Supporting Information

Nickel-Catalyzed Three-Component Olefin Reductive Dicarbofunctionalization to Access Alkylborates

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1. General Information

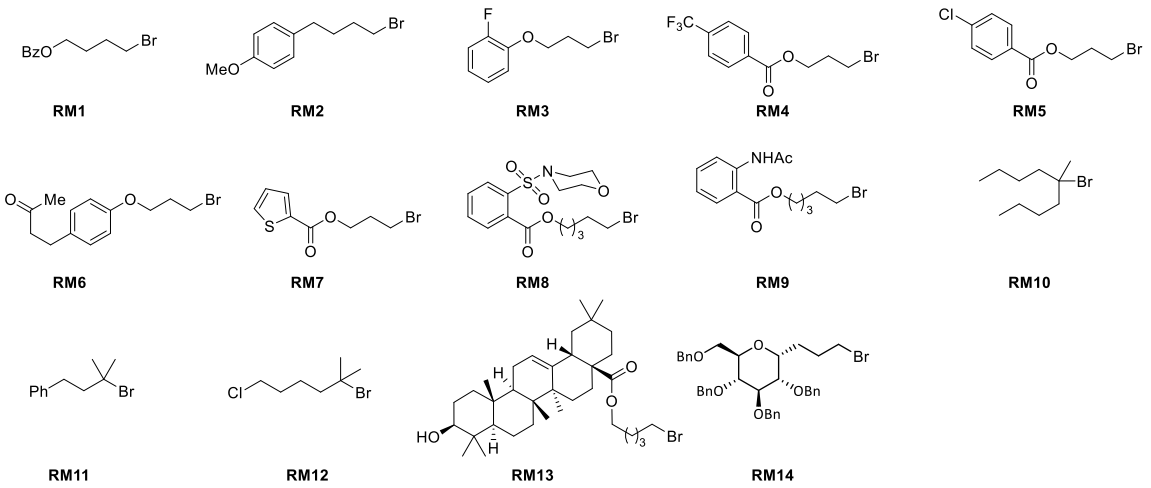
1.1. Materials

All the reactions were carried out in oven-dried Schlenk tubes under an argon atmosphere (purity ≥ 99.999%). The following chemicals were purchased and used as received: nickel(II) bromide 2-methoxyethyl ether complex (CAS: 312696-09-6, Aldrich); Manganese powder, 99.3% (metals basis) (CAS: 7439-96-5, Alfa Aesar); *N*,*N*-Dimethylethanamide (CAS: 217-19-5, Adamas-beta,); 4,4,5,5-tetramethyl-2-vinyl-1,3,2-dioxaborolane (CAS:75927-49-0, Accela); 2-bromo-2-methylpropane (CAS: 507-19-7, Energy Chemical); sodium iodide (CAS: 7681-82-5, Aladdin). Other commercially available reagents were obtained from Adamas-beta, TCI and Alfa Aesar Chemical Company.

1.2 Analytical Methods

^{1}H NMR, ^{13}C NMR, ^{11}B NMR and ^{19}F NMR spectra were recorded on a Bruker 400 MHz and 500 MHz spectrometer at 295 K in $CDCl_3$ unless otherwise noted. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity, integration, and coupling constant (Hz). Data for ^{13}C NMR were reported as follows: chemical shift (δ ppm), multiplicity, and coupling constant (Hz). Data for ^{11}B NMR were reported as follows: chemical shift (δ ppm), coupling constant (Hz). Chemical shifts were reported using the residual solvent $CHCl_3$ as the internal reference for ^{1}H NMR (δ = 7.260 ppm) and $CDCl_3$ peak as the internal reference for ^{13}C NMR (δ = 77.160 ppm). Gas chromatographic (GC) analysis was acquired on a Shimadzu GC-2014 Series GC System equipped with a flame-ionization detector. HRMS analysis was performed on Finnigan LCQ advantage Max Series MS System and Water XEVO G2 Q-TOF (Waters Corporation). Thin-layer chromatography was performed with silica gel 60 F254 plates eluting with solvents indicated, visualized by a 254 nm UV lamp Flash chromatography was performed using silica 60 (230-400 mesh).

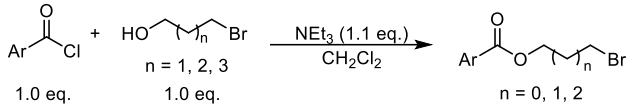
2. Preparation of Substrates



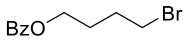
List of Alkyl Bromides

2.1. Preparation of Primary Alkyl Bromides

Procedure A:



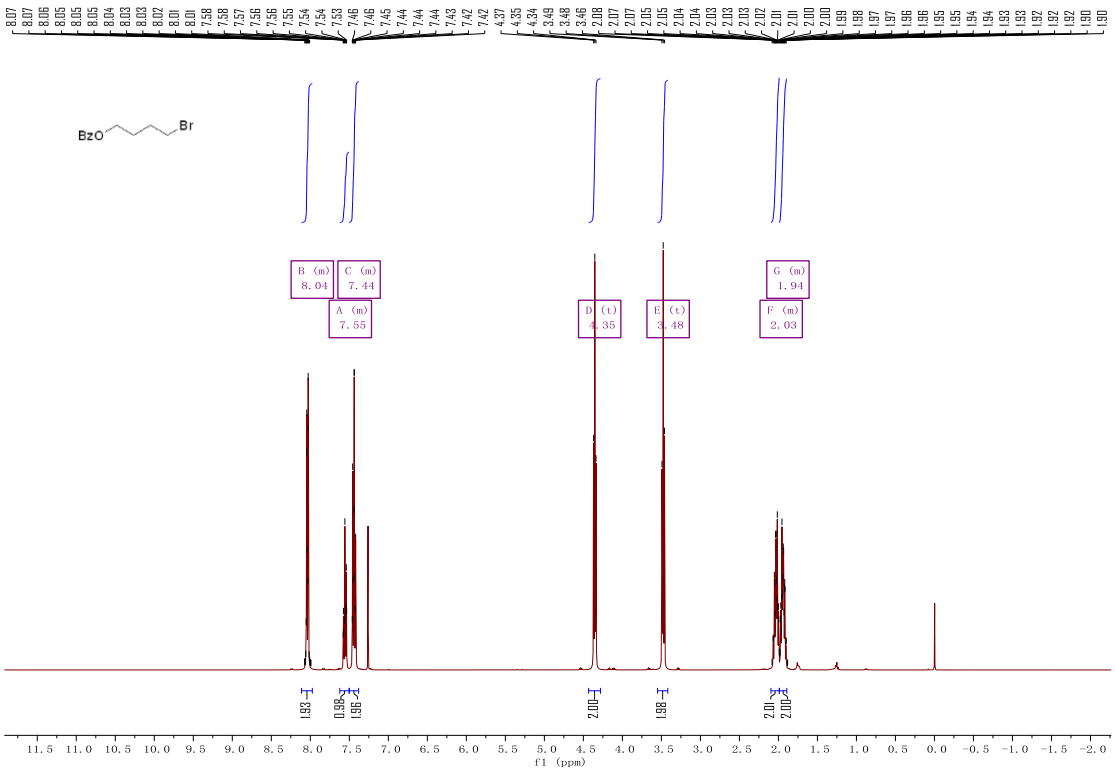
According to the reported literature,[1] primary alkyl bromides were conveniently synthesized under slightly modified reaction conditions.



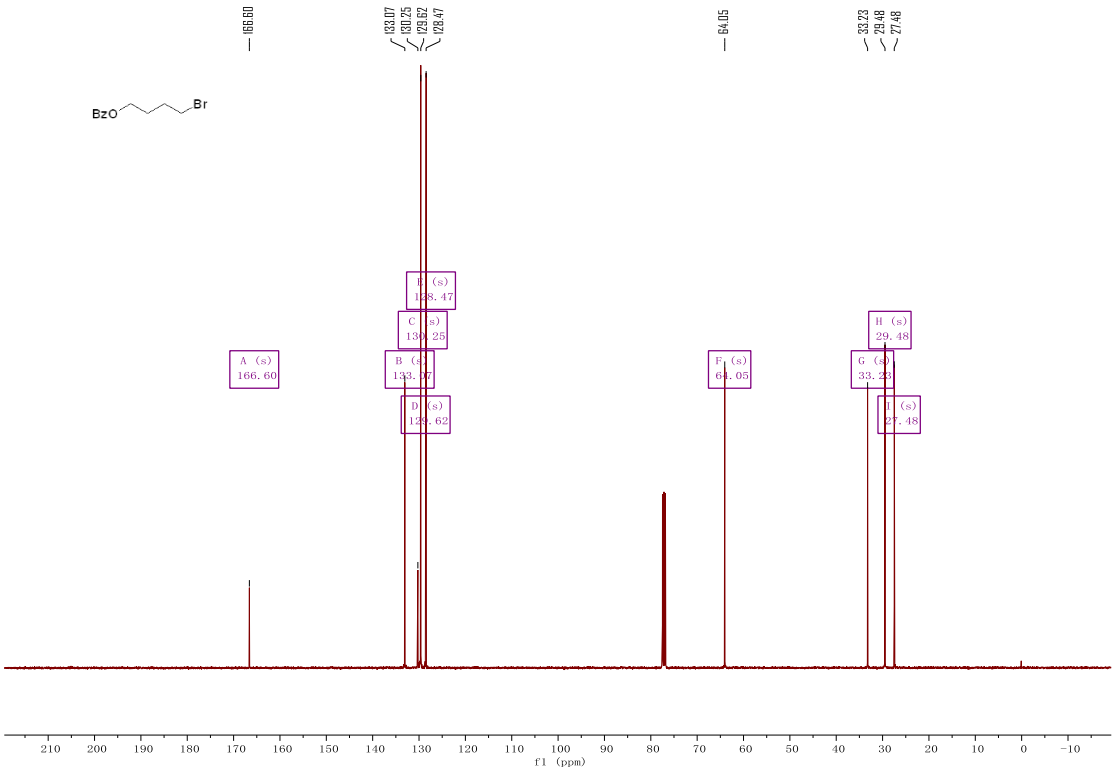
4-bromobutyl benzoate (**RM1**)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 – 7.95 (m, 2H), 7.60 – 7.50 (m, 1H), 7.49 – 7.35 (m, 2H), 4.35 (t, *J* = 6.2 Hz, 2H), 3.48 (t, *J* = 6.5 Hz, 2H), 2.10 – 1.97 (m, 2H), 1.98 – 1.88 (m, 2H).

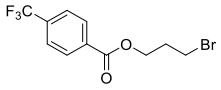
^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.60, 133.07, 130.25, 129.62, 128.47, 64.05, 33.23, 29.48, 27.48.



^{1}H NMR spectra for **RM1**



^{13}C NMR spectra for **RM1**

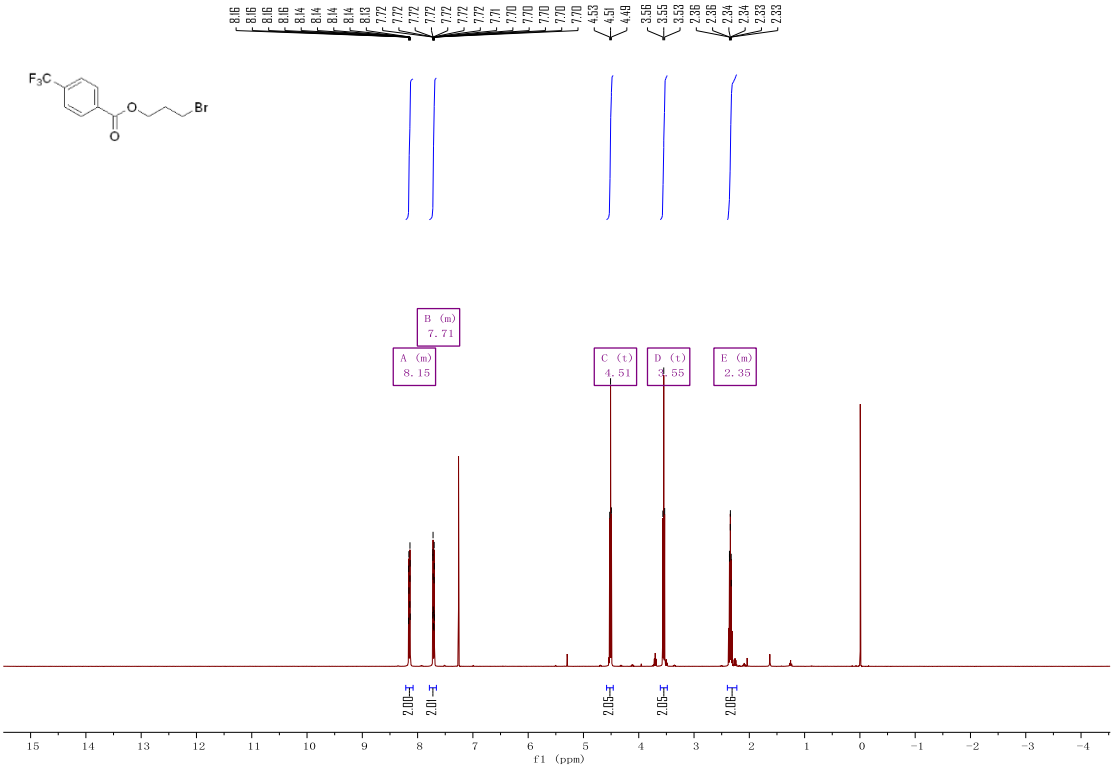


3-bromopropyl 4-(trifluoromethyl)benzoate (**RM4**)

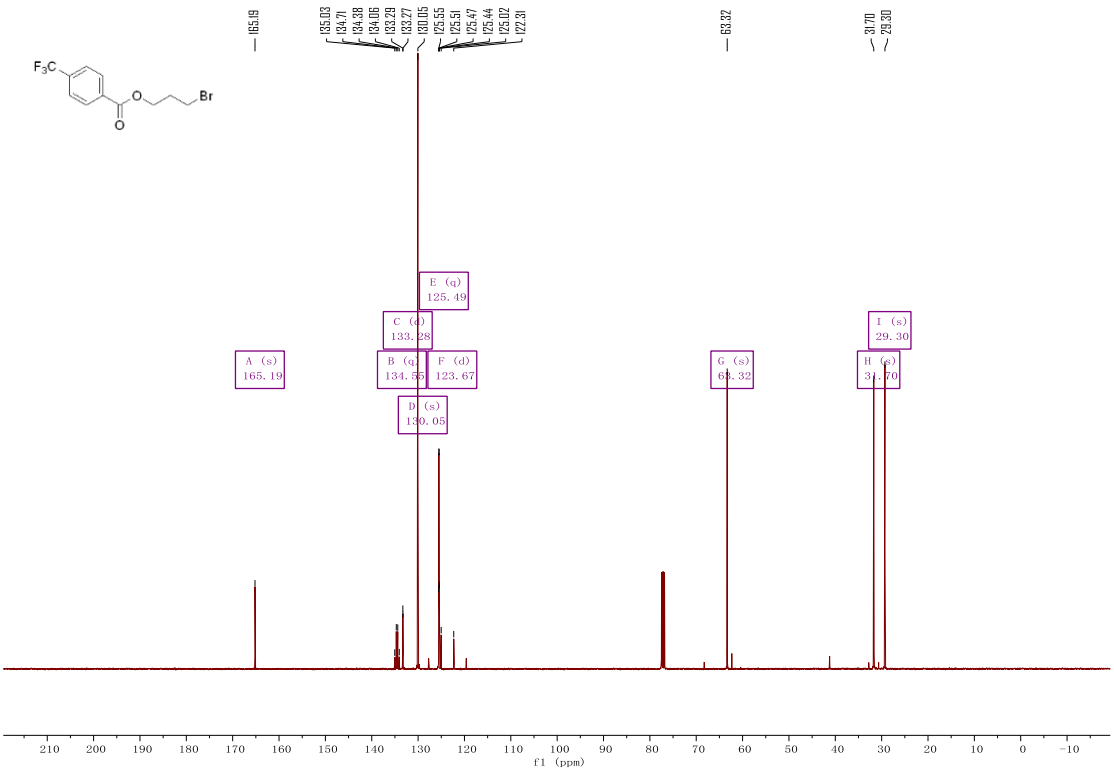
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.29 – 8.00 (m, 2H), 7.84 – 7.63 (m, 2H), 4.51 (t, *J* = 6.1 Hz, 2H), 3.55 (t, *J* = 6.5 Hz, 2H), 2.61 – 1.81 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.19, 134.55 (q, *J* = 32.7 Hz), 133.28 (d, *J* = 1.5 Hz), 130.05, 125.49 (q, *J* = 3.8 Hz), 123.67 (d, *J* = 272.7 Hz), 63.32, 31.70, 29.30.

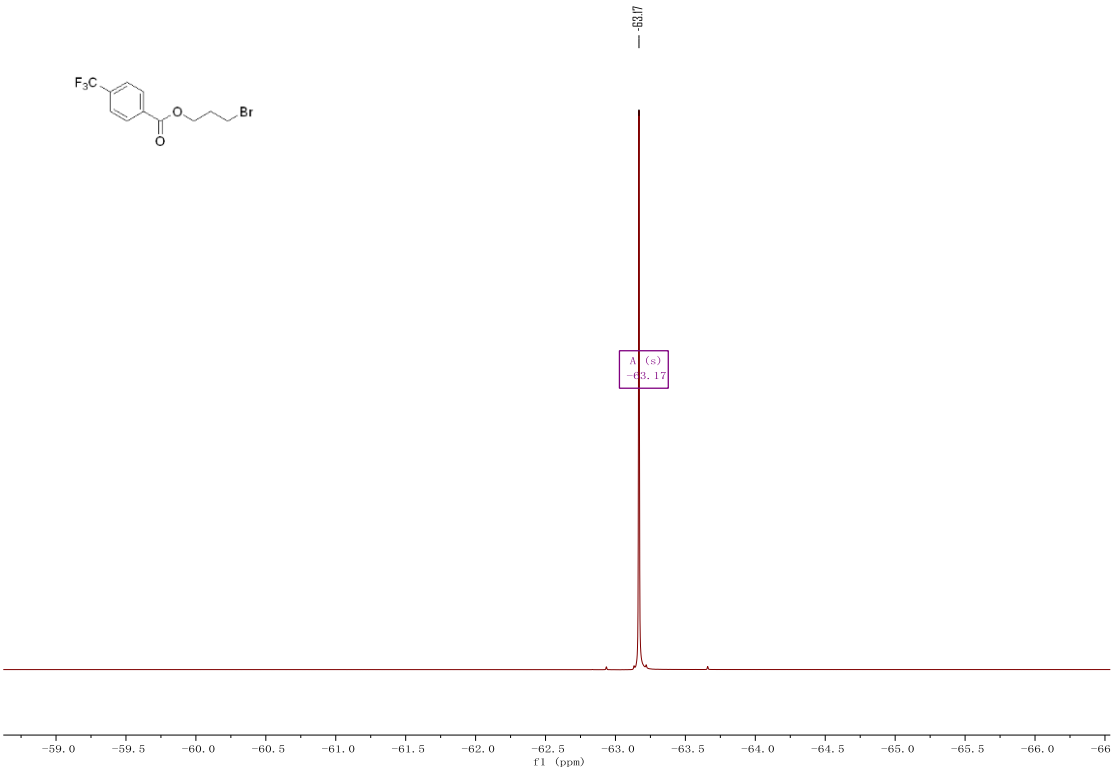
^{19}F NMR (376 MHz, Chloroform-*d*) δ -63.17.



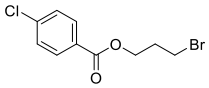
^{1}H NMR spectra for **RM4**



^{13}C NMR spectra for **RM4**



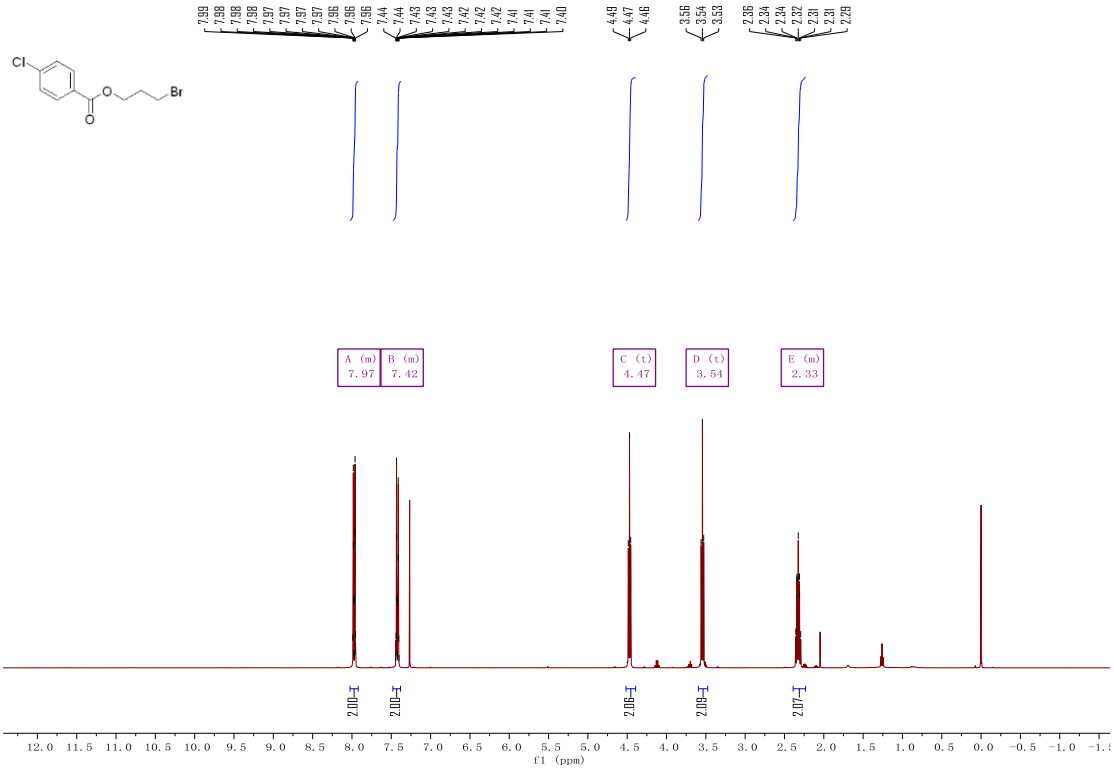
^{19}F NMR spectra for **RM4**



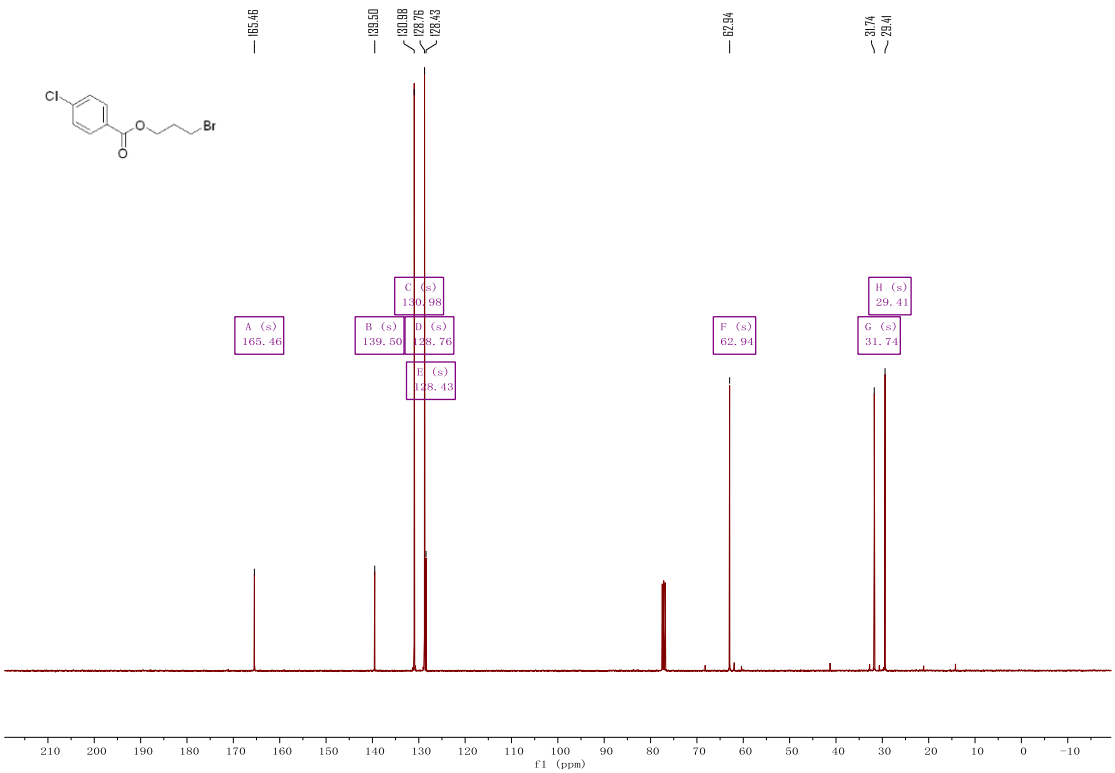
3-bromopropyl 4-chlorobenzoate (**RM5**)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 – 7.90 (m, 2H), 7.48 – 7.38 (m, 2H), 4.47 (t, *J* = 6.1 Hz, 2H), 3.54 (t, *J* = 6.5 Hz, 2H), 2.69 – 2.18 (m, 2H).

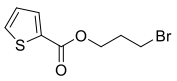
^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.46, 139.50, 130.98, 128.76, 128.43, 62.94, 31.74, 29.41.



^{1}H NMR spectra for **RM5**



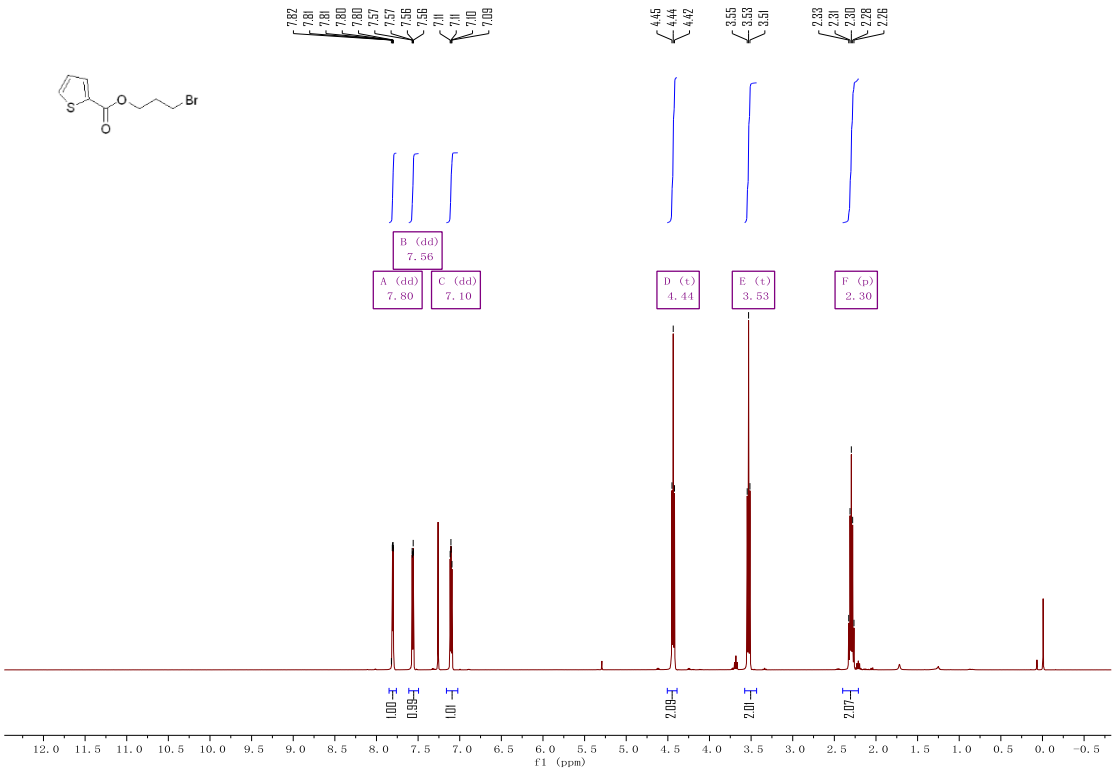
^{13}C NMR spectra for **RM5**



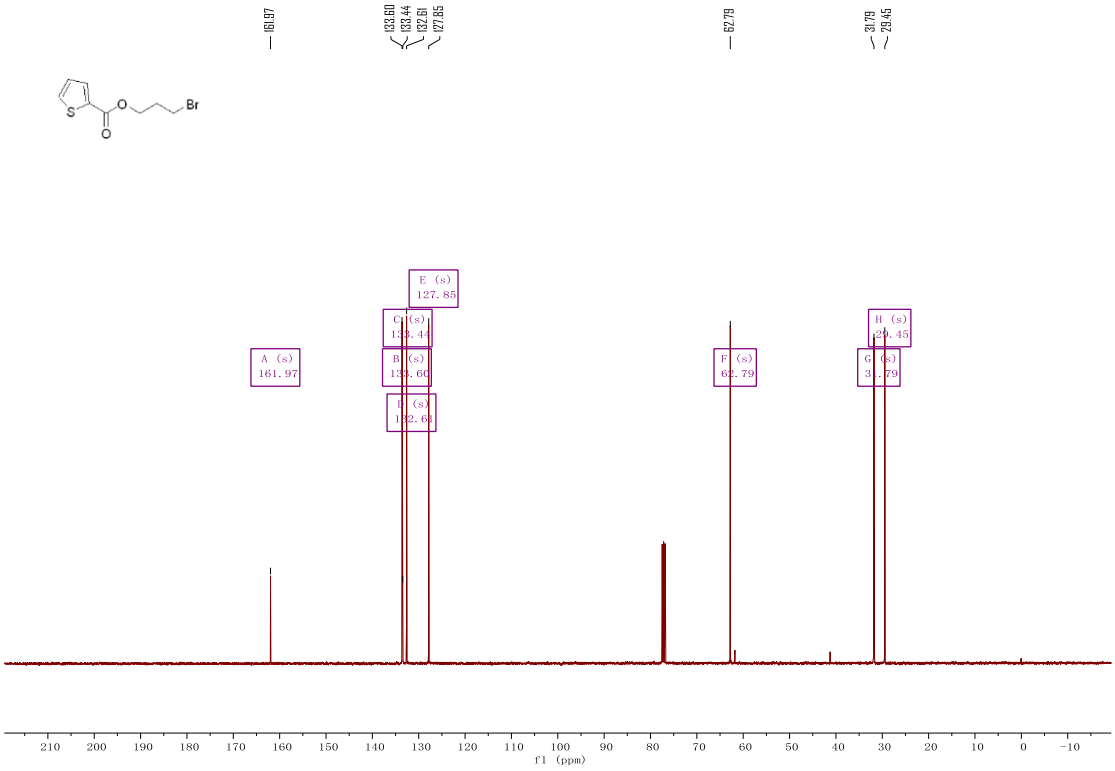
3-bromopropyl thiophene-2-carboxylate (**RM7**)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (dd, *J* = 3.7, 1.3 Hz, 1H), 7.56 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.10 (dd, *J* = 5.0, 3.7 Hz, 1H), 4.44 (t, *J* = 6.0 Hz, 2H), 3.53 (t, *J* = 6.5 Hz, 2H), 2.30 (p, *J* = 6.3 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.97, 133.60, 133.44, 132.61, 127.85, 62.79, 31.79, 29.45.

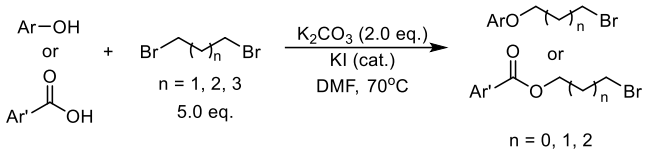


^{1}H NMR spectra for **RM7**

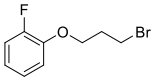


^{13}C NMR spectra for **RM7**

Procedure B:



To a stirred suspension of selective Phenol or Benzoic acid (10 mmol) in DMF, K_2CO_3 (20 mmol) and KI (1 mmol) were added at room temperature. The reaction was stirred for additional 0.5 hours at room temperature, dibromoalkanes (50 mmol) were added. The mixture was stirred at 70 ℃ for 5-10 h, the mixture was extracted with ethyl acetate, washed with saturated NaCl solution, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The resulting mixture was isolated by flash chromatography or recrystallization.

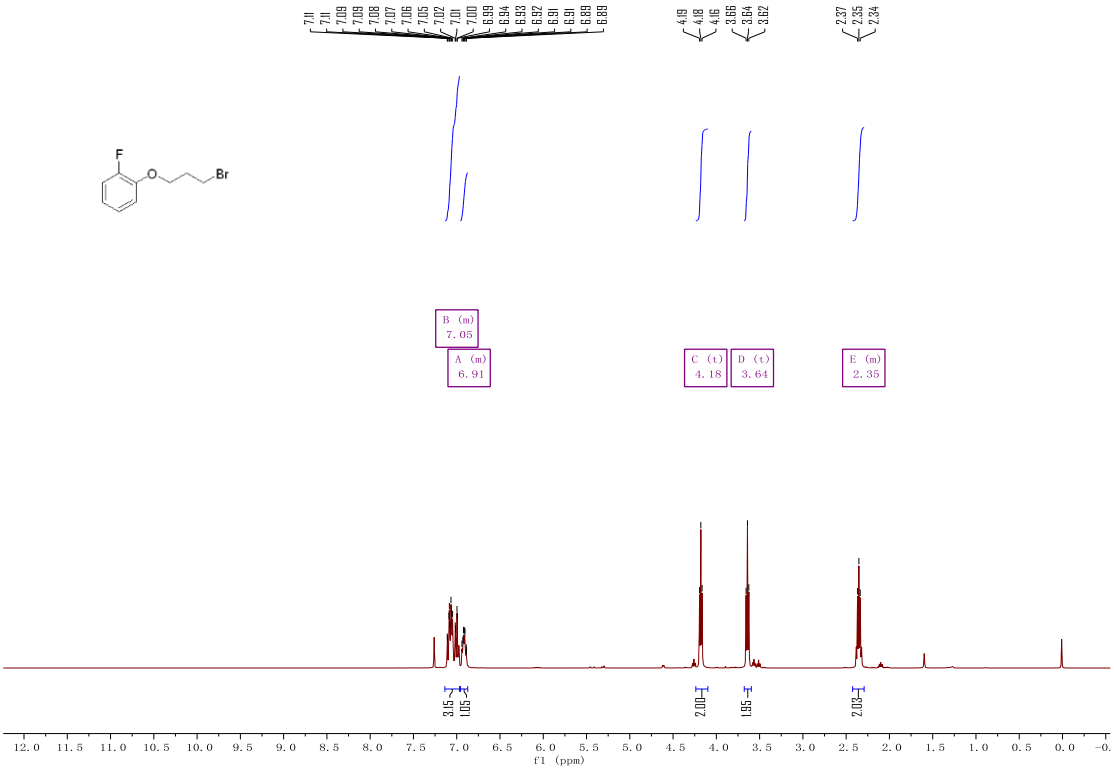


1-(3-bromopropoxy)-2-fluorobenzene (**RM3**)

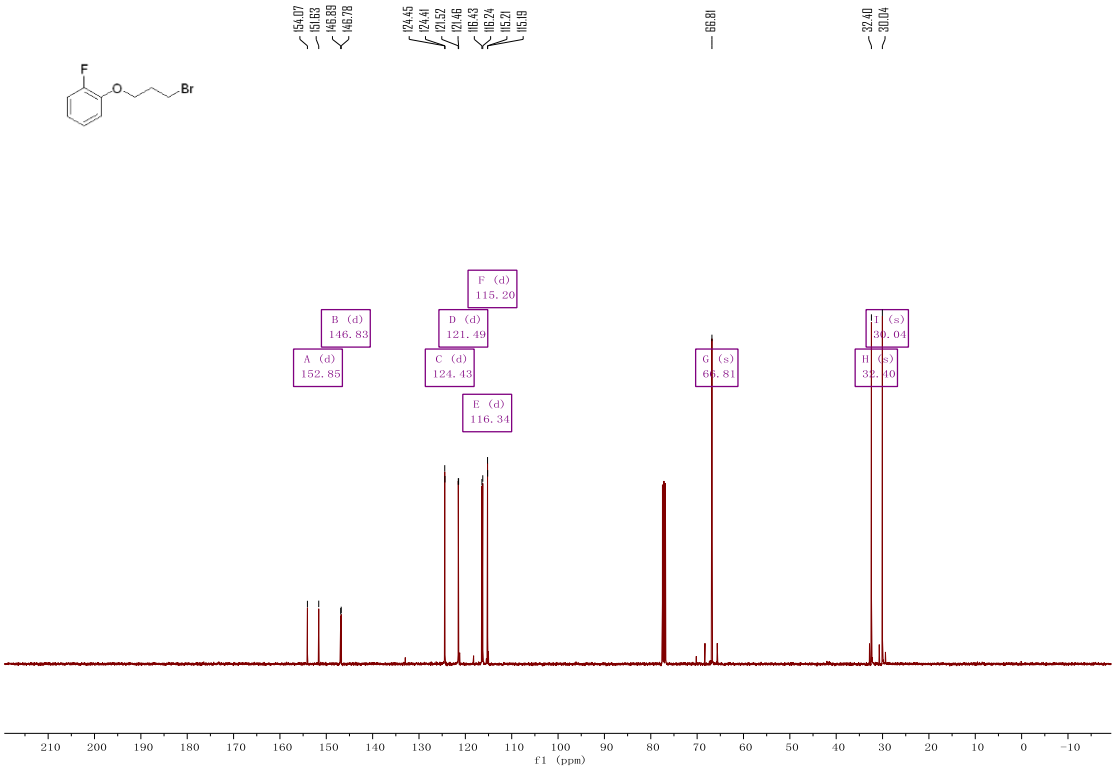
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.14 – 6.98 (m, 3H), 6.96 – 6.85 (m, 1H), 4.18 (t, *J* = 5.8 Hz, 2H), 3.64 (t, *J* = 6.4 Hz, 2H), 2.50 – 2.13 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.85 (d, *J* = 245.4 Hz), 146.83 (d, *J* = 10.6 Hz), 124.43 (d, *J* = 4.0 Hz), 121.49 (d, *J* = 6.8 Hz), 116.34 (d, *J* = 18.3 Hz), 115.20 (d, *J* = 1.8 Hz), 66.81, 32.40, 30.04.

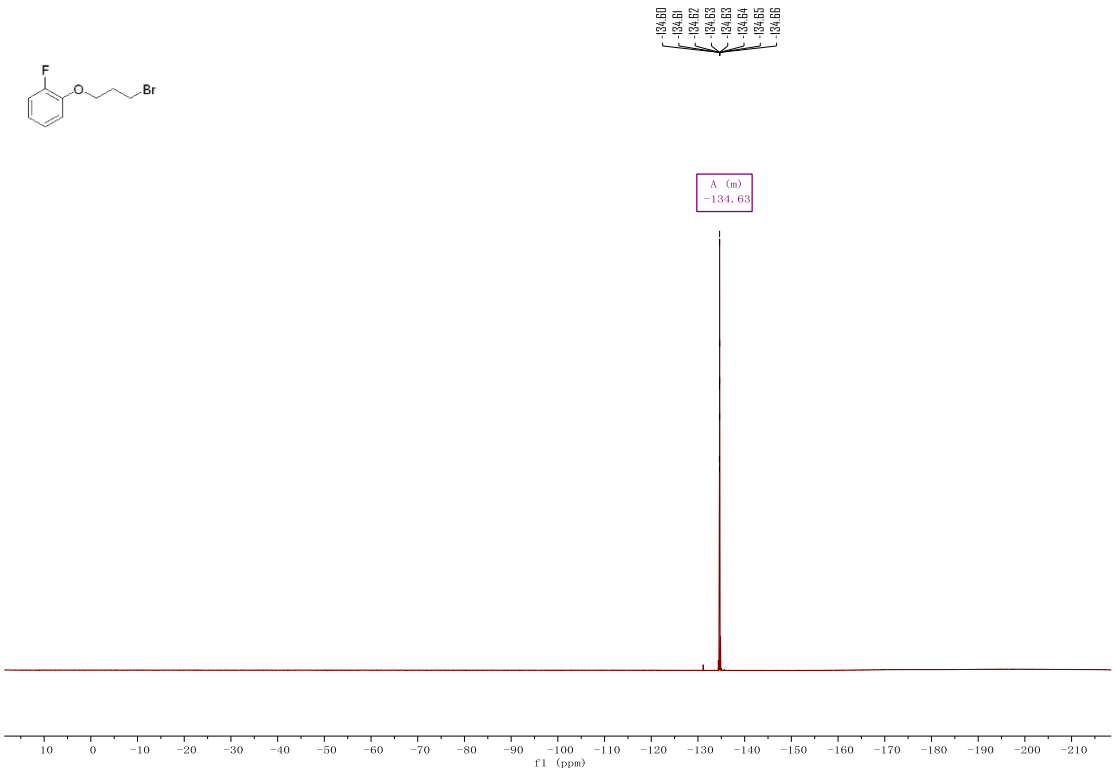
^{19}F NMR (376 MHz, Chloroform-*d*) δ -134.42 – -135.07 (m).



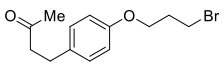
^{1}H NMR spectra for **RM3**



^{13}C NMR spectra for **RM3**



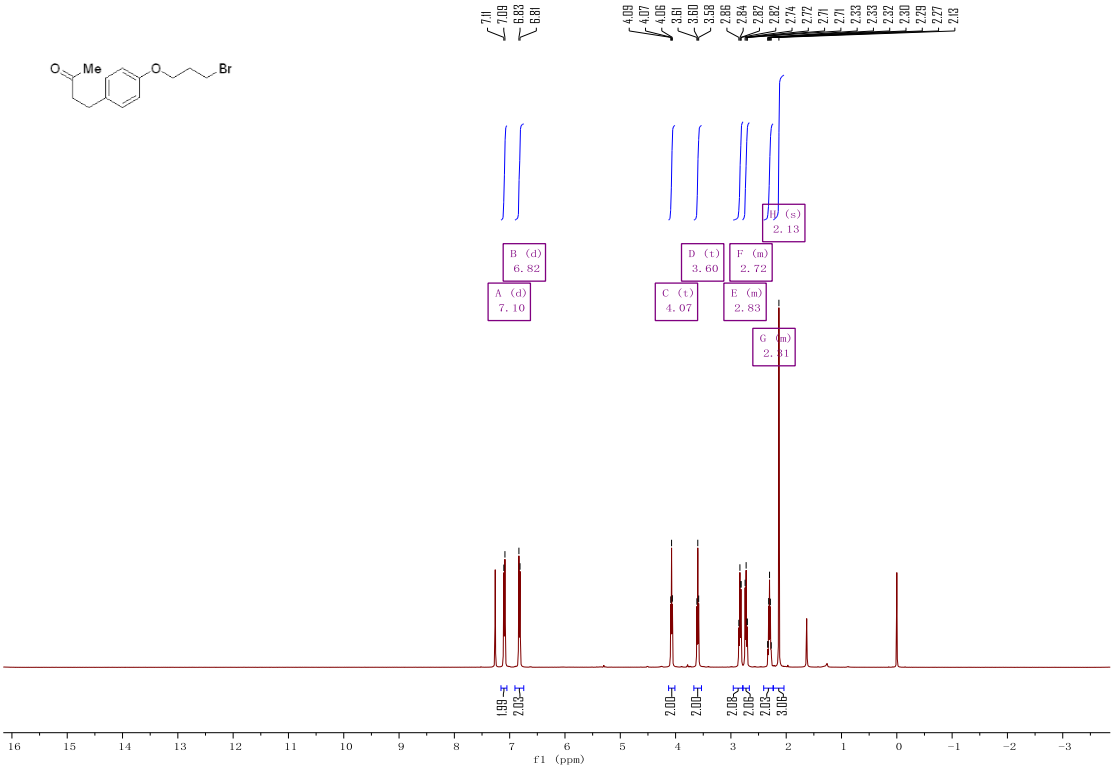
^{19}F NMR spectra for **RM3**



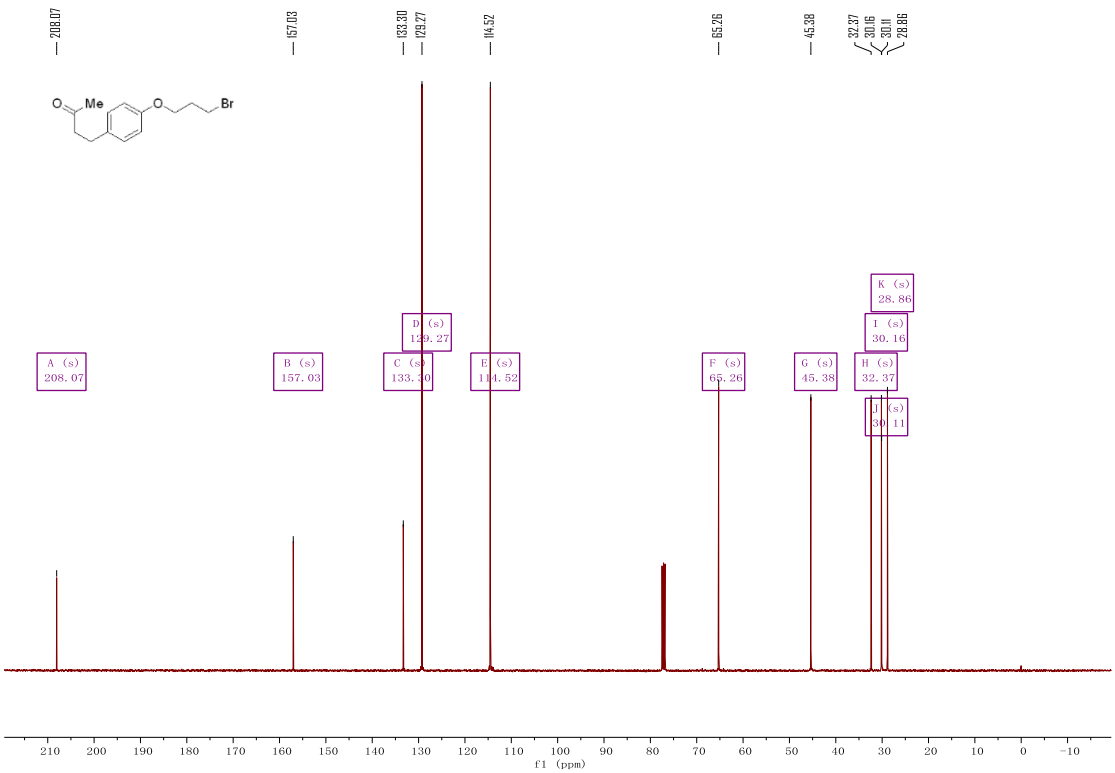
4-(4-(3-bromopropoxy)phenyl)butan-2-one (**RM6**)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.10 (d, *J* = 8.0 Hz, 2H), 6.82 (d, *J* = 8.0 Hz, 2H), 4.07 (t, *J* = 5.9 Hz, 2H), 3.60 (t, *J* = 6.4 Hz, 2H), 2.93 – 2.80 (m, 2H), 2.78 – 2.55 (m, 2H), 2.38 – 2.25 (m, 2H), 2.13 (s, 3H).

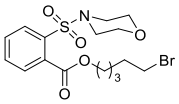
^{13}C NMR (101 MHz, Chloroform-*d*) δ 208.07, 157.03, 133.30, 129.27, 114.52, 65.26, 45.38, 32.37, 30.16, 30.11, 28.86.



^{1}H NMR spectra for **RM6**



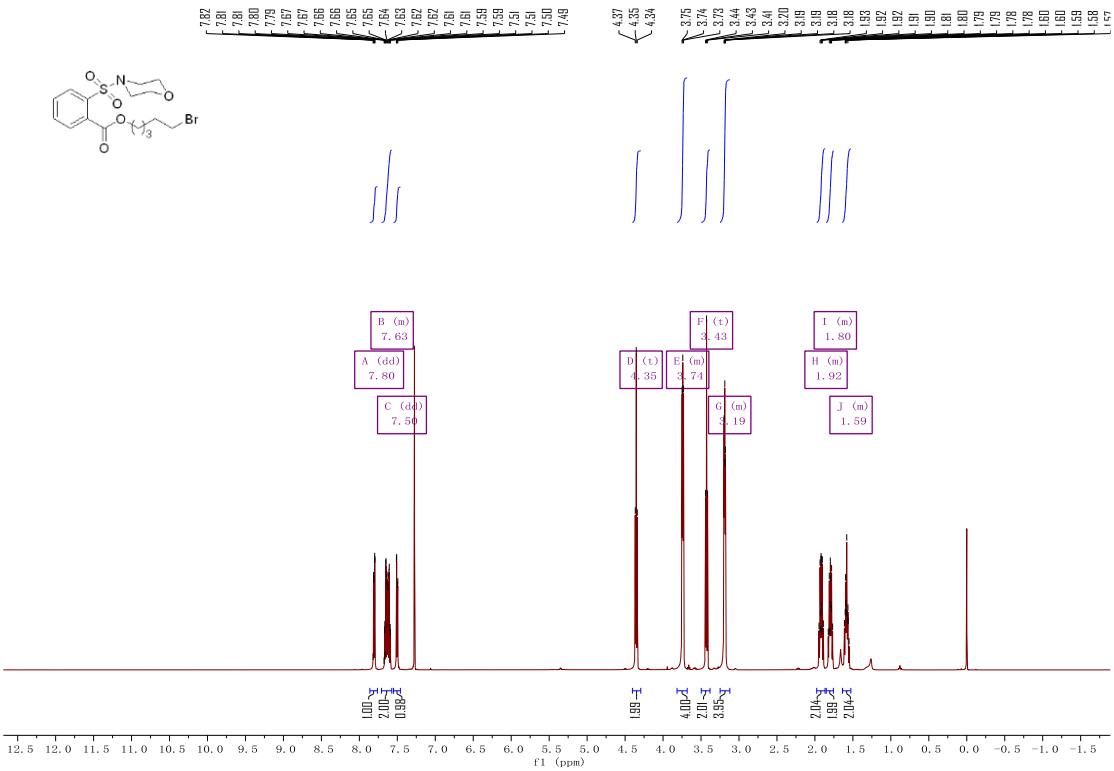
^{13}C NMR spectra for **RM6**



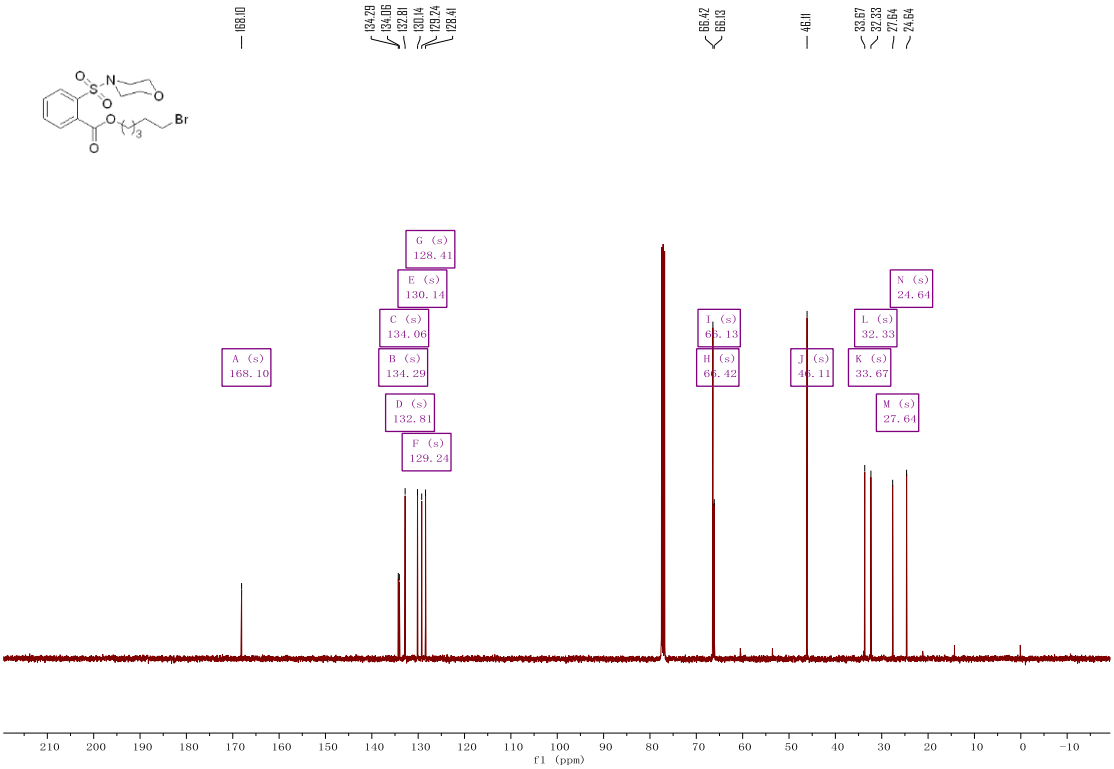
5-bromopentyl 2-(morpholinosulfonyl)benzoate (**RM8**)

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.80 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.69 – 7.55 (m, 2H), 7.50 (dd, *J* = 7.3, 1.6 Hz, 1H), 4.35 (t, *J* = 6.6 Hz, 2H), 3.84 – 3.55 (m, 4H), 3.43 (t, *J* = 6.7 Hz, 2H), 3.23 – 3.07 (m, 4H), 1.99 – 1.85 (m, 2H), 1.86 – 1.71 (m, 2H), 1.63 – 1.50 (m, 2H).

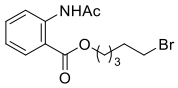
^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.10, 134.29, 134.06, 132.81, 130.14, 129.24, 128.41, 66.42, 66.13, 46.11, 33.67, 32.33, 27.64, 24.64.



^{1}H NMR spectra for **RM8**



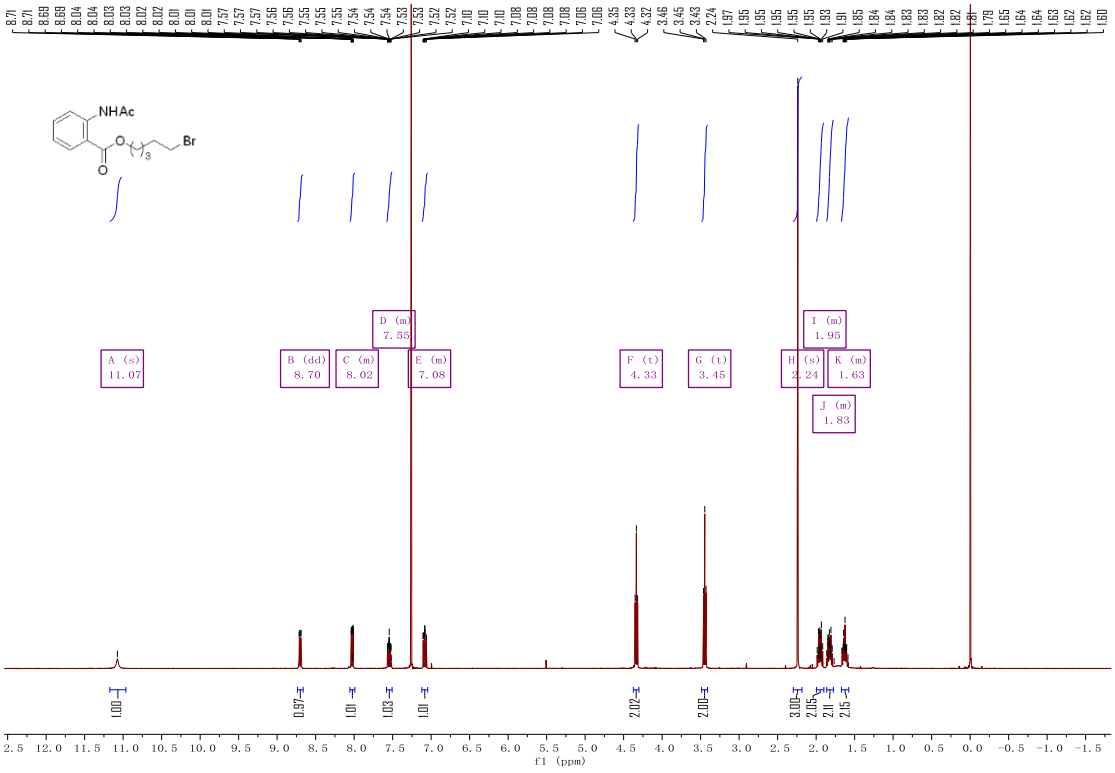
^{13}C NMR spectra for **RM8**



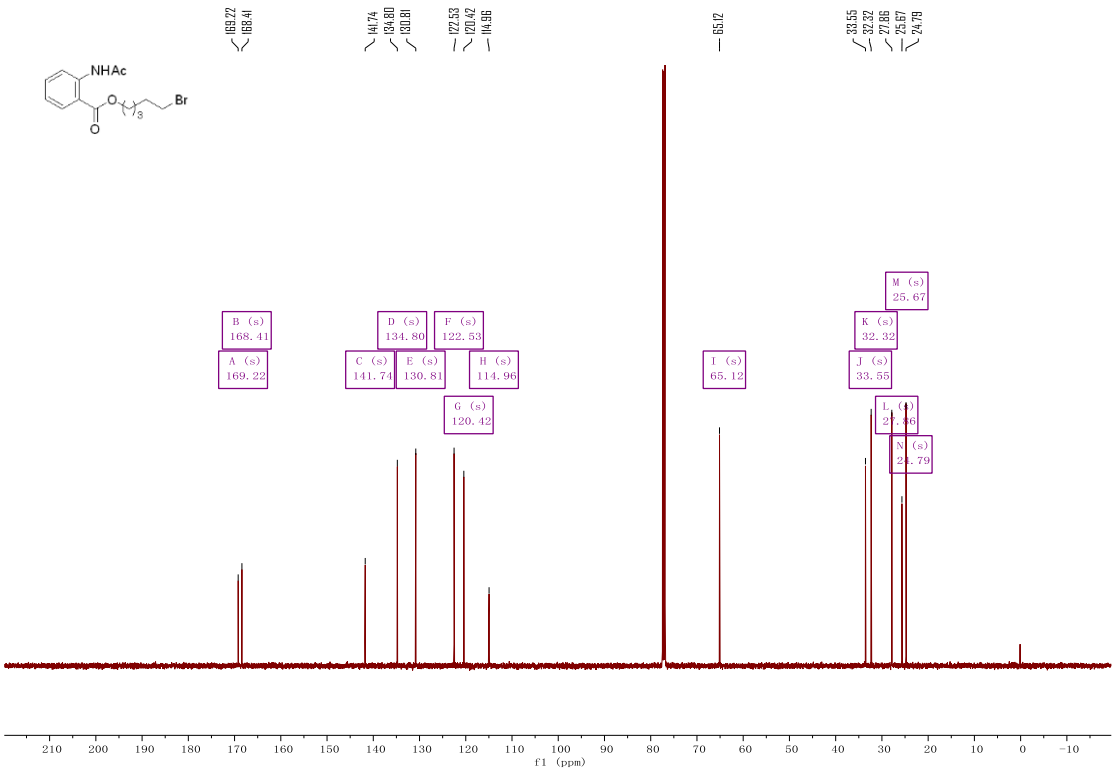
5-bromopentyl 2-acetamidobenzoate (**RM9**)

^{1}H NMR (500 MHz, Chloroform-*d*) δ 11.07 (s, 1H), 8.70 (dd, *J* = 8.5, 1.1 Hz, 1H), 8.09 – 7.88 (m, 1H), 7.62 – 7.44 (m, 1H), 7.17 – 7.04 (m, 1H), 4.33 (t, *J* = 6.5 Hz, 2H), 3.45 (t, *J* = 6.7 Hz, 2H), 2.24 (s, 3H), 2.03 – 1.89 (m, 2H), 1.88 – 1.73 (m, 2H), 1.68 – 1.58 (m, 2H).

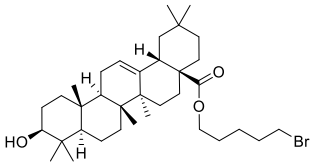
^{13}C NMR (126 MHz, Chloroform-*d*) δ 169.22, 168.41, 141.74, 134.80, 130.81, 122.53, 120.42, 114.96, 65.12, 33.55, 32.32, 27.86, 25.67, 24.79.



^{1}H NMR spectra for **RM9**



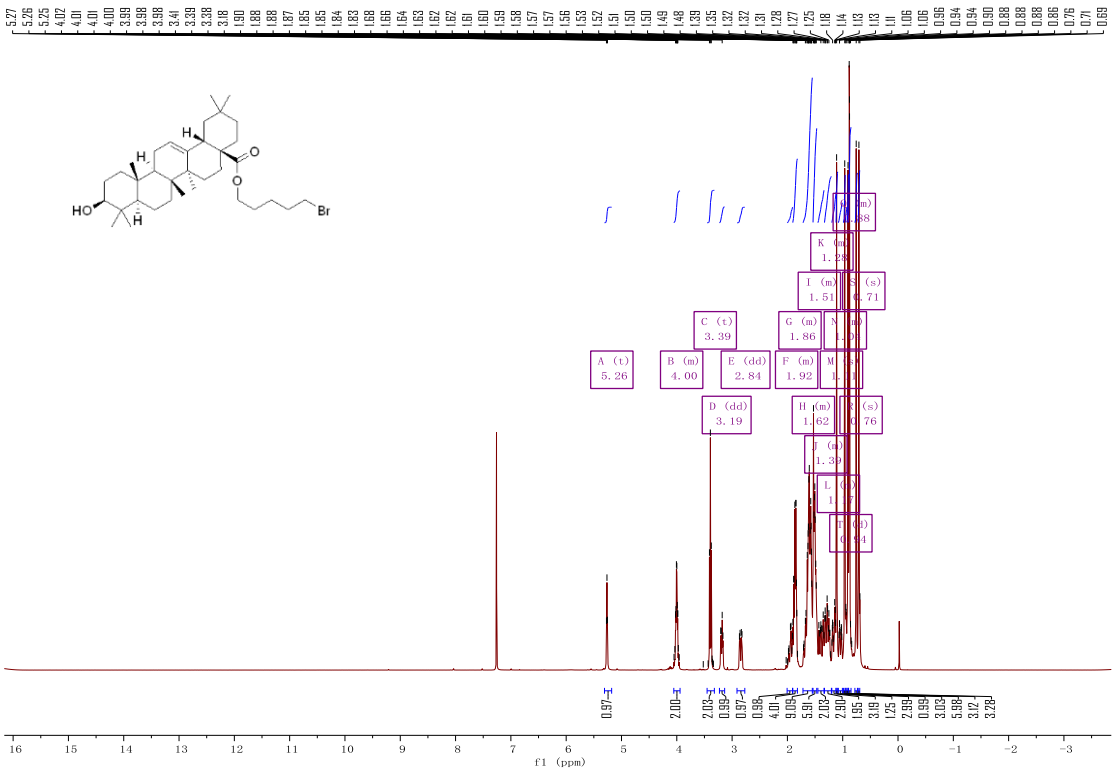
^{13}C NMR spectra for **RM9**



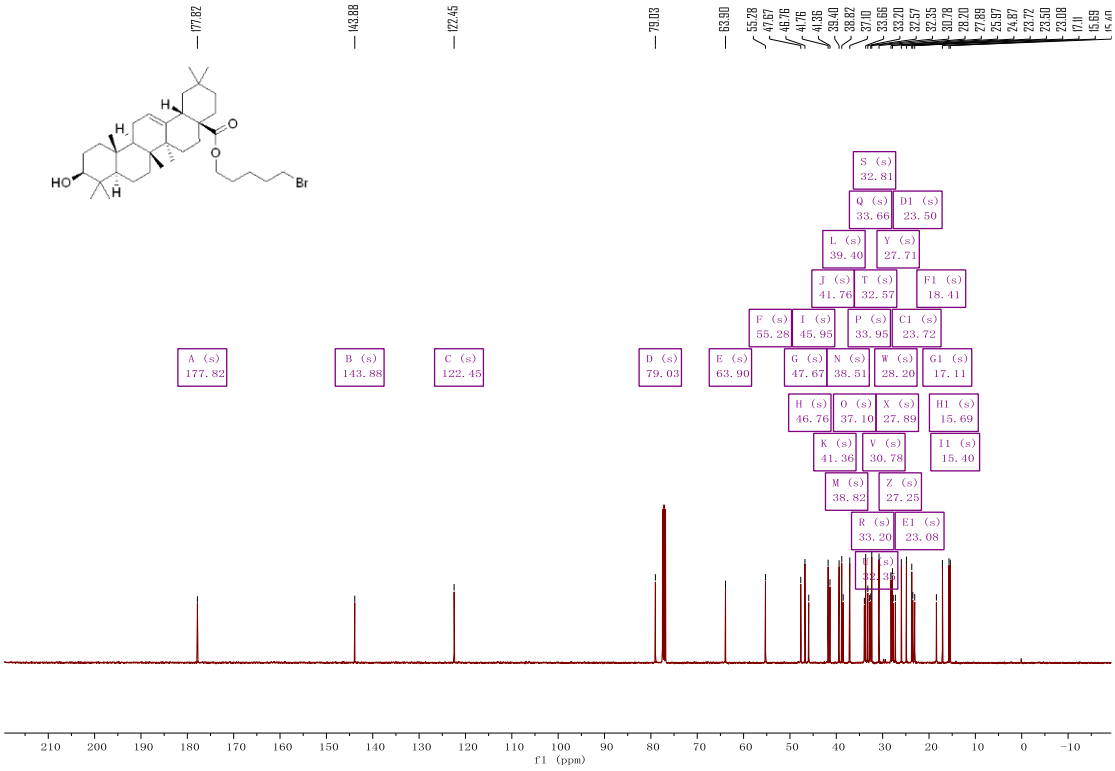
5-bromopentyl (4a*S*,6a*S*,6b*R*,8a*R*,10*S*,12a*R*,12b*R*,14b*S*)-10-hydroxy-2,2,6a,6b,9,9,12a-heptamethyl-1,3,4,5,6,6a,6b,7,8,8a,9,10,11,12,12a,12b,13,14b-octadecahydropicene-4a(2*H*)-carboxylate (**RM13**)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.26 (t, *J* = 3.6 Hz, 1H), 4.09 – 3.91 (m, 2H), 3.39 (t, *J* = 6.7 Hz, 2H), 3.19 (dd, *J* = 11.2, 4.8 Hz, 1H), 2.84 (dd, *J* = 13.9, 4.5 Hz, 1H), 2.01 – 1.86 (m, 1H), 1.91 – 1.79 (m, 4H), 1.73 – 1.55 (m, 9H), 1.55 – 1.47 (m, 6H), 1.45 – 1.34 (m, 2H), 1.33 – 1.20 (m, 3H), 1.20 – 1.12 (m, 2H), 1.11 (s, 3H), 1.09 – 0.99 (m, 1H), , 0.96 (s, 3H), δ 0.94 (d, *J* = 2.4 Hz, 1H) 0.90 (s, 3H), 0.91 – 0.81 (m, 6H), 0.76 (s, 3H), 0.71 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.82, 143.88, 122.45, 79.03, 63.90, 55.28, 47.67, 46.76, 45.95, 41.76, 41.36, 39.40, 38.82, 38.51, 37.10, 33.95, 33.66, 33.20, 32.81, 32.57, 32.35, 30.78, 28.20, 27.89, 27.71, 27.25, 25.97, 24.87, 23.72, 23.50, 23.08, 18.41, 17.11, 15.69, 15.40.

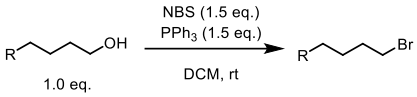


^{1}H NMR spectra for **RM13**

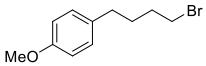


^{13}C NMR spectra for **RM13**

Procedure C:



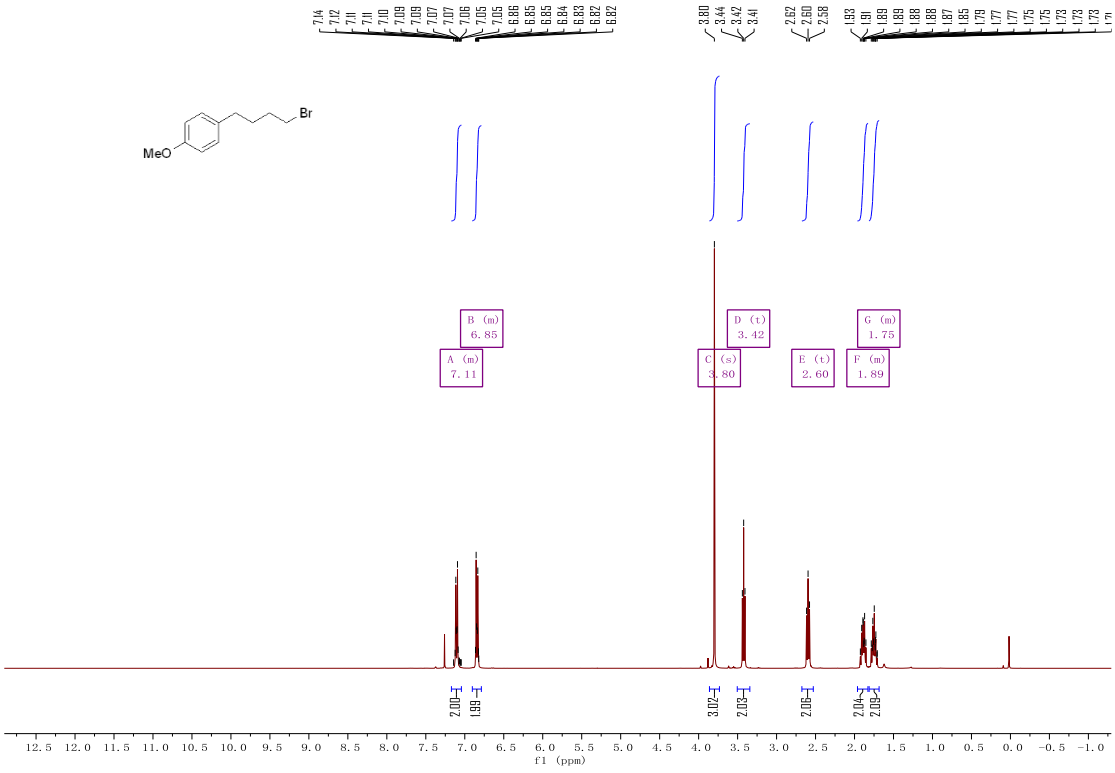
PPh_3 was added to a solution of NBS in DCM at 0°C. Primary alcohols were added and stirred for 12 h at room temperature. The mixture was washed with saturated NaCl solution, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The resulting mixture was isolated by flash chromatography.



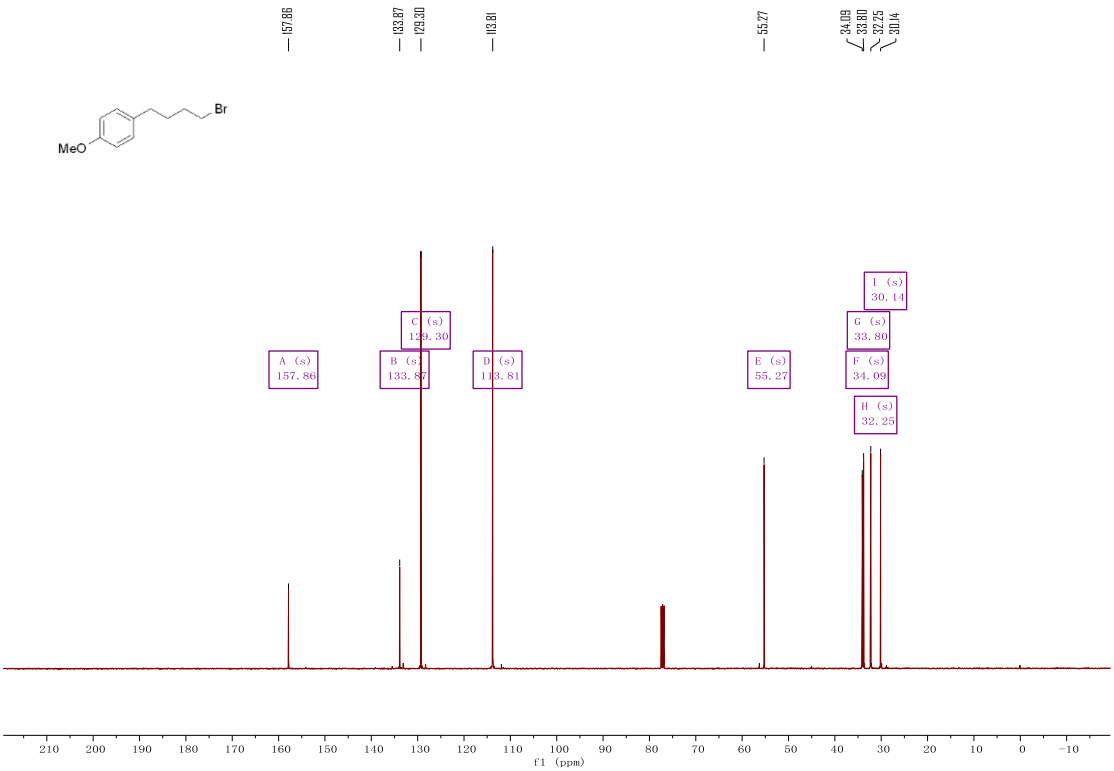
1-(4-bromobutyl)-4-methoxybenzene (**RM2**)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.15 – 7.00 (m, 2H), 6.91 – 6.71 (m, 2H), 3.80 (s, 3H), 3.42 (t, *J* = 6.7 Hz, 2H), 2.60 (t, *J* = 7.6 Hz, 2H), 1.96 – 1.83 (m, 2H), 1.82 – 1.67 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.86, 133.87, 129.30, 113.81, 55.27, 34.09, 33.80, 32.25, 30.14.

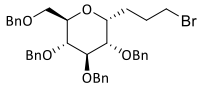


^{1}H NMR spectra for **RM2**



^{13}C NMR spectra for **RM2**

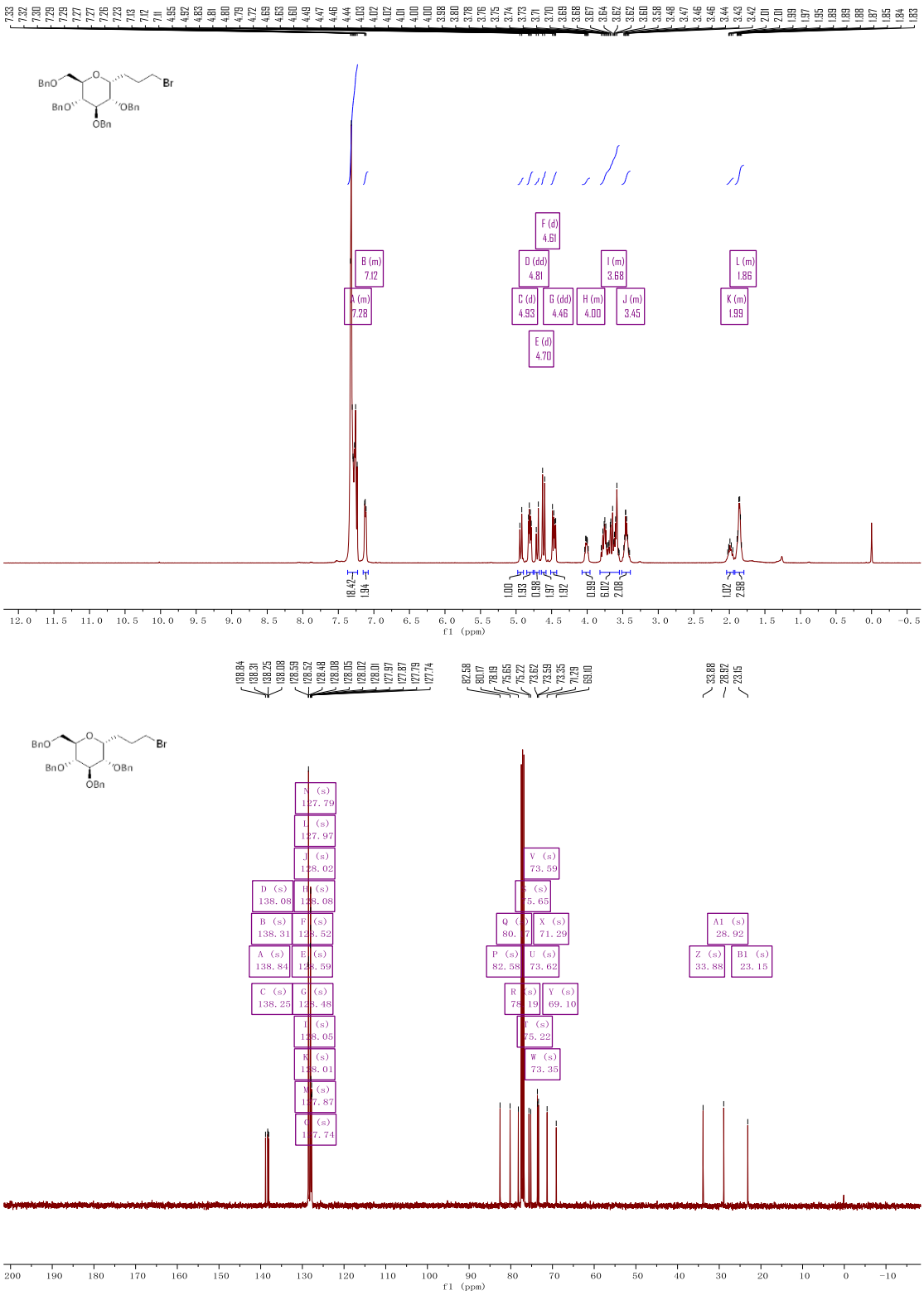
Compound **RM14** was prepared according to literature method.[2]



(2*R*,3*R*,4*R*,5*S*,6*R*)-3,4,5-tris(benzyloxy)-2-((benzyloxy)methyl)-6-(3-bromopropyl)tetrahydro-2*H*-pyran (**RM14**)

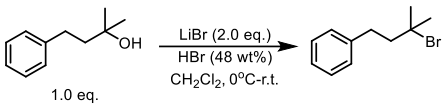
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.20 (m, 18H), 7.16 – 7.07 (m, 2H), 4.93 (d, J = 10.9 Hz, 1H), 4.81 (dd, J = 10.8, 4.8 Hz, 2H), 4.70 (d, J = 11.6 Hz, 1H), 4.61 (d, J = 11.9 Hz, 2H), 4.46 (dd, J = 11.4, 6.7 Hz, 2H), 4.08 – 3.94 (m, 1H), 3.84 – 3.54 (m, 6H), 3.51 – 3.38 (m, J = 4.7 Hz, 2H), 2.06 – 1.93 (m, 1H), 1.91 – 1.78 (m, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.84, 138.31, 138.25, 138.08, 128.59, 128.52, 128.48, 128.08, 128.05, 128.02, 128.01, 127.97, 127.87, 127.79, 127.74, 82.58, 80.17, 78.19, 75.65, 75.22, 73.62, 73.59, 73.35, 71.29, 69.10, 33.88, 28.92, 23.15.

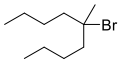


2.2. Preparation of Tertiary Alkyl Bromides

Procedure D:



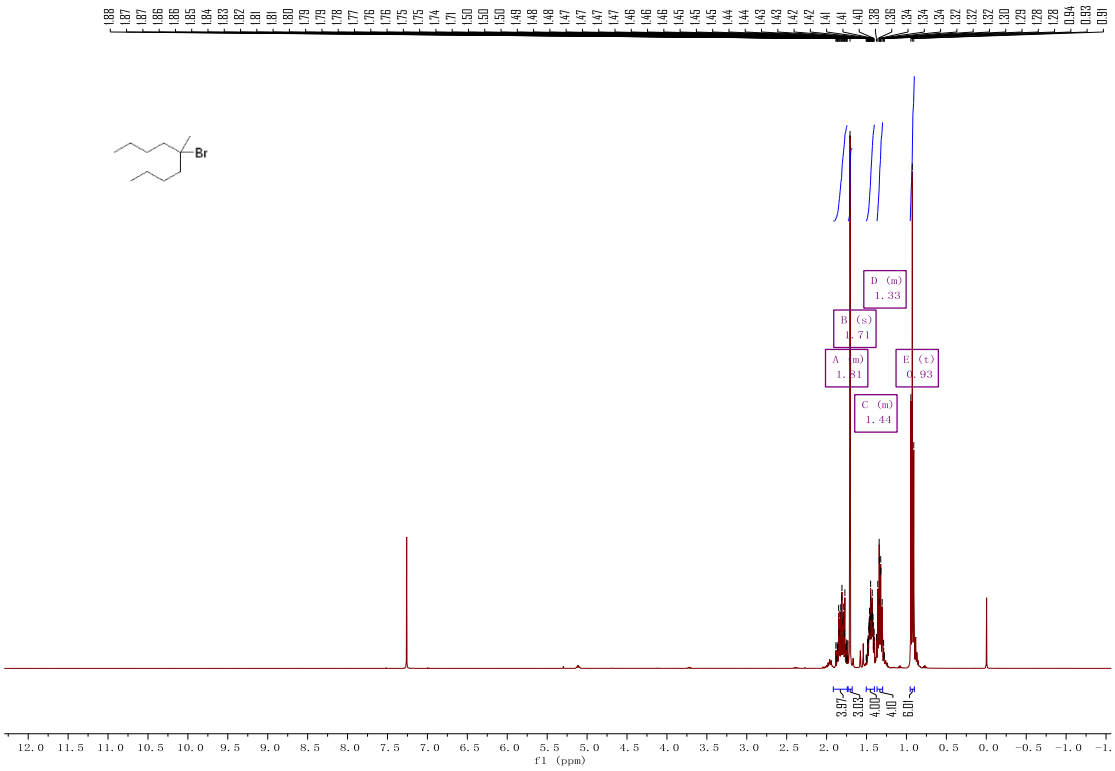
The tertiary alkyl bromides were prepared according to previously reported procedure.[3]



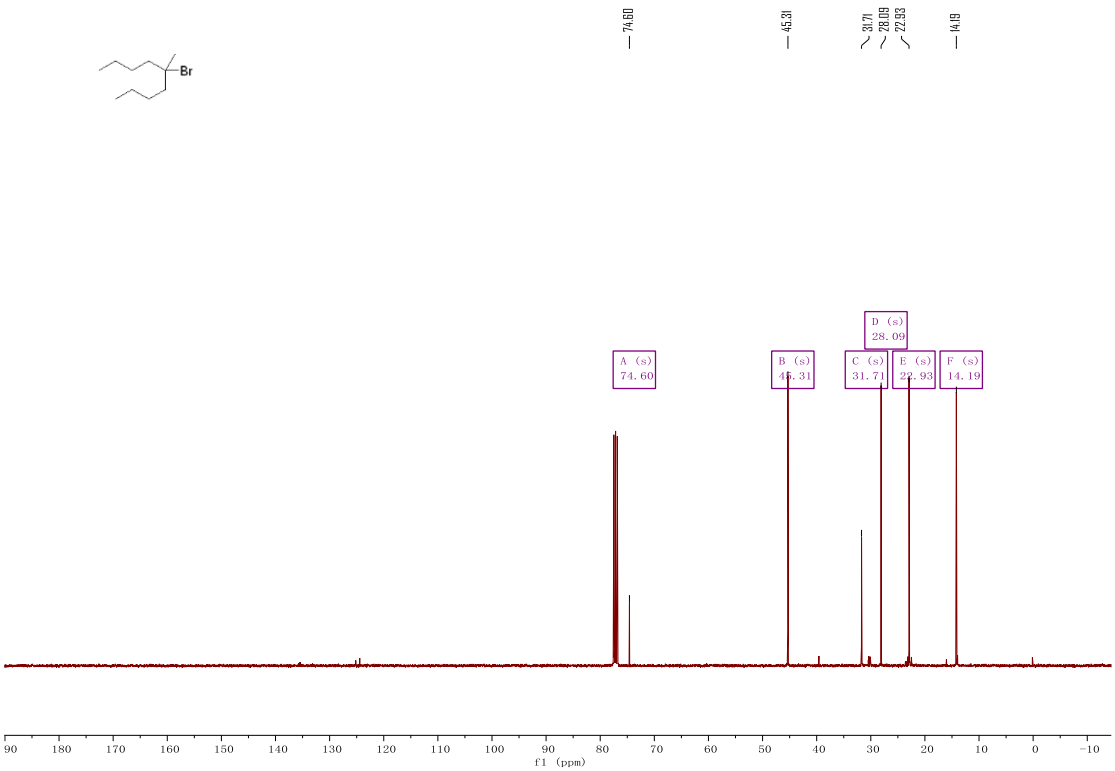
5-bromo-5-methylnonane (**RM10**)

^{1}H NMR (500 MHz, Chloroform-*d*) δ 1.90 – 1.74 (m, 4H), 1.71 (s, 3H), 1.51 – 1.39 (m, 4H), 1.37 – 1.28 (m, 4H), 0.93 (t, *J* = 7.3 Hz, 6H).

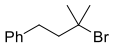
^{13}C NMR (101 MHz, Chloroform-*d*) δ 74.60, 45.31, 31.71, 28.09, 22.93, 14.19.



^{1}H NMR spectra for **RM10**



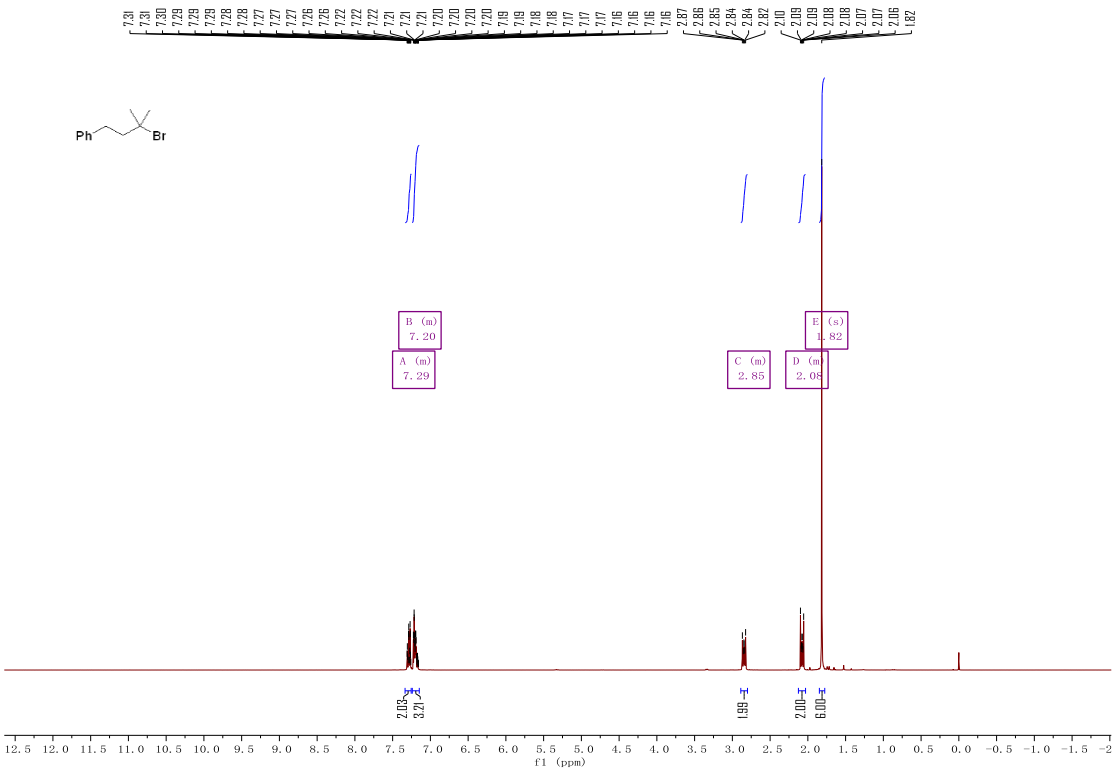
^{13}C NMR spectra for **RM10**



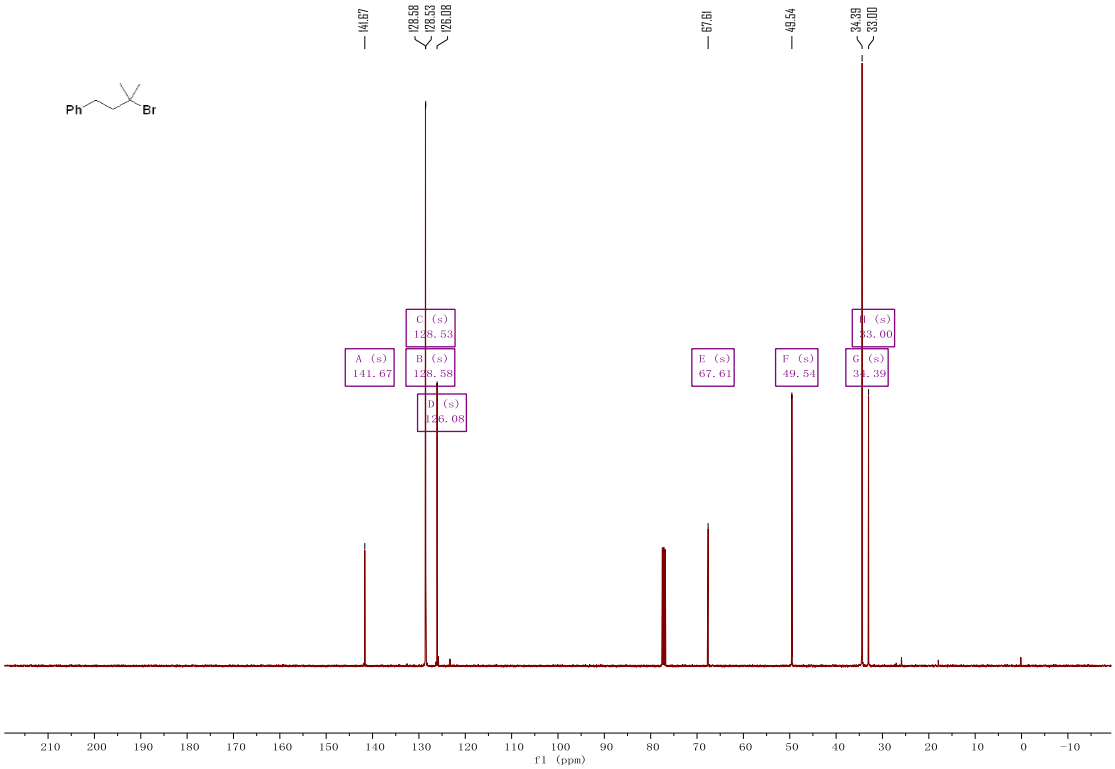
(3-bromo-3-methylbutyl)benzene (**RM11**)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.24 (m, 2H), 7.24 – 7.15 (m, 3H), 2.90 – 2.80 (m, 3H), 2.12 – 2.03 (m, 3H), 1.82 (s, 6H).

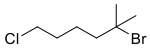
^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.67, 128.58, 128.53, 126.08, 67.61, 49.54, 34.39, 33.00.



^{1}H NMR spectra for **RM11**



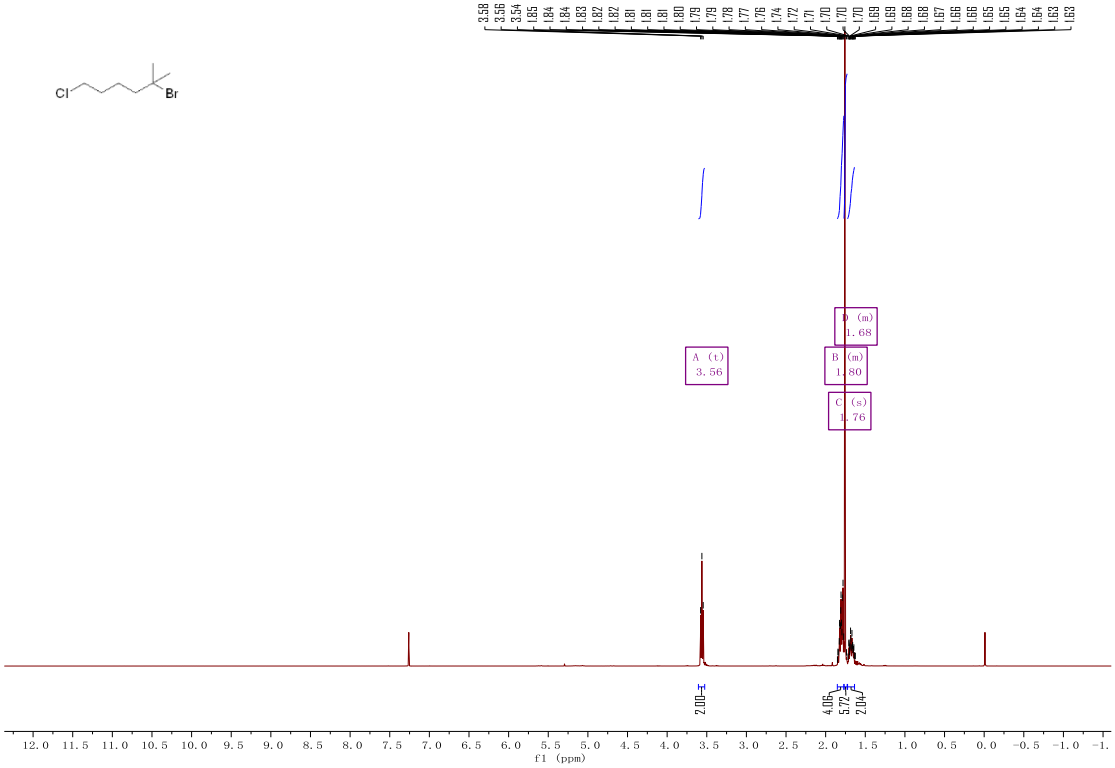
^{13}C NMR spectra for **RM11**



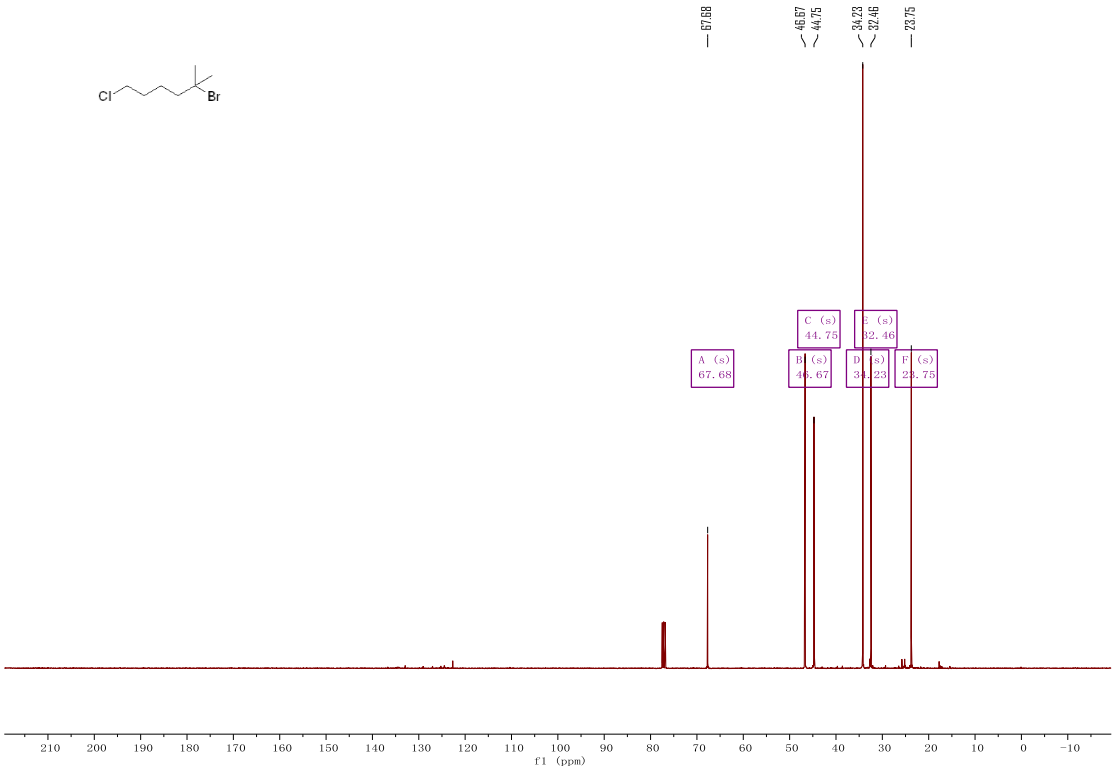
5-bromo-1-chloro-5-methylhexane (**RM12**)

^{1}H NMR (500 MHz, Chloroform-*d*) δ 3.56 (t, *J* = 6.6 Hz, 2H), 1.85 – 1.78 (m, 4H), 1.76 (s, 6H), 1.72 – 1.63 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 67.68, 46.67, 44.75, 34.23, 32.46, 23.75.



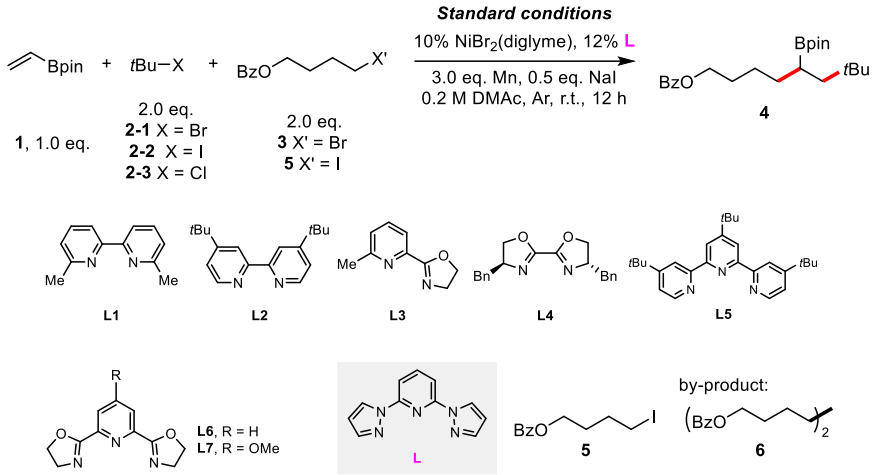
^{1}H NMR spectra for **RM12**



^{13}C NMR spectra for **RM12**

3. General Procedure for Table 1

Optimization of the Reaction Conditions



entry	nickel source	ligand	reductant	additive	solvent	X	X'	by-product yield of **6** (mmol)	yield of **3** (%)
1	**$NiBr_2$(diglyme)**	**L**	**Mn**	**NaI**	**DMAc**	**Br**	**Br**	**0.018**	**88 (83[b])**
2	$NiBr_2$(diglyme)	none	Mn	NaI	DMAc	Br	Br	< 0.010	N.R.
3	$NiBr_2$(diglyme)	L1	Mn	NaI	DMAc	Br	Br	< 0.010	< 2
4	$NiBr_2$(diglyme)	L2	Mn	NaI	DMAc	Br	Br	0.017	< 2
5	$NiBr_2$(diglyme)	L3	Mn	NaI	DMAc	Br	Br	0.012	8
6	$NiBr_2$(diglyme)	L4	Mn	NaI	DMAc	Br	Br	0.025	14
7	$NiBr_2$(diglyme)	L5	Mn	NaI	DMAc	Br	Br	0.052	19
8	$NiBr_2$(diglyme)	L6	Mn	NaI	DMAc	Br	Br	0.038	35
9	$NiBr_2$(diglyme)	L7	Mn	NaI	DMAc	Br	Br	0.031	63
10	none	L	Mn	NaI	DMAc	Br	Br	N.R	N.R.
11	$NiCl_2(PPh_3)_2$	L	Mn	NaI	DMAc	Br	Br	0.017	49
12	NiI_2	L	Mn	NaI	DMAc	Br	Br	0.036	83
13	$Ni(COD)_2$	L	Mn	NaI	DMAc	Br	Br	0.020	79
14	$NiBr_2$(diglyme)	L	Zn	NaI	DMAc	Br	Br	0.018	76
15	$NiBr_2$(diglyme)	L	B_2Pin_2 + LiOMe	NaI	DMAc	Br	Br	0.012	44
16	$NiBr_2$(diglyme)	L	B_2Pin_2 + K_3PO_4	NaI	DMAc	Br	Br	0.015	50
17	$NiBr_2$(diglyme)	L	DEMS + Na_2CO_3	NaI	DMAc	Br	Br	< 0.010	11
18	$NiBr_2$(diglyme)	L	Mn	20% NaI	DMAc	Br	Br	< 0.010	45
19	$NiBr_2$(diglyme)	L	Mn	30% TBAI	DMAc	Br	Br	0.018	82
20	$NiBr_2$(diglyme)	L	Mn	NaI	DMF	Br	Br	0.010	87

21	$NiBr_2$(diglyme)	L	Mn	NaI	NMP	Br	Br	0.010	72
22	$NiBr_2$(diglyme)	L	Mn	NaI	THF	Br	Br	N.R	< 2
23	$NiBr_2$(diglyme)	L	Mn	NaI	1,4-Dioxane	Br	Br	N.R	< 2
24	$NiBr_2$(diglyme)	L	Mn	NaI	CH_3CN	Br	Br	N.R	< 2
25	$NiBr_2$(diglyme)	L	Mn	NaI	DMSO	Br	Br	< 0.010	< 2
26	$NiBr_2$(diglyme)	L	Mn	NaI	DMAc	I	Br	0.080	< 2
27	$NiBr_2$(diglyme)	L	Mn	NaI	DMAc	Cl	Br	< 0.010	< 2
28[c]	$NiBr_2$(diglyme)	L	Mn	NaI	DMAc	Cl	Br	< 0.010	< 2
29	$NiBr_2$(diglyme)	L	Mn	NaI	DMAc	Br	I	0.070	54
30[d]	$NiBr_2$(diglyme)	L	Mn	NaI	DMAc	Br	Br	< 0.010	52
31[e]	$NiBr_2$(diglyme)	L	Mn	NaI	DMAc	Br	Br	0.036	76

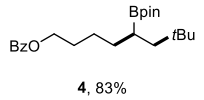
[a] Conditions: **1** (0.1 mmol, 1.0 equiv), **2** (0.2 mmol, 2.0 equiv), nickel source (0.01 mmol, 10 mol%), ligand (0.012 mmol, 12 mol%), Mn (0.3 mmol, 3.0 equiv), base (0.3 mmol, 3.0 equiv), solvent (0.5 mL), **3** (0.2 mmol, 2.0 equiv), rt, 12 h. Bis(4-methoxyphenyl)methanone was used as an internal standard. GC yield. [b] Isolated yield. [c] 20% Cp_2TiCl_2 as additive. [d] ratio of **1** : **2** : **3** = 1 : 1 : 1. [e] ratio of **1** : **2** : **3** = 1 : 1.5 : 2. Bpin = 4,4,5,5-tetramethyl-1,3-dioxaborolane. BzO = benzoyloxy. Diglyme = 2-methoxyethyl ether. THF = tetrahydrofuran. DMAc = *N*,*N*-dimethylacetamide. NMP = 1-methylpyrrolidin-2-one. DMSO = dimethyl sulfoxide.. N.R. = no reaction.

4. General Procedure for Olefin Reductive Dicarbofunctionalization

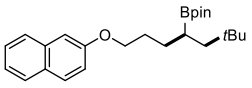
General Procedure 1: $NiBr_2$(diglyme) (0.020 mmol, 10 mol%, 7.1 mg), Ligand (0.024 mmol, 12 mol%, 5.0 mg), Mn (0.6 mmol, 3.0 equiv., 33.0 mg) and NaI (0.1 mmol, 0.5 equiv., 15.0 mg) were added to a Schlenk tube equipped with a stir bar. The Schlenk tube was evacuated and filled with argon (three cycles). To these solids, 1 mL DMAc (0.2 M) was added under argon atmosphere. Then, 4,4,5,5-tetramethyl-2-vinyl-1,3,2-dioxaborolane (0.2 mmol, 1.0 equiv.) and tertiary alkyl bromide (0.4 mmol, 2.0 equiv.) were added and stirred at room temperature (20-25 ℃) for 10 min, primary alkyl bromides or corresponding aryl iodides (0.4 mmol, 2.0 equiv.) were added under argon atmosphere. The mixture was stirred at room temperature for 12 hours, and purified by column chromatography to afford the desired product.

General Procedure 2: $NiBr_2$(diglyme) (0.020 mmol, 10 mol%, 7.1 mg), Ligand (0.024 mmol, 12 mol%, 5.0 mg), NaI (0.1 mmol, 0.5 equiv., 15.0 mg) and Mn (0.6 mmol, 3.0 equiv., 33.0 mg) were added to a Schlenk tube equipped with a stir bar. The Schlenk tube was evacuated and filled with argon (three cycles). To these solids, 1 mL DMAc (0.2 M) was added under argon atmosphere. Then, 4,4,5,5-tetramethyl-2-vinyl-1,3,2-dioxaborolane (0.2 mmol, 1.0 equiv.) and tertiary alkyl bromide (0.4 mmol, 2.0 equiv.) were added and stirred at room temperature (20-25 ℃) for 10 min, primary alkyl bromide (0.4 mmol, 2.0 equiv.) were added under argon atmosphere. The mixture was stirred at room temperature for 12 hours, and purified by column chromatography to afford the crude product. To a solution of crude product in THF (1 mL) and H_2O (1 mL) was added $NaBO_3 \cdot 4H_2O$ (154 mg, 1mmol) at room temperature. The reaction mixture was then stirred at room temperature for 12 hours. The reaction mixture was diluted with H_2O followed by extraction with EtOAc, dried with anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel to give the final product.

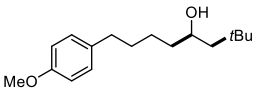
5. Examples Described in Scheme 2



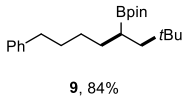
4, 83%



7, 76%



8, 66% (70%[b])



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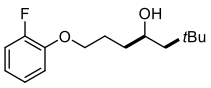
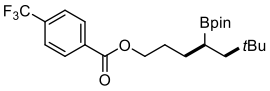
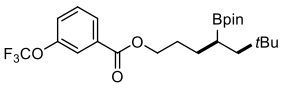


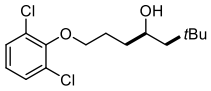
10, 61% (73%[b])



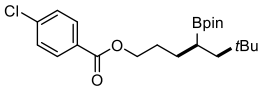
11, 73%



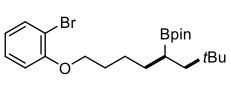
12, 68%



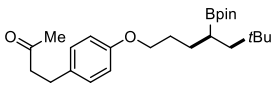
13, 64% (74%[b])



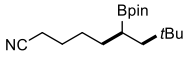
14, 80%



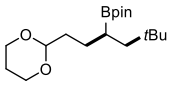
15, 70%



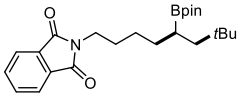
16, 74%



17, 76%



18, 67%



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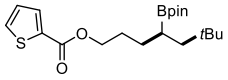
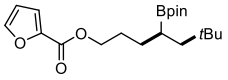
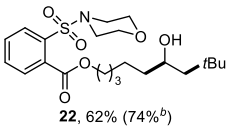


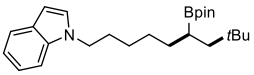
20, 70%



21, 68%



22, 62% (74%[b])



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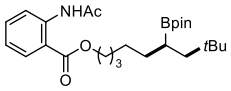
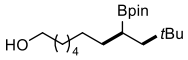
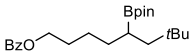


24, 66%



25, 60%



7,7-dimethyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octyl benzoate (**4**)

Following general procedure 1. The product was isolated by column chromatography as colorless oil (64.5 mg, 0.166 mmol, 83%).

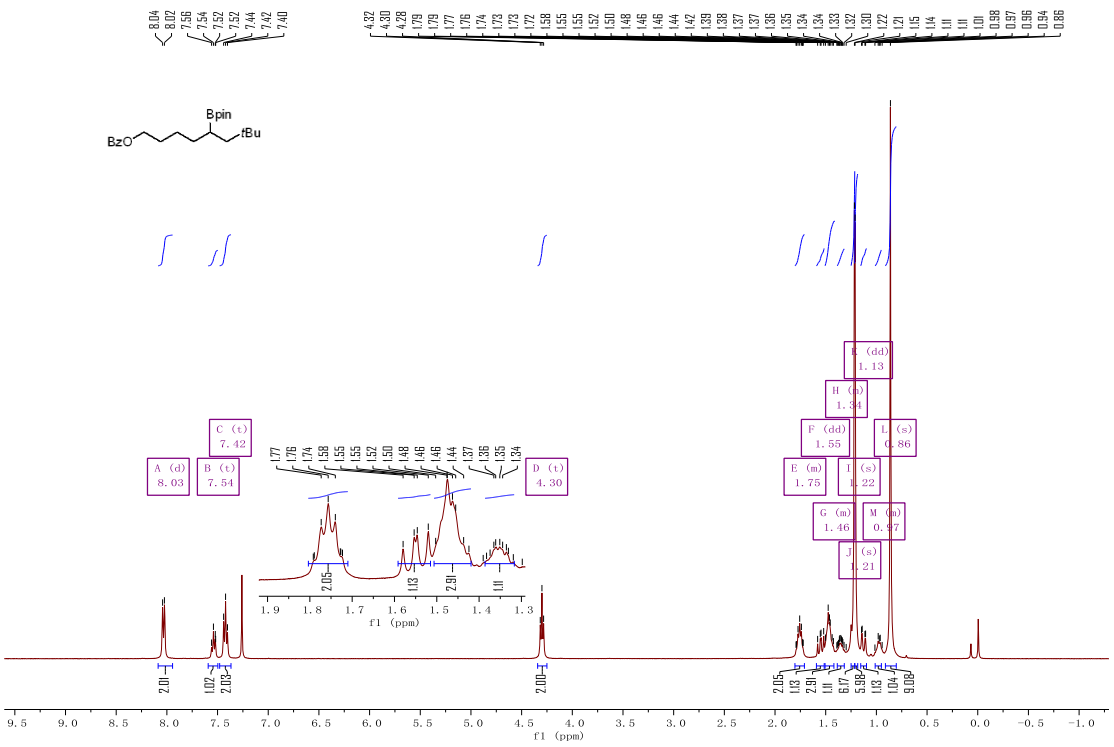
Rf (petroleum ether : acetone = 15 : 1) = 0.50.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 7.2 Hz, 2H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 4.30 (t, *J* = 6.6 Hz, 2H), 1.85 – 1.66 (m, 2H), 1.55 (dd, *J* = 13.4, 10.4 Hz, 1H), 1.53 – 1.40 (m, 3H), 1.41 – 1.28 (m, 1H), 1.22 (s, 6H), 1.21 (s, 6H), 1.13 (dd, *J* = 13.5, 2.5 Hz, 1H), 1.04 – 0.92 (m, 1H), 0.86 (s, 9H).

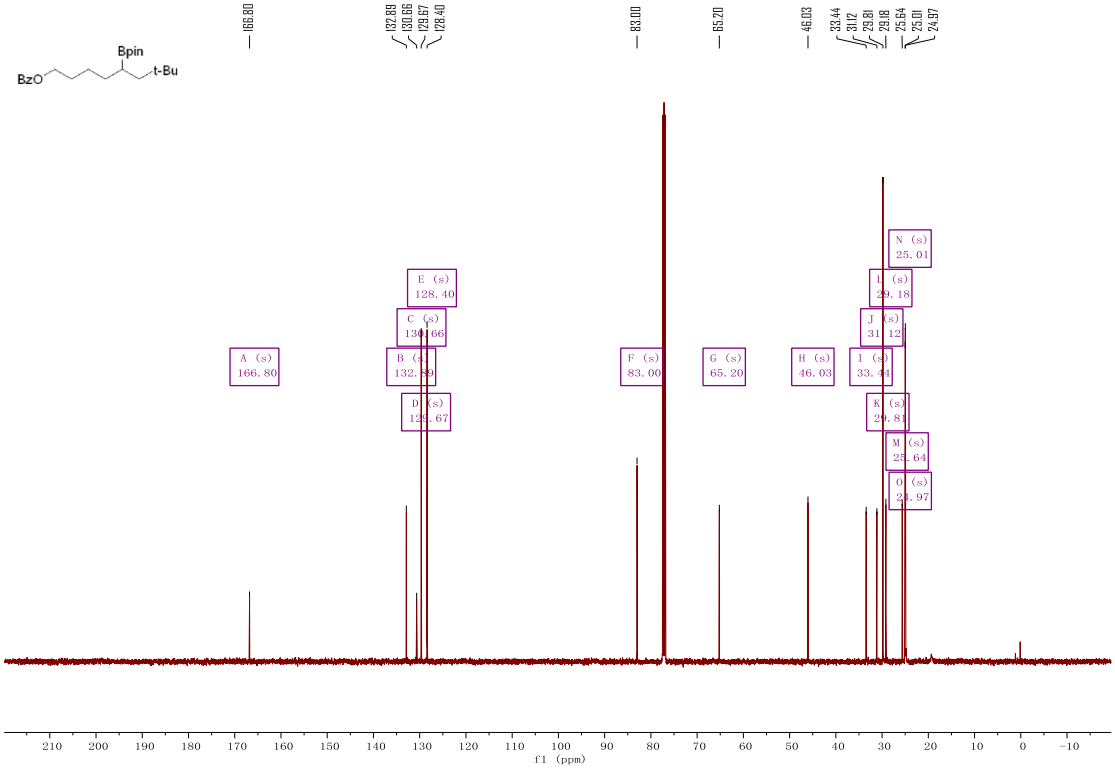
^{13}C NMR (126 MHz, Chloroform-*d*) δ 166.80, 132.89, 130.66, 129.67, 128.40, 83.00, 65.20, 46.03, 33.44, 31.12, 29.81, 29.18, 25.64, 25.01, 24.97.

^{11}B NMR (128 MHz, Chloroform-*d*) 35.02.

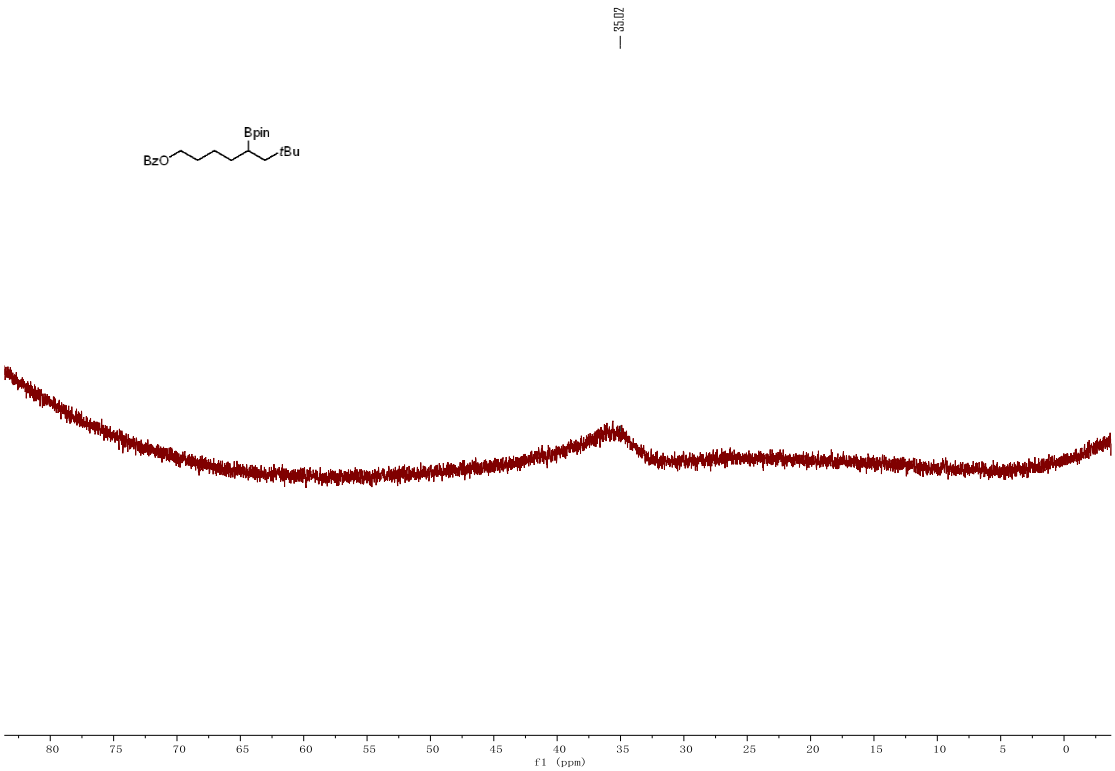
HRMS (ESI) calculated for $C_{23}H_{37}BO_4$ $[M+H]^+$: 389.2858, found: 389.2847.



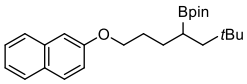
^{1}H NMR spectra for **4**



^{13}C NMR spectra for **4**



^{11}B NMR spectra for **4**



2-(6,6-dimethyl-1-(naphthalen-2-yloxy)heptan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**7**)

Following general procedure 1. The product was isolated by column chromatography as white solid (60.2 mg, 0.152 mmol, 76%).

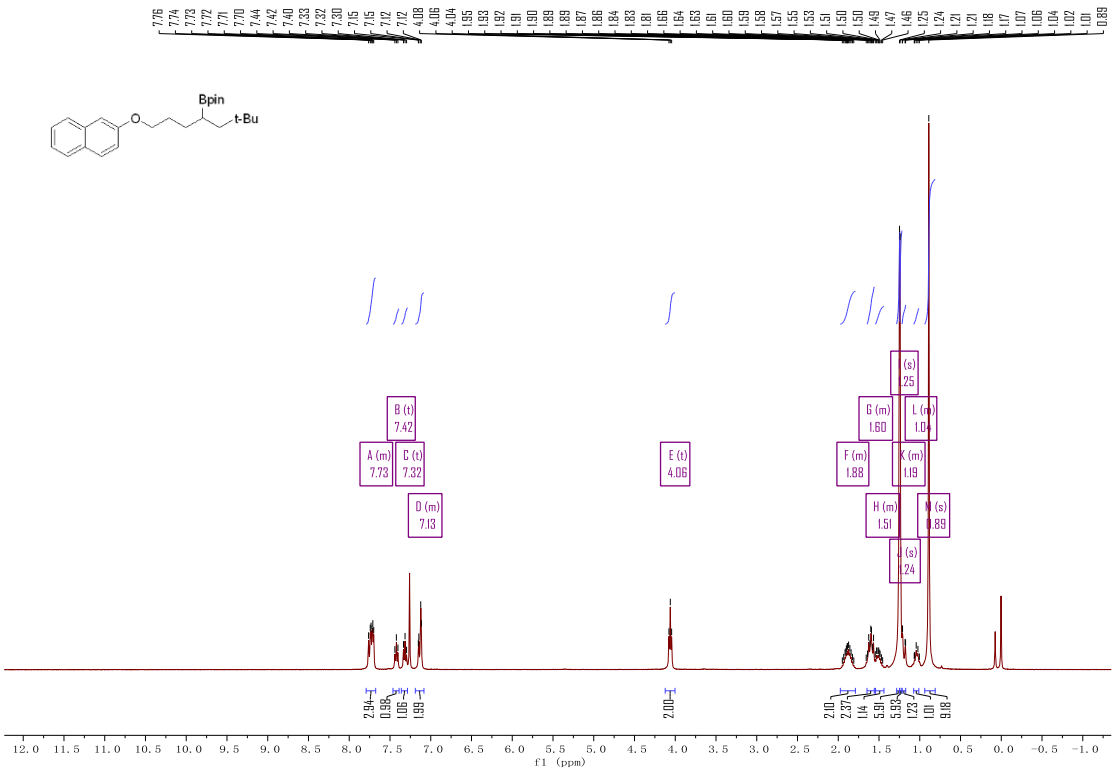
Rf (petroleum ether : ethyl acetate = 20 : 1) = 0.45

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 – 7.66 (m, 3H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.18 – 7.10 (m, 2H), 4.06 (t, *J* = 6.6 Hz, 2H), 2.07 – 1.76 (m, 2H), 1.69 – 1.55 (m, 2H), 1.57 – 1.43 (m, 1H), 1.25 (s, 6H), 1.24 (s, 6H), 1.22 – 1.16 (m, 1H), 1.08 – 1.00 (m, 1H), 0.89 (s, 9H).

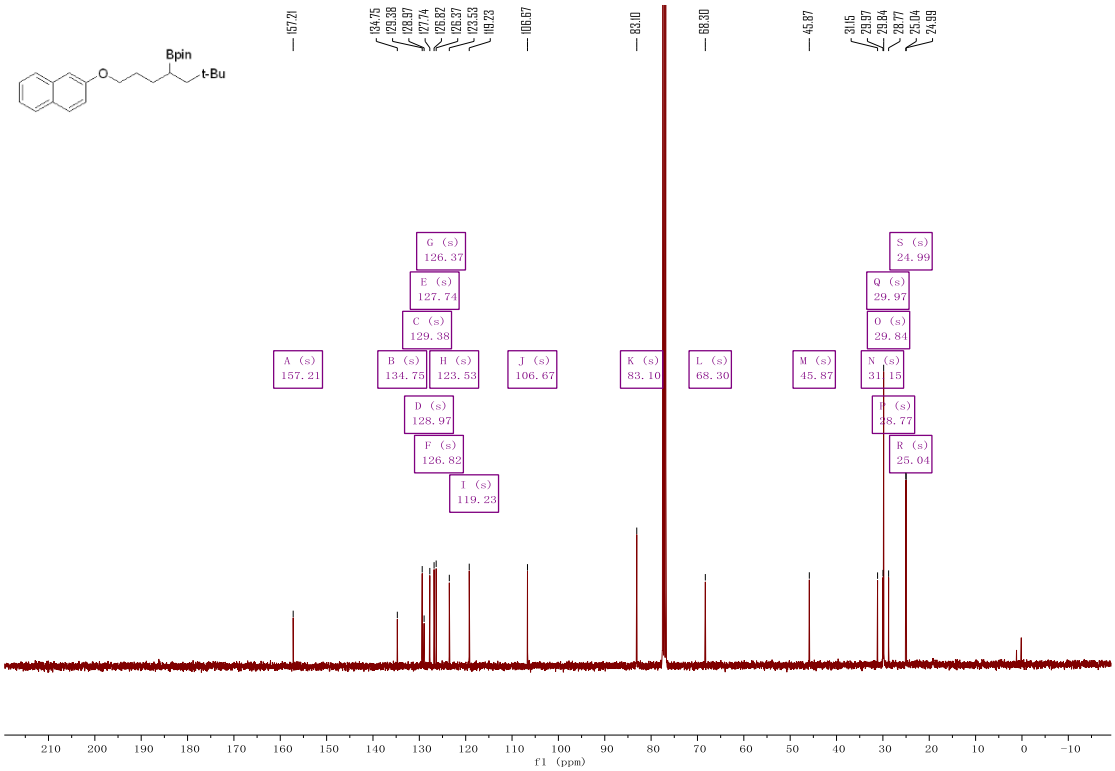
^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.21, 134.75, 129.38, 128.97, 127.74, 126.82, 126.37, 123.53, 119.23, 106.67, 83.10, 68.30, 45.87, 31.15, 29.97, 29.84, 28.77, 25.04, 24.99.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 35.15

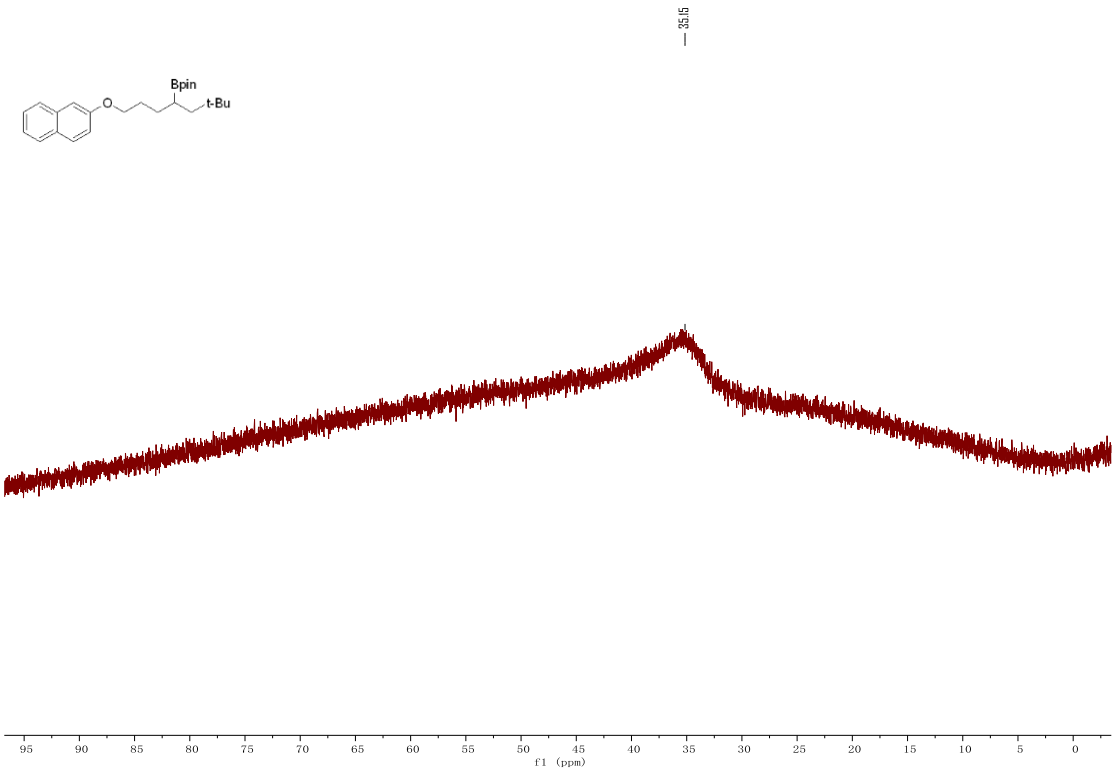
HRMS (ESI) calculated for $C_{25}H_{37}BO_3$ $[M+H]^+$: 397.2909, found: 397.2899.



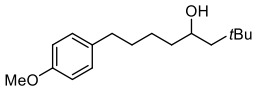
^{1}H NMR spectra for **7**



^{13}C NMR spectra for **7**



^{11}B NMR spectra for **7**



8-(4-methoxyphenyl)-2,2-dimethyloctan-4-ol (**8**)

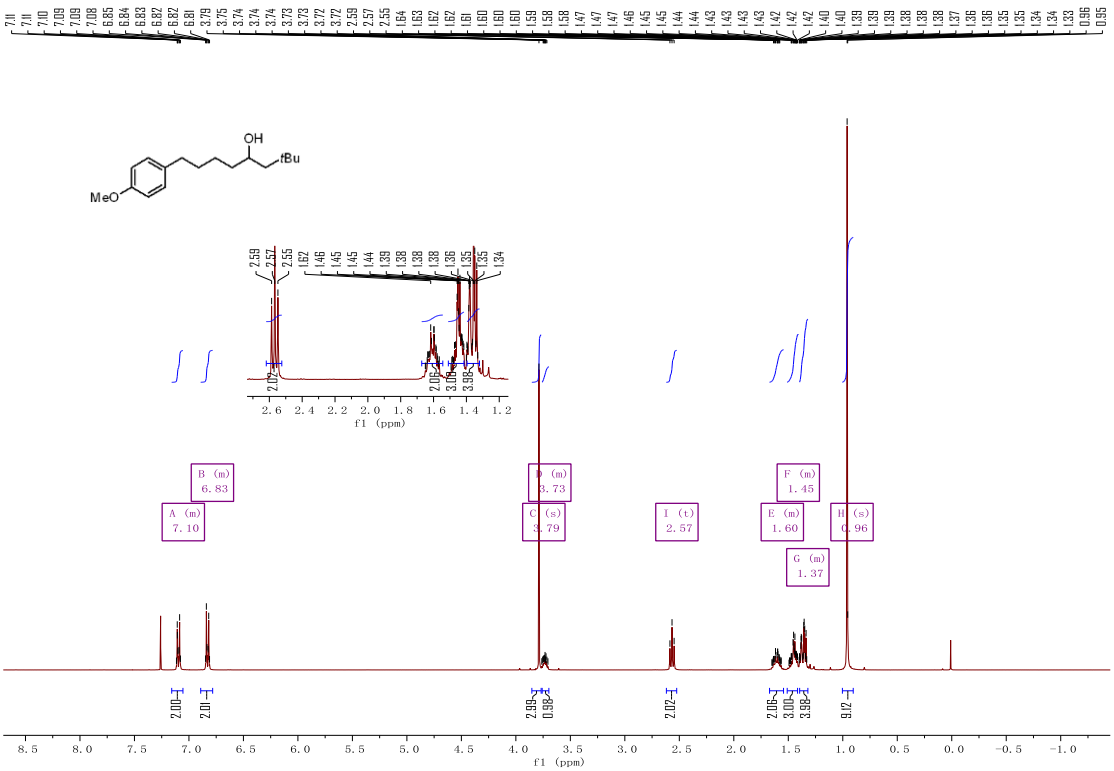
Following general procedure 2. The product was isolated by column chromatography as colorless oil (34.9 mg, 0.132 mmol, 66%).

Rf (petroleum ether : ethyl acetate = 5 : 1) = 0.50

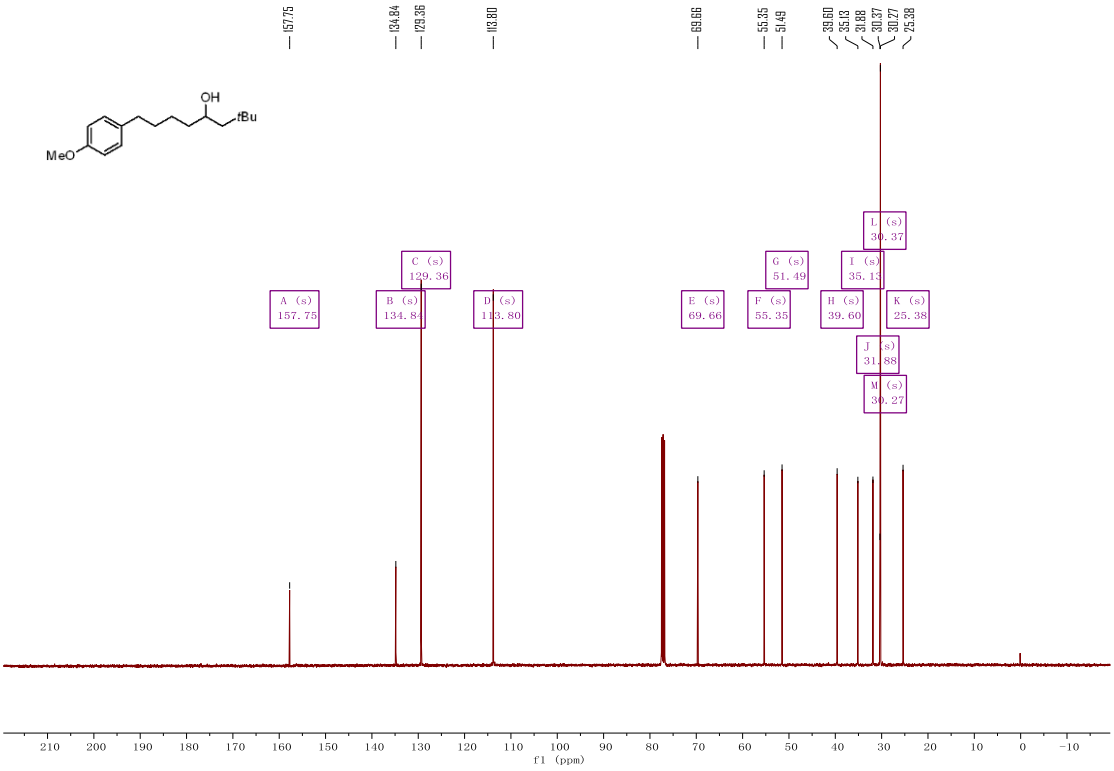
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.14 – 7.06 (m, 2H), 6.87 – 6.79 (m, 2H), 3.79 (s, 3H), 3.77 – 3.70 (m, 1H), 2.57 (t, *J* = 7.7 Hz, 2H), 1.70 – 1.54 (m, 2H), 1.52 – 1.39 (m, 3H), 1.40 – 1.30 (m, 4H), 0.96 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.75, 134.84, 129.36, 113.80, 69.66, 55.35, 51.49, 39.60, 35.13, 31.88, 30.37, 30.27, 25.38.

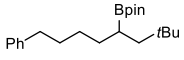
HRMS (ESI) calculated for $C_{22}H_{38}O_2B$ $[M+Na]^+$: 287.1982, found: 287.1987.



^{1}H NMR spectra for 8



^{13}C NMR spectra for **8**



2-(2,2-dimethyl-8-phenyloctan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**9**)

Following general procedure 1. The product was isolated by column chromatography as colorless oil (57.9 mg, 0.168 mmol, 84%).

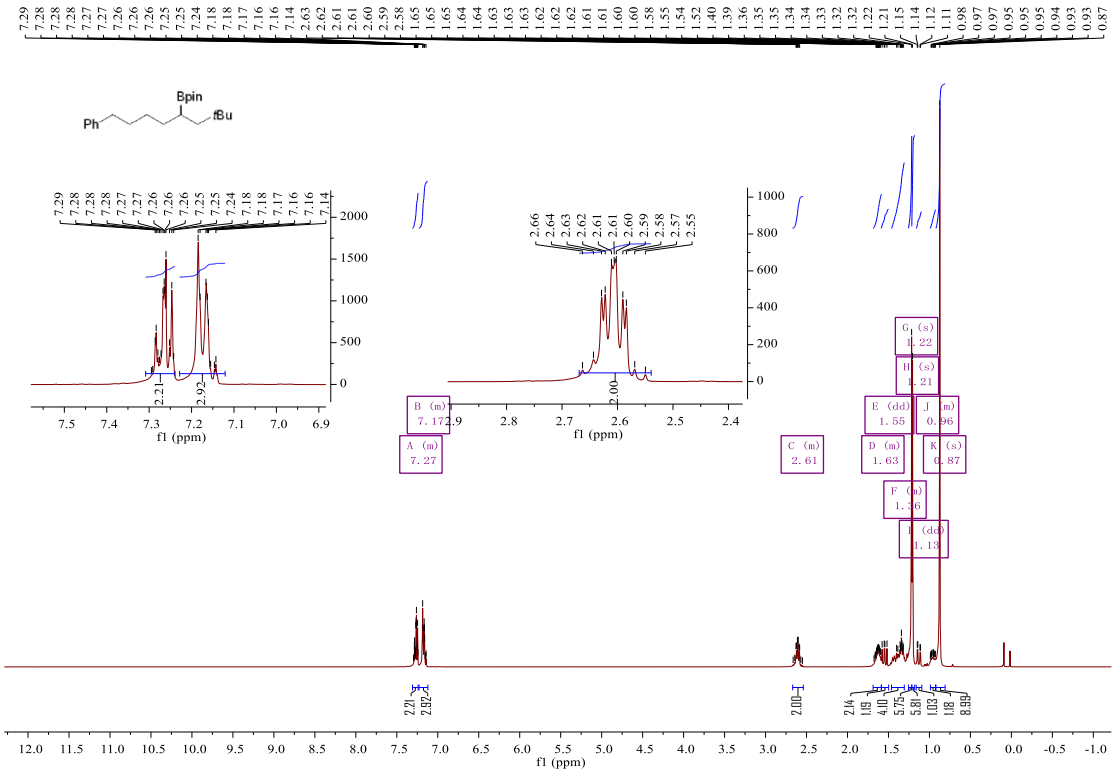
Rf (petroleum ether : ethyl acetate = 20 : 1) = 0.50

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.23 (m, 2H), 7.22 – 7.10 (m, 3H), 2.67 – 2.54 (m, 2H), 1.68 – 1.60 (m, 2H), 1.55 (dd, *J* = 13.4, 10.5 Hz, 1H), 1.48 – 1.30 (m, 4H), 1.22 (s, 6H), 1.21 (s, 6H), 1.13 (dd, *J* = 13.4, 2.5 Hz, 1H), 1.01 – 0.91 (m, 1H), 0.87 (s, 9H).

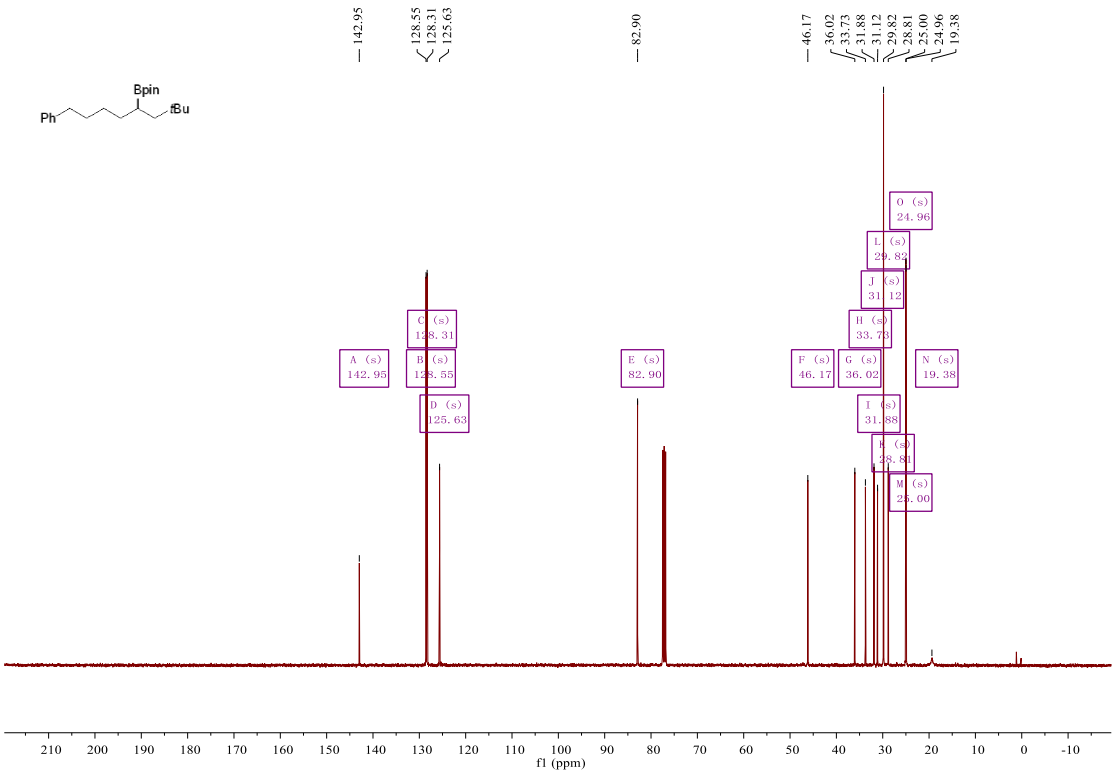
^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.95, 128.55, 128.31, 125.63, 82.90, 46.17, 36.02, 33.73, 31.88, 31.12, 29.82, 28.81, 25.00, 24.96, 19.38.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 33.75

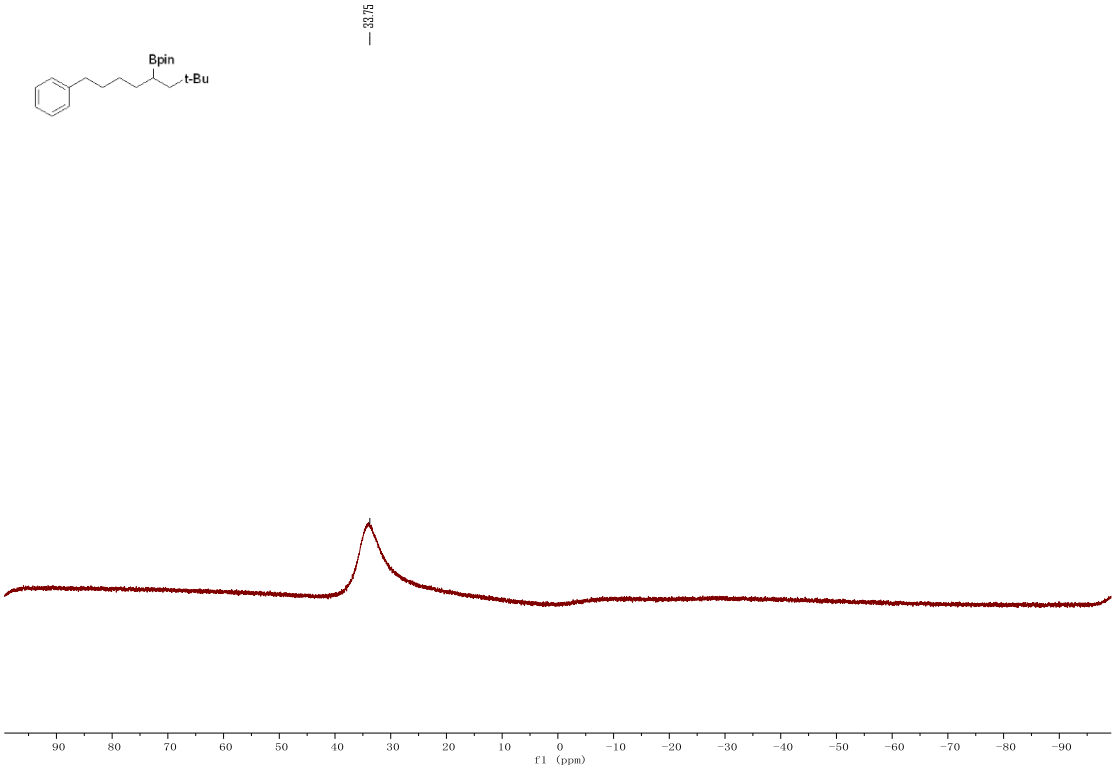
HRMS (ESI) calculated for $C_{22}H_{38}O_2B$ $[M+H]^+$: 345.2959, found: 345.2951.



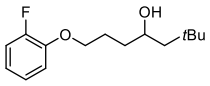
^{1}H NMR spectra for **9**



^{13}C NMR spectra for **9**



^{11}B NMR spectra for **9**



1-(2-fluorophenoxy)-6,6-dimethylheptan-4-ol (**10**)

Following general procedure 2. The product was isolated by column chromatography as colorless oil (31.0 mg, 0.122 mmol, 61%).

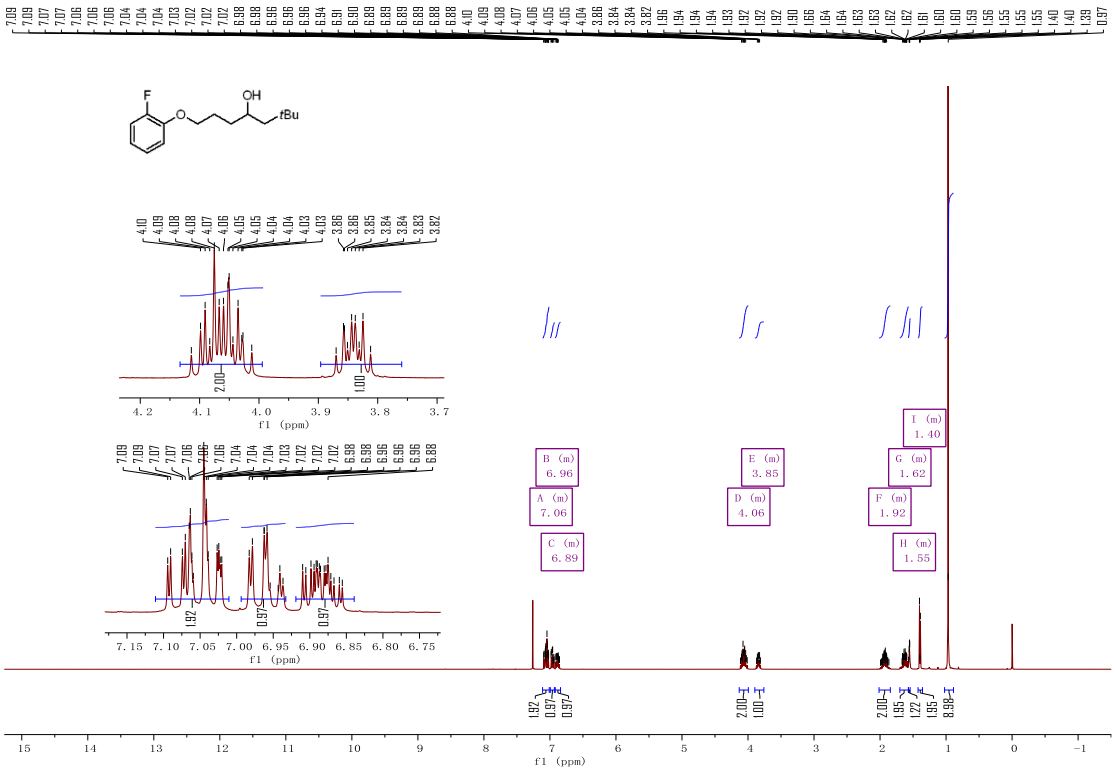
Rf (petroleum ether : ethyl acetate = 5 : 1) = 0.45

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.10 – 7.01 (m, 2H), 7.01 – 6.91 (m, 1H), 6.92 – 6.84 (m, 1H), 4.18 – 3.96 (m, 2H), 3.89 – 3.69 (m, 1H), 2.05 – 1.82 (m, 2H), 1.72 – 1.57 (m, 2H), 1.59 – 1.52 (m, 1H), 1.42 – 1.37 (m, 2H), 0.97 (s, 9H).

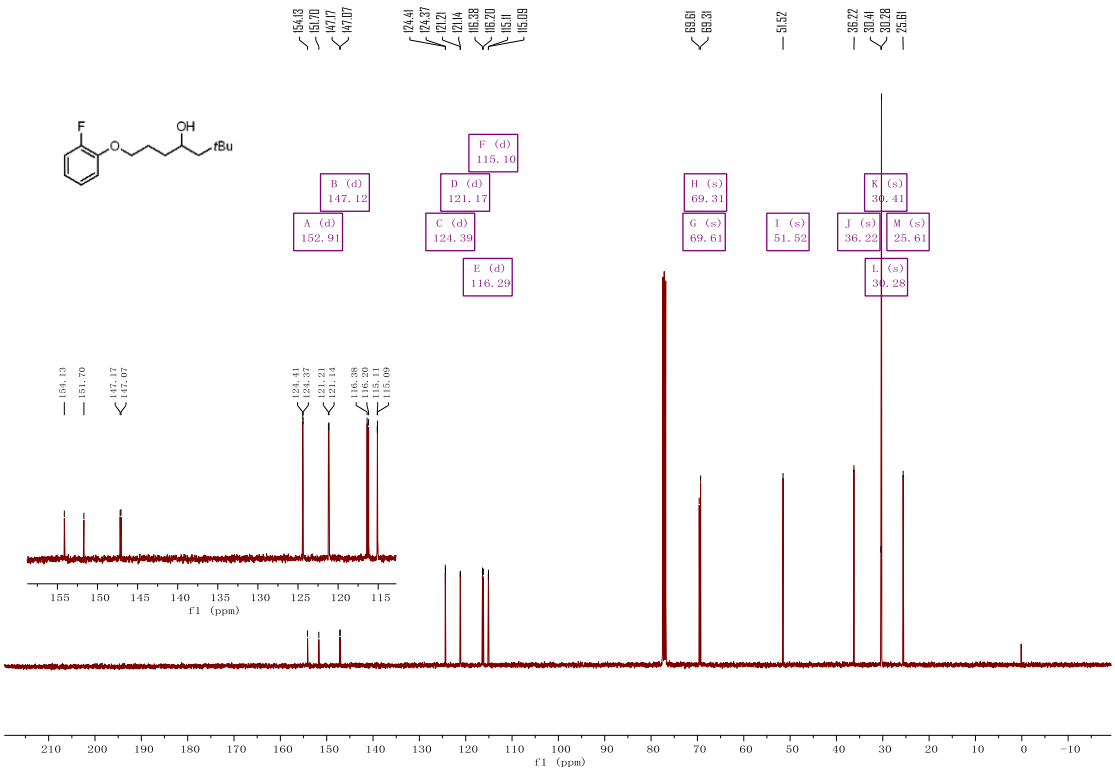
^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.91 (d, *J* = 245.2 Hz), 147.12 (d, *J* = 10.6 Hz), 124.39 (d, *J* = 3.9 Hz), 121.17 (d, *J* = 6.9 Hz), 116.29 (d, *J* = 18.3 Hz), 115.10 (d, *J* = 1.9 Hz), 69.61, 69.31, 51.52, 36.22, 30.41, 30.28, 25.61.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -134.75 – -134.83 (m).

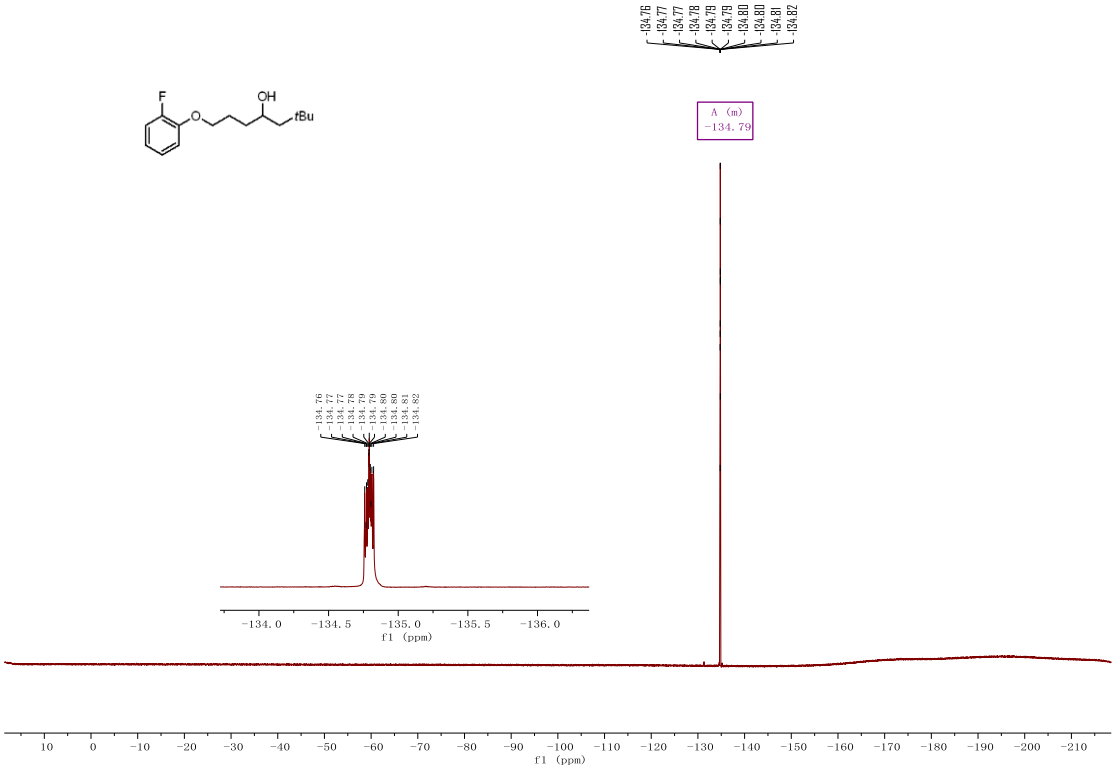
HRMS (ESI) calculated for $C_{15}H_{23}FO_2$ $[M+Na]^+$: 277.1574, found: 277.1580.



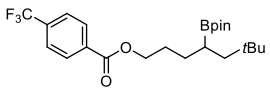
^{1}H NMR spectra for **10**



^{13}C NMR spectra for **10**



^{19}F NMR spectra for **10**



6,6-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptyl 4-(trifluoromethyl)benzoate (**11**)

Following general procedure 1. The product was isolated by column chromatography as colorless oil (64.6 mg, 0.146 mmol, 73%).

Rf (petroleum ether : acetone = 15 : 1) = 0.6

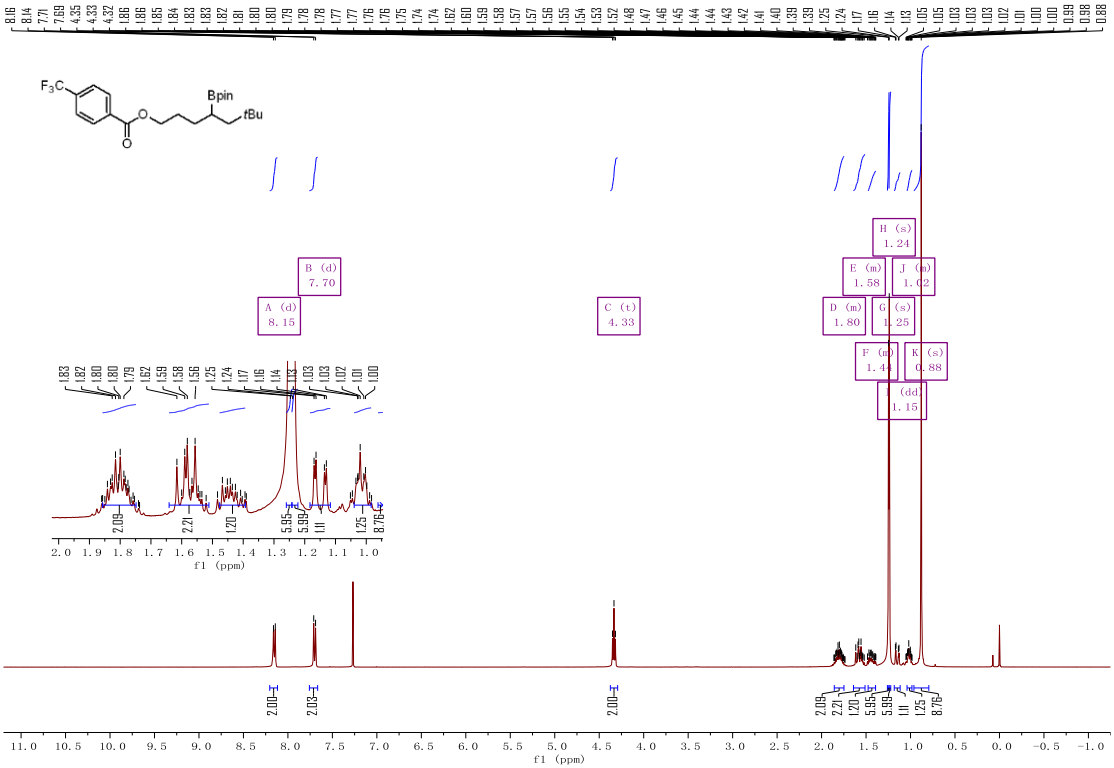
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.15 (d, *J* = 8.1 Hz, 2H), 7.70 (d, *J* = 8.2 Hz, 2H), 4.33 (t, *J* = 6.6 Hz, 2H), 1.86 – 1.73 (m, 2H), 1.64 – 1.51 (m, 2H), 1.49 – 1.37 (m, 1H), 1.25 (s, 6H), 1.24 (s, 6H), 1.15 (dd, *J* = 13.4, 2.6 Hz, 1H), 1.07 – 0.96 (m, 1H), 0.88 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 165.54, 134.42 (q, *J* = 32.7 Hz), 133.89, 130.09, 125.47 (q, *J* = 3.7 Hz), 123.81 (d, *J* = 272.5 Hz), 83.14, 66.01, 45.88, 31.14, 29.97, 29.80, 28.23, 25.02, 24.97.

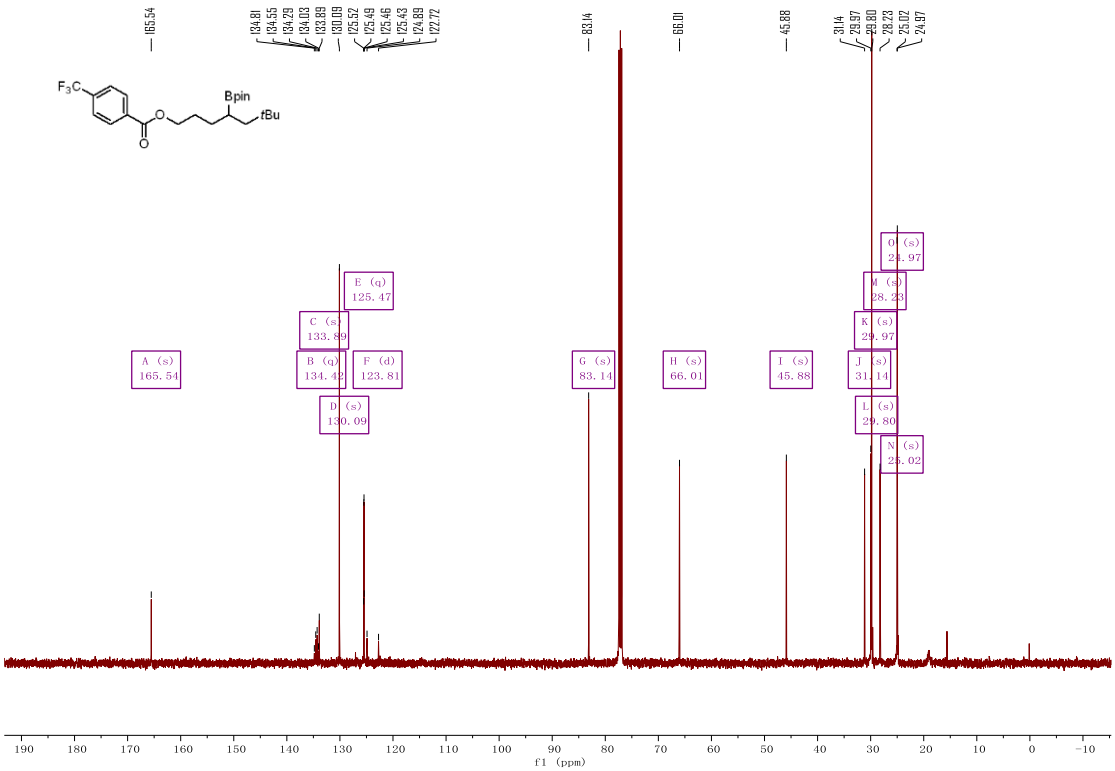
^{19}F NMR (376 MHz, Chloroform-*d*) δ -63.08.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 35.40.

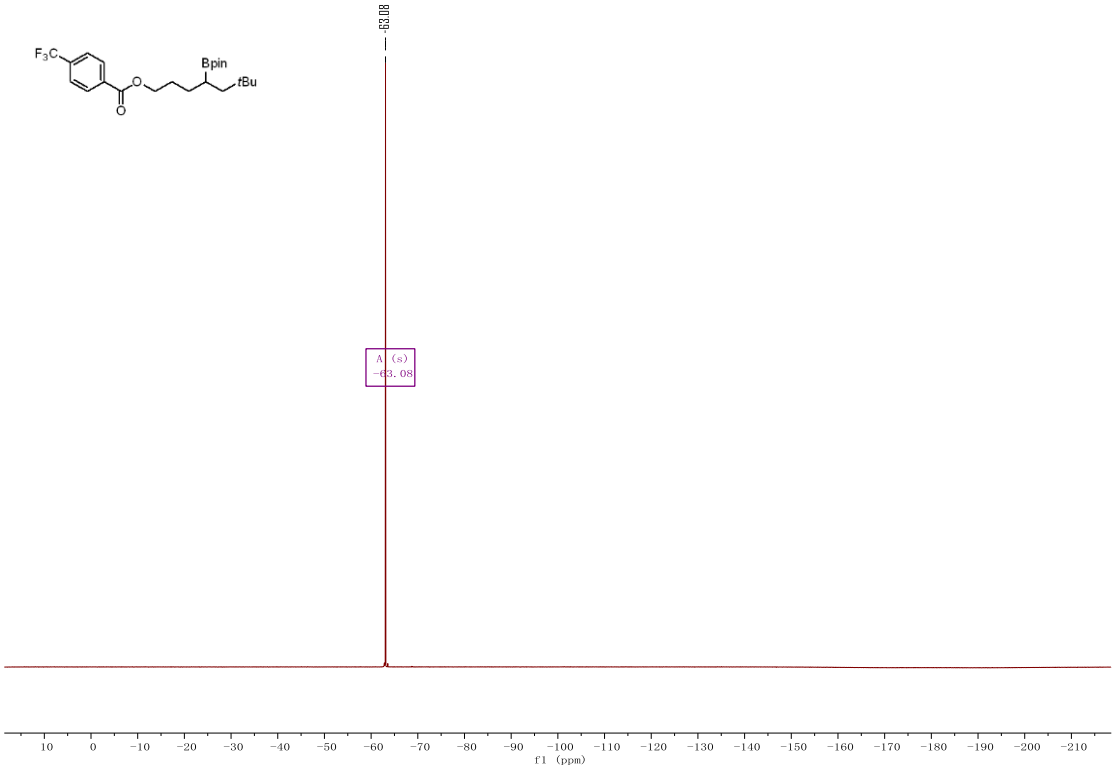
HRMS (ESI) calculated for $C_{23}H_{34}BF_3O_4$ $[M+H]^+$: 443.2575, found: 443.2567.



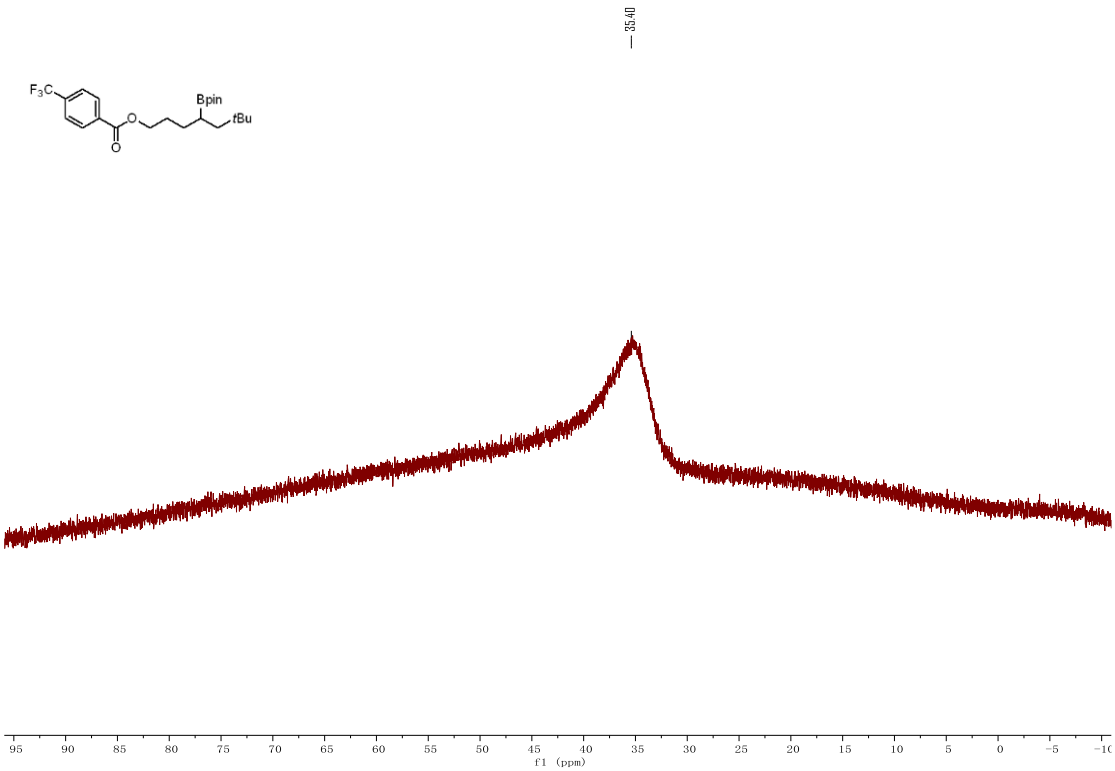
^{1}H NMR spectra for **11**



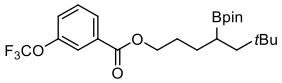
^{13}C NMR spectra for **11**



^{19}F NMR spectra for **11**



^{11}B NMR spectra for **11**



6,6-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptyl 3-(trifluoromethoxy)benzoate (**12**)

Following general procedure 1. The product was isolated by column chromatography as colorless oil (62.3 mg, 0.136 mmol, 68%).

Rf (petroleum ether : acetone = 15 : 1) = 0.50

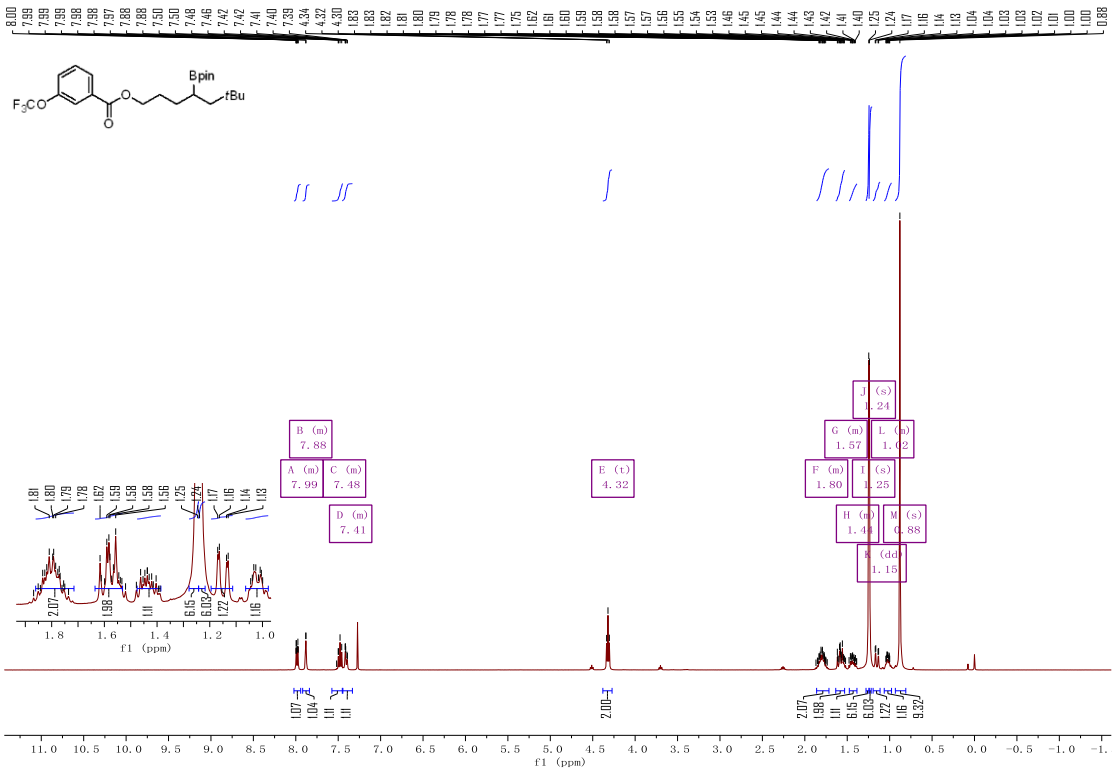
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 – 7.95 (m, 1H), 7.91 – 7.85 (m, 1H), 7.54 – 7.44 (m, 1H), 7.44 – 7.37 (m, 1H), 4.32 (t, *J* = 6.5 Hz, 2H), 1.87 – 1.73 (m, 2H), 1.65 – 1.51 (m, 2H), 1.50 – 1.37 (m, 1H), 1.25 (s, 6H), 1.24 (s, 6H), 1.15 (dd, *J* = 13.4, 2.5 Hz, 1H), 1.05 – 0.98 (m, 1H), 0.88 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.37, 149.32 (d, *J* = 1.9 Hz), 132.75, 129.96, 128.06, 125.35, 122.22, 120.55 (q, *J* = 258.0 Hz), 83.12, 65.96, 45.86, 31.14, 29.97, 29.79, 28.22, 25.00, 24.95, 19.04.

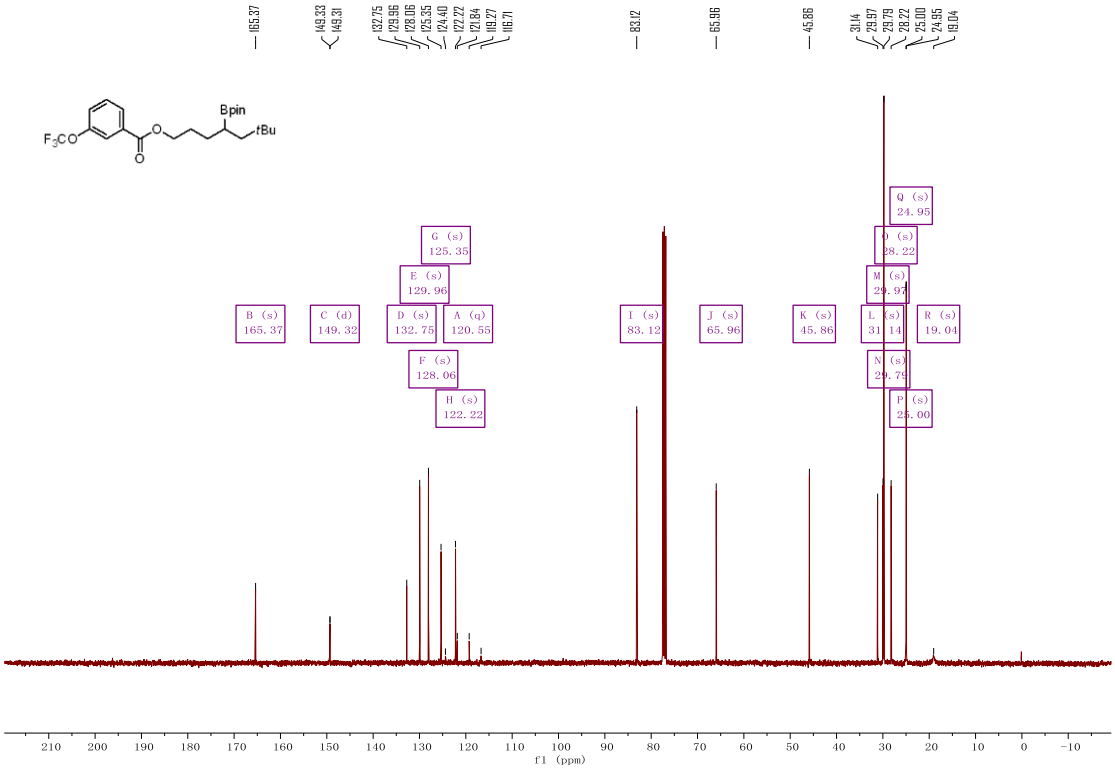
^{19}F NMR (376 MHz, Chloroform-*d*). δ -57.93.

^{11}B NMR (128 MHz, Chloroform-*d*). δ 35.42.

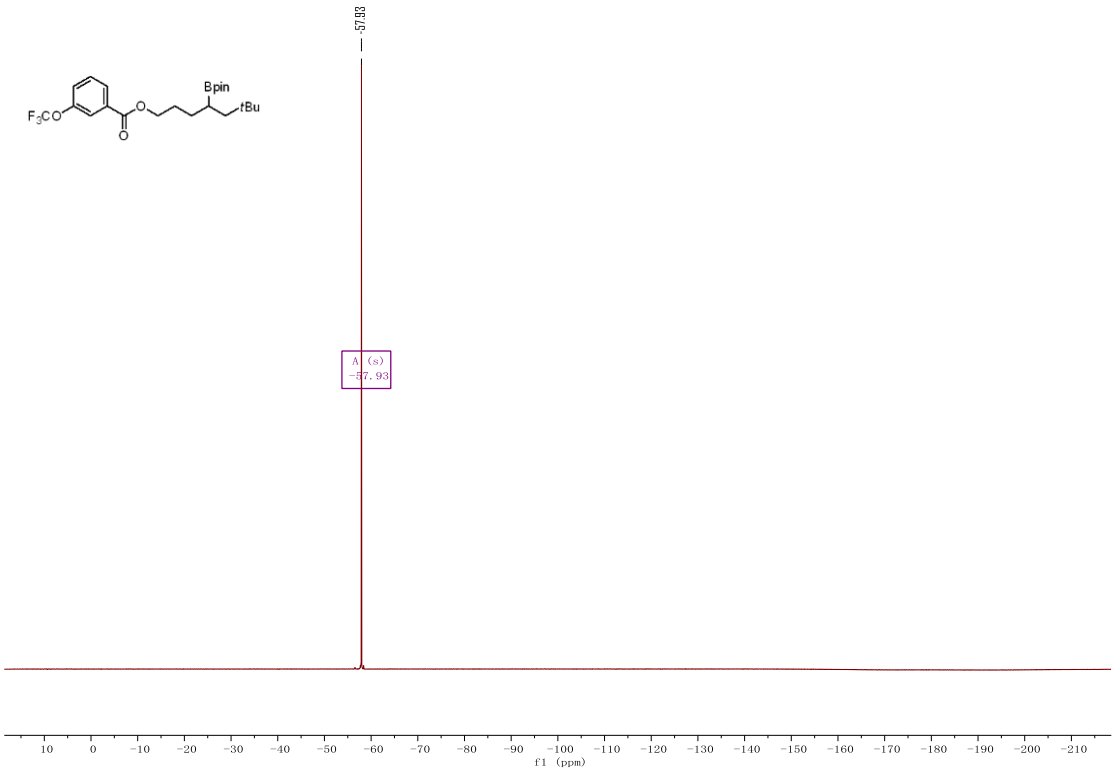
HRMS (ESI) calculated for $C_{23}H_{34}BF_3O_5$ $[M+H]^+$: 459.2524, found: 459.2511



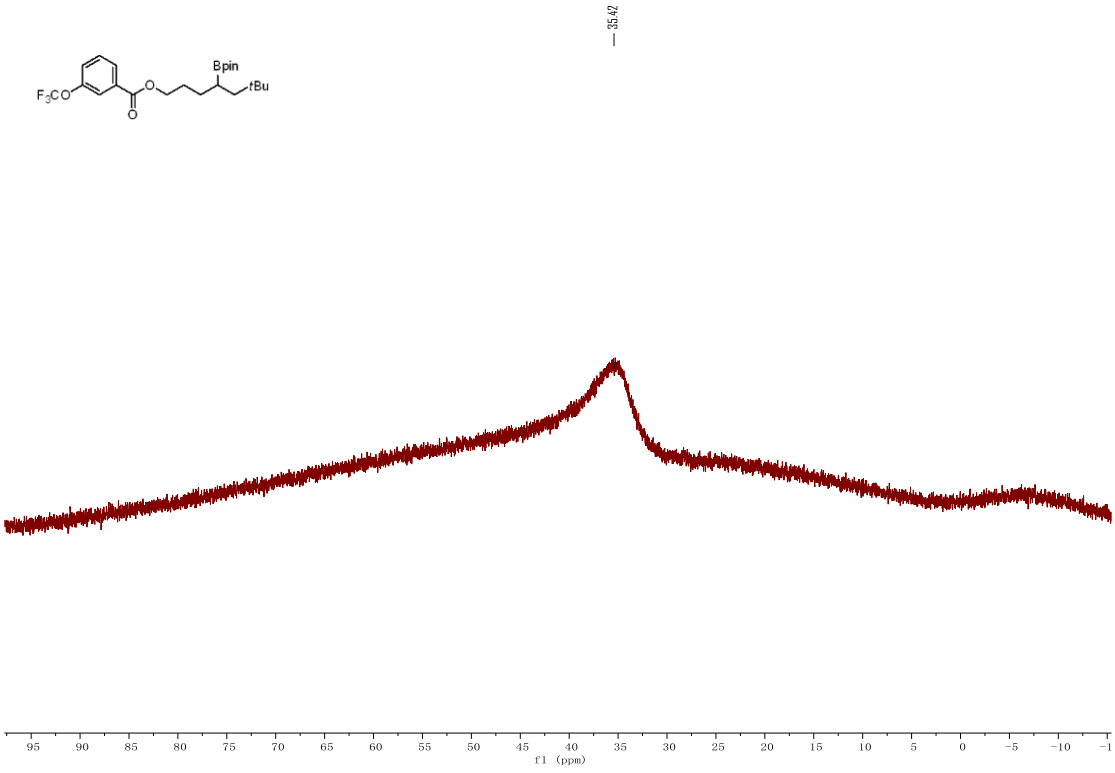
^{1}H NMR spectra for **12**



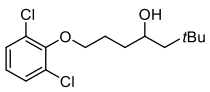
^{13}C NMR spectra for **12**



^{19}F NMR spectra for **12**



^{11}B NMR spectra for **12**



1-(2,6-dichlorophenoxy)-6,6-dimethylheptan-4-ol (**13**)

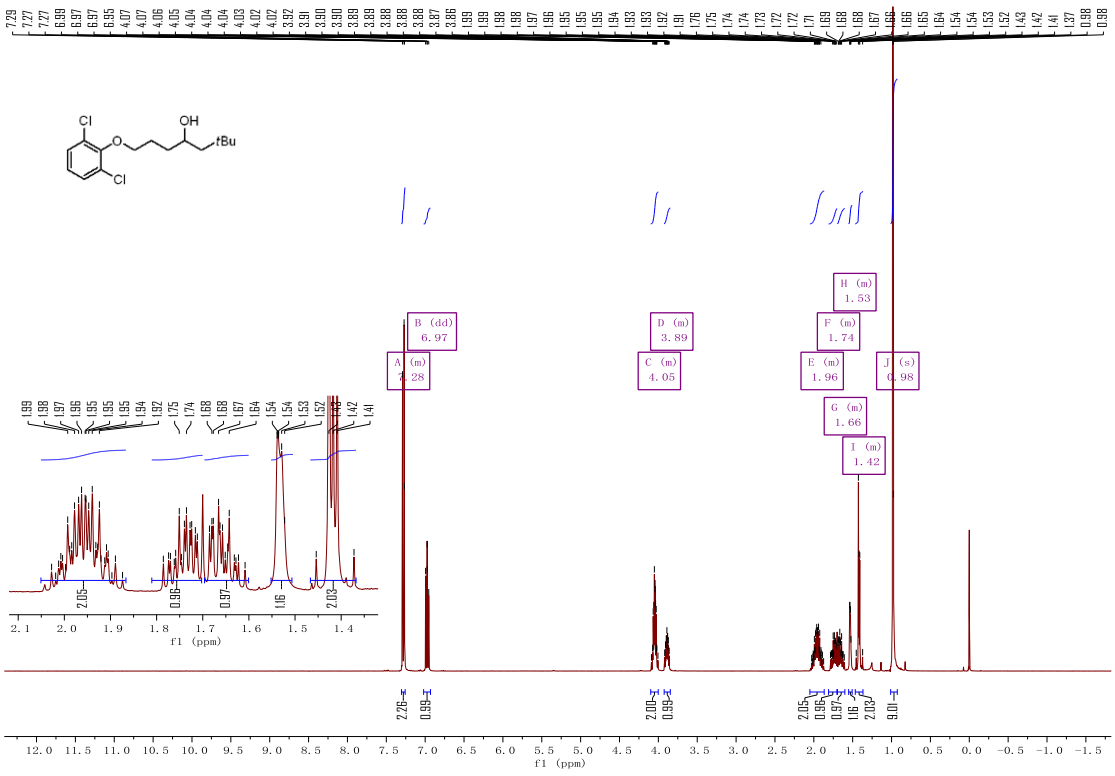
Following general procedure 2. The product was isolated by column chromatography as colorless oil (39.1 mg, 0.128 mmol, 64%).

Rf (petroleum ether : ethyl acetate = 5 : 1) = 0.45

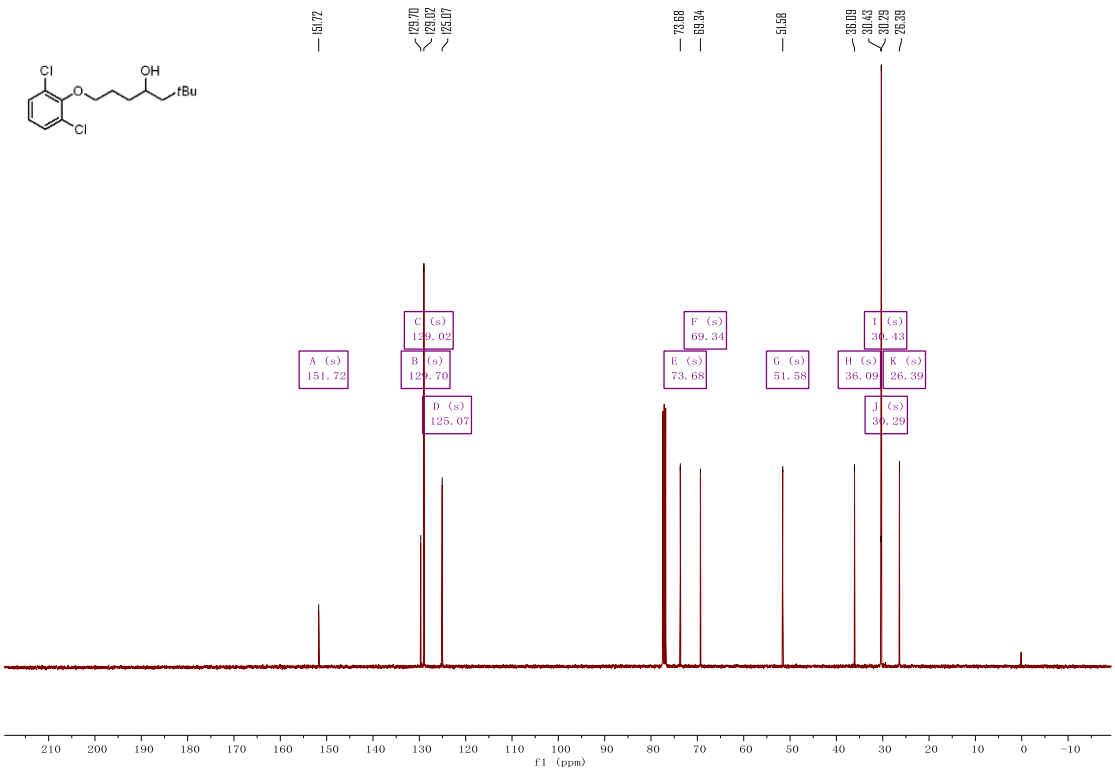
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.24 (m, 2H), 6.97 (dd, *J* = 8.4, 7.8 Hz, 1H), 4.13 – 3.98 (m, 2H), 3.94 – 3.84 (m, 1H), 2.04 – 1.86 (m, 2H), 1.79 – 1.70 (m, 1H), 1.69 – 1.60 (m, 1H), 1.56 – 1.49 (m, 1H), 1.46 – 1.34 (m, 2H), 0.98 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.72, 129.70, 129.02, 125.07, 73.68, 69.34, 51.58, 36.09, 30.43, 30.29, 26.39.

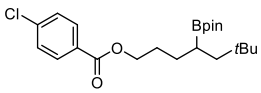
HRMS (ESI) calculated for $C_{15}H_{22}Cl_2O_2$ $[M+H]^+$: 305.1070, found: 305.1075



^{1}H NMR spectra for **13**



^{13}C NMR spectra for **13**



6,6-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptyl 4-chlorobenzoate (**14**)

Following general procedure 1. The product was isolated by column chromatography as colorless oil (65.4 mg, 0.160 mmol, 80%).

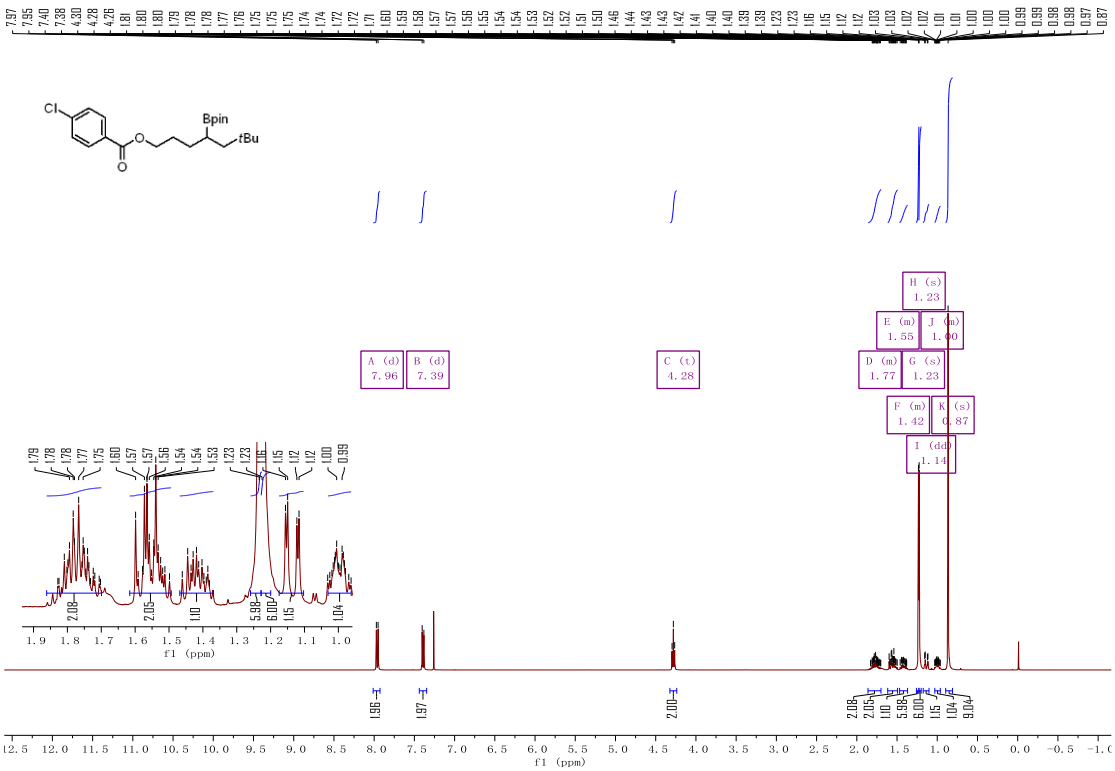
Rf (petroleum ether : acetone = 20 : 1) = 0.4

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 8.6 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 4.28 (t, *J* = 6.5 Hz, 2H), 1.86 – 1.69 (m, 2H), 1.62 – 1.49 (m, 2H), 1.46 – 1.38 (m, 1H), 1.23 (s, 6H), 1.23 (s, 6H), 1.14 (dd, *J* = 13.4, 2.5 Hz, 1H), 1.04 – 0.96 (m, 1H), 0.87 (s, 9H).

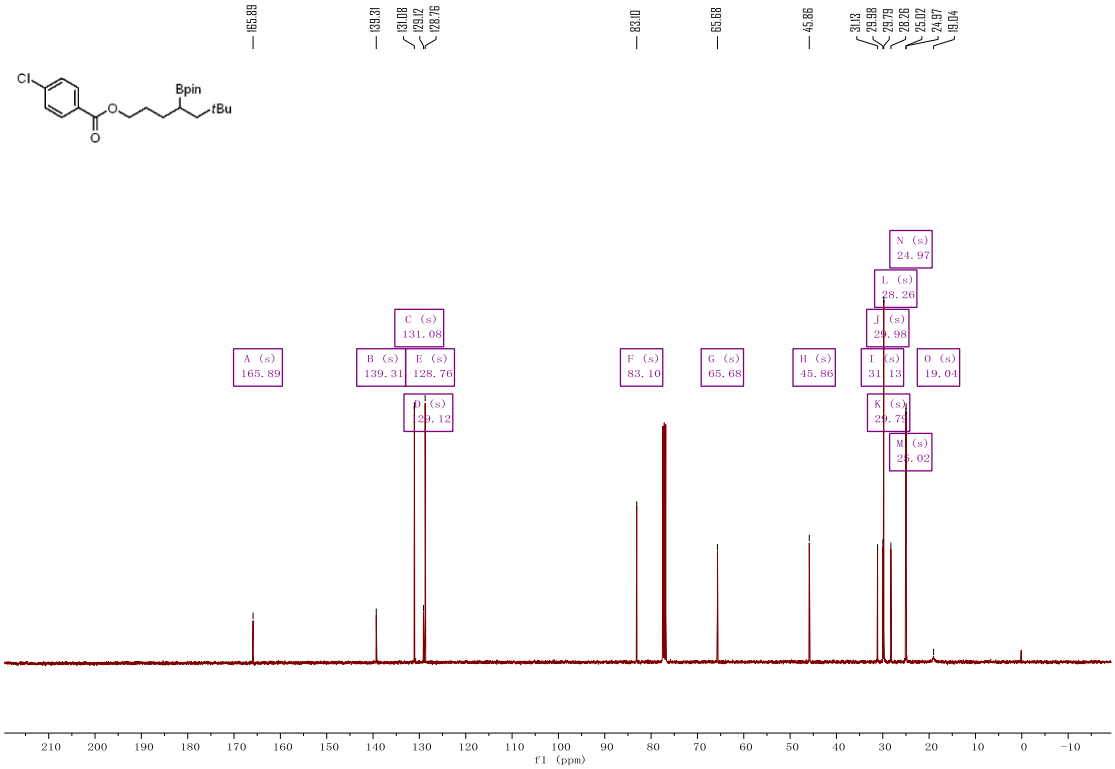
^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.89, 139.31, 131.08, 129.12, 128.76, 83.10, 65.68, 45.86, 31.13, 29.98, 29.79, 28.26, 25.02, 24.97, 19.04.

^{11}B NMR (128 MHz, Chloroform-*d*). δ 34.04.

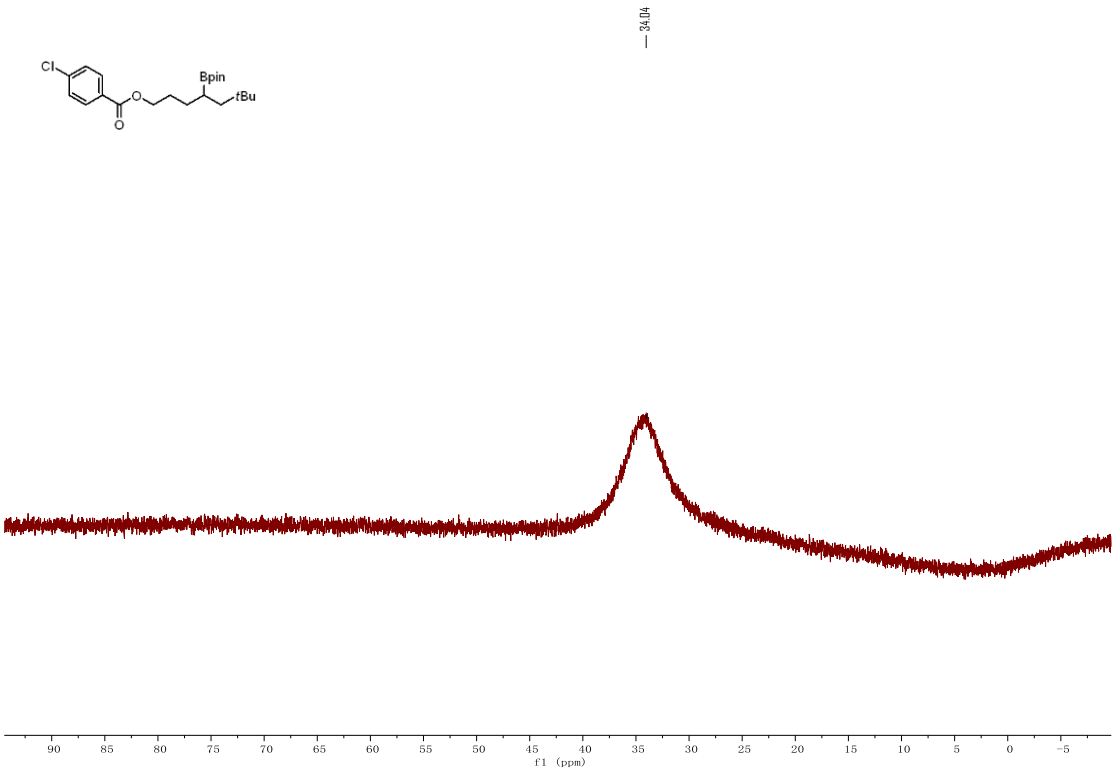
HRMS (ESI) calculated for $C_{23}H_{34}BClO_4$ $[M+H]^+$: 409.2311, found: 409.2317



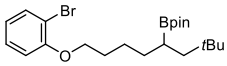
^{1}H NMR spectra for **14**



^{13}C NMR spectra for **14**



^{11}B NMR spectra for **14**



2-(8-(2-bromophenoxy)-2,2-dimethyloctan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**15**)

Following general procedure 1. The product was isolated by column chromatography as colorless oil (61.5 mg, 0.140 mmol, 70%).

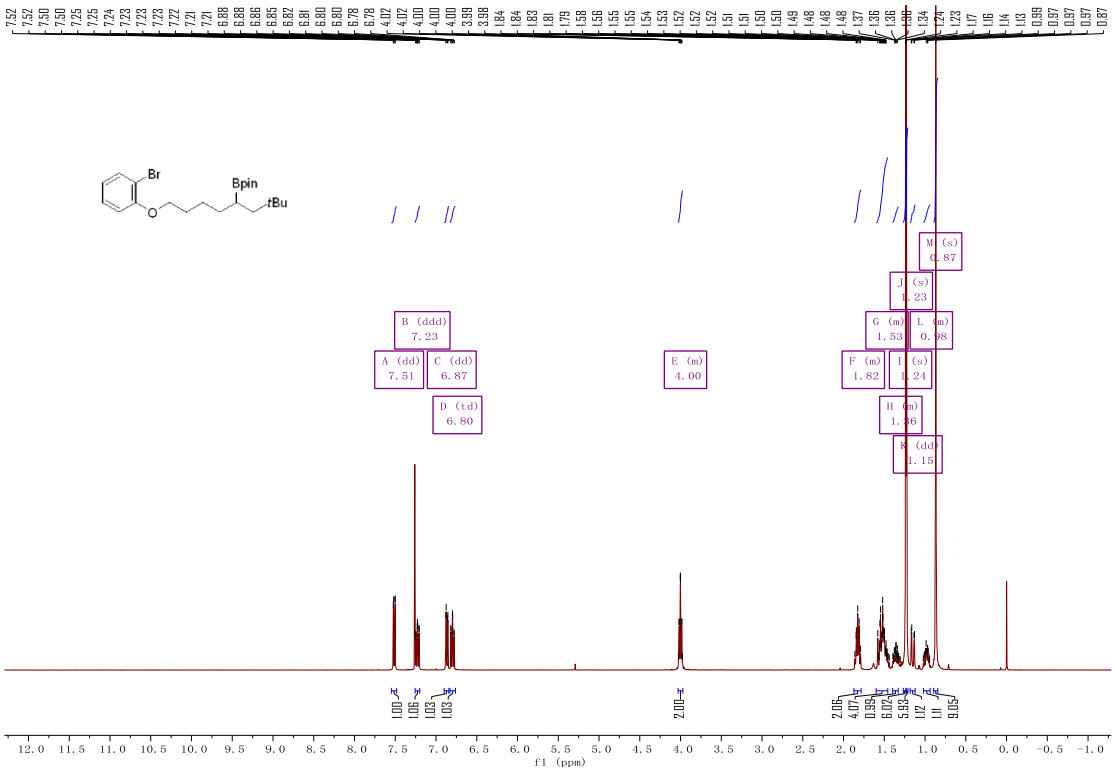
Rf (petroleum ether : acetone = 20 : 1) = 0.5

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.23 (ddd, *J* = 8.2, 7.4, 1.7 Hz, 1H), 6.87 (dd, *J* = 8.3, 1.4 Hz, 1H), 6.80 (td, *J* = 7.6, 1.4 Hz, 1H), 4.06 – 3.94 (m, 2H), 1.90 – 1.77 (m, 2H), 1.60 – 1.43 (m, 4H), 1.42 – 1.28 (m, 1H), 1.24 (s, 6H), 1.23 (s, 6H), 1.15 (dd, *J* = 13.4, 2.5 Hz, 1H), 1.04 – 0.92 (m, 1H), 0.87 (s, 9H).

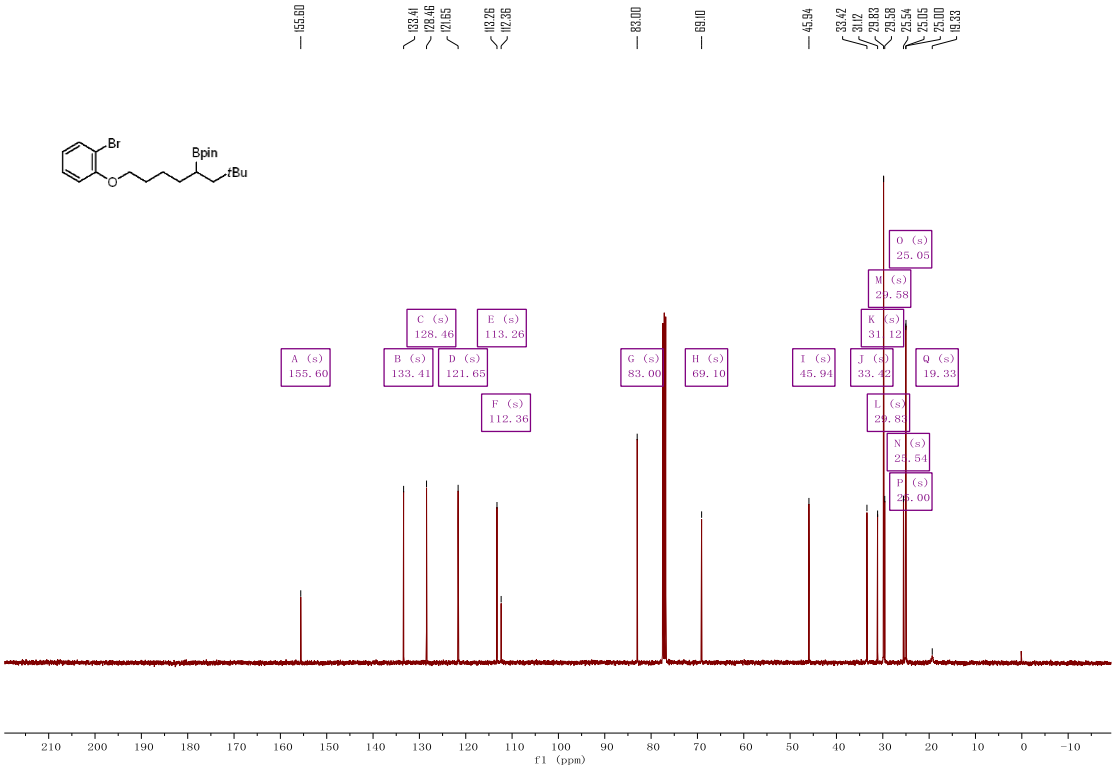
^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.60, 133.41, 128.46, 121.65, 113.26, 112.36, 83.00, 69.10, 45.94, 33.42, 31.12, 29.83, 29.58, 25.54, 25.05, 25.00, 19.33.

^{11}B NMR (128 MHz, Chloroform-*d*). δ 33.87

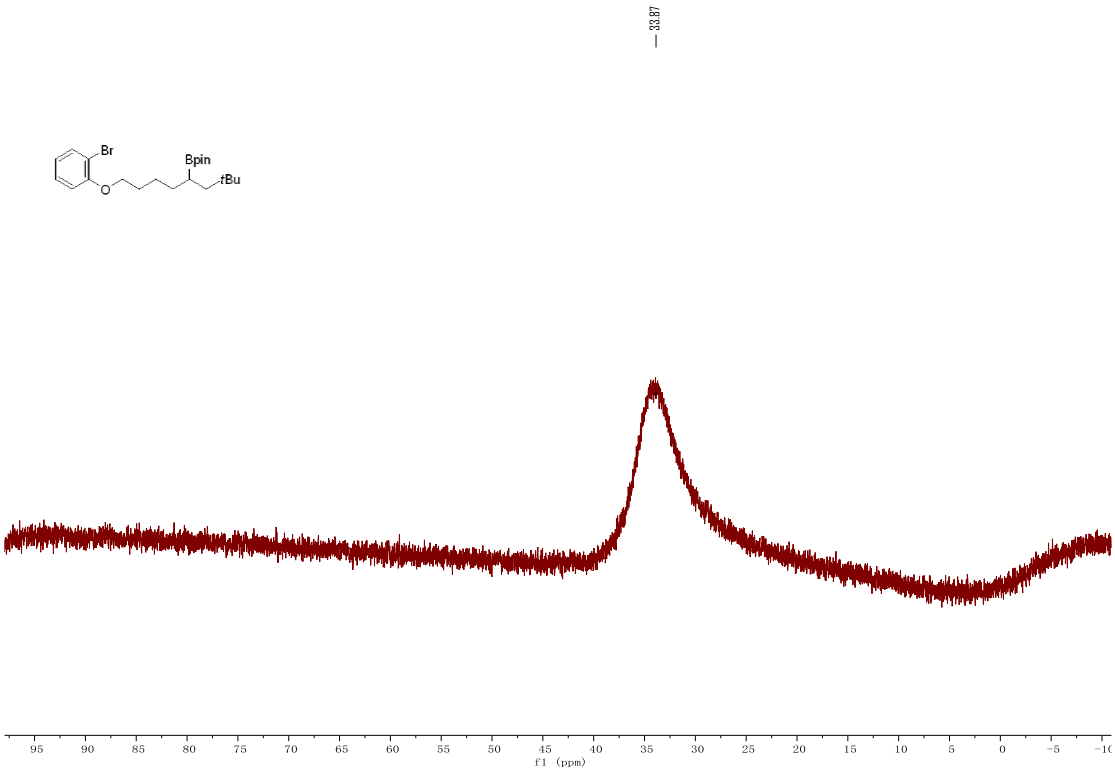
HRMS (ESI) calculated for $C_{22}H_{36}BBrO_3$ $[M+H]^+$: 439.2014, found: 439.2008



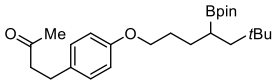
^{1}H NMR spectra for **15**



^{13}C NMR spectra for **15**



^{11}B NMR spectra for **15**



4-(4-((6,6-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptyl)oxy)phenyl)butan-2-one (**16**)

Following general procedure 1. The product was isolated by column chromatography as colorless oil (61.6 mg, 0.148 mmol, 74%).

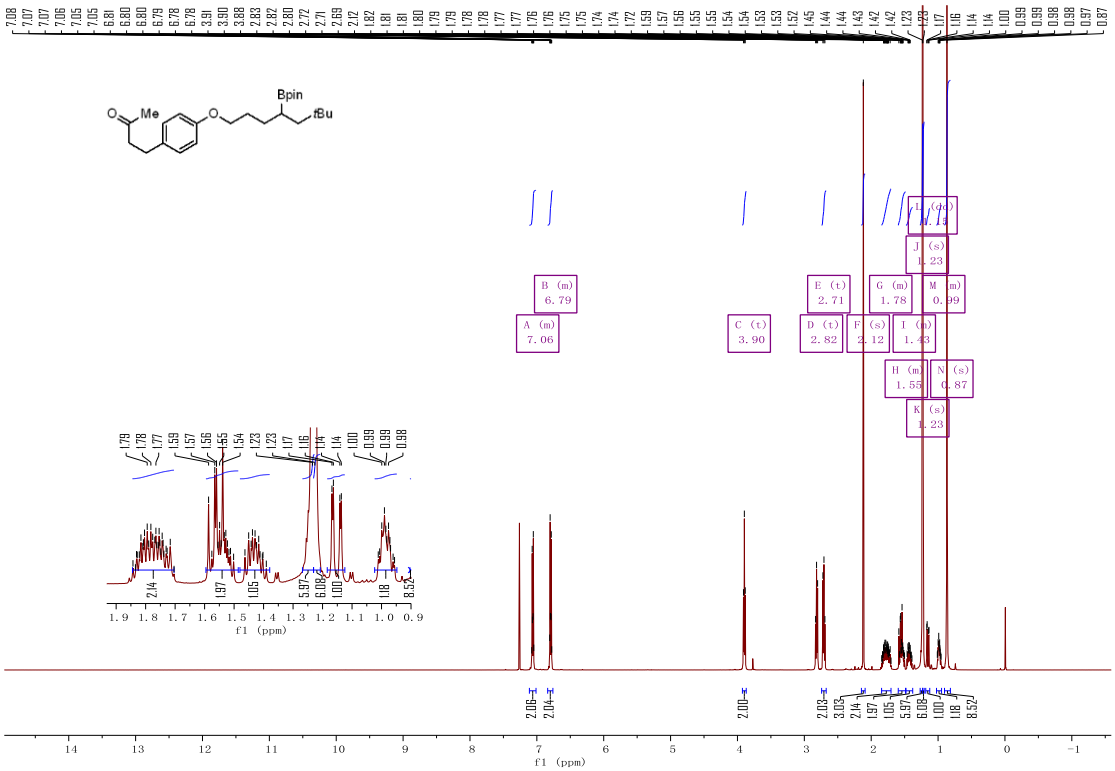
Rf (petroleum ether : ethyl acetate = 10 : 1) = 0.50

^{1}H NMR (500 MHz, Chloroform-*d*) 7.09 – 7.04 (m, 2H), 6.82 – 6.76 (m, 2H), 3.90 (t, *J* = 6.6 Hz, 2H), 2.82 (t, *J* = 7.5 Hz, 2H), 2.71 (t, *J* = 7.5 Hz, 2H), 2.12 (s, 3H), 1.87 – 1.69 (m, 2H), 1.59 – 1.49 (m, 1H), 1.48 – 1.37 (m, 1H), 1.23 (s, 6H), 1.23 (s, 6H), 1.15 (dd, *J* = 13.4, 2.5 Hz,1H), 1.02 – 0.95 (m, 1H), 0.87 (s, 9H).

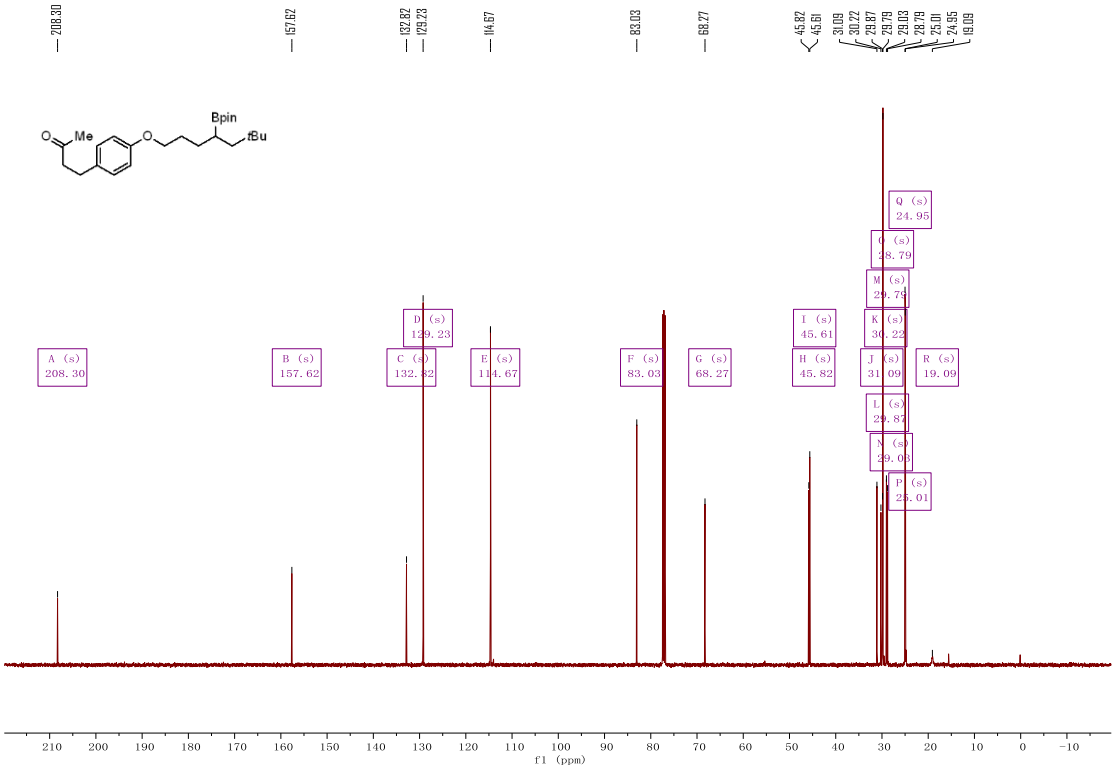
^{13}C NMR (126 MHz, Chloroform-*d*) δ 208.30, 157.62, 132.82, 129.23, 114.67, 83.03, 68.27, 45.82, 45.61, 31.09, 30.22, 29.87, 29.79, 29.03, 28.79, 25.01, 24.95, 19.09.

^{11}B NMR (128 MHz, Chloroform-*d*). δ 35.64

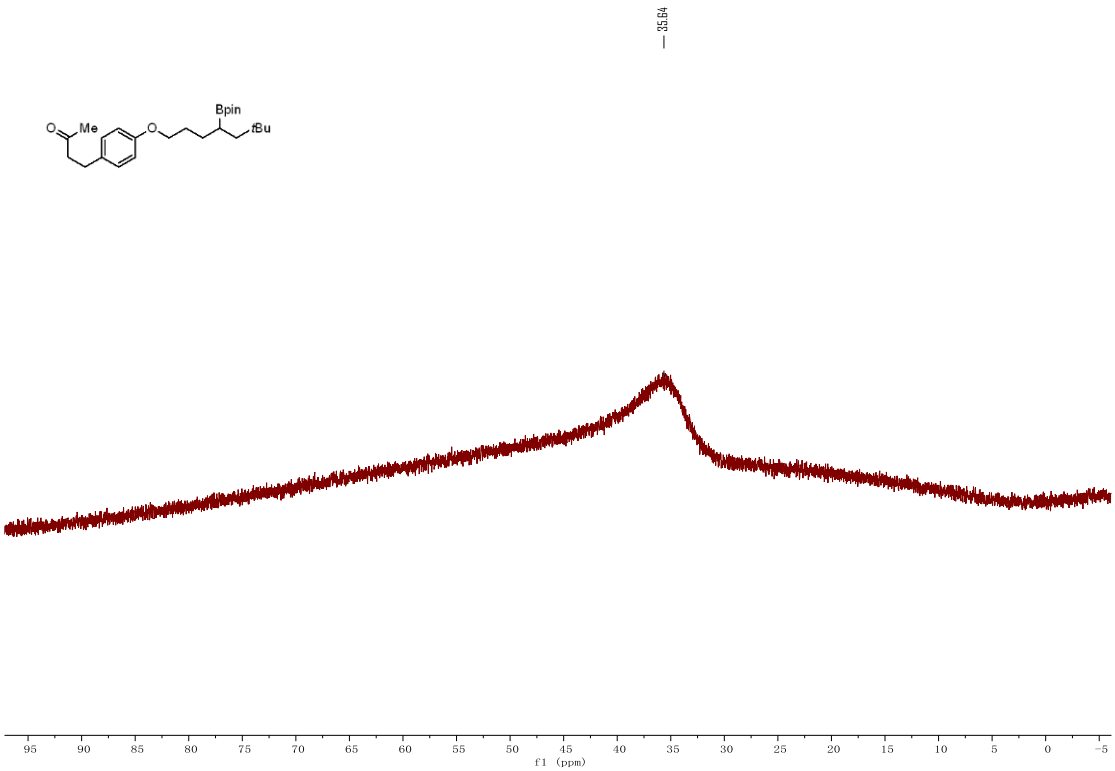
HRMS (ESI) calculated for $C_{25}H_{41}BO_4$ $[M+H]^+$: 417.3171, found: 417.3169



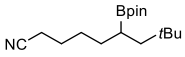
^{1}H NMR spectra for **16**



^{13}C NMR spectra for **16**



^{11}B NMR spectra for **16**



8,8-dimethyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nonanenitrile (**17**)
Following general procedure 1. The product was isolated by column chromatography as colorless oil (44.6 mg, 0.152 mmol, 76%).

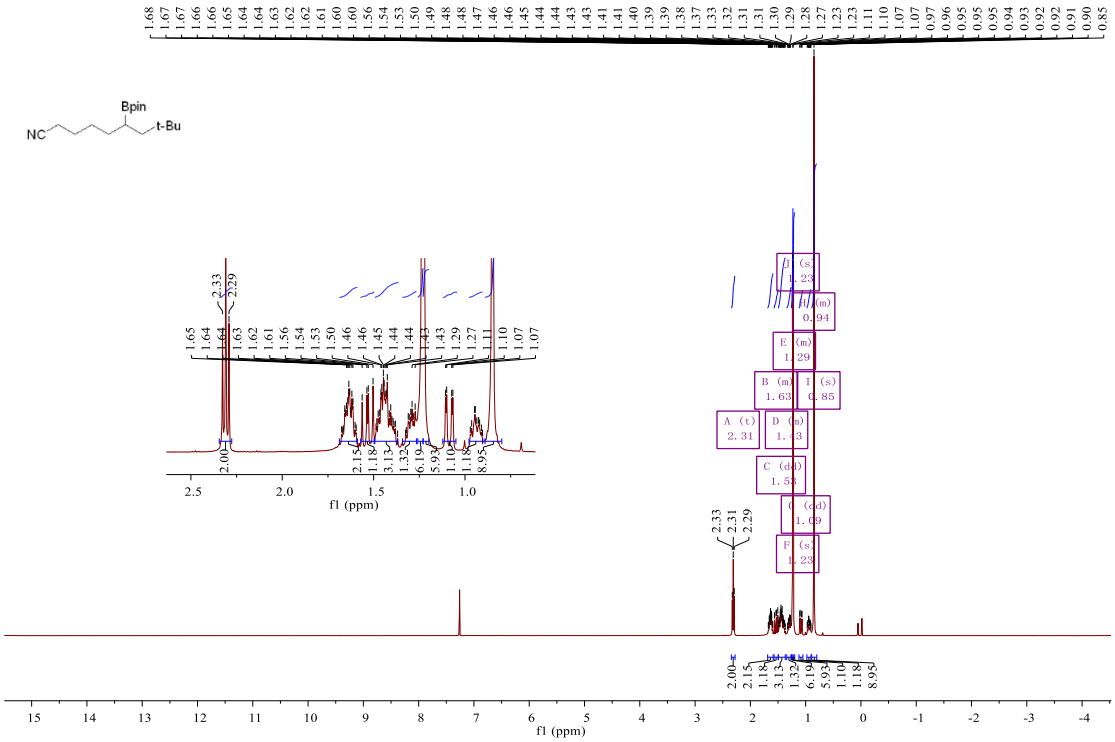
Rf (petroleum ether : ethyl acetate = 10 : 1) = 0.40

^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.31 (t, *J* = 7.1 Hz, 2H), 1.70 – 1.57 (m, 2H), 1.53 (dd, *J* = 13.4, 10.4 Hz, 1H), 1.51 – 1.36 (m, 3H), 1.35 – 1.25 (m, 1H), 1.23 (s, 6H), 1.23 (s, 6H), 1.09 (dd, *J* = 13.5, 2.6 Hz, 1H), 0.99 – 0.88 (m, 1H), 0.85 (s, 9H).

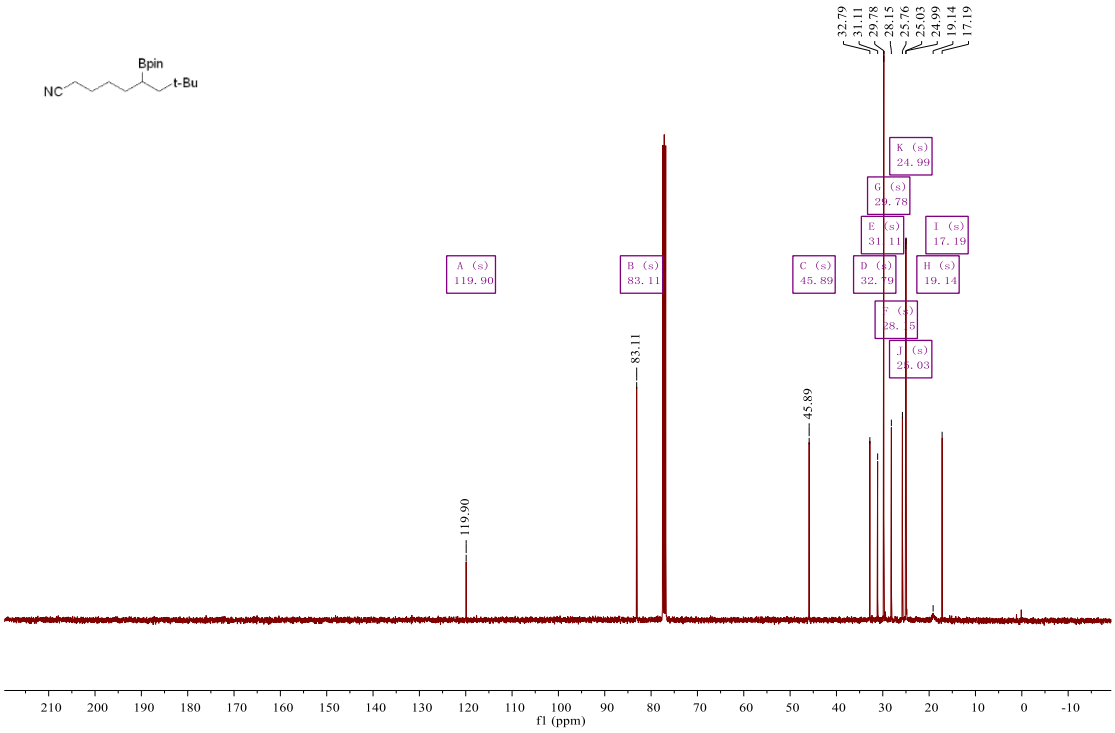
^{13}C NMR (101 MHz, Chloroform-*d*) δ 119.90, 83.11, 45.89, 32.79, 31.11, 29.78, 28.15, 25.76, 25.03, 24.99, 19.14, 17.19.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 34.06

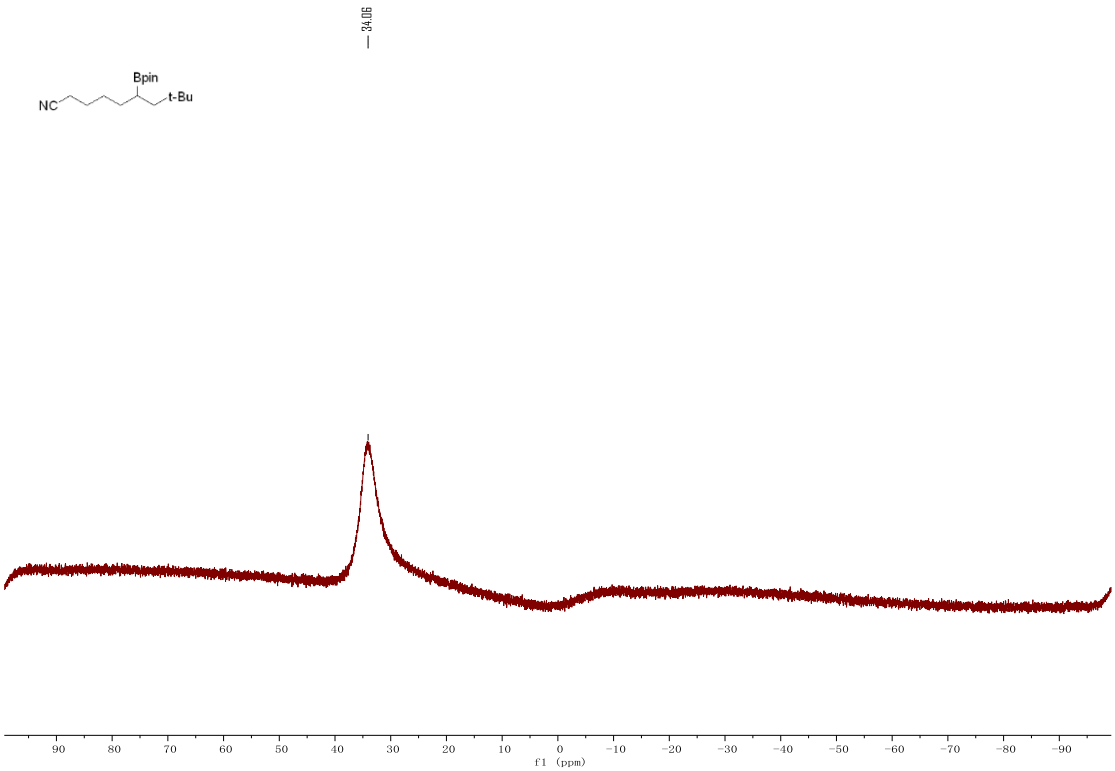
HRMS (ESI) calculated for $C_{17}H_{32}BNO_2$ $[M+H]^+$: 294.2599, found: 294.2595.



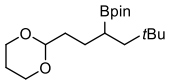
^{1}H NMR spectra for **17**



^{13}C NMR spectra for **17**



^{11}B NMR spectra for **17**



2-(1-(1,3-dioxan-2-yl)-5,5-dimethylhexan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**18**)

Following general procedure 1. The product was isolated by column chromatography as colorless oil (43.7 mg, 0.134 mmol, 67%).

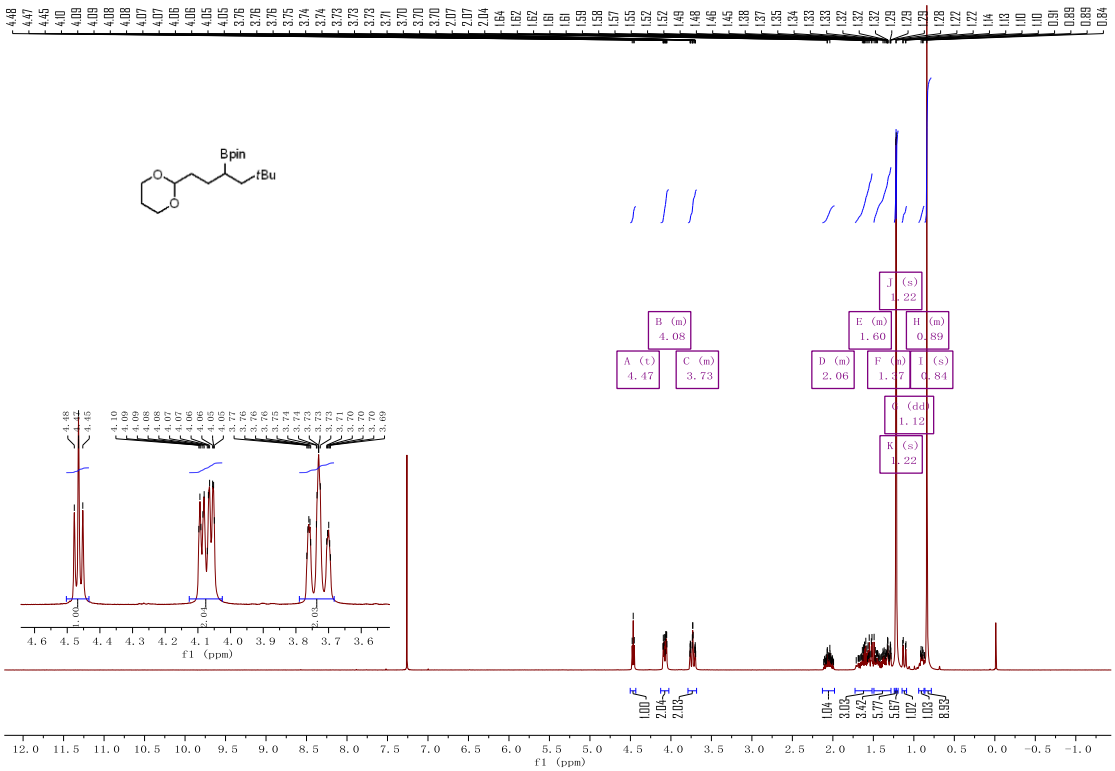
Rf (petroleum ether : ethyl acetate = 10 : 1) = 0.40

^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.47 (t, *J* = 5.2 Hz, 1H), 4.19 – 3.96 (m, 2H), 3.85 – 3.64 (m, 2H), 2.14 – 1.98 (m, 1H), 1.75 – 1.51 (m, 3H), 1.49 – 1.28 (m, 3H), 1.22 (s, 6H), 1.22 (s, 6H), 1.12 (dd, *J* = 13.5, 2.4 Hz, 1H), 0.93 – 0.87 (m, 1H), 0.84 (s, 9H).

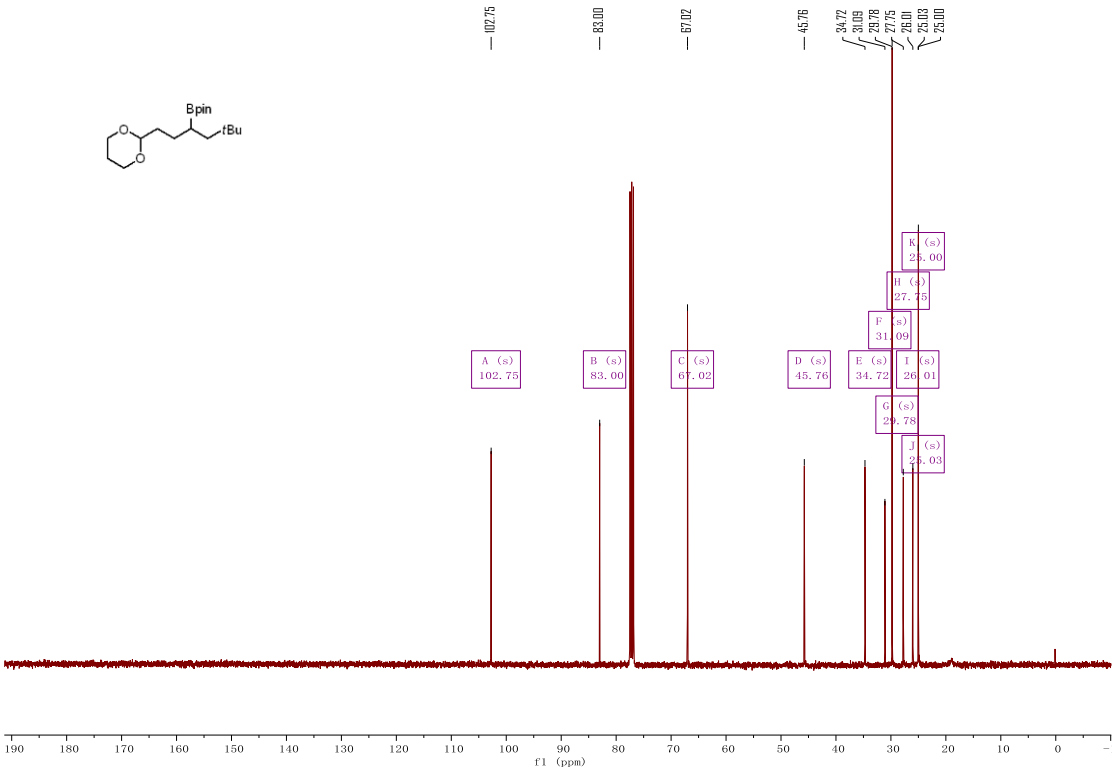
^{13}C NMR (101 MHz, Chloroform-*d*) δ 102.75, 83.00, 67.02, 45.76, 34.72, 31.09, 29.78, 27.75, 26.01, 25.03, 25.00.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 34.42

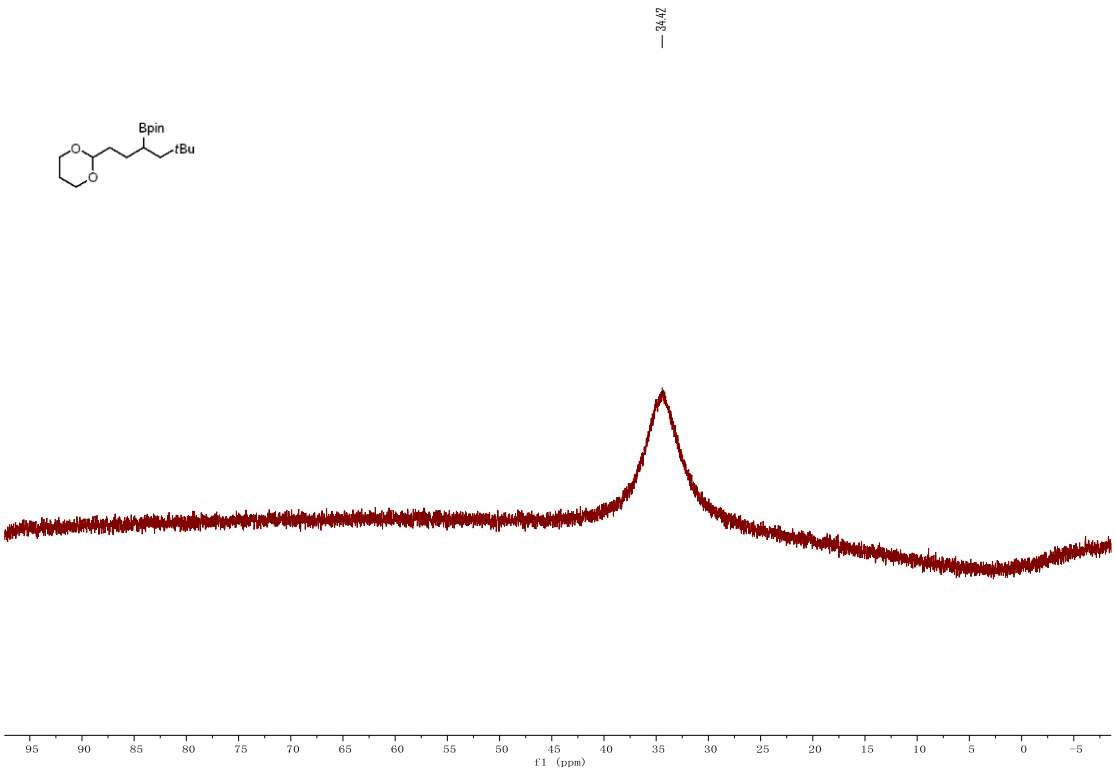
HRMS (ESI) calculated for $C_{18}H_{35}BO_4$ $[M+H]^+$: 327.2701, found: 327.2692.



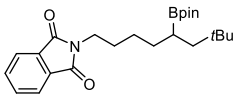
^{1}H NMR spectra for **18**



^{13}C NMR spectra for **18**



^{11}B NMR spectra for **18**



2-(7,7-dimethyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octyl)isoindoline-1,3-dione (**19**)

Following general procedure 1. The product was isolated by column chromatography as colorless oil (62.0 mg, 0.150 mmol, 75%).

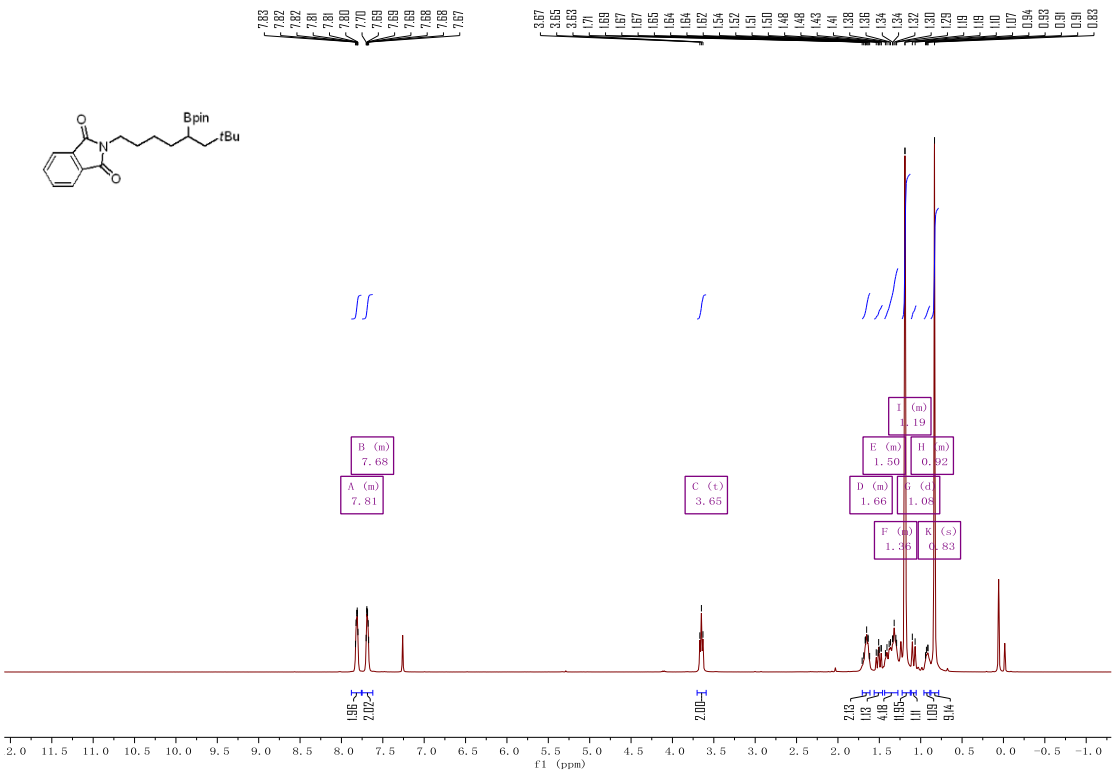
Rf (petroleum ether : ethyl acetate = 5 : 1) = 0.55

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 – 7.78 (m, 2H), 7.72 – 7.64 (m, 2H), 3.65 (t, *J* = 7.5 Hz, 2H), 1.73 – 1.59 (m, 2H), 1.57 – 1.45 (m, 1H), 1.45 – 1.27 (m, 4H), 1.23 – 1.14 (m, 12H), 1.08 (d, *J* = 13.4 Hz, 1H), 0.96 – 0.89 (m, 1H), 0.83 (s, 12H).

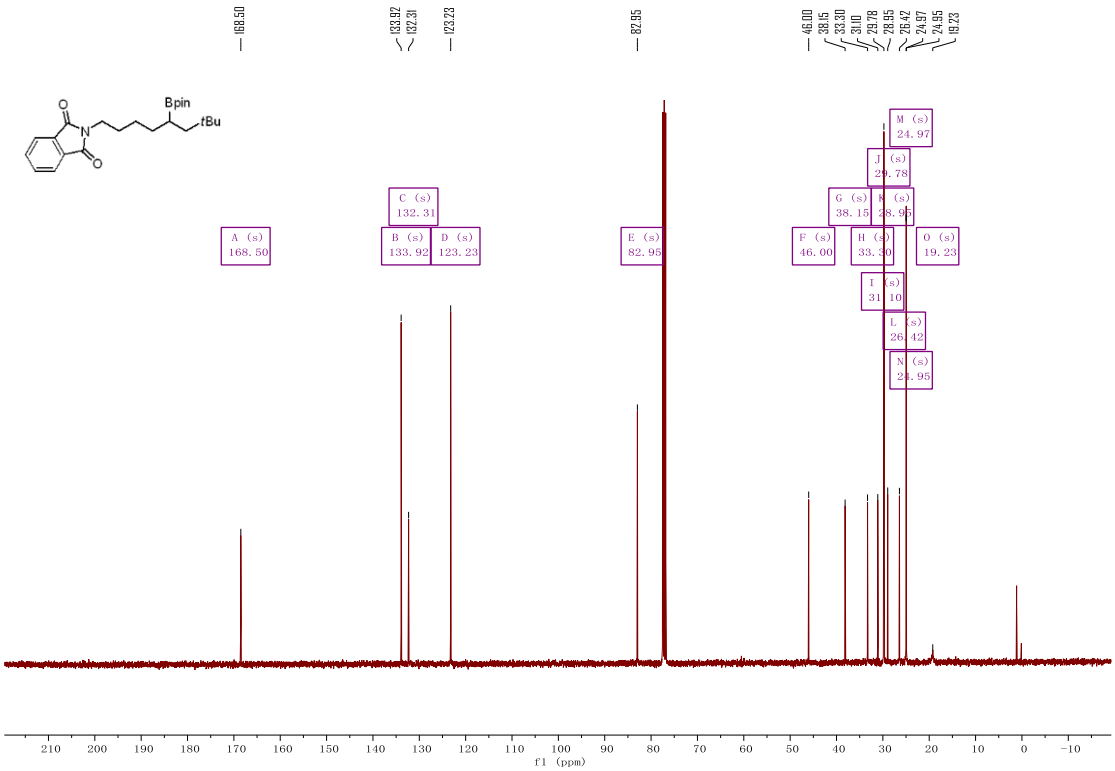
^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.50, 133.92, 132.31, 123.23, 82.95, 46.00, 38.15, 33.30, 31.10, 29.78, 28.95, 26.42, 24.97, 24.95, 19.23.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 35.04

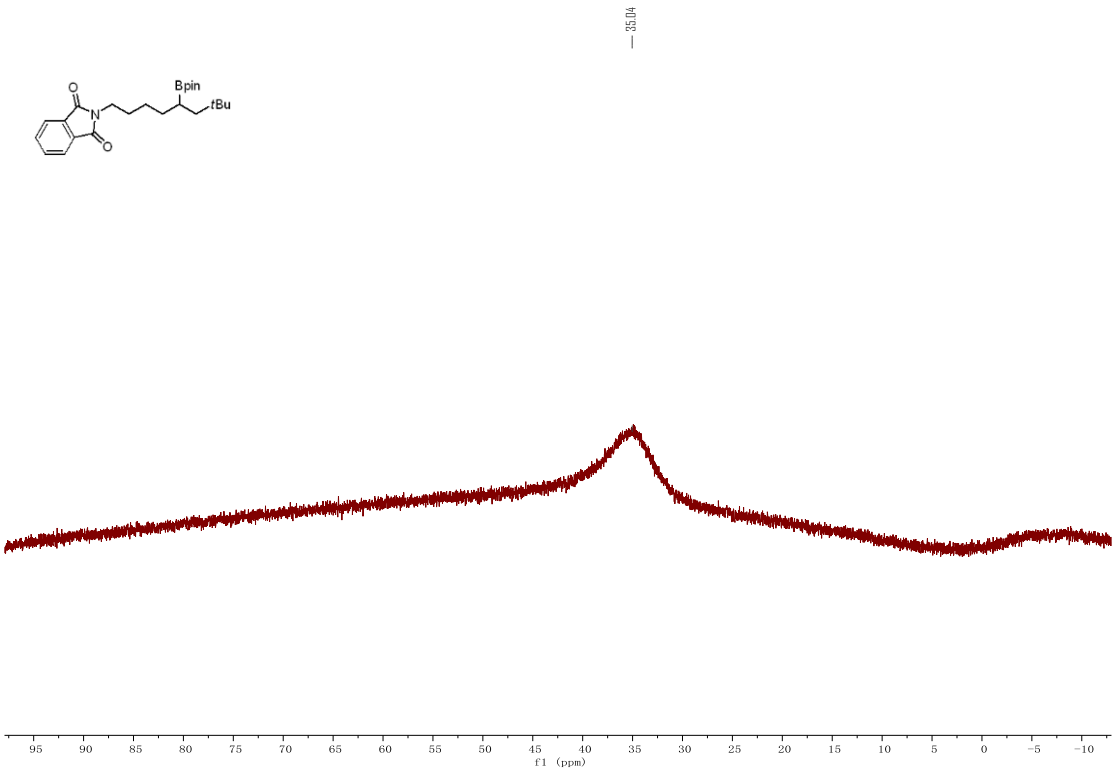
HRMS (ESI) calculated for $C_{24}H_{36}BNO_4$ $[M+H]^+$: 414.2810, found: 414.2799.



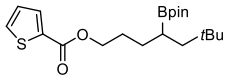
^{1}H NMR spectra for **19**



^{13}C NMR spectra for **19**



^{11}B NMR spectra for **19**



6,6-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptyl thiophene-2-carboxylate (**20**)

Following general procedure 1. The product was isolated by column chromatography as colorless oil (53.2 mg, 0.140 mmol, 70%).

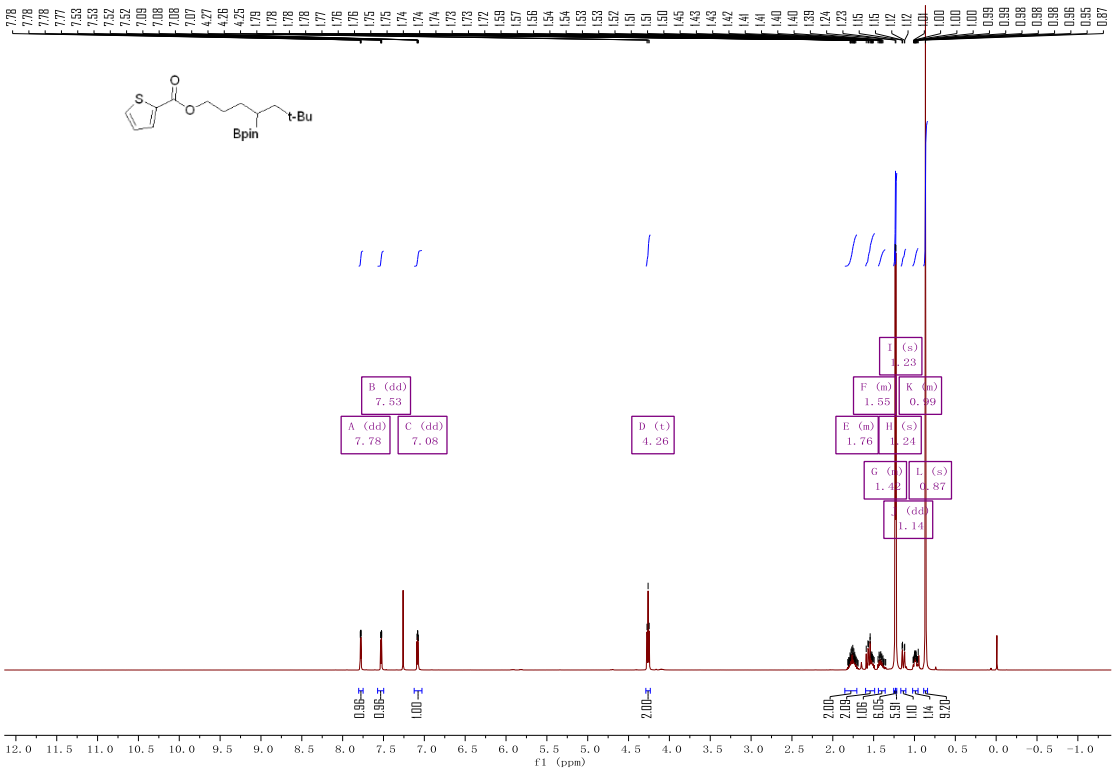
Rf (petroleum ether : ethyl acetate = 10 : 1) = 0.45

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.78 (dd, *J* = 3.7, 1.3 Hz, 1H), 7.53 (dd, *J* = 4.9, 1.3 Hz, 1H), 7.08 (dd, *J* = 5.0, 3.7 Hz, 1H), 4.26 (t, *J* = 6.6 Hz, 2H), 1.86 – 1.67 (m, 2H), 1.61 – 1.48 (m, 2H), 1.46 – 1.33 (m, 1H), 1.24 (s, 6H), 1.23 (s, 6H), 1.14 (dd, *J* = 13.4, 2.6 Hz, 1H), 1.04 – 0.94 (m, 1H), 0.87 (s, 9H).

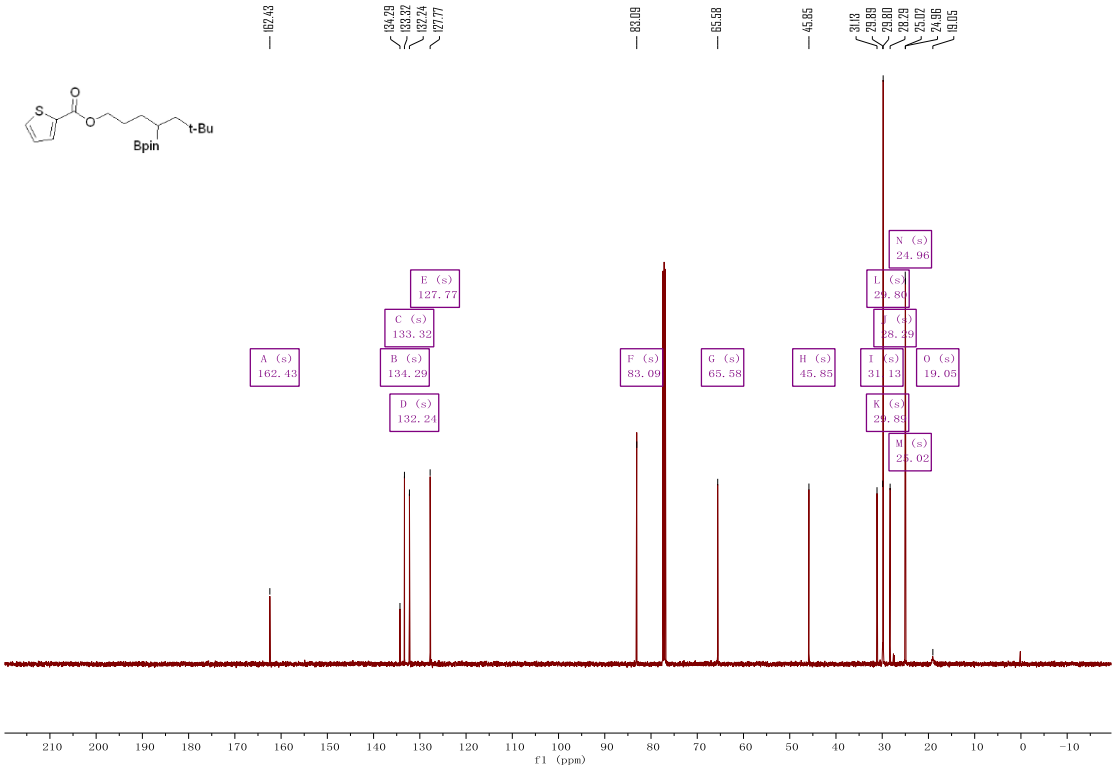
^{13}C NMR (126 MHz, Chloroform-*d*) δ 162.43, 134.29, 133.32, 132.24, 127.77, 83.09, 65.58, 45.85, 31.13, 29.89, 29.80, 28.29, 25.02, 24.96, 19.05

^{11}B NMR (128 MHz, Chloroform-*d*) δ 33.87

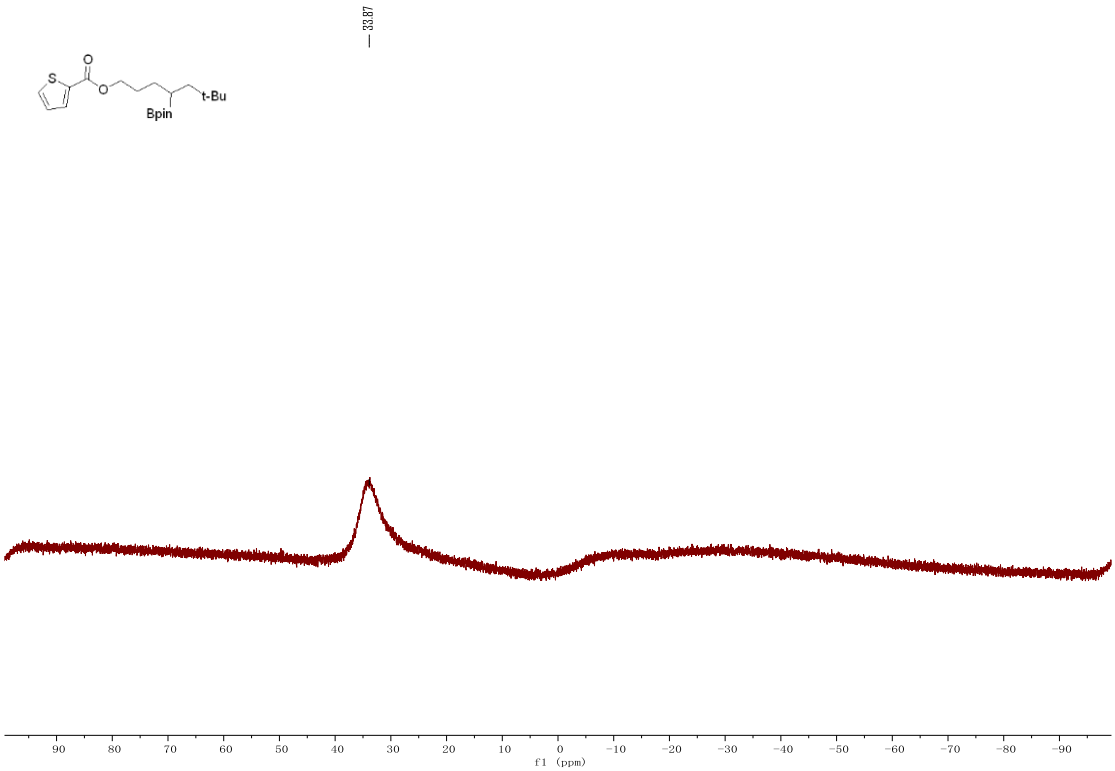
HRMS (ESI) calculated for $C_{20}H_{33}BO_4S$ $[M+H]^+$: 381.2265, found: 381.2254



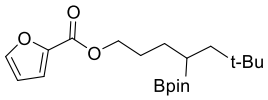
^{1}H NMR spectra for **20**



^{13}C NMR spectra for **20**



^{11}B NMR spectra for **20**



6,6-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptyl furan-2-carboxylate (**21**)

Following general procedure 1. The product was isolated by column chromatography as colorless oil (49.5 mg, 0.136 mmol, 68%).

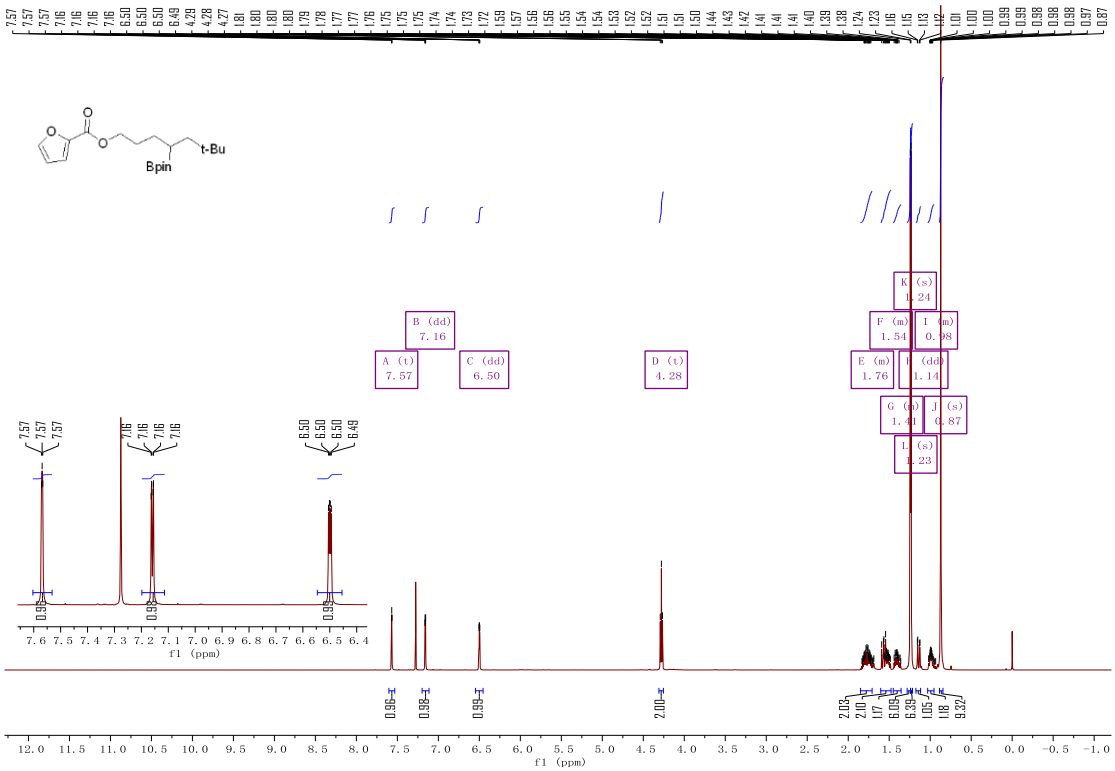
Rf (petroleum ether : ethyl acetate = 10 : 1) = 0.45

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.57 (t, *J* = 1.2 Hz, 1H), 7.16 (dd, *J* = 3.5, 0.8 Hz, 1H), 6.50 (dd, *J* = 3.5, 1.7 Hz, 1H), 4.28 (t, *J* = 6.7 Hz, 2H), 1.87 – 1.65 (m, 2H), 1.60 – 1.47 (m, 2H), 1.46 – 1.33 (m, 1H), 1.24 (s, 6H), 1.23 (s, 6H), 1.14 (dd, *J* = 13.4, 2.5 Hz, 1H), 1.05 – 0.92 (m, 1H), 0.87 (s, 9H).

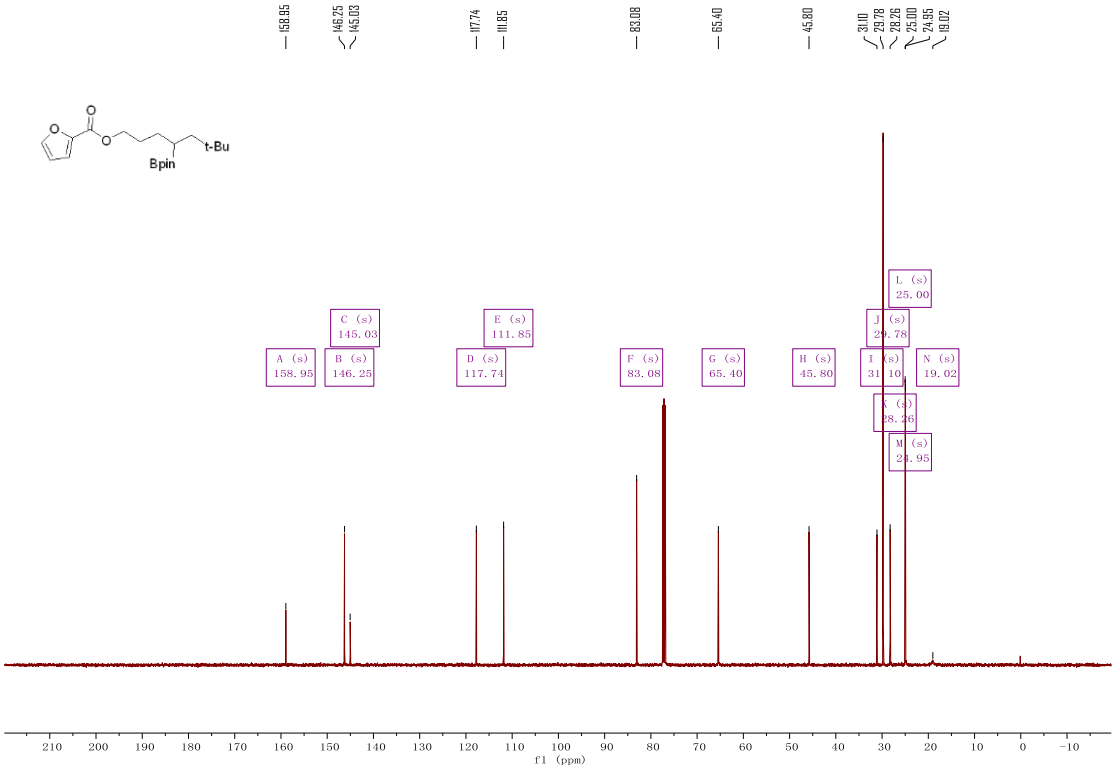
^{13}C NMR (126 MHz, Chloroform-*d*) δ 158.95, 146.25, 145.03, 117.74, 111.85, 83.08, 65.40, 45.80, 31.10, 29.78, 28.26, 25.00, 24.95, 19.02.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 33.86

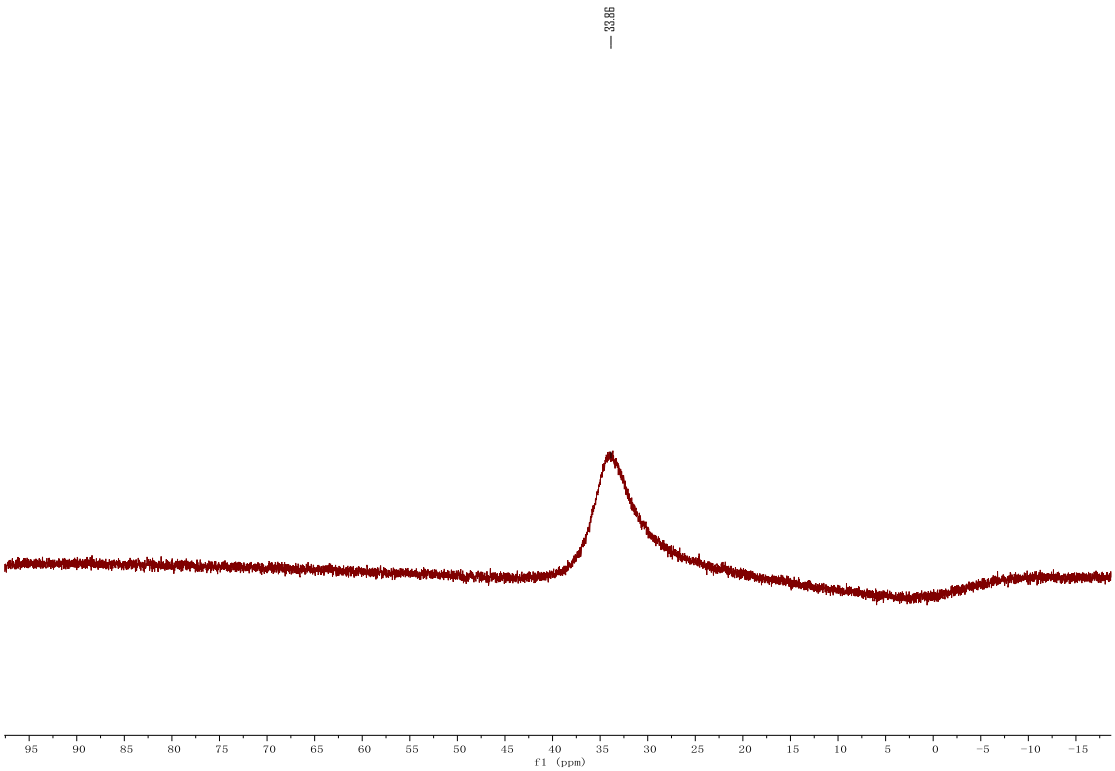
HRMS (ESI) calculated for $C_{20}H_{33}BO_5$ $[M+H]^+$: 365.2494, found: 365.2484



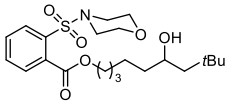
^{1}H NMR spectra for **21**



^{13}C NMR spectra for **21**



^{11}B NMR spectra for **21**



6-hydroxy-8,8-dimethylnonyl 2-(morpholinosulfonyl)benzoate (**22**)

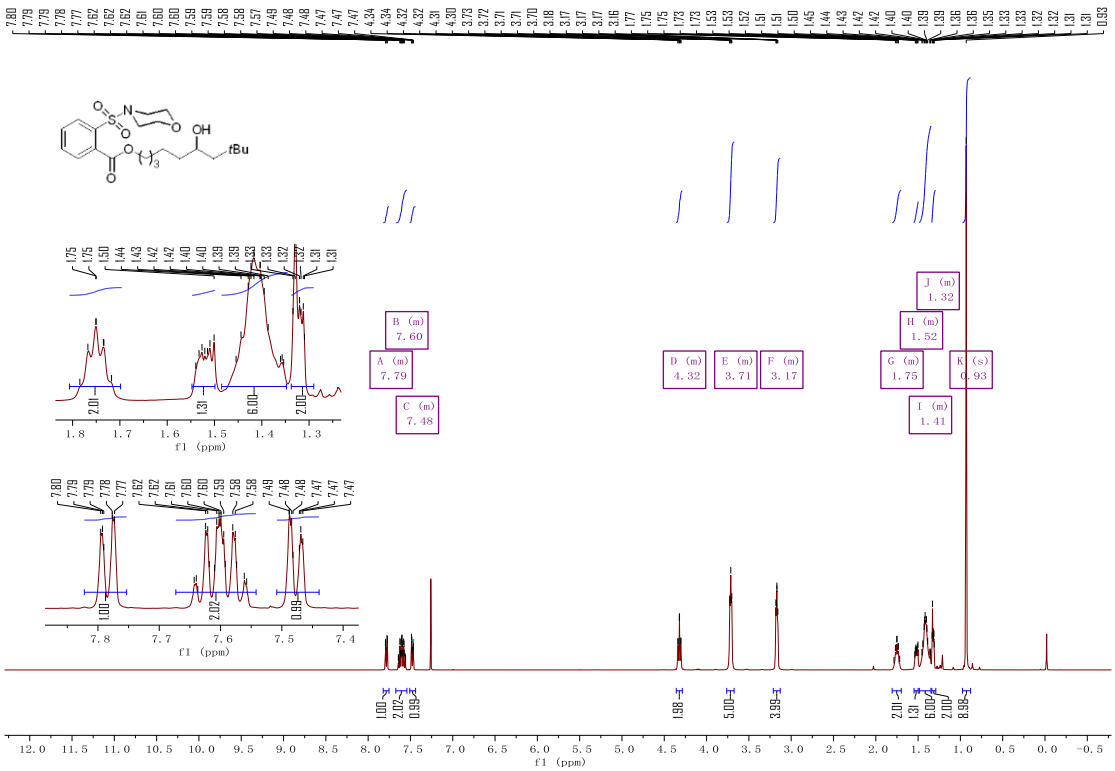
Following general procedure 2. The product was isolated by column chromatography as colorless oil (51.3 mg, 0.124 mmol, 62%).

Rf (petroleum ether : acetone = 2 : 1) = 0.60

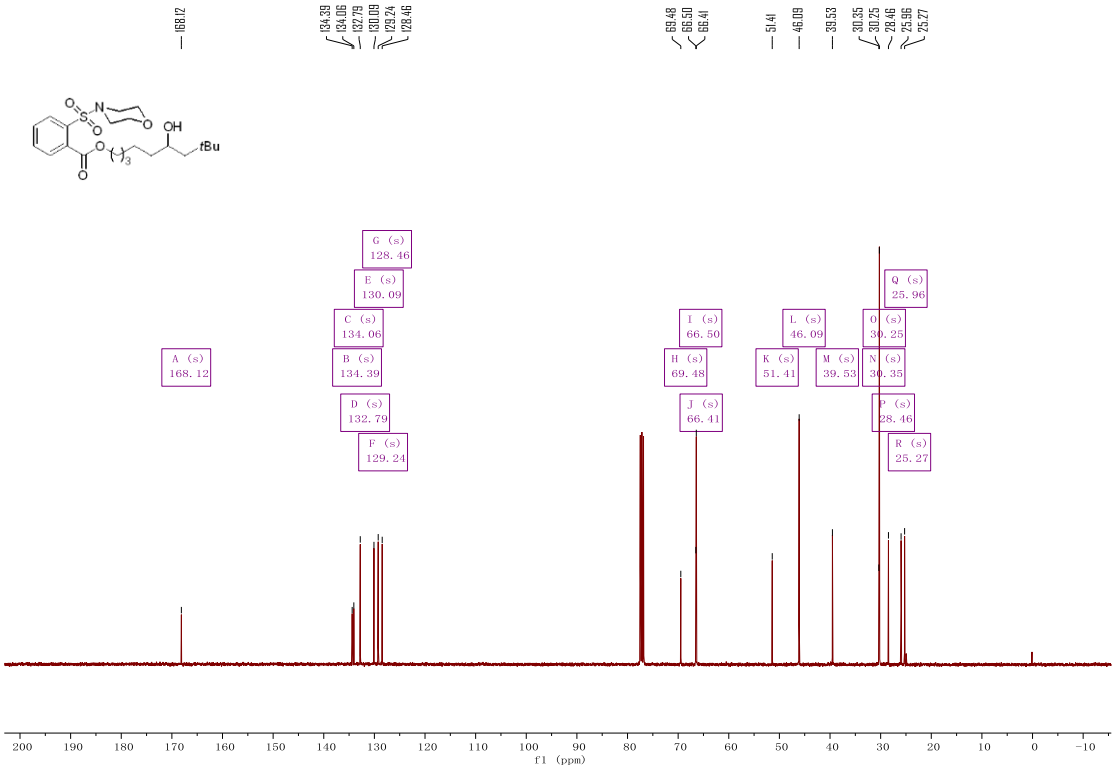
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 – 7.71 (m, 1H), 7.67 – 7.53 (m, 2H), 7.51 – 7.44 (m, 1H), 4.44 – 4.21 (m, 2H), 3.78 – 3.66 (m, 5H), 3.31 – 3.03 (m, 4H), 1.81 – 1.69 (m, 2H), 1.56 – 1.48 (m, 1H), 1.48 – 1.33 (m, 6H), 1.36 – 1.29 (m, 2H), 0.93 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.12, 134.39, 134.06, 132.79, 130.09, 129.24, 128.46, 69.48, 66.50, 66.41, 51.41, 46.09, 39.53, 30.35, 30.25, 28.46, 25.96, 25.27.

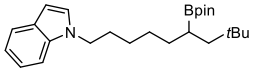
HRMS (ESI) calculated for $C_{22}H_{35}NO_6S$ $[M+H]^+$: 442.2258, found: 442.2263



^{1}H NMR spectra for **22**



^{13}C NMR spectra for **22**



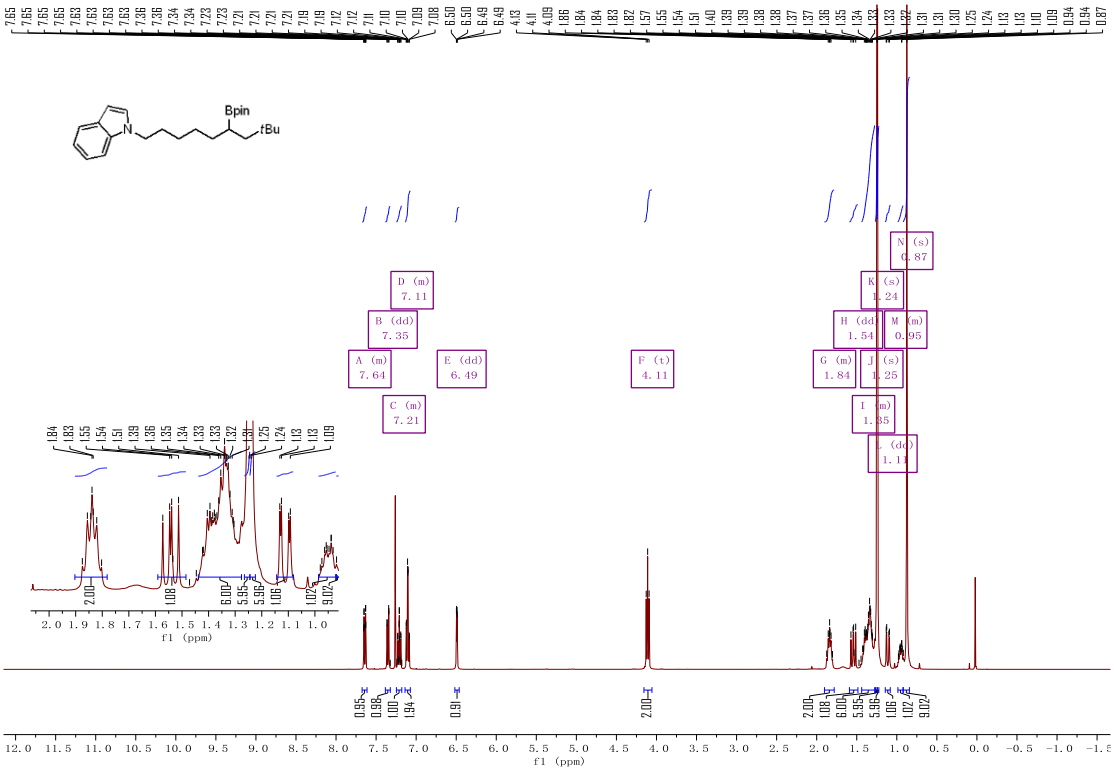
1-(8,8-dimethyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nonyl)-1H-indole (**23**) Following general procedure 1. The product was isolated by column chromatography as colorless oil (53.3 mg, 0.134 mmol, 67%).

Rf (petroleum ether : acetone = 5 : 1) = 0.60

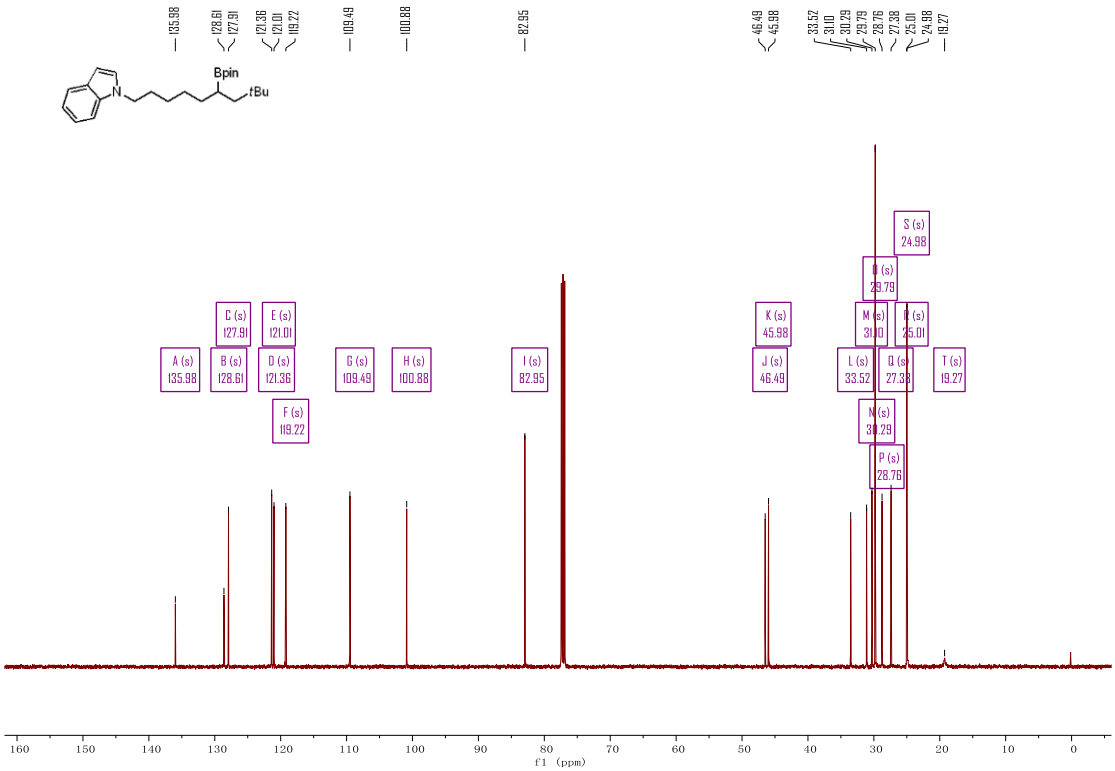
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 – 7.57 (m, 1H), 7.35 (dd, *J* = 8.3, 1.0 Hz, 1H), 7.26 – 7.16 (m, 1H), 7.13 – 7.07 (m, 2H), 6.49 (dd, *J* = 3.2, 0.8 Hz, 1H), 4.11 (t, *J* = 7.2 Hz, 2H), 1.93 – 1.73 (m, 2H), 1.54 (dd, *J* = 13.4, 10.4 Hz, 1H), 1.45 – 1.30 (m, 6H), 1.25 (s, 6H), 1.24 (s, 6H), 1.11 (dd, *J* = 13.4, 2.5 Hz, 1H), 1.00 – 0.90 (m, 1H), 0.87 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 135.98, 128.61, 127.91, 121.36, 121.01, 119.22, 109.49, 100.88, 82.95, 46.49, 45.98, 33.52, 31.10, 30.29, 29.79, 28.76, 27.38, 25.01, 24.98, 19.2

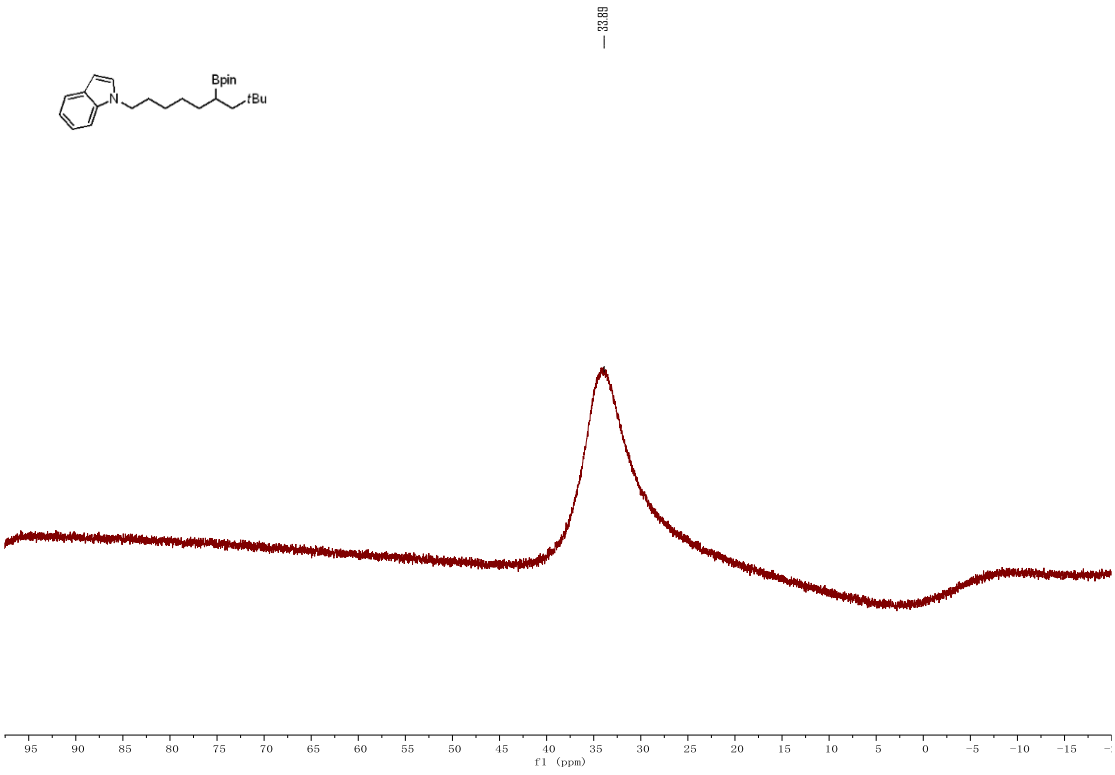
^{11}B NMR (128 MHz, Chloroform-*d*) δ 33.89



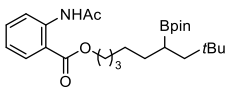
^{1}H NMR spectra for **23**



^{13}C NMR spectra for **23**



^{11}B NMR spectra for **23**



8,8-dimethyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nonyl 2-acetamidobenzoate (**24**)

Following general procedure 1. The product was isolated by column chromatography as colorless oil (60.6 mg, 0.132 mmol, 66%).

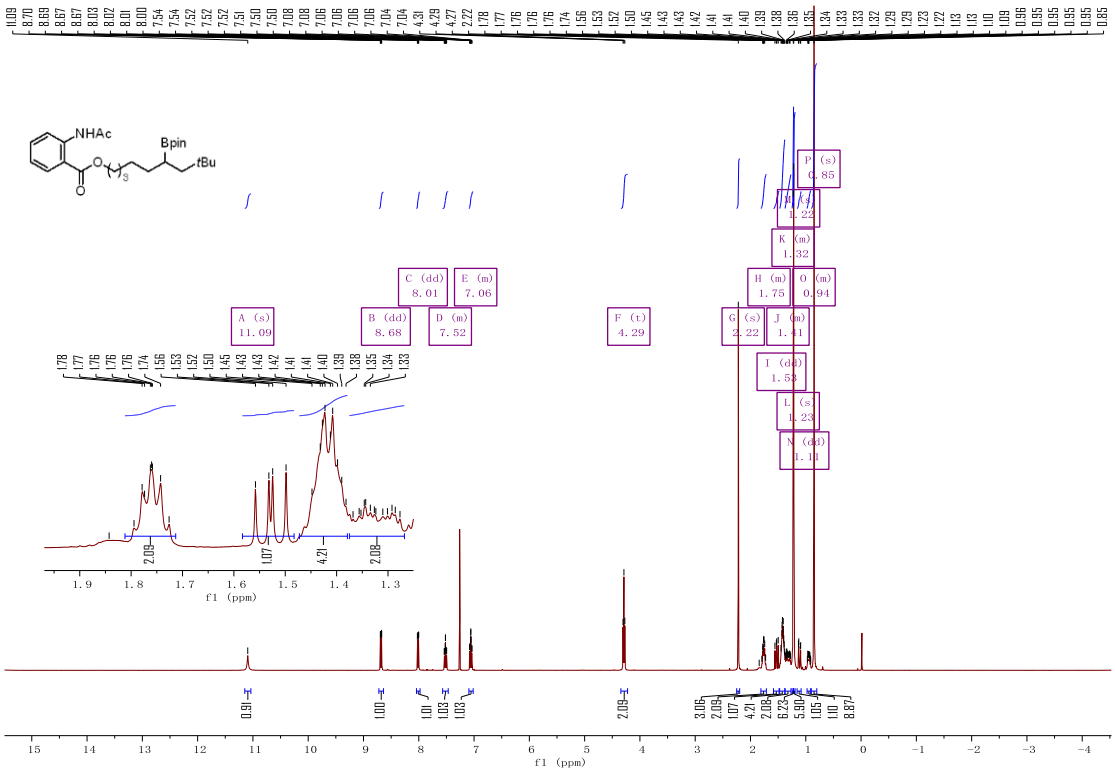
Rf (petroleum ether : acetone = 10 : 1) = 0.30

^{1}H NMR (400 MHz, Chloroform-*d*) δ 11.09 (s, 1H), 8.68 (dd, *J* = 8.5, 1.2 Hz, 1H), 8.01 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.64 – 7.41 (m, 1H), 7.21 – 6.77 (m, 1H), 4.29 (t, *J* = 6.6 Hz, 2H), 2.22 (s, 3H), 1.86 – 1.65 (m, 2H), 1.53 (dd, *J* = 13.4, 10.4 Hz, 1H), 1.47 – 1.38 (m, 4H), 1.37 – 1.27 (m, 2H), 1.23 (s, 6H), 1.22 (s, 6H), 1.11 (dd, *J* = 13.4, 2.4 Hz, 1H), 0.99 – 0.89 (m, 1H), 0.85 (s, 9H).

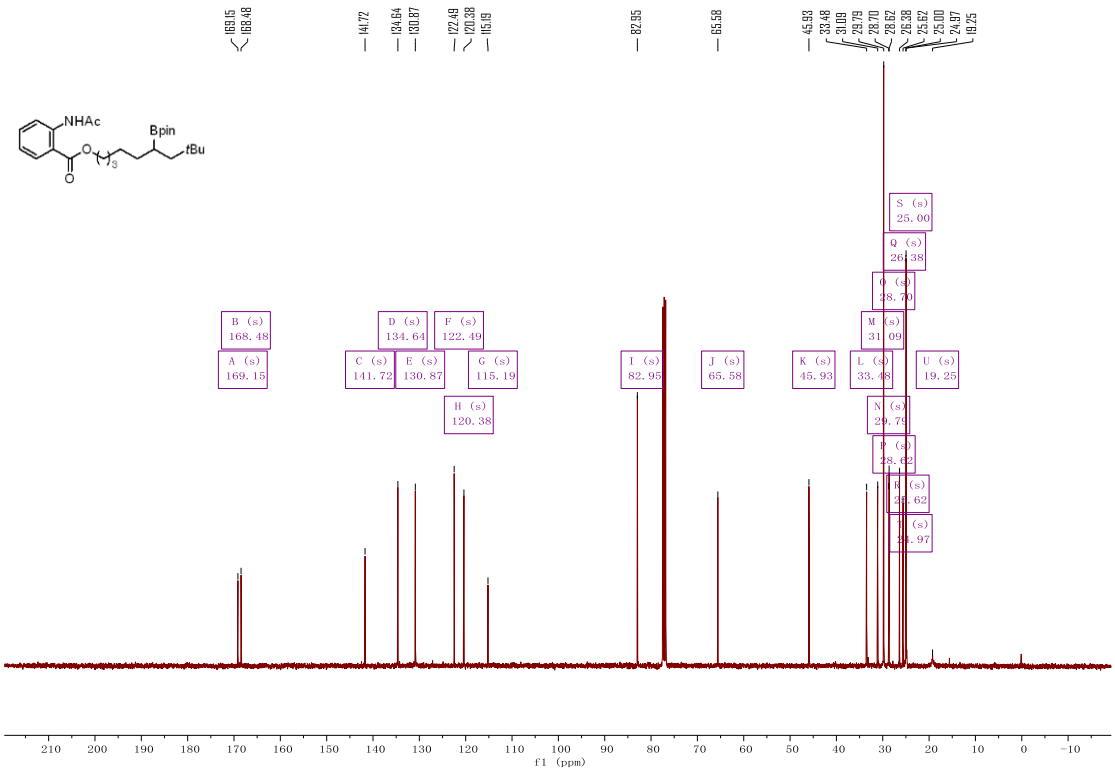
^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.15, 168.48, 141.72, 134.64, 130.87, 122.49, 120.38, 115.19, 82.95, 65.58, 45.93, 33.48, 31.09, 29.79, 28.70, 28.62, 26.38, 25.62, 25.00, 24.97, 19.25.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 34.17.

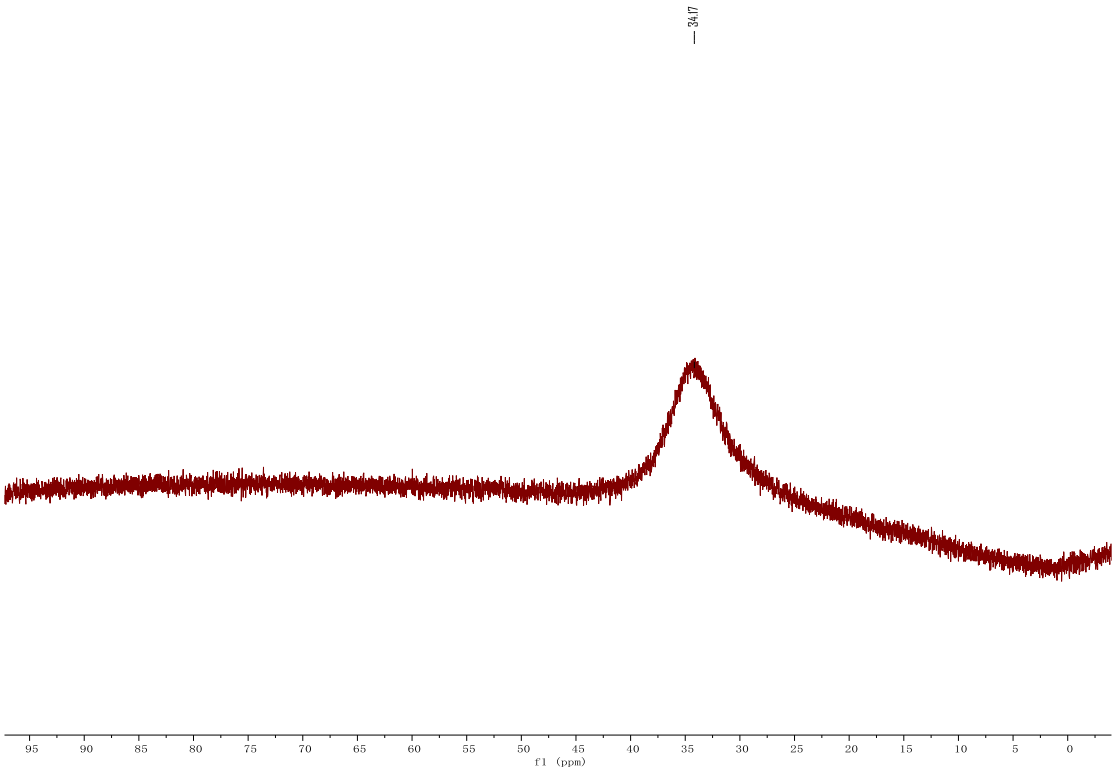
HRMS (ESI) calculated for $C_{26}H_{42}BNO_5$ $[M+H]^+$: 460.3229, found: 460.3212



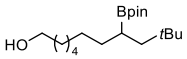
^{1}H NMR spectra for **24**



^{13}C NMR spectra for **24**



^{11}B NMR spectra for **24**



10,10-dimethyl-8-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)undecan-1-ol (**25**)
Following general procedure 1. The product was isolated by column chromatography as colorless oil (39.2 mg, 0.120 mmol, 60%).

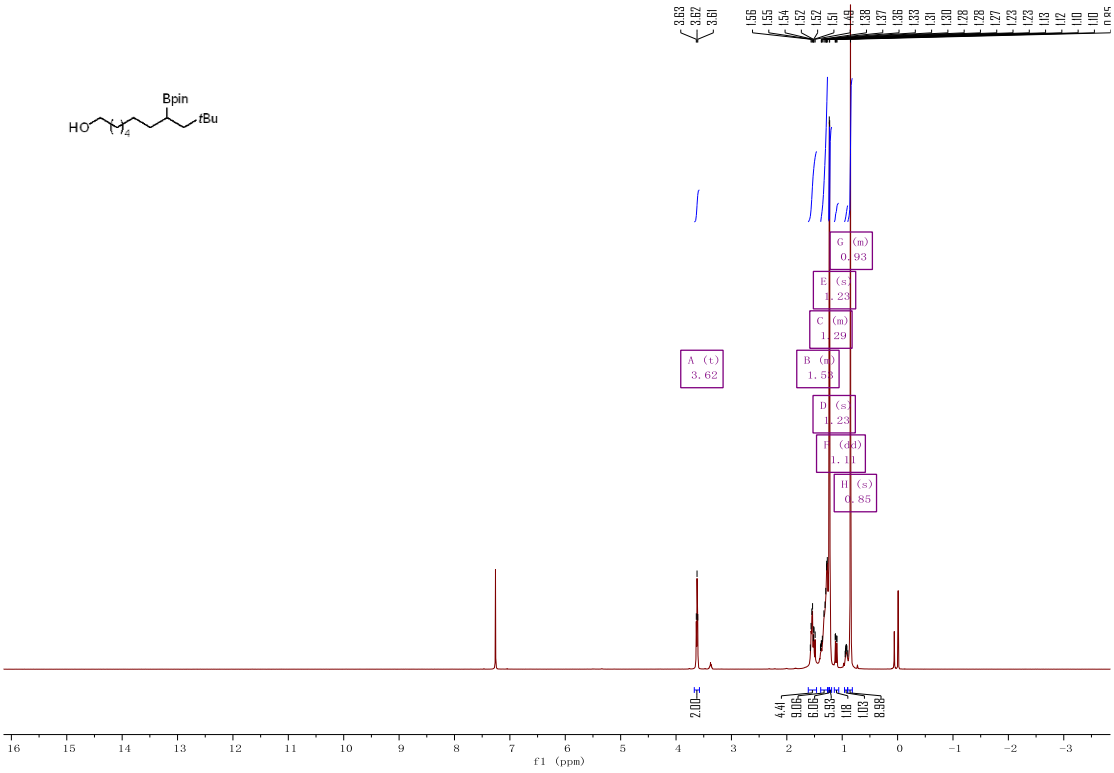
Rf (petroleum ether : Ethyl acetate = 5 : 1) = 0.40

^{1}H NMR (500 MHz, Chloroform-*d*) δ 3.62 (t, *J* = 6.6 Hz, 2H), 1.62 – 1.45 (m, 4H), 1.41 – 1.26 (m, 9H), 1.23 (s, 6H), 1.23 (s, 6H), 1.11 (dd, *J* = 13.4, 2.4 Hz, 1H), 0.95 – 0.89 (m, 1H), 0.85 (s, 9H).

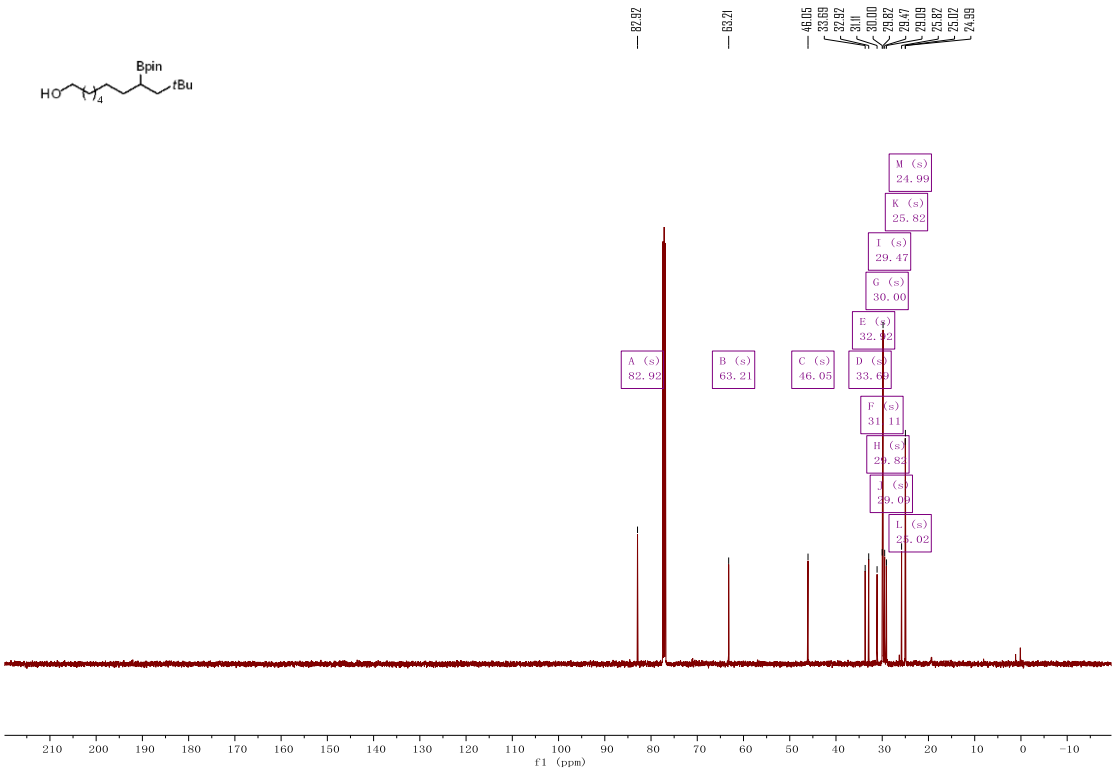
^{13}C NMR (126 MHz, Chloroform-*d*) δ 82.92, 63.21, 46.05, 33.69, 32.92, 31.11, 30.00, 29.82, 29.47, 29.09, 25.82, 25.02, 24.99.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 35.55

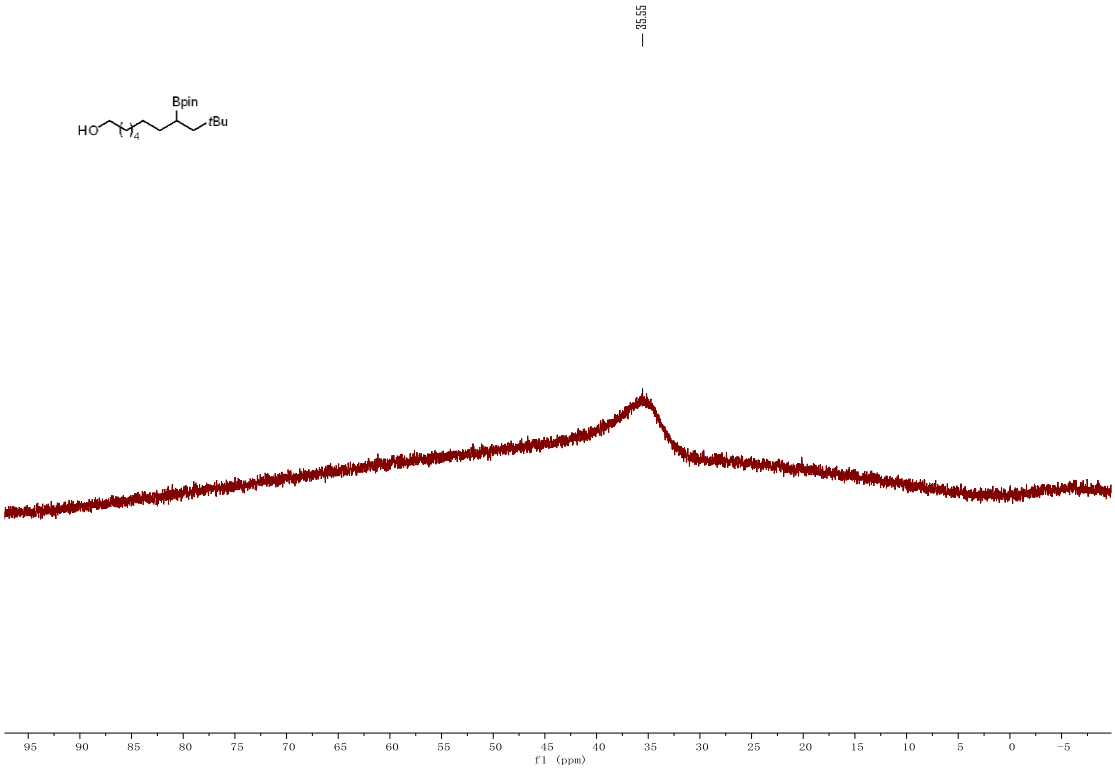
HRMS (ESI) calculated for $C_{19}H_{39}BO_3$ $[M+H]^+$: 327.3065, found: 327.3053



^{1}H NMR spectra for **25**

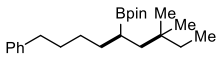


^{13}C NMR spectra for **25**

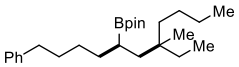


^{11}B NMR spectra for **25**

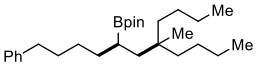
6. Examples Described in Scheme 3



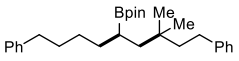
26, 82%



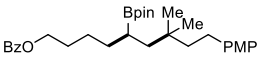
27, 75% (d.r. = 1:1)



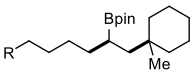
28, 68%



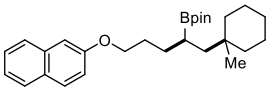
29, 55%



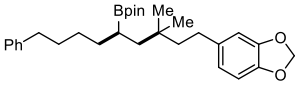
30, 59%



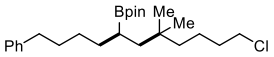
31, R = Ph, 78%
32, R = OBz, 77%



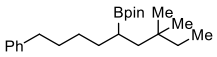
33, 67%



34, 51%



35, 76%



2-(7,7-dimethyl-1-phenylnonan-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**26**)
Following general procedure 1. The product was isolated by column chromatography as colorless oil (63.2 mg, 0.164 mmol, 82%).

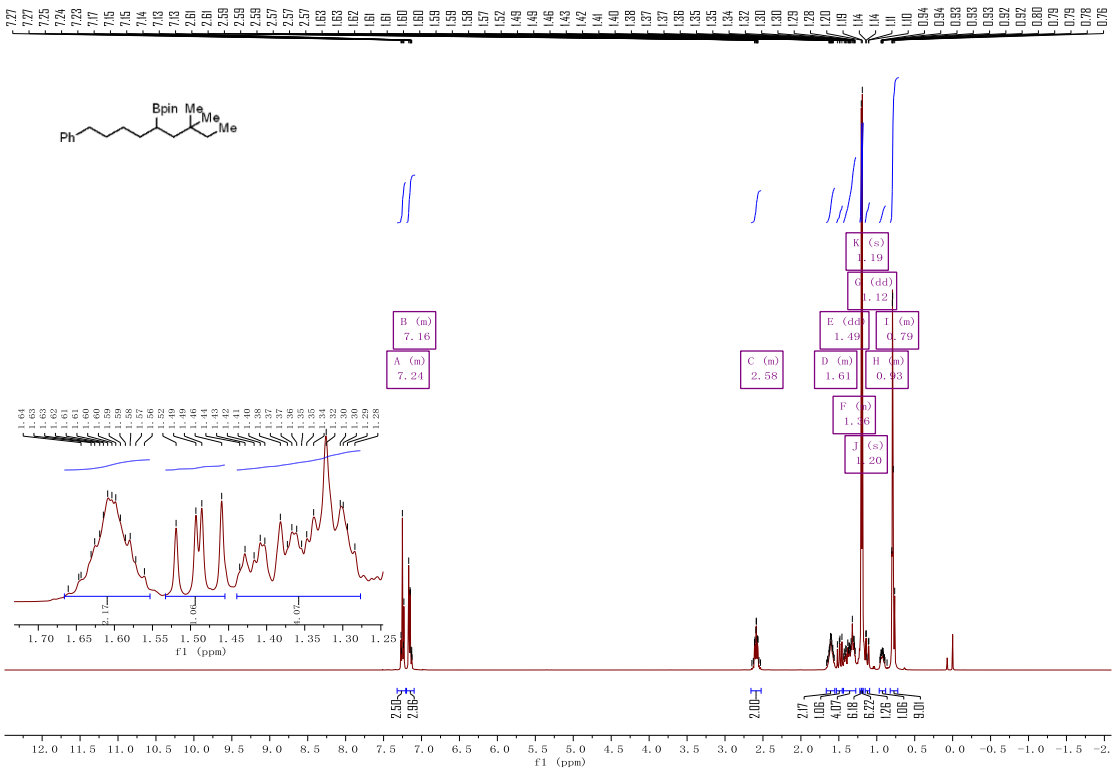
Rf (petroleum ether : ethyl acetate = 20 : 1) = 0.50

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 – 7.20 (m, 2H), 7.19 – 7.10 (m, 3H), 2.71 – 2.45 (m, 2H), 1.66 – 1.56 (m, 2H), 1.49 (dd, *J* = 13.5, 10.4 Hz, 1H), 1.44 – 1.27 (m, 4H), 1.20 (s, 6H), 1.19 (s, 6H), 1.12 (dd, *J* = 13.6, 2.6 Hz, 1H), 0.99 – 0.87 (m, 1H), 0.86 – 0.71 (m, 9H).

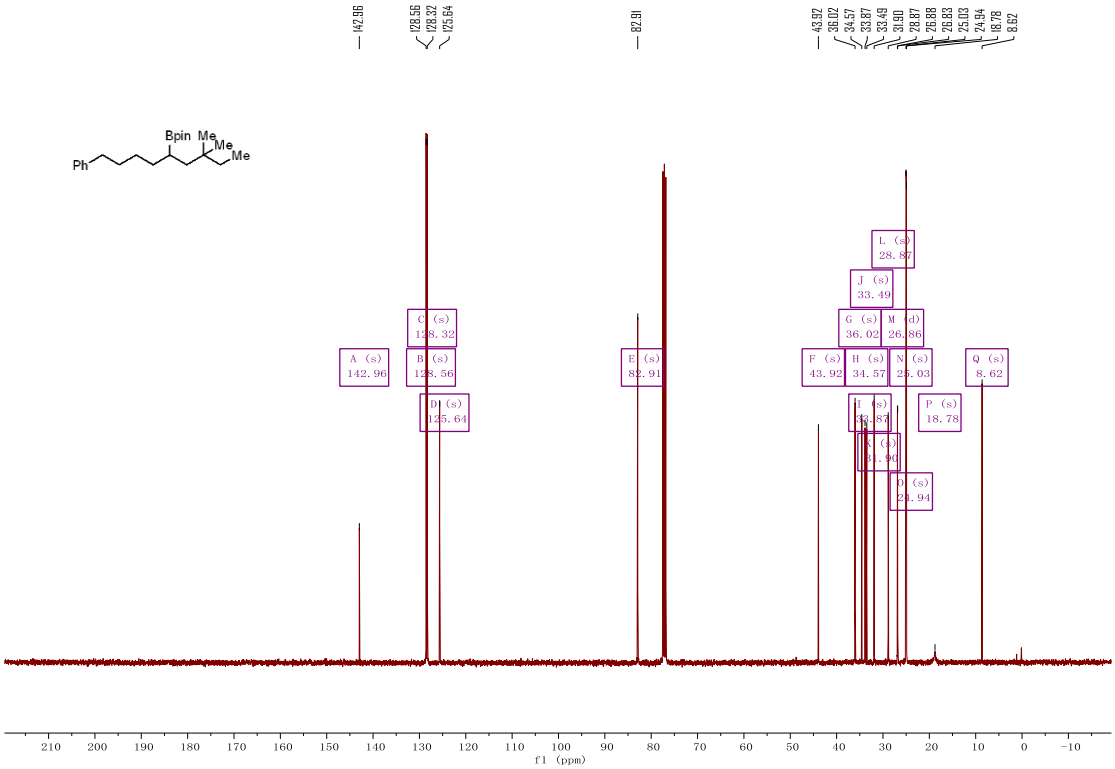
^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.96, 128.56, 128.32, 125.64, 82.91, 43.92, 36.02, 34.57, 33.87, 33.49, 31.90, 28.87, 26.86 (d, *J* = 4.8 Hz), 25.03, 24.94, 18.78, 8.62.

^{11}B NMR (128 MHz, Chloroform-*d*) 34.12

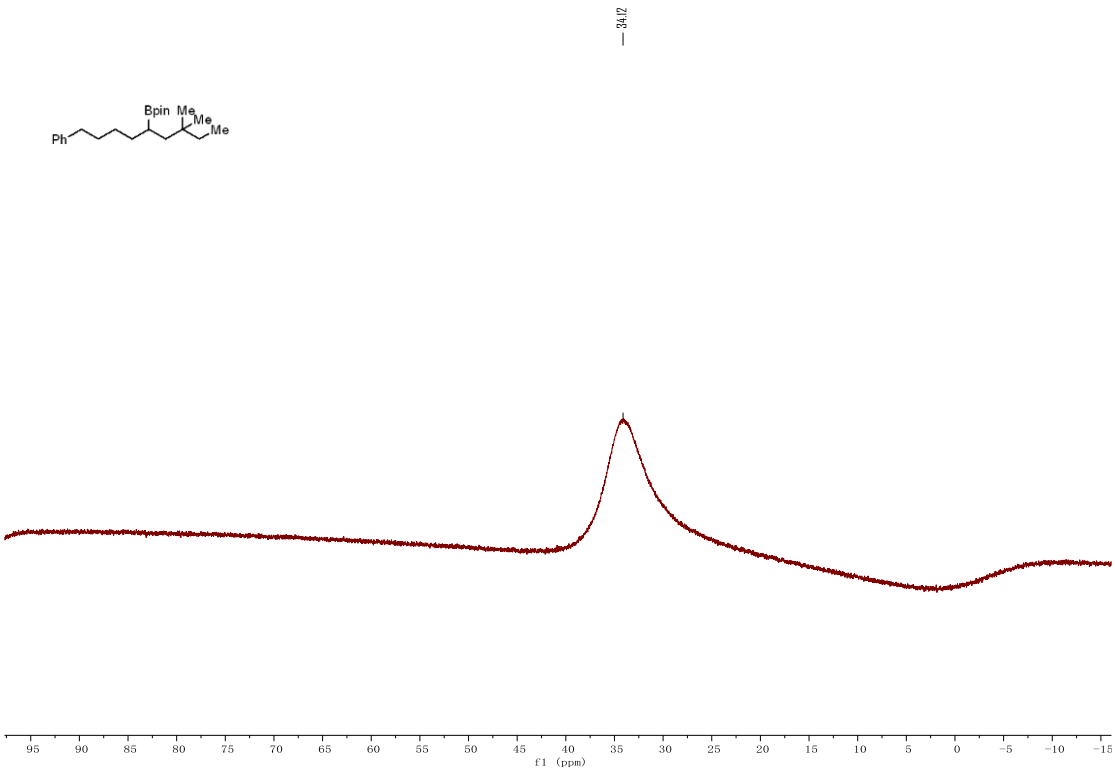
HRMS (ESI) calculated for $C_{23}H_{39}BO_2$ $[M+Na]^+$: 381.2935, found: 381.2941.



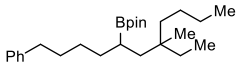
^{1}H NMR spectra for **26**



^{13}C NMR spectra for **26**



^{11}B NMR spectra for **26**



2-(7-ethyl-7-methyl-1-phenylundecan-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**27**)

Following general procedure 1. The product was isolated by column chromatography as colorless oil (60.1 mg, 0.150 mmol, 75%).

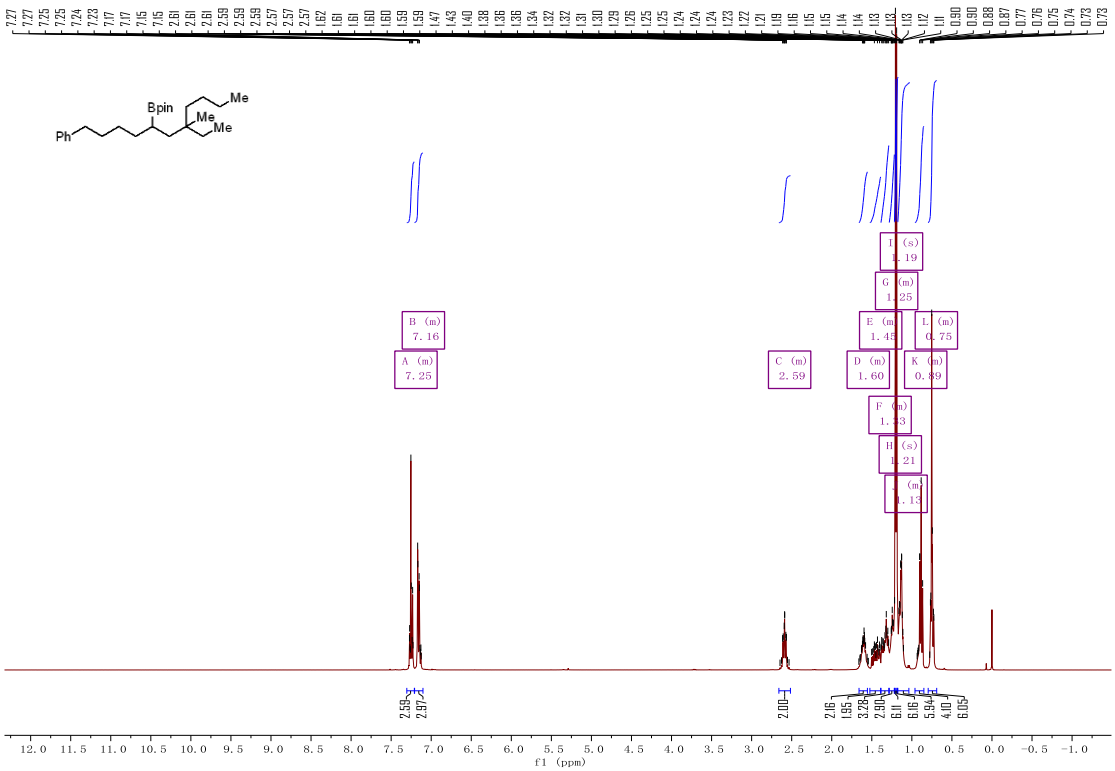
Rf (petroleum ether : ethyl acetate = 20 : 1) = 0.50

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 – 7.20 (m, 2H), 7.19 – 7.11 (m, 3H), 2.68 – 2.49 (m, 2H), 1.67 – 1.53 (m, 2H), 1.52 – 1.39 (m, 2H), 1.38 – 1.28 (m, 3H), 1.28 – 1.21 (m, 3H), 1.21 (s, 6H), 1.19 (s, 6H), 1.18 – 1.08 (m, 6H), 0.97 – 0.84 (m, 4H), 0.79 – 0.69 (m, 6H).

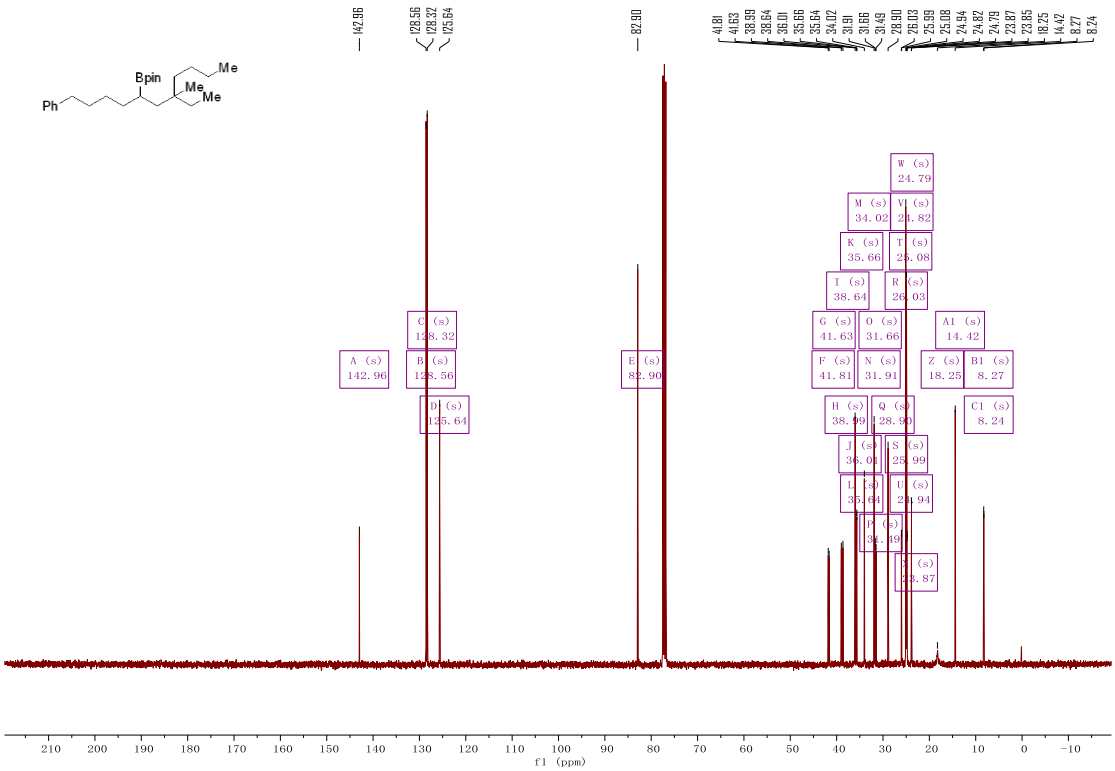
^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.96, 128.56, 128.32, 125.64, 82.90, 41.81, 41.63, 38.99, 38.64, 36.01, 35.66, 35.64, 34.02, 31.91, 31.66, 31.49, 28.90, 26.03, 25.99, 25.08, 24.94, 24.82, 24.79, 23.87, 23.85, 18.25, 14.42, 8.27, 8.24.

^{11}B NMR (128 MHz, Chloroform-*d*) 33.71

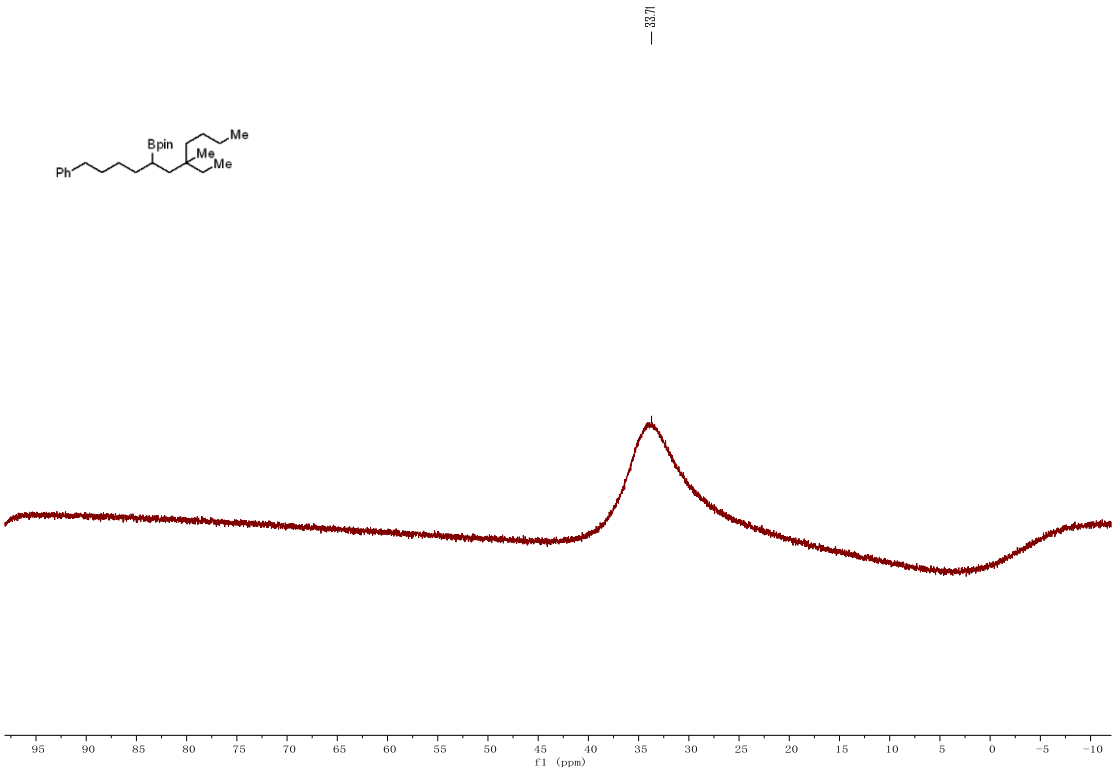
HRMS (ESI) calculated for $C_{26}H_{45}BO_2$ $[M+Na]^+$: 423.3405, found: 423.3410.



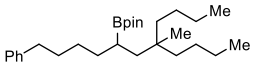
^{1}H NMR spectra for **27**



^{13}C NMR spectra for **27**



^{11}B NMR spectra for **27**



2-(7-butyl-7-methyl-1-phenylundecan-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**28**)

Following general procedure 1. The product was isolated by column chromatography as colorless oil (58.3 mg, 0.136 mmol, 68%).

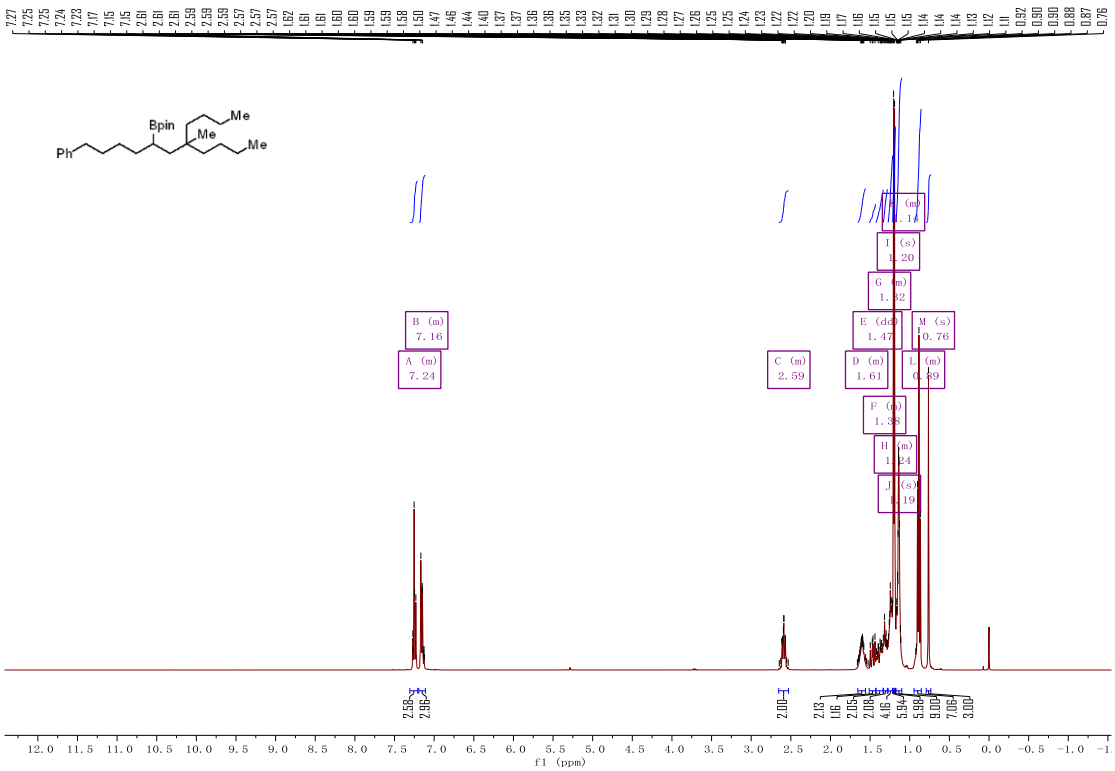
Rf (petroleum ether : ethyl acetate = 20 : 1) = 0.50

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 – 7.20 (m, 2H), 7.19 – 7.10 (m, 3H), 2.67 – 2.49 (m, 2H), 1.69 – 1.55 (m, 2H), 1.47 (dd, *J* = 13.7, 10.2 Hz, 1H), 1.43 – 1.34 (m, 2H), 1.34 – 1.28 (m, 2H), 1.27 – 1.22 (m, 4H), 1.20 (s, 6H), 1.19 (s, 6H), 1.19 – 1.09 (m, 9H), 0.95 – 0.84 (m, 7H), 0.76 (s, 3H).

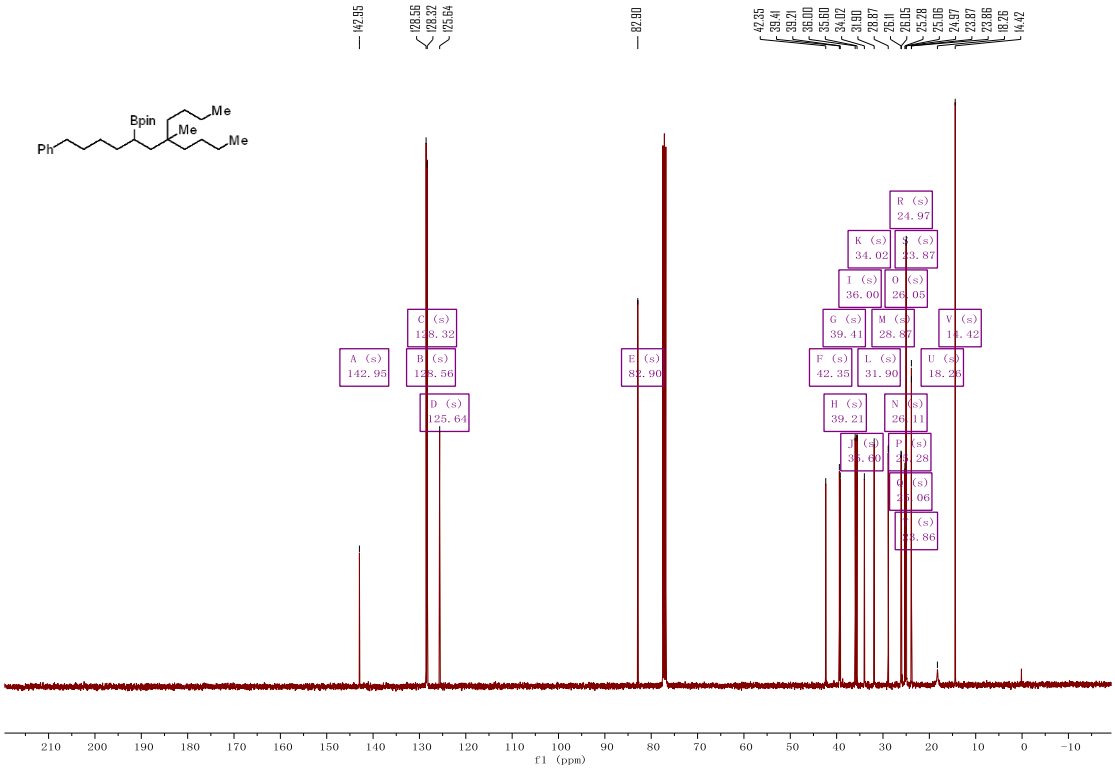
^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.95, 128.56, 128.32, 125.64, 82.90, 42.35, 39.41, 39.21, 36.00, 35.60, 34.02, 31.90, 28.87, 26.11, 26.05, 25.28, 25.06, 24.97, 23.87, 23.86, 18.26, 14.42.

^{11}B NMR (128 MHz, Chloroform-*d*) 34.50

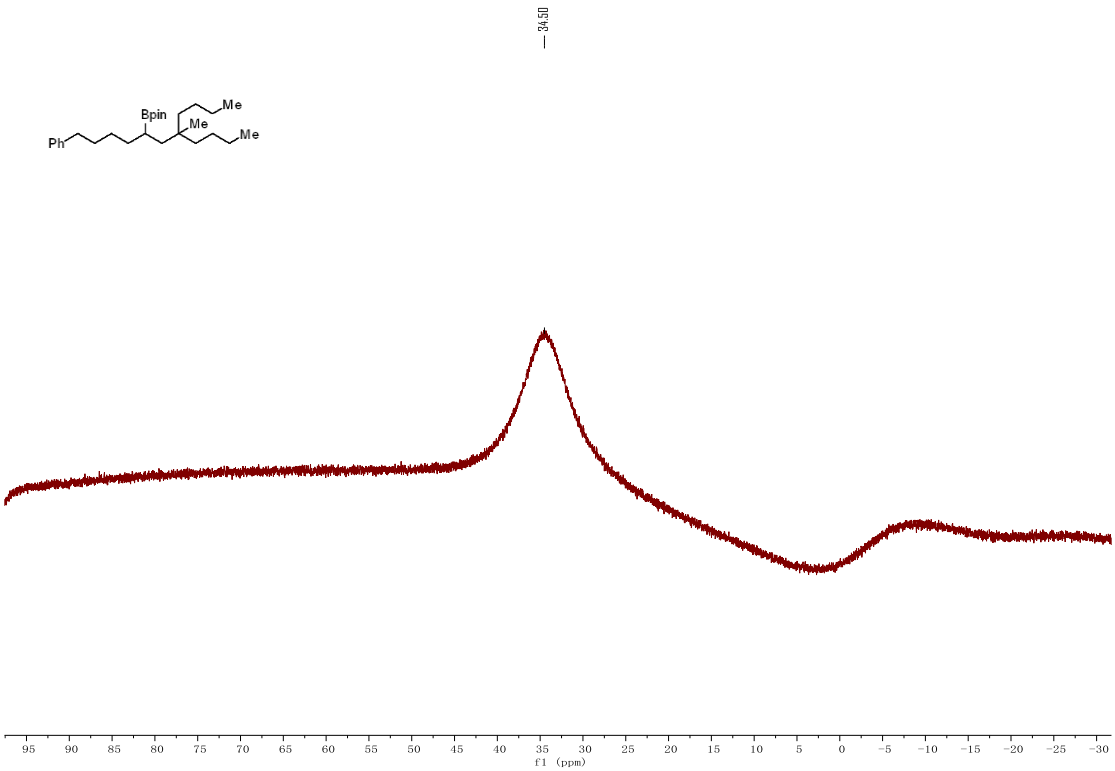
HRMS (ESI) calculated for $C_{28}H_{49}BO_2$ $[M+Na]^+$: 429.3898, found: 429.3904.



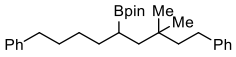
^{1}H NMR spectra for **28**



^{13}C NMR spectra for **28**



^{11}B NMR spectra for **28**



2-(3,3-dimethyl-1,9-diphenylnonan-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**29**) Following general procedure 1. The product was isolated by column chromatography as colorless oil (47.8 mg, 0.110 mmol, 55%).

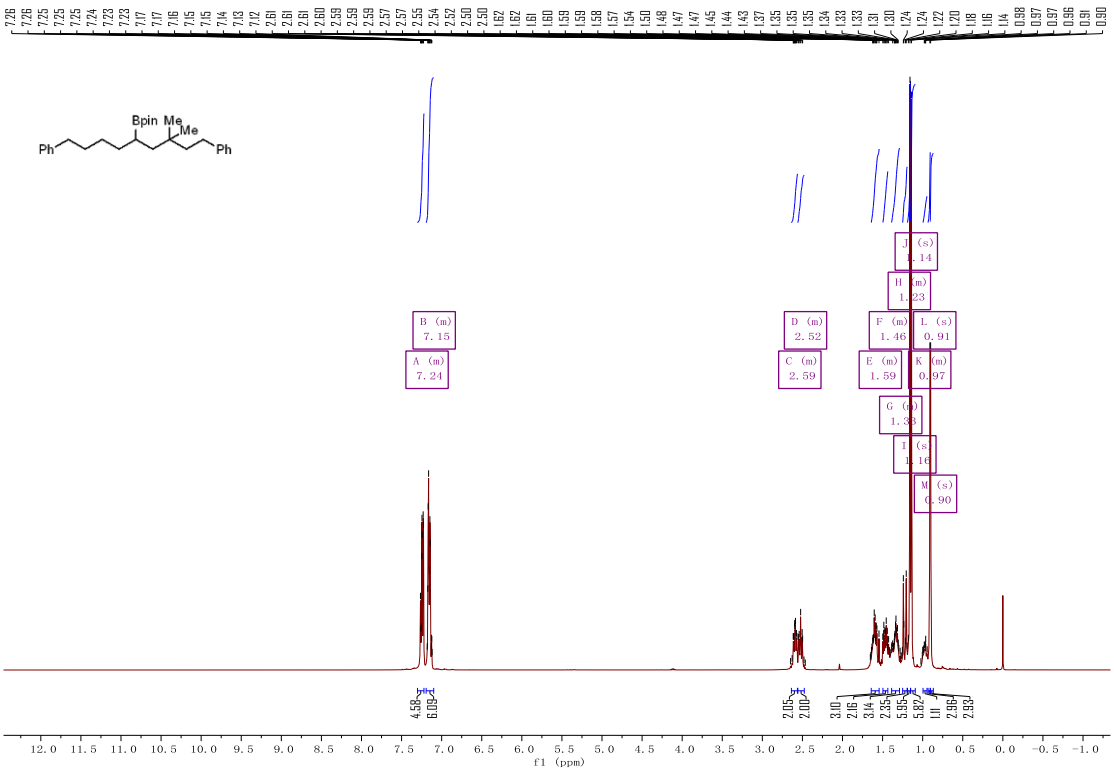
Rf (petroleum ether : ethyl acetate = 20 : 1) = 0.50

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 – 7.21 (m, 4H), 7.19 – 7.09 (m, 6H), 2.67 – 2.54 (m, 2H), 2.56 – 2.46 (m, 2H), 1.67 – 1.52 (m, 3H), 1.51 – 1.41 (m, 2H), 1.39 – 1.29 (m, 3H), 1.29 – 1.19 (m, 2H), 1.16 (s, 6H), 1.14 (s, 6H), 1.03 – 0.94 (m, 1H), 0.91 (s, 3H), 0.90 (s, 3H).

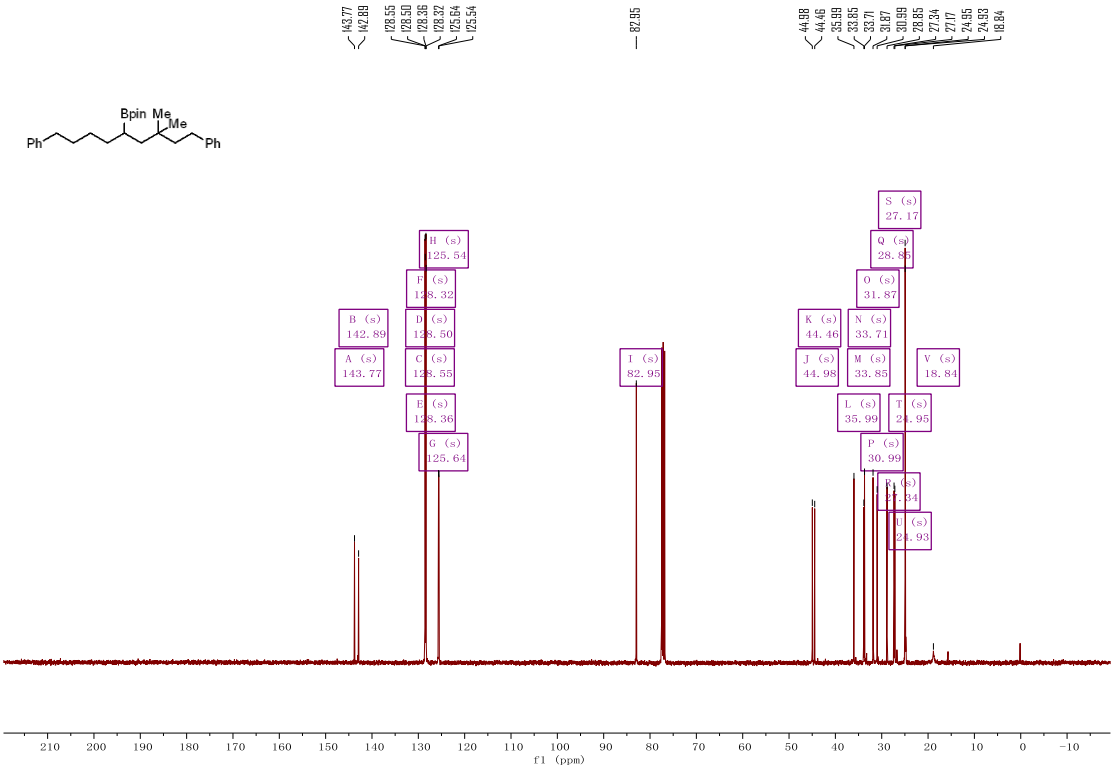
^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.77, 142.89, 128.55, 128.50, 128.36, 128.32, 125.64, 125.54, 82.95, 44.98, 44.46, 35.99, 33.85, 33.71, 31.87, 30.99, 28.85, 27.34, 27.17, 24.95, 24.93, 18.84.

^{11}B NMR (128 MHz, Chloroform-*d*) 35.56

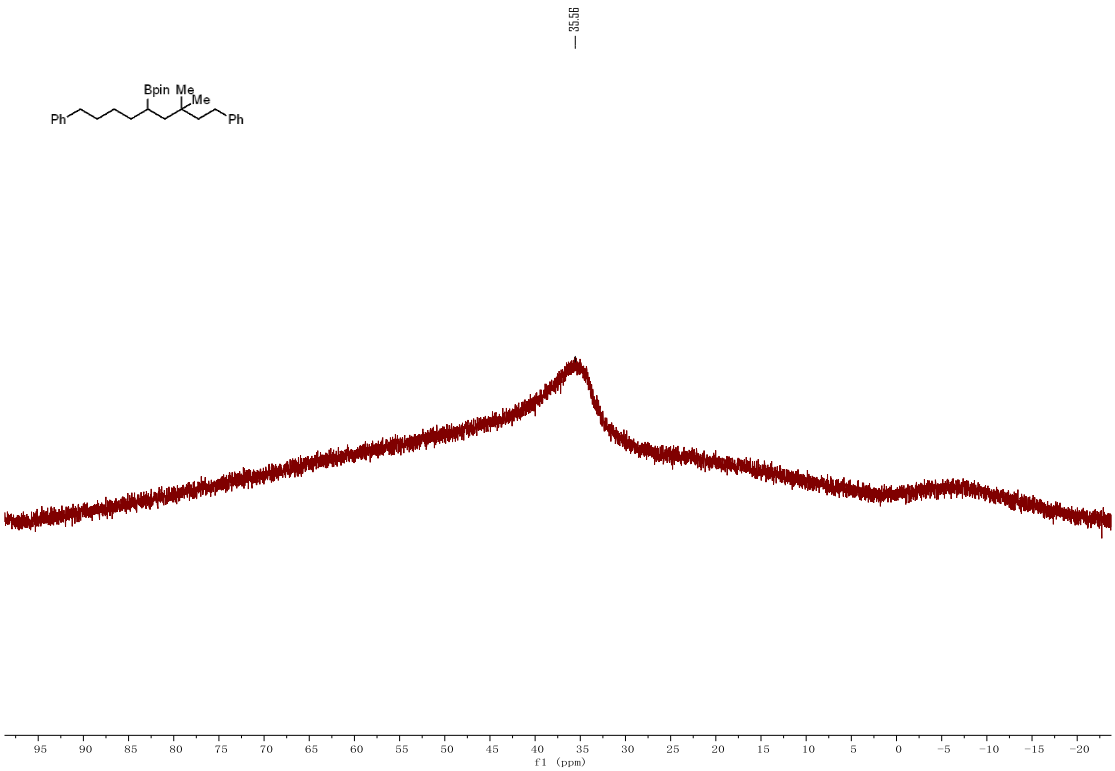
HRMS (ESI) calculated for $C_{29}H_{43}BO_2$ $[M+H]^+$:435.3429, found: 435.3434.



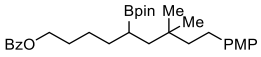
^{1}H NMR spectra for **29**



^{13}C NMR spectra for **29**



^{11}B NMR spectra for **29**



9-(4-methoxyphenyl)-7,7-dimethyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nonyl benzoate (**30**)

Following general procedure 1. The product was isolated by column chromatography as colorless oil (60.0 mg, 0.118 mmol, 59%).

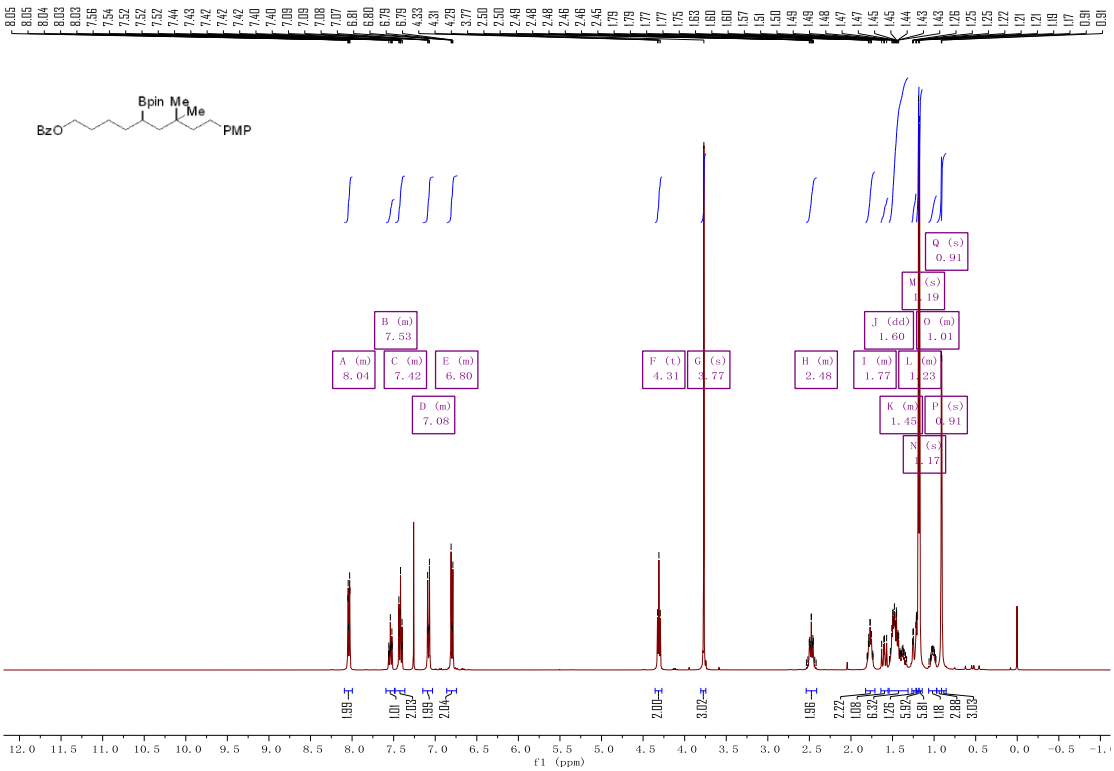
Rf (petroleum ether : acetone = 15 : 1) = 0.45

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12 – 7.94 (m, 2H), 7.61 – 7.47 (m, 1H), 7.46 – 7.34 (m, 2H), 7.15 – 7.05 (m, 2H), 6.89 – 6.73 (m, 2H), 4.31 (t, *J* = 6.6 Hz, 2H), 3.77 (s, 3H), 2.56 – 2.38 (m, 2H), 1.83 – 1.70 (m, 2H), 1.60 (dd, *J* = 13.5, 10.4 Hz, 1H), 1.54 – 1.31 (m, 6H), 1.27 – 1.21 (m, 1H), 1.19 (s, 6H), 1.17 (s, 6H), 1.08 – 0.96 (m, 1H), 0.91 (s, 3H), 0.91 (s, 3H).

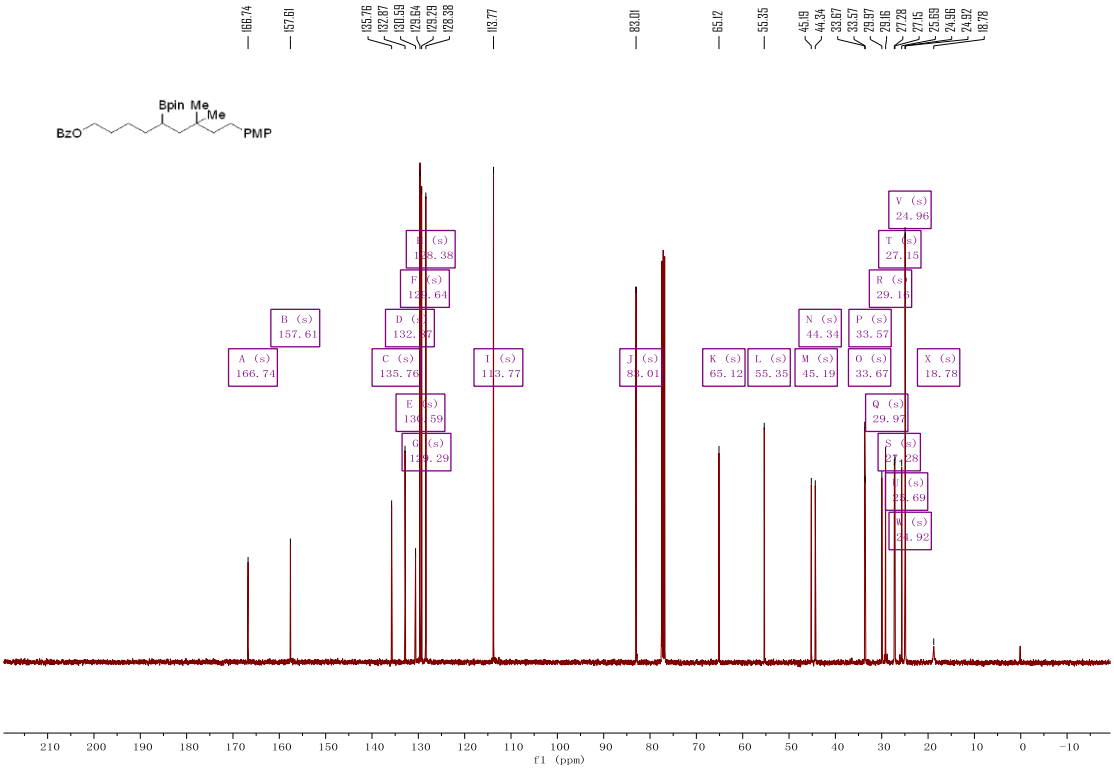
^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.74, 157.61, 135.76, 132.87, 130.59, 129.64, 129.29, 128.38, 113.77, 83.01, 65.12, 55.35, 45.19, 44.34, 33.67, 33.57, 29.97, 29.16, 27.28, 27.15, 25.69, 24.96, 24.92, 18.78.

^{11}B NMR (128 MHz, Chloroform-*d*) 34.18

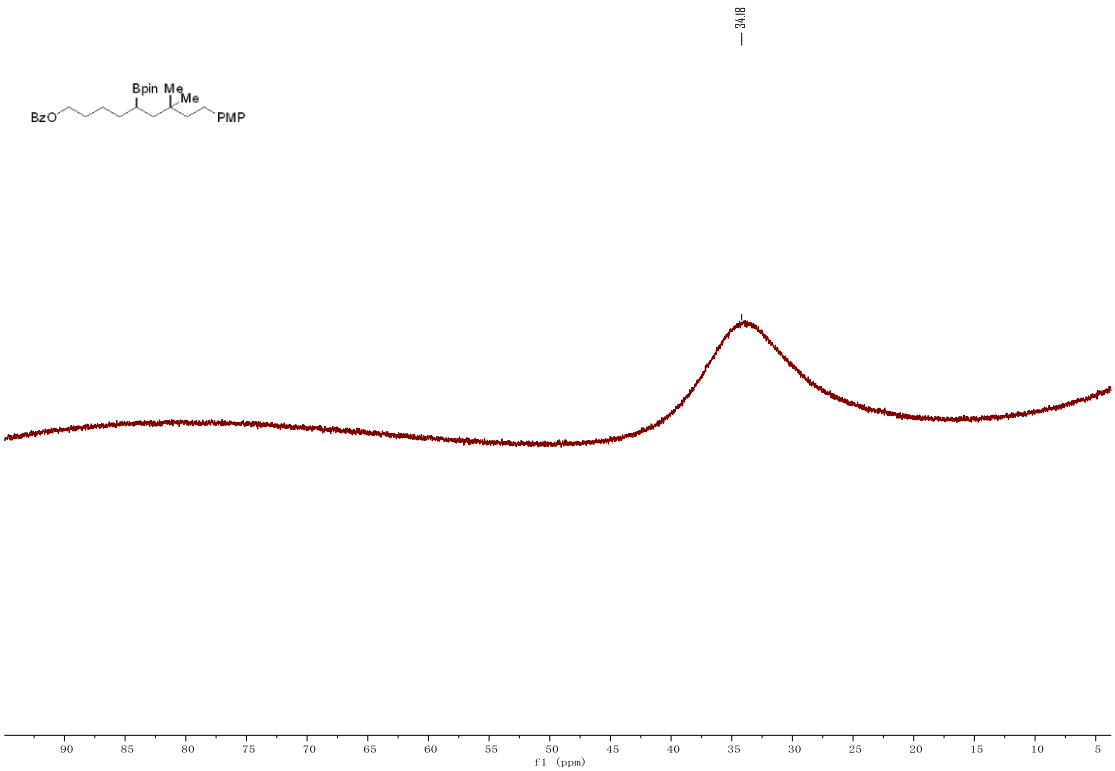
HRMS (ESI) calculated for $C_{31}H_{45}BO_5$ $[M+Na]^+$:531.3252, found: 531.3258.



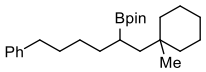
^{1}H NMR spectra for **30**



^{13}C NMR spectra for **30**



^{11}B NMR spectra for **30**



4,4,5,5-tetramethyl-2-(1-(1-methylcyclohexyl)-6-phenylhexan-2-yl)-1,3,2-dioxaborolane (**31**)

Following general procedure 1. The product was isolated by column chromatography as colorless oil (60.0 mg, 0.156 mmol, 78%).

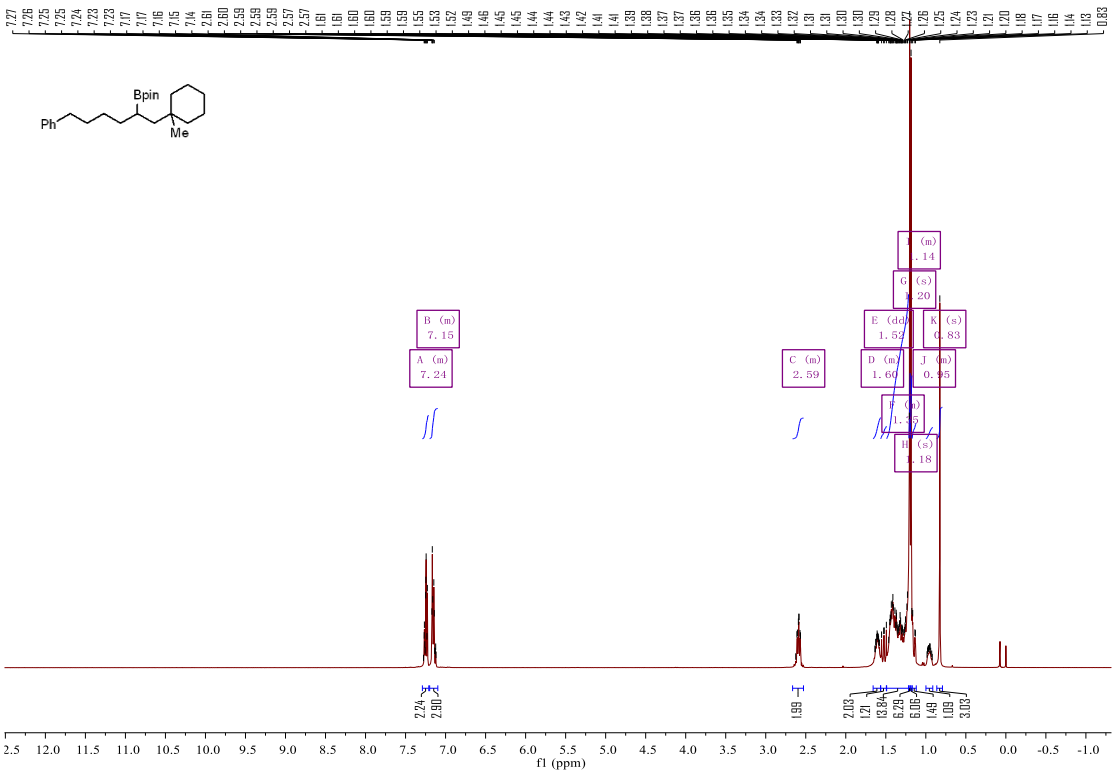
Rf (petroleum ether : ethyl acetate = 20 : 1) = 0.50

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 – 7.21 (m, 2H), 7.18 – 7.09 (m, 3H), 2.74 – 2.47 (m, 2H), 1.67 – 1.57 (m, 2H), 1.52 (dd, *J* = 13.5, 10.4 Hz, 1H), 1.47 – 1.23 (m, 14H), 1.20 (s, 6H), 1.18 (s, 6H), 1.17 – 1.12 (m, 1H), 1.01 – 0.90 (m, 1H), 0.83 (s, 3H).

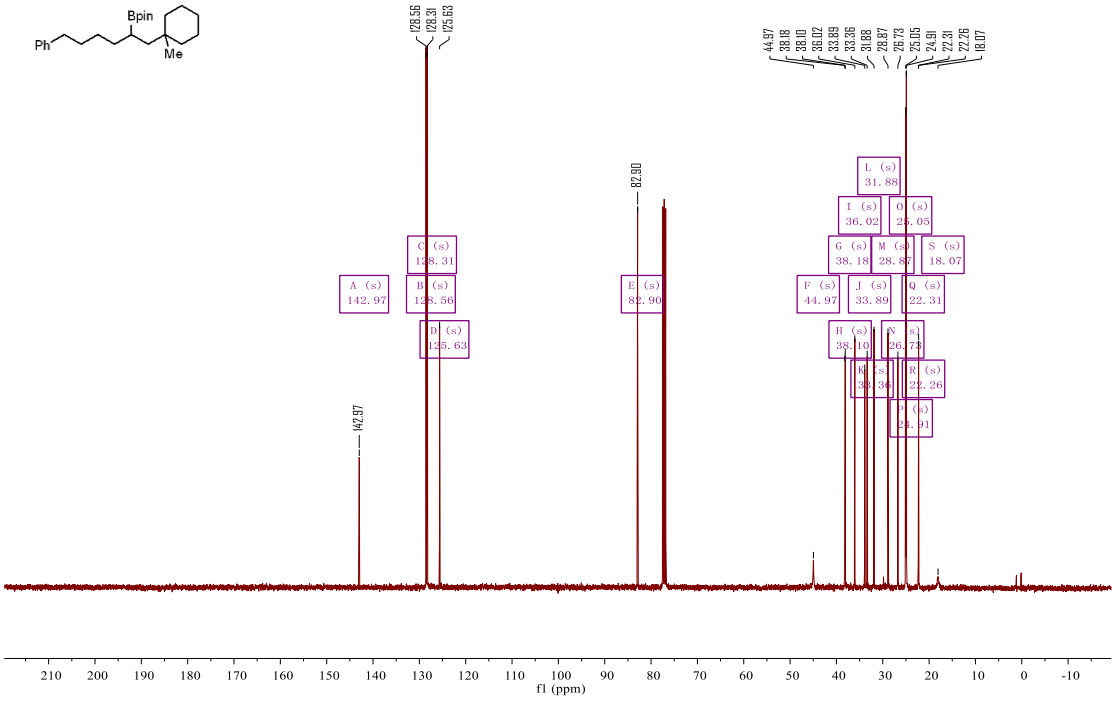
^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.97, 128.56, 128.31, 125.63, 82.90, 44.97, 38.18, 38.10, 36.02, 33.89, 33.36, 31.88, 28.87, 26.73, 25.05, 24.91, 22.31, 22.26, 18.07.

^{11}B NMR (128 MHz, Chloroform-*d*) 33.74

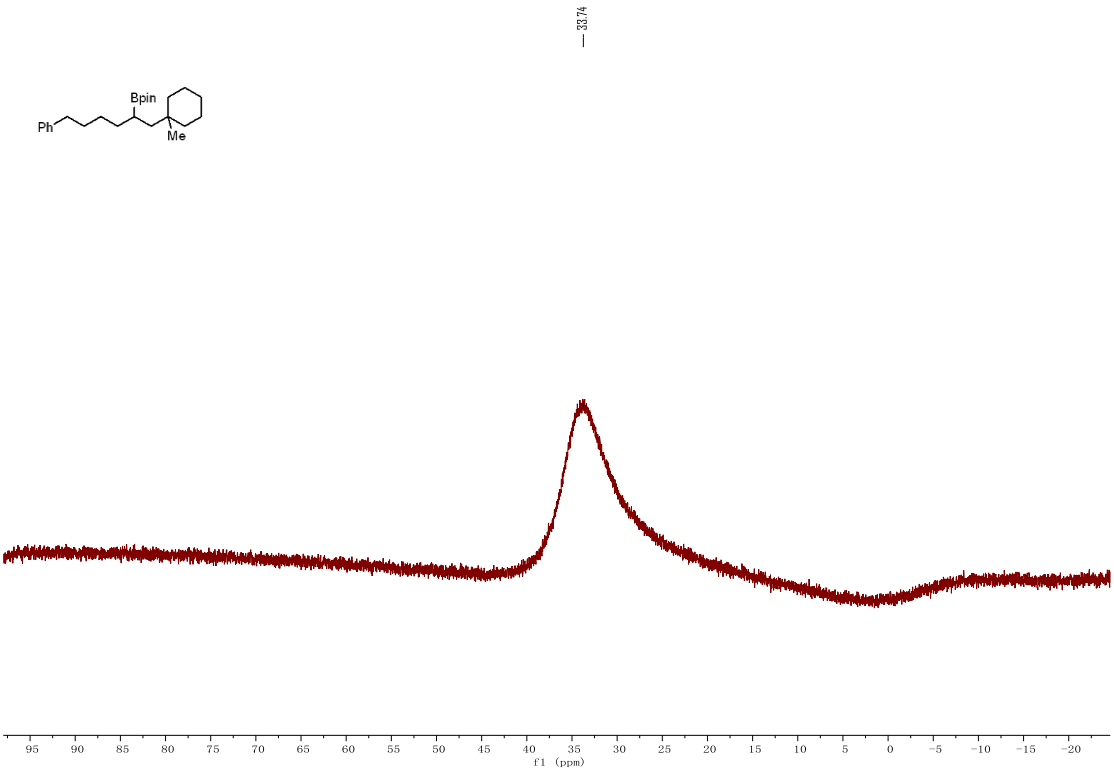
HRMS (ESI) calculated for $C_{25}H_{41}BO_2$ $[M+H]^+$:385.3272, found: 385.3264.



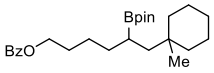
^{1}H NMR spectra for **31**



^{13}C NMR spectra for **31**



^{11}B NMR spectra for **31**



6-(1-methylcyclohexyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl benzoate (**32**)

Following general procedure 1. The product was isolated by column chromatography as colorless oil (66.0 mg, 0.154 mmol, 77%).

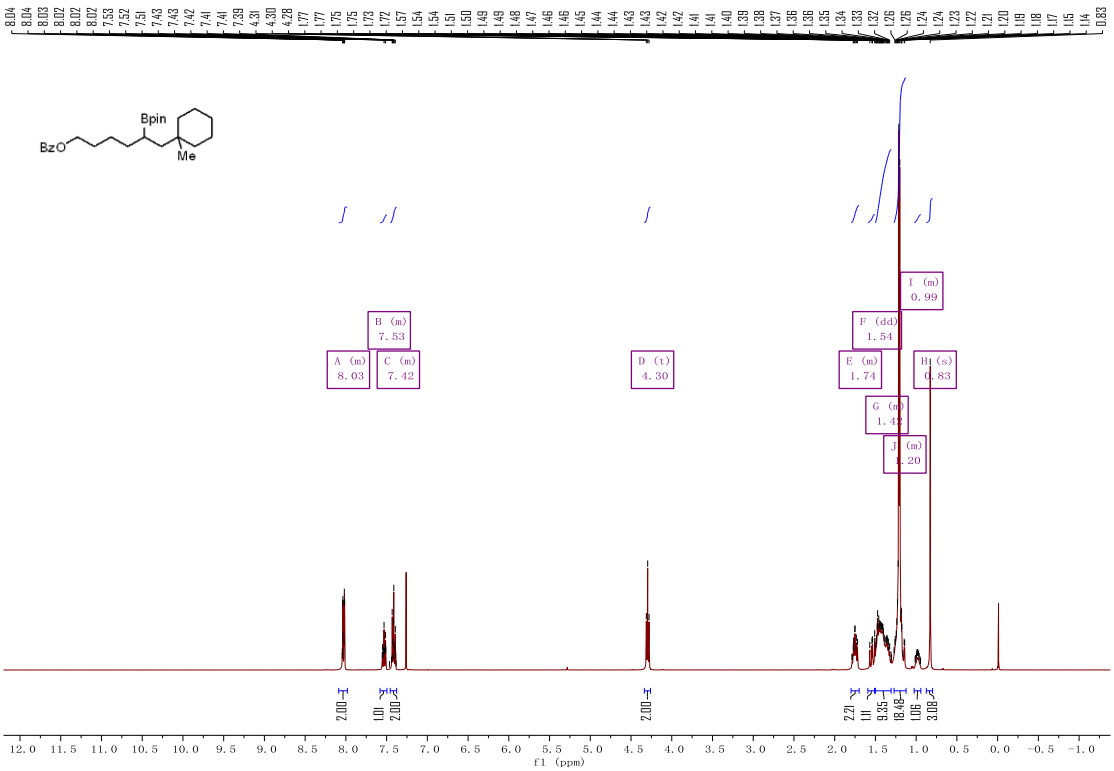
Rf (petroleum ether : acetone = 15 : 1) = 0.55

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 – 7.99 (m, 2H), 7.58 – 7.48 (m, 1H), 7.46 – 7.35 (m, 2H), 4.30 (t, *J* = 6.6 Hz, 2H), 1.81 – 1.70 (m, 2H), 1.54 (dd, *J* = 13.5, 10.4 Hz, 1H), 1.50 – 1.30 (m, 9H), 1.27 – 1.11 (m, 18H), 1.04 – 0.92 (m, 1H), 0.83 (s, 3H).

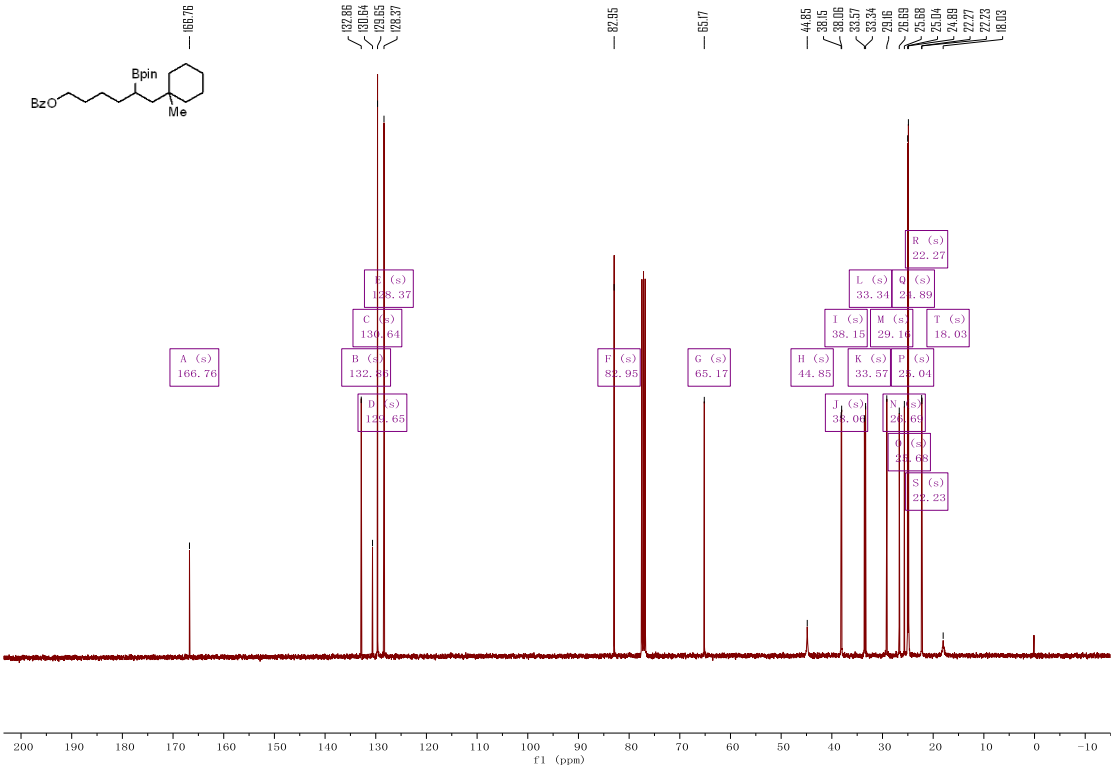
^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.76, 132.86, 130.64, 129.65, 128.37, 82.95, 65.17, 44.85, 38.15, 38.06, 33.57, 33.34, 29.16, 26.69, 25.68, 25.04, 24.89, 22.27, 22.23, 18.03.

^{11}B NMR (128 MHz, Chloroform-*d*) 36.23

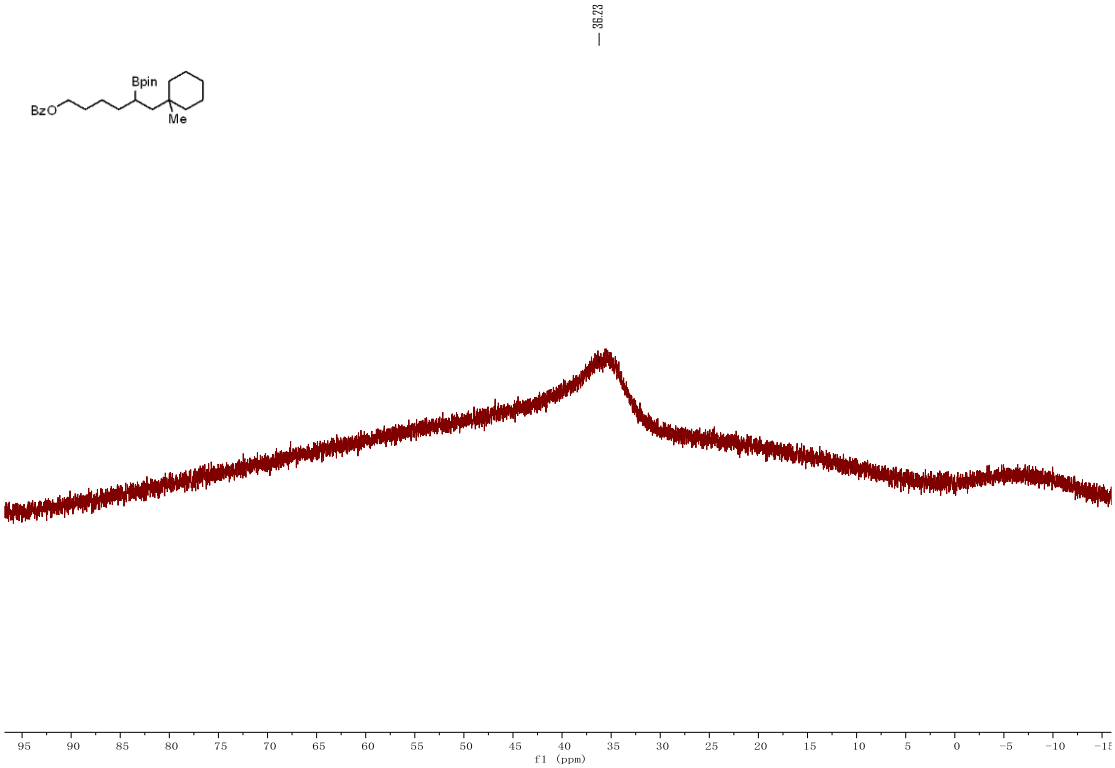
HRMS (ESI) calculated for $C_{26}H_{41}BO_4$ $[M+Na]^+$:451.2990, found: 451.2996.



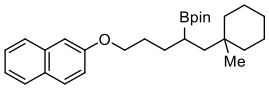
^{1}H NMR spectra for **32**



^{13}C NMR spectra for **32**



^{11}B NMR spectra for **32**



4,4,5,5-tetramethyl-2-(1-(1-methylcyclohexyl)-5-(naphthalen-2-yloxy)pentan-2-yl)-1,3,2-dioxaborolane (**33**)

Following general procedure 1. The product was isolated by column chromatography as white solid (58.5 mg, 0.134 mmol, 67%).

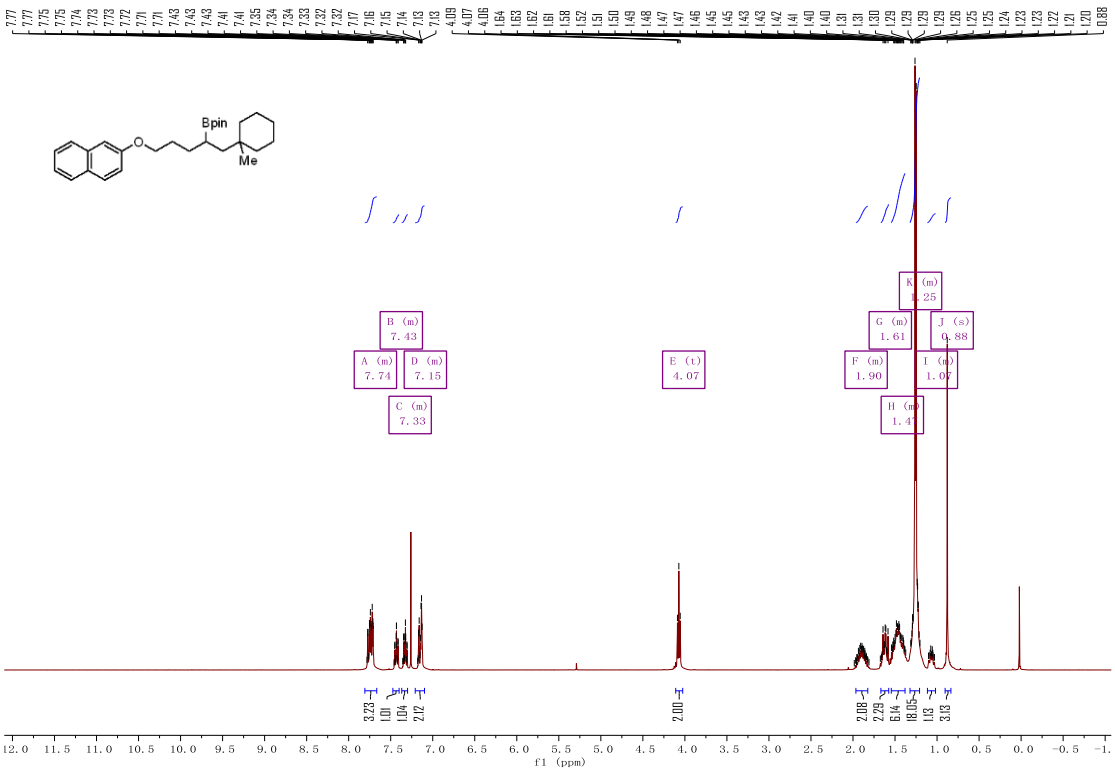
Rf (petroleum ether : ethyl acetate = 20 : 1) = 0.50

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 – 7.68 (m, 3H), 7.48 – 7.39 (m, 1H), 7.38 – 7.28 (m, 1H), 7.18 – 7.10 (m, 2H), 4.07 (t, *J* = 6.6 Hz, 2H), 1.99 – 1.78 (m, 2H), 1.68 – 1.56 (m, 2H), 1.56 – 1.35 (m, 6H), 1.34 – 1.18 (m, 18H), 1.11 – 1.01 (m, 1H), 0.88 (s, 3H).

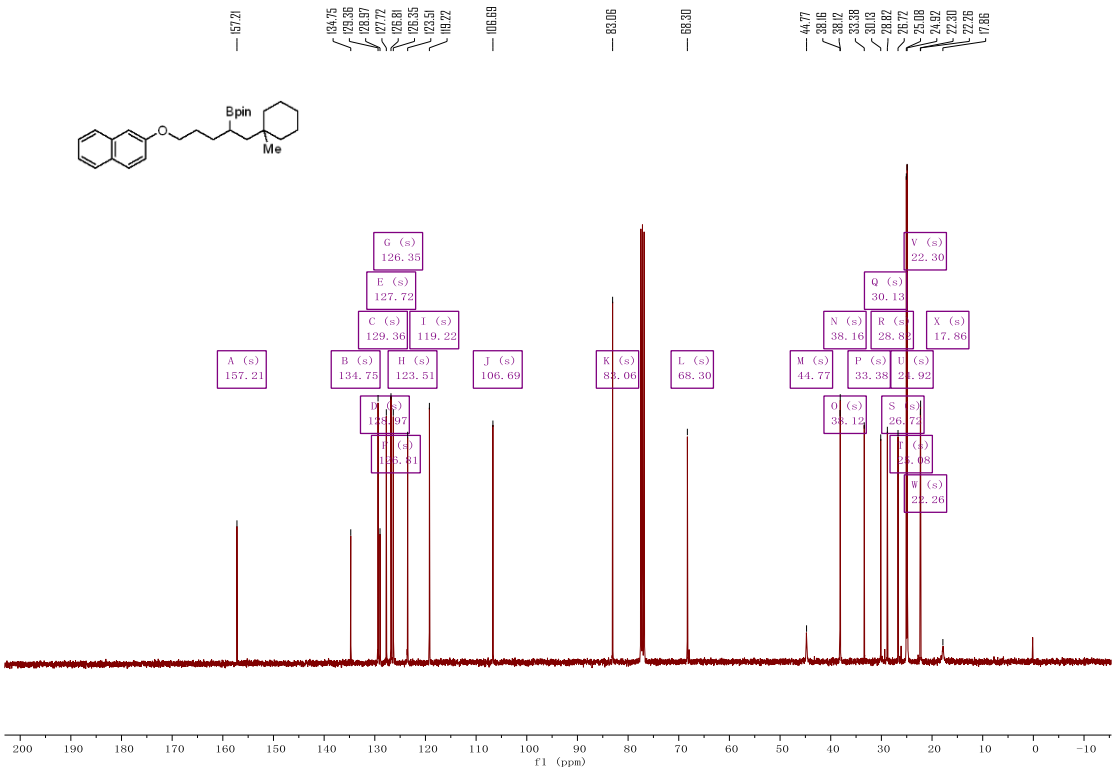
^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.21, 134.75, 129.36, 128.97, 127.72, 126.81, 126.35, 123.51, 119.22, 106.69, 83.06, 68.30, 44.77, 38.16, 38.12, 33.38, 30.13, 28.82, 26.72, 25.08, 24.92, 22.30, 22.26, 17.86.

^{11}B NMR (128 MHz, Chloroform-*d*) 37.18

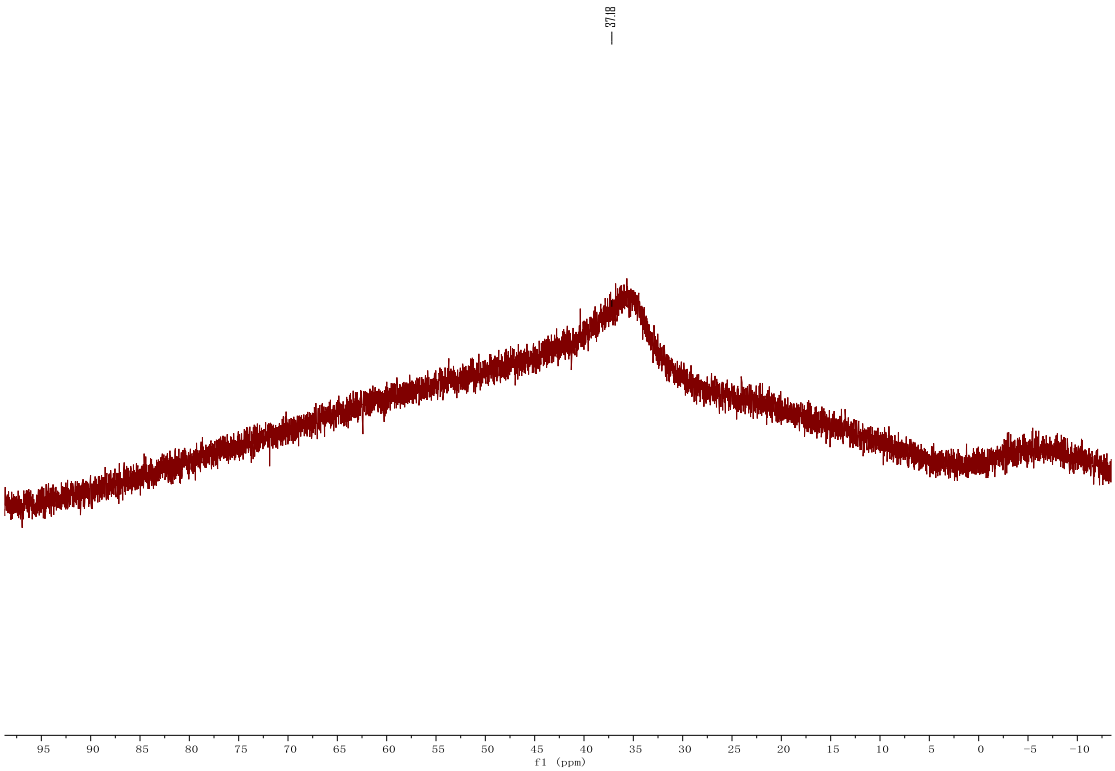
HRMS (ESI) calculated for $C_{28}H_{41}BO_3$ $[M+H]^+$:437.3222, found: 437.3227.



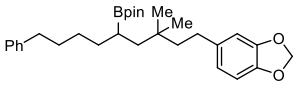
^{1}H NMR spectra for **33**



^{13}C NMR spectra for **33**



^{11}B NMR spectra for **33**



2-(1-(benzo[*d*][1,3]dioxol-5-yl)-3,3-dimethyl-9-phenylnonan-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**34**)

Following general procedure 1. The product was isolated by column chromatography as colorless oil (48.8 mg, 0.102 mmol, 51%).

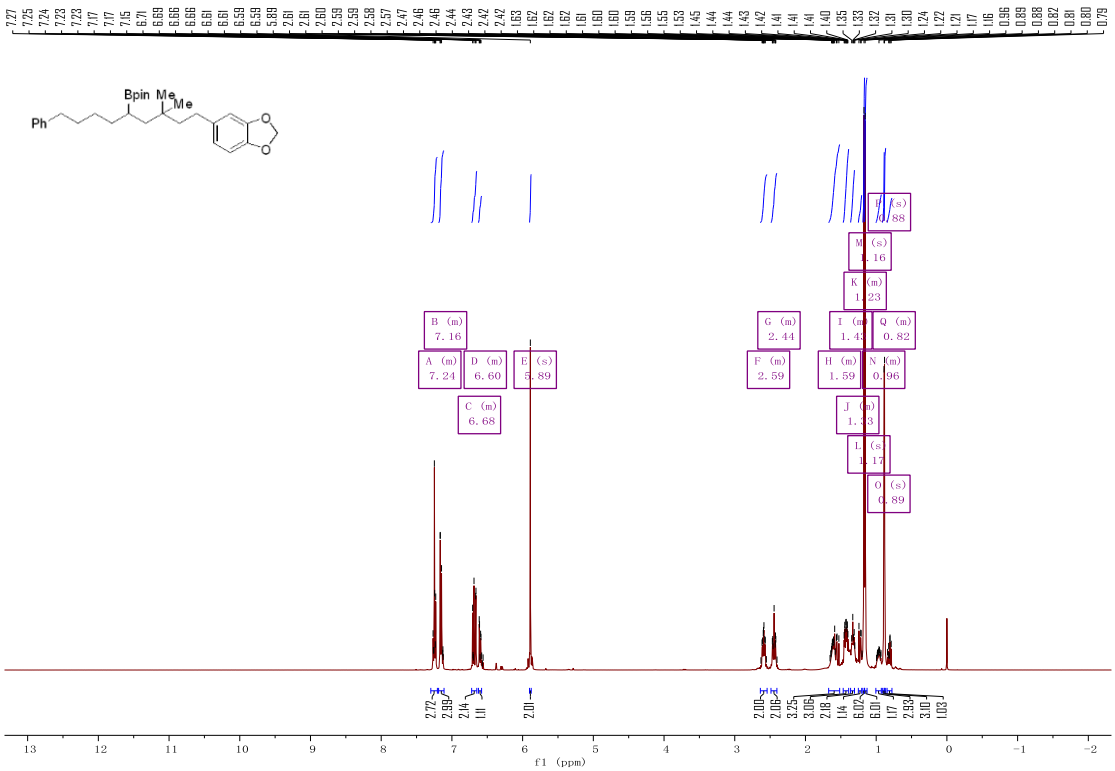
Rf (petroleum ether : acetone = 15 : 1) = 0.45

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.21 (m, 2H), 7.20 – 7.09 (m, 3H), 6.77 – 6.64 (m, 2H), 6.62 – 6.55 (m, 1H), 5.89 (s, 2H), 2.64 – 2.54 (m, 2H), 2.48 – 2.39 (m, 2H), 1.66 – 1.51 (m, 33H), 1.48 – 1.38 (m, 3H), 1.36 – 1.30 (m, 2H), 1.25 – 1.20 (m, 1H), 1.17 (s, 6H), 1.16 (s, 6H), 1.02 – 0.91 (m, 1H), 0.89 (s, 3H), 0.88 (s, 3H), 0.85 – 0.76 (m, 1H).

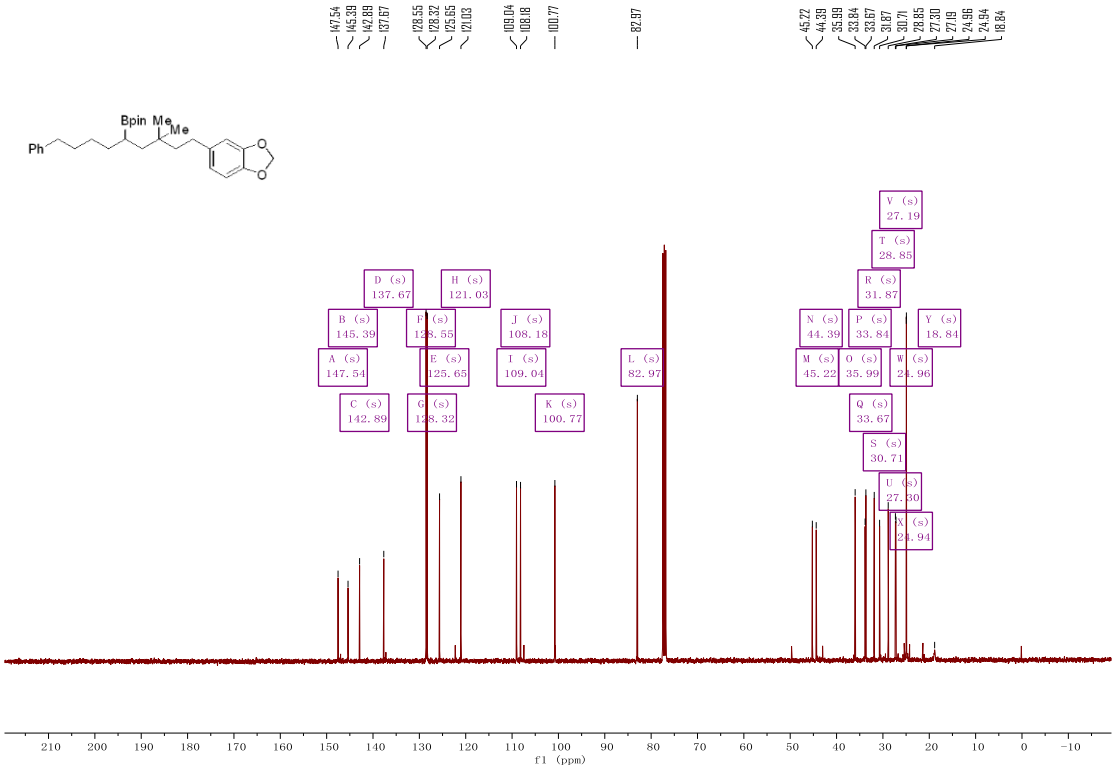
^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.54, 145.39, 142.89, 137.67, 128.55, 128.32, 125.65, 121.03, 109.04, 108.18, 100.77, 82.97, 45.22, 44.39, 35.99, 33.84, 33.67, 31.87, 30.71, 28.85, 27.30, 27.19, 24.96, 24.94, 18.84.

^{11}B NMR (128 MHz, Chloroform-*d*) 35.58

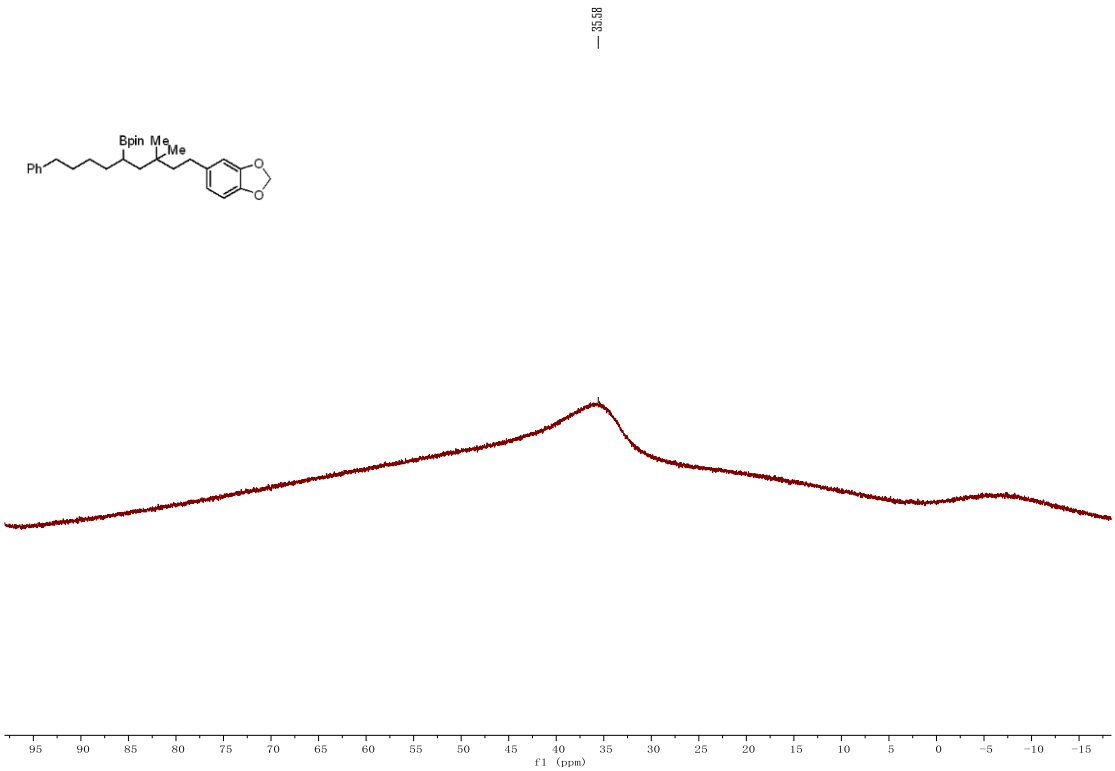
HRMS (ESI) calculated for $C_{30}H_{43}BO_4$ $[M+H]^+$:501.3147, found: 501.3152.



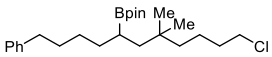
^{1}H NMR spectra for **34**



^{13}C NMR spectra for **34**



^{11}B NMR spectra for **34**



2-(11-chloro-7,7-dimethyl-1-phenylundecan-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**35**)

Following general procedure 1. The product was isolated by column chromatography as colorless oil (64.0 mg, 0.152 mmol, 76%).

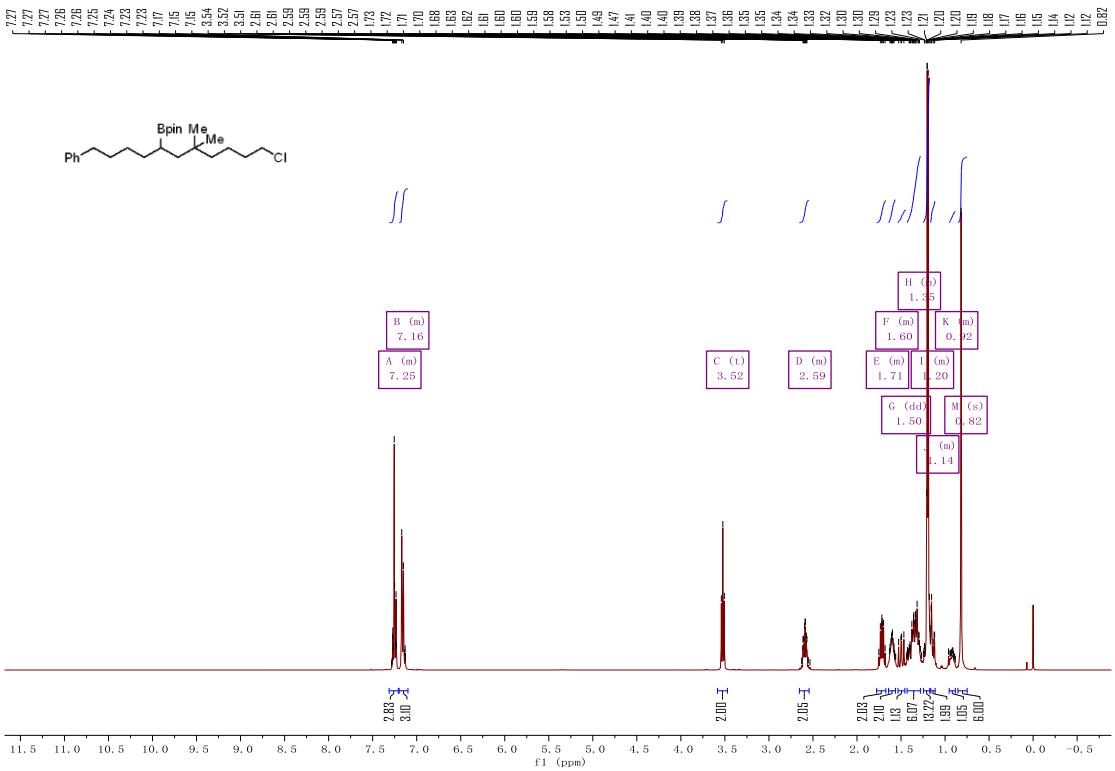
Rf (petroleum ether : ethyl acetate = 20 : 1) = 0.50

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 – 7.21 (m, 2H), 7.19 – 7.11 (m, 3H), 3.52 (t, *J* = 6.7 Hz, 2H), 2.66 – 2.51 (m, 2H), 1.78 – 1.67 (m, 2H), 1.65 – 1.56 (m, 2H), 1.50 (dd, *J* = 13.5, 10.4 Hz, 1H), 1.45 – 1.26 (m, 6H), 1.27 – 1.15 (m, 13H), 1.16 – 1.11 (m, 2H), 0.97 – 0.87 (m, 1H), 0.82 (s, 6H).

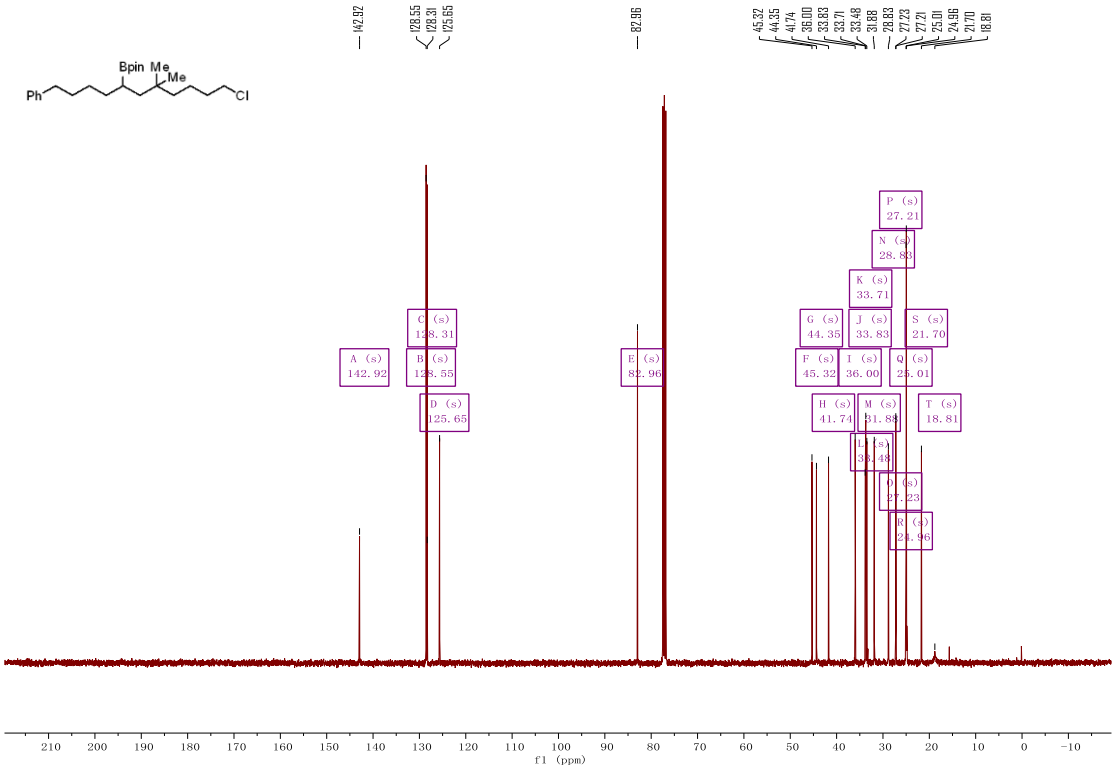
^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.92, 128.55, 128.31, 125.65, 82.96, 45.32, 44.35, 41.74, 36.00, 33.83, 33.71, 33.48, 31.88, 28.83, 27.23, 27.21, 25.01, 24.96, 21.70, 18.81.

^{11}B NMR (128 MHz, Chloroform-*d*) 35.35

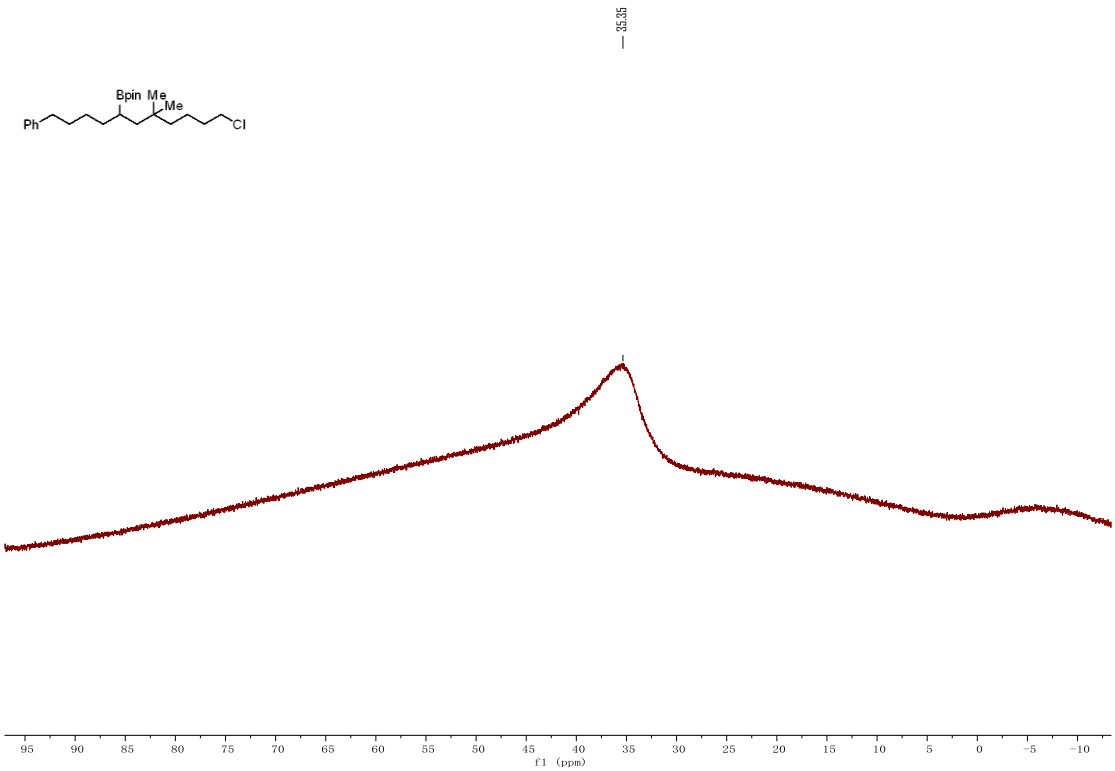
HRMS (ESI) calculated for $C_{25}H_{42}BClO_2$ $[M+H]^+$:421.3039, found: 421.3045.



^{1}H NMR spectra for **35**

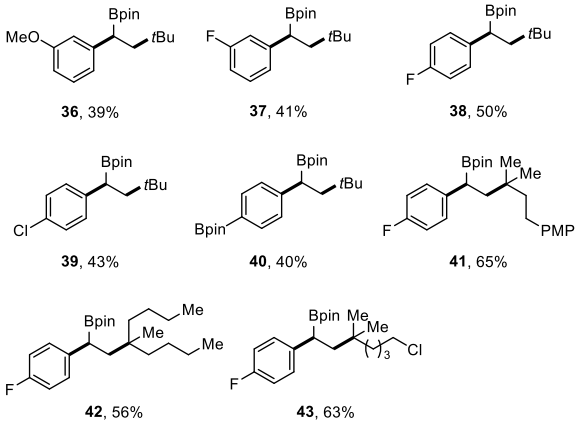


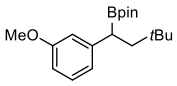
^{13}C NMR spectra for **35**



^{11}B NMR spectra for **35**

7. Examples Described in Scheme 4





2-(1-(3-methoxyphenyl)-3,3-dimethylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**36**)

Following general procedure 1. The product was isolated by column chromatography as white solid (24.8 mg, 0.078 mmol, 39%).

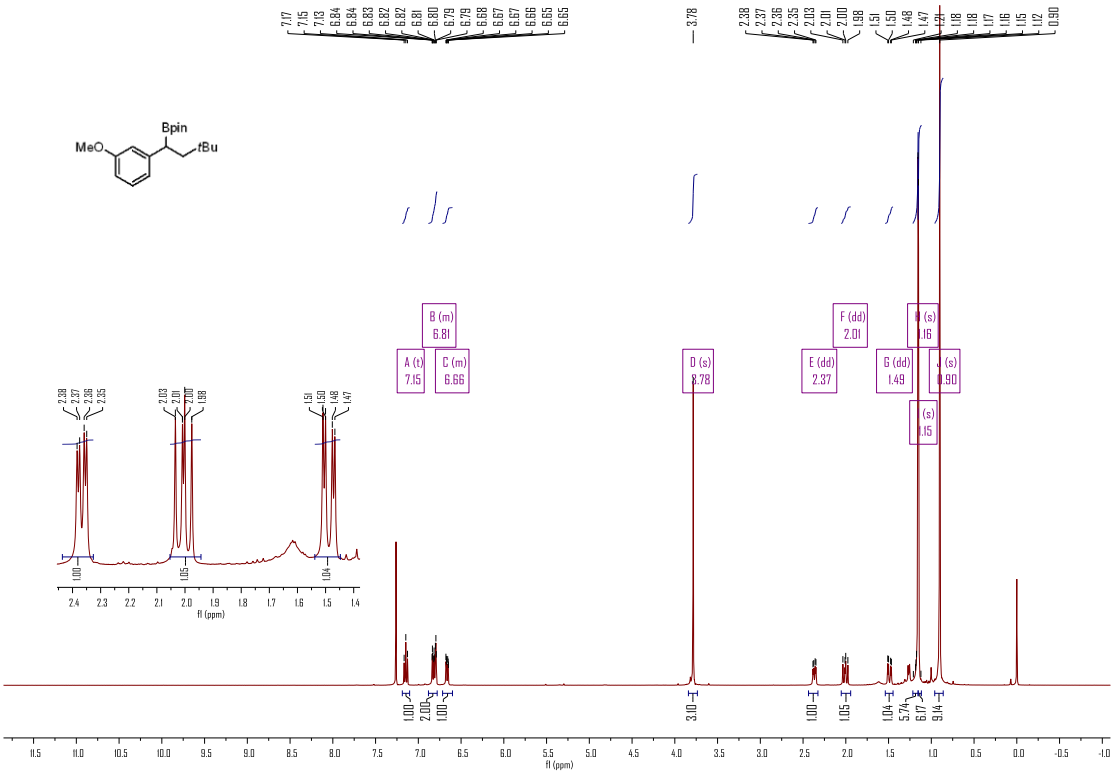
Rf (petroleum ether : dichloromethane = 1 : 1) = 0.45

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.15 (t, *J* = 7.9 Hz, 1H), 6.87 – 6.77 (m, 2H), 6.71 – 6.62 (m, 1H), 3.78 (s, 3H), 2.37 (dd, *J* = 10.1, 3.7 Hz, 1H), 2.01 (dd, *J* = 13.3, 10.1 Hz, 1H), 1.49 (dd, *J* = 13.3, 3.6 Hz, 1H), 1.16 (s, 6H), 1.15 (s, 6H), 0.90 (s, 9H).

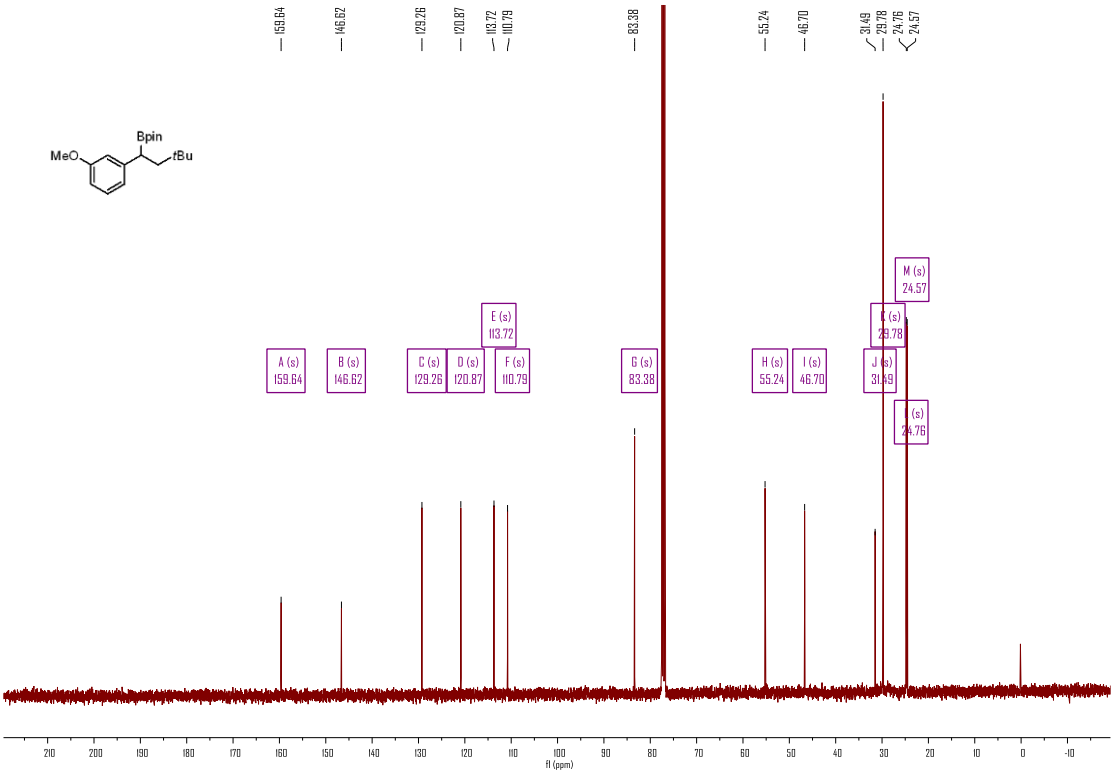
^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.64, 146.62, 129.26, 120.87, 113.72, 110.79, 83.38, 55.24, 46.70, 31.49, 29.78, 24.76, 24.57.

^{11}B NMR (128 MHz, Chloroform-*d*) 33.35

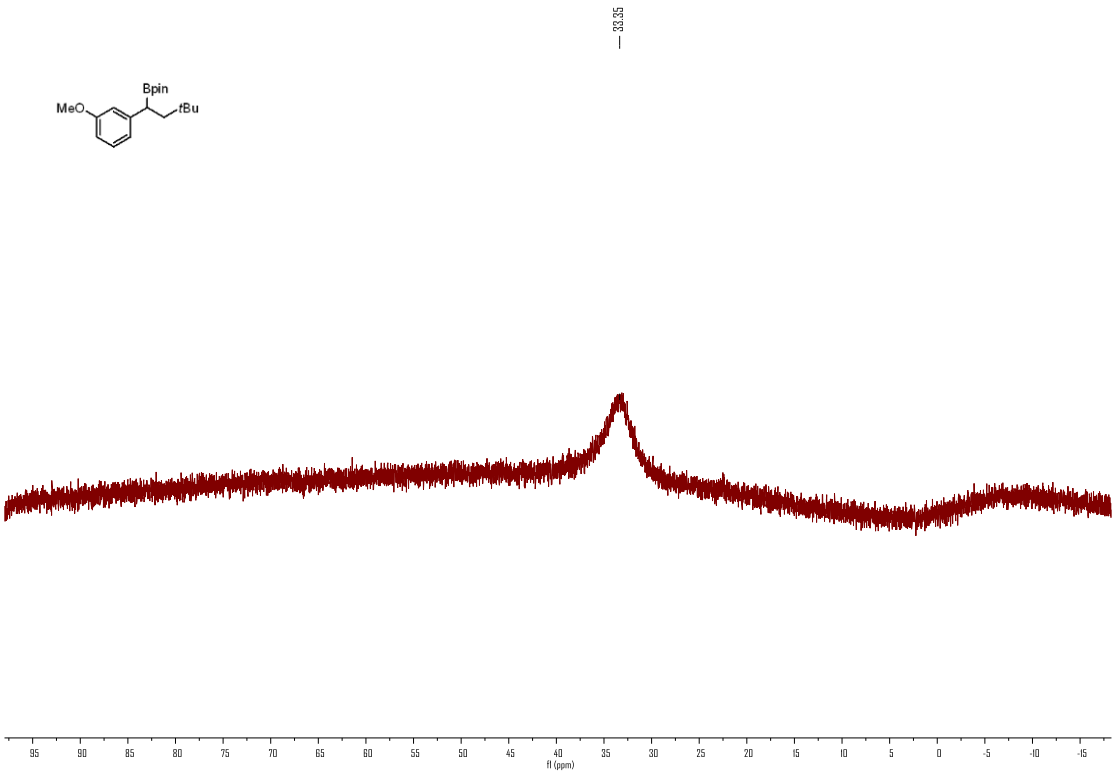
HRMS (ESI) calculated for $C_{19}H_{31}BO_3$ $[M+H]^+$: 319.2439 found: 319.2430.



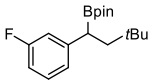
^{1}H NMR spectra for **36**



^{1}H NMR spectra for **36**



^{11}B NMR spectra for **36**



2-(1-(3-fluorophenyl)-3,3-dimethylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**37**) Following general procedure 1. The product was isolated by column chromatography as white solid (25.1 mg, 0.082 mmol, 41%).

Rf (petroleum ether : ethyl acetate = 20 : 1) = 0.50

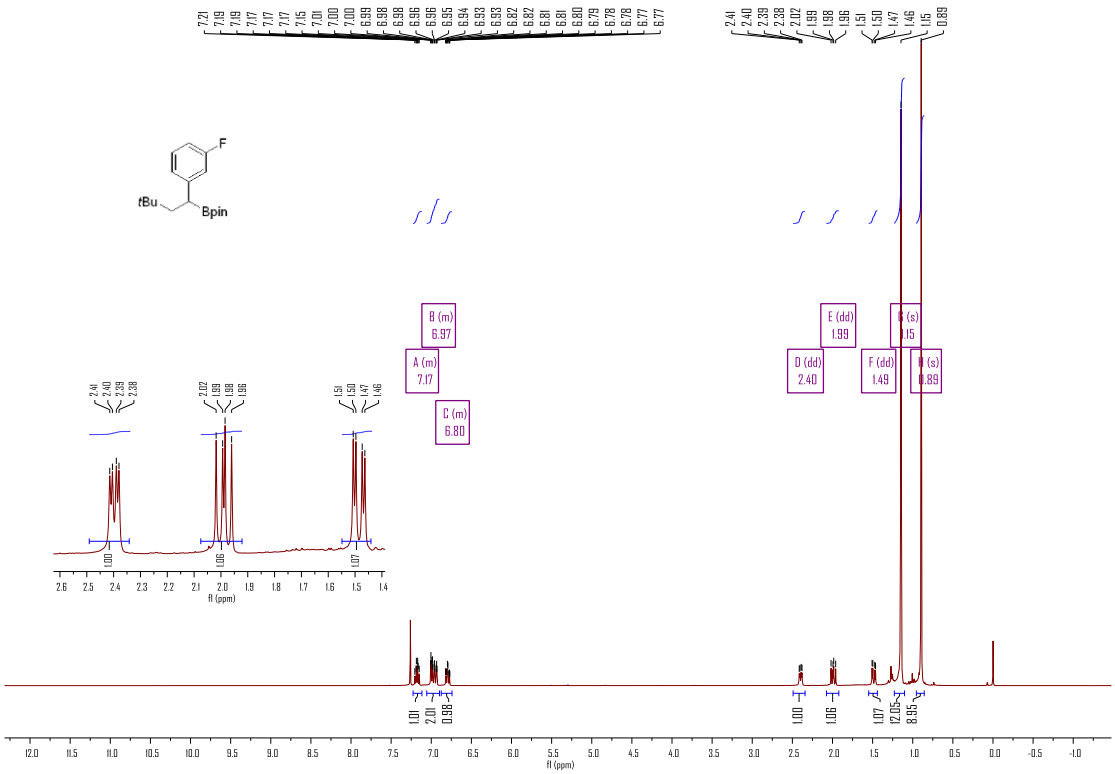
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 – 7.13 (m, 1H), 7.03 – 6.92 (m, 2H), 6.85 – 6.72 (m, 1H), 2.40 (dd, *J* = 9.8, 4.0 Hz, 1H), 1.99 (dd, *J* = 13.3, 9.8 Hz, 1H), 1.49 (dd, *J* = 13.4, 4.0 Hz, 1H), 1.15 (s, 12H), 0.89 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.90 (d, *J* = 244.4 Hz), 147.56 (d, *J* = 7.1 Hz), 129.49 (d, *J* = 8.4 Hz), 123.88 (d, *J* = 2.8 Hz), 114.89 (d, *J* = 21.1 Hz), 111.82 (d, *J* = 21.1 Hz), 83.40, 46.29, 31.40, 29.65, 24.56, 24.43.

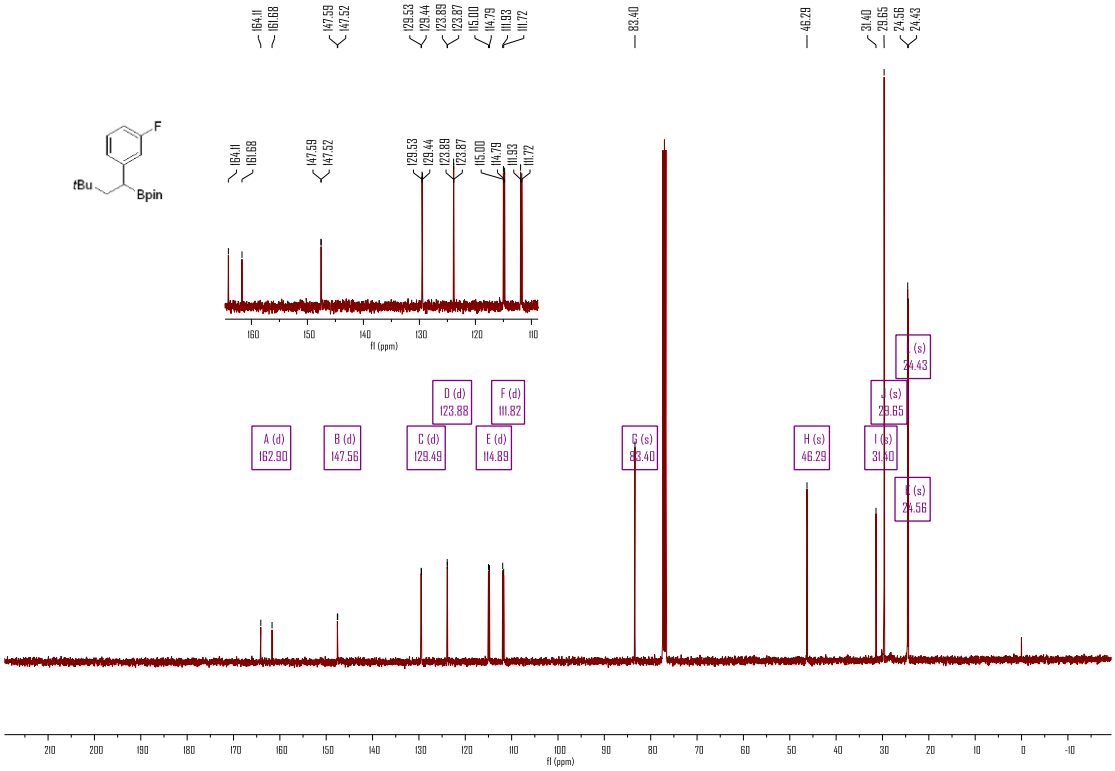
^{11}B NMR (128 MHz, Chloroform-*d*) 32.94

^{19}F NMR (376 MHz, Chloroform-*d*) δ -105.54 – -125.70 (m).

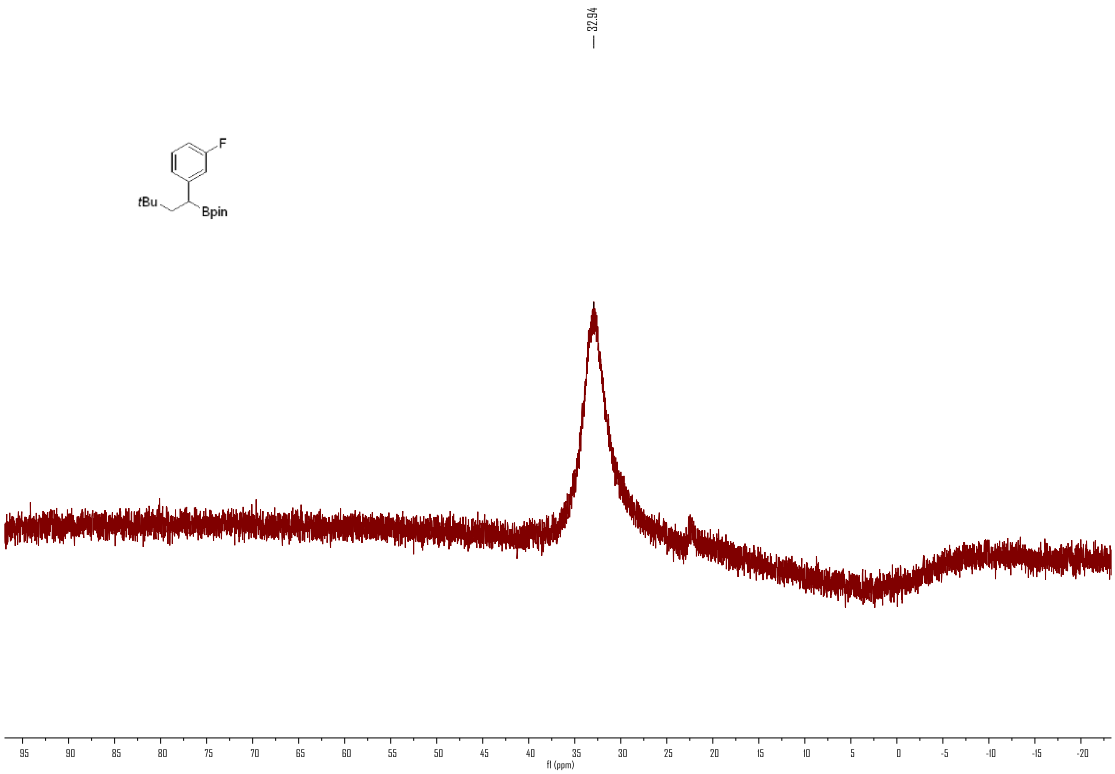
HRMS (ESI) calculated for $C_{18}H_{28}BFO_2$ $[M+H]^+$: 307.2239 found: 307.2241.



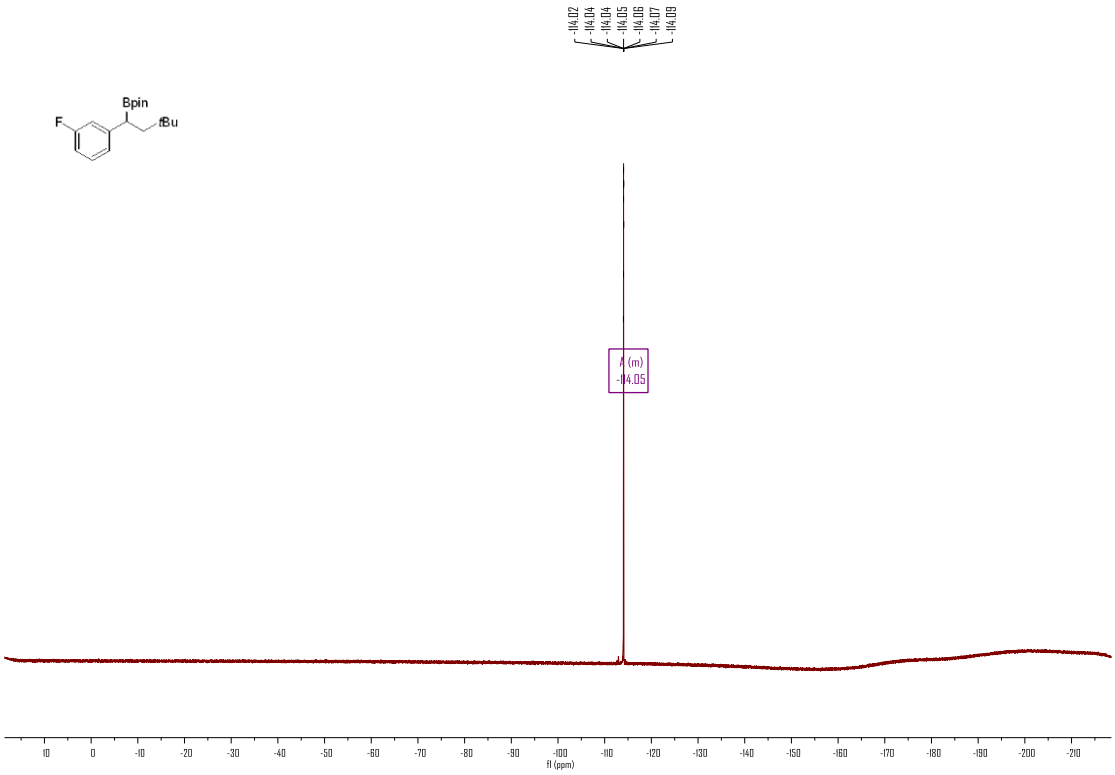
^{1}H NMR spectra for **37**



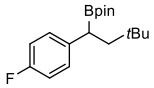
^{13}C NMR spectra for **37**



^{11}B NMR spectra for **37**



^{19}F NMR spectra for **37**



2-(1-(4-fluorophenyl)-3,3-dimethylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**38**) Following general procedure 1. The product was isolated by column chromatography as white solid (30.6 mg, 0.100 mmol, 50%).

Rf (petroleum ether : ethyl acetate = 20 : 1) = 0.55

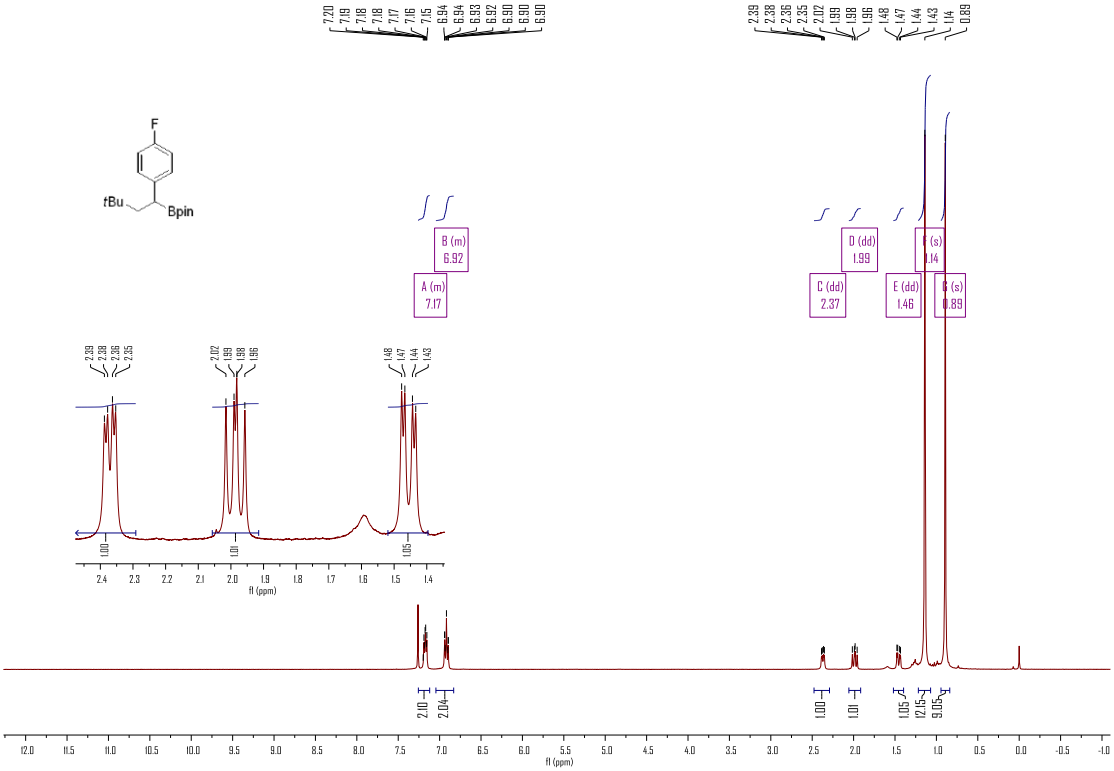
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.22 – 7.11 (m, 2H), 6.97 – 6.85 (m, 2H), 2.37 (dd, *J* = 9.9, 4.0 Hz, 1H), 1.99 (dd, *J* = 13.3, 9.9 Hz, 1H), 1.46 (dd, *J* = 13.3, 4.0 Hz, 1H), 1.14 (s, 12H), 0.89 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.81 (d, *J* = 242.3 Hz), 140.35 (d, *J* = 3.2 Hz), 129.35 (d, *J* = 7.7 Hz), 114.91 (d, *J* = 20.9 Hz), 83.27, 46.65, 31.35, 29.65, 24.54, 24.42.

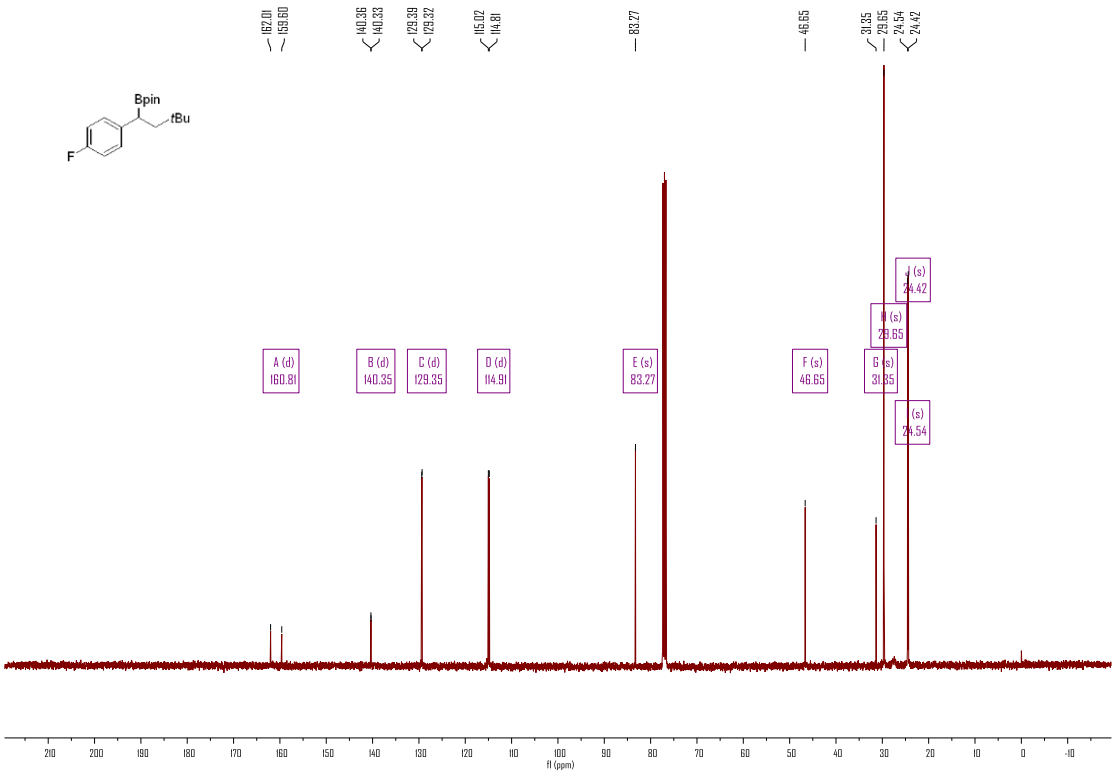
^{11}B NMR (128 MHz, Chloroform-*d*) 33.74

^{19}F NMR (376 MHz, Chloroform-*d*) δ -118.97 – -119.09 (m)

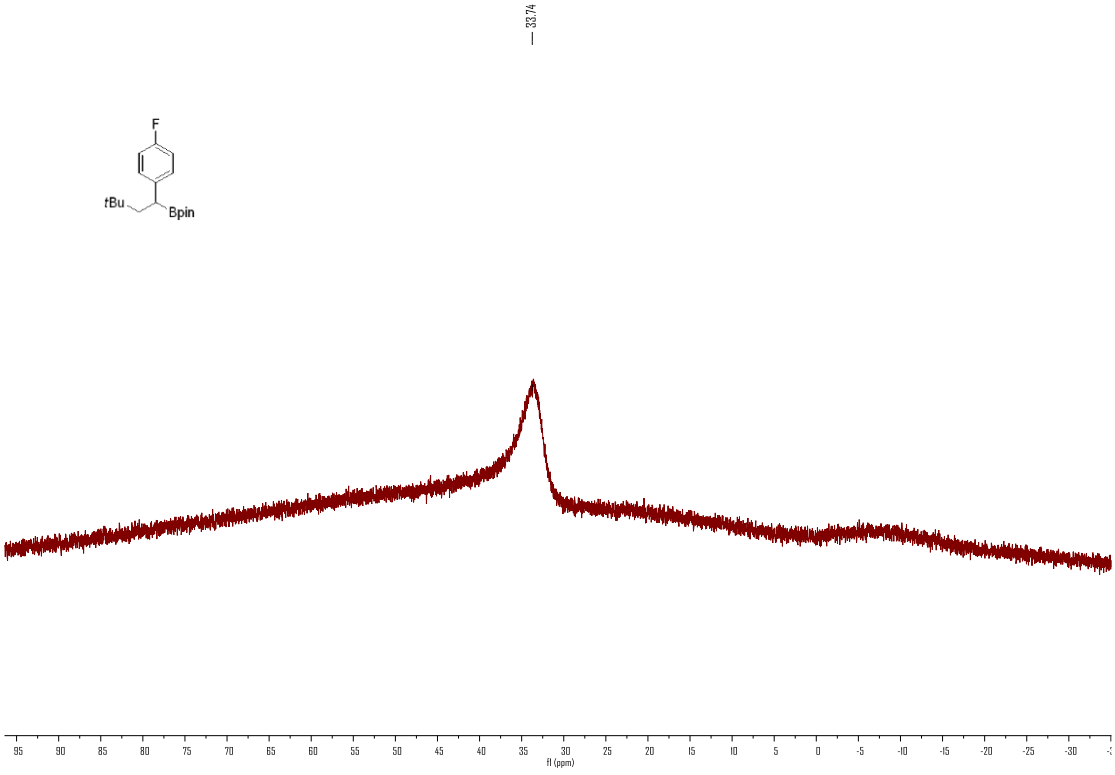
HRMS (ESI) calculated for $C_{18}H_{28}BFO_2$ $[M+H]^+$: 307.2239 found: 307.2236.



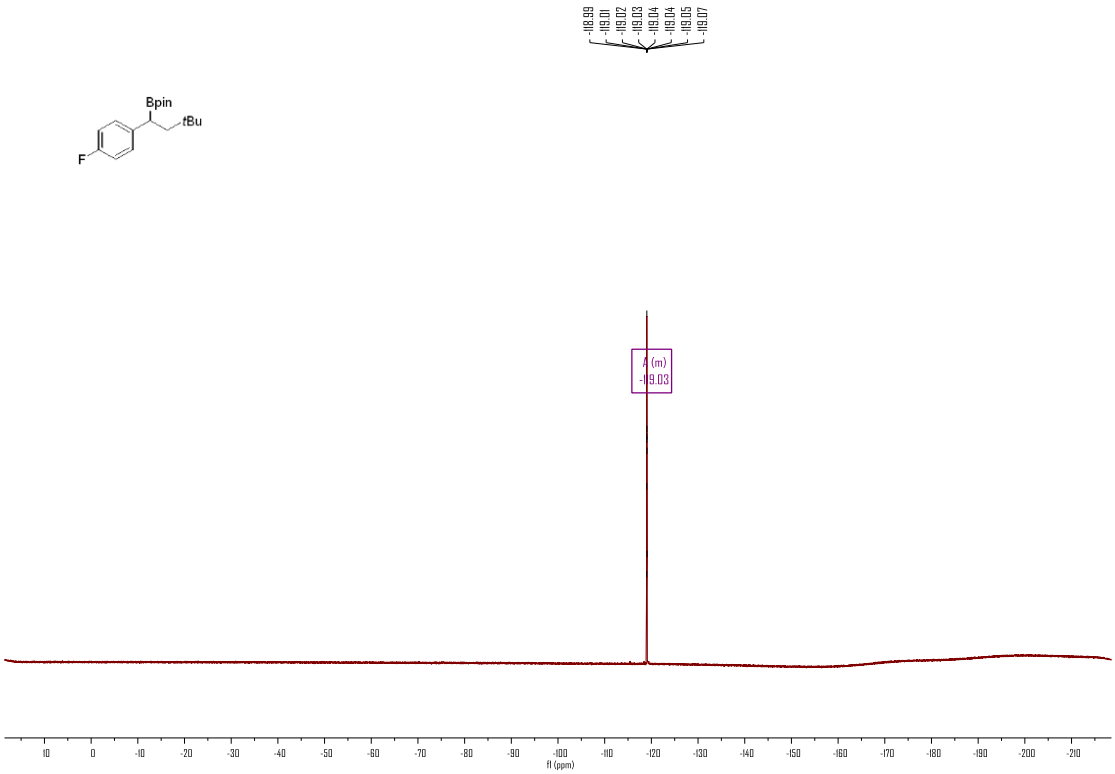
^{1}H NMR spectra for **38**



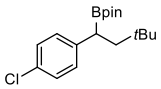
^{13}C NMR spectra for **38**



^{11}B NMR spectra for **38**



^{19}F NMR spectra for **38**



2-(1-(4-chlorophenyl)-3,3-dimethylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane(**39**) Following general procedure 1. The product was isolated by column chromatography as colorless oil (27.8 mg, 0.086 mmol, 43%).

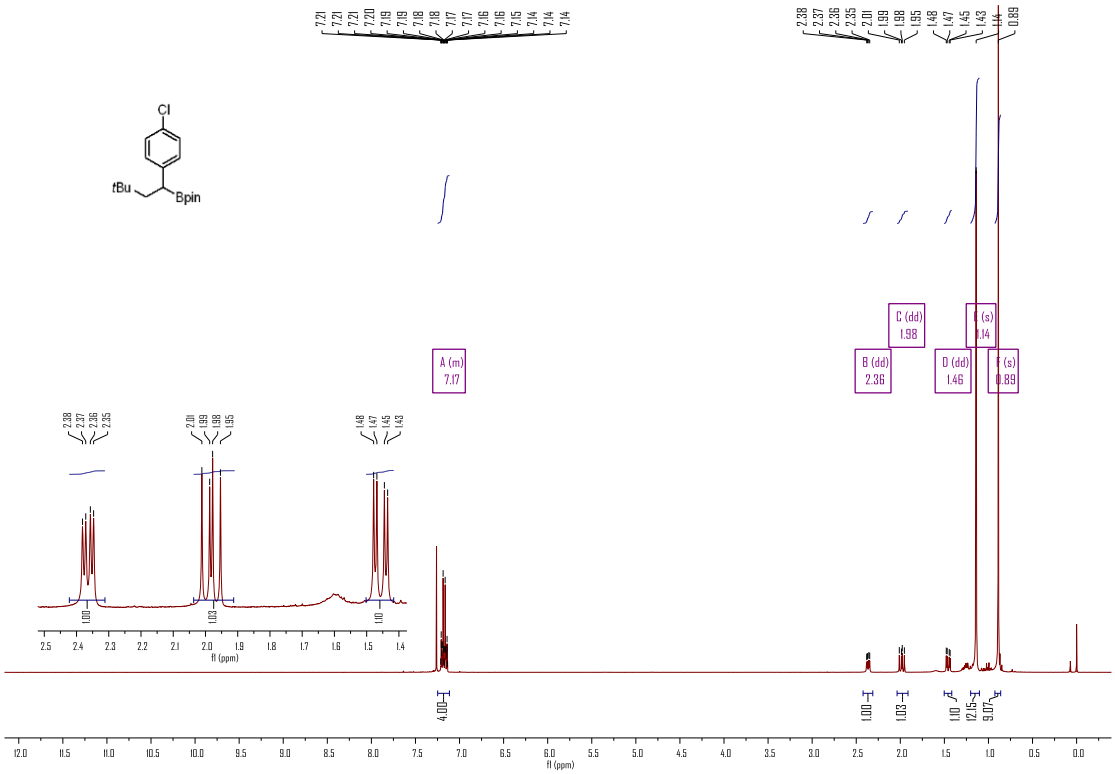
Rf (petroleum ether : ethyl acetate = 20 : 1) = 0.55

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 – 7.09 (m, 4H), 2.36 (dd, *J* = 9.7, 4.0 Hz, 1H), 1.98 (dd, *J* = 13.3, 9.7 Hz, 1H), 1.46 (dd, *J* = 13.3, 4.1 Hz, 1H), 1.14 (s, 12H), 0.89 (s, 9H).

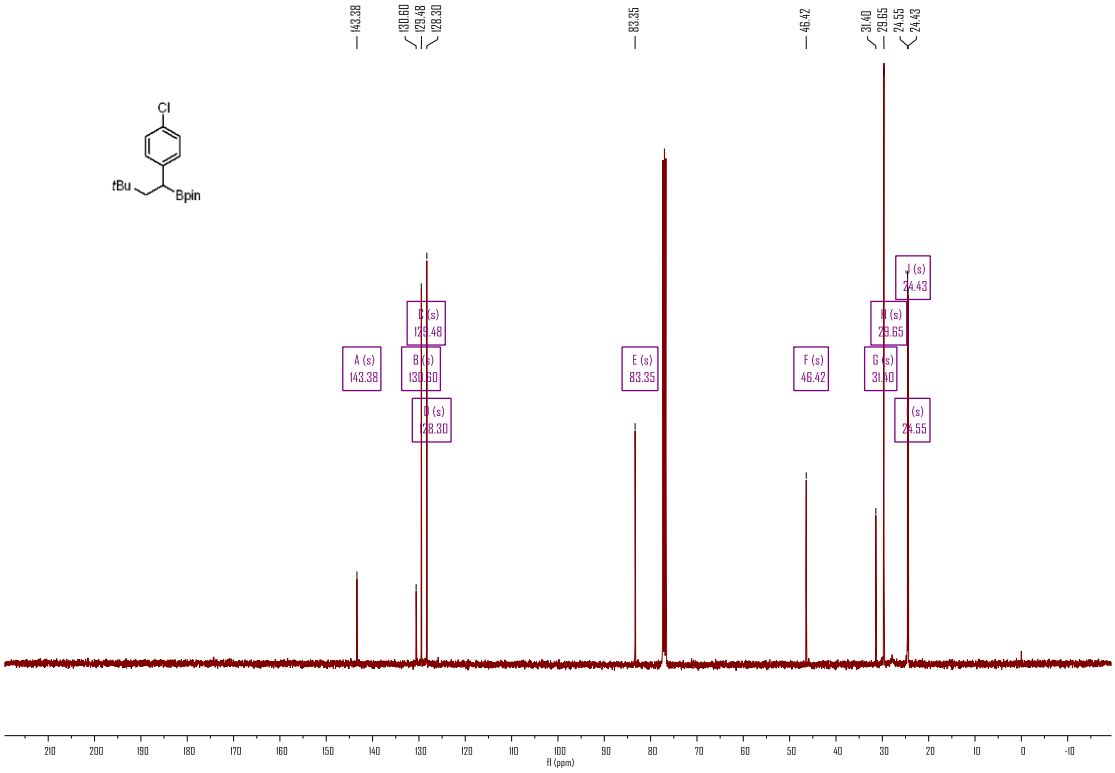
^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.38, 130.60, 129.48, 128.30, 83.35, 46.42, 31.40, 29.65, 24.55, 24.43.

^{11}B NMR (128 MHz, Chloroform-*d*) 33.26

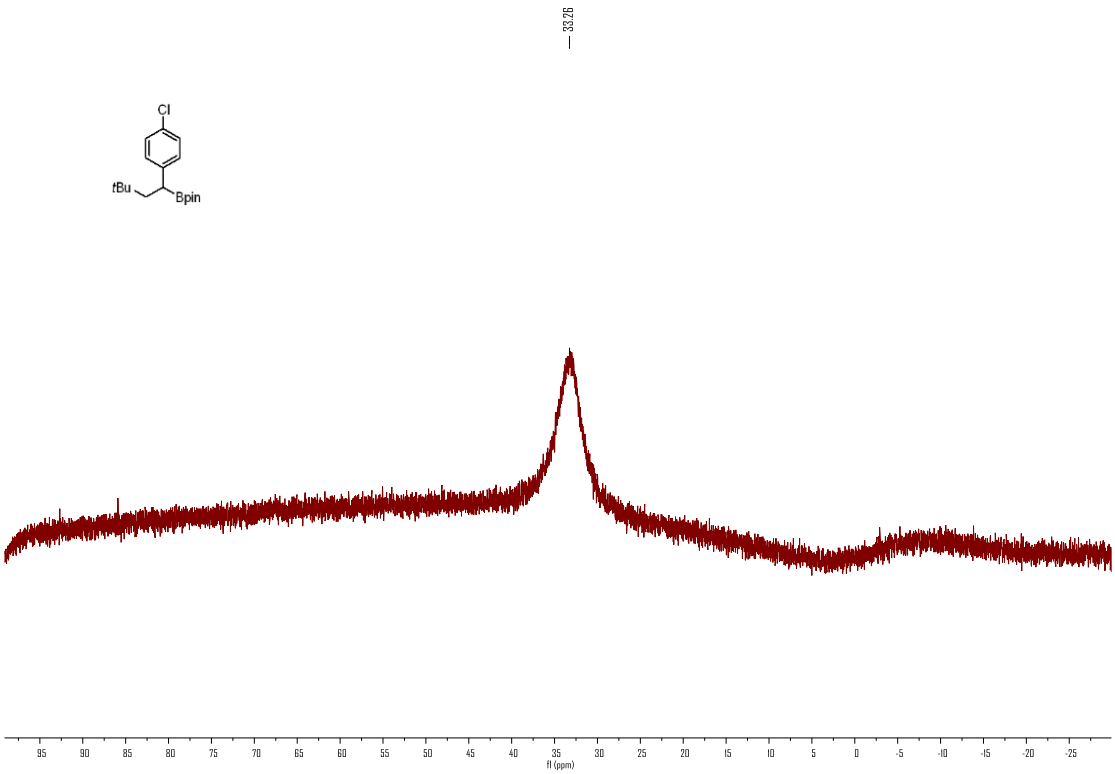
HRMS (ESI) calculated for $C_{18}H_{28}BClO_2$ $[M+H]^+$: 323.1944 found: 323.1949.



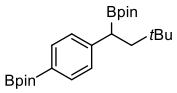
^{1}H NMR spectra for **39**



^{13}C NMR spectra for **39**



^{11}B NMR spectra for **39**



2-(4-(3,3-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane(**40**)

Following general procedure 1. The product was isolated by column chromatography as white solid (33.1 mg, 0.080 mmol, 40%).

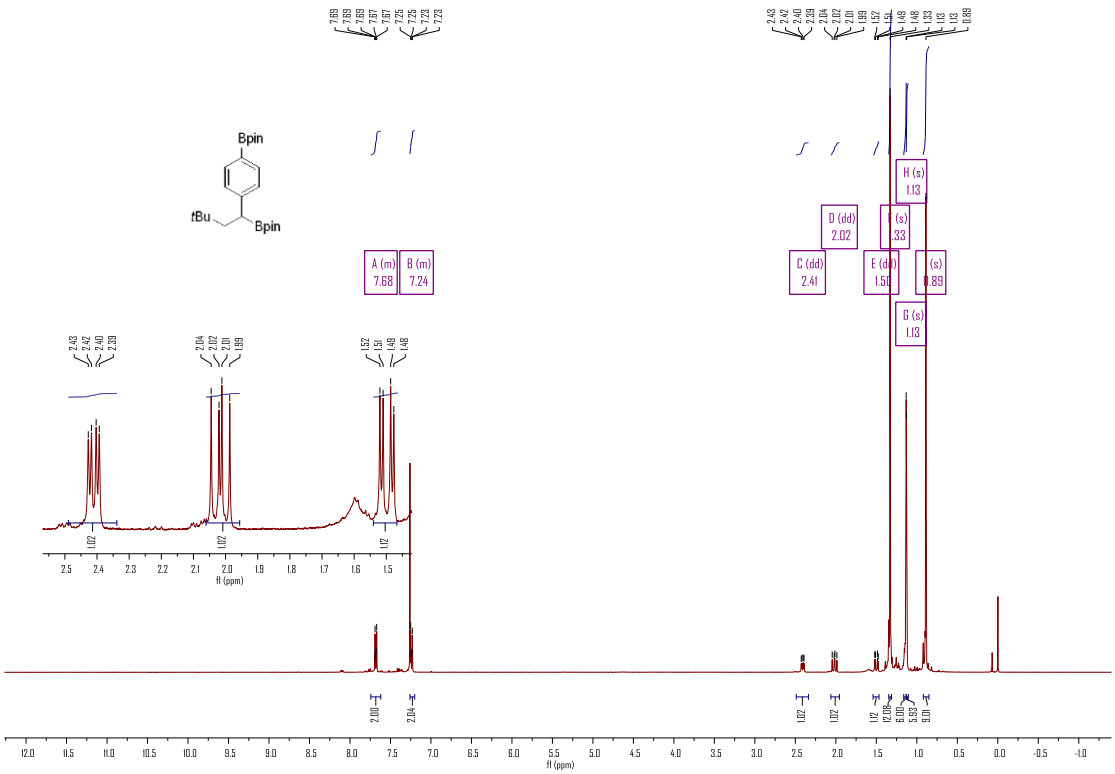
Rf (petroleum ether : ethyl acetate = 10 : 1) = 0.50

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 – 7.66 (m, 2H), 7.25 – 7.22 (m, 2H), 2.41 (dd, *J* = 9.7, 3.9 Hz, 1H), 2.02 (dd, *J* = 13.4, 9.8 Hz, 1H), 1.50 (dd, *J* = 13.3, 3.9 Hz, 1H), 1.33 (s, 12H), 1.13 (s, 6H), 1.13 (s, 6H), 0.89 (s, 9H).

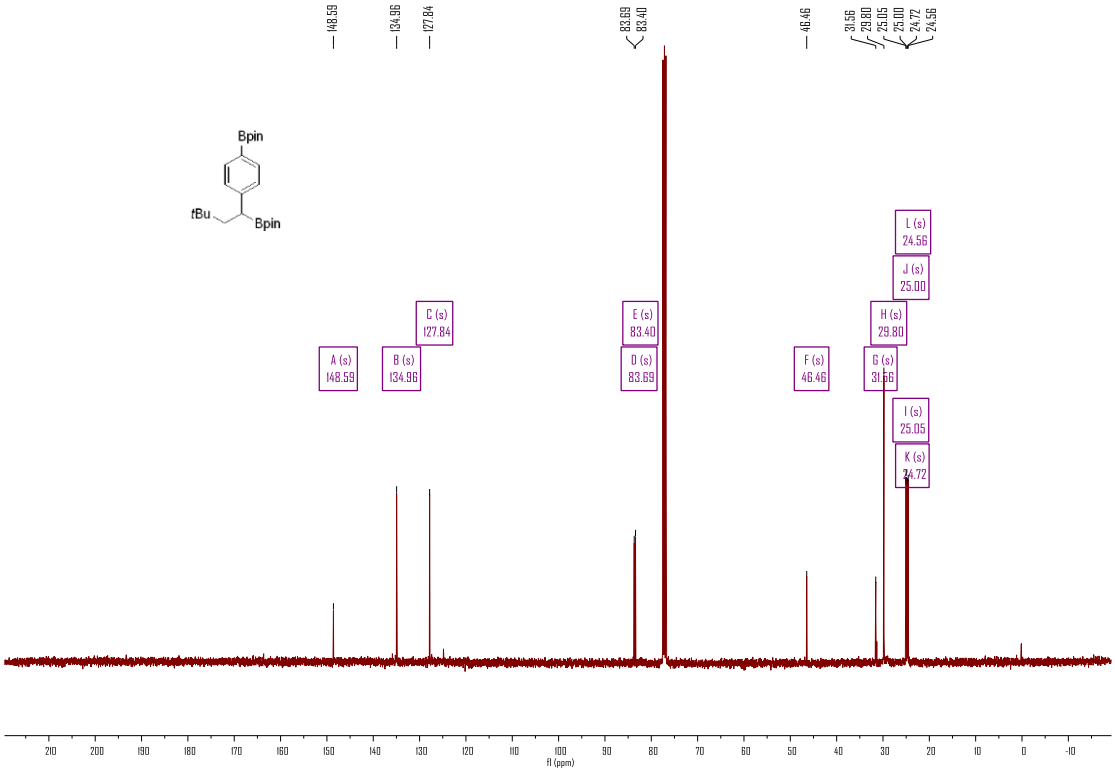
^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.59, 134.96, 127.84, 83.69, 83.40, 46.46, 31.56, 29.80, 25.05, 25.00, 24.72, 24.56

^{11}B NMR (128 MHz, Chloroform-*d*) 31.90

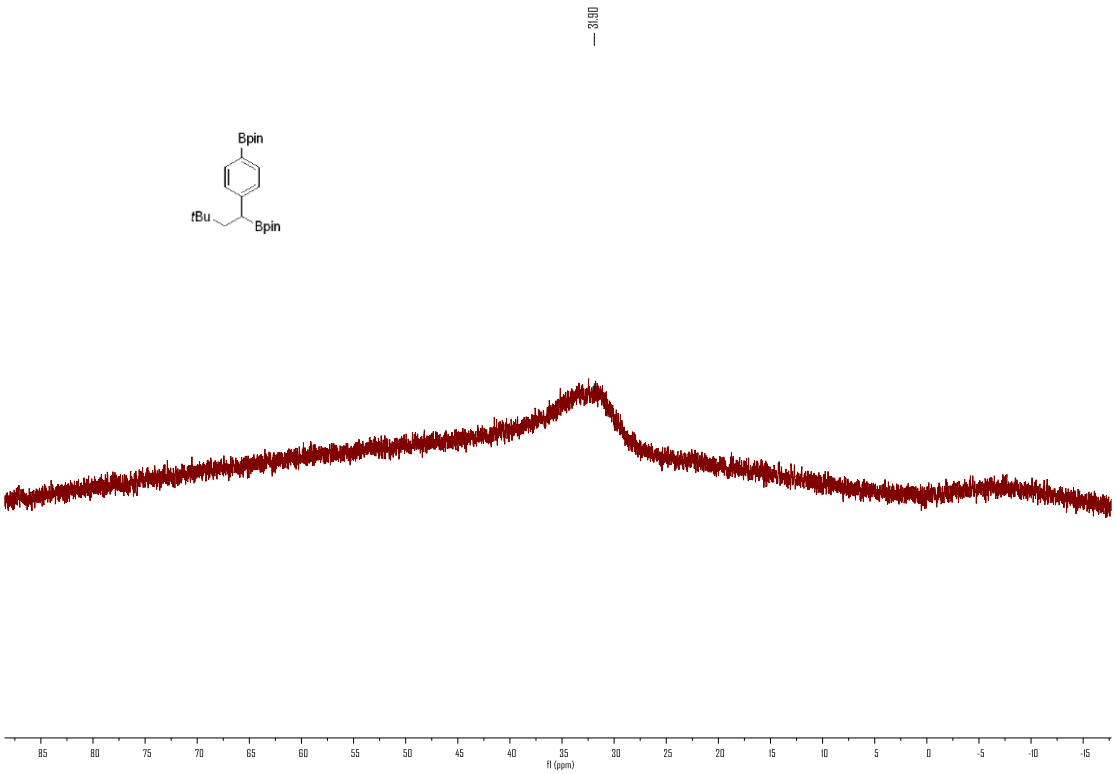
HRMS (ESI) calculated for $C_{24}H_{40}B_2O_4$ $[M+H]^+$: 415.3186 found: 415.3182.



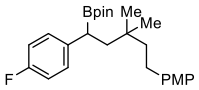
^{1}H NMR spectra for **40**



^{13}C NMR spectra for **40**



^{11}B NMR spectra for **40**



2-(1-(4-fluorophenyl)-5-(4-methoxyphenyl)-3,3-dimethylpentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**41**)

Following general procedure 1. The product was isolated by column chromatography as colorless oil (55.4 mg, 0.130 mmol, 65%).

Rf (petroleum ether : ethyl acetate = 20 : 1) = 0.45

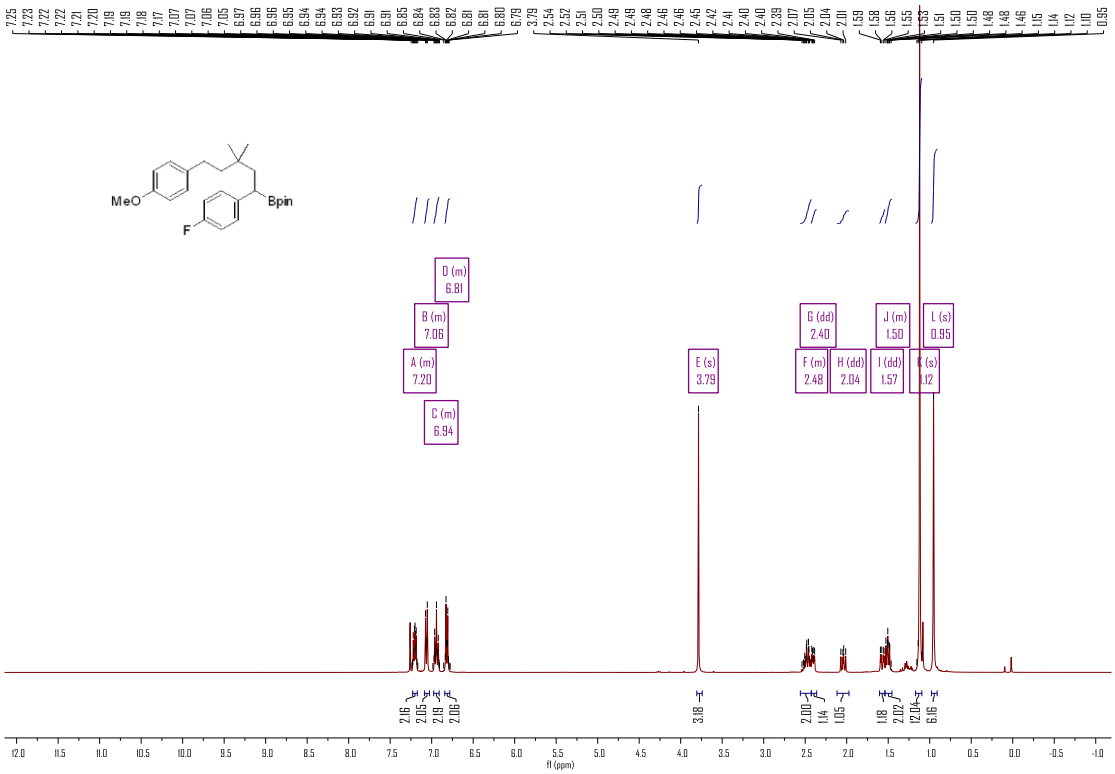
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24 – 7.16 (m, 2H), 7.09 – 7.03 (m, 2H), 6.99 – 6.90 (m, 2H), 6.85 – 6.77 (m, 2H), 3.79 (s, 3H), 2.56 – 2.44 (m, 2H), 2.40 (dd, *J* = 9.8, 3.8 Hz, 1H), 2.04 (dd, *J* = 13.4, 9.7 Hz, 1H), 1.57 (dd, *J* = 13.4, 3.9 Hz, 1H), 1.54 – 1.45 (m, 2H), 1.12 (s, 12H), 0.95 (s, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.97 (d, *J* = 242.4 Hz), 157.67, 140.42 (d, *J* = 3.2 Hz), 135.59, 129.52 (d, *J* = 7.5 Hz), 129.28, 115.11 (d, *J* = 21.0 Hz), 113.81, 83.44, 55.36, 44.97, 44.95, 34.08, 29.92, 27.41, 27.27, 24.64, 24.50.

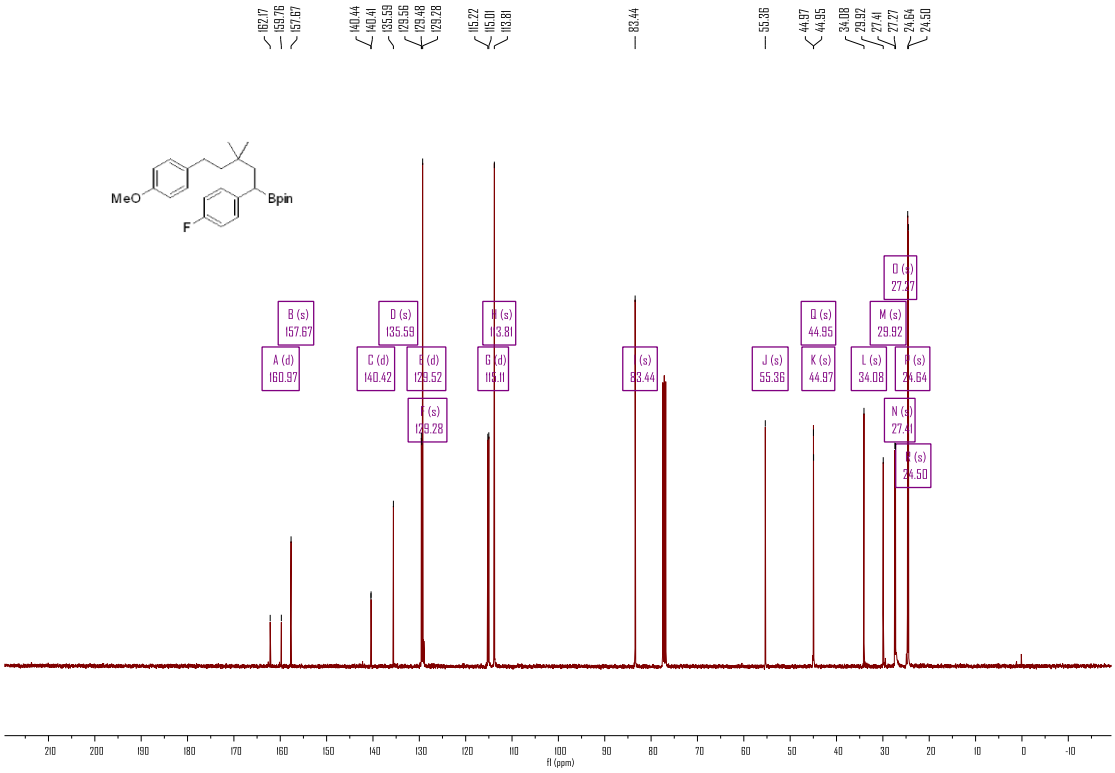
^{11}B NMR (128 MHz, Chloroform-*d*) 31.62.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -112.03 – -129.04 (m).

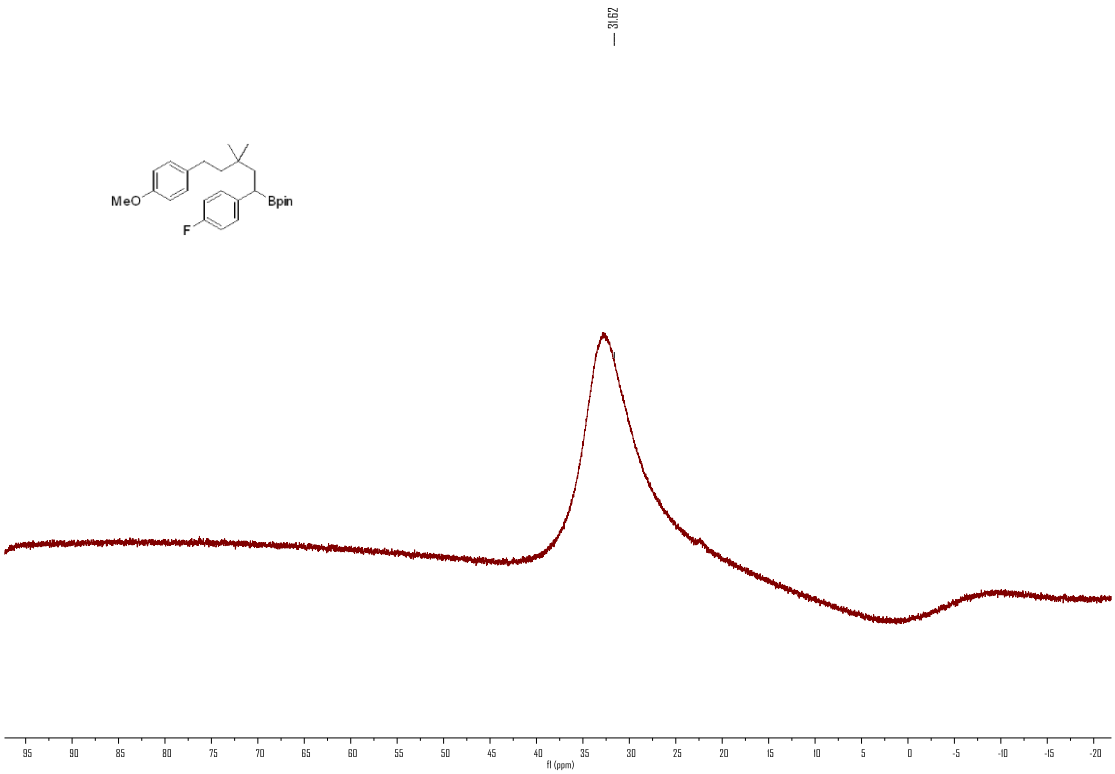
HRMS (ESI) calculated for $C_{26}H_{36}BFO_3$ $[M+Na]^+$: 449.2634, found: 449.2639.



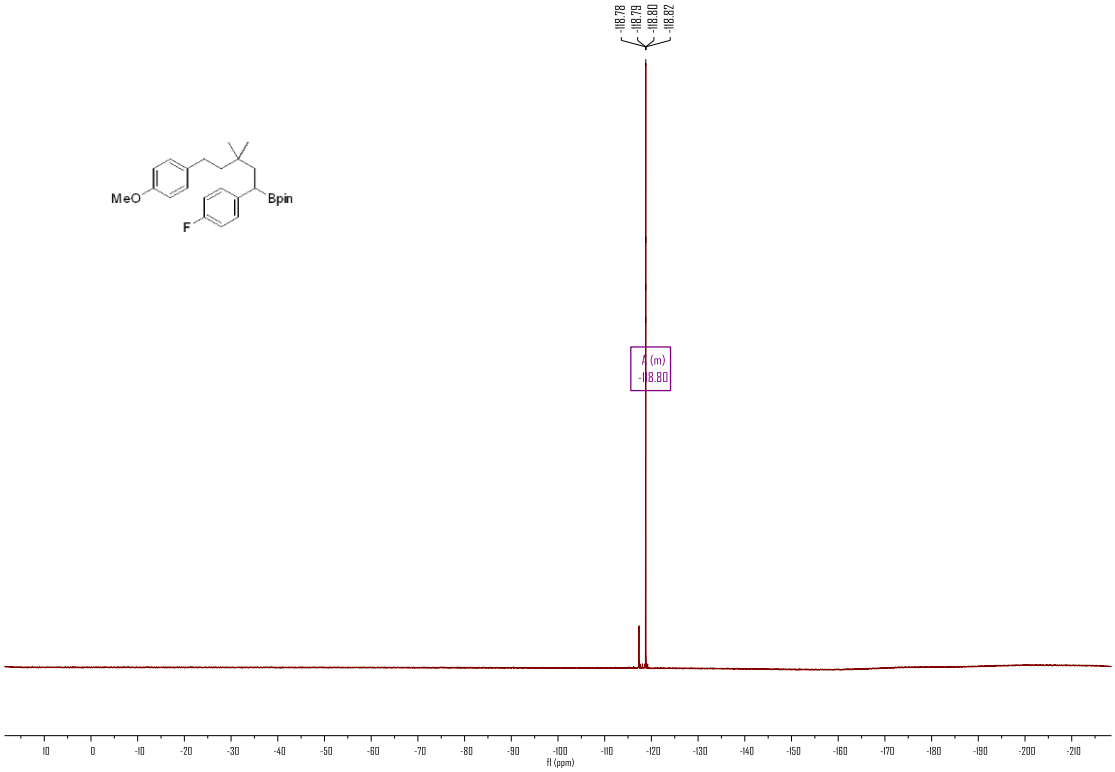
^{1}H NMR spectra for **41**



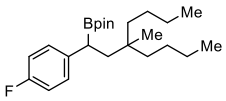
^{13}C NMR spectra for **41**



^{11}B NMR spectra for **41**



^{19}F NMR spectra for **41**



2-(3-butyl-1-(4-fluorophenyl)-3-methylheptyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**42**)

Following general procedure 1. The product was isolated by column chromatography as colorless oil (43.7 mg, 0.112 mmol, 56%).

Rf (petroleum ether : ethyl acetate = 20 : 1) = 0.50

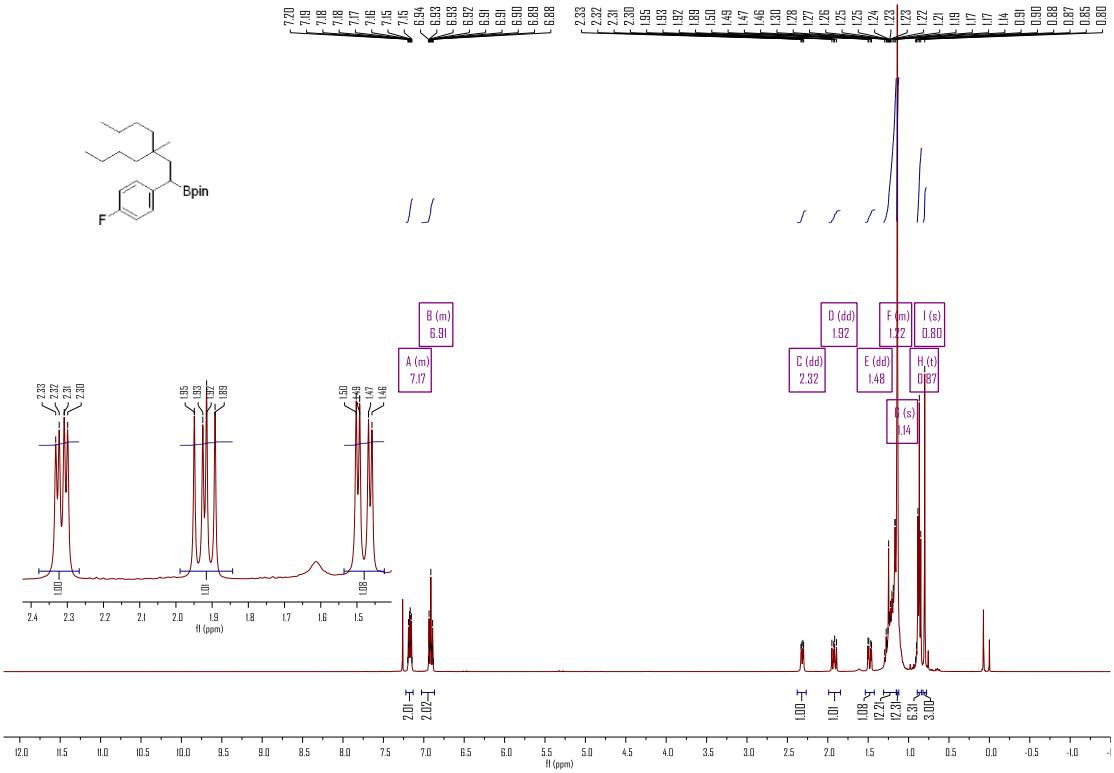
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.21 – 7.11 (m, 2H), 6.97 – 6.87 (m, 2H), 2.32 (dd, *J* = 9.4, 3.8 Hz, 1H), 1.92 (dd, *J* = 13.6, 9.4 Hz, 1H), 1.48 (dd, *J* = 13.6, 3.9 Hz, 1H), 1.30 – 1.15 (m, 12H), 1.14 (s, 12H), 0.87 (t, *J* = 7.0 Hz, 6H), 0.80 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.93 (d, *J* = 242.2 Hz), 140.75 (d, *J* = 3.2 Hz), 129.57 (d, *J* = 7.5 Hz), 115.02 (d, *J* = 20.9 Hz), 83.39, 42.87, 39.39, 39.24, 36.11, 26.02, 25.99, 25.29, 24.74, 24.51, 23.80, 23.79, 14.37.

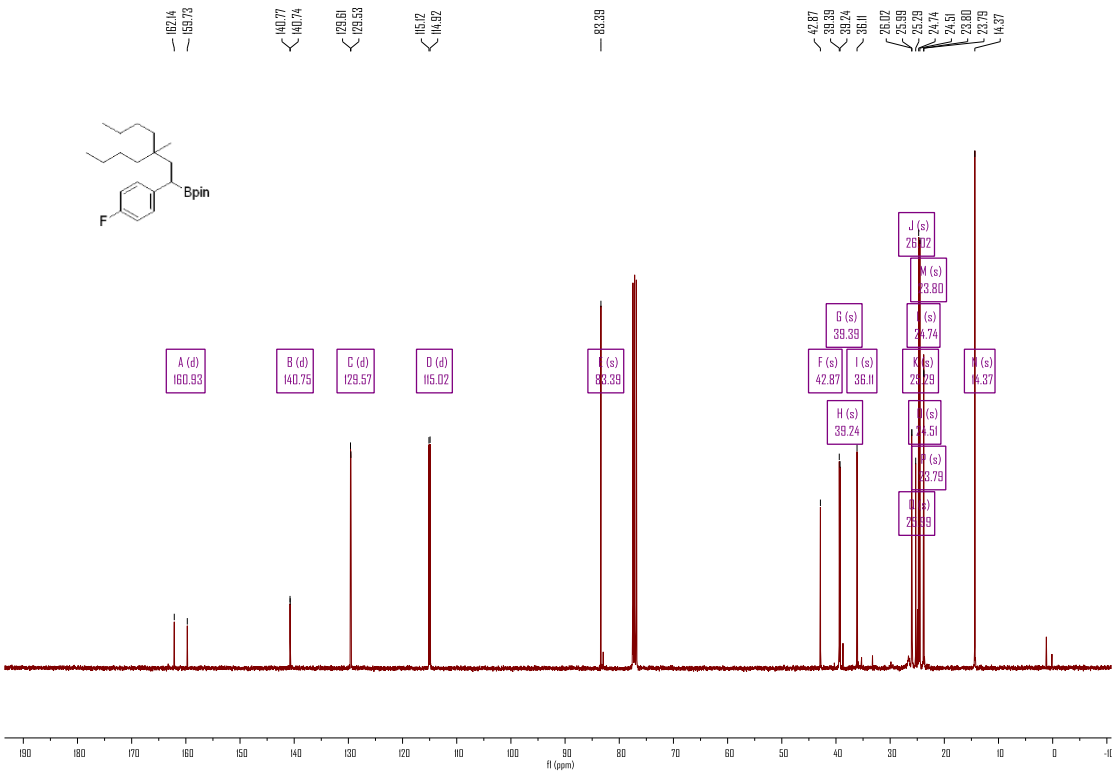
^{11}B NMR (128 MHz, Chloroform-*d*) 32.42

^{19}F NMR (376 MHz, Chloroform-*d*) δ -108.47 – -121.51 (m).

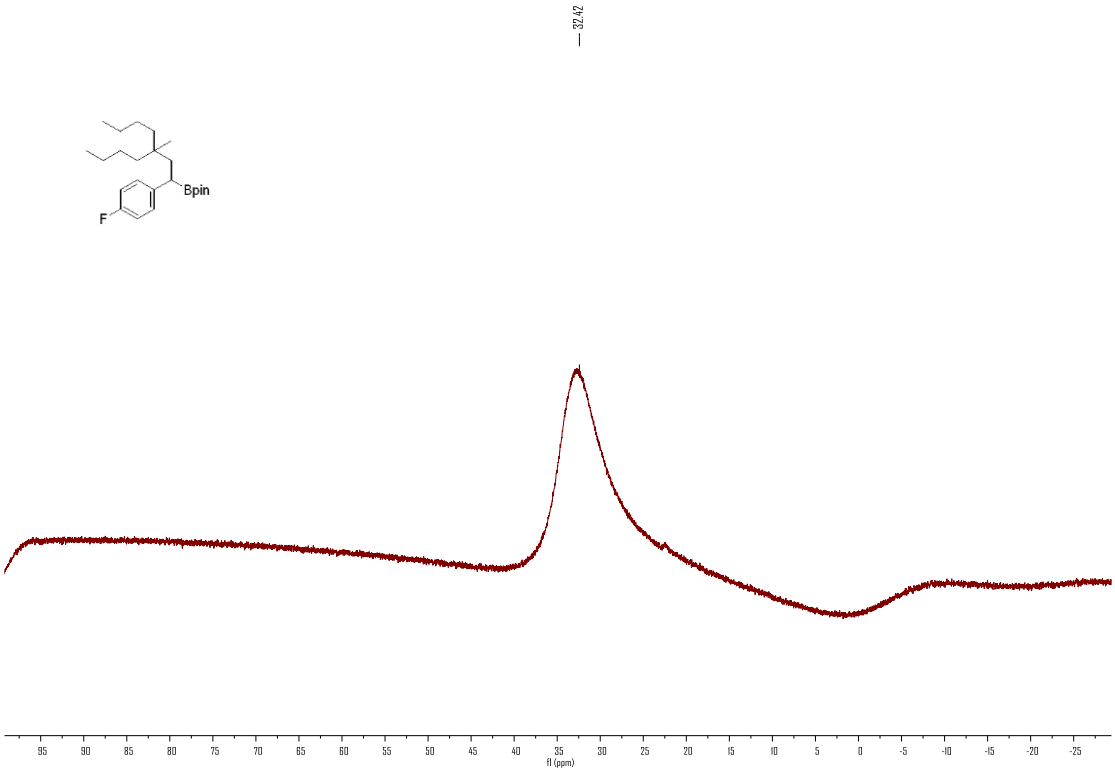
HRMS (ESI) calculated for $C_{24}H_{40}BFO_2$ $[M+Na]^+$: 413.2998, found: 413.3003.



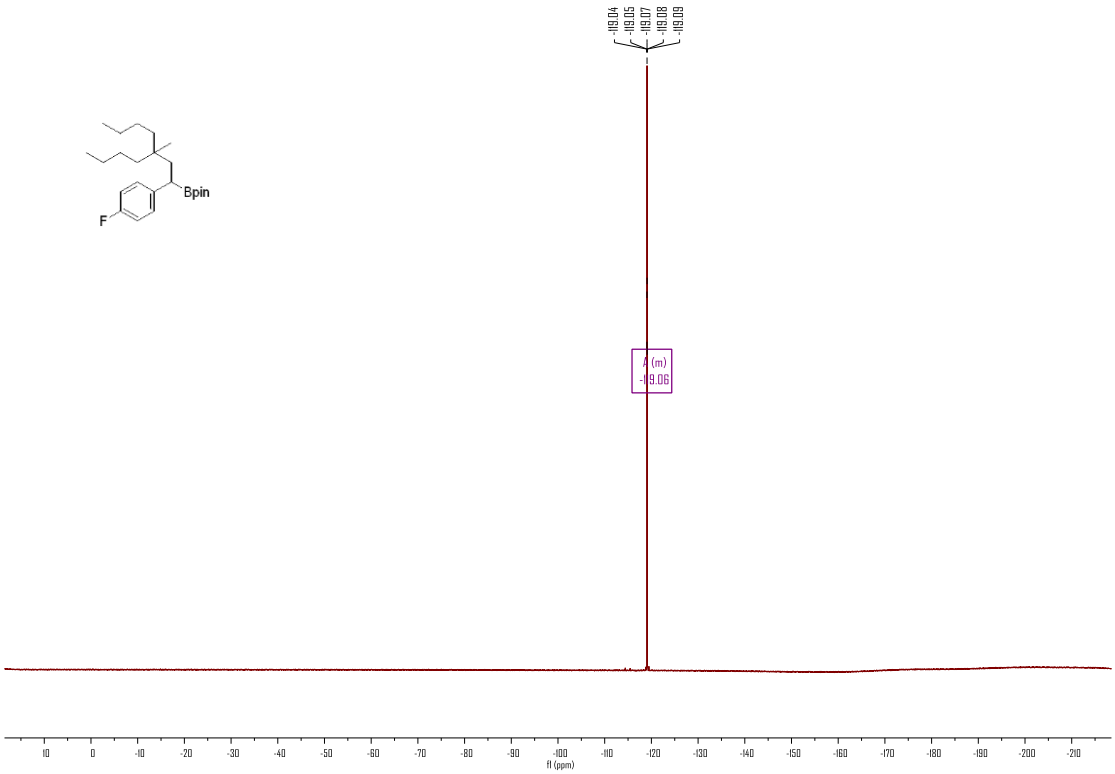
^{1}H NMR spectra for **42**



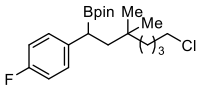
^{13}C NMR spectra for **42**



^{11}B NMR spectra for **42**



^{19}F NMR spectra for **42**



2-(7-chloro-1-(4-fluorophenyl)-3,3-dimethylheptyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**43**)

Following general procedure 1. The product was isolated by column chromatography as colorless oil (48.2 mg, 0.126 mmol, 63%).

Rf (petroleum ether : ethyl acetate = 20 : 1) = 0.50

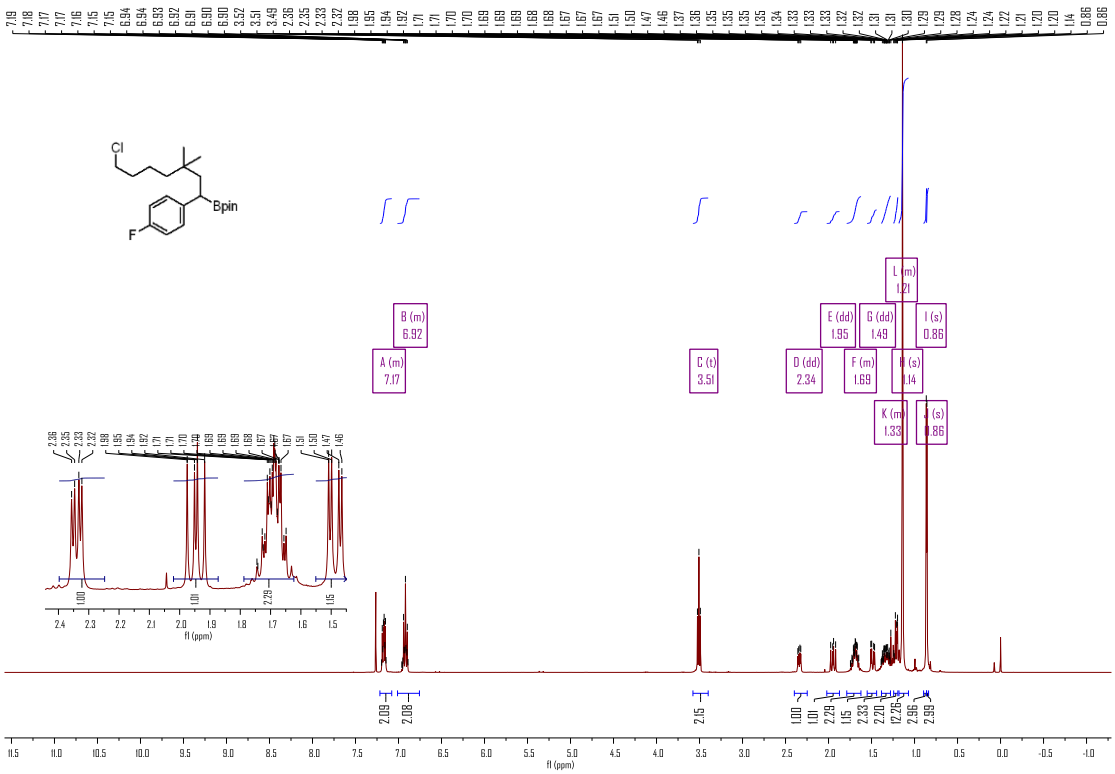
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.22 – 7.10 (m, 2H), 6.98 – 6.87 (m, 2H), 3.51 (t, *J* = 6.7 Hz, 2H), 2.34 (dd, *J* = 9.6, 4.0 Hz, 1H), 1.95 (dd, *J* = 13.5, 9.6 Hz, 1H), 1.77 – 1.63 (m, 2H), 1.49 (dd, *J* = 13.5, 4.0 Hz, 1H), 1.41 – 1.26 (m, 2H), 1.25 – 1.19 (m, 2H), 1.14 (s, 12H), 0.86 (s, 3H), 0.86 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.95 (d, *J* = 242.5 Hz), 140.39 (d, *J* = 3.2 Hz), 129.51 (d, *J* = 7.7 Hz), 115.09 (d, *J* = 20.9 Hz), 83.44, 45.23, 44.81, 41.59, 33.90, 33.59, 27.32, 24.68, 24.53, 21.63.

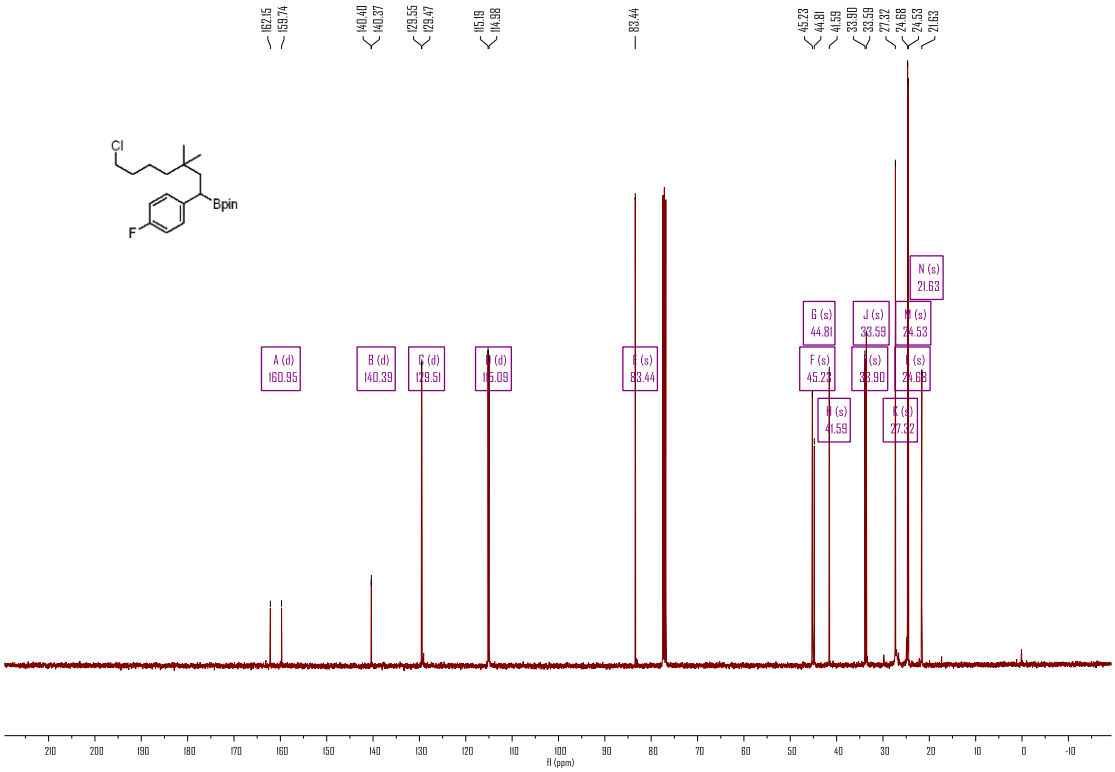
^{11}B NMR (128 MHz, Chloroform-*d*) 32.98

^{19}F NMR (376 MHz, Chloroform-*d*) δ -106.17 – -132.59 (m).

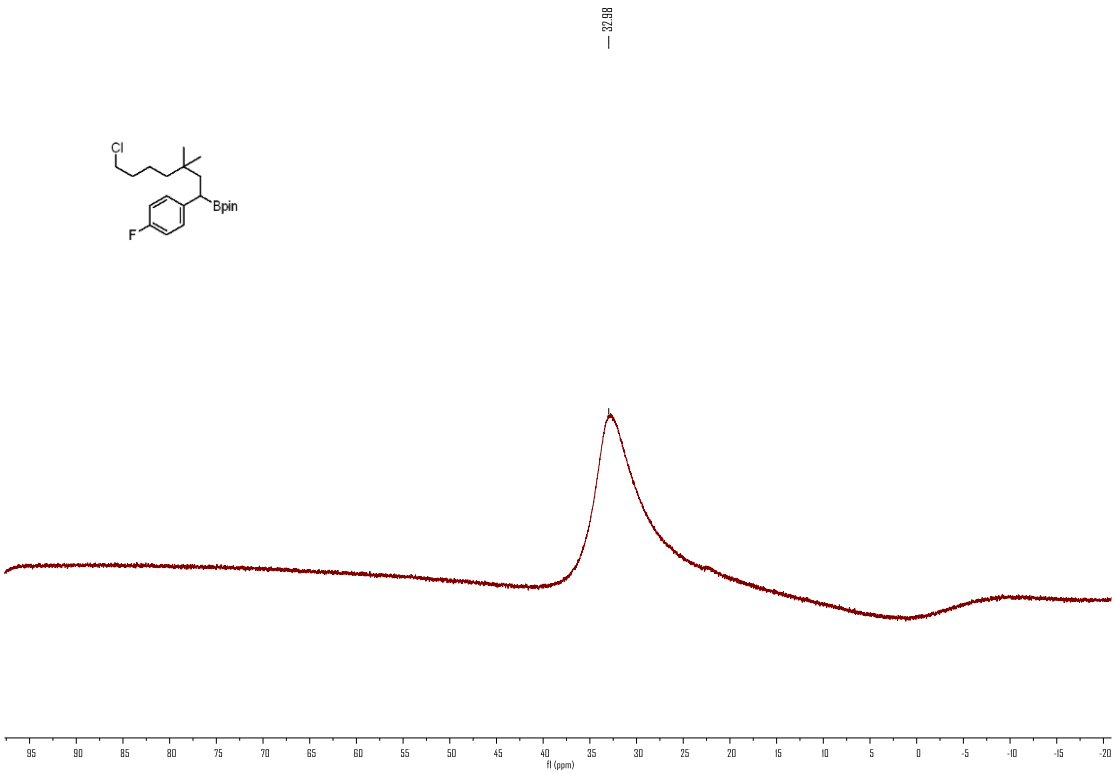
HRMS (ESI) calculated for $C_{21}H_{33}BClFO_2$ $[M+H]^+$: 383.2319, found: 383.2324.



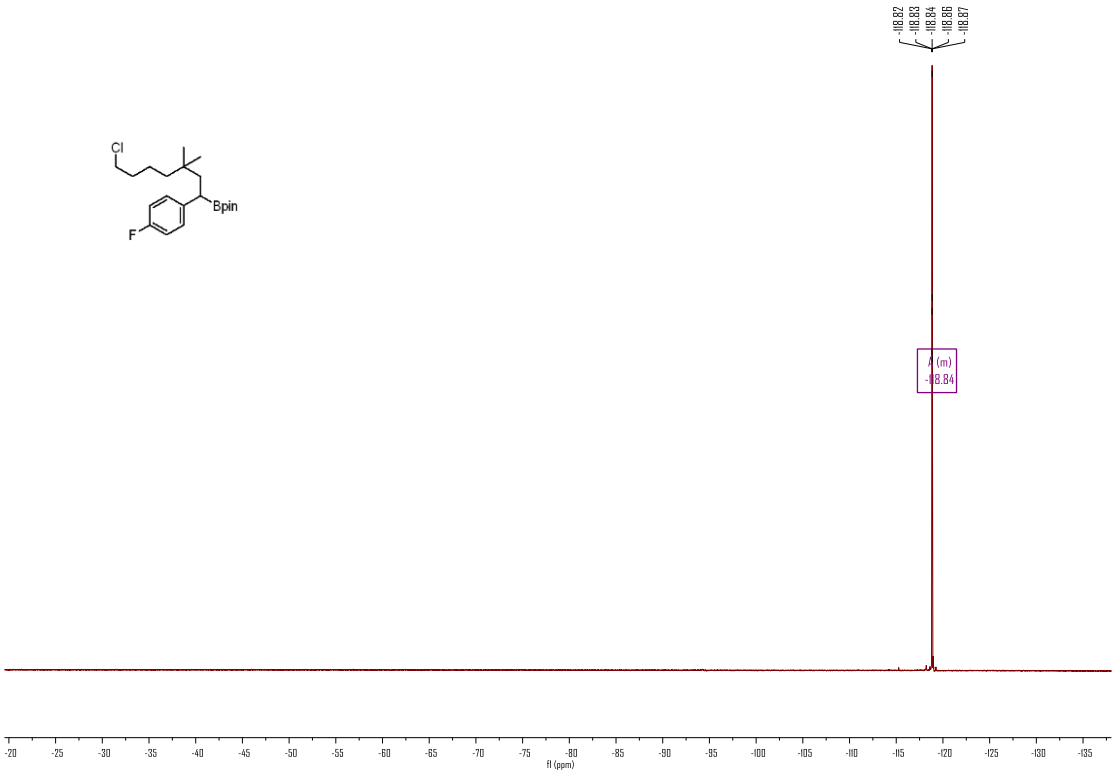
^{1}H NMR spectra for **43**



^{13}C NMR spectra for **43**



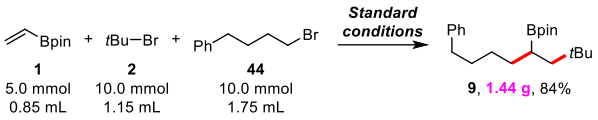
^{11}B NMR spectra for **43**



^{19}F NMR spectra for **43**

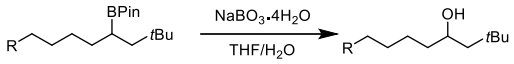
8. Examples Described in Scheme 5

8.1. One-Pot Synthesis at Gram Scale

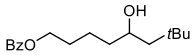


$NiBr_2$(diglyme) (10 mol%, 175 mg), Ligand (12 mol%, 125 mg), NaI (0.5 equiv., 375 mg), and Mn (3.0 equiv., 825 mg) were added to a Schlenk tube equipped with a stir bar. The Schlenk tube was evacuated and filled with argon (three cycles). To these solids, DMAc (0.2 M) was added under argon atmosphere. Then, 4,4,5,5-tetramethyl-2-vinyl-1,3,2-dioxaborolane (1.0 equiv., 0.85 mL) and 2-bromo-2-methylpropane (2.0 equiv., 1.15 mL) were added and stirred at room temperature (20-25 °C) for 10 minutes, (4-bromobutyl)benzene were added under argon atmosphere. The mixture was stirred at room temperature for 12 hours. The mixture was filtered through celite and concentrated the product was purified by column chromatography to afford the desired compound **9** as colorless oil (1.44 g, 4.20 mmol, 84%).

8.2. Alkylborate Transformation



To a solution of secondary boronates in THF (1 mL) and H_2O (1 mL) was added $NaBO_3 \cdot 4H_2O$ (154 mg, 1 mmol) at room temperature. The reaction mixture was then stirred at room temperature for 12 hours. The reaction mixture was diluted with H_2O followed by extraction with EtOAc, dried with anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel to give the final product.



5-hydroxy-7,7-dimethyloctyl benzoate (**45**)

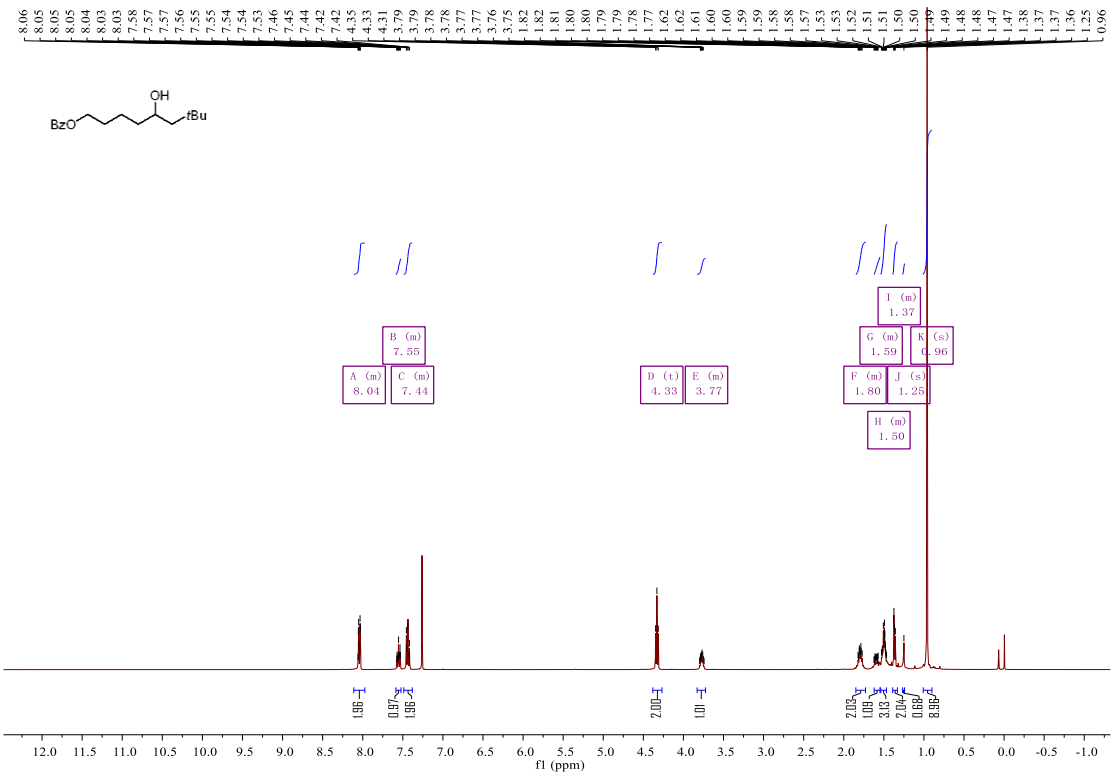
The product 45 was isolated by column chromatography as colorless oil (44.0 mg, 0.158 mmol, 79%).

Rf (petroleum ether : ethyl acetate = 5 : 1) = 0.45

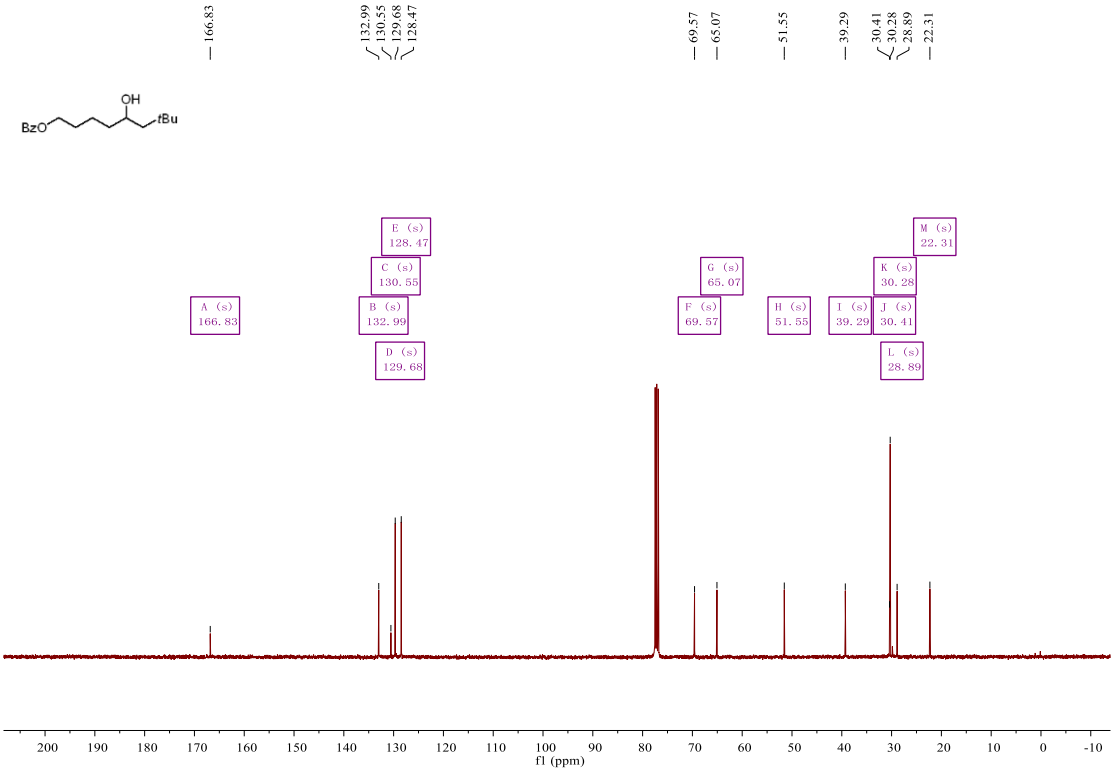
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 – 8.00 (m, 2H), 7.60 – 7.51 (m, 1H), 7.46 – 7.41 (m, 2H), 4.33 (t, *J* = 6.6 Hz, 2H), 3.86 – 3.62 (m, 1H), 1.91 – 1.73 (m, 2H), 1.65 – 1.55 (m, 1H), 1.55 – 1.44 (m, 3H), 1.41 – 1.32 (m, 2H), 1.25 (s, 1H), 0.96 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.83, 132.99, 130.55, 129.68, 128.47, 69.57, 65.07, 51.55, 39.29, 30.41, 30.28, 28.89, 22.31.

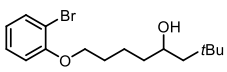
HRMS (ESI) calculated for $C_{17}H_{26}O_3$ $[M+H]^+$: 279.1955, found: 279.1948.



^{1}H NMR spectra for **45**



^{13}C NMR spectra for **45**



8-(2-bromophenoxy)-2,2-dimethyloctan-4-ol (**46**)

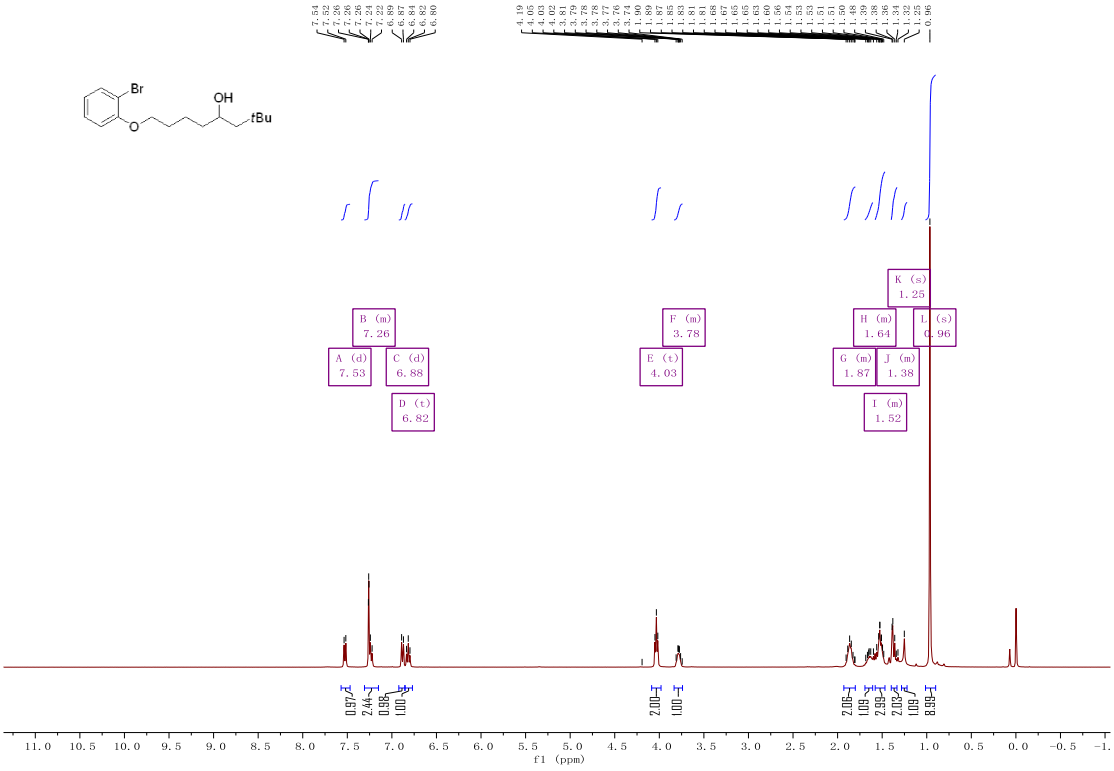
The product 46 was isolated by column chromatography as colorless oil (56.0 mg, 0.170 mmol, 85%).

Rf (petroleum ether : ethyl acetate = 5 : 1) = 0.50

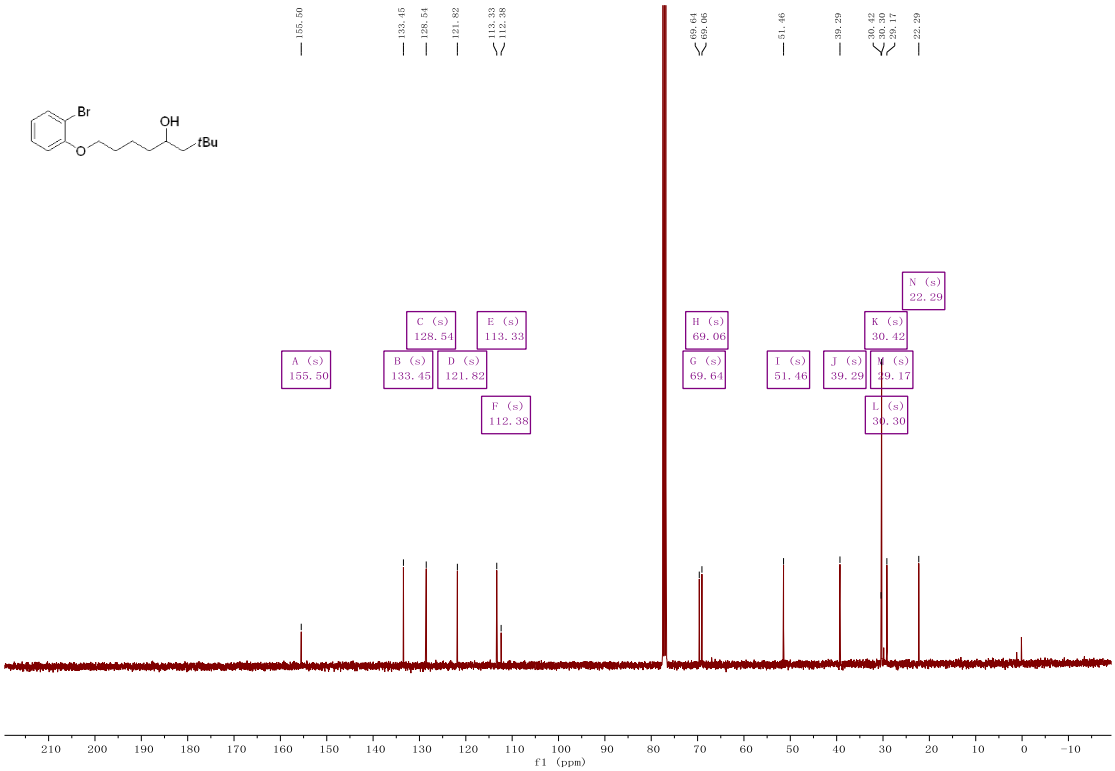
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 7.8 Hz, 1H), 7.29 – 7.15 (m, 2H), 6.88 (d, *J* = 8.2 Hz, 1H), 6.82 (t, *J* = 7.6 Hz, 1H), 4.03 (t, *J* = 6.4 Hz, 2H), 3.85 – 3.65 (m, 1H), 1.96 – 1.78 (m, 2H), 1.70 – 1.59 (m, 1H), 1.58 – 1.45 (m, 3H), 1.41 – 1.32 (m, 2H), 1.25 (s, 1H), 0.96 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.50, 133.45, 128.54, 121.82, 113.33, 112.38, 69.64, 69.06, 51.46, 39.29, 30.42, 30.30, 29.17, 22.29.

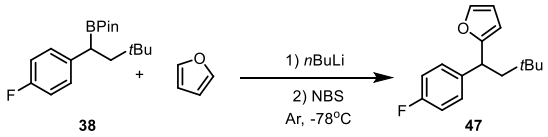
HRMS (ESI) calculated for $C_{16}H_{22}BrO_2$ $[M+Na]^+$: 351.0930, found: 351.0936.



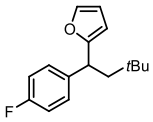
^{1}H NMR spectra for **46**



^{13}C NMR spectra for **46**



A 10 mL screw-cap test tube equipped with a magnetic stirrer was filled with argon, a solution of furan (22 μL, 0.3 mmol, 1.5 equiv.) in THF (1 mL) was added by syringe. Then *n*BuLi (2.4 M in hexanes, 125 μL, 0.25 mmol, 1.25 equiv.) was added at -78 °C. The resulting mixture was warmed up to room temperature and stirred for 1h. The reaction mixture was then cooled to -78 °C and a solution of **38** (72 μL, 0.2 mmol, 1.0 equiv.) in THF (1.0 mL) was added dropwise, and stirred at -78 °C for 1 h, at which time a solution of NBS (71 mg, 0.4 mmol, 2.0 equiv.) in THF (1 mL) was added dropwise. The resulting solution was stirred at -78 °C for 1 h, then quenched with saturated aqueous sodium thiosulfate solution, extracted with EtOAc and dried with anhydrous Na_2SO_4. Combined organic layers were concentrated in vacuo and purified by flash column chromatography on silica gel to give **47** (28.6mg, 0.116mmol, 58%) as a colorless oil.



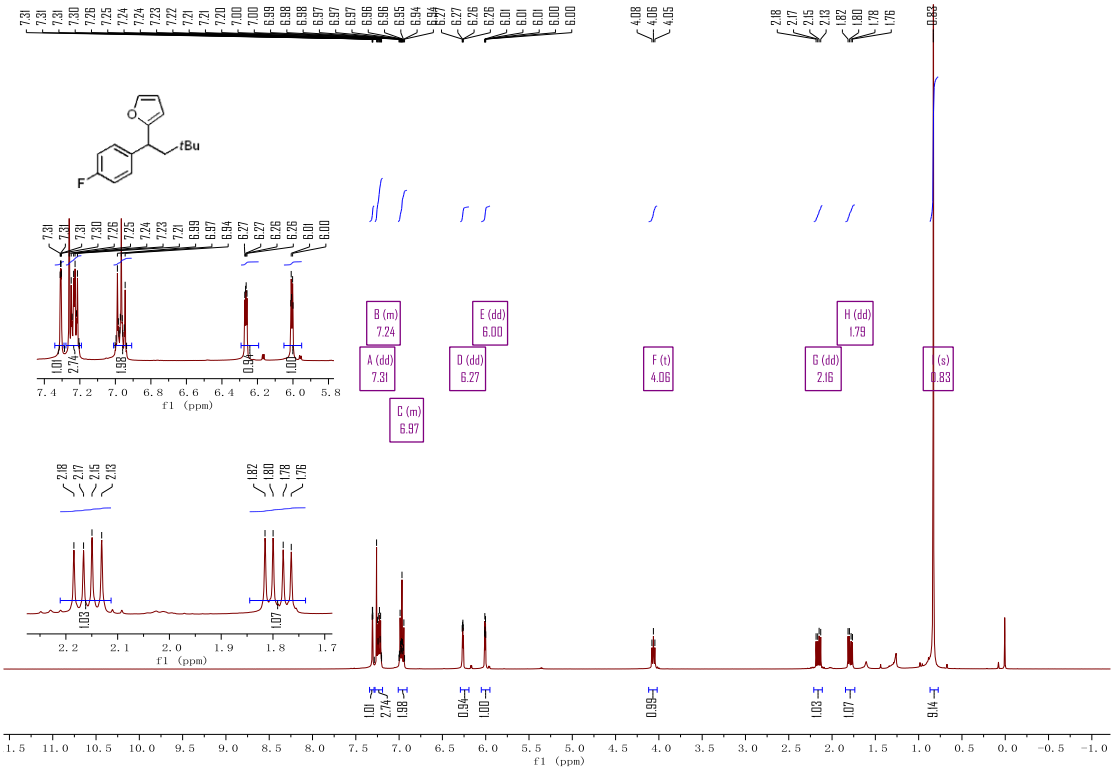
2-(1-(4-fluorophenyl)-3,3-dimethylbutyl)furan (**47**)

Rf (petroleum ether) = 0.75

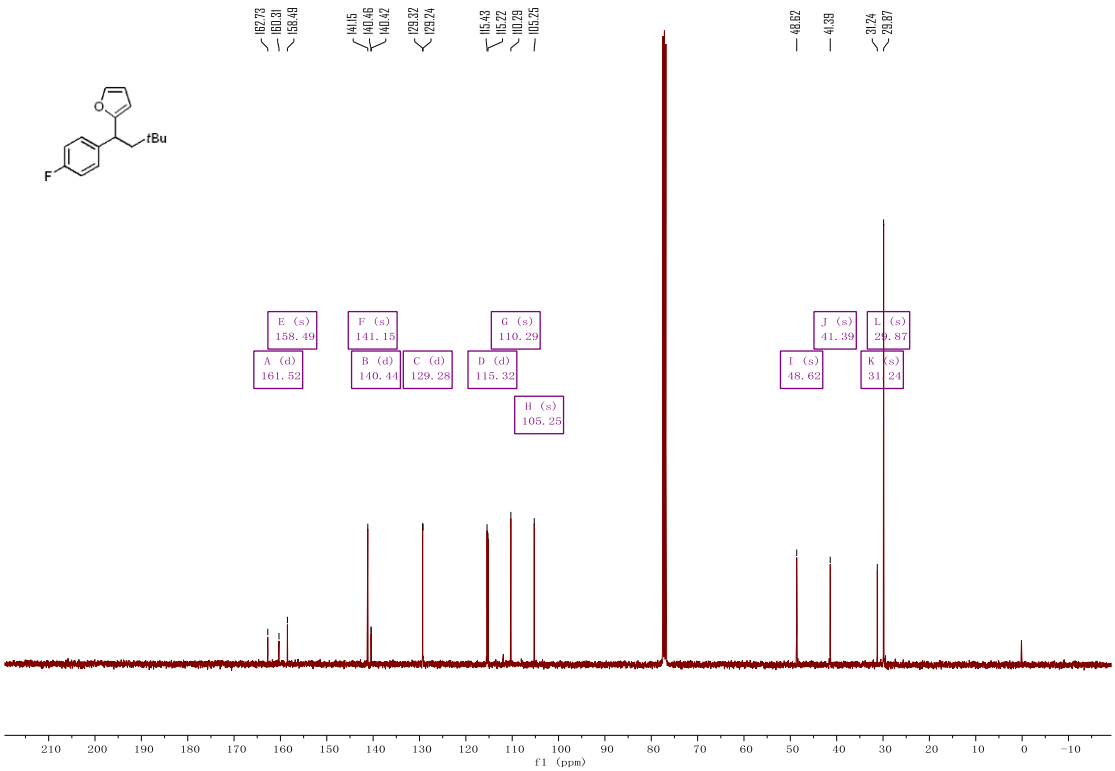
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 (dd, *J* = 1.9, 0.9 Hz, 1H), 7.26 – 7.19 (m, 2H), 7.01 – 6.92 (m, 2H), 6.27 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.00 (dd, *J* = 3.2, 0.9 Hz, 1H), 4.06 (t, *J* = 6.8 Hz, 1H), 2.16 (dd, *J* = 14.0, 7.5 Hz, 1H), 1.79 (dd, *J* = 14.0, 6.2 Hz, 1H), 0.83 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.52 (d, *J* = 244.0 Hz), 158.49, 141.15, 140.44 (d, *J* = 3.2 Hz), 129.28 (d, *J* = 7.9 Hz), 115.32 (d, *J* = 21.2 Hz), 110.29, 105.25, 48.62, 41.39, 31.24, 29.87.

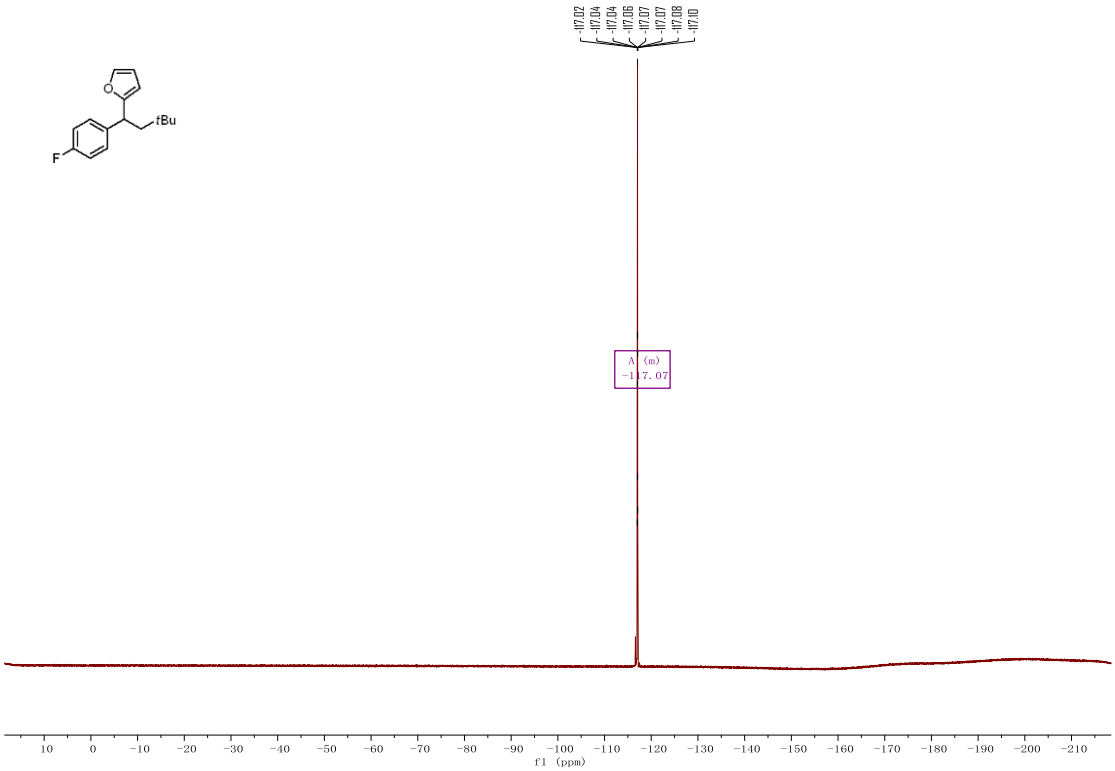
^{19}F NMR (376 MHz, Chloroform-*d*) δ -116.99 – -117.23 (m).



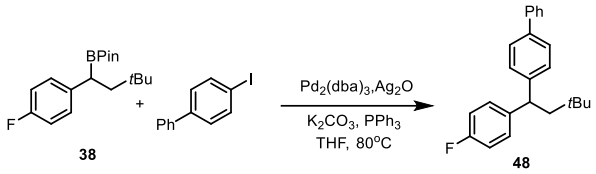
^{1}H NMR spectra for **47**



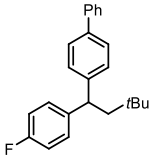
^{13}C NMR spectra for **47**



^{19}F NMR spectra for **47**



Compound **48** was prepared according to previously reported procedure.[4] $Pd_2(dba)_3$ (0.01 mmol, 5 mol%, 9.2 mg), PPh_3 (0.08 mmol, 40 mol%, 21 mg), K_2CO_3 (0.3 mmol, 1.5 equiv., 41.5 mg), Ag_2O (0.3 mmol, 1.5 equiv., 69.5 mg), 4-iodobiphenyl (0.4 mmol, 2.0 equiv., 112 mg) and compound **38** (0.2 mmol, 1.0 equiv., 61.2 mg) were added to a Schlenk tube equipped with a stir bar. The Schlenk tube was evacuated and filled with argon (three cycles). To these solids, 2 mL THF was added under argon atmosphere. The mixture was stirred at 80°C for 16 hours, and purified by column chromatography to afford compound **48** (34.6 mg, 0.104 mmol, 52%) as a white solid.



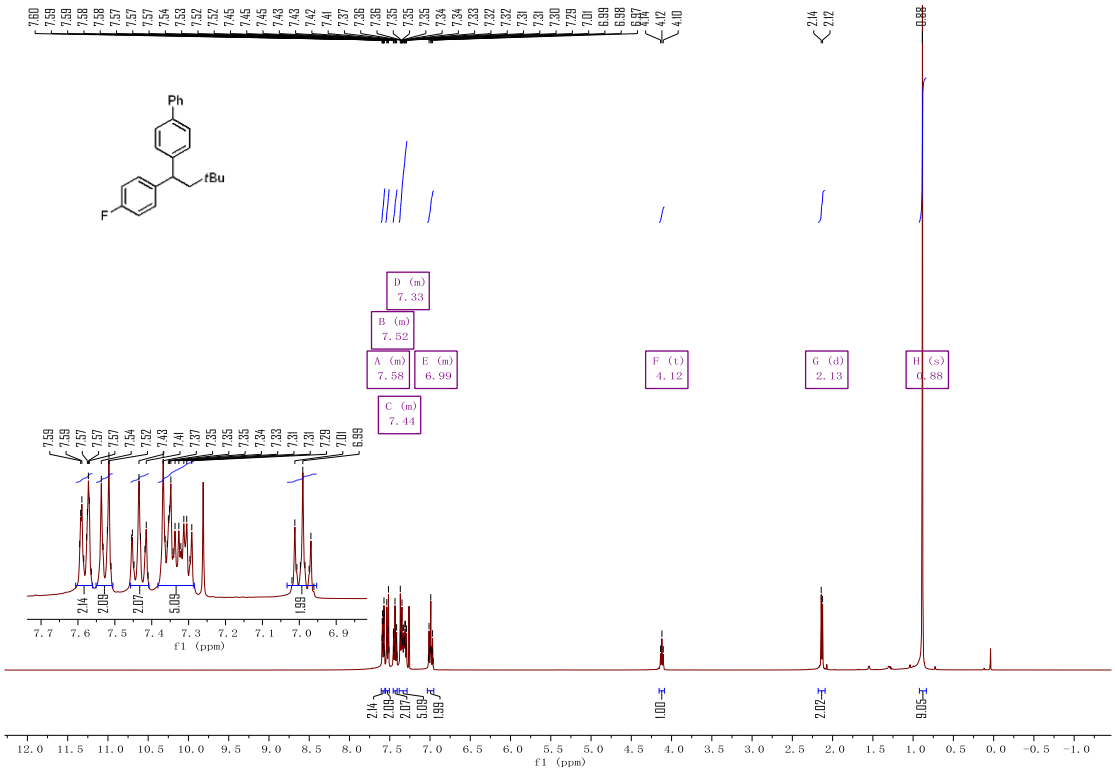
4-(1-(4-fluorophenyl)-3,3-dimethylbutyl)-1,1'-biphenyl (**48**)

Rf (petroleum ether) = 0.65

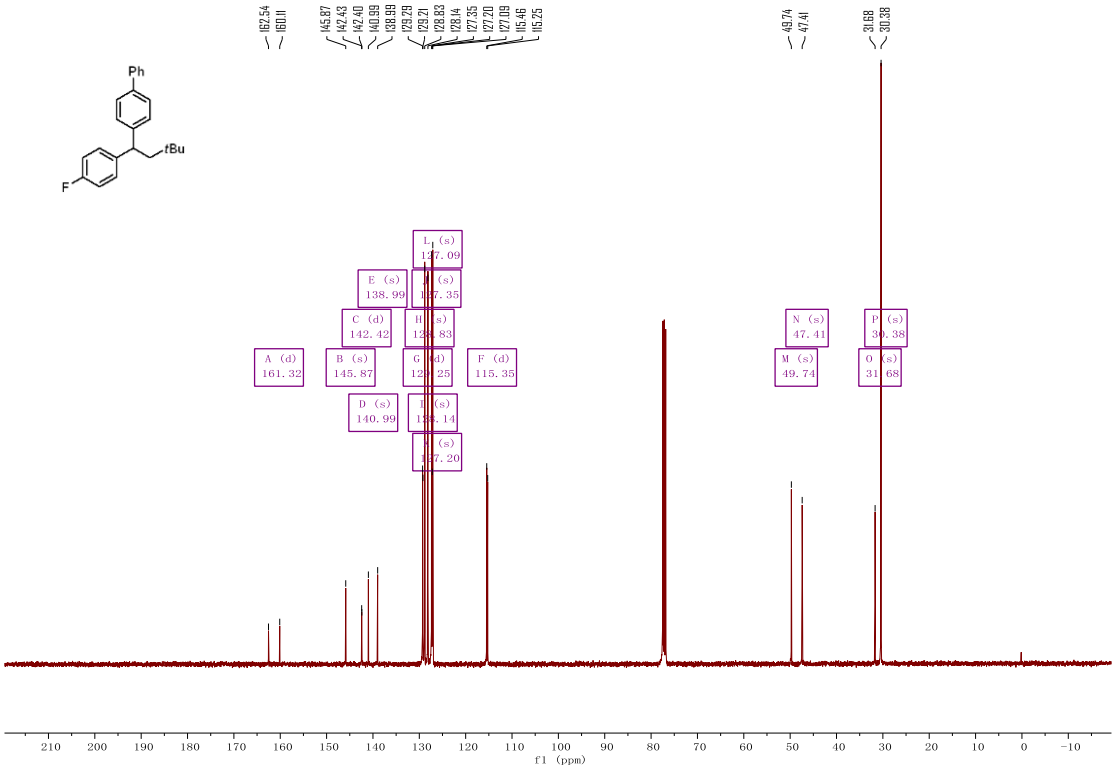
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 – 7.56 (m, 2H), 7.55 – 7.49 (m, 2H), 7.47 – 7.40 (m, 2H), 7.38 – 7.27 (m, 5H), 7.03 – 6.95 (m, 2H), 4.12 (t, *J* = 6.7 Hz, 1H), 2.13 (d, *J* = 6.7 Hz, 2H), 0.88 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.32 (d, *J* = 244.0 Hz), 145.87, 142.42 (d, *J* = 3.3 Hz), 140.99, 138.99, 129.25 (d, *J* = 7.8 Hz), 128.83, 128.14, 127.35, 127.20, 127.09, 115.35 (d, *J* = 21.0 Hz), 49.74, 47.41, 31.68, 30.38.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -117.38 – -117.58 (m).

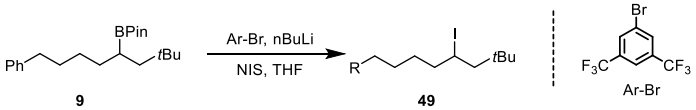


^{1}H NMR spectra for **48**

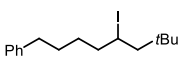


^{13}C NMR spectra for **48**

^{19}F NMR spectra for **48**



To a solution of 1- bromo- 3,5- bis(trifluoromethyl)benzene (69 μL, 0.40 mmol, 2.0 equiv) in THF (1.0 mL) at -78 ℃ was added n-BuLi (167 μL, 0.40 mmol, 2.0 equiv., 2.4 M in hexane) slowly under Ar atmosphere. The mixture was stirred at –78 ℃ for 1 hour, and then a solution of **9** (72 μL, 0.20 mmol 1.0 equiv) in THF (1.0 mL) was added. The mixture was stirred to stir at -78 ºC for 30 min and at room temperature for 30 min. Then, a solution of NIS (95 mg, 0.40 mmol, 2.0 equiv) in THF (1.0 mL) was added dropwise to the reaction mixture at the same temperature. The resulting mixture was stirred for further 1 hour. Then the reaction was quenched with saturated aqueous sodium thiosulfate solution (2.0 mL). The mixture was extracted with ethyl acetate twice. The combined organic layers were combined, dried over Na_2SO_4, and concentrated in vacuo. The product **49** was isolated by flash column chromatography as colorless oil (42.0 mg, 0.122 mmol, 61%).

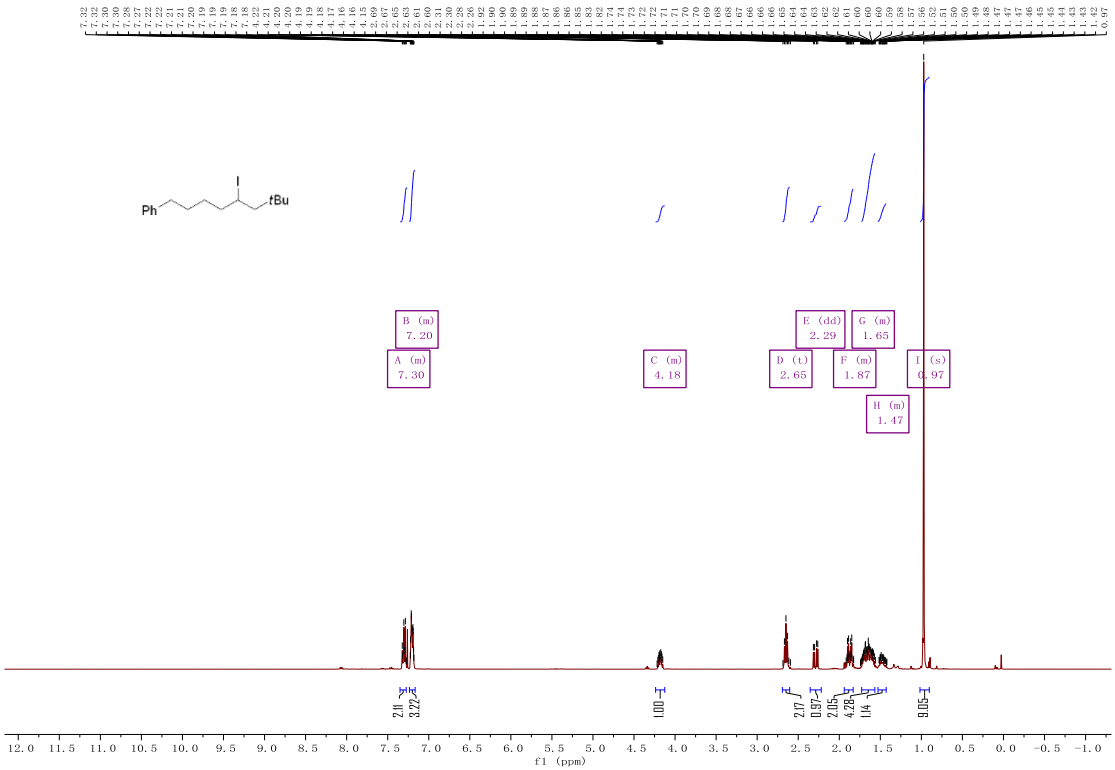


(5-iodo-7,7-dimethyloctyl)benzene (**49**)

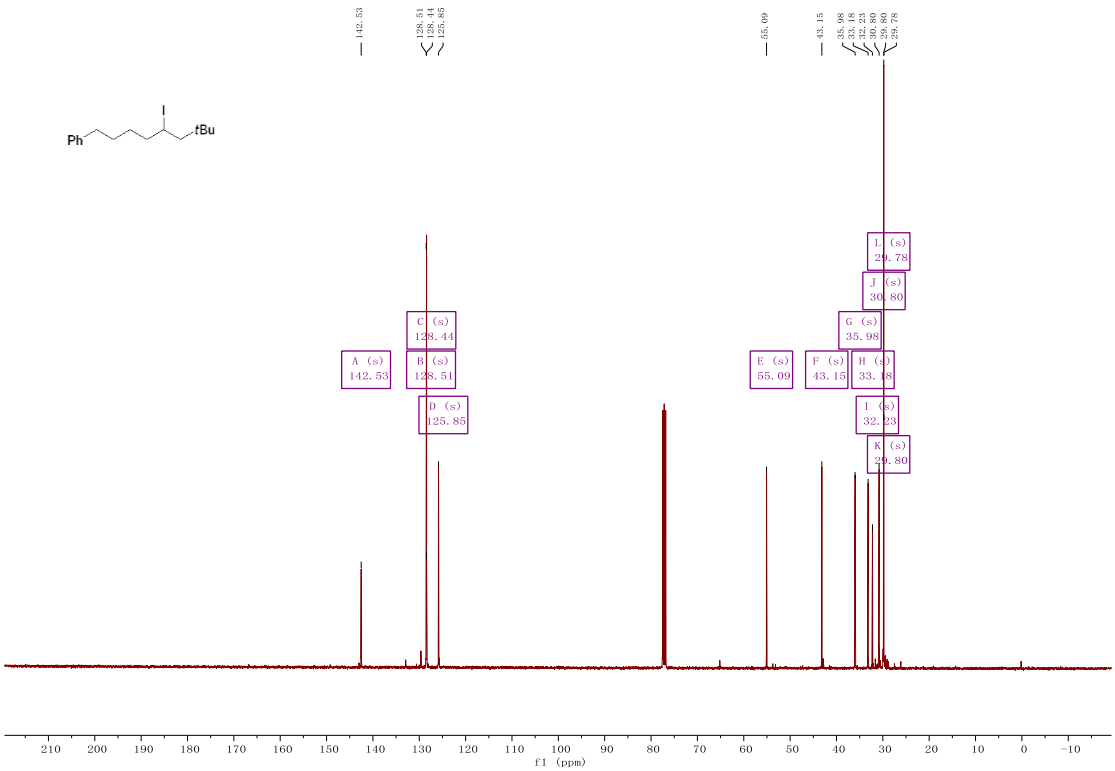
Rf (petroleum ether) = 0.70

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.27 (m, 2H), 7.25 – 7.15 (m, 3H), 4.25 – 4.11 (m, 1H), 2.65 (t, *J* = 7.5 Hz, 2H), 2.29 (dd, *J* = 15.4, 5.9 Hz, 1H), 1.92 – 1.82 (m, 2H), 1.74 – 1.52 (m, 4H), 1.52 – 1.41 (m, 1H), 0.97 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.53, 128.51, 128.44, 125.85, 55.09, 43.15, 35.98, 33.18, 32.23, 30.80, 29.80, 29.78.

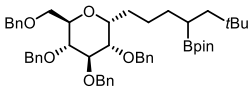


^{1}H NMR spectra for **49**



^{13}C NMR spectra for **49**

8.3. Late-Stage Functionalization



2-(6,6-dimethyl-1-((2*R*,3*S*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)heptan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**50**)

Following general procedure 1. The product was isolated by column chromatography as colorless oil (119.6 mg, 0.154 mmol, 77%, d.r. = 1:1).

Rf (petroleum ether : acetone = 5 : 1) = 0.50.

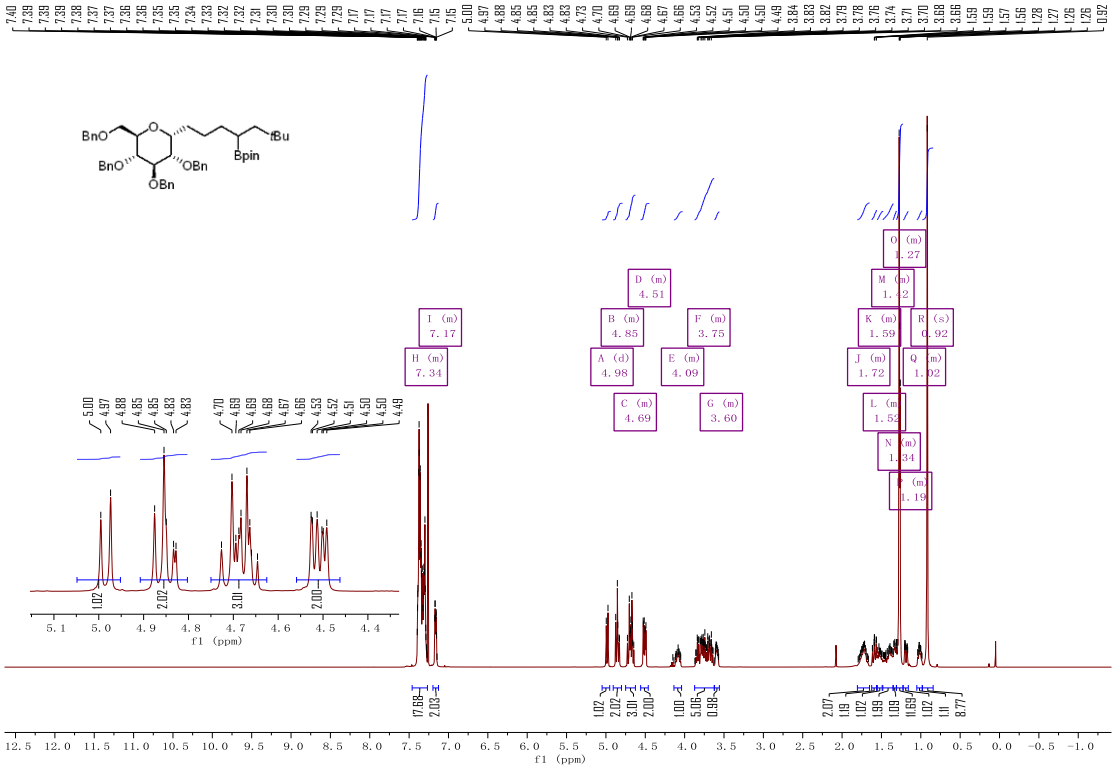
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.51 – 7.27 (m, 18H), 7.18 – 7.15 (m, 2H), 4.98 (d, *J* = 10.9 Hz, 1H), 4.92 – 4.79 (m, 2H), 4.77 – 4.62 (m, 3H), 4.57 – 4.42 (m, 2H), 4.15 – 4.02 (m, 1H), 3.88 – 3.65 (m, 5H), 3.63 – 3.52 (m, 1H), 1.81 – 1.66 (m, 2H), 1.63 – 1.56 (m, 1H), 1.55 – 1.49 (m, 1H), 1.48 – 1.36 (m, 2H), 1.35 – 1.31 (m, 1H), 1.30 – 1.23 (m, 12H), 1.21 – 1.16 (m, 1H), 1.05 – 0.98 (m, 1H), 0.92 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 138.88, 138.38, 138.34, 138.32, 138.07, 138.06, 128.47, 128.45, 128.43, 128.40, 128.04, 128.02, 128.00, 127.98, 127.95, 127.89,

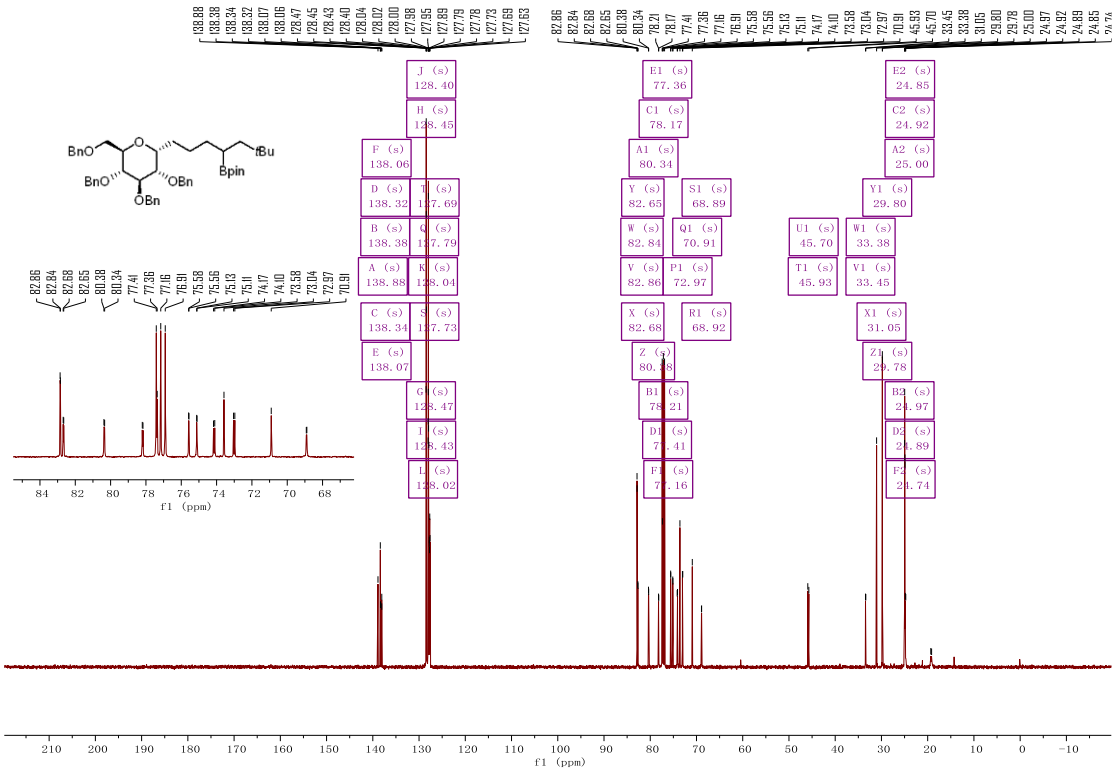
127.79, 127.78, 127.73, 127.69, 127.63, 82.86, 82.84, 82.68, 82.65, 80.38, 80.34, 78.21, 78.17, 77.41, 77.36, 77.16, 76.91, 75.58, 75.56, 75.13, 75.11, 74.17, 74.10, 73.58, 73.04, 72.97, 70.91, 68.92, 68.89, 45.93, 45.70, 33.45, 33.38, 31.05, 29.80, 29.78, 25.00, 24.97, 24.92, 24.89, 24.85, 24.74.

^{11}B NMR (128 MHz, Chloroform-*d*) 37.48

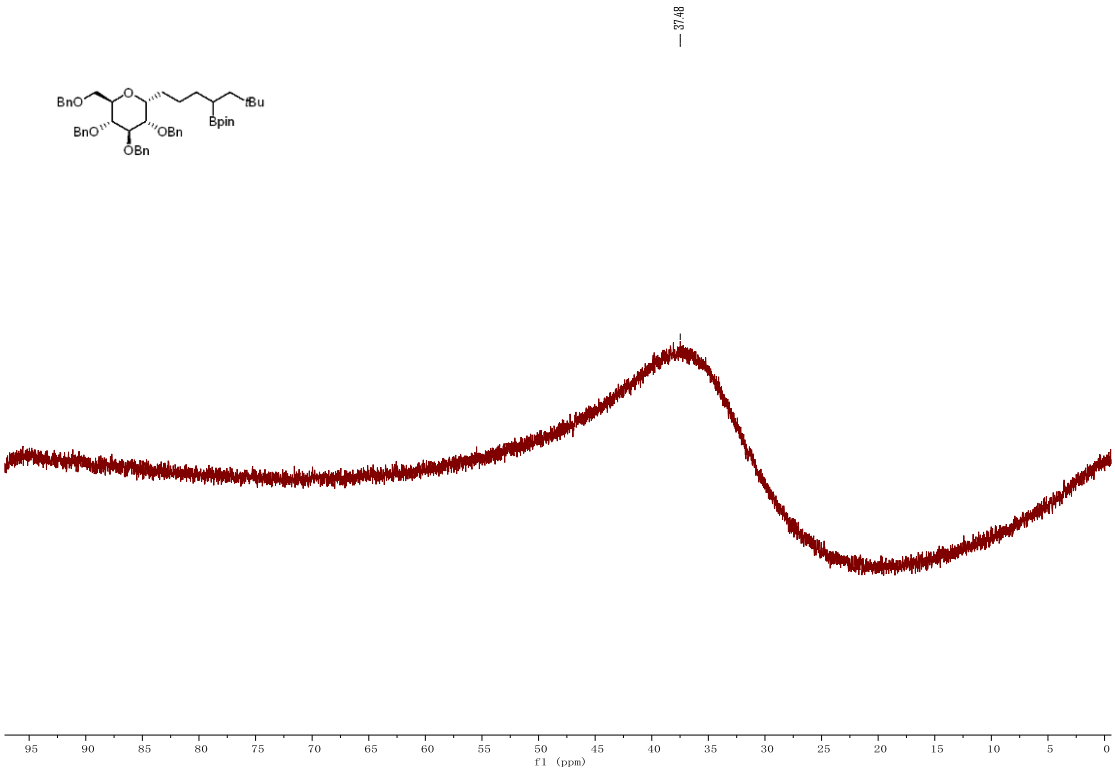
HRMS (ESI) calculated for $C_{49}H_{65}BO_7$ $[M+Na]^+$: 799.4716, found: 799.4721.



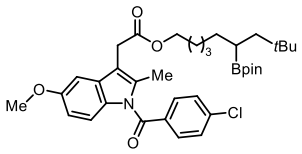
^{1}H NMR spectra for **50**



^{13}C NMR spectra for **50**



^{11}B NMR spectra for **50**



8,8-dimethyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nonyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate (**51**)

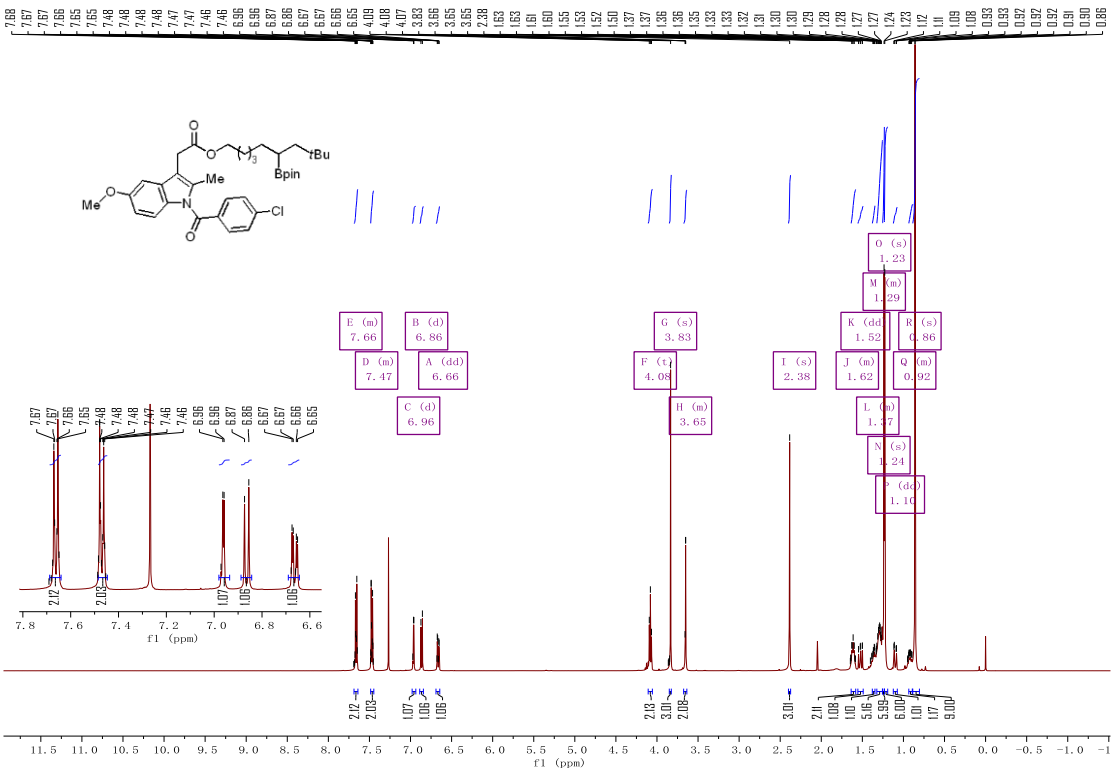
Following general procedure 1. The product was isolated by column chromatography as colorless oil (89.3 mg, 0.140 mmol, 70%).

Rf (petroleum ether : acetone = 4 : 1) = 0.60.

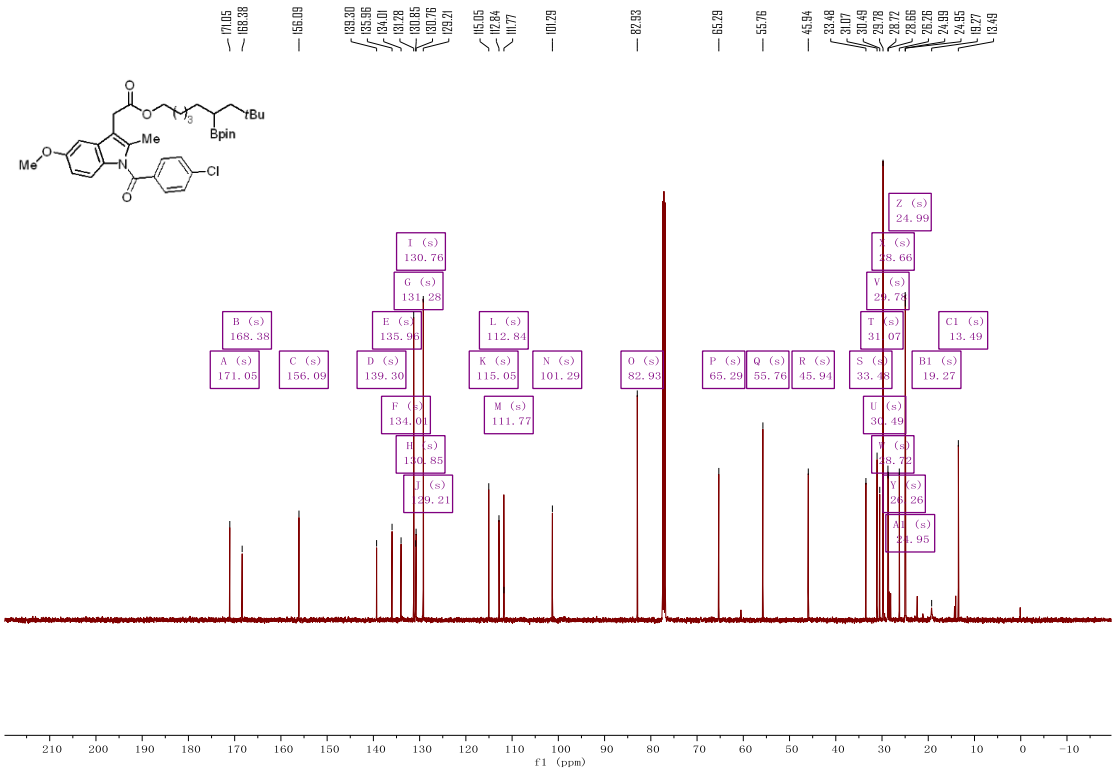
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.69 – 7.61 (m, 2H), 7.50 – 7.44 (m, 2H), 6.96 (d, *J* = 2.6 Hz, 1H), 6.86 (d, *J* = 9.0 Hz, 1H), 6.66 (dd, *J* = 9.0, 2.5 Hz, 1H), 4.08 (t, *J* = 6.7 Hz, 2H), 3.83 (s, 3H), 3.70 – 3.61 (m, 2H), 2.38 (s, 3H), 1.66 – 1.57 (m, 2H), 1.52 (dd, *J* = 13.4, 10.5 Hz, 1H), 1.42 – 1.34 (m, 1H), 1.33 – 1.26 (m, 5H), 1.24 (s, 6H), 1.23 (s, 6H), 1.10 (dd, *J* = 13.3, 2.4 Hz, 1H), 0.97 – 0.88 (m, 1H), 0.86 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 171.05, 168.38, 156.09, 139.30, 135.96, 134.01, 131.28, 130.85, 130.76, 129.21, 115.05, 112.84, 111.77, 101.29, 82.93, 65.29, 55.76, 45.94, 33.48, 31.07, 30.49, 29.78, 28.72, 28.66, 26.26, 24.99, 24.95, 19.27, 13.49.

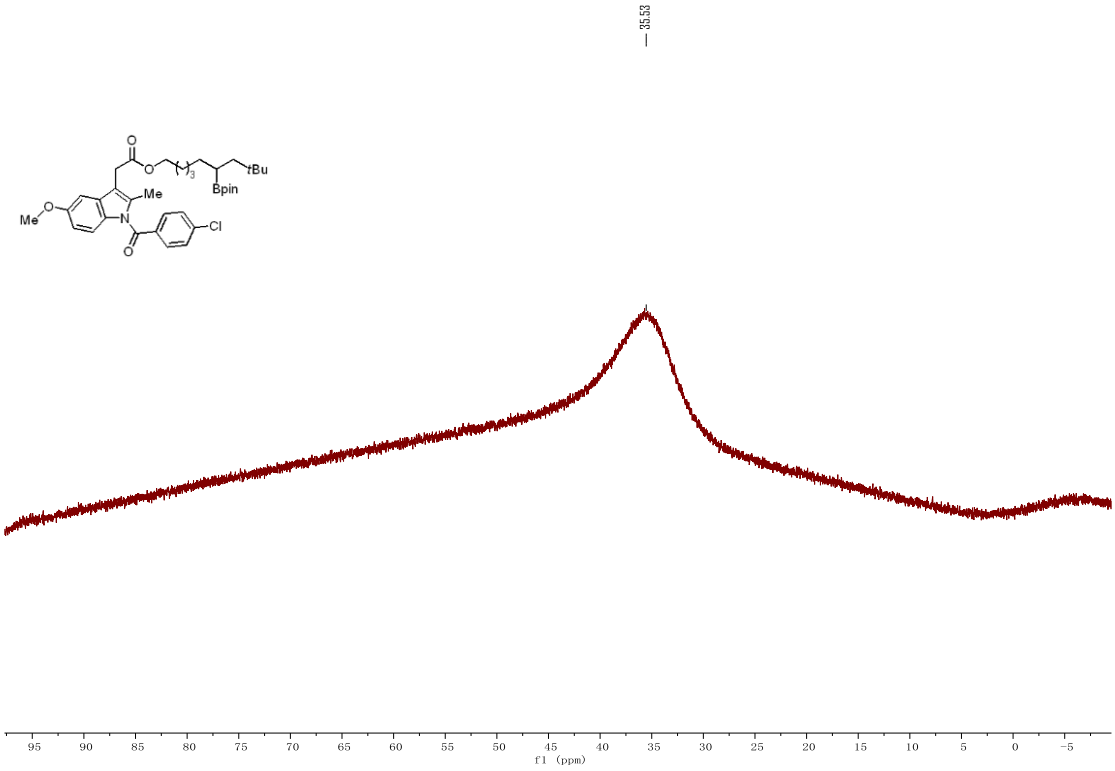
^{11}B NMR (128 MHz, Chloroform-*d*) 35.53



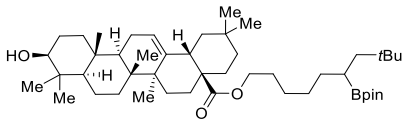
^{1}H NMR spectra for **51**



^{13}C NMR spectra for **51**



^{11}B NMR spectra for **51**



8,8-dimethyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nonyl (4a*S*,6a*S*,6b*R*,8a*R*,10*S*,12a*R*,12b*R*,14b*S*)-10-hydroxy-2,2,6a,6b,9,9,12a-heptamethyl-1,3,4,5,6,6a,6b,7,8,8a,9,10,11,12,12a,12b,13,14b-octadecahydropicene-4a(2*H*)-carboxylate (**52**)

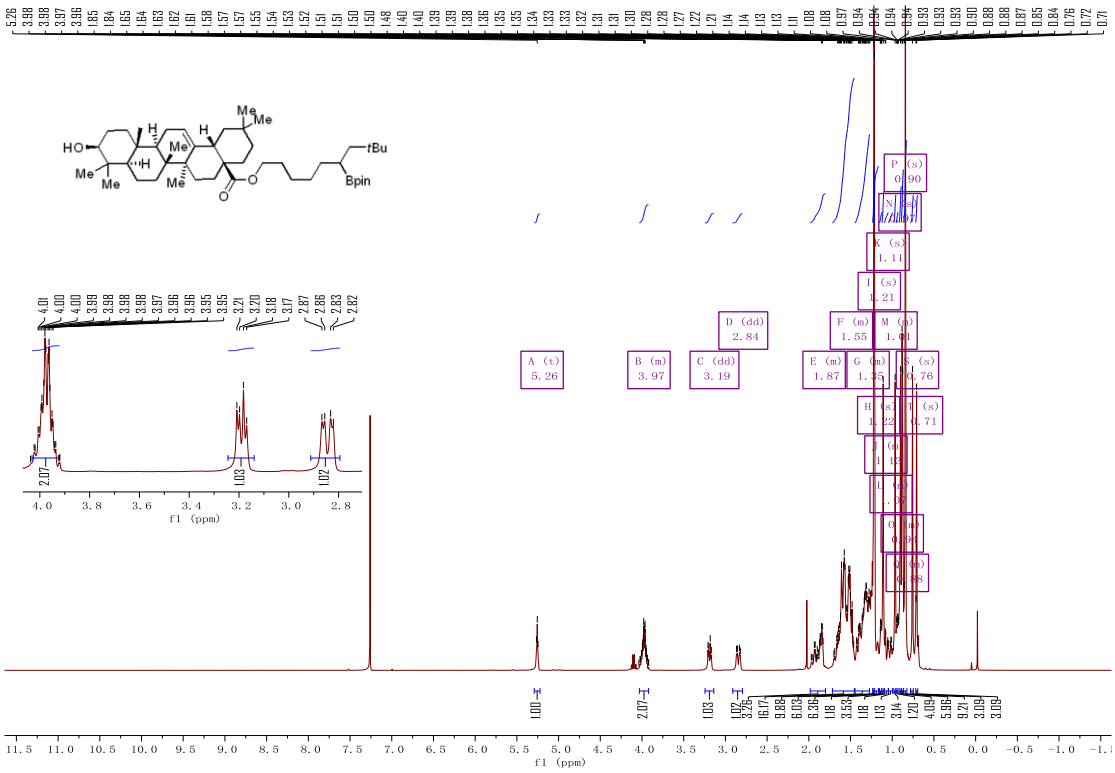
Following general procedure 1. The product was isolated by column chromatography as colorless oil (69.3 mg, 0.094 mmol, 47%, d.r. = 1:1).

Rf (petroleum ether : acetone = 5 : 1) = 0.50.

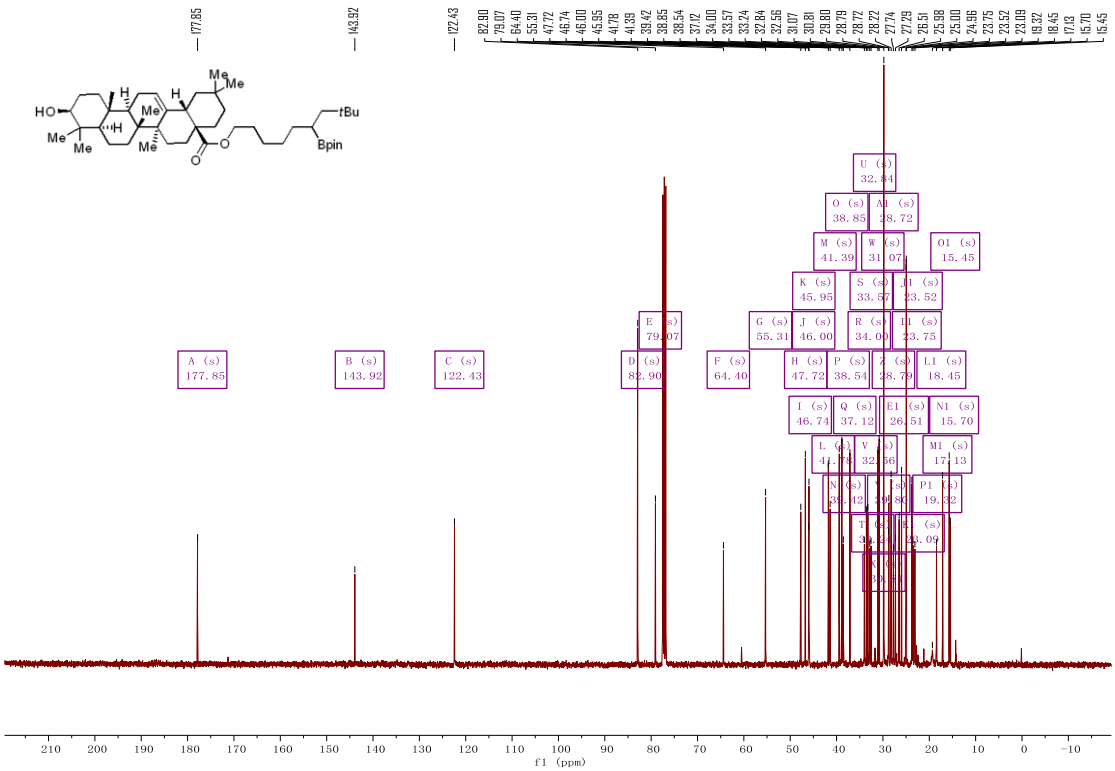
^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.26 (t, *J* = 3.7 Hz, 1H), 4.06 – 3.85 (m, 2H), 3.19 (dd, *J* = 11.0, 4.8 Hz, 1H), 2.84 (dd, *J* = 13.9, 4.5 Hz, 1H), 2.01 – 1.81 (m, 3H), 1.72 – 1.45 (m, 16H), 1.45 – 1.27 (m, 10H), 1.22 (s, 6H), 1.21 (s, 6H), 1.15 – 1.13 (m, 1H), 1.11 (s, 3H), 1.09 – 1.05 (m, 1H), 1.04 – 0.99 (m, 1H), 0.97 (s, 3H), 0.97 – 0.90 (m, 1H), 0.90 (s, 4H), 0.90 – 0.85 (m, 6H), 0.84 (s, 9H), 0.76 (s, 3H), 0.71 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.85, 143.92, 122.43, 82.90, 79.07, 64.40, 55.31, 47.72, 46.74, 46.00, 45.95, 41.78, 41.39, 39.42, 38.85, 38.54, 37.12, 34.00, 33.57, 33.24, 32.84, 32.56, 31.07, 30.81, 29.80, 28.79, 28.72, 28.22, 27.74, 27.29, 26.51, 25.98, 25.00, 24.96, 23.75, 23.52, 23.09, 19.32, 18.45, 17.13, 15.70, 15.45.

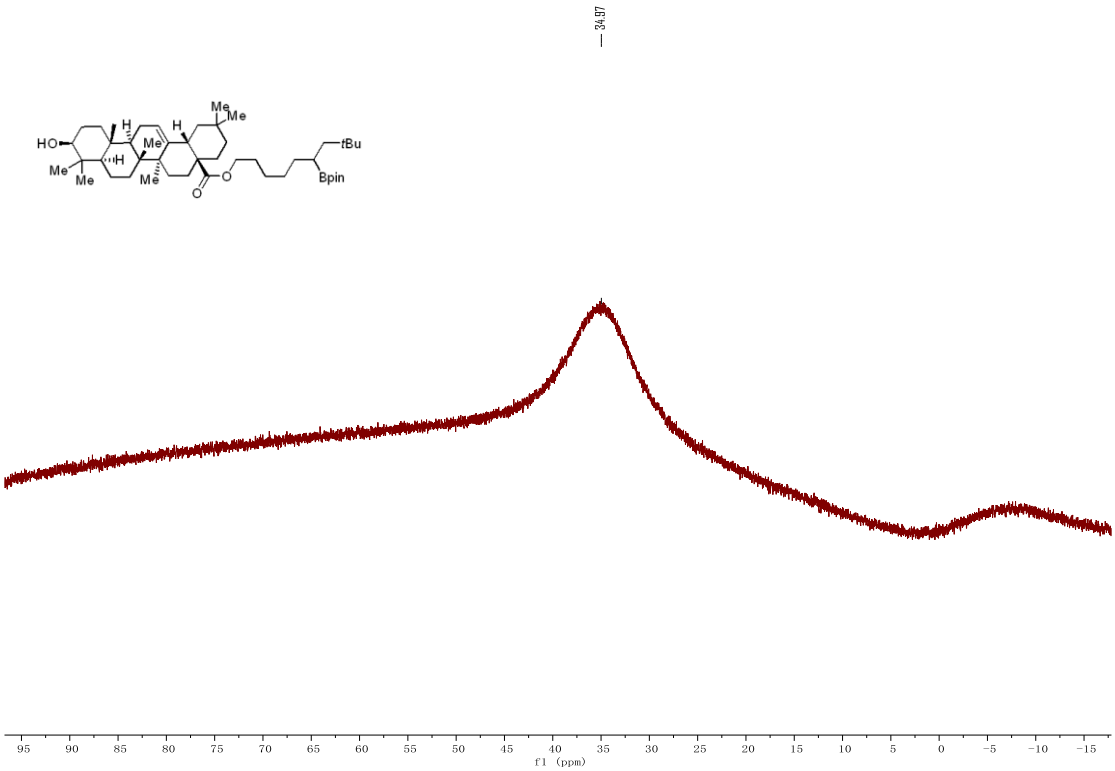
^{11}B NMR (128 MHz, Chloroform-*d*) 34.97



^{1}H NMR spectra for **52**



^{13}C NMR spectra for **52**

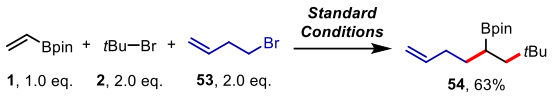


^{11}B NMR spectra for **52**

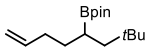
9. Examples Described in Scheme 6

9.1. Olefin Competition Experiments

a.



Following general procedure 1, **54** was obtained as colorless oil (33.5 mg, 0.126 mmol 63%).



2-(2,2-dimethyloct-7-en-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**54**)

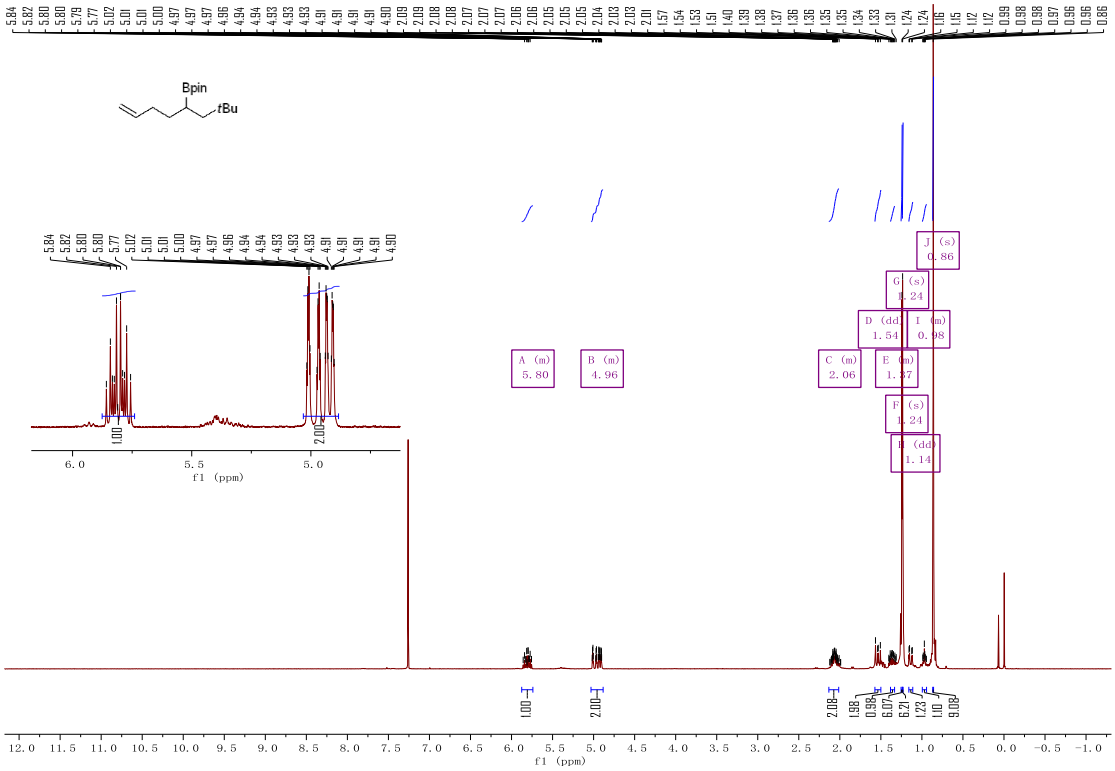
Rf (petroleum ether : acetone = 50 : 1) = 0.40

^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.91 – 5.71 (m, 1H), 5.06 – 4.86 (m, 2H), 2.12 – 1.98 (m, 2H), 1.54 (dd, *J* = 13.4, 10.4 Hz, 2H), 1.43 – 1.29 (m, 1H), 1.24 (s, 6H), 1.24 (s, 6H), 1.14 (dd, *J* = 13.4, 2.5 Hz, 1H), 1.00 – 0.93 (m, 1H), 0.86 (s, 9H).

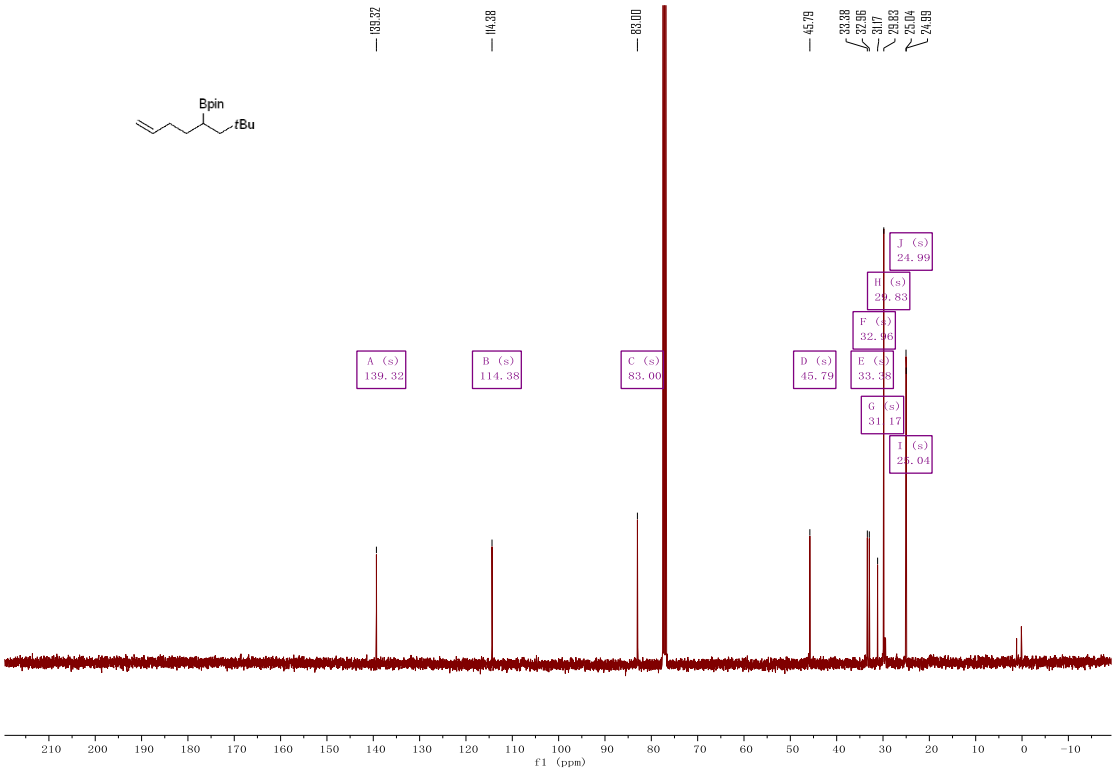
13C NMR (101 MHz, Chloroform-*d*) δ 139.32, 114.38, 83.00, 45.79, 33.38, 32.96, 31.17, 29.83, 25.04, 24.99.

^{11}B NMR (128 MHz, Chloroform-*d*) 34.57.

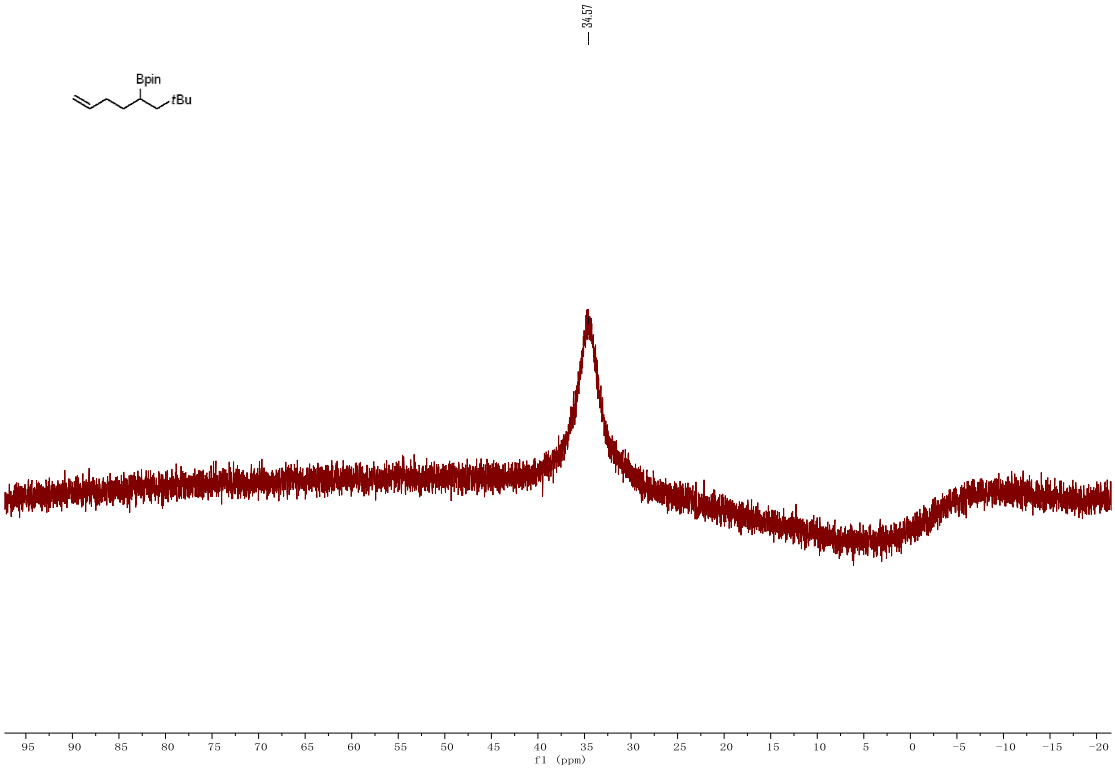
HRMS (ESI) calculated for $C_{16}H_{31}BO_2$ $[M+H]^+$: 267.2490, found: 267.2495.



^{1}H NMR spectra for **54**

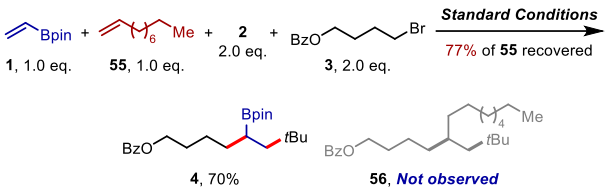


^{13}C NMR spectra for **54**



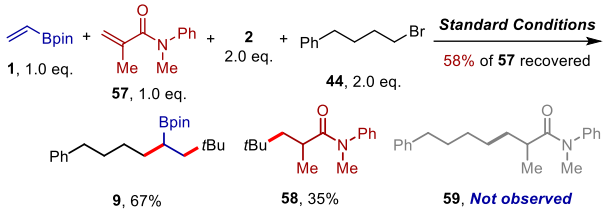
^{11}B NMR spectra for **54**

b.



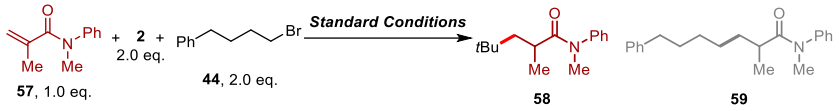
Following the procedure: $NiBr_2$(diglyme) (0.020 mmol, 10 mol%, 7.1 mg), Ligand (0.024 mmol, 12 mol%, 5.0 mg), NaI (0.1 mmol, 0.5 equiv., 15.0 mg) and Mn (0.6 mmol, 3.0 equiv., 33.0 mg) were added to a Schlenk tube equipped with a stir bar. The Schlenk tube was evacuated and filled with argon (three cycles). To these solids, 1 mL DMAc (0.2 M) was added under argon atmosphere. Then, dec-1-ene (0.2 mmol, 1.0 equiv., 38 μL), 4,4,5,5-tetramethyl-2-vinyl-1,3,2-dioxaborolane (0.2 mmol, 1.0 equiv., 34 μL) and tertiary alkyl bromide (0.4 mmol, 2.0 equiv., 46 μL) were added and stirred at room temperature (20-25 °C) for 10 min, 4-bromobutyl benzoate (0.4 mmol, 2.0 equiv., 75 μL) were added under argon atmosphere. The mixture was stirred at room temperature for 12 hours. Compound **4** was obtained in 70% yield (54.4 mg, 0.140 mmol). Compound **56** was not observed, and compound **55** was recovered on 77%.

c.



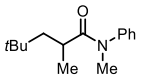
Following the procedure: $NiBr_2$(diglyme) (0.020 mmol, 10 mol%, 7.1 mg), Ligand (0.024 mmol, 12 mol%, 5.0 mg), NaI (0.1 mmol, 0.5 equiv., 15.0 mg), **57** (0.2 mmol, 1.0 equiv., 35.0 mg) and Mn (0.6 mmol, 3.0 equiv., 33.0 mg) were added to a Schlenk tube equipped with a stir bar. The Schlenk tube was evacuated and filled with argon (three cycles). To these solids, 1 mL DMAc (0.2 M) was added under argon atmosphere. Then, 4,4,5,5-tetramethyl-2-vinyl-1,3,2-dioxaborolane (0.2 mmol, 1.0 equiv., 34 μL) and tertiary alkyl bromide (0.4 mmol, 2.0 equiv., 46 μL) were added and stirred at room temperature (20-25 °C) for 10 min, (4-bromobutyl)benzene (0.4 mmol, 2.0 equiv., 70 μL) were added under argon atmosphere. The mixture was stirred at room temperature for 12 hours. Compound **9** was obtained in 67% yield (46.1 mg, 0.134 mmol), compound **58** was obtained as colorless oil on 35% (16.4 mg, 0.07 mmol). Compound **59** was not observed, and compound **57** was recovered on 58%.

d.



entry	deviation from standard conditions	yield of **58** (%)[a]	yield of **59** (%)
1	without **44**, $NiBr_2$(diglyme) and ligand	< 2	< 2
2	without **44**	50	< 2
3	without **2**, $NiBr_2$(diglyme) and ligand	N.R.[b]	
4	without **2**	N.R.[b]	

[a] Following general procedure 1., 0.2 mmol scale. Isolated yield. [b] Recovery rate of compound **57** was more than 95%.



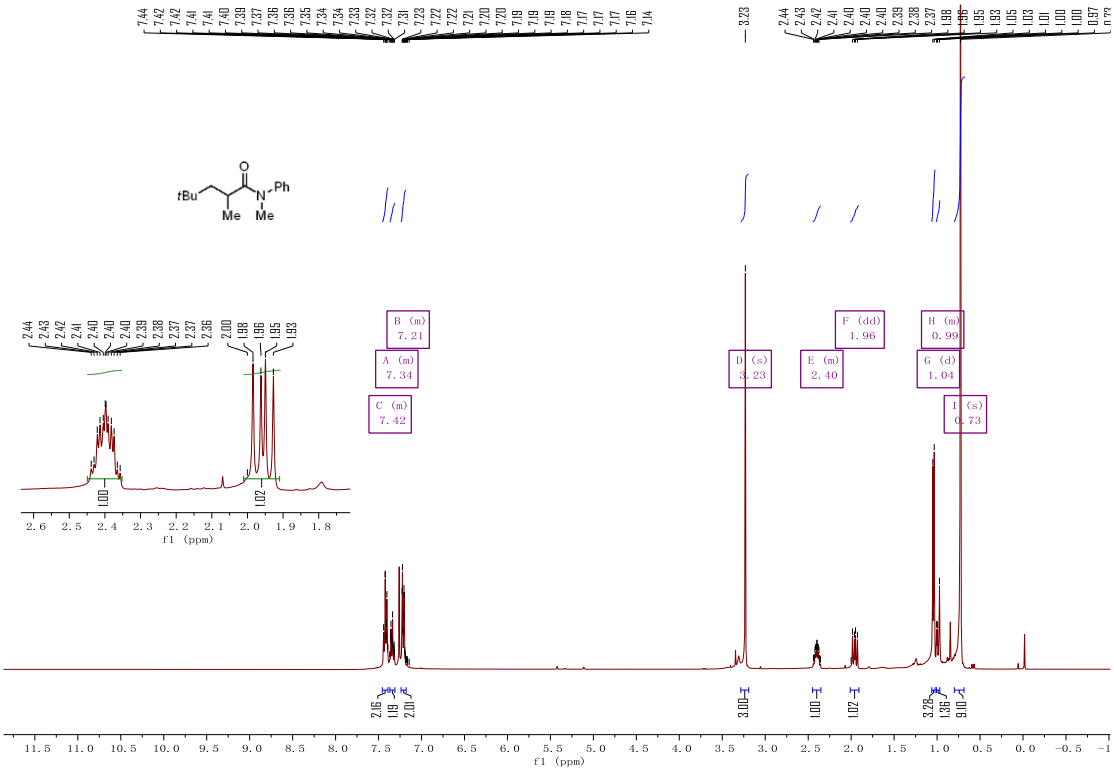
N,2,4,4-tetramethyl-*N*-phenylpentanamide (**58**)

Rf (petroleum ether : acetone : acetic acid= 5 : 1 : 0.5) = 0.40

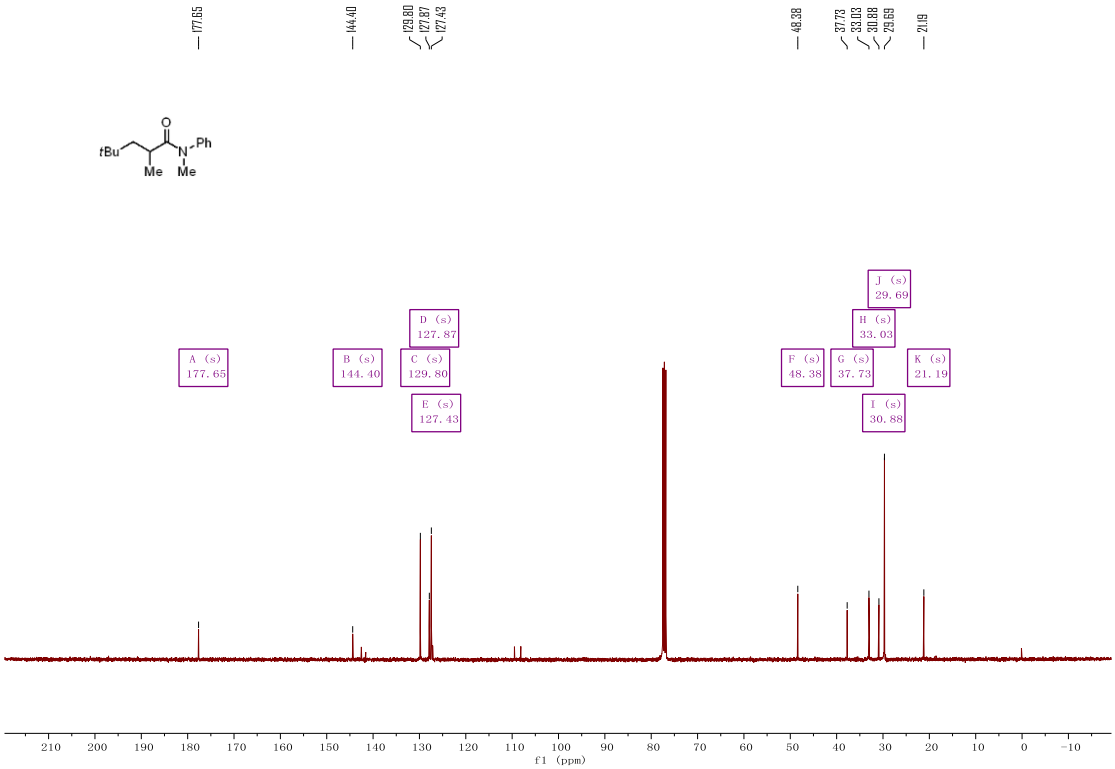
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 – 7.37 (m, 2H), 7.37 – 7.30 (m, 1H), 7.24 – 7.14 (m, 2H), 3.23 (s, 3H), 2.46 – 2.30 (m, 1H), 1.96 (dd, *J* = 14.0, 8.9 Hz, 1H), 1.04 (d, *J* = 6.9 Hz, 3H), 1.03 – 0.95 (m, 1H), 0.73 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.65, 144.40, 129.80, 127.87, 127.43, 48.38, 37.73, 33.03, 30.88, 29.69, 21.19.

HRMS (ESI) calculated for $C_{15}H_{23}NO$ $[M+H]^+$: 234.1852, found: 234.1858.

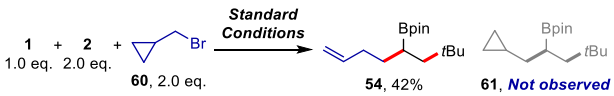


^{1}H NMR spectra for **58**



^{13}C NMR spectra for **58**

9.2. Radical Clock Experiment



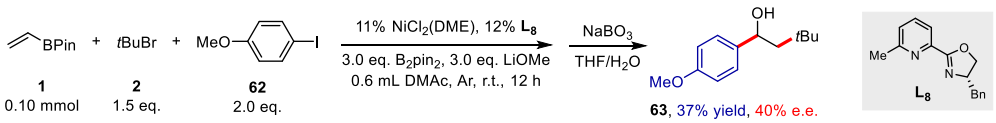
Following general procedure 1. Compound **61** was not observed. Compound **54** was isolated by column chromatography as colorless oil (22.3 mg, 0.084 mmol, 42%).

9.3. Non-metallic Reductant Experiment

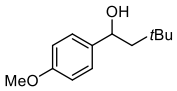
Following the procedure: $NiBr_2$(diglyme) (0.020 mmol, 10 mol%, 7.1 mg), Ligand (0.024 mmol, 12 mol%, 5.0 mg), NaI (0.1 mmol, 0.5 equiv., 15.0 mg) and TDAE (TDAE = 1,1,2,2-tetrakis(dimethylamino)ethylene) (0.3 mmol, 3.0 equiv., 140 μL) were added to a Schlenk tube equipped with a stir bar. The Schlenk tube was evacuated and filled with argon (three cycles). To these solids, 1.0 mL DMAc (0.2 M) was added

under argon atmosphere. Then, 4,4,5,5-tetramethyl-2-vinyl-1,3,2-dioxaborolane (0.2 mmol, 1.0 equiv., 34 μL) and **2** (0.4 mmol, 2.0 equiv., 46 μL) was added and stirred at room temperature (20-25 ℃) for 10 min, **63** (0.4 mmol, 2.0 equiv., 75 μL) were added under argon atmosphere. The mixture was stirred at room temperature for 12 hours, and compound **4** was detected by GC.

10. Stereochemical Control



General Procedure 3: $NiCl_2$(DME) (0.020 mmol, 10 mol%, 2.4 mg), **L_8** (0.024 mmol, 12 mol%, 3.1 mg), 1-iodo-4-methoxybenzene (0.2 mmol, 2.0 equiv., 46.8mg), B_2pin_2 (0.3 mmol, 3.0 equiv., 76.2 mg) and LiOMe (0.6 mmol, 3.0 equiv., 11.4 mg) were added to a Schlenk tube equipped with a stir bar. The Schlenk tube was evacuated and filled with argon (three cycles). To these solids, 0.6 mL DMAc was added under argon atmosphere. Then, 2-bromo-2-methylpropane (0.15 mmol, 1.5 equiv., 17 μL) was added and stirred at room temperature (20-25 °C) for 10 min, 4,4,5,5-tetramethyl-2-vinyl-1,3,2-dioxaborolane (0.1 mmol, 1.0 equiv., 17 μL) were added under argon atmosphere. The mixture was stirred at room temperature for 12 hours, and purified by column chromatography to afford the crude product. To a solution of the crude product in THF (1 mL) and H_2O (1 mL) was added $NaBO_3{\cdot}4H_2O$ (154 mg, 1mmol) at room temperature. The reaction mixture was then stirred at room temperature for 12 hours. The reaction mixture was diluted with H_2O followed by extraction with EtOAc, dried with anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel to give the final product **63** (7.7 mg, 0.037 mmol, 37% yield, 40% ee).



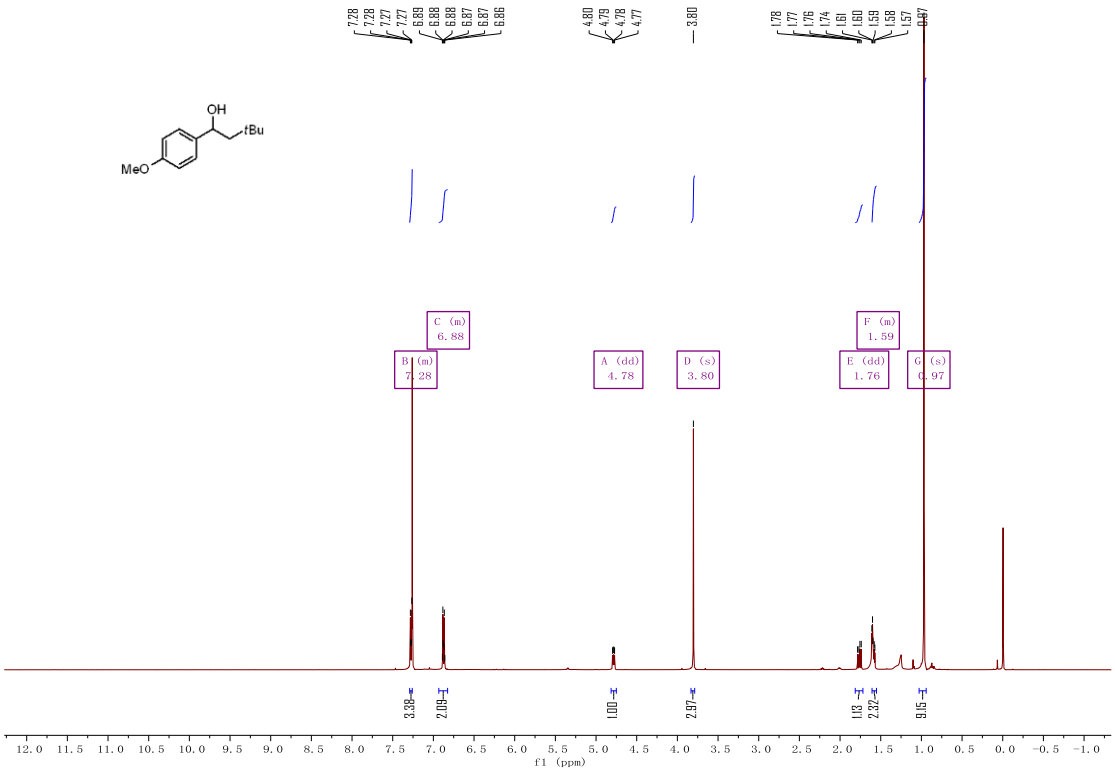
1-(4-methoxyphenyl)-3,3-dimethylbutan-1-ol (**63**)

Rf (petroleum ether : ethyl acetate= 5 : 1) = 0.50

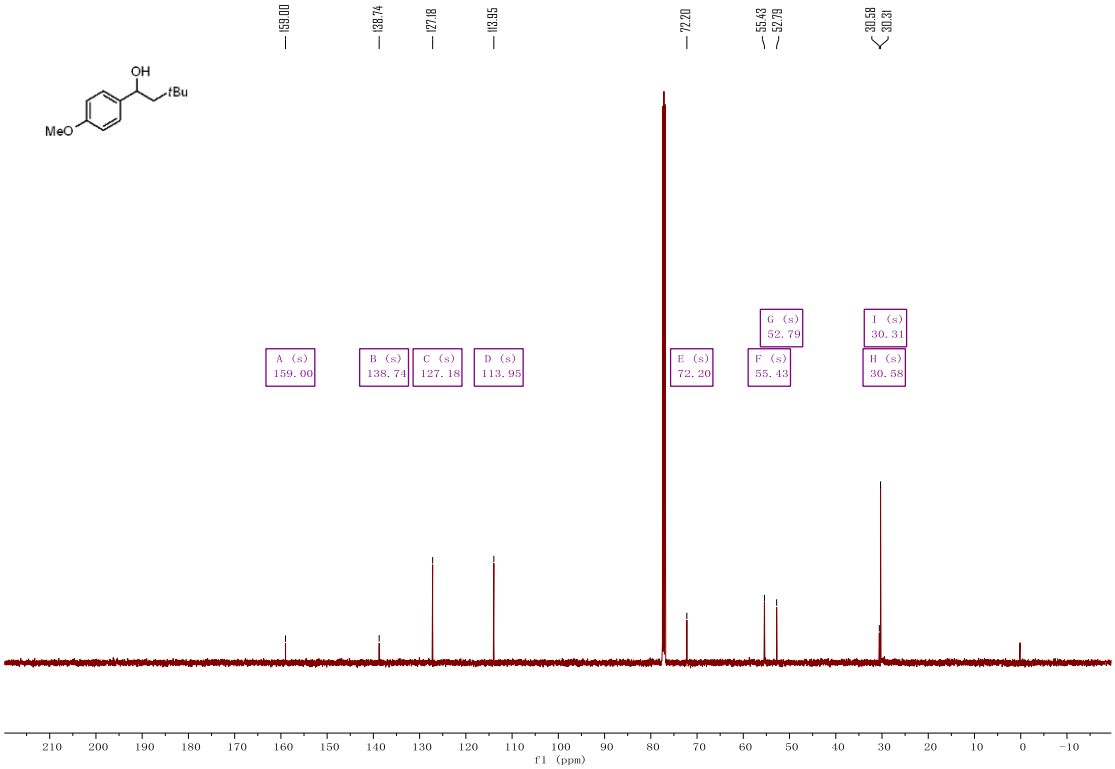
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.31 – 7.26 (m, 2H), 6.92 – 6.74 (m, 2H), 4.78 (dd, *J* = 8.2, 4.0 Hz, 1H), 3.80 (s, 3H), 1.76 (dd, *J* = 14.4, 8.2 Hz, 1H), 1.66 – 1.50 (m, 2H), 0.97 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 159.00, 138.74, 127.18, 113.95, 72.20, 55.43, 52.79, 30.58, 30.31.

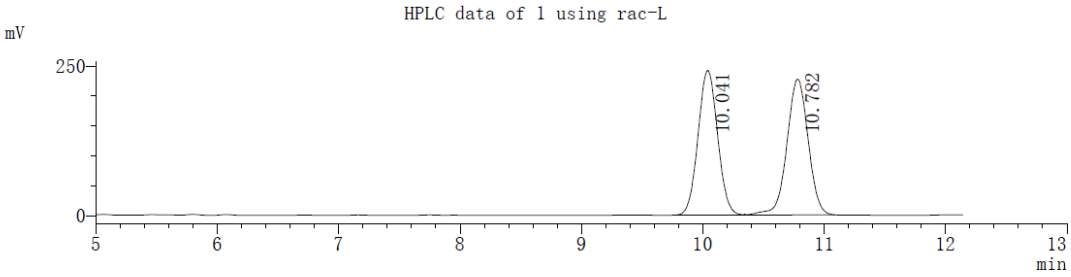
HPLC analysis: The ee was determined to be 40% on a CHIRALPAK AD-H column (4.0% *i*PrOH in hexane, 1.0 mL/min, 40 °C); retention times for compound obtained using **L_8**: 9.89 min (major), 10.539 min (minor).



^{1}H NMR spectra for **63**

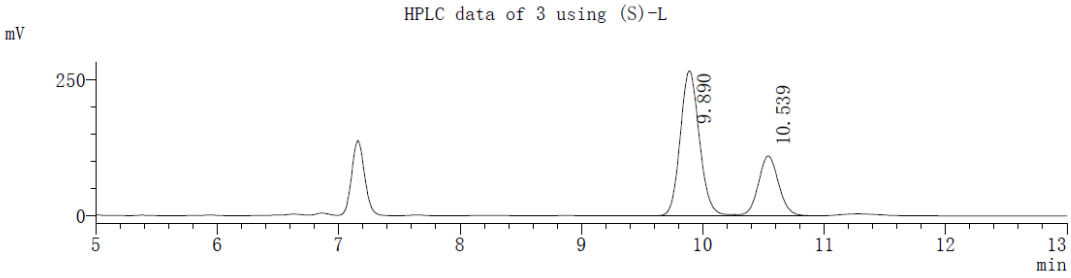


^{13}C NMR spectra for **63**



检测器A 214nm

Peak[#]	RetTime[min]	Height[uV]	Width[min]	Area[uV*s]	Area[%]
1	10.041	242273	0.174	2712811	49.523
2	10.782	227250	0.186	2765117	50.477

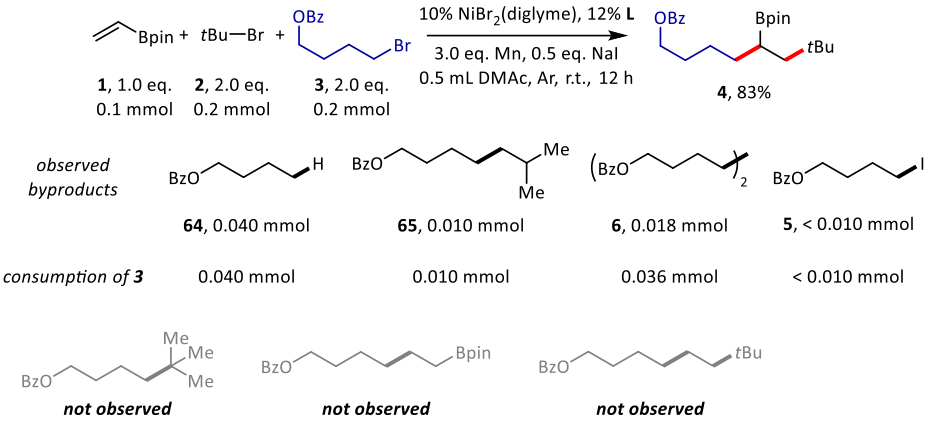


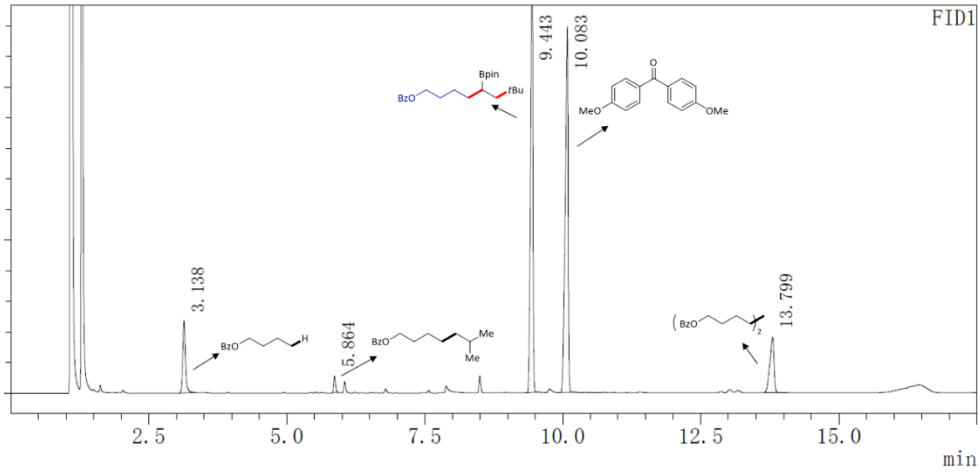
检测器A 214nm

Peak[#]	RetTime[min]	Height[uV]	Width[min]	Area[uV*s]	Area[%]
1	9.890	266768	0.168	2920891	69.802
2	10.539	109868	0.177	1263670	30.198

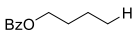
HPLC spectra for **63**

11. Calculation of Mass Balance





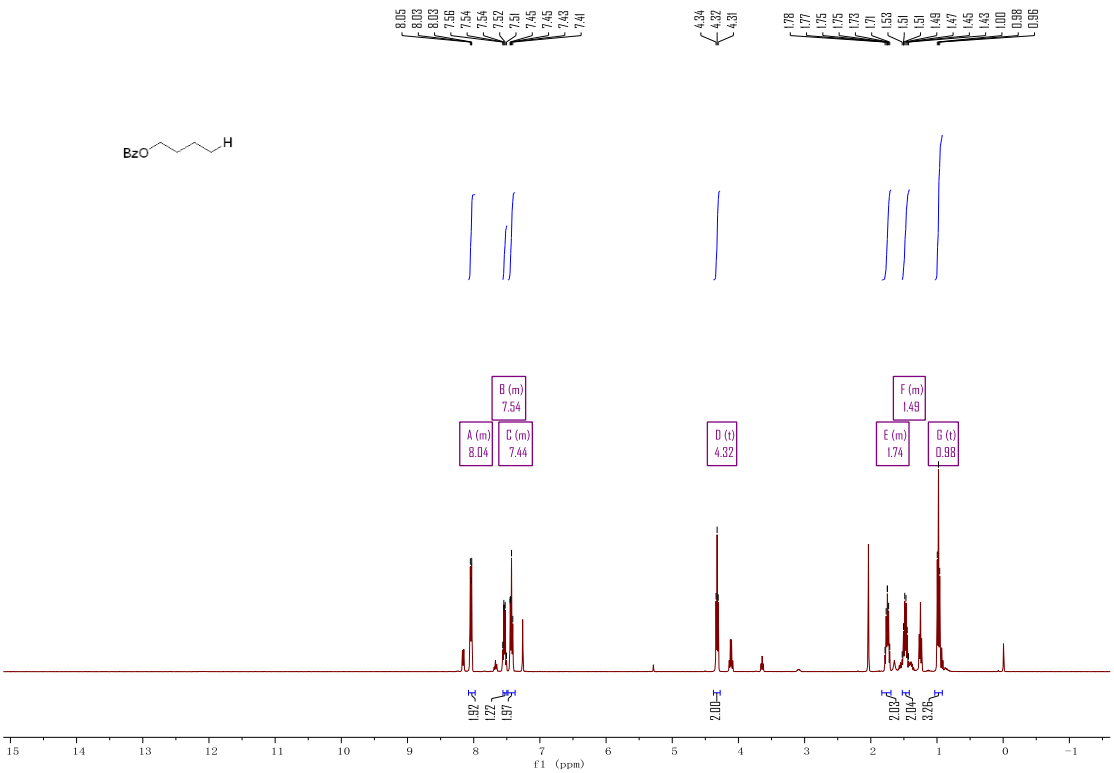
Following general procedure 1. Primary alkyl bromides were converted to both protonation products and homo-coupling products through the side reactions.



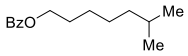
butyl benzoate (**64**)

Rf (petroleum ether : ethyl acetate= 20 : 1) = 0.70

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 – 7.97 (m, 2H), 7.57 – 7.49 (m, 1H), 7.47 – 7.36 (m, 2H), 4.32 (t, *J* = 6.6 Hz, 2H), 1.83 – 1.68 (m, 2H), 1.53 – 1.41 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H).



^{1}H NMR spectra for **64**

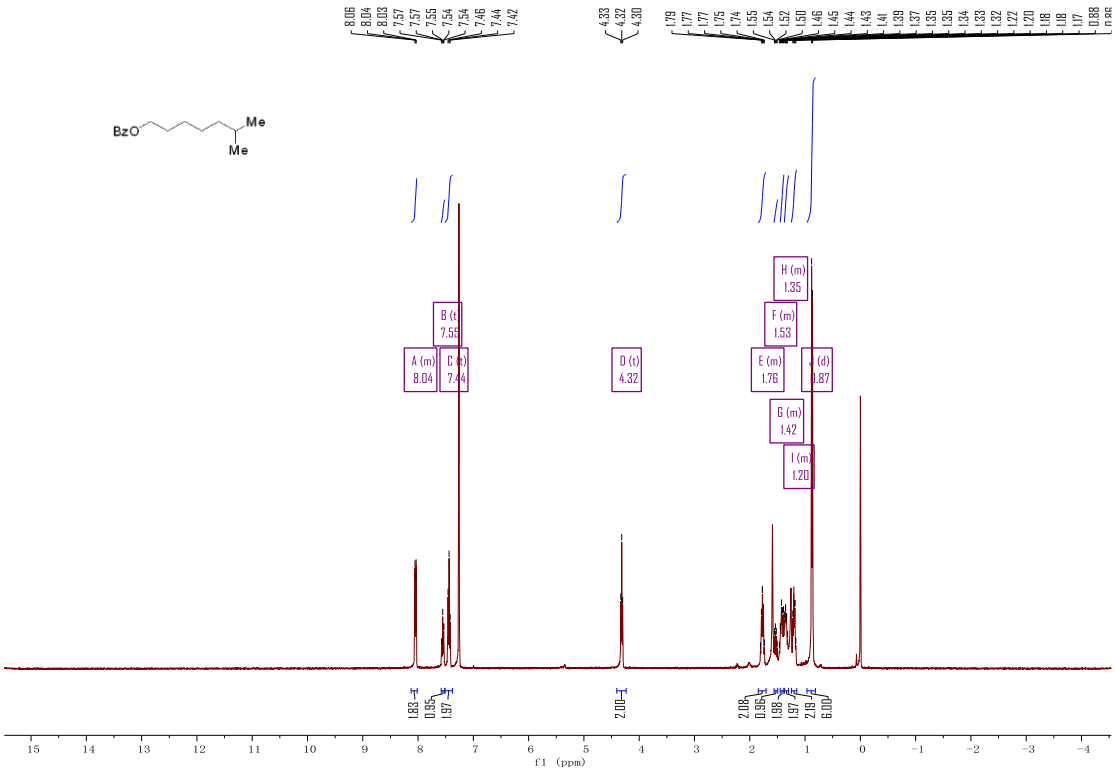


6-methylheptyl benzoate (**65**)

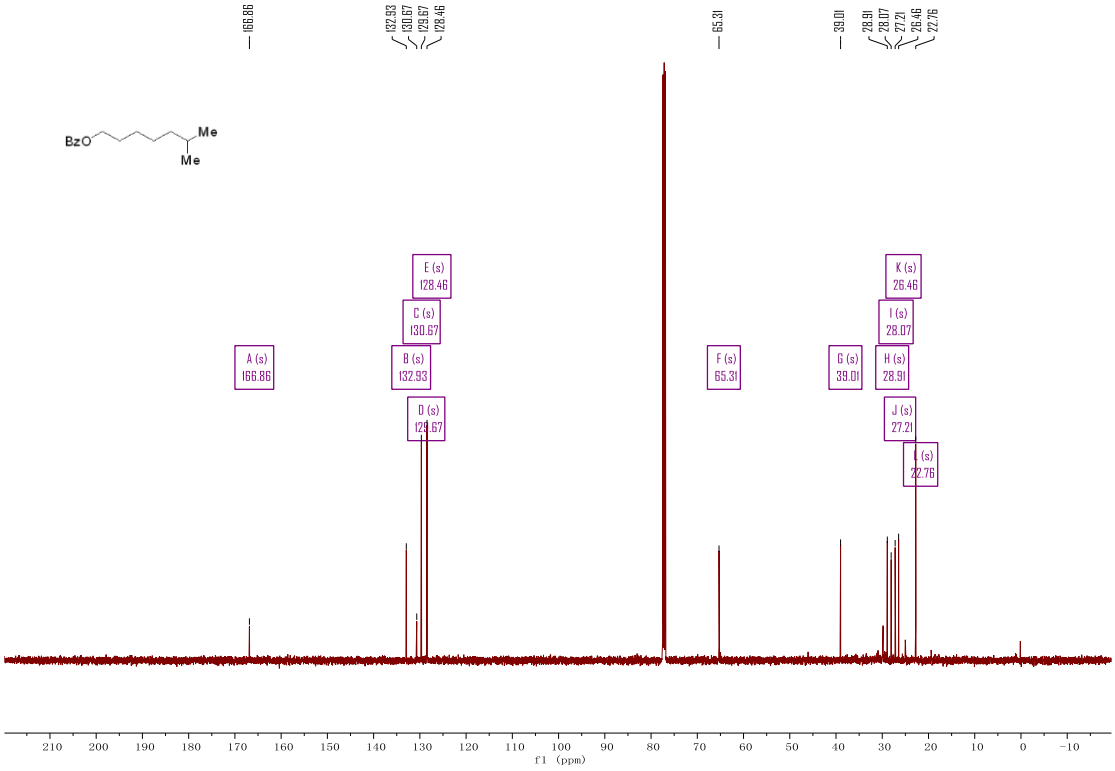
Rf (petroleum ether : ethyl acetate= 20 : 1) = 0.80

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.15 – 7.94 (m, 2H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 4.32 (t, *J* = 6.7 Hz, 2H), 1.84 – 1.70 (m, 2H), 1.56 – 1.48 (m, 1H), 1.46 – 1.39 (m, 2H), 1.40 – 1.29 (m, 2H), 1.24 – 1.14 (m, 2H), 0.87 (d, *J* = 6.6 Hz, 6H).

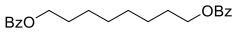
^{13}C NMR (126 MHz, Chloroform-*d*) δ 166.86, 132.93, 130.67, 129.67, 128.46, 65.31, 39.01, 28.91, 28.07, 27.21, 26.46, 22.76.



^{1}H NMR spectra for **65**



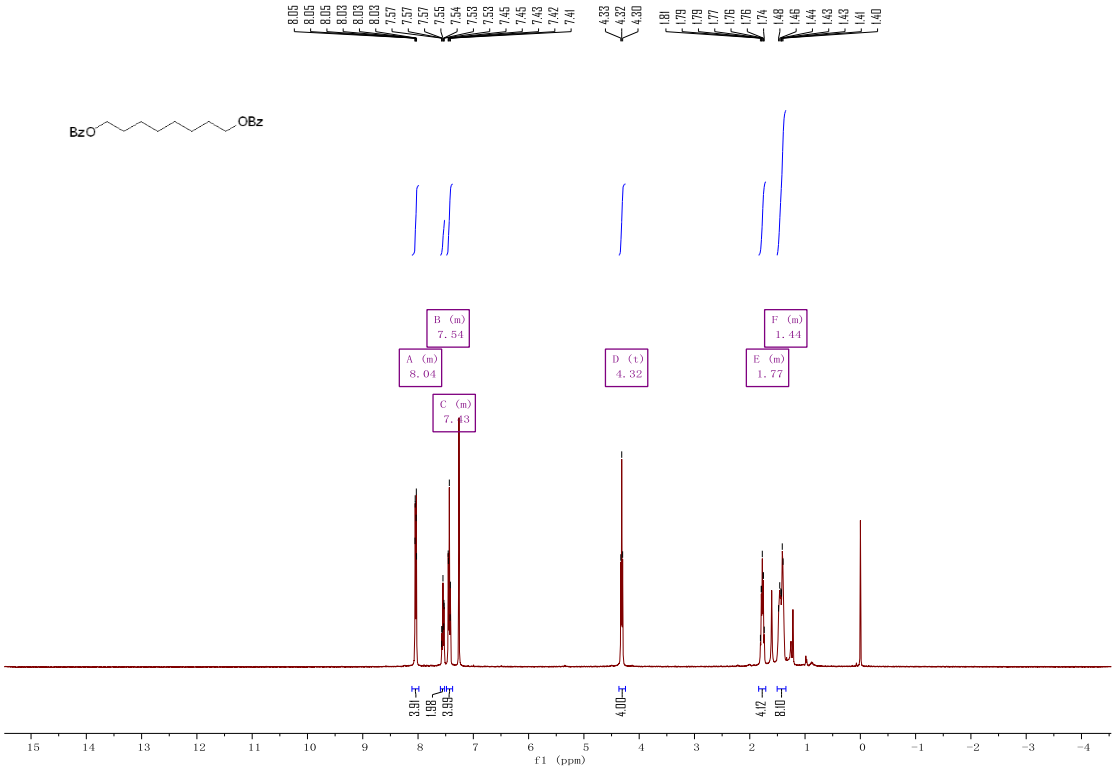
^{13}C NMR spectra for **65**



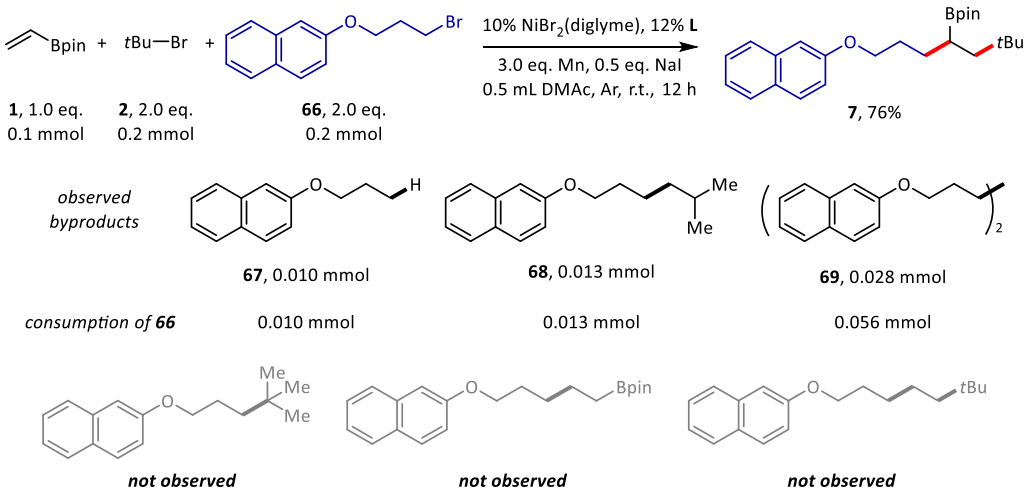
octane-1,8-diyl dibenzoate (**6**)

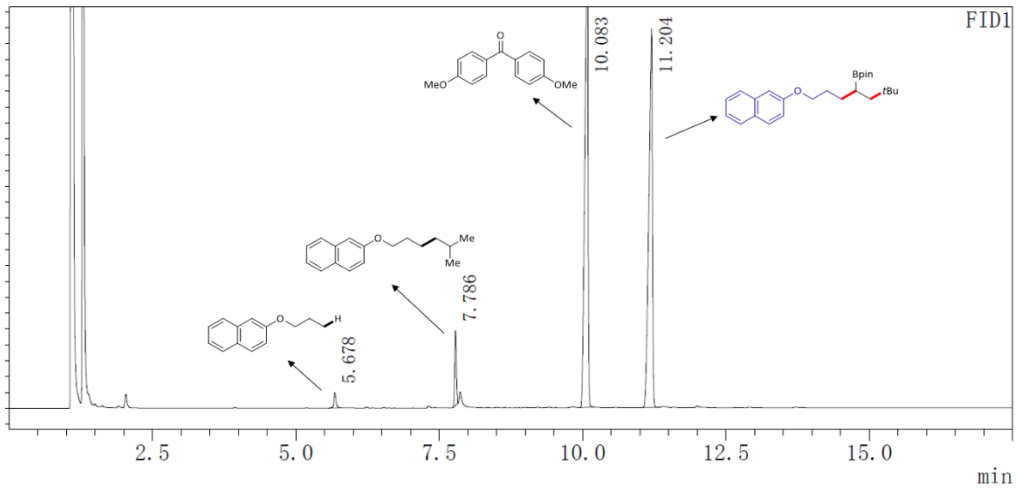
Rf (petroleum ether : ethyl acetate= 20 : 1) = 0.40

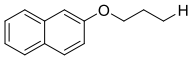
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.13 – 7.89 (m, 4H), 7.65 – 7.51 (m, 2H), 7.48 – 7.40 (m, 4H), 4.32 (t, *J* = 6.6 Hz, 4H), 1.83 – 1.72 (m, 4H), 1.53 – 1.32 (m, 8H).



^{1}H NMR spectra for **6**





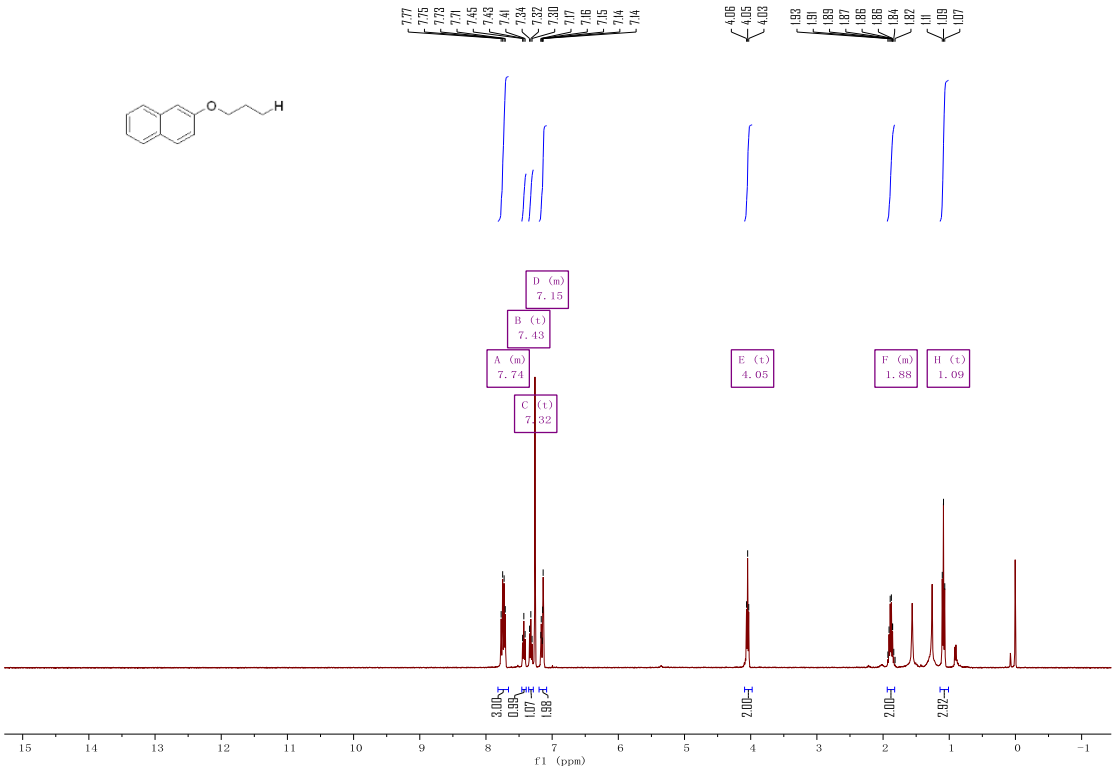


2-propoxynaphthalene (**67**)

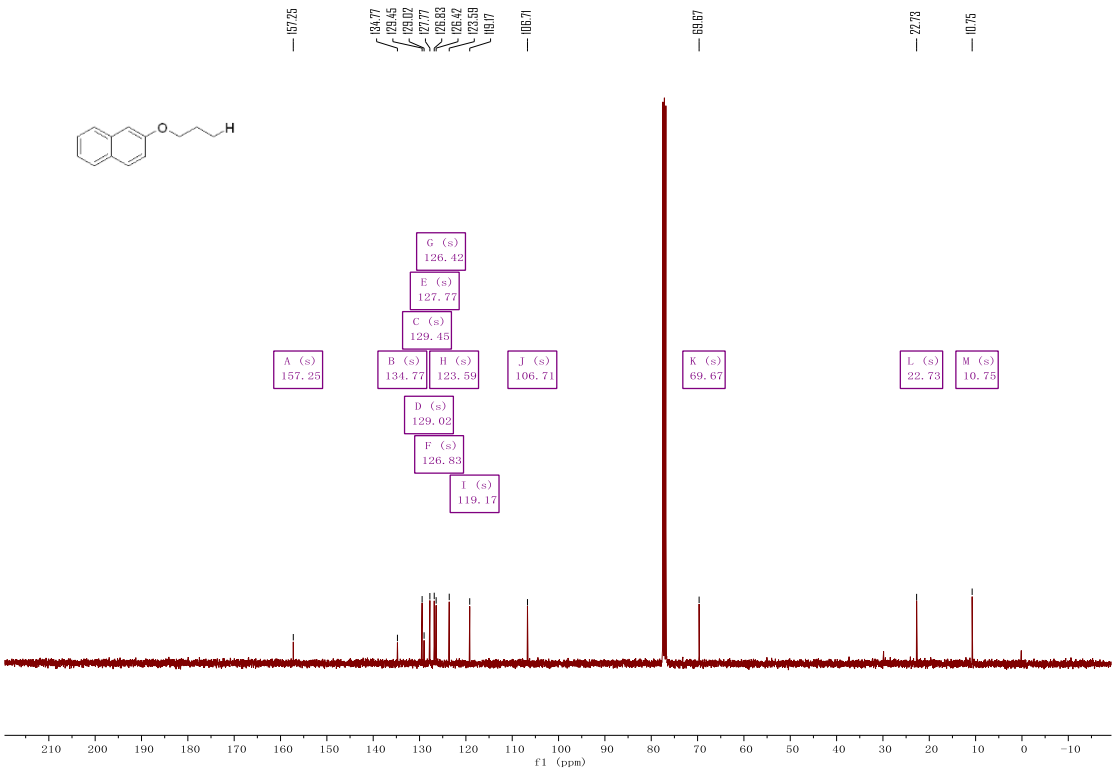
Rf (petroleum ether : ethyl acetate= 100 : 1) = 0.50

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 – 7.67 (m, 3H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.19 – 7.13 (m, 2H), 4.05 (t, *J* = 6.6 Hz, 2H), 1.95 – 1.79 (m, 2H), 1.09 (t, *J* = 7.5 Hz, 3H).

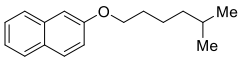
^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.25, 134.77, 129.45, 129.02, 127.77, 126.83, 126.42, 123.59, 119.17, 106.71, 69.67, 22.73, 10.75.



^{1}H NMR spectra for **67**



^{13}C NMR spectra for **67**

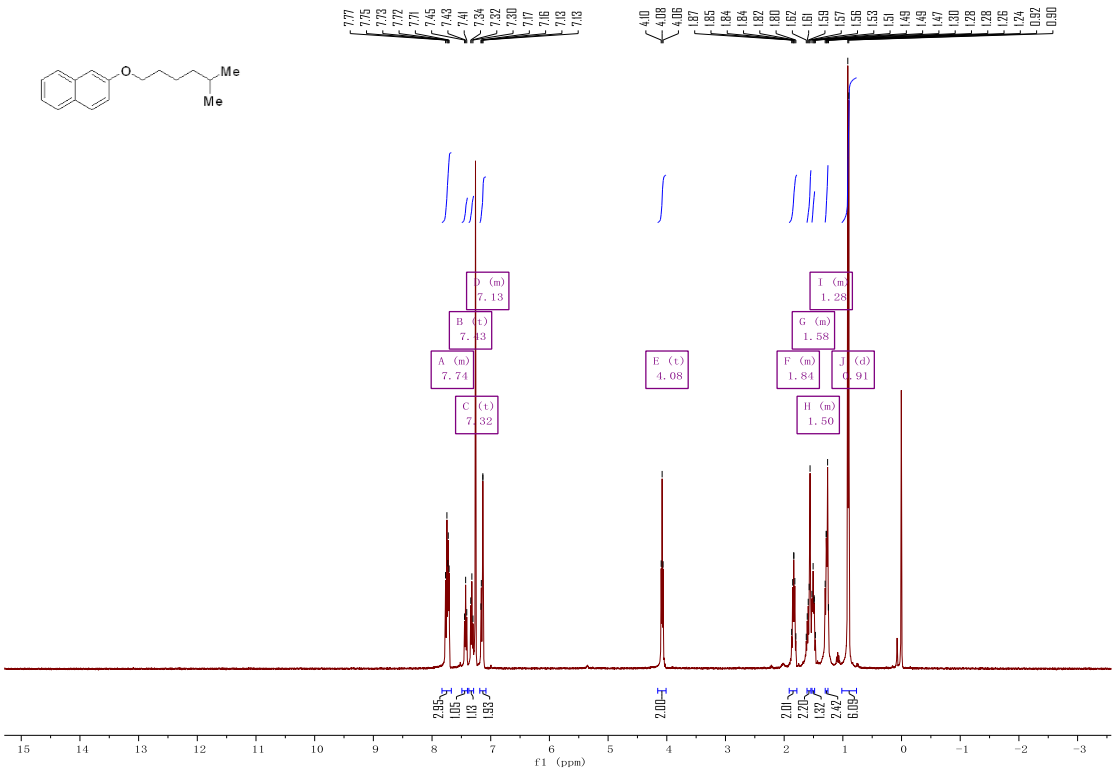


2-((5-methylhexyl)oxy)naphthalene (**68**)

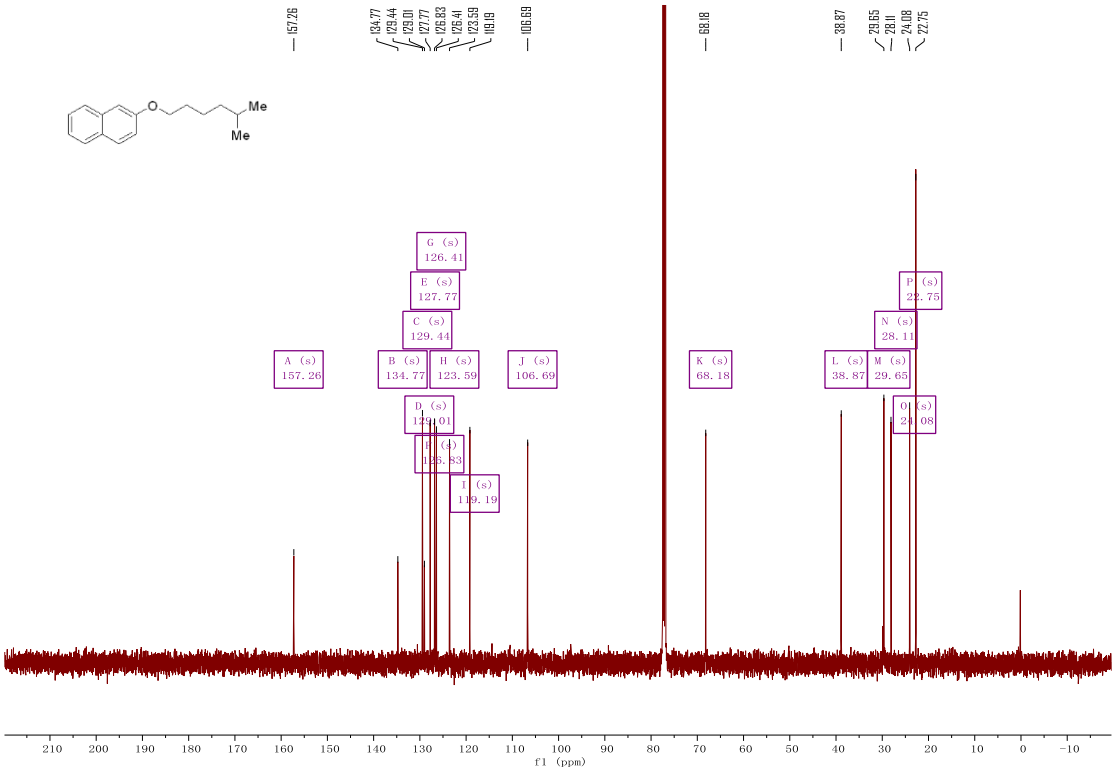
Rf (petroleum ether : ethyl acetate= 100 : 1) = 0.55

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 – 7.65 (m, 3H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.19 – 7.09 (m, 2H), 4.08 (t, *J* = 6.5 Hz, 2H), 1.94 – 1.74 (m, 2H), 1.64 – 1.54 (m, 2H), 1.55 – 1.44 (m, 1H), 1.32 – 1.21 (m, 2H), 0.91 (d, *J* = 6.6 Hz, 6H).

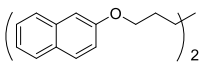
^{13}C NMR (126 MHz, Chloroform-*d*) δ 157.26, 134.77, 129.44, 129.01, 127.77, 126.83, 126.41, 123.59, 119.19, 106.69, 68.18, 38.87, 29.65, 28.11, 24.08, 22.75.



^{1}H NMR spectra for **68**



^{13}C NMR spectra for **68**

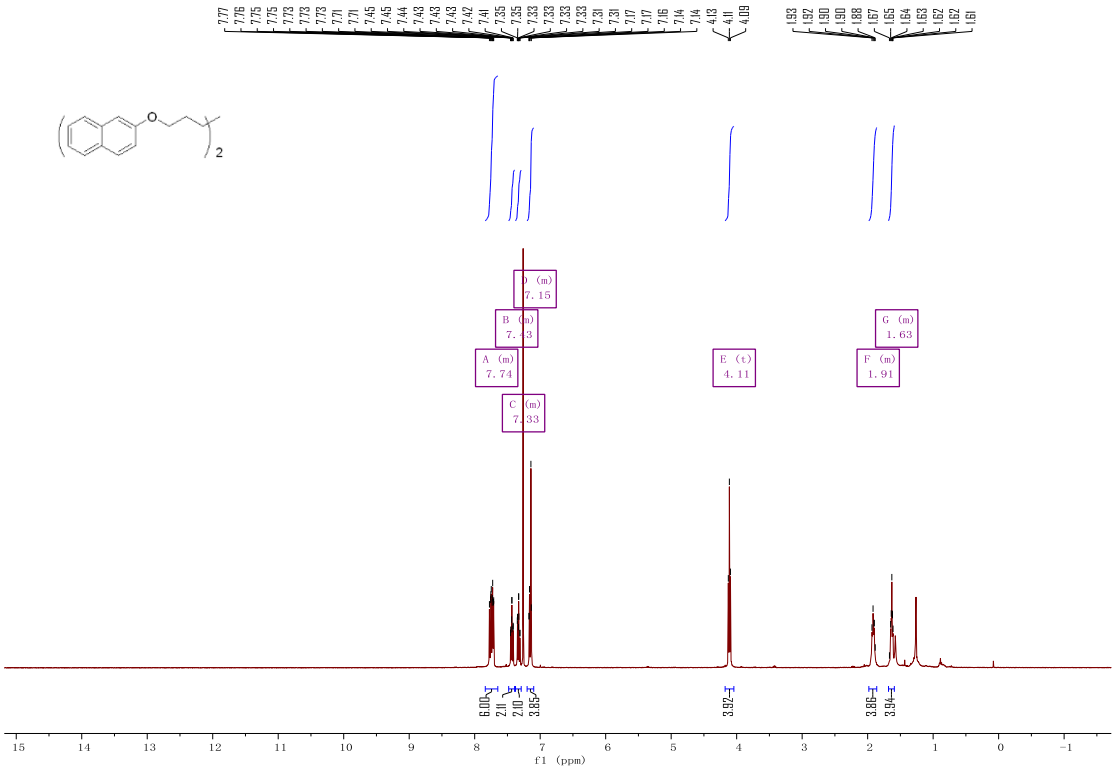


1,6-bis(naphthalen-2-yloxy)hexane (**69**)

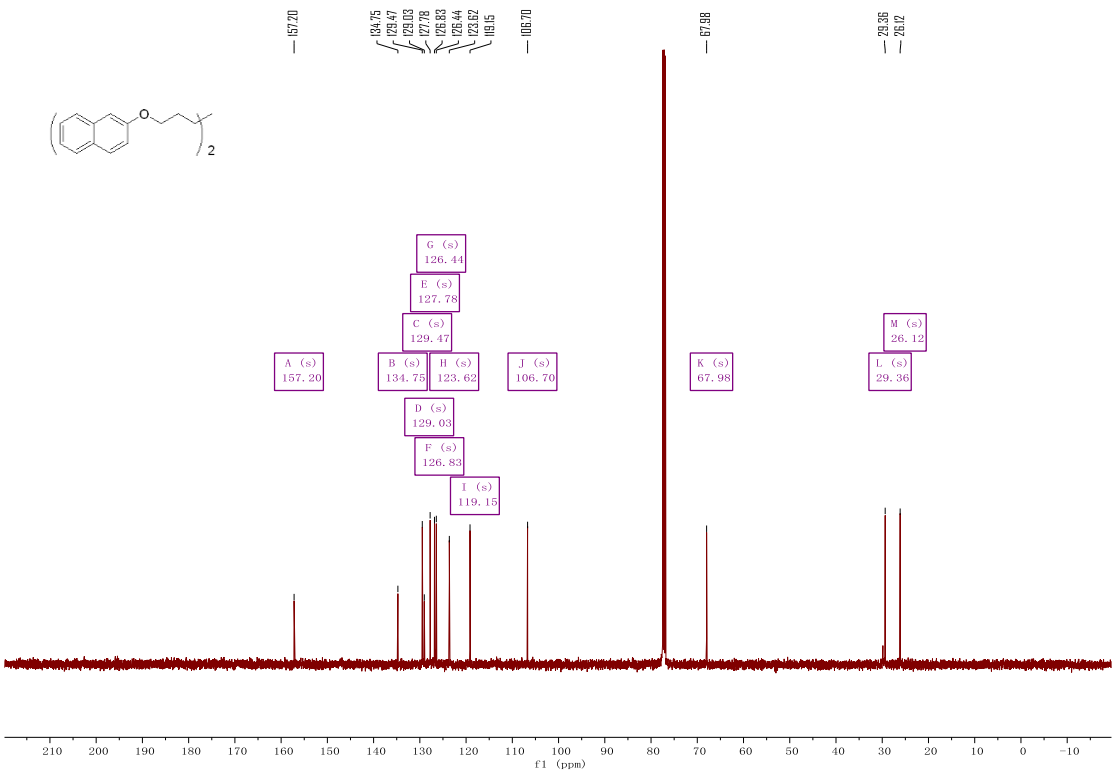
Rf (petroleum ether : ethyl acetate= 20 : 1) = 0.55

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 – 7.65 (m, 6H), 7.48 – 7.39 (m, 2H), 7.37 – 7.28 (m, 2H), 7.19 – 7.09 (m, 4H), 4.11 (t, *J* = 6.5 Hz, 4H), 2.00 – 1.79 (m, 4H), 1.70 – 1.58 (m, 4H).

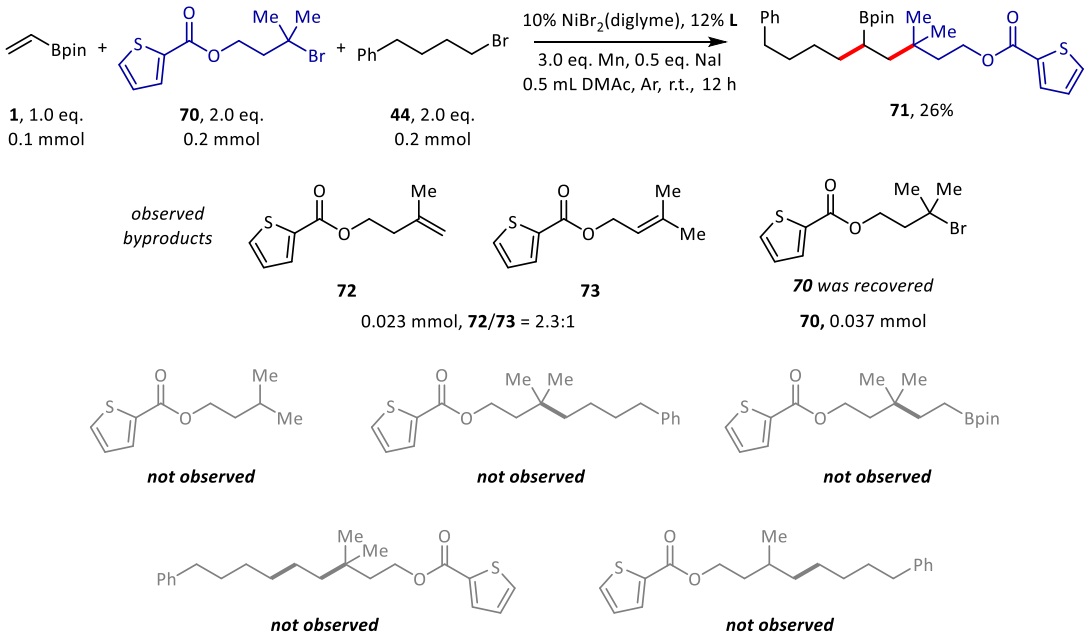
^{13}C NMR (126 MHz, Chloroform-*d*) δ 157.20, 134.75, 129.47, 129.03, 127.78, 126.83, 126.44, 123.62, 119.15, 106.70, 67.98, 29.36, 26.12.



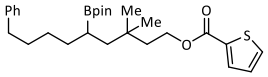
^{1}H NMR spectra for **69**



^{13}C NMR spectra for **69**



Following general procedure 1. Tertiary alkyl bromides were converted to dehydrohalogenation products.



3,3-dimethyl-9-phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nonyl

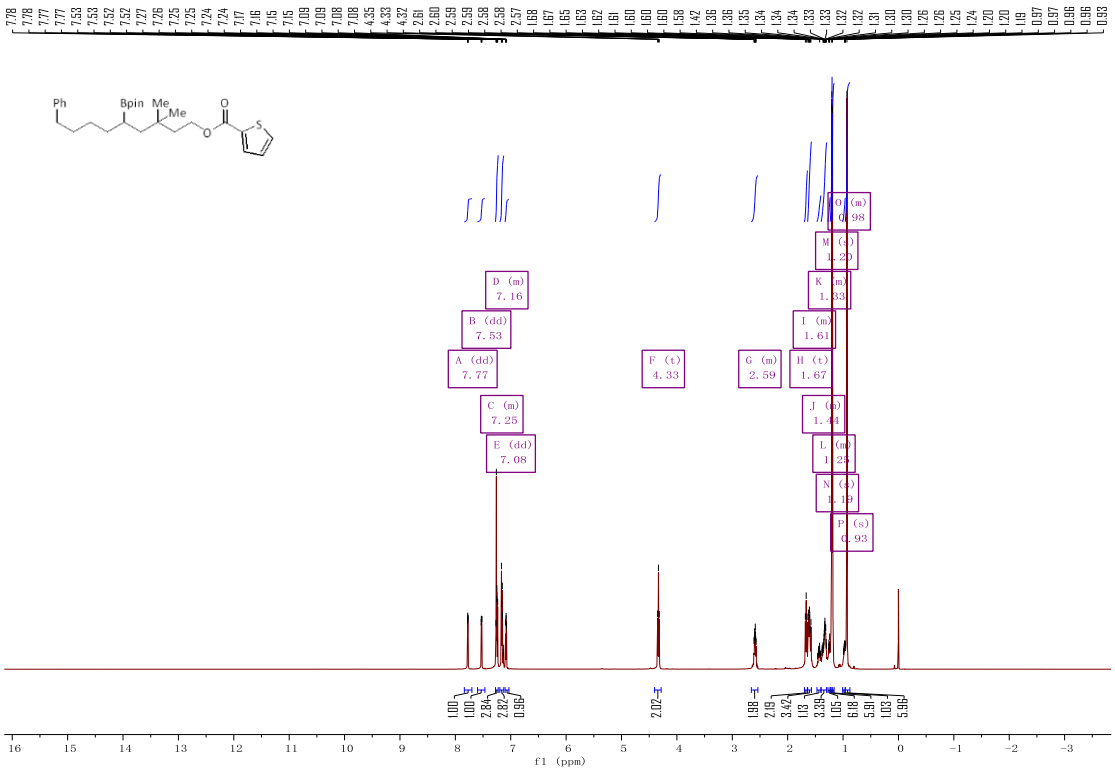
thiophene-2-carboxylate (**71**)

Rf (petroleum ether : acetone= 15 : 1) = 0.45

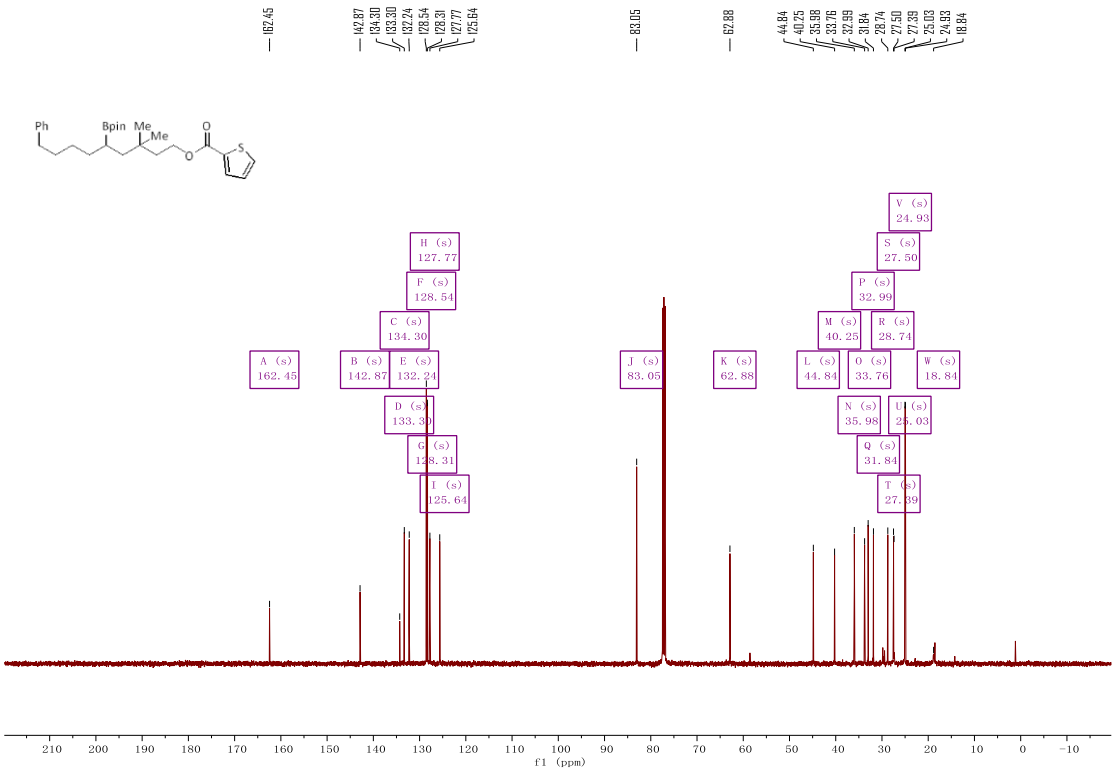
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.77 (dd, *J* = 3.7, 1.3 Hz, 1H), 7.53 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.29 – 7.22 (m, 2H), 7.19 – 7.12 (m, 3H), 7.08 (dd, *J* = 5.0, 3.7 Hz, 1H), 4.33 (t, *J* = 7.5 Hz, 2H), 2.72 – 2.49 (m, 2H), 1.67 (t, *J* = 7.5 Hz, 2H), 1.64 – 1.57 (m, 3H), 1.47 – 1.40 (m, 1H), 1.40 – 1.29 (m, 3H), 1.27 – 1.24 (m, 1H), 1.20 (s, 6H), 1.19 (s, 6H), 1.01 – 0.95 (m, 1H), 0.93 (s, 6H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 162.45, 142.87, 134.30, 133.30, 132.24, 128.54, 128.31, 127.77, 125.64, 83.05, 62.88, 44.84, 40.25, 35.98, 33.76, 32.99, 31.84, 28.74, 27.50, 27.39, 25.03, 24.93, 18.84.

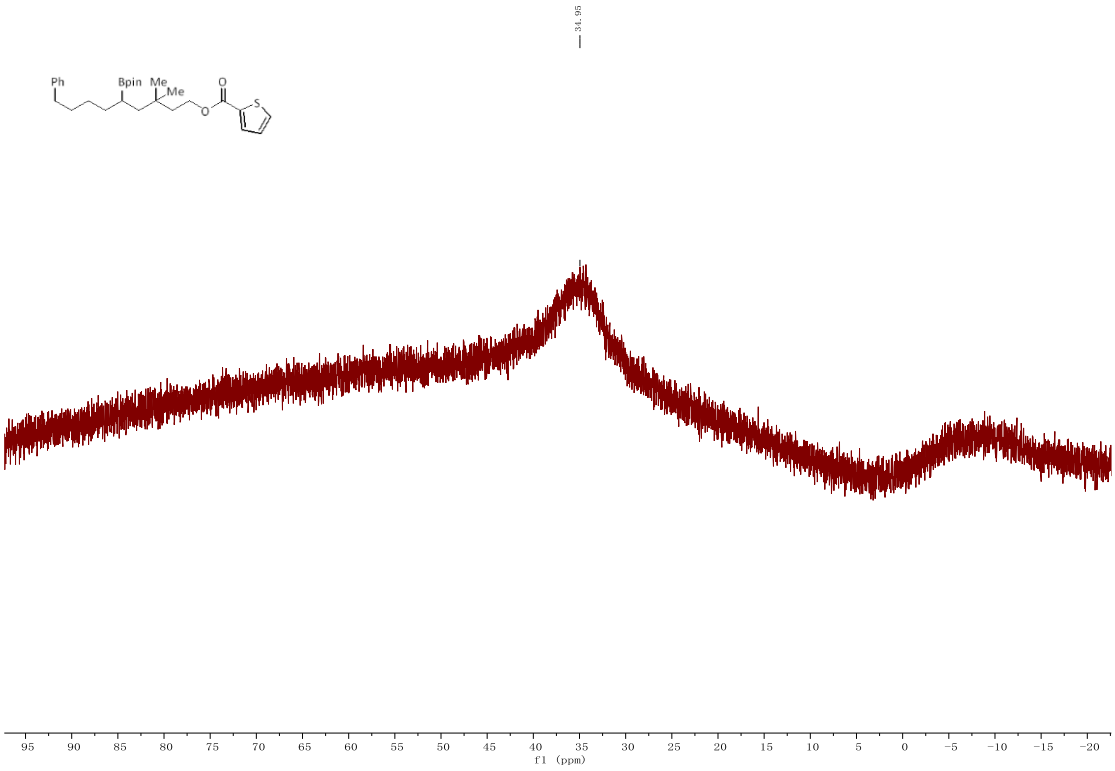
^{11}B NMR (128 MHz, Chloroform-*d*) δ 34.95.



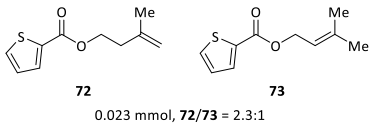
^{1}H NMR spectra for **71**



^{13}C NMR spectra for **71**



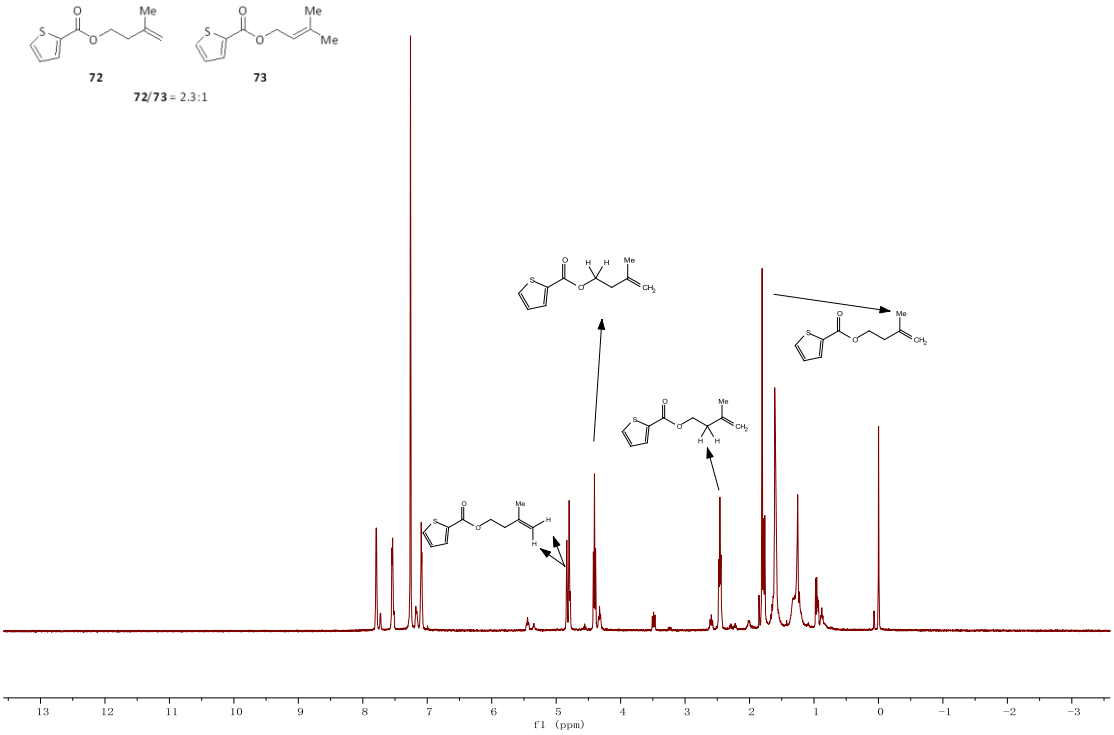
^{11}B NMR spectra for **71**



3-methylbut-3-en-1-yl thiophene-2-carboxylate (**72**)

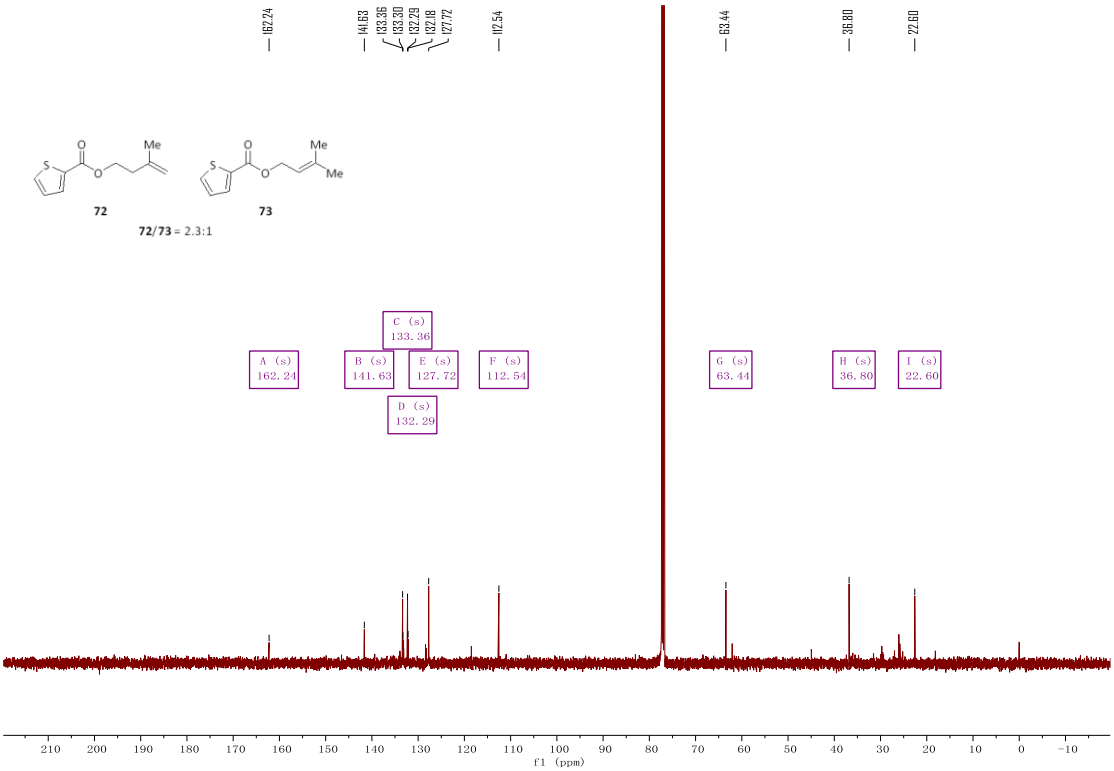
3-methylbut-2-en-1-yl thiophene-2-carboxylate (**73**)

Rf (petroleum ether : acetone= 15 : 1) = 0.60

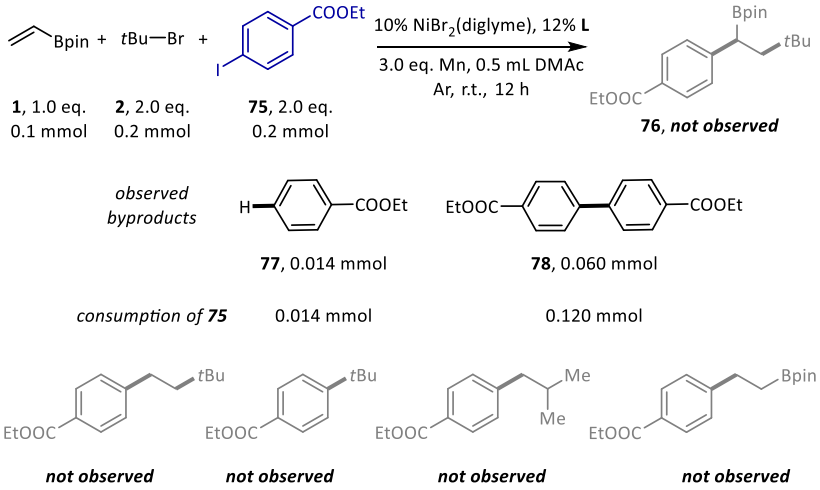


^{1}H NMR spectra for **72, 73**

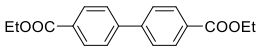
^{13}C NMR (126 MHz, Chloroform-*d*) δ 162.24, 141.63, 133.36, 132.29, 127.72, 112.54, 63.44, 36.80, 22.60.



^{13}C NMR spectra for **72, 73**



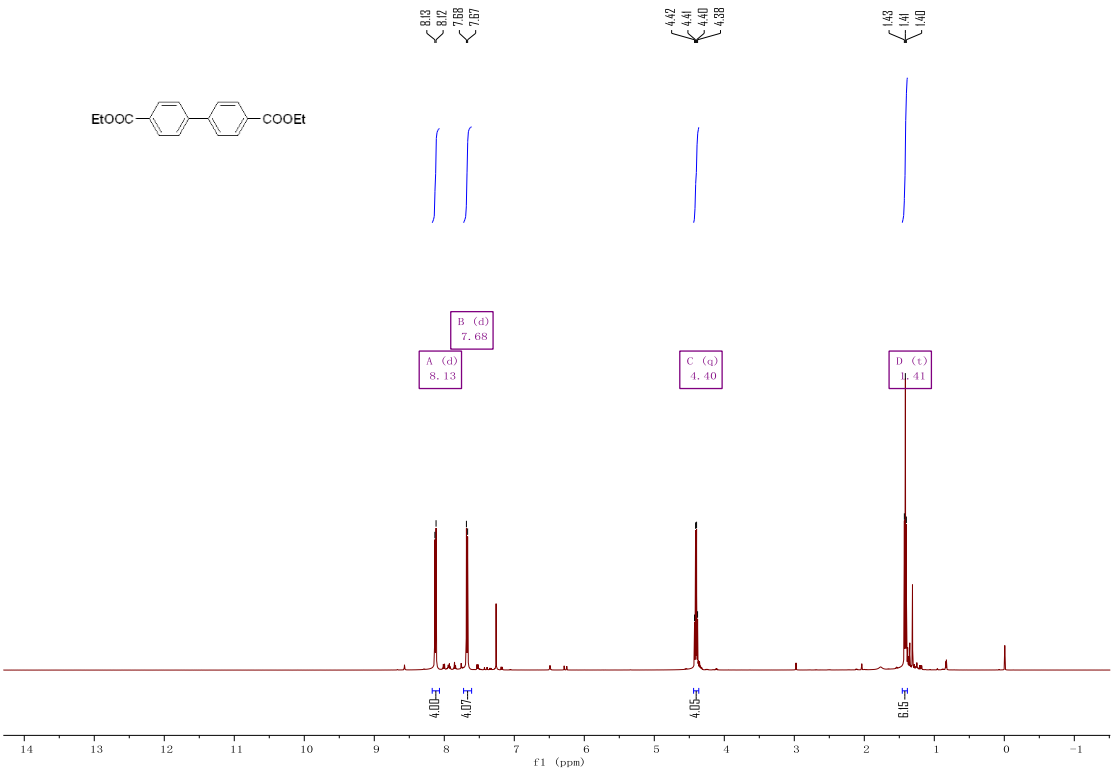
Following general procedure 1. Aryl iodides were converted to both protonation products and homo-coupling products.



diethyl [1,1'-biphenyl]-4,4'-dicarboxylate (**78**)

Rf (petroleum ether : acetone= 15 : 1) = 0.40

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.13 (d, *J* = 8.5 Hz, 4H), 7.68 (d, *J* = 8.5 Hz, 4H), 4.40 (q, *J* = 7.1 Hz, 4H), 1.41 (t, *J* = 7.1 Hz, 6H).



^{1}H NMR spectra for **78**

12. References

1. K. Miura, M. Tomita, Y. Yamada and A. Hosomi, *J. Org. Chem.*, 2007, **72**, 787.
2. X. X. Wang, L. Li, T. J. Gong, B. Xiao, X. Lu and Y. Fu, *Org. Lett.*, 2019, **21**, 4298.
3. W. Yu, L. Chen, J. Tao, T. Wang and J. Fu, *Chem. Commun.*, 2019, **55**, 5918.