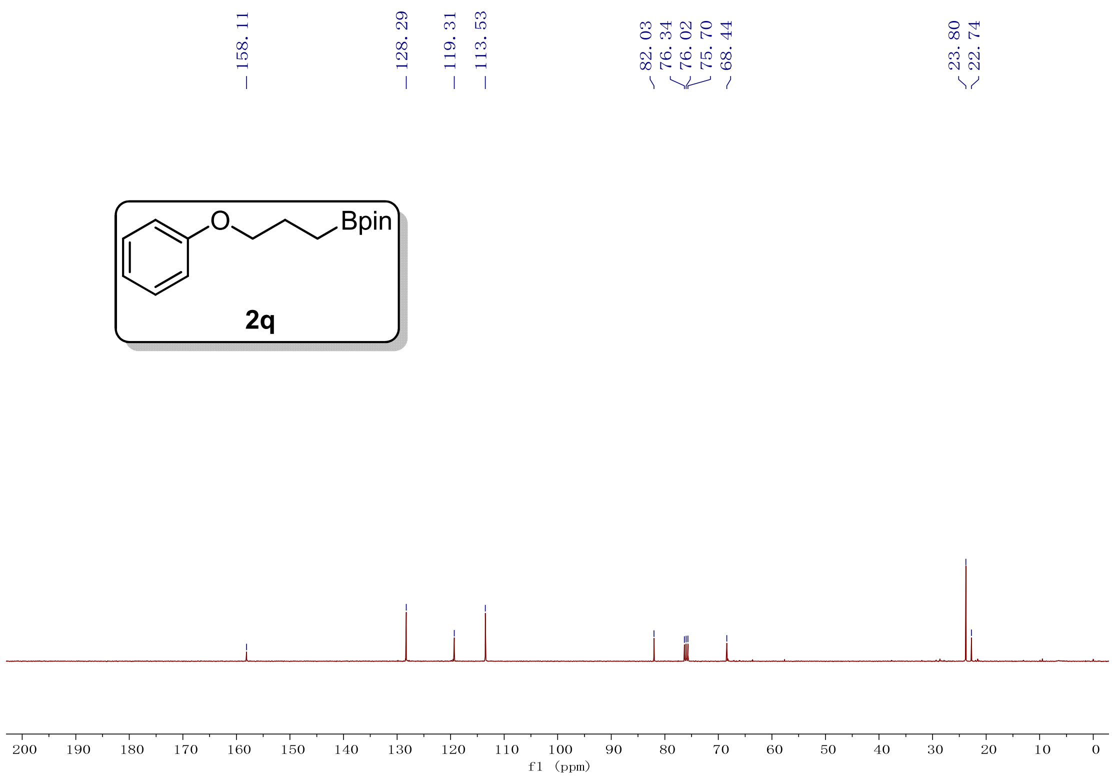

157.54
136.57
128.86
113.59
83.07
77.37
77.05
76.73
55.25
29.06
24.83
Bpin
MeO
2o
f1 (ppm)

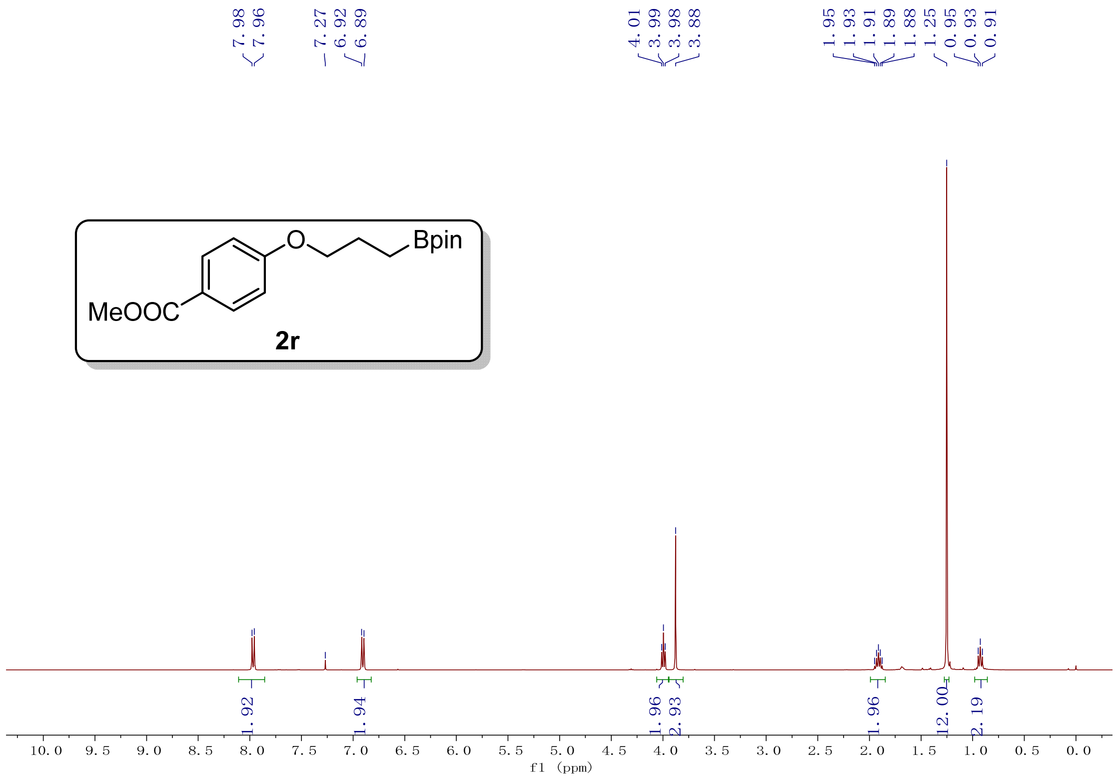

7.28
3.68
3.66
3.65
3.62
3.61
3.47
3.46
3.45
2.32
2.30
2.30
2.28
1.67
1.65
1.63
1.61
1.61
1.59
1.48
1.48
1.47
1.46
1.45
1.45
1.44
1.43
1.42
1.41
1.41
1.40
1.39
1.38
1.37
1.37
1.36
1.36
1.35
1.34
1.33
1.33
1.33
1.31
1.31
1.28
1.24
0.80
0.78
0.76
O
N
O
Bpin
2p
4.22
2.02
2.09
2.00
2.10
4.04
11.13
1.78
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

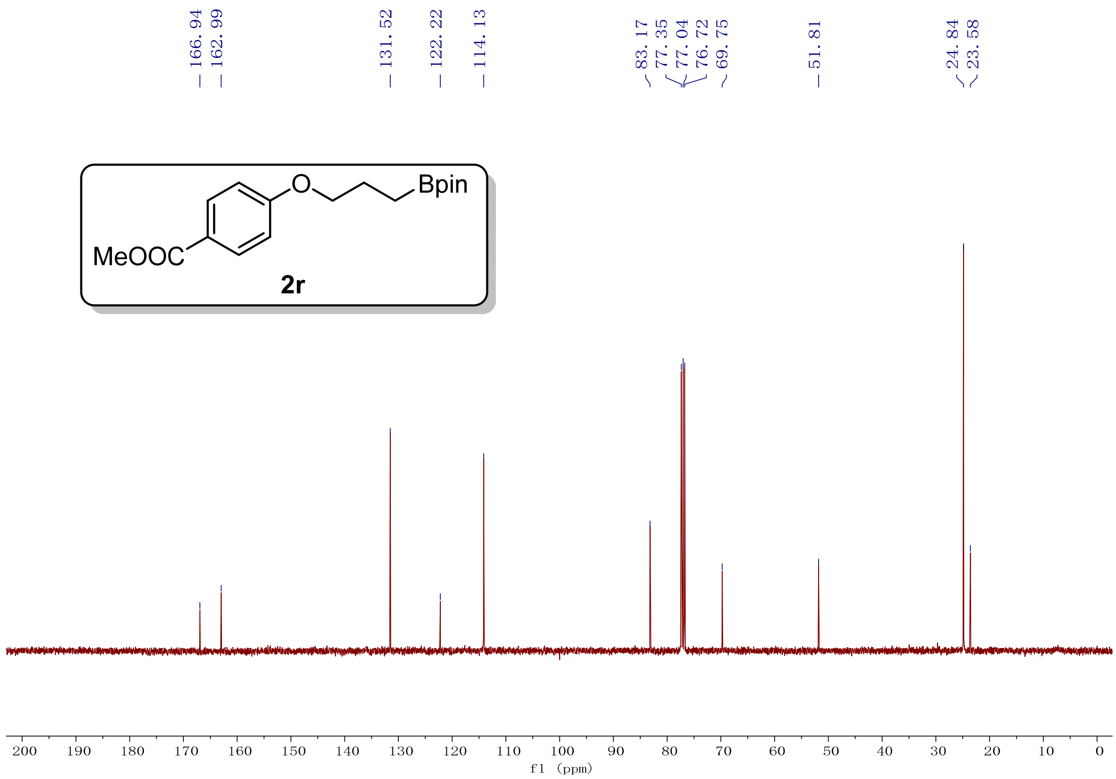

171.90
82.90
77.37
77.05
76.74
66.96
66.70
46.06
41.84
33.10
32.19
25.06
24.82
23.74
O
N
O
Bpin
2p
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

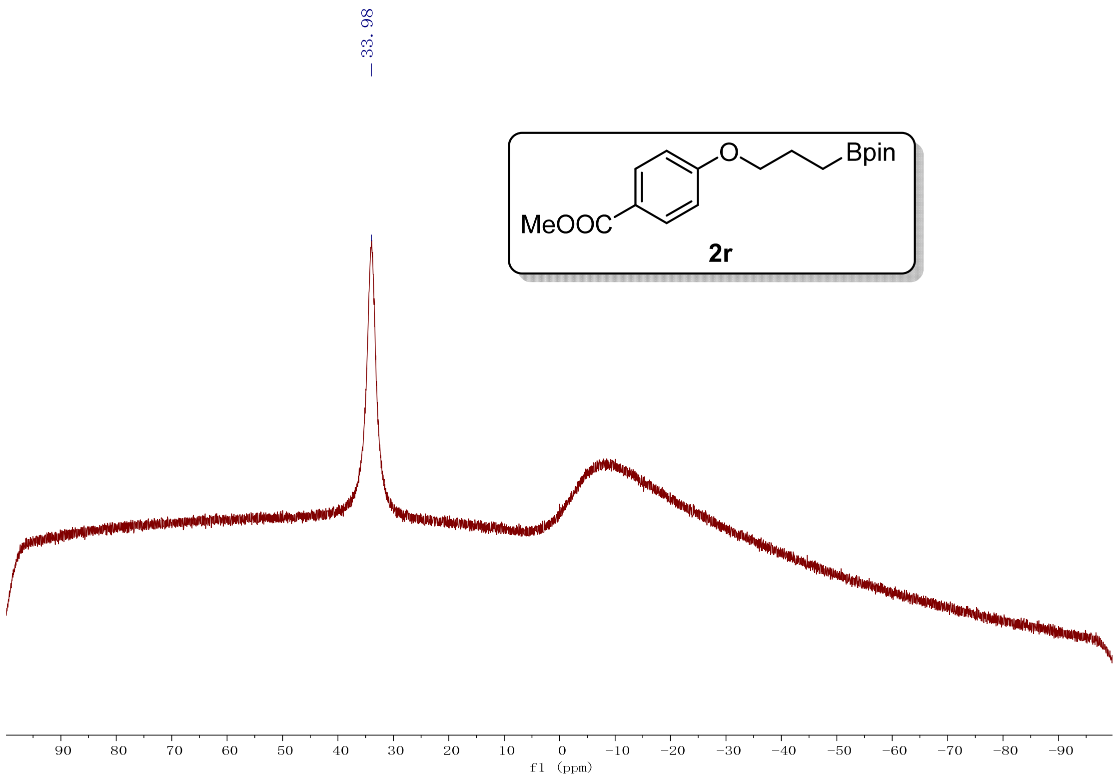

34.15
O
N
O
Bpin
2p
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)


7.18
7.18
7.17
7.15
6.82
6.81
6.80
6.80
3.87
3.85
3.83
1.84
1.82
1.80
1.80
1.16
0.86
0.84
0.82
O
Bpin
2q
2.15
3.14
2.00
1.91
11.44
2.12
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

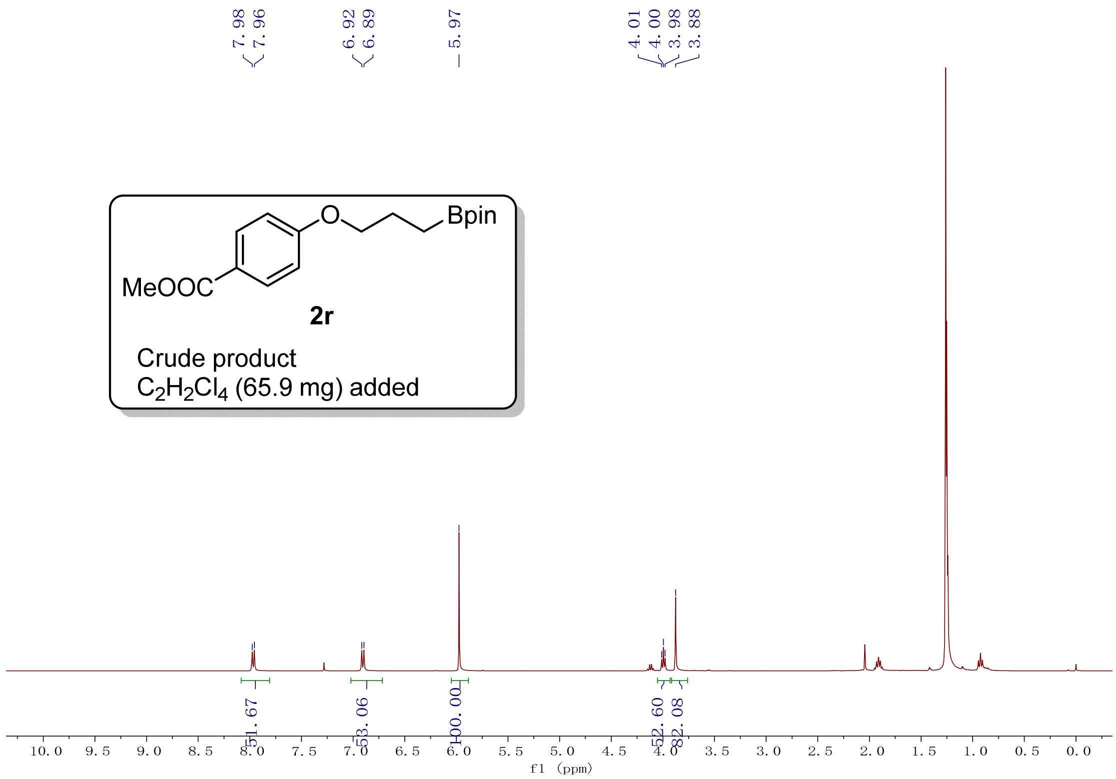

158.11
128.29
119.31
113.53
82.03
76.34
76.02
75.70
68.44
23.80
22.74
O
Bpin
2q
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.98
7.96
7.27
6.92
6.89
4.01
3.99
3.98
3.88
1.95
1.93
1.91
1.89
1.88
1.25
0.95
0.93
0.91
O
Bpin
MeOOC
2r
1.92
1.94
1.96
2.93
1.96
12.00
2.19
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

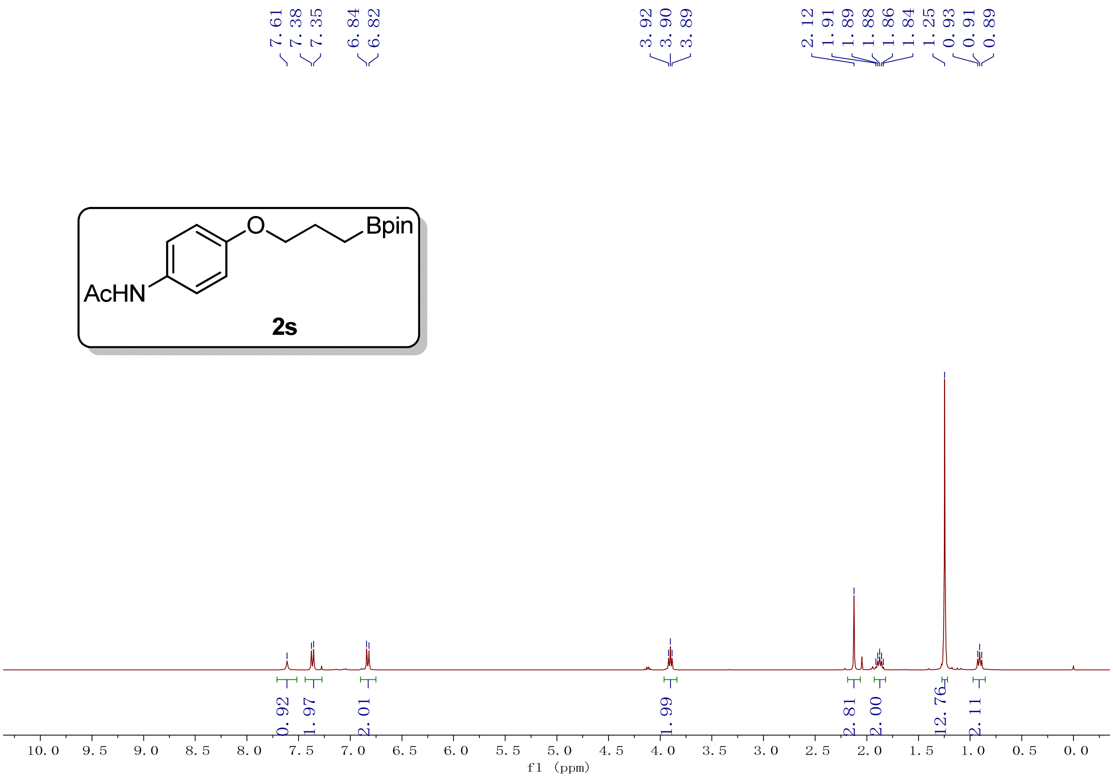

166.94
162.99
131.52
122.22
114.13
83.17
77.35
77.04
76.72
69.75
51.81
24.84
23.58
O
Bpin
MeOOC
2r
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

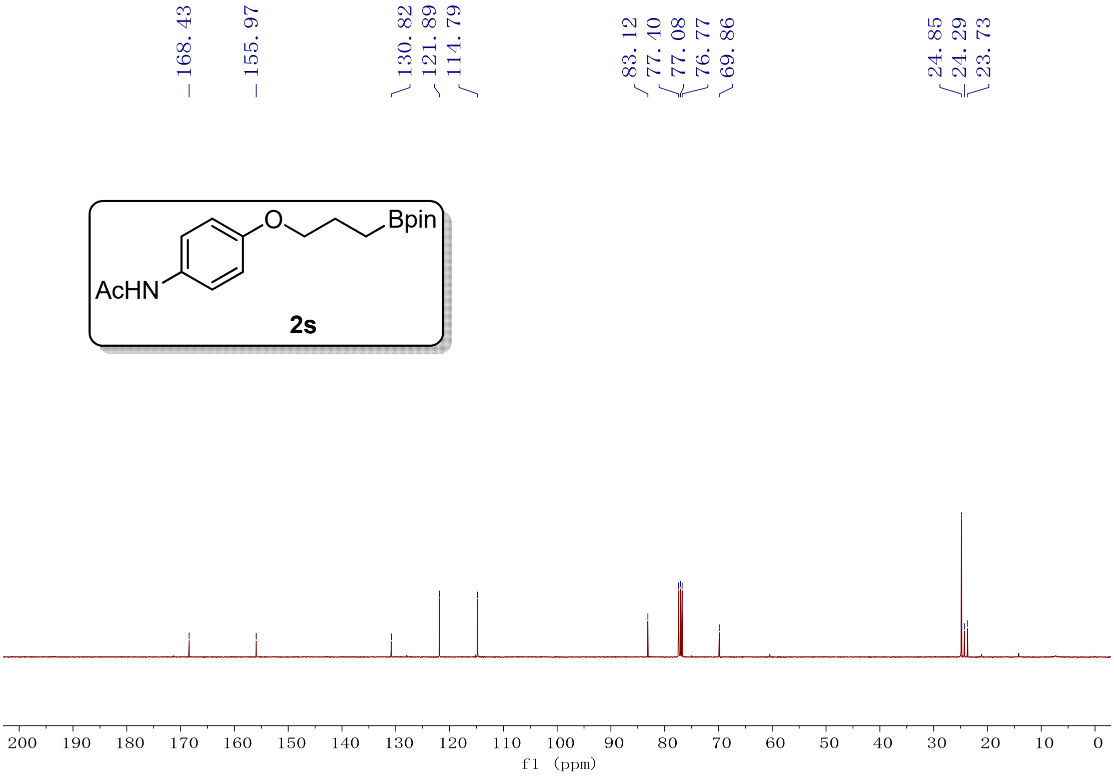


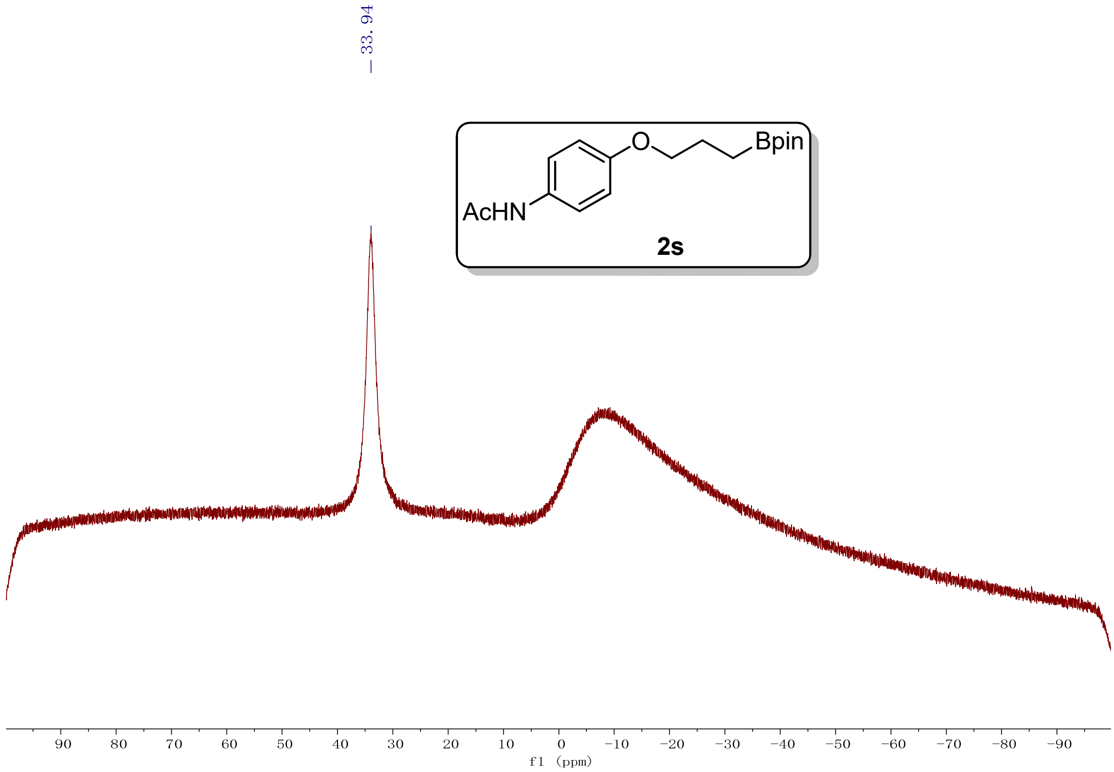
33.98
Bpin
MeOOC
2r
f1 (ppm)

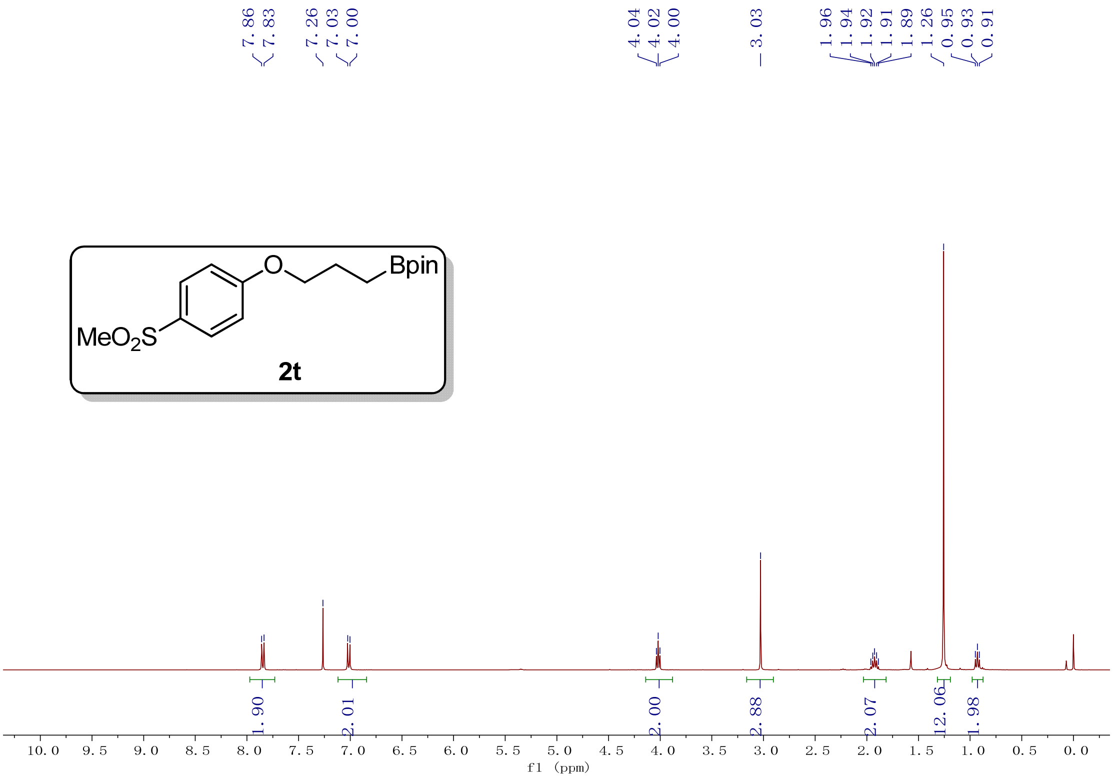


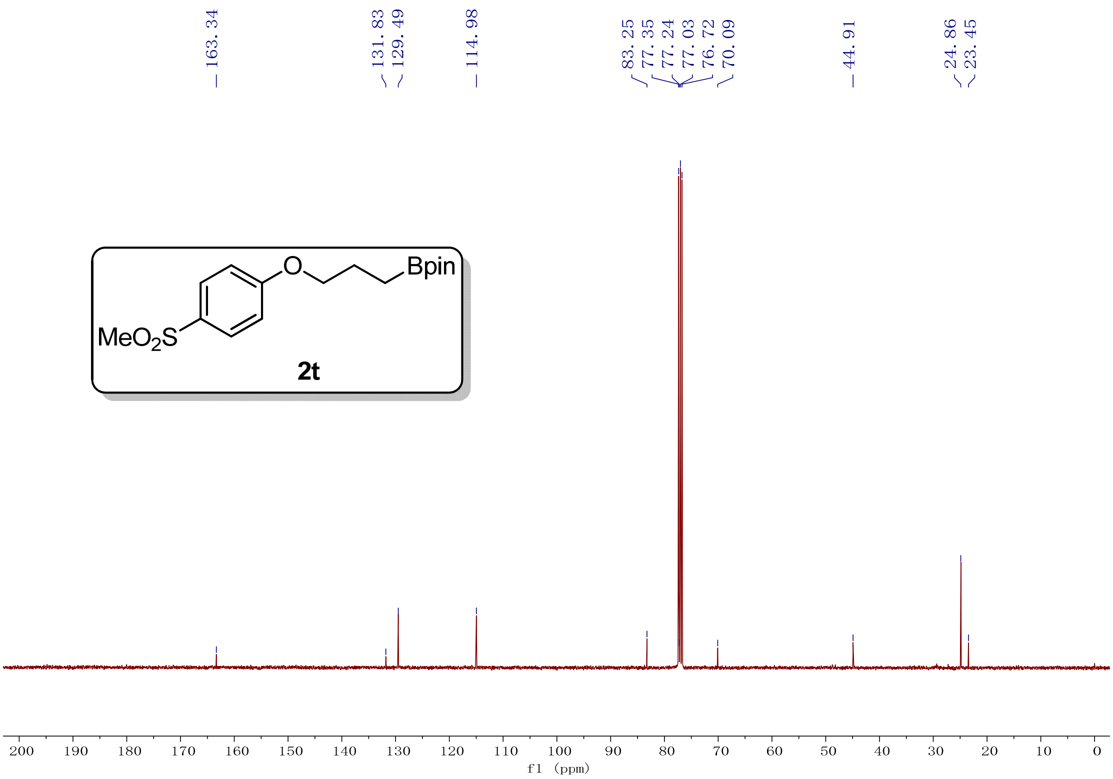
7.98
7.96
6.92
6.89
5.97
4.01
4.00
3.98
3.88
Bpin
MeOOC
2r
Crude product
C2H2Cl4 (65.9 mg) added
51.67
53.06
100.00
52.60
82.08
f1 (ppm)

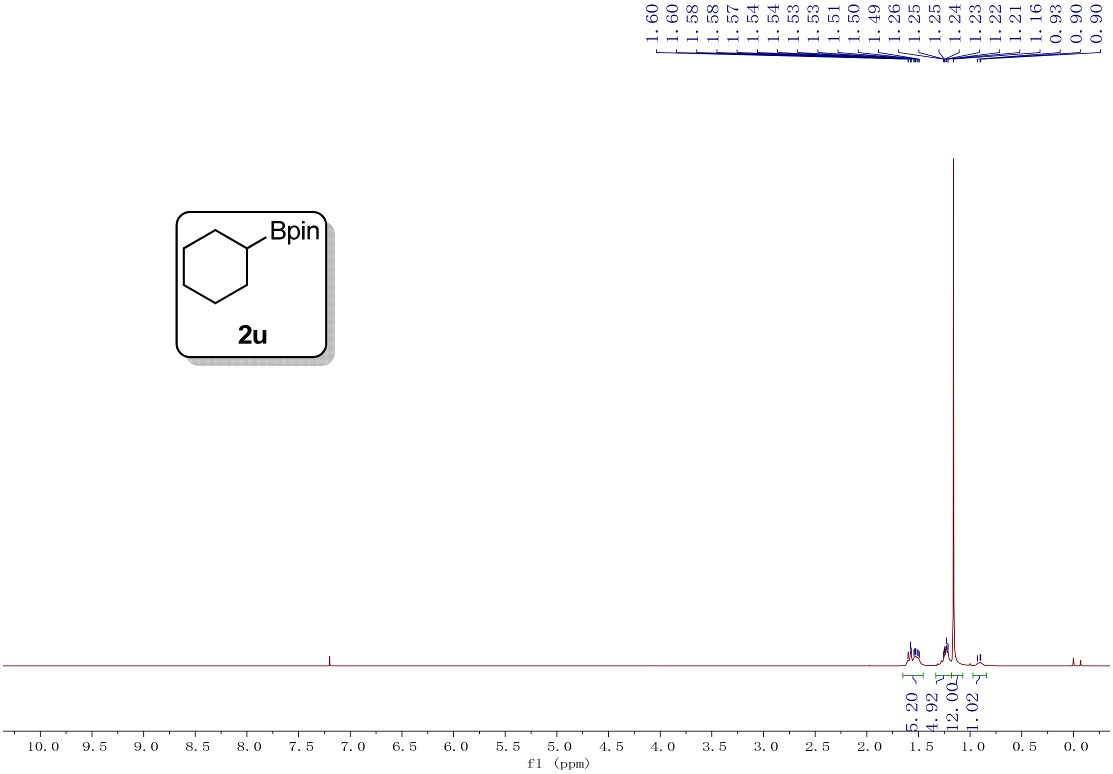

7.61
7.38
7.35
6.84
6.82
3.92
3.90
3.89
2.12
1.91
1.89
1.88
1.86
1.84
1.25
0.93
0.91
0.89
O
Bpin
AcHN
2s
0.92
1.97
2.01
1.99
2.81
2.00
12.76
2.11
f1 (ppm)


168.43
155.97
130.82
121.89
114.79
83.12
77.40
77.08
76.77
69.86
24.85
24.29
23.73
O
Bpin
AcHN
2s
f1 (ppm)

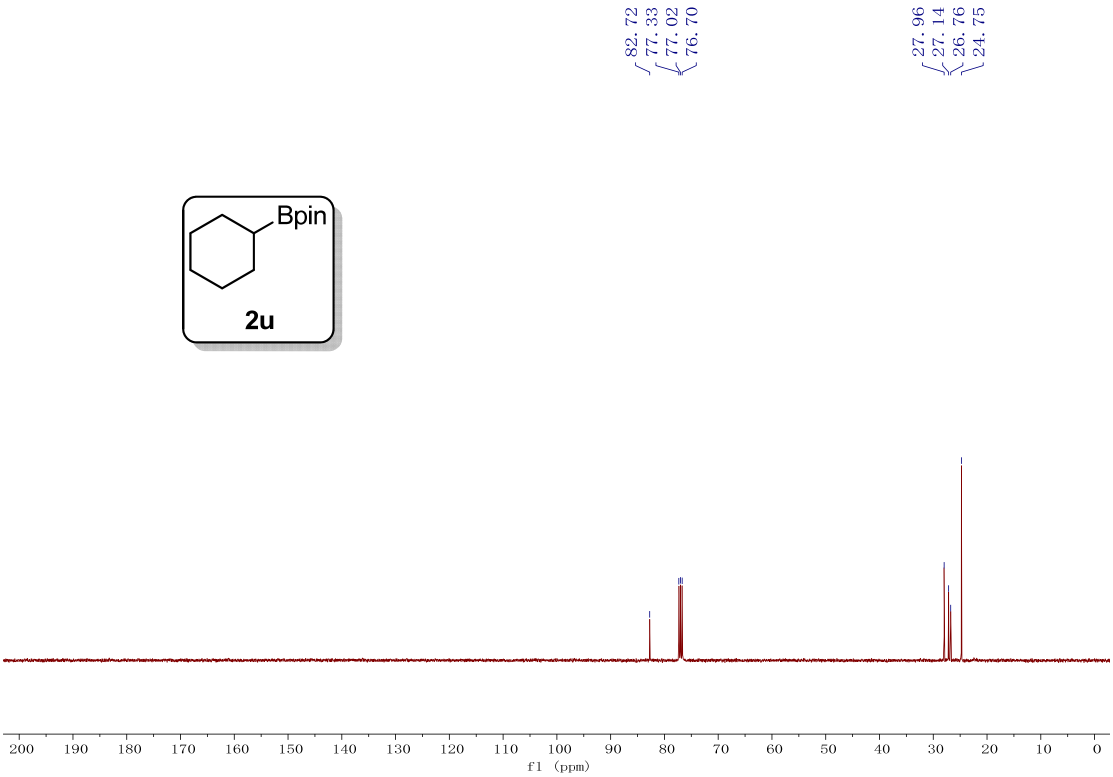

33.94
AcHN
O
Bpin
2s
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)


7.86
7.83
7.26
7.03
7.00
4.04
4.02
4.00
3.03
1.96
1.94
1.92
1.91
1.89
1.26
0.95
0.93
0.91
MeO2S
O
Bpin
2t
1.90
2.01
2.00
2.88
2.07
12.06
1.98
f1 (ppm)


163.34
131.83
129.49
114.98
83.25
77.35
77.24
77.03
76.72
70.09
44.91
24.86
23.45
MeO2S
O
Bpin
2t
f1 (ppm)

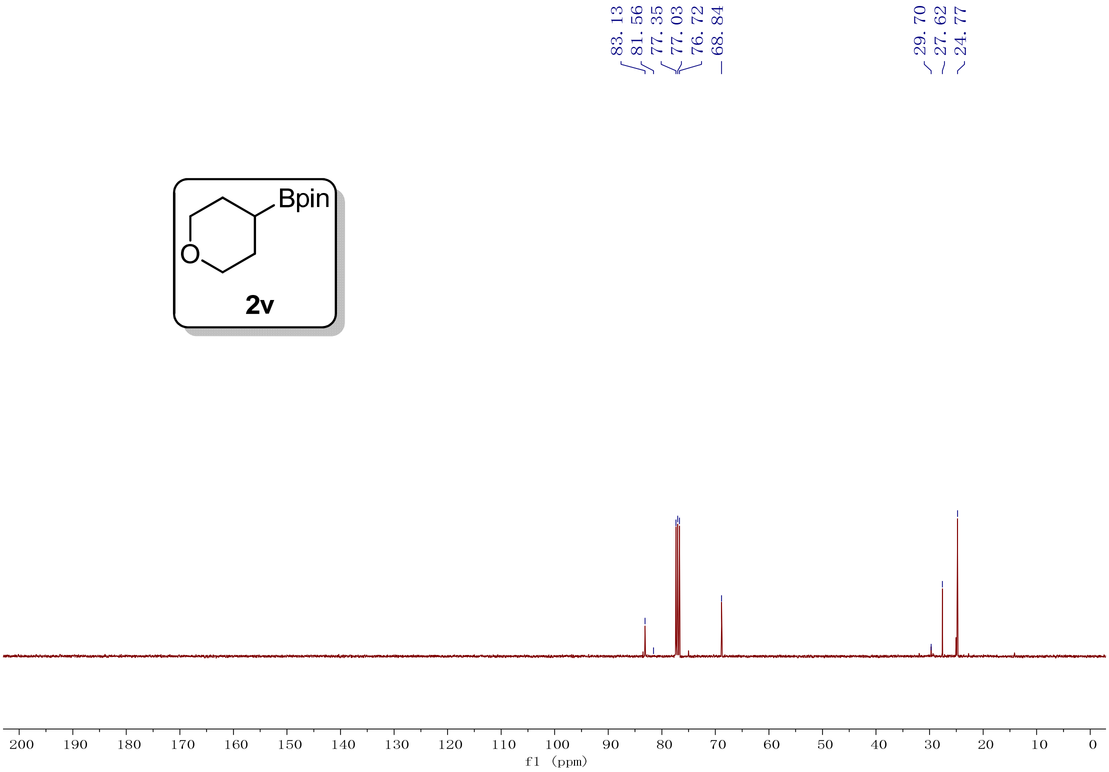


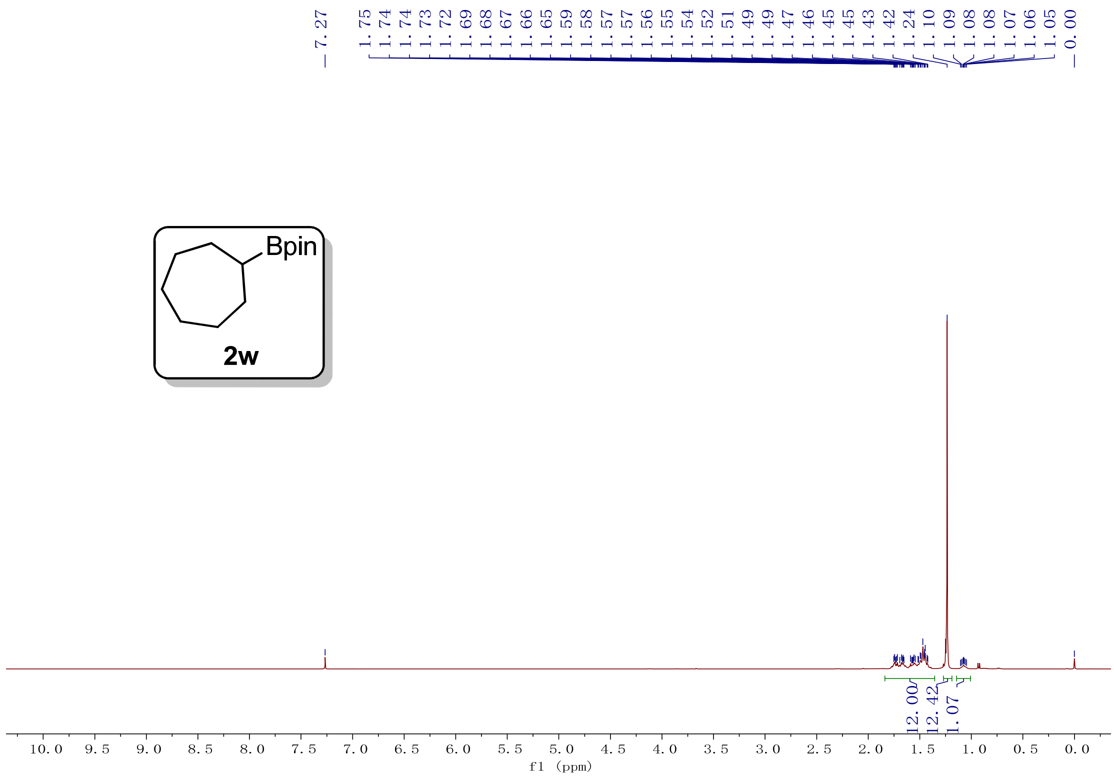
Bpin
2u
1.60 1.60 1.58 1.58 1.57 1.54 1.54 1.53 1.53 1.51 1.50 1.49 1.26 1.25 1.25 1.24 1.23 1.22 1.21 1.16 0.93 0.90 0.90
5.20 4.92 12.00 1.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

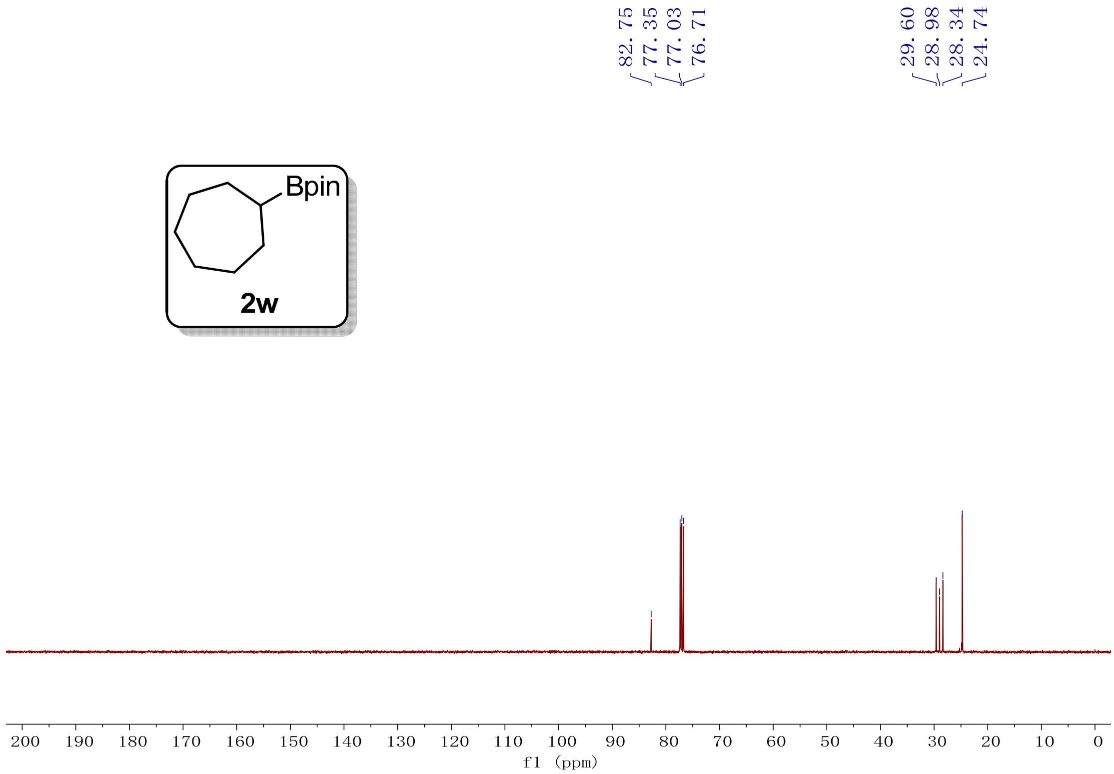


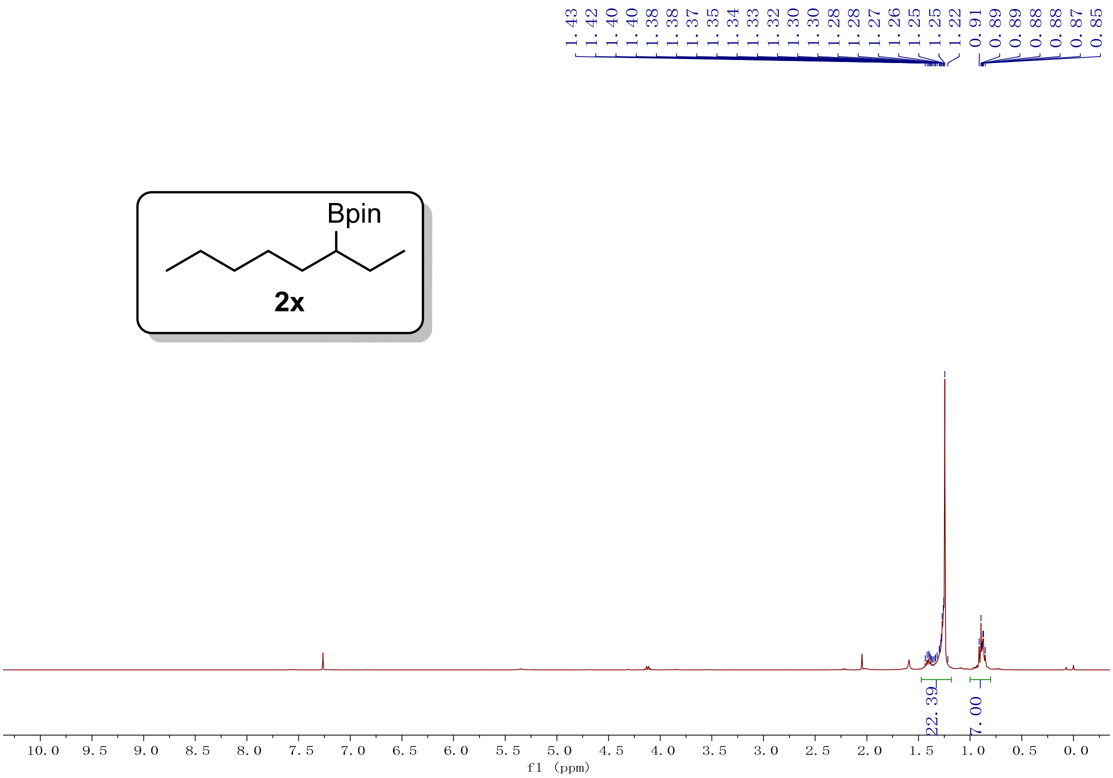
82.72 77.33 77.02 76.70
27.96 27.14 26.76 24.75
Bpin
2u
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

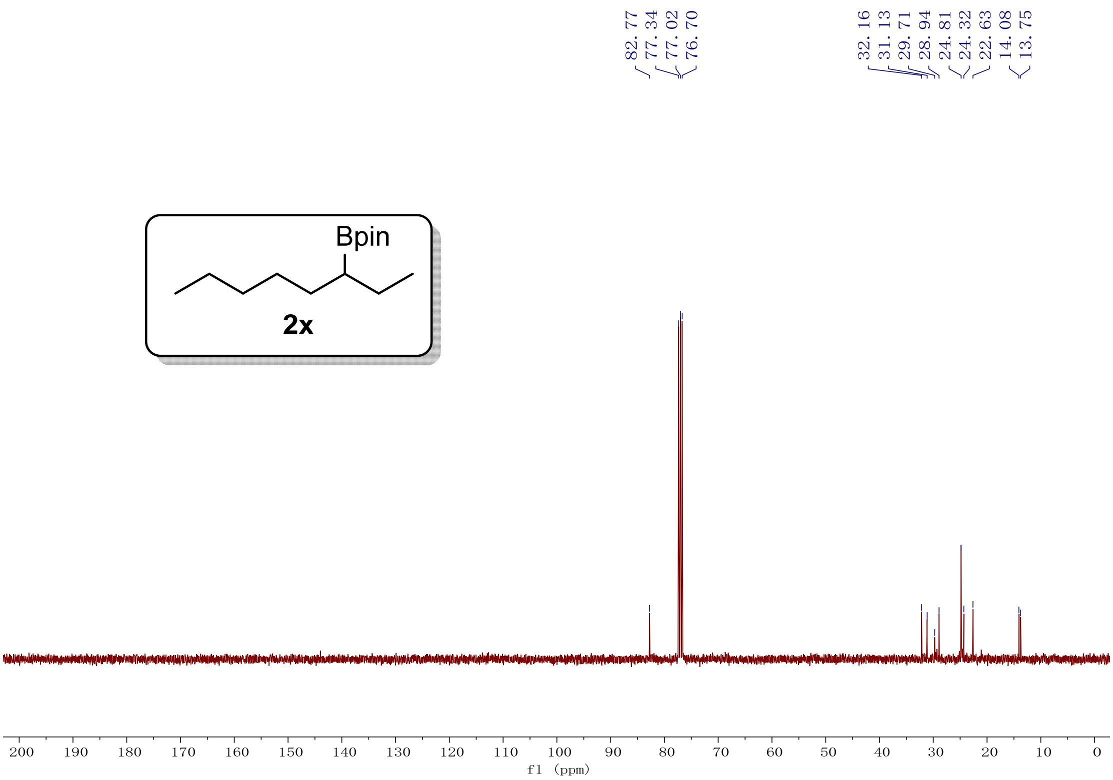

7.27
3.84
3.83
3.82
3.81
3.80
3.50
3.48
3.47
3.47
3.45
3.44
1.64
1.63
1.61
1.61
1.60
1.24
1.23
1.21
1.19
Bpin
O
2v
1.70
1.75
4.00
13.68
f1 (ppm)

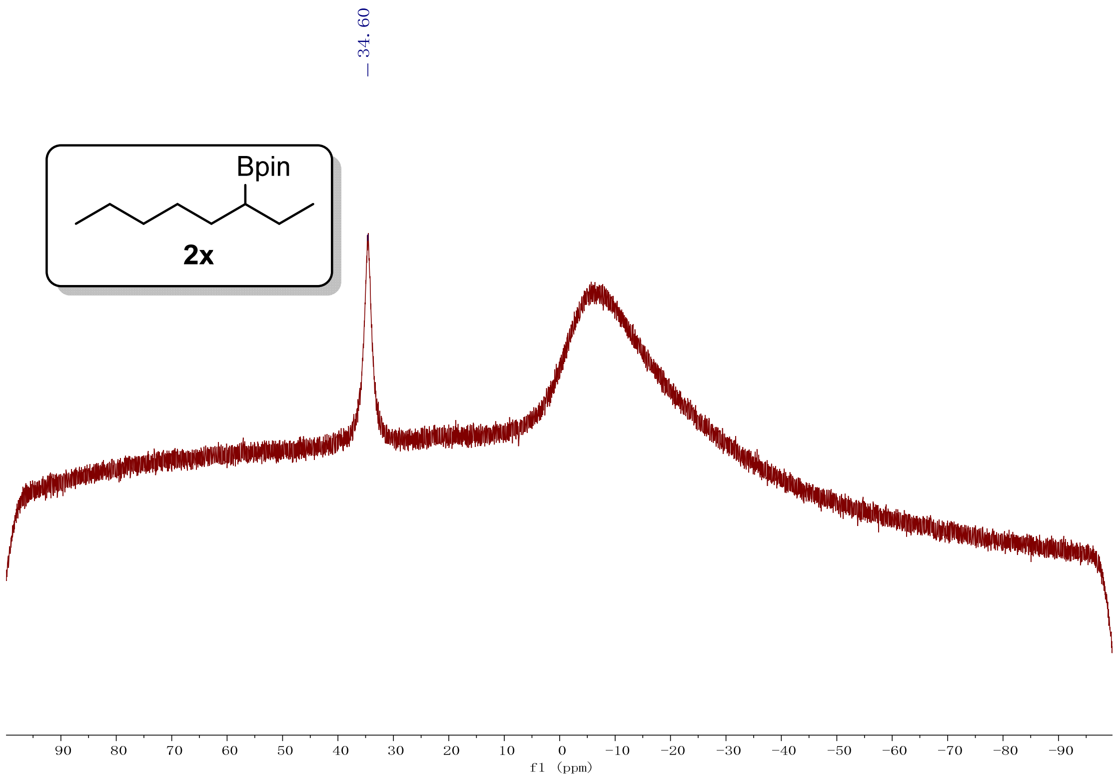

83.13
81.56
77.35
77.03
76.72
68.84
29.70
27.62
24.77
Bpin
O
2v
f1 (ppm)

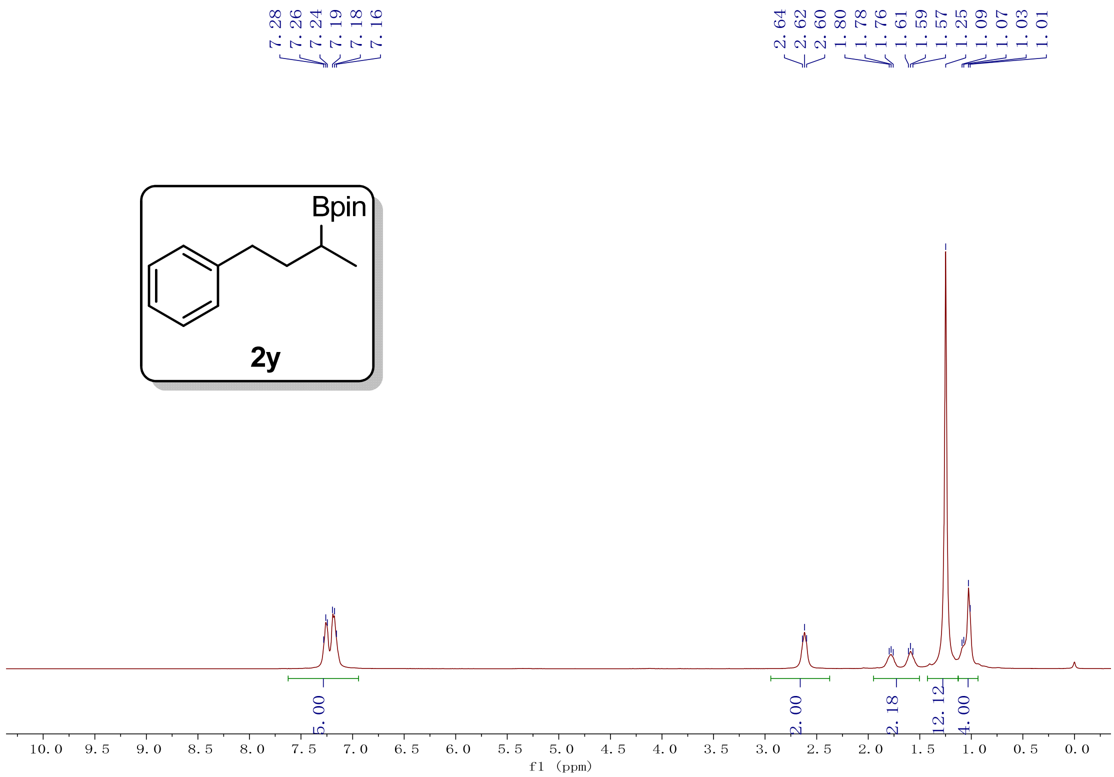

7.27
1.75 1.74 1.74 1.73 1.72 1.69 1.68 1.67 1.66 1.65 1.59 1.58 1.57 1.57 1.56 1.55 1.54 1.52 1.51 1.49 1.49 1.47 1.46 1.45 1.45 1.43 1.42 1.24 1.10 1.09 1.08 1.08 1.07 1.06 1.05
0.00
Bpin
2w
12.00
12.42
1.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

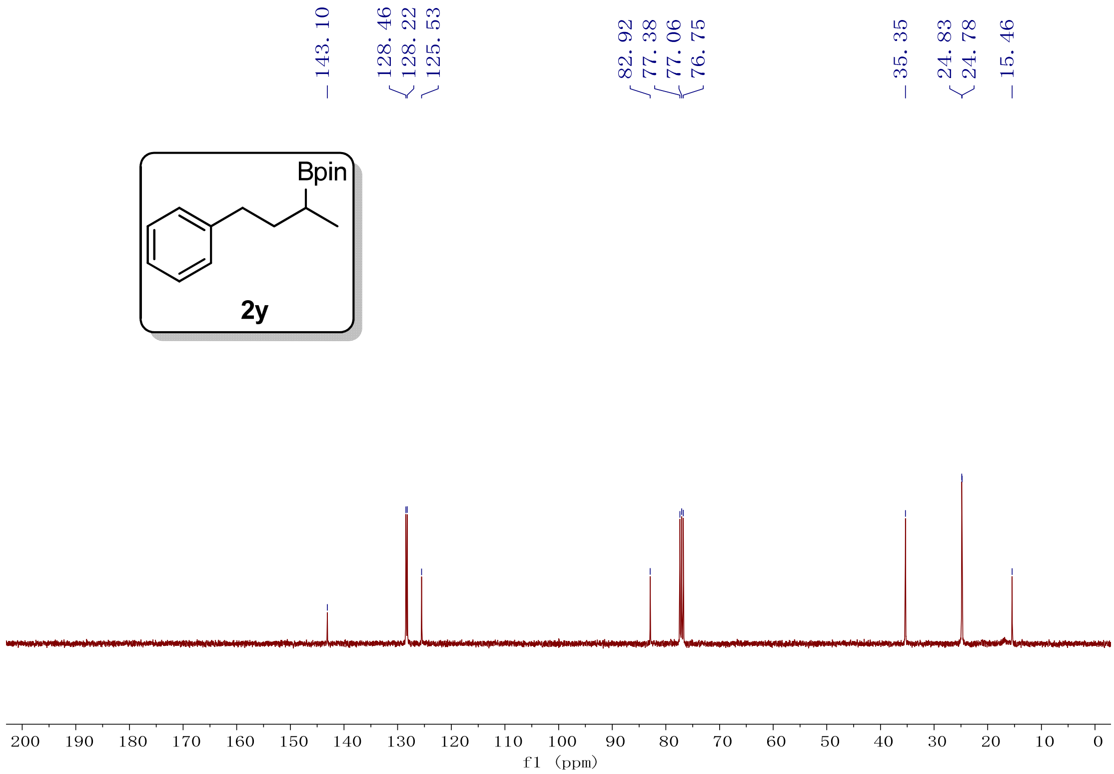

82.75
77.35
77.03
76.71
29.60
28.98
28.34
24.74
Bpin
2w
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

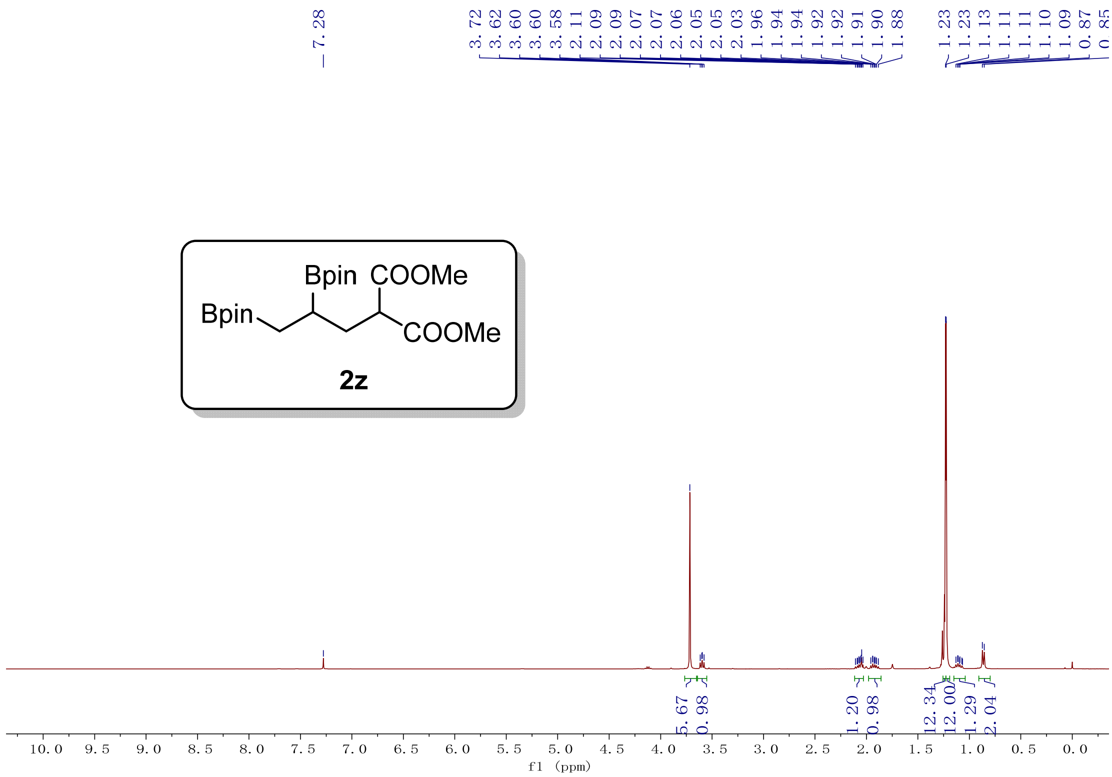

1.43
1.42
1.40
1.38
1.38
1.37
1.35
1.34
1.33
1.32
1.30
1.30
1.28
1.28
1.27
1.26
1.25
1.25
1.22
0.91
0.89
0.89
0.88
0.88
0.87
0.85
Bpin
2x
22.39
7.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

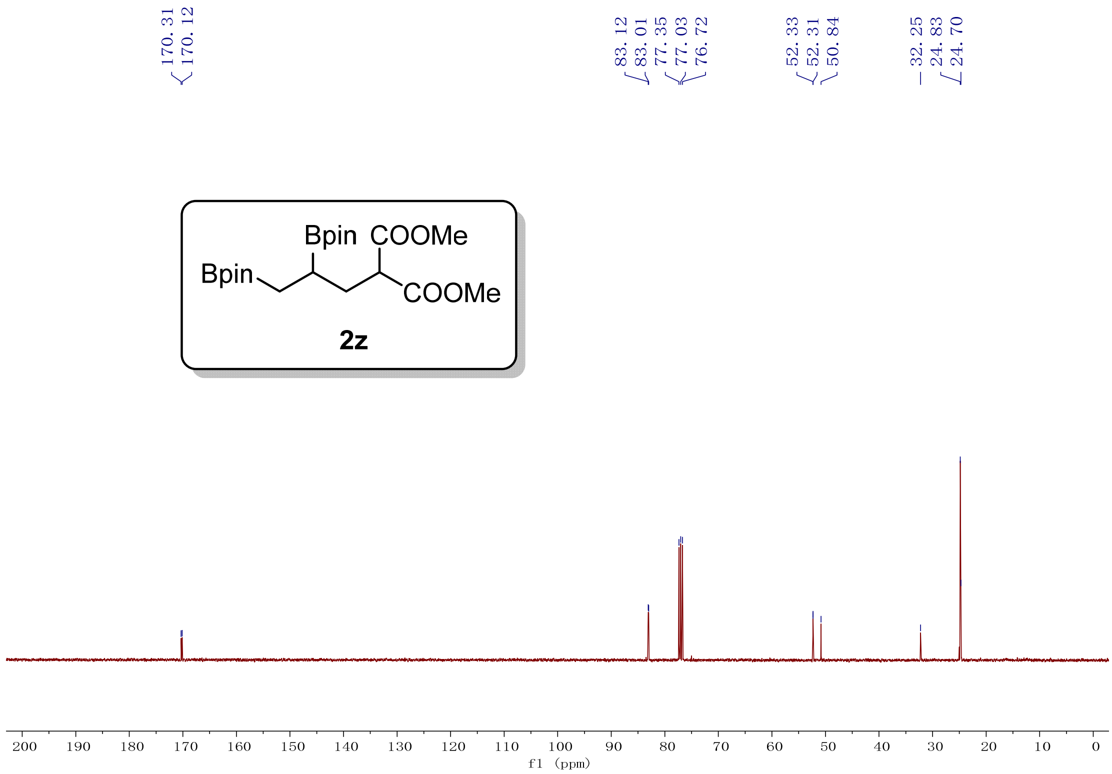

82.77
77.34
77.02
76.70
32.16
31.13
29.71
28.94
24.81
24.32
22.63
14.08
13.75
Bpin
2x
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

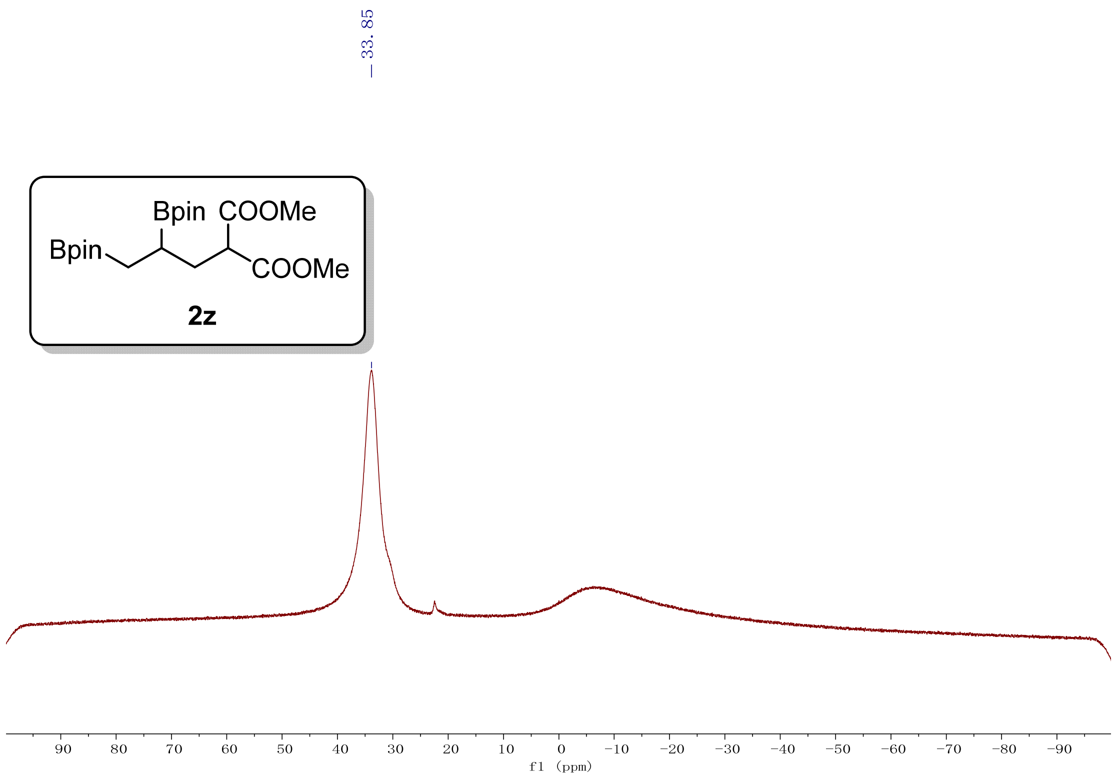

34.60
Bpin
2x
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)


7.28
7.26
7.24
7.19
7.18
7.16
2.64
2.62
2.60
1.80
1.78
1.76
1.61
1.59
1.57
1.25
1.09
1.07
1.03
1.01
Bpin
2y
5.00
2.00
2.18
12.12
4.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

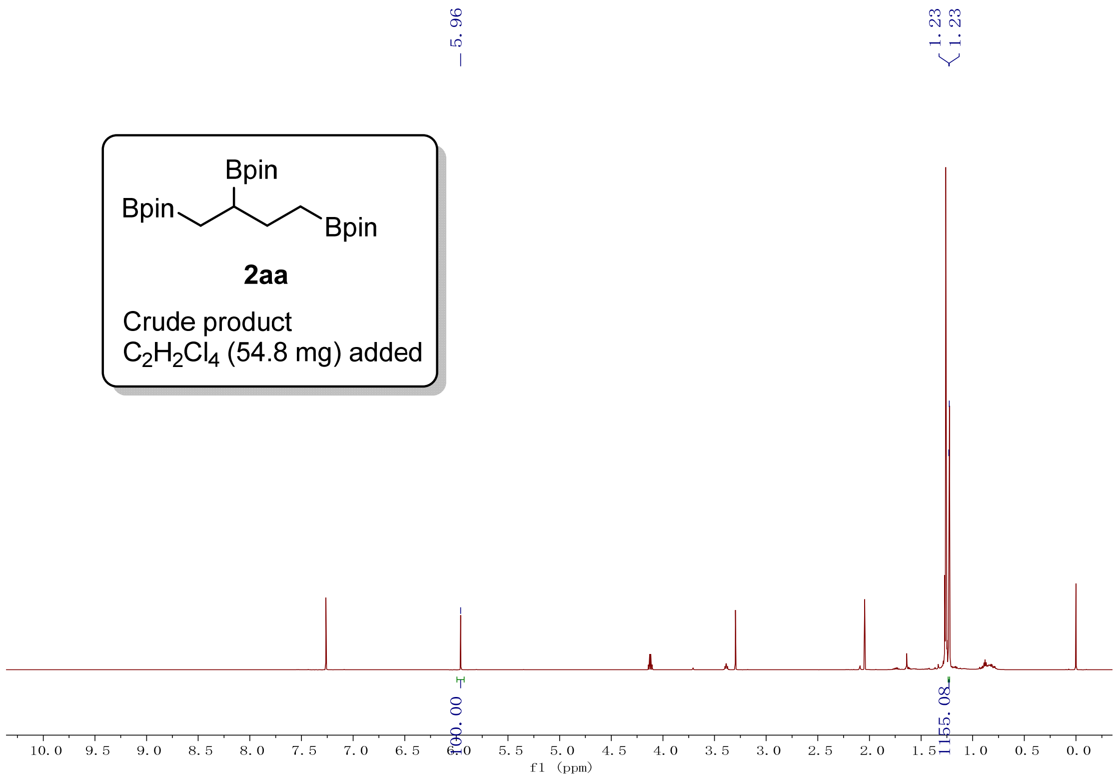

143.10
128.46
128.22
125.53
82.92
77.38
77.06
76.75
35.35
24.83
24.78
15.46
Bpin
2y
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.28
3.72 3.62 3.60 3.60 3.58 2.11 2.09 2.09 2.07 2.07 2.06 2.05 2.05 2.03 1.96 1.94 1.94 1.92 1.92 1.91 1.90 1.88
1.23 1.23 1.13 1.11 1.11 1.10 1.09 0.87 0.85
Bpin
Bpin
COOMe
COOMe
2z
5.67
0.98
1.20
0.98
12.34
12.00
1.29
2.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


170.31 170.12
83.12 83.01 77.35 77.03 76.72
52.33 52.31 50.84
32.25 24.83 24.70
Bpin
Bpin
COOMe
COOMe
2z
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



— 33.85
Bpin
Bpin
COOMe
COOMe
2z
90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90
f1 (ppm)



5.96
1.23
1.23
Bpin
Bpin
Bpin
2aa
Crude product
$C_2H_2Cl_4$ (54.8 mg) added
100.00
1155.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

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