Supporting Information: Structure-Modified Germatranes for Pd-Catalyzed Biaryl Synthesis

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General Reagent Information

GeO_2, triethanolamine, trimethylamine, EtOAc, petroleum ether(60-90 ^oC) were purchased from Sinopharm Chemical Reagent Co., Ltd. TBAF-H_2O was purchased from Adamas Reagent Co., Ltd. $PhGeCl_3$, DMAc and Cs_2CO_3 were purchased from TCI Shanghai. 2-Methyltetrahydrofuran (99%, SuperDry, J&KSeal), 1,1-dimethyloxirane, 2,6-bis(tert-butyl)pyridine, allylpalladium chloride dimer, and Grignard reagents were purchased from J&K Scientific Ltd. $Pd(OAc)_2$, SPhos, DavePhos and *N*-(2-methoxyphenyl)-2-(di-*t*-butylphosphino)pyrrole were purchased from Strem. $Pd(Ph_3P)_2Cl_2$ was purchased from Energy Chemical. Silica gel (HG/T2354-2010) from Branch Qingdao Haiyang Chemical Co., Ltd. Reagents and solvents were used as received unless otherwise noted.

General Analytical Information

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker Avance 400 spectrometer at ambient temperature in $CDCl_3$ unless otherwise noted. Data for ^{1}H-NMR are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration. Data for ^{13}C-NMR are reported in terms of chemical shift (δ ppm), multiplicity, and coupling constant (Hz). High resolution MS analysis were performed on an Acquity UPLC-Xevo G2 QTof instrument. Single crystal structure analysis were performed on an Oxford diffraction Gemini S Ultra instrument. 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. Column chromatographic purification of products was accomplished using forced-flow chromatography on silica gel.

General Procedural Information

General procedure A for the preparation of phenyl germatranes from $PhGeCl_3$

All reactions were performed in glassware under an atmosphere of Ar. Triethanolamine analogues (1.0 eq.) and triethylamine (3.0 eq.) were added to the solution of $PhGeCl_3$ (1.0 eq.) in toluene (0.15 M) at room temperature. The resulting mixture was stirred in ice-salt bath for 12 h then moved to room temperature for 12 h. The reaction mixture was poured into a separatory funnel containing a mixture of water and EtOAc. The organic layer was separated, washed with brine, dried over Na_2SO_4, and filtered. Solvent was removed under reduced pressure to provide the crude product. The resulting phenyl germatrane was isolated by silica gel column chromatography or recrystallization.

*General procedure B for the preparation of aryl germatranes from **Ge**-Cl (**IV**)*

Grignard reagents (2.0 eq.) were added to the suspension of ***Ge***-Cl (**IV**) (1 eq.) in

anhydrous THF (0.5 M) under 0 °C. The resulting mixture was stirred in 0 °C for 6 h then moved to room temperature for 6 h. The reaction mixture was poured into a separatory funnel containing a mixture of water and EtOAc. The organic layer was separated, washed with brine, dried over Na_2SO_4, and filtered. Solvent was removed under reduced pressure to provide the crude product. The resulting aryl germatranes was purified by silica gel column chromatography.

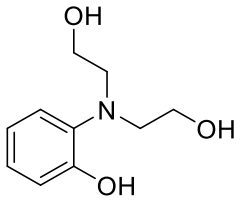
*General procedure C for the preparation of aryl germatranes from **Ge**-H (**II**)*

All reactions were performed in glassware under an atmosphere of Ar. ***Ge***-H (**II**) (1.0 eq.), $Pd(Ph_3P)_2Cl_2$ (5.0 mol%, for aryl iodides) or $Pd(OAc)_2$ (5.0 mol%, for aryl bromides and aryl triflates) and ligand (10 mol%, SPhos for aryl bromide, DavePhos for aryl triflates), Cs_2CO_3 (1.1 eq.) were weighed out on the benchtop, and transferred to an oven-dried Schlenk tube with stir bar. The Schlenk tube was evacuated and backfilled three times with argon. The aryl halide/triflate (1.1 eq.) was then added to the Schlenk tube via microsyringe, followed by DMAc (0.2 M). If the aryl halide/triflate was a solid, it was weighed out on the benchtop alongside the other solids. The Schlenk tube was sealed with a Teflon stopper and stirred at room temperature for 2 h (aryl iodides), or 4 h (aryl bromides and aryl triflates). The reaction mixture was poured into a separatory funnel containing a mixture of water and EtOAc. The organic layer was separated, washed with brine, dried over Na_2SO_4, and filtered. Solvent was removed under reduced pressure to provide the crude product. The resulting aryl germatranes was purified by silica gel column chromatography or recrystallization.

General procedure D for cross-coupling reactions

All reactions were performed in glassware under an atmosphere of Ar. Aryl germatranes (1.1 eq.), $Pd(Ph_3P)_2Cl_2$ (5.0 mol%, for aryl iodides and aryl bromides) or allylpalladium chloride dimer (2.5 mol%, for aryl chlorides) and *N*-(2-methoxyphenyl)-2-(di-*t*-butylphosphino)pyrrole (10 mol%, for aryl chlorides) were weighed out on the benchtop, and transferred to an oven-dried Schlenk tube with stir bar. The Schlenk tube was evacuated and backfilled three times with argon. The aryl halide (1.0 eq.) was then added to the Schlenk tube via microsyringe, followed by the solution of TBAF-H_2O (4.0 eq., 1.23 M in THF) in THF (0.2 M, for aryl iodides) or the solution of TBAF-H_2O (4.0 eq., 1.22 M in 2-methyltetrahydrofuran) in 2-methyltetrahydrofuran (0.2 M for aryl bromides and 0.33 M for aryl chlorides). If the aryl halide was a solid, it was weighed out on the benchtop alongside the other solids. The Schlenk tube was sealed with a Teflon stopper and stirred at 80 °C (for aryl iodides and aryl bromides) or 85 °C (for aryl chlorides) for 12 h. The reaction mixture was poured into a separatory funnel containing a mixture of water and EtOAc. The organic layer was separated, washed with brine, dried over Na_2SO_4, and filtered. Solvent was removed under reduced pressure to provide the crude product. The crude product was purified by silica gel column chromatography.

Preparation and Characterization

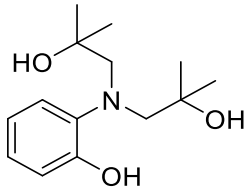


2,2'-((2-hydroxyphenyl)azanediyl)bis(ethan-1-ol). 2-Bromoethanol (4.26 mL, 60 mmol) was added to the suspension of 2-aminophenol (2.18 g, 20 mmol), $CaCO_3$ (4.00 g, 40 mmol) and KI (332 mg, 2 mmol) in water (28 mL). The resulting mixture was refluxed for 8 h. The reaction mixture was poured into a separatory funnel containing a mixture of water and EtOAc. The organic layer was separated, washed with brine, dried over Na_2SO_4, and filtered. Solvent was removed under reduced pressure to provide the crude product. The resulting 2,2'-((2-hydroxyphenyl)azanediyl)bis(ethan-1-ol) was purified by silica gel column chromatography (Petroleum ether : EtOAc=1:1, Rf~0.5) as light red oil (2.80 g, 71%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 – 7.10 (m, 1H), 7.08 – 7.02 (m, 1H), 6.95 – 6.90 (m, 1H), 6.88 – 6.82 (m, 1H), 3.63 – 3.55 (m, 4H), 3.15 – 3.06 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.4 , 136.7 , 126.5 , 123.2 , 120.2 , 115.7 , 59.7 , 57.2 .

Known compound.[1]

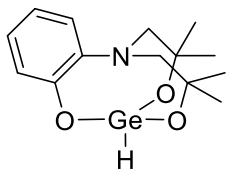


I: 1,1'-((2-hydroxyphenyl)azanediyl)bis(2-methylpropan-2-ol). 2-Aminophenol (17.5 g, 160 mmol), 1,1-dimethyloxirane (42.7 mL, 480 mmol) and water (1.2 mL) were added to the seal reaction tube, the resulting mixture was stirred at 120 ºC for 1 d. The excess 1,1-dimethyloxirane was removed under reduced pressure to provide the crude product. The resulting **I** was purified by silica gel column chromatography (Petroleum ether : EtOAc=2:1, Rf~0.4) as light red oil (35.2 g, 87%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.19 (m, 1H), 7.05 – 7.00 (m, 1H), 6.94 – 6.90 (m, 1H), 6.85 – 6.80 (m, 1H), 3.11 (s, 4H), 1.17 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.5 , 141.8 , 126.1 , 123.9 , 120.1 , 116.0 , 71.3 , 68.4 , 28.5 .

HRMS (ESI) calcd for $C_{14}H_{24}NO_3^+$ [$(M+H)^+$] 254.1756, found 254.1751.



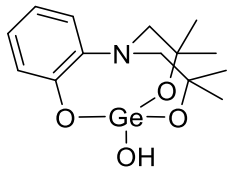
II: 4,4,12,12-tetramethyl-4,5-dihydro-2,6-(epoxyethano)benzo[d][1,3,6,2]dioxazagermocine. The reaction was performed in glassware under an atmosphere of Ar. **I** (5.07 g, 20 mmol) and triethylamine (11 mL, 80 mmol) were added to the suspension of $CsGeCl_3$[2] (6.24 g, 20 mmol) in

anhydrous toluene (200 mL, 0.1 M). The resulting mixture was stirred at 80 °C for 12 h. Solvent was removed under reduced pressure to provide the crude product. The resulting ***Ge***-H (**II**) was purified by silica gel column chromatography (Petroleum ether : EtOAc=2:1, Rf~0.6) as white solid (5.63 g, 87%). Melting point: 69.3-78.6 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.24 (m, 1H), 7.21 – 7.15 (m, 1H), 7.01 – 6.98 (m, 1H), 6.92 – 6.86 (m, 1H), 6.12 (s, 1H), 3.32 – 3.01 (m, 4H), 1.35 (s, 6H), 0.98 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.5 , 138.8 , 128.9 , 122.3 , 120.3 , 116.6 , 69.7 , 68.9 , 30.3 , 30.0 .

HRMS (ESI) calcd for $C_{14}H_{21}{}^{74}GeNO_3Na^+$ [$(M+Na)^+$] 348.0631, found 348.0642.

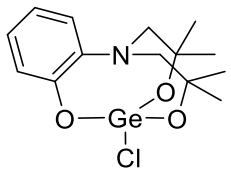


III: 4,4,12,12-tetramethyl-4,5-dihydro-2,6-(epoxyethano)benzo[d][1,3,6,2]dioxazagermocin-2-ol. I (5.07 g, 20 mmol) was added to the suspension of GeO_2 (2.30 g, 22 mmol) in solvent (40 mL, 0.5 M, acetonitrile : water = 1:1). The resulting mixture was stirred at 90 °C for 12 h. The reaction mixture was poured into a separatory funnel containing a mixture of water and EtOAc. The organic layer was separated, washed with brine, dried over Na_2SO_4, and filtered. Solvent was removed under reduced pressure to provide the product ***Ge***-OH (**III**) as white solid (5.57 g, 82%). Melting point: 58.4-67.5 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.24 (m, 1H), 7.24 – 7.19 (m, 1H), 7.07 – 7.03 (m, 1H), 6.94 – 6.89 (m, 1H), 3.33 – 3.07 (m, 4H), 1.37 (s, 6H), 1.01 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.8 , 138.0 , 129.5 , 122.0 , 120.7 , 117.1 , 70.2 , 69.7 , 30.0 , 29.6 .

HRMS (ESI) calcd for $C_{14}H_{21}{}^{74}GeNO_4Na^+$ [$(M+Na)^+$] 364.0580, found 364.0580.

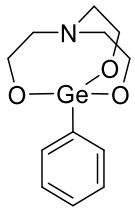


IV: 2-chloro-4,4,12,12-tetramethyl-4,5-dihydro-2,6-(epoxyethano)benzo[d][1,3,6,2]dioxaza-germocine. $SOCl_2$ (1.47 mL, 20 mmol) was added to the solution of ***Ge***-OH (**III**) (3.40 g, 10 mmol) in DCM (20 mL, 0.5 M) at 0 °C. The resulting mixture was stirred at 0 °C for 2 h. Solvent was removed under reduced pressure to provide the product ***Ge***-Cl(**IV**) as light red solid (quantitative). Melting point: 165.0-172.3 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.28 (m, 1H), 7.28 – 7.23 (m, 1H), 7.12 – 7.08 (m, 1H), 7.00 – 6.94 (m, 1H), 3.44 – 3.14 (m, 4H), 1.43 (s, 6H), 1.07 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.5 , 137.4 , 129.9 , 121.8 , 121.4 , 117.1 , 71.5 , 70.3 , 29.9 , 29.5 .

HRMS (ESI) calcd for $C_{14}H_{20}Cl^{74}GeNO_3Na^+$ [$(M+Na)^+$] 382.0241, found 382.0251.

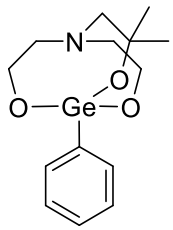


1a: 1-phenyl-2,8,9-trioxa-5-aza-1-germabicyclo[3.3.3]undecane. The general procedure A was employed on 1 mmol scale by using triethanolamine, the product was isolated by recrystallization from DCM as white solid (203 mg, 69%). Melting point: 230.3-238.9 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.68 (m, 2H), 7.35 – 7.28 (m, 3H), 3.88 (t, *J* = 5.7 Hz, 6H), 2.90 (t, *J* = 5.7 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.3 , 133.6 , 129.0 , 127.9 , 56.8 , 51.7 .

HRMS (ESI) calcd for $C_{12}H_{17}{}^{74}GeNO_3Na^+$ [$(M+Na)^+$] 320.0318, found 320.0283.

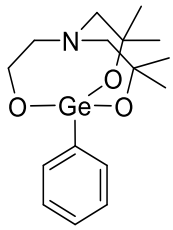


1b: 3,3-dimethyl-1-phenyl-2,8,9-trioxa-5-aza-1-germabicyclo[3.3.3]undecane. The general procedure A was employed on 1 mmol scale by using 2,2'-((2-hydroxy-2-methylpropyl)azanediyl)-bis(ethan-1-ol)[3], the product was isolated by silica gel column chromatography (Petroleum ether : EtOAc=4:1, Rf~0.4) as white solid (242 mg, 75%). Melting point: 123.9-127.2 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.71 (m, 2H), 7.34 – 7.28 (m, 3H), 3.92 – 3.79 (m, 4H), 3.02 – 2.90 (m, 4H), 2.73 (s, 2H), 1.35 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.9 , 133.7 , 128.9 , 127.9 , 68.5 , 62.8 , 57.4 , 55.9 , 31.3 .

HRMS (ESI) calcd for $C_{14}H_{21}{}^{74}GeNO_3Na^+$ [$(M+Na)^+$] 348.0631, found 348.0634.

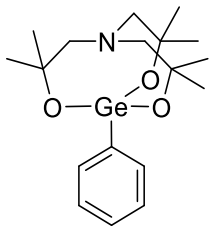


1c: 3,3,7,7-tetramethyl-1-phenyl-2,8,9-trioxa-5-aza-1-germabicyclo[3.3.3]undecane. The general procedure A was employed on 1 mmol scale by using 1,1'-((2-hydroxyethyl)azanediyl)-bis(2-methylpropan-2-ol)[3], the product was isolated by silica gel column chromatography (Petroleum ether : EtOAc=4:1, Rf~0.5) as white solid (237 mg, 67%). Melting point: 133.4-135.1 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.74 (m, 2H), 7.34 – 7.26 (m, 3H), 3.85 (t, *J* = 5.6 Hz, 2H), 3.03 (t, *J* = 5.6 Hz, 2H), 2.90 – 2.73 (m, 4H), 1.38 – 1.30 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.6 , 133.8 , 128.7 , 127.8 , 68.8 , 66.5 , 60.0 , 57.9 , 31.3 , 30.6 .

HRMS (ESI) calcd for $C_{16}H_{25}{}^{74}GeNO_3Na^+$ [$(M+Na)^+$] 376.0944, found 376.0947.

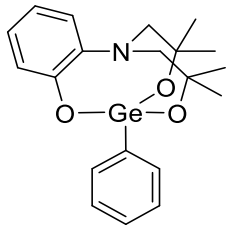


1d: 3,3,7,7,10,10-hexamethyl-1-phenyl-2,8,9-trioxa-5-aza-1-germabicyclo[3.3.3]undecane. The general procedure A was employed on 1 mmol scale by using 1,1',1''-nitrilotris(2-methylpropan-2-ol)[3], the product was isolated by silica gel column chromatography (Petroleum ether : EtOAc=4:1, Rf~0.5) as white solid (274 mg, 72%). Melting point: 193.7-195.6 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.75 (m, 2H), 7.34 – 7.23 (m, 3H), 2.91 (s, 6H), 1.31 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.5 , 133.9 , 128.6 , 127.7 , 70.1 , 69.0 , 30.7 .

HRMS (ESI) calcd for $C_{18}H_{29}{}^{74}GeNO_3Na^+$ [$(M+Na)^+$] 404.1257, found 404.1261.

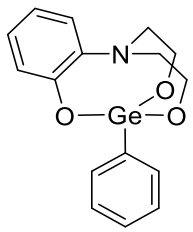


1e: 4,4,12,12-tetramethyl-2-phenyl-4,5-dihydro-2,6-(epoxyethano)benzo[d][1,3,6,2]dioxazagermocine. The general procedure A was employed on 1 mmol scale by using **I**, the product was isolated by silica gel column chromatography (Petroleum ether : EtOAc=6:1, Rf~0.5) as white solid (323 mg, 80%). Melting point: 202.6-203.9 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.86 (m, 2H), 7.42 – 7.31 (m, 3H), 7.29 – 7.25 (m, 1H), 7.19 – 7.12 (m, 1H), 7.02 – 6.97 (m, 1H), 6.90 – 6.83 (m, 1H), 3.31 – 3.05 (m, 4H), 1.35 (s, 6H), 1.01 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.9 , 139.4 , 139.3 , 134.2 , 129.3 , 128.7 , 128.0 , 122.6 , 120.0 , 116.9 , 70.1 , 68.9 , 30.4 , 30.0 .

HRMS (ESI) calcd for $C_{20}H_{25}{}^{74}GeNO_3Na^+$ [$(M+Na)^+$] 424.0944, found 424.0955.



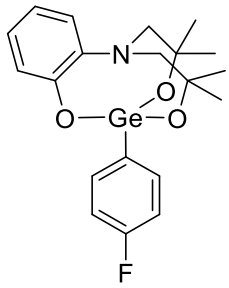
1f: 2-phenyl-4,5-dihydro-2,6-(epoxyethano)benzo[d][1,3,6,2]dioxazagermocine. The general procedure A was employed on 1 mmol scale by using 2,2'-((2-hydroxyphenyl)azanediyl)bis(ethan-1-ol), the product was isolated by silica gel column chromatography (Petroleum ether : EtOAc=2:1, Rf~0.4) as white solid (223 mg, 65%). Melting point: 135.1-141.2 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.78 (m, 2H), 7.44 – 7.33 (m, 3H), 7.31 – 7.25 (m, 1H), 7.22 – 7.14 (m, 1H), 7.07 – 7.02 (m, 1H), 6.91 – 6.85 (m, 1H), 3.92 – 3.82 (m, 2H), 3.72 – 3.61 (m, 2H),

3.37 – 3.27 (m, 2H), 3.15 – 3.03 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.0 , 138.0 , 133.9 , 133.4 , 129.6 , 129.0 , 128.1 , 122.9 , 120.0 , 116.8 , 57.6 , 56.0 .

HRMS (ESI) calcd for $C_{16}H_{17}{}^{74}GeNO_3Na^+$ [$(M+Na)^+$] 368.0318, found 368.0313.



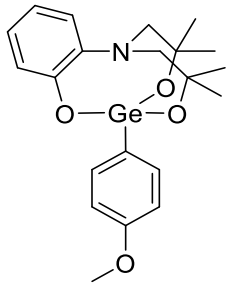
1g: 2-(4-fluorophenyl)-4,4,12,12-tetramethyl-4,5-dihydro-2,6-(epoxyethano)benzo[d][1,3,6,2]-dioxazagermocine. The general procedure B was employed on 1 mmol scale by using (4-fluorophenyl)magnesium bromide, the product was isolated by silica gel column chromatography (Petroleum ether : EtOAc=6:1, Rf~0.5) as white solid (338 mg, 81%). Melting point: 174.1-175.0 ^oC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.86 (m, 2H), 7.30 – 7.27 (m, 1H), 7.20 – 7.14 (m, 1H), 7.12 – 7.04 (m, 2H), 7.02 – 6.98 (m, 1H), 6.92 – 6.86 (m, 1H), 3.33 – 3.07 (m, 4H), 1.36 (s, 6H), 1.02 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.9 (d, *J* = 246.9 Hz), 153.8 , 139.1 , 136.1 (d, *J* = 7.4 Hz), 134.9 (d, *J* = 3.8 Hz), 128.8 , 122.5 , 120.1 , 116.9 , 114.9 (d, *J* = 19.8 Hz), 70.1 , 68.9 , 30.4 , 29.9 .

^{19}F NMR (376 MHz, $CDCl_3$) δ -112.31 .

HRMS (ESI) calcd for $C_{20}H_{24}F^{74}GeNO_3Na^+$ [$(M+Na)^+$] 442.0850, found 442.0868.

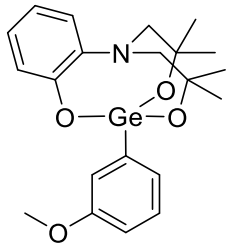


1h: 2-(4-methoxyphenyl)-4,4,12,12-tetramethyl-4,5-dihydro-2,6-(epoxyethano)benzo[d]-[1,3,6,2]dioxazagermocine. The general procedure B was employed on 1 mmol scale by using (4-methoxyphenyl)magnesium bromide, the product was isolated by silica gel column chromatography (Petroleum ether : EtOAc=6:1, Rf~0.4) as white solid (236 mg, 55%). Melting point: 139.3-145.4 ^oC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.7 Hz, 2H), 7.28 – 7.24 (m, 1H), 7.17 – 7.12 (m, 1H), 7.00 – 6.97 (m, 1H), 6.94 (d, *J* = 8.7 Hz, 2H), 6.89 – 6.83 (m, 1H), 3.80 (s, 3H), 3.30 – 3.04 (m, 4H), 1.34 (s, 6H), 1.00 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5 , 152.9 , 138.3 , 134.5 , 129.6 , 127.6 , 121.6 , 118.9 , 115.8 , 112.7 , 69.0 , 67.7 , 54.1 , 29.3 , 28.9 .

HRMS (ESI) calcd for $C_{21}H_{27}{}^{74}GeNO_4Na^+$ [$(M+Na)^+$] 454.1050, found 454.1052.

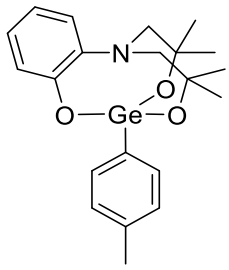


1i: 2-(3-methoxyphenyl)-4,4,12,12-tetramethyl-4,5-dihydro-2,6-(epoxyethano)benzo[d]-[1,3,6,2]dioxazagermocine. The general procedure B was employed on 1 mmol scale by using (3-methoxyphenyl)magnesium bromide, the product was isolated by silica gel column chromatography (Petroleum ether : EtOAc=6:1, Rf~0.4) as white solid (271 mg, 63%). Melting point: 127.6-132.5 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.44 (m, 2H), 7.35 – 7.30 (m, 1H), 7.29 – 7.26 (m, 1H), 7.19 – 7.13 (m, 1H), 7.03 – 6.98 (m, 1H), 6.93 – 6.85 (m, 2H), 3.84 (s, 3H), 3.32 – 3.07 (m, 4H), 1.36 (s, 6H), 1.01 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0 , 153.9 , 140.6 , 139.3 , 129.0 , 128.7 , 126.6 , 122.5 , 120.0 , 119.6 , 116.9 , 114.9 , 70.1 , 68.9 , 55.2 , 30.4 , 30.0 .

HRMS (ESI) calcd for $C_{21}H_{27}{}^{74}GeNO_4Na^+$ [$(M+Na)^+$] 454.1050, found 454.1052.

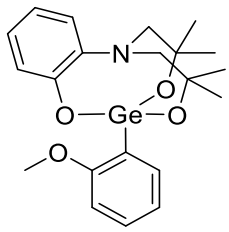


1j: 4,4,12,12-tetramethyl-2-(p-tolyl)-4,5-dihydro-2,6-(epoxyethano)benzo[d][1,3,6,2]dioxaza-germocine. The general procedure C was employed on 0.2 mmol scale by using 1-iodo-4-methylbenzene, 1-bromo-4-methylbenzene, or p-tolyl trifluoromethanesulfonate as substrate, the product was isolated by silica gel column chromatography (Petroleum ether : EtOAc=6:1, Rf~0.5) as white solid (66.2 mg, 80%; 72.8 mg, 88%; 56.3 mg, 68%). Melting point: 157.2-161.7 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.9 Hz, 2H), 7.30 – 7.26 (m, 1H), 7.20 (d, *J* = 7.5 Hz, 2H), 7.18 – 7.13 (m, 1H), 7.02 – 6.97 (m, 1H), 6.90 – 6.84 (m, 1H), 3.32 – 3.05 (m, 4H), 2.34 (s, 3H), 1.35 (s, 6H), 1.01 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.0 , 139.4 , 139.0 , 135.8 , 134.1 , 128.8 , 128.6 , 122.7 , 120.0 , 116.9 , 70.1 , 68.8 , 30.4 , 30.0 .

HRMS (ESI) calcd for $C_{21}H_{27}{}^{74}GeNO_3Na^+$ [$(M+Na)^+$] 438.1100, found 438.1098.



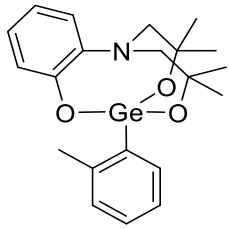
1k: 2-(2-methoxyphenyl)-4,4,12,12-tetramethyl-4,5-dihydro-2,6-(epoxyethano)benzo[d]-

[1,3,6,2]dioxazagermocine. The general procedure C was employed on 0.2 mmol scale by using 1-iodo-2-methoxybenzene as substrate, the product was isolated by silica gel column chromatography (Petroleum ether : EtOAc=6:1, Rf~0.4) as white solid (79.9 mg, 93%). Melting point: 157.5-164.8 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.97 (m, 1H), 7.36 – 7.30 (m, 1H), 7.29 – 7.25 (m, 1H), 7.18 – 7.11 (m, 1H), 7.03 – 6.99 (m, 1H), 6.99 – 6.94 (m, 1H), 6.94 – 6.89 (m, 1H), 6.88 – 6.83 (m, 1H), 3.83 (s, 3H), 3.30 – 3.04 (m, 4H), 1.36 (s, 6H), 1.01 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1 , 154.1 , 139.6 , 135.9 , 130.9 , 128.4 , 127.3 , 122.8 , 120.7 , 119.7 , 116.8 , 111.8 , 70.0 , 69.0 , 55.9 , 30.2 , 29.8 .

HRMS (ESI) calcd for $C_{21}H_{27}{}^{74}GeNO_4Na^+$ [$(M+Na)^+$] 454.1050, found 454.1050.

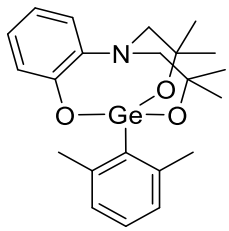


1l: 4,4,12,12-tetramethyl-2-(o-tolyl)-4,5-dihydro-2,6-(epoxyethano)benzo[d][1,3,6,2]dioxaza-germocine. The general procedure C was employed on 0.2 mmol scale by using 1-bromo-2-methylbenzene or o-tolyl trifluoromethanesulfonate as substrate, the product was isolated by silica gel column chromatography (Petroleum ether : EtOAc=6:1, Rf~0.5) as white solid (69.5 mg, 84%; 68.7 mg, 83%). Melting point: 170.1-172.3 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.10 (m, 1H), 7.29 – 7.23 (m, 2H), 7.22 – 7.12 (m, 3H), 7.02 – 6.96 (m, 1H), 6.90 – 6.83 (m, 1H), 3.30 – 3.02 (m, 4H), 2.65 (s, 3H), 1.36 (s, 6H), 1.00 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.8 , 143.2 , 139.4 , 138.3 , 135.0 , 130.2 , 129.4 , 128.5 , 124.7 , 122.7 , 119.9 , 116.8 , 69.5 , 69.0 , 30.3 , 30.1 , 23.4 .

HRMS (ESI) calcd for $C_{21}H_{27}{}^{74}GeNO_3Na^+$ [$(M+Na)^+$] 438.1100, found 438.1099.

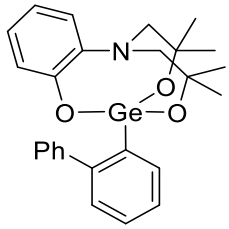


1m: 2-(2,6-dimethylphenyl)-4,4,12,12-tetramethyl-4,5-dihydro-2,6-(epoxyethano)benzo[d]-[1,3,6,2]dioxazagermocine. The general procedure C was employed on 2 mmol scale by using 2-bromo-1,3-dimethylbenzene as substrate, the product was isolated by silica gel column chromatography (Petroleum ether : EtOAc=6:1, Rf~0.5) as white solid (436 mg, 51%). Melting point: 142.8-147.8 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.26 (m, 1H), 7.17 – 7.10 (m, 2H), 7.03 – 7.00 (m, 2H), 6.98 – 6.95 (m, 1H), 6.89 – 6.84 (m, 1H), 3.27 – 3.00 (m, 4H), 2.68 (s, 6H), 1.36 (s, 6H), 0.99 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.0 , 143.9 , 139.6 , 137.7 , 129.0 , 128.3 , 123.1 , 120.0 , 116.8 , 69.7 , 69.2 , 30.6 , 30.3 , 25.5 .

HRMS (ESI) calcd for $C_{22}H_{29}{}^{74}GeNO_3Na^+$ [$(M+Na)^+$] 452.1257, found 452.1256.

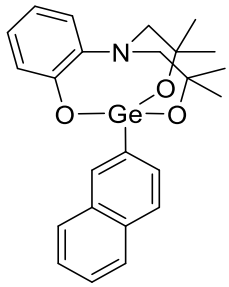


1n: 2-([1,1'-biphenyl]-2-yl)-4,4,12,12-tetramethyl-4,5-dihydro-2,6-(epoxyethano)benzo[d]-[1,3,6,2]dioxazagermocine. The general procedure C was employed on 0.2 mmol scale by using 2-bromo-1,1'-biphenyl as substrate, the product was isolated by silica gel column chromatography (Petroleum ether : EtOAc=6:1, Rf~0.6) as white solid (70.4 mg, 74%). Melting point: 170.3-172.4 ^{o}C.

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.24 – 8.18 (m, 1H), 7.55 – 7.49 (m, 2H), 7.33 – 7.26 (m, 2H), 7.23 – 7.14 (m, 4H), 7.11 – 7.07 (m, 1H), 7.05 – 6.99 (m, 1H), 6.75 – 6.68 (m, 2H), 3.07 – 2.78 (m, 4H), 1.05 (s, 6H), 0.68 (s, 6H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 170.1 , 152.7 , 147.2 , 144.3 , 138.1 , 136.8 , 136.8 , 134.5 , 129.5 , 128.8 , 127.9 , 127.3 , 126.0 , 125.2 , 125.2 , 121.4 , 118.6 , 115.7 , 68.0 , 67.7 , 59.4 , 29.1 , 29.0 , 20.0 .

HRMS (ESI) calcd for $C_{26}H_{29}{}^{74}GeNO_3Na^+$ [(M+Na)$^+$] 500.1257, found 500.1257.

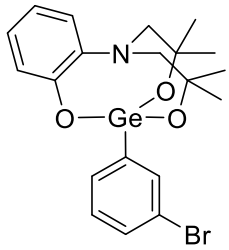


1o: 4,4,12,12-tetramethyl-2-(naphthalen-2-yl)-4,5-dihydro-2,6-(epoxyethano)benzo[d]-[1,3,6,2]dioxazagermocine. The general procedure C was employed on 0.2 mmol scale by using naphthalen-2-yl trifluoromethanesulfonate as substrate, the product was isolated by silica gel column chromatography (Petroleum ether : EtOAc=6:1, Rf~0.5) as white solid (88.2 mg, 98%). Melting point: 159.4-170.2 ^{o}C.

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.44 (s, 1H), 8.02 – 7.95 (m, 1H), 7.93 – 7.86 (m, 1H), 7.88 – 7.81 (m, 1H), 7.83 – 7.75 (m, 1H), 7.48 – 7.40 (m, 2H), 7.26 – 7.19 (m, 1H), 7.20 – 7.11 (m, 1H), 7.05 – 6.97 (m, 1H), 6.91 – 6.82 (m, 1H), 3.23 – 3.01 (m, 4H), 1.35 (s, 6H), 1.02 (s, 6H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 152.7 , 138.2 , 136.1 , 133.6 , 133.0 , 132.2 , 129.7 , 127.6 , 127.4 , 126.6 , 126.1 , 125.0 , 124.4 , 121.6 , 119.1 , 115.7 , 68.8 , 67.8 , 29.3 , 28.9 .

HRMS (ESI) calcd for $C_{24}H_{27}{}^{74}GeNO_3Na^+$ [(M+Na)$^+$] 474.1100, found 474.1108.

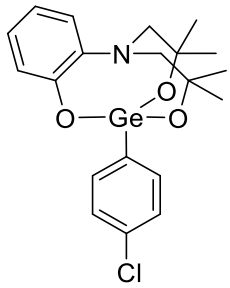


1p: 2-(3-bromophenyl)-4,4,12,12-tetramethyl-4,5-dihydro-2,6-(epoxyethano)benzo[d]-[1,3,6,2]dioxazagermocine. The general procedure C was employed on 5 mmol scale by using 1-bromo-3-iodobenzene as substrate, the product was isolated by silica gel column chromatography (Petroleum ether : EtOAc=6:1, Rf~0.5) as white solid (1.79 g, 75%). Melting point: 128.2-132.7 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.98 (m, 1H), 7.85 – 7.80 (m, 1H), 7.51 – 7.46 (m, 1H), 7.29 – 7.25 (m, 2H), 7.20 – 7.14 (m, 1H), 7.02 – 6.98 (m, 1H), 6.91 – 6.86 (m, 1H), 3.32 – 3.07 (m, 4H), 1.36 (s, 6H), 1.01 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.6 , 142.4 , 139.0 , 136.8 , 132.7 , 132.2 , 129.7 , 128.8 , 122.8 , 122.5 , 120.3 , 116.9 , 70.1 , 69.0 , 30.3 , 30.0 .

HRMS (ESI) calcd for $C_{20}H_{24}Br^{74}GeNO_3Na^+$ [$(M+Na)^+$] 502.0049, found 502.0046.

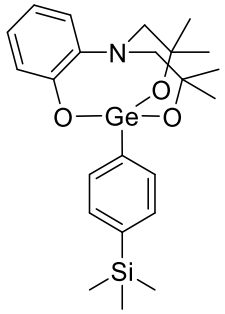


1q: 2-(4-chlorophenyl)-4,4,12,12-tetramethyl-4,5-dihydro-2,6-(epoxyethano)benzo[d]-[1,3,6,2]dioxazagermocine. The general procedure C was employed on 0.2 mmol scale by using 1-bromo-4-chlorobenzene as substrate, the product was isolated by silica gel column chromatography (Petroleum ether : EtOAc=6:1, Rf~0.5) as white solid (64.3 mg, 74%). Melting point: 139.7-142.8 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.3 Hz, 2H), 7.29 – 7.25 (m, 1H), 7.19 – 7.14 (m, 1H), 7.02 – 6.97 (m, 1H), 6.91 – 6.86 (m, 1H), 3.32 – 3.05 (m, 4H), 1.35 (s, 6H), 1.01 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.6 , 138.1 , 136.9 , 134.6 , 134.4 , 127.8 , 127.0 , 121.5 , 119.2 , 115.8 , 69.0 , 67.9 , 29.3 , 28.9 .

HRMS (ESI) calcd for $C_{20}H_{24}Cl^{74}GeNO_3Na^+$ [$(M+Na)^+$] 458.0554, found 458.0553.

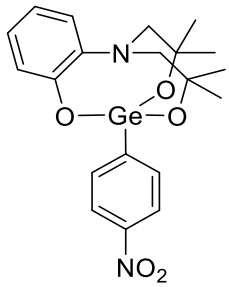


1r: 4,4,12,12-tetramethyl-2-(4-(trimethylsilyl)phenyl)-4,5-dihydro-2,6-(epoxyethano)benzo-[d][1,3,6,2]dioxazagermocine. The general procedure C was employed on 2 mmol scale by using (4-bromophenyl)trimethylsilane as substrate, the product was isolated by silica gel column chromatography (Petroleum ether : EtOAc=6:1, Rf~0.5) as white solid (680 mg, 72%). Melting point: 152.7-159.2 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.29 – 7.26 (m, 1H), 7.19 – 7.13 (m, 1H), 7.02 – 6.98 (m, 1H), 6.90 – 6.85 (m, 1H), 3.32 – 3.06 (m, 4H), 1.35 (s, 6H), 1.01 (s, 6H), 0.24 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.0 , 141.3 , 139.8 , 139.3 , 133.2 , 132.9 , 128.6 , 122.6 , 119.9 , 116.9 , 70.0 , 68.8 , 30.4 , 30.0 , -1.2 .

HRMS (ESI) calcd for $C_{23}H_{33}{}^{74}GeNO_3SiNa^+$ [$(M+Na)^+$] 496.1339, found 496.1350.

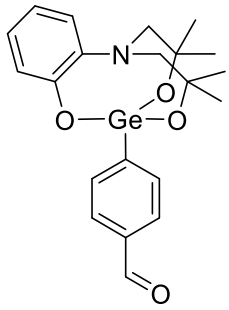


1s: 4,4,12,12-tetramethyl-2-(4-nitrophenyl)-4,5-dihydro-2,6-(epoxyethano)benzo[d][1,3,6,2]-dioxazagermocine. The general procedure C was employed on 0.2 mmol scale by using 1-bromo-4-nitrobenzene as substrate, the product was isolated by silica gel column chromatography (Petroleum ether : EtOAc=6:1, Rf~0.4) as white solid (75.6 mg, 85%). Melting point: 188.6-190.1 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.7 Hz, 2H), 8.10 (d, *J* = 8.7 Hz, 2H), 7.33 – 7.29 (m, 1H), 7.22 – 7.17 (m, 1H), 7.03 – 6.98 (m, 1H), 6.95 – 6.89 (m, 1H), 3.39 – 3.11 (m, 4H), 1.38 (s, 6H), 1.03 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.3 , 148.7 , 148.6 , 138.8 , 135.3 , 129.0 , 122.5 , 122.4 , 120.6 , 116.8 , 70.1 , 69.1 , 30.3 , 30.0 .

HRMS (ESI) calcd for $C_{20}H_{25}{}^{74}GeN_2O_5^+$ [$(M+H)^+$] 447.0975, found 447.0983.

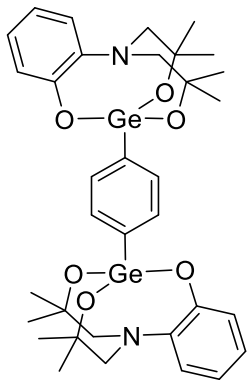


1t: 4-(4,4,12,12-tetramethyl-4,5-dihydro-2,6-(epoxyethano)benzo[d][1,3,6,2]dioxazagermocin-2-yl)benzaldehyde. The general procedure C was employed on 0.2 mmol scale by using 4-bromobenzaldehyde as substrate, the product was isolated by silica gel column chromatography (Petroleum ether : EtOAc=6:1, Rf~0.4) as white solid (70.2 mg, 82%). Melting point: 146.0-151.3 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.03 (s, 1H), 8.10 (d, *J* = 7.5 Hz, 2H), 7.88 (d, *J* = 7.5 Hz, 2H), 7.32 – 7.27 (m, 1H), 7.22 – 7.15 (m, 1H), 7.03 – 6.98 (m, 1H), 6.94 – 6.87 (m, 1H), 3.37 – 3.10 (m, 4H), 1.38 (s, 6H), 1.03 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 193.0 , 153.5 , 147.9 , 139.0 , 136.7 , 134.9 , 128.9 , 128.9 , 122.5 , 120.4 , 116.8 , 70.1 , 69.0 , 30.3 , 30.0 .

HRMS (ESI) calcd for $C_{21}H_{26}{}^{74}GeNO_4^+$ [(M+H)$^+$] 430.1074, found 430.1070.

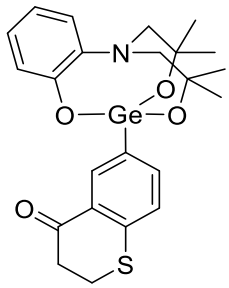


1u: 1,4-bis(4,4,12,12-tetramethyl-4,5-dihydro-2,6-(epoxyethano)benzo[d][1,3,6,2]dioxazagermocin-2-yl)benzene. The general procedure C was employed on 0.2 mmol scale by using 1,4-diiodobenzene or 1,4-dibromobenzene as substrate, the product was isolated by recrystallization from DCM as white solid (127 mg, 88%; 98.2 mg, 68%). Melting point > 305 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 4H), 7.29 – 7.25 (m, 2H), 7.18 – 7.13 (m, 2H), 7.00 – 6.96 (m, 2H), 6.89 – 6.83 (m, 2H), 3.31 – 3.06 (m, 8H), 1.34 (s, 12H), 1.00 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.2 , 140.3 , 139.4 , 133.5 , 128.5 , 122.7 , 119.8 , 117.0 , 70.1 , 68.8 , 30.4 , 30.0 .

HRMS (ESI) calcd for $C_{33}H_{45}{}^{74}Ge_2N_2O_6^+$ [(M+H)$^+$] 725.1701, found 725.1708.

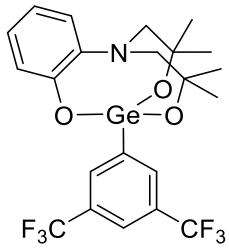


1v: 6-(4,4,12,12-tetramethyl-4,5-dihydro-2,6-(epoxyethano)benzo[d][1,3,6,2]dioxaza-germocin-2-yl)thiochroman-4-one. The general procedure C was employed on 0.2 mmol scale by using 6-bromothiochroman-4-one as substrate, the product was isolated by silica gel column chromatography (Petroleum ether : EtOAc=2:1, Rf~0.5) as white solid (69.0 mg, 71%). Melting point: 161.0-166.1 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 – 8.58 (m, 1H), 7.95 – 7.90 (m, 1H), 7.32 – 7.26 (m, 2H), 7.20 – 7.14 (m, 1H), 7.02 – 6.98 (m, 1H), 6.91 – 6.86 (m, 1H), 3.24 – 3.19 (m, 2H), 3.32 – 3.08 (m, 4H), 3.00 – 2.95 (m, 2H), 1.35 (s, 6H), 1.01 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 194.2 , 153.6 , 143.2 , 139.0 , 139.0 , 136.5 , 135.2 , 130.4 , 128.8 , 127.1 , 122.5 , 120.2 , 116.9 , 70.0 , 69.0 , 39.8 , 30.3 , 30.0 , 26.6 .

HRMS (ESI) calcd for $C_{23}H_{27}{}^{74}GeNO_4SNa^+$ [(M+Na)$^+$] 510.0770, found 510.0768.



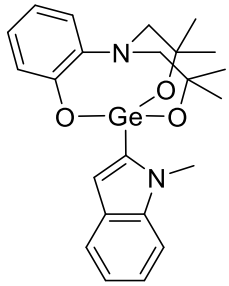
1w: 2-(3,5-bis(trifluoromethyl)phenyl)-4,4,12,12-tetramethyl-4,5-dihydro-2,6-(epoxyethano)-benzo[d][1,3,6,2]dioxazagermocine. The general procedure C was employed on 2 mmol scale by using 1-bromo-3,5-bis(trifluoromethyl)benzene as substrate, the product was isolated by silica gel column chromatography (Petroleum ether : EtOAc=6:1, Rf~0.5) as white solid (857 mg, 80%). Melting point: 160.8-164.6 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 2H), 7.86 (s, 1H), 7.32 – 7.28 (m, 1H), 7.24 – 7.18 (m, 1H), 7.06 – 7.01 (m, 1H), 6.96 – 6.90 (m, 1H), 3.38 – 3.11 (m, 4H), 1.39 (s, 6H), 1.04 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.2 , 143.1 , 138.7 , 134.7 – 134.3 (m), 130.4 (q, *J* = 32.7 Hz), 129.1 , 123.9 (q, *J* = 272.8 Hz), 123.2 – 122.8 (m), 122.4 , 120.7 , 116.8 , 70.1 , 69.3 , 30.3 , 29.9 .

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.59 .

HRMS (ESI) calcd for $C_{22}H_{24}F_6{}^{74}GeNO_3^+$ [(M+H)$^+$] 538.0872, found 538.0876.

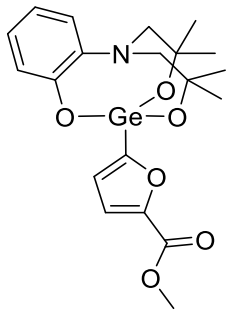


1x: 4,4,12,12-tetramethyl-2-(1-methyl-1H-indol-2-yl)-4,5-dihydro-2,6-(epoxyethano)benzo-[d][1,3,6,2]dioxazagermocine. The general procedure C was employed on 2 mmol scale by using 2-iodo-1-methyl-1H-indole as substrate, the product was isolated by silica gel column chromatography (Petroleum ether : EtOAc=6:1, Rf~0.5) as white solid (607 mg, 67%). Melting point: 175.0-182.3 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.60 (m, 1H), 7.35 – 7.31 (m, 1H), 7.30 – 7.27 (m, 1H), 7.21 – 7.16 (m, 2H), 7.12 (s, 1H), 7.06 – 7.01 (m, 2H), 6.93 – 6.87 (m, 1H), 4.01 (s, 3H), 3.34 – 3.09 (m, 4H), 1.38 (s, 6H), 1.04 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.5 , 139.6 , 139.2 , 139.0 , 128.8 , 128.3 , 122.5 , 121.5 , 120.9 , 120.3 , 118.6 , 116.9 , 111.3 , 109.2 , 69.9 , 69.2 , 33.2 , 30.3 , 30.0 .

HRMS (ESI) calcd for $C_{23}H_{28}{}^{74}GeN_2O_3Na^+$ [(M+Na)$^+$] 477.1209, found 477.1207.

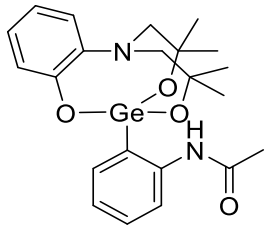


1y: methyl 5-(4,4,12,12-tetramethyl-4,5-dihydro-2,6-(epoxyethano)benzo[d][1,3,6,2]dioxaza-germocin-2-yl)furan-2-carboxylate. The general procedure C was employed on 5 mmol scale by using methyl 5-bromofuran-2-carboxylate as substrate, the product was isolated by silica gel column chromatography (Petroleum ether : EtOAc=2:1, Rf~0.3) as white solid (1.99 g, 89%). Melting point: 147.2-152.8 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.27 (m, 1H), 7.23 – 7.17 (m, 2H), 7.06 – 7.02 (m, 1H), 7.01 – 6.99 (m, 1H), 6.93 – 6.88 (m, 1H), 3.89 (s, 3H), 3.35 – 3.10 (m, 4H), 1.37 (s, 6H), 1.02 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.0 , 159.6 , 153.1 , 147.8 , 138.5 , 129.1 , 122.1 , 121.6 , 120.5 , 117.9 , 117.1 , 70.0 , 69.3 , 51.7 , 30.2 , 29.9 .

HRMS (ESI) calcd for $C_{20}H_{25}{}^{74}GeNO_6Na^+$ [(M+Na)$^+$] 472.0791, found 472.0789.

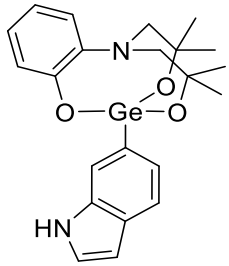


1z: N-(2-(4,4,12,12-tetramethyl-4,5-dihydro-2,6-(epoxyethano)benzo[d][1,3,6,2]dioxazagermocin-2-yl)phenyl)acetamide. The general procedure C was employed on 0.2 mmol scale by using N-(2-bromophenyl)acetamide as substrate, the product was isolated by silica gel column chromatography (Petroleum ether : EtOAc=1:1, Rf~0.3) as white solid (70.4 mg, 77%). Melting point: 177.8-181.5 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.10 (s, 1H), 8.47 – 8.36 (m, 1H), 7.89 – 7.81 (m, 1H), 7.40 – 7.35 (m, 1H), 7.32 – 7.28 (m, 1H), 7.21 – 7.16 (m, 1H), 7.14 – 7.09 (m, 1H), 7.01 – 6.97 (m, 1H), 6.94 – 6.89 (m, 1H), 3.35 – 3.10 (m, 4H), 2.13 (s, 3H), 1.40 (s, 6H), 1.06 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1 , 153.3 , 142.2 , 138.8 , 135.6 , 130.3 , 129.0 , 127.7 , 123.4 , 122.5 , 120.6 , 116.9 , 69.6 , 69.6 , 30.4 , 30.0 , 25.1 .

HRMS (ESI) calcd for $C_{22}H_{29}{}^{74}GeN_2O_4^+$ [$(M+H)^+$] 459.1339, found 459.1340.

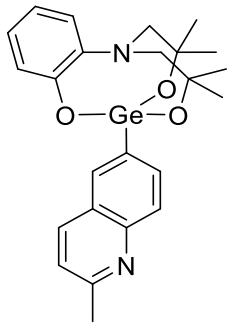


1a': 2-(1H-indol-6-yl)-4,4,12,12-tetramethyl-4,5-dihydro-2,6-(epoxyethano)benzo[d][1,3,6,2]-dioxazagermocine. The general procedure C was employed on 2 mmol scale by using 6-bromo-1H-indole as substrate, the product was isolated by silica gel column chromatography (Petroleum ether : EtOAc=2:1, Rf~0.3) as white solid (650 mg, 74%). Melting point: 190.2-196.1 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 8.04 – 7.99 (m, 1H), 7.67 – 7.61 (m, 2H), 7.29 – 7.26 (m, 1H), 7.17 – 7.12 (m, 1H), 7.10 – 7.07 (m, 1H), 7.02 – 6.99 (m, 1H), 6.90 – 6.85 (m, 1H), 6.47 – 6.42 (m, 1H), 3.29 – 3.07 (m, 4H), 1.37 (s, 6H), 1.04 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.1 , 139.5 , 135.9 , 131.4 , 128.9 , 128.6 , 124.7 , 124.5 , 122.8 , 120.3 , 120.0 , 117.2 , 116.9 , 102.1 , 70.0 , 68.9 , 30.5 , 30.1 .

HRMS (ESI) calcd for $C_{22}H_{26}{}^{74}GeN_2O_3Na^+$ [$(M+Na)^+$] 463.1053, found 463.1050.

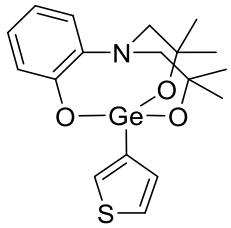


1b': 4,4,12,12-tetramethyl-2-(2-methylquinolin-6-yl)-4,5-dihydro-2,6-(epoxyethano)benzo[d]-[1,3,6,2]dioxazagermocine. The general procedure C was employed on 0.2 mmol scale by using 6-bromo-2-methylquinoline as substrate, the product was isolated by silica gel column chromatography (Petroleum ether : EtOAc=2:1, Rf~0.3) as white solid (83.7 mg, 90%). Melting point: 171.3-177.8 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 8.23 – 8.18 (m, 1H), 8.14 – 8.10 (m, 1H), 8.08 – 8.04 (m, 1H), 7.31 – 7.26 (m, 2H), 7.21 – 7.15 (m, 1H), 7.05 – 7.01 (m, 1H), 6.93 – 6.87 (m, 1H), 3.35 – 3.11 (m, 4H), 2.76 (s, 3H), 1.39 (s, 6H), 1.05 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.0 , 152.7 , 147.3 , 138.1 , 136.2 , 135.8 , 133.7 , 133.3 , 127.7 , 126.7 , 125.2 , 121.5 , 120.7 , 119.2 , 115.8 , 69.0 , 68.0 , 29.3 , 29.0 , 24.3 .

HRMS (ESI) calcd for $C_{24}H_{29}{}^{74}GeN_2O_3^+$ [$(M+H)^+$] 467.1390, found 467.1386.

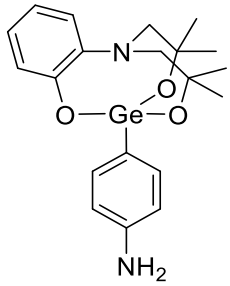


1c': 4,4,12,12-tetramethyl-2-(thiophen-3-yl)-4,5-dihydro-2,6-(epoxyethano)benzo[d][1,3,6,2]-dioxazagermocine. The general procedure C was employed on 2 mmol scale by using 3-bromothiophene as substrate, the product was isolated by silica gel column chromatography (Petroleum ether : EtOAc=6:1, Rf~0.5) as white solid (633 mg, 78%). Melting point: 159.4-163.9 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.84 (m, 1H), 7.49 – 7.46 (m, 1H), 7.42 – 7.39 (m, 1H), 7.30 – 7.26 (m, 1H), 7.19 – 7.14 (m, 1H), 7.02 – 6.99 (m, 1H), 6.91 – 6.86 (m, 1H), 3.32 – 3.08 (m, 4H), 1.36 (s, 6H), 1.01 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.8 , 139.1 , 137.8 , 132.5 , 131.6 , 128.7 , 125.0 , 122.5 , 120.1 , 116.9 , 70.0 , 68.9 , 304 , 30.0 .

HRMS (ESI) calcd for $C_{18}H_{23}{}^{74}GeNO_3SNa^+$ [$(M+Na)^+$] 430.0508, found 430.0507.

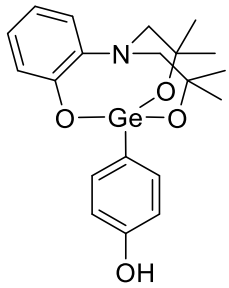


1d': 4-(4,4,12,12-tetramethyl-4,5-dihydro-2,6-(epoxyethano)benzo[d][1,3,6,2]dioxaza-germocin-2-yl)aniline. The general procedure C was employed on 0.2 mmol scale by using 4-bromoaniline as substrate, the product was isolated by silica gel column chromatography (Petroleum ether : EtOAc=2:1, Rf~0.3) as white solid (60.5 mg, 73%). Melting point: 173.1-176.0 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.7 Hz, 2H), 7.29 – 7.25 (m, 1H), 7.17 – 7.12 (m, 1H), 7.01 – 6.97 (m, 1H), 6.89 – 6.83 (m, 1H), 6.71 (d, *J* = 7.7 Hz, 2H), 3.47 (brs, 2H), 3.29 – 3.05 (m, 4H), 1.34 (s, 6H), 1.00 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.1 , 147.4 , 139.4 , 135.3 , 128.5 , 127.8 , 122.7 , 119.9 , 116.9 , 115.0 , 70.0 , 68.8 , 30.4 , 30.0 .

HRMS (ESI) calcd for $C_{20}H_{27}{}^{74}GeN_2O_3^+$ [$(M+H)^+$] 417.1233, found 417.1232.

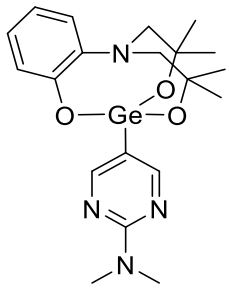


1e': 4-(4,4,12,12-tetramethyl-4,5-dihydro-2,6-(epoxyethano)benzo[d][1,3,6,2]dioxaza-germocin-2-yl)phenol. The general procedure C was employed on 0.2 mmol scale by using 4-bromophenol as substrate, the product was isolated by silica gel column chromatography (Petroleum ether : EtOAc=2:1, Rf~0.3) as white solid (69.1 mg, 83%). Melting point: 218.6-222.7 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.7 Hz, 2H), 7.36 – 7.31 (m, 1H), 7.25 – 7.19 (m, 1H), 7.09 – 7.04 (m, 1H), 6.96 – 6.90 (m, 1H), 6.78 (d, *J* = 7.7 Hz, 2H), 5.62 (brs, 1H), 3.38 – 3.13 (m, 4H), 1.42 (s, 6H), 1.07 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.8 , 153.8 , 139.2 , 135.5 , 129.8 , 128.7 , 122.6 , 120.0 , 116.9 , 115.4 , 70.0 , 68.9 , 30.3 , 30.0 .

HRMS (ESI) calcd for $C_{20}H_{25}{}^{74}GeNO_4Na^+$ [$(M+Na)^+$] 440.0893, found 440.0891.



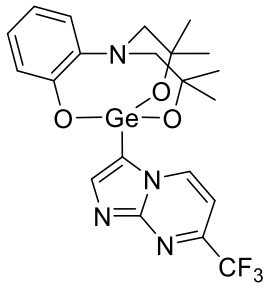
1f': N,N-dimethyl-5-(4,4,12,12-tetramethyl-4,5-dihydro-2,6-(epoxyethano)benzo[d][1,3,6,2]-

dioxazagermocin-2-yl)pyrimidin-2-amine. The general procedure C was employed on 0.2 mmol scale by using 5-bromo-N,N-dimethylpyrimidin-2-amine as substrate, the product was isolated by silica gel column chromatography (Petroleum ether : EtOAc=2:1, Rf~0.3) as white solid (65.0 mg, 73%). Melting point: 154.4-158.6 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (s, 2H), 7.29 – 7.25 (m, 1H), 7.20 – 7.15 (m, 1H), 6.99 – 6.95 (m, 1H), 6.91 – 6.86 (m, 1H), 3.30 – 3.09 (m, 4H), 3.19 (s, 6H), 1.33 (s, 6H), 0.98 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6 , 153.6 , 139.0 , 128.8 , 122.5 , 120.2 , 116.8 , 70.1 , 68.9 , 37.1 , 30.3 , 29.9 .

HRMS (ESI) calcd for $C_{20}H_{29}{}^{74}GeN_4O_3^+$ [$(M+H)^+$] 447.1451, found 447.1450.



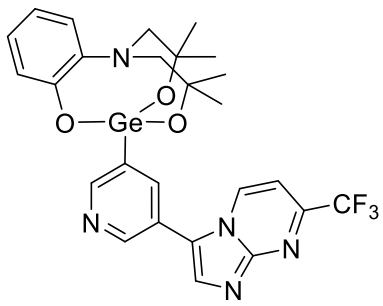
1g': 4,4,12,12-tetramethyl-2-(7-(trifluoromethyl)imidazo[1,2-a]pyrimidin-3-yl)-4,5-dihydro-2,6-(epoxyethano)benzo[d][1,3,6,2]dioxazagermocine. The general procedure C was employed on 1 mmol scale by using 3-bromo-7-(trifluoromethyl)imidazo[1,2-a]pyrimidine (**2b**) as substrate, the product was isolated by silica gel column chromatography (EtOAc, Rf~0.5) as white solid (387 mg, 76%). Melting point: 197.1-202.6 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.25 – 9.18 (m, 1H), 8.35 (s, 1H), 7.39 – 7.34 (m, 1H), 7.26 – 7.19 (m, 2H), 7.02 – 6.93 (m, 2H), 3.46 – 3.20 (m, 4H), 1.41 (s, 6H), 1.07 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.7 , 149.2 , 146.2 , 138.3 , 137.7 , 129.4 , 123.6 , 122.4 , 121.1 , 116.7 , 104.2 , 70.0 , 69.6 , 30.3 , 29.9 .

^{19}F NMR (376 MHz, $CDCl_3$) δ -68.13 .

HRMS (ESI) calcd for $C_{21}H_{24}F_3{}^{74}GeN_4O_3^+$ [$(M+H)^+$] 511.1013, found 511.1021.



1h': 4,4,12,12-tetramethyl-2-(5-(7-(trifluoromethyl)imidazo[1,2-a]pyrimidin-3-yl)pyridin-3-yl)-4,5-dihydro-2,6-(epoxyethano)benzo[d][1,3,6,2]dioxazagermocine. The general procedure C was employed on 0.5 mmol scale by using 3-(5-bromopyridin-3-yl)-7-(trifluoromethyl)-imidazo-[1,2-a]pyrimidine (**2c**) as substrate, the product was isolated by silica gel column chromatography (EtOAc, Rf~0.4) as white solid (217 mg, 74%). Melting point: 274.9-281.8 ºC.

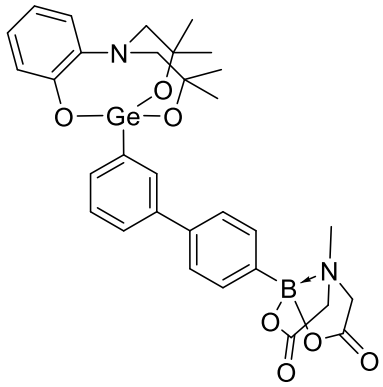
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.24 – 9.20 (m, 1H), 9.10 – 9.06 (m, 1H), 8.89 – 8.85 (m, 1H), 8.70 – 8.66 (m, 1H), 8.12 (s, 1H), 7.33 – 7.29 (m, 1H), 7.25 – 7.23 (m, 1H), 7.23 – 7.19 (m, 1H), 7.05 –

7.02 (m, 1H), 6.95 – 6.90 (m, 1H), 3.39 – 3.13 (m, 4H), 1.40 (s, 6H), 1.05 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.6 , 153.4 , 147.8 , 147.6 , 146.9 , 146.6 (q, *J* = 37.1 Hz), 140.3 , 138.8 , 135.8 , 134.4 , 129.02 , 128.1 , 122.4 , 120.5 (q, *J* = 275.3 Hz), 120.5 , 116.9 , 107.9 , 105.0 , 70.1 , 69.2 , 30.3 , 30.0 .

^{19}F NMR (376 MHz, $CDCl_3$) δ -68.33 .

HRMS (ESI) calcd for $C_{26}H_{27}F_3{}^{74}GeN_5O_3^+$ [$(M+H)^+$] 588.1278, found 588.1276.

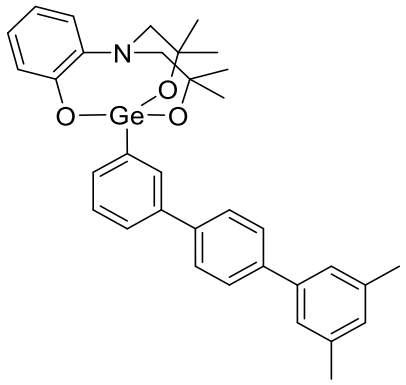


1i': 4-methyl-8-(3'-(4,4,12,12-tetramethyl-4,5-dihydro-2,6-(epoxyethano)benzo[d][1,3,6,2]dioxazagermocin-2-yl)-[1,1'-biphenyl]-4-yl)dihydro-4λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-b][1,3,2]oxazaborole-2,6(3H,5H)-dione. The reaction was performed in glassware under an atmosphere of Ar. **1p** (527 mg, 1.1 mmol), 4,4,5,5-tetramethyl-2-[4-(BMIDA)phenyl]-1,3,2-dioxaborolane (359 mg, 1.0 mmol), $Pd_2(dba)_3$ (11.5 mg, 2.5 mol%), SPhos (20.6 mg, 10 mol%) and K_2CO_3 (415 mg, 3.0 mmol) were weighed out on the benchtop, and transferred to an oven-dried Schlenk tube with stir bar. The Schlenk tube was evacuated and backfilled three times with argon. Acetonitrile (5 mL, 0.2 M) was then added to the Schlenk tube. The resulting mixture was stirred at 50 °C for 12 h. The reaction mixture was poured into a separatory funnel containing a mixture of water and EtOAc. The organic layer was separated, washed with brine, dried over Na_2SO_4, and filtered. Solvent was removed under reduced pressure to provide the crude product. The resulting **1i'** was isolated by silica gel column chromatography (EtOAc, Rf~0.4) as white solid (517 mg, 82%). Melting point: 167.2-173.5 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.92 – 7.87 (m, 1H), 7.65 (d, *J* = 8.3 Hz, 2H), 7.60 – 7.54 (m, 3H), 7.49 – 7.43 (m, 1H), 7.30 – 7.26 (m, 1H), 7.19 – 7.13 (m, 1H), 7.02 – 6.97 (m, 1H), 6.91 – 6.85 (m, 1H), 4.05 – 3.72 (m, 4H), 3.34 – 3.07 (m, 4H), 2.53 (s, 3H), 1.36 (s, 6H), 1.01 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0 , 153.8 , 143.1 , 140.1 , 139.2 , 133.6 , 132.9 , 132.7 , 128.8 , 128.5 , 128.2 , 127.3 , 122.6 , 120.2 , 116.9 , 70.0 , 68.9 , 61.8 , 47.7 , 30.4 , 30.0 .

HRMS (ESI) calcd for $C_{31}H_{35}B^{74}GeN_2O_7Na^+$ [$(M+Na)^+$] 655.1647, found 655.1656.

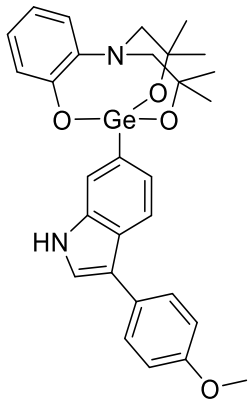


1j': 2-(3'',5''-dimethyl-[1,1':4',1''-terphenyl]-3-yl)-4,4,12,12-tetramethyl-4,5-dihydro-2,6-(epoxyethano)benzo[d][1,3,6,2]dioxazagermocine. The reaction was performed in glassware under an atmosphere of Ar. **1i'** (126 mg, 0.2 mmol), $Pd(OAc)_2$ (2.2 mg, 5 mol%) and SPhos (8.2 mg, 10 mol%) were weighed out on the benchtop, and transferred to an oven-dried Schlenk tube with stir bar. The Schlenk tube was evacuated and backfilled three times with argon. The 1-bromo-3,5-dimethylbenzene (33 μL, 0.24 mmol) was then added to the Schlenk tube via microsyringe, followed by K_3PO_4 (0.5 mL, 3.0 M aq., 7.5 eq.) and dioxane (2.5 mL). The resulting mixture was stirred at 60 °C for 12 h. The reaction mixture was poured into a separatory funnel containing a mixture of water and EtOAc. The organic layer was separated, washed with brine, dried over Na_2SO_4, and filtered. Solvent was removed under reduced pressure to provide the crude product. The resulting **1j'** was isolated by silica gel column chromatography (Petroleum ether : EtOAc=4:1, Rf~0.5) as thick oil (83 mg, 72%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.92 – 7.89 (m, 1H), 7.72 – 7.65 (m, 4H), 7.64 – 7.61 (m, 1H), 7.50 – 7.46 (m, 1H), 7.30 – 7.25 (m, 3H), 7.19 – 7.14 (m, 1H), 7.05 – 6.99 (m, 2H), 6.91 – 6.86 (m, 1H), 3.34 – 3.09 (m, 4H), 2.40 (s, 6H), 1.38 (s, 6H), 1.03 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.9 , 140.9 , 140.8 , 140.2 , 140.0 , 139.8 , 139.3 , 138.2 , 133.3 , 132.9 , 128.8 , 128.7 , 128.3 , 128.2 , 127.7 , 127.4 , 125.0 , 122.6 , 120.0 , 116.9 , 70.0 , 68.9 , 30.4 , 30.0 , 21.4 .

HRMS (ESI) calcd for $C_{34}H_{37}{}^{74}GeNO_3Na^+$ [$(M+Na)^+$] 604.1883, found 604.1886.



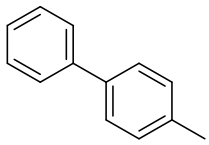
1k': 2-(3-(4-methoxyphenyl)-1H-indol-6-yl)-4,4,12,12-tetramethyl-4,5-dihydro-2,6-(epoxyethano)benzo[d][1,3,6,2]dioxazagermocine. 2,6-Bis(tert-butyl)pyridine (54 μL, 0.24 mmol) was added to the suspension of di(4-methoxyphenyl)iodonium tosylate[4] (123 mg, 0.24 mmol), **1a'** (87.8 mg, 0.2 mmol) and CuCl (1.0 mg, 5 mol%) in DCM (1.0 mL, 0.2 M). The resulting mixture was

stirred at 35 °C for 48 h. The reaction mixture was poured into a separatory funnel containing a mixture of water and EA. The organic layer was separated, washed with brine, dried over Na_2SO_4, and filtered. Solvent was removed under reduced pressure to provide the crude product. The resulting **1k'** was isolated by silica gel column chromatography (Petroleum ether : EtOAc=2:1, Rf~0.3) as thick oil (89.6 mg, 82%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.83 (m, 2H), 7.81 (s, 1H), 7.67 – 7.63 (m, 2H), 7.23 – 7.11 (m, 4H), 7.02 – 6.97 (m, 3H), 6.95 – 6.90 (m, 1H), 3.85 (s, 3H), 3.29 – 3.09 (m, 4H), 1.38 (s, 6H), 1.08 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.6 , 152.7 , 141.3 , 138.0 , 129.6 , 129.5 , 129.1 , 128.6 , 128.6 , 122.2 , 121.1 , 121.0 , 119.4 , 119.0 , 117.7 , 117.1 , 114.9 , 114.1 , 70.4 , 70.1 , 55.4 , 30.1 , 29.7 .

HRMS (ESI) calcd for $C_{29}H_{33}{}^{74}GeN_2O_4^+$ [$(M+H)^+$] 547.1652, found 547.1652.

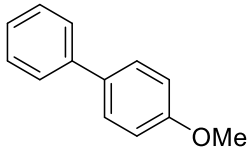


3a: 4-methyl-1,1'-biphenyl. The general procedure D was employed on 0.2 mmol scale by using **1e** and 1-chloro-4-methylbenzene as substrates, the product was isolated by silica gel column chromatography (Petroleum ether, Rf~0.7) as thick oil (23.9 mg, 71%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.55 (m, 2H), 7.51 – 7.47 (m, 2H), 7.45 – 7.40 (m, 2H), 7.34 – 7.29 (m, 1H), 7.27 – 7.23 (m, 2H), 2.39 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.2 , 138.4 , 137.0 , 129.5 , 128.7 , 127.0 , 127.0 , 127.0 , 21.1 .

Known compound.[5]

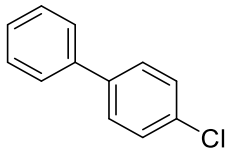


3b: 4-methoxy-1,1'-biphenyl. The general procedure D was employed on 0.2 mmol scale by using **1e** and 1-bromo-4-methoxybenzene as substrates, the product was isolated by silica gel column chromatography (Petroleum ether : EtOAc=50:1, Rf~0.5) as thick oil (35.0 mg, 95%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.49 (m, 4H), 7.43 – 7.37 (m, 2H), 7.32 – 7.27 (m, 1H), 6.97 (d, *J* = 8.4 Hz, 2H), 3.83 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.1 , 139.8 , 132.7 , 127.7 , 127.1 , 125.7 , 125.6 , 113.1 , 54.3 .

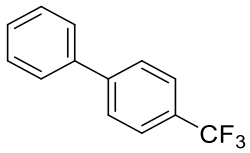
Known compound.[6]



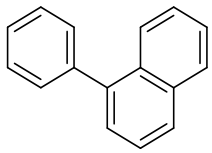
3c: 4-chloro-1,1'-biphenyl. The general procedure D was employed on 0.2 mmol scale by using **1e** and 1-bromo-4-chlorobenzene as substrates, the product was isolated by silica gel column chromatography (Petroleum ether, Rf~0.7) as thick oil (36.6 mg, 97%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.48 (m, 4H), 7.45 – 7.32 (m, 5H).

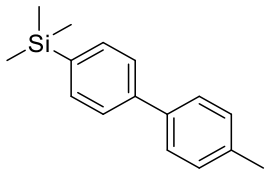
^{13}C NMR (101 MHz, $CDCl_3$) δ 140.0 , 139.6 , 133.4 , 128.9 , 128.9 , 128.4 , 127.6 , 127.0 .
Known compound.[7]



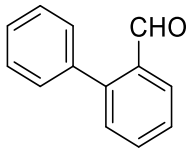
3d: 4-(trifluoromethyl)-1,1'-biphenyl. The general procedure D was employed on 0.2 mmol scale by using **1e** and 1-bromo-4-(trifluoromethyl)benzene as substrates, the product was isolated by silica gel column chromatography (Petroleum ether, Rf~0.7) as thick oil (41.3 mg, 93%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.65 (m, 4H), 7.60 – 7.56 (m, 2H), 7.49 – 7.43 (m, 2H), 7.42 – 7.37 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.8 – 143.6 (m), 138.7 , 128.3 (q, *J* = 32.4 Hz), 127.9 , 127.1 , 126.4 , 126.2 , 124.7 – 124.6 (m), 123.3 (q, *J* = 273.1).
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.36 .
Known compound.[8]



3e: 1-phenylnaphthalene. The general procedure D was employed on 0.2 mmol scale by using **1e** and 1-bromonaphthalene as substrates, the product was isolated by silica gel column chromatography (Petroleum ether, Rf~0.6) as thick oil (38.8 mg, 95%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.86 (m, 2H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.52 – 7.44 (m, 6H), 7.43 – 7.37 (m, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 140.8 , 140.3 , 133.8 , 131.6 , 130.1 , 128.3 , 127.6 , 127.2 , 126.9 , 126.0 , 125.8 , 125.4 .
Known compound.[9]



3f: trimethyl(4'-methyl-[1,1'-biphenyl]-4-yl)silane. The general procedure D was employed on 0.2 mmol scale by using **1r** and 1-bromo-4-methylbenzene as substrates, the product was isolated by silica gel column chromatography (Petroleum ether, Rf~0.7) as thick oil (43.3 mg, 90%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.55 (m, 4H), 7.53 – 7.46 (m, 2H), 7.27 – 7.21 (m, 2H), 2.39 (s, 3H), 0.30 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 141.5 , 138.8 , 138.3 , 137.1 , 133.8 , 129.5 , 127.0 , 126.3 , 21.1 , -1.1 .
Known compound.[10]

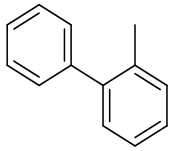


3g: [1,1'-biphenyl]-2-carbaldehyde. The general procedure D was employed on 0.2 mmol scale by using **1e** and 2-bromobenzaldehyde as substrates, the product was isolated by silica gel column chromatography (Petroleum ether : EtOAc=40:1, Rf~0.4) as thick oil (35.7 mg, 98%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.02 – 9.95 (m, 1H), 8.06 – 8.00 (m, 1H), 7.67 – 7.62 (m, 1H), 7.52 – 7.44 (m, 5H), 7.41 – 7.37 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.5 , 146.0 , 137.8 , 133.7 , 133.6 , 130.8 , 130.1 , 128.4 , 128.1 , 127.8 , 127.6 .

Known compound.[9]

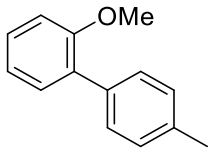


3h: 2-methyl-1,1'-biphenyl. The general procedure D was employed on 0.2 mmol scale by using **1e** and 1-bromo-2-methylbenzene as substrates, the product was isolated by silica gel column chromatography (Petroleum ether, Rf~0.7) as thick oil (29.6 mg, 88%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 2H), 7.35 – 7.30 (m, 3H), 7.27 – 7.22 (m, 4H), 2.27 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.9 , 140.9 , 134.3 , 129.2 , 128.7 , 128.1 , 127.0 , 126.2 , 125.7 , 124.7 , 19.4 .

Known compound.[9]

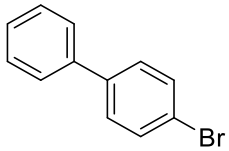


3i: 2-methoxy-4'-methyl-1,1'-biphenyl. The general procedure D was employed on 0.2 mmol scale by using **1k** and 1-bromo-4-methylbenzene as substrates, the product was isolated by silica gel column chromatography (Petroleum ether : EtOAc=50:1, Rf~0.5) as thick oil (38.9 mg, 98%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.40 (m, 2H), 7.32 – 7.27 (m, 2H), 7.23 – 7.20 (m, 2H), 7.03 – 6.99 (m, 1H), 6.98 – 6.95 (m, 1H), 3.80 (s, 3H), 2.38 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5 , 136.6 , 135.6 , 130.8 , 130.7 , 129.4 , 128.8 , 128.4 , 120.8 , 111.2 , 55.5 , 21.3 .

Known compound.[11]



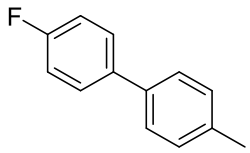
3j: 4-bromo-1,1'-biphenyl. The general procedure D was employed on 0.2 mmol scale by using **1e**

and 1-bromo-4-iodobenzene as substrates, the product was isolated by silica gel column chromatography (Petroleum ether, Rf~0.7) as white solid (34.0 mg, 73%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.51 (m, 4H), 7.47 – 7.41 (m, 4H), 7.38 – 7.33 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.1 , 140.0 , 131.9 , 128.9 , 128.8 , 127.7 , 127.0 , 121.5 .

Known compound.[5]



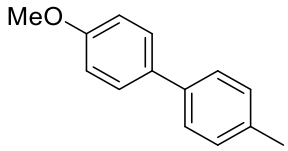
3k: 4-fluoro-4'-methyl-1,1'-biphenyl. The general procedure D was employed on 0.2 mmol scale by using **1g** and 1-chloro-4-methylbenzene as substrates, the product was isolated by silica gel column chromatography (Petroleum ether, Rf~0.7) as thick oil (23.1 mg, 62%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.47 (m, 2H), 7.43 (d, *J* = 7.7 Hz, 2H), 7.23 (d, *J* = 7.7 Hz, 2H), 7.14 – 7.05 (m, 2H), 2.38 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3 (d, *J* = 246.0 Hz), 137.4 , 137.3 (d, *J* = 3.2 Hz), 137.0 , 129.5 , 128.4 (d, *J* = 8.0 Hz), 126.8 , 115.5 (d, *J* = 21.4 Hz), 21.1 .

^{19}F NMR (376 MHz, $CDCl_3$) δ -116.27 .

Known compound.[12]

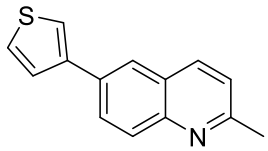


3l: 4-methoxy-4'-methyl-1,1'-biphenyl. The general procedure D was employed on 0.2 mmol scale by using **1h** and 1-chloro-4-methylbenzene as substrates, the product was isolated by silica gel column chromatography (Petroleum ether : EtOAc=50:1, Rf~0.5) as thick oil (25.0 mg, 63%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 7.6 Hz, 2H), 7.22 (d, *J* = 7.6 Hz, 2H), 6.96 (d, *J* = 8.4 Hz, 2H), 3.83 (s, 3H), 2.38 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9 , 136.9 , 135.3 , 132.7 , 128.4 , 126.9 , 125.5 , 113.1 , 54.3 , 20.0 .

Known compound.[13]

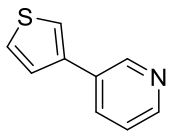


3m: 2-methyl-6-(thiophen-3-yl)quinolone. The general procedure D was employed on 0.2 mmol scale by using **1c'** and 6-bromo-2-methylquinoline as substrates, the product was isolated by silica gel column chromatography (Petroleum ether : EtOAc=3:1, Rf~0.5) as thick oil (39.6 mg, 88%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 8.01 (m, 2H), 7.96 – 7.92 (m, 2H), 7.58 – 7.55 (m, 1H), 7.51 – 7.48 (m, 1H), 7.44 – 7.41 (m, 1H), 7.30 – 7.26 (m, 1H), 2.75 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8 , 147.1 , 141.6 , 136.3 , 133.1 , 129.0 , 128.6 , 126.7 , 126.6 , 126.3 , 124.2 , 122.5 , 121.0 , 25.3 .

HRMS (ESI) calcd for $C_{14}H_{12}NS^+$ [(M+H)$^+$] 226.0690, found 226.0685.

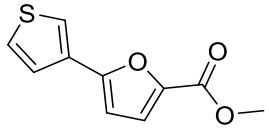


3n: 3-(thiophen-3-yl)pyridine. The general procedure D was employed on 0.2 mmol scale by using **1c'** and 3-bromopyridine as substrates, the product was isolated by silica gel column chromatography (Petroleum ether : EtOAc=2:1, Rf~0.5) as thick oil (30.3 mg, 94%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (s, 1H), 8.56 – 8.51 (m, 1H), 7.90 – 7.84 (m, 1H), 7.55 – 7.51 (m, 1H), 7.47 – 7.42 (m, 1H), 7.42 – 7.38 (m, 1H), 7.36 – 7.30 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.1 , 147.6 , 138.8 , 133.6 , 131.6 , 127.0 , 125.9 , 123.7 , 121.5 .

Known compound.[14]

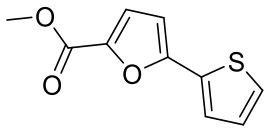


3o & 3t: methyl 5-(thiophen-3-yl)furan-2-carboxylate. The general procedure D was employed on 0.2 mmol scale by using **1c'** and methyl 5-bromofuran-2-carboxylate, or **1y** and 3-bromothiophene as substrates, the product was isolated by silica gel column chromatography (Petroleum ether : EtOAc=10:1, Rf~0.3) as thick oil (3o, 34.1 mg, 82%; 3t, 30.4 mg, 73%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.68 (m, 1H), 7.41 – 7.35 (m, 2H), 7.24 – 7.20 (m, 1H), 6.58 – 6.54 (m, 1H), 3.91 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2 , 154.4 , 142.9 , 131.3 , 126.7 , 124.9 , 122.1 , 120.0 , 106.7 , 51.8 .

HRMS (ESI) calcd for $C_{10}H_9O_3S^+$ [(M+H)$^+$] 209.0272, found 209.0272.

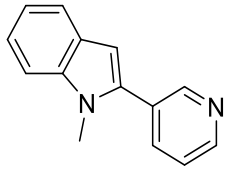


3p: methyl 5-(thiophen-2-yl)furan-2-carboxylate. The general procedure D was employed on 0.2 mmol scale by using **1y** and 2-bromothiophene as substrates, the product was isolated by silica gel column chromatography (Petroleum ether : EtOAc=10:1, Rf~0.3) as thick oil (25.0 mg, 60%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.43 (m, 1H), 7.36 – 7.31 (m, 1H), 7.23 – 7.20 (m, 1H), 7.09 – 7.05 (m, 1H), 6.60 – 6.55 (m, 1H), 3.91 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0 , 153.0 , 143.0 , 132.2 , 127.9 , 126.3 , 125.1 , 120.1 , 106.8 , 51.9 .

Known compound.[15]

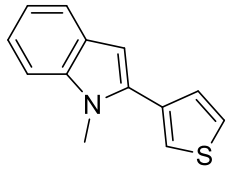


3q: 1-methyl-2-(pyridin-3-yl)-1H-indole. The general procedure D was employed on 0.2 mmol scale by using **1x** and 3-bromopyridine as substrates, the product was isolated by silica gel column chromatography (Petroleum ether : EtOAc=2:1, Rf~0.6) as thick oil (30.4 mg, 73%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 – 8.75 (m, 1H), 8.69 – 8.60 (m, 1H), 7.86 – 7.78 (m, 1H), 7.68 – 7.62 (m, 1H), 7.44 – 7.36 (m, 2H), 7.31 – 7.26 (m, 1H), 7.19 – 7.14 (m, 1H), 6.66 – 6.60 (m, 1H), 3.75 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.8 , 148.7 , 138.6 , 137.6 , 136.5 , 129.0 , 127.8 , 123.4 , 122.4 , 120.8 , 120.2 , 109.8 , 102.9 , 31.2 .

Known compound.[16]

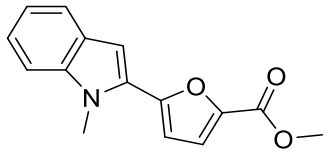


3r: 1-methyl-2-(thiophen-3-yl)-1H-indole. The general procedure D was employed on 0.2 mmol scale by using **1x** and 3-bromothiophene as substrates, the product was isolated by silica gel column chromatography (Petroleum ether, Rf~0.6) as thick oil (31.1 mg, 73%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.57 (m, 1H), 7.43 – 7.36 (m, 1H), 7.39 – 7.33 (m, 1H), 7.36 – 7.29 (m, 1H), 7.28 – 7.16 (m, 2H), 7.17 – 7.08 (m, 1H), 6.58 (s, 1H), 3.76 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.1 , 136.4 , 133.4 , 128.5 , 127.9 , 125.9 , 123.3 , 121.8 , 120.5 , 119.9 , 109.5 , 101.5 , 31.2 .

Known compound.[17]

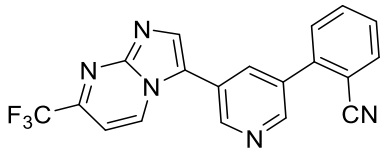


3s: methyl 5-(1-methyl-1H-indol-2-yl)furan-2-carboxylate. The general procedure D was employed on 0.2 mmol scale by using **1x** and methyl 5-bromofuran-2-carboxylate as substrates, the product was isolated by silica gel column chromatography (Petroleum ether : EtOAc=10:1, Rf~0.4) as thick oil (23.0 mg, 45%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.58 (m, 1H), 7.39 – 7.31 (m, 1H), 7.31 – 7.21 (m, 2H), 7.18 – 7.09 (m, 1H), 6.93 (s, 1H), 6.71 – 6.67 (m, 1H), 3.96 (s, 3H), 3.92 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1 , 151.2 , 143.6 , 138.7 , 129.5 , 127.4 , 123.0 , 121.1 , 120.3 , 119.7 , 109.6 , 109.4 , 103.4 , 52.0 , 31.7 .

HRMS (ESI) calcd for $C_{15}H_{14}NO_3^+$ $[(M+H)^+]$ 256.0974, found 256.0974.



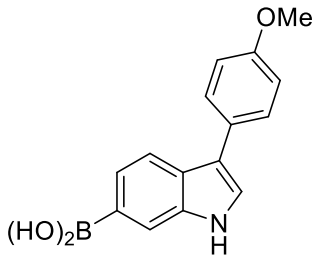
3u: 2-(5-(7-(trifluoromethyl)imidazo[1,2-a]pyrimidin-3-yl)pyridin-3-yl)benzonitrile. The general procedure D was employed on 0.2 mmol scale by using **1h'** and 2-bromobenzonitrile as substrates, the product was isolated by silica gel column chromatography (EtOAc, Rf~0.4) as light yellow solid (52.6 mg, 72%). Melting point: 181.9-188.4 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.30 – 9.25 (m, 1H), 8.83 – 8.79 (m, 1H), 8.78 – 8.74 (m, 1H), 8.65 – 8.61 (m, 1H), 8.20 (s, 1H), 7.87 – 7.82 (m, 1H), 7.78 – 7.72 (m, 1H), 7.65 – 7.60 (m, 1H), 7.59 – 7.53 (m, 1H), 7.29 – 7.26 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.1 , 147.6 (q, *J* = 37.5 Hz), 147.3 , 146.9 , 146.2 , 141.2 , 135.0 , 134.3 , 134.2 , 134.0 , 133.3 , 130.1 , 128.8 , 128.5 , 120.4 (d, *J* = 275.2 Hz), 118.2 , 111.5 , 108.5 , 105.4 – 105.1 (m).

^{19}F NMR (376 MHz, $CDCl_3$) δ -68.41 .

HRMS (ESI) calcd for $C_{19}H_{11}F_3N_5^+$ [$(M+H)^+$] 366.0967, found 366.0965.

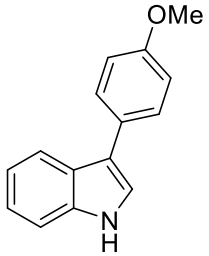


4a: (3-(4-methoxyphenyl)-1*H*-indol-6-yl)boronic acid. 2,6-Bis(tert-butyl)pyridine (54 μL, 0.24 mmol) was added to the suspension of di(4-methoxyphenyl)iodonium tosylate[4] (123 mg, 0.24 mmol), indole-6-boronic acid (32.2 mg, 0.2 mmol) and CuCl (1.0 mg, 5 mol%) in DCM (1.0 mL, 0.2 M). The resulting mixture was stirred at 35 °C for 48 h. The reaction mixture was poured into a separatory funnel containing a mixture of water and EA. The organic layer was separated, washed with brine, dried over Na_2SO_4, and filtered. Solvent was removed under reduced pressure to provide the crude product. The resulting **4a** was isolated by silica gel column chromatography (Petroleum ether : EtOAc=1:1, Rf~0.3) as thick oil (29.3 mg, 55%).

^{1}H NMR (400 MHz, Acetone-d6) δ 10.44 (s, 1H), 8.05 (s, 1H), 7.87 – 7.84 (m, 1H), 7.67 – 7.65 (m, 1H), 7.63 (d, J = 8.9 Hz, 2H), 7.58 – 7.56 (m, 1H), 7.03 (d, J = 8.9 Hz, 2H), 7.01 (s, 2H), 3.83 (s, 3H).

^{13}C NMR (101 MHz, Acetone-d6) δ 157.9 , 137.2 , 128.7 , 128.0 , 127.4 , 125.2 , 123.0 , 118.2 , 118.1 , 116.7 , 114.1 , 54.6 .

HRMS (ESI) calcd for $C_{15}H_{15}BNO_3^+$ [$(M+H)^+$] 268.1145, found 268.1137.

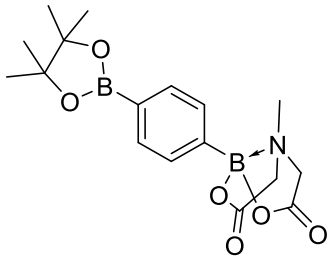


4b: 3-(4-methoxyphenyl)-1*H*-indole. 2,6-Bis(tert-butyl)pyridine (54 μL, 0.24 mmol) was added to the suspension of di(4-methoxyphenyl)iodonium tosylate[4] (123 mg, 0.24 mmol), indole-6-boronic acid (32.2 mg, 0.2 mmol) and CuCl (1.0 mg, 5 mol%) in DCM (1.0 mL, 0.2 M). The resulting mixture was stirred at 35 °C for 48 h. The reaction mixture was poured into a separatory funnel containing a mixture of water and EA. The organic layer was separated, washed with brine, dried over Na_2SO_4, and filtered. Solvent was removed under reduced pressure to provide the crude product. The resulting **4b** was isolated by silica gel column chromatography (Petroleum ether : EtOAc=4:1, Rf~0.4) as thick oil (6.7 mg, 15%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.91 – 7.87 (m, 1H), 7.59 (d, J = 8.8 Hz, 2H), 7.46 – 7.39 (m, 1H), 7.31 – 7.29 (m, 1H), 7.25 – 7.22 (m, 1H), 7.20 – 7.16 (m, 1H), 7.00 (d, J = 8.8 Hz, 2H), 3.86 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.1 , 136.5 , 128.6 , 128.1 , 125.9 , 122.3 , 121.1 , 120.1 , 119.7 , 118.0 , 114.2 , 111.3 , 55.4 .

HRMS (ESI) calcd for $C_{15}H_{14}NO^+$ [$(M+H)^+$] 224.1075, found 224.1068.



4,4,5,5-tetramethyl-2-[4-(BMIDA)phenyl]-1,3,2-dioxaborolane. All reactions were performed in oven-dried glassware under an atmosphere of Ar. (4-bromophenyl)boronic acid (2.01 g, 10 mmol) and 2,2'-(methylazanediyl)diacetic acid (1.47 g, 10 mmol) were weighed out on the benchtop, and transferred to an oven-dried Schlenk tube with stir bar. The Schlenk tube was evacuated and backfilled three times with argon. DMSO (15 mL) was then added to the Schlenk tube, followed by toluene (150 mL). The resulting mixture was stirred at 60 °C for 12 h. The reaction mixture was poured into a separatory funnel containing a mixture of water and EtOAc. The organic layer was separated, washed with brine, dried over Na_2SO_4, and filtered. Solvent was removed under reduced pressure to provide the crude product. The 4-bromophenyl MIDA boronate was isolated by recrystallization from DCM as white solid[18] (1.78 g, 57%). 4-Bromophenyl MIDA boronate (1.25 g, 4 mmol), $B_2(pin)_2$ (4.06 g, 16 mmol), $Pd(dppf)Cl_2$ (151 mg, 5 mol%) and KOAc (800 mg, 8 mmol) were weighed out on the benchtop, and transferred to an oven-dried Schlenk tube with stir bar. The Schlenk tube was evacuated and backfilled three times with argon. The DMF (40 mL, 0.1 M) was then added to the Schlenk tube. The resulting mixture was stirred at 90 °C for 24 h. The reaction mixture was poured into a separatory funnel containing a mixture of water and DCM. The organic

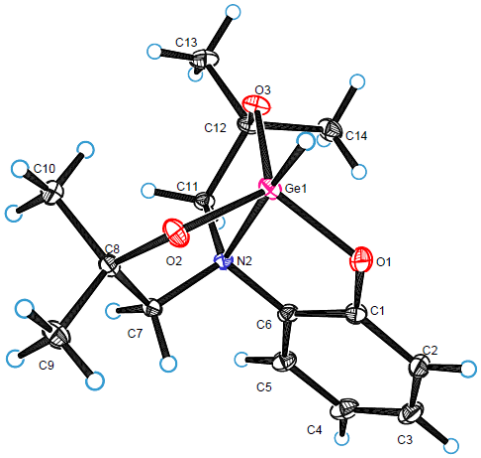
layer was separated, washed with brine, dried over Na_2SO_4, and filtered. Solvent was removed under reduced pressure to provide the crude product. The resulting 4,4,5,5-tetramethyl-2-[4-(BMIDA)phenyl]-1,3,2-dioxaborolane was isolated by recrystallization from DCM as off-white solid (690 mg, 48%). Melting point: 268.6-275.6 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 1H), 4.06 – 3.72 (m, 4H), 2.51 (s, 3H), 1.35 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5 , 134.5 , 131.5 , 83.9 , 61.8 , 47.6 , 24.9 .

HRMS (ESI) calcd for $C_{17}H_{24}B_2NO_6^+$ $[(M+H)^+]$ 360.1790, found 360.1790.

Crystal Structure and Data of II



II Ge–H

Table S1 Crystal data and structure refinement for **II**.

Identification code	**II**
Empirical formula	$C_{14}H_{21}GeNO_3$
Formula weight	323.91
Temperature/K	150(1)
Crystal system	orthorhombic
Space group	Pbca
a/Å	13.7717(2)
b/Å	11.15180(10)
c/Å	18.9206(2)
α /°	90
β /°	90
γ /°	90
Volume/Å3	2905.81(6)
Z	8
ρ calcg/cm3	1.481
μ /mm-1	2.904
F(000)	1344.0
Crystal size/mm3	0.240 × 0.220 × 0.220
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.348 to 142.298
Index ranges	-16 ⩽ h ⩽ 10, -13 ⩽ k ⩽ 11, -14 ⩽ l ⩽ 23
Reflections collected	7116
Independent reflections	2744 [Rint = 0.0215, Rsigma = 0.0206]
Data/restraints/parameters	2744/0/181
Goodness-of-fit on F2	1.054
Final R indexes [I>=2σ (I)]	R1 = 0.0288, wR2 = 0.0803
Final R indexes [all data]	R1 = 0.0306, wR2 = 0.0820
Largest diff. peak/hole / e Å-3	0.60/-0.48

Table S2 Fractional Atomic Coordinates (×104) and Equivalent Isotropic Displacement Parameters (Å2×103) for **II**. Ueq is defined as 1/3 of of the trace of the orthogonalised UIJ tensor.

Atom	x	y	z	U(eq)
Ge1	4006.9(2)	5506.2(2)	3434.5(2)	17.40(12)
O3	5013.2(9)	4865.1(11)	3896.2(7)	21.3(3)
O2	2832.6(10)	5528.2(10)	3851.8(8)	22.1(3)
O1	4014.9(10)	5526.3(11)	2460.1(8)	25.2(3)
N2	3641.1(10)	3591.6(13)	3249.6(8)	15.0(3)
C6	3685.2(13)	3438.0(16)	2488.8(9)	17.9(4)
C11	4371.7(12)	2890.6(15)	3650.8(9)	17.3(4)
C7	2627.7(13)	3462.9(16)	3514.2(9)	17.6(4)
C12	5290.9(13)	3645.6(16)	3773.2(10)	19.8(4)
C5	3532.1(13)	2350.7(17)	2151.2(10)	23.6(4)
C1	3849.2(14)	4487.0(16)	2112.0(11)	21.8(4)
C8	2403.1(13)	4421.2(15)	4073.5(10)	18.7(4)
C4	3543.7(15)	2309(2)	1417.2(11)	30.1(5)
C10	2775.4(14)	4100.4(18)	4809.8(10)	24.4(4)
C2	3846.1(16)	4441.7(19)	1373.5(12)	27.9(5)
C14	5974.8(13)	3597(2)	3139.3(12)	26.8(5)
C13	5796.9(15)	3192.3(19)	4437.8(11)	29.2(5)
C3	3695.7(15)	3358(2)	1037.8(11)	30.8(5)
C9	1303.8(14)	4602.8(18)	4096.6(12)	26.7(5)

Table S3 Anisotropic Displacement Parameters (Å2×103) for **II**. The Anisotropic displacement factor exponent takes the form: -2π2[h2a*2U11+2hka*b*U12+…].

Atom	U11	U22	U33	U23	U13	U12
Ge1	14.58(16)	14.81(16)	22.81(17)	1.18(7)	-0.09(8)	-0.51(7)
O3	17.4(6)	17.2(6)	29.4(7)	-3.8(6)	-5.6(5)	0.5(5)
O2	18.8(7)	16.3(6)	31.3(8)	-0.3(5)	4.0(6)	-0.6(5)
O1	30.0(8)	22.5(7)	23.1(7)	7.1(5)	-1.7(6)	-5.6(5)
N2	13.1(7)	17.5(7)	14.4(7)	1.8(6)	-1.9(6)	0.2(6)
C6	13.5(8)	23.5(9)	16.9(9)	0.1(7)	-1.6(6)	3.1(7)
C11	16.4(9)	16.7(8)	18.9(8)	2.1(7)	-4.0(7)	1.3(7)
C7	14.7(9)	19.6(9)	18.5(8)	1.1(7)	-1.8(7)	-2.4(7)
C12	16.1(8)	17.9(8)	25.4(9)	-1.5(7)	-4.1(7)	1.9(7)
C5	23.5(9)	24.9(9)	22.3(9)	-2.3(8)	-4.1(8)	6.0(8)
C1	16.4(8)	27.8(11)	21.2(10)	3.3(7)	-1.8(7)	0.6(7)
C8	15.6(9)	19.4(9)	21.1(9)	1.3(7)	1.3(7)	-2.4(7)
C4	28.9(11)	37.5(12)	23.9(10)	-9.7(9)	-5.8(8)	9.3(9)
C10	23.4(9)	31.2(10)	18.6(9)	-0.8(8)	1.1(7)	-1.7(8)
C2	21.5(10)	40.4(13)	21.7(10)	9.4(8)	-0.2(9)	0.1(8)
C14	16(1)	31.2(11)	33.3(12)	-3.7(9)	2.8(8)	1.9(7)
C13	26.5(10)	29.2(10)	32.0(11)	-1.0(9)	-13.4(9)	3.0(8)
C3	24.8(10)	51.5(13)	16.1(9)	-1.5(9)	-1.2(7)	6.6(10)
C9	16.8(9)	29.7(10)	33.4(11)	-1.3(8)	3.1(8)	1.4(8)

Table S4 Bond Lengths for **II**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ge1	O3	1.7873(13)	C6	C1	1.388(3)
Ge1	O2	1.7998(14)	C11	C12	1.538(2)
Ge1	O1	1.8439(16)	C7	C8	1.535(2)
Ge1	N2	2.2216(15)	C12	C13	1.524(3)
O3	C12	1.432(2)	C12	C14	1.526(3)
O2	C8	1.432(2)	C5	C4	1.390(3)
O1	C1	1.352(2)	C1	C2	1.398(3)
N2	C6	1.451(2)	C8	C10	1.527(3)
N2	C11	1.483(2)	C8	C9	1.528(3)
N2	C7	1.490(2)	C4	C3	1.389(3)
C6	C5	1.387(3)	C2	C3	1.381(3)

Table S5 Bond Angles for **II**.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
O3	Ge1	O2	119.19(6)	O3	C12	C13	107.65(15)
O3	Ge1	O1	119.27(6)	O3	C12	C14	109.04(15)
O2	Ge1	O1	116.35(6)	C13	C12	C14	110.77(16)
O3	Ge1	N2	82.44(5)	O3	C12	C11	108.94(14)
O2	Ge1	N2	83.02(5)	C13	C12	C11	108.61(15)
O1	Ge1	N2	81.69(6)	C14	C12	C11	111.74(15)
C12	O3	Ge1	120.51(11)	C6	C5	C4	119.22(19)
C8	O2	Ge1	119.21(11)	O1	C1	C6	119.97(18)
C1	O1	Ge1	118.39(12)	O1	C1	C2	121.20(18)
C6	N2	C11	114.66(14)	C6	C1	C2	118.82(18)
C6	N2	C7	111.18(13)	O2	C8	C10	109.30(15)
C11	N2	C7	114.38(14)	O2	C8	C9	107.66(15)
C6	N2	Ge1	105.08(11)	C10	C8	C9	109.73(17)
C11	N2	Ge1	105.79(10)	O2	C8	C7	108.36(15)
C7	N2	Ge1	104.60(10)	C10	C8	C7	113.46(15)
C5	C6	C1	121.67(17)	C9	C8	C7	108.15(16)
C5	C6	N2	123.64(17)	C3	C4	C5	119.34(19)
C1	C6	N2	114.63(16)	C3	C2	C1	119.46(19)
N2	C11	C12	110.31(14)	C2	C3	C4	121.48(19)
N2	C7	C8	110.69(14)				

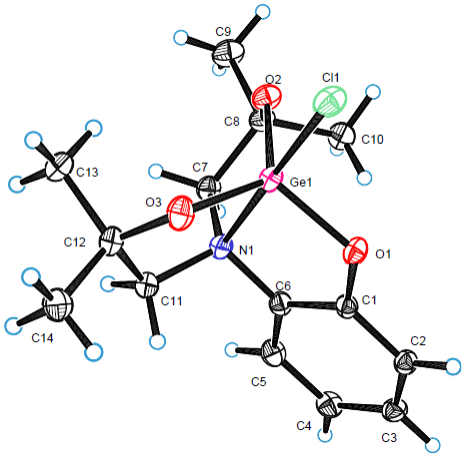
Table S6 Torsion Angles for **II**.

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
O2	Ge1	O3	C12	95.85(13)	Ge1	O3	C12	C11	-36.20(19)
O1	Ge1	O3	C12	-57.78(14)	N2	C11	C12	O3	36.7(2)
N2	Ge1	O3	C12	18.25(13)	N2	C11	C12	C13	153.68(15)
O3	Ge1	O2	C8	-57.82(15)	N2	C11	C12	C14	-83.84(18)
O1	Ge1	O2	C8	96.56(14)	C1	C6	C5	C4	0.0(3)
N2	Ge1	O2	C8	19.45(13)	N2	C6	C5	C4	176.89(17)
O3	Ge1	O1	C1	74.39(14)	Ge1	O1	C1	C6	-0.4(2)
O2	Ge1	O1	C1	-79.97(14)	Ge1	O1	C1	C2	-179.96(15)
N2	Ge1	O1	C1	-2.05(13)	C5	C6	C1	O1	-178.67(17)
C11	N2	C6	C5	62.2(2)	N2	C6	C1	O1	4.2(3)
C7	N2	C6	C5	-69.5(2)	C5	C6	C1	C2	0.9(3)
Ge1	N2	C6	C5	177.89(15)	N2	C6	C1	C2	-176.25(17)
C11	N2	C6	C1	-120.77(17)	Ge1	O2	C8	C10	85.40(16)
C7	N2	C6	C1	107.55(18)	Ge1	O2	C8	C9	-155.46(13)
Ge1	N2	C6	C1	-5.06(18)	Ge1	O2	C8	C7	-38.70(19)
C6	N2	C11	C12	92.34(18)	N2	C7	C8	O2	40.03(19)
C7	N2	C11	C12	-137.53(15)	N2	C7	C8	C10	-81.55(18)
Ge1	N2	C11	C12	-22.96(16)	N2	C7	C8	C9	156.47(15)
C6	N2	C7	C8	-137.85(15)	C6	C5	C4	C3	-0.8(3)
C11	N2	C7	C8	90.33(18)	O1	C1	C2	C3	178.55(19)
Ge1	N2	C7	C8	-24.94(15)	C6	C1	C2	C3	-1.0(3)
Ge1	O3	C12	C13	-153.79(13)	C1	C2	C3	C4	0.2(3)
Ge1	O3	C12	C14	85.99(16)	C5	C4	C3	C2	0.7(3)

Table S7 Hydrogen Atom Coordinates (Å×104) and Isotropic Displacement Parameters (Å2×103) for **II**.

Atom	x	y	z	U(eq)
H11A	4538	2171	3390	21
H11B	4101	2650	4102	21
H7A	2543	2672	3719	21
H7B	2177	3542	3123	21
H5	3423	1658	2413	28
H4	3451	1585	1182	36
H10A	3472	4077	4805	37
H10B	2528	3329	4945	37
H10C	2560	4694	5143	37
H2	3945	5136	1111	33
H14A	5642	3881	2726	40
H14B	6183	2785	3064	40
H14C	6530	4095	3229	40
H13A	6397	3617	4501	44
H13B	5927	2350	4391	44
H13C	5386	3324	4840	44
H3	3696	3330	547	37
H9A	1147	5194	4447	40
H9B	993	3858	4214	40
H9C	1080	4870	3643	40
H1	4227(17)	6720(20)	3514(11)	21(6)

Crystal Structure and Data of IV



IV Ge–Cl

Table S8 Crystal data and structure refinement for **IV**.

Identification code	**IV**
Empirical formula	$C_{14}H_{20}ClGeNO_3$
Formula weight	358.35
Temperature/K	150(1)
Crystal system	monoclinic
Space group	P21/n
a/Å	14.8342(3)
b/Å	13.3798(3)
c/Å	16.4653(4)
α /°	90
β /°	96.777(2)
γ /°	90
Volume/Å3	3245.18(13)
Z	4
ρ calcg/cm3	1.467
μ /mm-1	4.138
F(000)	1472.0
Crystal size/mm3	0.250 × 0.220 × 0.200
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.59 to 142.576
Index ranges	-16 ⩽ h ⩽ 18, -13 ⩽ k ⩽ 16, -20 ⩽ l ⩽ 18
Reflections collected	12642
Independent reflections	6131 [Rint = 0.0368, Rsigma = 0.0450]
Data/restraints/parameters	6131/0/369
Goodness-of-fit on F2	1.035
Final R indexes [I>=2σ (I)]	R1 = 0.0421, wR2 = 0.1081
Final R indexes [all data]	R1 = 0.0500, wR2 = 0.1132
Largest diff. peak/hole / e Å-3	1.42/-0.81

Table S9 Fractional Atomic Coordinates (×104) and Equivalent Isotropic Displacement Parameters (Å2×103) for **IV**. Ueq is defined as 1/3 of of the trace of the orthogonalised UIJ tensor.

Atom	x	y	z	U(eq)
Ge1	7122.9(2)	5360.1(3)	1474.2(2)	24.59(11)
Cl1	7118.7(5)	6823.7(6)	879.1(5)	33.99(18)
Cl2	7653.0(6)	3947.3(6)	6057.8(5)	35.17(19)
O1	6151.7(14)	4899.8(17)	818.1(12)	26.7(4)
O2	6975.0(15)	5847.2(17)	2450.8(13)	30.9(5)
O3	8195.0(15)	4986(2)	1206.1(15)	35.2(5)
N1	7100.4(17)	3923(2)	2055.9(15)	27.7(5)
C1	5864.2(19)	3962(2)	984.1(17)	23.5(6)
C5	6023(2)	2482(3)	1836(2)	33.0(7)
C6	6308.3(19)	3429(2)	1638.1(18)	25.6(6)
C2	5123(2)	3538(2)	513.5(18)	26.1(6)
C8	6613(2)	5179(3)	3021.8(18)	29.1(7)
C7	7044(2)	4147(3)	2934.2(18)	30.1(7)
C3	4836(2)	2598(2)	717(2)	30.1(7)
C4	5278(2)	2064(3)	1372(2)	33.9(7)
C12	8658(2)	4195(3)	1673(2)	34.8(7)
C11	7956(2)	3420(3)	1882(2)	33.9(7)
C10	5579(2)	5161(3)	2844(2)	36.2(7)
C9	6905(3)	5582(3)	3875(2)	42.4(8)
C13	9209(3)	4647(3)	2418(3)	44.8(9)
C14	9289(2)	3698(3)	1122(3)	49.6(10)

Table S10 Anisotropic Displacement Parameters (Å2×103) for **IV**. The Anisotropic displacement factor exponent takes the form: -2π2[h2a*2U11+2hka*b*U12+…].

Atom	U11	U22	U33	U23	U13	U12
Ge1	21.77(18)	30.4(2)	21.08(18)	1.63(13)	0.31(13)	-2.90(13)
Cl1	39.5(4)	31.9(4)	29.3(4)	4.1(3)	-1.4(3)	-9.0(3)
Cl2	51.4(5)	23.1(4)	32.0(4)	-1.1(3)	9.0(3)	9.4(3)
O1	25.1(10)	30.3(12)	23.3(10)	3.8(9)	-2.1(8)	-2.8(9)
O2	36.9(12)	32.1(12)	23.6(10)	0.0(9)	2.8(9)	-3.8(9)
O3	24.5(11)	43.3(14)	38.0(12)	3.0(11)	4.6(9)	-2.4(10)
N1	26.8(12)	29.3(14)	25.9(13)	0.4(11)	-0.9(10)	0.9(10)
C1	21.5(13)	28.5(16)	21.0(13)	-1.3(12)	4.1(10)	3.7(11)
C5	34.9(17)	32.1(18)	32.3(16)	6.6(14)	4.8(13)	3.3(13)
C6	25.0(14)	29.1(16)	22.6(14)	0.4(12)	2.9(11)	3.0(12)
C2	25.4(14)	30.7(16)	22.1(13)	-0.2(12)	1.8(11)	1.6(12)
C8	34.9(16)	32.1(17)	20.3(14)	-1.0(13)	3.5(12)	-1.3(13)
C7	35.1(16)	31.4(17)	22.3(14)	2.8(13)	-2.3(12)	1.4(13)
C3	26.6(15)	28.4(16)	35.4(16)	-5.1(13)	3.4(12)	-4.5(12)
C4	35.2(17)	26.2(16)	40.8(18)	3.9(14)	7.0(14)	-3.3(13)
C12	23.8(15)	36.7(19)	42.2(19)	-4.4(15)	-2.9(13)	1.7(13)
C11	28.3(16)	35.6(18)	36.3(17)	-6.2(15)	-3.1(13)	4.6(13)
C10	35.6(18)	43(2)	31.7(17)	-1.5(15)	8.4(14)	0.4(15)
C9	56(2)	49(2)	22.7(16)	-4.3(15)	3.9(15)	-3.5(18)
C13	34.8(18)	42(2)	54(2)	-10.3(18)	-9.8(16)	-3.2(15)
C14	26.2(17)	56(2)	68(3)	-21(2)	8.1(16)	-0.4(16)

Table S11 Bond Lengths for **IV**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ge1	O3	1.772(2)	C1	C2	1.389(4)
Ge1	O2	1.772(2)	C1	C6	1.391(4)
Ge1	O1	1.804(2)	C5	C4	1.384(5)
Ge1	N1	2.151(3)	C5	C6	1.387(5)
Ge1	Cl1	2.1895(9)	C2	C3	1.381(5)
O1	C1	1.363(4)	C8	C9	1.520(4)
O2	C8	1.446(4)	C8	C10	1.528(5)
O3	C12	1.436(4)	C8	C7	1.535(5)
N1	C6	1.449(4)	C3	C4	1.393(5)
N1	C7	1.489(4)	C12	C13	1.517(5)
N1	C11	1.493(4)	C12	C14	1.530(5)
C12	C11	1.536(5)			

Table S12 Bond Angles for **IV**.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
O3	Ge1	O2	122.73(11)	O1	C1	C6	119.8(3)
O3	Ge1	O1	115.55(11)	C2	C1	C6	119.5(3)
O2	Ge1	O1	119.55(10)	C4	C5	C6	119.0(3)
O3	Ge1	N1	85.43(11)	C5	C6	C1	121.4(3)
O2	Ge1	N1	85.11(10)	C5	C6	N1	123.9(3)
O1	Ge1	N1	84.72(10)	C1	C6	N1	114.6(3)
O3	Ge1	Cl1	95.51(9)	C3	C2	C1	118.9(3)
O2	Ge1	Cl1	94.76(8)	O2	C8	C9	107.1(3)
O1	Ge1	Cl1	94.44(7)	O2	C8	C10	109.1(3)
N1	Ge1	Cl1	178.95(7)	C9	C8	C10	110.7(3)
C1	O1	Ge1	116.15(18)	O2	C8	C7	107.7(2)
C8	O2	Ge1	117.22(19)	C9	C8	C7	109.2(3)
C12	O3	Ge1	117.5(2)	C10	C8	C7	112.8(3)
C6	N1	C7	114.7(2)	N1	C7	C8	110.1(2)
C6	N1	C11	111.3(2)	C2	C3	C4	121.7(3)
C7	N1	C11	115.0(2)	C5	C4	C3	119.5(3)
C6	N1	Ge1	104.53(18)	O3	C12	C13	108.4(3)
C7	N1	Ge1	104.92(19)	O3	C12	C14	106.9(3)
C11	N1	Ge1	105.0(2)	C13	C12	C14	110.1(3)
O1	C1	C2	120.7(3)	O3	C12	C11	108.9(2)
C13	C12	C11	113.8(3)	C14	C12	C11	108.5(3)
N1	C11	C12	110.7(3)				

Table S13 Torsion Angles for **IV**.

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
O3	Ge1	O1	C1	83.7(2)	O1	C1	C2	C3	-178.1(3)
O2	Ge1	O1	C1	-80.0(2)	C6	C1	C2	C3	1.0(4)
N1	Ge1	O1	C1	1.37(19)	Ge1	O2	C8	C9	157.0(2)
Cl1	Ge1	O1	C1	-177.99(18)	Ge1	O2	C8	C10	-83.2(3)
O3	Ge1	O2	C8	-101.8(2)	Ge1	O2	C8	C7	39.6(3)
O1	Ge1	O2	C8	60.7(2)	C6	N1	C7	C8	-89.1(3)
N1	Ge1	O2	C8	-20.4(2)	C11	N1	C7	C8	139.8(3)
Cl1	Ge1	O2	C8	158.5(2)	Ge1	N1	C7	C8	25.0(3)
O2	Ge1	O3	C12	61.0(3)	O2	C8	C7	N1	-40.6(3)
O1	Ge1	O3	C12	-102.1(2)	C9	C8	C7	N1	-156.7(3)
N1	Ge1	O3	C12	-20.2(2)	C10	C8	C7	N1	79.8(3)
Cl1	Ge1	O3	C12	160.3(2)	C1	C2	C3	C4	-0.9(5)
Ge1	O1	C1	C2	-179.9(2)	C6	C5	C4	C3	0.3(5)
Ge1	O1	C1	C6	1.0(3)	C2	C3	C4	C5	0.2(5)
C4	C5	C6	C1	-0.2(5)	Ge1	O3	C12	C13	-86.9(3)
C4	C5	C6	N1	-177.2(3)	Ge1	O3	C12	C14	154.5(2)
O1	C1	C6	C5	178.6(3)	Ge1	O3	C12	C11	37.4(3)
C2	C1	C6	C5	-0.5(4)	C6	N1	C11	C12	134.1(3)
O1	C1	C6	N1	-4.1(4)	C7	N1	C11	C12	-93.3(3)
C2	C1	C6	N1	176.8(3)	Ge1	N1	C11	C12	21.5(3)
C7	N1	C6	C5	-64.0(4)	O3	C12	C11	N1	-37.0(4)
C11	N1	C6	C5	68.8(4)	C13	C12	C11	N1	84.1(3)
Ge1	N1	C6	C5	-178.3(2)	C14	C12	C11	N1	-153.0(3)
C7	N1	C6	C1	118.8(3)	Ge1	N1	C6	C1	4.5(3)
C11	N1	C6	C1	-108.4(3)					

Table S14 Hydrogen Atom Coordinates (Å×104) and Isotropic Displacement Parameters (Å2×103) for **IV**.

Atom	x	y	z	U(eq)
H21A	6019	6454	7825	30
H21B	6808	7181	8162	30
H5	6327	2133	2274	40
H2	4825	3881	69	31
H16	4770	5970	4940	39
H7A	7648	4136	3233	36
H7B	6682	3640	3165	36
H3	4335	2316	408	36
H4	5075	1431	1497	41
H25A	7983	7566	7447	33
H25B	7389	8162	6756	33
H19	5730	8402	6870	38
H17	3917	7399	5052	44
H28A	9424	7292	7031	58
H28B	9171	8238	6490	58
H28C	9565	7286	6102	58
H11A	7824	2962	1427	41
H11B	8204	3037	2357	41
H24A	6165	5075	8687	49
H24B	6770	5761	9302	49
H24C	7110	4691	9096	49
H10A	5345	5823	2901	54
H10B	5334	4720	3222	54
H10C	5408	4928	2296	54
H27A	8263	7149	5036	49
H27B	7819	8112	5358	49
H27C	7269	7110	5268	49
H18	4394	8626	5998	47
H23A	8500	5388	8767	55
H23B	8239	6518	8834	55
H23C	8535	6101	8016	55
H9A	7549	5688	3945	64
H9B	6749	5108	4274	64
H9C	6600	6203	3947	64
H13A	9656	5093	2245	67
H13B	9505	4124	2748	67
H13C	8813	5011	2732	67
H14A	8940	3468	630	74
H14B	9590	3140	1404	74
H14C	9733	4173	988	74

Table S15 Solvent masks information for **IV**.

Number	X	Y	Z	Volume	Electron count	Content
1	0.500	0.000	1.000	81	32	
2	0.083	0.180	0.146	9	0	
3	0.583	0.319	0.646	9	0	
4	1.000	0.500	0.500	81	31	
5	0.417	0.680	0.354	9	0	
6	0.917	0.819	0.854	9	0	

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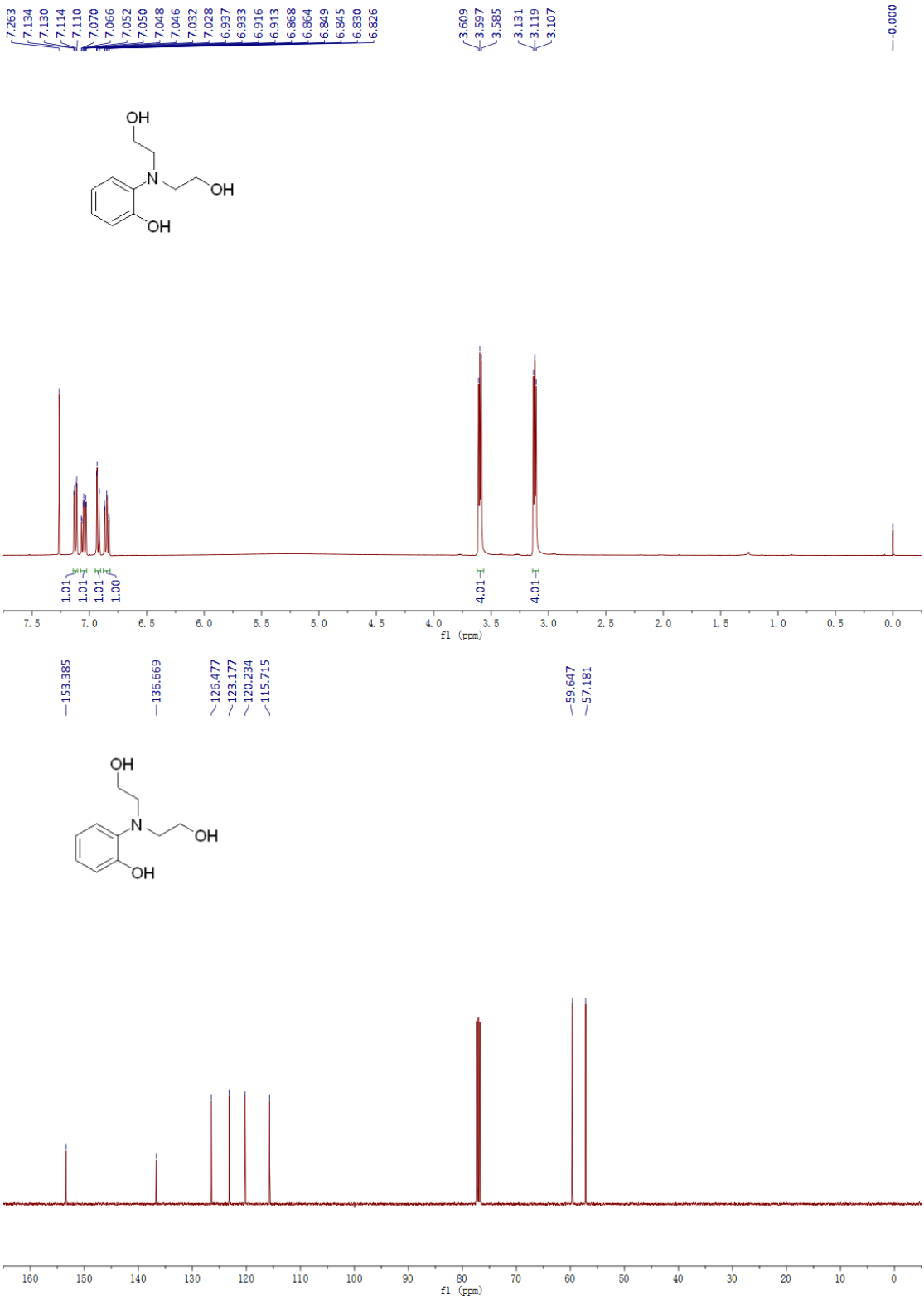
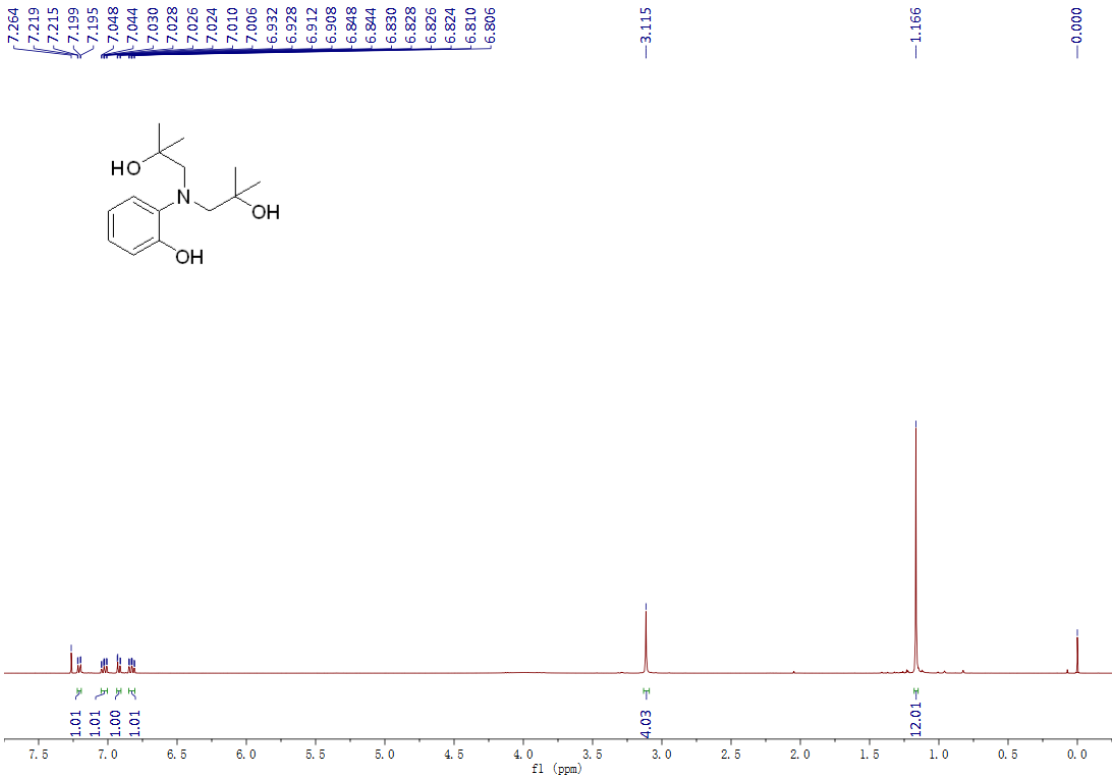
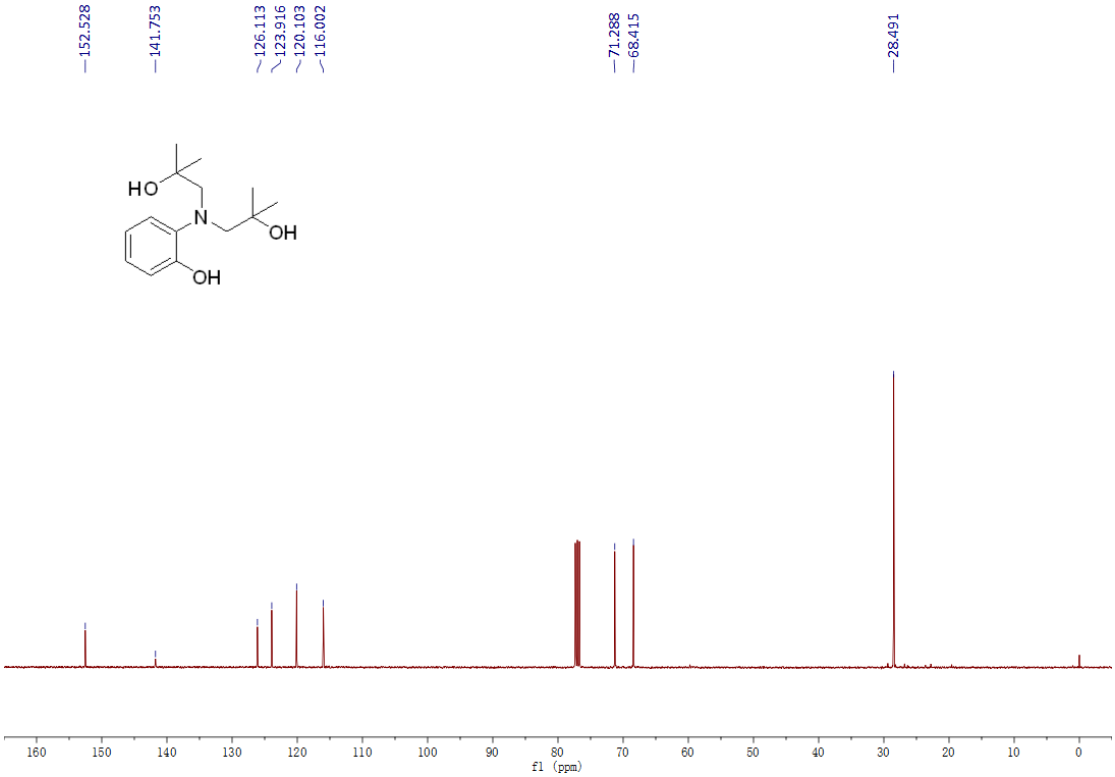
^{1}H and ^{13}C NMR Spectra

2,2'-((2-hydroxyphenyl)azanediyl)bis(ethan-1-ol)

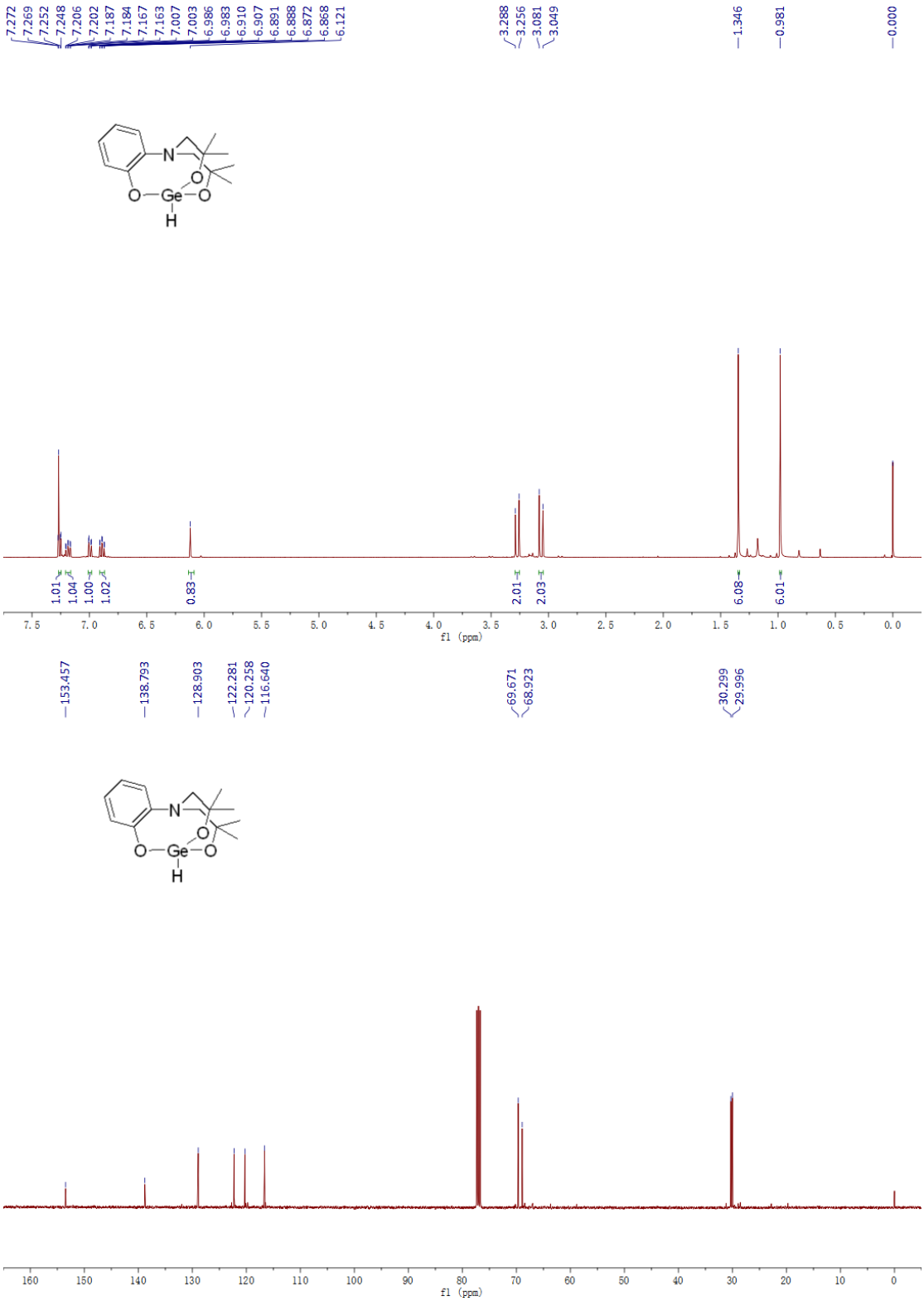


I: 1,1'-((2-hydroxyphenyl)azanediyl)bis(2-methylpropan-2-ol)

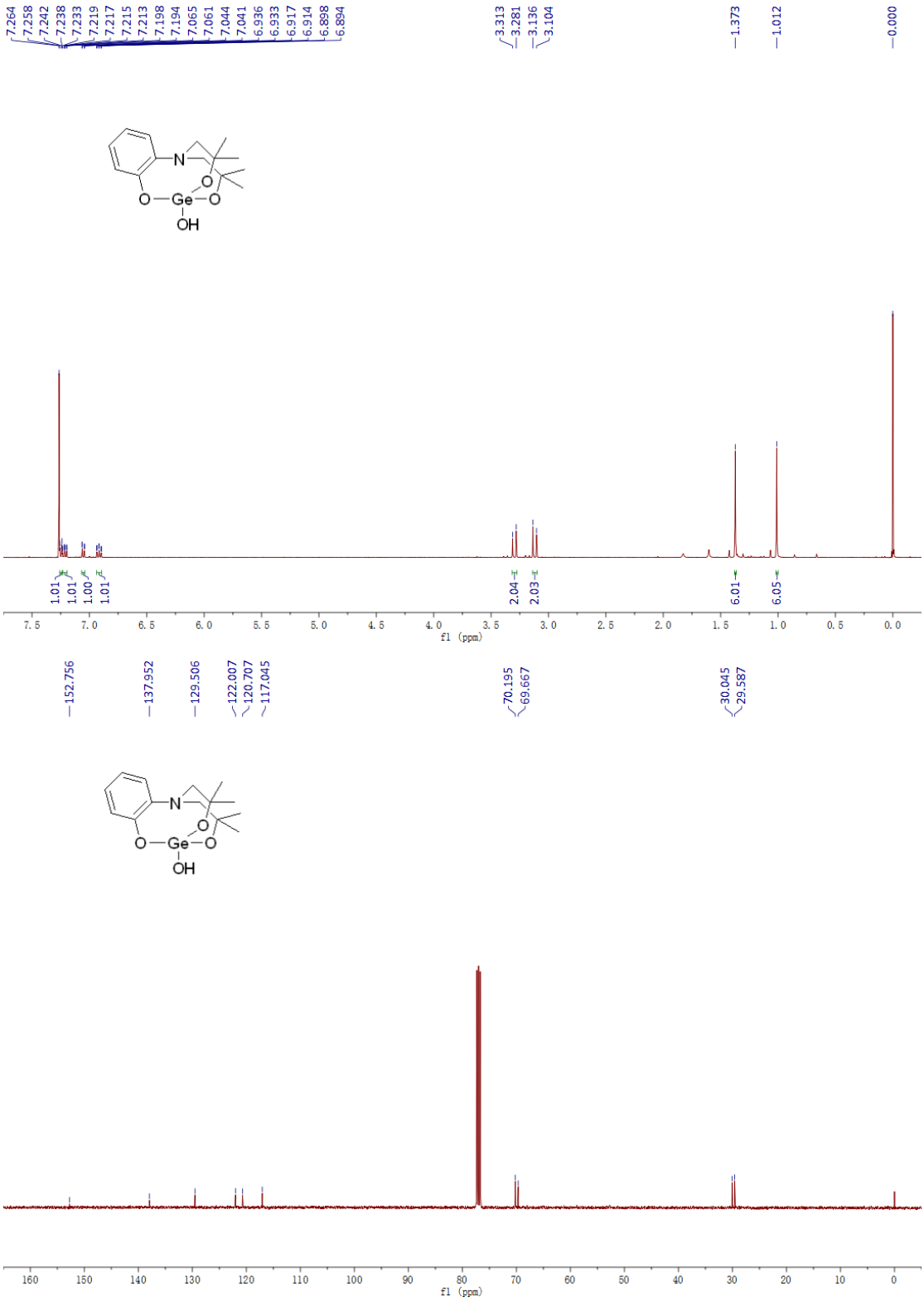




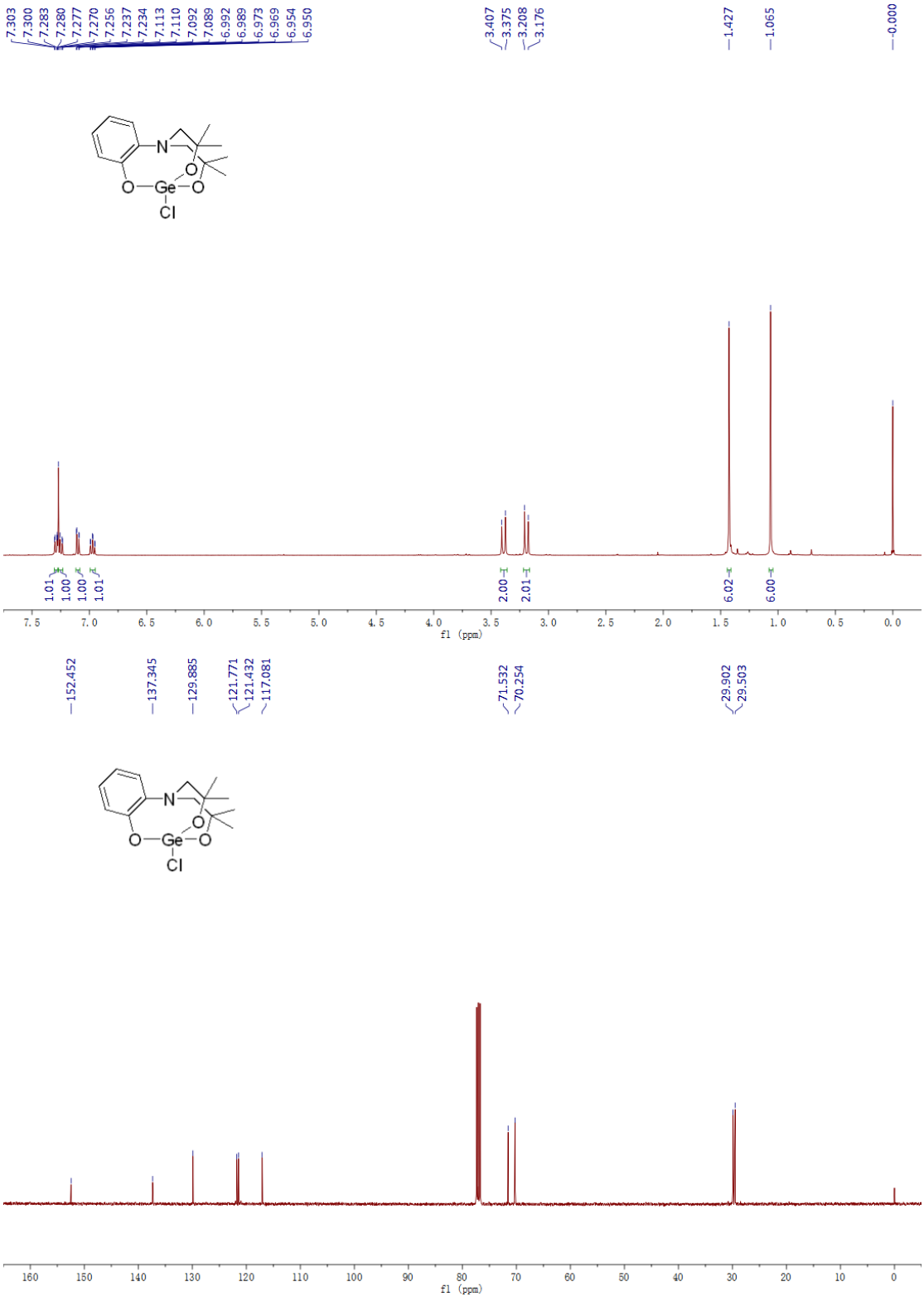
II: 4,4,12,12-tetramethyl-4,5-dihydro-2,6-(epoxyethano)benzo[d][1,3,6,2]dioxazagermocine



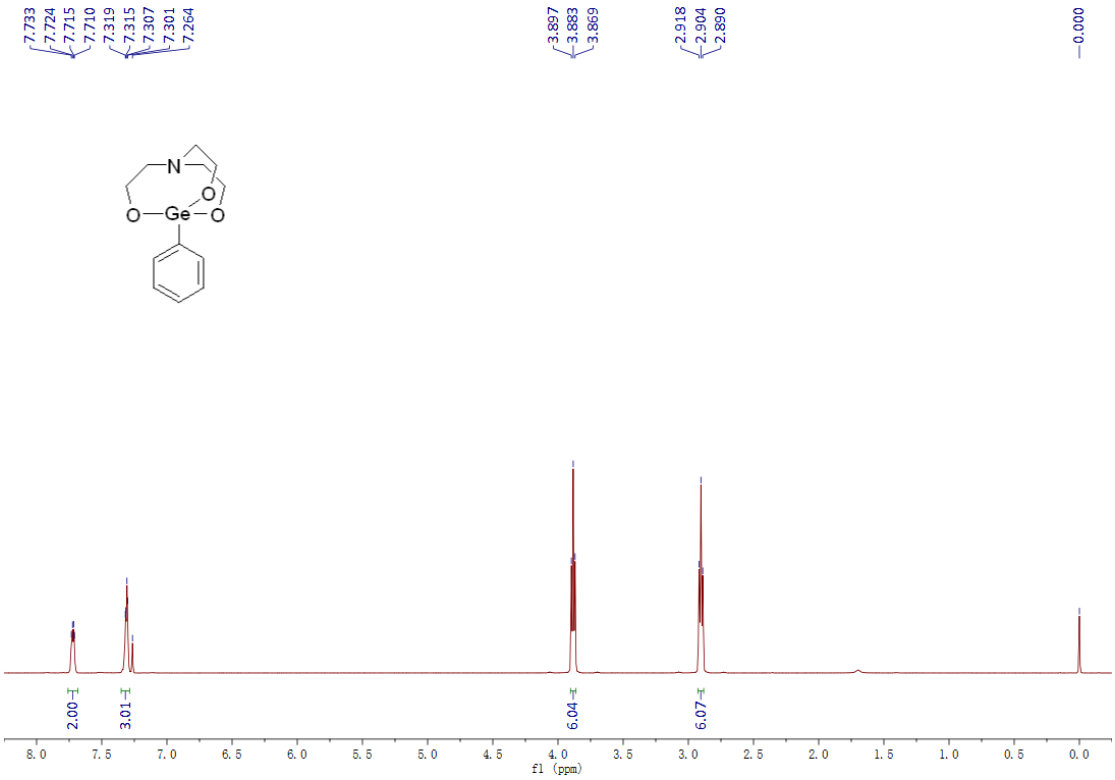
III: 4,4,12,12-tetramethyl-4,5-dihydro-2,6-(epoxyethano)benzo[d][1,3,6,2]dioxazagermocin-2-ol

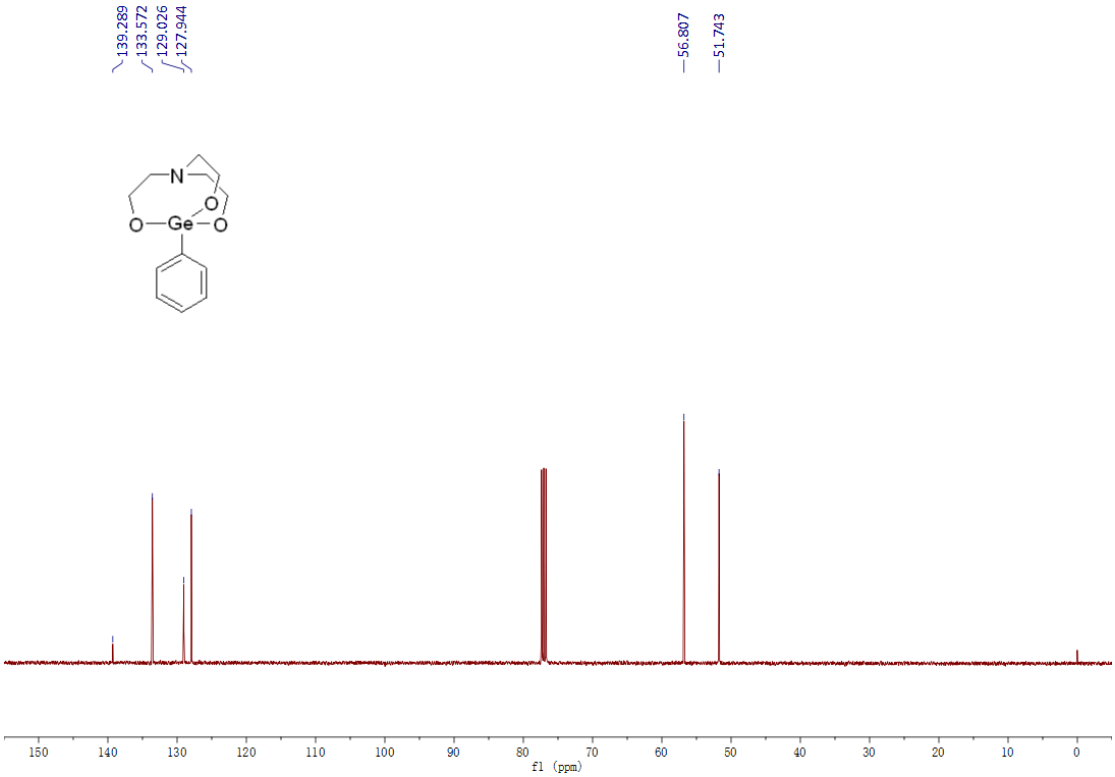


IV: 2-chloro-4,4,12,12-tetramethyl-4,5-dihydro-2,6-(epoxyethano)benzo[d][1,3,6,2]dioxaza-germocine

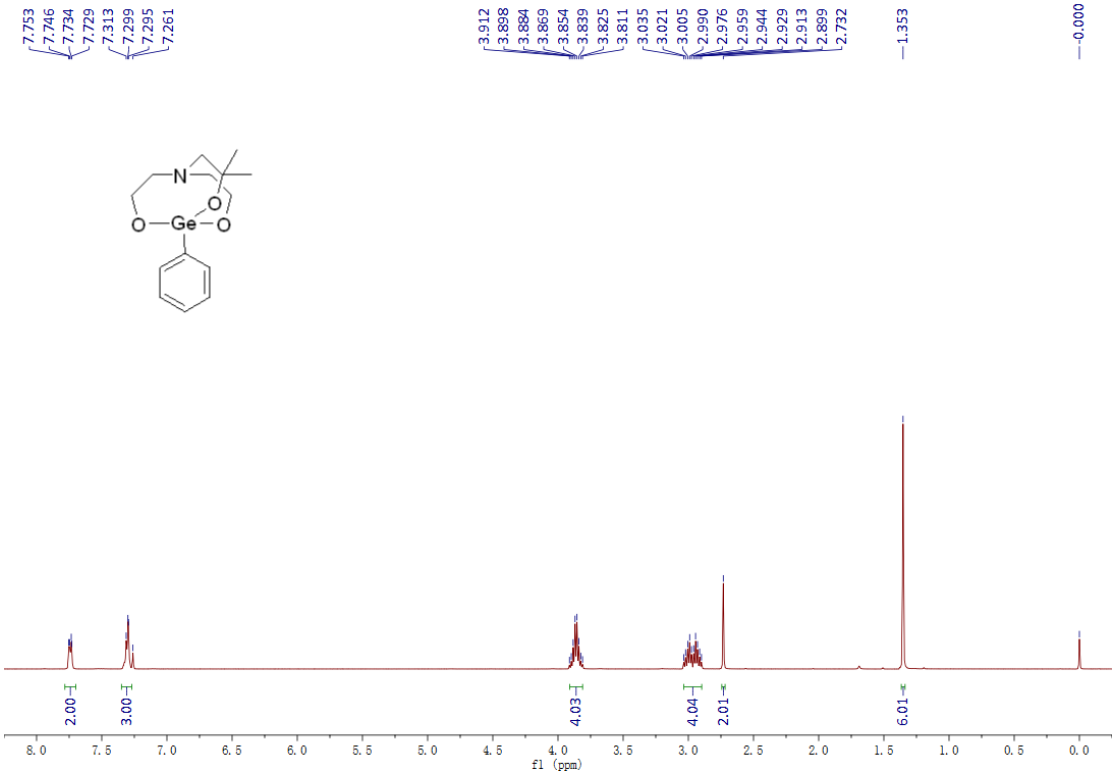


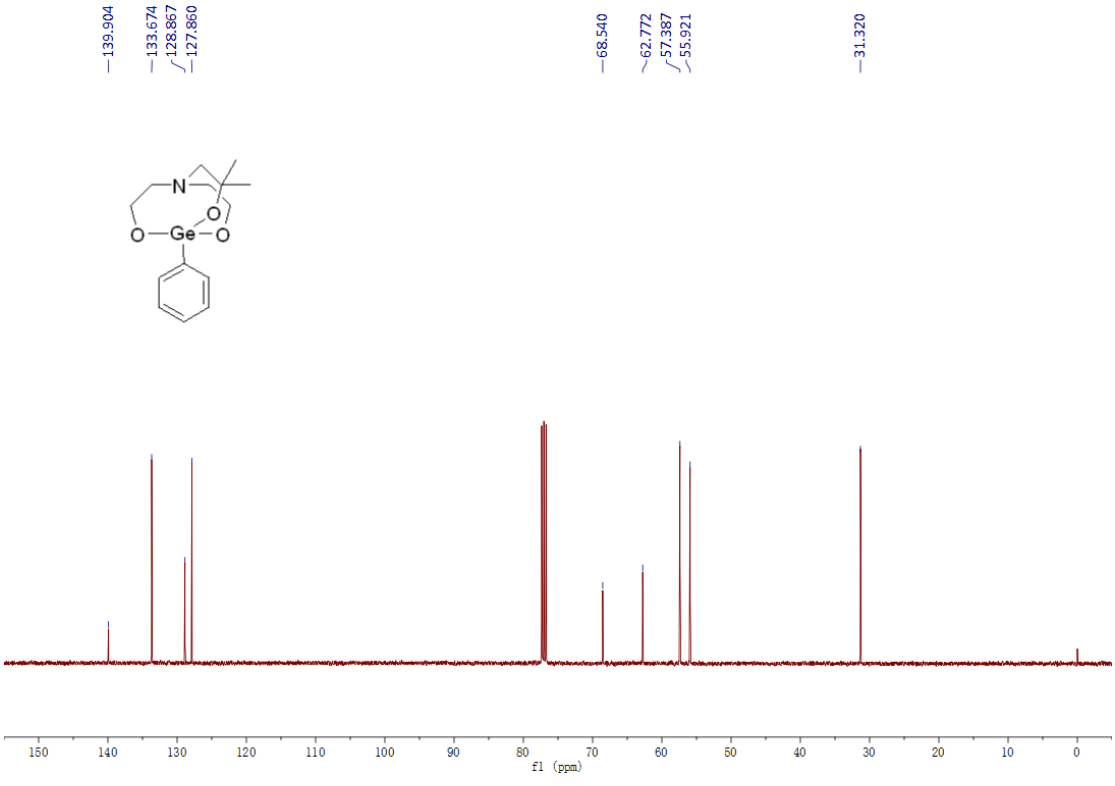
1a: 1-phenyl-2,8,9-trioxa-5-aza-1-germabicyclo[3.3.3]undecane



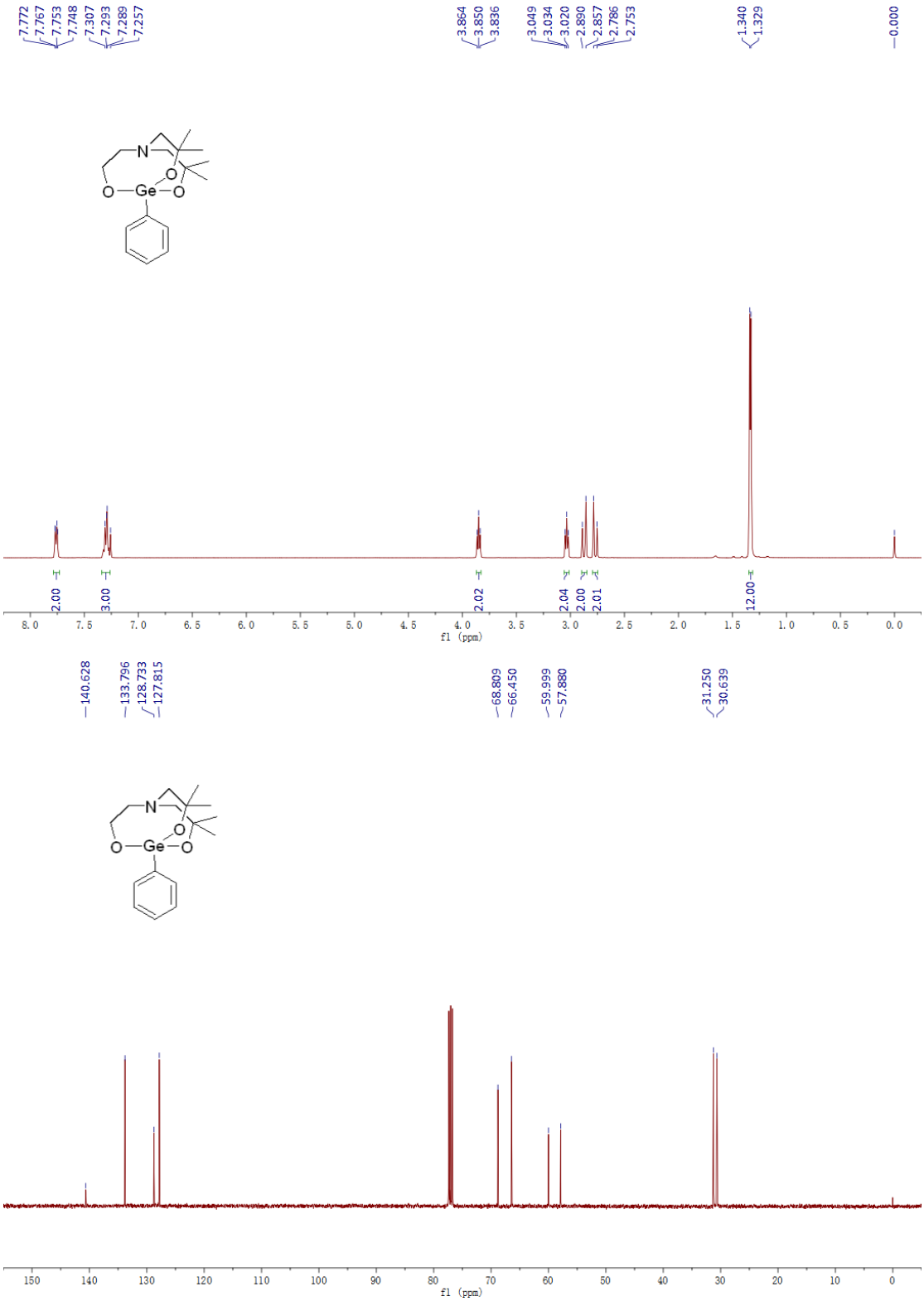


1b: 3,3-dimethyl-1-phenyl-2,8,9-trioxa-5-aza-1-germabicyclo[3.3.3]undecane

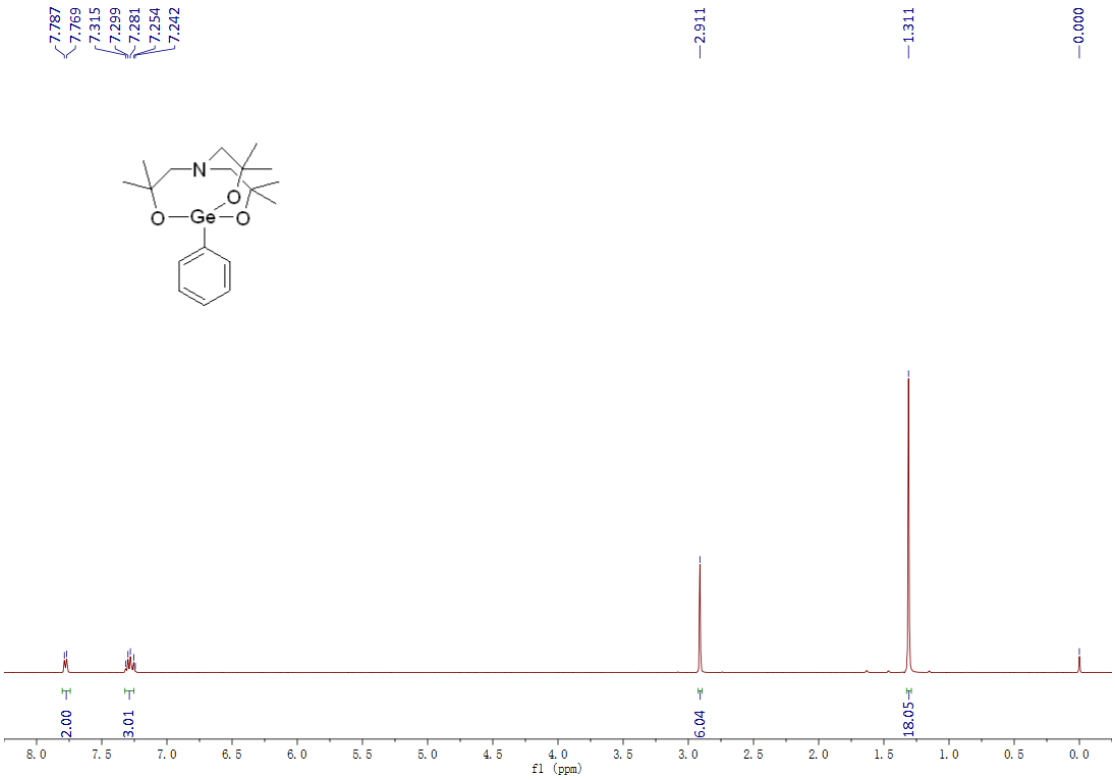


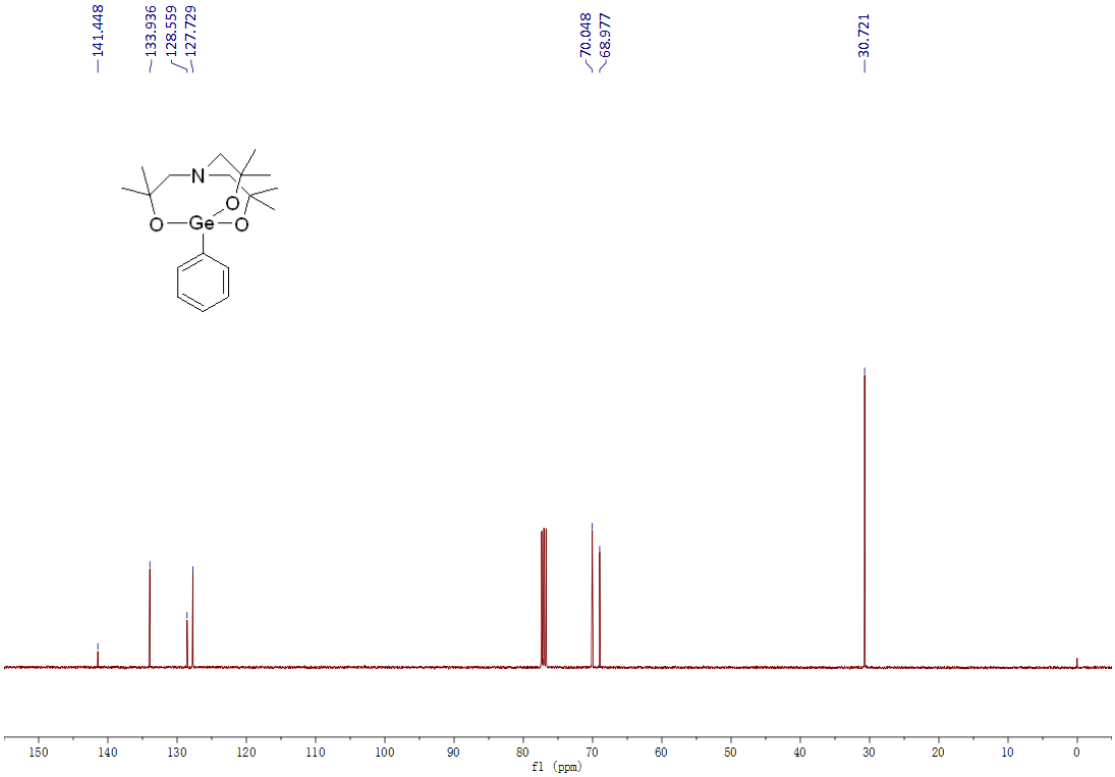


1c: 3,3,7,7-tetramethyl-1-phenyl-2,8,9-trioxa-5-aza-1-germabicyclo[3.3.3]undecane

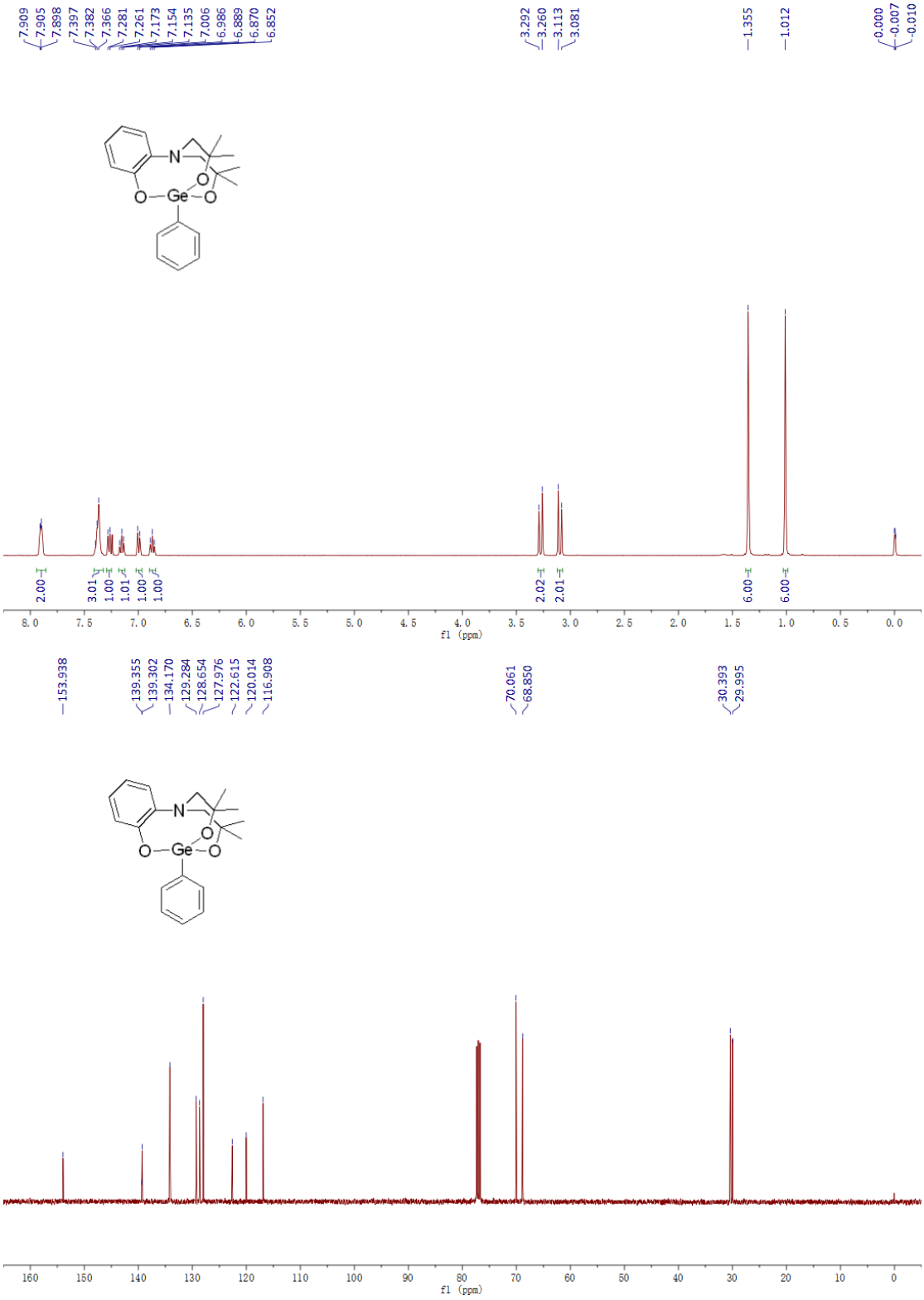


1d: 3,3,7,7,10,10-hexamethyl-1-phenyl-2,8,9-trioxa-5-aza-1-germabicyclo[3.3.3]undecane

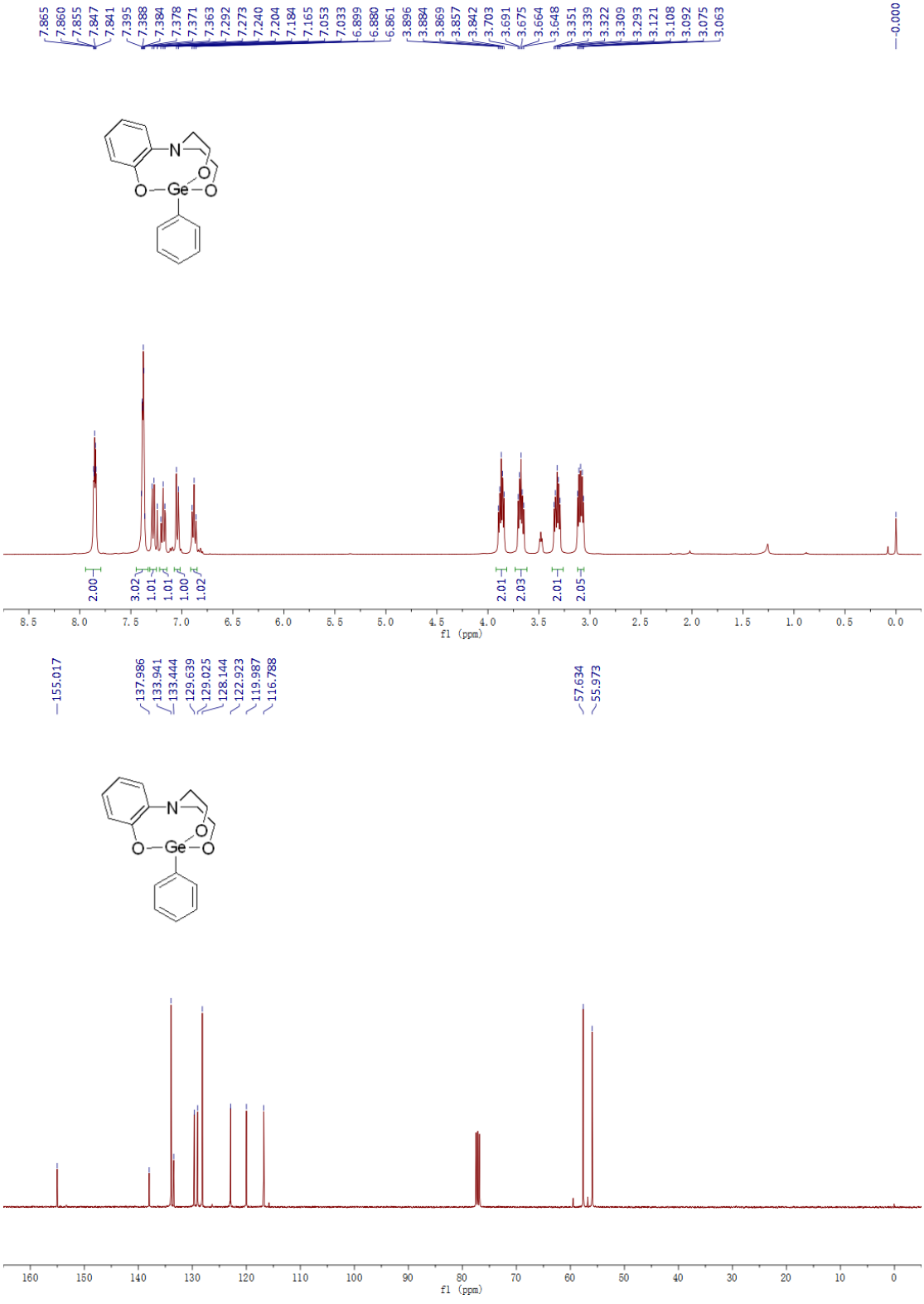




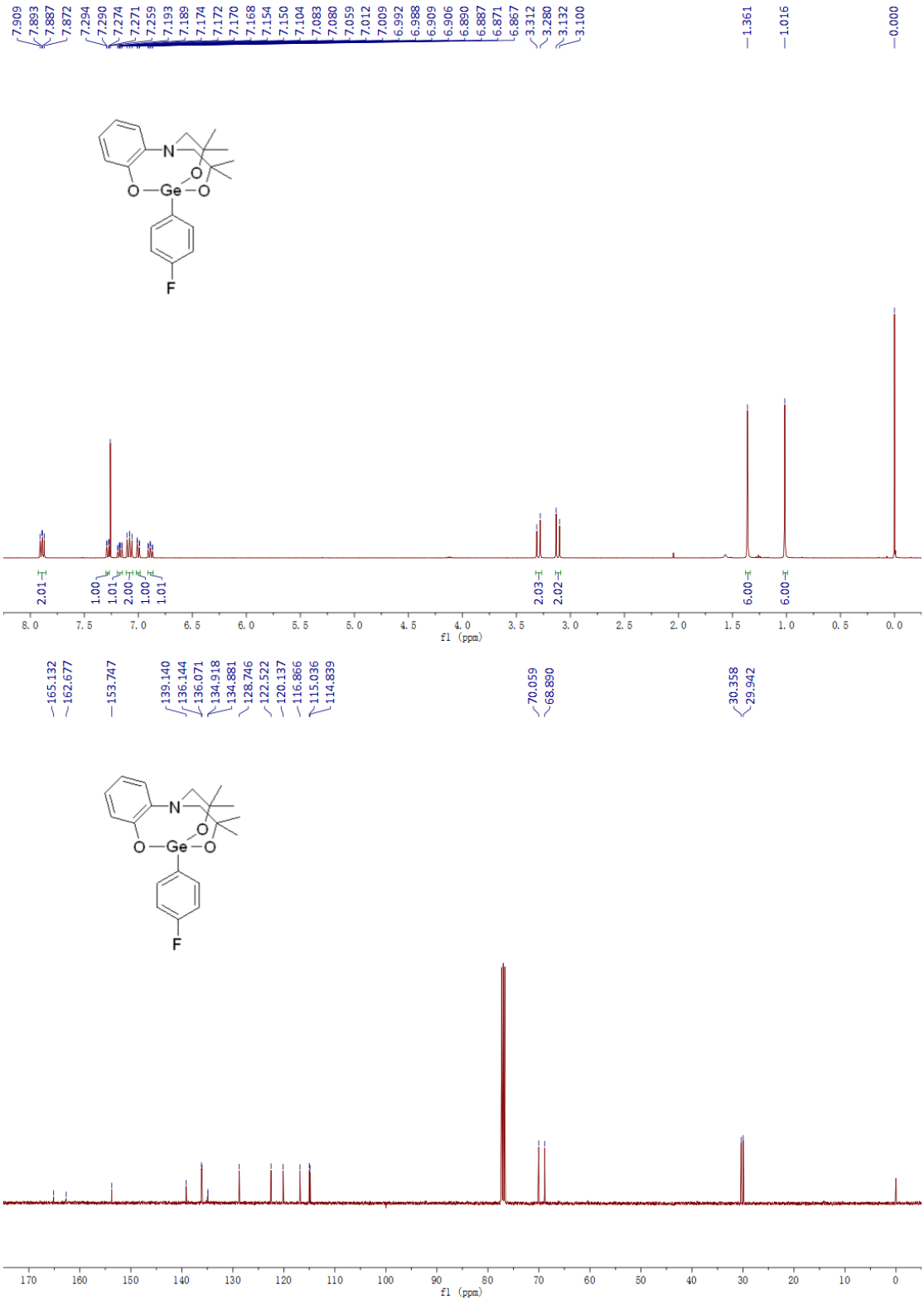
1e: 4,4,12,12-tetramethyl-2-phenyl-4,5-dihydro-2,6-(epoxyethano)benzo[d][1,3,6,2]dioxazagermocine



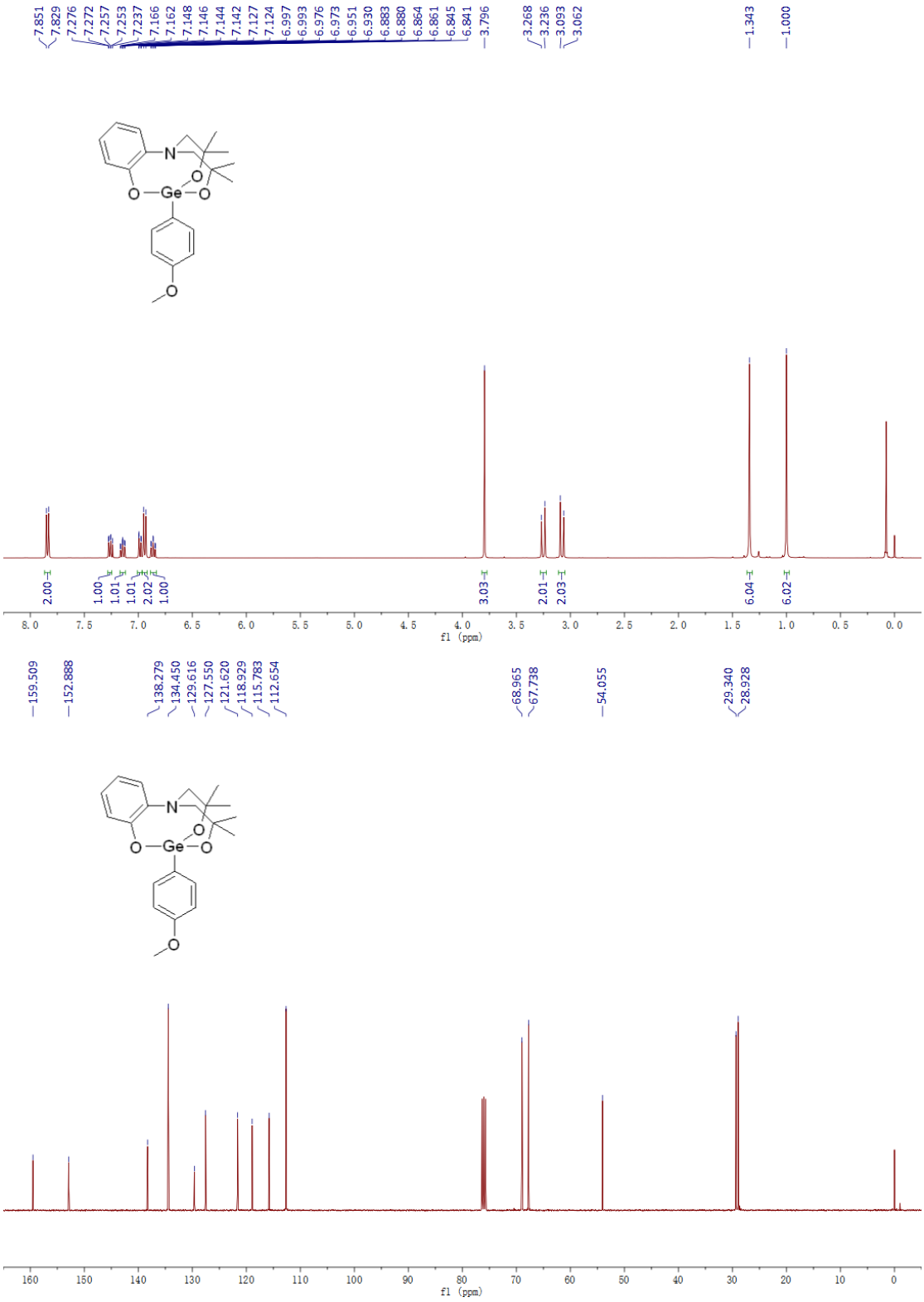
1f: 2-phenyl-4,5-dihydro-2,6-(epoxyethano)benzo[d][1,3,6,2]dioxazagermocine



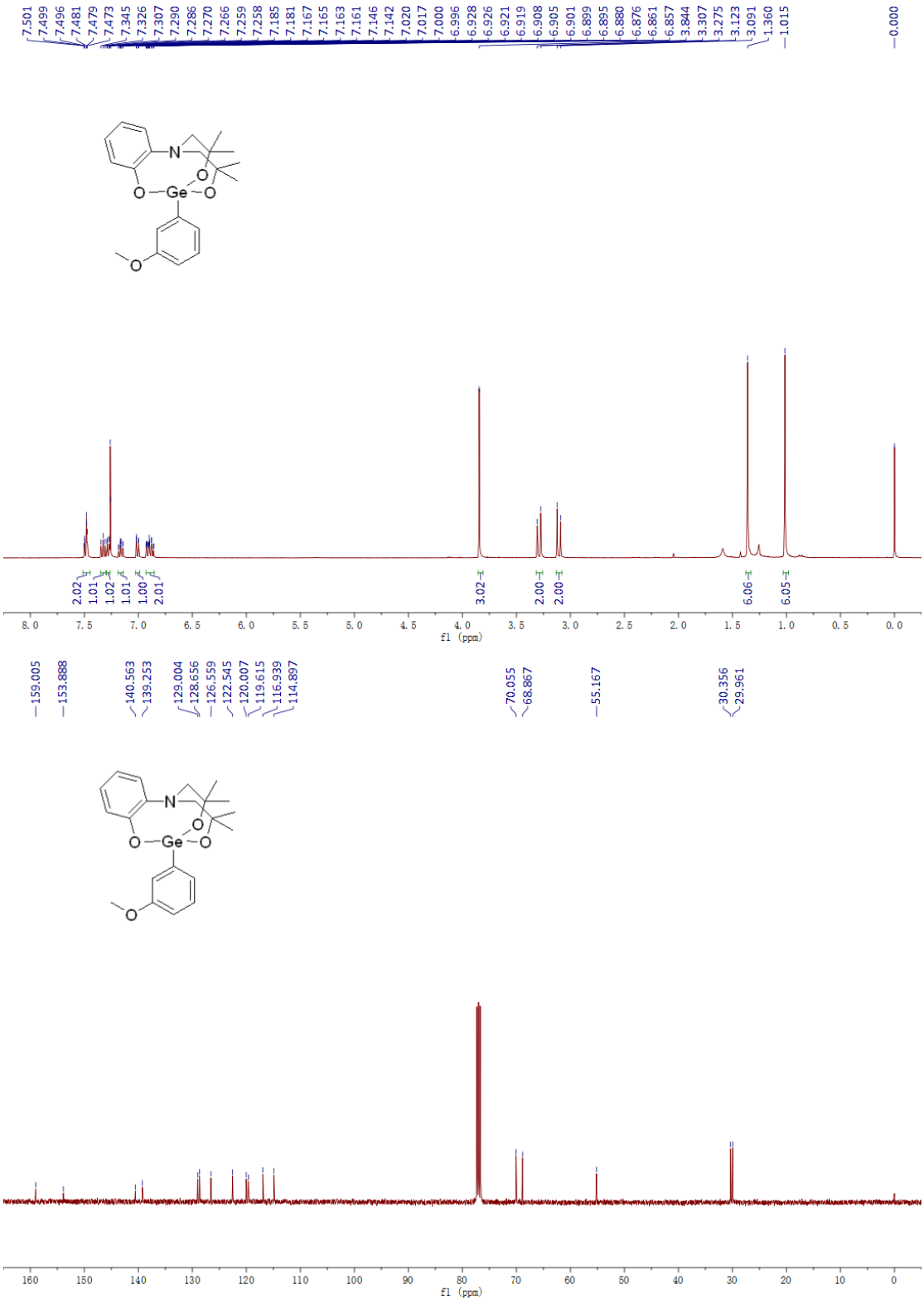
1g: 2-(4-fluorophenyl)-4,4,12,12-tetramethyl-4,5-dihydro-2,6-(epoxyethano)benzo[d][1,3,6,2]-dioxazagermocine



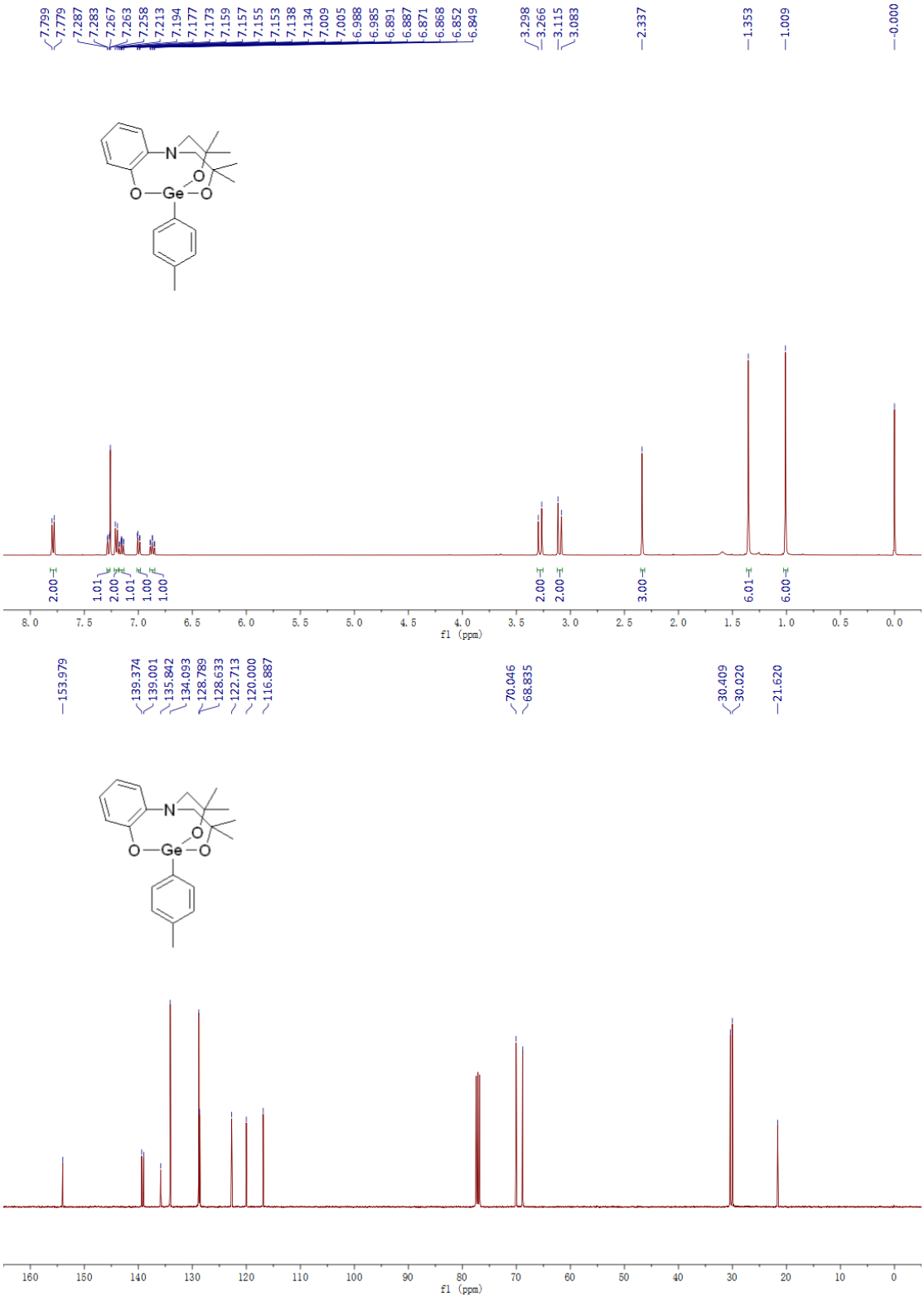
1h: 2-(4-methoxyphenyl)-4,4,12,12-tetramethyl-4,5-dihydro-2,6-(epoxyethano)benzo[d]-[1,3,6,2]dioxazagermocine



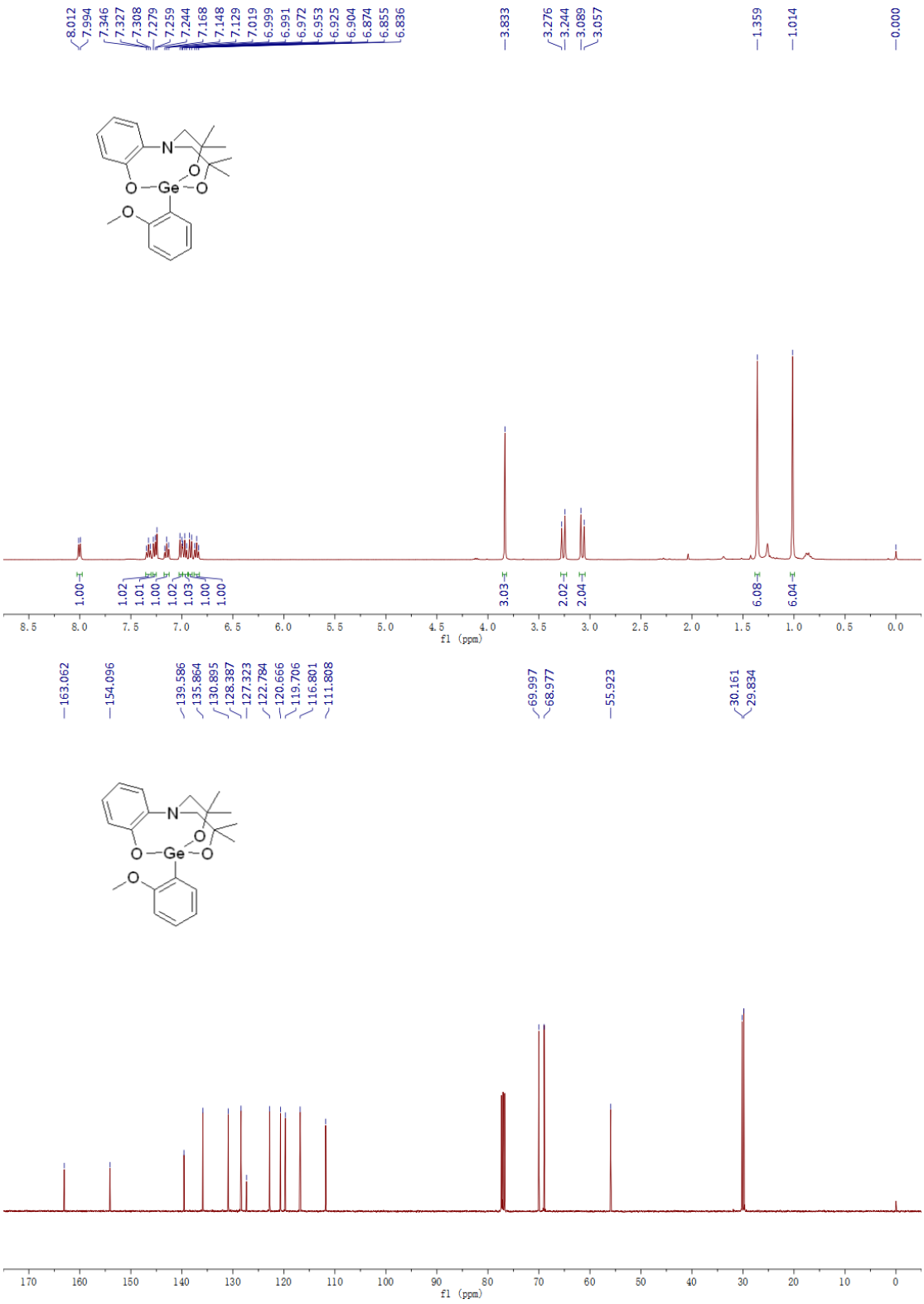
1i: 2-(3-methoxyphenyl)-4,4,12,12-tetramethyl-4,5-dihydro-2,6-(epoxyethano)benzo[d]-[1,3,6,2]dioxazagermocine



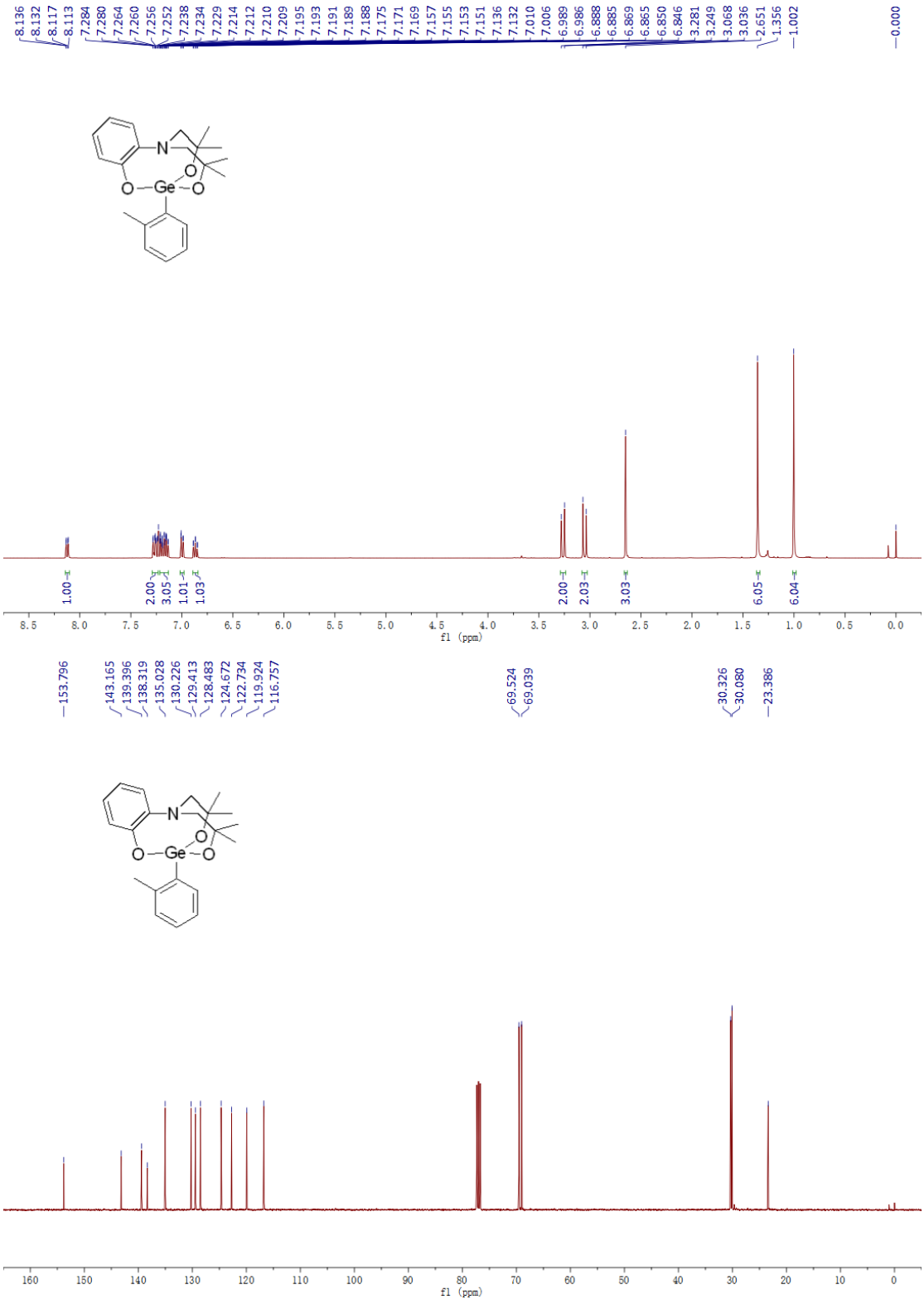
1j: 4,4,12,12-tetramethyl-2-(p-tolyl)-4,5-dihydro-2,6-(epoxyethano)benzo[d][1,3,6,2]dioxaza-germocine



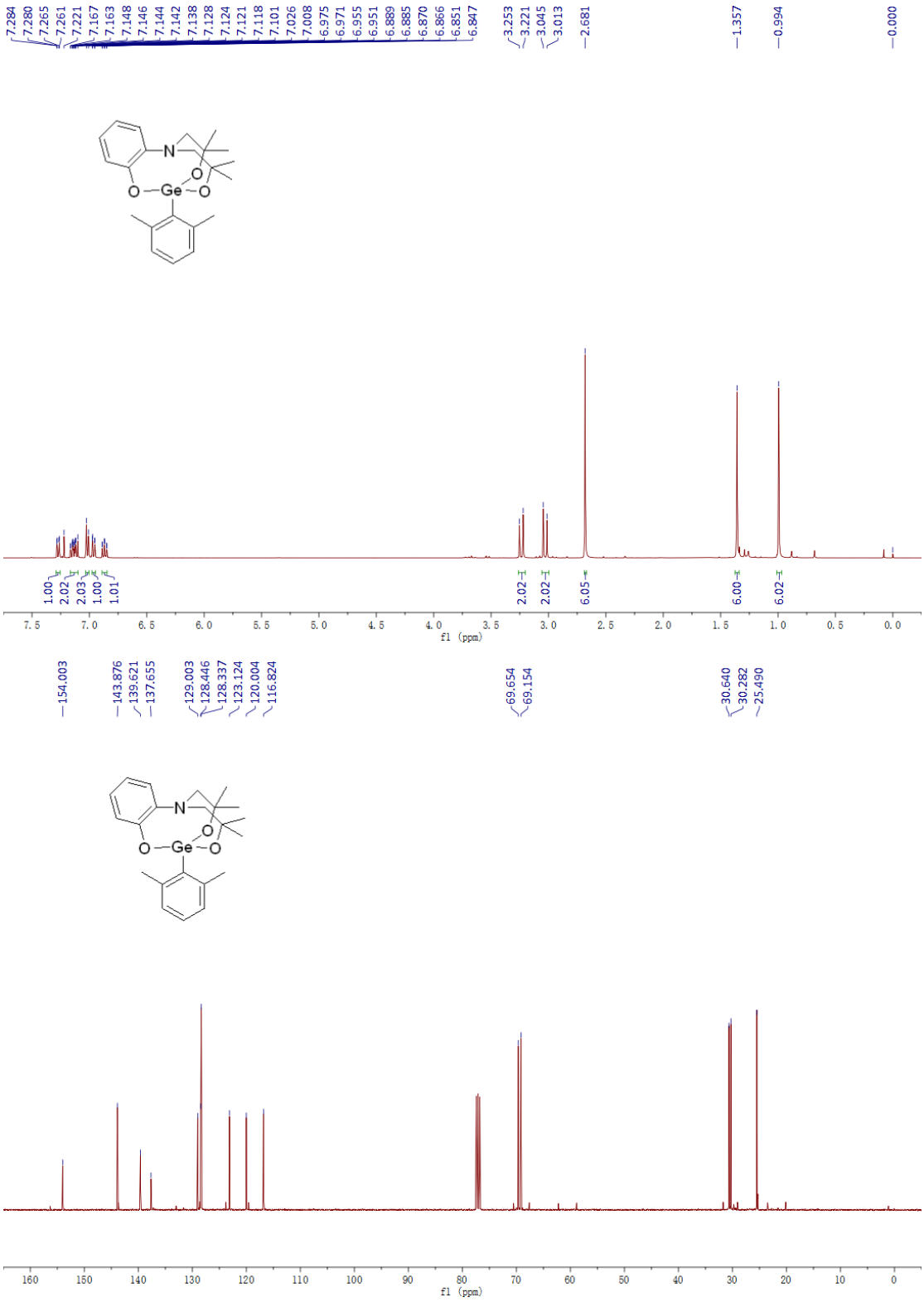
1k: 2-(2-methoxyphenyl)-4,4,12,12-tetramethyl-4,5-dihydro-2,6-(epoxyethano)benzo[d]-[1,3,6,2]dioxazagermocine



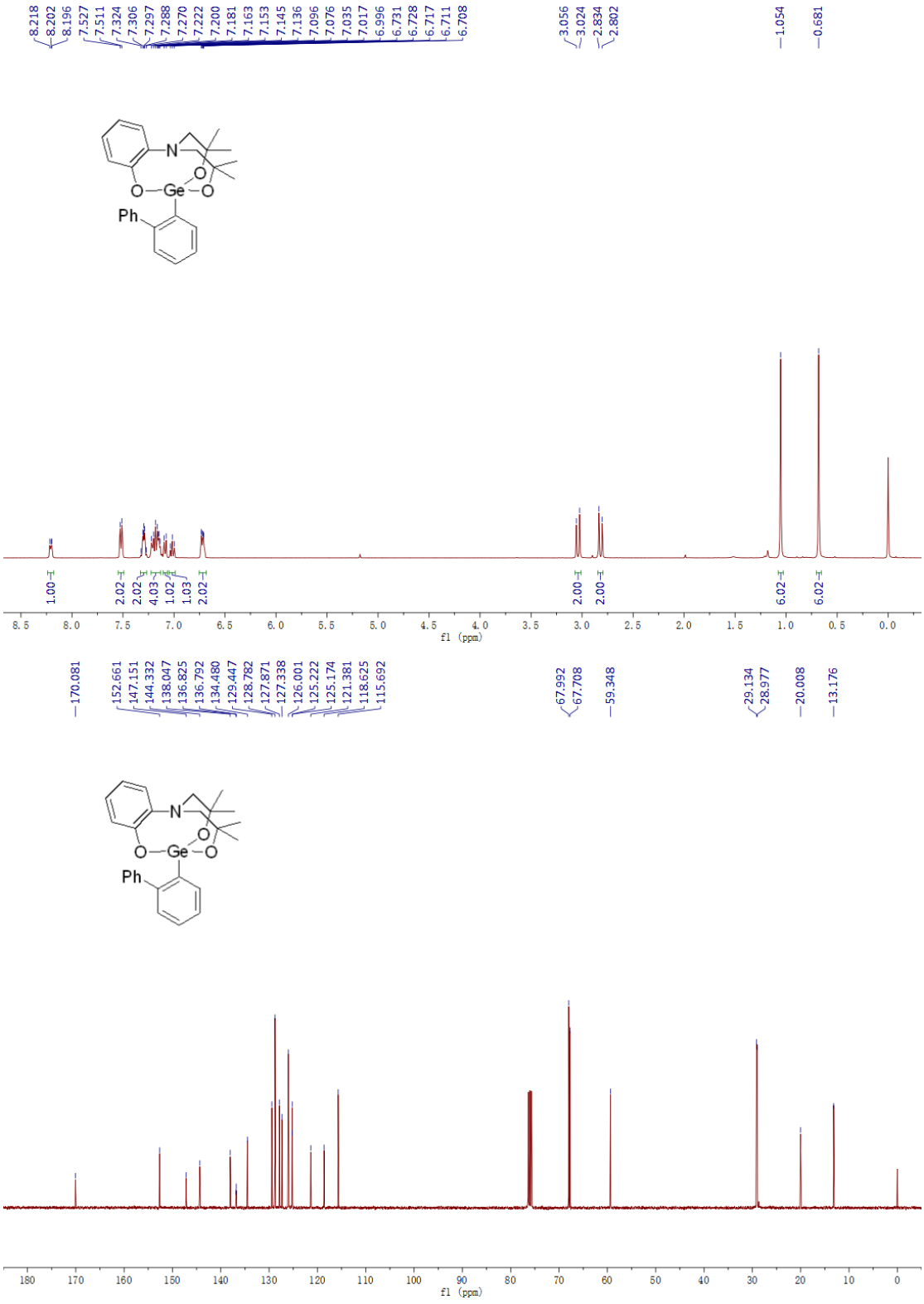
1l: 4,4,12,12-tetramethyl-2-(o-tolyl)-4,5-dihydro-2,6-(epoxyethano)benzo[d][1,3,6,2]dioxaza-germocine



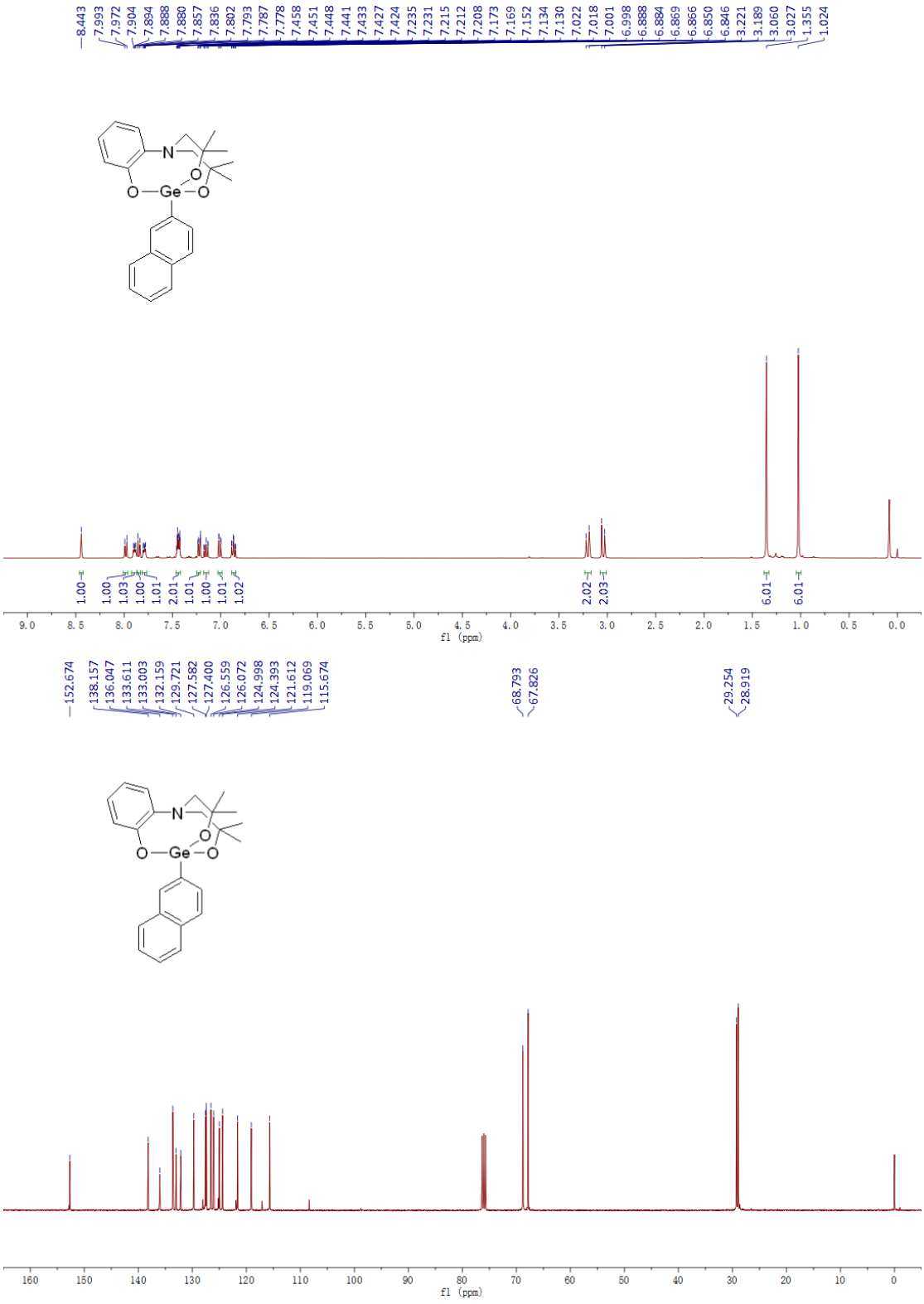
1m: 2-(2,6-dimethylphenyl)-4,4,12,12-tetramethyl-4,5-dihydro-2,6-(epoxyethano)benzo[d]-[1,3,6,2]dioxazagermocine



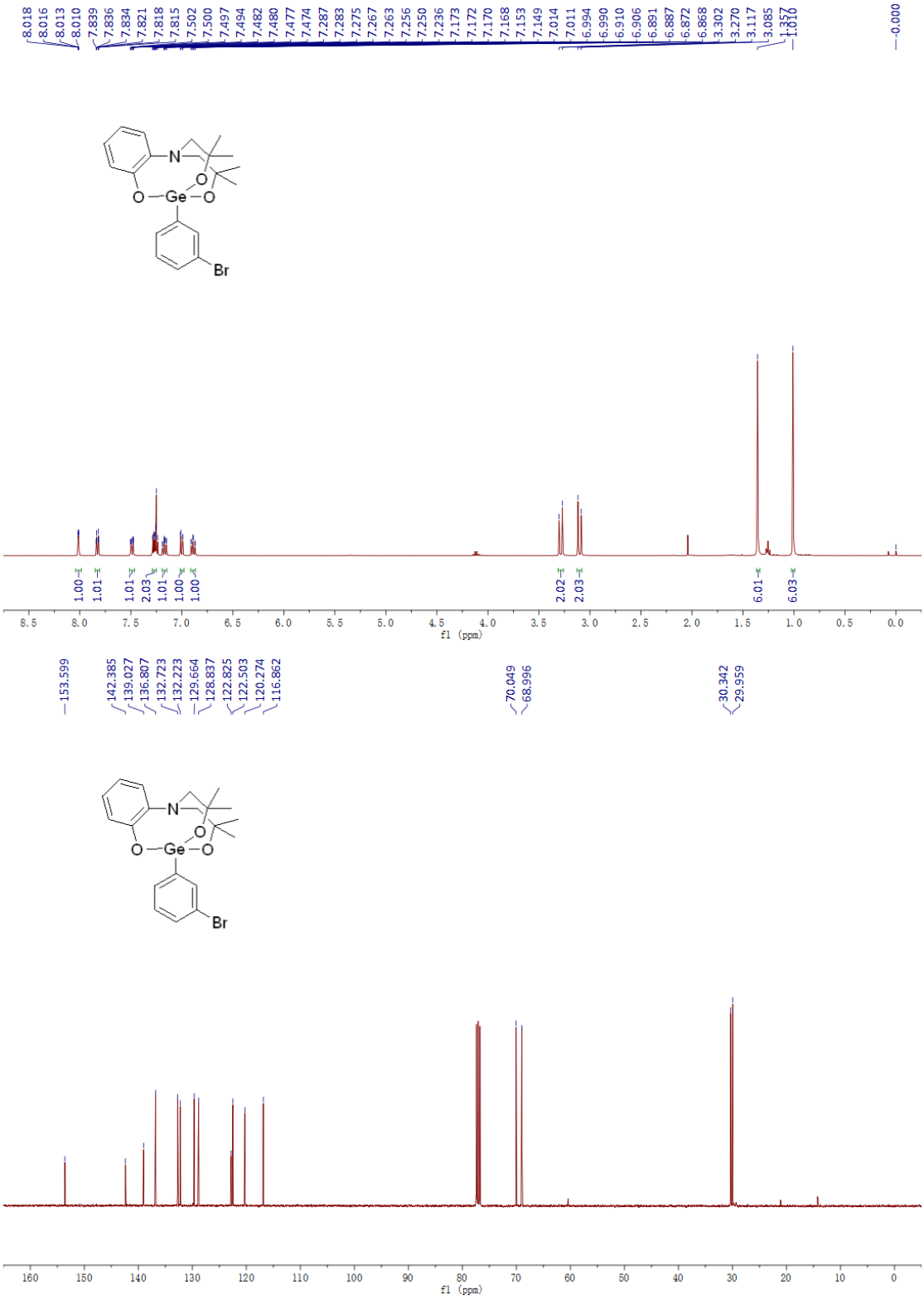
1n: 2-([1,1'-biphenyl]-2-yl)-4,4,12,12-tetramethyl-4,5-dihydro-2,6-(epoxyethano)benzo[d]-[1,3,6,2]dioxazagermocine



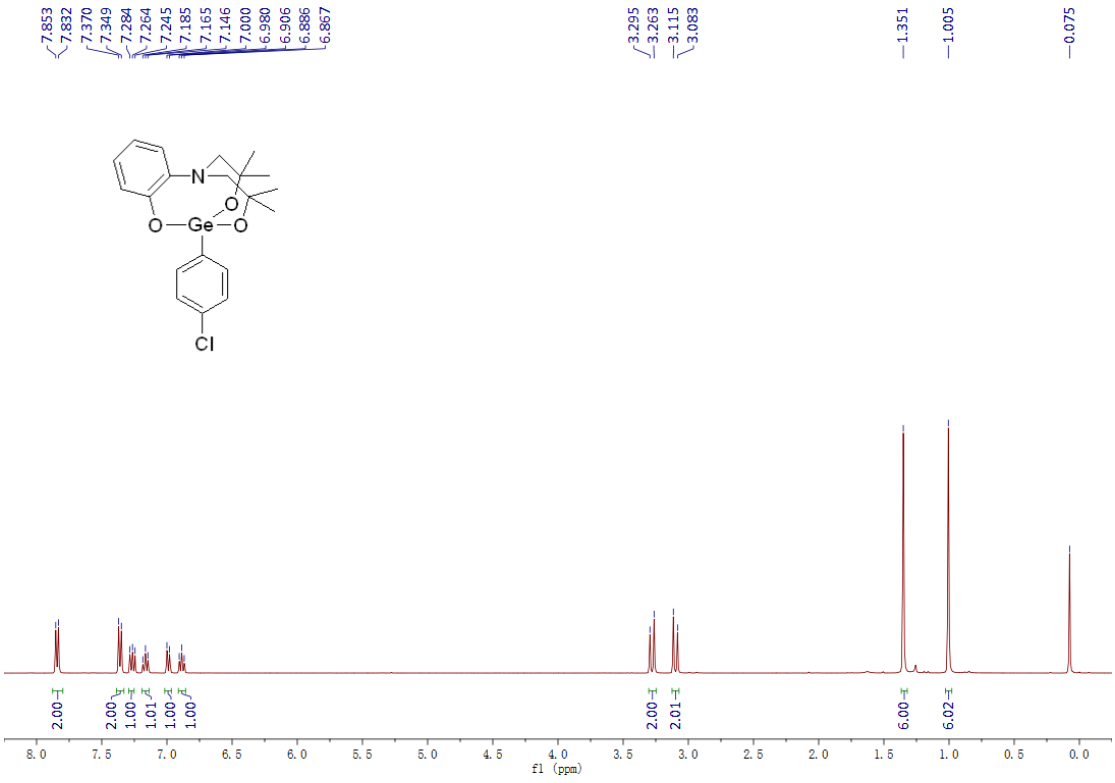
1o: 4,4,12,12-tetramethyl-2-(naphthalen-2-yl)-4,5-dihydro-2,6-(epoxyethano)benzo[d]-[1,3,6,2]dioxazagermocine

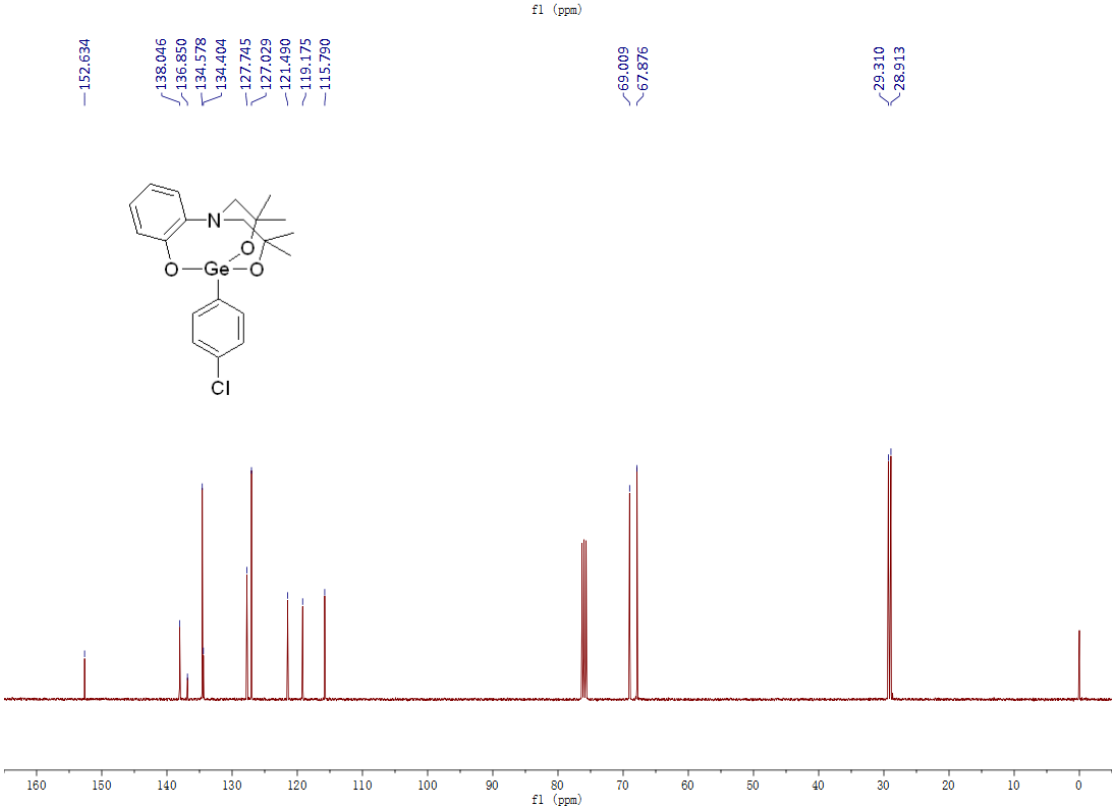


1p: 2-(3-bromophenyl)-4,4,12,12-tetramethyl-4,5-dihydro-2,6-(epoxyethano)benzo[d]-[1,3,6,2]dioxazagermocine

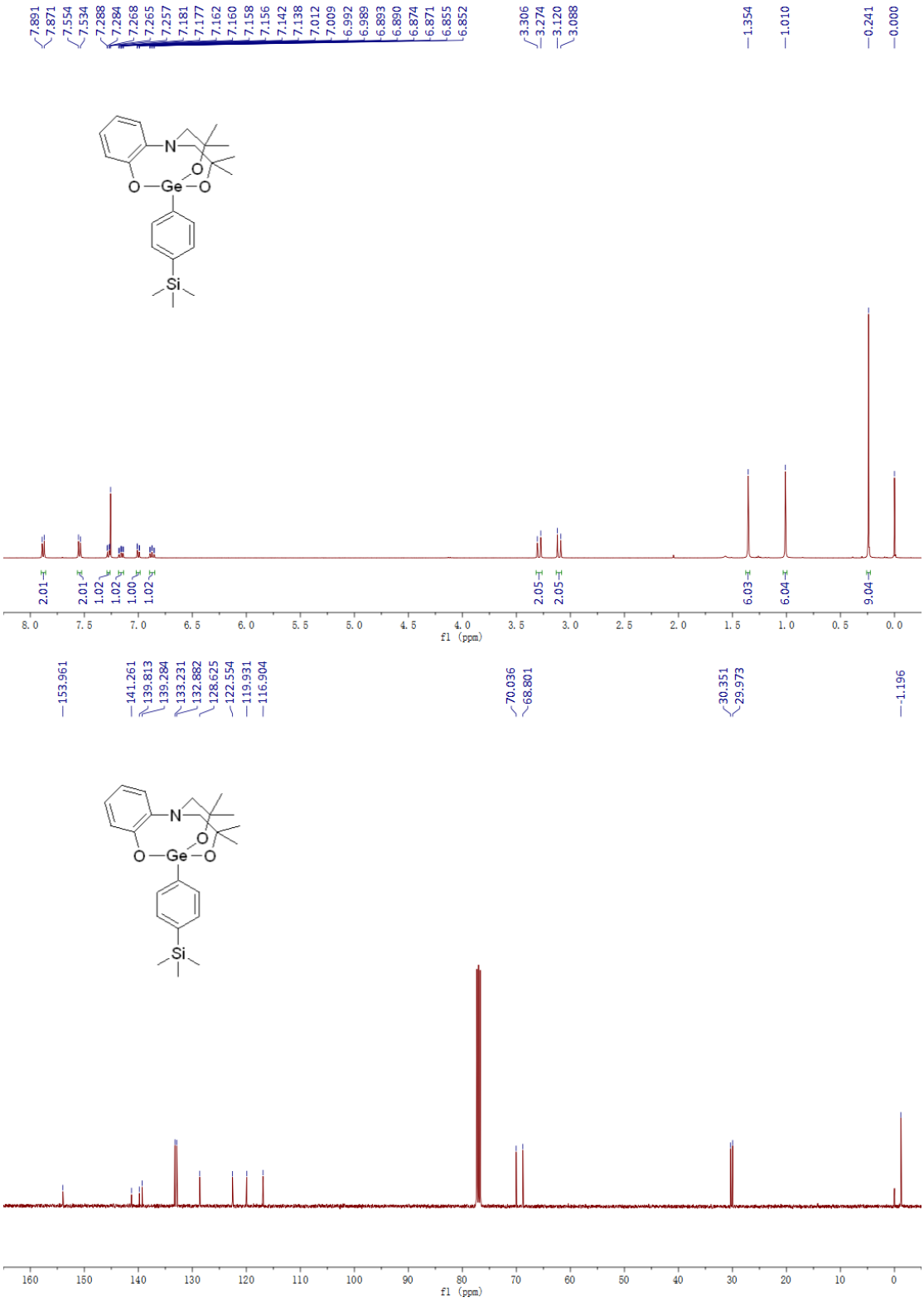


1q: 2-(4-chlorophenyl)-4,4,12,12-tetramethyl-4,5-dihydro-2,6-(epoxyethano)benzo[d]-[1,3,6,2]dioxazagermocine

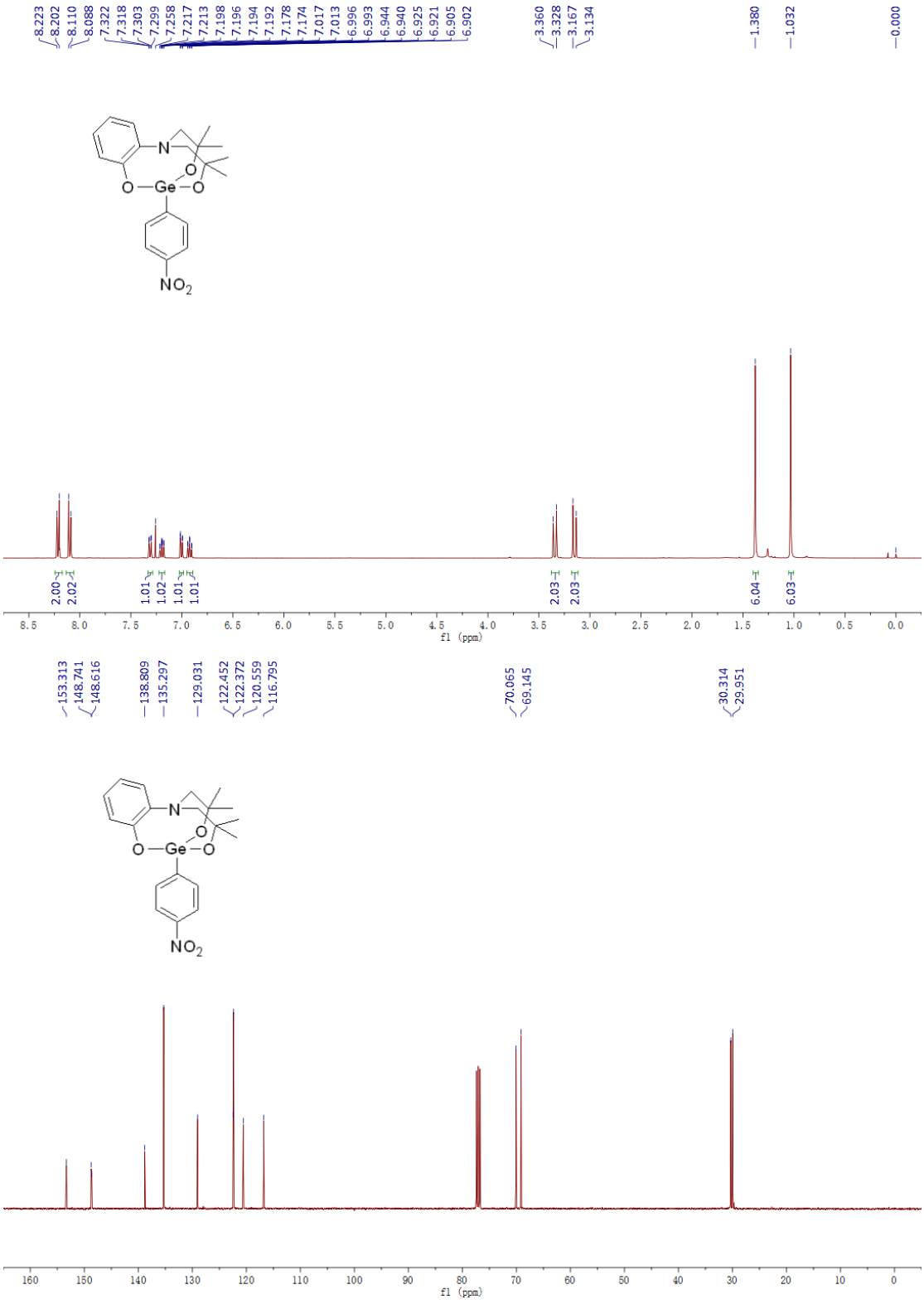




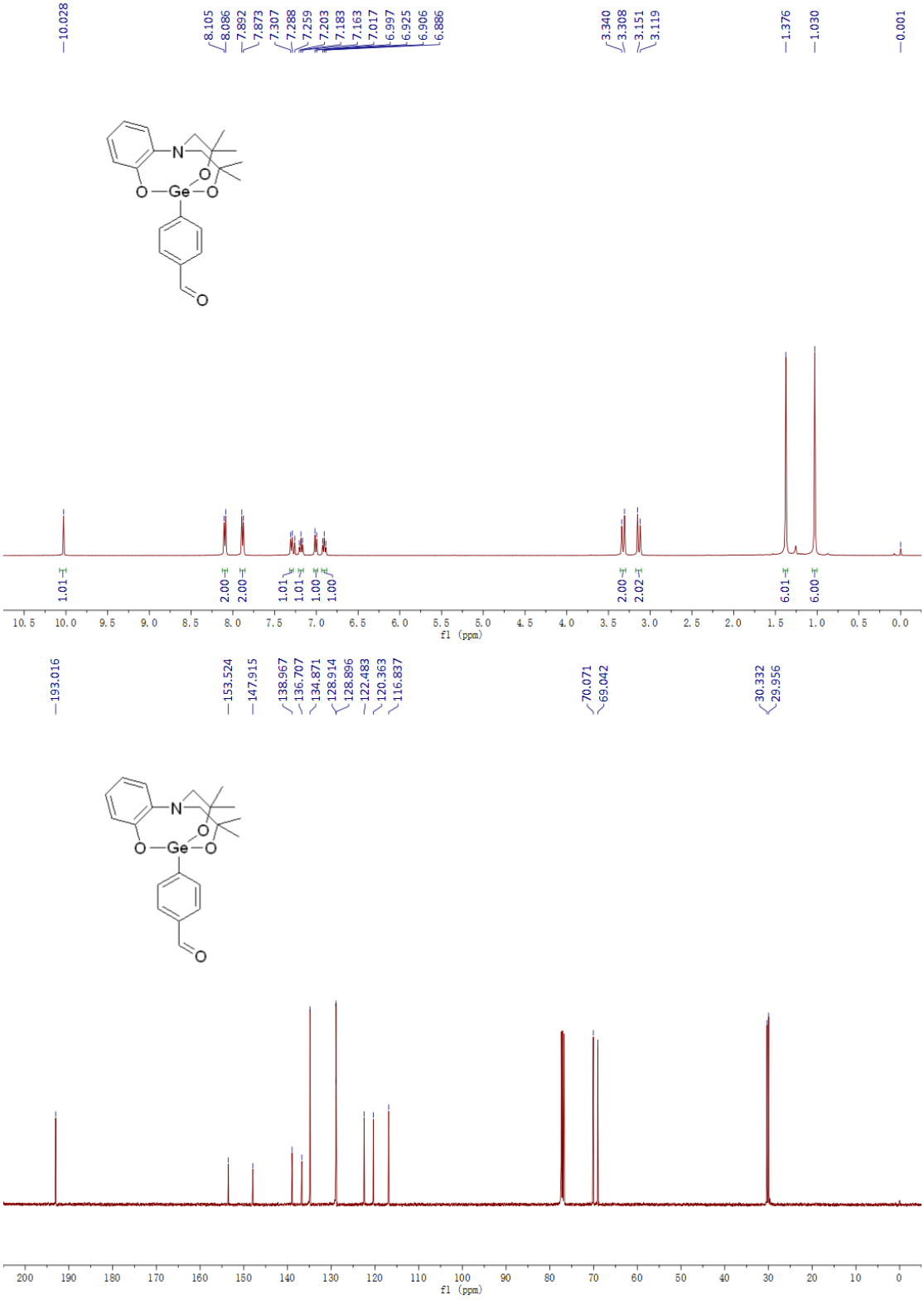
1r: 4,4,12,12-tetramethyl-2-(4-(trimethylsilyl)phenyl)-4,5-dihydro-2,6-(epoxyethano)benzo-[d][1,3,6,2]dioxazagermocine



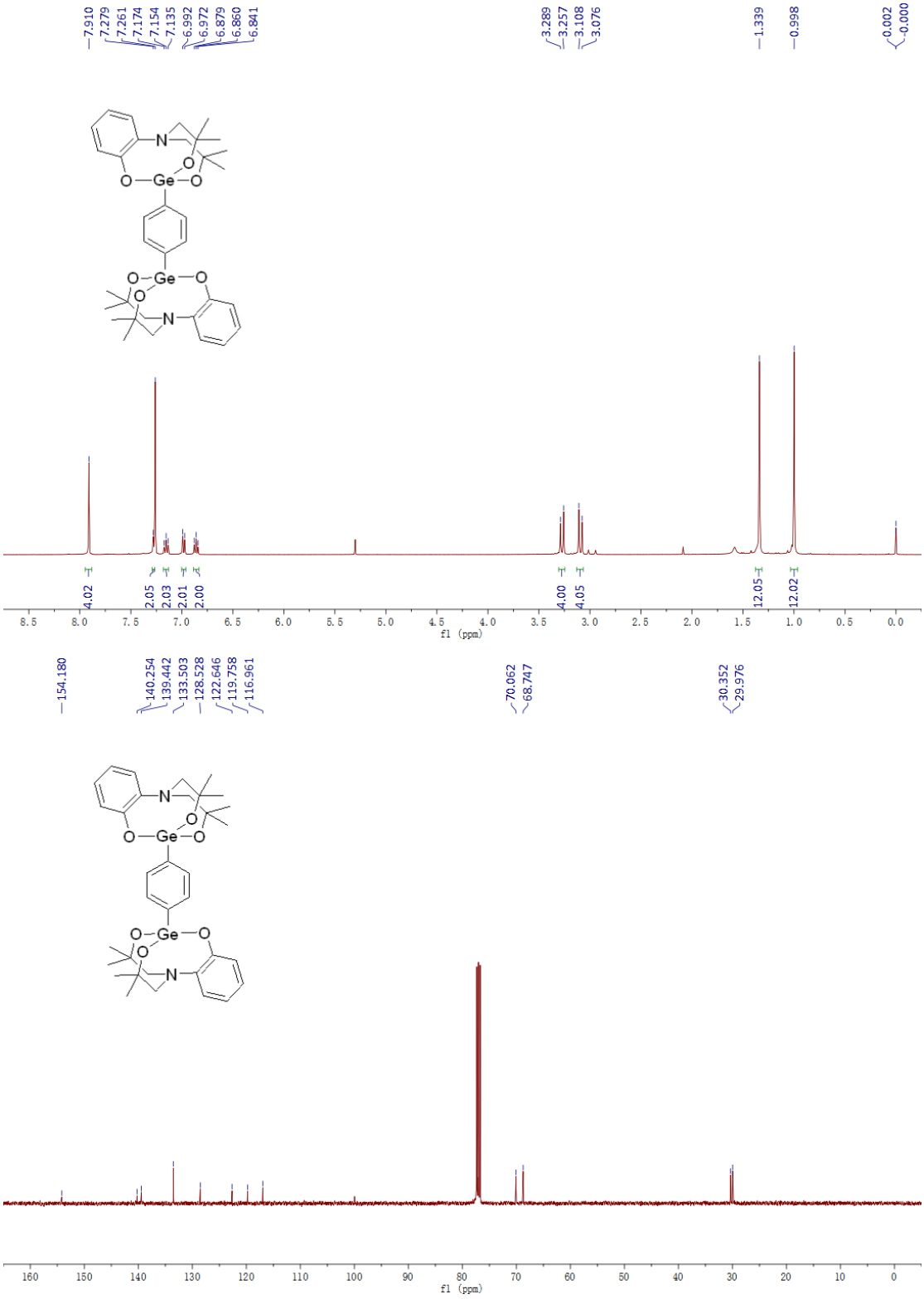
1s: 4,4,12,12-tetramethyl-2-(4-nitrophenyl)-4,5-dihydro-2,6-(epoxyethano)benzo[d][1,3,6,2]-dioxazagermocine



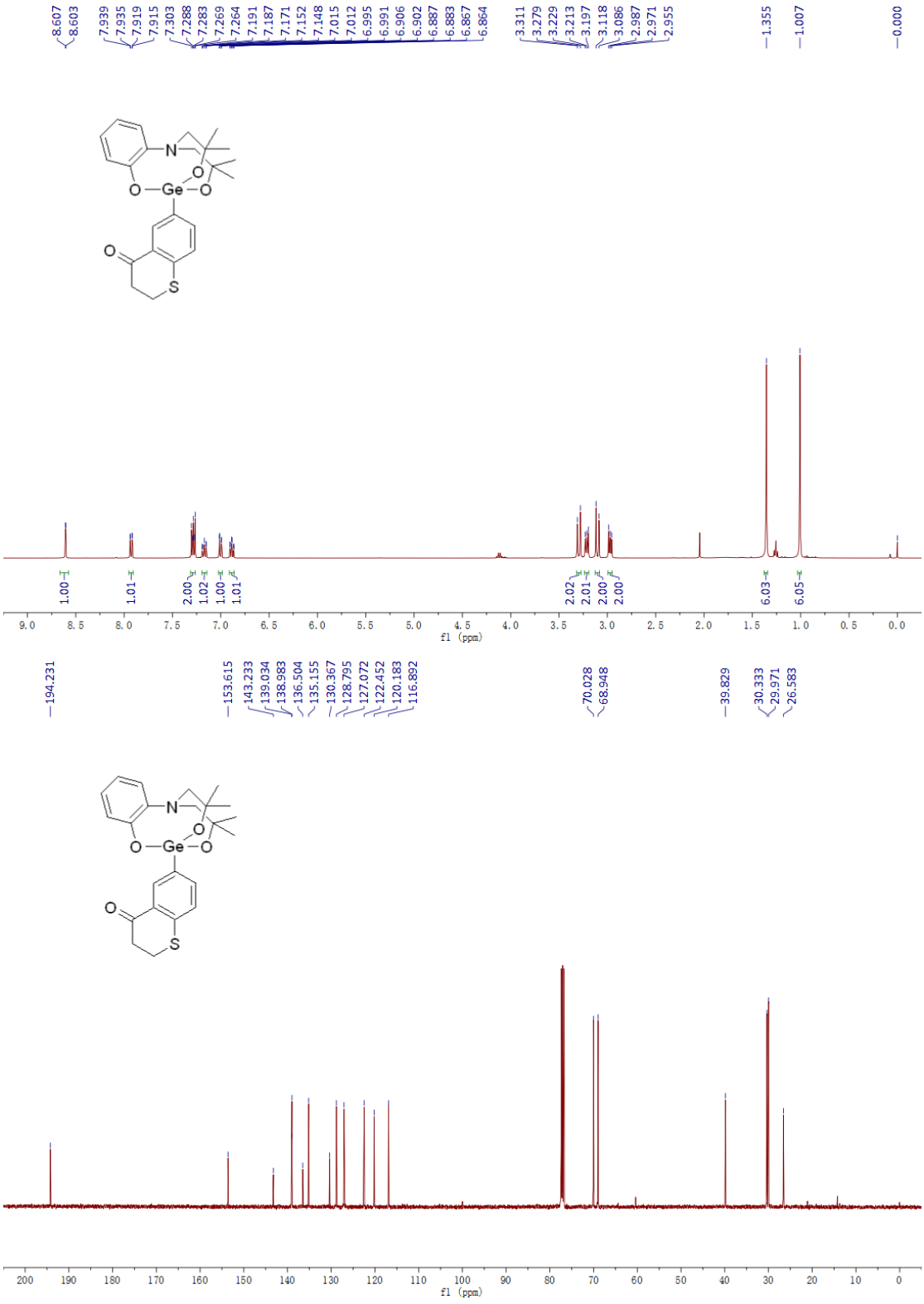
1t: 4-(4,4,12,12-tetramethyl-4,5-dihydro-2,6-(epoxyethano)benzo[d][1,3,6,2]dioxaza-germocin-2-yl)benzaldehyde



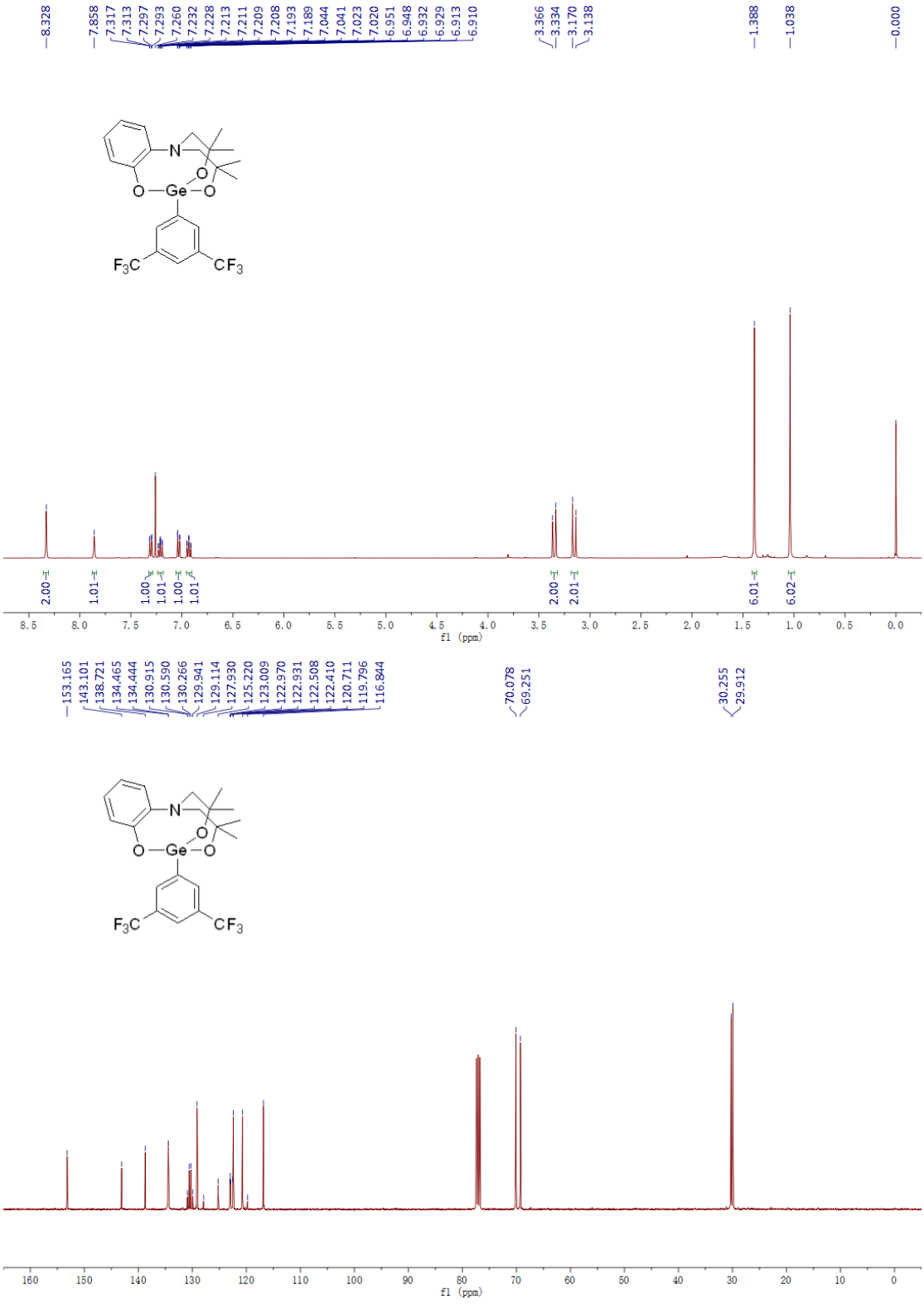
1u: 1,4-bis(4,4,12,12-tetramethyl-4,5-dihydro-2,6-(epoxyethano)benzo[d][1,3,6,2]dioxaza-germocin-2-yl)benzene



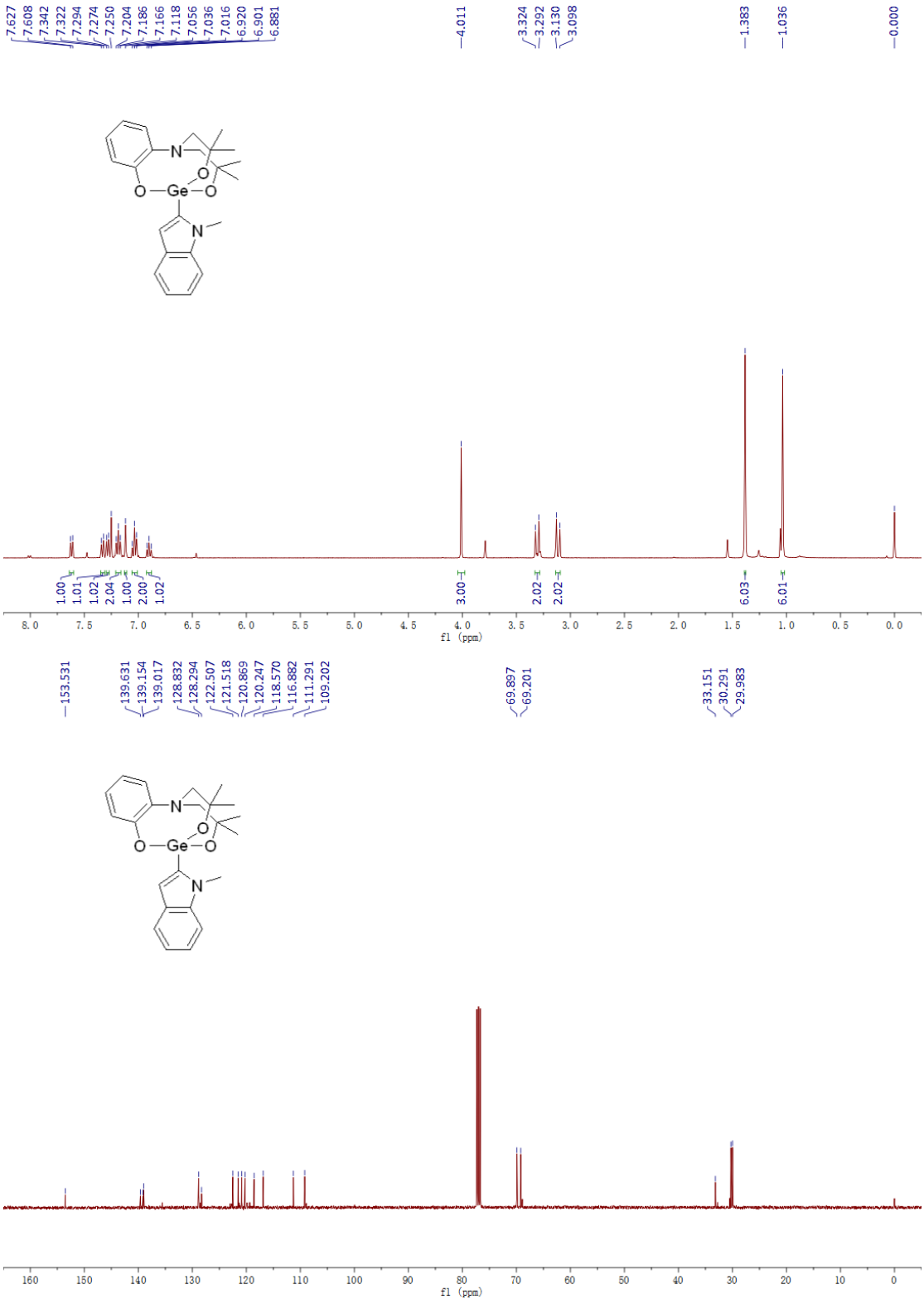
1v: 6-(4,4,12,12-tetramethyl-4,5-dihydro-2,6-(epoxyethano)benzo[d][1,3,6,2]dioxaza-germocin-2-yl)thiochroman-4-one



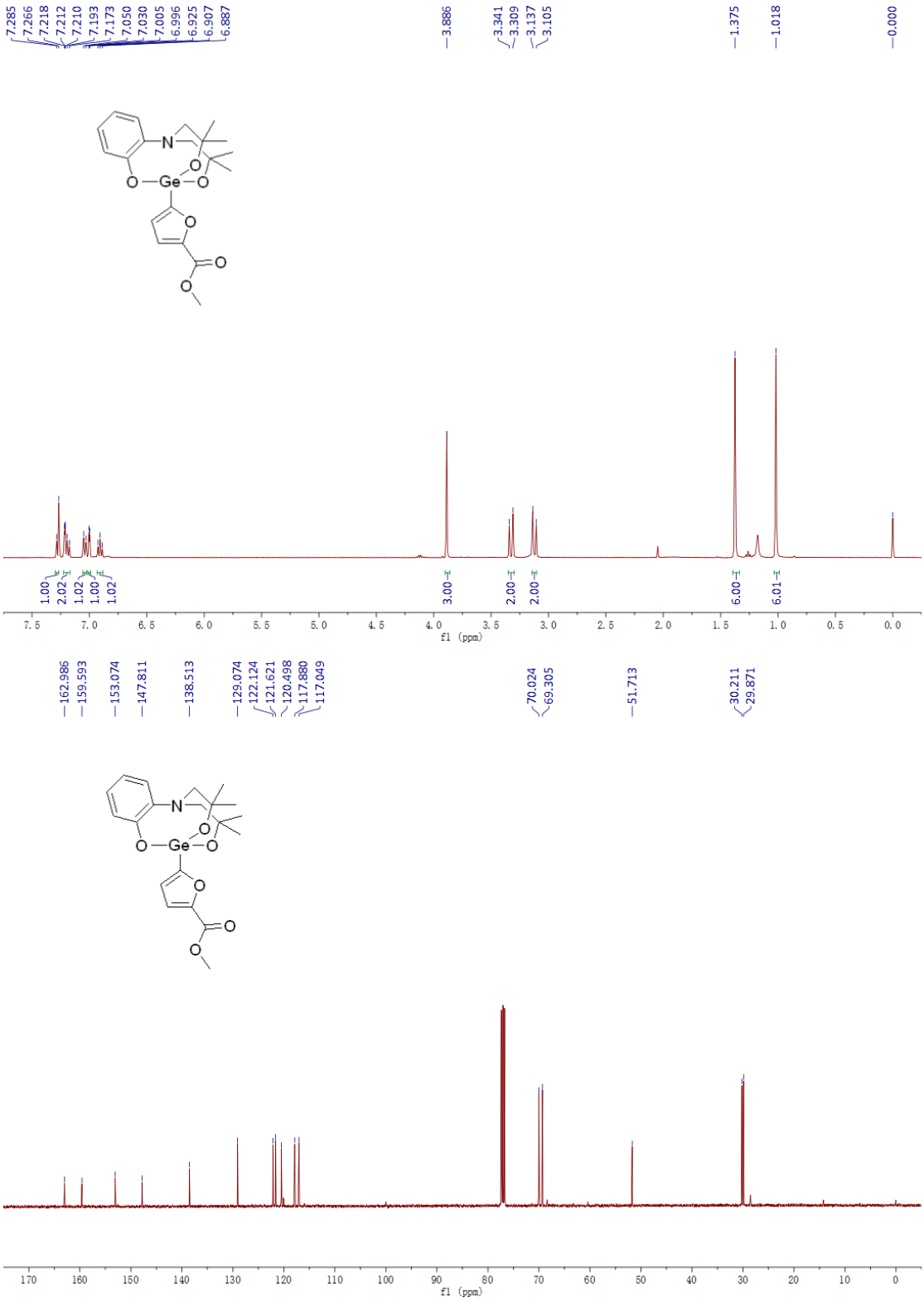
1w: 2-(3,5-bis(trifluoromethyl)phenyl)-4,4,12,12-tetramethyl-4,5-dihydro-2,6-(epoxyethano)-benzo[d][1,3,6,2]dioxazagermocine



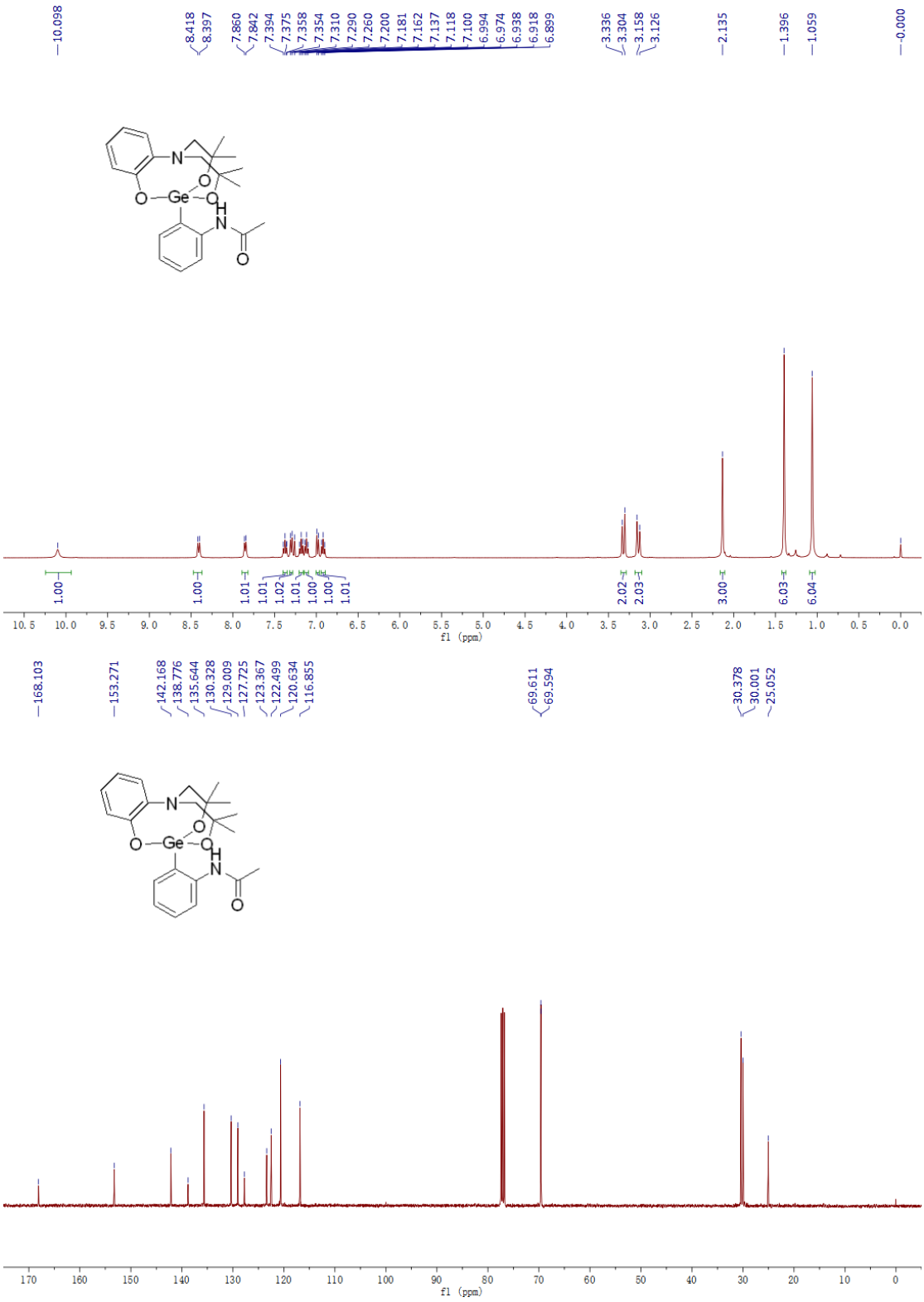
1x: 4,4,12,12-tetramethyl-2-(1-methyl-1H-indol-2-yl)-4,5-dihydro-2,6-(epoxyethano)benzo-[d][1,3,6,2]dioxazagermocine



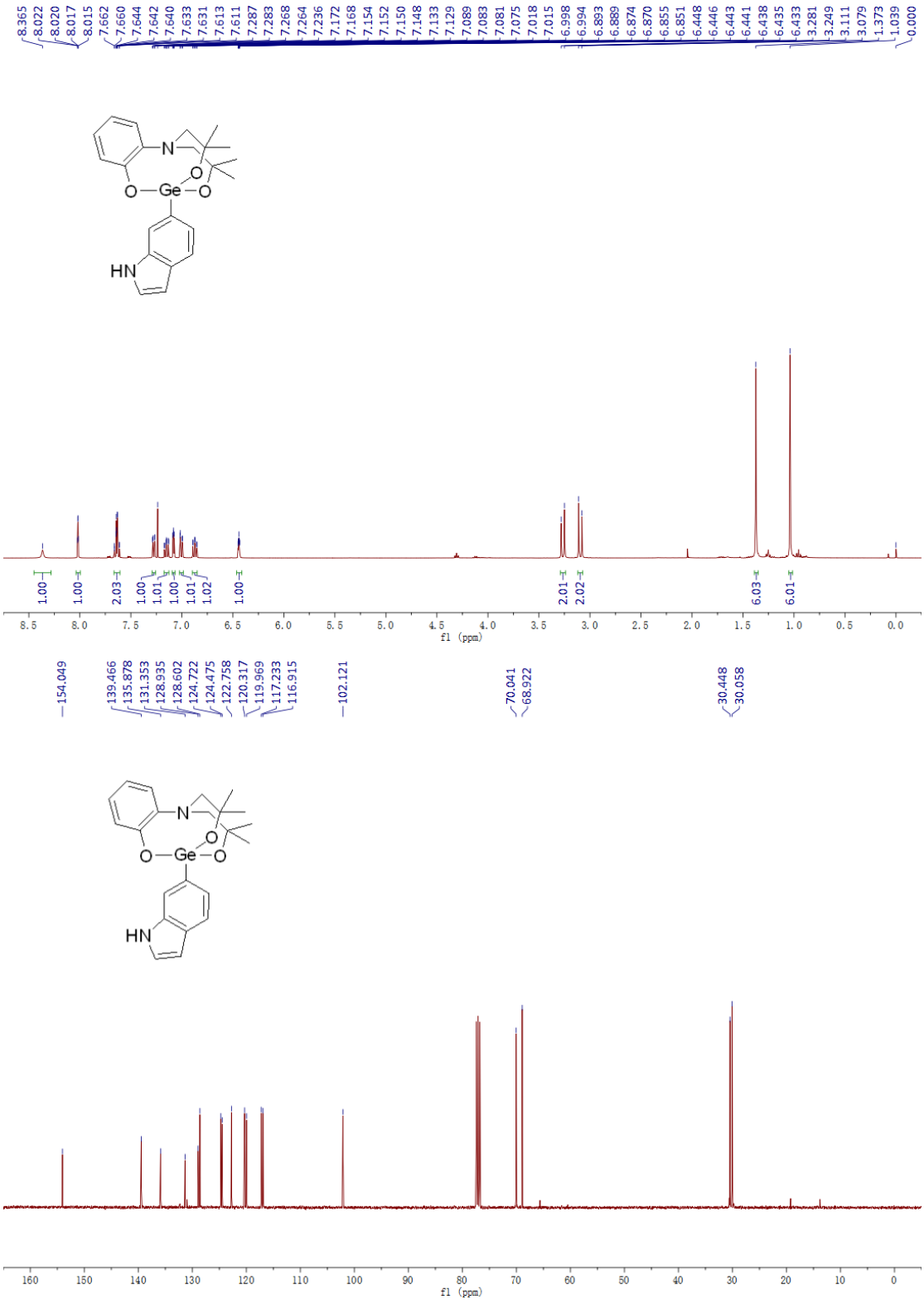
1y: methyl 5-(4,4,12,12-tetramethyl-4,5-dihydro-2,6-(epoxyethano)benzo[d][1,3,6,2]dioxaza-germocin-2-yl)furan-2-carboxylate



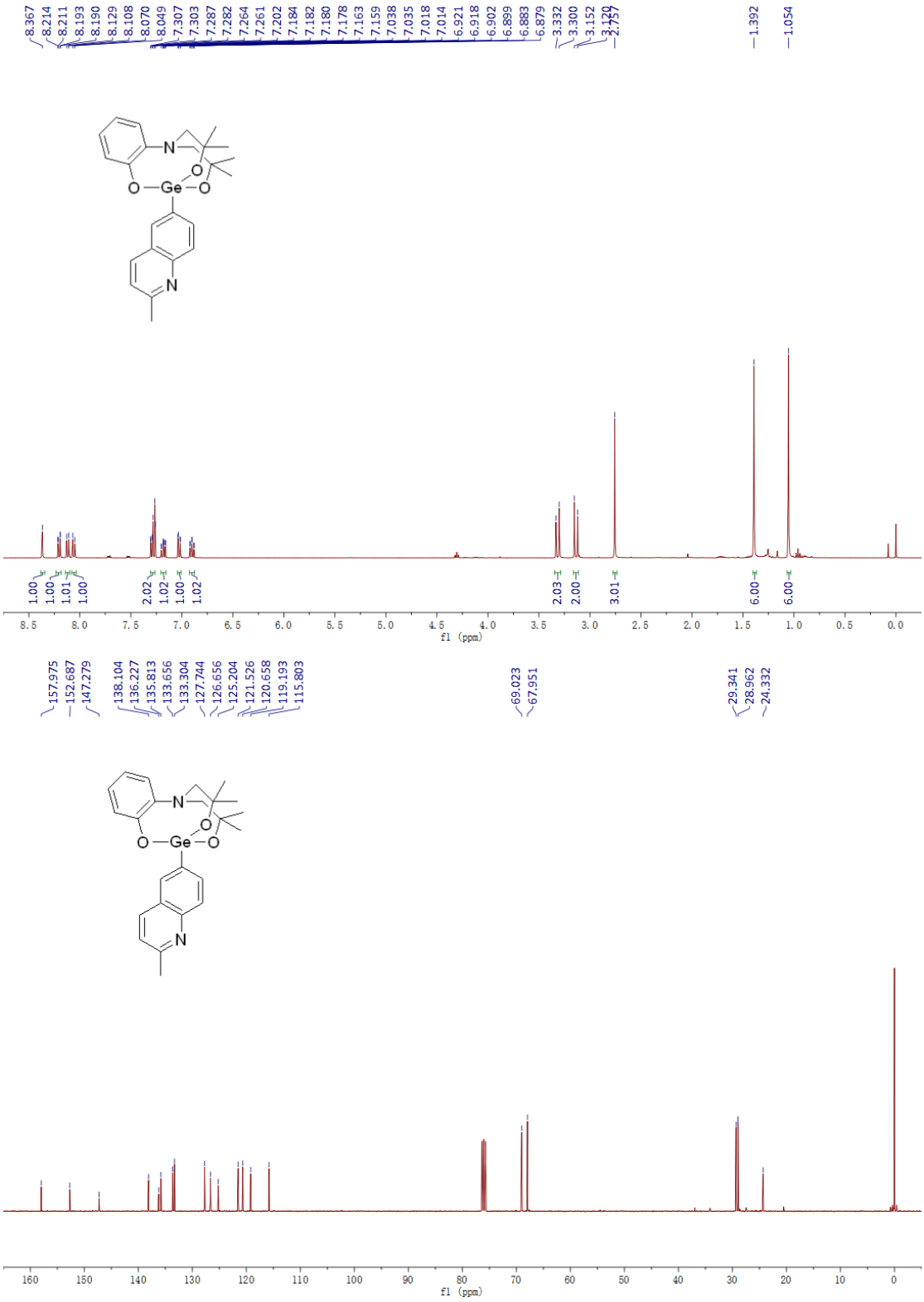
1z: N-(2-(4,4,12,12-tetramethyl-4,5-dihydro-2,6-(epoxyethano)benzo[d][1,3,6,2]dioxazagermocin-2-yl)phenyl)acetamide



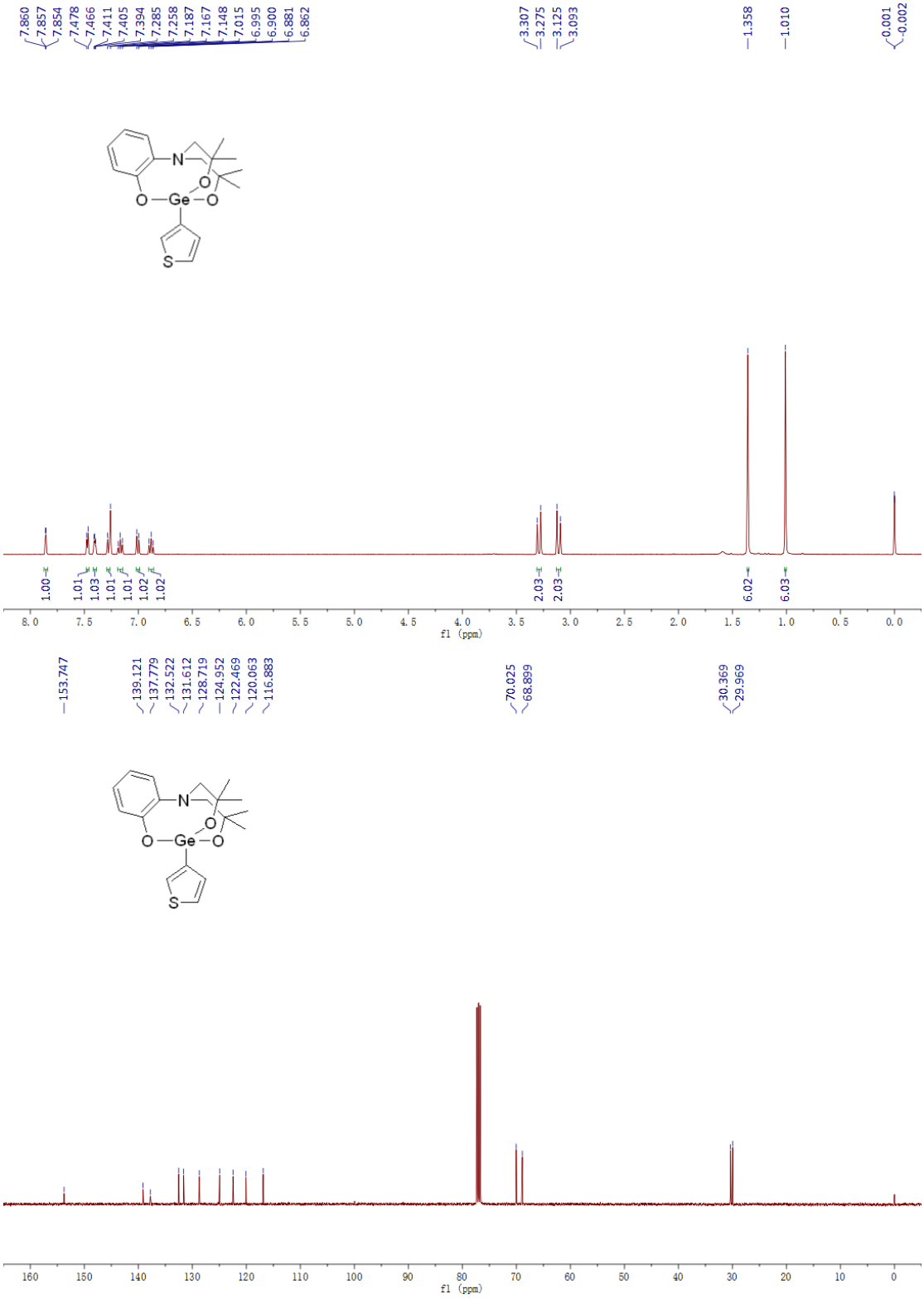
1a’: 2-(1H-indol-6-yl)-4,4,12,12-tetramethyl-4,5-dihydro-2,6-(epoxyethano)benzo[d][1,3,6,2]-dioxazagermocine



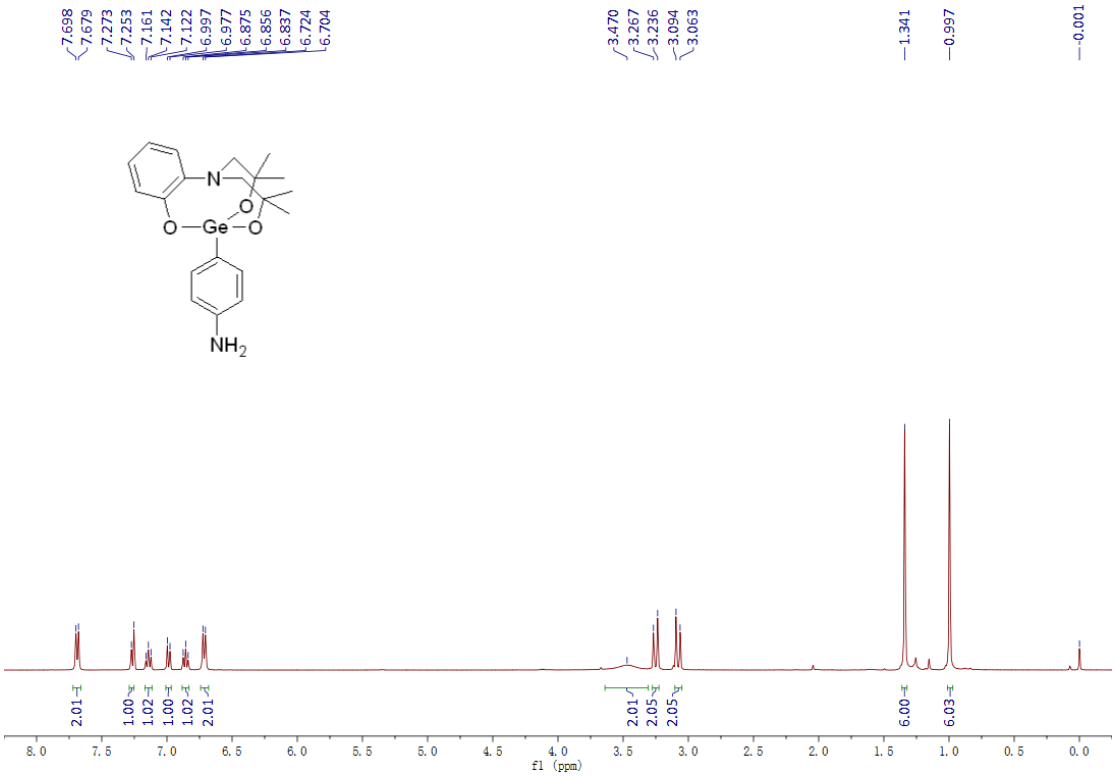
1b': 4,4,12,12-tetramethyl-2-(2-methylquinolin-6-yl)-4,5-dihydro-2,6-(epoxyethano)benzo[d]-[1,3,6,2]dioxazagermocine

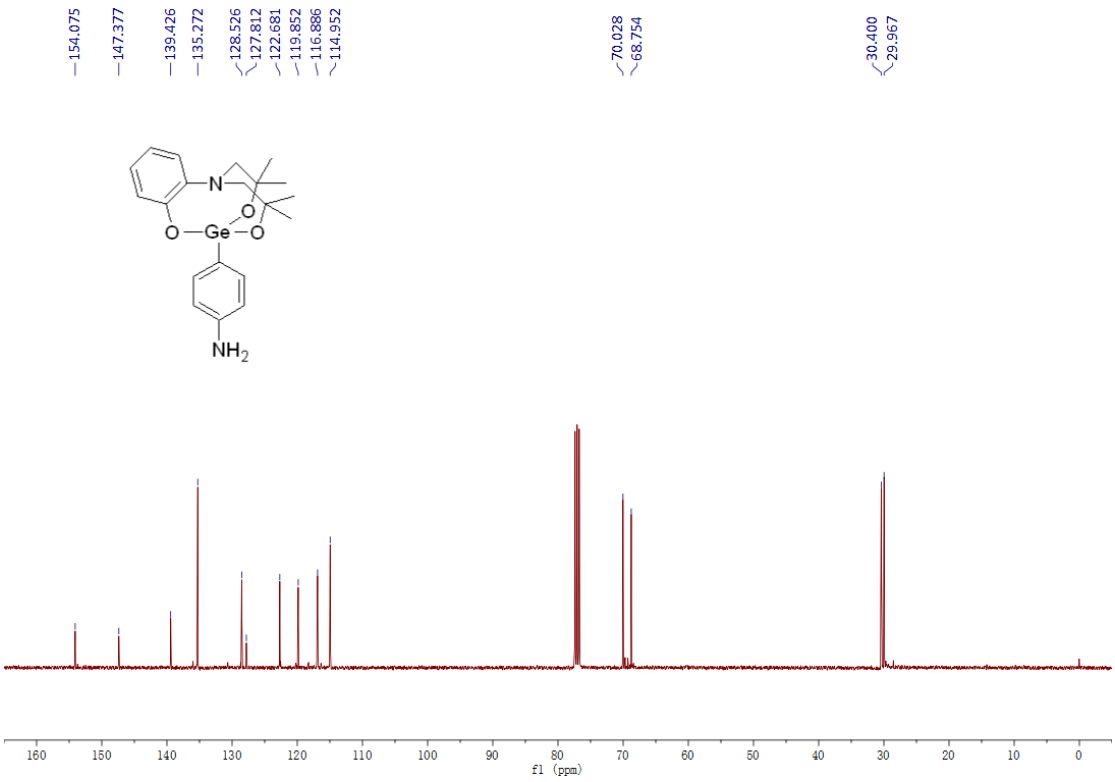


1c’: 4,4,12,12-tetramethyl-2-(thiophen-3-yl)-4,5-dihydro-2,6-(epoxyethano)benzo[d][1,3,6,2]-dioxazagermocine

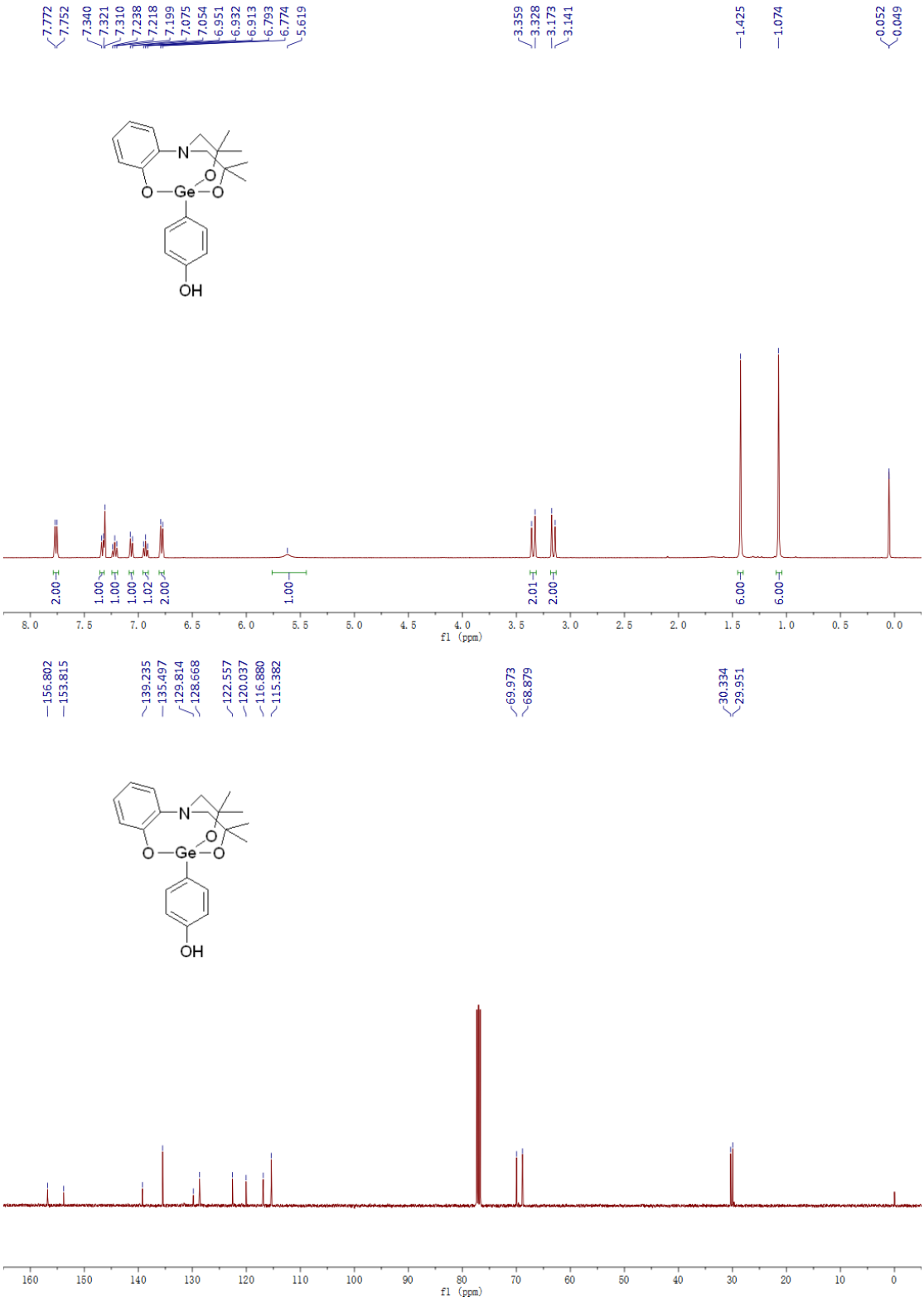


1d’: 4-(4,4,12,12-tetramethyl-4,5-dihydro-2,6-(epoxyethano)benzo[d][1,3,6,2]dioxaza-germocin-2-yl)aniline

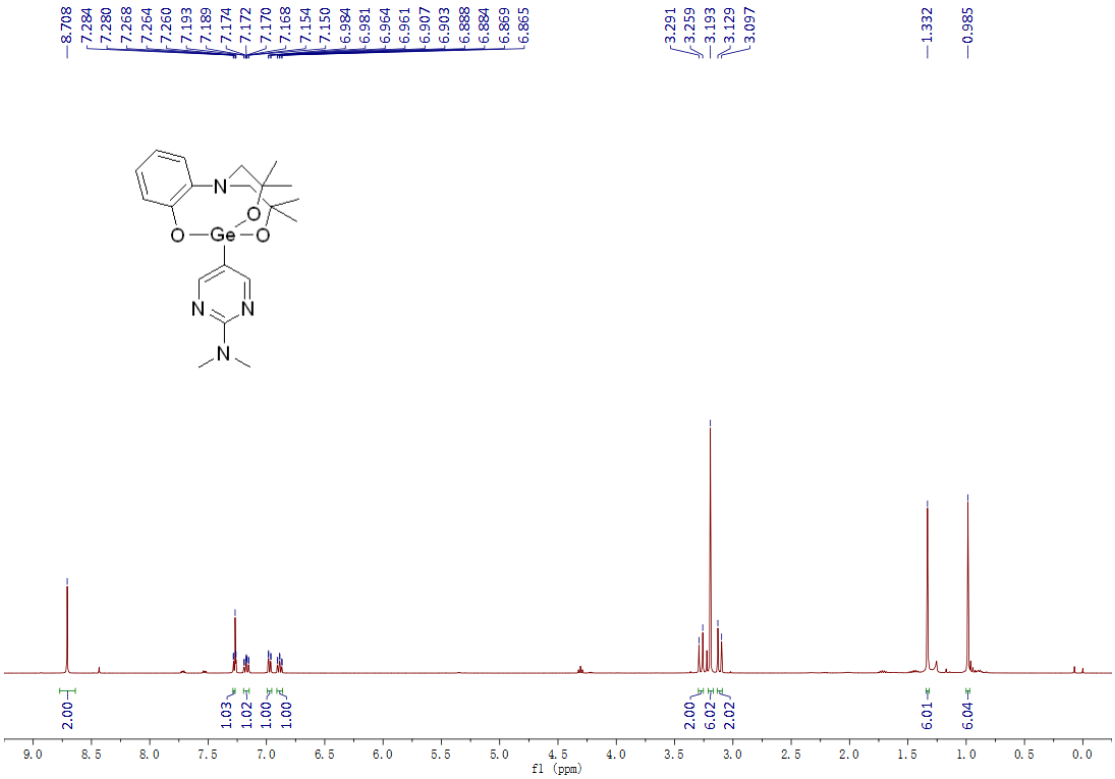


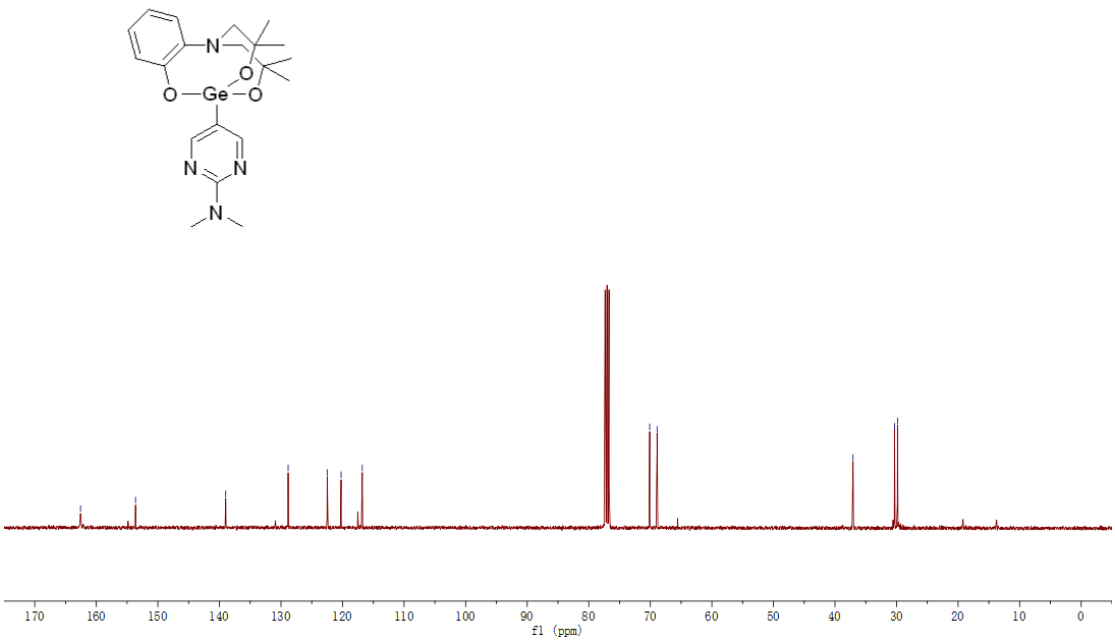


1e’: 4-(4,4,12,12-tetramethyl-4,5-dihydro-2,6-(epoxyethano)benzo[d][1,3,6,2]dioxaza-germocin-2-yl)phenol

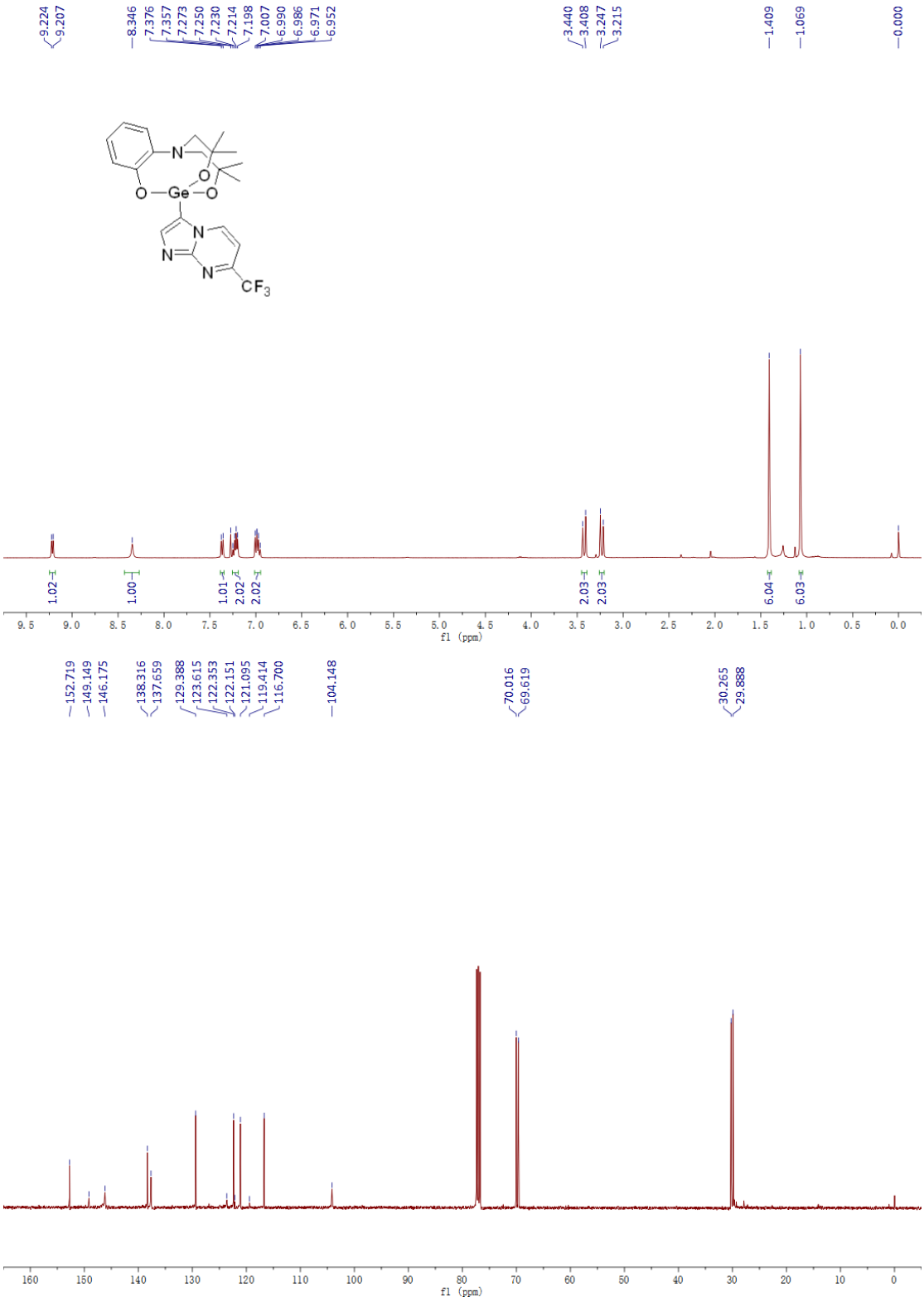


1f’: N,N-dimethyl-5-(4,4,12,12-tetramethyl-4,5-dihydro-2,6-(epoxyethano)benzo[d][1,3,6,2]-dioxazagermocin-2-yl)pyrimidin-2-amine

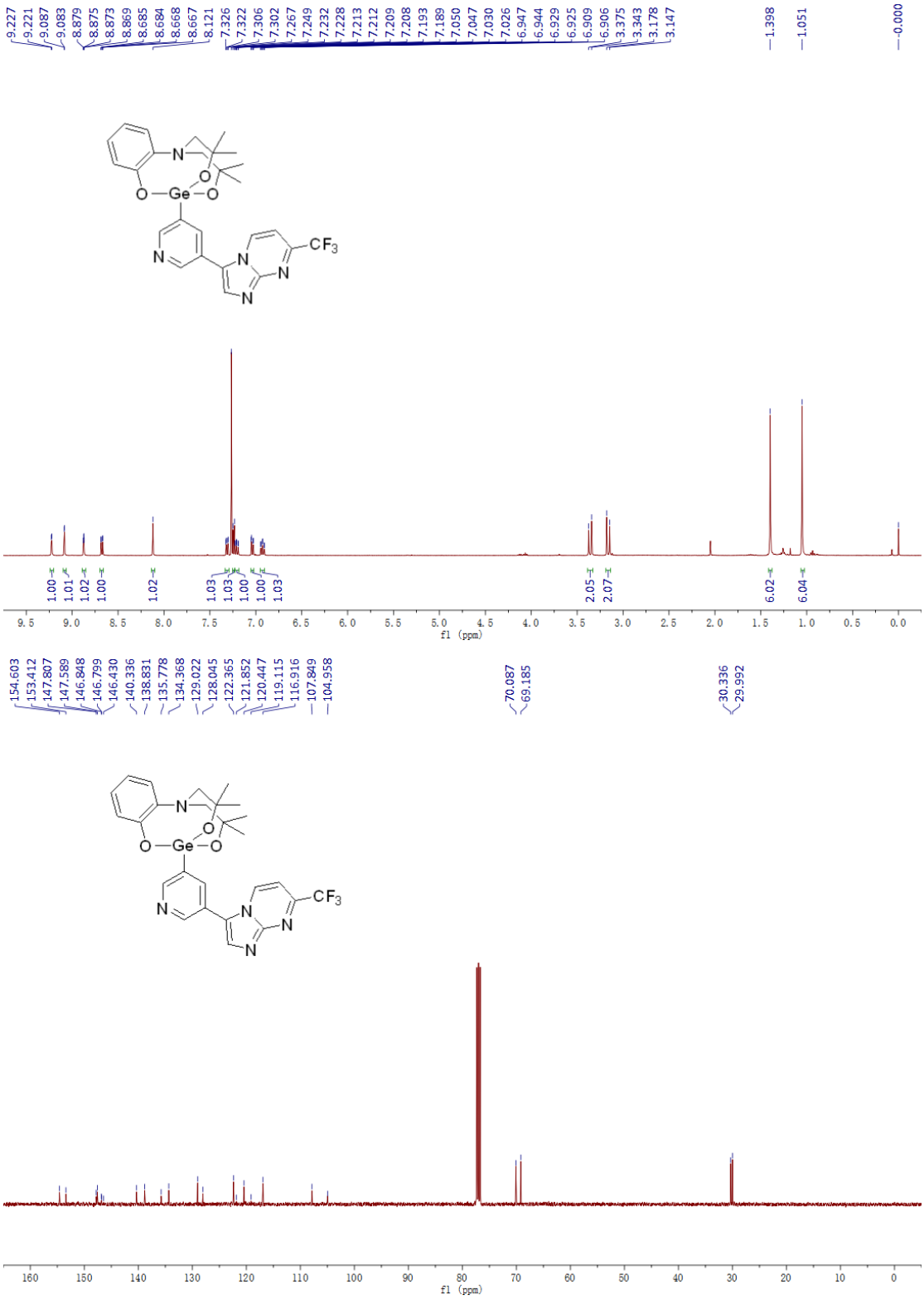




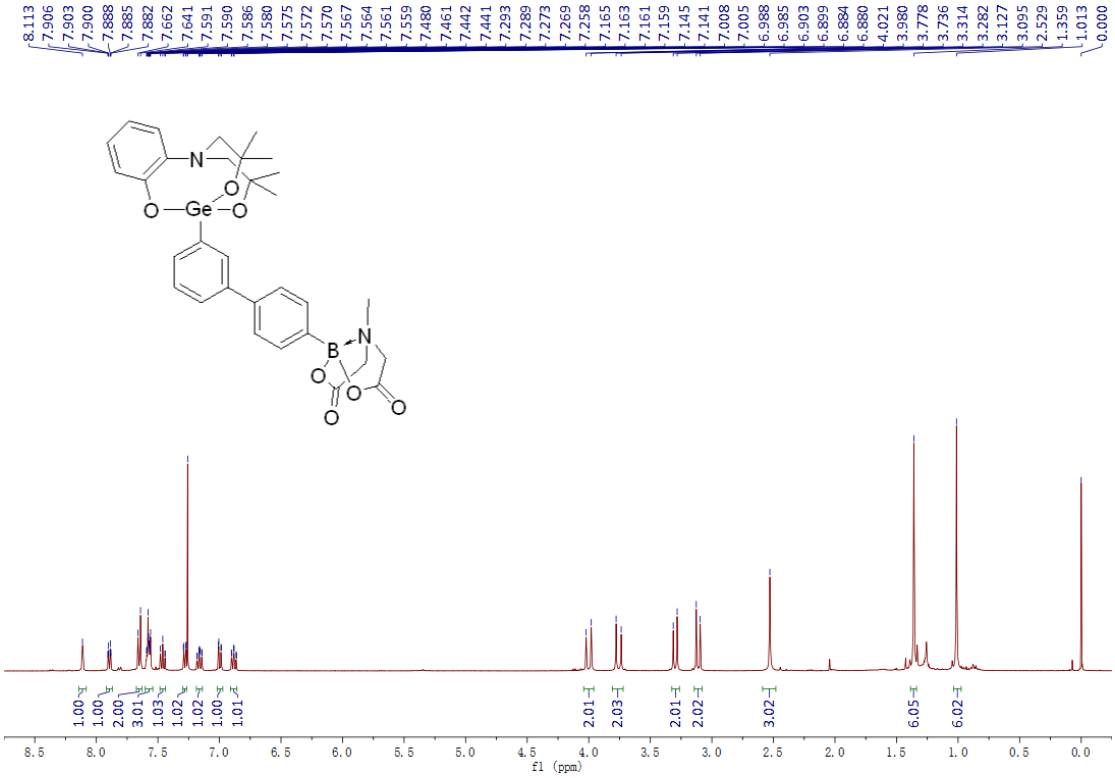
1g’: 4,4,12,12-tetramethyl-2-(7-(trifluoromethyl)imidazo[1,2-a]pyrimidin-3-yl)-4,5-dihydro-2,6-(epoxyethano)benzo[d][1,3,6,2]dioxazagermocine

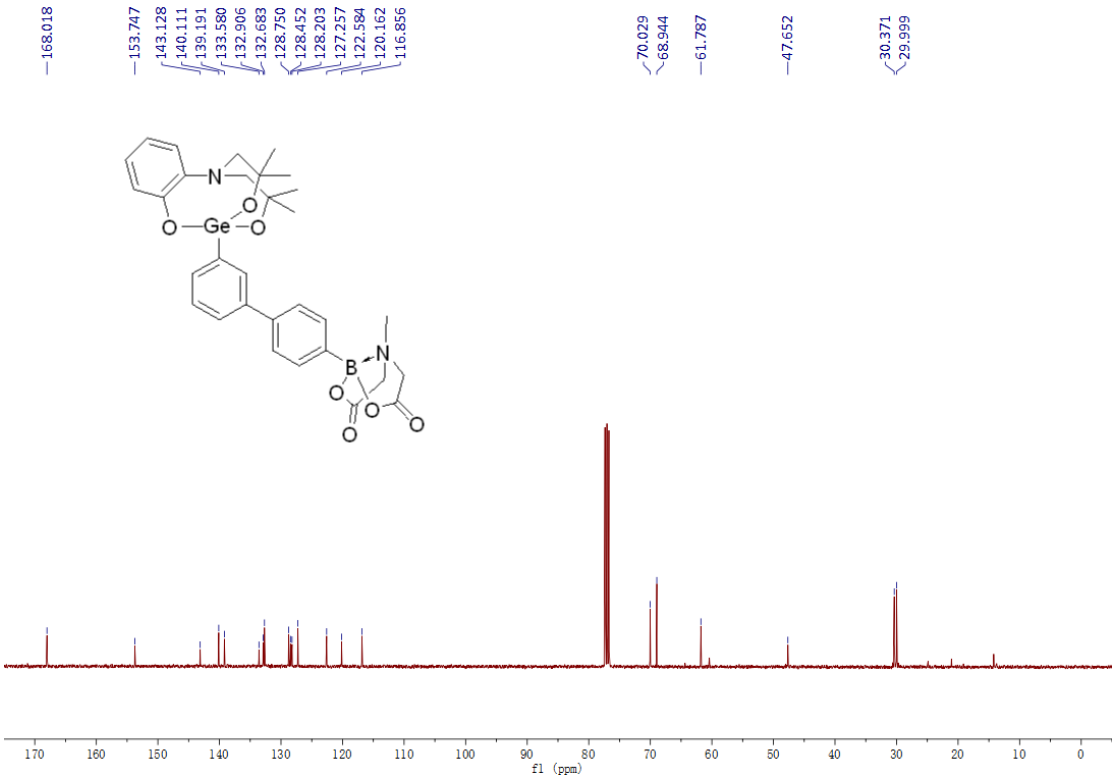


1h’: 4,4,12,12-tetramethyl-2-(5-(7-(trifluoromethyl)imidazo[1,2-a]pyrimidin-3-yl)pyridin-3-yl)-4,5-dihydro-2,6-(epoxyethano)benzo[d][1,3,6,2]dioxazagermocine

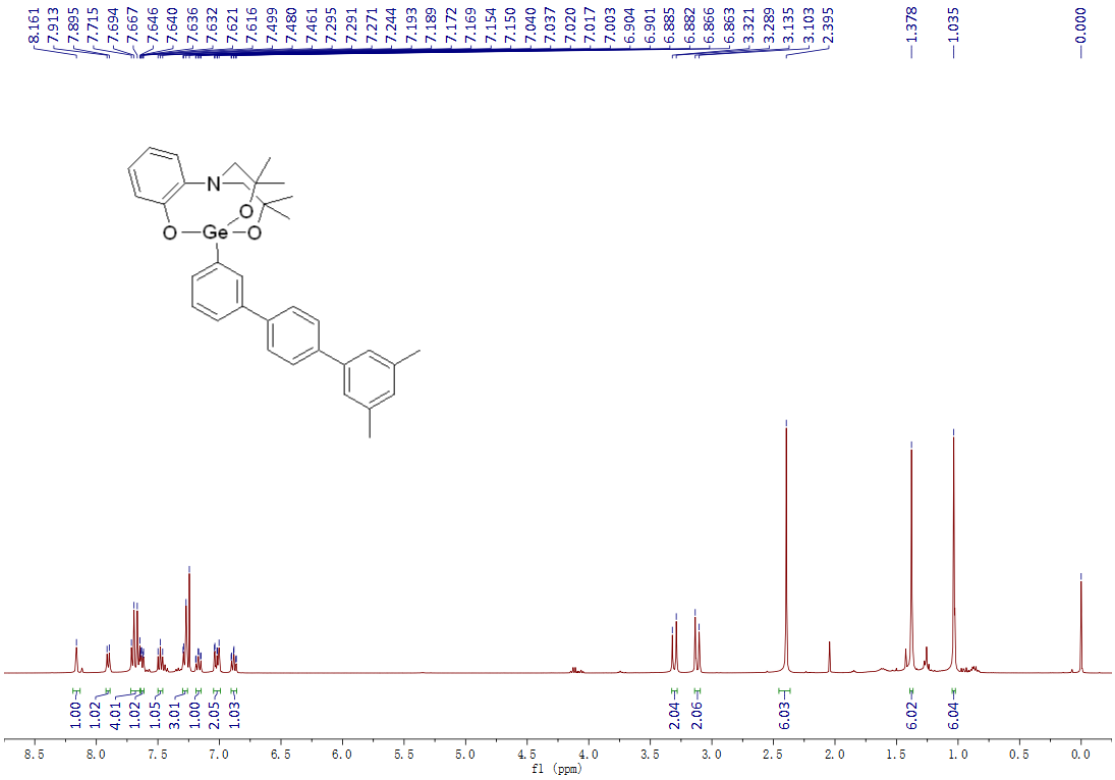


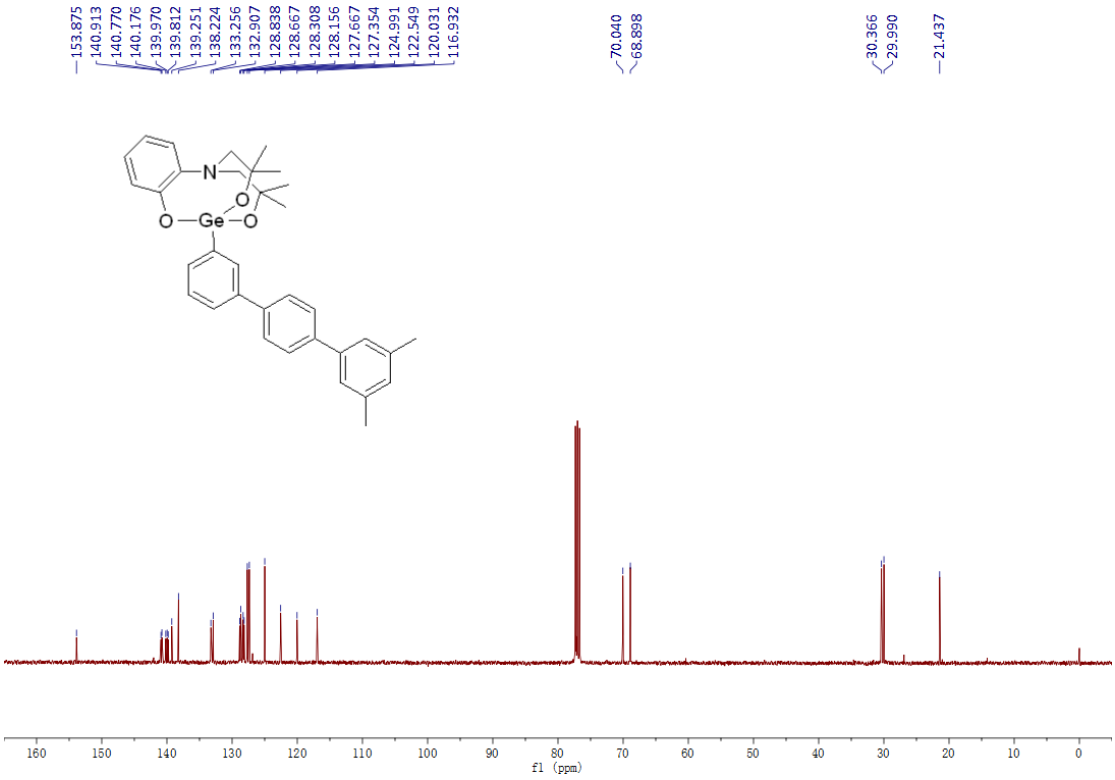
1i': 4-methyl-8-(3'-(4,4,12,12-tetramethyl-4,5-dihydro-2,6-(epoxyethano)benzo[d][1,3,6,2]dioxazagermocin-2-yl)-[1,1'-biphenyl]-4-yl)dihydro-4λ⁴,8λ⁴-[1,3,2]oxazaborolo[2,3-b][1,3,2]oxazaborole-2,6(3H,5H)-dione



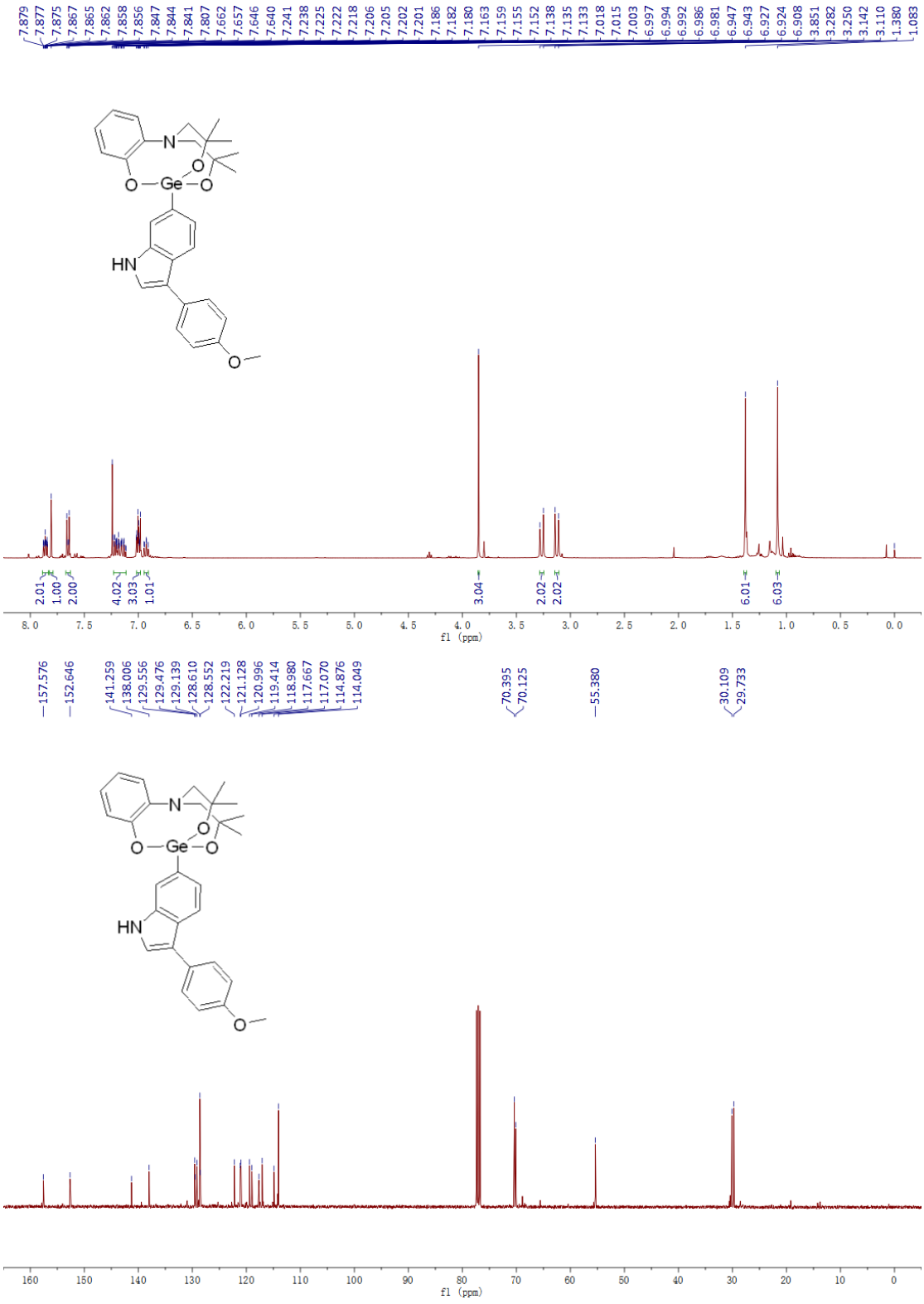


1j’: 2-(3'',5''-dimethyl-[1,1':4',1''-terphenyl]-3-yl)-4,4,12,12-tetramethyl-4,5-dihydro-2,6-(epoxyethano)benzo[d][1,3,6,2]dioxazagermocine

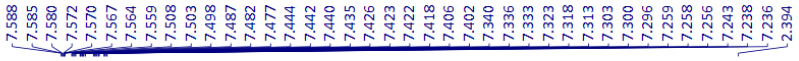


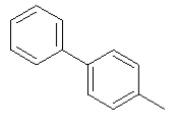


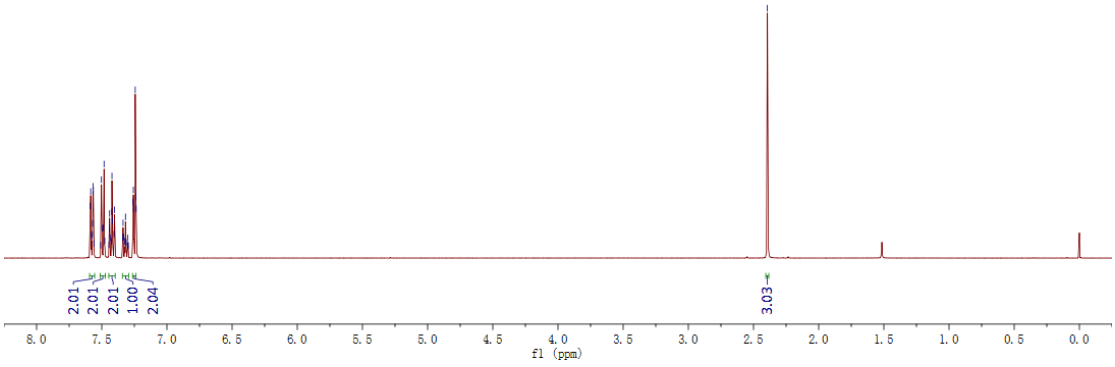
1k’: 2-(3-(4-methoxyphenyl)-1H-indol-6-yl)-4,4,12,12-tetramethyl-4,5-dihydro-2,6-(epoxy-ethano)benzo[d][1,3,6,2]dioxazagermocine.

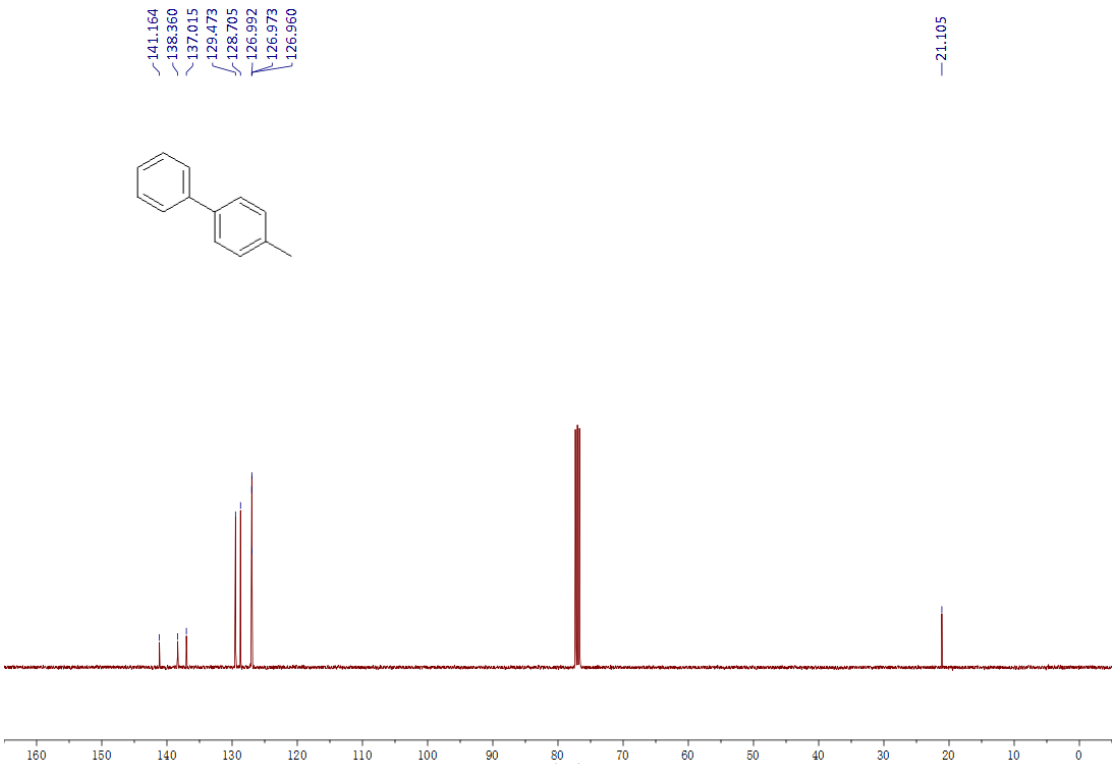


3a: 4-methyl-1,1'-biphenyl

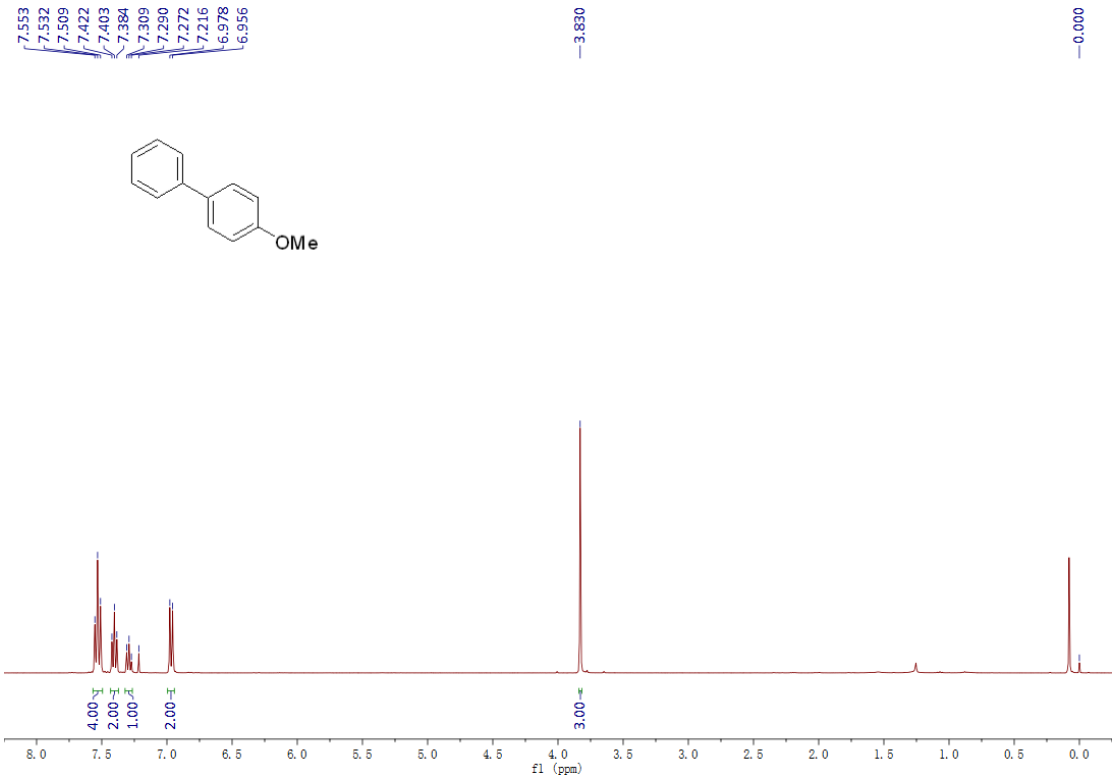


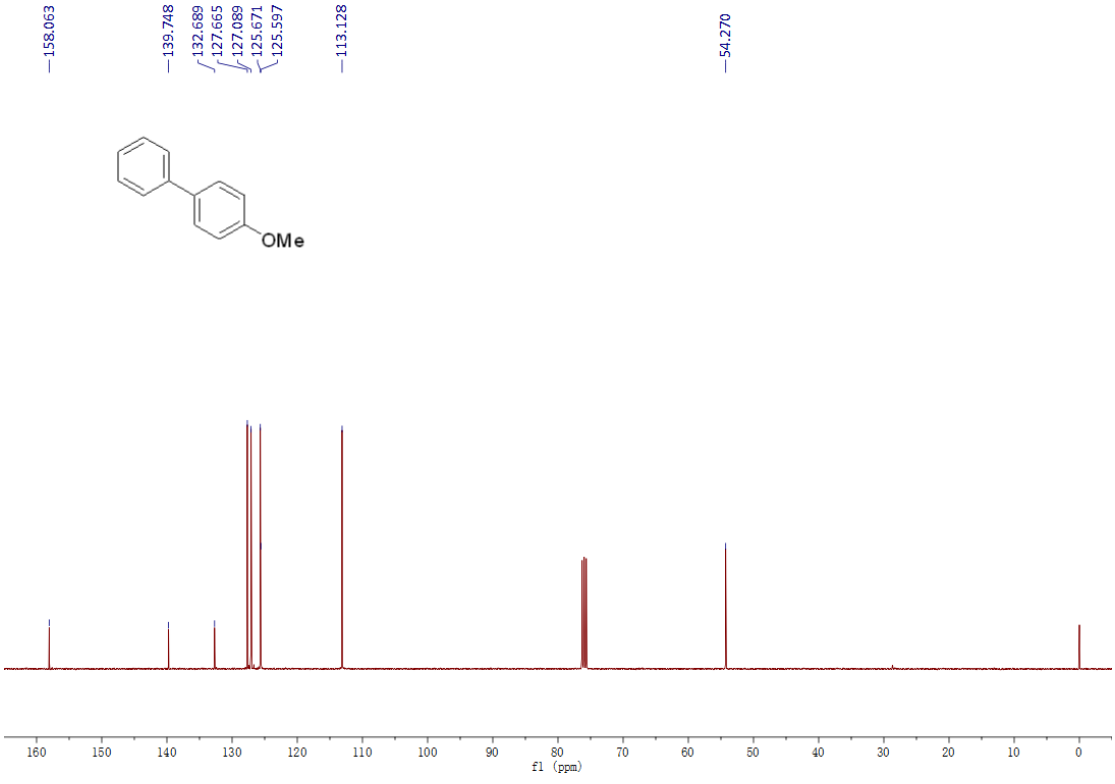




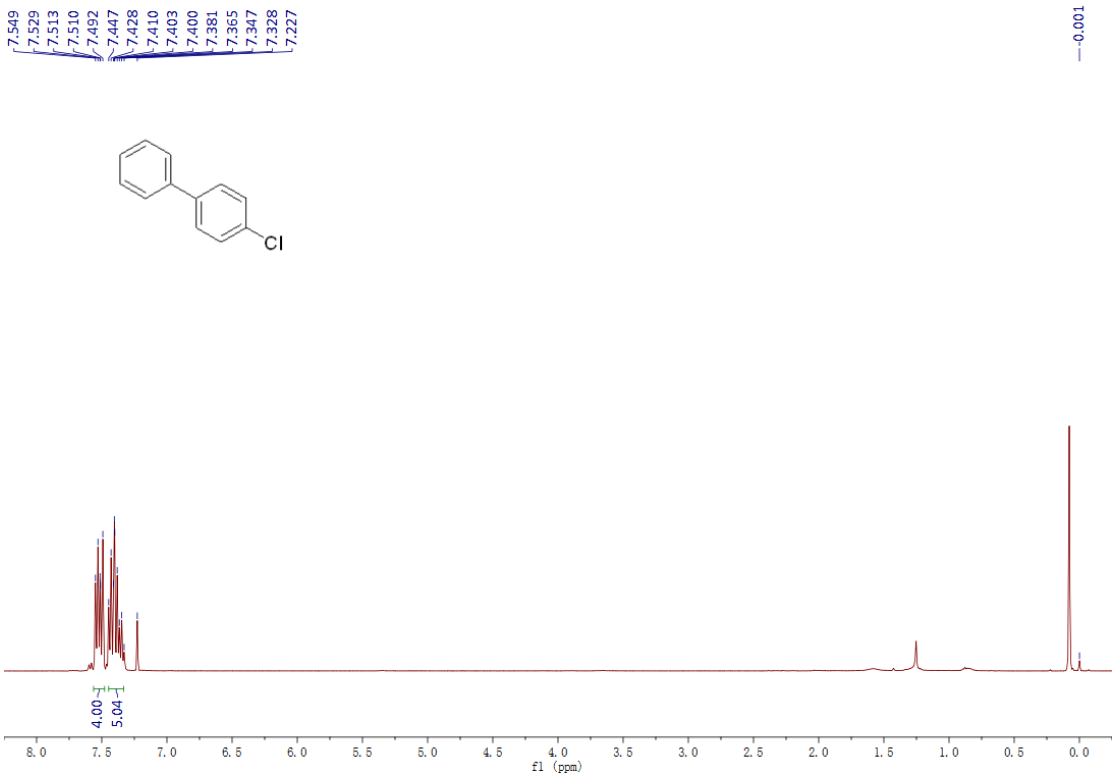


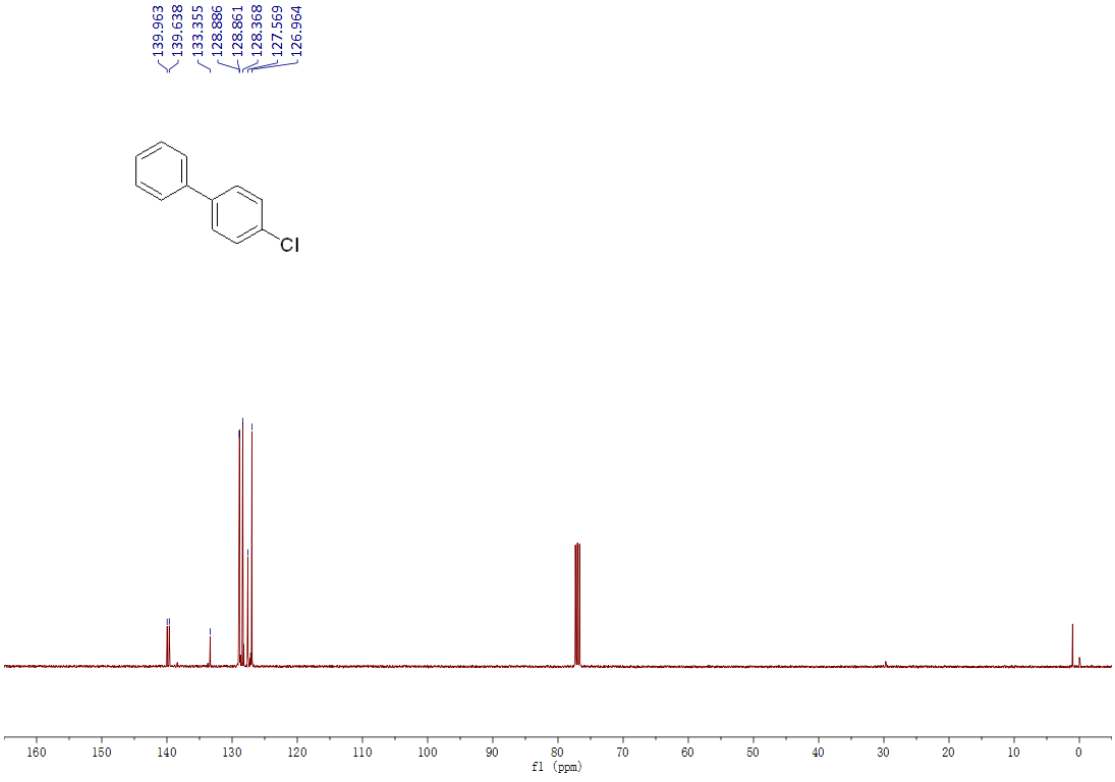
3b: 4-methoxy-1,1'-biphenyl



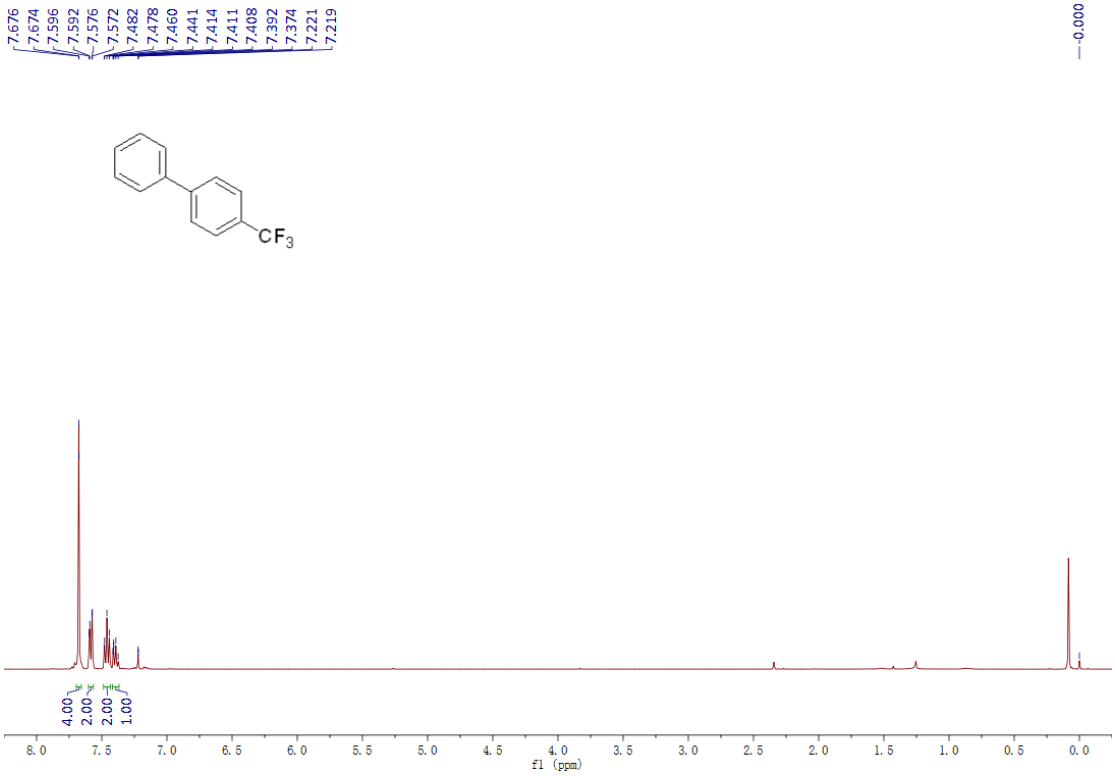


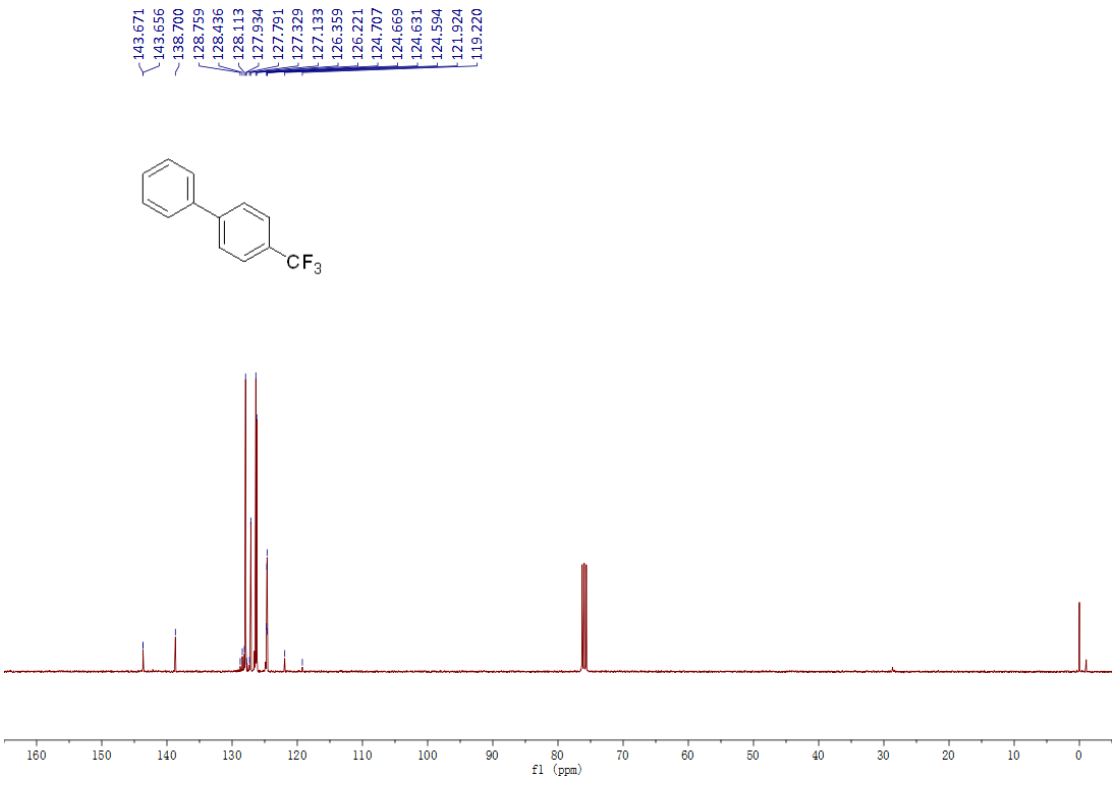
3c: 4-chloro-1,1'-biphenyl



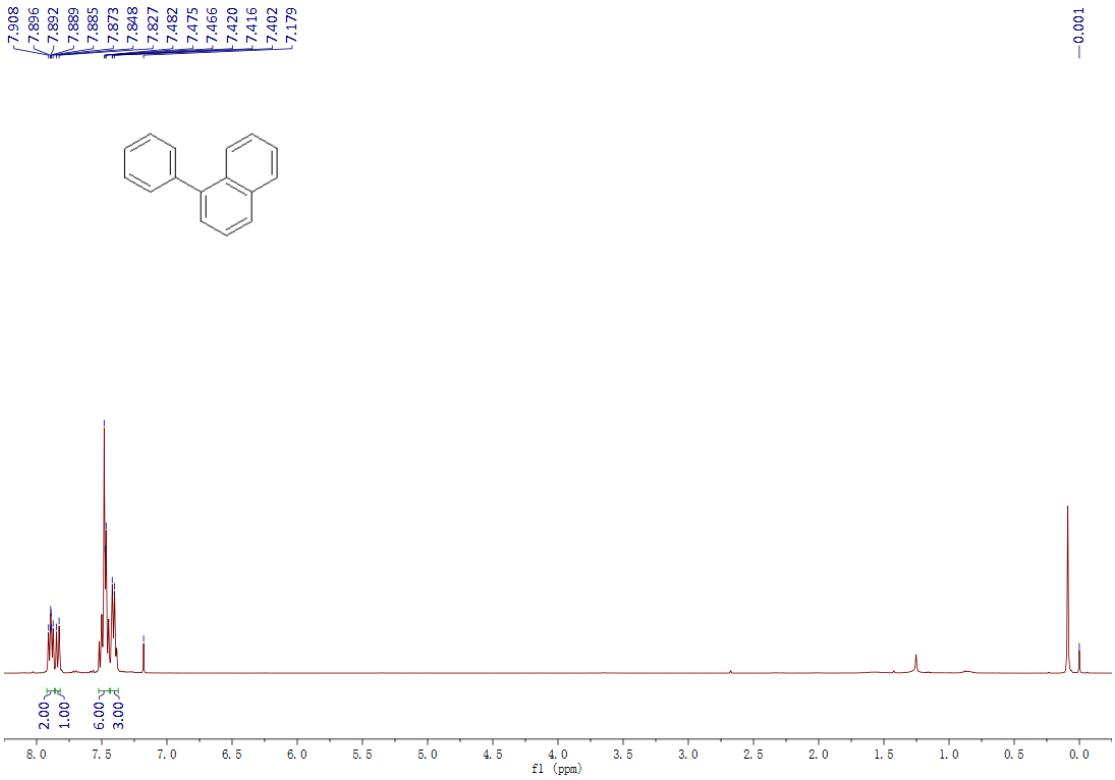


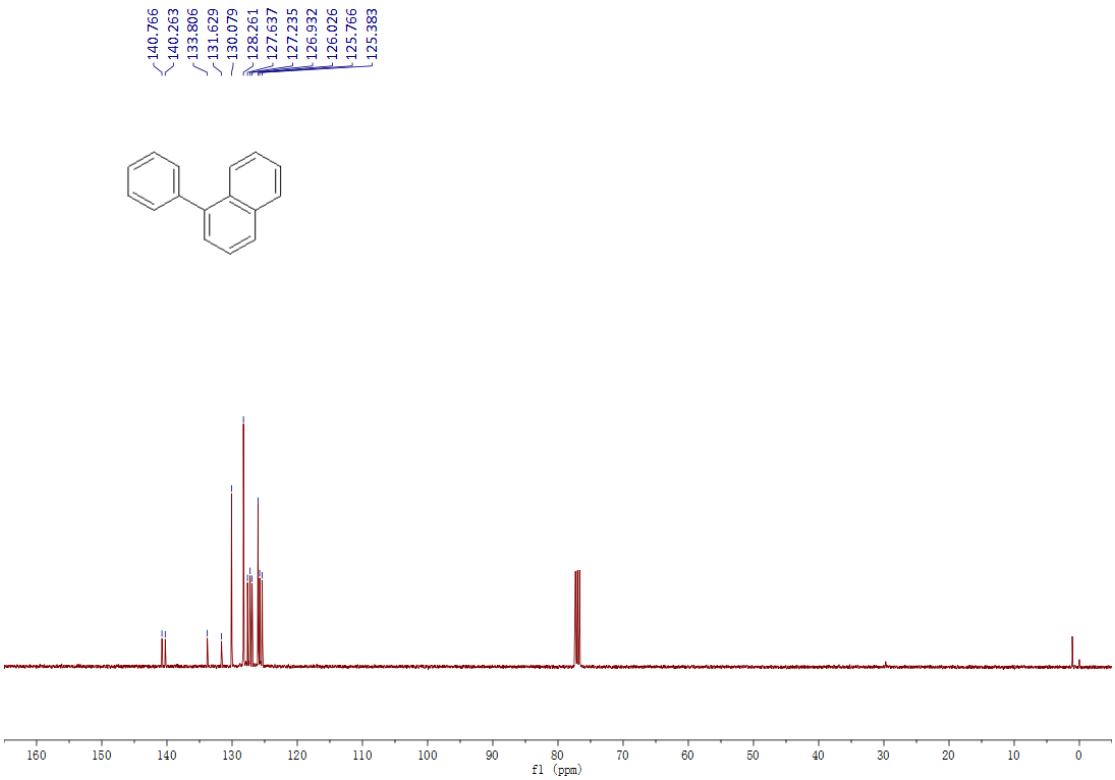
3d: 4-(trifluoromethyl)-1,1'-biphenyl



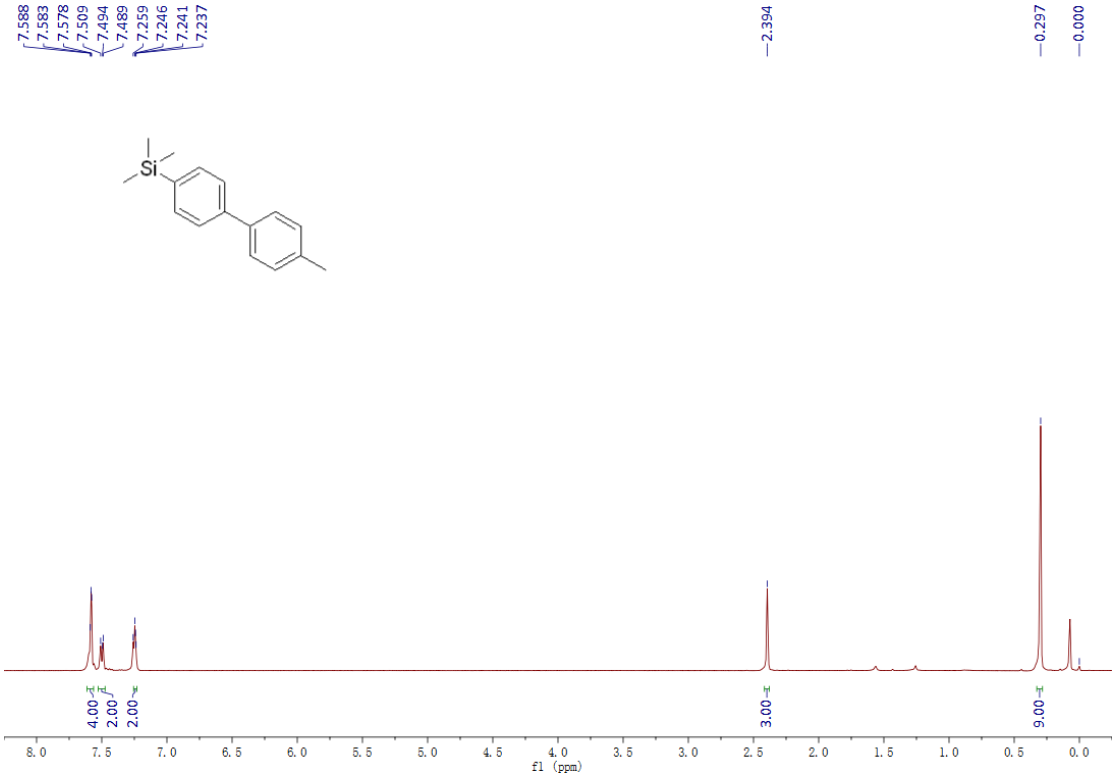


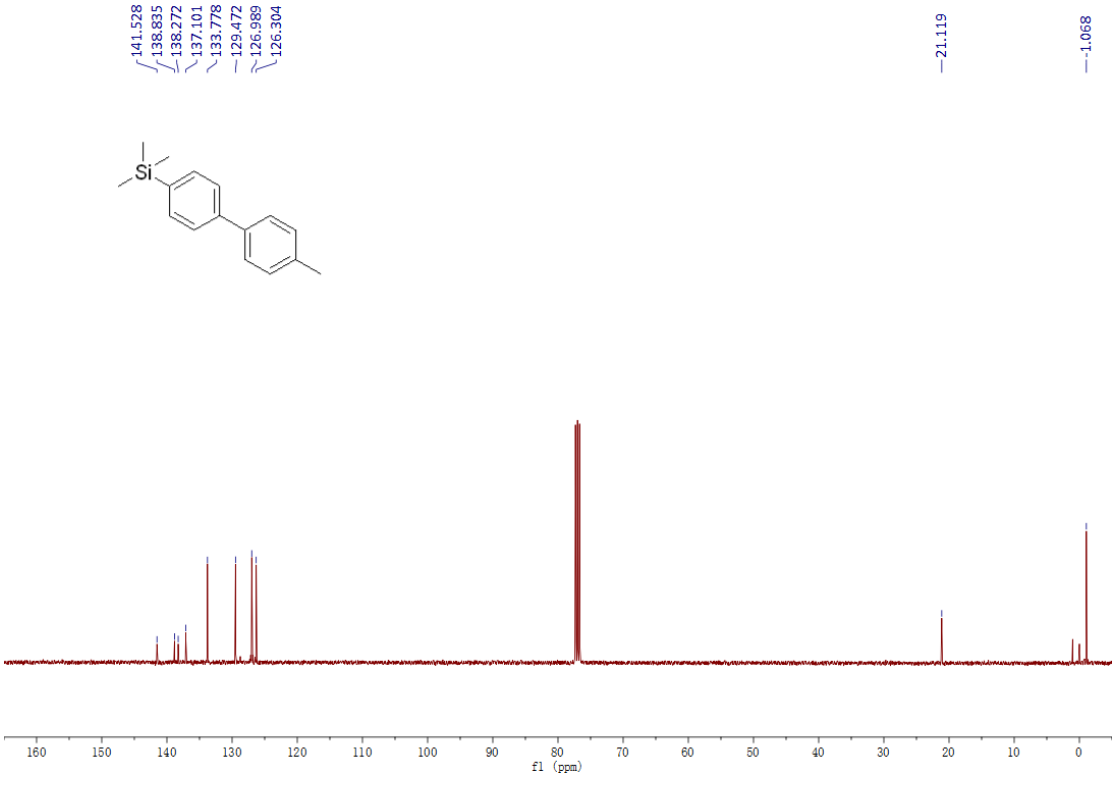
3e: 1-phenylnaphthalene



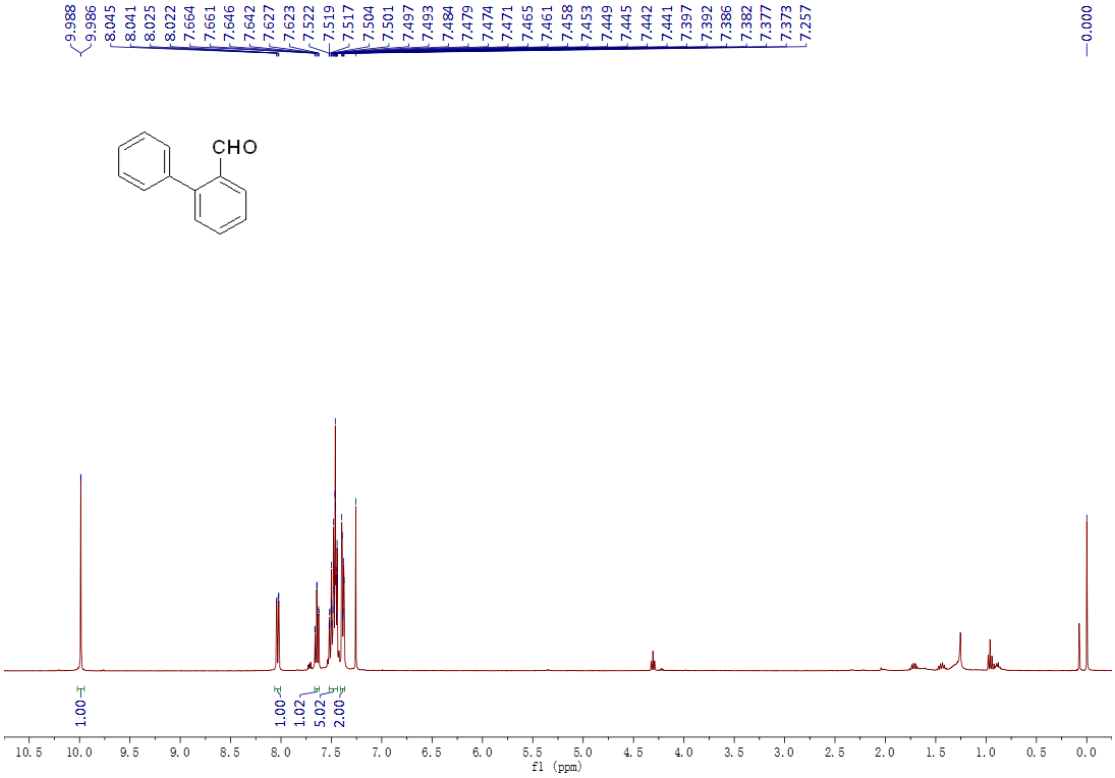


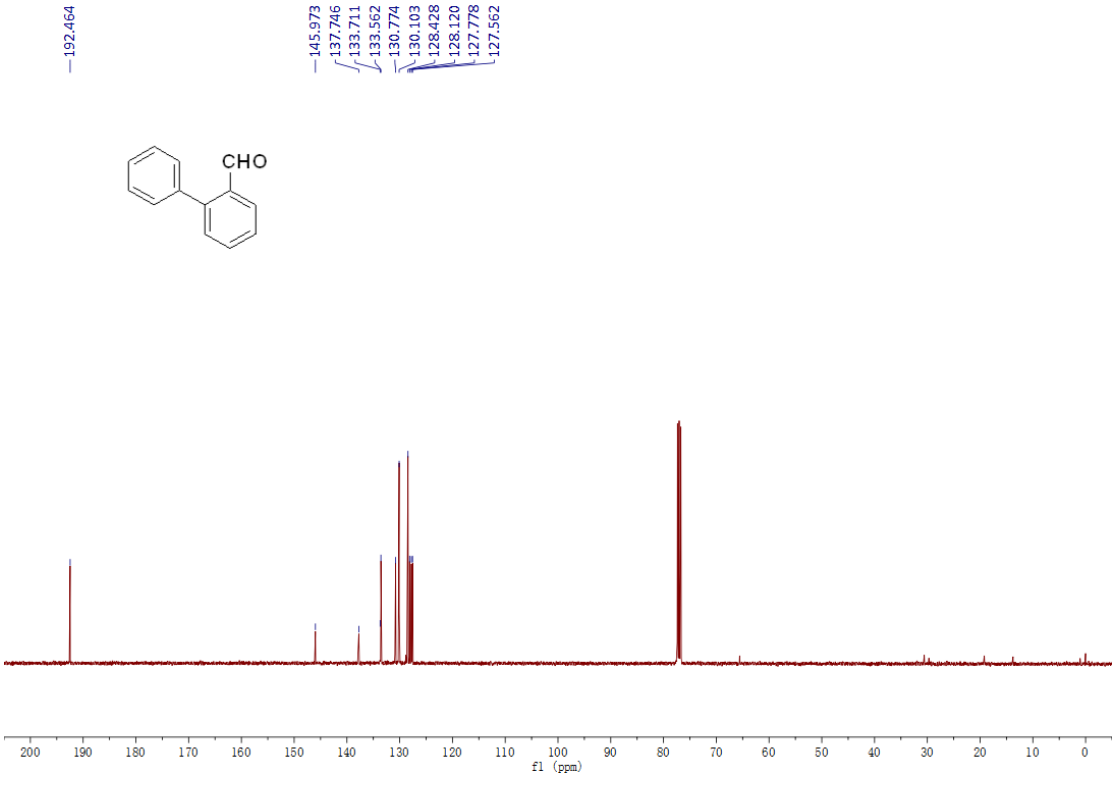
3f: trimethyl(4'-methyl-[1,1'-biphenyl]-4-yl)silane



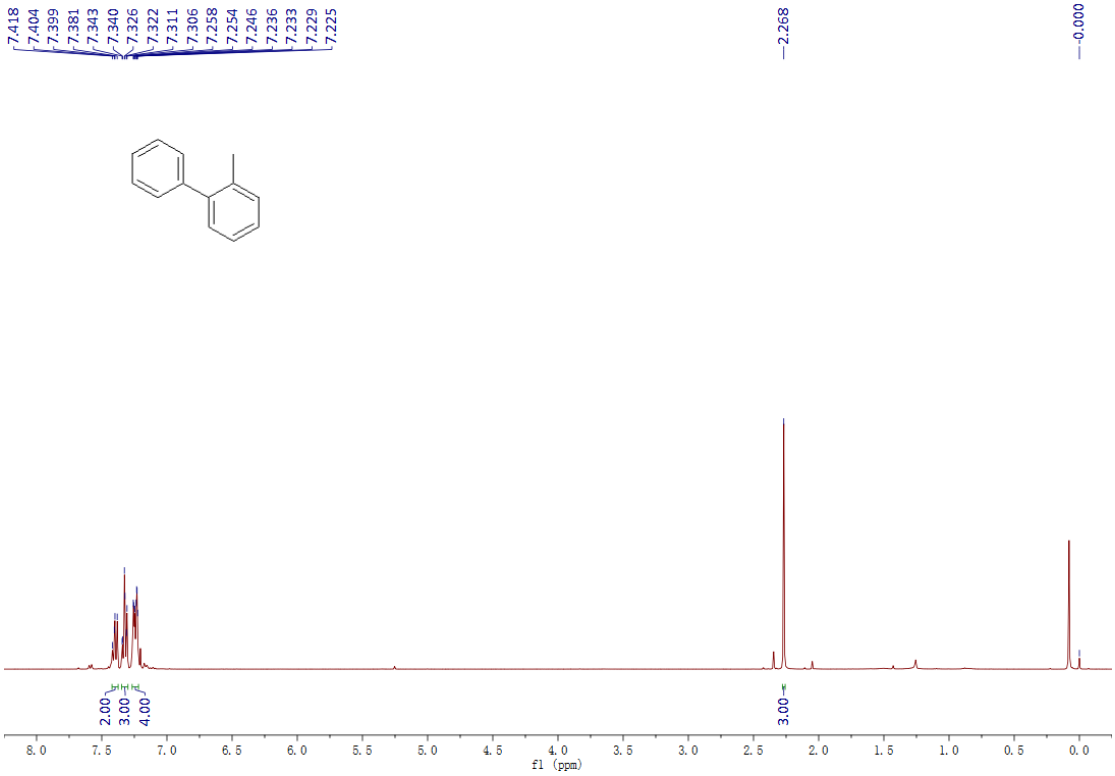


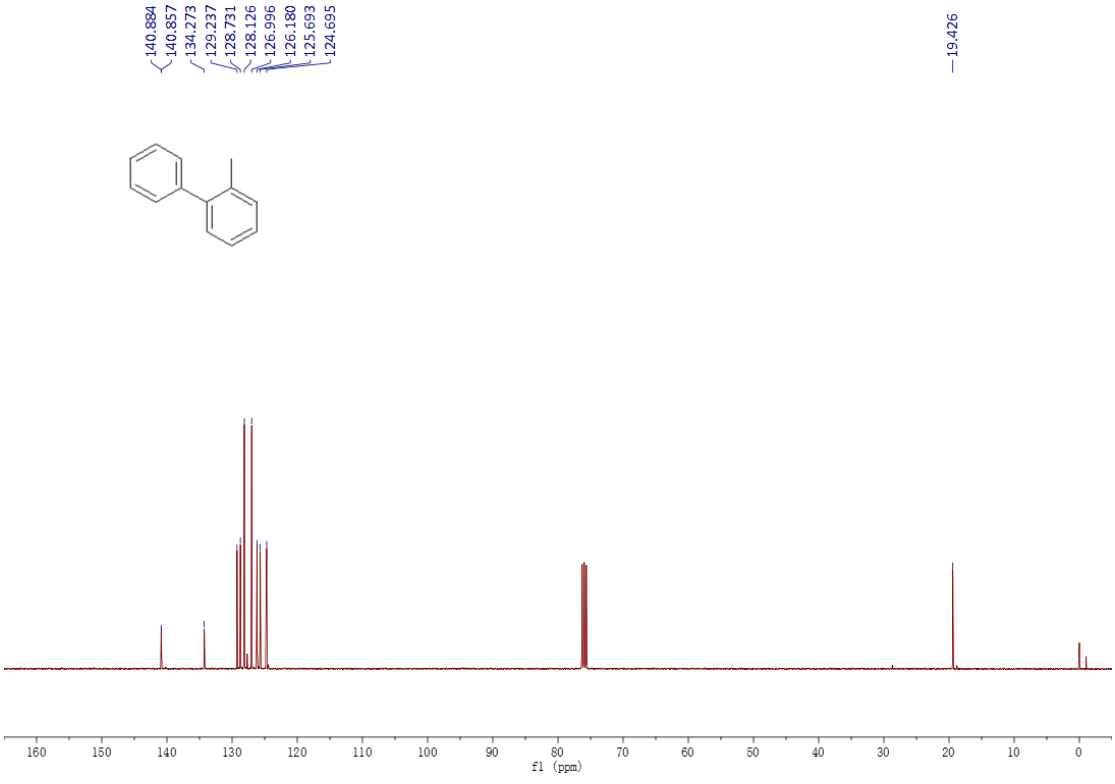
3g: [1,1'-biphenyl]-2-carbaldehyde



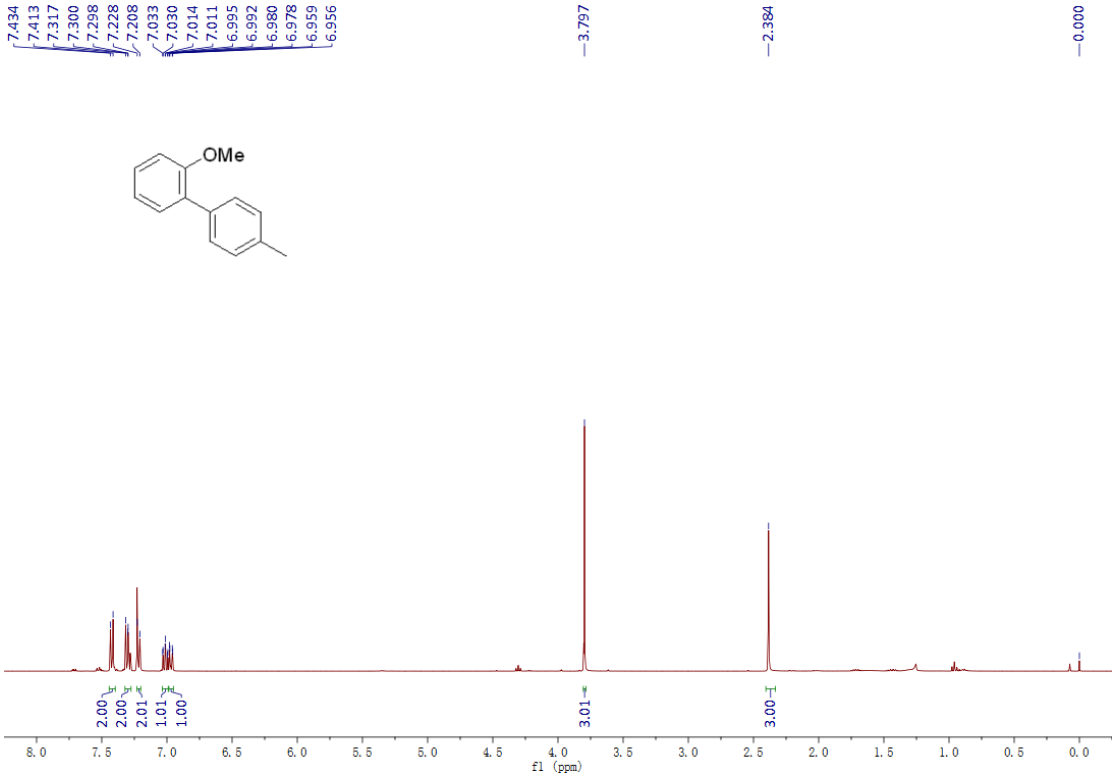


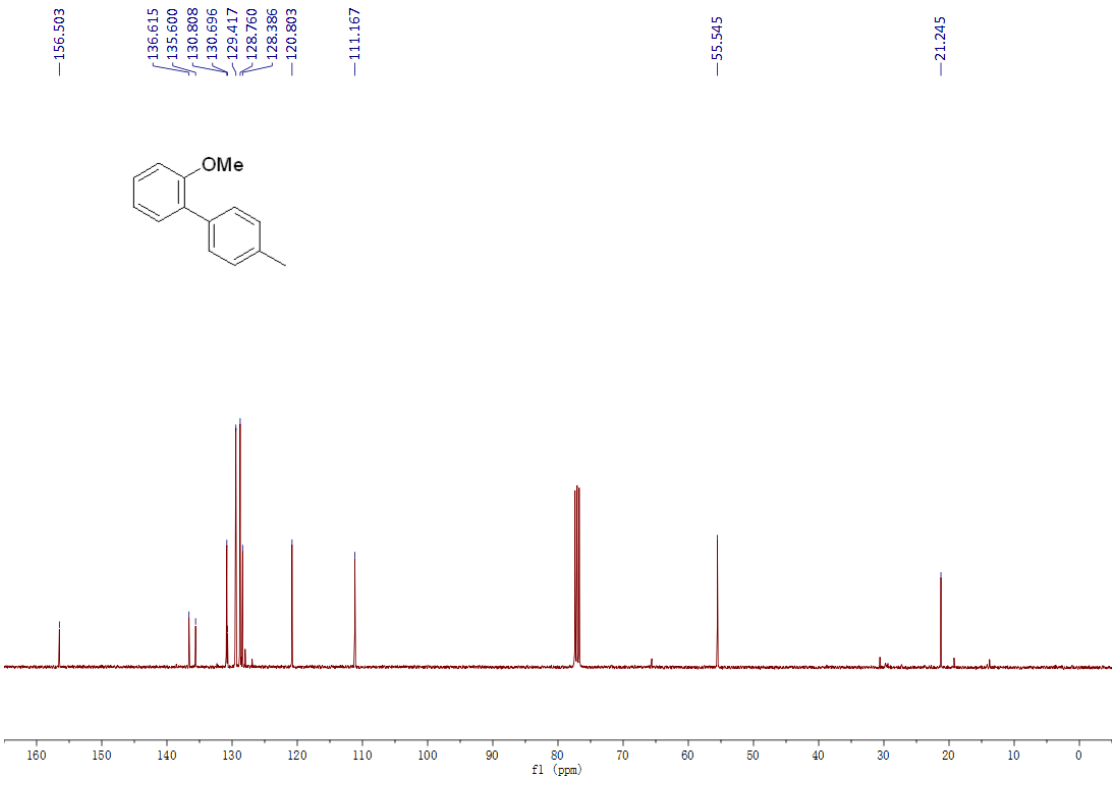
3h: 2-methyl-1,1'-biphenyl



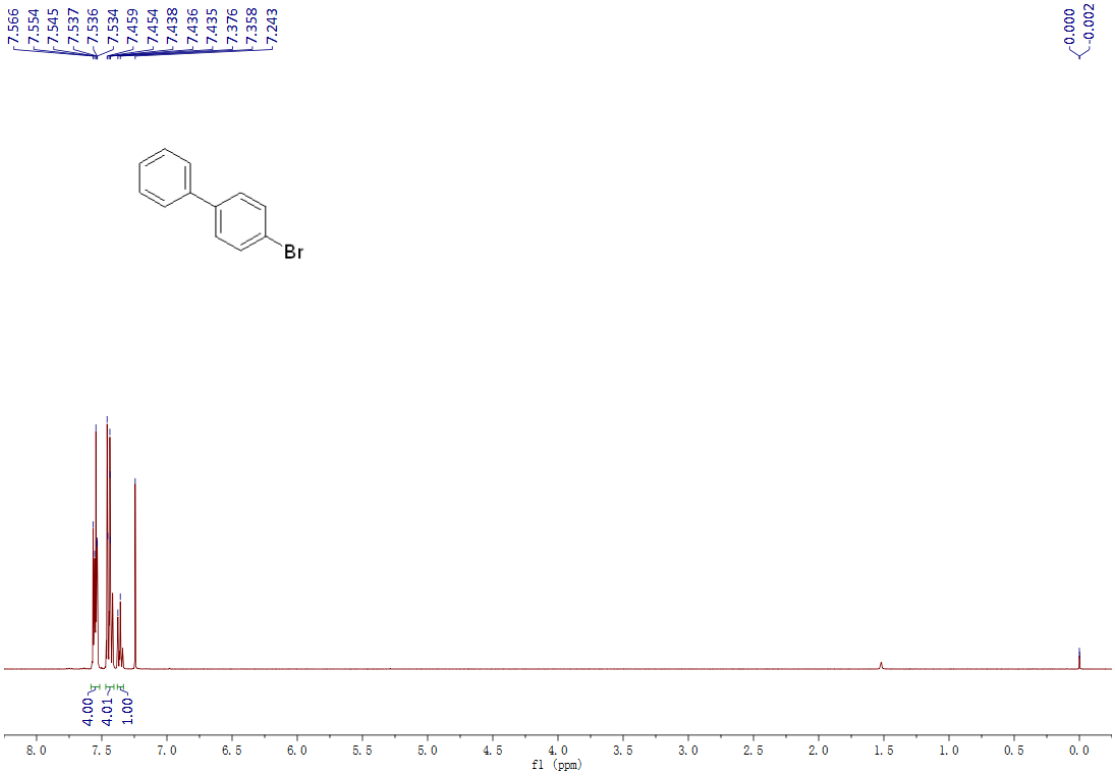


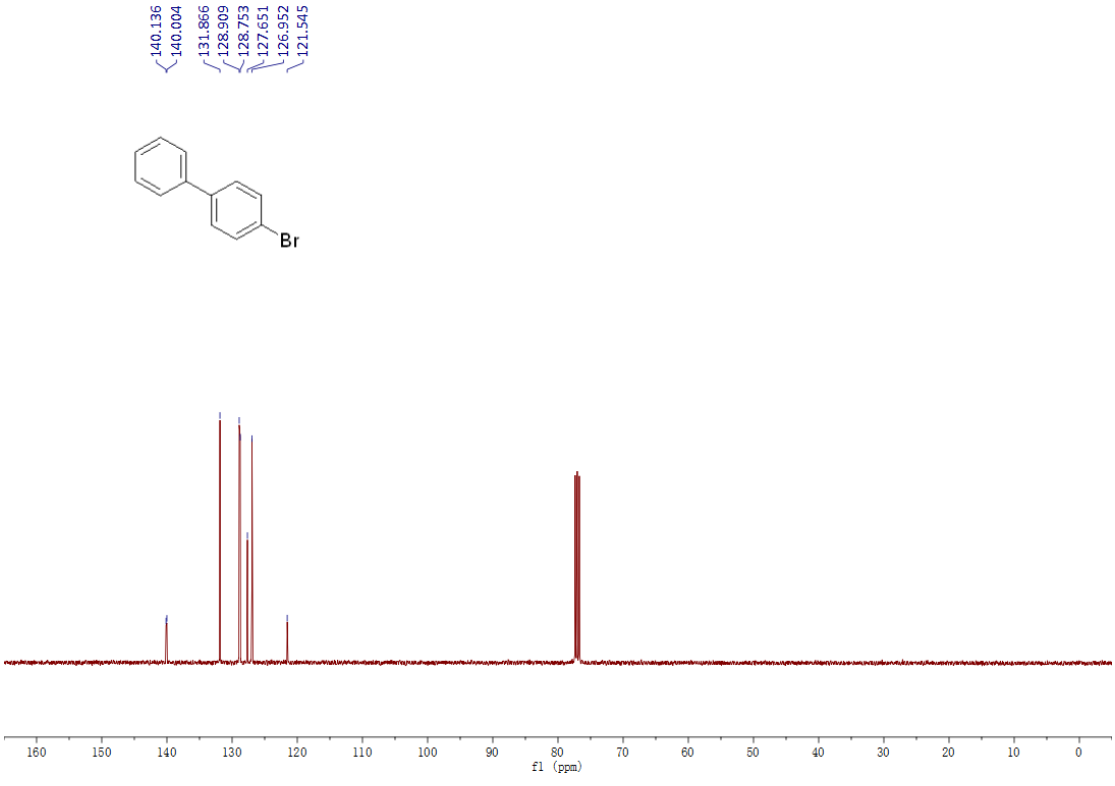
3i: 2-methoxy-4'-methyl-1,1'-biphenyl



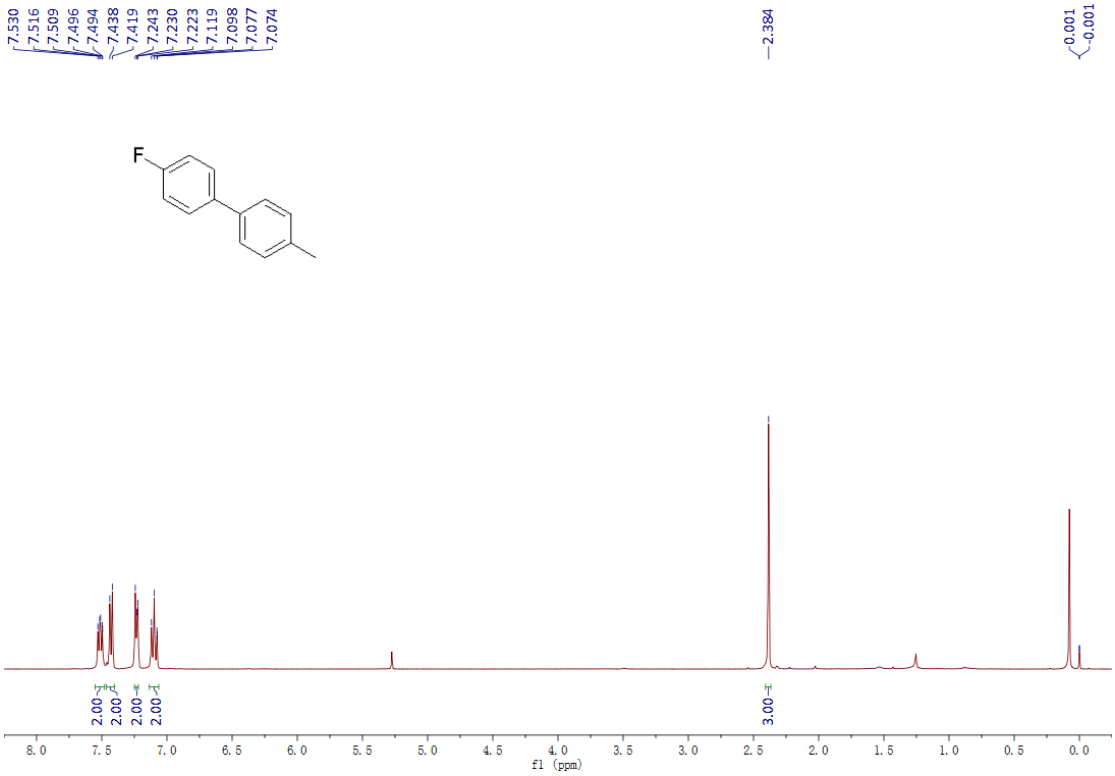


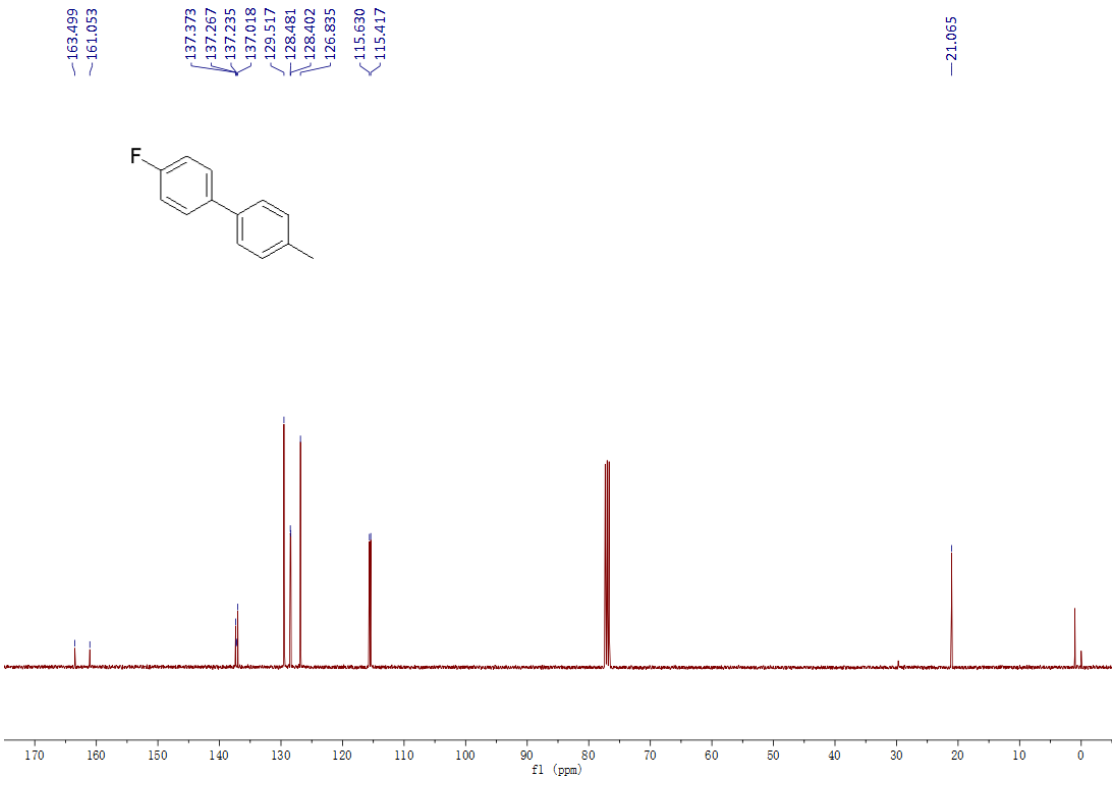
3j: 4-bromo-1,1'-biphenyl



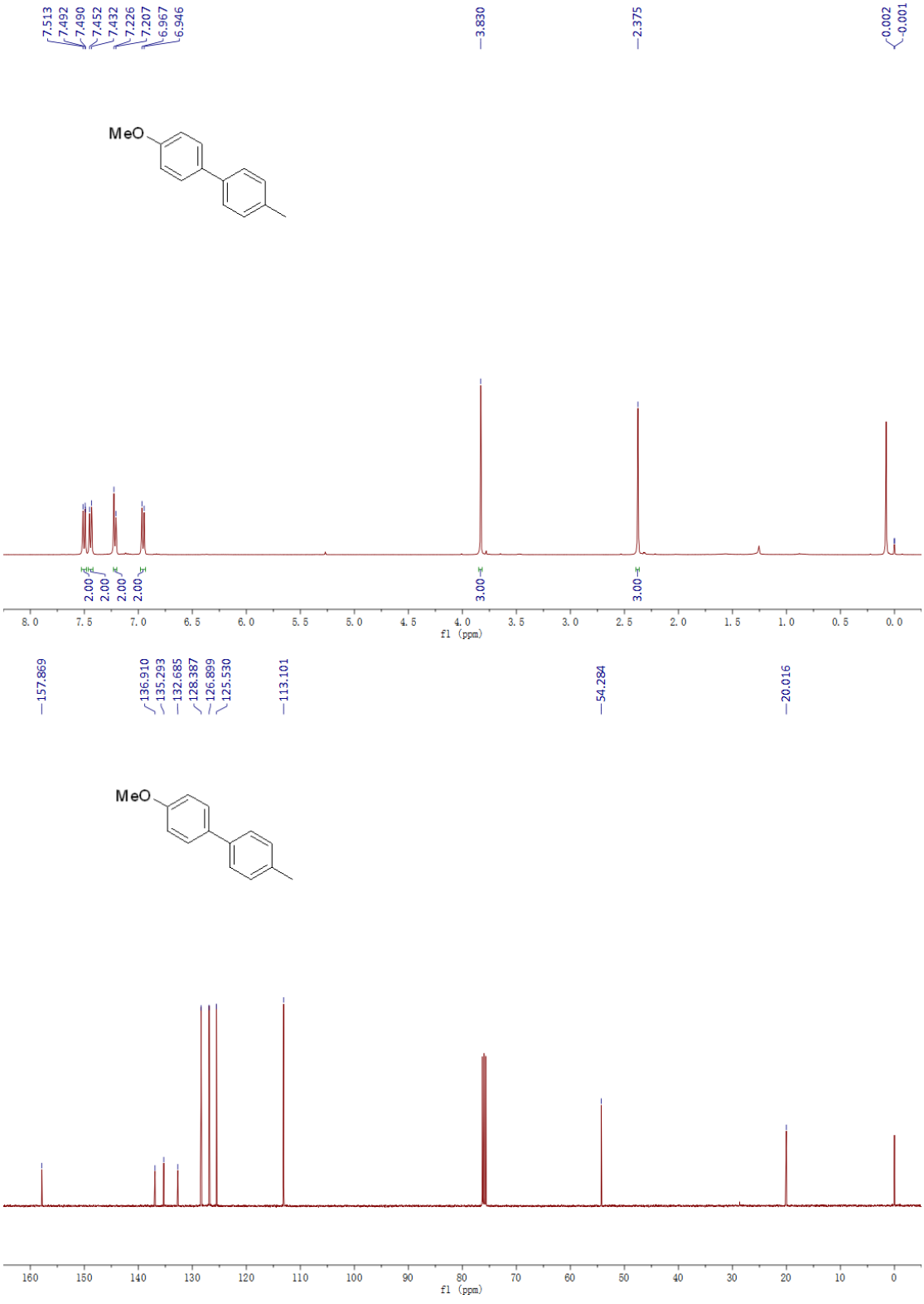


3k: 4-fluoro-4'-methyl-1,1'-biphenyl

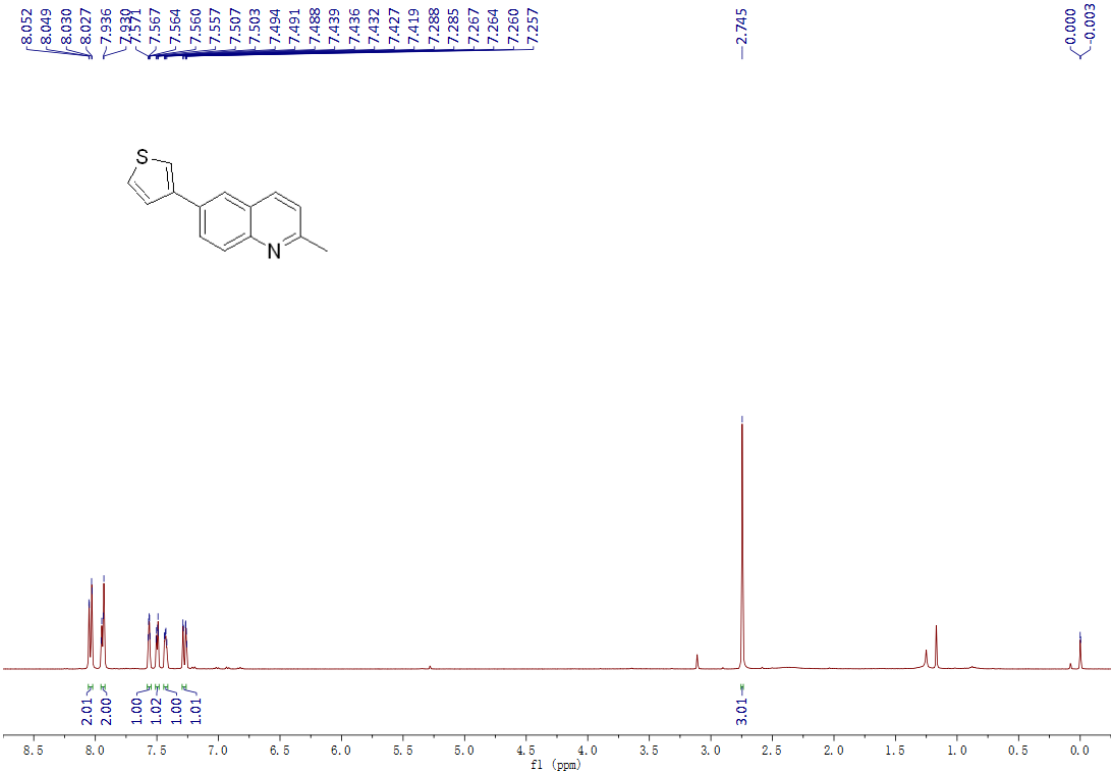


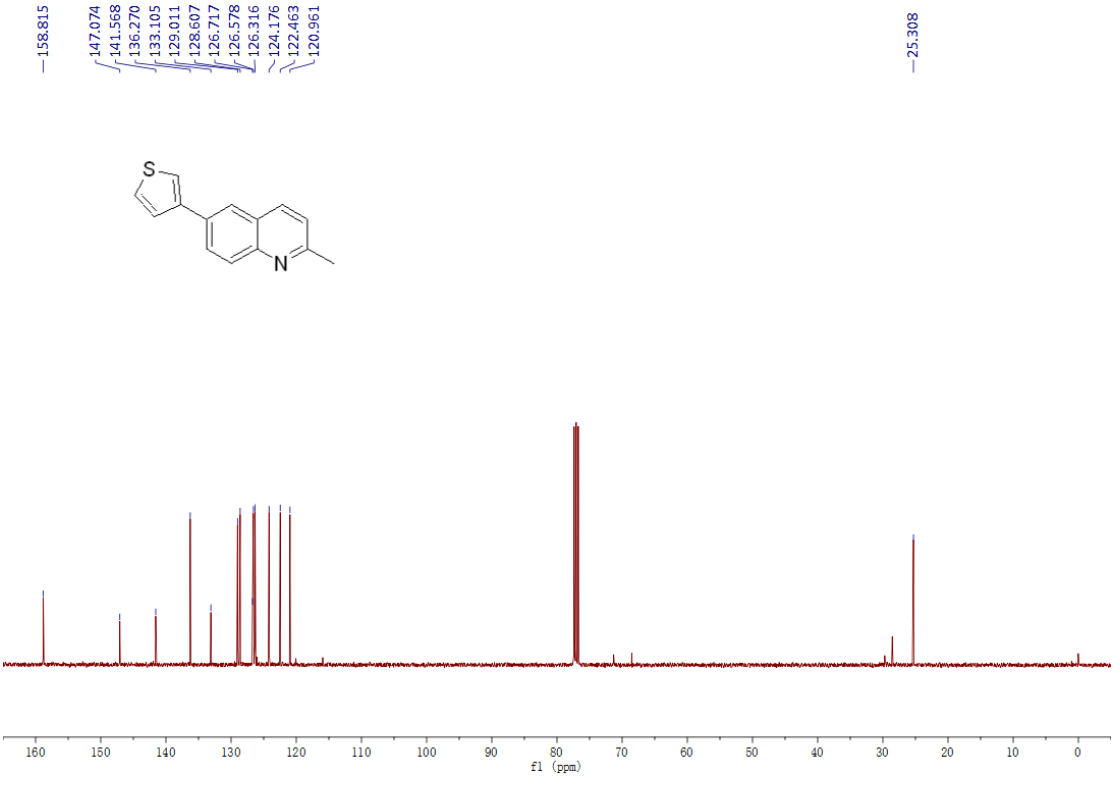


3l: 4-methoxy-4'-methyl-1,1'-biphenyl

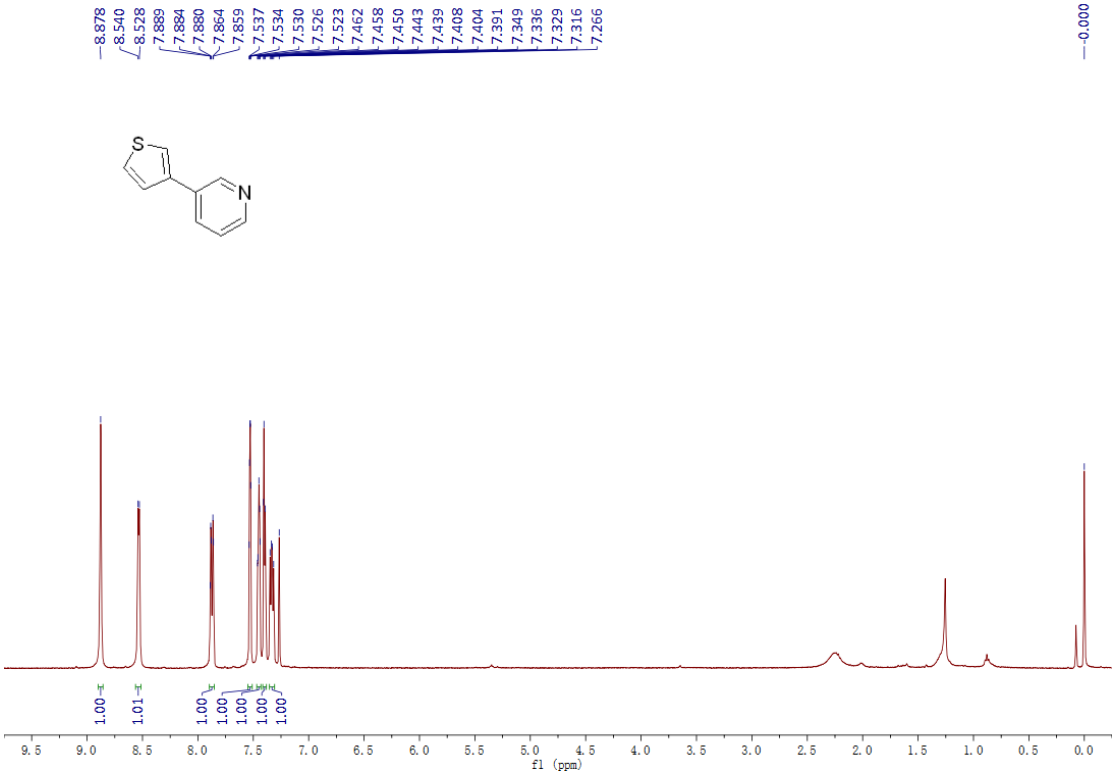


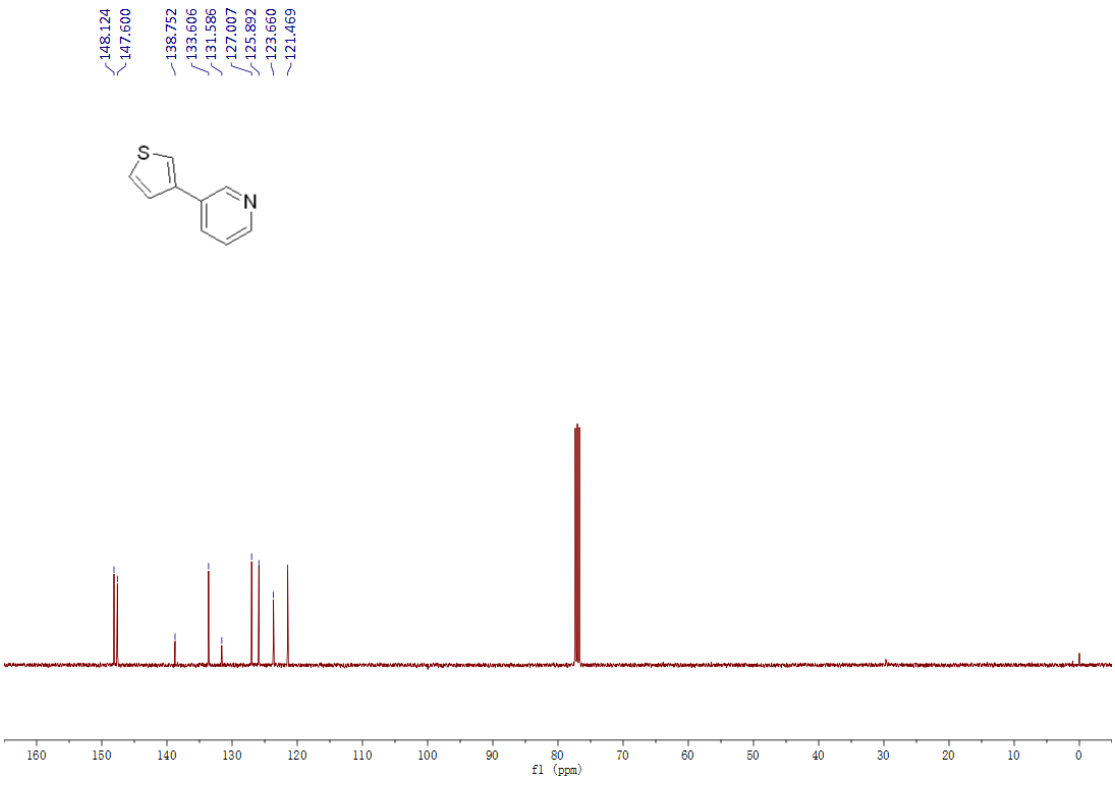
3m: 2-methyl-6-(thiophen-3-yl)quinolone



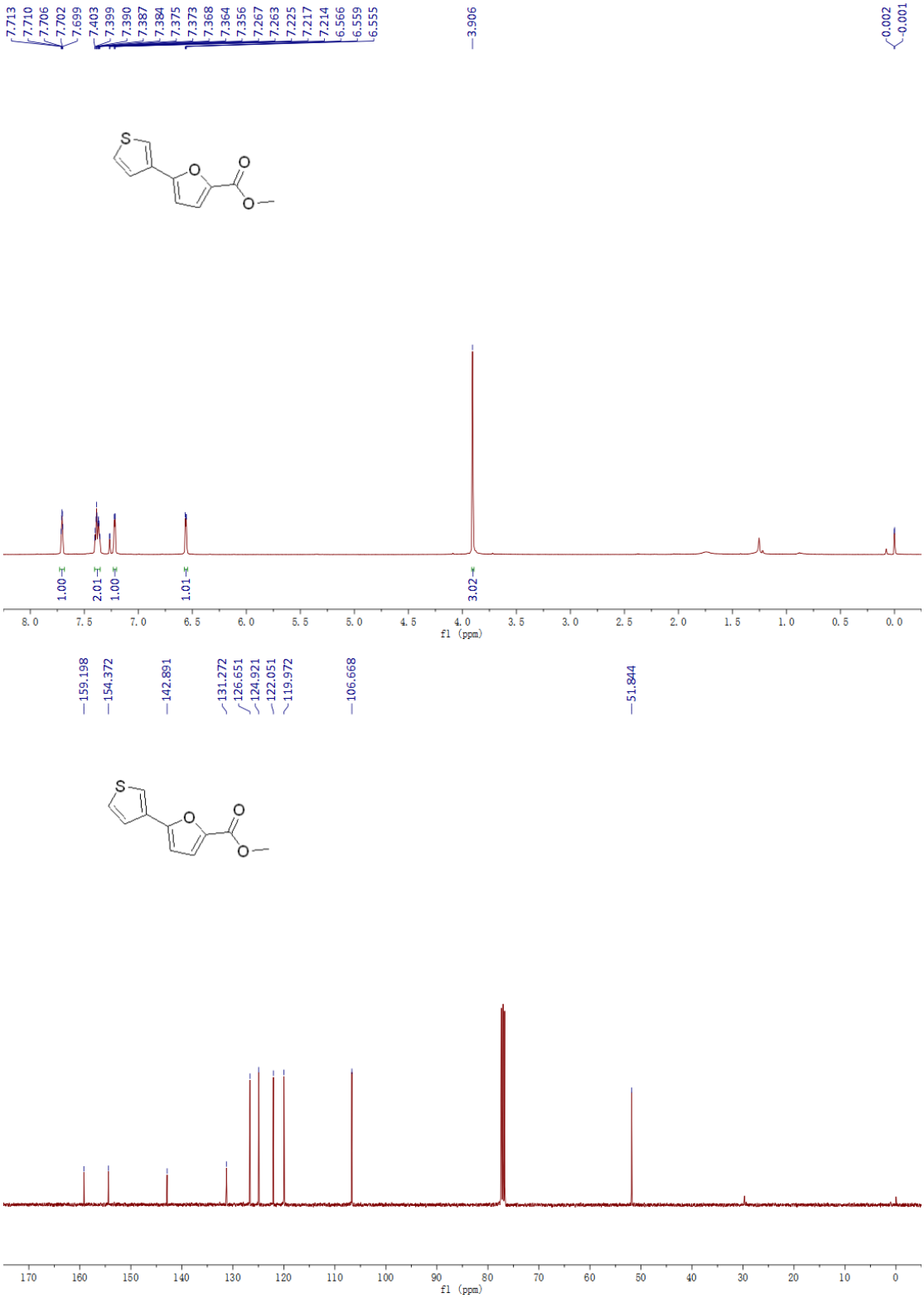


3n: 3-(thiophen-3-yl)pyridine

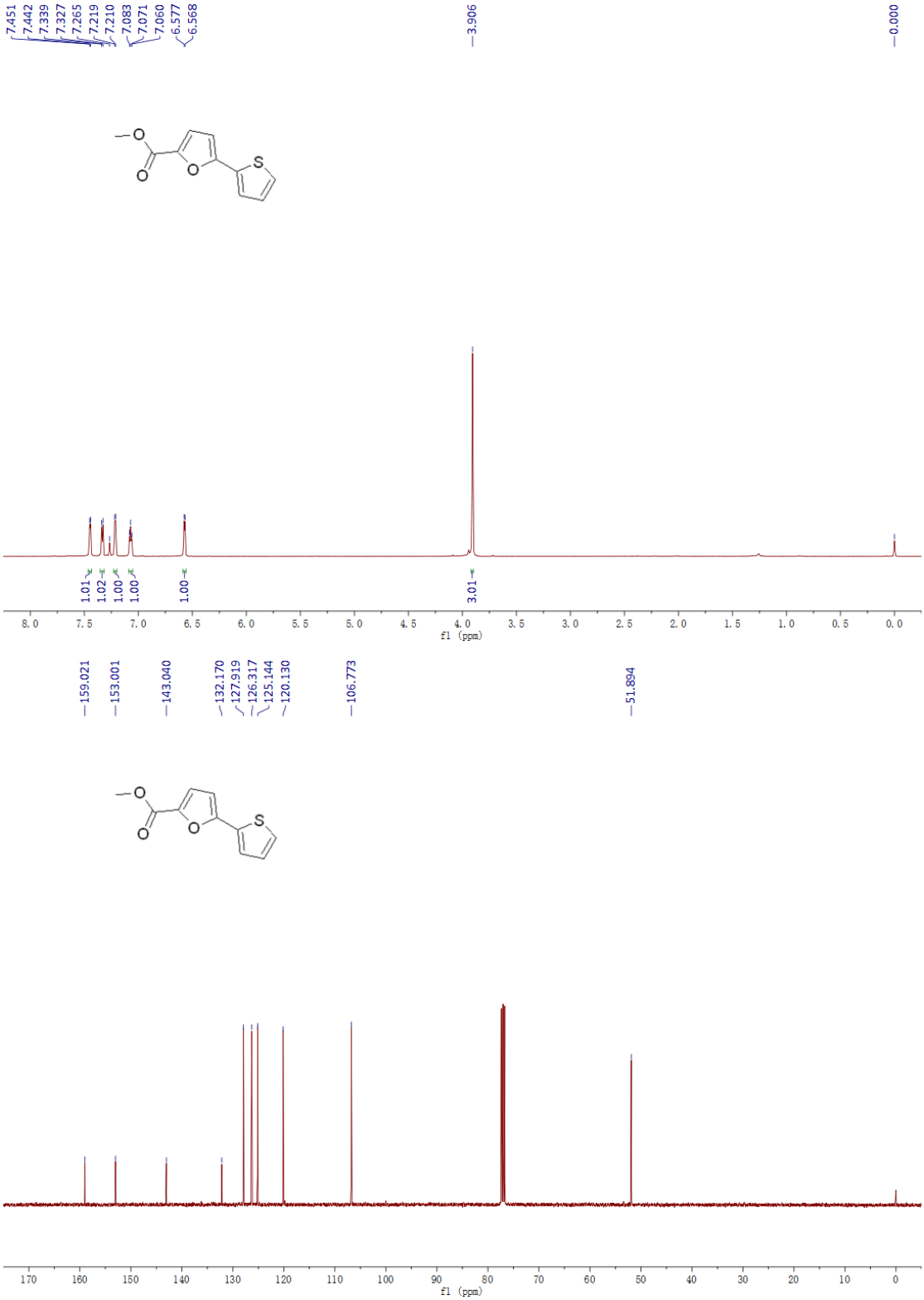




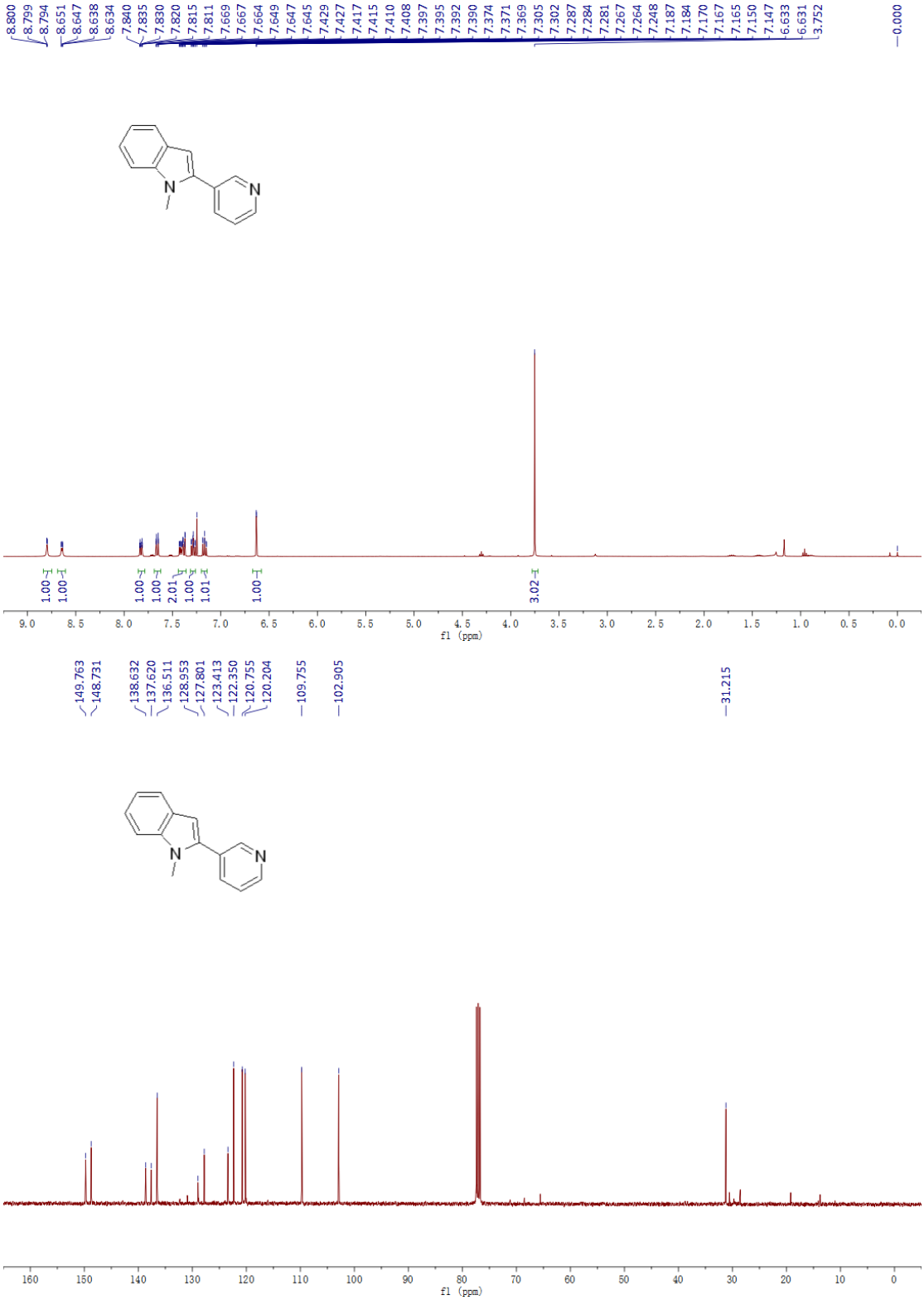
3o & 3t: methyl 5-(thiophen-3-yl)furan-2-carboxylate



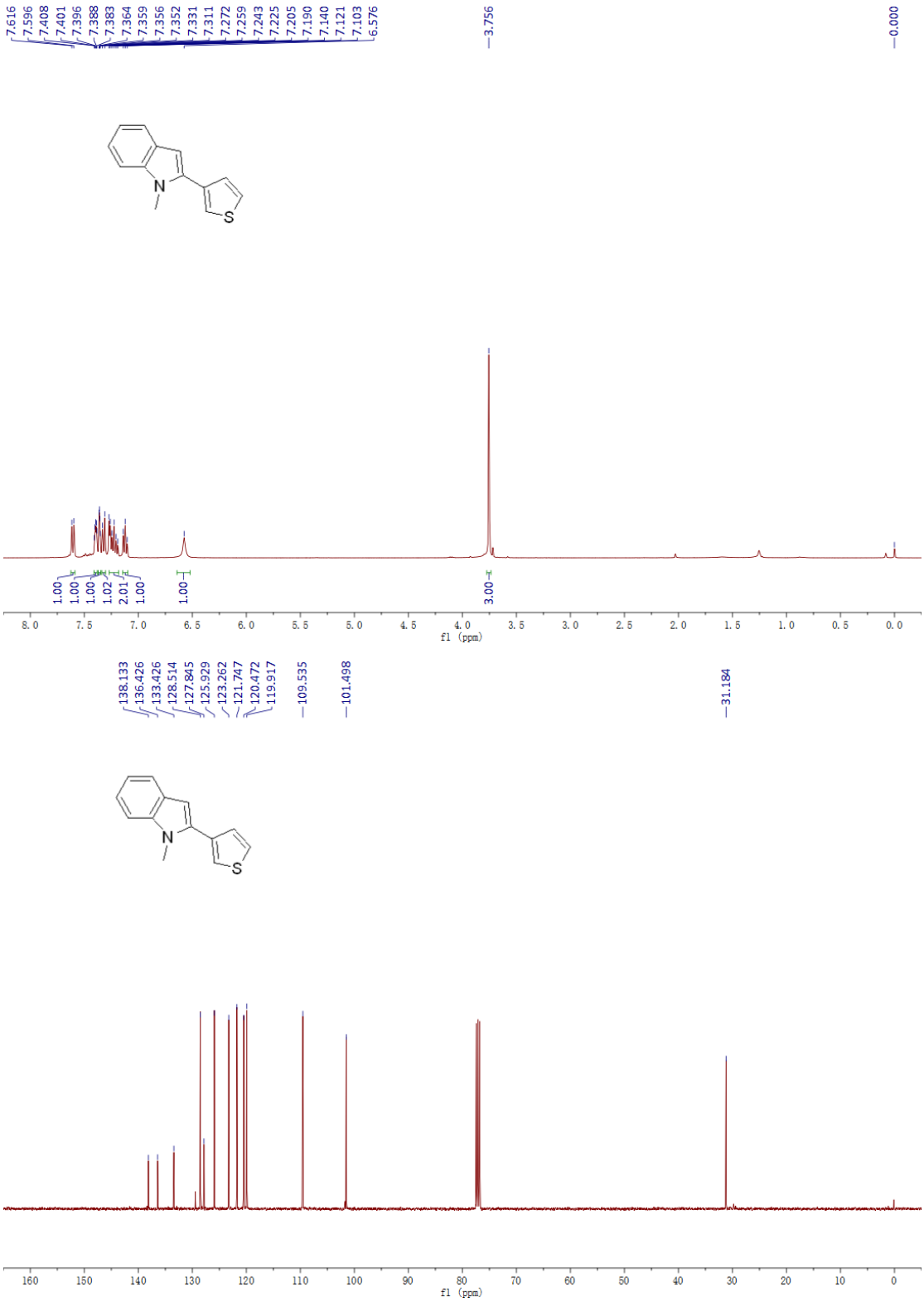
3p: methyl 5-(thiophen-2-yl)furan-2-carboxylate



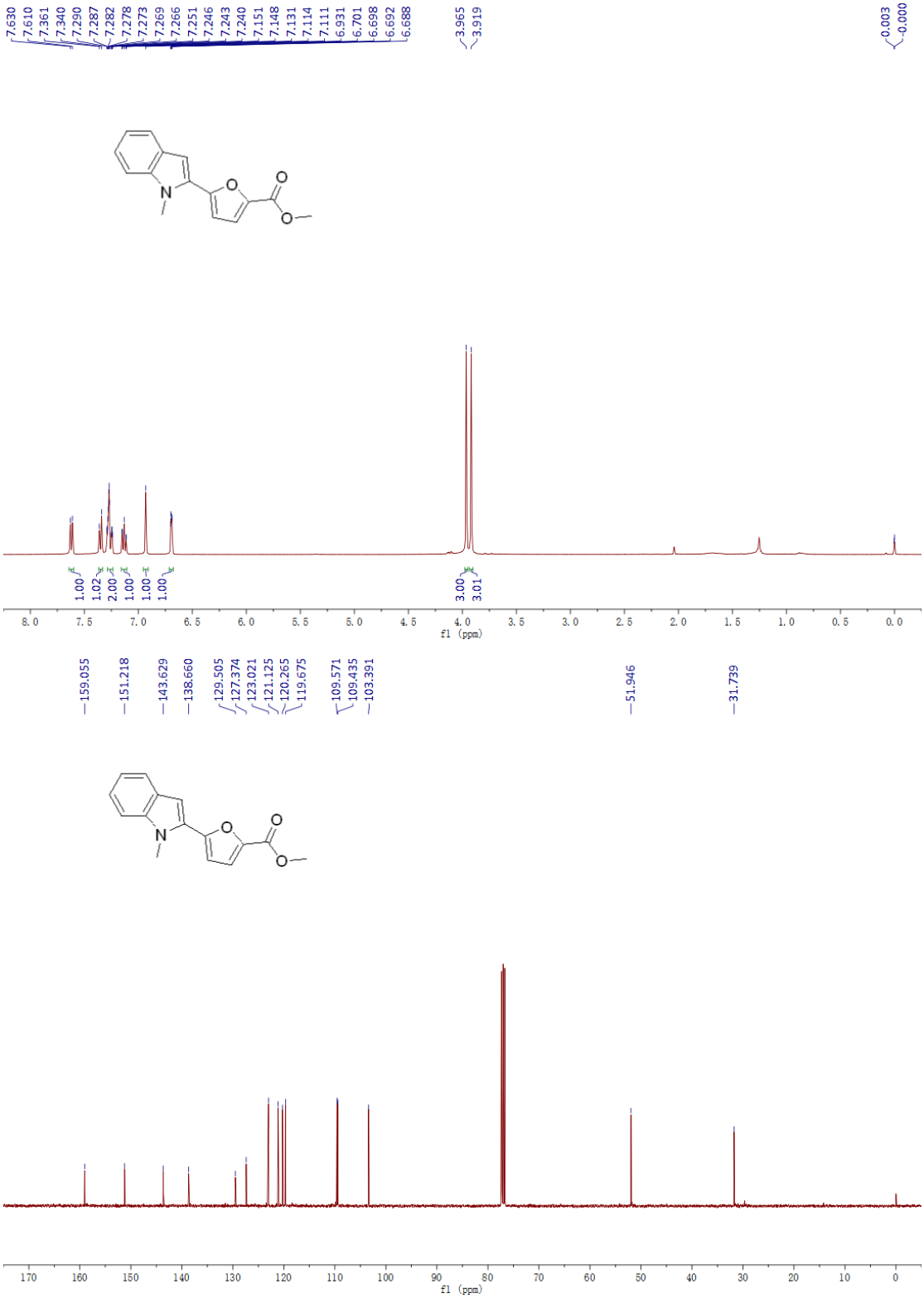
3q: 1-methyl-2-(pyridin-3-yl)-1H-indole



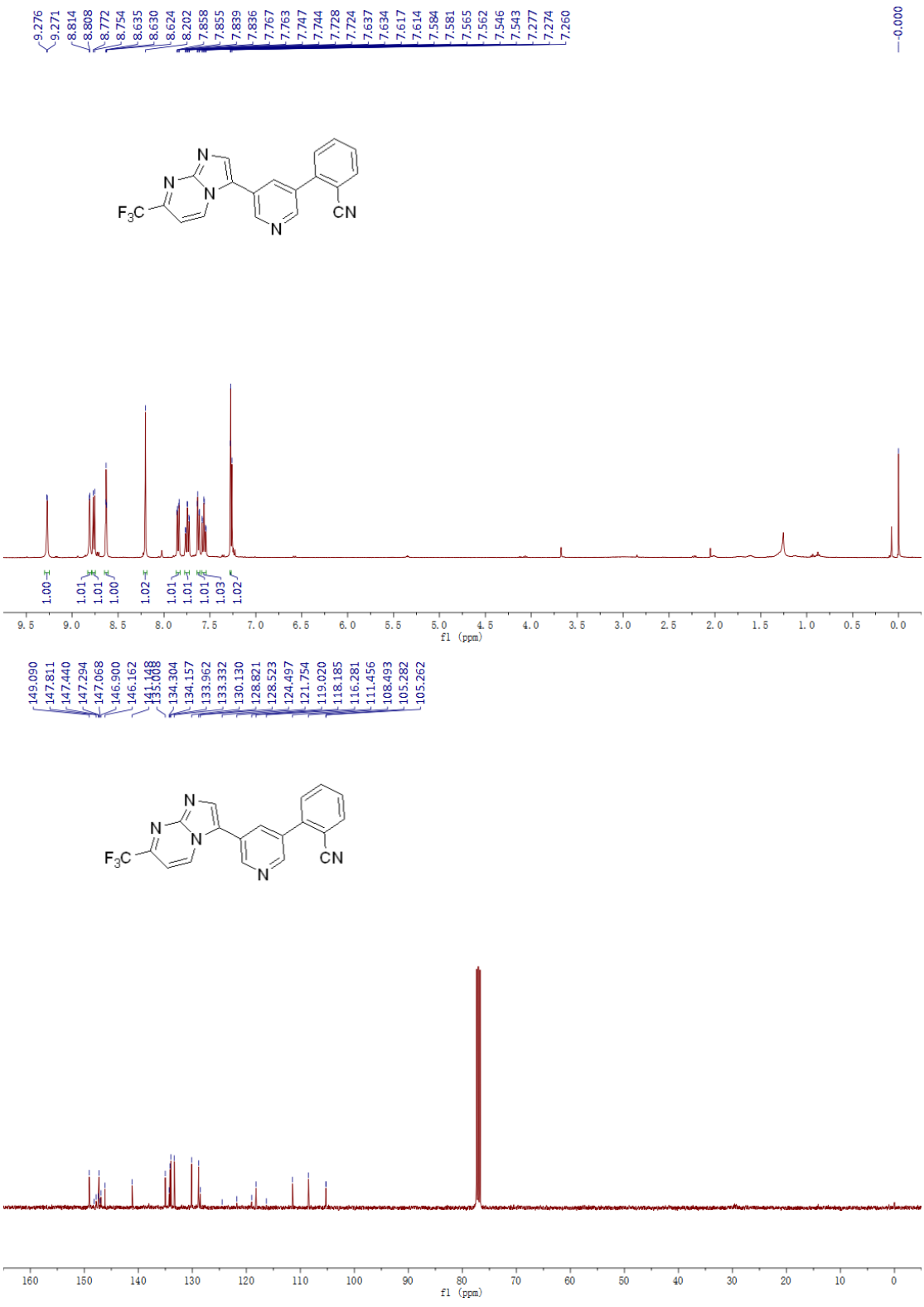
3r: 1-methyl-2-(thiophen-3-yl)-1H-indole



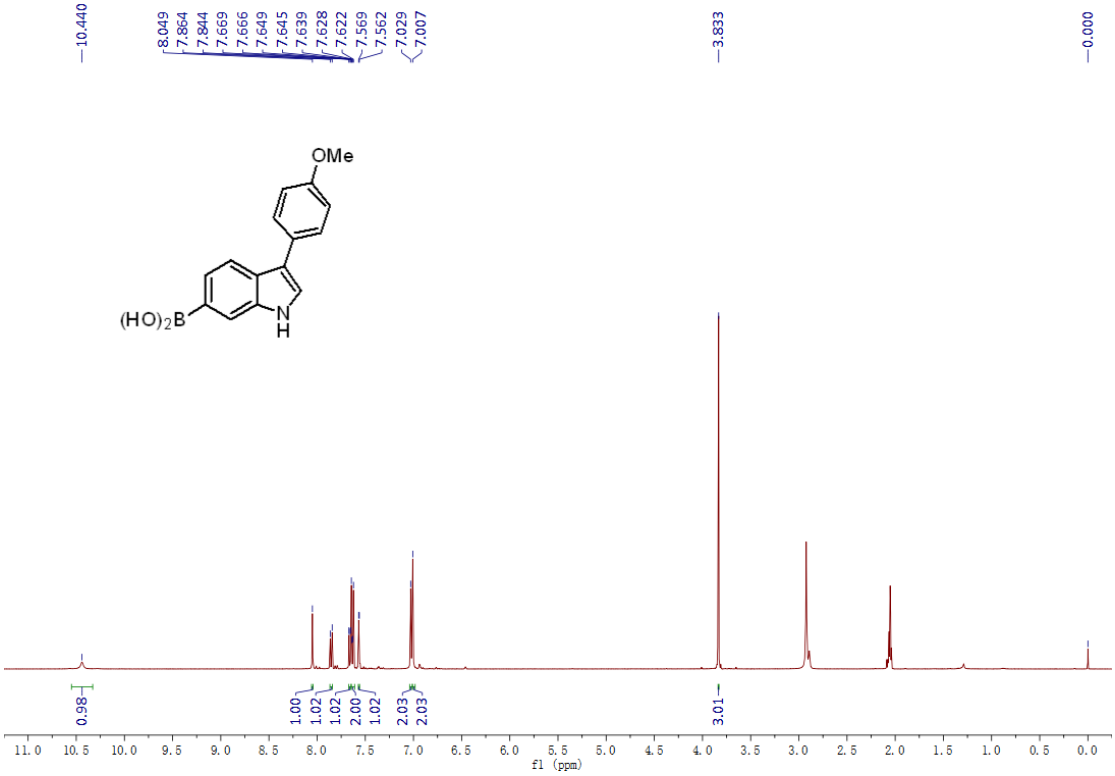
3s: methyl 5-(1-methyl-1H-indol-2-yl)furan-2-carboxylate

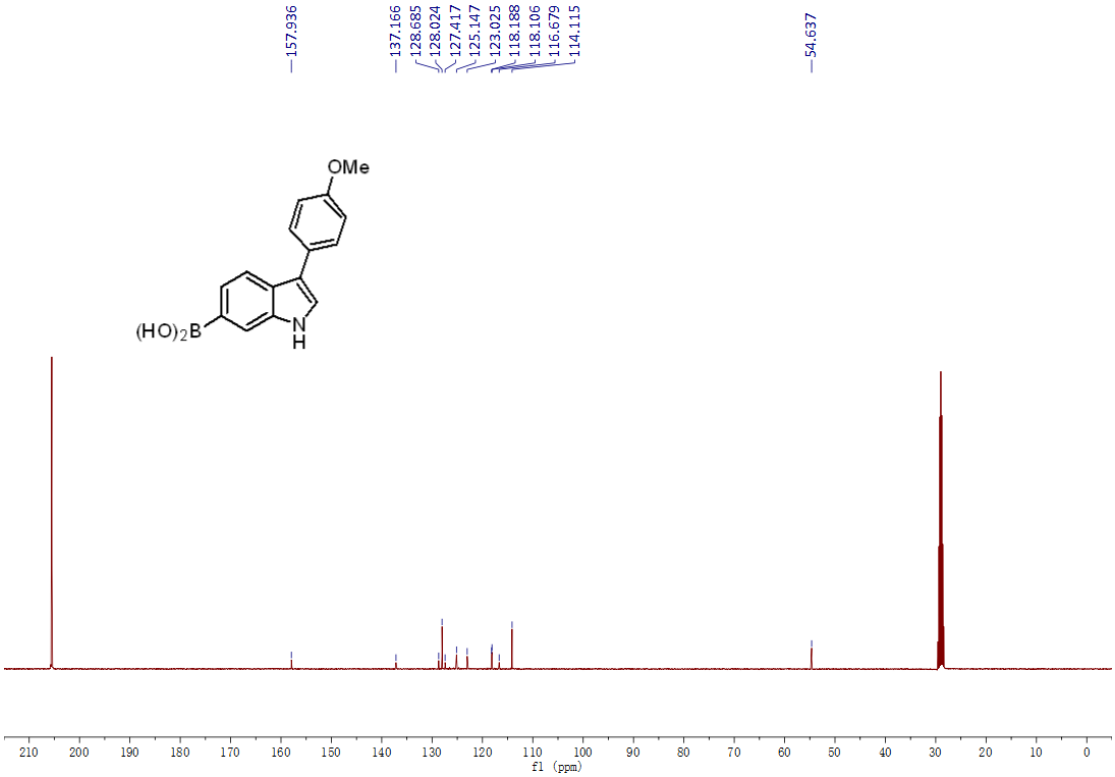


3u: 2-(5-(7-(trifluoromethyl)imidazo[1,2-a]pyrimidin-3-yl)pyridin-3-yl)benzonitrile

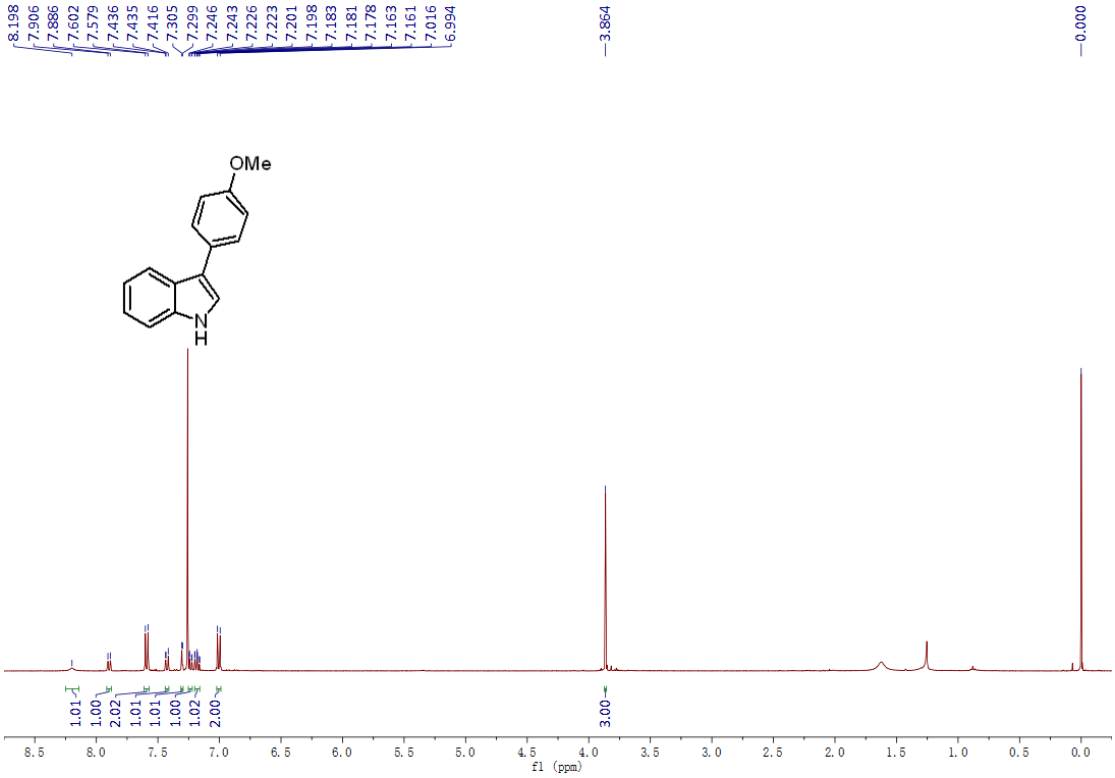


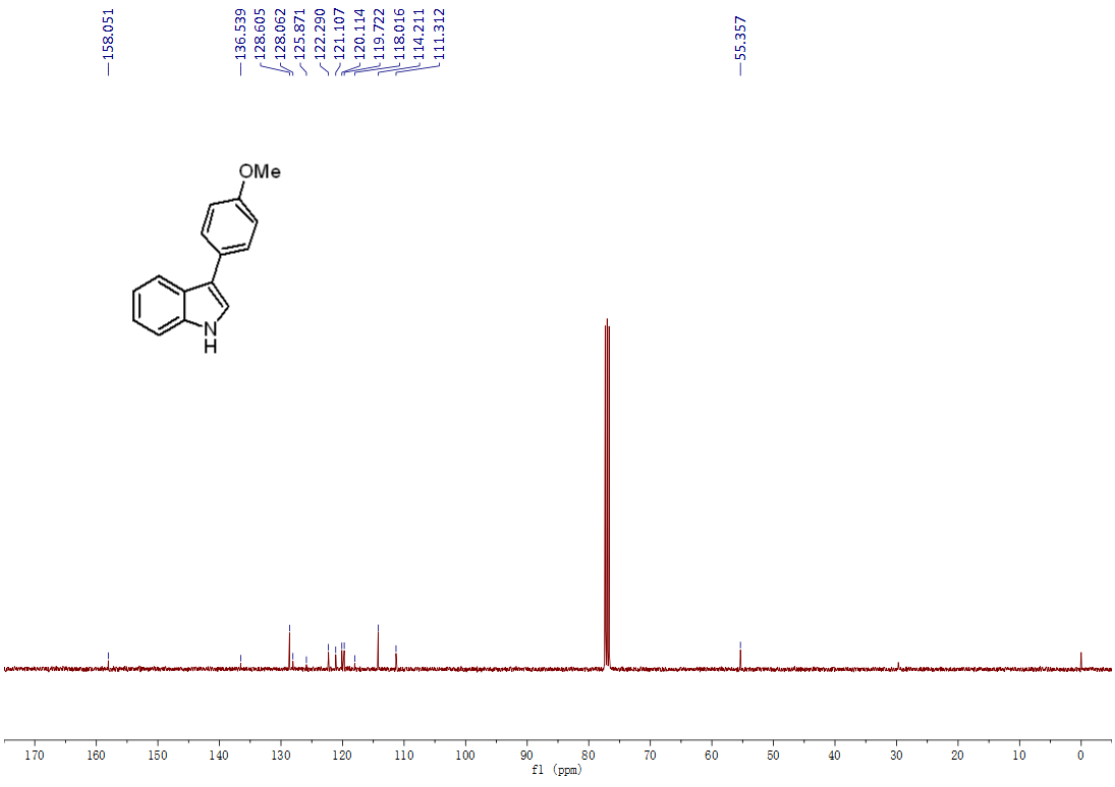
4a: (3-(4-methoxyphenyl)-1*H*-indol-6-yl)boronic acid





4b: 3-(4-methoxyphenyl)-1*H*-indole





4,4,5,5-tetramethyl-2-[4-(BMIDA)phenyl]-1,3,2-dioxaborolane