Supporting Information

for

Base-Controlled Highly Selective Synthesis of Alkyl 1,2-Bis(boronates) or 1,1,2-Tris(boronates) from Terminal Alkynes

Guoliang Gao[a], Jianxiang Yan[a], Kai Yang[a], Fener Chen[b] and Qiuling Song[a, c]*

[a] Institute of Next Generation Matter Transformation, College of Chemical Engineering and College of Material Sciences at Huaqiao University, Xiamen, Fujian, 361021, P. R. China

[b] Department of Chemistry, Fudan University, Shanghai, 200433, P. R. China.

[c] Key Laboratory of Green Pesticide and Agricultural Bioengineering, Ministry of Education, Guizhou University, Guiyang, 550025, China

Email: qsong@hqu.edu.cn

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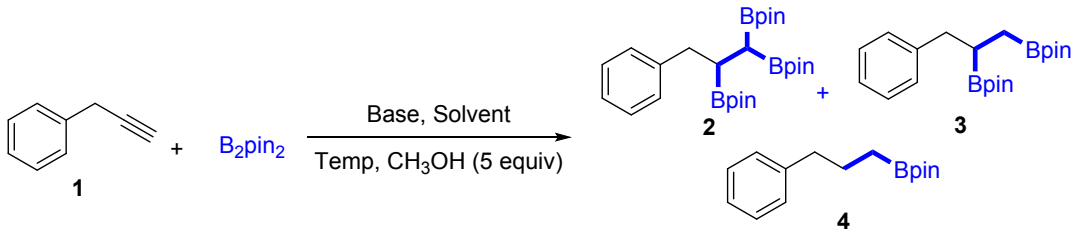
General Information

All experiments were conducted with a Schlenk tube. Flash column chromatography was performed over silica gel (200-300 mesh). ^{1}H NMR spectra were recorded on a Bruker AVIII-500M spectrometers, chemical shifts (in ppm) were referenced to $CDCl_3$ (δ = 7.26 ppm) and DMSO-d_6 (δ = 2.50 ppm) as internal standards. ^{13}C NMR spectra were obtained by using the same NMR spectrometers and were calibrated with $CDCl_3$ (δ = 77.0 ppm), DMSO-d_6 (δ = 39.6 ppm). Unless otherwise noted, materials obtained from commercial suppliers were used without further purification, and the most starting materials were purchased from Energy.

Condition Screenings

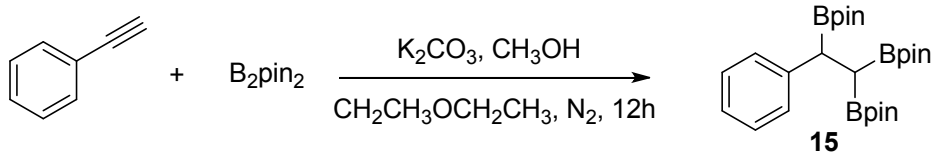
Table S1. Optimization of reaction conditions.[a]



Entry	Base	Solvent	Temperature (°C)	GC yield (%)		
				2	**3**	**4**
1	Cs_2CO_3	CH_3CN	60	10	48	trace
2	**Cs_2CO_3**	**CH_3CN**	**80**	**0**	**(77)[b]**	**<5**
3	Cs_2CO_3	CH_3CN	90	10	48	trace
4	Cs_2CO_3	CH_3CN	100	trace	46	12
5	CsF	CH_3CN	80	<5	50	<5
6	K_3PO_4	CH_3CN	80	<5	42	<5
7	Na_2CO_3	CH_3CN	80	0	55	<5
8	Li_2CO_3	CH_3CN	80	<5	63	trace
9	K_2CO_3	CH_3CN	80	38	44	<5
10[c]	K_2CO_3	Dioxane	80	44	32	<5
11[c]	K_2CO_3	THF	80	46	15	0
12[c]	K_2CO_3	$C_2H_5OC_2H_5$	80	60	<5	0
13[c]	K_2CO_3	MTBE	80	54	10	0
14[c]	K_2CO_3	$C_2H_5OC_2H_5$	70	68	trace	<5
15[c]	**K_2CO_3**	**$C_2H_5OC_2H_5$**	**50**	**(82)[b]**	**<5**	**0**
16[c]	K_2CO_3	$C_2H_5OC_2H_5$	40	67	trace	0
17[d]	**K_2CO_3**	**$C_2H_5OC_2H_5$**	**60**	**80 (72)[b]**	**<5**	**0**
18[e]	**Cs_2CO_3**	**CH_3CN**	**80**	**0**	**(82)[b]**	**<5**

[a] Conditions: 3-phenyl-1-propyne (**1**) (0.2 mmol), B_2pin_2 (3 equiv), base (4 equiv), solvent (2 mL), 12 h, N_2. [b] Isolated yields. [c] 1.5 equiv of K_2CO_3 and 4.5 equiv of B_2pin_2 were used. [d] K_2CO_3 (0.6 equiv), B_2pin_2 (2.5 equiv), CH_3OH, Et_2O, 60 °C, 12 h. [e] 1.5 equiv of Cs_2CO_3 and 2 equiv of B_2pin_2 were used.

Table S2. Condition optimization for the synthesis of 1,1,2-Tris(boronates) from arylacetylenes

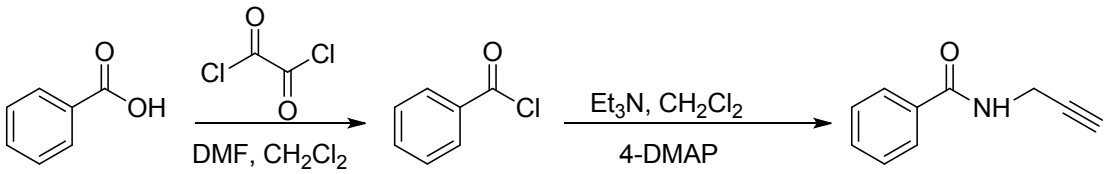


15

Entry	K_2CO_3 (equiv)	B_2pin_2 (equiv)	Temp (^oC)	Conversion (%)	Yield (%)[a]
1	1	3	50	100	92
2	0.5	3	50	100	93
3	0.2	3	50	>98	86
4	0.1	3	50	70	60
5	0.3	2	50	100	94 (90)
6	0.2	1.8	50	80	74
7	0.3	2	40	90	86
8	0.3	2	rt	60	50

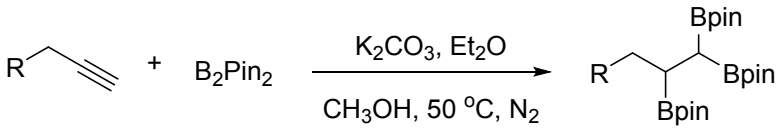
Conditions: [a] only by GC

General Procedures

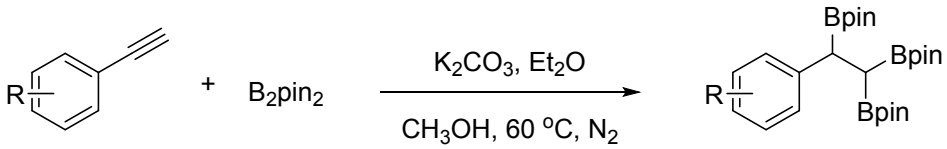


General procedure A: the synthesis of amido acetylene from acyl chloride and propargylic amine: To a solution of propargylic amine (10 mmol, 1.0 equiv.) in CH_2Cl_2, trimethylamine (1.4 mL, 10 mmol, 1.0 equiv.) and 4-dimethylaminopyridine (24.4 mg, 0.2 mmol, 0.02 equiv.) were added. The resulting mixture was cooled to 0 ^oC, and the acid chloride (10 mmol, 1.0 equiv.) was added. The mixture was stirred for 30 min at 0 ^oC and 3 h at room temperature. H_2O (15 mL) was added, and the aqueous layer was extracted with another (3*15 mL) of CH_2Cl_2. The combined organic extracts were washed with saturated $NaHCO_3$, H_2O and brine, dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by

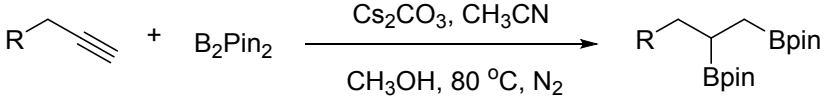
column chromatography on silica.[1]



General procedure B: the synthesis of alkyl 1,1,2-tris(boronates) from terminal alkyl alkynes and B_2pin_2 : In air, a 25 mL Schlenk tube was charged with B_2pin_2 (2.5 equiv) and K_2CO_3 (0.6 equiv). The flask was evacuated and filled with nitrogen for three cycles. Et_2O (3 mL), terminal alkyl alkynes (0.2 mmol) and CH_3OH (40 uL, 5 equiv) were added. The reaction was allowed to stir at 50 °C for 12 hours. Upon completion, the reaction mixture was diluted with ethyl acetate, filtered through a silica gel plug, rinsed with ethyl acetate, and concentrated in vacuo. The crude reaction mixture was purified on silica gel to afford the desired product.

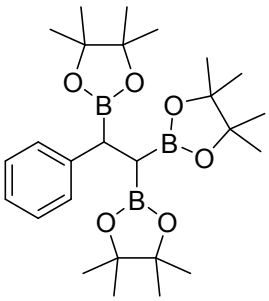


General procedure C: the synthesis of alkyl 1,1,2-tris(boronates) from arylacetylenes and B_2pin_2 : In air, a 25 mL Schlenk tube was charged with B_2pin_2 (2.0 equiv) and K_2CO_3 (0.3 equiv). The flask was evacuated and filled with nitrogen for three cycles. Et_2O (3 mL), terminal alkyl alkynes (0.2 mmol) and CH_3OH (40 uL, 5 equiv) were added. The reaction was allowed to stir at 60 °C for 12 hours. Upon completion, the reaction mixture was diluted with ethyl acetate, filtered through a silica gel plug, rinsed with ethyl acetate, and concentrated in vacuo. The crude reaction mixture was purified on silica gel to afford the desired product.

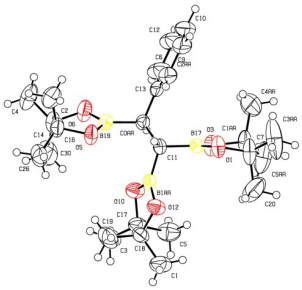


General procedure D: the synthesis of alkyl 1,2-bis(boronates) from terminal alkyl alkynes and B_2pin_2 : In air, a 25 mL schlenk tube was charged with B_2pin_2 (101 mg, 2 equiv) and Cs_2CO_3 (98 mg, 1.5 equiv). The flask was evacuated and filled with nitrogen for three cycles. Then CH_3CN (3 mL), terminal alkyl alkynes (0.2 mmol) and CH_3OH (40 uL, 5 equiv) were added subsequently. The reaction was allowed to stir at 80 ^oC for 12 hours. Upon completion, the reaction mixture was diluted with ethyl acetate, filtered through a silica gel plug, rinsed with ethyl acetate, and concentrated in vacuo. The crude reaction mixture was purified on silica gel to afford the desired product.

X-Ray crystallographic data of compound 15



15



CCDC: 1551784

Bond precision: C-C = 0.0060 A Wavelength=0.71073

Cell: a=10.7089(7) b=11.6927(9) c=13.5483(11)
alpha=114.506(8) beta=99.354(6) gamma=104.113(6)
Temperature: 291 K

	Calculated	Reported
Volume	1428.7(2)	1428.7(2)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C26 H43 B3 O6	C26 H43 B3 O6
Sum formula	C26 H43 B3 O6	C26 H43 B3 O6
Mr	484.03	484.03
Dx,g cm-3	1.125	1.125
Z	2	2
Mu (mm-1)	0.076	0.076
F000	524.0	524.3
F000'	524.25	
h,k,lmax	12,13,16	12,13,16
Nref	5032	5025
Tmin,Tmax		
Tmin'		

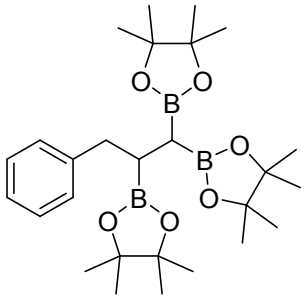
Correction method= Not given

Data completeness= 0.999 Theta(max)= 25.000

R(reflections)= 0.0702(3551) wR2(reflections)= 0.2191(5025)

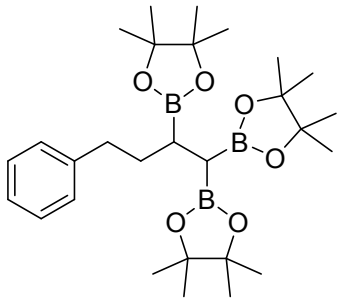
S = 1.046 Npar= 328

Characterization Data for Products



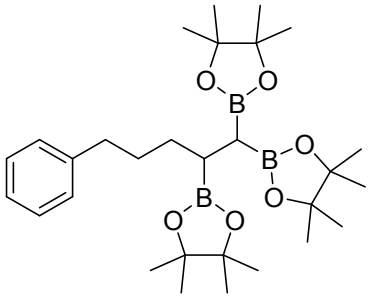
2

2,2',2''-(3-phenylpropane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)[3](CAS: 1638158-42-5). The reaction was performed following the general procedure B. Colorless oil, 82% yield (81.7 mg). ^{1}H NMR (500 MHz, CDCl3) δ 7.24 – 7.15 (m, 4H), 7.10 (t, J = 6.9 Hz, 1H), 2.79 (dd, J = 13.3, 6.9 Hz, 1H), 2.71 (dd, J = 13.3, 8.7 Hz, 1H), 1.68 (dd, J = 15.9, 8.9 Hz, 1H), 1.22 (s, 24H), 1.11 (d, J = 16.3 Hz, 12H), 0.85 (d, J = 9.3 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.6, 129.3, 127.8, 125.3, 82.8, 82.7, 39.1, 25.0, 24.9, 24.8, 24. ^{11}B NMR: δ = 36.4 (br).



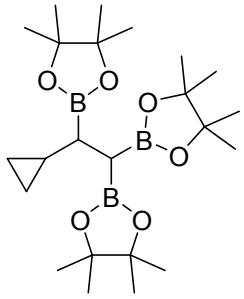
5

2,2',2''-(4-phenylbutane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)[3](CAS: 1638158-43-6). The reaction was performed following the general procedure B. White solid, 77% yield (78.8 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (t, *J* = 7.5 Hz, 2H), 7.16 (d, *J* = 6.9 Hz, 2H), 7.12 (t, *J* = 7.2 Hz, 1H), 2.70 – 2.62 (m, 1H), 2.56 – 2.47 (m, 1H), 1.81 – 1.67 (m, 2H), 1.45 (dd, *J* = 15.5, 7.9 Hz, 1H), 1.24 (d, *J* = 2.8 Hz, 12H), 1.21 (d, *J* = 3.6 Hz, 24H), 0.95 (d, *J* = 10.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.7, 128.4, 128.0, 125.2, 83.4, 82.7, 82.6, 35.6, 35.2, 25.1, 24.5. ^{11}B NMR: δ = 36.2 (br).



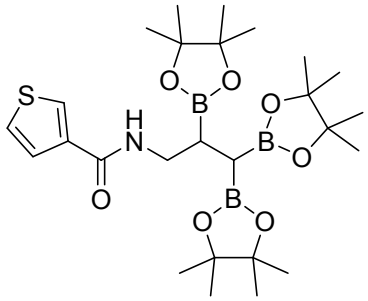
6

2,2',2''-(5-phenylpentane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane). The reaction was performed following the general procedure B. Colorless oil, 66% yield (69.4 mg). ^{1}H NMR (500 MHz, CDCl3) δ 7.23 (t, J = 7.5 Hz, 2H), 7.16 (s, 1H), 7.15 – 7.10 (m, 2H), 2.59 – 2.54 (m, 2H), 1.69 (dd, J = 9.3, 7.2 Hz, 2H), 1.62 – 1.53 (m, 2H), 1.21 (s, 24H), 1.18 (s, 1H), 1.16 (s, 12H), 1.05 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.3, 128.3, 128.1, 125.3, 82.8, 82.6, 36.9, 32.9, 29.5, 24.9, 24.7. ^{11}B NMR: δ = 36.3 (br). HRMS-(DART) for: $^{12}C_{29}{}^{1}H_{49}{}^{10}B_{3}{}^{16}O_{6}[M+H]^{+}$: calculated: 524.3990, found: 524.3990.



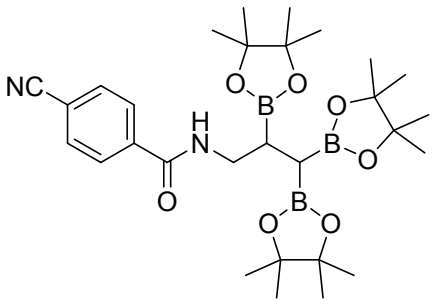
7

2,2',2''-(2-cyclopropylethane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)[3](CAS: 1638158-32-3). The reaction was performed following the general procedure B. Colorless oil, 50% yield (44.8 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.25 (s, 24H), 1.21 (t, *J* = 4.0 Hz, 12H), 1.19 (s, 4H), 0.89 (dd, *J* = 34.6, 8.3 Hz, 1H), 0.66 (d, *J* = 5.6 Hz, 1H), 0.34 (d, *J* = 6.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 83.46, 82.9, 82.5, 24.9, 14.9, 6.2, 4.2. ^{11}B NMR: δ = 36.4 (br).



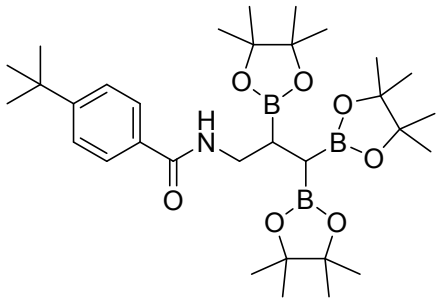
8

N-(2,3,3-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)thiophene-3-carboxamide. The reaction was performed following the general procedure B. Colorless oil, 70% yield (76.6 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (ddd, *J* = 6.1, 3.0, 1.3 Hz, 1H), 7.35 (dd, *J* = 5.1, 1.3 Hz, 1H), 7.30 – 7.27 (m, 1H), 6.80 (s, 1H), 3.68 – 3.56 (m, 1H), 3.32 (ddd, *J* = 12.9, 8.1, 4.5 Hz, 1H), 1.50 – 1.39 (m, 1H), 1.24 (d, *J* = 4.6 Hz, 12H), 1.22 (d, *J* = 6.5 Hz, 24H), 0.93 (d, *J* = 2.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.7, 138.2, 127.7, 126.1, 125.9, 83.4, 83.2, 42.7, 24.8, 24.5. ^{11}B NMR: δ = 36.5 (br). HRMS-(DART) for: $^{12}C_{26}{}^{1}H_{44}{}^{10}B_3{}^{14}N{}^{16}O_7{}^{32}S[M+H]^+$: calculated: 545.3299, found: 545.3298.



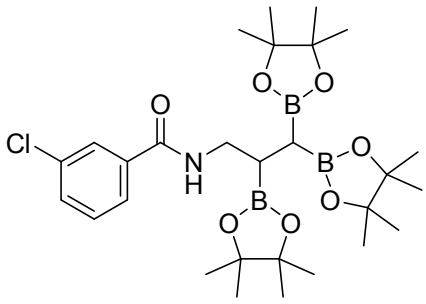
9

4-cyano-N-(2,3,3-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)benzamide. The reaction was performed following the general procedure B. Colorless oil, 56% yield (63.4 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.5 Hz, 2H), 7.70 (d, *J* = 8.5 Hz, 2H), 7.36 (s, 1H), 3.75 (dt, *J* = 13.1, 6.5 Hz, 1H), 3.37 – 3.32 (m, 1H), 1.62 (dd, *J* = 14.2, 6.9 Hz, 1H), 1.23 – 1.21 (m, 24H), 1.20 (d, *J* = 1.5 Hz, 12H), 0.90 (d, *J* = 6.9 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.0, 139.5, 132.2, 127.6, 118.2, 114.5, 83.5, 83.3, 42.8, 24.8, 24.6. ^{11}B NMR: δ = 36.7 (br). HRMS-(DART) for: $^{12}C_{29}{}^{1}H_{45}{}^{10}B_3{}^{14}N_2{}^{16}O_7[M+H]^+$: calculated: 564.3688, found: 564.3688.



10

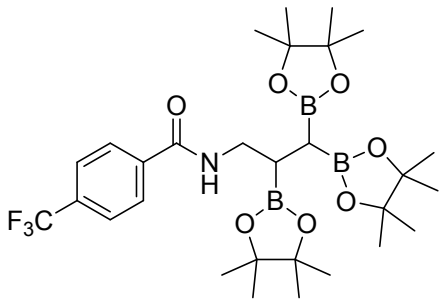
4-(tert-butyl)-N-(2,3,3-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)benzamide. The reaction was performed following the general procedure B. Colorless oil, 67% yield (80.0 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.5 Hz, 2H), 7.41 (t, *J* = 8.1 Hz, 2H), 7.13 (s, 1H), 3.73 (dt, *J* = 12.8, 6.3 Hz, 1H), 3.36 – 3.29 (m, 1H), 1.62 (dd, *J* = 14.3, 7.5 Hz, 1H), 1.32 (s, 9H), 1.26 (s, 12H), 1.21 (d, *J* = 5.9 Hz, 24H), 0.90 – 0.87 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.9, 154.4, 132.3, 126.6, 125.3, 83.4, 83.2, 42.9, 34.8, 31.2, 25.26, 24.51. ^{11}B NMR: δ = 36.4 (br). HRMS-(DART) for: $^{12}C_{32}{}^{1}H_{54}{}^{10}B_3{}^{14}N{}^{16}O_7[M+H]^+$: calculated: 595.4361, found: 595.4361.



11

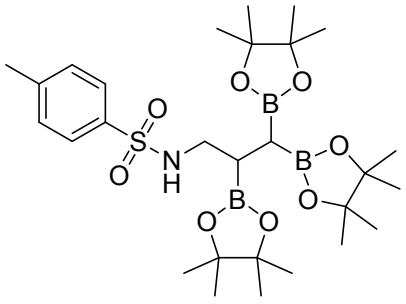
3-chloro-N-(2,3,3-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)benzamide. The reaction was performed following the general procedure B. Colorless oil, 60% yield (69.0 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 1.7 Hz, 1H), 7.68 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.35 (d, *J* = 7.2 Hz, 1H), 7.06 (s, 1H), 3.76 – 3.64 (m, 1H), 3.36 – 3.30 (m, 1H), 1.25 (d, *J* = 9.7 Hz, 12H), 1.22 (t, *J* = 5.1 Hz, 24H), 0.96 (t, *J* = 7.4 Hz, 1H), 0.91 – 0.87 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.6, 137.3, 134.5, 131.0, 129.7, 127.1, 125.2, 83.5, 83.2, 43.1, 24.9,

24.5. ^{11}B NMR: δ = 36.5 (br). HRMS-(DART) for: $^{12}C_{28}{}^{1}H_{45}{}^{10}B_3Cl^{14}N^{16}O_7[M+H]^+$: calculated: 573.3345, found: 573.3345.



12

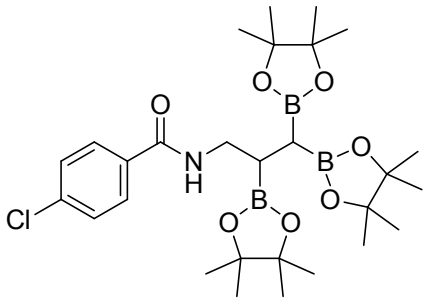
4-(trifluoromethyl)-N-(2,3,3-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)benzamide. The reaction was performed following the general procedure B. Colorless oil, 55% yield (67.0 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.2 Hz, 2H), 7.68 (d, *J* = 8.1 Hz, 2H), 7.09 (s, 1H), 3.66 (dt, *J* = 13.1, 6.5 Hz, 1H), 3.40 – 3.34 (m, 1H), 1.51 – 1.47 (m, 1H), 1.25 (d, *J* = 1.8 Hz, 12H), 1.22 (t, *J* = 4.8 Hz, 24H), 0.98 – 0.95 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.7, 138.6, 127.4, 125.4, 123.2, 83.5, 83.3, 43.2, 24.8, 24.2. ^{11}B NMR: δ = 36.7 (br). HRMS-(DART) for: $^{12}C_{29}{}^{1}H_{45}{}^{10}B_3{}^{18}F_3{}^{14}N^{16}O_7[M+H]^+$: calculated: 607.3609, found: 607.3609.



13

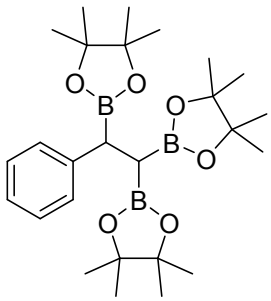
4-methyl-N-(2,3,3-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)benzenesulfonamide. The reaction was performed following the general procedure B. Colorless oil, 44% yield (52.0 mg). ^{1}H NMR (500 MHz, CDCl3) δ 7.74 (d, J = 8.2 Hz, 2H), 7.27 (s, 1H), 7.25 (s, 1H), 5.50 (s, 1H), 3.06 (dt, J = 11.5, 6.8 Hz, 1H), 2.92 (ddd, J = 11.6, 7.4, 4.5 Hz, 1H), 2.40 (s, 3H), 1.48 – 1.42 (m, 1H), 1.19 (s,

24H), 1.17 (d, J = 4.8 Hz, 12H), 0.75 (d, J = 6.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.6, 137.3, 129.4, 127.2, 83.5, 77.3, 76.8, 46.1, 24.8, 24.6. ^{11}B NMR: δ = 36.5 (br). HRMS-(DART) for: $^{12}C_{28}{}^{1}H_{48}{}^{10}B_3{}^{14}N^{16}O_8{}^{32}S[M+H]^+$: calculated: 589.3562, found: 589.3563.



14

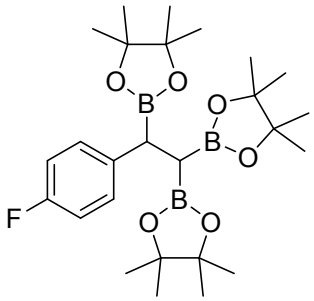
4-chloro-N-(2,3,3-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)benzamide. The reaction was performed following the general procedure B. Colorless oil, 50% yield (57.5 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 – 7.71 (m, 2H), 7.37 (d, *J* = 8.6 Hz, 2H), 7.21 (s, 1H), 3.74 (dt, *J* = 13.0, 6.4 Hz, 1H), 3.35 – 3.30 (m, 1H), 1.24 (d, *J* = 1.7 Hz, 12H), 1.22 (d, *J* = 2.3 Hz, 24H), 0.95 (dd, *J* = 10.1, 7.1 Hz, 1H), 0.91 – 0.87 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.9, 137.1, 133.6, 128.6, 128.3, 83.5, 83.3, 43.1, 25.1, 24.4. ^{11}B NMR: δ = 36.8 (br). HRMS-(DART) for: $^{12}C_{28}{}^{1}H_{45}{}^{10}B_3Cl^{14}N^{16}O_7[M+H]^+$: calculated: 573.3345, found: 573.3346.



15

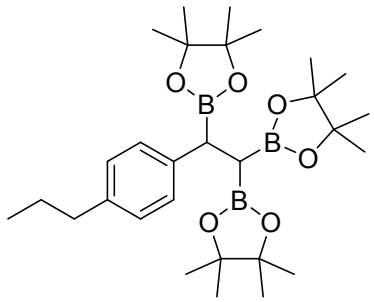
2,2',2''-(2-phenylethane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)[3](CAS: 1638158-49-2). The reaction was performed following the general procedure C. Colorless oil, 90% yield (87.2 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (dd, *J* = 8.1, 1.2 Hz, 2H), 7.15 (t, *J* = 7.7 Hz, 2H), 7.02 (t, *J* = 7.2 Hz, 1H), 2.66

(d, J = 12.8 Hz, 1H), 1.45 – 1.41 (m, 1H), 1.23 (d, J = 6.4 Hz, 12H), 1.13 (d, J = 10.6 Hz, 12H), 0.93 (d, J = 9.3 Hz, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.2, 128.5, 127.8, 124.6, 83.0, 82.61, 24.9, 24.8, 24.6, 24.5. ^{11}B NMR: δ = 37.1 (br).



16

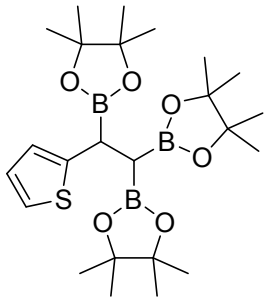
2,2',2''-(2-(4-fluorophenyl)ethane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane). The reaction was performed following the general procedure C. Colorless oil, 92% yield (92.4 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (dd, J = 8.7, 5.6 Hz, 2H), 6.86 (t, J = 8.8 Hz, 2H), 2.64 (d, J = 12.8 Hz, 1H), 1.42 – 1.37 (m, 1H), 1.23 (d, J = 6.0 Hz, 12H), 1.13 (d, J = 9.1 Hz, 12H), 0.95 (d, J = 12.4 Hz, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.7, 159.8, 140.9, 129.7, 114.5, 114.4, 83.1, 82.7, 24.8, 24.6, 24.4, 24.2. ^{11}B NMR: δ = 37.5 (br). HRMS-(DART) for: $^{12}C_{26}{}^{1}H_{42}{}^{10}B_3{}^{18}F^{16}O_6[M+H]^+$: calculated: 500.3426, found: 500.3425.



17

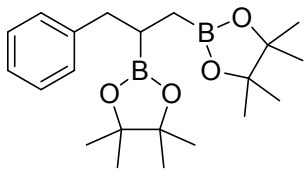
2,2',2''-(2-(4-propylphenyl)ethane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane). The reaction was performed following the general procedure C. Colorless oil, 93% yield (97.9 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 (d, J = 8.0 Hz, 2H), 6.96 (d, J = 8.0 Hz, 2H), 2.61 (d, J = 12.8 Hz, 1H), 2.47 (t, J = 7.5 Hz, 2H), 1.54

(dd, *J* = 15.4, 7.0 Hz, 2H), 1.41 (d, *J* = 12.8 Hz, 1H), 1.23 (d, *J* = 7.0 Hz, 12H), 1.14 (d, *J* = 10.7 Hz, 12H), 0.92 (s, 12H), 0.86 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.3, 138.7, 128.3, 127.9, 82.9, 82.6, 37.6, 25.0, 24.8, 24.3, 13.7. ^{11}B NMR: δ = 37.2 (br). HRMS-(DART) for: $^{12}C_{29}{}^{1}H_{49}{}^{10}B_3{}^{16}O_6[M+H]^+$: calculated: 524.3990, found: 524.3989.



18

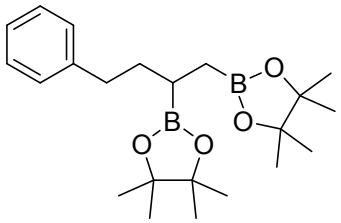
2,2',2''-(2-(thiophen-2-yl)ethane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane). The reaction was performed following the general procedure C. Colorless oil, 89% yield (87.3 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.97 (dd, *J* = 5.1, 1.1 Hz, 1H), 6.81 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.78 (d, *J* = 3.4 Hz, 1H), 3.00 (d, *J* = 12.3 Hz, 1H), 1.28 (s, 1H), 1.22 (d, *J* = 3.8 Hz, 12H), 1.17 (d, *J* = 5.6 Hz, 12H), 1.03 (d, *J* = 8.3 Hz, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 126.2, 123.5, 121.9, 83.3, 83.1, 82.8, 31.4, 29.7, 24.9, 24.3. ^{11}B NMR: δ = 37.4 (br). HRMS-(DART) for: $^{12}C_{24}{}^{1}H_{41}{}^{10}B_3{}^{16}O_6{}^{32}S[M+H]^+$: calculated: 488.3085, found: 488.3085.



19

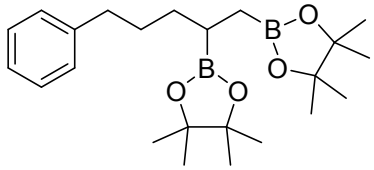
2,2'-(3-phenylpropane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)[2] (CAS: 1172611-59-4). The reaction was performed following the general procedure D. Colorless oil, 82% yield (61.1 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 – 7.21 (m, 2H), 7.19 (t, *J* = 4.1 Hz, 2H), 7.13 (t, *J* = 6.9 Hz, 1H), 2.79 (dd, *J* = 13.4, 7.4 Hz, 1H), 2.60 (dd, *J* = 13.4, 8.4 Hz, 1H), 1.45 (dt, *J* = 12.7, 6.4 Hz, 1H), 1.22 (s, 13H), 1.17 (d,

J = 11.0 Hz, 12H), 0.82 (d, *J* = 7.7 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.3, 129.1, 127.9, 125.4, 82.9, 39.5, 24.9, 24.8, 24.6. ^{11}B NMR: δ = 30.4 (br).



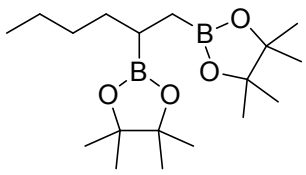
20

2,2'-(4-phenylbutane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)[5] (CAS:1888337-29-8). The reaction was performed following the general procedure D. Colorless oil, 78% yield (60.3 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (t, *J* = 7.5 Hz, 2H), 7.19 (d, *J* = 7.0 Hz, 2H), 7.15 (t, *J* = 7.3 Hz, 1H), 2.63 (t, *J* = 8.3 Hz, 2H), 1.84 – 1.76 (m, 1H), 1.69 – 1.61 (m, 1H), 1.25 (d, *J* = 9.3 Hz, 24H), 0.97 (dd, *J* = 15.8, 9.7 Hz, 1H), 0.90 (dd, *J* = 9.5, 6.4 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.3, 128.4, 128.1, 125.4, 82.9, 35.9, 35.3, 29.7, 24.8, 24.6. ^{11}B NMR: δ = 30.3 (br).



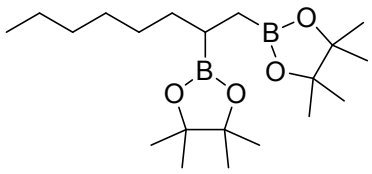
21

2,2'-(5-phenylpentane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane).[5] The reaction was performed following the general procedure D. Colorless oil, 81% yield (64.8 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, *J* = 7.4 Hz, 2H), 7.17 (s, 1H), 7.17 – 7.12 (m, 2H), 2.61 – 2.57 (m, 2H), 1.63 (d, *J* = 5.1 Hz, 2H), 1.40 – 1.28 (m, 2H), 1.22 (d, *J* = 8.5 Hz, 24H), 0.89 – 0.84 (m, 1H), 0.80 (dd, *J* = 15.8, 5.9 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.0, 128.4, 128.1, 125.4, 82.8, 83.2, 36.1 , 33.5, 30.7, 24.8, 24.6. ^{11}B NMR: δ = 30.6 (br). HRMS-(DART) for: $^{12}C_{23}{}^{1}H_{38}{}^{10}B_2{}^{16}O_4[M+H]^+$: calculated: 399.2056, found: 399.2057.



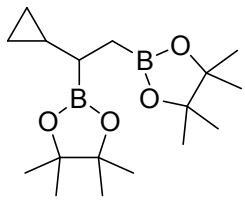
22

2,2'-(hexane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)[6](CAS: 1198172-03-0). The reaction was performed following the general procedure D. Colorless oil, 76% yield (51.4 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.35 – 1.28 (m, 2H), 1.26 (dd, *J* = 6.7, 3.3 Hz, 4H), 1.22 (d, *J* = 3.2 Hz, 24H), 0.87 – 0.84 (m, 3H), 0.83 (d, *J* = 3.9 Hz, 1H), 0.78 (dd, *J* = 15.7, 5.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 82.7, 82.5, 82.2, 33.5, 31.1, 24.8, 24.4, 22.9, 14.1. ^{11}B NMR: δ = 30.6 (br).



23

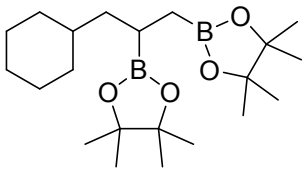
2,2'-(octane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)[7](CAS: 1240790-15-1). The reaction was performed following the general procedure D. Colorless oil, 68% yield (49.8 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.35 – 1.28 (m, 2H), 1.26 (dd, *J* = 6.7, 3.3 Hz, 4H), 1.22 (d, *J* = 3.2 Hz, **2**4H), 0.87 – 0.84 (m, 3H), 0.83 (d, *J* = 3.9 Hz, 1H), 0.78 (dd, *J* = 15.7, 5.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 82.7, 82.4, 33.8, 31.8, 29.5, 28.8, 24.8, 24.4, 22.6, 14.1. ^{11}B NMR: δ = 30.2 (br).



24

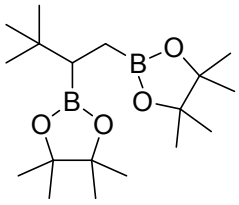
2,2'-(1-cyclopropylethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane).[8] The reaction was performed following the general procedure D. Colorless oil, 77% yield (49.6 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.23 (d, *J* = 11.1 Hz, 24H), 0.93 (d, *J* = 7.9 Hz, 2H), 0.69 (td, *J* = 8.1, 3.9 Hz, 1H), 0.45 (dd, *J* = 17.3,

8.0 Hz, 1H), 0.37 (dt, *J* = 8.0, 6.6 Hz, 2H), 0.14 – 0.08 (m, 1H), 0.06 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 82.8, 82.4, 25.1, 24.6, 14.8, 4.7, 4.2. ^{11}B NMR: δ = 29.5 (br). HRMS-(DART) for: $^{12}C_{17}{}^{1}H_{32}{}^{10}B_2{}^{16}O_4[M+H]^+$: calculated: 321.3258, found: 321.3257.



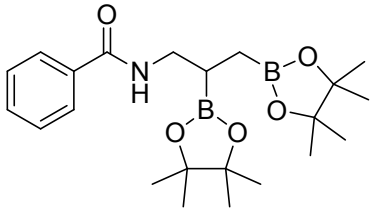
25

2,2'-(3-cyclohexylpropane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane). The reaction was performed following the general procedure D. Colorless oil, 78% yield (59.0 mg). ^1H NMR (500 MHz, $CDCl_3$) δ 1.69 – 1.63 (m, 5H), 1.32 (s, 2H), 1.26 (d, *J* = 11.5 Hz, 4H), 1.22 (d, *J* = 3.6 Hz, 24H), 1.15 – 1.08 (m, 2H), 0.79 (t, *J* = 7.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 82.7, 82.4, 41.4, 36.4, 33.6, 33.3, 26.8, 26.5, 24.8. ^{11}B NMR: δ = 30.0 (br). HRMS-(DART) for: $^{12}C_{21}{}^{1}H_{40}{}^{10}B_2{}^{16}O_4[M+H]^+$: calculated: 377.3258, found: 377.3257.



26

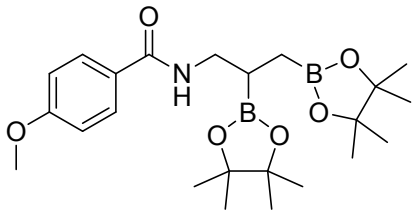
2,2'-(3,3-dimethylbutane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)[9](CAS: 1391742-85-0). The reaction was performed following the general procedure D. Colorless oil, 69% yield (46.7 mg). ^1H NMR (500 MHz, $CDCl_3$) δ 1.23 (s, 24H), 1.20 – 1.17 (m, 9H), 1.10 – 1.04 (m, 1H), 0.99 (s, 1H), 0.88 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 83.5, 82.8, 32.3, 29.1, 25.3, 24.9, 24.6. ^{11}B NMR: δ = 29.4 (br).



27

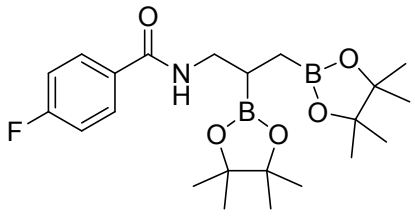
N-(2,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)benzamide.

The reaction was performed following the general procedure D. Colorless oil, 80% yield (66.4 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.2 Hz, 2H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 5.34 (s, 1H), 4.04 – 4.01 (m, 2H), 3.92 – 3.86 (m, 1H), 1.21 (d, *J* = 6.1 Hz, 24H), 1.13 – 1.05 (m, 1H), 0.87 (t, *J* = 6.9 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.0, 135.2, 130.9, 128.3, 126.8, 83.43 , 83.2, 43.1, 24.8. 24.7. ^{11}B NMR: δ = 33.3 (br). HRMS-(DART) for: $^{12}C_{22}{}^{1}H_{35}{}^{10}B_2{}^{14}N^{16}O_5[M+H]^+$: calculated: 414.2847, found: 414.2847.



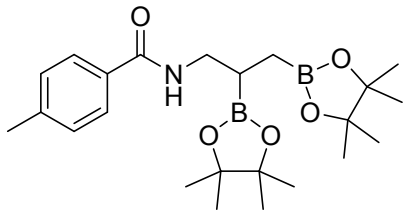
28

N-(2,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)-4-methoxybenzamide. The reaction was performed following the general procedure D. Colorless oil, 89% yield (79.3 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.9 Hz, 2H), 6.90 (s, 1H), 6.88 (s, 2H), 3.83 (s, 3H), 3.62 (dt, *J* = 13.0, 6.5 Hz, 1H), 3.41 – 3.23 (m, 1H), 1.52 – 1.41 (m, 1H), 1.24 – 1.21 (m, 24H), 0.94 (qd, *J* = 16.3, 7.2 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.6, 161.8, 128.6, 127.5, 113.5, 83.4, 83.2, 55.3, 43.0 , 24.8. ^{11}B NMR: δ = 33.4 (br). HRMS-(DART) for: $^{12}C_{23}{}^{1}H_{37}{}^{10}B_2{}^{14}N^{16}O_6[M+H]^+$: calculated: 444.2952, found: 444.2953.



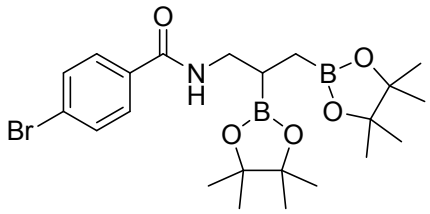
29

N-(2,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)-4-fluorobenzamide. The reaction was performed following the general procedure D. Light yellow oil, 81% yield (70.2 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 8.8, 5.3 Hz, 2H), 7.07 (t, *J* = 8.6 Hz, 2H), 5.43 (s, 1H), 3.61 (dt, *J* = 13.0, 6.5 Hz, 1H), 3.41 – 3.21 (m, 1H), 1.23 – 1.20 (m, 24H), 0.94 (qd, *J* = 16.3, 7.1 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.0, 129.1, 115.4, 115.2, 83.5, 83.3, 82.9, 75.0, 43.1, 24.8, 24.5. ^{11}B NMR: δ = 33.5 (br). HRMS-(DART) for: $^{12}C_{22}{}^{1}H_{34}{}^{10}B_2{}^{18}F{}^{14}N{}^{16}O_5[M+H]^+$: calculated: 432.2753, found: 432.2573.



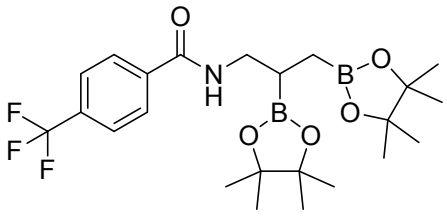
30

N-(2,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)-4-methylbenzamide. The reaction was performed following the general procedure D. Colorless oil, 70% yield (60.1 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.92 (s, 1H), 3.63 (dt, *J* = 13.0, 6.5 Hz, 1H), 3.36 (ddd, *J* = 12.8, 8.0, 4.4 Hz, 1H), 2.38 (s, 3H), 1.23 (dd, *J* = 10.7, 3.0 Hz, 24H), 0.99 – 0.90 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.9, 141.3, 129.0, 126.8, 83.4, 83.2, 43.0, 24.8, 21.4. ^{11}B NMR: δ = 33.7 (br). HRMS-(DART) for: $^{12}C_{23}{}^{1}H_{37}{}^{10}B_2{}^{14}N{}^{16}O_5[M+H]^+$: calculated: 428.3003, found: 428.3003.



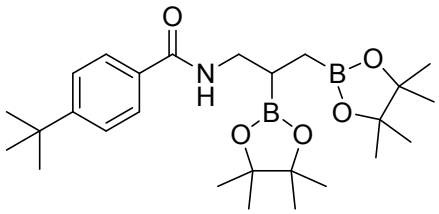
31

N-(2,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)-4-bromobenzamide. The reaction was performed following the general procedure D. Light yellow oil, 77% yield (76.0 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 – 7.64 (m, 2H), 7.57 – 7.53 (m, 2H), 6.98 (s, 1H), 3.63 (dt, *J* = 13.1, 6.5 Hz, 1H), 3.39 – 3.31 (m, 1H), 1.50 – 1.43 (m, 1H), 1.26 – 1.19 (m, 24H), 0.95 (qd, *J* = 16.3, 7.1 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.9, 134.1, 131.6, 128.5, 125.6, 83.5, 83.3, 43.2, 24.8. ^{11}B NMR: δ = 33.4 (br). HRMS-(DART) for: $^{12}C_{22}{}^{1}H_{34}{}^{10}B_2Br^{14}N^{16}O_5[M+H]^+$: calculated: 492.1952, found: 492.1953.



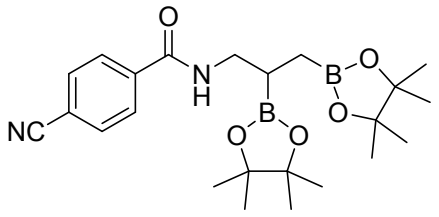
32

N-(2,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)-4-(trifluoromethyl)benzamide. The reaction was performed following the general procedure D. Light yellow oil, 77% yield (74.4 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.1 Hz, 2H), 7.66 (d, *J* = 8.2 Hz, 2H), 7.11 (s, 1H), 3.65 (dt, *J* = 13.1, 6.5 Hz, 1H), 3.39 – 3.33 (m, 1H), 1.47 (dd, *J* = 14.1, 7.2 Hz, 1H), 1.22 (dd, *J* = 14.9, 3.2 Hz, 24H), 0.99 – 0.90 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.7, 138.4, 132.6, 127.3, 125.38 (q, *J* = 3.7 Hz), 83.5, 83.3, 43.2, 24.8. ^{11}B NMR: δ = 33.4 (br). HRMS-(DART) for: $^{12}C_{23}{}^{1}H_{34}{}^{10}B_2{}^{18}F_3{}^{14}N^{16}O_5[M+H]^+$: calculated: 482.2721, found: 482.2720.



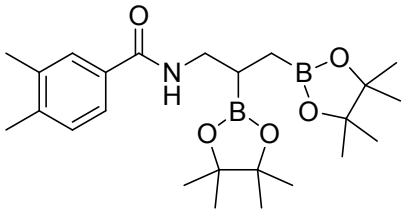
33

N-(2,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)-4-(tert-butyl)benzamide. The reaction was performed following the general procedure D. Colorless oil, 88% yield (82.6 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.2 Hz, 2H), 6.93 (s, 1H), 3.62 (dt, *J* = 13.0, 6.5 Hz, 1H), 3.35 (ddd, *J* = 12.8, 8.0, 4.4 Hz, 1H), 2.93 (dd, *J* = 13.8, 6.9 Hz, 1H), 1.45 (t, *J* = 6.7 Hz, 1H), 1.26 – 1.22 (m, 24H), 1.21 (d, *J* = 4.5 Hz, 9H), 0.93 (qd, *J* = 16.3, 7.1 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.9, 152.1, 132.7, 126.9, 126.4, 83.4, 83.2, 42.9, 34.0, 24.8, 24.5, 23.8. ^{11}B NMR: δ = 33.5 (br). HRMS-(DART) for: $^{12}C_{26}{}^{1}H_{43}{}^{10}B_2{}^{14}N{}^{16}O_5[M+H]^+$: calculated: 469.3316, found: 469.3316.



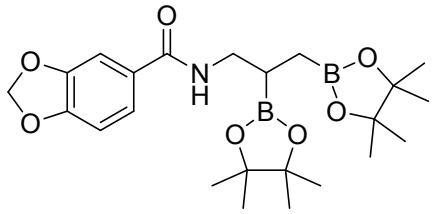
34

N-(2,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)-4-cyanobenzamide. The reaction was performed following the general procedure D. Light yellow oil, 90% yield (79.3 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.5 Hz, 2H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.12 (s, 1H), 3.64 (dt, *J* = 13.1, 6.5 Hz, 1H), 3.40 – 3.33 (m, 1H), 1.23 (dd, *J* = 12.6, 2.9 Hz, 24H), 1.00 – 0.90 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.1, 139.1, 132.3, 127.5, 118.1, 114.6, 83.6, 83.3, 43.3, 24.8. ^{11}B NMR: δ = 33.5 (br). HRMS-(DART) for: $^{12}C_{23}{}^{1}H_{34}{}^{10}B_2{}^{14}N_2{}^{16}O_5[M+H]^+$: calculated: 439.2799, found: 439.2804.



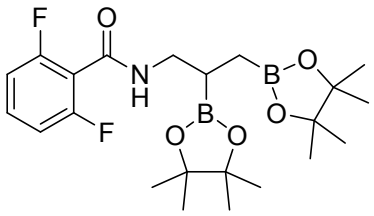
35

N-(2,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)-3,4-dimethylbenzamide. The reaction was performed following the general procedure D. Colorless oil, 80% yield (70.9 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 1.4 Hz, 1H), 7.49 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.15 (d, *J* = 7.8 Hz, 1H), 6.92 (s, 1H), 3.63 (dt, *J* = 13.0, 6.5 Hz, 1H), 3.34 (ddd, *J* = 12.9, 8.2, 4.4 Hz, 1H), 2.28 (s, 6H), 1.50 – 1.42 (m, 1H), 1.23 (dd, *J* = 10.3, 6.3 Hz, 24H), 0.94 (qd, *J* = 16.3, 7.2 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.1, 139.9, 136.6, 132.6, 129.5, 128.1, 124.2, 83.4, 83.2, 42.9, 24.9, 24.6, 24.5, 19.8. ^{11}B NMR: δ = 33.5 (br). HRMS-(DART) for: $^{12}C_{24}{}^{1}H_{39}{}^{10}B_2{}^{14}N^{16}O_5[M+H]^+$: calculated: 442.3160, found: 442.3157.



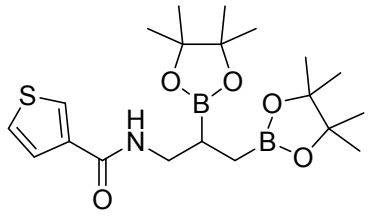
36

N-(2,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)benzo[d][1,3]dioxole-5-carboxamide. The reaction was performed following the general procedure D. Colorless oil, 77% yield (70.7 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (d, *J* = 1.7 Hz, 1H), 7.28 (d, *J* = 1.7 Hz, 1H), 7.25 (d, *J* = 1.6 Hz, 1H), 6.89 (s, 1H), 5.98 (s, 2H), 3.57 (dt, *J* = 13.0, 6.5 Hz, 2H), 3.34 – 3.28 (m, 2H), 1.20 (s, 24H), 0.94 – 0.91 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.4, 149.9, 147.7, 129.3, 121.3, 107.8, 107.5, 101.5, 83.4, 83.2, 74.9, 43.1, 24.7, 24.5. ^{11}B NMR: δ = 33.6 (br). HRMS-(DART) for: $^{12}C_{23}{}^{1}H_{35}{}^{10}B_2{}^{14}N^{16}O_7[M+H]^+$: calculated: 458.2745, found: 458.2751.



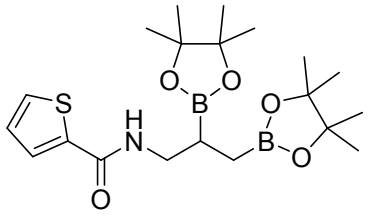
37

N-(2,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)-2,6-difluorobenzamide. The reaction was performed following the general procedure D. Light yellow oil, 82% yield (74.0 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (ddd, *J* = 8.4, 7.4, 4.2 Hz, 1H), 6.93 – 6.89 (m, 2H), 6.75 (s, 1H), 3.60 (dt, *J* = 13.2, 6.6 Hz, 1H), 3.46 – 3.41 (m, 1H), 1.46 (p, *J* = 7.0 Hz, 1H), 1.20 (d, *J* = 15.7 Hz, 24H), 0.98 – 0.89 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.9, 160.0, 158.9 (d, *J* = 7.2 Hz), 131.1 (t, *J* = 10.2 Hz), 115.0, 111.8, 83.5, 83.2, 74.9, 43.0, 24.9, 24.6. ^{11}B NMR: δ = 33.6 (br). HRMS-(DART) for: $^{12}C_{22}{}^{1}H_{33}{}^{10}B_2{}^{18}F_2{}^{14}N{}^{16}O_5[M+H]^+$: calculated: 450.2658, found: 450.2655.



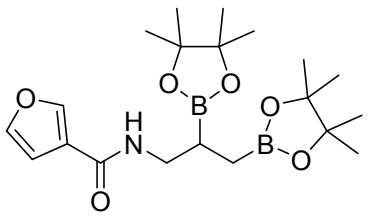
38

N-(2,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)thiophene-3-carboxamide. The reaction was performed following the general procedure D. Light yellow oil, 86% yield (72.4 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 3.0, 1.2 Hz, 1H), 7.32 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.27 (dd, *J* = 4.8, 2.7 Hz, 1H), 6.85 (s, 1H), 3.55 (dt, *J* = 13.1, 6.5 Hz, 1H), 3.32 – 3.26 (m, 1H), 1.18 (s, 24H), 0.89 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.7, 138.2, 127.6, 126.1, 125.9, 83.4, 83.2, 42.7, 25.1, 24.6, 24.5. ^{11}B NMR: δ = 33.4 (br). HRMS-(DART) for: $^{12}C_{20}{}^{1}H_{33}{}^{10}B_2{}^{14}N{}^{16}O_5{}^{32}S[M+H]^+$: calculated: 420.2411, found: 420.2410.



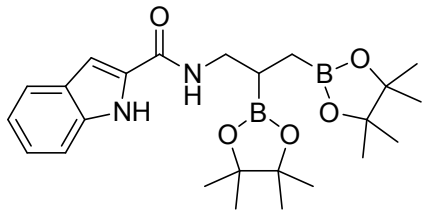
39

N-(2,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)thiophene-2-carboxamide. The reaction was performed following the general procedure D. Light yellow oil, 79% yield (66.6 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 3.7 Hz, 1H), 7.41 (d, *J* = 5.0 Hz, 1H), 7.03 (t, *J* = 4.3 Hz, 1H), 6.82 (s, 1H), 3.60 (dt, *J* = 13.0, 6.5 Hz, 1H), 3.30 (ddd, *J* = 12.9, 8.3, 4.5 Hz, 1H), 1.48 – 1.41 (m, 1H), 1.24 – 1.20 (m, 24H), 0.97 – 0.86 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.5, 139.7, 129.2, 127.5, 127.3, 83.4, 83.2, 42.9, 24.8. ^{11}B NMR: δ = 33.7 (br). HRMS-(DART) for: $^{12}C_{20}{}^{1}H_{33}{}^{10}B_2{}^{14}N^{16}O_5{}^{32}S[M+H]^+$: calculated: 420.2411, found: 420.2410.



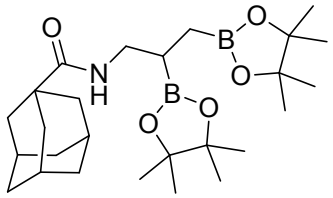
40

N-(2,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)furan-3-carboxamide. The reaction was performed following the general procedure D. Colorless oil, 82% yield (66.5 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.36 (s, 1H), 6.67 (s, 1H), 6.53 (s, 1H), 4.06 (q, *J* = 7.2 Hz, 1H), 3.52 (dt, *J* = 13.1, 6.5 Hz, 1H), 3.24 (ddd, *J* = 13.0, 8.3, 4.5 Hz, 1H), 1.18 (s, 24H), 0.87 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.3, 144.5, 143.4, 122.9, 108.1, 83.4, 83.2, 82.8, 74.9, 42.4, 24.8, 24.5, 24.4. ^{11}B NMR: δ = 33.7 (br). HRMS-(DART) for: $^{12}C_{20}{}^{1}H_{33}{}^{10}B_2{}^{14}N^{16}O_6[M+H]^+$: calculated: 404.2639, found: 404.2640.



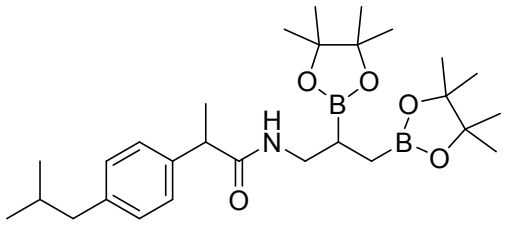
41

N-(2,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)-1H-indole-2-carboxamide. The reaction was performed following the general procedure D. Light yellow oil, 66% yield (60.0 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.73 (s, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 8.3 Hz, 1H), 7.29 (d, *J* = 7.9 Hz, 1H), 7.12 (t, *J* = 5.9 Hz, 1H), 6.83 (d, *J* = 34.8 Hz, 1H), 5.71 – 5.50 (m, 1H), 4.28 – 4.11 (m, 1H), 3.68 (dt, *J* = 13.1, 6.6 Hz, 1H), 3.40 (ddd, *J* = 12.9, 8.1, 4.6 Hz, 1H), 1.28 – 1.25 (m, 24H), 1.03 – 0.88 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.4, 136.3, 131.4, 127.6, 124.0, 121.6, 120.3, 112.0, 101.4, 83.5, 83.3, 75.0, 42.7, 24.8, 24.5. ^{11}B NMR: δ = 33.6 (br). HRMS-(DART) for: $^{12}C_{24}{}^{1}H_{36}{}^{10}B_2{}^{14}N_2{}^{16}O_5[M+H]^+$: calculated: 453.2956, found: 453.2957.



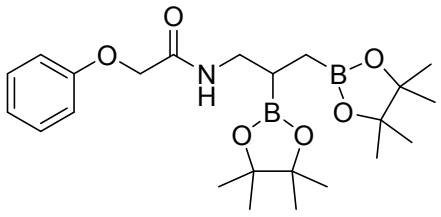
42

(3r,5r,7r)-N-(2,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)adamantane-1-carboxamide. The reaction was performed following the general procedure D. Colorless oil, 61% yield (57.7 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.27 (s, 1H), 3.40 (dt, *J* = 12.7, 6.2 Hz, 1H), 3.10 (ddd, *J* = 13.0, 8.7, 4.4 Hz, 1H), 2.00 (s, 3H), 1.82 (d, *J* = 2.6 Hz, 6H), 1.71 – 1.65 (m, 6H), 1.24 – 1.21 (m, 24H), 0.88 – 0.81 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.5, 83.3, 83.1, 42.3, 40.5, 39.2, 36.6, 28.2, 24.8, 24.4. ^{11}B NMR: δ = 33.1 (br). HRMS-(DART) for: $^{12}C_{26}{}^{1}H_{45}{}^{10}B_2{}^{14}N^{16}O_5[M+H]^+$: calculated: 472.3629, found: 472.3629.



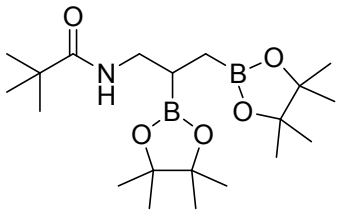
43

N-(2,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)-2-(4-isobutylphenyl)propanamide. The reaction was performed following the general procedure D. Colorless oil, 66% yield (65.9 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (d, *J* = 7.8 Hz, 2H), 7.07 (d, *J* = 7.9 Hz, 2H), 5.94 (s, 1H), 3.49 (dd, *J* = 7.2, 3.5 Hz, 1H), 3.33 (dt, *J* = 12.9, 6.4 Hz, 1H), 3.10 (ddd, *J* = 12.9, 8.6, 4.1 Hz, 1H), 2.41 (d, *J* = 7.1 Hz, 2H), 1.83 (dd, *J* = 13.4, 6.7 Hz, 1H), 1.47 (d, *J* = 7.1 Hz, 3H), 1.23 (d, *J* = 14.0 Hz, 24H), 0.88 (d, *J* = 6.6 Hz, 6H), 0.76 (dd, *J* = 16.2, 7.6 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.1, 140.3, 138.8, 129.5, 127.4, 83.1, 75.0, 46.9, 45.0, 42.6, 30.2, 24.9, 24.4, 22.4, 18.6. ^{11}B NMR: δ = 33.9 (br). HRMS-(DART) for: $^{12}C_{28}{}^{1}H_{47}{}^{10}B_2{}^{14}N^{16}O_5[M+H]^+$: calculated: 498.3786, found: 498.3790.



44

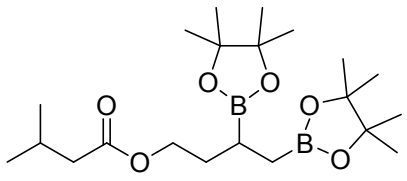
N-(2,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)-2-phenoxyacetamide. The reaction was performed following the general procedure D. Colorless oil, 60% yield (53.4 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.26 (m, 2H), 7.16 (s, 1H), 6.98 (t, *J* = 7.3 Hz, 1H), 6.88 (d, *J* = 8.3 Hz, 2H), 4.44 (s, 2H), 3.50 (dt, *J* = 13.0, 6.5 Hz, 1H), 3.24 (ddd, *J* = 13.2, 8.5, 4.8 Hz, 1H), 1.20 (s, 24H), 0.90 – 0.79 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.9, 157.4, 129.7, 121.8, 114.6, 83.4, 83.1, 67.4, 41.9, 24.8, 24.5. ^{11}B NMR: δ = 33.5 (br). HRMS-(DART) for: $^{12}C_{23}{}^{1}H_{37}{}^{10}B_2{}^{14}N^{16}O_6[M+H]^+$: calculated: 444.2952, found: 444.2953.



45

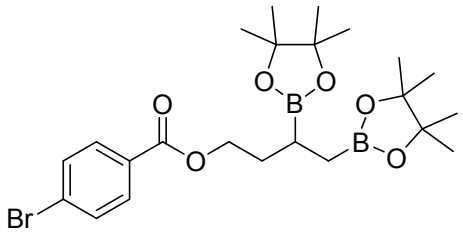
N-(2,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)pivalamide.

The reaction was performed following the general procedure D. Colorless oil, 70% yield (55.3 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.39 (s, 1H), 3.37 (dt, *J* = 12.6, 6.2 Hz, 1H), 3.05 (ddd, *J* = 13.1, 8.9, 4.3 Hz, 1H), 1.20 (s, 9H), 1.18 (s, 24H), 0.85 – 0.76 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.0, 83.3, 83.1, 82.9, 75.0, 42.5, 38.6, 27.5, 24.9, 24.5, 24.5. ^{11}B NMR: δ = 33.2 (br). HRMS-(DART) for: $^{12}C_{20}{}^{1}H_{39}{}^{10}B_2{}^{14}N^{16}O_5[M+H]^+$: calculated: 394.3160, found: 394.3172.



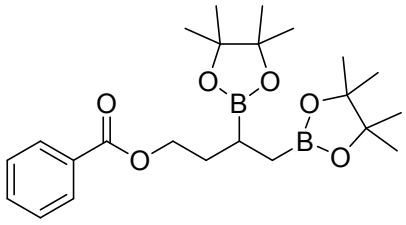
46

3,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl 3-methylbutanoate. The reaction was performed following the general procedure D. Colorless oil, 66% yield (54.2 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.08 (dd, *J* = 13.6, 6.9 Hz, 2H), 2.15 (d, *J* = 6.8 Hz, 2H), 2.07 (dd, *J* = 13.2, 6.8 Hz, 1H), 1.80 (dd, *J* = 13.1, 7.0 Hz, 1H), 1.62 (dd, *J* = 13.8, 6.9 Hz, 1H), 1.22 (d, *J* = 1.5 Hz, 24H), 0.93 (d, *J* = 6.6 Hz, 6H), 0.88 (d, *J* = 6.2 Hz, 1H), 0.85 (d, *J* = 6.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.3, 129.6, 115.3, 83.5, 82.9, 63.8, 43.5, 32.1, 25.7, 25.07, 24.55, 22.4. ^{11}B NMR: δ = 33.4 (br). HRMS-(DART) for: $^{12}C_{21}{}^{1}H_{40}{}^{10}B_2{}^{16}O_6[M+H]^+$: calculated: 409.3156, found: 409.3173.



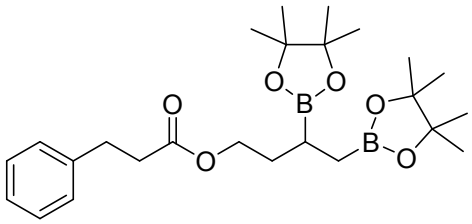
47

3,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl 4-bromobenzoate. The reaction was performed following the general procedure D. Colorless oil, 78% yield (79.3 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.6 Hz, 2H), 7.55 (d, *J* = 8.6 Hz, 2H), 4.36 – 4.30 (m, 2H), 1.94 (dd, *J* = 13.9, 6.5 Hz, 1H), 1.76 (dd, *J* = 13.8, 6.9 Hz, 1H), 1.23 (d, *J* = 3.4 Hz, 24H), 0.96 – 0.92 (m, 1H), 0.92 – 0.88 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.9, 131.5, 131.2, 129.6, 83.1, 82.7, 65.0, 32.1, 24.8, 24.4. ^{11}B NMR: δ = 33.6 (br). HRMS-(DART) for: $^{12}C_{23}{}^{1}H_{35}{}^{10}B_2Br^{16}O_6[M+H]^+$: calculated: 507.1949, found: 507.1951.



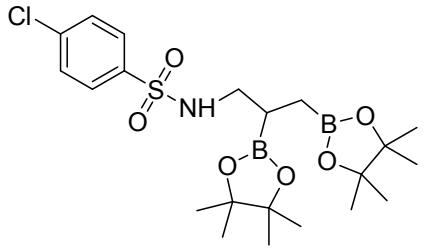
48

3,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butylbenzoate. The reaction was performed following the general procedure D. Colorless oil, 67% yield (57.7 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 9.5 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.0 Hz, 2H), 4.30 (dd, *J* = 17.1, 7.2 Hz, 2H), 1.92 (dd, *J* = 13.8, 6.4 Hz, 1H), 1.74 (dd, *J* = 13.8, 6.9 Hz, 1H), 1.22 (s, 24H), 0.89 (dd, *J* = 11.5, 7.6 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.7, 132.6, 130.7, 129.58, 128.2, 83.5, 83.0, 64.7, 32.1, 25.1, 24.6, 24.5. ^{11}B NMR: δ = 33.6 (br). HRMS-(DART) for: $^{12}C_{23}{}^{1}H_{36}{}^{10}B_2{}^{16}O_6[M+H]^+$: calculated: 429.2843, found: 429.2841.



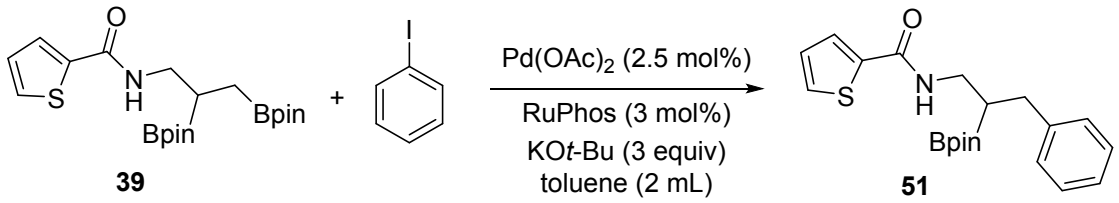
49

3,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl 3-phenylpropanoate. The reaction was performed following the general procedure D. Colorless oil, 67% yield (61.4 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 2H), 7.20 (d, *J* = 1.4 Hz, 2H), 7.19 (s, 1H), 3.67 (s, 2H), 2.94 (d, *J* = 8.1 Hz, 2H), 2.65 – 2.62 (m, 2H), 1.65 (s, 1H), 1.49 – 0.97 (m, 24H), 0.07 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.5, 139.6, 129.2, 127.5, 127.3, 83.4, 83.2, 60.3, 42.8, 25.1, 24.6, 24.5, 20.9, 14.1. ^{11}B NMR: δ = 33.4 (br). HRMS-(DART) for: $^{12}C_{25}{}^{1}H_{40}{}^{10}B_2{}^{16}O_6[M+H]^+$: calculated: 457.3156, found: 457.3158.

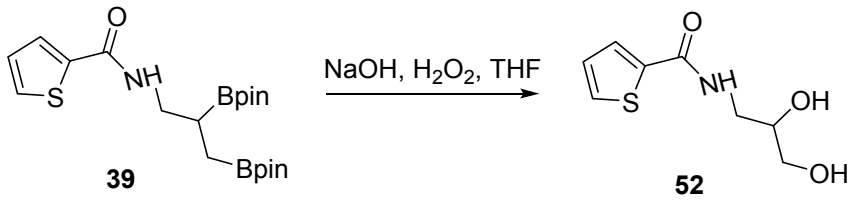


50

N-(2,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)-4-chlorobenzenesulfonamide. The reaction was performed following the general procedure D. Light yellow oil, 60% yield (58.2 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 – 7.78 (m, 2H), 7.48 – 7.44 (m, 2H), 5.29 (s, 1H), 3.02 – 2.90 (m, 2H), 1.20 (t, *J* = 3.7 Hz, 24H), 0.85 (dd, *J* = 16.7, 7.6 Hz, 1H), 0.79 (dd, *J* = 16.3, 6.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.7 (d, *J* = 8.4 Hz), 129.2, 128.6, 83.6, 83.4, 46.4, 24.8, 24.4. ^{11}B NMR: δ = 33.9 (br). HRMS-(DART) for: $^{12}C_{21}{}^{1}H_{34}{}^{10}B_2Cl^{14}N^{16}O_6{}^{32}S[M+H]^+$: calculated: 484.2127, found: 484.2126.

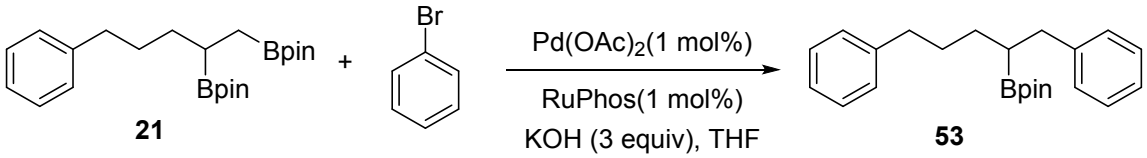


To an oven-dried 25 mL round bottom flask with magnetic stir bar in the dry box was added the 1,2-bis(boronate) **39** (84.2mg, 0.2 mmol), toluene (2 mL), KO*t*-Bu (54 mg, 0.6 mmol), $Pd(OAc)_2$ (1.2 mg, 5 μmol), RuPhos (2.8 mg, 6 μmol) and iodobenzene (32 μL, 0.3 mmol). The flask was sealed with a rubber septum, removed from the dry box, and heated to 80 °C in an oil bath for 12 hours. The reaction mixture was cooled to room temperature and H_2O (2 mL) was added. The layers were allowed to seperate and the aqueous layer was extracted with dichloromethane (3 x 10 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The crude material was purified on SiO_2 gel to afford compound **51** as a colorless oil (46.9 mg, 63% yield).[10] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.37 (dd, *J* = 3.7, 1.1 Hz, 1H), 7.26 (t, *J* = 3.5 Hz, 2H), 7.23 (d, *J* = 6.7 Hz, 2H), 7.17 (t, *J* = 7.0 Hz, 1H), 7.05 (dd, *J* = 4.9, 3.7 Hz, 1H), 6.51 (s, 1H), 3.54 – 3.45 (m, 2H), 2.88 (dd, *J* = 13.9, 6.9 Hz, 1H), 2.71 (dd, *J* = 13.9, 8.4 Hz, 1H), 1.22 (d, *J* = 1.3 Hz, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.5, 141.1, 139.4, 129.4, 128.9, 128.3, 127.6, 126.0, 83.7, 40.5, 34.9, 24.8. HRMS-(DART) for: $^{12}C_{19}{}^{1}H_{24}{}^{10}B^{14}N^{16}O_3{}^{32}S[M+H]^+$: calculated: 371.1836, found: 371.1837.

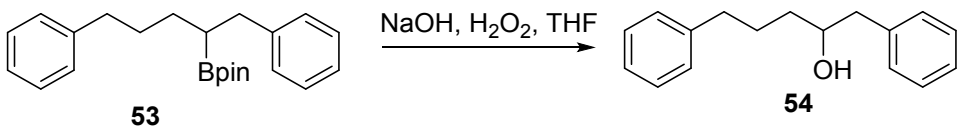


The 1,2-bis(boronate) **39** (84.2 mg, 0.2 mmol) was transferred to a 25-mL round bottom flask and cooled to 0 °C (ice/water) and charged with 3 M sodium hydroxide (2 mL), and 30% hydrogen peroxide (1 mL). The reaction was gradually warmed to room temperature and allowed to stir for 4 h at which time the vial was diluted with

ethyl acetate and the aqueous and organic layers were separated. The aqueous layer was extracted with ethyl acetate (3 x 10 mL) and the combined organic layers were dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The crude material was purified on flash chromatography to afford compound **52** as a white solid (35.4 mg, 88% yield).[10] ^{1}H NMR (500 MHz, DMSO) δ 8.46 (t, J = 5.7 Hz, 1H), 7.79 (dd, J = 3.7, 1.1 Hz, 1H), 7.73 (dd, J = 5.0, 1.1 Hz, 1H), 7.13 (dd, J = 5.0, 3.7 Hz, 1H), 4.86 (s, 1H), 4.60 (s, 1H), 3.63 – 3.59 (m, 1H), 3.32 (s, 1H), 3.17 – 3.11 (m, 1H), 1.23 (s, 2H). 13C NMR (125 MHz, DMSO) δ 161.5, 140.2, 130.7, 128.2, 127.9, 70.5, 64.0, 42.9.

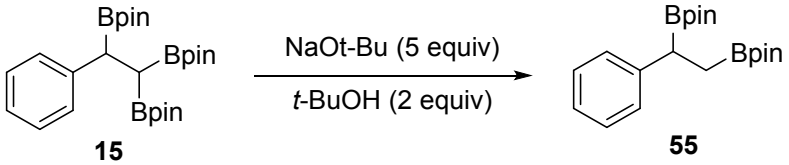


To an oven-dried 25 mL round bottom flask with magnetic stir bar in the dry box was added the 1,2-bis(boronate) **21** (80.0 mg, 0.2 mmol), THF (2 mL), KOH (54 mg, 0.6 mmol), $Pd(OAc)_2$ (1.2 mg, 2 μ mol), RuPhos (2.8 mg, 3 μmol) and bromobenzene (29 μL, 0.3 mmol). The flask was sealed with a rubber septum, removed from the dry box, and heated to 70^{o}C in an oil bath for 12 hours. The reaction mixture was cooled to room temperature and H_2O (2 mL) was added. The layers were allowed to be separated and the aqueous layer was extracted with dichloromethane (3 x 10 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The crude material was purified by flash chromatography to afford compound **53** as a colorless oil, (63.0 mg, 90% yield).[10] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, *J* = 7.7 Hz, 2H), 7.26 – 7.20 (m, 4H), 7.17 (d, *J* = 7.2 Hz, 4H), 2.71 (qd, *J* = 13.5, 7.9 Hz, 2H), 2.59 (dt, *J* = 13.7, 8.0 Hz, 2H), 1.72 – 1.62 (m, 2H), 1.50 (dd, *J* = 9.5, 5.3 Hz, 1H), 1.17 (s, 6H), 1.14 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.7, 142.2, 128.8, 128.3, 128.2, 128.0, 125.6, 125.5, 82.9, 37.3, 36.1, 31.0, 30.8, 24.8, 24.7.



53 **54**

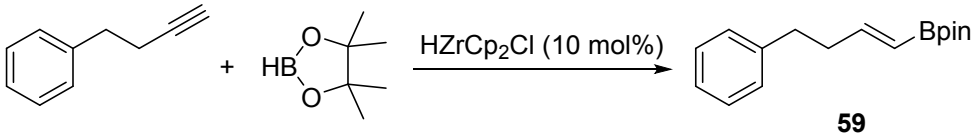
The boronates **53** (0.16 mmol, 52.5 mg) was transferred to a 25-mL round bottom flask and cooled to 0 ^{o}C (ice/water) and charged with 3 M sodium hydroxide (2 mL), and 30% hydrogen peroxide (1 mL). The reaction was gradually warmed to room temperature and allowed to stir for 4 h at which time the vial was diluted with ethyl acetate and the aqueous and organic layers were separated. The aqueous layer was extracted with ethyl acetate (3 x 10 mL) and the combined organics were dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The crude material was purified by flash chromatography to afford compound **54** as a white solid, (38.1 mg, 88% yield).[12] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 15.3, 7.6 Hz, 3H), 7.26 (t, *J* = 7.6 Hz, 2H), 7.20 (t, *J* = 7.1 Hz, 5H), 3.88 – 3.81 (m, 1H), 2.83 (dd, *J* = 13.5, 4.2 Hz, 1H), 2.65 (dd, *J* = 13.6, 8.3 Hz, 3H), 1.91 – 1.81 (m, 1H), 1.72 (ddd, *J* = 21.1, 14.5, 6.8 Hz, 1H), 1.59 – 1.56 (m, 1H), 1.52 (d, *J* = 3.9 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.3 , 138.5, 129.4, 128.6, 128.4, 128.3, 126.5, 125.7, 72.5, 44.0, 36.4, 35.8, 27.6.



15 **55**

To an oven-dried 2-dram vial equipped with magnetic stir bar in the glovebox was added 1,1,2-tris(boronates) **15** (96.8 mg, 0.2 mmol) and NaOt-Bu (5.0 equiv.), followed immediately by t-BuOH (2 equiv.), and the toluene (2 mL) was added. The vial was sealed with a polypropylene cap, taped, and removed from the glovebox. The mixture was reacted at room temperature for 12 hours. The pure 1,2-bis(boronates) product **55** was isolated by flash chromatography as a colorless oil (60.1mg, 84% yield).[12] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (d, *J* = 4.4 Hz, 4H), 7.11 – 7.07 (m, 1H), 2.52 (dd, *J* = 11.0, 5.7 Hz, 1H), 1.38 (dd, *J* = 16.0, 11.1 Hz, 1H), 1.20 (s, 12H), 1.18

(d, J = 7.7 Hz, 12H), 1.11 (dd, J = 16.0, 5.7 Hz, 1H). ^{13}C NMR (125MHz, $CDCl_3$) δ 145.4, 128.1, 127.9, 124.9, 83.2, 83.0, 24.9, 24.7, 24.6, 24.5.



59

To an oven-dried 2-dram vial equipped with magnetic stir bar in the glovebox was added alkyne (1.1 equiv, 28 uL) and pinacol borane (1.0 mmol, 20 uL), followed immediately by Schwartz's reagent (0.10 equiv, 18mg). The vial was sealed with a polypropylene cap, taped, and removed from the glovebox. The mixture was heated in an oil bath to 60^{o}C for 14 hours, at which point it was cooled to room temperature. The pure vinyl(boronate) products were isolated by flash chromatography to afford compound **59** as a colorless oil (47.9 mg, 88% yield).[12] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, J = 7.4 Hz, 2H), 7.20 – 7.16 (m, 3H), 6.70 (dt, J = 18.0, 6.2 Hz, 1H), 5.50 (d, J = 18.0 Hz, 1H), 2.76 – 2.71 (m, 2H), 2.48 (dd, J = 16.0, 7.9 Hz, 2H), 1.27 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.3, 141.7, 128.2, 125.8, 82.9, 82.1, 37.4, 34.5, 24.7, 24.4. ^{11}B NMR: δ = 28.5 (br).

References

(1) N. S. Gulykina, T. M. Dolgina, G. N. Bondarenko, I. P. Beletskaya, Russian *J. Org. Chem.* **2003**, *39*, 797-807.

(2) A . Bonet, C . Sole, H. Gulyás, E. Fernández, *Org. Biomol.*

Chem., **2012**, *10*, 6621 – 6623.

(3) O. V. Gutov, W. Bury, D. A. Gomez-Gualdron, V. Krungleviciute, D. Fairen-Jimenez, J. E. Mondloch, A. A. Sarjeant, S. S. Al-Juaid, R. Q. Snurr, J. T. Hupp, T. Yildirim, O. K. Farha, *Chem. Eur. J.* **2014**, *20*, 12389-12393.

(4) M. C.Hsu, A. J. Junia, A. R. Haight, W. Zhang, *J. Org. Chem.* **2004**, *69*, 3907-3911.

(5) C. Y. Huang, A. G. Doyle, *J. Am. Chem. Soc.* **2012**, *134*, 9541-9544.

(6) A. Bonet, H. Gulyás, E. Fernández, *Angew. Chem. Int. Ed.* **2010**, *49*, 5130-5134.

(7) Y. Lee, H. Jang, A. Hoveyda, *J. Am. Chem. Soc.* **2009**, *131*, 18234-18235.

(8) S. R. Inglis, E. C. Y. Woon, A. L. Thompson, C. J. Schofield, *J. Org. Chem.* **2010**, *75*, 468-471.

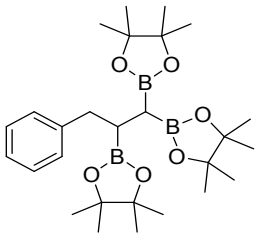
(9) K. K. Tanabe, M. S. Ferrandon, N. A. Siladke, S. J. Kraft, G. Zhang, J. Niklas, O. G. Poluektov, S. J. Lopykinski, E. E. Bunel, T. R. Krause, J. T. Miller, A. S. Hock, S. T. Nguyen, *Angew. Chem. Int. Ed.* **2014**, *53*, 12055-12058.

(10) Blaisdell, T. P.; Morken, J. P. *J. Am. Chem. Soc.* **2015**, *137*, 8712-8715.

(11) K. Yang and Q. L. Song. *Green Chem.* **2016**, *18*, 932-936.

(12) J. R. Coombs, L. Zhang, J. P. Morken, *J. Am. Chem. Soc.* **2014**, *136*, 16140-16143.

Spectroscopic Data



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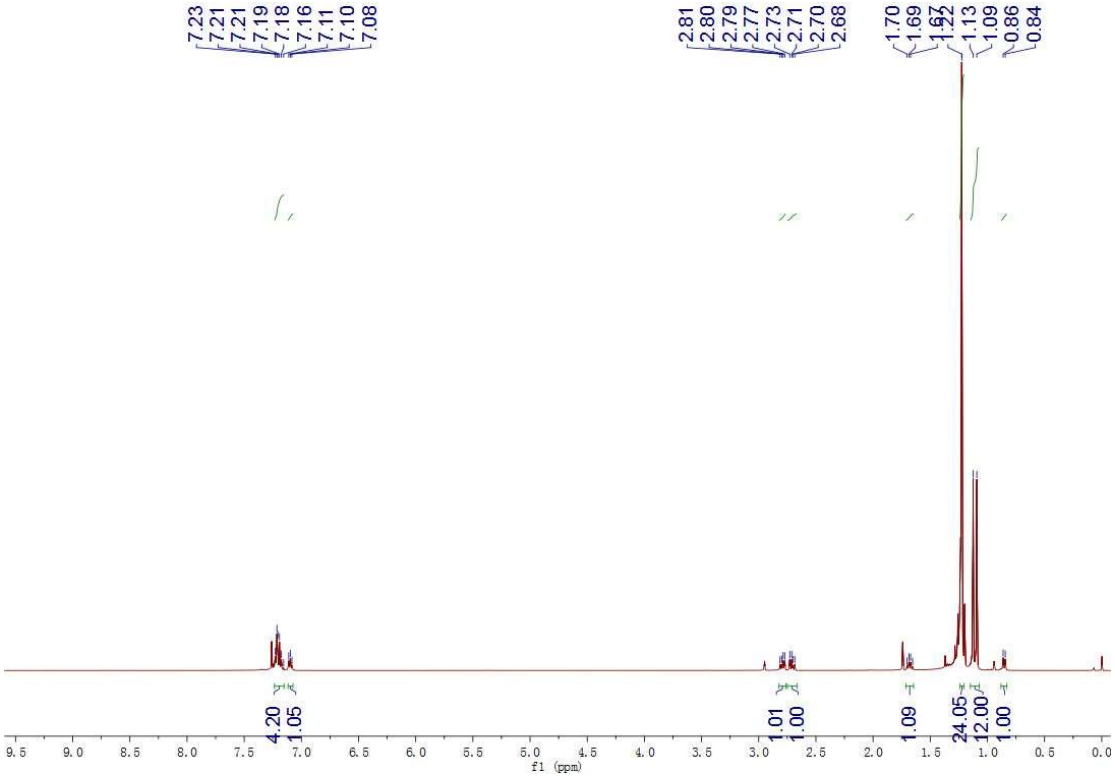
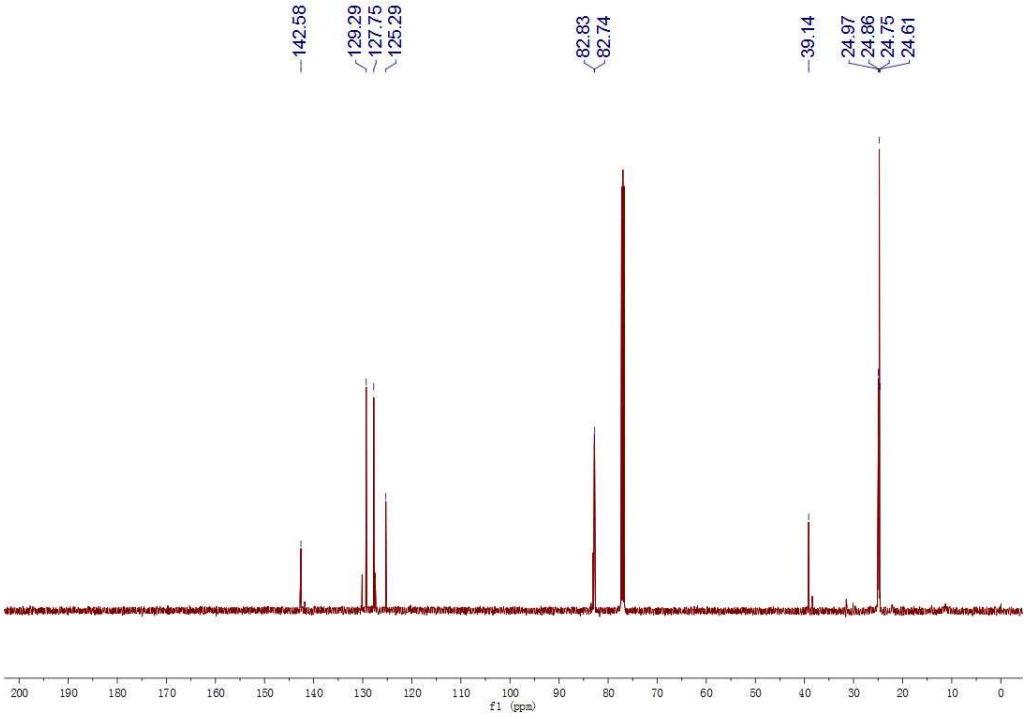
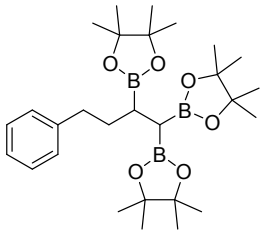
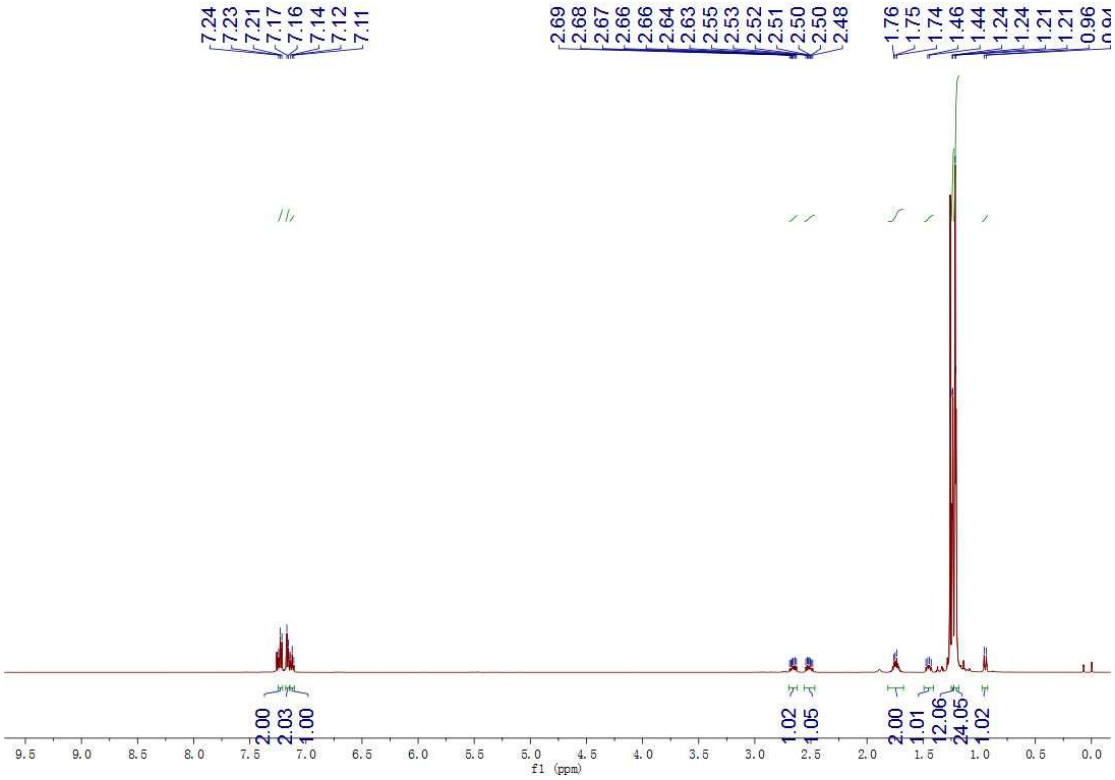






5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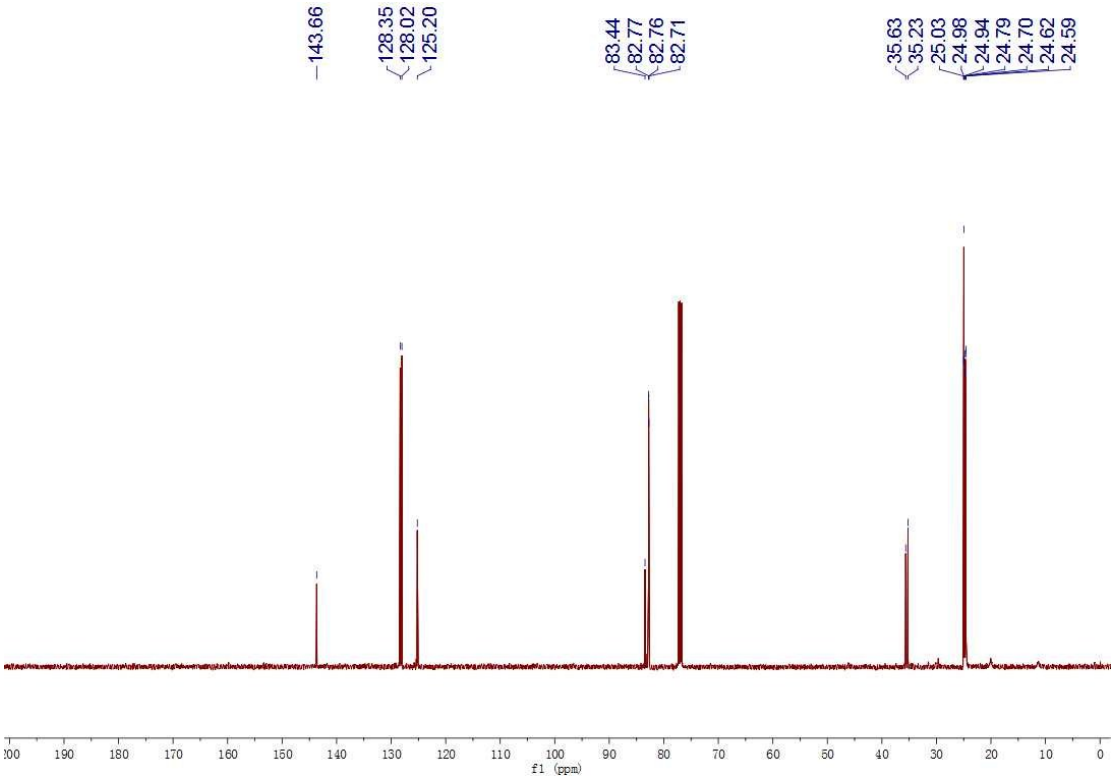
f1 (ppm)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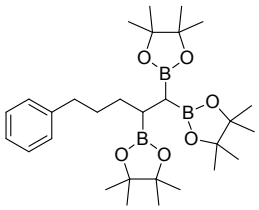
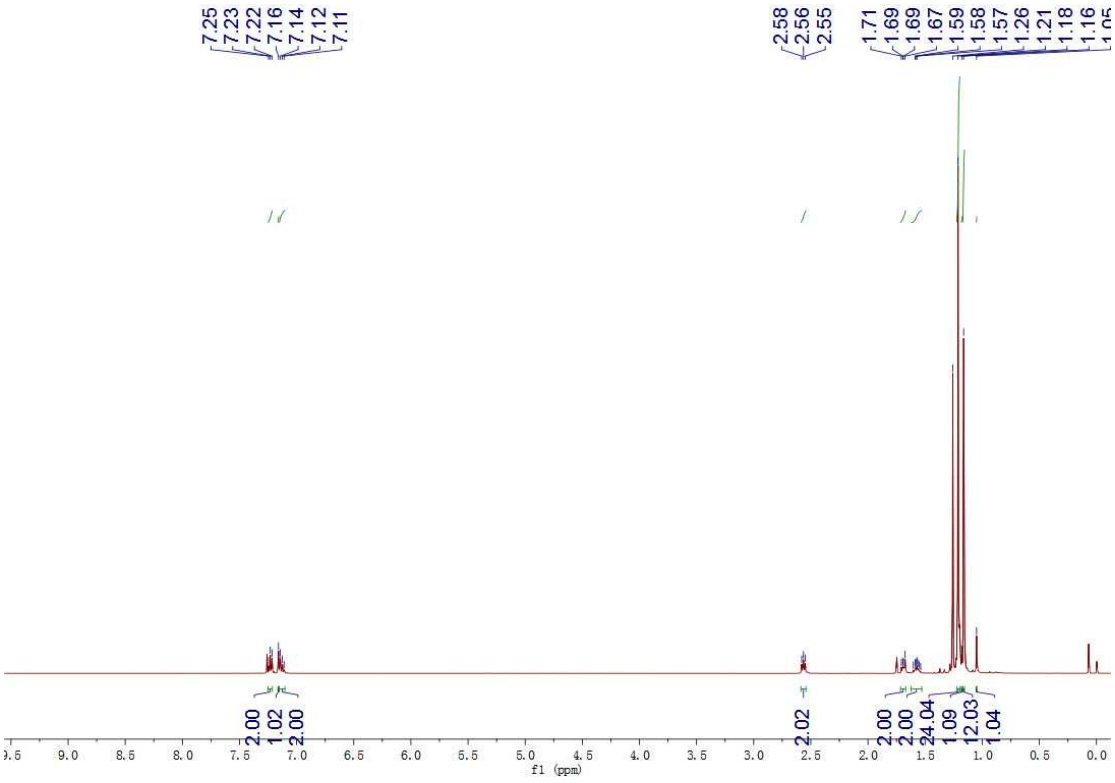


6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1.71
1.69
1.69
1.67
1.59
1.58
1.57
1.26
1.21
1.18
1.16
2.00
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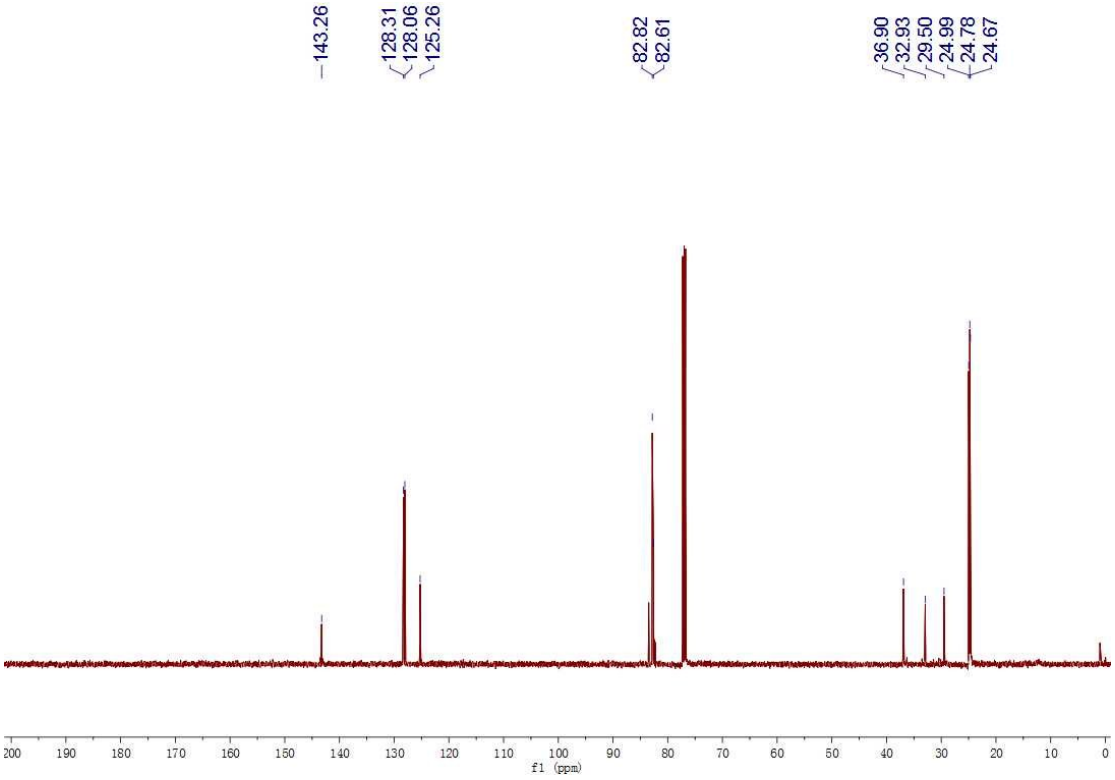
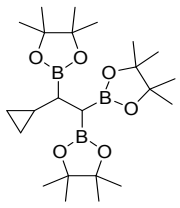
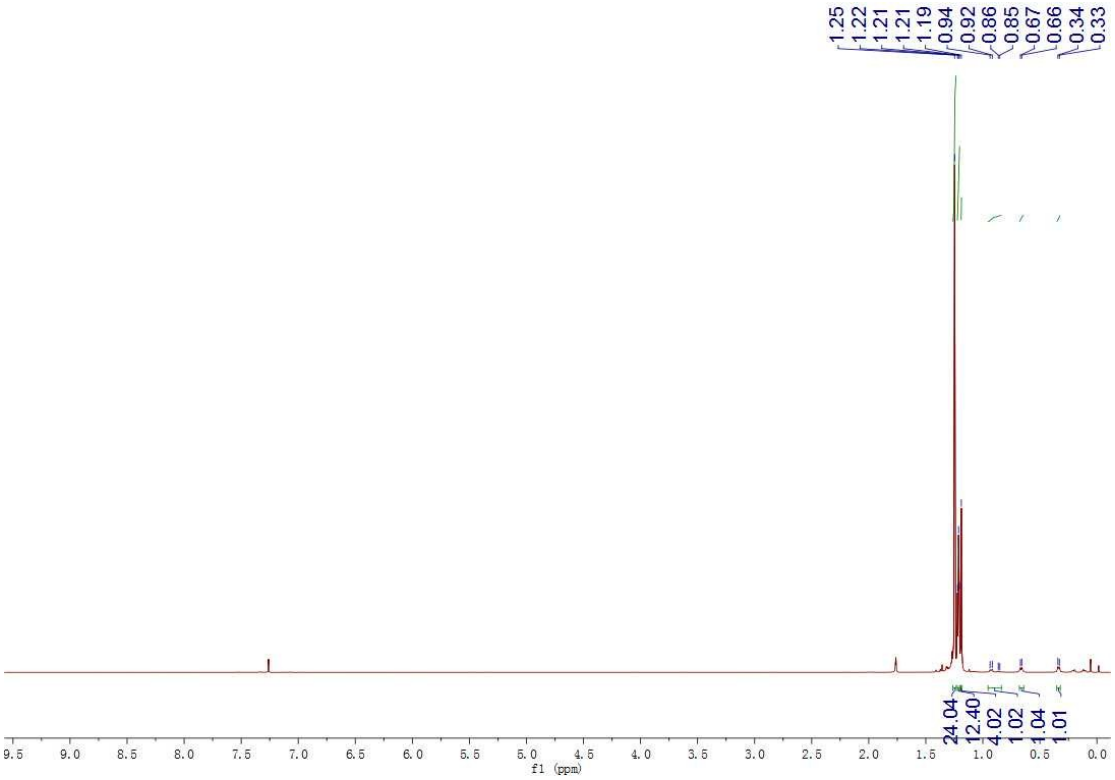
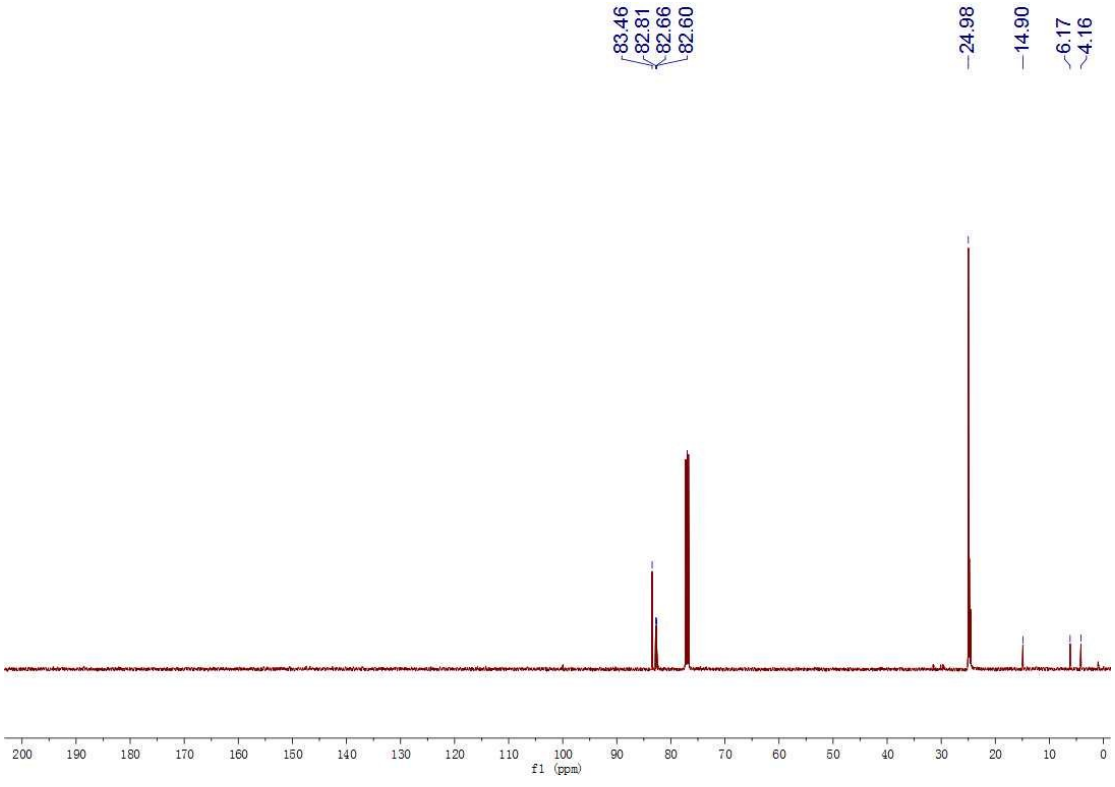
2.00
2.02
2.00
2.00
24.04
1.09
12.03
1.04
f1 (ppm)

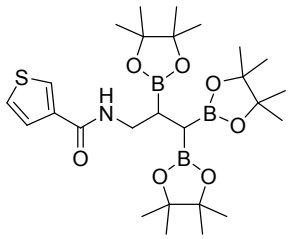

143.26
128.31
128.06
125.26
82.82
82.61
36.90
32.93
29.50
24.99
24.78
24.67
f1 (ppm)



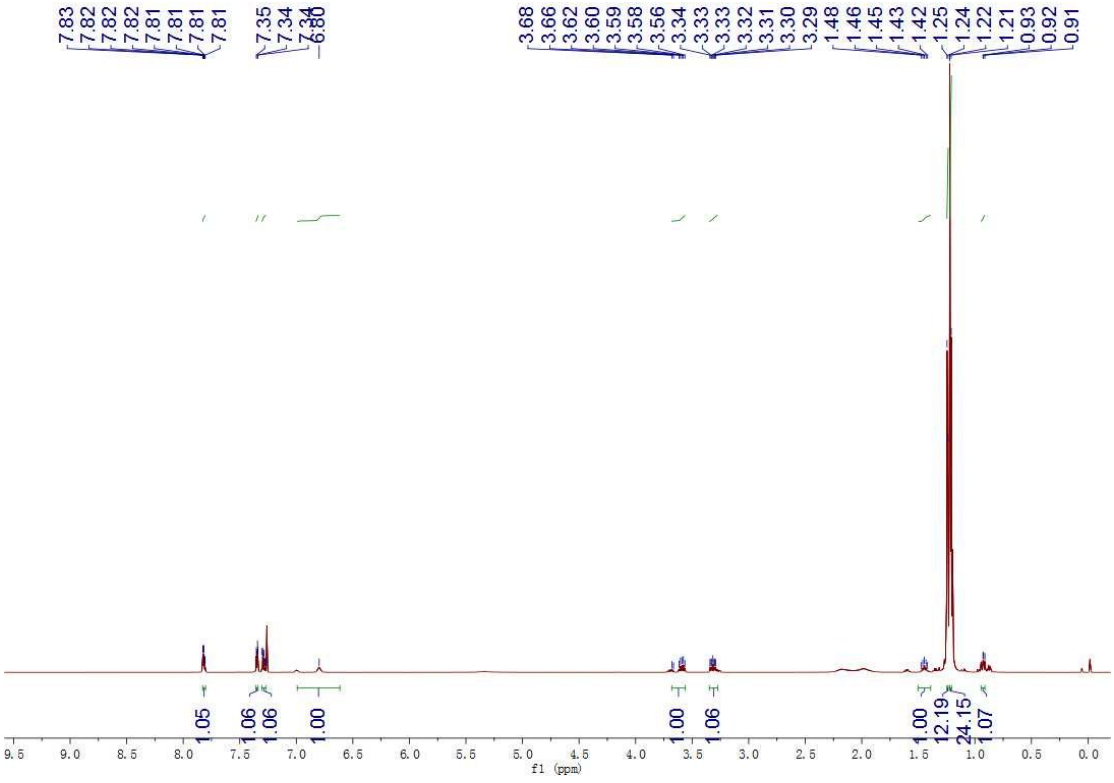
7


1.25
1.22
1.21
1.21
1.19
0.94
0.92
0.86
0.85
0.67
0.66
0.34
0.33
24.04
12.40
4.02
1.02
1.04
1.01
f1 (ppm)


83.46
82.81
82.66
82.60
24.98
14.90
6.17
4.16
f1 (ppm)



8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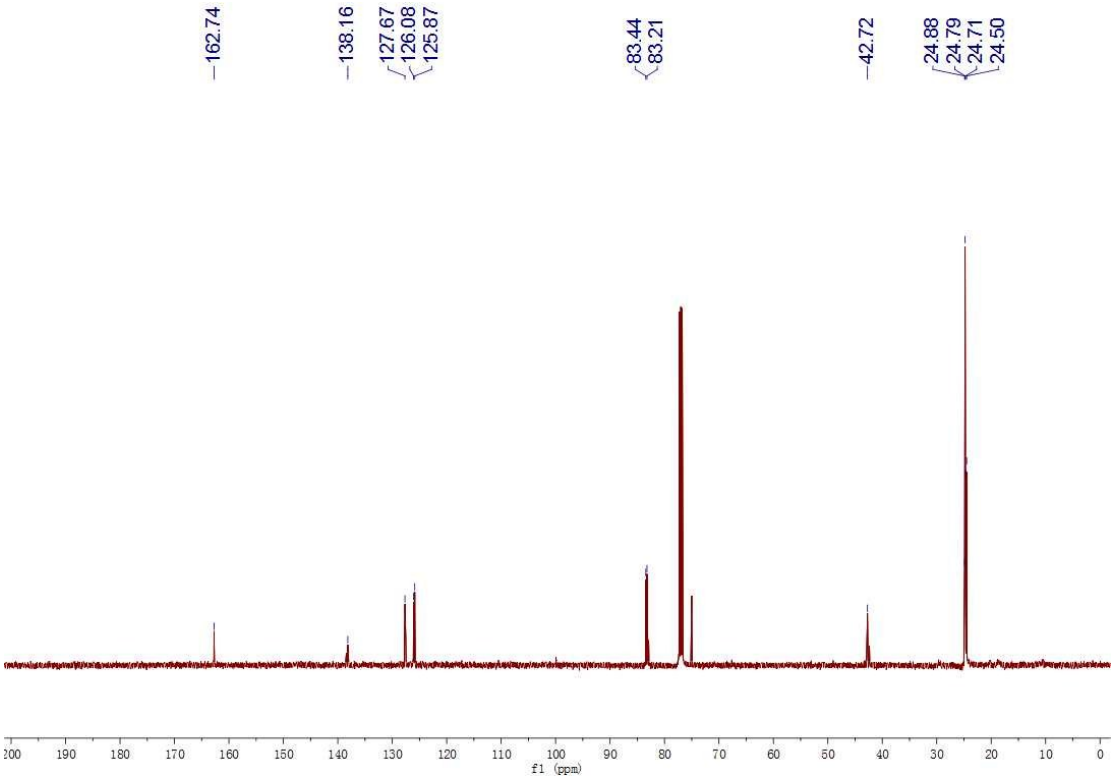
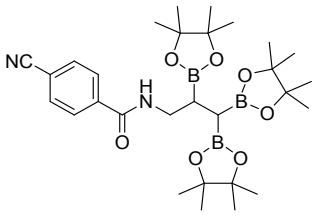
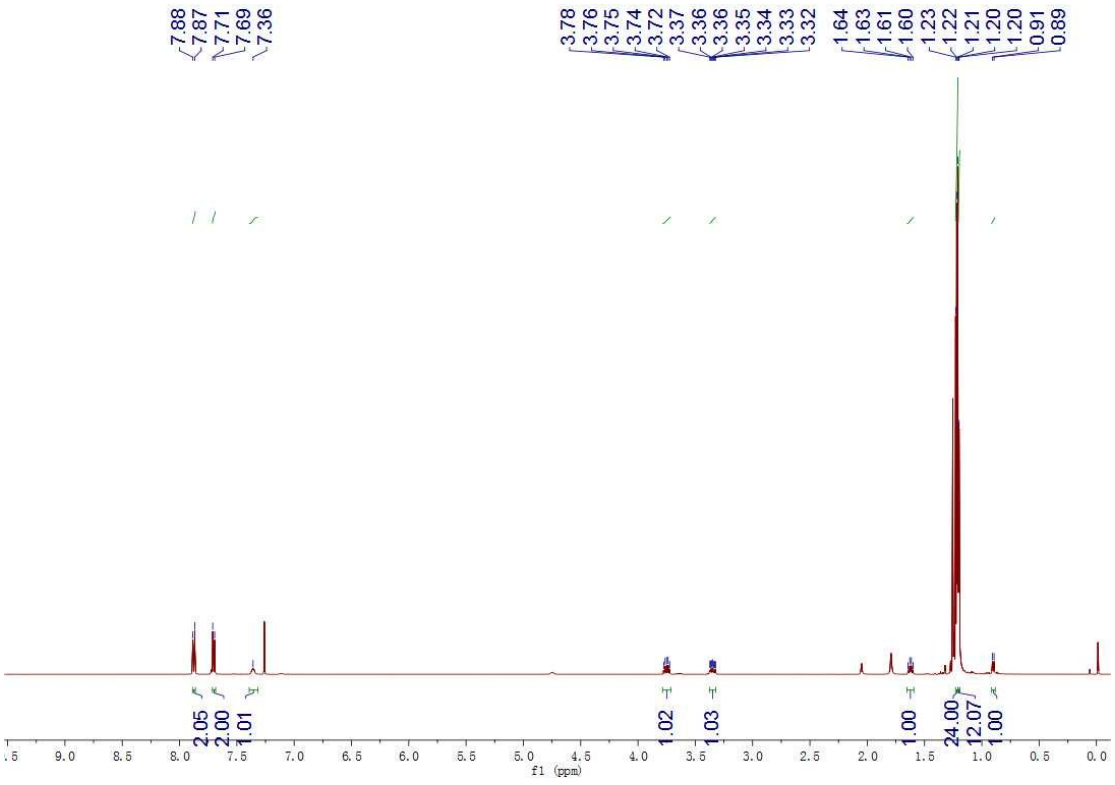
7.82
7.82
7.82
7.81
7.81
7.81
7.35
7.34
7.34
6.80
3.68
3.66
3.62
3.60
3.59
3.58
3.56
3.34
3.33
3.33
3.32
3.31
3.30
3.29
1.48
1.46
1.45
1.43
1.42
1.25
1.24
1.22
1.21
0.93
0.92
0.91
1.05
1.06
1.06
1.00
1.00
1.06
1.00
12.19
24.15
1.07
f1 (ppm)


162.74
138.16
127.67
126.08
125.87
83.44
83.21
42.72
24.88
24.79
24.71
24.50
f1 (ppm)



9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7.71
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3.78
3.76
3.75
3.74
3.72
3.37
3.36
3.36
3.35
3.34
3.33
3.32
1.64
1.63
1.61
1.60
1.23
1.22
1.21
1.20
1.20
0.91
0.89
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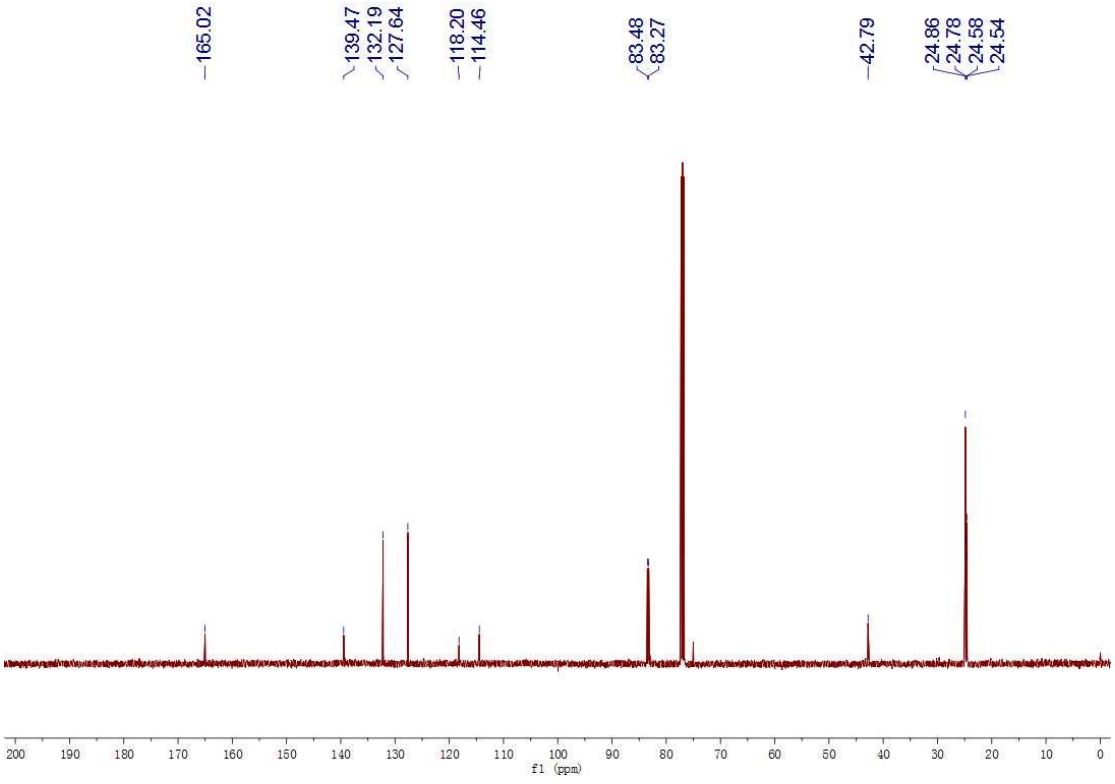
2.00
1.01
1.02
1.03
1.00
24.00
12.07
1.00
f1 (ppm)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83.27
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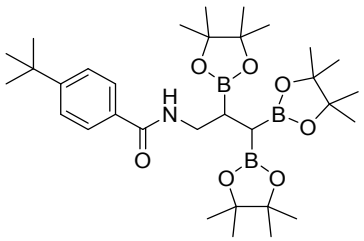
24.78
24.58
24.54
f1 (ppm)



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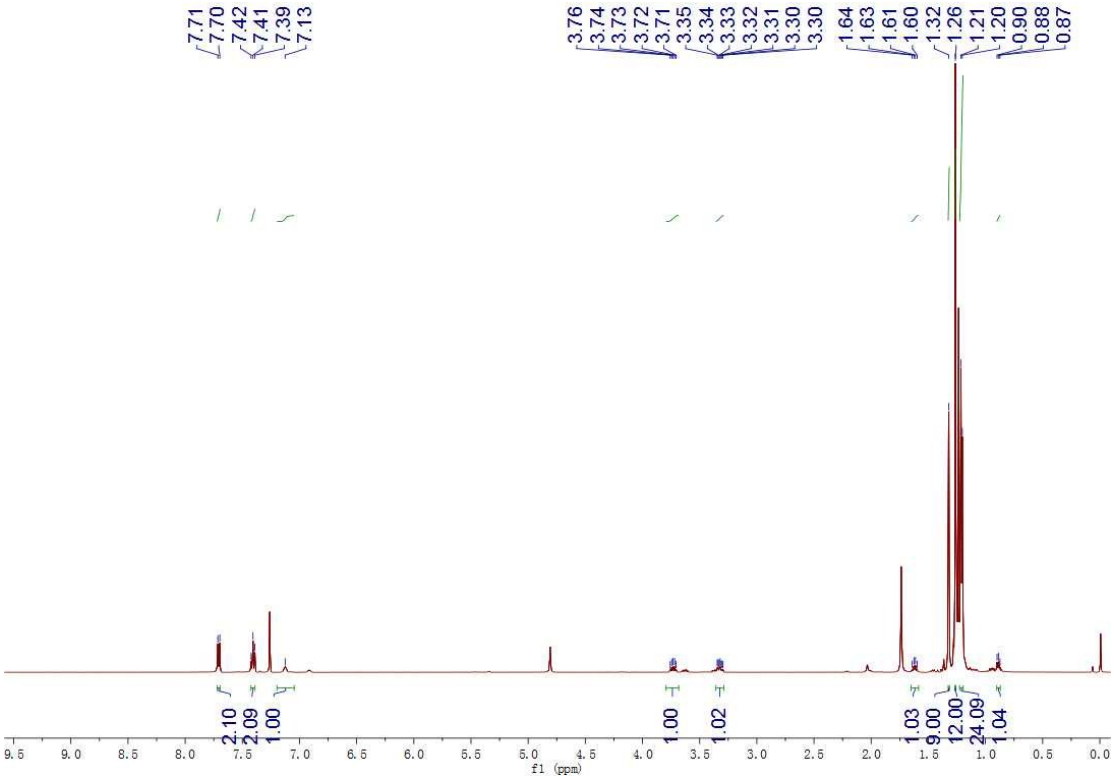
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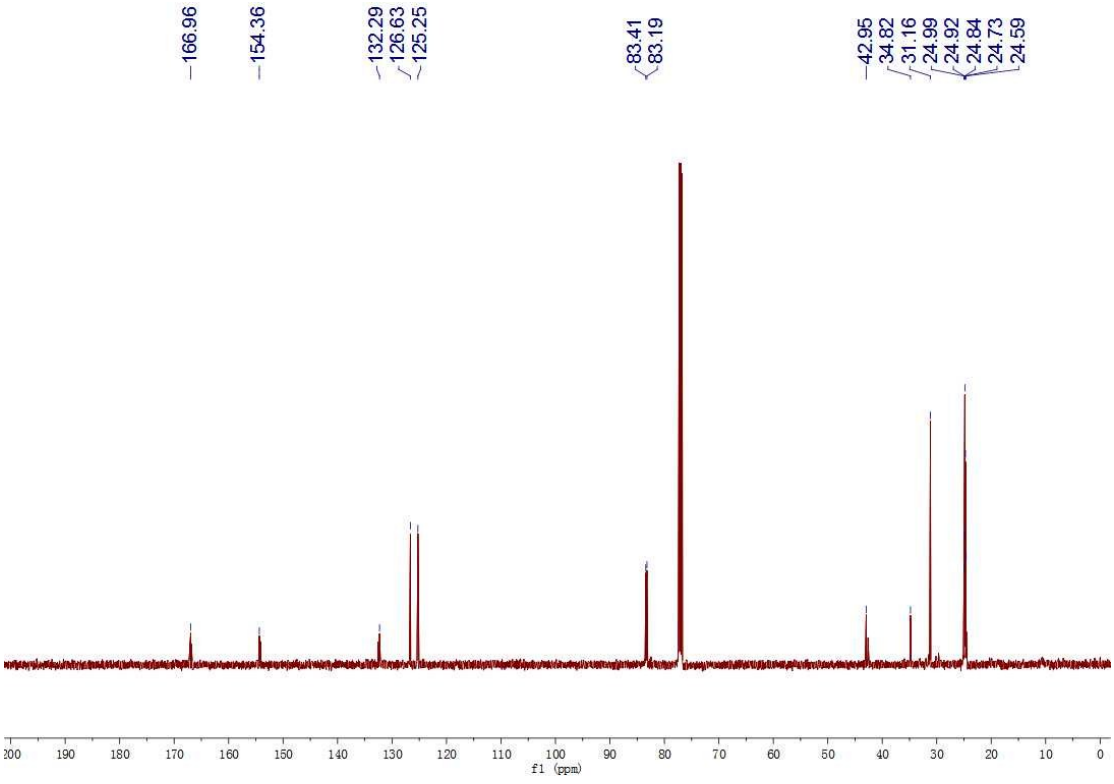
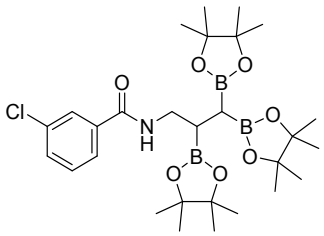
7.70
7.42
7.41
7.39
7.13
3.76
3.74
3.73
3.72
3.71
3.35
3.34
3.33
3.32
3.31
3.30
3.30
1.64
1.63
1.61
1.60
1.32
1.26
1.21
1.20
0.90
0.88
0.87
2.10
2.09
1.00
1.00
1.02
1.03
9.00
12.00
24.09
1.04
f1 (ppm)


166.96
154.36
132.29
126.63
125.25
83.41
83.19
42.95
34.82
31.16
24.99
24.92
24.84
24.73
24.59
f1 (ppm)



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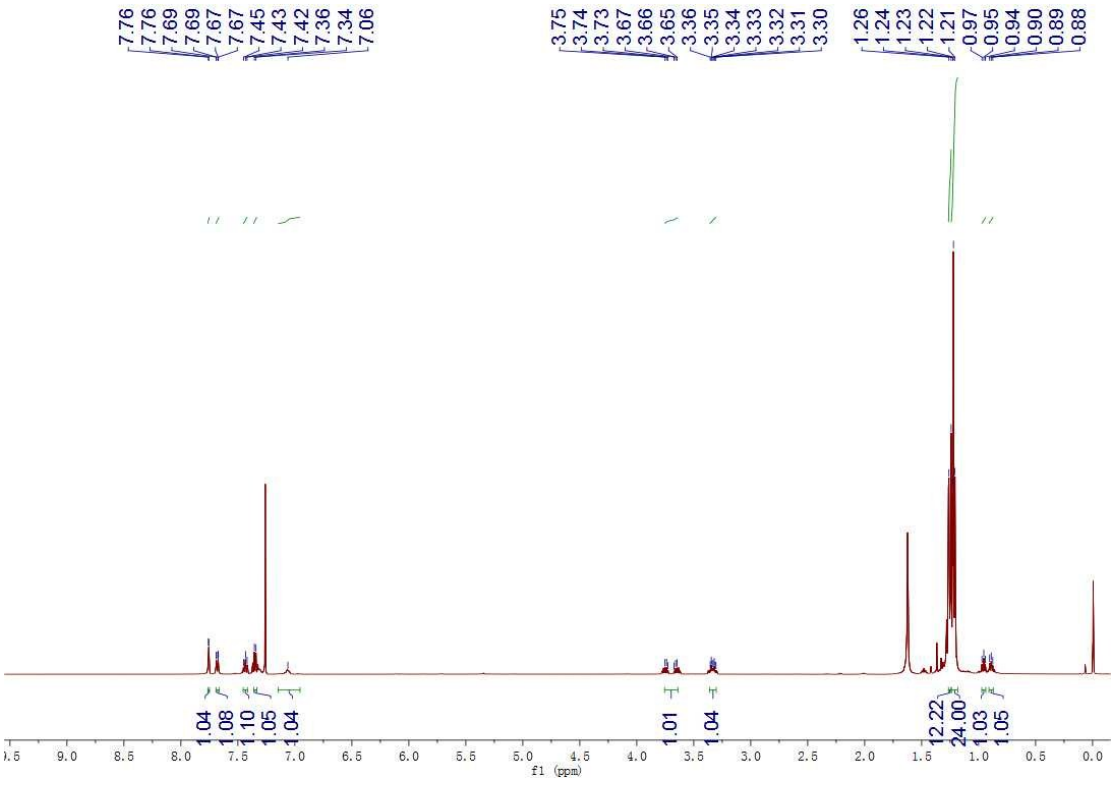
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7.69
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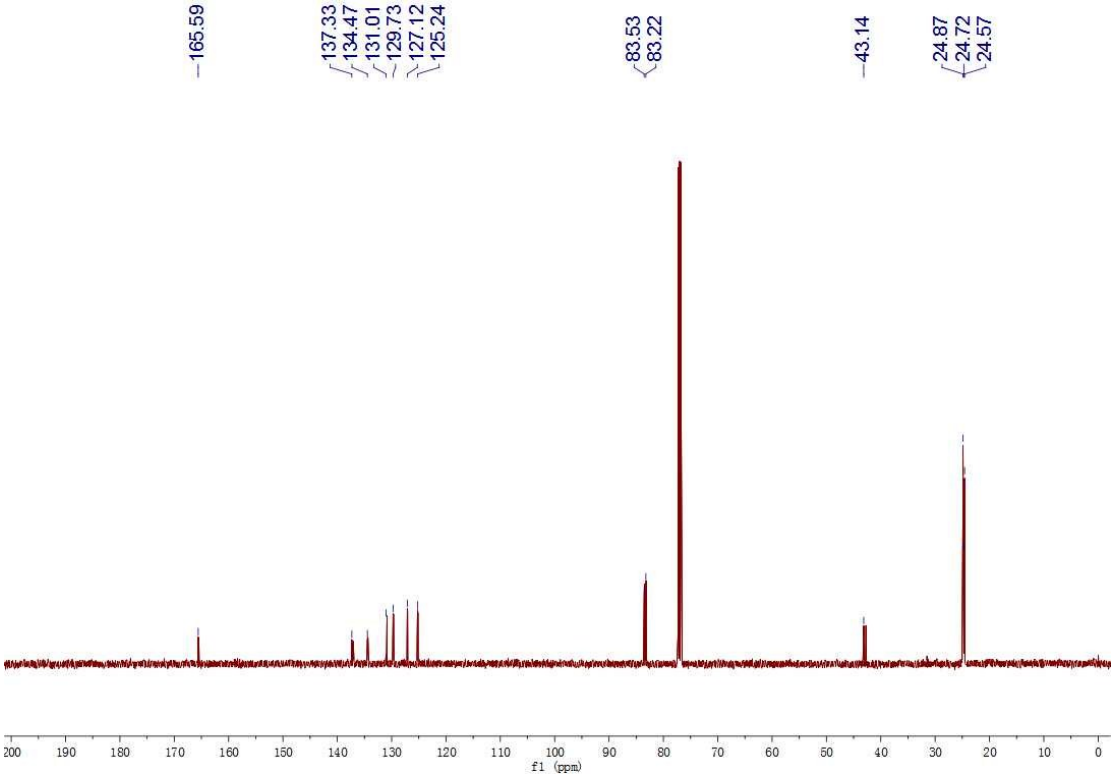
7.67
7.45
7.43
7.42
7.36
7.34
7.06
3.75
3.74
3.73
3.67
3.66
3.65
3.36
3.35
3.34
3.33
3.32
3.31
3.30
1.26
1.24
1.23
1.22
1.21
0.97
0.95
0.94
0.90
0.89
0.88
1.04
1.08
1.10
1.05
1.04
1.01
1.04
12.22
24.00
1.03
1.05
f1 (ppm)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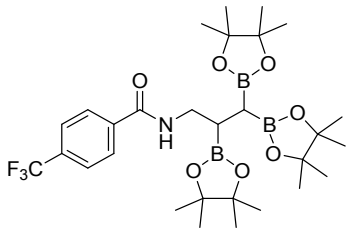
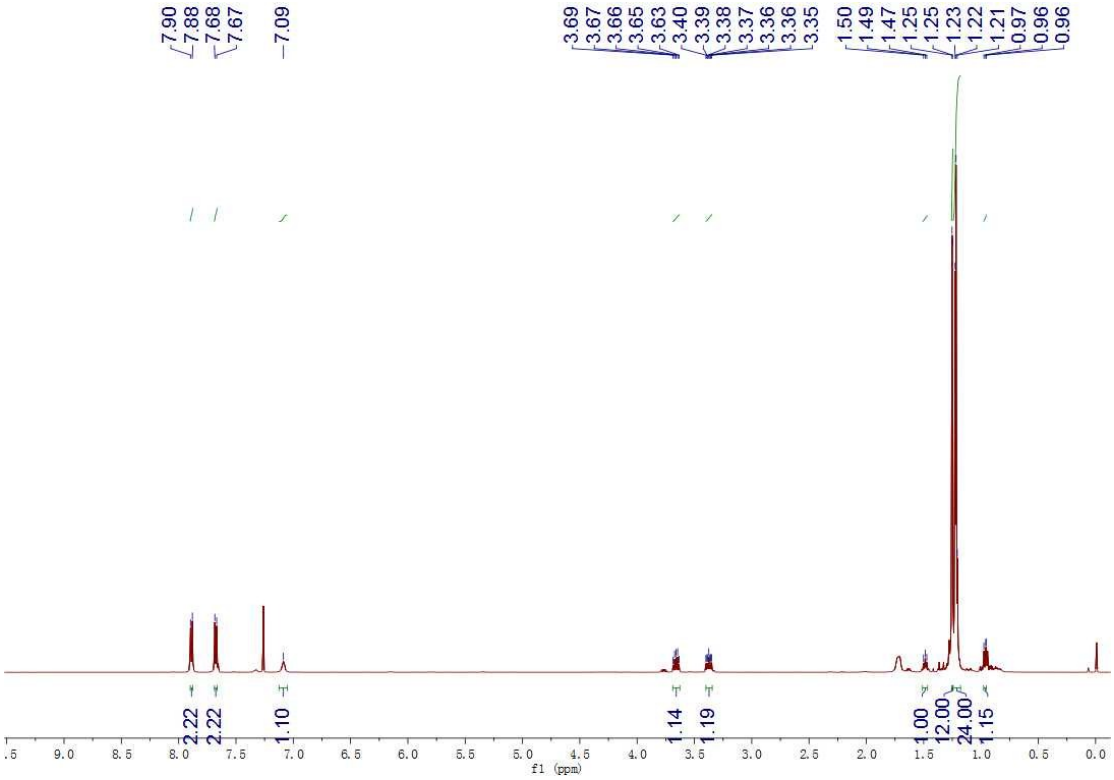
137.33
134.47
131.01
129.73
127.12
125.24
83.53
83.22
43.14
24.87
24.72
24.57
f1 (ppm)



12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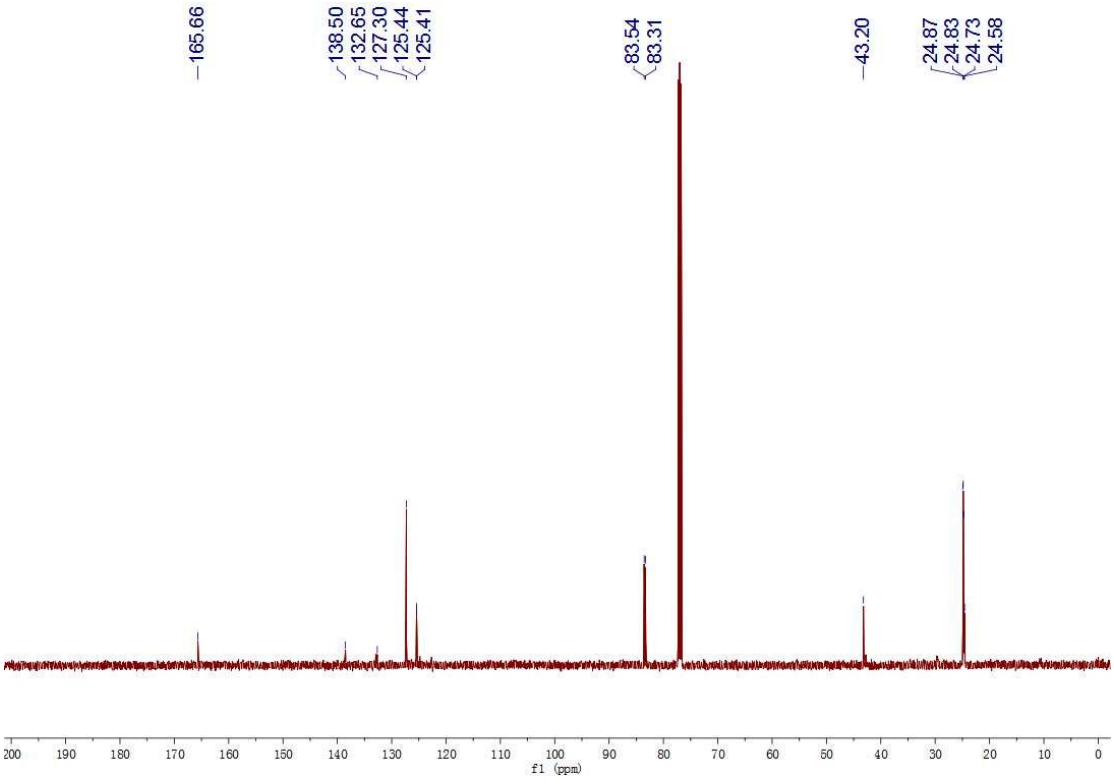
7.09
3.69
3.67
3.66
3.65
3.63
3.40
3.39
3.38
3.37
3.36
3.36
3.35
1.50
1.49
1.47
1.25
1.25
1.23
1.22
1.21
0.97
0.96
0.96
2.22
2.22
1.10
1.14
1.19
1.00
12.00
24.00
1.15
f1 (ppm)


165.66
138.50
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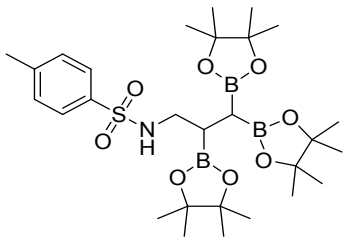
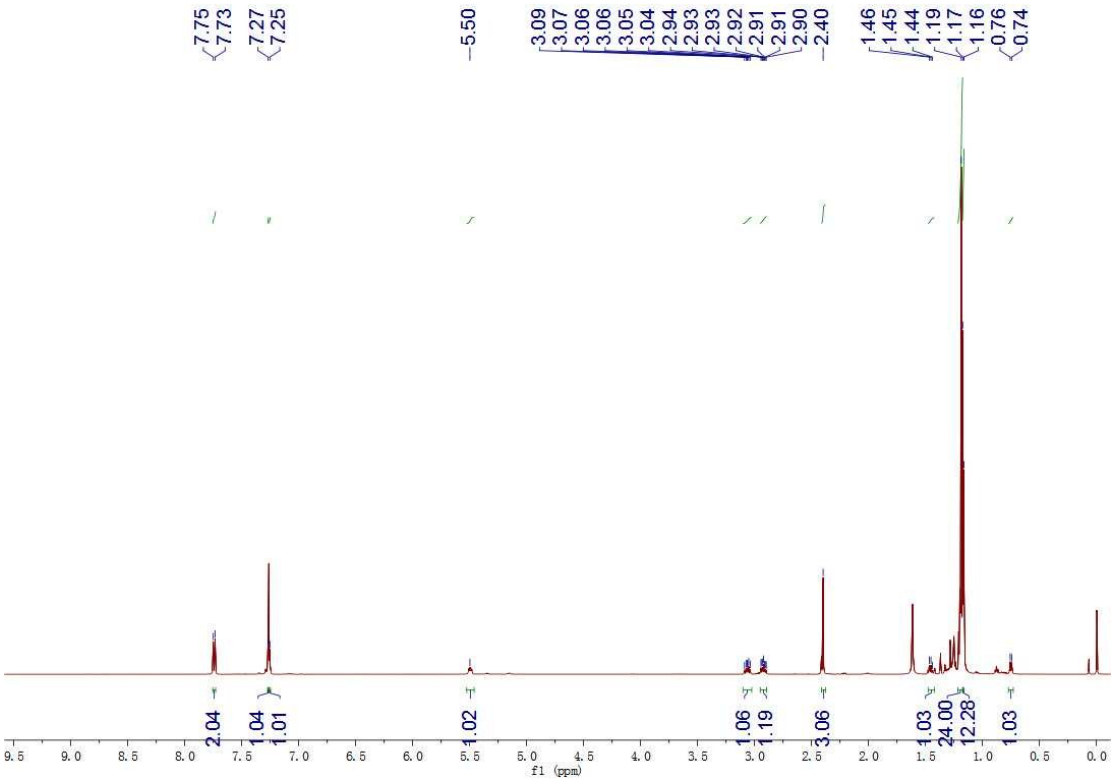
127.30
125.44
125.41
83.54
83.31
43.20
24.87
24.83
24.73
24.58
f1 (ppm)



13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3.07
3.06
3.06
3.05
3.04
2.94
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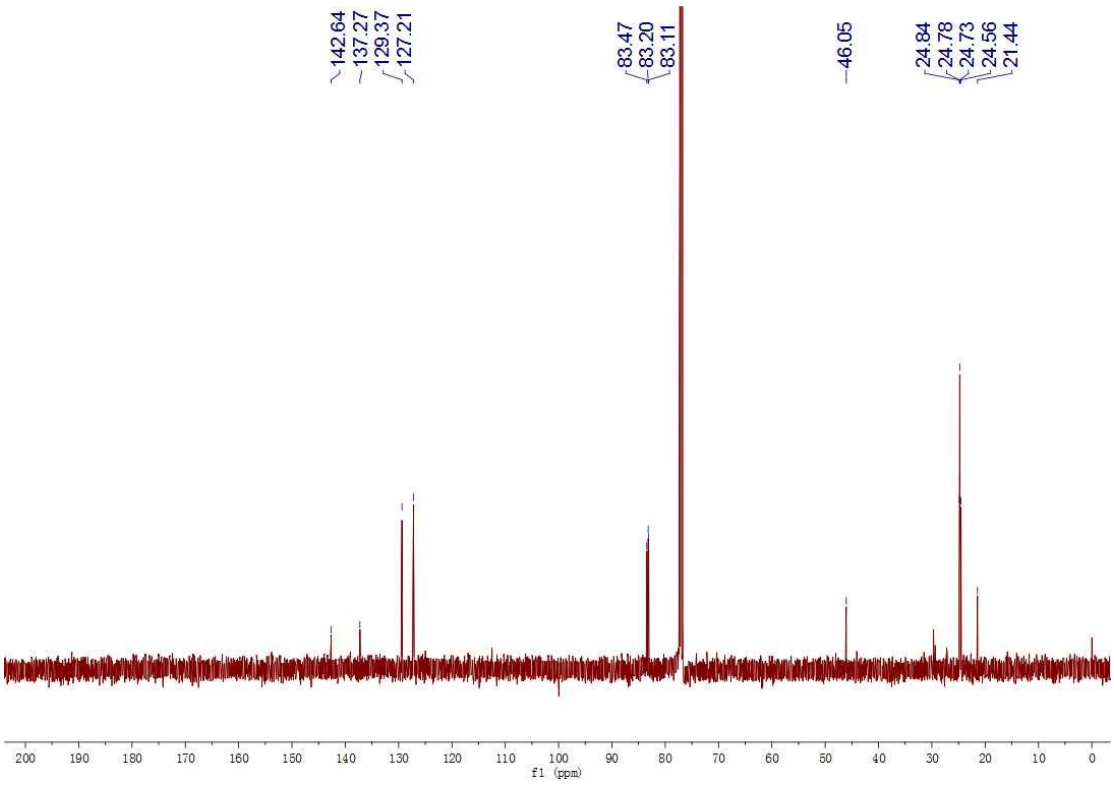
2.93
2.92
2.91
2.91
2.90
2.40
1.46
1.45
1.44
1.19
1.17
1.16
0.76
0.74
2.04
1.04
1.01
1.02
1.06
1.19
3.06
1.03
24.00
12.28
1.03
f1 (ppm)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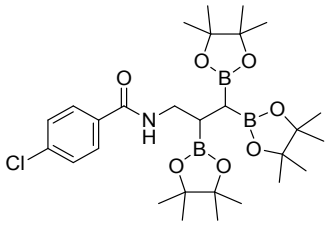
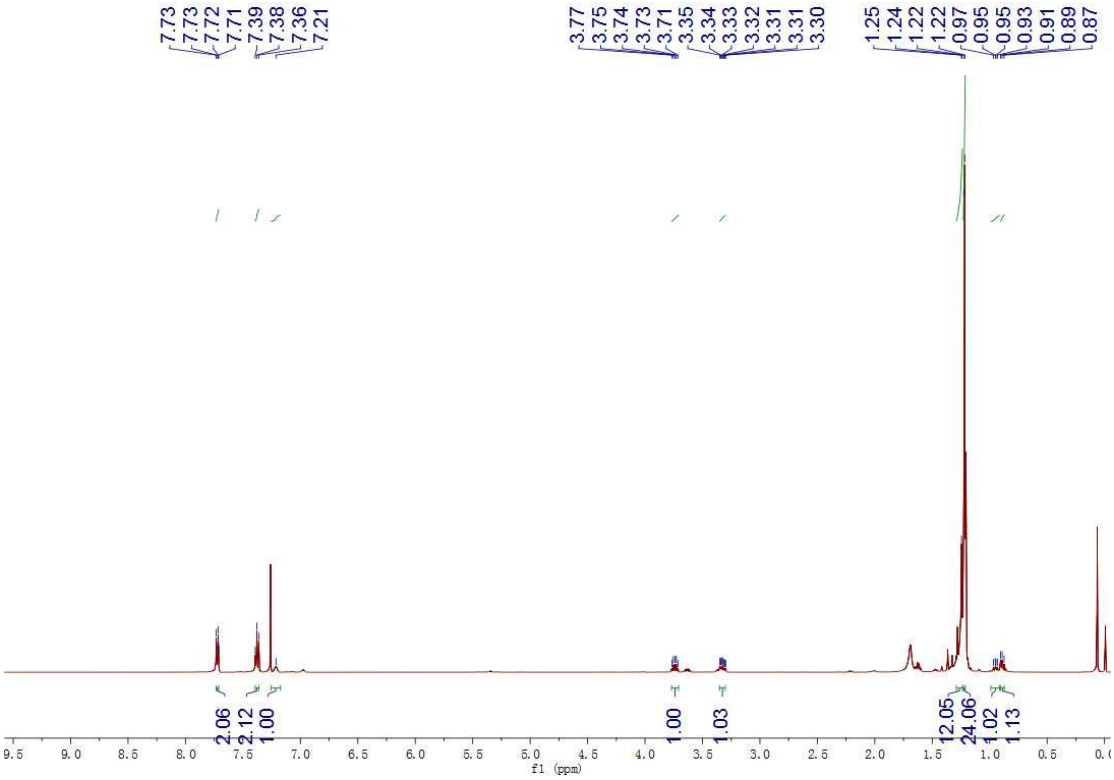
83.20
83.11
46.05
24.84
24.78
24.73
24.56
21.44
f1 (ppm)



14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7.21
3.77
3.75
3.74
3.73
3.71
3.35
3.34
3.33
3.32
3.31
3.31
3.30
1.25
1.24
1.22
1.22
0.97
0.95
0.95
0.93
0.91
0.89
0.87
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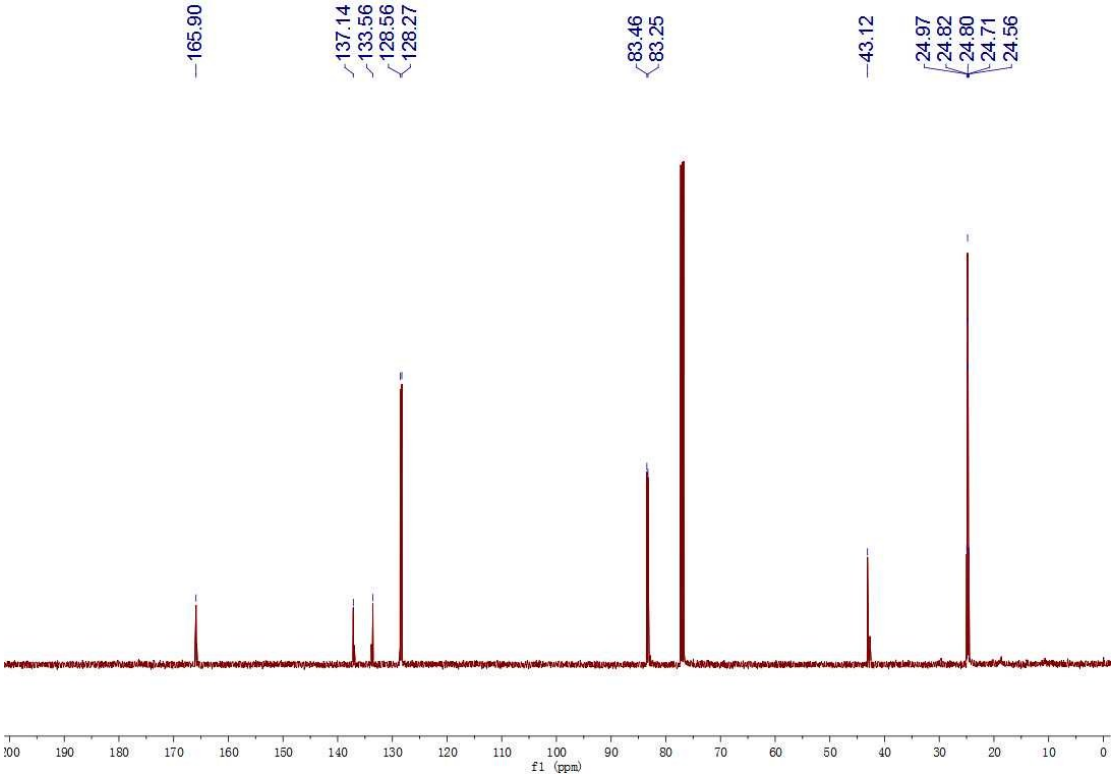
2.12
1.00
1.00
1.03
12.05
24.06
1.02
1.13
f1 (ppm)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128.27
83.46
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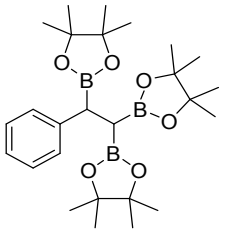
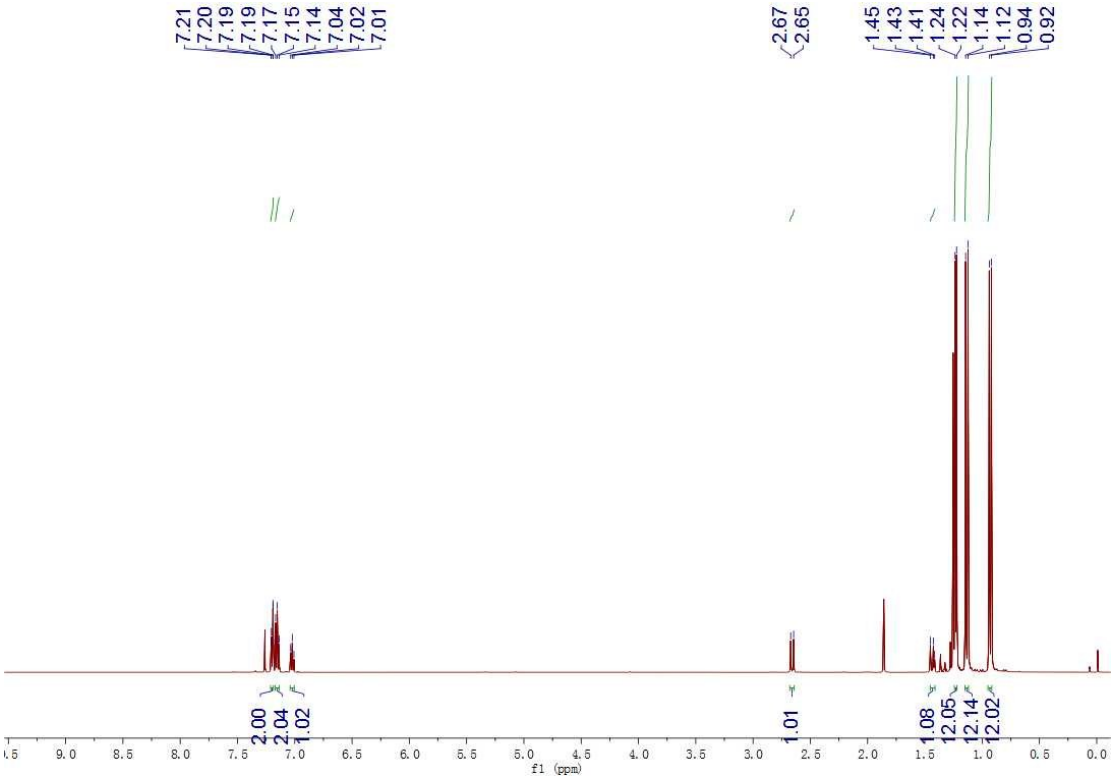
43.12
24.97
24.82
24.80
24.71
24.56
f1 (ppm)



15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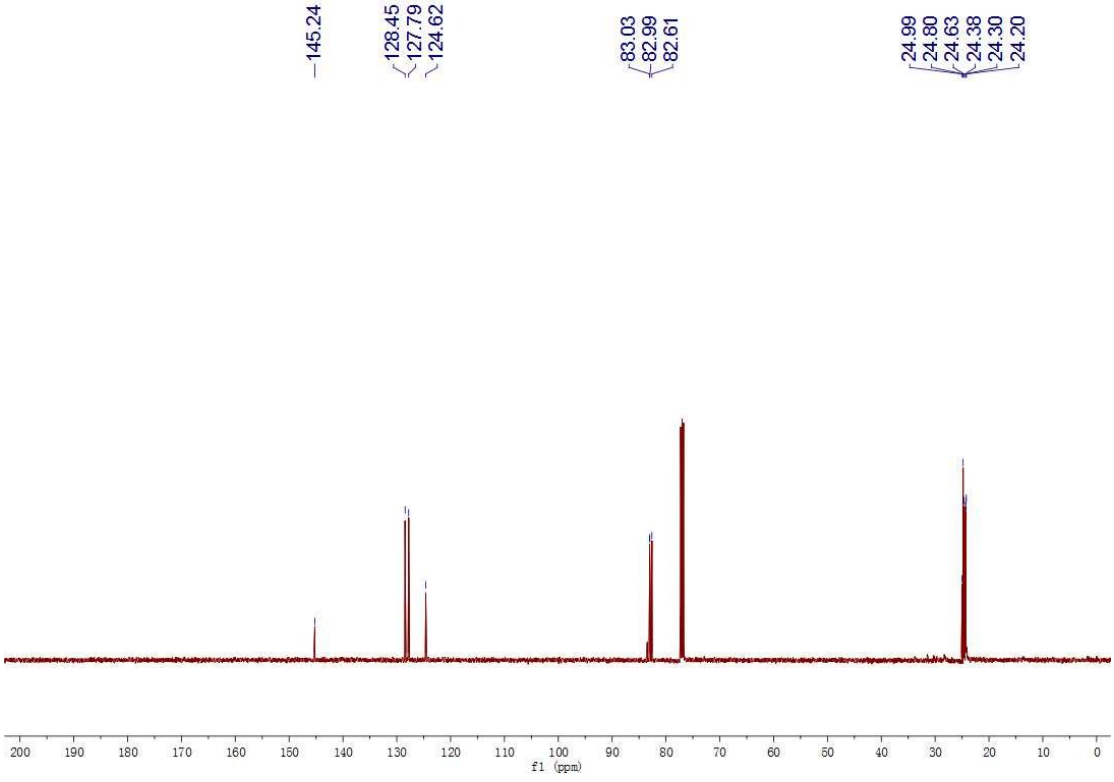
7.19
7.19
7.17
7.15
7.14
7.04
7.02
7.01
2.67
2.65
1.45
1.43
1.41
1.24
1.22
1.14
1.12
0.94
0.92
2.00
2.04
1.02
1.01
1.08
12.05
12.14
12.02
f1 (ppm)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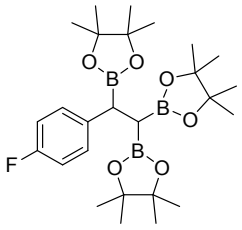
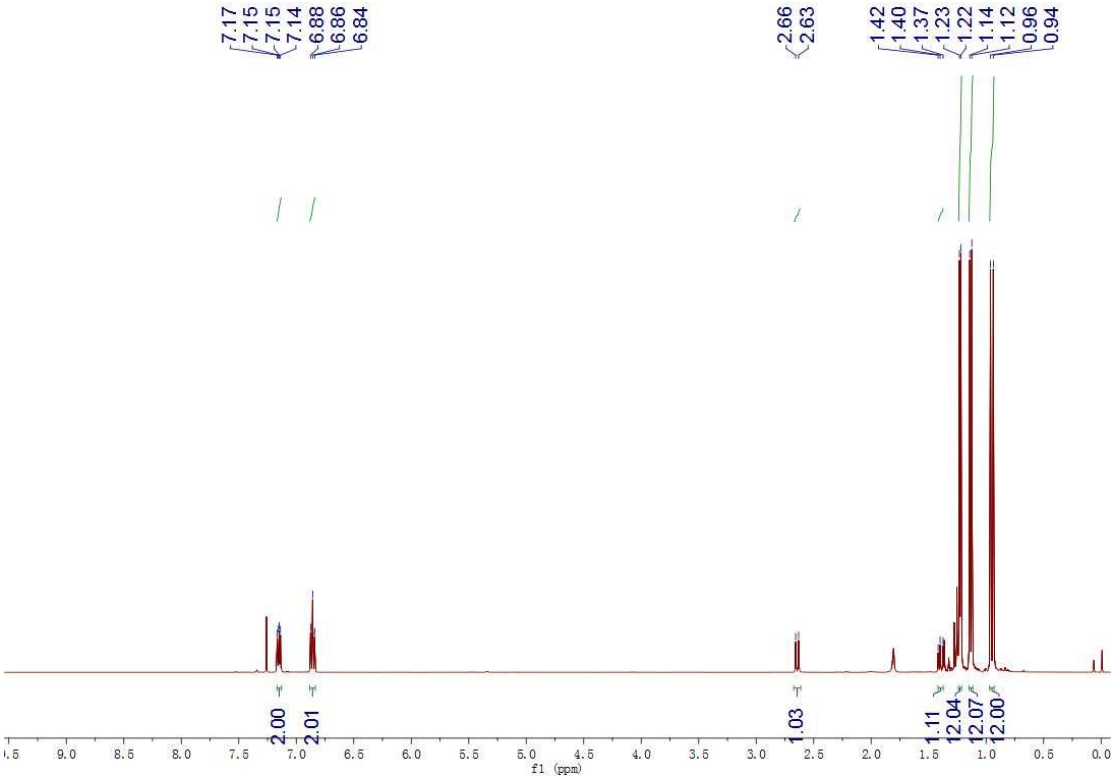
82.61
24.99
24.80
24.63
24.38
24.30
24.20
f1 (ppm)


O
B
O
O
B
O
F
B
O
O

16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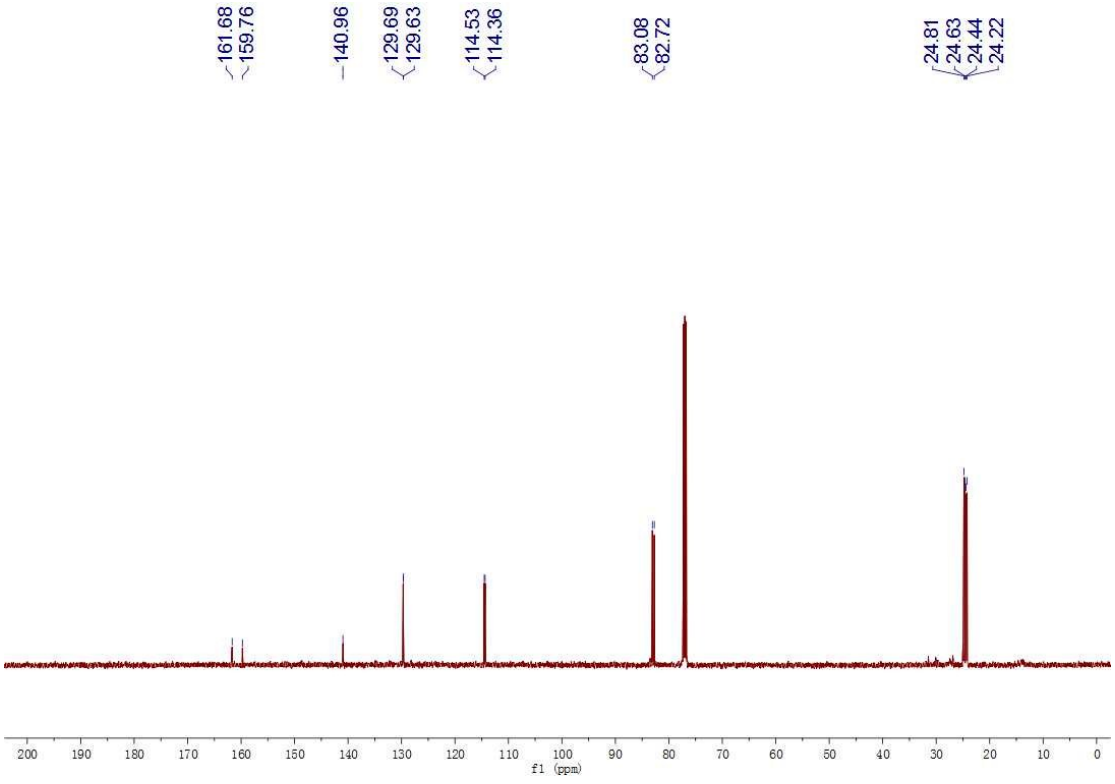
6.86
6.84
2.66
2.63
1.42
1.40
1.37
1.23
1.22
1.14
1.12
0.96
0.94
2.00
2.01
1.03
1.11
12.04
12.07
12.00
f1 (ppm)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83.08
82.72
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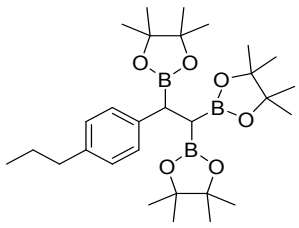
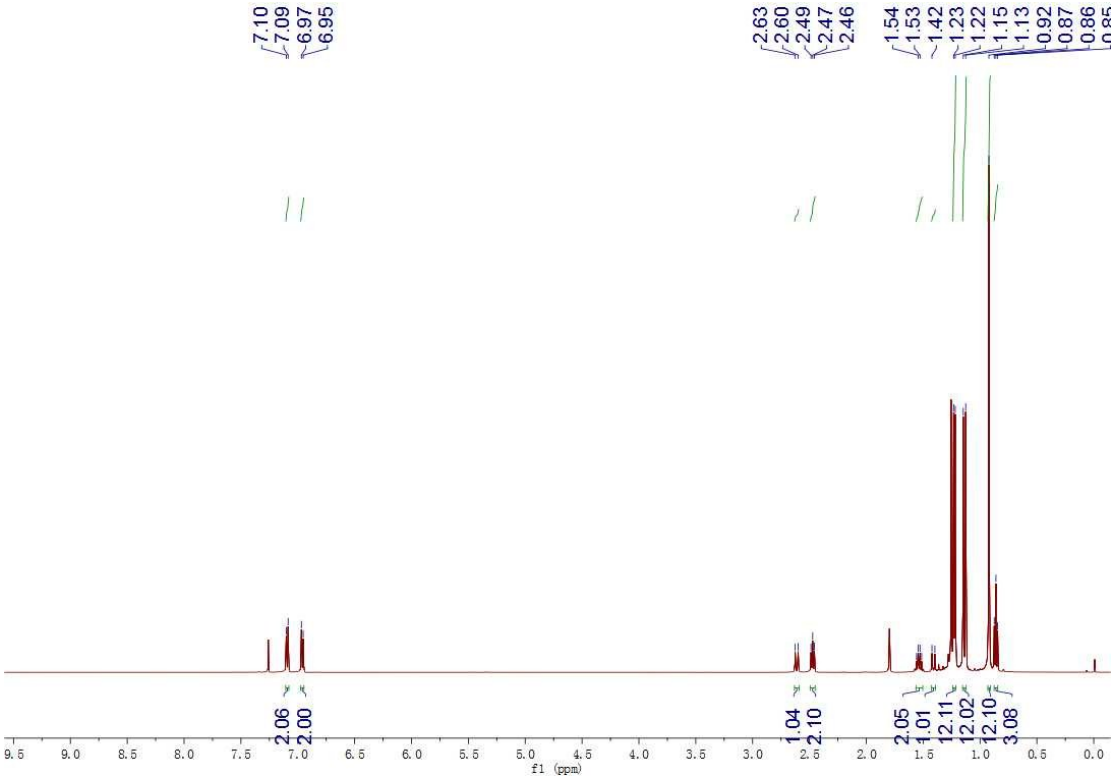
24.63
24.44
24.22
f1 (ppm)



17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6.97
6.95
2.63
2.60
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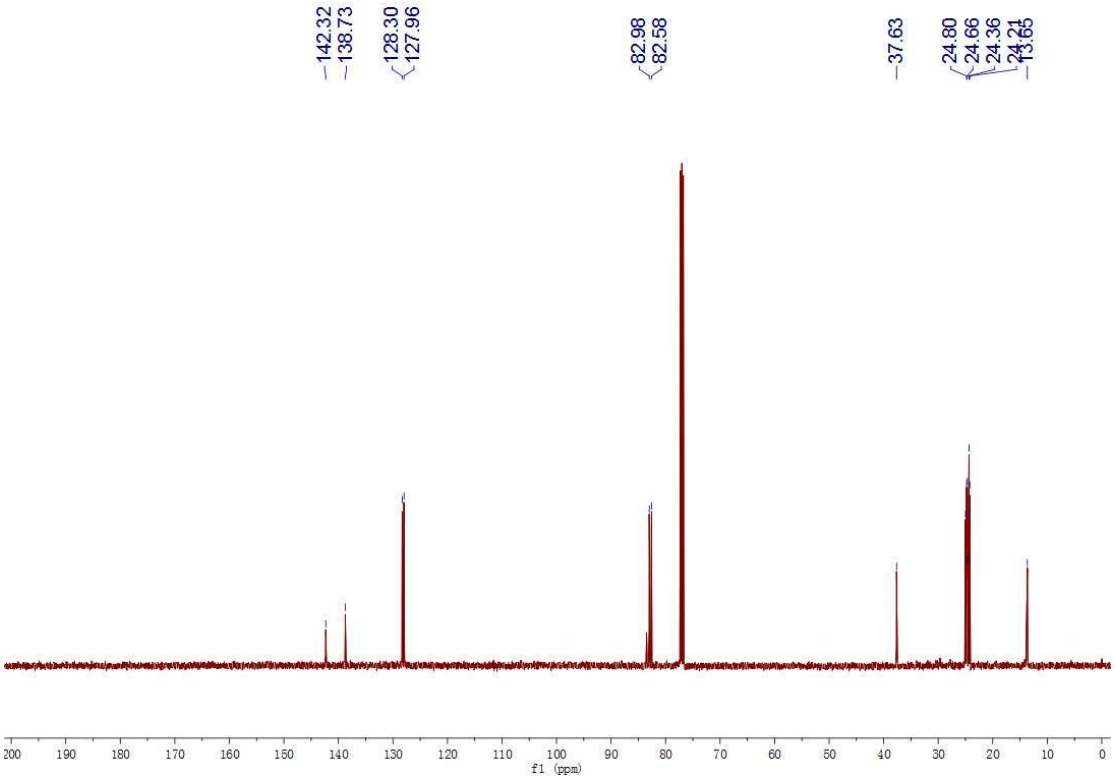
2.47
2.46
1.54
1.53
1.42
1.23
1.22
1.15
1.13
0.92
0.87
0.86
2.06
2.00
1.04
2.10
2.05
1.01
12.11
12.02
12.10
3.08
f1 (ppm)


142.32
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128.30
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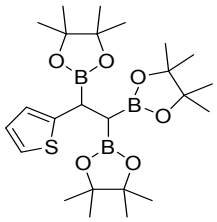
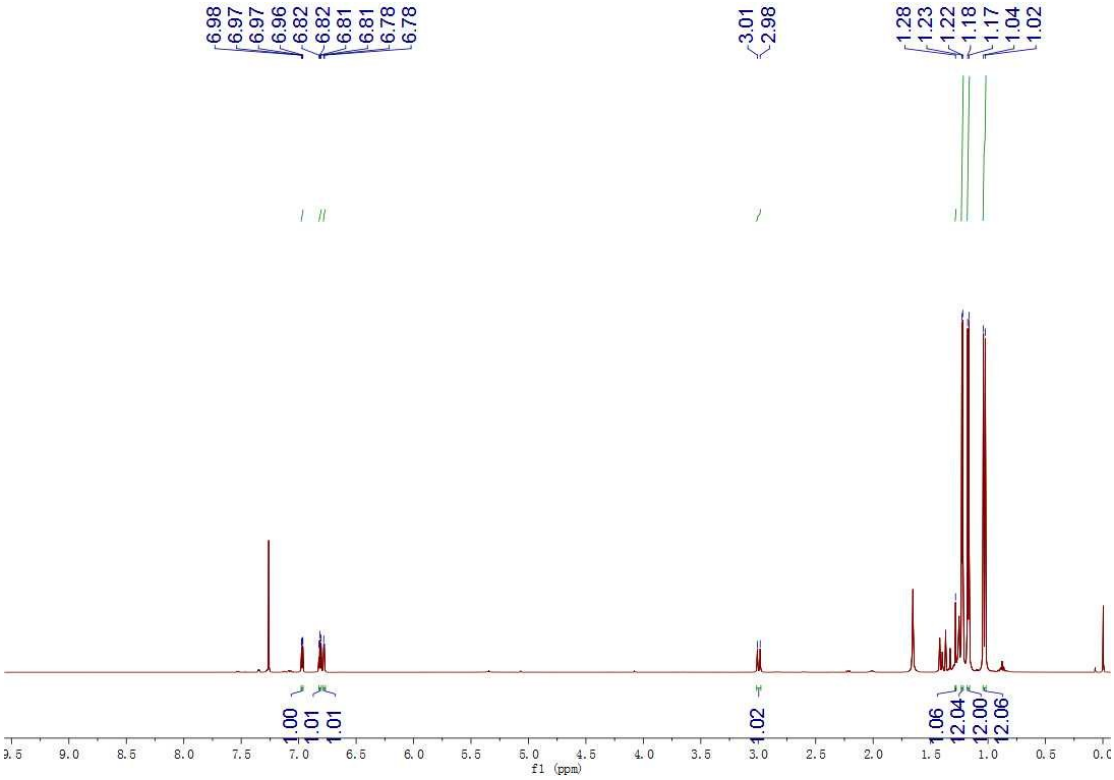
82.58
37.63
24.80
24.66
24.36
24.21
13.85
f1 (ppm)



18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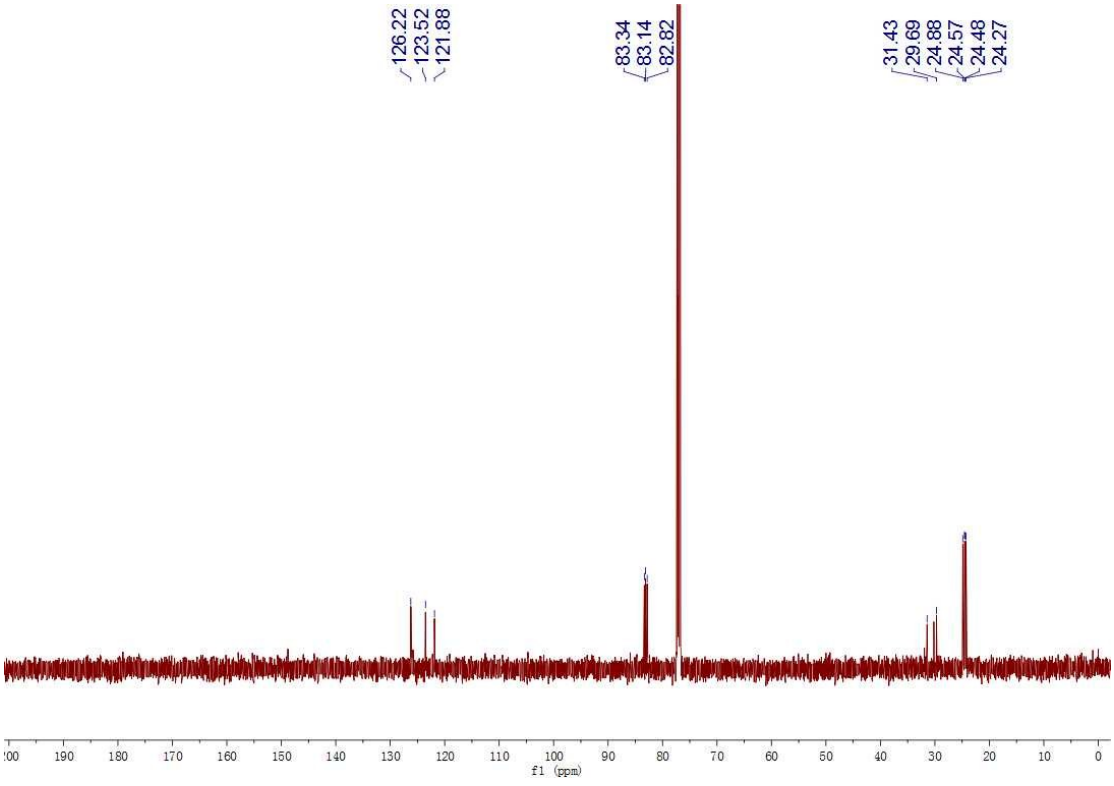
6.97
6.96
6.82
6.82
6.81
6.81
6.78
6.78
3.01
2.98
1.28
1.23
1.22
1.18
1.17
1.04
1.02
1.00
1.01
1.01
1.02
1.06
12.04
12.00
12.06
f1 (ppm)


126.22
123.52
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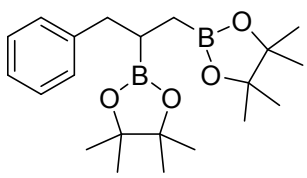
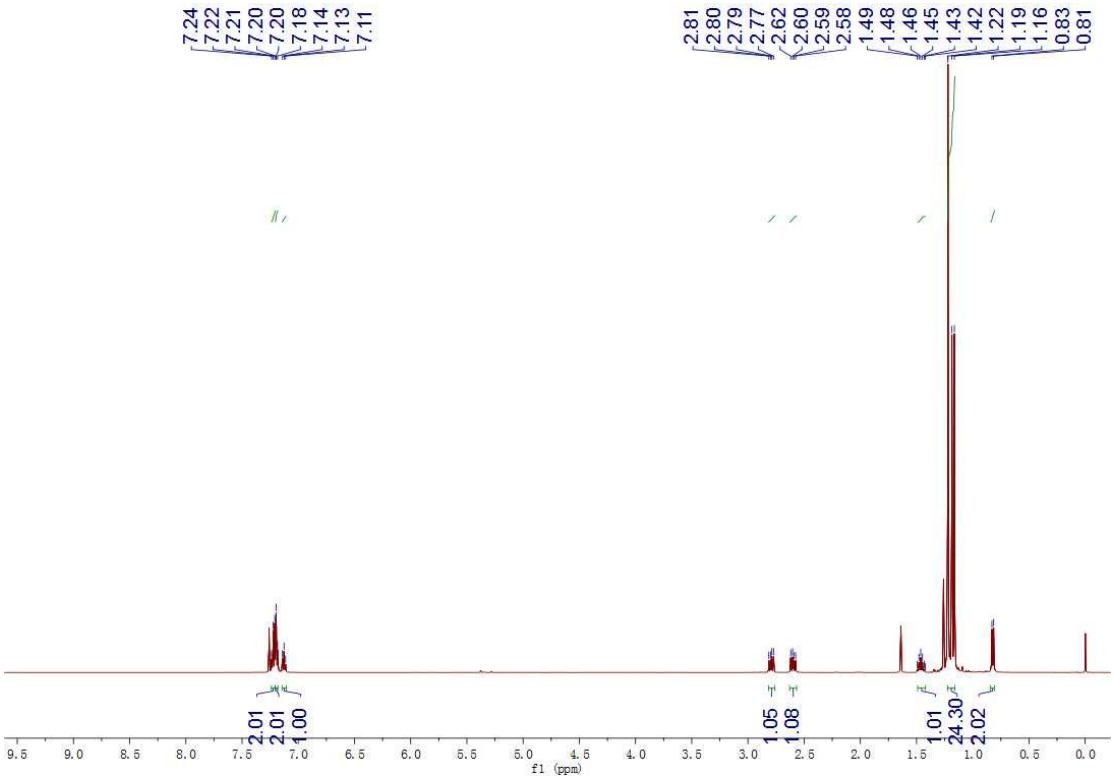
83.14
82.82
31.43
29.69
24.88
24.57
24.48
24.27
f1 (ppm)



19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7.13
7.11
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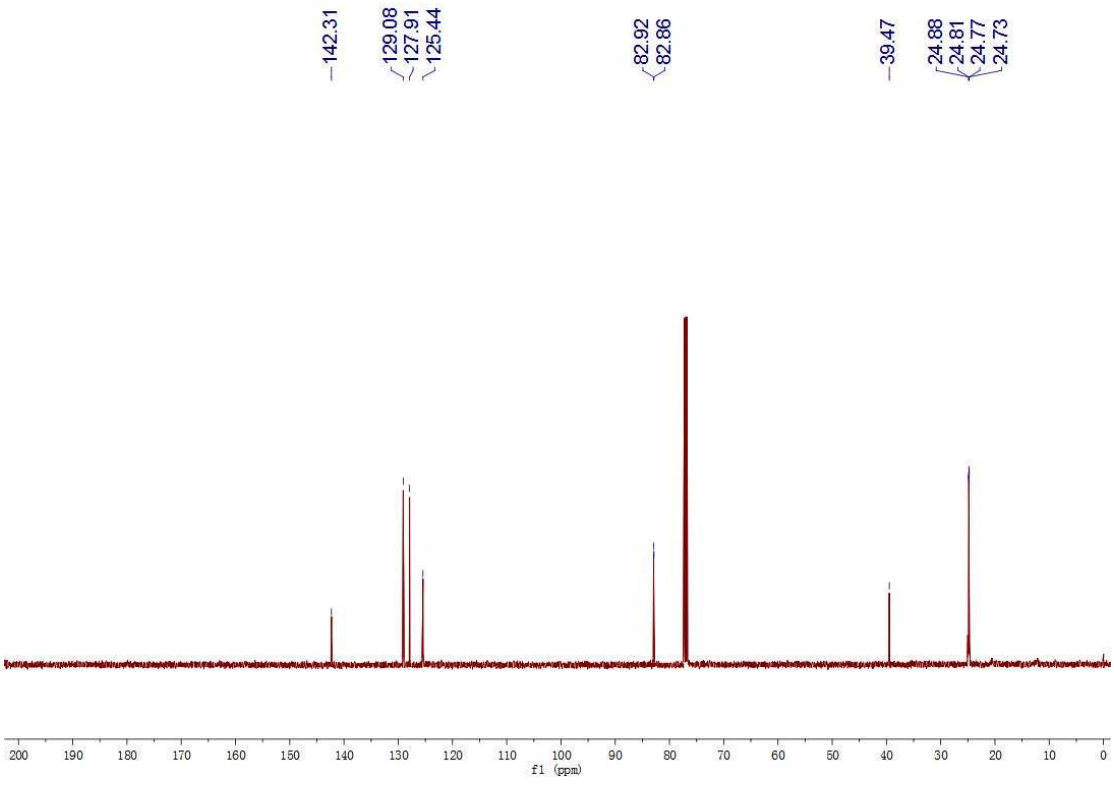
2.80
2.79
2.77
2.62
2.60
2.59
2.58
1.49
1.48
1.46
1.45
1.43
1.42
1.22
1.19
1.16
0.83
0.81
2.01
2.01
1.00
1.05
1.08
1.01
24.30
2.02
f1 (ppm)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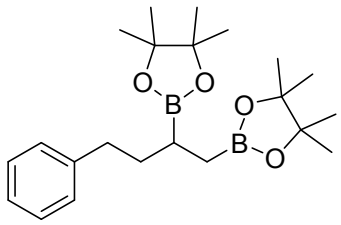
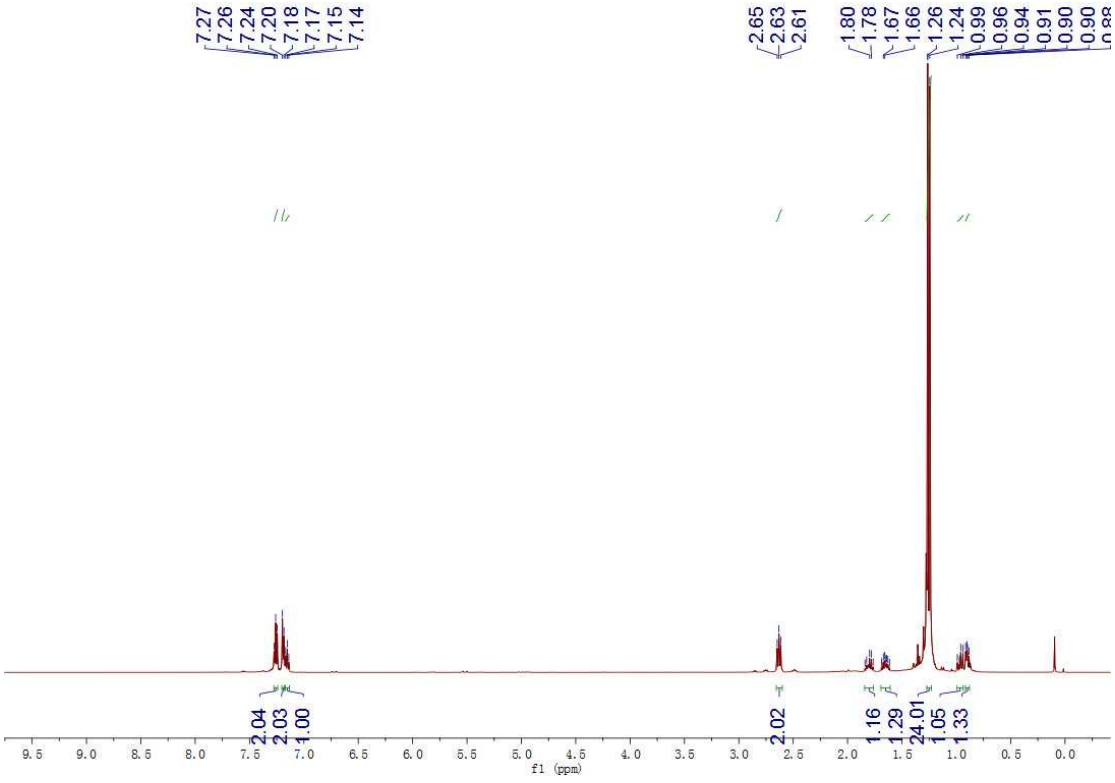
82.92
82.86
39.47
24.88
24.81
24.77
24.73
f1 (ppm)



20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7.18
7.17
7.15
7.14
2.65
2.63
2.61
1.80
1.78
1.67
1.66
1.26
1.24
0.99
0.96
0.94
0.91
0.90
0.90
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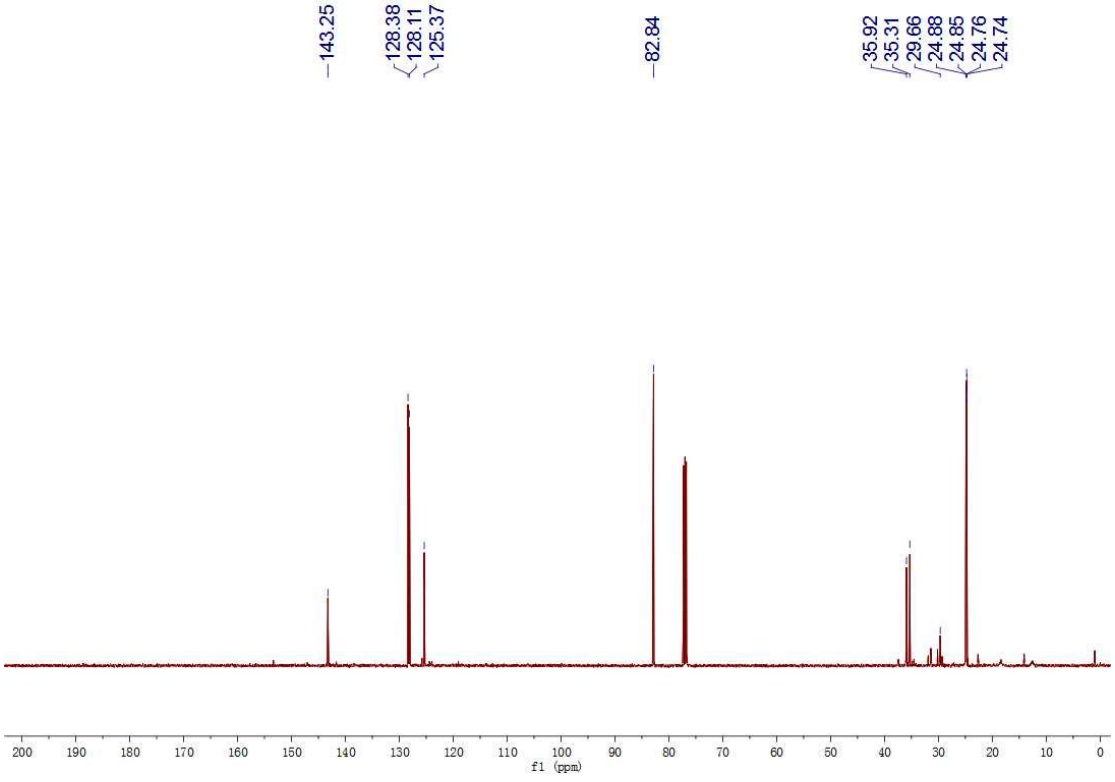
2.03
1.00
2.02
1.16
1.29
24.01
1.05
1.33
f1 (ppm)


143.25
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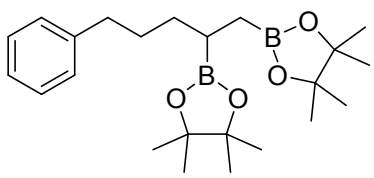
35.31
29.66
24.88
24.85
24.76
24.74
f1 (ppm)



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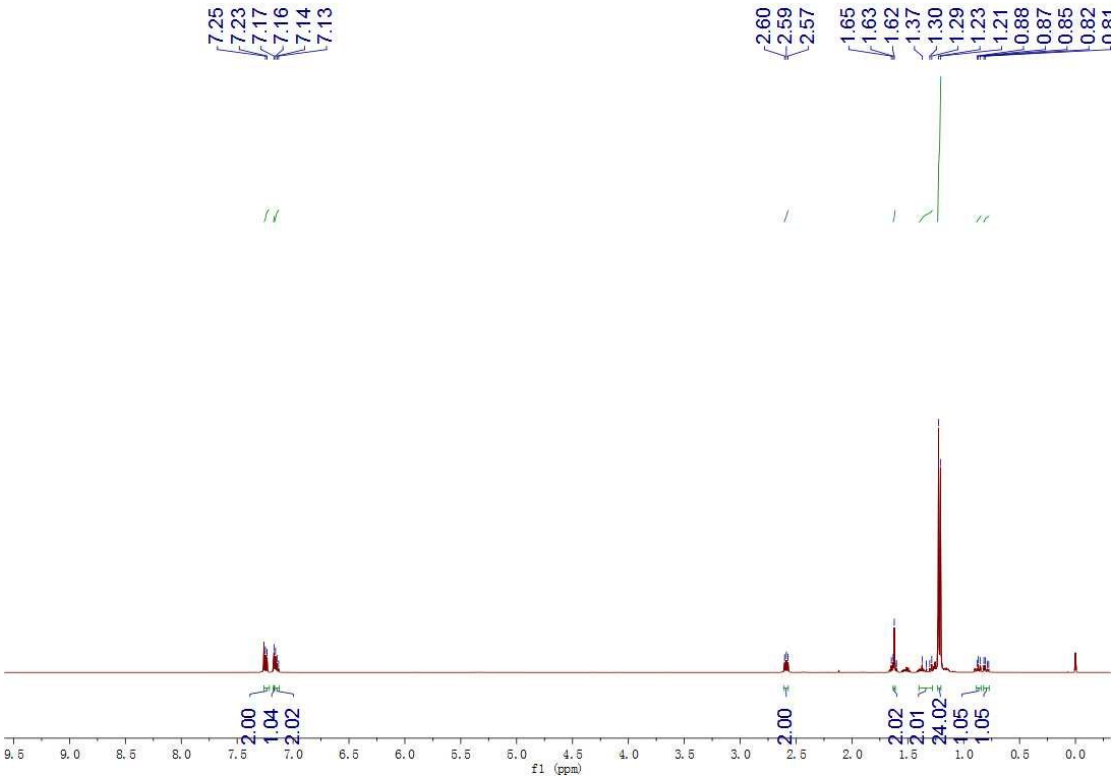
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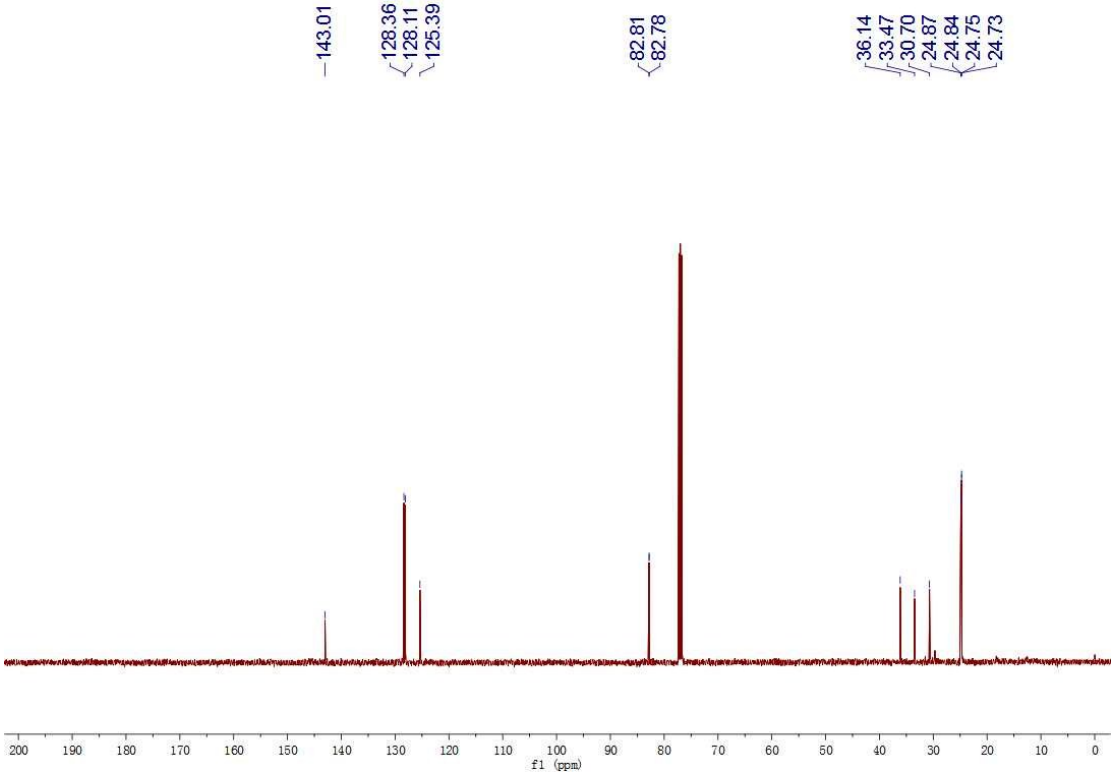
7.23
7.17
7.16
7.14
7.13
2.60
2.59
2.57
1.65
1.63
1.62
1.37
1.30
1.29
1.23
1.21
0.88
0.87
0.85
0.82
2.00
1.04
2.02
2.00
2.02
2.01
24.02
1.05
1.05
f1 (ppm)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128.36
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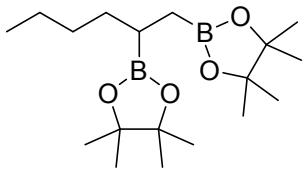
82.78
36.14
33.47
30.70
24.87
24.84
24.75
24.73
f1 (ppm)



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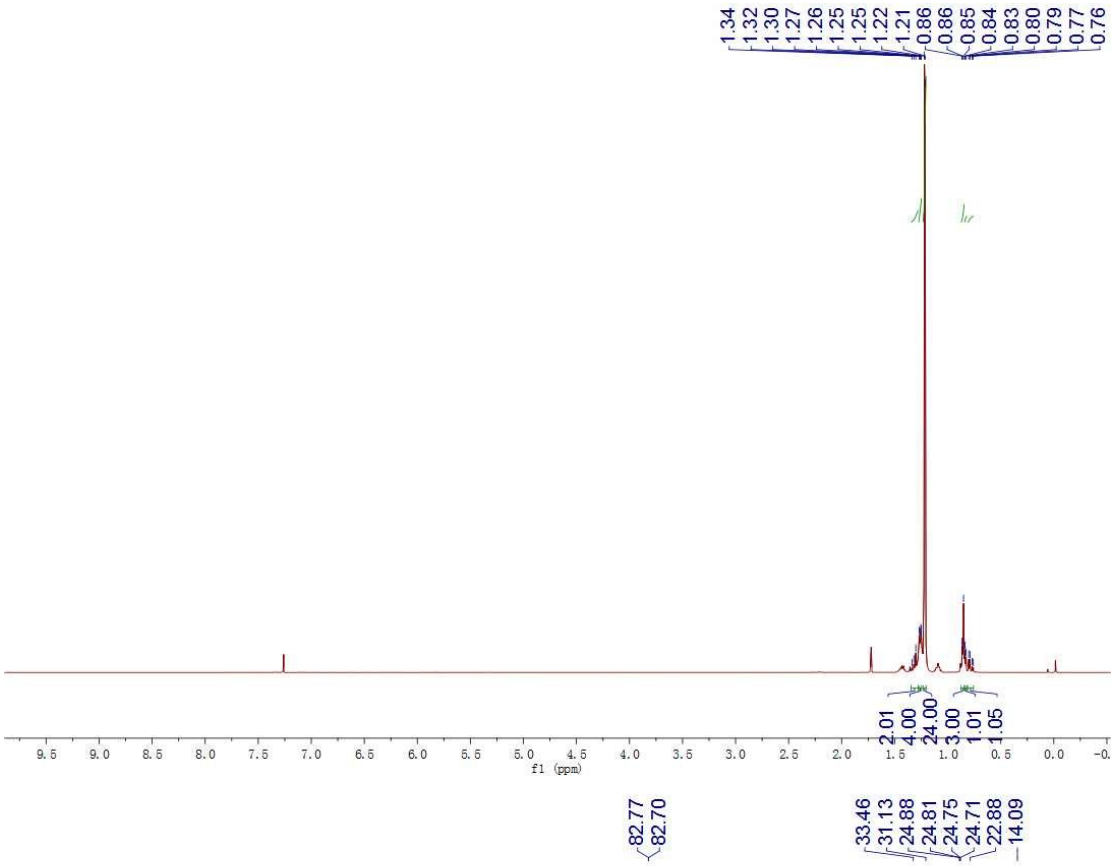
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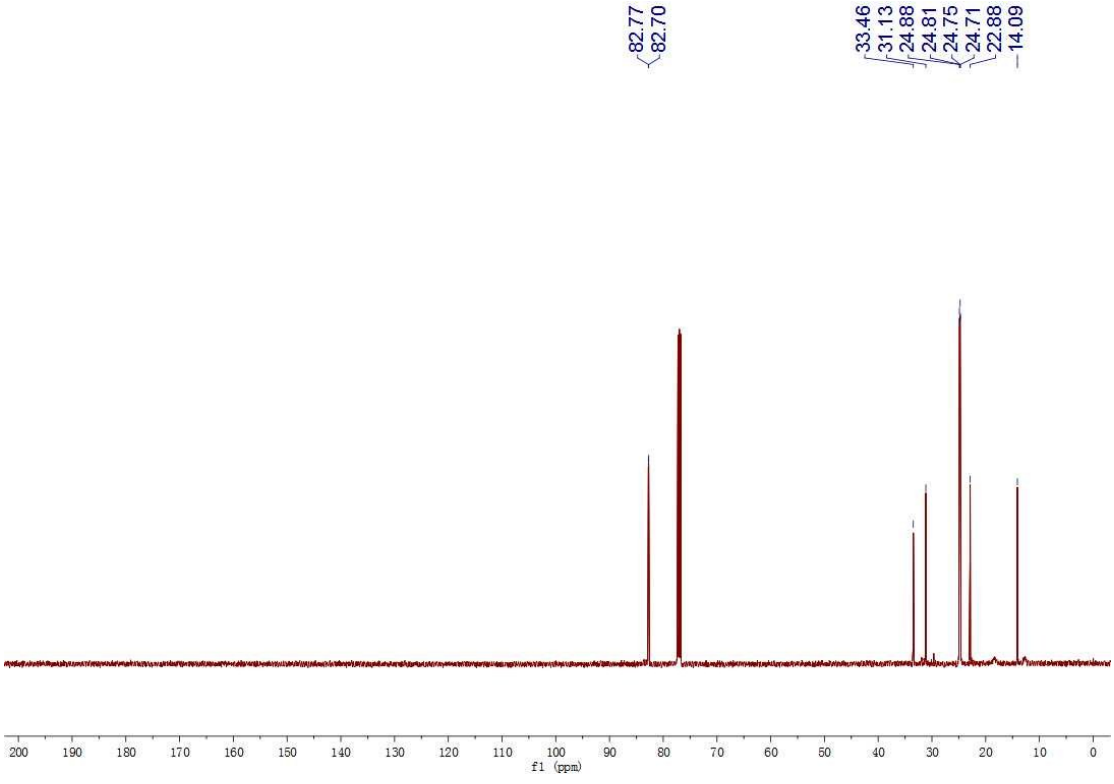
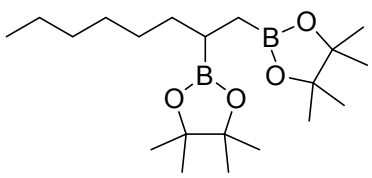
1.32
1.30
1.27
1.26
1.25
1.25
1.22
1.21
0.86
0.86
0.85
0.84
0.83
0.80
0.79
0.77
0.76
2.01
4.00
24.00
3.00
1.01
1.05
f1 (ppm)


82.77
82.70
33.46
31.13
24.88
24.81
24.75
24.71
22.88
14.09
f1 (ppm)



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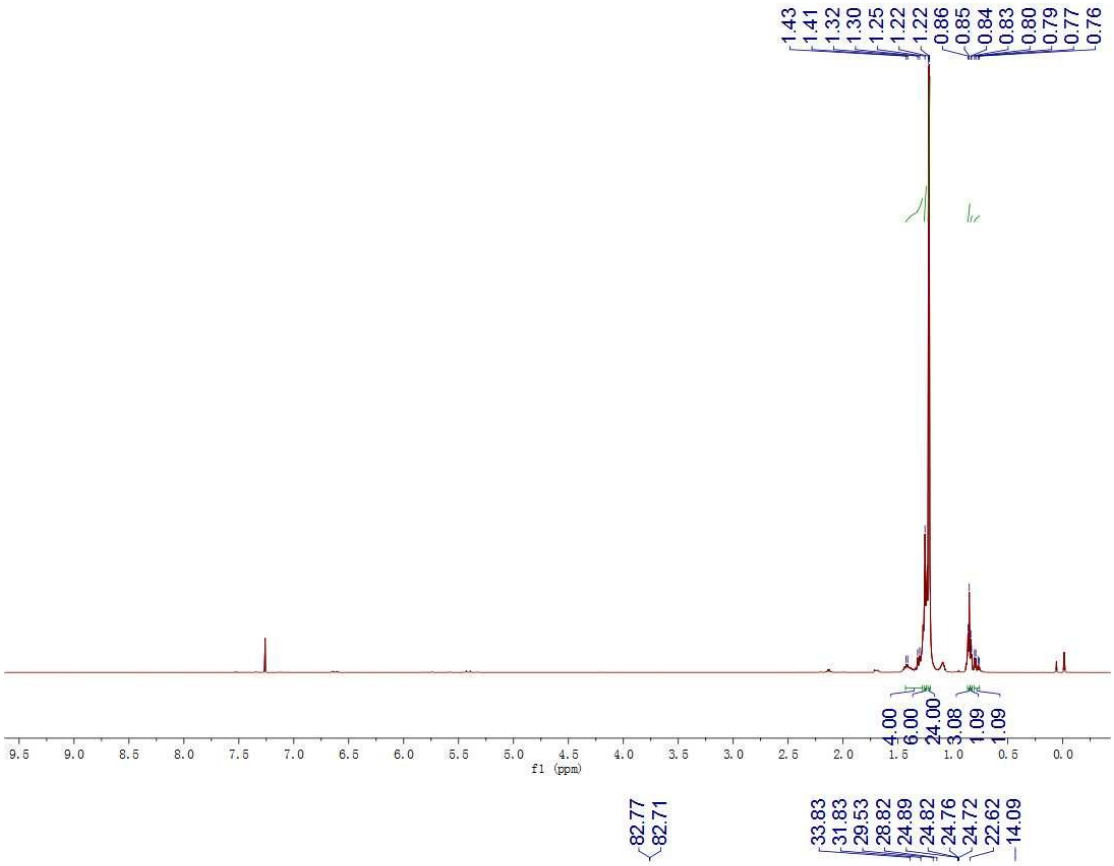
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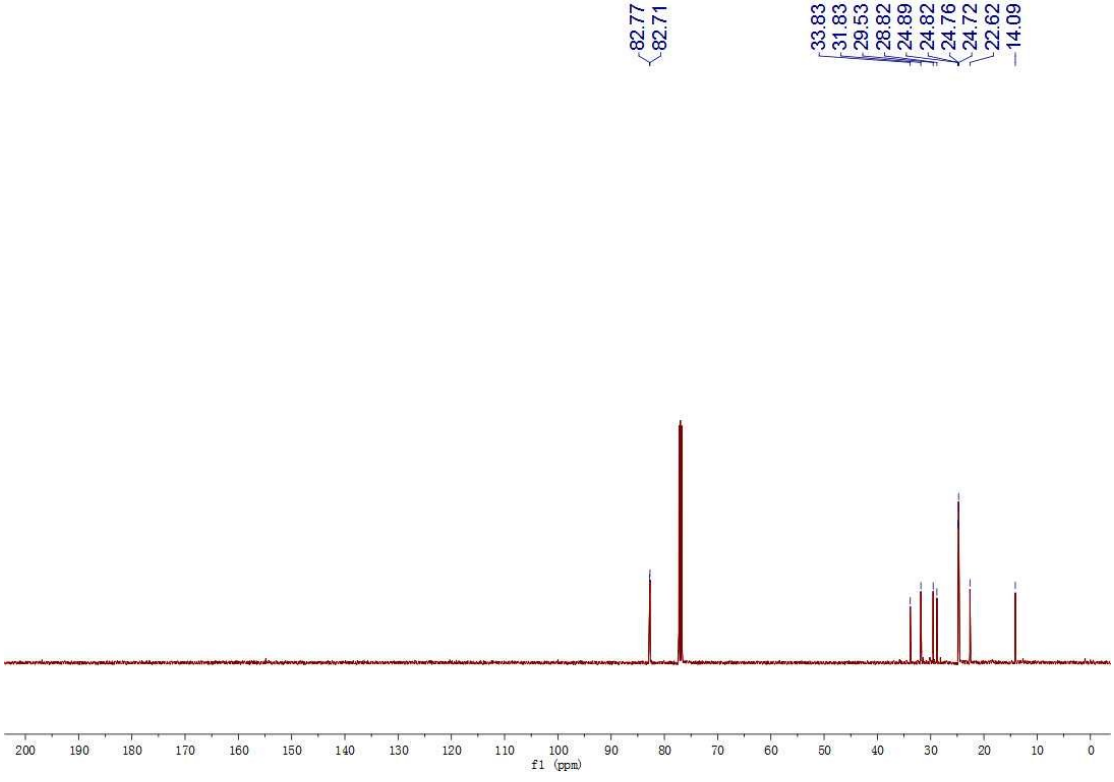
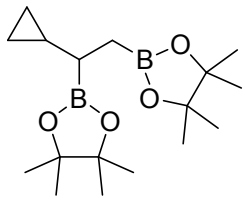
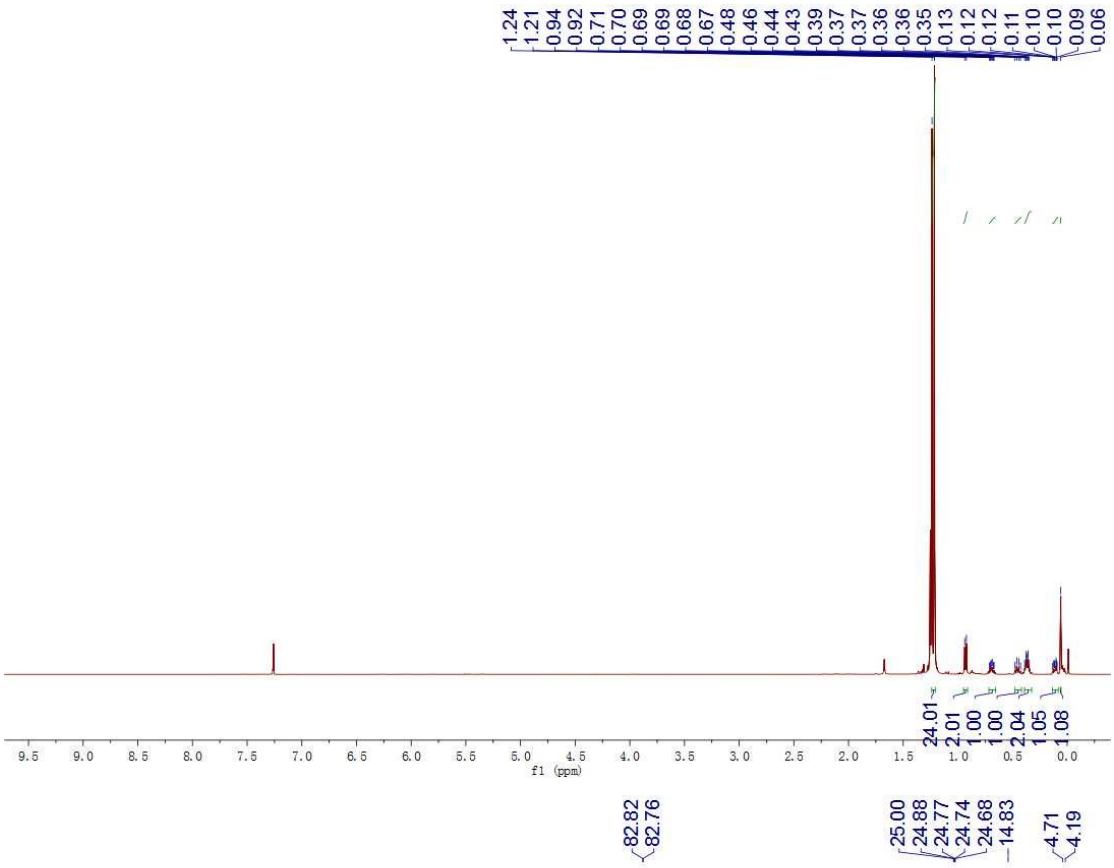
1.41
1.32
1.30
1.25
1.22
1.22
0.86
0.85
0.84
0.83
0.80
0.79
0.77
0.76
4.00
6.00
24.00
3.08
1.09
1.09
f1 (ppm)


82.77
82.71
33.83
31.83
29.53
28.82
24.89
24.82
24.76
24.72
22.62
14.09
f1 (ppm)



24


1.24
1.21
0.94
0.92
0.71
0.70
0.69
0.69
0.68
0.67
0.48
0.46
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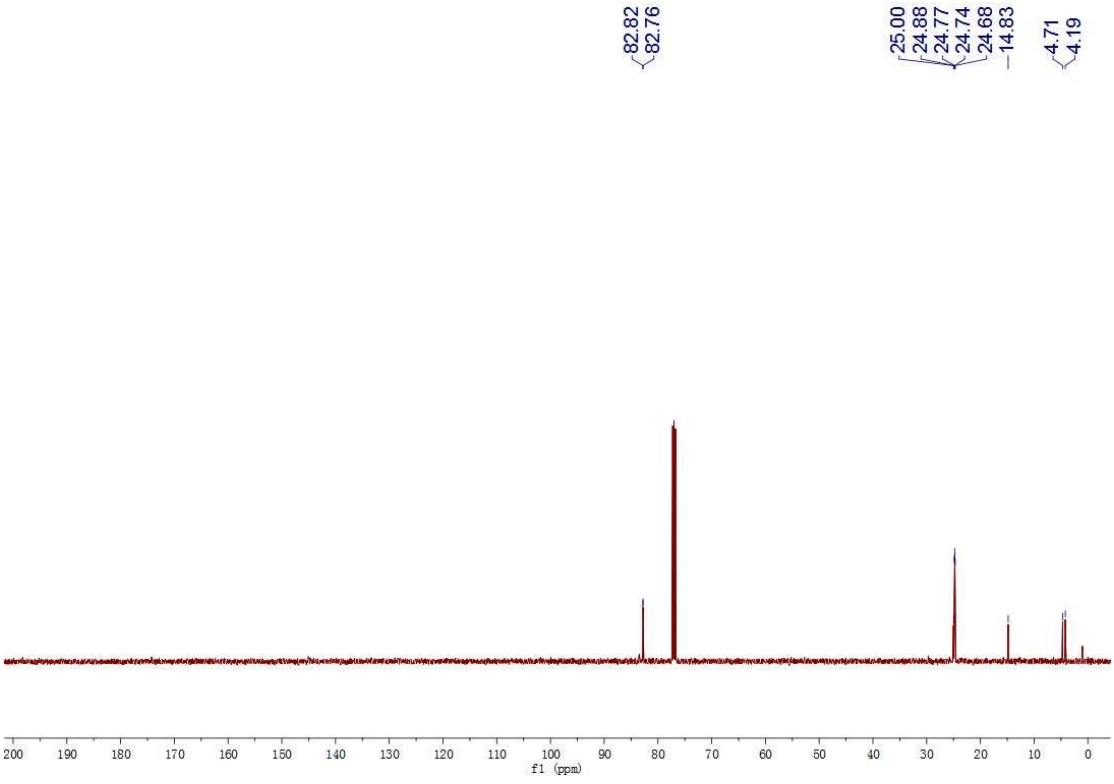
0.43
0.39
0.37
0.37
0.36
0.36
0.35
0.13
0.12
0.12
0.11
0.10
0.10
0.09
0.06
24.01
2.01
1.00
1.00
2.04
1.05
1.08
f1 (ppm)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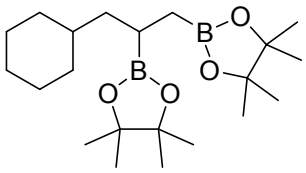
82.76
25.00
24.88
24.77
24.74
24.68
14.83
4.71
4.19
f1 (ppm)



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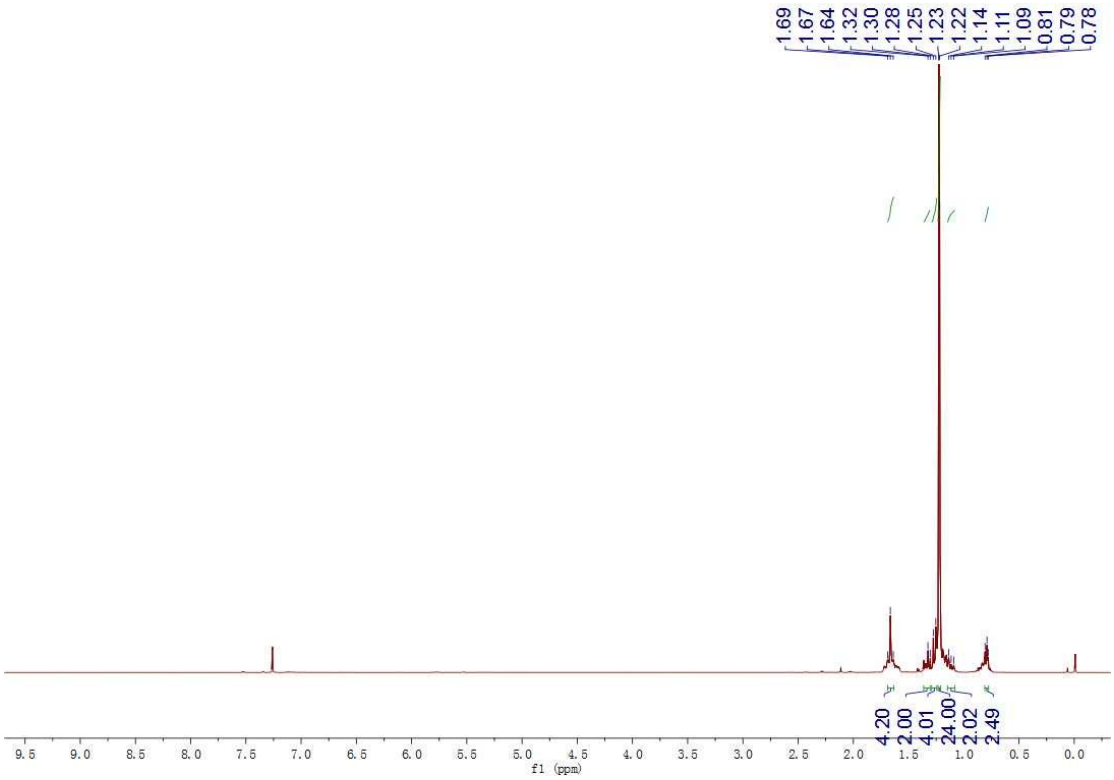
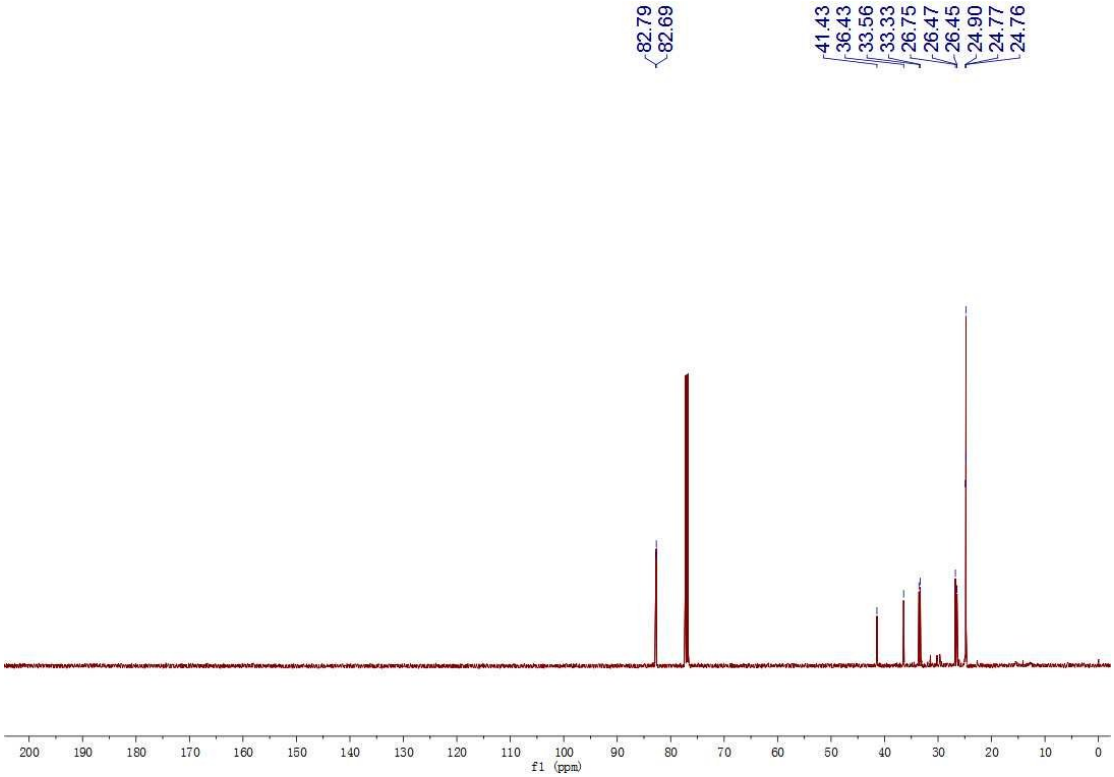

1.69
1.67
1.64
1.32
1.30
1.28
1.25
1.23
1.22
1.14
1.11
1.09
0.81
0.79
0.78
4.20
2.00
4.01
24.00
2.02
2.49
f1 (ppm)


82.79
82.69
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36.43
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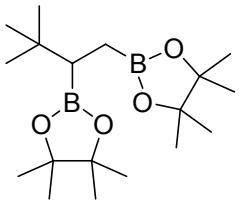
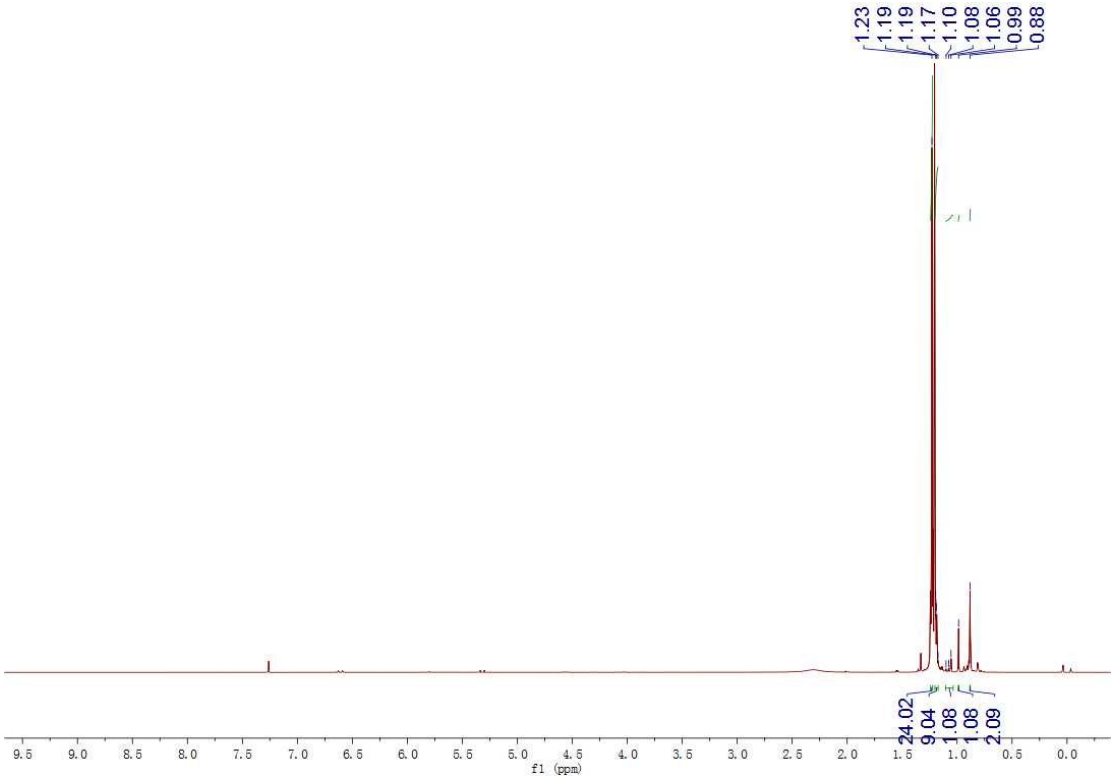
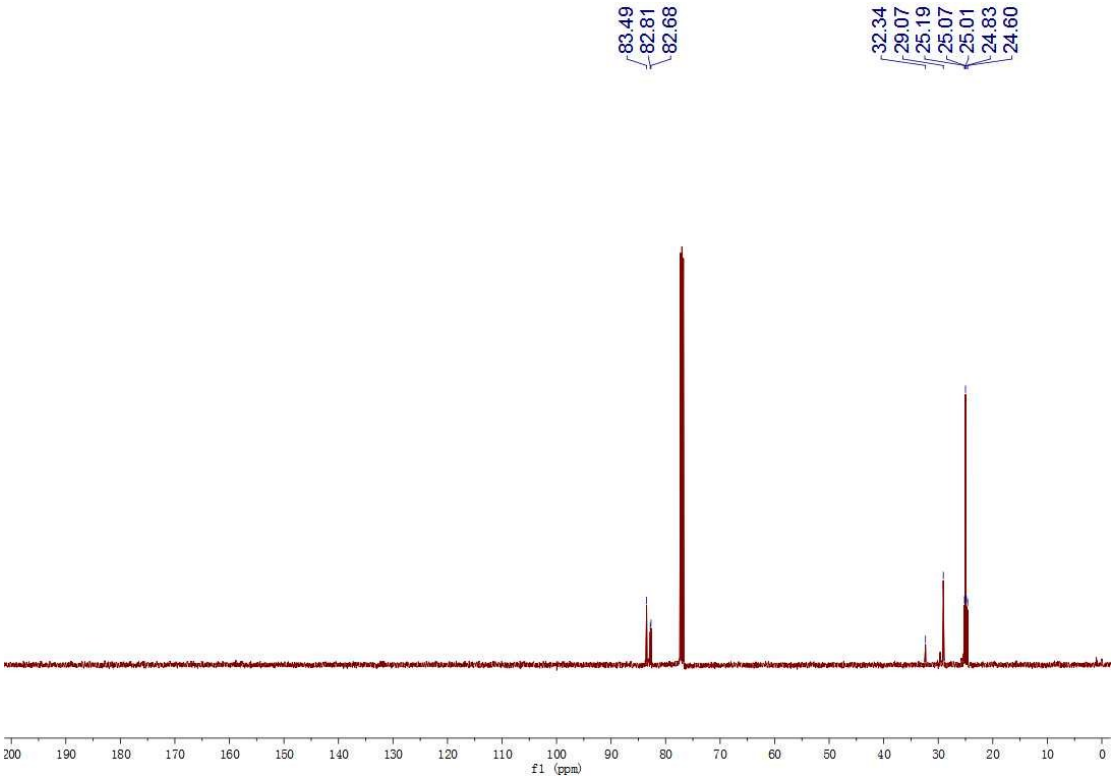
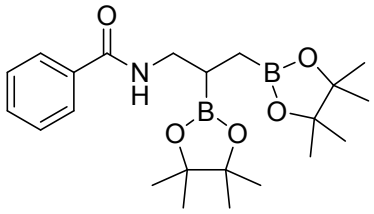
33.33
26.75
26.47
26.45
24.90
24.77
24.76
f1 (ppm)



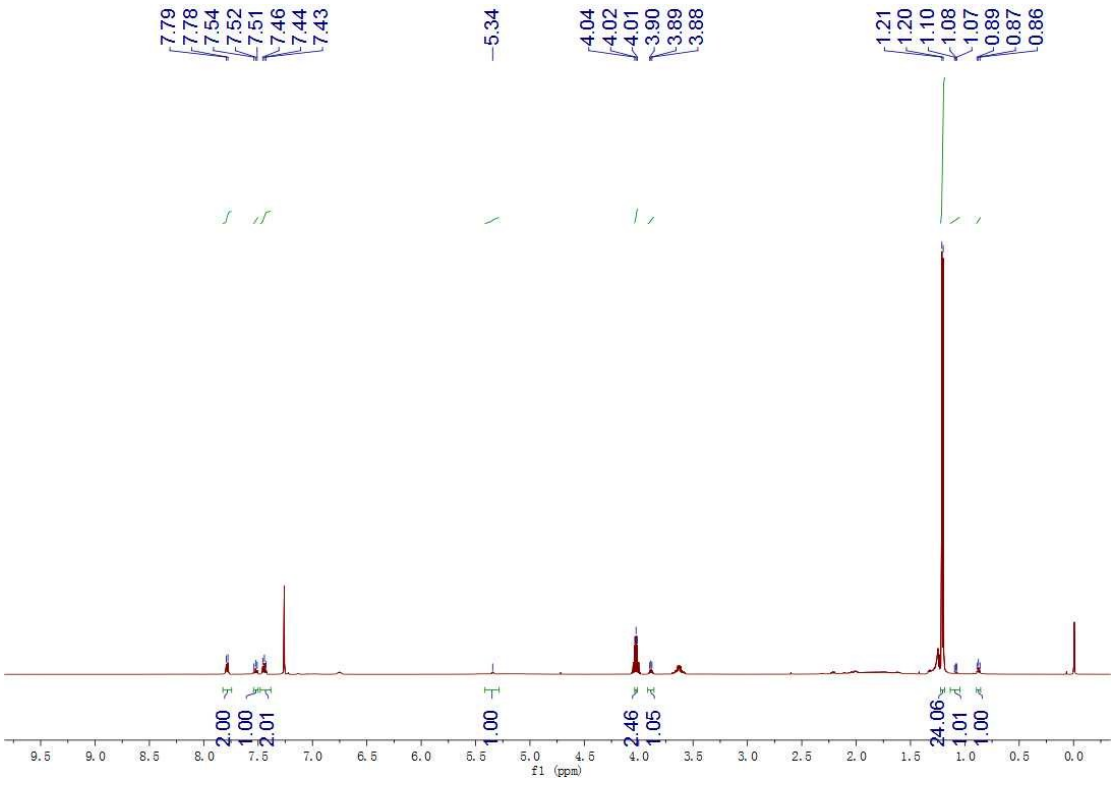
26


1.23
1.19
1.19
1.17
1.10
1.08
1.06
0.99
0.88
24.02
9.04
1.08
1.08
2.09
f1 (ppm)


83.49
82.81
82.68
32.34
29.07
25.19
25.07
25.01
24.83
24.60
f1 (ppm)



27


7.79
7.78
7.54
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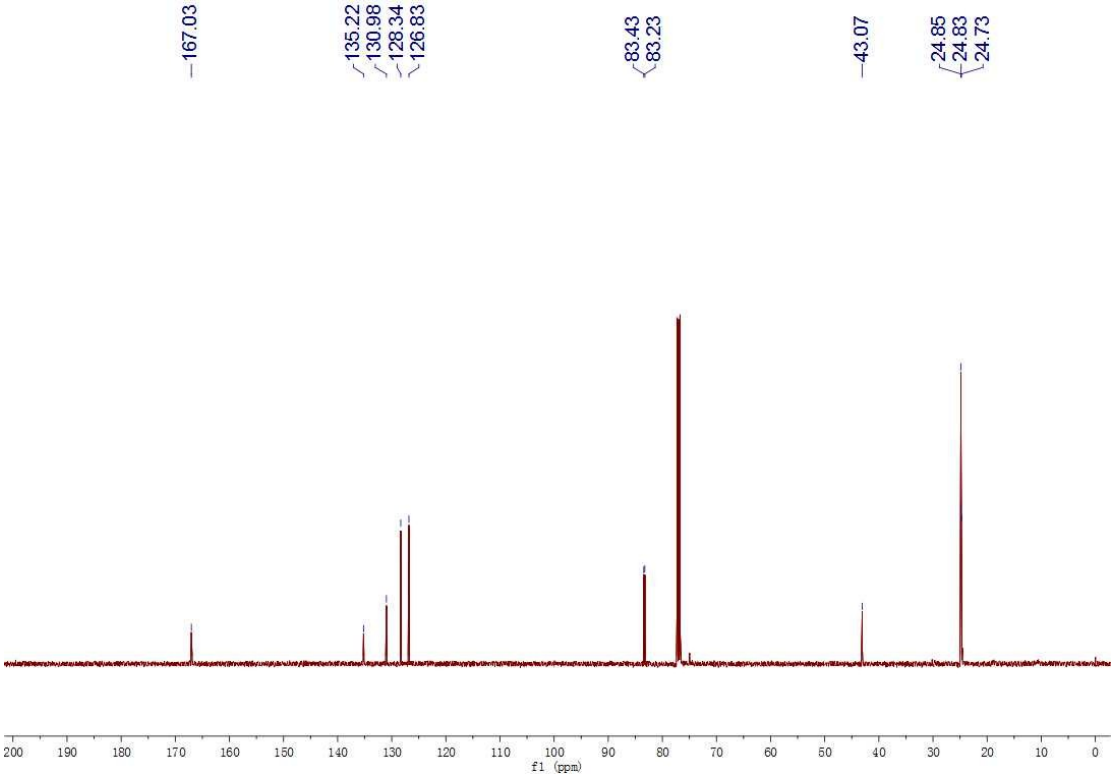
7.51
7.46
7.44
7.43
5.34
4.04
4.02
4.01
3.90
3.89
3.88
1.21
1.20
1.10
1.08
1.07
0.89
0.87
0.86
2.00
1.00
2.01
1.00
2.46
1.05
24.06
1.01
1.00
f1 (ppm)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135.22
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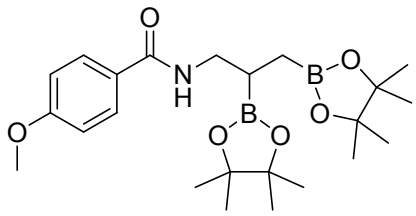
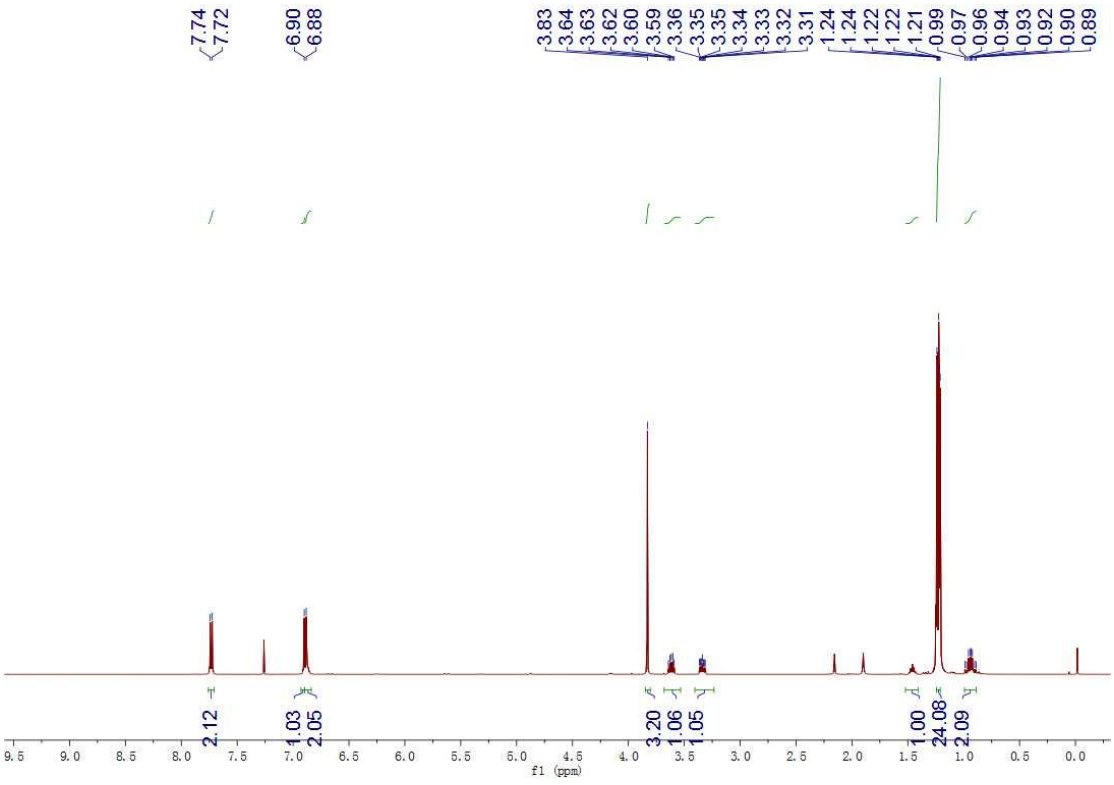
128.34
126.83
83.43
83.23
43.07
24.85
24.83
24.73
f1 (ppm)



28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6.88
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3.64
3.63
3.62
3.60
3.59
3.36
3.35
3.35
3.34
3.33
3.32
3.31
1.24
1.24
1.22
1.22
1.21
0.99
0.97
0.96
0.94
0.93
0.92
0.90
0.89
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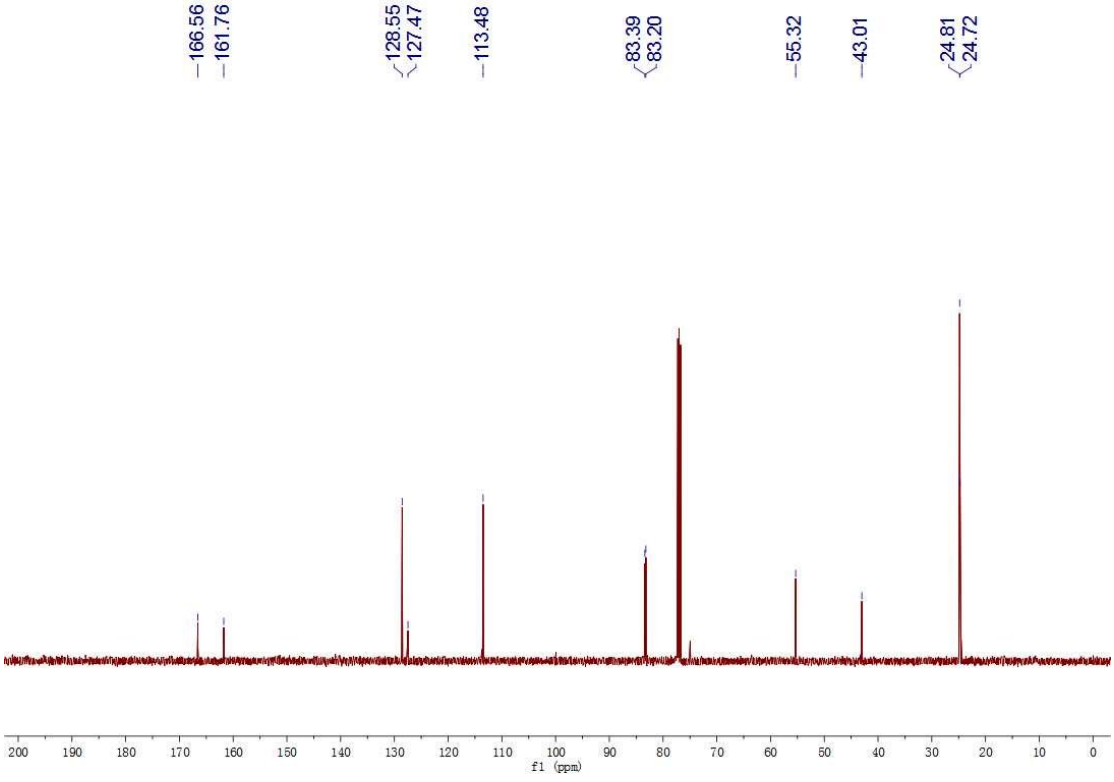
1.03
2.05
3.20
1.06
1.05
1.00
24.08
2.09
f1 (ppm)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55.32
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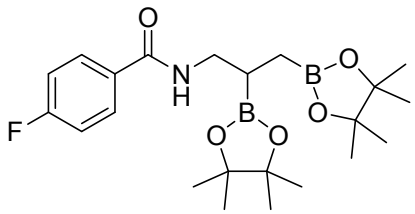
24.81
24.72
f1 (ppm)



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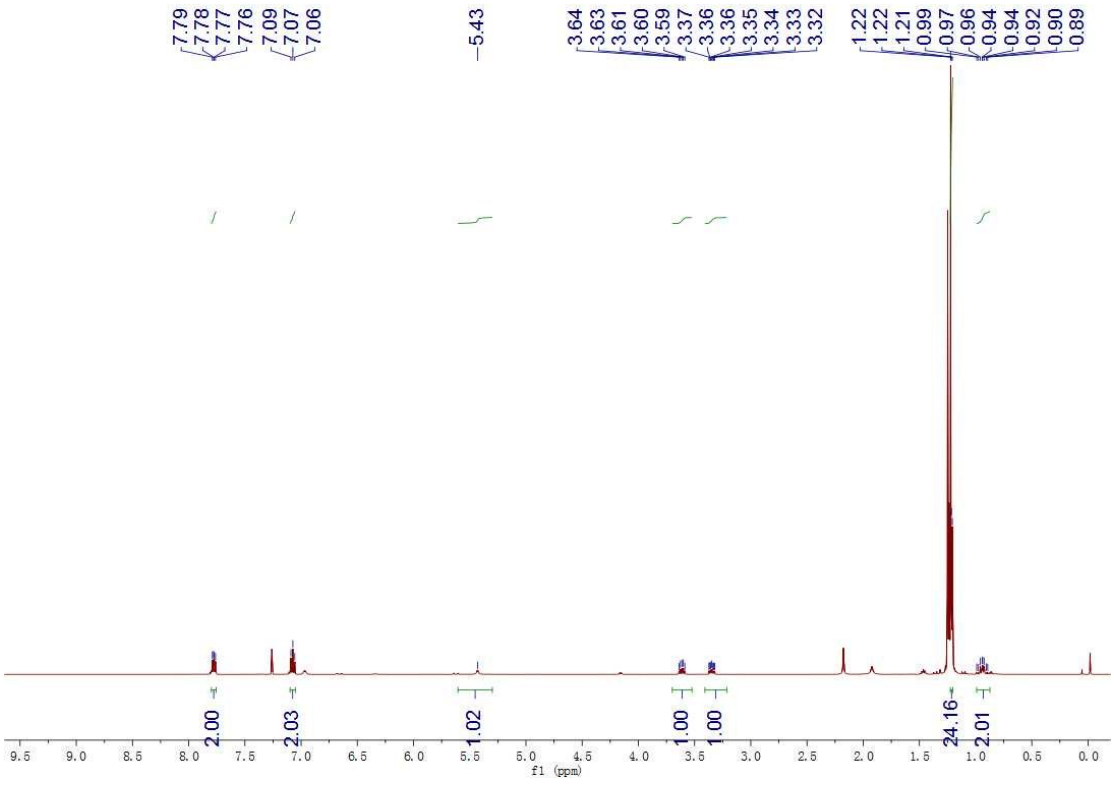
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7.78
7.77
7.76
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7.06
5.43
3.64
3.63
3.61
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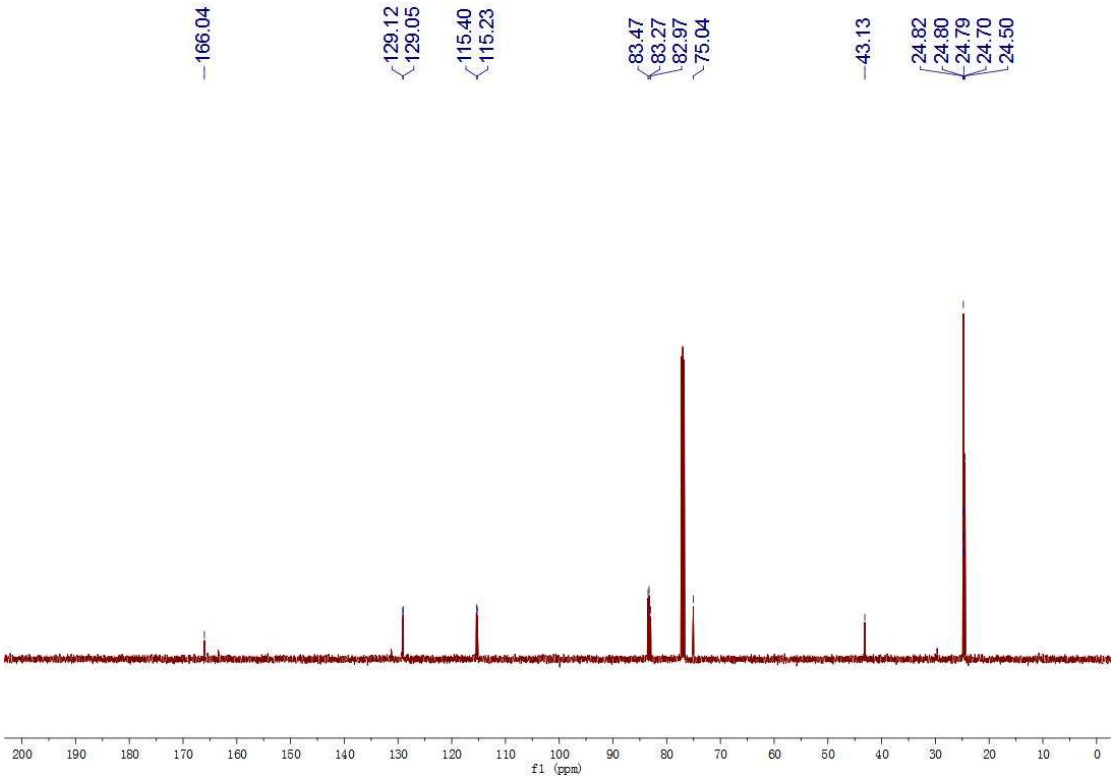
3.37
3.36
3.36
3.35
3.34
3.33
3.32
1.22
1.22
1.21
0.99
0.97
0.96
0.94
0.94
0.92
0.90
0.89
2.00
2.03
1.02
1.00
1.00
24.16
2.01
f1 (ppm)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129.05
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43.13
24.82
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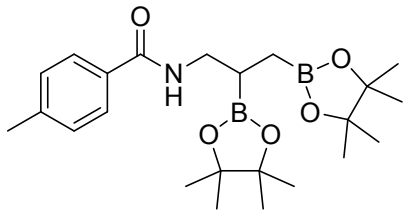
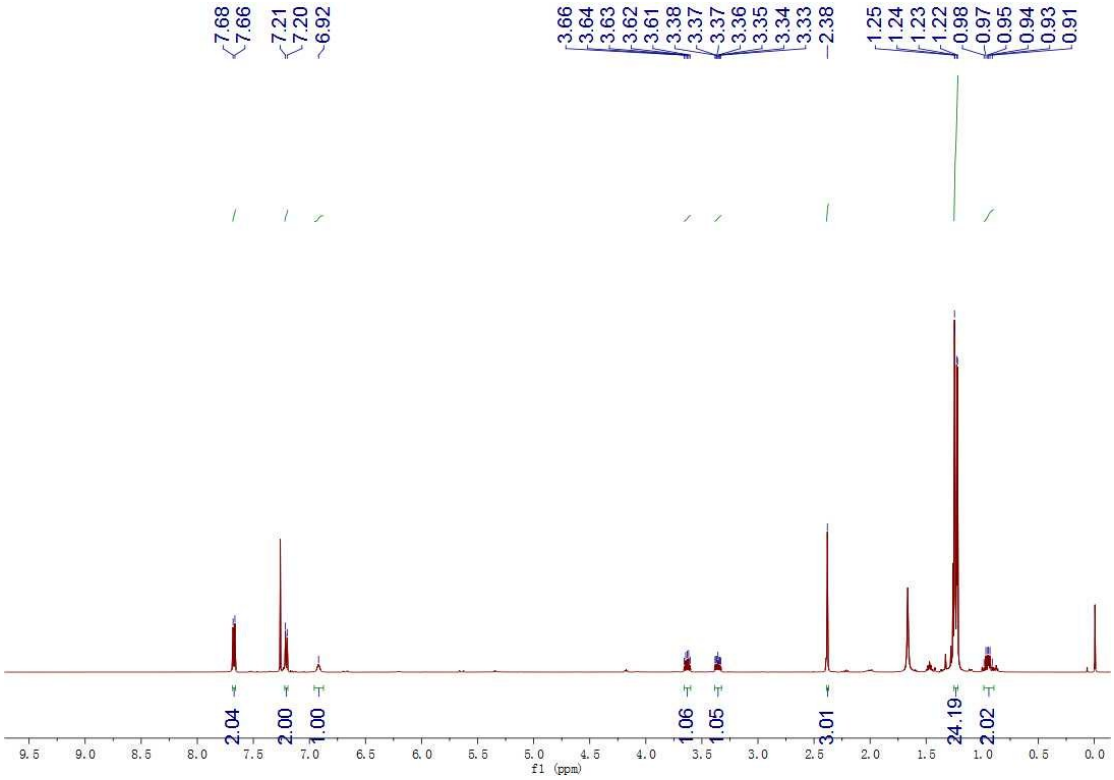
24.50
f1 (ppm)



30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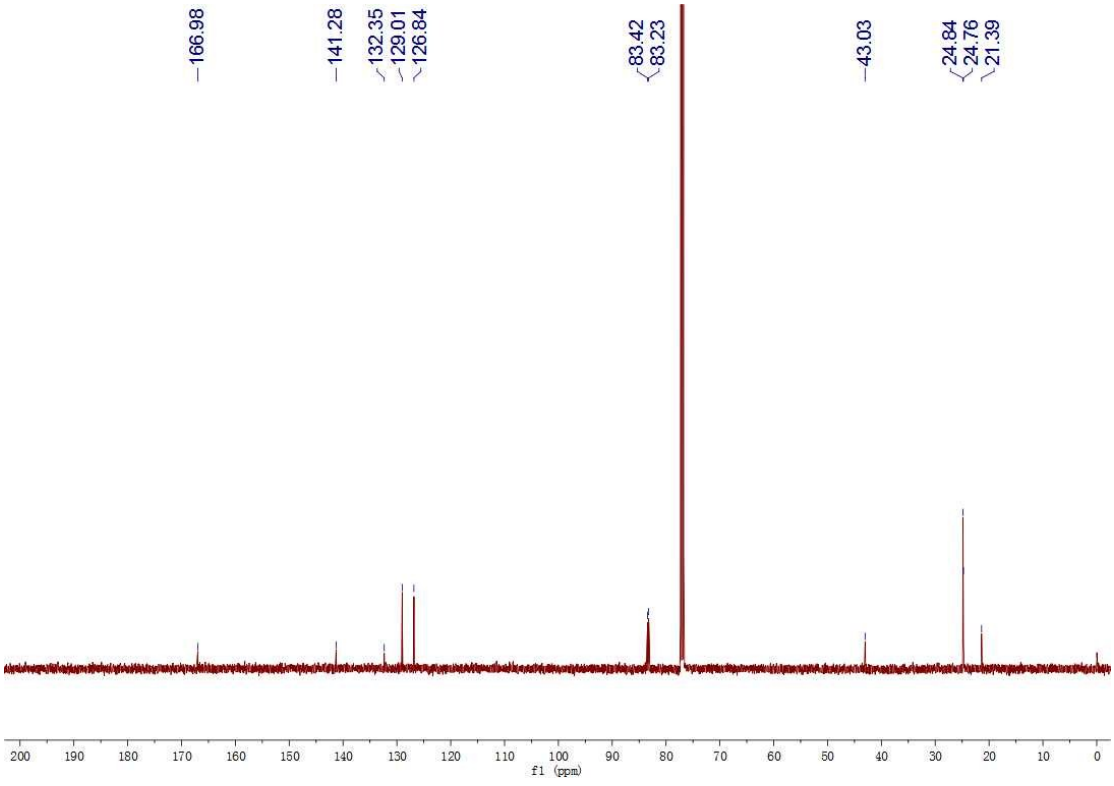
3.64
3.63
3.62
3.61
3.38
3.37
3.37
3.36
3.35
3.34
3.33
2.38
1.25
1.24
1.23
1.22
0.98
0.97
0.95
0.94
0.93
0.91
2.04
2.00
1.00
1.06
1.05
3.01
24.19
2.02
f1 (ppm)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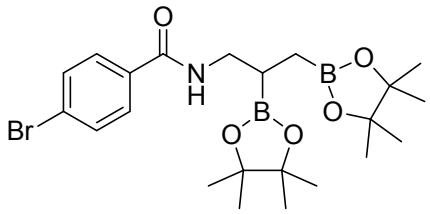
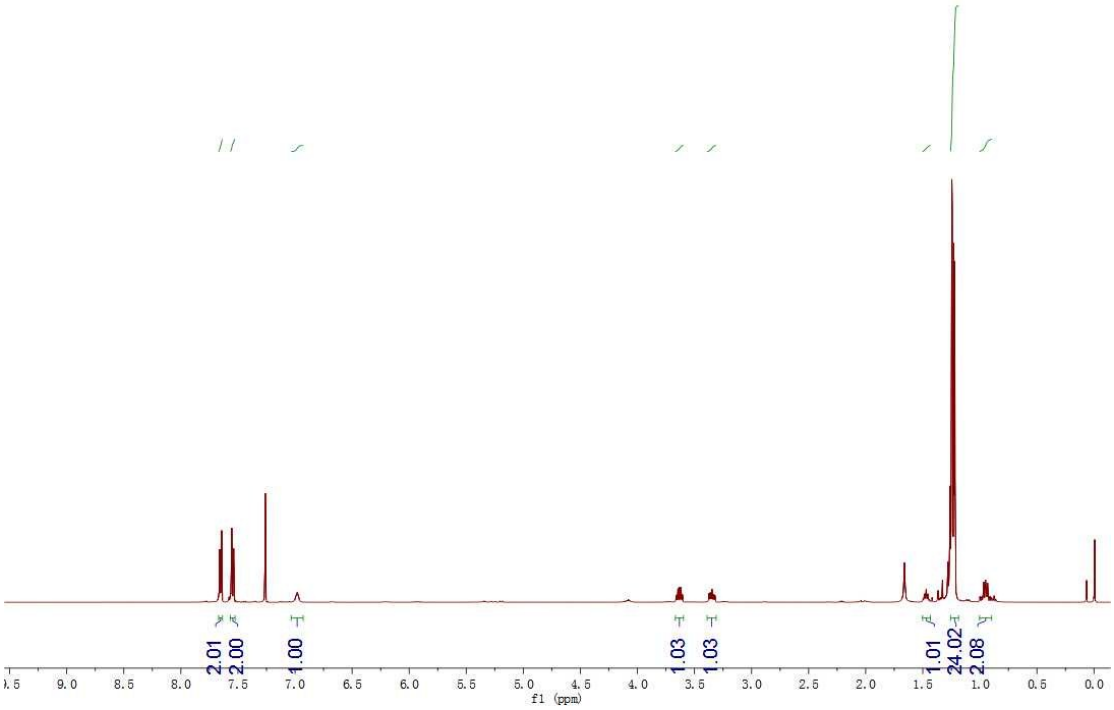
83.23
43.03
24.84
24.76
21.39
f1 (ppm)



31


2.01
2.00
1.00
1.03
1.03
1.01
24.02
2.08
f1 (ppm)


165.99
134.06
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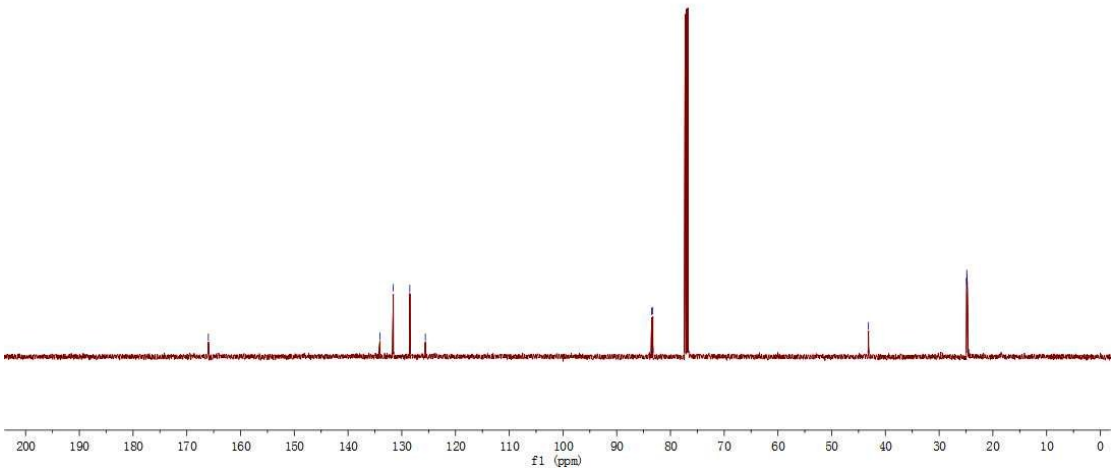
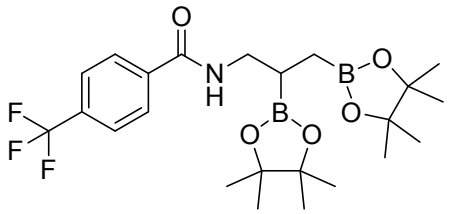
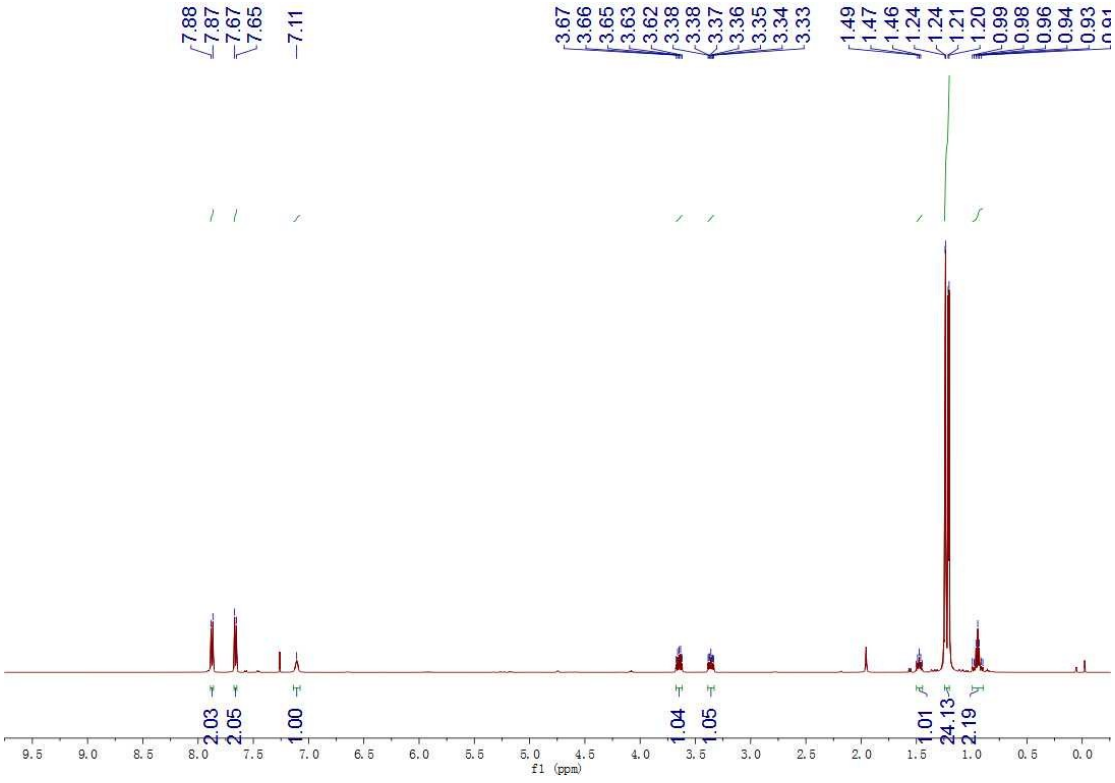
83.29
43.15
24.87
24.86
24.83
24.75


f1 (ppm)



32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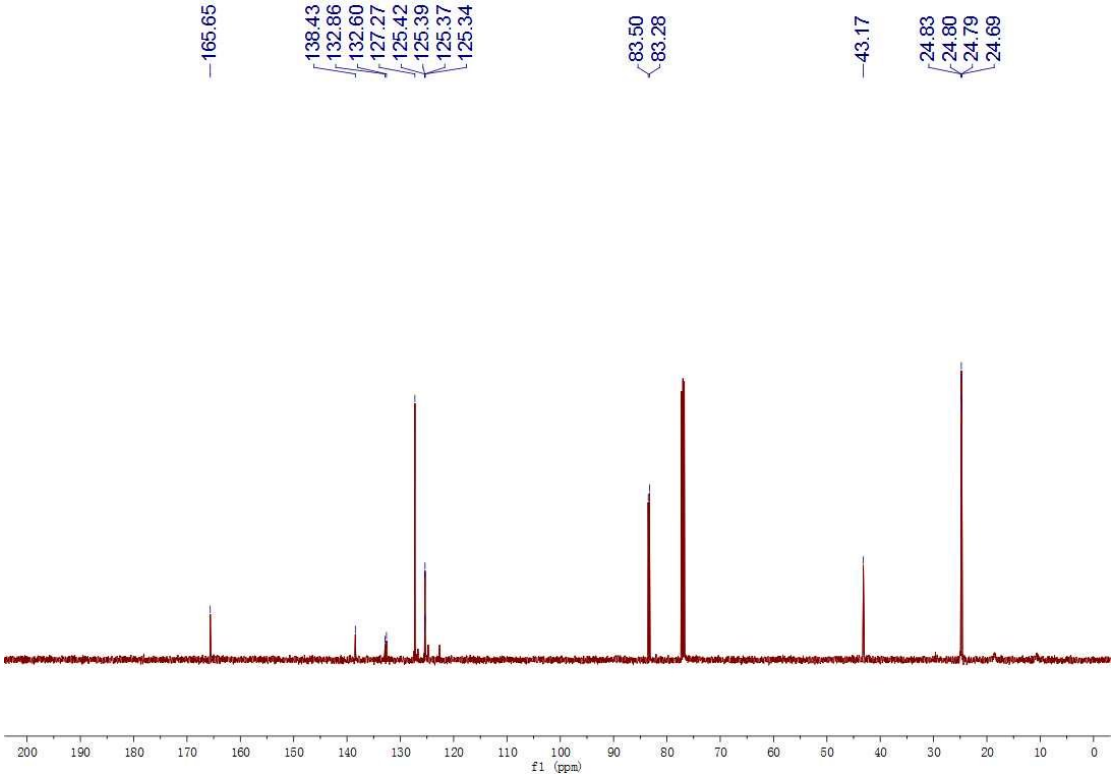
3.38
3.38
3.37
3.36
3.35
3.34
3.33
1.49
1.47
1.46
1.24
1.24
1.21
1.20
0.99
0.98
0.96
0.94
0.93
2.03
2.05
1.00
1.04
1.05
1.01
24.13
2.19
f1 (ppm)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132.86
132.60
127.27
125.42
125.39
125.37
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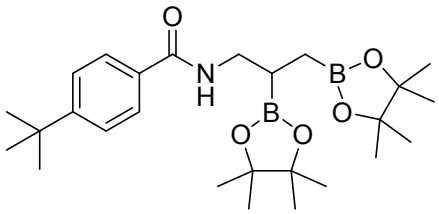
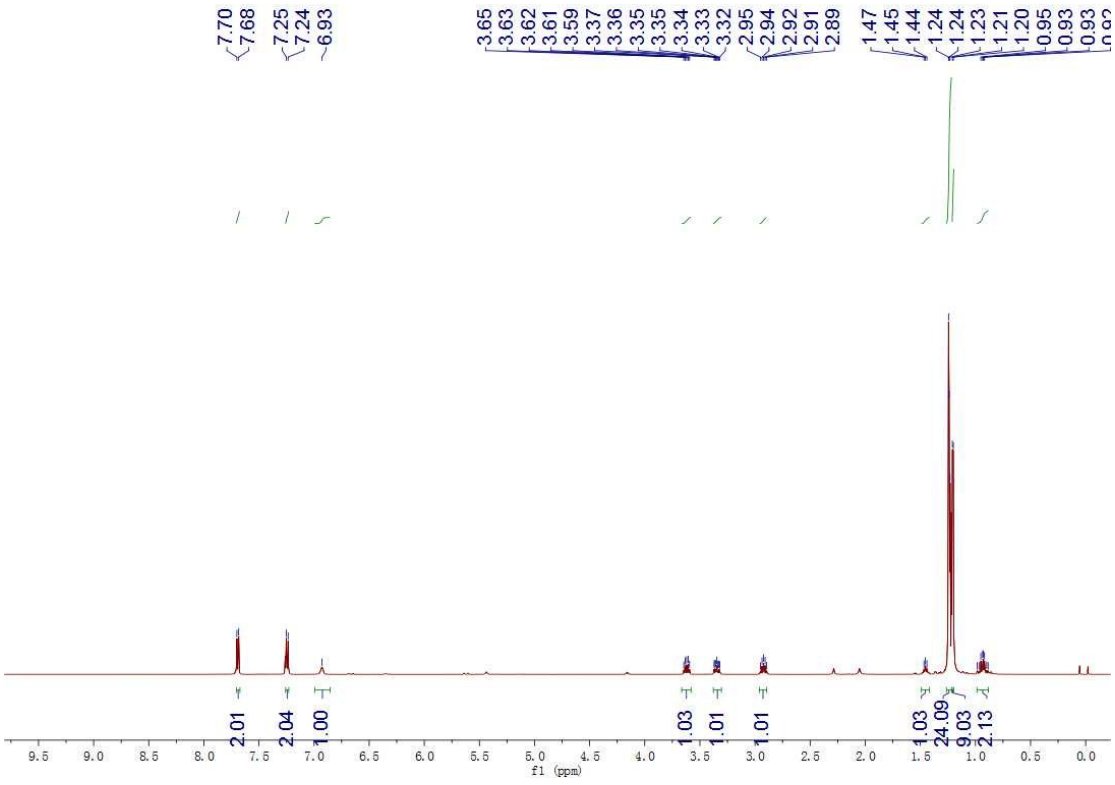
83.28
43.17
24.83
24.80
24.79
24.69
f1 (ppm)



33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3.65
3.63
3.62
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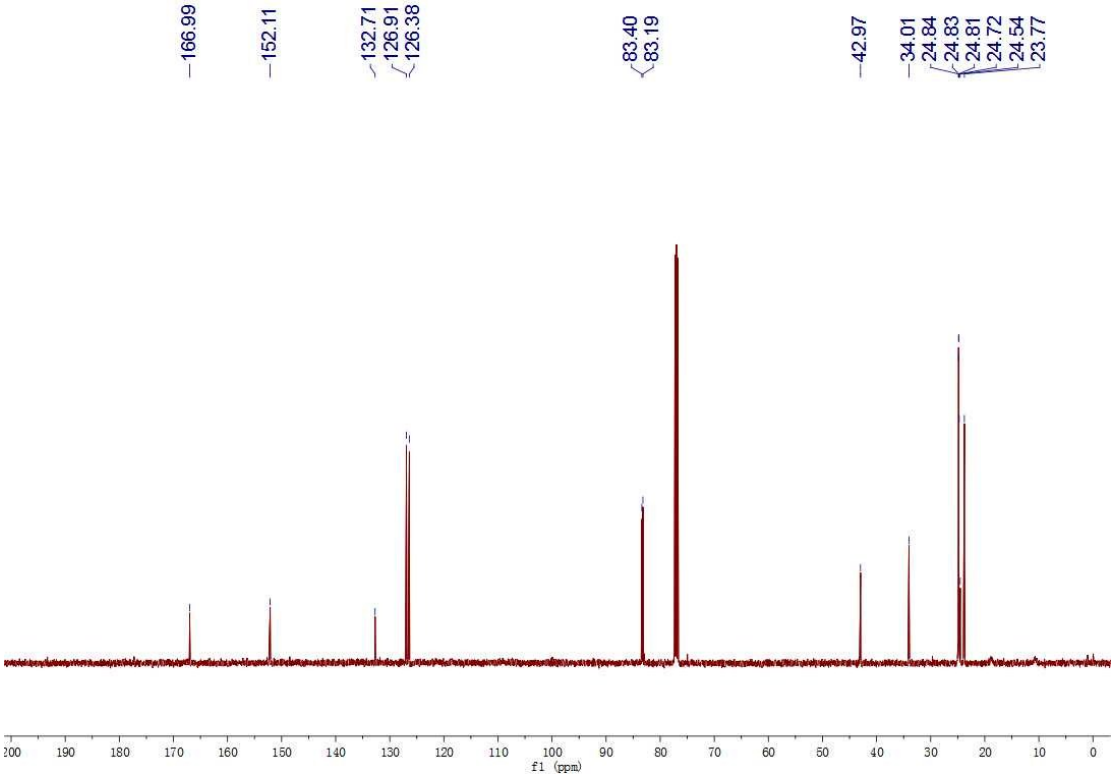
3.59
3.37
3.36
3.35
3.35
3.34
3.33
3.32
2.95
2.94
2.92
2.91
2.89
1.47
1.45
1.44
1.24
1.24
1.23
1.21
1.20
0.95
0.93
0.93
2.01
2.04
1.00
1.03
1.01
1.01
1.03
24.09
9.03
2.13
f1 (ppm)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152.11
132.71
126.91
126.38
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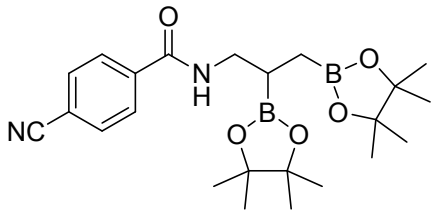
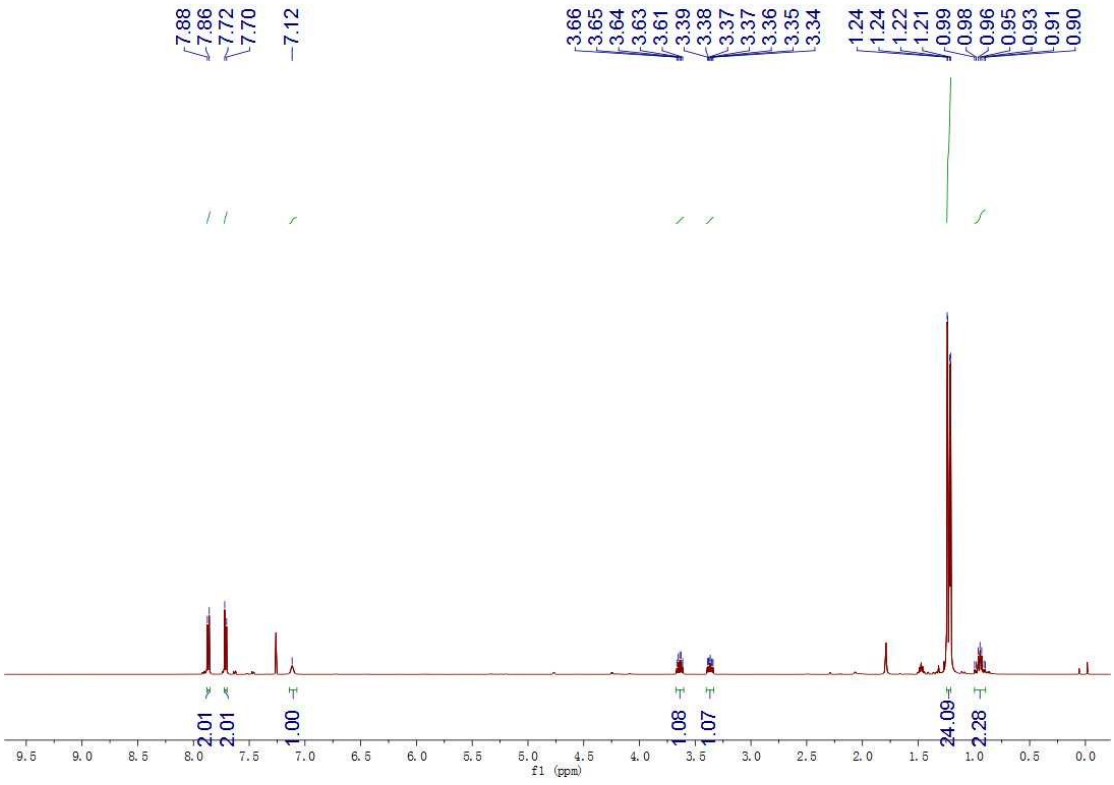
24.84
24.83
24.81
24.72
24.54
23.77
f1 (ppm)



34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3.64
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3.61
3.39
3.38
3.37
3.37
3.36
3.35
3.34
1.24
1.24
1.22
1.21
0.99
0.98
0.96
0.95
0.93
0.91
0.90
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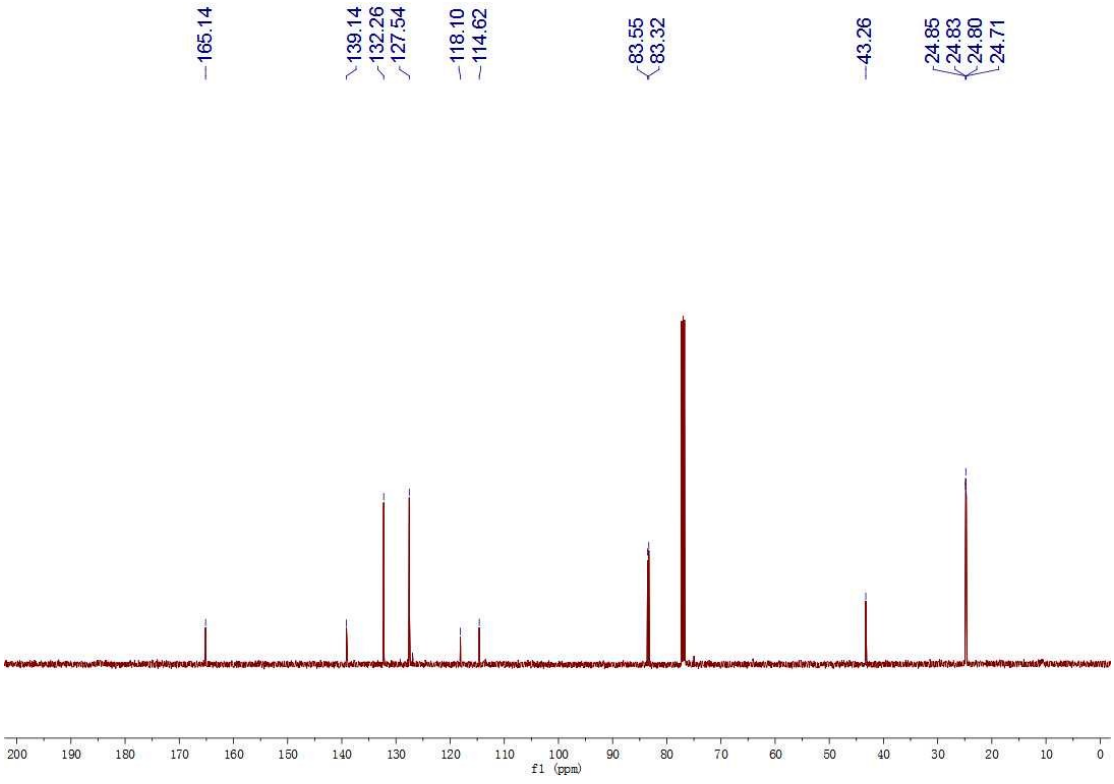
2.01
1.00
1.08
1.07
24.09
2.28
f1 (ppm)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139.14
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127.54
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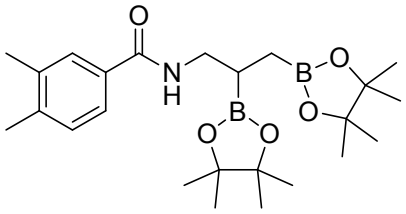
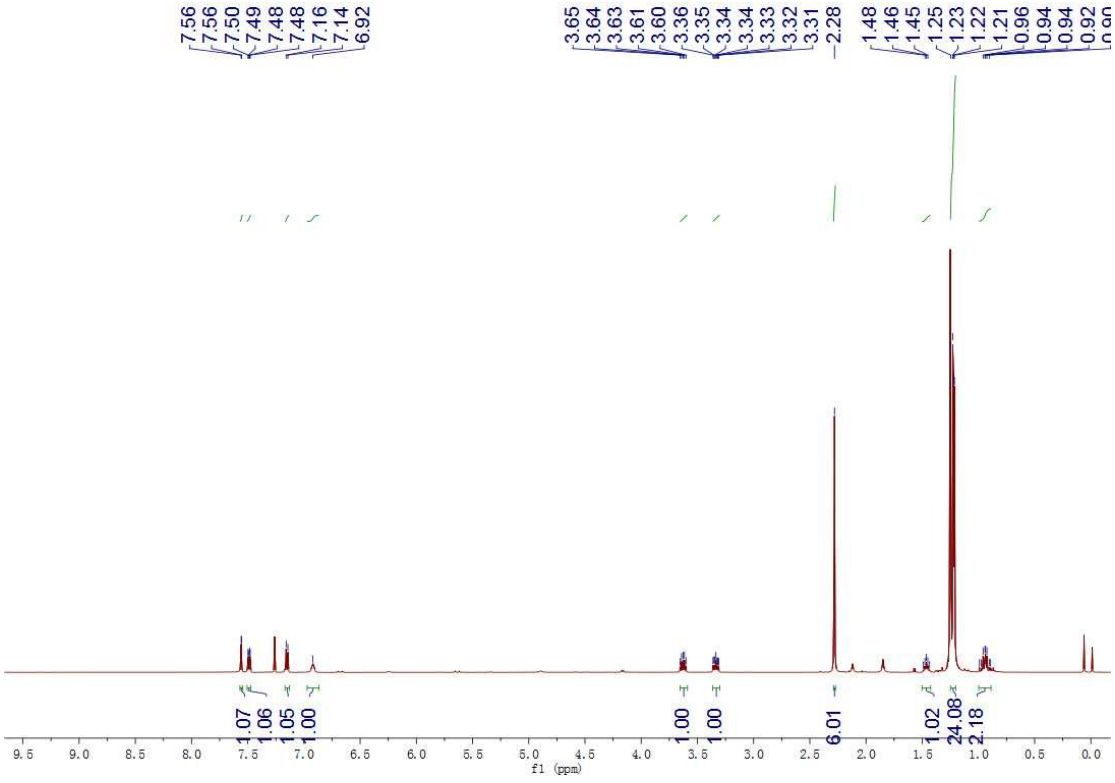
83.32
43.26
24.85
24.83
24.80
24.71
f1 (ppm)



35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7.48
7.16
7.14
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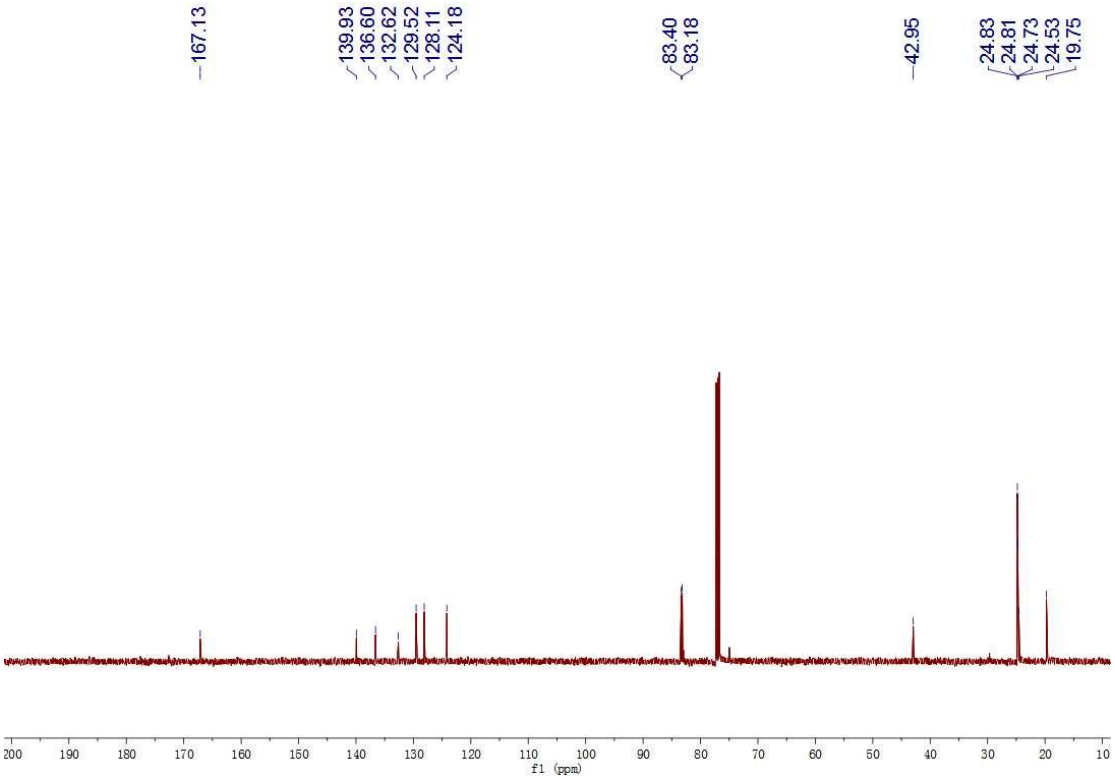
3.64
3.63
3.61
3.60
3.36
3.35
3.34
3.34
3.33
3.32
3.31
2.28
1.48
1.46
1.45
1.25
1.23
1.22
1.21
0.96
0.94
0.94
0.92
1.07
1.06
1.05
1.00
1.00
1.00
6.01
1.02
24.08
2.18
f1 (ppm)


167.13
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136.60
132.62
129.52
128.11
124.18
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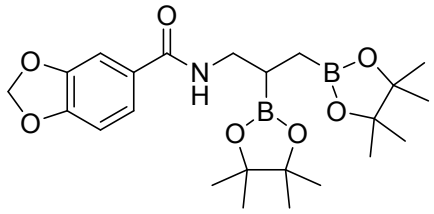
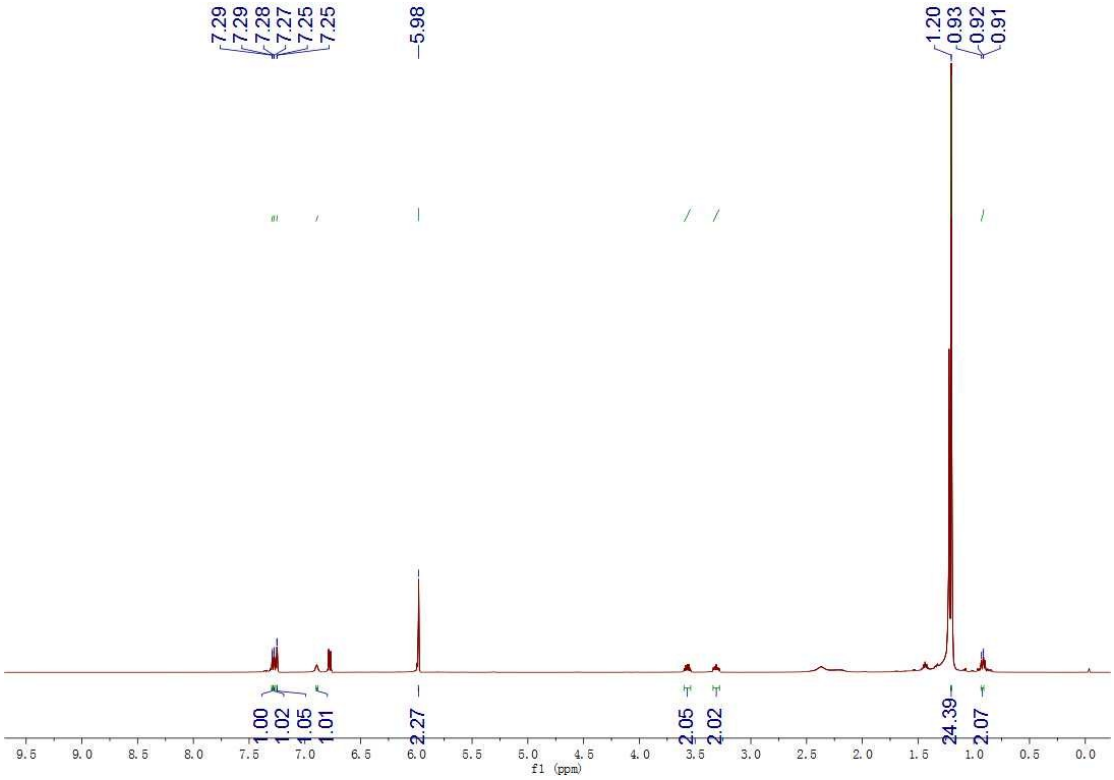
83.18
42.95
24.83
24.81
24.73
24.53
19.75
f1 (ppm)



36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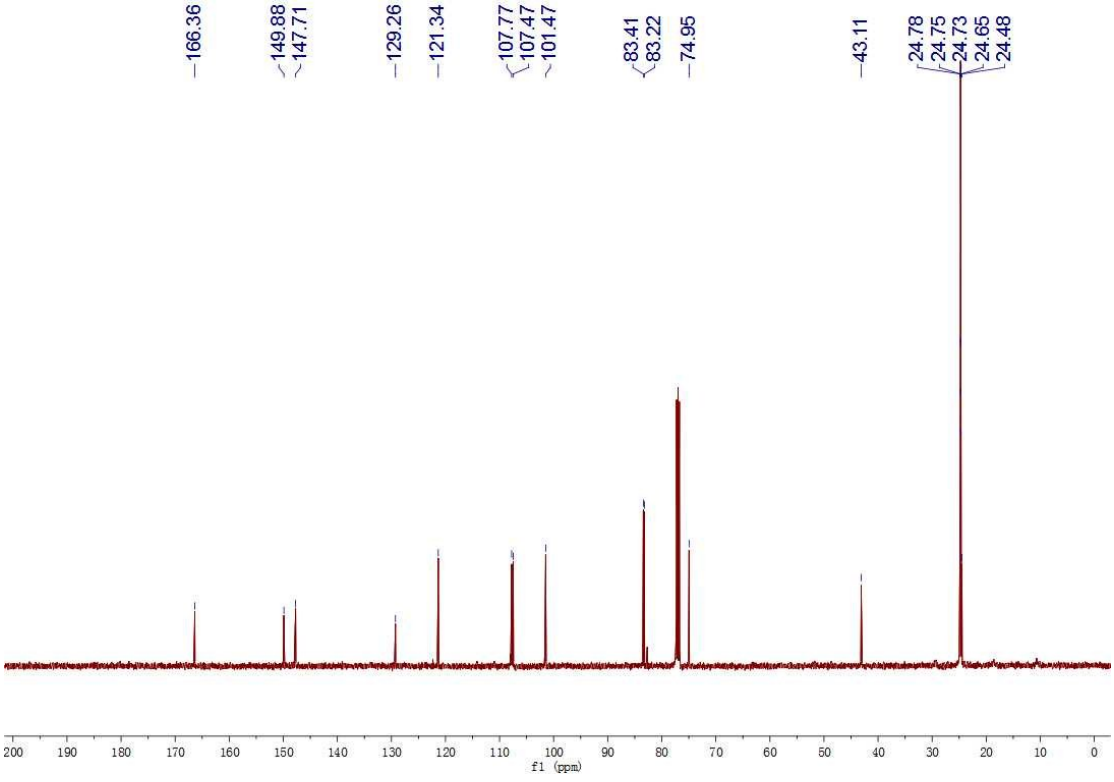
7.29
7.28
7.27
7.25
7.25
5.98
1.20
0.93
0.92
0.91
1.00
1.02
1.05
1.01
2.27
2.05
2.02
24.39
2.07
f1 (ppm)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147.71
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121.34
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101.47
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83.22
74.95
43.11
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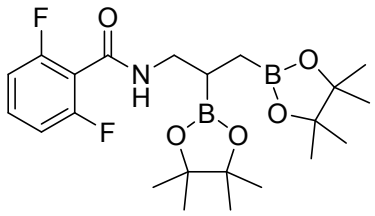
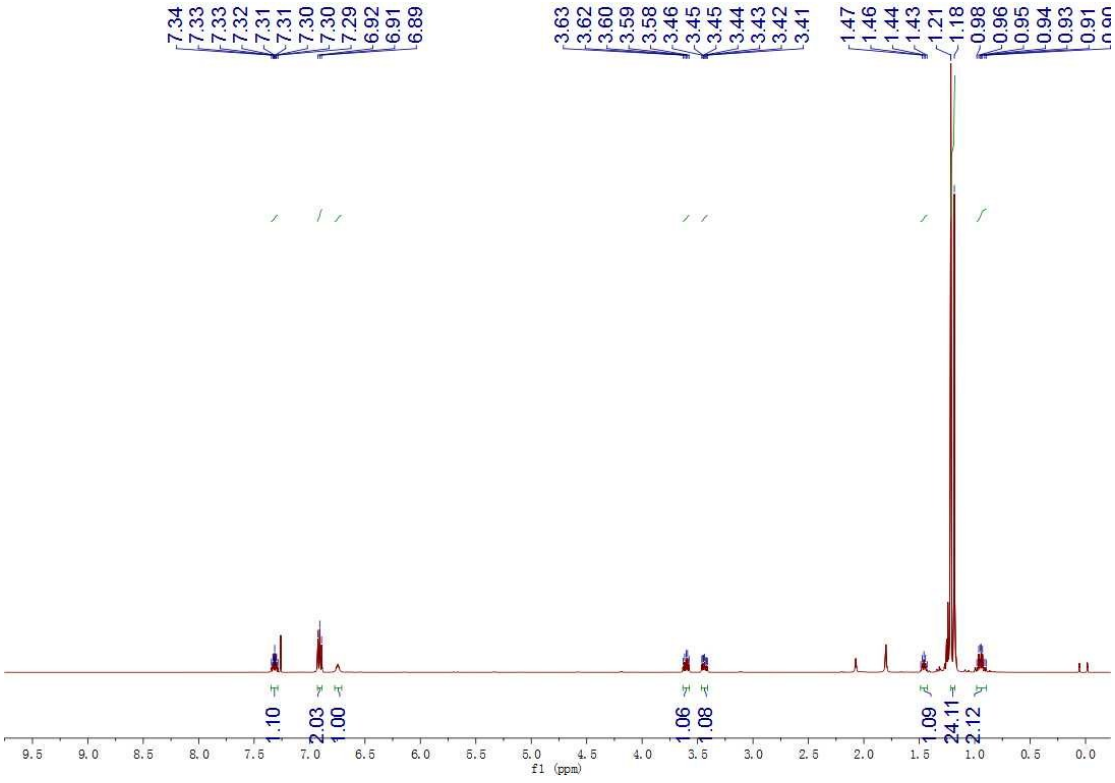
24.75
24.73
24.65
24.48
f1 (ppm)



37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7.33
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7.31
7.31
7.30
7.30
7.29
6.92
6.91
6.89
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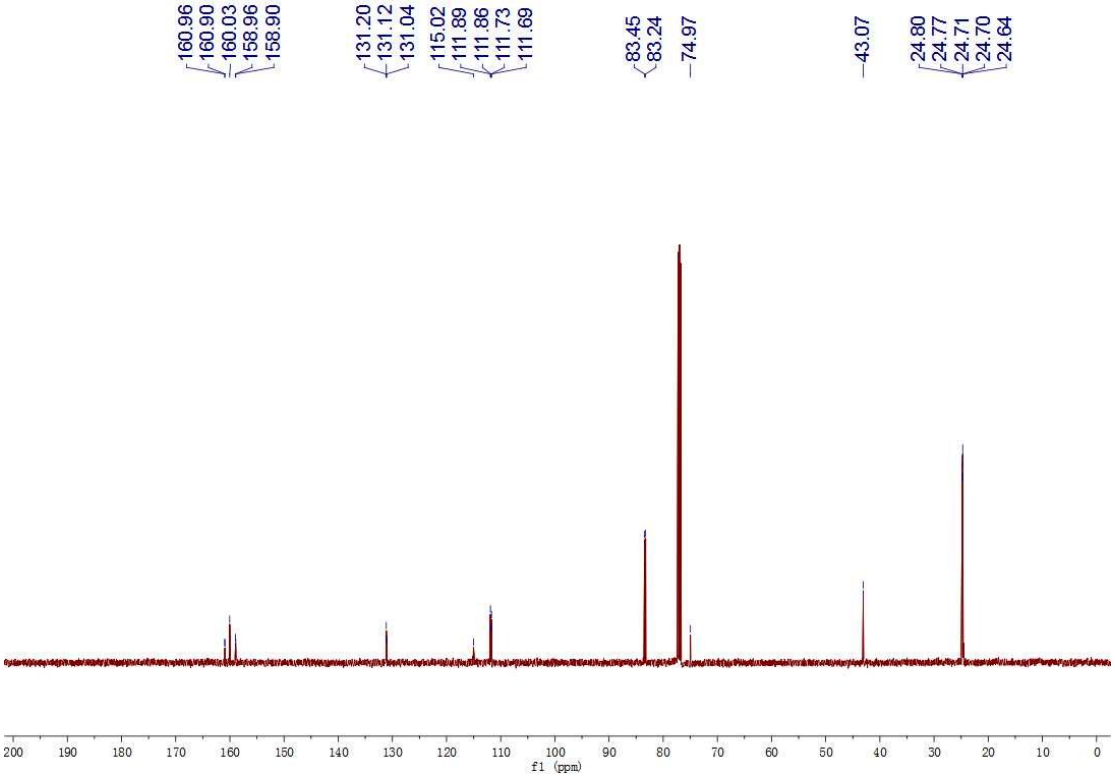
3.62
3.60
3.59
3.58
3.46
3.45
3.45
3.44
3.43
3.42
3.41
1.47
1.46
1.44
1.43
1.21
1.18
0.98
0.96
0.95
0.94
0.93
0.91
1.10
2.03
1.00
1.06
1.08
1.09
24.11
2.12
f1 (ppm)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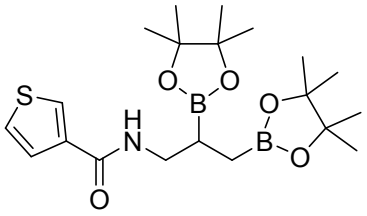
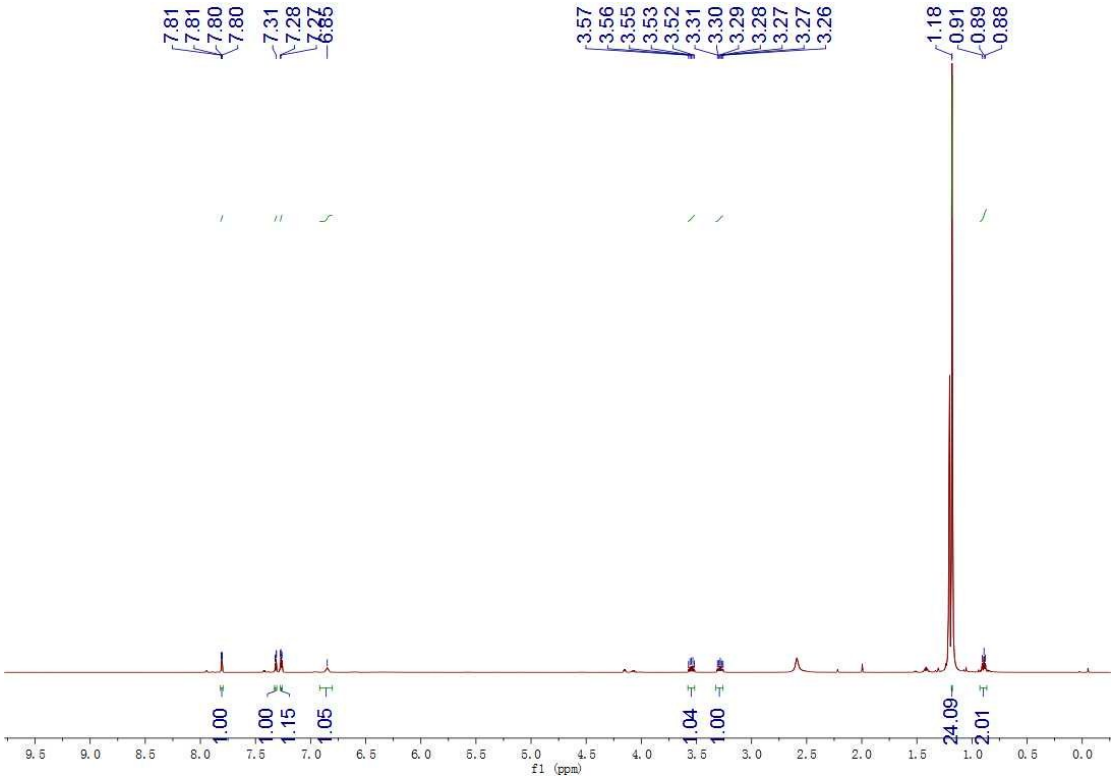
160.90
160.03
158.96
158.90
131.20
131.12
131.04
115.02
111.89
111.86
111.73
111.69
83.45
83.24
74.97
43.07
24.80
24.77
24.71
24.70
24.64
f1 (ppm)



38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7.81
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7.80
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7.28
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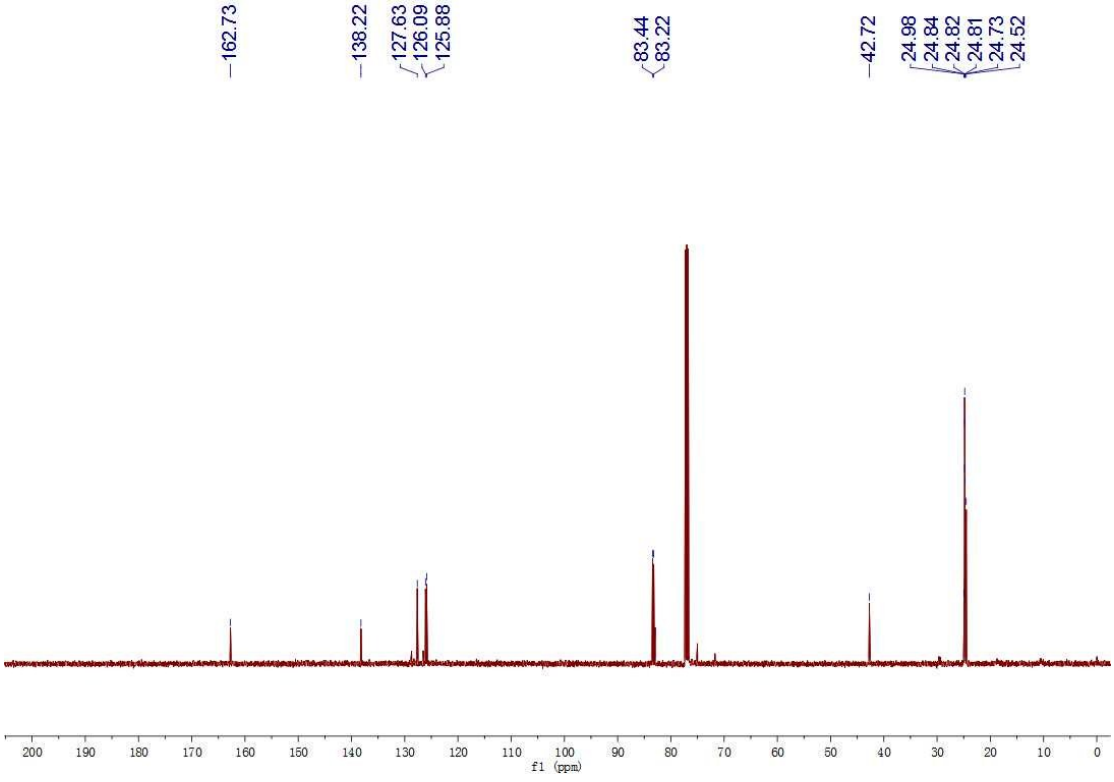
3.56
3.55
3.53
3.52
3.31
3.30
3.29
3.28
3.27
3.27
3.26
1.18
0.91
0.89
0.88
1.00
1.00
1.15
1.05
1.04
1.00
24.09
2.01
f1 (ppm)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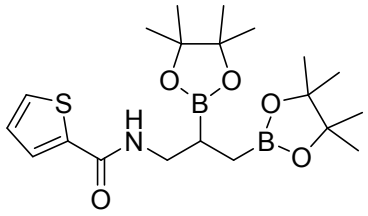
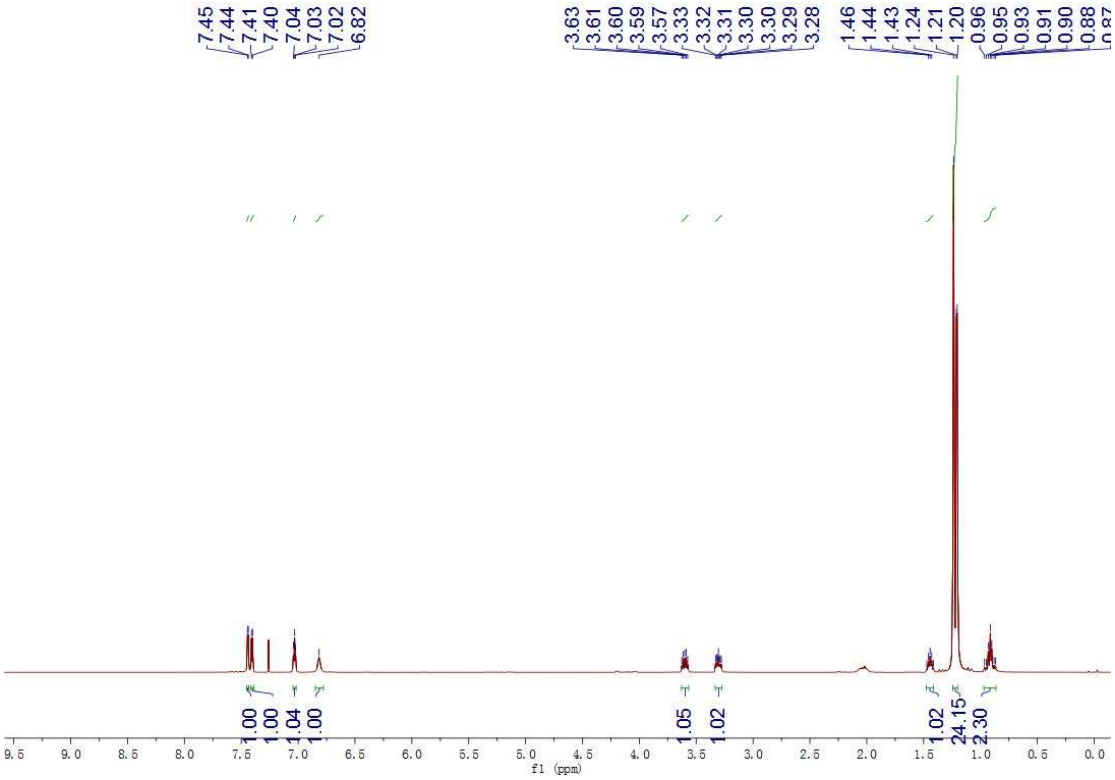
138.22
127.63
126.09
125.88
83.44
83.22
42.72
24.98
24.84
24.82
24.81
24.73
24.52
f1 (ppm)



39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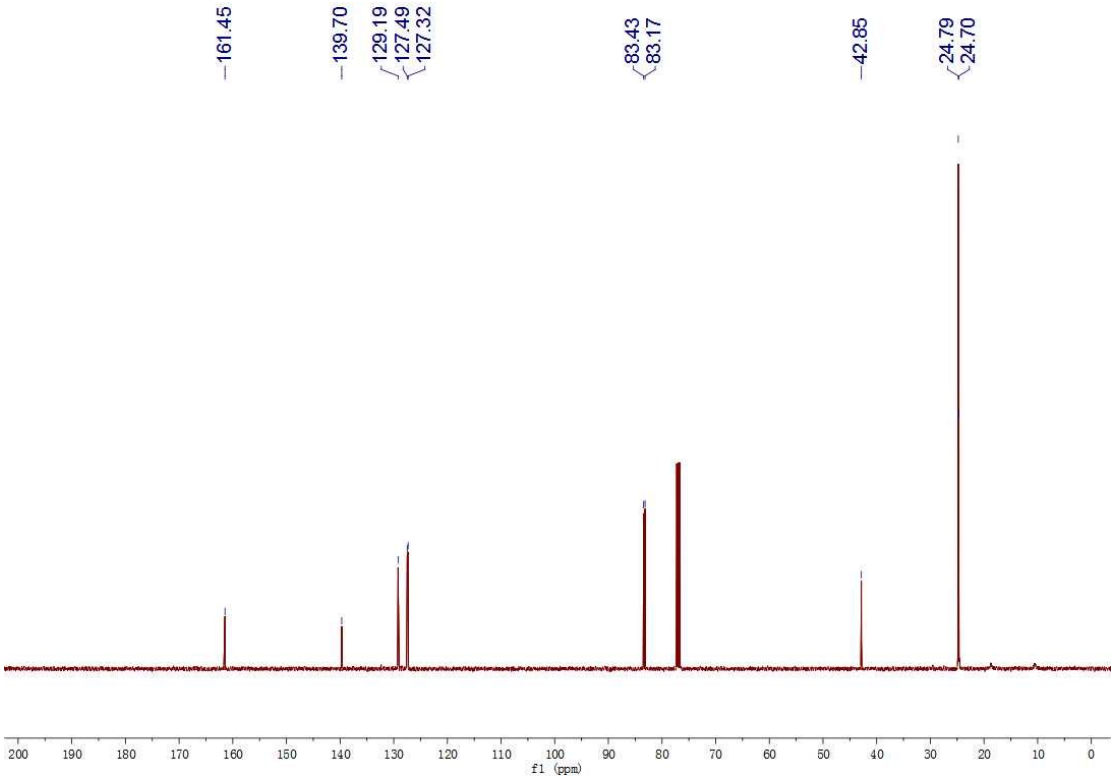
7.04
7.03
7.02
6.82
3.63
3.61
3.60
3.59
3.57
3.33
3.32
3.31
3.30
3.30
3.29
3.28
1.46
1.44
1.43
1.24
1.21
1.20
0.96
0.95
0.93
0.91
0.90
0.88
1.00
1.00
1.04
1.00
1.05
1.02
1.02
24.15
2.30
f1 (ppm)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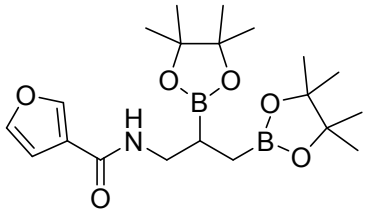
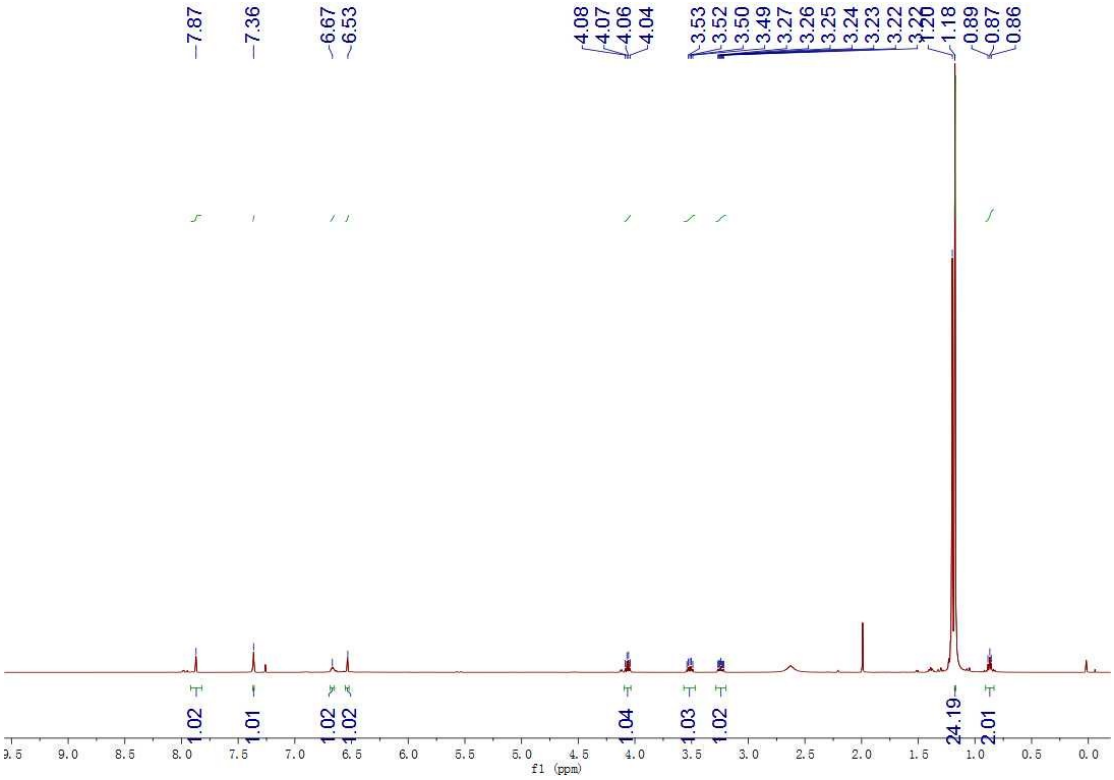
127.49
127.32
83.43
83.17
42.85
24.79
24.70
f1 (ppm)



40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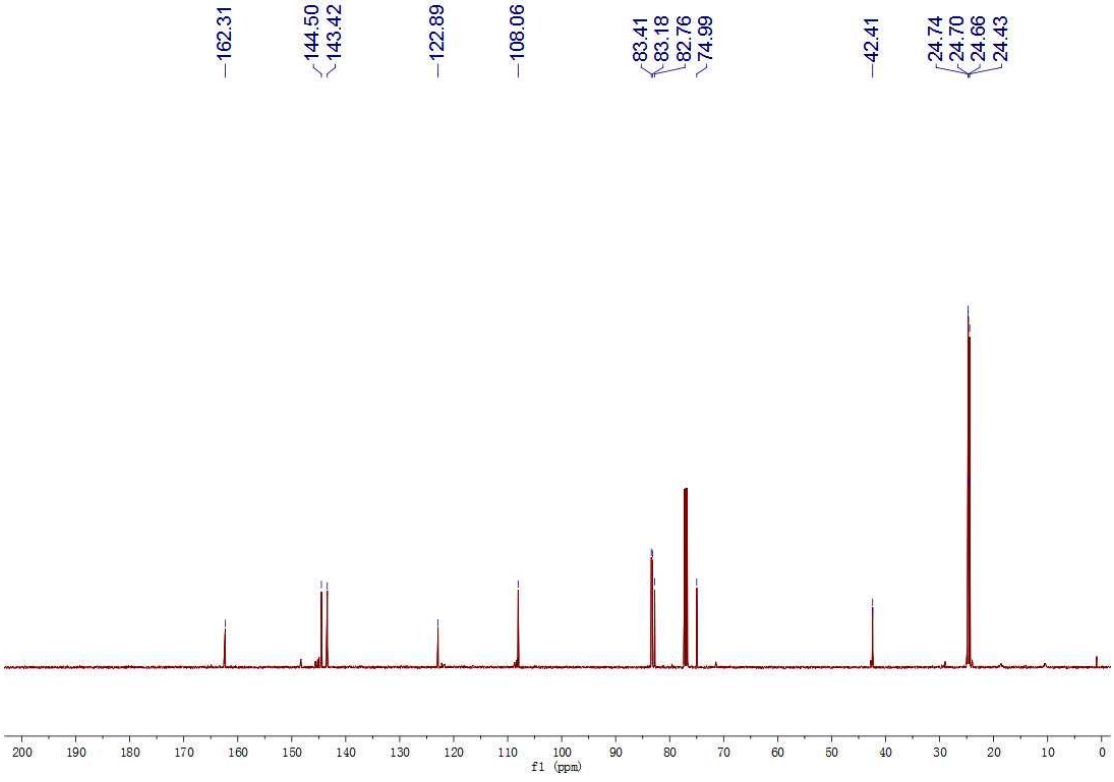
4.07
4.06
4.04
3.53
3.52
3.50
3.49
3.27
3.26
3.25
3.24
3.23
3.22
1.20
1.18
0.89
0.87
0.86
1.02
1.01
1.02
1.02
1.04
1.03
1.02
24.19
2.01
f1 (ppm)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143.42
122.89
108.06
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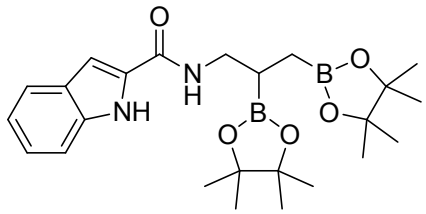
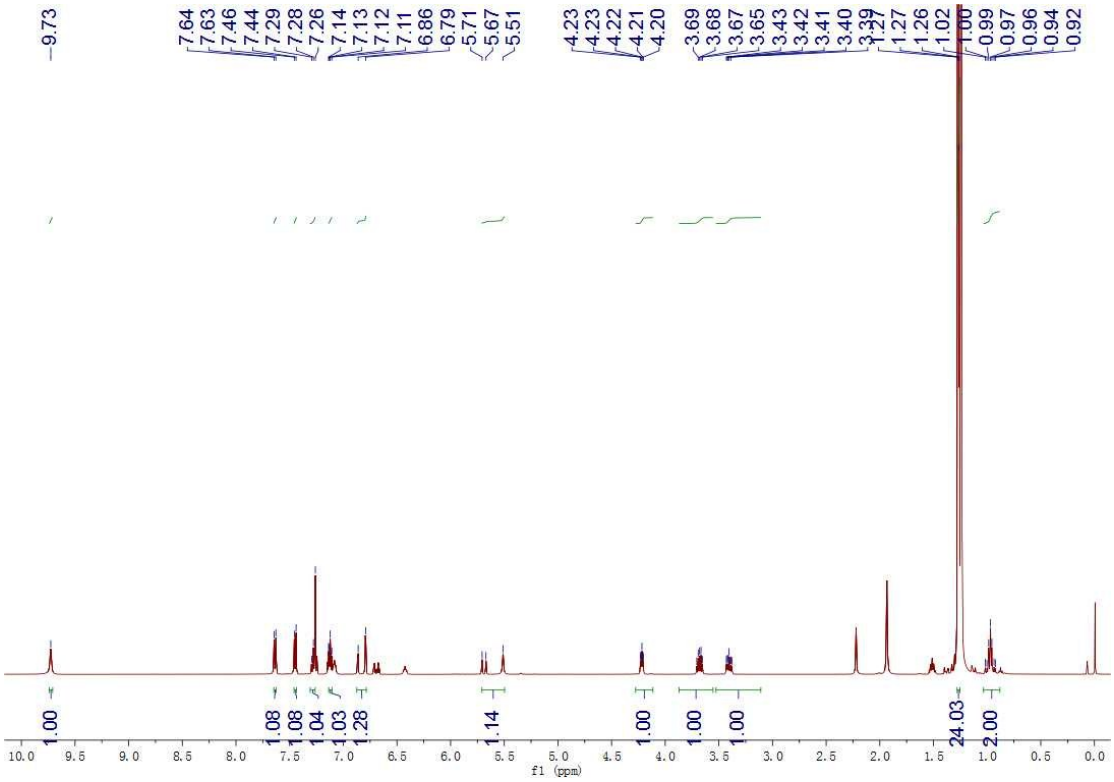
83.18
82.76
74.99
42.41
24.74
24.70
24.66
24.43
f1 (ppm)



41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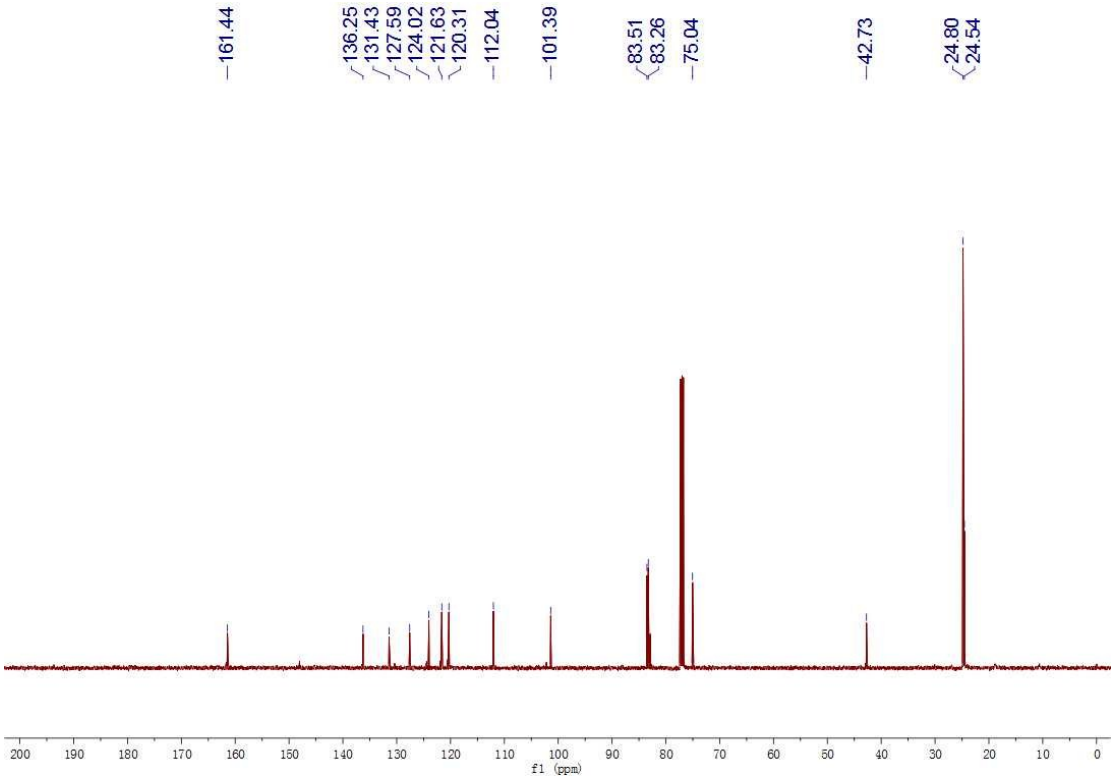
7.28
7.26
7.14
7.13
7.12
7.11
6.86
6.79
5.71
5.67
5.51
4.23
4.23
4.22
4.21
4.20
3.69
3.68
3.67
3.65
3.43
3.42
3.41
3.40
3.39
1.27
1.26
1.02
1.00
0.99
0.97
0.96
0.94
0.92
1.00
1.08
1.08
1.04
1.03
1.28
1.14
1.00
1.00
1.00
24.03
2.00
f1 (ppm)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136.25
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127.59
124.02
121.63
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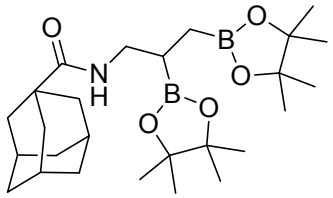
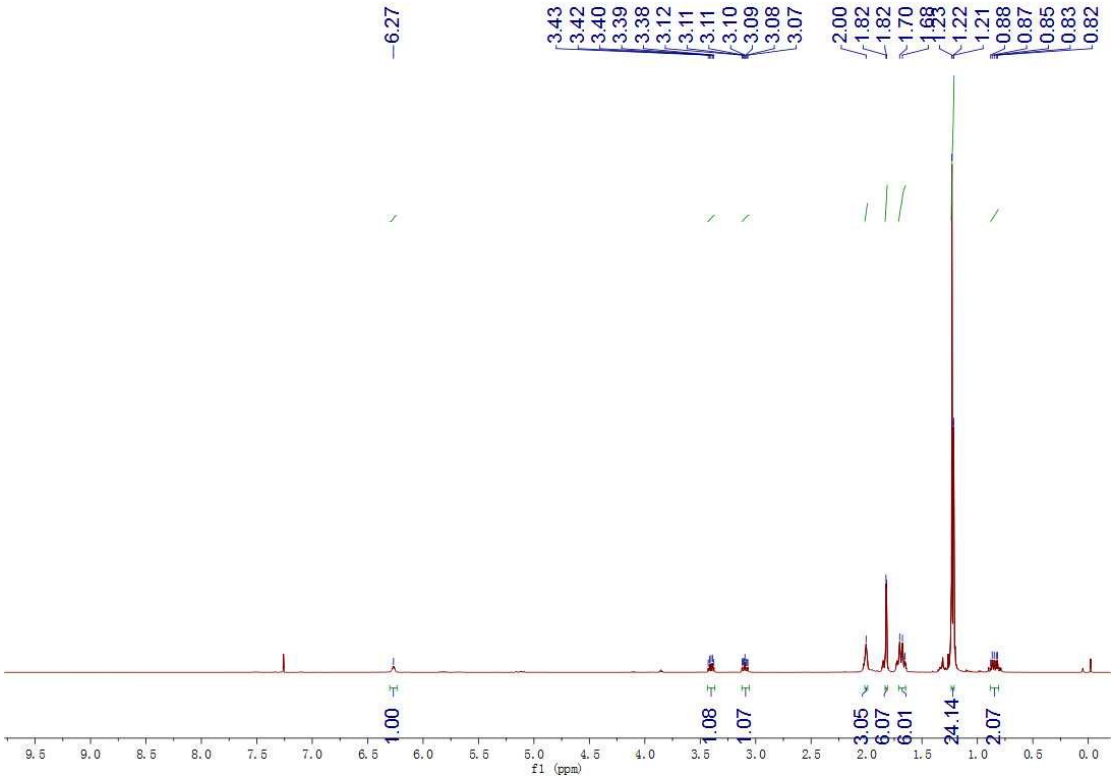
112.04
101.39
83.51
83.26
75.04
42.73
24.80
24.54
f1 (ppm)



42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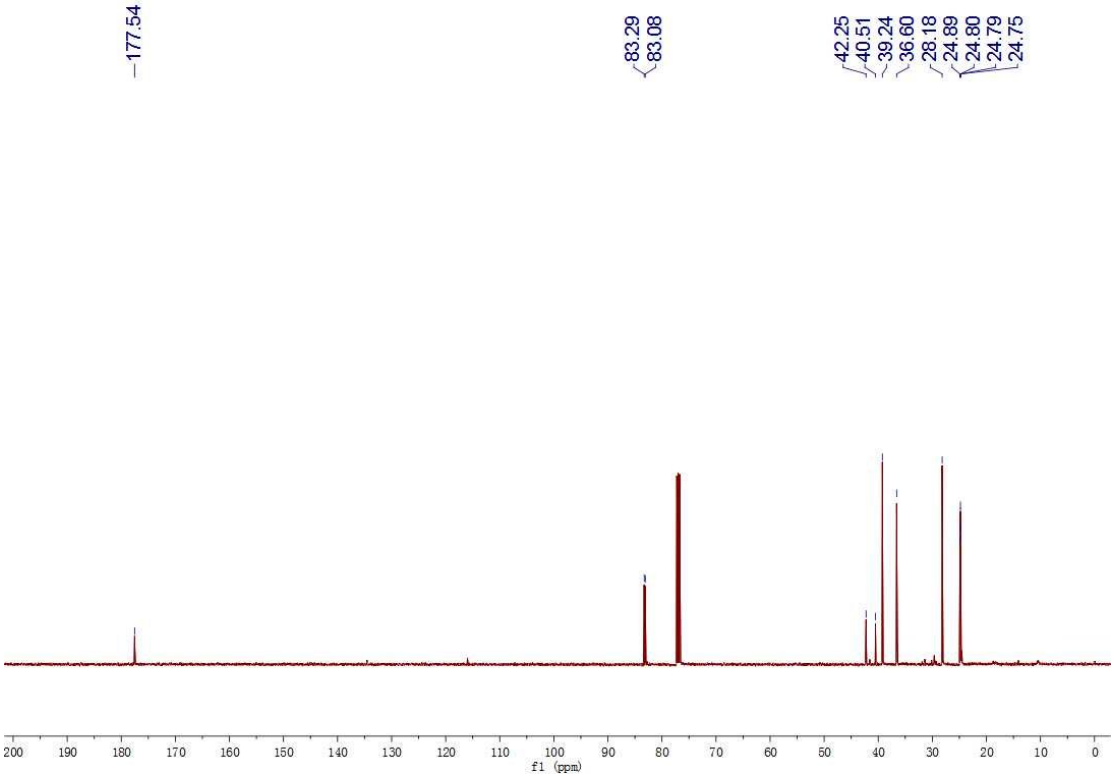
3.38
3.12
3.11
3.11
3.10
3.09
3.08
3.07
2.00
1.82
1.82
1.70
1.22
1.21
0.88
0.87
0.85
0.83
0.82
1.00
1.08
1.07
3.05
6.07
6.01
24.14
2.07
f1 (ppm)


177.54
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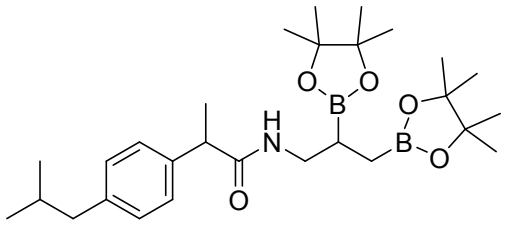
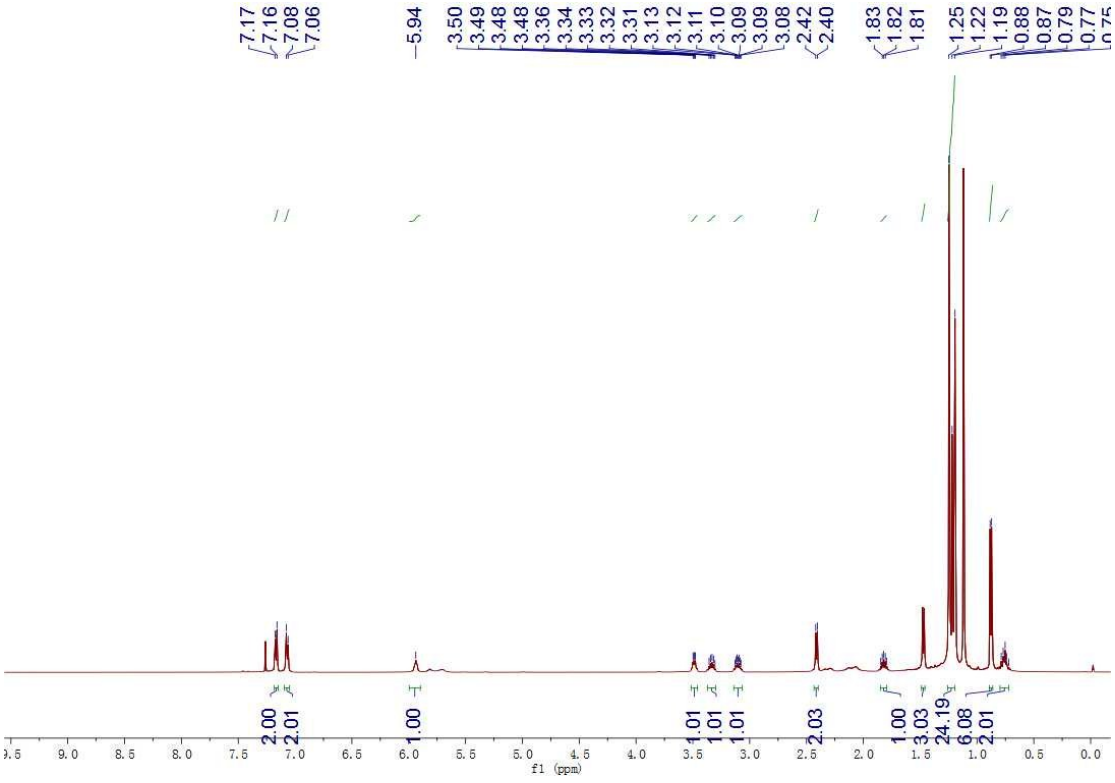
39.24
36.60
28.18
24.89
24.80
24.79
24.75
f1 (ppm)



43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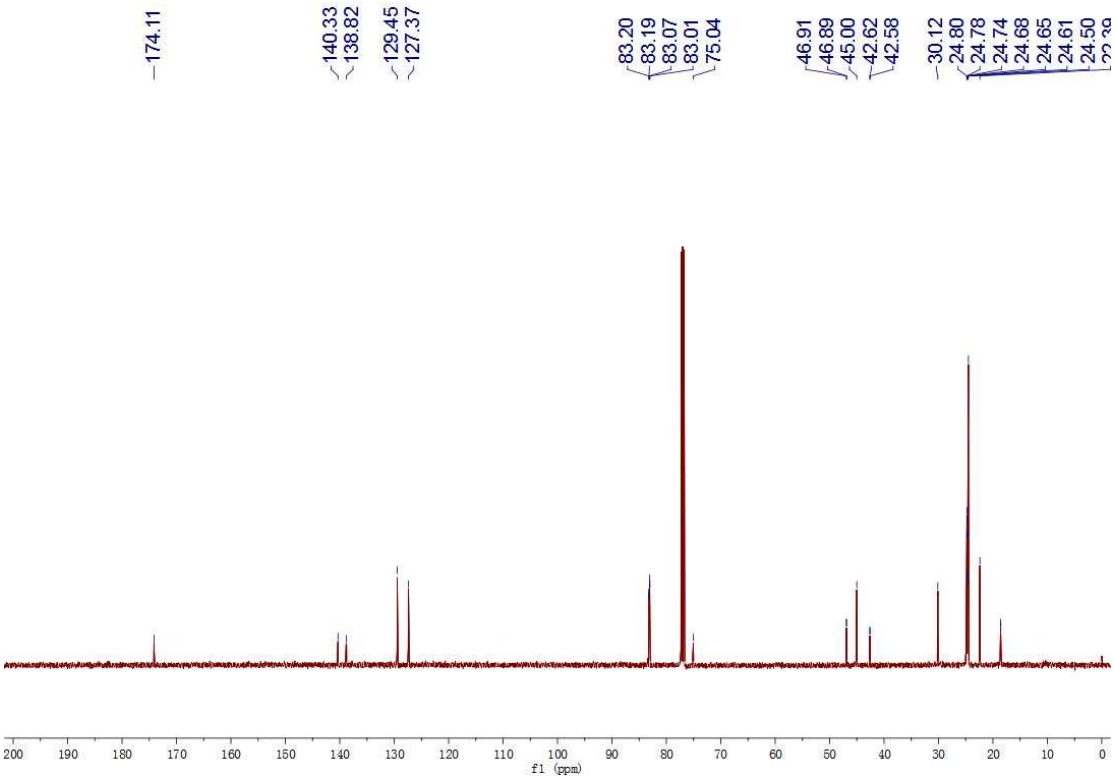
3.36
3.34
3.33
3.32
3.31
3.13
3.12
3.11
3.10
3.09
3.09
3.08
2.42
2.40
1.83
1.82
1.81
1.25
1.22
1.19
0.88
0.87
0.79
0.77
2.00
2.01
1.00
1.01
1.01
1.01
2.03
1.00
3.03
24.19
6.08
2.01
f1 (ppm)


174.11
140.33
138.82
129.45
127.37
83.20
83.19
83.07
83.01
75.04
46.91
46.89
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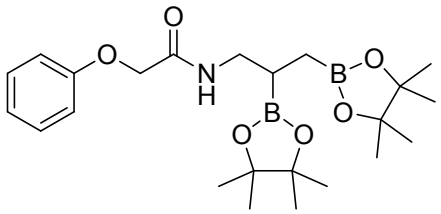
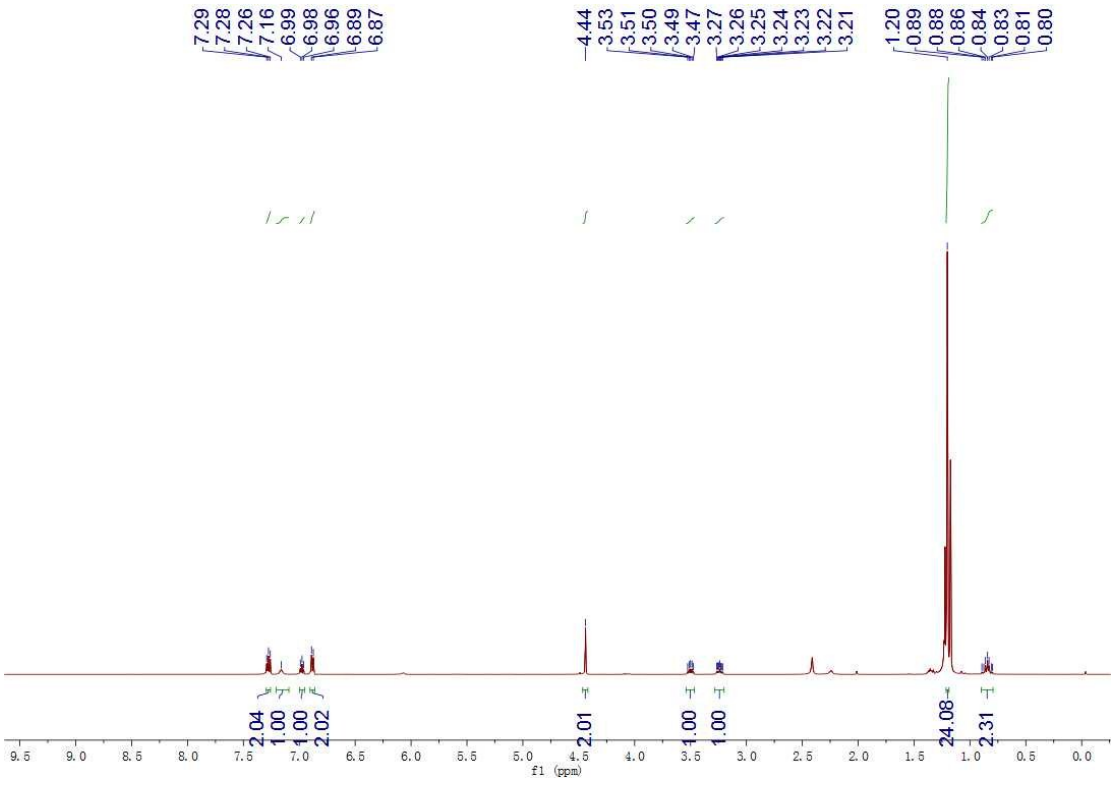
24.68
24.65
24.61
24.50
f1 (ppm)



44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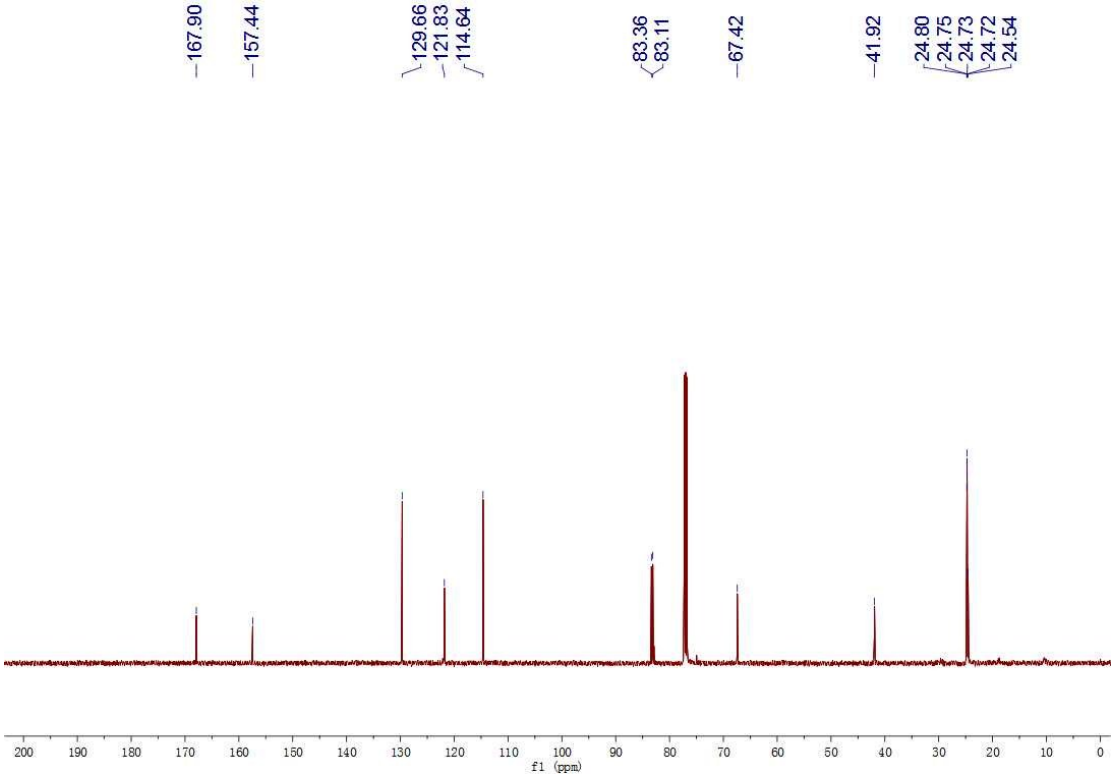
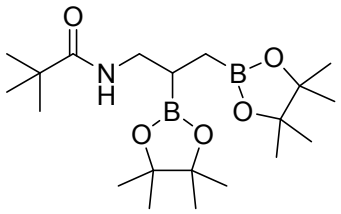
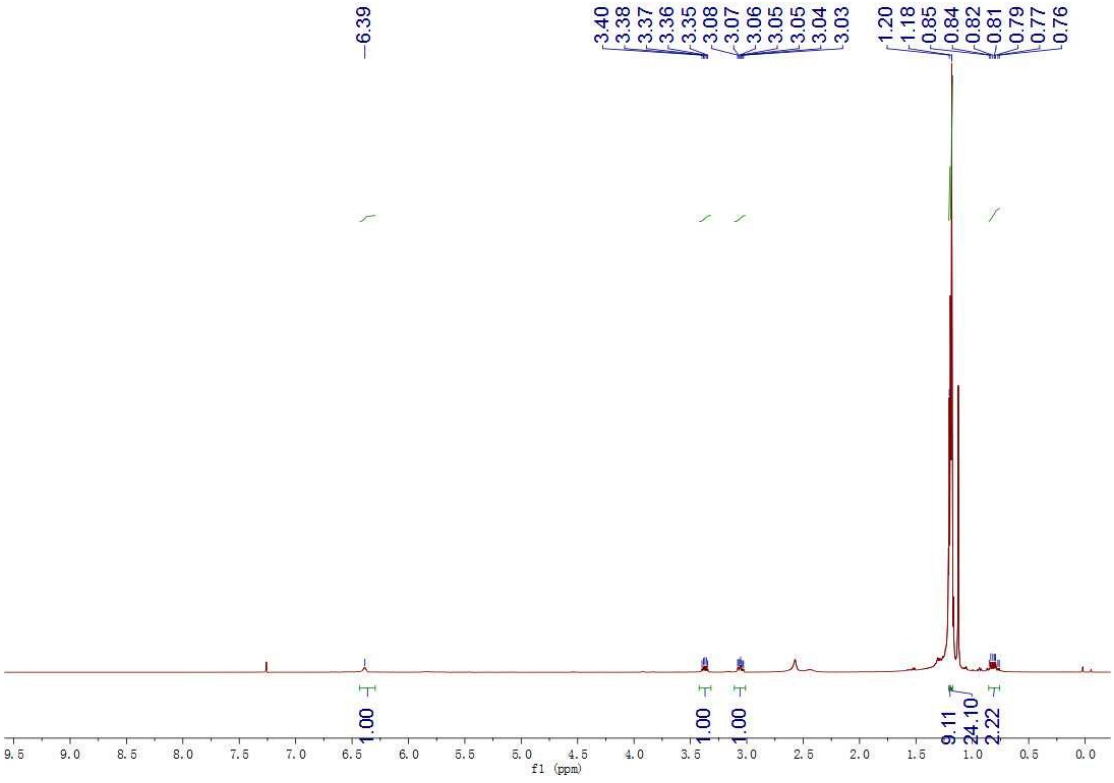
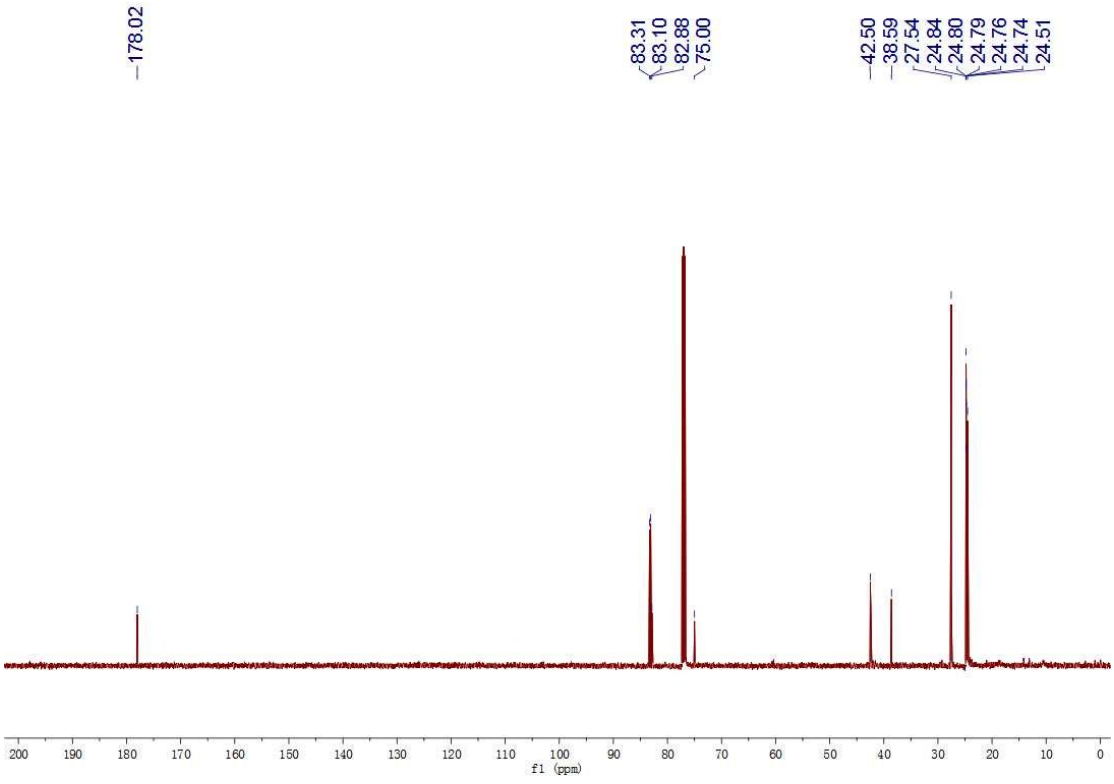
3.50
3.49
3.47
3.27
3.26
3.25
3.24
3.23
3.22
3.21
1.20
0.89
0.88
0.86
0.84
0.83
0.81
0.80
2.04
1.00
1.00
2.02
2.01
1.00
1.00
24.08
2.31
f1 (ppm)

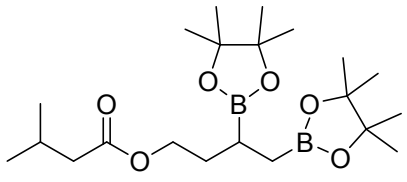

167.90
157.44
129.66
121.83
114.64
83.36
83.11
67.42
41.92
24.80
24.75
24.73
24.72
24.54
f1 (ppm)



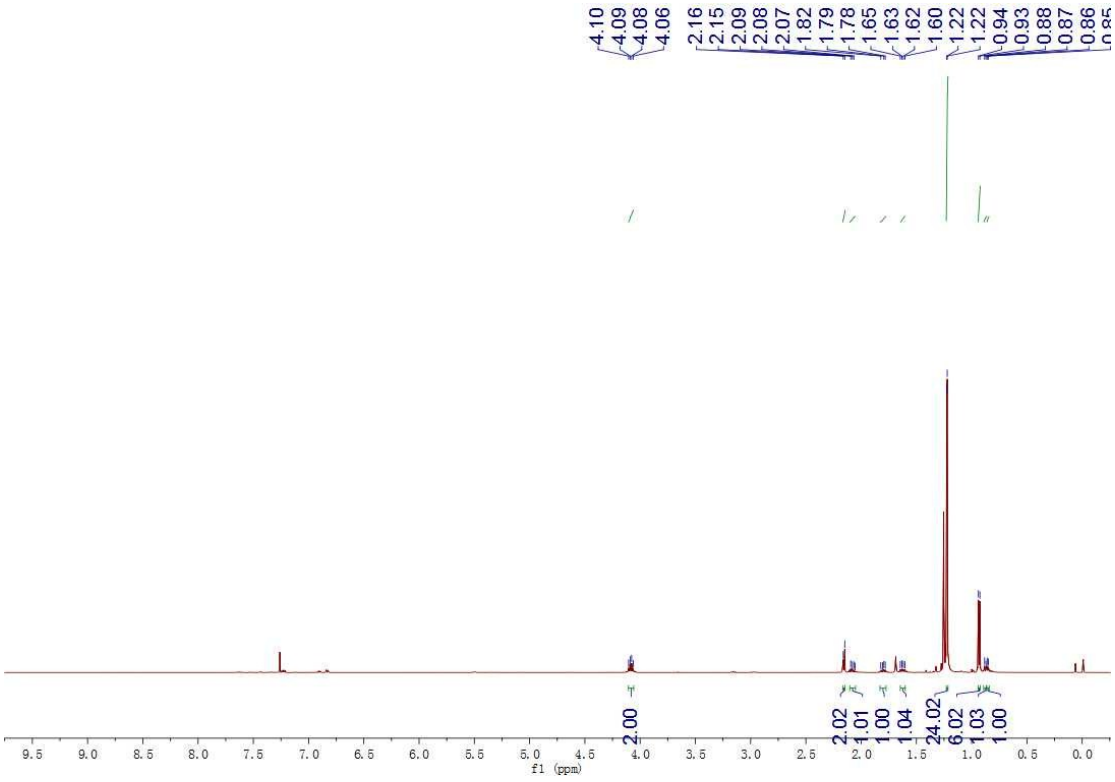
45

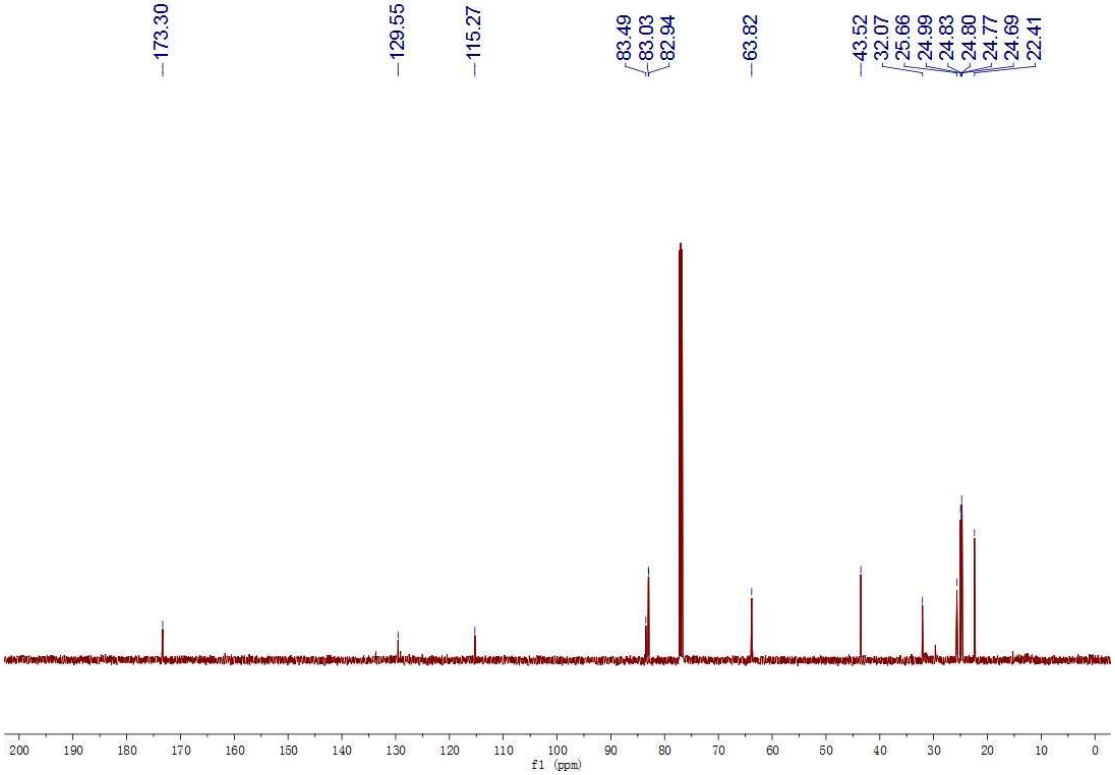

6.39
3.40
3.38
3.37
3.36
3.35
3.08
3.07
3.06
3.05
3.05
3.04
3.03
1.20
1.18
0.85
0.84
0.82
0.81
0.79
0.77
0.76
1.00
1.00
1.00
9.11
24.10
2.22
f1 (ppm)

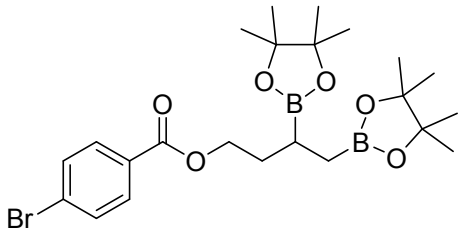

178.02
83.31
83.10
82.88
75.00
42.50
38.59
27.54
24.84
24.80
24.79
24.76
24.74
24.51
f1 (ppm)



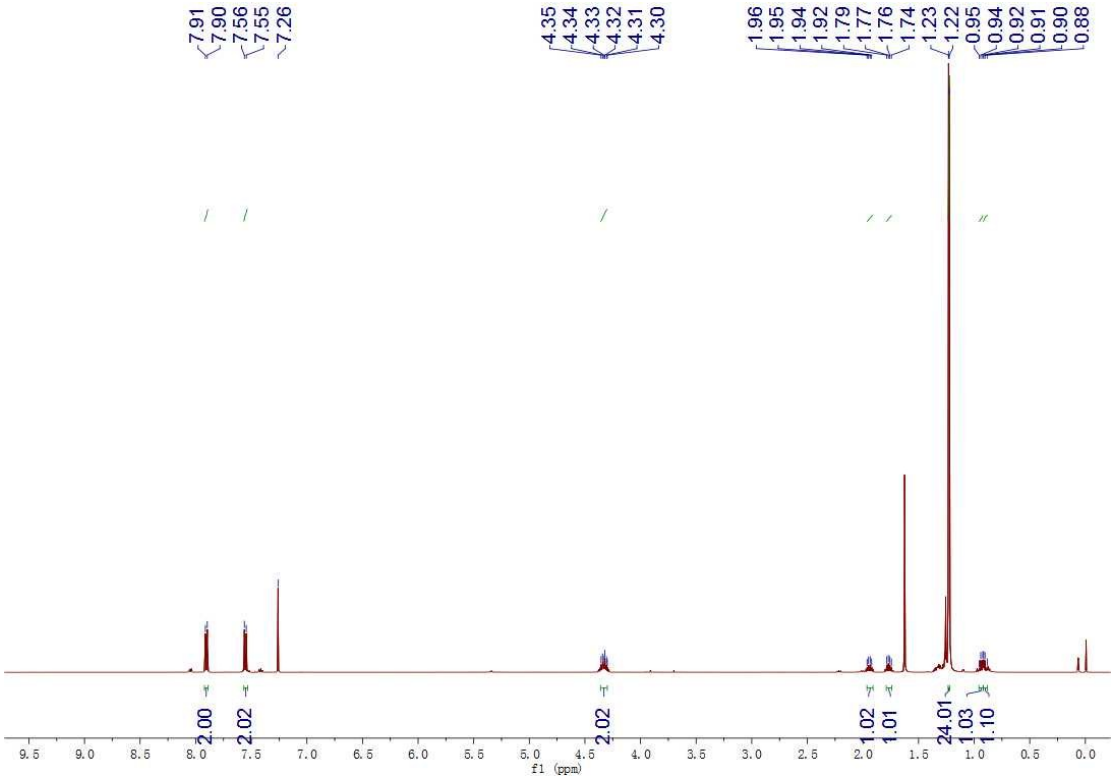
46

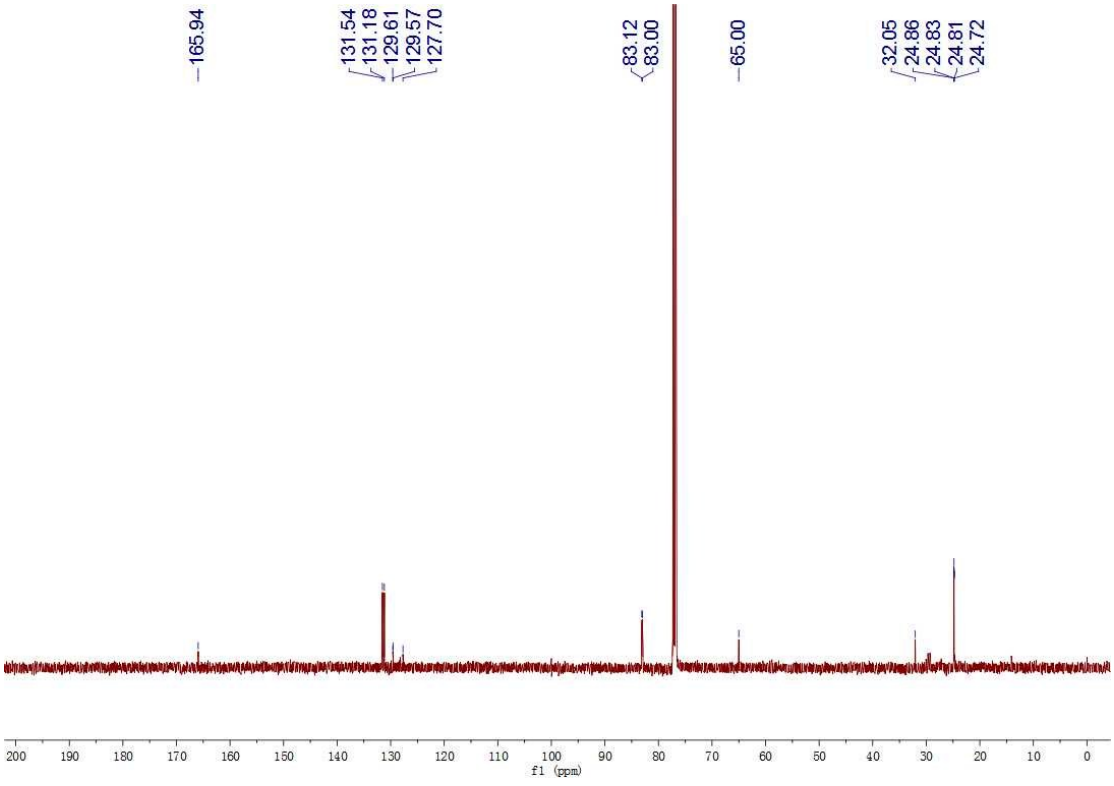

4.10
4.09
4.08
4.06
2.16
2.15
2.09
2.08
2.07
1.82
1.79
1.78
1.65
1.63
1.62
1.60
1.22
1.22
0.94
0.93
0.88
0.87
0.86
2.00
2.02
1.01
1.00
1.04
24.02
6.02
1.03
1.00
f1 (ppm)

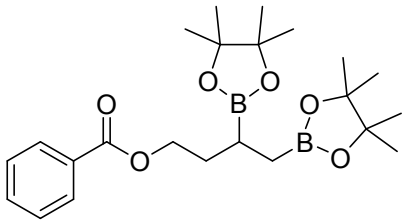

173.30
129.55
115.27
83.49
83.03
82.94
63.82
43.52
32.07
25.66
24.99
24.83
24.80
24.77
24.69
22.41
f1 (ppm)


O
O
B
O
O
B
O
Br

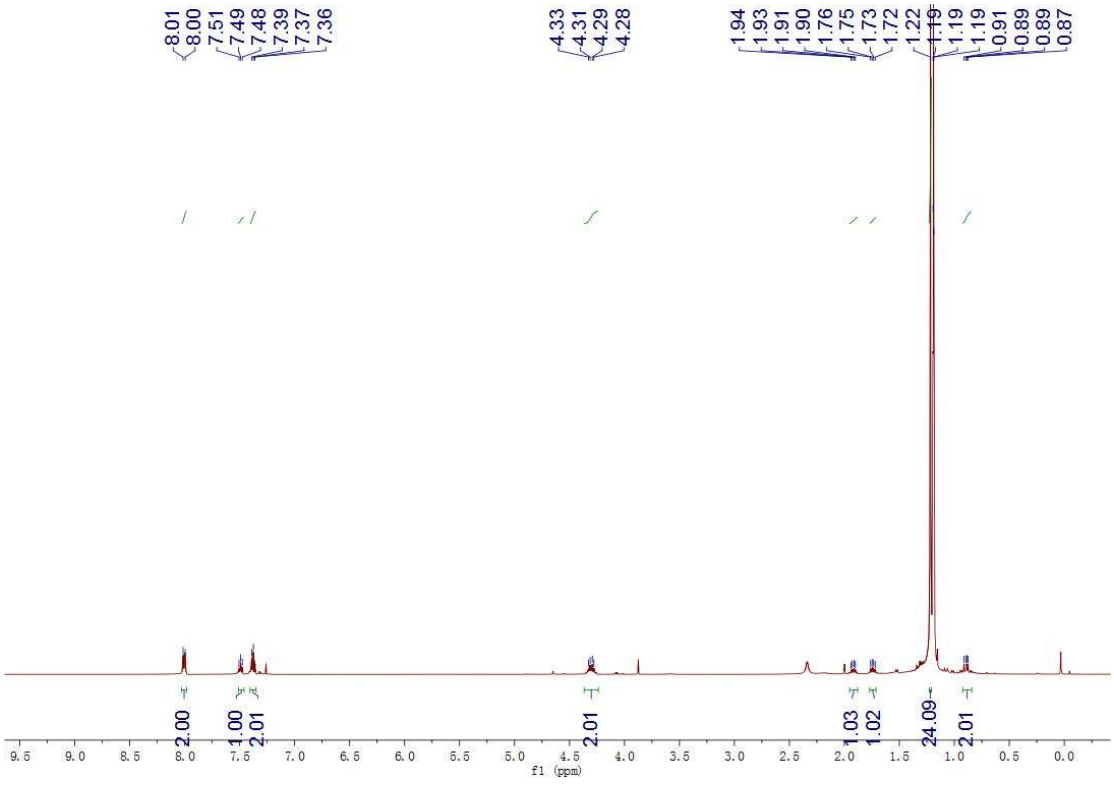
47

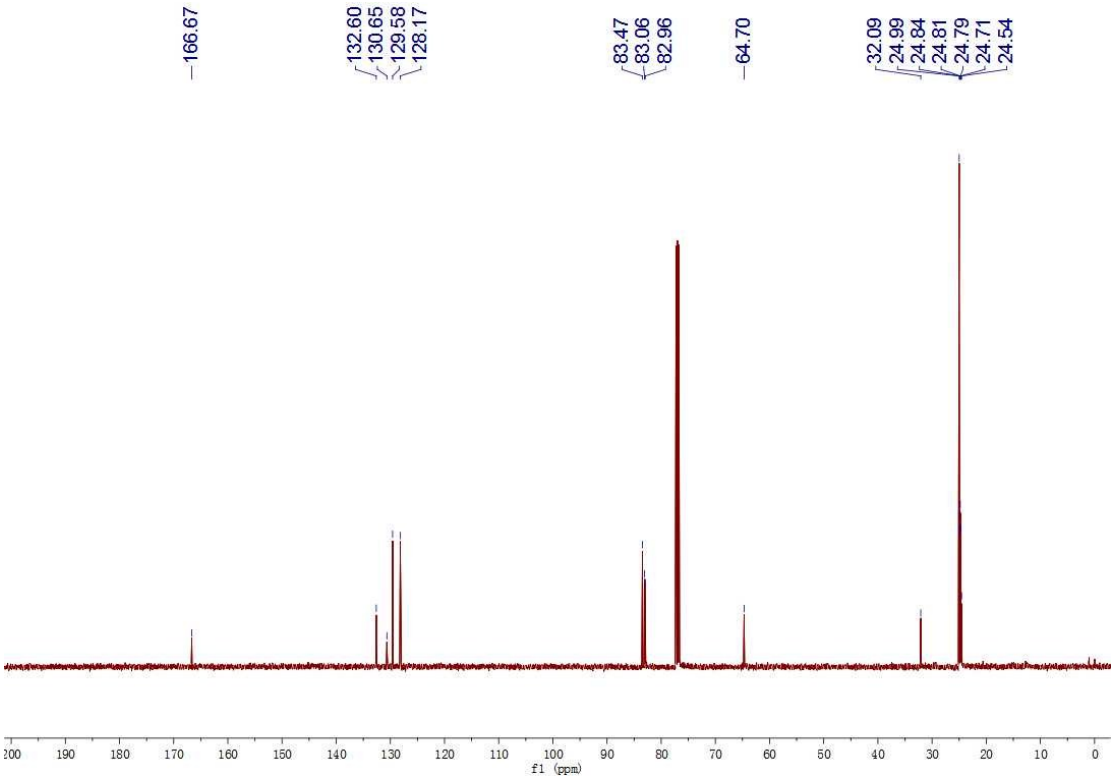

7.91
7.90
7.56
7.55
7.26
4.35
4.34
4.33
4.32
4.31
4.30
1.96
1.95
1.94
1.92
1.79
1.77
1.76
1.74
1.23
1.22
0.95
0.94
0.92
0.91
0.90
0.88
2.00
2.02
2.02
1.02
1.01
24.01
1.03
1.10
f1 (ppm)

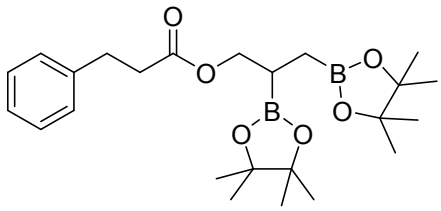

165.94
131.54
131.18
129.61
129.57
127.70
83.12
83.00
65.00
32.05
24.86
24.83
24.81
24.72
f1 (ppm)



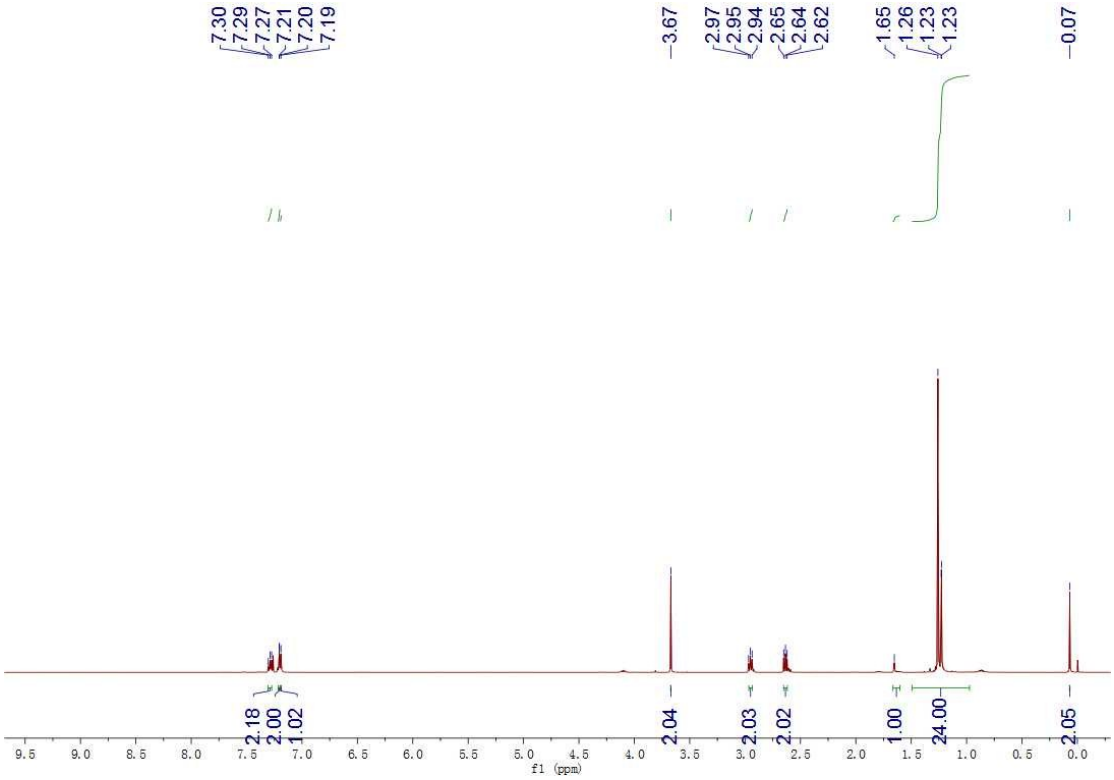
48

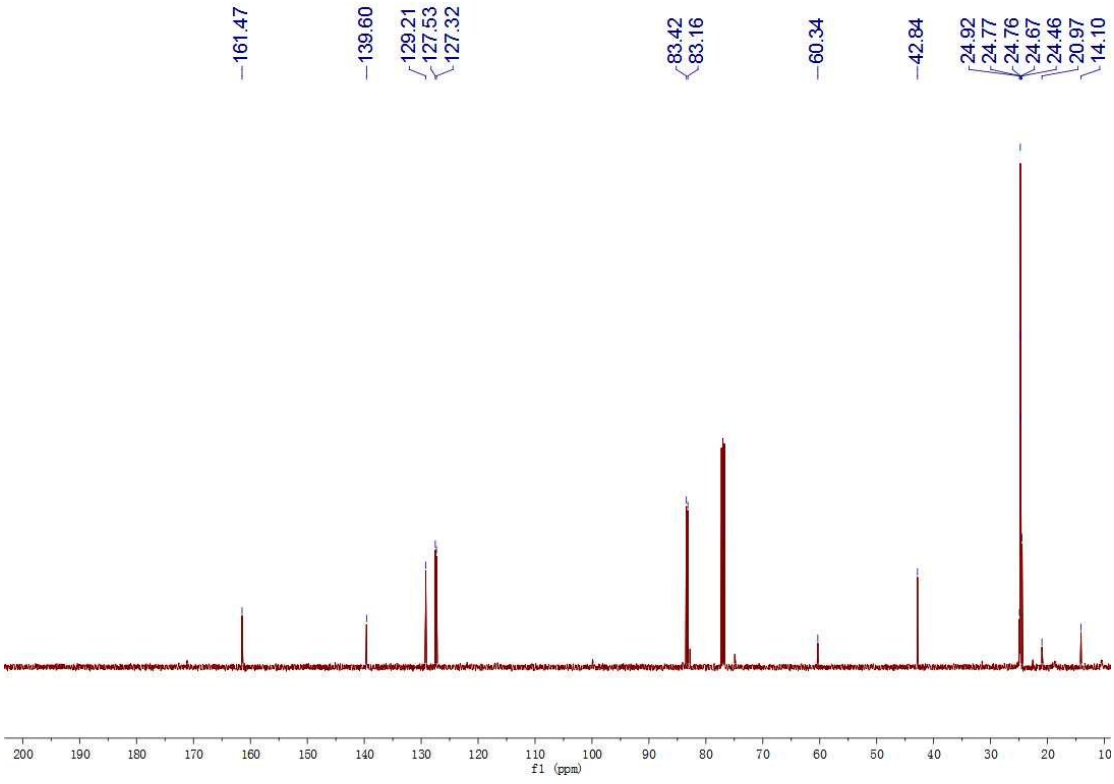

8.01
8.00
7.51
7.49
7.48
7.39
7.37
7.36
4.33
4.31
4.29
4.28
1.94
1.93
1.91
1.90
1.76
1.75
1.73
1.72
1.22
1.19
1.19
1.19
0.91
0.89
0.89
0.87
2.00
1.00
2.01
2.01
1.03
1.02
24.09
2.01
f1 (ppm)

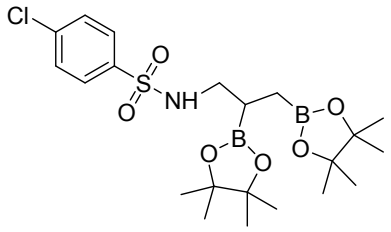

166.67
132.60
130.65
129.58
128.17
83.47
83.06
82.96
64.70
32.09
24.99
24.84
24.81
24.79
24.71
24.54
f1 (ppm)



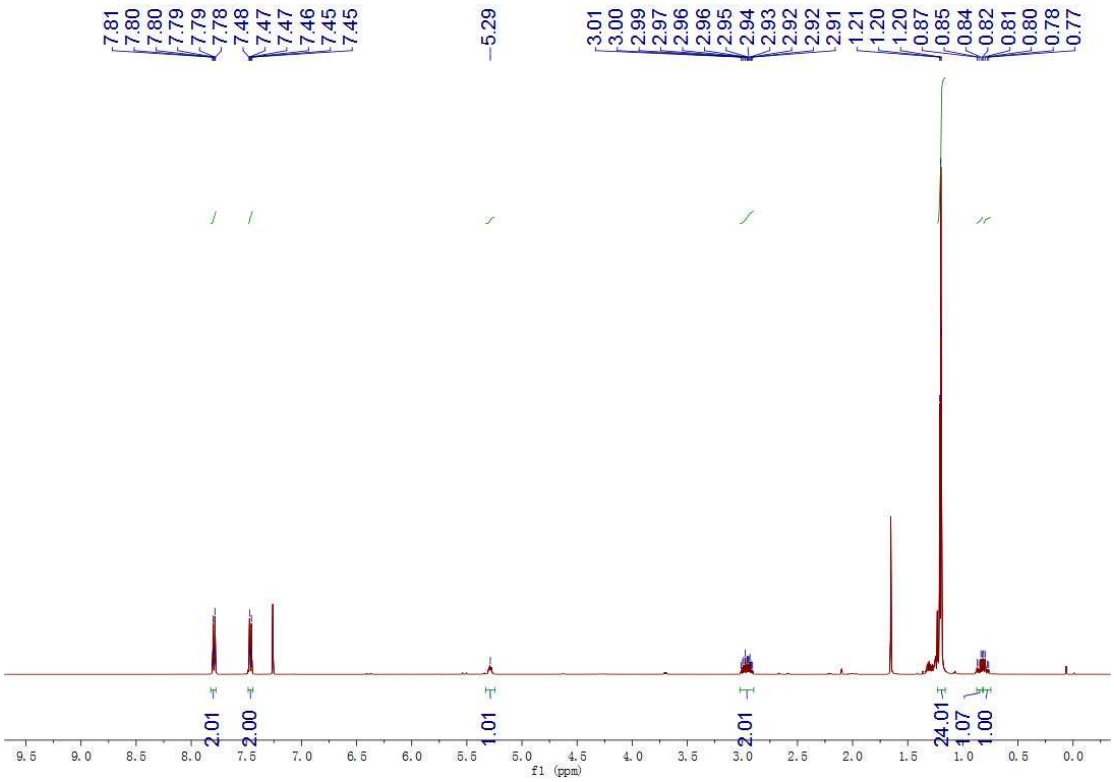
49

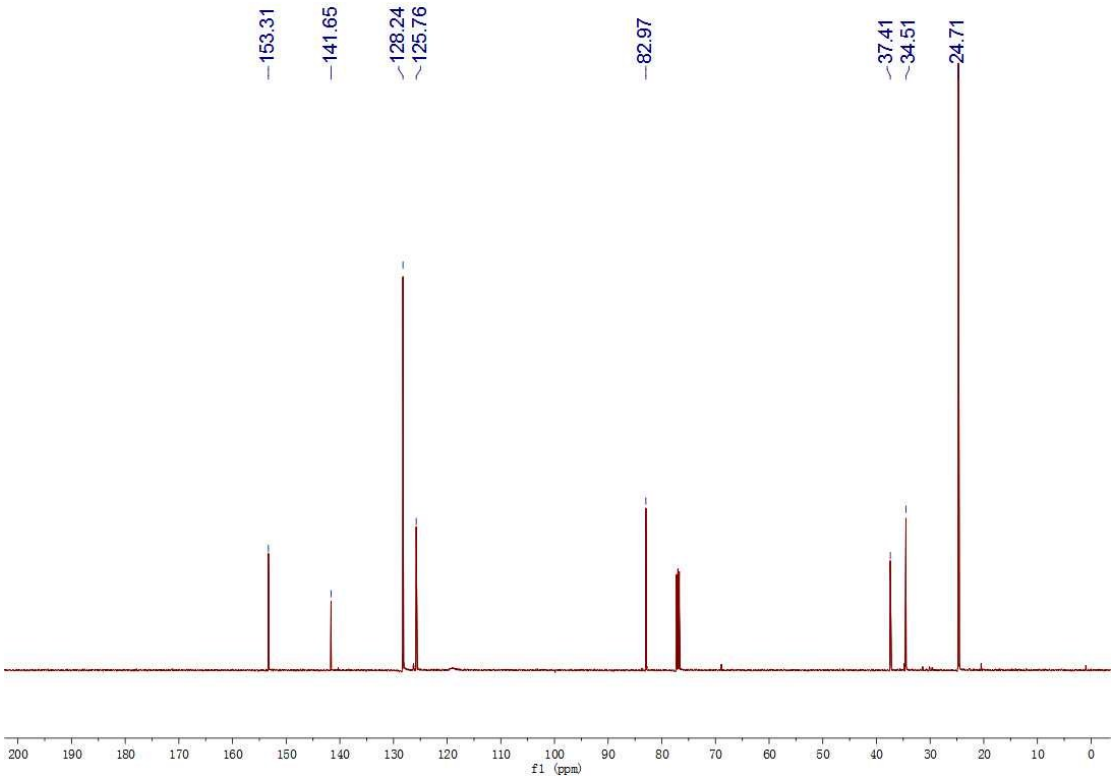

7.30
7.29
7.27
7.21
7.20
7.19
3.67
2.97
2.95
2.94
2.65
2.64
2.62
1.65
1.26
1.23
1.23
0.07
2.18
2.00
1.02
2.04
2.03
2.02
1.00
24.00
2.05
f1 (ppm)

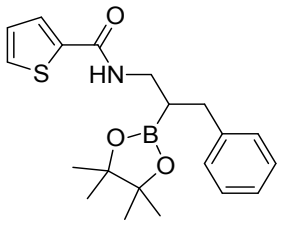

161.47
139.60
129.21
127.53
127.32
83.42
83.16
60.34
42.84
24.92
24.77
24.76
24.67
24.46
20.97
14.10
f1 (ppm)


Cl
O
O
S
NH
B
O
O
B
O
O

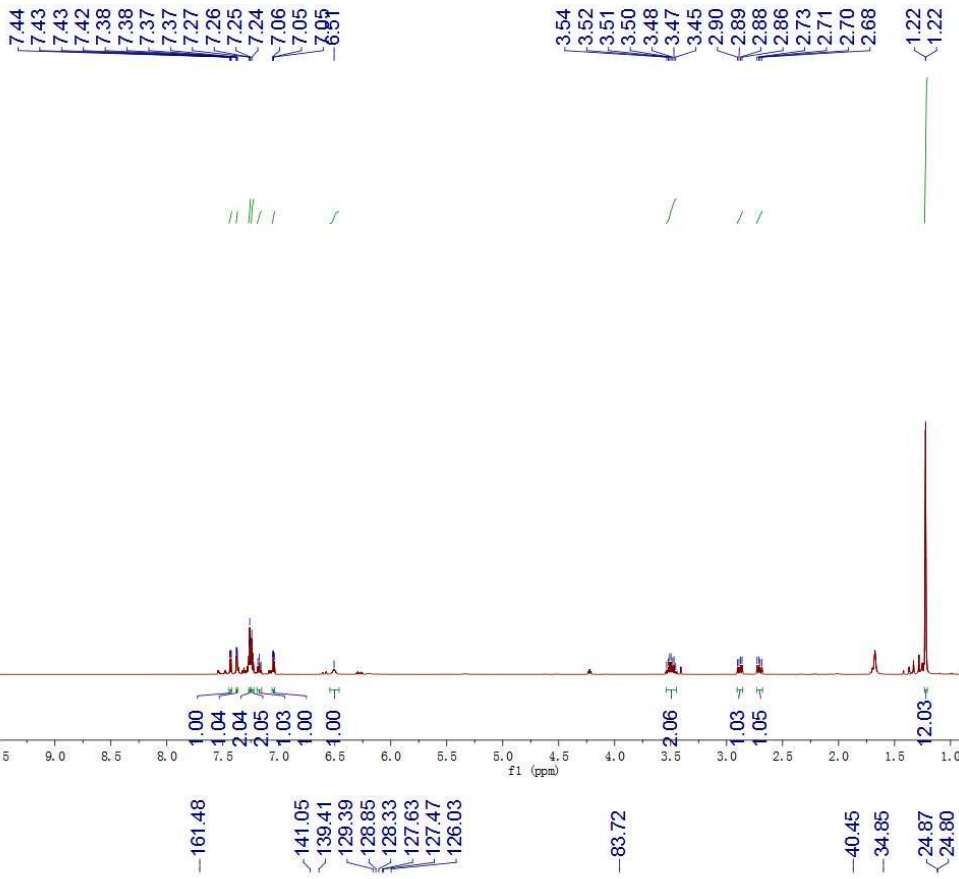
50

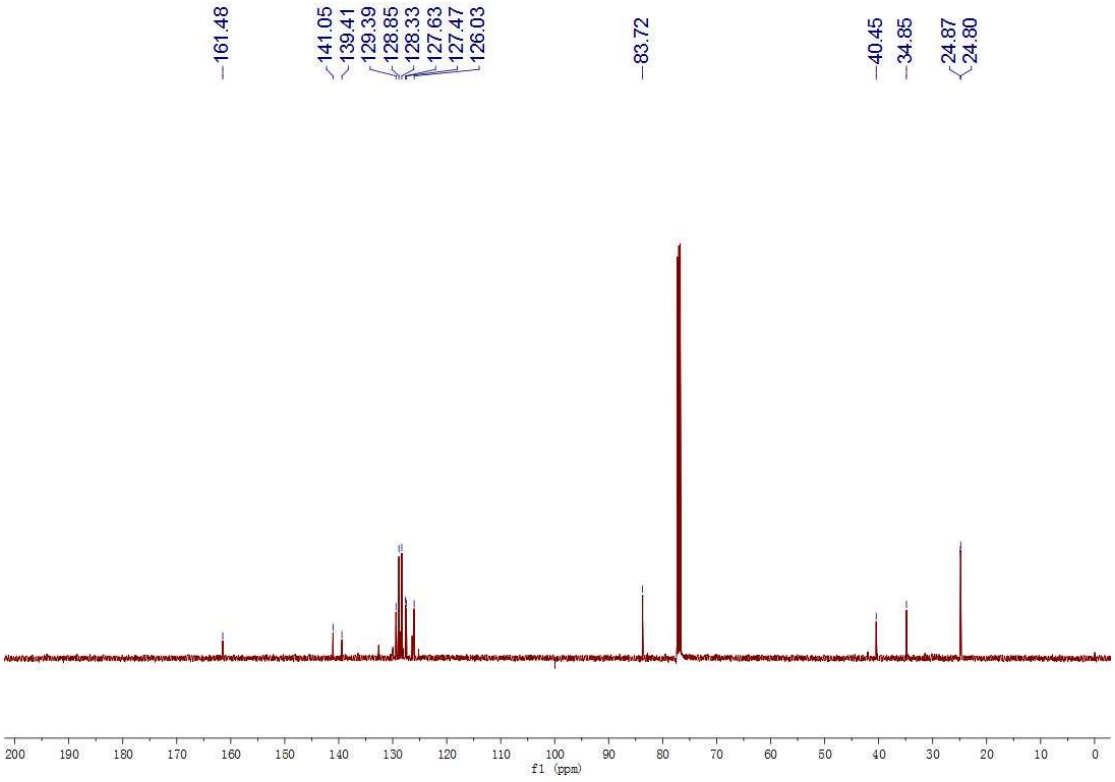

7.81
7.80
7.80
7.79
7.79
7.78
7.48
7.47
7.47
7.46
7.45
7.45
5.29
3.01
3.00
2.99
2.97
2.96
2.96
2.95
2.94
2.93
2.92
2.92
2.91
1.21
1.20
1.20
0.87
0.85
0.84
0.82
0.81
0.80
0.78
0.77
2.01
2.00
1.01
2.01
24.01
1.07
1.00
f1 (ppm)

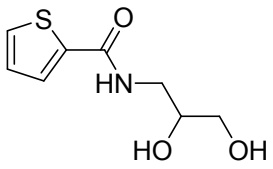

153.31
141.65
128.24
125.76
82.97
37.41
34.51
24.71
f1 (ppm)



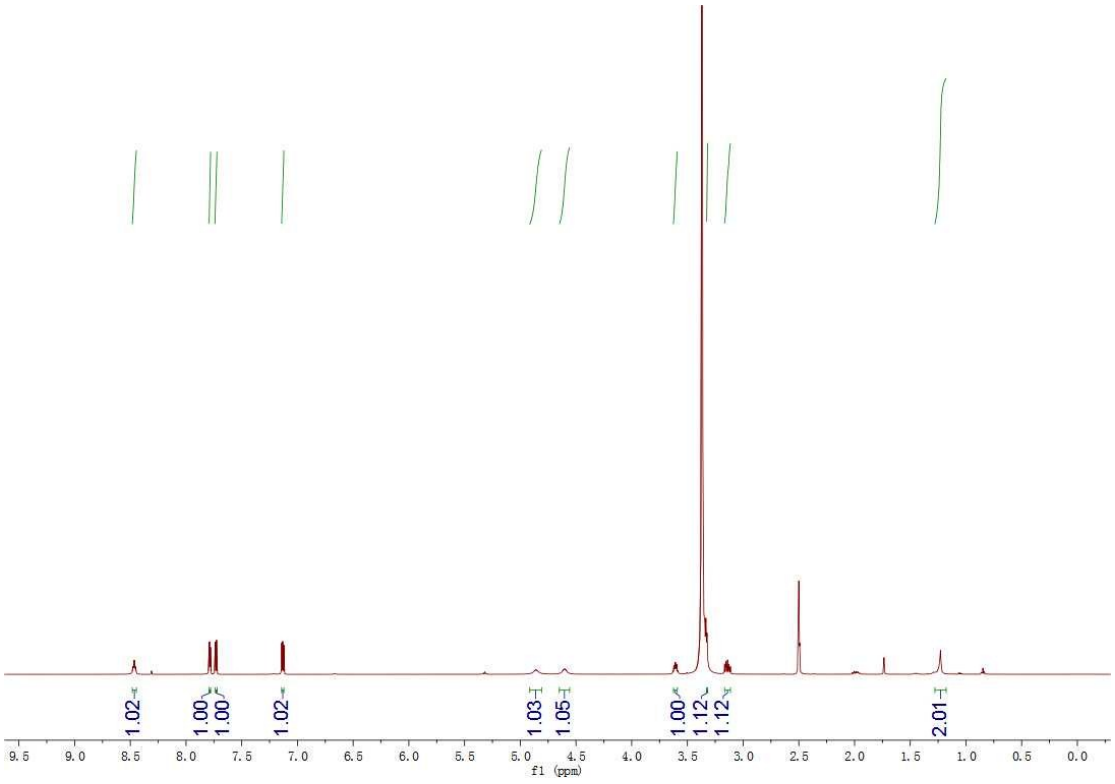
51

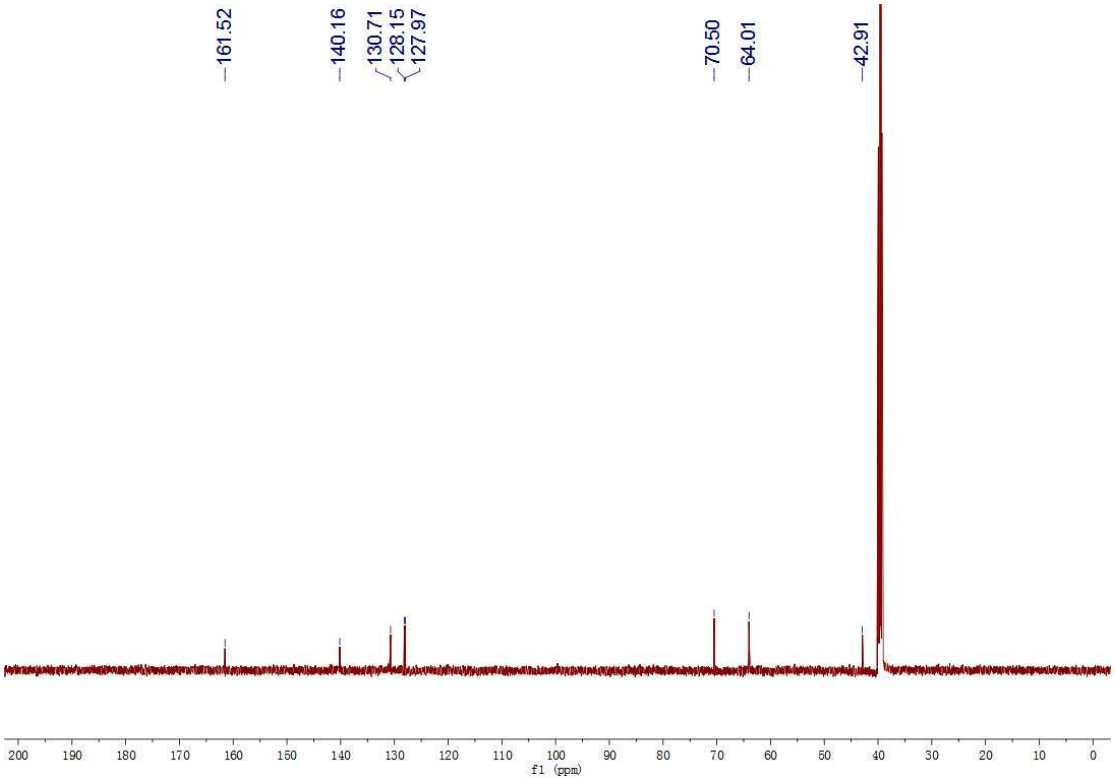

7.44
7.43
7.43
7.42
7.38
7.38
7.37
7.37
7.27
7.26
7.25
7.24
7.06
7.05
6.51
3.54
3.52
3.51
3.50
3.48
3.47
3.45
2.90
2.89
2.88
2.86
2.73
2.71
2.70
2.68
1.22
1.22
1.00
1.04
2.04
2.05
1.03
1.00
1.00
2.06
1.03
1.05
12.03
f1 (ppm)

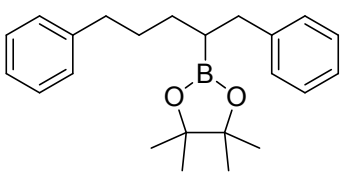

161.48
141.05
139.41
129.39
128.85
128.33
127.63
127.47
126.03
83.72
40.45
34.85
24.87
24.80
f1 (ppm)


S
O
HN
HO
OH

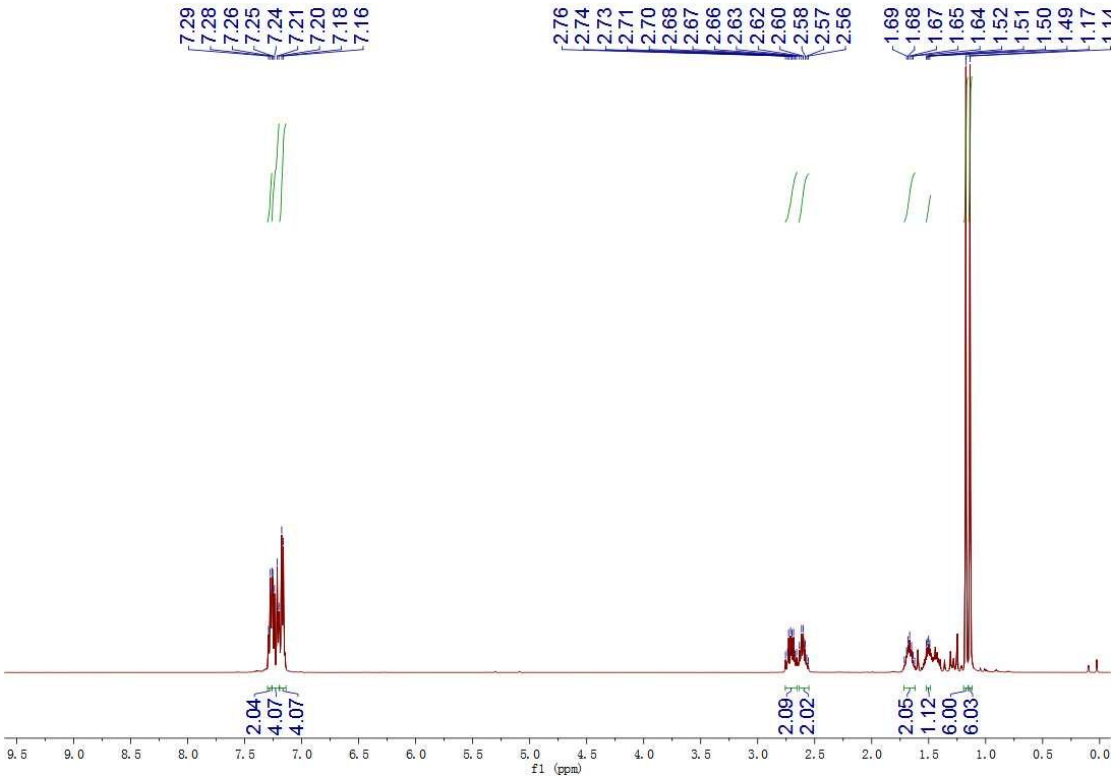
52


1.02
1.00
1.00
1.02
1.03
1.05
1.00
1.12
1.12
2.01
f1 (ppm)


161.52
140.16
130.71
128.15
127.97
70.50
64.01
42.91
f1 (ppm)


B
O
O

53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7.28
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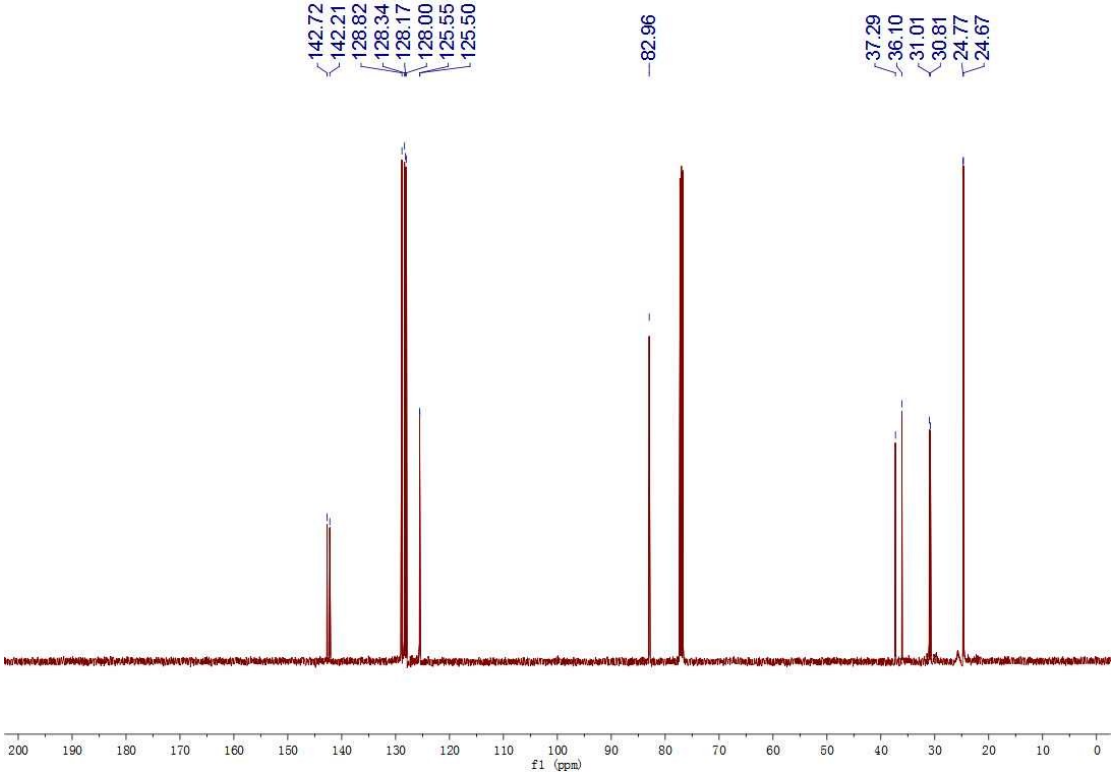
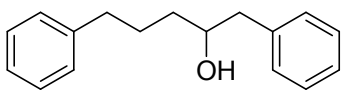
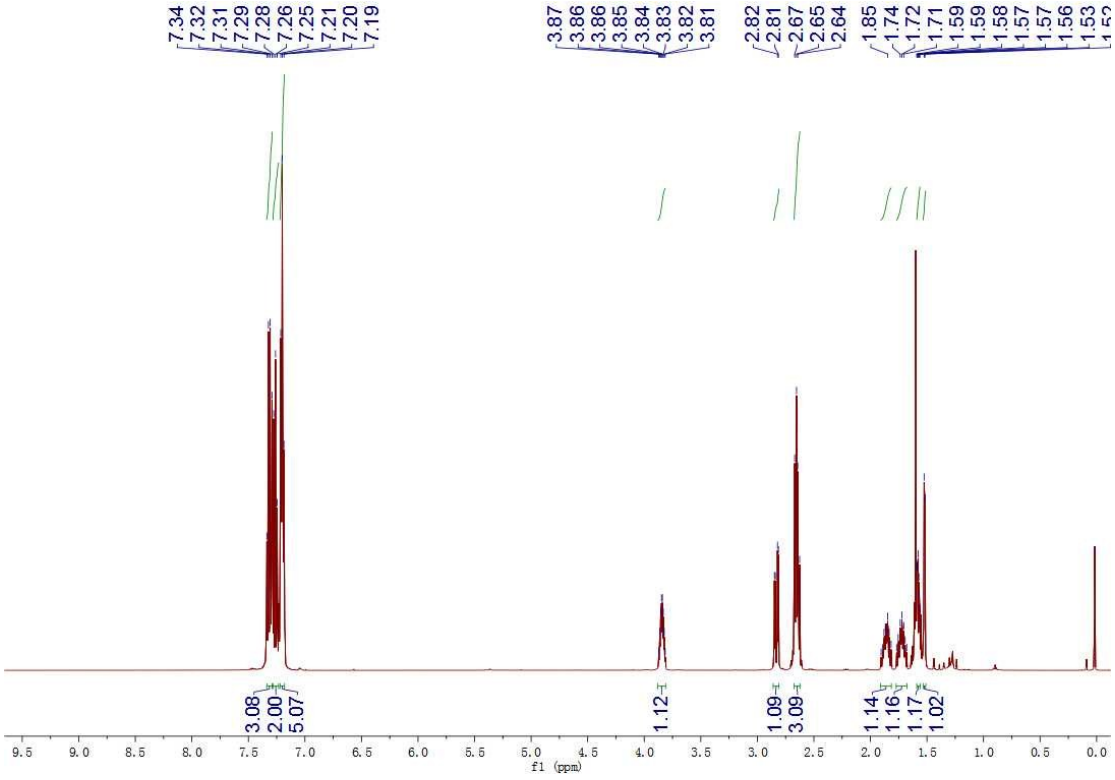
7.25
7.24
7.21
7.20
7.18
7.16
2.76
2.74
2.73
2.71
2.70
2.68
2.67
2.66
2.63
2.62
2.60
2.58
2.57
2.56
1.69
1.68
1.67
1.65
1.64
1.52
1.51
1.50
1.49
1.17
2.04
4.07
4.07
2.09
2.02
2.05
1.12
6.00
6.03
f1 (ppm)


142.72
142.21
128.82
128.34
128.17
128.00
125.55
125.50
82.96
37.29
36.10
31.01
30.81
24.77
24.67
f1 (ppm)


OH

54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7.28
7.26
7.25
7.21
7.20
7.19
3.87
3.86
3.86
3.85
3.84
3.83
3.82
3.81
2.82
2.81
2.67
2.65
2.64
1.85
1.74
1.72
1.71
1.59
1.59
1.58
1.57
1.57
1.56
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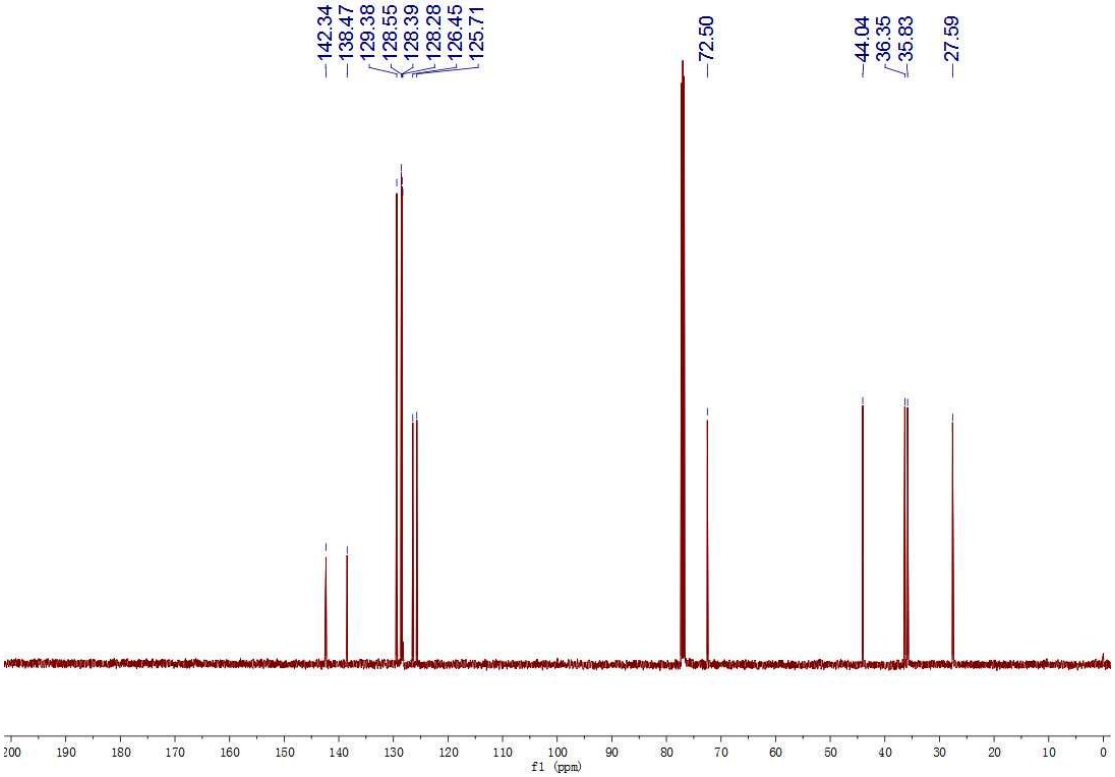
1.14
1.16
1.17
1.02
f1 (ppm)


142.34
138.47
129.38
128.55
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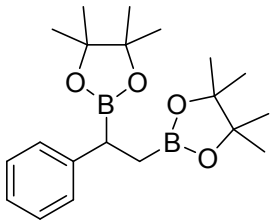
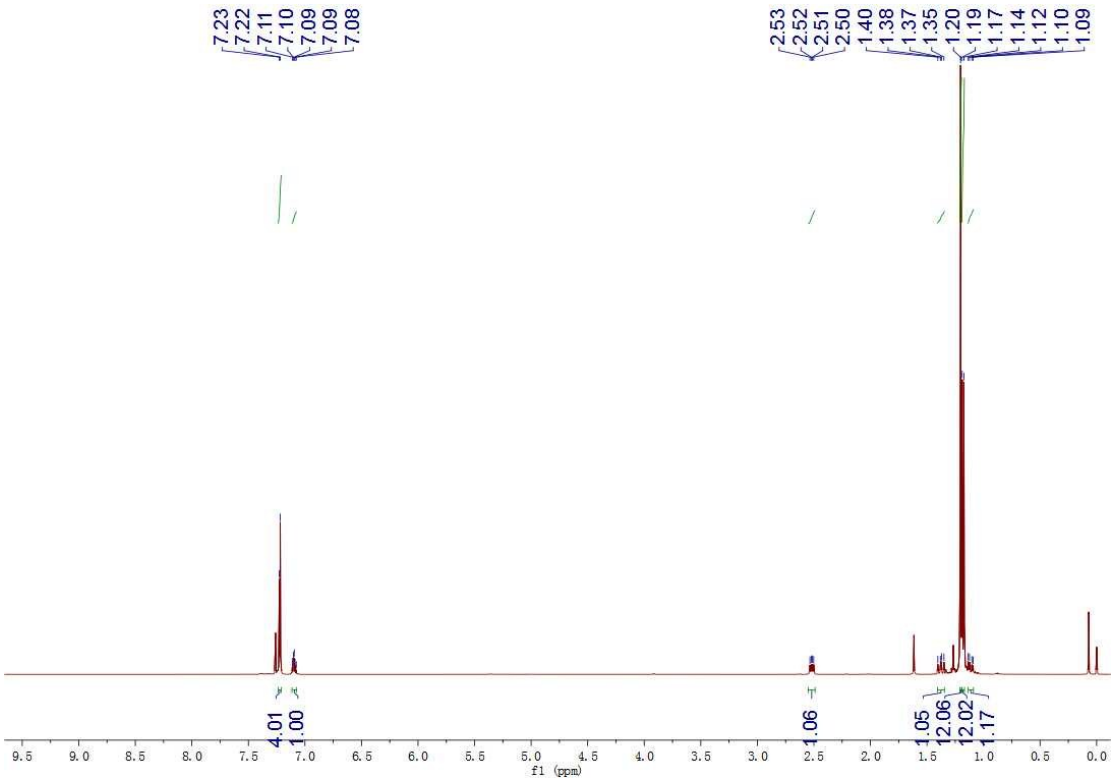
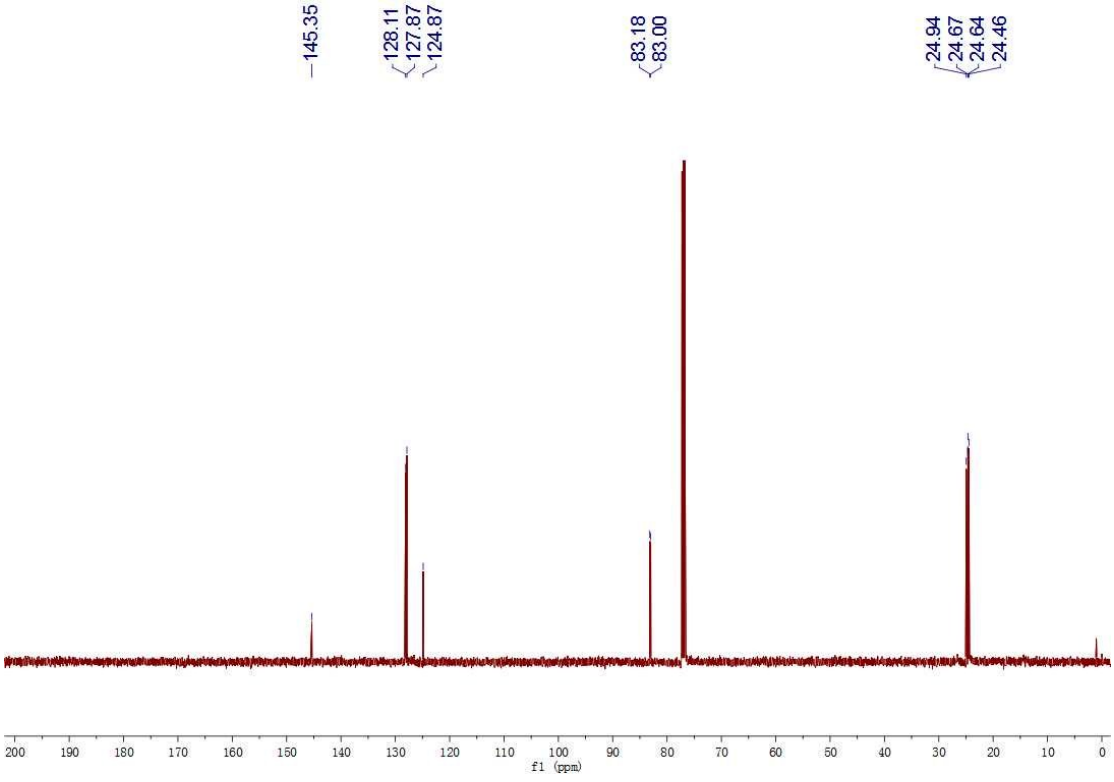
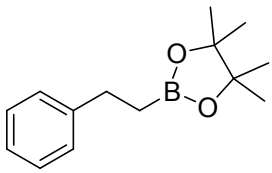
128.28
126.45
125.71
72.50
44.04
36.35
35.83
27.59
f1 (ppm)



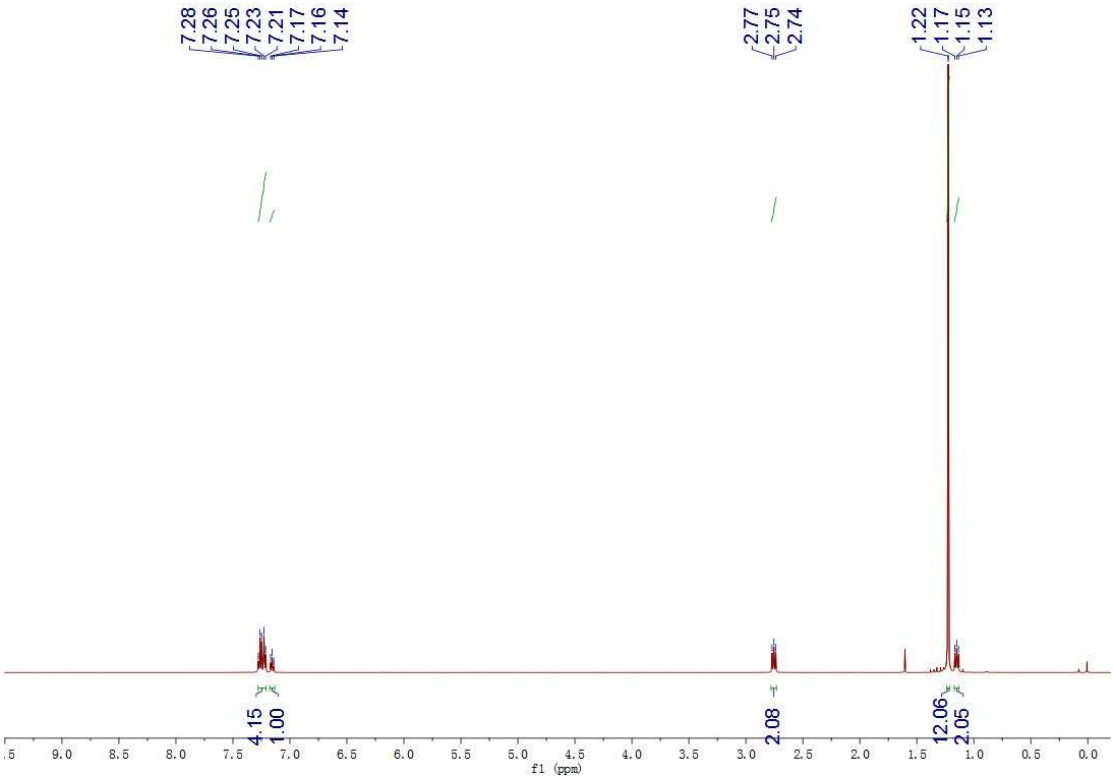
55


7.23
7.22
7.11
7.10
7.09
7.09
7.08
2.53
2.52
2.51
2.50
1.40
1.38
1.37
1.35
1.20
1.19
1.17
1.14
1.12
1.10
1.09
4.01
1.00
1.06
1.05
12.06
12.02
1.17
f1 (ppm)


145.35
128.11
127.87
124.87
83.18
83.00
24.94
24.67
24.64
24.46
f1 (ppm)



57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7.26
7.25
7.23
7.21
7.17
7.16
7.14
2.77
2.75
2.74
1.22
1.17
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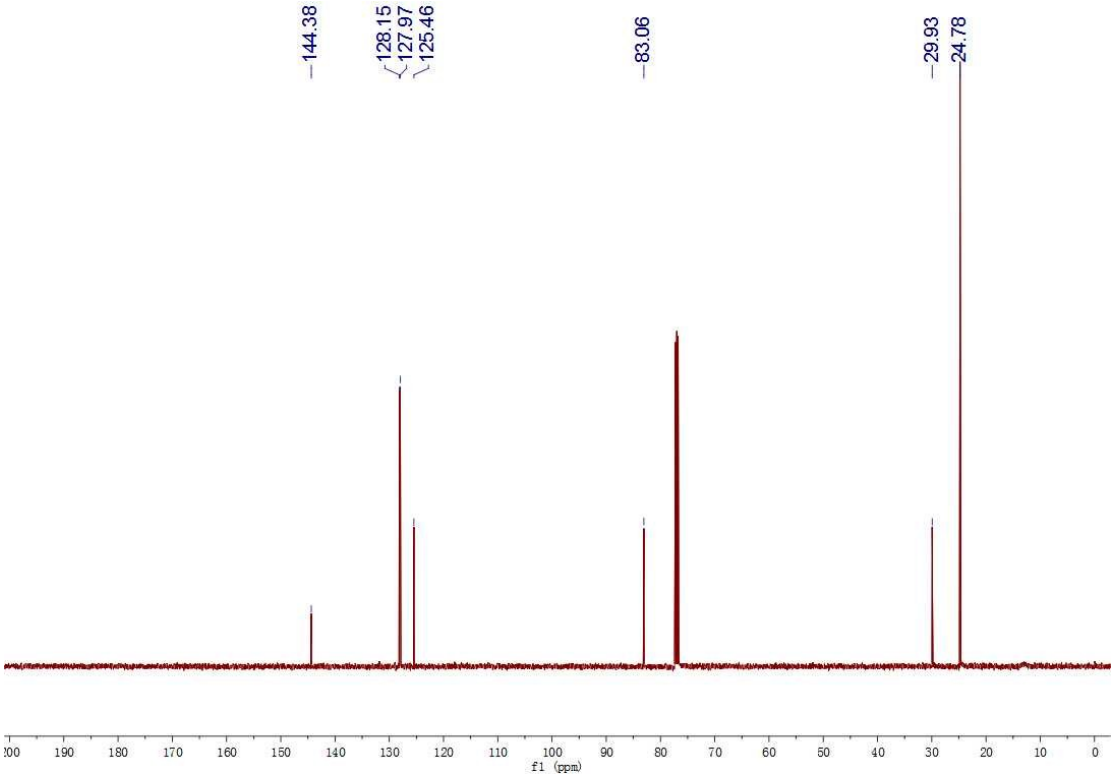
4.15
1.00
2.08
12.06
2.05
f1 (ppm)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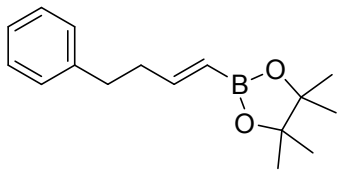
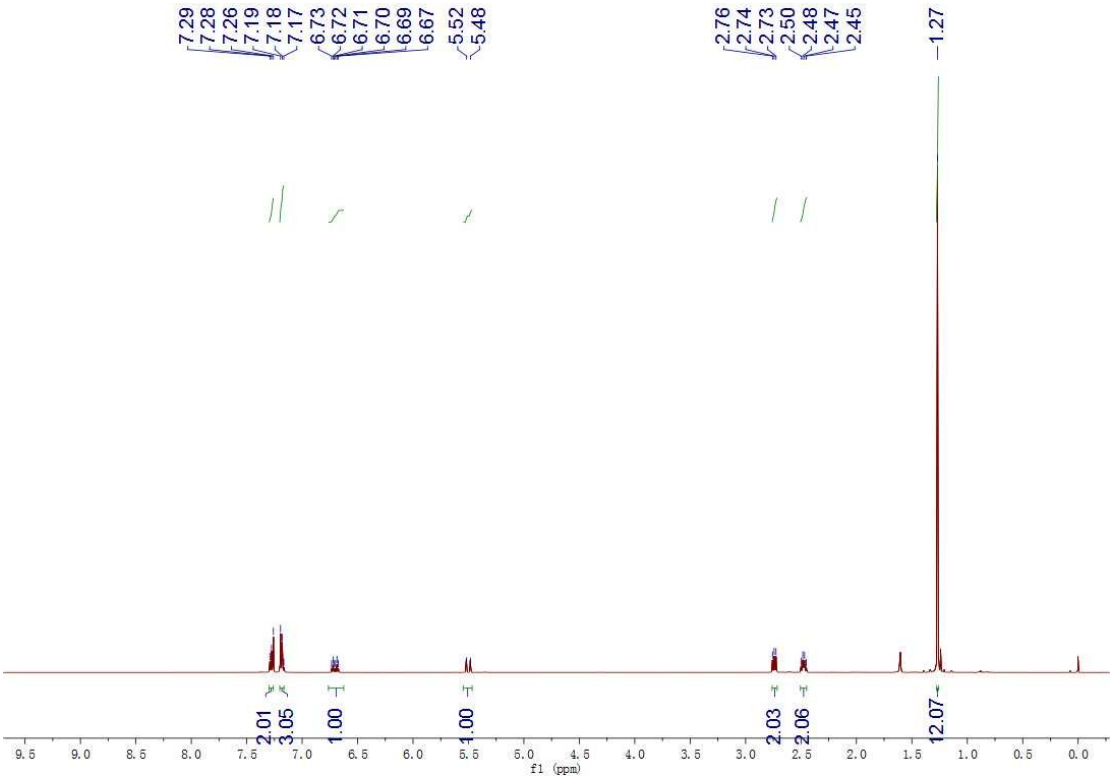
125.46
83.06
29.93
24.78
f1 (ppm)



59


7.29
7.28
7.26
7.19
7.18
7.17
6.73
6.72
6.71
6.70
6.69
6.67
5.52
5.48
2.76
2.74
2.73
2.50
2.48
2.47
2.45
1.27
2.01
3.05
1.00
1.00
2.03
2.06
12.07
f1 (ppm)