Tertiary Cyclopropyl Carbagermatranes: Synthesis and Cross-Coupling

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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. THF was freshly distilled before used. DMAc、CH_3CN and dioxane were purchased from J&K. 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}HNMR spectra were reported in parts per million relative to tetramethylsilane ($\delta = 0$). Data for ^{1}HNMR 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). 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 or preparative TLC (Thin-layer chromatogram) on silica gel.

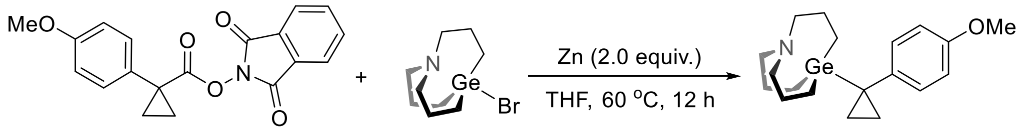
2. Experimental Procedure and Compound Characterization Data for Scheme 2

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 °C for 2 hours and stored under argon atmosphere.

2.2 Table 1. Condition optimization of decarboxylative carbagermatranation[a]

To an oven-dried screw-cap tube equipped with stir bar was charged with ***Ge***-Br[1] (0.1 mmol, 29.2 mg, 1.0 equiv.), α-(4-methoxy)phenylcyclopropane carboxylic acid NHP ester (**1a**) (0.2 mmol, 67.5 mg, 2.0 equiv.) 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. Mesitylene (0.1 mmol) was added as internal standard for NMR analysis.



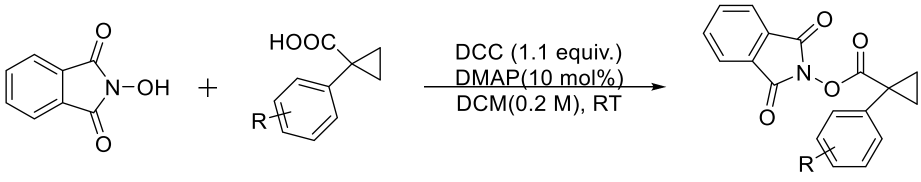
1a, 2.0 equiv. ***Ge*-Br**,1.0 equiv. **2a**

Entry	Change of standard conditions	Yield/%[c]
1	None	98[b]
2	CH_3CN instead of THF	70
3	Dioxane instead of THF	24
4	Toluene instead of THF	<5
5	DMAc instead of THF	37
6	DMAc/THF(v/v) = 1/1 instead of THF	41
7	1.0 equiv. of Zn dust was used	39
8	3.0 equiv. of Zn dust was used	94
9	1.0 equiv. of NHP ester was used	47
10	RT instead of 60 °C	71

[a] All reactions were performed on 0.1 mmol scale, solvent (0.2 M). [b] Yield were determined by ^{1}H-NMR using mesitylene as internal standard. [c] Isolated yield.

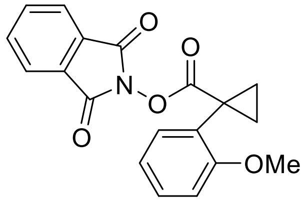
2.3 Preparation of α-arylcyclopropane carboxylic acid NHP esters and characterization

1a, **1d**, **1g** and **1m** were synthesized according reported literatures.[2-4] **1b**, **1c**, **1e**, **1f**, **1h**, **1l** and **1n-1r** were synthesized as follow:



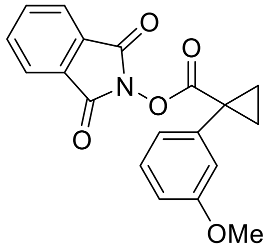
(1.1 equiv.) **(1.0 equiv.)** **1**

General procedure A for the preparation of α-arylcyclopropane carboxylic acid NHP esters: To a solution of NHPI (N-Hydroxyphthalimide, 1.1 equiv.), α-arylcyclopropane 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 rinsed with additional CH_2Cl_2, filtrate was collected and concentrated under reduced pressure. Further purification can be accomplished by silica gel column chromatography or recrystallization as needed.



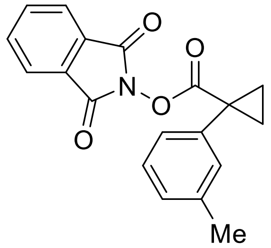
1,3-dioxoisoindolin-2-yl 1-(2-methoxyphenyl)cyclopropane-1-carboxylate (1b). 5 mmol 1-(2-methoxyphenyl)cyclopropane-1-carboxylic acid[5] was applied in the general procedure A. Purified by recrystallization from DCM/MeOH to give title compound as white solid in 80% yield.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.85 – 7.79 (m, 2H), 7.76 – 7.70 (m, 1H), 7.32 (m, 2H), 6.97 – 6.90 (m, 2H), 3.97 (s, 3H), 1.85 (q, *J* = 4.4 Hz, 2H), 1.38 (q, *J* = 4.4 Hz, 2H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 171.29, 161.95, 159.42, 134.67, 130.02, 129.47, 129.05, 125.69, 123.82, 120.19, 110.51, 55.77, 23.38, 18.23. **HRMS (ESI)**: Exact mass calculated for $C_{19}H_{15}NO_5$ $[M+H]^+$ 338.1028, found 338.10217.



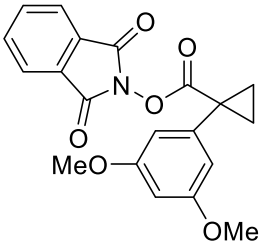
1,3-dioxoisoindolin-2-yl 1-(3-methoxyphenyl)cyclopropane-1-carboxylate (1c). 5 mmol 1-(3-methoxyphenyl)cyclopropane-1-carboxylic acid was applied in the general procedure A. Purified by recrystallization from DCM/MeOH to give title compound as white solid in 87% yield.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.88 – 7.81 (m, 2H), 7.79 – 7.71 (m, 2H), 7.28 – 7.24 (m, 1H), 7.08 (m, 2H), 6.85 (m, 1H), 3.83 (s, 3H), 1.89 (q, *J* = 4.3 Hz, 2H), 1.49 (q, *J* = 4.3 Hz, 2H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 171.12, 161.98, 159.57, 138.49, 134.79, 129.54, 129.02, 123.97, 122.78, 116.18, 113.80, 55.39, 27.45, 18.87. **HRMS (ESI)**: Exact mass calculated for $C_{19}H_{15}NO_5$ $[M+H]^+$ 338.1028, found 338.10237.



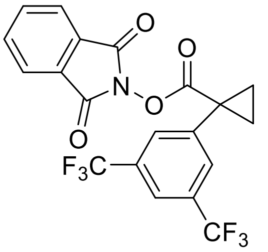
1,3-dioxoisoindolin-2-yl 1-(m-tolyl)cyclopropane-1-carboxylate (1e). 5 mmol 1-(3-tolyl)cyclopropane-1-carboxylic acid[6] was applied in the general procedure A. Purified by recrystallization from DCM/MeOH to give title compound as white solid in 85% yield.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.87 – 7.81 (m, 2H), 7.77 – 7.71 (m, 2H), 7.35 – 7.30 (m, 2H), 7.28 – 7.22 (m, 1H), 7.12 (d, *J* = 7.4 Hz, 1H), 2.36 (s, 3H), 1.89 (q, *J* = 4.2 Hz, 2H), 1.48 (q, *J* = 4.3 Hz, 2H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 171.28, 162.00, 138.20, 136.95, 134.77, 131.39, 129.01, 128.84, 128.45, 127.74, 123.95, 27.32, 21.47, 18.80. **HRMS (ESI)**: Exact mass calculated for $C_{19}H_{15}NO_4$ $[M+H]^+$ 322.1079, found 322.10719.



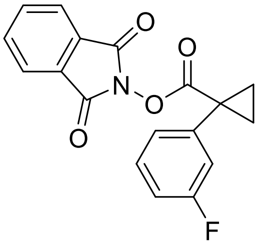
1,3-dioxoisoindolin-2-yl 1-(3,5-dimethoxyphenyl)cyclopropane-1-carboxylate (1f). 5 mmol 1-(3,5-dimethoxyphenyl)cyclopropane-1-carboxylic acid[7] was applied in the general procedure A. Purified by silica gel column chromatography using petroleum ether/ethyl acetate = 3/1 as eluent to give title compound as light yellow solid in 92% yield.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.89 – 7.81 (m, 2H), 7.80 – 7.71 (m, 2H), 6.67 (d, *J* = 2.1 Hz, 2H), 6.40 (m, 1H), 3.81 (s, 6H), 1.93 – 1.82 (q, *J* = 4.3 Hz, 2H), 1.48 (q, *J* = 4.3 Hz, 2H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 171.03, 161.95, 160.69, 139.15, 134.78, 129.01, 123.95, 108.49, 100.27, 55.49, 27.64, 18.85. **HRMS (ESI)**: Exact mass calculated for $C_{20}H_{17}NO_6$ $[M+H]^+$ 368.1134, found 368.1128.

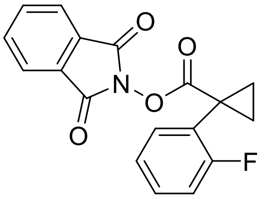


1,3-dioxoisoindolin-2-yl 1-(3,5-bis(trifluoromethyl)phenyl)cyclopropane-1-carboxylate (1h). 5 mmol 1-(3,5-bis(trifluoromethyl)phenyl)cyclopropane-1-carboxylic acid[7] was applied in the general procedure A. Purified by silica gel column chromatography using petroleum ether/ethyl acetate = 4/1 as eluent to give title compound as white solid in 61% yield.

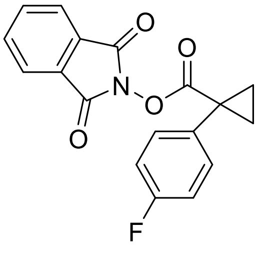
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.99 (s, 2H), 7.88 (m, *J* = 5.5, 3.1 Hz, 2H), 7.84 (s, 1H), 7.79 (m, 2H), 2.07 (q, *J* = 4.6 Hz, 2H), 1.58 (q, *J* = 4.7 Hz, 2H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 169.83, 161.81, 139.62, 135.00, 132.04 (q, J_{CF} = 33.5 Hz), 130.94 (d, J_{CF} = 2.7 Hz), 128.91, 127.28, 124.16, 123.21 (d, J_{CF} = 273.7 Hz), 122.27 (d, J_{CF} = 3.8 Hz), 121.85, 119.14, 27.12, 18.85. **^{19}F NMR (376 MHz, CDCl$_3$)** δ -62.78. **HRMS (ESI)**: Exact mass calculated for $C_{20}H_{11}F_6NO_4$ $[M+H]^+$ 444.0671, found 444.06587.



1,3-dioxoisoindolin-2-yl 1-(3-fluorophenyl)cyclopropane-1-carboxylate (1i). 5 mmol 1-(3-fluorophenyl)cyclopropane-1-carboxylic acid was applied in the general procedure A. Purified by silica gel column chromatography using petroleum ether/ethyl acetate = 5/1 as eluent to give title compound as white solid in 70% yield.
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.87 – 7.82 (m, 2H), 7.78 – 7.72 (m, 2H), 7.34 – 7.29 (m, 2H), 7.22 (m, 1H), 7.03 – 6.97 (m, 1H), 1.92 (q, J = 4.4 Hz, 2H), 1.49 (q, J = 4.4 Hz, 2H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 170.64, 162.6 (d, J_{CF} = 247.5 Hz), 161.90, 139.35 (d, J_{CF} = 7.8 Hz,), 134.84, 130.05 (d, J_{CF} = 8.4 Hz), 128.93, 126.36 (d, J_{CF} = 2.9 Hz), 123.99, 117.66 (d, J_{CF} = 21.7 Hz), 115.13 (d, J_{CF} = 20.9 Hz), 27.12, 18.88. **^{19}F NMR (376 MHz, CDCl$_3$)** δ -112.83. **HRMS (ESI)**: Exact mass calculated for $C_{18}H_{12}FNO_4$ [M+H]$^+$ 326.0829, found 326.08219.



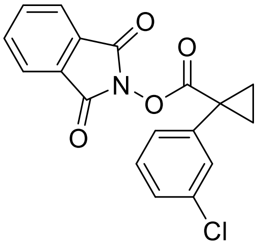
1,3-dioxoisoindolin-2-yl 1-(2-fluorophenyl)cyclopropane-1-carboxylate (1j). 5 mmol 1-(2-fluorophenyl)cyclopropane-1-carboxylic acid[8] was applied in the general procedure A. Purified by silica gel column chromatography using petroleum ether/ethyl acetate = 5/1 as eluent to give title compound as white solid in 71% yield.
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.87 – 7.81 (m, 2H), 7.78 – 7.72 (m, 2H), 7.42 (m, 1H), 7.32 (m, 1H), 7.16 – 7.07 (m, 2H), 1.96 (q, J = 4.5 Hz, 2H), 1.49 (q, J = 4.5 Hz, 2H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 170.28, 162.62 (d, J_{CF} = 251.5 Hz), 161.83, 134.79, 131.79 (d, J_{CF} = 3.1 Hz), 130.15 (d, J_{CF} = 8.2 Hz), 128.96, 124.52 (d, J_{CF} = 14.4 Hz), 124.14 (d, J_{CF} = 3.7 Hz), 123.95, 115.74 (d, J_{CF} = 21.2 Hz), 22.13, 18.60. **^{19}F NMR (376 MHz, CDCl$_3$)** δ -113.18. **HRMS (ESI)**: Exact mass calculated for $C_{18}H_{12}FNO_4$ [M+H]$^+$ 326.0829, found 326.08219.



1,3-dioxoisoindolin-2-yl 1-(4-fluorophenyl)cyclopropane-1-carboxylate (1k). 5

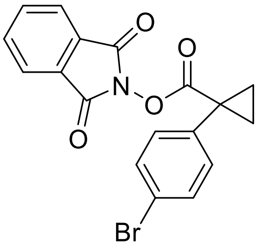
mmol 1-(4-fluorophenyl)cyclopropane-1-carboxylic acid was applied in the general procedure A. Purified by silica gel column chromatography using petroleum ether/ethyl acetate = 5/1 as eluent to give title compound as white solid in 77% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.82 (m, 2H), 7.79 – 7.73 (m, 2H), 7.52 – 7.46 (m, 2H), 7.08 – 7.01 (m, 2H), 1.91 (q, J = 4.3 Hz, 2H), 1.46 (q, J = 4.4 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.02, 162.42 (d, J_{CF} = 247.5 Hz), 161.97, 134.84, 132.91 (d, J_{CF} = 3.3 Hz), 132.45 (d, J_{CF} = 8.3 Hz), 128.99, 124.02, 115.52 (d, J_{CF} = 21.6 Hz), 26.71, 18.99. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -113.82. **HRMS (ESI)**: Exact mass calculated for $C_{18}H_{12}FNO_4$ $[M+H]^+$ 326.0829, found 326.08206.



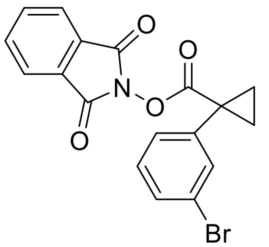
1,3-dioxoisoindolin-2-yl 1-(3-chlorophenyl)cyclopropane-1-carboxylate (1l). 5 mmol 1-(3-chlorophenyl)cyclopropane-1-carboxylic acid was applied in the general procedure A. Purified by recrystallization from DCM/MeOH to give title compound as white solid in 78% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.82 (m, 2H), 7.79 – 7.73 (m, 2H), 7.50 (s, 1H), 7.44 – 7.39 (m, 1H), 7.29 (m, 2H), 1.92 (q, J = 4.3 Hz, 2H), 1.48 (q, J = 4.4 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.62, 161.93, 139.02, 134.86, 134.28, 130.77, 129.86, 129.03, 128.37, 124.04, 27.16, 18.82. **HRMS (ESI)**: Exact mass calculated for $C_{18}H_{12}ClNO_4$ $[M+H]^+$ 342.0533, found 342.05243.



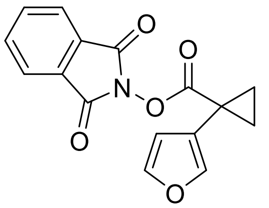
1,3-dioxoisoindolin-2-yl 1-(4-bromophenyl)cyclopropane-1-carboxylate (1n). 5 mmol 1-(4-bromophenyl)cyclopropane-1-carboxylic acid was applied in the general procedure A. Purified by recrystallization from DCM/MeOH to give title compound as white solid in 62% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.81 (m, 2H), 7.78 – 7.73 (m, 2H), 7.48 (d, J = 8.4 Hz, 2H), 7.39 (d, J = 8.4 Hz, 2H), 1.90 (q, J = 4.3 Hz, 2H), 1.45 (q, J = 4.4 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.66, 161.89, 136.07, 134.84, 132.37, 131.72, 128.90, 123.99, 122.16, 26.86, 18.86. **HRMS (ESI)**: Exact mass calculated for $C_{18}H_{12}BrNO_4$ $[M+H]^+$ 386.0028, found 386.00168.



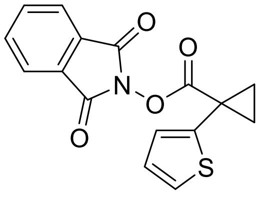
1,3-dioxoisoindolin-2-yl 1-(3-bromophenyl)cyclopropane-1-carboxylate (1o). 5 mmol 1-(3-bromophenyl)cyclopropane-1-carboxylic acid was applied in the general procedure A. Purified by recrystallization from DCM/MeOH to give title compound as white solid in 63% yield.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.89 – 7.83 (m, 2H), 7.79 – 7.74 (m, 2H), 7.66 (m, 1H), 7.49 – 7.43 (m, 2H), 7.23 (t, *J* = 9.9, 5.9 Hz, 1H), 1.92 (q, *J* = 4.4 Hz, 2H), 1.49 (q, *J* = 4.4 Hz, 2H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 170.62, 161.92, 139.26, 134.87, 133.63, 131.29, 130.14, 129.54, 128.98, 124.05, 122.40, 27.11, 18.85. **HRMS (ESI)**: Exact mass calculated for $C_{18}H_{12}BrNO_4$ $[M+H]^+$ 386.0028, found 386.0031.



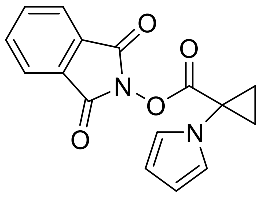
1,3-dioxoisoindolin-2-yl 1-(furan-3-yl)cyclopropane-1-carboxylate (1p). 5 mmol 1-(furan-3-yl)cyclopropane-1-carboxylic acid was applied in the general procedure A. Purified by recrystallization from DCM/MeOH to give title compound as white solid in 89% yield.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.90 – 7.84 (m, 2H), 7.80 – 7.74 (m, 2H), 7.52 (s, 1H), 7.37 (t, *J* = 1.7 Hz, 1H), 6.50 (m, 1H), 1.90 (q, *J* = 4.3 Hz, 2H), 1.41 (q, *J* = 4.4 Hz, 2H). **^{13}C NMR (101 MHz, CDCl3)** δ 170.32, 162.02, 143.08, 141.25, 134.85, 129.04, 124.02, 122.50, 111.19, 19.66, 18.63. **HRMS (ESI)**: Exact mass calculated for $C_{16}H_{11}NO_4S$ $[M+H]^+$ 298.0715, found 298.0711.



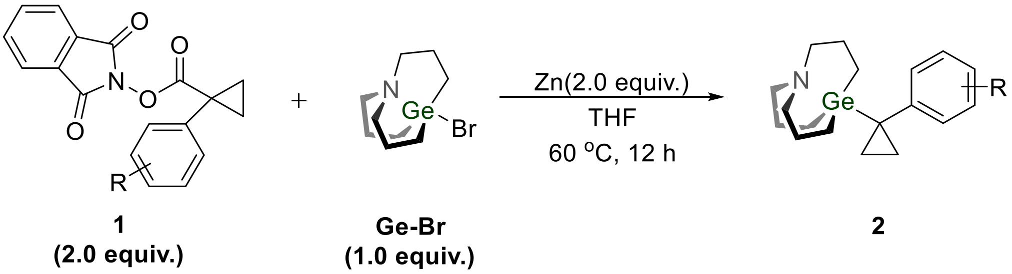
1,3-dioxoisoindolin-2-yl 1-(thiophen-2-yl)cyclopropane-1-carboxylate (1q). 5mmol 1-(thiophen-2-yl)cyclopropane-1-carboxylic acid was applied in the general procedure A. Purified by recrystallization from DCM/MeOH to give title compound as white solid in 76% yield.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.88 – 7.82 (m, 2H), 7.79 – 7.73 (m, 2H), 7.28 – 7.22 (m, 1H), 7.15 (dd, *J* = 3.6, 1.1 Hz, 1H), 6.96 (dd, *J* = 5.2, 3.6 Hz, 1H), 2.02 (q, *J* = 4.3 Hz, 2H), 1.61 (q, *J* = 4.4 Hz, 2H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 170.17, 161.88, 140.36, 134.84, 128.94, 128.39, 126.72, 125.84, 124.00, 22.01, 21.28. **HRMS (ESI)**: Exact mass calculated for $C_{16}H_{11}NO_4S$ $[M+H]^+$ 314.0487, found 314.04783.

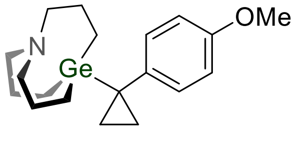


1,3-dioxoisoindolin-2-yl 1-(1H-pyrrol-1-yl)cyclopropane-1-carboxylate (1r). 5 mmol 1-(1H-pyrrol-1-yl)cyclopropane-1-carboxylic acid was applied in the general procedure A. Purified by silica gel column chromatography using petroleum ether/ethyl acetate = 4/1 as eluent to give title compound as light yellow solid in 84% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.83 (m, 2H), 7.80 – 7.75 (m, 2H), 6.90 (t, *J* = 2.2 Hz, 2H), 6.20 (t, *J* = 2.2 Hz, 2H), 2.02 (q, *J* = 5.2 Hz, 2H), 1.81 (q, *J* = 4.8 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.24, 161.62, 134.94, 128.85, 124.09, 122.58, 109.54, 39.35, 19.59. **HRMS (ESI)**: Exact mass calculated for $C_{16}H_{12}N_2O_4$ $[M+H]^+$ 297.0875, found 297.08663.

2.4 Procedure for decarboxylative carbagermatranation and characterization



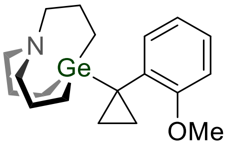
General procedure B for decarboxylative carbagermatranation: To an oven-dried screw-cap tube equipped with stir bar was charged with ***Ge*-Br** (0.2 mmol, 58.4 mg, 1.0 equiv.), corresponding NHP ester (0.4 mmol, 2.0 equiv.) and Zn powder (0.4 mmol, 26 mg, 2.0 equiv.). The tube was vacuumed and backfilled with argon for three cycles, then 1.0 mL THF was added through syringe and the tube was sealed with a teflon stopper and stirred at 60 °C 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.



5-(1-(4-methoxyphenyl)cyclopropyl)-1-aza-5-germabicyclo[3.3.3]undecane (2a).

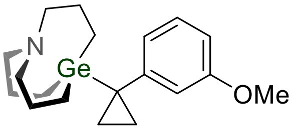
Synthesized by general procedure B, purified by silica gel column chromatography using petroleum ether/ethyl acetate = 100/1 as eluent to give title compound as light yellow oil in 98% yield.

^{1}H NMR (400 MHz, C_6D_6) δ 6.98 – 6.92 (m, 2H), 6.57 – 6.51 (m, 2H), 3.08 (s, 3H), 1.83 – 1.72 (t, *J* = 6.0 Hz, 6H), 1.06 (m, 6H), 0.55 – 0.46 (m, 4H), 0.44 – 0.35 (t, *J* = 6.6 Hz, 6H). **^{13}C NMR (101 MHz, C_6D_6)** δ 157.35, 142.20, 131.08, 113.61, 54.77, 53.59, 23.83, 20.29, 9.86, 9.62. **HRMS (ESI)**: Exact mass calculated for $C_{19}H_{29}GeNO$ $[M+H]^+$ 362.1539, found 362.1537.



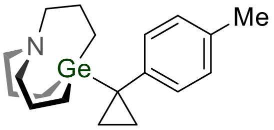
5-(1-(2-methoxyphenyl)cyclopropyl)-1-aza-5-germabicyclo[3.3.3]undecane (2b). Synthesized by general procedure B, purified by silica gel column chromatography using petroleum ether/ethyl acetate = 100/1 as eluent to give title compound as light yellow solid in 62% yield.

^{1}H NMR (400 MHz, C_6D_6) δ 7.03 (d, *J* = 7.3 Hz, 1H), 6.76 (t, *J* = 7.4 Hz, 1H), 6.63 (t, *J* = 7.4 Hz, 1H), 6.32 (d, *J* = 8.1 Hz, 1H), 3.18 (s, 3H), 1.86 – 1.76 (t, *J* = 5.6 Hz, 6H), 1.09 (m, 6H), 0.69 – 0.57 (m, 4H), 0.52 – 0.42 (t, *J* = 6.6 Hz, 6H). **^{13}C NMR (101 MHz, C_6D_6)** δ 158.92, 138.40, 131.73, 125.55, 120.49, 110.29, 54.57, 53.73, 24.05, 17.22, 10.77, 10.12. **HRMS (ESI)**: Exact mass calculated for $C_{19}H_{29}GeNO$ $[M+H]^+$ 362.1539, found 362.1531.

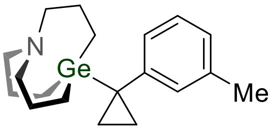


5-(1-(3-methoxyphenyl)cyclopropyl)-1-aza-5-germabicyclo[3.3.3]undecane (2c). Synthesized by general procedure B, purified by silica gel column chromatography using petroleum ether/ethyl acetate = 100/1 as eluent to give title compound as colorless oil in 70% yield.

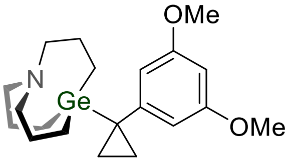
^{1}H NMR (400 MHz, C_6D_6) δ 6.88 (s, 1H), 6.76 (m, 1H), 6.72 – 6.68 (m, 1H), 6.37 – 6.32 (m, 1H), 3.14 (s, 3H), 1.78 – 1.71 (t, J = 6.0 Hz, 6H), 1.08 – 0.98 (m, 6H), 0.57 – 0.54 (m, 2H), 0.50 – 0.46 (m, 2H), 0.40 (t, *J* = 6.6 Hz, 6H). **^{13}C NMR (101 MHz, C_6D_6)** δ 159.88, 152.05, 128.85, 122.94, 116.43, 109.80, 54.65, 53.58, 23.80, 21.80, 9.89, 9.59. **HRMS (ESI)**: Exact mass calculated for $C_{19}H_{29}GeNO$ $[M+H]^+$ 362.1539, found 362.1544



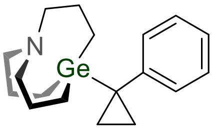
5-(1-(p-tolyl)cyclopropyl)-1-aza-5-germabicyclo[3.3.3]undecane (2d). Synthesized by general procedure B, purified by silica gel column chromatography using petroleum ether as eluent to give title compound as white solid in 96% yield.
^{1}H NMR (400 MHz, C_6D_6) δ 6.84 (d, *J* = 8.0 Hz, 2H), 6.62 (d, *J* = 7.9 Hz, 2H), 1.77 (s, 3H), 1.66 – 1.60 (t, *J* = 5.8 Hz, 6H), 0.92 (m, 6H), 0.43 – 0.35 (m, 4H), 0.30 – 0.23 (t, *J* = 6.6 Hz, 6H). **^{13}C NMR (101 MHz, C_6D_6)** δ 147.25, 133.41, 130.31, 128.77, 53.59, 23.83, 21.13, 20.97, 9.85, 9.51. **HRMS (ESI)**: Exact mass calculated for $C_{19}H_{29}GeN$ $[M+H]^+$ 366.1044, found 346.1585.



5-(1-(m-tolyl)cyclopropyl)-1-aza-5-germabicyclo[3.3.3]undecane (2e). Synthesized by general procedure B, purified by silica gel column chromatography using petroleum ether as eluent to give title compound as white solid in 68% yield.
^{1}H NMR (400 MHz, C_6D_6) δ 7.15 (m, 3H), 6.87 (d, J = 6.4 Hz, 1H), 2.22 (s, 3H), 2.08 – 2.01 (t, *J* = 5.6 Hz, 6H), 1.37 – 1.28 (m, 6H), 0.80 (m, 4H), 0.72 – 0.65 (t, *J* = 6.6 Hz, 6H). **^{13}C NMR (101 MHz, C_6D_6)** δ 150.33, 137.00, 131.14, 127.98, 127.66, 125.36, 53.63, 23.86, 21.71, 21.49, 9.90, 9.51. **HRMS (ESI)**: Exact mass calculated for $C_{19}H_{29}GeN$ $[M+H]^+$ 346.1590, found 346.1582.

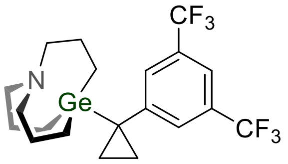


5-(1-(3,5-dimethoxyphenyl)cyclopropyl)-1-aza-5-germabicyclo[3.3.3]undecane (2f). Synthesized by general procedure B, purified by silica gel column chromatography using petroleum ether/ethyl acetate = 30/1 as eluent to give title compound as colorless oil in 58% yield.
^{1}H NMR (400 MHz, C_6D_6) δ 6.40 (m, 2H), 6.11 (m, 1H), 3.14 (s, 6H), 1.76 (t, J = 5.8 Hz, 6H), 1.04 (m, 6H), 0.59 (m, 2H), 0.48 (m, 2H), 0.45 – 0.40 (t, J = 6.6 Hz, 6H). **^{13}C NMR (101 MHz, C_6D_6)** δ 161.60, 160.95, 152.76, 108.66, 104.46, 98.06, 96.98, 54.77, 53.61, 23.83, 22.24, 9.97, 9.70. **HRMS (ESI)**: Exact mass calculated for $C_{20}H_{31}GeNO_2$ $[M+H]^+$ 392.1645, found 392.1649.



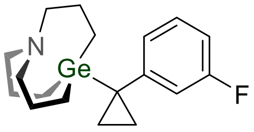
5-(1-phenylcyclopropyl)-1-aza-5-germabicyclo[3.3.3]undecane (2g). Synthesized by general procedure B, purified by silica gel column chromatography using petroleum ether as eluent to give title compound as colorless oil in 63% yield.

^{1}H NMR (400 MHz, C_6D_6) δ 7.04 (d, *J* = 7.7 Hz, 2H), 6.92 (m, 2H), 6.75 (m, 1H), 1.83 – 1.71 (t, *J* = 5.8 Hz, 6H), 1.11 – 0.98 (m, 6H), 0.49 (m, 4H), 0.42 – 0.33 (t, *J* = 6.6 Hz, 6H). **^{13}C NMR (101 MHz, C_6D_6)** δ 150.38, 130.41, 128.02, 124.50, 53.61, 23.81, 21.60, 9.87, 9.48. **HRMS (ESI)**: Exact mass calculated for $C_{18}H_{27}GeN$ [M+H]$^+$ 332.1434, found 332.1421.



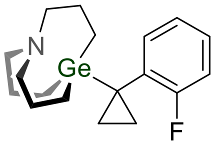
5-(1-(3,5-bis(trifluoromethyl)phenyl)cyclopropyl)-1-aza-5-germabicyclo[3.3.3]undecane (2h). Synthesized by general procedure B, using 3.0 equivalent Zn powder instead, purified by silica gel column chromatography using petroleum ether as eluent to give title compound as white solid in 61% yield.

^{1}H NMR (400 MHz, C_6D_6) δ 7.46 (s, 2H), 7.39 (s, 1H), 1.73 – 1.65 (t, *J* = 5.8 Hz, 6H), 1.02 – 0.93 (m, 6H), 0.40 (m, 2H), 0.28 (m, 2H), 0.26 – 0.20 (t, *J* = 6.6 Hz, 6H). **^{13}C NMR (101 MHz, C_6D_6)** δ 153.82, 131.10 (q, J_{CF} = 32.5 Hz), 130.18 (d, J_{CF} = 2.5 Hz), 128.53, 124.47 (d, J_{CF} = 273.7 Hz), 120.40, 118.05, 118.01, 117.98, 117.94, 117.90, 53.34, 23.41, 22.45, 9.99, 9.58. **^{19}F NMR (376 MHz, C_6D_6)** δ -62.45. **HRMS (ESI)**: Exact mass calculated for $C_{20}H_{25}F_6GeN$ [M+H]$^+$ 468.1181, found 468.1179.



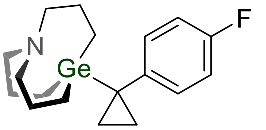
5-(1-(3-fluorophenyl)cyclopropyl)-1-aza-5-germabicyclo[3.3.3]undecane (2i). Synthesized by general procedure B, using 3.0 equivalent Zn powder instead, purified by silica gel column chromatography using petroleum ether as eluent to give title compound as colorless oil in 78% yield.

^{1}H NMR (400 MHz, C_6D_6) δ 6.83 – 6.77 (m, 1H), 6.73 – 6.64 (m, 2H), 6.46 – 6.39 (m, 1H), 1.75 – 1.69 (t, *J* = 6.0 Hz, 6H), 1.00 (m, 6H), 0.44 – 0.39 (m, 4H), 0.34 – 0.27 (t, *J* = 6.6 Hz, 6H). **^{13}C NMR (101 MHz, C_6D_6)** δ 163.17 (d, J_{CF} = 244.4 Hz), 153.53 (d, J_{CF} = 7.1 Hz), 129.27 (d, J_{CF} = 8.6 Hz), 125.96 (d, J_{CF} = 2.5 Hz), 116.94 (d, J_{CF} = 20.0 Hz), 111.26 (d, J_{CF} = 21.1 Hz), 53.49, 23.66, 21.84, 21.82, 12.10, 9.79, 9.58. **^{19}F NMR (376 MHz, C_6D_6)** δ -114.46. **HRMS (ESI)**: Exact mass calculated for $C_{18}H_{26}FGeN$ [M+H]$^+$ 350.1339, found 350.1339



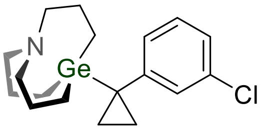
5-(1-(2-fluorophenyl)cyclopropyl)-1-aza-5-germabicyclo[3.3.3]undecane (2j). Synthesized by general procedure B, using 3.0 equivalent Zn powder instead, purified by silica gel column chromatography using petroleum ether as eluent to give title compound as colorless oil in 59% yield.

^{1}H NMR (400 MHz, C$_6$D$_6$) δ 6.94 (t, J = 7.6 Hz, 1H), 6.67 – 6.51 (m, 3H), 1.80 – 1.70 (t, J = 5.8 Hz, 6H), 1.10 – 0.99 (m, 6H), 0.56 (d, J = 10.6 Hz, 4H), 0.47 – 0.38 (t, J = 6.4 Hz, 6H). **^{13}C NMR (101 MHz, C$_6$D$_6$)** δ 162.60 (d, J_{CF} = 246.4 Hz), 137.39 (d, J_{CF} = 14.1 Hz), 132.65 (d, J_{CF} = 4.9 Hz), 125.85 (d, J_{CF} = 8.0 Hz), 123.71 (d, J_{CF} = 3.4 Hz), 115.37 (d, J_{CF} = 22.6 Hz), 53.57, 23.76, 15.93, 9.88. **^{19}F NMR (376 MHz, C$_6$D$_6$)** δ -113.18. **HRMS (ESI)**: Exact mass calculated for $C_{18}H_{26}FGeN$ [M+H]$^+$ 350.1339, found 350.1330.



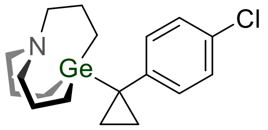
5-(1-(4-fluorophenyl)cyclopropyl)-1-aza-5-germabicyclo[3.3.3]undecane (2k). Synthesized by general procedure B, using 3.0 equivalent Zn powder instead, purified by silica gel column chromatography using petroleum ether as eluent to give title compound as colorless oil in 77% yield.

^{1}H NMR (400 MHz, C$_6$D$_6$) δ 6.83 – 6.76 (m, 2H), 6.60 – 6.53 (m, 2H), 1.80 – 1.72 (t, J = 5.8 Hz, 6H), 1.08 – 0.98 (m, 6H), 0.46 – 0.38 (m, 4H), 0.31 (t, J = 6.6 Hz, 6H). **^{13}C NMR (101 MHz, C$_6$D$_6$)** δ 160.79 (d, J_{CF} = 242.4 Hz), 146.00 (d, J_{CF} = 3.0 Hz), 131.43 (d, J_{CF} = 7.5 Hz), 114.63 (d, J_{CF} = 20.8 Hz), 53.54, 23.73, 20.59, 9.77, 9.59. **^{19}F NMR (376 MHz, C$_6$D$_6$)** δ -119.42. **HRMS (ESI)**: Exact mass calculated for $C_{18}H_{26}FGeN$ [M+H]$^+$ 350.1339, found 350.1335.



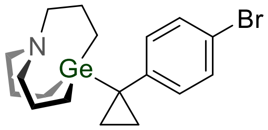
5-(1-(3-chlorophenyl)cyclopropyl)-1-aza-5-germabicyclo[3.3.3]undecane (2l). Synthesized by general procedure B, using 3.0 equivalent Zn powder instead, purified by silica gel column chromatography using petroleum ether as eluent to give title compound as colorless oil in 75% yield.

^{1}H NMR (400 MHz, C$_6$D$_6$) δ 7.40 (m, 1H), 7.06 – 6.98 (m, 2H), 6.88 (m, 1H), 2.01 – 1.94 (t, J = 6.0 Hz, 6H), 1.29 – 1.21 (m, 6H), 0.70 – 0.63 (m, 4H), 0.58 – 0.53 (t, J = 6.6 Hz, 6H). **^{13}C NMR (101 MHz, C$_6$D$_6$)** δ 153.00, 133.82, 130.39, 129.24, 128.52, 124.61, 53.46, 23.64, 21.77, 9.77, 9.51. **HRMS (ESI)**: Exact mass calculated for $C_{18}H_{26}ClGeN$ [M+H]$^+$ 366.1044, found 366.1041



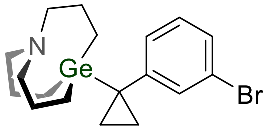
5-(1-(4-chlorophenyl)cyclopropyl)-1-aza-5-germabicyclo[3.3.3]undecane (2m). Synthesized by general procedure B, using 3.0 equivalent Zn powder instead, purified by silica gel column chromatography using petroleum ether as eluent to give title compound as colorless oil in 54% yield.

^{1}H NMR (400 MHz, C_6D_6) δ 6.94 – 6.87 (d, J = 8.0 Hz, 2H), 6.78 (d, J = 8.2 Hz, 2H), 1.84 – 1.76 (t, J = 5.8 Hz, 6H), 1.11 – 1.01 (m, 6H), 0.44 (m, 4H), 0.36 – 0.28 (t, J = 6.6 Hz, 6H). **^{13}C NMR (101 MHz, C_6D_6)** δ 149.04, 131.60, 129.98, 53.56, 23.72, 21.09, 9.81, 9.53. **HRMS (ESI)**: Exact mass calculated for $C_{18}H_{26}ClGeN$ [M+H]$^{+}$ 366.1044, found 366.1033.



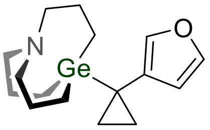
5-(1-(4-bromophenyl)cyclopropyl)-1-aza-5-germabicyclo[3.3.3]undecane (2n). Synthesized by general procedure B, using 3.0 equivalent Zn powder instead, purified by silica gel column chromatography using petroleum ether as eluent to give title compound as colorless oil in 66% yield.

^{1}H NMR (400 MHz, C_6D_6) δ 7.00 (d, *J* = 8.0 Hz, 2H), 6.68 (d, *J* = 8.1 Hz, 2H), 1.79 – 1.71 (t, J = 5.8 Hz, 6H), 1.07 – 0.97 (m, 6H), 0.40 (m, 4H), 0.32 – 0.23 (t, J = 6.6 Hz, 6H). **^{13}C NMR (101 MHz, C_6D_6)** δ 149.56, 132.05, 131.02, 117.98, 53.55, 23.71, 21.18, 9.80, 9.49. **HRMS (ESI)**: Exact mass calculated for $C_{18}H_{26}BrGeN$ [M+H]$^{+}$ 410.0539, found 410.0537.



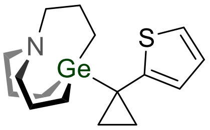
5-(1-(3-bromophenyl)cyclopropyl)-1-aza-5-germabicyclo[3.3.3]undecane (2o). Synthesized by general procedure B, using 3.0 equivalent Zn powder instead, purified by silica gel column chromatography using petroleum ether as eluent to give title compound as colorless oil in 82% yield.

^{1}H NMR (400 MHz, C_6D_6) δ 7.29 (m, 1H), 6.88 (s, 1H), 6.80 (d, *J* = 7.6 Hz, 1H), 6.54 (t, *J* = 7.8 Hz, 1H), 1.74 – 1.66 (t, J = 6.0 Hz, 6H), 0.98 (m, 6H), 0.41 – 0.34 (m, 4H), 0.31 – 0.25 (t, J = 6.4 Hz, 6H). **^{13}C NMR (101 MHz, C_6D_6)** δ 153.33, 133.31, 129.55, 128.94, 127.52, 122.28, 53.45, 23.64, 21.80, 9.76, 9.52. **HRMS (ESI)**: Exact mass calculated for $C_{18}H_{26}BrGeN$ [M+H]$^{+}$ 410.0539, found 410.0526.



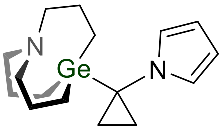
5-(1-(furan-3-yl)cyclopropyl)-1-aza-5-germabicyclo[3.3.3]undecane (2p). Synthesized by general procedure B, using DMAc as solvent instead at 80 °C, purified by silica gel column chromatography using petroleum ether/ethyl acetate = 100/1 as eluent to give title compound as colorless oil in 39% yield.

^{1}H NMR (400 MHz, C_6D_6) δ 6.90 – 6.87 (m, 1H), 6.85 (m, 1H), 5.96 (m, 1H), 1.84 – 1.77 (t, J = 5.8 Hz, 6H), 1.12 – 1.02 (m, 6H), 0.40 – 0.33 (m, 10H). **^{13}C NMR (101 MHz, C_6D_6)** δ 142.11, 139.61, 133.43, 112.65, 53.77, 23.77, 10.04, 9.34. **HRMS (ESI)**: Exact mass calculated for $C_{16}H_{25}GeNO$ [M+H]$^+$ 322.1226, found 322.1223.



5-(1-(thiophen-2-yl)cyclopropyl)-1-aza-5-germabicyclo[3.3.3]undecane (2q). Synthesized by general procedure B, purified by silica gel column chromatography using petroleum ether as eluent to give title compound as colorless oil in 97% yield.

^{1}H NMR (400 MHz, C_6D_6) δ 6.37 – 6.31 (m, 3H), 1.63 – 1.55 (t, J = 5.8 Hz, 6H), 0.89 (m, 6H), 0.49 (m, 2H), 0.33 (m, 2H), 0.31 – 0.24 (t, J = 6.6 Hz, 6H). **^{13}C NMR (101 MHz, C_6D_6)** δ 155.73, 126.52, 123.93, 121.26, 53.68, 23.89, 23.72, 23.54, 15.33, 11.65, 10.12. **HRMS (ESI)**: Exact mass calculated for $C_{16}H_{25}GeNS$ [M+H]$^+$ 338.0998, found 338.0993.



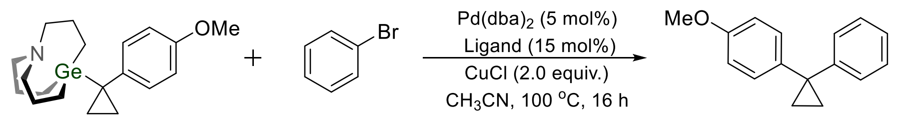
5-(1-(1H-pyrrol-1-yl)cyclopropyl)-1-aza-5-germabicyclo[3.3.3]undecane (2r). Synthesized by general procedure B, purified by silica gel column chromatography using petroleum ether as eluent to give title compound as light yellow oil in 51% yield.

^{1}H NMR (400 MHz, C_6D_6) δ 6.46 (m, 2H), 6.05 (m, 2H), 1.74 – 1.65 (t, J = 5.8 Hz, 6H), 0.98 (m, 6H), 0.67 – 0.58 (m, 2H), 0.28 (t, J = 6.6 Hz, 8H). **^{13}C NMR (101 MHz, C_6D_6)** δ 121.54, 107.47, 53.41, 35.46, 23.36, 10.27, 9.89. **HRMS (ESI)**: Exact mass calculated for $C_{16}H_{26}GeN_2$ [M+H]$^+$ 321.1386, found 321.1376.

3. Experimental Procedure of Cross-Coupling Reactions and Compound Characterization Data for Scheme 3

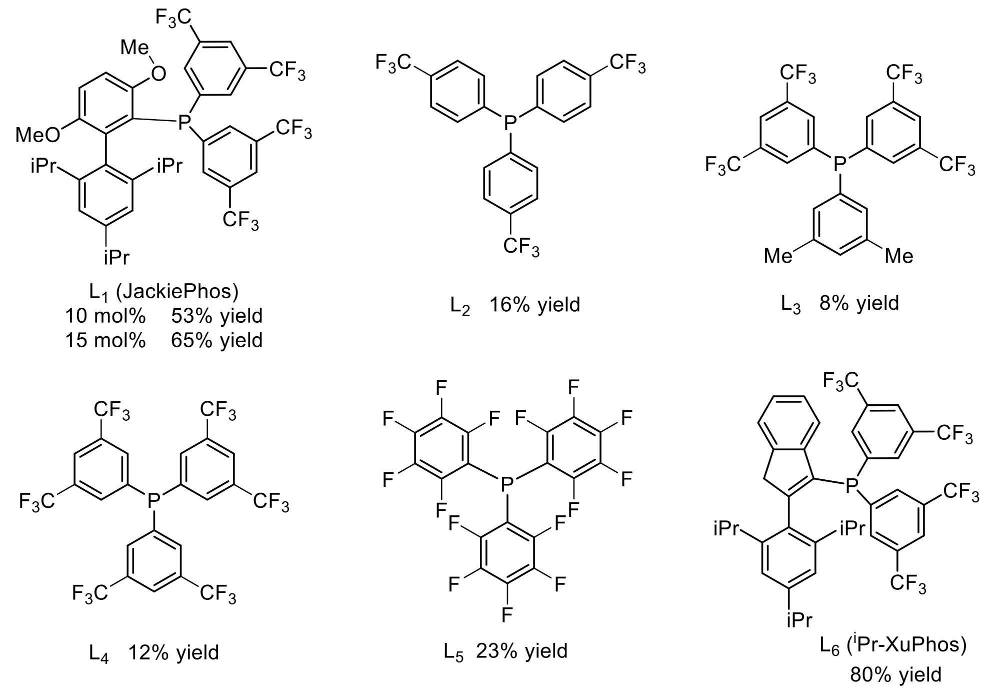
3.1 Table 2-3. Condition optimization of cross-coupling reactions

Palladium catalyst, ligand, and CuCl were weighed and transferred to a screw-cap tube with stir bar. The tube was evacuated and backfilled three times with argon, then 5-(1-(4-methoxyphenyl)cyclopropyl)-1-aza-5-germabicyclo[3.3.3]undecane (**2a**) (0.05 mmol, 18 mg, 1.0 equiv.), bromobenzene (0.06 mmol, 6.5 μL, 1.2 equiv.) and solvent (0.5 mL) were added and the screw-cap tube was sealed with a teflon stopper and heated to 100 °C for 16 hours. At the end of the reaction, the reaction mixture was cooled to room temperature and added saturated sodium chloride aqueous solution, extracted with ethyl acetate. Organic layer was separated and calculated yield by GC based on benzophenone as internal standard.



2a **(1.0 equiv.)** **(1.2 equiv.)** **3a**

Table 2. Ligand Optimization of Cross-Coupling Reactions[a,b]



L$_1$ (JackiePhos)
10 mol% 53% yield
15 mol% 65% yield

L$_2$ 16% yield

L$_3$ 8% yield

L$_4$ 12% yield

L$_5$ 23% yield

L$_6$ (^{i}Pr-XuPhos)
80% yield

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[a] All reactions were carried out in 0.05 mmol scale. [b] Yields of 3a were determined by GC using benzophenone as internal standard.

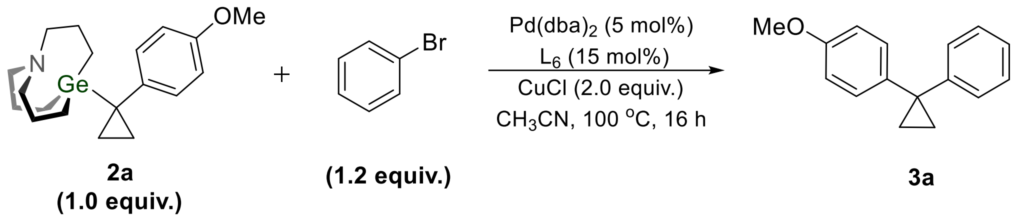
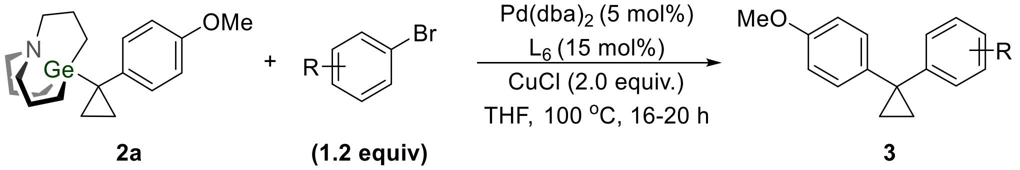


Table 3. Condition Optimization of Cross-Coupling Reactions[a]

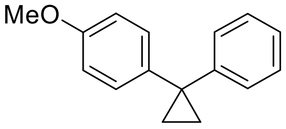
Entry	Change of standard conditions	Yield/%[b]
1	$Pd(OAc)_2$ instead of $Pd(dba)_2$	64
2	$Pd_2(dba)_3$ instead of $Pd(dba)_2$	61
3	$PdCl_2$ instead of $Pd(dba)_2$	34
4	0.2 equiv. of CuCl was used	22
5	1.0 equiv. of CuCl was used	30
6	No CuCl	trace
7	2.0 equiv. of KF as additive	51
8	Toluene instead of CH_3CN	65
9	Dioxane instead of CH_3CN	92
10	THF instead of CH_3CN	**96**
11	DMF instead of CH_3CN	12

[a] All reactions were carried out in 0.05 mmol scale. [b] Yields of 3a were determined by GC using benzophenone as internal standard.

3.2 Preparation and characterization data of cross-coupling product

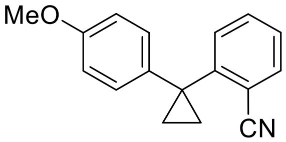


General procedure C for cross-coupling reaction: $Pd(dba)_2$ (0.01 mmol, 5.8 mg, 5 mol%), ^{i}Pr-XuPhos (L_6) (0.03 mmol, 23.3 mg, 15 mol%), CuCl (0.4 mmol, 39.6 mg, 2.0 equiv.) and aryl bromide (0.24 mmol, 1.2 equiv.) (If aryl bromide is liquid, added it after filling with argon) were weighed and transferred to a screw-cap tube with stir bar. The tube was evacuated and backfilled three times with argon, then 5-(1-(4-methoxyphenyl)cyclopropyl)-1-aza-5-germabicyclo[3.3.3]undecane (**2a**) (0.20 mmol, 72 mg, 1.0 equiv.) and THF (1.0 mL) were added, the screw-cap tube was sealed with a teflon stopper and heated to 100 °C for 16 hours. At the end of the reaction, the reaction mixture was cooled to room temperature and added saturated sodium chloride aqueous solution, 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 preparative TLC.



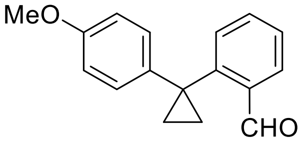
1-methoxy-4-(1-phenylcyclopropyl)benzene (3a). Prepared according to general procedure C outlined above, purified by preparative TLC using petroleum ether/ethyl acetate = 100/1 as eluent to give title compound as colorless oil in 90% yield. 3a is an known compound, and NMR data of 3a matched with previous report.[9]

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.19 – 7.05 (m, 4H), 6.76 – 6.71 (m, 1H), 3.68 (s, 2H), 1.17 (s, 2H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 157.97, 146.38, 137.86, 129.97, 128.32, 128.00, 125.83, 113.75, 55.36, 29.27, 16.47. **HRMS (ESI)**: Exact mass calculated for $C_{16}H_{16}O$ $[M+H]^+$ 225.1279, found 225.12733.



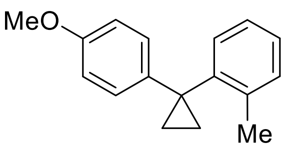
2-(1-(4-methoxyphenyl)cyclopropyl)benzonitrile (3b). Prepared according to general procedure C outlined above and reaction stopped after 20 hours, purified by preparative TLC using petroleum ether/ethyl acetate = 30/1 as eluent to give title compound as colorless oil in 71% yield.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.66 – 7.50 (m, 3H), 7.31 – 7.23 (m, 3H), 6.81 – 6.76 (m, 2H), 3.74 (s, 3H), 1.44 – 1.37 (m, 2H), 1.36 – 1.30 (m, 2H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 158.16, 149.47, 136.18, 133.50, 132.91, 131.40, 129.02, 127.14, 118.50, 114.36, 113.84, 55.32, 29.19, 15.25. **HRMS (ESI)**: Exact mass calculated for $C_{17}H_{15}NO$ $[M+H]^+$ 250.1232, found 250.1231.



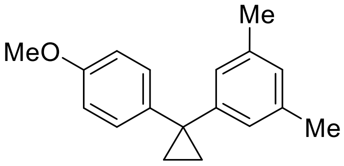
2-(1-(4-methoxyphenyl)cyclopropyl)benzaldehyde (3c). Prepared according to general procedure C outlined above and reaction stopped after 20 hours, purified by preparative TLC using petroleum ether/ethyl acetate = 20/1 as eluent to give title compound as colorless oil in 58% yield.

^{1}H NMR (400 MHz, CDCl$_3$) δ 10.61 (s, 1H), 7.91 (d, J = 7.6 Hz, 1H), 7.58 (m, 2H), 7.41 (m, 1H), 6.94 – 6.88 (m, 2H), 6.78 – 6.72 (m, 2H), 3.73 (s, 3H), 1.48 – 1.36 (m, 4H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 192.62, 157.75, 147.72, 143.46, 137.81, 135.22, 134.29, 131.63, 130.63, 129.09, 128.52, 128.06, 127.56, 126.89, 125.53, 113.97, 55.37, 26.13, 17.46. **HRMS (ESI)**: Exact mass calculated for $C_{17}H_{16}O_2$ $[M+H]^+$ 253.1229, found 253.12218.



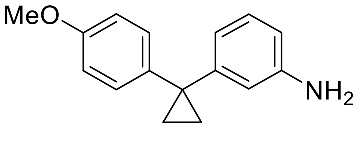
1-(1-(4-methoxyphenyl)cyclopropyl)-2-methylbenzene (3d). Prepared according to general procedure C outlined above and reaction stopped after 20 hours, purified by preparative TLC using petroleum ether/ethyl acetate = 100/1 as eluent to give title compound as colorless oil in 63% yield.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.36 – 7.31 (m, 1H), 7.13 – 7.04 (m, 3H), 6.83 – 6.78 (m, 2H), 6.68 – 6.62 (m, 2H), 3.65 (s, 3H), 2.15 (s, 3H), 1.21 (m, 2H), 1.16 (m, 2H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 157.36, 141.06, 138.11, 134.14, 133.05, 128.66, 128.22, 127.66, 126.81, 125.96, 125.85, 125.61, 113.61, 55.28, 26.96, 17.72, 1.18. **HRMS (ESI)**: Exact mass calculated for $C_{17}H_{18}O$ [M+H]$^+$: 239.1436, found 239.1430.



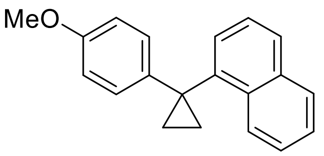
1-(1-(4-methoxyphenyl)cyclopropyl)-3,5-dimethylbenzene (3e). Prepared according to general procedure C outlined above, purified by preparative TLC using petroleum ether/ethyl acetate = 100/1 as eluent to give title compound as colorless oil in 72% yield.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.12 – 7.08 (m, 2H), 6.77 – 6.68 (m, 5H), 3.68 (s, 3H), 2.17 (s, 6H), 1.17 – 1.09 (m, 4H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 157.87, 146.27, 138.18, 137.78, 129.85, 127.62, 126.00, 113.70, 55.35, 29.18, 21.48, 16.24. **HRMS (ESI)**: Exact mass calculated for $C_{18}H_{20}O$ [M+H]$^+$ 253.1592, found 253.1582.

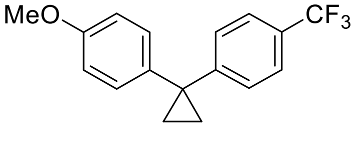


3-(1-(4-methoxyphenyl)cyclopropyl)aniline (3f). Prepared according to general procedure C outlined above, purified by preparative TLC using petroleum ether/ethyl acetate = 8/1 as eluent to give title compound as colorless oil in 65% yield.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.21 – 7.15 (m, 2H), 7.03 (t, J = 7.7 Hz, 1H), 6.85 – 6.77 (m, 2H), 6.58 (d, J = 7.8 Hz, 1H), 6.47 (m, 2H), 3.77 (s, 3H), 1.29 – 1.16 (m, 4H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 157.89, 147.63, 146.28, 137.92, 129.98, 129.21, 118.11, 115.13, 113.66, 112.76, 55.35, 29.15, 16.39. **HRMS (ESI)**: Exact mass calculated for $C_{16}H_{17}NO$ [M+H]$^+$ 240.1388, found 240.13820.

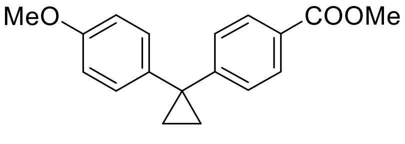


1-(1-(4-methoxyphenyl)cyclopropyl)naphthalene (3g). Prepared according to general procedure C outlined above, purified by preparative TLC using petroleum ether/ethyl acetate = 100/1 as eluent to give title compound as colorless oil in 87% yield. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.18 (m, 1H), 7.86 – 7.74 (m, 2H), 7.61 (m, 1H), 7.48 – 7.35 (m, 3H), 6.95 – 6.89 (m, 2H), 6.71 – 6.65 (m, 2H), 3.67 (s, 3H), 1.54 – 1.33 (m, 4H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 157.36, 141.06, 138.11, 134.14, 133.05, 128.66, 128.22, 127.66, 126.81, 125.96, 125.85, 125.61, 113.61, 55.28, 26.96, 17.72, 1.18. **HRMS (ESI)**: Exact mass calculated for $C_{20}H_{18}O$ [M+H]$^+$ 275.1436, found 275.1427.

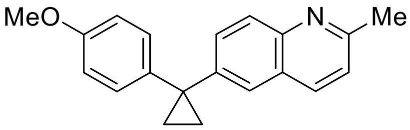


1-methoxy-4-(1-(4-(trifluoromethyl)phenyl)cyclopropyl)benzene (3h). Prepared according to general procedure C outlined above, purified by preparative TLC using petroleum ether/ethyl acetate = 100/1 as eluent to give title compound as colorless oil in 78% yield. 3h is an known compound, and NMR data of 3j matched with previous report. [9a]

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.39 (m, 2H), 7.17 – 7.09 (m, 4H), 6.78 – 6.73 (m, 2H), 3.69 (s, 3H), 1.26 – 1.16 (m, 4H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 158.34, 150.73(q, J = 1.0 Hz), 136.63, 127.94 (q, J = 33.0 Hz), 127.86, 125.26 (q, J = 15.0 Hz), 124.46(q, J = 270.1 Hz), 113.98, 55.38, 29.24, 16.95. **^{19}F NMR (376 MHz, CDCl$_3$)** δ -62.23. **HRMS (ESI)**: Exact mass calculated for $C_{17}H_{15}F_3O$ [M+H]$^+$ 293.1153, found 293.1140.



Methyl 4-(1-(4-methoxyphenyl)cyclopropyl)benzoate (3i). Prepared according to general procedure C outlined above, purified by preparative TLC using petroleum ether/ethyl acetate = 30/1 as eluent to give title compound as colorless oil in 92% yield. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.90 (d, *J* = 8.3 Hz, 2H), 7.19 (m, 4H), 6.87 – 6.81 (m, 2H), 3.87 (s, 3H), 3.78 (s, 3H), 1.36 – 1.25 (m, 4H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 167.12, 158.24, 152.07, 136.65, 130.41, 129.61, 127.47, 127.35, 113.89, 55.34, 52.08, 29.34, 17.19. **HRMS (ESI)**: Exact mass calculated for $C_{18}H_{18}O_3$ [M+H]$^+$ 283.1334, found 283.1332.

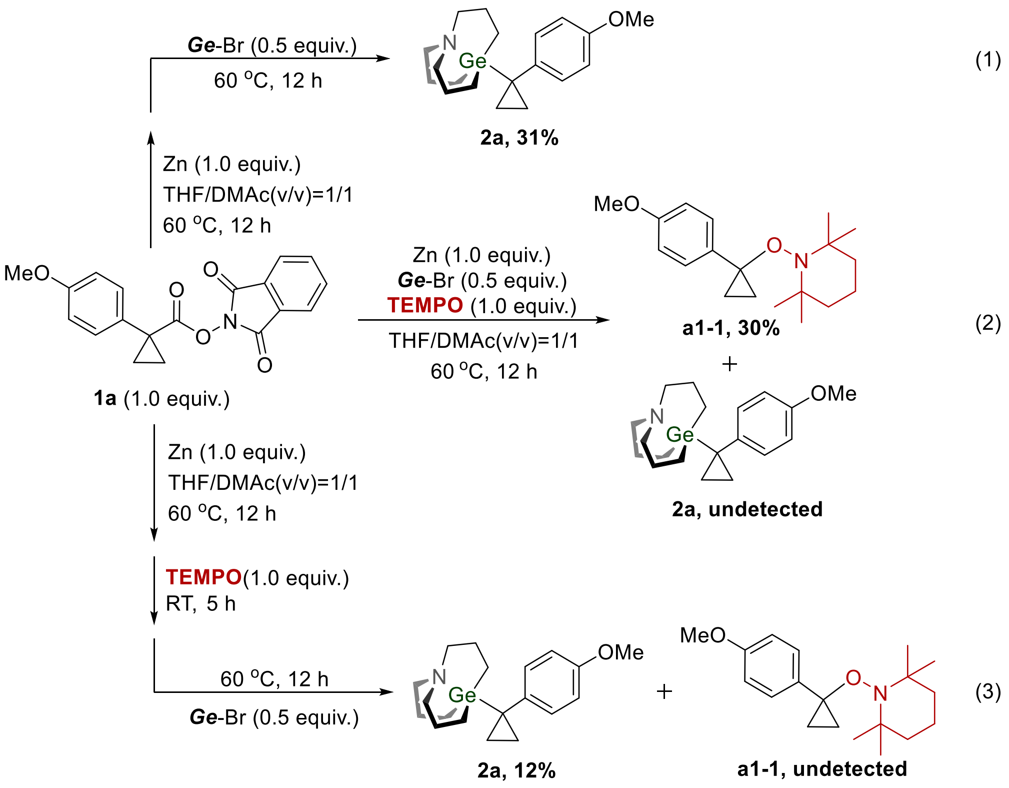


6-(1-(4-methoxyphenyl)cyclopropyl)-2-methylquinoline (3j). Prepared according to general procedure C outlined above, purified by preparative TLC using petroleum ether/ethyl acetate = 6/1 as eluent to give title compound as light yellow oil in 59% yield.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.92 (m, 2H), 7.55 – 7.50 (m, 2H), 7.25 – 7.20 (m, 3H), 6.87 – 6.81 (m, 2H), 3.78 (s, 3H), 2.71 (s, 3H), 1.39 – 1.30 (m, 4H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 157.89, 147.63, 146.28, 145.91, 137.92, 129.98, 129.21, 118.11, 115.13, 113.66, 112.76, 55.35, 29.15, 16.39. **HRMS (ESI)**: Exact mass calculated for $C_{20}H_{19}NO$ [M+H]$^+$ 290.1545, found 290.15347.

4. Mechanism Experiment

4.1 Scheme 4. TEMPO captures experiment

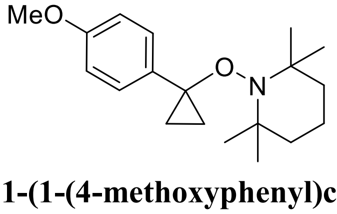


Equation (1): To an oven-dried screw-cap tube equipped with stir bar was charged with 1,3-dioxoisoindolin-2-yl 1-(4-methoxyphenyl)cyclopropane-1-carboxylate (**1a**) (0.3 mmol, 101.2 mg, 1.0 equiv.) and Zn powder (0.3 mmol, 19.5 mg, 1.0 equiv.). The tube was vacuumed and backfilled with argon for three cycles. Then DMAc (0.75 mL) and

THF (0.75 mL) were added through syringe and the tube was sealed with a teflon stopper and stirred at 60 ºC for 12 hours. 12 hours later, a clean yellow solution was obtained, to which ***Ge***-Br (0.15 mmol, 43.8 mg, 0.5 equiv.) was added under argon atmosphere. The mixture was stirred at 60 ºC 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 ether/ethyl acetate = 100/1 as eluent to give 2a in 31% yield.

Equation (2): To an oven-dried screw-cap tube equipped with stir bar was charged with 1,3-dioxoisoindolin-2-yl 1-(4-methoxyphenyl)cyclopropane-1-carboxylate (**1a**) (0.3 mmol, 101.2 mg, 1.0 equiv.), Zn powder (0.3 mmol, 19.5 mg, 1.0 equiv.), ***Ge***-Br (0.15 mmol, 43.8 mg, 0.5 equiv.) and TEMPO (0.3 mmol, 46.9 mg, 1.0 equiv.). The tube was vacuumed and backfilled with argon for three cycles, then DMAc (0.75 mL) and THF (0.75 mL) were added through syringe and the tube was sealed with a teflon stopper and stirred at 60 ºC for 12 hours. 12 hours later, quenched with NH_4Cl (sat, aq), then 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/ethyl acetate = 10/1 as eluent to give TEMPO-captured product (a1-1) in 30% yield and **2a** was not detected.

Equation (3): To an oven-dried screw-cap tube equipped with stir bar was charged with 1,3-dioxoisoindolin-2-yl 1-(4-methoxyphenyl)cyclopropane-1-carboxylate (**1a**) (0.3 mmol, 101.2 mg, 1.0 equiv.) and Zn powder (0.3 mmol, 19.5 mg, 1.0 equiv.). The tube was vacuumed and backfilled with argon for three cycles, then DMAc (0.75 mL) and THF (0.75 mL) were added through syringe and the tube was sealed with a teflon stopper and stirred at 60 ºC for 12 hours. 12 hours later, a clean yellow solution was obtained, to which TEMPO (0.3 mmol, 46.9 mg, 1.0 equiv.) was added under argon atmosphere. The mixture was stirred at room temperature for 5 hours followed by the addition of ***Ge***-Br (0.15 mmol, 43.8 mg, 0.5 equiv.) under argon atmosphere and stirred for further 12 hours at 60 ºC. 12 hours later, 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/ethyl acetate = 100/1 as eluent to give **2a** in 12% yield and TEMPO-captured product (**a1-1**) was not detected.

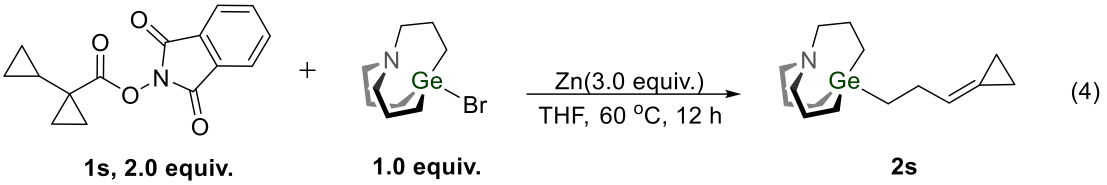


1-(1-(4-methoxyphenyl)cyclopropoxy)-2,2,6,6-tetramethylpiperidine (a1-1).

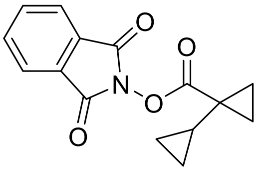
Purified by preparative TLC using petroleum ether/ethyl acetate = 10/1 as eluent to give title compound as colorless oil.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.30 (d, *J* = 7.3 Hz, 2H), 6.85 (d, *J* = 7.3 Hz, 2H), 3.80 (s, 3H), 1.67 – 1.54 (m, 4H), 1.51 (d, *J* = 14.1 Hz, 1H), 1.43 (d, *J* = 12.2 Hz, 2H), 1.33 (d, *J* = 11.7 Hz, 1H), 1.13 (s, 2H), 1.01 (s, 6H), 0.82 (s, 6H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 174.34, 158.59, 132.05, 131.60, 113.43, 60.13, 55.33, 38.81, 31.79, 27.81, 20.38, 16.93, 16.26. **HRMS (ESI)**: Exact mass calculated for $C_{19}H_{29}NO_2$ $[M+H]^+$ 304.2277, found 304.2280.

4.2 Radical probe experiments



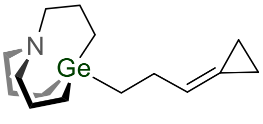
Equation 4: To an oven-dried screw-cap tube equipped with stir bar was charged with **1s** (0.6 mmol, 162.8 mg), ***Ge*-Br** (0.3 mmol, 87.6 mg) and Zn powder (0.9 mmol, 58.5 mg). The tube was vacuumed and backfilled with argon for three cycles. THF (1.5 mL) was added through syringe and the tube was sealed with a teflon stopper and stirred at 60 °C 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 **2s** in 72% yield as colorless oil.



1,3-dioxoisoindolin-2-yl [1,1'-bi(cyclopropane)]-1-carboxylate (1s).

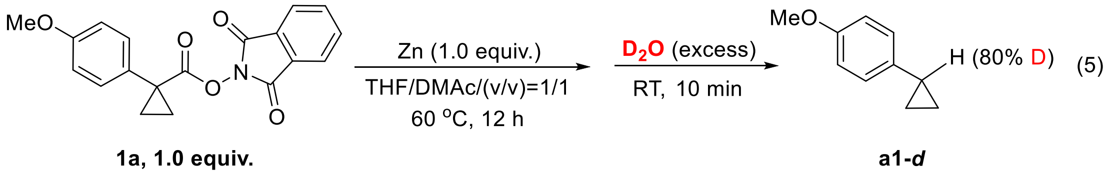
2 mmol 1-(2-methoxyphenyl)cyclopropane-1-carboxylic acid was applied in the general procedure A. Purified by recrystallization from DCM/MeOH to give title compound as white solid in 81% yield.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.92 – 7.85 (m, 2H), 7.82 – 7.75 (m, 2H), 1.66 – 1.59 (m, 1H), 1.41 (q, *J* = 4.4 Hz, 2H), 0.87 (q, *J* = 4.4 Hz, 2H), 0.61 – 0.53 (m, 2H), 0.23 – 0.14 (m, 2H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 172.28, 162.28, 134.79, 129.18, 124.02, 23.68, 14.99, 10.90, 3.09. **HRMS (ESI)**: Exact mass calculated for $C_{15}H_{13}NO_4$ $[M+H]^+$ 272.0923, found 272.0928.

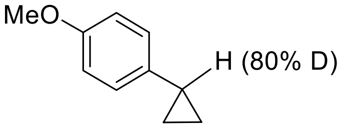


5-(3-cyclopropylidenepropyl)-1-aza-5-germabicyclo[3.3.3]undecane (2s).
^{1}H NMR (400 MHz, C_6D_6) δ 6.09 – 5.99 (m, 1H), 2.51 – 2.41 (m, 2H), 2.21 – 2.14 (m, 6H), 1.42 (m, 6H), 1.02 (m, 4H), 0.81 – 0.74 (m, 2H), 0.73 – 0.66 (m, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.28, 162.28, 134.79, 129.18, 124.02, 23.68, 14.99, 10.90, 3.09. **HRMS (ESI)**: Exact mass calculated for $C_{15}H_{27}GeN$ $[M+H]^+$ 296.1434, found 296.1440.

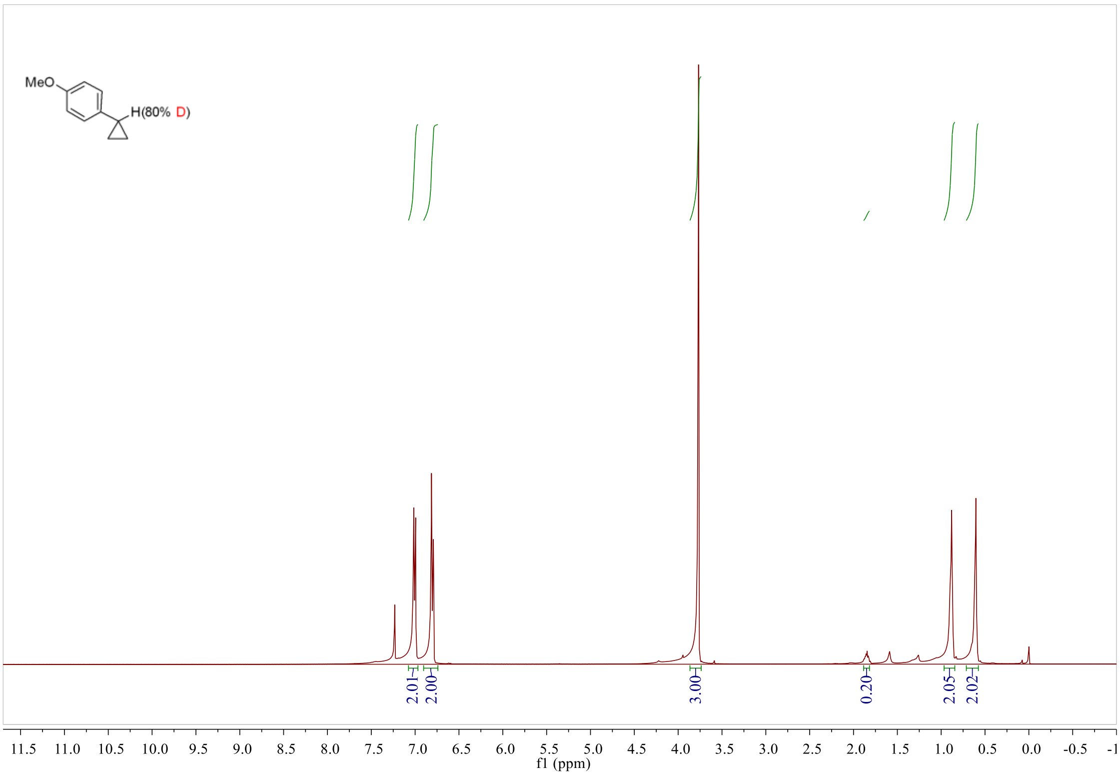
4.3 Deuterium labeling studies

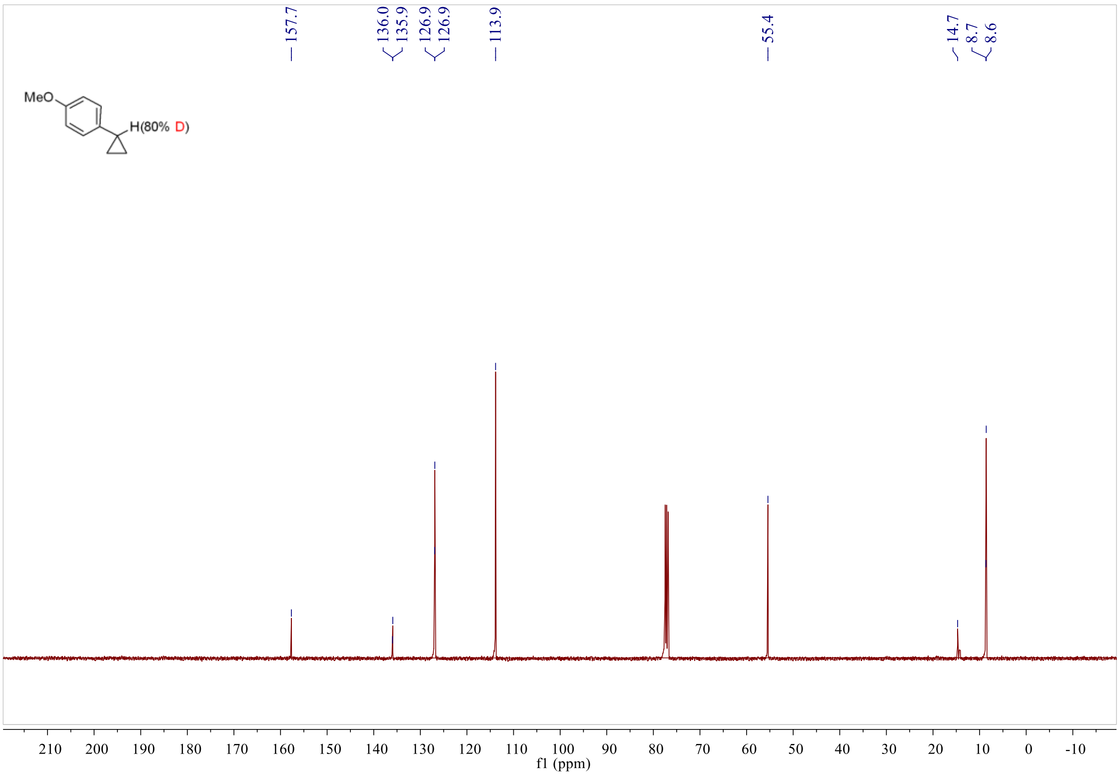


Equation 5: To an oven-dried screw-cap tube equipped with stir bar was charged with **1a** (0.3 mmol, 101.2 mg, 1.0 equiv) and Zn powder (0.3 mmol, 19.5 mg, 1.0 equiv). The tube was vacuumed and backfilled with argon for three cycles, then THF (0.75 mL) and DMAc (0.75 mL) were added through syringe and the tube was sealed with a teflon stopper and stirred at 60 °C for 12 hours. 12 hours later, the reaction mixture was cooled to room temperature and excess of D_2O was added to the reaction solution under argon atmosphere. The mixture was stirred for further 10 minutes, then 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 TLC using petroleum ether/ethyl acetate = 100/1 as eluent to give deuteration compound **a1-*d*** as colorless oil in 61% yield.



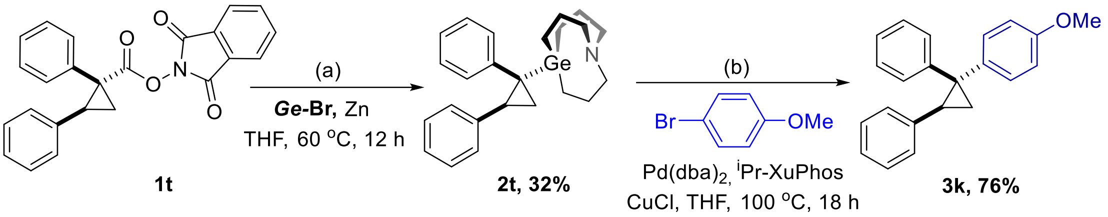
1-(cyclopropyl-1-d)-4-methoxybenzene (a1-*d*). Colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 (m, 2H), 6.74 – 6.69 (m, 2H), 3.68 (s, 3H), 1.75 (m, 0.2H), 0.80 (m, 2H), 0.52 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.67, 135.97, 135.91, 126.93, 126.89, 113.85, 55.42, 14.71, 8.65, 8.57. **HRMS (ESI)**: Exact mass calculated for $C_{10}H_{11}DO$ $[M+H]^+$ 150.1029, found 150.1051.


MeO
H(80% D)
2.01
2.00
3.00
0.20
2.05
2.02
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


157.7
136.0
135.9
126.9
126.9
113.9
55.4
14.7
8.7
8.6
MeO
H(80% D)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

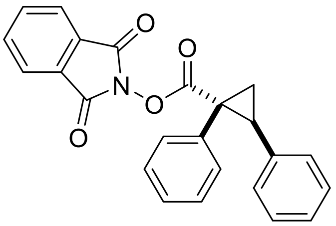
5. Stereospecific Cross-Coupling Reaction and Orthogonality Demonstration

5.1 Scheme 5. Stereospecific cross-coupling reaction



Reaction (a): To an oven-dried screw-cap tube equipped with stir bar was charged with ***Ge***-Br (0.2 mmol, 58.4 mg, 1.0 equiv.), cis-1,3-dioxoisoindolin-2-yl 1,2-diphenylcyclopropane-1-carboxylate (**1t**) (0.4 mmol, 123.6 mg, 2.0 equiv.) and Zn powder (0.4 mmol, 26 mg, 2.0 equiv.). The tube was vacuumed and backfilled with argon for three cycles, then 1.0 mL THF was added through syringe and the tube was sealed with a teflon stopper and stirred at 60 °C 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 preparative TLC using petroleum ether as eluent to give **2t** in 32% yield as white solid.

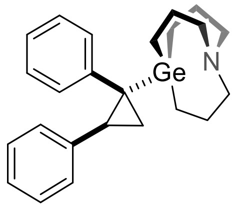
Reaction (b): To an oven-dried screw-cap tube equipped with stir bar was added $Pd(dba)_2$ (0.01 mmol, 5.75 mg, 5 mol%), ^{i}Pr-XuPhos (0.03 mmol, 23.2 mg, 15 mol%), CuCl (0.4 mmol, 39.6 mg, 2.0 equiv.) and cis-5-(1,2-diphenylcyclopropyl)-1-aza-5-germabicyclo[3.3.3]undecane (**2t**) (0.20 mmol, 81.2 mg, 1.0 equiv.). The tube was vacuumed and backfilled with argon for three cycles, then 4-bromoanisole (0.22 mmol, 42.4 mg, 1.1 equiv) and THF (1.0 mL) were added through syringe and the screw-cap tube was sealed with a teflon stopper and heated to 100 °C for 18 hours. At the end of the reaction, the reaction mixture was cooled to room temperature and added saturated sodium chloride aqueous solution, extracted with ethyl acetate three times. Organic layer was separated, dried over Na_2SO_4, concentrated under reduced pressure to give crude product, which was purified by preparative TLC using petroleum ether/ethyl acetate = 50/1 as eluent to give **3k** in 76% yield as white solid.



Cis-1,3-dioxoisoindolin-2-yl 1,2-diphenylcyclopropane-1-carboxylate (1t). 5 mmol cis-1,2-diphenylcyclopropane-1-carboxylic acid[10] was applied in the general procedure A. Purified by silica gel column chromatography using petroleum ether/ethyl acetate =

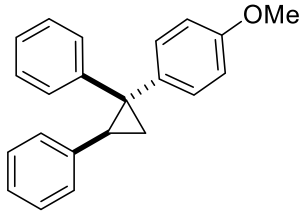
5/1 as eluent to give title compound as white solid in 86% yield.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.89 – 7.84 (m, 2H), 7.80 – 7.75 (m, 2H), 7.23 – 7.15 (m, 5H), 7.10 (m, 3H), 6.89 – 6.84 (m, 2H), 3.39 (dd, *J* = 9.4, 7.8 Hz, 1H), 2.38 (dd, *J* = 9.5, 5.4 Hz, 1H), 2.19 (dd, *J* = 7.7, 5.4 Hz, 1H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 170.52, 162.01, 134.96, 134.83, 132.34, 132.18, 129.04, 128.39, 128.08, 127.98, 127.89, 127.04, 124.01, 35.41, 35.31, 21.84. **HRMS (ESI)**: Exact mass calculated for $C_{24}H_{17}NO_4$ [M+H]$^+$ 384.1236, found 384.1230.



Cis-5-(1,2-diphenylcyclopropyl)-1-aza-5-germabicyclo[3.3.3]undecane(2t). Synthesized according to reaction (a) to give title compound as white solid in 32% yield.

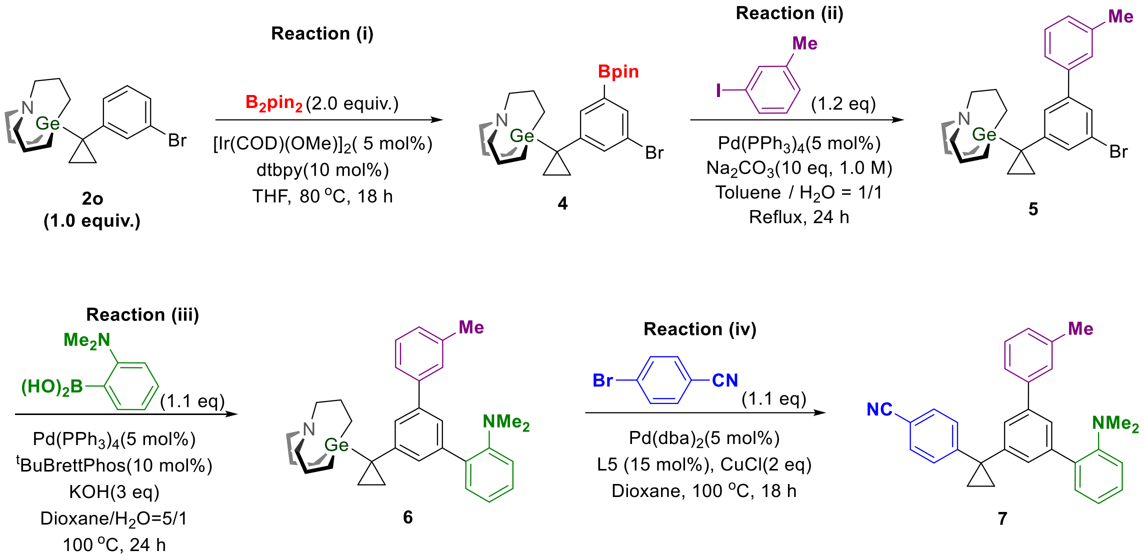
^{1}H NMR (400 MHz, C$_6$D$_6$) δ 6.79 – 6.57 (m, 8H), 6.55 – 6.49 (m, 2H), 1.99 (m, 1H), 1.79 – 1.69 (m, 6H), 1.18 – 1.09 (m, 2H), 1.08 – 1.00 (m, 6H), 0.46 – 0.34 (m, 6H). **^{13}C NMR (101 MHz, C$_6$D$_6$)** δ 144.60, 141.50, 138.65, 131.08, 129.34, 127.96, 127.72, 125.98, 125.04, 124.32, 53.59, 33.98, 26.39, 24.69, 23.83, 18.16, 11.53, 9.99. **HRMS (ESI)**: Exact mass calculated for $C_{24}H_{17}GeNO_4$ [M+H]$^+$ 408.1747, found 408.1738.



Cis-(1-(4-methoxyphenyl)cyclopropane-1,2-diyl)dibenzene (3k). Synthesized according to reaction (b) to give title compound as white solid in 76% yield. **3k** is an known compound, and can also be synthesized based on reported literature.[11]

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.27 – 7.21 (m, 2H), 7.12 – 6.99 (m, 8H), 6.89 – 6.78 (m, 4H), 3.74 (s, 3H), 2.80 (dd, *J* = 8.9, 6.5 Hz, 1H), 1.92 (dd, *J* = 6.5, 5.4 Hz, 1H), 1.73 (dd, *J* = 9.0, 5.3 Hz, 1H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 157.91, 140.78, 139.43, 138.94, 131.01, 128.75, 128.03, 128.00, 127.73, 126.21, 125.62, 113.83, 55.39, 38.88, 32.18, 20.69. **HRMS (ESI)**: Exact mass calculated for $C_{20}H_{19}NO$ [M+H]$^+$ 301.1592, found 301.1588.

5.2 Scheme 6. Orthogonal reactivity with boron reagents

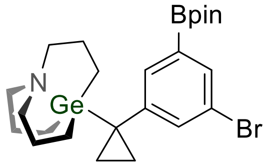


Reaction (i) : $[Ir(COD)(OMe)]_2$ (0.01 mmol, 6.63 mg, 5 mol%), dtbpy (4,4'-Di-tert-butyl-2,2'-dipyridyl, 0.02 mmol, 5.4 mg, 10 mol%), B_2pin_2 (0.4 mmol, 101.6 mg, 2.0 equiv.) were weighed and transferred to a screw-cap tube with stir bar. The tube was evacuated and backfilled three times with argon, then THF (1.0 mL) and 5-(1-(3-bromophenyl)cyclopropyl)-1-aza-5-germabicyclo[3.3.3]undecane (**2o**) (0.20 mmol, 81.80 mg, 1.0 equiv.) were added and the screw-cap tube was sealed with a teflon stopper and heated to 80 °C for 18 hours. At the end of the reaction, the reaction mixture was cooled to room temperature and purified by preparative TLC using petroleum ether/ethyl acetate = 50/1 as eluent to give 4 as white solid in 92% yield.

Reaction (ii): To an oven-dried screw-cap tube equipped with stir bar was added $Pd(PPh_3)_4$ (0.01 mmol, 11.6 mg, 5 mol%), Na_2CO_3 (2.0 mmol, 212 mg, 10.0 equiv.) and 5-(1-(3-bromo-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)phenyl)cyclopropyl)-1-aza-5-germabicyclo[3.3.3]undecane (**4**) (0.2 mmol, 107 mg, 1.0 equiv.) were weighed and transferred to a screw-cap tube with stir bar. The tube was evacuated and backfilled three times with argon, then 1-iodo-3-methylbenzene (0.24 mmol, 31.4 μl, 1.2 equiv.) was added by microsyringe, toluene (2.0 mL) and H_2O (2.0 mL) were added through syringe. Then the screw-cap tube was sealed with a teflon stopper and heated to 100 °C for 24 hours. At the end of the reaction, the reaction mixture was cooled to room temperature and extracted with ethyl acetate three times. Organic layer was separated, dried over Na_2SO_4, concentrated under reduced pressure to give crude product, which was purified by preparative TLC using petroleum ether as eluent to give **5** in 90% yield as colorless liquid.

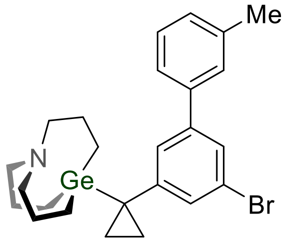
Reaction (iii): To an oven-dried screw-cap tube equipped with stir bar was added $Pd(PPh_3)_4$ (0.01 mmol, 11.6 mg, 5 mol%), ^{t}BuBrettPhos (0.02 mmol, 9.7 mg, 10 mol%), KOH (0.6 mmol, 33.7 mg, 3.0 equiv.) and (2-(dimethylamino)phenyl)boronic acid (0.22 mmol, 36.3 mg, 1.1 equiv.). The tube was evacuated and backfilled three times with argon, then 5-(1-(5-bromo-3'-methyl-[1,1'-biphenyl]-3-yl)cyclopropyl)-1-aza-5-germabicyclo[3.3.3]undecane (**5**) (0.2 mmol, 99.8 mg, 1.0 equiv.), dioxane (1.0 mL) and H_2O (0.2 mL) were added through syringe and the screw-cap tube was sealed with a teflon stopper and heated to 100 °C for 24 hours. At the end of the reaction, the reaction mixture was cooled to room temperature and extracted with ethyl acetate three times. Organic layer was separated, dried over Na_2SO_4, concentrated under reduced pressure to give crude product, which was purified by preparative TLC using petroleum ether/ethyl acetate = 50/1 as eluent to give **6** in 78% yield as colorless liquid.

Reaction (iv): To an oven-dried screw-cap tube equipped with stir bar was added $Pd(dba)_2$ (0.01 mmol, 5.75 mg, 5 mol%), ^{i}Pr-XuPhos (L_6) (0.03 mmol, 23.2 mg, 15 mol%), CuCl (0.4 mmol, 39.6 mg, 2.0 equiv.) and 4-bromobenzonitrile (0.22 mmol, 40.1 mg, 1.1 equiv.). The tube was vacuumed and backfilled with argon for three cycles, then 5'-(1-(1-aza-5-germabicyclo[3.3.3]undecan-5-yl)cyclopropyl)-N,N,3''-trimethyl-[1,1':3',1''-terphenyl]-2-amine (**6**) (0.20 mmol, 108 mg, 1.0 equiv) and THF (1.0 mL) were added through syringe and the screw-cap tube was sealed with a teflon stopper and heated to 100 °C for 18 hours. At the end of the reaction, the reaction mixture was cooled to room temperature and extracted with ethyl acetate three times. Organic layer was separated, dried over Na_2SO_4, concentrated under reduced pressure to give crude product, which was purified by preparative TLC using petroleum ether/ethyl acetate = 20/1 as eluent to give **7** in 64% yield as white solid.



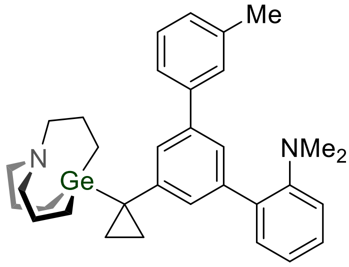
5-(1-(3-bromo-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2 yl)phenyl)cyclopropyl)-1-aza-5-germabicyclo[3.3.3]undecane (4). Synthesized according to reaction (i) to give title compound as white solid in 92% yield.

^{1}H NMR (400 MHz, C_6D_6) δ 7.89 (m, 1H), 7.73 (s, 1H), 7.44 (m, 1H), 1.68 (t, J = 5.8 Hz, 6H), 0.99 – 0.89 (m, 6H), 0.83 – 0.78 (m, 12H), 0.42 – 0.36 (m, 4H), 0.33 – 0.25 (t, J = 6.4 Hz, 6H). **^{13}C NMR (101 MHz, C_6D_6)** δ 152.97, 136.24, 135.41, 134.07, 122.40, 83.94, 53.43, 24.96, 23.65, 21.74, 9.79, 9.57. **^{11}B NMR (128 MHz, C_6D_6)** δ 30.16. **HRMS (ESI)**: Exact mass calculated for $C_{24}H_{37}BBrGeNO_2$ $[M+H]^+$ 536.1391, found 536.1383.



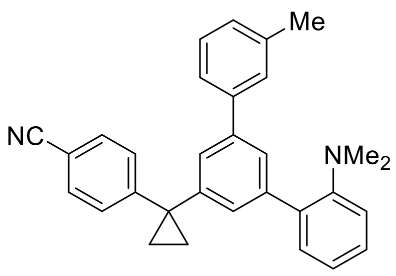
5-(1-(5-bromo-3'-methyl-[1,1'-biphenyl]-3-yl)cyclopropyl)-1-aza-5-germabicyclo[3.3.3]undecane (5). Synthesized according to reaction (ii) to give title compound as colorless liquid in 90% yield.

^{1}H NMR (400 MHz, C_6D_6) δ 7.31 – 7.25 (m, 3H), 7.02 (m, 1H), 6.85 – 6.81 (m, 2H), 6.68 (d, *J* = 7.4 Hz, 1H), 1.84 (m, 3H), 1.71 – 1.64 (t, J = 5.8 Hz, 6H), 0.96 (m, 6H), 0.47 – 0.40 (m, 4H), 0.36 – 0.30 (m, 6H). **^{13}C NMR (101 MHz, C_6D_6)** δ 153.67, 153.62, 146.99, 143.91, 143.29, 143.05, 140.85, 140.77, 140.37, 138.48, 132.10, 132.02, 129.09, 129.06, 129.02, 128.75, 128.61, 128.01, 127.94, 127.88, 127.68, 127.51, 127.48, 126.62, 126.56, 124.78, 124.74, 124.10, 123.37, 122.79, 122.76, 53.47, 23.67, 22.10, 21.49, 21.45, 15.61, 9.83, 9.68, 9.48, 1.43. **HRMS (ESI)**: Exact mass calculated for $C_{25}H_{33}BrGeN$ [M+H]$^+$ 500.1008, found 500.1013.



5'-(1-(1-aza-5-germabicyclo[3.3.3]undecan-5-yl)cyclopropyl)-N,N,3''-trimethyl-[1,1':3',1''-terphenyl]-2-amine (6). Synthesized according to reaction (iii) to give title compound as colorless liquid in 78% yield.

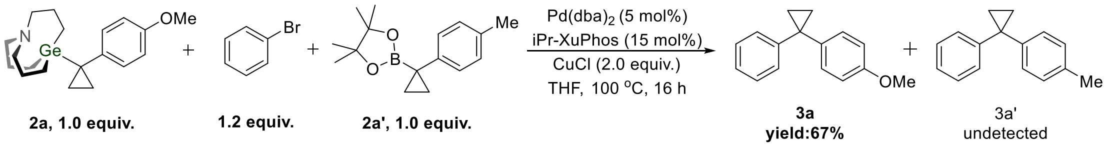
^{1}H NMR (400 MHz, C_6D_6) δ 7.42 (m, 3H), 7.29 (s, 1H), 7.17 – 7.12 (m, 2H), 6.94 – 6.89 (m, 2H), 6.71 (m, 2H), 6.65 (m, 1H), 2.18 (m, 6H), 1.88 (m, 3H), 1.79 – 1.73 (t, J = 5.8 Hz, 6H), 1.04 (m, 6H), 0.62 – 0.59 (m, 2H), 0.54 – 0.51 (m, 2H), 0.48 – 0.40 (m, 6H). **^{13}C NMR (101 MHz, C_6D_6)** δ 151.77, 151.64, 150.71, 144.70, 143.18, 142.48, 142.34, 142.13, 142.09, 141.44, 138.30, 135.59, 132.20, 130.19, 129.04, 129.01, 128.44, 127.61, 127.55, 125.45, 125.35, 124.90, 124.02, 123.49, 122.13, 122.01, 117.97, 53.61, 43.50, 43.45, 23.91, 21.81, 21.60, 9.86, 9.68, 9.50. **HRMS (ESI)**: Exact mass calculated for $C_{33}H_{43}GeN_2$ [M+H]$^+$ 541.2638, found 541.2654.



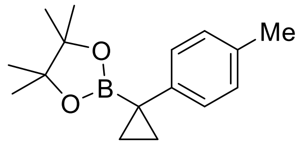
4-(1-(2-(dimethylamino)-3''-methyl-[1,1':3',1''-terphenyl]-5'-yl)cyclopropyl)benzonitrile (7). Synthesized according to reaction (iv) to give title compound as white solid in 64% yield.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.68 (d, *J* = 6.9 Hz, 1H), 7.57 – 7.50 (m, 3H), 7.42 (m, 3H), 7.34 – 7.25 (m, 5H), 7.15 (d, *J* = 7.4 Hz, 1H), 7.02 (m, 2H), 2.53 (s, 6H), 2.41 (s, 3H), 1.49 (m, 2H), 1.36 (m, 2H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 152.02, 151.94, 151.27, 144.18, 144.07, 142.70, 141.87, 141.72, 141.07, 138.47, 133.64, 132.11, 131.60, 128.95, 128.92, 128.88, 128.80, 128.44, 128.30, 128.23, 128.01, 127.49, 127.22, 126.17, 125.97, 125.92, 124.34, 121.63, 119.17, 117.85, 43.49, 30.41, 21.64, 17.45. **HRMS (ESI)**: Exact mass calculated for $C_{31}H_{29}N_2$ $[M+H]^+$ 429.2331, found 429.2337.

5.3 Competitive experiment with boron reagent



To an oven-dried screw-cap tube equipped with stir bar was added Pd(dba)$_2$ (0.01 mmol, 5.75 mg, 5 mol%), ^{i}Pr-XuPhos (0.03 mmol, 23.2 mg, 15 mol%), CuCl (0.4 mmol, 39.6 mg, 2.0 equiv.) and 4,4,5,5-tetramethyl-2-(1-(p-tolyl)cyclopropyl)-1,3,2-dioxaborolane (0.20 mmol, 51.6 mg, 1.0 equiv.). The tube was vacuumed and backfilled with argon for three cycles, then 5-(1-(4-methoxyphenyl)cyclopropyl)-1-aza-5-germabicyclo[3.3.3]undecane (**2a**) (0.20 mmol, 72 mg, 1.0 equiv.), bromobenzene (0.24 mmol, 25.4 μL, 1.2 equiv.) and THF (1.0 mL) were added through syringe and the screw-cap tube was sealed with a teflon stopper and heated to 100 °C for 16 hours. At the end of the reaction, the reaction mixture was cooled to room temperature and added saturated sodium chloride aqueous solution, extracted with ethyl acetate three times. Organic layer was separated, dried over Na$_2$SO$_4$, concentrated under reduced pressure to give crude product, which was purified by preparative TLC using petroleum ether/ethyl acetate = 100/1 as eluent to give **3a** in 67% yield as colorless oil.



4,4,5,5-tetramethyl-2-(1-(p-tolyl)cyclopropyl)-1,3,2-dioxaborolane (2a’). Synthesized based on reported literature[12], purified by preparative TLC using petroleum ether/ethyl acetate = 50/1 as eluent to give title compound as white solid in 69% yield.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.15 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 2.29 (s, 3H), 1.21 (s, 12H), 1.10 – 1.04 (m, 2H), 0.90 – 0.85 (m, 2H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 172.28, 162.28, 134.79, 129.18, 124.02, 23.68, 14.99, 10.90, 3.09. **^{11}B NMR (128 MHz, CDCl$_3$)** δ 33.84. **HRMS (ESI)**: Exact mass calculated for $C_{16}H_{23}BO_2$ $[M+Na]^+$ 281.1689, found 281.1688.

6. Reference

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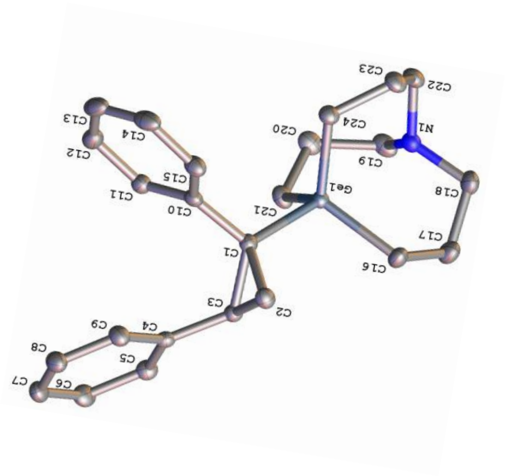
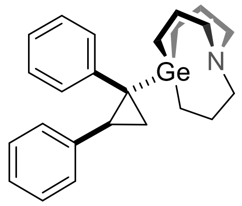
7. X-Ray Crystallographic Data and NMR Spectra

7.1 X-ray crystallographic data of 2t and 3k





2t

Figure S1. X-ray structure of compound 2t

Table S1. Crystal data and structure refinement for C24H31GeN (2t)

Identification code	C24 H31 Ge N	
Empirical formula	C24 H31 Ge N	
Formula weight	406.09	
Temperature	173.0 K	
Wavelength	1.34139 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 15.7360(11) Å	α = 90 °.
	b = 10.2256(7) Å	ß = 117.508(3) °.
	c = 14.5955(11) Å	γ = 90 °.
Volume	2083.0(3) $Å^3$	
Z	4	
Density (calculated)	1.295 Mg/m^3	
Absorption coefficient	1.381 mm^{-1}	
F(000)	856	
Crystal size	0.1 x 0.06 x 0.05 mm^3	
Theta range for data collection	4.795 to 54.931 °.	
Index ranges	-19<=h<=19, -12<=k<=12, -17<=l<=14	
Reflections collected	20026	
Independent reflections	3925 [R(int) = 0.0625]	
Completeness to theta = 53.594 °	99.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7508 and 0.5062	
Refinement method	Full-matrix least-squares on F^2	

Data / restraints / parameters	3925 / 0 / 235
Goodness-of-fit on F^2	1.069
Final R indices [I>2sigma(I)]	R1 = 0.0411, wR2 = 0.1135
R indices (all data)	R1 = 0.0441, wR2 = 0.1175
Extinction coefficient	n/a
Largest diff. peak and hole	0.776 and -1.008 e.Å^{-3}

Experimental. Single colourless prism-shaped crystals of 2t were recrystallized from CH_3CN by saturated solution at r.t.

Table S2. Atomic coordinates (x10^4) and equivalent isotropic displacement parameters (Å^{2}x10^3) for 2t. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U(eq)
Ge(1)	8096(1)	5957(1)	7021(1)	25(1)
N(1)	8311(1)	3531(2)	6644(1)	32(1)
C(1)	7894(1)	7831(2)	7290(2)	27(1)
C(2)	8602(2)	8487(2)	8272(2)	32(1)
C(3)	7643(1)	8062(2)	8171(2)	27(1)
C(4)	6911(1)	9020(2)	8120(2)	27(1)
C(5)	6189(2)	8589(2)	8342(2)	33(1)
C(6)	5487(2)	9432(3)	8309(2)	41(1)
C(7)	5495(2)	10734(2)	8057(2)	41(1)
C(8)	6205(2)	11180(2)	7837(2)	40(1)
C(9)	6907(2)	10330(2)	7867(2)	34(1)
C(10)	7433(2)	8645(2)	6327(2)	28(1)
C(11)	6442(2)	8685(2)	5720(2)	35(1)
C(12)	6033(2)	9385(3)	4794(2)	46(1)
C(13)	6606(2)	10033(2)	4459(2)	51(1)
C(14)	7584(2)	10004(2)	5052(2)	47(1)
C(15)	7994(2)	9324(2)	5980(2)	37(1)
C(16)	9104(2)	5309(2)	8366(2)	39(1)
C(17)	9098(2)	3828(2)	8513(2)	48(1)
C(18)	9105(2)	3085(2)	7614(2)	43(1)
C(19)	7382(2)	2962(2)	6408(2)	41(1)
C(20)	6604(2)	3991(2)	5906(2)	39(1)
C(21)	6813(2)	5198(2)	6590(2)	35(1)
C(22)	8527(2)	3625(2)	5779(2)	37(1)

C(23)	9053(2)	4903(2)	5853(2)	37(1)
C(24)	8489(2)	6076(2)	5929(2)	31(1)

Table S3. Bond lengths [Å] for 2t

Ge(1)-C(1)	2.0110(19)	C(12)-C(13)	1.378(4)
Ge(1)-C(16)	1.982(2)	C(13)-H(13)	0.9500
Ge(1)-C(21)	1.975(2)	C(13)-C(14)	1.374(4)
Ge(1)-C(24)	1.962(2)	C(14)-H(14)	0.9500
N(1)-C(18)	1.463(3)	C(14)-C(15)	1.388(3)
N(1)-C(19)	1.459(3)	C(15)-H(15)	0.9500
N(1)-C(22)	1.454(3)	C(16)-H(16A)	0.9900
C(1)-C(2)	1.506(3)	C(16)-H(16B)	0.9900
C(1)-C(3)	1.528(3)	C(16)-C(17)	1.531(3)
C(1)-C(10)	1.500(3)	C(17)-H(17A)	0.9900
C(2)-H(2A)	0.9900	C(17)-H(17B)	0.9900
C(2)-H(2B)	0.9900	C(17)-C(18)	1.520(4)
C(2)-C(3)	1.511(3)	C(18)-H(18A)	0.9900
C(3)-H(3)	1.0000	C(18)-H(18B)	0.9900
C(3)-C(4)	1.487(3)	C(19)-H(19A)	0.9900
C(4)-C(5)	1.390(3)	C(19)-H(19B)	0.9900
C(4)-C(9)	1.389(3)	C(19)-C(20)	1.521(3)
C(5)-H(5)	0.9500	C(20)-H(20A)	0.9900
C(5)-C(6)	1.385(3)	C(20)-H(20B)	0.9900
C(6)-H(6)	0.9500	C(20)-C(21)	1.524(3)
C(6)-C(7)	1.383(4)	C(21)-H(21A)	0.9900
C(7)-H(7)	0.9500	C(21)-H(21B)	0.9900
C(7)-C(8)	1.374(4)	C(22)-H(22A)	0.9900
C(8)-H(8)	0.9500	C(22)-H(22B)	0.9900
C(8)-C(9)	1.391(3)	C(22)-C(23)	1.524(3)
C(9)-H(9)	0.9500	C(23)-H(23A)	0.9900
C(10)-C(11)	1.394(3)	C(23)-H(23B)	0.9900
C(10)-C(15)	1.391(3)	C(23)-C(24)	1.527(3)
C(11)-H(11)	0.9500	C(24)-H(24A)	0.9900
C(11)-C(12)	1.397(3)	C(24)-H(24B)	0.9900
C(12)-H(12)	0.9500		

Table S4. Bond angles [°] for 2t

C(16)-Ge(1)-C(1)	104.58(9)	C(8)-C(7)-C(6)	119.4(2)
C(21)-Ge(1)-C(1)	101.91(8)	C(8)-C(7)-H(7)	120.3
C(21)-Ge(1)-C(16)	114.69(10)	C(7)-C(8)-H(8)	119.8
C(24)-Ge(1)-C(1)	103.67(8)	C(7)-C(8)-C(9)	120.3(2)
C(24)-Ge(1)-C(16)	114.63(10)	C(9)-C(8)-H(8)	119.8
C(24)-Ge(1)-C(21)	115.11(10)	C(4)-C(9)-C(8)	121.1(2)
C(19)-N(1)-C(18)	114.8(2)	C(4)-C(9)-H(9)	119.4
C(22)-N(1)-C(18)	115.10(18)	C(8)-C(9)-H(9)	119.4
C(22)-N(1)-C(19)	115.55(19)	C(11)-C(10)-C(1)	121.81(19)
C(2)-C(1)-Ge(1)	119.73(14)	C(15)-C(10)-C(1)	120.28(19)
C(2)-C(1)-C(3)	59.71(13)	C(15)-C(10)-C(11)	117.8(2)
C(3)-C(1)-Ge(1)	115.88(13)	C(10)-C(11)-H(11)	119.7
C(10)-C(1)-Ge(1)	113.43(14)	C(10)-C(11)-C(12)	120.7(2)
C(10)-C(1)-C(2)	118.00(17)	C(12)-C(11)-H(11)	119.7
C(10)-C(1)-C(3)	120.09(16)	C(11)-C(12)-H(12)	119.8
C(1)-C(2)-H(2A)	117.7	C(13)-C(12)-C(11)	120.4(3)
C(1)-C(2)-H(2B)	117.7	C(13)-C(12)-H(12)	119.8
C(1)-C(2)-C(3)	60.87(13)	C(12)-C(13)-H(13)	120.3
H(2A)-C(2)-H(2B)	114.8	C(14)-C(13)-C(12)	119.5(2)
C(3)-C(2)-H(2A)	117.7	C(14)-C(13)-H(13)	120.3
C(3)-C(2)-H(2B)	117.7	C(13)-C(14)-H(14)	119.8
C(1)-C(3)-H(3)	113.7	C(13)-C(14)-C(15)	120.4(2)
C(2)-C(3)-C(1)	59.42(13)	C(15)-C(14)-H(14)	119.8
C(2)-C(3)-H(3)	113.7	C(10)-C(15)-H(15)	119.4
C(4)-C(3)-C(1)	123.68(17)	C(14)-C(15)-C(10)	121.2(2)
C(4)-C(3)-C(2)	122.02(17)	C(14)-C(15)-H(15)	119.4
C(4)-C(3)-H(3)	113.7	Ge(1)-C(16)-H(16A)	108.6
C(5)-C(4)-C(3)	118.47(18)	Ge(1)-C(16)-H(16B)	108.6
C(9)-C(4)-C(3)	123.88(19)	H(16A)-C(16)-H(16B)	107.6
C(9)-C(4)-C(5)	117.66(19)	C(17)-C(16)-Ge(1)	114.54(17)
C(4)-C(5)-H(5)	119.3	C(17)-C(16)-H(16A)	108.6
C(6)-C(5)-C(4)	121.3(2)	C(17)-C(16)-H(16B)	108.6
C(6)-C(5)-H(5)	119.3	C(16)-C(17)-H(17A)	109.3
C(5)-C(6)-H(6)	119.9	C(16)-C(17)-H(17B)	109.3
C(7)-C(6)-C(5)	120.2(2)	H(17A)-C(17)-H(17B)	107.9
C(7)-C(6)-H(6)	119.9	C(18)-C(17)-C(16)	111.7(2)
C(6)-C(7)-H(7)	120.3	C(18)-C(17)-H(17A)	109.3

C(18)-C(17)-H(17B)	109.3	C(20)-C(21)-H(21A)	108.8
N(1)-C(18)-C(17)	109.68(19)	C(20)-C(21)-H(21B)	108.8
N(1)-C(18)-H(18A)	109.7	H(21A)-C(21)-H(21B)	107.7
N(1)-C(18)-H(18B)	109.7	N(1)-C(22)-H(22A)	109.8
C(17)-C(18)-H(18A)	109.7	N(1)-C(22)-H(22B)	109.8
C(17)-C(18)-H(18B)	109.7	N(1)-C(22)-C(23)	109.38(18)
H(18A)-C(18)-H(18B)	108.2	H(22A)-C(22)-H(22B)	108.2
N(1)-C(19)-H(19A)	109.8	C(23)-C(22)-H(22A)	109.8
N(1)-C(19)-H(19B)	109.8	C(23)-C(22)-H(22B)	109.8
N(1)-C(19)-C(20)	109.50(19)	C(22)-C(23)-H(23A)	109.4
H(19A)-C(19)-H(19B)	108.2	C(22)-C(23)-H(23B)	109.4
C(20)-C(19)-H(19A)	109.8	C(22)-C(23)-C(24)	111.36(18)
C(20)-C(19)-H(19B)	109.8	H(23A)-C(23)-H(23B)	108.0
C(19)-C(20)-H(20A)	109.4	C(24)-C(23)-H(23A)	109.4
C(19)-C(20)-H(20B)	109.4	C(24)-C(23)-H(23B)	109.4
C(19)-C(20)-C(21)	111.3(2)	Ge(1)-C(24)-H(24A)	108.5
H(20A)-C(20)-H(20B)	108.0	Ge(1)-C(24)-H(24B)	108.5
C(21)-C(20)-H(20A)	109.4	C(23)-C(24)-Ge(1)	114.94(15)
C(21)-C(20)-H(20B)	109.4	C(23)-C(24)-H(24A)	108.5
Ge(1)-C(21)-H(21A)	108.8	C(23)-C(24)-H(24B)	108.5
Ge(1)-C(21)-H(21B)	108.8	H(24A)-C(24)-H(24B)	107.5
C(20)-C(21)-Ge(1)	113.95(15)		

Table S5. Anisotropic displacement parameters (Å^{2}x 10^3) for 2t. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2hka^{*}\ b^{*}\ U^{12}\ ]$

	U^{11}	**U^{22}**	**U^{33}**	**U^{23}**	**U^{13}**	**U^{12}**
Ge(1)	25(1)	25(1)	25(1)	1(1)	12(1)	3(1)
N(1)	36(1)	30(1)	34(1)	1(1)	18(1)	5(1)
C(1)	26(1)	26(1)	29(1)	0(1)	14(1)	1(1)
C(2)	29(1)	31(1)	35(1)	-2(1)	14(1)	0(1)
C(3)	30(1)	25(1)	25(1)	1(1)	13(1)	0(1)
C(4)	29(1)	29(1)	22(1)	-2(1)	11(1)	-1(1)
C(5)	34(1)	32(1)	33(1)	0(1)	16(1)	-3(1)
C(6)	29(1)	55(1)	42(1)	0(1)	19(1)	2(1)
C(7)	36(1)	50(1)	37(1)	2(1)	17(1)	14(1)

C(8)	52(1)	33(1)	40(1)	5(1)	26(1)	9(1)
C(9)	40(1)	31(1)	38(1)	3(1)	24(1)	2(1)
C(10)	37(1)	24(1)	28(1)	-2(1)	18(1)	4(1)
C(11)	39(1)	34(1)	32(1)	0(1)	17(1)	6(1)
C(12)	56(2)	42(1)	31(1)	-3(1)	12(1)	15(1)
C(13)	88(2)	34(1)	32(1)	5(1)	28(1)	15(1)
C(14)	81(2)	30(1)	48(2)	3(1)	45(2)	2(1)
C(15)	48(1)	28(1)	44(1)	3(1)	30(1)	3(1)
C(16)	44(1)	36(1)	26(1)	2(1)	8(1)	9(1)
C(17)	63(2)	40(1)	34(1)	8(1)	15(1)	14(1)
C(18)	49(1)	33(1)	43(1)	7(1)	18(1)	14(1)
C(19)	50(1)	28(1)	54(2)	-6(1)	32(1)	-5(1)
C(20)	32(1)	38(1)	49(2)	8(1)	21(1)	-7(1)
C(21)	32(1)	31(1)	47(1)	-1(1)	22(1)	0(1)
C(22)	43(1)	36(1)	39(1)	-3(1)	24(1)	5(1)
C(23)	37(1)	42(1)	42(1)	1(1)	27(1)	4(1)
C(24)	33(1)	32(1)	33(1)	1(1)	19(1)	1(1)

Table S6. Hydrogen coordinates (x10^{4}) and isotropic displacement parameters (Å^{2}x10^{3}) for 2t.

	x	**y**	**z**	**U(eq)**
H(2A)	8712	9436	8244	38
H(2B)	9174	7981	8743	38
H(3)	7675	7254	8572	32
H(5)	6177	7698	8521	39
H(6)	4997	9114	8459	49
H(7)	5016	11315	8037	49
H(8)	6215	12073	7663	48
H(9)	7393	10652	7711	41
H(11)	6040	8232	5939	42
H(12)	5356	9415	4393	55
H(13)	6327	10496	3823	61
H(14)	7982	10453	4826	56
H(15)	8671	9323	6385	44
H(16A)	9738	5566	8434	47
H(16B)	9026	5746	8927	47
H(17A)	9668	3576	9160	58
H(17B)	8521	3583	8579	58

H(18A)	9720	3235	7600	51
H(18B)	9041	2136	7701	51
H(19A)	7388	2642	7051	49
H(19B)	7250	2210	5934	49
H(20A)	5979	3617	5777	47
H(20B)	6562	4248	5232	47
H(21A)	6752	4961	7215	42
H(21B)	6324	5872	6212	42
H(22A)	7925	3596	5120	44
H(22B)	8931	2876	5791	44
H(23A)	9154	4999	5235	45
H(23B)	9689	4879	6469	45
H(24A)	7908	6184	5257	37
H(24B)	8885	6871	6048	37

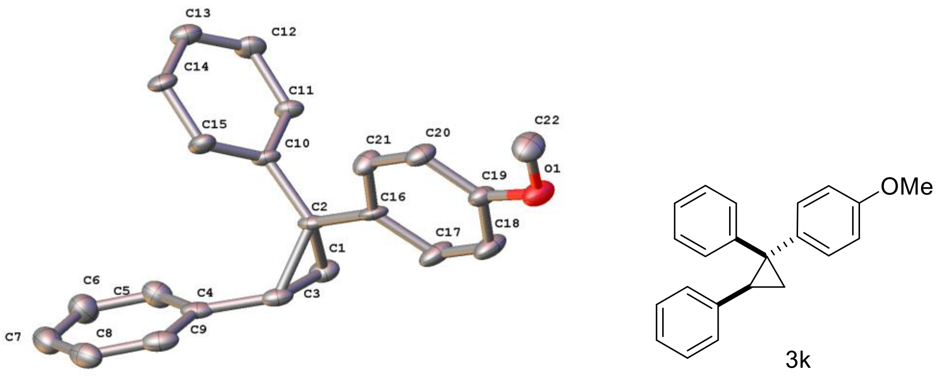


Figure S2. X-ray structure of compound 3k

Table S7. Crystal data and structure refinement for C22H20O (3k)

Identification code	C22 H20 O	
Empirical formula	C22 H20 O	
Formula weight	300.38	
Temperature	173.0 K	
Wavelength	1.34139 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 32.854(6) Å	α = 90 °.
	b = 5.8699(12) Å	β = 90 °.
	c = 34.286(6) Å	γ = 90°.
Volume	6612(2) $Å^3$	

Z	16
Density (calculated)	1.207 Mg/m^3
Absorption coefficient	0.357 mm^{-1}
F(000)	2560
Crystal size	0.05 x 0.01 x 0.01 mm^3
Theta range for data collection	3.242 to 55.052 °.
Index ranges	-39<=h<=24, -7<=k<=3, -41<=l<=34
Reflections collected	21701
Independent reflections	6044 [R(int) = 0.1322]
Completeness to theta = 53.594 °	96.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7508 and 0.1560
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6044 / 0 / 417
Goodness-of-fit on F^2	0.977
Final R indices [I>2sigma(I)]	R1 = 0.1063, wR2 = 0.2407
R indices (all data)	R1 = 0.2265, wR2 = 0.3178
Extinction coefficient	n/a
Largest diff. peak and hole	0.367 and -0.337 e.Å^{-3}

Experimental. Single colourless prism-shaped crystals of 3k were recrystallized from petroleum ether by saturated solution at rt.

Table S8. Atomic coordinates (x10^4) and equivalent isotropic displacement parameters (Å^{2}x10^3) for 3k. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	**y**	**z**	**U(eq)**
O(1)	4474(1)	333(8)	6766(1)	57(1)
C(1)	4369(2)	6597(9)	5191(2)	43(2)
C(2)	4136(2)	4475(8)	5303(2)	32(1)
C(3)	4494(2)	4348(8)	5012(2)	39(1)
C(4)	4444(2)	3817(9)	4590(2)	40(1)
C(5)	4249(2)	5265(10)	4329(2)	52(2)
C(6)	4217(2)	4735(12)	3939(2)	60(2)
C(7)	4385(2)	2697(12)	3798(2)	58(2)
C(8)	4572(2)	1226(11)	4052(2)	56(2)

C(9)	4605(2)	1791(10)	4444(2)	50(2)
C(10)	3704(1)	4326(8)	5165(2)	32(1)
C(11)	3431(2)	5975(9)	5281(2)	36(1)
C(12)	3024(2)	5897(10)	5171(2)	46(2)
C(13)	2892(2)	4154(10)	4931(2)	46(2)
C(14)	3160(2)	2479(9)	4816(2)	42(1)
C(15)	3566(2)	2571(9)	4930(2)	41(1)
C(16)	4218(1)	3430(9)	5700(2)	35(1)
C(17)	4532(2)	4128(10)	5938(2)	54(2)
C(18)	4613(2)	3077(11)	6289(2)	57(2)
C(19)	4367(2)	1277(9)	6413(2)	40(1)
C(20)	4053(2)	573(10)	6182(2)	46(2)
C(21)	3975(2)	1652(9)	5828(2)	43(2)
C(22)	4253(2)	-1647(11)	6882(2)	61(2)
O(2)	3061(1)	8599(6)	6047(1)	45(1)
C(1A)	3083(2)	3136(9)	7710(2)	44(2)
C(2A)	3320(1)	5166(8)	7578(1)	29(1)
C(3A)	2997(2)	5448(8)	7892(2)	36(1)
C(4A)	3086(2)	6038(9)	8305(2)	34(1)
C(5A)	2901(2)	7947(9)	8464(2)	46(2)
C(6A)	2970(2)	8641(10)	8845(2)	52(2)
C(7A)	3239(2)	7358(11)	9074(2)	51(2)
C(8A)	3428(2)	5439(10)	8922(2)	52(2)
C(9A)	3352(2)	4776(9)	8544(2)	47(2)
C(10A)	3763(1)	5339(8)	7683(1)	30(1)
C(11A)	3919(2)	7281(9)	7864(2)	36(1)
C(12A)	4330(2)	7456(11)	7948(2)	50(2)
C(13A)	4591(2)	5689(11)	7861(2)	49(2)
C(14A)	4444(2)	3772(11)	7679(2)	48(2)
C(15A)	4031(2)	3578(9)	7598(2)	40(1)
C(16A)	3225(2)	6093(9)	7175(2)	32(1)
C(17A)	3384(2)	5019(9)	6840(2)	39(1)
C(18A)	3322(2)	5873(9)	6475(2)	40(1)
C(19A)	3094(2)	7856(9)	6426(2)	37(1)
C(20A)	2925(2)	8945(9)	6745(2)	43(1)
C(21A)	2996(2)	8039(9)	7114(2)	39(1)
C(22A)	2843(2)	10679(9)	5979(2)	52(2)

Table S9. Bond lengths [Å] for 3k

O(1)-C(19)	1.377(6)	C(1)-H(1B)	0.9900
O(1)-C(22)	1.426(7)	C(1)-C(2)	1.511(7)
C(1)-H(1A)	0.9900	C(1)-C(3)	1.512(7)

C(2)-C(3)	1.542(7)	C(22)-H(22B)	0.9800
C(2)-C(10)	1.498(6)	C(22)-H(22C)	0.9800
C(2)-C(16)	1.517(7)	O(2)-C(19A)	1.375(6)
C(3)-H(3)	1.0000	O(2)-C(22A)	1.435(6)
C(3)-C(4)	1.489(8)	C(1A)-H(1AA)	0.9900
C(4)-C(5)	1.391(8)	C(1A)-H(1AB)	0.9900
C(4)-C(9)	1.395(8)	C(1A)-C(2A)	1.492(7)
C(5)-H(5)	0.9500	C(1A)-C(3A)	1.521(7)
C(5)-C(6)	1.378(8)	C(2A)-C(3A)	1.519(6)
C(6)-H(6)	0.9500	C(2A)-C(10A)	1.506(6)
C(6)-C(7)	1.403(8)	C(2A)-C(16A)	1.519(7)
C(7)-H(7)	0.9500	C(3A)-H(3A)	1.0000
C(7)-C(8)	1.373(8)	C(3A)-C(4A)	1.486(7)
C(8)-H(8)	0.9500	C(4A)-C(5A)	1.387(7)
C(8)-C(9)	1.388(8)	C(4A)-C(9A)	1.407(7)
C(9)-H(9)	0.9500	C(5A)-H(5A)	0.9500
C(10)-C(11)	1.378(6)	C(5A)-C(6A)	1.386(8)
C(10)-C(15)	1.385(7)	C(6A)-H(6A)	0.9500
C(11)-H(11)	0.9500	C(6A)-C(7A)	1.400(8)
C(11)-C(12)	1.390(7)	C(7A)-H(7A)	0.9500
C(12)-H(12)	0.9500	C(7A)-C(8A)	1.387(8)
C(12)-C(13)	1.383(7)	C(8A)-H(8A)	0.9500
C(13)-H(13)	0.9500	C(8A)-C(9A)	1.376(7)
C(13)-C(14)	1.377(7)	C(9A)-H(9A)	0.9500
C(14)-H(14)	0.9500	C(10A)-C(11A)	1.395(7)
C(14)-C(15)	1.392(6)	C(10A)-C(15A)	1.388(6)
C(15)-H(15)	0.9500	C(11A)-H(11A)	0.9500
C(16)-C(17)	1.379(7)	C(11A)-C(12A)	1.385(7)
C(16)-C(21)	1.385(7)	C(12A)-H(12A)	0.9500
C(17)-H(17)	0.9500	C(12A)-C(13A)	1.378(8)
C(17)-C(18)	1.379(7)	C(13A)-H(13A)	0.9500
C(18)-H(18)	0.9500	C(13A)-C(14A)	1.374(8)
C(18)-C(19)	1.395(7)	C(14A)-H(14A)	0.9500
C(19)-C(20)	1.367(7)	C(14A)-C(15A)	1.390(7)
C(20)-H(20)	0.9500	C(15A)-H(15A)	0.9500
C(20)-C(21)	1.393(7)	C(16A)-C(17A)	1.408(7)
C(21)-H(21)	0.9500	C(16A)-C(21A)	1.384(7)
C(22)-H(22A)	0.9800	C(17A)-H(17A)	0.9500

C(17A)-C(18A)	1.362(7)	C(20A)-C(21A)	1.394(7)
C(18A)-H(18A)	0.9500	C(21A)-H(21A)	0.9500
C(18A)-C(19A)	1.394(7)	C(22A)-H(22D)	0.9800
C(19A)-C(20A)	1.383(7)	C(22A)-H(22E)	0.9800
C(20A)-H(20A)	0.9500	C(22A)-H(22F)	0.9800

Table S10. Bond angles [°] for 3k

C(19)-O(1)-C(22)	116.4(4)	C(8)-C(7)-C(6)	119.6(6)
H(1A)-C(1)-H(1B)	114.7	C(8)-C(7)-H(7)	120.2
C(2)-C(1)-H(1A)	117.6	C(7)-C(8)-H(8)	120.0
C(2)-C(1)-H(1B)	117.6	C(7)-C(8)-C(9)	120.0(6)
C(2)-C(1)-C(3)	61.3(3)	C(9)-C(8)-H(8)	120.0
C(3)-C(1)-H(1A)	117.6	C(4)-C(9)-H(9)	119.3
C(3)-C(1)-H(1B)	117.6	C(8)-C(9)-C(4)	121.5(6)
C(1)-C(2)-C(3)	59.4(3)	C(8)-C(9)-H(9)	119.3
C(1)-C(2)-C(16)	118.1(4)	C(11)-C(10)-C(2)	119.0(5)
C(10)-C(2)-C(1)	116.7(5)	C(11)-C(10)-C(15)	118.4(5)
C(10)-C(2)-C(3)	121.1(4)	C(15)-C(10)-C(2)	122.6(4)
C(10)-C(2)-C(16)	115.2(4)	C(10)-C(11)-H(11)	119.1
C(16)-C(2)-C(3)	115.2(4)	C(10)-C(11)-C(12)	121.7(5)
C(1)-C(3)-C(2)	59.3(3)	C(12)-C(11)-H(11)	119.1
C(1)-C(3)-H(3)	113.5	C(11)-C(12)-H(12)	120.4
C(2)-C(3)-H(3)	113.5	C(13)-C(12)-C(11)	119.2(5)
C(4)-C(3)-C(1)	123.2(5)	C(13)-C(12)-H(12)	120.4
C(4)-C(3)-C(2)	123.6(4)	C(12)-C(13)-H(13)	120.1
C(4)-C(3)-H(3)	113.5	C(14)-C(13)-C(12)	119.9(5)
C(5)-C(4)-C(3)	123.3(5)	C(14)-C(13)-H(13)	120.1
C(5)-C(4)-C(9)	117.6(6)	C(13)-C(14)-H(14)	119.9
C(9)-C(4)-C(3)	119.0(5)	C(13)-C(14)-C(15)	120.2(5)
C(4)-C(5)-H(5)	119.3	C(15)-C(14)-H(14)	119.9
C(6)-C(5)-C(4)	121.5(6)	C(10)-C(15)-C(14)	120.5(5)
C(6)-C(5)-H(5)	119.3	C(10)-C(15)-H(15)	119.7
C(5)-C(6)-H(6)	120.1	C(14)-C(15)-H(15)	119.7
C(5)-C(6)-C(7)	119.8(6)	C(17)-C(16)-C(2)	122.9(5)
C(7)-C(6)-H(6)	120.1	C(17)-C(16)-C(21)	117.9(5)
C(6)-C(7)-H(7)	120.2	C(21)-C(16)-C(2)	119.1(5)

C(16)-C(17)-H(17)	119.1
C(16)-C(17)-C(18)	121.9(5)
C(18)-C(17)-H(17)	119.1
C(17)-C(18)-H(18)	120.2
C(17)-C(18)-C(19)	119.6(5)
C(19)-C(18)-H(18)	120.2
O(1)-C(19)-C(18)	115.2(5)
C(20)-C(19)-O(1)	125.5(5)
C(20)-C(19)-C(18)	119.3(5)
C(19)-C(20)-H(20)	119.8
C(19)-C(20)-C(21)	120.4(5)
C(21)-C(20)-H(20)	119.8
C(16)-C(21)-C(20)	120.9(5)
C(16)-C(21)-H(21)	119.6
C(20)-C(21)-H(21)	119.6
O(1)-C(22)-H(22A)	109.5
O(1)-C(22)-H(22B)	109.5
O(1)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
C(19A)-O(2)-C(22A)	117.6(4)
H(1AA)-C(1A)-H(1AB)	114.8
C(2A)-C(1A)-H(1AA)	117.7
C(2A)-C(1A)-H(1AB)	117.7
C(2A)-C(1A)-C(3A)	60.5(3)
C(3A)-C(1A)-H(1AA)	117.7
C(3A)-C(1A)-H(1AB)	117.7
C(1A)-C(2A)-C(3A)	60.7(3)
C(1A)-C(2A)-C(10A)	119.1(4)
C(1A)-C(2A)-C(16A)	117.0(4)
C(3A)-C(2A)-C(16A)	117.7(4)
C(10A)-C(2A)-C(3A)	119.9(4)
C(10A)-C(2A)-C(16A)	113.0(4)
C(1A)-C(3A)-H(3A)	113.0
C(2A)-C(3A)-C(1A)	58.8(3)
C(2A)-C(3A)-H(3A)	113.0
C(4A)-C(3A)-C(1A)	124.4(5)
C(4A)-C(3A)-C(2A)	124.4(4)
C(4A)-C(3A)-H(3A)	113.0
C(5A)-C(4A)-C(3A)	118.5(5)
C(5A)-C(4A)-C(9A)	118.0(5)
C(9A)-C(4A)-C(3A)	123.6(5)
C(4A)-C(5A)-H(5A)	118.8
C(6A)-C(5A)-C(4A)	122.3(6)
C(6A)-C(5A)-H(5A)	118.8
C(5A)-C(6A)-H(6A)	120.9
C(5A)-C(6A)-C(7A)	118.3(6)
C(7A)-C(6A)-H(6A)	120.9
C(6A)-C(7A)-H(7A)	119.7
C(8A)-C(7A)-C(6A)	120.5(6)
C(8A)-C(7A)-H(7A)	119.7
C(7A)-C(8A)-H(8A)	119.9
C(9A)-C(8A)-C(7A)	120.1(6)
C(9A)-C(8A)-H(8A)	119.9
C(4A)-C(9A)-H(9A)	119.6
C(8A)-C(9A)-C(4A)	120.8(5)
C(8A)-C(9A)-H(9A)	119.6
C(11A)-C(10A)-C(2A)	121.0(4)
C(15A)-C(10A)-C(2A)	120.9(5)
C(15A)-C(10A)-C(11A)	118.0(5)
C(10A)-C(11A)-H(11A)	119.7
C(12A)-C(11A)-C(10A)	120.7(5)
C(12A)-C(11A)-H(11A)	119.7
C(11A)-C(12A)-H(12A)	119.8
C(13A)-C(12A)-C(11A)	120.4(6)
C(13A)-C(12A)-H(12A)	119.8
C(12A)-C(13A)-H(13A)	120.1
C(14A)-C(13A)-C(12A)	119.8(5)
C(14A)-C(13A)-H(13A)	120.1
C(13A)-C(14A)-H(14A)	120.0
C(13A)-C(14A)-C(15A)	120.0(5)
C(15A)-C(14A)-H(14A)	120.0
C(10A)-C(15A)-H(15A)	119.5
C(14A)-C(15A)-C(10A)	121.1(5)
C(14A)-C(15A)-H(15A)	119.5

C(17A)-C(16A)-C(2A)	120.5(5)	C(19A)-C(20A)-H(20A)	120.8
C(21A)-C(16A)-C(2A)	122.8(5)	C(19A)-C(20A)-C(21A)	118.3(5)
C(21A)-C(16A)-C(17A)	116.7(5)	C(21A)-C(20A)-H(20A)	120.8
C(16A)-C(17A)-H(17A)	119.1	C(16A)-C(21A)-C(20A)	122.8(5)
C(18A)-C(17A)-C(16A)	121.9(5)	C(16A)-C(21A)-H(21A)	118.6
C(18A)-C(17A)-H(17A)	119.1	C(20A)-C(21A)-H(21A)	118.6
C(17A)-C(18A)-H(18A)	120.1	O(2)-C(22A)-H(22D)	109.5
C(17A)-C(18A)-C(19A)	119.9(5)	O(2)-C(22A)-H(22E)	109.5
C(19A)-C(18A)-H(18A)	120.1	O(2)-C(22A)-H(22F)	109.5
O(2)-C(19A)-C(18A)	115.0(5)	H(22D)-C(22A)-H(22E)	109.5
O(2)-C(19A)-C(20A)	124.6(5)	H(22D)-C(22A)-H(22F)	109.5
C(20A)-C(19A)-C(18A)	120.4(5)	H(22E)-C(22A)-H(22F)	109.5

Table S11. Anisotropic displacement parameters (Å^{2}x 10^3) for 3k. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2hka^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	39(3)	75(3)	57(3)	19(2)	-8(2)	-14(2)
C(1)	34(4)	38(3)	57(4)	7(3)	1(3)	-9(3)
C(2)	17(3)	27(3)	50(3)	-2(2)	9(2)	-6(2)
C(3)	22(3)	35(3)	59(4)	10(3)	5(3)	-3(2)
C(4)	22(3)	35(3)	63(4)	11(3)	12(3)	-4(2)
C(5)	54(4)	51(4)	52(4)	0(3)	12(3)	2(3)
C(6)	59(5)	68(5)	54(4)	0(4)	4(3)	3(4)
C(7)	59(5)	64(4)	52(4)	-8(4)	14(3)	-15(4)
C(8)	53(4)	46(4)	70(5)	-15(4)	20(3)	-10(3)
C(9)	30(4)	38(3)	83(5)	11(3)	10(3)	-4(3)
C(10)	14(3)	30(3)	52(3)	4(3)	3(2)	1(2)
C(11)	21(3)	34(3)	52(4)	4(3)	4(2)	3(2)
C(12)	30(4)	46(3)	61(4)	3(3)	2(3)	11(3)
C(13)	28(3)	49(4)	62(4)	6(3)	0(3)	-1(3)
C(14)	20(3)	48(4)	58(4)	1(3)	1(3)	-8(3)
C(15)	22(3)	47(3)	53(4)	-7(3)	-1(2)	1(2)
C(16)	13(3)	37(3)	55(4)	4(3)	4(2)	-4(2)
C(17)	32(4)	58(4)	71(4)	18(3)	-16(3)	-17(3)
C(18)	35(4)	70(4)	66(4)	18(4)	-13(3)	-22(3)
C(19)	25(3)	49(3)	46(4)	7(3)	-3(2)	-5(3)
C(20)	30(3)	48(4)	61(4)	9(3)	-5(3)	-12(3)
C(21)	38(4)	41(3)	50(4)	10(3)	-9(3)	-16(3)
C(22)	63(5)	60(4)	59(4)	19(3)	0(3)	-19(4)

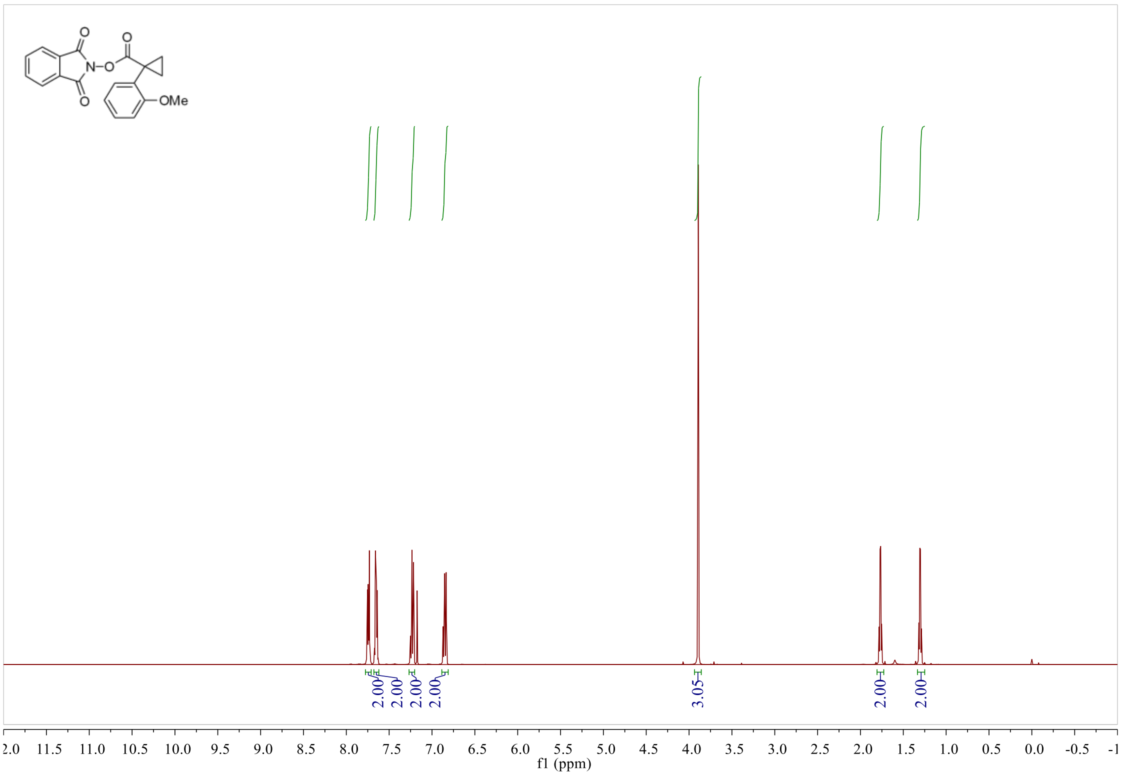
O(2)	40(3)	45(2)	50(3)	-3(2)	-6(2)	5(2)
C(1A)	39(4)	31(3)	63(4)	-1(3)	9(3)	-9(3)
C(2A)	16(3)	28(3)	43(3)	-1(2)	-2(2)	-3(2)
C(3A)	18(3)	36(3)	52(4)	-1(3)	0(2)	3(2)
C(4A)	14(3)	40(3)	49(3)	0(3)	8(2)	-2(2)
C(5A)	40(4)	44(3)	55(4)	-1(3)	9(3)	4(3)
C(6A)	52(4)	44(4)	60(4)	-5(3)	6(3)	11(3)
C(7A)	42(4)	55(4)	56(4)	-8(3)	2(3)	4(3)
C(8A)	46(4)	62(4)	47(4)	5(3)	-5(3)	9(3)
C(9A)	41(4)	38(3)	62(4)	6(3)	8(3)	11(3)
C(10A)	17(3)	25(3)	48(3)	1(2)	3(2)	6(2)
C(11A)	26(3)	36(3)	46(3)	1(3)	1(2)	-1(2)
C(12A)	37(4)	56(4)	57(4)	-2(3)	-5(3)	-17(3)
C(13A)	25(3)	71(5)	50(4)	13(3)	-7(3)	-1(3)
C(14A)	26(3)	56(4)	61(4)	3(3)	2(3)	17(3)
C(15A)	29(3)	36(3)	54(4)	3(3)	4(3)	12(2)
C(16A)	16(3)	31(3)	48(3)	-8(3)	-4(2)	4(2)
C(17A)	28(3)	33(3)	55(4)	-9(3)	1(2)	3(2)
C(18A)	27(3)	46(3)	48(4)	-6(3)	2(2)	3(2)
C(19A)	25(3)	39(3)	47(4)	-4(3)	-6(2)	1(2)
C(20A)	40(4)	42(3)	47(4)	0(3)	-8(3)	8(3)
C(21A)	29(3)	34(3)	55(4)	-5(3)	0(3)	8(2)
C(22A)	52(4)	50(4)	54(4)	2(3)	-12(3)	8(3)

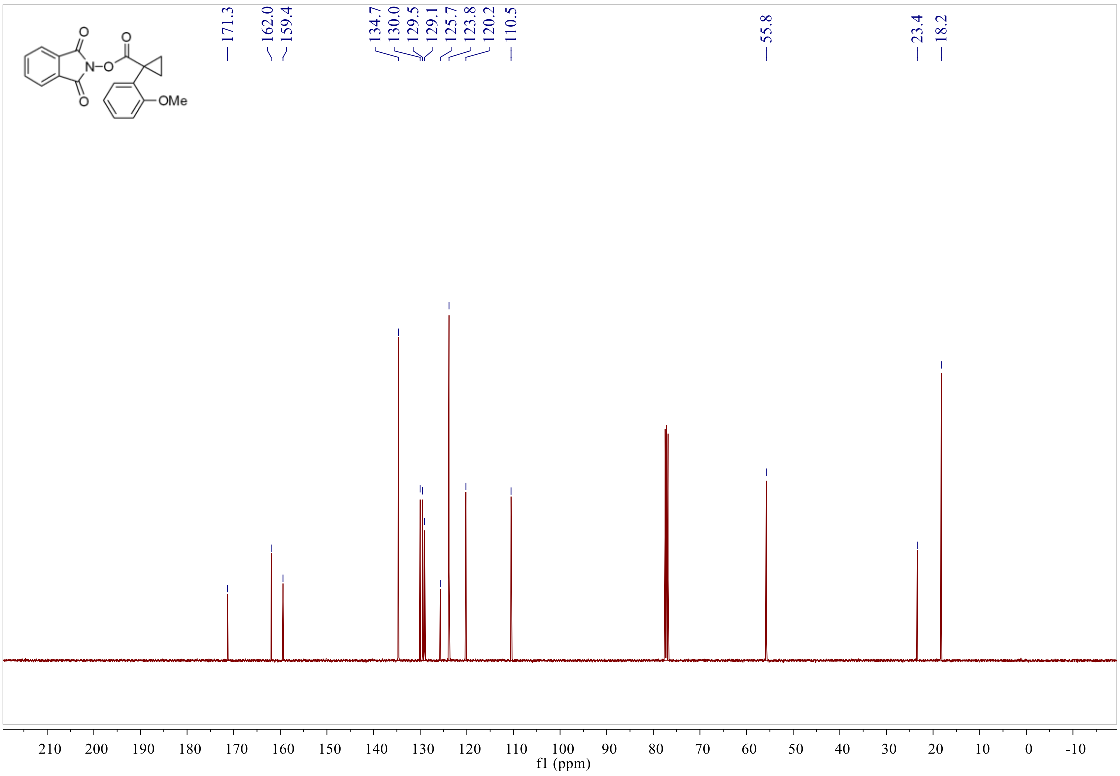
Table S12. Hydrogen coordinates (x10^4) and isotropic displacement parameters (Å^{2}x 10^3) for 3k.

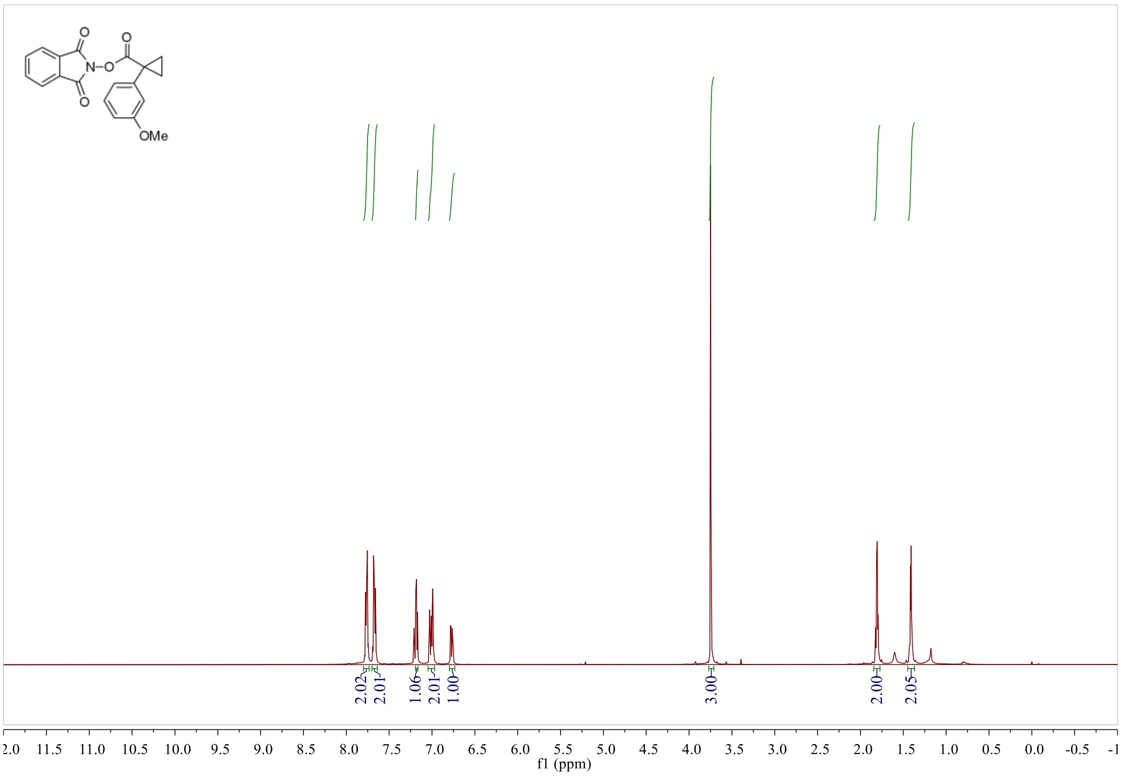
	x	y	z	U(eq)
H(1A)	4552	7272	5390	52
H(1B)	4231	7716	5021	52
H(3)	4748	3698	5128	46
H(5)	4135	6652	4422	63
H(6)	4082	5747	3765	72
H(7)	4369	2337	3528	70
H(8)	4679	-178	3960	68
H(9)	4740	776	4617	61
H(11)	3524	7197	5439	43
H(12)	2839	7027	5260	55
H(13)	2617	4112	4846	56
H(14)	3067	1255	4658	50
H(15)	3749	1422	4846	49
H(17)	4698	5369	5858	64

H(18)	4834	3575	6446	68
H(20)	3886	-661	6263	55
H(21)	3752	1163	5672	52
H(22A)	4274	-2810	6678	91
H(22B)	3966	-1249	6922	91
H(22C)	4367	-2242	7126	91
H(1AA)	3226	1987	7871	53
H(1AB)	2877	2507	7528	53
H(3A)	2741	6164	7793	43
H(5A)	2719	8810	8307	56
H(6A)	2840	9954	8947	62
H(7A)	3292	7806	9335	61
H(8A)	3609	4581	9080	62
H(9A)	3480	3452	8443	56
H(11A)	3741	8496	7931	43
H(12A)	4433	8802	8067	60
H(13A)	4871	5796	7927	59
H(14A)	4625	2579	7609	57
H(15A)	3931	2219	7483	48
H(17A)	3538	3660	6870	46
H(18A)	3434	5117	6255	48
H(20A)	2764	10277	6713	51
H(21A)	2882	8789	7334	47
H(22D)	2863	11091	5703	78
H(22E)	2960	11898	6139	78
H(22F)	2556	10469	6050	78

7.2 NMR spectra







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O
O
OMe
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11.5
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8.5
8.0
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6.0
5.5
5.0
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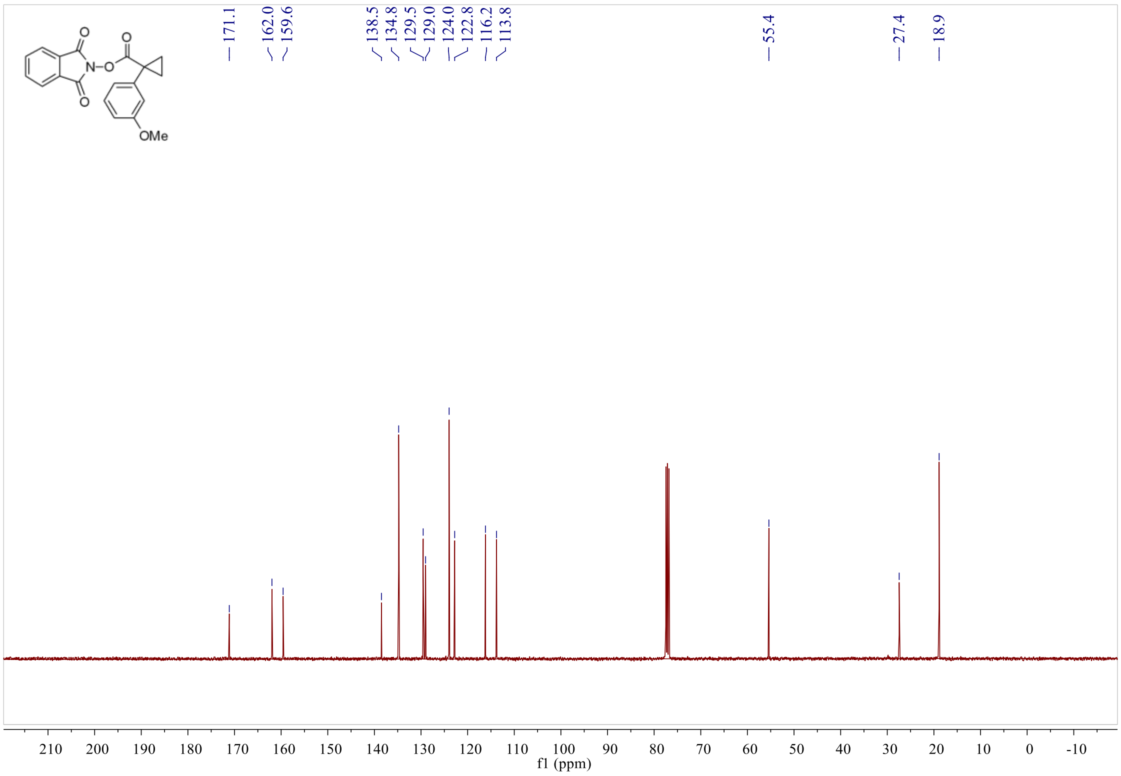

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159.6
138.5
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129.5
129.0
124.0
122.8
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113.8
55.4
27.4
18.9
O
N
O
O
O
OMe
210
200
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180
170
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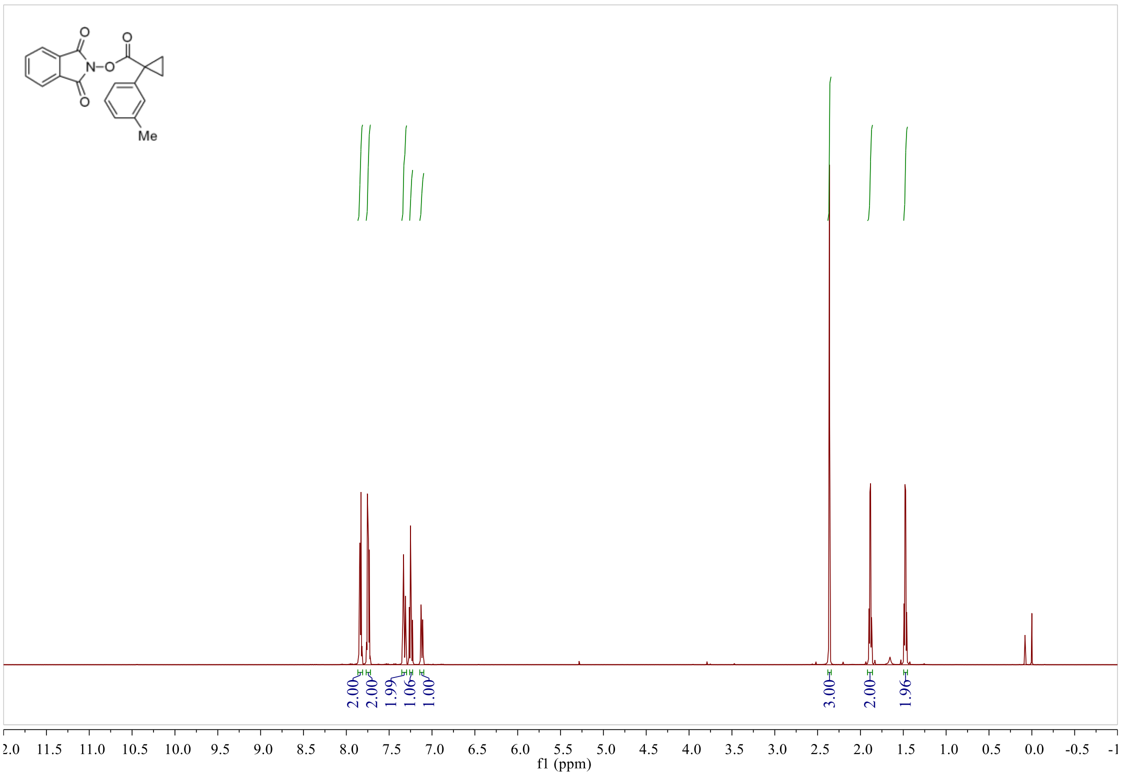
f1 (ppm)



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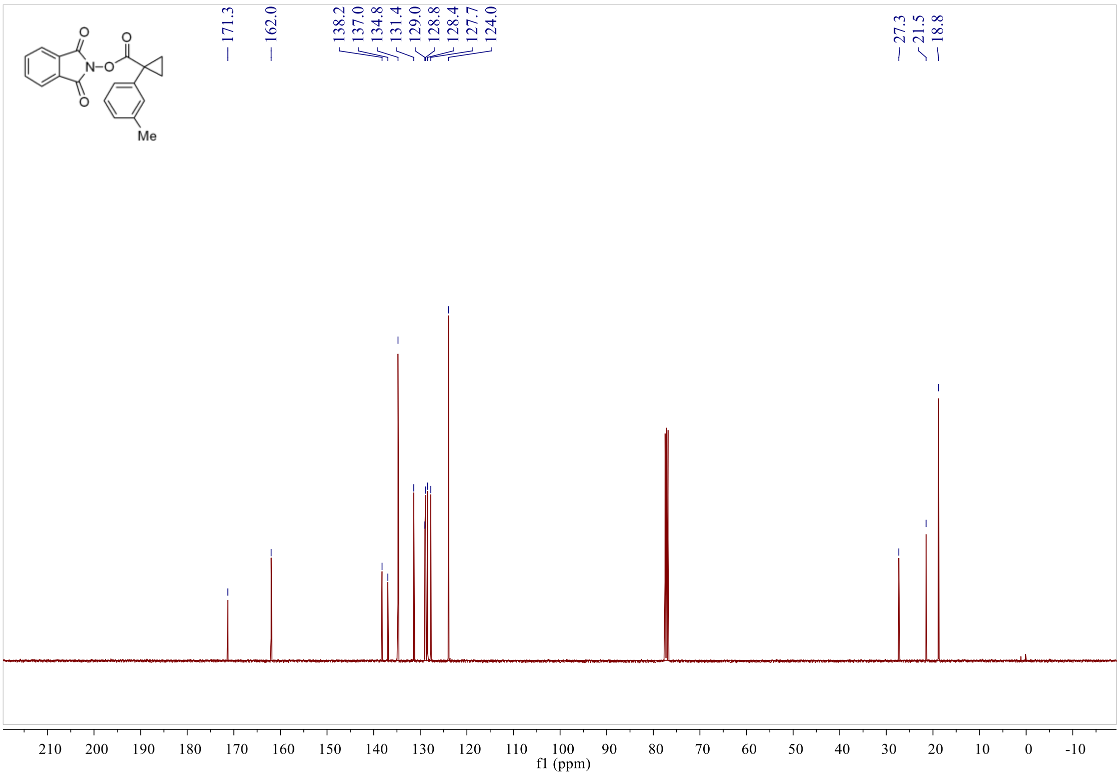

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21.5
18.8
O
N
O
O
O
Me
210
200
190
180
170
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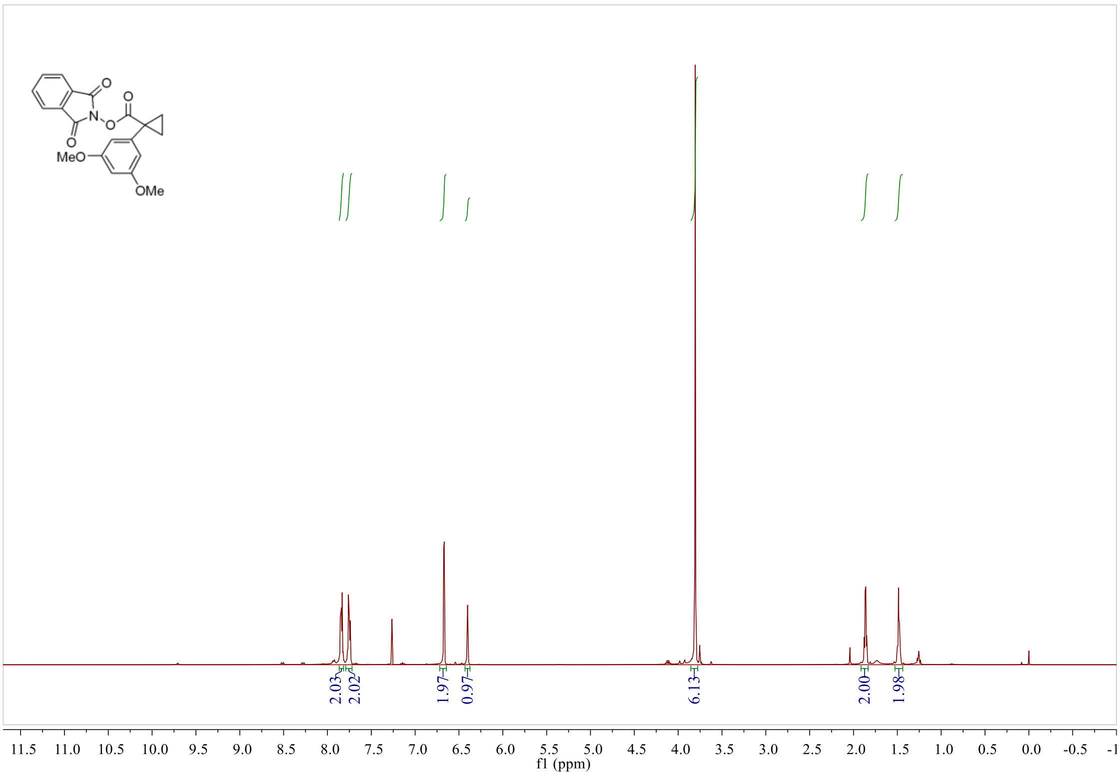
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8.0
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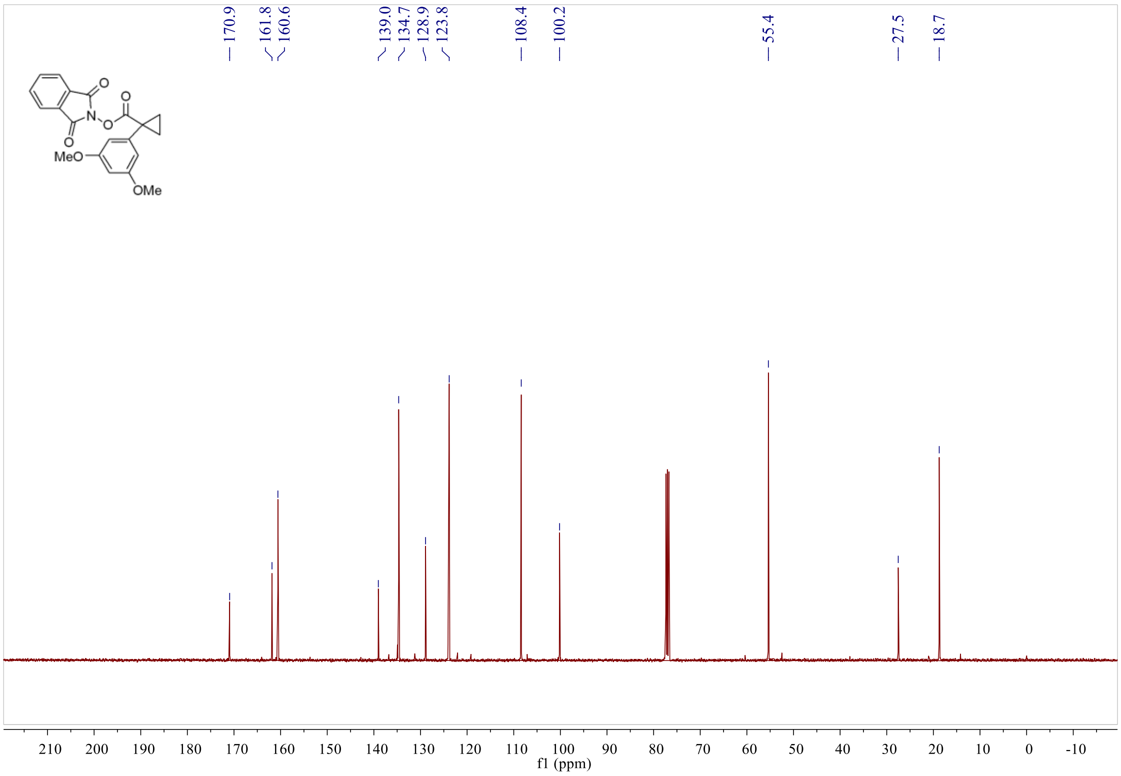
f1 (ppm)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123.8
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55.4
27.5
18.7
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O
O
O
MeO
OMe
210
200
190
180
170
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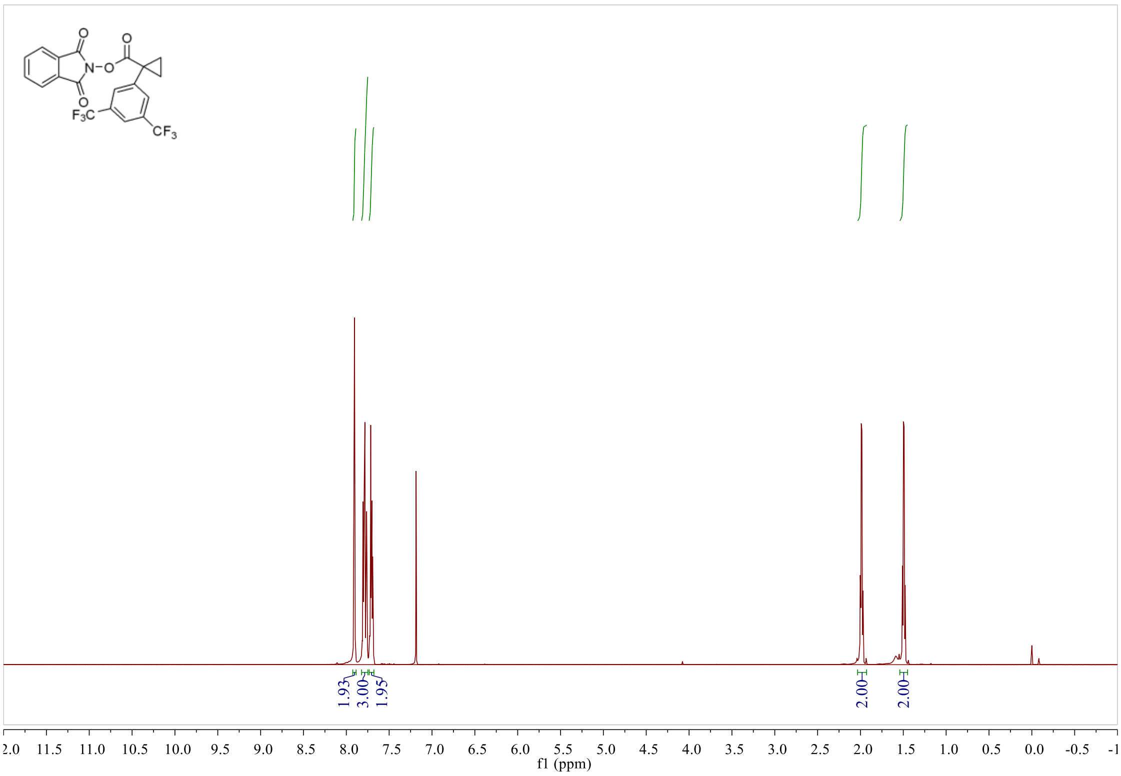
f1 (ppm)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10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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2.0
1.5
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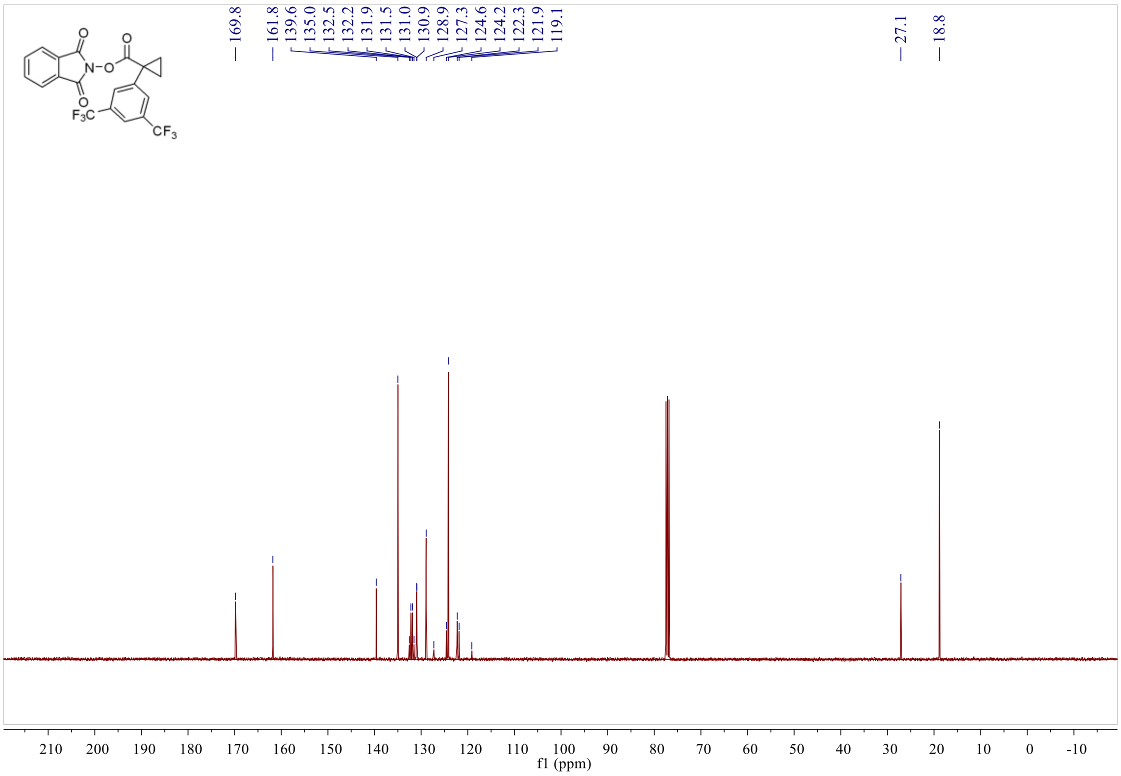
0.0
-0.5
-1
f1 (ppm)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128.9
127.3
124.6
124.2
122.3
121.9
119.1
27.1
18.8
O
N
O
O
O
F3C
CF3
210
200
190
180
170
160
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140
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100
90
80
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60
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40
30
20
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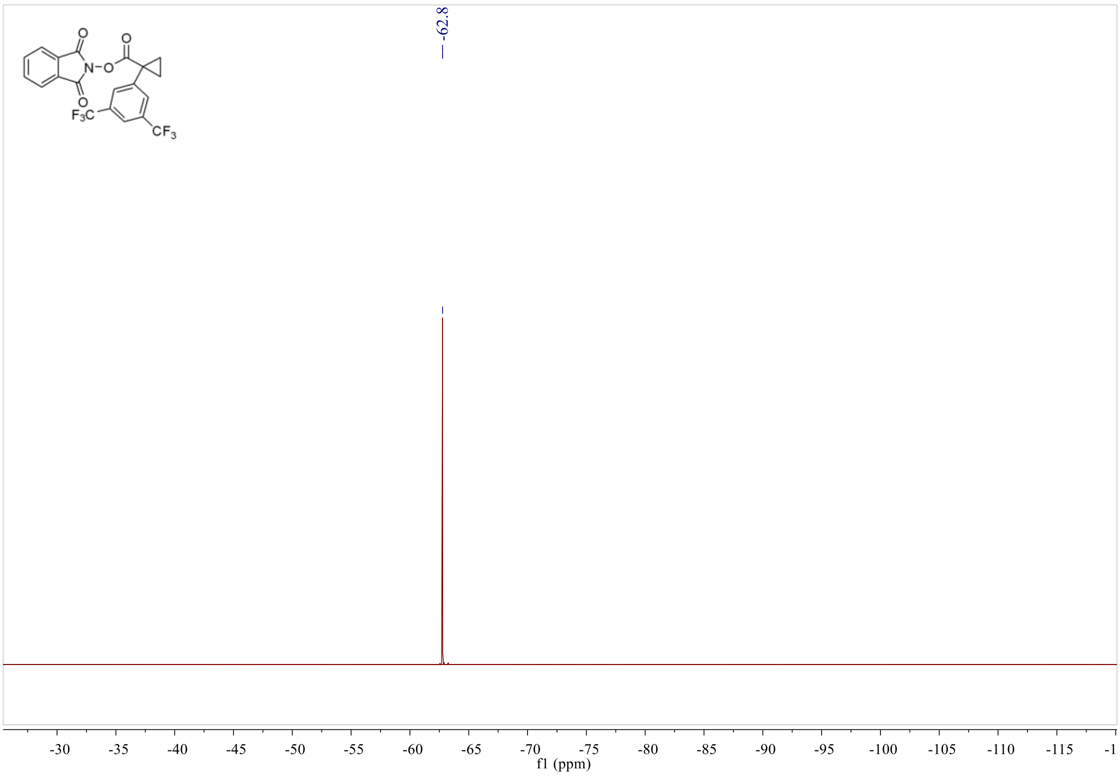
0
-10
f1 (ppm)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CF3
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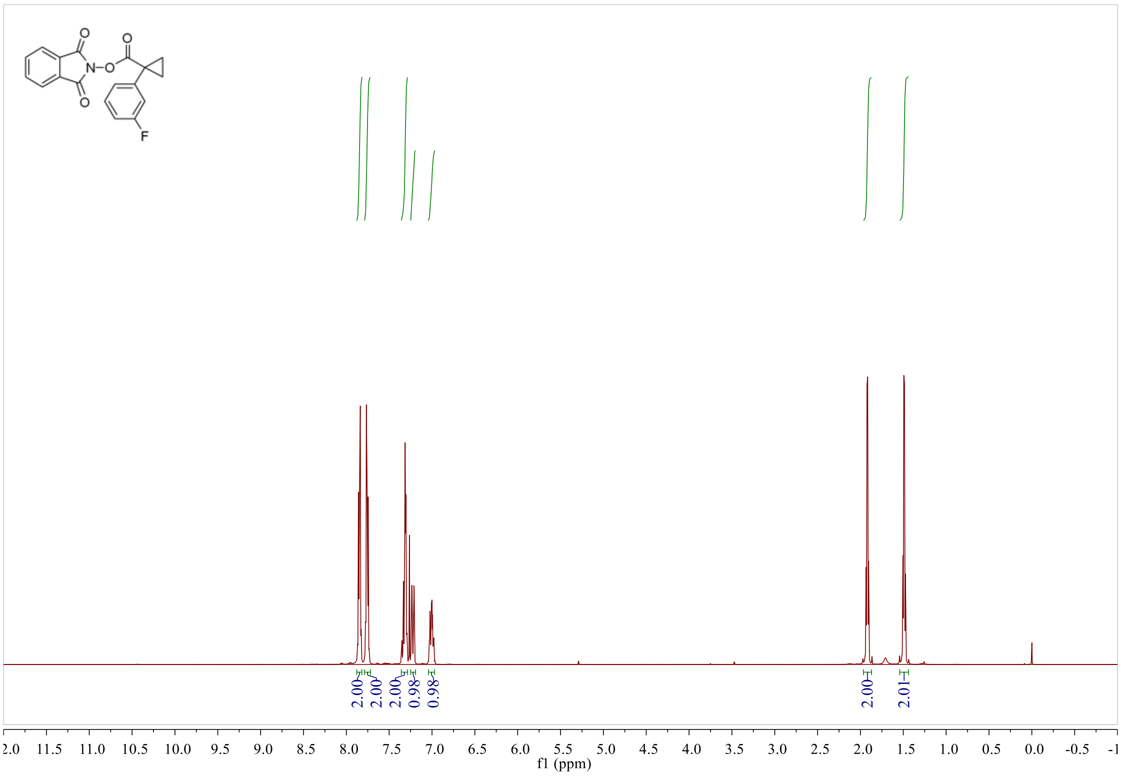
-105
-110
-115
f1 (ppm)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O
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9.5
9.0
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8.0
7.5
7.0
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6.0
5.5
5.0
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2.0
1.5
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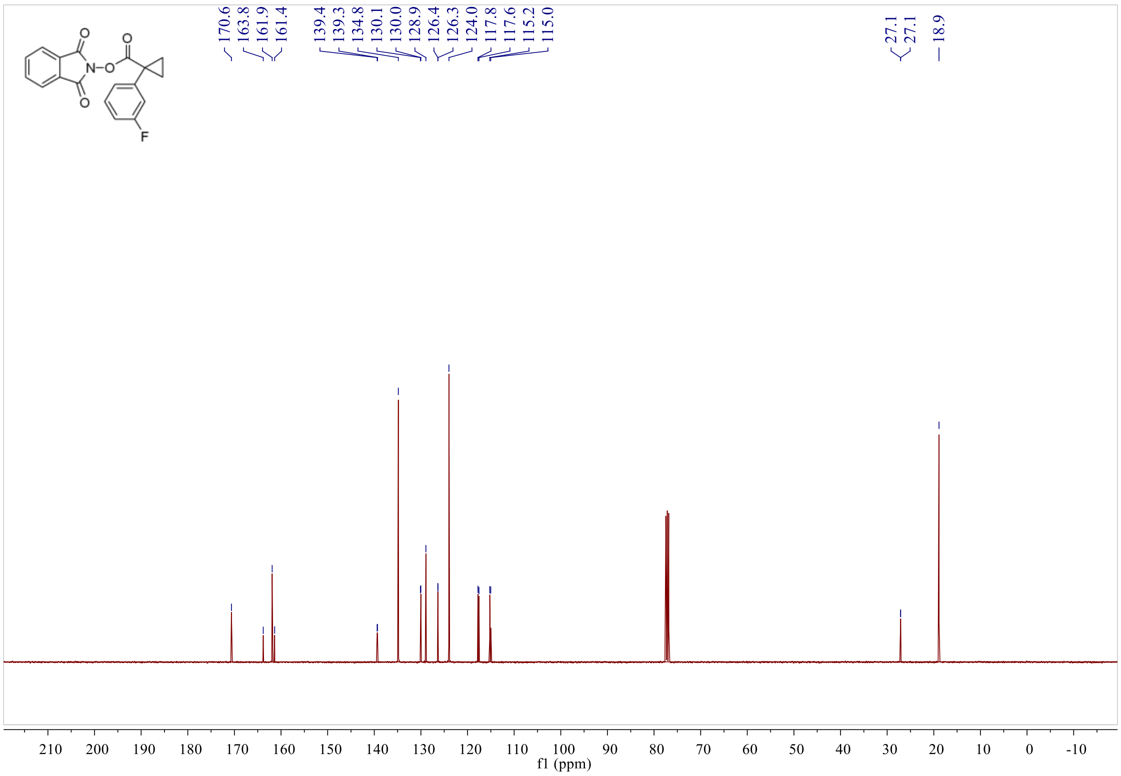
0.5
0.0
-0.5
f1 (ppm)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139.4
139.3
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130.0
128.9
126.4
126.3
124.0
117.8
117.6
115.2
115.0
27.1
27.1
18.9
O
N
O
F
210
200
190
180
170
160
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140
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120
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100
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80
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30
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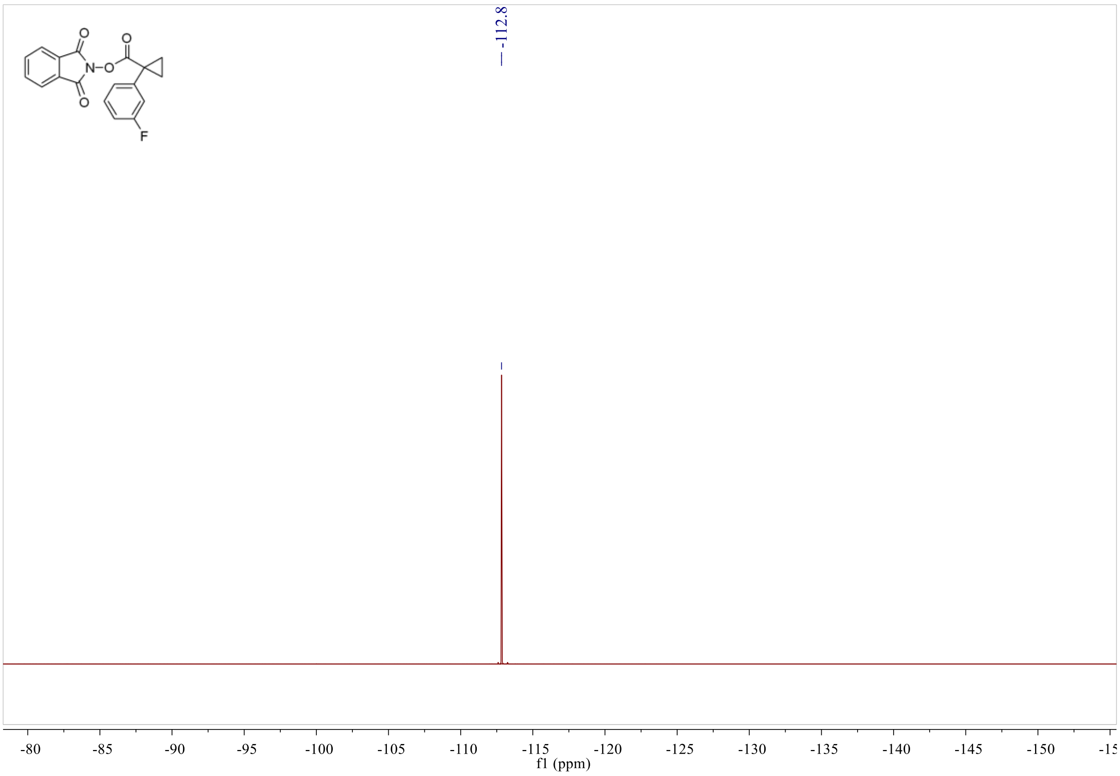
0
-10
f1 (ppm)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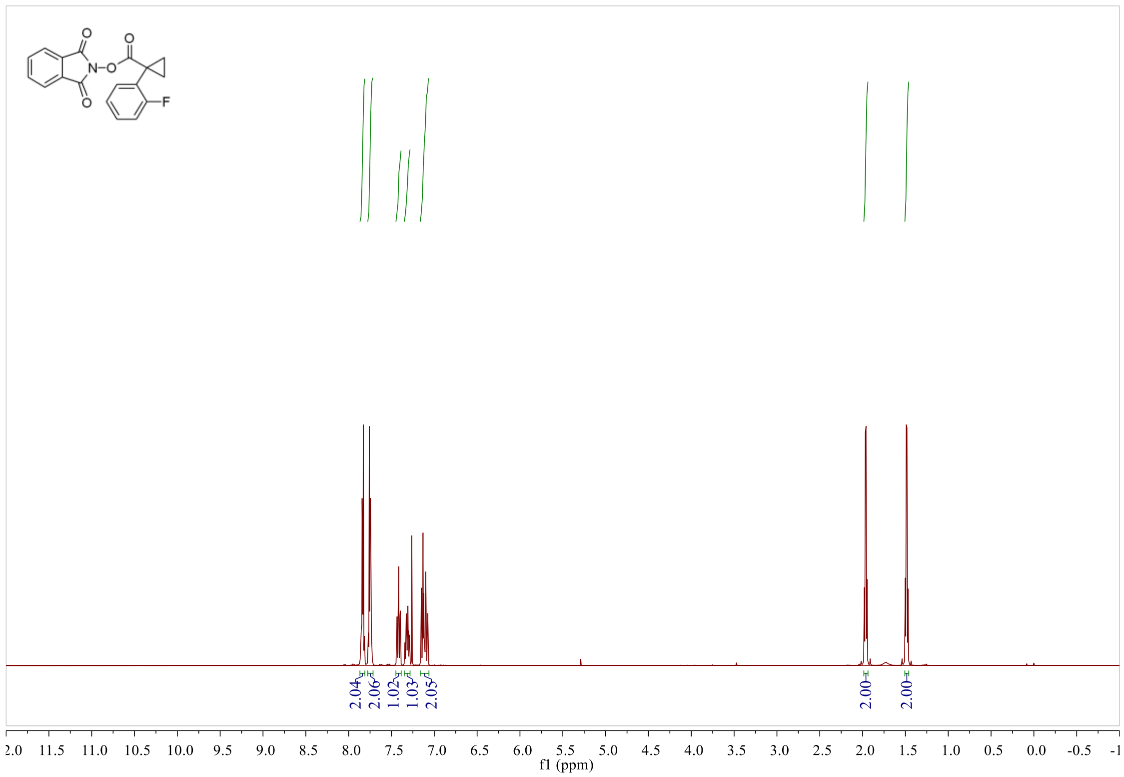
f1 (ppm)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1.03
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2.00
2.00
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11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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1.5
1.0
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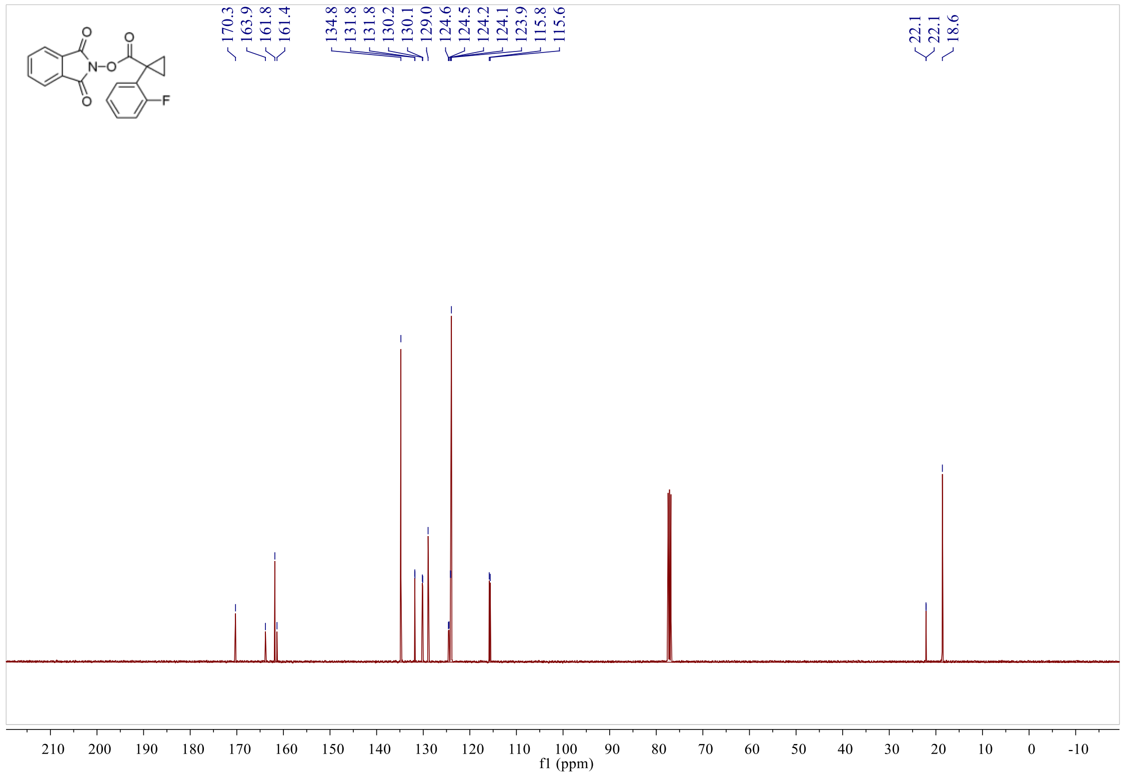
-1
f1 (ppm)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129.0
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124.5
124.2
124.1
123.9
115.8
115.6
22.1
22.1
18.6
O
N
O
O
O
F
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200
190
180
170
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100
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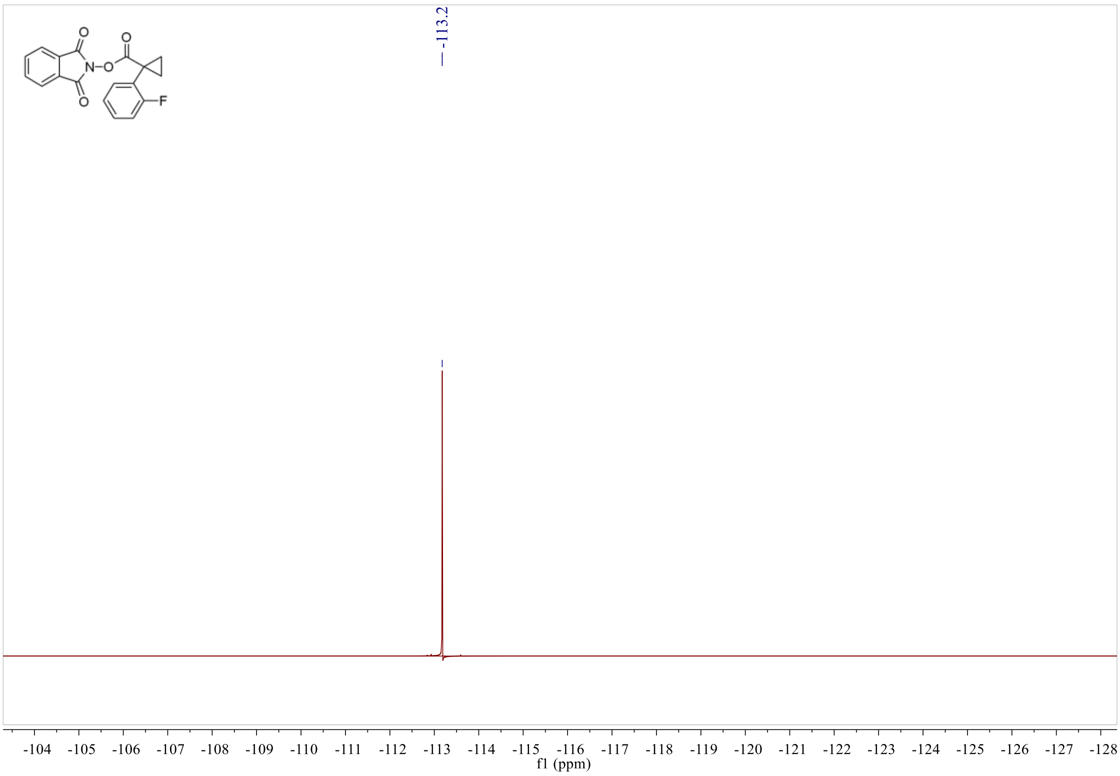
30
20
10
0
-10
f1 (ppm)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O
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O
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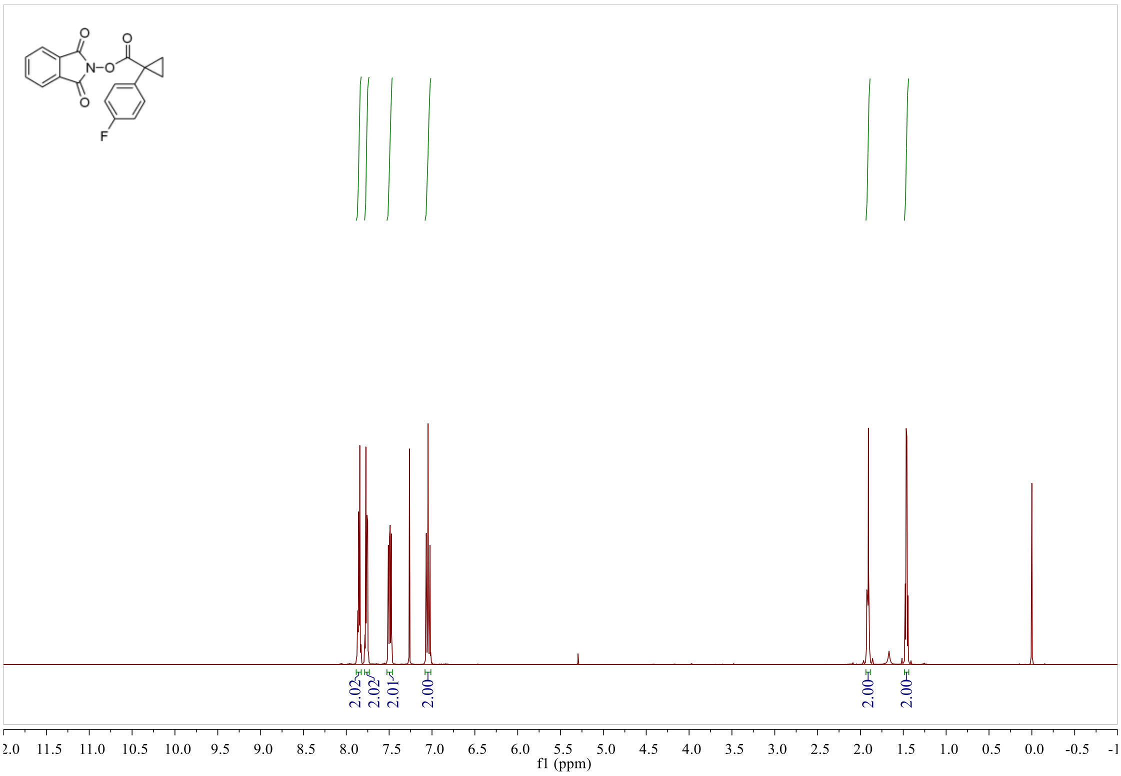
f1 (ppm)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N
O
O
O
F
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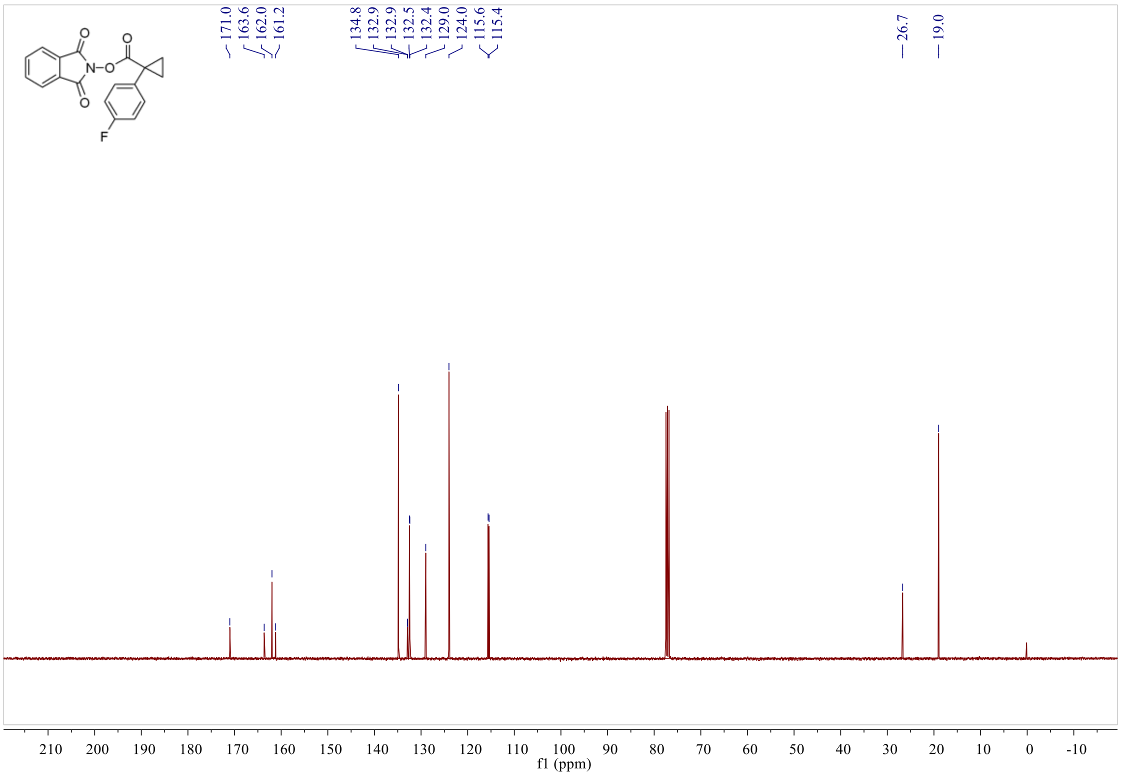
2.02
2.01
2.00
2.00
2.00
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)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162.0
161.2
134.8
132.9
132.9
132.5
132.4
129.0
124.0
115.6
115.4
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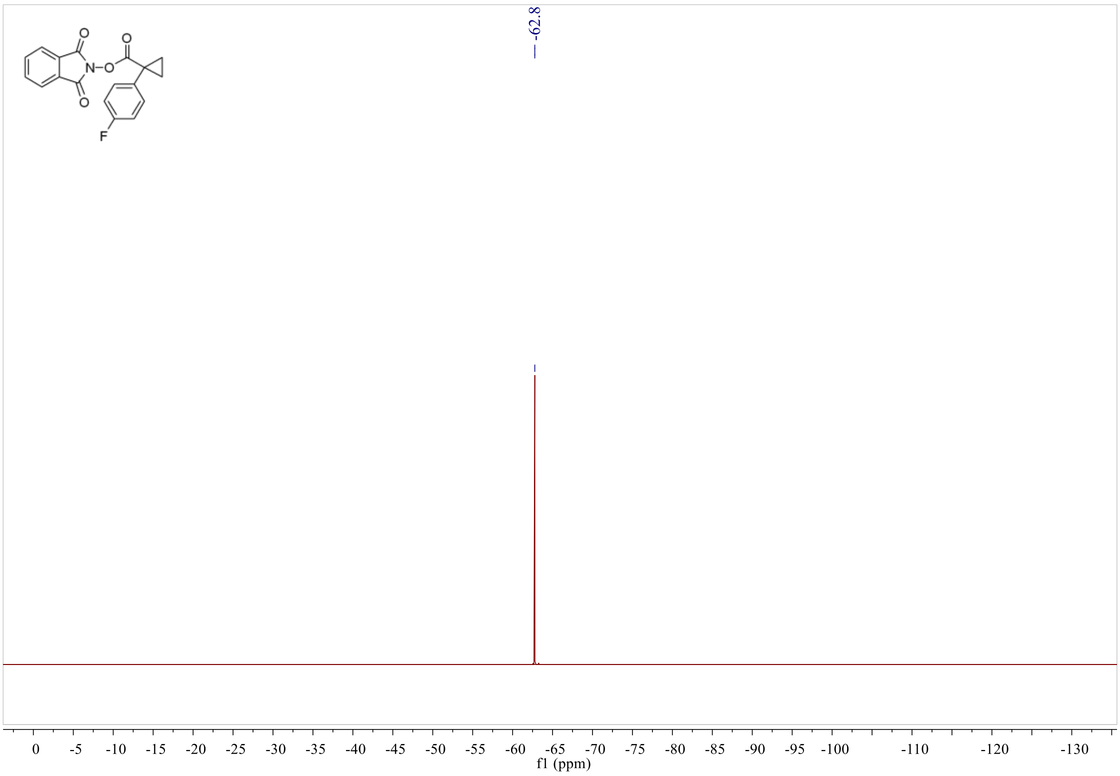
19.0
O
N
O
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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O
F
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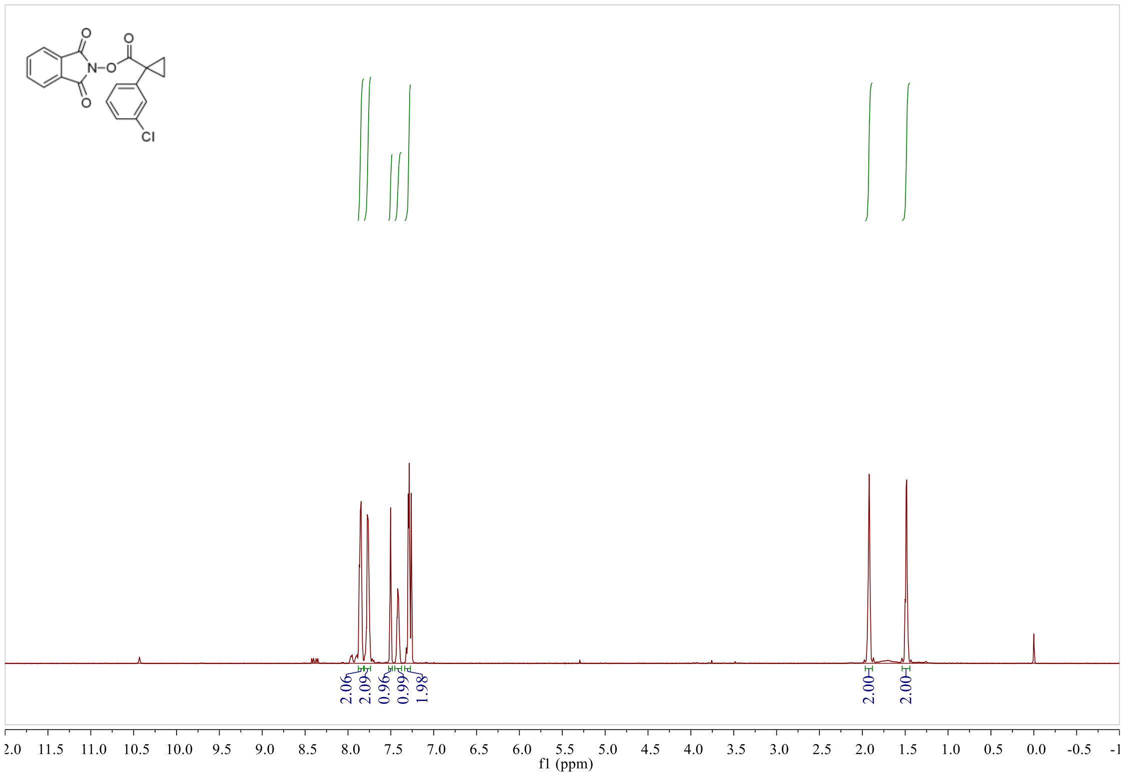
f1 (ppm)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O
O
O
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11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
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6.5
6.0
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5.0
4.5
4.0
3.5
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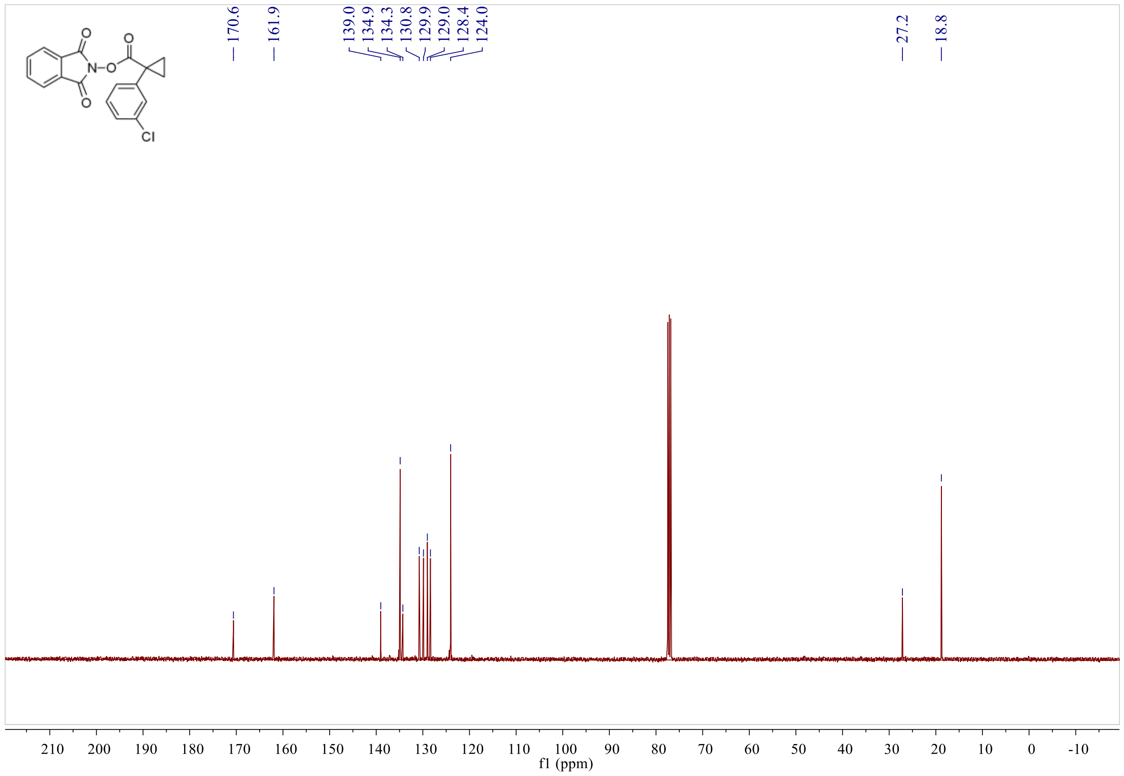
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)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O
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134.9
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130.8
129.9
129.0
128.4
124.0
27.2
18.8
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
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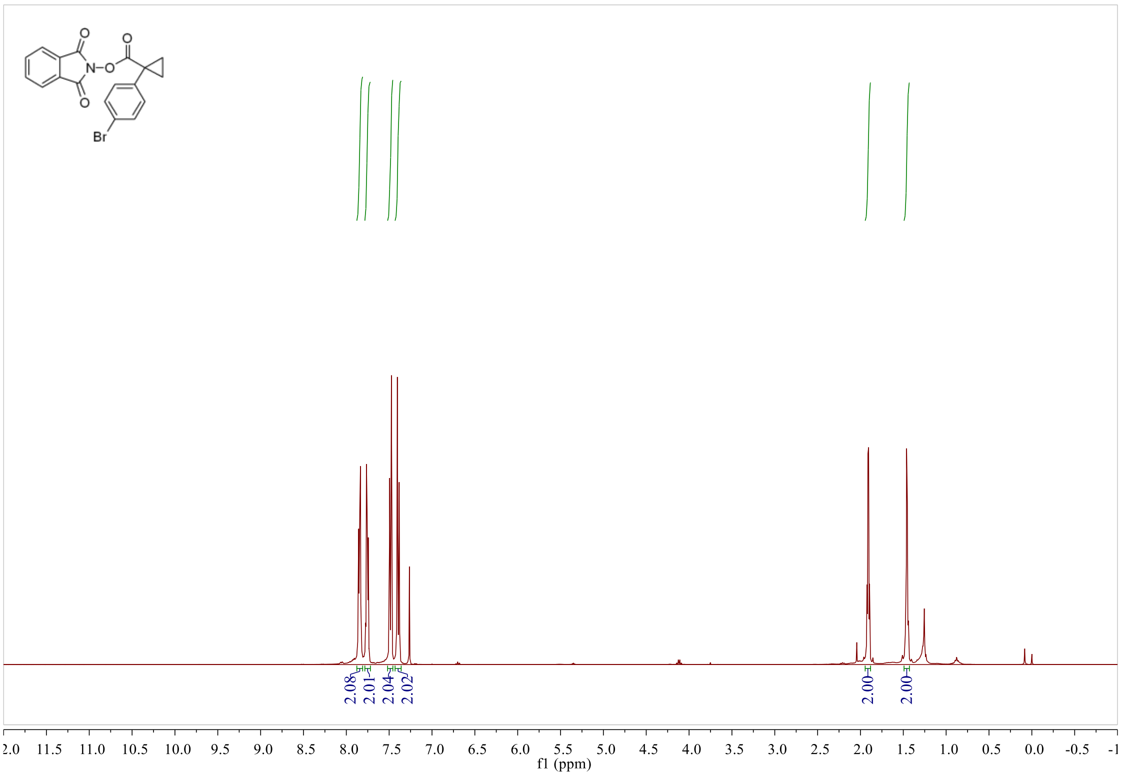
-10
f1 (ppm)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2.00
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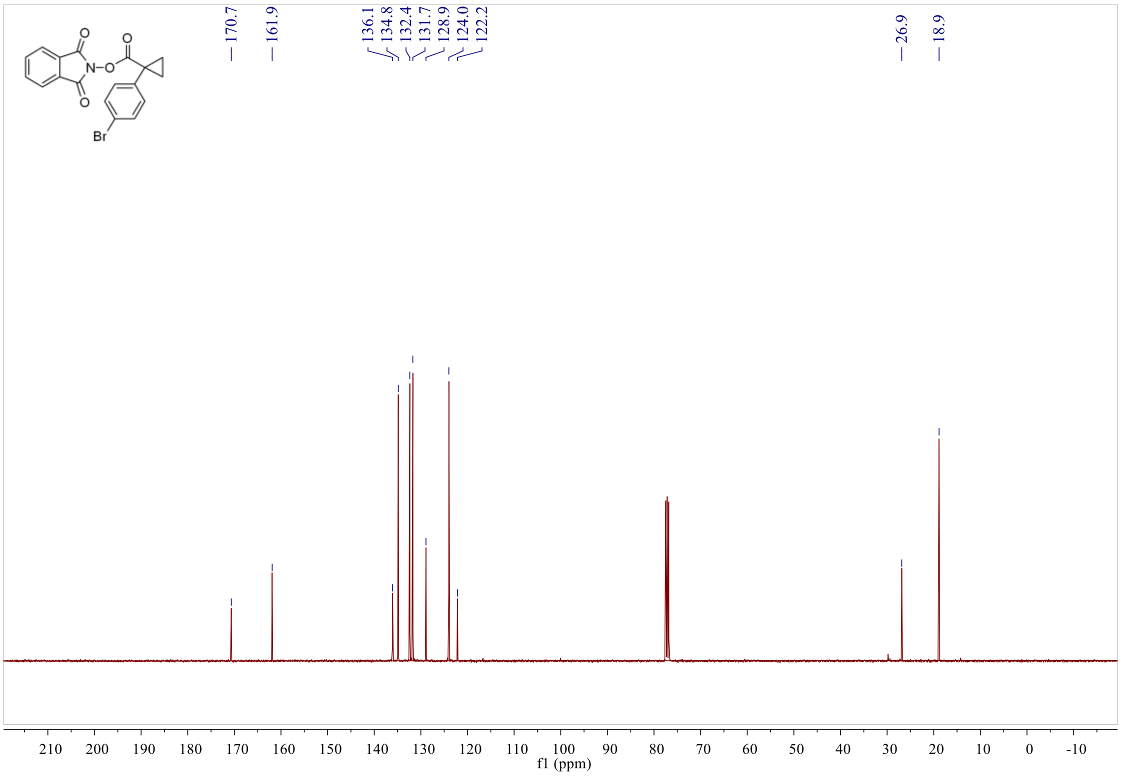
f1 (ppm)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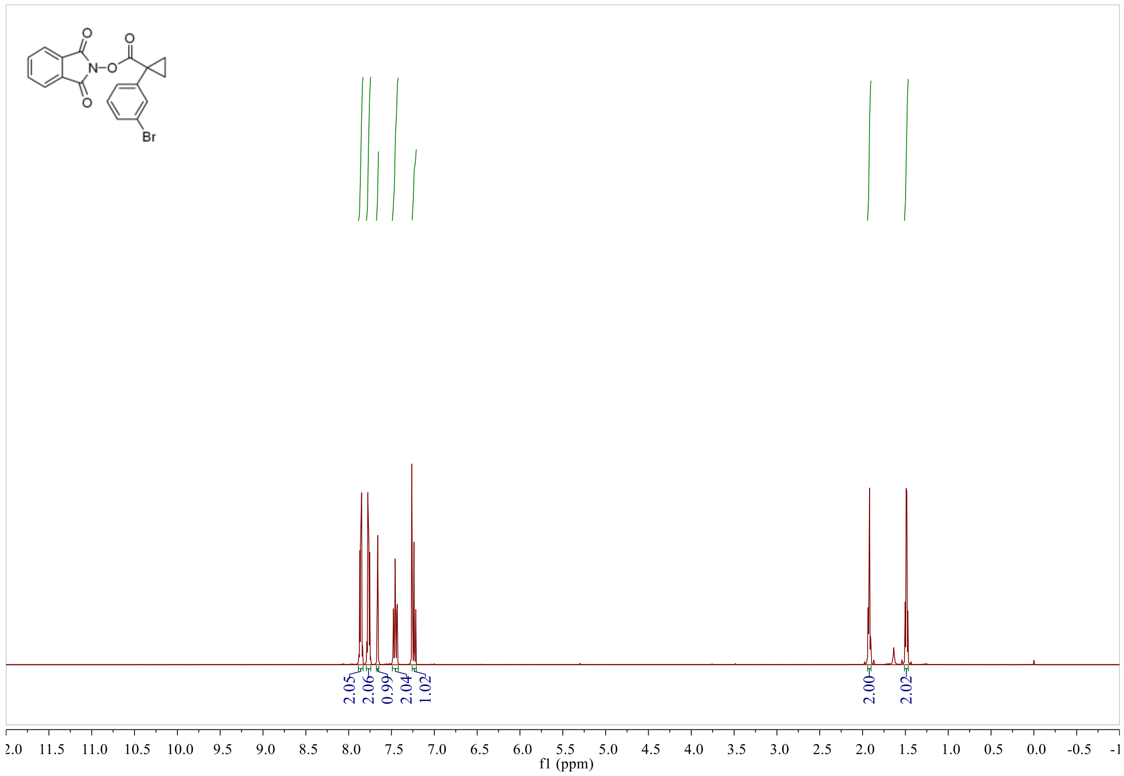
O
O
O
Br
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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2.02
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10.5
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8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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2.0
1.5
1.0
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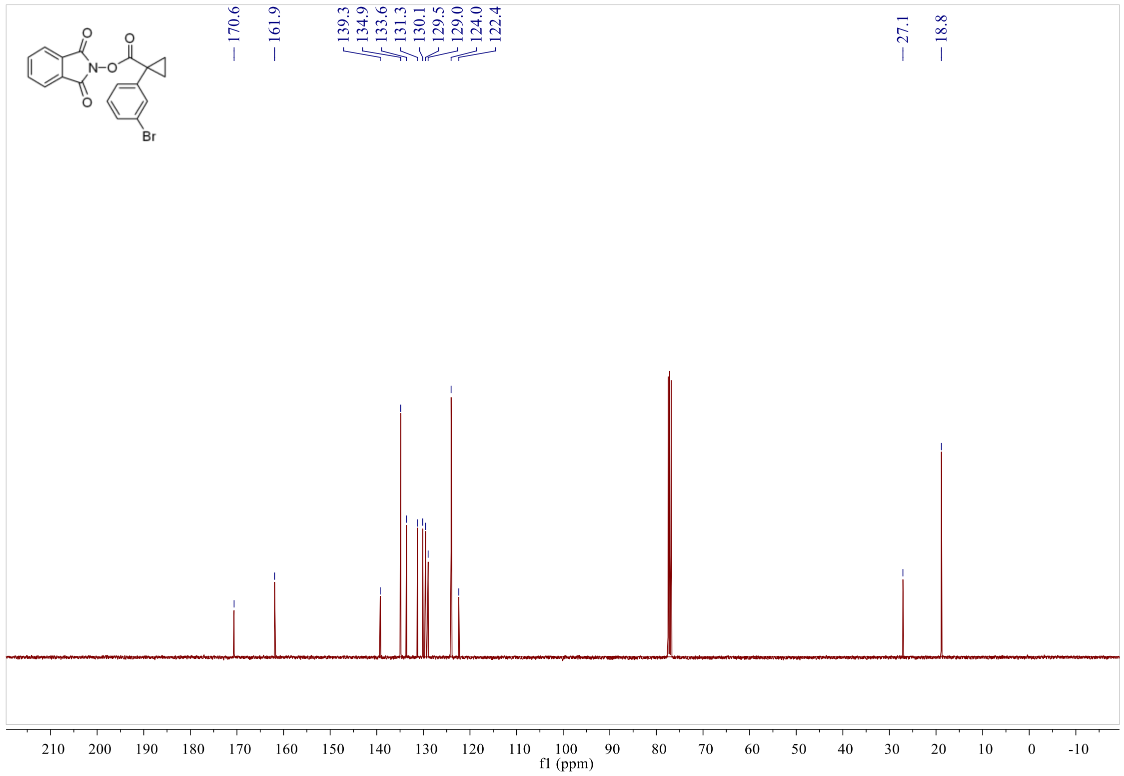
f1 (ppm)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129.5
129.0
124.0
122.4
27.1
18.8
210
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190
180
170
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100
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80
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30
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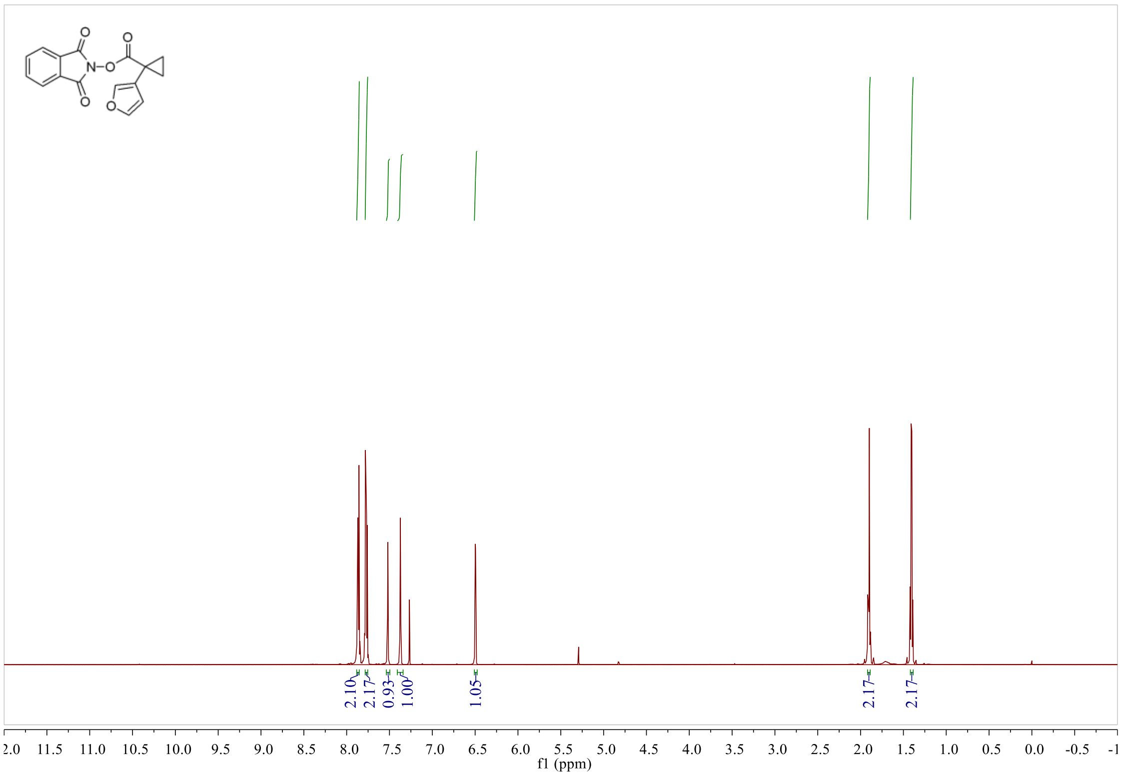
f1 (ppm)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6.0
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5.0
4.5
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2.0
1.5
1.0
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0.0
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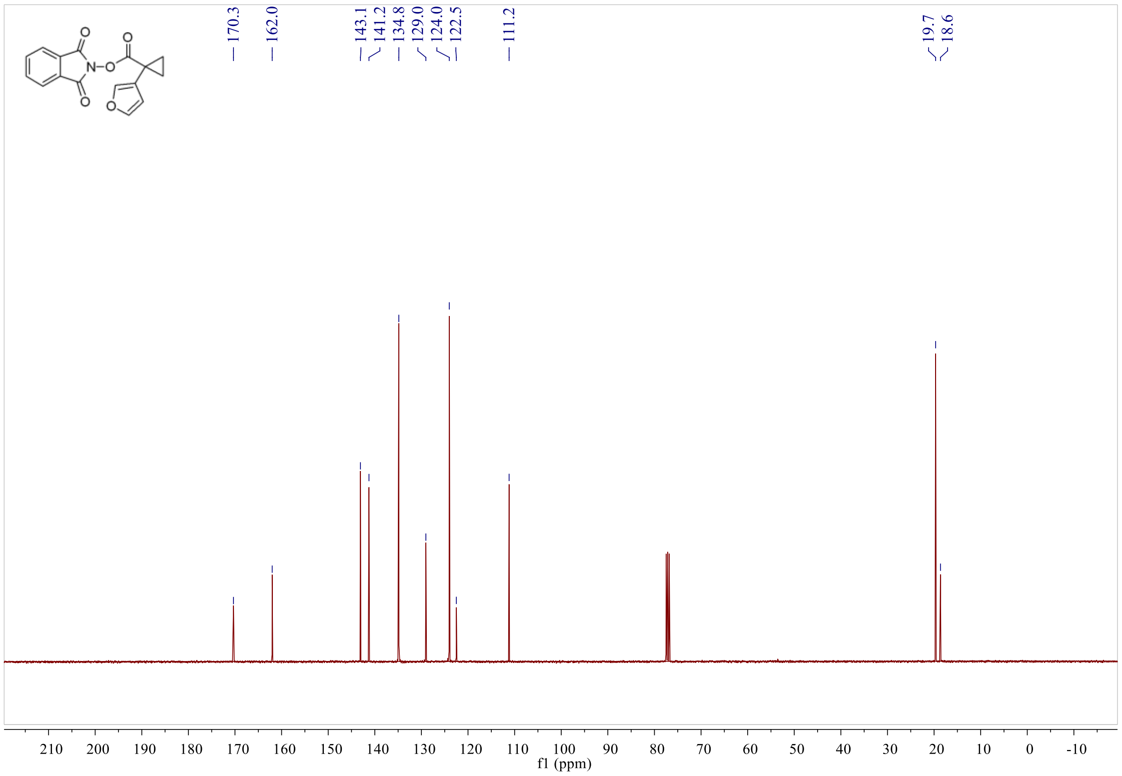
-1
f1 (ppm)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O
N
O
O
O
O
210
200
190
180
170
160
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140
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100
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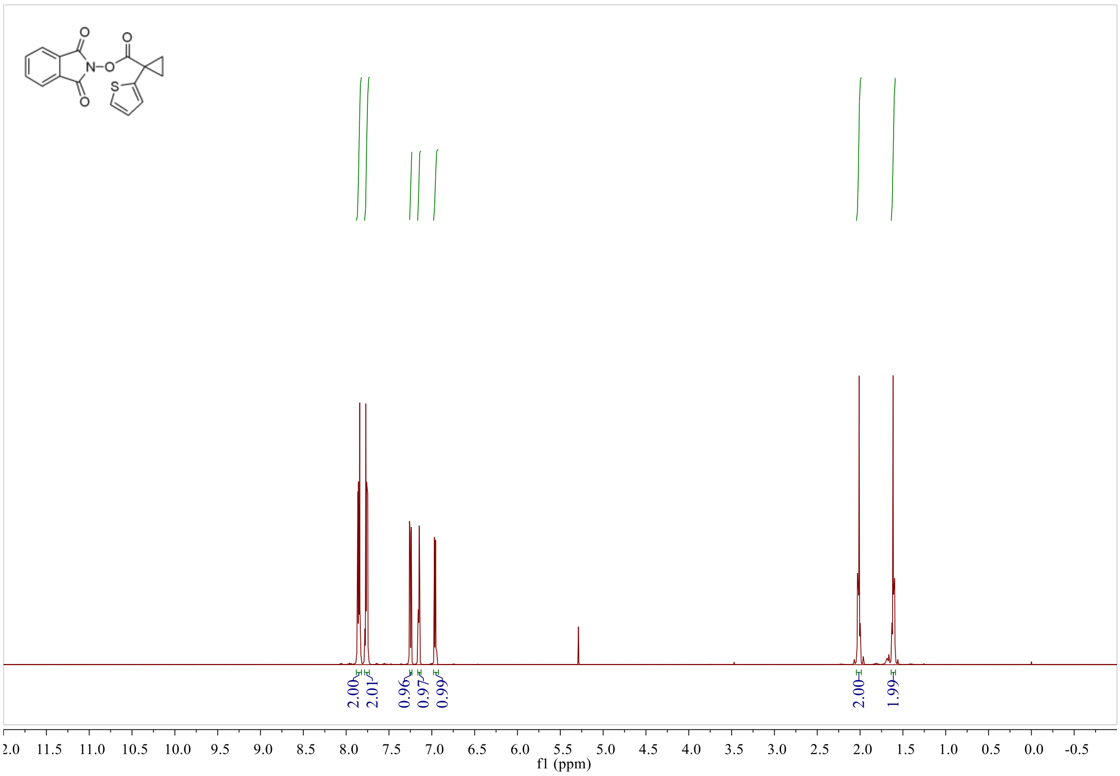
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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2.5
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0.5
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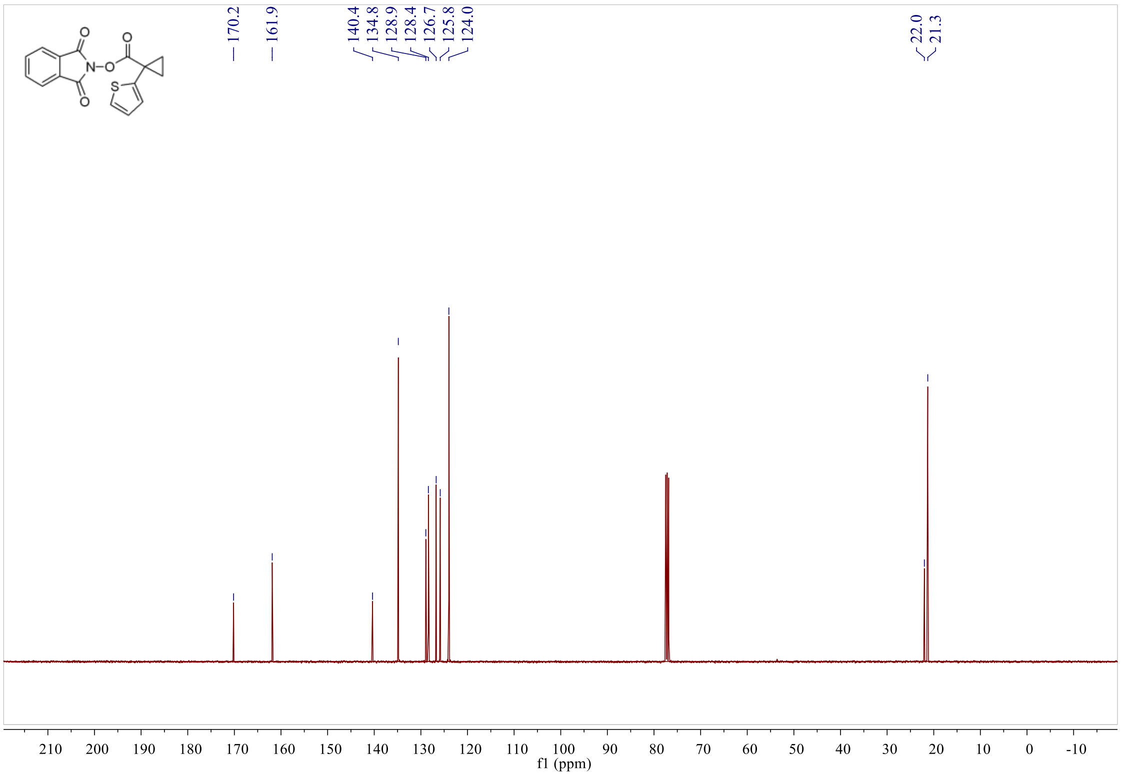
f1 (ppm)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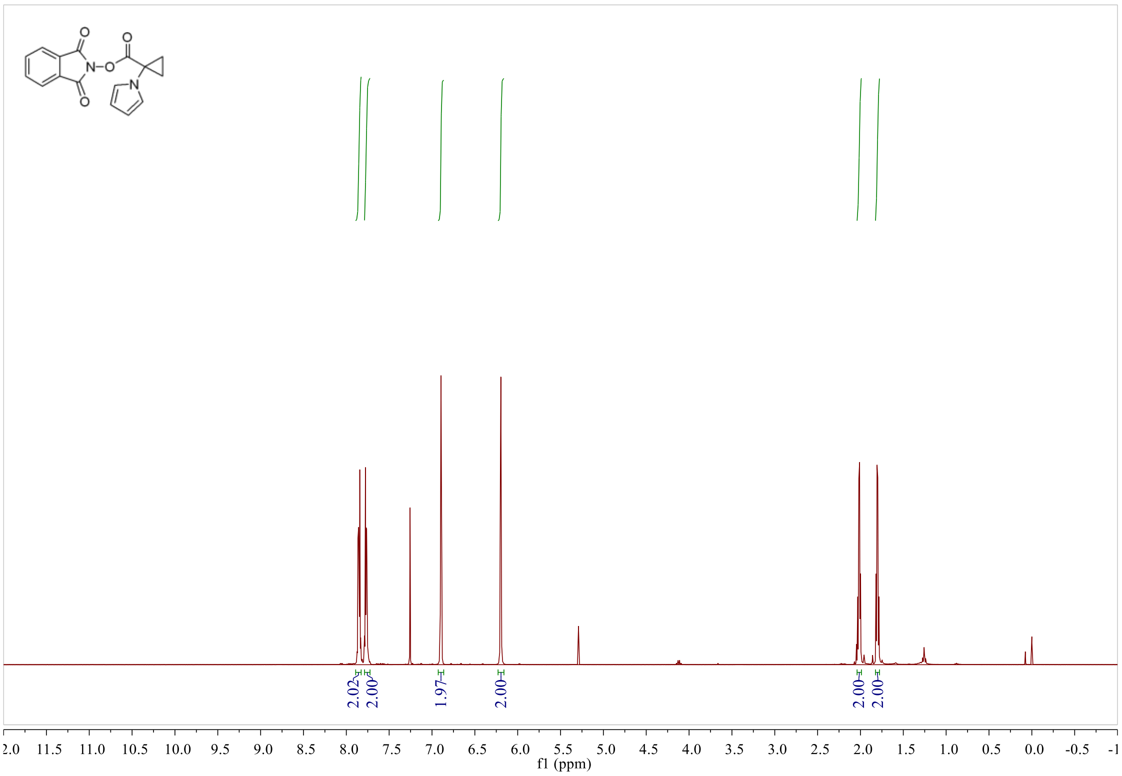
126.7
125.8
124.0
22.0
21.3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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2.00
1.97
2.00
2.00
2.00
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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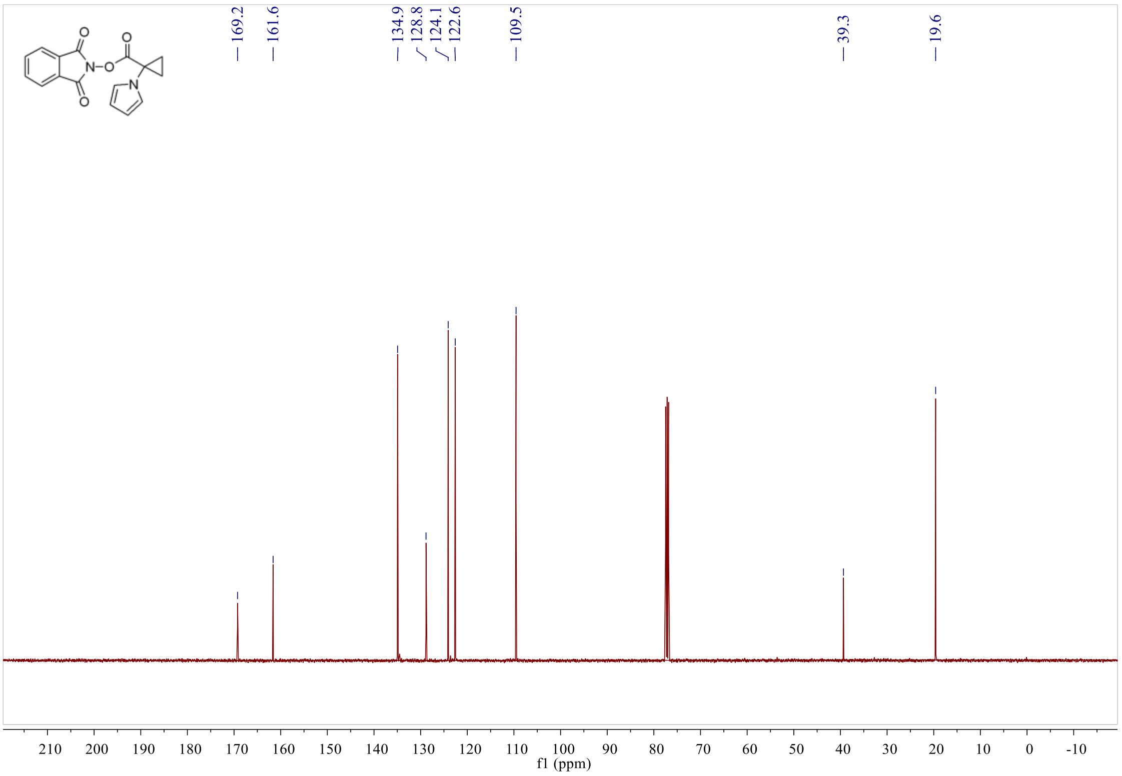
0.0
-0.5
-1
f1 (ppm)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124.1
122.6
109.5
39.3
19.6
210
200
190
180
170
160
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100
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80
70
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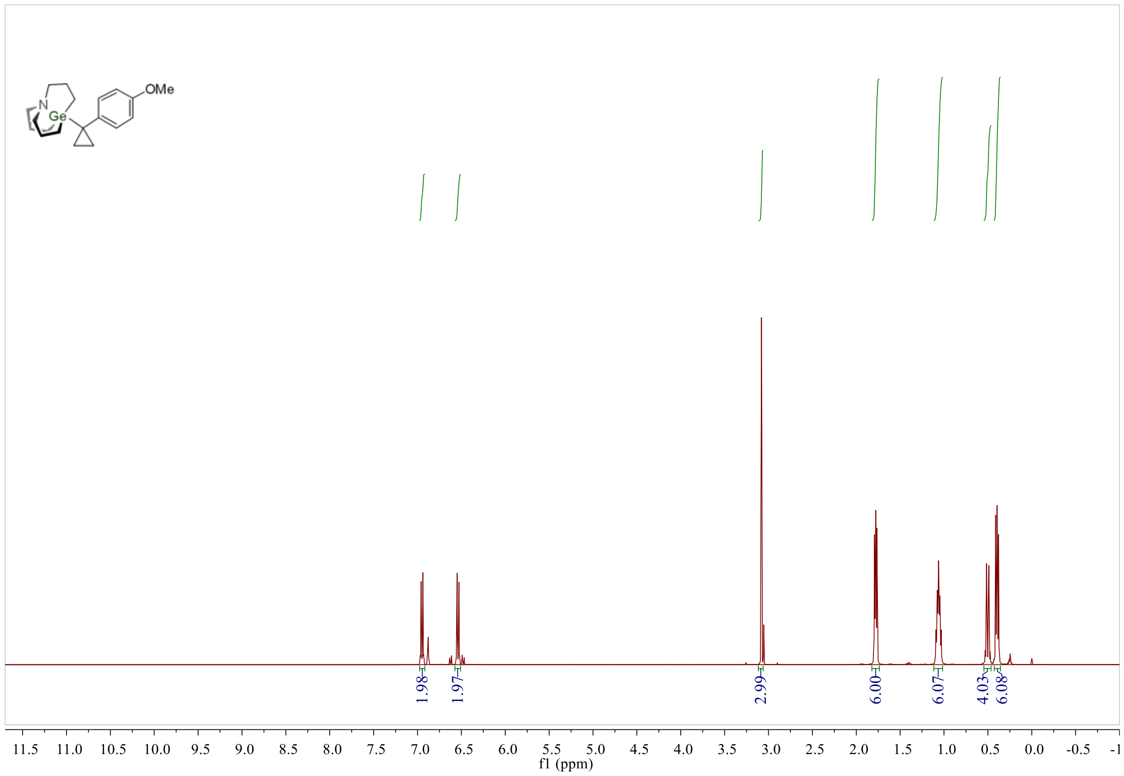
50
40
30
20
10
0
-10
f1 (ppm)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Ge
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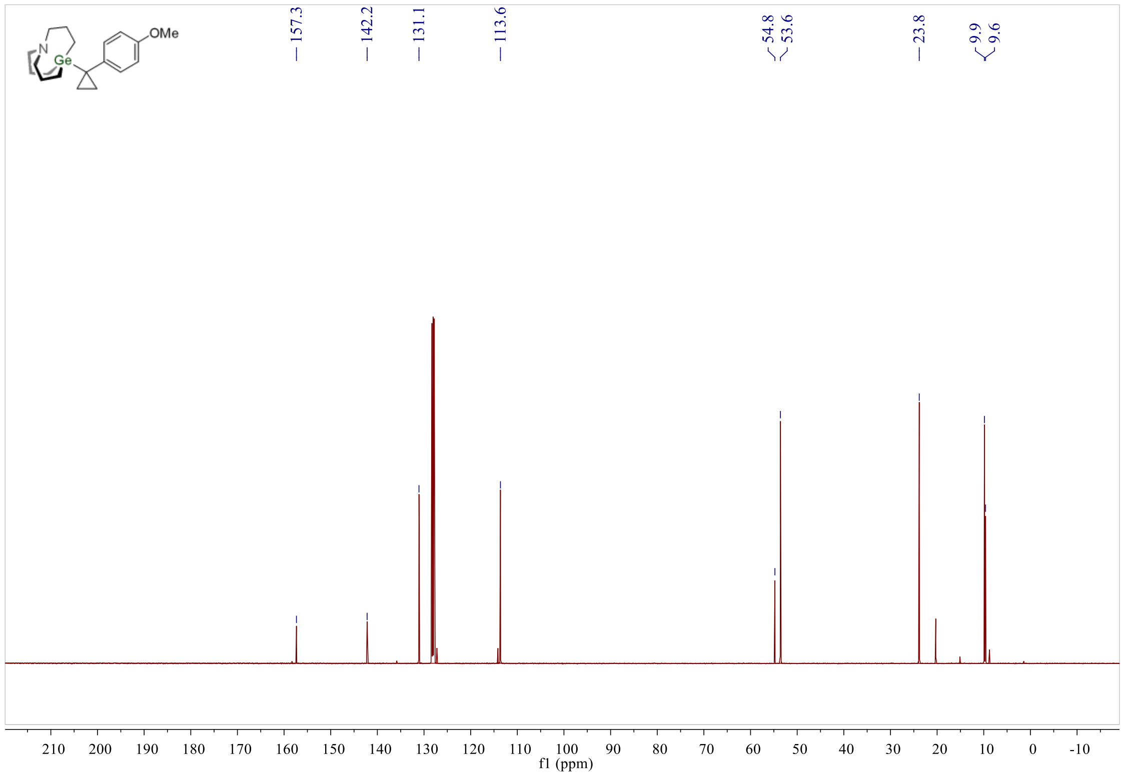
2.99
6.00
6.07
4.03
6.08
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)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Ge
157.3
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131.1
113.6
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23.8
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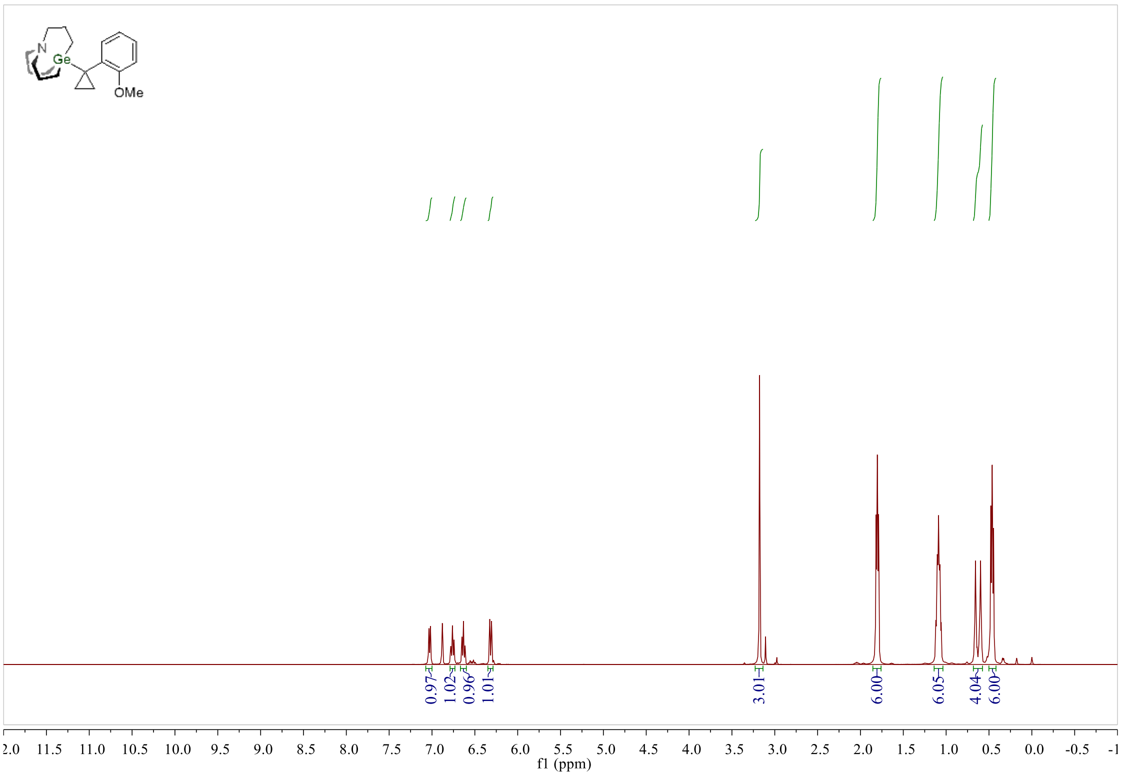
9.6
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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Ge
OMe
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0.96
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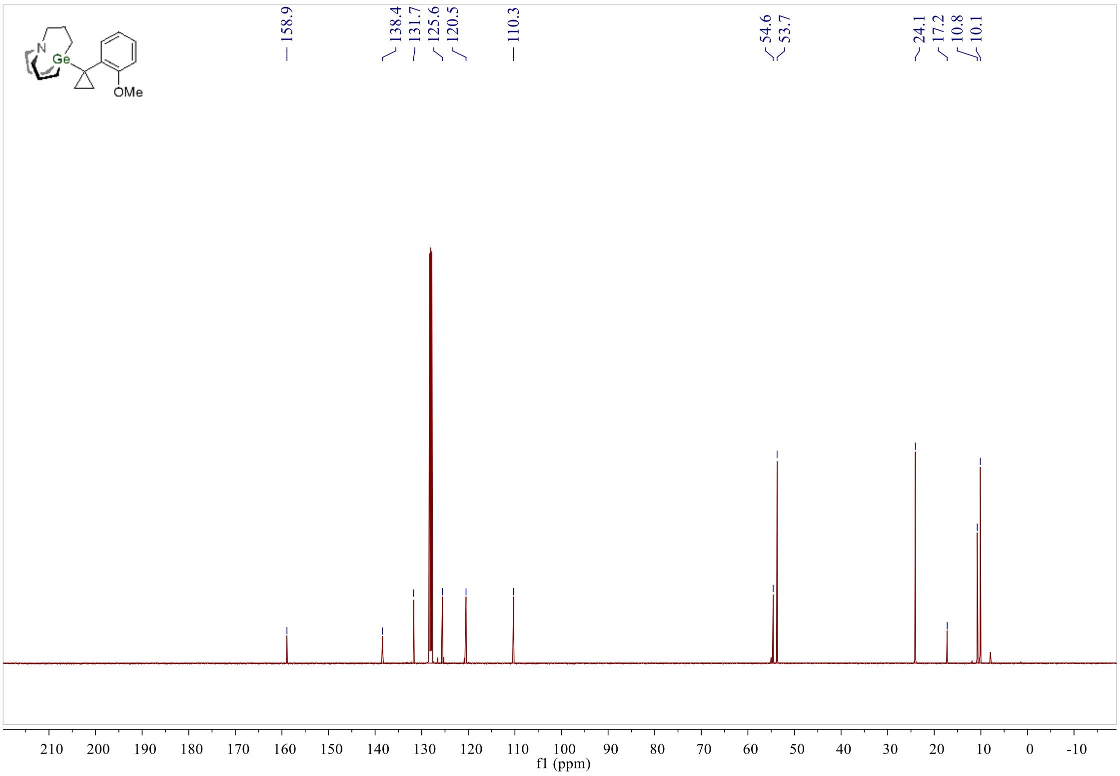
3.01
6.00
6.05
4.04
6.00
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)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Ge
OMe
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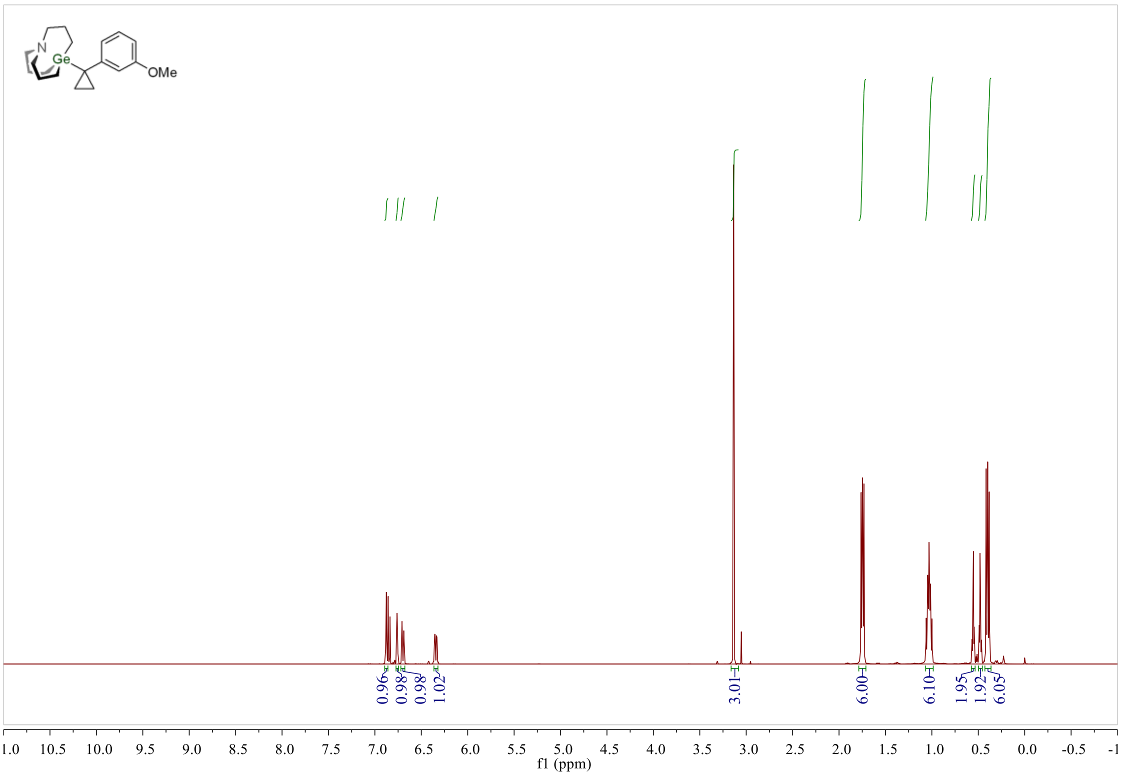
131.7
125.6
120.5
110.3
54.6
53.7
24.1
17.2
10.8
10.1
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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Ge
OMe
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0.98
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3.01
6.00
6.10
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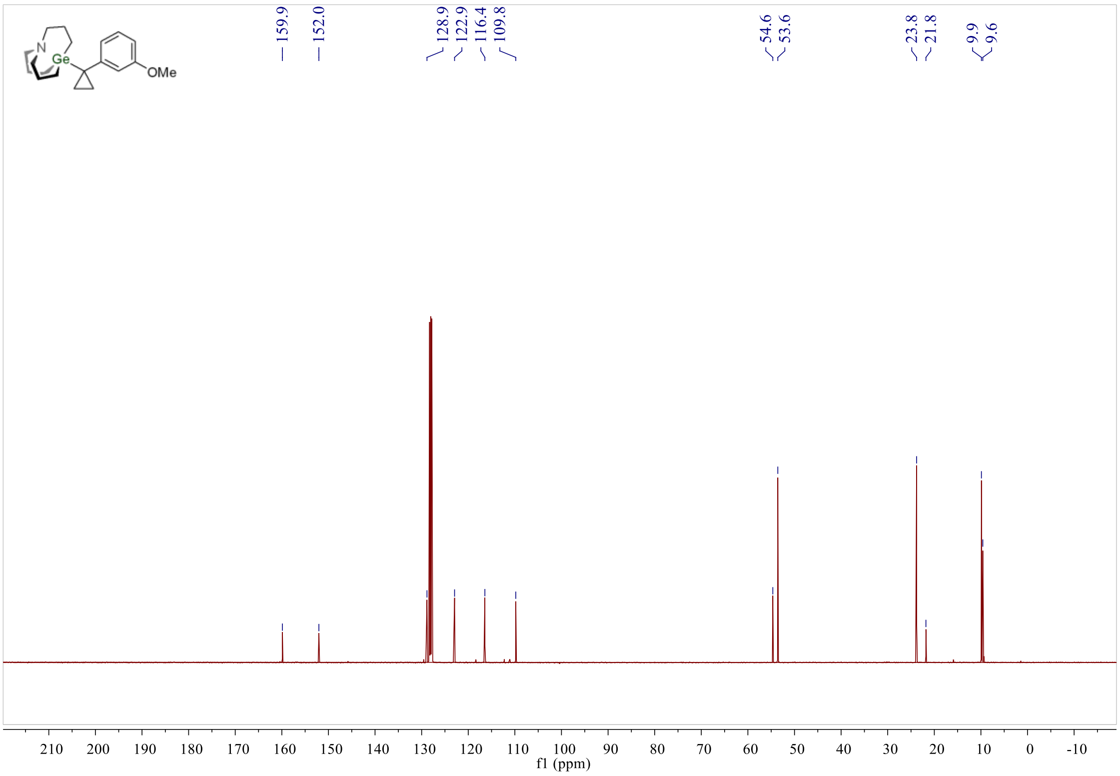
1.92
6.05
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)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Ge
OMe
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128.9
122.9
116.4
109.8
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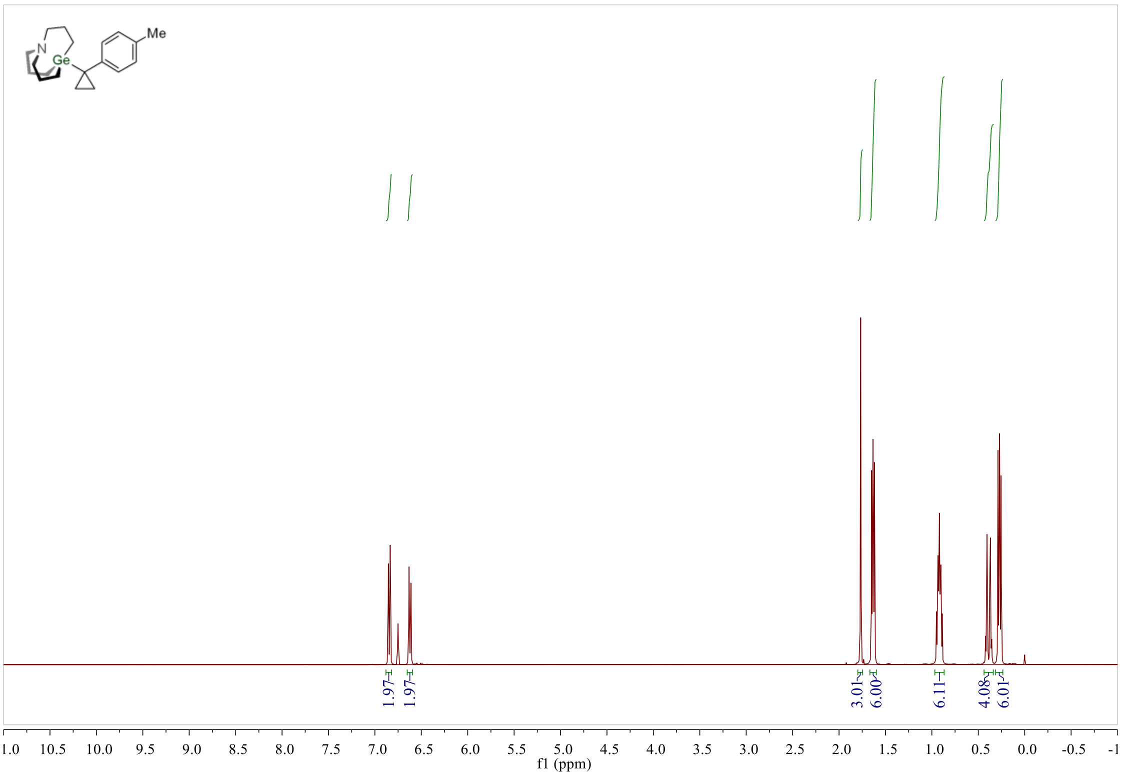
53.6
23.8
21.8
9.9
9.6
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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Ge
Me
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1.97
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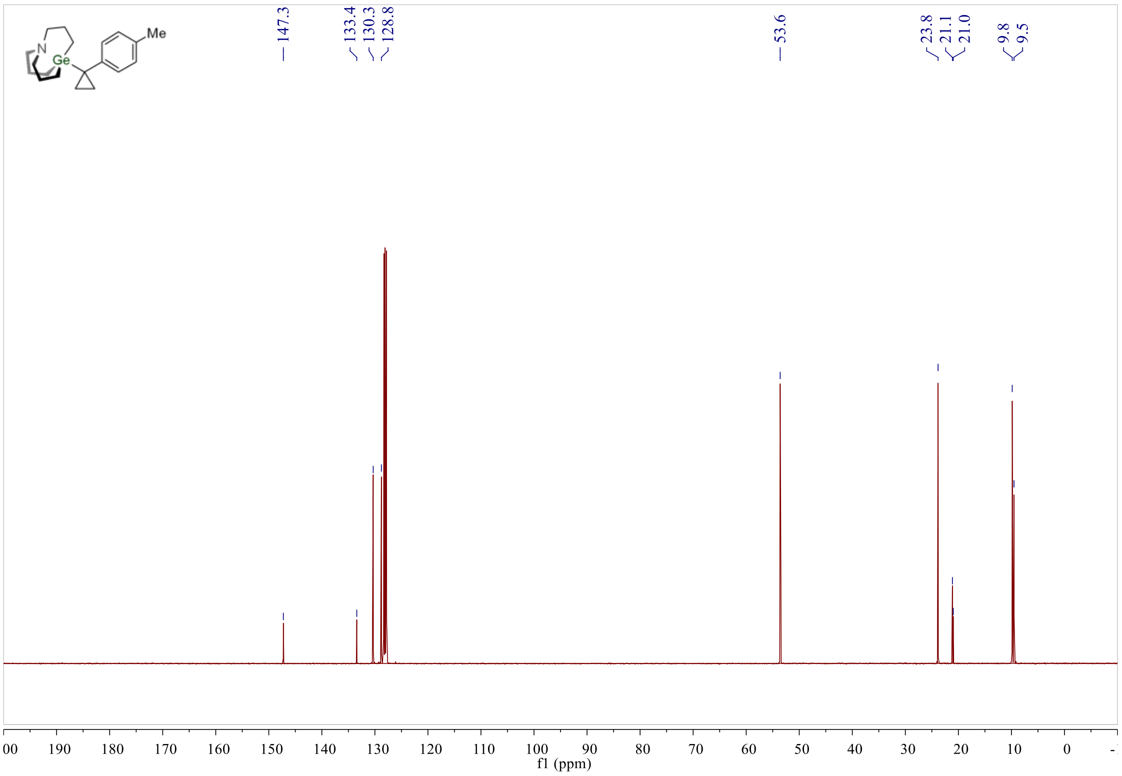
6.00
6.11
4.08
6.01
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


N
Ge
Me
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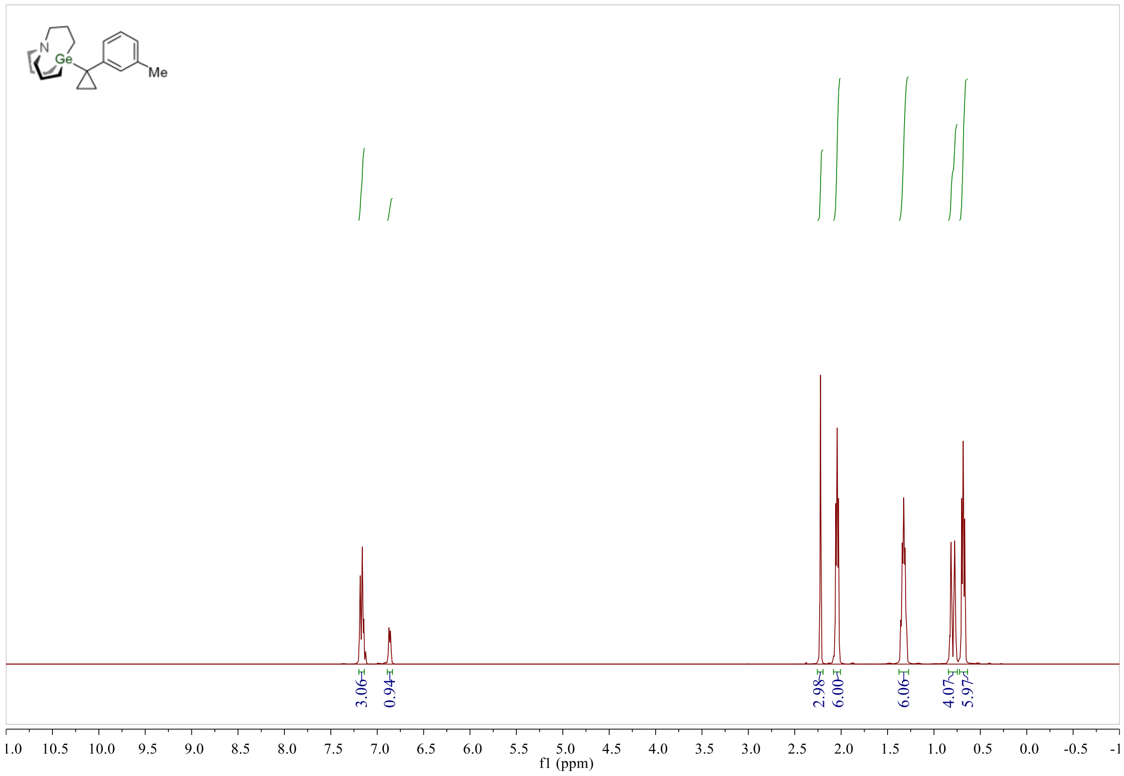
133.4
130.3
128.8
53.6
23.8
21.1
21.0
9.8
9.5
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-
f1 (ppm)


N
Ge
Me
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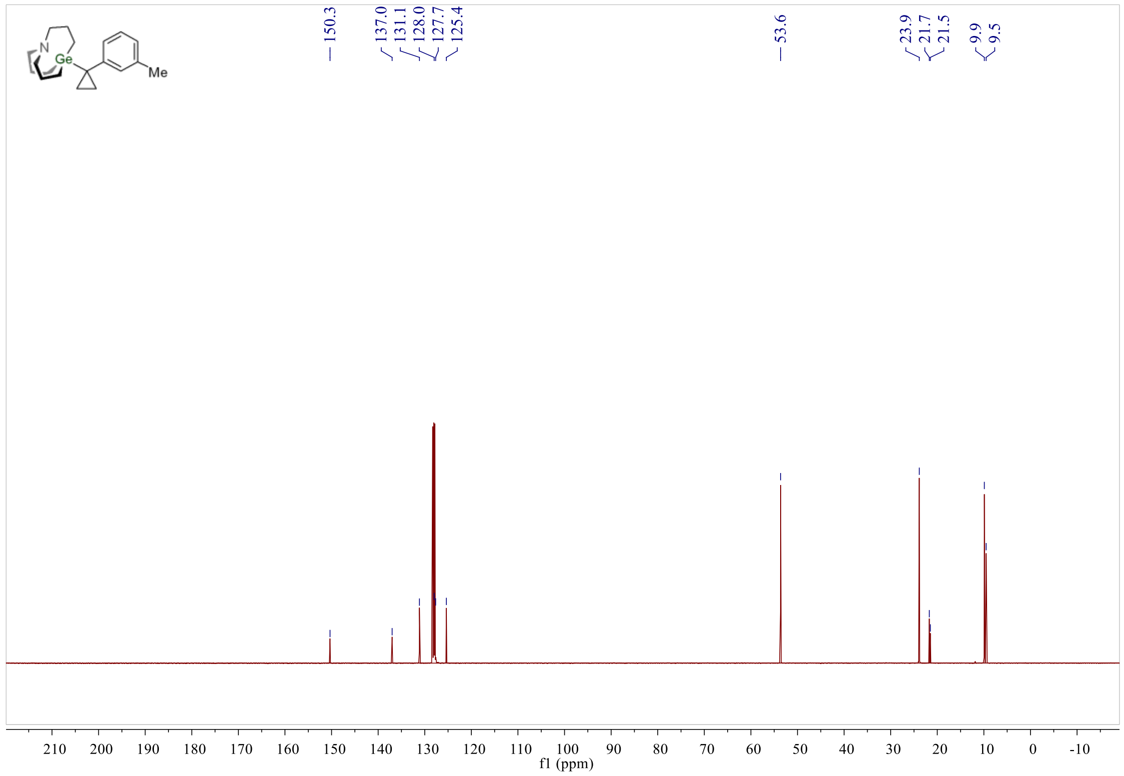
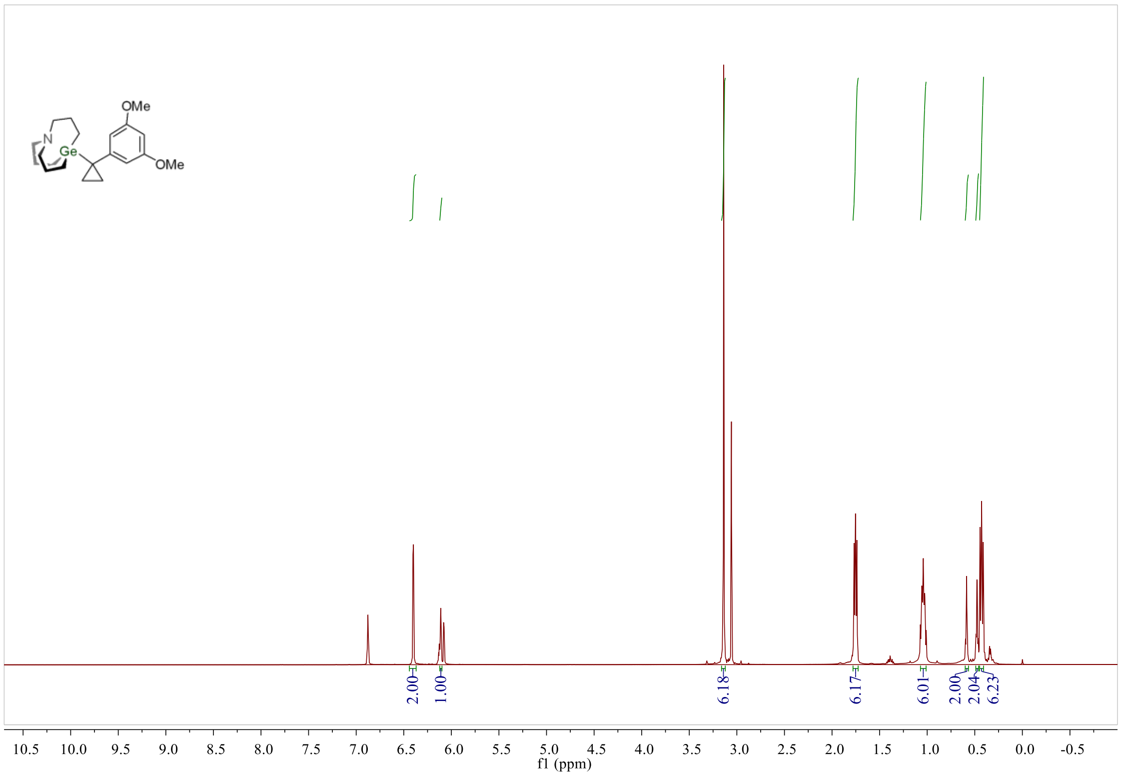
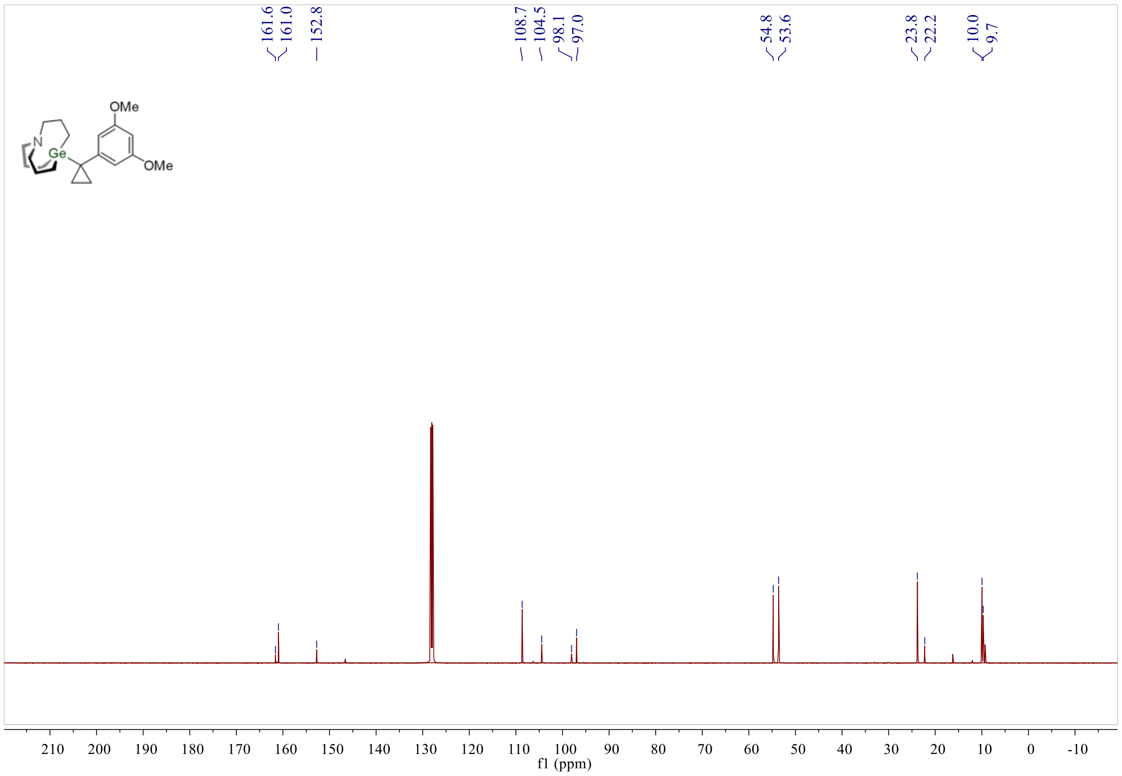
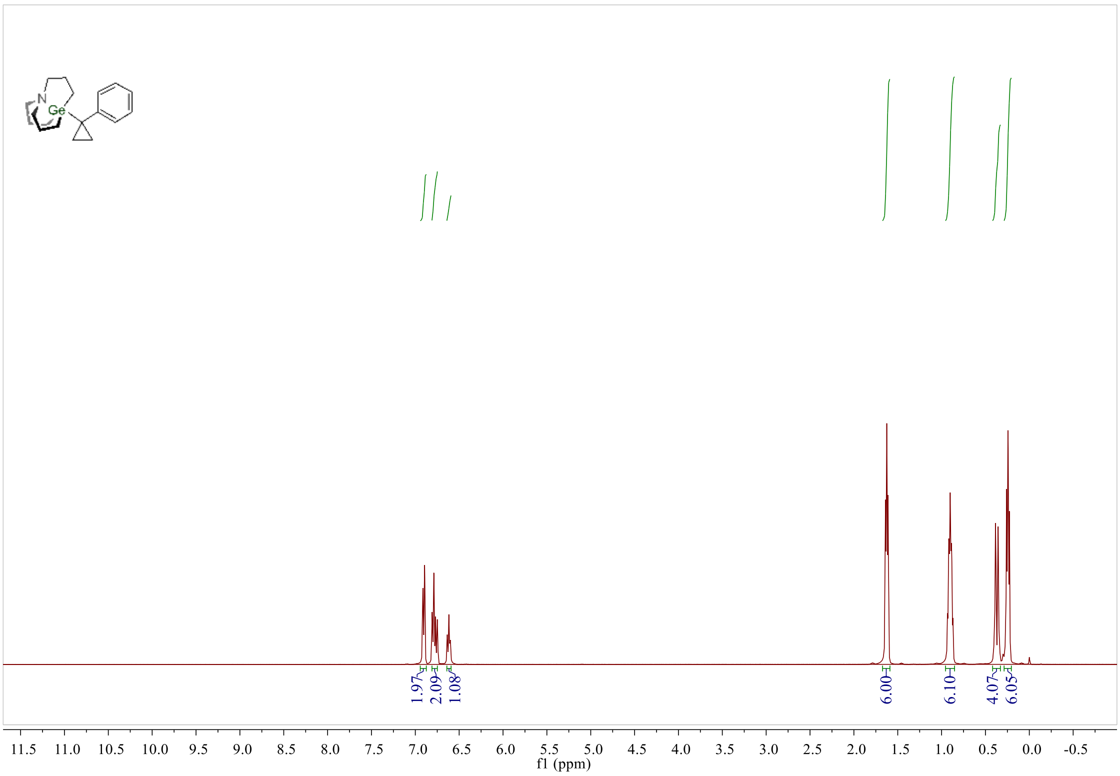
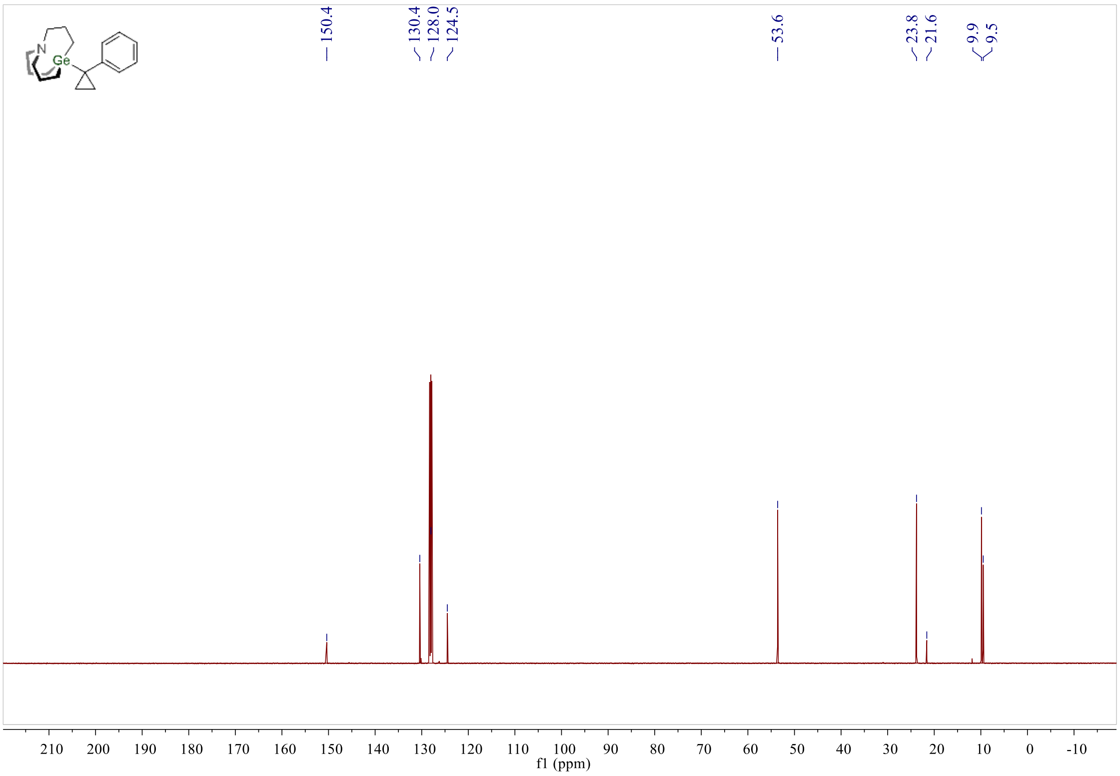
0.94
2.98
6.00
6.06
4.07
5.97
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

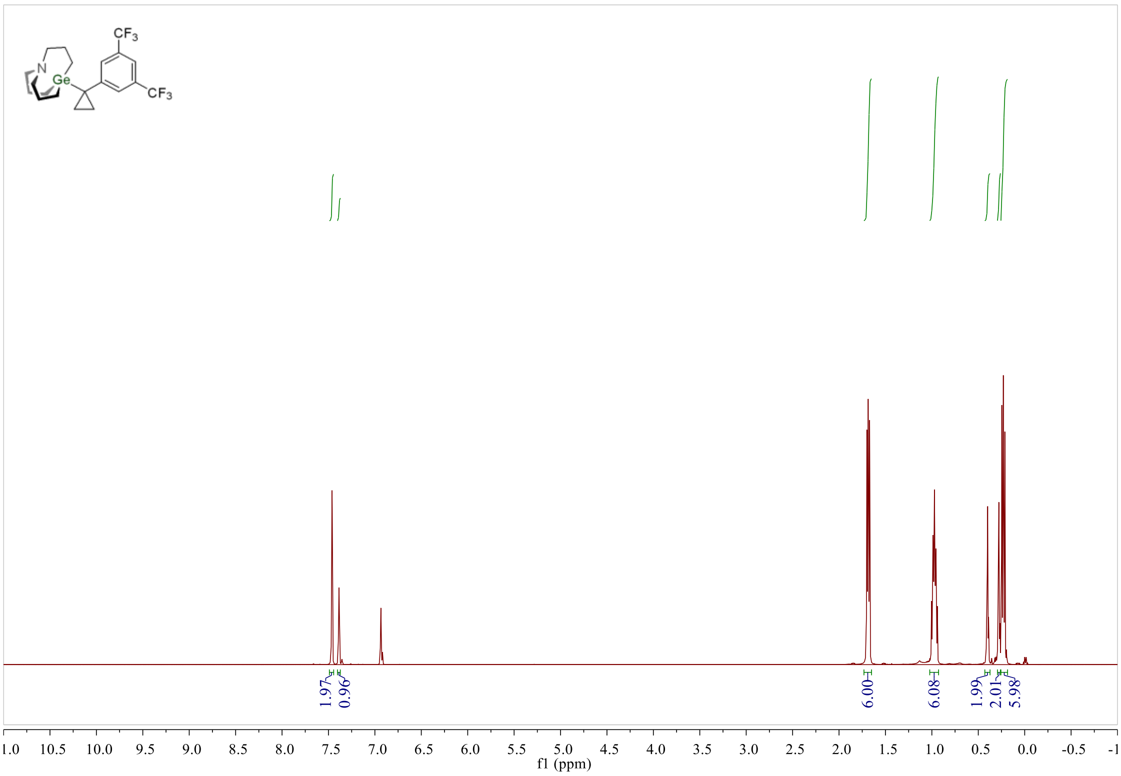

N
Ge
Me
150.3
137.0
131.1
128.0
127.7
125.4
53.6
23.9
21.7
21.5
9.9
9.5
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

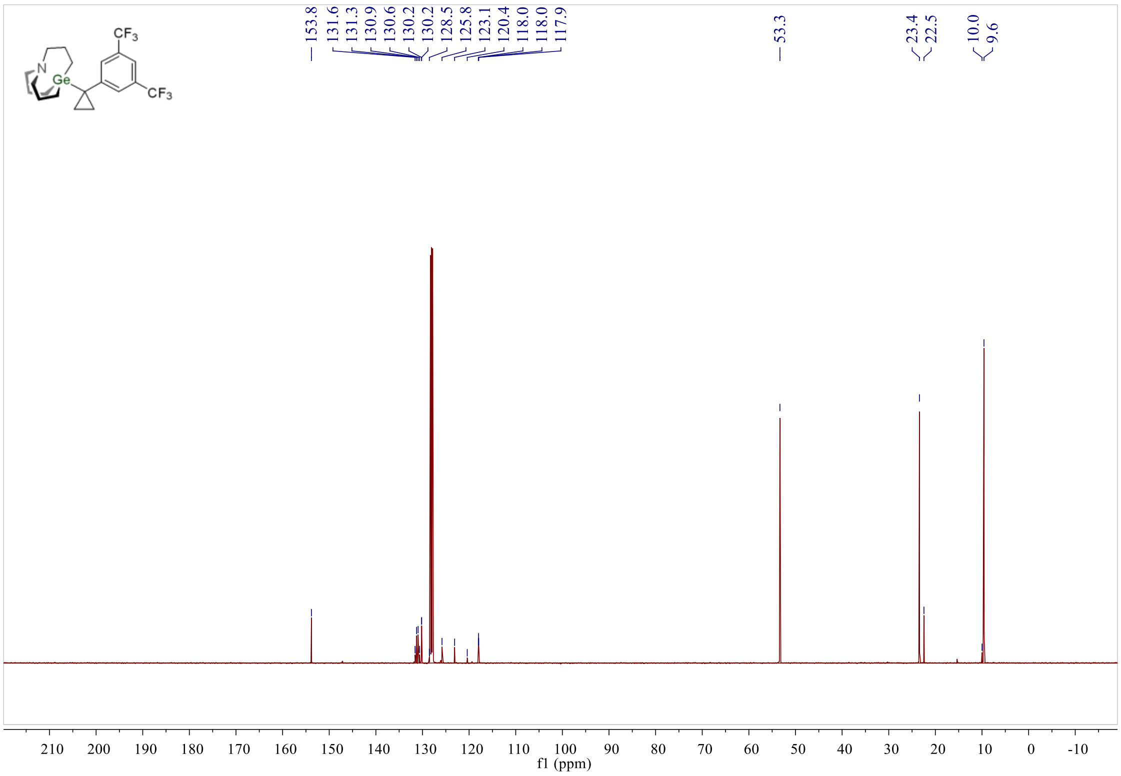

OMe
N
Ge
OMe
2.00
1.00
6.18
6.17
6.01
2.00
2.04
6.23
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

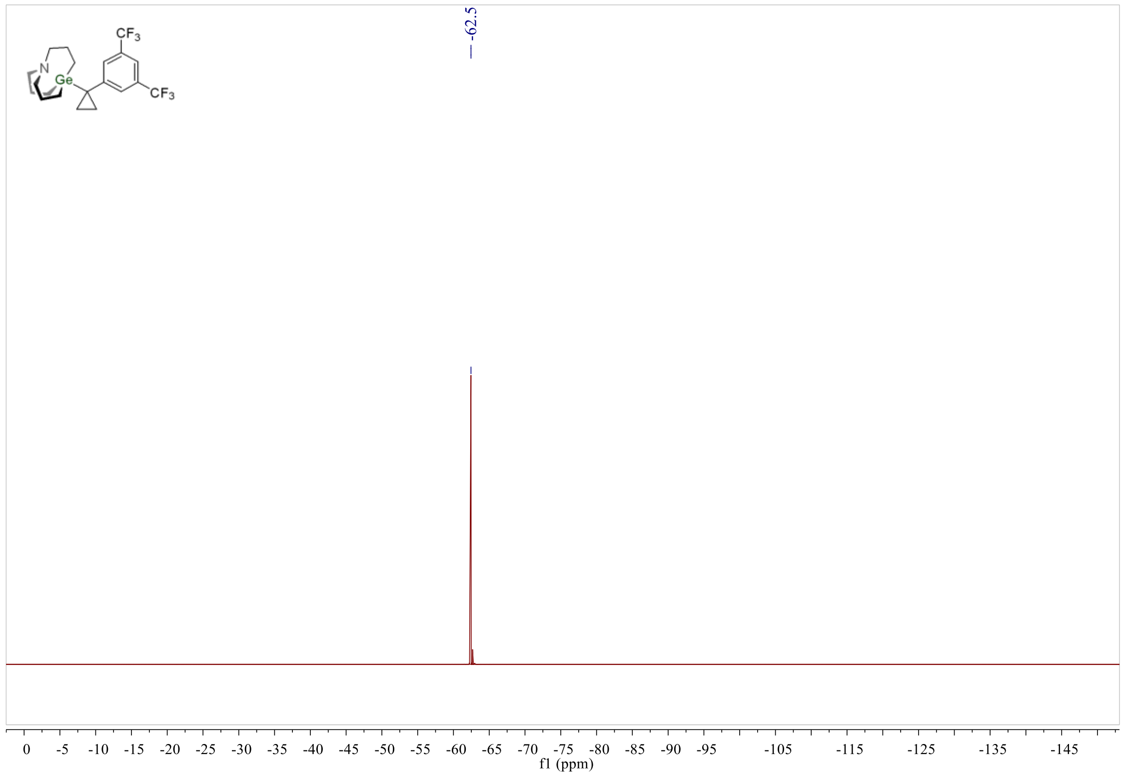

161.6
161.0
152.8
108.7
104.5
98.1
97.0
54.8
53.6
23.8
22.2
10.0
9.7
OMe
N
Ge
OMe
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

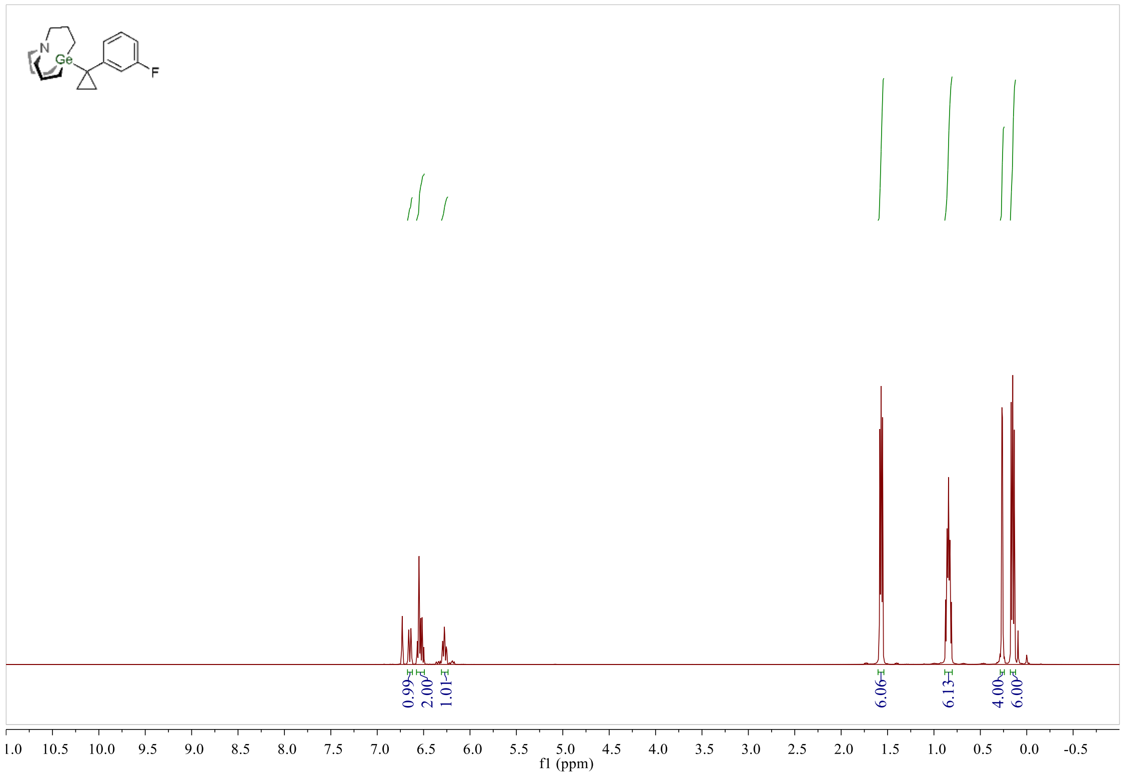

N
Ge
1.97
2.09
1.08
6.00
6.10
4.07
6.05
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

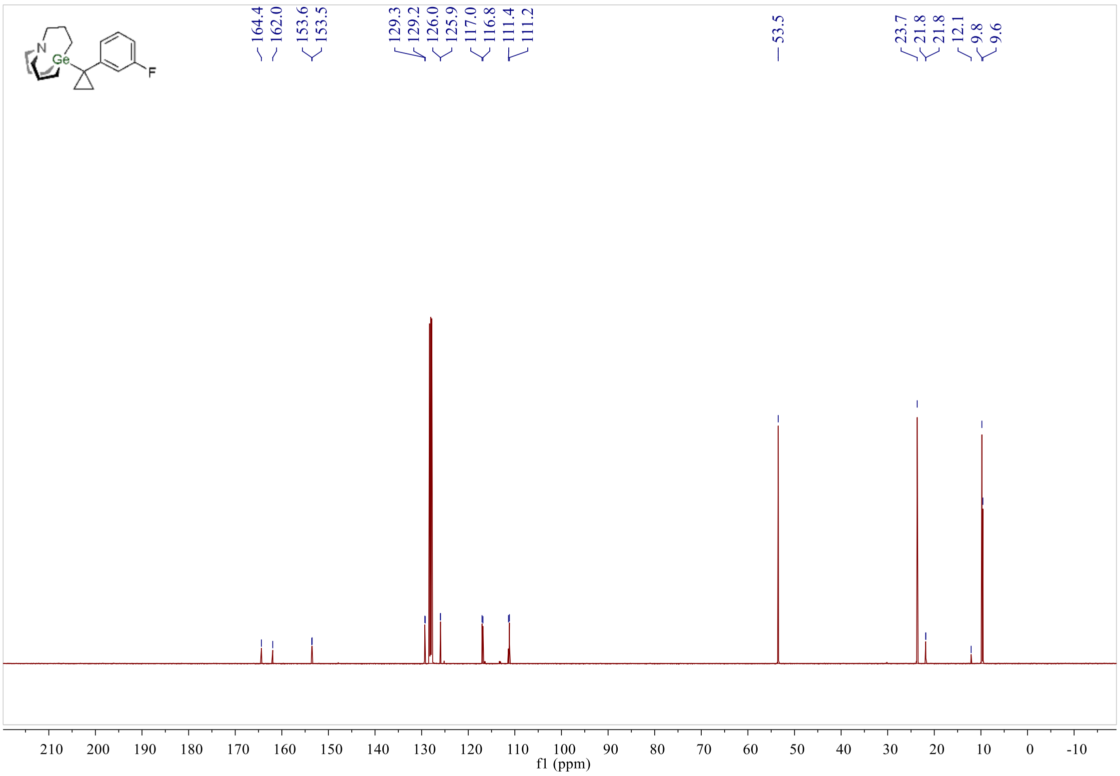

N
Ge
150.4
130.4
128.0
124.5
53.6
23.8
21.6
9.9
9.5
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


CF3
N
Ge
CF3
1.97
0.96
6.00
6.08
1.99
2.01
5.98
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


153.8
131.6
131.3
130.9
130.6
130.2
130.2
128.5
125.8
123.1
120.4
118.0
118.0
117.9
53.3
23.4
22.5
10.0
9.6
CF3
N
Ge
CF3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


CF3
CF3
N
Ge
-62.5
0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -105 -115 -125 -135 -145
f1 (ppm)


N
Ge
F
0.99
2.00
1.01
6.06
6.13
4.00
6.00
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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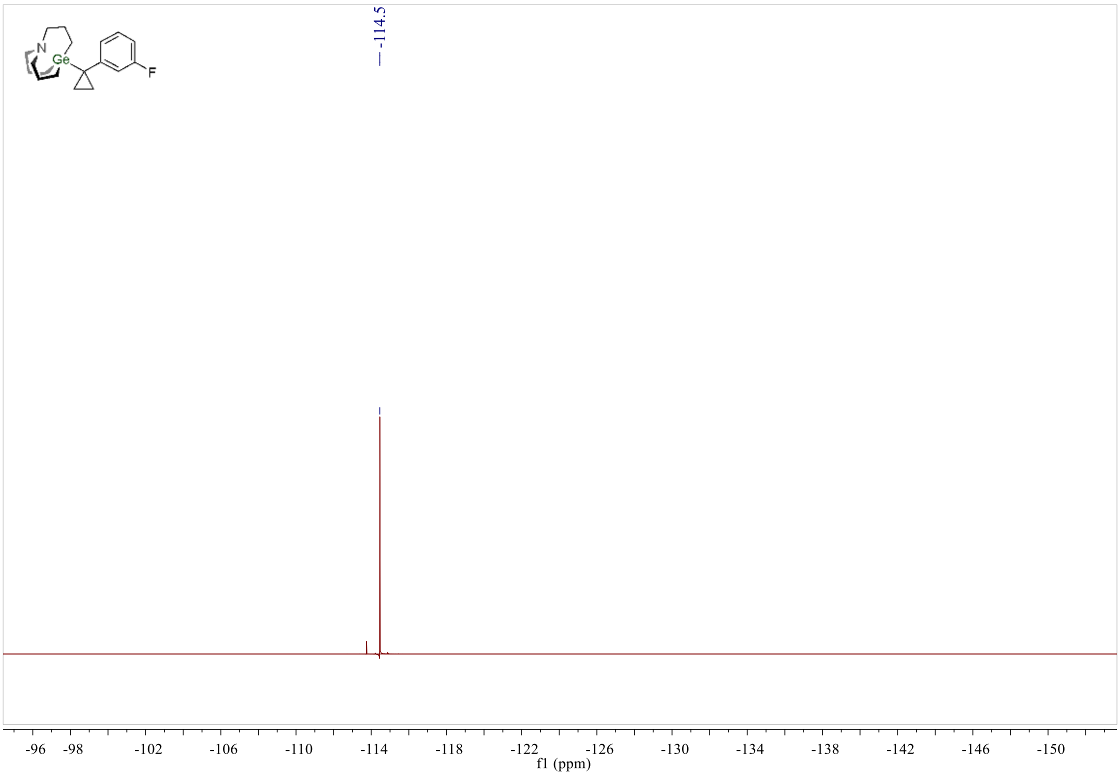
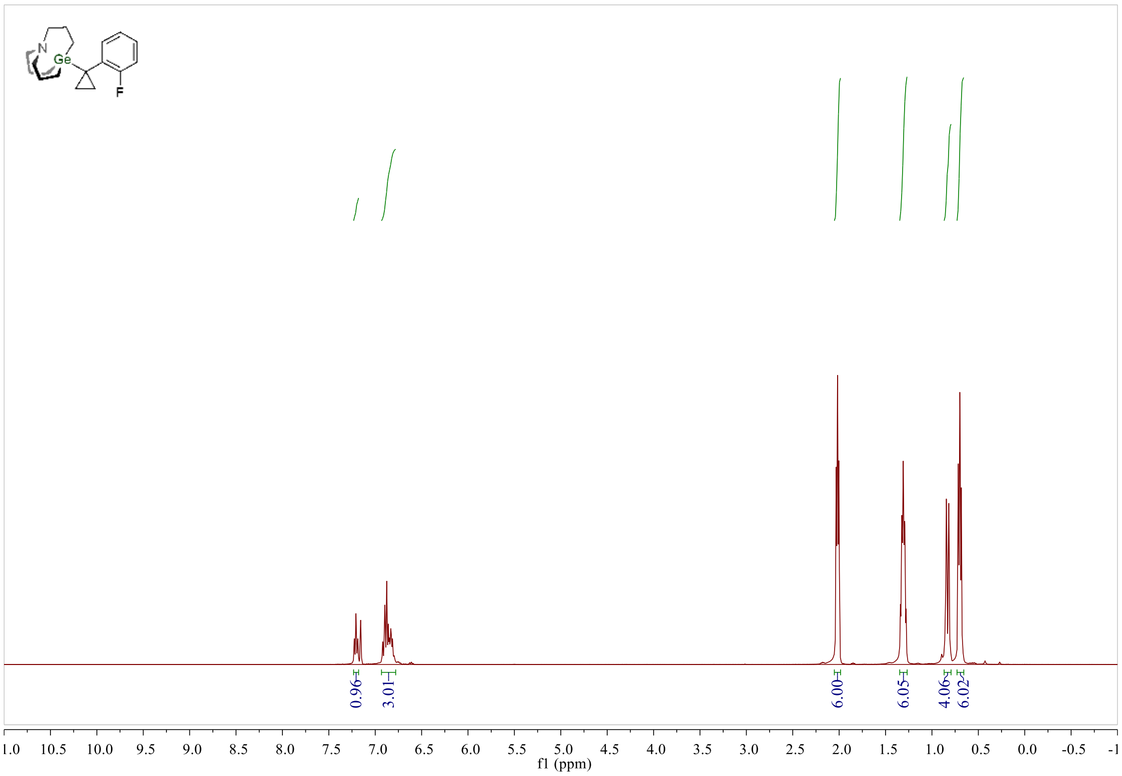
153.5
129.3
129.2
126.0
125.9
117.0
116.8
111.4
111.2
53.5
23.7
21.8
21.8
12.1
9.8
9.6
N
Ge
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-114.5
N
Ge
F
-96 -98 -102 -106 -110 -114 -118 -122 -126 -130 -134 -138 -142 -146 -150
f1 (ppm)


Ge
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F
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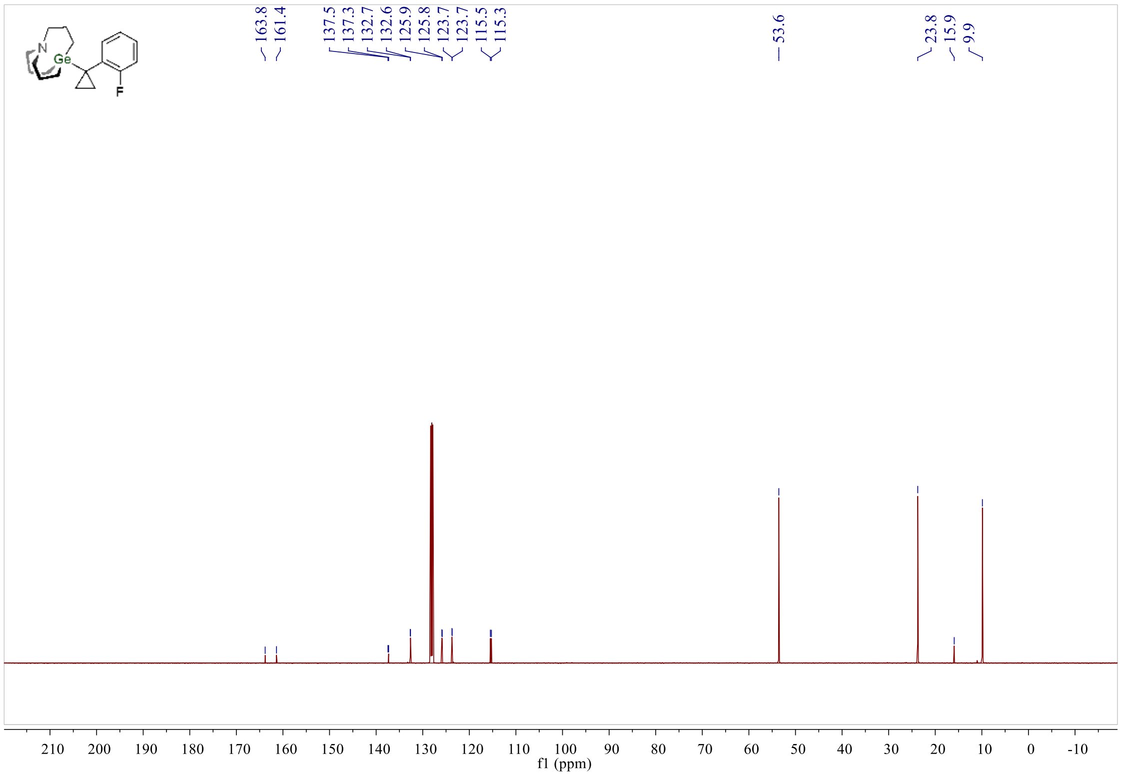
6.00
6.05
4.06
6.02
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


Ge
N
F
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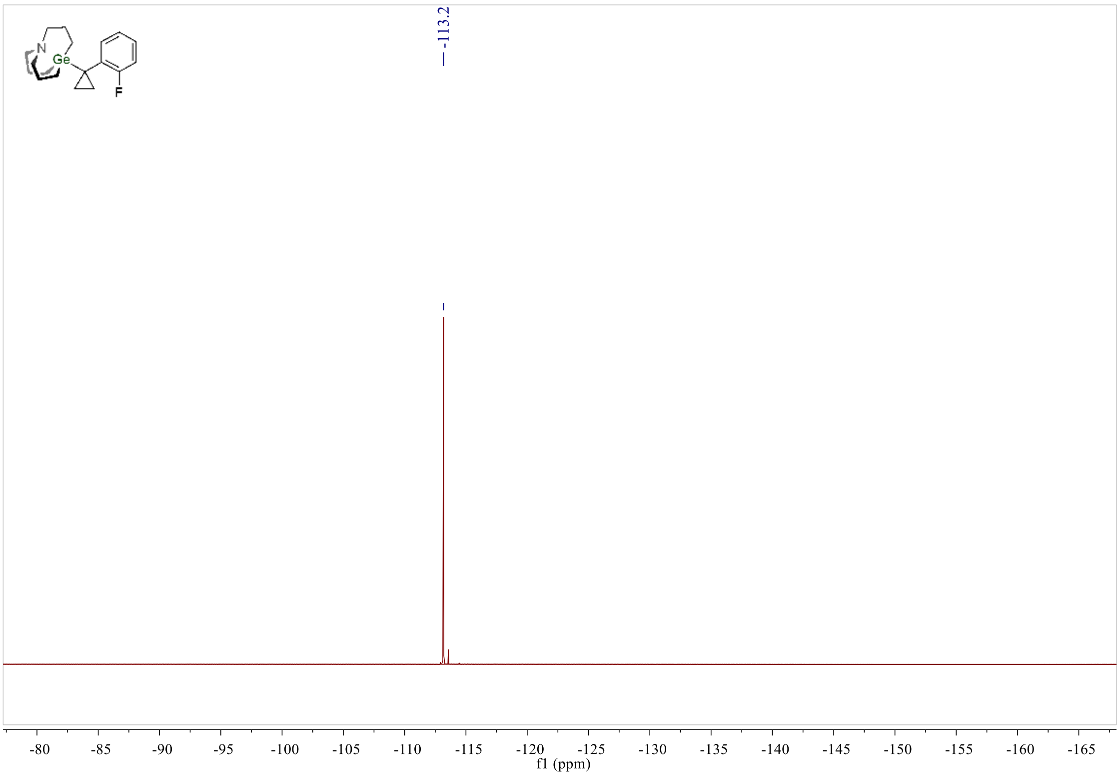
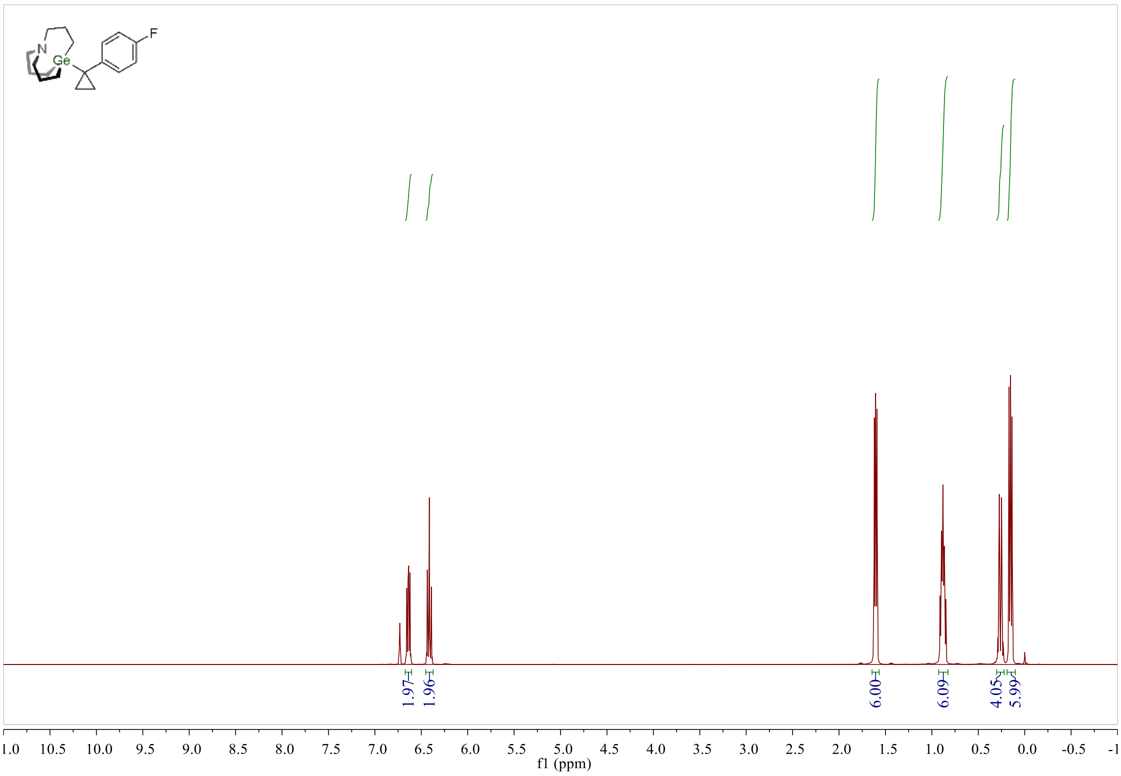
161.4
137.5
137.3
132.7
132.6
125.9
125.8
123.7
123.7
115.5
115.3
53.6
23.8
15.9
9.9
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



Ge
N
F
-113.2
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
-165
f1 (ppm)



F
N
Ge
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1.96
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6.09
4.05
5.99
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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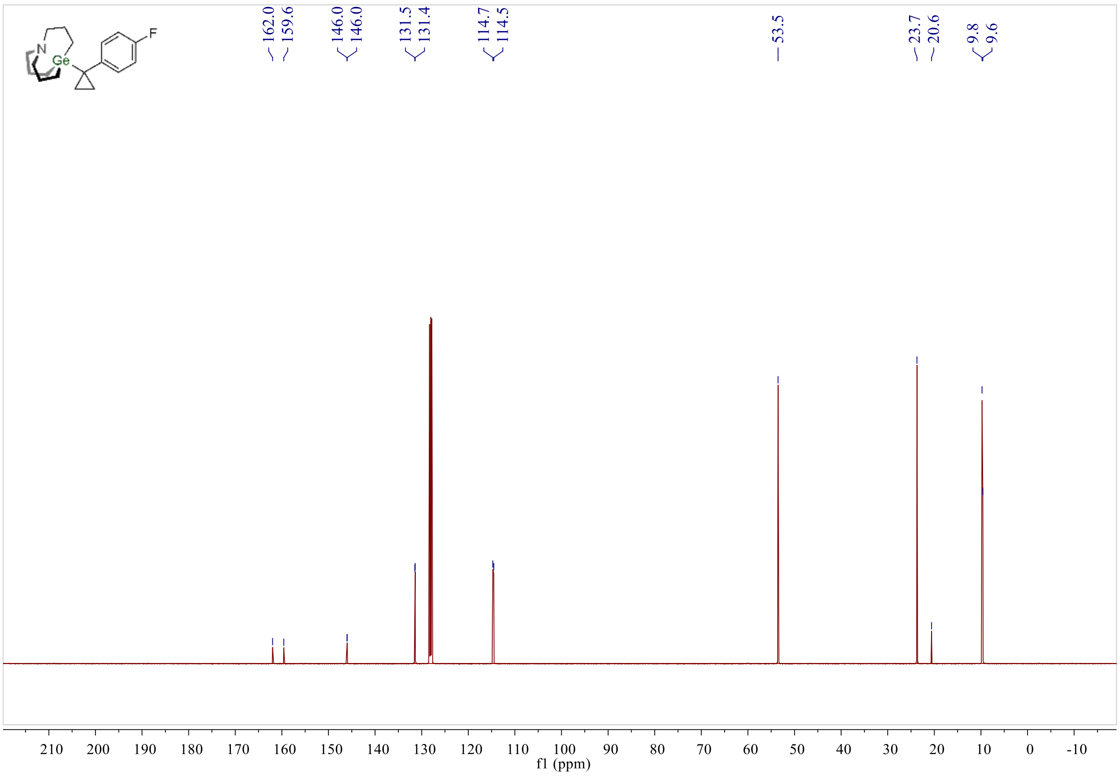
0.0
-0.5
-1
f1 (ppm)


F
N
Ge
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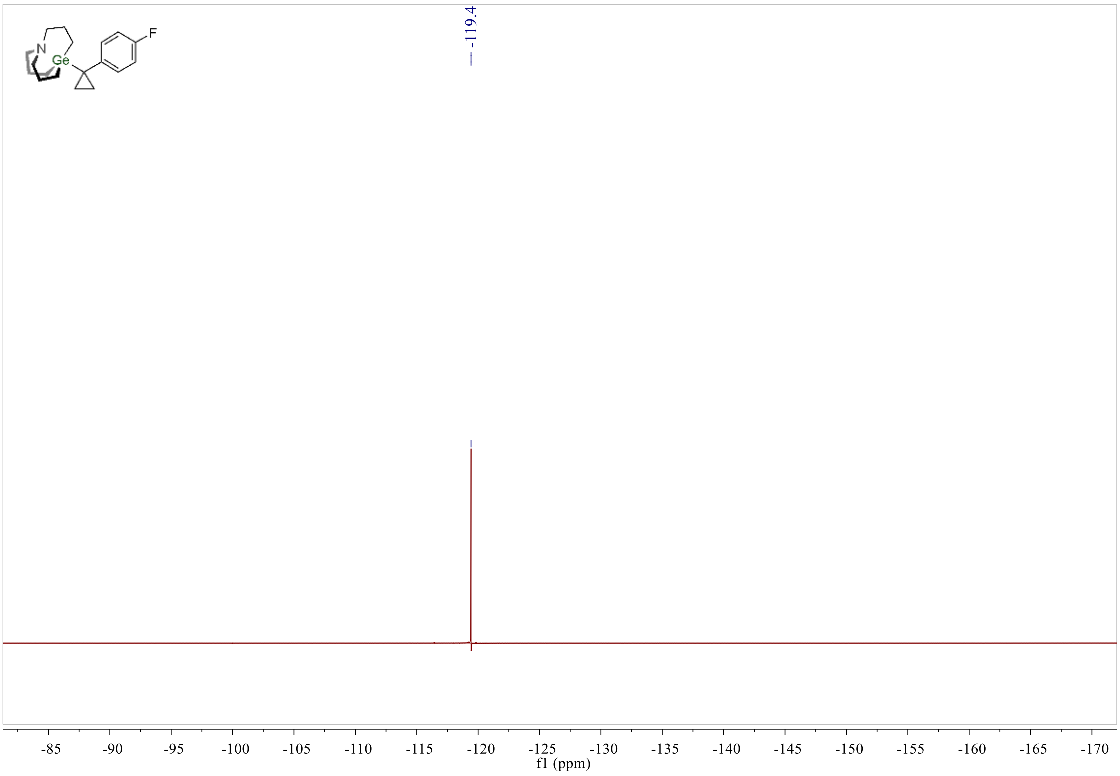
146.0
146.0
131.5
131.4
114.7
114.5
53.5
23.7
20.6
9.8
9.6
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


F
N
Ge
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-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
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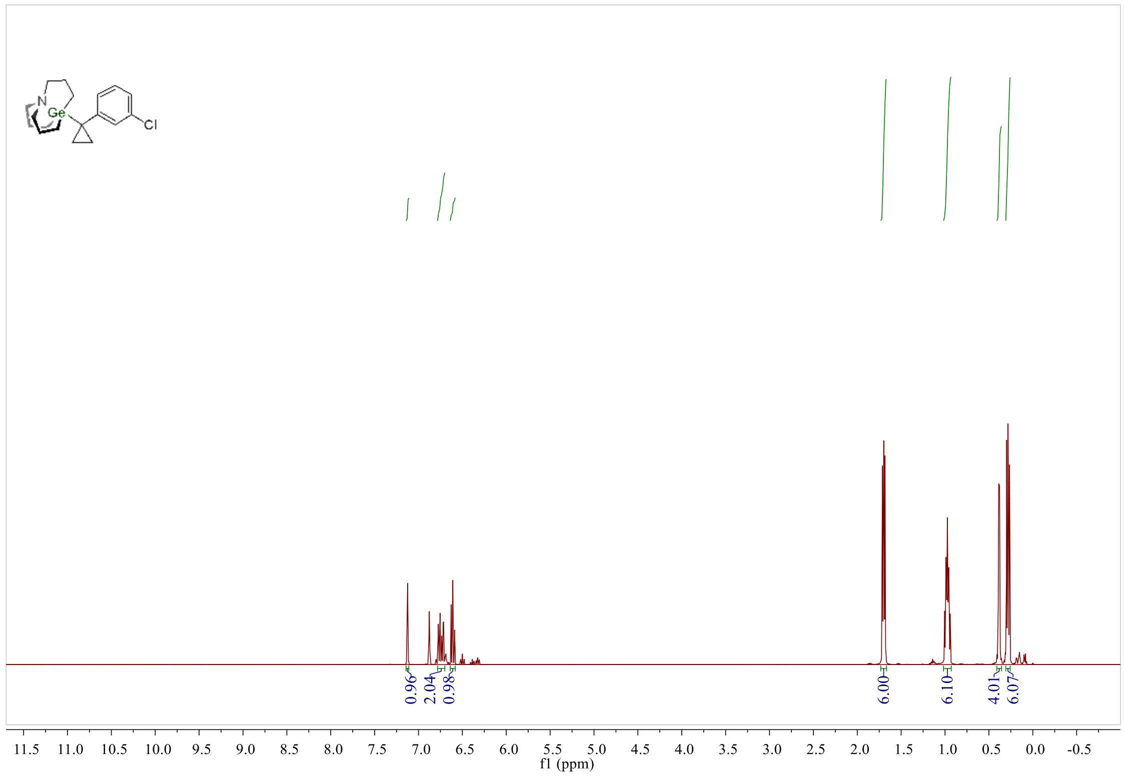
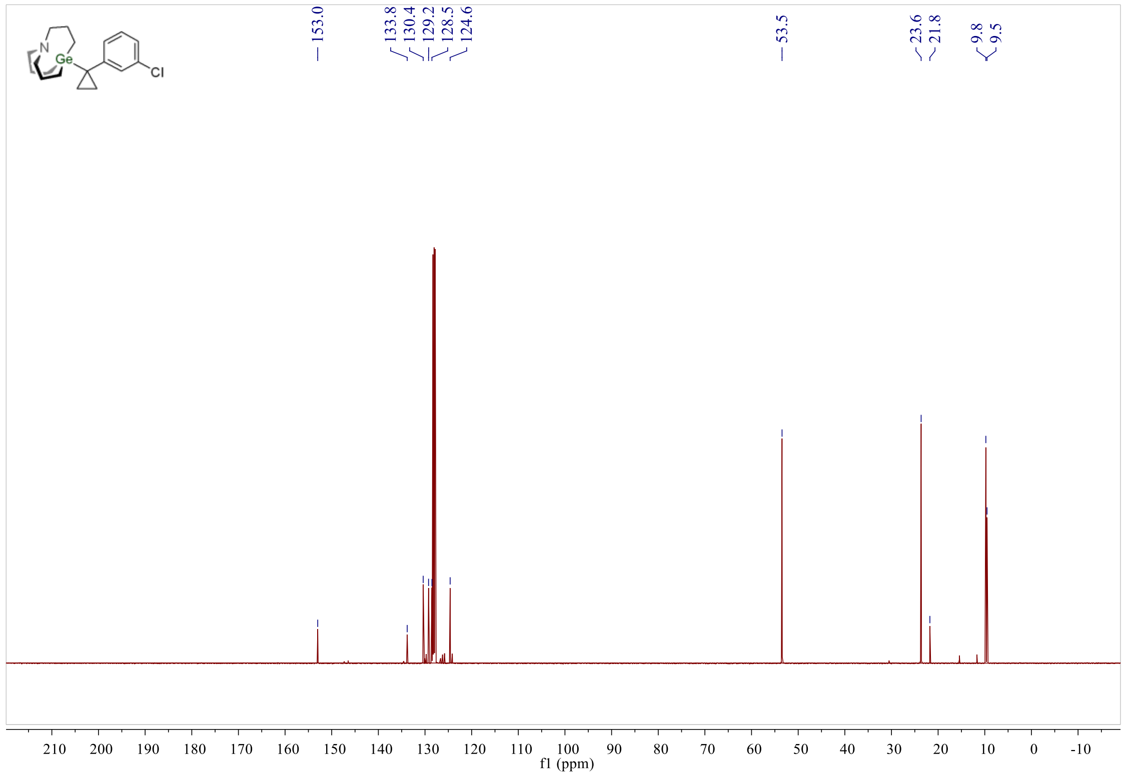
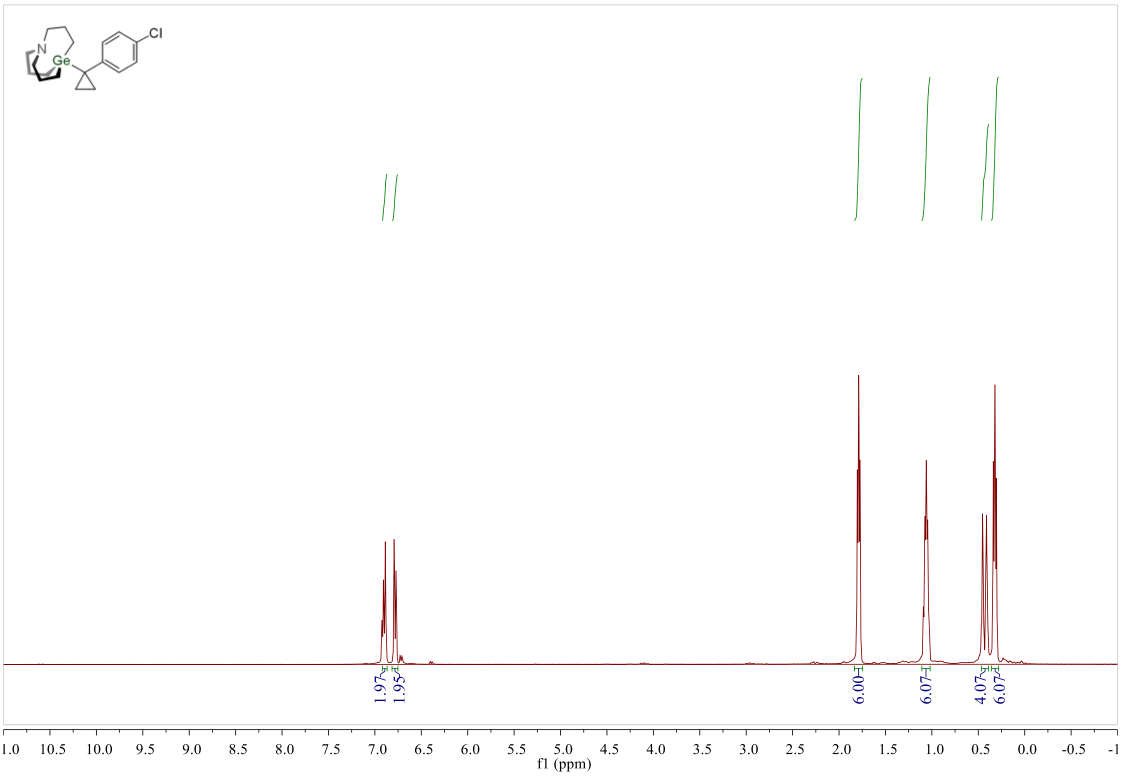
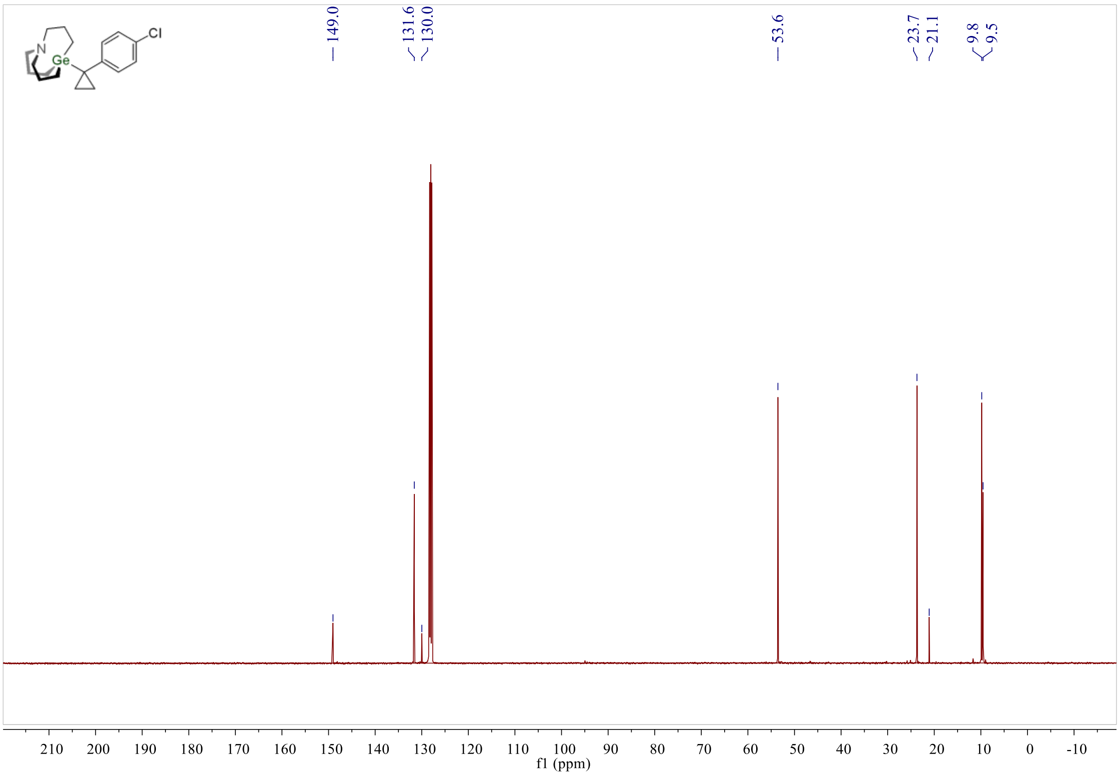
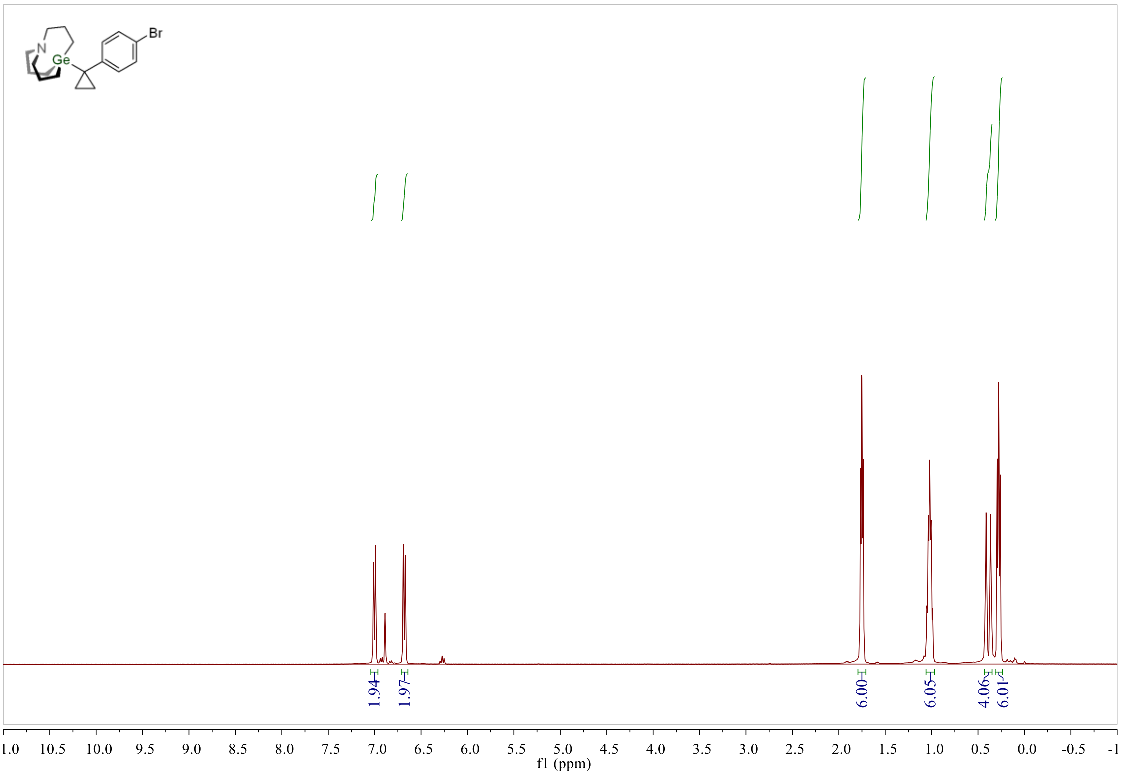
-160
-165
-170
f1 (ppm)


N
Ge
Cl
0.96
2.04
0.98
6.00
6.10
4.01
6.07
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


153.0
133.8
130.4
129.2
128.5
124.6
53.5
23.6
21.8
9.8
9.5
N
Ge
Cl
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Ge
N
Cl
1.97
1.95
6.00
6.07
4.07
6.07
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


Ge
N
Cl
149.0
131.6
130.0
53.6
23.7
21.1
9.8
9.5
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Br
N
Ge
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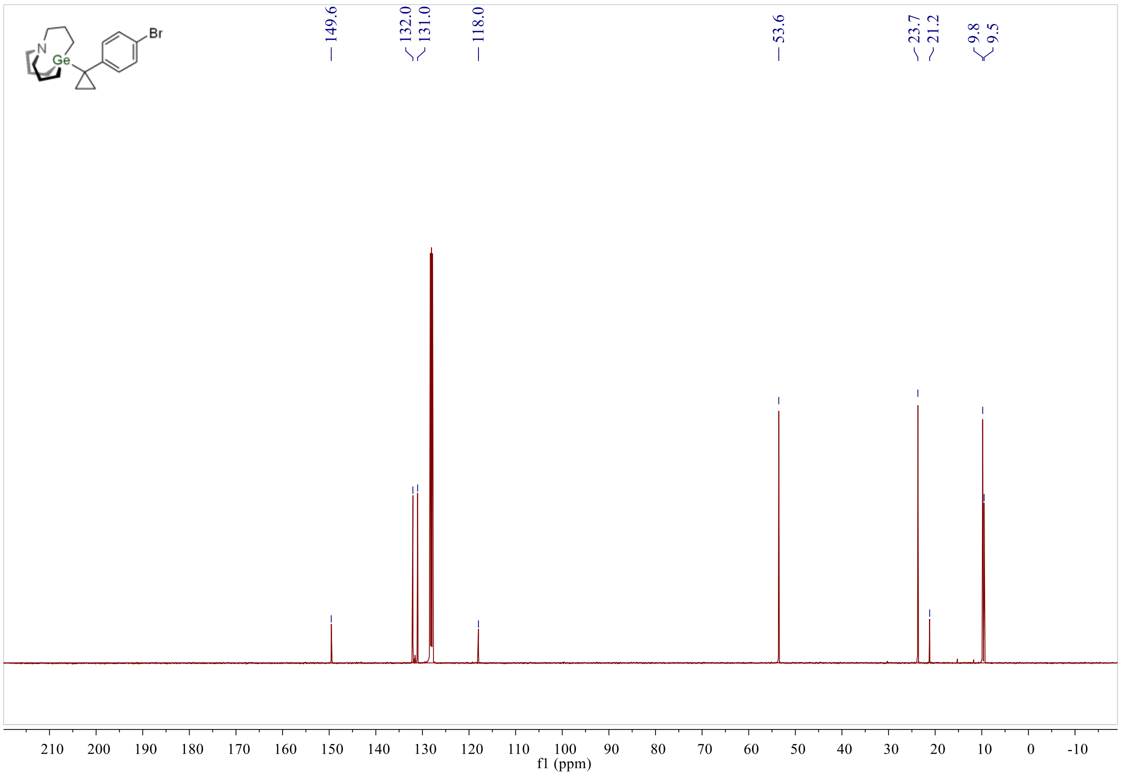
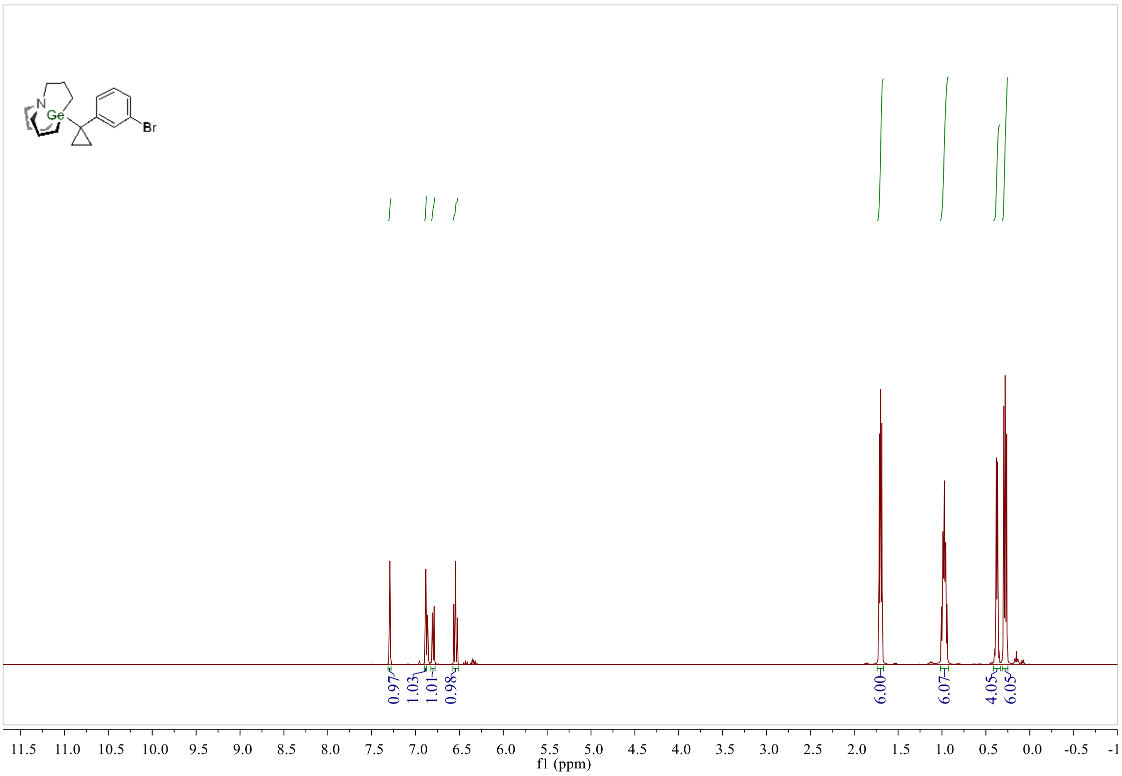
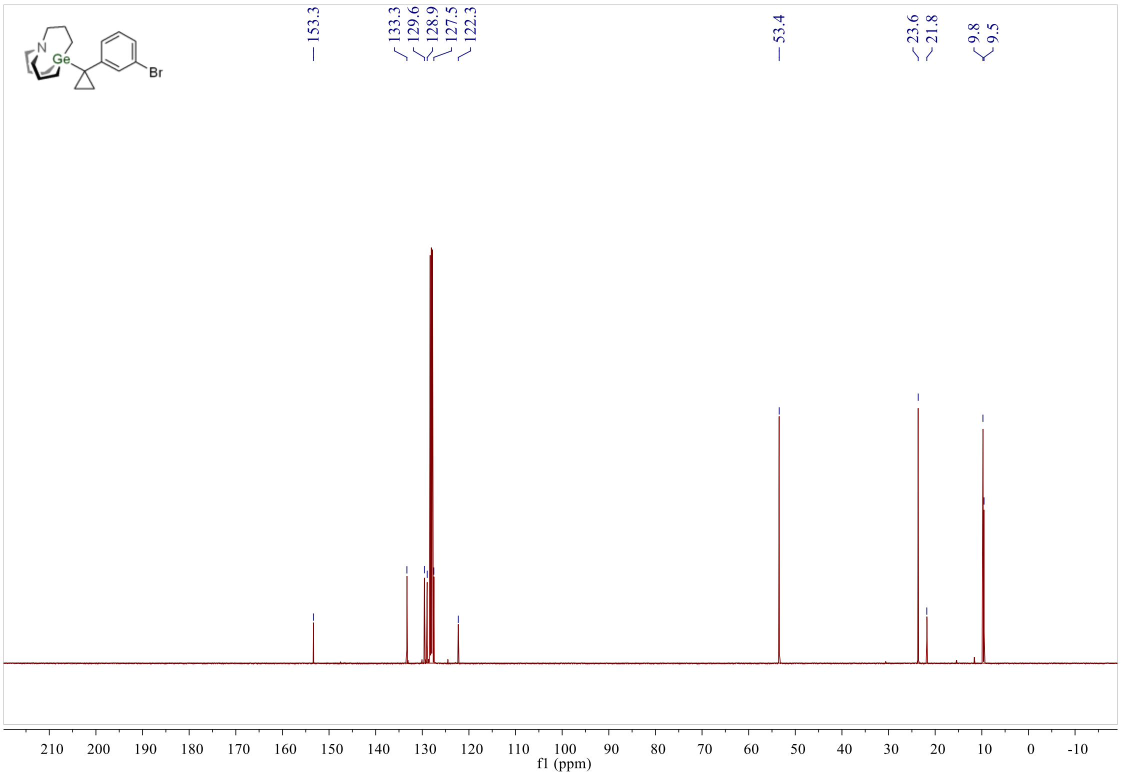
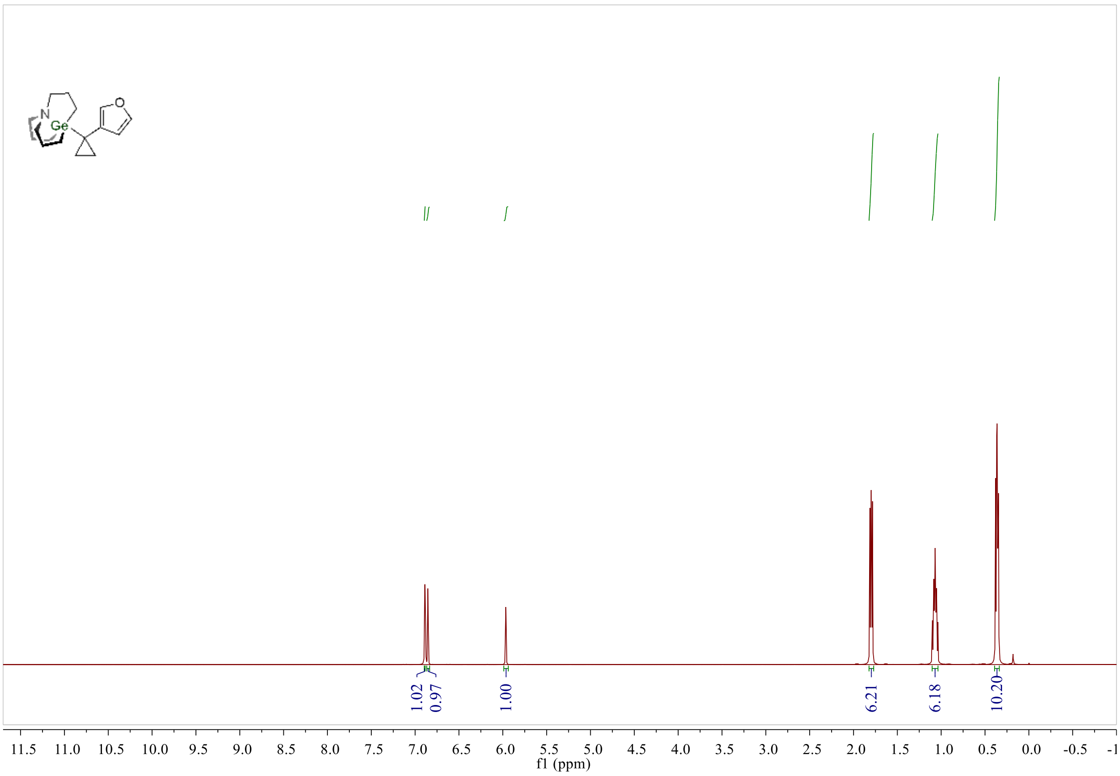
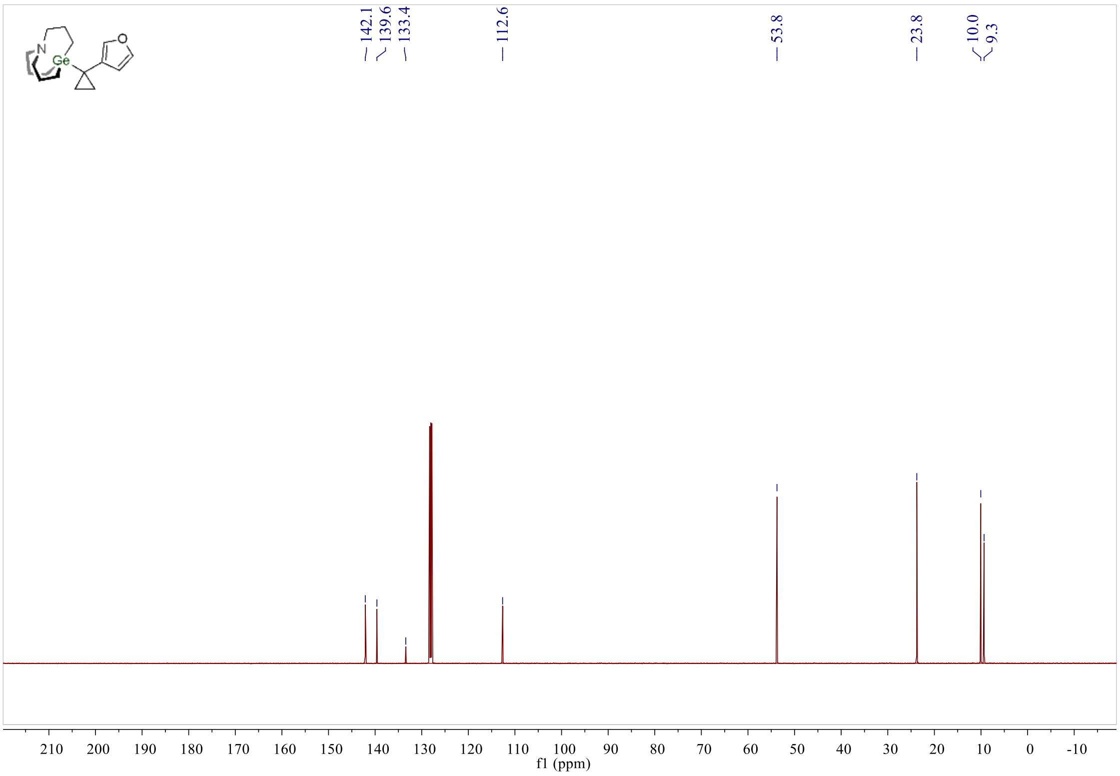
1.97
6.00
6.05
4.06
6.01
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

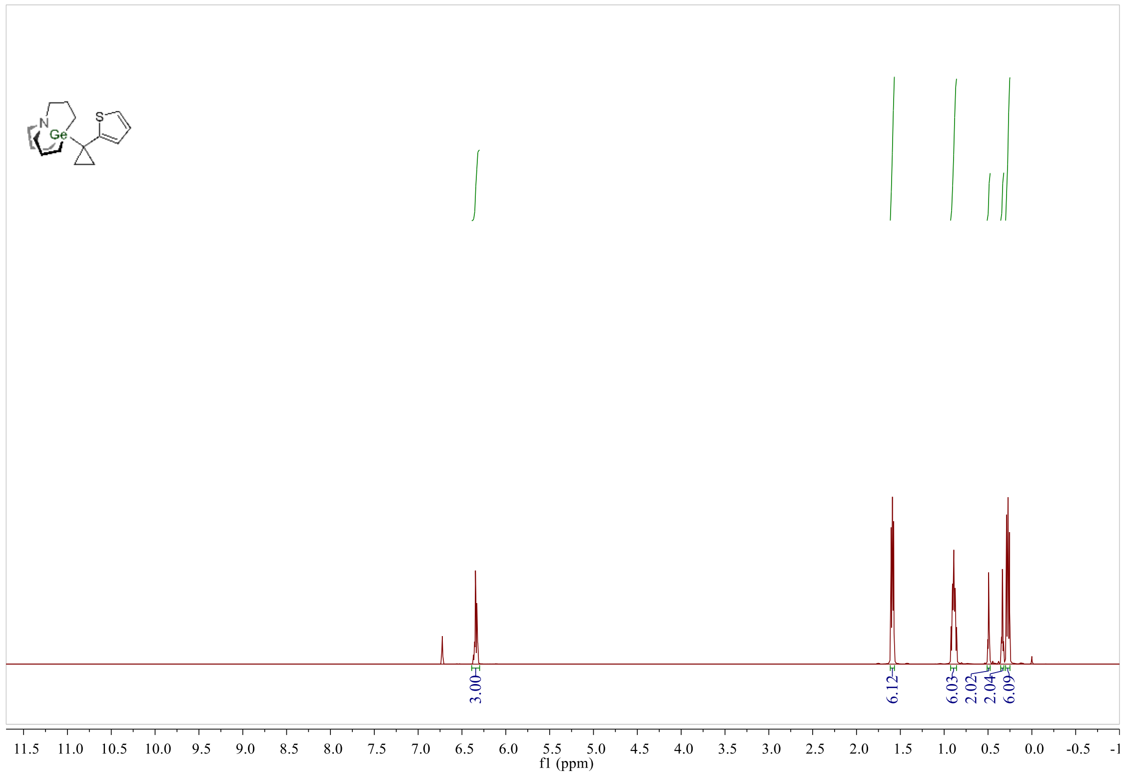

Br
N
Ge
149.6
132.0
131.0
118.0
53.6
23.7
21.2
9.8
9.5
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

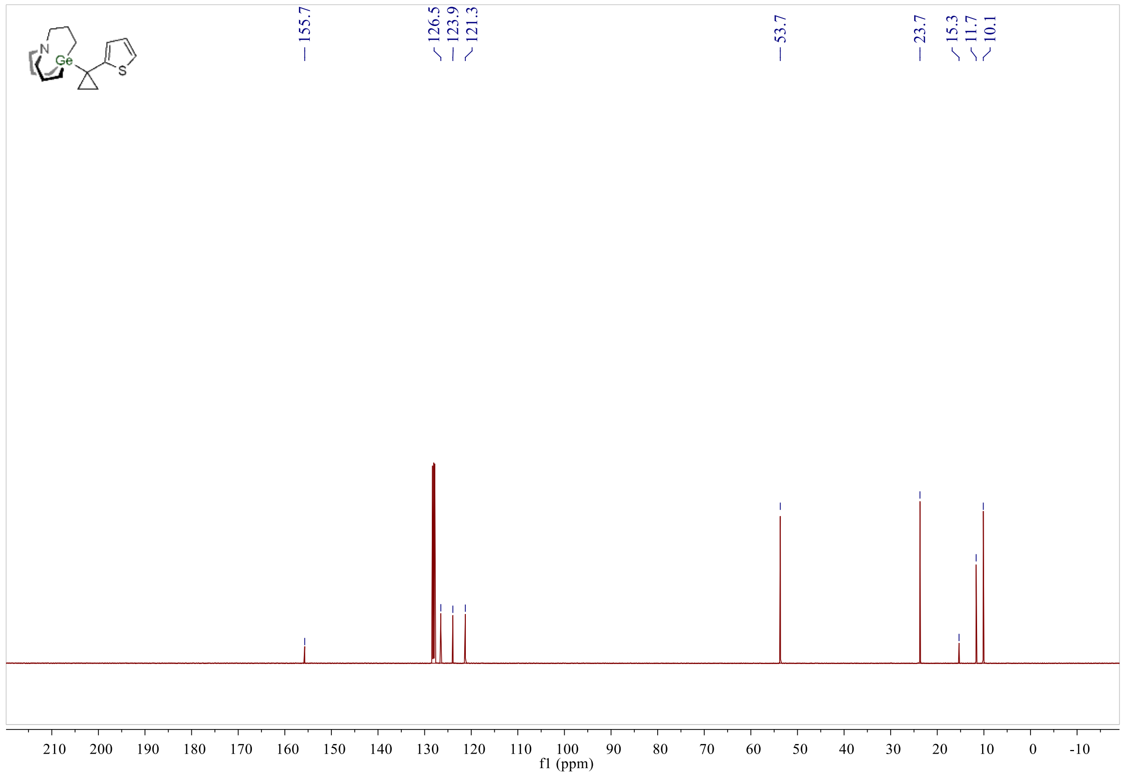

N
Ge
Br
0.97
1.03
1.01
0.98
6.00
6.07
4.05
6.05
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

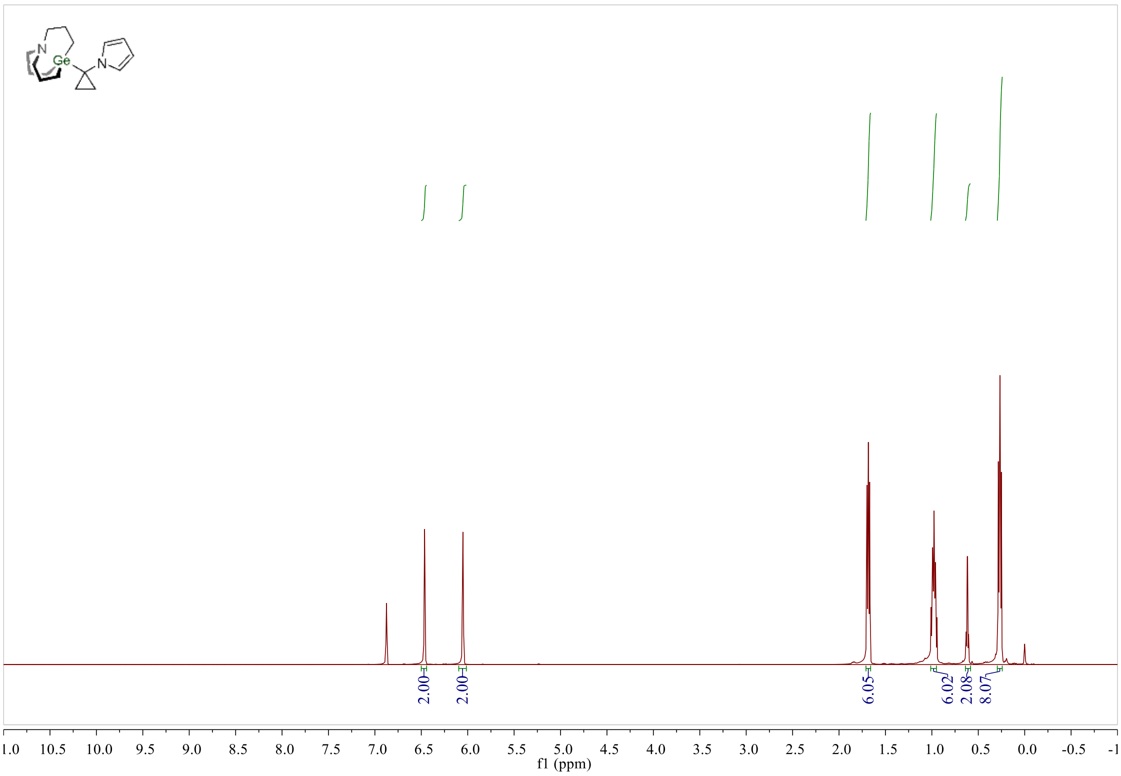

N
Ge
Br
153.3
133.3
129.6
128.9
127.5
122.3
53.4
23.6
21.8
9.8
9.5
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

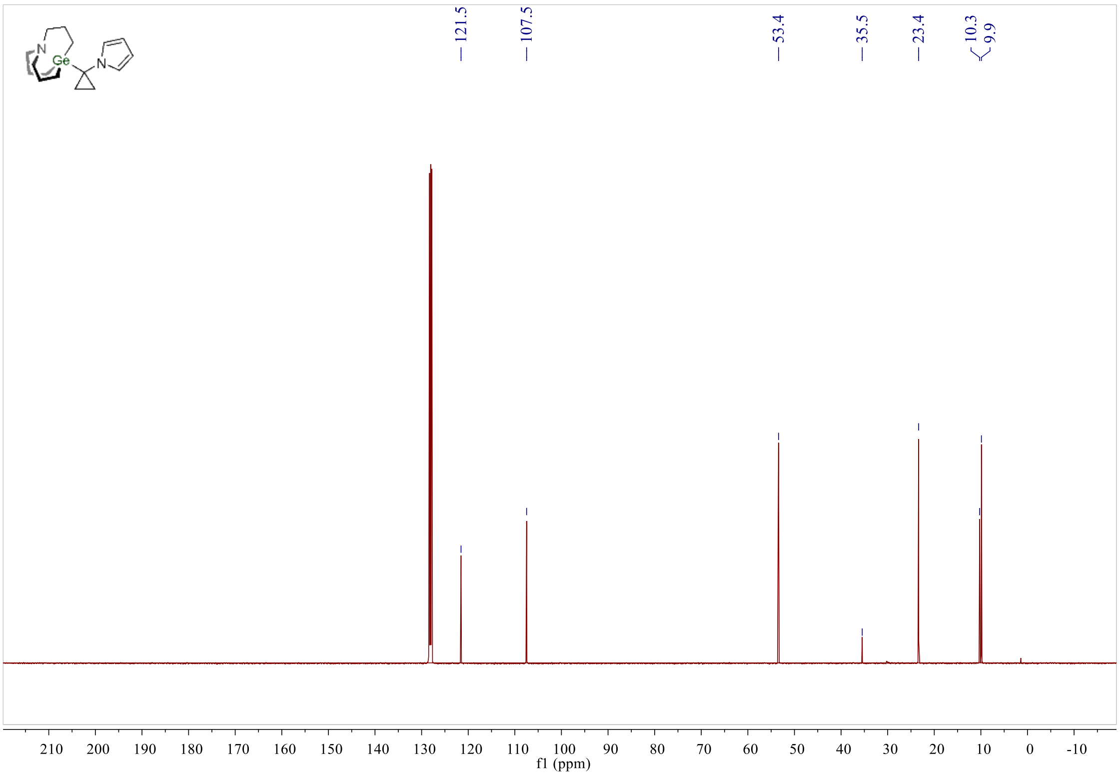

N
Ge
O
1.02
0.97
1.00
6.21
6.18
10.20
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

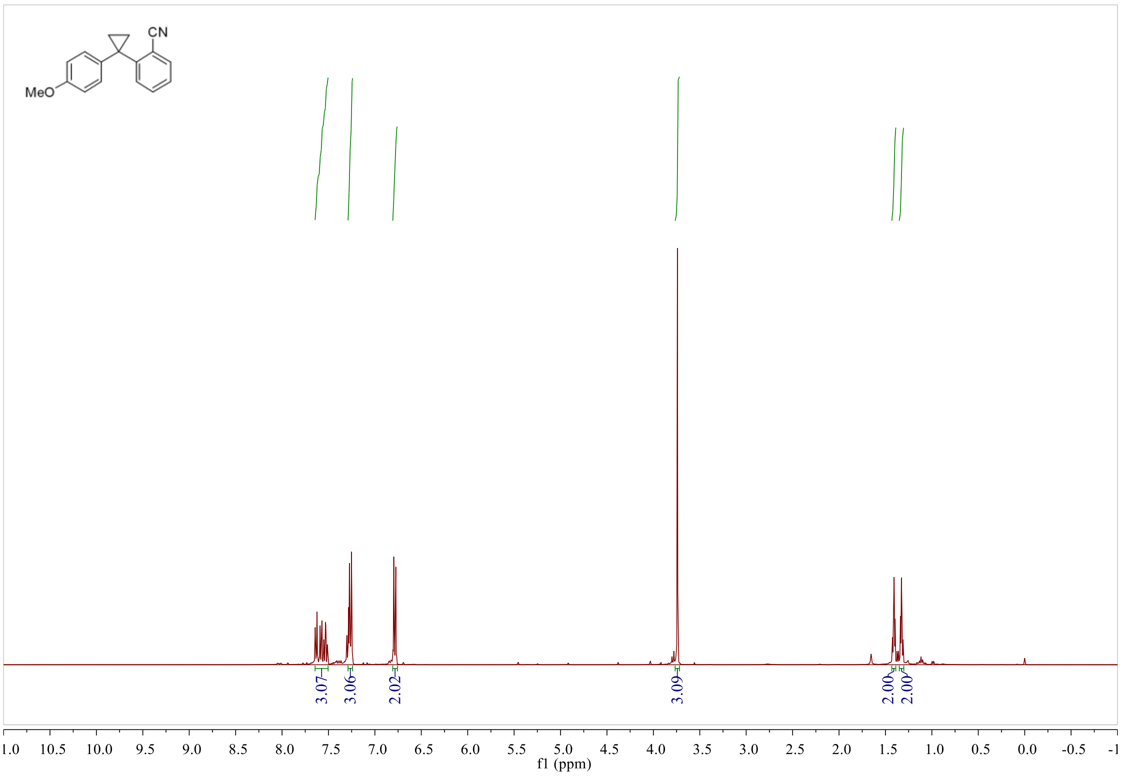

N
Ge
O
142.1
139.6
133.4
112.6
53.8
23.8
10.0
9.3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

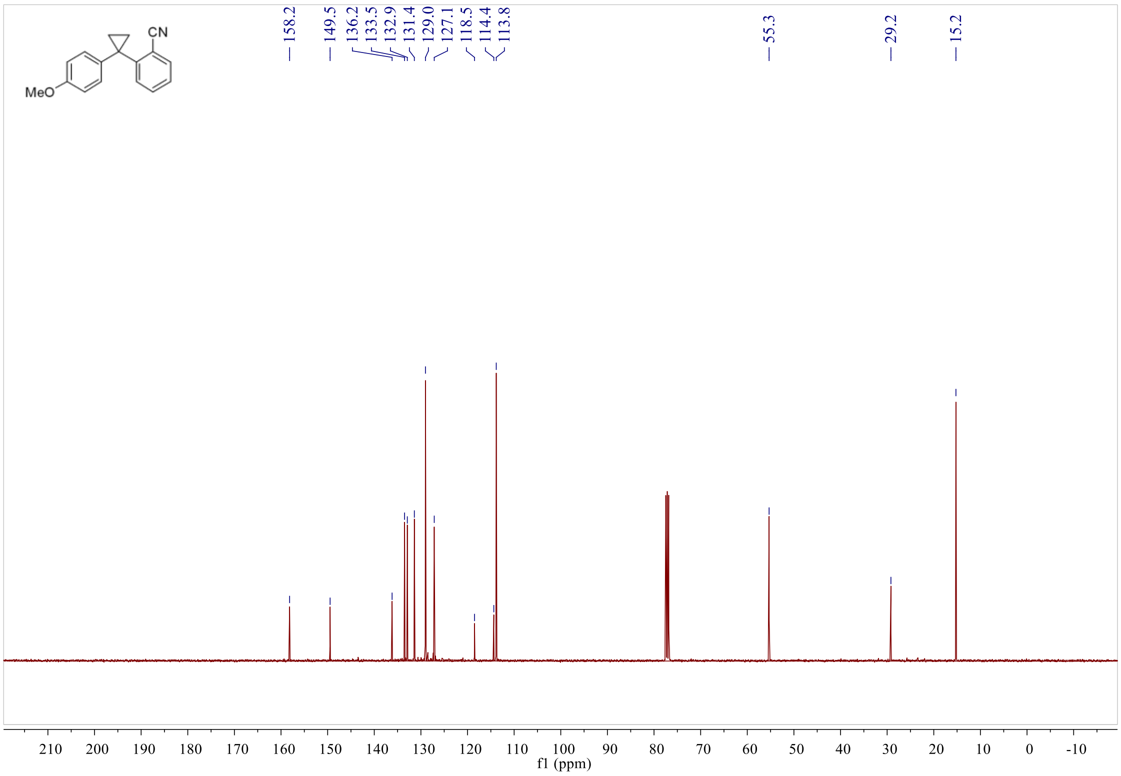

N
Ge
S
3.00
6.12
6.03
2.02
2.04
6.09
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

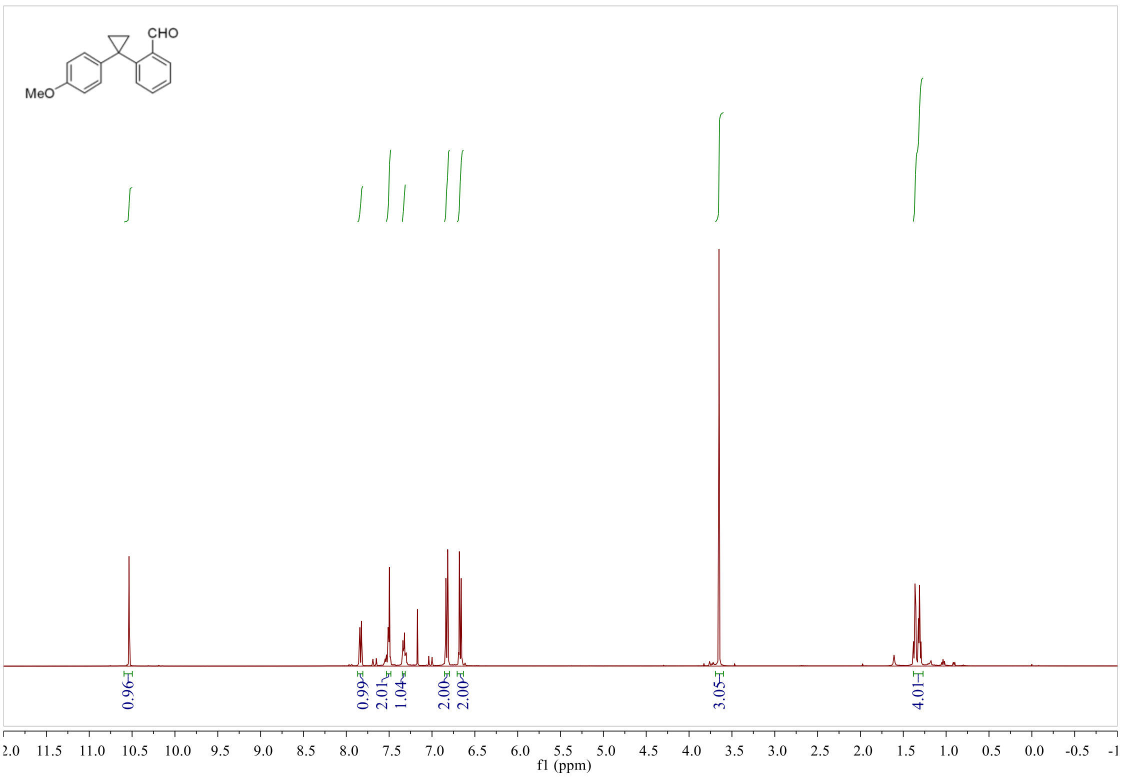

N
Ge
S
155.7
126.5
123.9
121.3
53.7
23.7
15.3
11.7
10.1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

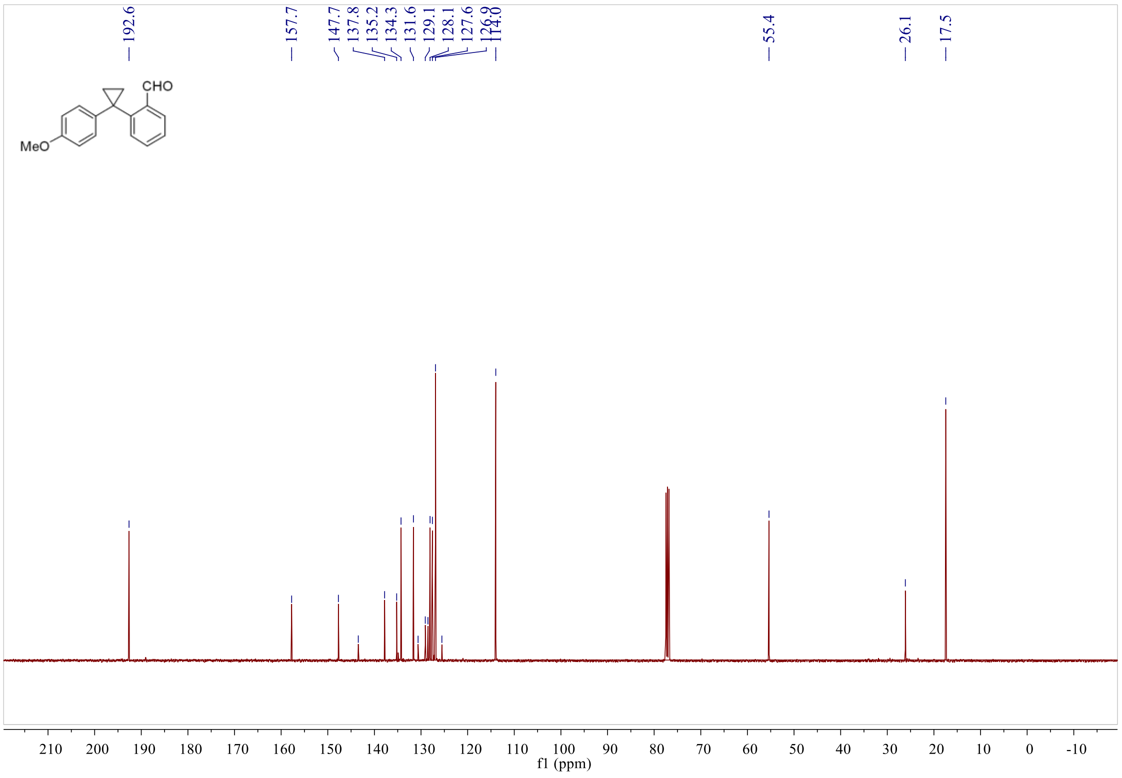

Ge
N
2.00
2.00
6.05
6.02
2.08
8.07
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

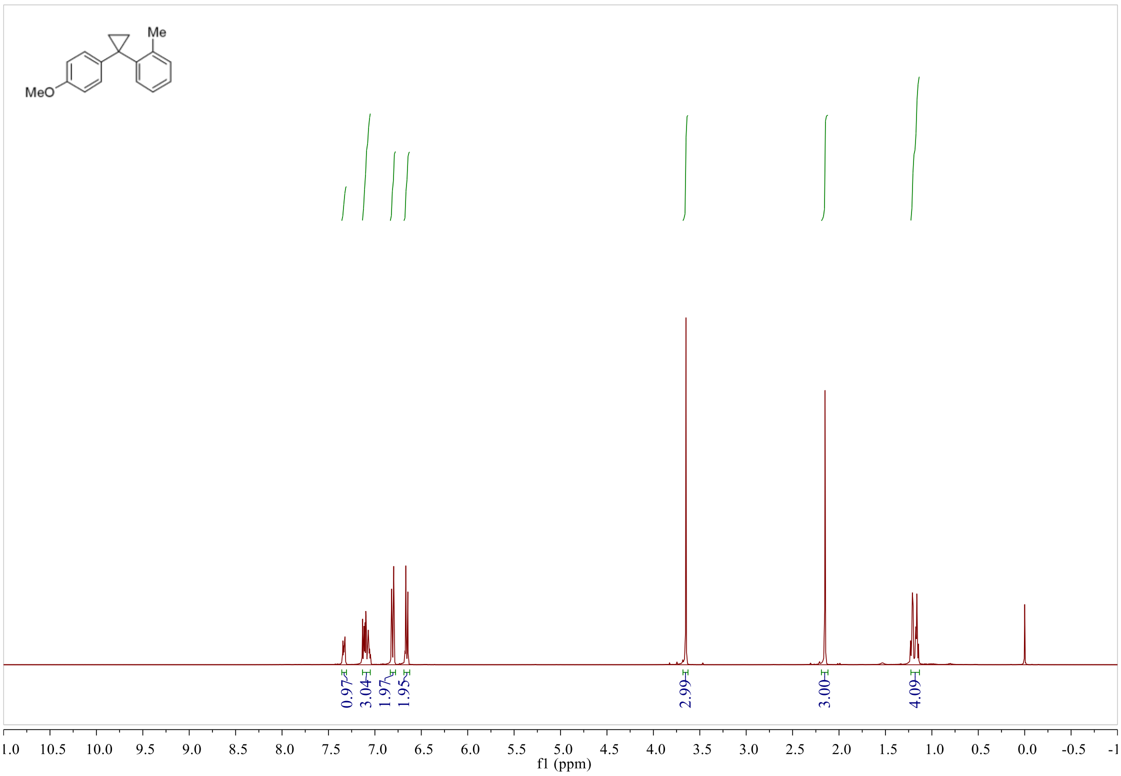

Ge
N
121.5
107.5
53.4
35.5
23.4
10.3
9.9
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

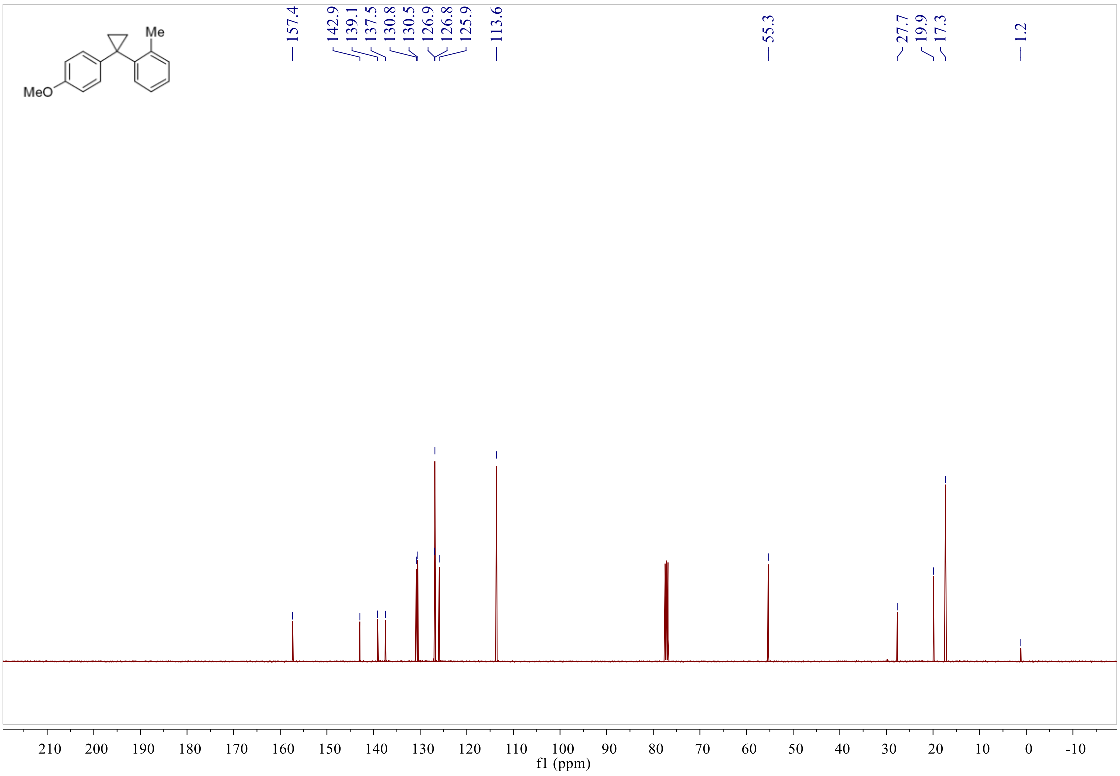

CN
MeO
3.07
3.06
2.02
3.09
2.00
2.00
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

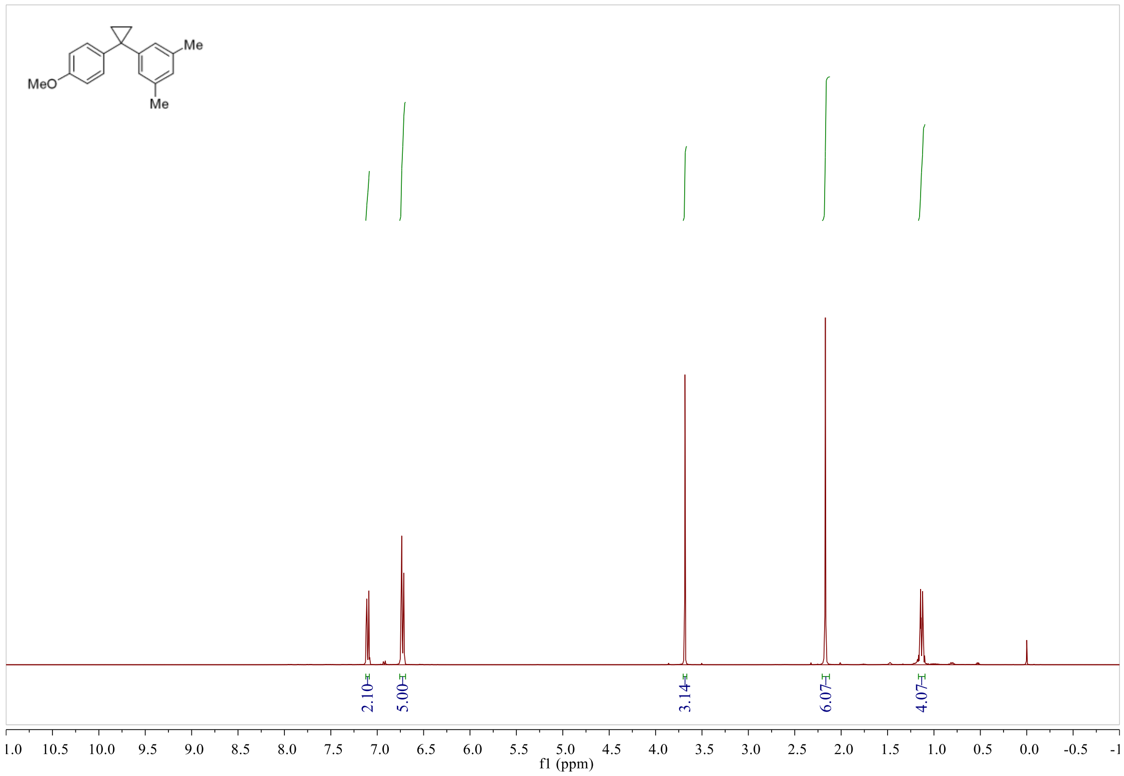

158.2
149.5
136.2
133.5
132.9
131.4
129.0
127.1
118.5
114.4
113.8
55.3
29.2
15.2
CN
MeO
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

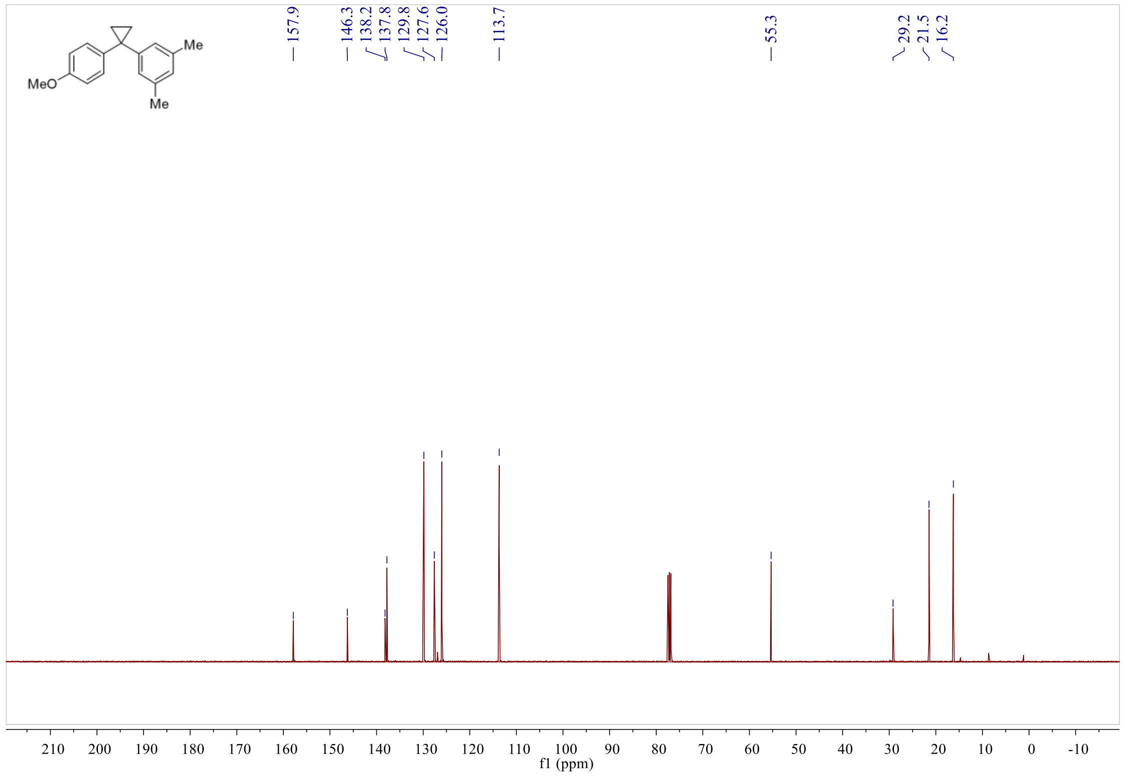

CHO
MeO
0.96
0.99
2.01
1.04
2.00
2.00
3.05
4.01
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

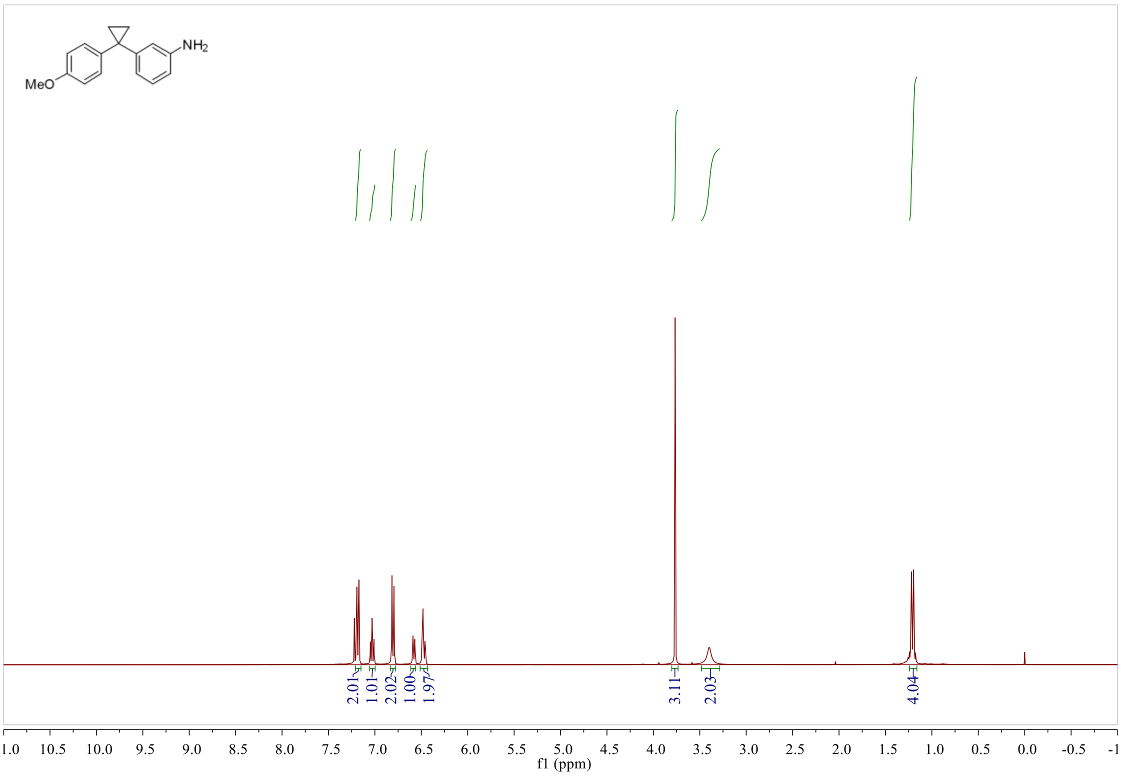

192.6
157.7
147.7
137.8
135.2
134.3
131.6
129.1
128.1
127.6
126.9
114.0
55.4
26.1
17.5
CHO
MeO
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

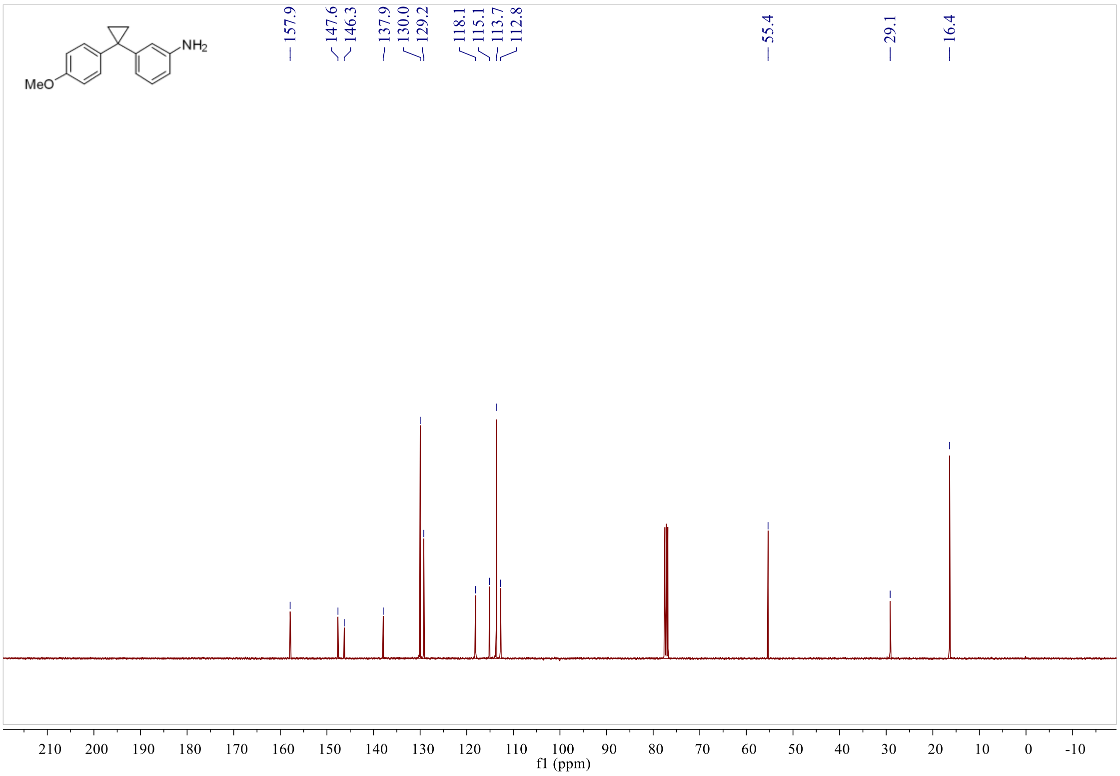

MeO
Me
0.97
3.04
1.97
1.95
2.99
3.00
4.09
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

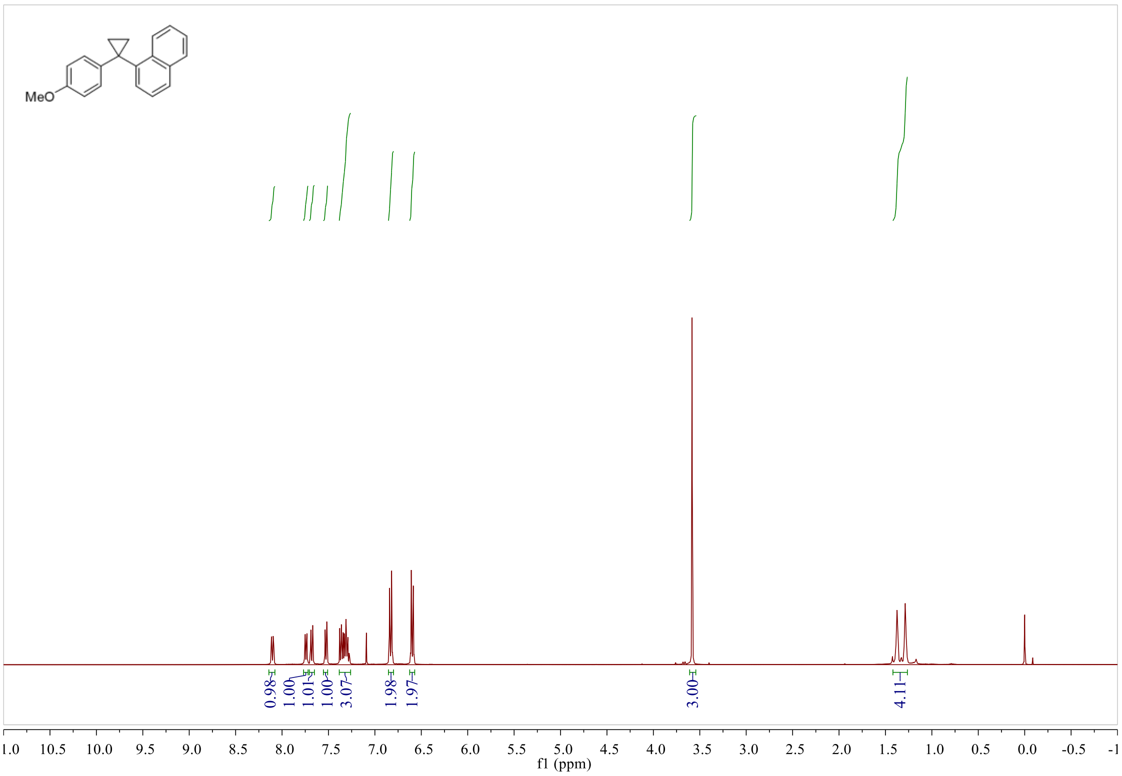

157.4
142.9
139.1
137.5
130.8
130.5
126.9
126.8
125.9
113.6
55.3
27.7
19.9
17.3
1.2
MeO
Me
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

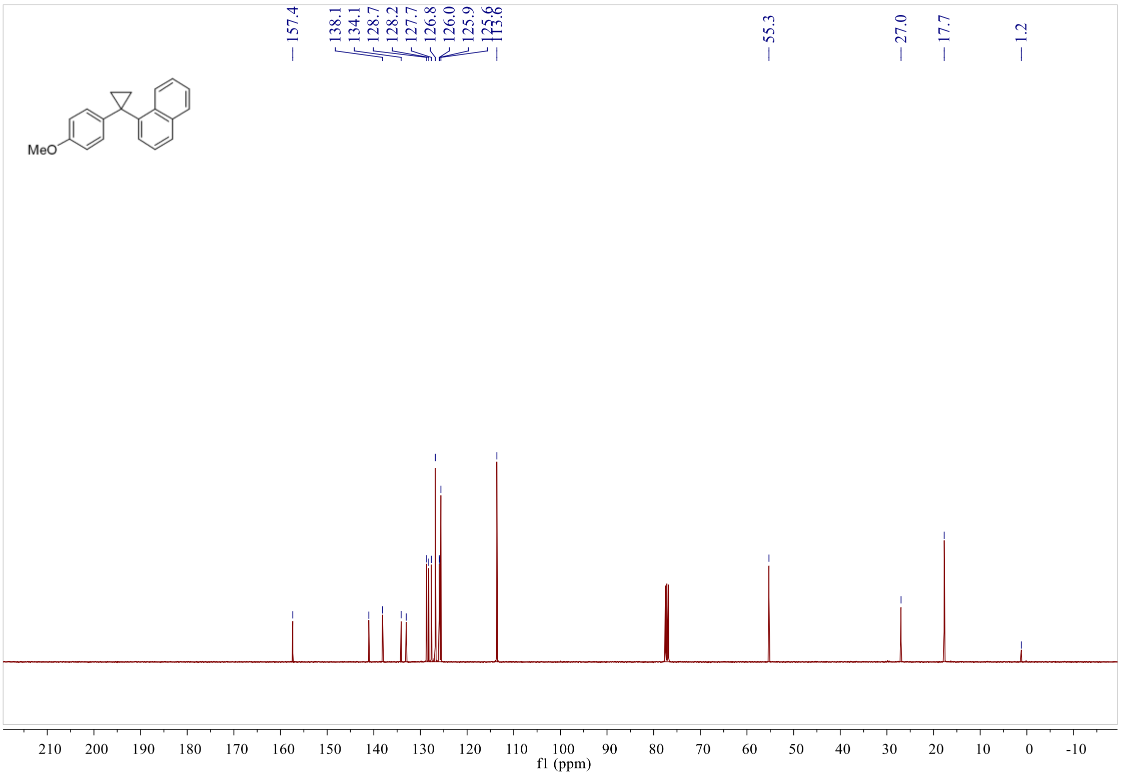

MeO
Me
Me
2.10
5.00
3.14
6.07
4.07
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

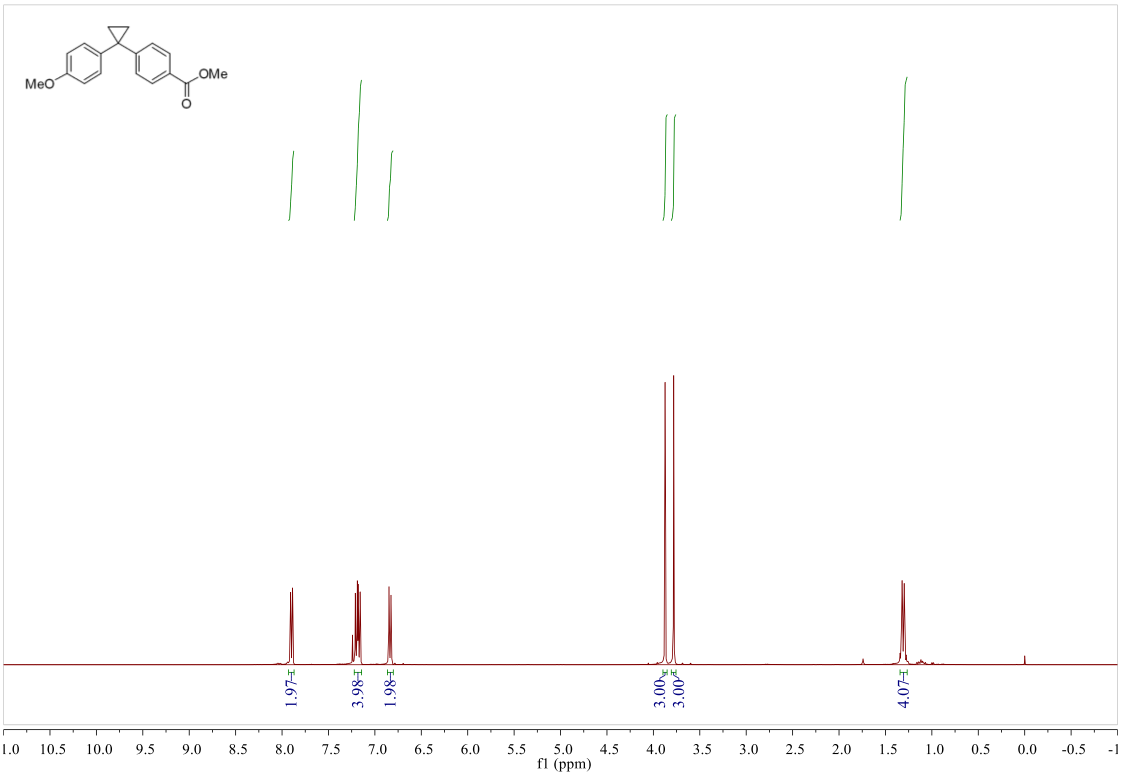

MeO
Me
Me
157.9
146.3
138.2
137.8
129.8
127.6
126.0
113.7
55.3
29.2
21.5
16.2
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

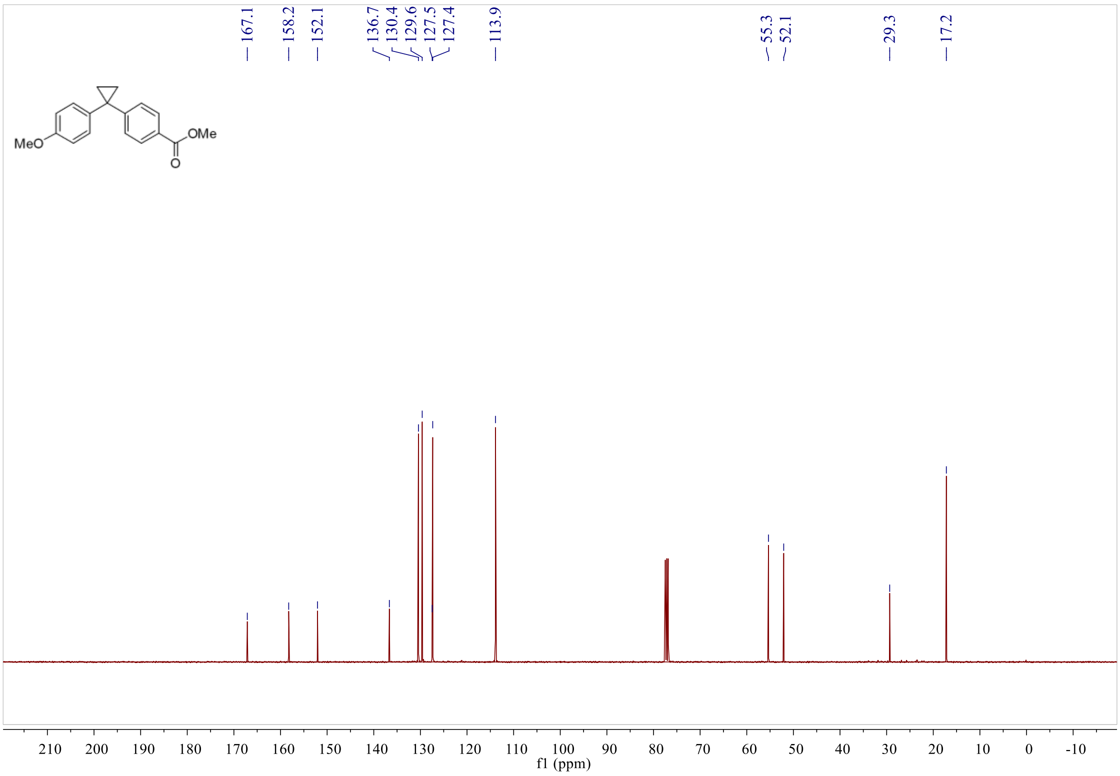

NH2
MeO
2.01
1.01
2.02
1.00
1.97
3.11
2.03
4.04
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

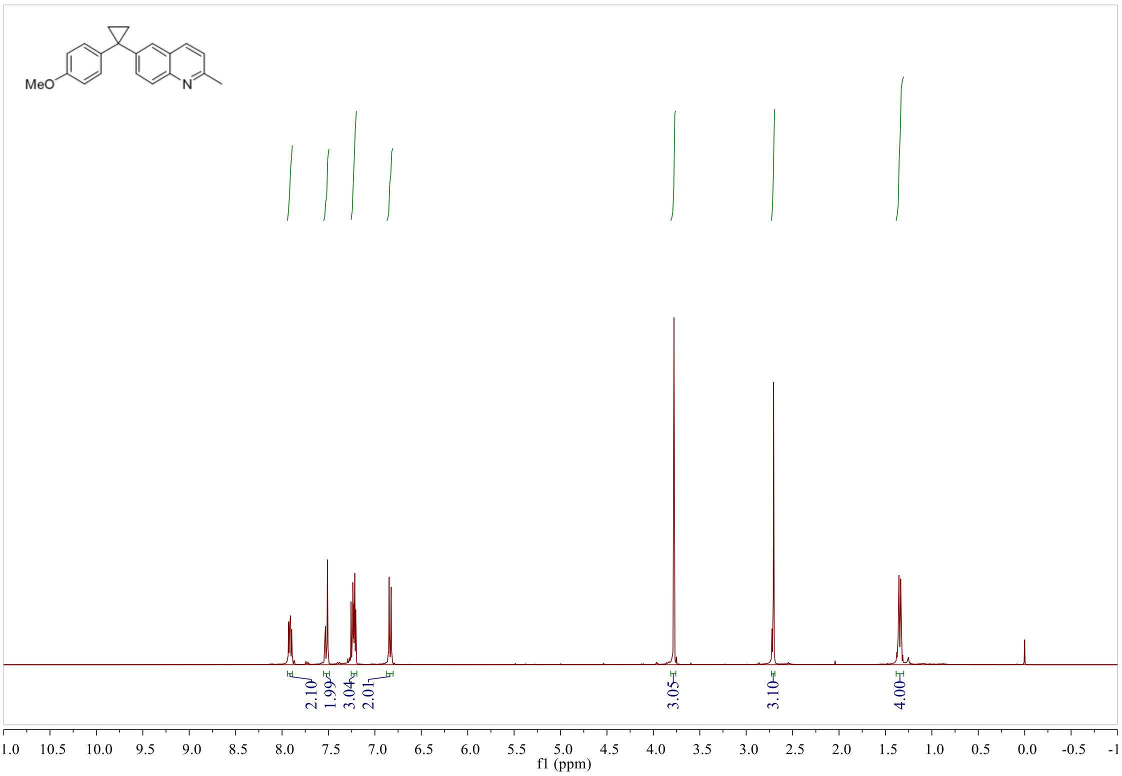

NH2
MeO
157.9
147.6
146.3
137.9
130.0
129.2
118.1
115.1
113.7
112.8
55.4
29.1
16.4
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

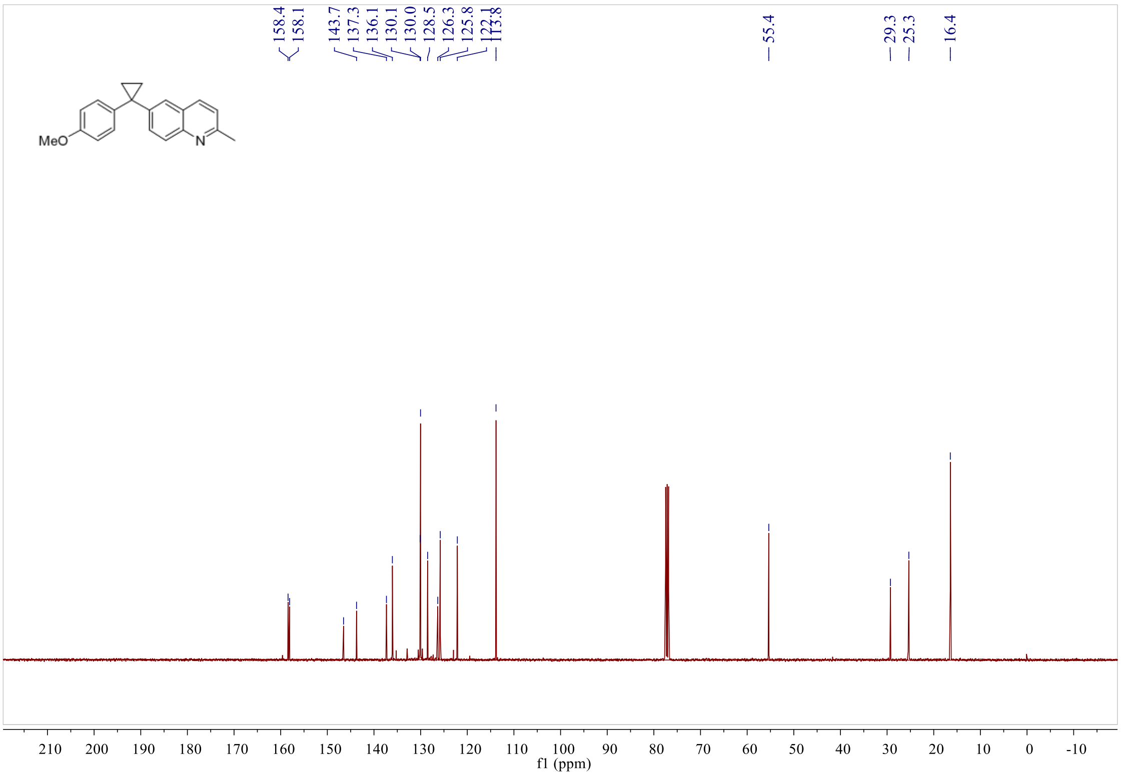

MeO
0.98
1.00
1.01
1.00
3.07
1.98
1.97
3.00
4.11
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

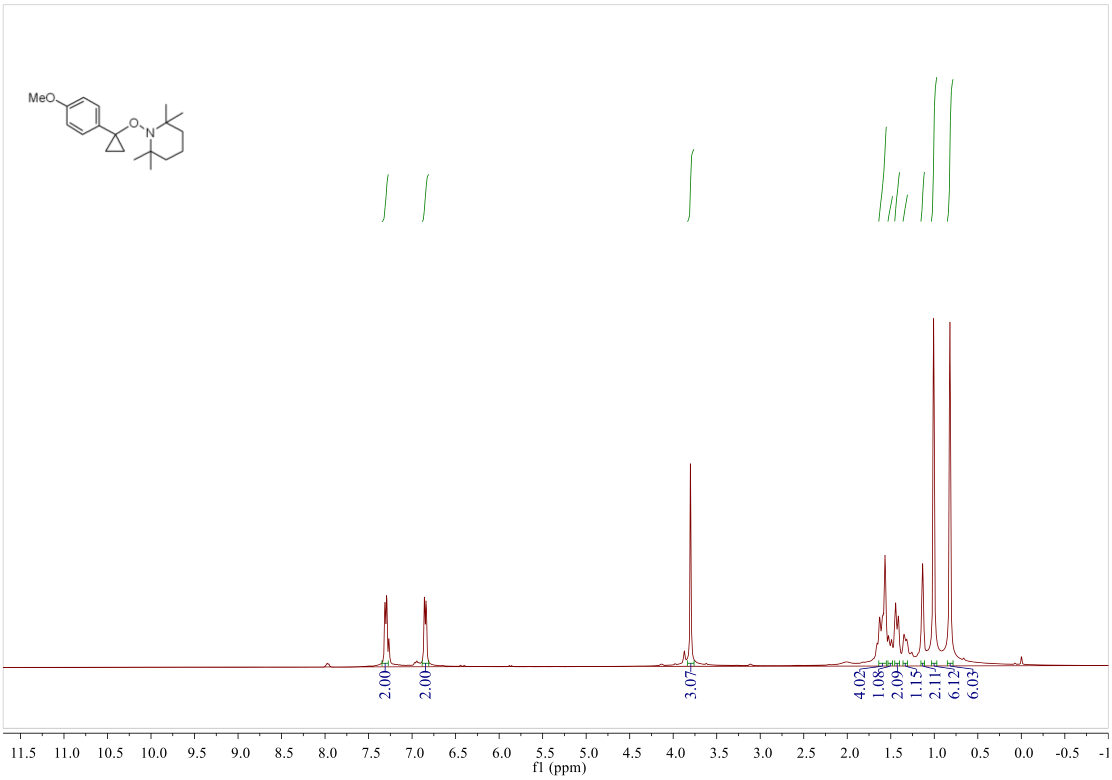

157.4
138.1
134.1
128.7
128.2
127.7
126.8
126.0
125.9
125.6
113.6
55.3
27.0
17.7
1.2
MeO
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

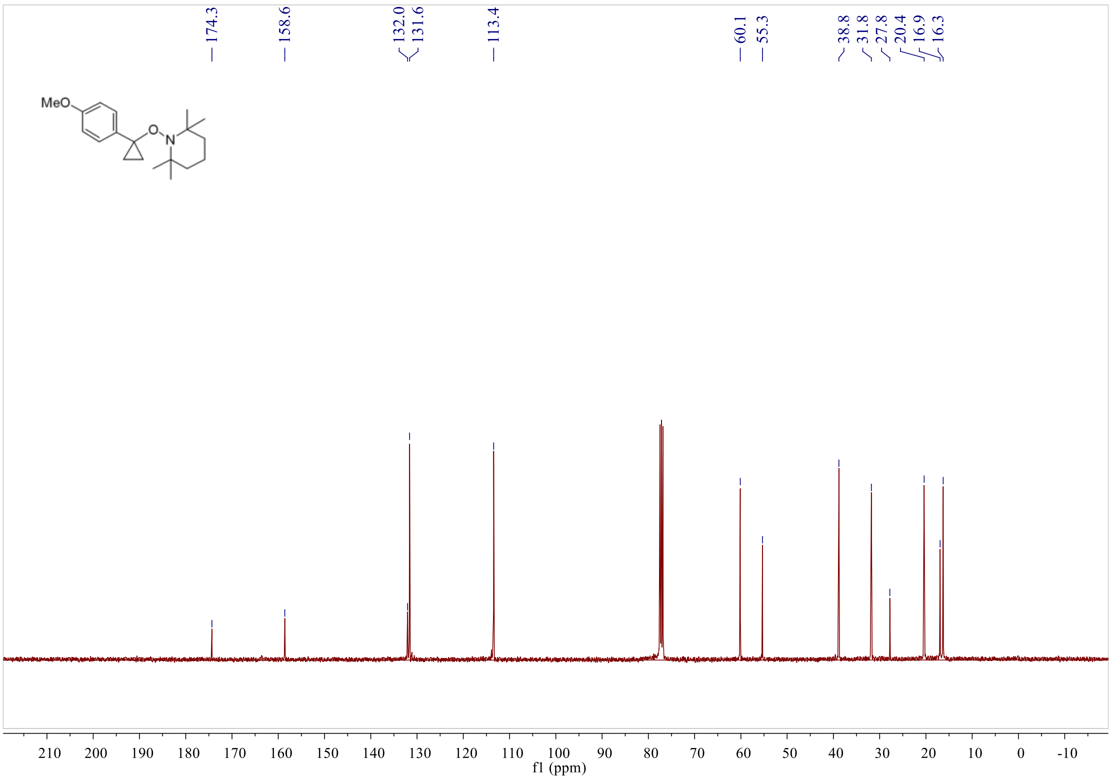

MeO
OMe
O
1.97
3.98
1.98
3.00
3.00
4.07
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

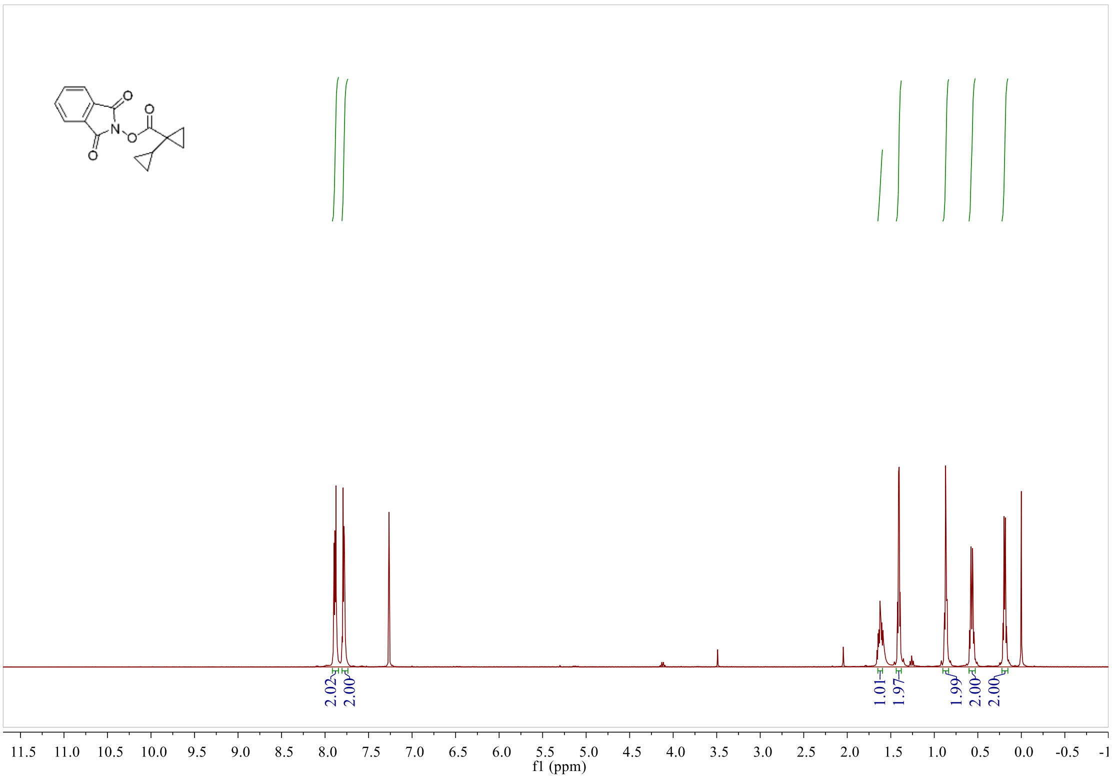

167.1
158.2
152.1
136.7
130.4
129.6
127.5
127.4
113.9
55.3
52.1
29.3
17.2
MeO
OMe
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

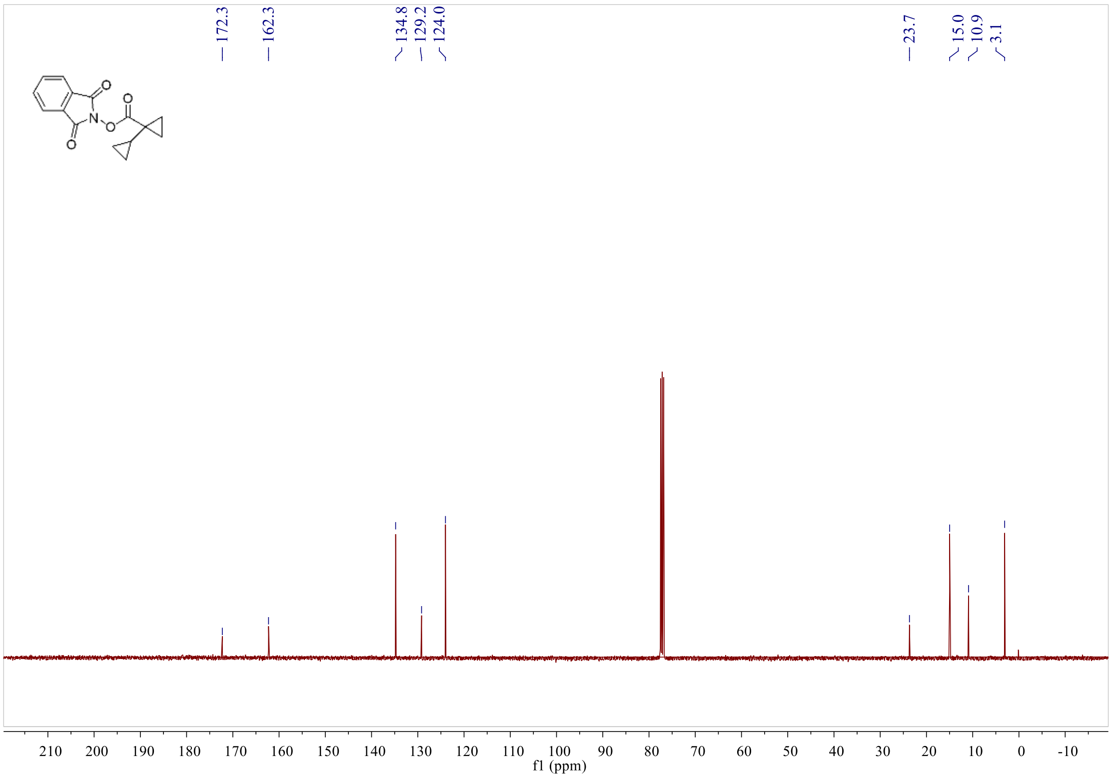

MeO
N
2.10
1.99
3.04
2.01
3.05
3.10
4.00
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

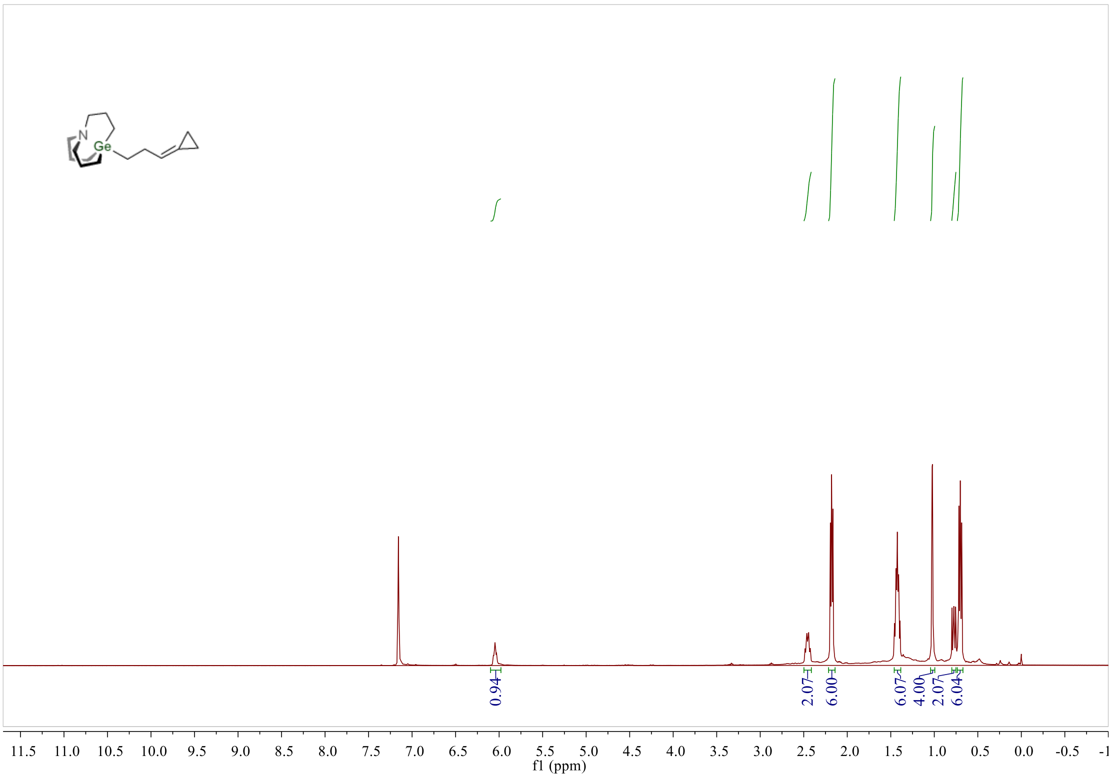

158.4
158.1
143.7
137.3
136.1
130.1
130.0
128.5
126.3
125.8
122.1
113.8
55.4
29.3
25.3
16.4
MeO
N
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


MeO
O
N
2.00
2.00
3.07
4.02
1.08
2.09
1.15
2.11
6.12
6.03
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

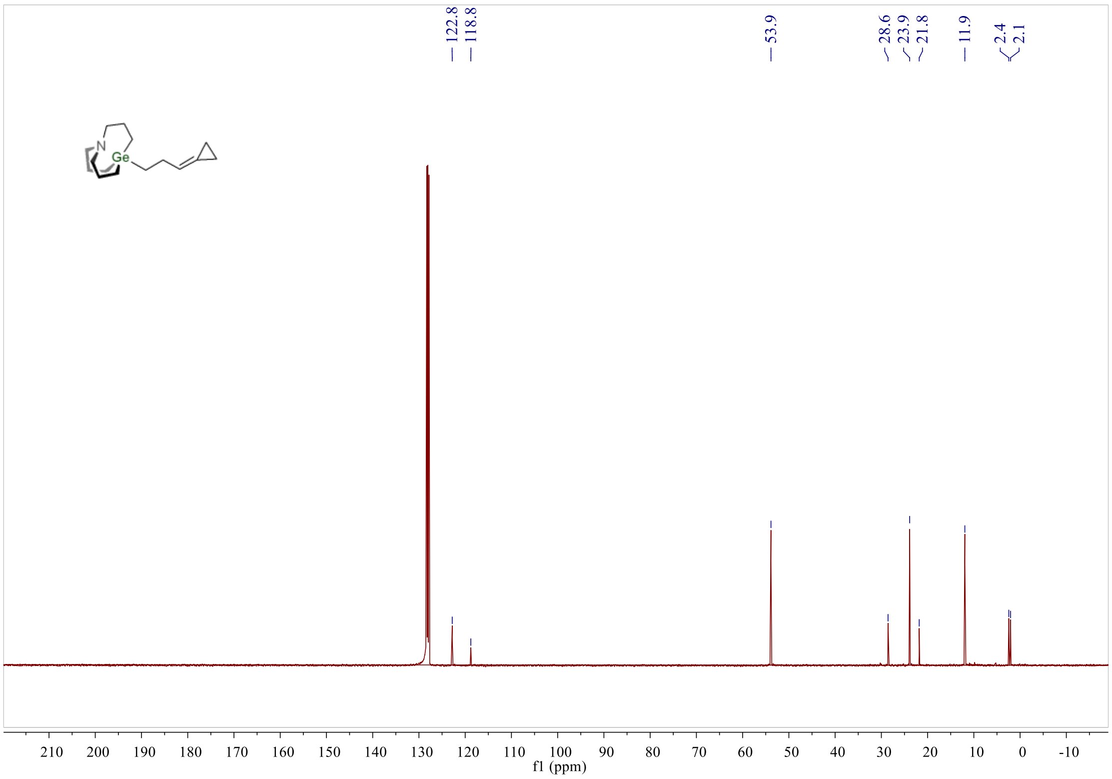

174.3
158.6
132.0
131.6
113.4
60.1
55.3
38.8
31.8
27.8
20.4
16.9
16.3
MeO
O
N
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


2.02
2.00
1.01
1.97
1.99
2.00
2.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

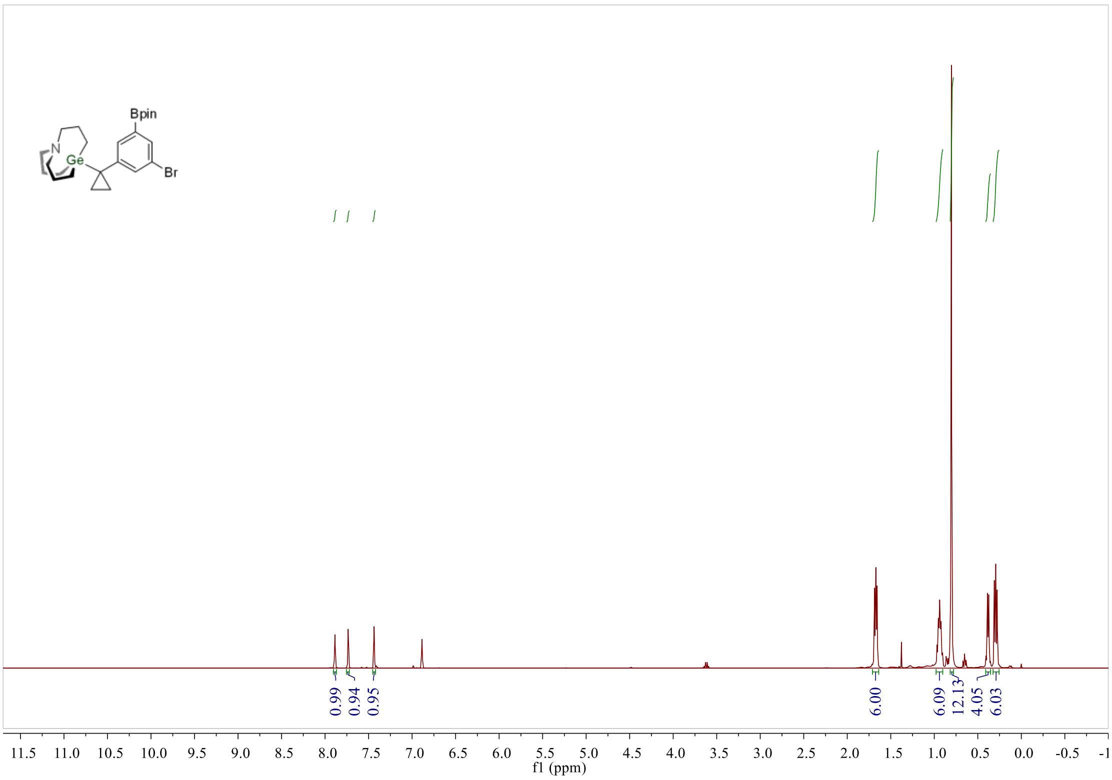

172.3
162.3
134.8
129.2
124.0
23.7
15.0
10.9
3.1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

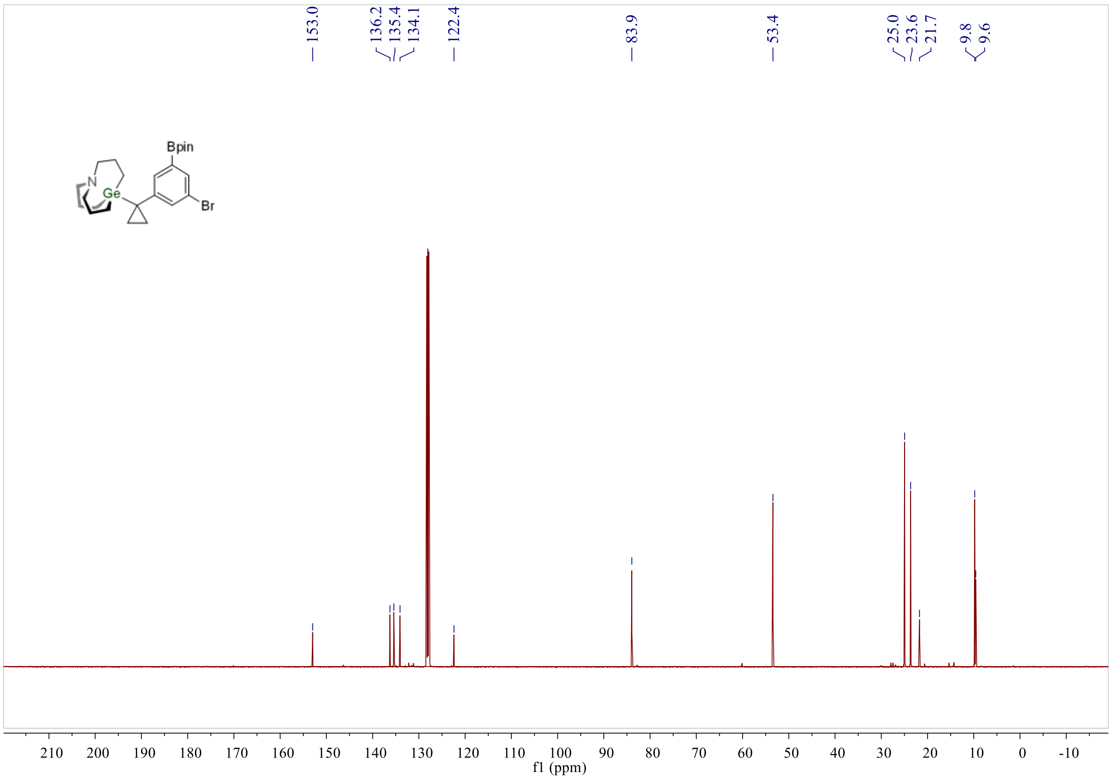


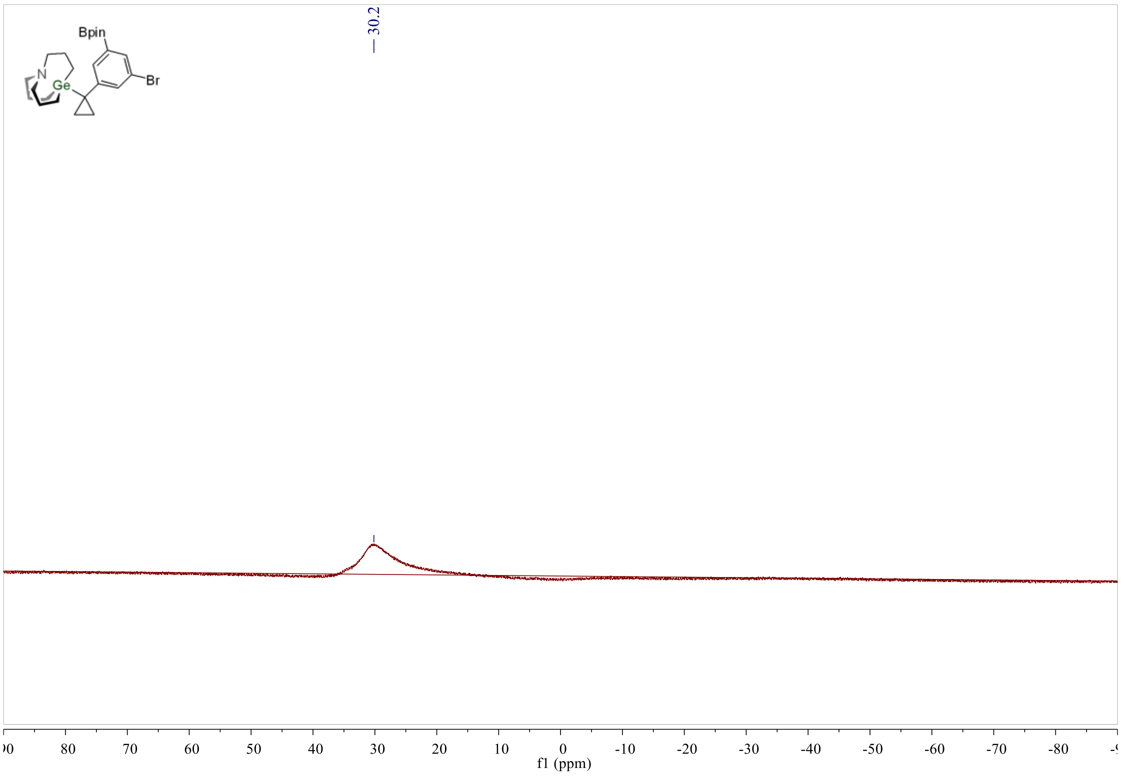
N
Ge
0.94
2.07
6.00
6.07
4.00
2.07
6.04
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

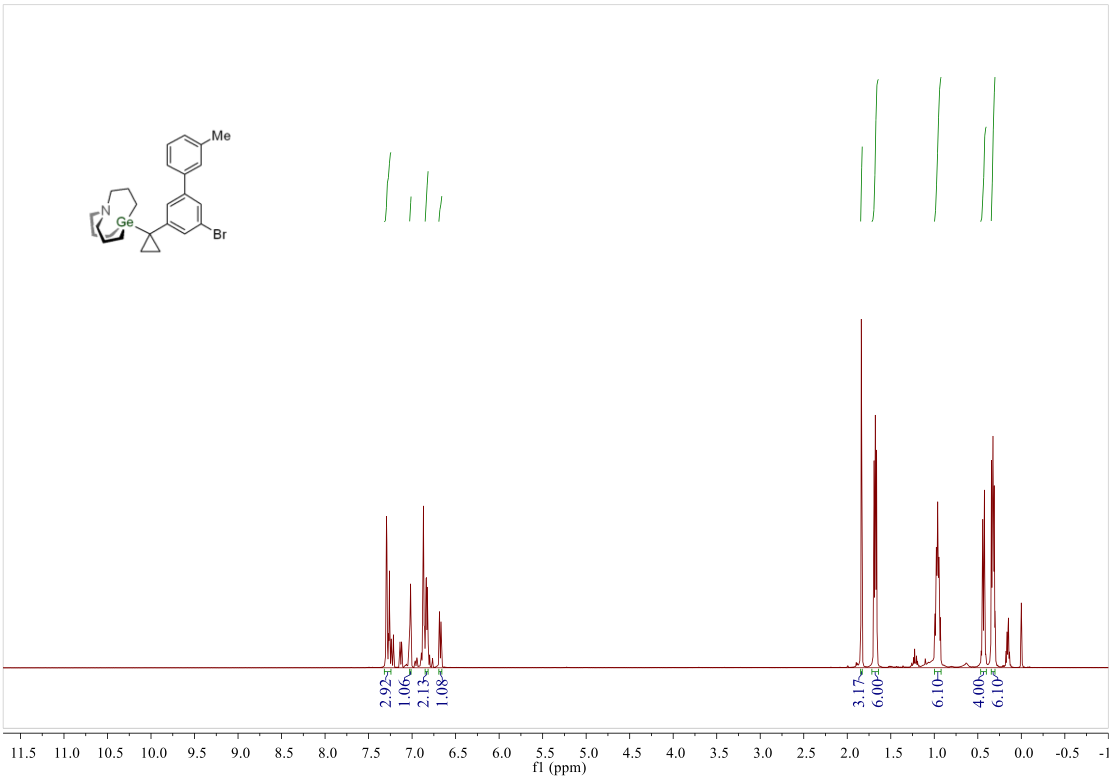


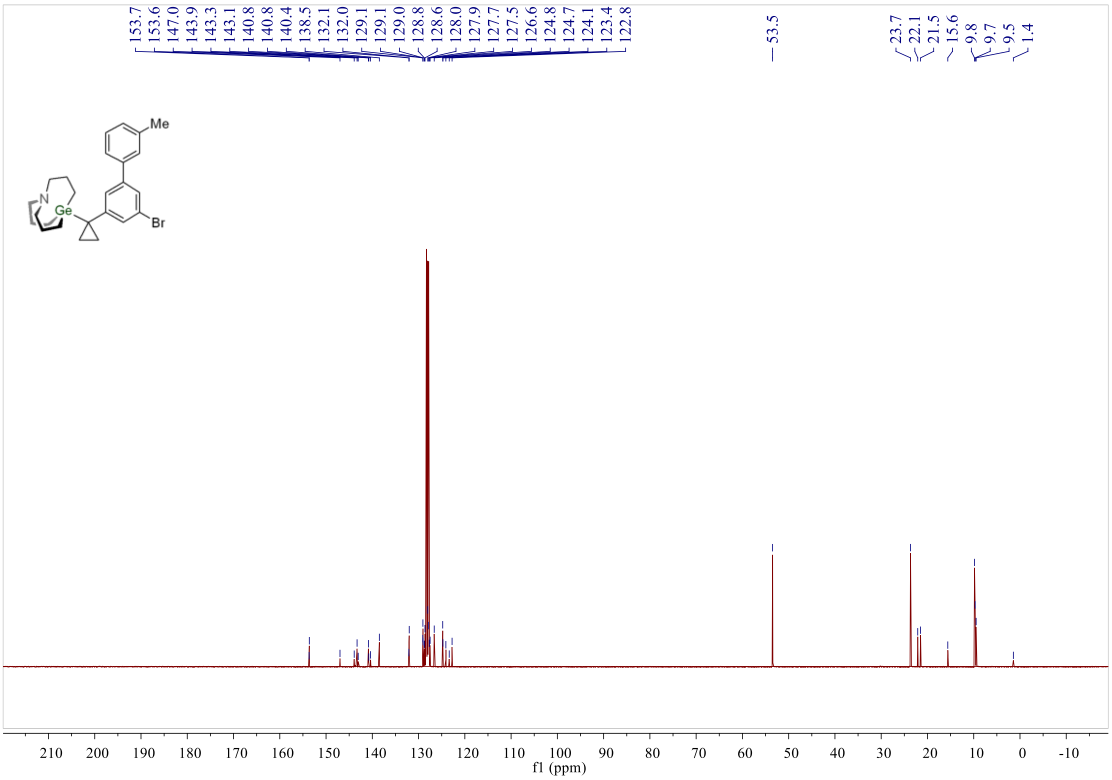
122.8
118.8
53.9
28.6
23.9
21.8
11.9
2.4
2.1
N
Ge
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

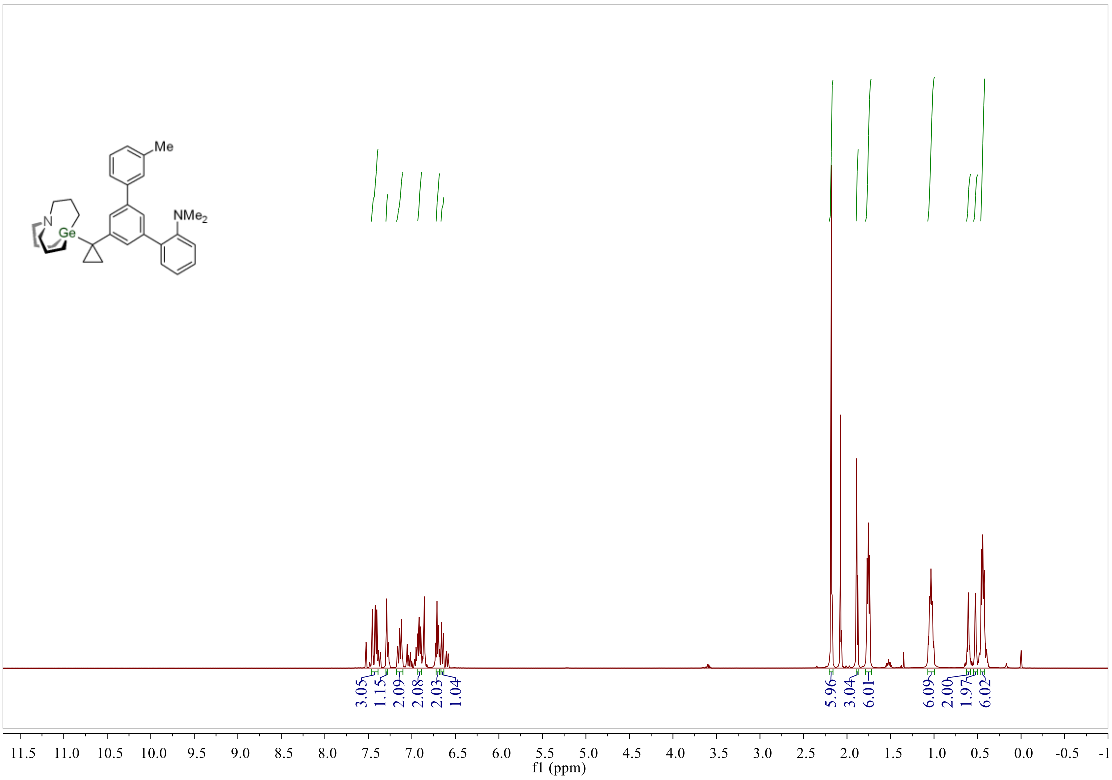

Bpin
N
Ge
Br
0.99
0.94
0.95
6.00
6.09
12.13
4.05
6.03
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

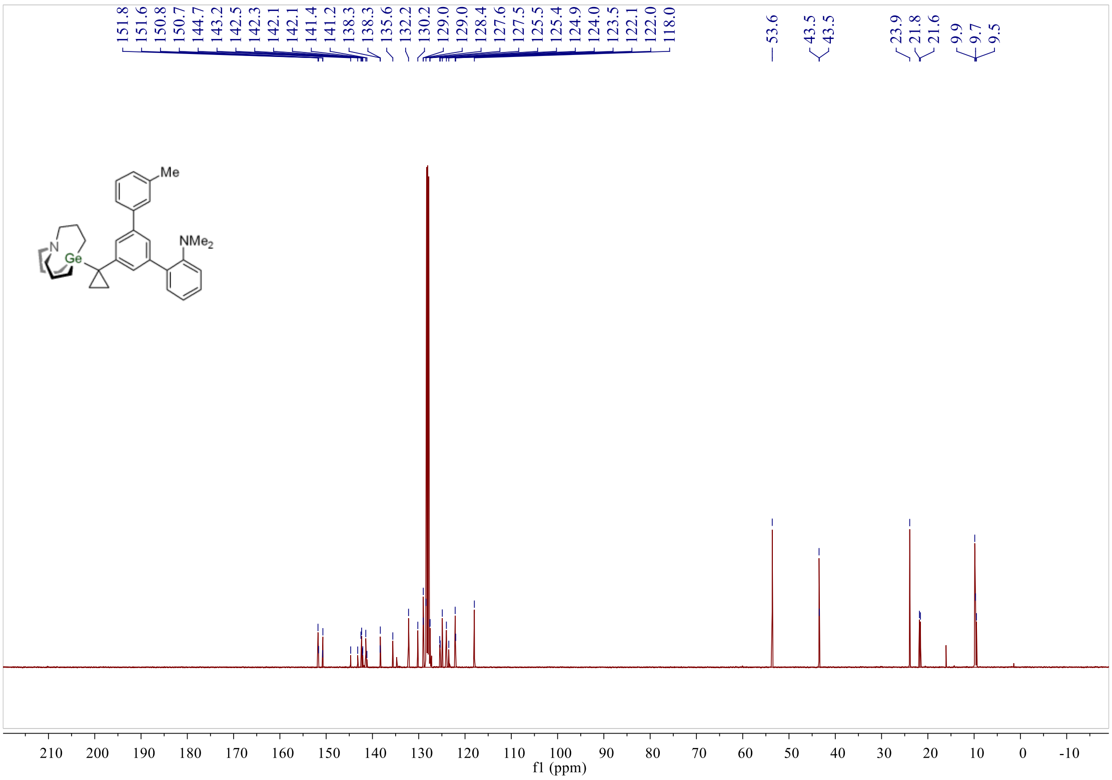

153.0
136.2
135.4
134.1
122.4
83.9
53.4
25.0
23.6
21.7
9.8
9.6
Bpin
N
Ge
Br
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

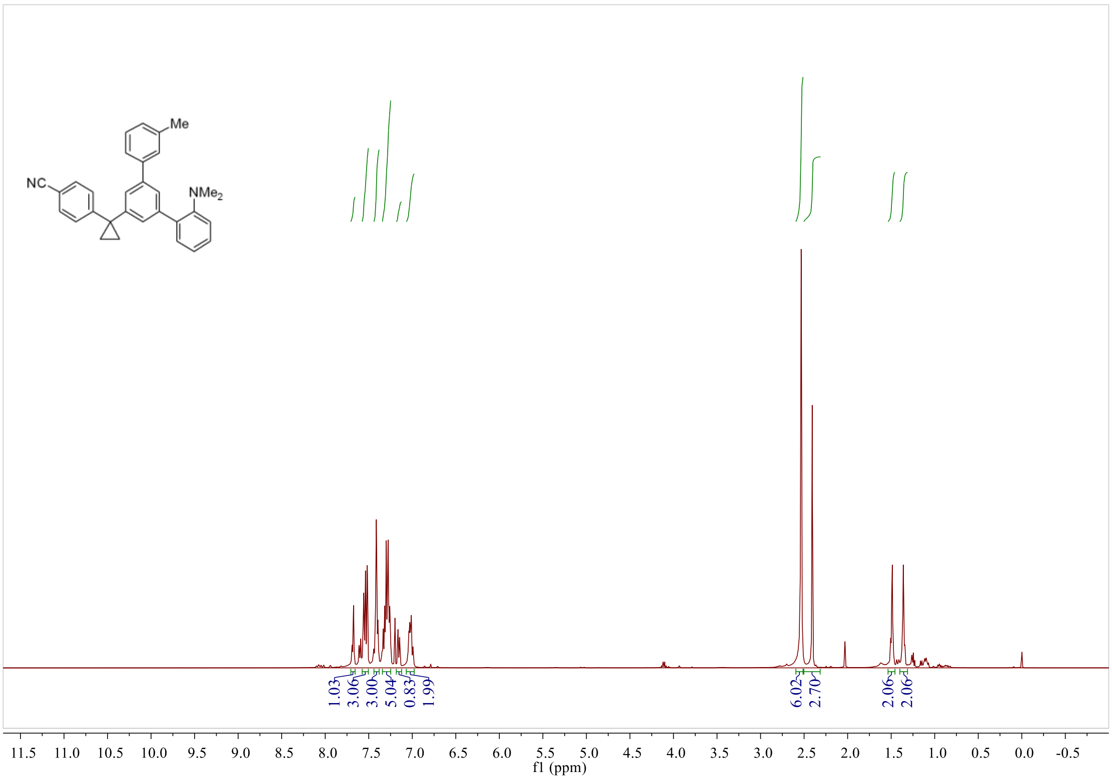

Bpin
N
Ge
Br
30.2
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

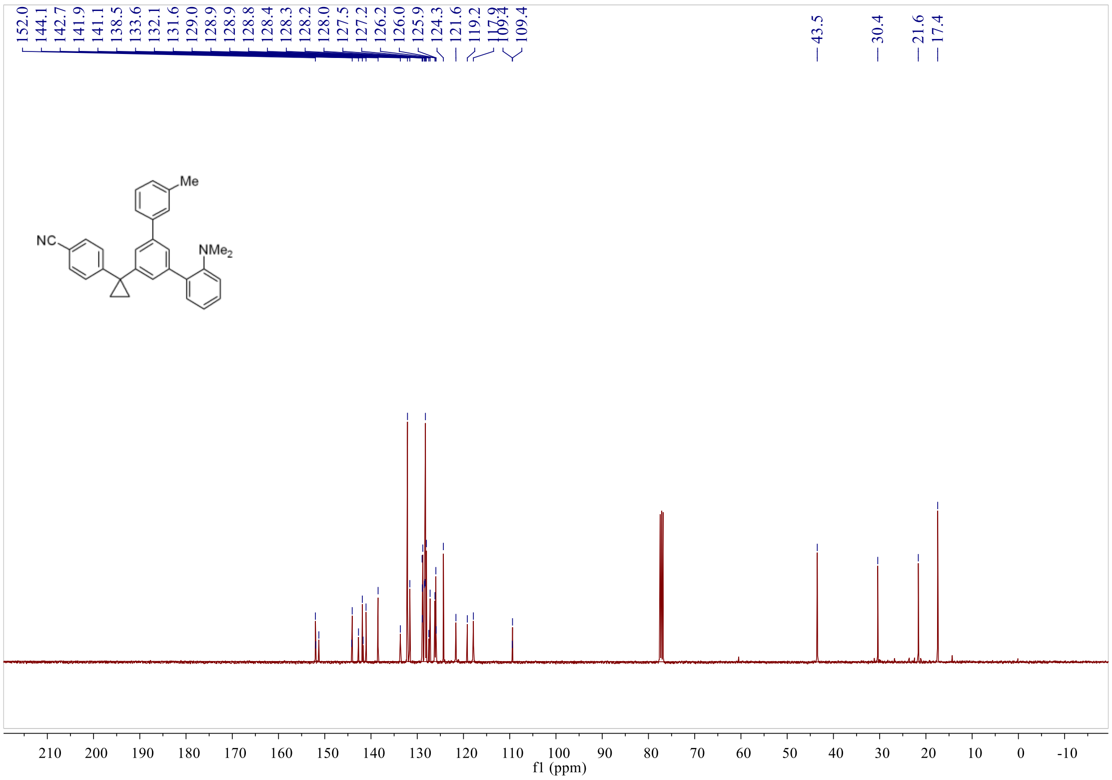

Me
N
Ge
Br
2.92
1.06
2.13
1.08
3.17
6.00
6.10
4.00
6.10
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

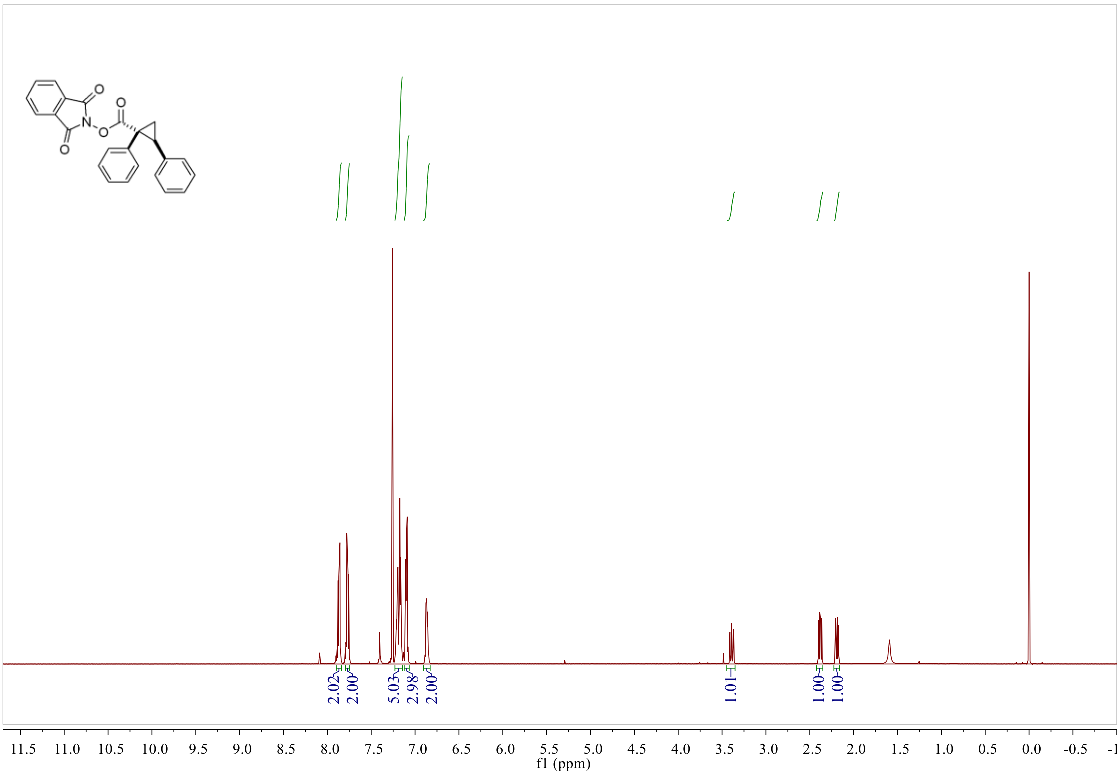

153.7
153.6
147.0
143.9
143.3
143.1
140.8
140.8
140.4
138.5
132.1
132.0
129.1
129.1
129.0
128.8
128.6
128.0
127.9
127.7
127.5
126.6
124.8
124.7
124.1
123.4
122.8
53.5
23.7
22.1
21.5
15.6
9.8
9.7
9.5
1.4
Me
N
Ge
Br
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

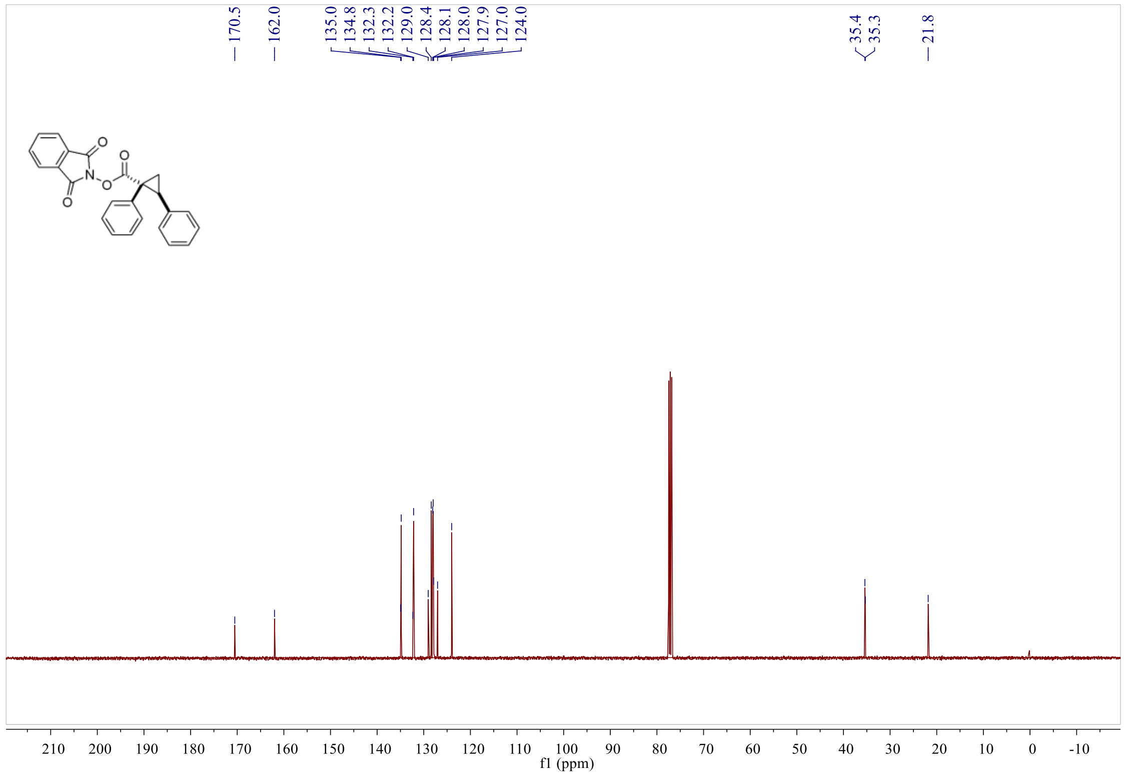

Me
N
Ge
NMe$_2$
3.05
1.15
2.09
2.08
2.03
1.04
5.96
3.04
6.01
6.09
2.00
1.97
6.02
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

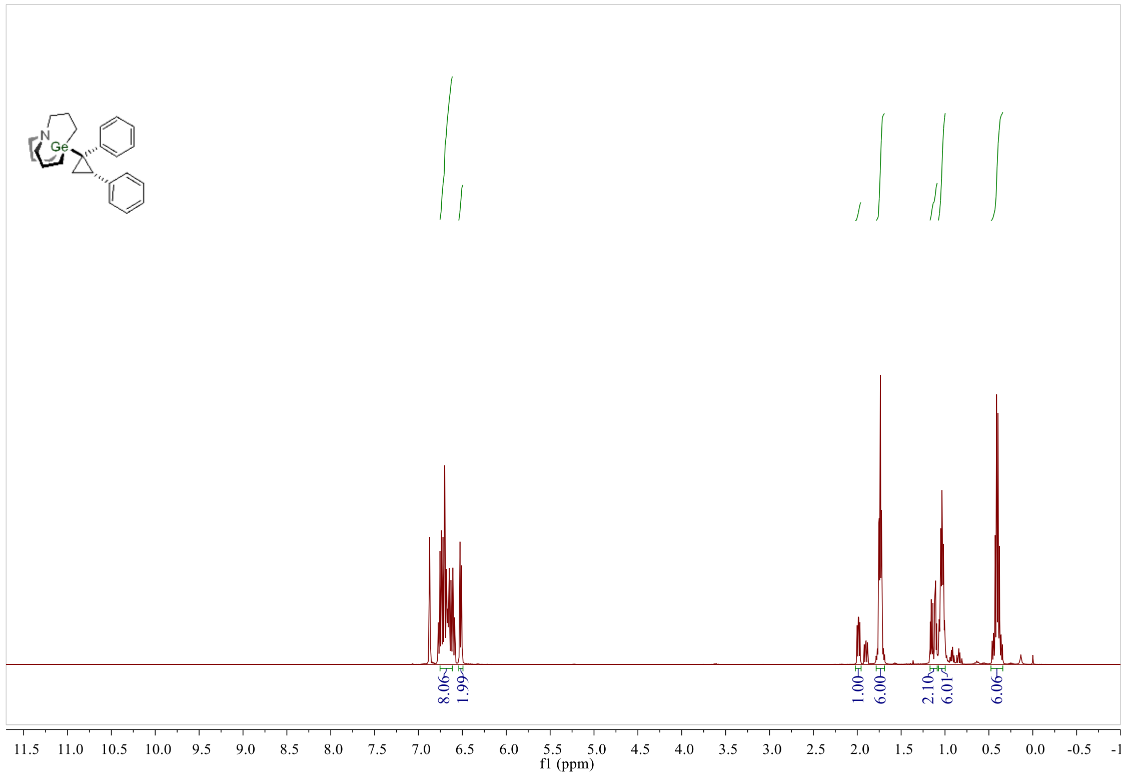

151.8
151.6
150.8
150.7
144.7
143.2
142.5
142.3
142.1
142.1
141.4
141.2
138.3
138.3
135.6
132.2
130.2
129.0
129.0
128.4
127.6
127.5
125.5
125.4
124.9
124.0
123.5
122.1
122.0
118.0
53.6
43.5
43.5
23.9
21.8
21.6
9.9
9.7
9.5
Me
NMe2
N
Ge
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

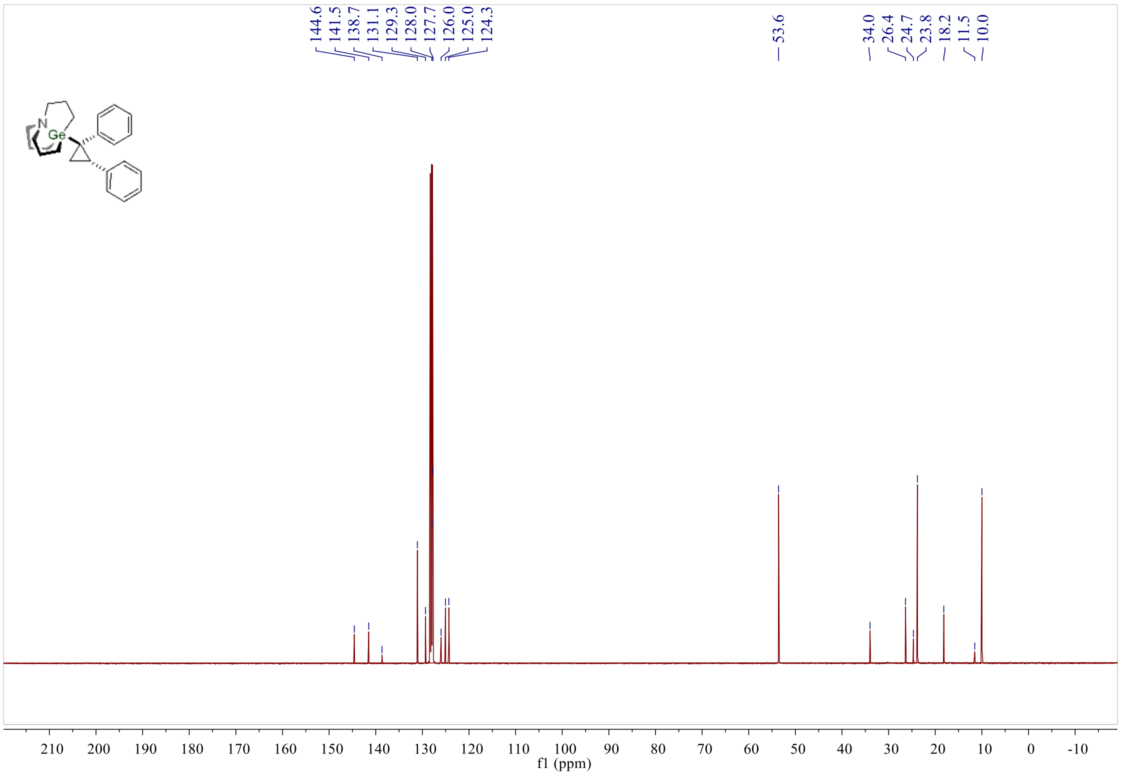

Me
NC
NMe2
1.03
3.06
3.00
5.04
0.83
1.99
6.02
2.70
2.06
2.06
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

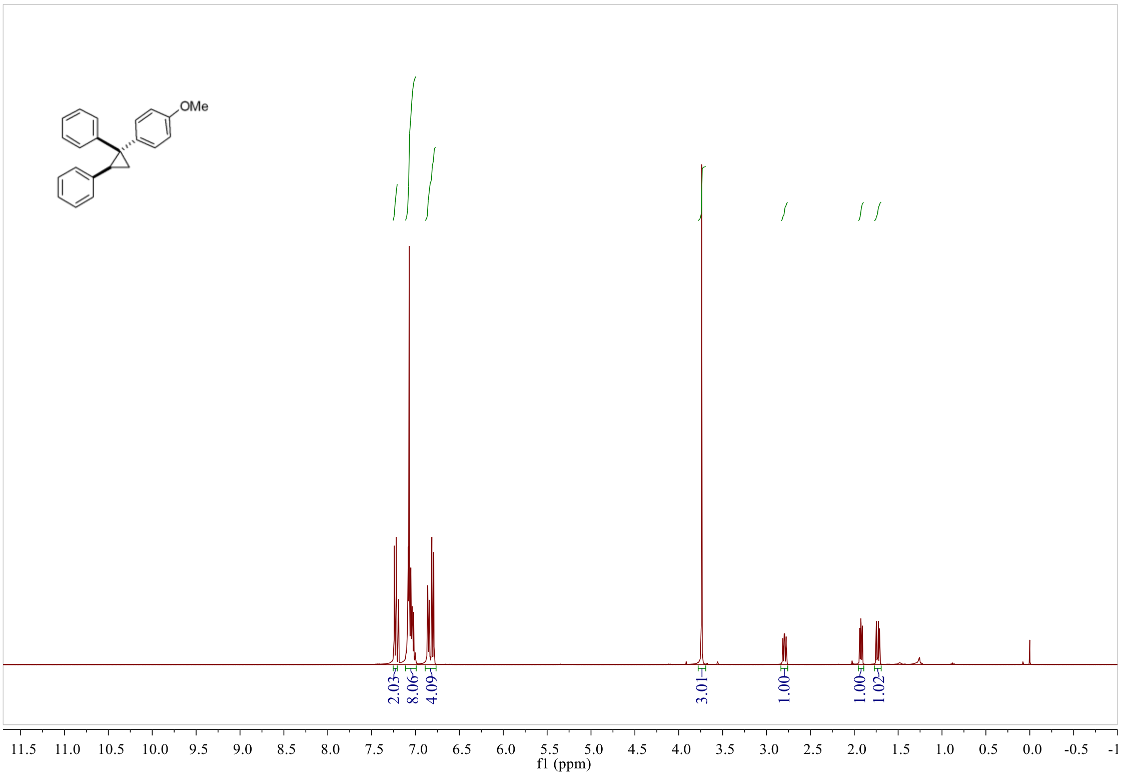

152.0
144.1
142.7
141.9
141.1
138.5
133.6
132.1
131.6
129.0
128.9
128.9
128.8
128.4
128.3
128.2
128.0
127.5
127.2
126.2
126.0
125.9
124.3
121.6
119.2
117.9
109.4
109.4
43.5
30.4
21.6
17.4
Me
NC
NMe$_2$
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

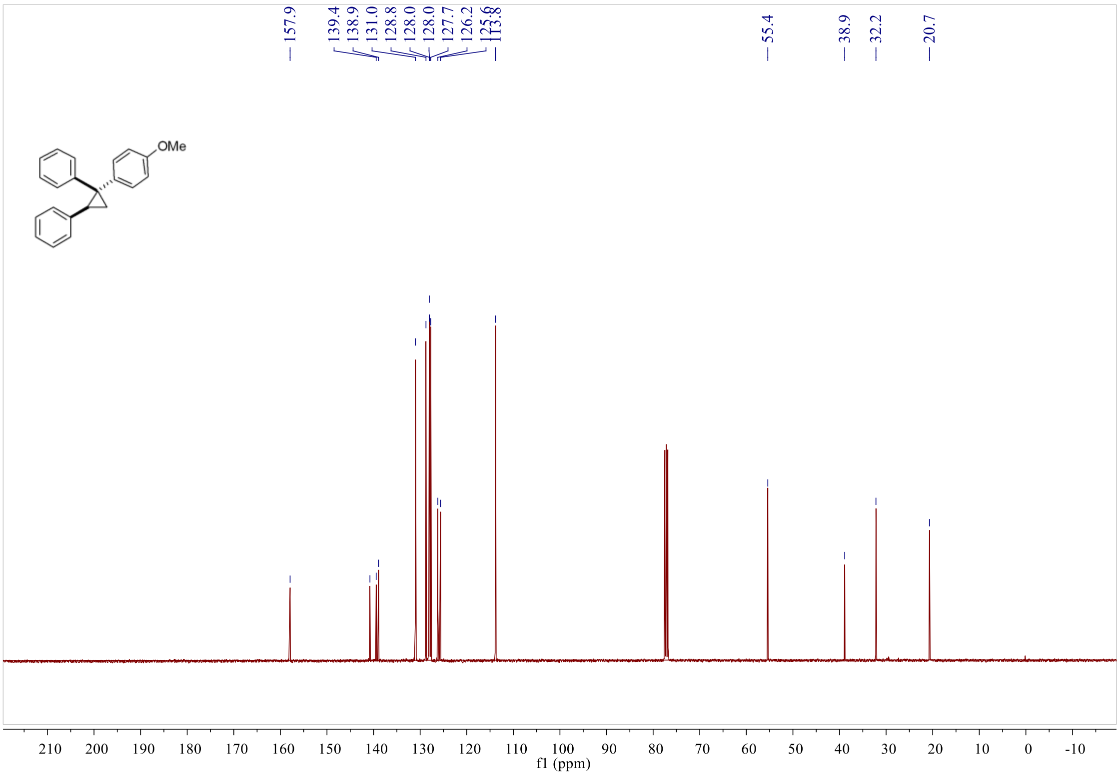

O
N
O
O
O
2.02
2.00
5.03
2.98
2.00
1.01
1.00
1.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

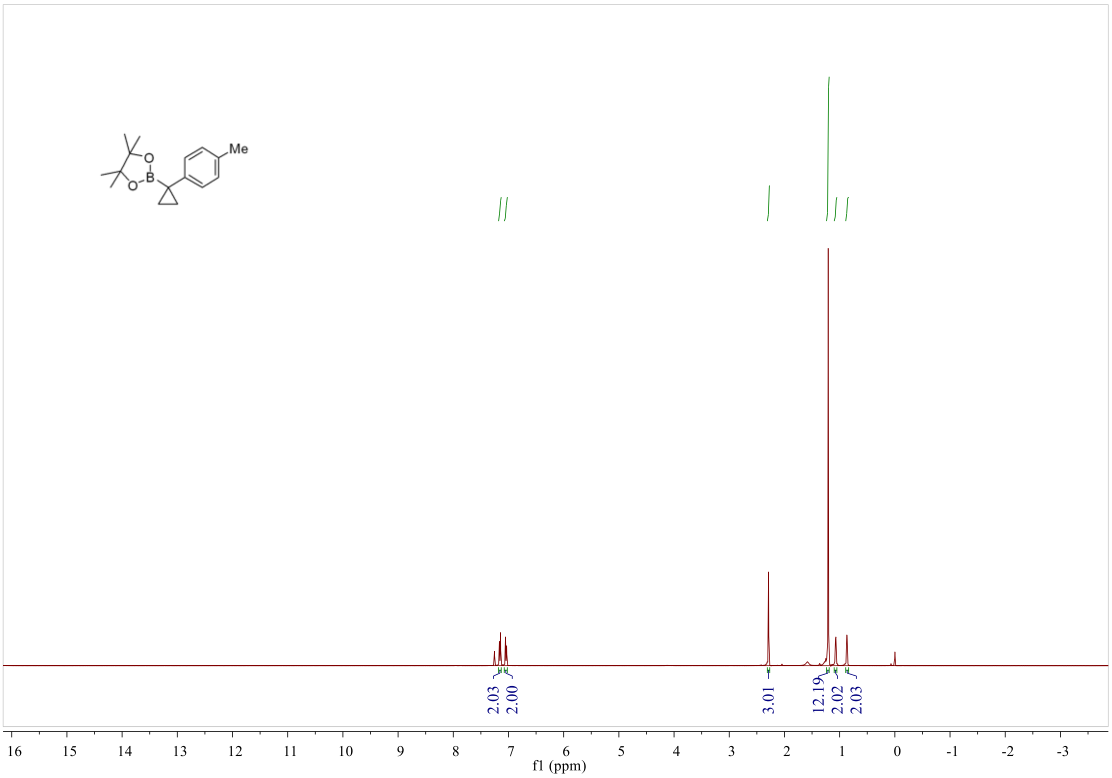

170.5
162.0
135.0
134.8
132.3
132.2
129.0
128.4
128.1
128.0
127.9
127.0
124.0
35.4
35.3
21.8
O
N
O
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

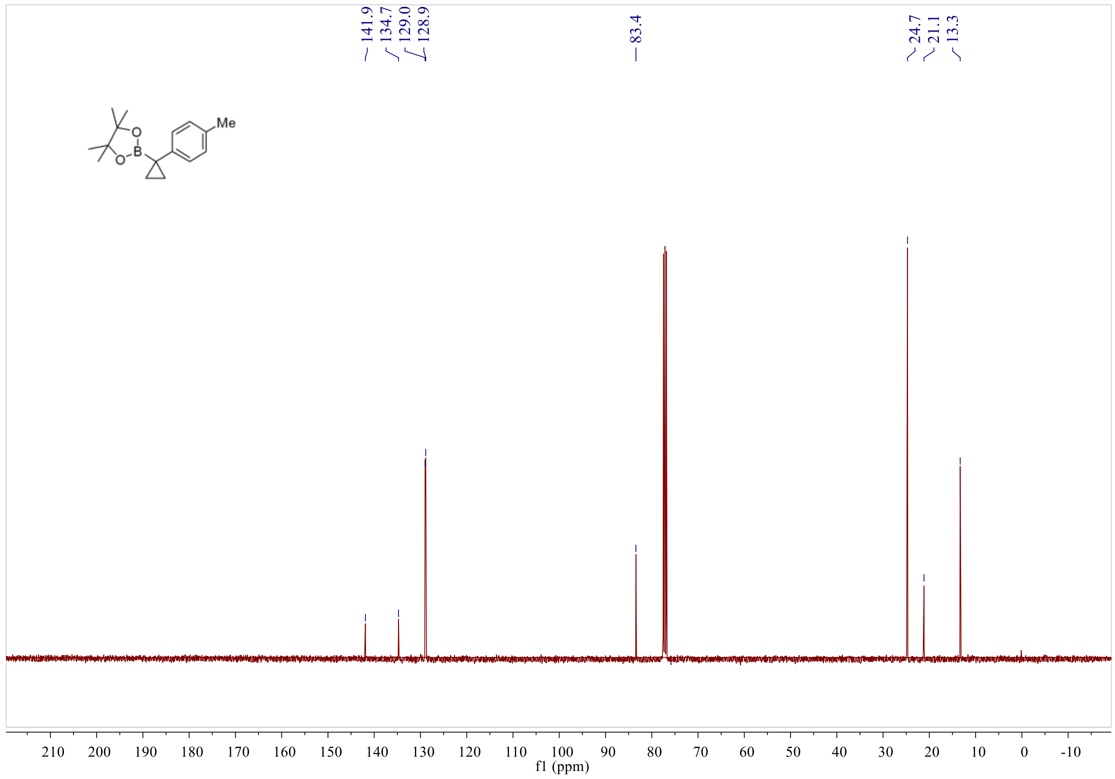

N
Ge
8.06
1.99
1.00
6.00
2.10
6.01
6.06
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

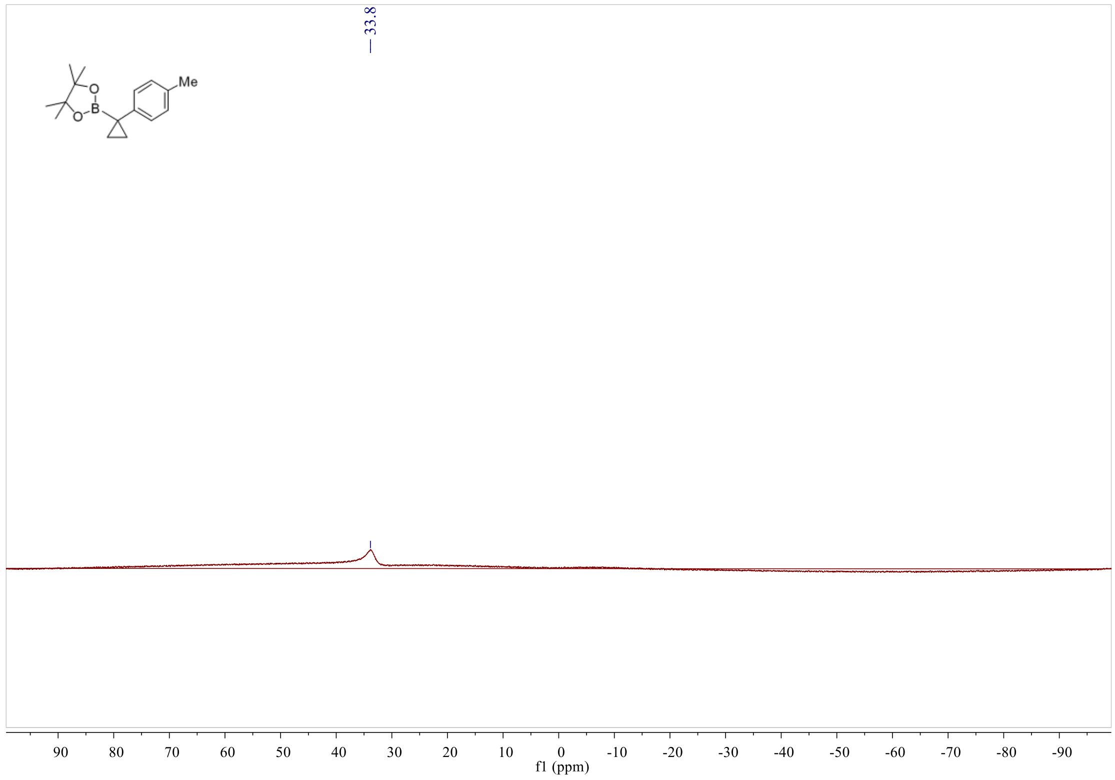

144.6
141.5
138.7
131.1
129.3
128.0
127.7
126.0
125.0
124.3
53.6
34.0
26.4
24.7
23.8
18.2
11.5
10.0
N
Ge
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


OMe
2.03
8.06
4.09
3.01
1.00
1.00
1.02
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


157.9
139.4
138.9
131.0
128.8
128.0
128.0
127.7
126.2
125.6
113.8
55.4
38.9
32.2
20.7
OMe
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Me
O
B
2.03
2.00
3.01
12.19
2.02
2.03
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)


141.9
134.7
129.0
128.9
83.4
24.7
21.1
13.3
Me
O
B
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


33.8
Me
O
B
O
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)