Supporting Information

Copper-Promoted Difunctionalization of Unactivated Alkenes with Silanes

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Table of Contents

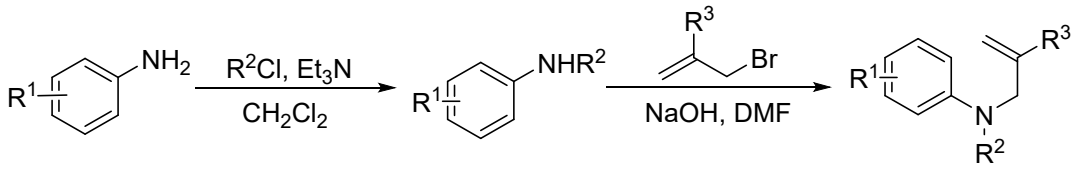
1. General Information

All manipulations were performed in 25 mL Schlenk tube equipped with a magnetic stir bar unless otherwise noted. Solvents and reagents were purchased from commercial sources and used as received. Flash column chromatography was performed using silica gel (60-Å pore size, 32-63 μm, standard grade). Analytical thin-layer chromatography was performed using glass plates pre-coated with 0.25 mm 230-400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Melting points were recorded by XT4A micro melting point Measurement Instruments, thermometer was unrevised. The transformation progress and mass spectra were indicated by GC (Shimadzu GC-2010 Plus) or GC-MS (Thermo Fisher Scientific DSQ II). NMR spectra were obtained on Bruker AVANCE III systems using $CDCl_3$ as a solvent, $CDCl_3$ as an internal standard substance, at 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR, and 376 MHz for ^{19}F NMR. High-resolution mass spectrometry (HRMS) data were obtained on an Agilent Technologies 1290-6540 UHPLC/Accurate-Mass Quadrupole Time-of Flight (Q-TOF) LC/MS using ESI as ion source. X-ray analysis was performed with a single-crystal X-ray diffractometer. Preparative TLC was performed on silica gel plates and developed with ethyl acetate/petroleum ether.

2. General Procedure

2.1 Substrate Synthesis

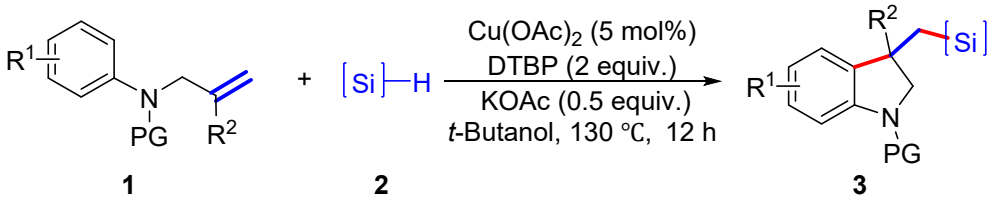
Anilides, sulfonamides, and substrates **1** were prepared according to literature procedures.[1]



A 250 mL flask, equipped with a magnetic stirring bar, was charged with aniline compound (20.0 mmol, 1.0 equiv.), CH_2Cl_2 (60.0 mL), and Et_3N (40.0 mmol, 2.0 equiv.), followed by the addition of acyl chloride (24.0 mmol, 1.2 equiv.) at 0 °C. The

reaction mixture was stirred at room temperature. After aniline compound was consumed, as indicated by TLC, the action mixture was quenched with aqueous $NaHCO_3$ (130 mL) and extracted with CH_2Cl_2 (130 mL) three times. The combined organic phase was washed with brine (70 mL). After removal of solvents, the solid of the crude product was further purified by washing with a petroleum ether/ethyl acetate mixture (7:1, v/v), affording *N*-acylaniline. To a stirred solution of *N*-acylaniline (15.0 mmol, 1.0 equiv.), and NaOH (22.5 mmol, 1.5 equiv.) in DMF (45.0 mL) was added 3-bromo-prop-1-ene (19.5 mmol, 1.3 equiv.), and the mixture was stirred at room temperature. After *N*-acylaniline was consumed, as indicated by TLC, the reaction mixture was quenched with brine (90 mL) and extracted with CH_2Cl_2 (90 mL) three times. The combined organic layers were dried with anhydrous Na_2SO_4, then filtered and concentrated under reduced pressure. The residue was purified by column chromatography (Petroleum/EtOAc = 8:1) on silica gel to afford **1a-1x**.

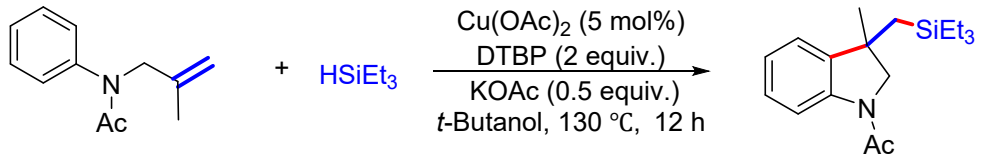
2.2 Experimental Procedure



1 **2** **3**

A dried 25 mL Schlenk tube equipped with a magnetic stir bar was charged with **1** (0.50 mmol, 1.0 equiv.), **2** (4.0 mmol, 8.0 equiv.), DTBP (1.0 mmol, 2.0 equiv.), KOAc (0.25 mmol, 0.5 equiv.), $Cu(OAc)_2$ (0.025 mmol, 5 mol%), and *t*-BuOH (3.0 mL). Subsequently, the tube was sealed and the resulting mixture was stirred at 130 °C for 12 h under Ar atmosphere. After cooling to room temperature, the reaction mixture was washed with water and extracted with CH_2Cl_2 three times. The combined organic layers dried over anhydrous Na_2SO_4, concentrated in vacuo. The crude products were purified by flash column chromatography on silica gel (Petroleum ether/EtOAc) to afford desired products **3**.

2.3 Scale-up Reaction

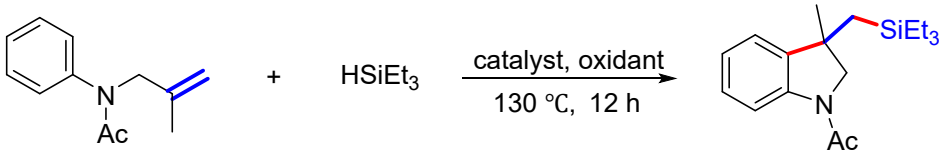


1a 0.946 g (5 mmol) **2a** 4.651 g (40 mmol) **3aa** 0.987 g (65%)

A mixture of *N*-(2-methyl-allyl)-*N*-phenylacetamide **1a** (0.946 g, 5.0 mmol, 1.0 equiv.), triethylsilane **2a** (4.651 g, 40 mmol, 8.0 equiv.), DTBP (1.462 g, 10 mmol, 2.0 equiv.), KOAc (0.245 g, 2.5 mmol, 0.5 equiv.), $Cu(OAc)_2$ (0.091g, 0.25 mmol, 5 mol%), *t*-BuOH (30 mL), was taken in a dry round-bottomed flask. The reaction mixture was then stirred at 130 °C for 12 h under an argon atmosphere. After cooling down to room temperature, the reaction mixture was washed with water and extracted with CH_2Cl_2 three times. The combined organic layers dried over anhydrous Na_2SO_4, concentrated in vacuo. Then the crude reaction mixture was purified by flash silica gel column chromatography (Petroleum/EtOAc = 60:1-30:1) to afford the desired product **3aa** (0.987 g, 65%).

3. Optimization of the reaction

Table S1. Reaction Optimization



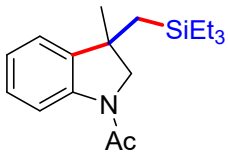
1a **2a** **3aa**

entry	**2a** (equiv.)	solvent	Catalyst (mol%)	Oxidant (equiv.)	Base (equiv.)	yield (%)[b]
1	10	*t*-Butanol	-	DTBP(3)	-	32
2	10	THF	-	DTBP(3)	-	17
3	10	DMSO	-	DTBP(3)	-	18
4	10	Benzene	-	DTBP(3)	-	16
5	10	Toluene	-	DTBP(3)	-	23
6	10	CH_3CN	-	DTBP(3)	-	trace
7	10	*t*-Butanol	CuI(10)	DTBP(3)	-	46
8	10	*t*-Butanol	CuBr(10)	DTBP(3)	-	44
9	10	*t*-Butanol	$Cu(OAc)_2$(10)	DTBP(3)	-	50
10	10	*t*-Butanol	$Cu(acac)_2$(10)	DTBP(3)	-	0

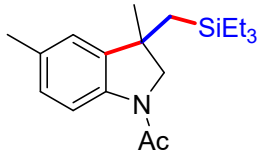
11	10	*t*-Butanol	$MnCl_2·4H_2O$(10)	DTBP(3)	-	16
12	10	*t*-Butanol	AgOAc(10)	DTBP(3)	-	trace
13	10	*t*-Butanol	$CoCl_2$(10)	DTBP(3)	-	trace
14	10	*t*-Butanol	$FeCl_2$(10)	DTBP(3)	-	trace
15	10	*t*-Butanol	Ni_2O_3(10)	DTBP(3)	-	19
16	10	*t*-Butanol	$Cu(OAc)_2$(10)	-	-	0
17	10	*t*-Butanol	$Cu(OAc)_2$(10)	TBHP(3)	-	trace
18	10	*t*-Butanol	$Cu(OAc)_2$(10)	TBPB(3)	-	24
19	10	*t*-Butanol	$Cu(OAc)_2$(10)	LPO(3)	-	27
20	10	*t*-Butanol	$Cu(OAc)_2$(10)	DTBP(3)	NaOAc(3)	57
21	10	*t*-Butanol	$Cu(OAc)_2$(10)	DTBP(3)	$NaHCO_3$(3)	19
22	10	*t*-Butanol	$Cu(OAc)_2$(10)	DTBP(3)	KOAc(3)	70
23	10	*t*-Butanol	$Cu(OAc)_2$(10)	DTBP(3)	K_3PO_4(3)	7
24	10	*t*-Butanol	$Cu(OAc)_2$(10)	DTBP(3)	Et_3N(3)	14
25	10	*t*-Butanol	$Cu(OAc)_2$(10)	DTBP(3)	DBU(3)	15
26	10	*t*-Butanol	$Cu(OAc)_2$(10)	DTBP(3)	Pyridine(3)	41
27	10	*t*-Butanol	$Cu(OAc)_2$(10)	DTBP(2.5)	KOAc(3)	74
28	10	*t*-Butanol	$Cu(OAc)_2$(10)	DTBP(2)	KOAc(3)	88
29	10	*t*-Butanol	$Cu(OAc)_2$(10)	DTBP(1.5)	KOAc(3)	35
30	12	*t*-Butanol	$Cu(OAc)_2$(10)	DTBP(2)	KOAc(3)	86
31	8	*t*-Butanol	$Cu(OAc)_2$(10)	DTBP(2)	KOAc(3)	88
32	6	*t*-Butanol	$Cu(OAc)_2$(10)	DTBP(2)	KOAc(3)	65
33	8	*t*-Butanol	$Cu(OAc)_2$(15)	DTBP(2)	KOAc(3)	72
34	8	*t*-Butanol	$Cu(OAc)_2$(5)	DTBP(2)	KOAc(3)	87
35	8	*t*-Butanol	$Cu(OAc)_2$(2)	DTBP(2)	KOAc(3)	75
36	8	*t*-Butanol	$Cu(OAc)_2$(5)	DTBP(2)	KOAc(1.5)	87
37	**8**	***t*-Butanol**	**$Cu(OAc)_2$(5)**	**DTBP(2)**	**KOAc(0.5)**	**88(80)**
38	8	*t*-Butanol	$Cu(OAc)_2$(5)	DTBP(2)	KOAc(0.25)	63

[a]Reaction conditions: **1a** (0.5 mmol, 1.0 equiv.), **2a**, oxidant, catalyst, base, solvent (3.0 mL), 130 ℃, under Ar, 12 h (DTBP = di-*tert*-butylperoxide, TBHP = *tert*-butyl hydroperoxide, TBPB = *tert*-butyl peroxybenzoate, LPO = dilauroyl peroxide). [b]Yields determined by GC analysis with naphthalene as the internal standard, isolated yield of **3aa** was shown in parentheses.

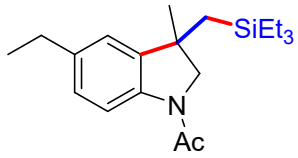
4. Characterization data of the products



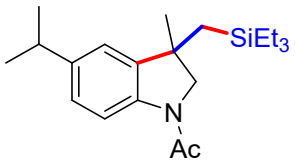
1-(3-methyl-3-((triethylsilyl)methyl)indolin-1-yl)ethan-1-one (3aa). White solid, 80% yield (121.6 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 10:1). M.p. = 47-49 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) present in 5.0:1 ratio of rotational isomer about the amide: δ 8.17 (d, *J* = 8.0 Hz, 1 H), 7.20-7.16 (m, 1 H), 7.14-7.12 (m, 1 H), 7.05-7.01 (m, 1 H), 3.93-3.83 (m, 0.33 H), 3.83-3.72 (m, 1.66 H), 2.44 (s, 0.50 H), 2.21 (s, 2.49 H), 1.33 (s, 2.54 H), 1.39 (s, 0.51 H), 1.17 (d, *J* = 14.8 Hz, 1 H), 1.07 (d, *J* = 14.8 Hz, 1 H), 0.88 (t, *J* = 8.0 Hz, 9 H), 0.51-0.36 (m, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm), major rotational isomer: δ 168.6, 141.8, 141.1, 127.6, 123.8, 122.0, 116.9, 63.4, 42.5, 30.9, 26.2, 24.2, 7.4, 4.4; minor rotational isomer: δ 168.4, 144.6, 140.0, 127.2, 123.4, 123.3, 114.0, 62.0, 40.9, 30.2, 25.3, 24.5, 7.3, 4.4; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{30}NOSi$ 304.2091; Found 304.2093.



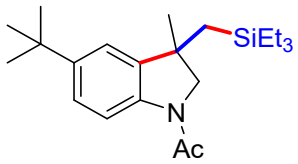
1-(3,5-dimethyl-3-((triethylsilyl)methyl)indolin-1-yl)ethan-1-one (3ba). Light yellow liquid, 81% yield (128.4 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) present in 5.0:1 ratio of rotational isomers about the amide: δ 8.03 (d, *J* = 8.4 Hz, 1 H), 6.99-6.93 (m, 2 H), 3.92-3.83 (m, 0.34 H), 3.81-3.71 (m, 1.69 H), 2.41 (s, 0.50 H), 2.31 (s, 3 H), 2.19 (s, 2.50 H), 1.38 (s, 2.52 H), 1.31 (s, 0.50 H), 1.16 (d, *J* = 15.2 Hz, 1 H), 1.05 (d, *J* = 15.2 Hz, 1 H), 0.88 (t, *J* = 8.0 Hz, 9 H), 0.52-0.39 (m, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm), major rotational isomer: δ 168.3, 141.9, 138.8, 133.4, 128.1, 122.6, 116.6, 63.5, 42.5, 30.8, 26.2, 24.1, 21.1, 7.4, 4.4; minor rotational isomer: δ 168.2, 144.8, 137.7, 133.1, 127.6, 124.0, 113.8, 62.1, 40.9, 30.1, 25.2, 24.4, 20.9, 7.3, 4.5; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{32}NOSi$ 318.2248; Found 318.2248.



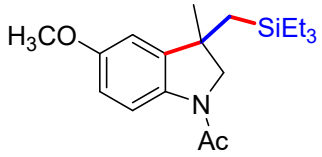
1-(5-ethyl-3-methyl-3-((triethylsilyl)methyl)indolin-1-yl)ethan-1-one (3ca). Light yellow liquid, 71% yield (117.4 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) present in 4.5:1 ratio of rotational isomers about the amide: δ 8.06 (d, *J* = 8.0 Hz, 1 H), 7.02-6.95 (m, 2 H), 3.92-3.84 (m, 0.36 H), 3.82-3.71 (m, 1.63 H), 2.64-2.58 (m, 2 H), 2.42 (s, 0.54 H), 2.19 (s, 2.46 H), 1.39 (s, 2.50 H), 1.33 (s, 0.55 H), 1.21 (t, *J* = 7.6 Hz, 3 H), 1.18-1.05 (m, 2 H), 0.88 (t, *J* = 7.8 Hz, 9 H), 0.50-0.37 (m, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm), major rotational isomer: δ 168.3, 141.8, 139.9, 139.1, 127.0, 121.5, 116.7, 63.6, 42.5, 31.0, 28.6, 26.2, 24.1, 15.9, 7.4, 4.3; minor rotational isomer: δ 144.7, 139.6, 138.0, 126.5, 122.8, 113.9, 62.2, 40.9, 30.3, 28.4, 25.2, 24.4, 4.4. **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{34}NOSi$ 332.2404; Found 332.2402.



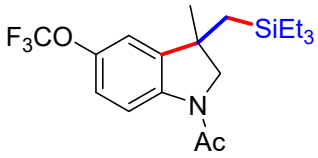
1-(5-isopropyl-3-methyl-3-((triethylsilyl)methyl)indolin-1-yl)ethan-1-one (3da). Light yellow liquid, 67% yield (116.1 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) present in 4.2:1 ratio of rotational isomers about the amide: δ 8.06 (d, *J* = 8.4 Hz, 1 H), 7.06-6.97 (m, 2 H), 3.92-3.84 (m, 0.38 H), 3.82-3.71 (m, 1.61 H), 2.92-2.84 (m, 1 H), 2.42 (s, 0.57 H), 2.19 (s, 2.41 H), 1.40 (s, 2.46 H), 1.33 (s, 0.59 H), 1.24-1.22 (m, 6 H), 1.16 (d, *J* = 14.8 Hz, 1 H), 1.07 (d, *J* = 15.2 Hz, 1 H), 0.87 (t, *J* = 7.8 Hz, 9 H), 0.49-0.34 (m, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm), major rotational isomer: δ 168.3, 144.6, 141.5, 139.2, 125.6, 120.0, 116.7, 63.7, 42.6, 34.0, 31.1, 26.3, 24.2, 24.1, 7.4, 4.3; minor rotational isomer: δ 144.5, 144.3, 138.1, 125.1, 121.3, 113.8, 62.3, 41.0, 33.8, 30.4, 25.3, 24.4, 4.4; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{36}NOSi$ 346.2561; Found 346.2560.



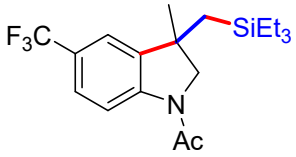
1-(5-(tert-butyl)-3-methyl-3-((triethylsilyl)methyl)indolin-1-yl)ethan-1-one (3ea). Light yellow liquid, 64% yield (114.3 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 15:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) present in 4.0:1 ratio of rotational isomers about the amide: δ 8.07 (d, *J* = 8.4 Hz, 1 H), 7.23-7.12 (m, 2 H), 3.92-3.85 (m, 0.40 H), 3.82-3.72 (m, 1.60 H), 2.42 (s, 0.60 H), 2.19 (s, 2.39 H), 1.40 (s, 2.44 H), 1.34 (s, 0.61 H), 1.30 (s, 9 H), 1.15 (d, *J* = 14.8 Hz, 1 H), 1.08 (d, *J* = 15.2 Hz, 1 H), 0.86 (t, *J* = 7.8 Hz, 9 H), 0.49-0.32 (m, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm), major rotational isomer: δ 168.3, 146.9, 141.0, 138.9, 124.6, 118.8, 116.3, 63.7, 42.7, 34.6, 31.5, 31.3, 26.4, 24.1, 7.5, 4.3; minor rotational isomer: δ 146.5, 144.0, 137.8, 124.1, 120.2, 113.5, 62.3, 41.0, 34.5, 31.5, 30.6, 25.3, 24.4, 4.4; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{38}NOSi$ 360.2717; Found 360.2717.



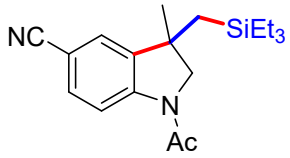
1-(5-methoxy-3-methyl-3-((triethylsilyl)methyl)indolin-1-yl)ethan-1-one (3fa). Light brown liquid, 70% yield (116.0 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) present in 6.3:1 ratio of rotational isomers about the amide: δ 8.08 (d, *J* = 8.8 Hz, 1 H), 6.74-6.67 (m, 2 H), 3.93-3.83 (m, 0.29 H), 3.81-3.71 (m, 4.83 H), 2.38 (s, 0.41 H), 2.17 (s, 2.59 H), 1.37 (s, 2.60 H), 1.30 (s, 0.41 H), 1.14 (d, *J* = 15.2 Hz, 1 H), 1.04 (d, *J* = 14.8 Hz, 1 H), 0.88 (t, *J* = 7.8 Hz, 9 H), 0.52-0.36 (m, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm), major rotational isomer: δ 167.9, 156.5, 143.5, 134.9, 117.5, 111.9, 108.5, 63.5, 55.6, 42.6, 30.7, 26.0, 23.9, 7.4, 4.3; minor rotational isomer: δ 156.3, 146.4, 133.7, 114.7, 111.7, 109.6, 62.2, 55.5, 41.2, 30.0, 25.0, 24.1, 7.3, 4.4; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{32}NO_2Si$ 334.2197; Found 334.2197.



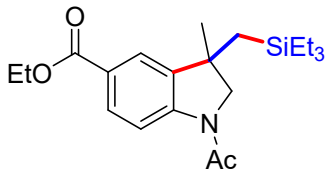
1-(3-methyl-3-((triethylsilyl)methyl)-5-(trifluoromethoxy)indolin-1-yl)ethan-1-one (3ga). Yellow liquid, 79% yield (153.7 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) present in 10.1:1 ratio of rotational isomers about the amide: δ 8.17 (d, *J* = 8.8 Hz, 1 H), 7.04-7.01 (m, 1 H), 6.95 (s, 1 H), 3.92-3.90 (m, 0.18 H), 3.86-3.76 (m, 1.82 H), 2.42 (s, 0.27 H), 2.20 (s, 2.72 H), 1.39 (s, 2.72 H), 1.33 (s, 0.27 H), 1.15 (d, *J* = 14.8 Hz, 1 H), 1.06 (d, *J* = 15.2 Hz, 1 H), 0.88 (t, *J* = 8.0 Hz, 9 H), 0.50-0.36 (m, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 168.7, 145.4, 143.7, 139.9, 120.6 (q, $^1J_{(C-F)}$ = 254.7 Hz), 120.4, 117.6, 115.5, 63.6, 42.7, 30.9, 26.2, 24.1, 7.4, 4.4; **^{19}F NMR** (376 MHz, $CDCl_3$, ppm): δ -61.58; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{29}F_3NO_2Si$ 388.1914; Found 388.1914.



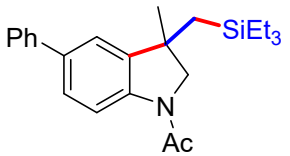
1-(3-methyl-3-((triethylsilyl)methyl)-5-(trifluoromethyl)indolin-1-yl)ethan-1-one (3ha). Yellow liquid, 43% yield (80.3 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) present in 10.5:1 ratio of rotational isomers about the amide: δ 8.25 (d, *J* = 8.4 Hz, 1 H), 7.47-7.44 (m, 1 H), 7.35 (s, 1 H), 3.87 (d, *J* = 10.0 Hz, 1 H), 3.80 (d, *J* = 10.0 Hz, 1 H), 2.46 (s, 0.26 H), 2.23 (s, 2.74 H), 1.42 (s, 2.74 H), 1.36 (s, 0.26 H), 1.18 (d, *J* = 14.8 Hz, 1 H), 1.08 (d, *J* = 14.8 Hz, 1 H), 0.88 (t, *J* = 8.0 Hz, 9 H), 0.52-0.35 (m, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 169.2, 143.9, 142.4, 125.7 (q, $^2J_{(C-F)}$ = 32.0 Hz), 125.3 (d, $^3J_{(C-F)}$ = 3.6 Hz), 124.4 (q, $^1J_{(C-F)}$ = 270.0 Hz), 119.2 (d, $^3J_{(C-F)}$ = 3.4 Hz), 116.6, 63.5, 42.6, 30.9, 26.2, 24.2, 7.3, 4.3; **^{19}F NMR** (376 MHz, $CDCl_3$, ppm): δ -58.12; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{29}F_3NOSi$ 372.1965; Found 372.1964.



1-acetyl-3-methyl-3-((triethylsilyl)methyl)indoline-5-carbonitrile (3ia). Colorless liquid, 48% yield (78.5 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 7:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.22 (d, *J* = 8.4 Hz, 1 H), 7.48-7.45 (m, 1 H), 7.37 (s, 1 H), 3.85 (d, *J* = 10.0 Hz, 1 H), 3.78 (d, *J* = 10.0 Hz, 1 H), 2.22 (s, 3 H), 1.38 (s, 3 H), 1.16 (d, *J* = 15.2 Hz, 1 H), 1.03 (d, *J* = 15.2 Hz, 1 H), 0.88 (t, *J* = 8.0 Hz, 9 H), 0.50-0.36 (m, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 169.4, 144.8, 143.1, 132.7, 126.0, 119.3, 117.1, 106.5, 63.3, 42.6, 30.7, 26.2, 24.3, 7.4, 4.4; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{29}N_2OSi$ 329.2044; Found 329.2042.

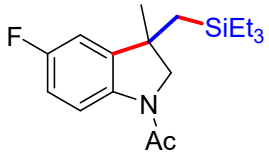


ethyl 1-acetyl-3-methyl-3-((triethylsilyl)methyl)indoline-5-carboxylate (3ja). Yellow liquid, 41% yield (76.9 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 7:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) present in 9.2:1 ratio of rotational isomers about the amide: δ 8.18 (d, *J* = 8.4 Hz, 1 H), 7.91-7.89 (m, 1 H), 7.80 (s, 1 H), 4.37-4.31 (m, 2 H), 3.87-3.77 (m, 2 H), 2.45 (s, 0.30 H), 2.22 (s, 2.75 H), 1.40-1.36 (m, 6 H), 1.20 (d, *J* = 14.8 Hz, 1 H), 1.07 (d, *J* = 15.2 Hz, 1 H), 0.87 (t, *J* = 7.8 Hz, 9 H), 0.50-0.37 (m, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 169.2, 166.4, 145.0, 142.1, 130.1, 125.8, 123.6, 116.1, 63.7, 60.8, 42.4, 30.9, 26.2, 24.3, 14.4, 7.4, 4.4; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{34}NO_3Si$ 376.2302; Found 376.2304.

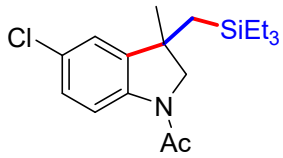


1-(3-methyl-5-phenyl-3-((triethylsilyl)methyl)indolin-1-yl)ethan-1-one (3la). Yellow liquid, 67% yield (127.4 mg). Column chromatography on silica gel

(Petroleum ether/EtOAc = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) present in 5.4:1 ratio of rotational isomers about the amide: δ 8.26 (d, *J* = 8.4 Hz, 1 H), 7.60-7.58 (m, 2 H), 7.46-7.30 (m, 5 H), 4.00-3.92 (m, 0.31 H), 3.89-3.79 (m, 1.68 H), 2.48 (s, 0.47 H), 2.24 (s, 2.55 H), 1.46 (s, 2.54 H), 1.40 (s, 0.47 H), 1.24 (d, *J* = 14.8 Hz, 1 H), 1.15 (d, *J* = 15.2 Hz, 1 H), 0.92 (t, *J* = 8.0 Hz, 9 H), 0.58-0.40 (m, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 168.6, 142.5, 141.2, 140.7, 137.0, 128.8, 126.9 (2 C), 126.7, 120.8, 117.1, 63.7, 42.7, 31.0, 26.4, 24.2, 7.5, 4.4; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{34}NOSi$ 380.2404; Found 380.2402.

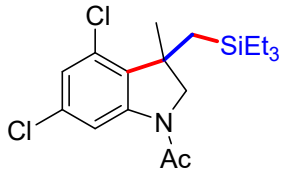


1-(5-fluoro-3-methyl-3-((triethylsilyl)methyl)indolin-1-yl)ethan-1-one (3ma). White solid, 83% yield (132.7 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 10:1). M.p. = 32-34 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) present in 9.0:1 ratio of rotational isomers about the amide: δ 8.14-8.11 (m, 1 H), 6.88-6.80 (m, 2 H), 3.96-3.85 (m, 0.20 H), 3.85-3.74 (m, 1.80 H), 2.40 (s, 0.30 H), 2.19 (s, 2.70 H), 1.38 (s, 2.69 H), 1.31 (s, 0.30 H), 1.14 (d, *J* = 14.8 Hz, 1 H), 1.04 (d, *J* = 15.2 Hz, 1 H), 0.89 (t, *J* = 7.8 Hz, 9 H), 0.52-0.42 (m, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 168.3, 159.6 (d, $^1J_{(C-F)}$ = 240.6 Hz), 144.0 (d, $^3J_{(C-F)}$ = 7.1 Hz), 137.2 (d, $^4J_{(C-F)}$ = 1.8 Hz), 117.8 (d, $^3J_{(C-F)}$ = 7.8 Hz), 113.7 (d, $^2J_{(C-F)}$ = 22.5 Hz), 109.3 (d, $^2J_{(C-F)}$ = 27.3 Hz), 63.4, 42.6, 30.6, 26.0, 23.9, 7.4, 4.3; **^{19}F NMR** (376 MHz, $CDCl_3$, ppm): δ -118.83; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{29}FNOSi$ 322.1997; Found 322.1995.

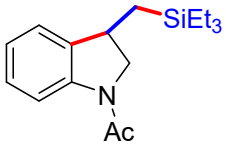


1-(5-chloro-3-methyl-3-((triethylsilyl)methyl)indolin-1-yl)ethan-1-one (3na). Yellow liquid, 90% yield (151.5 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 7:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) present in 8.7:1 ratio of rotational isomers about the amide: δ 8.10 (d, *J* = 8.4 Hz, 1 H), 7.15-7.07 (m,

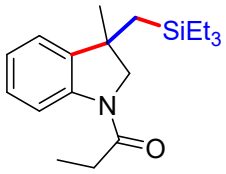
2 H), 3.94-3.84 (m, 0.21 H), 3.84-3.74 (m, 1.81 H), 2.41 (s, 0.31 H), 2.20 (s, 2.70 H), 1.38 (s, 2.70 H), 1.32 (s, 0.31 H), 1.15 (d, J = 15.2 Hz, 1 H), 1.04 (d, J = 15.2 Hz, 1 H), 0.90 (t, J = 8.0 Hz, 9 H), 0.53-0.38 (m, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 168.6, 143.9, 139.7, 128.6, 127.4, 122.4, 117.8, 63.4, 42.6, 30.6, 26.1, 24.0, 7.4, 4.3; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{29}ClNOSi$ 338.1701; Found 338.1700.



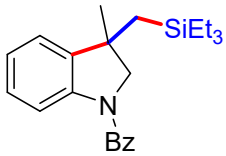
1-(4,6-dichloro-3-methyl-3-((triethylsilyl)methyl)indolin-1-yl)ethan-1-one (3pa). Colorless liquid, 47% yield (88.4 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 7:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 8.21 (d, J = 1.2 Hz, 1 H), 6.95 (d, J = 2.0 Hz, 1 H), 3.84 (d, J = 10.4 Hz, 1 H), 3.74 (d, J = 10.4 Hz, 1 H), 2.18 (s, 3 H), 1.54 (s, 3 H), 1.38-1.29 (m, 2 H), 0.88 (t, J = 7.8 Hz, 9 H), 0.45-0.40 (m, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 168.9, 143.8, 135.4, 133.9, 130.3, 124.9, 115.9, 64.1, 43.9, 28.8, 24.3, 23.7, 7.4, 4.3; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{28}Cl_2NOSi$ 372.1312; Found 372.1307.



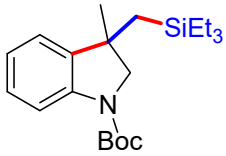
1-(3-((triethylsilyl)methyl)indolin-1-yl)ethan-1-one (3qa). White solid, 67% yield (97.0 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 7:1). M.p. = 51-53 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) present in 4.6:1 ratio of rotational isomers about the amide: δ 8.17 (d, J = 8.0 Hz, 1 H), 7.23-7.01 (m, 3 H), 4.39 (t, J = 10.6 Hz, 0.18 H), 4.16 (t, J = 9.2 Hz, 0.82 H), 3.57-3.31 (m, 2 H), 2.42 (s, 0.53 H), 2.21 (s, 2.46 H), 1.23-1.18 (m, 1 H), 0.98 (t, J = 7.8 Hz, 9 H), 0.88-0.82 (m, 1 H), 0.63-0.56 (m, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 168.5, 141.9, 137.9, 127.6, 123.7, 123.3, 116.8, 57.2, 36.4, 24.2, 18.3, 7.4, 3.9; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{28}NOSi$ 290.1935; Found 290.1932.



1-(3-methyl-3-((triethylsilyl)methyl)indolin-1-yl)propan-1-one (3ra). Yellow liquid, 79% yield (124.9 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) present in 7.1:1 ratio of rotational isomers about the amide: δ 8.20 (d, *J* = 8.0 Hz, 1 H), 7.20-7.12 (m, 2 H), 7.04-7.00 (m, 1 H), δ 3.93-3.86 (m, 0.24 H), 3.82-3.71 (m, 1.71 H), 2.69 (s, 0.24 H), 2.45-2.39 (m, 1.71 H), 1.38 (s, 2.64 H), 1.33 (s, 0.37 H), 1.23 (t, *J* = 7.4 Hz, 3 H), 1.17 (d, *J* = 15.2 Hz, 1 H), 1.06 (d, *J* = 15.2 Hz, 1 H), 0.88 (t, *J* = 7.8 Hz, 9 H), 0.49-0.39 (m, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 171.9, 141.7, 141.4, 127.6, 123.6, 122.0, 116.8, 62.4, 42.6, 30.9, 29.2, 26.1, 8.7, 7.4, 4.4; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{32}NOSi$ 318.2248; Found 318.2245.

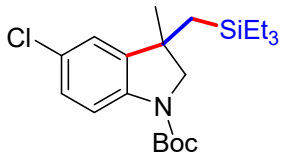


(3-methyl-3-((triethylsilyl)methyl)indolin-1-yl)(phenyl)methanone (3sa). Colorless liquid, 45% yield (81.7 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.08 (s, 1 H), 7.63-7.61 (m, 2 H), 7.55-7.52 (m, 3 H), 7.32-7.30 (m, 1 H), 7.21-7.15 (m, 1 H), 7.10-7.06 (m, 1 H), 3.91-3.85 (m, 2 H), 1.41 (s, 3 H), 1.23(d, *J* = 14.9 Hz, 1 H), 1.11 (d, *J* = 14.9 Hz, 1 H), 0.86 (t, *J* = 7.9 Hz, 9 H), 0.49-0.38 (m, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 168.0, 143.0, 141.5, 137.6, 130.1, 128.4, 127.1, 127.0, 123.9, 122.5, 116.7, 64.6, 42.4, 29.5, 25.2, 6.8, 4.0; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{32}NOSi$ 366.2248; Found 366.2244.

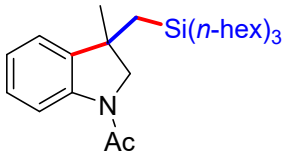


***tert*-butyl 3-methyl-3-((triethylsilyl)methyl)indoline-1-carboxylate (3ta).** Colorless liquid, 54% yield (97.6 mg). Column chromatography on silica gel (Petroleum

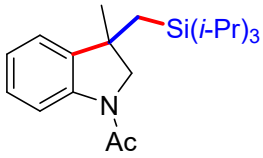
ether/EtOAc = 100:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.62 (s, 1 H), 7.17-7.10 (m, 2 H), 6.97-6.93 (m, 1 H), 3.78-3.65 (m, 2 H), 1.56 (s, 9 H), 1.36 (s, 3 H), 1.11-1.00 (m, 2 H), 0.87 (t, *J* = 8.0 Hz, 9 H), 0.43 (s, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 152.5, 142.6, 141.4, 127.4, 122.3, 114.6, 80.4, 61.9, 41.7, 30.8 (2 C), 28.5, 26.7, 7.4, 4.3; **HRMS (ESI-TOF)** *m/z*: $[M + Na]^+$ Calcd for $C_{21}H_{36}NO_2SiNa$ 384.2329; Found 384.2325.



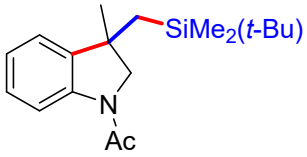
***tert*-butyl 5-chloro-3-methyl-3-((triethylsilyl)methyl)indoline-1-carboxylate (3ua).** Yellow liquid, 90% yield (178.6 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 100:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.53 (s, 1 H), 7.11-7.04 (m, 2 H), 3.78-3.65 (m, 2 H), 1.55 (s, 9 H), 1.35 (s, 3 H), 1.10 (d, *J* = 14.4 Hz, 1 H), 1.00 (d, *J* = 14.8 Hz, 1 H), 0.88 (t, *J* = 8.0 Hz, 9 H), 0.46-0.44 (m, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 152.3, 143.5, 140.0, 127.3, 122.6, 115.6, 80.7, 62.1, 41.8, 30.5 (2 C), 28.4, 26.5, 7.4, 4.3; **HRMS (ESI-TOF)** *m/z*: $[M + Na]^+$ Calcd for $C_{21}H_{35}ClNO_2SiNa$ 418.1940; Found 418.1939.



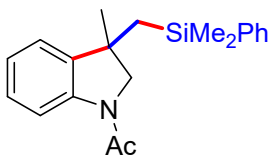
1-(3-methyl-3-((trihexylsilyl)methyl)indolin-1-yl)ethan-1-one (3ab). Light yellow liquid, 58% yield (136.5 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 7:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) present in 5.3:1 ratio of rotational isomers about the amide: δ 8.17 (d, *J* = 8.0 Hz, 1 H), 7.20-7.12 (m, 2 H), 7.05-7.01 (m, 1 H), 3.92-3.85 (m, 0.31 H), 3.83-3.72 (m, 1.66 H), 2.44 (s, 0.48 H), 2.21 (s, 2.55 H), 1.39-1.14 (m, 28 H), 1.05 (d, *J* = 14.8 Hz, 1 H), 0.88 (t, *J* = 6.8 Hz, 9 H), 0.48-0.34 (m, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 168.5, 141.8, 141.2, 127.6, 123.8, 122.0, 116.9, 63.4, 42.6, 33.6, 31.5, 31.0, 27.2, 24.2, 23.8, 22.6, 14.1, 13.6; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{30}H_{54}NOSi$ 472.3969; Found 472.3970.



1-(3-methyl-3-((triisopropylsilyl)methyl)indolin-1-yl)ethan-1-one (3ac). Colorless liquid, 31% yield (54.3 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) present in 5.1:1 ratio of rotational isomers about the amide: δ 8.17 (d, *J* = 8.0 Hz, 1 H), 7.24-7.16 (m, 2 H), 7.10-7.03 (m, 1 H), 4.01-3.92 (m, 0.33 H), 3.92-3.76 (m, 1.67 H), 2.44 (s, 0.49 H), 2.21 (s, 2.51 H), 1.41 (s, 2.51 H), 1.36 (s, 0.49 H), 1.28 (d, *J* = 15.2 Hz, 1 H), 1.15 (d, *J* = 15.2 Hz, 1 H), 1.06-1.03 (m, 21 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 168.6, 142.8, 140.9, 127.6, 123.9, 121.9, 116.9, 63.6, 42.5, 31.0, 24.3, 23.4, 19.1, 19.0, 11.9; **HRMS (ESI-TOF)** *m/z*: $[M + Na]^+$ Calcd for $C_{21}H_{36}NOSiNa$ 368.2380; Found 368.2378.

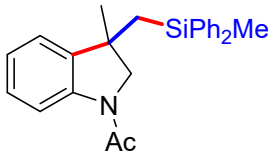


1-(3-((*tert*-butyldimethylsilyl)methyl)-3-methylindolin-1-yl)ethan-1-one (3ad). Colorless liquid, 25% yield (37.8 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) present in 5.1:1 ratio of rotational isomers about the amide: δ 8.18 (d, *J* = 8.0 Hz, 1 H), 7.21-7.17 (m, 1 H), 7.13-7.09 (m, 1 H), 7.06-7.02 (m, 1 H), 3.97-3.83 (m, 0.33 H), 3.83-3.74 (m, 1.67 H), 2.44 (s, 0.49 H), 2.21 (s, 2.49 H), 1.40 (s, 2.49 H), 1.34 (s, 0.49 H), 1.18-1.08 (m, 2 H), 0.83 (s, 9 H), 0.00 (s, 3 H), -0.18 (s, 0.50 H), -0.25 (s, 2.50 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 168.6, 141.7, 141.2, 127.7, 123.8, 122.2, 116.9, 63.2, 42.5, 31.4, 26.4, 26.2, 24.3, 16.5, -4.1, -4.9; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{30}NOSi$ 304.2091; Found 304.2092.

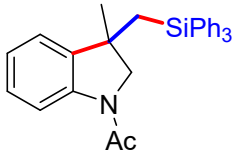


1-(3-((dimethyl(phenyl)silyl)methyl)-3-methylindolin-1-yl)ethan-1-one (3ae). Colorless liquid, 77% yield (125.0 mg). Column chromatography on silica gel

(Petroleum ether/EtOAc = 7:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) present in 9.2:1 ratio of rotational isomers about the amide: δ 8.18 (d, *J* = 8.0 Hz, 1 H), 7.46-7.35 (m, 5 H), 7.22-7.18 (m, 1 H), 7.12-7.10 (m, 1 H), 7.04-7.00 (m, 1 H), 3.90-3.80 (m, 0.19 H), 3.54-3.42 (m, 1.75 H), 2.39 (s, 0.29 H), 1.72 (s, 2.67 H), 1.42-1.27 (m, 5 H), 0.25 (s, 0.29 H), 0.19 (s, 3 H), -0.02 (s, 2.67 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 169.9, 142.7, 142.0, 140.2, 134.7, 130.3, 129.1, 128.9, 124.9, 123.4, 118.0, 63.5, 43.7, 33.1, 32.7, 24.9, -0.0, -1.7; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{26}NOSi$ 324.1778; Found 324.1774.



1-(3-methyl-3-((methyldiphenylsilyl)methyl)indolin-1-yl)ethan-1-one (3af). Colorless liquid, 66% yield (128.0 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 7:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) present in 12.6:1 ratio of rotational isomers about the amide: δ 8.17 (d, *J* = 8.0 Hz, 1 H), 7.50-7.30 (m, 10 H), 7.24-7.14 (m, 2 H), 7.05-7.02 (m, 1 H), 3.90-3.75 (m, 0.15 H), 3.57-3.38 (m, 1.85 H), 2.33 (s, 0.22 H), 1.77 (d, *J* = 15.2 Hz, 1 H), 1.63 (d, *J* = 14.8 Hz, 1 H), 1.58 (s, 2.78 H), 1.45 (s, 2.78 H), 1.31 (s, 0.22 H), 0.47 (s, 0.22 H), 0.19 (s, 2.78 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 168.8, 141.6, 140.7, 137.7, 136.8, 134.6, 134.3, 129.5, 129.3, 128.0, 127.9 (2 C), 123.8, 122.3, 116.9, 62.2, 42.5, 31.7, 29.8, 23.6, -3.9; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{25}H_{28}NOSi$ 386.1935; Found 386.1933.

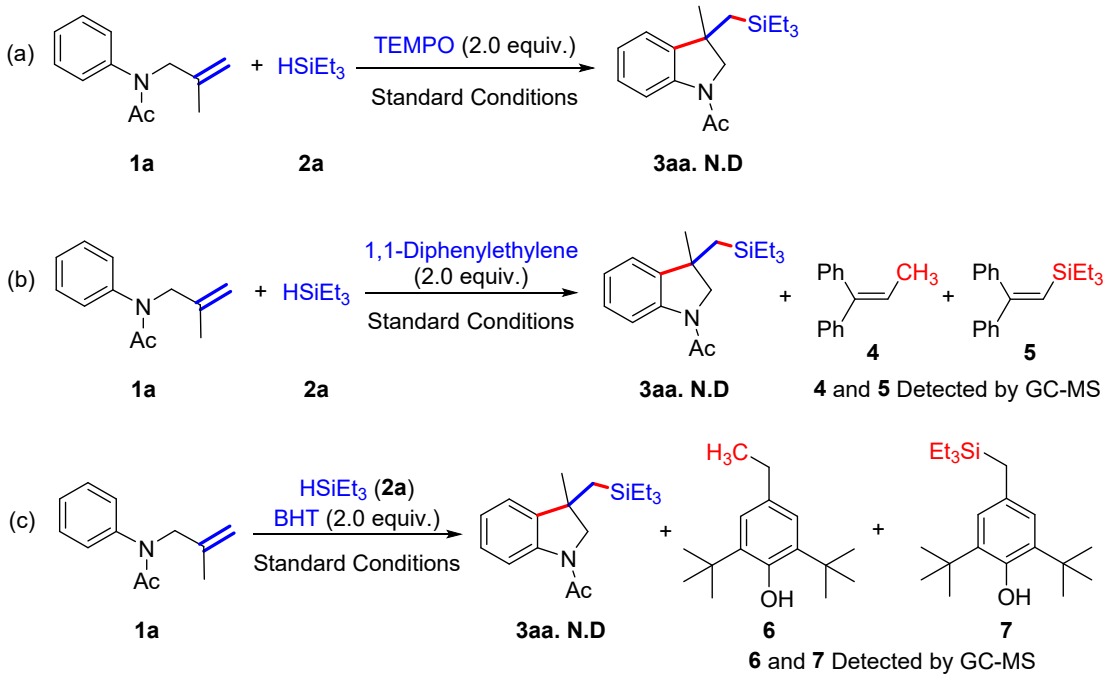


1-(3-methyl-3-((triphenylsilyl)methyl)indolin-1-yl)ethan-1-one (3ag). White solid, 78% yield (175.4 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 15:1). M.p. = 156-158 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) present in 14.0:1 ratio of rotational isomers about the amide: δ 8.11-8.09 (m, 1 H), 7.58-7.56 (m, 6 H), 7.44-7.35 (m, 9 H), 7.17-7.14 (m, 2 H), 6.99-6.95 (m, 1 H), 3.76-3.65 (m, 0.13 H), 3.51-3.18 (m, 1.90 H), 2.29 (s, 0.20 H), 2.16 (d, *J* = 15.2 Hz, 1 H), 1.95 (d, *J* = 15.2 Hz, 1

H), 1.71 (s, 2.80 H), 1.32 (s, 2.80 H), 1.28 (s, 0.20 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 168.6, 142.0, 141.0, 135.8, 134.8, 129.7, 128.1, 127.7, 123.8, 122.1, 116.8, 62.5, 42.7, 30.9, 27.0, 23.8; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{30}H_{30}NOSi$ 448.2091; Found 448.2093.

5. Radical trapping experiment

To study the reaction mechanism, several control experiments were carried out under the optimized reaction conditions (Scheme S2). When 2.0 equiv. of TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxyl) was added to the system, the reaction was completely inhibited. By adding 2.0 equiv. of radical scavenger 1,1-diphenylethylene to the reaction mixture, the reaction was totally suppressed and corresponding adducts **4** and **5** could be detected by GC-MS. When 2.0 equiv. of BHT (2,6-di-tert-butyl-4-methylphenol) was added to the reaction, no target product was obtained and GC-MS analysis indicated that compounds **6** and **7** were formed. These results showed that the reaction system proceeded in a free radical way.



Scheme S2. Radical trapping experiment

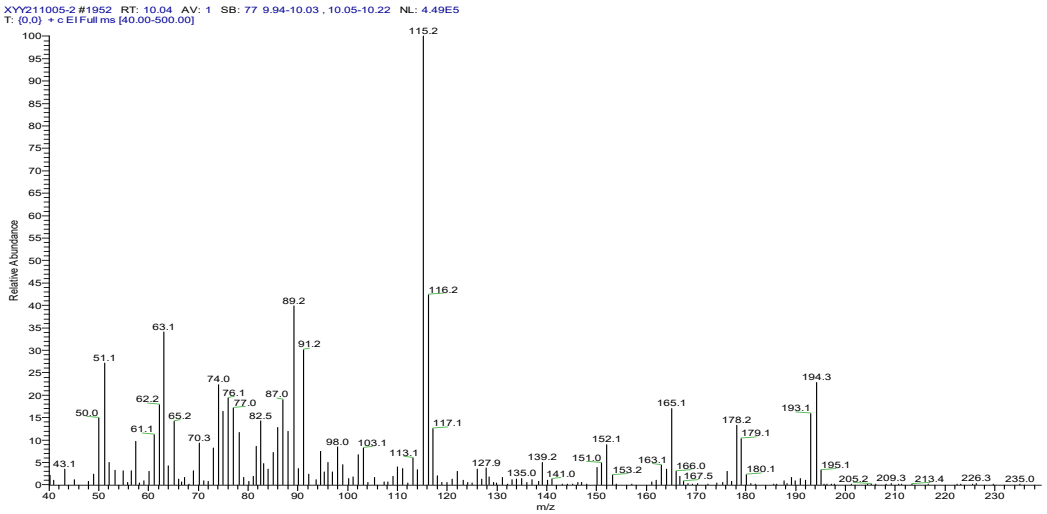


Figure S1. GC-MS (EI, m/z) of compound 4

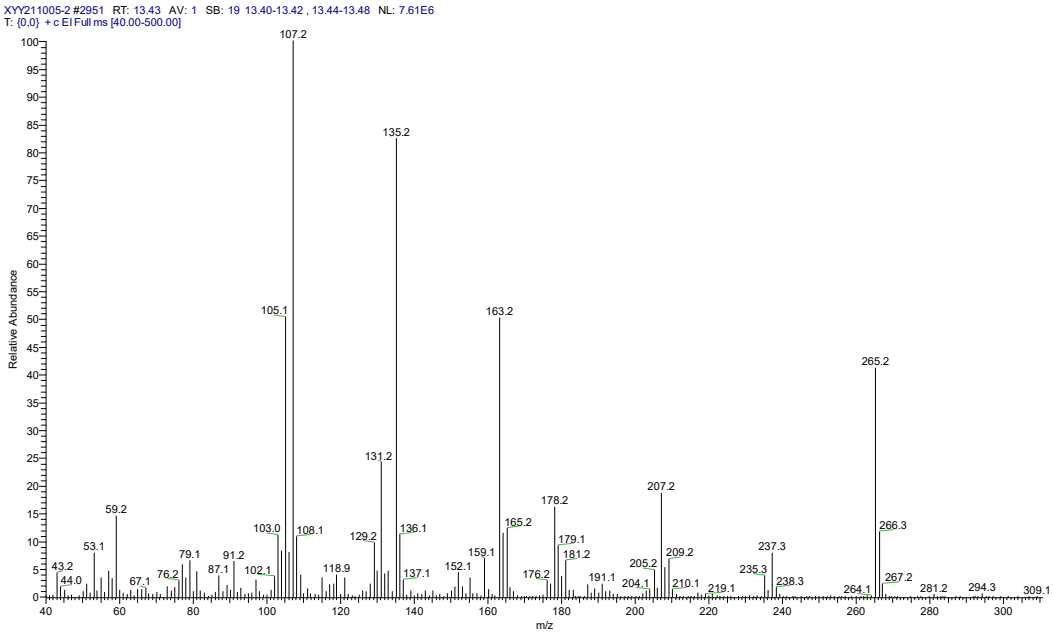


Figure S2. GC-MS (EI, m/z) of compound 5

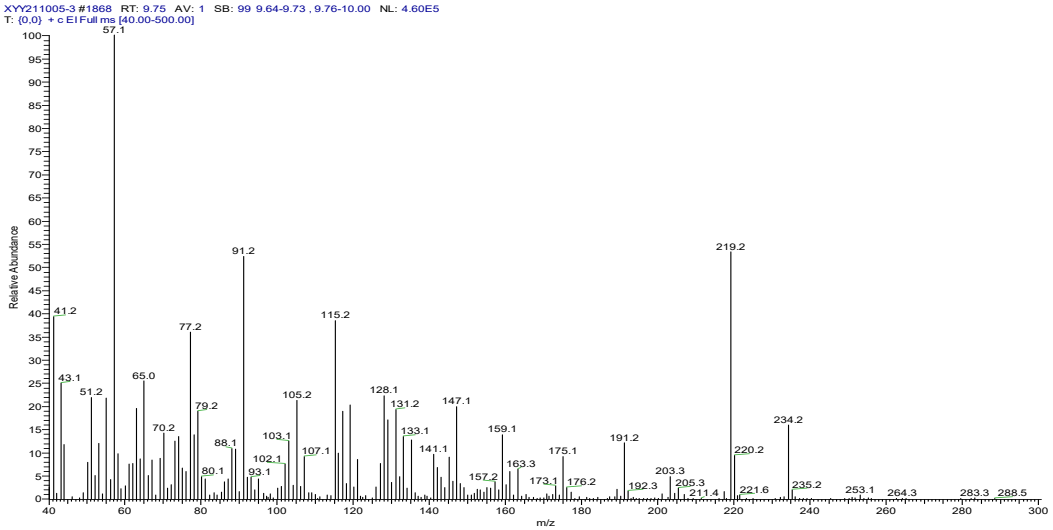


Figure S3. GC-MS (EI, m/z) of compound 6

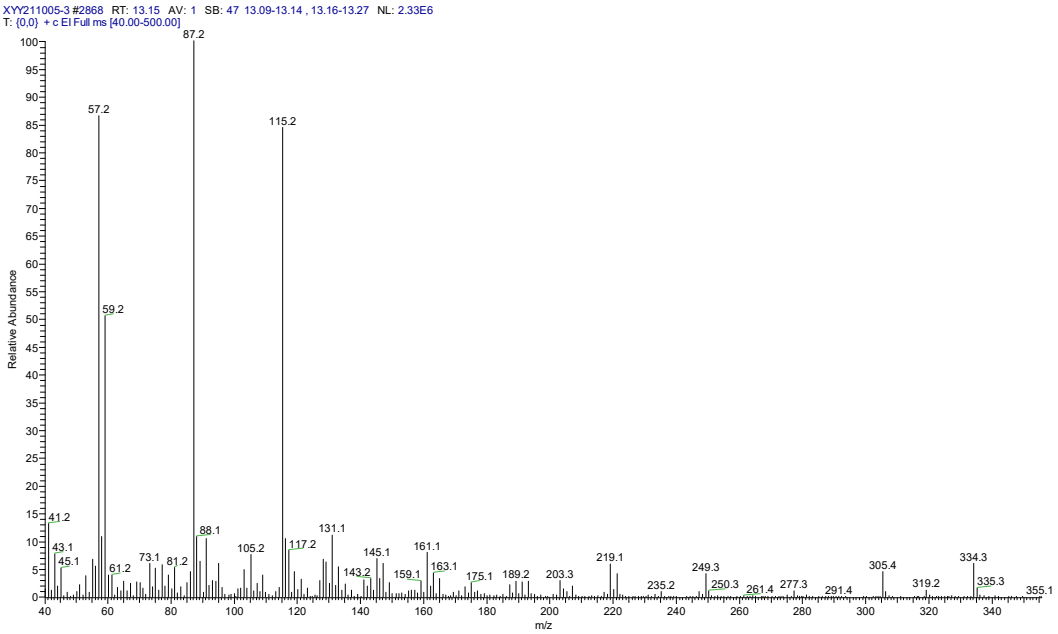


Figure S4. GC-MS (EI, m/z) of compound 7

6. X-Ray crystallographic data of 3aa

The product **3aa** was recrystallized from petroleum ether. Further information can be found in the CIF file. This crystal was deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC**2120950**.

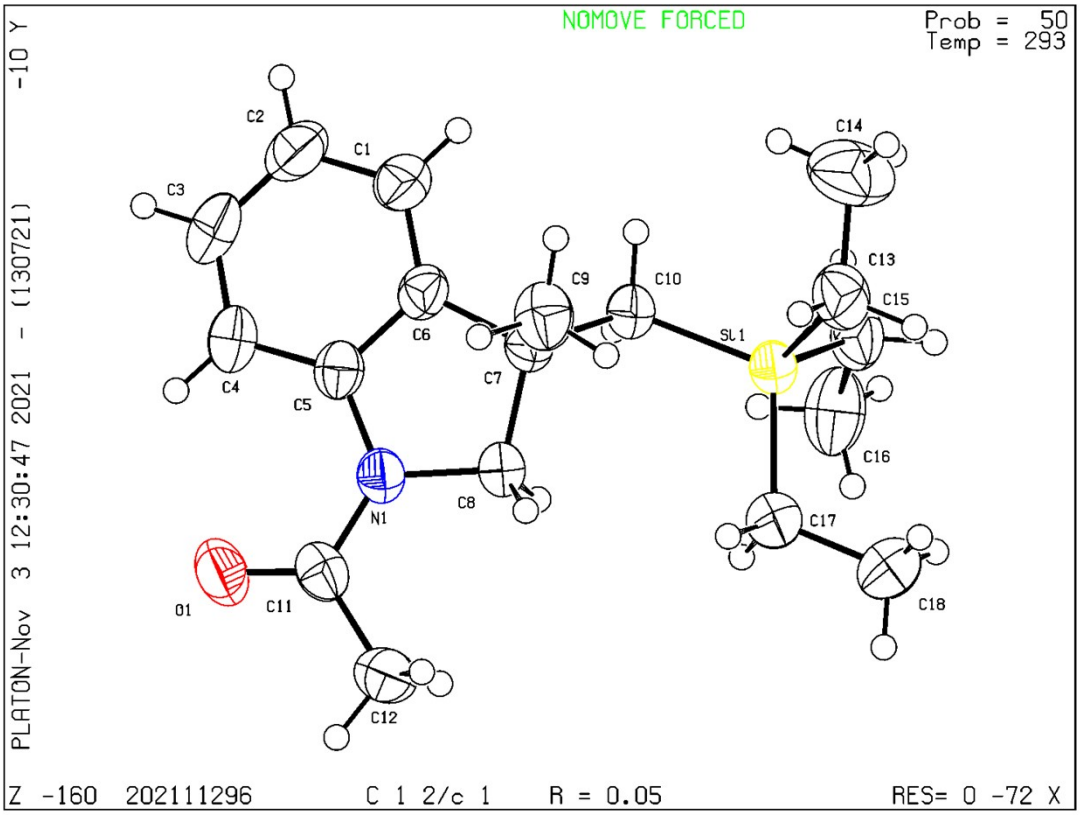


Figure S5. Single-crystal X-ray Molecular Structure of 3aa

Table S2. Crystal data and structure refinement for 3aa

Identification code	**3aa**
Empirical formula	$C_{18}H_{29}NOSi$
Formula weight	303.51
Temperature/K	293(2)
Crystal system	monoclinic
Space group	C2/c
a/Å	22.3463(8)
b/Å	7.5222(3)
c/Å	22.4194(11)
α/°	90
β/°	102.133(4)
γ/°	90
Volume/Å^3	3684.4(3)
Z	8
ρ_{calc}g/cm^3	1.094
μ/mm^{-1}	1.104
F(000)	1328.0
Crystal size/mm^3	0.18 × 0.08 × 0.06
Radiation	CuKα (λ = 1.54184)

2Θ range for data collection/°	8.068 to 134.14
Index ranges	$-26 \leq h \leq 26$, $-5 \leq k \leq 8$, $-26 \leq l \leq 26$
Reflections collected	12393
Independent reflections	3274 [R_{int} = 0.0402, R_{sigma} = 0.0365]
Data/restraints/parameters	3274/0/195
Goodness-of-fit on F^2	1.037
Final R indexes [I>=2σ (I)]	R_1 = 0.0470, wR_2 = 0.1276
Final R indexes [all data]	R_1 = 0.0606, wR_2 = 0.1415
Largest diff. peak/hole / e $Å^{-3}$	0.32/-0.17

7. References

1. a) D. Q. Liang, D. D. Ge, Y. P. Lv, W. Z. Huang, B. L. Wang and W. L. Li, *J Org Chem*., 2018, **83**, 4681-4691; b) D. Q. Liang, Q. S. Dong, P. H. Xu, Y. Dong, W. L. Li and Y. Ma, *J Org Chem*., 2018, **83**, 11978-11986; c) Y. N. Li, Y. Chang, Y. F. Li, C. Cao, J. S. Yang, B. L. Wang and D. Q. Liang, *Adv. Synth. Catal*., 2018, **360**, 2488-2492.

8. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of the products

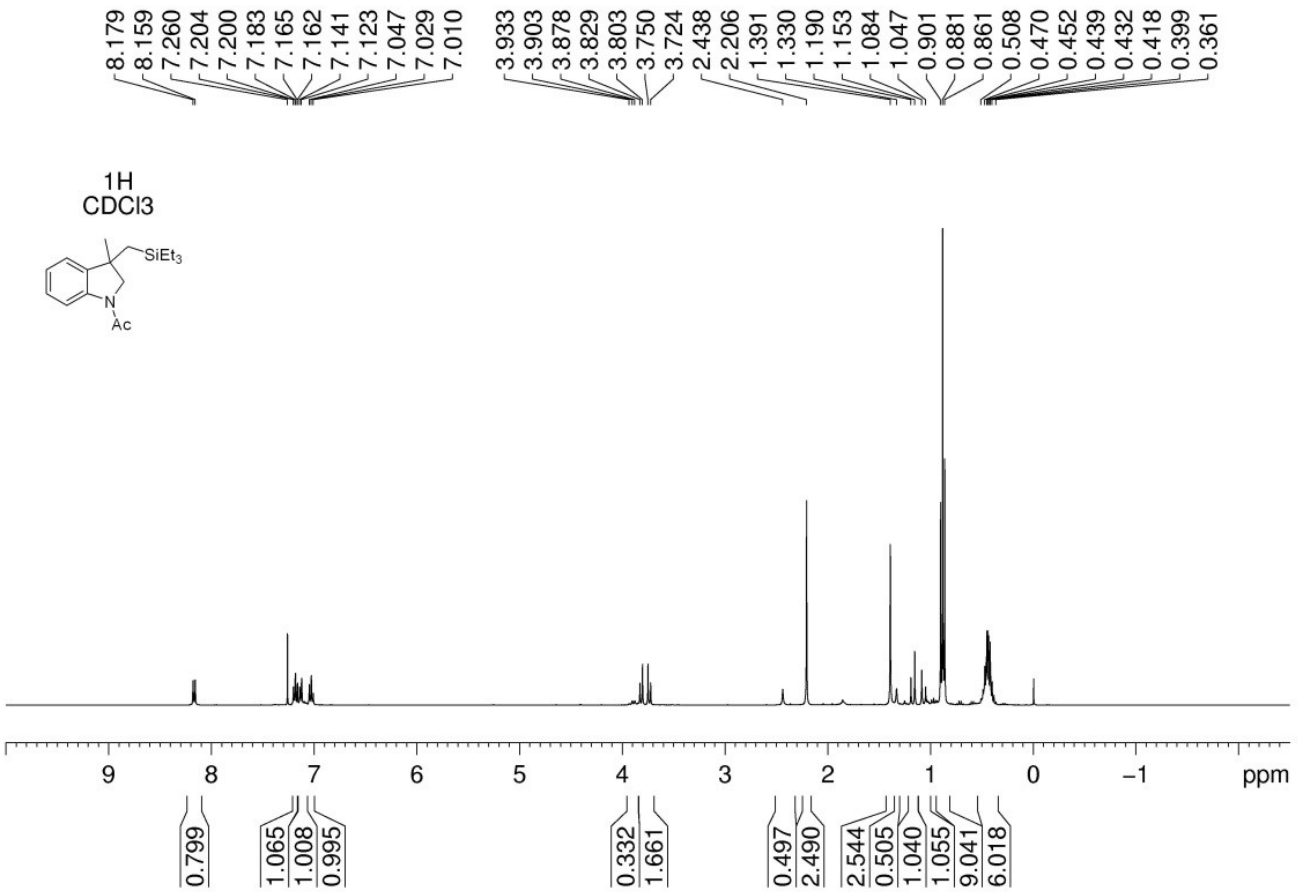


Figure S6. ^{1}H NMR (400 MHz, $CDCl_3$) of compound 3aa

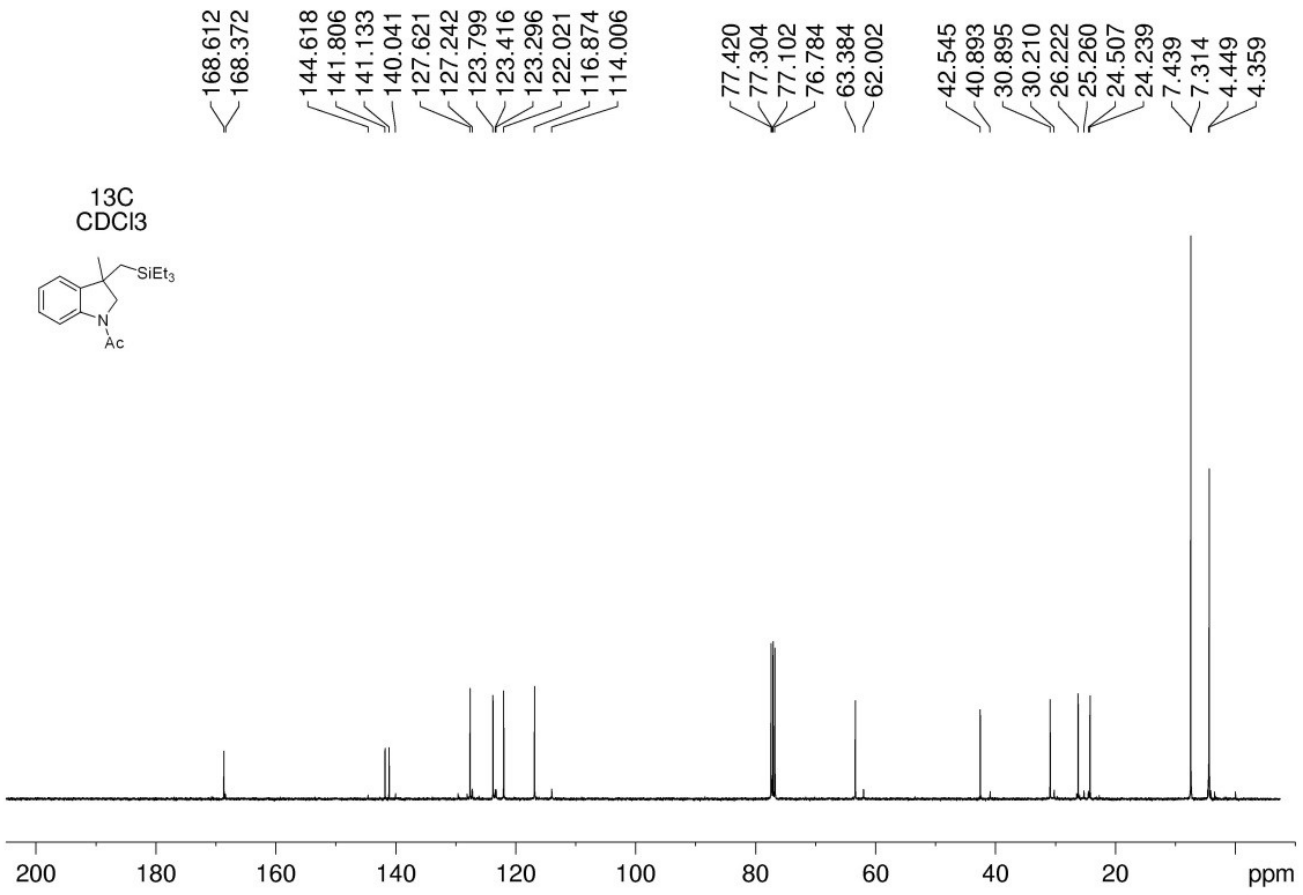


Figure S7. ^{13}C NMR (100 MHz, $CDCl_3$) of compound 3aa

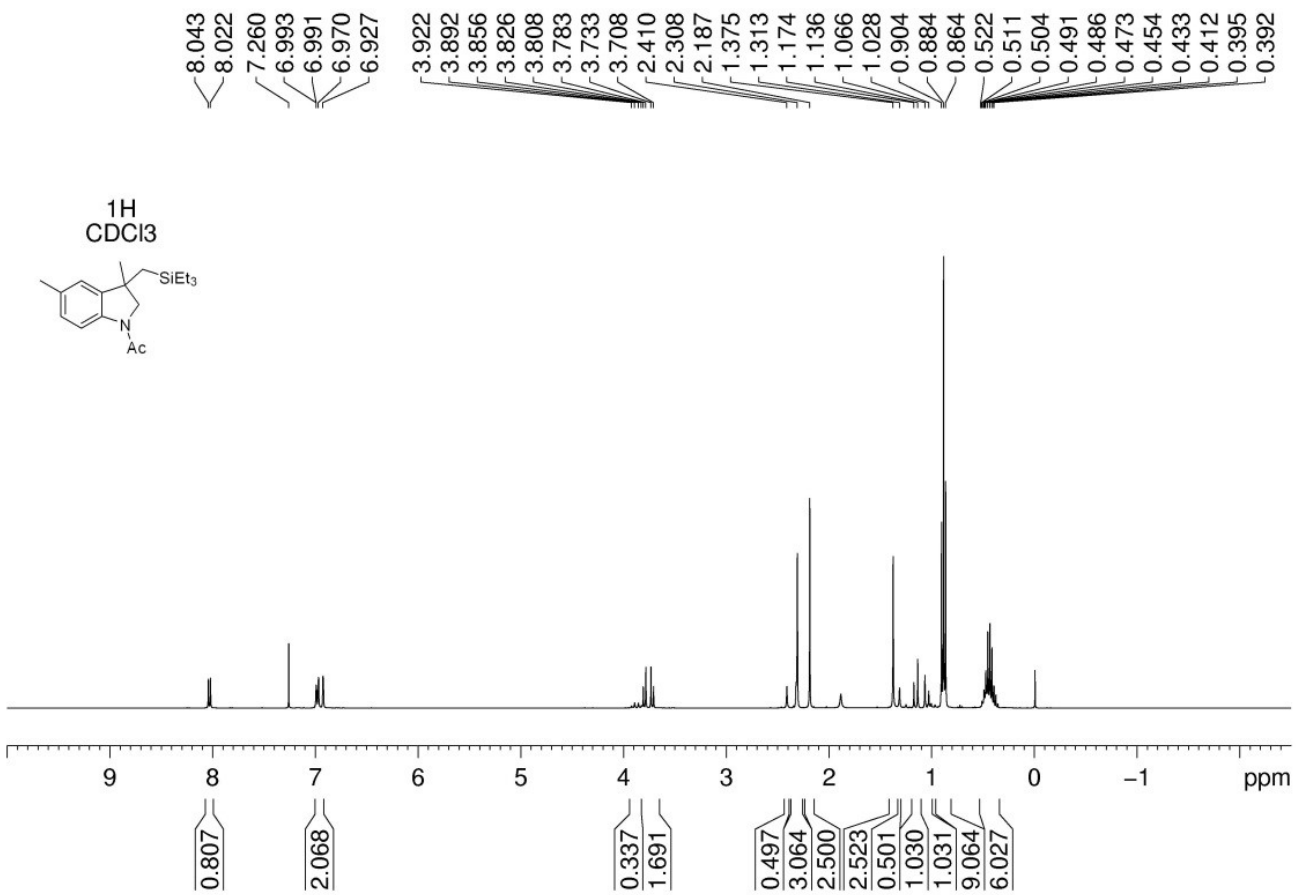


Figure S8.^{1}H NMR (400 MHz, $CDCl_3$) of compound 3ba

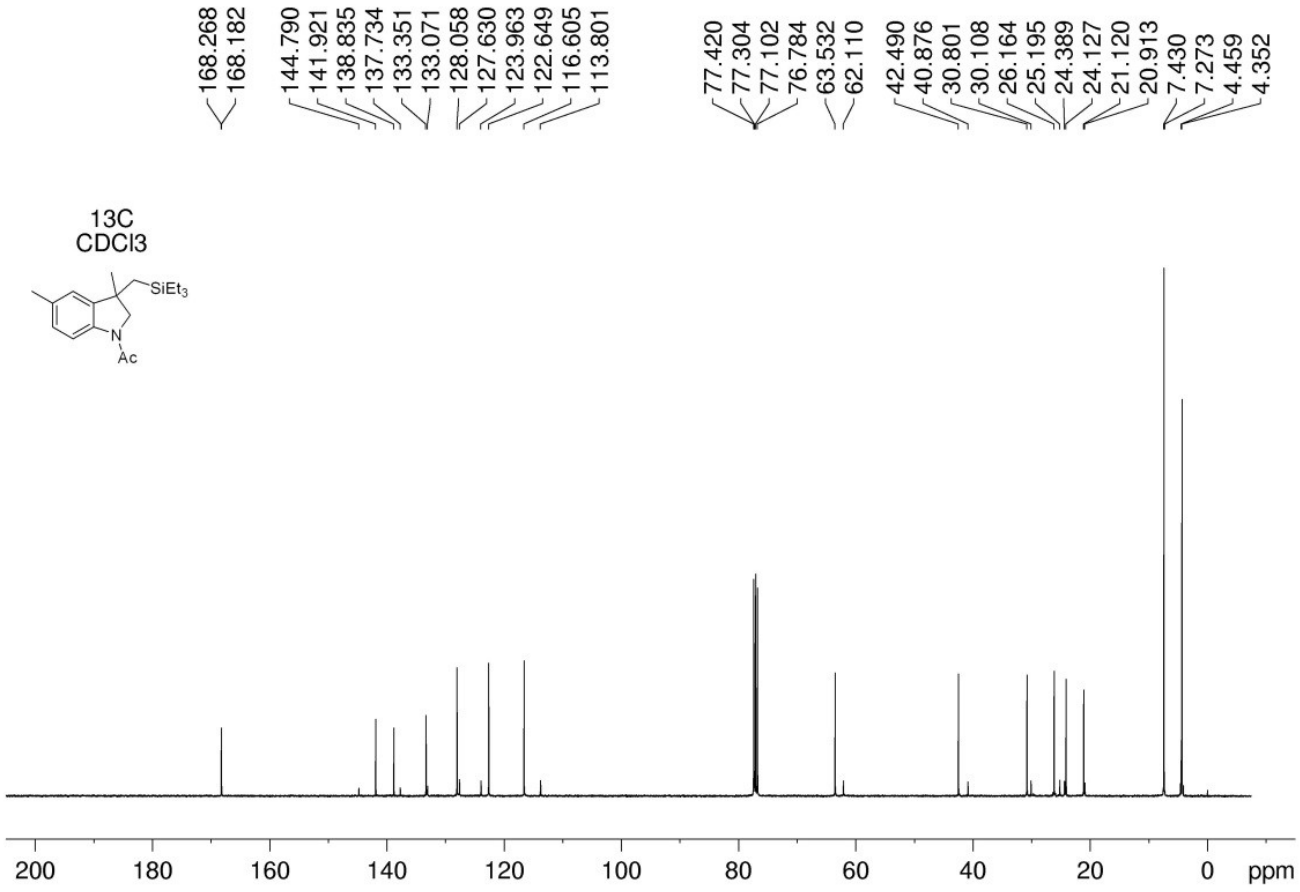


Figure S9. ^{13}C NMR (100 MHz, $CDCl_3$) of compound 3ba

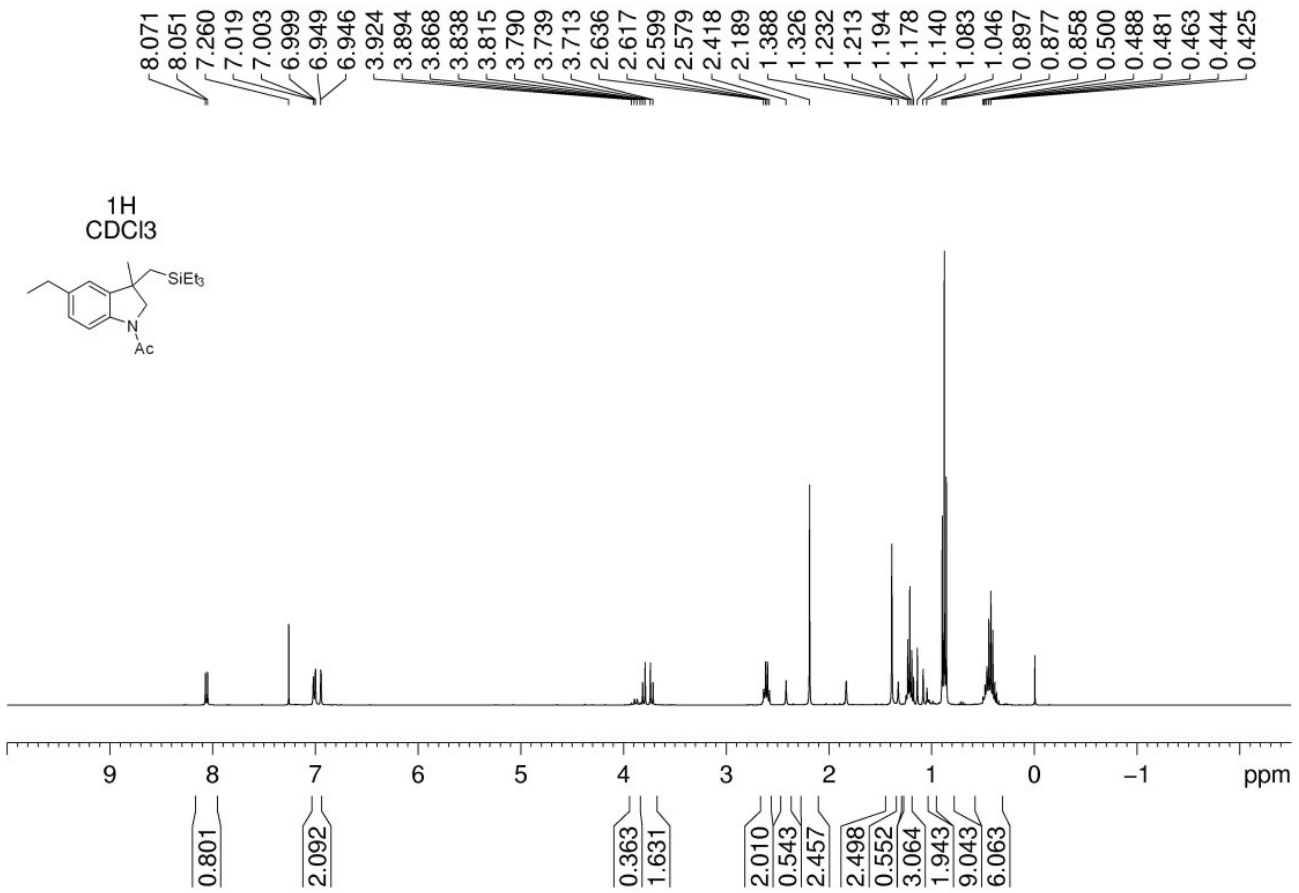


Figure S10. ^{1}H NMR (400 MHz, $CDCl_3$) of compound 3ca

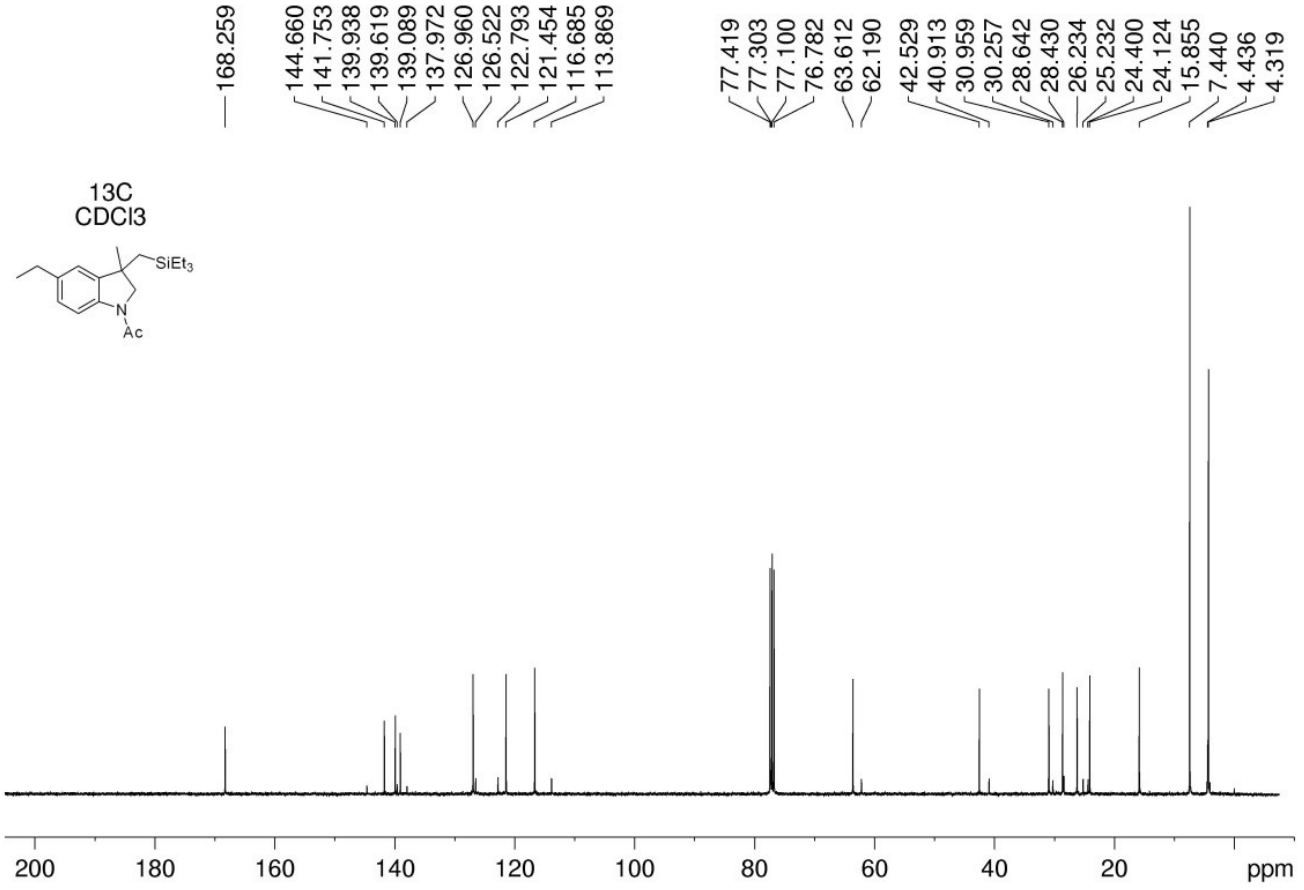


Figure S11. ^{13}C NMR (100 MHz, $CDCl_3$) of compound 3ca

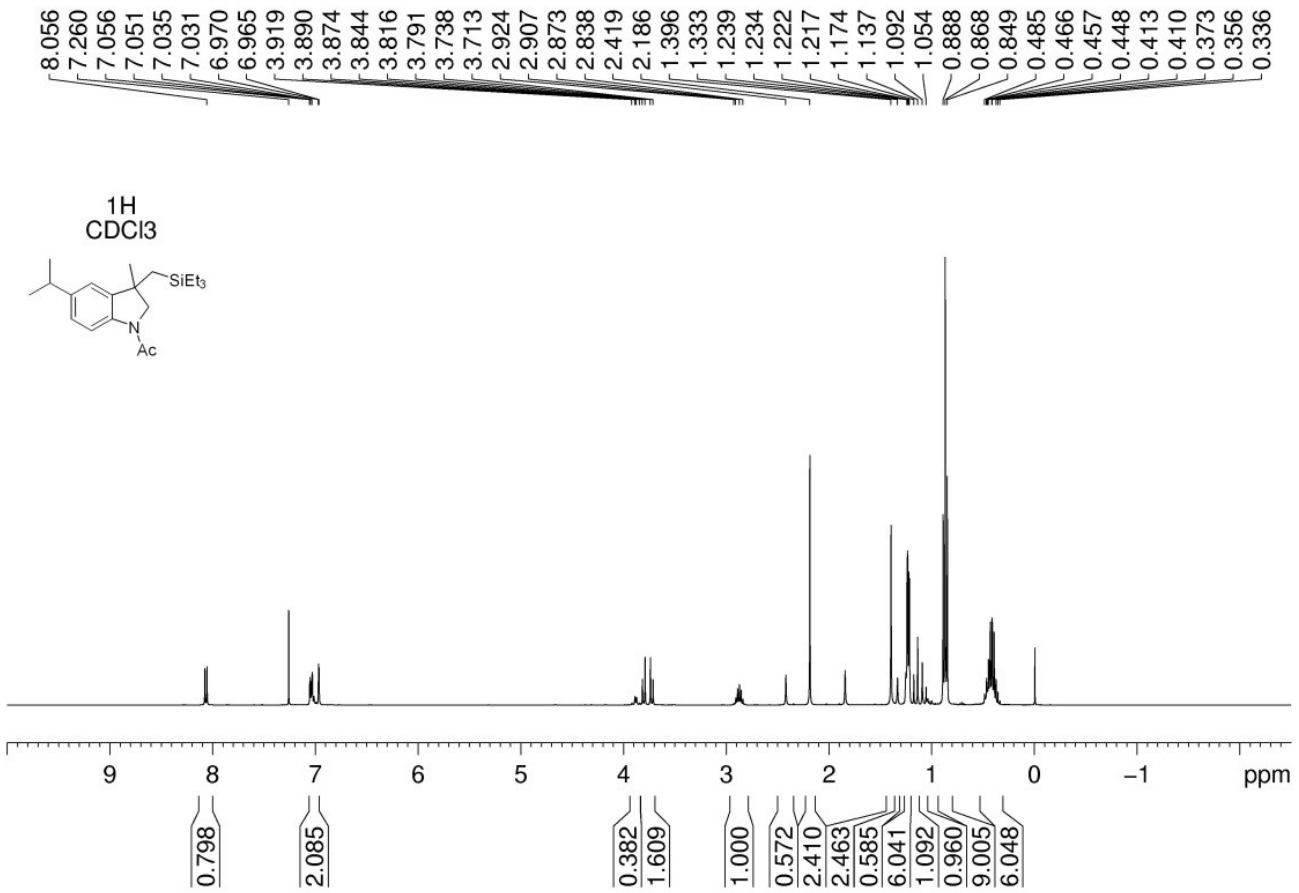


Figure S12. ^{1}H NMR (400 MHz, $CDCl_3$) of compound 3da

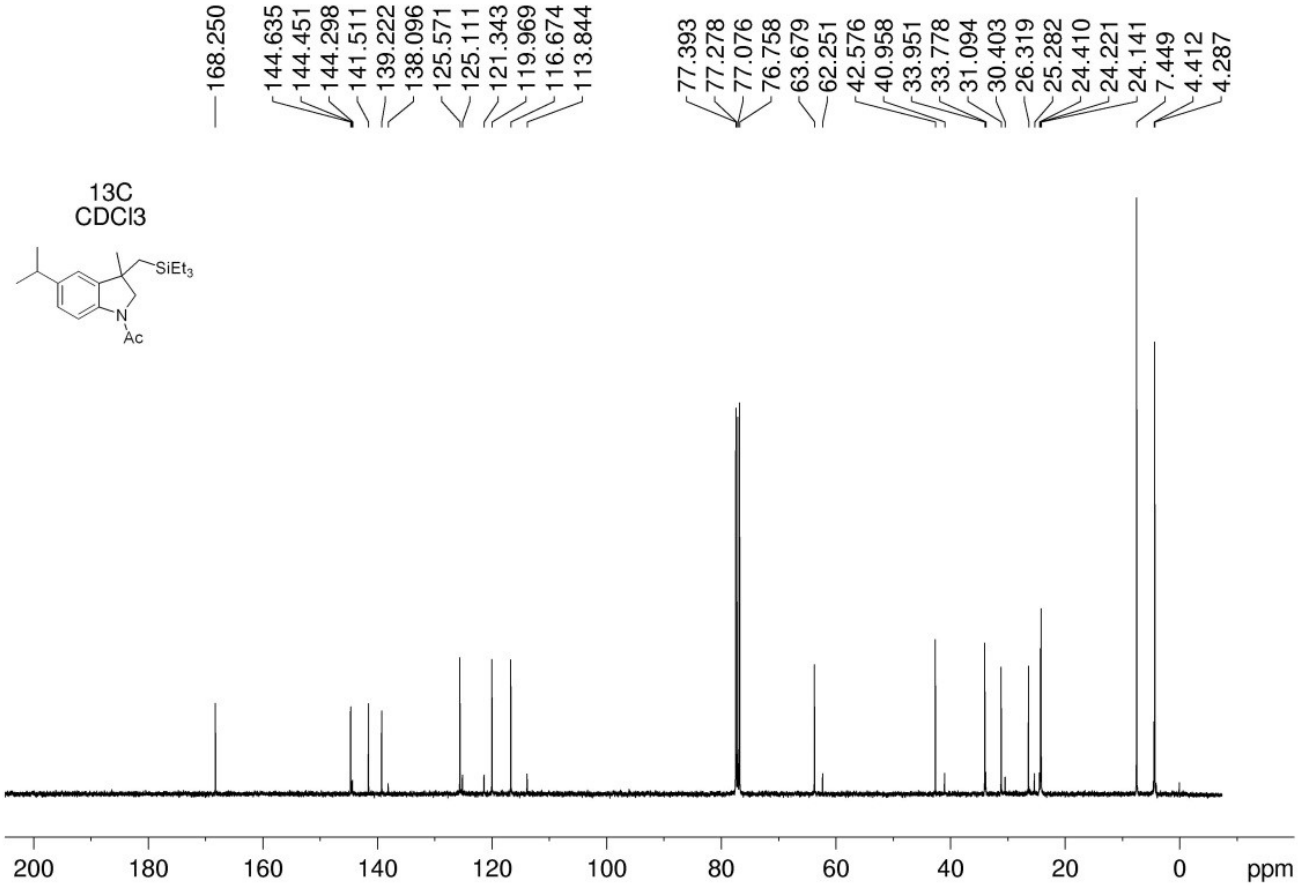


Figure S13. ^{13}C NMR (100 MHz, $CDCl_3$) of compound 3da

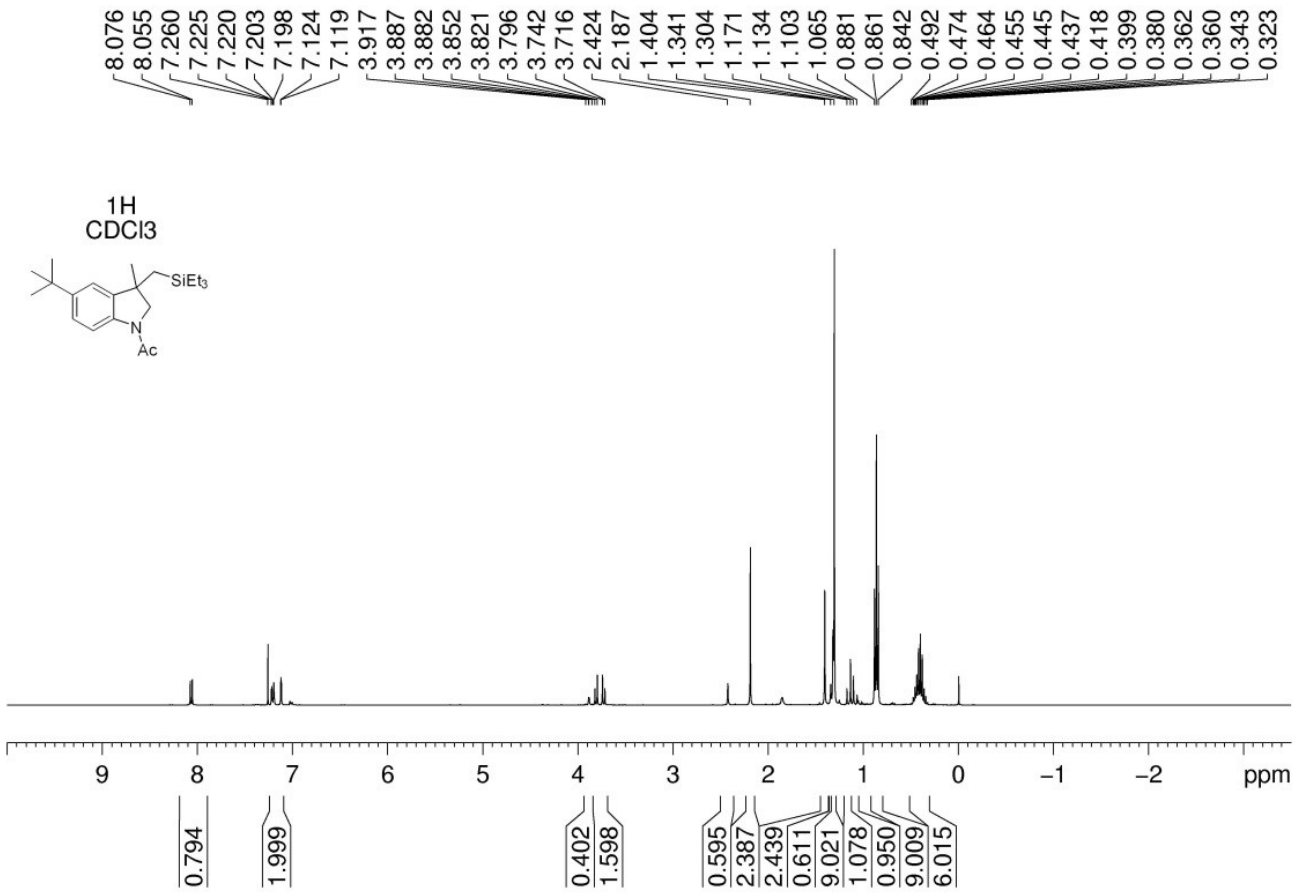


Figure S14. ^{1}H NMR (400 MHz, $CDCl_3$) of compound 3ea

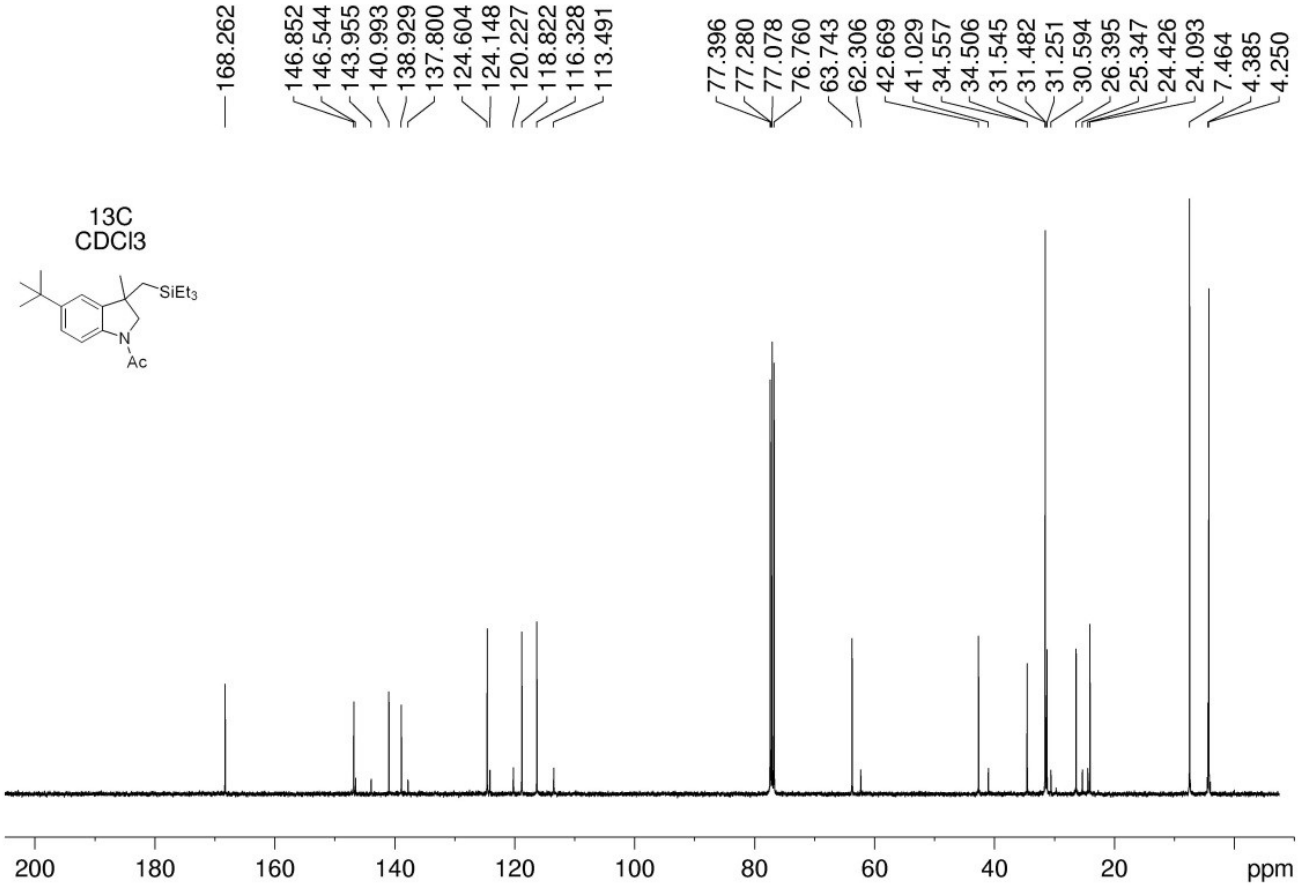


Figure S15. ^{13}C NMR (100 MHz, $CDCl_3$) of compound 3ea

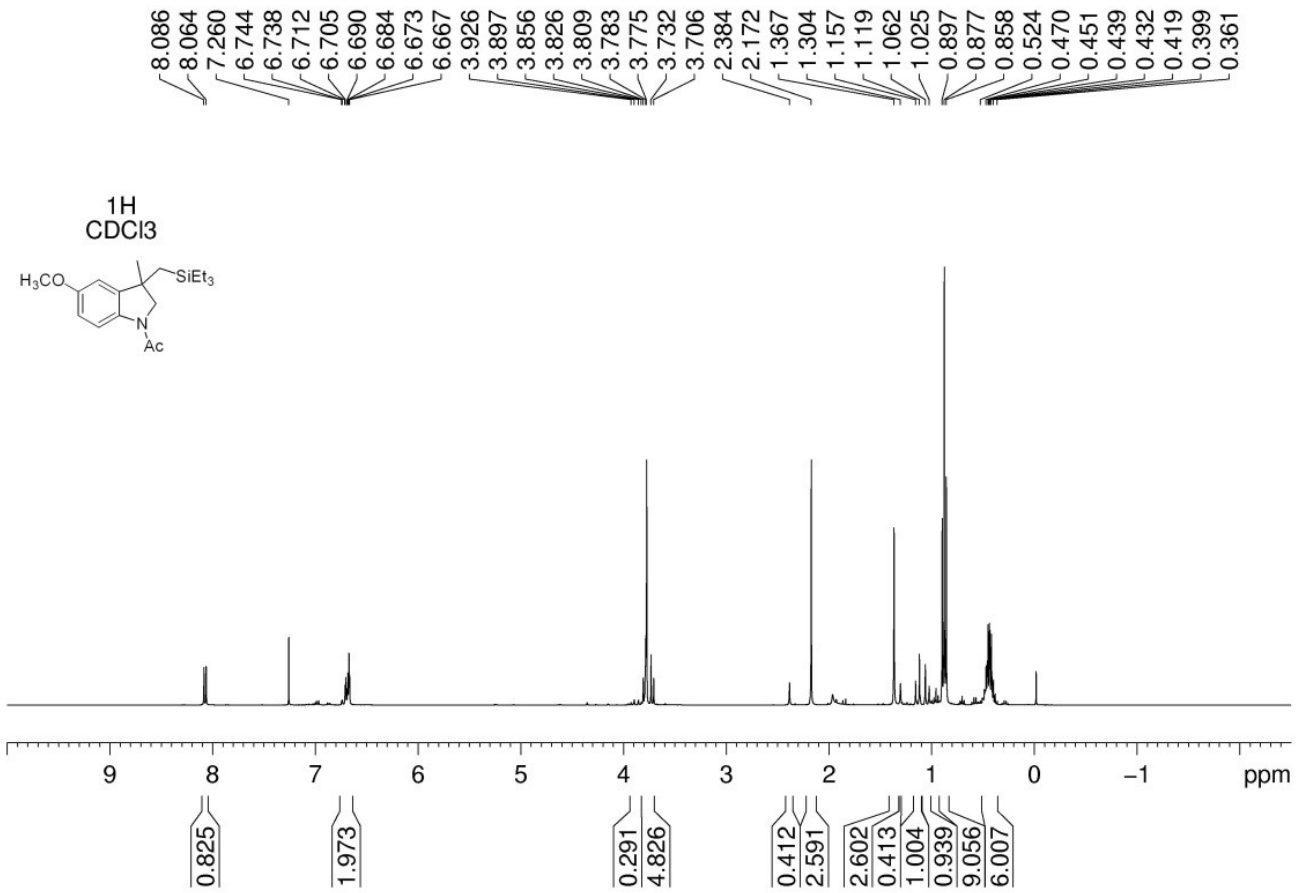


Figure S16. ^{1}H NMR (400 MHz, $CDCl_3$) of compound 3fa

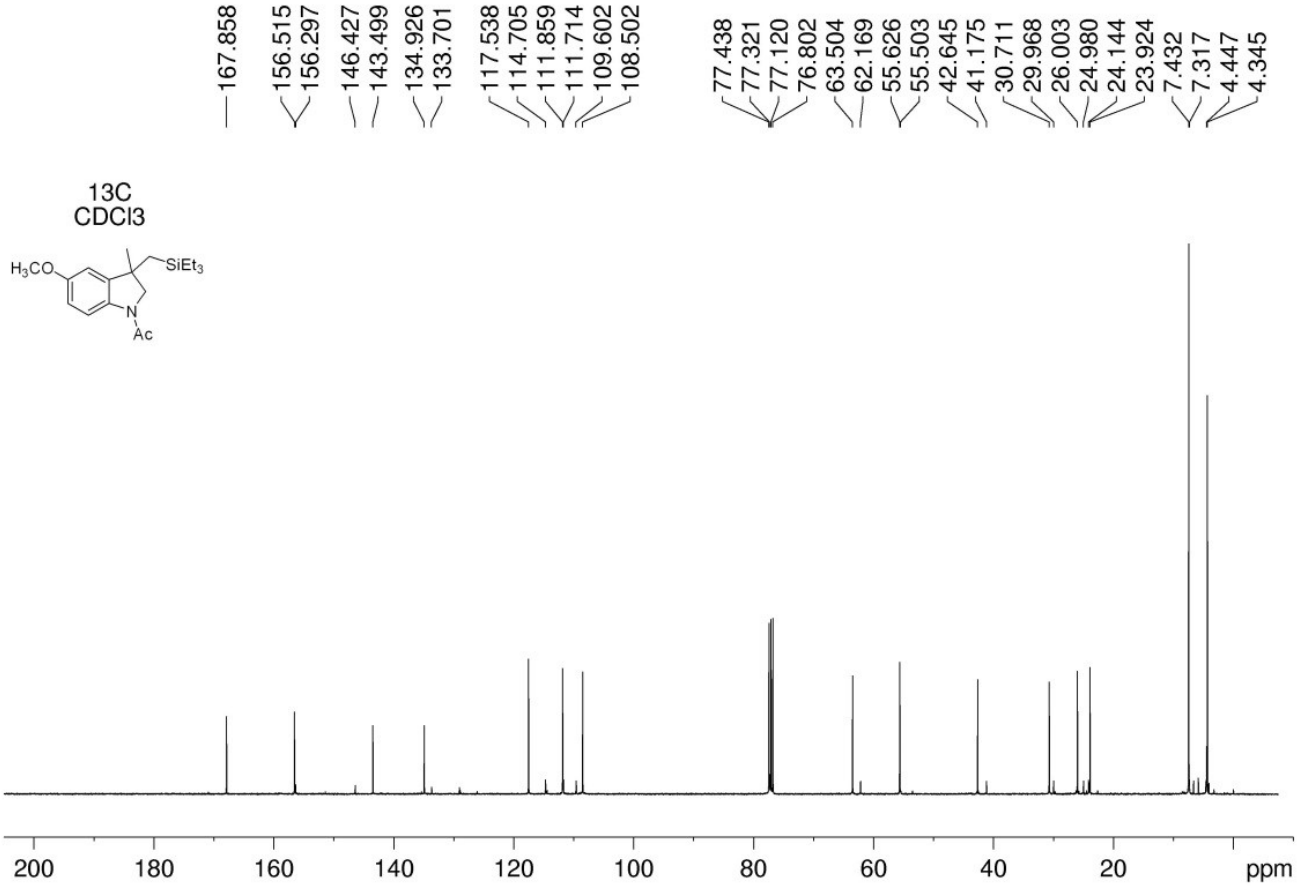


Figure S17. ^{13}C NMR (100 MHz, $CDCl_3$) of compound 3fa

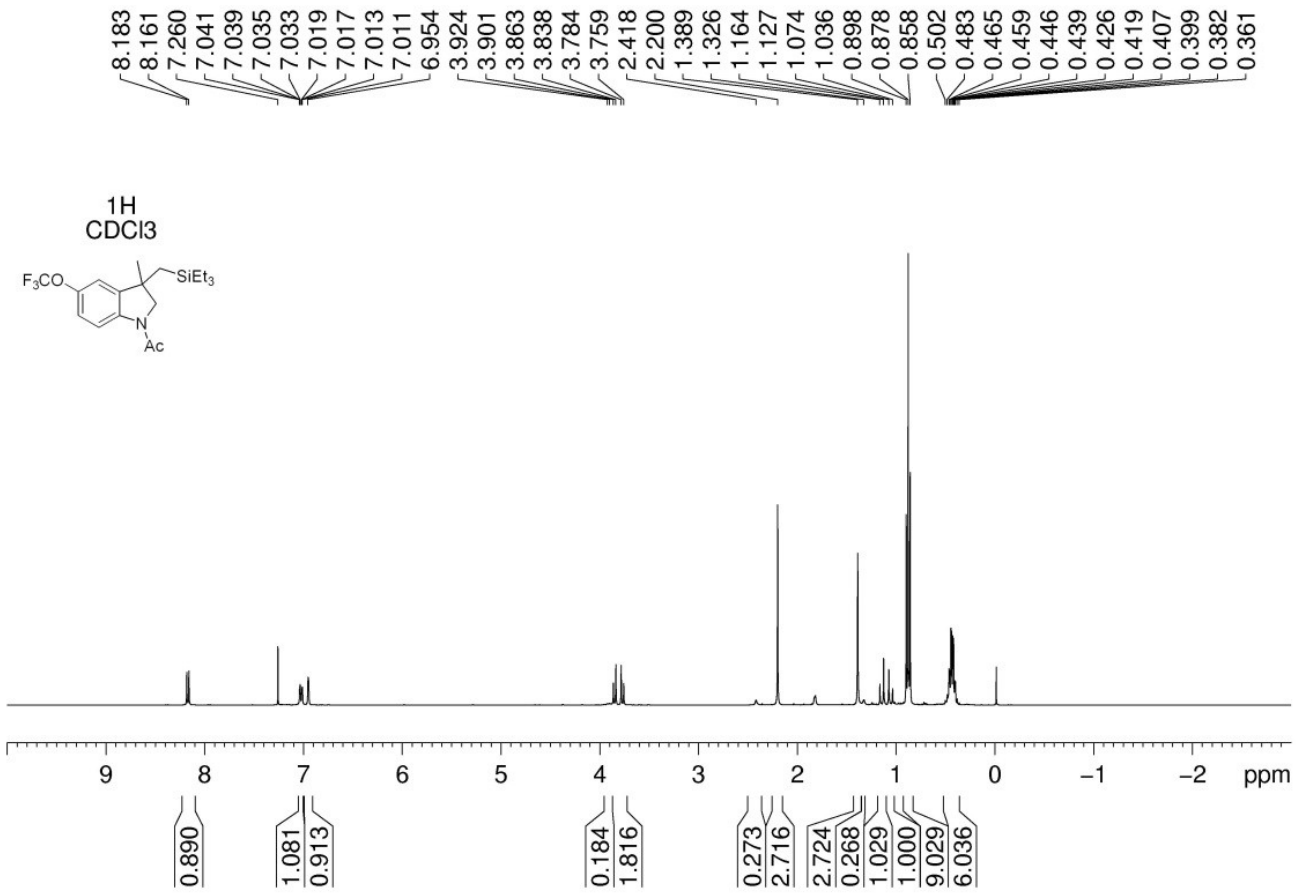


Figure S18. ^{1}H NMR (400 MHz, $CDCl_3$) of compound 3ga

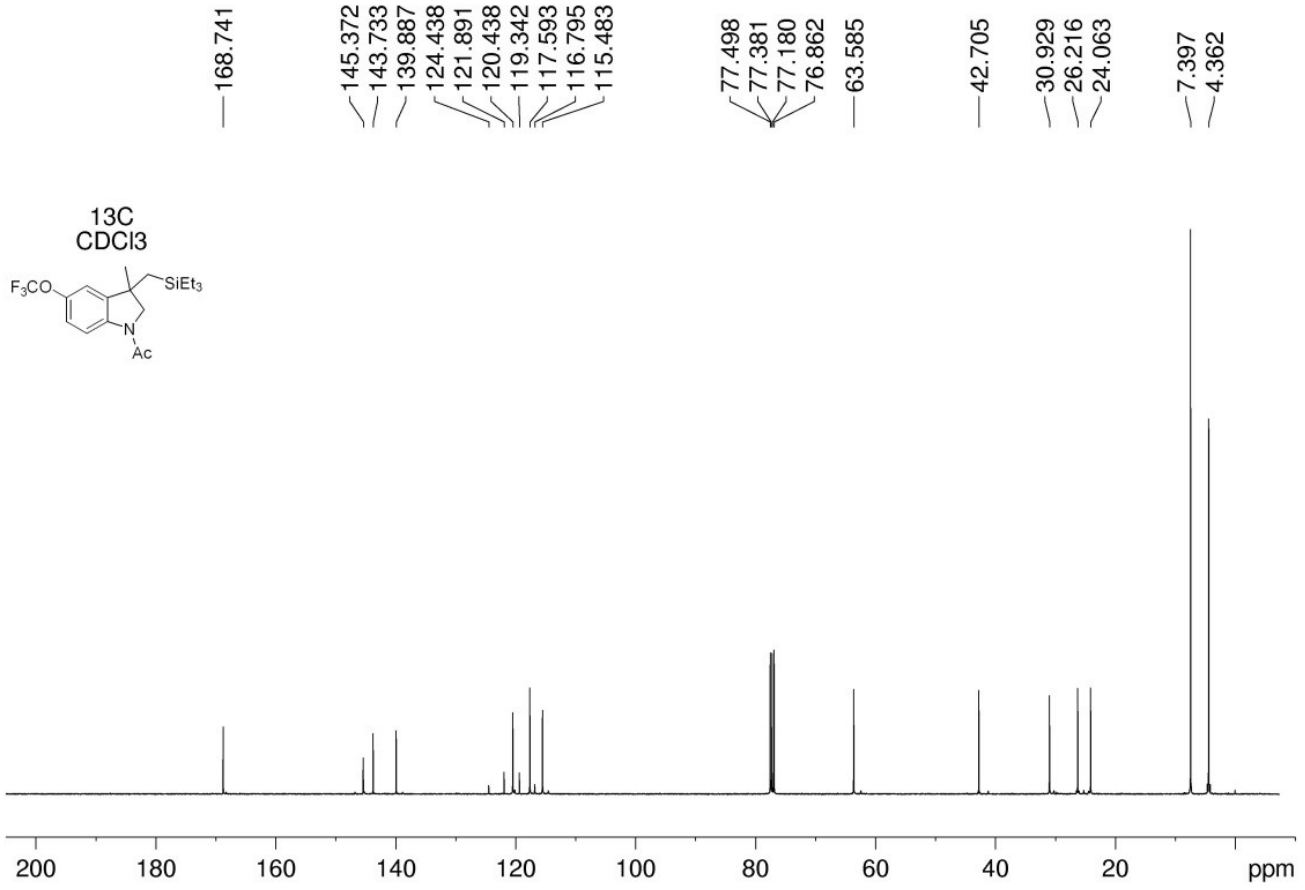


Figure S19. ^{13}C NMR (100 MHz, $CDCl_3$) of compound 3ga

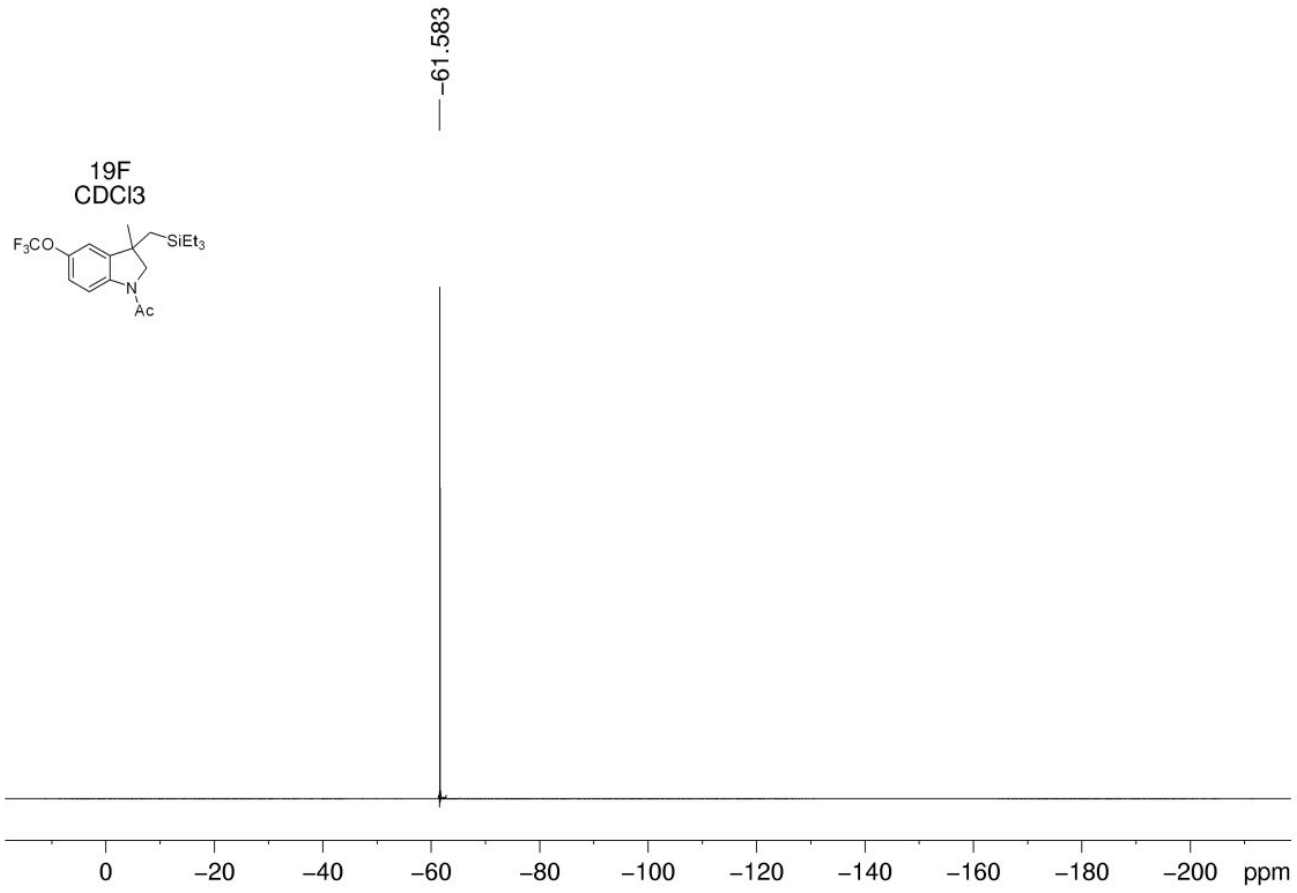


Figure S20. ^{19}F NMR (376 MHz, $CDCl_3$) of compound 3ga

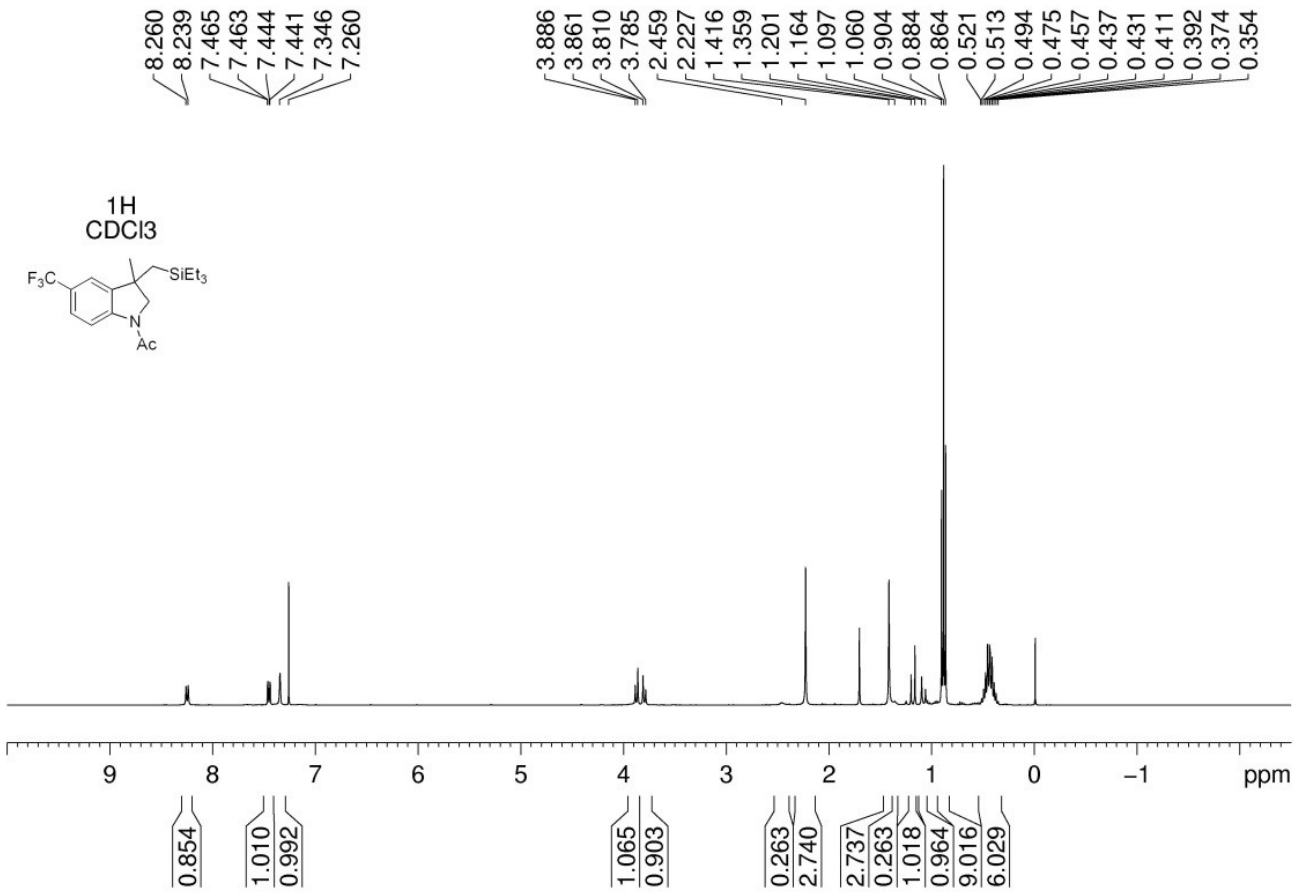


Figure S21. ^{1}H NMR (400 MHz, $CDCl_3$) of compound 3ha

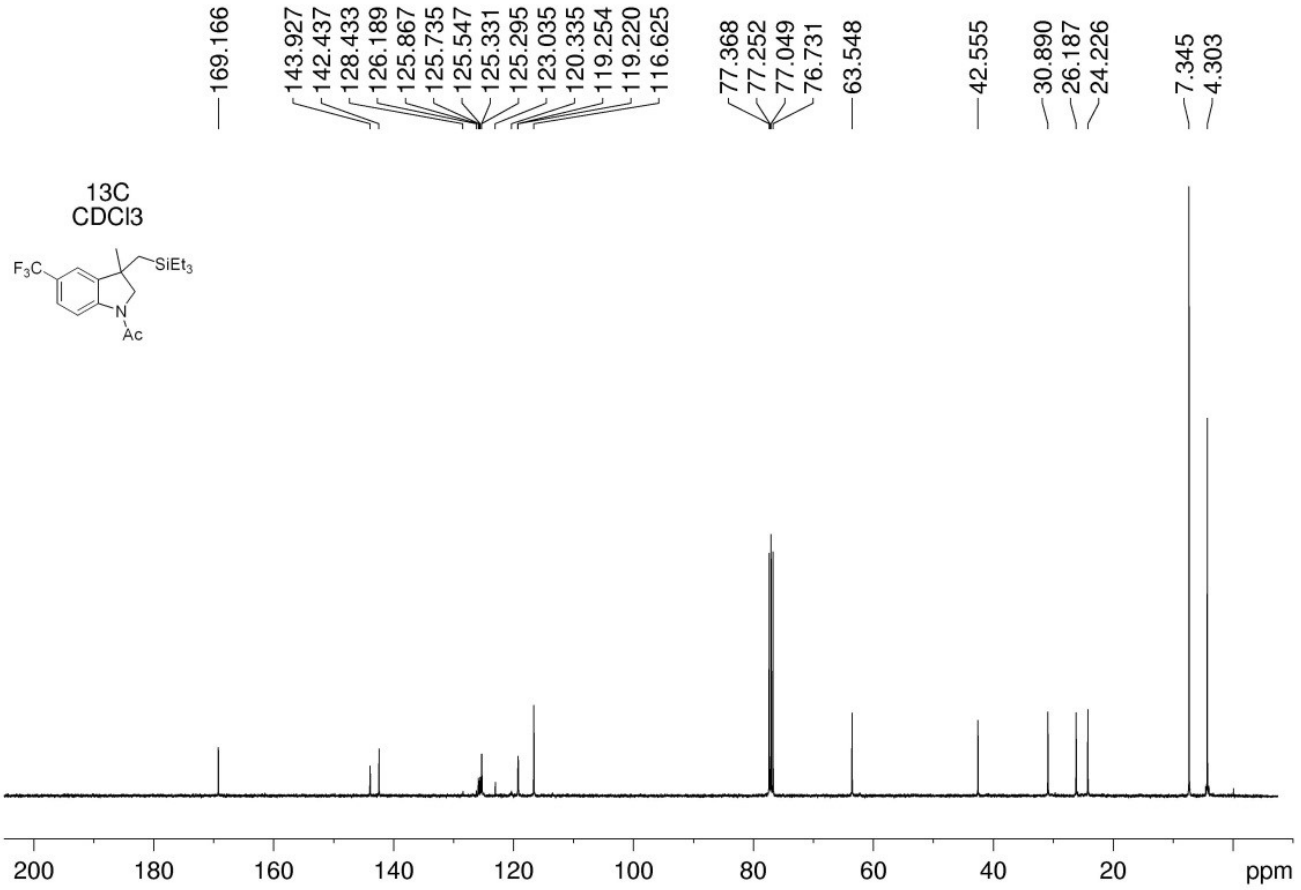


Figure S22. ^{13}C NMR (100 MHz, $CDCl_3$) of compound 3ha

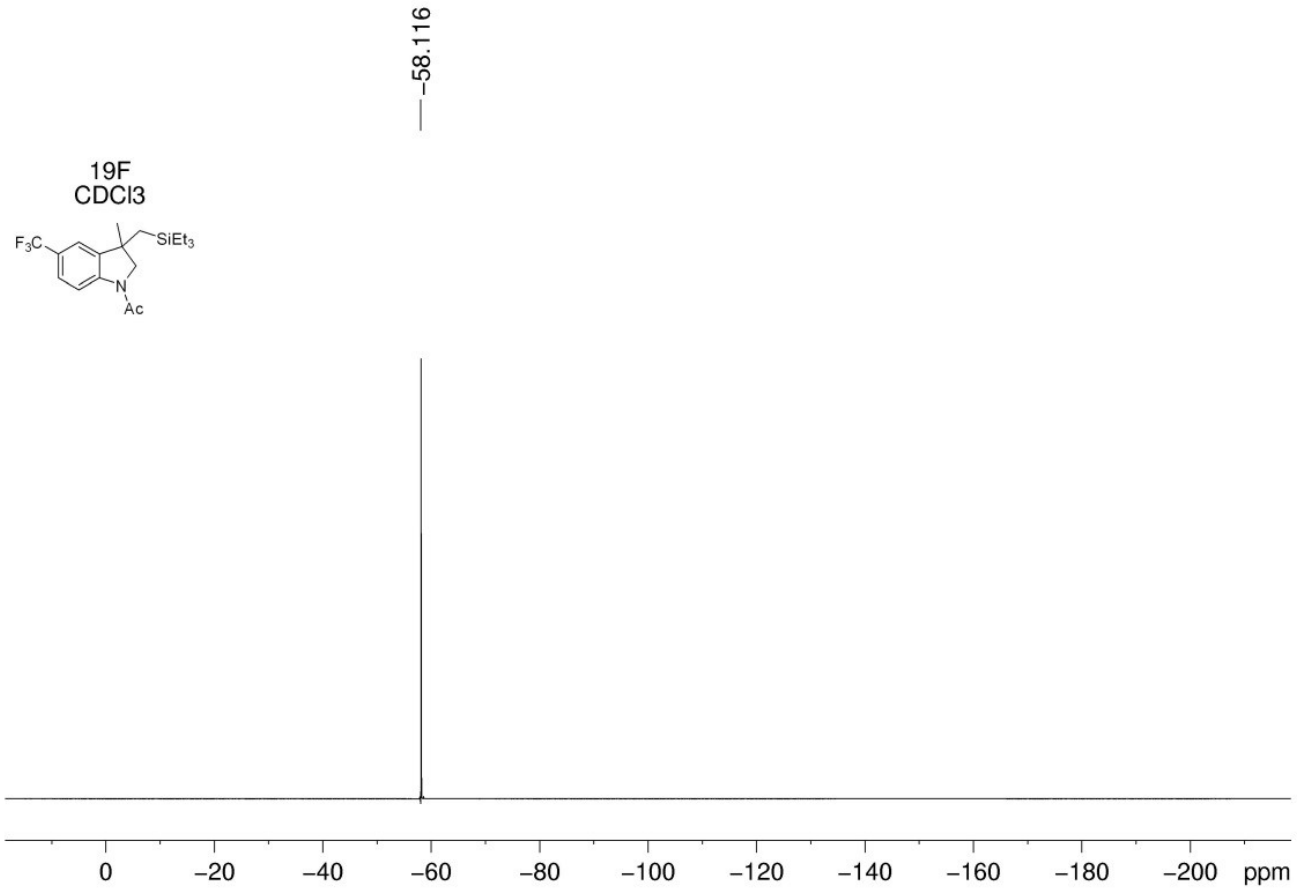


Figure S23. ^{19}F NMR (376 MHz, $CDCl_3$) of compound 3ha

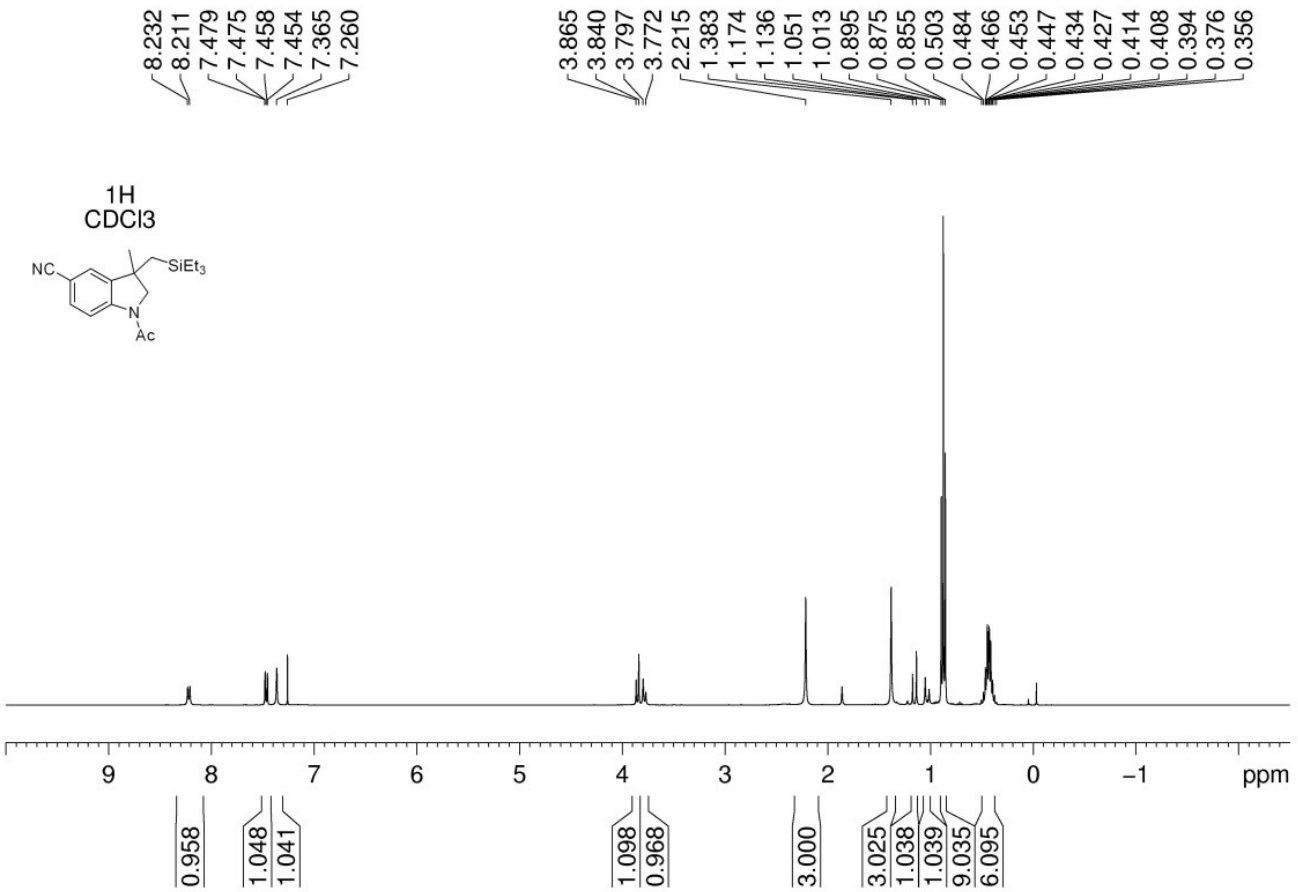


Figure S24. ^{1}H NMR (400 MHz, $CDCl_3$) of compound 3ia

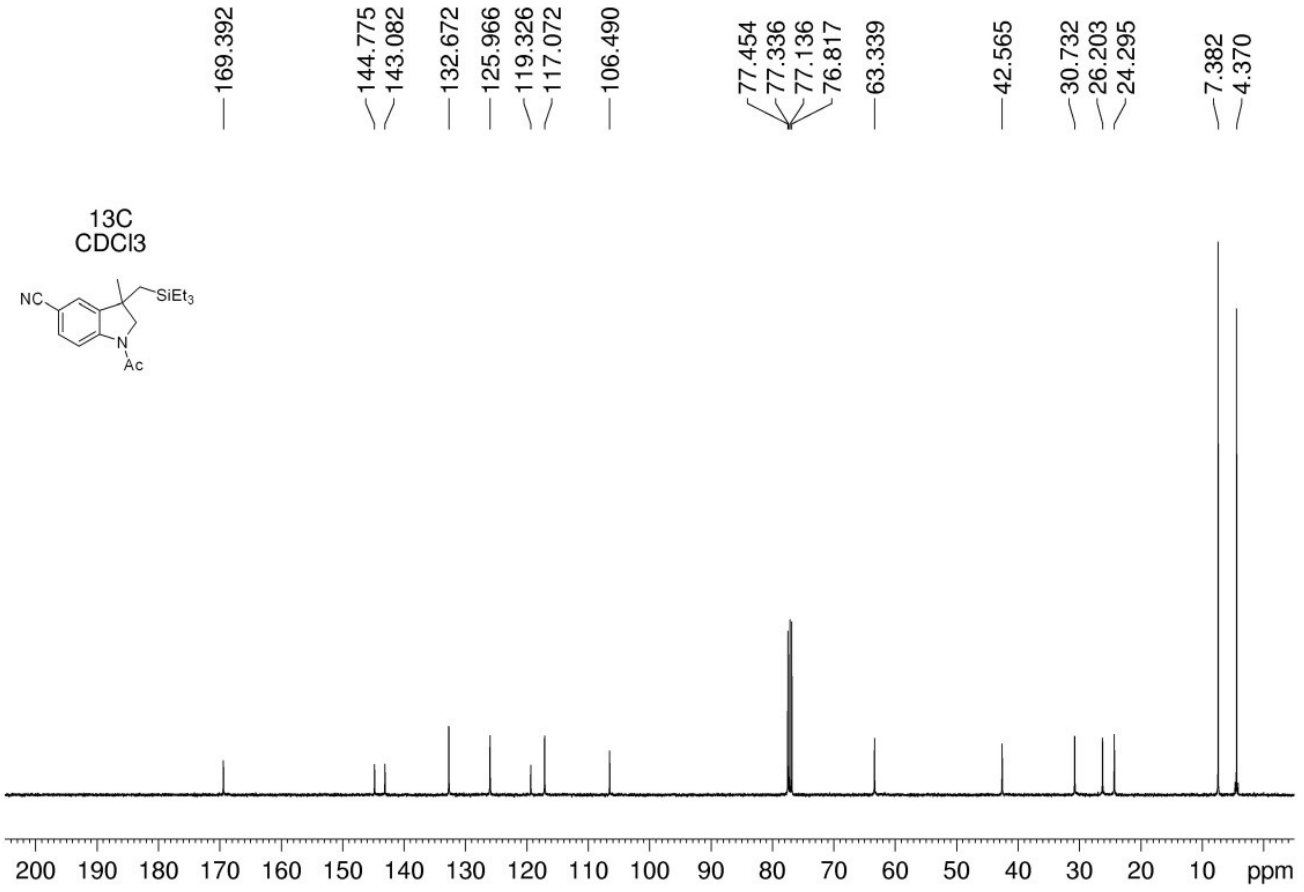


Figure S25. ^{13}C NMR (100 MHz, $CDCl_3$) of compound 3ia

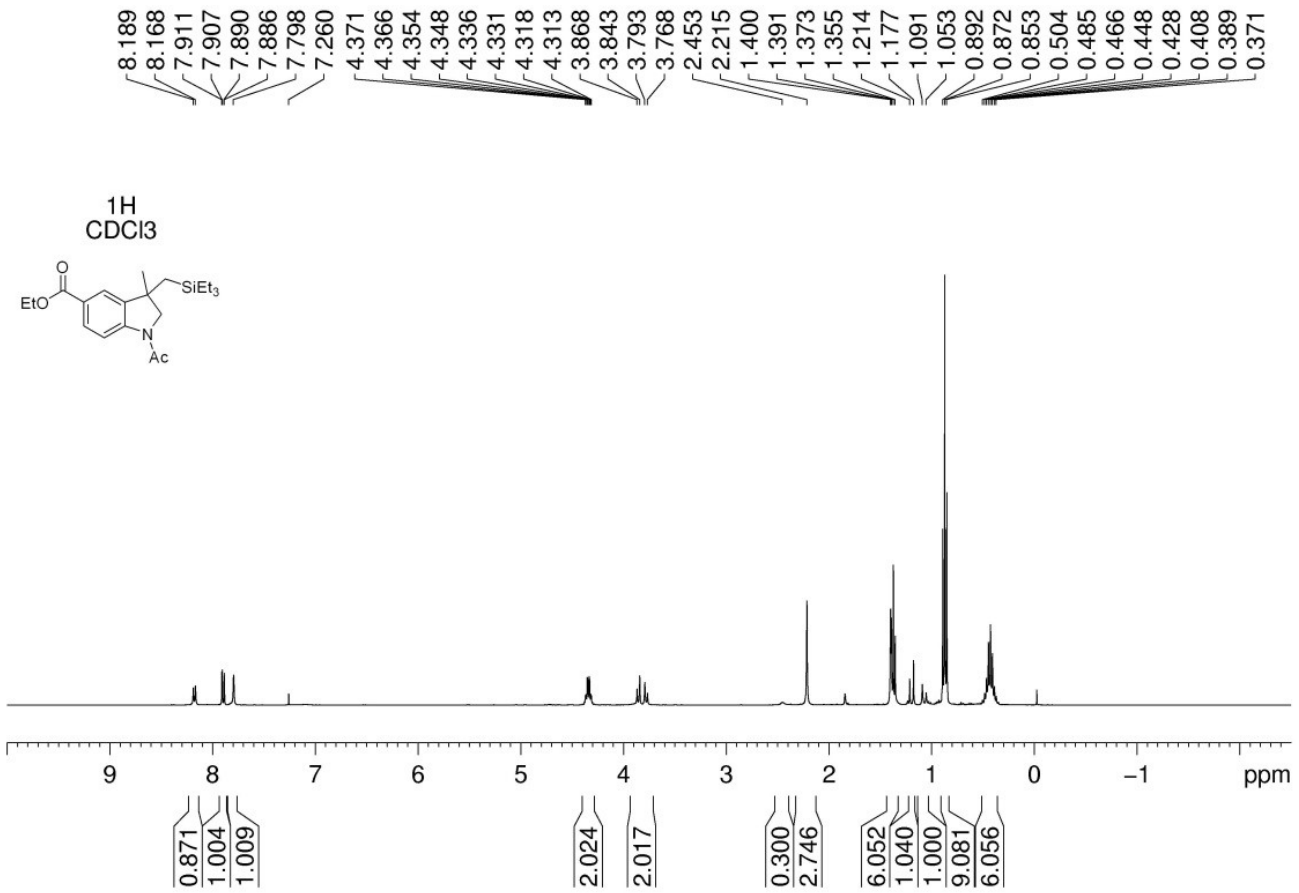


Figure S26. ^{1}H NMR (400 MHz, $CDCl_3$) of compound 3ja

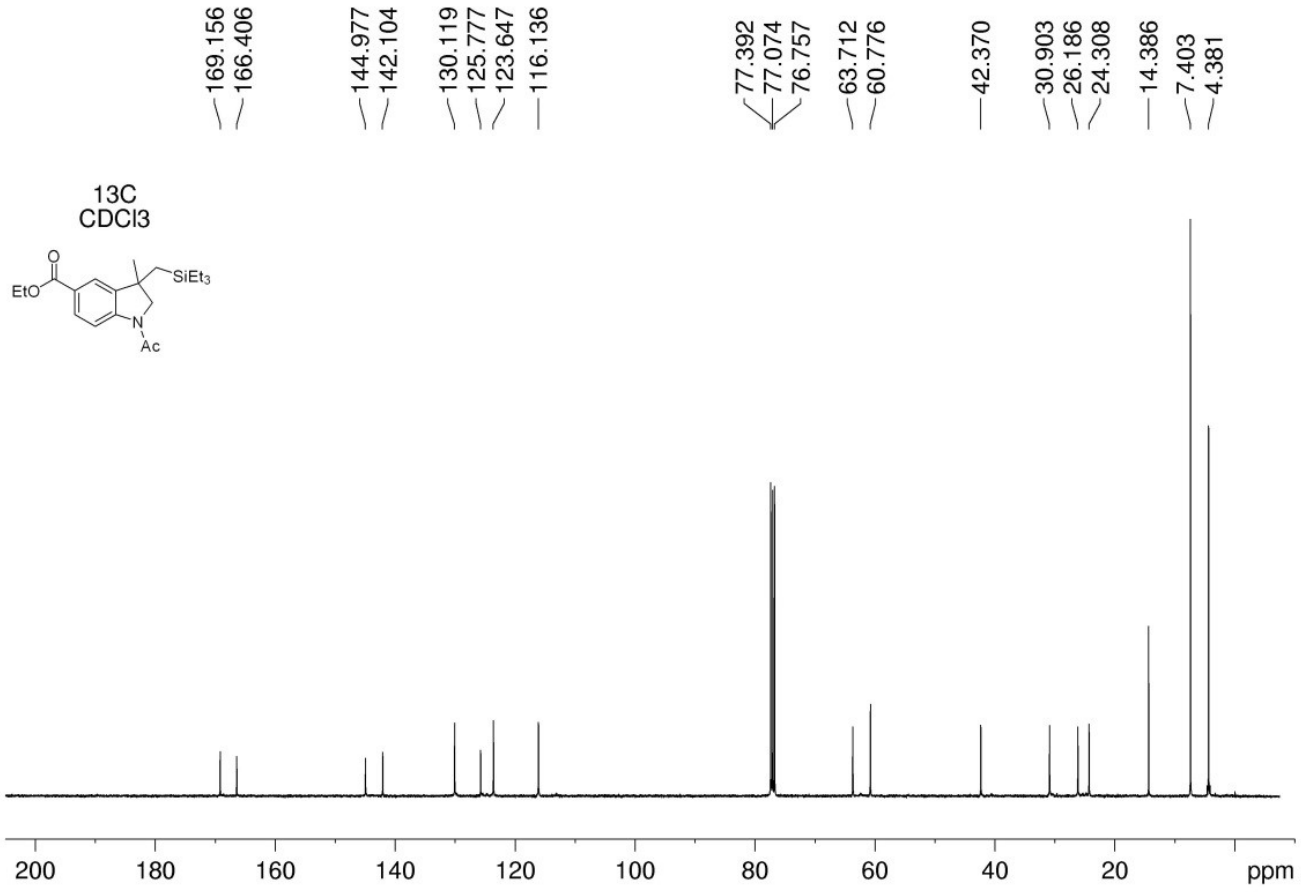


Figure S27. ^{13}C NMR (100 MHz, $CDCl_3$) of compound 3ja

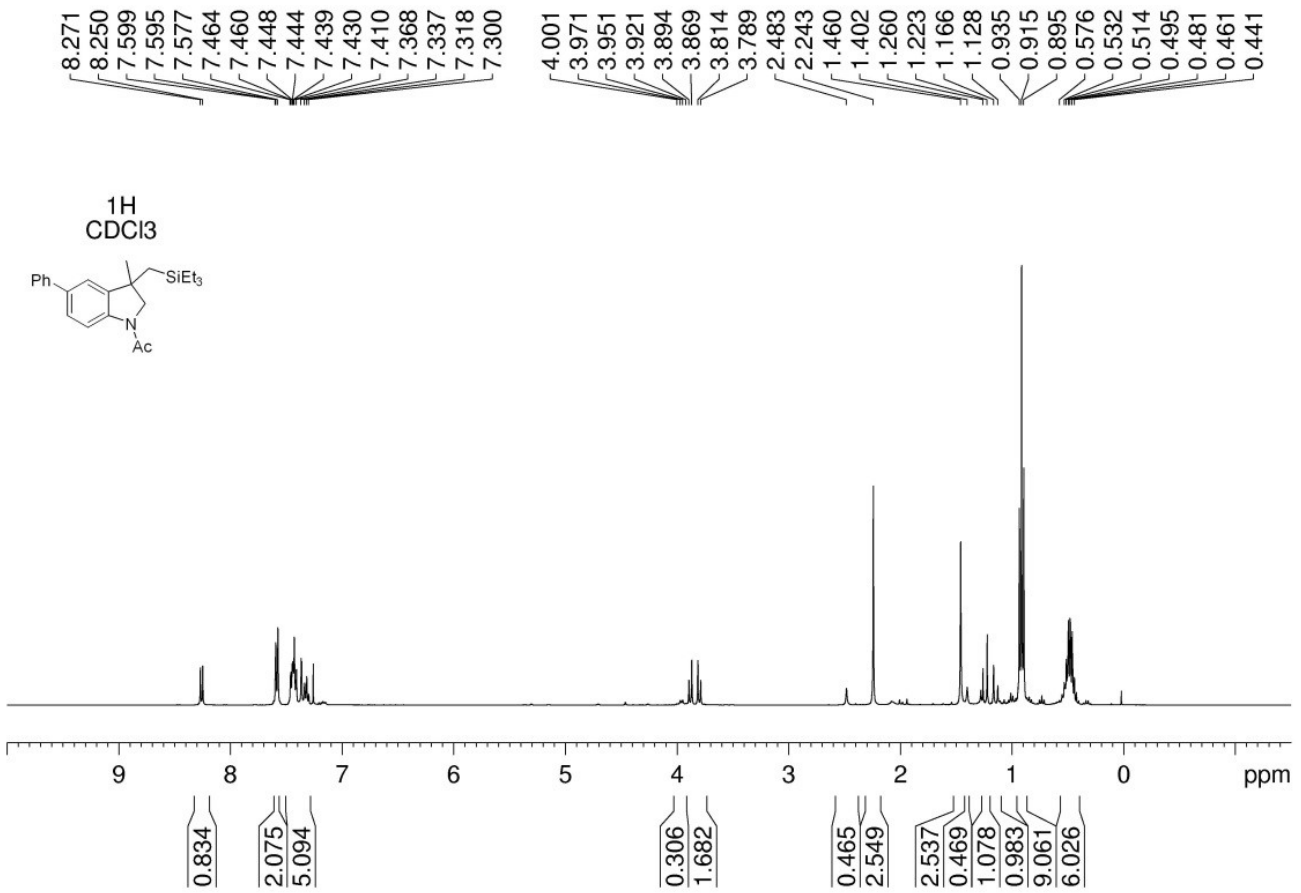


Figure S28. ^{1}H NMR (400 MHz, $CDCl_3$) of compound 3la

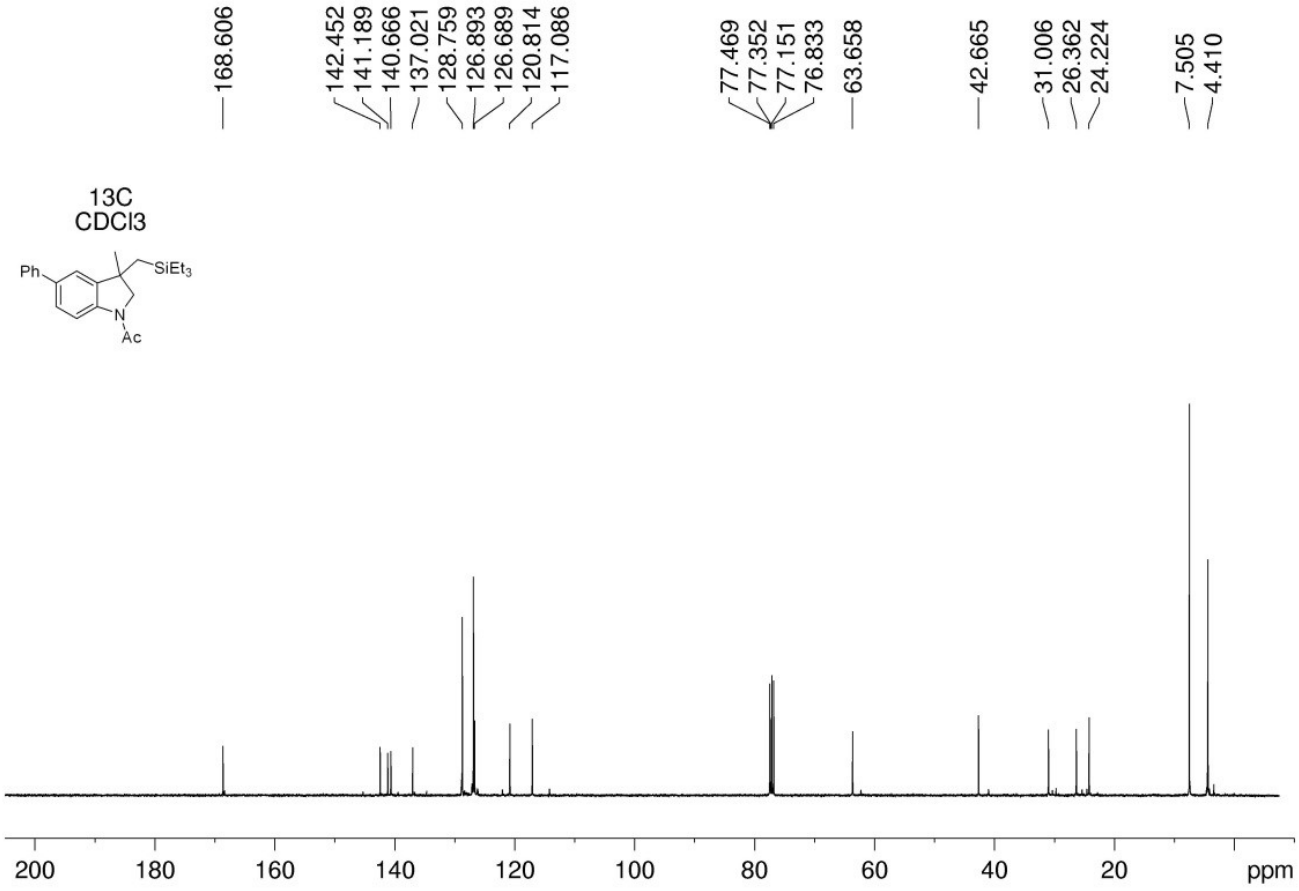


Figure S29. ^{13}C NMR (100 MHz, $CDCl_3$) of compound 3la

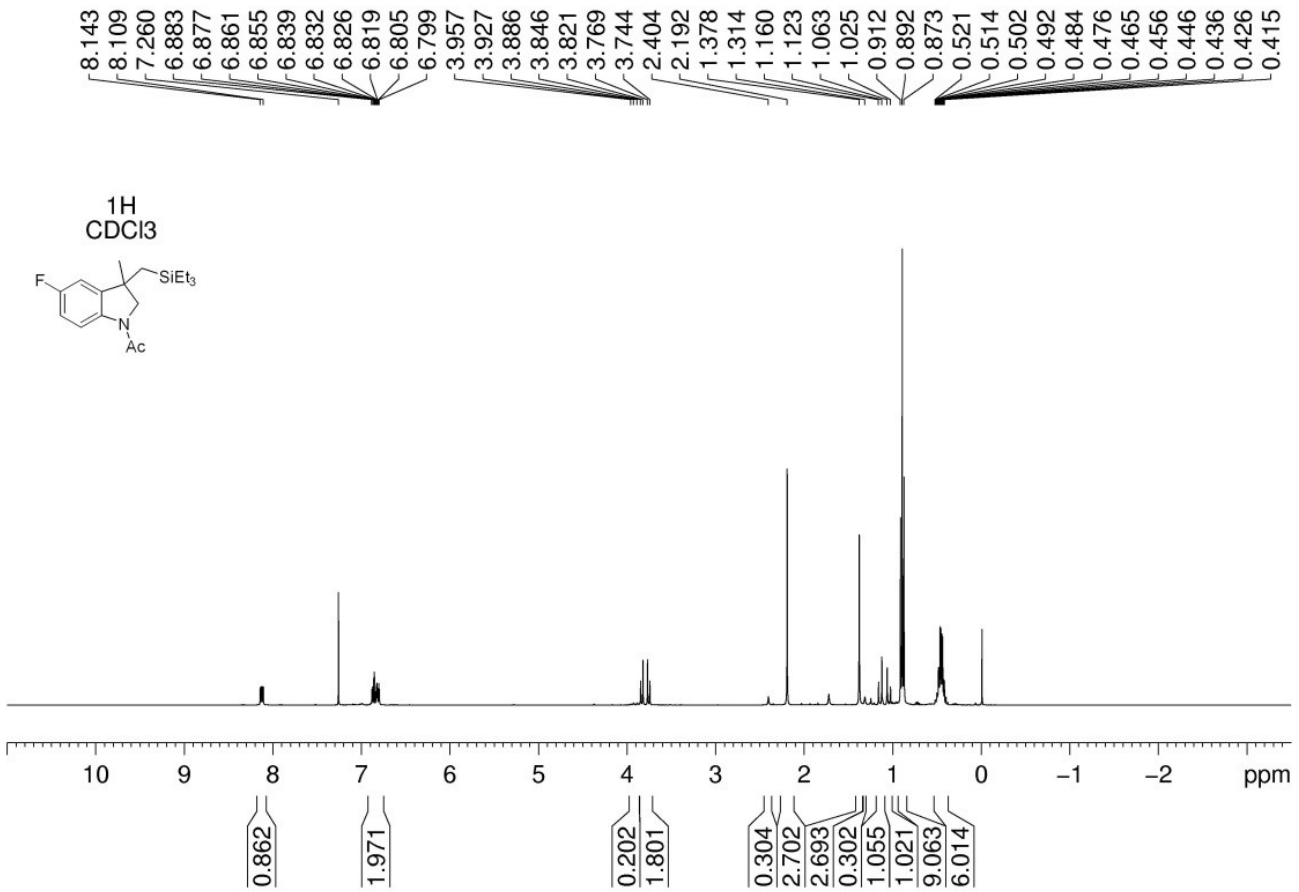


Figure S30. ^{1}H NMR (400 MHz, $CDCl_3$) of compound 3ma

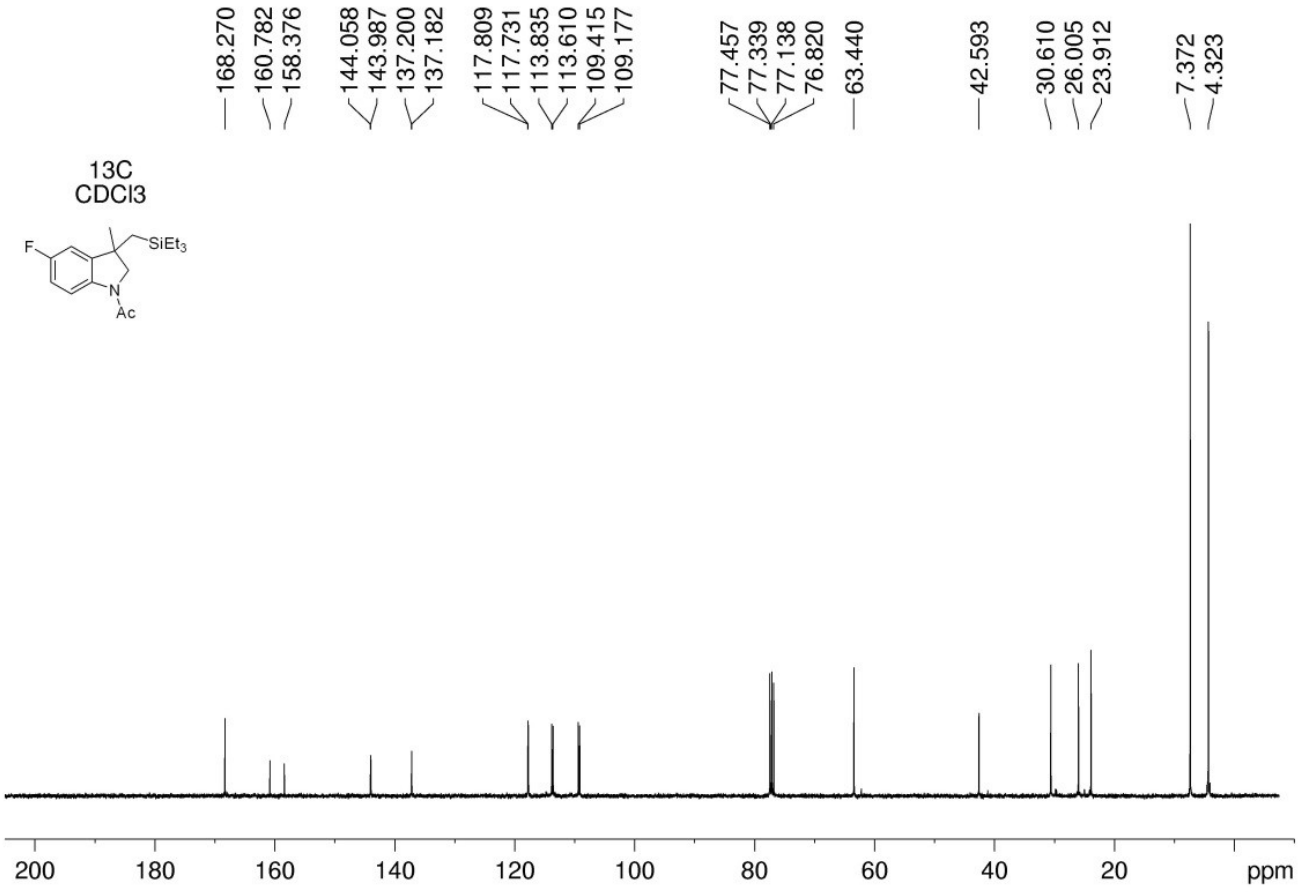


Figure S31. ^{13}C NMR (100 MHz, $CDCl_3$) of compound 3ma

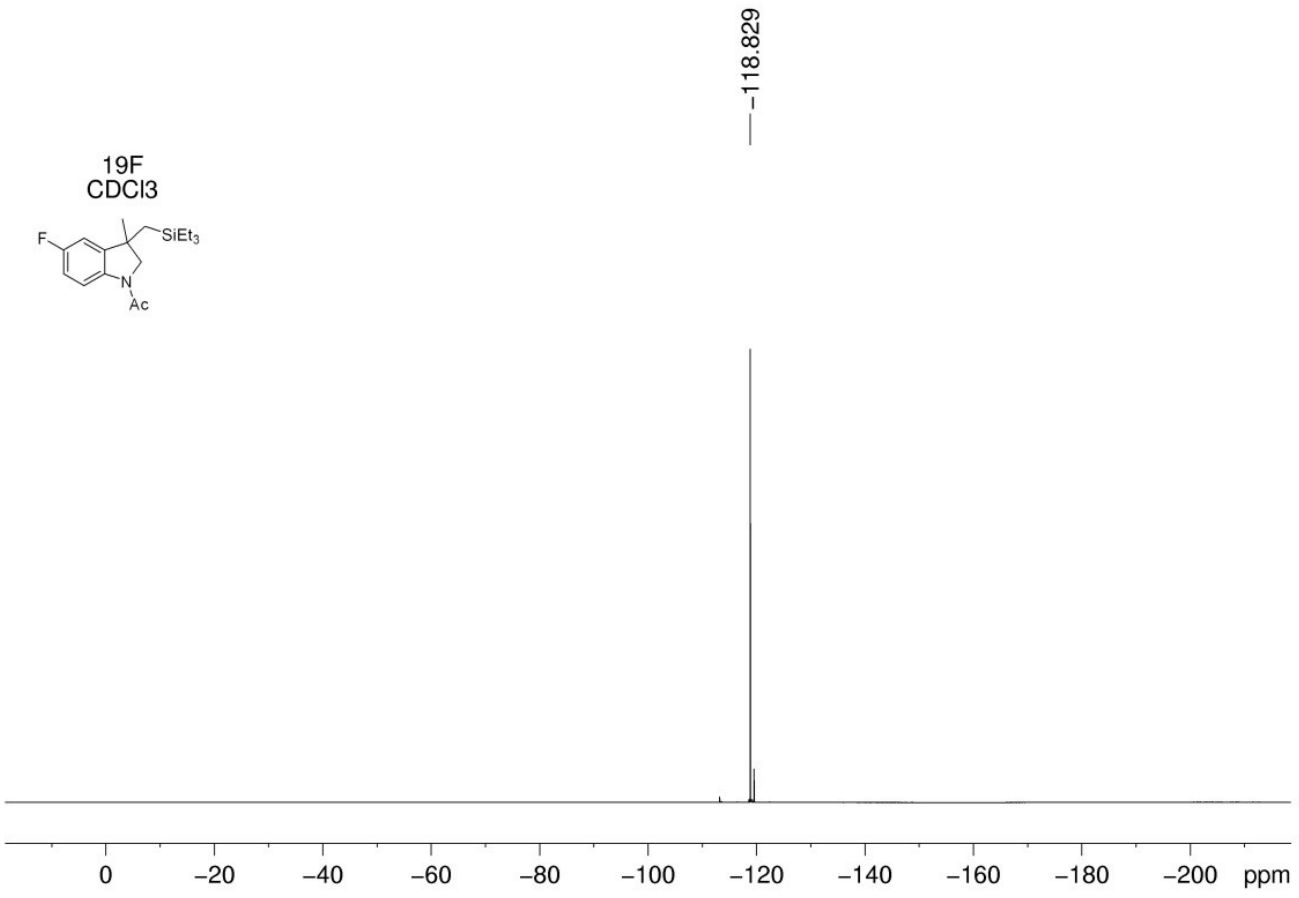


Figure S32. ^{19}F NMR (376 MHz, CDCl 3) of compound 3ma

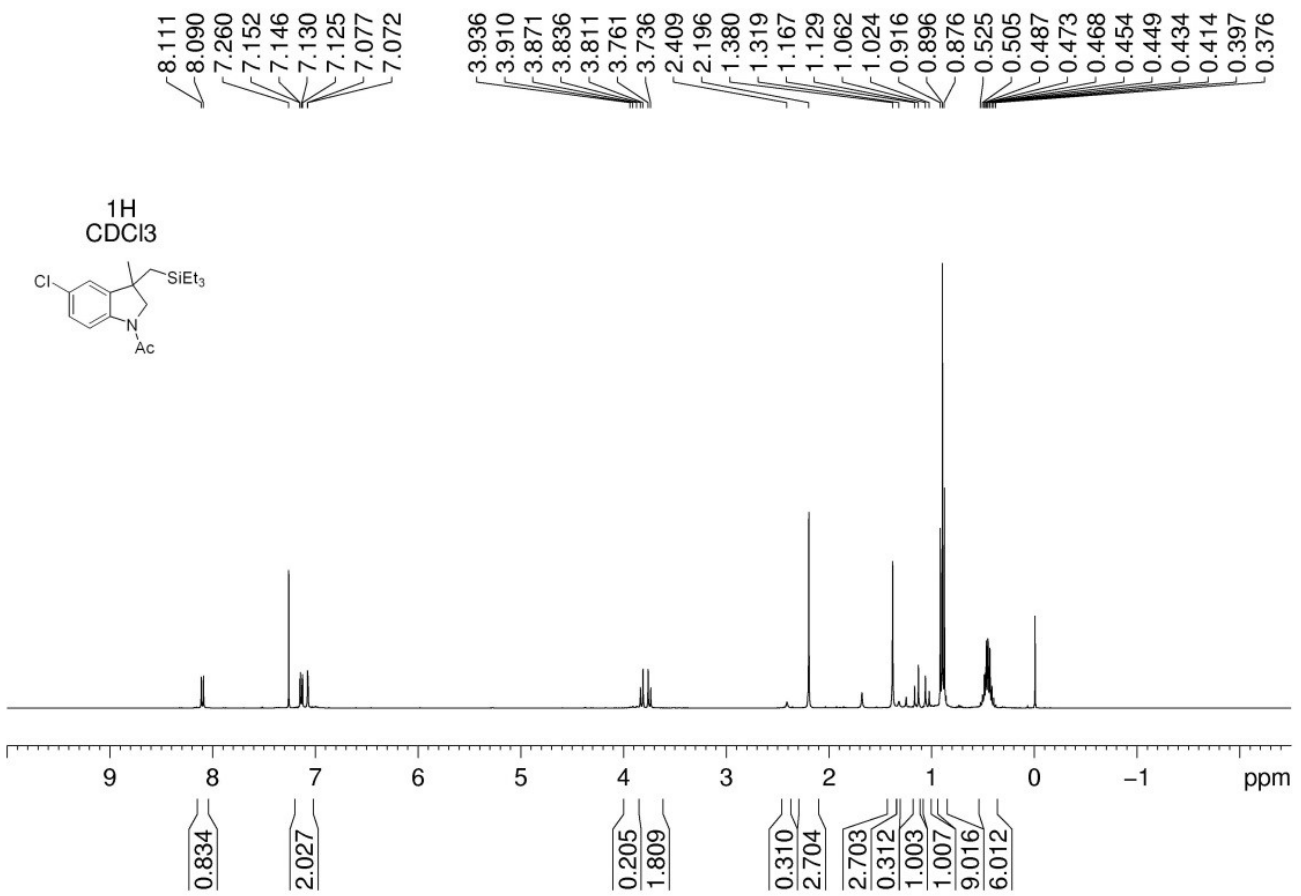


Figure S33. ^{1}H NMR (400 MHz, $CDCl_3$) of compound 3na

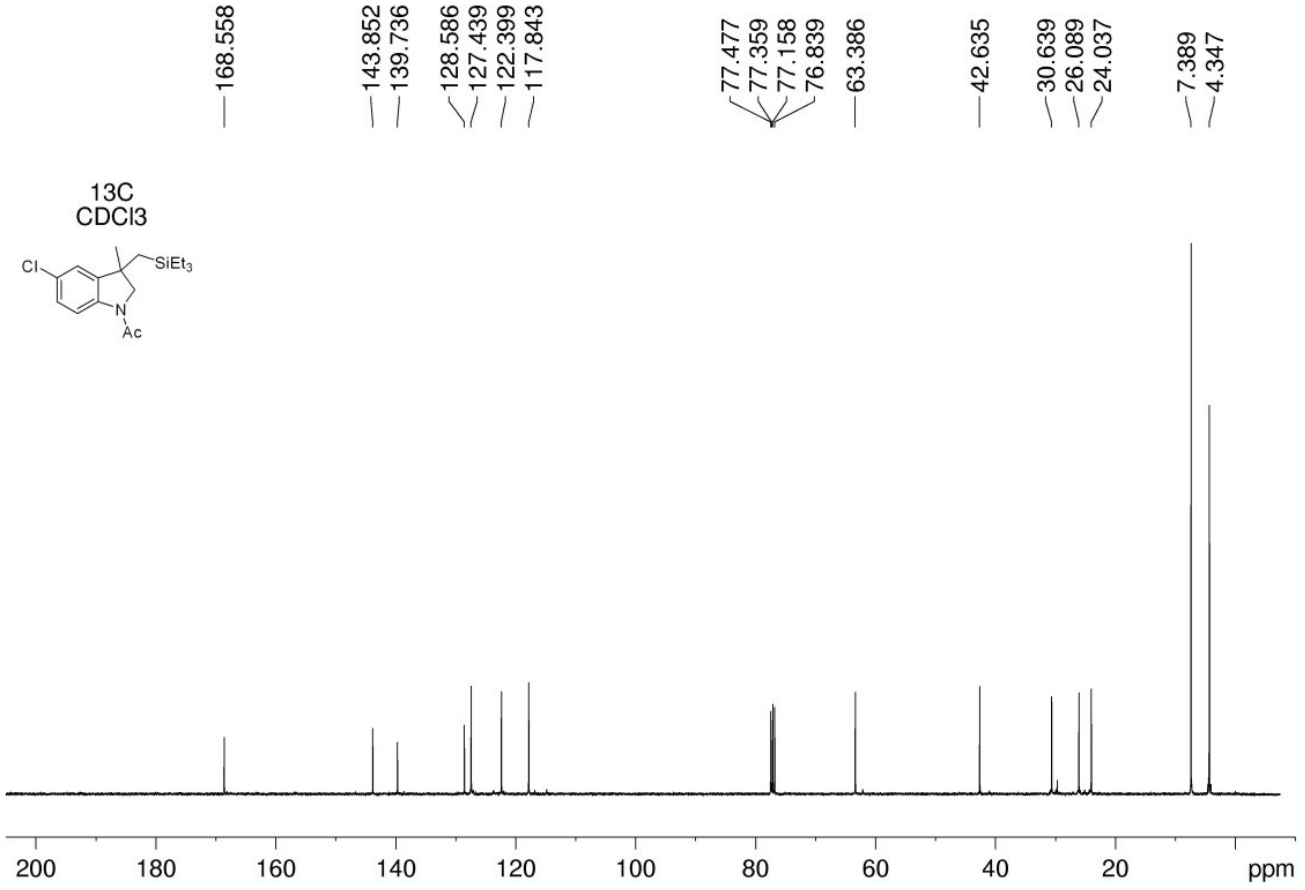


Figure S34. ^{13}C NMR (100 MHz, $CDCl_3$) of compound 3na

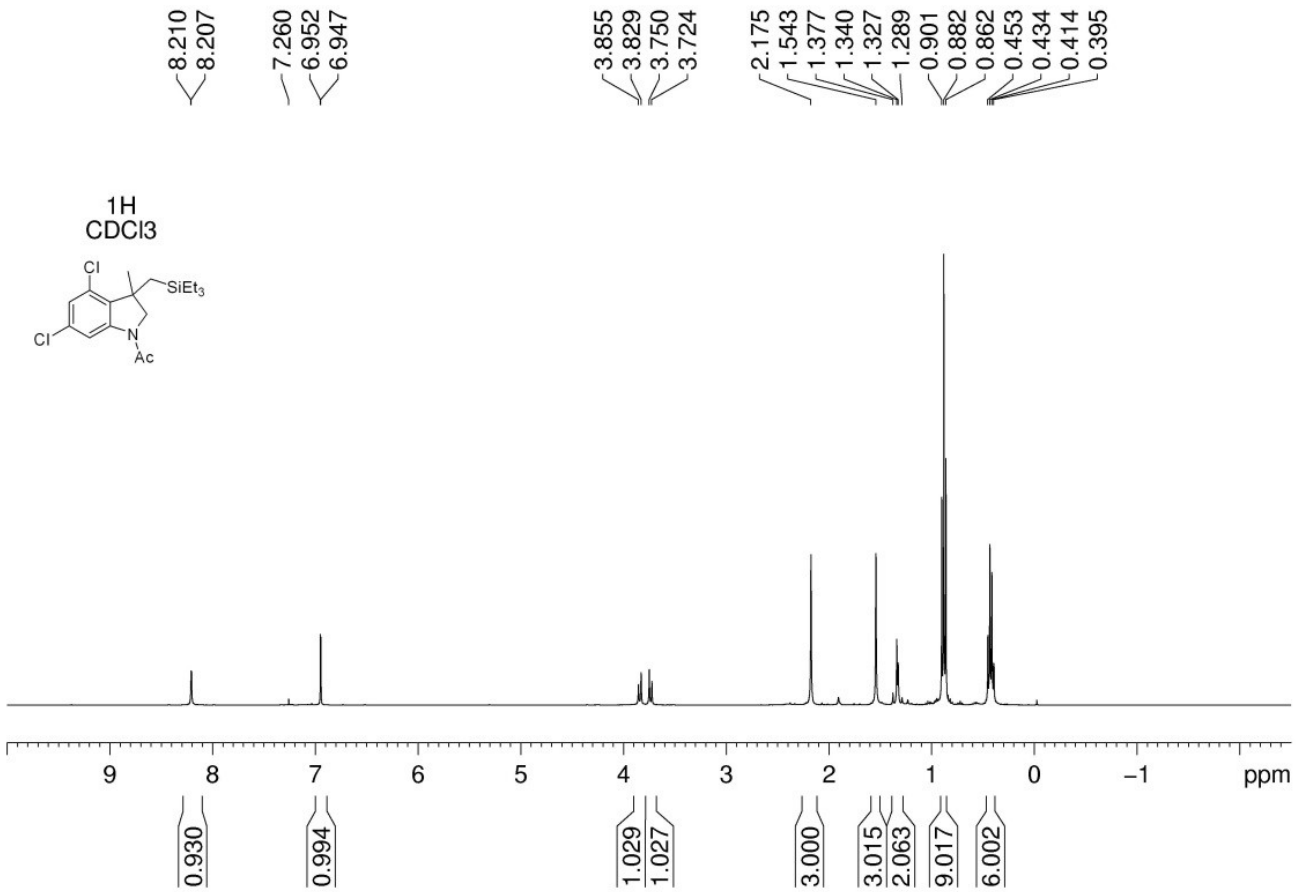


Figure S35. ^{1}H NMR (400 MHz, $CDCl_3$) of compound 3pa

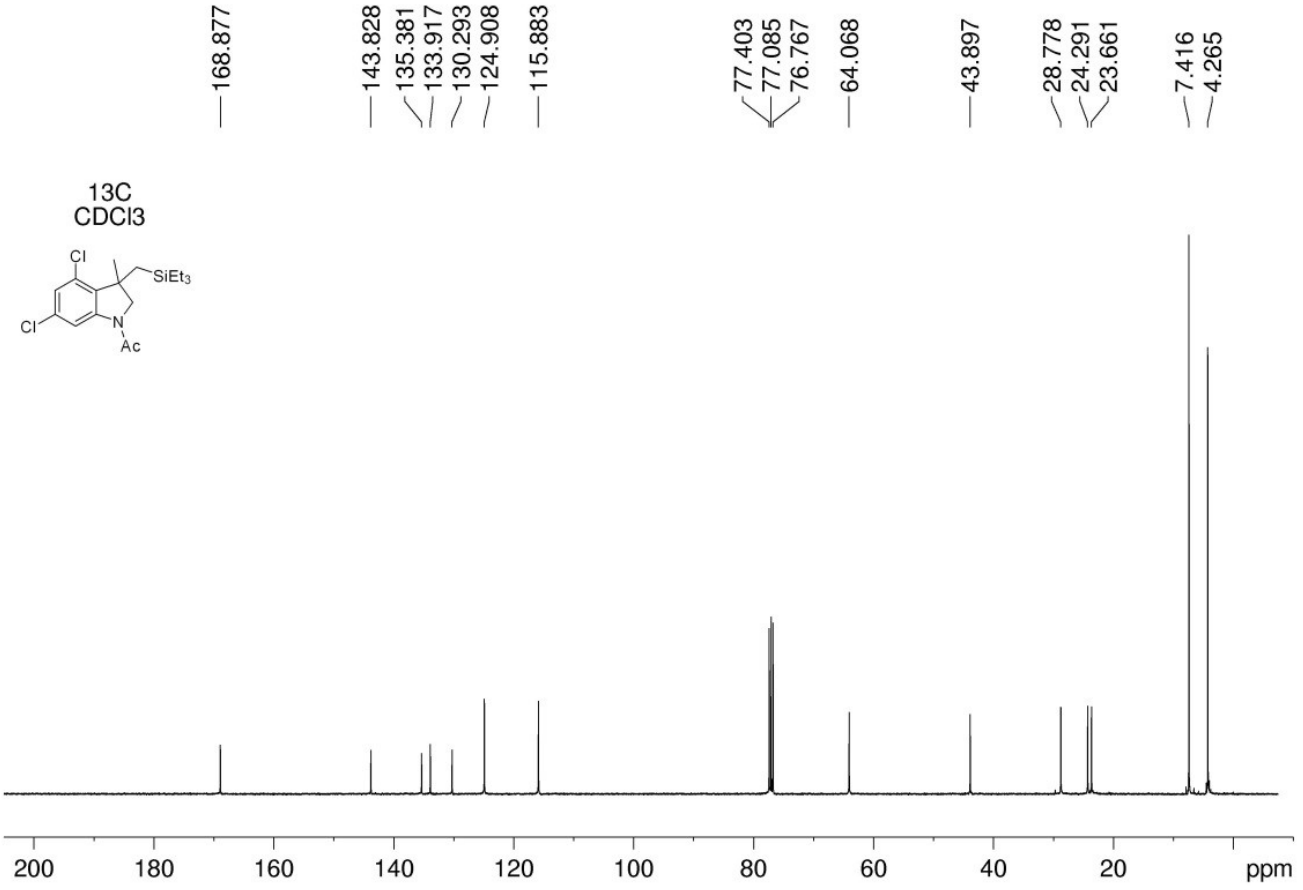


Figure S36. ^{13}C NMR (100 MHz, $CDCl_3$) of compound 3ba

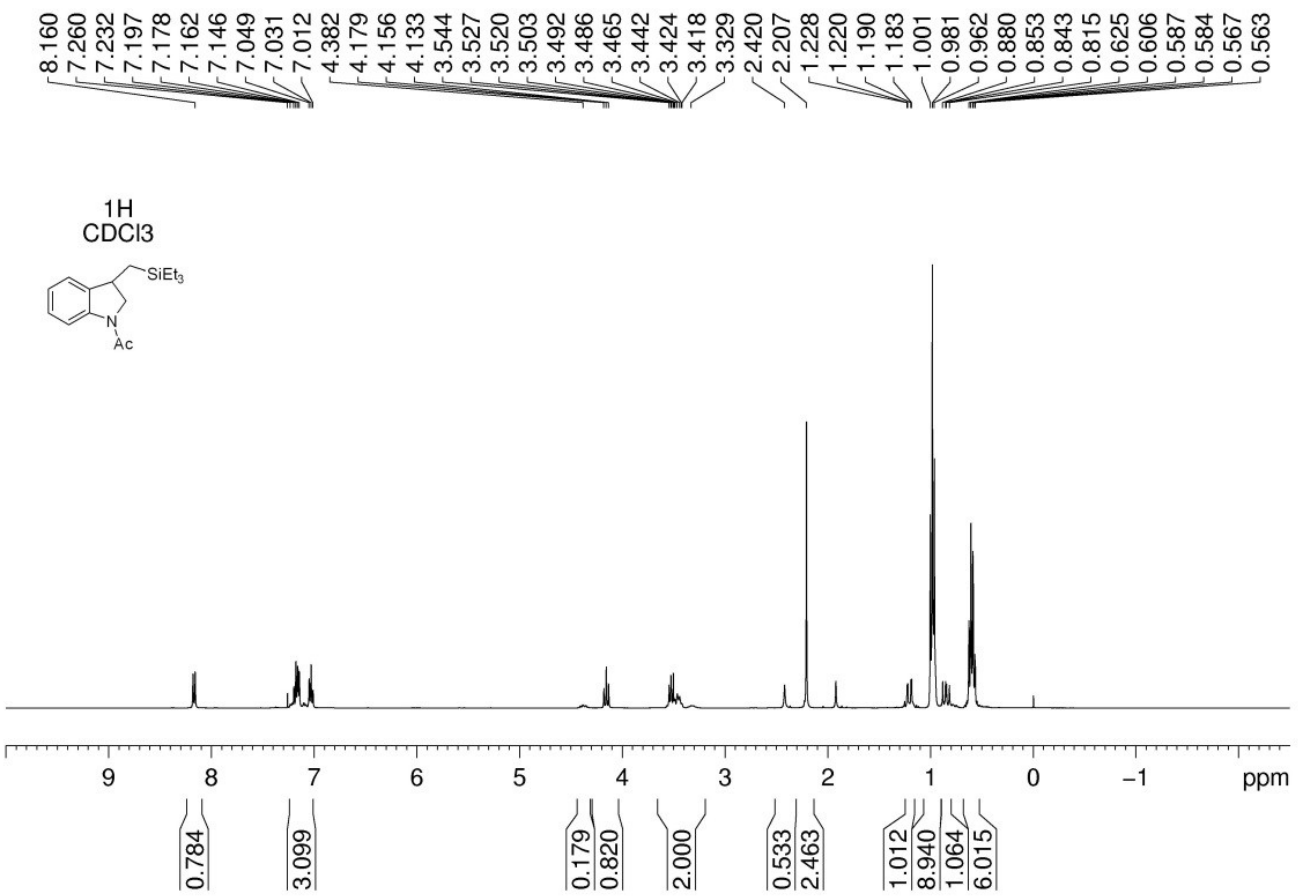


Figure S37. ^{1}H NMR (400 MHz, $CDCl_3$) of compound 3qa

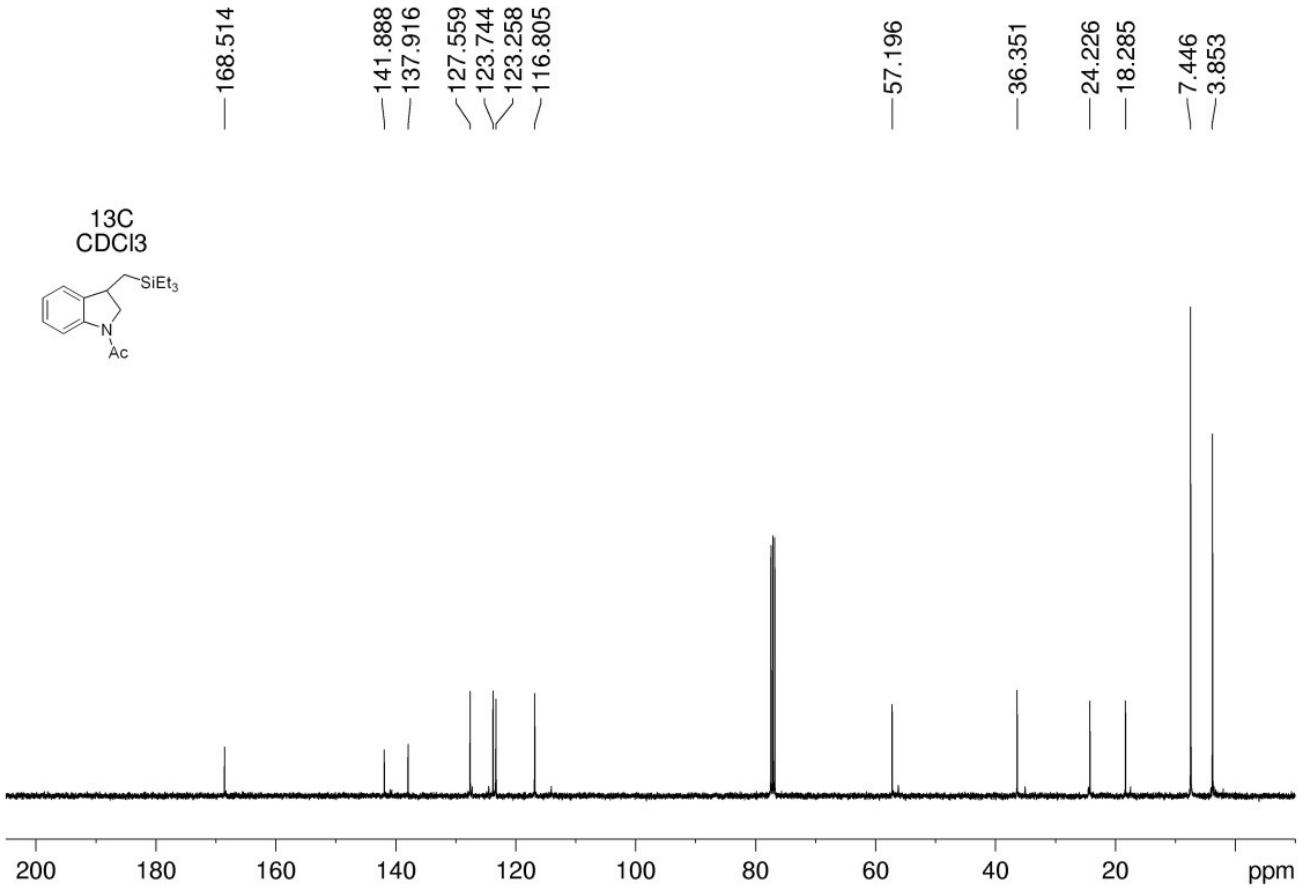


Figure S38. ^{13}C NMR (100 MHz, $CDCl_3$) of compound 3qa

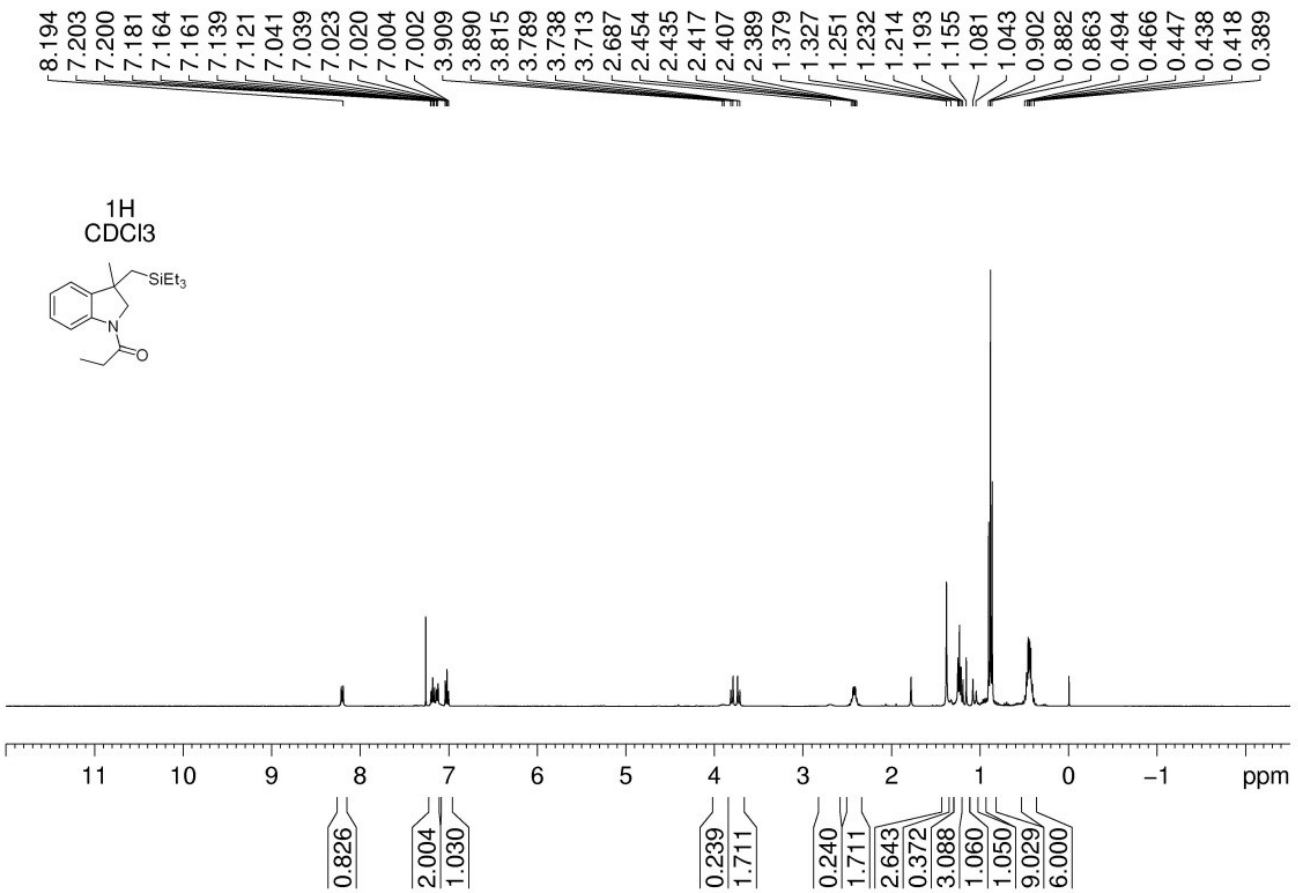


Figure S39. ^{1}H NMR (400 MHz, $CDCl_3$) of compound 3ra

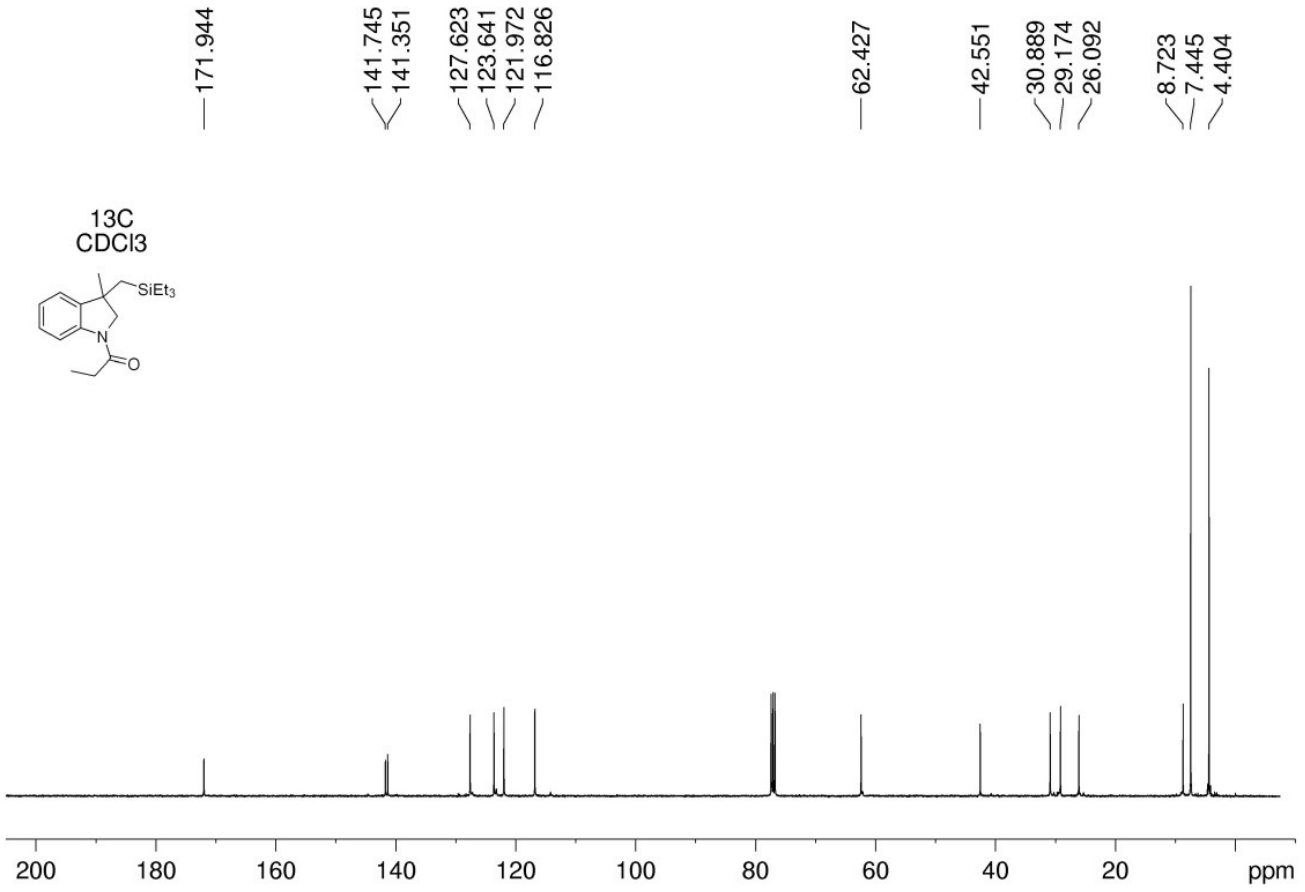


Figure S40. ^{13}C NMR (100 MHz, $CDCl_3$) of compound 3ra

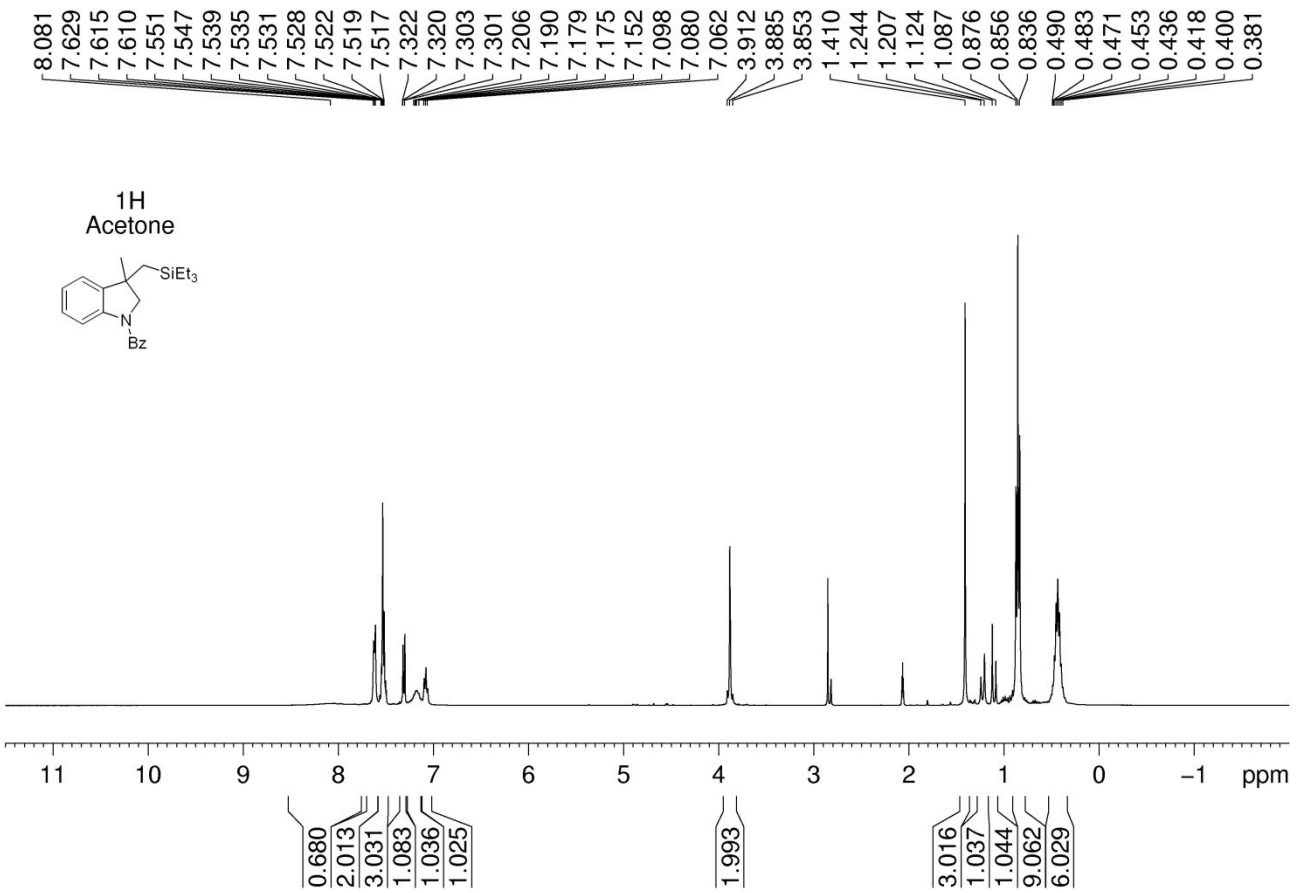


Figure S41. ^{1}H NMR (400 MHz, $CDCl_3$) of compound 3sa

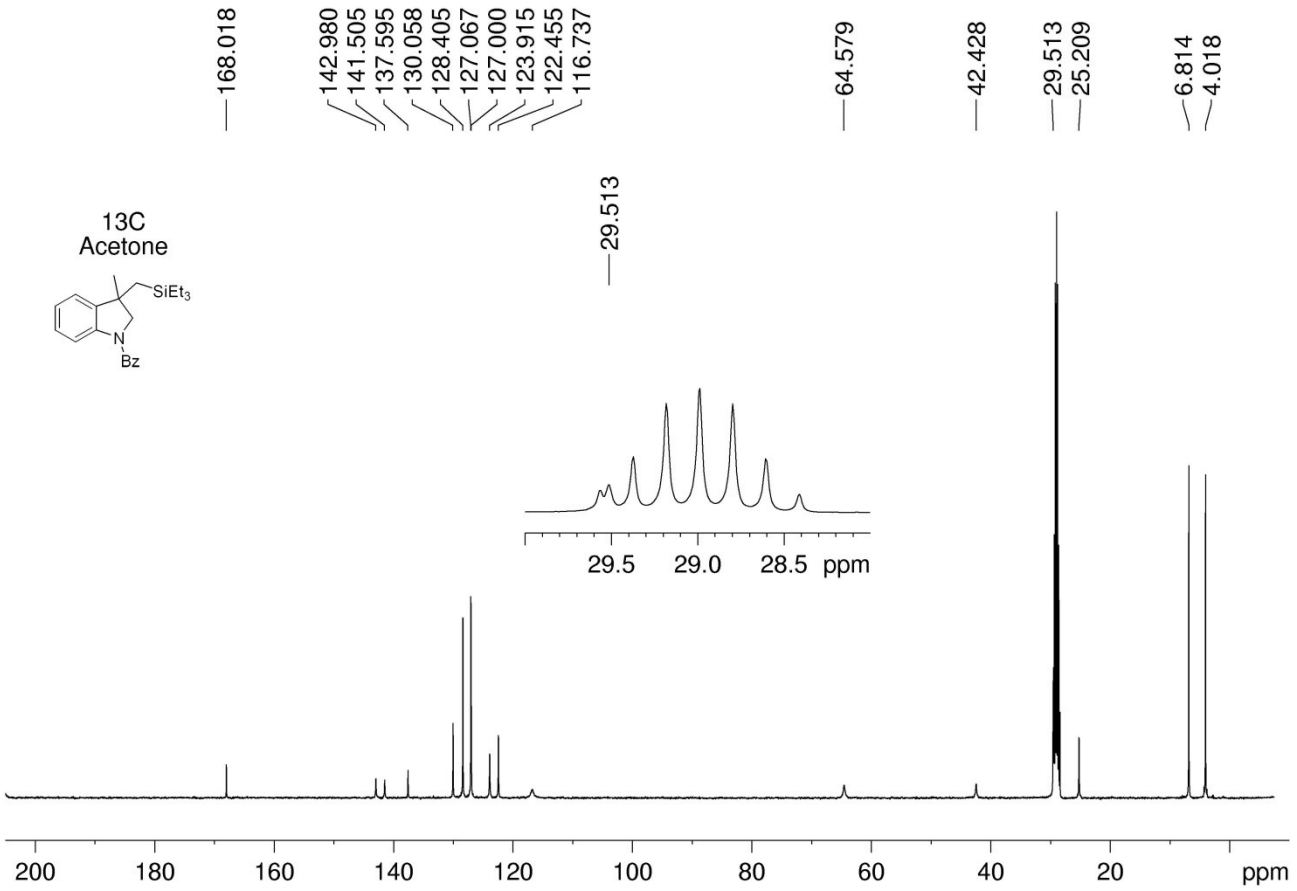


Figure S42. ^{13}C NMR (100 MHz, $CDCl_3$) of compound 3sa

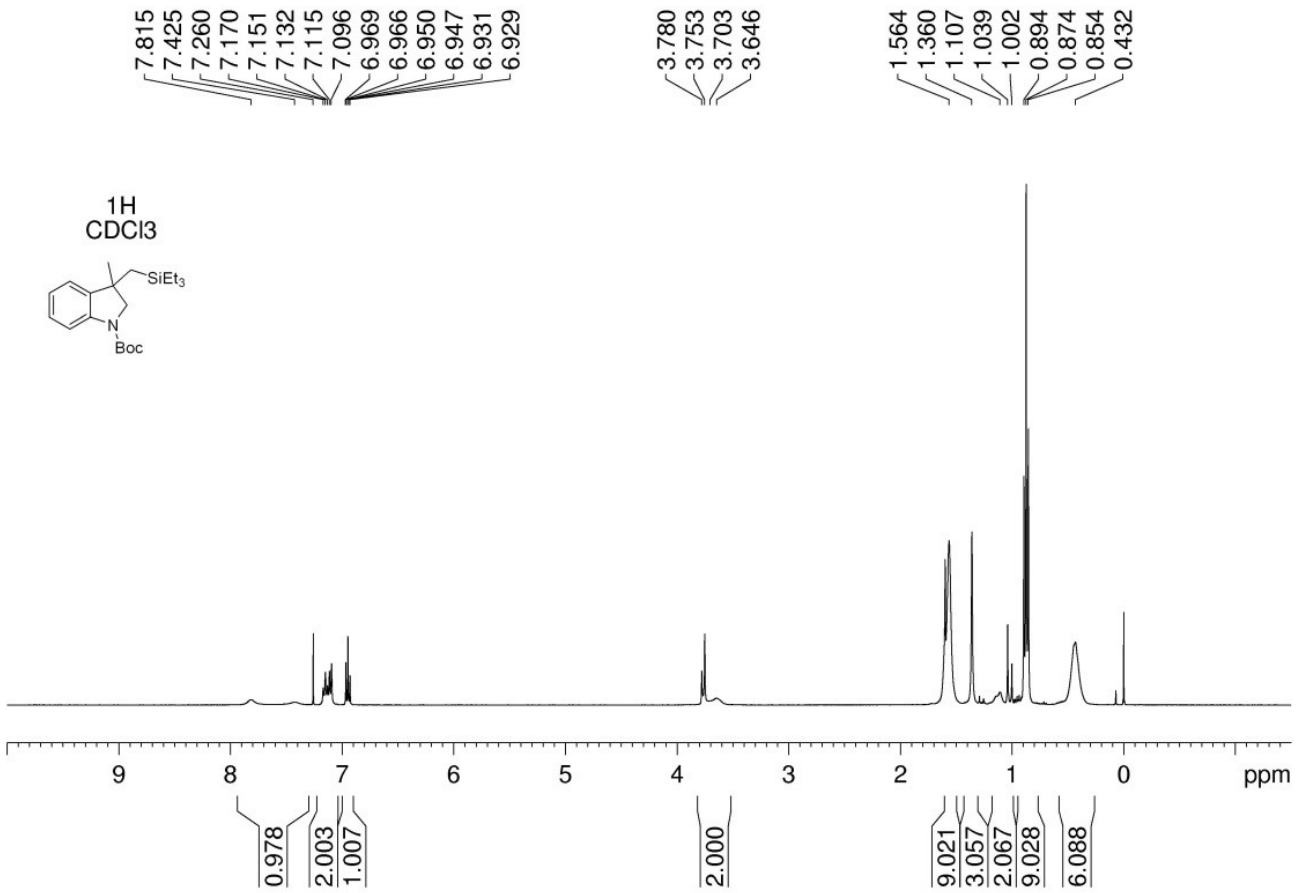


Figure S43. ^{1}H NMR (400 MHz, $CDCl_3$) of compound 3ta

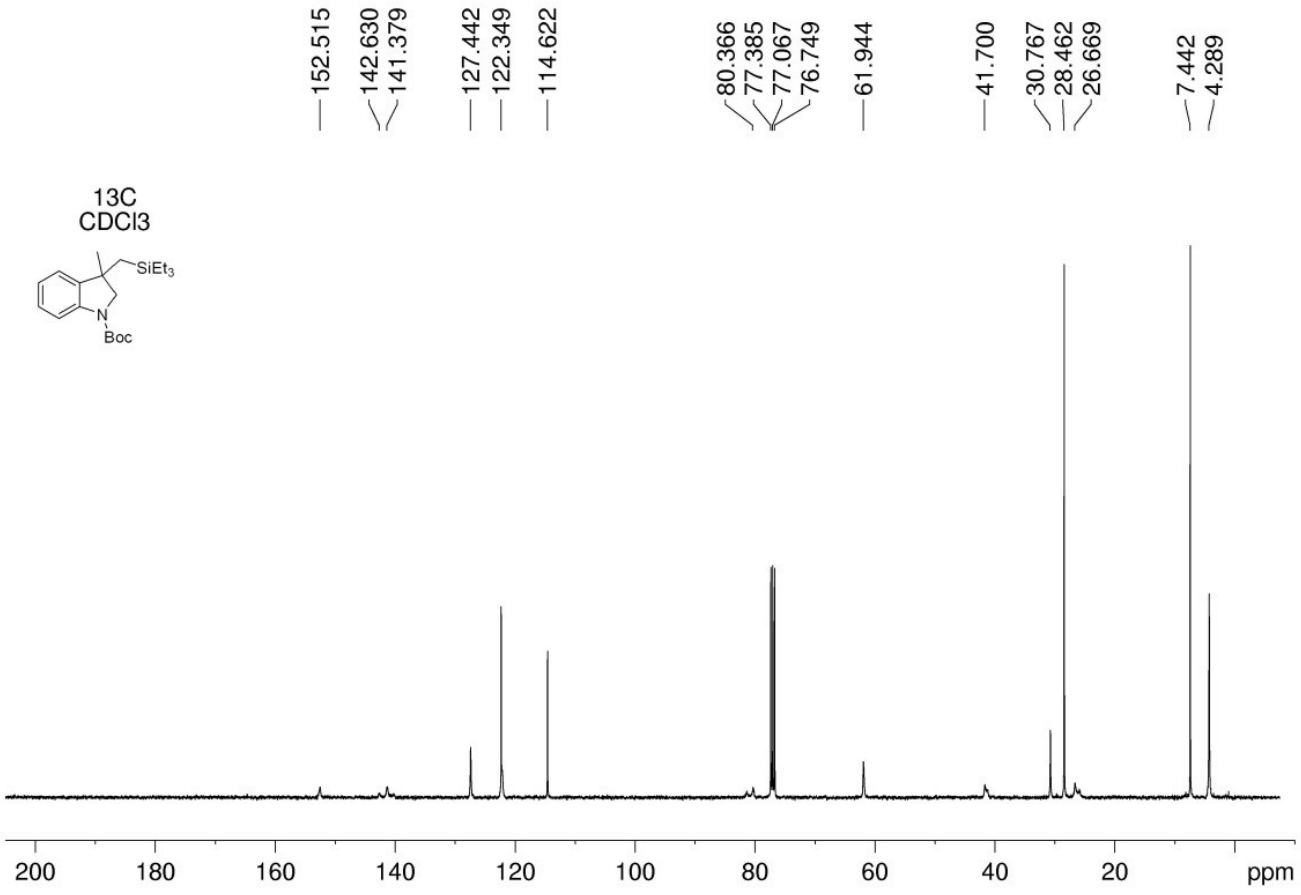


Figure S44. ^{13}C NMR (100 MHz, $CDCl_3$) of compound 3ta

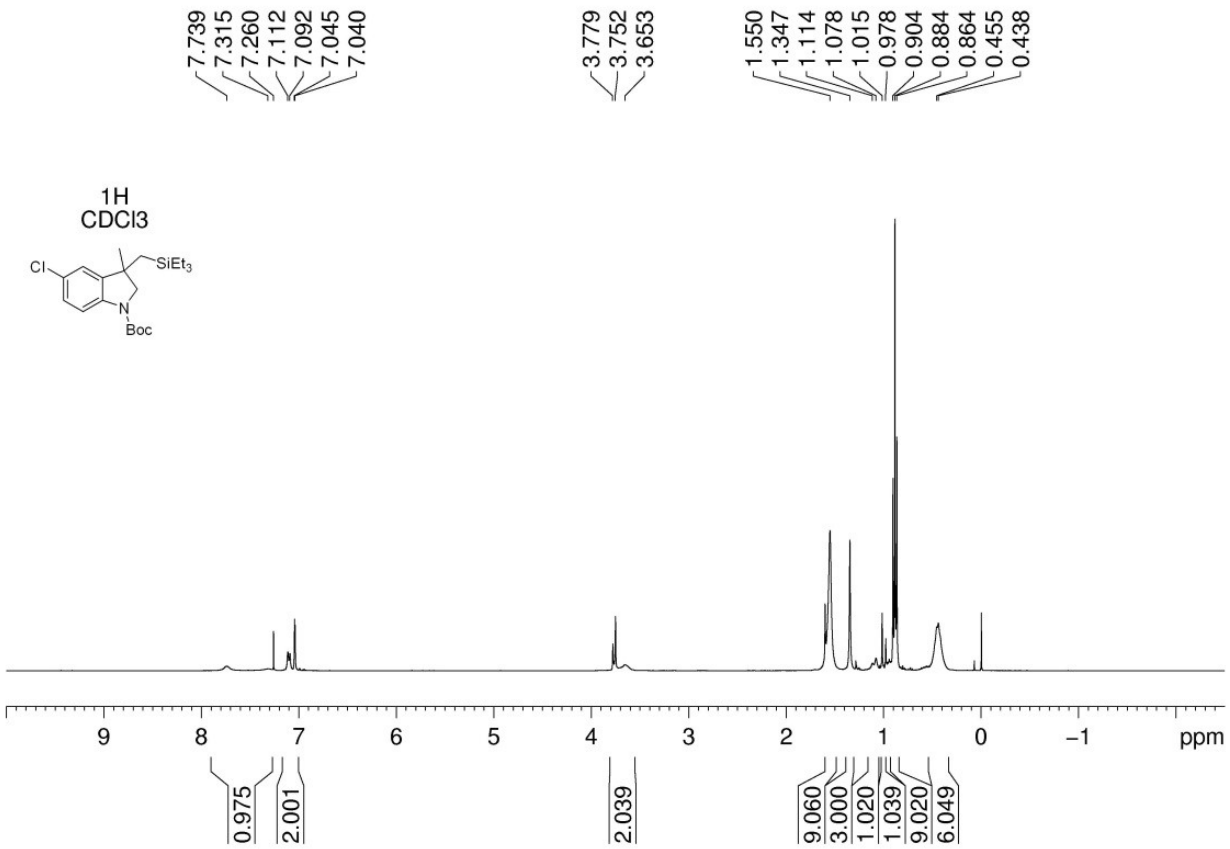


Figure S45. ^{1}H NMR (400 MHz, $CDCl_3$) of compound 3ua

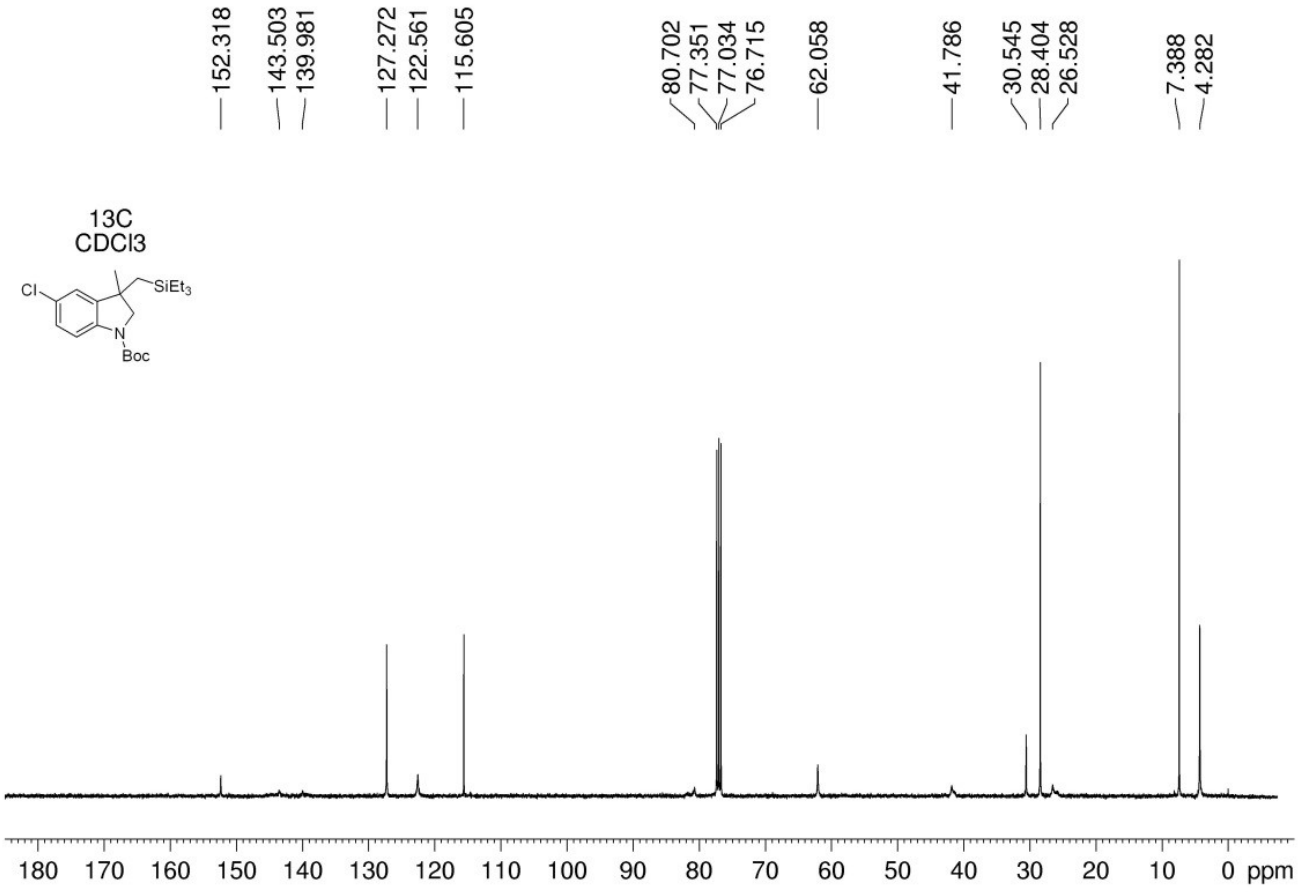


Figure S46. ^{13}C NMR (100 MHz, $CDCl_3$) of compound 3ua

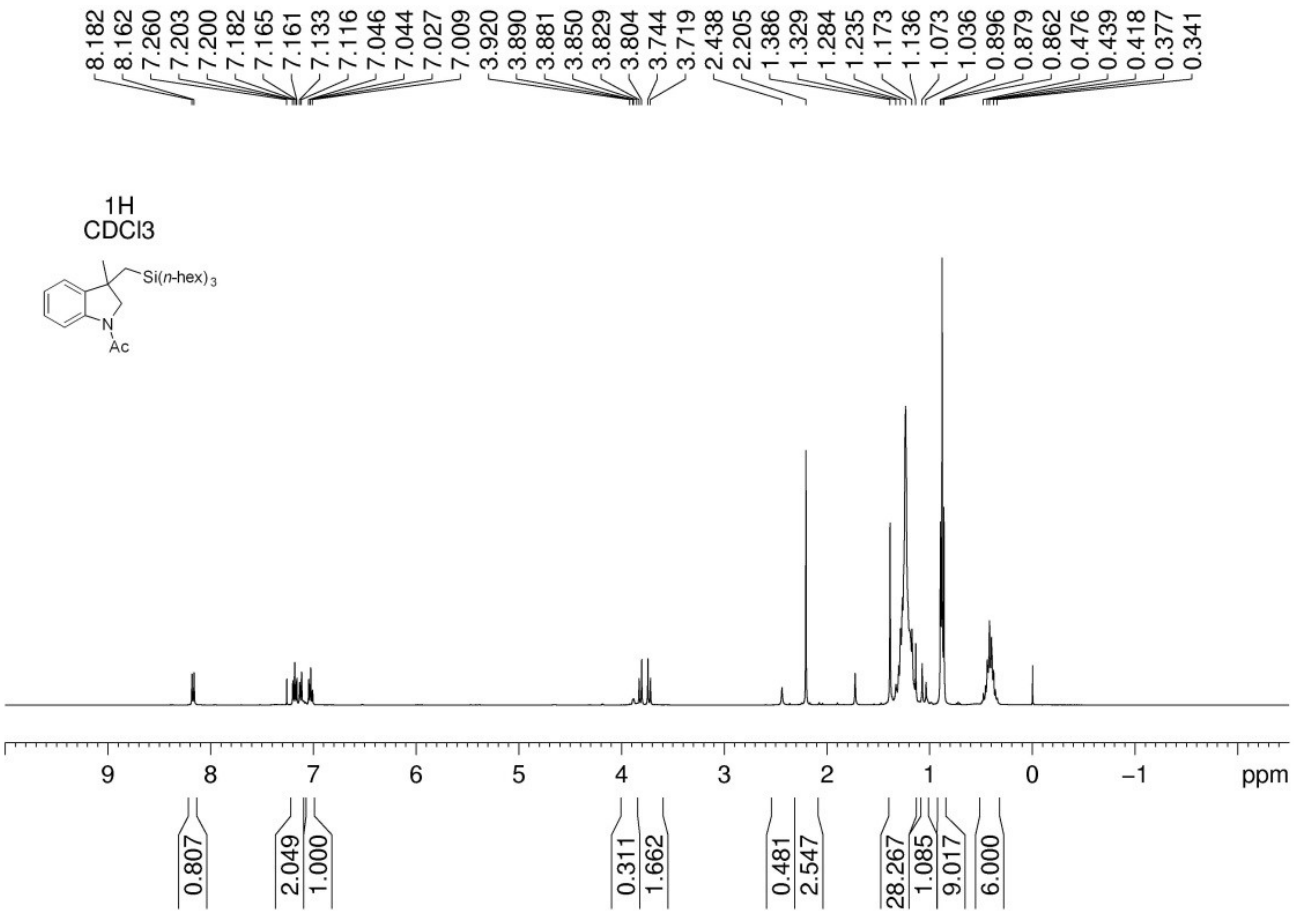


Figure S47. ^{1}H NMR (400 MHz, $CDCl_3$) of compound 3ab

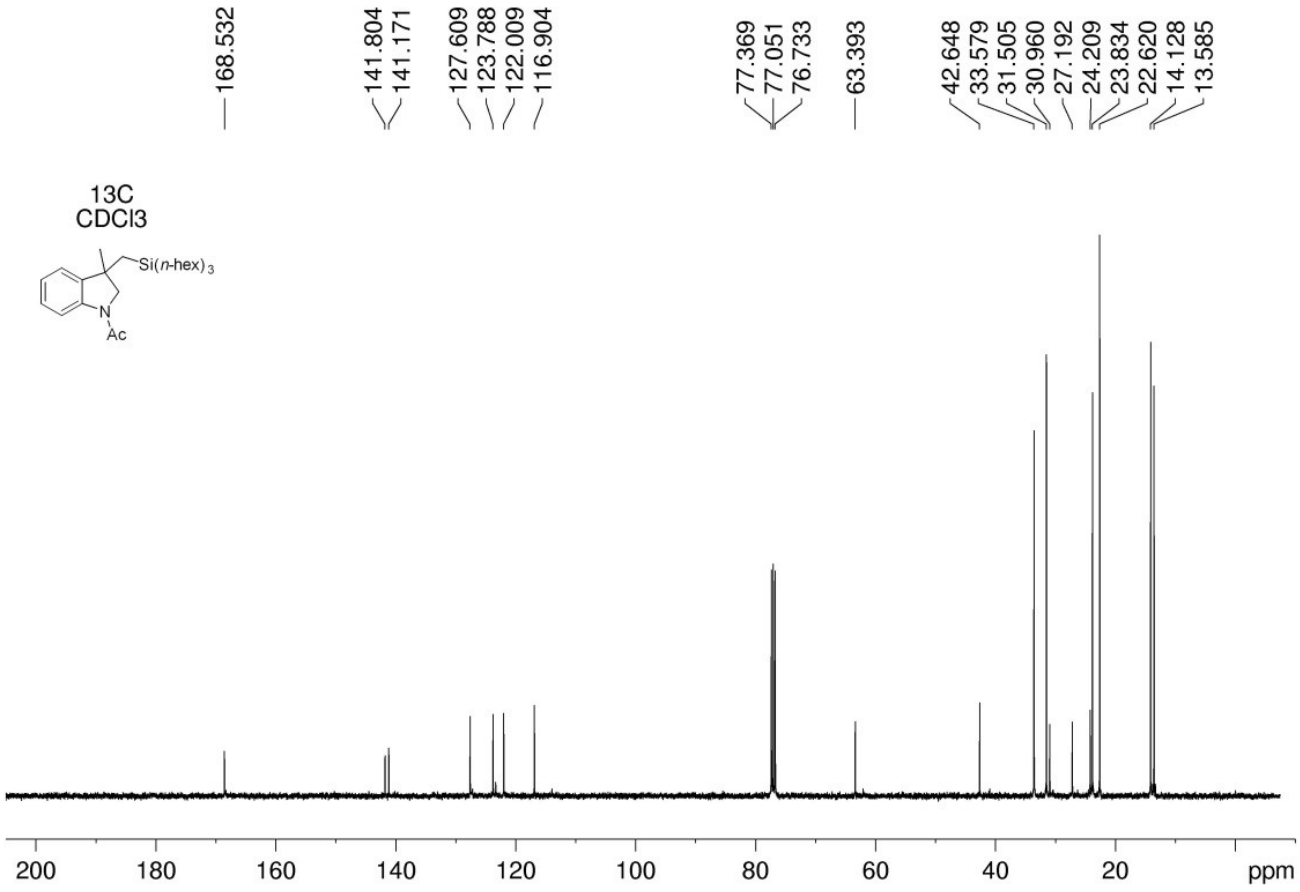


Figure S48. ^{13}C NMR (100 MHz, $CDCl_3$) of compound 3ab

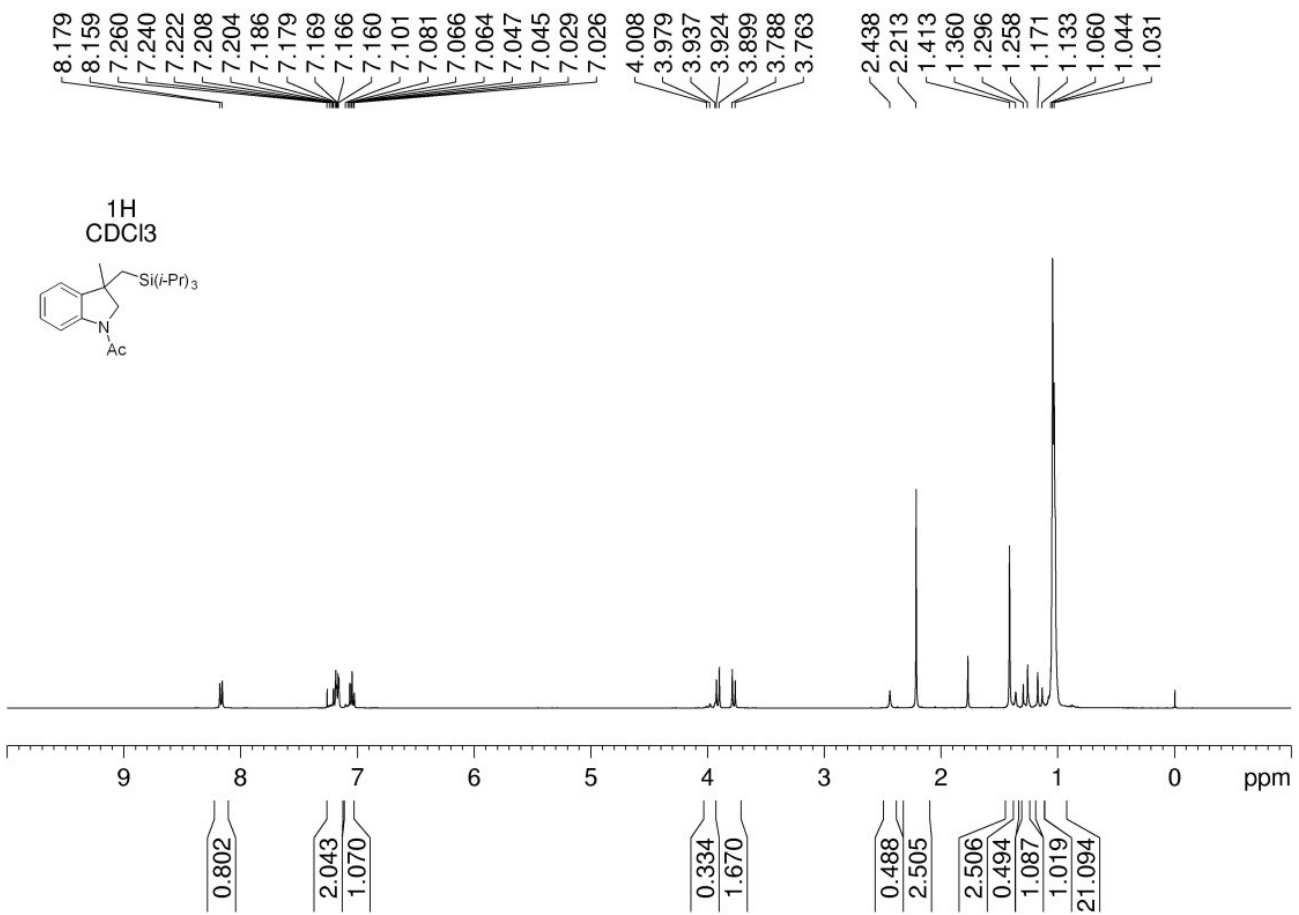


Figure S49. ^{1}H NMR (400 MHz, $CDCl_3$) of compound 3ac

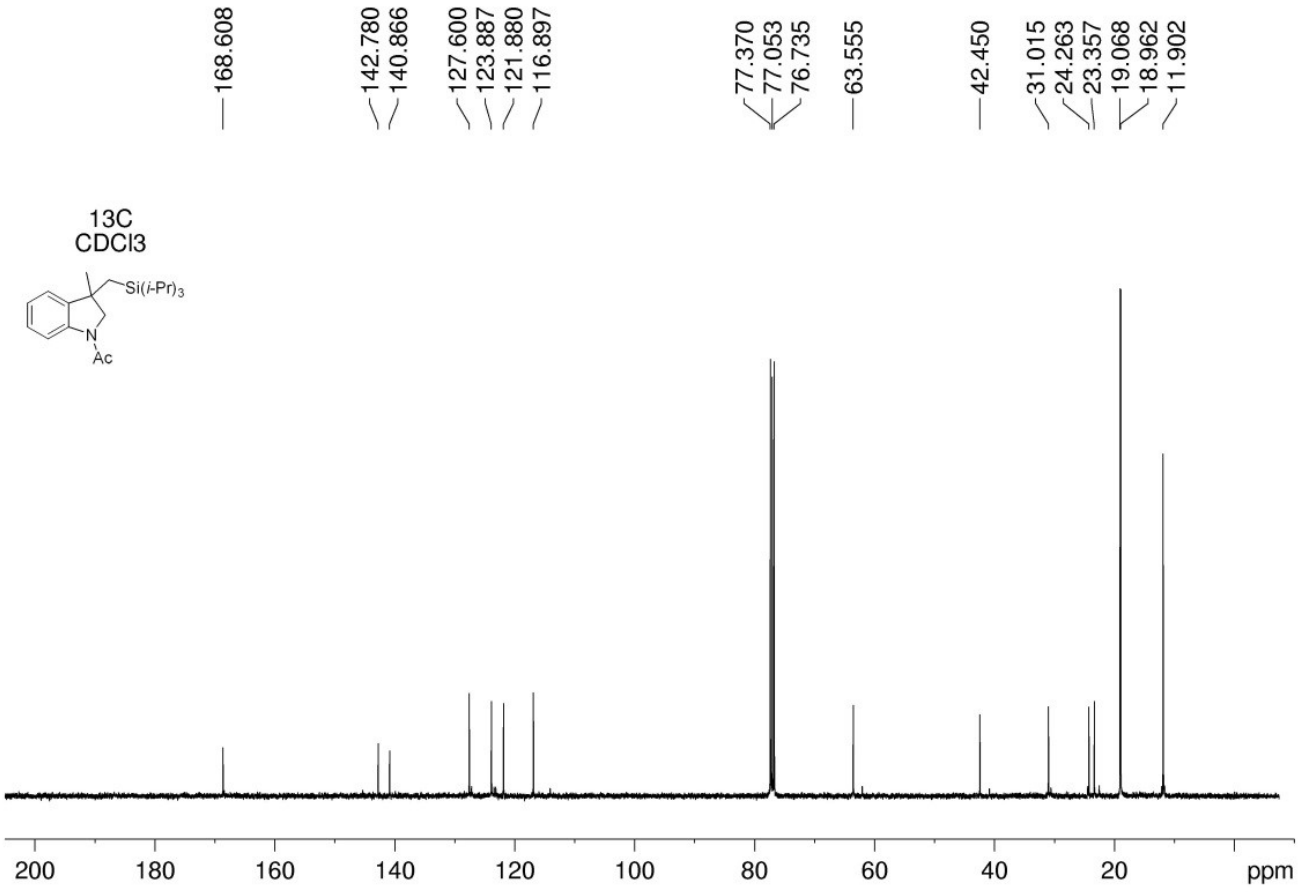


Figure S50. ^{13}C NMR (100 MHz, $CDCl_3$) of compound 3ac

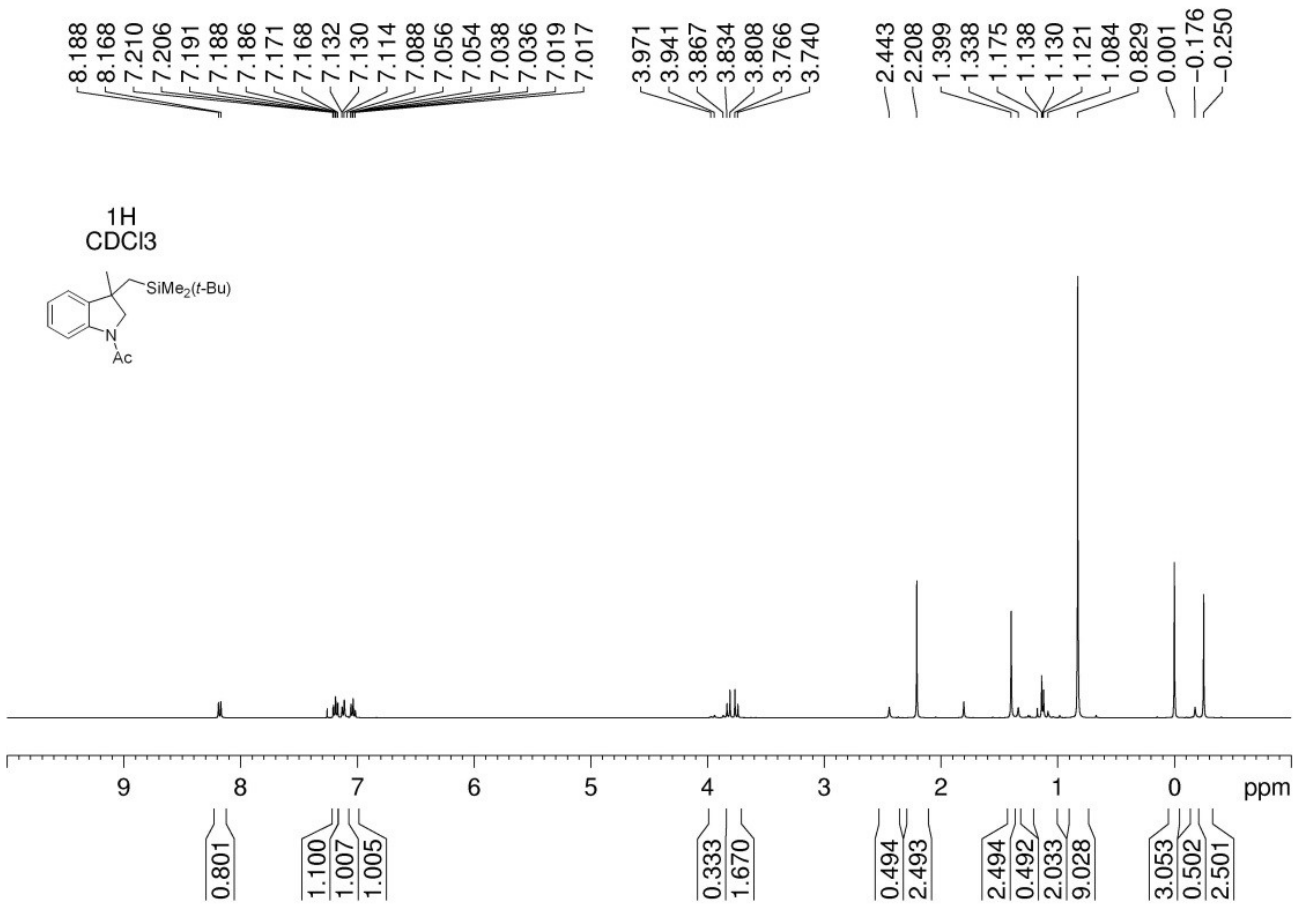


Figure S51. ^{1}H NMR (400 MHz, $CDCl_3$) of compound 3ad

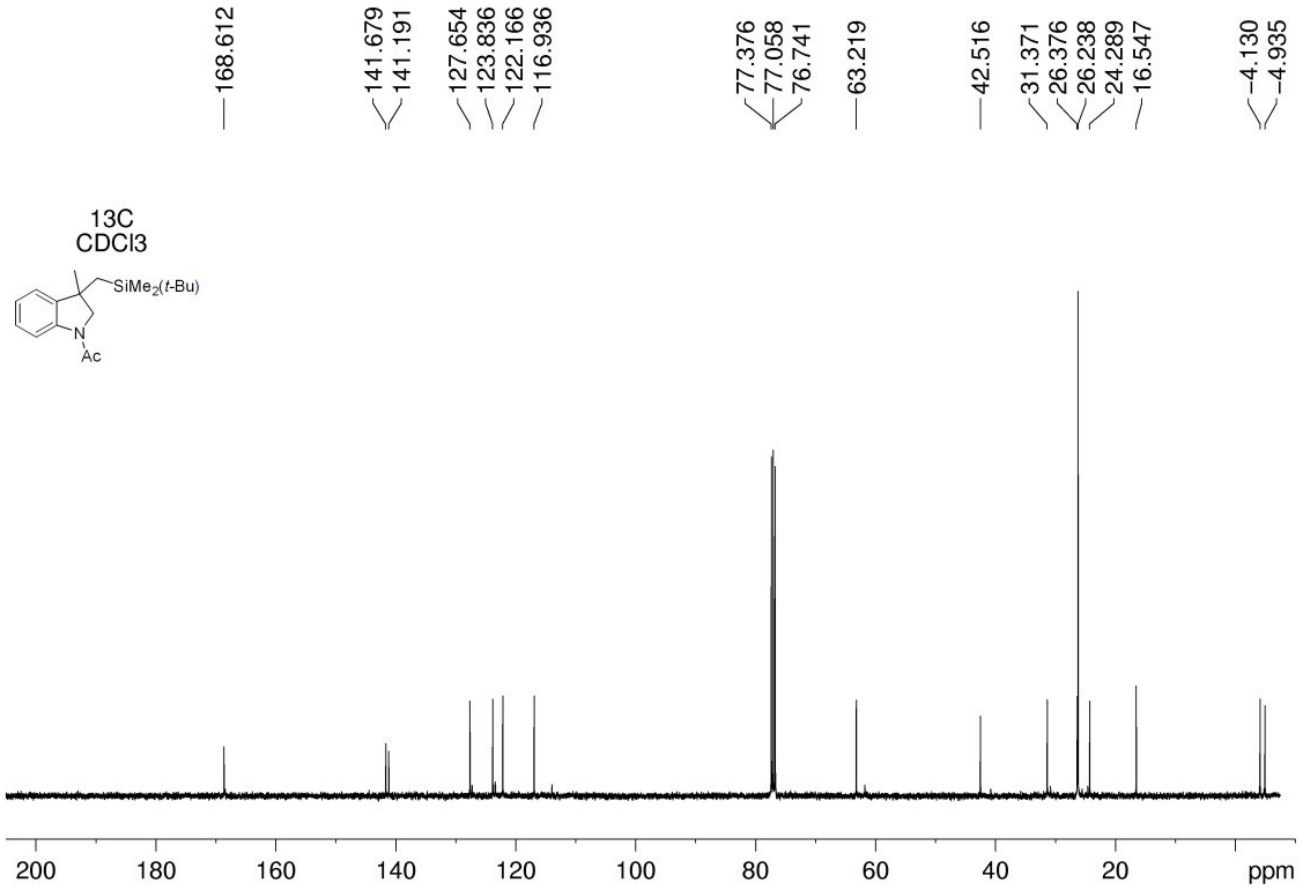


Figure S52. ^{13}C NMR (100 MHz, $CDCl_3$) of compound 3ad

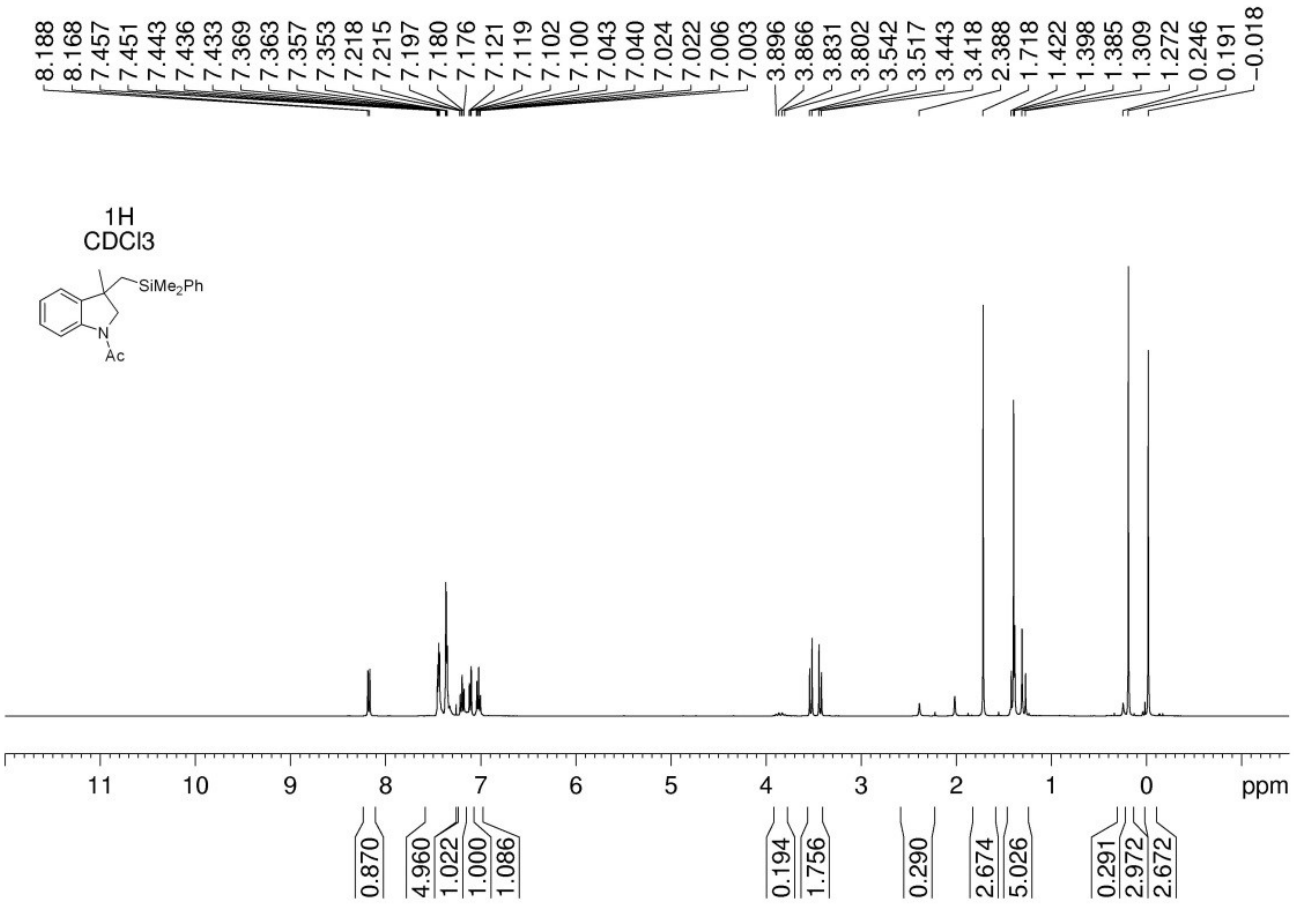


Figure S53. ^{1}H NMR (400 MHz, $CDCl_3$) of compound 3ae

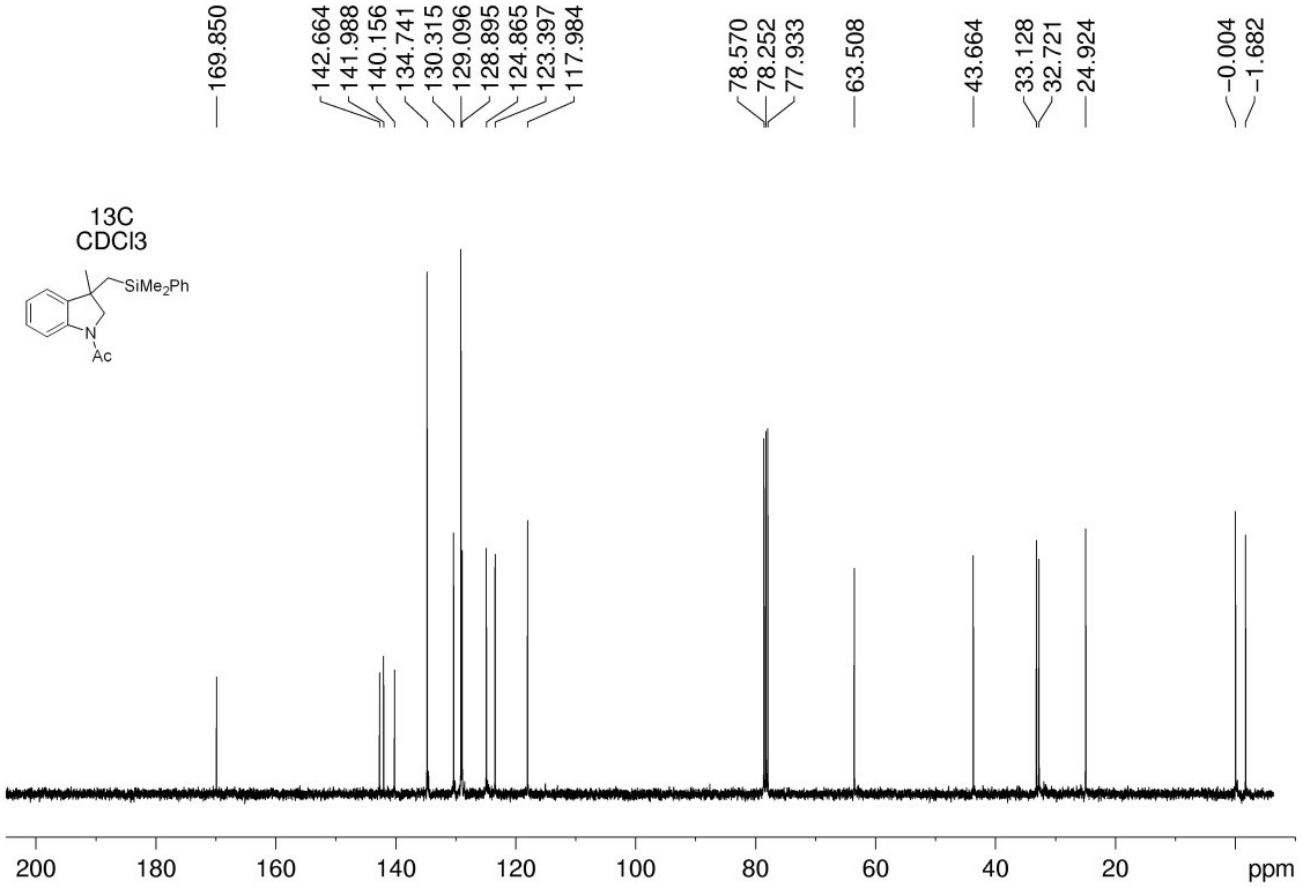


Figure S54. ^{13}C NMR (100 MHz, $CDCl_3$) of compound 3ae

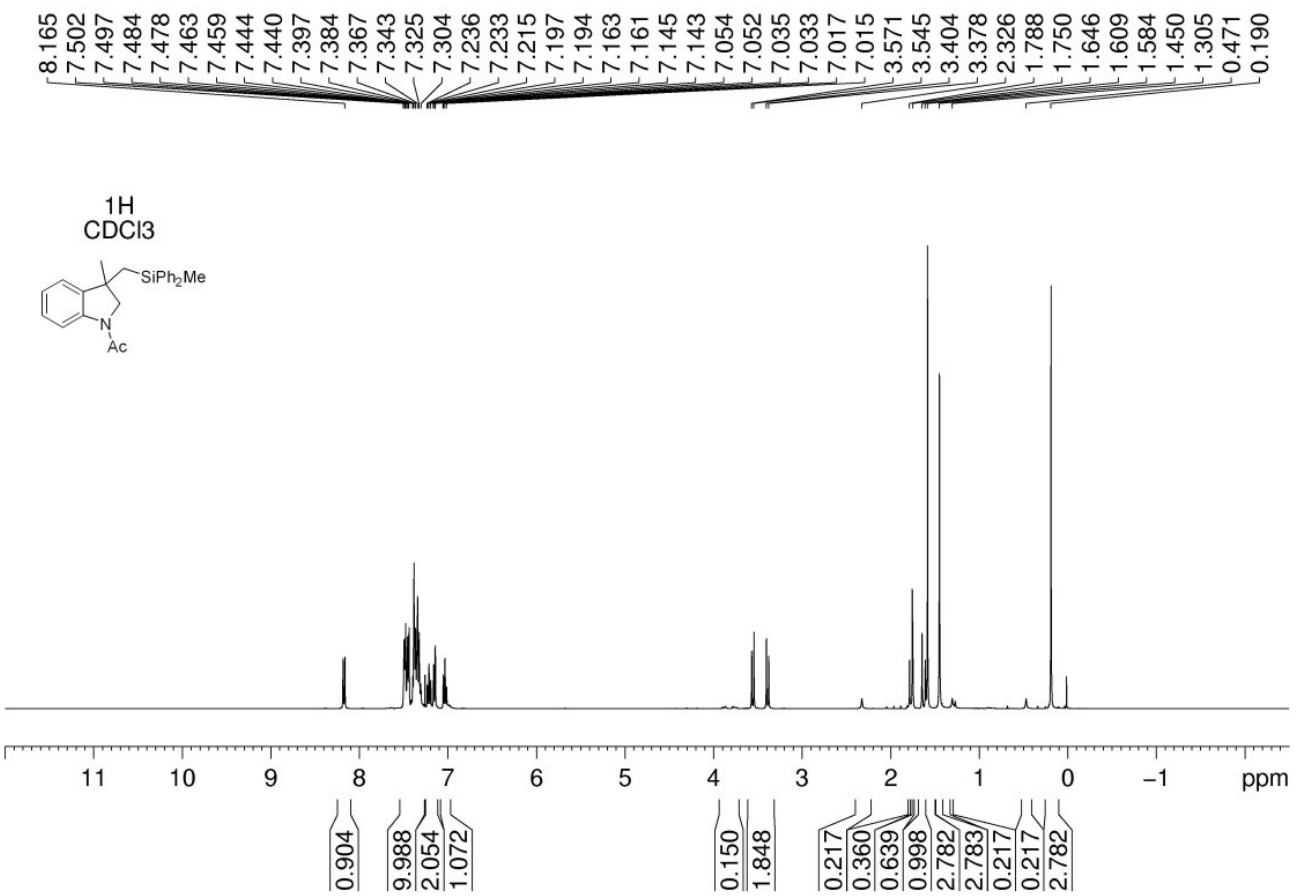


Figure S55. ^{1}H NMR (400 MHz, $CDCl_3$) of compound 3af

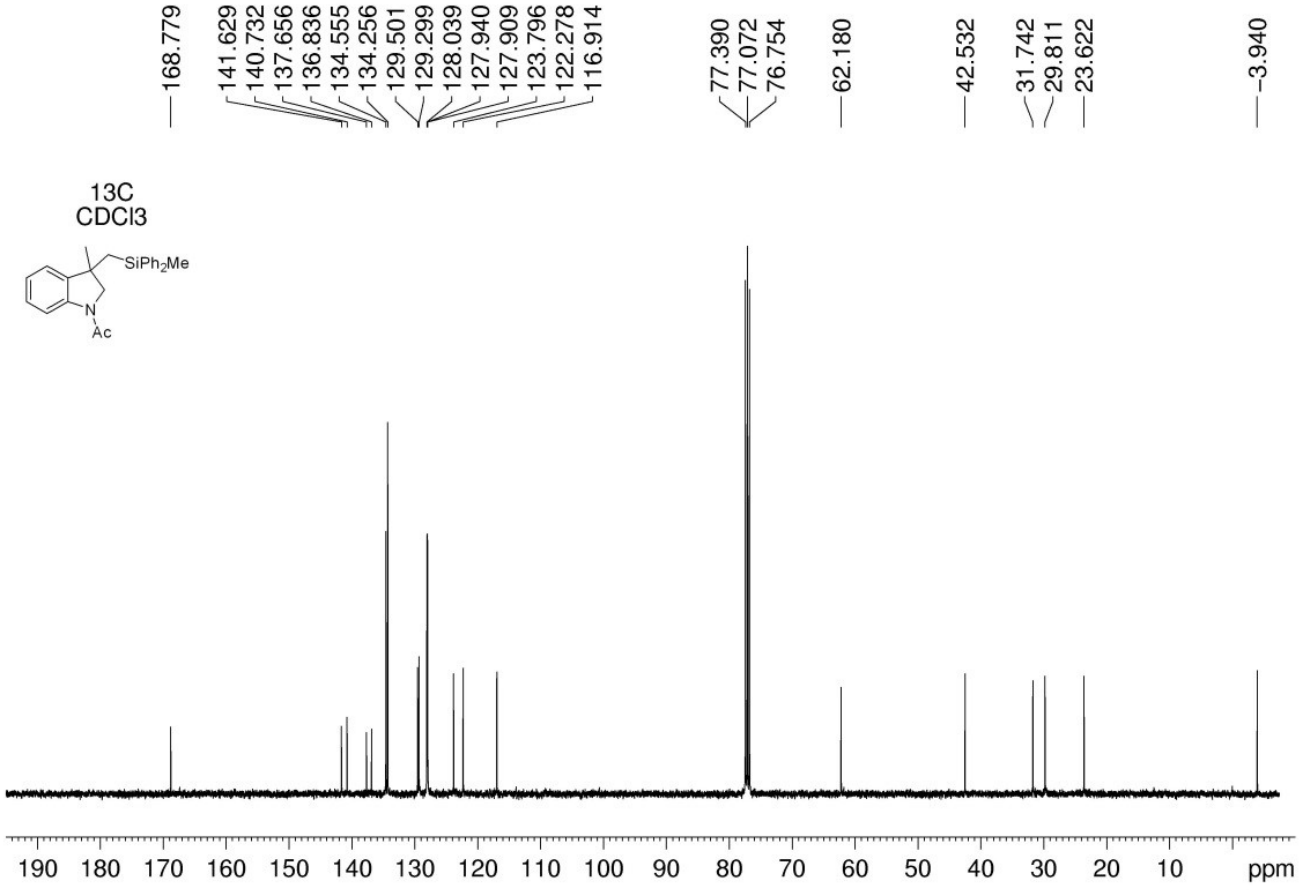


Figure S56. ^{13}C NMR (100 MHz, $CDCl_3$) of compound 3af

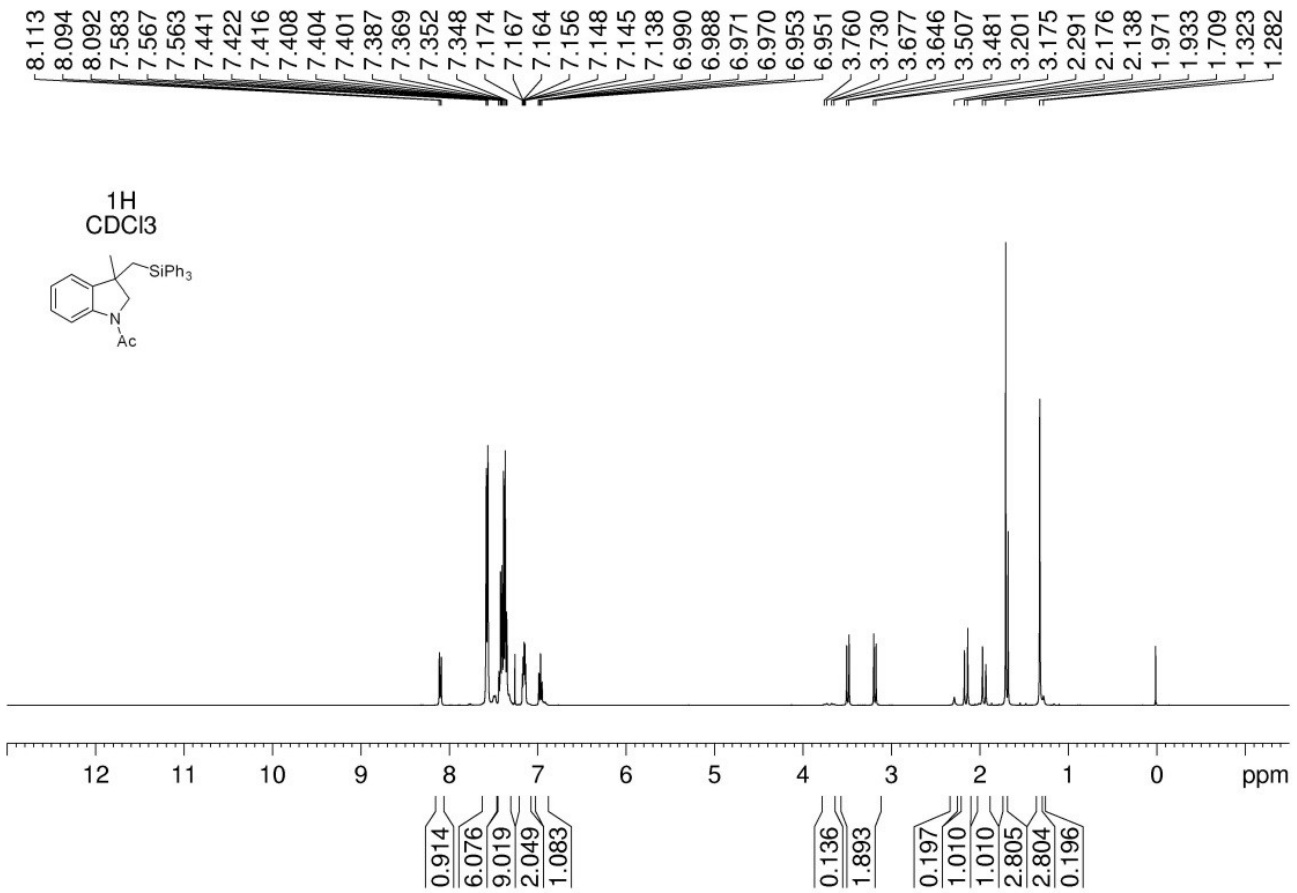


Figure S57. ^{1}H NMR (400 MHz, $CDCl_3$) of compound 3ag

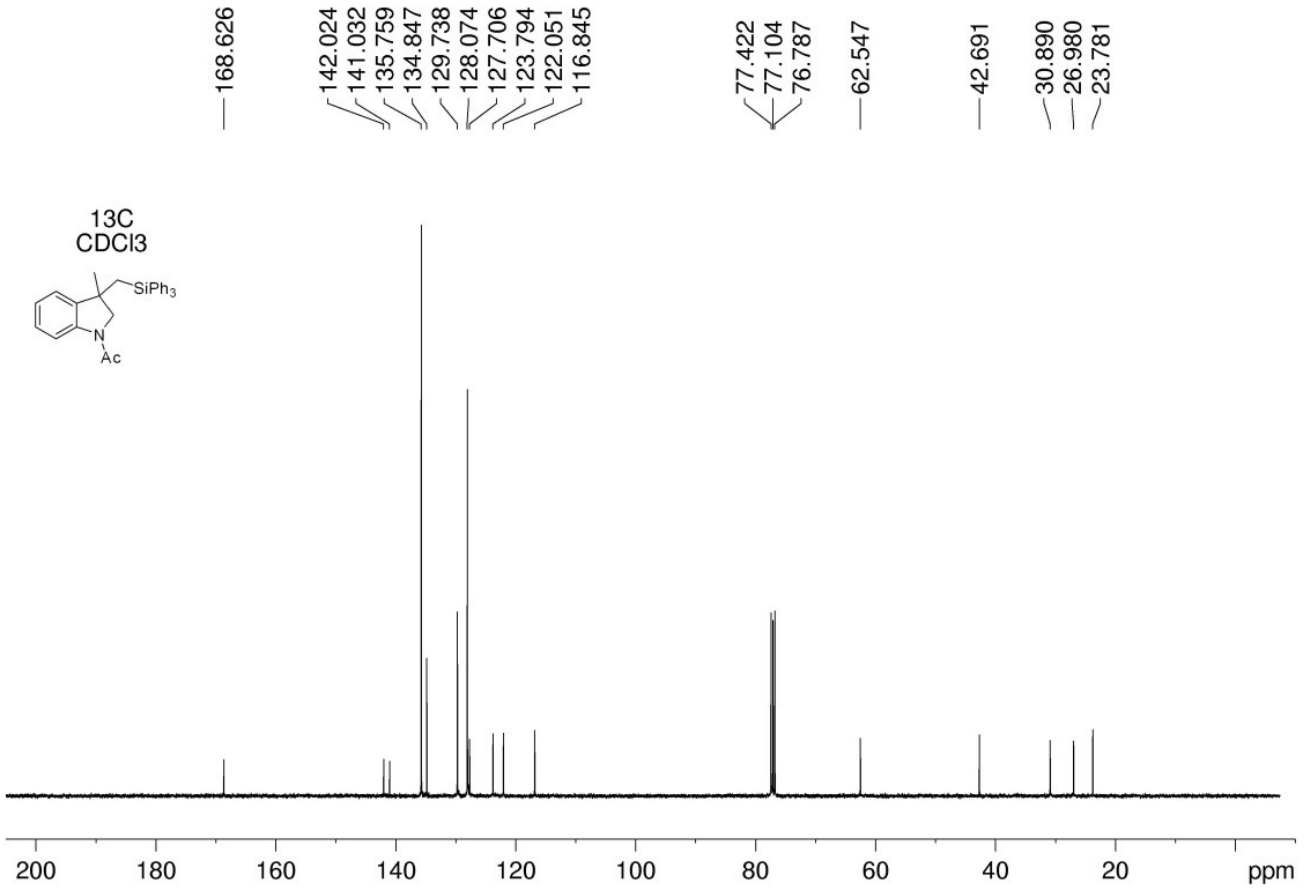


Figure S58. ^{13}C NMR (100 MHz, $CDCl_3$) of compound 3ag