

Supporting Information

Photoinduced Radical Gernyloximation of Activated Alkenes

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1 General Methods

All reagents were used without further purification. TLC was performed on silica gel plates (GF254, 200-300 mesh) using UV light (254/365 nm) for detection, and column chromatography was performed on silica gel (200-300 mesh). ^1H NMR (300 or 400 or 600 MHz), ^{13}C NMR (101 or 151 MHz), ^{19}F NMR (376 or 565 MHz) were measured on Bruker Avance 400 MHz spectrometer. All NMR spectra were recorded in CDCl_3 at room temperature ($20 \pm 3^\circ\text{C}$). To display multiplicities and signal forms correctly the following abbreviations were used: s = singlet, d = doublet, t = triplet, m = multiplet. ^1H NMR and ^{13}C NMR chemical shifts are quoted in parts per million (ppm) downfield from TMS. High-resolution mass spectra (HRMS) were taken with the Agilent Infinity II Q-TOF 6546 system. The UV spectra were recorded by using the Hitachi UH4150 UV-Vis-NIR Spectrophotometer.

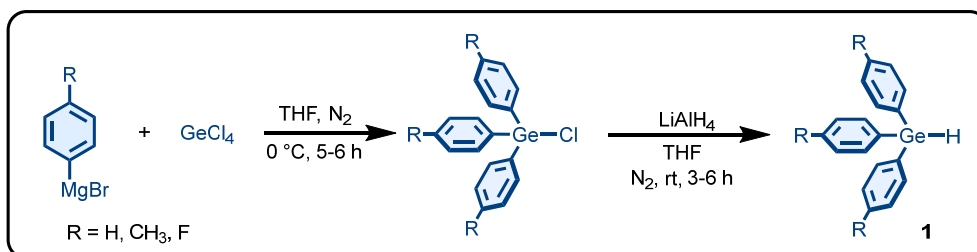
2. Experimental Procedures

2.1 Preparation of starting materials

2.1.1 General procedure for the synthesis of arylgermane **1**^{S1, 2}

Step 1: Under a nitrogen atmosphere at 0 °C, tetrahydrofuran (1.25 mL), germanium tetrachloride (1.0 mmol), and the Grignard reagent (3.0 equiv.) were sequentially added to the reaction flask. The mixture was stirred for 5–6 hours. The reaction was then quenched with 6 M HCl, followed by extraction with diethyl ether and saturated NaHCO₃ solution. The organic layer was dried over anhydrous Na₂SO₄, concentrated under reduced pressure, and purified by column chromatography to afford the desired product as a white solid.

Step 2: Under an inert nitrogen atmosphere and at ambient temperature, 1 mmol (0.34 g, 1 equiv.) of Ph₃GeCl was dissolved in 2.5 mL of THF. To the resulting suspension, 1 mmol (0.81 mL, 1 equiv.) of LiAlH₄ was added dropwise in 2.5 mL of THF. The reaction mixture was stirred at room temperature for a period of 3-6 hours to ensure complete reaction. Following this, 5 mL of 2 M H₂SO₄ was introduced dropwise to the mixture. The organic phase was then separated, and the aqueous layer was extracted with DCM in 3 × 10 mL. The combined organic phases were dried over anhydrous Na₂SO₄, and the solvent was subsequently removed under reduced pressure. The residual material was recrystallized from hexane, yielding the pure product **1** as a white crystalline solid. (Scheme S1)

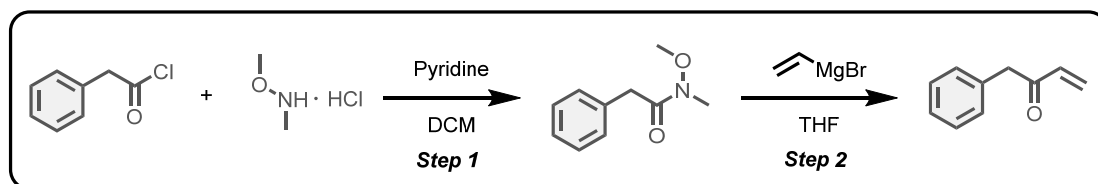


Scheme S1. General synthetic procedures for **1**

2.1.2 General procedure for the synthesis of 1-phenylbut-3-en-2-one^{S3}

Step 1: A Schlenk tube equipped with a magnetic stir bar was evacuated and backfilled with nitrogen 3 times. *N,O*-dimethylhydroxylamine hydrochloride (0.59 g, 6.0 mmol, 1.2 equiv.) was suspended in DCM (20 mL). At 0 °C phenylacetyl chloride (0.66 mL, 5.0 mmol, 1.0 equiv.) was slowly added. Pyridine (0.89 mL, 11 mmol, 2.2 equiv.) was added *via* syringe pump within 5 min. The reaction mixture was stirred at 0 °C for 5 min and at room temperature for 1 h. Afterwards, it was neutralized with HCl (2 M, 10 mL) and the organic layer was washed with HCl (2 M, 10 mL), H₂O (2 × 10 mL), saturated NaHCO₃ (2 × 10 mL), brine (10 mL) and dried with Na₂SO₄.

Step 2: *N*-methoxy-*N*-methyl-2-phenylacetamide was dissolved in THF (27 mL). At 0 °C vinyl magnesium bromide (1 M in THF, 8.0 mL, 8.0 mmol, 1.6 equiv.) was added within 15 min and the reaction mixture was stirred for 15 min at 0 °C. Saturated NH₄Cl (10 mL) was added carefully and the mixture was extracted with DCM (3 × 15 mL). The combined organic phases were washed with brine (10 mL), dried with Na₂SO₄, and concentrated. The crude product was purified by flash column chromatography (0.33 g, 2.3 mmol, 46% over two steps) and was obtained as a colorless oil. (Scheme S2)

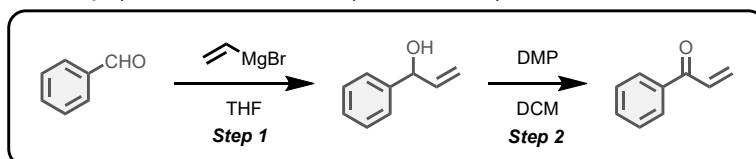


Scheme S2. General experimental procedures for 1-phenylbut-3-en-2-one

2.1.3 General procedure for the synthesis of 1-phenylprop-2-en-1-one^{S3}

Step 1: A Schlenk tube equipped with a magnetic stir bar was evacuated and backfilled with nitrogen 3 times. Benzaldehyde (5.0 mmol, 1.0 equiv.) was dissolved in THF (12.5 mL). At -78 °C vinyl magnesium bromide (1 M in THF, 5.5 mL, 5.5 mmol, 1.1 equiv.) was added dropwise and the reaction stirred for 1 hour at -78 °C. The reaction was neutralized by the addition of saturated NH₄Cl (8 mL) and warmed to room temperature. The mixture was extracted with Et₂O (3 × 15 mL). The combined organic layers were washed with brine (10 mL) and dried with Na₂SO₄. Flash column chromatography of the crude product (SiO₂, PE/EA 4:1) afforded methyl 4-(1-hydroxyallyl)benzoate as a colorless oil.

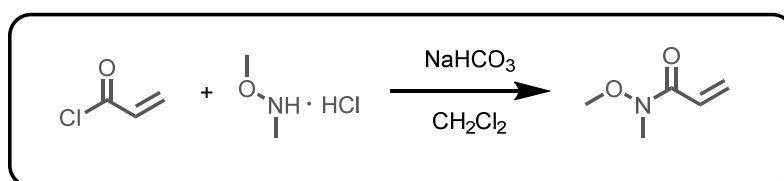
Step 2: The resulting methyl 4-(1-hydroxyallyl)benzoate was redissolved in DCM (25 mL) and DMP (3.2 g, 7.5 mmol, 1.5 equiv.) was carefully added at 0 °C. The reaction mixture was stirred for 2 hours at room temperature before it was neutralized with saturated Na₂S₂O₃ (5 mL) and saturated NaHCO₃ (5 mL) and stirred for another hour at room temperature. The phases were separated and the aqueous layer was extracted with DCM (3 × 10 mL). The combined organic phases were washed with brine (10 mL), dried with Na₂SO₄, and concentrated. Flash column chromatography (SiO₂, PE/EA 10:1) afforded methyl 4-acryloylbenzoate (0.73 g, 3.9 mmol, 77% over 2 steps) as a colorless oil. (Scheme S3)



Scheme S3. General synthetic procedures for 1-phenylprop-2-en-1-one

2.1.4 General procedure for the synthesis of *N*-Methoxy-*N*-methylacrylamide^{S3}

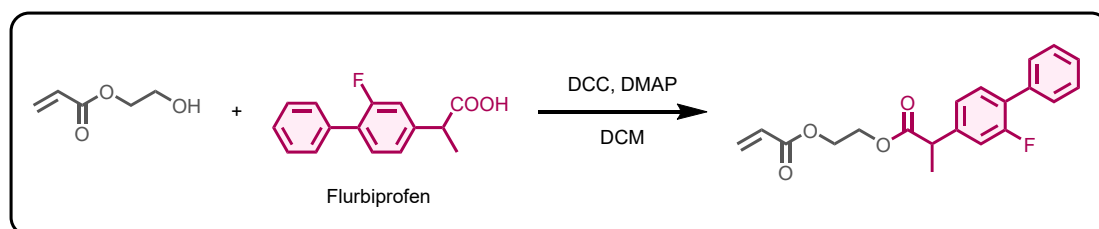
A Schlenk tube equipped with a magnetic stir bar was evacuated and backfilled with nitrogen 3 times. To a solution of acryloyl chloride (0.24 mL, 3.0 mmol, 1.0 equiv.) in DCM (2.5 mL) *N,O*-dimethylhydroxylamine hydrochloride (0.35 g, 3.6 mmol, 1.2 equiv.) and NaHCO₃ (0.63 g, 7.5 mmol, 2.5 equiv.) were added at 0 °C. The suspension was stirred at 0 °C for 3 hours before it was neutralized with HCl (2 M, 3 mL). The organic layer was separated and washed with saturated NaHCO₃ (3 mL) and brine (3 mL) and dried with Na₂SO₄. The crude product was purified by flash column chromatography (SiO₂, PE/EA 3:1) and *N*-methoxy-*N*-methylacrylamide (0.31 g, 2.7 mmol, 89%) was isolated as a colorless oil. (Scheme S4)



Scheme S4. General synthetic procedures for *N*-Methoxy-*N*-methylacrylamide

2.1.5 General procedure for the synthesis of carboxylic-acid-derived alkene (exemplified by flurbiprofen)

In a 50 mL round bottom flask, 2-hydroxyethyl acrylate (0.53 mL, 5 mmol, 1 equiv.), flurbiprofen (1.34 g, 5.5 mmol, 1.1 equiv.), and DMAP (0.03 g, 0.05 mmol, 0.01 equiv.) were dissolved in DCM (30 mL). The mixture was stirred at room temperature, and DCC (1.03 g, 5 mmol, 1 equiv.) was added dropwise. The reaction was allowed to proceed overnight under continuous stirring. The resulting esterified products were subsequently purified by silica gel column chromatography. (Scheme S5)

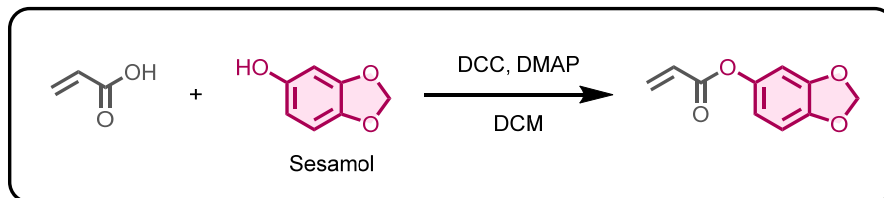


Scheme S5. General synthetic procedures for carboxylic-acid-derived alkenes

2.1.6 General procedure for the synthesis of phenol-derived alkene (exemplified by Sesamol)

In a 50 mL round-bottom flask, acrylic acid (0.34 mL, 5 mmol, 1 equiv.), sesamol (0.75 g, 5.5 mmol, 1.1 equiv.), DMAP (0.03 g, 0.05 mmol, 0.01 equiv.) were dissolved in DCM (30 mL). The

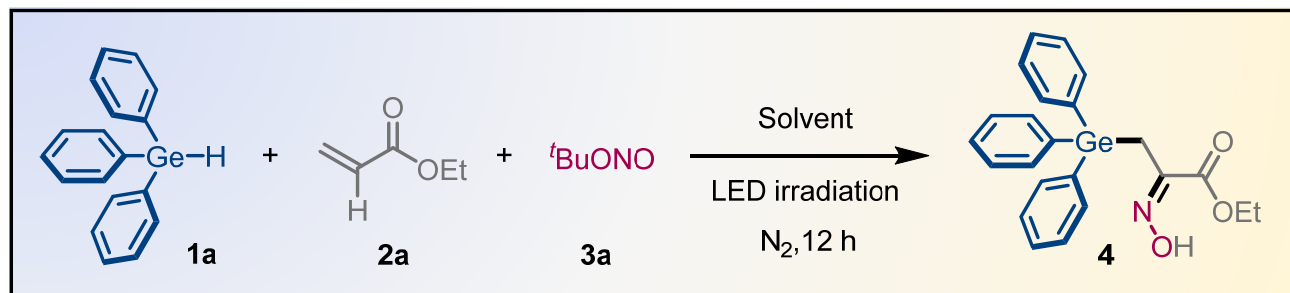
mixture was stirred at room temperature, and DCC (1.03 g, 5 mmol, 1 equiv.) was subsequently added dropwise. The reaction mixture was stirred overnight at room temperature to ensure complete esterification. The esterified products were purified by silica gel column chromatography using an appropriate solvent system. (Scheme S6)



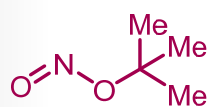
Scheme S6. General synthetic procedures for phenol-derived alkene

2.2 Optimization of reaction conditions

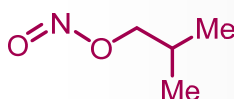
Table S1 Optimization of reaction conditions^a



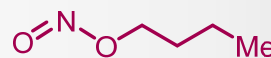
Optional Nitrites



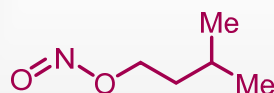
tert-butyl nitrite
3a



iso-butyl nitrite
3b



n-butyl nitrite
3c



iso-pentyl nitrite
3d



n-pentyl nitrite
3e



n-hexyl nitrite
3f

Entry	Comp.1 (equiv)	Comp.2 (equiv)	Comp.1 (equiv)	Solvent	LED light (W)	Yield (%) ^b
1	1a (3.0 equiv)	2a (1.0 equiv)	3a (10.0 equiv)	DCM	390 nm (20 W)	40
2	1a (3.0 equiv)	2a (1.0 equiv)	3a (10.0 equiv)	MeCN	390 nm (20 W)	15
3	1a (3.0 equiv)	2a (1.0 equiv)	3a (10.0 equiv)	EA	390 nm (20 W)	42
4	1a (3.0 equiv)	2a (1.0 equiv)	3a (10.0 equiv)	THF	390 nm (20 W)	55
5	1a (3.0 equiv)	2a (1.0 equiv)	3a (10.0 equiv)	DMF	390 nm (20 W)	trace
6	1a (3.0 equiv)	2a (1.0 equiv)	3a (10.0 equiv)	DMSO	390 nm (20 W)	trace
7	1a (3.0 equiv)	2a (1.0 equiv)	3a (10.0 equiv)	<i>n</i> -pentane	390 nm (20 W)	63
8	1a (3.0 equiv)	2a (1.0 equiv)	3a (10.0 equiv)	<i>n</i> -hexane	390 nm (20 W)	67
9	1a (3.0 equiv)	2a (1.0 equiv)	3a (10.0 equiv)	cyclohexane	390 nm (20 W)	58
10	1a (3.0 equiv)	2a (1.0 equiv)	3a (10.0 equiv)	<i>n</i> -hexane/H ₂ O (v/v = 10:1)	390 nm (20 W)	30
11	1a (3.0 equiv)	2a (1.0 equiv)	3a (10.0 equiv)	<i>n</i> -hexane/MeOH (v/v = 10:1)	390 nm (20 W)	59
12	1a (3.0 equiv)	2a (1.0 equiv)	3a (10.0 equiv)	<i>n</i> -hexane/EtOH (v/v = 10:1)	390 nm (20 W)	63
13	1a (3.0 equiv)	2a (1.0 equiv)	3a (10.0 equiv)	<i>n</i> -hexane/ <i>i</i> -PrOH (v/v = 10:1)	390 nm (20 W)	55
14	1a (3.0 equiv)	2a (1.0 equiv)	3a (10.0 equiv)	<i>n</i> -hexane/ <i>t</i> -BuOH (v/v = 10:1)	390 nm (20 W)	77
15	1a (3.0 equiv)	2a (1.0 equiv)	3a (10.0 equiv)	<i>n</i> -hexane/ <i>t</i> -BuOH (v/v = 2:1)	390 nm (20 W)	39
16	1a (3.0 equiv)	2a (1.0 equiv)	3a (10.0 equiv)	<i>n</i> -hexane/ <i>t</i> -BuOH (v/v = 5:1)	390 nm (20 W)	55
17	1a (3.0 equiv)	2a (1.0 equiv)	3a (10.0 equiv)	<i>n</i> -hexane/ <i>t</i> -BuOH (v/v = 20:1)	390 nm (20 W)	87
18	1a (3.0 equiv)	2a (1.0 equiv)	3a (10.0 equiv)	<i>n</i> -hexane/ <i>t</i> -BuOH (v/v = 50:1)	390 nm (20 W)	60
19	1a (5.0 equiv)	2a (1.0 equiv)	3a (10.0 equiv)	<i>n</i> -hexane/ <i>t</i> -BuOH	390 nm (20 W)	43

20	1a (1.0 equiv)	2a (1.0 equiv)	3a (10.0 equiv)	(v/v = 20:1) <i>n</i> -hexane/ ^t BuOH (v/v = 20:1)	390 nm (20 W)	15
21	1a (1.0 equiv)	2a (3.0 equiv)	3a (10.0 equiv)	<i>n</i> -hexane/ ^t BuOH (v/v = 20:1)	390 nm (20 W)	28
22	1a (1.0 equiv)	2a (5.0 equiv)	3a (10.0 equiv)	<i>n</i> -hexane/ ^t BuOH (v/v = 20:1)	390 nm (20 W)	30
23	1a (1.0 equiv)	2a (1.0 equiv)	3a (2.0 equiv)	<i>n</i> -hexane/ ^t BuOH (v/v = 20:1)	390 nm (20 W)	trace
24	1a (3.0 equiv)	2a (1.0 equiv)	3a (4.0 equiv)	<i>n</i> -hexane/ ^t BuOH (v/v = 20:1)	390 nm (20 W)	trace
25	1a (3.0 equiv)	2a (1.0 equiv)	3a (6.0 equiv)	<i>n</i> -hexane/ ^t BuOH (v/v = 20:1)	390 nm (20 W)	60
26	1a (3.0 equiv)	2a (1.0 equiv)	3a (8.0 equiv)	<i>n</i> -hexane/ ^t BuOH (v/v = 20:1)	390 nm (20 W)	70
27	1a (3.0 equiv)	2a (1.0 equiv)	3a (12.0 equiv)	<i>n</i> -hexane/ ^t BuOH (v/v = 20:1)	390 nm (20 W)	83
28	1a (3.0 equiv)	2a (1.0 equiv)	3a (10.0 equiv)	<i>n</i> -hexane/ ^t BuOH (v/v = 20:1)	--	0
29	1a (3.0 equiv)	2a (1.0 equiv)	3a (10.0 equiv)	<i>n</i> -hexane/ ^t BuOH (v/v = 20:1)	365 nm (20 W)	75
30	1a (3.0 equiv)	2a (1.0 equiv)	3a (10.0 equiv)	<i>n</i> -hexane/ ^t BuOH (v/v = 20:1)	400 nm (20 W)	70
31	1a (3.0 equiv)	2a (1.0 equiv)	3a (10.0 equiv)	<i>n</i> -hexane/ ^t BuOH (v/v = 20:1)	405 nm (20 W)	45
32	1a (3.0 equiv)	2a (1.0 equiv)	3a (10.0 equiv)	<i>n</i> -hexane/ ^t BuOH (v/v = 20:1)	410 nm (20 W)	20
33	1a (3.0 equiv)	2a (1.0 equiv)	3a (10.0 equiv)	<i>n</i> -hexane/ ^t BuOH (v/v = 20:1)	390 nm (10 W)	70
34	1a (3.0 equiv)	2a (1.0 equiv)	3a (10.0 equiv)	<i>n</i> -hexane/ ^t BuOH (v/v = 20:1)	390 nm (40 W)	66
35 ^c	1a (3.0 equiv)	2a (1.0 equiv)	3a (10.0 equiv)	<i>n</i> -hexane/ ^t BuOH (v/v = 20:1)	390 nm (20 W)	trace
36 ^d	1a (3.0 equiv)	2a (1.0 equiv)	3a (10.0 equiv)	<i>n</i> -hexane/ ^t BuOH (v/v = 20:1)	390 nm (20 W)	trace
37 ^e	1a (3.0 equiv)	2a (1.0 equiv)	3a (10.0 equiv)	<i>n</i> -hexane/ ^t BuOH (v/v = 20:1)	390 nm (20 W)	40
38 ^f	1a (3.0 equiv)	2a (1.0 equiv)	3a (10.0 equiv)	<i>n</i> -hexane/ ^t BuOH (v/v = 20:1)	390 nm (20 W)	28
39	1a (3.0 equiv)	2a (1.0 equiv)	3b (10.0 equiv)	<i>n</i> -hexane/ ^t BuOH (v/v = 20:1)	390 nm (20 W)	52
40	1a (3.0 equiv)	2a (1.0 equiv)	3c (10.0 equiv)	<i>n</i> -hexane/ ^t BuOH (v/v = 20:1)	390 nm (20 W)	50
41	1a (3.0 equiv)	2a (1.0 equiv)	3d (10.0 equiv)	<i>n</i> -hexane/ ^t BuOH (v/v = 20:1)	390 nm (20 W)	52
42	1a (3.0 equiv)	2a (1.0 equiv)	3e (10.0 equiv)	<i>n</i> -hexane/ ^t BuOH (v/v = 20:1)	390 nm (20 W)	40
43	1a (3.0 equiv)	2a (1.0 equiv)	3f (10.0 equiv)	<i>n</i> -hexane/ ^t BuOH (v/v = 20:1)	390 nm (20 W)	60

Reaction conditions: **1a** (0.3 mmol), **2a** (0.1 mmol), and **3a** (1.0 mmol) in solvent (1.5 mL) were irradiated with LED light under N₂ protection at room temperature for 12 hours unless otherwise noted. ^bThe yields of **4** were determined by ¹H NMR analysis using 1,1,2,2-tetrachloroethane an internal standard. ^dUnder O₂ atmosphere. ^eReaction time was 6 hours. ^fReaction time was 24 hours.

2.3 Photographs of the reaction vessel, Kessil lamp, and photoreaction device

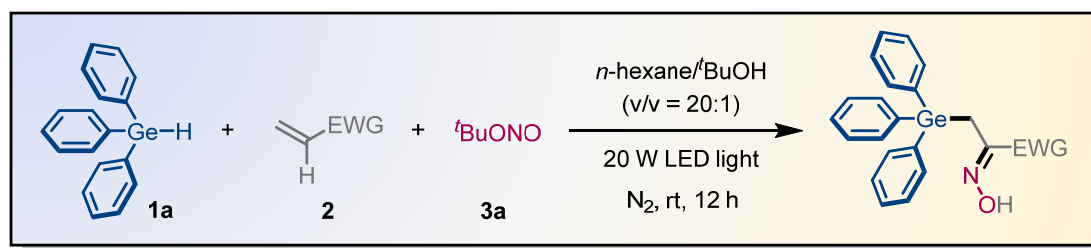
The experimental setup employs a 25 mL reaction vial as the reaction vessel. The photoreaction device consists of a stirrer, a fixed base, a reaction vessel, and a Kessil PR160L-390 nm lamp, positioned at a distance of 2 – 3 cm from the bottom of the reaction vessel to ensure optimal light exposure. More details regarding the assembly are provided in Figure S1.



Figure S1. Photographs of the reaction vessel, Kessil lamp, and photoreaction device. **A:** 25 mL reaction vial; **B:** Kessil PR160L-390 nm lamp, **C:** photoreactor.

2.4 Model reaction conditions

In a 25 mL Schlenk tube, a mixture of **1a** (0.1 0.3 mmol, 3.0 equiv.), **2** (0.1 mmol), and **3a** (1 mmol, 10 equiv.) in 1.5 mL hexane was prepared. The reaction mixture was stirred under irradiation with a 20 W 390 nm LED light source in N₂ atmosphere at room temperature for 12 hours. The progress of the reaction was monitored by TLC. Upon completion, the reaction mixture was concentrated under reduced pressure, and the resulting residue was purified by flash chromatography on silica gel using a gradient of petroleum ether and ethyl acetate as the eluent to afford the desired product. (Scheme S7)

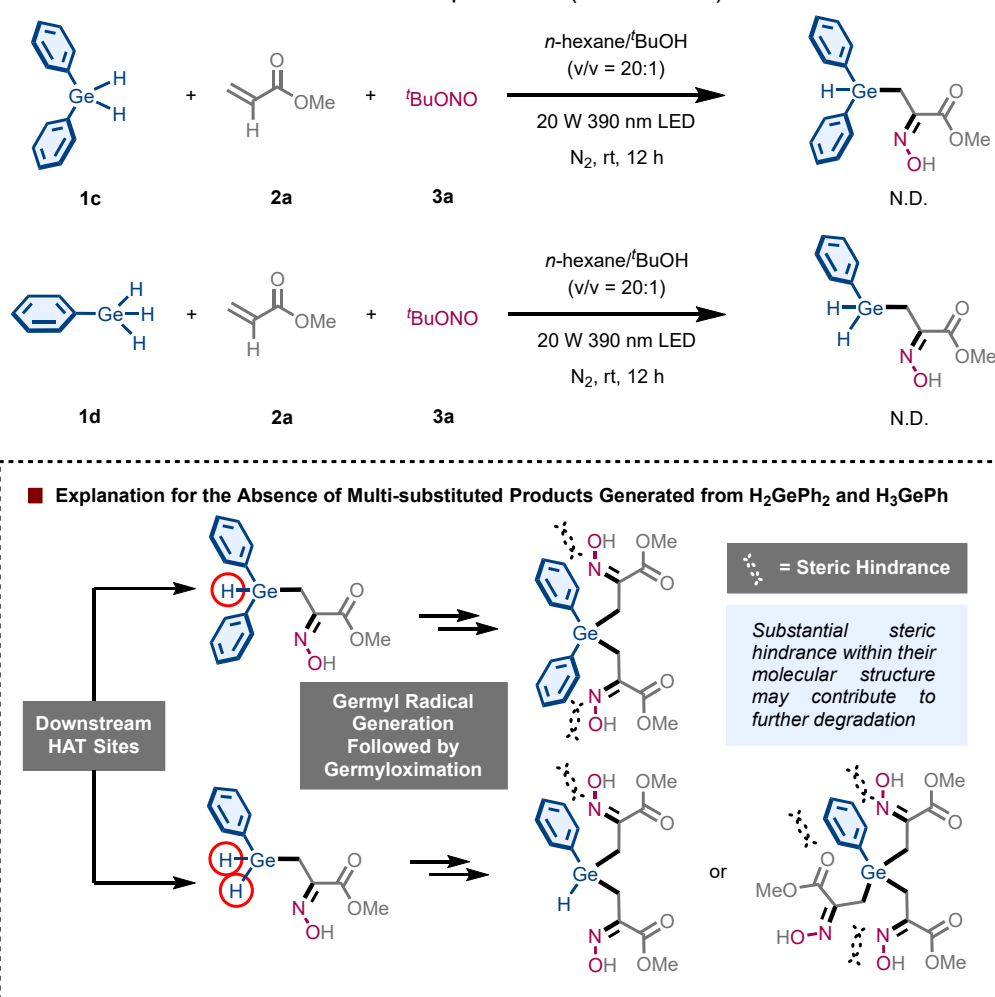


Scheme S7. Model reaction conditions

2.5 Substrate evaluation

2.5.1 Evaluation of the applicability by using Ph₂GeH₂ and PhGeH₃ as substrates

The failure in the synthesis of desired products from H₂GePh₂ and H₃GePh appears to stem from residual Ge–H bonds in the mono-substituted derivatives, which can serve as downstream hydrogen atom transfer (HAT) sites, consequently leading to the generation of new germanium-centered radicals. Therefore, the reaction does not stop at the synthesis of monosubstituted alkylgermanes, and it is plausible that the continued germyloximation lead to the formation of disubstituted or trisubstituted products. Substantial steric hindrance within their molecular structure may contribute to further degradation and byproduct generation, which is likely responsible for the absence of the desired products. (Scheme S8)

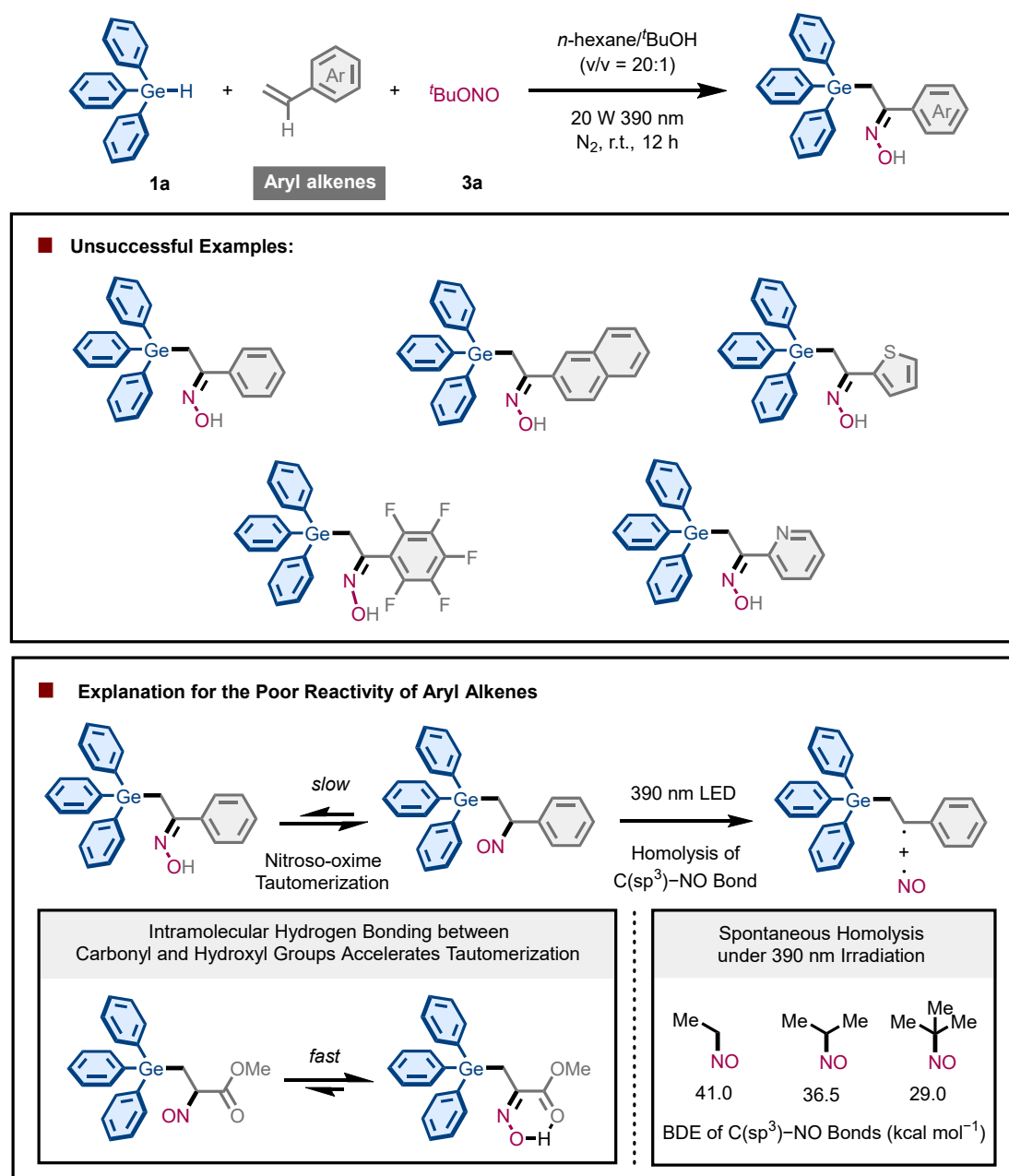


Scheme S8. Evaluation of the applicability by using Ph₂GeH₂ and PhGeH₃ substrates

2.5.2 Evaluation of aryl alkenes

A range of aryl alkenes, including styrene, 2-vinylnaphthalene, 2-ethenylthiophene, 2,3,4,5,6-pentafluorostyrene, and 2-vinylpyridine, were subjected to the standard reaction conditions. As illustrated in Scheme blow, neither electron-deficient nor electron-rich aryl alkenes yielded the

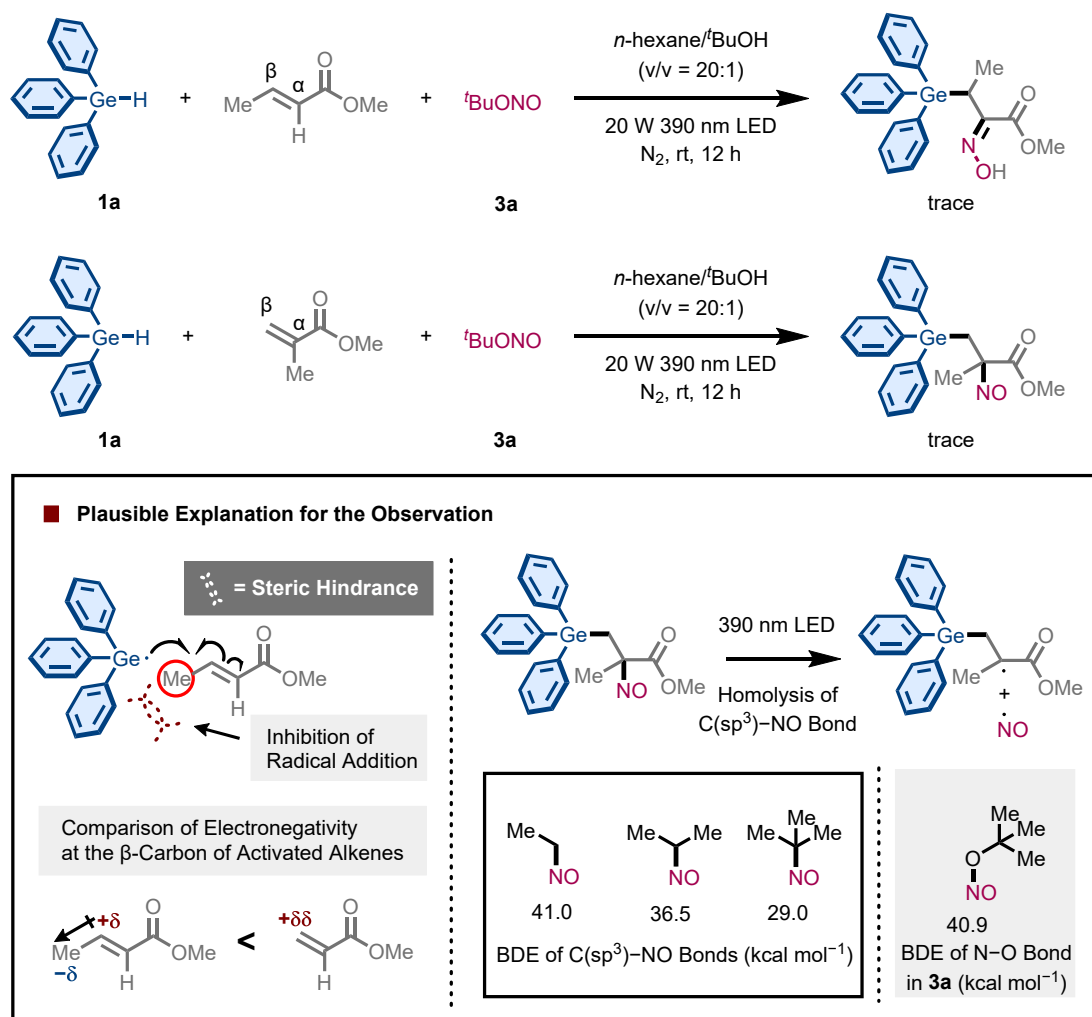
anticipated alkyl germane products. This experimental outcome can be attributed to the stability of the alkyl nitroso intermediates formed during the reaction process. In contrast, activated alkenes (e.g. methyl acrylate) possess a carbonyl group capable of establishing intramolecular hydrogen bonding with the oxime moiety, thereby facilitating rapid nitroso-oxime tautomerization and favoring the formation of thermodynamically stable α -germyloxime-type products. Lacking such structural feature, aryl alkenes preclude efficient tautomerization and lead to the accumulation of nitroso intermediates, which is characterized by labile $C(sp^3)$ -NO bonds^{S4-6} and readily undergo spontaneous homolysis under 390 nm light irradiation, ultimately hindering the synthesis of the target products. (Scheme S9)



Scheme S9. Evaluation of electron-deficient nor electron-rich aryl alkenes

2.5.3 Evaluation of activated alkene with substitution at the β - or α - position

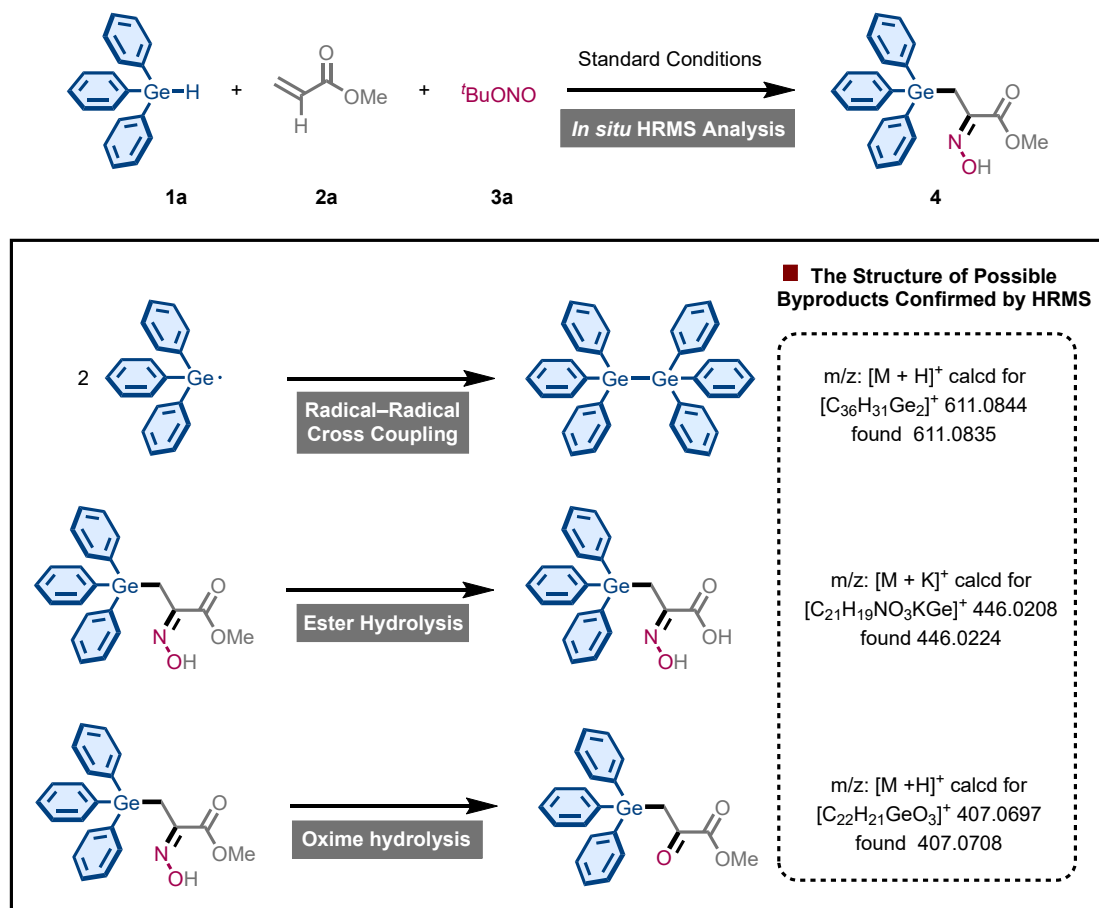
As illustrated in Scheme S10, incorporation of a methyl group at the β - or α -position of the alkene did not afford the anticipated gemyloximation or gemylnitrosation products. The likely explanation for this observation is that the presence of a β -methyl group in methylbut-2-enoate imposes considerable steric hindrance, impeding the addition of the triphenylgermyl radical, as well as diminishes the electronegativity at the β -carbon, thereby reducing its susceptibility to nucleophilic radical attack. In the case of methyl methacrylate, the absence of α -hydrogen atoms prevents the vital nitroso-oxime tautomerization, suggesting that the alkyl nitroso formation would predominate. However, the resultant gemylnitrosation product contains a $C(sp^3)$ –NO bond with a bond dissociation energy notably lower than that of the N–O bond in TBN, ^{S4-6} rendering it prone to homolytic cleavage under 390 nm light irradiation, resulting in rapid decomposition of the target product. (Scheme S10)



Scheme S10. Evaluation of activated alkene with substitution at the β - or α - position

2.6 In situ HRMS analysis on model reaction

Due to the inability to isolate and purify a single byproduct from the reaction mixture for structural confirmation, an *in situ* high-resolution mass spectrometry (HRMS) analysis was utilized on model reactions of **1a**, **2a**, and **3a** to identify possible byproduct structures. The HRMS signal peaks at 611.0835, 446.0224, and 407.0708 correspond to $[\text{C}_{36}\text{H}_{31}\text{Ge}_2]^+$, $[\text{C}_{21}\text{H}_{19}\text{NO}_3\text{KGe}]^+$, and $[\text{C}_{22}\text{H}_{21}\text{GeO}_3]^+$, suggesting the existence of hexaphenyldigermene, 2-(hydroxyimino)-3-(triphenylgermyl)propanoic acid, and methyl 2-oxo-3-(triphenylgermyl)propanoate, respectively. The generation of the former is attributed to radical-radical cross-coupling of two germyl radicals. While, the formation of the latter two are presumed to arise from hydrolysis of the ester and oxime groups. This comprehensive HRMS analysis provides a reasonable explanation for the moderate yields obtained in certain cases, as the formation of such byproducts competes with the desired transformation. (Scheme S11 and Figures S2)



Scheme S11. *In situ* HRMS analysis to confirmed the structure of possible byproducts

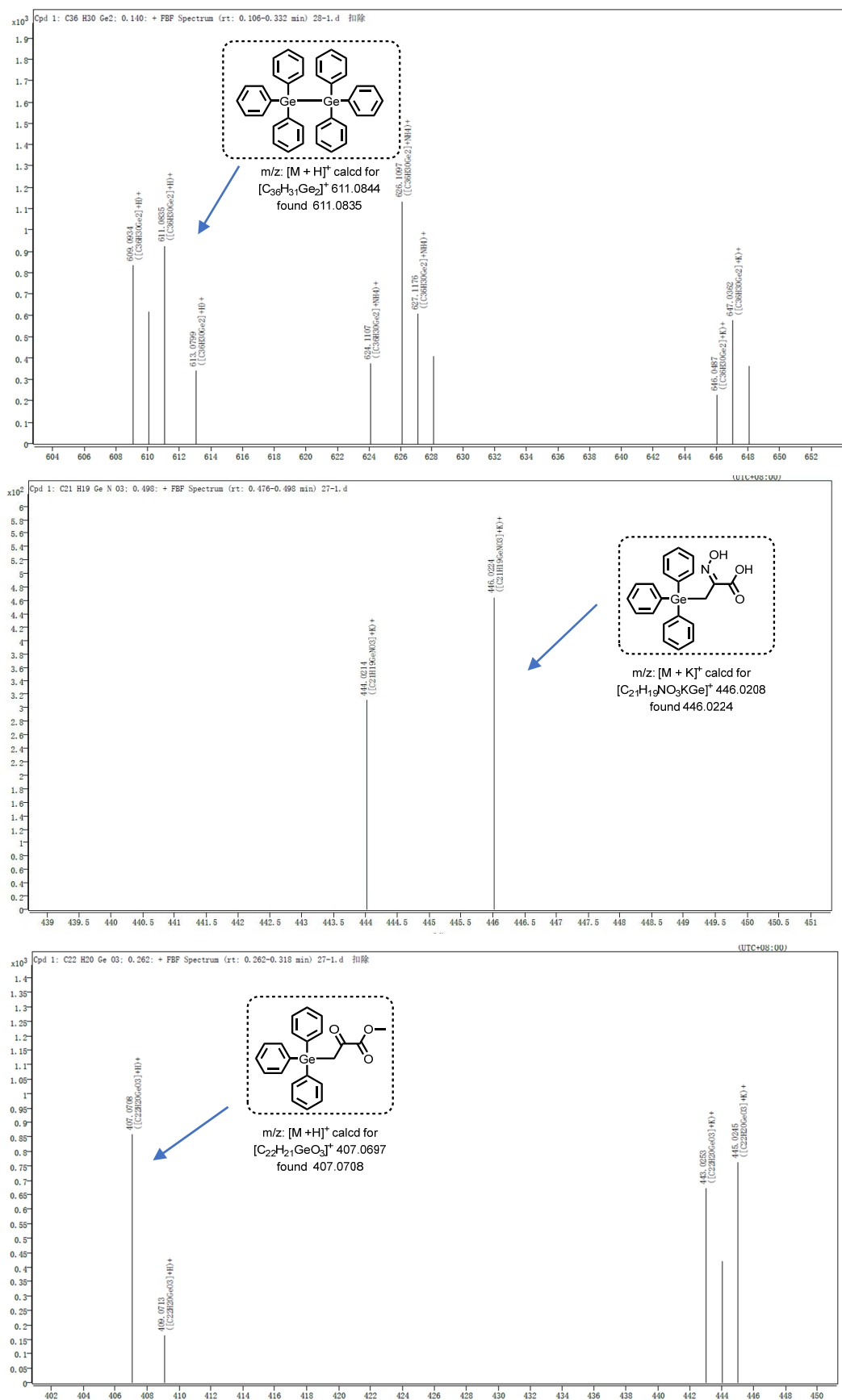


Figure S2. HRMS spectra

2.7 Synthetic application

2.7.1 The gram-scale preparation synthesis process

Compounds **1a** (3.0 equiv.), **2a** (4.0 mmol), **3a** (10.0 equiv.), and *n*-hexane/*i*BuOH (v/v = 20:1, 15 mL) were sequentially added to a 50 mL reaction flask. The mixture was stirred under a N₂ atmosphere at room temperature for 24 hours under irradiation with a 40 W, 390 nm light source. Upon completion of the reaction, the solvent was removed under reduced pressure using a rotary evaporator to afford a concentrated residue. The desired product **4** was isolated by silica gel column chromatography, yielding 1.17 g of the target compound with a separation yield of 67%. (Scheme S12A)

2.7.2 General procedure for the synthesis of **36**^{S7}

Methyl (*E*)-2-(hydroxyimino)-3-(triphenylgermyl)propanoate (10 mmol) dissolved in 15 mL DMF was added to NaH (0.6 in oil, 12 mmol, 1.2 equiv.) in 12 mL DMF dropwise. The mixture was stirred at 0 °C for an additional 2 hours. Then, haloalkanes (12 mmol, 1.2 equiv.) were added slowly, and the reaction mixture was stirred at room temperature overnight. The reaction was quenched by the addition of a saturated aqueous solution of NH₄Cl. The mixture was then diluted with water and extracted with EA (2 × 30 mL). The combined organic phases were washed with a saturated aqueous NaCl solution (25 mL) and dried over anhydrous Na₂SO₄. After filtration and removal of the solvents under reduced pressure, the crude product was purified by column chromatography to afford the desired product. (Scheme S12B)

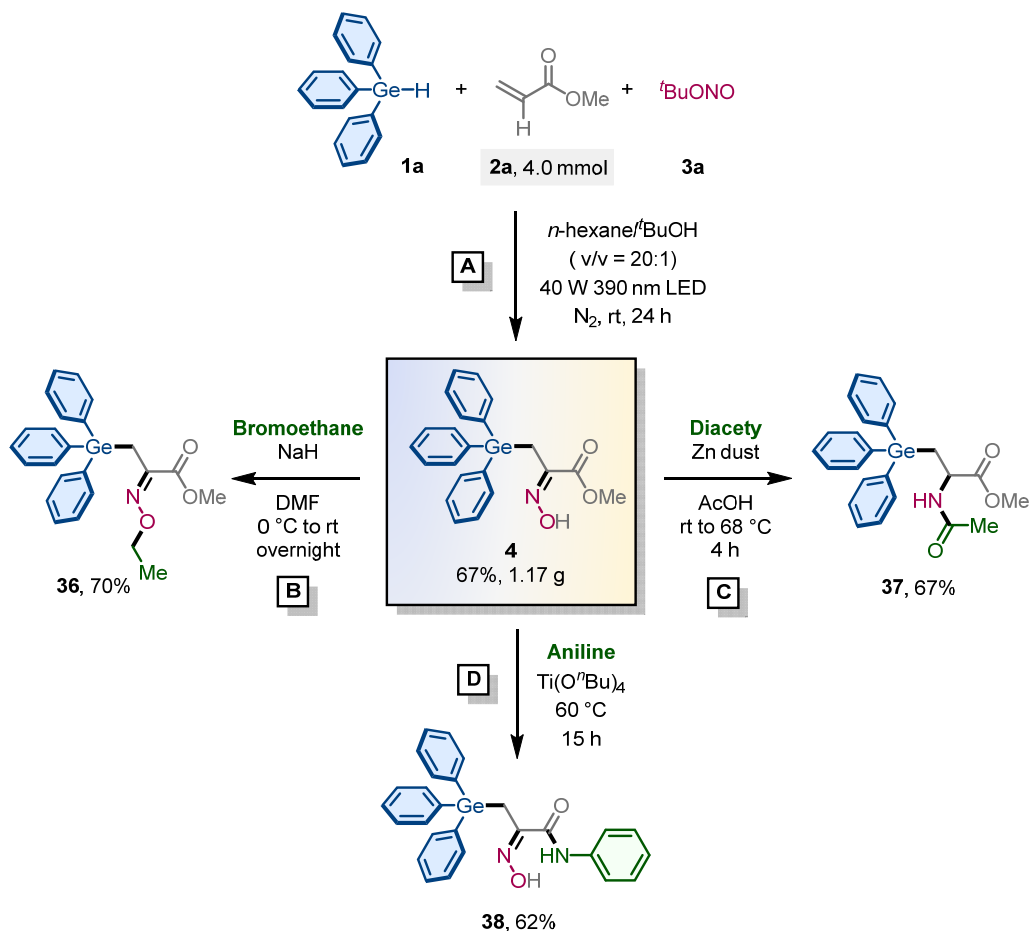
2.7.3 General procedure for the synthesis of **37**^{S3}

Methyl (*E*)-2-(hydroxyimino)-3-(triphenylgermyl)propanoate (0.15 mmol, 1.0 equiv.) was dissolved in a mixture of acetic acid (1.2 mL) and acetic anhydride (1.8 mmol, 12 equiv.). The reaction mixture was cooled to 0 °C and Zn (0.098 g, 1.5 mmol, 10 equiv.) was added. The mixture was stirred at room temperature for 3 hours, followed by heating at 68 °C for 1 hour using a heating mantle. Afterwards, the mixture was filtrated, and the residue was washed with DCM (3 mL). The filtrate was carefully neutralized with saturated NaHCO₃ (3 mL) and extracted with DCM (3 × 3 mL). The combined organic layers were washed with brine (4 mL), dried with Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel using a mixture of pentane and ethyl acetate (5:4 v/v) as the eluent. Methyl 2-acetamido-3-(triphenylgermyl)propanoate was isolated as a white solid. Scheme S12C)

2.7.4 General procedure for the synthesis of **38**^{S8}

A mixture of aniline (1.8 mL, 20 mmol), methyl pyruvate oxime (22 mmol), and Ti(OnBu)₄ (0.68 mL, 2.0 mmol) was stirred at 60 °C for 15 hours. Upon completion of the reaction, the

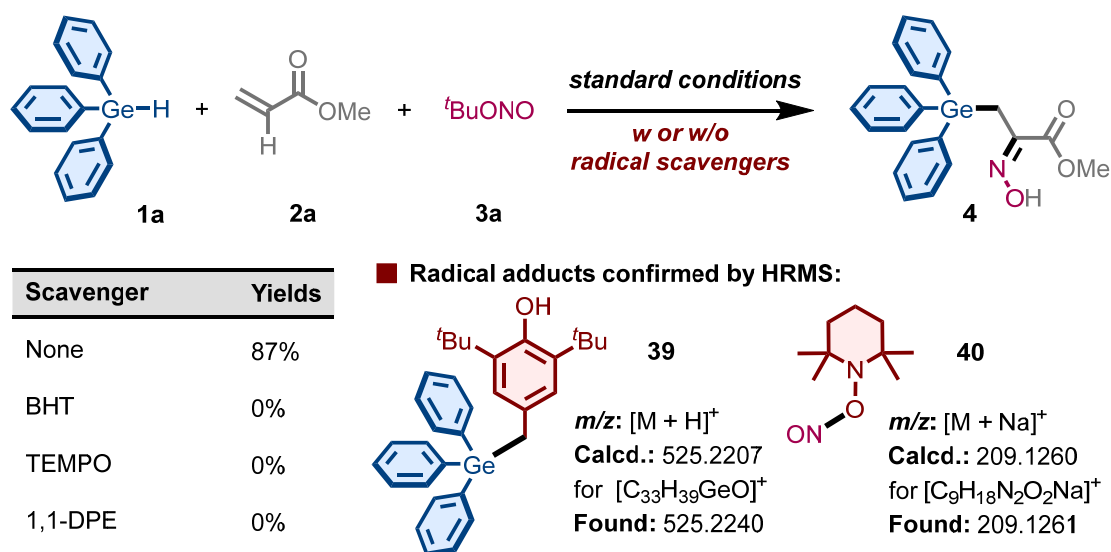
mixture was quenched with a saturated aqueous solution of NaHCO_3 (30 mL) and extracted with EA (3×80 mL). The combined organic layers were washed with water (2×30 mL), dried over anhydrous MgSO_4 , filtered, and concentrated under reduced pressure. The crude product was purified by trituration with hexane to afford the desired compound as a white solid. (Scheme S12D)



Scheme S12. Gram-scale synthesis and product derivatization

2.8 Radical scavenging experiments

In a reaction tube, a mixture of **1a** (0.3 mmol), **2a** (0.2 mmol), **3** (1 mmol), and radical scavengers (5.0 equiv.) in n-hexane/^tBuOH (20:1, 1.5 mL) was prepared. The reaction mixture was stirred under irradiation with a 20 W 390 nm Kessil light source at room temperature under N₂ atmosphere for 12 hours. The yields of **4** were determined by TLC and isolated yield analysis (Scheme S13). During the radical scavenger experiments, the formation of 1,1-DPE and TEMPO adducts (**39** and **40**) were confirmed by high-resolution mass spectrometry (HRMS), which aligns conclusively with the proposed reaction mechanism. (Figures S3–4)



Scheme S13. Radical scavenging experiments

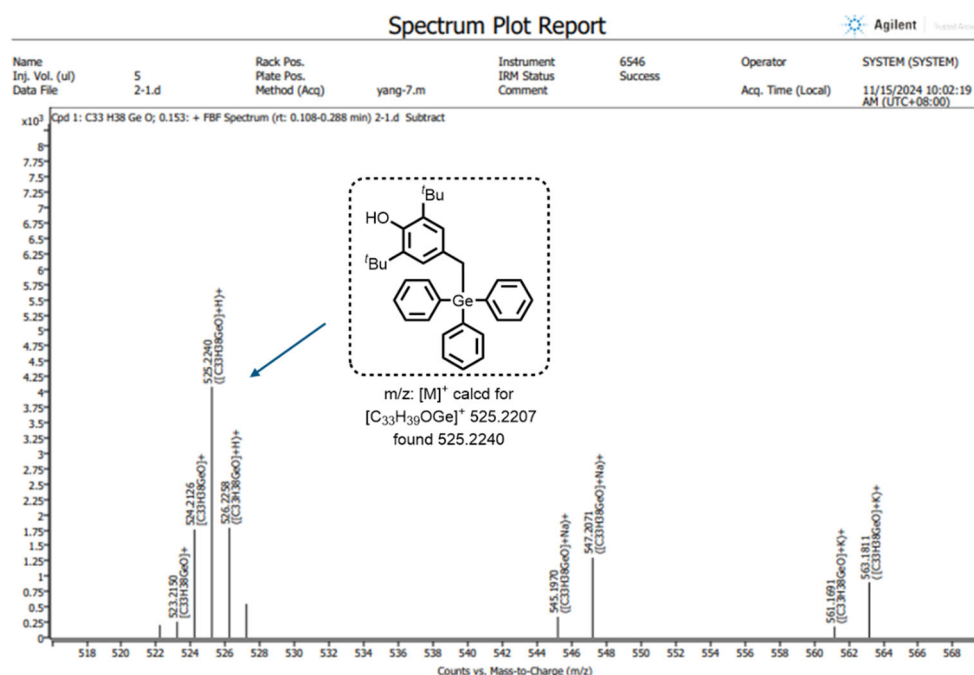


Figure S3. HR-MS spectrum of **39**

Spectrum Plot Report

Agilent Significant Figures

Name	Inj. Vol. (ul)	5	Rack Pos.	Plate Pos.	Method (Acq)	yang-7.m	Instrument	IRM Status	Comment	6546	Success	Operator	SYSTEM (SYSTEM)
Data File	4.d											Acq. Time (Local)	11/14/2024 9:05:19 PM (UTC+08:00)

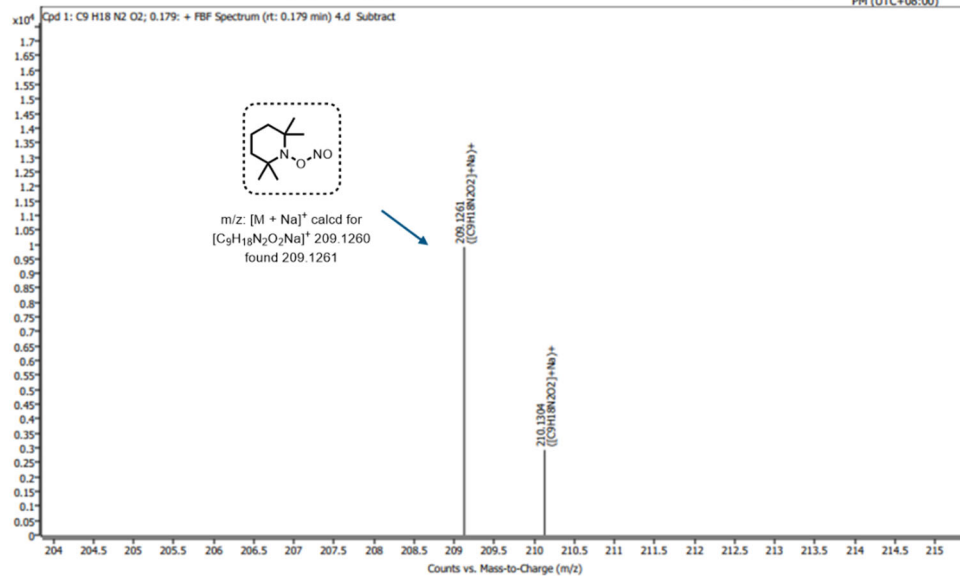


Figure S4. spectrum of 40

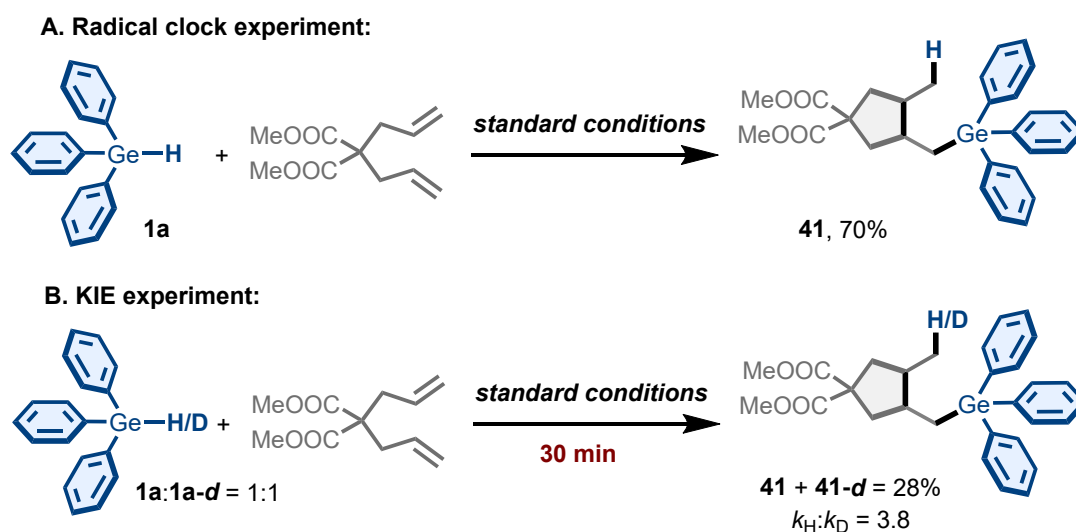
2.9 Radical clock and KIE experiments

2.9.1 Radical clock experiment

In a 25 mL reaction tube, a mixture of **1a** (0.3 mmol), 2,2-diallyl dimethyl dicarboxylate (0.1 mmol), ^tBuONO (1 mol) were added in n-hexane/^tBuOH (20:1, 1.5 mL) was prepared. The reaction mixture was irradiated with a 20 W 390 nm Kessil light source at room temperature under N₂ atmosphere for 12 hours. Upon completion, the mixture was purified by column chromatography on silica gel using a gradient of PE and EA as the eluent, yielding the desired product **41**. (Scheme S14A)

2.9.2 KIE experiment

In a 25 mL reaction tube, a mixture of **1a** (0.15 mmol), **1a-d** (0.15 mmol), 2,2-diallyl dimethyl dicarboxylate (0.1 mmol), and ^tBuONO (1 mol) in n-hexane/^tBuOH (v:v = 20:1, 1.5 mL) was prepared. The reaction mixture was irradiated with a 20 W 390 nm Kessil light source at room temperature under N₂ atmosphere for 12 hours. Upon completion, the mixture was purified by column chromatography on silica gel using a gradient of PE and EA as the eluent, affording the desired products **42** and **42-d**. The ratio of **42** to **42-d** was subsequently determined by ¹H NMR analysis. (Scheme S14B)

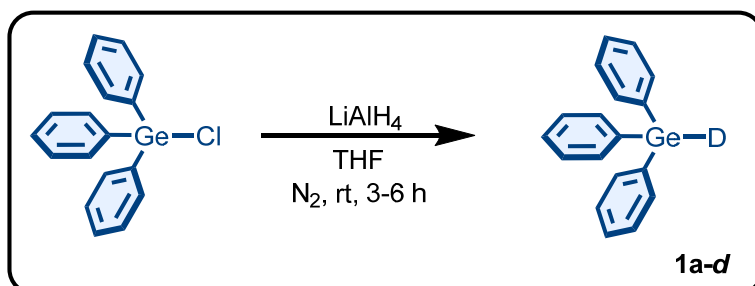


Scheme S14. Radical clock and KIE experiments

2.7.3 Synthesis of **1a-d**

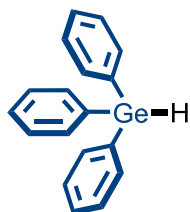
Under an inert nitrogen atmosphere and at ambient temperature, 1 mmol (0.34 g, 1 equiv.) of Ph₃GeCl was dissolved in 2.5 mL of THF. To the resulting suspension, 1 mmol (0.81 mL, 1 equiv.) of LiAlD₄ was added dropwise in 2.5 mL of THF. The reaction mixture was stirred at room temperature for a period of 3-6 hours to ensure complete reaction. Following this, 5 mL of 2 M H₂SO₄ was introduced dropwise to the mixture. The organic phase was then separated,

and the aqueous layer was extracted with DCM in 3×10 mL. The combined organic phases were dried over anhydrous Na_2SO_4 , and the solvent was subsequently removed under reduced pressure. The residual material was recrystallized from hexane, yielding the pure product **1a-d** as a white crystalline solid. (Scheme S15 and Figure S5–S6)



Scheme S15. Synthetic procedure for **1a-d**

2.7.4 Comparison of ^1H NMR data of **1** and **1a-d**



Triphenylgermane (1a)

Purification by flash column chromatography (PE) to provide **1a**. White solid. ^1H NMR (600 MHz, Chloroform-*d*) δ 7.50 – 7.43 (m, 6H), 7.37 – 7.25 (m, 9H), 7.18 (s, 1H).



Triphenylgermane-d (1a-d)

Purification by flash column chromatography (PE) to provide **1a-d**. White solid. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.75 – 7.57 (m, 6H), 7.52 – 7.41 (m, 9H).

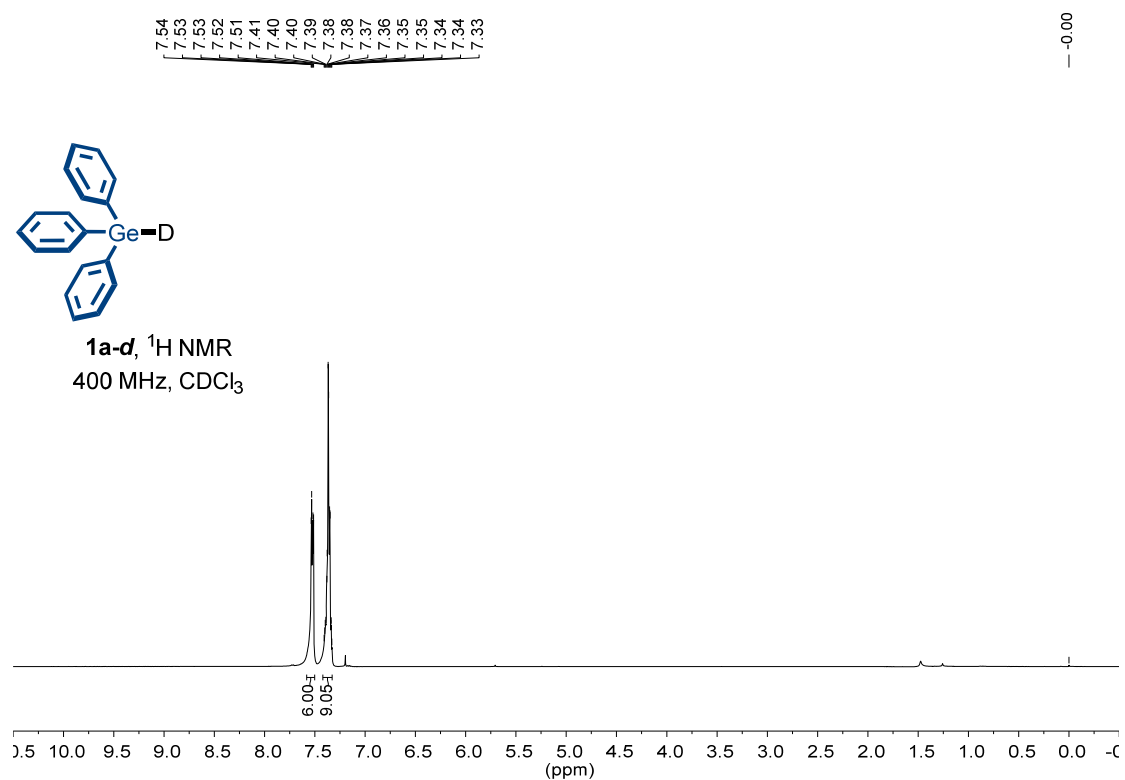
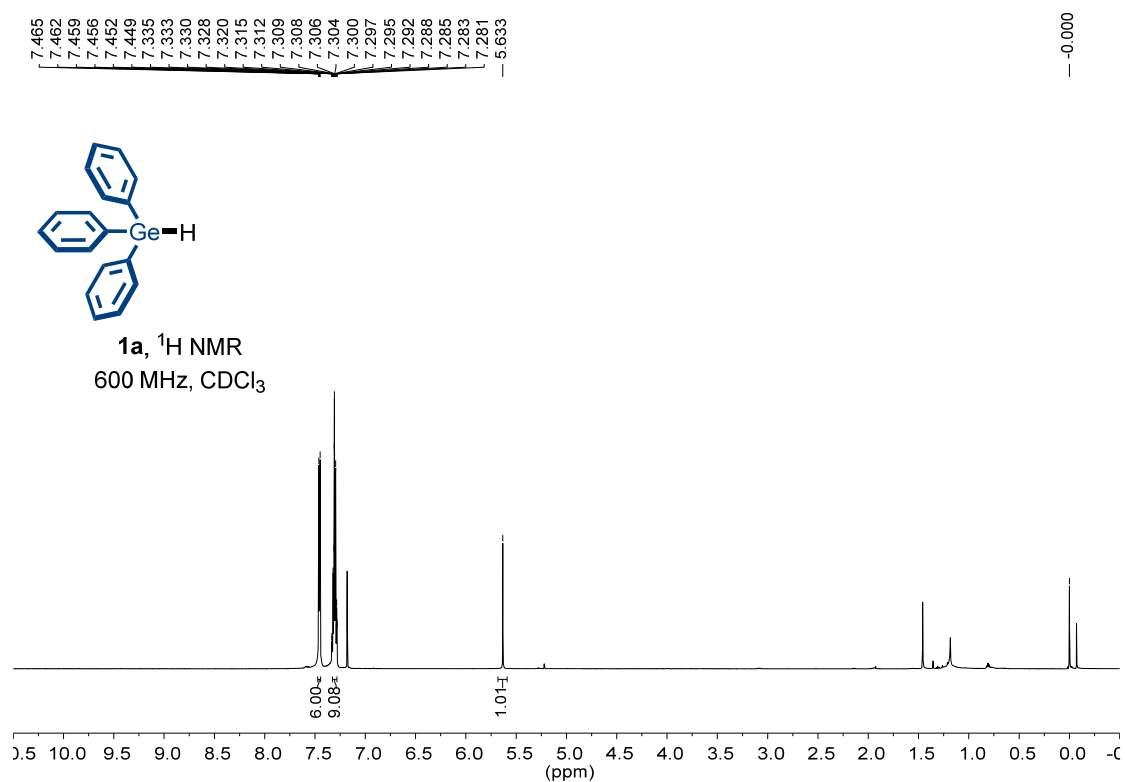


Figure S5. Comparison of ^1H NMR spectra of **1a** and **1a-d**

2.8.5 Determination of $k_H:k_D$ by ^1H NMR spectra of 41 and 41-d

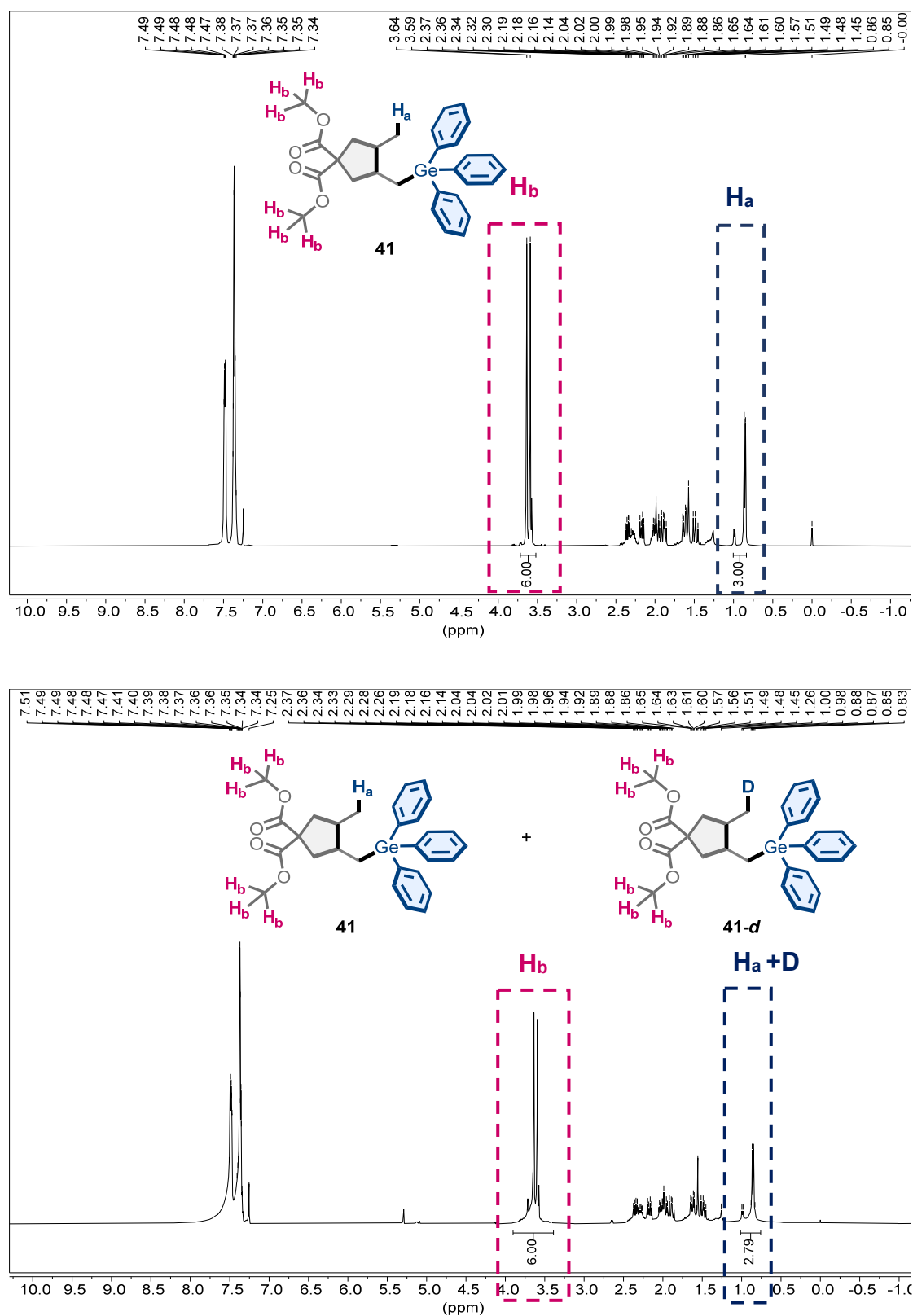


Figure S6. ^1H NMR spectra for radical clock and KIE experiments

$$k_H:k_D = 0.79/0.21 = 3.8$$

2.10 UV-vis absorption experiments

To further elucidate the role of *tert*-butanol, UV-vis absorption measurements of TBN were performed. As showcased in Figure S1, TBN dissolved in *tert*-butanol exhibits a pronounced red-shift in UV-vis spectrum and an increased absorption intensity at 390 nm compared to that in *n*-hexane, which may account for the increased yields with the use of cosolvents of *n*-hexane and *tert*-butanol. (Figure S7)

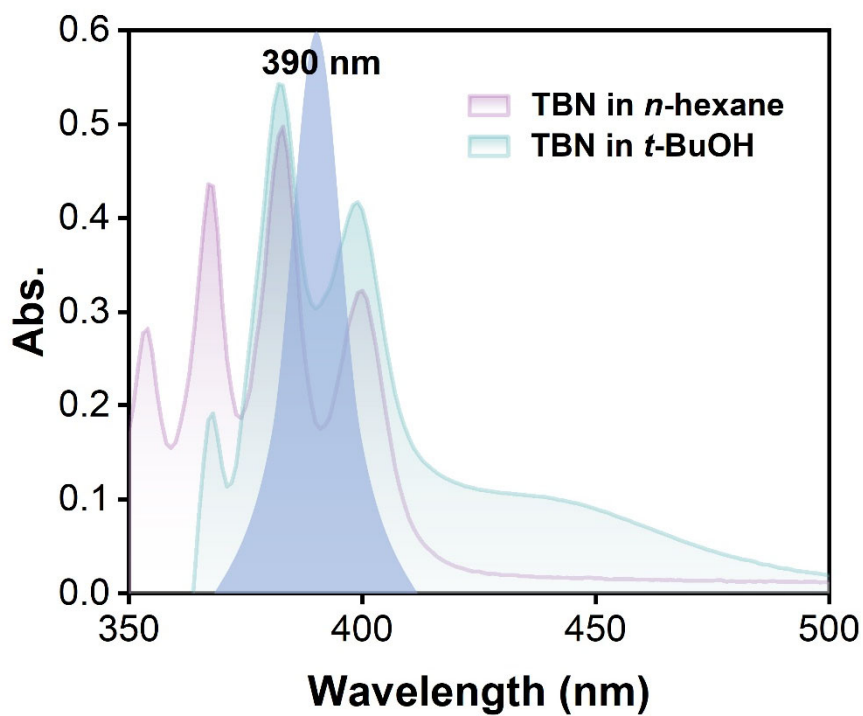


Figure S7 UV-vis absorption spectra of TBN

Two quartz cuvettes were prepared and designated as the sample cell and the reference cell. Hexane was added to the reference cell as the solvent to ensure minimal absorption in the UV-visible range. In the sample cell, six distinct 0.1 M nitrite ester solutions were introduced, ensuring homogeneity and the absence of bubbles. Initially, a blank scan of the reference cell was conducted to record the absorbance values of hexane across various wavelengths, which served as background correction data. Subsequently, the sample cell was placed in the spectrophotometer, and the wavelength was incrementally increased from the lower range, with absorbance values recorded at each wavelength. This procedure was repeated for each nitrite ester solution to ensure data reproducibility and accuracy. (Figure S8).

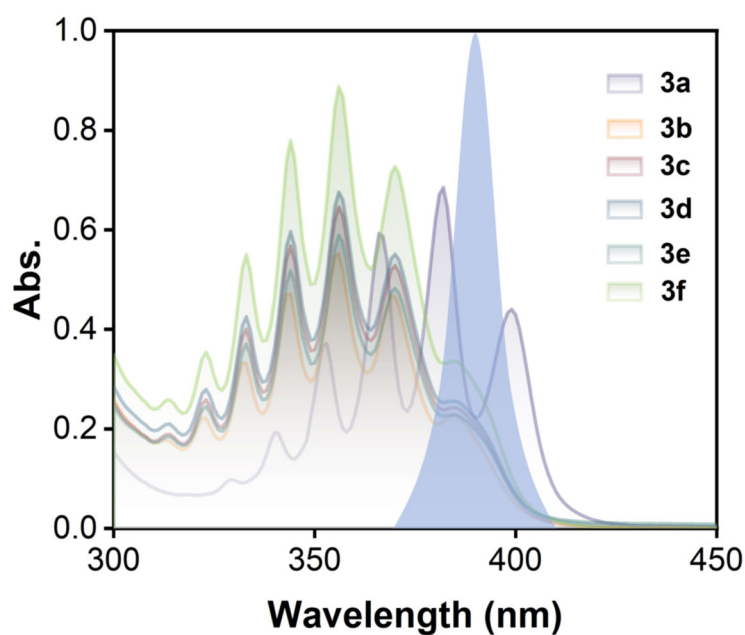


Figure S8. UV-visible spectral absorption experiments

2.11 LED on/off irradiation experiment

To 6 identical 25 mL reaction tubes, add **1a** (90.6mg, 0.3mmol), **2a** (8.4, 0.1mmol), ^tBuONO (0.12 mL, 1 mmol) in n-hexane/^tBuOH (20:1, 1.5 mL) in each tube. The reactions were irradiated with 390 nm Kessil light for 2 hours, after which the solvent was removed using a rotary evaporator. The yield of the first reaction was determined by ¹H NMR spectroscopy using 1,1,2,2-tetrachloroethane as an internal standard. The remaining five reactions were carried out in the dark for 2 hours. The second reaction was then sampled and processed identically, and its yield was determined by ¹H NMR. Subsequently, the 390 nm light was turned on, and the reaction was allowed to proceed for an additional 2 hours before determining the yield of the third reaction. This procedure was repeated iteratively until the reaction had proceeded for a total of 12 hours. The experimental data revealed that the reaction continued to progress even in the absence of light, suggesting the involvement of a radical chain mechanism in the reaction process. (Figure S8)

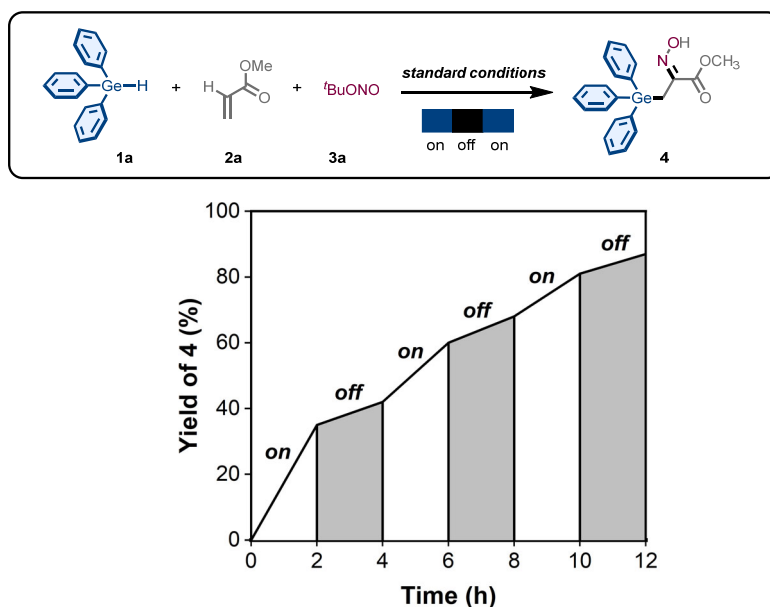
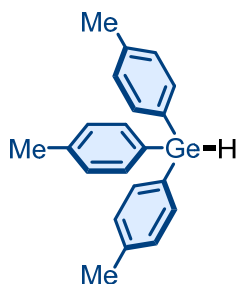


Figure S9. LED on/off irradiation experiments

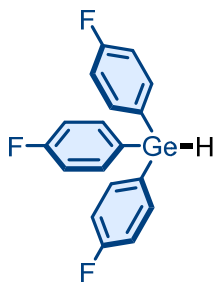
3 Characterization Data



tri-p-tolylgermane (1b)

Purification by flash column chromatography (PE) to provide **1b**. White solid (17 mg, 50% yield).

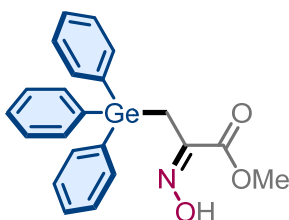
^1H NMR (300 MHz, Chloroform-*d*) δ 7.42 – 7.33 (m, 6H), 7.21 – 7.09 (m, 6H), 5.60 (s, 1H), 2.34 (s, 9H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 138.9, 135.1, 132.2, 129.1, 21.5. HRMS (ESI-TOF) *m/z*: $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{21}\text{H}_{22}\text{NaGe}^+$, 371.0825, found: 371.0805.



tris(4-fluorophenyl)germane (1c)

Purification by flash column chromatography (PE) to provide **1c**. White solid (22 mg, 60% yield).

^1H NMR (600 MHz, Chloroform-*d*) δ 7.49 – 7.36 (m, 6H), 7.14 – 6.96 (m, 6H), 5.70 (s, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 164.0 (d, $J = 248.9$ Hz), 136.9 (d, $J = 7.6$ Hz), 130.4 (d, $J = 3.8$ Hz), 115.9, 115.8. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -111.09. HRMS (ESI-TOF) *m/z*: $[\text{M} + \text{NH}_4]^+$ calcd for $\text{C}_{18}\text{H}_{17}\text{NF}_3\text{Ge}^+$, 378.0519, found: 378.0552.

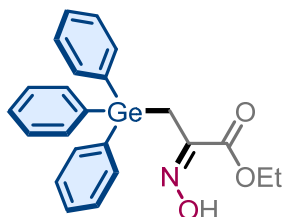


methyl-2-(hydroxyimino)-3-(triphenylgermyl)propanoate (4)

Purification by flash column chromatography (PE: EA, *v/v* = 5:1) to provide **4**. Colorless oil (37

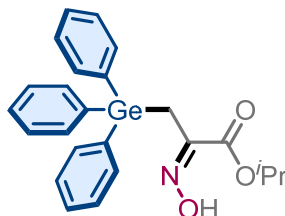
mg, 87% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 9.52 (s, 1H), 7.53 – 7.50 (m, 6H), 7.38 – 7.30 (m, 9H), 3.47 (s, 3H), 3.06 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.9, 151.9,

136.0, 134.9, 129.1, 128.1, 52.2, 14.2. HRMS (ESI-TOF) m/z : $[M + Na]^+$ calcd for $C_{22}H_{21}NO_3NaGe^+$, 444.0625, found: 444.0590.



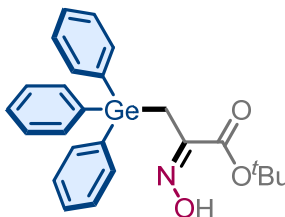
triphenyl(p-tolylethynyl)germane (5)

Purification by flash column chromatography (PE: EA, v/v = 5:1) to provide **5**. Colorless oil (34 mg, 79% yield). 1H NMR (400 MHz, Chloroform- d) δ 8.53 (s, 1H), 7.46 – 7.43 (m, 6H), 7.30 – 7.25 (m, 9H), 3.90 (q, J = 6.4 Hz, 2H), 2.99 (s, 2H), 1.00 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform- d) δ 163.5, 152.2, 135.8, 134.8, 129.2, 128.2, 61.6, 14.0, 13.9. HRMS (ESI-TOF) m/z : $[M + Na]^+$ calcd for $C_{23}H_{23}NO_3NaGe^+$, 458.0782, found: 458.0771.



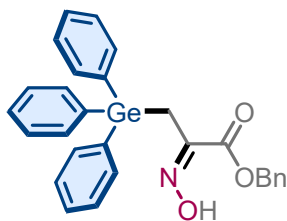
isopropyl-2-(hydroxyimino)-3-(triphenylgermyl)propanoate (6)

Purification by flash column chromatography (PE: EA, v/v = 5:1) to provide **6**. Colorless oil (34 mg, 75% yield). 1H NMR (400 MHz, Chloroform- d) δ 9.51 (s, 1H), 7.53 – 7.51 (m, 6H), 7.37 – 7.29 (m, 9H), 4.86 – 4.79 (m, 1H), 3.05 (s, 2H), 1.03 (d, J = 6.2 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform- d) δ 162.9, 151.6, 135.9, 129.1, 128.1, 69.3, 13.9. HRMS (ESI-TOF) m/z : $[M + Na]^+$ calcd for $C_{24}H_{25}NO_3NaGe^+$, 472.0938, found: 472.0949.



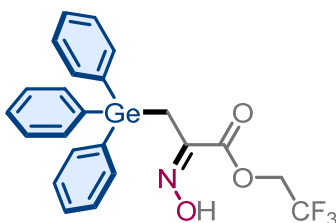
tert-butyl-2-(hydroxyimino)-3-(triphenylgermyl)propanoate (7)

Purification by flash column chromatography (PE: EA, v/v = 5:1) to provide **7**. Colorless oil (34 mg, 73% yield). 1H NMR (400 MHz, Chloroform- d) δ 9.53 (s, 1H), 7.45 – 7.43 (m, 6H), 7.22 – 7.30 (m, 9H), 2.95 (s, 2H), 1.17 (s, 9H). ^{13}C NMR (101 MHz, Chloroform- d) δ 162.4, 136.3, 134.9, 128.9, 128.1, 82.0, 27.7, 13.9. HRMS (ESI-TOF) m/z : $[M + Na]^+$ calcd for $C_{25}H_{27}NO_3NaGe^+$, 486.1095, found: 486.1108.



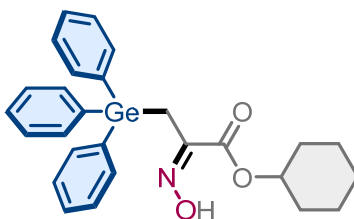
benzyl-2-(hydroxyimino)-3-(triphenylgermyl)propanoate (8)

Purification by flash column chromatography (PE: EA, v/v = 5:1) to provide **8**. Colorless oil (24 mg, 50% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 9.36 (s, 1H), 7.62 – 7.60 (m, 1H), 7.48 – 7.46 (m, 6H), 7.39 – 7.42 (m, 2H), 7.36 – 7.32 (m, 2H), 7.30 – 7.22 (m, 9H), 4.92 (s, 2H), 3.05 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.3, 151.6, 135.8, 135.2, 134.2, 130.1, 129.2, 128.5, 128.3, 128.2, 67.1, 14.1. HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{28}\text{H}_{25}\text{NO}_3\text{NaGe}^+$, 520.0938, found: 520.0952.



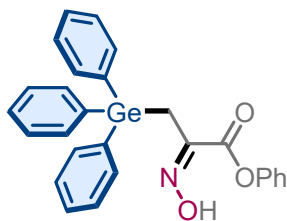
2,2,2-trifluoroethyl-2-(hydroxyimino)-3-(triphenylgermyl)propanoate (9)

Purification by flash column chromatography (PE: EA, v/v = 5:1) to provide **9**. Colorless oil (31 mg, 64% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.84 (s, 1H), 7.52 – 7.49 (m, 6H), 7.41 – 7.32 (m, 9H), 4.24 (q, J = 8.3 Hz, 2H), 3.07 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.0, 151.0, 135.4, 134.8, 129.3, 128.2, 122.6 (d, J = 277.7 Hz), 60.9 (d, J = 37.0 Hz), 14.2. HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{23}\text{H}_{20}\text{NO}_3\text{F}_3\text{NaGe}^+$, 512.0499, found: 512.0499.



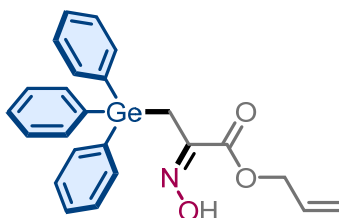
cyclohexyl-2-(hydroxyimino)-3-(triphenylgermyl)propanoate (10)

Purification by flash column chromatography (PE: EA, v/v = 5:1) to provide **10**. Colorless oil (29 mg, 60% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 9.65 (s, 1H), 7.53 – 7.51 (m, 6H), 7.37 – 7.29 (m, 9H), 4.63 – 4.59 (m, 1H), 3.05 (s, 2H), 1.61 – 1.58 (m, 5H), 1.27 – 1.17 (m, 5H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.9, 151.6, 135.9, 134.9, 129.1, 128.1, 74.0, 31.1, 25.3, 23.5, 13.9. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{27}\text{H}_{30}\text{NO}_3\text{Ge}^+$, 490.1432 found: 490.1433.



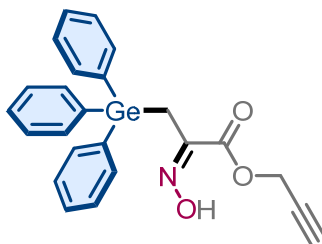
phenyl-2-(hydroxyimino)-3-(triphenylgermyl)propanoate (11)

Purification by flash column chromatography (PE: EA, v/v = 5:1) to provide **11**. Colorless oil (30 mg, 62% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.58 (s, 1H), 7.57 – 7.53 (m, 7H), 7.42 – 7.31 (m, 10H), 7.23 – 7.18 (m, 1H), 6.73 – 6.70 (m, 2H), 3.16 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.8, 135.6, 134.6, 132.2, 128.3, 126.3, 120.6, 108.5, 87.9, 34.1, 23.7. HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{27}\text{H}_{22}\text{NO}_3\text{NaGe}^+$, 506.0782, found: 506.0791.



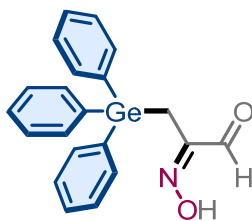
allyl-2-(hydroxyimino)-3-(triphenylgermyl)propanoate (12)

Purification by flash column chromatography (PE: EA, v/v = 5:1) to provide **12**. Colorless oil (24 mg, 54% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.43 (s, 1H), 7.53 – 7.50 (m, 6H), 7.40 – 7.32 (m, 9H), 5.74 – 5.64 (m, 1H), 5.16 (t, J = 8.0 Hz, 2H), 4.42 (d, J = 5.6 Hz, 2H), 3.07 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.2, 135.8, 134.8, 131.3, 129.2, 128.2, 118.9, 66.1, 53.4, 14.1. HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{24}\text{H}_{23}\text{NO}_3\text{NaGe}^+$, 470.0782, found: 470.0794.



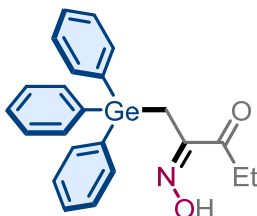
prop-2-yn-1-yl-2-(hydroxyimino)-3-(triphenylgermyl)propanoate (13)

Purification by flash column chromatography (PE: EA, v/v = 5:1) to provide **13**. Colorless oil (28 mg, 62% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.52 – 7.51 (m, 6H), 7.37 – 7.32 (m, 9H), 4.45 (s, 2H), 3.07 (s, 2H), 2.40 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.7, 151.7, 135.7, 134.8, 129.3, 128.2, 75.4, 52.9, 14.1. HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{24}\text{H}_{21}\text{NO}_3\text{NaGe}^+$, 468.0625, found: 468.0645.



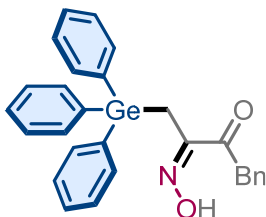
2-(hydroxyimino)-3-(triphenylgermyl)propanal (14)

Purification by flash column chromatography (PE: EA, v/v = 5:1) to provide **14**. Colorless oil (20 mg, 50% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 9.16 (s, 1H), 8.05 (s, 1H), 7.51 – 7.49 (m, 6H), 7.39 – 7.34 (m, 9H), 2.92 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.2, 135.7, 134.8, 129.3, 128.2, 10.9. HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{21}\text{H}_{19}\text{NO}_2\text{NaGe}^+$, 414.0520, found: 414.0501.



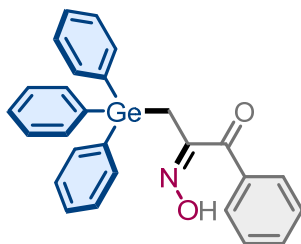
2-(hydroxyimino)-1-(triphenylgermyl)pentan-3-one (15)

Purification by flash column chromatography (PE: EA, v/v = 5:1) to provide **15**. Colorless oil (27 mg, 65% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.55 (s, 1H), 7.48 – 7.42 (m, 6H), 7.38 – 7.22 (m, 9H), 2.95 (s, 2H), 2.27 (q, J = 7.3 Hz, 2H), 0.73 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.2, 136.3, 134.85, 129.0, 128.0, 30.1, 11.6, 7.8. HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{23}\text{H}_{23}\text{NO}_2\text{NaGe}^+$, 442.0833, found: 442.0840.



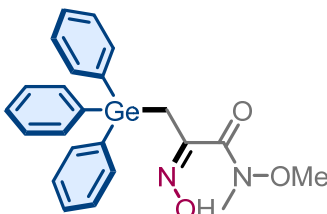
3-(hydroxyimino)-1-phenyl-4-(triphenylgermyl)butan-2-one (16)

Purification by flash column chromatography (PE: EA, v/v = 5:1) to provide **16**. Colorless oil (22 mg, 55% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.04 (s, 1H), 7.52 – 7.42 (m, 6H), 7.42 – 7.29 (m, 9H), 7.29 – 7.14 (m, 3H), 6.95 – 6.82 (m, 2H), 3.68 (s, 2H), 3.02 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 136.2, 134.9, 134.4, 129.7, 129.0, 128.1, 126.5, 43.3, 11.8. HRMS (ESI-TOF) m/z : $[\text{M} + \text{NH}_4]^+$ calcd for $\text{C}_{28}\text{H}_{29}\text{N}_2\text{O}_2\text{Ge}^+$, 449.1435, found: 449.1429.



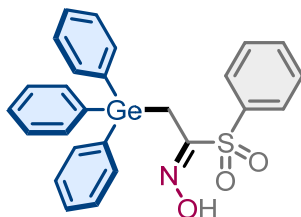
2-(hydroxyimino)-1-phenyl-3-(triphenylgermyl)propan-1-one (17)

Purification by flash column chromatography (PE: EA, v/v = 5:1) to provide **17**. Colorless oil (31 mg, 67% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.65 (s, 1H), 7.62 – 7.54 (m, 6H), 7.47 – 7.34 (m, 10H), 7.27 – 7.21 (m, 2H), 7.21 – 7.15 (m, 2H), 3.15 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.8, 159.3, 136.6, 136.1, 134.9, 132.2, 129.7, 129.2, 128.2, 127.8, 12.9. HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{27}\text{H}_{23}\text{NO}_2\text{NaGe}^+$, 490.0833, found: 490.0838.



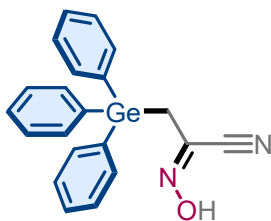
2-(hydroxyimino)-N-methoxy-N-methyl-3-(triphenylgermyl)propanamide (18)

Purification by flash column chromatography (PE: EA, v/v = 5:1) to provide **18**. Colorless oil (24 mg, 53% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.56 – 7.48 (m, 6H), 7.41 – 7.30 (m, 9H), 3.68 (s, 0.5H), 3.44 (s, 3H), 3.26 (s, 0.5H), 3.09 (s, 2H), 2.85 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.6, 136.2, 134.9, 129.1, 61.0, 26.1, 14.8. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{25}\text{NO}_3\text{Ge}^+$, 451.1071, found: 451.1070.



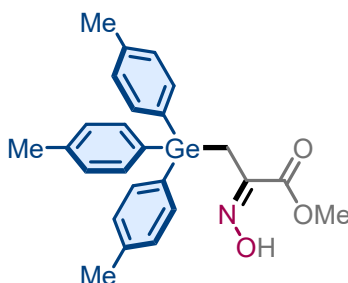
1-(phenylsulfonyl)-2-(triphenylgermyl)ethan-1-one oxime (19)

Purification by flash column chromatography (PE: EA, v/v = 5:1) to provide **19**. Colorless oil (27 mg, 53% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.77 (s, 1H), 7.60 – 7.51 (m, 6H), 7.49 – 7.34 (m, 12H), 7.29 – 7.23 (m, 2H), 3.05 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.1, 135.7, 134.9, 133.7, 129.2, 128.2, 13.8. HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{26}\text{H}_{23}\text{NO}_3\text{NaSGe}^+$, 526.0503, found: 526.0511.



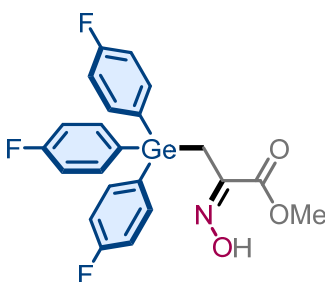
N-hydroxy-2-(triphenylgermyl)acetimidoyl cyanide (**20**)

Purification by flash column chromatography (PE: EA, v/v = 5:1) to provide **20**. Colorless oil (22 mg, 57% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.24 (s, 1H), 7.59 – 7.49 (m, 6H), 7.49 – 7.38 (m, 9H), 2.92 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.6, 134.9, 129.7, 128.5, 115.0, 18.4. HRMS (ESI-TOF) *m/z*: $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{21}\text{H}_{18}\text{N}_2\text{ONaGe}^+$, 411.0523, found: 411.0526.



methyl-2-(hydroxyimino)-3-(tri-p-tolylgermyl)propanoate (21)

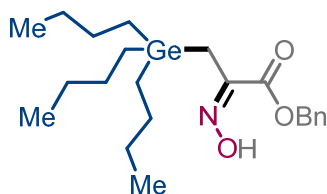
Purification by flash column chromatography (PE: EA, v/v = 5:1) to provide **21**. Colorless oil (43 mg, 91% yield). ^1H NMR (600 MHz, Chloroform-*d*) δ 8.73 (s, 1H), 7.40 – 7.37 (m, 6H), 7.18 – 7.12 (m, 6H), 3.51 (s, 3H), 3.02 (s, 2H), 2.34 (s, 9H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 164.0, 152.3, 138.9, 134.8, 132.5, 128.9, 52.3, 21.5, 14.4. HRMS (ESI-TOF) *m/z*: $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{25}\text{H}_{27}\text{NO}_3\text{NaGe}^+$, 486.1095, found: 486.1104.



methyl-2-(hydroxyimino)-3-(tris(4-fluorophenyl)germyl)propanoate (22)

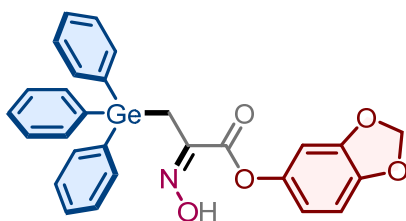
Purification by flash column chromatography (PE: EA, v/v = 5:1) to provide **22**. Colorless oil (24 mg, 50% yield). ^1H NMR (600 MHz, Chloroform-*d*) δ 9.26 (s, 1H), 7.53 – 7.34 (m, 6H), 7.11 – 6.96 (m, 6H), 3.56 (s, 3H), 3.02 (s, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 164.3 (d, J = 129.9 Hz), 163.1, 151.5, 136.5 (d, J = 7.5 Hz), 130.7 (d, J = 3.6 Hz), 115.6, 115.5, 52.5, 14.4. ^{19}F NMR

(565 MHz, Chloroform-*d*) δ -111.11. HRMS (ESI-TOF) m/z : $[M + H]^+$ calcd for $C_{22}H_{19}F_3NO_3Ge^+$, 476.0523, found: 476.0529.



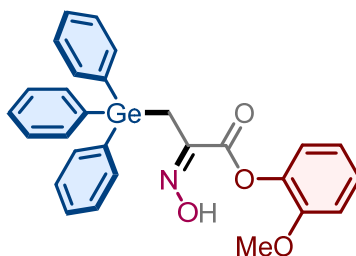
benzyl-2-(hydroxyimino)-3-(tributylgermyl)propanoate (23)

Purification by flash column chromatography (PE: EA, v/v = 5:1) to provide **23**. Colorless oil (26 mg, 60% yield). 1H NMR (600 MHz, Chloroform-*d*) δ 9.44 (s, 1H), 7.40 – 7.37 (m, 2H), 7.36 – 7.31 (m, 3H), 5.26 (s, 2H), 2.27 (s, 2H), 1.43 – 1.15 (m, 13H), 0.92 – 0.83 (m, 9H), 0.81 – 0.71 (m, 6H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 163.8, 153.2, 135.4, 128.5, 128.3, 67.2, 27.0, 26.4, 13.7, 13.7, 12.9. HRMS (ESI-TOF) m/z : $[M + H]^+$ calcd for $C_{22}H_{38}NO_3Ge^+$, 438.2058, found: 438.2087.



2-methoxyphenyl-2-(hydroxyimino)-3-(triphenylgermyl)propanoate (24)

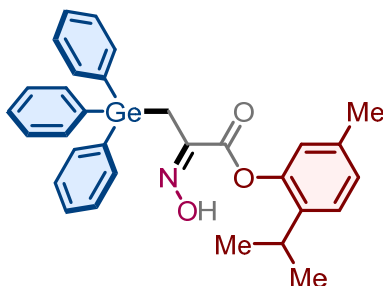
Purification by flash column chromatography (PE: EA, v/v = 5:1) to provide **24**. Colorless oil (30 mg, 57% yield). 1H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.54 (m, 6H), 7.49 – 7.25 (m, 9H), 6.66 (d, J = 8.0 Hz, 1H), 6.29 – 6.12 (m, 2H), 5.94 (s, 2H), 3.13 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.6, 151.3, 147.9, 145.59, 144.5, 135.7, 134.9, 129.3, 128.3, 113.8, 107.8, 103.5, 101.7, 14.4. HRMS (ESI-TOF) m/z : $[M + Na]^+$ calcd for $C_{28}H_{23}NO_5NaGe^+$, 550.0680, found: 550.0691.



benzo[d][1,3]dioxol-5-yl-2-(hydroxyimino)-3-(triphenylgermyl)propanoate (25)

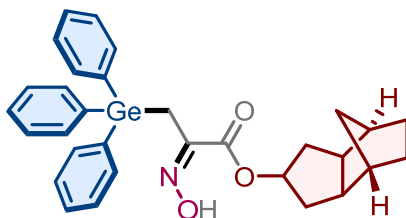
Purification by flash column chromatography (PE: EA, v/v = 5:1) to provide **25**. Colorless oil (26 mg, 50% yield). 1H NMR (400 MHz, Chloroform-*d*) δ 9.47 (s, 1H), 7.74 – 7.40 (m, 6H), 7.51 – 7.20 (m, 9H), 7.33 – 7.15 (m, 1H), 7.10 – 6.83 (m, 2H), 6.68 – 6.57 (m, 1H), 3.62 (s, 3H), 3.13

(s, 2H). ^{13}C NMR (101 MHz, Chloroform- d) δ 161.8, 151.2, 151.1, 139.4, 135.9, 134.9, 129.2, 128.2, 127.1, 122.7, 120.6, 112.4, 55.8, 14.4. HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{28}\text{H}_{25}\text{NO}_4\text{NaGe}^+$, 536.0888, found: 536.0940.



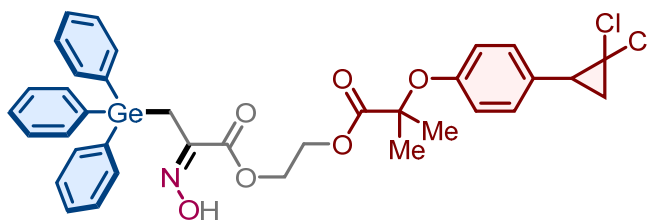
2-isopropyl-5-methylphenyl-2-(hydroxyimino)-3-(triphenylgermyl)propanoate (26)

Purification by flash column chromatography (PE: EA, v/v = 5:1) to provide **26**. Colorless oil (29 mg, 54% yield). ^1H NMR (600 MHz, Chloroform- d) δ 9.12 (s, 1H), 7.59 – 7.49 (m, 3H), 7.47 – 7.35 (m, 2H), 7.35 – 7.30 (m, 3H), 7.15 – 7.09 (m, 1H), 7.04 – 6.90 (m, 0H), 6.22 (s, 0H), 3.15 (s, 1H), 2.64 (p, J = 6.9 Hz, 1H), 2.26 (s, 1H), 1.04 (d, J = 6.9 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform- d) δ 162.7, 147.6, 137.1, 136.5, 135.8, 134.9, 129.2, 128.2, 127.4, 126.3, 122.4, 26.8, 23.1, 20.7, 14.5. HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{31}\text{H}_{31}\text{NO}_3\text{NaGe}^+$, 562.1408, found: 562.1419.



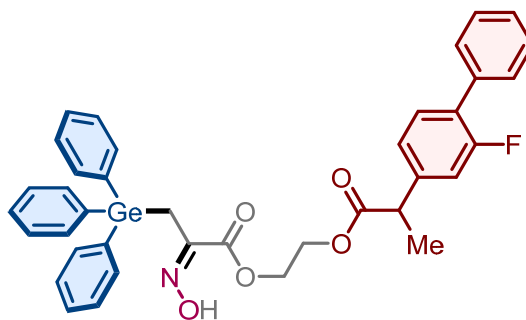
(3aR,4S,7R,7aS)-octahydro-1H-4,7-methanoinden-2-yl-2-(hydroxyimino)-3-(triphenylgermyl)propanoate (27)

Purification by flash column chromatography (PE: EA, v/v = 5:1) to provide **27**. Colorless oil (25 mg, 47% yield). ^1H NMR (400 MHz, Chloroform- d) δ 9.65 (s, 1H), 7.60 – 7.49 (m, 6H), 7.44 – 7.26 (m, 9H), 4.32 (m, 1H), 3.05 (s, 2H), 1.96 – 1.75 (m, 3H), 1.79 – 1.55 (m, 4H), 1.54 – 1.39 (m, 1H), 1.30 – 1.10 (m, 2H), 1.07 – 0.96 (m, 2H), 0.96 – 0.84 (m, 2H). ^{13}C NMR (101 MHz, Chloroform- d) δ 163.2, 151.5, 135.9, 134.9, 129.1, 128.2, 78.5, 47.2, 45.8, 42.8, 39.5, 38.6, 31.9, 31.6, 29.3, 27.7, 13.8. HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{31}\text{H}_{33}\text{NO}_3\text{NaGe}^+$, 564.1564, found: 564.1578.



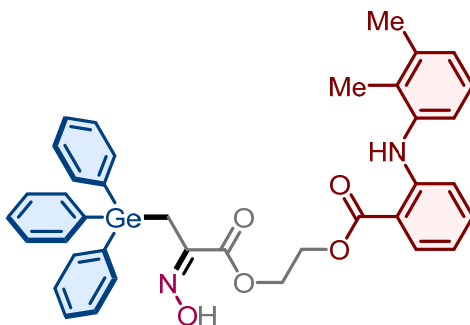
2-((2-(4-(2,2-dichlorocyclopropyl)phenoxy)-2-methylpropanoyl)oxy)ethyl-2-(hydroxyimino)-3-(triphenylgermyl)propanoate (28)

Purification by flash column chromatography (PE: EA, v/v = 5:1) to provide **28**. Colorless oil (35 mg, 49% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 9.83 (s, 1H), 7.70 – 7.49 (m, 6H), 7.49 – 7.30 (m, 9H), 7.17 – 7.07 (m, 2H), 6.93 – 6.78 (m, 2H), 4.19 – 4.13 (m, 2H), 4.09 – 4.05 (m, 2H), 3.06 (s, 2H), 2.83 (t, J = 10.7, 8.3 Hz, 1H), 1.79 (d, J = 7.8 Hz, 2H), 1.60 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.9, 163.1, 154.8, 151.1, 135.7, 134.9, 129.7, 129.3, 128.4, 128.2, 118.9, 79.2, 62.7, 62.6, 60.9, 34.8, 25.9, 25.4, 14.1. HRMS (ESI-TOF) m/z : $[\text{M} + \text{NH}_4]^+$ calcd for $\text{C}_{36}\text{H}_{35}\text{NO}_6\text{NaCl}_2\text{Ge}^+$, 744.0945, found: 744.0969.



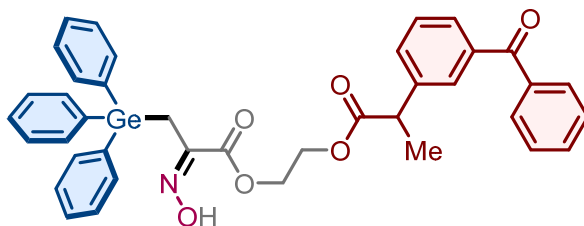
2-((2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoyl)oxy)ethyl-2-(hydroxyimino)-3-(triphenylgermyl)propanoate (29)

Purification by flash column chromatography (PE: EA, v/v = 5:1) to provide **29**. Colorless oil (29 mg, 43% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 9.22 (s, 1H), 7.54 – 7.45 (m, 8H), 7.43 – 7.38 (m, 3H), 7.38 – 7.27 (m, 10H), 7.17 – 6.98 (m, 2H), 4.16 – 3.91 (m, 4H), 3.68 (q, J = 7.1 Hz, 1H), 3.02 (s, 2H), 1.48 (d, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.7, 163.2, 160.9, 158.4, 151.4, 141.4 (d, J = 7.6 Hz), 135.8, 135.4, 134.8, 130.8 (d, J = 4.0 Hz), 129.2, 128.9 (d, J = 2.9 Hz), 128.5, 128.2, 127.7, 123.6 (d, J = 3.3 Hz), 115.3 (d, J = 23.6 Hz), 62.8, 62.3, 44.8, 18.3, 14.0. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -117.44. HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{38}\text{H}_{34}\text{NO}_5\text{NaGe}^+$, 700.1525, found: 700.1525.



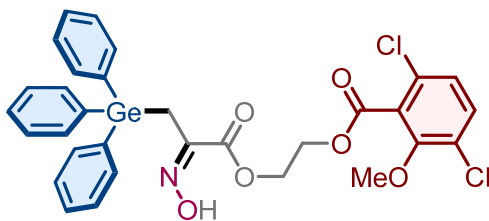
2-((2-(hydroxyimino)-3-(triphenylgermyl)propanoyl)oxy)ethyl 2-((2,3-dimethylphenyl)amino)benzoate (30)

Purification by flash column chromatography (PE: EA, v/v = 5:1) to provide **30**. Colorless oil (30 mg, 45% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 9.15 (s, 1H), 7.91 (d, J = 8.1, 1.6 Hz, 1H), 7.60 – 7.44 (m, 6H), 7.44 – 7.28 (m, 9H), 7.25 – 7.18 (m, 2H), 7.17 – 7.06 (m, 2H), 7.05 – 7.00 (m, 1H), 6.72 (d, J = 8.5 Hz, 1H), 6.61 (t, J = 7.5 Hz, 1H), 4.32 – 4.21 (m, 4H), 3.05 (s, 2H), 2.32 (s, 3H), 2.16 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.2, 149.6, 138.7, 138.2, 135.7, 134.8, 134.4, 132.6, 131.8, 129.2, 126.9, 125.9, 123.3, 116.1, 113.6, 110.3, 63.3, 61.9, 20.6, 14.1, 14.0. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{38}\text{H}_{37}\text{N}_2\text{O}_5\text{Ge}^+$, 675.1909, found: 675.1943.



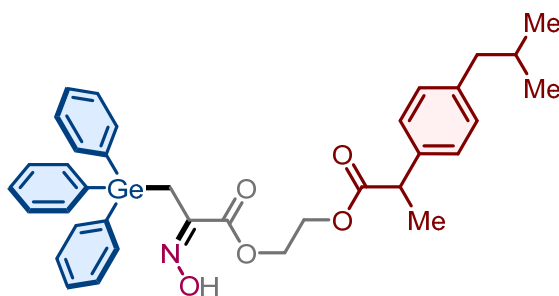
2-((2-(3-benzoylphenyl)propanoyl)oxy)ethyl-2-(hydroxyimino)-3-(triphenylgermyl)propanoate (31)

Purification by flash column chromatography (PE: EA, v/v = 5:1) to provide **31**. Colorless oil (31 mg, 45% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 10.68 (s, 1H), 7.80 – 7.71 (m, 2H), 7.66 – 7.54 (m, 2H), 7.48 – 7.42 (m, 10H), 7.42 – 7.26 (m, 10H), 4.08 – 3.99 (m, 2H), 3.84 (q, J = 8.0 Hz, 1H), 3.80 – 3.68 (m, 2H), 2.76 (s, 2H), 1.51 (d, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 196.7, 173.7, 163.1, 147.5, 140.6, 137.9, 137.4, 135.4, 134.1, 132.7, 131.5, 130.2, 129.4, 129.3, 129.1, 128.5, 128.4, 62.7, 61.8, 45.2, 18.4, 18.3. HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{39}\text{H}_{35}\text{NO}_6\text{NaGe}^+$, 710.1568, found: 710.1632.



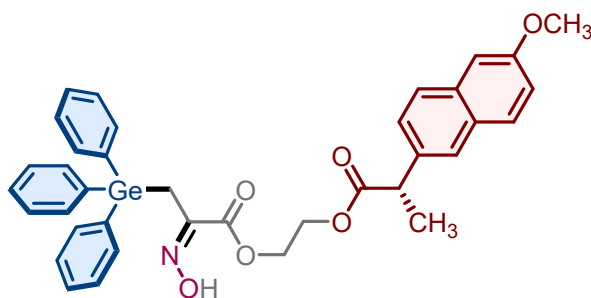
2-((2-(2-(hydroxyimino)-3-(triphenylgermyl)propanoyl)oxy)ethyl 3,6-dichloro-2-methoxybenzoate (32)

Purification by flash column chromatography (PE: EA, v/v = 5:1) to provide **32**. Colorless oil (31 mg, 47% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 9.42 (s, 1H), 7.56 – 7.46 (m, 6H), 7.45 – 7.28 (m, 10H), 7.07 (d, J = 8.7 Hz, 1H), 4.53 – 4.23 (m, 2H), 4.23 – 4.10 (m, 2H), 3.82 (s, 3H), 3.04 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.2, 163.2, 153.9, 151.4, 135.7, 134.1, 132.0, 129.8, 129.2, 128.5, 128.2, 126.8, 125.8, 63.2, 62.8, 62.3, 14.0. HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{31}\text{H}_{27}\text{NO}_6\text{NaCl}_2\text{Ge}^+$, 676.0319, found: 676.0336.



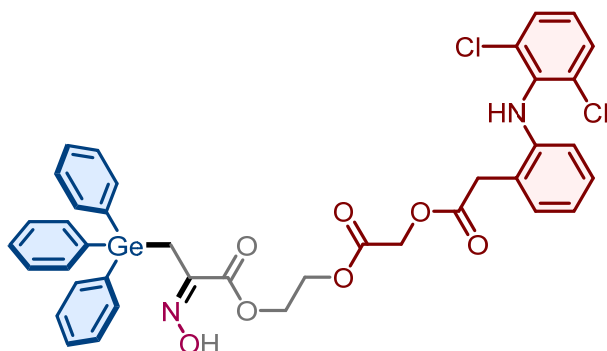
2-((2-(2-(4-isobutylphenyl)propanoyl)oxy)ethyl-2-(hydroxyimino)-3- triphenylgermyl) propanoate (33)

Purification by flash column chromatography (PE: EA, v/v = 5:1) to provide **33**. Colorless oil (39 mg, 61% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 9.70 (s, 1H), 7.66 – 7.51 (m, 6H), 7.45 – 7.29 (m, 9H), 7.27 – 7.17 (m, 2H), 7.16 – 7.05 (m, 2H), 4.12 – 3.88 (m, 4H), 3.69 (q, J = 7.2 Hz, 1H), 3.02 (s, 2H), 2.40 (d, J = 7.0 Hz, 2H), 1.96 – 1.80 (m, 1H), 1.44 (d, J = 7.0 Hz, 3H), 0.87 (d, J = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.5, 163.2, 151.3, 140.7, 137.4, 135.8, 134.8, 129.4, 129.2, 128.2, 127.2, 62.9, 61.9, 45.0, 44.9, 30.2, 22.4, 18.5, 14.0. HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{36}\text{H}_{39}\text{NO}_5\text{NaGe}^+$, 662.1932, found: 662.1949.



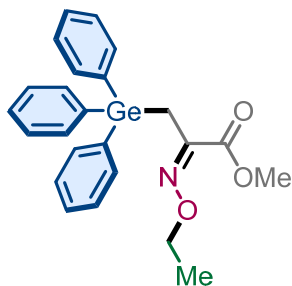
(S)-2-((2-(6-methoxynaphthalen-2-yl)propanoyl)oxy)ethyl-2-(hydroxyimino)-3-(triphenylgermyl)propanoate (**34**)

Purification by flash column chromatography (PE: EA, v/v = 5:1) to provide **34**. Colorless oil (37 mg, 56% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 9.75 (s, 1H), 7.78 – 7.57 (m, 4H), 7.52 – 7.39 (m, 6H), 7.39 – 7.23 (m, 5H), 7.14 – 7.03 (m, 2H), 4.14 – 4.01 (m, 2H), 4.01 – 3.93 (m, 2H), 3.84 (s, 3H), 3.78 (q, J = 7.1 Hz, 1H), 2.91 (s, 2H), 1.53 (d, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.4, 163.2, 157.7, 151.1, 135.8, 135.3, 133.8, 129.4, 129.3, 128.9, 128.2, 127.3, 126.2, 126.1, 119.1, 105.7, 62.9, 62.1, 55.3, 45.3, 18.5, 13.9. HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{37}\text{H}_{35}\text{NO}_6\text{NaGe}^+$, 686.1568, found: 686.1574.



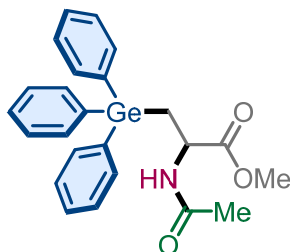
4-((triphenylgermyl)ethynyl)phenyl 2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoate (**35**)

Purification by flash column chromatography (PE: EA, v/v = 5:1) to provide **35**. Colorless oil (39 mg, 49% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 9.40 (s, 1H), 7.62 – 7.43 (m, 7H), 7.42 – 7.27 (m, 10H), 7.26 – 7.19 (m, 1H), 7.17 – 7.04 (m, 1H), 6.99 – 6.88 (m, 2H), 6.62 – 6.50 (m, 1H), 4.54 (s, 2H), 4.13 – 4.01 (m, 4H), 3.90 (s, 2H), 3.04 (s, 2H), 2.03 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.4, 167.2, 163.2, 151.4, 142.8, 137.9, 135.7, 134.9, 131.0, 129.6, 129.3, 128.9, 124.1, 123.9, 122.2, 118.5, 62.7, 62.5, 60.9, 38.0, 14.1. HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{39}\text{H}_{34}\text{N}_2\text{O}_7\text{NaCl}_2\text{Ge}^+$, 809.0847, found: 809.0856.



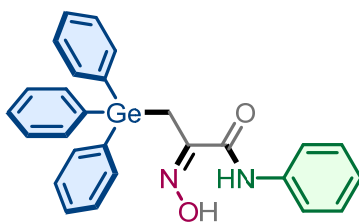
methyl-2-(ethoxyimino)-3-(triphenylgermyl)propanoate (36)

Purification by flash column chromatography (PE: EA, v/v = 5:1). Colorless oil (31 mg, 70% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.58 – 7.47 (m, 6H), 7.44 – 7.33 (m, 9H), 4.02 (q, J = 7.1 Hz, 2H), 3.58 (s, 3H), 3.04 (s, 2H), 1.05 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.2, 150.7, 135.9, 134.8, 129.2, 128.1, 70.9, 52.5, 15.1, 14.2. HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{24}\text{H}_{25}\text{NO}_3\text{NaGe}^+$, 472.0938, found: 472.0950.



methyl (R)-2-acetamido-3-(triphenylgermyl)propanoate (37)

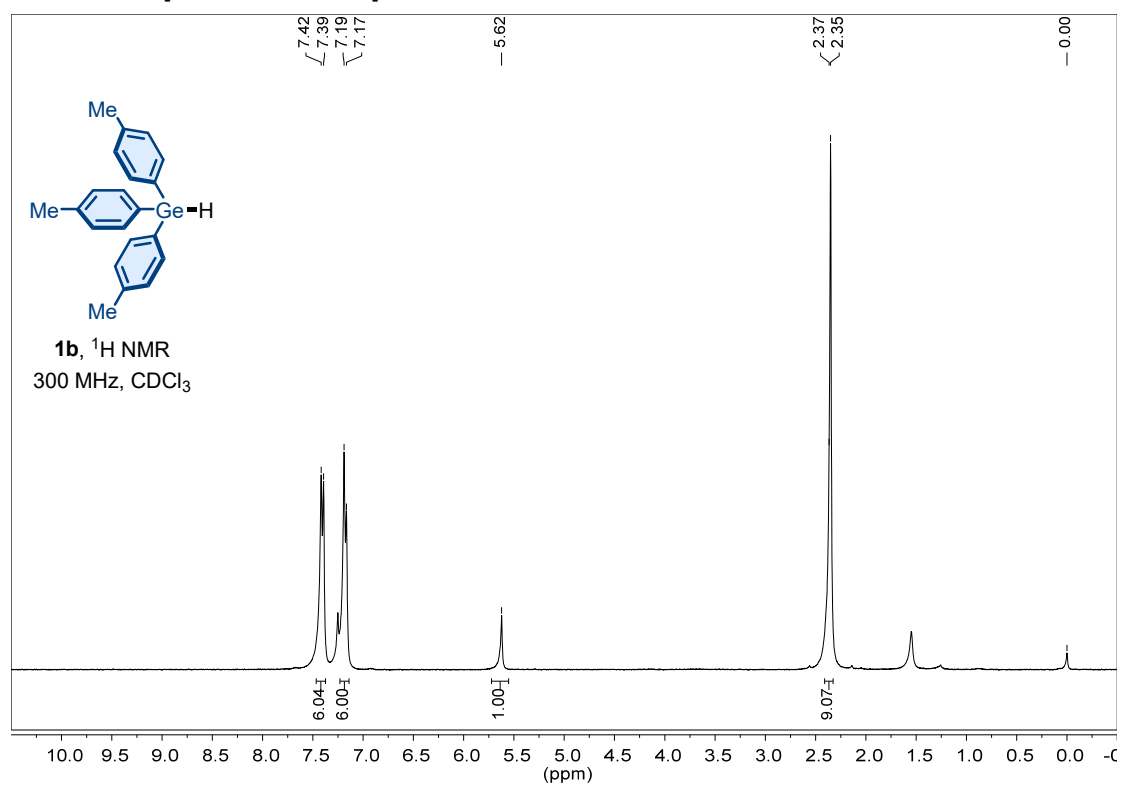
Purification by flash column chromatography (PE: EA, v/v = 5:1). Colorless oil (30 mg, 67% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.55 – 7.47 (m, 6H), 7.46 – 7.36 (m, 9H), 5.65 (d, J = 7.6 Hz, 1H), 4.87 – 4.76 (m, 1H), 3.43 (s, 3H), 2.13 (dd, J = 14.1, 5.9 Hz, 1H), 1.93 (dd, J = 14.1, 8.9 Hz, 1H), 1.58 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.2, 169.2, 135.9, 134.8, 129.2, 128.4, 51.9, 50.1, 22.5, 18.1. HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{24}\text{H}_{25}\text{NO}_3\text{NaGe}^+$, 472.0938, found: 472.0937.



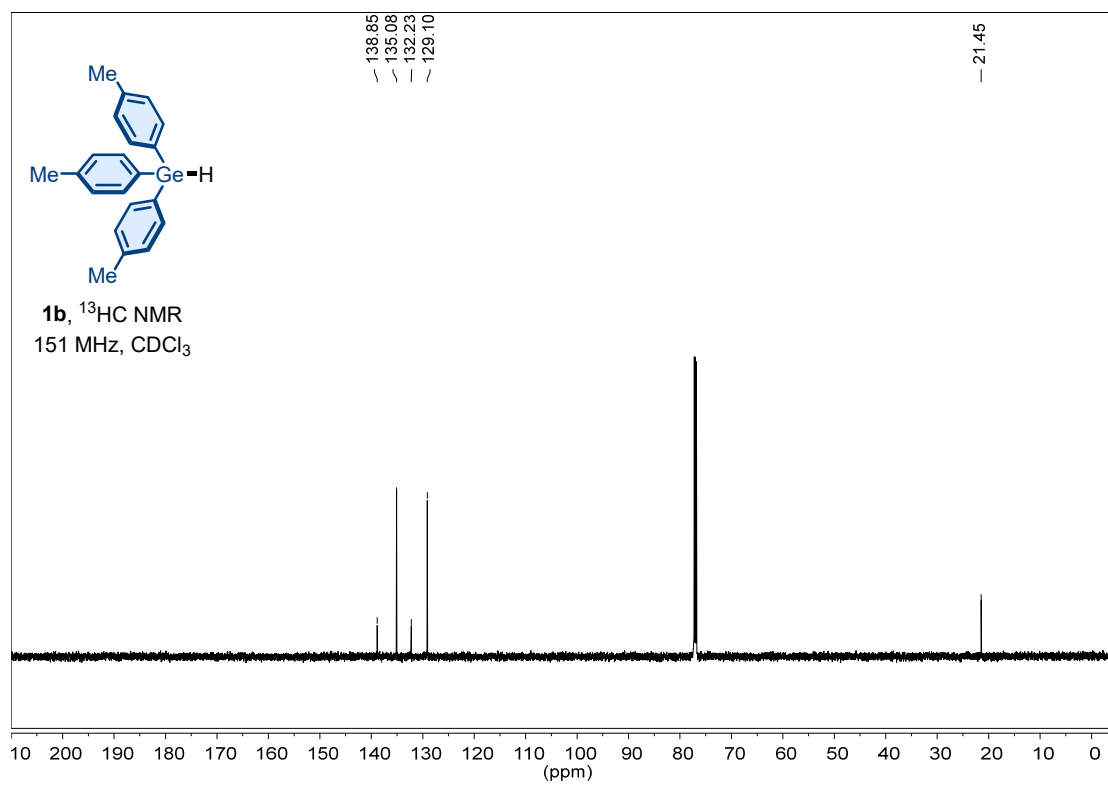
2-(hydroxyimino)-N-phenyl-3-(triphenylgermyl)propanamide (38)

Purification by flash column chromatography (PE: EA, v/v = 5:1). Colorless oil (30 mg, 62% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.11 (s, 1H), 7.68 – 7.45 (m, 6H), 7.42 – 7.20 (m, 11H), 7.30 – 7.22 (m, 2H), 7.07 (t, J = 7.3 Hz, 1H), 3.17 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.7, 155.5, 137.2, 136.0, 134.9, 129.2, 128.9, 128.1, 124.2, 119.9, 12.6. HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{27}\text{H}_{24}\text{N}_2\text{O}_2\text{NaGe}^+$, 505.0942, found: 505.0949.

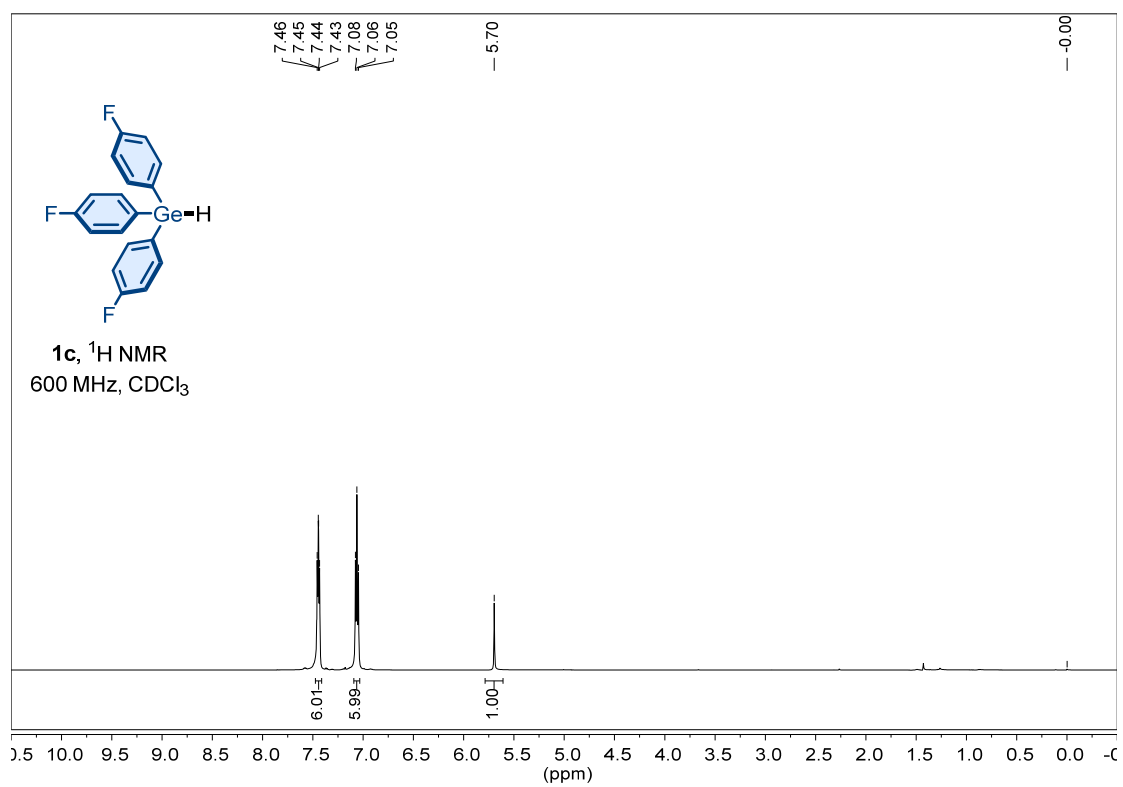
4 NMR Spectrum Copies



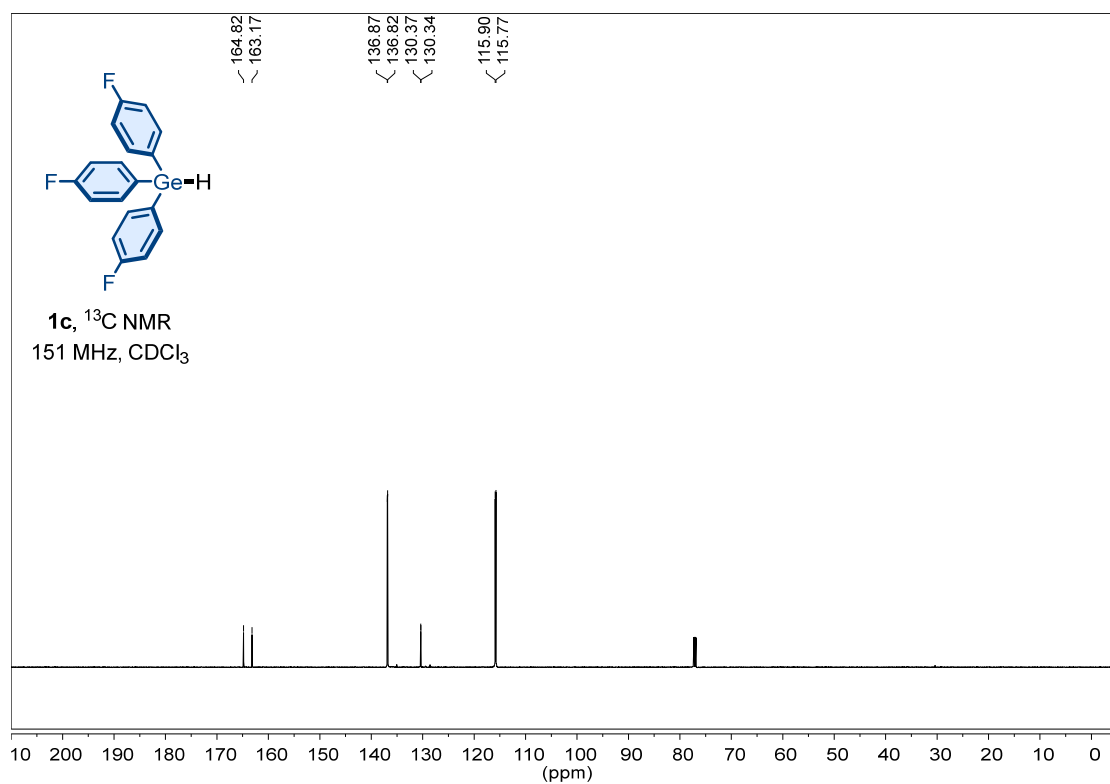
^1H NMR spectrum of **1a**



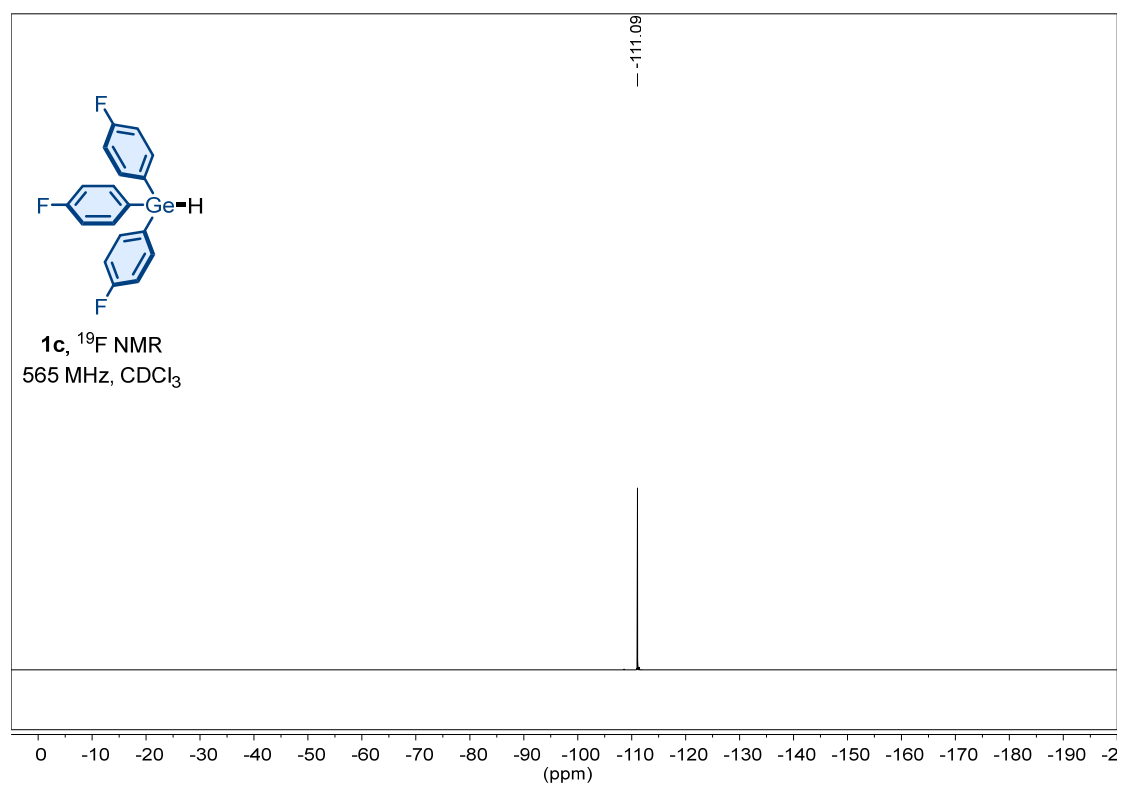
^{13}C NMR spectrum of **1b**



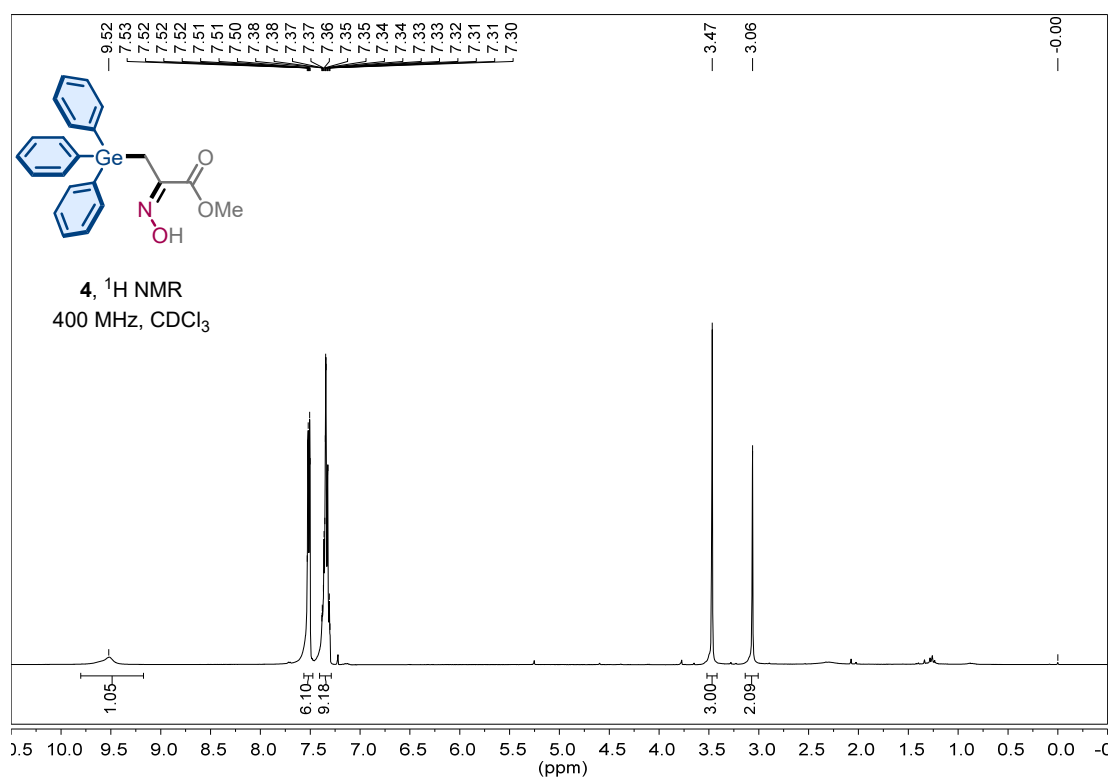
^1H NMR spectrum of **1c**



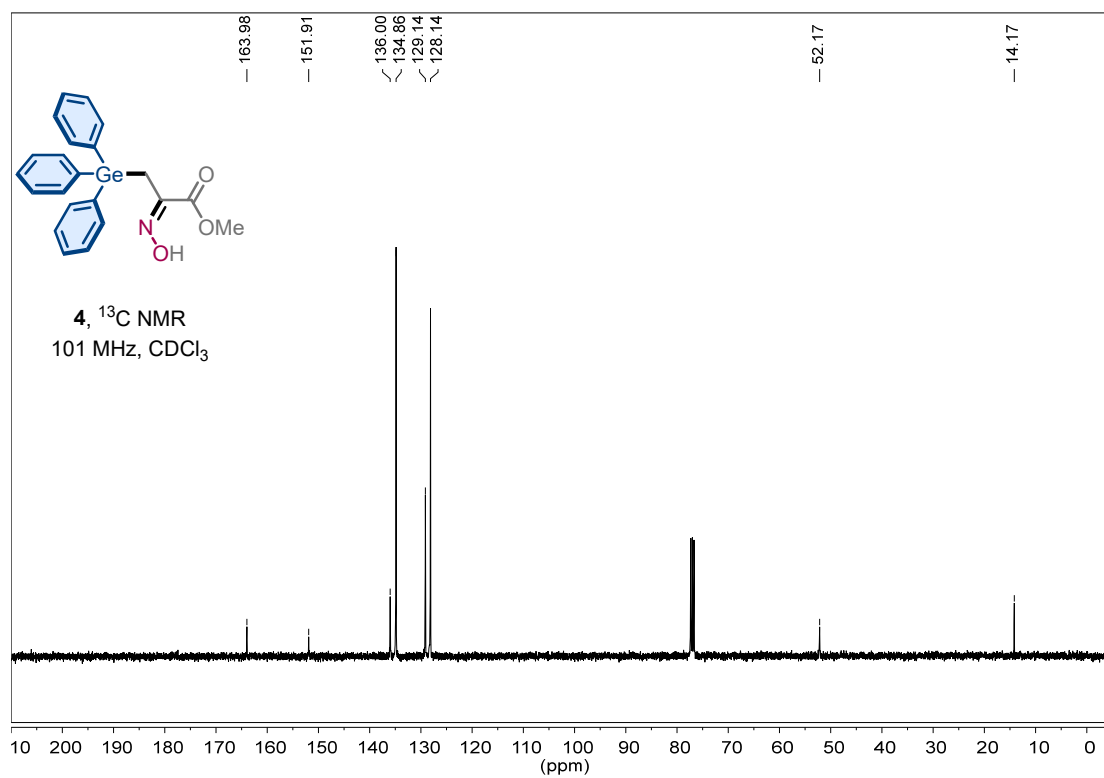
^{13}C NMR spectrum of **1c**



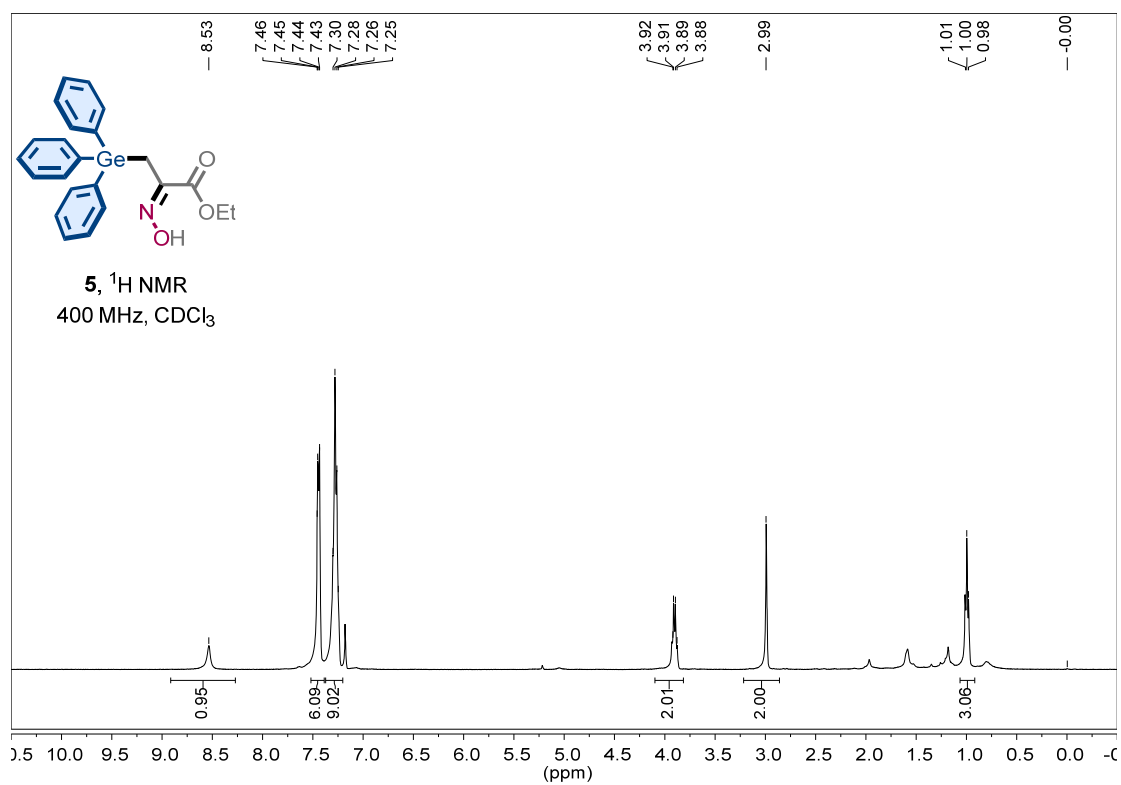
^{19}F NMR spectrum of **1c**



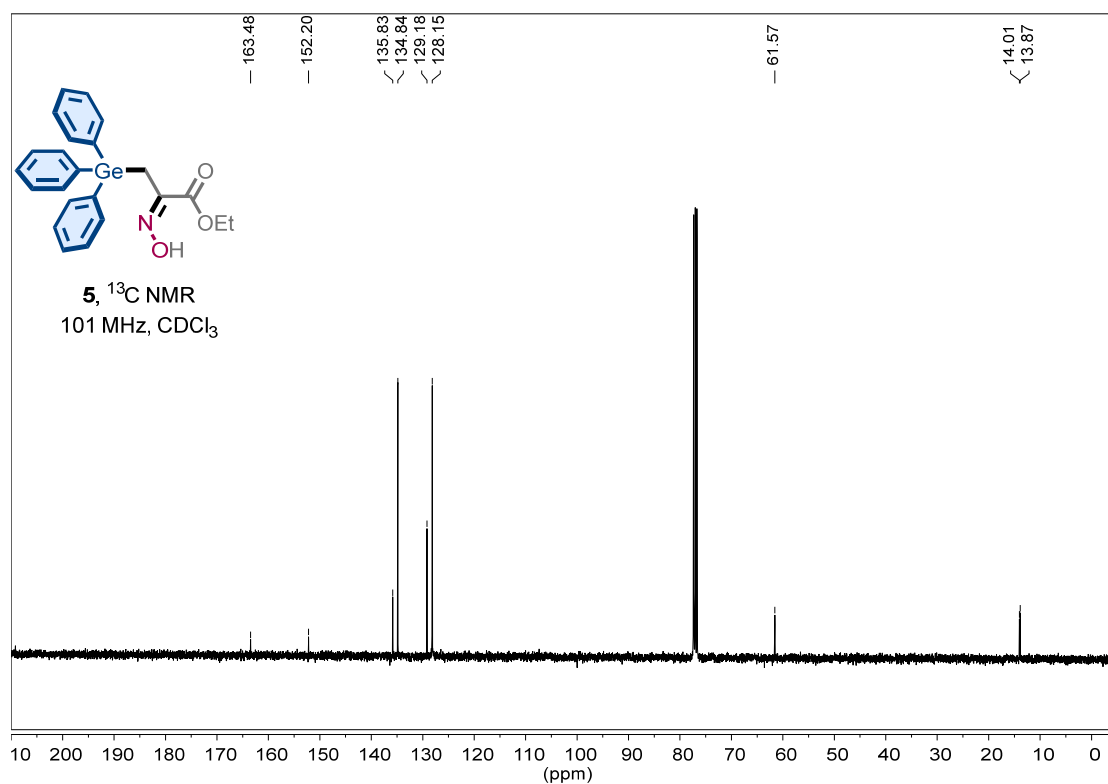
^1H NMR spectrum of **4**



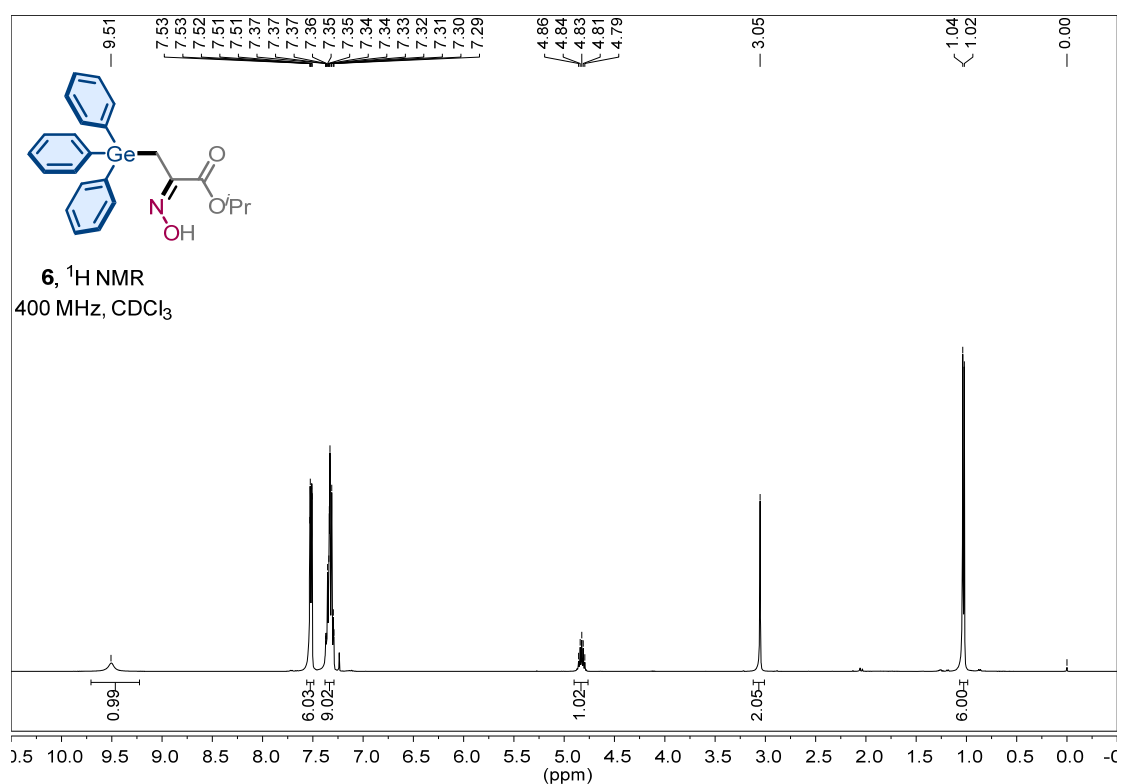
^{13}C NMR spectrum of **4**



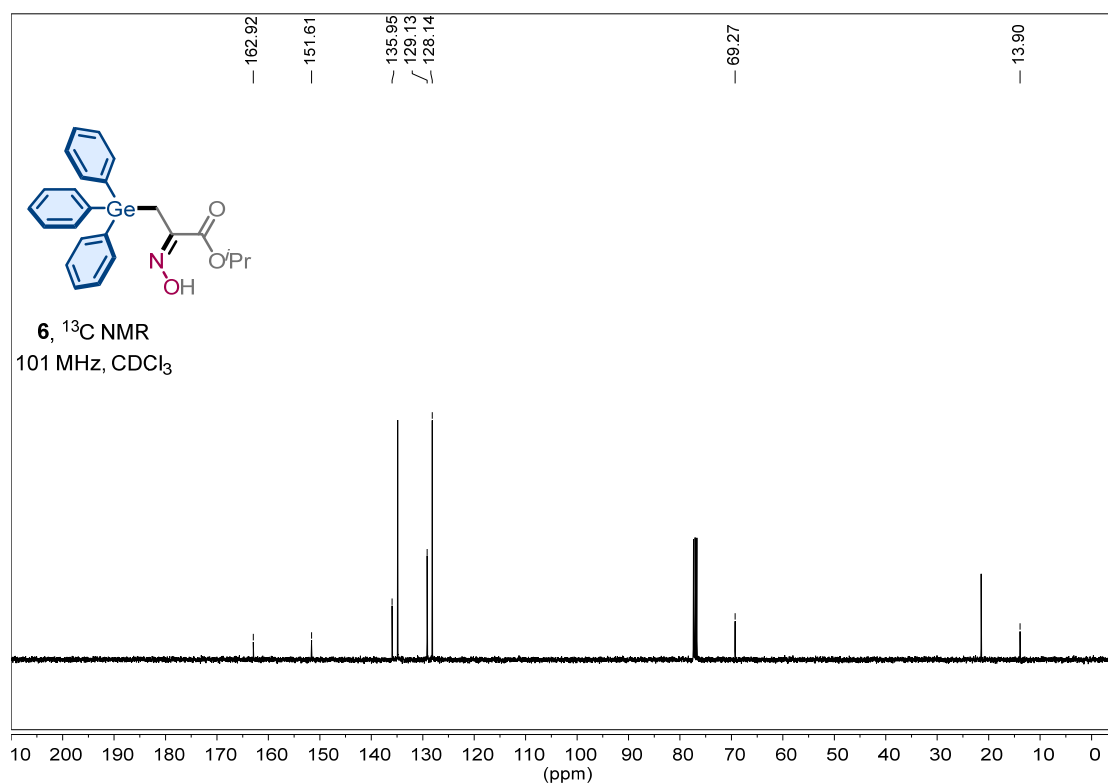
^1H NMR spectrum of **5**



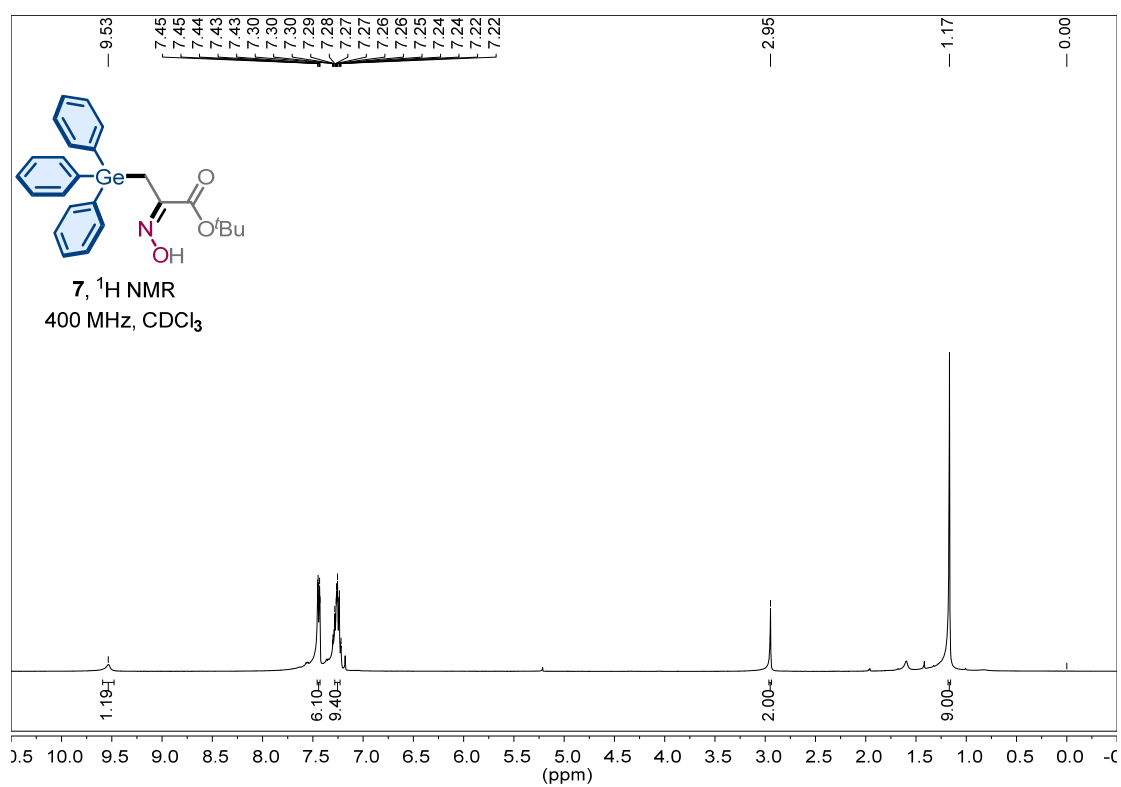
^{13}C NMR spectrum of **5**



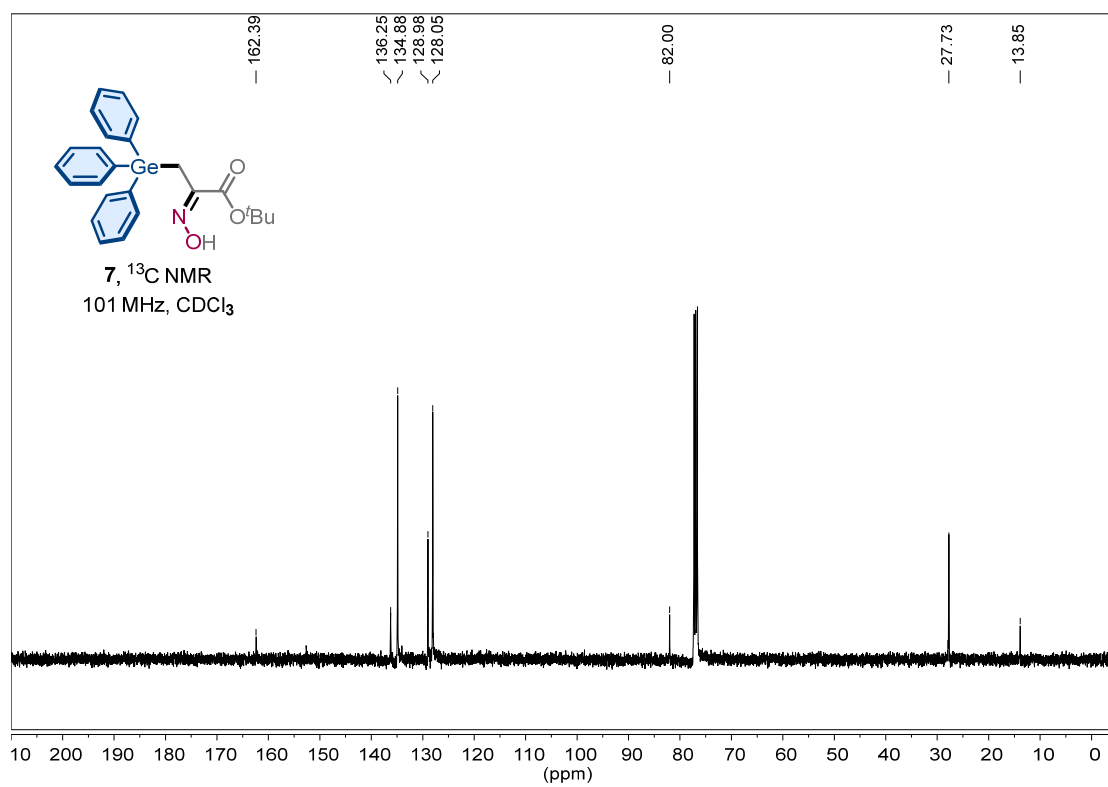
^1H NMR spectrum of **6**



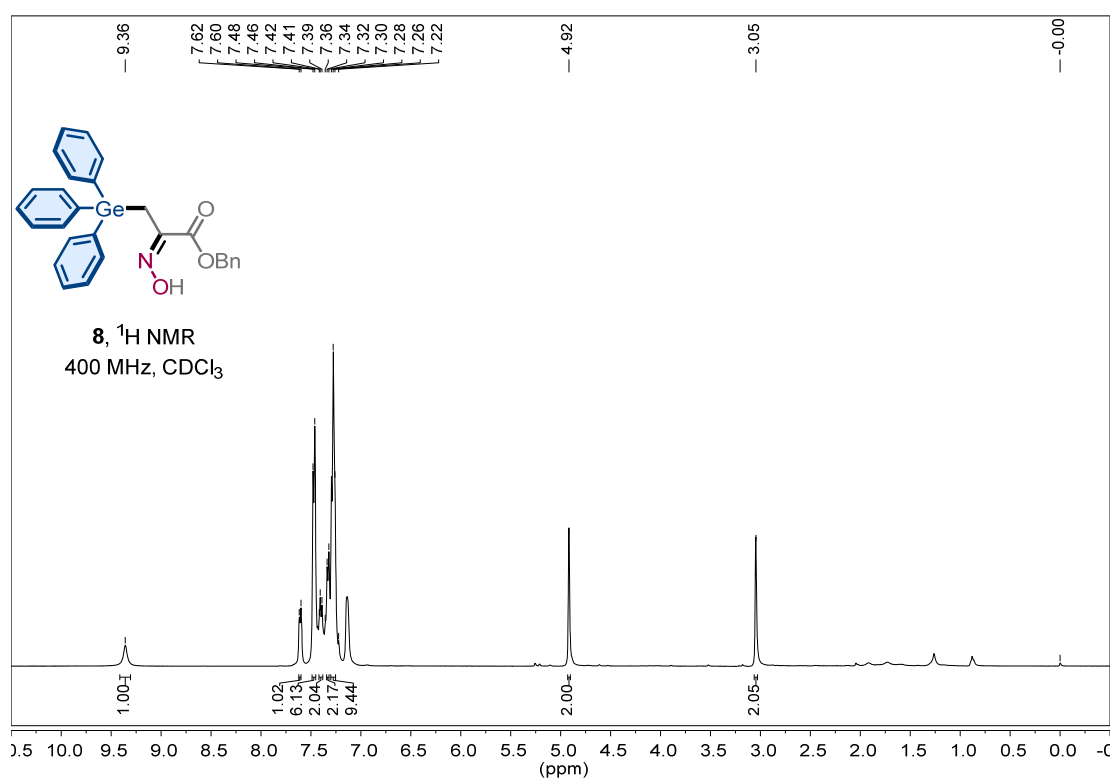
^{13}C NMR spectrum of **6**



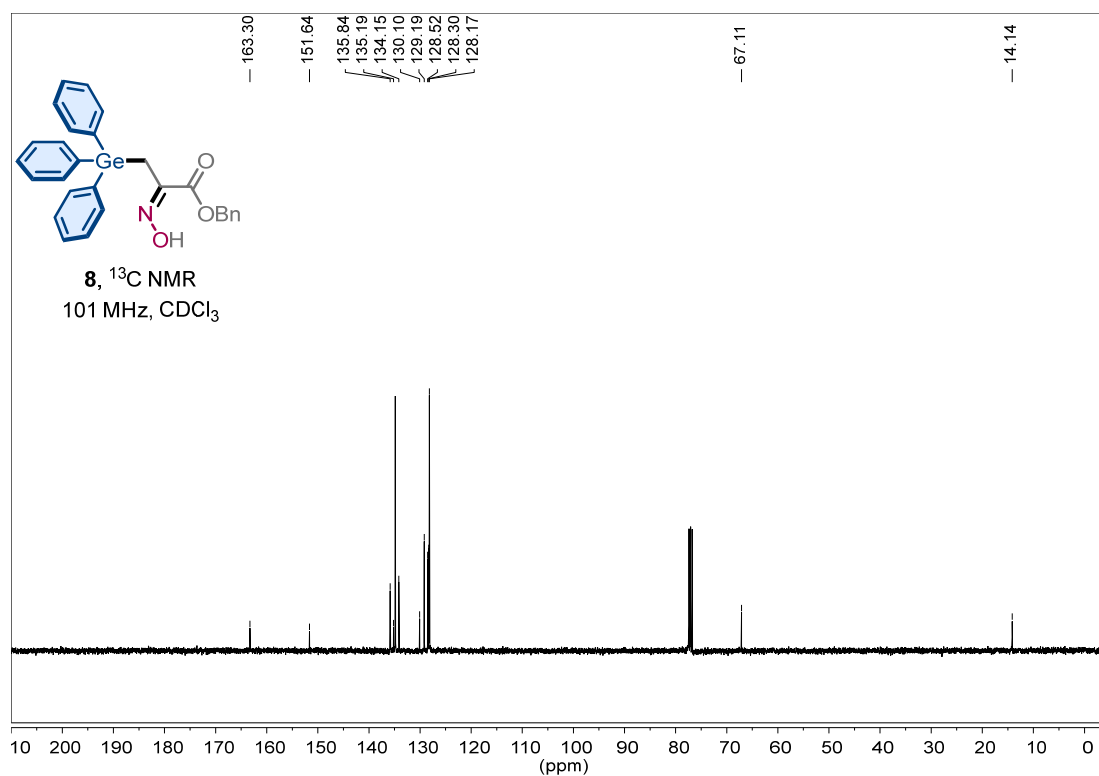
^1H NMR spectrum of **7**



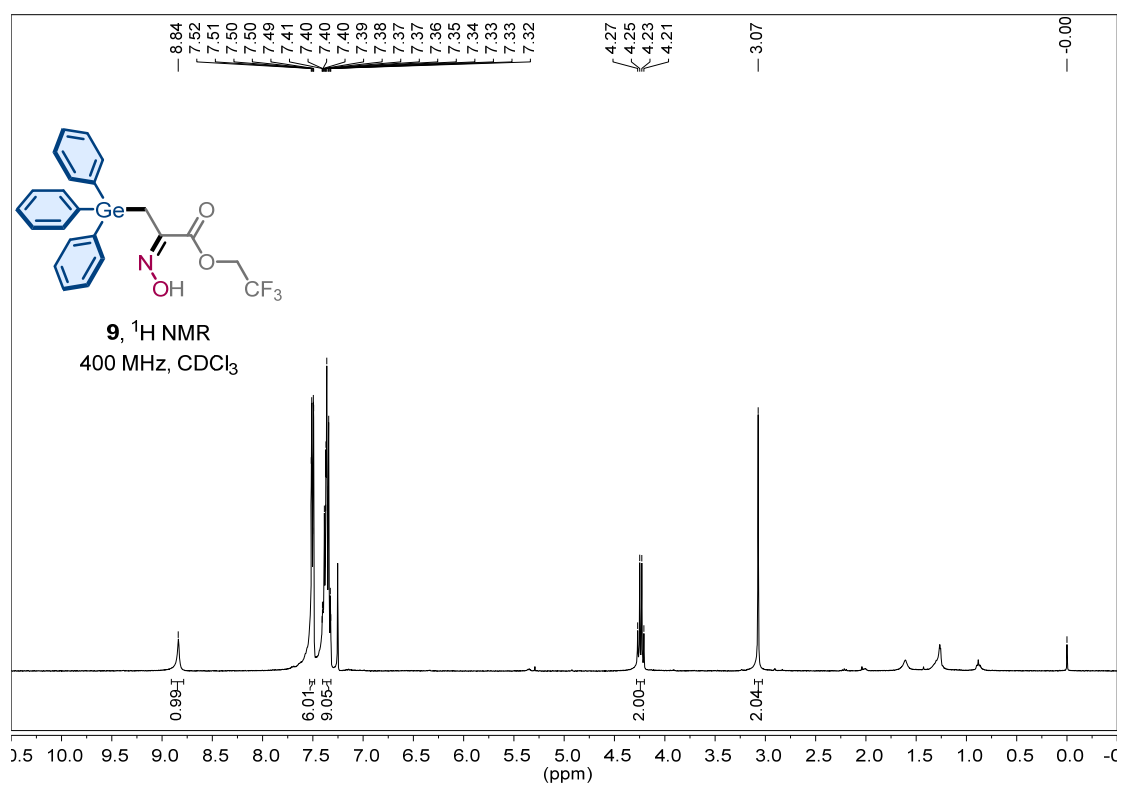
^{13}C NMR spectrum of **7**



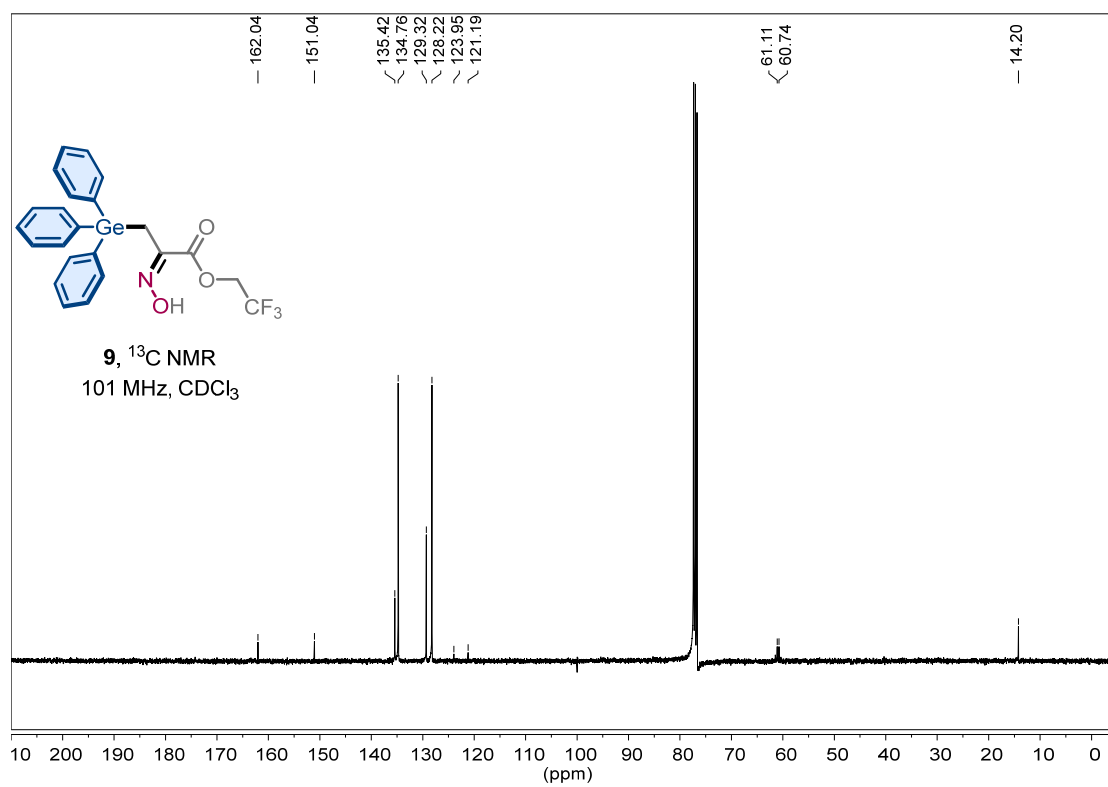
^1H NMR spectrum of **8**



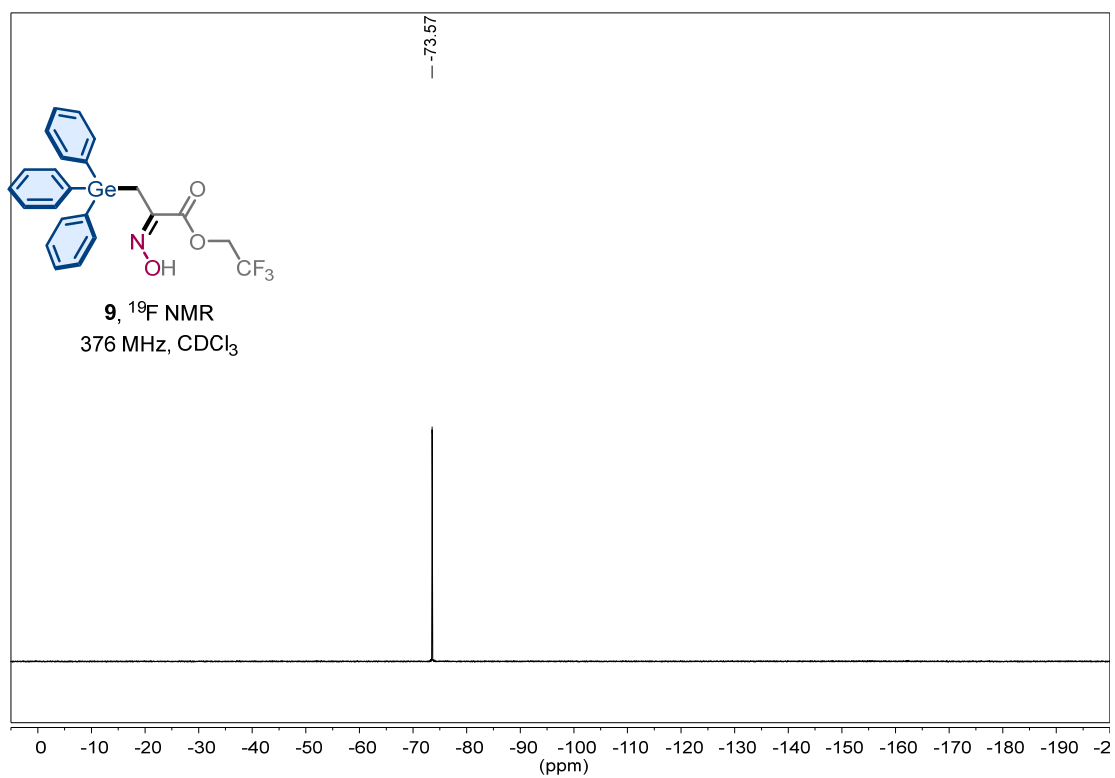
^{13}C NMR spectrum of **8**



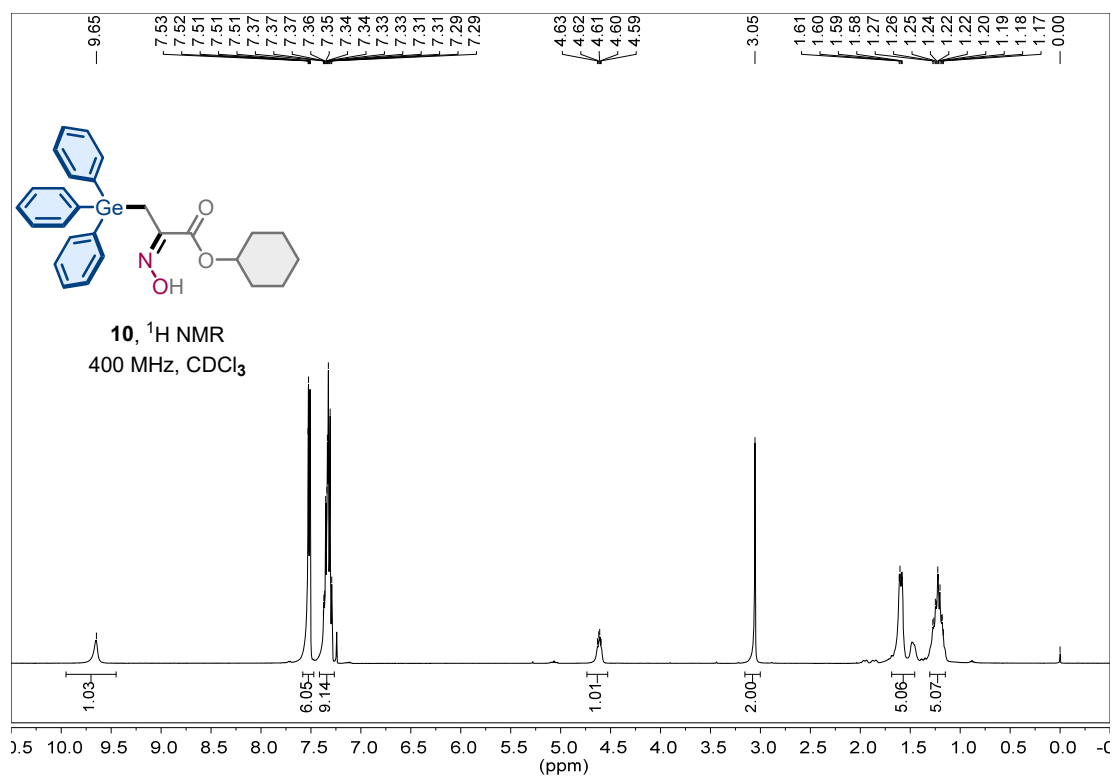
^1H NMR spectrum of **9**



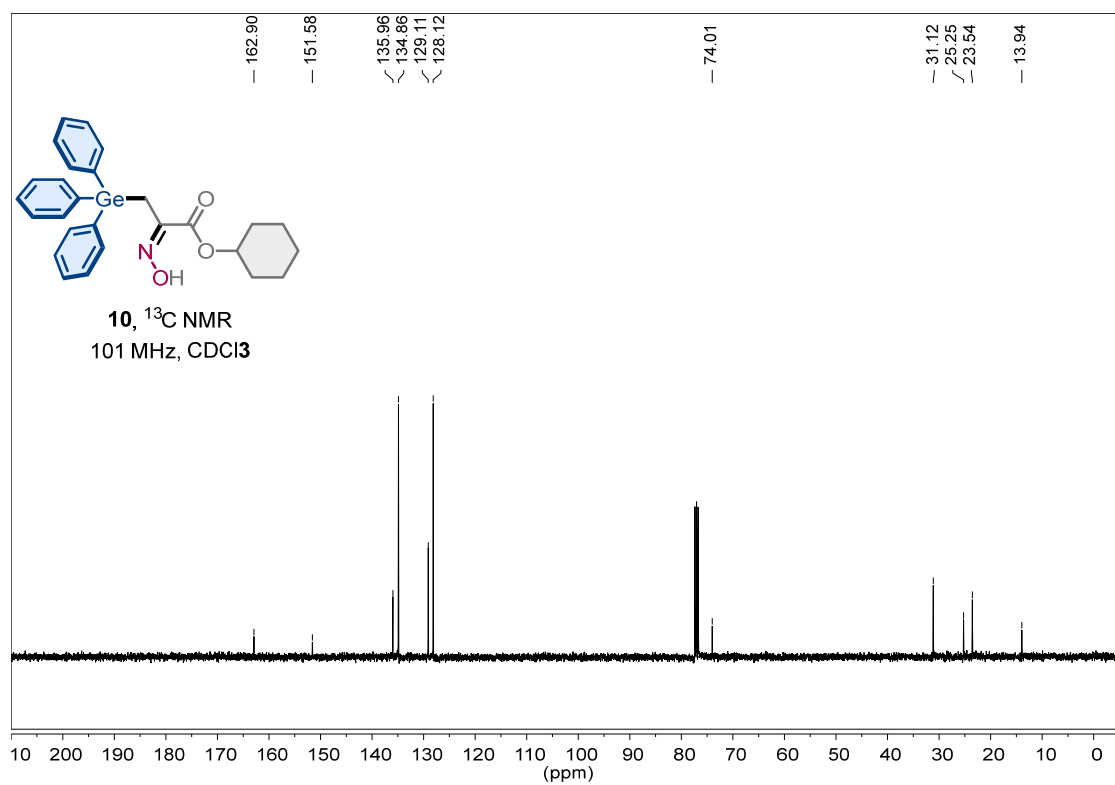
^{13}C NMR spectrum of **9**



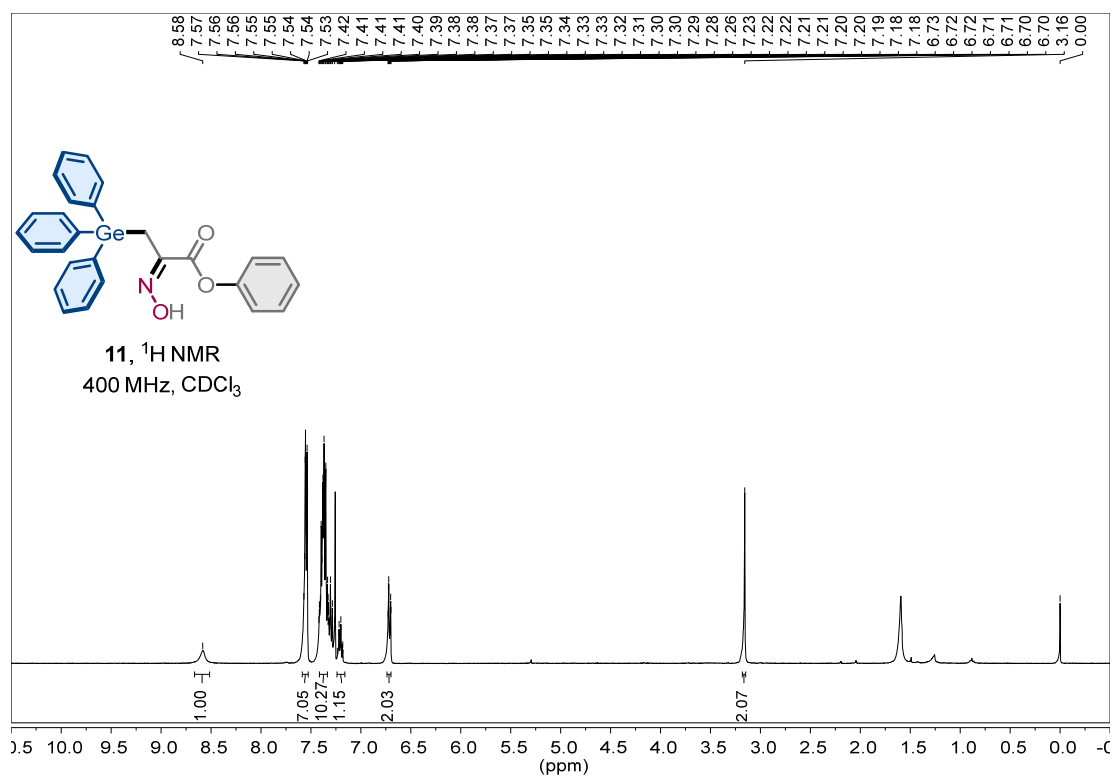
^{19}F NMR spectrum of **9**



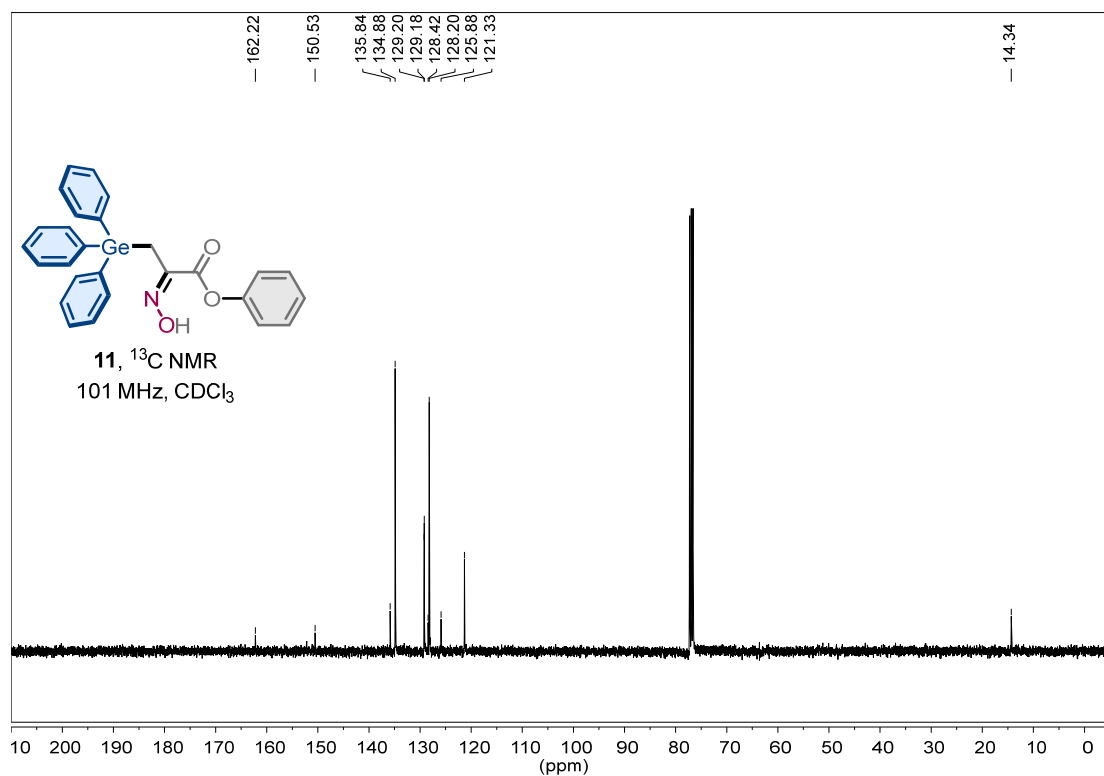
^1H NMR spectrum of **10**



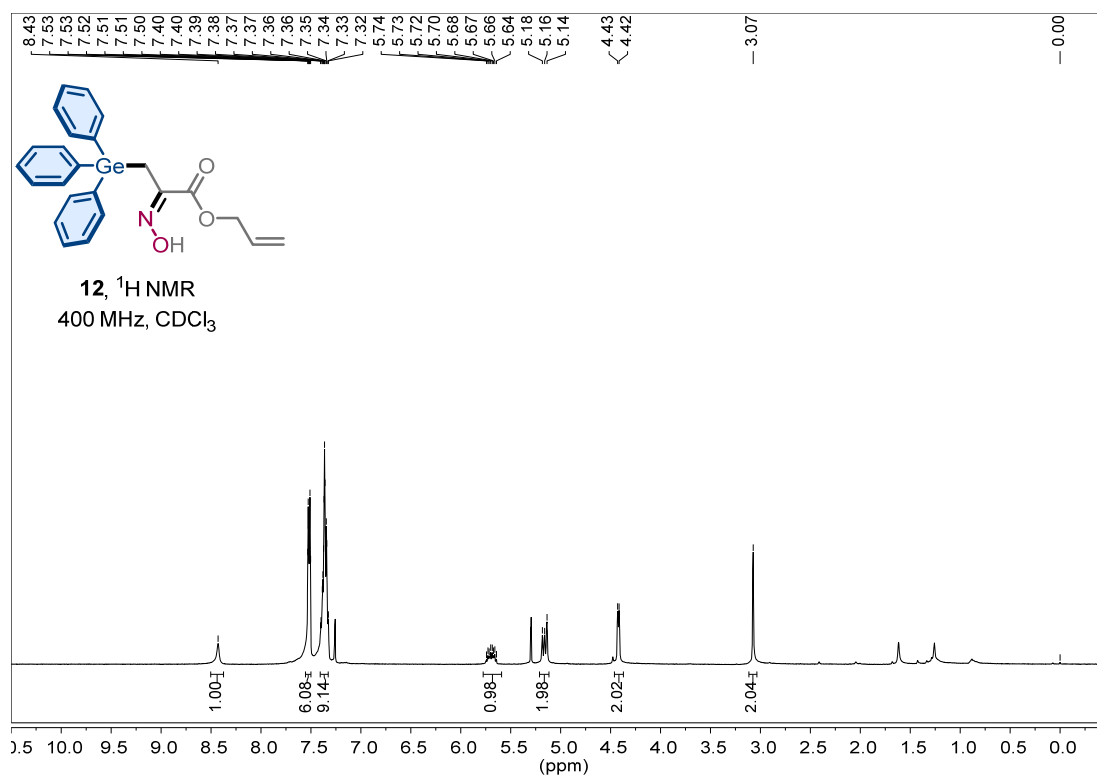
^{13}C NMR spectrum of **10**



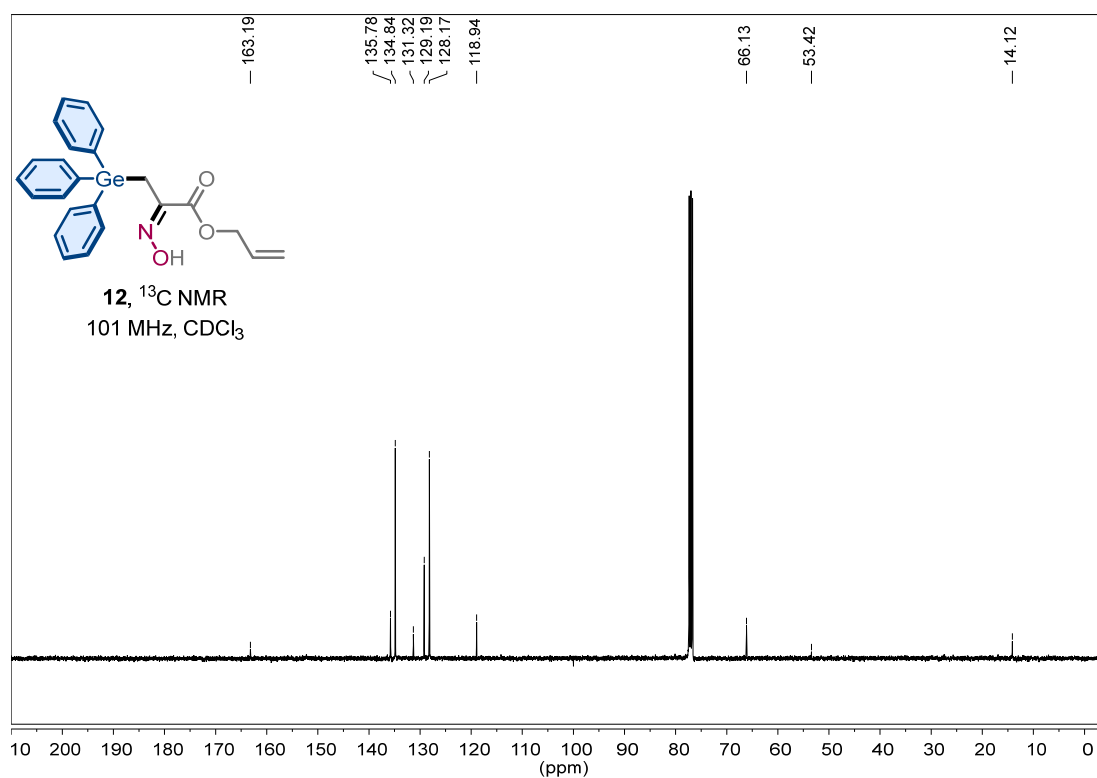
^1H NMR spectrum of **11**



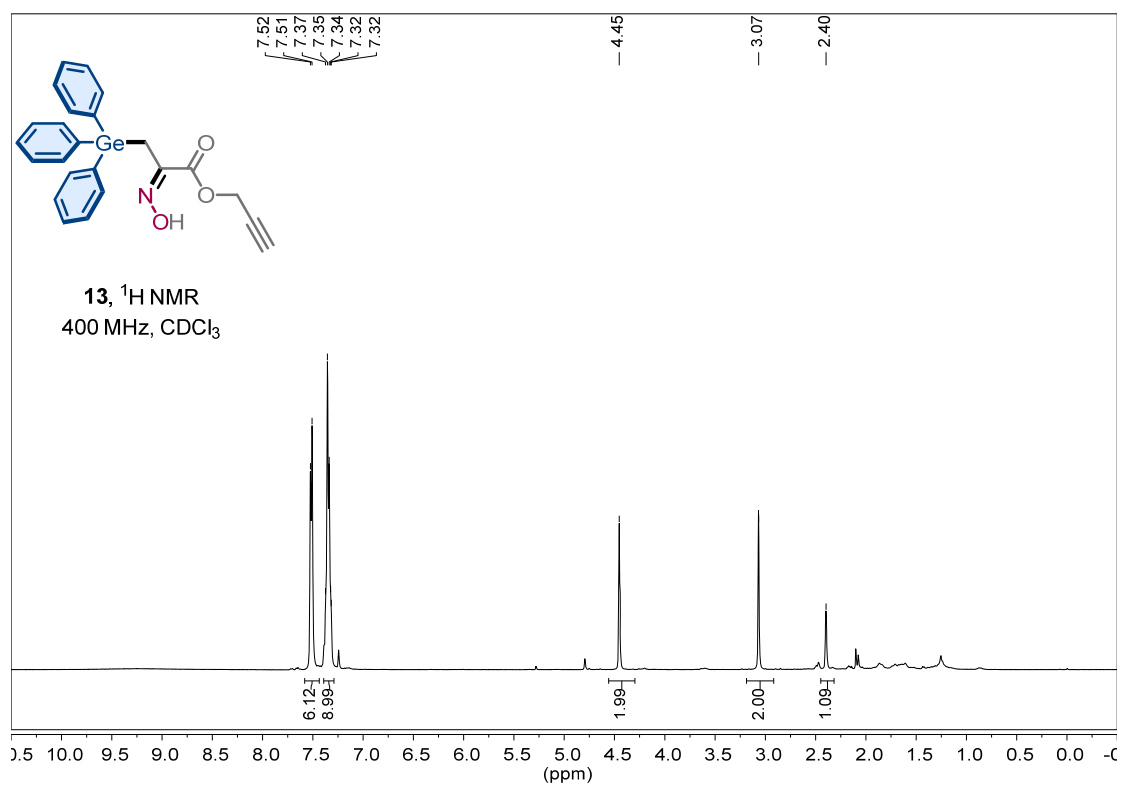
^{13}C NMR spectrum of **11**



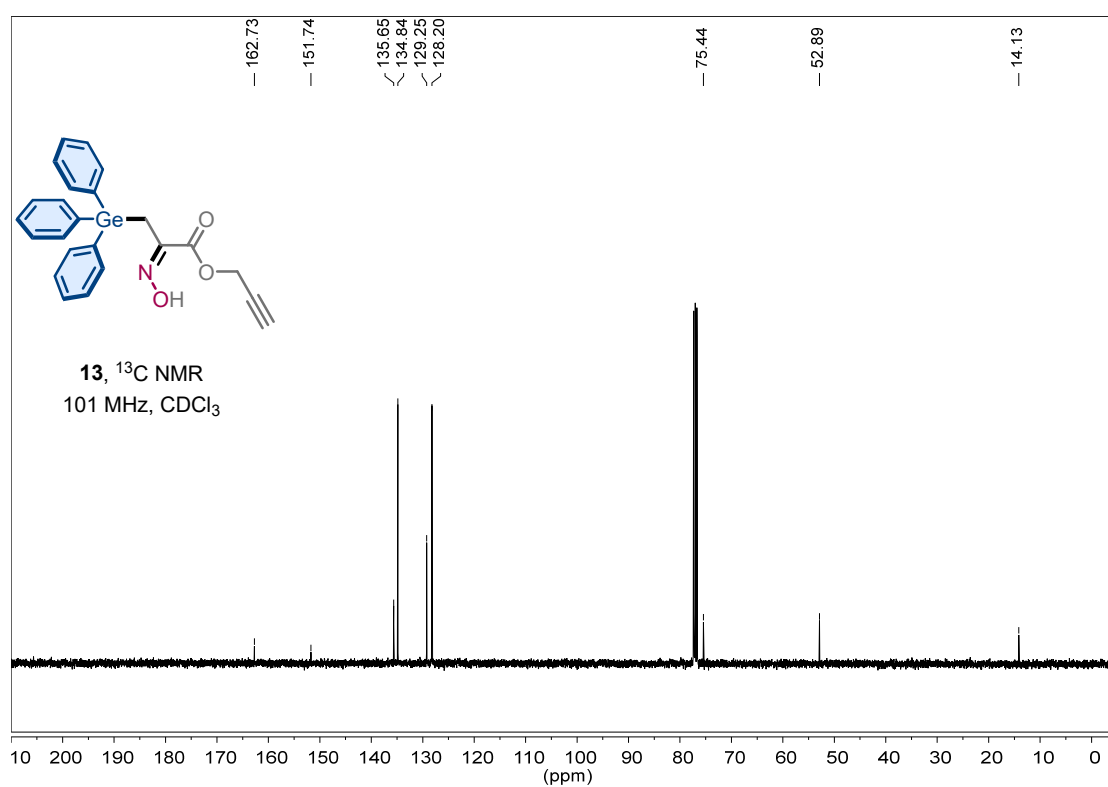
^1H NMR spectrum of **12**



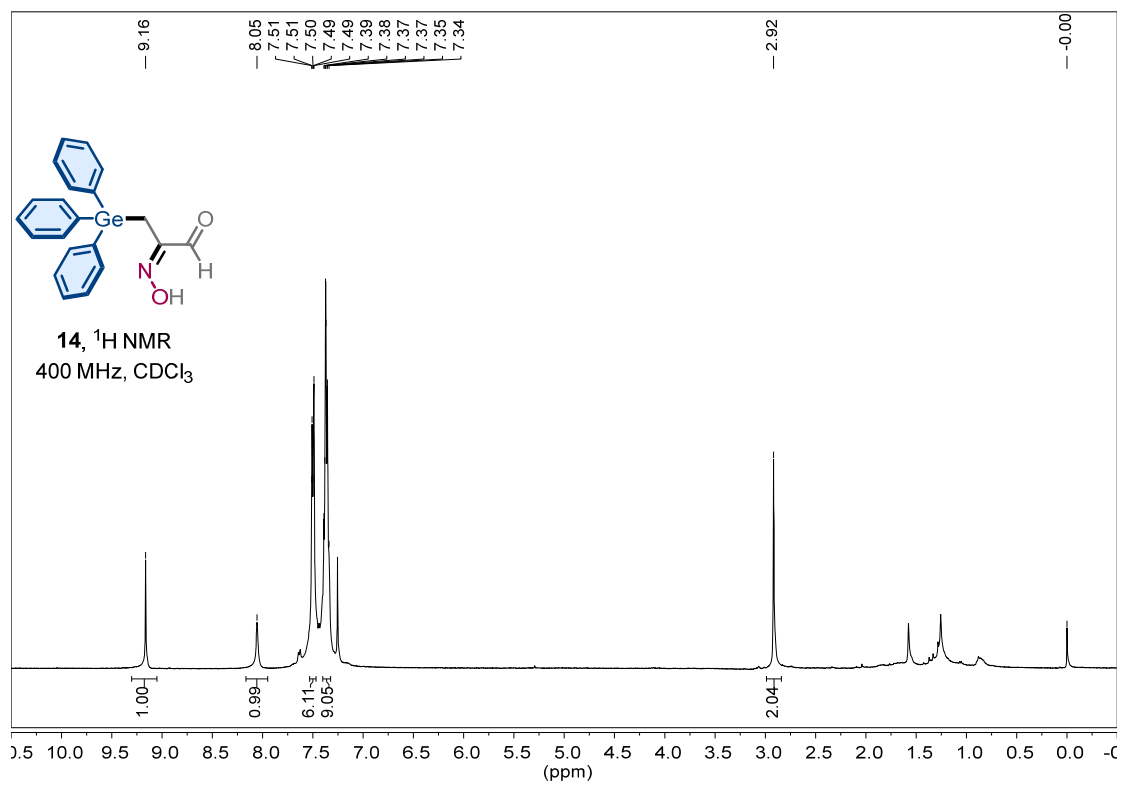
^{13}C NMR spectrum of **12**



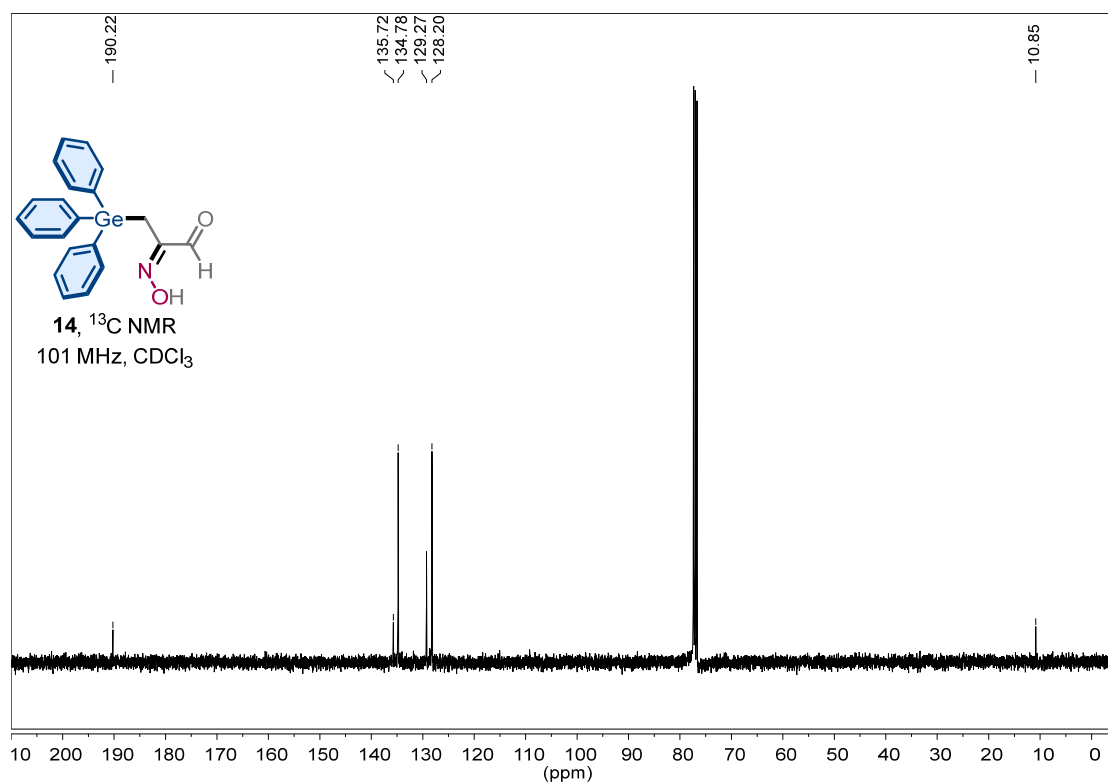
^1H NMR spectrum of **13**



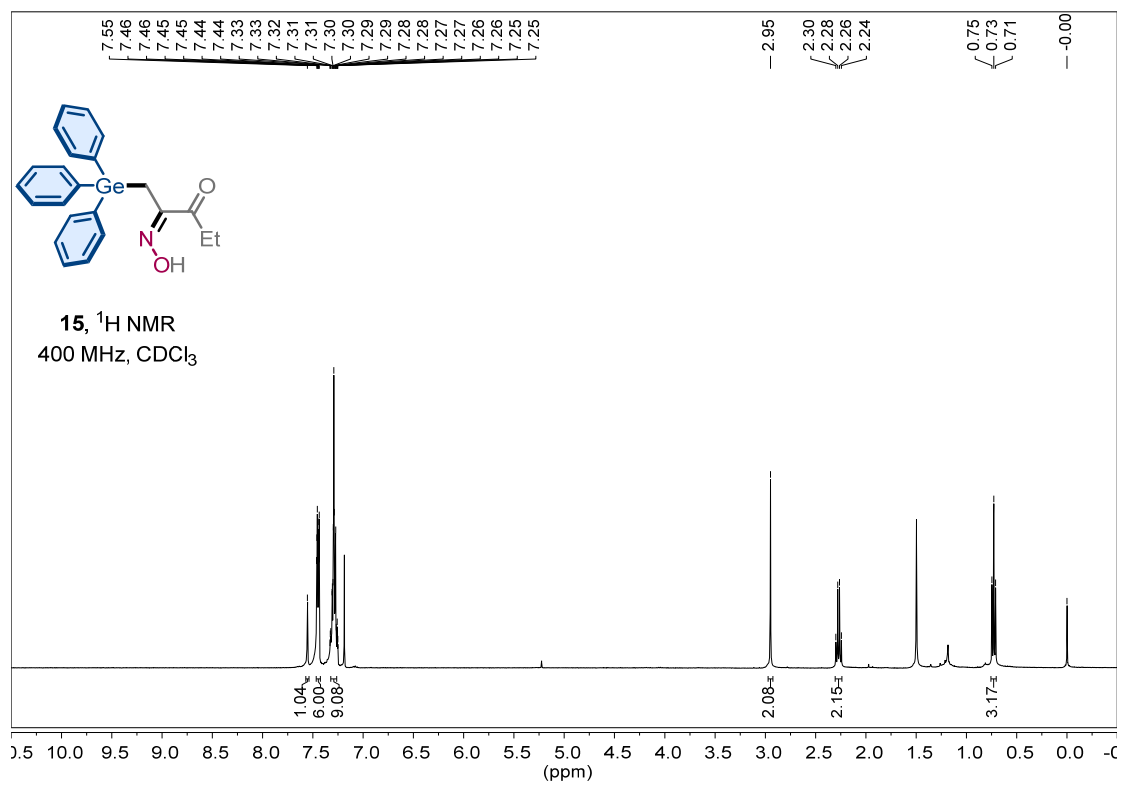
^{13}C NMR spectrum of **13**



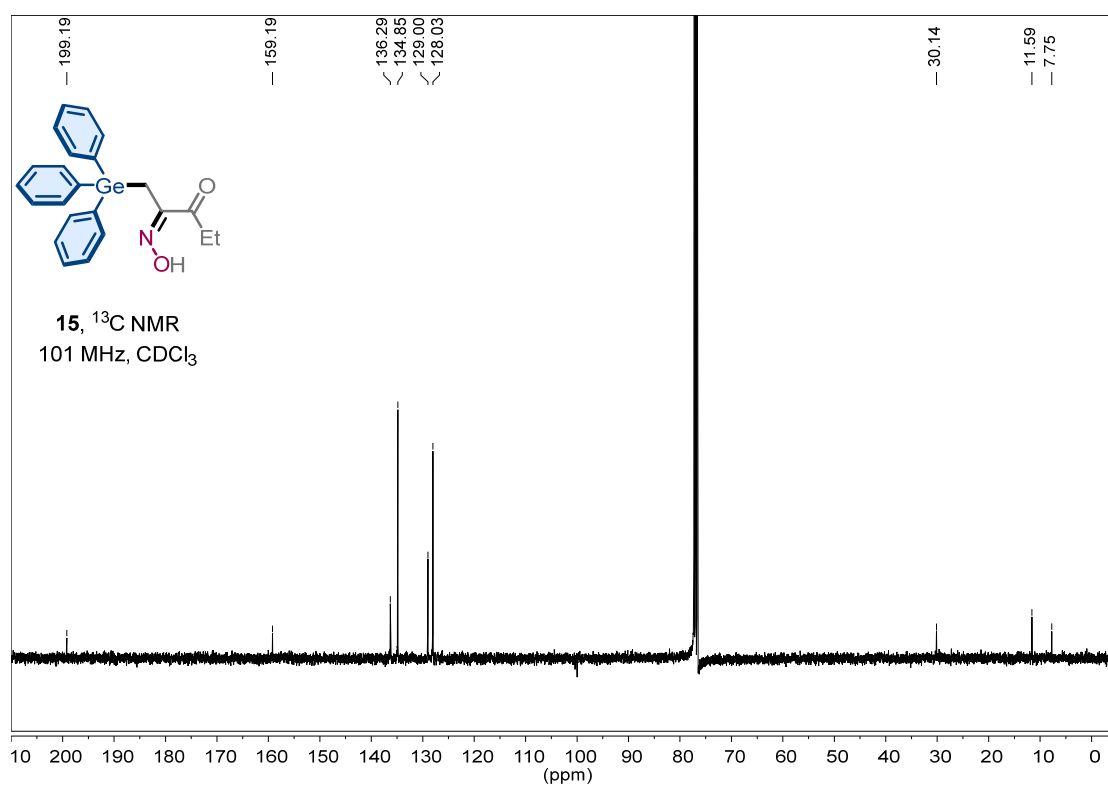
^1H NMR spectrum of **14**



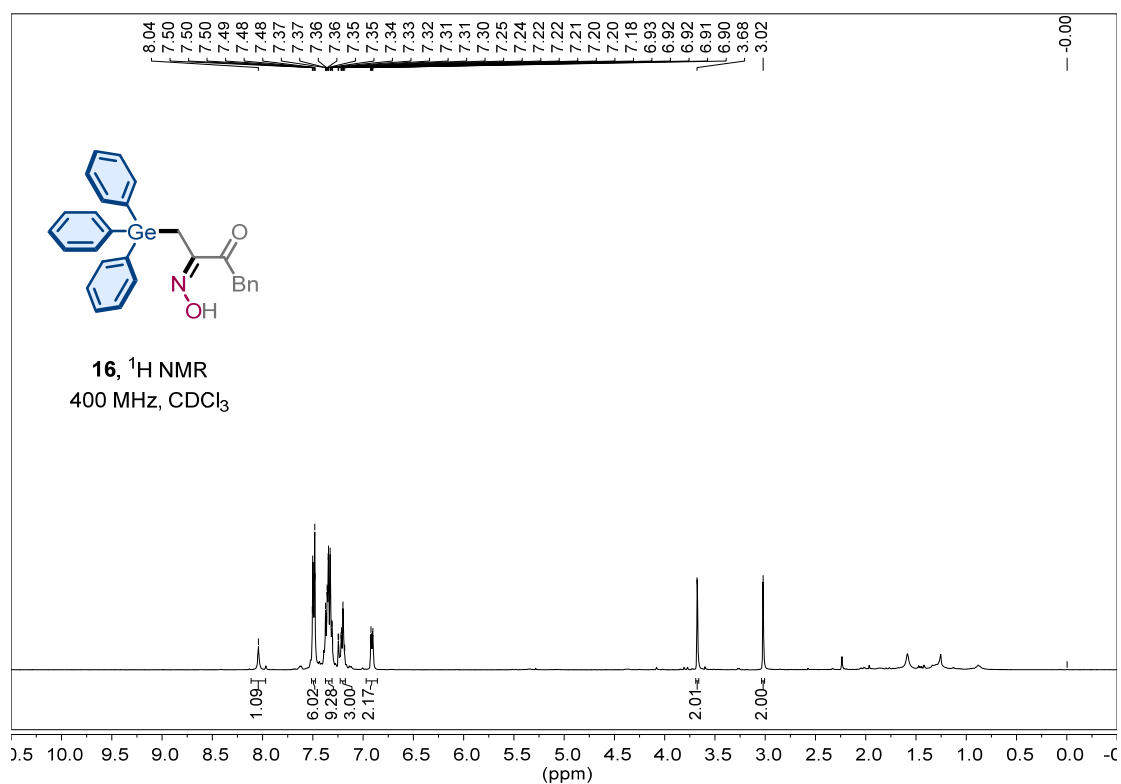
^{13}C NMR spectrum of **14**



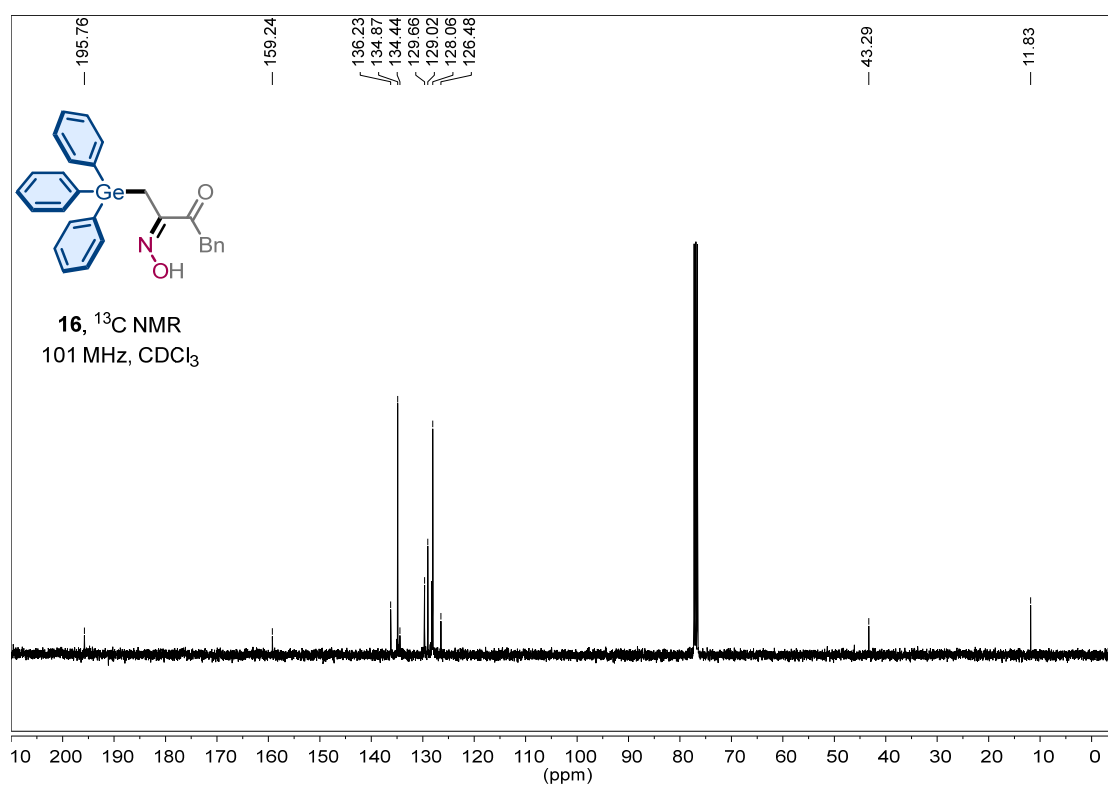
^1H NMR spectrum of **15**



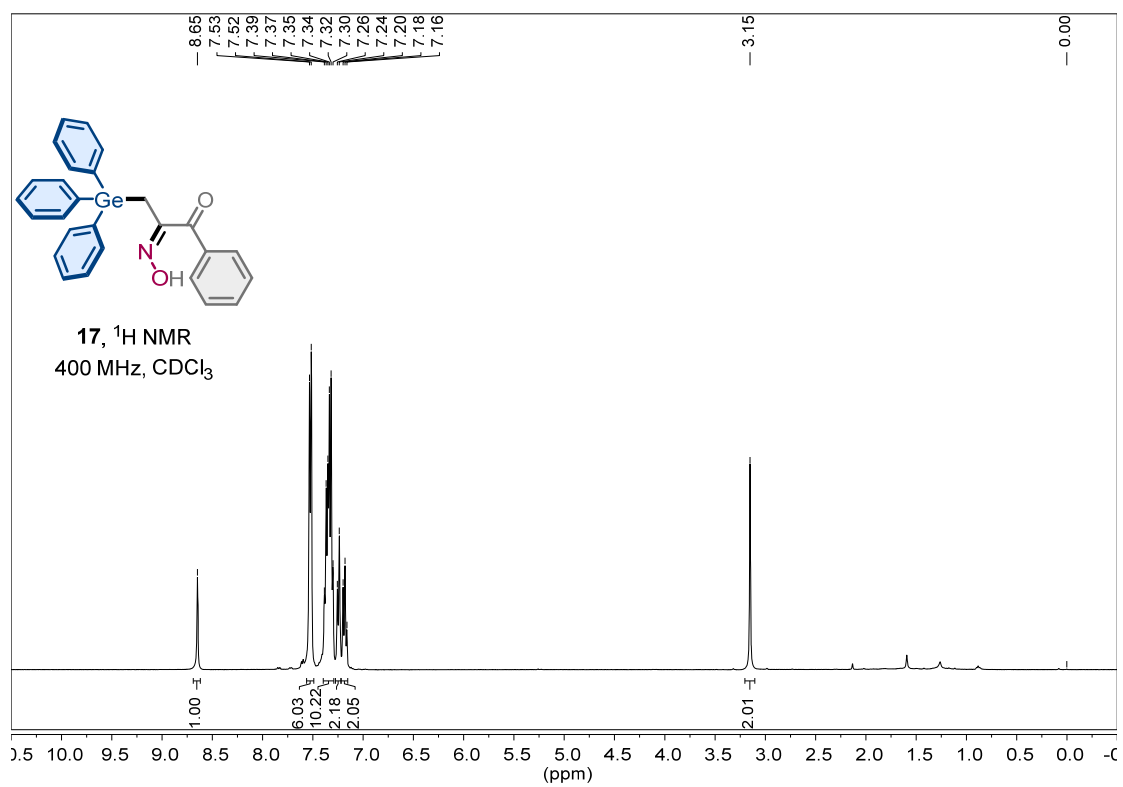
^{13}C NMR spectrum of **15**



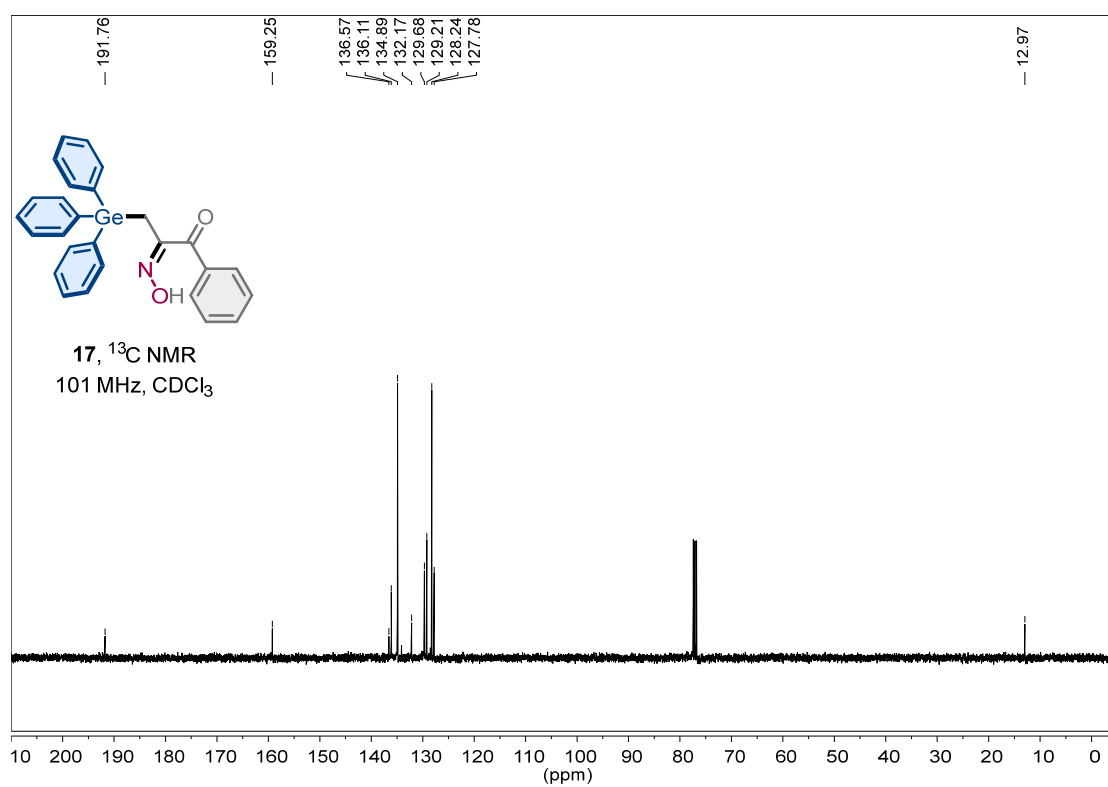
^1H NMR spectrum of **16**



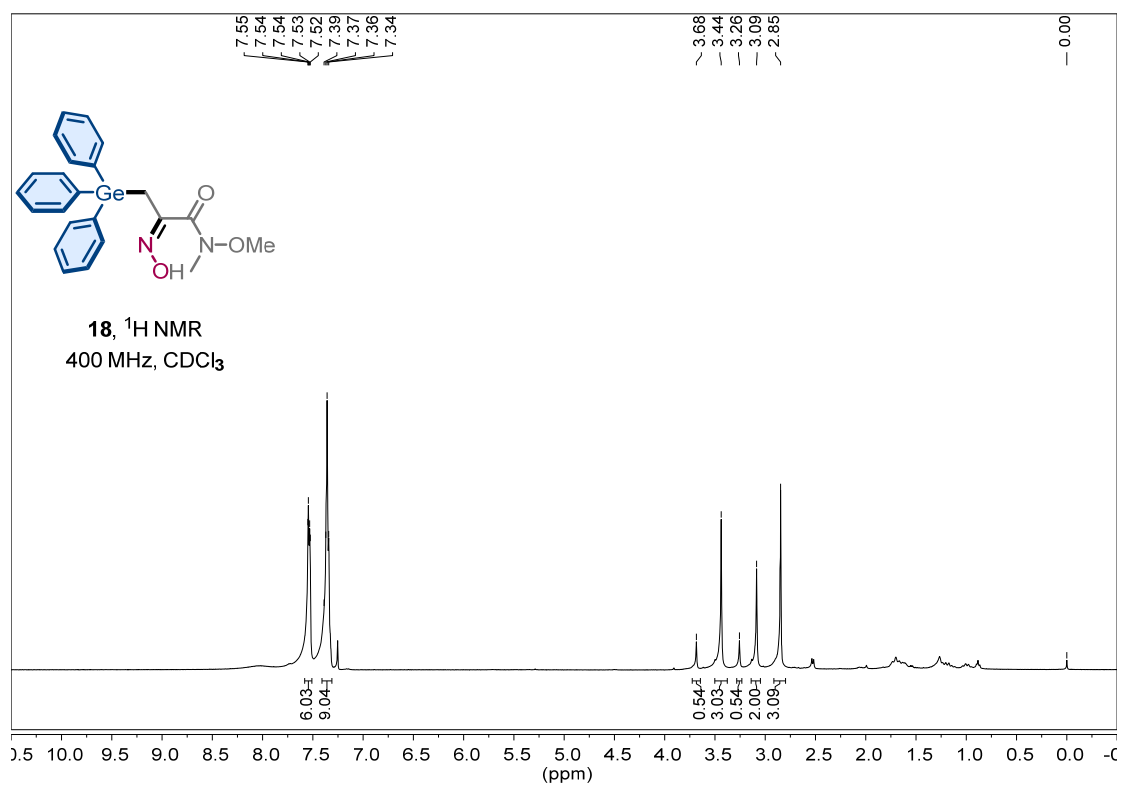
^{13}C NMR spectrum of **16**



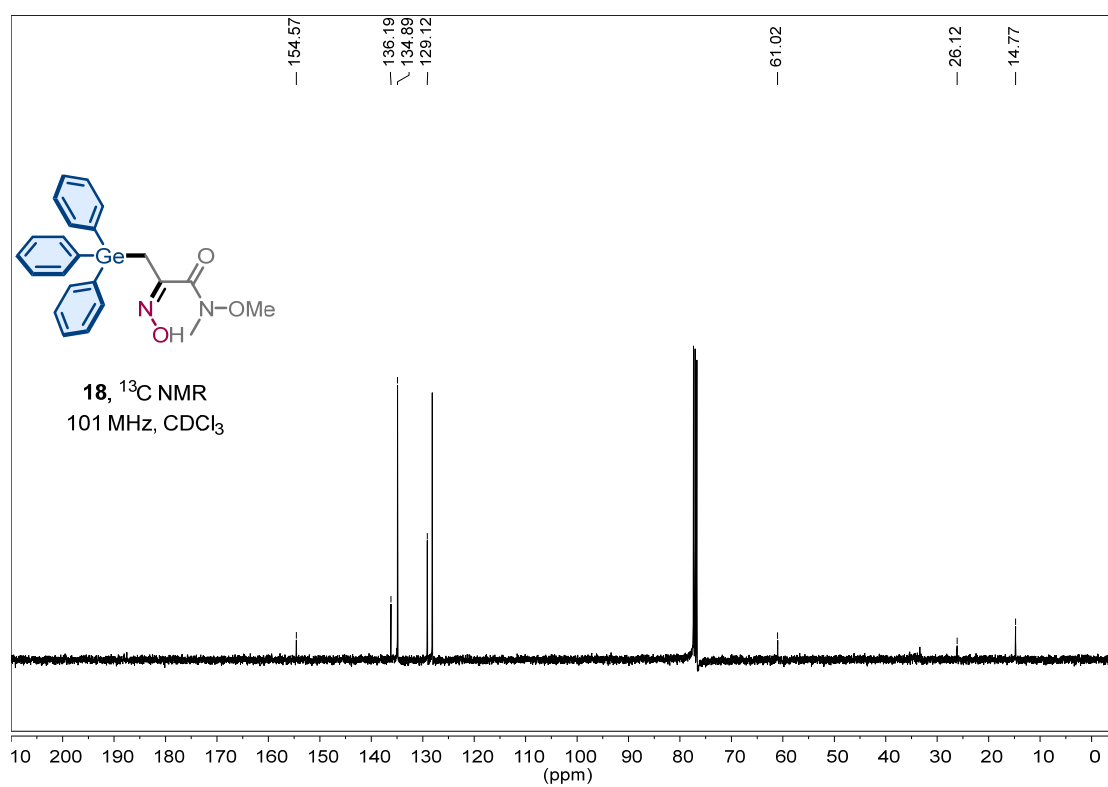
^1H NMR spectrum of **17**



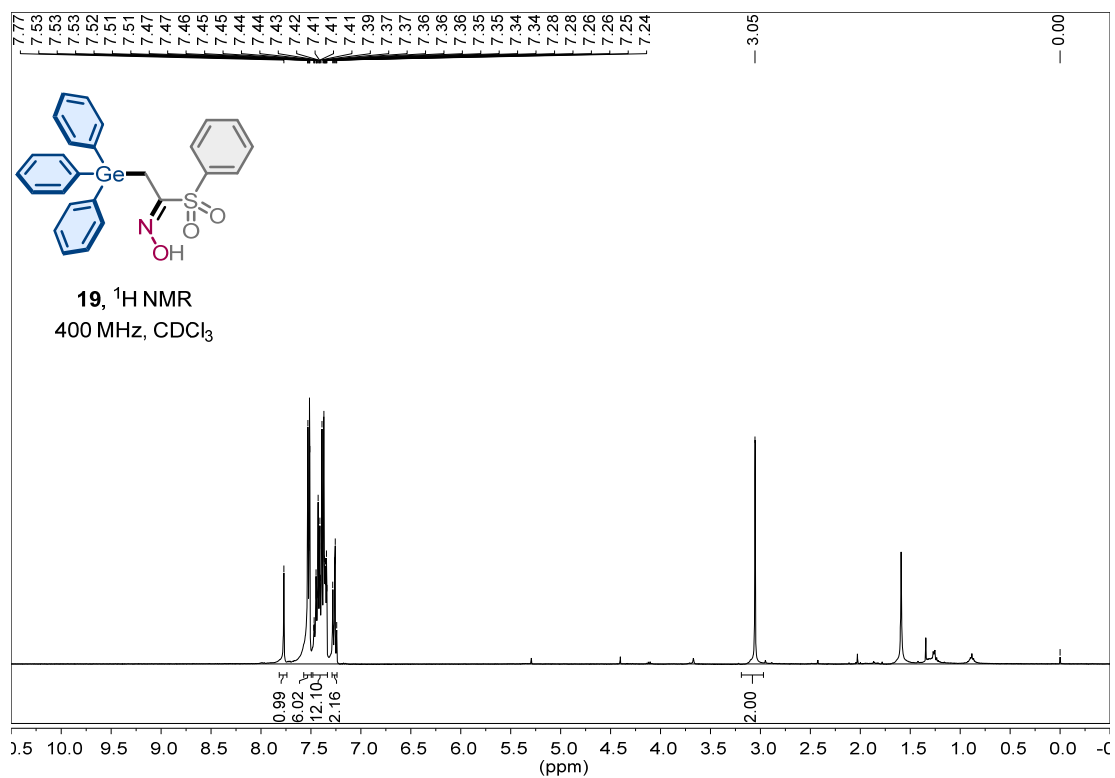
^{13}C NMR spectrum of **17**



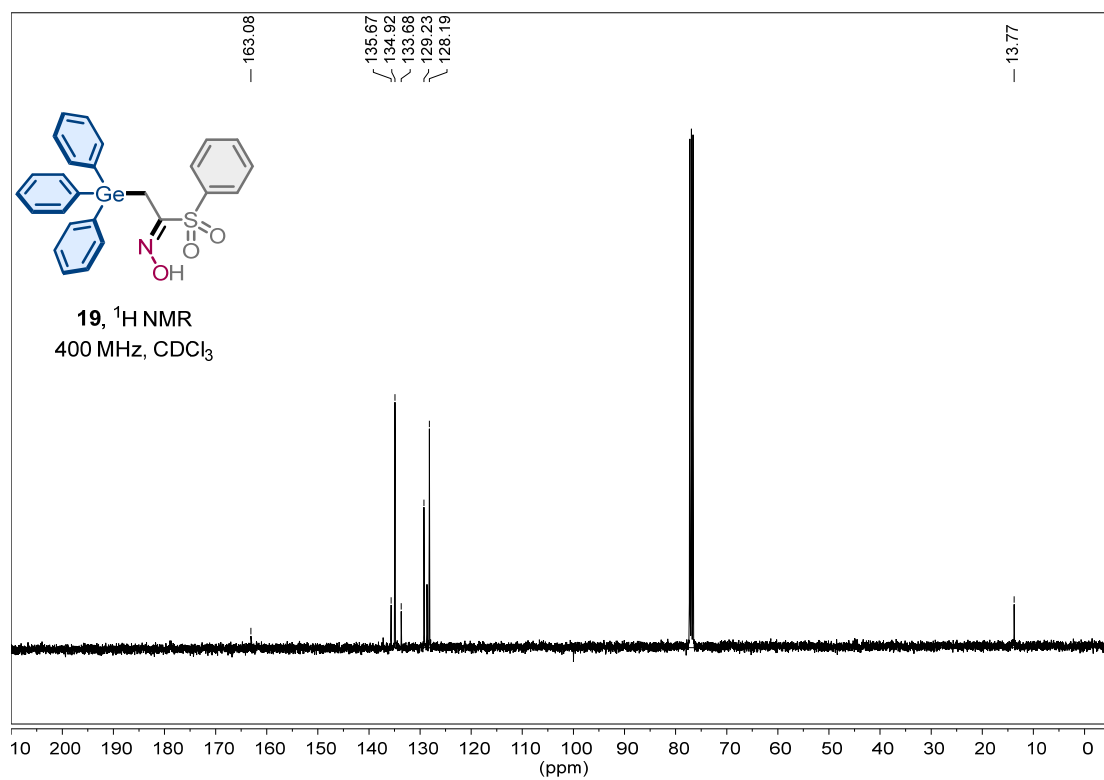
^1H NMR spectrum of **18**



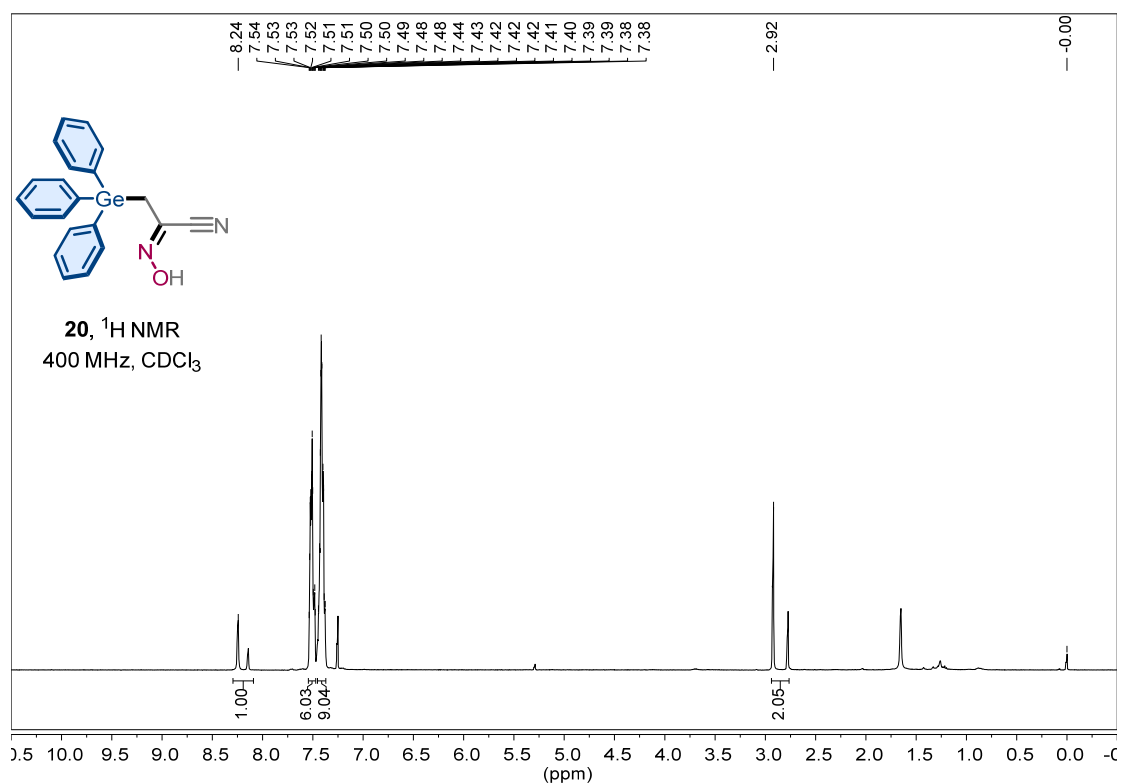
^{13}C NMR spectrum of **18**



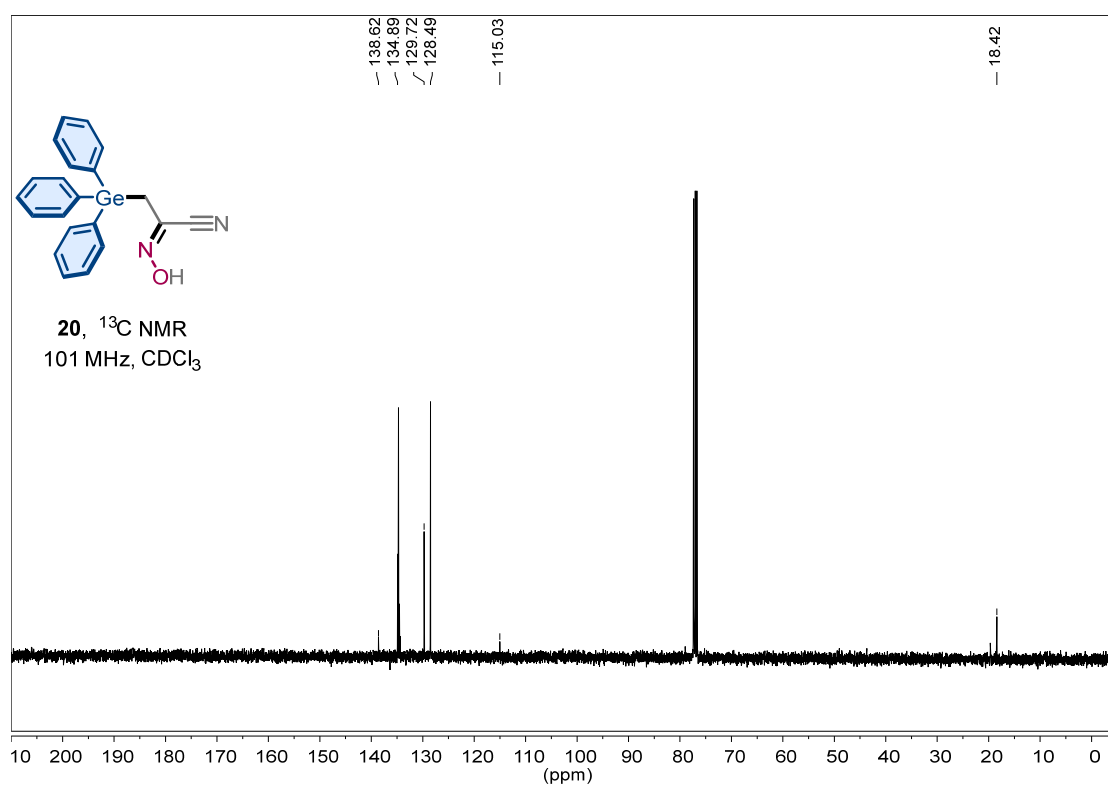
¹H NMR spectrum of **19**



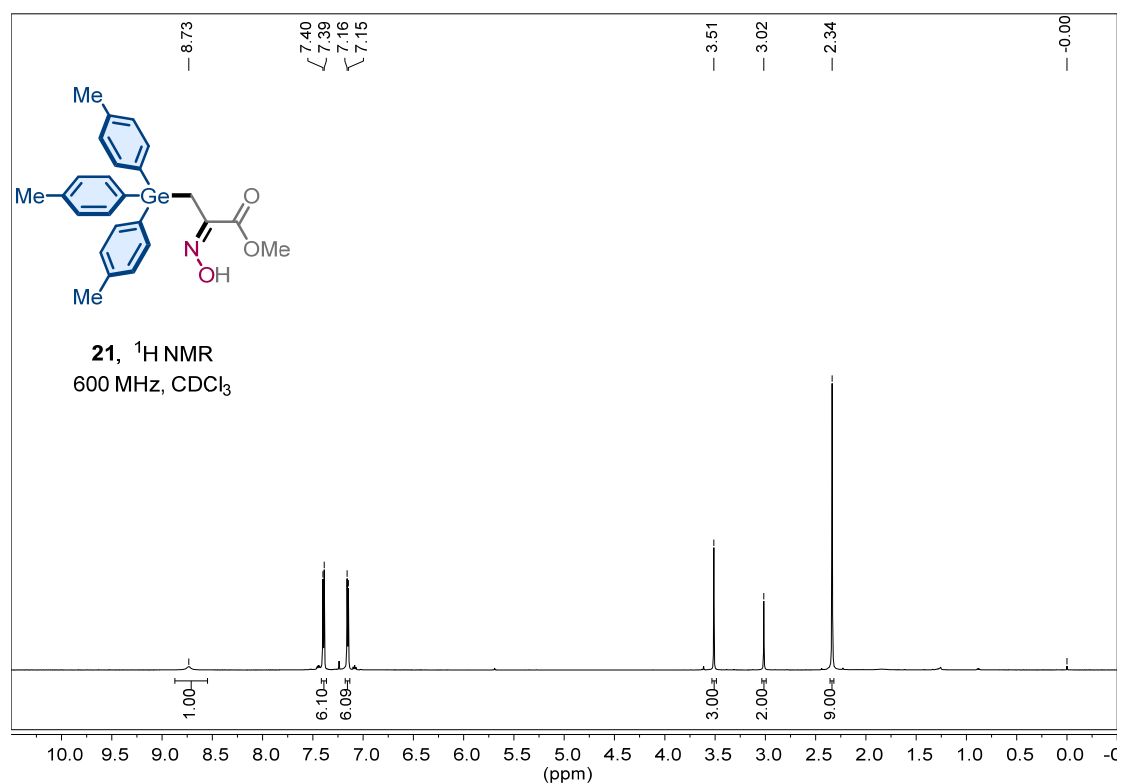
¹³C NMR spectrum of **19**



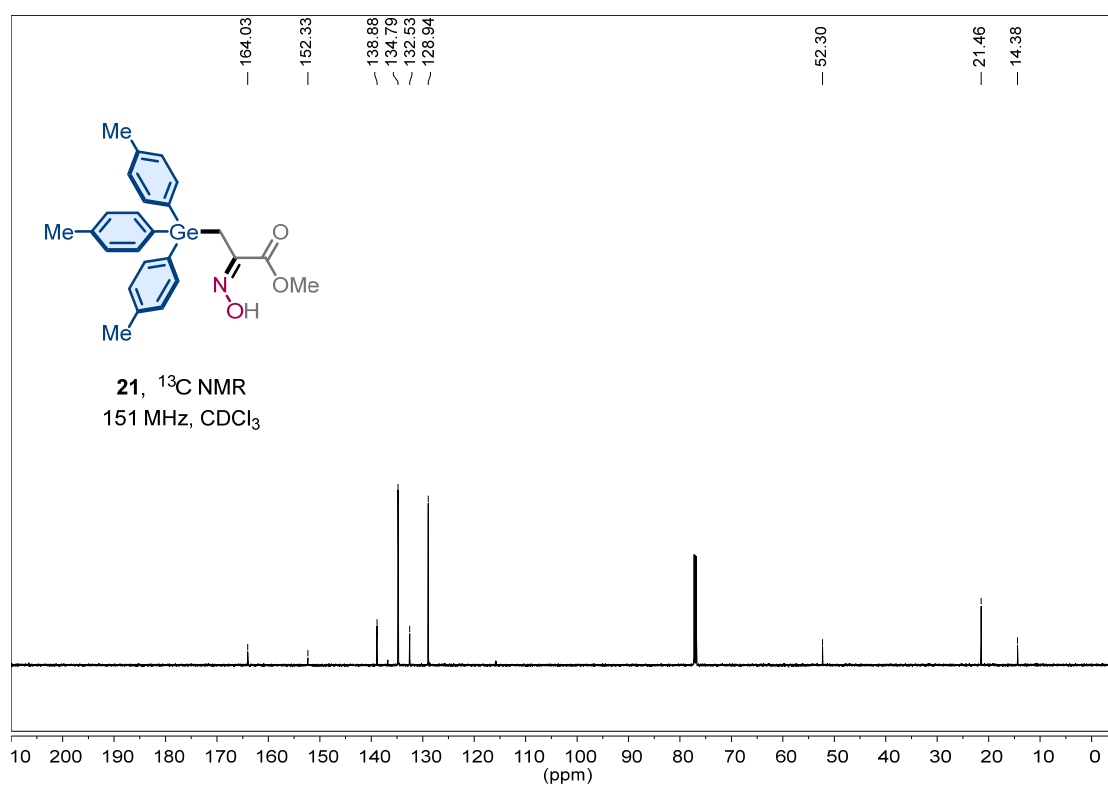
^1H NMR spectrum of **20**



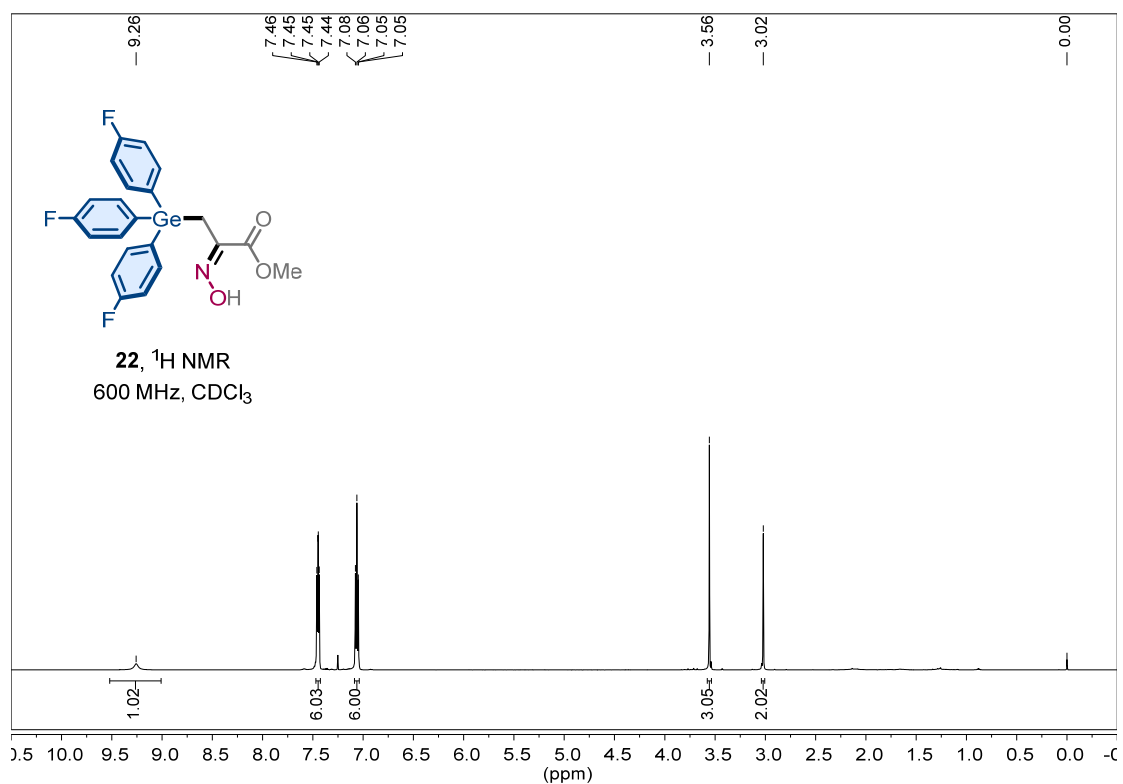
^{13}C NMR spectrum of **20**



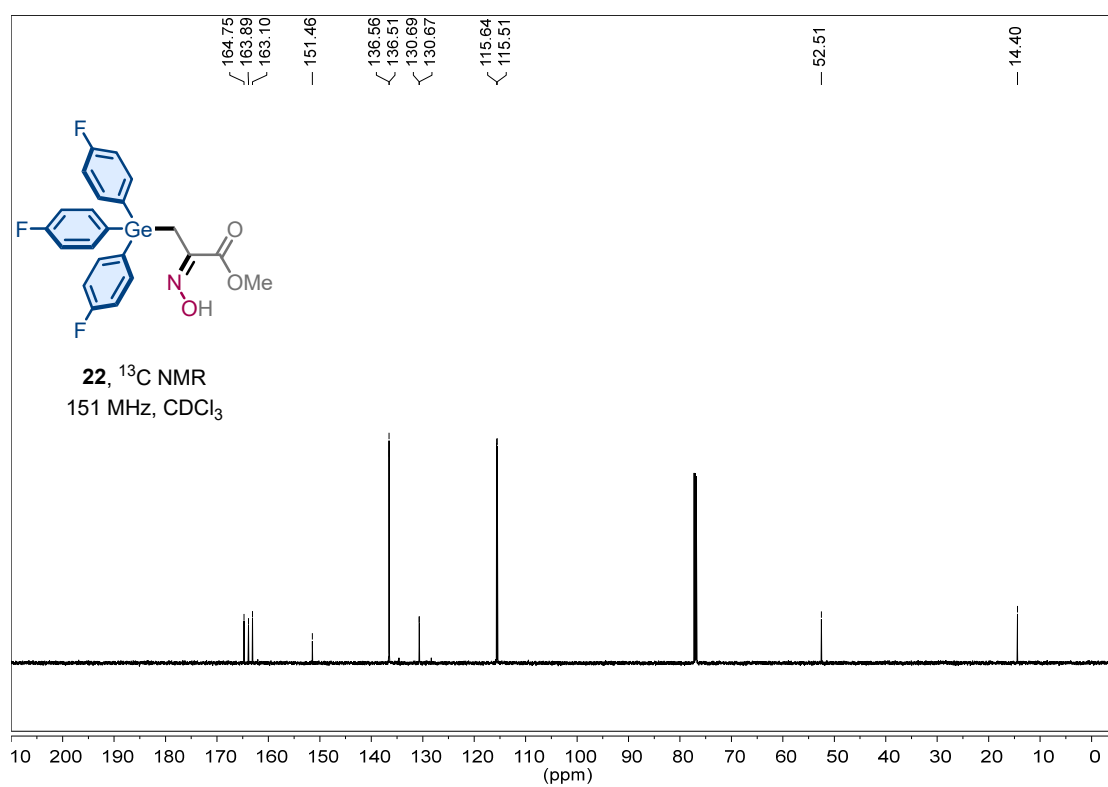
^1H NMR spectrum of **21**



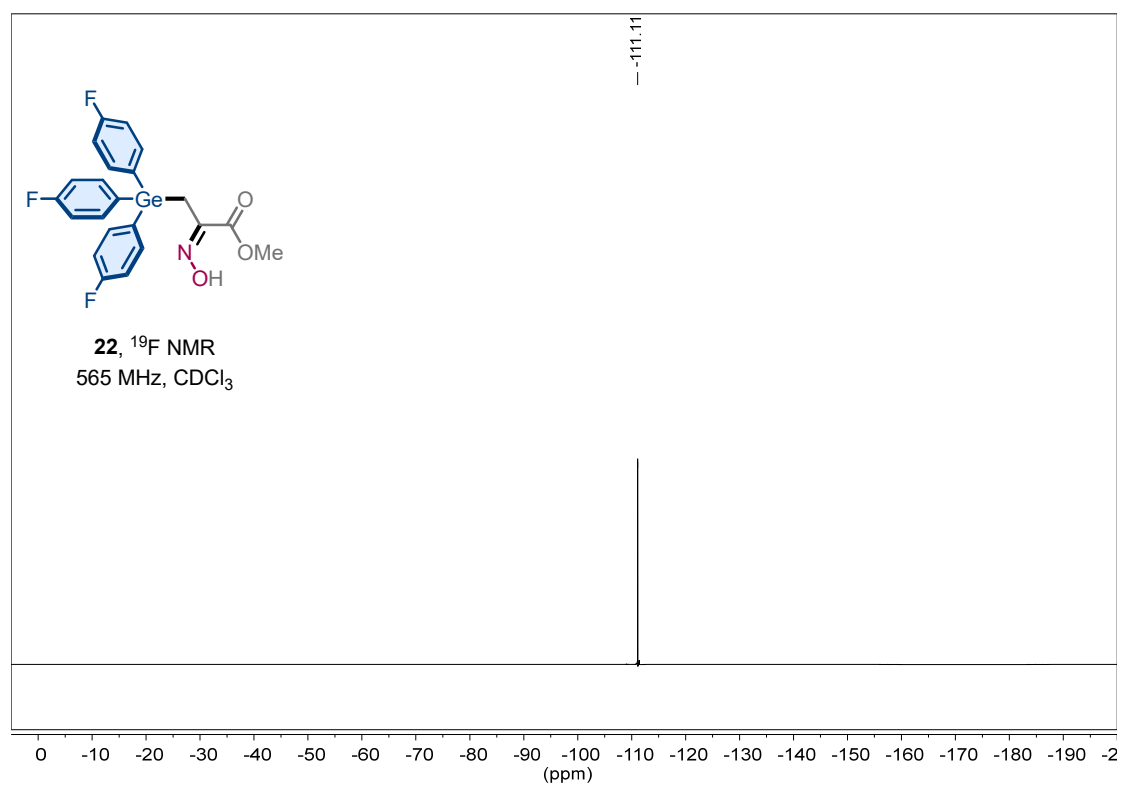
^{13}C NMR spectrum of **21**



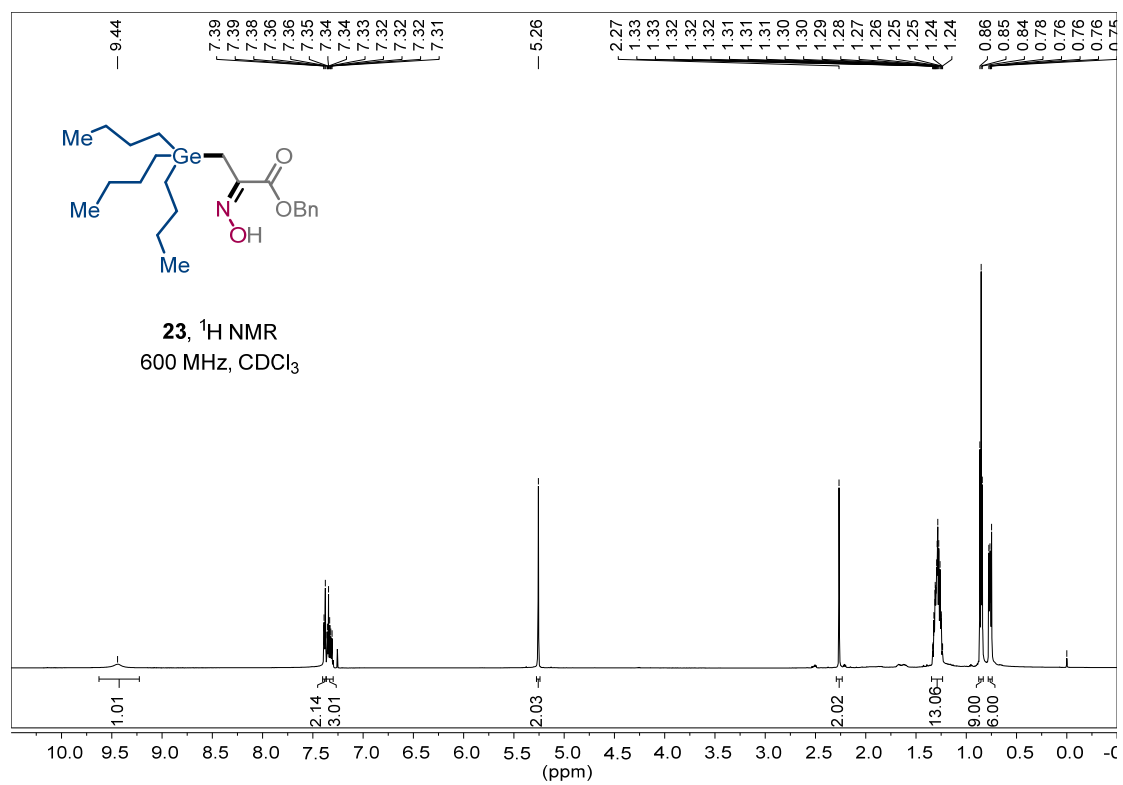
^1H NMR spectrum of **22**



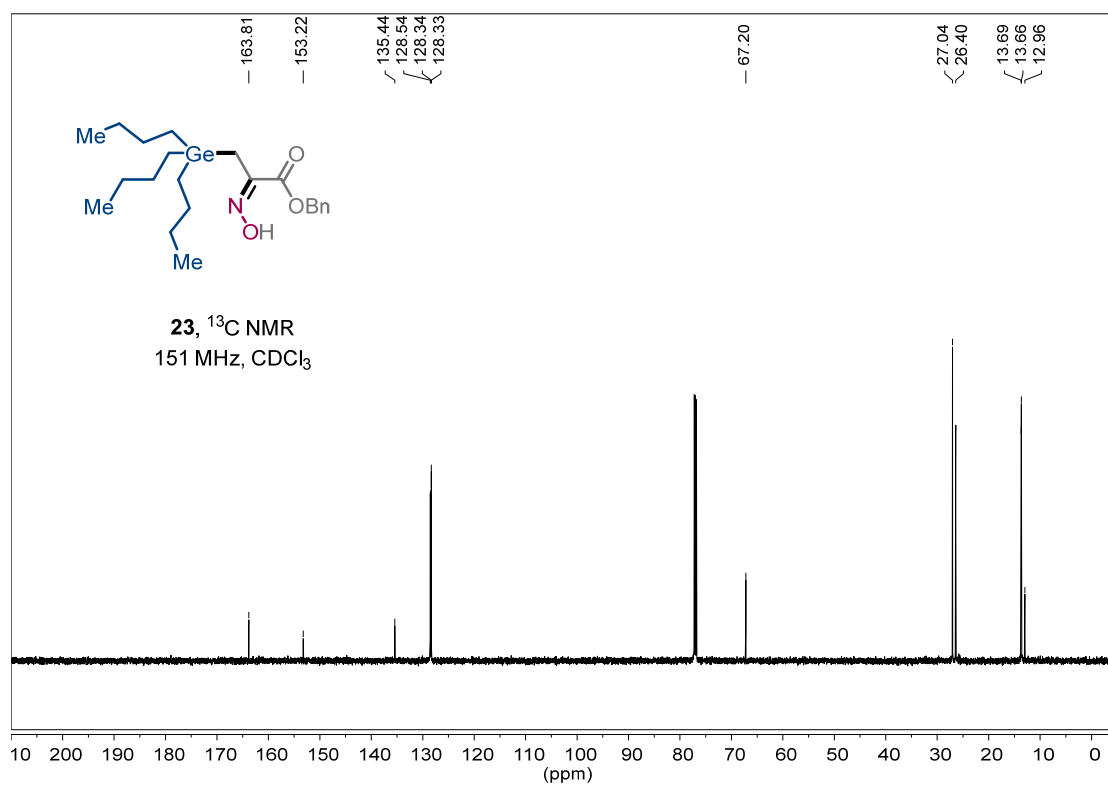
^{13}C NMR spectrum of **22**



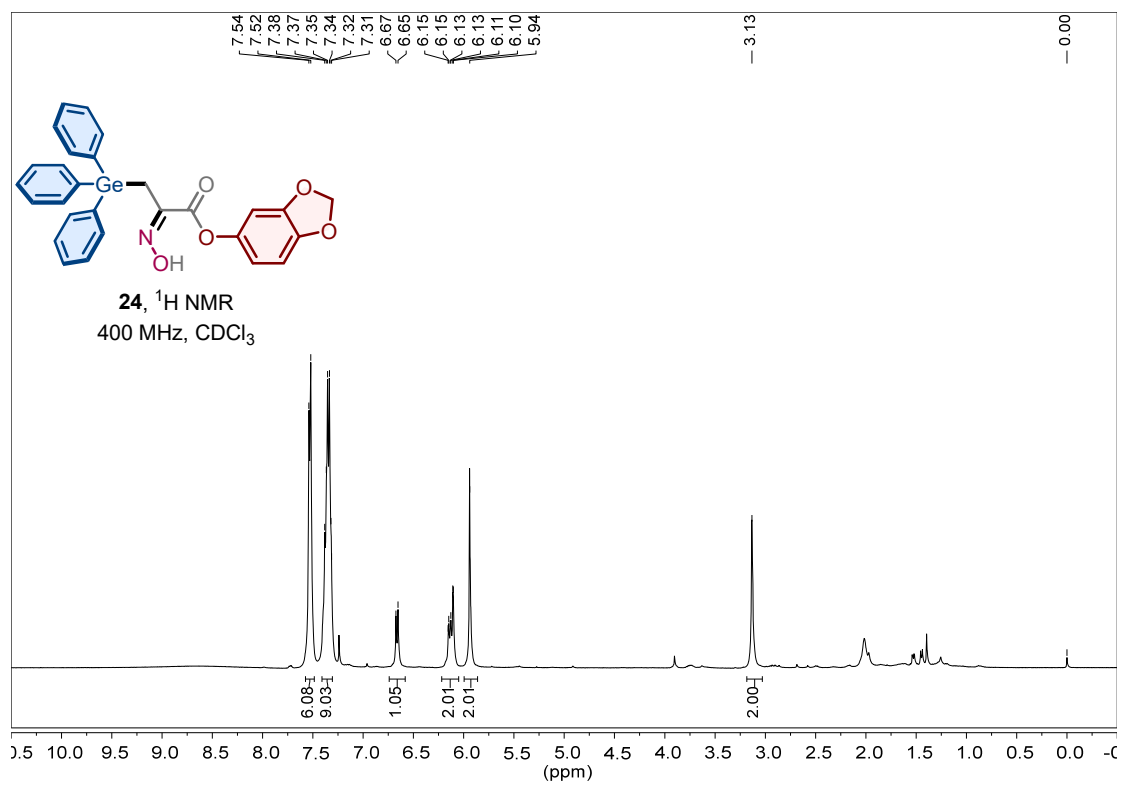
^{19}F NMR spectrum of **22**



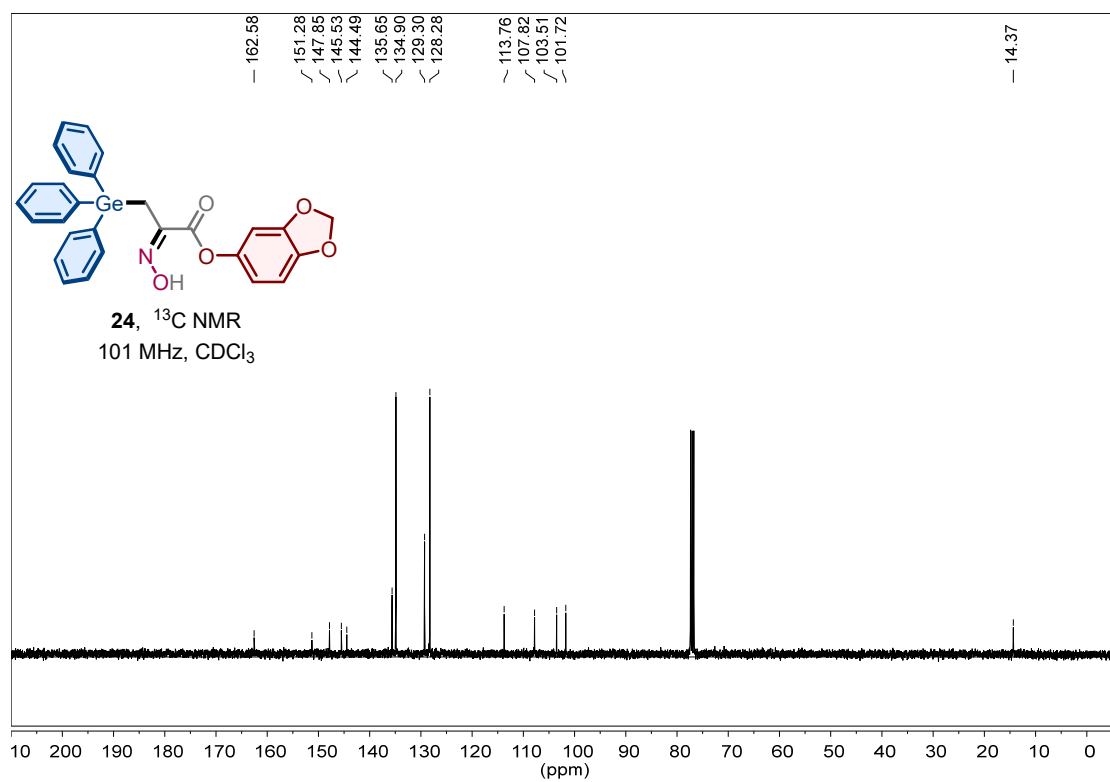
^1H NMR spectrum of **23**



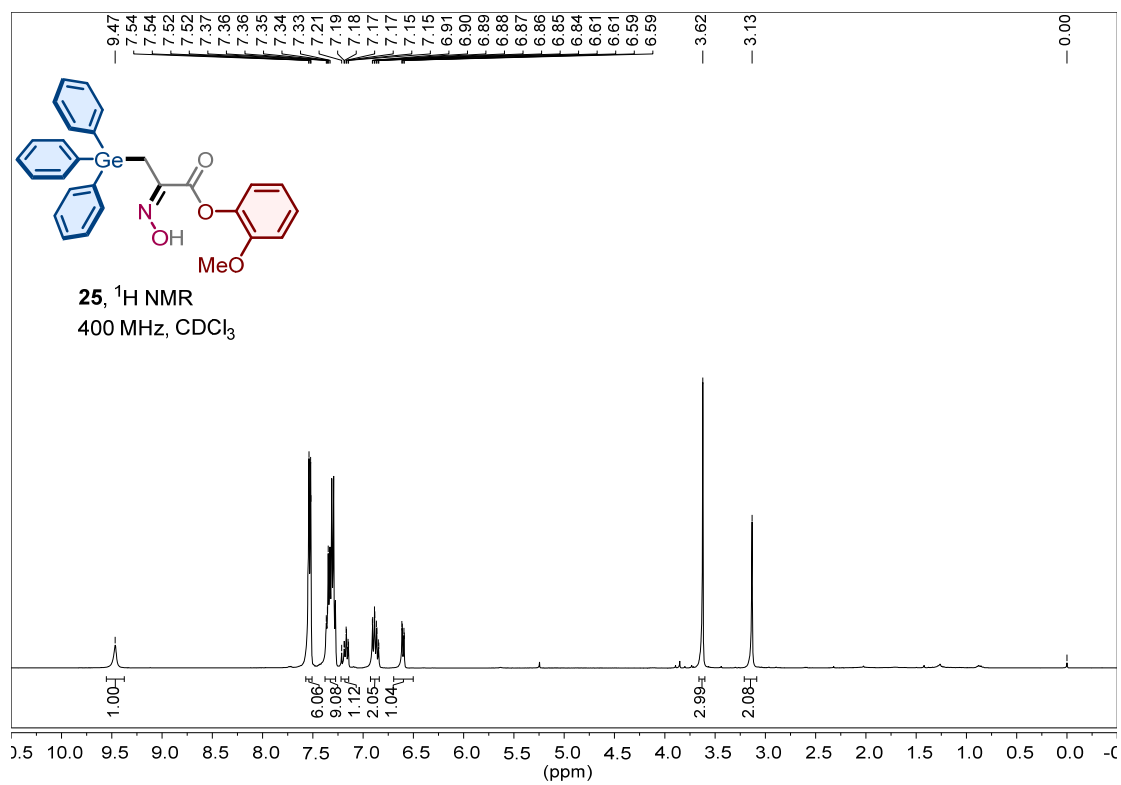
^{13}C NMR spectrum of **23**



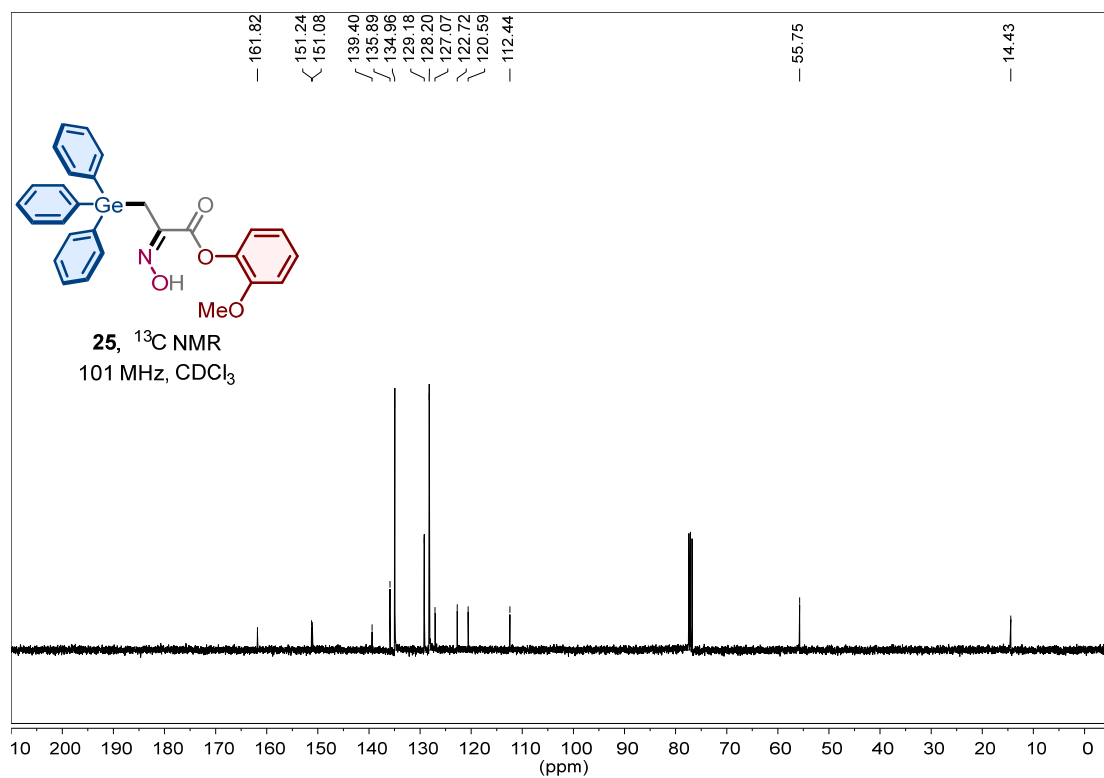
^1H NMR spectrum of **24**



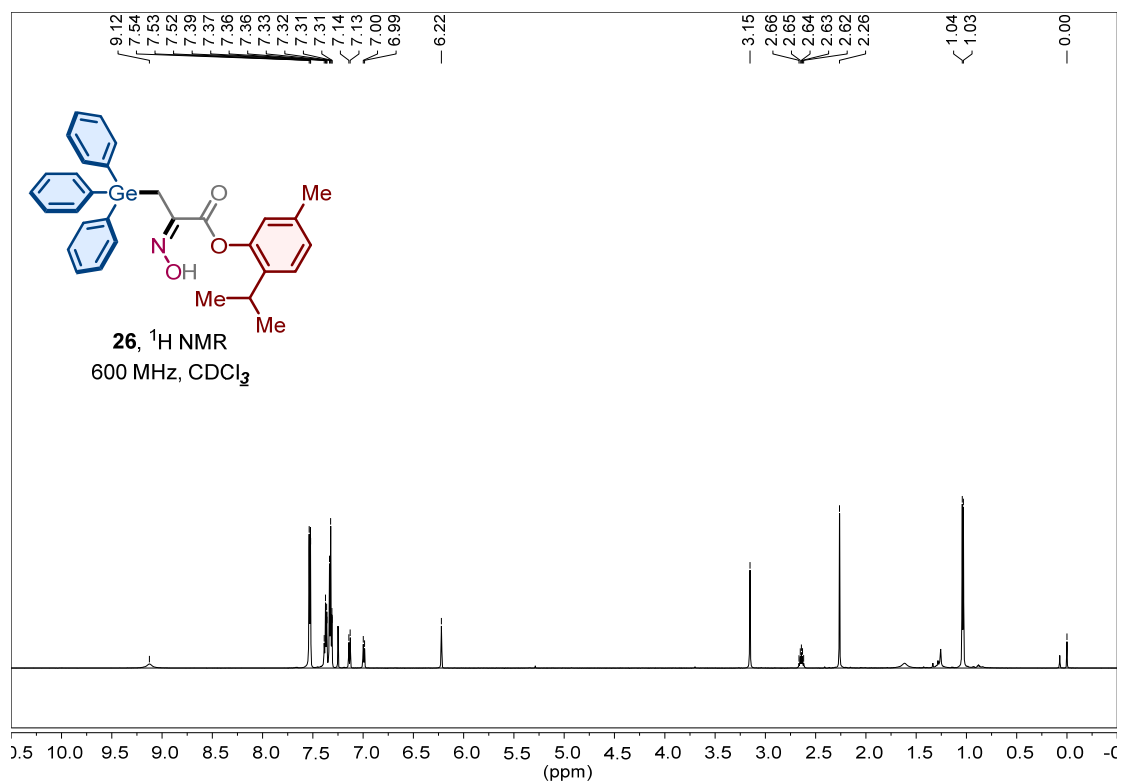
^{13}C NMR spectrum of **24**



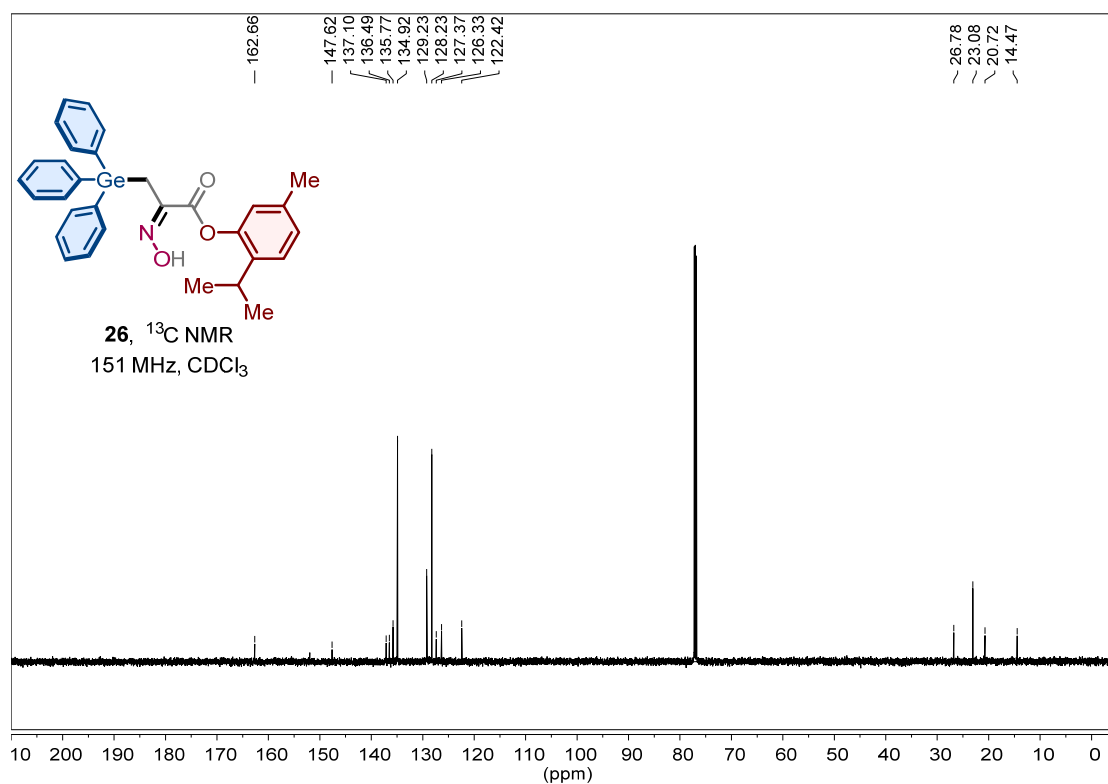
^1H NMR spectrum of **25**



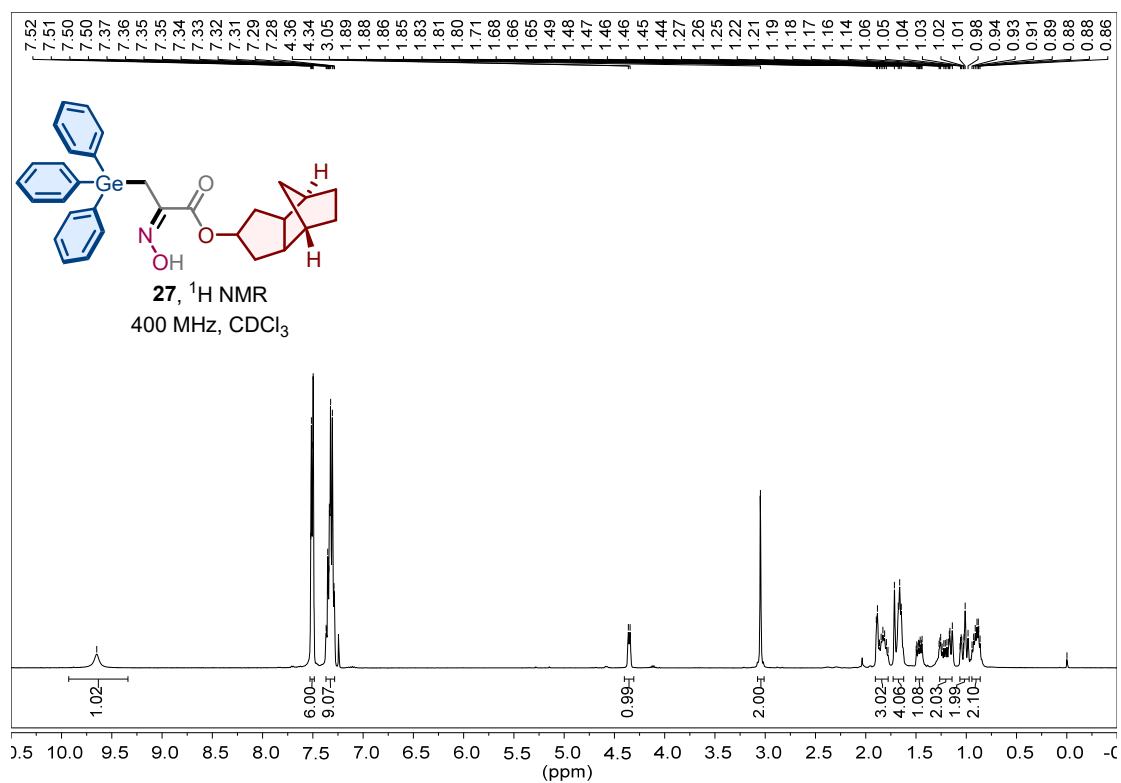
^{13}C NMR spectrum of **25**



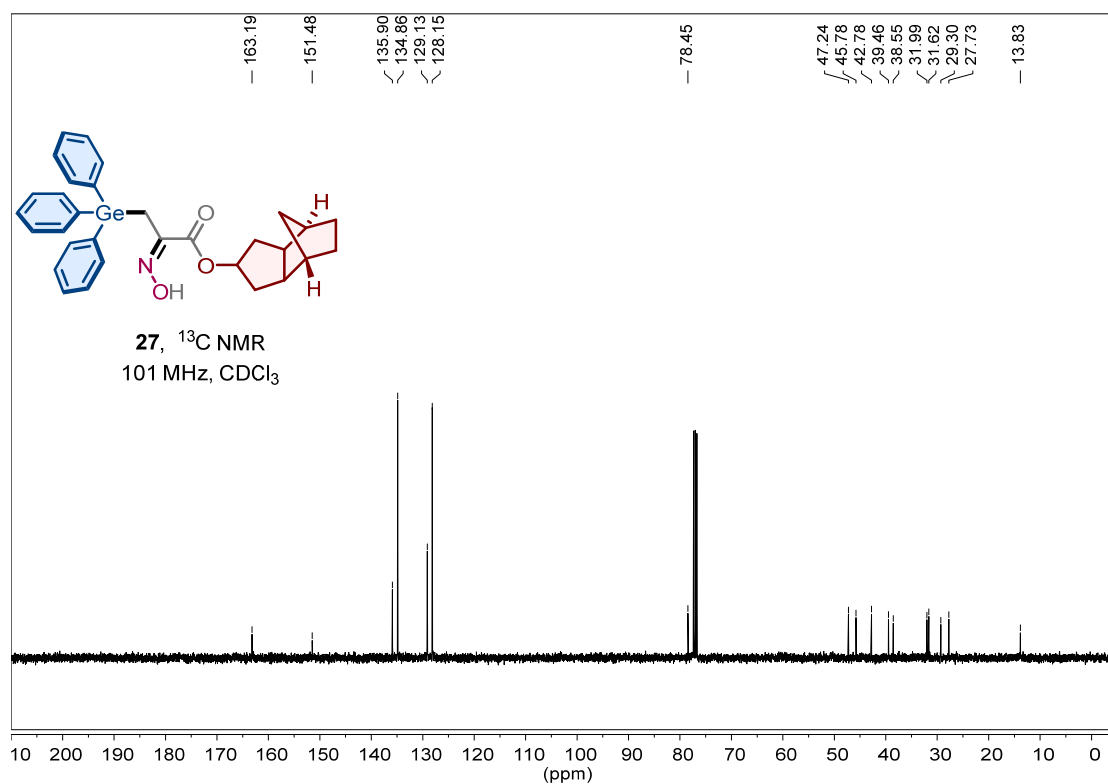
^1H NMR spectrum of **26**



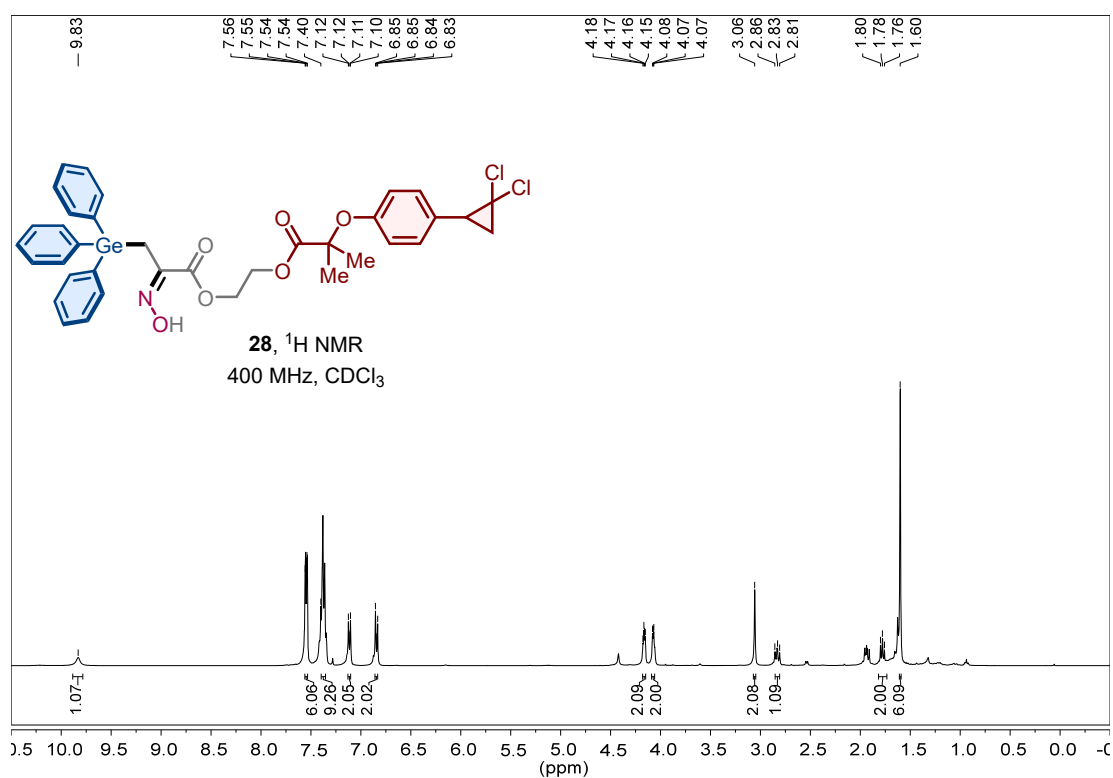
^{13}C NMR spectrum of **26**



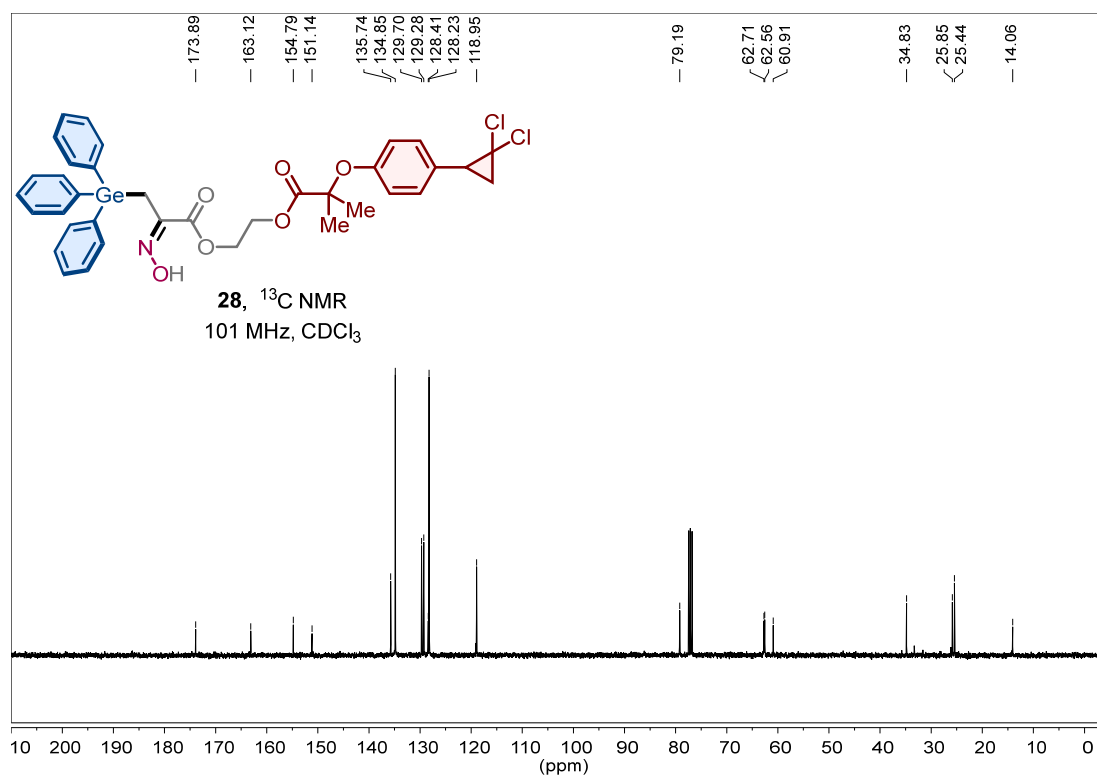
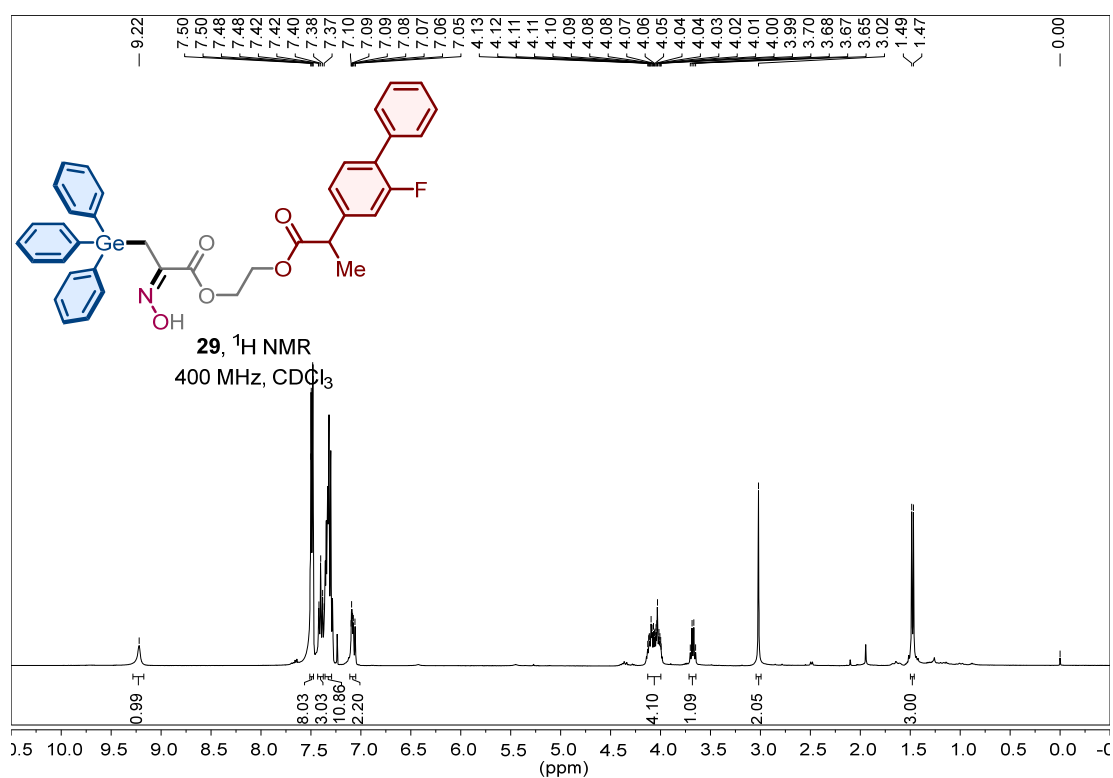
^1H NMR spectrum of **27**

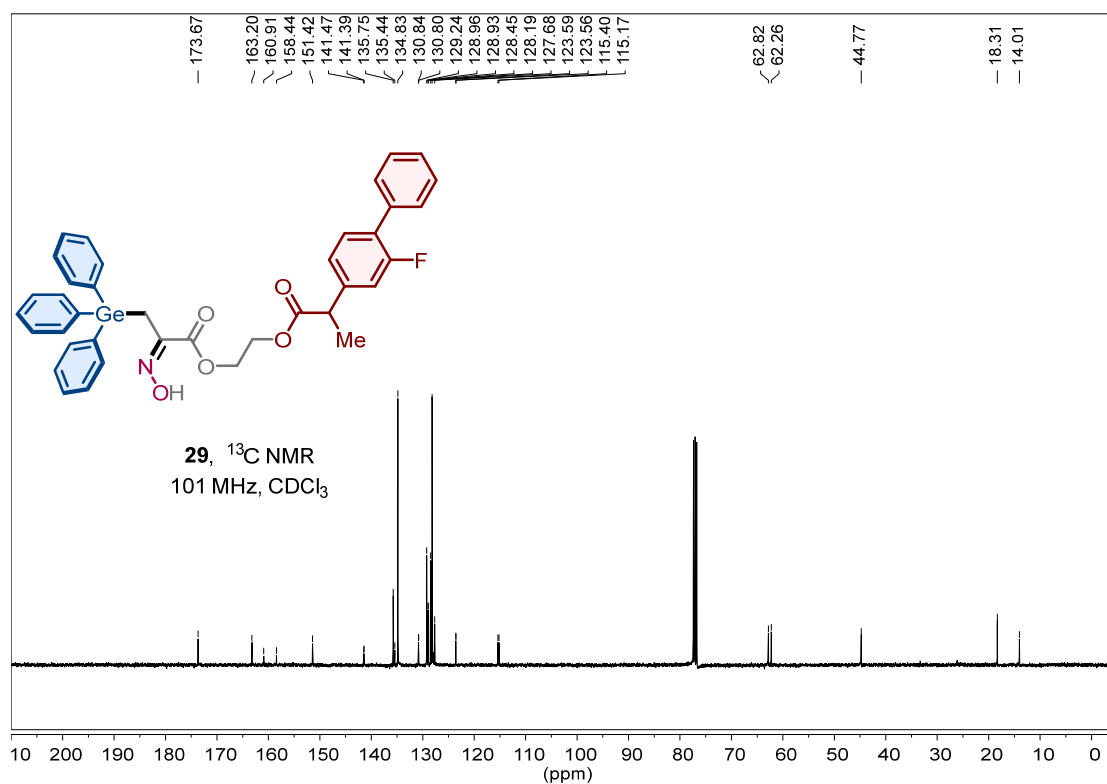


^{13}C NMR spectrum of **27**

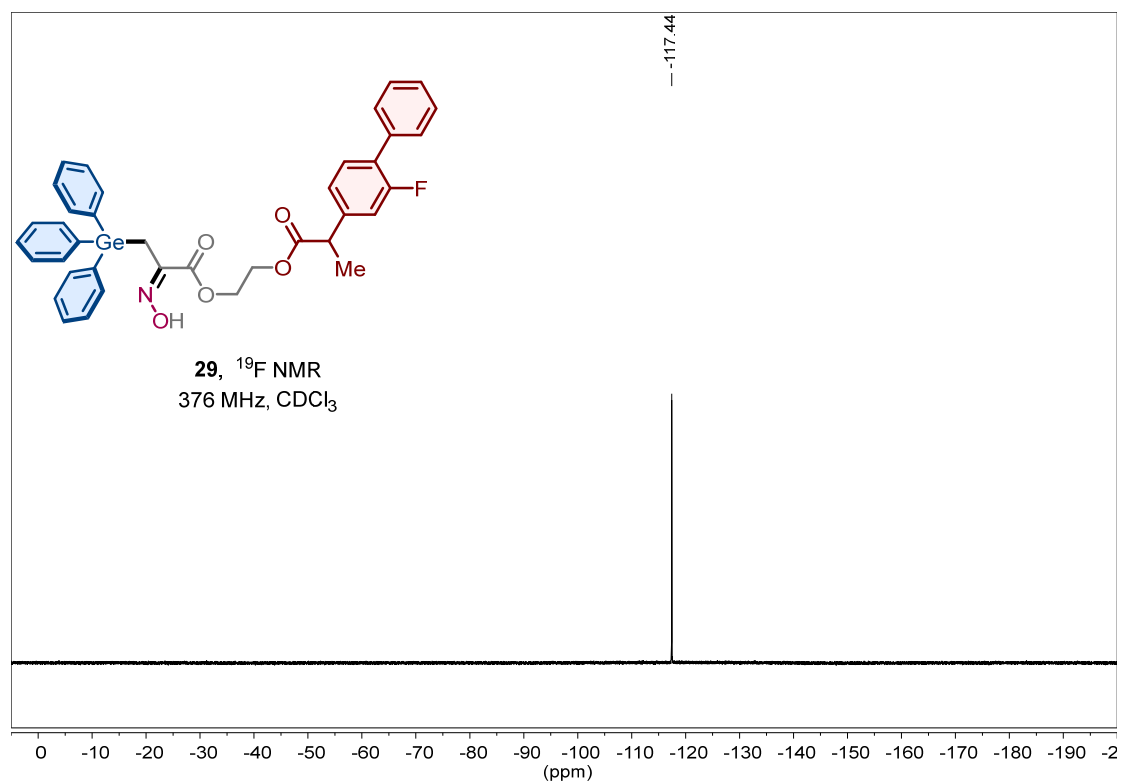


^1H NMR spectrum of **28**

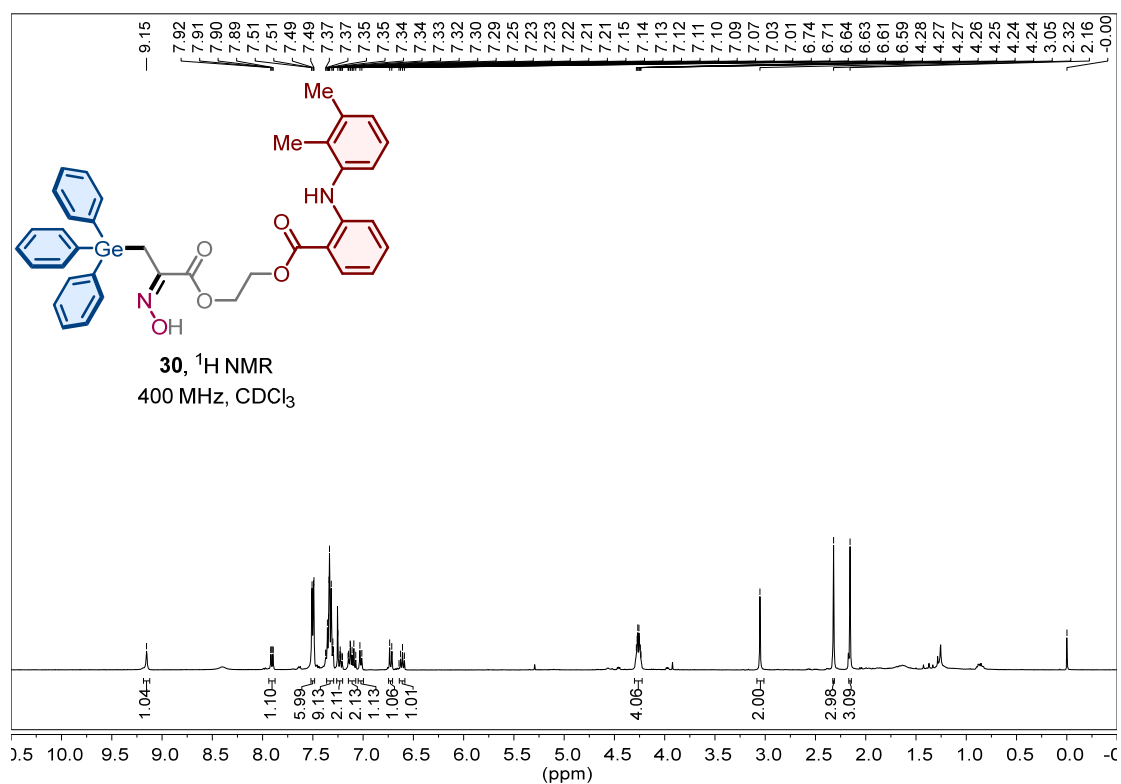
 ^{13}C NMR spectrum of **28**¹H NMR spectrum of **29**



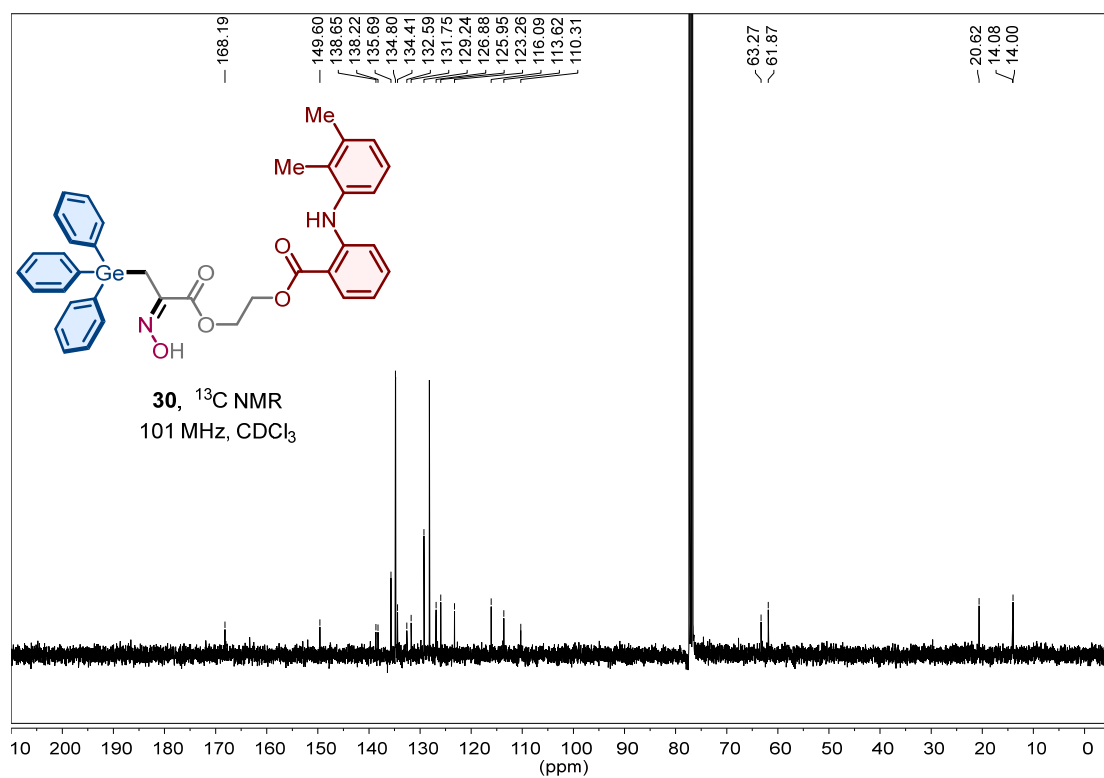
^{13}C NMR spectrum of **29**



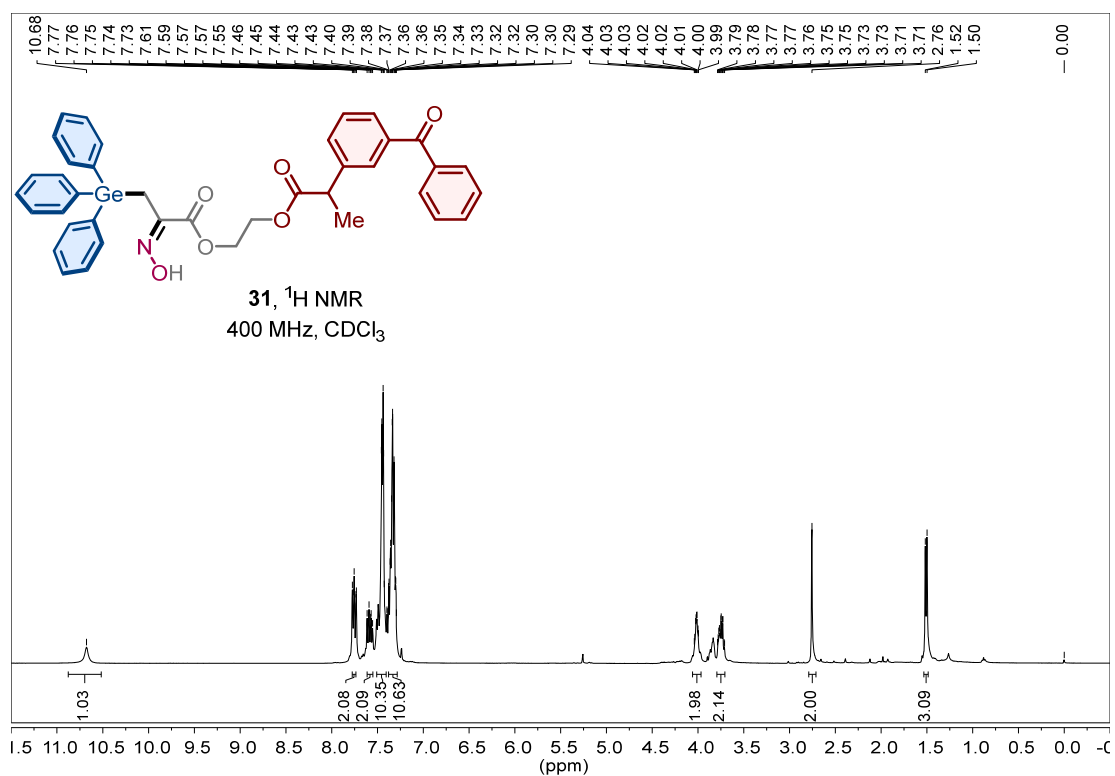
^{19}F NMR spectrum of **29**



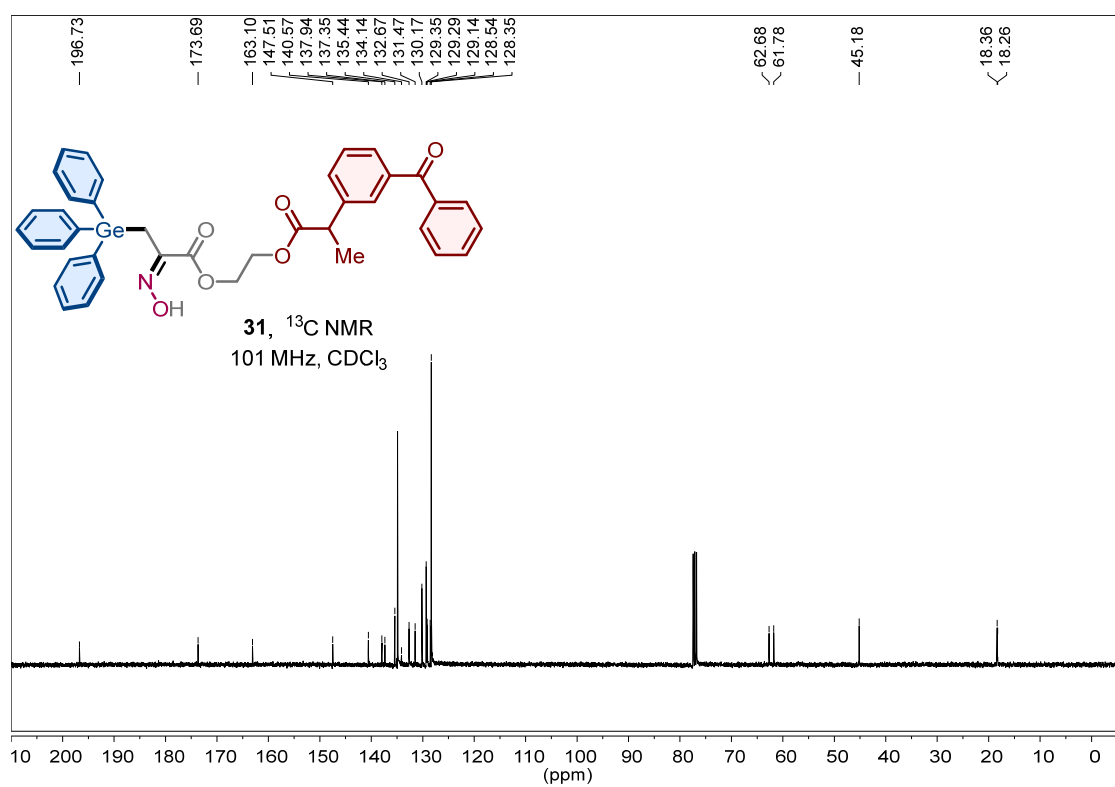
^1H NMR spectrum of **30**



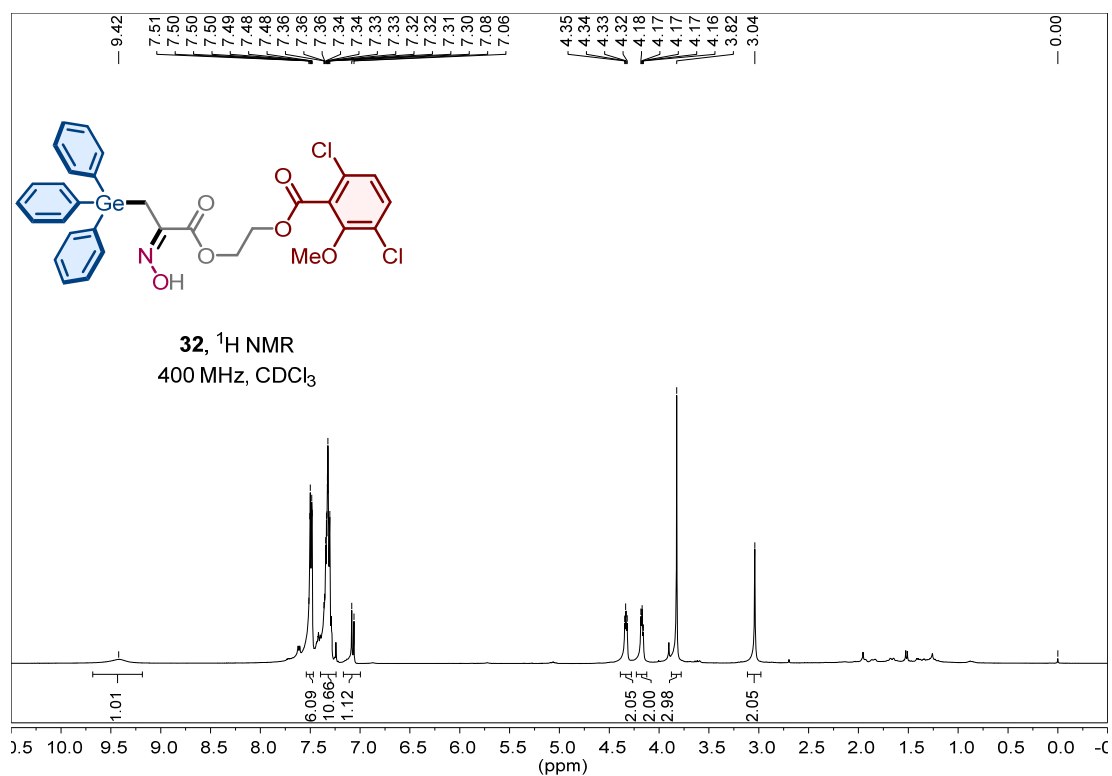
^{13}C NMR spectrum of **30**



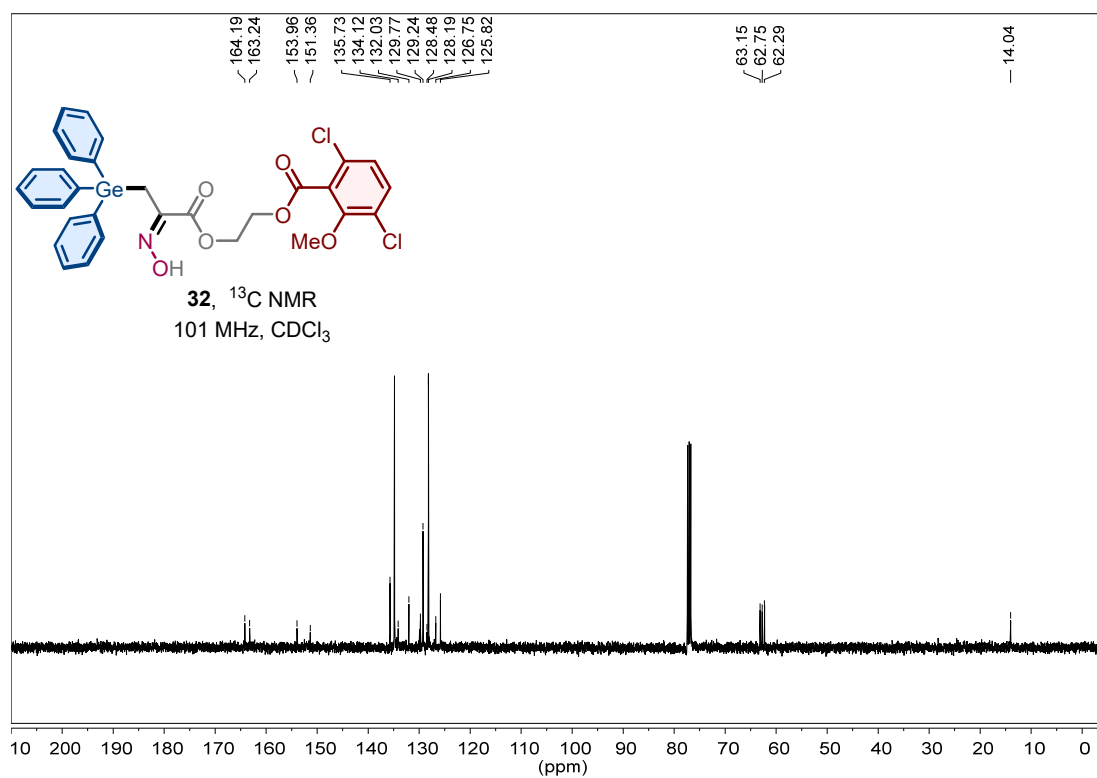
^1H NMR spectrum of **31**



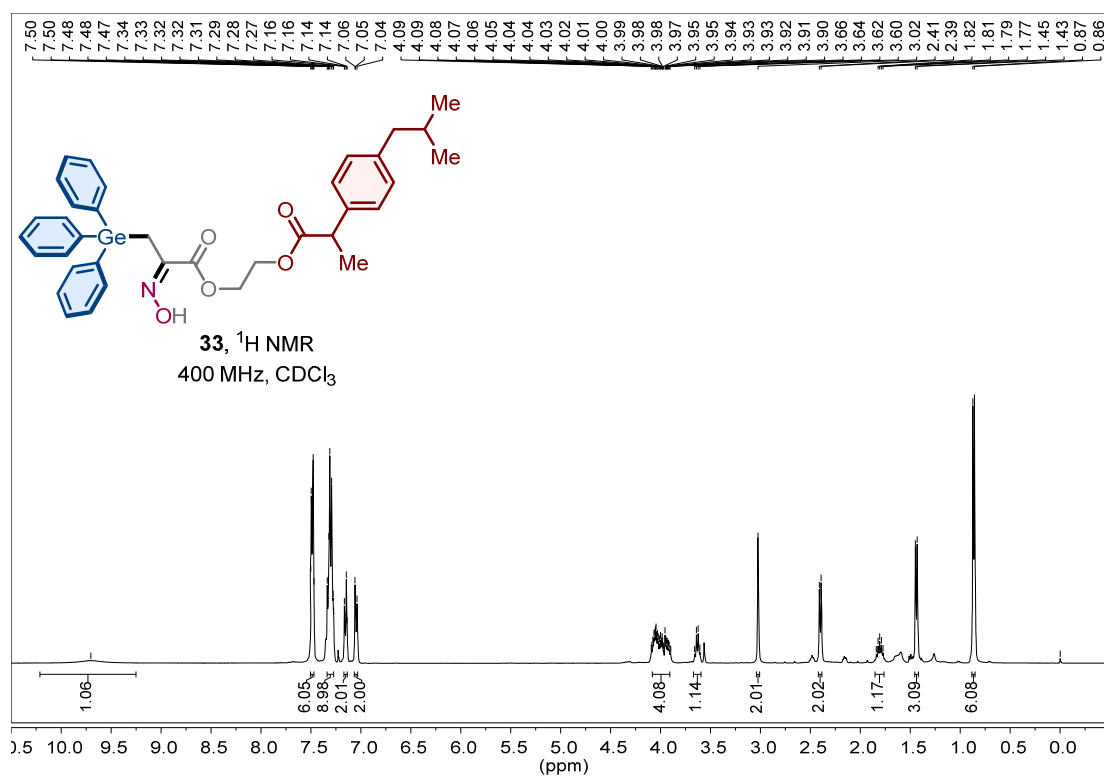
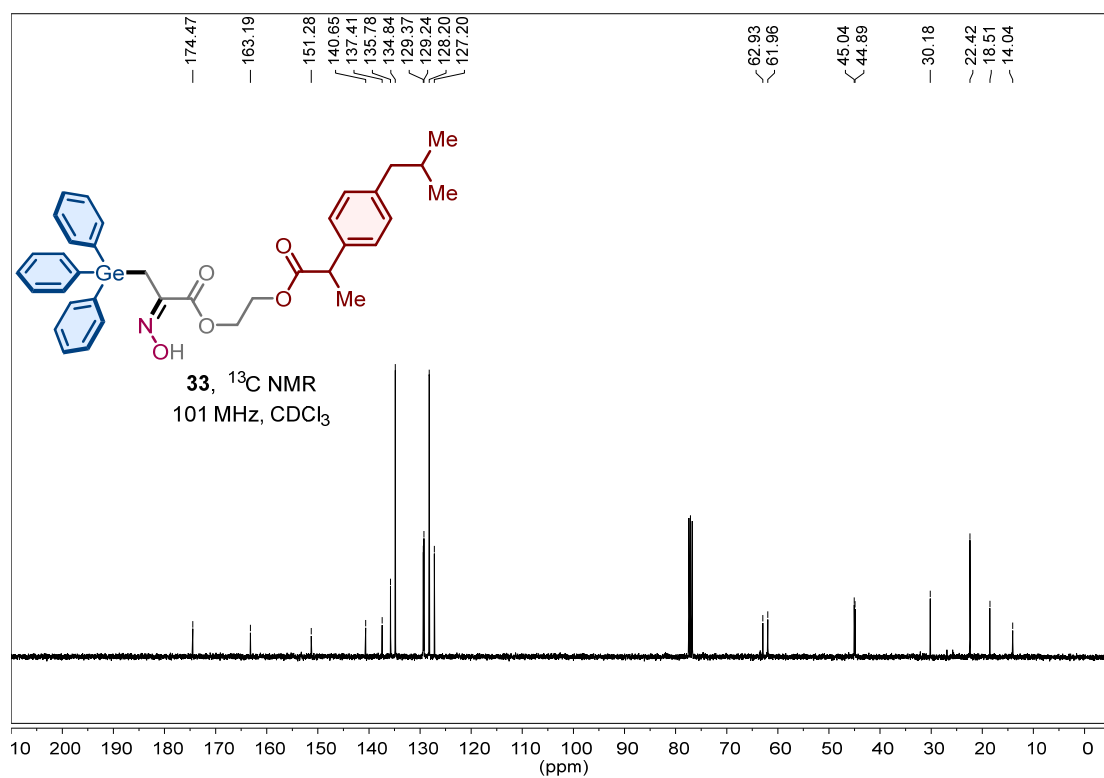
^{13}C NMR spectrum of **31**



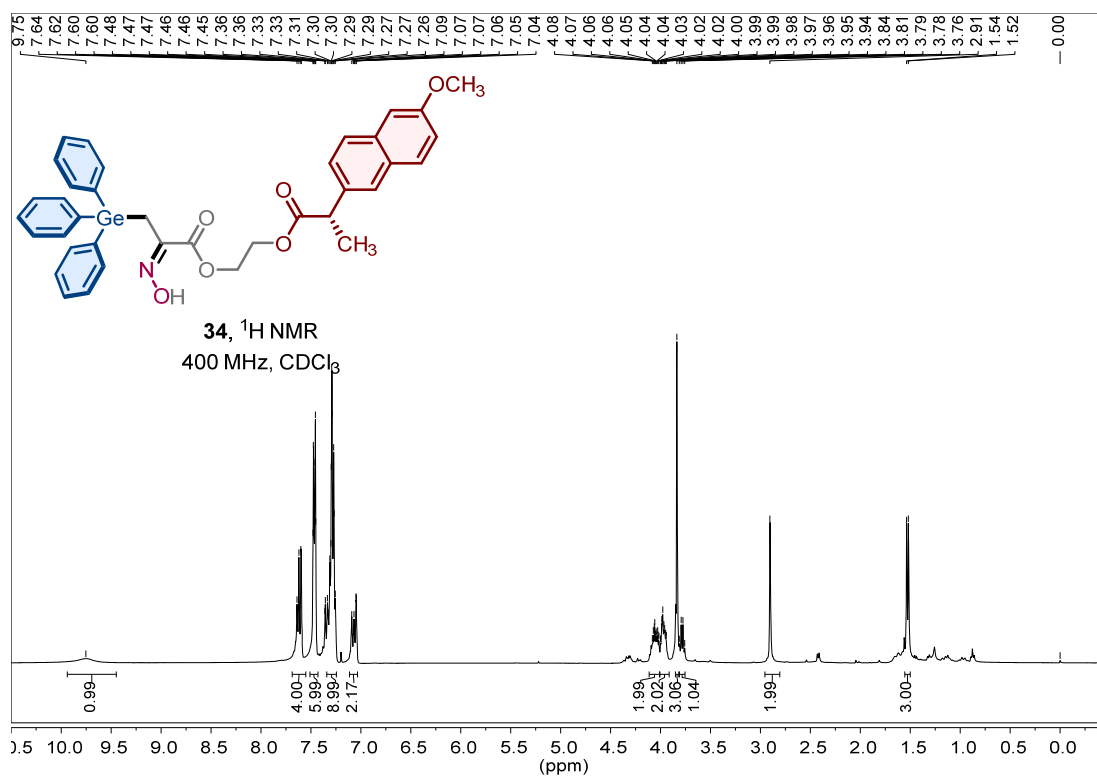
^1H NMR spectrum of **32**



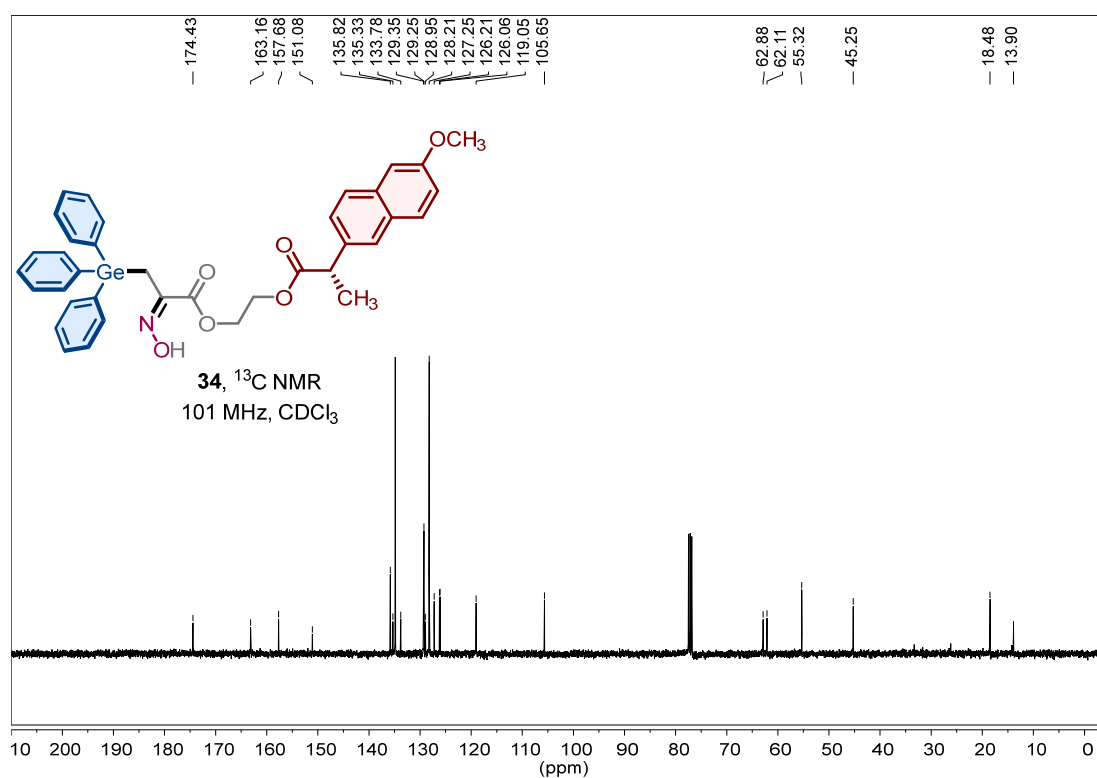
^{13}C NMR spectrum of **32**

¹H NMR spectrum of **33**

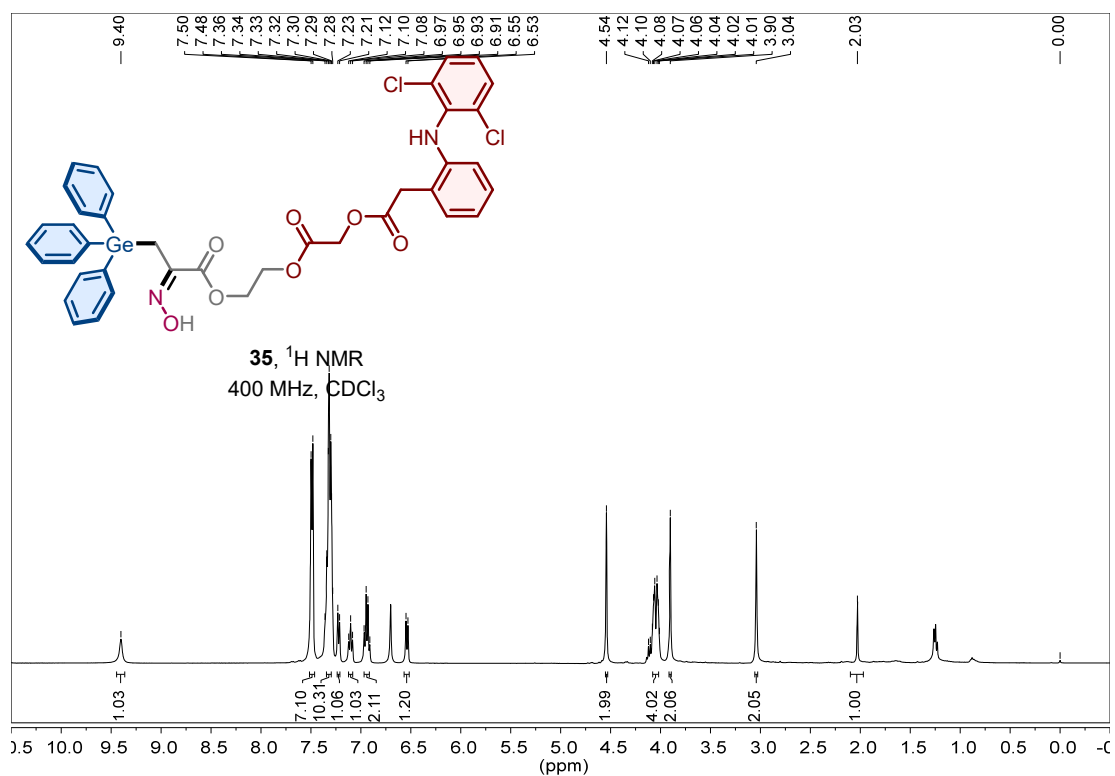
¹³C NMR spectrum of **33**



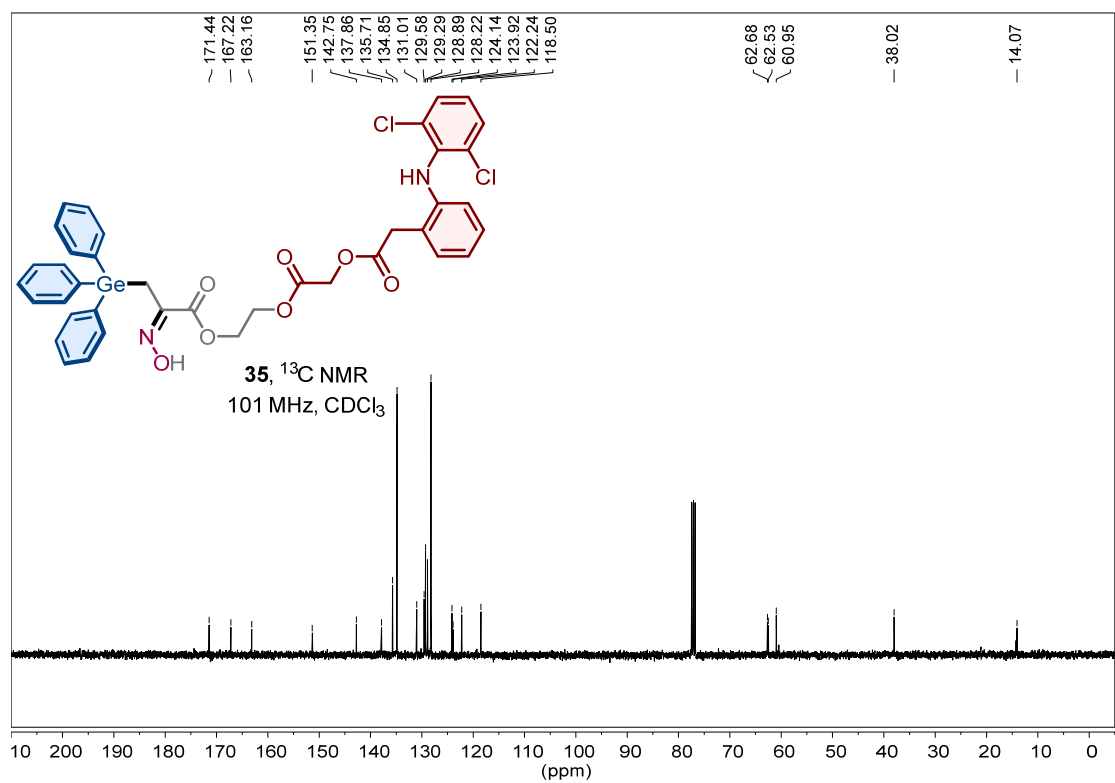
^1H NMR spectrum of **34**



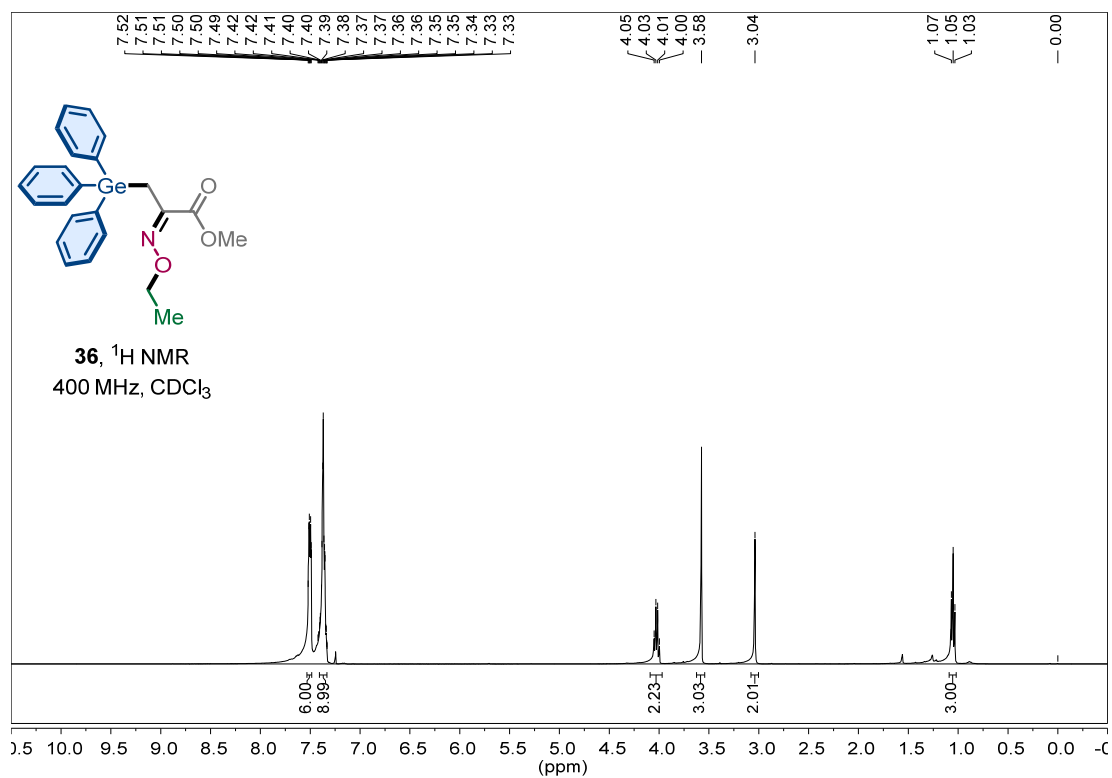
^{13}C NMR spectrum of **34**



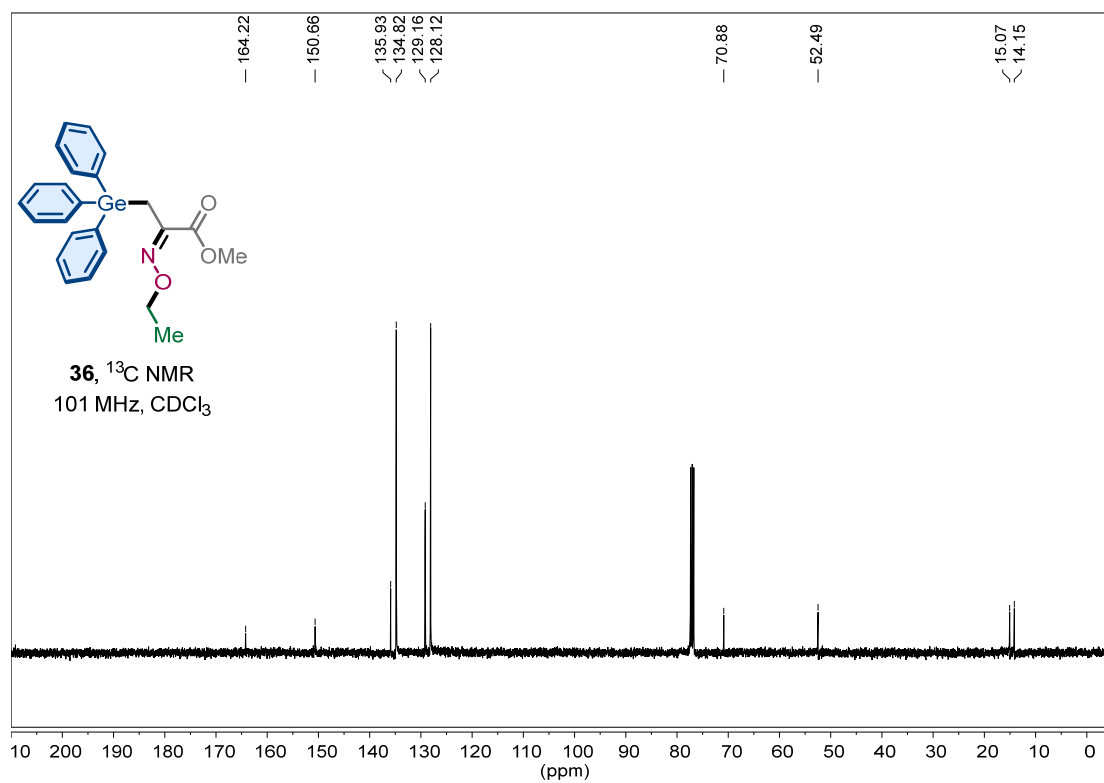
^1H NMR spectrum of **35**



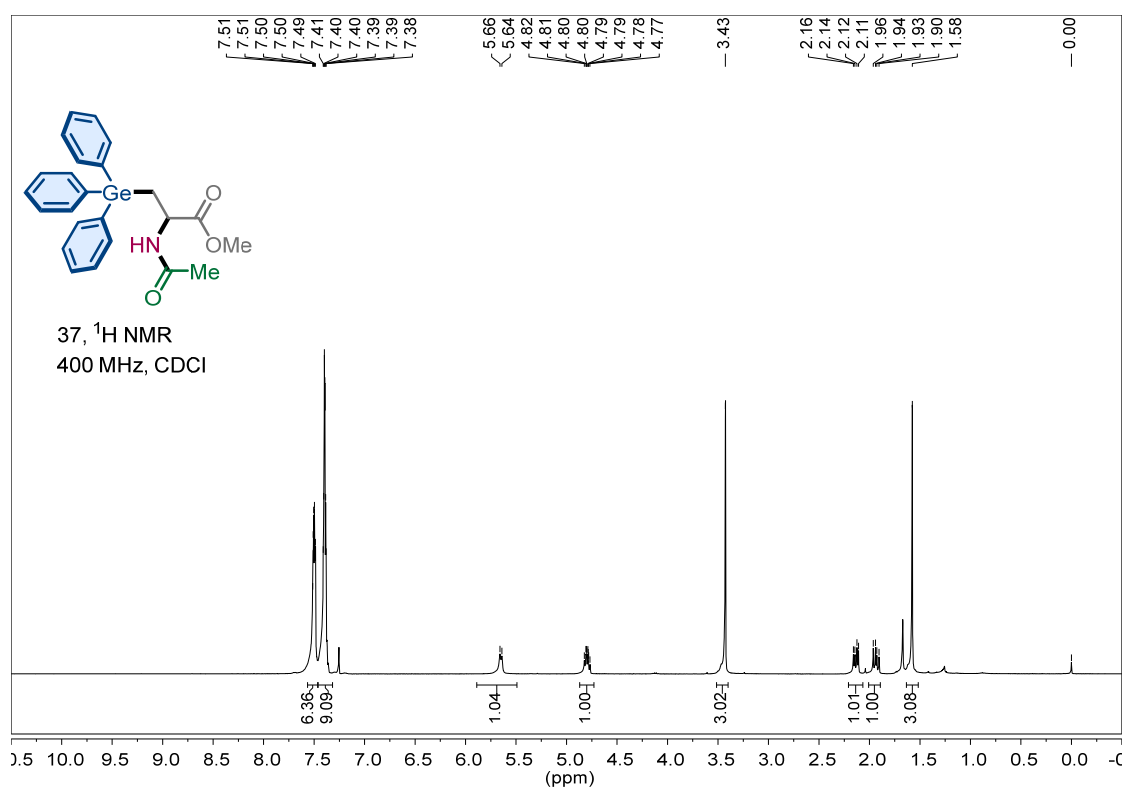
^{13}C NMR spectrum of **35**



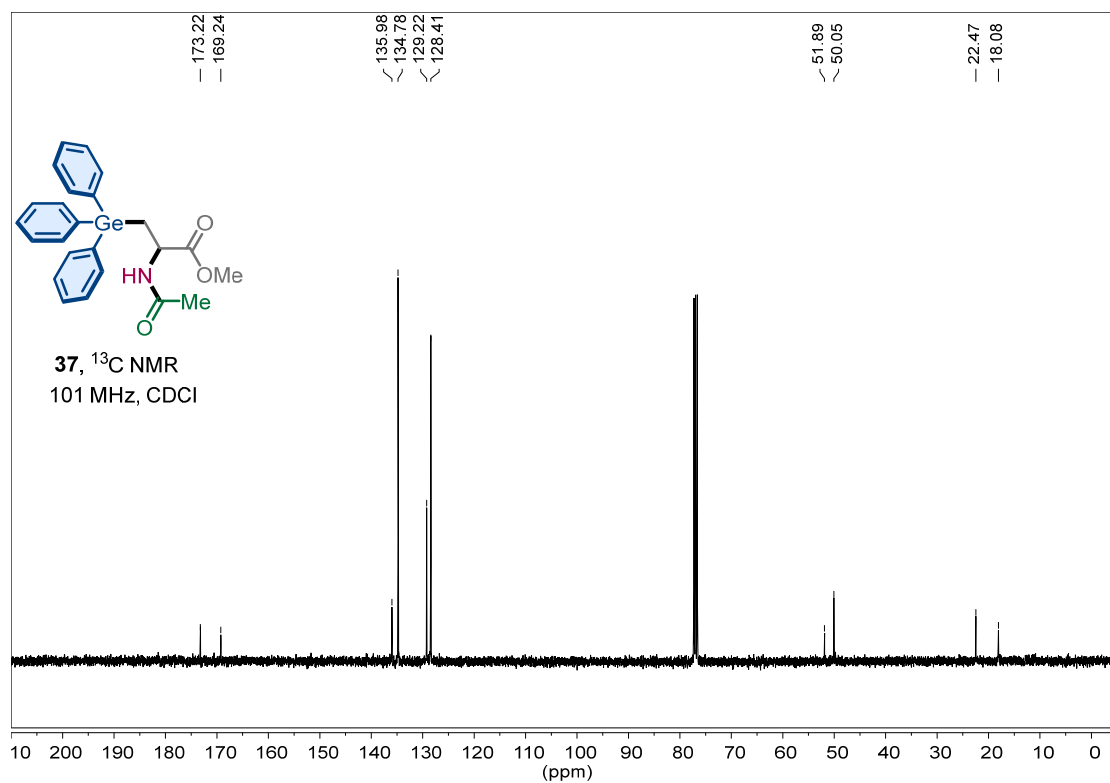
^1H NMR spectrum of **36**



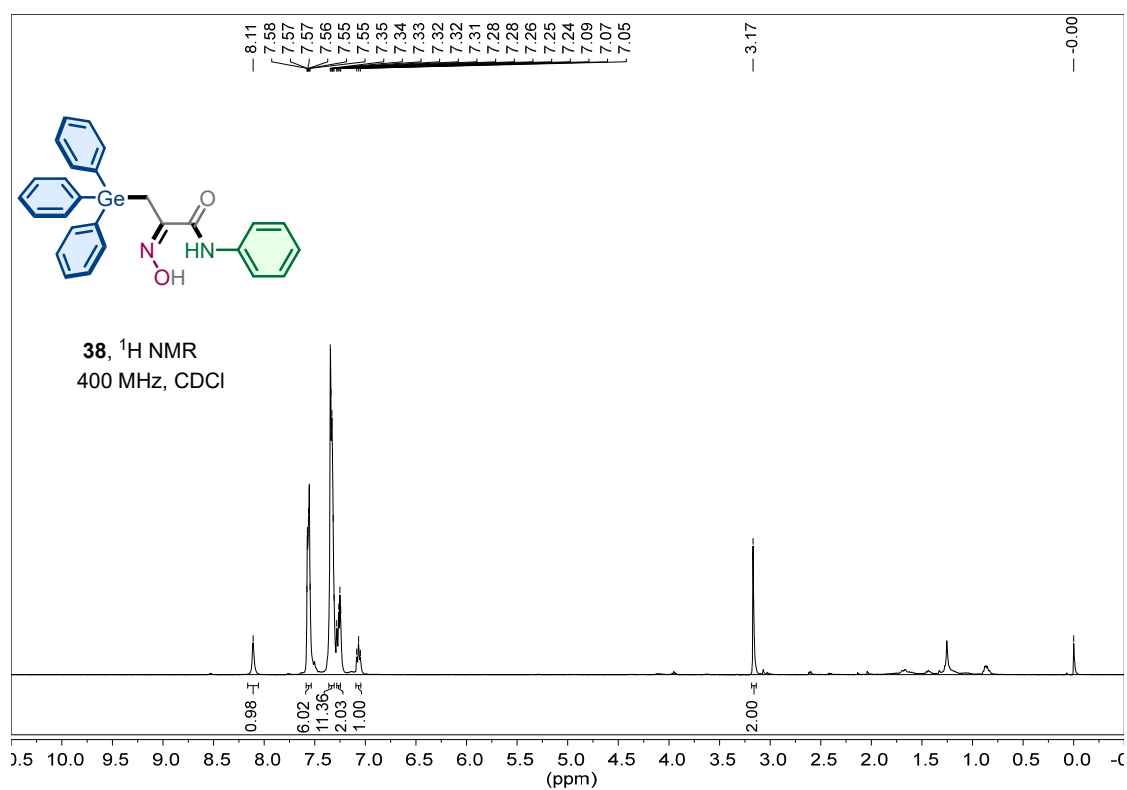
^{13}C NMR spectrum of **36**



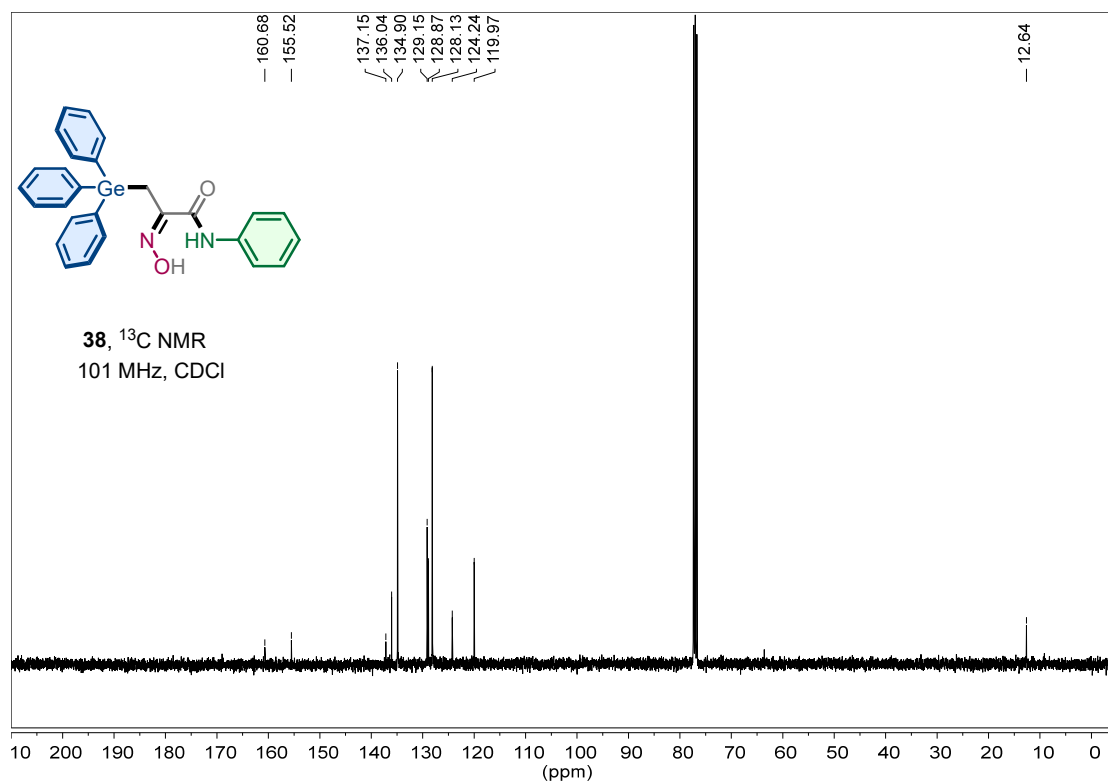
^1H NMR spectrum of **37**



^{13}C NMR spectrum of **37**



^1H NMR spectrum of **38**



^{13}C NMR spectrum of **38**

5 References

- S1. K. V. Zaitsev, A. V. Kharcheva, K. Lam, Z. Zhanabil, G. Issabayeva, Y. F. Oprunenko, A. V. Churakov, G. S. Zaitseva and S. S. Karlov, Donor-acceptor molecular oligogermanes: novel properties and structural aspects. *J. Organomet. Chem.* **2018**, 867, 228-237.
- S2. M. L. Amadoruge, E. K. Short, C. Moore, A. L. Rheingold and C. S. Weinert, Structural, spectral, and electrochemical investigations of para-tolyl-substituted oligogermanes. *J. Organomet. Chem.* **2010**, 695, 1813-182314.
- S3. S. Plöger and A. Studer, Visible-Light-Mediated Radical Silyl-Oximation of Activated Alkenes Using *tert*-Butyl Nitrite and Silanes. *Org. Lett.* **2022**, 24, 8568-857246.
- S4. P. J. Carmichael, B. G. Gowenlock and C. A. F. Johnson, Carbon–nitrogen bond dissociation energy values in C-nitrosocompounds. *Int. J. Chem. Kinet.* **2004**, 4, 339-3433.
- S5. L. Batt, K. Christie, R. T. Milne and A. J. Summers, Heats of formation of C1–C4 alkyl nitrites (RONO) and their RO–NO bond dissociation energies. *Int. J. Chem. Kinet.* **2004**, 6, 877-8856.
- S6. P. J. Carmichael, B. G. Gowenlock and C. A. F. Johnson, C–N Bond Dissociation Energies in Some Halogenated C-Nitroso-compounds and in Di-*t*-Butyl Nitroxide. *J. Chem. Soc., Perkin Trans. 2*, **1973**, 14, 1853-1856.
- S7. Z.-y. Liu, Y. Pan, P. Zou, H.-c. Huang, Y. Chen and Y. Chen, Hypervalent Iodine Reagents Enable C–H Alkynylation with Iminophenylacetic Acids via Alkoxy Radicals. *Org. Lett.* **2022**, 24, 5951-595632.
- S8. S. Y. Kim and H. N. Lim, Methyl Pyruvate Oxime as a Carbonyl Synthon: Synthesis of Ureas, Carbamates, Thiocarbamates, and Anilides. *Org. Lett.* **2024**, 26, 3850-385418.