Zn-Mediated Decarboxylative Carbagermatranation of Aliphatic N-Hydroxyphthalimide Esters: Evidence for alkylzinc Intermediate

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Supporting Information

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1. General information

1.1 Reagent information

All of the reagents were purchased from commercial source and used without further purification unless otherwise noted. DMF was purchased from Sigma-Aldrich. THF was freshly distilled before used. Zn powder was activated before used. Silica gel (300-400 mesh, pH = 6-7, HG/T2354-2010) was purchased from Branch Qingdao Haiyang Chemical Co., Ltd. Reagents and solvents were used as received unless otherwise noted.

1.2 Analytical information

^{1}H-NMR spectra were recorded on 400 MHz spectrometers. Chemical shifts of ^{1}H-NMR spectra were reported in parts per million relative to tetramethylsilane (δ = 0) or the residual solvent peak for DMF (δ = 8.03 ppm), CD_2Cl_2 (δ = 5.32 ppm). Data for ^{1}H-NMR were reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration. ^{13}C-NMR spectra were recorded on 101 MHz spectrometers. Chemical shifts were reported in parts per million relative to the solvent resonance as the internal standard ($CDCl_3$, δ 77.2 ppm; C_6D_6, δ 128.1 ppm; $(CD_3)_2CO$, δ 30.0 ppm & δ 206.3 ppm; CD_2Cl_2 δ 53.8 ppm). Data for ^{13}C-NMR are reported in terms of chemical shift (δ ppm), multiplicity, and coupling constant (Hz). High-resolution mass spectra (HRMS) were recorded on an Acquity UPLC-Xevo G2 QTof instrument with ESI mode unless otherwise stated. Gas chromatographic (GC) analysis was acquired on a Shimadzu GC-2014 Series GC system equipped with a flame-ionization detector. Organic solutions were concentrated under reduced pressure on a Buchi rotary evaporator. Chromatographic purification of products was accomplished using column chromatography on silica gel.

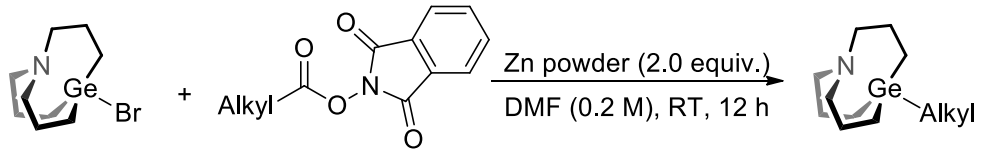
2. Experimental Procedure and Compound Characterization Data for Table 1-3

2.1 Activation of Zn powder

To a 100 mL round-bottom flask was charged with 10 g Zn powder followed by the addition of 20 mL HCl (5% aq), stirred at room temperature for 2 hours, then filtered and washed with H_2O, ethanol and ethyl ether three times respectively, then dried under vacuum at 120 ºC for 2 hours and stored under argon atmosphere.

2.2 Condition optimization

To an oven-dried screw-cap tube equipped with stir bar was charged with 0.1 mmol ***Ge***Br[1], corresponding NHP ester and Zn powder. The tube was vacuumed and backfilled with argon for three cycles. Solvent was added through syringe and the tube was sealed with a teflon stopper and stirred at indicated temperature for indicated time. The reaction was quenched with NH_4Cl (sat, aq), extracted with ethyl acetate. Organic layer was separated, dried over Na_2SO_4 and concentrated under reduced pressure. 0.1 mmol mesitylene was added as internal standard for NMR analysis.



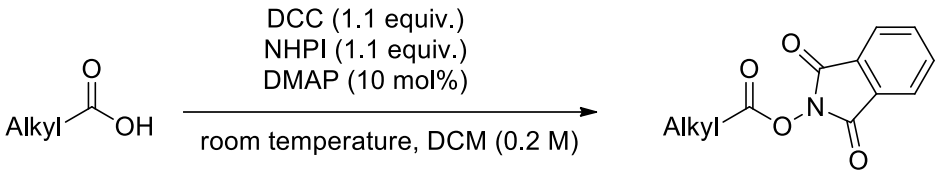
1.0 equiv. **1** ***Ge***Br 2.0 equiv. **2** **3**

Entry	Variations	Yield [%]
Alkyl = ^{n}Pr		
1	none	99
2	Mn powder instead of Zn powder	0
3	Mg powder instead of Zn powder	0
4	TDAE instead of Zn powder	0
5	THF instead of DMF	57
6	DMAc instead of DMF	56
7	1.0 equiv. of NHPI ester was used	42
8	1.5 equiv. of NHPI ester was used	65
Alkyl = ^{s}Bu		
9	none	<5
10	60 ^{o}C instead of RT	32
11	DMAc instead of DMF, 60 ^{o}C	8
12	THF instead of DMF, 60 ^{o}C	68
13	THF instead of DMF, 60 ^{o}C, 18 h	70
14	THF instead of DMF, 60 ^{o}C, 18 h, 3.0 equiv. Zn powder	80

2.3 Preparation of alkyl carboxylic acid NHP esters and characterization

2a-c, **2e-f**, **2q-ac**, **2af-aj**, **2am-2ap**, **2as** and **2au** were synthesized according reported literatures.[2-12]

2d, **2g-p**, **2ad-ae**, **2ak-al**, **2aq-ar, 2at** and **2av** were synthesized as follow:



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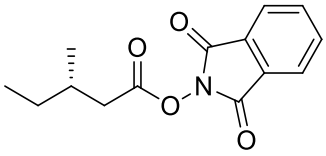
General procedure A:

To a solution of NHPI (N-Hydroxyphthalimide, 1.1 equiv.), alkyl carboxylic acid (1.0 equiv.) and DMAP (4-Dimethylaminopyridine, 10 mol%) in DCM (0.2 M) was added DCC (Dicyclohexylcarbodiimide, 1.1 equiv.). The resulting mixture was stirred at room temperature and monitored by TLC technique. After the alkyl carboxylic acid was consumed, the mixture was filtered through a pad of silica gel, and filtrate was collected and concentrated under reduced pressure. Further purification can be accomplished by silica gel column chromatography or recrystallization as needed.

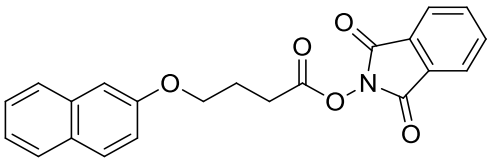


1,3-dioxoisoindolin-2-yl (S)-3-methylpentanoate (2d). 10 mmol (S)-3-methylpentanoic acid[13] was applied in the general procedure A. Purified by silica gel column chromatography using petroleum ether/ethyl acetate = 8/1 as eluent. Isolated in 85% yield as 2.24 g white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.86 (m, 2H), 7.81 – 7.76 (m, 2H), 2.70 – 2.62 (m, 1H), 2.50 – 2.42 (m, 1H), 2.08 – 1.98 (m, 1H), 1.56 – 1.45 (m, 1H), 1.42 – 1.31 (m, 1H), 1.09 (d, *J* = 6.7 Hz, 3H), 0.96 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 162.1, 134.8, 129.0, 124.0, 38.0, 32.3, 29.3, 19.2, 11.3.

HRMS (ESI) *m/z* ([M+H]$^+$) Calcd for $C_{14}H_{16}NO_4$: 262.1079; Found: 262.1101.

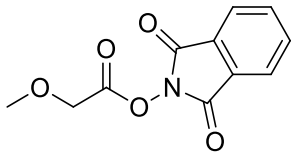


1,3-dioxoisoindolin-2-yl 4-(naphthalen-2-yloxy)butanoate (2g). 10 mmol 4-(naphthalen-2-yloxy)butanoic acid[14] was applied in the general procedure A. Purified by silica gel column chromatography using petroleum ether/ethyl acetate = 4/1 as eluent. Isolated in 90% yield as 3.37 g white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.83 (m, 2H), 7.78 – 7.70 (m, 5H), 7.46 – 7.40 (m, 1H), 7.35 – 7.30 (m, 1H), 7.19 – 7.14 (m, 2H), 4.19 (t, *J* = 6.0 Hz, 2H), 2.95 (t, *J* = 7.3 Hz, 2H), 2.38 – 2.27 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 161.9, 156.6, 134.8, 134.5, 129.5, 129.0, 128.9, 127.6, 126.8, 126.4, 124.0, 123.7, 118.8, 106.7, 66.0, 27.9, 24.5.

HRMS (ESI) *m/z* ([M+Na]$^+$) Calcd for $C_{22}H_{17}NNaO_5$: 398.1004; Found: 398.1006.

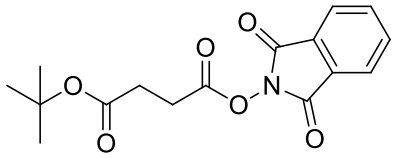


1,3-dioxoisoindolin-2-yl 2-methoxyacetate (2h). 5 mmol 2-methoxyacetic acid was applied in the general procedure A. Purified by recrystallization from DCM/MeOH. Isolated in 66% yield as 775 mg white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.87 (m, 2H), 7.84 – 7.79 (m, 2H), 4.46 (s, 2H), 3.55 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 161.7, 135.0, 128.8, 124.1, 67.7, 59.9.

HRMS (ESI) *m/z* ([M+Na]$^+$) Calcd for $C_{11}H_9NNaO_5$: 258.0378; Found: 258.0383.

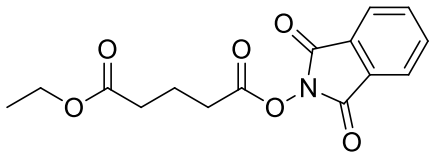


Tert-butyl (1,3-dioxoisoindolin-2-yl) succinate (2i). 28.5 mmol 4-(tert-butoxy)-4-oxobutanoic acid was applied in the general procedure A. Purified by recrystallization from DCM/MeOH. Isolated in 85% yield as 7.8 g white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.86 (m, 2H), 7.82 – 7.77 (m, 2H), 2.98 (t, *J* = 7.0 Hz, 2H), 2.70 (t, *J* = 7.0 Hz, 2H), 1.48 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 168.9, 161.8, 134.9, 128.9, 124.1, 81.5, 30.0, 28.0, 26.6.

HRMS (ESI) *m/z* ([M+Na]$^+$) Calcd for $C_{16}H_{17}NNaO_6$: 342.0954; Found: 342.0955.

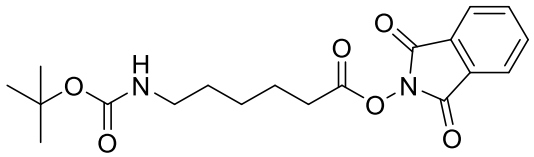


1,3-dioxoisoindolin-2-yl ethyl glutarate (2j). To a solution of 285mg (1.6 mmol) ethyl 5-chloro-5-oxopentanoate in 8 mL DCM was added 287 mg (1.76 mmol) NHPI, followed by addition of 0.244 mL (1.76 mmol) Et_3N over 10 min. The resulting mixture was then stirred at room temperature overnight. After the reaction was finished, the mixture was concentrated under reduced pressure to give crude product, which was purified by silica gel column chromatography using petroleum ether/ethyl acetate = 4/1 as eluent to give 305 mg white solid in 62% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.87 (m, 2H), 7.83 – 7.77 (m, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 2.78 (t, *J* = 7.3 Hz, 2H), 2.50 (t, *J* = 7.3 Hz, 2H), 2.17 – 2.05 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6, 169.2, 162.0, 134.9, 129.0, 124.1, 60.7, 32.8, 30.2, 20.0, 14.3.

HRMS (ESI) *m/z* ([M+Na]$^+$) Calcd for $C_{15}H15NNaO_6$: 328.0797; Found: 328.0794.

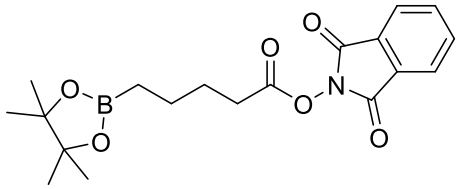


1,3-dioxoisoindolin-2-yl 6-((tert-butoxycarbonyl)amino)hexanoate (2k). 10 mmol 6-((tert-butoxycarbonyl)amino)hexanoic acid was applied in the general procedure A. Purified by silica gel chromatography using petroleum ether/ethyl acetate = 2/1 as eluent. Isolated in 70% yield as 2.63 g white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.86 (m, 2H), 7.85 – 7.77 (m, 2H), 4.67 (s, 1H), 3.15 (s, 2H), 2.68 (t, *J* = 7.3 Hz, 2H), 1.86 – 1.77 (m, 2H), 1.60 – 1.40 (m, 13H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 162.1, 156.1, 134.9, 129.0, 124.1, 79.2, 40.3, 31.0, 29.6, 28.5, 26.0, 24.4.

HRMS (ESI) *m/z* ([M+Na]$^+$) Calcd for $C_{19}H_{24}N_2NaO_6$: 399.1532; Found: 399.1535.

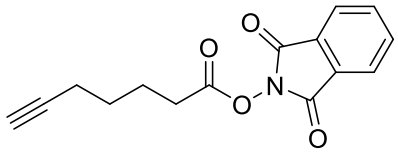


1,3-dioxoisoindolin-2-yl 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanoate (2l). To a 25 mL oven-dried screw-cap tube was charged with 0.05 mmol (46.2 mg) $Rh(PPh_3)_3Cl$. The tube was then vacuumed and backfilled with argon for three cycles. 5 mL THF, 5 mmol **2f** in 2 mL DCM and 5 mmol (0.725 mL) H-Bpin was added through syringe sequentially. The resulting mixture was then stirred at 0 ^{o}C, allowed to warm up slowly to room temperature overnight. After the reaction was complete, the mixture was concentrated under reduced pressure to give crude product, which was purified by silica gel column chromatography using petroleum ether/ethyl acetate = 4/1 as eluent to give 600 mg white solid in 32% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.86 (m, 2H), 7.82 – 7.76 (m, 2H), 2.67 (t, *J* = 7.6 Hz, 2H), 1.85 – 1.75 (m, 2H), 1.61 – 1.52 (m, 2H), 1.25 (s, 12H), 0.84 (t, *J* = 7.8 Hz, 2H).

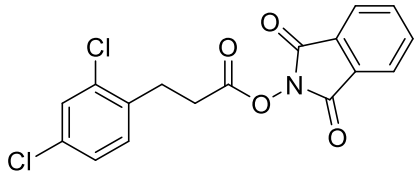
^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 162.1, 134.8, 129.0, 124.0, 83.2, 30.9, 27.2, 24.9, 23.6.

HRMS (ESI) *m/z* ([M+Na]$^+$) Calcd for $C_{19}H_{24}BNNaO_6$: 396.1594; Found: 396.1603.

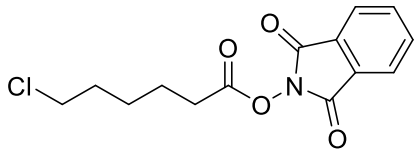


1,3-dioxoisoindolin-2-yl hept-6-ynoate (2m). 5 mmol hept-6-ynoic acid was applied in the general procedure A. Purified by silica gel column chromatography using petroleum ether/ethyl acetate = 4/1 as eluent. Isolated in 90% yield as 1.23 g white solid.

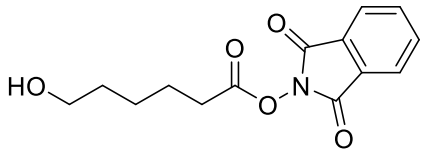
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.85 (m, 2H), 7.83 – 7.76 (m, 2H), 2.75 – 2.68 (m, 2H), 2.31 – 2.23 (m, 2H), 2.00 – 1.98 (m, 1H), 1.97 – 1.87 (m, 2H), 1.74 – 1.64 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 162.0, 134.9, 128.9, 124.0, 83.6, 69.1, 30.5, 27.4, 23.7, 18.1.
HRMS (ESI) *m/z* ([M+Na]$^+$) Calcd for $C_{15}H_{13}NNaO_4$: 294.0742; Found: 294.0743.



1,3-dioxoisoindolin-2-yl 3-(2,4-dichlorophenyl)propanoate (2n). 4.56 mmol 3-(2,4-dichlorophenyl)propanoic acid was applied in the general procedure A. Purified by recrystallization from DCM/MeOH. Isolated in 84% yield as 1.39g white solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.84 (m, 2H), 7.82 – 7.76 (m, 2H), 7.37 (s, 1H), 7.29 – 7.25 (m, 1H), 7.23 – 7.19 (m, 1H), 3.17 (t, *J* = 7.5 Hz, 2H), 2.99 (t, *J* = 7.5 Hz, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 161.9, 135.3, 134.9, 134.6, 133.4, 131.6, 129.5, 128.9, 127.5, 124.1, 30.6, 28.1.
HRMS (ESI) *m/z* ([M+Na]$^+$) Calcd for $C_{17}H_{11}NNaO_4$: 385.9963; Found: 385.9954.

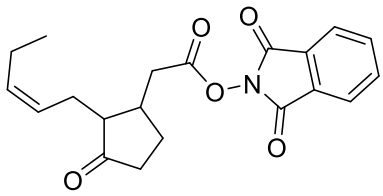


1,3-dioxoisoindolin-2-yl 6-chlorohexanoate. (2o). 6.67 mmol of 6-chlorohexanoic acid was applied in the general procedure A. Purified by recrystallization from DCM/MeOH. Isolated in 81% yield as 1.6 g white solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.85 (m, 2H), 7.83 – 7.77 (m, 2H), 3.62 – 3.53 (m, 2H), 2.76 – 2.66 (m, 2H), 1.90 – 1.77 (m, 4H), 1.66 – 1.54 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 162.1, 134.9, 129.0, 124.1, 44.7, 32.2, 30.9, 26.2, 24.1.
HRMS (ESI) *m/z* ([M+H]$^+$) Calcd for $C_{14}H_{15}ClNO_4$: 296.0690; Found: 296.0691.

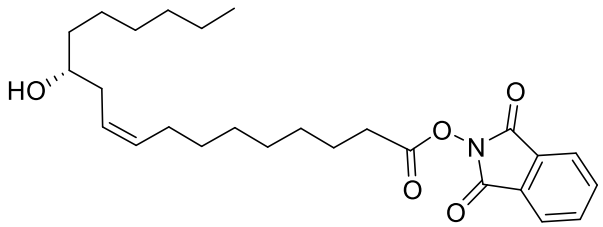


1,3-dioxoisoindolin-2-yl 6-hydroxyhexanoate (2p). 10 mmol of 6-hydroxyhexanoic acid[15] was applied in the general procedure A. Purified silica gel column chromatography using petroleum ether/ethyl acetate = 1/1 as eluent. Isolated in 27% yield as 750 mg white solid.

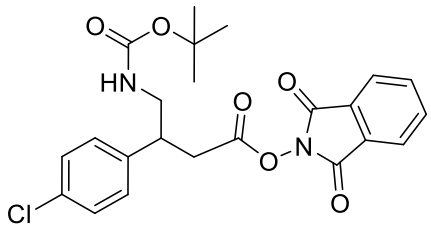
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.86 (m, 2H), 7.83 – 7.78 (m, 2H), 3.67 (t, *J* = 6.3 Hz, 2H), 2.70 (t, *J* = 7.3 Hz, 2H), 2.30 (s, 1H), 1.90 – 1.77 (m, 2H), 1.70 – 1.48 (m, 4H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 162.1, 134.9, 128.8, 124.0, 62.3, 32.1, 31.0, 25.0, 24.4.
HRMS (ESI) *m/z* ([M+Na]$^+$) Calcd for $C_{14}H_{16}NNaO_5$: 300.0848; Found: 300.0845.



1,3-dioxo-2,3-dihydro-1H-inden-2-yl (Z)-2-(3-oxo-2-(pent-2-en-1-yl)cyclopentyl)acetate (2ad). 3.2 mmol Jasmonic acid was applied in the general procedure A. Purified by silica gel column chromatography using petroleum ether/ethyl actate = 3:1 as eluent. Isolated in 43% yield as 468 mg viscous oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.87 (m, 2H), 7.85 – 7.79 (m, 2H), 5.57 – 5.46 (m, 1H), 5.37 – 5.25 (m, 1H), 3.09 (dd, *J* = 15.2, 3.7 Hz, 1H), 2.65 (dd, *J* = 15.2, 9.1 Hz, 1H), 2.53 – 2.33 (m, 4H), 2.24 – 1.97 (m, 4H), 1.74 – 1.58 (m, 2H), 1.01 – 0.96 (t, *J* = 7.5 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 218.3, 168.2, 162.0, 135.0, 134.7, 129.0, 124.8, 124.2, 53.9, 38.3, 37.8, 35.8, 26.9, 25.6, 20.8, 14.2.
HRMS (ESI) *m/z* ([M+Na]$^+$) Calcd for $C_{10}H_{21}NNaO_5$: 378.1317; Found: 378.1322.



1,3-dioxoisoindolin-2-yl (R,Z)-12-hydroxyoctadec-9-enoate (2ae). 10 mmol Ricinoleic acid was applied in the general procedure A. Purified by silica gel column chromatography using petroleum ether/ethyl acetate = 4/1 as eluent. Isolated in 40% yield as 1.8 g viscous oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.86 (m, 2H), 7.82 – 7.77 (m, 2H), 5.62 – 5.53 (m, 1H), 5.45 – 5.37 (m, 1H), 3.65 – 3.58 (m, 1H), 2.66 (t, *J* = 7.5 Hz, 2H), 2.22 (t, *J* = 6.6 Hz, 2H), 2.10 – 2.01 (m, 2H), 1.84 – 1.73 (m, 2H), 1.65 (s, 1H), 1.51 – 1.24 (m, 18H), 0.88 (t, *J* = 6.7 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 162.2, 134.9, 133.5, 129.1, 125.4, 124.1, 71.6, 37.0, 35.5, 32.0, 31.1, 29.7, 29.5, 29.1, 29.1, 28.9, 27.5, 25.9, 24.8, 22.8, 14.2.
HRMS (ESI) *m/z* ([M+Na]$^+$) Calcd for $C_{26}H_{37}NNaO_5$: 466.2569; Found: 466.2562.

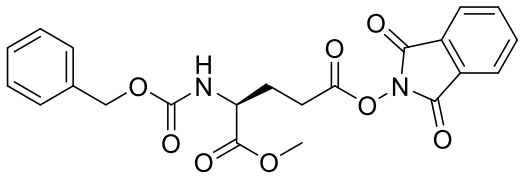


1,3-dioxoisoindolin-2-yl 4-((tert-butoxycarbonyl)amino)-3-(4-chlorophenyl)butanoate (2ak). To a solution of 14 mmol (560 mg) NaOH in dixoane/H_2O (14 mL/14 mL) was added 4.68 mmol (1 g) Baclofen. Then the solution was cooled to 0 ^oC followed by the addition of 4.9 mmol (1.125 mL) $(Boc)_2O$. After the addition of $(Boc)_2O$, the resulting solution was stirred at room temperature. 4 hours later, the solution was acidified by diluted HCl (aq) to pH = 2, extracted with ethyl ether (30 mL x 3), then the organic layer was combined, washed with brine, dried over Na_2SO_4, concentrated under reduced pressure to give viscous oil. The oil was dissolved in 23 mL DCM, followed by the addition of 5.5 mmol (896 mg) NHPI, 0.55 mmol (61 mg) DMAP and 5.5 mmol (1.13 g) DCC sequentially, and allowed to stir at room temperature until the reaction was complete. The resulting mixture was filtered through a pad of silica gel, and filtrate was collected and concentrated under reduced pressure. Purified by silica gel column chromatography using petroleum ether/ethyl acetate = 3/1 as eluent. Isolated in 51% yield (two steps) as 1.1 g white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.83 (m, 2H), 7.80 – 7.75 (m, 2H), 7.35 – 7.31 (m, 2H), 7.22 (d, *J* = 8.3 Hz, 2H), 4.75 (s, 1H), 3.57 – 3.33 (m, 3H), 3.06 (dd, *J* = 15.9, 6.0 Hz, 1H), 2.94 (dd, *J* = 15.9, 8.0 Hz, 1H), 1.41 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 161.8, 156.0, 138.7, 134.9, 133.4, 129.2, 129.1, 128.9, 124.1, 79.8, 45.5, 42.0, 35.1, 28.4.

HRMS (ESI) *m/z* ([M+Na]$^+$) Calcd for $C_{23}H_{23}ClN_2NaO_6$: 481.1142; Found: 481.1143.

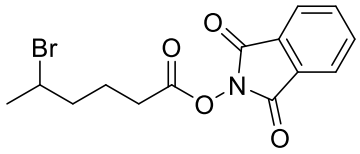


5-(1,3-dioxoisoindolin-2-yl) 1-methyl ((benzyloxy)carbonyl)-L-glutamate (2al). 10 mmol Cbz-Glu-OMe was applied in the general procedure A. Purified by silica gel column chromatography using petroleum ether/ethyl acetate = 1/1 as eluent. Isolate in 45% yield as 2 g light yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.84 (m, 2H), 7.82 – 7.75 (m, 2H), 7.39 – 7.28 (m, 5H), 5.64 (d, *J* = 8.1 Hz, 1H), 5.12 (s, 2H), 4.55 – 4.46 (m, 1H), 3.75 (s, 3H), 2.88 – 2.69 (m, 2H), 2.43 – 2.32 (m, 1H), 2.23 – 2.09 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.9, 168.9, 161.9, 156.1, 136.1, 134.9, 128.9, 128.6, 128.3, 128.2, 124.1, 67.3, 53.1, 52.9, 27.5, 27.4.

HRMS (ESI) *m/z* ([M+Na]$^+$) Calcd for $C_{22}H_{20}N_2NaO_8$: 463.1117; Found: 463.1123.

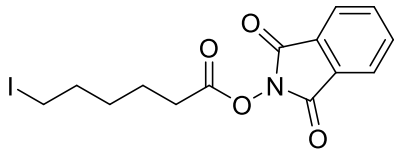


1,3-dioxoisoindolin-2-yl 5-bromohexanoate (2aq). 43 mmol (5 g) *δ*-Hexalactone was dissolve in 10 mL 33 wt% HBr/HOAc in a 100 mL round-bottom falsk and stirred at room temperature for 48 hours. The resulting solution was neutralized with Na_2CO_3 (aq), acidified with diluted HCl (aq) to pH = 1, extracted with DCM (30 mL x 3). The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure to give viscous liquid. The liquid was dissolved in 70 mL DCM, followed by the addition of 14 mmol (2.28 g) NHPI, 1.4 mmol (170 mg) DMAP and 14 mmol (2.88 g) DCC sequentially and allowed to stir at room temperature until the reaction was complete. The resulting mixture was filtered through a pad of silica gel, and filtrate was collected and concentrated under reduced pressure. Purified by silica gel column chromatography using petroleum ether/ethyl acetate = 8/1 as eluent. Isolated in 7% yield (two steps) as 1.05 g white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.86 (m, 2H), 7.83 – 7.77 (m, 2H), 4.22 – 4.12 (m, 1H), 2.76 – 2.70 (m, 2H), 2.11 – 1.89 (m, 4H), 1.75 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 162.0, 134.9, 129.0, 124.1, 50.5, 39.7, 30.3, 26.5, 23.1.

HRMS (ESI) *m/z* ([M+Na]$^+$) Calcd for $C_{14}H_{14}BrNNaO_4$: 362.0004; Found: 362.0005.

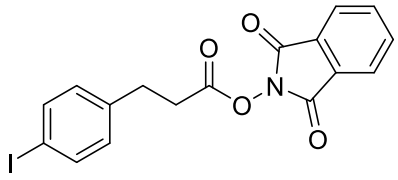


1,3-dioxoisoindolin-2-yl 6-iodohexanoate (2ar). To a 100 mL round-bottom flask equipped with a stir bar, 10 mmol (1.95 g) 6-bromohexanoic acid and 20 mmol (3 g) NaI was added followed by the addition of 20 mL acetone. Resulting mixture was allowed to reflux for 20 hours. Then solvent was removed under reduced pressure to give crude product, which was washed with 50 mL $Na_2S_2O_3$ (sat. aq) and extracted with ethyl ether （30 mL x 3）. Combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated under reduce pressure to give viscous oil. The oil was dissolved in 50 mL DCM followed by the addition of 11 mmol (1.79 g) NHPI, 1.1 mmol (134 mg) DMAP and 11 mmol (2.27 g) DCC sequentially and allowed to stir at room temperature until the reaction was complete. The resulting mixture was filtered through a pad of silica gel, and filtrate was collected and concentrated under reduced pressure. Purified by recrystallization from DCM/MeOH. Isolated in 77% yield (two steps) as 3 g light yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.86 (m, 2H), 7.83 – 7.76 (m, 2H), 3.22 (t, *J* = 7.0 Hz, 2H), 2.70 (t, *J* = 7.4 Hz, 2H), 1.95 – 1.77 (m, 4H), 1.62 – 1.52 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 162.0, 134.9, 129.0, 124.1, 33.1, 30.9, 29.7, 23.7, 6.2.

HRMS (ESI) *m/z* ([M+Na]$^+$) Calcd for $C_{14}H_{14}INNaO_4$: 409.9865; Found: 409.9860.

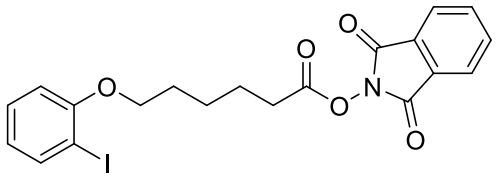


1,3-dioxoisoindolin-2-yl 3-(4-iodophenyl)propanoate (2at). 3.6 mmol 3-(4-iodophenyl)propanoic acid was applied in the general procedure. Purified by recrystallization from DCM/MeOH. Isolated in 91% yield as 1.38 g white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.85 (m, 2H), 7.84 – 7.77 (m, 2H), 7.65 (d, *J* = 8.3 Hz, 2H), 7.02 (d, *J* = 8.2 Hz, 2H), 3.08 – 3.01 (m, 2H), 2.99 – 2.92 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8, 162.0, 138.9, 137.9, 134.9, 130.5, 129.0, 124.1, 92.1, 32.5, 30.1.

HRMS (ESI) *m/z* ([M+Na]$^+$) Calcd for $C_{17}H_{12}INNaO_4$: 443.9709; Found: 443.9723.



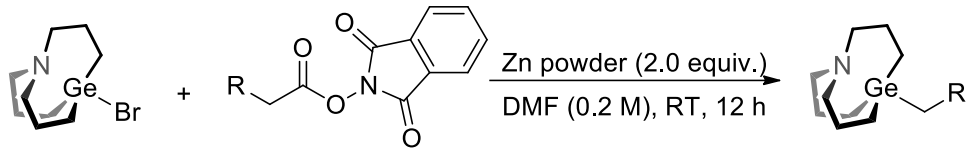
1,3-dioxoisoindolin-2-yl 6-(2-iodophenoxy)hexanoate (2av). In a 200 mL round-bottom flask equipped with a stir bar, 15 mmol (3.3 g) 2-Iodophenol was added followed by the addition of 37 mL 10% KOH (aq) and 45 mL EtOH. To this solution, 16.5 mmol (3.22 g) 6-bromohexanoic acid in 15 mL sat. K_2CO_3 was added. Resulting mixture was stirred at refluxed for 5 hours. After which, the mixture was cooled and acidified with diluted HCl (aq) slowly to pH = 2, extracted with ethyl ether （30 mL x 3）. Combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated under reduce pressure to give viscous oil. Purified by flash column chromatography gave target acid as 1.71g (5 mmol) solid, which was dissolved in 25 mL DCM followed by the addition of 5.5 mmol (896 mg) NHPI, 0.55 mmol (67 mg) DMAP and 5.5 mmol (1.13 g) DCC sequentially and allowed to stir at room temperature until the reaction was complete. The resulting mixture was filtered through a pad of silica gel, and filtrate was collected and concentrated under reduced pressure. Purified by recrystallization from DCM/MeOH. Isolated in 27% yield (two steps) as 2 g white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.85 (m, 2H), 7.82 – 7.74 (m, 3H), 7.31 – 7.25 (m, 1H), 6.82 – 6.76 (m, 1H), 6.72 – 6.65 (m, 1H), 4.04 (t, *J* = 6.2 Hz, 2H), 2.74 (t, *J* = 7.5 Hz, 2H), 1.96 – 1.86 (m, 4H), 1.76 – 1.68 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 162.0, 157.5, 139.4, 134.8, 129.5, 128.9, 124.0, 122.5, 112.1, 86.8, 68.7, 31.0, 28.6, 25.6, 24.4.

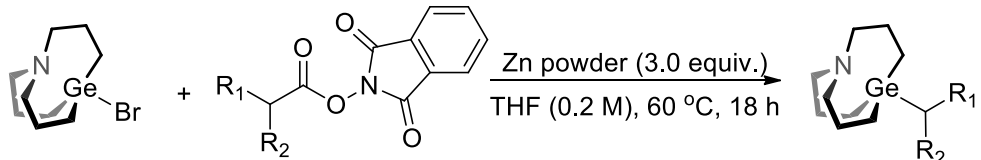
HRMS (ESI) *m/z* ([M+Na]$^+$) Calcd for $C_{20}H_{18}INNaO_5$: 502.0127; Found: 502.0133.

2.4 Procedure for decarboxylative carbagermatranation and characterization



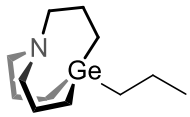
***1, Ge*Br** **2** **3**

General Method A: To an oven-dried screw-cap tube equipped with stir bar was charged with 0.1 mmol (29.2 mg) ***Ge***Br, 0.2 mmol corresponding NHP ester and 0.2 mmol (13 mg) Zn powder. The tube was vacuumed and backfilled with argon for three cycles. 0.5 mL DMF was added through syringe and the tube was sealed with a teflon stopper and stirred at room temperature for 12 hours. The reaction was quenched with NH_4Cl (sat, aq), extracted with ethyl acetate. Organic layer was separated, dried over Na_2SO_4, concentrated under reduced pressure to give crude product, which was purified by silica gel column chromatography.



***1, Ge*Br** **2** **3**

General Method B: To an oven-dried screw-cap tube equipped with stir bar was charged with 0.1 mmol (29.2 mg) ***Ge***Br, 0.2 mmol corresponding NHP ester and 0.3 mmol (19.5 mg) Zn powder. The tube was vacuumed and backfilled with argon for three cycles. 0.5 mL THF was added through syringe and the tube was sealed with a teflon stopper and stirred at 60 °C for 18 hours. The reaction was quenched with NH_4Cl (sat, aq), extracted with ethyl acetate. Organic layer was separated, dried over Na_2SO_4, concentrated under reduced pressure to give crude product, which was purified by silica gel column chromatography.

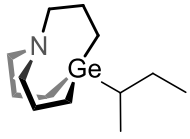


5-propyl-1-aza-5-germabicyclo[3.3.3]undecane (3a). Synthesized by Method A, purified by silica gel column chromatography using petroleum ether as eluent.

^{1}H NMR (400 MHz, C_6D_6) δ 2.20 – 2.13 (t, *J* = 5.8 Hz, 6H), 1.54 – 1.37 (m, 8H), 1.07 (t, *J* = 7.2 Hz, 3H), 0.70 – 0.63 (m, 6H), 0.62 – 0.54 (m, 2H).

^{13}C NMR (101 MHz, C_6D_6) δ 53.9, 24.8, 23.9, 19.4, 19.2, 11.9.

HRMS (ESI) *m/z* ([M+H]$^+$) Calcd for $C_{12}H_{26}{}^{74}GeN$: 258.1277; Found: 258.1283.

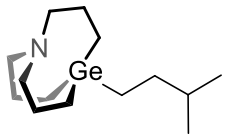


5-(sec-butyl)-1-aza-5-germabicyclo[3.3.3]undecane (3b). Synthesized by Method B, purified by silica gel column chromatography using petroleum ether as eluent

^{1}H NMR (400 MHz, C_6D_6) δ 2.24 – 2.15 (m, 6H), 1.71 – 1.60 (m, 1H), 1.49 – 1.39 (m, 6H), 1.33 – 1.23 (m, 1H), 1.11 (d, J = 7.4 Hz, 3H), 1.04 (t, *J* = 7.3 Hz, 3H), 0.73 – 0.63 (m, 6H), 0.63 – 0.54 (m, 1H).

^{13}C NMR (101 MHz, C_6D_6) δ 54.0, 27.8, 26.6, 24.0, 15.3, 14.1, 9.8.

HRMS (ESI) *m/z* ([M+H]$^+$) Calcd for $C_{13}H_{28}{}^{74}GeN$: 272.1434; Found: 272.1427.

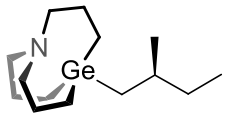


5-isopentyl-1-aza-5-germabicyclo[3.3.3]undecane (3c). Synthesized by Method A, purified by silica gel column chromatography using petroleum ether as eluent to give title compound as colorless oil in 97% yield, 28 mg.

^{1}H NMR (400 MHz, C_6D_6) δ 2.20 (t, *J* = 5.8 Hz, 6H), 1.59 – 1.39 (m, 7H), 1.38 – 1.30 (m, 2H), 1.00 (d, *J* = 6.6 Hz, 6H), 0.69 (t, *J* = 6.4 Hz, 6H), 0.59 – 0.51 (m, 2H).

^{13}C NMR (101 MHz, C_6D_6) δ 53.9, 35.3, 31.9, 23.9, 22.7, 19.2, 11.7.

HRMS (ESI) *m/z* ([M+H]$^+$) Calcd for $C_{14}H_{30}{}^{74}GeN$: 286.1590; Found: 286.1592.

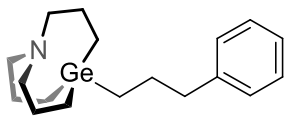


(S)-5-(2-methylbutyl)-1-aza-5-germabicyclo[3.3.3]undecane (3d). Synthesized by Method A, purified by silica gel column chromatography using petroleum ether as eluent to give title compound as colorless oil in 99% yield, 28 mg.

^{1}H NMR (400 MHz, C_6D_6) δ 2.20 (t, *J* = 5.6 Hz, 6H), 1.68 – 1.53 (m, 1H), 1.51 – 1.37 (m, 7H), 1.34 – 1.21 (m, 1H), 1.05 – 0.91 (m, 6H), 0.78 – 0.65 (m, 7H), 0.51 – 0.38 (m, 1H).

^{13}C NMR (101 MHz, C_6D_6) δ 54.0, 33.9, 32.8, 30.8, 24.0, 23.1, 13.0, 12.0.

HRMS (ESI) *m/z* ([M+H]$^+$) Calcd for $C_{14}H_{30}{}^{74}GeN$: 286.1590; Found: 286.1593.

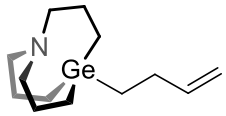


5-(3-phenylpropyl)-1-aza-5-germabicyclo[3.3.3]undecane (3e). Synthesized by Method A, purified by silica gel column chromatography using petroleum ether as eluent to give title compound as colorless oil in 81% yield, 24 mg.

^{1}H NMR (400 MHz, C_6D_6) δ 7.24 – 7.17 (m, 4H), 7.13 – 7.06 (m, 1H), 2.64 (t, *J* = 7.6 Hz, 2H), 2.17 (t, *J* = 5.7 Hz, 6H), 1.78 – 1.68 (m, 2H), 1.45 – 1.36 (m, 6H), 0.64 (t, *J* = 6.5 Hz, 6H), 0.60 – 0.53 (m, 2H).

^{13}C NMR (101 MHz, C_6D_6) δ 143.6, 128.9, 128.6, 125.9, 53.8, 41.1, 28.5, 23.8, 21.8, 11.8.

HRMS (ESI) *m/z* ([M+H]$^+$) Calcd for $C_{18}H_{30}{}^{74}GeN$: 334.1590; Found: 286.1543.

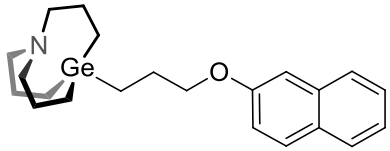


5-(but-3-en-1-yl)-1-aza-5-germabicyclo[3.3.3]undecane (3f). Synthesized by Method A, purified by silica gel column chromatography using petroleum ether as eluent to give title compound as colorless oil in 95% yield, 26 mg.

^{1}H NMR (400 MHz, C_6D_6) δ 6.02 (ddt, *J* = 16.6, 10.0, 6.4 Hz, 1H), 5.13 (ddd, *J* = 17.0, 3.8, 1.6 Hz, 1H), 5.00 (ddt, *J* = 10.1, 2.3, 1.2 Hz, 1H), 2.28 – 2.11 (m, 8H), 1.52 – 1.31 (m, 6H), 0.77 – 0.55 (m, 8H).

^{13}C NMR (101 MHz, C_6D_6) δ 143.2, 112.3, 53.8, 30.4, 23.8, 21.0, 11.9.

HRMS (ESI) *m/z* ([M+H]$^+$) Calcd for $C_{13}H_{26}{}^{74}GeN$: 270.1277; Found: 270.1284.

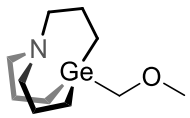


5-(3-(naphthalen-2-yloxy)propyl)-1-aza-5-germabicyclo[3.3.3]undecane (3g). Synthesized by Method A, purified by silica gel column chromatography using petroleum ether as eluent to give title compound as colorless oil in 68% yield, 27 mg.

^{1}H NMR (400 MHz, C_6D_6) δ 7.69 – 7.58 (m, 2H), 7.54 (d, *J* = 8.9 Hz, 1H), 7.35 – 7.26 (m, 2H), 7.24 – 7.11 (m, 2H), 3.86 (t, *J* = 6.9 Hz, 2H), 2.16 (t, *J* = 5.8 Hz, 6H), 1.95 – 1.85 (m, 2H), 1.47 – 1.37 (m, 6H), 0.67 (t, *J* = 5.8 Hz, 6H), 0.62 – 0.51 (m, 2H).

^{13}C NMR (101 MHz, C_6D_6) δ 158.0, 135.5, 129.8, 129.5, 128.2, 127.1, 126.5, 123.6, 119.7, 107.0, 71.5, 53.8, 25.8, 23.8, 17.4, 11.8.

HRMS (ESI) *m/z* ([M+H]$^+$) Calcd for $C_{22}H_{32}{}^{74}GeNO$: 400.1696; Found: 400.1697.

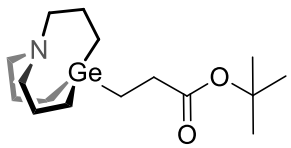


5-(methoxymethyl)-1-aza-5-germabicyclo[3.3.3]undecane (3h). Synthesized by Method A, purified by silica gel column chromatography using petroleum ether as eluent to give title compound as colorless oil in 66% yield, 17 mg.

^{1}H NMR (400 MHz, C_6D_6) δ 3.31 (s, 3H), 3.13 (s, 2H), 2.12 (t, *J* = 5.8 Hz, 6H), 1.47 – 1.37 (m, 6H), 0.82 (t, *J* = 6.6 Hz, 6H).

^{13}C NMR (101 MHz, C_6D_6) δ 72.8, 63.3, 53.9, 23.5, 10.6

HRMS (ESI) *m/z* ([M+H]$^+$) Calcd for $C_{13}H_{24}{}^{74}GeNO$: 260.1070; Found: 260.1064.



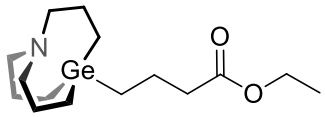
Tert-butyl 3-(1-aza-5-germabicyclo[3.3.3]undecan-5-yl)propanoate (3i). Synthesized by Method A, purified by silica gel column chromatography using

petroleum ether/ethyl acetate = 50/1 as eluent to give title compound as colorless oil in 78% yield, 27 mg.

^{1}H NMR (400 MHz, C_6D_6) δ 2.36 – 2.30 (m, 2H), 2.11 (t, *J* = 5.8 Hz, 6H), 1.45 (s, 9H), 1.39 – 1.30 (m, 6H), 0.93 – 0.86 (m, 2H), 0.62 – 0.55 (m, 6H).

^{13}C NMR (101 MHz, C_6D_6) δ 174.9, 78.8, 53.7, 32.1, 28.3, 23.7, 16.8, 11.6.

HRMS (ESI) *m/z* ([M+H]$^+$) Calcd for $C_{16}H_{32}{}^{74}GeNO_2$: 344.1645; Found: 344.1643.

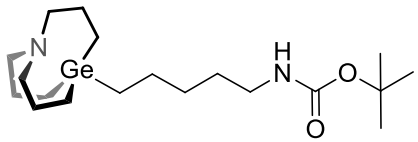


Ethyl 4-(1-aza-5-germabicyclo[3.3.3]undecan-5-yl)butanoate (3j). Synthesized by Method A, purified by silica gel column chromatography using petroleum ether/ethyl acetate = 20/1 as eluent to give title compound as colorless oil in 80% yield, 26 mg.

^{1}H NMR (400 MHz, Acetone-*d*$_6$) δ 4.06 (q, *J* = 7.1 Hz, 2H), 2.43 (t, *J* = 5.7 Hz, 6H), 2.21 (t, *J* = 7.3 Hz, 2H), 1.65 – 1.51 (m, 8H), 1.20 (t, *J* = 7.1 Hz, 3H), 0.66 (t, *J* = 6.6 Hz, 6H), 0.39 – 0.29 (m, 2H).

^{13}C NMR (101 MHz, Acetone-*d*$_6$) δ 173.8, 60.3, 54.4, 39.1, 24.1, 22.2, 22.0, 14.8, 12.2.

HRMS (ESI) *m/z* ([M+H]$^+$) Calcd for $C_{15}H_{30}{}^{74}GeNO_2$: 330.1488; Found: 330.1478.

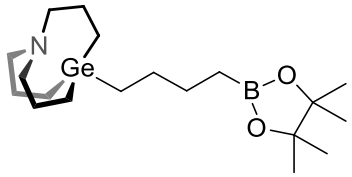


Tert-butyl (5-(1-aza-5-germabicyclo[3.3.3]undecan-5-yl)pentyl)carbamate (3k). Synthesized by Method A, purified by silica gel column chromatography using petroleum ether/ethyl acetate = 10/1 as eluent to give title compound as colorless oil in 75% yield, 30 mg.

^{1}H NMR (400 MHz, Acetone-*d*$_6$) δ 5.88 (s, 1H), 3.08 – 2.97 (m, 2H), 2.43 (t, *J* = 5.7 Hz, 6H), 1.59 – 1.51 (m, 6H), 1.46 (m, 2H), 1.39 (s, 9H), 1.35 – 1.23 (m, 4H), 0.65 (t, *J* = 6.5 Hz, 6H), 0.39 – 0.31 (m, 2H).

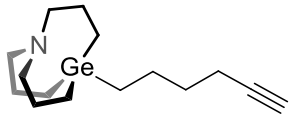
^{13}C NMR (101 MHz, Acetone-*d*$_6$) δ 156.7, 78.3, 54.4, 41.3, 32.1, 30.8, 28.8, 26.1, 24.2, 22.3, 12.3.

HRMS (ESI) *m/z* ([M+H]$^+$) Calcd for $C_{19}H_{39}{}^{74}GeN_2O_2$: 401.2223; Found: 401.2200.

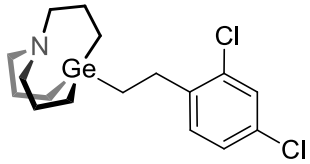


5-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)-1-aza-5-germabicyclo[3.3.3]undecane (3l). Synthesized by Method A, purified by silica gel column chromatography using petroleum ether/ethyl acetate = 20/1 as eluent to give title compound as colorless oil in 70% yield, 28 mg.

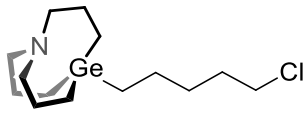
^{1}H NMR (400 MHz, Acetone-d_6) δ 2.43 (t, *J* = 5.7 Hz, 6H), 1.59 – 1.50 (m, 6H), 1.39 – 1.24 (m, 4H), 1.21 (s, 12H), 0.70 – 0.62 (m, 8H), 0.38 – 0.32 (m, 2H).
^{13}C NMR (101 MHz, Acetone-d_6) δ 83.5, 54.5, 29.4, 29.1, 25.3, 24.2, 22.2, 12.3.
HRMS (ESI) *m/z* ([M+H]$^+$) Calcd for $C_{19}H_{39}B^{74}GeNO_2$: 398.2286; Found: 398.2284.



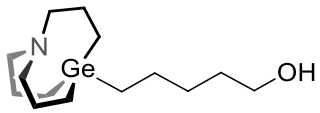
5-(hex-5-yn-1-yl)-1-aza-5-germabicyclo[3.3.3]undecane (3m). Synthesized by Method A, purified by silica gel column chromatography using petroleum ether as eluent to give title compound as colorless oil in 65% yield, 19 mg.
^{1}H NMR (400 MHz, C_6D_6) δ 2.20 – 2.15 (m, 6H), 2.08 (td, *J* = 6.9, 2.7 Hz, 2H), 1.81 (t, *J* = 2.7 Hz, 1H), 1.56 – 1.37 (m, 10H), 0.67 – 0.60 (m, 6H), 0.46 – 0.40 (m, 2H).
^{13}C NMR (101 MHz, C_6D_6) δ 84.9, 68.7, 53.8, 33.2, 25.1, 23.8, 21.2, 18.5, 11.8
HRMS (ESI) *m/z* ([M+H]$^+$) Calcd for $C_{15}H_{28}{}^{74}GeN$: 296.1434; Found: 296.1439.



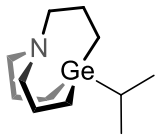
5-(2,4-dichlorophenethyl)-1-aza-5-germabicyclo[3.3.3]undecane (3n). Synthesized by Method A, purified by silica gel column chromatography using petroleum ether as eluent to give title compound as colorless oil in 80% yield, 31 mg.
^{1}H NMR (400 MHz, C_6D_6) δ 7.26 (d, *J* = 2.2 Hz, 1H), 6.92 (dd, *J* = 8.2, 2.2 Hz, 1H), 6.79 (d, *J* = 8.2 Hz, 1H), 2.69 – 2.59 (m, 2H), 2.16 (t, *J* = 5.7 Hz, 6H), 1.46 – 1.37 (m, 6H), 0.74 – 0.63 (m, 8H).
^{13}C NMR (101 MHz, C_6D_6) δ 134.5, 131.7, 130.8, 129.4, 127.3, 53.8, 29.5, 23.7, 22.1, 11.7.
HRMS (ESI) *m/z* ([M+H]$^+$) Calcd for $C_{17}H_{26}Cl_2{}^{74}GeN$: 388.0654; Found: 388.0641.



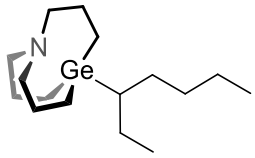
5-(5-chloropentyl)-1-aza-5-germabicyclo[3.3.3]undecane (3o). Synthesized by Method A, purified by silica gel column chromatography using petroleum ether as eluent to give title compound as colorless oil in 79% yield, 25 mg.
^{1}H NMR (400 MHz, C_6D_6) δ 3.18 (t, *J* = 6.8 Hz, 2H), 2.19 (t, *J* = 5.7 Hz, 6H), 1.61 – 1.52 (m, 2H), 1.49 – 1.39 (m, 6H), 1.37 – 1.24 (m, 4H), 0.65 (t, *J* = 6.6 Hz, 6H), 0.49 – 0.41 (m, 2H).
^{13}C NMR (101 MHz, C_6D_6) δ 53.8, 45.2, 32.8, 31.5, 25.2, 23.8, 21.6, 11.8.
HRMS (ESI) *m/z* ([M+H]$^+$) Calcd for $C_{14}H_{29}Cl^{74}GeN$: 320.1200; Found: 320.1200.



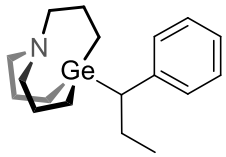
5-(1-aza-5-germabicyclo[3.3.3]undecan-5-yl)pentan-1-ol (3p). Synthesized by Method A, purified by silica gel column chromatography using petroleum ether/ethyl acetate = 4/1 as eluent to give title compound as colorless oil in 33% yield, 10 mg.
^{1}H NMR (400 MHz, Acetone-d_6) δ 3.55 – 3.46 (m, 2H), 2.43 (t, J = 5.7 Hz, 6H), 1.60 – 1.44 (m, 8H), 1.37 – 1.26 (m, 4H), 0.65 (t, J = 6.6 Hz, 6H), 0.40 – 0.32 (m, 2H).
^{13}C NMR (101 MHz, Acetone-d_6) δ 62.6, 54.3, 33.7, 31.1, 26.2, 24.1, 22.3, 12.1.
HRMS (ESI) *m/z* ([M+H]$^+$) Calcd for $C_{14}H_{30}{}^{74}GeNO$: 302.1539; Found: 302.1539.



5-isopropyl-1-aza-5-germabicyclo[3.3.3]undecane (3q). Synthesized by Method B, purified by silica gel column chromatography using petroleum ether as eluent to give title compound as colorless oil in 80% yield, 21 mg.
^{1}H NMR (400 MHz, C_6D_6) δ 2.18 (t, J = 2.8 Hz, 6H), 1.47 – 1.39 (m, 6H), 1.14 (d, J = 7.3 Hz, 6H), 0.81 – 0.72 (m, 1H), 0.68 – 0.64 (m, 6H).
^{13}C NMR (101 MHz, C_6D_6) δ 53.9, 23.9, 20.0, 19.4, 9.2.
HRMS (ESI) *m/z* ([M+H]$^+$) Calcd for $C_{12}H_{26}{}^{74}GeN$: 258.1277; Found: 258.1276.

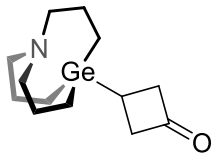


5-(heptan-3-yl)-1-aza-5-germabicyclo[3.3.3]undecane (3r). Synthesized by Method B at 90 ºC instead of 60 ºC, purified by silica gel column chromatography using petroleum ether as eluent to give title compound as colorless oil in 57% yield, 18 mg.
^{1}H NMR (400 MHz, C_6D_6) δ 2.21 (t, J = 5.7 Hz, 6H), 1.72 – 1.28 (m, 14H), 1.05 – 0.95 (m, 6H), 0.72 (t, J = 6.5 Hz, 6H), 0.67 – 0.59 (m, 1H).
^{13}C NMR (101 MHz, C_6D_6) δ 54.1, 33.9, 32.2, 30.6, 24.1, 24.0, 23.7, 14.5, 14.3, 11.1.
HRMS (ESI) *m/z* ([M+H]$^+$) Calcd for $C_{16}H_{34}{}^{74}GeN$: 314.1903; Found: 314.1892.

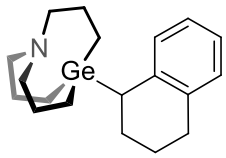


5-(1-phenylpropyl)-1-aza-5-germabicyclo[3.3.3]undecane (3s). Synthesized by Method B, purified by silica gel column chromatography using petroleum ether as eluent to give title compound as colorless oil in 66% yield, 22 mg.

^{1}H NMR (400 MHz, C_6D_6) δ 7.27 – 7.21 (m, 2H), 7.12 – 7.07 (m, 2H), 7.06 – 7.01 (m, 1H), 2.15 – 1.96 (m, 6H), 1.93 – 1.76 (m, 3H), 1.43 – 1.23 (m, 6H), 0.99 (t, *J* = 7.0 Hz, 3H), 0.70 – 0.61 (m, 6H).
^{13}C NMR (101 MHz, C_6D_6) δ 147.2, 127.7, 123.7, 53.7, 45.4, 24.2, 23.9, 15.1, 10.3.
HRMS (ESI) *m/z* ([M+H]$^+$) Calcd for $C_{18}H_{30}{}^{74}GeN$: 334.1590; Found: 334.1590.



3-(1-aza-5-germabicyclo[3.3.3]undecan-5-yl)cyclobutan-1-one (3t). Synthesized by Method B, purified by silica gel column chromatography using petroleum ether/ethyl acetate = 10/1 as eluent to give title compound as colorless oil in 42% yield, 12 mg.
^{1}H NMR (400 MHz, C_6D_6) δ 3.06 – 2.88 (m, 2H), 2.75 – 2.62 (m, 2H), 2.06 (t, *J* = 5.9 Hz, 6H), 1.37 – 1.24 (m, 6H), 1.13 – 1.01 (m, 1H), 0.48 (t, *J* = 6.6 Hz, 6H).
^{13}C NMR (101 MHz, C_6D_6) δ 206.9, 53.7, 50.1, 23.4, 13.9, 9.9
HRMS (ESI) *m/z* ([M+H]$^+$) Calcd for $C_{13}H_{24}{}^{74}GeNO$: 284.1070; Found: 284.1073.



5-(1,2,3,4-tetrahydronaphthalen-1-yl)-1-aza-5-germabicyclo[3.3.3]undecane (3u). Synthesized by Method B, purified by silica gel column chromatography using petroleum etheras eluent to give title compound as colorless oil in 66% yield, 23 mg.
^{1}H NMR (400 MHz, C_6D_6) δ 7.13 – 6.98 (m, 4H), 2.84 – 2.65 (m, 2H), 2.39 – 2.33 (m, 1H), 2.17 – 2.07 (m, 3H), 2.07 – 1.89 (m, 5H), 1.73 – 1.63 (m, 2H), 1.44 – 1.23 (m, 6H), 0.72 – 0.61 (m, 6H).
^{13}C NMR (101 MHz, C_6D_6) δ 143.7, 135.5, 129.5, 127.5, 125.5, 123.5, 53.9, 36.7, 30.3, 26.7, 24.1, 23.0, 11.8.
HRMS (ESI) *m/z* ([M+H]$^+$) Calcd for $C_{19}H_{30}{}^{74}GeN$: 346.1590; Found: 346.1577.

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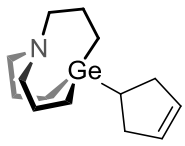
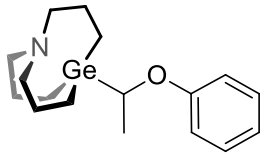
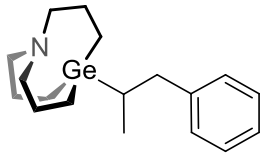


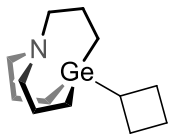
5-(cyclopent-3-en-1-yl)-1-aza-5-germabicyclo[3.3.3]undecane (3v). Synthesized by Method B, purified by silica gel column chromatography using petroleum ether as eluent to give title compound as colorless oil in 71% yield, 20 mg.
^{1}H NMR (400 MHz, C_6D_6) δ 5.89 (s, 2H), 2.70 – 2.59 (m, 2H), 2.35 – 2.23 (m, 2H), 2.17 (t, *J* = 5.8 Hz, 6H), 1.47 – 1.31 (m, 7H), 0.66 (t, *J* = 6.6 Hz, 6H).
^{13}C NMR (101 MHz, C_6D_6) δ 131.7, 53.9, 36.2, 27.3, 23.8, 10.1.
HRMS (ESI) *m/z* ([M+Na]$^+$) Calcd for $C_{14}H_{25}{}^{74}GeNNa$: 304.1096; Found: 304.1117.



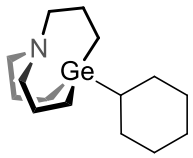
5-(1-phenoxyethyl)-1-aza-5-germabicyclo[3.3.3]undecane (3w). Synthesized by Method B at 90 ^{o}C instead, purified by silica gel column chromatography using petroleum ether as eluent to give title compound as colorless oil in 38% yield, 13 mg.
^{1}H NMR (400 MHz, C_6D_6) δ 7.22 – 7.17 (m, 2H), 7.06 – 7.01 (m, 2H), 6.87 – 6.80 (m, 1H), 3.95 (q, *J* = 7.0 Hz, 1H), 2.10 (t, *J* = 5.9 Hz, 6H), 1.48 – 1.32 (m, 9H), 0.86 – 0.70 (m, 6H).
^{13}C NMR (101 MHz, C_6D_6) δ 160.9, 129.7, 120.0, 115.9, 72.1, 53.8, 23.5, 16.5, 9.5.
HRMS (ESI) *m/z* ([M+H]$^{+}$) Calcd for $C_{17}H_{28}{}^{74}GeNO$: 336.1383; Found: 336.1380.



5-(1-phenylpropan-2-yl)-1-aza-5-germabicyclo[3.3.3]undecane (3x). Synthesized by Method B, purified by silica gel column chromatography using petroleum ether as eluent to give title compound as colorless oil in 36% yield, 12 mg.
^{1}H NMR (400 MHz, C_6D_6) δ 7.26 – 7.09 (m, 5H), 2.93 (dd, *J* = 13.6, 3.6 Hz, 1H), 2.31 (dd, *J* = 13.5, 11.0 Hz, 1H), 2.17 (t, *J* = 6.5 Hz, 6H), 1.48 – 1.38 (m, 6H), 1.02 – 0.89 (m, 4H), 0.65 (t, *J* = 6.5 Hz, 6H).
^{13}C NMR (101 MHz, C_6D_6) δ 144.2, 129.3, 128.4, 125.7, 53.9, 40.1, 27.9, 23.9, 15.3, 9.6.
HRMS (ESI) *m/z* ([M+H]$^{+}$) Calcd for $C_{18}H_{30}{}^{74}GeN$: 334.1590; Found: 334.1592.



5-cyclobutyl-1-aza-5-germabicyclo[3.3.3]undecane (3y). Synthesized by Method B, purified by silica gel column chromatography using petroleum ether as eluent to give title compound as colorless oil in 86% yield, 23.0 mg.
^{1}H NMR (400 MHz, C_6D_6) δ 2.28 – 2.16 (m, 9H), 2.15 – 1.99 (m, 3H), 1.91 – 1.80 (m, 1H), 1.49 – 1.39 (m, 6H), 0.69 (t, *J* = 6.6 Hz, 6H).
^{13}C NMR (101 MHz, C_6D_6) δ 53.9, 28.8, 25.3, 23.9, 23.6, 9.6.
HRMS (ESI) *m/z* ([M+H]$^{+}$) Calcd for $C_{13}H_{26}{}^{74}GeN$: 270.1277; Found: 270.1281.

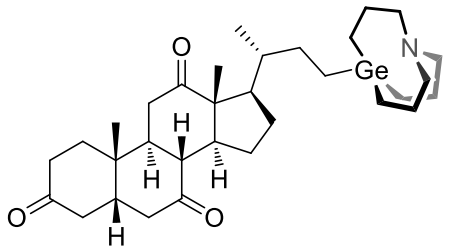


5-cyclohexyl-1-aza-5-germabicyclo[3.3.3]undecane (3z). Synthesized by Method B, purified by silica gel column chromatography using petroleum ether as eluent to give title compound as colorless oil in 30% yield, 9 mg.

^{1}H NMR (400 MHz, C_6D_6) δ 2.19 (t, *J* = 5.8 Hz, 6H), 1.87 – 1.74 (m, 5H), 1.49 – 1.40 (m, 6H), 1.36 – 1.19 (m, 5H), 0.68 – 0.57 (m, 7H).

^{13}C NMR (101 MHz, C_6D_6) δ 53.9, 32.4, 29.4, 29.3, 27.9, 23.9, 9.2.

HRMS (ESI) *m/z* ([M+H]$^+$) Calcd for $C_{15}H_{30}{}^{74}GeN$: 298.1590; Found: 298.1580.

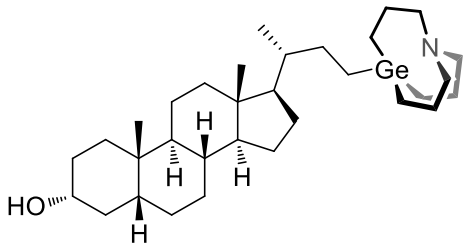


(5S,8R,9S,10S,13R,14S,17R)-17-((R)-4-(1-aza-5-germabicyclo[3.3.3]undecan-5-yl)butan-2-yl)-10,13-dimethyldodecahydro-3H-cyclopenta[a]phenanthrene-3,7,12(2H,4H)-trione (3aa). Synthesized by Method A using 1.0 mL DMF as solvent instead, purified by silica gel column chromatography using petroleum ether/ethyl acetate = 8/1 as eluent to give title compound as white solid in 72% yield, 41 mg.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 2.97 – 2.80 (m, 3H), 2.41 (t, *J* = 5.8 Hz, 6H), 2.36 – 2.07 (m, 8H), 2.03 – 1.92 (m, 4H), 1.84 – 1.74 (m, 1H), 1.64 – 1.58 (m, 1H), 1.57 – 1.48 (m, 6H), 1.46 – 1.36 (m, 4H), 1.32 – 1.22 (m, 2H), 1.19 – 1.03 (m, 5H), 0.79 (d, *J* = 6.5 Hz, 3H), 0.63 (t, *J* = 6.5 Hz, 6H), 0.43 (td, *J* = 13.0, 4.1 Hz, 1H), 0.17 (td, *J* = 12.7, 4.6 Hz, 1H).

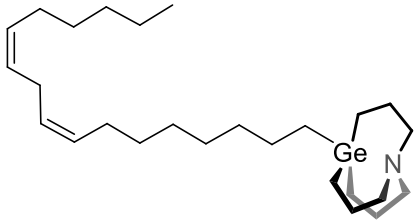
^{13}C NMR (101 MHz, CD_2Cl_2) δ 212.5, 209.3, 209.3, 57.2, 54.1, 52.3, 49.4, 47.2, 46.0, 45.7, 45.4, 43.2, 39.2, 39.1, 36.9, 36.4, 35.6, 31.0, 28.1, 25.6, 23.9, 22.1, 18.8, 17.2, 12.1, 11.8.

HRMS (ESI) *m/z* ([M+H]$^+$) Calcd for $C_{32}H_{52}{}^{74}GeNO_3$: 572.3159; Found: 572.3163.

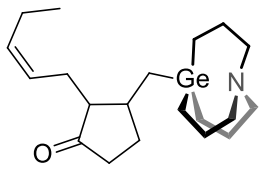


(3R,5R,8R,9S,10S,13R,14S,17R)-17-((R)-4-(1-aza-5-germabicyclo[3.3.3]undecan-5-yl)butan-2-yl)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-3-ol (3ab). Synthesized by Method A using 0.5 mL THF as solvent instead, 55% yield was determined by ^{1}H NMR spectra using mesitylene as internal standard. Purification by silica gel column chromatography using petroleum ether/ethyl acetate = 4/1 as eluent resulted in 30 mg white solid mixture of target product and protonation product with a ratio of 2.1/1. Adjusted yield of corresponding carbagermatranes was 43%.

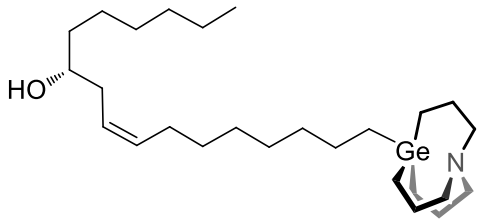
HRMS (ESI) *m/z* ([M+H]$^+$) Calcd for $C_{32}H_{58}{}^{74}GeNO$: 546.3730; Found: 546.3741.



5-((8Z,11Z)-heptadeca-8,11-dien-1-yl)-1-aza-5-germabicyclo[3.3.3]undecane (3ac). Synthesized by Method A, purified by silica gel column chromatography using petroleum ether as eluent to give title compound as colorless oil in 95%, 42 mg.
^{1}H NMR (400 MHz, C_6D_6) δ 5.53 – 5.43 (m, 4H), 2.94 – 2.84 (m, 2H), 2.19 (t, *J* = 5.8 Hz, 6H), 2.15 – 2.02 (m, 4H), 1.51 – 1.23 (m, 22H), 0.89 (t, *J* = 6.9 Hz, 3H), 0.70 (t, *J* = 6.5 Hz, 6H), 0.63 – 0.55 (m, 2H).
^{13}C NMR (101 MHz, C_6D_6) δ 130.6, 130.4, 128.5, 128.4, 53.9, 34.7, 31.9, 30.3, 29.9, 29.9, 29.8, 27.8, 27.6, 26.2, 26.1, 23.9, 23.0, 22.0, 14.3, 11.9.
HRMS (ESI) *m/z* ([M+H]$^+$) Calcd for $C_{26}H_{50}{}^{74}GeN$: 450.3155; Found: 450.3126.

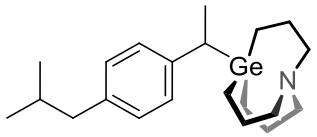


(Z)-3-((1-aza-5-germabicyclo[3.3.3]undecan-5-yl)methyl)-2-(pent-2-en-1-yl)cyclopentan-1-one (3ad). Synthesized by Method A at 60 °C instead, purified by silica gel column chromatography using petroleum ether/ethyl acetate = 10/1 as eluent to give title compound as colorless oil in 74% yield, 28 mg.
^{1}H NMR (400 MHz, C_6D_6) δ 5.58 – 5.43 (m, 2H), 2.59 – 2.49 (m, 1H), 2.46 – 2.37 (m, 1H), 2.26 – 2.06 (m, 9H), 1.86 – 1.72 (m, 3H), 1.58 – 1.51 (m, 1H), 1.48 – 1.35 (m, 6H), 1.04 – 0.88 (m, 5H), 0.71 – 0.58 (m, 6H), 0.22 (dd, *J* = 13.3, 11.0 Hz, 1H).
^{13}C NMR (101 MHz, C_6D_6) δ 218.1, 133.1, 126.6, 58.8, 53.8, 39.3, 38.4, 30.5, 27.7, 25.0, 23.8, 21.1, 14.6, 13.0.
HRMS (ESI) *m/z* ([M+H]$^+$) Calcd for $C_{20}H_{36}{}^{74}GeNO$: 380.2009; Found: 380.2006.

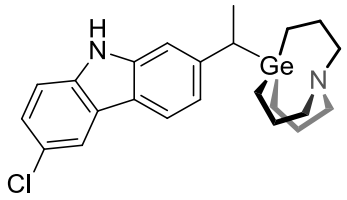


(R,Z)-17-(1-aza-5-germabicyclo[3.3.3]undecan-5-yl)heptadec-9-en-7-ol (3ae). Synthesized by Method A, purified by silica gel column chromatography using petroleum ether/ethyl acetate = 8/1 as eluent to give title compound as colorless oil in 47% yield, 22 mg.

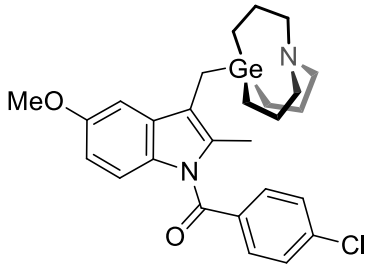
^{1}H NMR (400 MHz, Acetone-d_6) δ 5.51 – 5.39 (m, 2H), 3.61 – 3.52 (m, 1H), 3.40 (d, J = 5.0 Hz, 1H), 2.43 (t, J = 5.8 Hz, 6H), 2.27 – 2.14 (m, 2H), 1.60 – 1.51 (m, 6H), 1.50 – 1.43 (m, 2H), 1.40 – 1.24 (m, 20H), 0.89 (t, J = 6.8 Hz, 3H), 0.65 (t, J = 6.5 Hz, 6H), 0.39 – 0.32 (m, 2H).
^{13}C NMR (101 MHz, Acetone-d_6) δ 131.9, 127.2, 71.6, 54.3, 37.8, 36.4, 34.9, 32.7, 30.5, 28.0, 26.5, 26.2, 24.1, 23.3, 22.2, 14.4, 12.2.
HRMS (ESI) *m/z* ([M+H]$^+$) Calcd for $C_{26}H_{52}{}^{74}GeNO$: 468.3261; Found: 468.3267.



5-(1-(4-isobutylphenyl)ethyl)-1-aza-5-germabicyclo[3.3.3]undecane (3af). Synthesized by Method B, purified by silica gel column chromatography using petroleum ether eluent to give title compound as colorless thick oil in 81% yield, 31 mg.
^{1}H NMR (400 MHz, C_6D_6) δ 7.13 – 7.04 (m, 4H), 2.41 (d, J = 7.2 Hz, 2H), 2.13 – 1.99 (m, 7H), 1.87 – 1.76 (m, 1H), 1.48 (d, J = 7.5 Hz, 3H), 1.40 – 1.26 (m, 6H), 0.88 (d, J = 6.4 Hz, 6H), 0.75 – 0.61 (m, 6H).
^{13}C NMR (101 MHz, C_6D_6) δ 146.7 136.4, 129.0, 126.7, 53.7, 45.5, 35.0, 30.7, 23.9, 22.7, 16.6, 10.0.
HRMS (ESI) *m/z* ([M+H]$^+$) Calcd for $C_{21}H_{36}{}^{74}GeN$: 376.2060; Found: 376.2039.



2-(1-(1-aza-5-germabicyclo[3.3.3]undecan-5-yl)ethyl)-6-chloro-9H-carbazole (3ag). Synthesized by Method B, purified by silica gel column chromatography using petroleum ether/ethyl acetate = 10/1 as eluent to give title compound as yellow thick oil in 70% yield, 31 mg.
^{1}H NMR (400 MHz, C_6D_6) δ 7.97 (d, J = 2.0 Hz, 1H), 7.72 (d, J = 8.1 Hz, 1H), 7.35 – 7.30 (m, 1H), 7.04 – 6.98 (m, 1H), 6.88 (s, 1H), 6.76 (d, J = 8.5 Hz, 1H), 6.50 (s, 1H), 2.30 (q, J = 7.4 Hz, 1H), 2.14 – 2.00 (m, 6H), 1.61 (d, J = 7.4 Hz, 3H), 1.45 – 1.29 (m, 6H), 0.81 – 0.68 (m, 6H).
^{13}C NMR (101 MHz, C_6D_6) δ 149.0, 141.2, 138.1, 125.6, 124.9, 124.7, 120.2, 120.1, 119.8, 119.1, 111.4, 107.9, 53.7, 36.5, 23.9, 16.9, 10.1.
HRMS (ESI) *m/z* ([M+H]$^+$) Calcd for $C_{23}H_{30}Cl^{74}GeN_2$: 443.1309; Found: 443.1276.

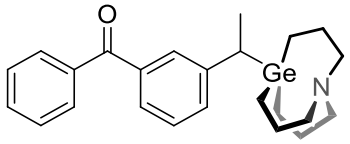


(3-((1-aza-5-germabicyclo[3.3.3]undecan-5-yl)methyl)-5-methoxy-2-methyl-1H-indol-1-yl)(4-chlorophenyl)methanone (3ah). Synthesized by Method A, purified by silica gel column chromatography using petroleum ether/ethyl acetate = 6/1 as eluent to give title compound as yellow thick oil in 89% yield, 47 mg.

^{1}H NMR (400 MHz, C_6D_6) δ 7.27 – 7.21 (m, 2H), 7.13 (d, *J* = 2.5 Hz, 1H), 7.06 (d, *J* = 8.9 Hz, 1H), 6.97 – 6.92 (m, 2H), 6.65 – 6.61 (m, 1H), 3.52 (s, 3H), 2.35 (s, 3H), 2.06 (t, *J* = 5.9 Hz ,6H), 1.97 (s, 2H), 1.40 – 1.27 (m, 6H), 0.75 (t, *J* = 6.6 Hz, 6H).

^{13}C NMR (101 MHz, C_6D_6) δ 167.6, 156.4, 138.1, 135.6, 132.8, 131.8, 131.3, 130.5, 128.9, 122.1, 115.4, 110.6, 103.3, 55.3, 53.5, 23.7, 19.2, 14.5, 13.4.

HRMS (ESI) *m/z* ([M+H]$^+$) Calcd for $C_{27}H_{34}Cl^{74}GeN_2O_2$: 527.1521; Found: 527.1522.

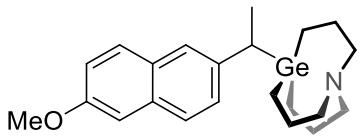


(3-(1-(1-aza-5-germabicyclo[3.3.3]undecan-5-yl)ethyl)phenyl)(phenyl)methanone (3ai). Synthesized by Method B, purified by silica gel column chromatography using petroleum ether/ethyl acetate = 20/1 as eluent to give title compound as white solid in 57% yield, 24 mg.

^{1}H NMR (400 MHz, C_6D_6) δ 7.88 – 7.83 (m, 2H), 7.79 (s, 1H), 7.54 (d, *J* = 7.4 Hz, 1H), 7.21 – 7.04 (m, 5H), 2.09 – 1.94 (m, 7H), 1.39 (d, *J* = 7.4 Hz, 3H), 1.35 – 1.21 (m, 6H), 0.67 – 0.54 (m, 6H).

^{13}C NMR (101 MHz, C_6D_6) δ 196.5, 150.1, 138.9, 137.9, 131.9, 130.5, 130.4, 127.9, 125.6, 53.6, 35.5, 23.7, 16.3, 9.9.

HRMS (ESI) *m/z* ([M+H]$^+$) Calcd for $C_{24}H_{32}{}^{74}GeNO$: 424.1696; Found: 424.1682.

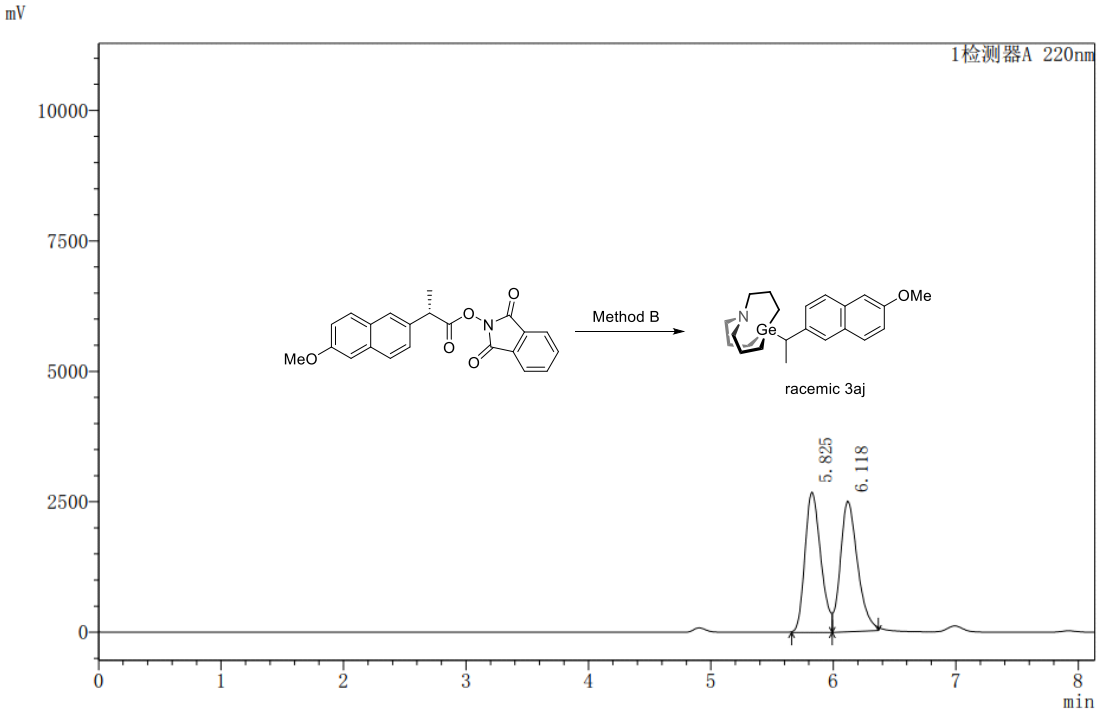


5-(1-(6-methoxynaphthalen-2-yl)ethyl)-1-aza-5-germabicyclo[3.3.3]undecane (3aj). Synthesized by Method B from enantiomerically pure naproxen NHP ester, purified by silica gel column chromatography using petroleum ether as eluent to give racemic product as white solid in 75% yield, 30 mg, 0% ee.

^{1}H NMR (400 MHz, C_6D_6) δ 7.68 – 7.57 (m, 2H), 7.50 (s, 1H), 7.34 (d, *J* = 8.5 Hz, 1H), 7.24 – 7.19 (m, 1H), 7.00 (s, 1H), 3.42 (s, 3H), 2.24 (q, *J* = 7.4 Hz, 1H), 2.12 – 1.96 (m, 6H), 1.58 (d, *J* = 7.4 Hz, 3H), 1.41 – 1.23 (m, 6H), 0.77 – 0.63 (m, 6H).

^{13}C NMR (101 MHz, C_6D_6) δ 157.1, 144.9, 132.5, 130.2, 129.1, 127.9, 126.4, 123.6, 118.9, 106.2, 54.8, 53.7, 35.5, 23.8, 16.7, 10.1.
HRMS (ESI) *m/z* ([M+H]$^+$) Calcd for $C_{22}H_{32}{}^{74}GeNO$: 400.1696; Found: 400.1694.

Column	CHIRALCEL AD-H(ADH0CE-TD152)
Column size	0.46 cm I.D. × 25 cm L
Injection	2.5 uL
Mobile phase	Hexane / Isopropanol = 100 / 0(V /V)
Flow rate	0.7 mL / min
Wave length	UV 220 nm
Temperature	25 ºC



Peak#	Ret. Time	Area	Area%	T.Plate#	Tailing F.	Height
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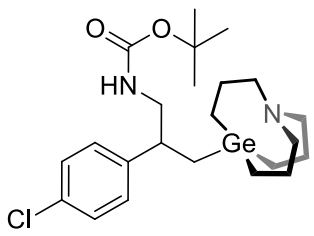
2	6.118	24489258	50.189	8513	--	2503917



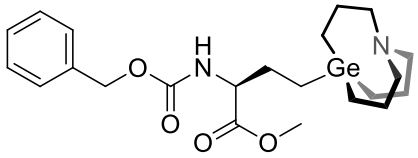
Tert-butyl (3-(1-aza-5-germabicyclo[3.3.3]undecan-5-yl)-2-(4-chlorophenyl)propyl)carbamate (3ak). Synthesized by Method A at 60 ºC instead,

purified by silica gel column chromatography using petroleum ether/ethyl acetate = 10/1 as eluent to give title compound as white solid in 31% yield, 15 mg.

^{1}H NMR (400 MHz, Acetone-d_6) δ 7.28 (d, J = 8.1 Hz, 2H), 7.21 (d, J = 8.2 Hz, 2H), 5.72 (s, 1H), 3.25 – 3.17 (m, 1H), 3.13 – 3.03 (m, 1H), 3.01 – 2.91 (m, 1H), 2.36 (t, J = 5.7 Hz, 6H), 1.51 – 1.42 (m, 6H), 1.33 (s, 9H), 0.80 – 0.65 (m, 2H), 0.60 – 0.41 (m, 6H).

^{13}C NMR (101 MHz, Acetone-d_6) δ 156.6, 146.3, 131.9, 130.6, 129.0, 78.4, 54.4, 50.3, 43.6, 28.7, 27.6, 24.1, 13.0.

HRMS (ESI) *m/z* ([M+Na]$^+$) Calcd for $C_{23}H_{37}Cl^{74}GeN_2NaO_2$: 505.1653; Found: 505.1648.



Methyl (S)-2-(((benzyloxy)carbonyl)amino)-4-(1-aza-5-germabicyclo[3.3.3]undecan-5-yl)butanoate (3al). Synthesized by Method A at 60 °C instead of room temperature, purified by silica gel column chromatography using petroleum ether/ethyl acetate = 3/1 as eluent to give title compound as colorless thick oil in 53% yield, 25 mg.

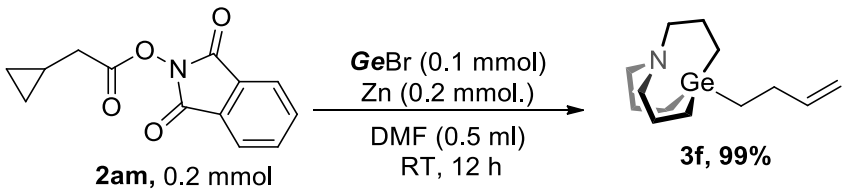
^{1}H NMR (400 MHz, Acetone-d_6) δ 7.40 – 7.28 (m, 5H), 6.48 (d, J = 7.6 Hz, 1H), 5.07 (s, 2H), 4.14 – 4.06 (m, 1H), 3.67 (s, 3H), 2.42 (t, J = 6.6 Hz, 6H), 1.84 – 1.61 (m, 2H), 1.59 – 1.50 (m, 6H), 0.66 (t, J = 6.6 Hz, 6H), 0.46 – 0.29 (m, 2H).

^{13}C NMR (101 MHz, Acetone-d_6) δ 173.9, 157.1, 138.4, 129.3, 128.7, 66.7, 58.2, 54.4, 52.1, 29.1, 24.0, 17.4, 12.1.

HRMS (ESI) *m/z* ([M+H]$^+$) Calcd for $C_{22}H_{35}{}^{74}GeN_2O_4$: 465.1809; Found: 465.1810.

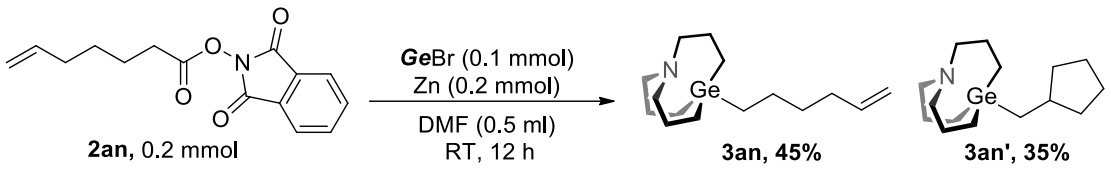
3. Experimental Procedure and Compound Characterization Data for scheme 2-6

3.1 Scheme 2. Radical probe experiments

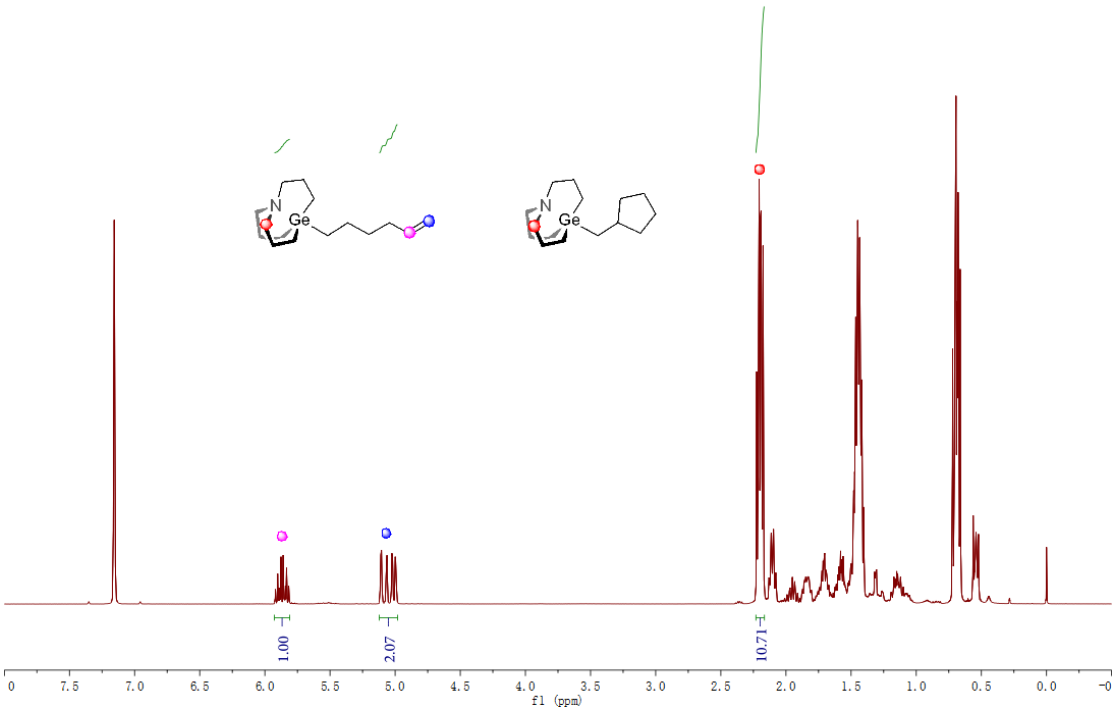


To an oven-dried screw-cap tube equipped with stir bar was charged with 0.1 mmol (29.2 mg) ***Ge***Br, 0.2 mmol (49 mg) **2am** and 0.2 mmol (13 mg) Zn powder. The tube was vacuumed and backfilled with argon for three cycles. 0.5 mL DMF was added through syringe and the tube was sealed with a teflon stopper and stirred at room temperature for 12 hours. The reaction was quenched with NH_4Cl (sat, aq), extracted with ethyl acetate. Organic layer was separated, dried over Na_2SO_4, concentrated under

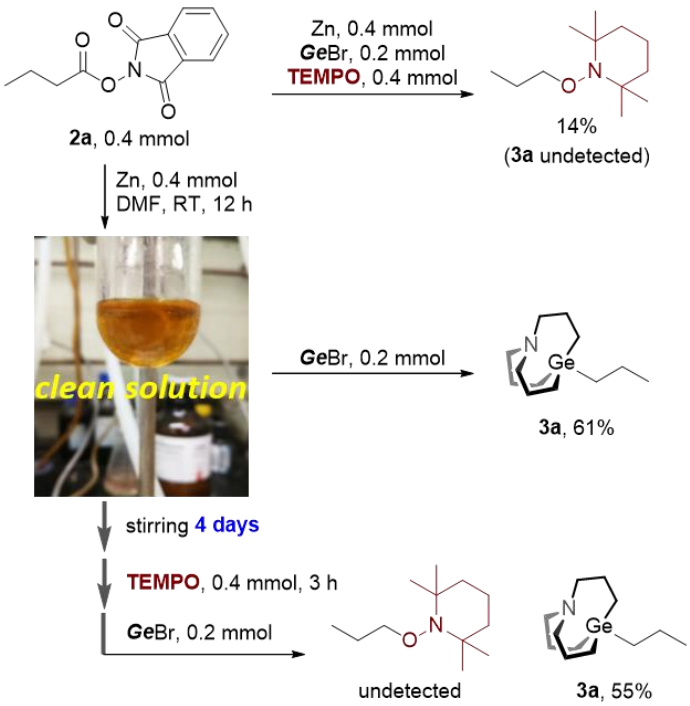
reduced pressure to give crude product, which was purified by silica gel column chromatography using petroleum ether as eluent to give **3f** in 99% yield as 26.6 mg colorless oil.



To an oven-dried screw-cap tube equipped with stir bar was charged with 0.1 mmol (29.2 mg) ***Ge***Br, 0.2 mmol (54.6 mg) **2an** and 0.2 mmol Zn (13 mg) powder. The tube was vacuumed and backfilled with argon for three cycles. 0.5 mL DMF was added through syringe and the tube was sealed with a teflon stopper and stirred at room temperature for 12 hours. The reaction was quenched with NH_4Cl (sat, aq), extracted with ethyl acetate. Organic layer was separated, dried over Na_2SO_4, concentrated under reduced pressure to give crude product, which was purified by silica gel column chromatography give inseparable mixture of **3an** and **3an'** in total 80% yield as 23.7 mg colorless oil. The ratio was determined by ^1H NMR spectra.



3.2 Scheme 3. Ruling-out of radical involvement in Ge-C bond formation step



Upper: To an oven-dried screw-cap tube equipped with stir bar was charged with 0.4 mmol (93.2 mg) **2a**, 0.2 mmol (58.4 mg) ***Ge***Br and 0.4 mmol (26 mg) Zn powder. The tube was vacuumed and backfilled with argon for three cycles. 1.0 mL DMF was added through syringe and the tube was sealed with a teflon stopper and stirred at room temperature for 12 hours. GC analysis detected 14% of TEMPO-captured product and **3a** was not detected.

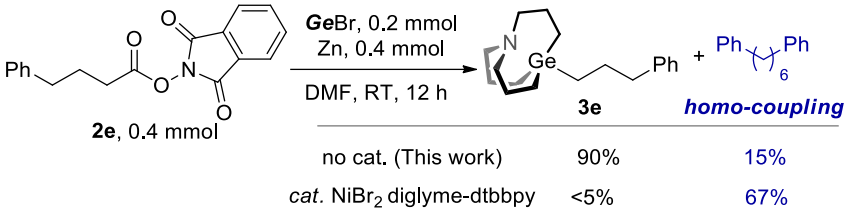
The TEMPO-captured product is a known compound, and can be synthesized based on reported literature[16]. ^{1}H NMR (400 MHz, CDCl3) δ 3.69 (t, J = 6.7 Hz, 2H), 1.59 – 1.49 (m, 4H), 1.47 – 1.42 (m, 4H), 1.15 (s, 6H), 1.10 (s, 6H), 0.94 (t, J = 7.4 Hz, 2H). ^{13}C NMR (101 MHz, CDCl3) δ 78.4, 59.8, 39.8, 33.2, 22.1, 20.2, 17.3, 11.1. NMR data of Synthesized TEMPO-captured product matched with previous report[17]. GC response factor was determined using this synthesized compound as analyte and benzophenone as internal standard.

Middle: To an oven-dried screw-cap tube equipped with stir bar was charged with 0.4 mmol (93.2 mg) **2a** and 0.4 mmol (26 mg) Zn powder. The tube was vacuumed and backfilled with argon for three cycles. 1.0 mL DMF was added through syringe and the tube was sealed with a teflon stopper and stirred at room temperature for 12 hours. 12 hours later, a clean yellow solution was obtained, to which 0.2 mmol ***Ge***Br (58.4 mg) was added under argon atmosphere. The mixture was stirred for further 12 hours, then quenched with NH_4Cl (sat, aq), extracted with ethyl acetate. Organic layer was separated, dried over Na_2SO_4, concentrated under reduced pressure to give crude

product, which was purified by silica gel column chromatography using petroleum as eluent in 61% yield, colorless oil, 31.2 mg.

Under: To an oven-dried screw-cap tube equipped with stir bar was charged with 0.4 mmol (93.2 mg) **2a** and 0.4 mmol (26 mg) Zn powder. The tube was vacuumed and backfilled with argon for three cycles. 1.0 mL DMF was added through syringe and the tube was sealed with a teflon stopper and stirred at room temperature for 12 hours. 12 hours later, a clean yellow solution was obtained, which was further stirred at room temperature for 4 days followed by the addition of 0.4 mmol (62.5 mg) TEMPO under argon atmosphere. After TEMPO was added, the mixture was stirred at room temperature for 3 hours followed by the addition of 0.2 mmol (58.4 mg) ***Ge***Br under argon atmosphere and stirred for further 12 hours. TEMPO-captured product was not detected by GC-MS analysis. The reaction was quenched with NH_4Cl (sat, aq), extracted with ethyl acetate. Organic layer was separated, dried over Na_2SO_4, concentrated under reduced pressure to give crude product, which was purified by silica gel column chromatography using petroleum ether as eluent in 55% yield, colorless oil, 28 mg.

3.3 Scheme 4. Interference experiment with Ni catalyst

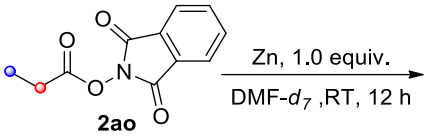


Without catalyst: To an oven-dried screw-cap tube equipped with stir bar was charged with 0.2 mmol (58.4 mg) ***Ge***Br, 0.4 mmol (123.6 mg) **2e** and 0.4 mmol (26 mg) Zn powder. The tube was vacuumed and backfilled with argon for three cycles. 1.0 mL DMF was added through syringe and the tube was sealed with a teflon stopper and stirred at room temperature for 12 hours. Yields were determined by GC analysis using benzophenone internal standard.

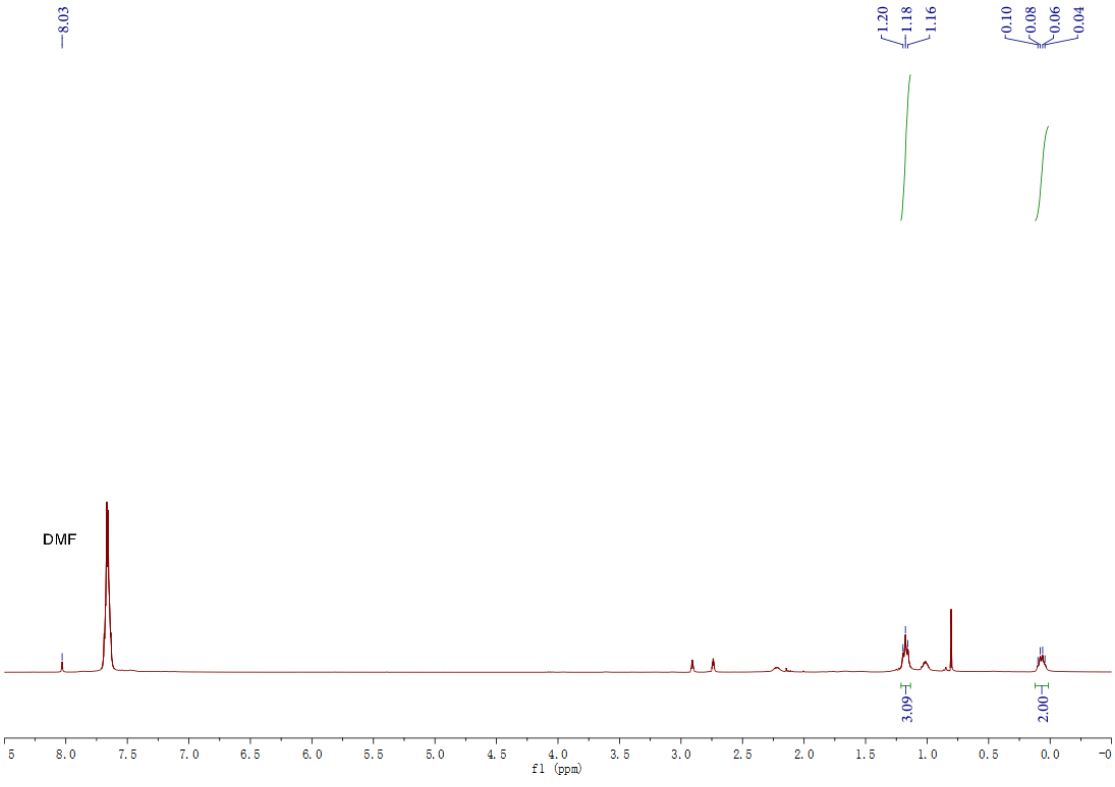
With Ni catalyst: To an oven-dried screw-cap tube equipped with stir bar was charged with 0.02 mmol (7 mg) $NiBr_2$ diglyme, 0.024 mmol (6.4 mg) 4,4'-di-tert-butyl-2,2'-bipyridine, 0.2 mmol (58.4 mg) ***Ge***Br, 0.4 mmol (123.6 mg) **2e** and 0.4 mmol (26 mg) Zn powder. The tube was vacuumed and backfilled with argon for three cycles. 0.5 mL DMF was added through syringe and the tube was sealed with a teflon stopper and stirred at room temperature for 12 hours. Yields were determined by GC analysis using benzophenone internal standard.

3.4 Scheme 5. Comparison of ^{1}H-NMR spectra of alkyl zinc reagent of our strategy and classic alkyl zinc regent

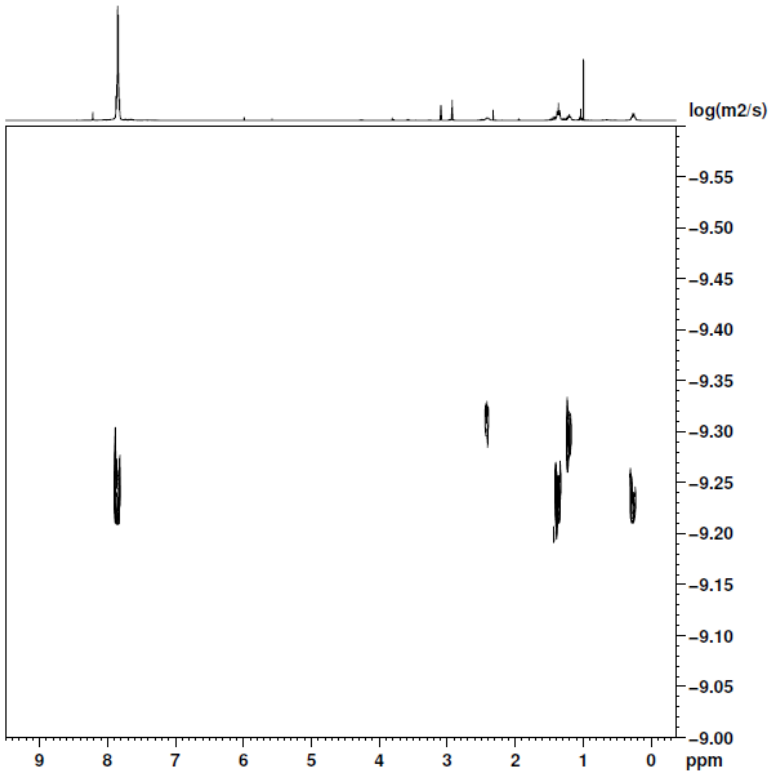
a) Zinc-mediating decarboxylation of NHP esters



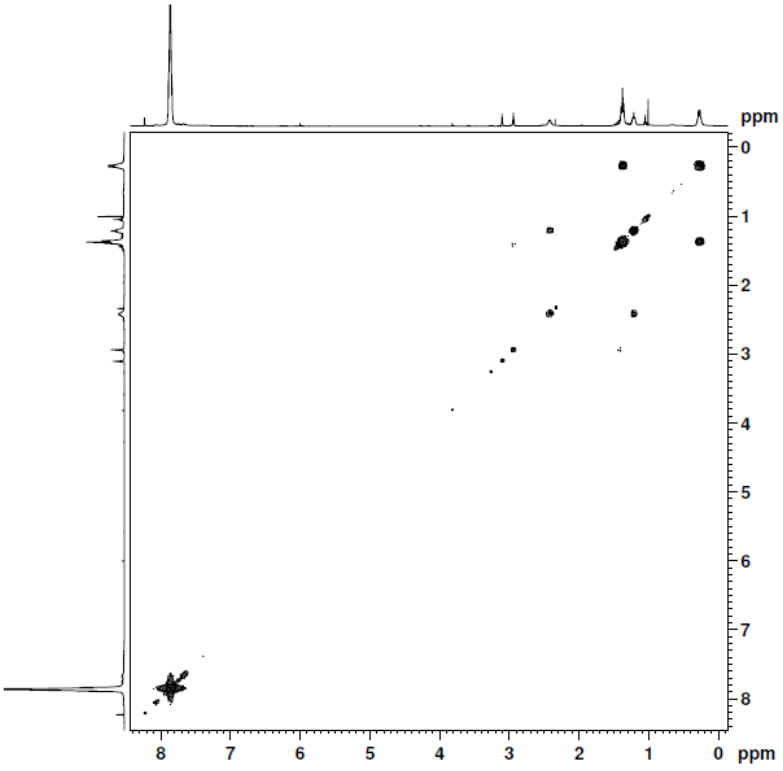
To an oven-dried screw-cap tube equipped with stir bar was charged with 0.02 mmol (43.8 mg) **2ao** and 0.2 mmol (13 mg) Zn powder. The tube was vacuumed and backfilled with argon for three cycles. 0.5 mL DMF-d_7 was added through syringe and the tube was sealed with a teflon stopper and stirred at room temperature for 12 hours. Under argon atmosphere, the resulting solution was transferred to NMR tube for analysis. **^{1}H NMR** (400 MHz, DMF-d_7) δ -CH_3 1.18 (t, J = 7.9 Hz, 3H), -CH_2-Zn 0.07 (q, J = 7.5 Hz, 2H).



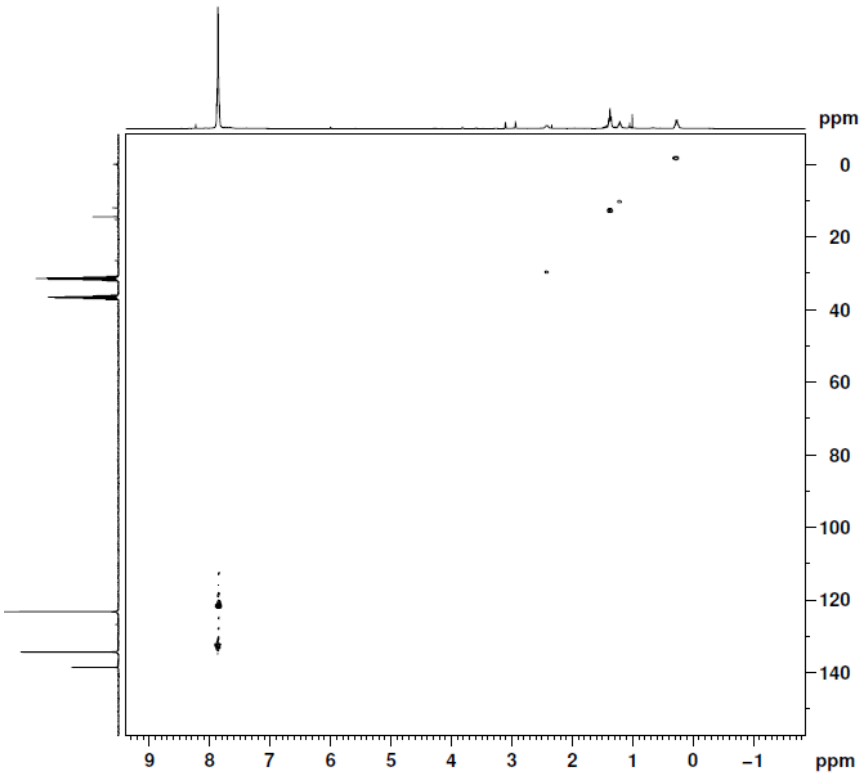
^{1}H NMR spectra for **scheme 5a**



DOSY spectra for **scheme 5a**

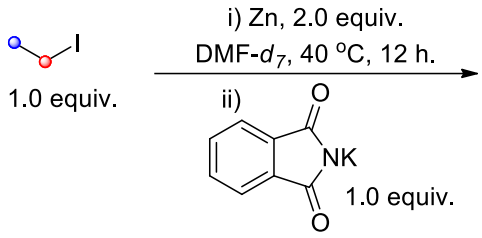


^{1}H-^{1}H COSY spectra for **scheme 5a**



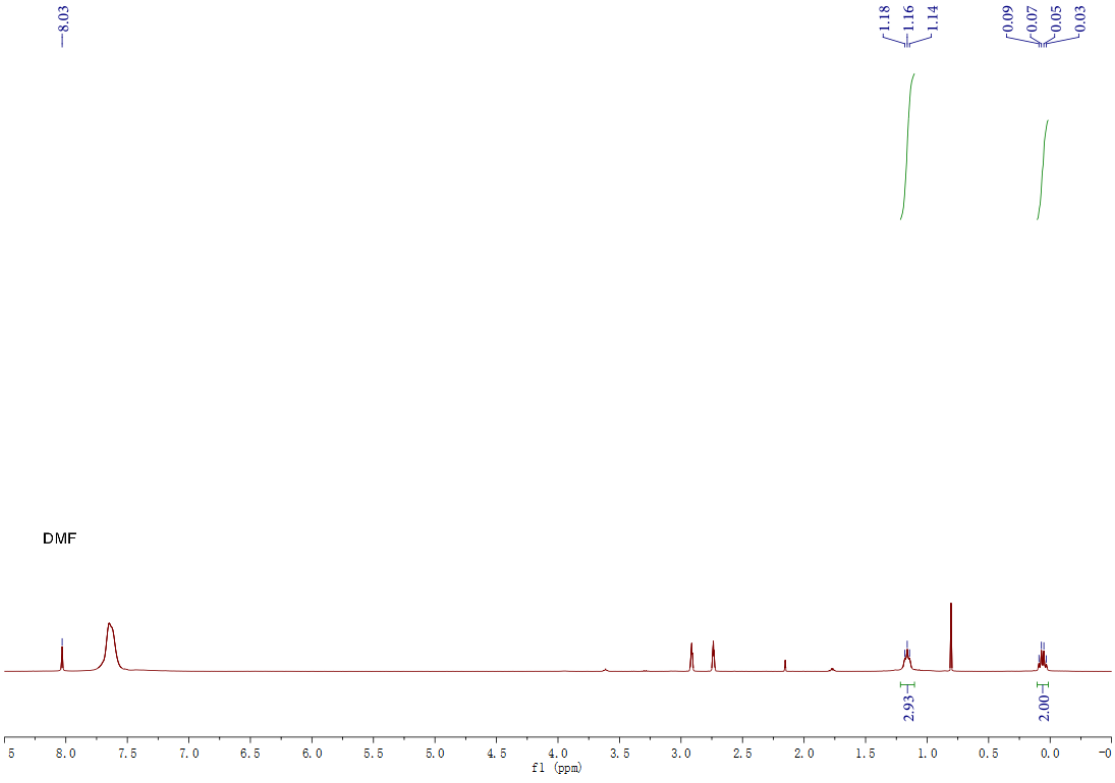
HSQC spectra for **scheme 5a**

b) Classic synthesis of alkyl zinc

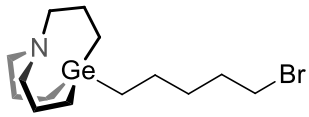


To an oven-dried screw-cap tube equipped with stir bar was charged with 0.3 mmol (19.5 mg) Zn powder. The tube was vacuumed and backfilled with argon for three cycles then 1.0 mL THF was added through syringe. To this mixture was added 0.05 mmol (4.3 µL) 1,2-dibromoethane followed by stirring at 65 °C for 5 minutes. Then the mixture was cooled, and 0.05 mmol (6.3 µL) TMSCl was added and stirred at room temperature for 15 minutes. Following, THF was removed under vacuum and 1.0 mL DMF-d_7 and 0.15 mmol (12 µL) iodoethane was added through syringe. The tube was sealed with a teflon stopper and stirred at 40 °C for 12 hours. When the mixture was cooled, 0.15 mmol (27.8 mg) Potassium phthalimide was added and stirred for 3 hours. Under argon atmosphere, the resulting solution was transferred to NMR tube for

analysis. **^{1}H NMR** (400 MHz, DMF-d_7) δ -CH_3 1.16 (t, J = 7.6 Hz, 3H), -CH_2-Zn 0.06 (q, J = 8.0 Hz, 2H).



3.5 Scheme 6. Br/I-containing substrates and orthogonal experiment with Suzuki cross-coupling reaction

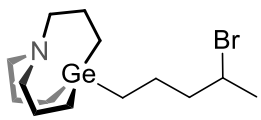


5-(5-bromopentyl)-1-aza-5-germabicyclo[3.3.3]undecane (3ap). Synthesized by Method A, purified by silica gel column chromatography using petroleum ether as eluent to give title compound as colorless oil in 77% yield, 28 mg.

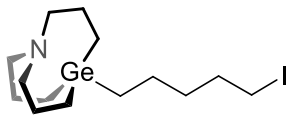
^{1}H NMR (400 MHz, C_6D_6) δ 3.03 (t, J = 6.9 Hz, 2H), 2.19 (t, J = 5.8 Hz, 6H), 1.67 – 1.57 (m, 2H), 1.47 – 1.39 (m, 6H), 1.34 – 1.22 (m, 4H), 0.65 (t, J = 6.6 Hz, 6H), 0.46 – 0.39 (m, 2H).

^{13}C NMR (101 MHz, C_6D_6) δ 53.8, 34.0, 33.0, 32.8, 25.1, 23.8, 21.6, 11.8.

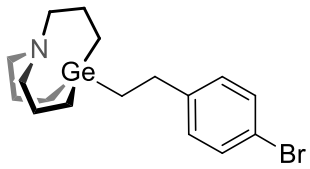
HRMS (ESI) *m/z* ([M+H]$^+$) Calcd for $C_{14}H_{29}Br^{74}GeN$: 364.0695; Found: 364.0677.



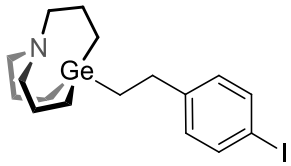
5-(4-bromopentyl)-1-aza-5-germabicyclo[3.3.3]undecane (3aq). Synthesized by Method A, purified by silica gel column chromatography using petroleum ether as eluent to give title compound as colorless oil in 87% yield, 32 mg.
^{1}H NMR (400 MHz, C_6D_6) δ 3.99 – 3.89 (m, 1H), 2.18 (t, *J* = 5.8 Hz 6H), 1.87 – 1.75 (m, 1H), 1.62 – 1.37 (m, 12H), 0.66 (t, *J* = 6.5 Hz, 6H), 0.51 – 0.26 (m, 2H).
^{13}C NMR (101 MHz, C_6D_6) δ 53.8, 51.8, 45.8, 26.6, 24.2, 23.8, 20.9, 11.8.
HRMS (ESI) *m/z* ([M+H]$^+$) Calcd for $C_{14}H_{29}Br^{74}GeN$: 364.0695; Found: 364.0667.



5-(5-iodopentyl)-1-aza-5-germabicyclo[3.3.3]undecane (3ar). Synthesized by Method A, purified by silica gel column chromatography using petroleum ether as eluent to give title compound as colorless oil in 27% yield, 11 mg.
^{1}H NMR (400 MHz, C_6D_6) δ 2.79 (t, *J* = 7.1 Hz, 2H), 2.19 (t, *J* = 5.7 Hz, 6H), 1.63 – 1.53 (m, 2H), 1.49 – 1.39 (m, 6H), 1.30 – 1.20 (m, 4H), 0.65 (t, *J* = 6.5 Hz, 6H), 0.47 – 0.39 (m, 2H).
^{13}C NMR (101 MHz, C_6D_6) δ 53.5, 34.8, 33.4, 24.5, 23.5, 21.2, 11.5, 6.8.
HRMS (ESI) *m/z* ([M+H]$^+$) Calcd for $C_{14}H_{29}I^{74}GeN$: 412.0566; Found: 412.0499.

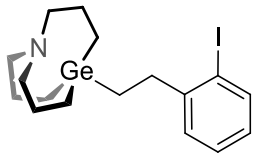


5-(4-bromophenethyl)-1-aza-5-germabicyclo[3.3.3]undecane (3as). Synthesized by Method A using 0.5 mL THF as solvent instead, purified by silica gel column chromatography using petroleum ether as eluent to give title compound as colorless oil in 68% yield, 27 mg.
^{1}H NMR (400 MHz, C_6D_6) δ 7.31 (d, *J* = 8.1 Hz, 2H), 6.83 (d, *J* = 8.1 Hz, 2H), 2.48 (t, *J* = 8.8 Hz, 2H), 2.16 (t, *J* = 5.7 Hz, 6H), 1.45 – 1.35 (m, 6H), 0.73 – 0.65 (m, 2H), 0.61 (t, *J* = 6.5 Hz, 6H).
^{13}C NMR (101 MHz, C_6D_6) δ 145.9, 131.6, 130.1, 119.2, 53.8, 31.6, 23.8, 23.7, 11.7.
HRMS (ESI) *m/z* ([M+Na]$^+$) Calcd for $C_{17}H_{26}Br^{74}GeNNa$: 420.0358; Found: 420.0326.

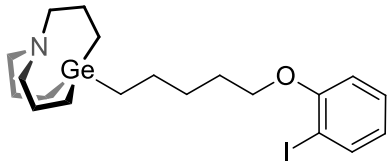


5-(4-iodophenethyl)-1-aza-5-germabicyclo[3.3.3]undecane (3at). Synthesized by Method A, purified by silica gel column chromatography using petroleum ether as eluent to give title compound as colorless oil in 70% yield, 31 mg.

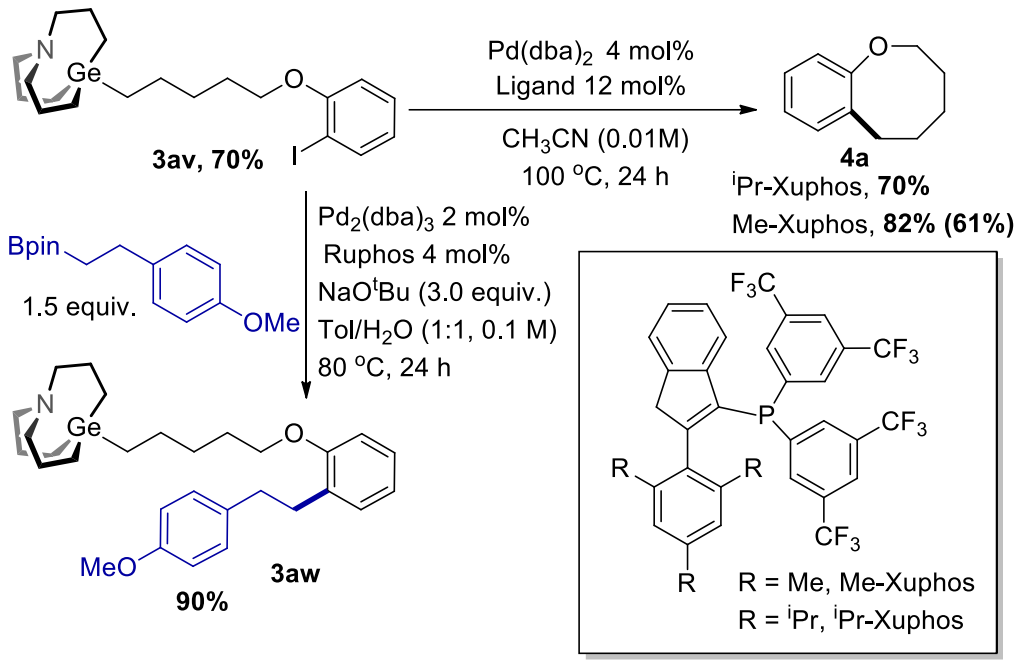
^{1}H NMR (400 MHz, C_6D_6) δ 7.53 – 7.44 (m, 2H), 6.75 – 6.65 (m, 2H), 2.51 – 2.41 (m, 2H), 2.15 (t, *J* = 5.8 Hz, 6H), 1.44 – 1.33 (m, 6H), 0.71 – 0.64 (m, 2H), 0.60 (t, *J* = 6.6 Hz, 6H).
^{13}C NMR (101 MHz, C_6D_6) δ 146.6, 137.6, 130.4, 90.3, 53.8, 31.7, 23.8, 23.7, 11.7.
HRMS (ESI) *m/z* ([M+H]$^+$) Calcd for $C_{17}H_{27}I^{74}GeN$: 446.0400; Found: 446.0391.

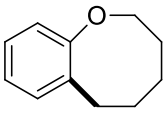


5-(2-iodophenethyl)-1-aza-5-germabicyclo[3.3.3]undecane (3au). Synthesized by Method A using 0.5 mL THF as solvent instead, purified by silica gel column chromatography using petroleum ether as eluent to give title compound as colorless oil in 64% yield, 29 mg.
^{1}H NMR (400 MHz, C_6D_6) δ 7.77 – 7.68 (m, 1H), 7.09 – 7.05 (m, 1H), 7.03 – 6.96 (m, 1H), 6.54 – 6.48 (m, 1H), 2.80 – 2.72 (m, 2H), 2.16 (t, *J* = 5.8 Hz, 6H), 1.46 – 1.36 (m, 6H), 0.85 – 0.75 (m, 2H), 0.72 (t, *J* = 6.6 Hz, 6H).
^{13}C NMR (101 MHz, C_6D_6) δ 149.4, 139.8, 129.1, 128.6, 127.3, 100.7, 53.8, 37.8, 23.8, 23.1, 11.8.
HRMS (ESI) *m/z* ([M+H]$^+$) Calcd for $C_{17}H_{27}I^{74}GeN$: 446.0400; Found: 446.0380.



5-(5-(2-iodophenoxy)pentyl)-1-aza-5-germabicyclo[3.3.3]undecane (3av). Synthesized by Method A using 0.5 mL THF as solvent instead, purified by silica gel column chromatography using petroleum ether as eluent to give title compound as colorless oil in 70% yield, 35 mg.
^{1}H NMR (400 MHz, C_6D_6) δ 7.72 – 7.67 (m, 1H), 6.98 – 6.92 (m, 1H), 6.42 – 6.36 (m, 2H), 3.58 (t, *J* = 6.5 Hz, 2H), 2.20 (t, *J* = 5.8 Hz, 6H), 1.74 – 1.66 (m, 2H), 1.56 – 1.40 (m, 10H), 0.69 (t, *J* = 6.5 Hz, 6H), 0.63 – 0.54 (m, 2H).
^{13}C NMR (101 MHz, C_6D_6) δ 158.2, 139.8, 129.4, 122.4, 112.2, 87.2, 69.3, 53.9, 30.8, 29.4, 25.8, 23.9, 21.9, 11.9.
HRMS (ESI) *m/z* ([M+H]$^+$) Calcd for $C_{20}H_{33}{}^{74}GeINO$: 504.0819; Found: 504.0824.





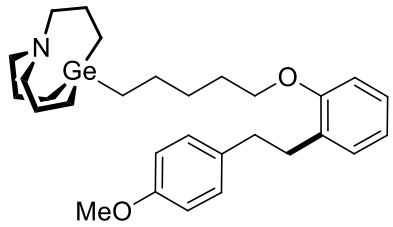
3,4,5,6-tetrahydro-2H-benzo[*b*]oxocine (**4a**). To an oven-dried screw-cap tube equipped with stir bar was added 0.1 mmol (50.2 mg) **3av**, 0.004 mmol (2.3 mg) $Pd(dba)_2$ and 0.012 mmol (8.3 mg) Me-Xuphos or (9.3 mg) ^{i}Pr-Xuphos. The tube was vacuumed and backfilled with argon for three cycles. 10 mL CH_3CN was added through syringe and the tube was sealed with a teflon stopper and stirred at 100 °C for 24 hours. When the reaction was finished, solvent was removed under reduced pressure. 70% ^{1}H NMR yield was determined using mesitylene as internal standard for ^{i}Pr-Xuphos. For Me-Xuphos 82% ^{1}H NMR yield was determined using mesitylene as internal standard. Resulting crude was purified by silica gel column chromatography using petroleum ether as eluent to give **4a** in 61% yield as colorless liquid, 10 mg. Isolated yield lost due to the low volatility.

^{1}H NMR (400 MHz, CDCl3) δ 7.21 – 7.15 (m, 1H), 7.14 – 7.11 (m, 1H), 7.07 – 7.01 (m, 2H), 4.09 (t, *J* = 5.5 Hz, 2H), 2.79 – 2.73 (m, 2H), 1.73 – 1.57 (m, 4H), 1.52 – 1.45 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.8, 137.6, 129.9, 127.7, 124.5, 121.7, 76.6, 31.7, 30.6, 27.9, 26.9.

HRMS (ESI) *m/z* ($[M+H]^+$) Calcd for $C_{11}H_{15}O$: 163.1123; Found: 163.0397.

GC-MS (EI) *m/z* (M^+) Calcd for $C_{11}H_{14}O$: 162.10; Found: 162.17.



5-(5-(2-(4-methoxyphenethyl)phenoxy)pentyl)-1-aza-5-germabicyclo[3.3.3]undecane (3aw) To an oven-dried screw-cap tube equipped with stir bar was charged with 0.1 mmol (50.2 mg) **3av**, 0.002 mmol (1.8 mg) $Pd_2(dba)_3$, 0.004 mmol (1.9 mg) Ruphos and 0.3 mmol (28.8 mg) NaO^tBu. The tube was vacuumed and backfilled with argon for three cycles. 0.15 mmol (39.2 mg) 2-(4-methoxyphenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and 1.0 mL toluene/H_2O = 1/1 was added through syringe and the tube was sealed with a teflon stopper and stirred at 80 ^oC for 24 hours. When the reaction was finished, the mixture was extracted with ethyl acetate/brine, organic phase was collected, dried over Na_2SO_4, concentrated under reduced pressure to give crude product, which was purified by silica gel column chromatography using petroleum ether/ethyl acetate = 80/1 as eluent to give **3aw** in 90% yield as colorless thick oil, 46 mg.

^{1}H NMR (400 MHz, C_6D_6) δ 7.14 – 7.08 (m, 3H), 7.08 – 7.04 (m, 1H), 6.88 – 6.83 (m, 1H), 6.82 – 6.77 (m, 2H), 6.70 – 6.67 (m, 1H), 3.73 (t, *J* = 6.4 Hz, 2H), 3.33 (s, 3H), 3.11 – 3.04 (m, 2H), 3.02 – 2.93 (m, 2H), 2.18 (t, *J* = 5.8 Hz, 6H), 1.80 – 1.70 (m, 2H), 1.57 – 1.38 (m, 10H), 0.68 (t, *J* = 6.5 Hz, 6H), 0.59 – 0.53 (m, 2H).

^{13}C NMR (101 MHz, C_6D_6) δ 158.5, 157.6, 134.9, 130.7, 130.4, 129.8, 127.5, 120.5, 114.2, 111.5, 68.0, 54.8, 53.8, 36.1, 33.9, 31.1, 29.7, 25.9, 23.9, 22.0, 11.9.

HRMS (ESI) *m/z* ([M+Na]$^+$) Calcd for $C_{29}H_{43}{}^{74}GeNNaO_2$: 534.2403; Found: 534.2403.

4. Reference

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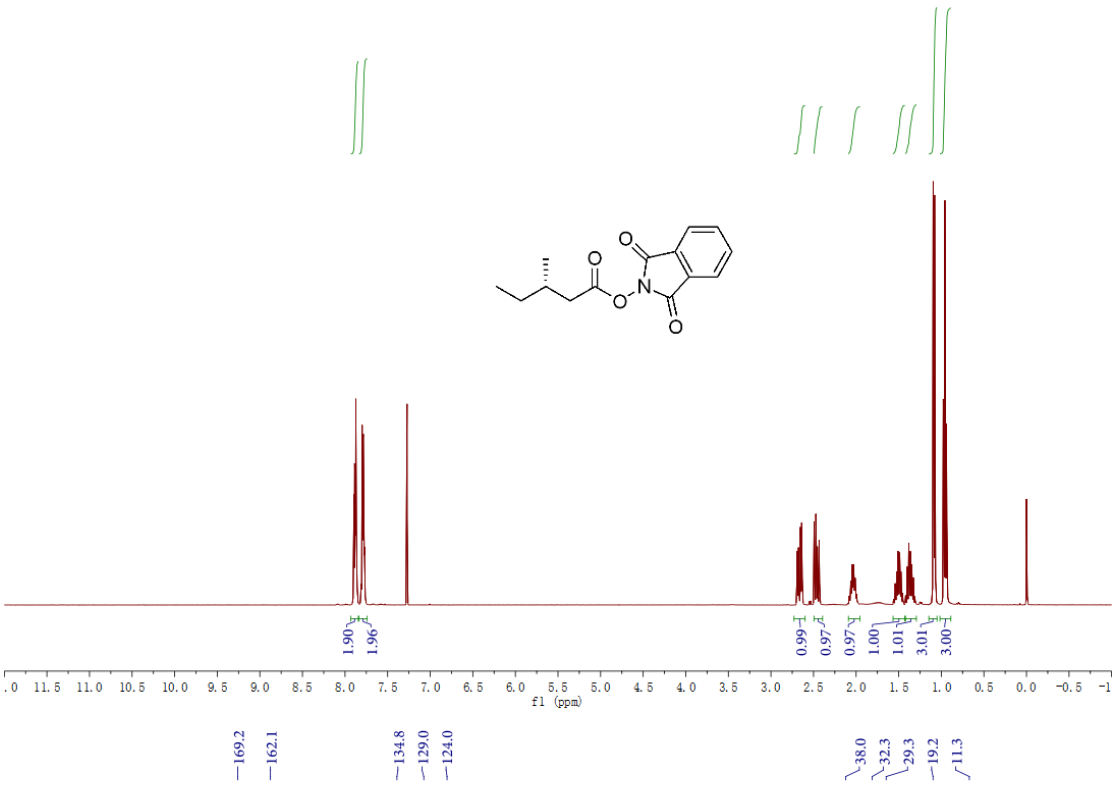
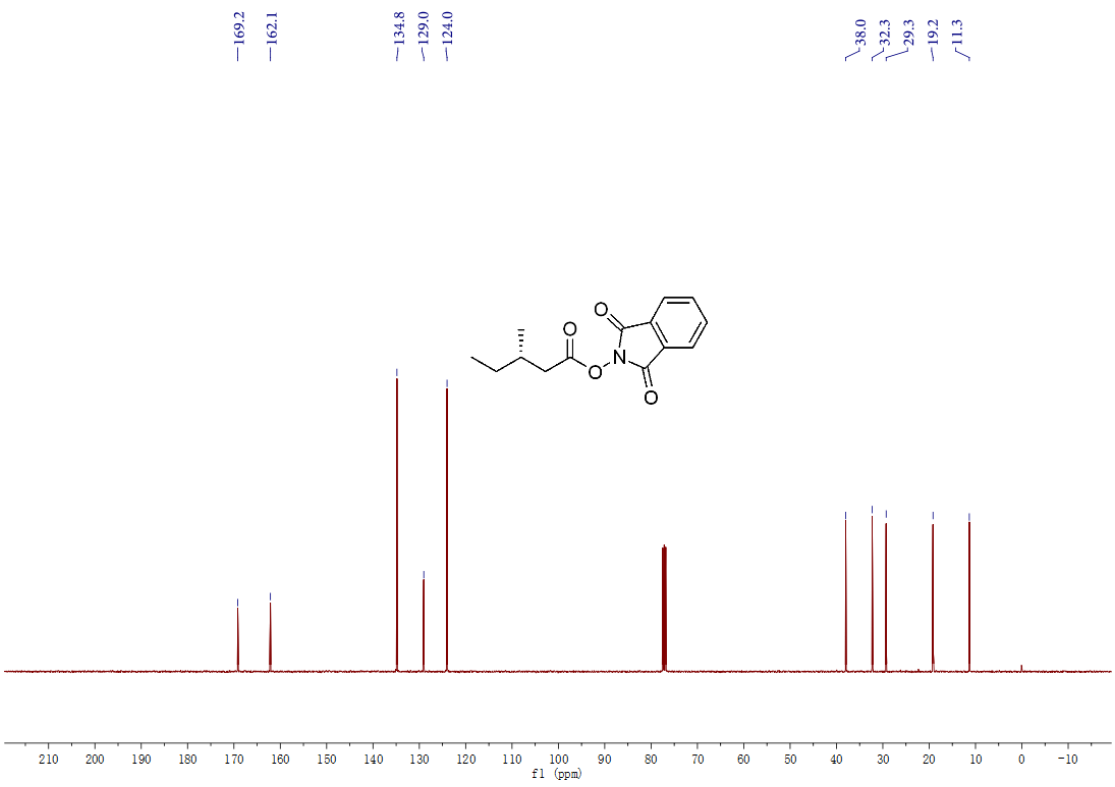
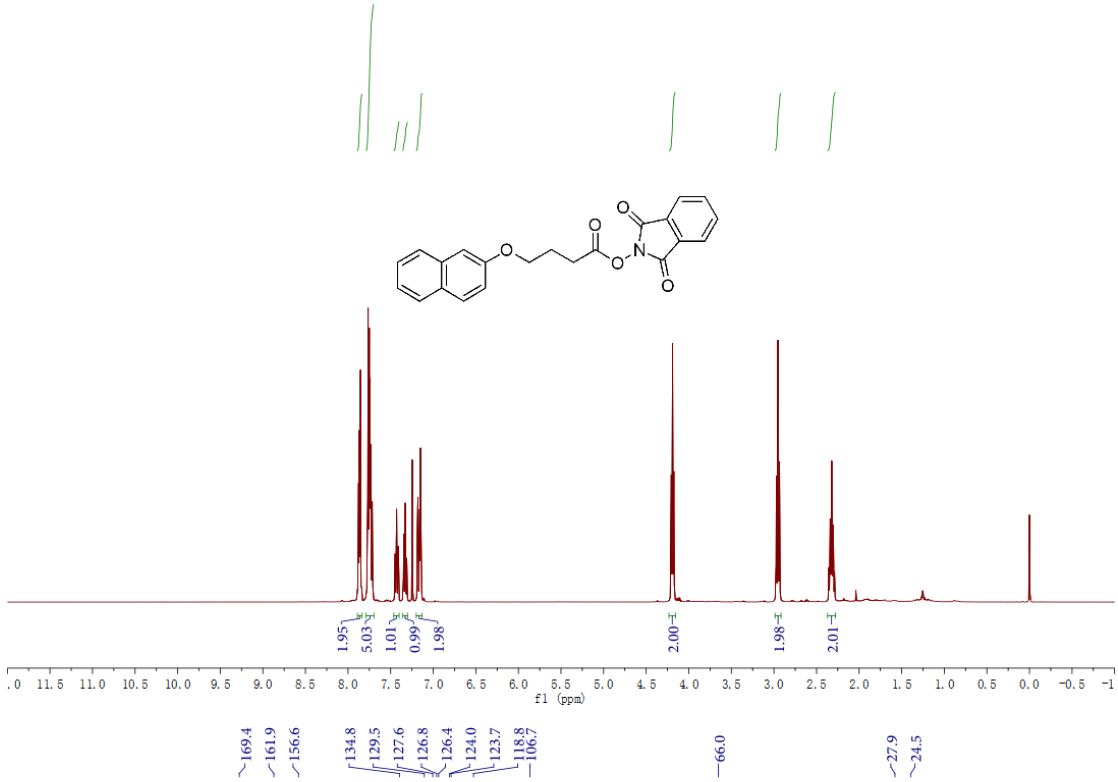
5. NMR spectra



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5.03
1.01
0.99
1.98
2.00
1.98
2.01
f1 (ppm)
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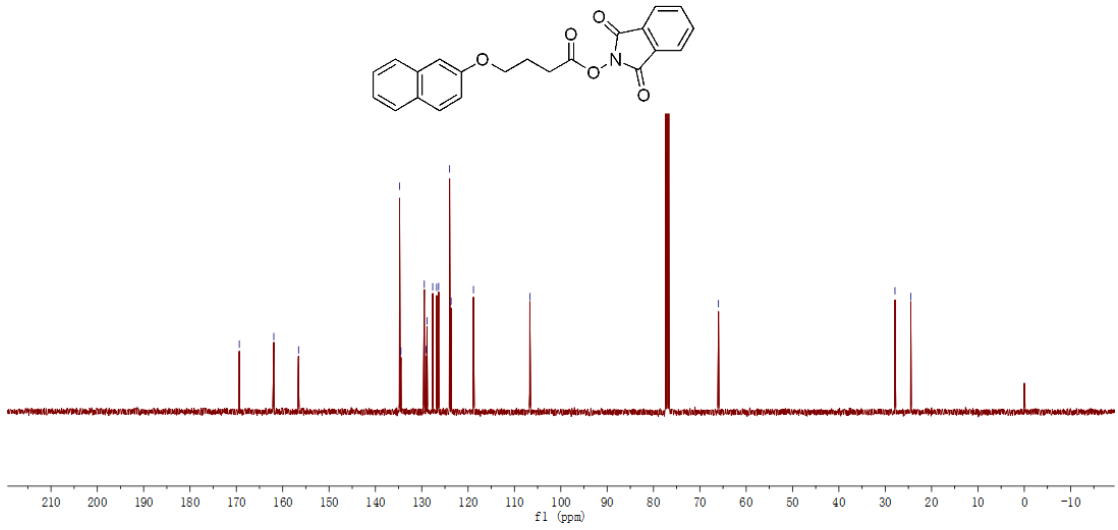
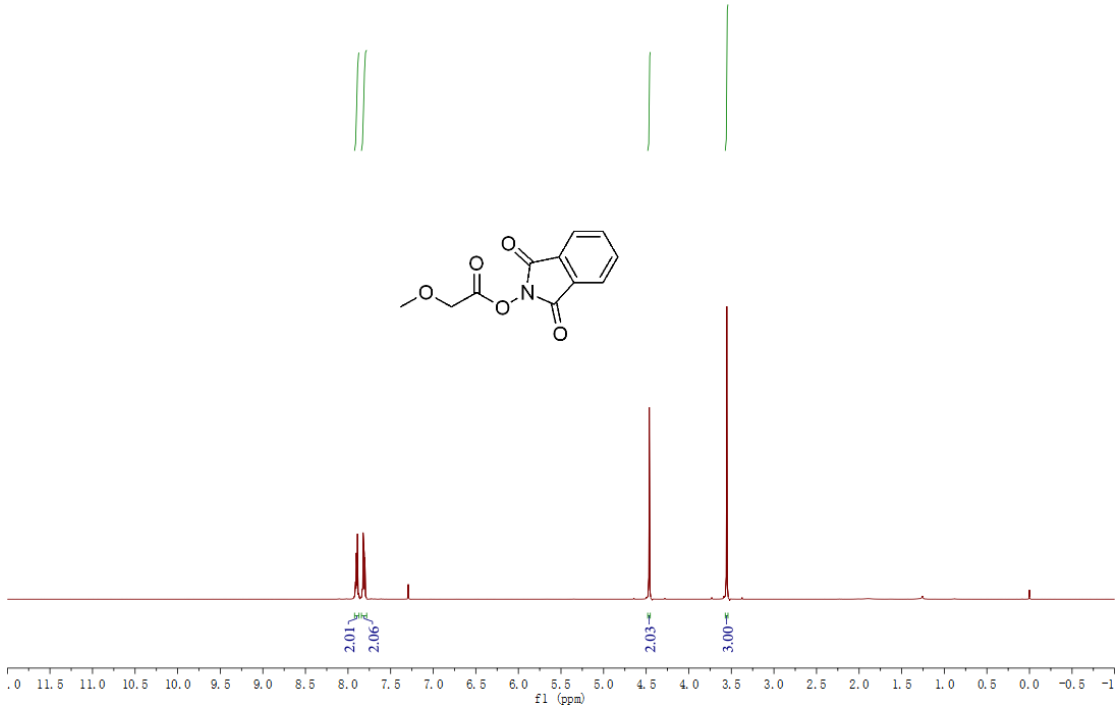
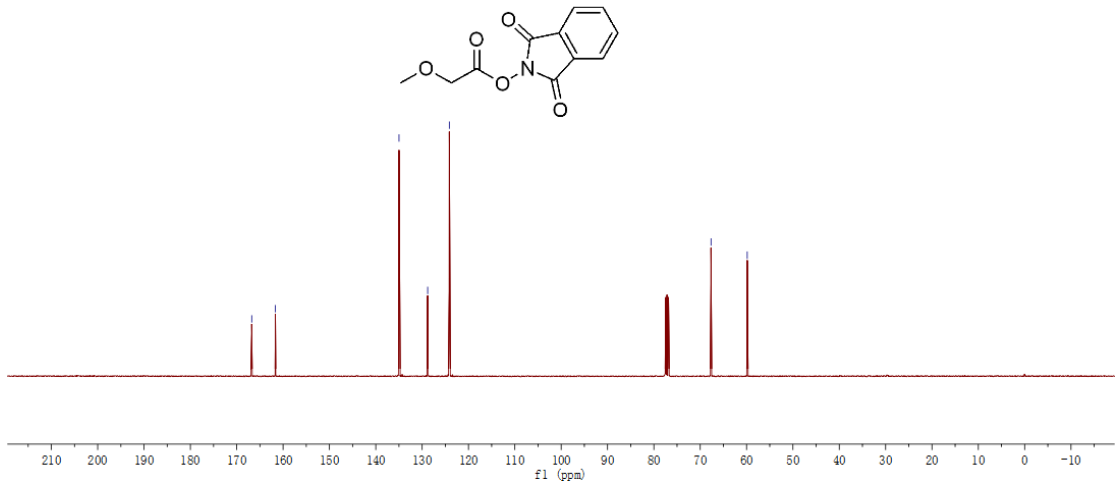
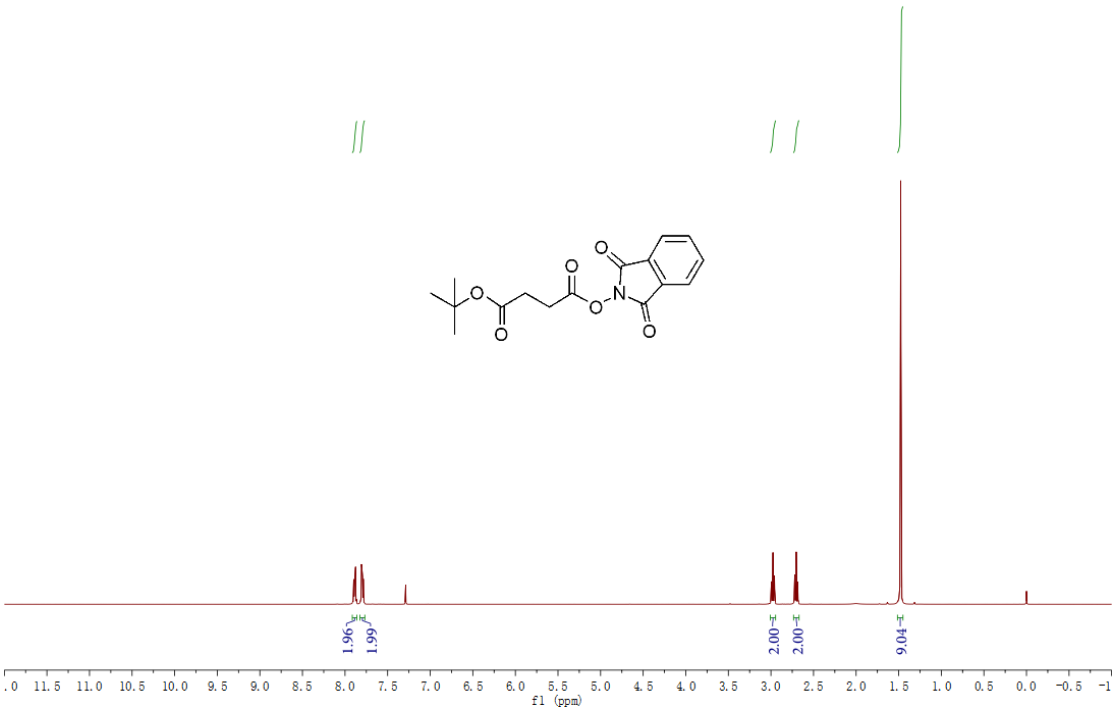
134.8
129.5
127.6
126.8
126.4
124.0
123.7
118.8
106.7
66.0
27.9
24.5

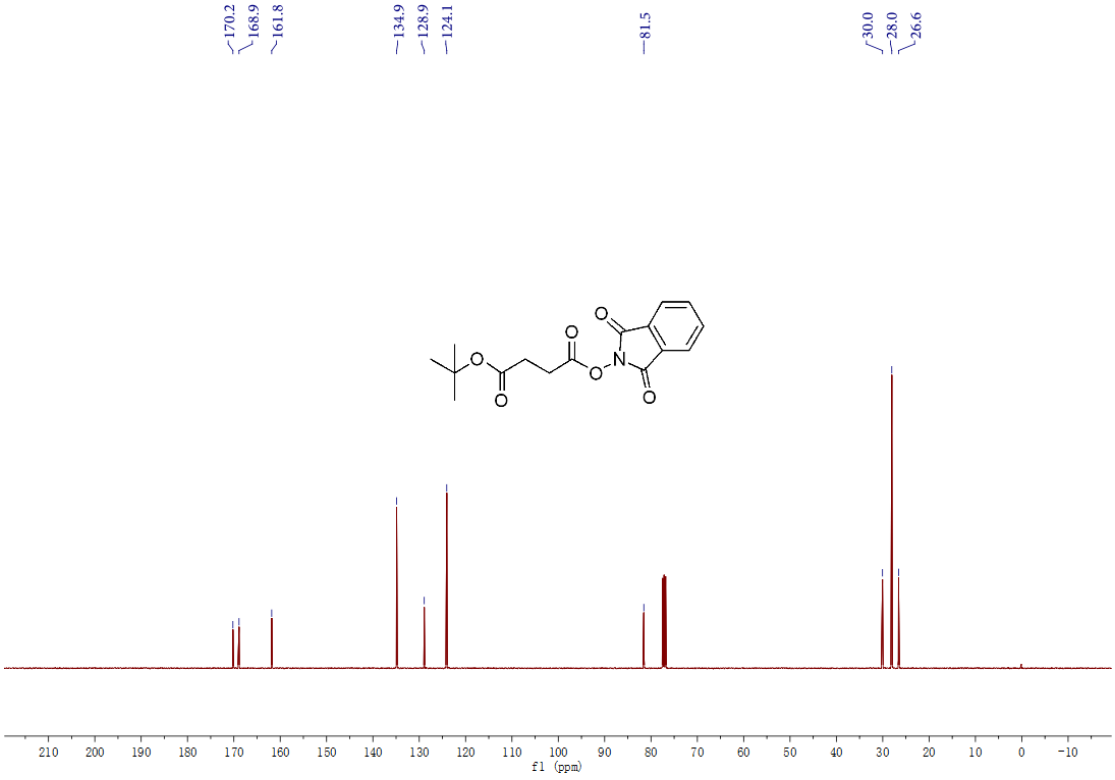

f1 (ppm)

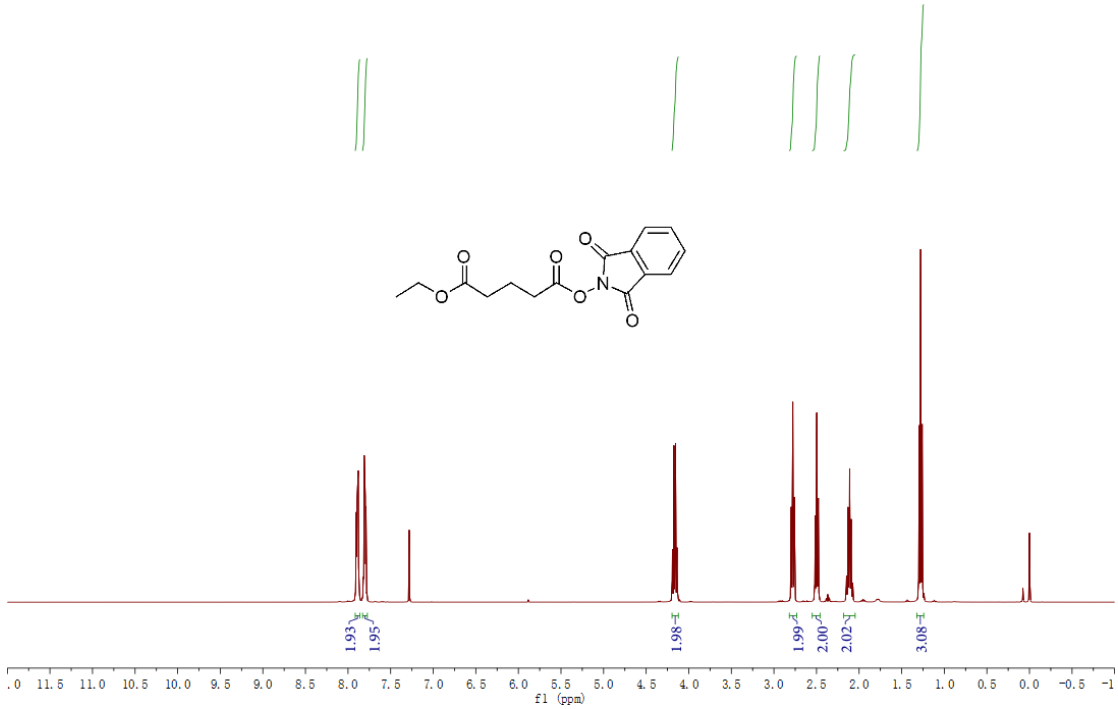

2.01
2.06
2.03
3.00
f1 (ppm)

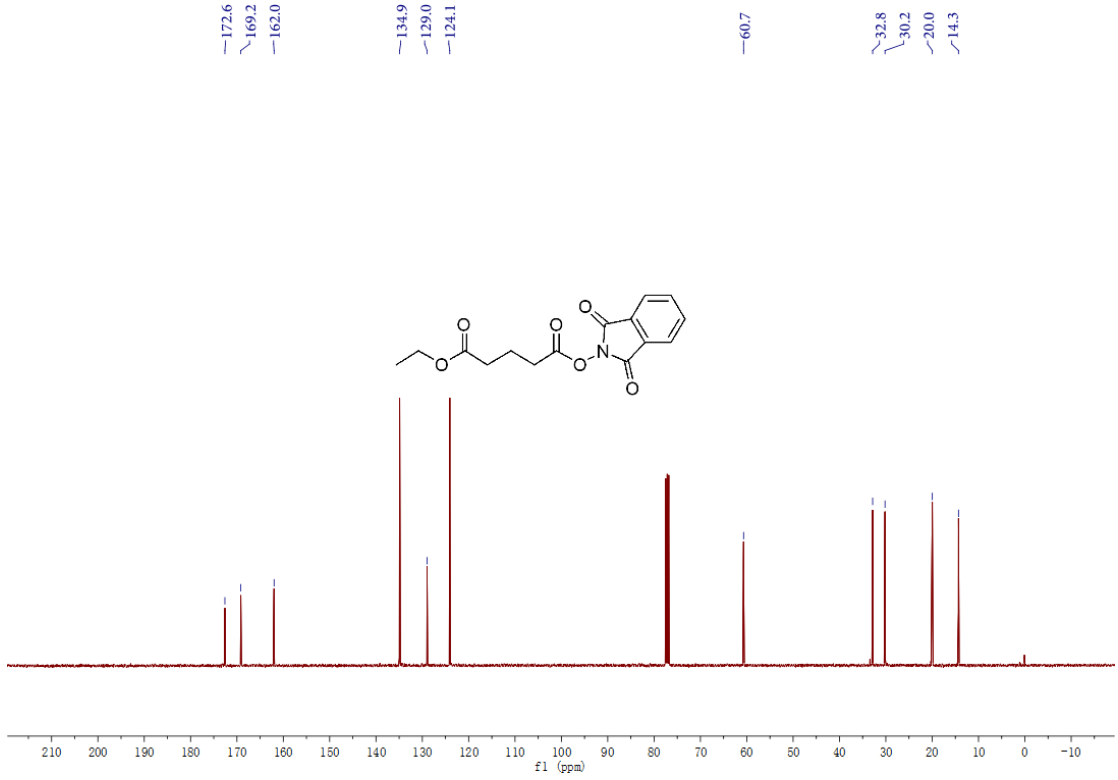

166.8
161.7
135.0
128.8
124.1
67.7
59.9

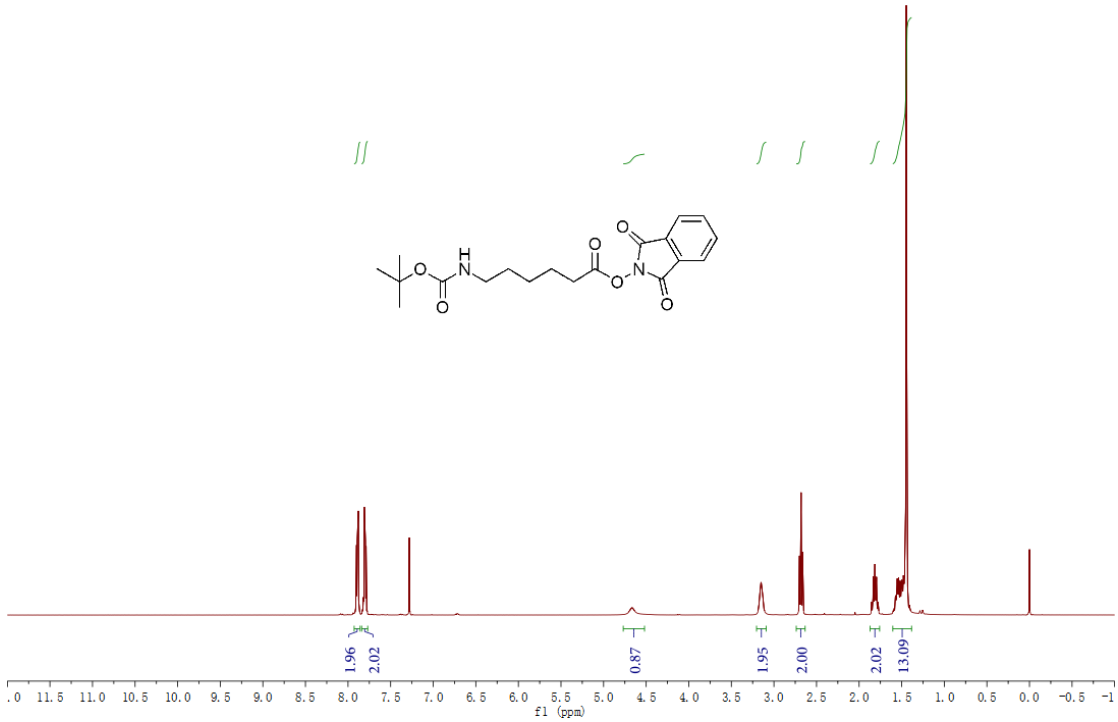

f1 (ppm)

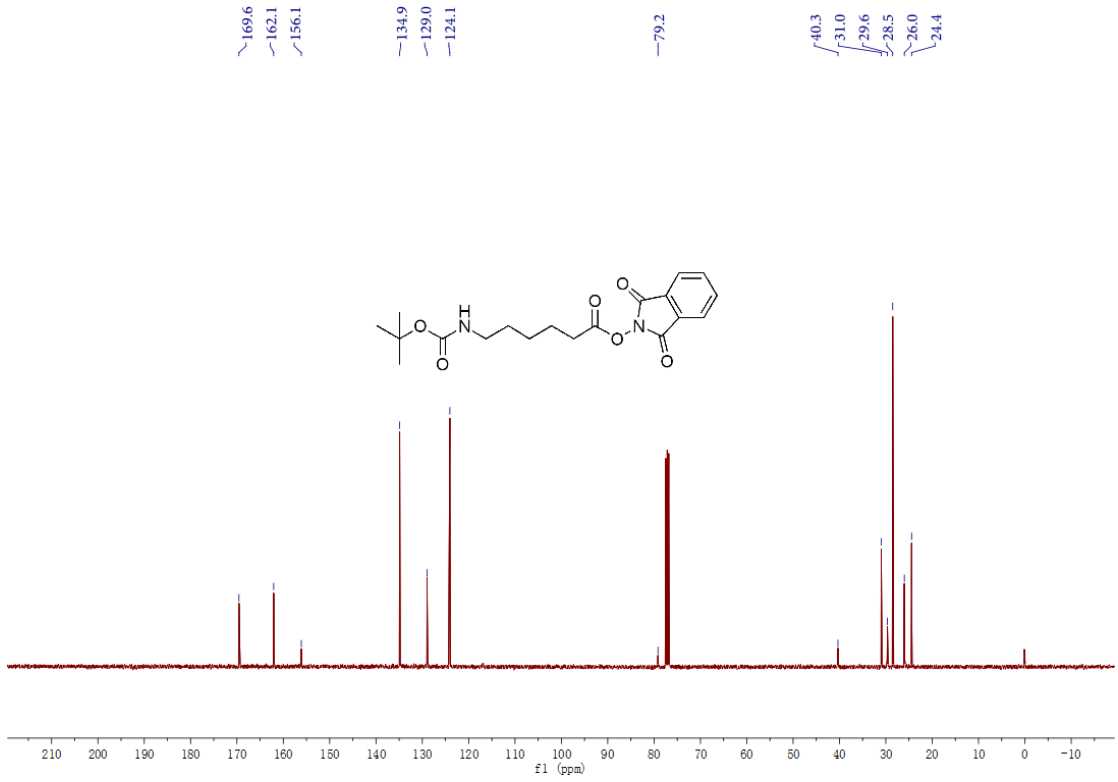

1.96
1.99
2.00
2.00
9.04
f1 (ppm)

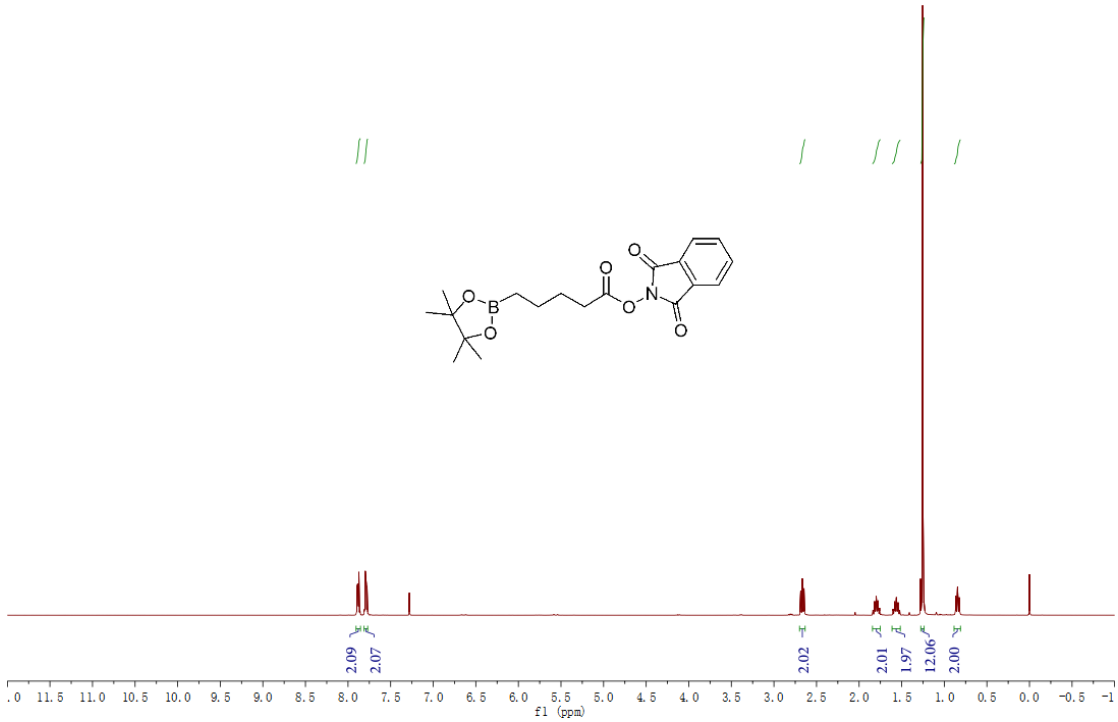

170.2
168.9
161.8
134.9
128.9
124.1
81.5
30.0
28.0
26.6
f1 (ppm)

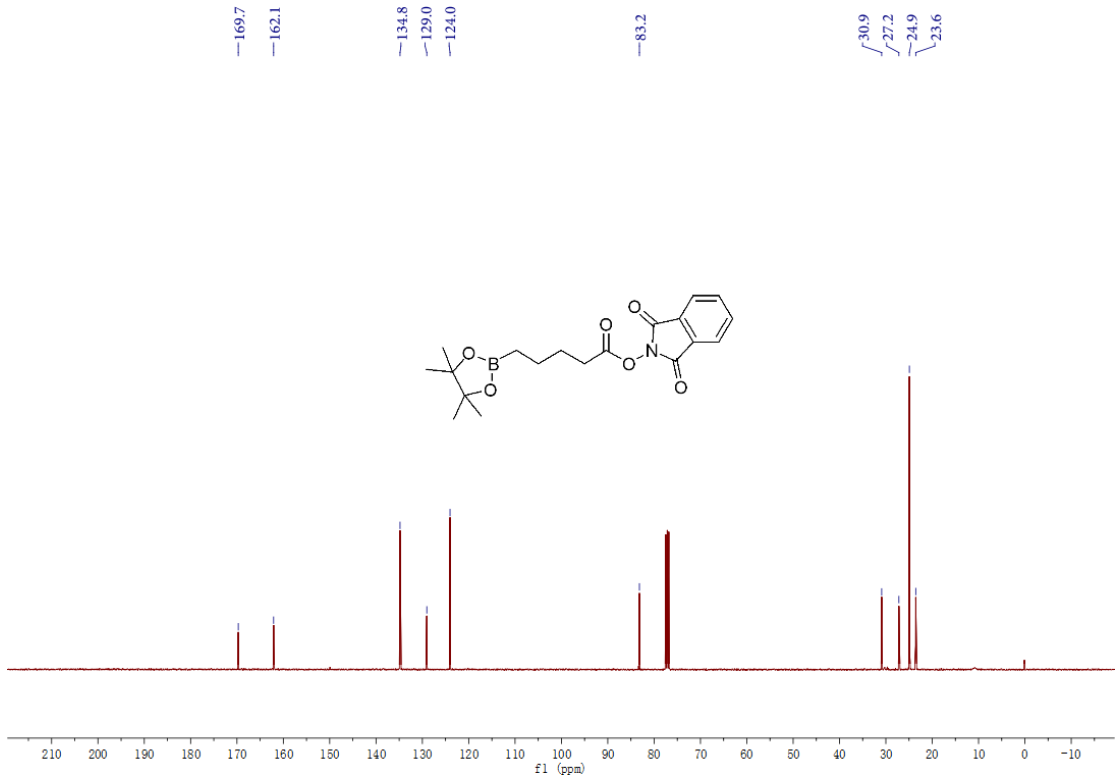

1.93
1.95
1.98
1.99
2.00
2.02
3.08
f1 (ppm)

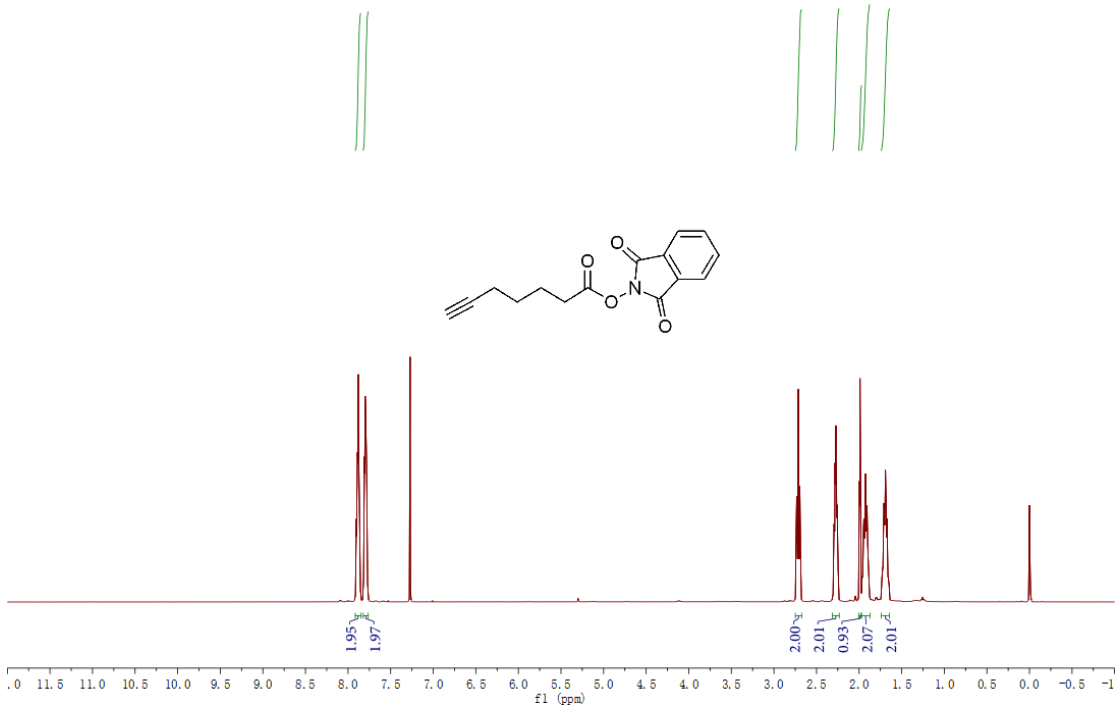

172.6
169.2
162.0
134.9
129.0
124.1
60.7
32.8
30.2
20.0
14.3
f1 (ppm)


1.96
2.02
0.87
1.95
2.00
2.02
13.09
f1 (ppm)

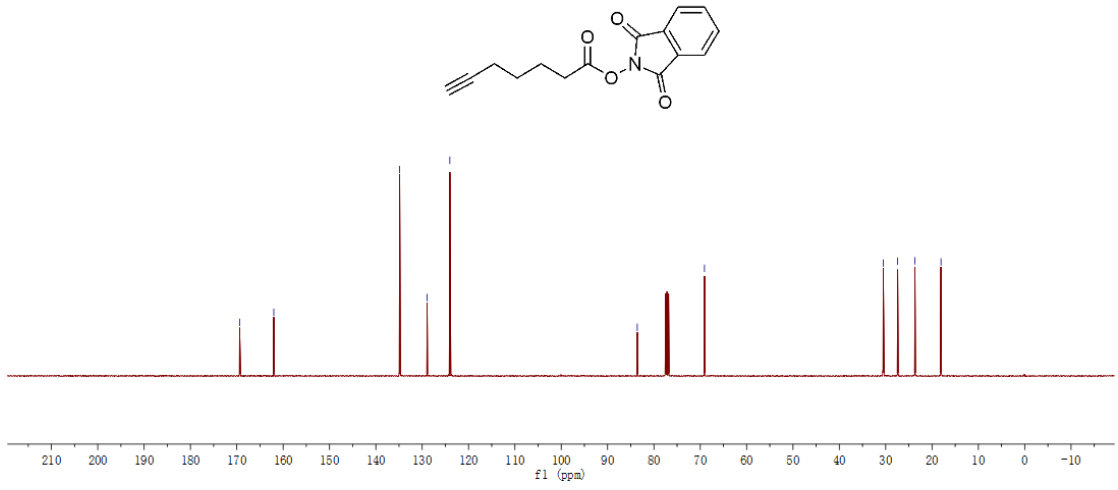

169.6
162.1
156.1
134.9
129.0
124.1
79.2
40.3
31.0
29.6
28.5
26.0
24.4
f1 (ppm)

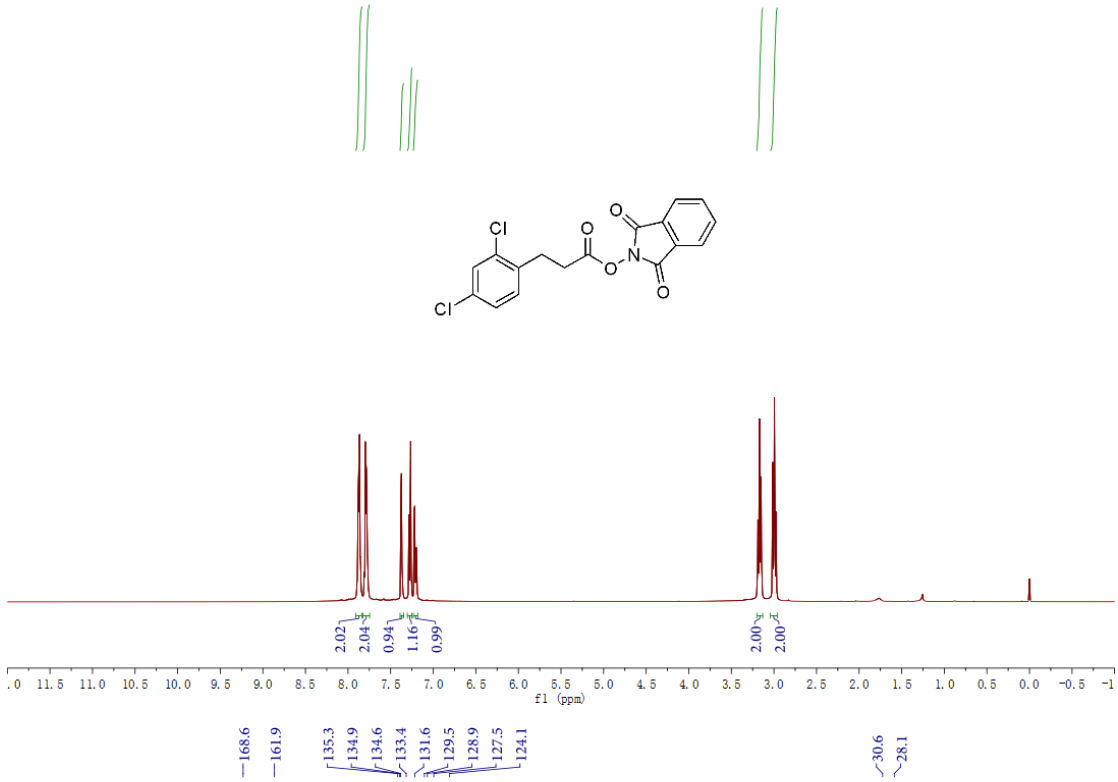

2.09
2.07
2.02
2.01
1.97
12.06
2.00
f1 (ppm)

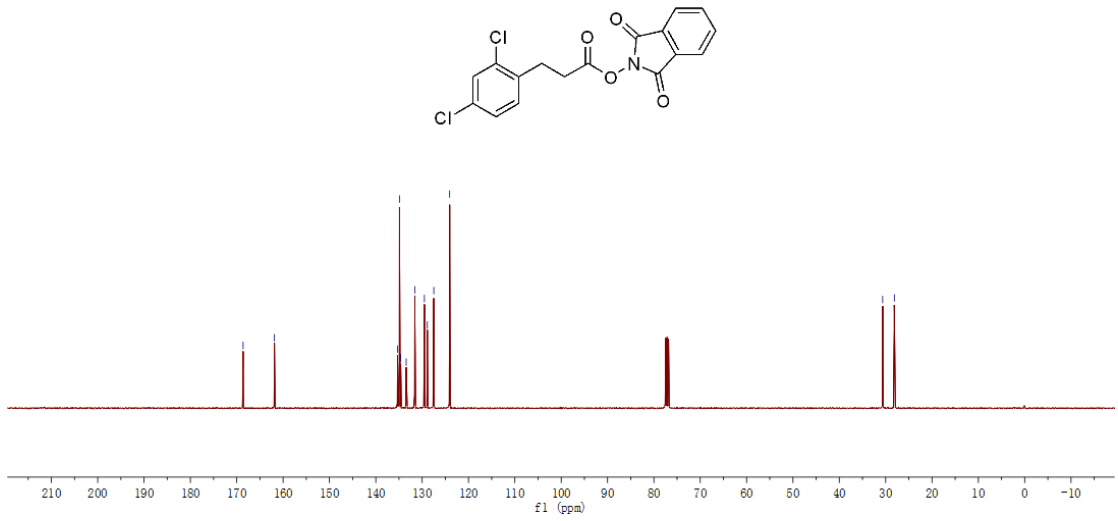

169.7
162.1
134.8
129.0
124.0
83.2
30.9
27.2
24.9
23.6
f1 (ppm)

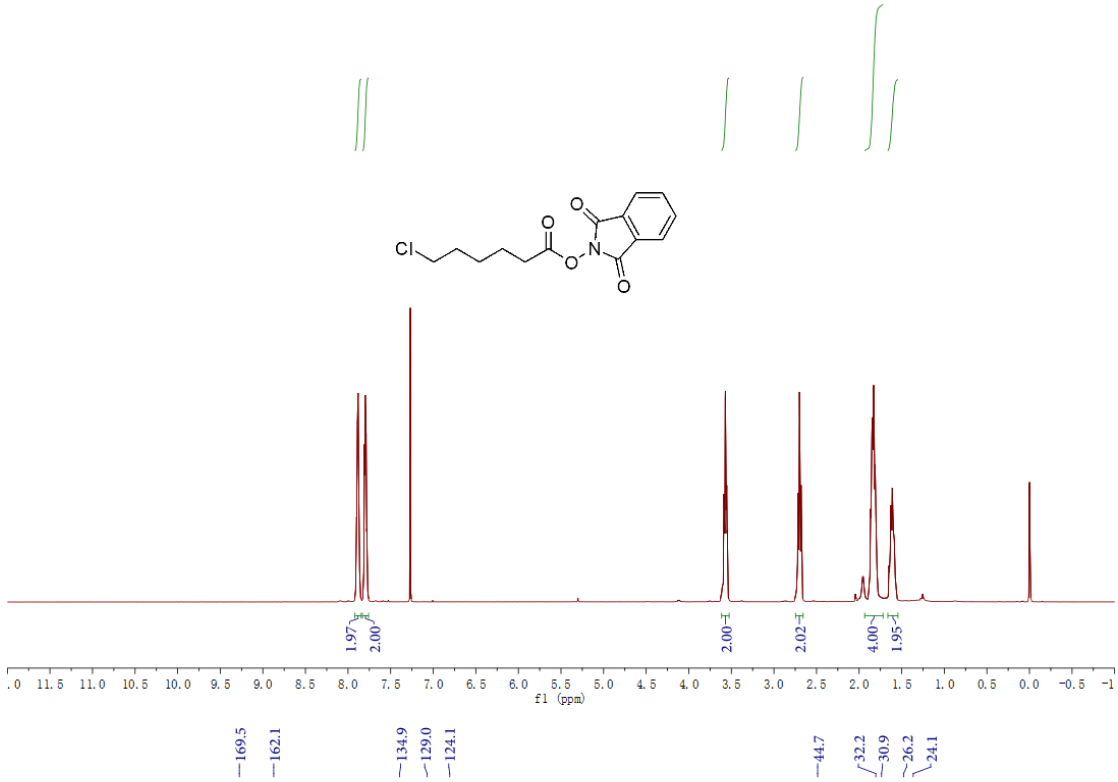

1.95
1.97
2.00
2.01
0.93
2.07
2.01
f1 (ppm)

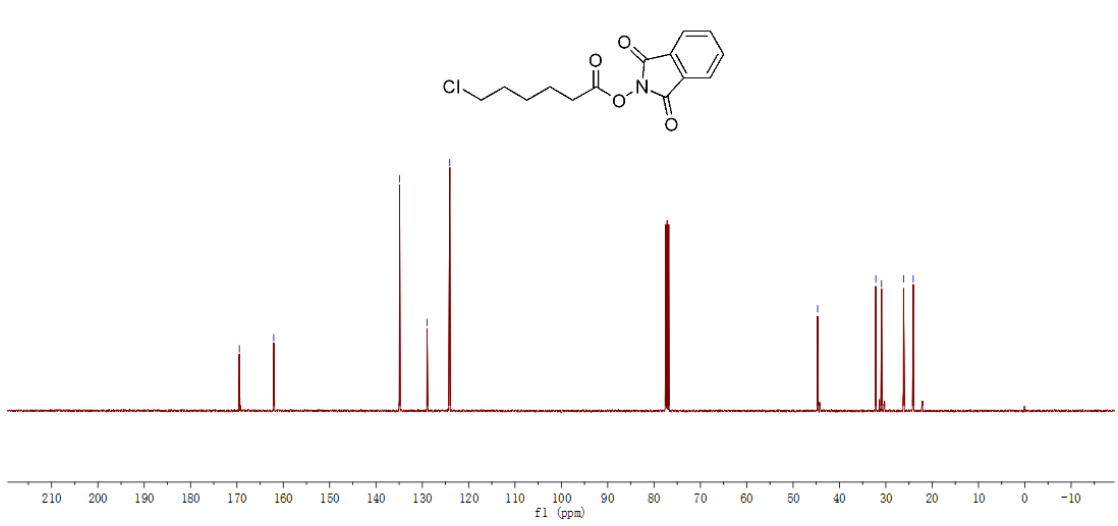

169.4
162.0
134.9
128.9
124.0
83.6
69.1
30.5
27.4
23.7
18.1

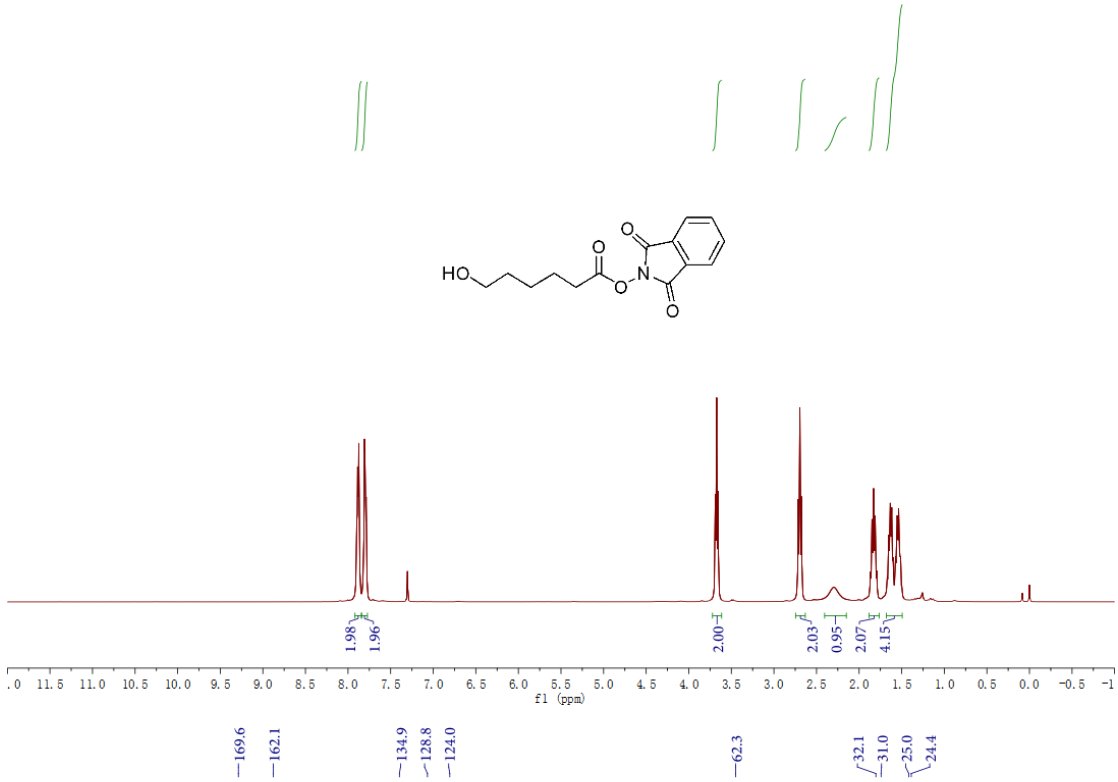

f1 (ppm)

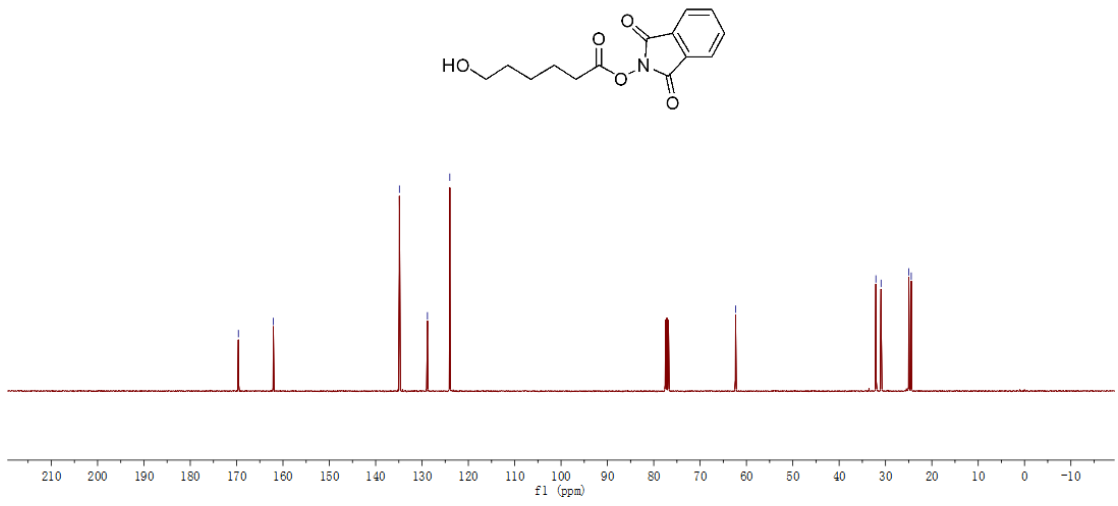

Cl
Cl
O
O
N
O
O
2.02
2.04
0.94
1.16
0.99
2.00
2.00
f1 (ppm)

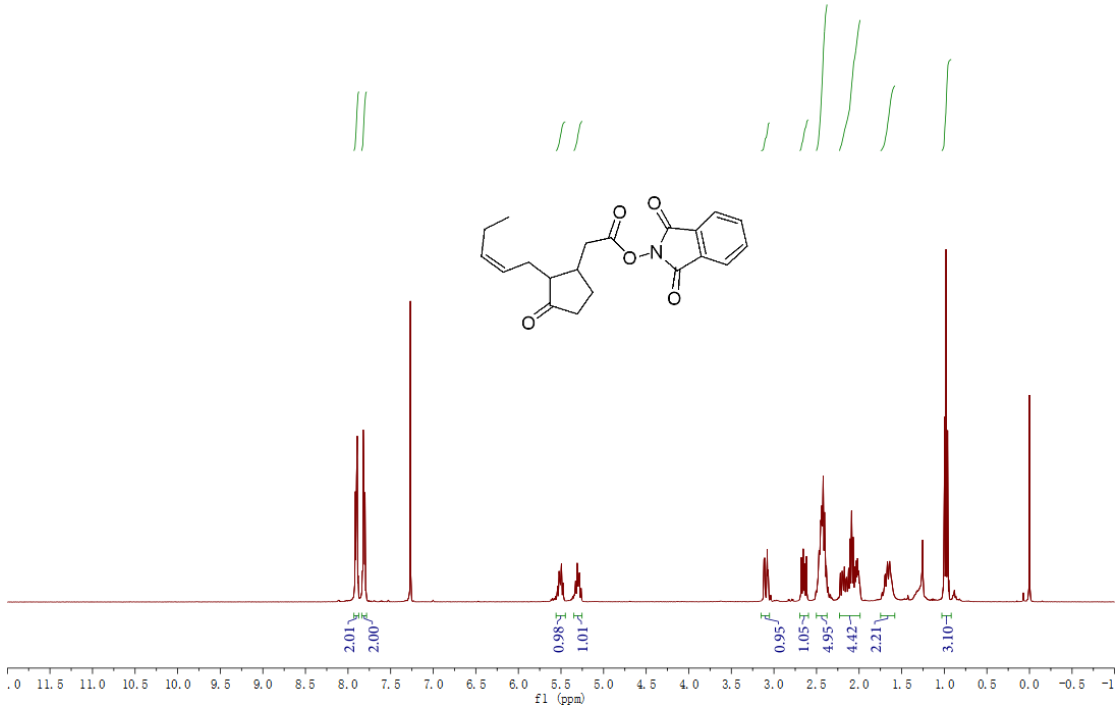

168.6
161.9
135.3
134.9
134.6
133.4
131.6
129.5
128.9
127.5
124.1
30.6
28.1
Cl
Cl
O
O
N
O
O
f1 (ppm)

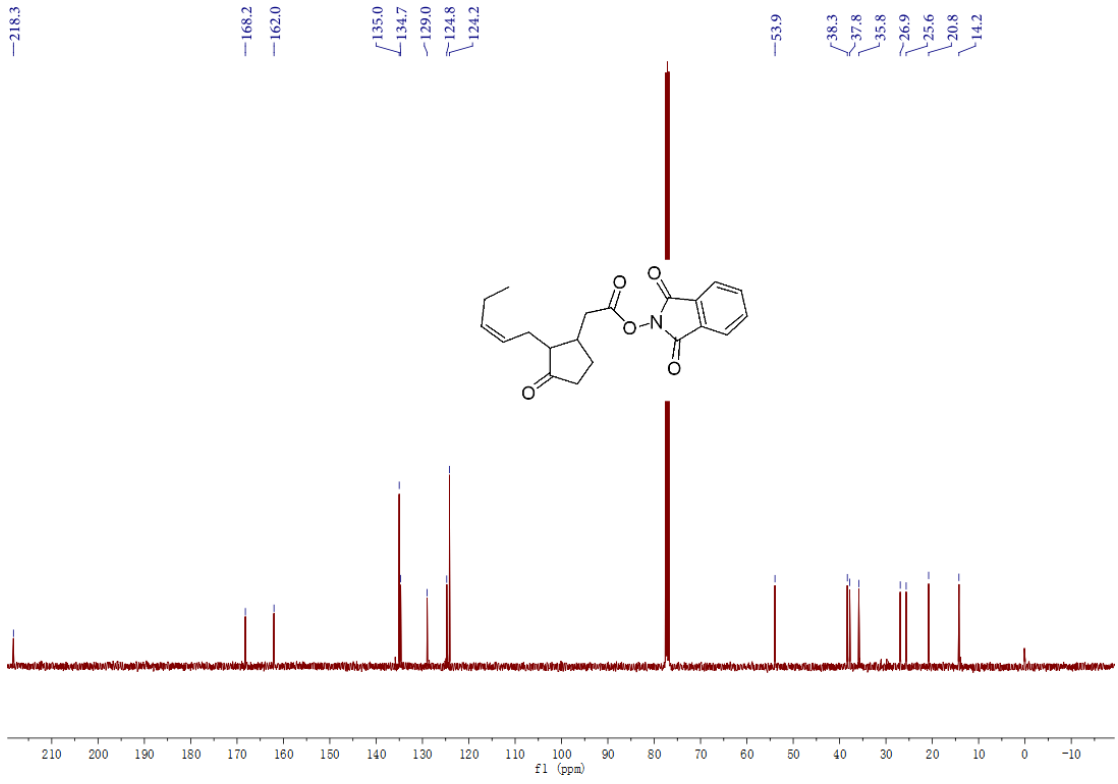

Cl
O
N
O
O
O
1.97
2.00
2.00
2.02
4.00
1.95
f1 (ppm)

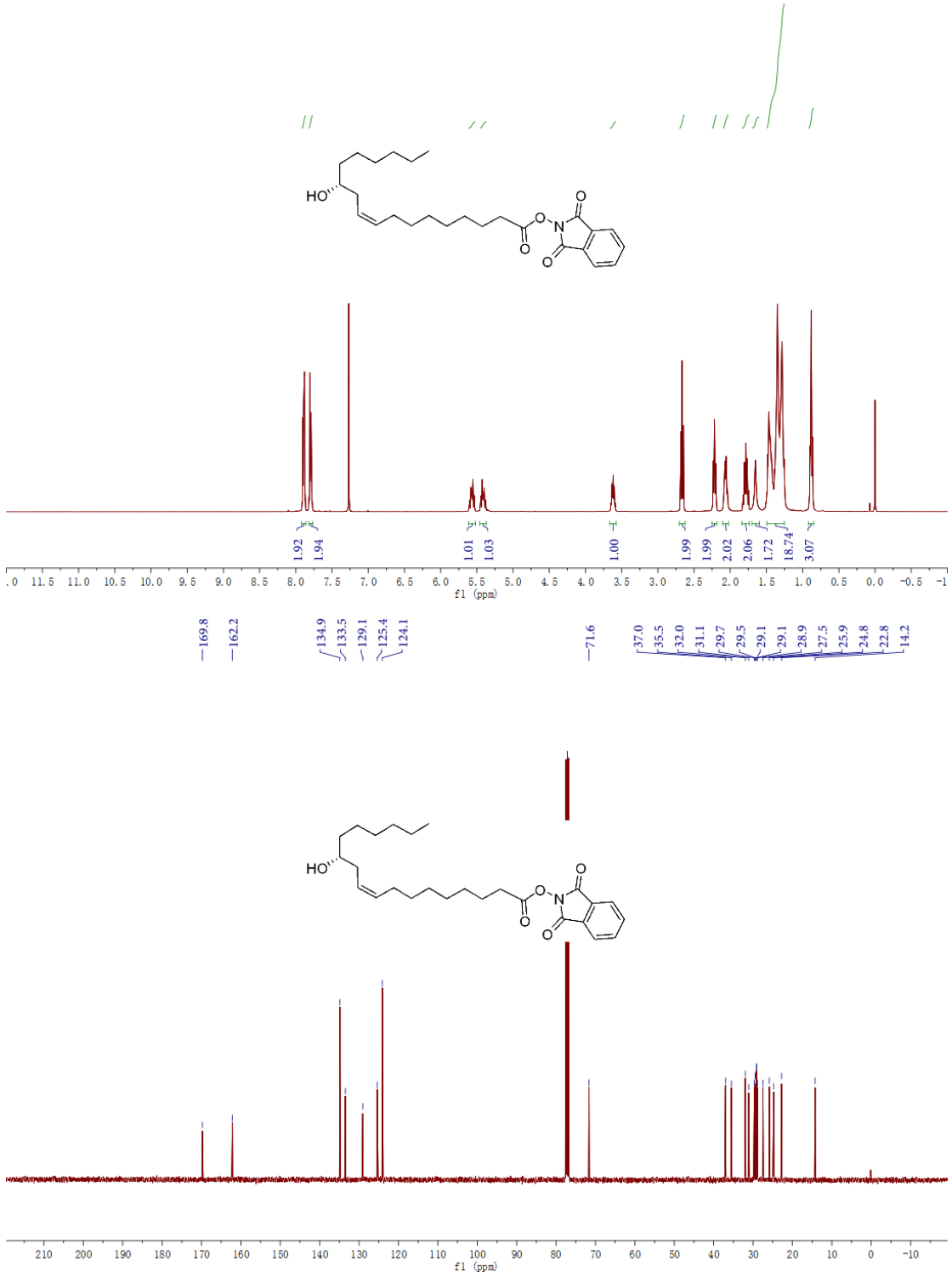

169.5
162.1
134.9
129.0
124.1
44.7
32.2
30.9
26.2
24.1
Cl
O
N
O
O
O
f1 (ppm)

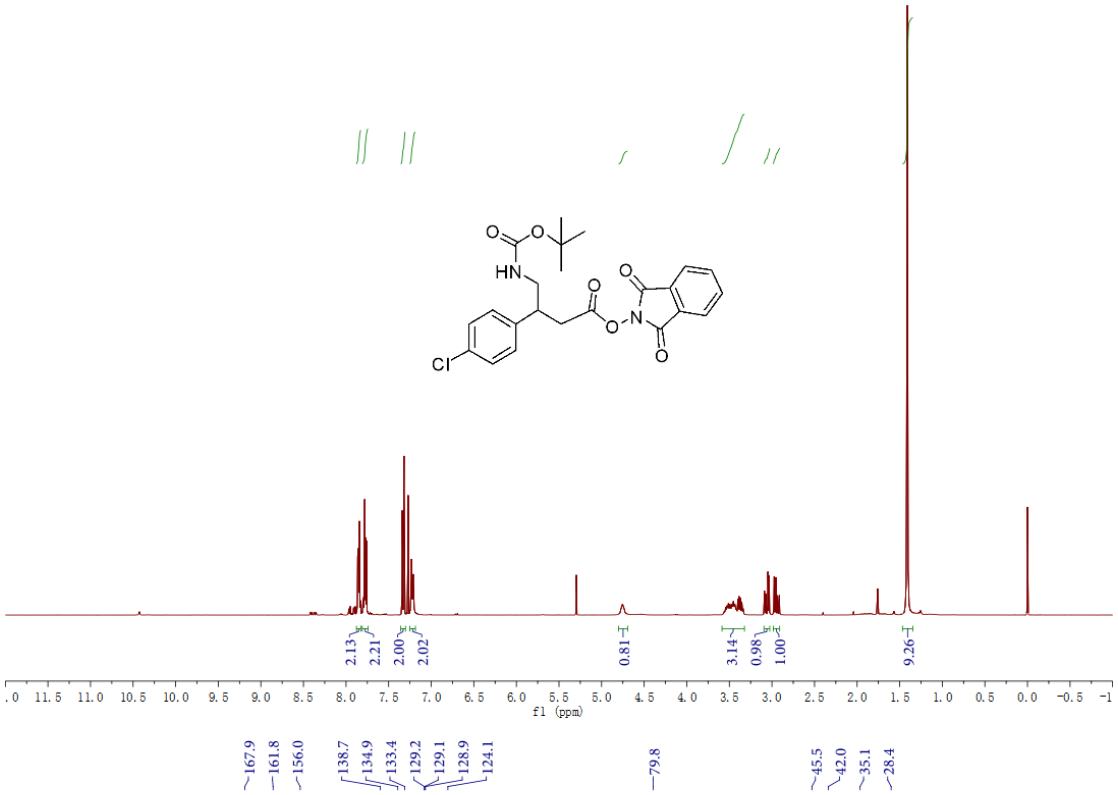

HO
O
O
N
O
O
1.98
1.96
2.00
2.03
0.95
2.07
4.15
f1 (ppm)


169.6
162.1
134.9
128.8
124.0
62.3
32.1
31.0
25.0
24.4
HO
O
O
N
O
O
f1 (ppm)

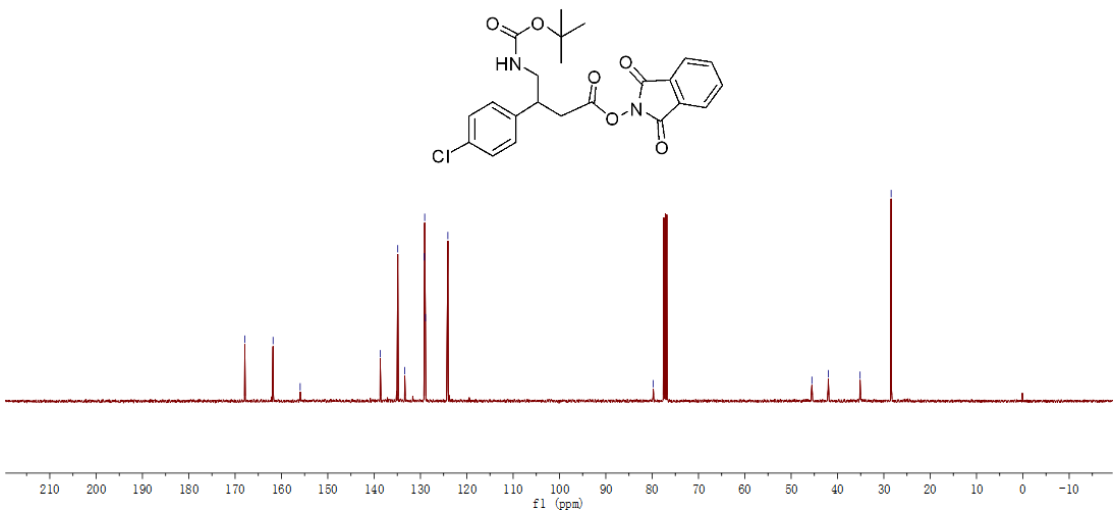

2.01
2.00
0.98
1.01
0.95
1.05
4.95
4.42
2.21
3.10
f1 (ppm)

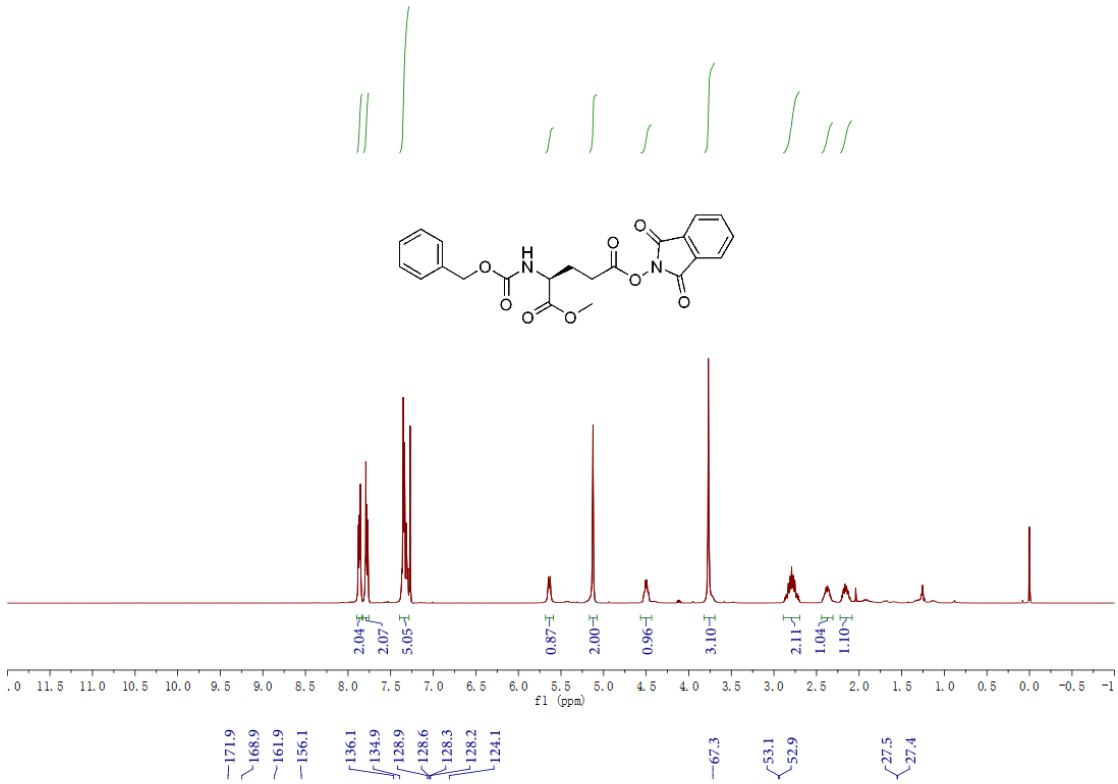

218.3
168.2
162.0
135.0
134.7
129.0
124.8
124.2
53.9
38.3
37.8
35.8
26.9
25.6
20.8
14.2
f1 (ppm)

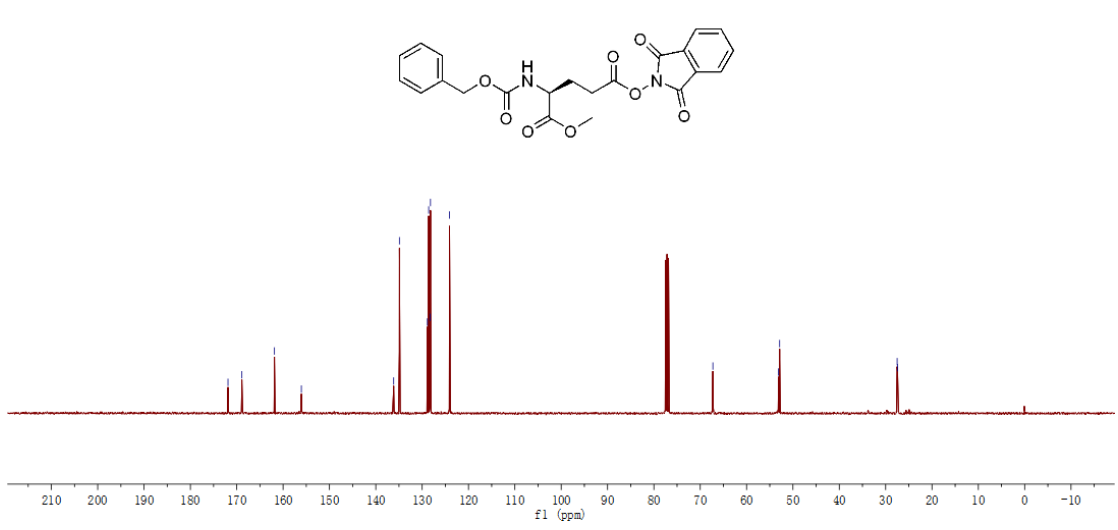

HO
O
O
N
O
O
1.92
1.94
1.01
1.03
1.00
1.99
1.99
2.02
2.06
1.72
18.74
3.07
f1 (ppm)
169.8
162.2
134.9
133.5
129.1
125.4
124.1
71.6
37.0
35.5
32.0
31.1
29.7
29.5
29.1
29.1
28.9
27.5
25.9
24.8
22.8
14.2
f1 (ppm)

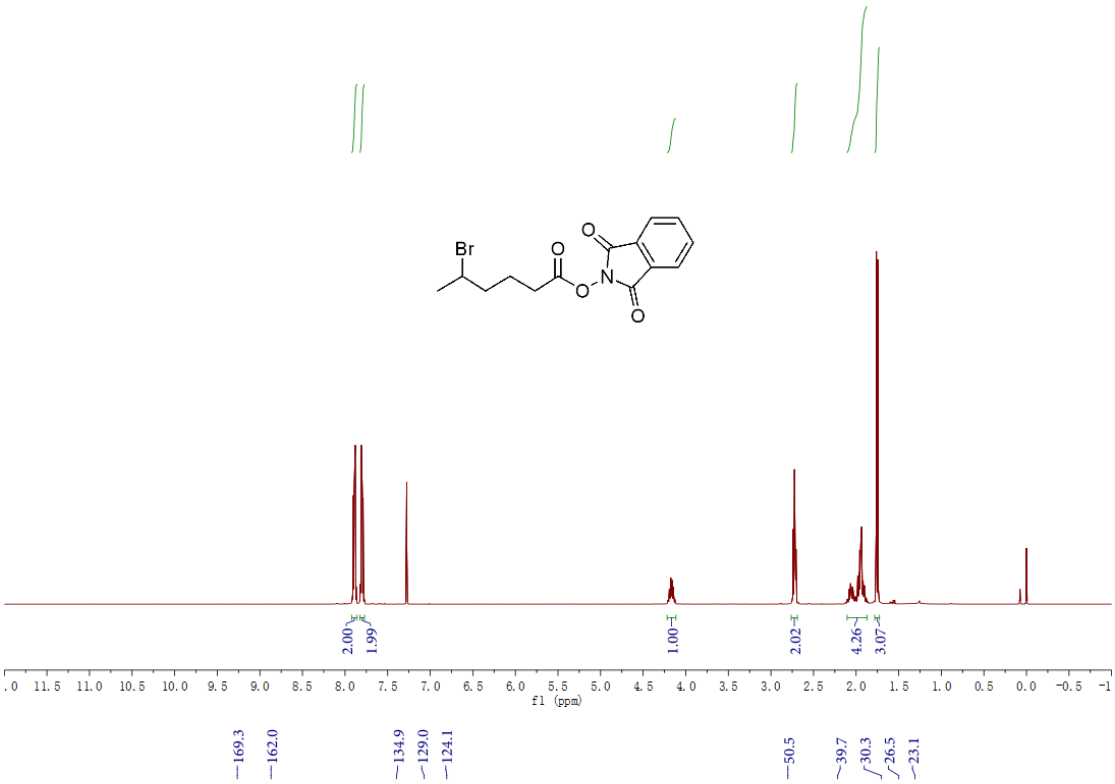

HN
O
O
O
O
O
N
O
Cl
2.13
2.21
2.00
2.02
0.81
3.14
0.98
1.00
9.26
f1 (ppm)

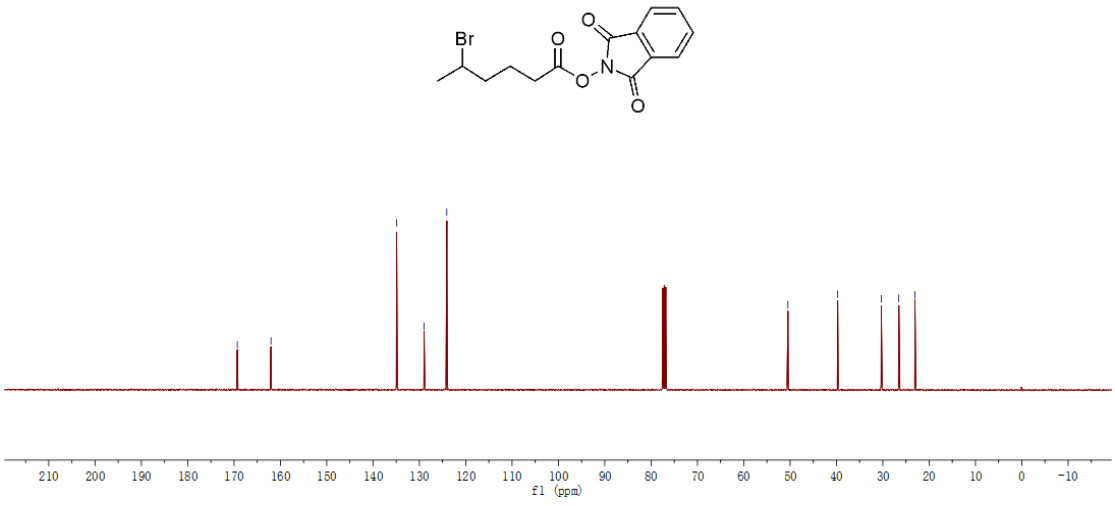
167.9
161.8
156.0
138.7
134.9
133.4
129.2
129.1
128.9
124.1
79.8
45.5
42.0
35.1
28.4

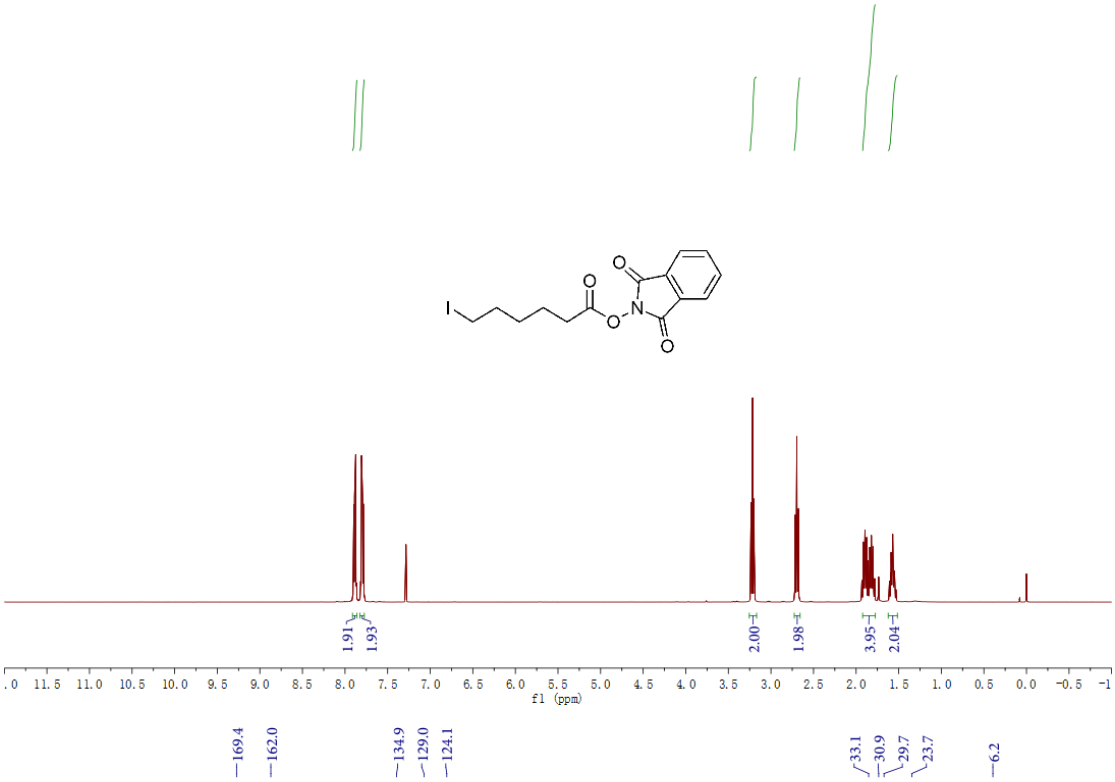

HN
O
O
O
O
O
N
O
Cl
f1 (ppm)

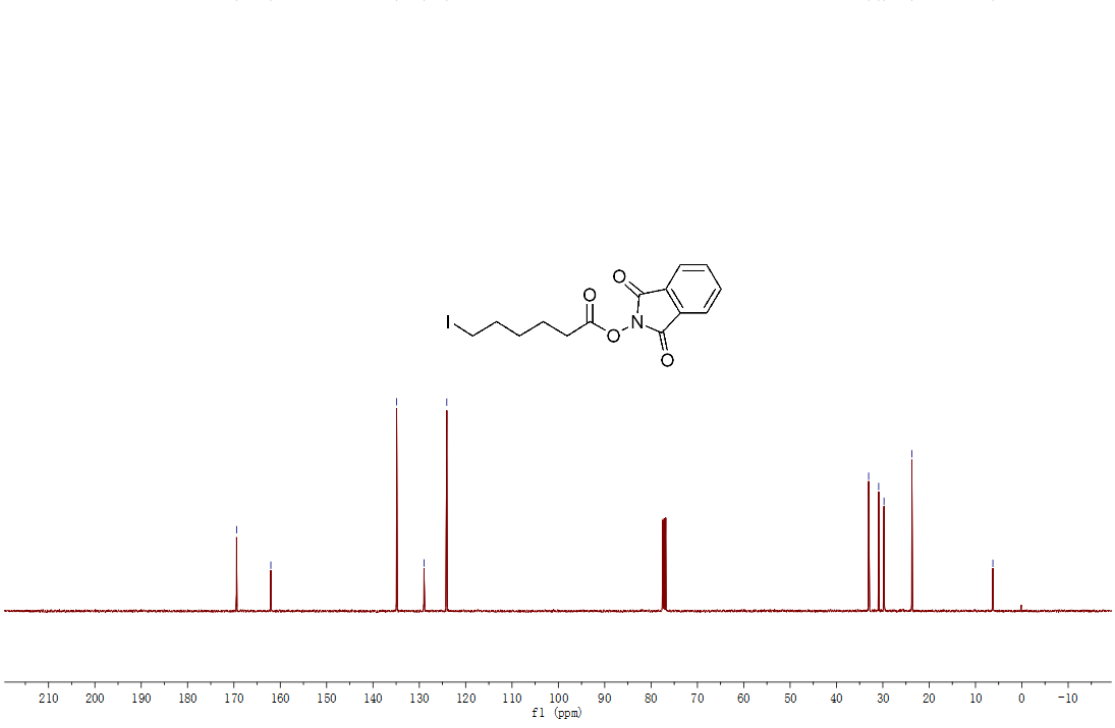

2.04
2.07
5.05
0.87
2.00
0.96
3.10
2.11
1.04
1.10
f1 (ppm)

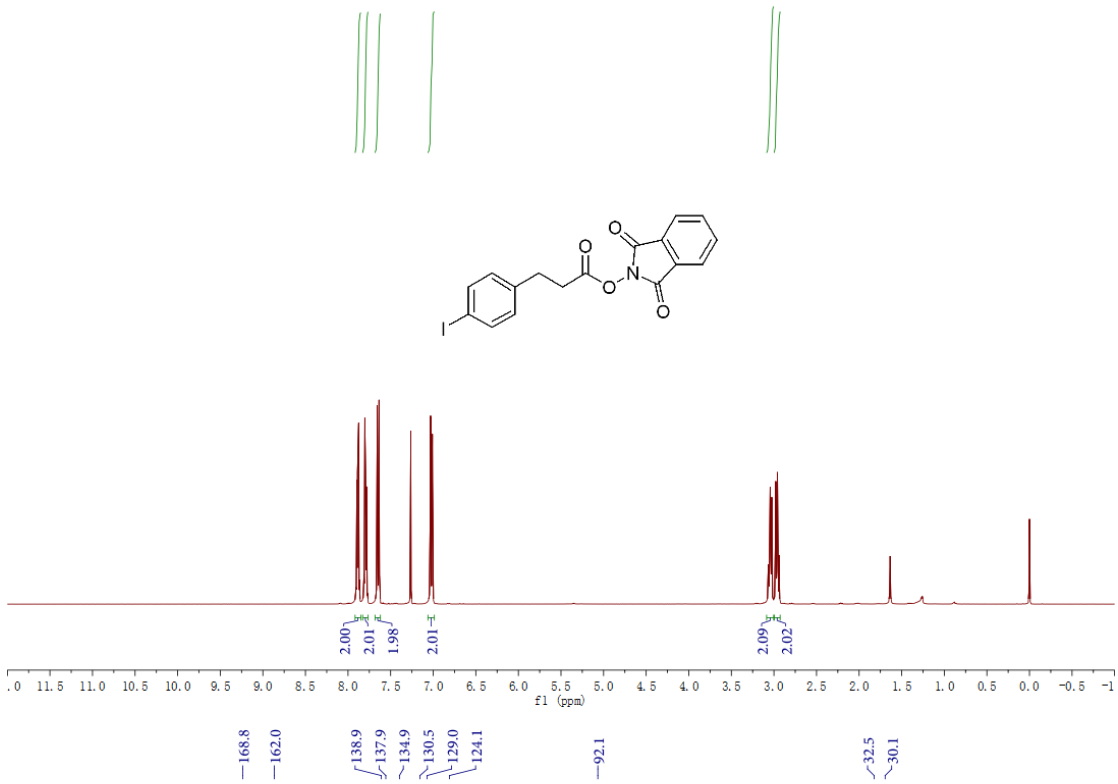

171.9
168.9
161.9
156.1
136.1
134.9
128.9
128.6
128.3
128.2
124.1
67.3
53.1
52.9
27.5
27.4
f1 (ppm)

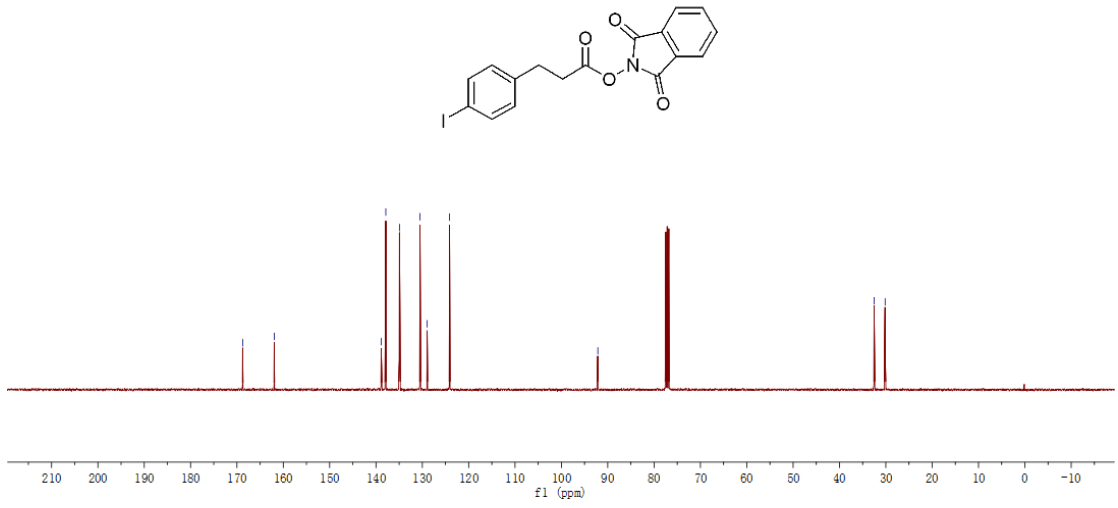

Br
O
O
N
O
O
2.00
1.99
1.00
2.02
4.26
3.07
f1 (ppm)

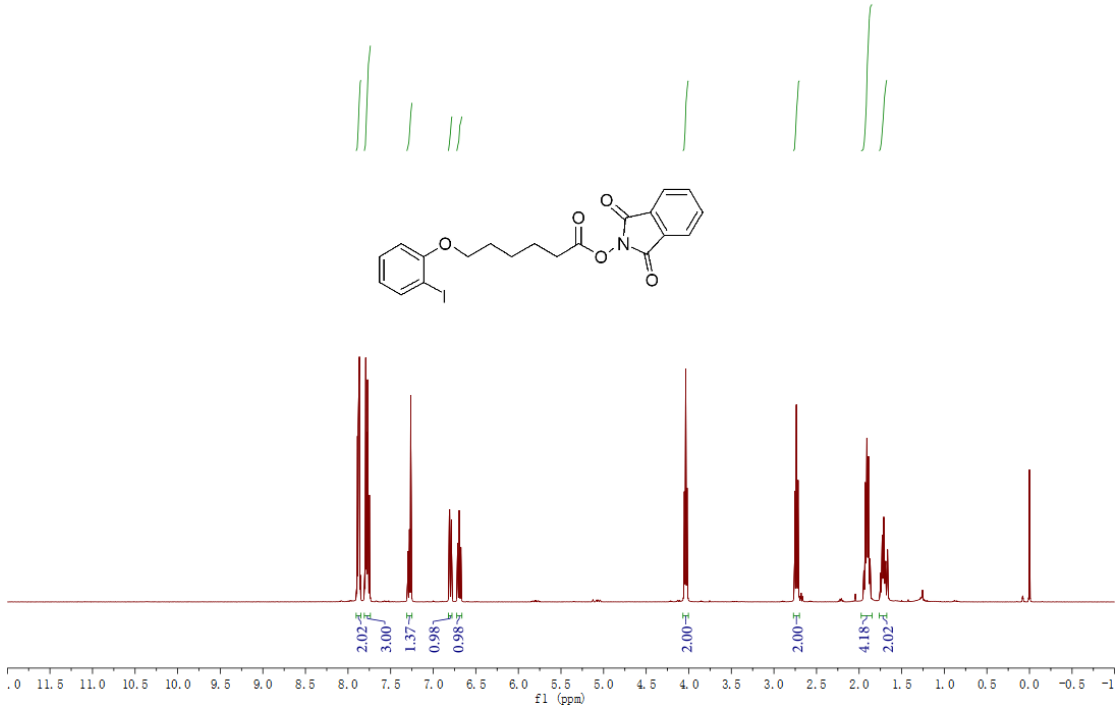

Br
O
O
N
O
O
169.3
162.0
134.9
129.0
124.1
50.5
39.7
30.3
26.5
23.1
f1 (ppm)


I
O
O
N
O
O
1.91
1.93
2.00
1.98
3.95
2.04
f1 (ppm)

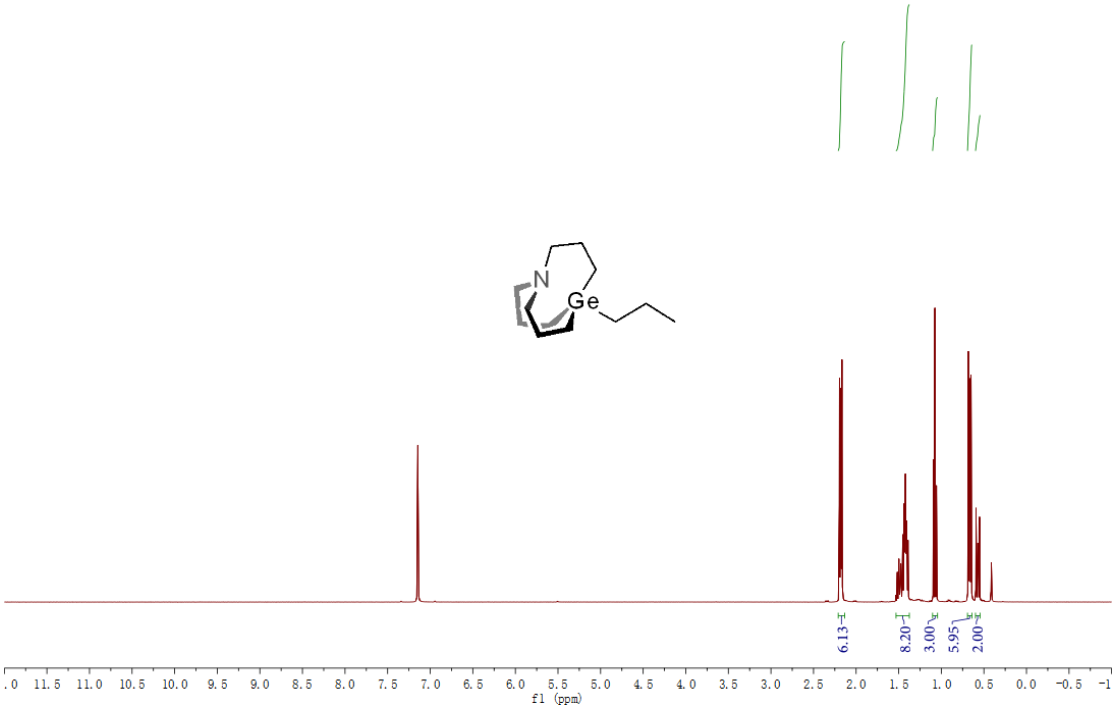

169.4
162.0
134.9
129.0
124.1
33.1
30.9
29.7
23.7
6.2
I
O
O
N
O
O
f1 (ppm)

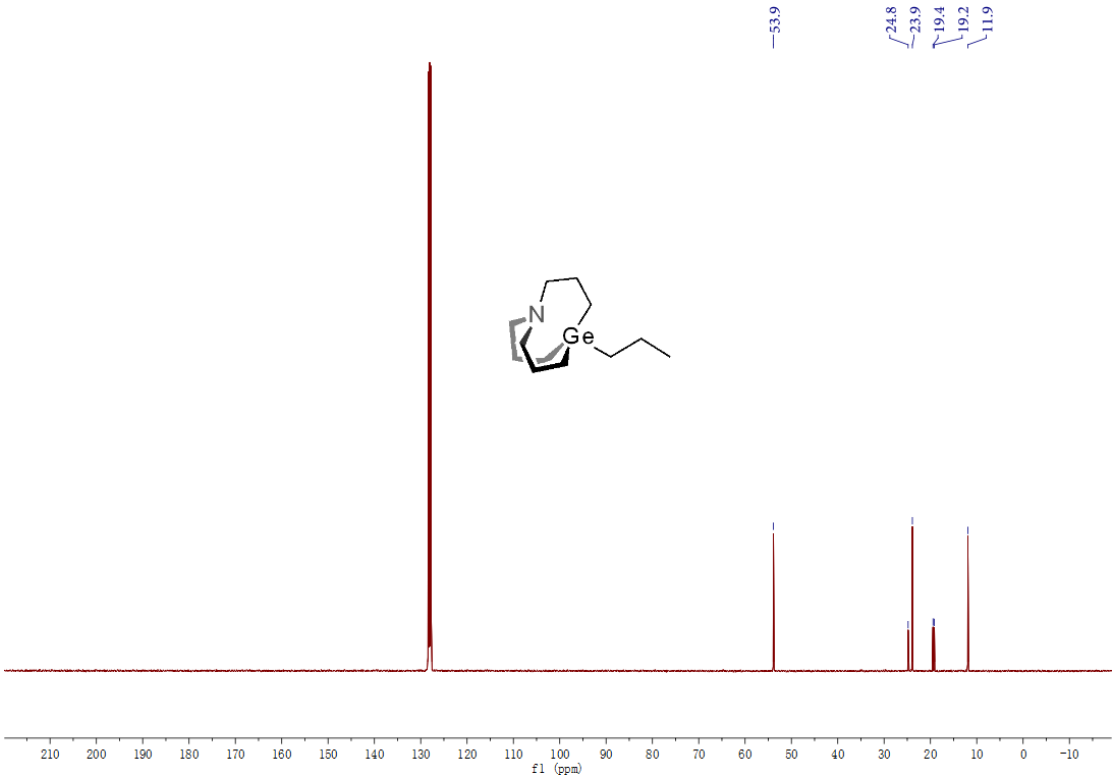

2.00
2.01
1.98
2.01
2.09
2.02
f1 (ppm)

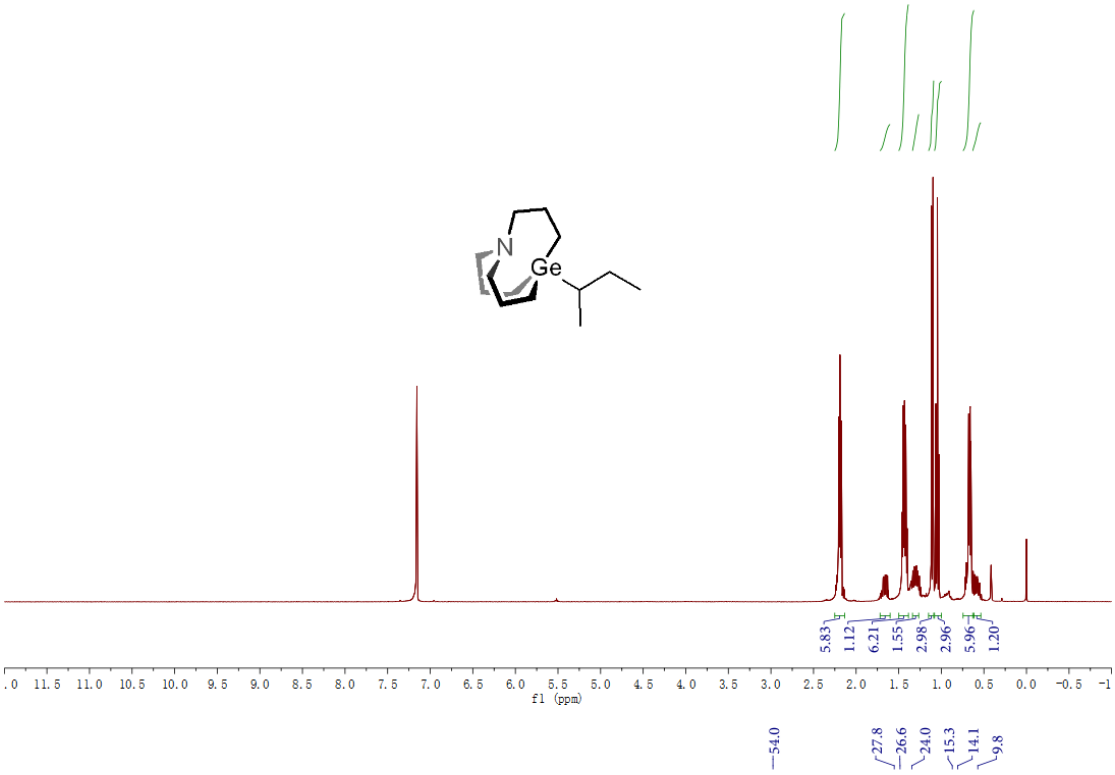

168.8
162.0
138.9
137.9
134.9
130.5
129.0
124.1
92.1
32.5
30.1
f1 (ppm)

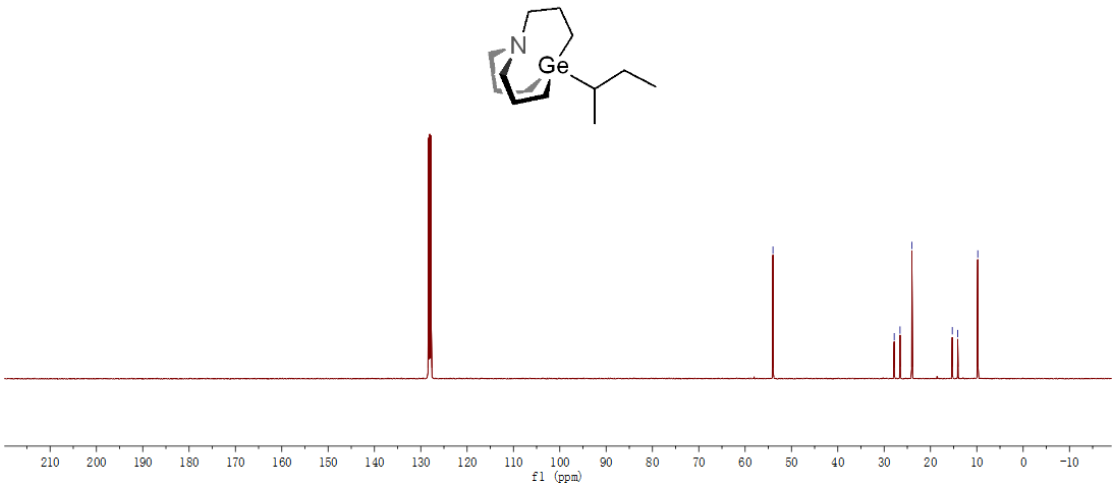

2.02
3.00
1.37
0.98
0.98
2.00
2.00
4.18
2.02
f1 (ppm)

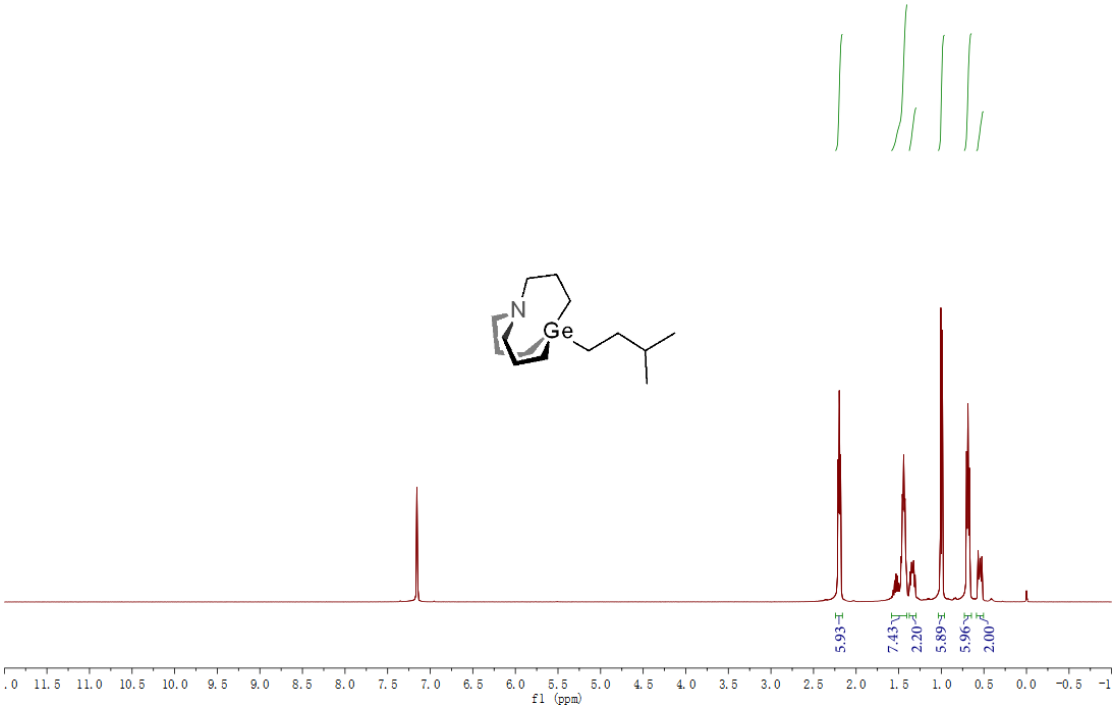
169.6
162.0
157.5
139.4
134.8
129.5
128.9
124.0
122.5
112.1
86.8
68.7
31.0
28.6
25.6
24.4
f1 (ppm)

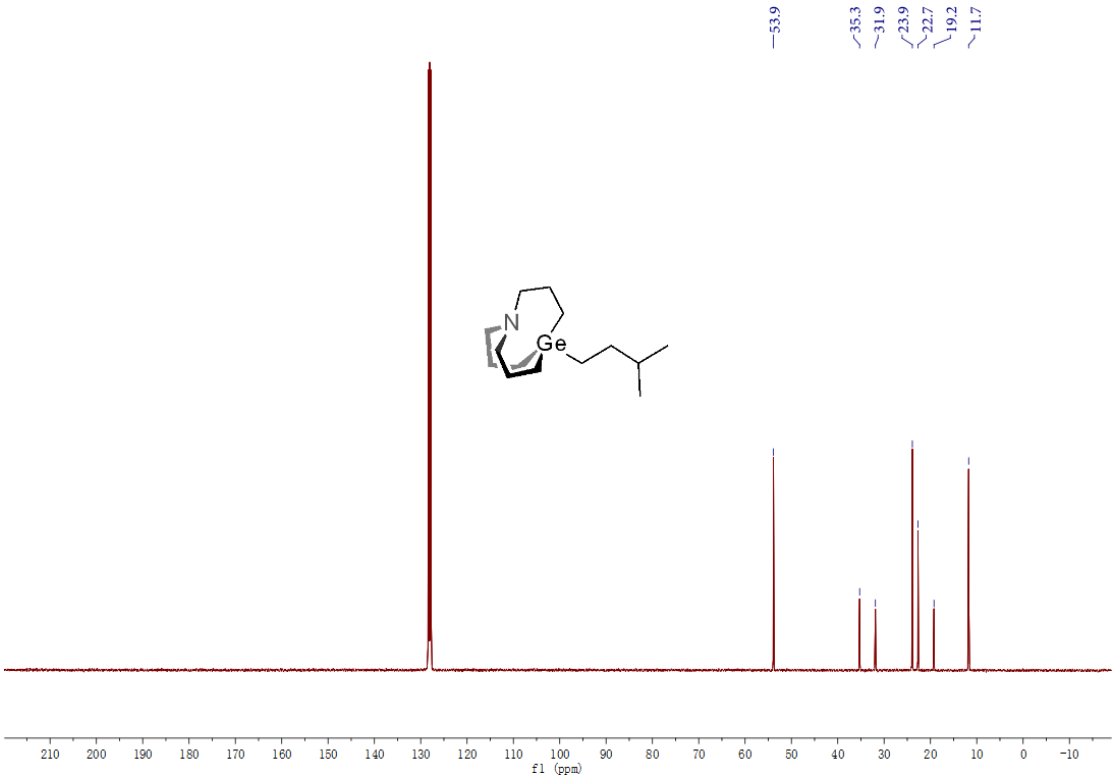

N
Ge
6.13
8.20
3.00
5.95
2.00
f1 (ppm)

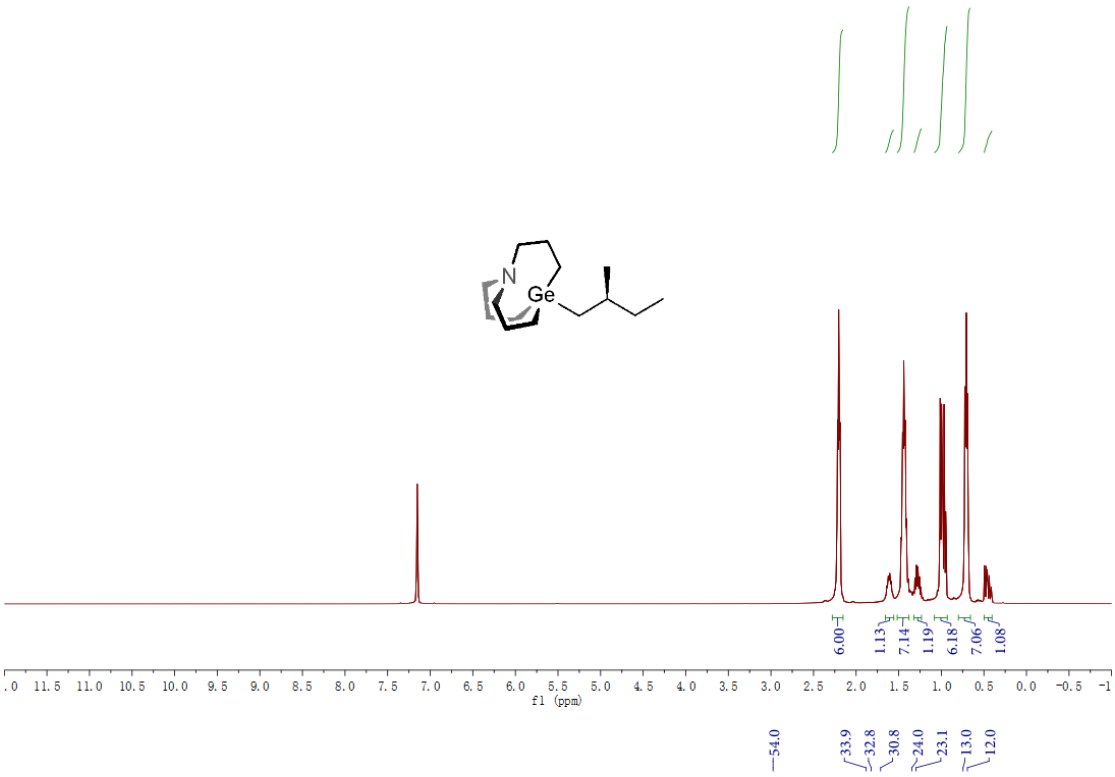

53.9
24.8
23.9
19.4
19.2
11.9
N
Ge
f1 (ppm)

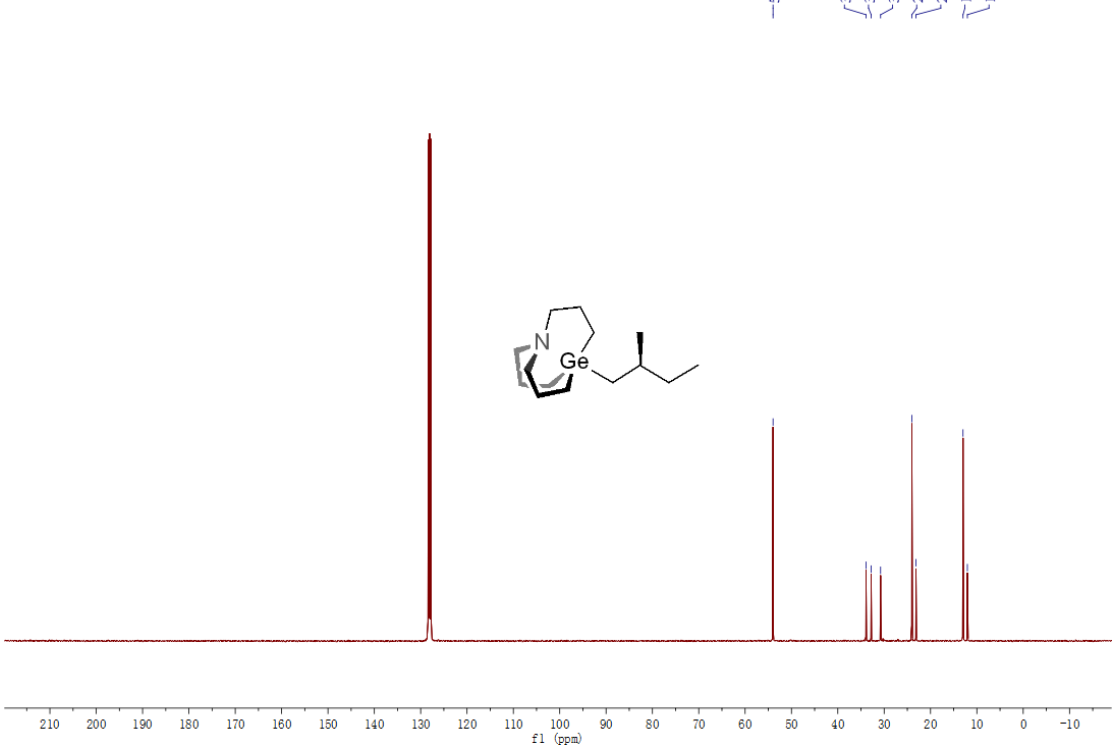

N
Ge
5.83
1.12
6.21
1.55
2.98
2.96
5.96
1.20
f1 (ppm)

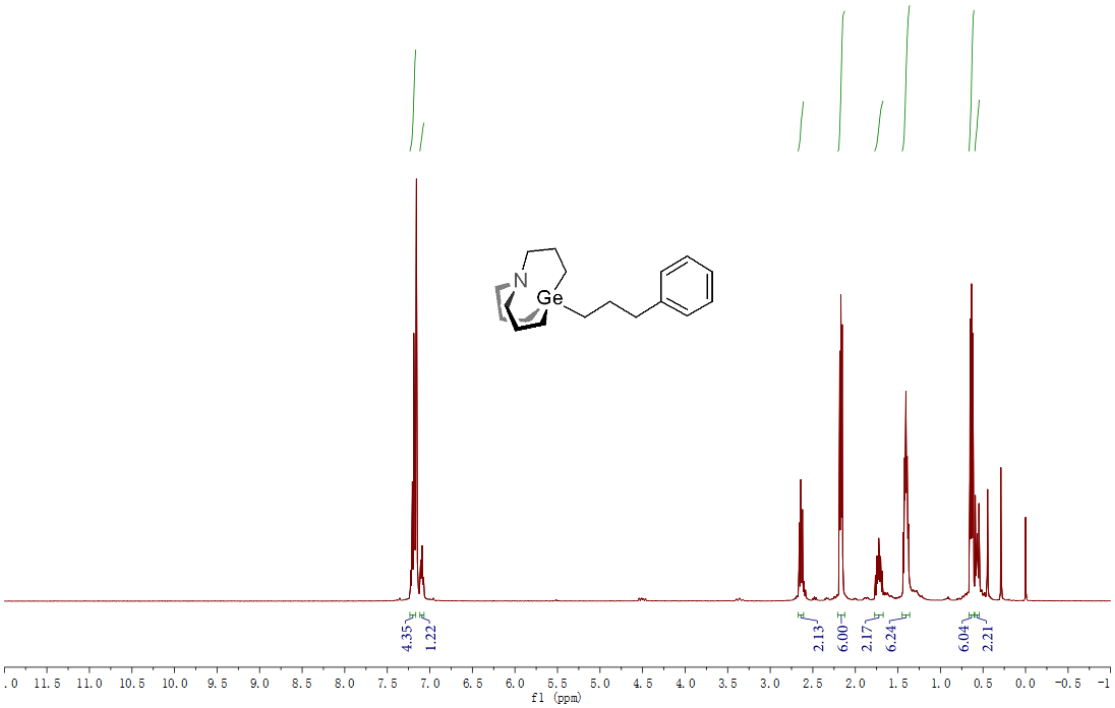

N
Ge
54.0
27.8
26.6
24.0
15.3
14.1
9.8
f1 (ppm)

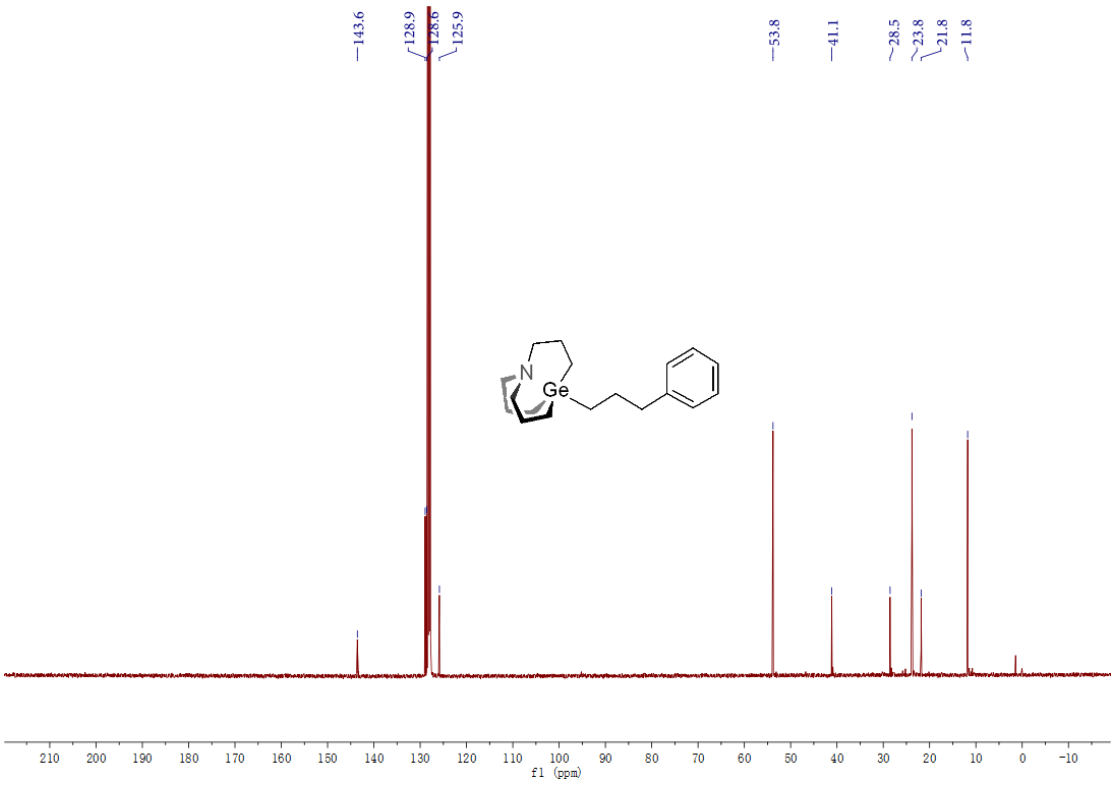

N
Ge
5.93
7.43
2.20
5.89
5.96
2.00
f1 (ppm)

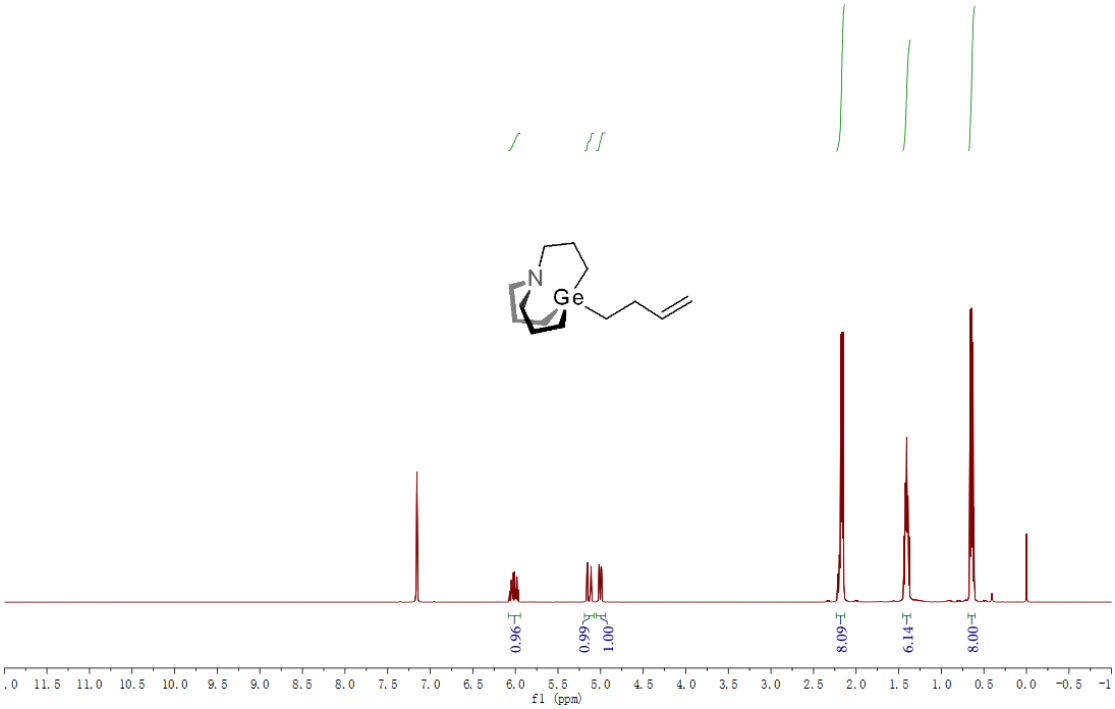

53.9
35.3
31.9
23.9
22.7
19.2
11.7
N
Ge
f1 (ppm)

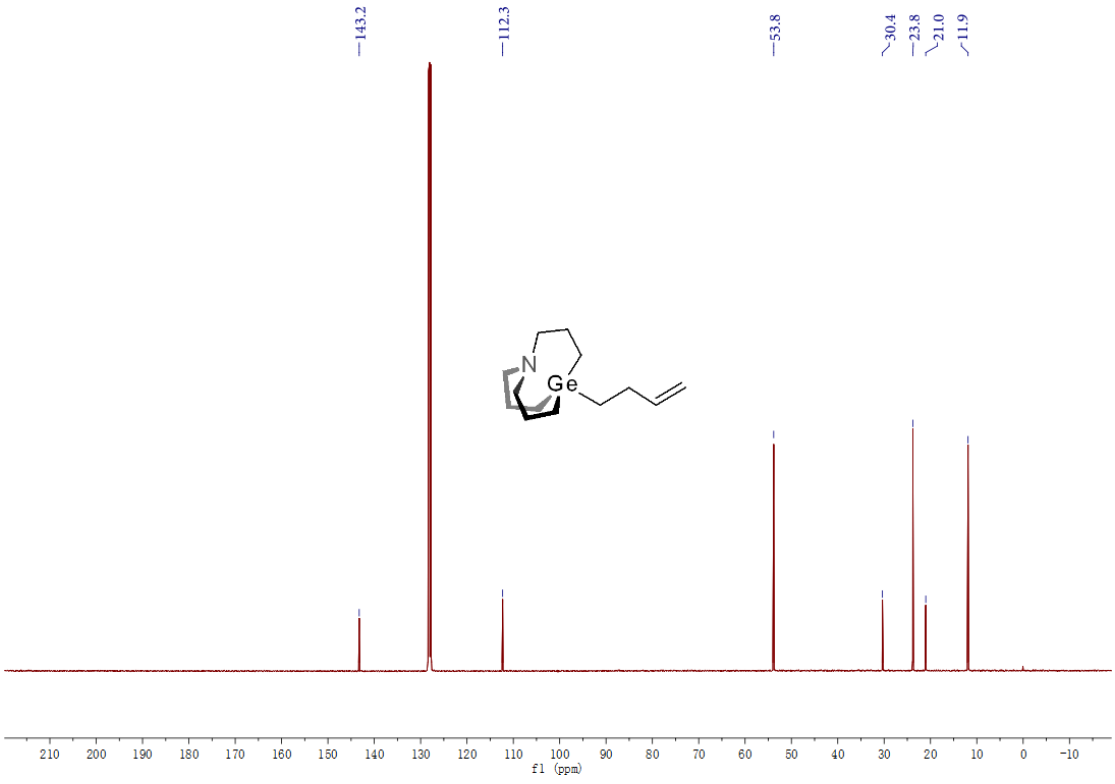

N
Ge
6.00
1.13
7.14
1.19
6.18
7.06
1.08
f1 (ppm)

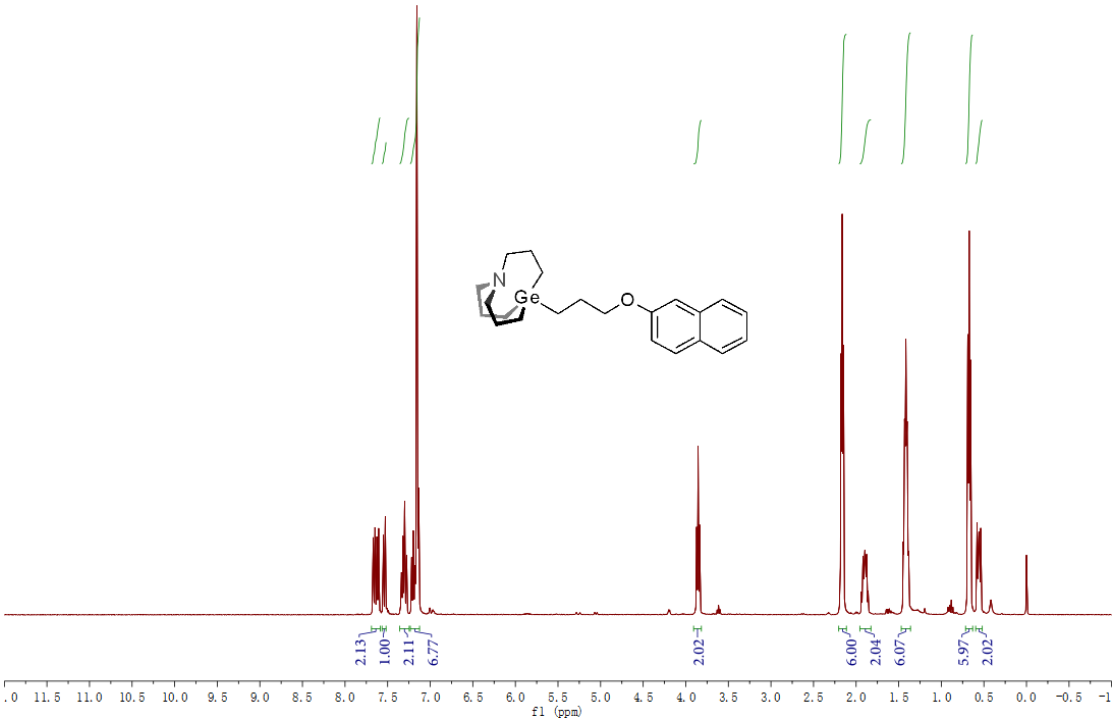

54.0
33.9
32.8
30.8
24.0
23.1
13.0
12.0
N
Ge
f1 (ppm)

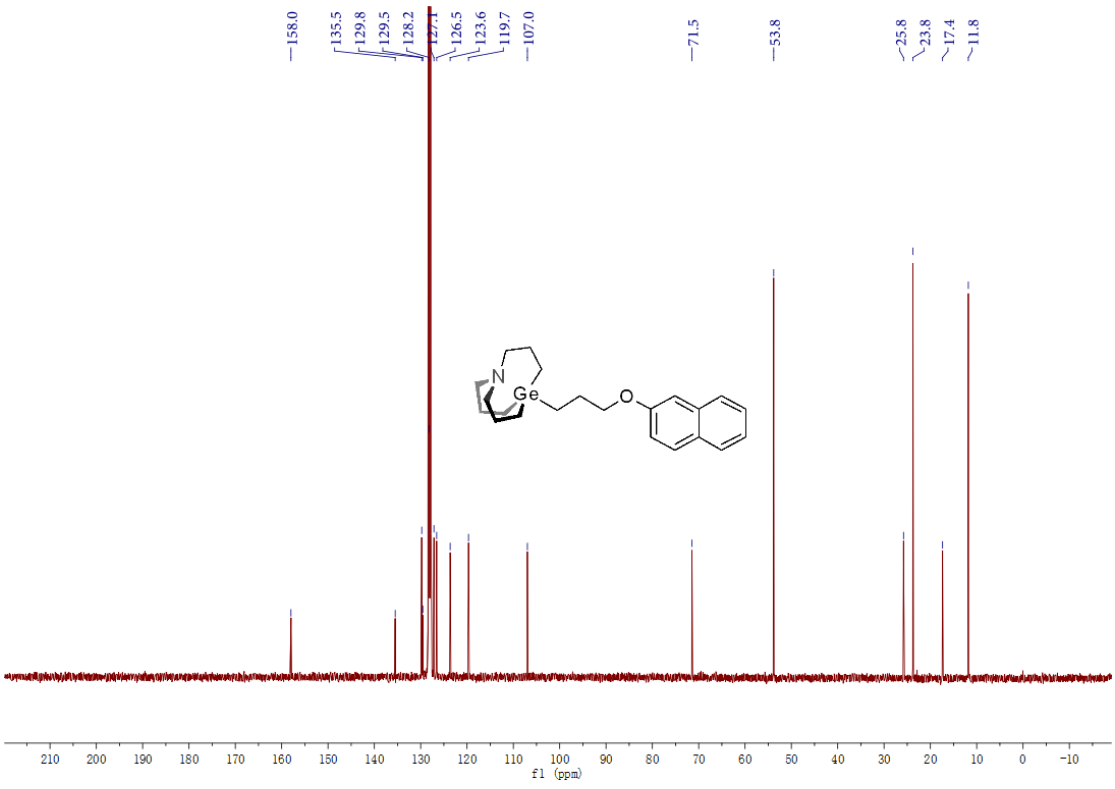

N
Ge
4.35
1.22
2.13
6.00
2.17
6.24
6.04
2.21
f1 (ppm)

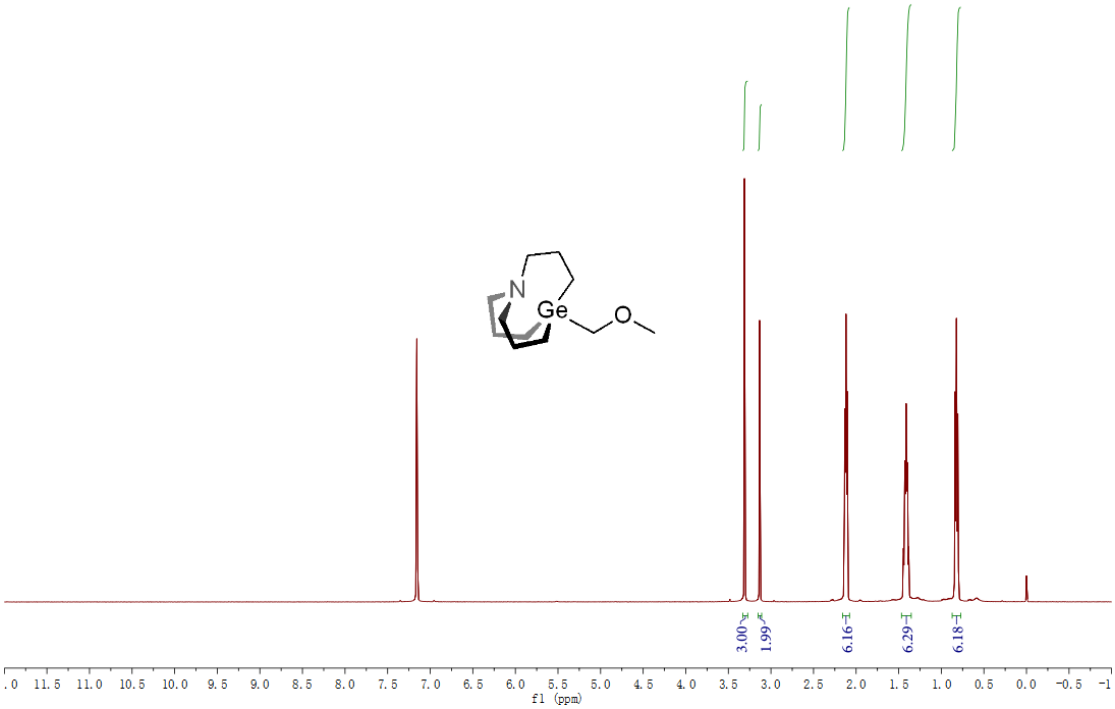

143.6
128.9
128.6
125.9
53.8
41.1
28.5
23.8
21.8
11.8
N
Ge
f1 (ppm)

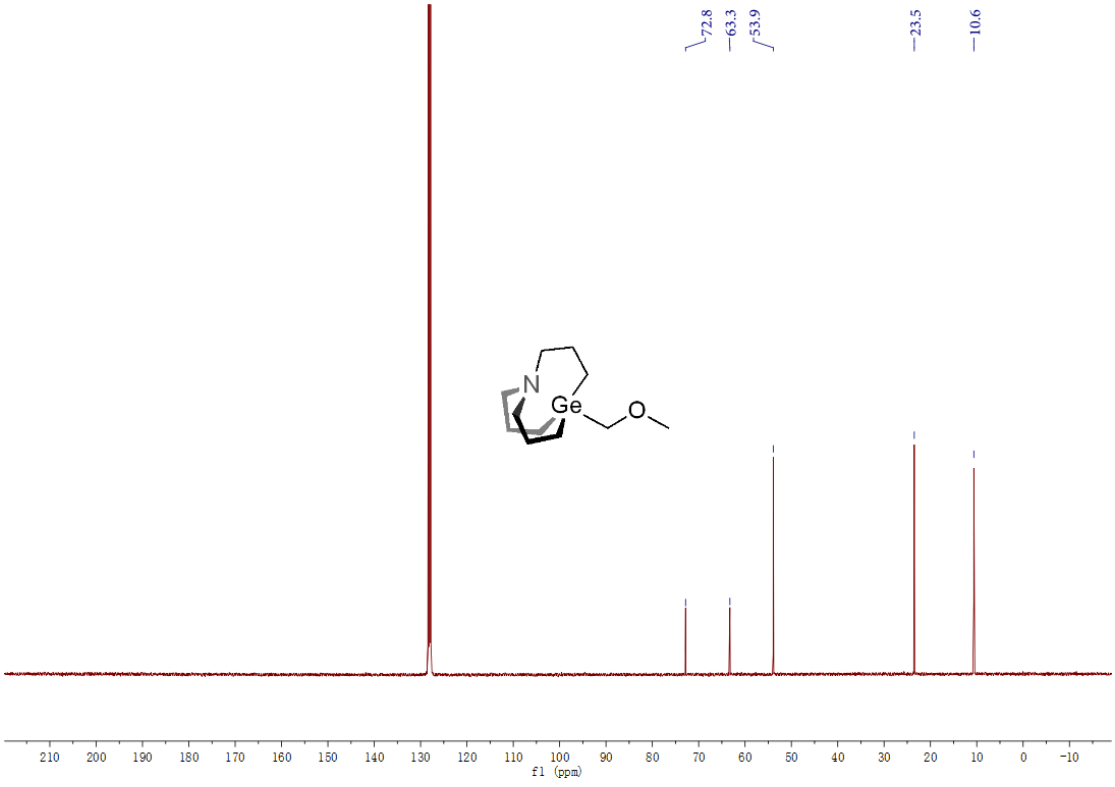

N
Ge
0.96
0.99
1.00
8.09
6.14
8.00
f1 (ppm)

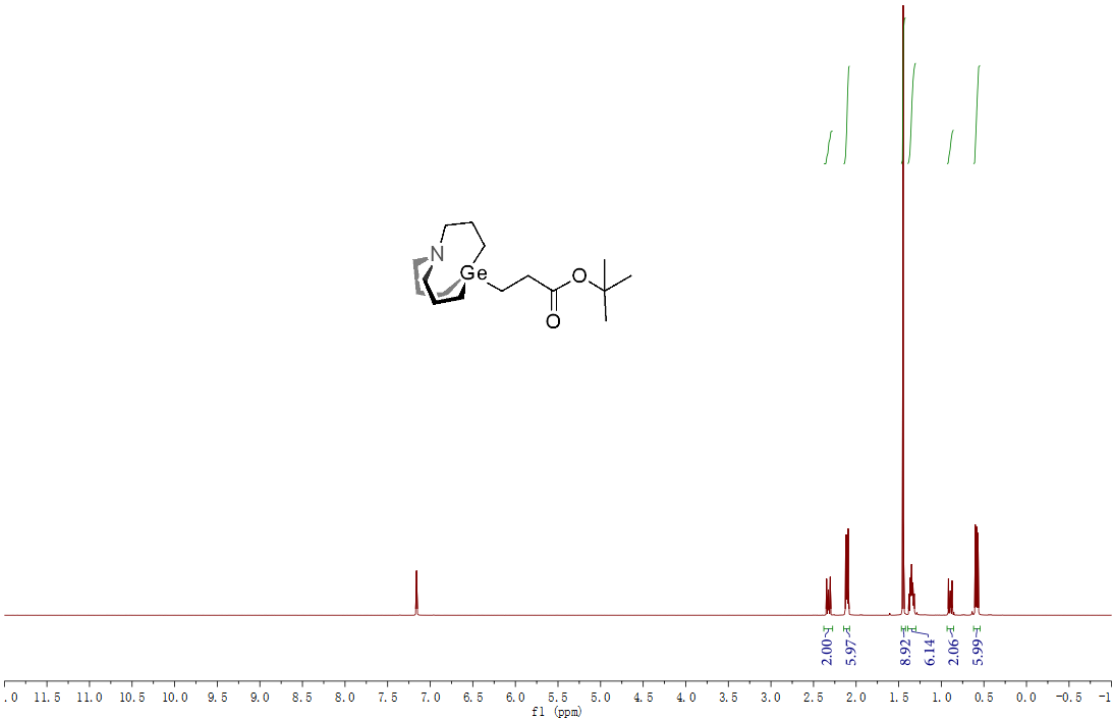

143.2
112.3
53.8
30.4
23.8
21.0
11.9
N
Ge
f1 (ppm)

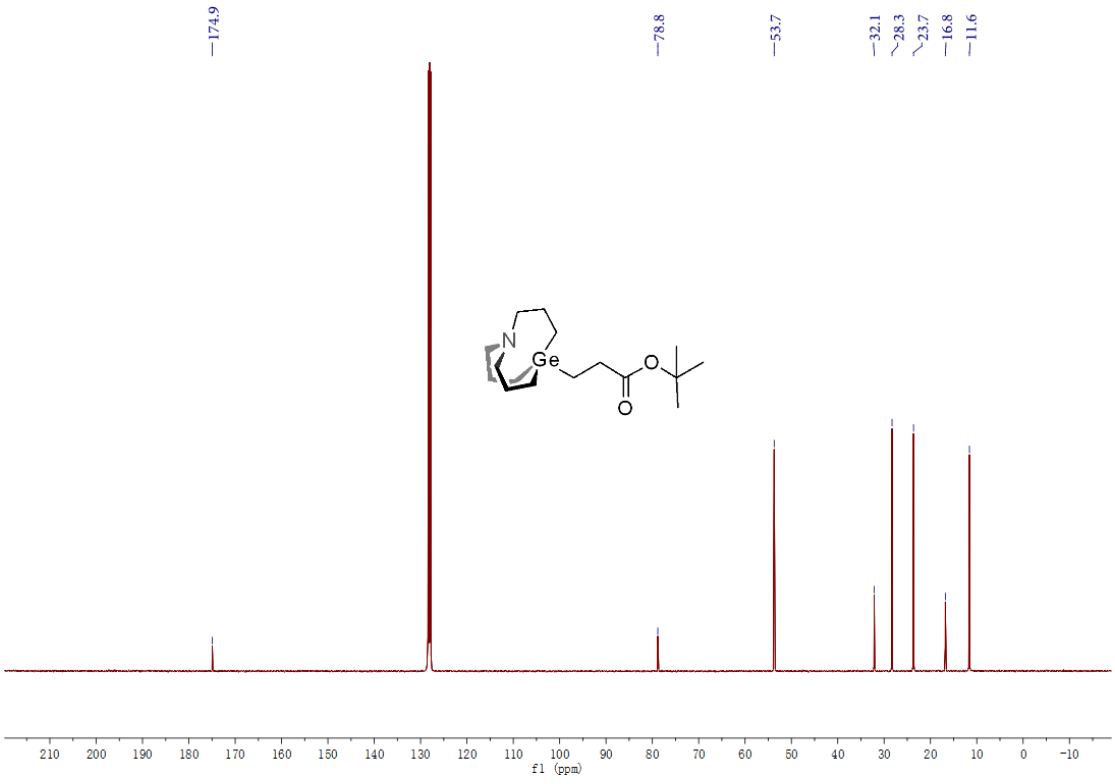

N
Ge
O
2.13
1.00
2.11
6.77
2.02
6.00
2.04
6.07
5.97
2.02
f1 (ppm)

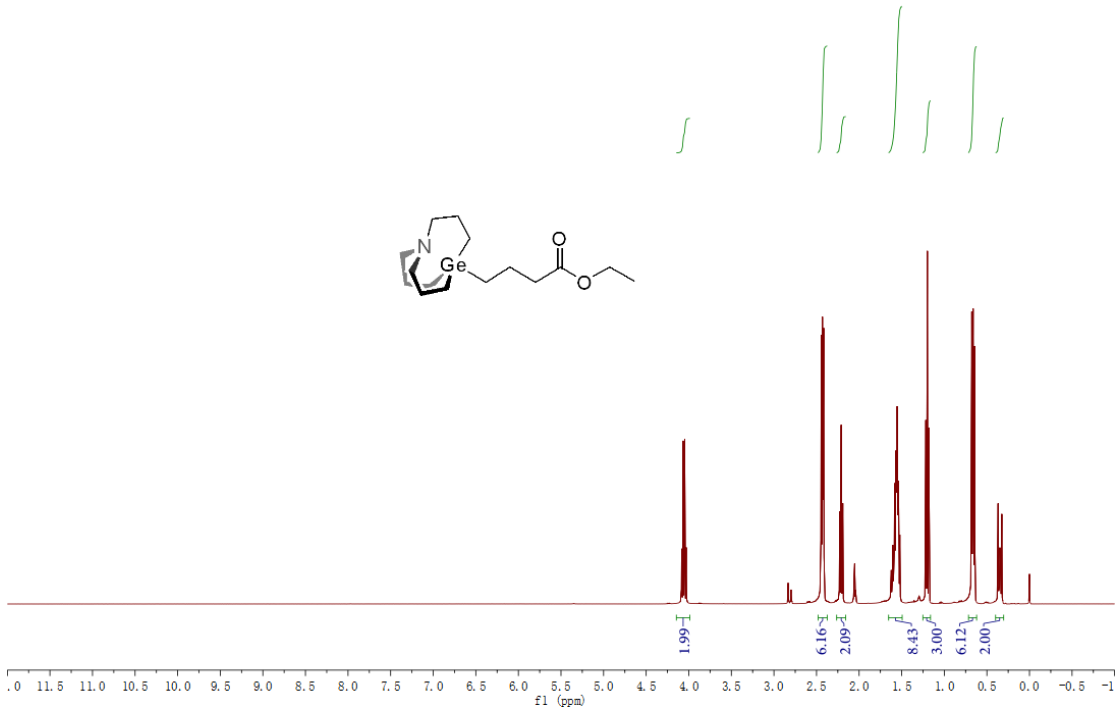

158.0
135.5
129.8
129.5
128.2
127.1
126.5
123.6
119.7
107.0
71.5
53.8
25.8
23.8
17.4
11.8
N
Ge
O
f1 (ppm)

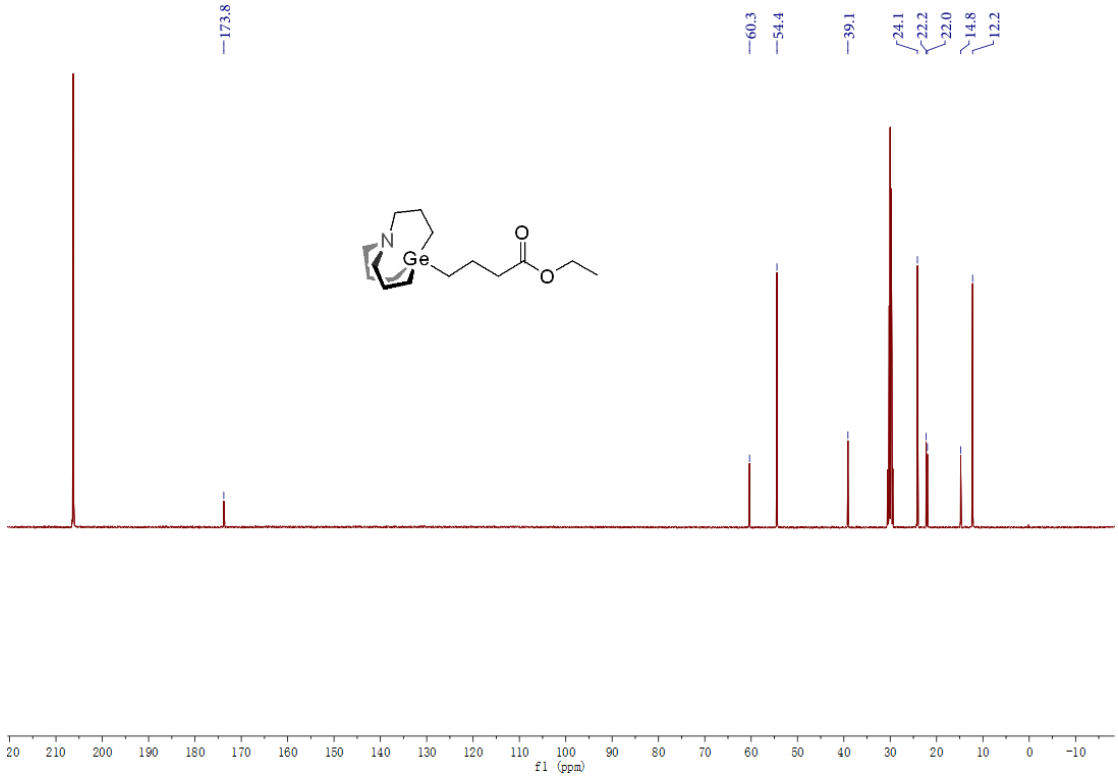

N
Ge
O
3.00
1.99
6.16
6.29
6.18
f1 (ppm)

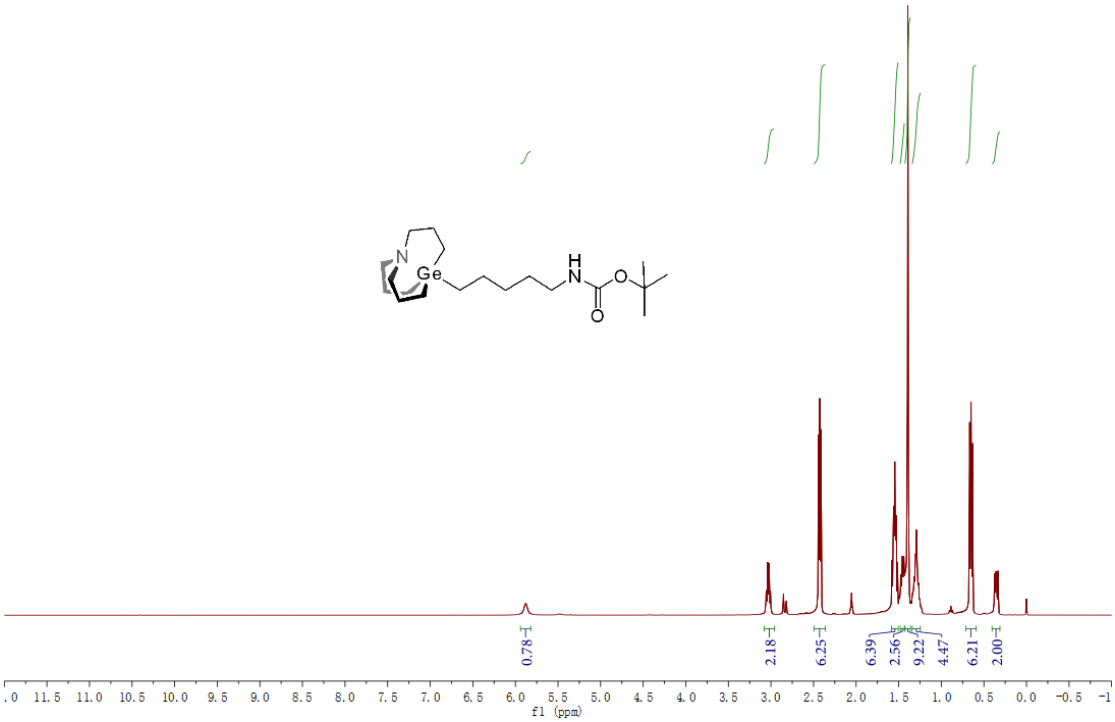

72.8
63.3
53.9
23.5
10.6
N
Ge
O
f1 (ppm)

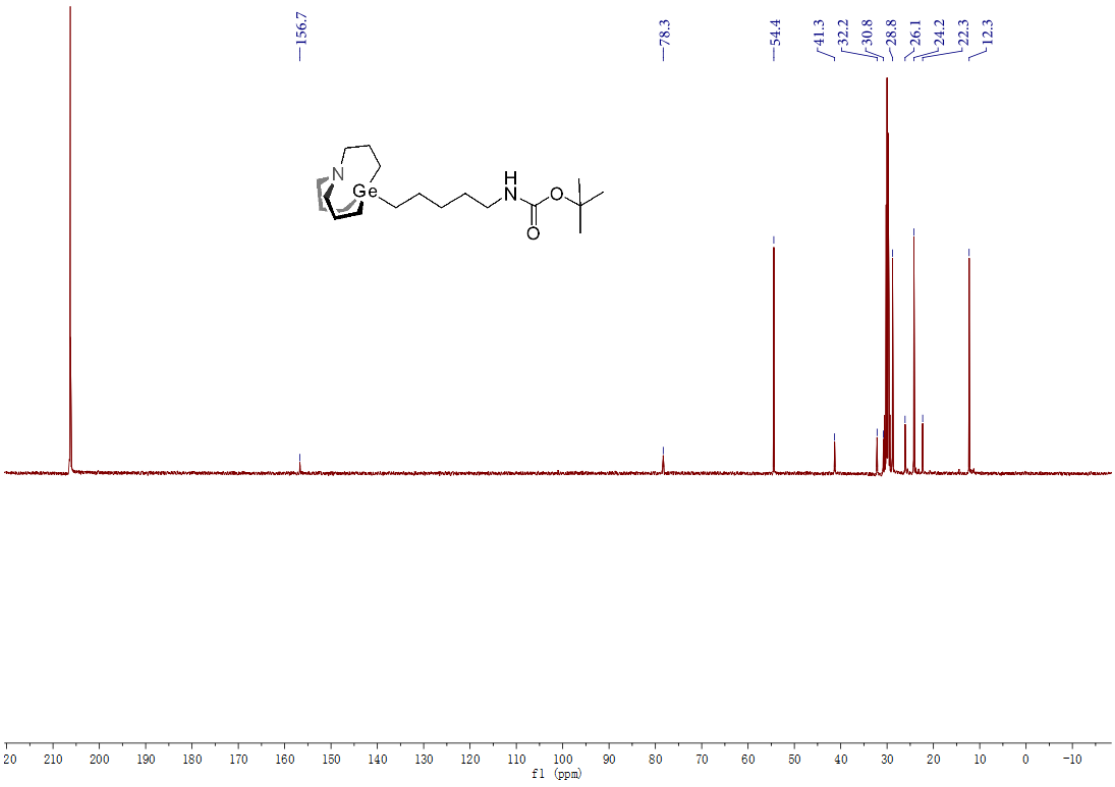

N
Ge
O
O
2.00
5.97
8.92
6.14
2.06
5.99
f1 (ppm)

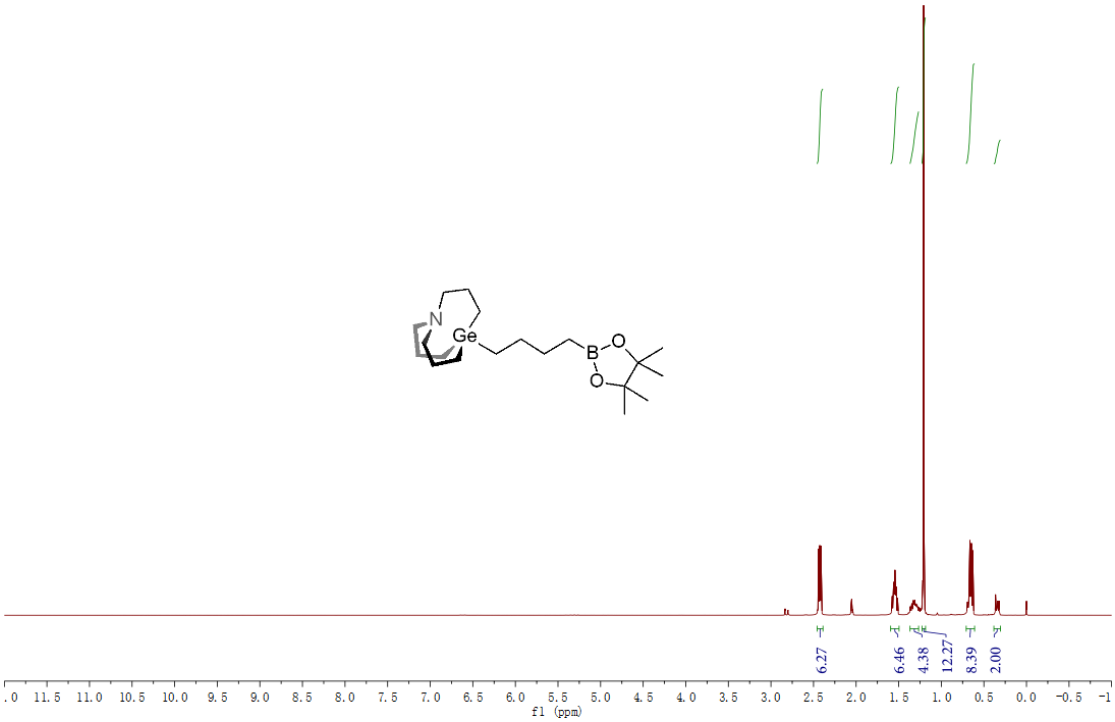

174.9
78.8
53.7
32.1
28.3
23.7
16.8
11.6
N
Ge
O
O
f1 (ppm)

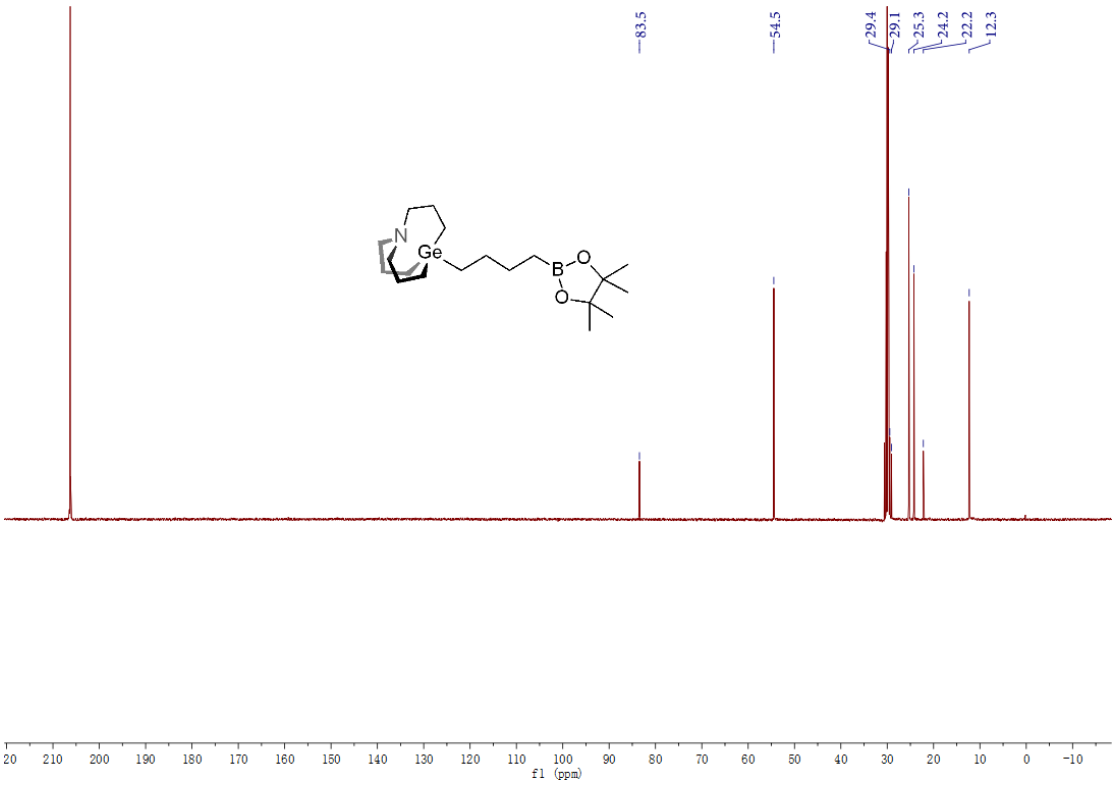

N
Ge
O
O
1.99
6.16
2.09
8.43
3.00
6.12
2.00
f1 (ppm)

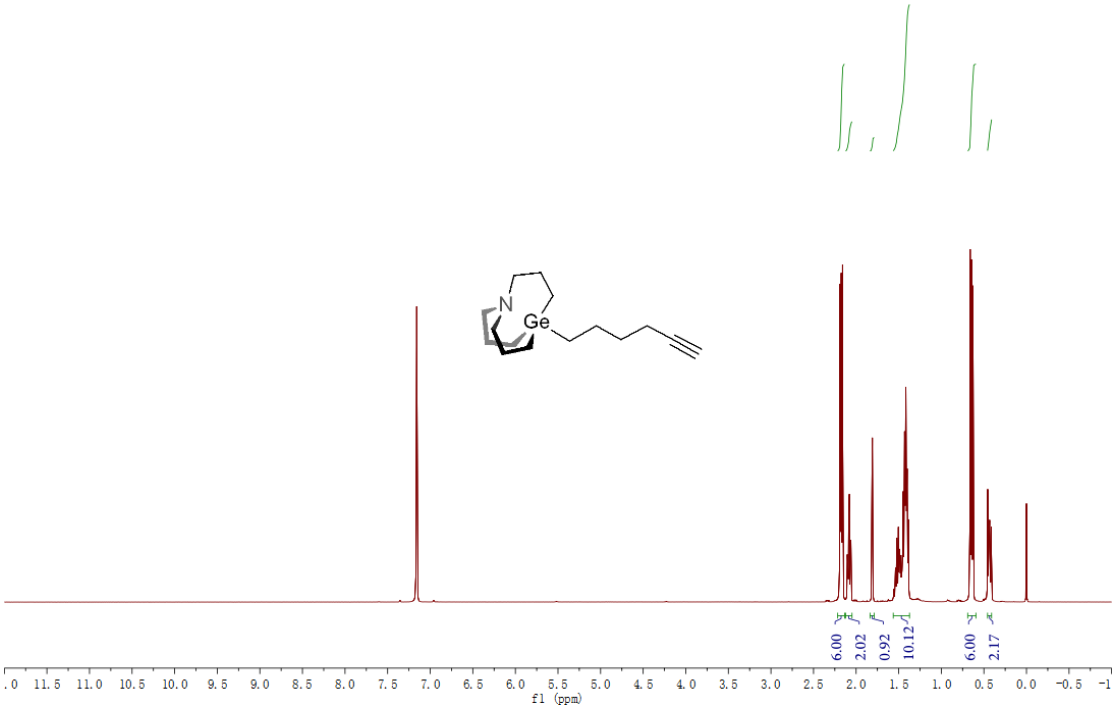

173.8
60.3
54.4
39.1
24.1
22.2
22.0
14.8
12.2
N
Ge
O
O
f1 (ppm)

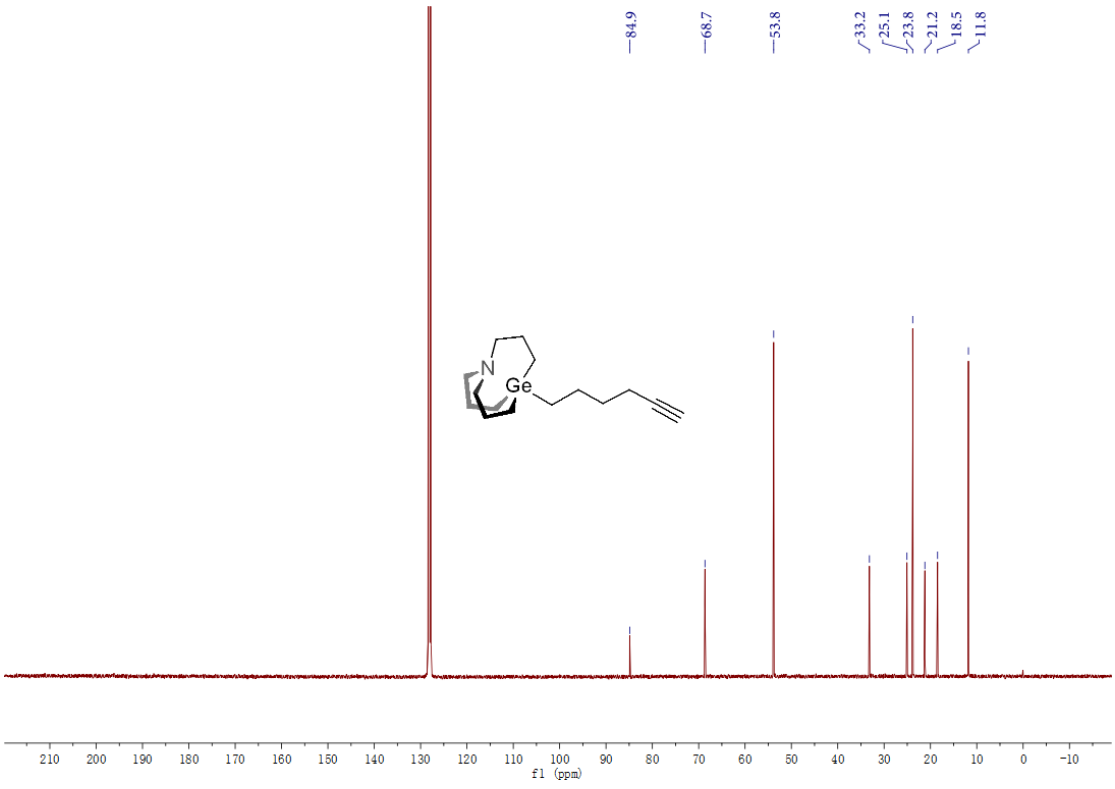

0.78
2.18
6.25
6.39
2.56
9.22
4.47
6.21
2.00
f1 (ppm)

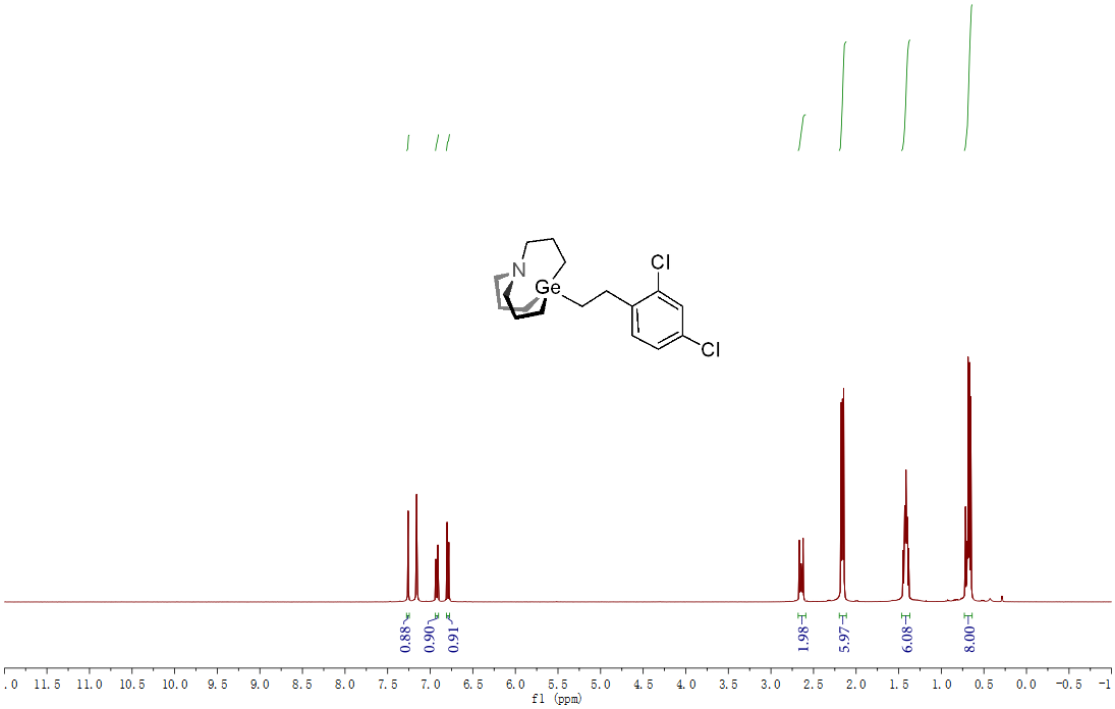

156.7
78.3
54.4
41.3
32.2
30.8
28.8
26.1
24.2
22.3
12.3
f1 (ppm)

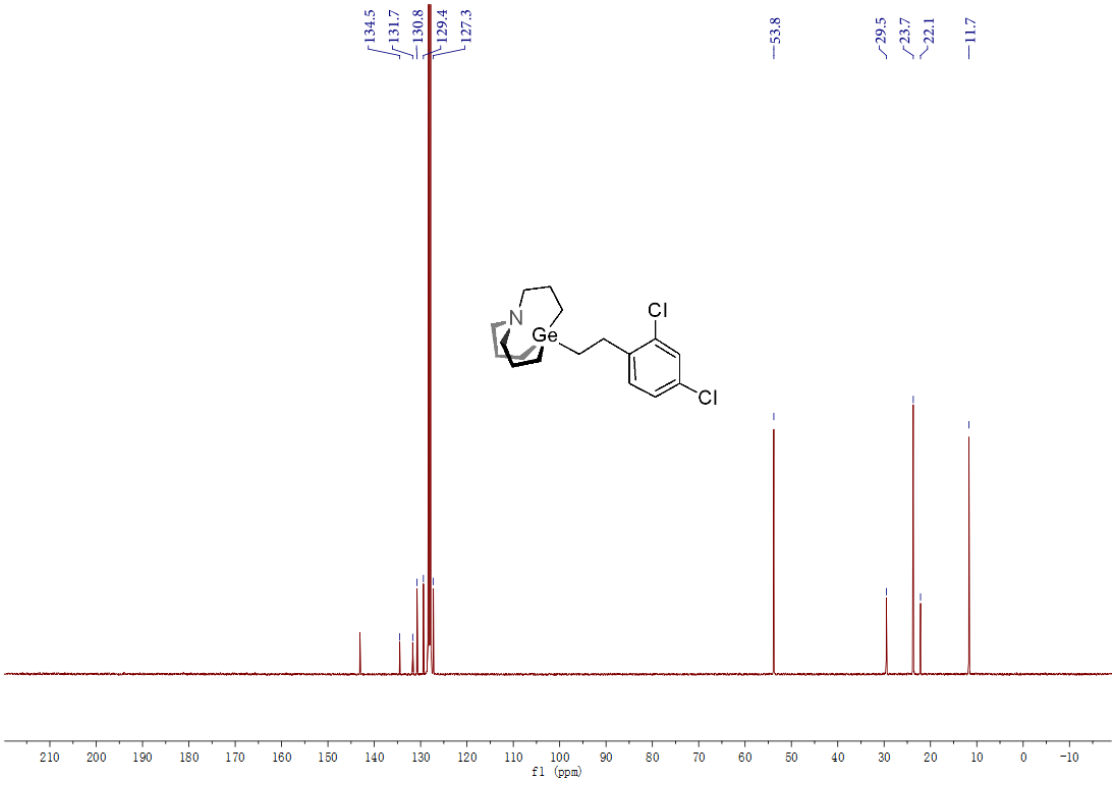

6.27
6.46
4.38
12.27
8.39
2.00
f1 (ppm)

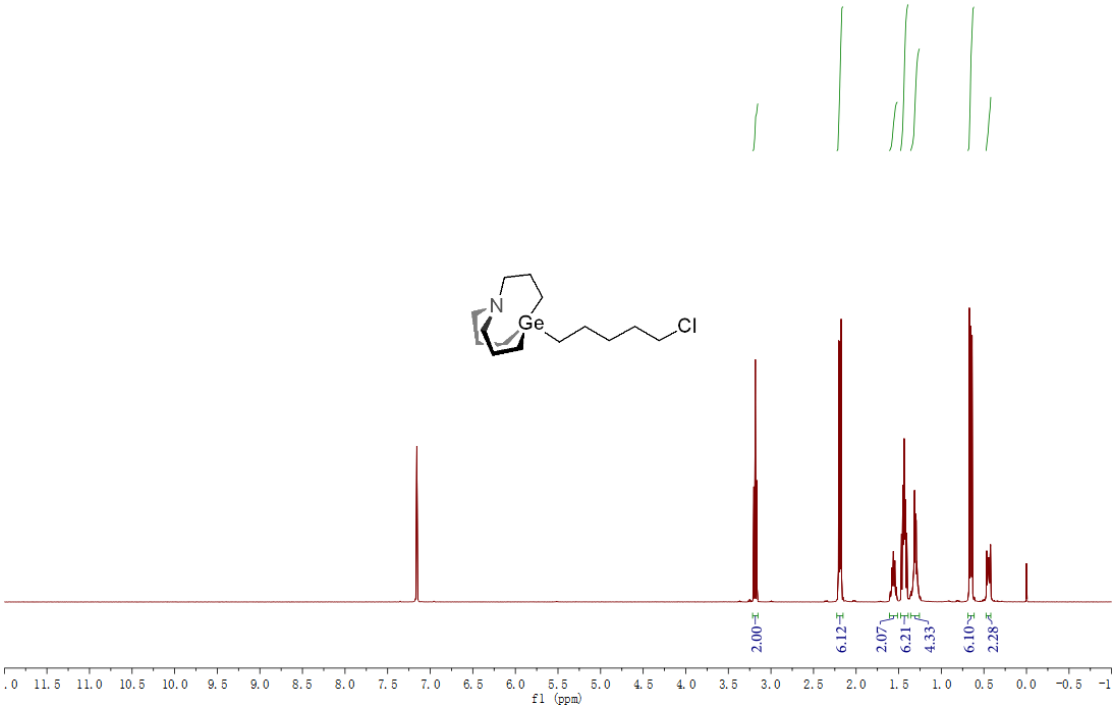

83.5
54.5
29.4
29.1
25.3
24.2
22.2
12.3
f1 (ppm)

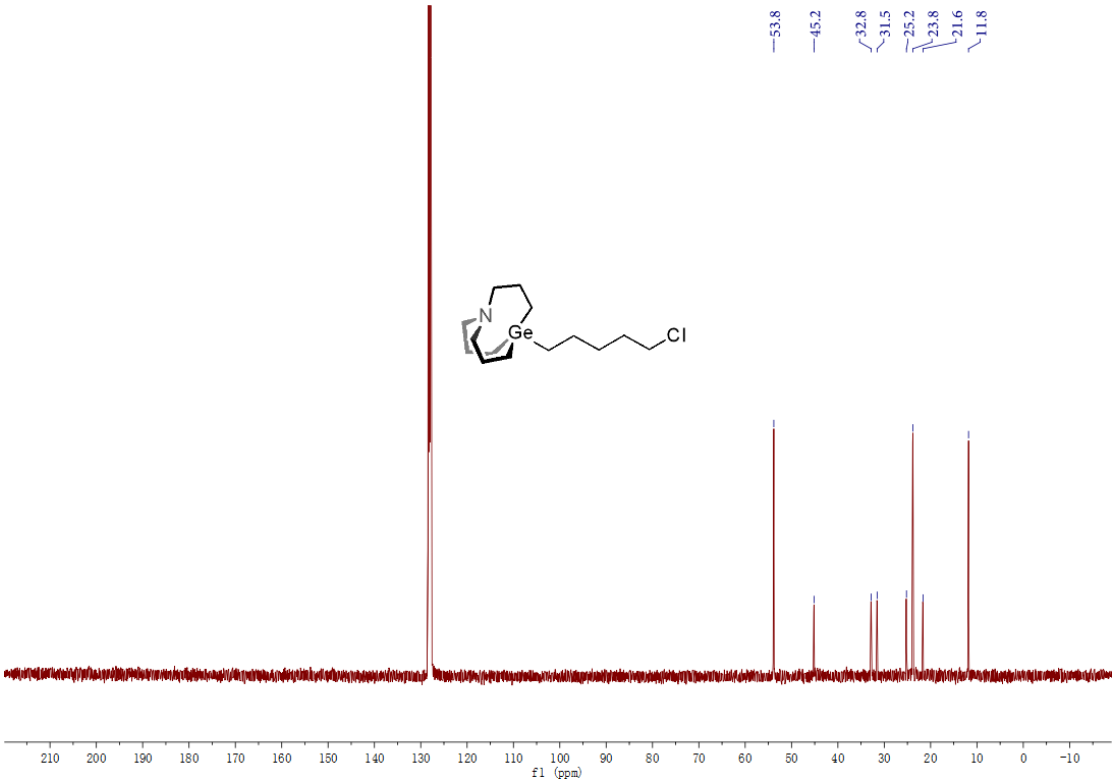

N
Ge
6.00
2.02
0.92
10.12
6.00
2.17
f1 (ppm)

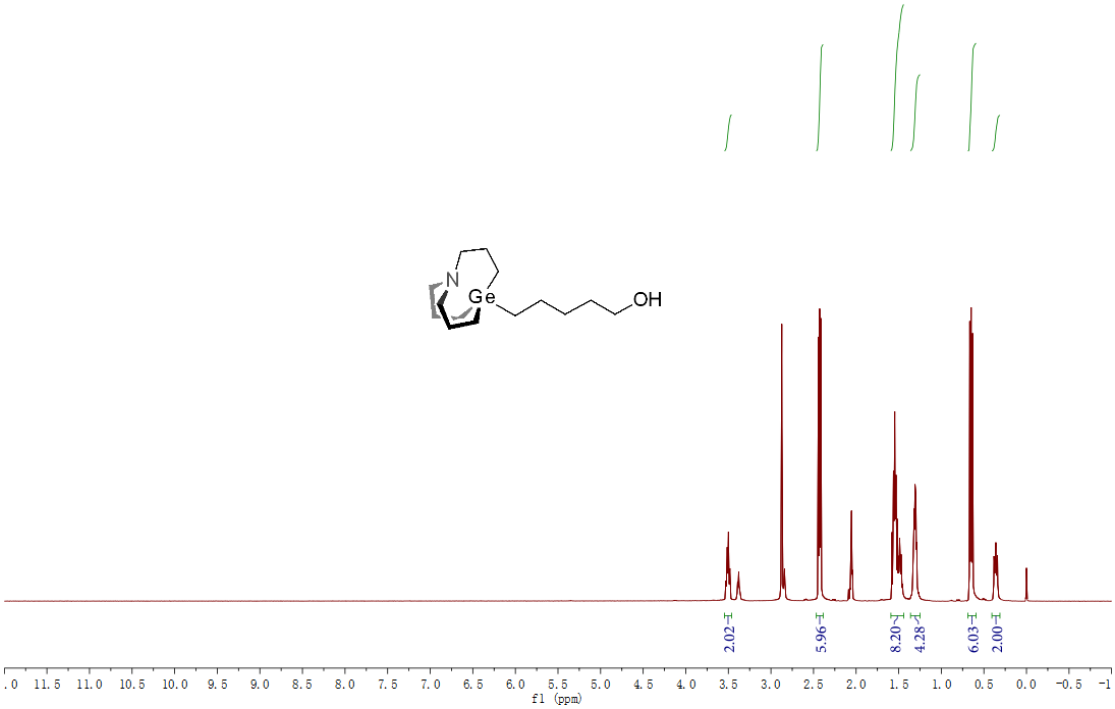

84.9
68.7
53.8
33.2
25.1
23.8
21.2
18.5
11.8
N
Ge
f1 (ppm)

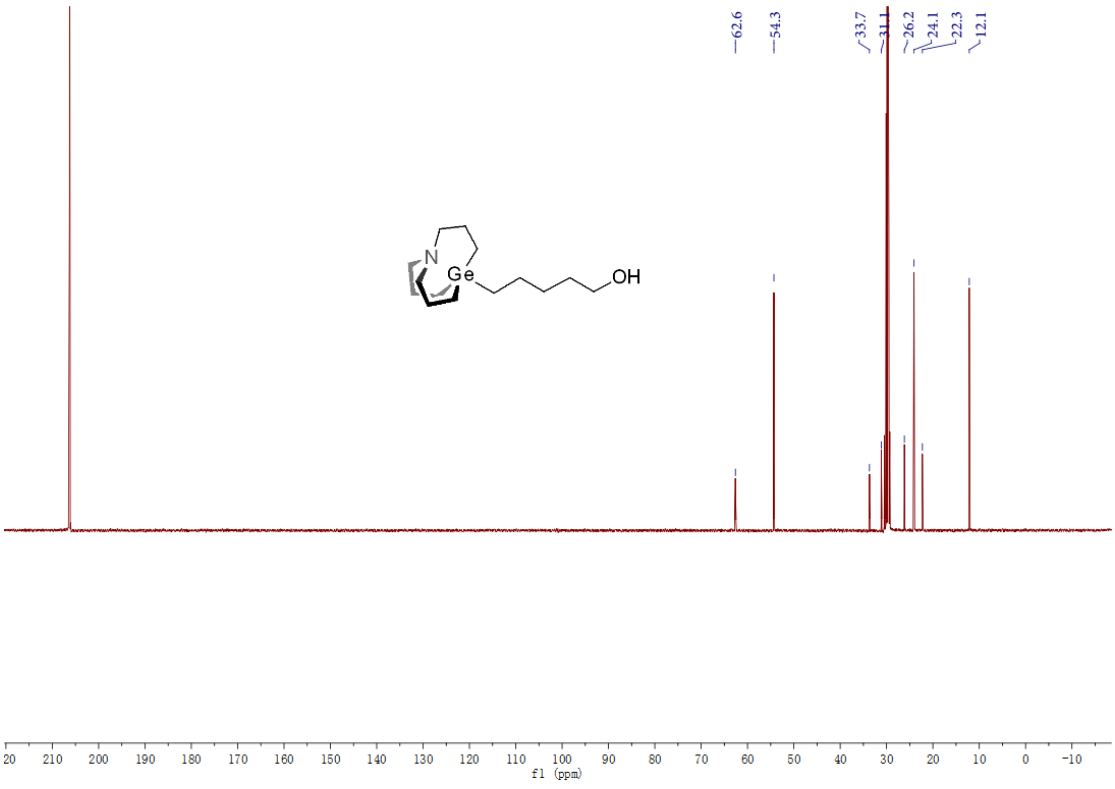

N
Ge
Cl
Cl
0.88
0.90
0.91
1.98
5.97
6.08
8.00
f1 (ppm)

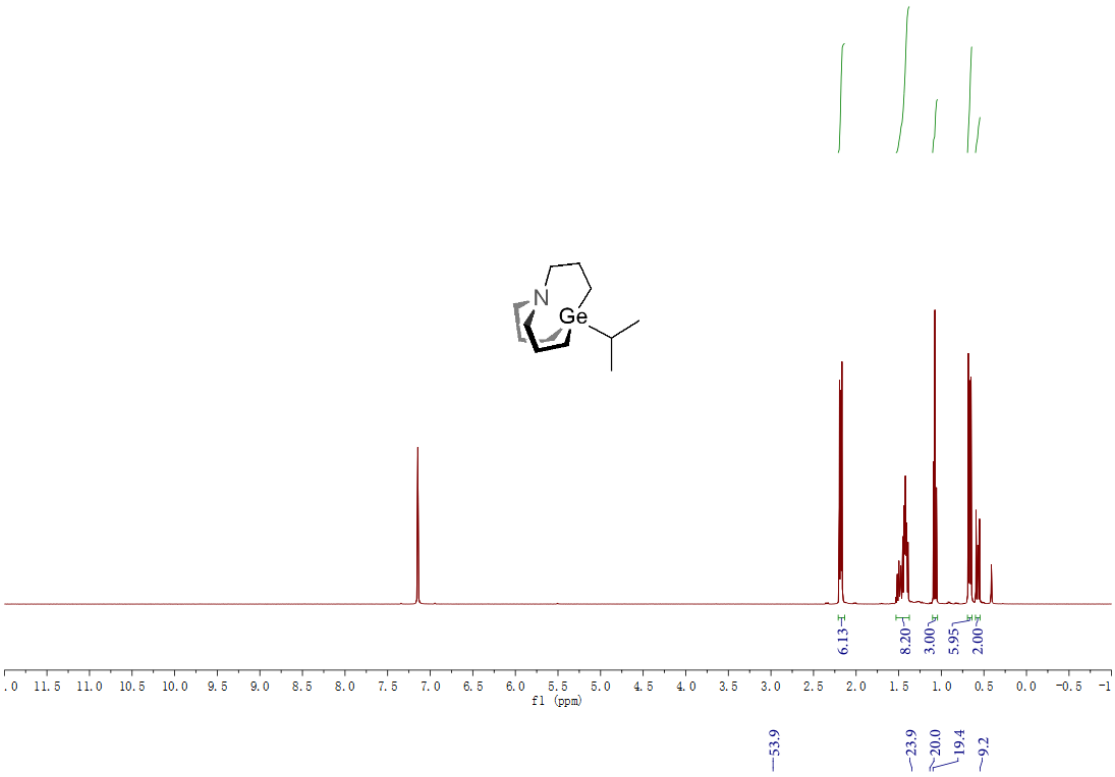

134.5
131.7
130.8
129.4
127.3
53.8
29.5
23.7
22.1
11.7
N
Ge
Cl
Cl
f1 (ppm)

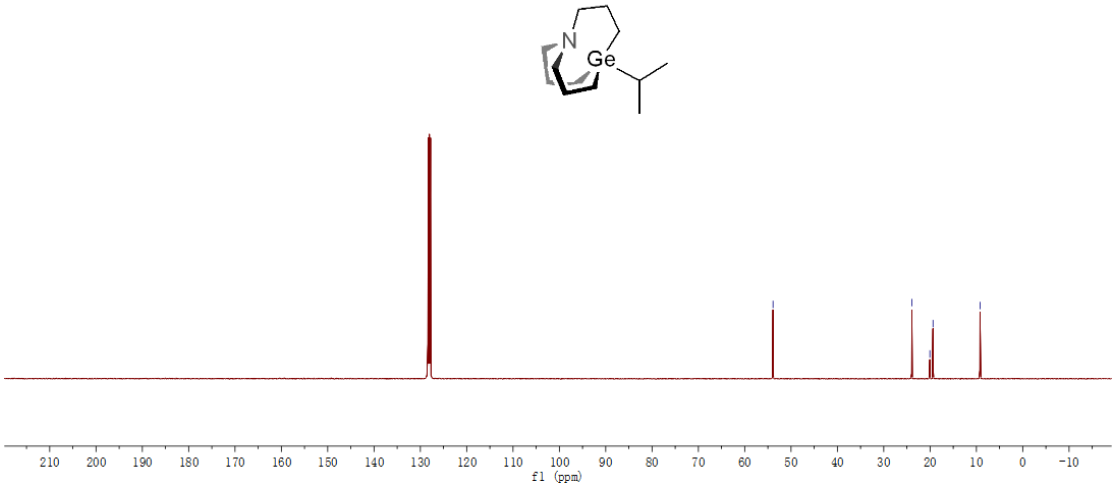

N
Ge
Cl
2.00
6.12
2.07
6.21
4.33
6.10
2.28
f1 (ppm)

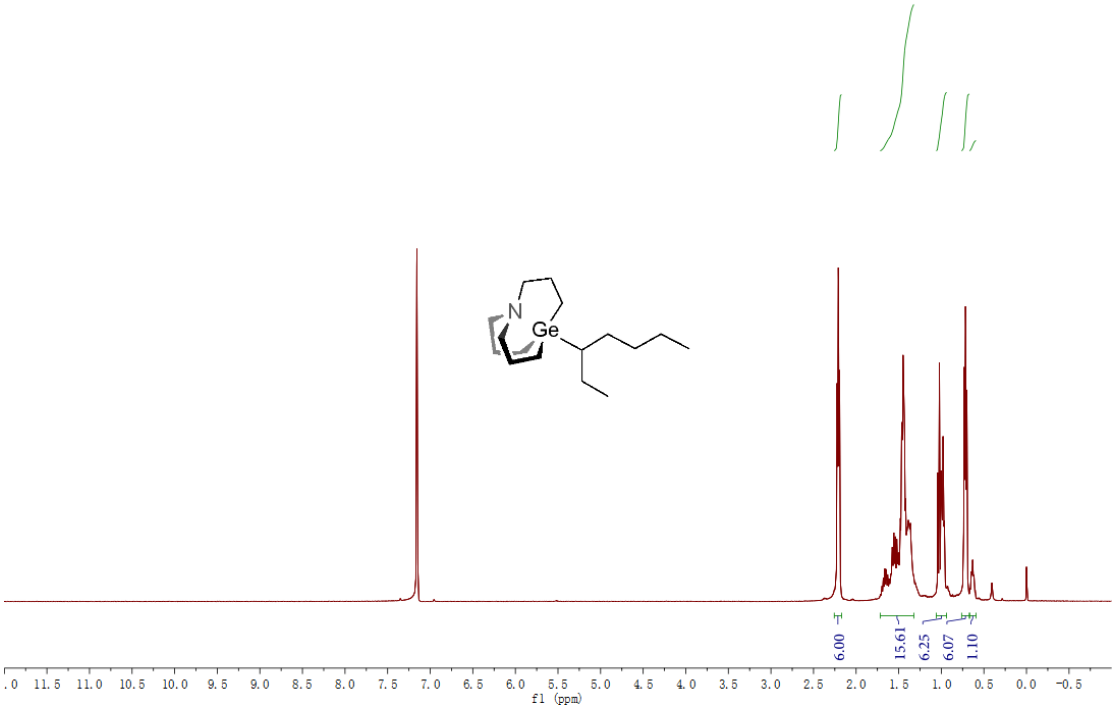

53.8
45.2
32.8
31.5
25.2
23.8
21.6
11.8
N
Ge
Cl
f1 (ppm)

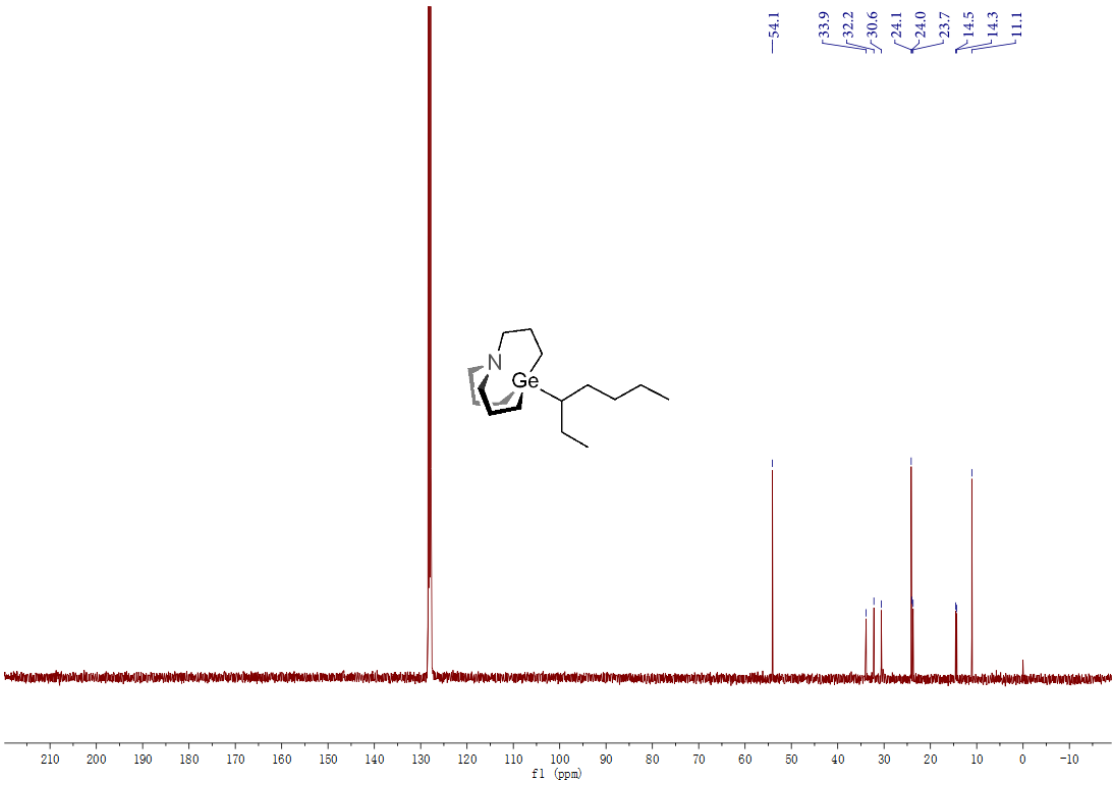

N
Ge
OH
2.02
5.96
8.20
4.28
6.03
2.00
f1 (ppm)

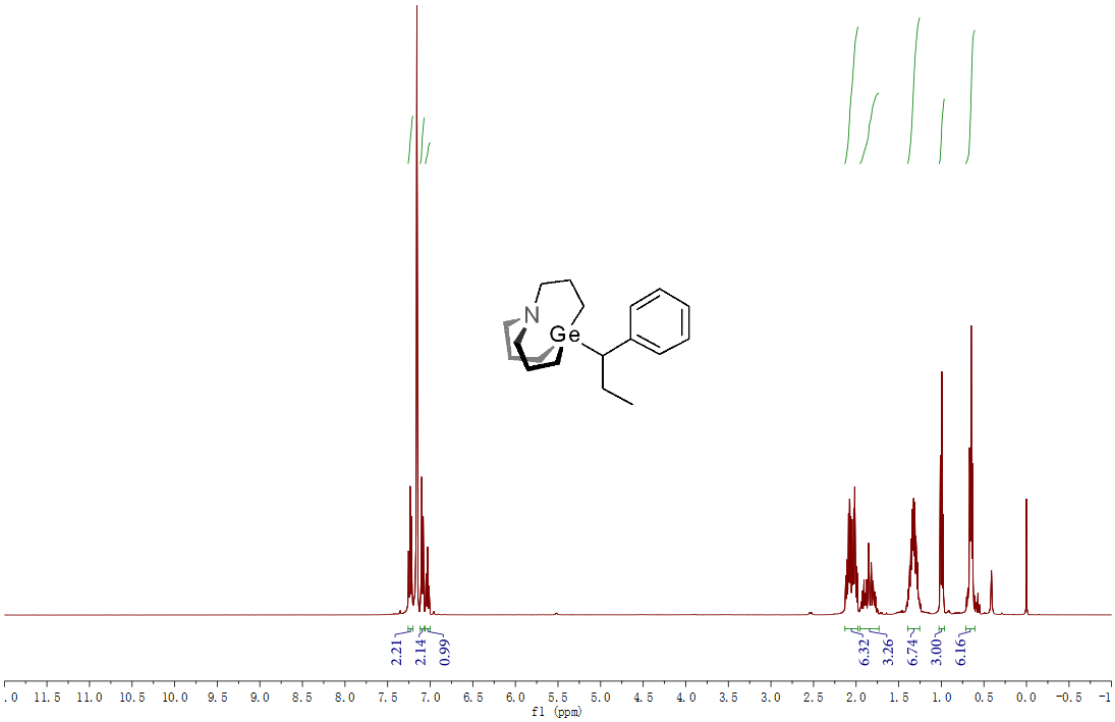

62.6
54.3
33.7
31.1
26.2
24.1
22.3
12.1
N
Ge
OH
f1 (ppm)

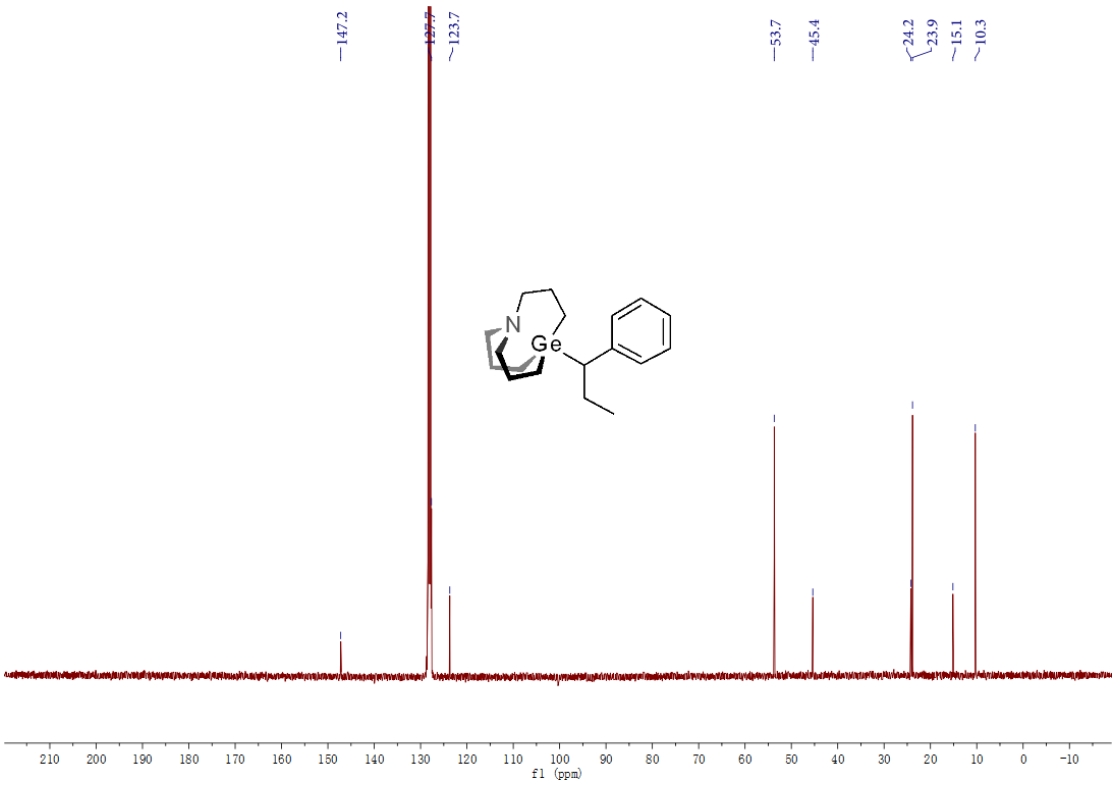

N
Ge
6.13
8.20
3.00
5.95
2.00
f1 (ppm)

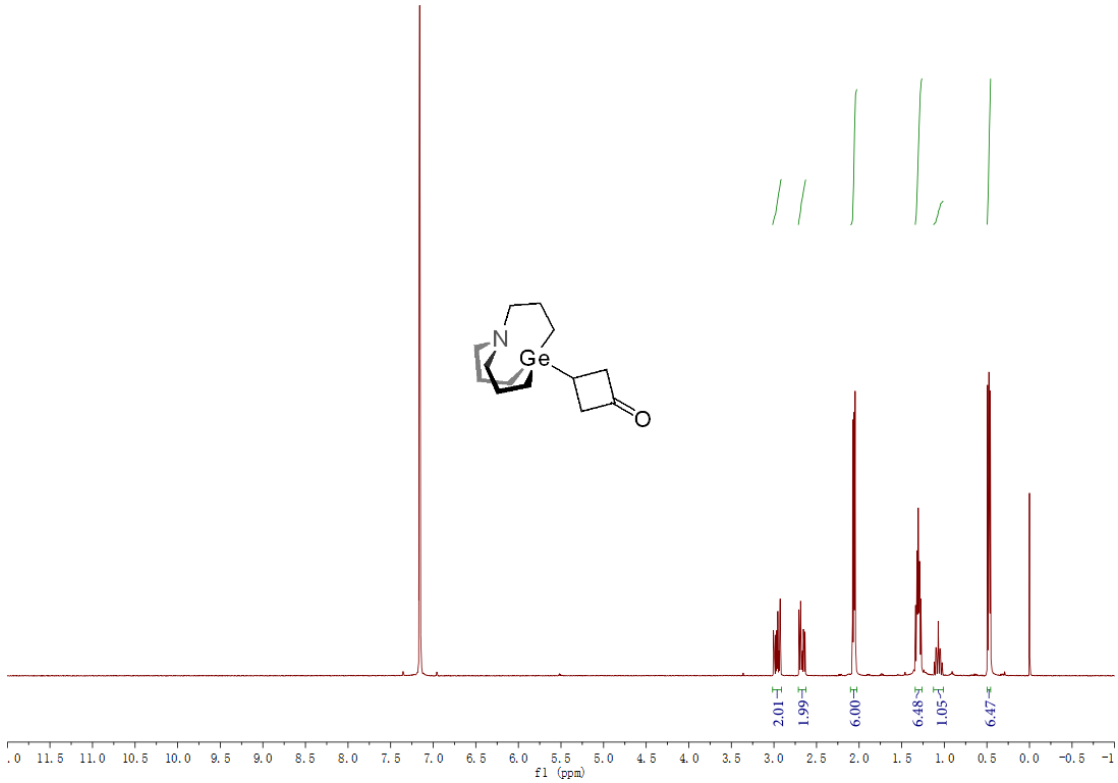

53.9
23.9
20.0
19.4
9.2
N
Ge
f1 (ppm)

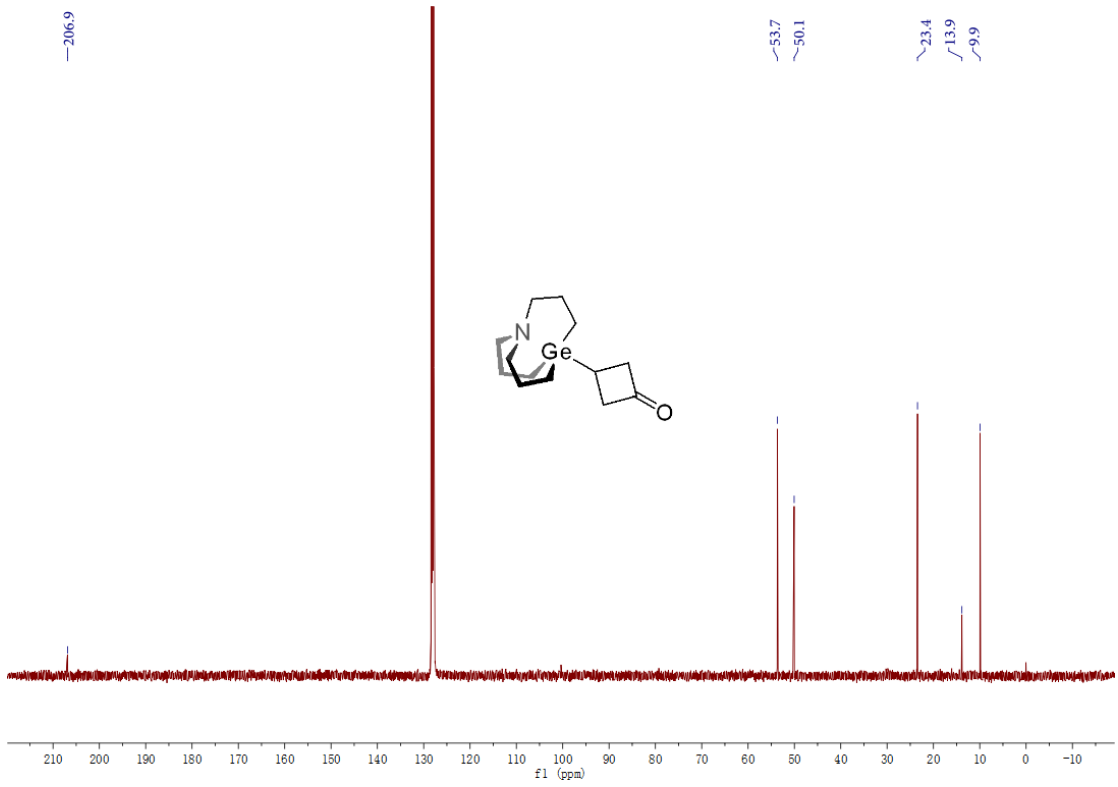

N
Ge
6.00
15.61
6.25
6.07
1.10
f1 (ppm)

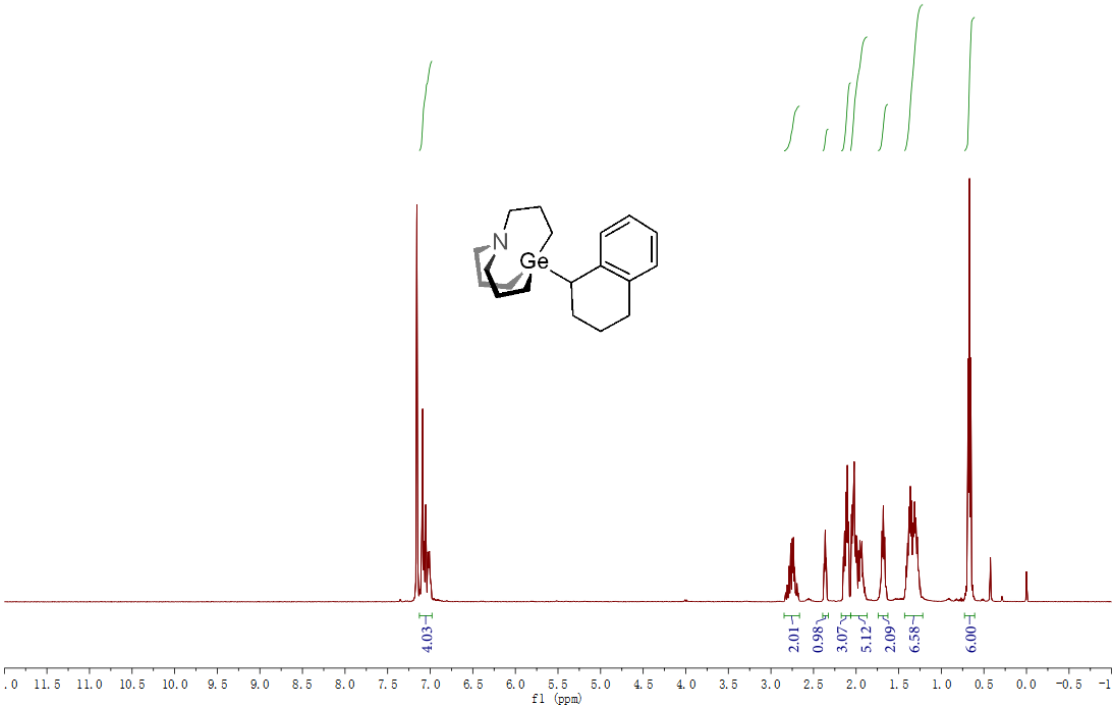

54.1
33.9
32.2
30.6
24.1
24.0
23.7
14.5
14.3
11.1
N
Ge
f1 (ppm)

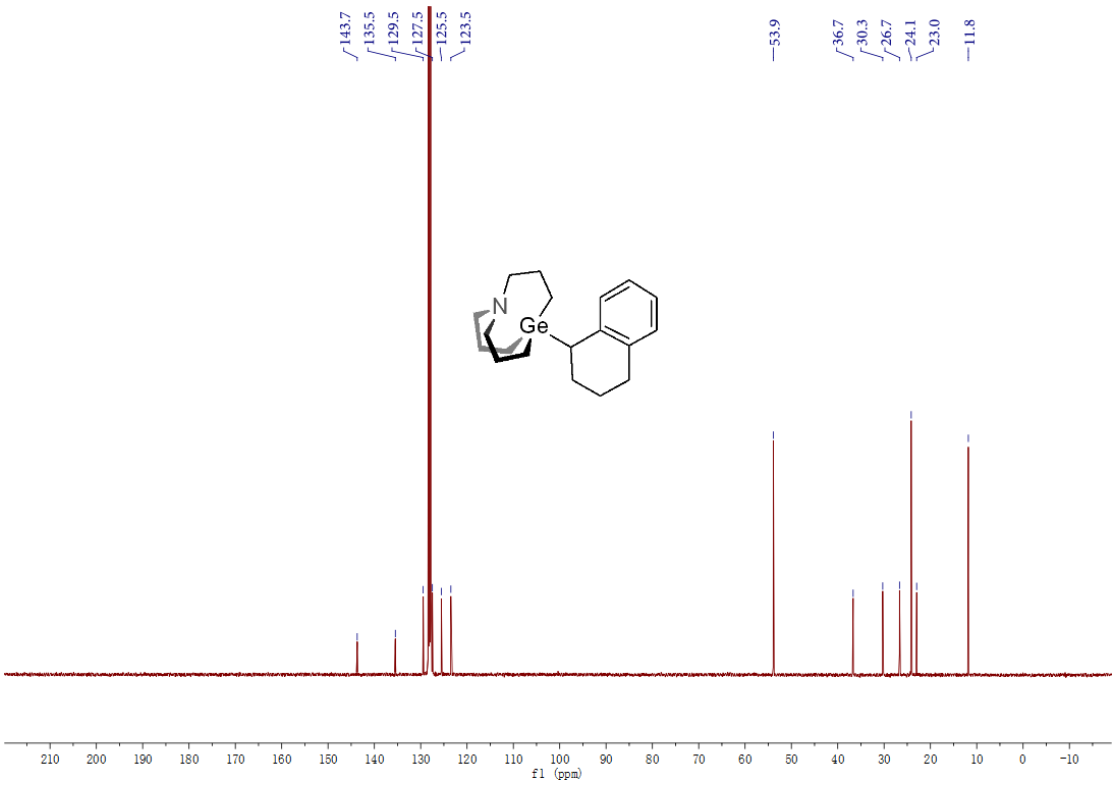

N
Ge
2.21
2.14
0.99
6.32
3.26
6.74
3.00
6.16
f1 (ppm)

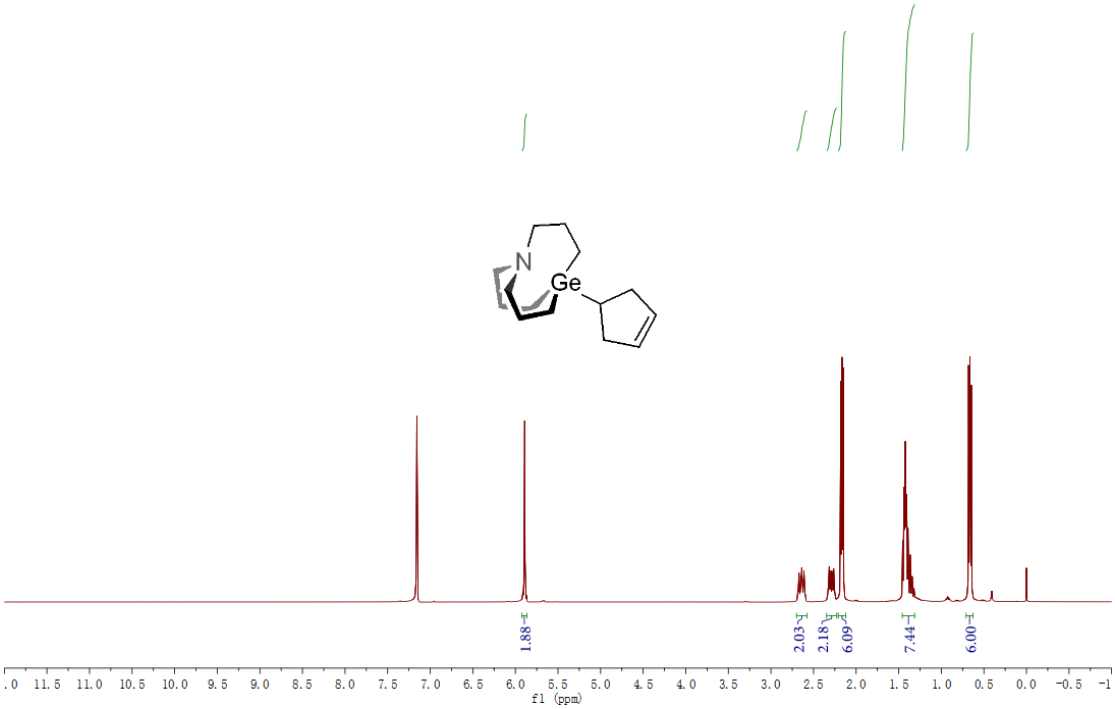

147.2
127.7
123.7
53.7
45.4
24.2
23.9
15.1
10.3
N
Ge
f1 (ppm)

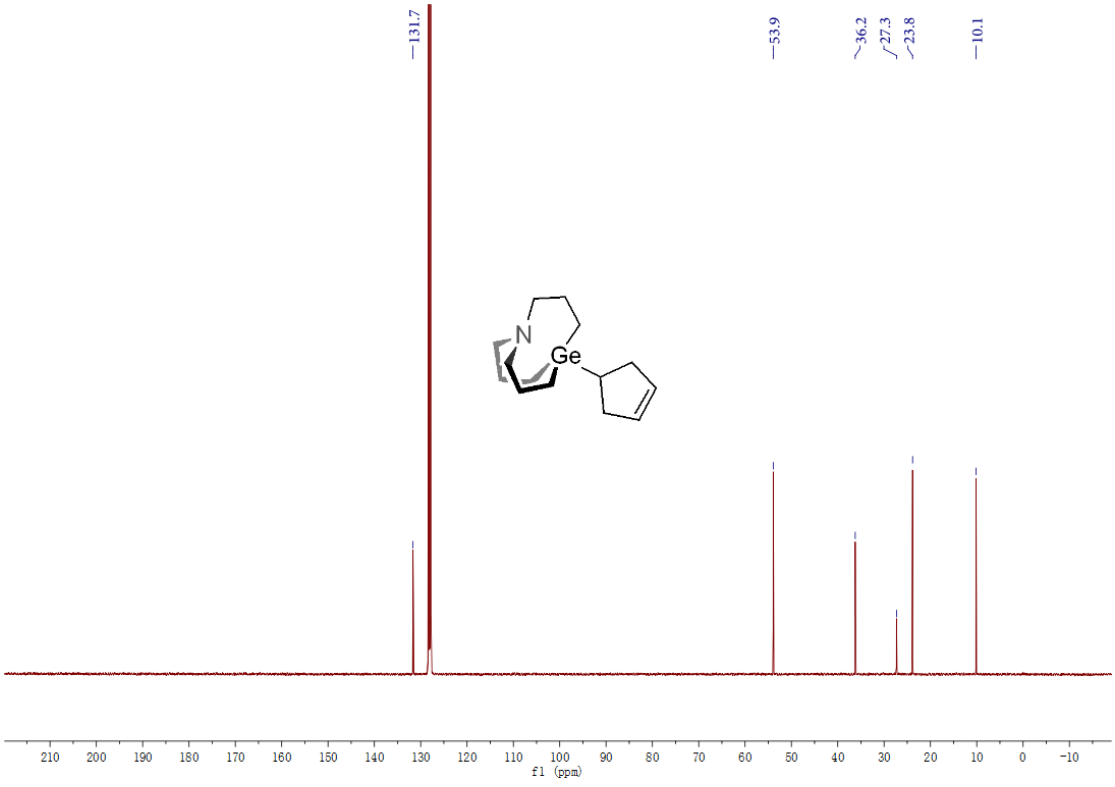

N
Ge
O
2.01
1.99
6.00
6.48
1.05
6.47
f1 (ppm)

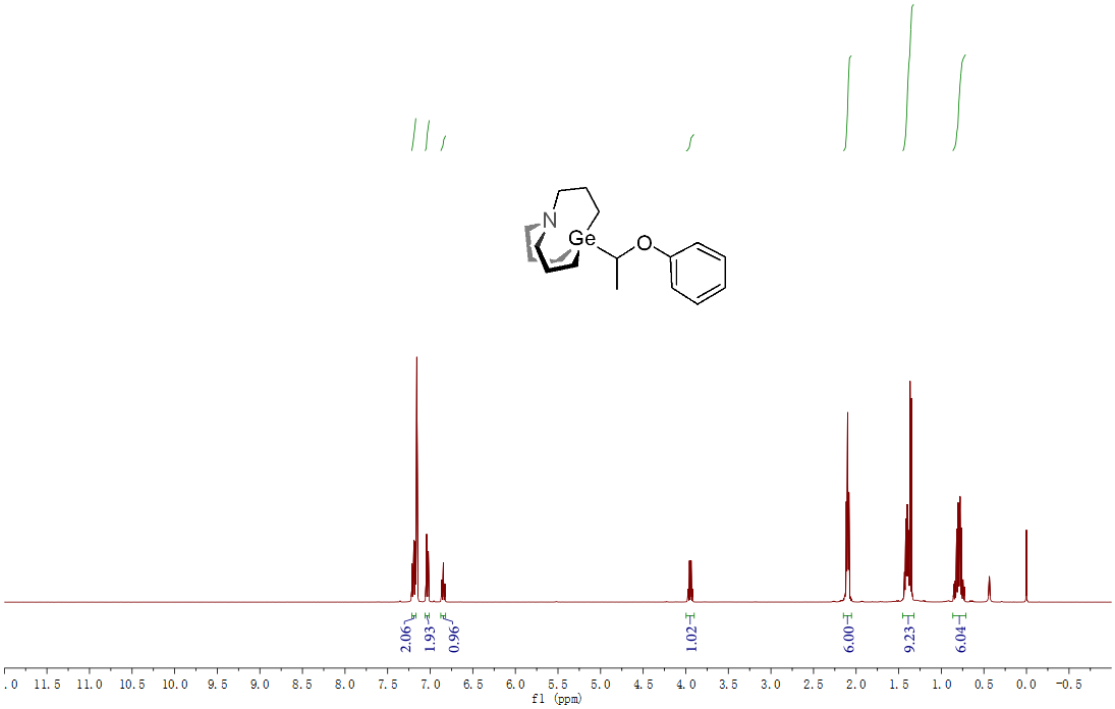

206.9
53.7
50.1
23.4
13.9
9.9
N
Ge
O
f1 (ppm)

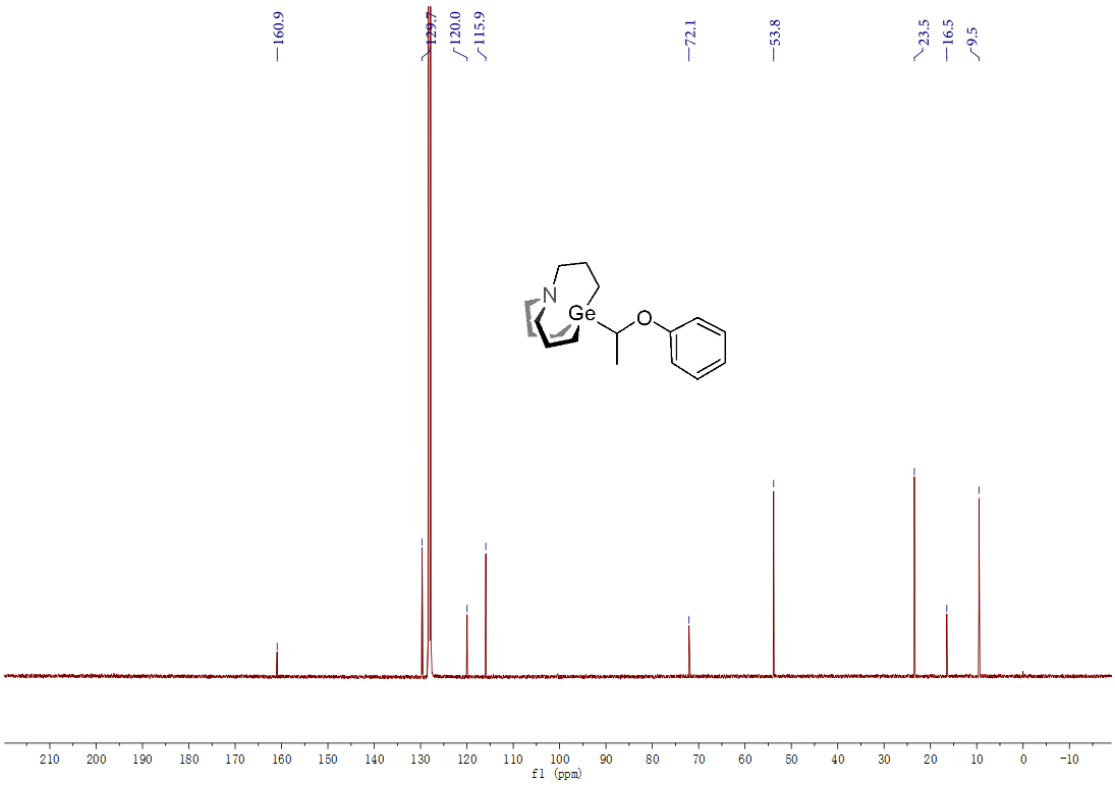

N
Ge
4.03
2.01
0.98
3.07
5.12
2.09
6.58
6.00
f1 (ppm)

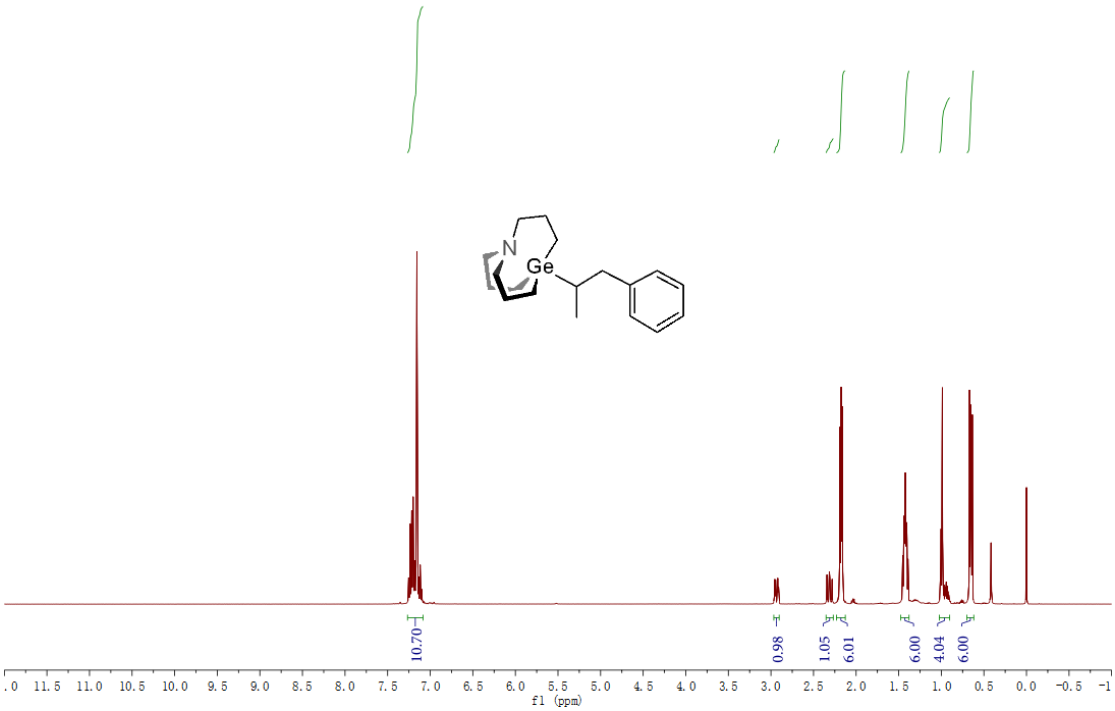

143.7
135.5
129.5
127.5
125.5
123.5
53.9
36.7
30.3
26.7
24.1
23.0
11.8
N
Ge
f1 (ppm)

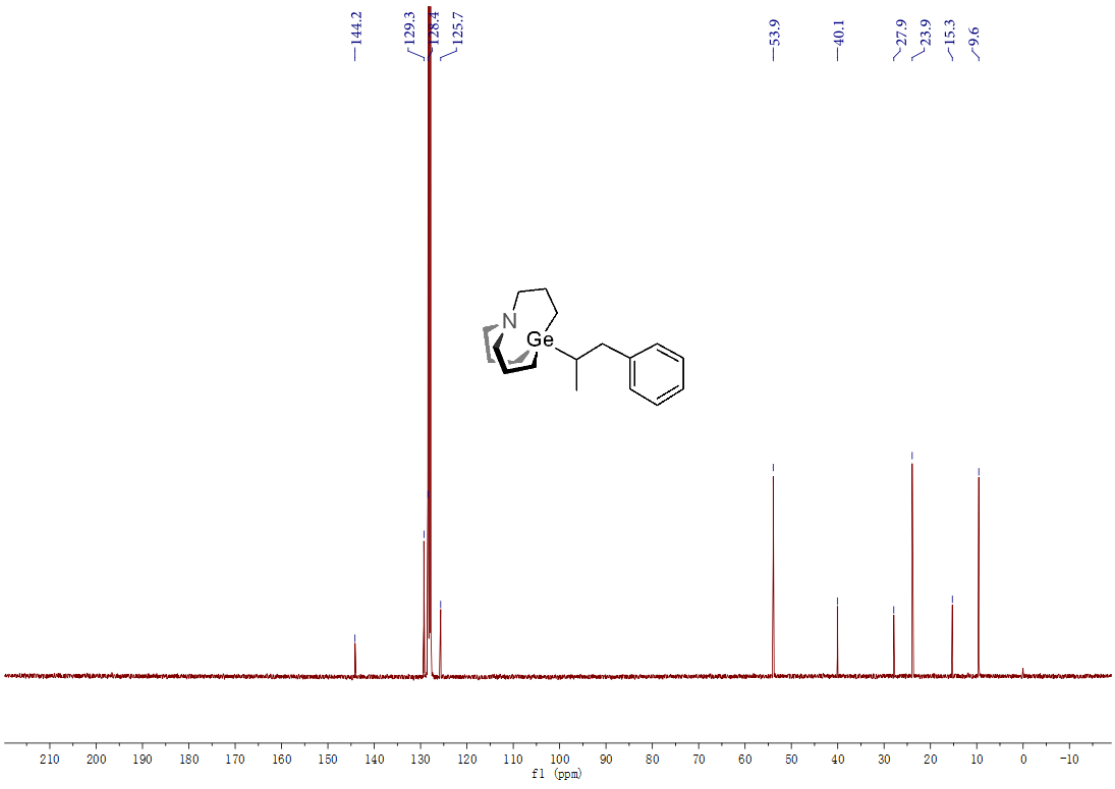

N
Ge
1.88
2.03
2.18
6.09
7.44
6.00
f1 (ppm)

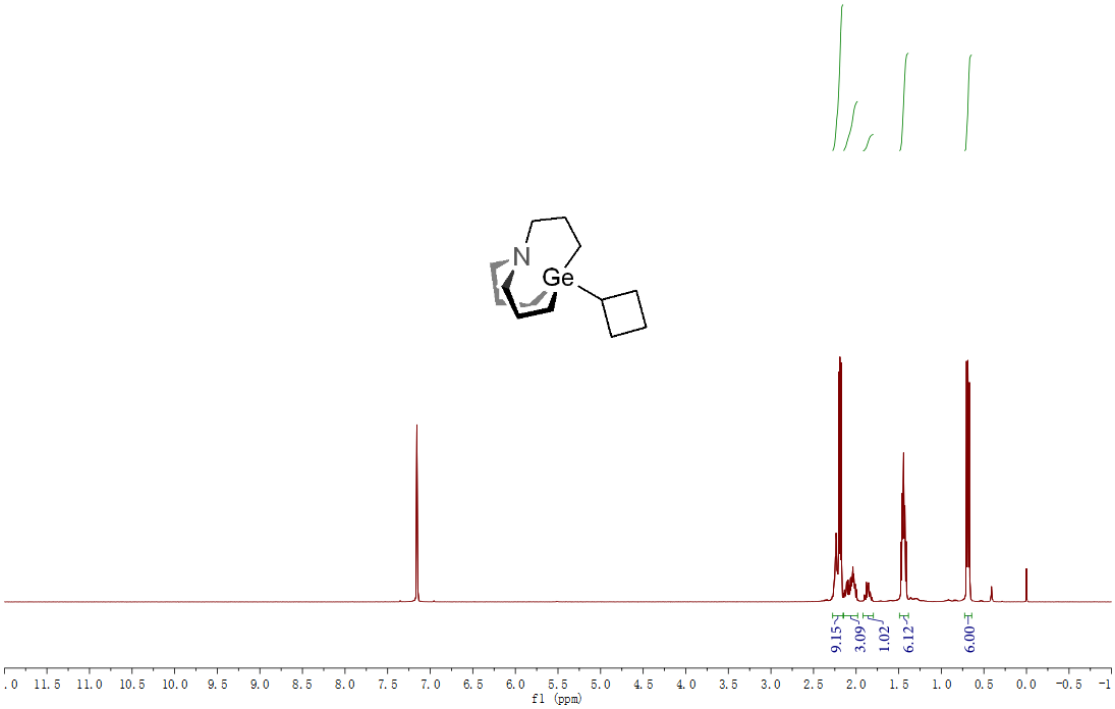

131.7
53.9
36.2
27.3
23.8
10.1
N
Ge
f1 (ppm)

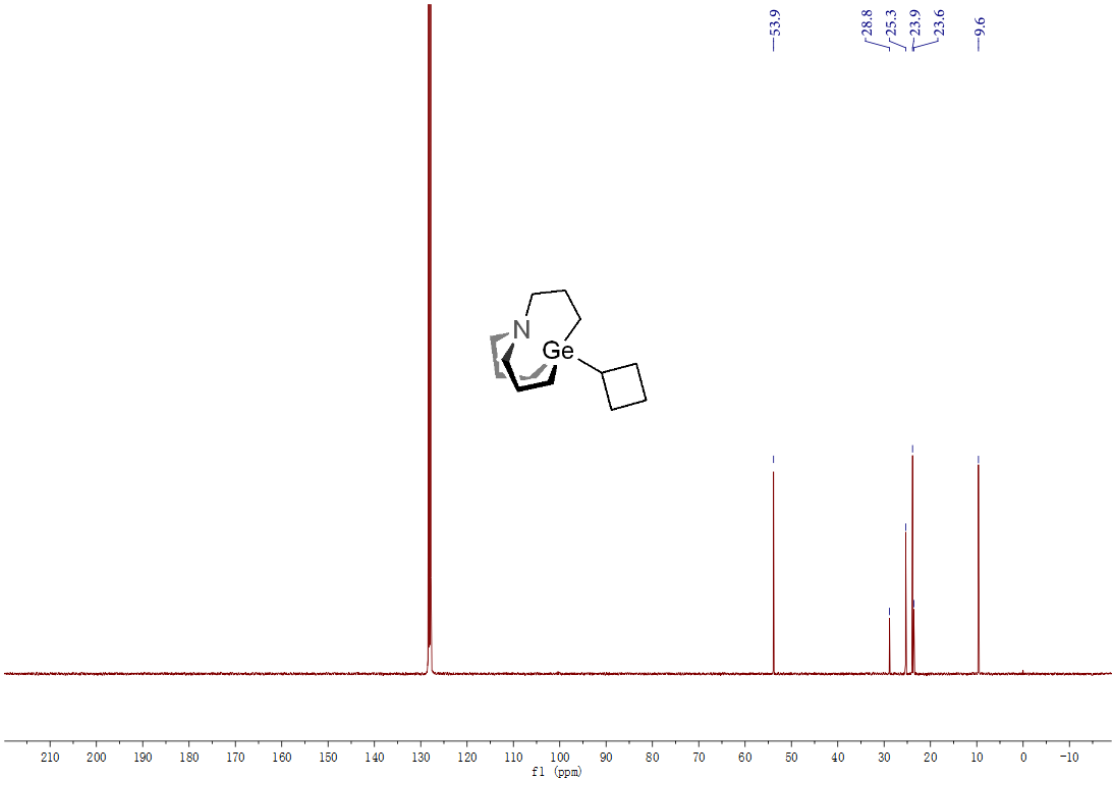

N
Ge
O
2.06
1.93
0.96
1.02
6.00
9.23
6.04
f1 (ppm)

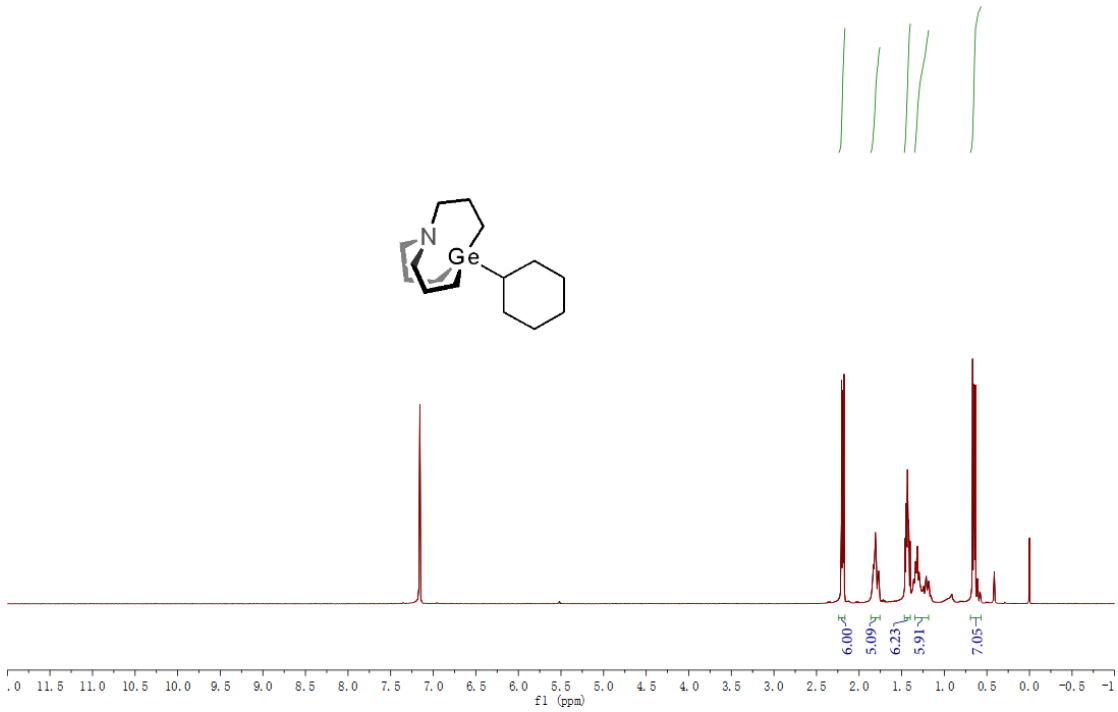

160.9
129.7
120.0
115.9
72.1
53.8
23.5
16.5
9.5
N
Ge
O
f1 (ppm)

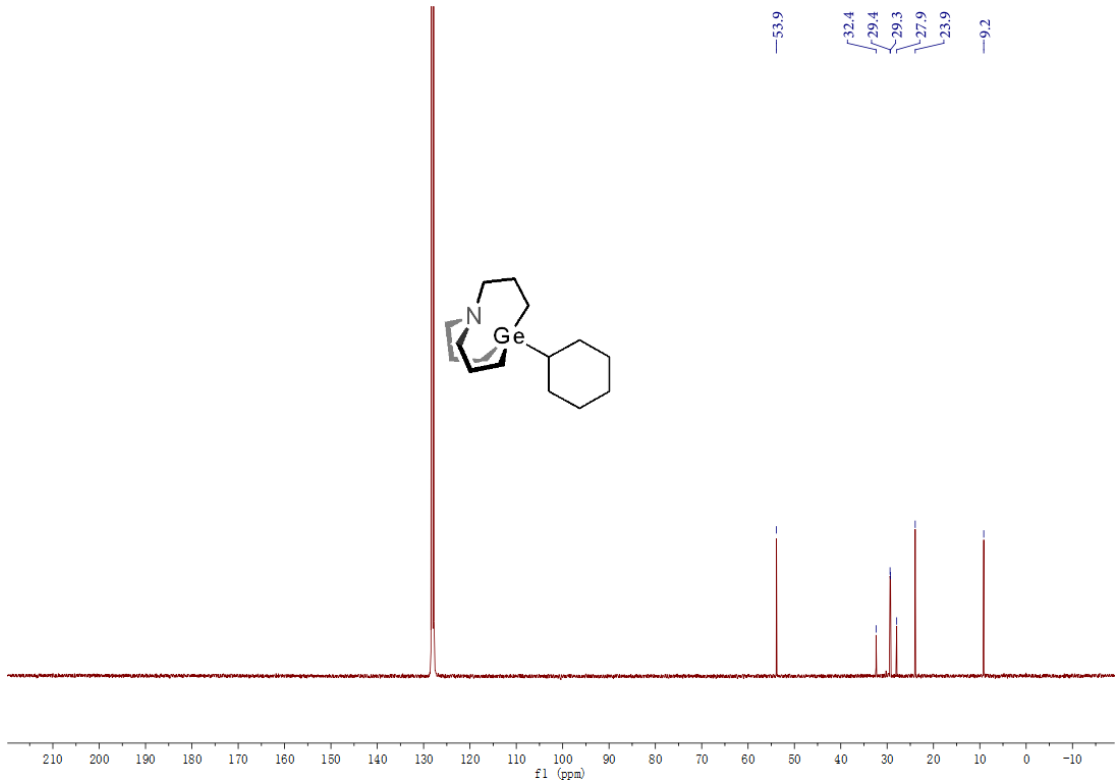

N
Ge
10.70
0.98
1.05
6.01
6.00
4.04
6.00
f1 (ppm)

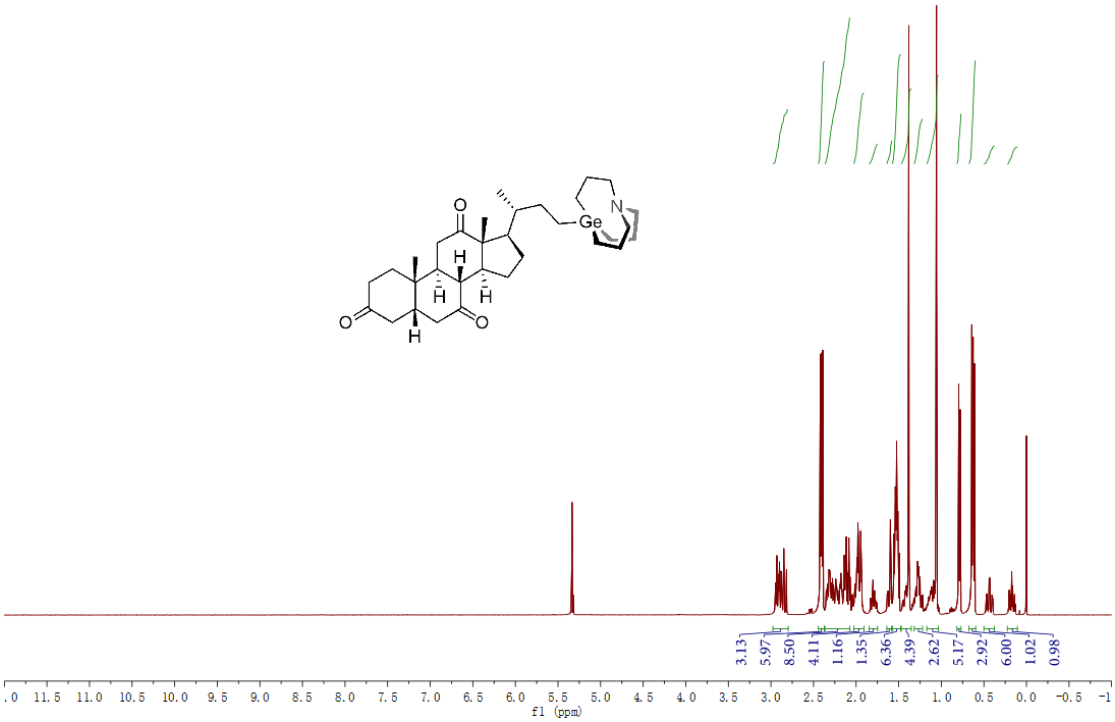

144.2
129.3
128.4
125.7
53.9
40.1
27.9
23.9
15.3
9.6
N
Ge
f1 (ppm)


N
Ge
9.15
3.09
1.02
6.12
6.00
f1 (ppm)

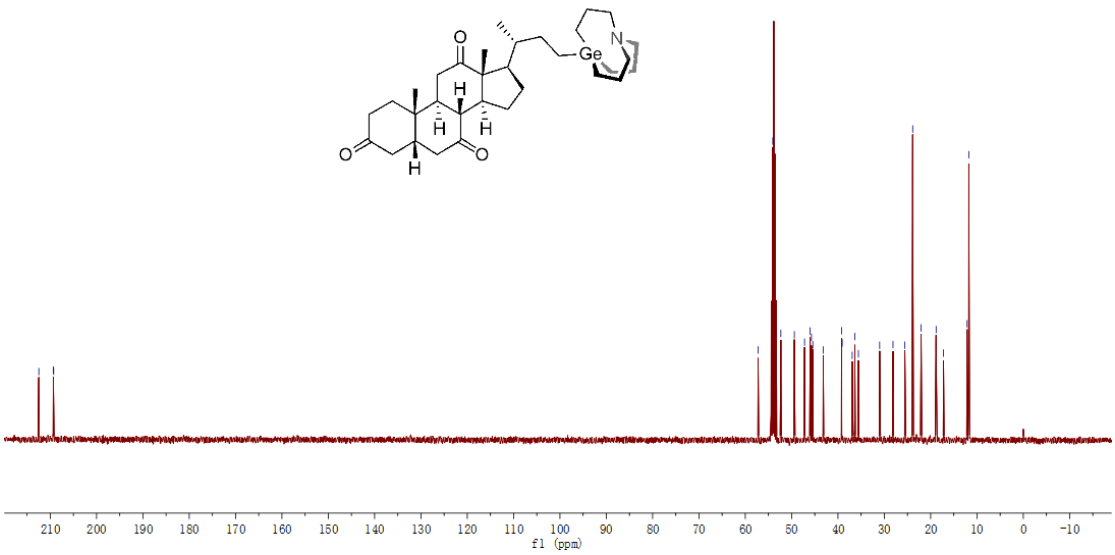

53.9
28.8
25.3
23.9
23.6
9.6
N
Ge
f1 (ppm)

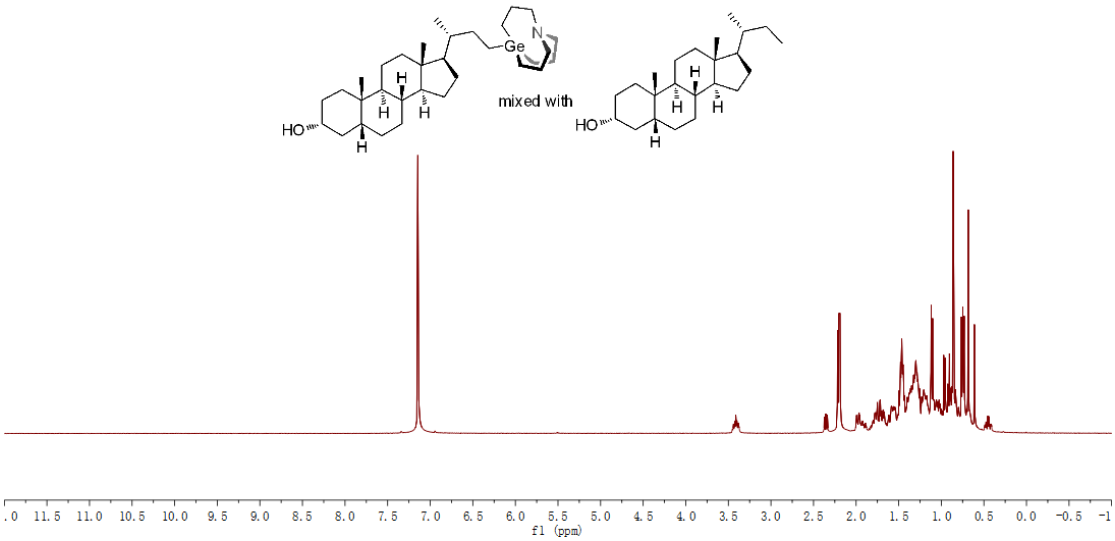

N
Ge
6.00
5.09
6.23
5.91
7.05
f1 (ppm)

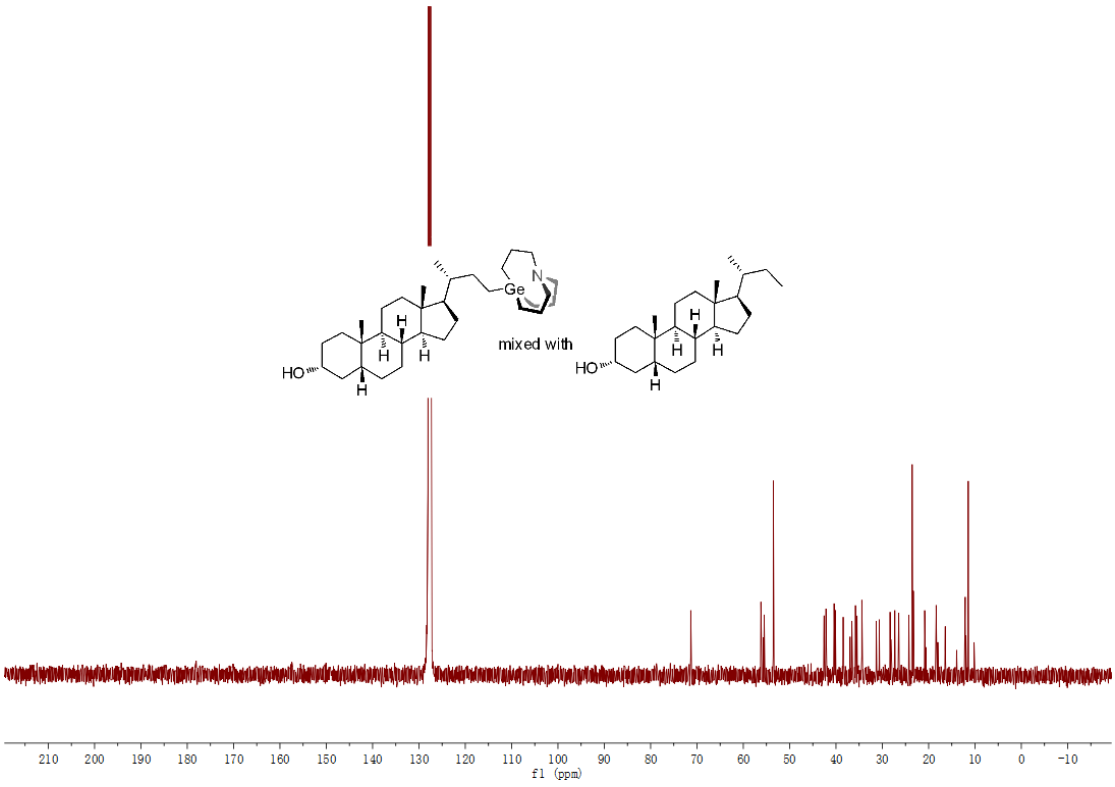

53.9
32.4
29.4
29.3
27.9
23.9
9.2
N
Ge
f1 (ppm)

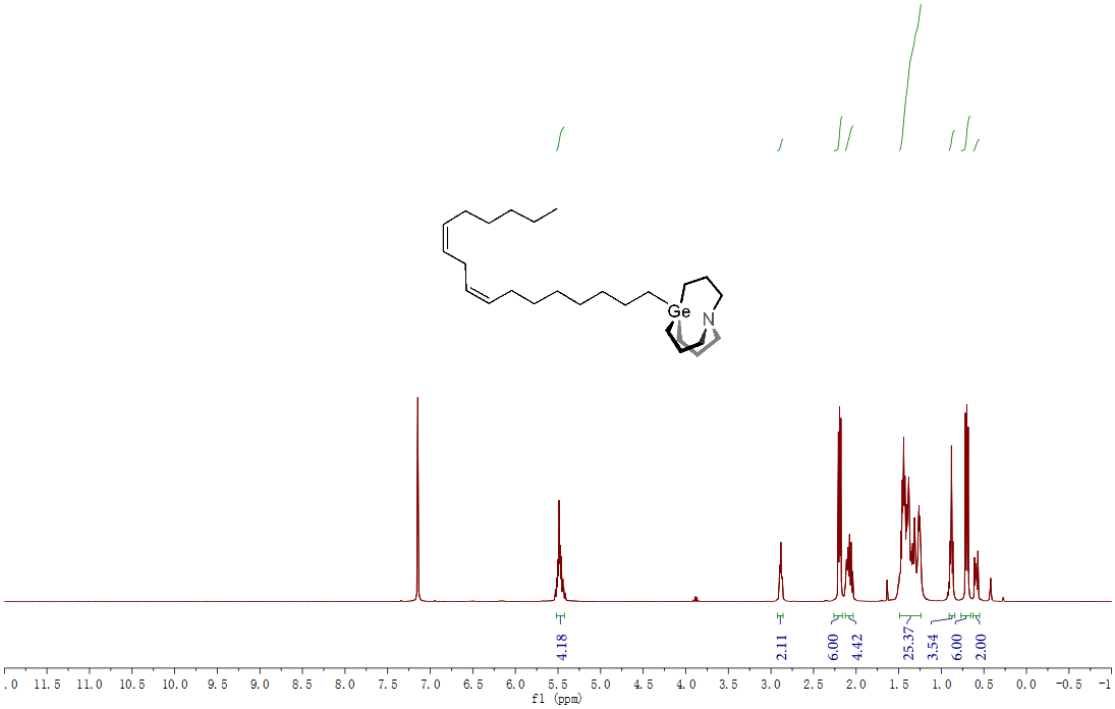

O
Ge
N
H
H
H
O
O
H
3.13
5.97
8.50
4.11
1.16
1.35
6.36
4.39
2.62
5.17
2.92
6.00
1.02
0.98
f1 (ppm)

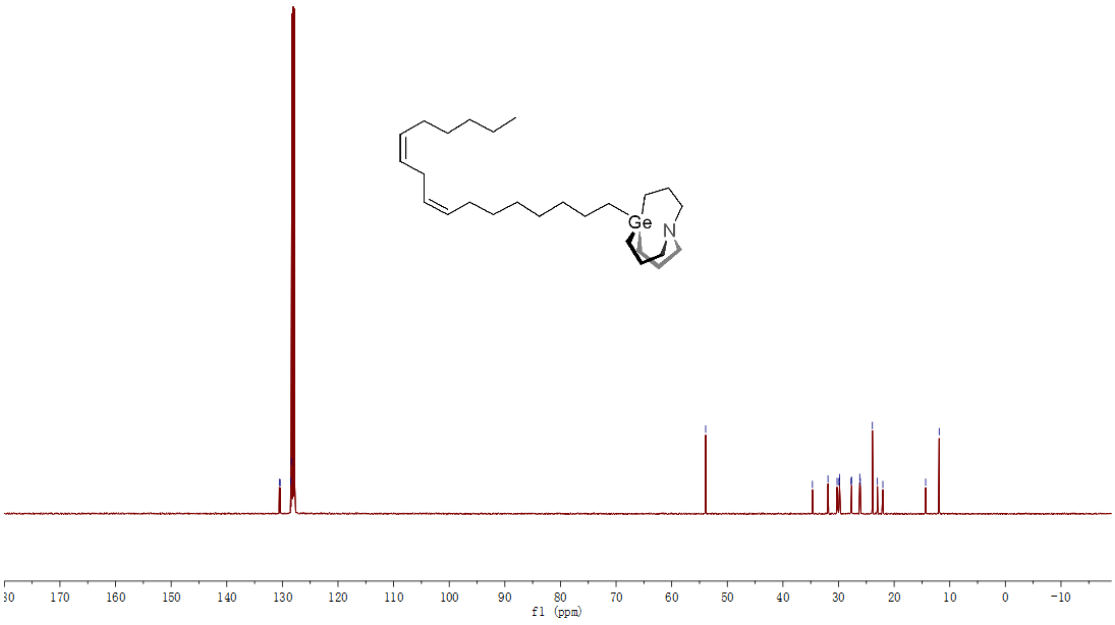

212.5
209.3
209.3
57.2
54.1
52.3
49.4
47.2
46.0
45.7
45.4
43.2
39.2
39.1
36.9
36.4
35.6
31.0
28.1
25.6
23.9
22.1
18.8
17.2
12.1
11.8

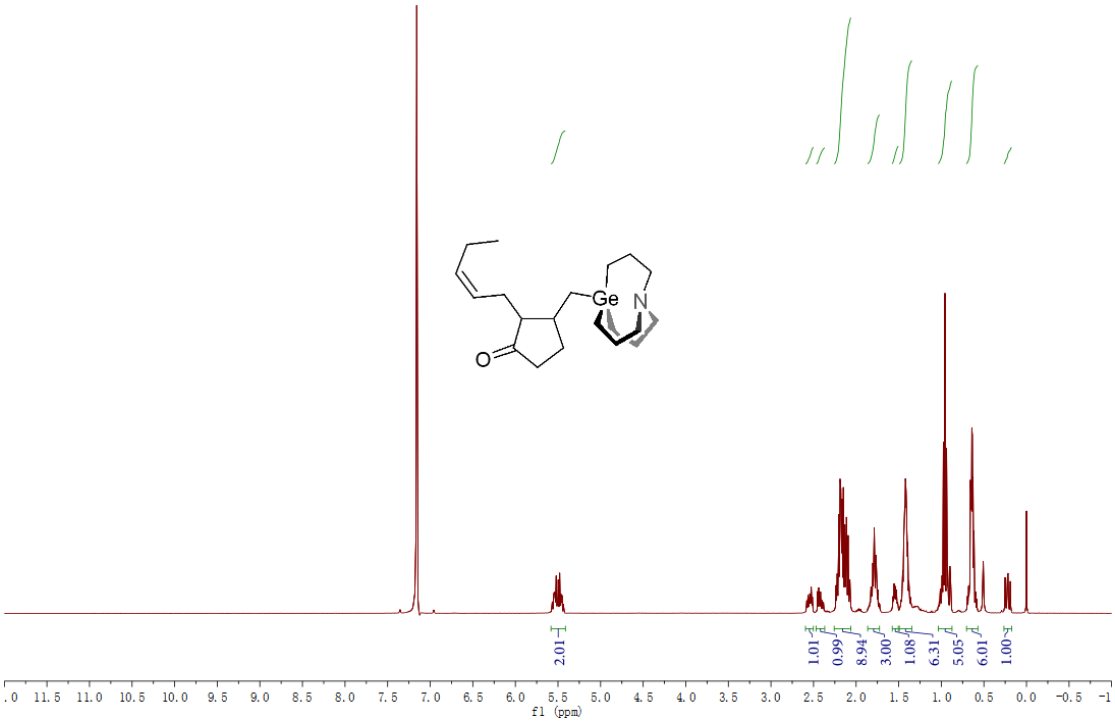

O
Ge
N
H
H
H
O
O
H
f1 (ppm)

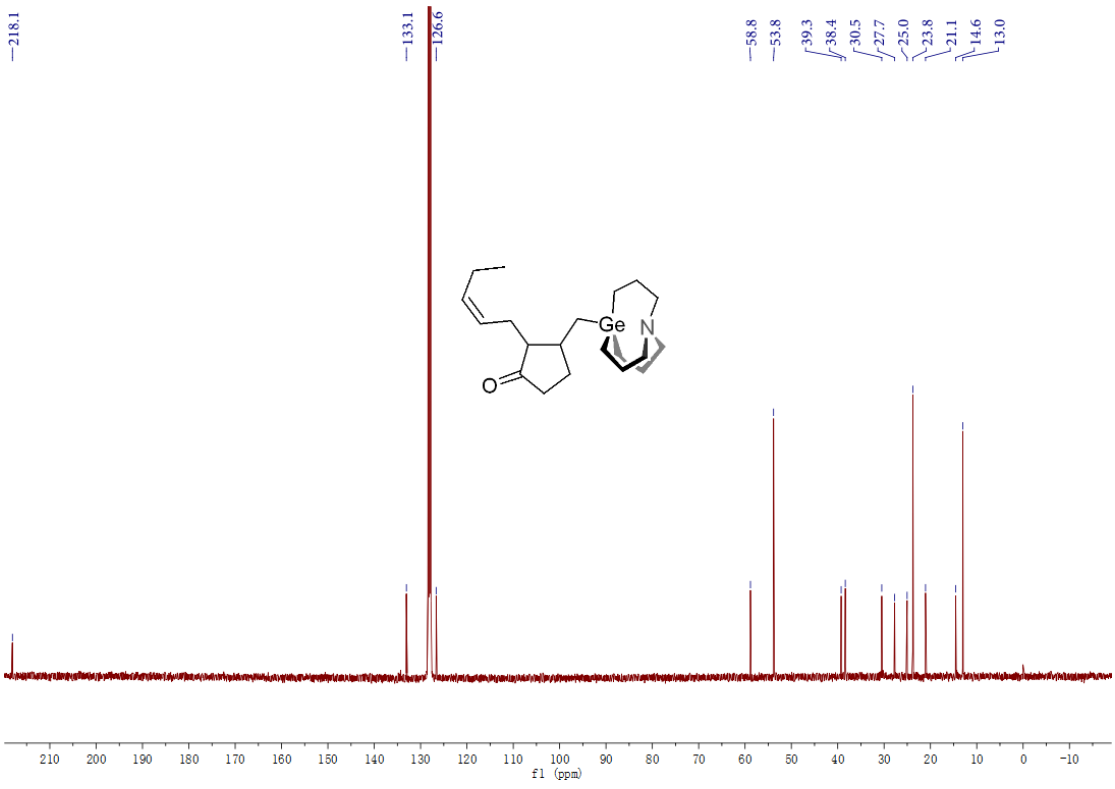

Ge
N
HO
H
mixed with
HO
H
f1 (ppm)

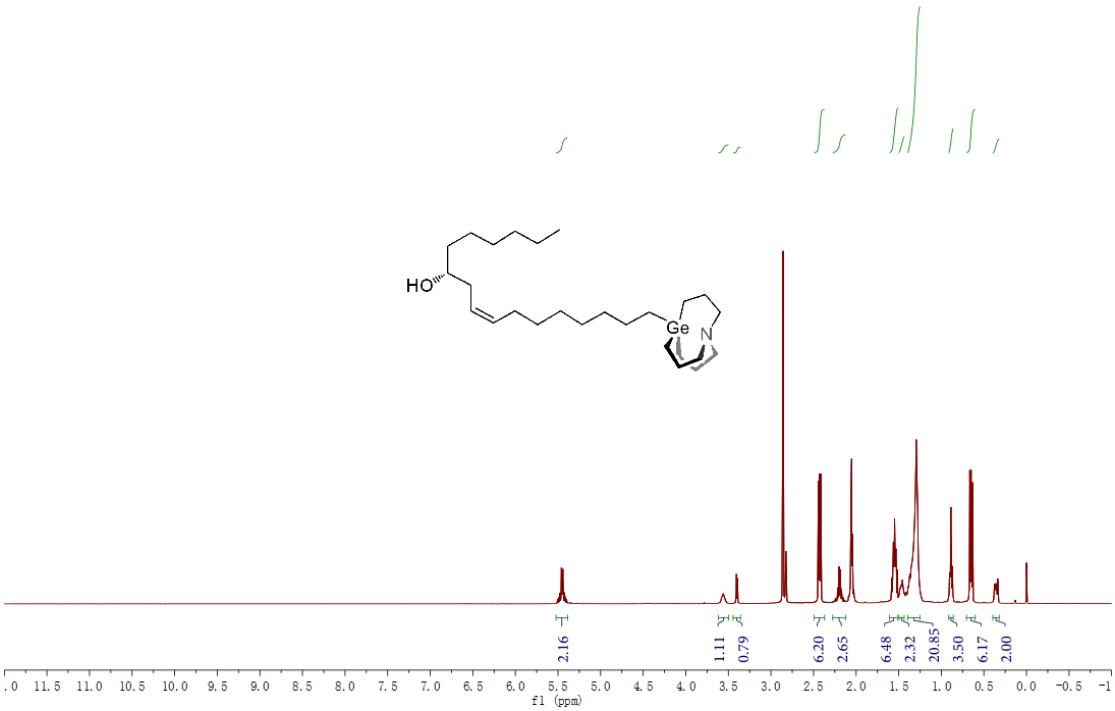

Ge
N
HO
H
mixed with
HO
H
f1 (ppm)

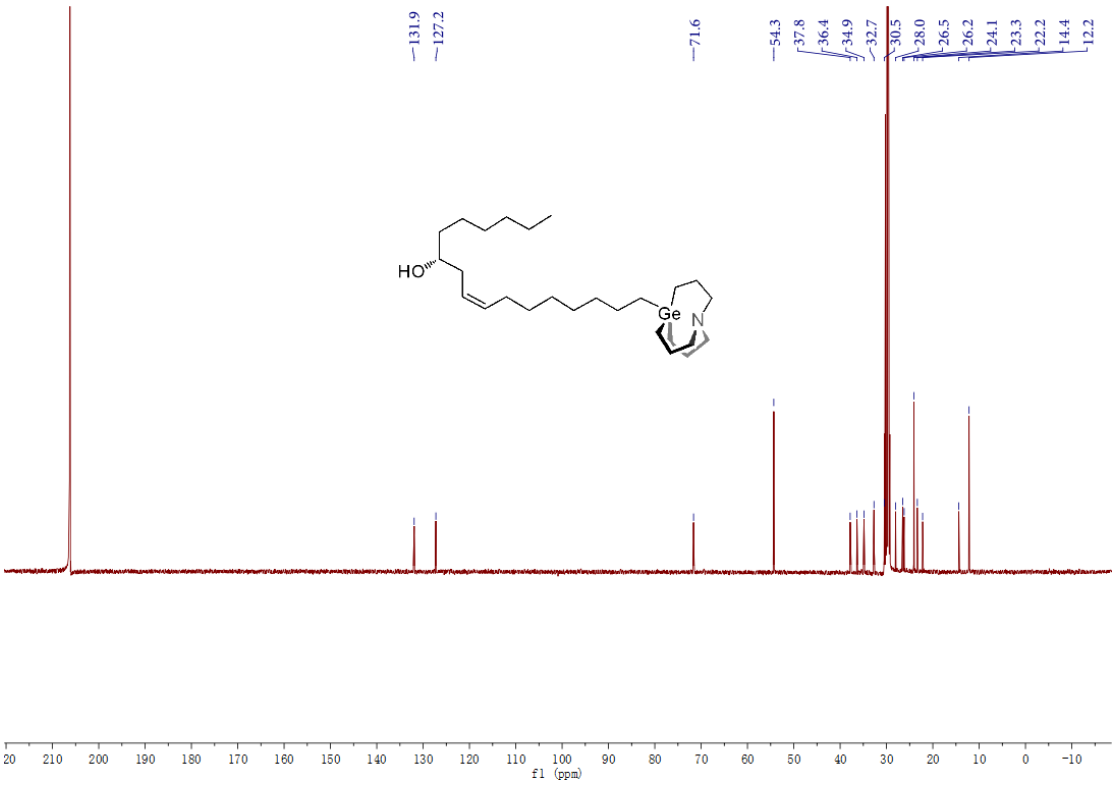

Ge
N
4.18
2.11
6.00
4.42
25.37
3.54
6.00
2.00
f1 (ppm)

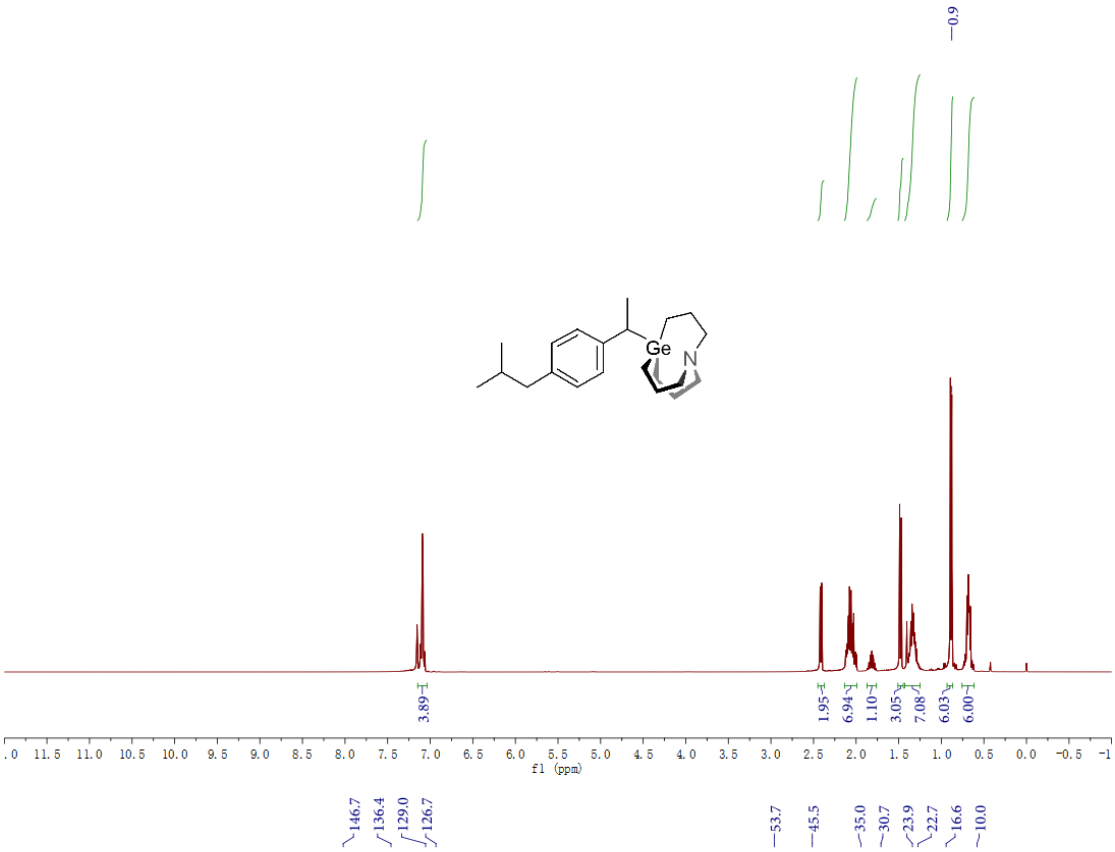

130.6
130.4
128.5
128.4
53.9
34.7
31.9
30.3
29.9
29.9
29.8
27.8
27.6
26.2
26.1
23.9
23.0
22.0
14.3
11.9
Ge
N
f1 (ppm)

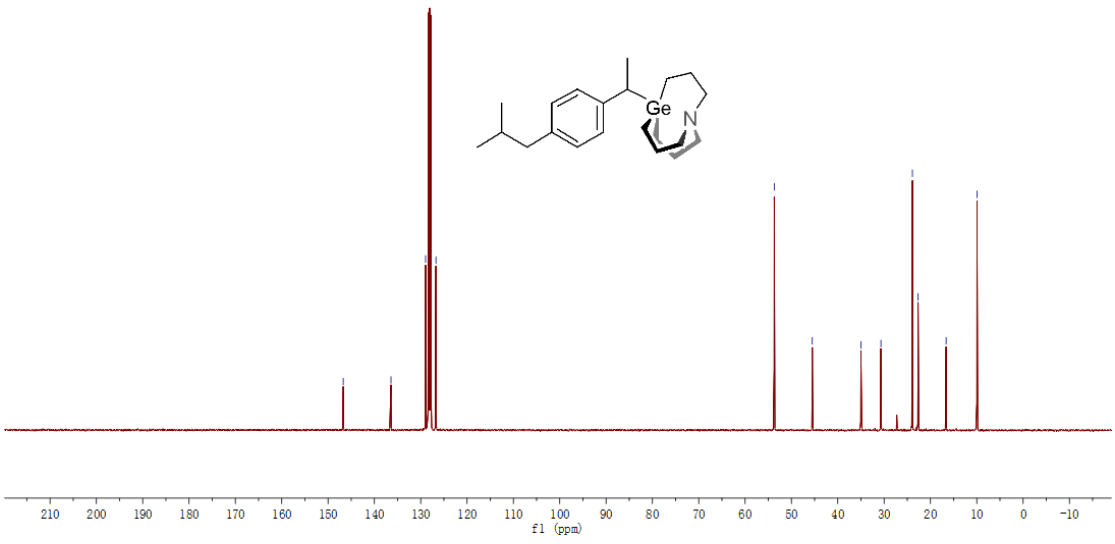

Ge
N
O
2.01
1.01
0.99
8.94
3.00
1.08
6.31
5.05
6.01
1.00
f1 (ppm)

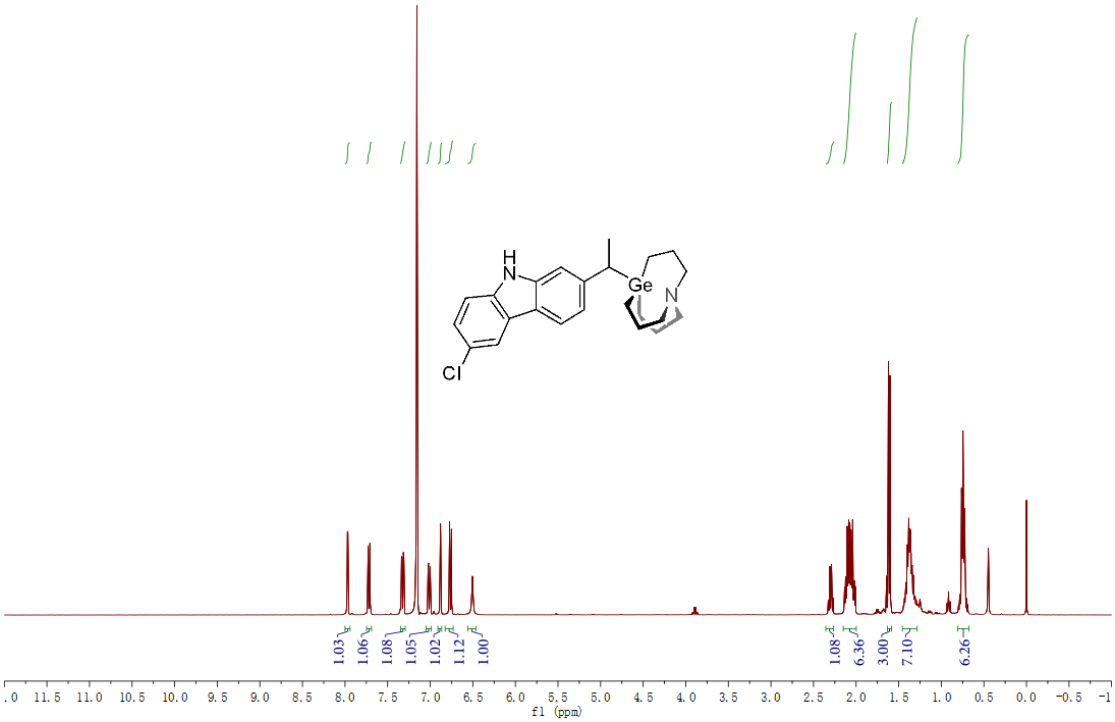

218.1
133.1
126.6
58.8
53.8
39.3
38.4
30.5
27.7
25.0
23.8
21.1
14.6
13.0
Ge
N
O
f1 (ppm)

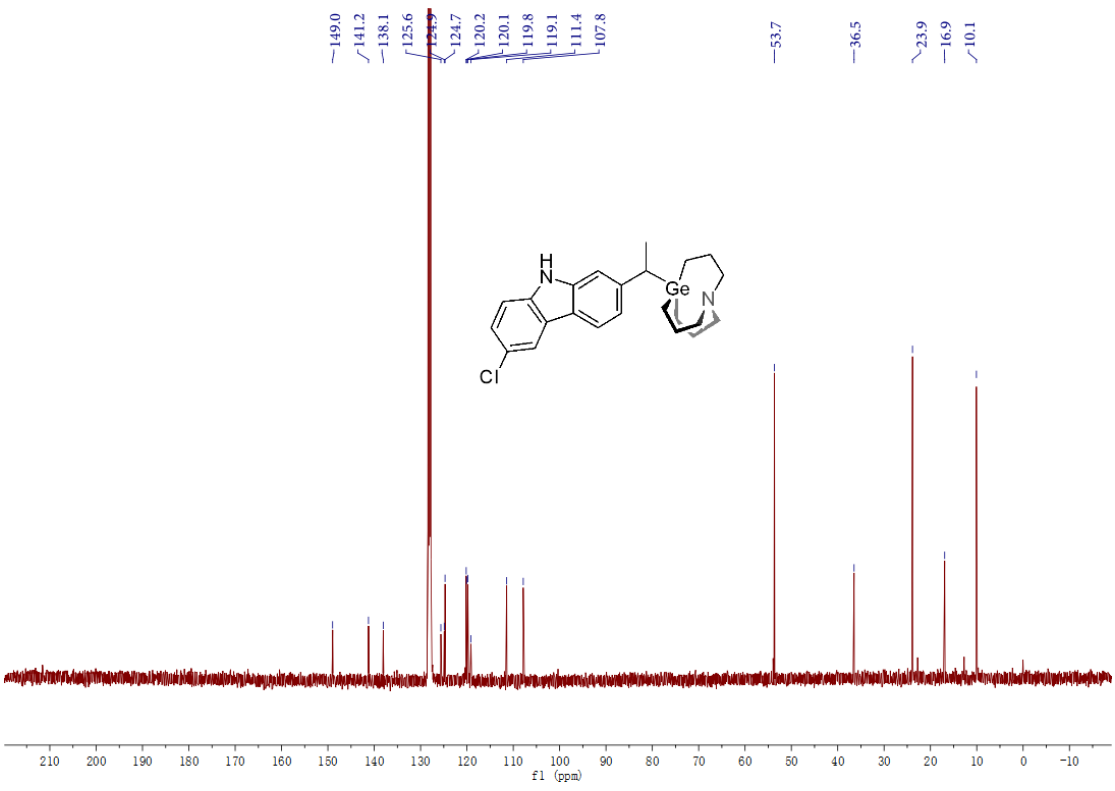

HO
Ge
N
2.16
1.11
0.79
6.20
2.65
6.48
2.32
20.85
3.50
6.17
2.00
f1 (ppm)

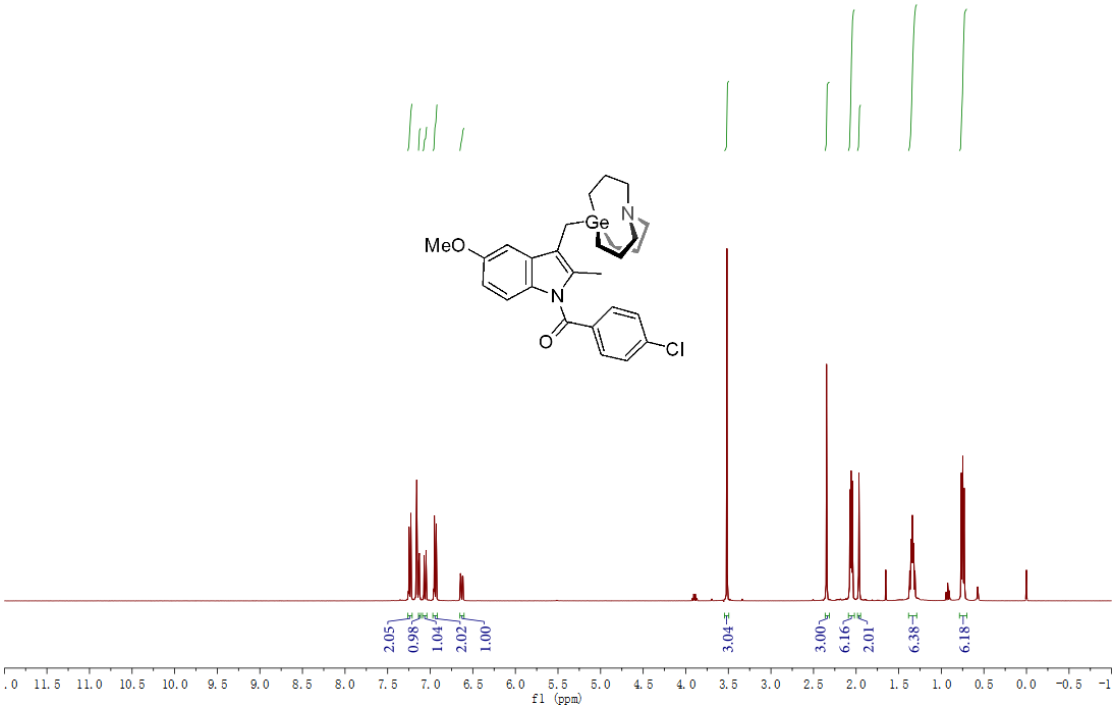

131.9
127.2
71.6
54.3
37.8
36.4
34.9
32.7
30.5
28.0
26.5
26.2
24.1
23.3
22.2
14.4
12.2
HO
Ge
N
f1 (ppm)

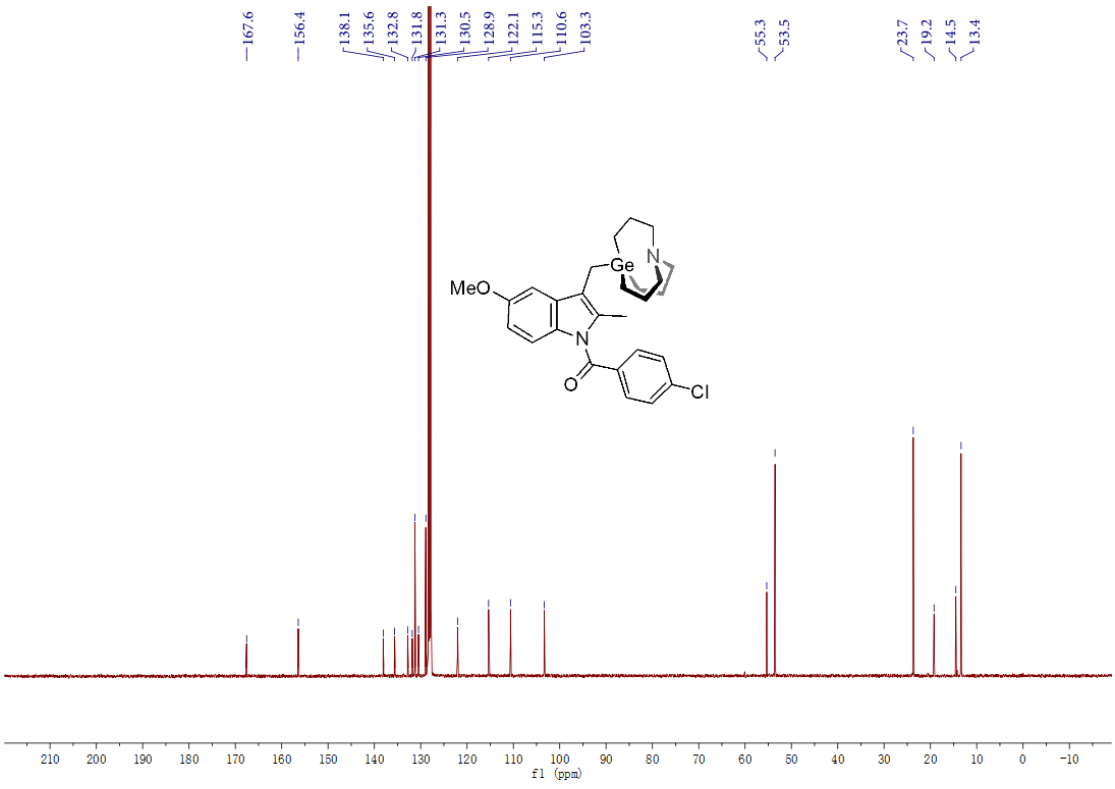

0.9
Ge
N
3.89
1.95
6.94
1.10
3.05
7.08
6.03
6.00
f1 (ppm)

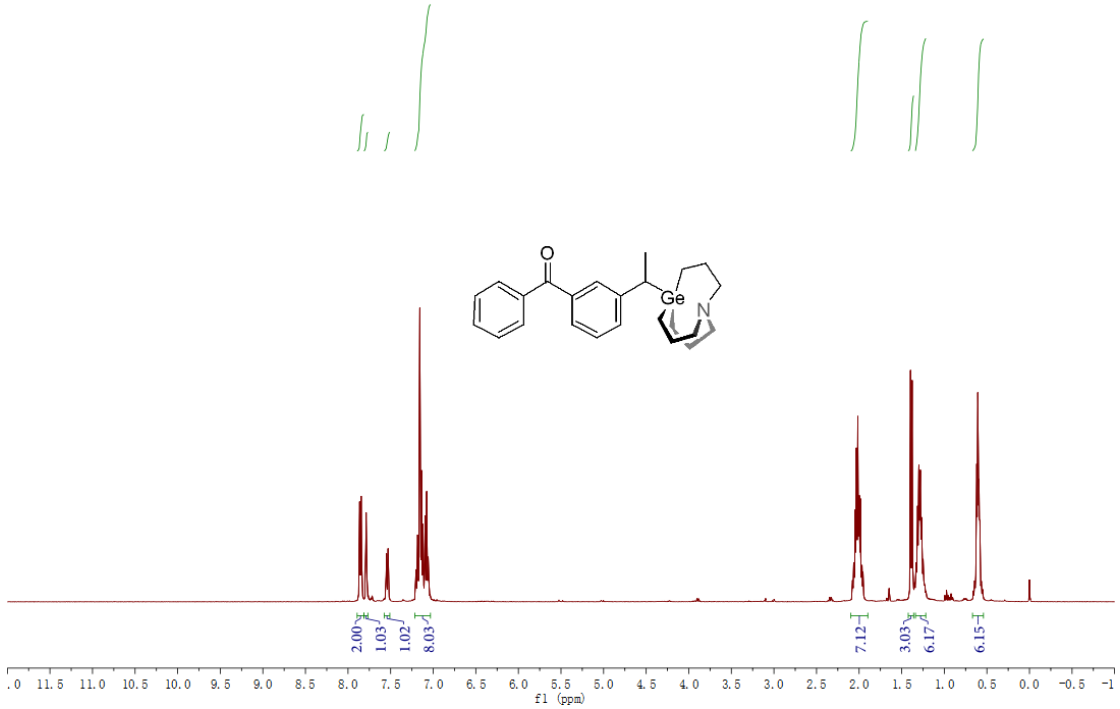

146.7
136.4
129.0
126.7
53.7
45.5
35.0
30.7
23.9
22.7
16.6
10.0
Ge
N
f1 (ppm)

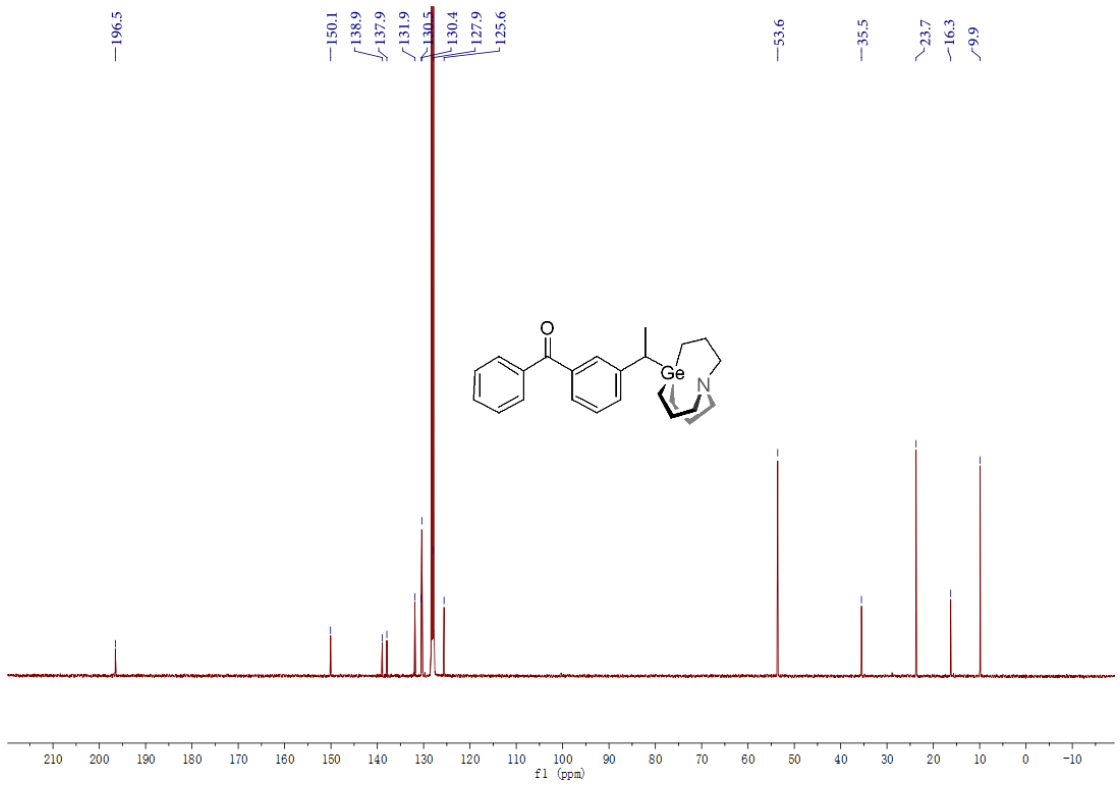

H
N
Ge
N
Cl
1.03
1.06
1.08
1.05
1.02
1.12
1.00
1.08
6.36
3.00
7.10
6.26
f1 (ppm)

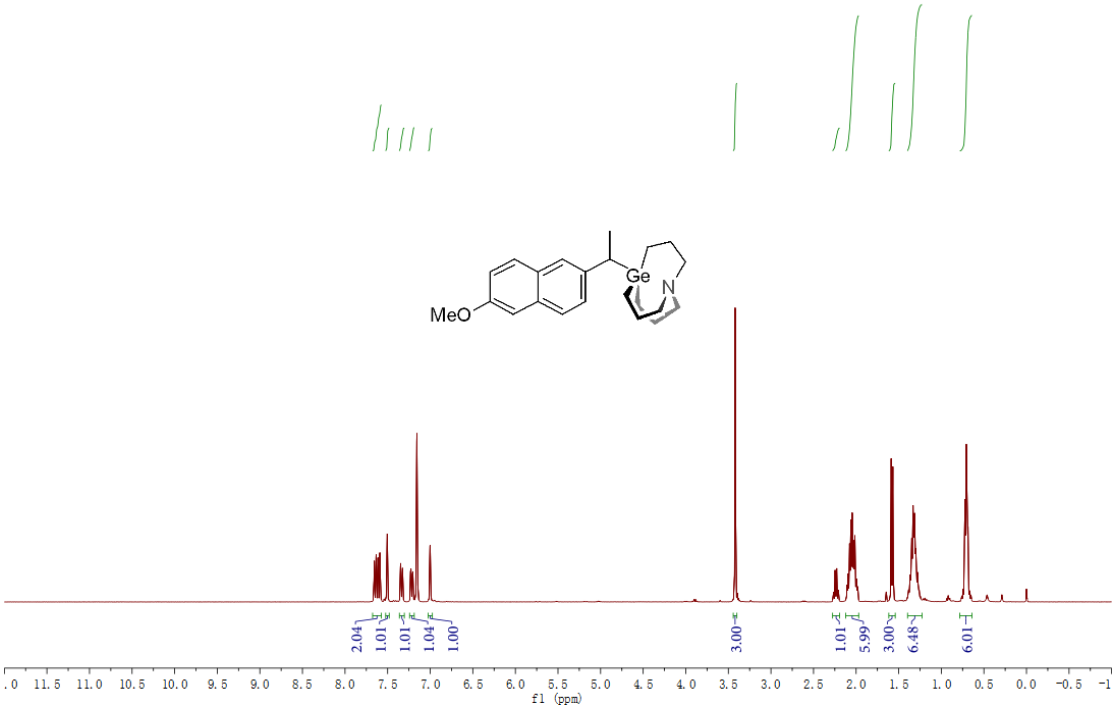

149.0
141.2
138.1
125.6
124.9
124.7
120.2
120.1
119.8
119.1
111.4
107.8
53.7
36.5
23.9
16.9
10.1
H
N
Ge
N
Cl
f1 (ppm)

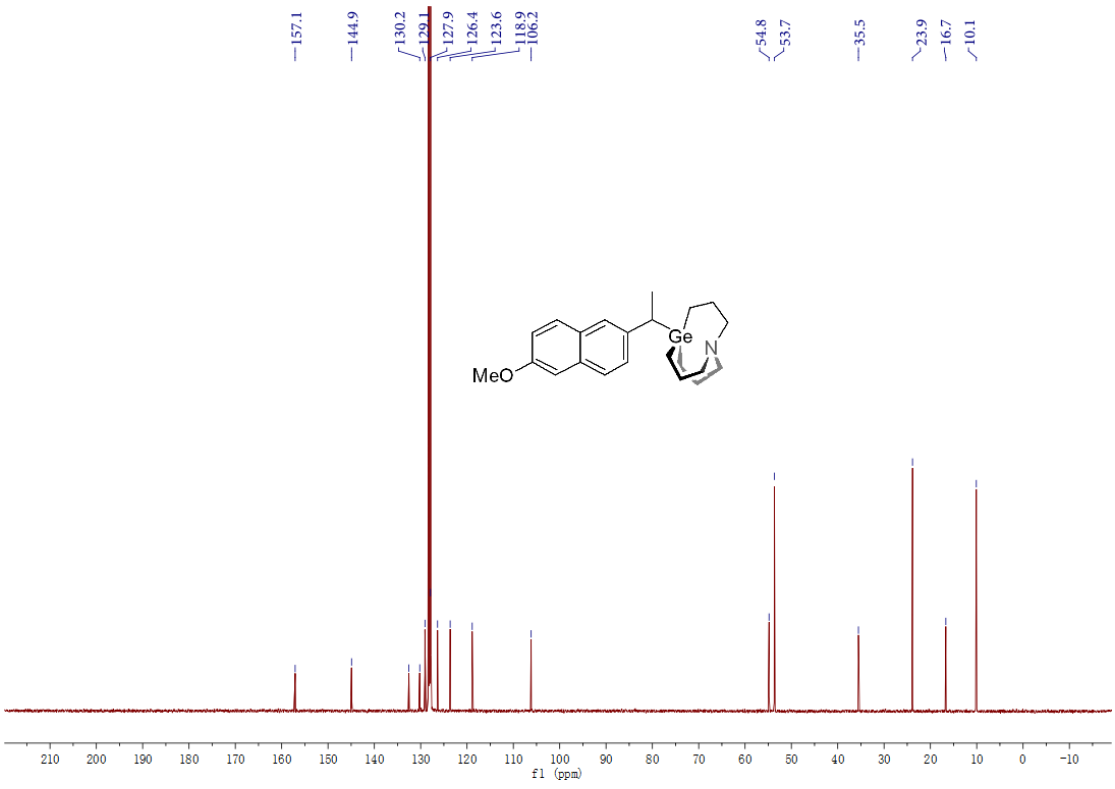

Ge
N
MeO
N
O
Cl
2.05
0.98
1.04
2.02
1.00
3.04
3.00
6.16
2.01
6.38
6.18
f1 (ppm)

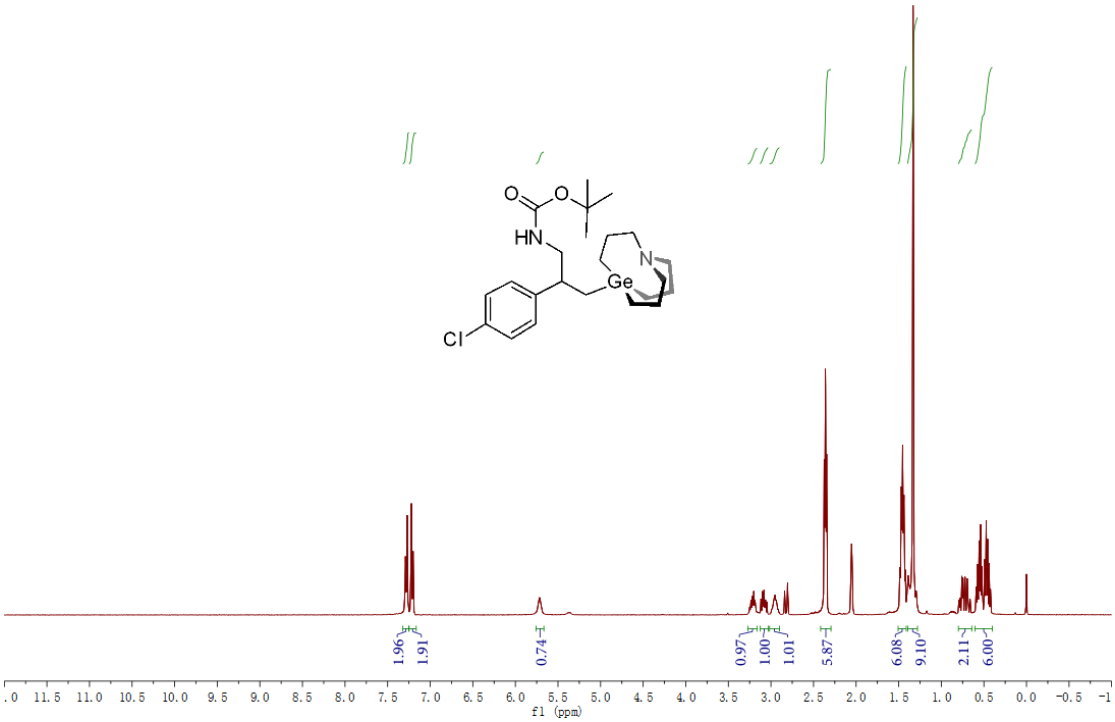

167.6
156.4
138.1
135.6
132.8
131.8
131.3
130.5
128.9
122.1
115.3
110.6
103.3
55.3
53.5
23.7
19.2
14.5
13.4
Ge
N
MeO
N
O
Cl
f1 (ppm)

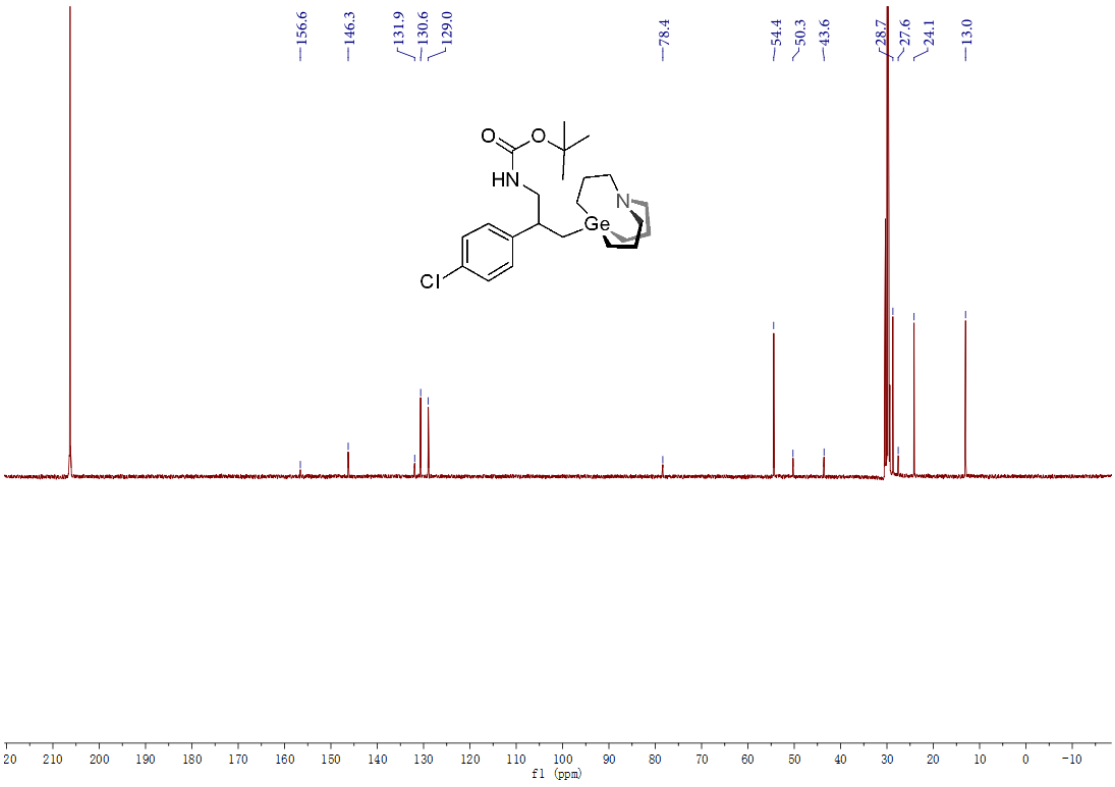

O
Ge
N
2.00
1.03
1.02
8.03
7.12
3.03
6.17
6.15
f1 (ppm)

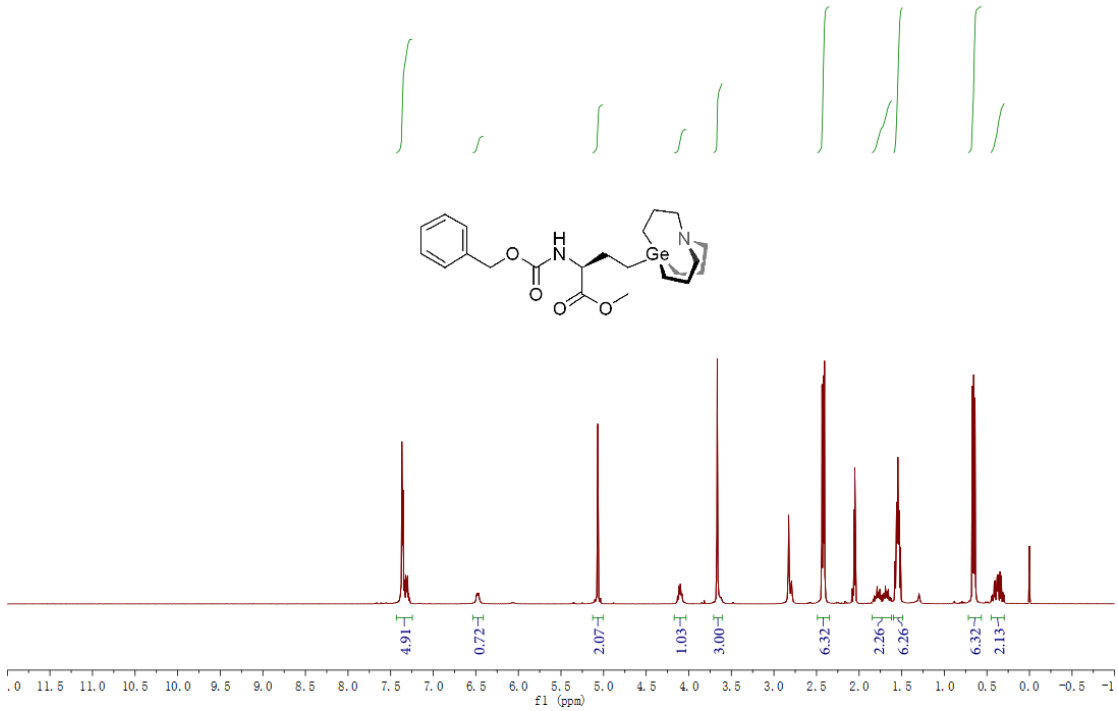

196.5
150.1
138.9
137.9
131.9
130.5
130.4
127.9
125.6
53.6
35.5
23.7
16.3
9.9
O
Ge
N
f1 (ppm)

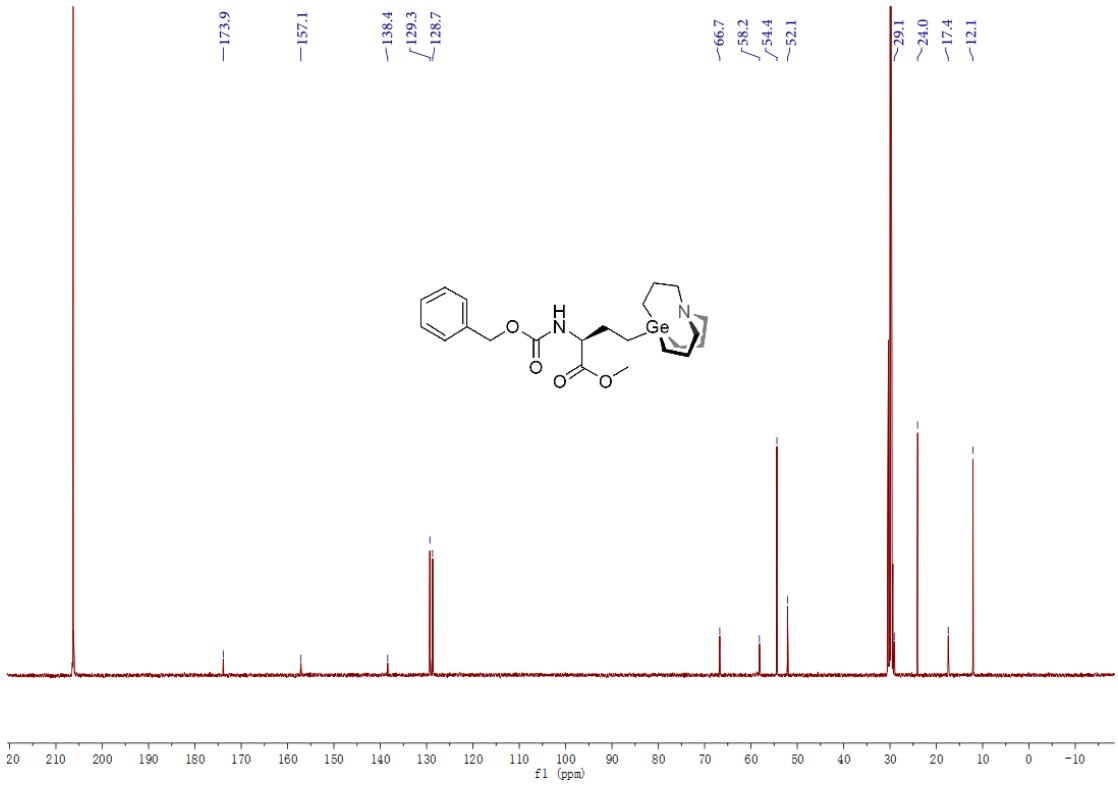

MeO
Ge
N
2.04
1.01
1.01
1.04
1.00
3.00
1.01
5.99
3.00
6.48
6.01
f1 (ppm)

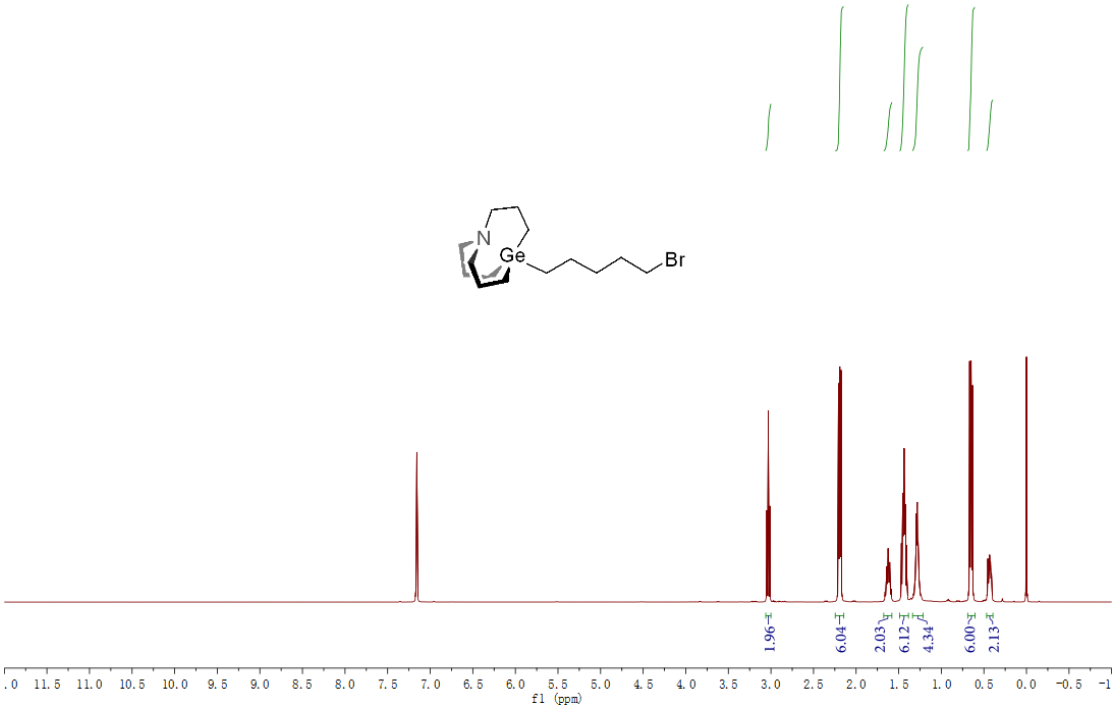

157.1
144.9
130.2
129.1
127.9
126.4
123.6
118.9
106.2
54.8
53.7
35.5
23.9
16.7
10.1
MeO
Ge
N
f1 (ppm)

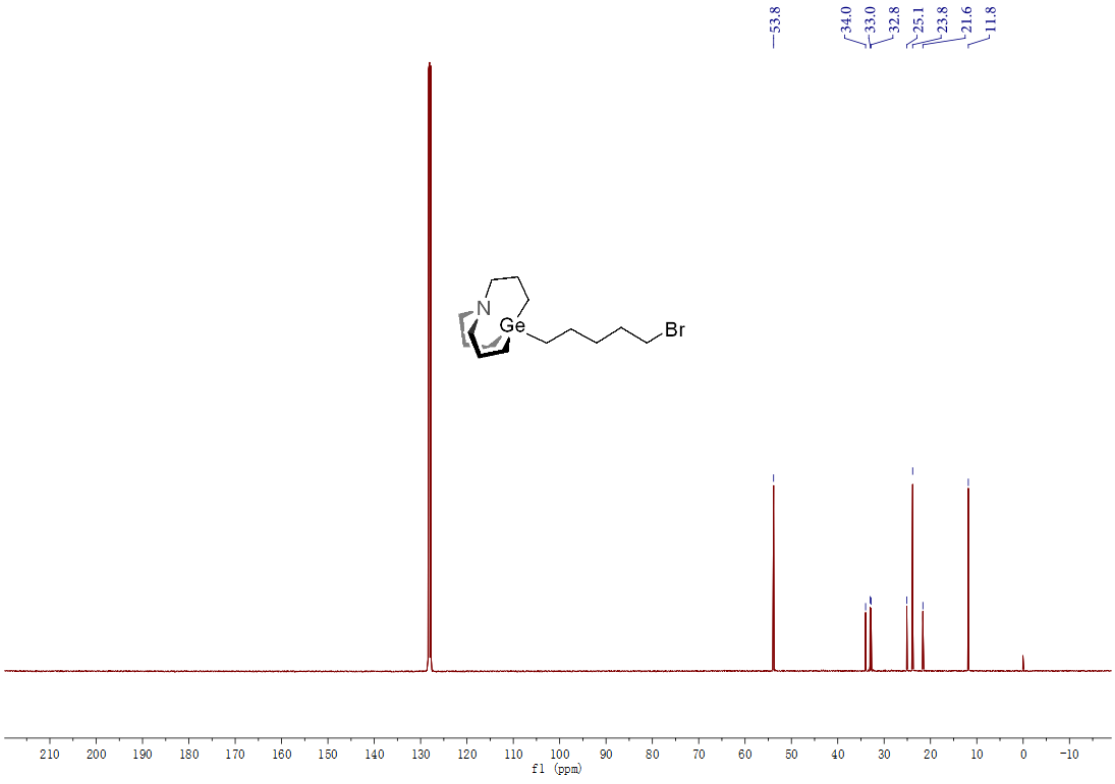

O
O
HN
N
Ge
Cl
1.96
1.91
0.74
0.97
1.00
1.01
5.87
6.08
9.10
2.11
6.00
f1 (ppm)

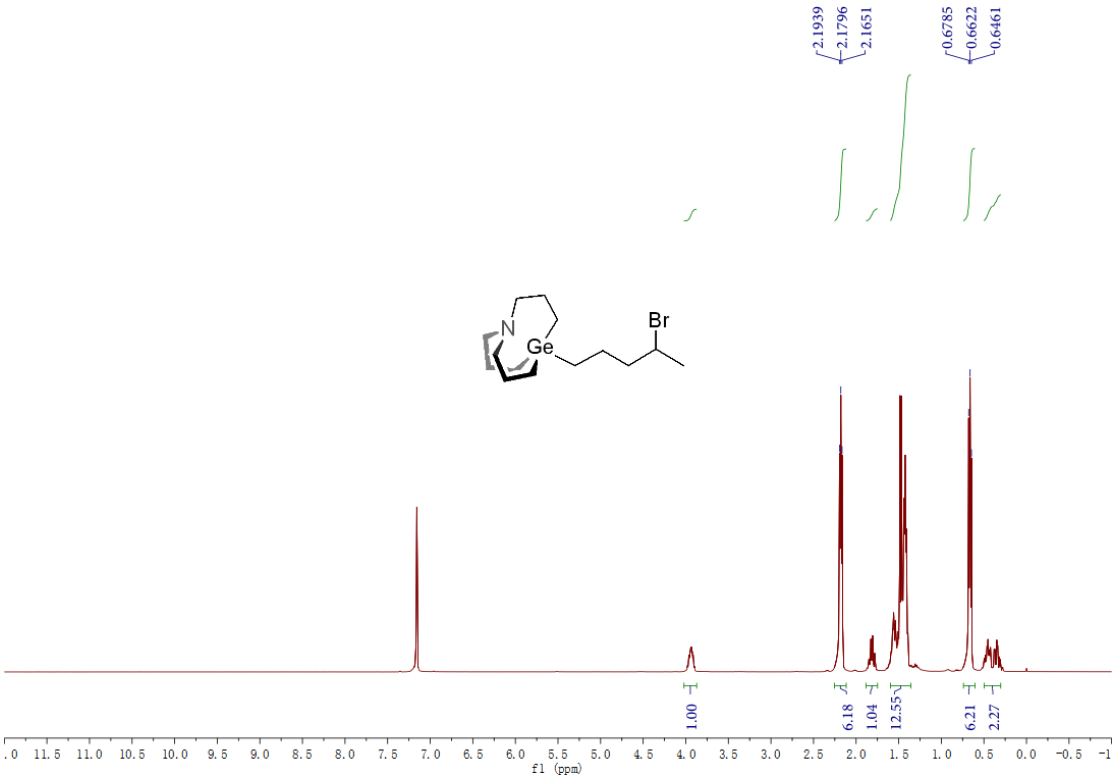

156.6
146.3
131.9
130.6
129.0
78.4
54.4
50.3
43.6
28.7
27.6
24.1
13.0
O
O
HN
N
Ge
Cl
f1 (ppm)

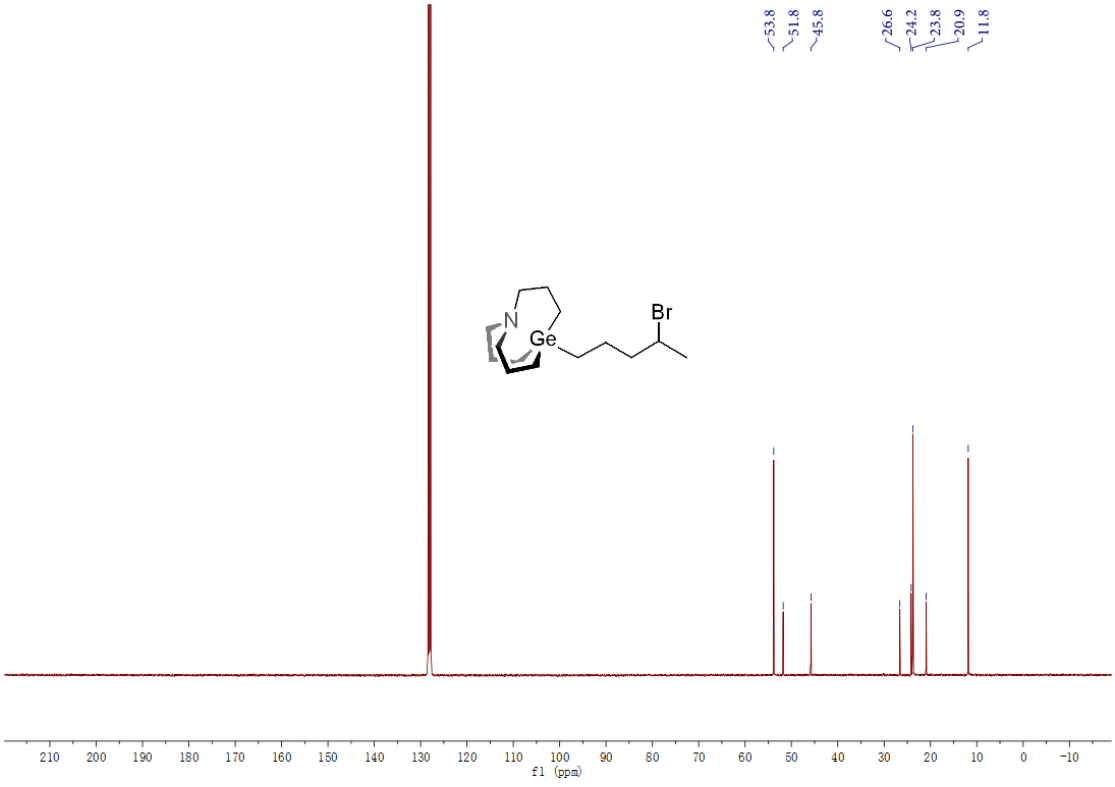

4.91
0.72
2.07
1.03
3.00
6.32
2.26
6.26
6.32
2.13
f1 (ppm)

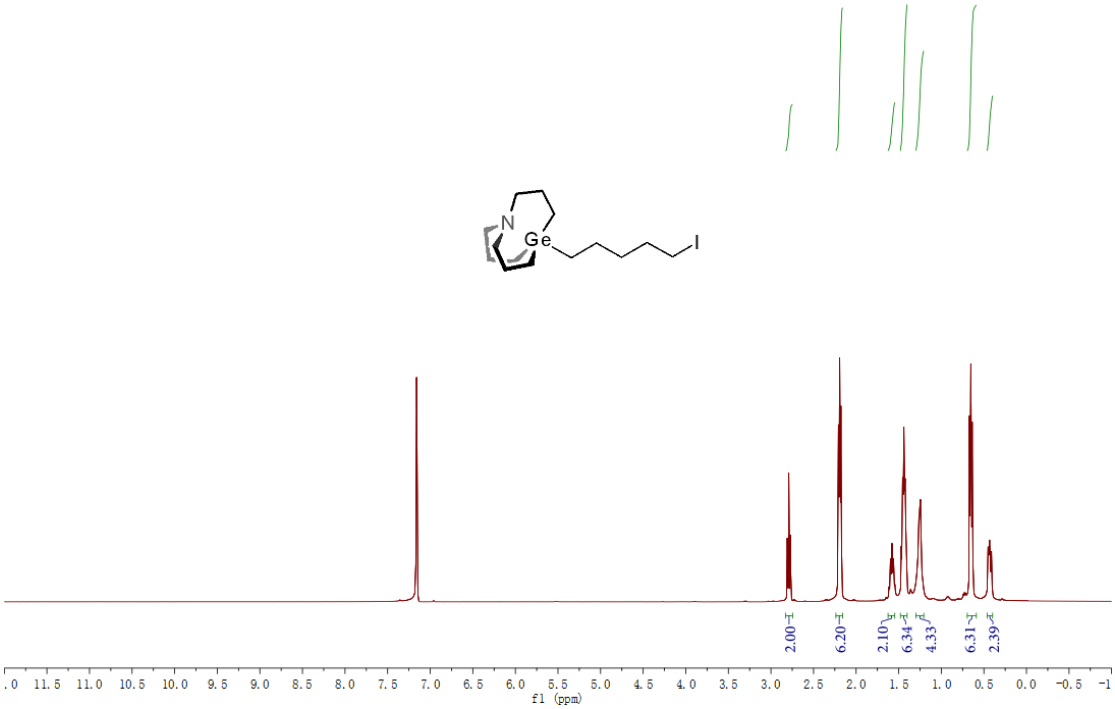

173.9
157.1
138.4
129.3
128.7
66.7
58.2
54.4
52.1
29.1
24.0
17.4
12.1
f1 (ppm)

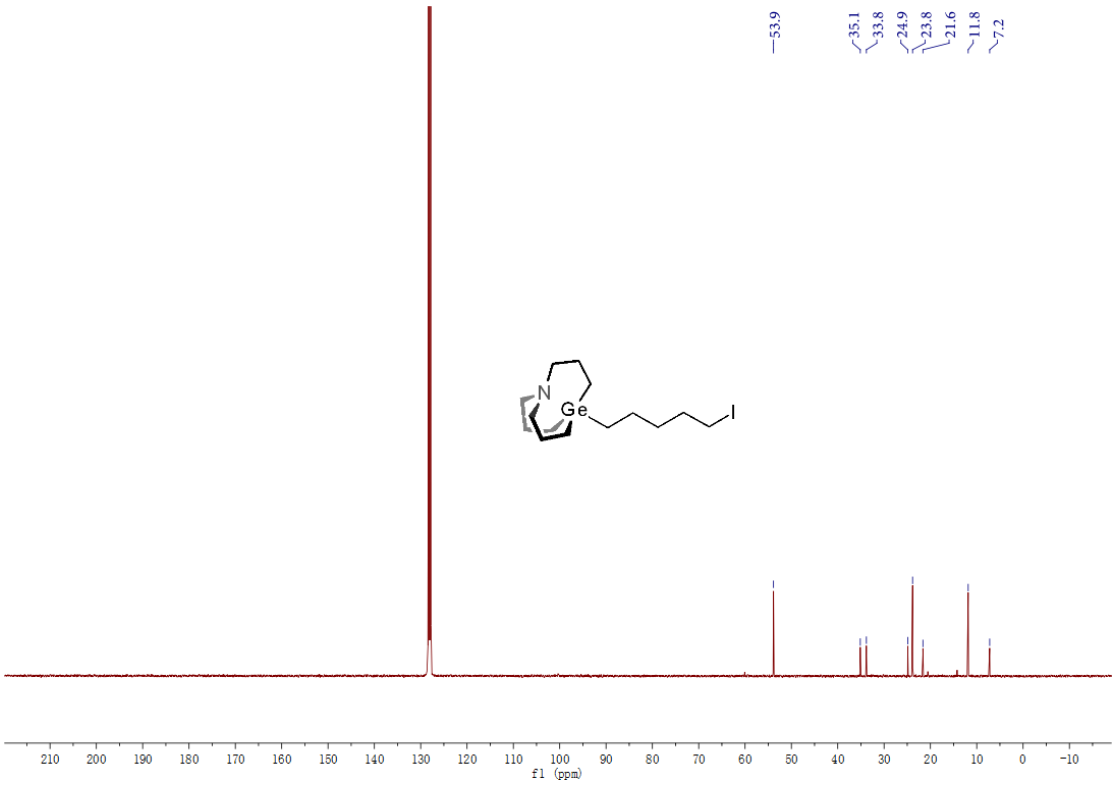

N
Ge
Br
1.96
6.04
2.03
6.12
4.34
6.00
2.13
f1 (ppm)

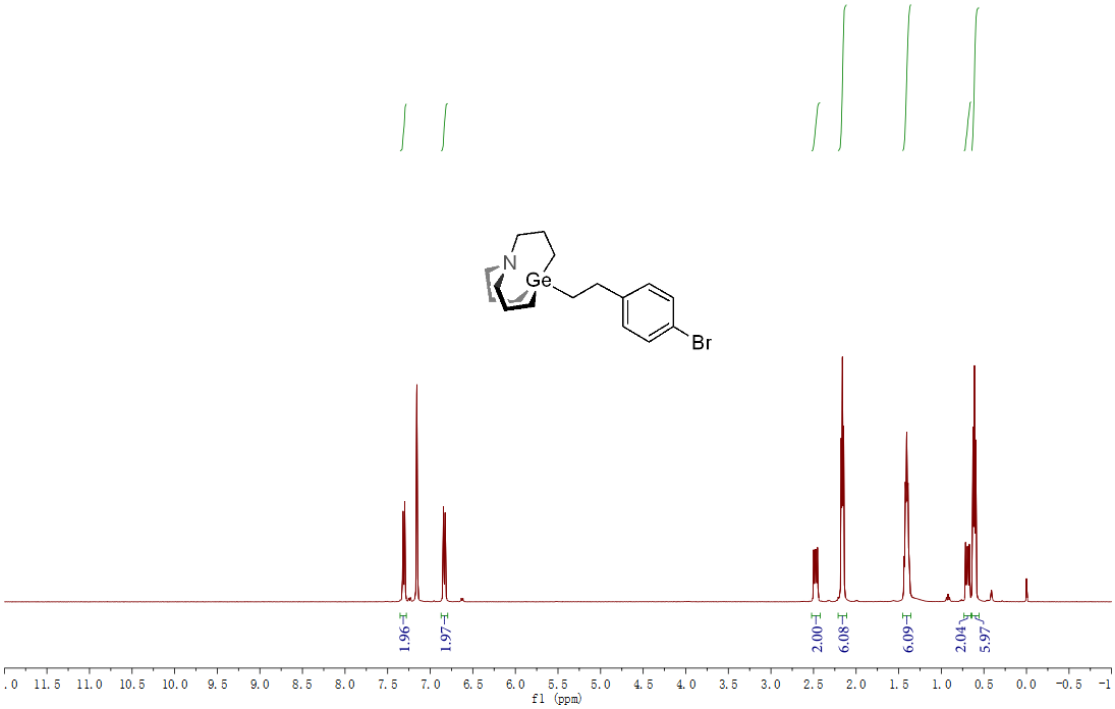

53.8
34.0
33.0
32.8
25.1
23.8
21.6
11.8
N
Ge
Br
f1 (ppm)

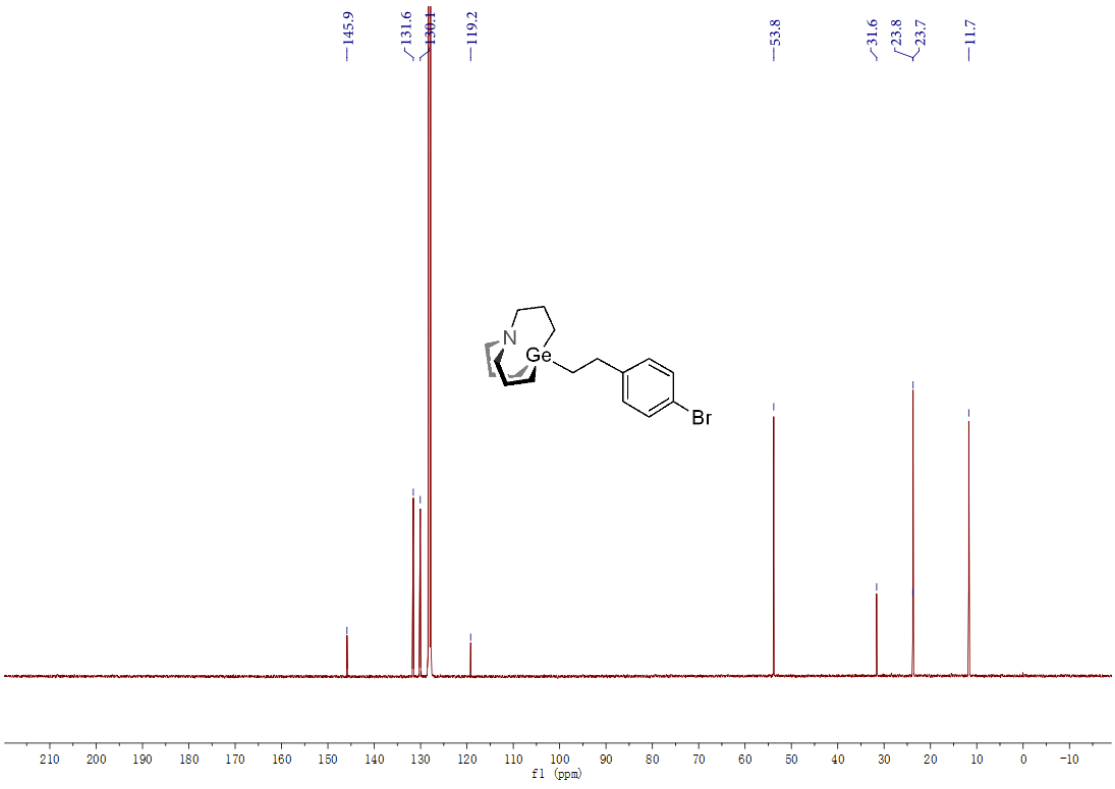

2.1939
2.1796
2.1651
0.6785
0.6622
0.6461
N
Ge
Br
1.00
6.18
1.04
12.55
6.21
2.27
f1 (ppm)

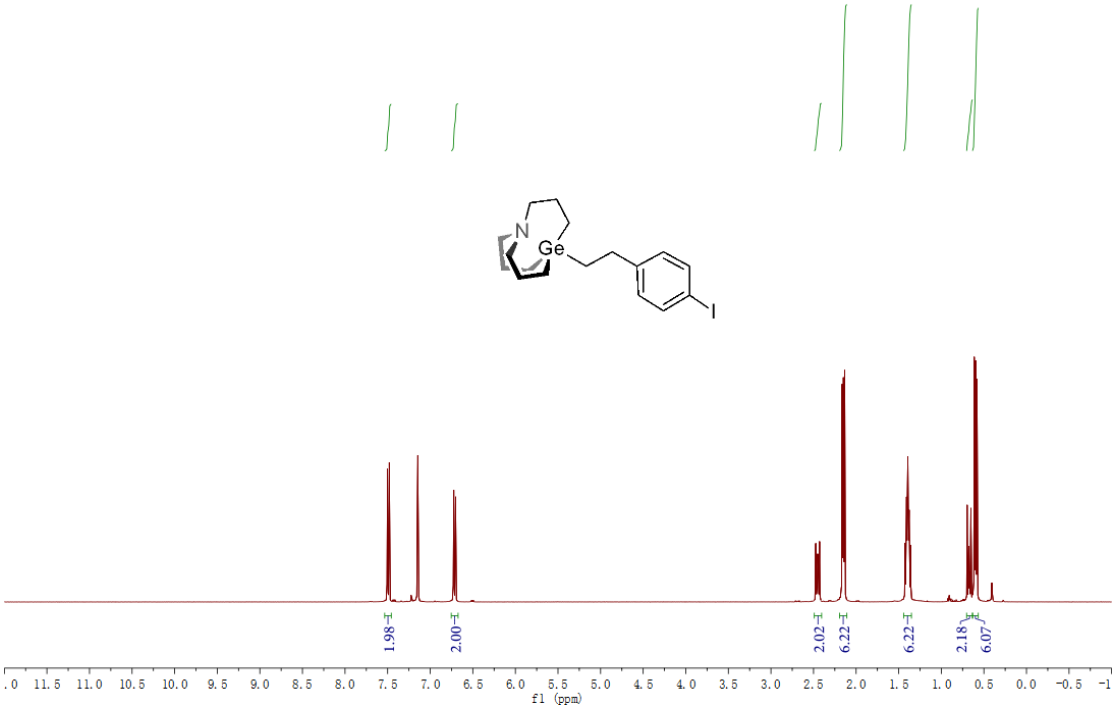

53.8
51.8
45.8
26.6
24.2
23.8
20.9
11.8
N
Ge
Br
f1 (ppm)

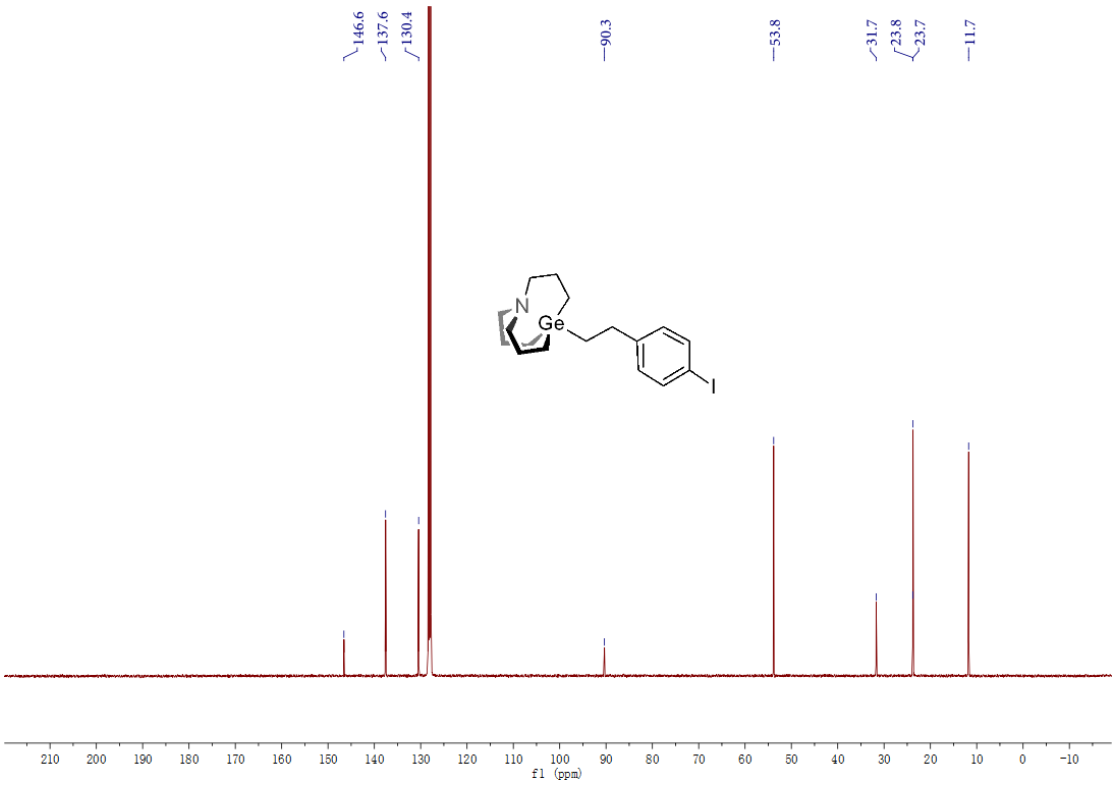

N
Ge
I
2.00
6.20
2.10
6.34
4.33
6.31
2.39
f1 (ppm)

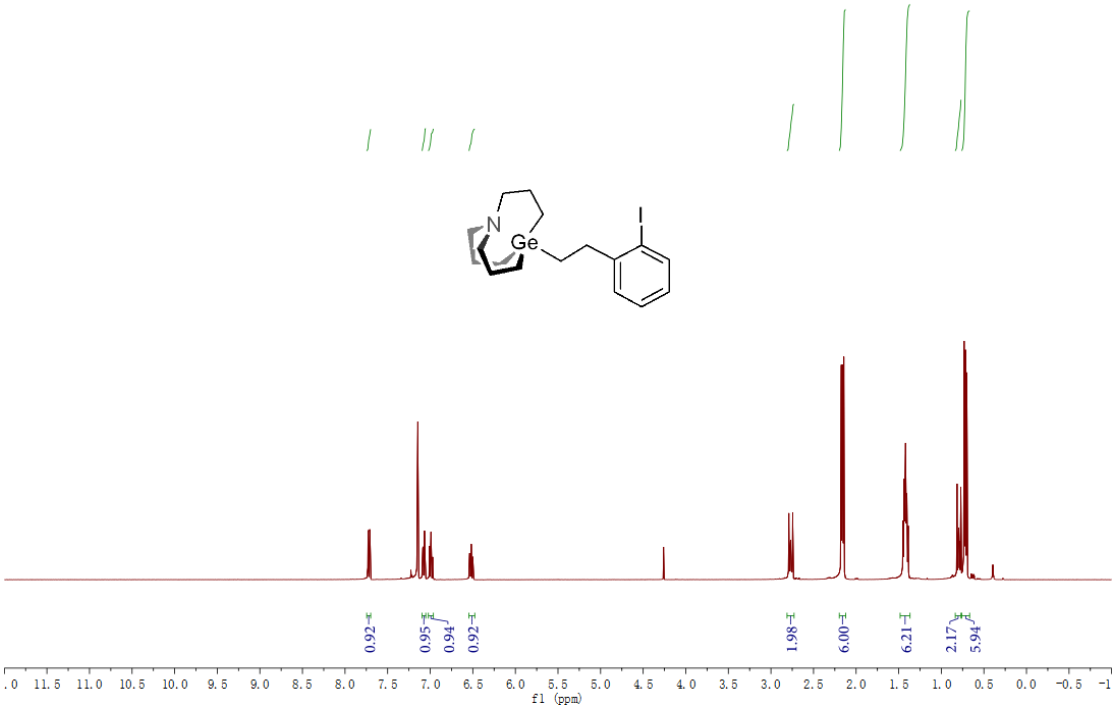

53.9
35.1
33.8
24.9
23.8
21.6
11.8
7.2
N
Ge
I
f1 (ppm)

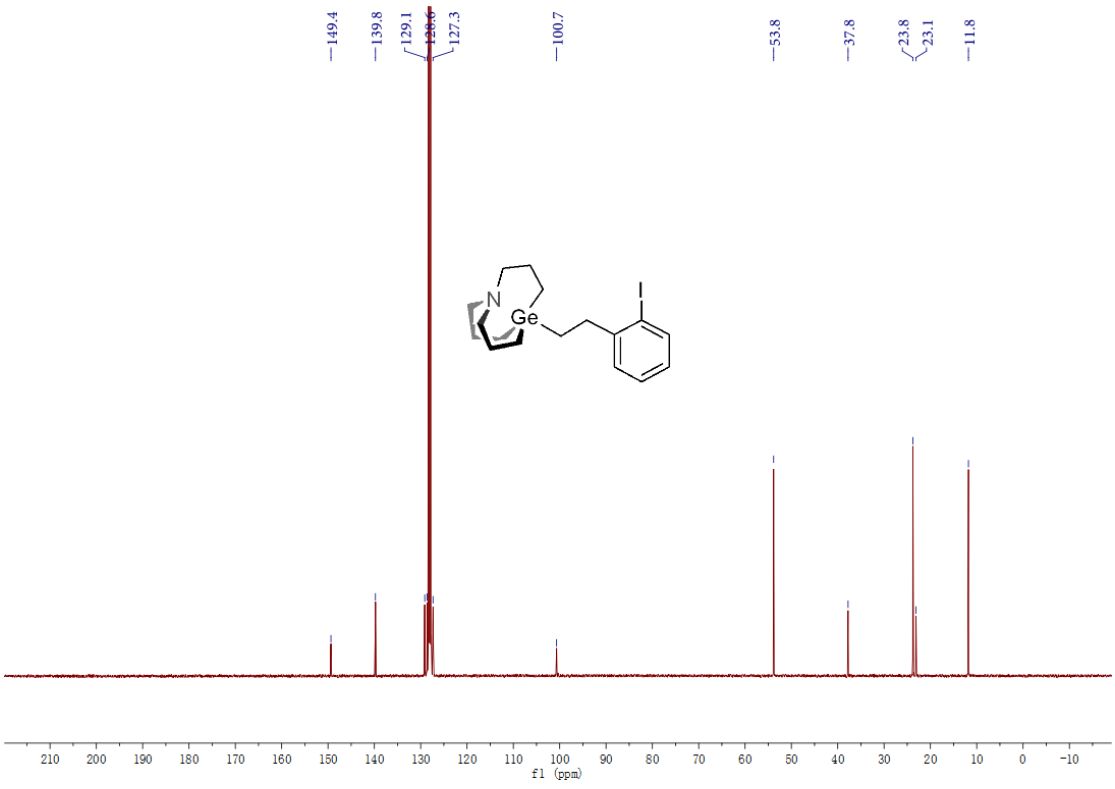

N
Ge
Br
1.96
1.97
2.00
6.08
6.09
2.04
5.97
f1 (ppm)


145.9
131.6
130.1
119.2
53.8
31.6
23.8
23.7
11.7
N
Ge
Br
f1 (ppm)

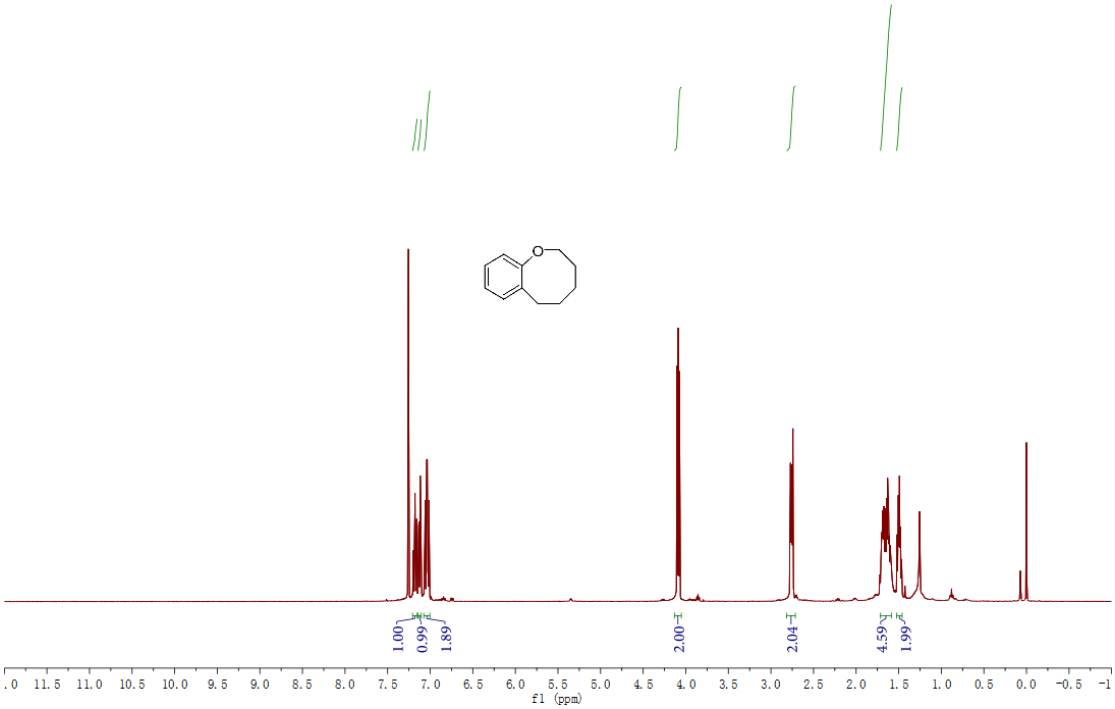

N
Ge
I
1.98
2.00
2.02
6.22
6.22
2.18
6.07
f1 (ppm)

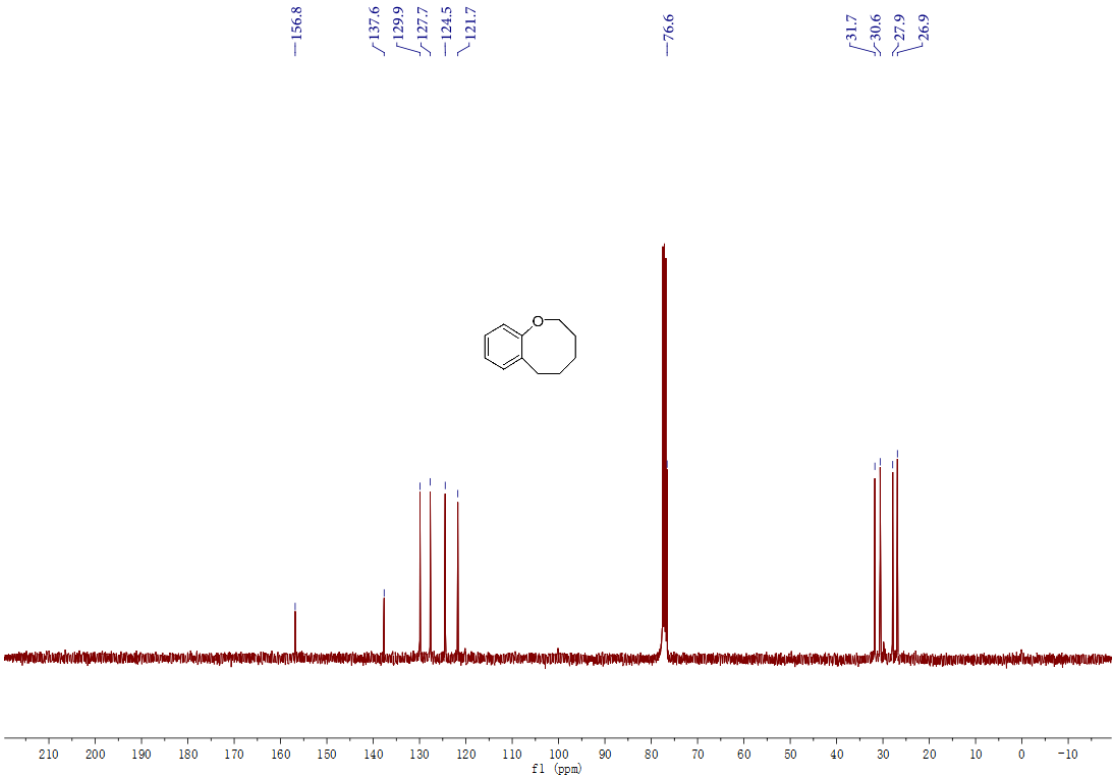

146.6
137.6
130.4
90.3
53.8
31.7
23.8
23.7
11.7
N
Ge
I
f1 (ppm)

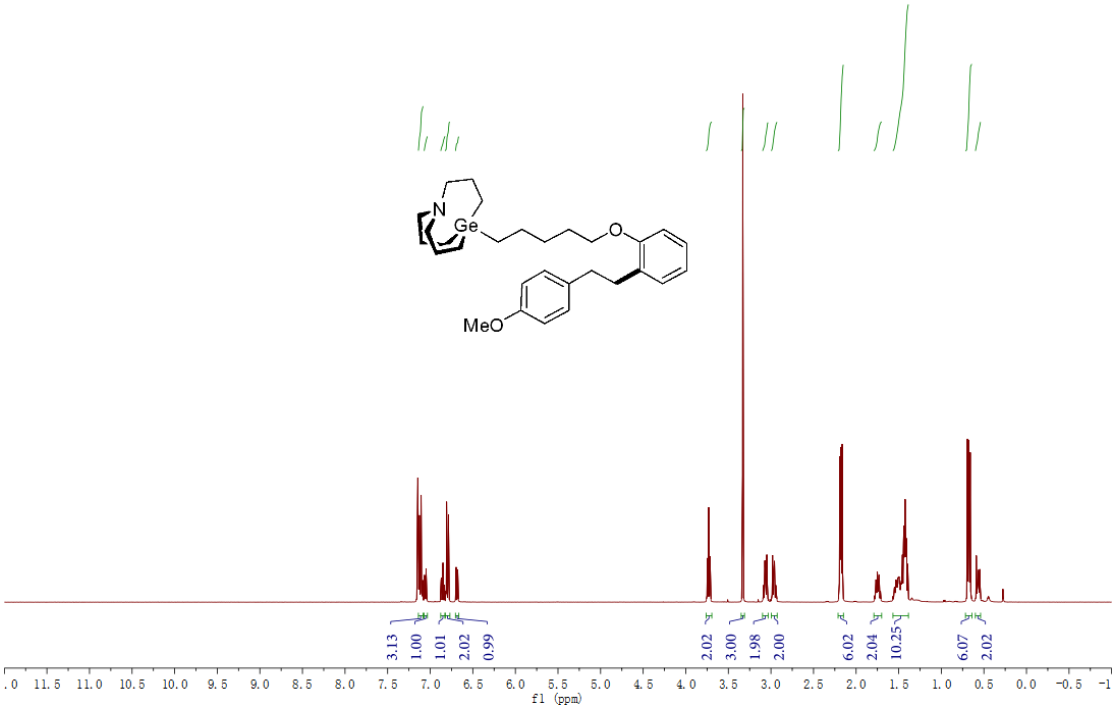

N
Ge
I
0.92
0.95
0.94
0.92
1.98
6.00
6.21
2.17
5.94
f1 (ppm)

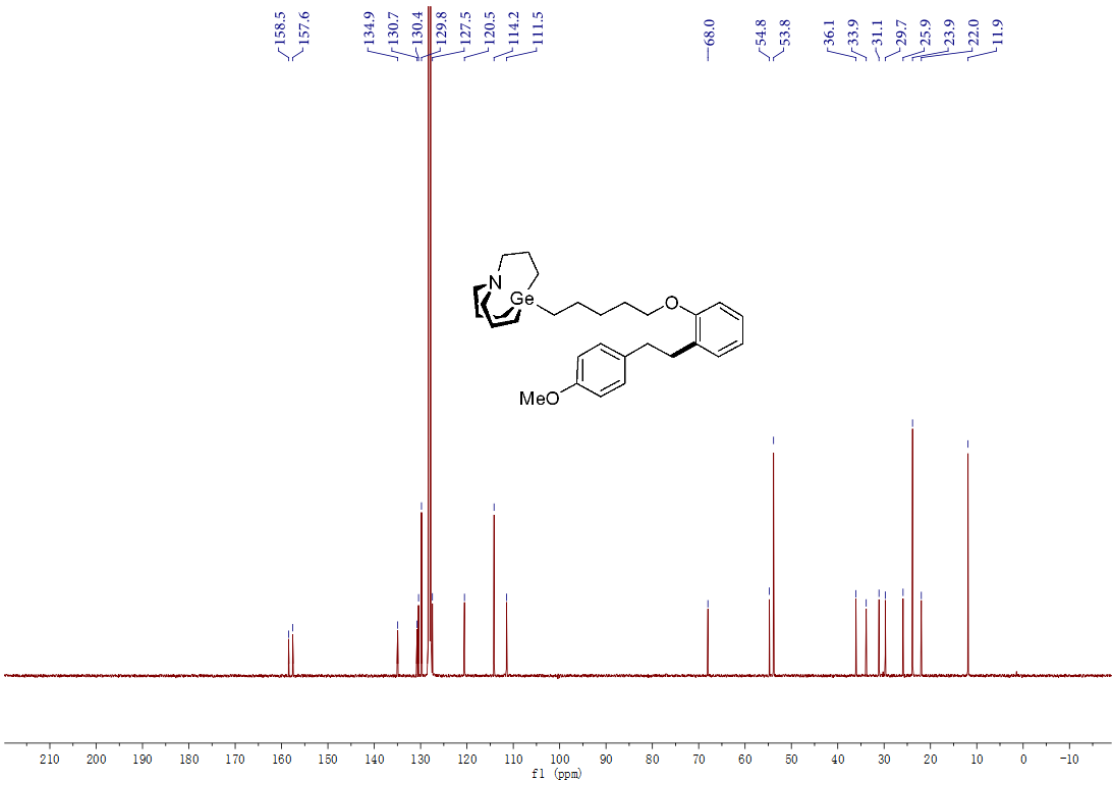

149.4
139.8
129.1
128.6
127.3
100.7
53.8
37.8
23.8
23.1
11.8
N
Ge
I
f1 (ppm)


N
Ge
O
I
1.00
1.04
2.05
2.07
5.98
2.08
10.24
6.14
2.13
f1 (ppm)
158.2
139.8
130.4
122.4
112.2
87.2
69.3
53.9
30.8
29.4
25.8
23.9
21.9
11.9
f1 (ppm)


1.00
0.99
1.89
2.00
2.04
4.59
1.99
f1 (ppm)


156.8
137.6
129.9
127.7
124.5
121.7
76.6
31.7
30.6
27.9
26.9
f1 (ppm)


Ge
N
O
MeO
3.13
1.00
1.01
2.02
0.99
2.02
3.00
1.98
2.00
6.02
2.04
10.25
6.07
2.02
f1 (ppm)


158.5
157.6
134.9
130.7
130.4
129.8
127.5
120.5
114.2
111.5
68.0
54.8
53.8
36.1
33.9
31.1
29.7
25.9
23.9
22.0
11.9
Ge
N
O
MeO
f1 (ppm)