Supporting Information

Facile synthesis of β-germyl-α-amino amides via Pd(II)-catalyzed primary and secondary C(sp^3)–H bonds germylation

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1. General Information

Toluene was dried by Sodium, distilled under reduced pressure and stored under nitrogen. $Pd(OAc)_2$ (Stream), Ag_2CO_3 (Adamas), BINA-PO_2H (Adamas) were purchased from above mentioned company and used without additional purification. Other chemical reagents were commercially available and directly used without any further purification. NMR spectra were recorded on a Bruke Avance operating for ^1H NMR at 400 MHz, ^{13}C NMR at 100 MHz, and ^{19}F NMR at 376 MHz, using TMS as internal standard. The peaks were internally referenced to TMS (0.00 ppm) or residual undeuterated solvent signal (7.26 ppm for ^1H NMR and 77.16 ppm for ^{13}C NMR). The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet, b = broad. High resolution mass spectroscopy (HRMS) analyses were performed at a Thermo Scientific Exactive Plus. Inc mass instrument (ESI).

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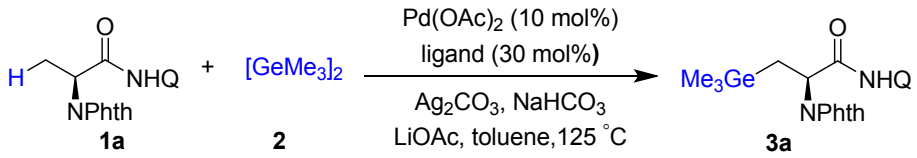
2. Experimental Section

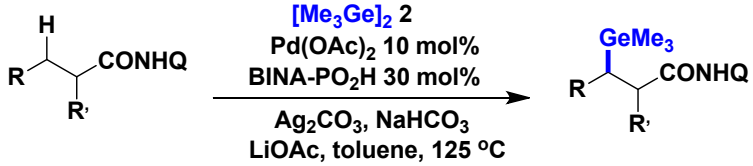
2.1 Optimization for C(sp^3)-H Germylation



Entry[a]	Ligand	$[GeMe_3]_2$	Yield of 3a
1	AdCOOH	5.0 eq.	37%
2	PivOH	5.0 eq.	42%
3	$MesCO_2H$	5.0 eq.	46%
4	N-Boc-Val-OH	5.0 eq.	55%
5	N-Boc-Ile-OH	5.0 eq.	58%
6	N-Boc-Ala-OH	5.0 eq.	45%
7	BINA-PO_2H	5.0 eq.	71%[b]
8	BINA-PO_2H	3.0 eq.	38%
9	BINA-PO_2H	1.5 eq.	20%

[a] The reactions were carried out **1a** (0.10 mmol), **2** (0.50 mmol), $Pd(OAc)_2$ (0.010 mmol), ligand (0.03 mmol), Ag_2CO_3 (0.20 mmol), $NaHCO_3$ (0.20 mmol), LiOAc (0.05 mmol), toluene (1.0 mL), air, 125 °C, 12 h. Yield of ^1H NMR. [b] Isolated yield.

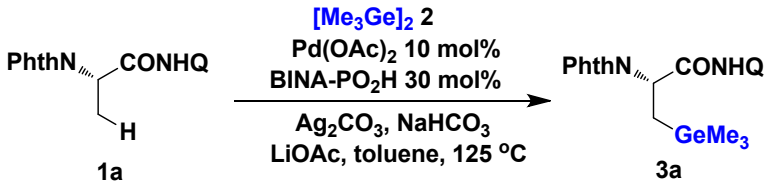
2.2 General Procedure for C(sp^3)-H Germylation



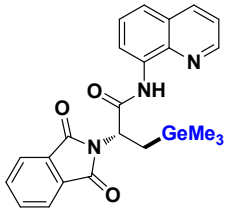
To an oven-dried 50 mL screw-capped vial was added substrate amides (0.15 mmol), hexamethylgermane (0.75 mmol), $Pd(OAc)_2$ (3.5 mg, 0.015 mmol), BINA-PO_2H (15.2 mg, 0.045 mmol), Ag_2CO_3 (82.8 mg, 0.3 mmol), $NaHCO_3$ (25.2 mg, 0.3 mmol), LiOAc (4.7 mg, 0.075 mmol), toluene (1.0 mL). The mixture was stirred for 10 h at 125 °C under air followed by cooling. The resulting mixture was filtered through a

celite pad and concentrated in *vacuo*. The residue was purified by preparative TLC using hexane/EtOAc as the eluent to afford the product**.**

2.3 Scale-up Reaction for C(sp^3)-H Germylation

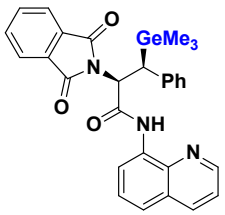


To an oven-dried 50 mL screw-capped vial was added substrate amides (1.0 mmol), hexamethylgermane (5.0 mmol), $Pd(OAc)_2$ (23 mg, 0.1 mmol), BINA-PO_2H (0.3 mmol), Ag_2CO_3 (2.0 mmol), $NaHCO_3$ (2.0 mmol), LiOAc (1.0 mmol), toluene (5.0 mL). The mixture was stirred for 24 h at 125 °C under air followed by cooling. The resulting mixture was filtered through a celite pad and concentrated in *vacuo*. The residue was purified by flash column chromatography using hexane/EtOAc as the eluent to afford the product **3a** in 65% yield**.**



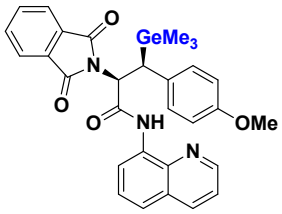
(R)-2-(1,3-dioxoisoindolin-2-yl)-N-(quinolin-8-yl)-3-(trimethylgermyl)propanamide 3a

^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.47 (br, 1H), 8.75 (dd, *J*=4.4, 1.6, 1H), 8.72 (t, *J*=4.4, 1H), 8.14 (dd, *J*=8.4, 1.6, 1H), 7.89 (dd, *J*=5.6, 3.1, 2H), 7.74 (dd, *J*=5.6, 3.1, 2H), 7.50 (d, *J*=4.4, 2H), 7.43 (dd, *J*=8.4, 4.4, 1H), 5.23 (dd, *J*=12.0, 5.6, 1H), 2.20 (dd, *J*=13.6, 12.0, 1H), 1.80 (dd, *J*=13.6, 5.6, 1H), 0.18 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 168.37, 168.19, 148.51, 138.75, 136.41, 134.34, 134.20, 132.11, 128.03, 127.45, 123.71, 122.00, 121.74, 116.79, 53.25, 17.21, -1.80; **HRMS** (EI-TOF) calcd for $C_{23}H_{23}N_3O_3GeNa$ $(M+Na)^+$: 486.0843, found: 486.0833.



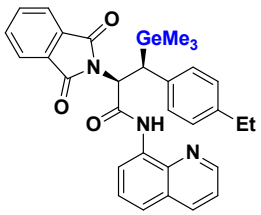
(2R,3S)-2-(1,3-dioxoisoindolin-2-yl)-3-phenyl-N-(quinolin-8-yl)-3-(trimethylgermyl)propanamide 3b

^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.85 (s, 1H), 8.90 (dd, *J*=4.4, 1.6, 1H), 8.80 (dd, *J*=5.6, 3.2, 1H), 8.14 (dd, *J*=8.4, 1.6, 1H), 7.71-7.68 (m, 2H), 7.59-7.53-7.50 (m, 2H), 7.53-7.50 (m, 2H), 7.45 (dd, *J*=8.4, 4.4, 1H), 7.14-7.08 (m, 4H), 6.97-6.93 (m, 1H), 5.64 (d, *J*=13.6, 1H), 4.00 (d, *J*=13.6, 1H), 0.13 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 168.24, 167.14, 148.78, 140.29, 138.93, 136.28, 134.56, 134.06, 131.44, 128.43, 128.06, 127.38, 125.41, 123.45, 122.23, 121.77, 117.39, 59.42, 36.62, -2.19; **HRMS** (EI-TOF) calcd for $C_{29}H_{27}N_3O_3Ge$ Na $(M+Na)^+$: 562.1162, found: 562.1147.



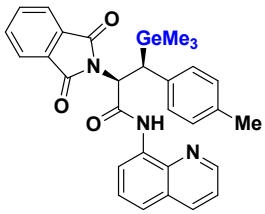
(2R,3S)-2-(1,3-dioxoisoindolin-2-yl)-3-(4-methoxyphenyl)-N-(quinolin-8-yl)-3-(trimethylgermyl)propanamide 3c

dr~15:1 estimated by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$)δ = 10.86 (br, 1H), 8.90 (dd, *J*=4.4, 1.6, 1H), 8.79 (dd, *J*=5.6, 3.2, 1H), 8.14 (dd, *J*=8.4, 1.6, 1H), 7.71 (dd, *J*=5.6, 3.0, 2H), 7.58 (dd, *J*=5.6, 3.0, 2H), 7.52-7.50 (m, 2H), 7.45 (dd, *J*=8.4, 4.4, 1H), 5.57 (d, *J*=13.6, 1H), 3.93 (d, *J*=13.6, 1H), 3.66 (s, 3H), 0.12 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 168.26, 167.22, 157.33, 148.76, 138.93, 136.26, 134.58, 134.07, 132.19, 131.47, 128.06, 127.38, 123.47, 122.21, 121.75, 117.39, 113.89, 59.71, 55.18, 35.54, -2.21; **HRMS** (EI-TOF) calcd for $C_{30}H_{29}N_3O_4GeNa$ $(M+Na)^+$: 592.1268, found: 592.1254.



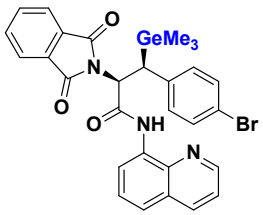
(2R,3S)-2-(1,3-dioxoisoindolin-2-yl)-3-(4-ethylphenyl)-N-(quinolin-8-yl)-3-(trimethylgermyl)propanamide 3d

^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.86 (br, 1H), 8.90 (dd, *J*=4.4, 1.6, 1H), 8.80 (dd, *J*=5.6, 3.2, 1H), 8.14 (dd, *J*=8.4, 1.6, 1H), 7.70 (dd, *J*=5.6, 3.2, 2H), 7.57 (dd, *J*=5.6, 3.2, 2H), 7.53-7.51 (m, 2H), 7.45 (dd, *J*=8.4, 4.4, 1H), 6.99 (d, *J*=8.4, 2H), 6.93 (d, *J*=8.0, 2H), 5.61 (d, *J*=13.6, 1H), 3.95 (d, *J*=13.6, 1H), 2.44 (d, *J*=7.6, 2H), 1.04 (t, *J*=7.6, 3H), 0.13 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 168.30, 167.28, 148.77, 141.18, 138.95, 137.15, 136.26, 134.61, 133.98, 131.53, 128.06, 127.83, 127.38, 123.42, 122.20, 121.75, 117.40, 59.69, 36.15, 28.33, 15.44, -2.17; **HRMS** (EI-TOF) calcd for $C_{31}H_{31}N_3O_3Ge$ Na $(M+Na)^+$: 590.1475, found: 590.1460.



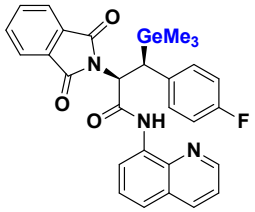
(2R,3S)-2-(1,3-dioxoisoindolin-2-yl)-N-(quinolin-8-yl)-3-(p-tolyl)-3-(trimethylgermyl)propanamide 3e

dr ~ 12.5:1 estimated by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$)δ = 10.86 (br, 1H), 8.90 (dd, *J*=4.4, 1.6, 1H), 8.79 (dd, *J*=5.6, 3.2, 1H), 8.14 (dd, *J*=8.4, 1.6, 1H), 7.70 (td, *J*=5.6, 2.4, 2H), 7.58 (dd, *J*=5.6, 3.2, 2H), 7.53-7.50 (m, 2H), 7.45 (dd, *J*=8.4, 4.4, 1H), 6.98 (d, *J*=8.0, 2H), 6.92 (d, *J*=8.0, 2H), 5.61 (d, *J*=13.6, 1H), 3.96 (d, *J*=13.6, 1H), 2.15 (s, 3H), 0.12 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 168.25, 167.24, 148.77, 138.95, 136.93, 136.26, 134.74, 134.60, 134.01, 131.52, 129.14, 128.06, 127.38, 123.47, 122.20, 121.75, 117.39, 59.61, 36.08, 21.02, -2.21; **HRMS** (EI-TOF) calcd for $C_{30}H_{29}N_3O_3Ge$ Na $(M+Na)^+$: 576.1318, found: 576.1302.



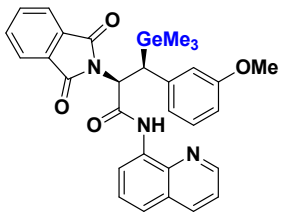
(2R,3S)-3-(4-bromophenyl)-2-(1,3-dioxoisoindolin-2-yl)-N-(quinolin-8-yl)-3-(trimethylgermyl)propanamide 3f

dr ~ 4:1 estimated by ^{1}H NMR. ^{1}H NMR of main product (400 MHz, $CDCl_3$) δ = 10.78 (br, 1H), 8.88 (dd, *J*=4.4, 1.6, 1H), 8.79-8.76 (m, 1H), 8.14 (dd, *J*=8.4, 1.6, 1H), 7.73 (dd, *J*=5.6, 3.2, 2H), 7.62 (dd, *J*=5.6, 3.2, 2H), 7.52 (d, *J*=4.0, 2H), 7.45 (dd, *J*=8.4, 4.4, 1H), 7.27-7.25 (m, 2H), 6.98 (d, *J*=8.4, 2H), 5.58 (d, *J*=13.6, 1H), 4.00 (d, *J*=13.6, 1H), 0.13 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 168.19, 166.76, 148.79, 139.63, 138.89, 136.31, 134.44, 134.27, 134.07, 131.59, 131.36, 128.44, 128.07, 127.39, 123.63, 123.47, 122.33, 121.81, 119.03, 117.39, 58.95, 36.12, -2.19, -2.22; **HRMS** (EI-TOF) calcd for $C_{29}H_{26}BrN_3O_3Ge$ Na $(M+Na)^+$: 640.0267, found: 640.0248.



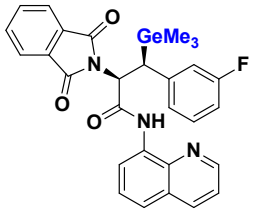
(2R,3S)-2-(1,3-dioxoisoindolin-2-yl)-3-(4-fluorophenyl)-N-(quinolin-8-yl)-3-(trimethylgermyl)propanamide 3g

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.82 (s, 1H), 8.88 (dd, *J* = 4.0, 1.6 Hz, 1H), 8.79 (dd, *J* = 5.2, 3.6 Hz, 1H), 8.14 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.72 (dd, *J* = 5.6, 3.2 Hz, 2H), 7.61 (dd, *J* = 5.6, 3.2 Hz, 2H), 7.45 (dd, *J* = 8.4, 4.2 Hz, 1H), 7.05 (dd, *J* = 8.8, 5.2 Hz, 2H), 6.83 (t, *J* = 8.8 Hz, 2H), 5.58 (d, *J* = 13.6 Hz, 1H), 3.98 (d, *J* = 13.6 Hz, 1H), 0.14 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.20, 166.90, 160.85, 148.78, 138.91, 136.30, 136.12(d, *J* = 3.1 Hz),134.49, 134.22, 131.36, 128.94, 128.06, 127.39, 123.54, 122.04 (d, *J* = 50.1 Hz), 117.38, 115.33(d, *J* = 21.1 Hz), 59.39, 35.76, -2.21; ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.79; **HRMS** (EI-TOF) calcd for $C_{29}H_{26}FN_3O_3GeNa$ $(M+Na)^+$: 580.1068, found: 580.1057.



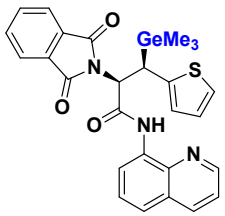
(2R,3S)-2-(1,3-dioxoisoindolin-2-yl)-3-(3-methoxyphenyl)-N-(quinolin-8-yl)-3-(trimethylgermyl)propanamide 3h

D.r. = 15:1 estimated by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.86 (br, 1H), 8.89 (dd, *J*=4.4, 1.6, 1H), 8.80 (dd, *J*=5.6, 3.2, 1H), 8.14 (dd, *J*=8.4, 1.6, 1H), 7.71 (dd, *J*=5.6, 3.2, 2H), 7.58 (dd, *J*=5.6, 3.2, 2H), 7.53-7.51 (m, 2H), 7.45 (dd, *J*=8.4, 4.4, 1H), 5.73 (d, *J*=13.2, 0H), 5.63 (d, *J*=13.6, 1H), 3.98 (d, *J*=13.6, 1H), 3.71 (s, 3H), 0.15 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 168.23, 167.08, 159.56, 148.77, 141.90, 138.93, 136.27, 134.56, 134.08, 131.48, 129.38, 128.06, 127.37, 123.48, 122.23, 121.76, 117.40, 111.65, 59.37, 55.24, 36.75, -2.13; **HRMS** (EI-TOF) calcd for $C_{30}H_{29}N_3O_4Ge$ Na $(M+Na)^+$: 592.1268, found: 592.1254.



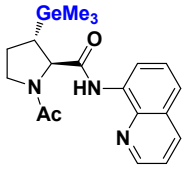
(2R,3S)-2-(1,3-dioxoisoindolin-2-yl)-3-(3-fluorophenyl)-N-(quinolin-8-yl)-3-(trimethylgermyl)propanamide 3i

dr~14:1 estimated by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.80 (br, 1H), 8.88 (dd, *J*=4.4, 1.6, 1H), 8.78 (dd, *J*=5.2, 4.0, 1H), 8.14 (dd, *J*=8.4, 1.6, 1H), 7.73 (dd, *J*=5.6, 3.1, 2H), 7.60 (dd, *J*=5.6, 3.2, 2H), 7.53-7.51 (m, 2H), 7.44 (dd, *J*=8.4, 4.2, 1H), 7.10 (td, *J*=8.0, 6.4, 1H), 6.88 (d, *J*=8.0, 1H), 6.82 (dt, *J*=10.0, 2.0, 1H), 6.67 (td, *J*=8.4, 2.0, 1H), 5.60 (d, *J*=13.5, 1H), 4.03 (d, *J*=13.6, 1H), 0.15 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 168.13, 166.75, 162.81 (d, *J*=244.2), 148.78, 143.27 (d, *J*=7.3), 138.87, 136.29, 134.43, 134.19, 131.36, 129.89, 128.04 (s, 3H), 127.36, 123.56, 122.31, 121.79, 117.36, 112.45 (d, *J*=21.1), 59.02, 36.59, -2.17; ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.97; **HRMS** (EI-TOF) calcd for $C_{29}H_{26}N_3O_3Ge$ Na $(M+Na)^+$: 580.1068, found: 580.1051.



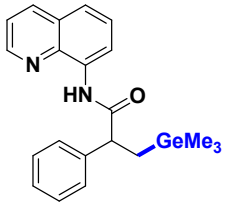
(2R,3R)-2-(1,3-dioxoisoindolin-2-yl)-N-(quinolin-8-yl)-3-(thiophen-2-yl)-3-(trimethylgermyl)propanamide 3j

dr ~ 4:1 estimated by ^{1}H NMR. ^{1}H NMR of the main product (400 MHz, $CDCl_3$) δ = 10.84 (s, 1H), 8.90 (dd, *J*=4.4, 1.6, 1H), 8.78 (t, *J*=4.4, 1H), 8.14 (dd, *J*=8.4, 1.6, 1H), 8.07 (dd, *J*=8.4, 1.6, 0H), 7.77-7.74 (m, 2H), 7.62 (dd, *J*=5.6, 3.2, 2H), 7.52 (d, *J*=4.4, 2H), 7.45 (dd, *J*=8.4, 4.4, 1H), 6.88 (d, *J*=5.2, 1H), 6.76-6.72 (m, 2H), 5.48 (d, *J*=13.2, 1H), 4.34 (d, *J*=13.2, 1H), 0.20 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 168.20, 166.67, 148.81, 143.39, 138.93, 136.28, 134.50, 134.15, 131.52, 128.06, 127.36, 126.82, 124.13, 123.92, 123.56, 122.34, 122.31, 121.78, 117.45, 60.76, 31.29, -2.20; **HRMS** (EI-TOF) calcd for $C_{27}H_{25}SN_3O_3GeNa$ $(M+Na)^+$: 568.0726, found: 568.0707.



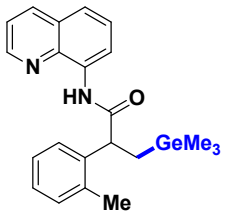
(2R,3S)-1-acetyl-N-(quinolin-8-yl)-3-(trimethylgermyl)pyrrolidine-2-carboxamide 3k

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.93 (br, 1H), 8.55 (dd, *J* = 4.0, 1.6 Hz, 1H), 8.31 (d, *J* = 8.4 Hz, 1H), 8.01 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.78 (dd, *J* = 12.4, 7.6 Hz, 2H), 7.59-7.37 (m, 5H), 7.29 (dd, *J* = 8.0, 4.0 Hz, 1H), 4.64 (t, *J* = 7.6 Hz, 1H), 1.82 (dd, *J* = 14.8, 7.2 Hz, 1H), 1.52 (dd, *J* = 14.8, 8.4 Hz, 1H), -0.06 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.29, 148.13, 138.54, 137.63, 136.16, 134.77, 134.40, 131.69, 129.19, 128.14, 127.89, 127.41, 126.61, 125.81, 125.77, 123.60, 121.50, 121.34, 116.17, 46.81, 20.75, -1.03; **HRMS** (EI-TOF) calcd for $C_{19}H_{25}N_3O_2Ge$ Na $(M+Na)^+$: 424.1056, found: 424.1037.



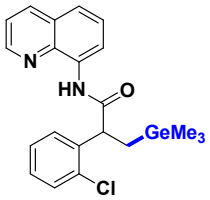
2-phenyl-N-(quinolin-8-yl)-3-(trimethylgermyl)propanamide 5a

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.93 (br, 1H),8.76- 8.74 (m, 2H), 8.10 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.51-7.24 (m, 8H), 3.85 (dd, *J* = 9.2, 7.2 Hz, 1H), 1.75 (dd, *J* = 13.6, 6.8 Hz, 1H), 1.51 (dd, *J* = 13.6, 9.2 Hz, 1H), 0.05 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.18, 148.26, 141.57, 138.64, 136.36, 134.76, 128.97, 128.09, 128.01, 127.51, 127.45, 121.62, 121.46, 116.40, 51.81, 21.39, -1.73; **HRMS** (EI-TOF) calcd for $C_{21}H_{24}N_2OGeNa$ $(M+Na)^+$: 417.0998, found: 417.0980.



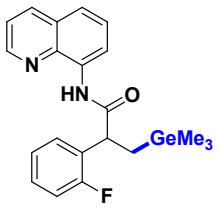
N-(quinolin-8-yl)-2-(o-tolyl)-3-(trimethylgermyl)propanamide 5b

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.87 (br, 1H), 8.74 (d, *J* = 7.4 Hz, 1H), 8.68 (d, *J* = 2.8 Hz, 1H), 8.09 (d, *J* = 7.2 Hz, 1H), 7.55-7.43 (m, 3H), 7.37 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.25-7.17 (m, 3H), 4.11 (dd, *J* = 8.4, 7.6 Hz, 1H), 2.52 (s, 3H), 1.79 (dd, *J* = 13.6, 7.2 Hz, 1H), 1.50 (dd, *J* = 13.6, 9.2 Hz, 1H), 0.07 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.32, 148.24, 139.57, 138.62, 136.31, 135.91, 134.81, 130.95, 127.98, 127.54, 127.50, 127.24, 126.80, 121.58, 121.38, 116.31, 47.30, 20.73, 20.17, -1.59; **HRMS** (EI-TOF) calcd for $C_{22}H_{26}N_2OGe$ Na $(M+Na)^+$: 431.1155, found: 431.1139.



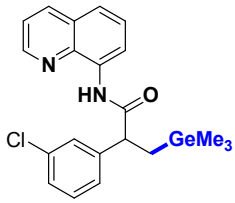
2-(2-chlorophenyl)-N-(quinolin-8-yl)-3-(trimethylgermyl)propanamide 5c

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.85 (br, 1H), 8.83-8.79 (m, 2H), 8.16 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.56-7.44 (m, 3H), 2.58-2.51 (m, 1H), 1.87-1.78 (m, 1H), 1.60-1.53 (m, 1H), 1.40-1.25 (m, 8H), 1.13 (dd, *J* = 14.8, 8.8 Hz, 1H), 0.91-0.82 (m, 4H), 0.03 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.71, 148.30, 138.63, 136.45, 134.75, 128.09, 127.63, 121.67, 121.36, 116.59, 45.31, 36.74, 31.85, 29.49, 27.69, 22.74, 21.11, 14.19, -0.94; **HRMS** (EI-TOF) calcd for $C_{21}H_{23Cl}N_2OGeNa$ $(M+Na)^+$: 451.0608, found: 451.0588.



2-(2-fluorophenyl)-N-(quinolin-8-yl)-3-(trimethylgermyl)propanamide 5d

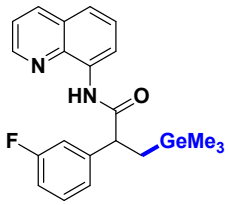
^{1}H NMR (400 MHz, $CDCl_3$) δ10.04 (br, 1H), 8.78-8.74 (m, 2H), 8.11 (d, *J* = 8.0 Hz, 1H), 7.58 (t, *J* = 6.8 Hz, 1H), 7.52-7.45 (m, 2H), 7.41 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.24-7.21 (m, 1H), 7.16 (t, *J* = 7.2 Hz, 1H), 7.07 (t, *J* = 7.2 Hz, 1H), 4.27 (dd, *J* = 8.4, 7.6 Hz, 1H), 1.75 (dd, *J* = 13.6, 7.2 Hz, 1H), 1.51 (dd, *J* = 13.6, 8.8 Hz, 1H), 0.08 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) 172.28, 161.41 (d, *J* = 243.2 Hz), 148.38, 138.65, 136.32, 134.74, 129.36 (d, *J* = 3.8 Hz), 128.84 (d, *J* = 8.3 Hz), 128.52 (d, *J* = 14.6 Hz),128.01, 127.46, 124.74 (d, *J* = 3.5 Hz), 121.63 (d, *J* = 8.3 Hz), 116.52, 115.73, 115.50, 43.03 (d, *J* = 2.6 Hz), 20.17, -1.81; ^{19}F NMR (376 MHz, $CDCl_3$) δ -118.12; **HRMS** (EI-TOF) calcd for $C_{21}H_{23F}N_2OGe$ Na $(M+Na)^+$: 435.0904, found: 435.0888.



2-(3-chlorophenyl)-N-(quinolin-8-yl)-3-(trimethylgermyl)propanamide 5e

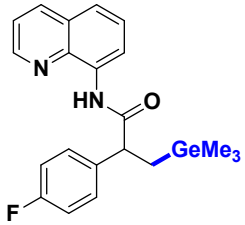
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.96 (br, 1H), 8.77 (dd, *J* = 4.0, 1.6 Hz, 1H), 8.73 (dd, *J* = 7.2, 1.6 Hz, 1H), 8.12 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.52-7.38 (m, 5H), 7.30-7.23 (m, 2H), 3.83 (t, *J* = 8.0 Hz, 1H), 1.73 (dd, *J* = 13.6, 7.2 Hz, 1H), 1.46 (dd, *J* = 13.6, 8.8 Hz, 1H), 0.08 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.35, 148.32, 143.72, 138.54, 136.52, 134.74, 134.49, 130.15, 128.19, 128.04, 127.62, 127.52, 126.27, 121.72,

116.62, 51.47, 21.52, -1.70; **HRMS** (EI-TOF) calcd for $C_{21}H_{23}ClN_2OGeNa$ $(M+Na)^+$: 451.0608, found: 451.0588.



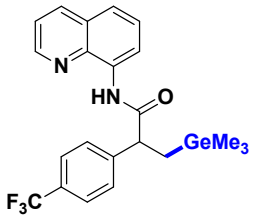
2-(3-fluorophenyl)-N-(quinolin-8-yl)-3-(trimethylgermyl)propanamide 5f

^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.95 (br, 1H), 8.77 (dd, *J*=4.4, 1.6, 1H), 8.73 (dd, *J*=7.2, 1.6, 1H), 8.12 (dd, *J*=8.4, 1.6, 1H), 7.52-7.46 (m, 2H), 7.42 (dd, *J*=8.4, 4.4, 1H), 7.34-7.22 (m, 3H), 6.98-6.93 (m, 1H), 3.84 (dd, *J*=8.4, 7.6, 1H), 1.73 (dd, *J*=13.6, 7.2, 1H), 1.47 (dd, *J*=13.7, 8.8, 1H), 0.07 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 172.45, 164.44, 161.99, 148.36, 144.21, 144.14, 138.61, 136.43, 134.56, 130.41, 130.33, 128.03, 127.50, 123.81, 123.78, 121.71, 121.67, 116.50, 115.09, 114.87, 114.48, 114.27, 51.53, 51.51, 21.44, -1.72; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -112.59.; **HRMS** (EI-TOF) calcd for $C_{21}H_{23}FN_2OGeNa$ $(M+Na)^+$: 435.0904, found: 435.0886.



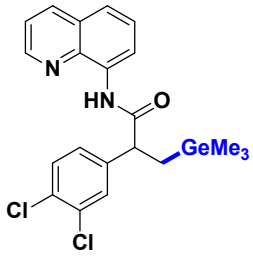
2-(4-fluorophenyl)-N-(quinolin-8-yl)-3-(trimethylgermyl)propanamide 5g

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.93 (br, 1H), 8.76 (dd, *J*=4.4, 1.6, 1H), 8.73 (dd, *J*=7.2, 1.6, 1H), 8.12 (dd, *J*=8.4, 1.6, 1H), 7.52-7.41 (m, 5H), 7.07-7.02 (m, 2H), 3.84 (dd, *J*=9.2, 6.8, 1H), 1.72 (dd, *J*=13.6, 6.8, 1H), 1.48 (dd, *J*=13.6, 9.2, 1H), 0.06 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.03, 163.49, 161.05, 148.33, 138.61, 137.36, 137.32, 136.44, 134.60, 129.63, 129.55, 128.03, 127.50, 121.69, 121.63, 116.46, 115.86, 115.65, 51.00, 21.61, -1.71; ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.46; **HRMS** (EI-TOF) calcd for $C_{21}H_{23}FN_2OGeNa$ $(M+Na)^+$: 435.0904, found: 435.0856.



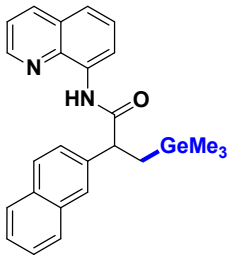
N-(quinolin-8-yl)-2-(4-(trifluoromethyl)phenyl)-3-(trimethylgermyl)propanamide 5h

^{1}H NMR (400 MHz, $CDCl_3$) δ10.47 (br, 1H), 8.75 (dd, *J*=4.4, 1.6, 1H), 8.72 (t, *J*=4.4, 1H), 8.14 (dd, *J*=8.4, 1.6, 1H), 7.89 (dd, *J*=5.2, 3.2, 2H), 7.74 (dd, *J*=5.2, 3.2, 2H), 7.50 (d, *J*=4.4, 2H), 7.43 (dd, *J*=8.4, 4.4, 1H), 5.23 (dd, *J*=12.0, 5.6, 1H), 2.20 (dd, *J*=13.6, 12.0, 1H), 1.80 (dd, *J*=13.6, 5.6, 1H), 0.18 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ172.22, 148.37, 142.66, 138.60, 136.45, 134.44, 131.54,131.22 (q, *J*=32.0), 129.39, 128.03, 127.48, 124.87 (q, *J*=3.8), 124.32 (q, *J*=3.8), 124.25 (q, *J*=270.8), 121.78 (d, *J*=1.8), 116.55, 51.63, 21.67, -1.73; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.52; **HRMS** (EI-TOF) calcd for $C_{22}H_{23}F_3N_2OGeNa$ $(M+Na)^+$: 485.0872, found: 485.0856.



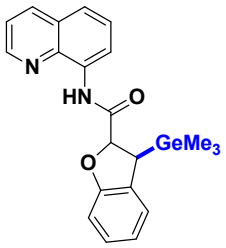
2-(3,4-dichlorophenyl)-N-(quinolin-8-yl)-3-(trimethylgermyl)propanamide 5i

^{1}H NMR (400 MHz, $CDCl_3$) δ9.95 (br, 1H), 8.79 (dd, *J*=4.4, 1.6, 1H), 8.71 (dd, *J*=6.8, 2.4, 1H), 8.14 (dd, *J*=8.0, 1.6, 1H), 7.62 (d, *J*=2.0, 1H), 7.53-7.34 (m, 5H), 3.80 (t, *J*=8.0, 1H), 1.73 (dd, *J*=13.6, 8.0, 1H), 1.42 (dd, *J*=13.6, 8.4, 1H), 0.10 (s, 9H).; **^{13}C NMR** (100 MHz, $CDCl_3$) δ171.92, 148.44, 142.05, 138.57, 136.51, 134.38, 132.89, 131.45, 130.78, 129.97, 128.05, 127.50, 127.40, 121.86, 121.79, 116.60, 50.99, 21.60, -1.64; **HRMS** (EI-TOF) calcd for $C_{21}H_{22}Cl_2N_2OGeNa$ $(M+Na)^+$: 485.2019, found: 485.0196.



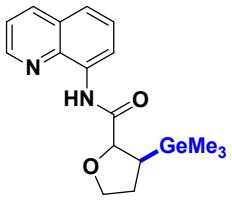
2-(naphthalen-2-yl)-N-(quinolin-8-yl)-3-(trimethylgermyl)propanamide 5j

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.95 (s, 1H), 8.86-8.84 (m, 2H), 8.15 (dd, *J*=8.4, 1.6, 1H), 7.58-7.53 (m, 2H), 7.45 (dd, *J*=8.4, 4.4, 1H), 7.15-7.05 (m, 3H), 6.91 (td, *J*=7.6, 0.8, 1H), 5.53 (d, *J*=9.2, 1H), 3.36 (d, *J*=9.2, 1H), 0.15 (s, 9H).; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.04, 148.24, 139.15, 138.60, 136.32, 134.70, 133.76, 132.89, 128.75, 127.97, 127.95, 127.79, 127.47, 126.79, 126.26, 126.10, 125.88, 121.59, 121.49, 116.40, 51.93, 21.35, -1.62; **HRMS** (EI-TOF) calcd for $C_{25}H_{26}N_2OGeNa$ $(M+Na)^+$: 476.1155, found: 476.1140.



N-(quinolin-8-yl)-3-(trimethylgermyl)-2,3-dihydrobenzofuran-2-carboxamide 5k

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.95 (s, 1H), 8.86-8.84 (m, 2H), 8.15 (dd, *J*=8.4, 1.6, 1H), 7.58-7.53 (m, 2H), 7.45 (dd, *J*=8.4, 4.4, 1H), 7.15-7.05 (m, 3H), 6.91 (td, *J*=7.6, 0.8, 1H), 5.53 (d, *J*=9.2, 1H), 3.36 (d, *J*=9.2, 1H), 0.15 (s, 9H).; **^{13}C NMR** (100 MHz, $CDCl_3$) δ168.52, 157.73, 148.80, 138.95, 136.27, 133.90, 130.96, 128.15, 127.38, 126.95, 123.60, 122.33, 121.84, 121.73, 116.91, 110.05, 86.08, 36.63, -1.75; **HRMS** (EI-TOF) calcd for $C_{21}H_{22}N_2O_2Na$ $(M+Na)^+$: 431.0791, found: 431.0773.

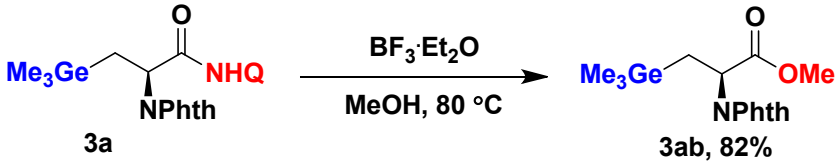


N-(quinolin-8-yl)-3-(trimethylgermyl)tetrahydrofuran-2-carboxamide 5l

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.82 (br, 1H), 8.85 (dd, *J*=4.4, 1.6, 1H), 8.77 (dd, *J*=6.4, 2.8, 1H), 8.14 (dd, *J*=8.4, 1.6, 1H), 7.55-7.49 (m, 2H), 7.44 (dd, *J*=8.4, 4.4, 1H),

4.74-4.72 (m, 1H), 4.47-4.43 (m, 1H), 3.90-3.84 (m, 1H), 2.12-2.04 (m, 1H), 1.91-1.82 (m, 2H), 0.23 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.65, 148.74, 139.04, 136.26, 134.17, 128.16, 127.42, 121.88, 121.70, 116.47, 82.21, 69.57, 32.62, 28.53, -1.78; **HRMS** (EI-TOF) calcd for $C_{17}H_{22}N_2O_2GeNa$ $(M+Na)^+$: 383.0791, found: 383.0777.

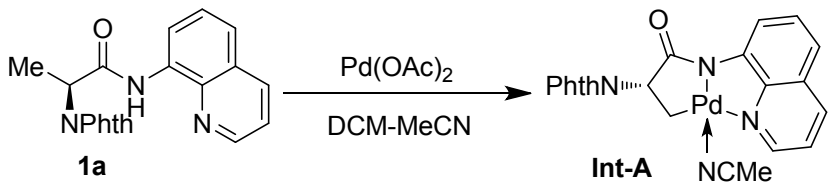
2.4 Removal of Directing Group



To an oven-dried 50 mL round-bottomed flask was added substrate **3a** (0.1 mmol), $BF_3{\cdot}Et_2O$ (1.0 mmol) in MeOH (1 mL). The flask was stirred for 12 h at 80 °C. The crude product was purified by prepared column chromatography(R_f = 0.7, EtOAc/PE = 1/5) to afford **3ab** (31.0 mg, 85%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 – 7.84 (m, 2H), 7.77 – 7.71 (m, 2H), 4.97 (dd, *J* = 11.1, 5.7 Hz, 1H), 3.72 (s, 3H), 1.80 (dd, *J* = 14.1, 11.1 Hz, 1H), 1.69 (dd, *J* = 14.1, 5.7 Hz, 1H), 0.10 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 170.87, 167.42, 134.02, 131.71, 123.34, 52.65, 49.85, 16.98, -2.23. **HRMS** (EI-TOF) calcd for $C_{15}H_{19}GeNNaO_4$ $(M+Na)^+$: 374.0424, found: 374.0415.

2.5 Mechanistic Investigation

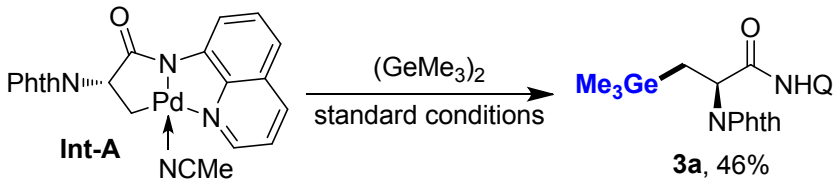
Synthesis of Palladacycle Int-A



To an oven-dried 50 mL round-bottomed flask was added substrate **1a** (1.0 mmol), $Pd(OAc)_2$ (1.0 mmol) in DCM (10 mL) and MeCN (5 mL). The flask was stirred for 12 h at 60 °C followed by cooling. The purified product was collected by filtration, washed with MeCN, diethyl ether and dried under vacuum to afford **Int-A** (392 mg,

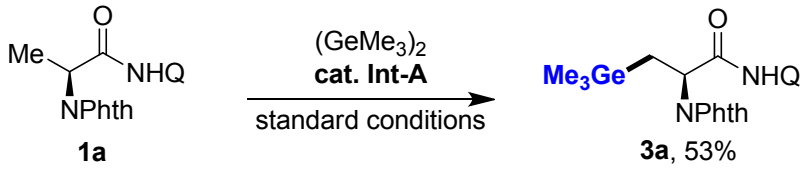
80%) as yellow power.[1] ^{1}H NMR (501 MHz, $CDCl_3$) δ 8.93 (d, *J* = 7.5 Hz, 1H), 8.18 (s, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.83 (s, 2H), 7.68 (s, 2H), 7.40 (t, *J* = 8.0 Hz, 1H), 7.19 (d, *J* = 7.5 Hz, 1H), 7.15 (dd, *J* = 7.5, 4.5 Hz, 1H), 5.32 (t, *J* = 10.0 Hz, 1H), 2.40 (t, *J* = 9.0 Hz, 1H), 2.32 (s, 3H),1.95 (t, *J* = 8.0 Hz, 1H).

Stoichiometric Reaction of Int-A



To an oven-dried 50 mL screw-capped vial was added **Int-A** (0.1 mmol), **2** (0.5 mmol), BINA-PO_2H (0.03 mmol), Ag_2CO_3 (0.2 mmol), $NaHCO_3$ (0.2 mmol), LiOAc (0.05 mmol), toluene (1.0 mL). The mixture was stirred for 10 h at 125 °C under air followed by cooling. The resulting mixture was filtered through a celite pad and concentrated in *vacuo*. The product **3a** was obtained in 52% yield (determined by ^{1}H NMR).

Catalytic Reaction of Int-A

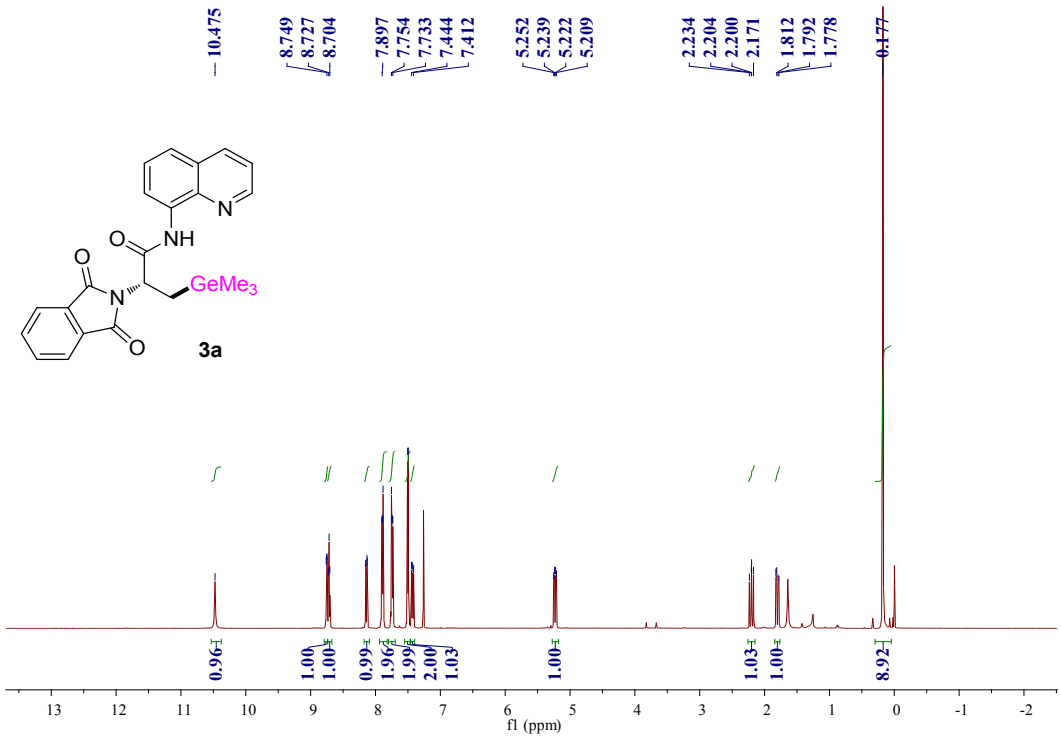


To an oven-dried 50 mL screw-capped vial was added **1a** (0.1 mmol),**2** (0.5 mmol), **Int-A** (0.01 mmol), BINA-PO_2H (0.03 mmol), Ag_2CO_3 (0.2 mmol), $NaHCO_3$ (0.2 mmol), LiOAc (0.05 mmol), toluene (1.0 mL). The mixture was stirred for 10 h at 125 °C under air followed by cooling. The resulting mixture was filtered through a celite pad and concentrated in *vacuo*. The product **3a** was obtained in 28% yield (determined by ^{1}H NMR yield).

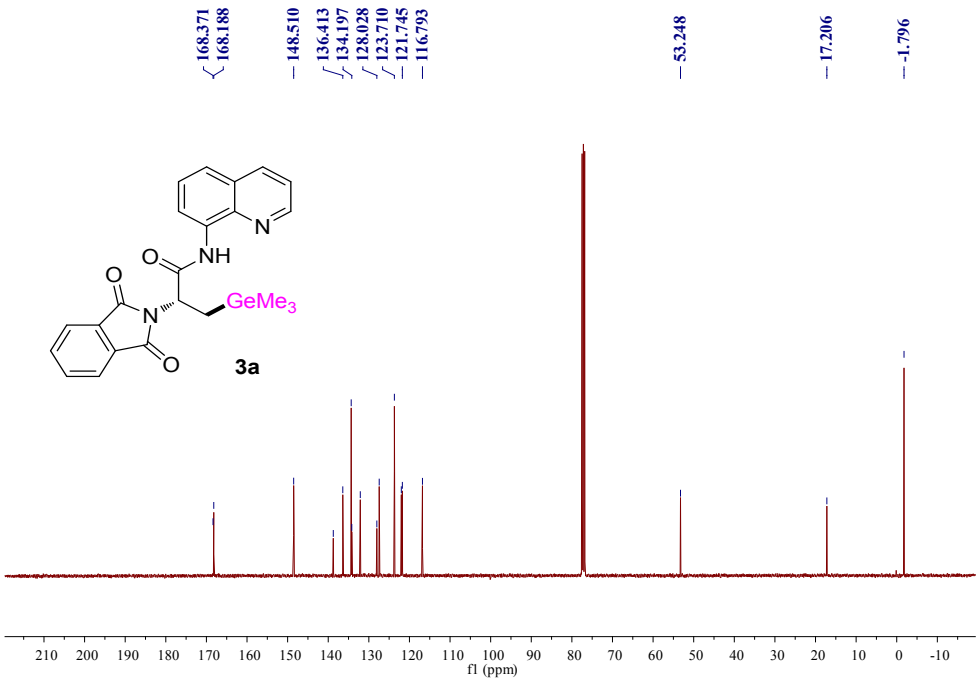
3. References:

1. Liu, Y.-J.; Liu, Y.-H.; Zhang, Z.-Z.; Chen, K.; Shi, B.-F., *Angew. Chem. Int. Ed.* **2016**, *55*, 13859.

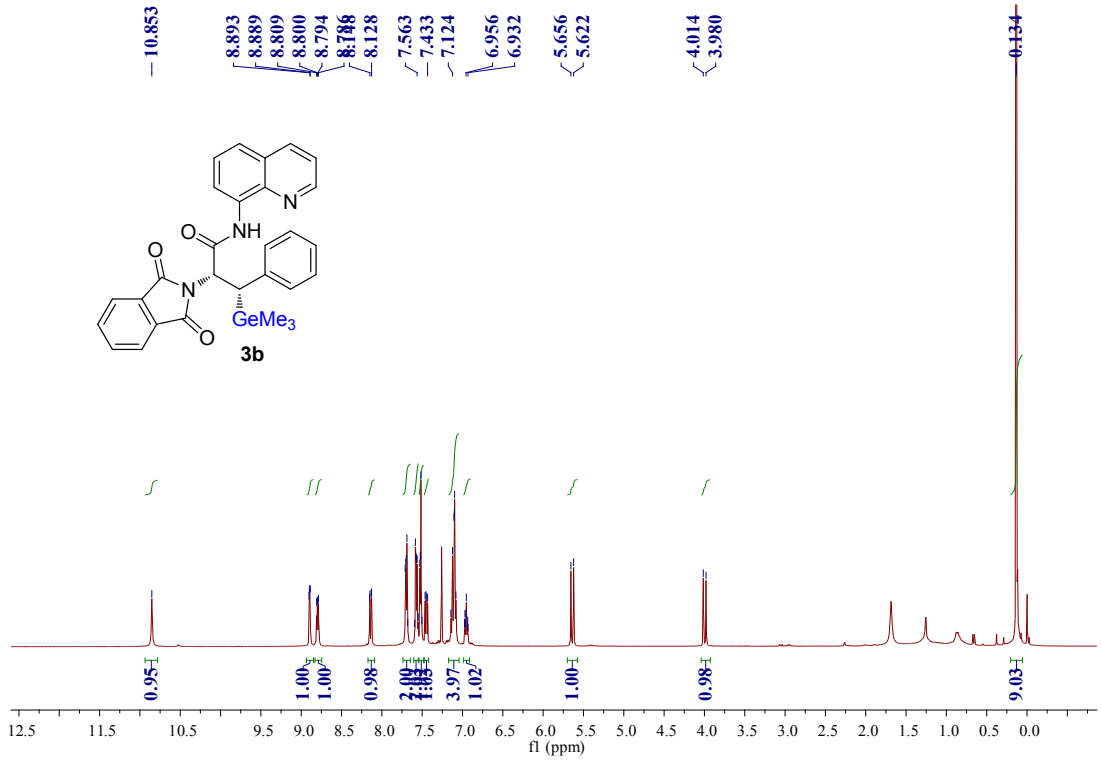
4. NMR Spectra



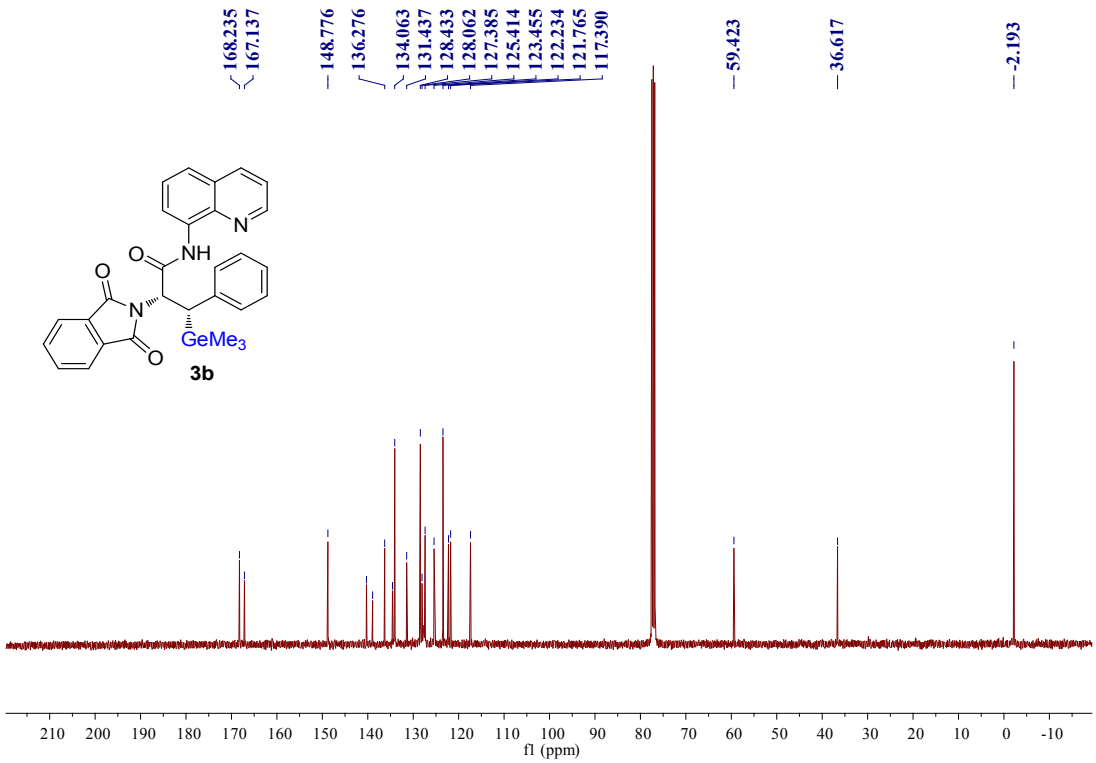
^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.47 (br, 1H), 8.75 (dd, *J*=4.4, 1.6, 1H), 8.72 (t, *J*=4.4, 1H), 8.14 (dd, *J*=8.4, 1.6, 1H), 7.89 (dd, *J*=5.6, 3.1, 2H), 7.74 (dd, *J*=5.6, 3.1, 2H), 7.50 (d, *J*=4.4, 2H), 7.43 (dd, *J*=8.4, 4.4, 1H), 5.23 (dd, *J*=12.0, 5.6, 1H), 2.20 (dd, *J*=13.6, 12.0, 1H), 1.80 (dd, *J*=13.6, 5.6, 1H), 0.18 (s, 9H).



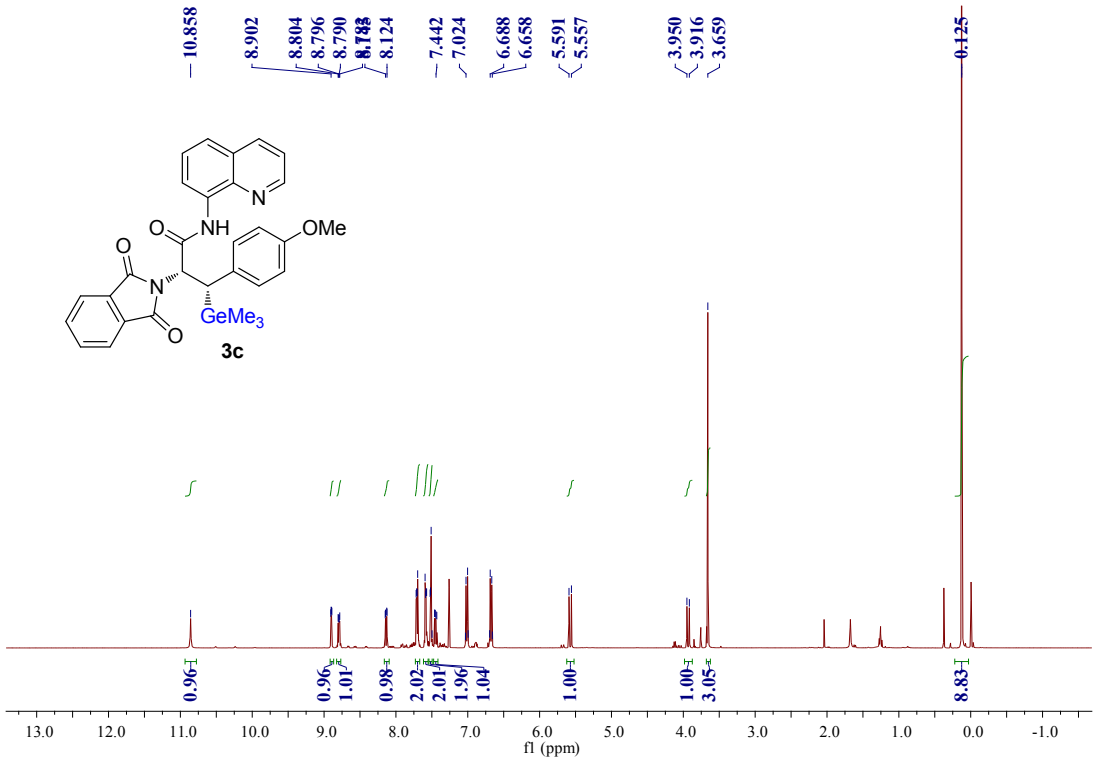
^{13}C NMR (101 MHz, $CDCl_3$) δ = 168.37, 168.19, 148.51, 138.75, 136.41, 134.34, 134.20, 132.11, 128.03, 127.45, 123.71, 122.00, 121.74, 116.79, 53.25, 17.21, -1.80.



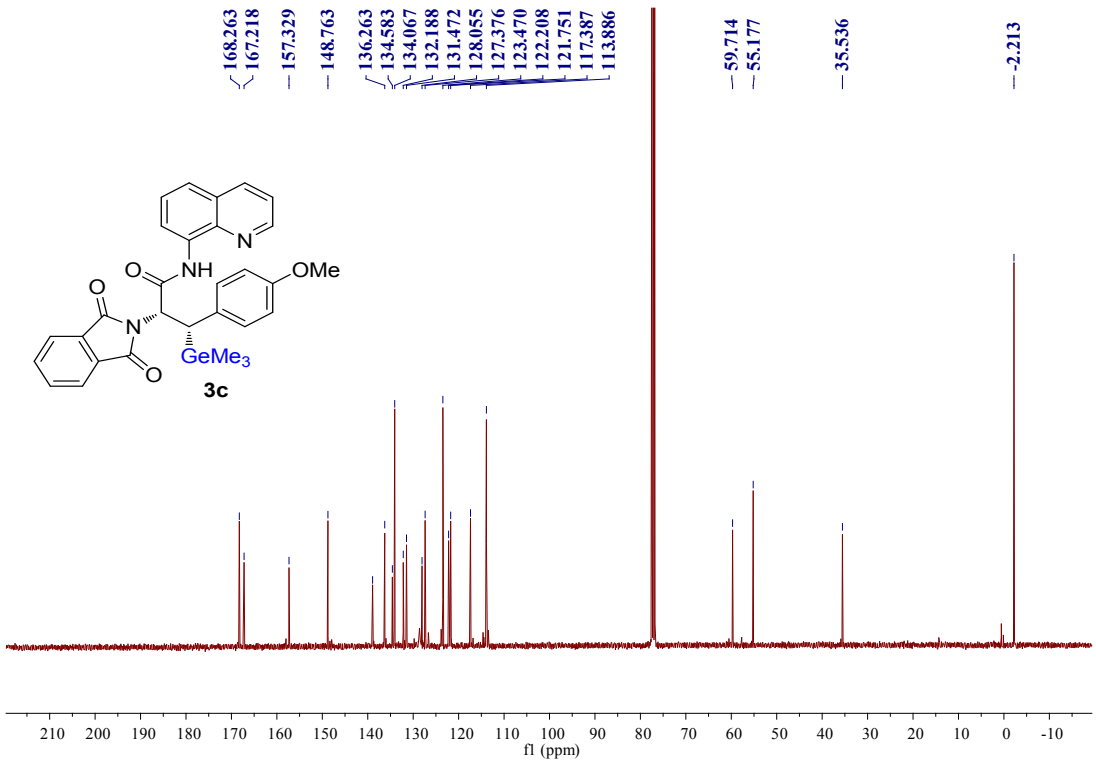
^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.85 (s, 1H), 8.90 (dd, *J*=4.4, 1.6, 1H), 8.80 (dd, *J*=5.6, 3.2, 1H), 8.14 (dd, *J*=8.4, 1.6, 1H), 7.71-7.68 (m, 2H), 7.59-7.53-7.50 (m, 2H), 7.53-7.50 (m, 2H), 7.45 (dd, *J*=8.4, 4.4, 1H), 7.14-7.08 (m, 4H), 6.97-6.93 (m, 1H), 5.64 (d, *J*=13.6, 1H), 4.00 (d, *J*=13.6, 1H), 0.13 (s, 9H).



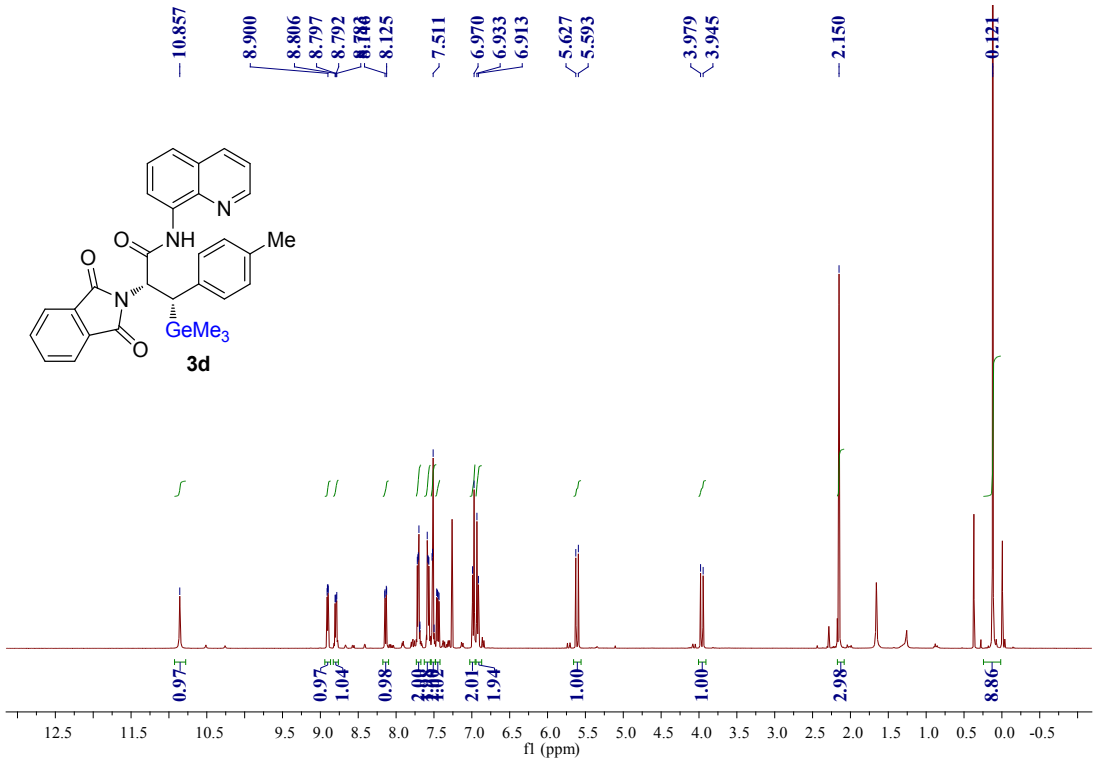
^{13}C NMR (101 MHz, $CDCl_3$) δ = 168.24, 167.14, 148.78, 140.29, 138.93, 136.28, 134.56, 134.06, 131.44, 128.43, 128.06, 127.38, 125.41, 123.45, 122.23, 121.77, 117.39, 59.42, 36.62, -2.19.



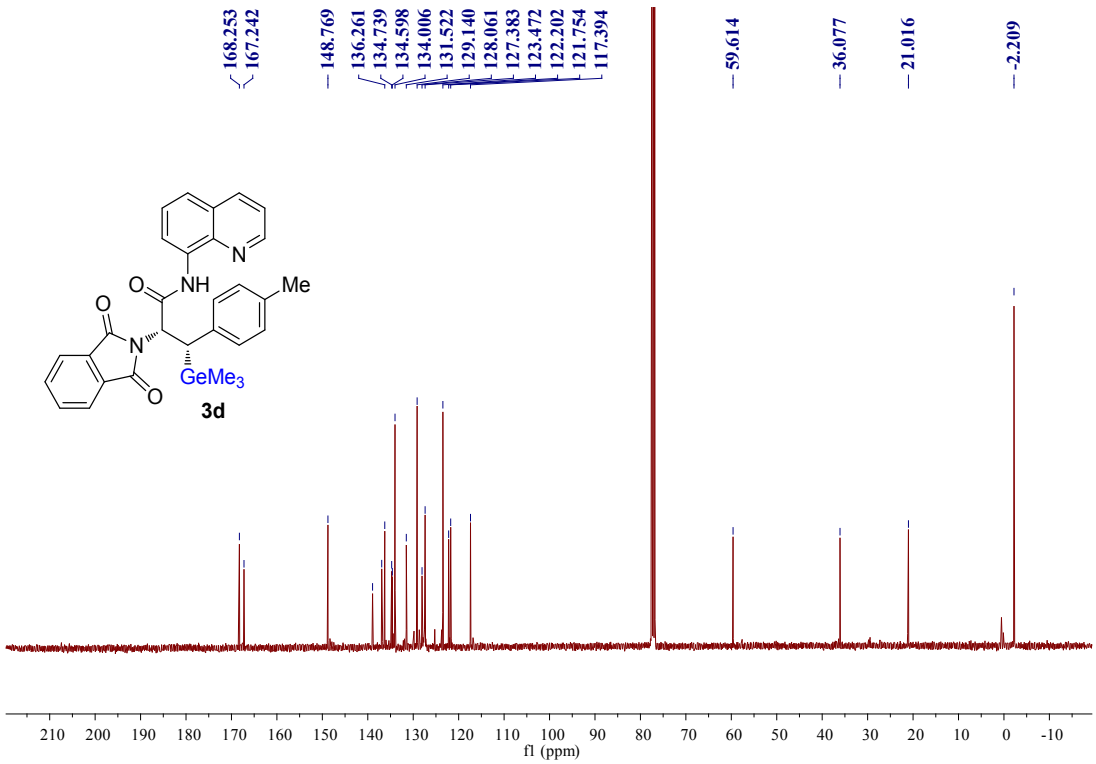
d.r. = 15:1 determined by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$)δ = 10.86 (br, 1H), 8.90 (dd, *J*=4.4, 1.6, 1H), 8.79 (dd, *J*=5.6, 3.2, 1H), 8.14 (dd, *J*=8.4, 1.6, 1H), 7.71 (dd, *J*=5.6, 3.0, 2H), 7.58 (dd, *J*=5.6, 3.0, 2H), 7.52-7.50 (m, 2H), 7.45 (dd, *J*=8.4, 4.4, 1H), 5.57 (d, *J*=13.6, 1H), 3.93 (d, *J*=13.6, 1H), 3.66 (s, 3H), 0.12 (s, 9H).



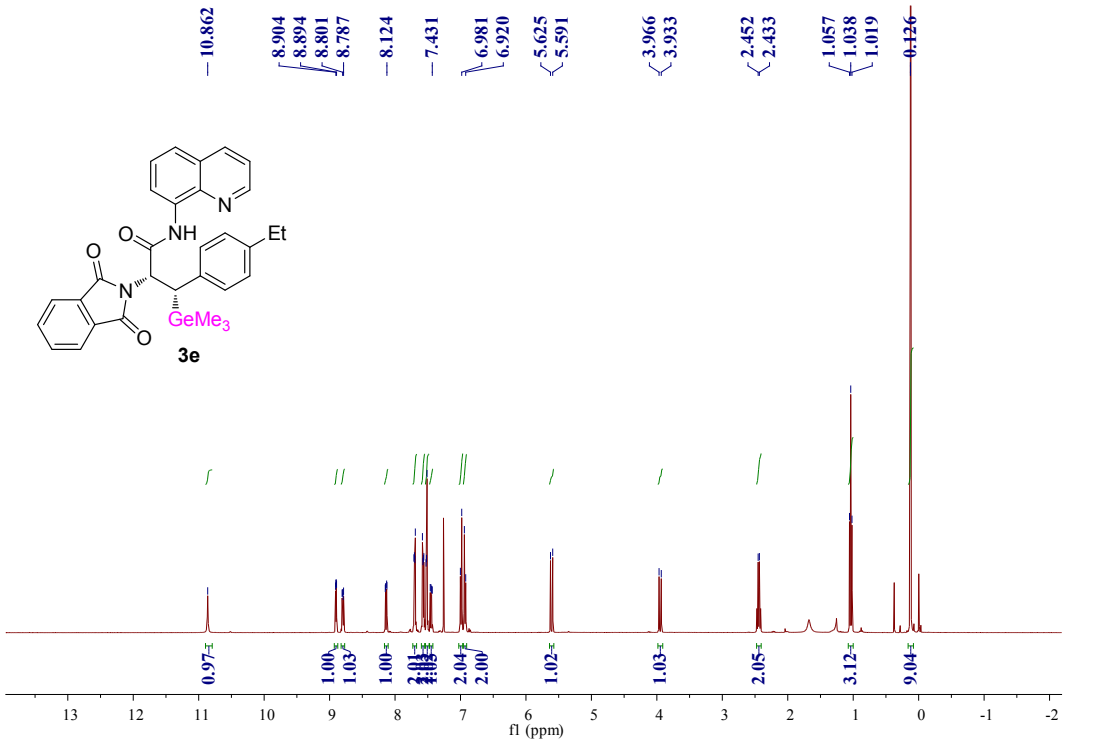
^{13}C NMR (101 MHz, $CDCl_3$) δ = 168.26, 167.22, 157.33, 148.76, 138.93, 136.26, 134.58, 134.07, 132.19, 131.47, 128.06, 127.38, 123.47, 122.21, 121.75, 117.39, 113.89, 59.71, 55.18, 35.54, -2.21.



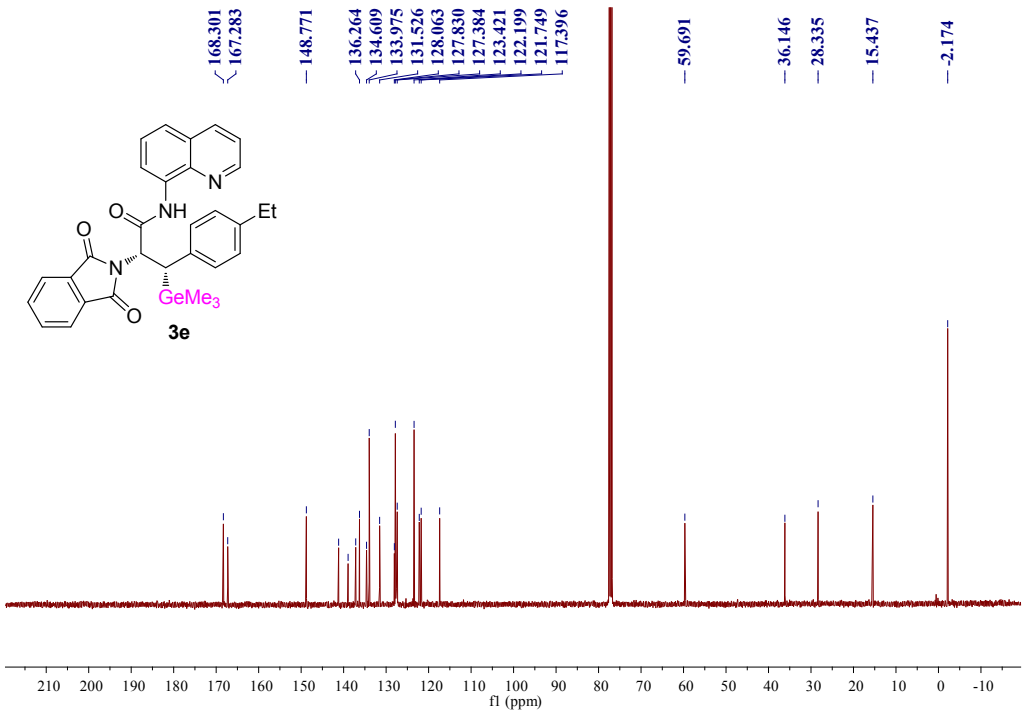
d.r. = 12.5:1 determined by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$)δ = 10.86 (br, 1H), 8.90 (dd, *J*=4.4, 1.6, 1H), 8.79 (dd, *J*=5.6, 3.2, 1H), 8.14 (dd, *J*=8.4, 1.6, 1H), 7.70 (td, *J*=5.6, 2.4, 2H), 7.58 (dd, *J*=5.6, 3.2, 2H), 7.53-7.50 (m, 2H), 7.45 (dd, *J*=8.4, 4.4, 1H), 6.98 (d, *J*=8.0, 2H), 6.92 (d, *J*=8.0, 2H), 5.61 (d, *J*=13.6, 1H), 3.96 (d, *J*=13.6, 1H), 2.15 (s, 3H), 0.12 (s, 9H).



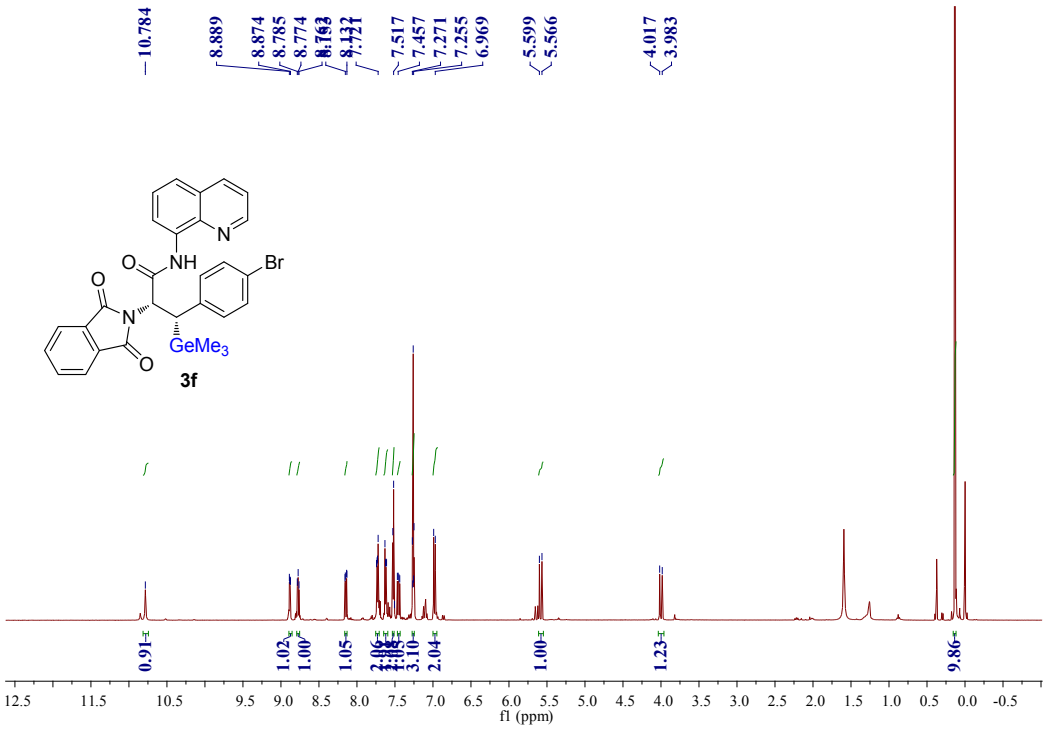
^{13}C NMR (101 MHz, $CDCl_3$) δ = 168.25, 167.24, 148.77, 138.95, 136.93, 136.26, 134.74, 134.60, 134.01, 131.52, 129.14, 128.06, 127.38, 123.47, 122.20, 121.75, 117.39, 59.61, 36.08, 21.02, -2.21.



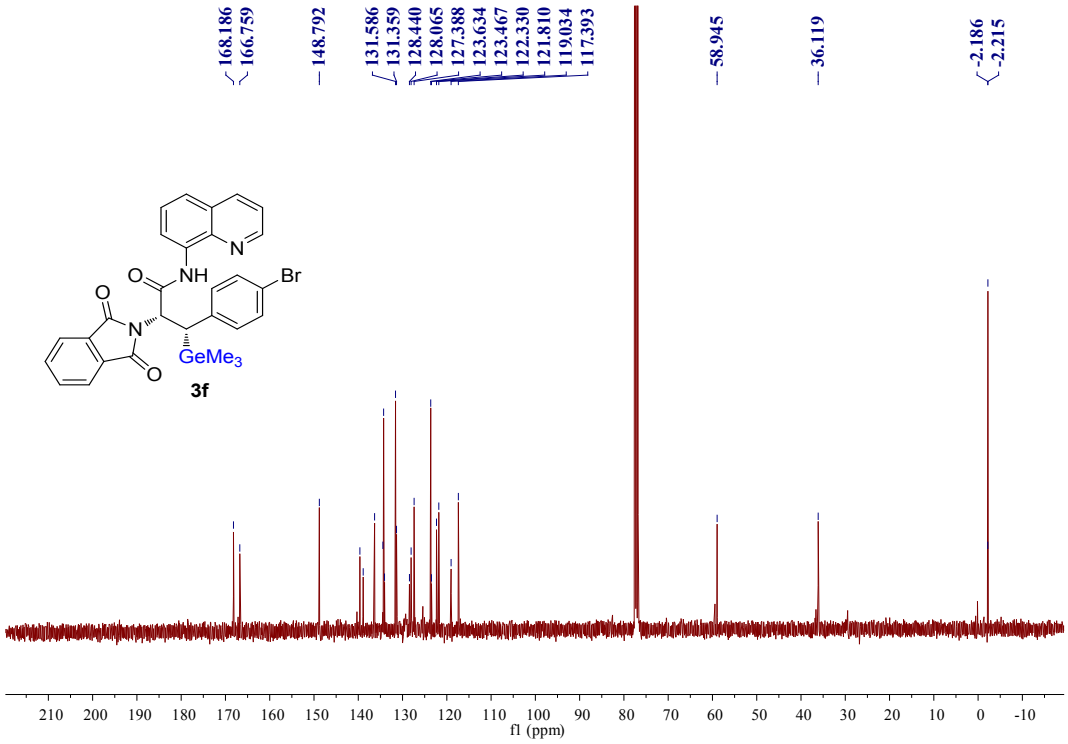
^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.86 (br, 1H), 8.90 (dd, *J*=4.4, 1.6, 1H), 8.80 (dd, *J*=5.6, 3.2, 1H), 8.14 (dd, *J*=8.4, 1.6, 1H), 7.70 (dd, *J*=5.6, 3.2, 2H), 7.57 (dd, *J*=5.6, 3.2, 2H), 7.53-7.51 (m, 2H), 7.45 (dd, *J*=8.4, 4.4, 1H), 6.99 (d, *J*=8.4, 2H), 6.93 (d, *J*=8.0, 2H), 5.61 (d, *J*=13.6, 1H), 3.95 (d, *J*=13.6, 1H), 2.44 (d, *J*=7.6, 2H), 1.04 (t, *J*=7.6, 3H), 0.13 (s, 9H).



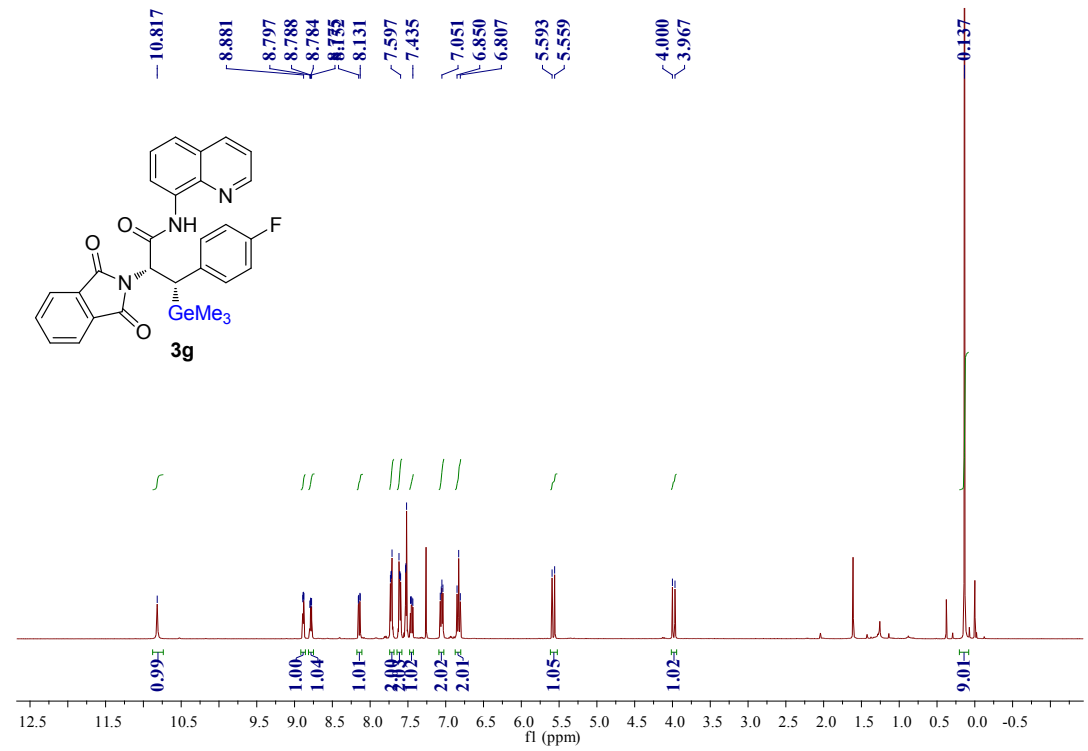
^{13}C NMR (101 MHz, $CDCl_3$) δ = 168.30, 167.28, 148.77, 141.18, 138.95, 137.15, 136.26, 134.61, 133.98, 131.53, 128.06, 127.83, 127.38, 123.42, 122.20, 121.75, 117.40, 59.69, 36.15, 28.33, 15.44, -2.17.



d.r. = 4:1 determined by ^{1}H NMR. ^{1}H NMR of main product (400 MHz, $CDCl_3$) δ = 10.78 (br, 1H), 8.88 (dd, *J*=4.4, 1.6, 1H), 8.79-8.76 (m, 1H), 8.14 (dd, *J*=8.4, 1.6, 1H), 7.73 (dd, *J*=5.6, 3.2, 2H), 7.62 (dd, *J*=5.6, 3.2, 2H), 7.52 (d, *J*=4.0, 2H), 7.45 (dd, *J*=8.4, 4.4, 1H), 7.27-7.25 (m, 2H), 6.98 (d, *J*=8.4, 2H), 5.58 (d, *J*=13.6, 1H), 4.00 (d, *J*=13.6, 1H), 0.13 (s, 9H).

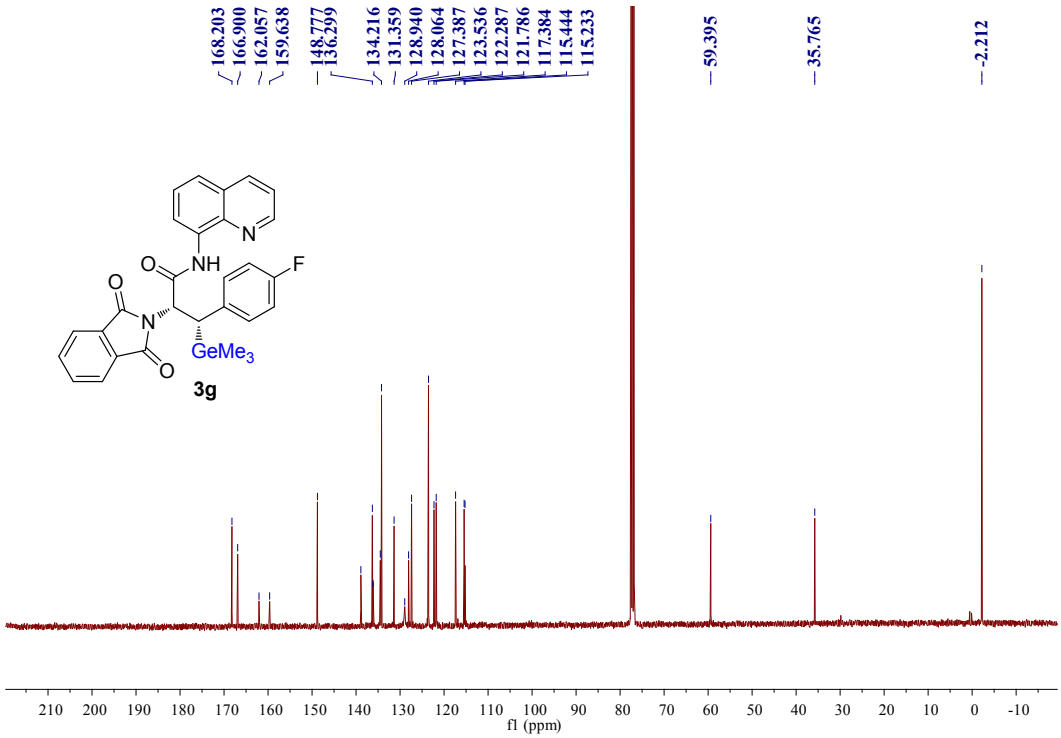


^{13}C NMR (101 MHz, $CDCl_3$) δ = 168.19, 166.76, 148.79, 139.63, 138.89, 136.31, 134.44, 134.27, 134.07, 131.59, 131.36, 128.44, 128.07, 127.39, 123.63, 123.47, 122.33, 121.81, 119.03, 117.39, 58.95, 36.12, -2.19, -2.22.

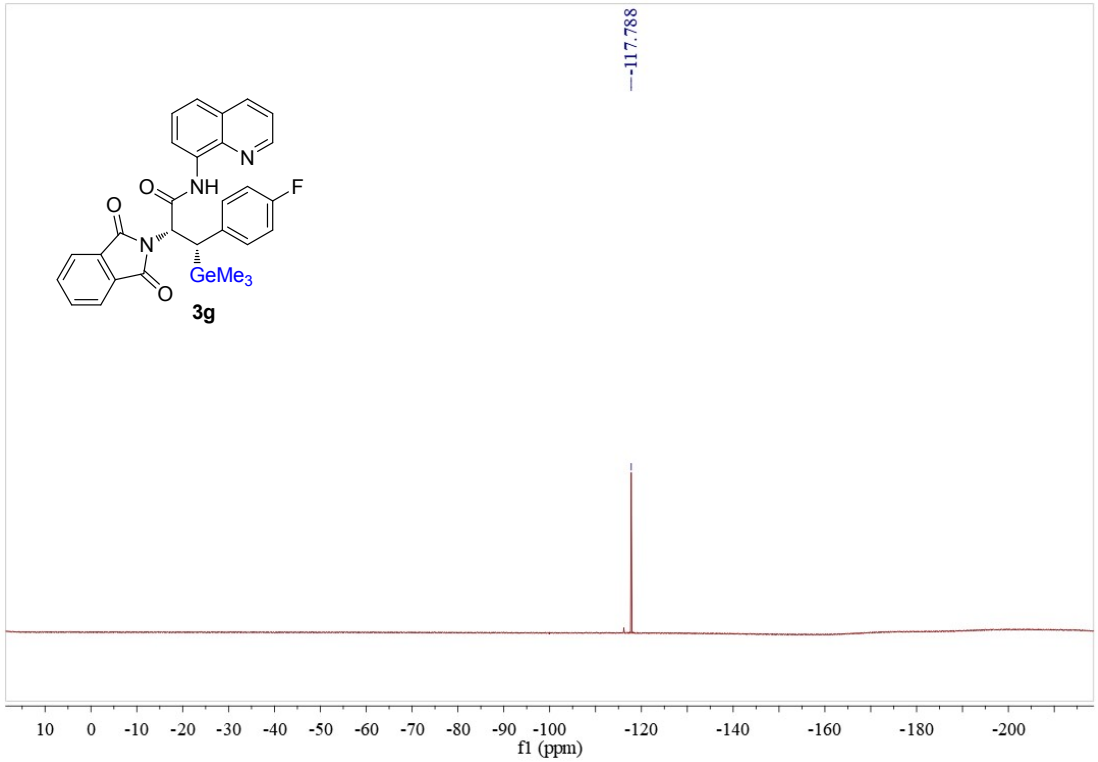


^{1}H NMR (400 MHz, $CDCl_3$) δ 10.82 (s, 1H), 8.88 (dd, *J* = 4.0, 1.6 Hz, 1H), 8.79 (dd, *J* = 5.2, 3.6 Hz, 1H), 8.14 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.72 (dd, *J* = 5.6, 3.2 Hz, 2H), 7.61 (dd, *J* = 5.6, 3.2 Hz, 2H), 7.45

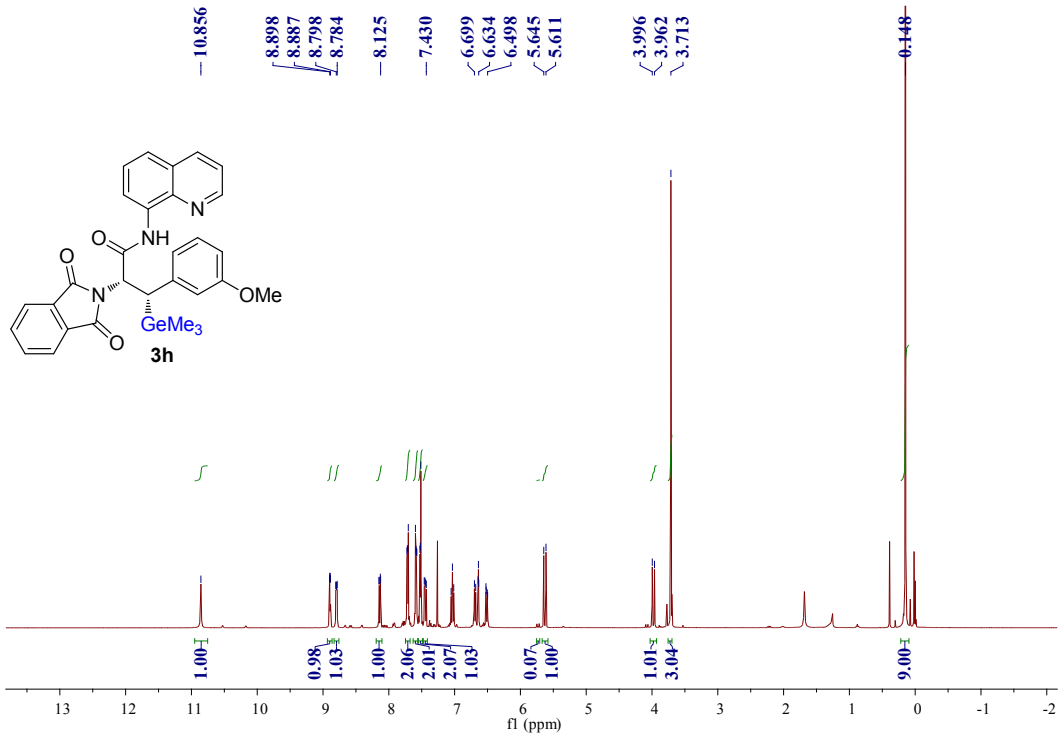
(dd, *J* = 8.4, 4.2 Hz, 1H), 7.05 (dd, *J* = 8.8, 5.2 Hz, 2H), 6.83 (t, *J* = 8.8 Hz, 2H), 5.58 (d, *J* = 13.6 Hz, 1H), 3.98 (d, *J* = 13.6 Hz, 1H), 0.14 (s, 9H).



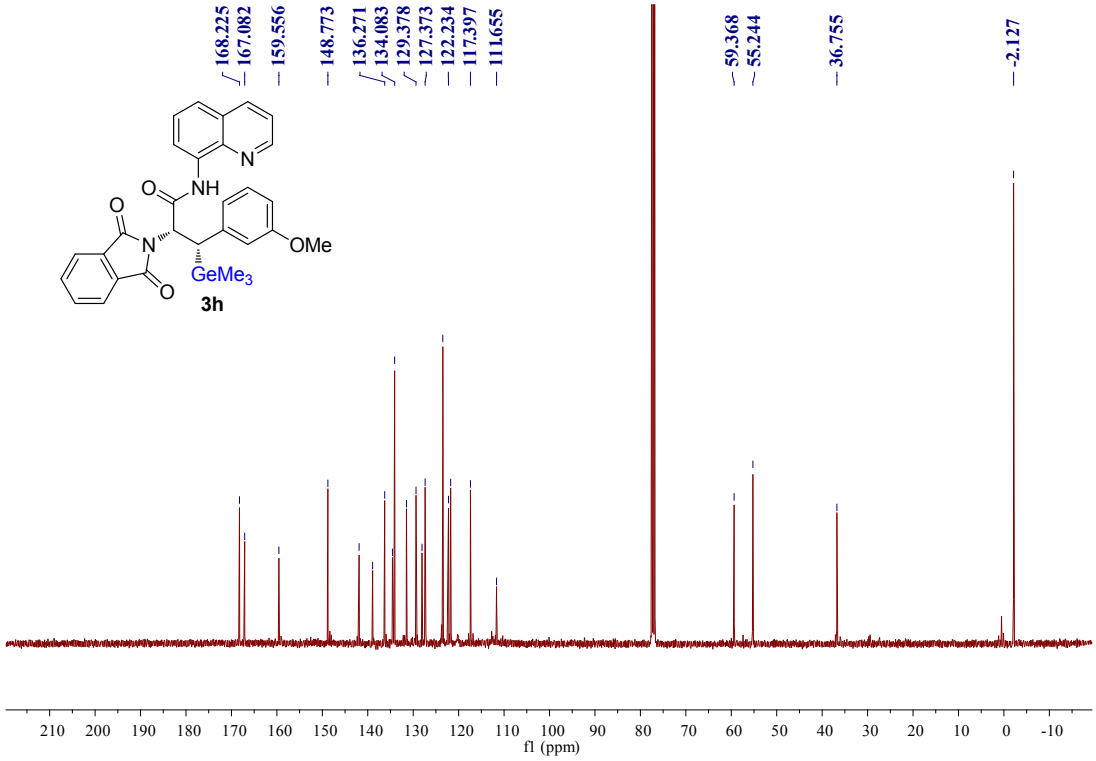
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.20, 166.90, 160.85, 148.78, 138.91, 136.30, 136.12(d, *J* = 3.1 Hz),134.49, 134.22, 131.36, 128.94, 128.06, 127.39, 123.54, 122.04 (d, *J* = 50.1 Hz), 117.38, 115.33(d, *J* = 21.1 Hz), 59.39, 35.76, -2.21.



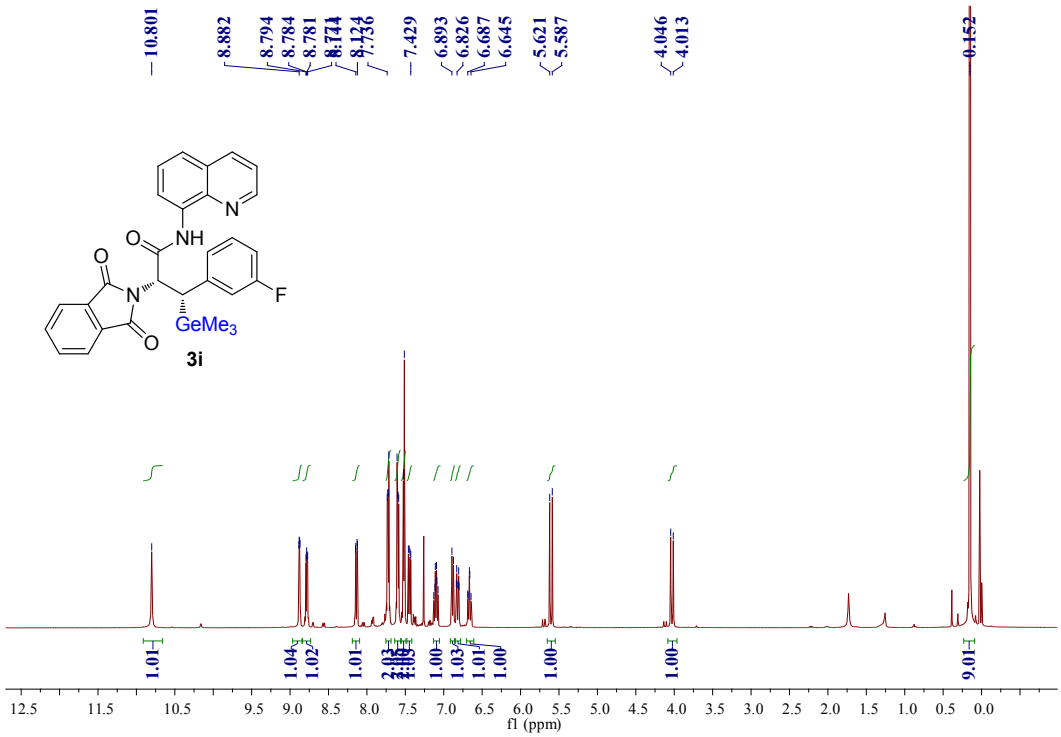
^{19}F NMR (376 MHz, $CDCl_3$) δ = -117.79.



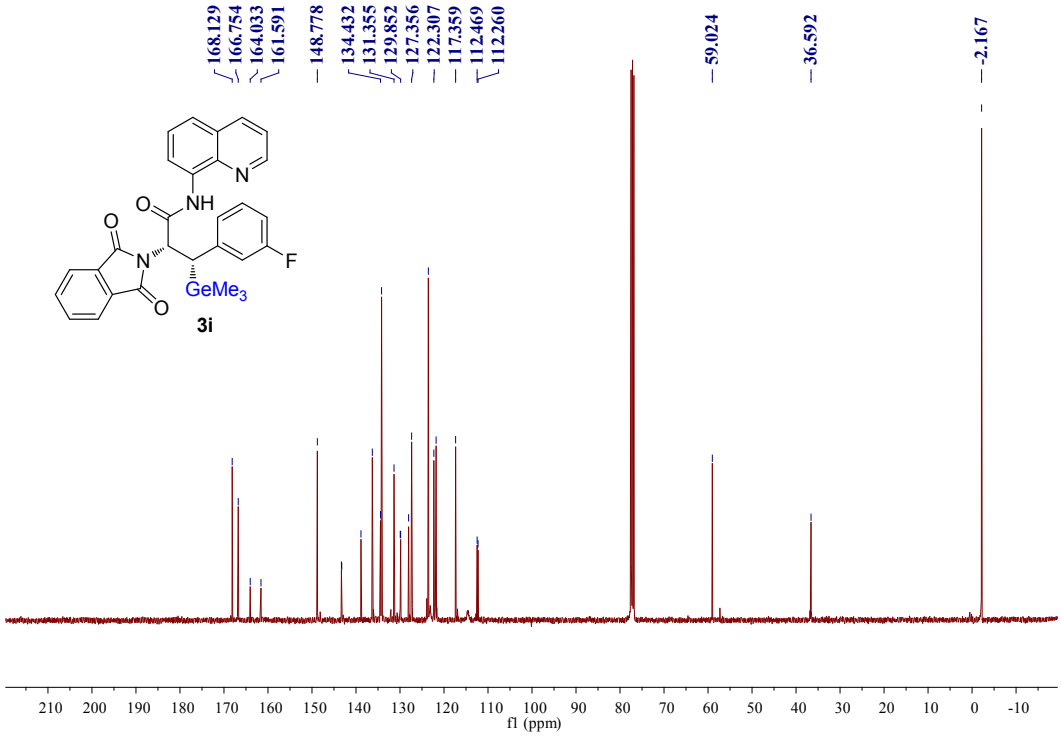
d.r. = 15:1 determined by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.86 (br, 1H), 8.89 (dd, *J*=4.4, 1.6, 1H), 8.80 (dd, *J*=5.6, 3.2, 1H), 8.14 (dd, *J*=8.4, 1.6, 1H), 7.71 (dd, *J*=5.6, 3.2, 2H), 7.58 (dd, *J*=5.6, 3.2, 2H), 7.53-7.51 (m, 2H), 7.45 (dd, *J*=8.4, 4.4, 1H), 5.73 (d, *J*=13.2, 0H), 5.63 (d, *J*=13.6, 1H), 3.98 (d, *J*=13.6, 1H), 3.71 (s, 3H), 0.15 (s, 9H).



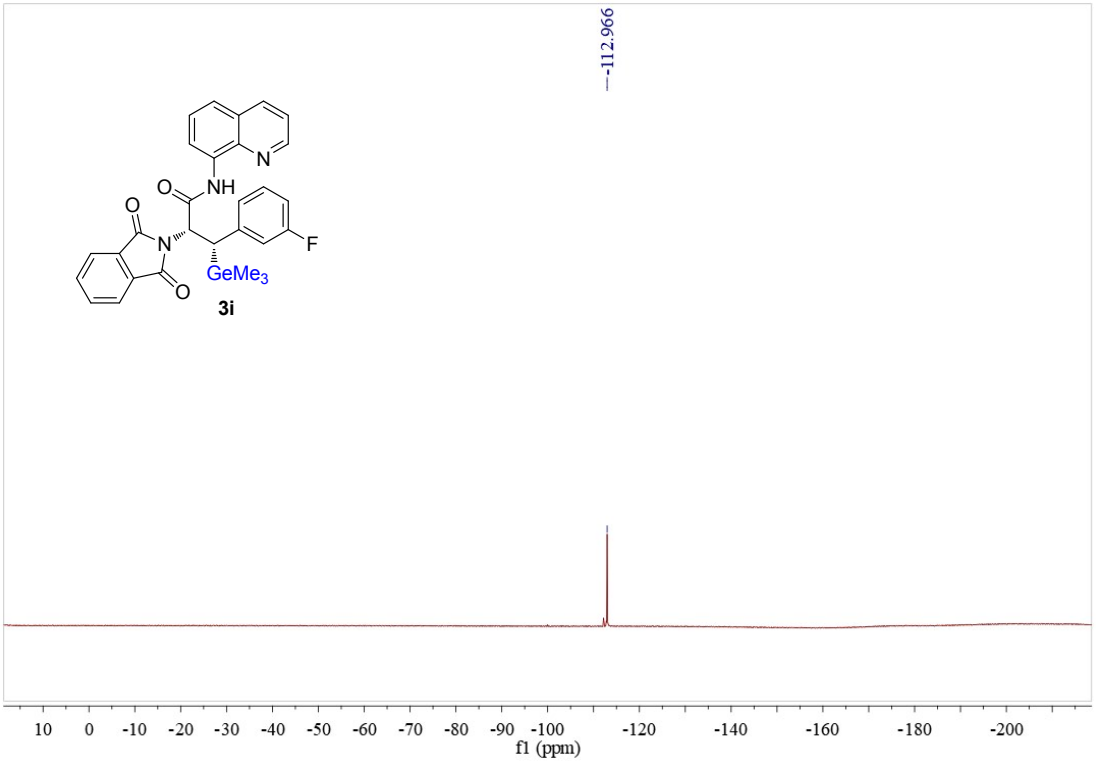
^{13}C NMR (101 MHz, $CDCl_3$) δ = 168.23, 167.08, 159.56, 148.77, 141.90, 138.93, 136.27, 134.56, 134.08, 131.48, 129.38, 128.06, 127.37, 123.48, 122.23, 121.76, 117.40, 111.65, 59.37, 55.24, 36.75, -2.13.



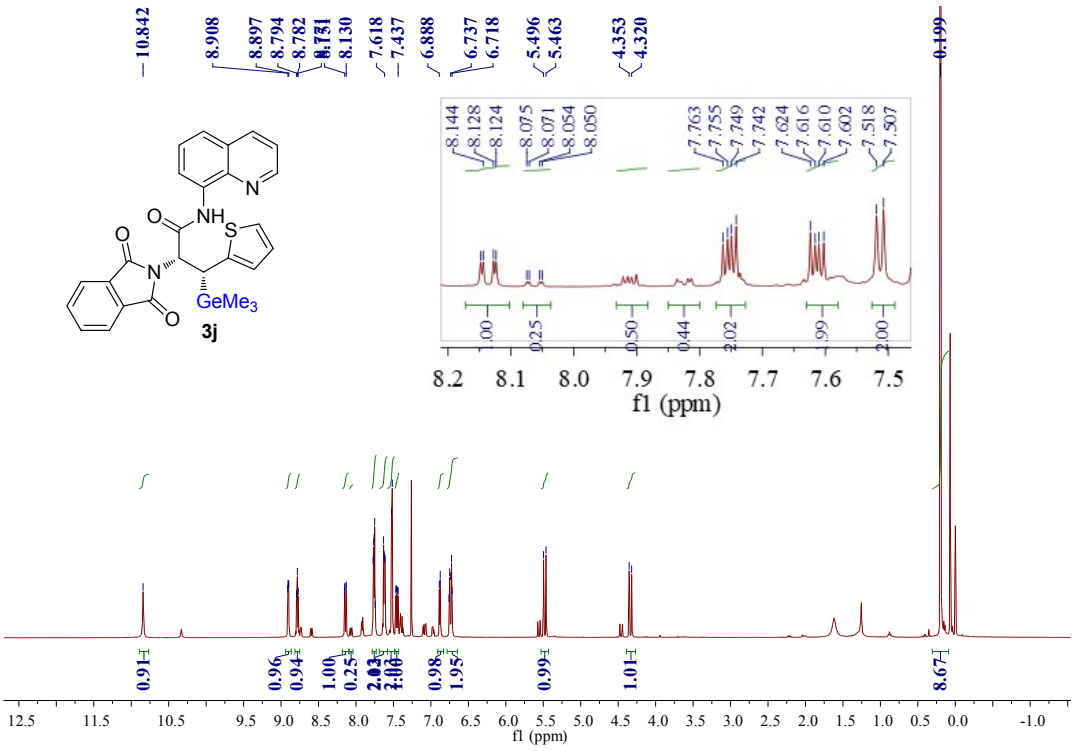
d.r. = 14:1 determined by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.80 (br, 1H), 8.88 (dd, *J*=4.4, 1.6, 1H), 8.78 (dd, *J*=5.2, 4.0, 1H), 8.14 (dd, *J*=8.4, 1.6, 1H), 7.73 (dd, *J*=5.6, 3.1, 2H), 7.60 (dd, *J*=5.6, 3.2, 2H), 7.53-7.51 (m, 2H), 7.44 (dd, *J*=8.4, 4.2, 1H), 7.10 (td, *J*=8.0, 6.4, 1H), 6.88 (d, *J*=8.0, 1H), 6.82 (dt, *J*=10.0, 2.0, 1H), 6.67 (td, *J*=8.4, 2.0, 1H), 5.60 (d, *J*=13.5, 1H), 4.03 (d, *J*=13.6, 1H), 0.15 (s, 9H).



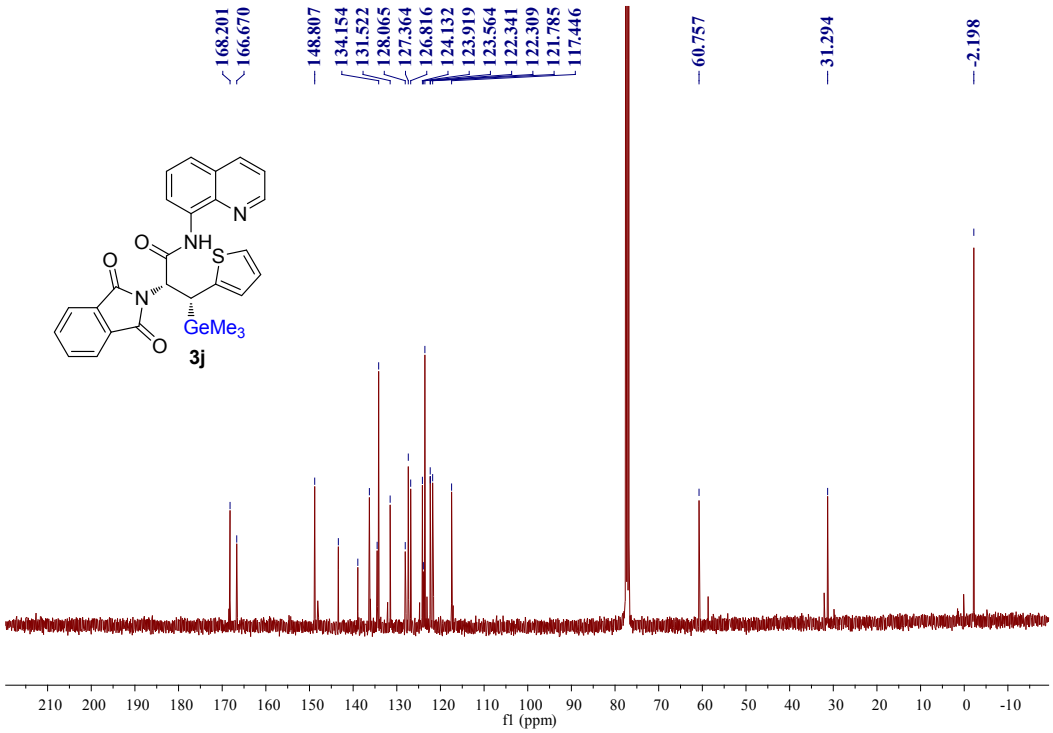
^{13}C NMR (101 MHz, $CDCl_3$) δ = 168.13, 166.75, 162.81 (d, *J*=244.2), 148.78, 143.27 (d, *J*=7.3), 138.87, 136.29, 134.43, 134.19, 131.36, 129.89, 128.04 (s, 3H), 127.36, 123.56, 122.31, 121.79, 117.36, 112.45 (d, *J*=21.1), 59.02, 36.59, -2.17



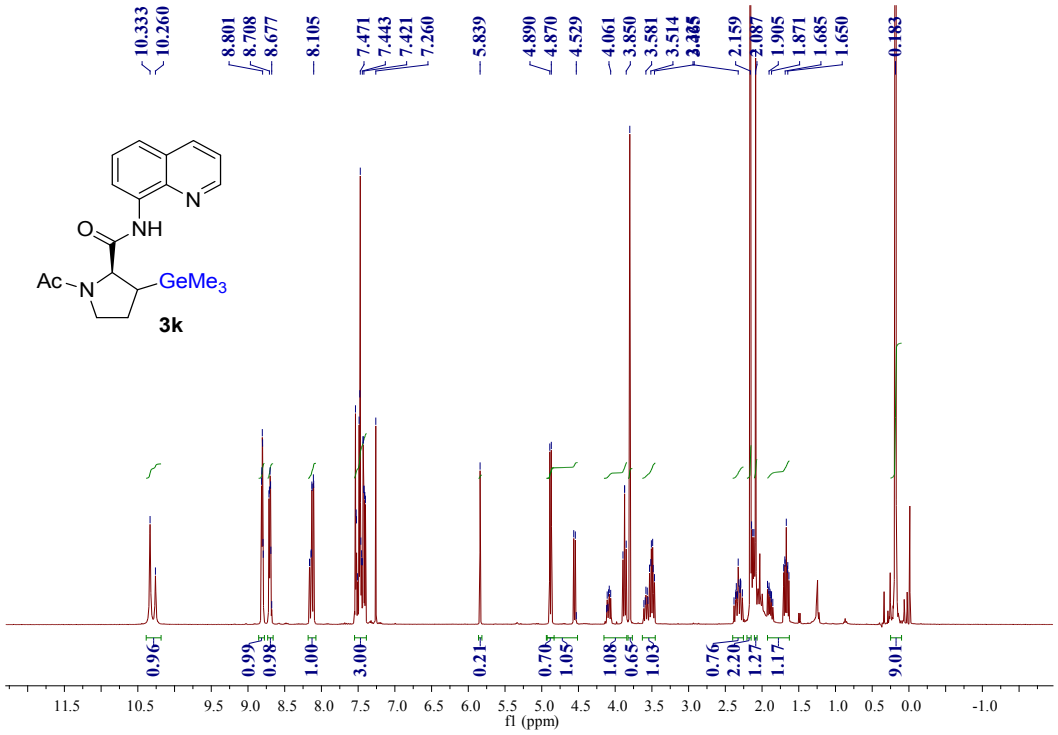
^{19}F NMR (376 MHz, $CDCl_3$) δ = -112.97.



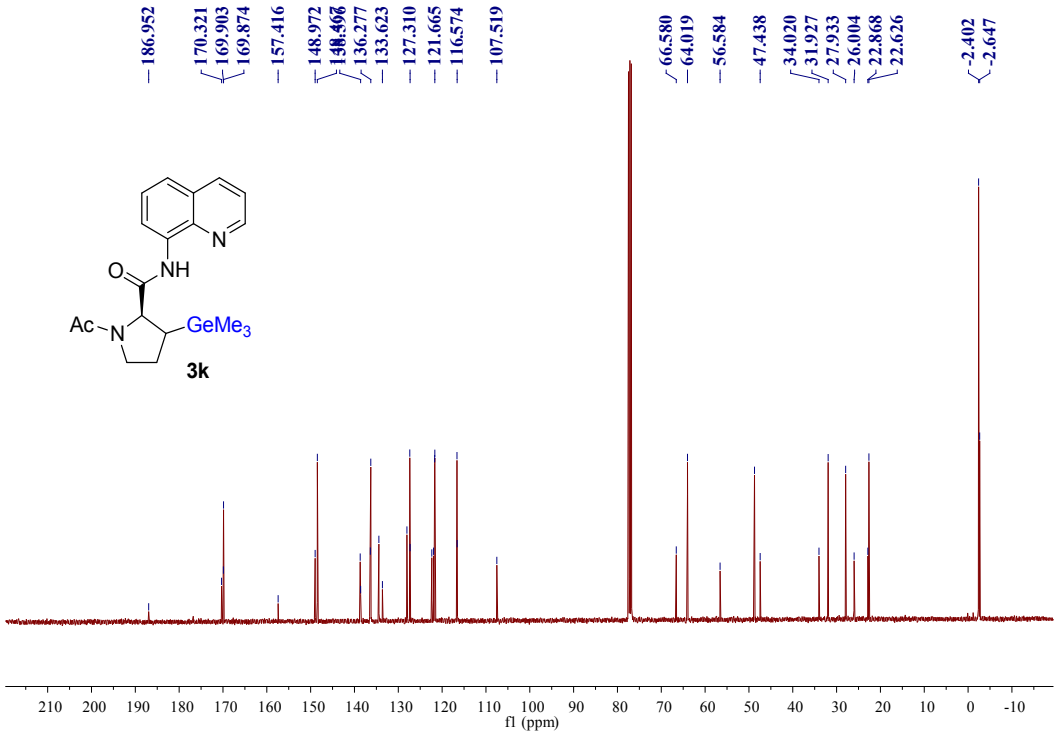
d.r. = 4:1 determined by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.84 (s, 1H), 8.90 (dd, *J*=4.4, 1.6, 1H), 8.78 (t, *J*=4.4, 1H), 8.14 (dd, *J*=8.4, 1.6, 1H), 8.07 (dd, *J*=8.4, 1.6, 0H), 7.77-7.74 (m, 2H), 7.62 (dd, *J*=5.6, 3.2, 2H), 7.52 (d, *J*=4.4, 2H), 7.45 (dd, *J*=8.4, 4.4, 1H), 6.88 (d, *J*=5.2, 1H), 6.76-6.72 (m, 2H), 5.48 (d, *J*=13.2, 1H), 4.34 (d, *J*=13.2, 1H), 0.20 (s, 9H).



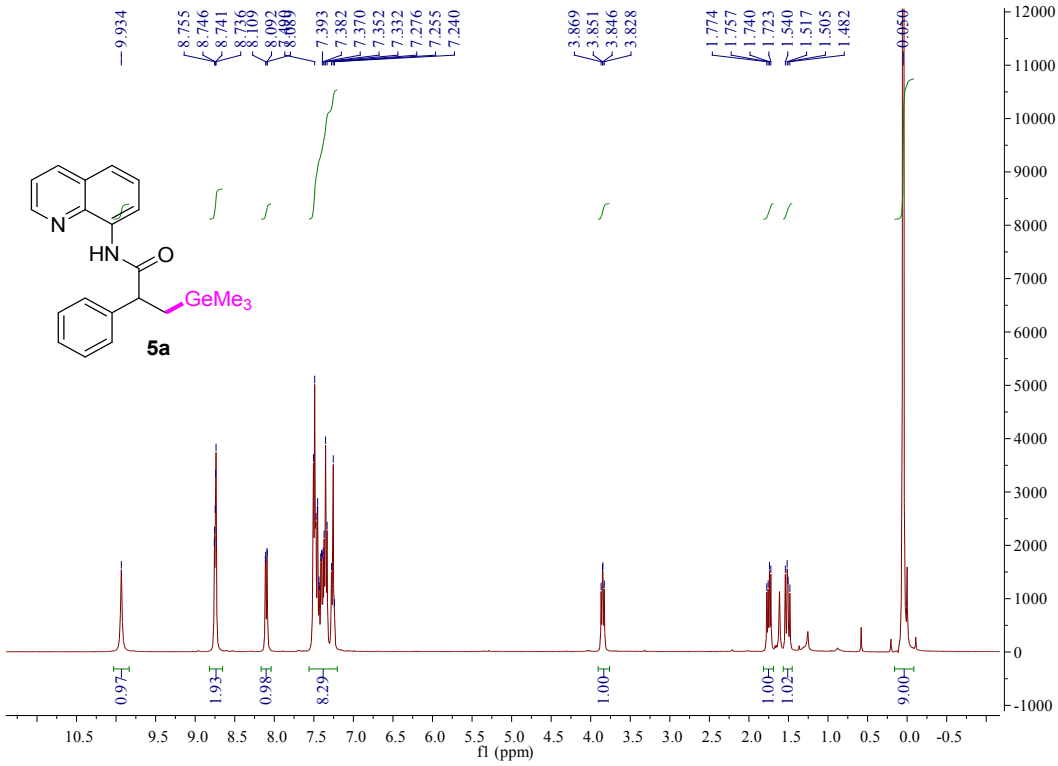
^{13}C NMR (101 MHz, $CDCl_3$) δ = 168.20, 166.67, 148.81, 143.39, 138.93, 136.28, 134.50, 134.15, 131.52, 128.06, 127.36, 126.82, 124.13, 123.92, 123.56, 122.34, 122.31, 121.78, 117.45, 60.76, 31.29, -2.20.



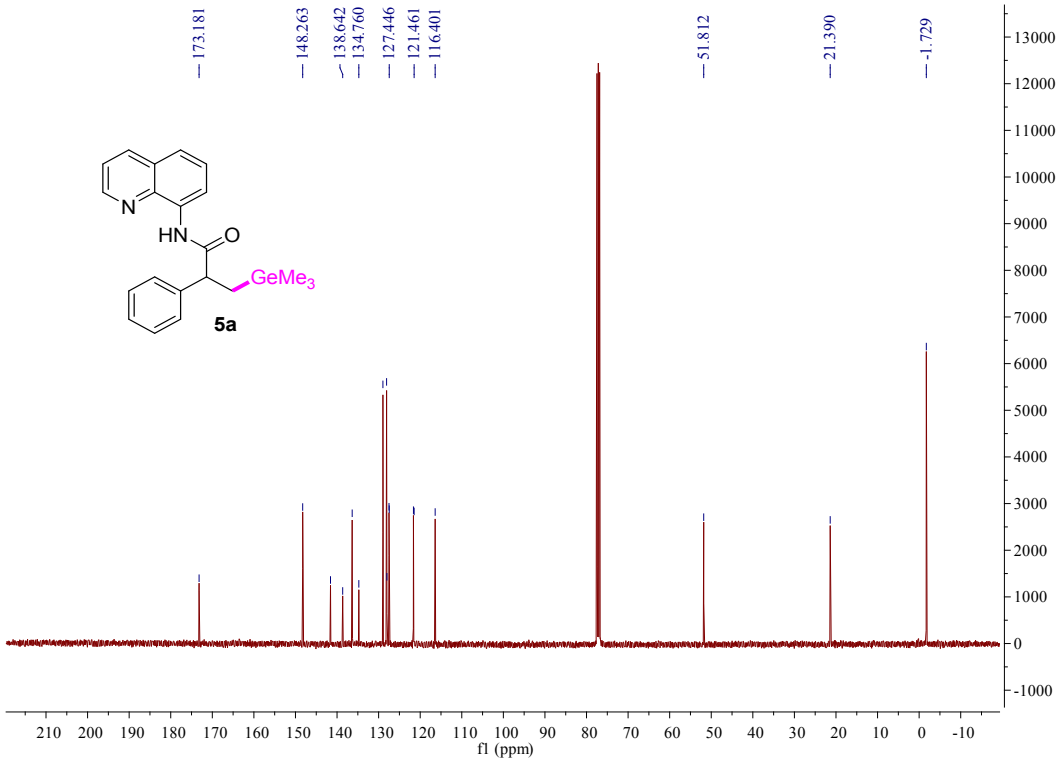
d.r. = 2.4:1 determined by ^{1}H NMR.^{1}H NMR(400 MHz, $CDCl_3$) δ = 10.27 (s, 1H), 8.81-8.79 (m, 1H), 8.72-8.68 (m, 1H), 8.12 (dd, *J*=8.4, 1.6, 1H), 7.54-7.40 (m, 3H), 5.84 (s, 0.21 H), 4.88 (d, *J*=8.4, 1H), 4.12-3.85 (m, 1H), 3.80 (s, 0.65 H), 3.61-3.47 (m, 1H), 2.38-2.27 (m, 0.76 H), 2.16 (s, 2H), 2.09 (s, 1H), 1.93-1.63 (m, 1H), 0.18 (s, 9H).



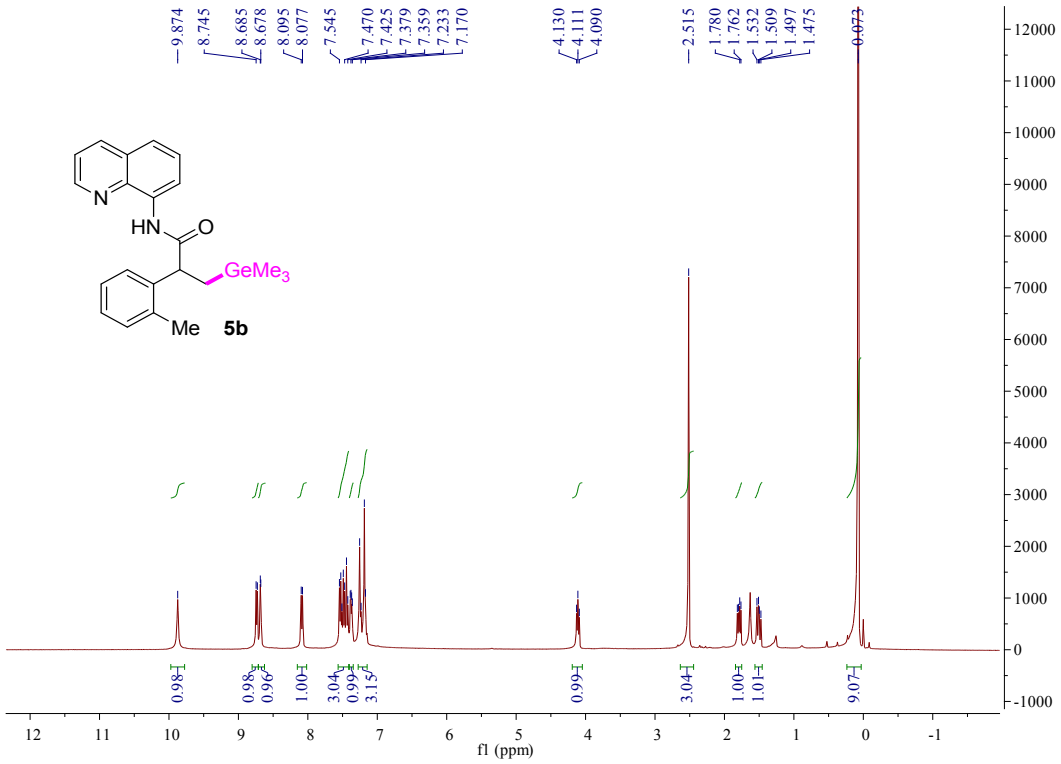
^{13}C NMR (101 MHz, $CDCl_3$) δ = 186.95, 170.32, 169.90, 169.87, 157.42, 148.97, 148.47, 138.69, 138.60, 136.38, 136.28, 134.43, 133.62, 128.03, 127.38, 127.31, 122.36, 121.95, 121.70, 121.67, 116.61, 116.57, 107.52, 66.58, 64.02, 56.58, 48.73, 47.44, 34.02, 31.93, 27.93, 26.00, 22.87, 22.63, -2.40, -2.65.



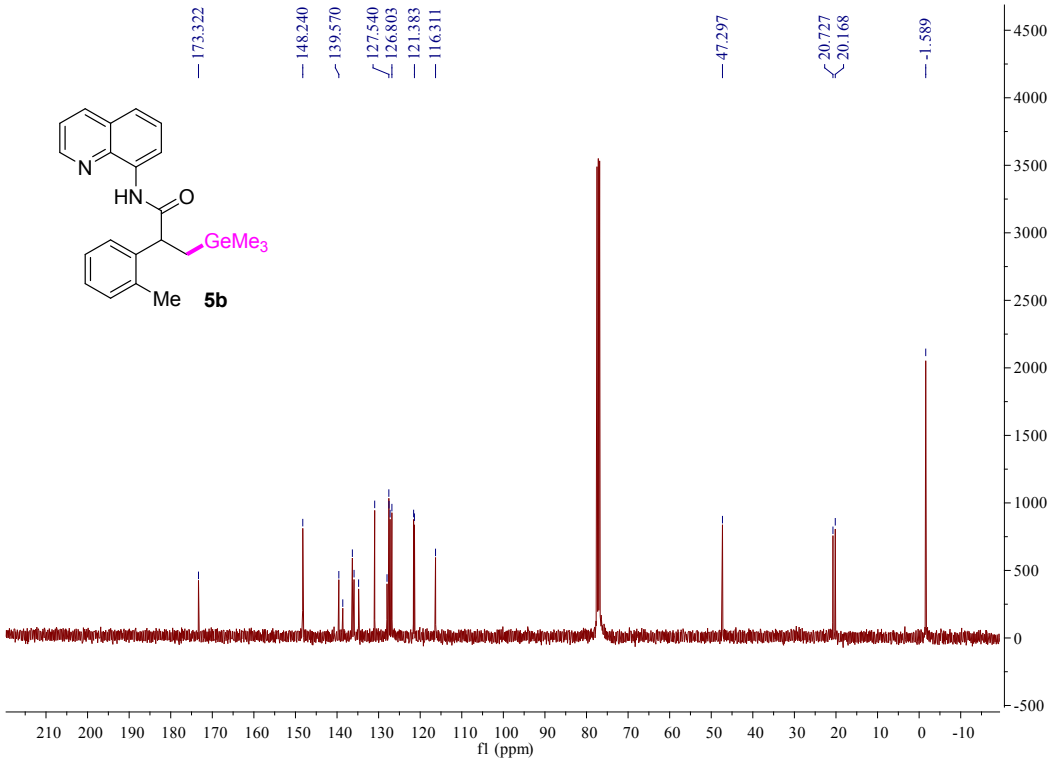
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.93 (br, 1H),8.76- 8.74 (m, 2H), 8.10 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.51-7.24 (m, 8H), 3.85 (dd, *J* = 9.2, 7.2 Hz, 1H), 1.75 (dd, *J* = 13.6, 6.8 Hz, 1H), 1.51 (dd, *J* = 13.6, 9.2 Hz, 1H), 0.05 (s, 9H).



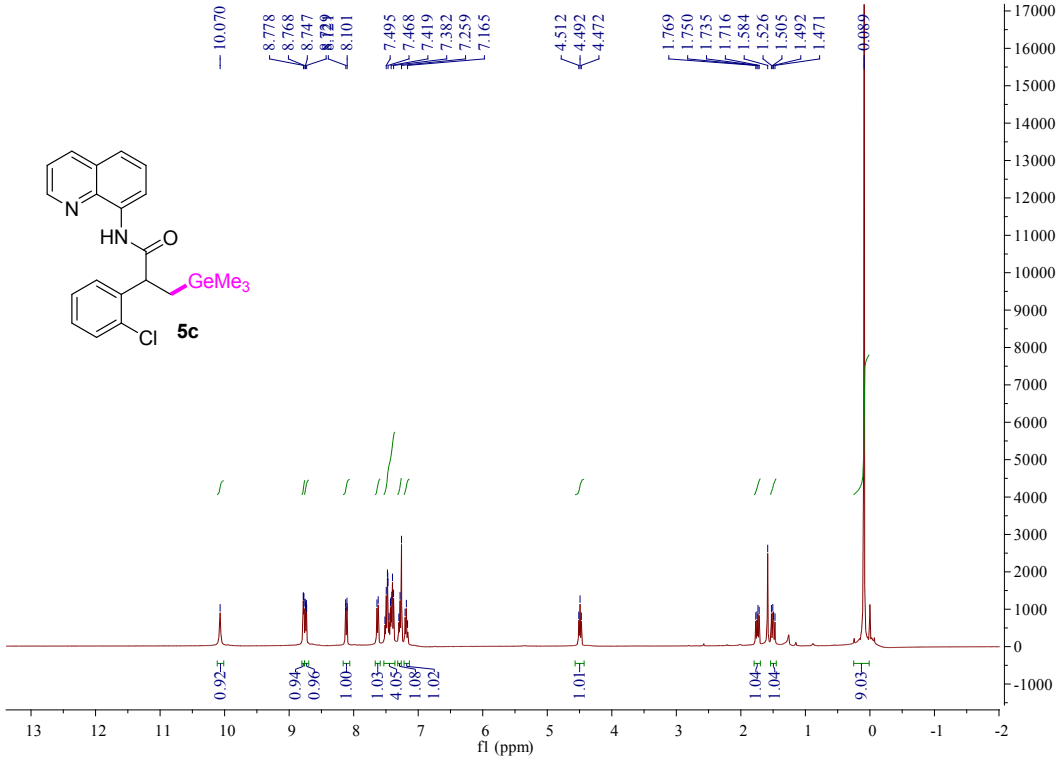
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.18, 148.26, 141.57, 138.64, 136.36, 134.76, 128.97, 128.09, 128.01, 127.51, 127.45, 121.62, 121.46, 116.40, 51.81, 21.39, -1.73



^{1}H NMR (400 MHz, $CDCl_3$) δ 9.87 (br, 1H), 8.74 (d, *J* = 7.4 Hz, 1H), 8.68 (d, *J* = 2.8 Hz, 1H), 8.09 (d, *J* = 7.2 Hz, 1H), 7.55-7.43 (m, 3H), 7.37 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.25-7.17 (m, 3H), 4.11 (dd, *J* = 8.4, 7.6 Hz, 1H), 2.52 (s, 3H), 1.79 (dd, *J* = 13.6, 7.2 Hz, 1H), 1.50 (dd, *J* = 13.6, 9.2 Hz, 1H), 0.07 (s, 9H).

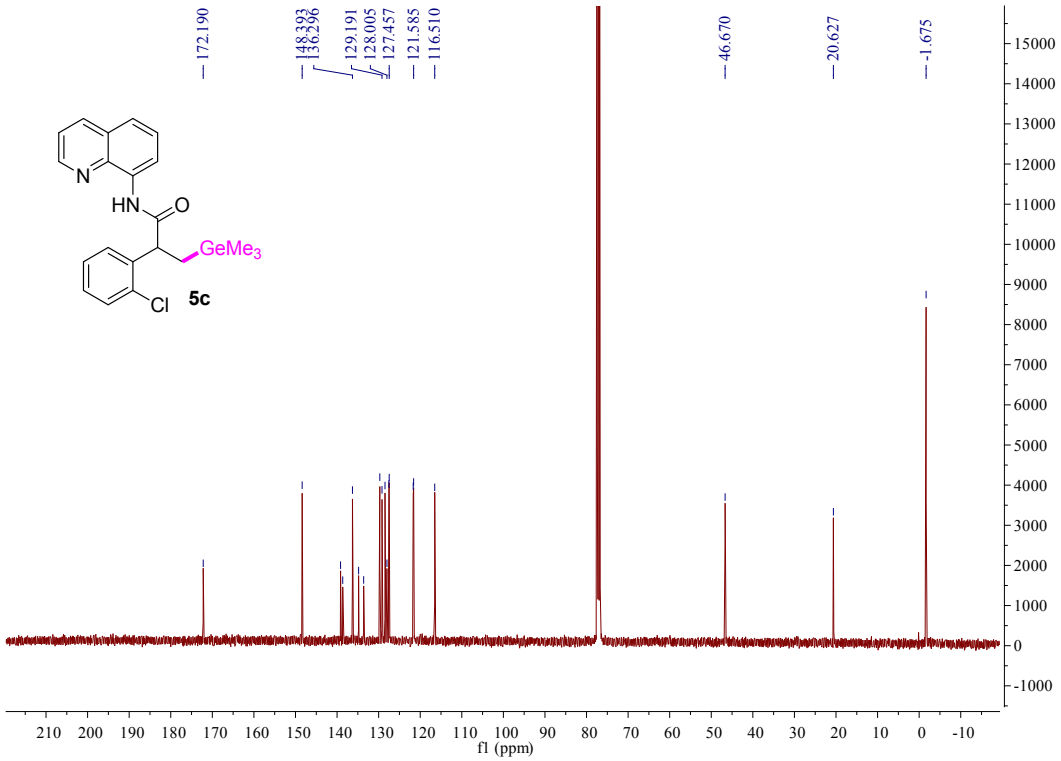


^{13}C NMR (101 MHz, $CDCl_3$) δ 173.32, 148.24, 139.57, 138.62, 136.31, 135.91, 134.81, 130.95, 127.98, 127.54, 127.50, 127.24, 126.80, 121.58, 121.38, 116.31, 47.30, 20.73, 20.17, -1.59

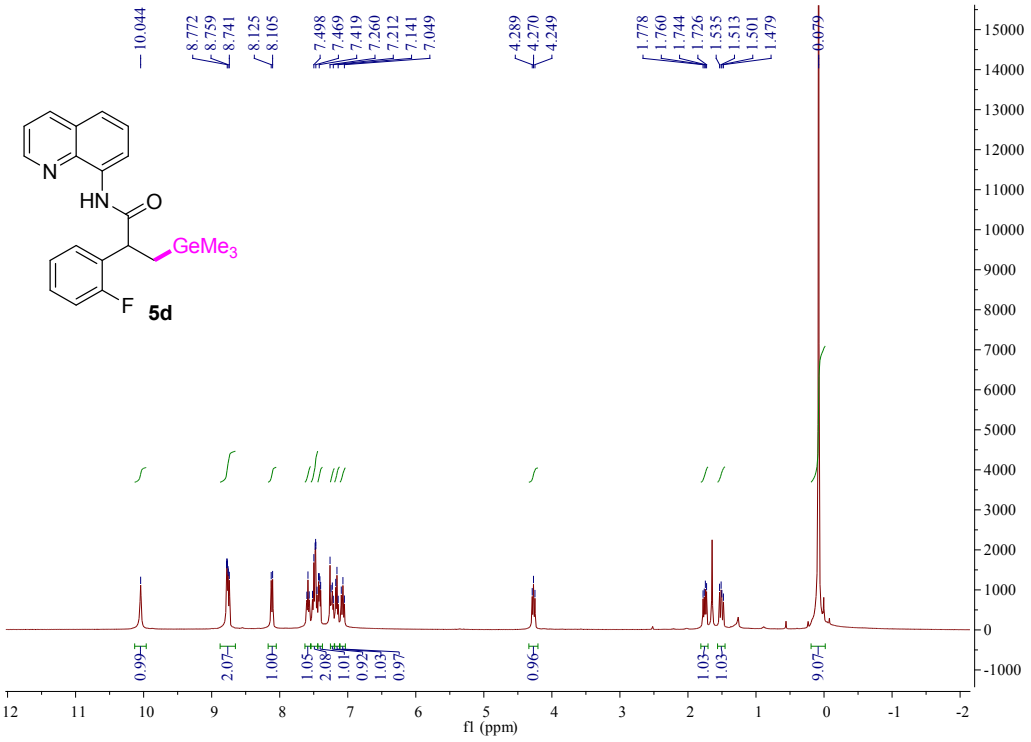


^{1}H NMR (400 MHz, $CDCl_3$) δ 10.07 (br, 1H), 8.77 (dd, J = 4.0, 1.6 Hz, 1H), 8.74 (dd, J = 7.2, 1.6 Hz, 1H), 8.11 (dd, J = 8.0, 1.2 Hz, 1H), 7.63 (d, J = 7.6 Hz, 1H), 752-7.38 (m, 4H), 7.29 (d, J = 7.6 Hz, 1H),

7.18 (t, *J* = 7.6 Hz, 1H), 4.49 (t, *J* = 8.0 Hz, 1H), 1.74 (dd, *J* = 13.6, 7.6 Hz, 1H), 1.50 (dd, *J* = 13.6, 8.4 Hz, 1H), 0.09 (s, 9H).

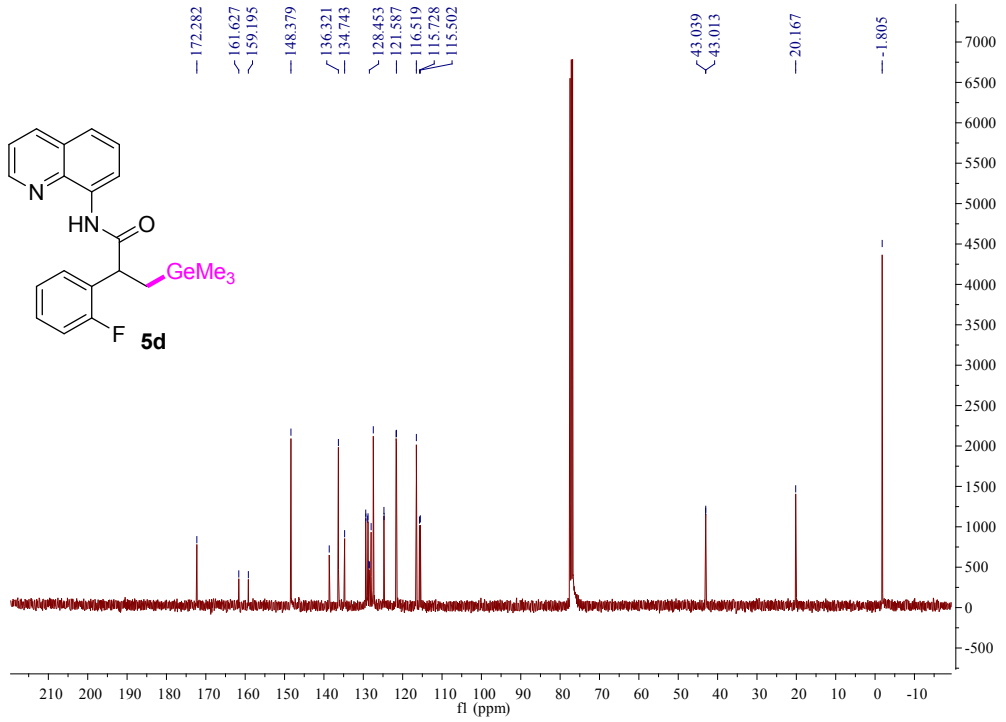


^{13}C NMR (101 MHz, $CDCl_3$) δ 172.19, 148.39, 139.16, 138.64, 136.30, 134.82, 133.60, 129.72, 129.19, 128.47, 128.01, 127.55, 127.46, 121.68, 121.59, 116.51, 46.67, 20.63, -1.68

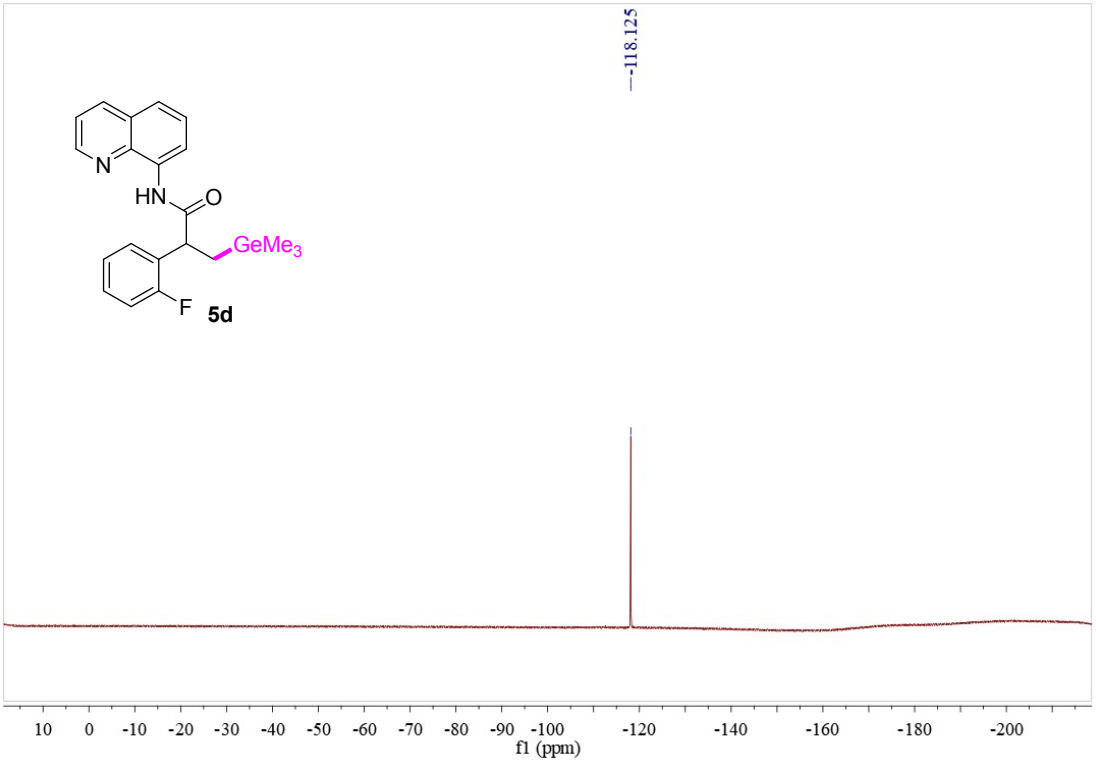


^{1}H NMR (400 MHz, $CDCl_3$) δ 10.04 (br, 1H), 8.78-8.74 (m, 2H), 8.11 (d, *J* = 8.0 Hz, 1H), 7.58 (t, *J* = 6.8 Hz, 1H), 7.52-7.45 (m, 2H), 7.41 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.24-7.21 (m, 1H), 7.16 (t, *J* = 7.2 Hz,

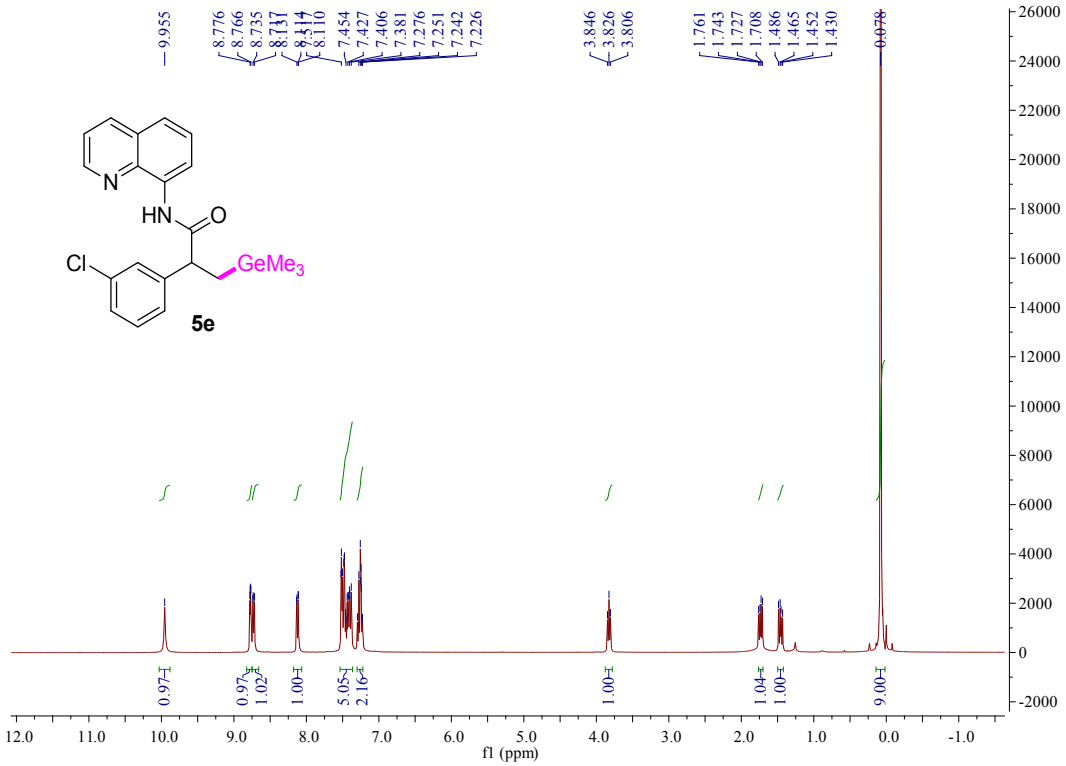
1H), 7.07 (t, *J* = 7.2 Hz, 1H), 4.27 (dd, *J* = 8.4, 7.6 Hz, 1H), 1.75 (dd, *J* = 13.6, 7.2 Hz, 1H), 1.51 (dd, *J* = 13.6, 8.8 Hz, 1H), 0.08 (s, 9H).



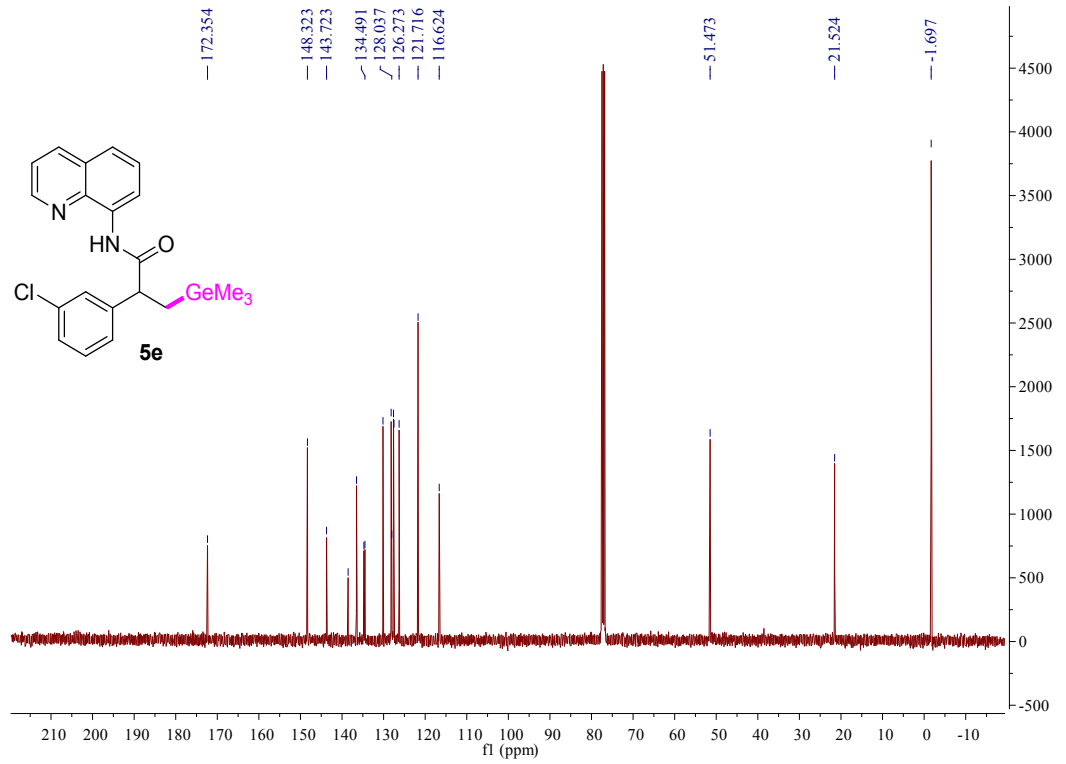
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.28, 161.41 (d, *J* = 243.2 Hz), 148.38, 138.65, 136.32, 134.74, 129.36 (d, *J* = 3.8 Hz), 128.84 (d, *J* = 8.3 Hz), 128.52 (d, *J* = 14.6 Hz),128.01, 127.46, 124.74 (d, *J* = 3.5 Hz), 121.63 (d, *J* = 8.3 Hz), 116.52, 115.73, 115.50, 43.03 (d, *J* = 2.6 Hz), 20.17, -1.81.



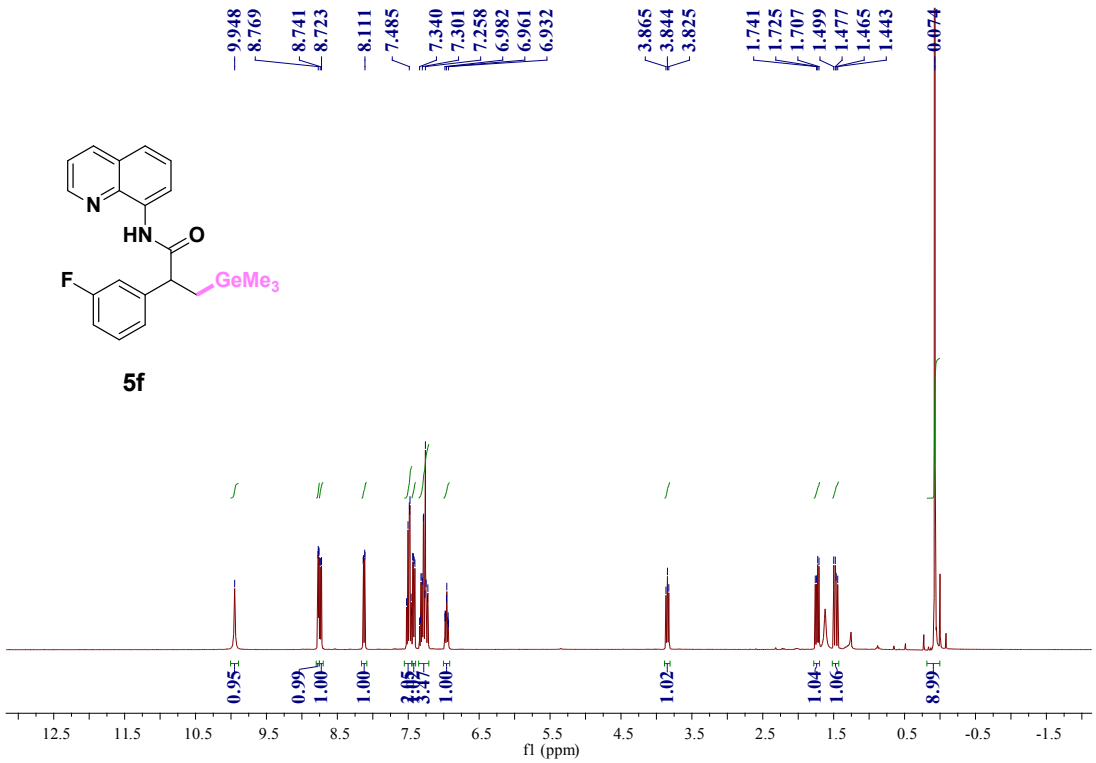
^{19}F NMR (376 MHz, $CDCl_3$) δ = -118.12.



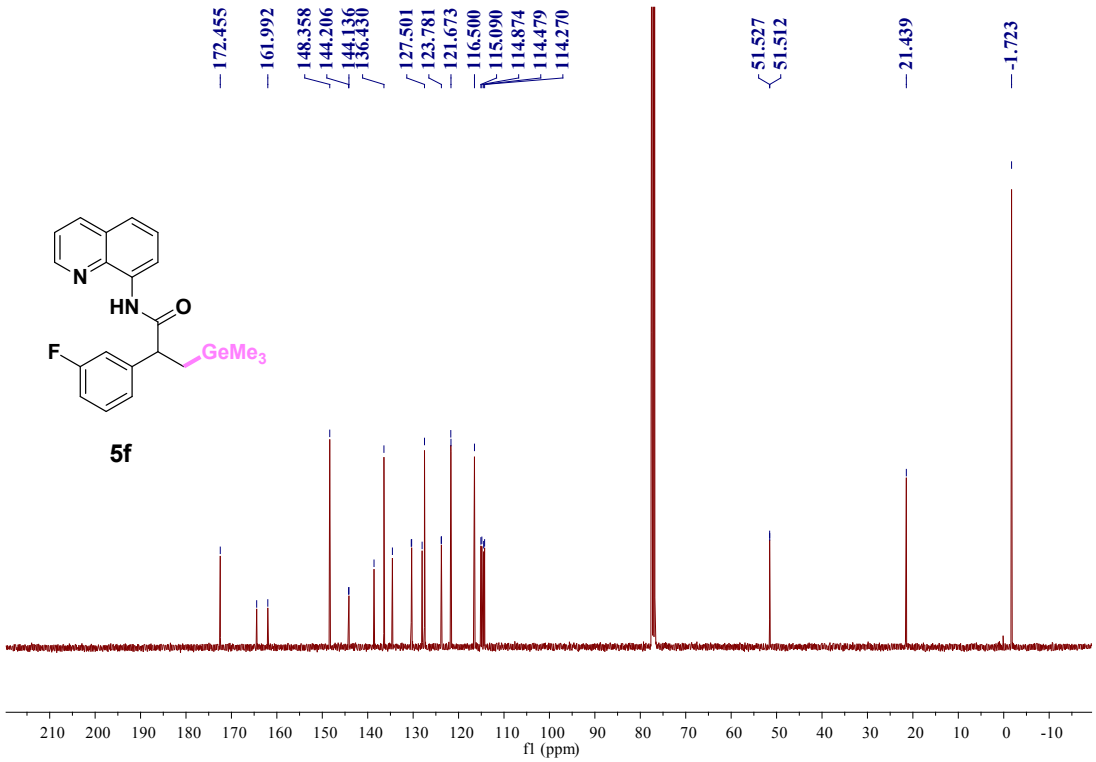
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.96 (br, 1H), 8.77 (dd, *J* = 4.0, 1.6 Hz, 1H), 8.73 (dd, *J* = 7.2, 1.6 Hz, 1H), 8.12 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.52-7.38 (m, 5H), 7.30-7.23 (m, 2H), 3.83 (t, *J* = 8.0 Hz, 1H), 1.73 (dd, *J* = 13.6, 7.2 Hz, 1H), 1.46 (dd, *J* = 13.6, 8.8 Hz, 1H), 0.08 (s, 9H).



^{13}C NMR (101 MHz, CDCl3) δ 172.35, 148.32, 143.72, 138.54, 136.52, 134.74, 134.49, 130.15, 128.19, 128.04, 127.62, 127.52, 126.27, 121.72, 116.62, 51.47, 21.52, -1.70.

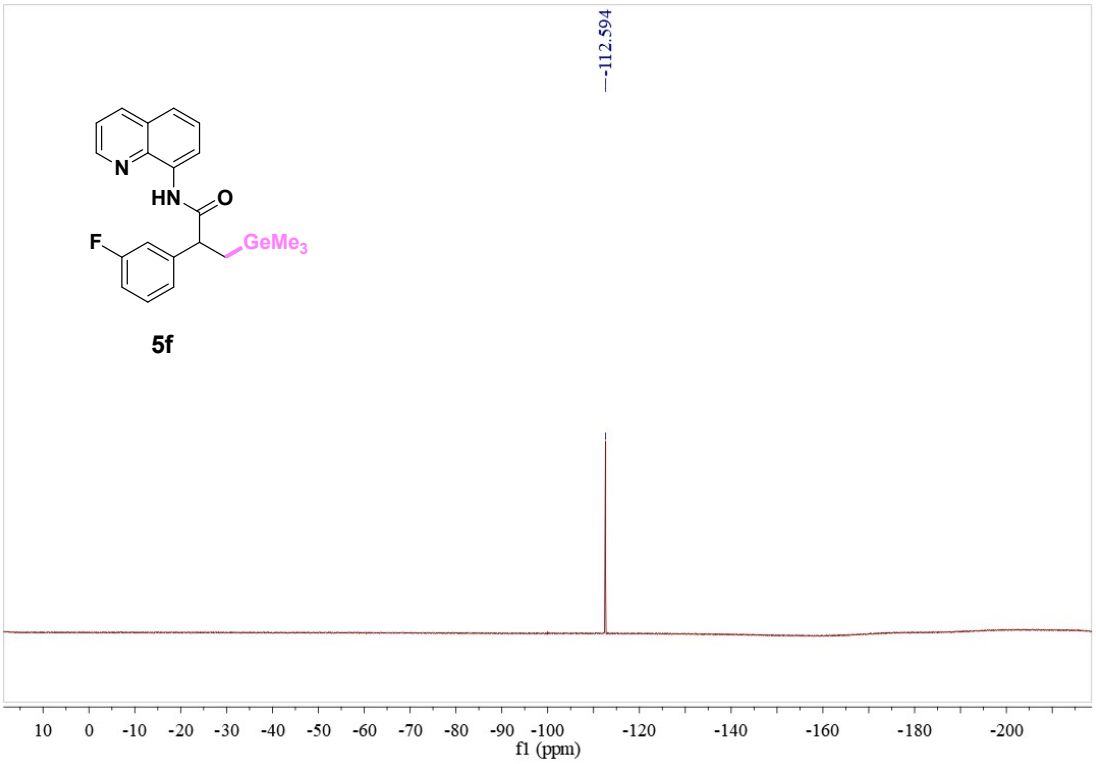


^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.95 (br, 1H), 8.77 (dd, *J*=4.4, 1.6, 1H), 8.73 (dd, *J*=7.2, 1.6, 1H), 8.12 (dd, *J*=8.4, 1.6, 1H), 7.52-7.46 (m, 2H), 7.42 (dd, *J*=8.4, 4.4, 1H), 7.34-7.22 (m, 3H), 6.98-6.93 (m, 1H), 3.84 (dd, *J*=8.4, 7.6, 1H), 1.73 (dd, *J*=13.6, 7.2, 1H), 1.47 (dd, *J*=13.7, 8.8, 1H), 0.07 (s, 9H).

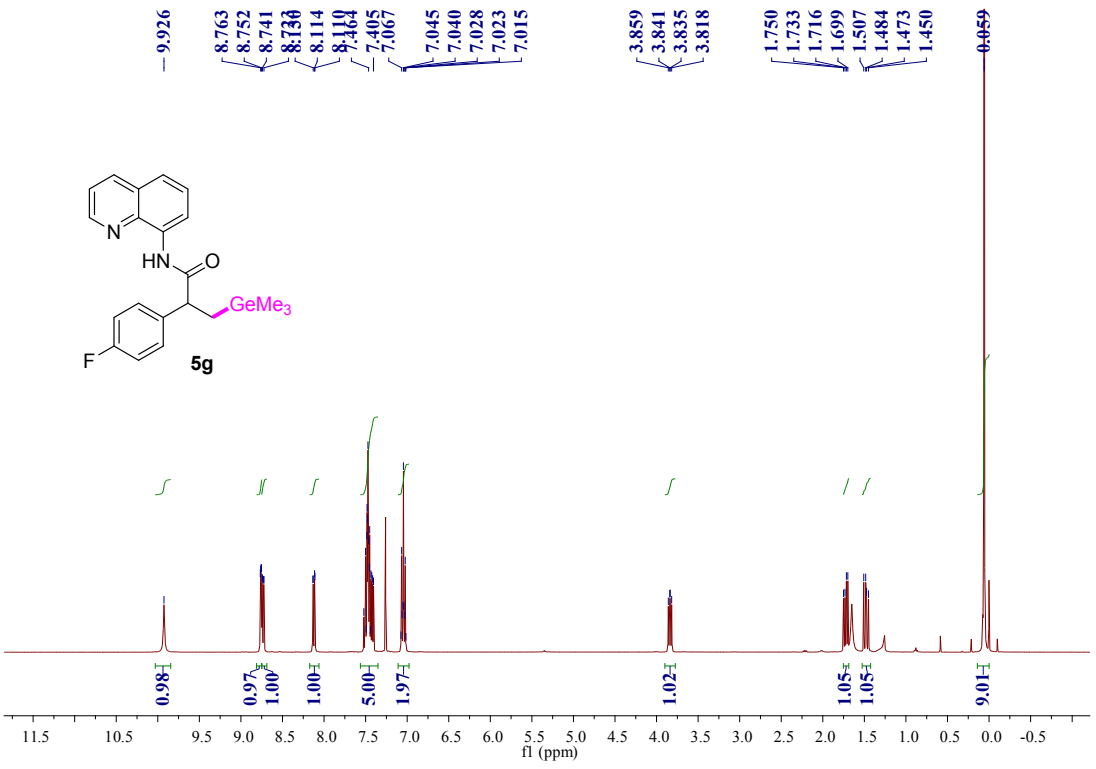


^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.45, 164.44, 161.99, 148.36, 144.21, 144.14, 138.61, 136.43,

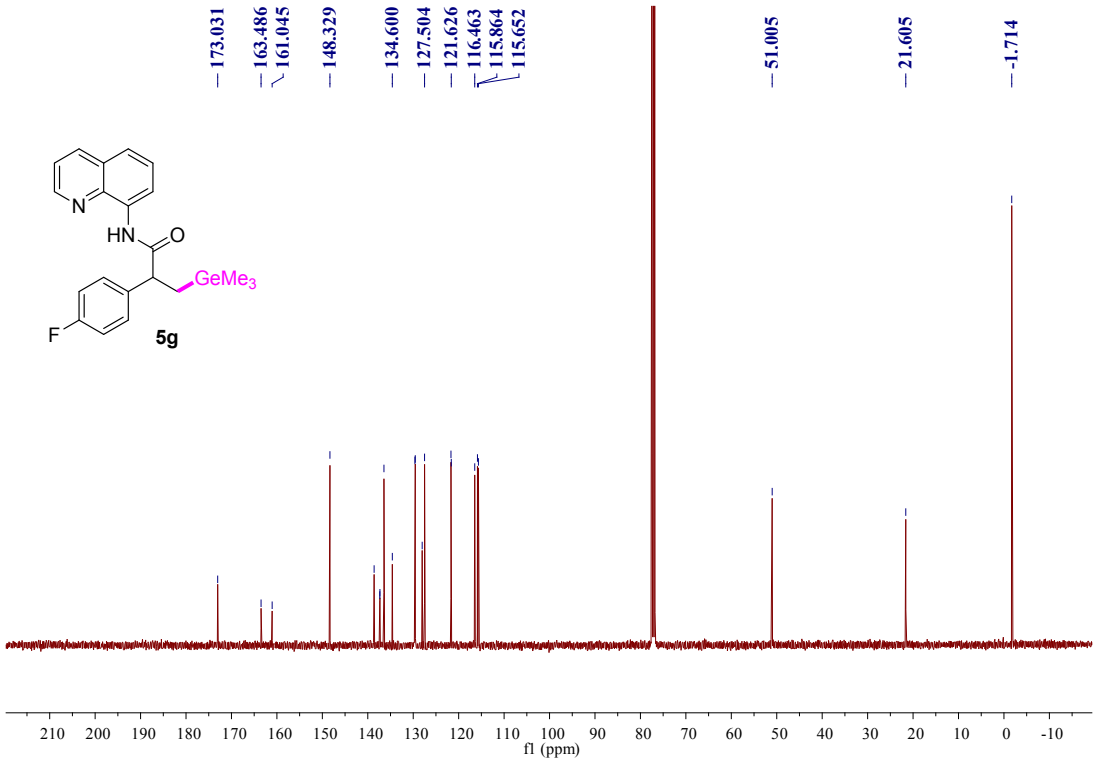
134.56, 130.41, 130.33, 128.03, 127.50, 123.81, 123.78, 121.71, 121.67, 116.50, 115.09, 114.87, 114.48, 114.27, 51.53, 51.51, 21.44, -1.72.



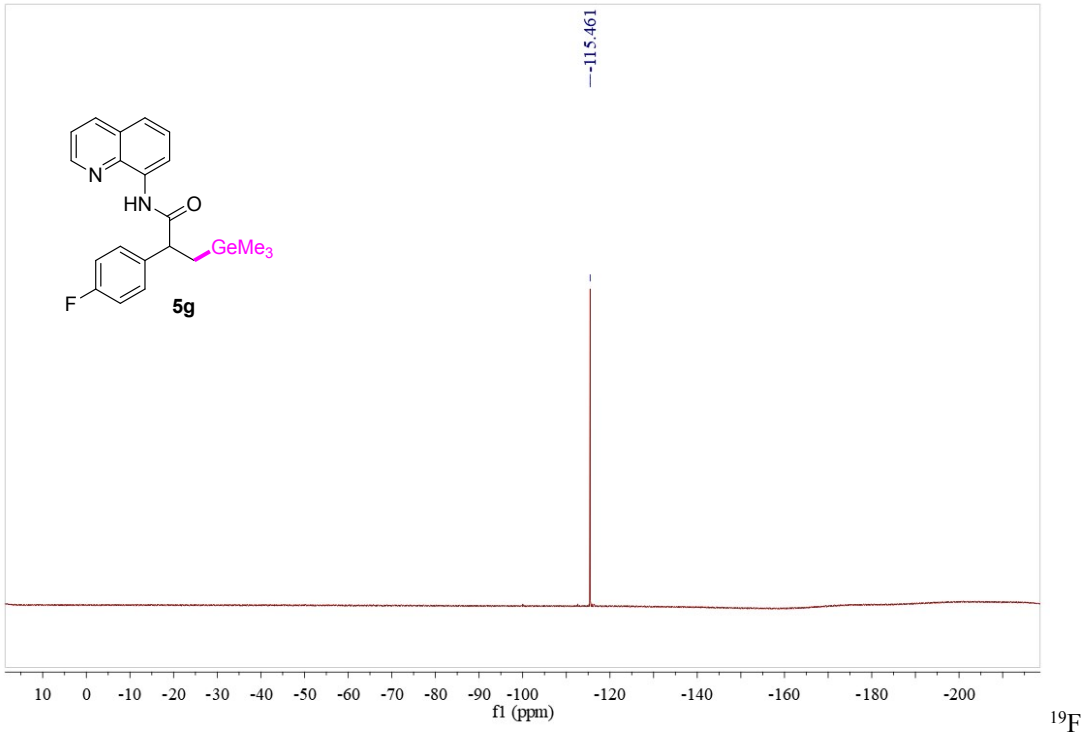
^{19}F NMR (376 MHz, $CDCl_3$) δ = -112.59.



^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.93 (br, 1H), 8.76 (dd, *J*=4.4, 1.6, 1H), 8.73 (dd, *J*=7.2, 1.6, 1H), 8.12 (dd, *J*=8.4, 1.6, 1H), 7.52-7.41 (m, 5H), 7.07-7.02 (m, 2H), 3.84 (dd, *J*=9.2, 6.8, 1H), 1.72 (dd, *J*=13.6, 6.8, 1H), 1.48 (dd, *J*=13.6, 9.2, 1H), 0.06 (s, 9H).

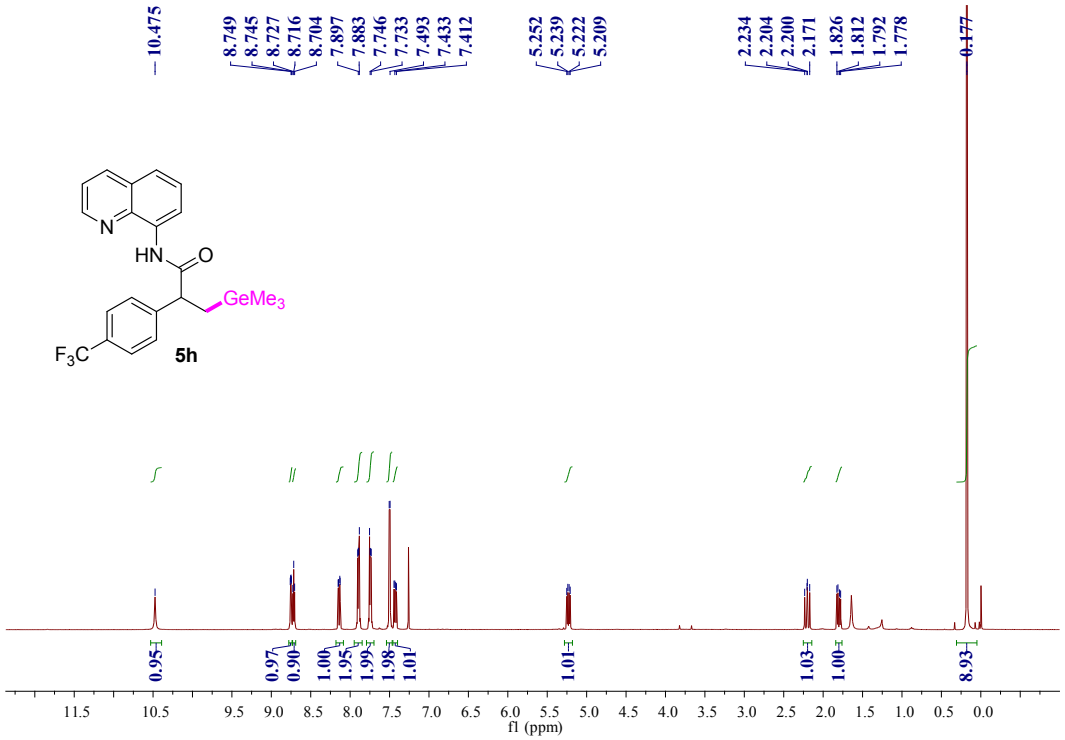


^{13}C NMR (101 MHz, $CDCl_3$) δ = 173.03, 163.49, 161.05, 148.33, 138.61, 137.36, 137.32, 136.44, 134.60, 129.63, 129.55, 128.03, 127.50, 121.69, 121.63, 116.46, 115.86, 115.65, 51.00, 21.61, -1.71.

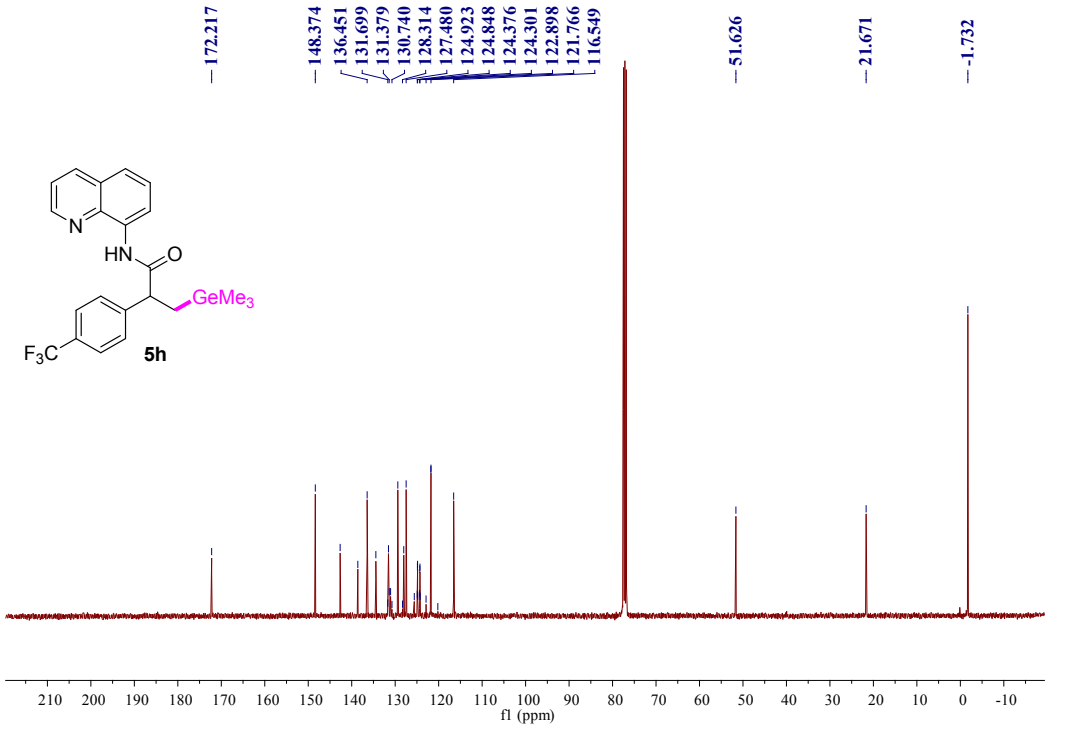


^{19}F

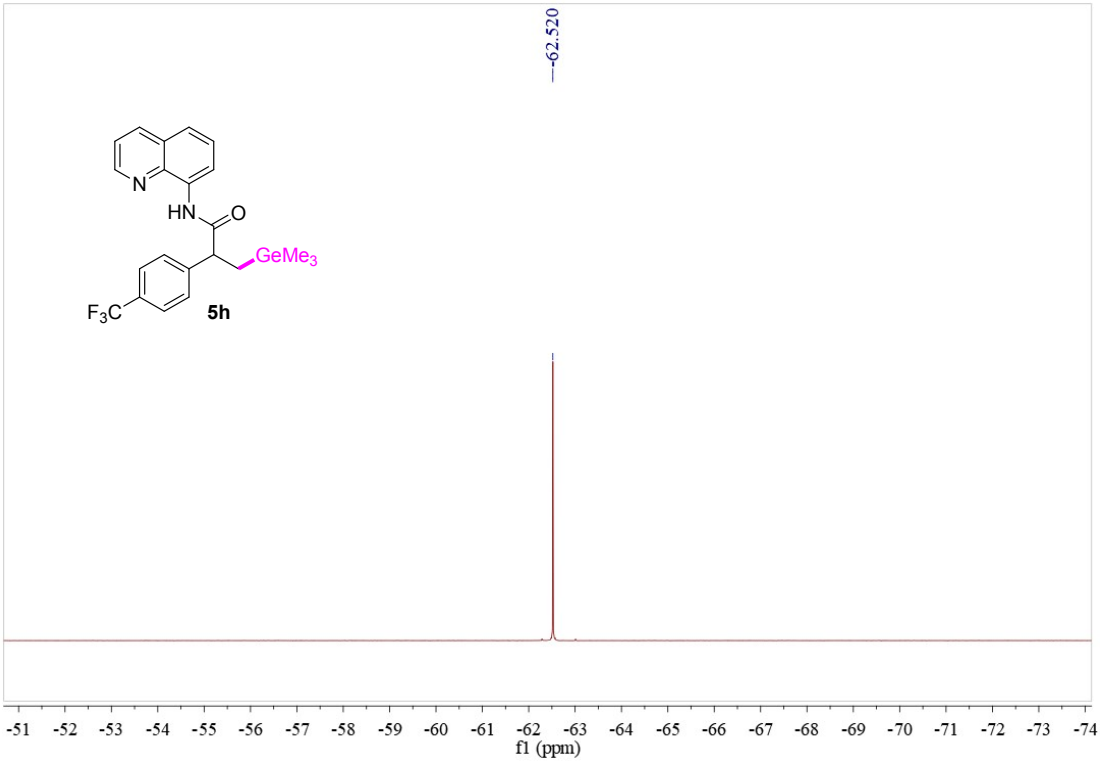
^{19}F NMR (376 MHz, $CDCl_3$) δ = -115.46.



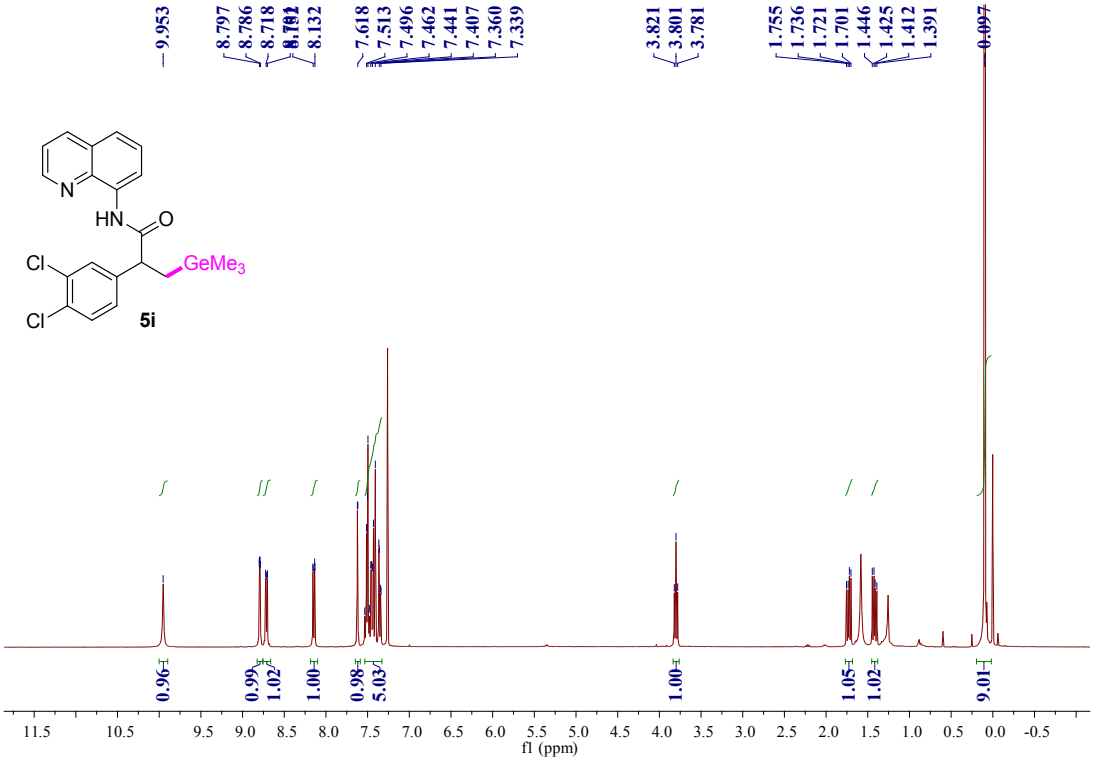
^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.47 (br, 1H), 8.75 (dd, *J*=4.4, 1.6, 1H), 8.72 (t, *J*=4.4, 1H), 8.14 (dd, *J*=8.4, 1.6, 1H), 7.89 (dd, *J*=5.2, 3.2, 2H), 7.74 (dd, *J*=5.2, 3.2, 2H), 7.50 (d, *J*=4.4, 2H), 7.43 (dd, *J*=8.4, 4.4, 1H), 5.23 (dd, *J*=12.0, 5.6, 1H), 2.20 (dd, *J*=13.6, 12.0, 1H), 1.80 (dd, *J*=13.6, 5.6, 1H), 0.18 (s, 9H).



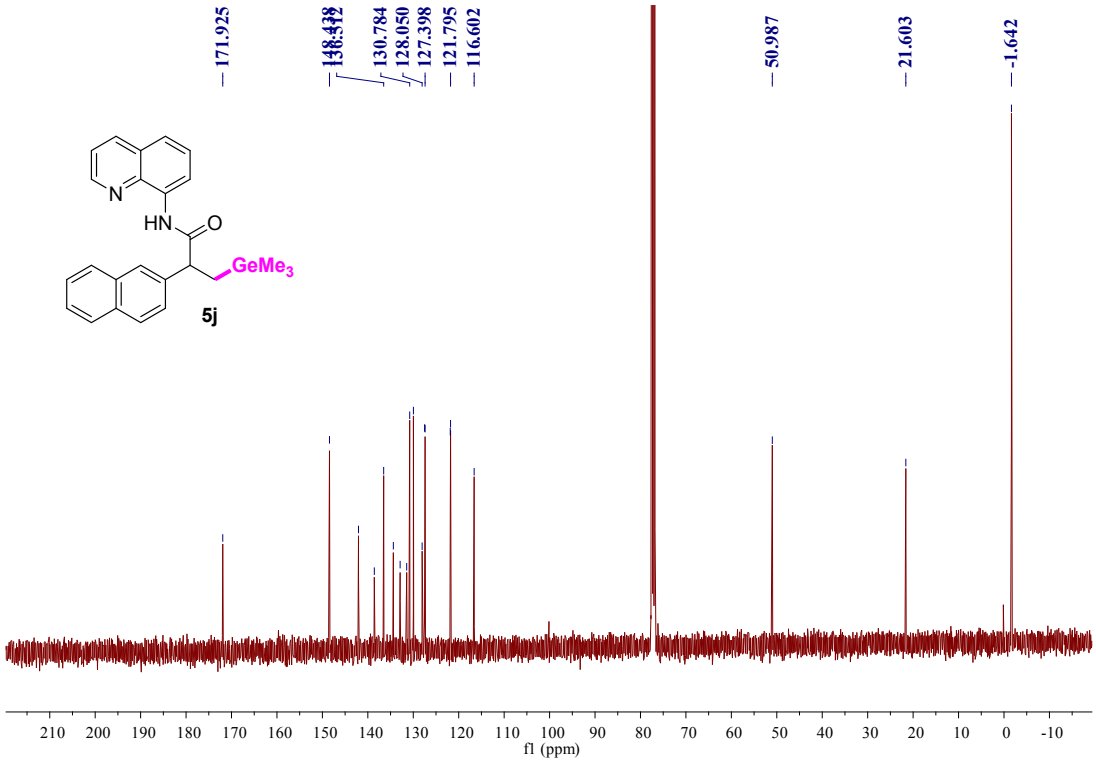
^{13}C NMR (101 MHz, CDCl3) δ = 172.22, 148.37, 142.66, 138.60, 136.45, 134.44, 131.54,131.22 (q, J=32.0), 129.39, 128.03, 127.48, 124.87 (q, J=3.8), 124.32 (q, J=3.8), 124.25 (q, J=270.8), 121.78 (d, J=1.8), 116.55, 51.63, 21.67, -1.73.



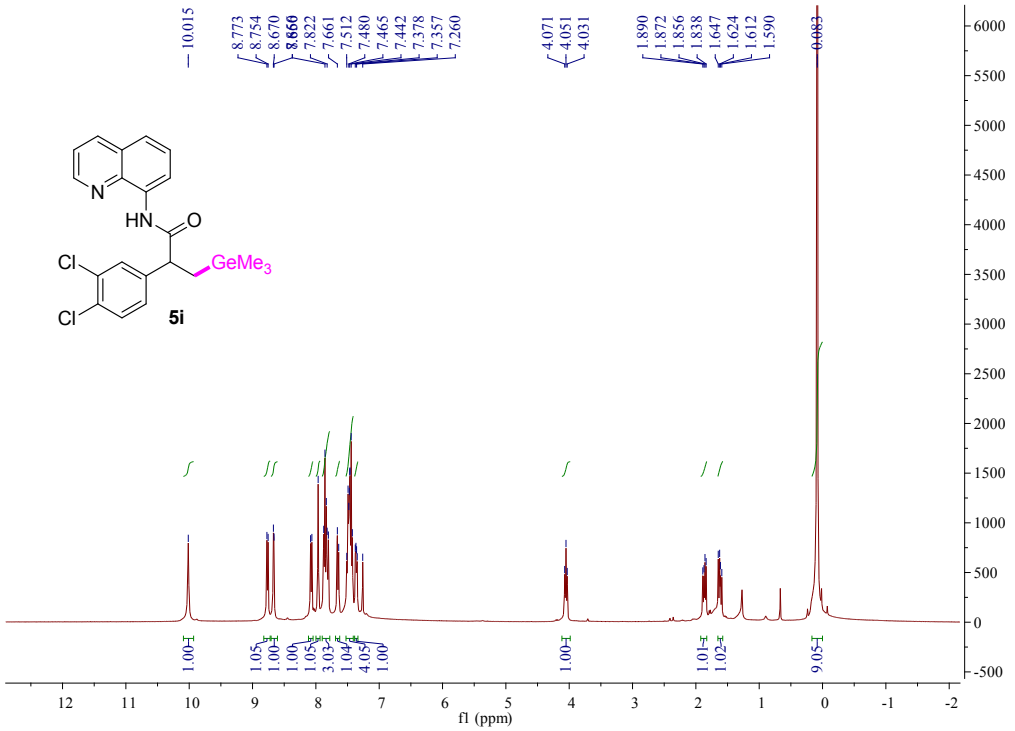
^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.52.



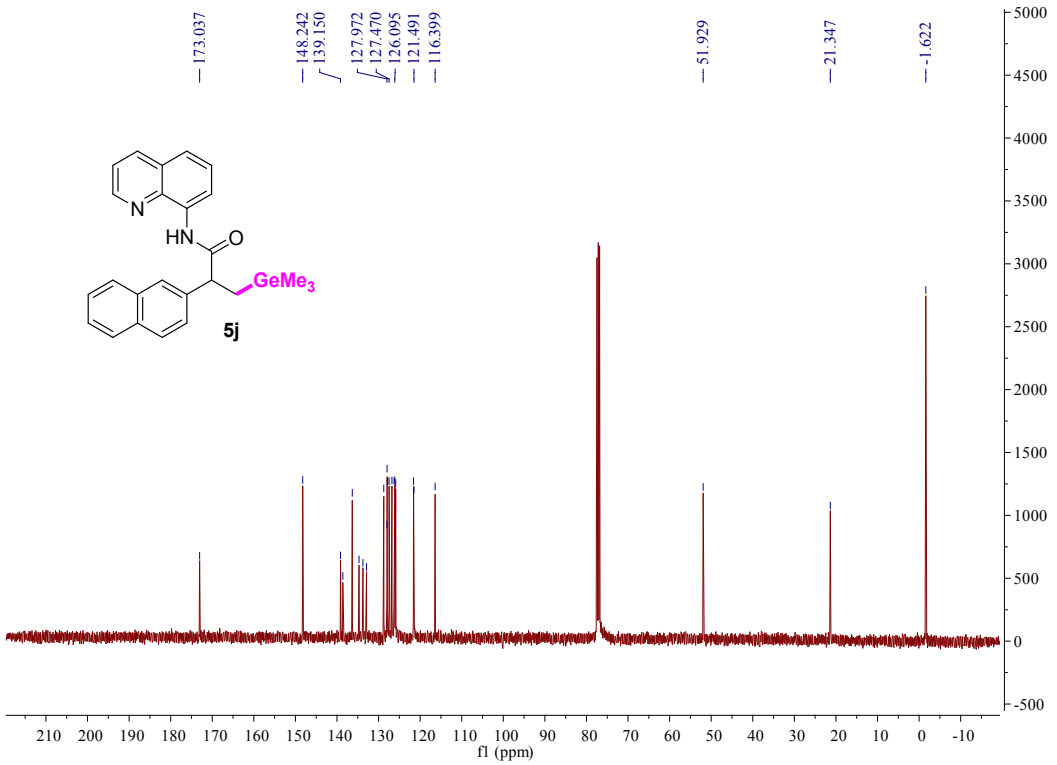
^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.95 (br, 1H), 8.79 (dd, *J*=4.4, 1.6, 1H), 8.71 (dd, *J*=6.8, 2.4, 1H), 8.14 (dd, *J*=8.0, 1.6, 1H), 7.62 (d, *J*=2.0, 1H), 7.53-7.34 (m, 5H), 3.80 (t, *J*=8.0, 1H), 1.73 (dd, *J*=13.6, 8.0, 1H), 1.42 (dd, *J*=13.6, 8.4, 1H), 0.10 (s, 9H).



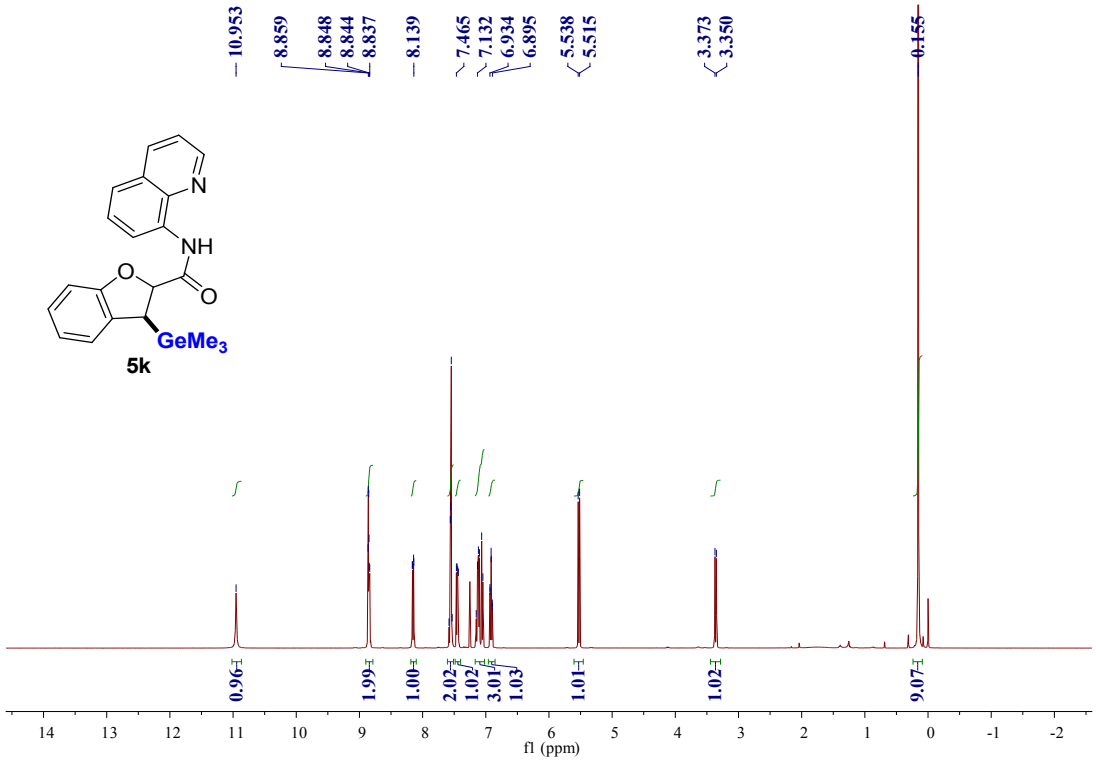
^{13}C NMR (101 MHz, $CDCl_3$) δ = 171.92, 148.44, 142.05, 138.57, 136.51, 134.38, 132.89, 131.45, 130.78, 129.97, 128.05, 127.50, 127.40, 121.86, 121.79, 116.60, 50.99, 21.60, -1.64.



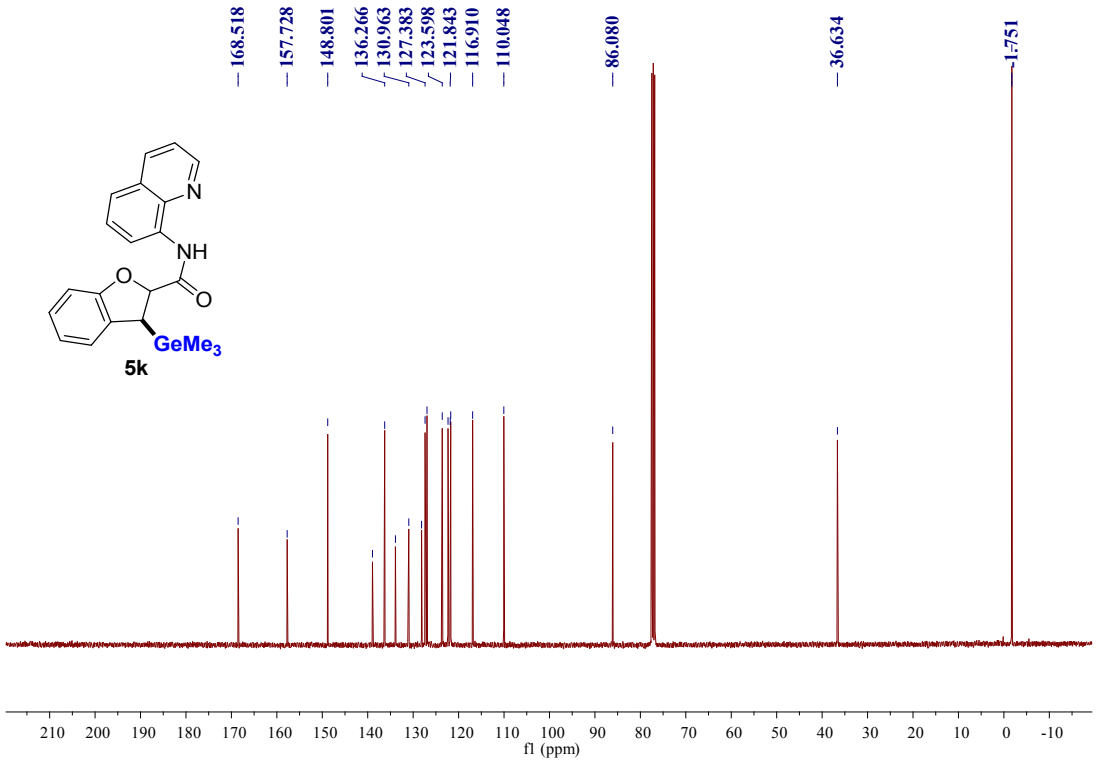
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.01 (br, 1H), 8.76 (d, *J* = 7.6 Hz, 1H), 8.67 (d, *J* = 4.0 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.96 (s, 1H), 7.88-7.80 (m, 3H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.51-7.42 (m, 4H), 7.36 (dd, *J* = 8.0, 4.0 Hz, 1H), 4.05 (t, *J* = 8.0 Hz, 1H), 1.86 (dd, *J* = 13.6, 7.2 Hz, 1H), 1.62 (dd, *J* = 13.6, 8.8 Hz, 1H), 0.08 (s, 9H).



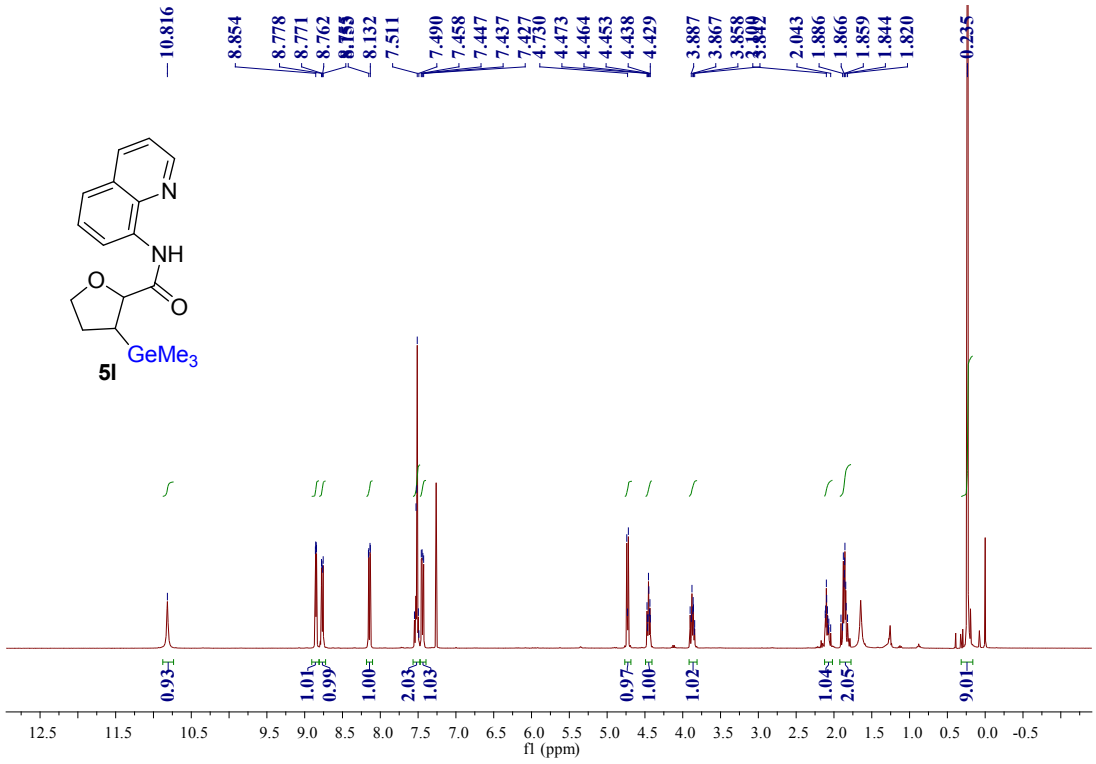
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.04, 148.24, 139.15, 138.60, 136.32, 134.70, 133.76, 132.89, 128.75, 127.97, 127.95, 127.79, 127.47, 126.79, 126.26, 126.10, 125.88, 121.59, 121.49, 116.40, 51.93, 21.35, -1.62



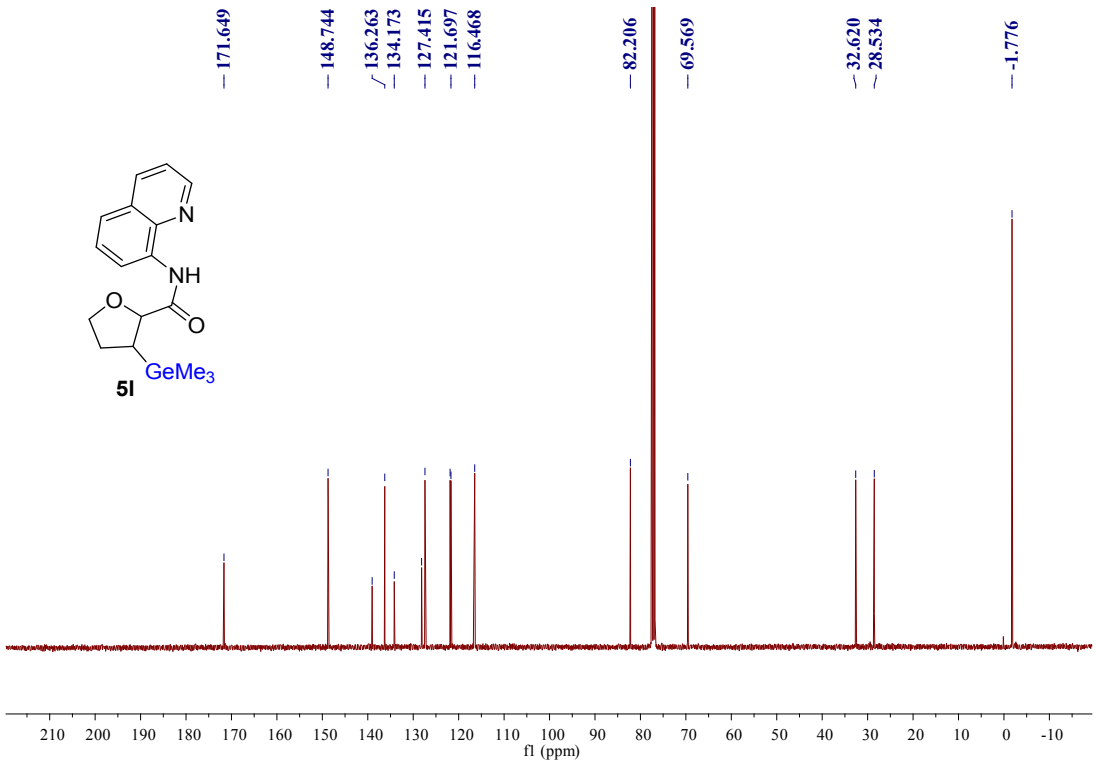
^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.95 (s, 1H), 8.86-8.84 (m, 2H), 8.15 (dd, *J*=8.4, 1.6, 1H), 7.58-7.53 (m, 2H), 7.45 (dd, *J*=8.4, 4.4, 1H), 7.15-7.05 (m, 3H), 6.91 (td, *J*=7.6, 0.8, 1H), 5.53 (d, *J*=9.2, 1H), 3.36 (d, *J*=9.2, 1H), 0.15 (s, 9H).



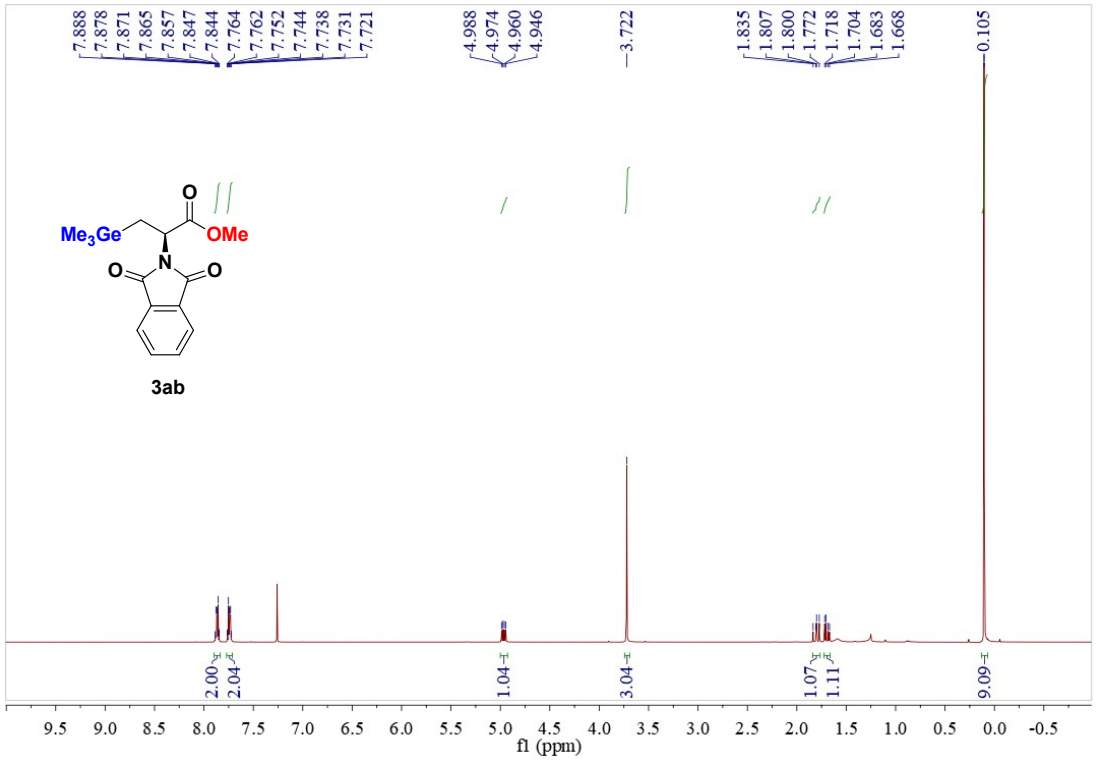
^{13}C NMR (101 MHz, $CDCl_3$) δ = 168.52, 157.73, 148.80, 138.95, 136.27, 133.90, 130.96, 128.15, 127.38, 126.95, 123.60, 122.33, 121.84, 121.73, 116.91, 110.05, 86.08, 36.63, -1.75.



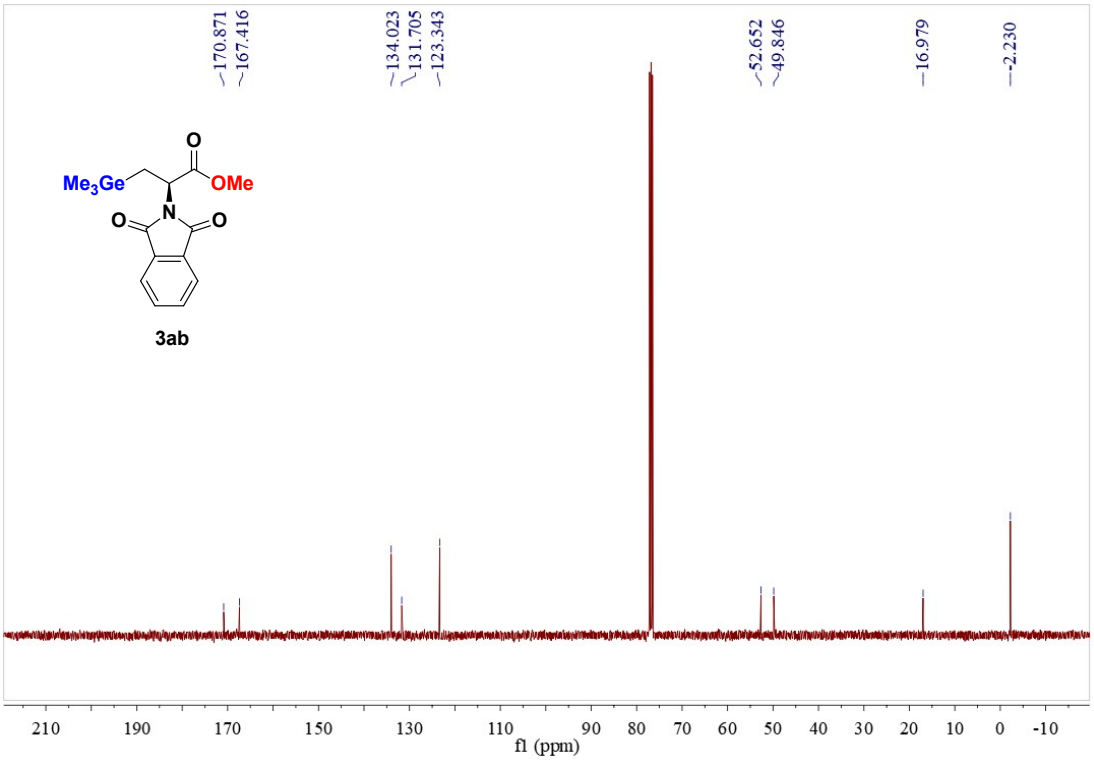
^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.82 (br, 1H), 8.85 (dd, *J*=4.4, 1.6, 1H), 8.77 (dd, *J*=6.4, 2.8, 1H), 8.14 (dd, *J*=8.4, 1.6, 1H), 7.55-7.49 (m, 2H), 7.44 (dd, *J*=8.4, 4.4, 1H), 4.74-4.72 (m, 1H), 4.47-4.43 (m, 1H), 3.90-3.84 (m, 1H), 2.12-2.04 (m, 1H), 1.91-1.82 (m, 2H), 0.23 (s, 9H).



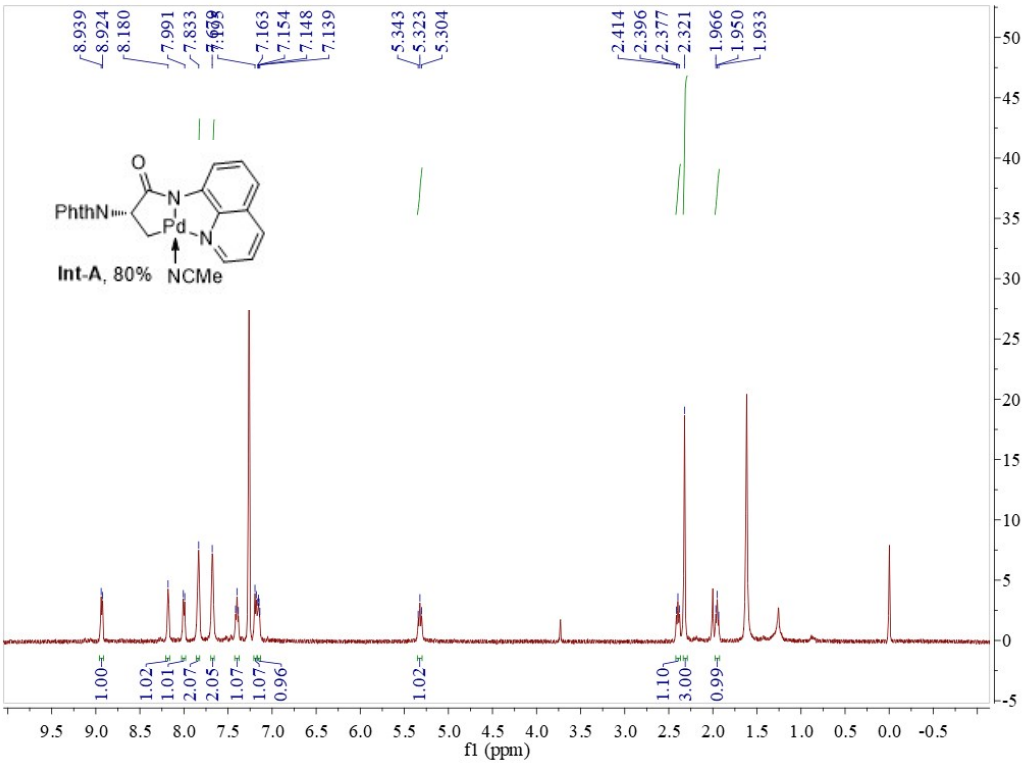
^{13}C NMR (101 MHz, $CDCl_3$) δ = 171.65, 148.74, 139.04, 136.26, 134.17, 128.16, 127.42, 121.88, 121.70, 116.47, 82.21, 69.57, 32.62, 28.53, -1.78.



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.84 (m, 2H), 7.77 – 7.71 (m, 2H), 4.97 (dd, *J* = 11.1, 5.7 Hz, 1H), 3.72 (s, 3H), 1.80 (dd, *J* = 14.1, 11.1 Hz, 1H), 1.69 (dd, *J* = 14.1, 5.7 Hz, 1H), 0.10 (s, 9H).



^{13}C NMR (101 MHz, $CDCl_3$) δ = 170.87, 167.42, 134.02, 131.71, 123.34, 52.65, 49.85, 16.98, -2.23.



^{1}H NMR (501 MHz, $CDCl_3$) δ 8.93 (d, *J* = 7.5 Hz, 1H), 8.18 (s, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.83 (s, 2H), 7.68 (s, 2H), 7.40 (t, *J* = 8.0 Hz, 1H), 7.19 (d, *J* = 7.5 Hz, 1H), 7.15 (dd, *J* = 7.5, 4.5 Hz, 1H), 5.32 (t, *J* = 10.0 Hz, 1H), 2.40(t, *J* = 9.0 Hz, 1H)2.32 (s, 3H),1.95(t, *J* = 8.0 Hz, 1H).