Supporting Information

$Me_3SiSiMe_2(O^nBu)$: A Disilane Reagent for the Synthesis of Diverse Silacycles via Brook- and Retro-Brook-Type Rearrangement

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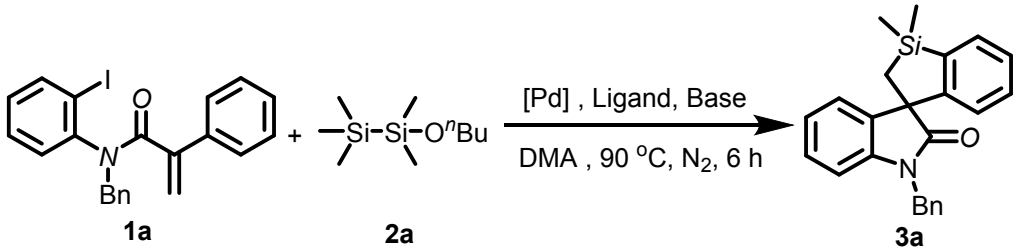
Table of Contenes

1. General Information

^{1}H-NMR and ^{13}C-NMR spectra were recorded at room temperature using a Bruker Avance-500 instruments (^{1}H NMR at 500 MHz and ^{13}C NMR at 125 MHz), NMR spectra of all products were reported in ppm with reference to solvent signals [^{1}H NMR: $CD(H)Cl_3$ (7.26 ppm), ^{13}C NMR: $CD(H)Cl_3$ (77.00 ppm)]. Signal patterns are indicated as s or brs, singlet; d, doublet; t, triplet, and m, multiplet. HPLC/Q-TOF-MS analysis was performed with an Agilent 1290 LC system coupled with a 6530Q-TOF/MS accurate-mass spectrometer (Agilent Technologies, USA). The mass spectrometry was performed in the positive electrospray ionization (ESI+) mode. Reactions were monitored by thin-layer chromatography Column chromatography (petroleum ether/ethyl acetate) was performed on silica gel (200-300 mesh). Analytical grade solvents and commercially available reagents were purchased from commercial sources and used directly without further purification unless otherwise stated.

2. Optimization of the Reaction Condition.

Table S1. Optimization of Reaction Conditions Silylaton of 1'-benzyl-1,1-dimethyl-1,2-dihydrospiro[benzo[b]silole-3,3'-indolin]-2'-one[a]

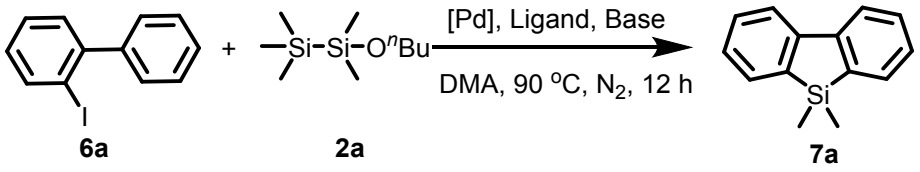


Entry	[Pd]	Ligand	Base	Solvent	Yield (%)[b]
1	$Pd(OAc)_2$		K_2CO_3	DMF	66
2	$Pd(OAc)_2$			DMF	ND
3	$PdCl_2$		K_2CO_3	DMF	20
4	$Pd(TFA)_2$		K_2CO_3	DMF	trace
5	$Pd(dba)_2$		K_2CO_3	DMF	15
6	$Pd(OAc)_2$		Na_2CO_3	DMF	0
7	$Pd(OAc)_2$		$KHCO_3$	DMF	0

8	$Pd(OAc)_2$		K_3PO_4	DMF	0
9	$Pd(OAc)_2$		Cs_2CO_3	DMF	0
10	$Pd(OAc)_2$	PPh_3	K_2CO_3	DMF	72
11		PPh_3	K_2CO_3	DMF	ND
12	$Pd(OAc)_2$	P(o-tol)$_3$	K_2CO_3	DMF	55
13	$Pd(OAc)_2$	X-Phos	K_2CO_3	DMF	50
14	$Pd(OAc)_2$	P^{t}Bu$_3$	K_2CO_3	DMF	68
15	$Pd(OAc)_2$	PPh_3	K_2CO_3	DMA	81
16	$Pd(OAc)_2$	PPh_3	K_2CO_3	MeCN	trace
17	$Pd(OAc)_2$	PPh_3	K_2CO_3	Toluene	trace
18[c]	$Pd(OAc)_2$	PPh_3	K_2CO_3	DMA	71
19[d]	$Pd(OAc)_2$	PPh_3	K_2CO_3	DMA	76
20[e]	$Pd(OAc)_2$	PPh_3	K_2CO_3	DMA	60

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), Pd catalyst (10 mol%), ligand (20 mol%), base (3 equiv), and solvent (2 mL) at 90 °C under N_2 for 6 h. [b] Isolated yield. [c] 80 °C. [d] 100 °C. [e] $Pd(OAc)_2$ (5 mmol%)

Table S2. Optimization of Reaction Conditions Silylaton of 2-iodobiphenyl[a]



6a **2a** **7a**

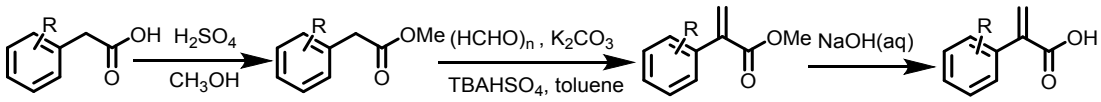
Entry	Catalyst	Ligand	Base	Solvent	Yield[b] (%)
1	$Pd(OAc)_2$		K_2CO_3	DMF	52
2	$PdCl_2$		K_2CO_3	DMF	trace
3	$PdCl_2(CH_3CN)_2$		K_2CO_3	DMF	17
4	$[PdCl(\pi\text{-allyl})]_2$		K_2CO_3	DMF	11
5	$Pd(OAc)_2$			DMF	ND
6	$Pd(OAc)_2$		Na_2CO_3	DMF	trace
7	$Pd(OAc)_2$		K_3PO_4	DMF	ND
8	$Pd(OAc)_2$		Cs_2CO_3	DMF	ND
9	$Pd(OAc)_2$		LiO^{t}Bu	DMF	ND
10	$Pd(OAc)_2$		$KHCO_3$	DMF	23
11	$Pd(OAc)_2$		K_2CO_3	DMA	46
12	$Pd(OAc)_2$		K_2CO_3	CH_3CN	trace
13	$Pd(OAc)_2$		K_2CO_3	Toluene	ND
14	$Pd(OAc)_2$		K_2CO_3	Dioxane	ND
15	$Pd(OAc)_2$	PPh_3	K_2CO_3	DMF	trace
16	$Pd(OAc)_2$	TFP	K_2CO_3	DMF	trace
17	$Pd(OAc)_2$	P^{t}Bu$_3$	K_2CO_3	DMF	50
18	$Pd(OAc)_2$	Xantphos	K_2CO_3	DMF	trace
19[c]	$Pd(OAc)_2$		K_2CO_3	DMF	48

20[d]	$Pd(OAc)_2$	K_2CO_3	DMF	50
21[e]	$Pd(OAc)_2$	K_2CO_3	DMF	64

[a] Reaction conditions: **6a** (0.2 mmol), **2a** (0.3 mmol), Pd catalyst (10 mol%), ligand (20 mol%), base (3 equiv), and solvent (2 mL) at 90 °C under N_2 for 12 h. [b] Isolated yield. [c] 80 °C. [d] 100 °C. [e] **6a** (0.24 mmol).

3. General Procedures for the Synthesis of Substrates

3.1General Procedures for the Synthesis of acrylamides[1,2] (1a-1u). (GP1)



Step I: A 50 mL round bottom flask equipped with a stir bar was charged with 2-phenylacetic acid derivatives (20 mmol), concentrated sulfuric acid (3 drops), and methanol (20 mL), then the mixture was heated to reflux for 6 hours. After that, the reaction mixture was allowed to cool down to room temperature. After the methanol was removed by rotary evaporation, the residue was diluted with ethyl acetate and treated with saturated sodium bicarbonate solution and brine. The organic layer was dried over anhydrous sodium sulfate and concentrated in vacuo to afford the corresponding methyl 2-phenylacetate derivatives.

Step II: To a solution of methyl phenylacetate derivatives (20 mmol) in anhydrous toluene (40 mL), K_2CO_3 (30 mmol, 1.5 equiv), tetrabutylammonium bisulfate (2.0 mmol, 10 mol%), and formaldehyde (30 mmol) were added. The reaction mixture was heated at 80 °C for 12 h, quenched with H_2O (100 mL), and extracted with EA (3×50 mL). The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure to afford the desired product as a colorless oil.

Step III: To a solution of prepared methyl 2-phenylacrylate derivatives in THF (10 mL), a solution of sodium hydrate (3.2 g, 80 mmol, 4.0 equiv) in water (10 mL) was added. The reaction mixture was heated at reflux for 2 hours and then cooled to 0 °C. Addition of concentrated hydrochloric acid resulted in precipitation of a white solid which was extracted with dichloromethane. The organic layer was dried over anhydrous sodium sulfate and concentrated in vacuo to afford 2-phenylacrylic acid derivatives

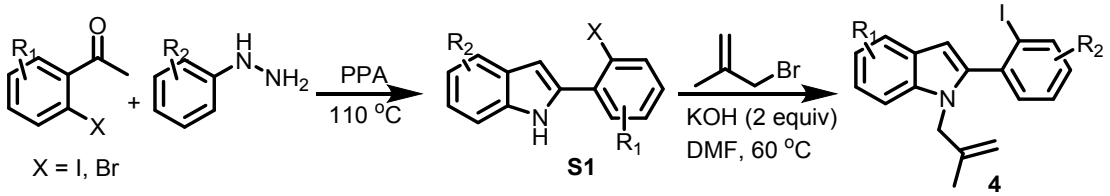
which was used directly in the next step.

Step IV: Oxalyl chloride (6 mmol, 2 equiv) was added dropwise to a solution of substituted 2-phenylacrylic acids (3 mmol) and DMF (4 drops) in CH_2Cl_2 at 0 °C. The reaction was maintained at 0 °C for about 5 minutes and then allowed to warm to room temperature and stirred for 1 h. The excess oxalyl chloride was removed under vacuum, and the resulting crude acid chloride was used in next step directly.

Step V: A solution of the substituted 2-iodoaniline derivativese (2 mmol), DMAP (0.1 mmol, 0.05 equiv) and TEA (4 mmol, 2.0 equiv) was prepared in CH_2Cl_2 (10 mL) and cooled to 0 °C. The acyl chloride solution was added dropwise into the solution. After 5 minutes, the reaction was allowed to warm to room temperature and stirred overnight. The reaction was quenched with saturated $NaHCO_3$ solution and extracted with CH_2Cl_2 twice. The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The resulting crude amide was used in next step without further purification.

Step VI: NaH (120 mg, 60% in mineral oil, 3.0 mmol, 1.5 equiv) was added to a solution of the above product in THF (8.0 mL) at 0 °C in portions. After stirring for 20 min at 0 °C, alkyl/benzyl halide (2.4 mmol, 1.2 equiv) was added dropwise and the reaction mixture was allowed to room temperature and stirred for another 2 h. After completion of the reaction (monitored by TLC), the residue was quenched with water and extracted into ethyl acetate. The organic layer was dried over anhydrous sodium sulfate, and the solution was evaporated to dryness. The crude product was purified by column chromatography (petroleum ether : ethyl acetate = 10:1) to provide the desired products**1a-1u**.

3.2 General Procedures for the Synthesis of alkene-tethered aryl halides[3] (4a-4h). (GP2)



Step I: A mixture of acetophenone (5.0 mmol), phenylhydrazine (6.0 mmol, 1.2

equiv) and polyphosphoric acid (PPA, 15.0 g) was added to a round bottom flask and stirred at 110 °C for 6 h. After the completion of the reaction, the residue was quenched with ice water and extracted into ethyl acetate. The organic phases were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was purified by silica gel column chromatography (petroleum ether/EtOAc = 30:1) to give the corresponding substituted indole **S1**.

Step II: A solution of **S1** (3.0 mmol) in DMF (5 mL) and powdered KOH (6.0 mmol, 3.0 equiv) was stirred at 60 °C for 10 min, cooled to room temperature, and treated with 3-bromo-2-methylprop-1-ene (4.5 mmol, 1.5 equiv). The reaction mixture was stirred at 60 °C for 12-18 h, poured onto ice and diluted with 15 mL of EtOAc. The combined organic layer was washed with H_2O, brine, dried by Na_2SO_4, concentrated in vacuo and purified by silica gel column chromatography (petroleum ether) to afford the desired product **4a-4h**.

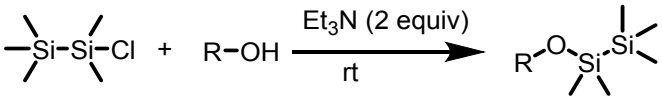
3.3 General Procedures for the Synthesis of 2-iodobiphenyls[4] (6b-6o). (GP3)

Step I: A 100 mL schlenk tube was charged with substituted 2-iodoaniline (3.0 mmol, 1 equiv), substituted phenylboronic acid (3.9 mmol, 1.3 equiv), $Pd(OAc)_2$, (0.15 mmol, 0.05 equiv), dppf (0.3 mmol, 0.1 equiv), Na_2CO_3 (12.0 mmol, 4 equiv), 1,4-dioxane (15.0 mL) and water (6.0 mL). The mixture was heated in an oil bath at 65 °C overnight. After the completion of the reaction, it was allowed to attain to room temperature, then the reaction mixture was filtered and the filtrate was washed by H_2O and brine. The combined organic layer was dried over anhydrous Na_2SO_4 and evaporated under vacuum. The crude product was purified by silica gel column chromatography (petroleum ether/EtOAc) to give the corresponding substituted 2-aminobiphenyls.

Step II: A solution of concn HCl (36-38%; 2.7 mmol, 1.35 equiv, 1mL) in water (4 mL) was added slowly to the prepared 2-aminobiphenyl (2.0 mmol) at 0 °C in portions. After stirring for 1 h at 0 °C, the aqueous solution of $NaNO_2$ (3.0 mmol, 1.5 equiv) was added to the reaction mixture below 5 °C within 10 min and stirred for 1 h. Then an aqueous solution of KI (4.0 mmol, 2 equiv) in water (4 mL) was added, and the reaction mixture was stirred at room temperature overnight. After the completion of the reaction,

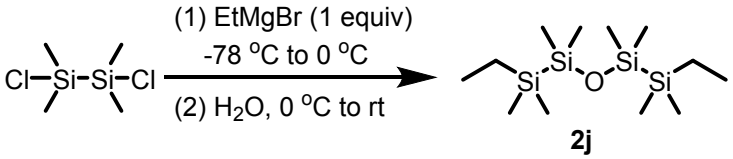
saturated aqueous $NaHCO_3$ was added to neutralize the acid and adjusted the solution to pH > 7. Then the residue was extracted into ethyl acetate (3×5 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was purified by silica gel column chromatography (petroleum ether unless otherwise noted) to give the desired 2-iodobiphenyls **6b-6o**.

3.4 General Procedures for the Synthesis disiloxanes (2a-2f, 2h)[5]. (GP4)



1-chloro-1,1,2,2,2-pentamethyldisilane (10 mmol) was added to a solution of Et_3N (20 mmol, 2 equiv) in ROH (40 mmol, 4 equiv) at 0 °C drop-wise. The reaction was stirred at room temperature for 10 h. After the completion of the reaction, the reaction mixture was filtered and the filtrate diluted in ethyl acetate, and washed with water. The combined organic layer was dried over anhydrous Na_2SO_4 and evaporated under vacuum. The crude product was purified by silica gel column chromatography (petroleum ether) to give the corresponding products **2a-2f, 2h.**

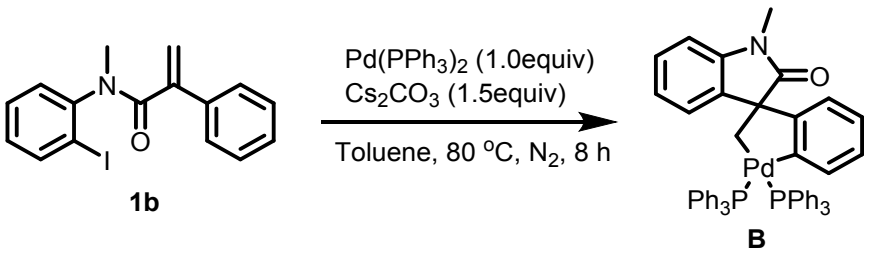
3.5 General Procedures for the Synthesis 1,3-Bis(ethyldimethylsilyl)-1,1,3,3-tetramethyldisiloxane. (GP5)



2j

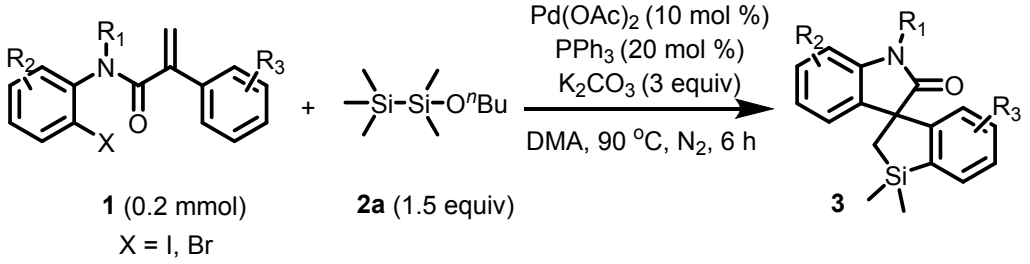
1,2-dichloro-1,1,2,2-tetramethyldisilane (2 mmol) was dissolved in dry diethyl ether (6 mL) and cooled to -78 °C, and then ethylmagnesium bromide (2 mmol, 1 equiv, 1.0 M) was added to the solution slowly. The reaction mixture was stirred at -78 °C to 0 °C for 2 h. Then the reaction was stirred overnight at room temperature after adding excess water. After the completion of the reaction, this reaction mixture was extracted with ethyl acetate (3 × 15 mL). The ethyl acetate extract was dried with Na_2SO_4 and concentrated in vacuo. The crude product was purified by column chromatography (petroleum ether) to afford the desired product **2j.**

3.6 General Procedures for the Synthesis Spiropalladcycle.[6](GP6)



To a flame dried 2 dram vial cooled under nitrogen, *N*-(2-iodophenyl)-*N*-methyl-2-phenylacrylamide **1b** (72.6 mg, 0.2 mmol, 1 equiv), $Pd(PPh_3)_4$ (231 mg, 0.2 mmol, 1 equiv), and Cs_2CO_3 (97.7 mg, 0.3 mmol, 1.5 equiv) were added and allowed to purge for 10 minutes. PhMe (2 mL, 0.1 M) was added and a teflon line screw cap was fitted on the two dram vial, sealed with Teflon tape and place in a preheated oil bath at 80 °C for 8 hours. The reaction mixture was cooled to room temperature. Once cooled, the reaction was passed through a plug of celite using DCM and concentrated in vacuo. Once solidified, hexane was used to triturate the compound. The mixture was passed through glass wool, and the collected solid was redissolved in DCM and concentrated in vacuo. The palladacycle **B** was recrystallized with Et_2O and hexanes to obtain a pale yellow solid (86.6 mg, 0.1 mmol, 50%).

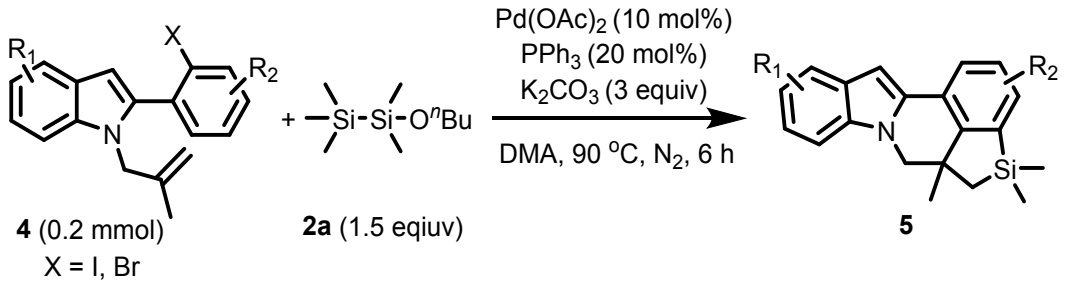
4. General Procedures of Synthesis Spiro[benzo[b]silole-3,3'-indolin]-2'-ones



The mixture of acrylamide **1** (0.2 mmol), 1-butoxy-1,1,2,2,2-pentamethyldisilane **2a** (61.2 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 0.1 equiv), PPh_3 (10.6 mg, 0.04 mmol, 0.2 equiv), and K_2CO_3 (82.8 mg, 0.6 mmol, 3 equiv) in DMA (2 mL) was stirred under nitrogen atmosphere at 90 °C for 6 h. After the completion of the reaction (monitored by TLC), the reaction mixture was filtered and the filtrate was washed by H_2O and brine. The combined organic layer was evaporated under reduced

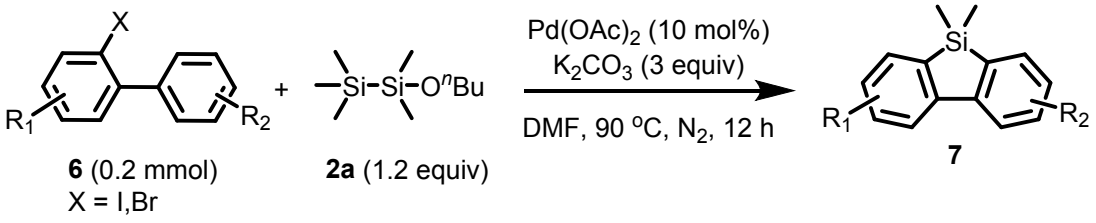
pressure, and the crude product was purified by column chromatography (petroleum ether: ethyl acetate = 30:1) to provide the products **3**.

5. General Procedures of Synthesis Indolo[2,1-a]silolo[4,3,2-de]isoquinolines



The mixture of alkene-tethered aryl halides **4** (0.2 mmol), 1-butoxy-1,1,2,2,2-pentamethyldisilane **2a** (61.2 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 0.1 equiv), PPh_3 (10.6 mg, 0.04 mmol, 0.2 equiv), and K_2CO_3 (82.8 mg, 0.6 mmol, 3.0 equiv) in DMA (2 mL) was stirred under nitrogen atmosphere at 90 °C for 6 h. After the completion of the reaction (monitored by TLC), the reaction mixture was filtered and the filtrate was washed by H_2O and brine. The combined organic layer was evaporated under reduced pressure and the crude product was purified by column chromatography (petroleum ether) to provide the products **5**.

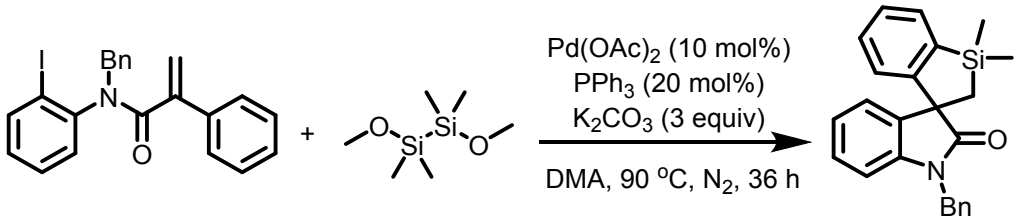
6. General Procedures of Synthesis Dibenzo[b,d]siloles.



The mixture of diphenyl **6** (0.2 mmol), 1-butoxy-1,1,2,2,2-pentamethyldisilane **2a** (49.4 mg, 0.24 mmol, 1.2 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 0.1 equiv), and K_2CO_3 (82.8 mg, 0.6 mmol, 3.0 equiv) in DMF (2 mL) was stirred under nitrogen atmosphere at 90 °C for 12 h. After the completion of the reaction (monitored by TLC), the reaction mixture was filtered and the filtrate was washed by H_2O and brine. The combined

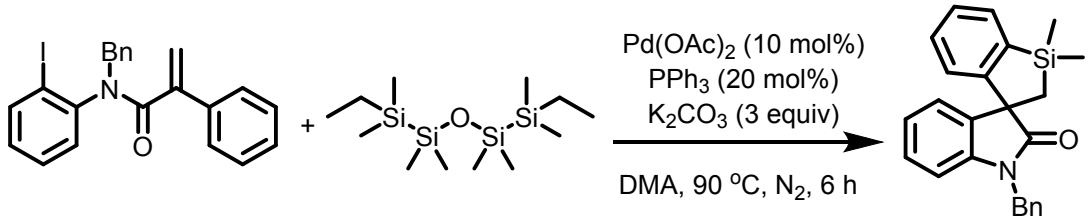
organic layer was evaporated under reduced pressure and the crude product was purified by column chromatography (petroleum) to provide the products **7**.

7. Mechanistic Studies



1a (0.2 mmol) **2h** (0.3 mmol) **3a**, 27%

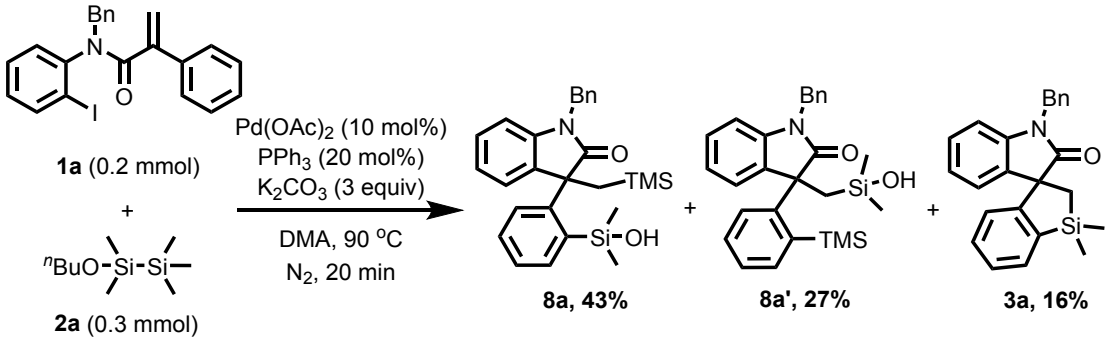
The mixture of acrylamide **1a** (87.8 mg, 0.2 mmol,), 1,2-dimethoxy-1,1,2,2-tetramethyldisilane **2h** (53.4 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 0.1 equiv), PPh_3 (10.6 mg, 0.04 mmol, 0.2 equiv), and K_2CO_3 (82.8 mg, 0.6 mmol, 3.0 equiv) in DMA (2 mL) was stirred under nitrogen atmosphere at 90 °C for 36 h. After the completion of the reaction (monitored by TLC), the reaction mixture was filtered and the filtrate was washed by H_2O and brine. The combined organic layer was evaporated under reduced pressure and the crude product was purified by column chromatography (petroleum ether: ethyl acetate = 20:1) to provide the desired product **3a** with a yield of 27 % (19.9 mg).



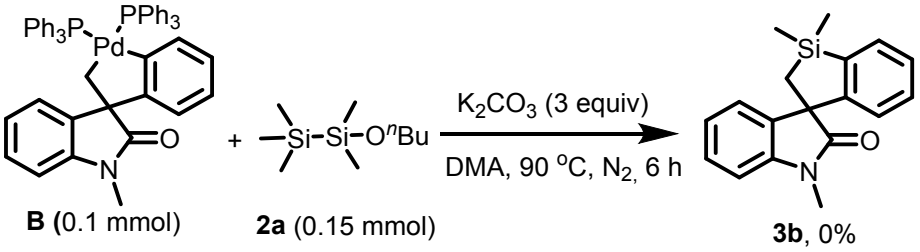
1a (0.2 mmol) **2i** (0.3 mmol) **3a**, 50%

The mixture of acrylamide **1a** (87.8 mg, 0.2 mmol,), 1,3-bis(ethyldimethylsilyl)-1,1,3,3-tetramethyldisiloxane **2i** (92.0 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 0.1 equiv), PPh_3 (10.6 mg, 0.04 mmol, 0.2 equiv), and K_2CO_3 (82.8 mg, 0.6 mmol, 3.0 equiv) in DMA (2 mL) was stirred under nitrogen atmosphere at 90 °C for 6 h. After the completion of the reaction (monitored by TLC), the reaction mixture was filtered and the filtrate was washed by H_2O and brine. The combined organic layer

was evaporated under reduced pressure and the crude product was purified by column chromatography (petroleum ether: ethyl acetate = 30:1) to provide the desired product **3a** with a yield of 50% (36.9 mg).

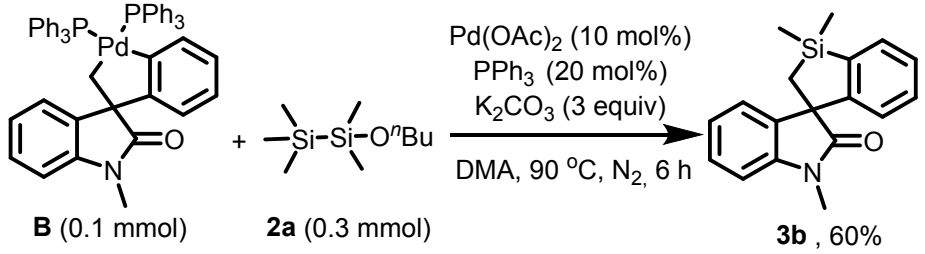


The mixture of acrylamide **1a** (87.8 mg, 0.2 mmol,), 1-butoxy-1,1,2,2,2-pentamethyldisilane **2a** (61.2 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 0.1 equiv), PPh_3 (10.6 mg, 0.04 mmol, 0.2 equiv) and K_2CO_3 (82.8 mg, 0.6 mmol, 3.0 equiv) in DMA (2 mL) was stirred under nitrogen atmosphere at 90 °C for 20min. After the completion of the reaction (monitored by TLC), the reaction mixture was filtered and the filtrate was washed by H_2O and brine. The combined organic layer was evaporated under reduced pressure and the crude product was purified by column chromatography and the products **8a**, **8a'** and **3a** were obtained with yields of 43%, 27%, and 16%, respectively.

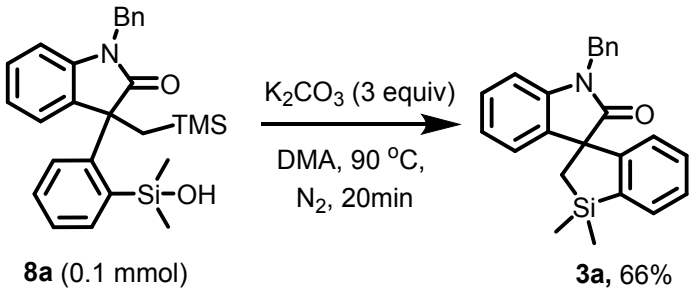


The mixture of palladacycle **B** (86.6 mg, 0.1 mmol,), 1-butoxy-1,1,2,2,2-pentamethyldisilane **2a** (30.6 mg, 0.15 mmol, 1.5 equiv) and K_2CO_3 (41.4 mg, 0.3 mmol, 3.0 equiv) in DMA (1 mL) was stirred under nitrogen atmosphere at 90°C for 6 h. After the completion of the reaction (monitored by TLC), the reaction mixture was filtered and the filtrate was washed by H_2O and brine. The combined organic layer was evaporated under reduced pressure and the crude product was purified by column

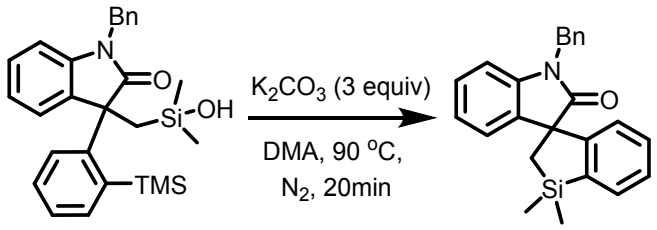
chromatography (petroleum ether: ethyl acetate = 20:1) to provide the desired product **3b** with a yield of 0 %.



The mixture of palladacycle **B** (86.6 mg, 0.1 mmol, 1 equiv), 1-butoxy-1,1,2,2,2-pentamethyldisilane **2a** (30.6 mg, 0.15 mmol, 1.5 equiv), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol, 0.1 equiv), PPh_3 (5.3 mg, 0.02 mmol, 0.2 equiv) and K_2CO_3 (41.4 mg, 0.3 mmol, 3.0 equiv) in DMA (1 mL) was stirred under nitrogen atmosphere at 90°C for 6 h. After the completion of the reaction (monitored by TLC), the reaction mixture was filtered and the filtrate was washed by H_2O and brine. The combined organic layer was evaporated under reduced pressure and the crude product was purified by column chromatography (petroleum ether: ethyl acetate = 20:1) to provide the desired product **3b** with a yield of 60 % (17.6 mg).

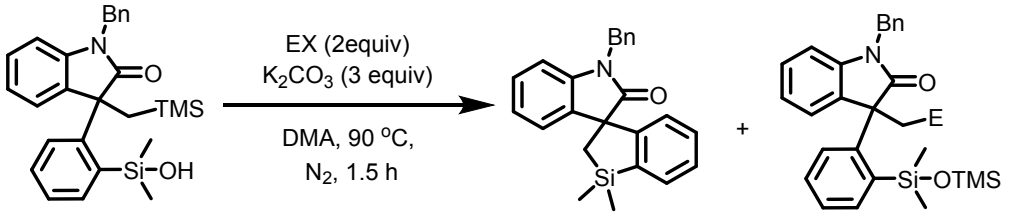


The mixture of **8a** (0.1 mmol, 46.0 mg) and K_2CO_3 (41.4 mg, 0.3 mmol, 3.0 equiv) in DMA (1 mL) was stirred under nitrogen atmosphere at 90 °C for 20min. After the completion of the reaction (monitored by TLC), the reaction mixture was filtered and the filtrate was washed by H_2O and brine. The combined organic layer was evaporated under reduced pressure and the crude product was purified by column chromatography (petroleum ether: ethyl acetate = 20:1) to provide the desired product **3a** with a yield of 66%.



8a' (0.1 mmol) **3a,** 60%

The mixture of **8a'** (46.0 mg , 0.1 mmol,) and K_2CO_3 (41.4 mg, 0.3 mmol, 3.0 equiv) in DMA (1 mL) was stirred under nitrogen atmosphere at 90 °C for 20min. After the completion of the reaction (monitored by TLC), the reaction mixture was filtered and the filtrate was washed by H_2O and brine. The combined organic layer was evaporated under reduced pressure and the crude product was purified by column chromatography (petroleum ether: ethyl acetate = 20:1) to provide the desired product **3a** with a yield of 60%.

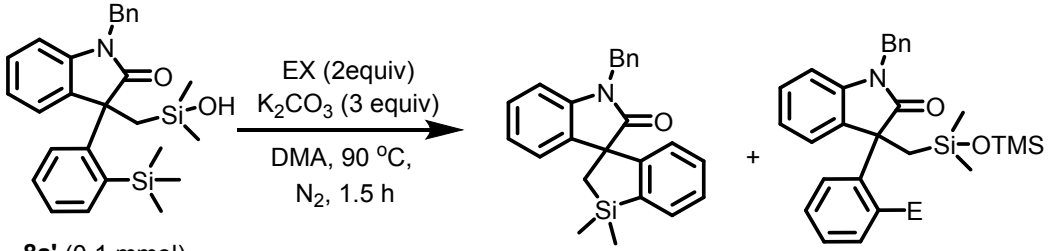


8a (0.1 mmol)

EX = MeI, **3a**, 74%
EX = BnBr, **3a**, 80%

F-1, 0%

The mixture of **8a** (46.0 mg, 0.1 mmol,)， MeI/BnBr (0.2 mmol) and K_2CO_3 (41.4 mg, 0.3 mmol, 3.0 equiv) in DMA (1 mL) was stirred under nitrogen atmosphere at 90 °C for 1.5 h. After the completion of the reaction (monitored by TLC), the reaction mixture was filtered and the filtrate was washed by H_2O and brine. The combined organic layer was evaporated under reduced pressure and the crude product was purified by column chromatography (petroleum ether: ethyl acetate = 20:1) to provide the product **3a**. However, the product **F-1** could not be detected.



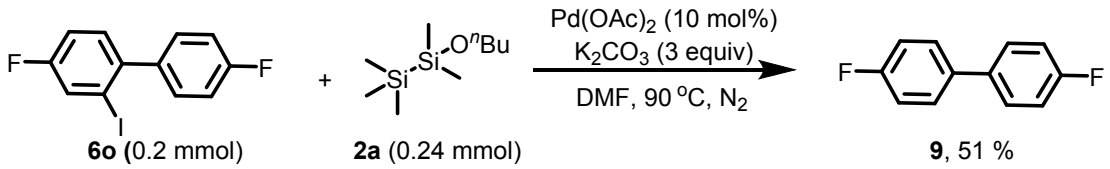
8a' (0.1 mmol)

EX = MeI, **3a**, 66%
EX = BnBr, **3a**, 64%

F'-2, 0%

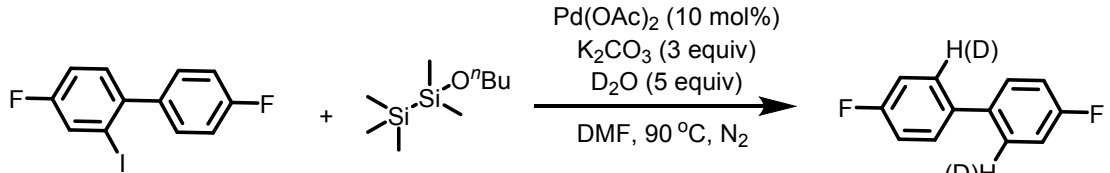
The mixture of **8a'** (0.1 mmol, 46.0 mg)， MeI/BnBr (0.2 mmol) and K_2CO_3

(41.4mg, 0.3 mmol, 3.0 equiv) in DMA (1 mL) was stirred under nitrogen atmosphere at 90 °C for 1.5 h. After the completion of the reaction (monitored by TLC), the reaction mixture was filtered and the filtrate was washed by H_2O and brine. The combined organic layer was evaporated under reduced pressure,and the crude product was purified by column chromatography (petroleum ether: ethyl acetate = 20:1) to provide the product **3a**. However, the product **F'-2** could not be detected.



6o (0.2 mmol) **2a** (0.24 mmol) **9**, 51 %

The mixture of **6o** (0.2 mmol, 63.2 mg), 1-butoxy-1,1,2,2,2-pentamethyldisilane **2a** (49.0 mg, 0.24 mmol, 1.2 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 0.1 equiv), and K_2CO_3 (82.8 mg, 0.6 mmol, 3.0 equiv), in DMF (2 mL) was stirred under nitrogen atmosphere at 90°C for 6 h. After the completion of the reaction (monitored by TLC), the reaction mixture was filtered and the filtrate was washed by H_2O and brine. The combined organic layer was evaporated under reduced pressure and the crude product was purified by column chromatography (petroleum ether) to provide the desired product **9** with a yield of 51% (19.3 mg).



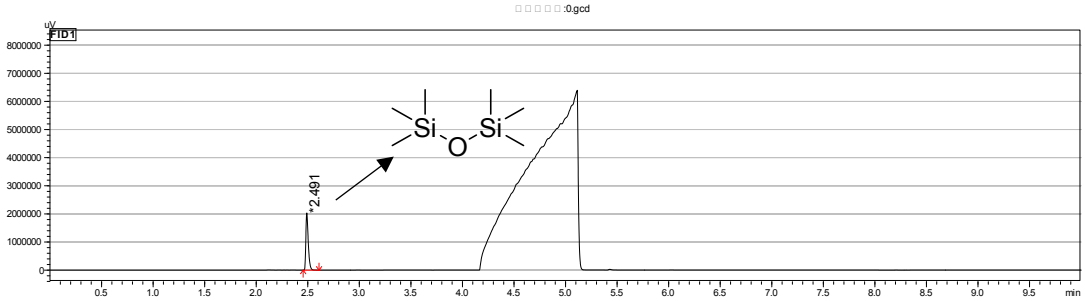
6o (0.2 mmol) **2a** (0.24 mmol) **9-D**, 47%

The mixture of **6o** (0.2 mmol, 63.2 mg), 1-butoxy-1,1,2,2,2-pentamethyldisilane **2a** (49.0 mg, 0.24 mmol, 1.2 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 0.1 equiv), D_2O (20.0 mg, 1.0 mmol, 5 equiv) and K_2CO_3 (82.8 mg, 0.6 mmol, 3.0 equiv), in DMF (2 mL) was stirred under nitrogen atmosphere at 90°C for 6 h. After the completion of the reaction (monitored by TLC), the reaction mixture was filtered and the filtrate was washed by H_2O and brine. The combined organic layer was evaporated under reduced pressure and the crude product was purified by column chromatography (petroleum

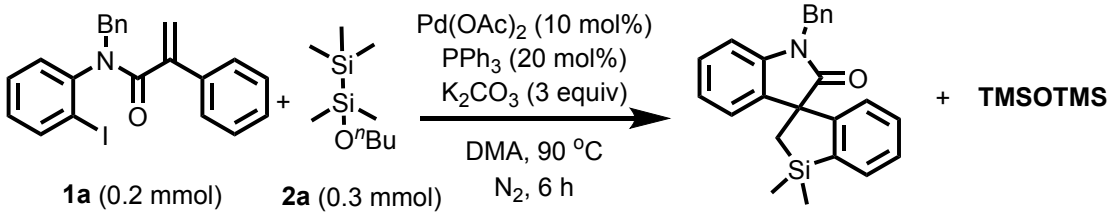
ether) to provide the desired product **9'** with a yield of 47% (18.0 mg).

The gas chromatograph data is shown as follows:

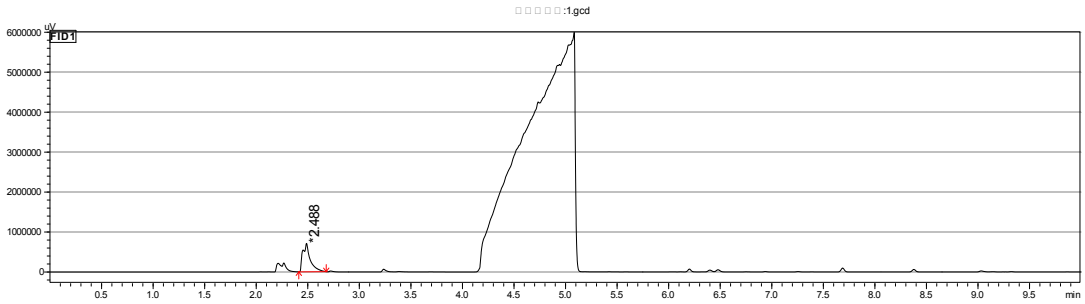
1. The mixture of TMSOTMS and DMA was analyzed by gas chromatograph.



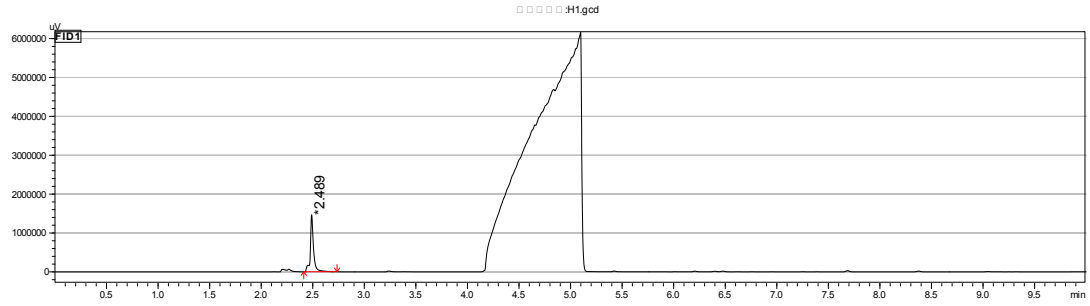
2. The mixture of **1a** (42.9 mg, 0.1 mmol), 1-butoxy-1,1,2,2,2-pentamethyldisilane **2a** (61.2 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 0.1 equiv), PPh_3 (10.6 mg, 0.04 mmol, 0.2 equiv) and K_2CO_3 (82.8 mg, 0.6 mmol, 3.0 equiv) in DMA (2 mL) was stirred under nitrogen atmosphere at 90 °C for 20min. After the completion of the reaction (monitored by TLC), the reaction mixture was filtered and the filtrate was analyzed by gas chromatograph.



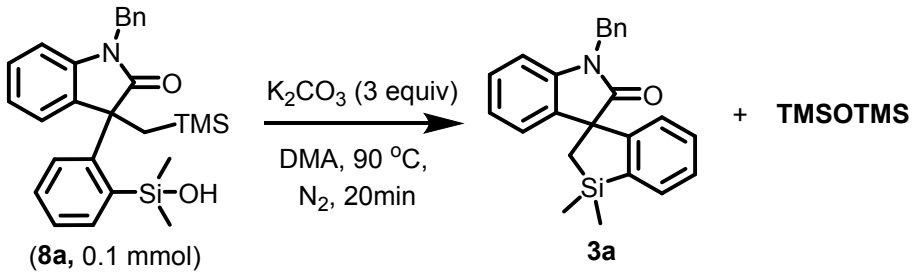
1a (0.2 mmol) **2a** (0.3 mmol)

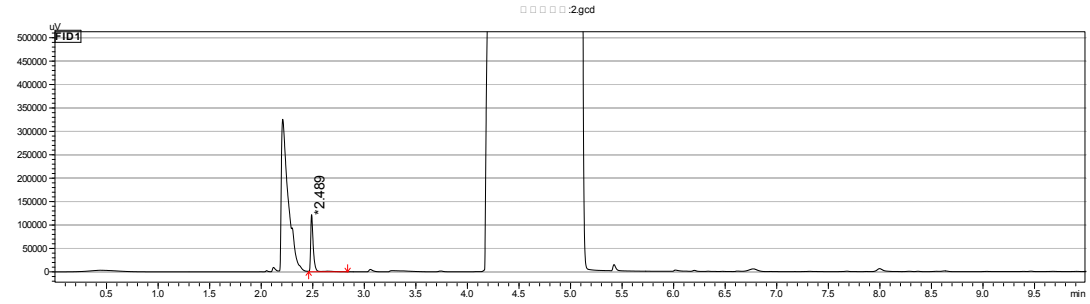


3. The mixture of 1 and 2 was analyzed by gas chromatograph.

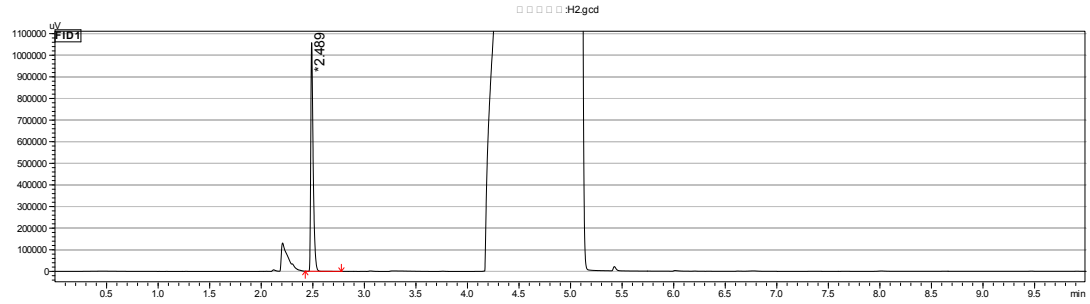


4. The mixture of **8a** (46.0 mg, 0.1 mmol) and K_2CO_3 (41.4 mg, 0.3 mmol, 3.0 equiv) in DMA (1 mL) was stirred under nitrogen atmosphere at 90 °C for 20 min. After the completion of the reaction (monitored by TLC), the reaction mixture was filtered and the filtrate was analyzed by gas chromatograph.

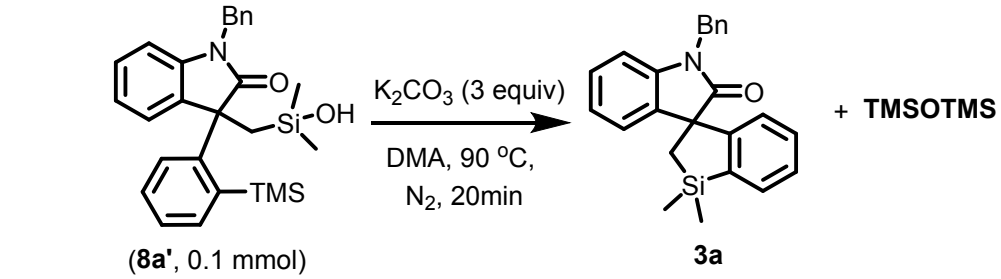




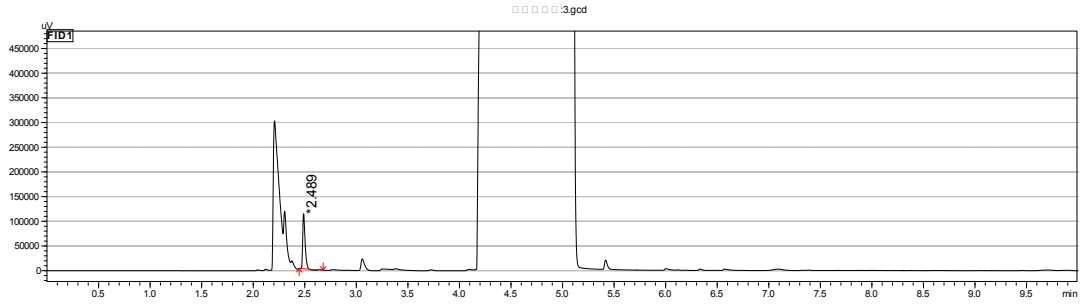
5. The mixture of 1 and 4 was analyzed by gas chromatograph.



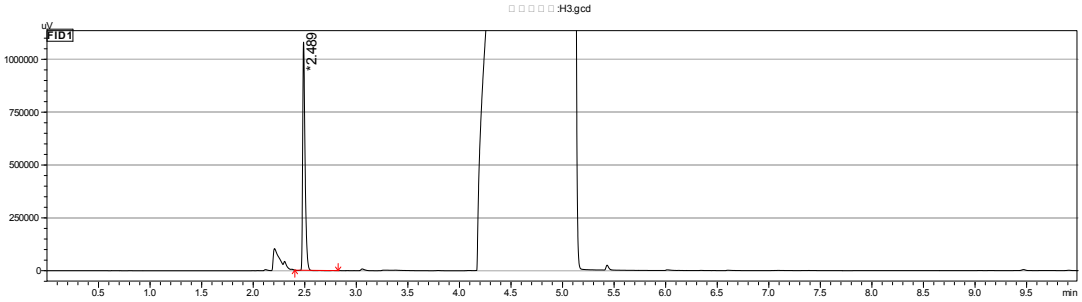
6. The mixture of **8a'** (46.0 mg, 0.1 mmol) and K_2CO_3 (41.4 mg, 0.3 mmol, 3.0 equiv) in DMA (1 mL) was stirred under nitrogen atmosphere at 90 °C for 20 min. After the completion of the reaction (monitored by TLC), the reaction mixture was filtered and the filtrate was analyzed by gas chromatograph.



(**8a'**, 0.1 mmol) **3a**

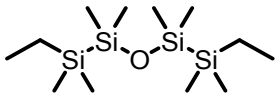


7. The mixture of 1 and 6 was analyzed by gas chromatograph.



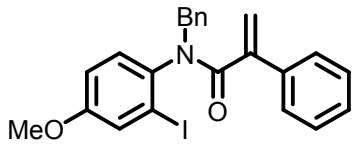
8. Characterization of the Substrates

1,3-bis(ethyldimethylsilyl)-1,1,3,3-tetramethyldisiloxane (2i)



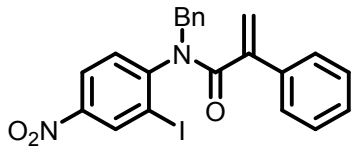
The title compound was prepared in line with **GP5**, purified on flash column chromatography using petroleum ether as the eluent, and was obtained as a colorless oil with a yield of 30%. R_f = 0.87 (petroleum ether). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 0.96 (t, *J* = 8.0 Hz, 6H), 0.57 (q, *J* = 8.0 Hz, 4H), 0.16 (s, 12H), 0.13 (s, 12H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 8.1, 6.5, 2.7, -4.8.

***N*-benzyl-*N*-(2-iodo-4-methoxyphenyl)-2-phenylacrylamide (1l)**



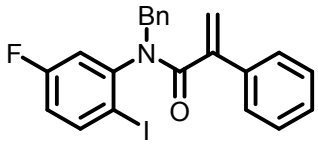
The title compound was prepared in line with **GP1**, purified on flash column chromatography using petroleum ether/EtOAc as the eluent, and was obtained as a white solid with a yield of 40%. R_f = 0.41 (petroleum ether : EtOAc = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.28-7.16 (m, 10H), 7.11-7.09 (m, 2H), 6.27 (dd, *J* = 3.0 Hz, 8.5 Hz, 1H), 5.95 (d, *J* = 8.5 Hz, 1H), 5.80 (d, *J* = 14.0 Hz, 1H), 5.62 (s, 1H), 5.32 (s, 1H), 4.00 (d, *J* = 14.0 Hz, 1H), 3.68 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.3, 158.7, 145.7, 137.0, 136.8, 135.7, 131.8, 129.5, 128.3, 128.3, 127.9, 127.6, 125.9, 124.3, 116.4, 113.5, 100.5, 55.5, 51.5.

***N*-benzyl-*N*-(2-iodo-4-nitrophenyl)-2-phenylacrylamide (1n)**



The title compound was prepared in line with **GP1**, purified on flash column chromatography using petroleum ether/EtOAc as the eluent, and was obtained as a yellow solid with a yield of 40%. R_f = 0.35 (petroleum ether : EtOAc = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.58 (s, 1H), 7.61 (dd, *J* = 2.5 Hz, 9.0 Hz, 1H), 7.28-7.17 (m, 9H), 7.06 (d, *J* = 7.5 Hz, 1H), 6.20 (d, *J* = 8.5 Hz, 1H), 5.83 (d, *J* =14.0 Hz, 1H), 5.70 (s, 1H), 5.39 (s, 1H), 4.11 (d, *J* = 14.0 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 169.1, 148.7, 146.4, 145.2, 136.0, 135.8, 134.7, 132.0, 129.4, 128.6, 128.6, 128.4, 128.1, 125.9, 122.7, 118.2, 99.9, 51.1.

***N*-benzyl-*N*-(5-fluoro-2-iodophenyl)-2-phenylacrylamide**

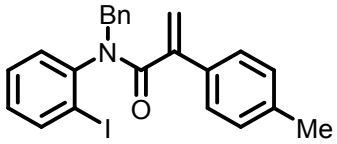


1f

The title compound was prepared in line with **GP1**, purified on flash column chromatography using petroleum ether/EtOAc as the eluent, and was obtained as a yellow solid with a yield of 40%. R_f = 0.35 (petroleum ether : EtOAc = 10:1). **^{1}H NMR**

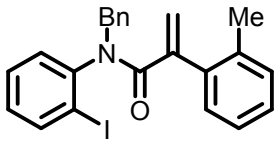
(500 MHz, $CDCl_3$) δ 7.70-7.67 (m, 2H), 7.28-7.19 (m, 8H), 7.08-7.06 (m, 2H), 6.62 (td, *J* = 3.0 Hz, 8.5 Hz, 1H), 5.84 (dd, *J* =3.0 Hz, 9.0 Hz, 1H), 5.79 (d, *J* = 14.5 Hz, 1 H), 5.36 (s, 1H), 4.06 (d, *J* = 14.5 Hz, 1H), **^{13}C NMR** (125 MHz, $CDCl_3$) δ 169.6, 161.82 (d, *J* = 248.5 Hz), 145.5, 144.3 (d, *J* =9.6 Hz), 140.2 (d, *J* =8.4 Hz), 136.7, 136.2, 129.3, 128.5, 128.4, 128.0 (d, *J* = 36.6 Hz), 125.7, 119.4 (d, *J* = 22.6 Hz), 117.6, 116.8 (d, *J* = 21.8 Hz), 93.5, 51.3.

***N*-benzyl-*N*-(2-iodophenyl)-2-(4-methoxyphenyl)acrylamide (1p)**



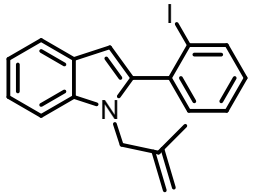
The title compound was prepared in line with **GP1**, purified on flash column chromatography using petroleum ether/EtOAc as the eluent, and was obtained as a white solid with a yield of 38%. R_f = 0.37 (petroleum ether : EtOAc = 10:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 1.6 Hz, 7.7 Hz, 1H), 7.26-7.25 (m, 6H), 7.02-6.98 (m, 4H), 6.85-6.77 (m, 2H), 6.14 (dd, *J* = 2.0 Hz, 7.5 Hz, 1H), 5.84 (d, *J* = 14.0 Hz, 1H), 5.56 (s, 1H), 5.28 (s, 1H), 4.05 (d, *J* = 14.0 Hz, 1H), 2.29 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.0, 145.2, 143.0, 139.7, 137.8, 136.7, 134.1, 131.8, 129.5, 129.1, 129.0, 128.3, 128.0, 127.6, 125.8, 115.5, 100.1, 51.3, 21.1.

***N*-benzyl-*N*-(2-iodophenyl)-2-(o-tolyl)acrylamide (1r)**



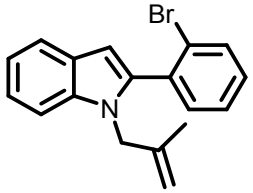
The title compound was prepared in line with **GP1**, purified on flash column chromatography using petroleum ether/EtOAc as the eluent, and was obtained as a white solid with a yield of 38%. R_f = 0.37 (petroleum ether : EtOAc = 10:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.8 Hz, 1H), 7.25-7.18 (m, 5H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 7.5 Hz, 1H), 6.79 (q, *J* = 7.0 Hz, 2H), 6.72 (t, *J* = 7.5 Hz, 1H), 6.50 (d, *J* = 7.5 Hz, 1H), 5.71 (d, *J* = 14.0 Hz, 1H), 5.27 (s, 1H), 3.98 (d, *J* = 14.0 Hz, 1H), 2.01 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.1, 146.7, 142.6, 139.6, 137.4, 136.7, 135.5, 131.74, 130.1, 129.7, 129.0, 128.3, 128.2, 127.9, 127.6, 127.3, 125.6, 124.0, 100.1, 52.0, 20.0.

2-(2-iodophenyl)-1-(2-meth ylallyl)-1*H*-indole (4a)



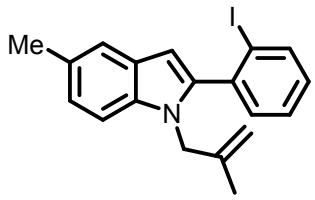
The title compound was prepared in line with **GP2**, purified on flash column chromatography using petroleum ether as the eluent, and was obtained as a colorless oil in an overall yield of 50%. R_f = 0.75 (petroleum ether). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.45-7.39 (m, 2H), 7.36 (d, *J* = 8.5 Hz, 1H), 7.25 (td, *J* = 1.0 Hz, 7.0 Hz, 1H), 7.18-7.11 (m, 2H), 6.53 (s, 1H), 4.78-4.77 (m, 1H), 4.61 (brs, 1H), 4.46 (s, 1H), 4.37 (brs, 1H), 1.53 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 142.2, 140.9, 139.1, 138.2, 136.7, 132.0, 130.0, 127.7, 121.7, 120.8, 119.8, 111.9, 110.4, 102.7, 101.4, 50.0, 20.0.

2-(2-bromophenyl)-1-(2-methylallyl)-1*H*-indole (4a')



The title compound was prepared in line with **GP2**, purified on flash column chromatography using petroleum ether as the eluent, and was obtained as a colorless oil in an overall yield of 45%. R_f = 0.77 (petroleum ether). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.73-7.69 (m, 2H), 7.45-7.37 (m, 3H), 7.31 (td, *J* = 2.0 Hz, 7.5 Hz, 1H), 7.26 (td, *J* = 1.0 Hz, 7.0 Hz, 1H), 7.20-7.16 (m, 1H), 6.58 (s, 1H), 4.79-4.78 (m, 1H), 4.54 (s, 2H), 4.49-4.80 (m, 1H), 1.53 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 140.9, 139.3, 136.8, 134.0, 132.8, 132.7, 130.0, 127.8, 127.0, 125.1, 121.7, 120.7, 119.8, 111.8, 110.4, 102.9, 49.9, 19.9.

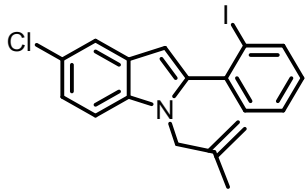
2-(2-iodophenyl)-5-methyl-1-(2-methylallyl)-1*H*-indole (4b)



The title compound was prepared in line with **GP2**, purified on flash column

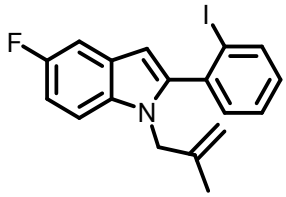
chromatography using petroleum ether as the eluent, and was obtained as a colorless oil in an overall yield of 42%. R_f = 0.80 (petroleum ether). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.0 Hz, 1H), 7.48 (s, 1H), 7.43-7.39 (m, 2H), 7.26 (d, *J* = 8.0 Hz, 1H), 7.14-7.11 (m, 1H), 7.08 (dd, *J* = 1.5 Hz, 8.0 Hz, 1H), 6.45 (s, 1H), 4.78-4.77 (m, 1H), 4.58 (brs, 1H), 4.47-4.46 (m, 1H), 4.35 (brs, 1H), 2.50 (s, 3H), 1.53 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 142.3, 141.0, 139.1, 138.3, 135.0, 131.9, 129.9, 129.0, 127.9, 127.7, 123.4, 120.4, 111.8, 110.1, 102.1, 101.5, 50.0, 21.4, 20.0.

5-chloro-2-(2-iodophenyl)-1-(2-methylallyl)-1*H*-indole (4c)



The title compound was prepared in line with **GP2**, purified on flash column chromatography using petroleum ether as the eluent, and was obtained as a colorless oil in an overall yield of 48%. R_f = 0.79 (petroleum ether). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 2.0 Hz, 1H)), 7.44-7.38 (m, 2H), 7.27 (d, *J* = 8.0 Hz, 1H), 7.19 (d, *J* = 2.0 Hz, 8.5 Hz, 2H), 7.15 (td, *J* = 2.0 Hz, 8.0 Hz, 1H), 6.47 (s, 1H), 4.79-4.78 (m, 1H), 4.58 (brs, 1H), 4.45-4.44 (m, 1H), 1.52 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 143.5, 140.6, 139.1, 137.6, 135.0, 131.8, 130.3, 128.6, 127.8, 125.5, 122.1, 120.1, 112.1, 111.5, 102.2, 101.2, 50.1, 20.0

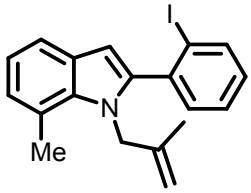
5-fluoro-2-(2-iodophenyl)-1-(2-methylallyl)-1*H*-indole (4d)



The title compound was prepared in line with method **GP2**, purified on flash column chromatography using petroleum ether as the eluent, and was obtained as a colorless oil in an overall yield of 51%. R_f = 0.81 (petroleum ether). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.0 Hz, 1H), 7.44-7.37(m, 2H), 7.31 (dd, *J* = 2.5 Hz, 9.5 Hz, 1H), 7.26 (dd, *J* = 4.5 Hz, 6.0 Hz, 1H), 7.14 (td, *J* = 1.5 Hz, 7.5 Hz, 1H), 6.98 (td, *J* = 2.5 Hz, 9.0 Hz, 1H), 6.48 (s, 1H), 4.79 (s, 1H), 4.58 (brs, 1H), 4.46 (s, 1H), 4.34 (brs, 1H), 1.51 (s,

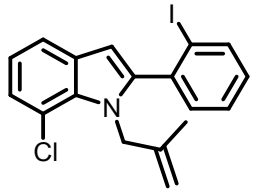
3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 158.0 (d, *J* = 233.0 Hz), 143.7, 140.7, 139.1, 137.8, 133.2, 131.8, 130.2, 127.9 (d, *J* = 10.0 Hz), 127.8, 112.1, 111.1 (d, *J* = 9.6 Hz), 110.1 (d, *J* = 26.0 Hz) 105.5 (d, *J* = 23.2 Hz) 102.6 (d, *J* = 4.6 Hz), 101.2, 50.2, 20.0.

2-(2-iodophenyl)-7-methyl-1-(2-methylallyl)-1*H*-indole (4e)



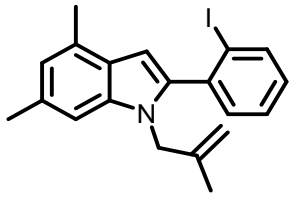
The title compound was prepared in line with method **GP2**, purified on flash column chromatography using petroleum ether as the eluent, and was obtained as a colorless oil in an overall yield of 27%. R_f = 0.78 (petroleum ether). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.39-7.38 (m, 2H), 7.13-7.10 (m, 1H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.96 (d, *J* = 7.0 Hz, 1H), 6.48 (s, 1H), 4.86 (d, *J* = 18.5 Hz, 1H), 4.74 (s, 1H), 4.19 (d, *J* = 18.0 Hz, 1H), 4.04 (s, 3H), 2.67 (s, 3H), 1.58 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 143.1, 142.8, 139.0, 138.4, 135.4, 132.0, 130.0, 128.5, 127.7, 124.9, 121.4, 119.9, 118.9, 110.5, 103.2, 101.6, 51.1, 19.8, 19.1.

7-chloro-2-(2-iodophenyl)-1-(2-methylallyl)-1*H*-indole (4f)



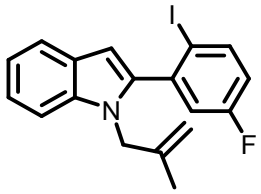
The title compound was prepared in line with **GP2**, purified on flash column chromatography using petroleum ether as the eluent, and was obtained as a colorless oil in an overall yield of 25%. R_f = 0.80 (petroleum ether). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.42-7.37 (m, 2H), 7.19 (d, *J* = 7.5 Hz, 1H), 7.15-7.12 (m, 1H), 7.04 (t, *J* = 8.0 Hz, 1H), 6.52 (s, 1H), 5.25 (d, *J* = 18.0 Hz, 1H), 4.70 (s, 1H), 4.28 (d, *J* = 17.5 Hz, 1H), 3.95 (s, 3H), 1.60 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 144.0, 142.9, 139.1, 137.6, 131.9, 130.8, 130.3, 127.7, 123.9, 120.5, 119.6, 117.1, 103.5, 101.3, 50.7, 19.9.

2-(2-iodophenyl)-4,6-dimethyl-1-(2-methylallyl)-1*H*-indole (4g)



The title compound was prepared in line with **GP2**, purified on flash column chromatography using petroleum ether as the eluent, and was obtained as a colorless oil in an overall yield of 38%. R_f = 0.79 (petroleum ether). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.0 Hz, 1H), 7.42-7.41 (m, 2H), 7.14-7.09 (m, 1H), 7.00 (s, 1H), 6.83 (s, 1H), 6.50 (s, 1H), 4.78-4.77 (m, 1H), 4.57 (brs, 1H), 4.46-4.45 (m, 1H), 4.33 (brs, 1H), 2.58 (s, 3H), 2.48 (s, 3H), 1.55 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 141.0, 141.0, 139.0, 138.5, 136.8, 132.0, 131.7, 129.8, 129.8, 127.7, 125.5, 122.1, 111.7, 107.9, 101.7, 101.1, 50.0, 21.9, 20.1, 18.6.

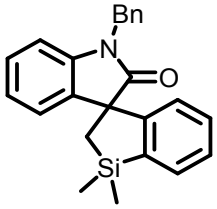
2-(5-fluoro-2-iodophenyl)-1-(2-methylallyl)-1*H*-indole (4h)



The title compound was prepared in line with **GP2**, purified on flash column chromatography using petroleum ether as the eluent, and was obtained as a colorless oil in an overall yield of 20%. R_f = 0.76 (petroleum ether). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 8.5 Hz, 1H), 7.26 (td, *J* = 1.0 Hz, 7.0 Hz, 1H), 7.19-7.14 (m, 2H), 6.90 (td, *J* = 3.0 Hz, 8.5 Hz, 1H), 6.54 (s, 1H), 4.80-4.79 (m, 1H), 4.52-4.43 (m, 3H), 1.55 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.4 (d, *J* = 247.5 Hz), 140.9, 140.8, 140.3 (d, *J* = 8.0 Hz), 140.1 (d, *J* = 8.1 Hz), 136.8, 127.6, 122.1, 120.9, 120.0, 119.2 (d, *J* = 21.9 Hz), 117.5 (d, *J* = 21.6 Hz), 112.0, 110.5, 103.0, 94.4 (d, *J* = 3.5 Hz), 50.0, 20.0.

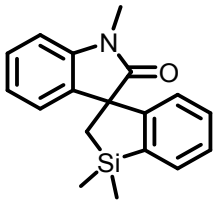
9. Characterization of the Products

1'-benzyl-1,1-dimethyl-1,2-dihydrospiro[benzo[*b*]silole-3,3'-indolin]-2'-one (**3a**):



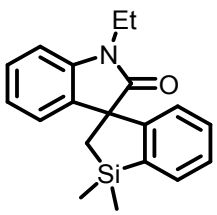
White solid, Mp = 109.2-110.8 °C. R_f = 0.51 (petroleum ether : EtOAc = 30:1). Yield = 81%, m = 59.8 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.0 Hz, 1H), 7.32-7.29 (m, 6H), 7.23-7.18 (m, 2H), 7.04-7.00 (m, 2H), 6.81 (d, *J* = 8.0 Hz, 1H), 6.59 (d, *J* = 7.5 Hz, 1H), 5.06 (d, *J* = 15.5 Hz, 1H), 4.84 (d, *J* = 15.5 Hz, 1H), 1.67 (d, *J* = 15.5 Hz, 1H), 1.36 (d, *J* = 15.0 Hz, 1H), 0.64 (s, 3H), 0.51 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 180.6, 151.7, 142.6, 141.2, 137.6, 136.2, 132.4, 130.1, 128.8, 127.8, 127.6, 127.4, 127.3, 124.7, 123.6, 123.1, 109.0, 59.6, 43.8, 24.4, -0.1, -0.6. **HRMS** (ESI-TOF) *m/z*: calcd for $C_{24}H_{24}NOSi^+$ $(M + H)^+$: 370.1622, found: 370.1629.

1,1,1'-trimethyl-1,2-dihydrospiro[benzo[*b*]silole-3,3'-indolin]-2'-one (**3b**)



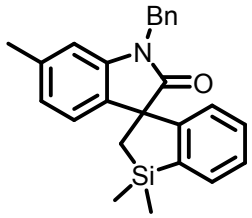
White solid, Mp = 135.5-137.0 °C. R_f = 0.53 (petroleum ether : EtOAc = 30:1). Yield = 65%, m = 38.2 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.0 Hz, 1H), 7.31 (td, *J* = 1.5 Hz, 7.5 Hz, 1H), 7.29-7.26 (m, 1H), 7.19 (td, *J* = 1.5 Hz, 8.0 Hz 1H), 7.07-7.02 (m, 2H), 6.93 (d, *J* = 7.5 Hz, 1H), 6.57 (d, *J* = 7.5 Hz, 1H), 3.26 (s, 3H), 1.59 (d, *J* = 15.5 Hz, 1H), 1.30 (d, *J* = 15.0 Hz, 1H), 0.62 (s, 3H), 0.49 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 180.5, 151.6, 143.6, 141.1, 137.5, 132.2, 130.1, 127.9, 127.4, 124.7, 123.5, 123.0, 107.9, 59.6, 26.5, 24.3, -0.1, -0.6. **HRMS** (ESI-TOF) *m/z*: calcd for $C_{18}H_{20}NOSi^+$ $(M + H)^+$: 294.1309, found: 294.1312.

1'-ethyl-1,1-dimethyl-1,2-dihydrospiro[benzo[*b*]silole-3,3'-indolin]-2'-one (**3c**)



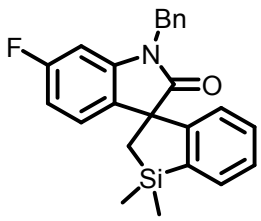
White solid, **Mp** = 88.5-90.6 °C. R_f = 0.51 (petroleum ether : EtOAc = 30:1). Yield = 67%, m = 41.2 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.0 Hz, 1H), 7.56-7.51 (m 2H), 7.44 (td, *J* = 1.0 Hz, 7.0 Hz, 1H), 7.31-7.27 (m, 2H), 7.20 (d, *J* = 8.0 Hz, 1H), 6.81 (d, *J* = 7.5 Hz, 1H), 4.12-3.99 (m, 2H), 1.84 (d, *J* = 15.0 Hz, 1H), 1.58-1.54 (m, 4H), 0.87 (s, 3H), 0.74 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 180.0, 151.6, 142.5, 141.0, 137.8, 132.1, 130.0, 127.7, 127.2, 124.5, 123.6, 122.7, 108.0, 59.4, 34.7, 23.9, 12.6, -0.2, -0.7. **HRMS** (ESI-TOF) *m/z*: calcd for $C_{19}H_{22}NOSi^+$ $(M + H)^+$: 308.1465, found: 308.1468.

1'-benzyl-1,1,6'-trimethyl-1,2-dihydrospiro[benzo[*b*]silole-3,3'-indolin]-2'-one (3e)



White solid, **Mp** = 147.1-148.6 °C. R_f = 0.48 (petroleum ether : EtOAc = 30:1). Yield = 73 %, m = 56 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.5 Hz, 1H), 7.37-7.29 (m, 6H), 7.23 (td, *J* = 1.0 Hz, 7.5 Hz, 1H), 6.93 (d, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 7.5 Hz, 1H), 6.65 (s, 1H), 6.63 (d, *J* = 7.5 Hz, 1H), 5.06 (d, *J* = 15.5 Hz, 1H), 4.84 (d, *J* = 15.5 Hz, 1H), 2.34 (s, 3H), 1.67 (d, *J* = 15.0 Hz, 1H), 1.36 (d, *J* = 15.0 Hz, 1H), 0.65 (s, 3H), 0.52 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 180.8, 151.8, 142.7, 141.0, 137.8, 136.3, 134.6, 132.2, 130.0, 128.7, 127.4, 127.3, 127.1, 124.6, 123.5, 123.2, 109.7, 59.3, 43.6, 24.4, 21.7, -0.2, -0.7. **HRMS** (ESI-TOF) *m/z*: calcd for $C_{25}H_{26}NOSi^+$ $(M + H)^+$: 384.1778, found: 384.1792.

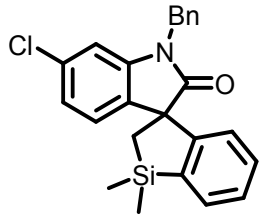
1'-benzyl-6'-fluoro-1,1-dimethyl-1,2-dihydrospiro[benzo[*b*]silole-3,3'-indolin]-2'-one (3f)



White solid, **Mp** = 127.3-131.9 °C. R_f = 0.49 (petroleum ether : EtOAc = 30:1). Yield

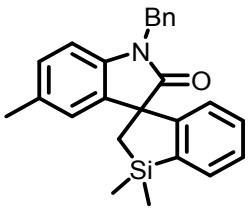
= 71%, m = 55.0 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.5 Hz, 1H), 7.37-7.29 (m, 6H), 7.24 (td, *J* = 1.0 Hz, 7.5 Hz, 1H), 6.98-6.95 (m, 1H), 6.71 (td, *J* = 2.0 Hz, 9.5 Hz, 1H), 6.60 (d, *J* = 8.0 Hz, 1H), 6.55 (td, *J* = 2.0 Hz, 8.0 Hz, 1H), 5.04 (d, *J* = 15.5 Hz, 1H), 4.81 (d, *J* = 16.0 Hz, 1H), 1.68 (d, *J* = 15.0 Hz, 1H), 1.35 (d, *J* = 15.5 Hz, 1H), 0.66 (s, 3H), 0.51 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 180.8, 162.6 (d, *J* = 243.0 Hz), 151.4, 144.0 (d, *J* = 11.5 Hz), 141.2, 135.7, 132.8 (d, *J* = 2.9 Hz), 132.5, 130.2, 128.9, 127.8, 127.6, 127.3, 124.6,124.5 (d, *J* = 9.6 Hz), 109.1 (d, *J* = 22.1 Hz), 97.7 (d, *J* = 27.4 Hz), 59.2, 44.0, 24.6, -0.1, -0.6. **HRMS** (ESI-TOF) *m/z*: calcd for $C_{24}H_{22}FNNaOSi^+$ $(M + Na)^+$: 410.1347, found: 410.1347.

1'-benzyl-6'-chloro-1,1-dimethyl-1,2-dihydrospiro[benzo[*b*]silole-3,3'-indolin]-2'-one (3g)



White solid, **Mp** = 148.3-148.7 °C. R_f = 0.47 (petroleum ether : EtOAc = 30:1). Yield = 76%, m = 61.4 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.0 Hz, 1H), 7.36-7.29 (m, 6H), 7.26 (td, *J* = 1.5 Hz, 7.5 Hz, 1H), 7.15 (dd, *J* = 2.0 Hz, 8.5 Hz, 1H), 7.03 (d, *J* = 2.0 Hz, 1H), 6.72 (d, *J* = 8.5 Hz, 1H), 6.61 (d, *J* = 8.0 Hz, 1H), 5.05 (d, *J* = 15.5 Hz, 1H), 4.84 (d, *J* = 15.5 Hz, 1H), 1.69 (d, *J* = 15.0 Hz, 1H), 1.36 (d, *J* = 15.0 Hz, 1H), 0.67 (s, 3H), 0.53 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 180.0, 150.7, 141.1, 141.0, 139.1, 135.7, 132.4, 130.2, 128.8, 128.3, 127.7, 127.6, 127.6, 127.2, 124.6, 124.0, 109.9, 59.6, 43.8, 24.4, -0.2, -0.7. **HRMS** (ESI-TOF) m/z: calcd for $C_{24}H_{22}ClNNaOSi^+$ $(M + Na)^+$: 426.1051, found: 426.1051.

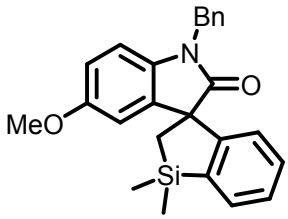
1'-benzyl-1,1,5'-trimethyl-1,2-dihydrospiro[benzo[*b*]silole-3,3'-indolin]-2'-one (3h)



White solid, **Mp** = 126.7-128.8 °C. R_f = 0.53 (petroleum ether : EtOAc = 30:1). Yield

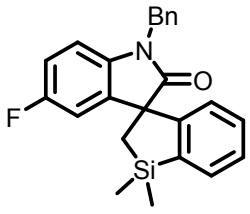
= 80%, m = 61.3 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.5 Hz, 1H), 7.36-7.28 (m, 6H), 7.25 (td, *J* = 1.0 Hz, 7.5 Hz, 1H), 7.01 (d, *J* = 9.0 Hz, 1H), 6.89 (s, 1H), 6.72 (d, *J* = 8.0 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 5.07 (d, *J* = 15.5 Hz, 1H), 4.85 (d, *J* = 15.5 Hz, 1H), 2.28 (s, 3H), 1.70 (d, *J* = 15.0 Hz, 1H), 1.39 (d, *J* = 15.0 Hz, 1H), 0.67 (s, 3H), 0.54 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 180.4, 151.7, 141.1, 140.1, 137.5, 136.2, 132.5, 132.2, 130.0, 128.7, 127.9, 127.4, 127.3, 127.2, 124.7, 124.2, 108.6, 59.6, 43.7, 24.3, 21.0, -0.2, -0.6. **HRMS** (ESI-TOF) m/z: calcd for $C_{25}H_{25}NNaOSi^+$ (M + Na)$^+$: 406.1598, found: 406.1596.

1'-benzyl-5'-methoxy-1,1-dimethyl-1,2-dihydrospiro[benzo[*b*]silole-3,3'-indolin]-2'-one (3i)



White solid, **Mp** = 107.7-109.6 °C. R_f = 0.43 (petroleum ether : EtOAc = 10:1). Yield = 79%, m = 63.1 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.5 Hz, 1H), 7.32-7.25 (m, 6H), 7.20 (td, *J* = 1.5 Hz, 8.0 Hz, 1H), 6.69-6.65 (m, 2H), 6.61-6.58 (m, 2H), 5.00 (d, *J* = 15.5 Hz, 1H), 4.79 (d, *J* = 15.5 Hz, 1H), 3.67 (s, 3H), 1.65 (d, *J* = 15.0 Hz, 1H), 1.32 (d, *J* = 15.0 Hz, 1H), 0.61 (s, 3H), 0.48 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 180.3, 156.3, 151.5, 141.1, 138.7, 136.2, 136.0, 132.3, 130.1, 128.7, 127.5, 127.4, 127.2, 124.7, 112.2, 110.6, 109.3, 60.0, 55.7, 43.8, 24.5, -0.2, -0.6. **HRMS** (ESI-TOF) m/z: calcd for $C_{25}H_{26}NNaO_2Si^+$ (M + Na)$^+$: 422.1547, found: 422.1545.

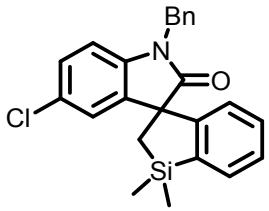
1'-benzyl-5'-fluoro-1,1-dimethyl-1,2-dihydrospiro[benzo[*b*]silole-3,3'-indolin]-2'-one (3j)



White solid, **Mp** = 121.0-122.6 °C. R_f = 0.50 (petroleum ether : EtOAc = 30:1). Yield = 74%, m = 57.3 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.5 Hz, 1H), 7.36-

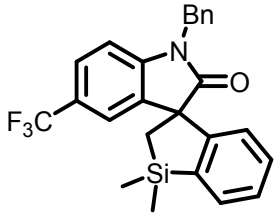
7.28 (m, 6H), 7.26-7.23 (m, 1H), 6.88 (td, *J* = 2.5 Hz, 8.5 Hz, 1H), 6.78 (dd, *J* = 2.5 Hz, 8.0 Hz, 1H), 6.70 (q, *J* = 4.0 Hz, 1H), 6.61 (d, *J* = 8.0 Hz, 1H), 5.05 (d, *J* = 15.5 Hz, 1H), 4.84 (d, *J* = 16.0 Hz, 1H), 1.79 (d, *J* = 15.0 Hz, 1H), 1.34 (d, *J* = 15.0 Hz, 1H), 0.65 (s, 3H), 0.51 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 180.2, 159.6 (d, *J* = 239.5 Hz), 150.9, 141.1, 139.0 (d, *J* = 7.7 Hz), 138.4 (d, *J* = 2.0 Hz), 135.8, 132.4, 130.2, 128.8, 127.6, 127.5, 127.2, 124.6, 113.9 (d, *J* = 23.3 Hz), 111.5 (d, *J* = 24.4 Hz) ,109.4 (d, *J* = 8.0 Hz), 59.8 (d, *J* = 1.9 Hz), 43.8, 24.4, -0.2, -0.7. **HRMS** (ESI-TOF) *m/z*: calcd for $C_{24}H_{23}FNOSi^+$ $(M + H)^+$: 387.1524, found: 387.1530.

1'-benzyl-5'-chloro-1,1-dimethyl-1,2-dihydrospiro[benzo[*b*]silole-3,3'-indolin]-2'-one (3k)



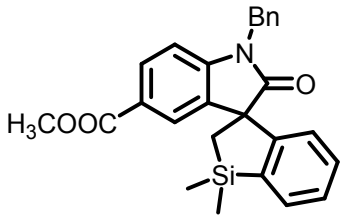
White solid, **Mp** = 137.0-139.0 °C. R_f = 0.47 (petroleum ether : EtOAc = 30:1). Yield = 74%, m = 59.5 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.0 Hz, 1H), 7.37-7.29 (m, 6H), 7.24 (td, *J* = 1.0 Hz, 7.5 Hz, 1H), 6.99 (td, *J* = 1.5 Hz, 8.0 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 6.81 (d, *J* = 1.5 Hz, 1H), 6.60 (d, *J* = 7.5 Hz, 1H), 5.03 (d, *J* = 15.5 Hz, 1H), 4.82 (d, *J* = 15.5 Hz, 1H), 1.67 (d, *J* = 15.0 Hz, 1H), 1.34 (d, *J* = 15.0 Hz, 1H), 0.65 (s, 3H), 0.51 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 180.5, 151.1, 143.8, 141.2, 135.9, 135.7, 133.4, 132.5, 130.2, 129.0, 127.8, 127.6, 127.3, 124.6, 124.5, 123.0, 109.5, 59.2, 43.9, 24.5, -0.1, -0.6. **HRMS** (ESI-TOF) *m/z*: calcd for $C_{24}H_{23}ClNOSi^+$ $(M + H)^+$: 404.1232, found: 404.1236.

1'-benzyl-1,1-dimethyl-5'-(trifluoromethyl)-1,2-dihydrospiro[benzo[*b*]silole-3,3'-indolin]-2'-one (3l)



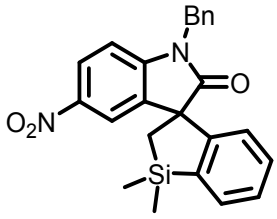
White solid, **Mp** = 128.4-129.2 °C. R_f = 0.45 (petroleum ether : EtOAc = 30:1). Yield = 63%, m = 55.1 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.0 Hz, 1H), 7.35 (d, *J* = 6.0 Hz, 1H), 7.35-7.32 (m, 3H), 7.32-7.29 (m, 4H), 7.26-7.25 (m, 1H), 6.89 (d, *J* = 8.5 Hz, 1H), 6.57 (d, *J* = 7.5 Hz, 1H), 5.08 (d, *J* = 15.5 Hz, 1H), 4.88 (d, *J* = 15.5 Hz, 1H), 1.68 (d, *J* = 15.0 Hz, 1H), 1.40-1.37 (d, *J* = 15.0 Hz, 1H), 0.66 (s, 3H), 0.53 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 180.3, 150.5, 145.6, 141.3, 137.9, 135.5, 132.5, 130.3, 128.9, 127.8, 127.7, 127.2, 125.5 (q, *J* = 3.9 Hz), 125.5 (q, *J* = 32.6 Hz), 124.5, 124.3 (q, *J* = 268.9 Hz), 120.6 (q, *J* = 3.5 Hz), 108.7, 59.4, 43.9, 24.6, -0.3, -0.7. **HRMS** (ESI-TOF) *m/z*: calcd for $C_{25}H_{23}F_3NOSi^+$ $(M + H)^+$: 438.1496, found: 438.1500.

Methyl 1'-benzyl-1,1-dimethyl-2'-oxo-1,2-dihydrospiro[benzo[*b*]silole-3,3'-indoline]-5'-carboxylate (3m)



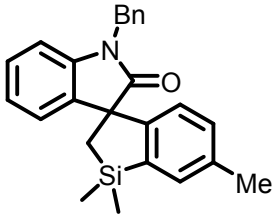
White solid, **Mp** = 147.4-148.3 °C. R_f = 0.54 (petroleum ether : EtOAc = 5 :1). Yield = 47%, m = 40.2 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 1.5 Hz, 8.5 Hz, 1H), 7.70 (d, *J* = 1.5 Hz, 1H), 7.67 (d, *J* = 7.0 Hz, 1H), 7.34-7.28 (m, 6H), 7.21 (td, *J* = 1.0 Hz, 7.5 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.53 (d, *J* = 8.0 Hz, 1H), 5.05 (d, *J* = 16.0 Hz, 1H), 4.86 (d, *J* = 8.0 Hz, 1H), 3.83 (s, 3H), 1.64 (d, *J* = 15.0 Hz, 1H), 1.39 (d, *J* = 15.5 Hz, 1H), 0.63 (s, 3H), 0.52 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 180.7, 166.8, 150.8, 146.8, 141.3, 137.5, 135.6, 132.5, 130.5, 130.2, 128.9, 127.8, 127.2, 125.0, 124.9, 124.6, 108.5, 59.3, 51.9, 43.9, 24.5, -0.3, -0.6. **HRMS** (ESI-TOF) *m/z*: calcd for $C_{26}H_{26}NO_3Si^+$ $(M + H)^+$: 428.1676, found: 428.1676.

1'-benzyl-1,1-dimethyl-5'-nitro-1,2-dihydrospiro[benzo[*b*]silole-3,3'-indolin]-2'-one (3n)



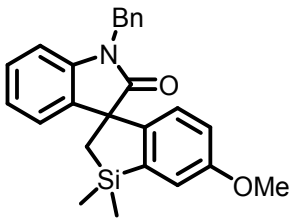
Yellow solid, **Mp** = 80.7-81.9 °C. R_f = 0.56 (petroleum ether : EtOAc = 5 :1). Yield = 31%, m = 25.7 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.15 (dd, *J* = 2.0 Hz, 8.5 Hz, 1H), 7.90 (d, *J* = 2.5 Hz, 1H), 7.68 (d, *J* = 7.0 Hz, 1H), 7.37-7.26 (m, 6H), 7.23 (td, *J* = 1.0 Hz, 7.5 Hz, 1H), 6.86 (d, *J* = 9.0 Hz, 1H), 6.52 (d, *J* = 7.5 Hz, 1H), 5.07 (d, *J* = 15.5 Hz, 1H), 4.89 (d, *J* = 15.5 Hz, 1H), 1.67 (d, *J* = 15.5 Hz, 1H), 1.39 (d, *J* = 15.5 Hz, 1H), 0.63 (s, 3H), 0.54 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 180.4, 149.8, 148.3, 143.9, 141.3, 138.4, 135.0, 132.7, 130.4, 129.0, 128.1, 128.0, 127.2, 125.0, 124.4, 119.5, 108.5, 59.3, 44.1, 24.6, -0.3, -0.7. **HRMS** (ESI-TOF) *m/z*: calcd for $C_{24}H_{23}N_2O_3Si^+$ $(M + H)^+$: 415.1472, found: 415.1475.

1'-benzyl-1,1,6-trimethyl-1,2-dihydrospiro[benzo[*b*]silole-3,3'-indolin]-2'-one (3o)



White solid, **Mp** = 142.0-143.9 °C. R_f = 0.51 (petroleum ether : EtOAc = 30 :1). Yield = 72%, m = 55.2 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.46 (s, 1H), 7.34-7.29 (m, 4H), 7.28-7.26 (m, 1H), 7.17 (td, *J* = 2.0 Hz, 8.0 Hz, 1H), 7.04-6.99 (m, 3H), 6.79 (d, *J* = 8.0 Hz, 1H), 6.48 (d, *J* = 8.0 Hz, 1H), 5.05 (d, *J* = 15.5 Hz, 1H), 4.82 (d, *J* = 15.5 Hz, 1H), 2.35 (s, 3H), 1.65 (d, *J* = 15.0 Hz, 1H), 1.35 (d, *J* = 15.0 Hz, 1H), 0.62 (s, 3H), 0.48 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 180.7, 148.8, 142.6, 141.1, 137.6, 136.9, 136.2, 132.8, 131.2, 128.7, 127.6, 127.5, 127.3, 124.4, 123.5, 123.0, 108.9, 59.1, 43.7, 24.5, 21.1, -0.18, -0.6. **HRMS** (ESI-TOF) m/z: calcd for $C_{25}H_{25}NNaOSi^+$ $(M + Na)^+$: 406.1598, found: 406.1597.

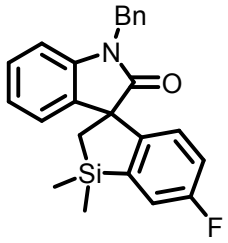
1'-benzyl-6-methoxy-1,1-dimethyl-1,2-dihydrospiro[benzo[*b*]silole-3,3'-indolin]-2'-one (3p)



White solid, **Mp** = 134.3-136.0 °C. R_f = 0.48 (petroleum ether : EtOAc = 10 :1). Yield

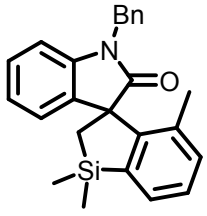
= 63%, m = 53.5 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.34-7.30 (m, 4H), 7.28-7.25 (m, 1H), 7.17 (td, *J* = 2.0 Hz, 8.0 Hz, 1H), 7.14 (d, *J* = 3.0 Hz, 1H), 7.04-6.99 (m, 2H), 6.80-6.76 (m, 2H), 6.50 (d, *J* = 8.5 Hz, 1H), 5.05 (d, *J* = 15.5 Hz, 1H), 4.83 (d, *J* = 15.5 Hz, 1H), 3.82 (s, 3H), 1.66 (d, *J* = 15.0 Hz, 1H), 1.37 (d, *J* = 15.0 Hz, 1H), 0.64 (s, 3H), 0.50 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 180.8, 159.1, 143.7, 142.9, 142.6, 137.6, 136.2, 128.8, 127.7, 127.6, 127.3, 125.7, 123.5, 123.0, 117.0, 115.9, 109.0, 58.8, 55.4, 43.7, 24.9, -0.2, -0.6. **HRMS** (ESI-TOF) *m/z*: calcd for $C_{25}H_{26}NO_2Si^+$ $(M + H)^+$: 400.1727, found: 400.1725.

1'-benzyl-6-fluoro-1,1-dimethyl-1,2-dihydrospiro[benzo[*b*]silole-3,3'-indolin]-2'-one (3q)



White solid, **Mp** = 117.3-118.6 °C. R_f = 0.48 (petroleum ether : EtOAc = 30 :1). Yield = 63%, m = 50.4 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.34-7.26 (m, 6H), 7.20-7.16 (m, 1H), 7.01 (d, *J* =4.0 Hz, 2H), 6.89 (td, *J* = 2.5 Hz, 8.5 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.52 (q, *J* = 4.5 Hz, 1H), 5.03 (d, *J* = 15.5 Hz, 1H), 4.83 (d, *J* = 16.0 Hz, 1H), 1.68 (d, *J* = 15.0 Hz, 1H), 1.37 (d, *J* = 15.0 Hz, 1H), 0.63 (s, 3H), 0.49 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 180.3, 162.5 (d, *J* = 246.8 Hz), 147.0, 144.1 (d, *J* = 5.0 Hz), 142.5, 137.2, 136.1, 128.8, 127.9, 127.6, 127.3, 126.3 (d, *J* = 7.8 Hz), 123.5, 123.1, 118.0 (d, *J* = 18.9 Hz), 117.4 (d, *J* = 22.8 Hz), 109.0, 58.9, 43.8, 24.9, -0.3, -0.8. **HRMS** (ESI-TOF) *m/z*: calcd for $C_{24}H_{22}FNNaOSi^+$ $(M + Na)^+$: 410.1347, found: 410.1345.

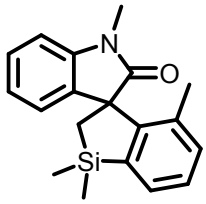
1'-benzyl-1,1,4-trimethyl-1,2-dihydrospiro[benzo[*b*]silole-3,3'-indolin]-2'-one (3r)



White solid, **Mp** = 169.4-170.4 °C. R_f = 0.51 (petroleum ether : EtOAc = 30 :1). Yield = 81%, m = 62.1 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.0 Hz, 1H), 7.41(d,

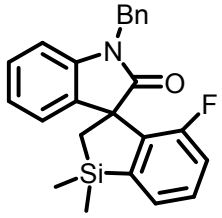
J = 7.5 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.30-7.24 (m, 2H), 7.17 (d, *J* = 8.0 Hz, 1H), 7.06 (d, *J* = 7.5 Hz, 1H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.85-6.83 (m, 2H), 5.21 (d, *J* = 15.5 Hz, 1H), 4.85 (d, *J* = 15.5 Hz, 1H), 1.76 (d, *J* = 15.0 Hz, 1H), 1.60 (s, 3H), 1.30-1.27 (d, *J* = 15.0 Hz, 1H), 0.51-0.49 (d, *J* = 12.5 Hz, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 181.0, 148.3, 142.4, 141.8, 136.7, 136.1, 135.3, 132.8, 129.6, 128.7, 128.0, 127.6, 127.6, 127.3, 122.9, 122.7, 108.9, 59.7, 44.0, 27.3, 19.1, -0.2, -0.7. **HRMS** (ESI-TOF) *m/z*: calcd for $C_{25}H_{25}NNaOSi^+$ $(M + Na)^+$: 406.1598, found: 406.1596.

1,1,1',4-tetramethyl-1,2-dihydrospiro[benzo[*b*]silole-3,3'-indolin]-2'-one (3s)



White solid, **Mp** = 144.6-145.5 °C. R_f = 0.47 (petroleum ether : EtOAc = 30 :1). Yield = 65%, m = 40.0 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.0 Hz, 1H), 7.28-7.22 (m, 2H), 7.05 (d, *J* = 7.0 Hz, 1H), 6.97 (td, *J* = 1.0 Hz, 8.0 Hz, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.83 (dd, *J* = 1.0 Hz, 7.5 Hz, 1H), 3.33 (s, 3H), 1.66 (d, *J* = 15.0 Hz, 1H), 1.60 (s, 3H), 1.20 (d, *J* = 15.0 Hz, 1H), 0.48 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 181.1, 148.6, 142.8, 142.2, 136.6, 135.2, 132.9, 129.7, 128.0, 127.5, 123.0, 122.8, 107.9, 59.5, 26.6, 26.5, 18.8, -0.1, -0.7. **HRMS** (ESI-TOF) *m/z*: calcd for $C_{19}H_{22}NOSi^+$ $(M + H)^+$: 308.1465, found: 308.1467.

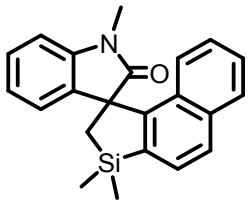
1'-benzyl-4-fluoro-1,1-dimethyl-1,2-dihydrospiro[benzo[*b*]silole-3,3'-indolin]-2'-one (3t)



White solid, **Mp** = 71.9-72.8 °C. R_f = 0.49 (petroleum ether : EtOAc = 30 :1). Yield = 70%, m = 52.3 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.40-7.27 (m, 7H), 7.13 (td, *J* = 1.0 Hz, 7.5 Hz, 1H), 6.95-6.88 (m, 3H), 6.75 (d, *J* = 7.5 Hz, 1H), 5.09 (d, *J* = 15.5 Hz, 1H), 4.97 (d, *J* = 15.5 Hz, 1H), 1.77 (d, *J* = 15.0 Hz, 1H), 1.32 (d, *J* = 15.0 Hz, 1H), 0.54 (s,

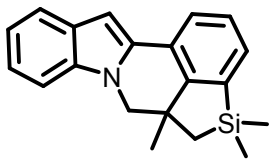
6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 180.3, 159.3 (d, *J* = 251.6 Hz), 145.1, 142.0, 137.3 (d, *J* = 11.1 Hz), 136.2, 136.0, 130.2 (d, *J* = 6.3 Hz), 128.7, 127.6, 127.5, 127.5, 127.4, 127.2 (d, *J* = 1.7 Hz), 122.6 (d, *J* = 4.5 Hz), 116.9 (d, *J* = 20.6 Hz), 109.1, 56.7, 44.1, 25.4, -0.3, -0.8. **HRMS** (ESI-TOF) *m/z*: calcd for $C_{24}H_{22}FNNaOSi^+$ $(M + Na)^+$: 410.1347, found: 410.1345.

1,3',3'-trimethyl-2',3'-dihydrospiro[indoline-3,1'-naphtho[2,1-*b*]silol]-2-one (3u)



White solid, **Mp** = 213.8-218.9 °C. R_f = 0.53 (petroleum ether : EtOAc = 10 :1). Yield = 70%, m = 48.1 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 8.5 Hz, 1H), 7.35 (s, 1H), 7.29 (td, *J* = 1.0 Hz, 7.5 Hz, 1H), 7.18-7.15 (s, 1H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.92 (td, *J* = 0.5 Hz, 7.5 Hz,1H), 6.83 (s, 2H), 3.44 (s, 3H), 1.78 (d, *J* = 14.5 Hz, 1H), 1.33 (d, *J* = 15.0 Hz, 1H), 0.54 (d, *J* = 8.0 Hz, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 181.5, 146.5, 142.1, 141.3, 138.0, 135.3, 130.2, 128.9, 128.9, 127.6, 127.5, 126.4, 125.9, 123.5, 122.9, 122.7, 108.3, 59.9, 27.5, 26.7, -0.3, -0.8. **HRMS** (ESI-TOF) *m/z*: calcd for $C_{22}H_{22}NOSi^+$ $(M + H)^+$: 344.1465, found: 344.1467.

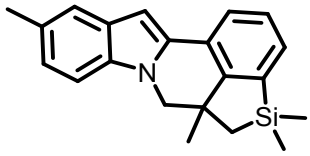
4,4,5a-trimethyl-4,5,5a,6-tetrahydroindolo[2,1-*a*]silolo[4,3,2-*de*]isoquinoline (5a)



Yellow solid, **Mp** = 161.9-163.8 °C. R_f = 0.71 (petroleum ether). Yield = 58%, m = 35.2 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 1.5 Hz, 7.5 Hz, 1H), 7.67-7.65 (m, 1H), 7.48 (dd, *J* = 1.5 Hz, 7.5 Hz, 1H), 7.38-7.33 (m, 2H), 7.25-7.21 (m, 1H), 7.14-7.11 (td, *J* = 1.0 Hz, 7.5 Hz, 1H), 6.91 (s, 1H), 4.41 (d, *J* = 11.5 Hz, 1H), 3.83 (d, *J* = 11.5 Hz, 1H), 1.27 (d, *J* = 14.0 Hz, 1H), 1.18 (s, 3H), 1.09 (d, *J* = 14.0 Hz, 1H), 0.48 (s, 3H), 0.41 (s, 3H) . **^{13}C NMR** (125 MHz, $CDCl_3$) δ 151.8, 137.8, 136.9, 135.0, 131.4, 128.8, 127.5, 126.1, 125.0, 121.5, 120.7, 119.6, 108.9, 96.4, 54.6, 43.3, 28.7, 25.7, -0.1, -1.1. **HRMS** (ESI-TOF) *m/z*: calcd for $C_{20}H_{22}NSi^+$ $(M + H)^+$: 304.1516, found:

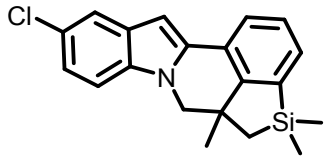
304.1524.

4,4,5a,10-tetramethyl-4,5,5a,6-tetrahydroindolo[2,1-*a*]silolo[4,3,2-*de*]isoquinoline (5b)



Yellow solid, **Mp** = 192.3-193.1 °C. R_f = 0.73 (petroleum ether). Yield = 45%, m = 28.6 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 1.0 Hz, 7.5 Hz, 1H), 7.46 (dd, *J* = 1.0 Hz, 7.5 Hz, 1H), 7.44 (s, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.26-7.24 (m, 1H), 7.05 (dd, *J* = 1.5 Hz, 8.5 Hz, 1H), 6.81 (s, 1H), 4.36 (d, *J* = 11.5 Hz, 1H), 3,80 (d, *J* = 11.5 Hz, 1H), 2.47 (s, 3H), 1.25 (d, *J* = 14.0 Hz, 1H), 1.16 (s, 3H), 1.08 (d, *J* = 14.0 Hz, 1H), 0.46 (s, 3H), 0.40 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 151.8, 137.8, 135.4, 135.0, 131.3, 129.1, 128.8, 127.5, 126.3, 124.9, 123.2, 120.3, 108.6, 95.9, 54.7, 43.4, 28.7, 25.7, 21.4, -0.1, -1.1. **HRMS** (ESI-TOF) *m/z*: calcd for $C_{21}H_{24}NSi^+$ $(M + H)^+$: 318.1673, found: 318.1677.

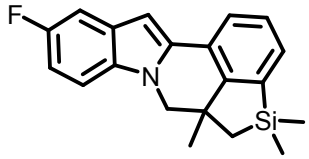
10-chloro-4,4,5a-trimethyl-4,5,5a,6-tetrahydroindolo[2,1-*a*]silolo[4,3,2 *de*]isoquinoline (5c)



Yellow solid, **Mp** = 191.6-194.0 °C. R_f = 0.69 (petroleum ether). Yield = 50%, m = 33.8 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 1.0 Hz, 7.5 Hz, 1H), 7.59 (d, *J* = 2.0 Hz, 1H), 7.48 (dd, *J* = 1.0 Hz, 7.0 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.25 (d, *J* = 9.0 Hz, 1 H), 7.15 (dd, *J* = 2.0 Hz, 8.5 Hz, 1H), 6.82 (s, 1H), 4.33 (d, *J* = 12.0 Hz, 1H), 3.80 (d, *J* = 12.0 Hz, 1H), 1.25 (d, *J* = 14.5 Hz, 1H), 1.15 (s, 3H), 1.07 (d, *J* = 14.0 Hz, 1H), 0.46 (s, 3H), 0.40 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 151.8, 137.9, 136.3, 135.4, 131.9, 129.7, 127.6, 125.7, 125.2, 125.1, 121.8, 119.9, 109.8, 95.9, 54.8, 43.3, 28.7, 25.7, -0.2, -1.1. **HRMS** (ESI-TOF) *m/z*: calcd for $C_{20}H_{21}ClNSi^+$ $(M + H)^+$: 338.1126, found: 338.1135.

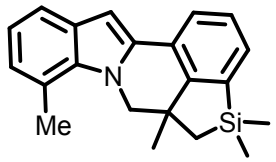
10-fluoro-4,4,5a-trimethyl-4,5,5a,6-tetrahydroindolo[2,1-*a*]silolo[4,3,2-

***de*]isoquinoline (5d)**



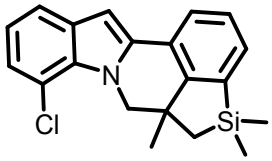
Yellow solid, **Mp** = 178.7-179.5 °C. R_f = 0.70 (petroleum ether). Yield = 55%, m = 35.4 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 1.0 Hz, 7.5 Hz, 1H), 7.49 (dd, *J* = 1.0 Hz, 7.0 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.29 (dd, *J* = 2.5 Hz, 9.5 Hz, 1H), 7.25 (t, *J* = 4.5 Hz, 1H), 6.96 (td, *J* = 2.5 Hz, 9.0 Hz, 1H), 6.85 (s, 1H), 4.33 (d, *J* = 11.5 Hz, 1H), 3.80 (d, *J* = 12.0 Hz, 1H), 1.26 (d, *J* = 14.0 Hz, 1H), 1.17 (s, 3H), 1.08 (d, *J* = 14.5 Hz, 1H), 0.47 (s, 3H), 0.41 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 157.9 (d, *J* = 232.8 Hz), 151.7, 137.8, 136.5, 133.6, 131.7, 128.9 (d, *J* = 10.3 Hz), 127.6, 125.8, 125.1, 109.8 (d, *J* = 26.3 Hz), 109.3 (d, *J* = 9.8 Hz), 105.3 (d, *J* = 23.4 Hz), 96.3 (d, *J* = 4.9 Hz), 54.8, 43.3, 28.7, 25.7, -0.1, -1.1. **HRMS** (ESI-TOF) *m/z*: calcd for $C_{20}H_{21}FNSi^+$ $(M + H)^+$: 322.1422, found: 322.1429.

4,4,5a,8-tetramethyl-4,5,5a,6-tetrahydroindolo[2,1-*a*]silolo[4,3,2-*de*]isoquinoline (5e)



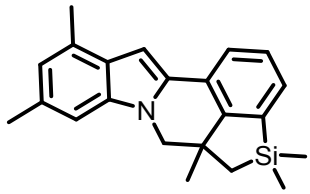
Yellow solid, **Mp** = 136.1-136.0 °C. R_f = 0.69 (petroleum ether). Yield = 40%, m = 25.4 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 1.0 Hz, 7.5 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.47 (dd, *J* = 1.0 Hz, 7.0 Hz, 1H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.01-6.98 (m, 1H), 6.93-6.92 (m, 2H), 4.97 (d, *J* = 12.0 Hz, 1H), 4.01 (d, *J* = 11.5 Hz, 1H), 2.82 (s, 3H), 1.24-1.21 (m, 4H), 1.05-1.03 (d, *J* = 14.0 Hz, 1H), 0.48 (s, 3H), 0.41 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 151.5, 137.5, 135.9, 135.3, 131.2, 129.3, 127.5, 126.2, 124.9, 124.8, 120.6, 119.6, 118.9, 97.5, 57.5, 43.4, 28.5, 25.8, 21.1, -0.1, -1.1. **HRMS** (ESI-TOF) m/z: calcd for $C_{21}H_{24}NSi^+$ $(M + H)^+$: 318.1673, found: 318.1671.

8-chloro-4,4,5a-trimethyl-4,5,5a,6-tetrahydroindolo[2,1-*a*]silolo[4,3,2-*de*]isoquinoline (5f)



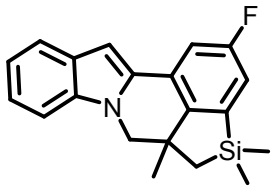
Yellow solid, **Mp** = 143.5-144.6 °C. R_f = 0.68 (petroleum ether). Yield = 44%, m = 29.7 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 1.5 Hz, 8.0 Hz, 1H), 7.72 (dd, *J* = 1.0 Hz, 7.5 Hz, 1H), 7.49 (dd, *J* = 1.5 Hz, 7.5 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.15 (dd, *J* = 1.0 Hz, 7.5 Hz, 1H), 6.99 (t, *J* = 2.5 Hz, 1H), 6.92 (s, 1H), 5.56 (d, *J* = 12.0 Hz, 1H), 3.93 (d, *J* = 12.5 Hz, 1H), 1.25 (d, *J* = 14.0 Hz, 1H), 1.22 (s, 3H), 1.05 (d, *J* = 14.5 Hz, 1H), 0.47 (s, 3H), 0.40 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 152.0, 137.7, 136.7, 132.3, 131.8, 131.7, 127.5, 125.5, 125.2, 123.6, 120.1, 119.4, 116.4, 97.6, 56.6, 43.2, 28.4, 25.7, -0.1, -1.1. **HRMS** (ESI-TOF) *m/z*: calcd for $C_{20}H_{21}ClNSi^+$ $(M + H)^+$: 338.1126, found: 338.1125.

4,4,5a,9,11-pentamethyl-4,5,5a,6-tetrahydroindolo[2,1-*a*]silolo[4,3,2 *de*]isoquinoline (5g)



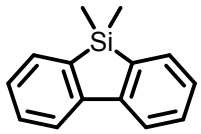
Yellow solid, **Mp** = 118.0-119.3 °C. R_f = 0.68 (petroleum ether). Yield = 40%, m = 26.5 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.5 Hz, 1H), 7.46 (d, *J* = 7.5 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.02 (s, 1H), 6.88 (s, 1H), 6.79 (s, 1H), 4.37 (d, *J* = 12.0 Hz, 1H), 3.79 (d, *J* = 12.0 Hz, 1H), 2.59 (s, 3H), 2.50 (s, 3H), 1.26 (d, *J* = 14.5 Hz, 1H), 1.18 (s, 3H), 1.09 (d, *J* = 14.0 Hz, 1H), 0.48 (s, 3H), 0.41 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 151.6, 137.7, 137.1, 133.9, 131.7, 131.0, 129.8, 127.5, 126.6, 126.4, 124.7, 121.8, 106.5, 94.9, 54.7, 43.3, 28.7, 25.7, 21.9, 18.7, -0.1, -1.1. **HRMS** (ESI-TOF) *m/z*: calcd for $C_{22}H_{26}NSi^+$ $(M + H)^+$: 332.1829, found: 332.1832.

2-fluoro-4,4,5a-trimethyl-4,5,5a,6-tetrahydroindolo[2,1-*a*]silolo[4,3,2-*de*]isoquinoline (5h)



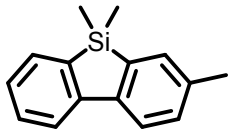
Yellow solid, **Mp** = 105.6-107.6 °C. R_f = 0.72 (petroleum ether). Yield = 40%, m = 25.7 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.5 Hz, 1H), 7.38-7.7.35 (m, 2H), 7.25-7.22 (m, 1H), 7.13-7.09 (m, 2H), 6.88 (s, 1H), 4.38 (d, *J* = 11.5 Hz, 1H), 3.80-3.77 (d, *J* = 12.0 Hz, 1H), 1.28 (d, *J* = 14.0 Hz, 1H), 1.15 (s, 3H), 1.11 (d, *J* = 14.0 Hz, 1H), 0.47 (s, 3H), 0.40 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.8 (d, *J* = 244.6 Hz), 147.2 (d, *J* = 2.3 Hz), 140.7 (d, *J* = 4.3 Hz), 137.0, 134.1, 128.7, 127.9 (d, *J* = 8.4 Hz), 122.0, 120.9, 119.9, 117.2 (d, *J* = 19.5 Hz), 111.6 (d, *J* = 23.9 Hz), 109.0, 97.3, 54.7, 43.0, 28.7, 26.0, -0.3, -1.2. **HRMS** (ESI-TOF) *m/z*: calcd for $C_{20}H_{22}FNSi^+$ $(M + H)^+$: 322.1422, found: 322.1421.

5,5-dimethyl-5H-dibenzo[*b,d*]silole (7a)[6]



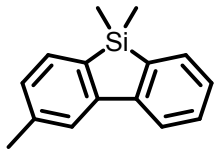
White solid, R_f = 0.71 (petroleum ether). Yield = 64%, m = 16.1 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.5 Hz, 2H), 7.65 (d, *J* = 7.0 Hz, 2H), 7.45 (td, *J* = 1.5 Hz, 7.5 Hz, 2H), 7.31-7.28 (m, 2H), 0.44 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 147.8, 138.9, 132.7, 130.1, 127.3, 120.8, -3.3.

3,5,5-trimethyl-5H-dibenzo[*b,d*]silole (7b)[7]



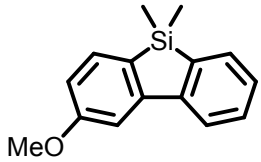
Brownish oil, R_f = 0.72 (petroleum ether). **7b**: Yield = 57%, m = 25.5 mg; Yield = 63%, m = 28.2 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.5 Hz, 1H), 7.74 (d, *J* = 7.5 Hz, 1H), 7.63 (d, *J* = 7.0 Hz, 1H), 7.47 (s, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.28-7.25 (m, 2H), 2.41 (s, 3H), -0.43 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 147.9, 145.2, 139.0, 138.6, 136.9, 133.4, 132.6, 130.9, 130.1, 126.9, 120.6, 120.5, 21.3, -3.2.

2,5,5-trimethyl-5H-dibenzo[*b,d*]silole (7c)[8]



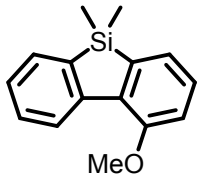
Yellow oil, R_f = 0.70 (petroleum ether). **7c**: Yield = 43%, m = 19.3 mg; Yield = 63%, m = 28.2 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.0 Hz, 1H), 7.66 (s, 1H), 7.63 (d, *J* = 7.0 Hz, 1H), 7.54 (d, *J* = 7.0 Hz, 1H), 7.43 (td, *J* = 1.0 Hz, 7.5 Hz, 1H), 7.28 (t, *J* = 8.0 Hz, 1H), 7.12 (d, *J* = 7.0 Hz, 1H), 2.43 (s, 3H), 0.42 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 148.1, 147.8, 140.1, 139.4, 135.4, 132.6, 132.6, 130.0, 128.3, 127.2, 121.7, 120.7, 21.8, -3.2.

2-methoxy-5,5-dimethyl-5H-dibenzo[*b,d*]silole (7d)



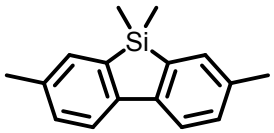
Colorless oil, R_f = 0.59 (petroleum ether). Yield = 50%, m = 24.0 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.5 Hz, 1H), 7.63 (d, *J* = 7.0 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.38 (d, *J* = 2.5 Hz, 1H), 7.29 (t, *J* = 7.5 Hz, 1H), 6.85 (td, *J* = 2.5 Hz, 8.0 Hz, 1H), 3.90 (s, 3H), -0.41 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 161.9, 149.8, 147.4, 140.2, 133.8, 132.6, 130.0, 129.8, 127.5, 120.8, 113.0, 107.0, 55.3, -3.0. **HRMS** (ESI-TOF) *m/z*: calcd for $C_{15}H_{17}OSi^+$ $(M + H)^+$: 241.1043, found: 241.1042

1-methoxy-5,5-dimethyl-5H-dibenzo[*b,d*]silole (7e)[9]



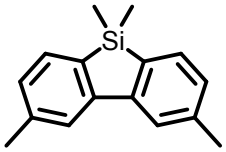
Colorless oil, R_f = 0.57 (petroleum ether). Yield = 40%, m = 25.7 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.56 (d, *J* = 8.0 Hz, 1H), 7.63-7.61 (m, 1H), 7.42 (td, *J* = 1.5 Hz, 7.5 Hz, 1H), 7.30-7.27 (m, 1H), 7.27-7.23 (m, 2H), 7.02 (td, *J* = 1.0 Hz, 8.0 Hz, 1H), 3.99 (s, 3H), 0.41 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 157.3, 147.7, 141.9, 138.9, 135.3, 132.0, 130.1, 128.4, 126.7, 126.4, 124.6, 113.4, 55.2, -3.2.

3,5,5,7-tetramethyl-5H-dibenzo[*b,d*]silole (7f)[10]



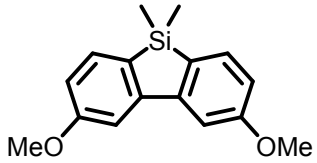
White solid, R_f = 0.69 (petroleum ether). Yield = 50%, m = 23.8 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.43 (s, 2H), 7.23 (d, *J* = 7.0 Hz, 2H), 2.38 (s, 6H), 0.41 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 145.3, 138.7, 136.4, 133.4, 130.9, 120.3, 21.3, -3.2.

2,5,5,8-tetramethyl-5H-dibenzo[*b,d*]silole (7g)[10]



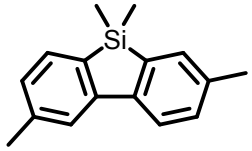
Colorless oil, R_f = 0.75 (petroleum ether). Yield = 44%, m =21.9 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.66 (s, 2H), 7.53 (d, *J* = 7.5 Hz, 2H), 7.12 (d, *J* = 7.0 Hz, 2H), 2.43 (s, 6H), 0.40 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 148.1, 140.0, 135.8, 132.6, 128.2, 121.6, 21.8, -3.1.

2,8-dimethoxy-5,5-dimethyl-5H-dibenzo[*b,d*]silole (7h)[11]



White solid, R_f = 0.51 (petroleum ether). Yield = 44%, m = 23.8 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 2.0 Hz, 2H), 6.85 (dd, *J* = 2.0 Hz, 7.5Hz, 2H), 3.89 (s, 6H), 0.38 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 161.8, 149.4, 133.7, 130.9, 113.0, 107.0, 55.3, -2.8.

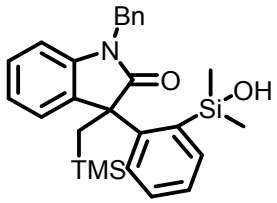
2,5,5,7-tetramethyl-5H-dibenzo[*b,d*]silole (7i)



White solid, **Mp** = 104.8-106.7 °C. R_f = 0.70 (petroleum ether). Yield = 55%, m = 26.2 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.0 Hz, 1H), 7.62 (s, 1H), 7.52 (d, *J* = 7.0 Hz, 1H), 7.44 (s, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.09 (d, *J* = 7.5 Hz, 1H), 2.42 (s, 3H), 2.39 (s, 3H), -0.40 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 148.2, 145.2, 140.0,

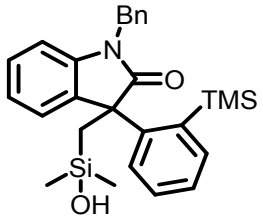
139.4, 136.8, 135.1, 133.4, 132.6, 130.8, 127.8, 121.4, 120.5, 21.8, 21.3, -3.1. **HRMS** (ESI-TOF) *m/z*: calcd for $C_{16}H_{19}Si^+$ $(M + H)^+$:239.1251, found: 239.1255.

1-benzyl-3-(2-(hydroxydimethylsilyl)phenyl)-3-((trimethylsilyl)methyl)indolin-2-one (8a)



White solid, **Mp** = 140.7-145.3 °C. R_f = 0.47 (petroleum ether : EtOAc = 30 :1). Yield = 43%, m = 19.7 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.5 Hz, 1H), 7.29-7.27 (m, 1H), 7.25-7.23 (m, 3H), 7.19-7.14 (m, 4H), 7.09 (t, *J* = 8.0 Hz, 1H), 6.96 (s, 1H), 6.86 (d, *J* = 7.5 Hz, 1H), 6.72 (d, *J* = 8.0 Hz, 1H), 5.24 (d, *J* =15.5 Hz, 1H), 4.56 (d, *J* =15.5 Hz, 1H), 3.09 (d, *J* = 14.0 Hz, 1H), 1.69 (brs, 1H), 1.51 (d, *J* = 14.5 Hz, 1H), 0.56 (s, 3H), 0.54 (s, 3H), -0.3 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 181.0, 148.6, 141.9, 140.8, 137.2, 135.5, 135.2, 128.7, 128.6, 128.3, 127.9, 127.7, 127.2, 126.3, 126.0, 123.4, 109.7, 57.2, 44.1, 27.3, 4.0, 3.2, -0.9. **HRMS** (ESI-TOF) *m/z*: calcd for $C_{27}H_{33}NNaO_2Si_2^+$ $(M + Na)^+$: 482.1942, found: 482.1942.

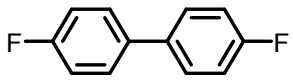
1-benzyl-3-((hydroxydimethylsilyl)methyl)-3-(2-(trimethylsilyl)phenyl)indolin-2-one (8a')



Colorless oil, R_f = 0.55 (petroleum ether : EtOAc = 5 :1). Yield = 27%, m = 12.4 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.76 (m, 1H), 7.29-7.27 (m, 1H), 7.35-7.30 (m, 4H), 7.28-7.26 (m, 1H), 7.23-7.22 (m, 2H), 7.19 (t, *J* = 8.0 Hz, 1H), 7.13-7.12 (m, 1H), 7.05-6.99 (m, 2H), 6.83 (d, *J* = 8.0 Hz, 1H), 4.94 (s, 2H), 2.29 (d, *J* =14.5 Hz, 1H), 2.12 (brs, 1H), 1.54 (d, *J* = 14.5 Hz, 1H), 0.36 (s, 9H), 0.02 (s, 3H), -0.2 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$,) δ 180.6, 146.7, 141.8, 138.7, 137.6, 137.3, 135.8, 129.0, 128.8, 128.7, 127.9, 127.7, 127.6, 126.3, 124.1, 123.1, 109.6, 56.9, 44.1, 30.9, 3.5, 1.3, 0.9. **HRMS**

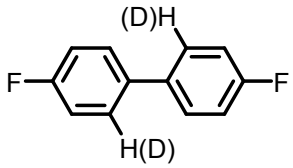
(ESI-TOF) *m/z*: calcd for $C_{27}H_{33}NNaO_2Si_2^+$ $(M + Na)^+$: 482.1942, found: 482.1940.

4,4'-difluoro-1,1'-biphenyl (9)[12]



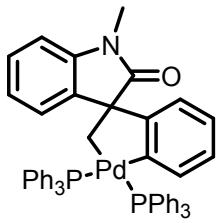
White soild, R_f = 0.7 (petroleum ether). Yield = 51%, m = 19.3 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.51-7.47 (m, 4H), 7.15-7.10 (m, 4H). **^{13}C NMR** (125 MHz, $CDCl_3$,) δ 162.4 (d, *J* = 245.0 Hz), 136.4 (d, *J* = 3.1 Hz), 128.5 (d, *J* = 8.1 Hz), 115.5 (d, *J* = 21.4 Hz).

product 9-D



White soild, R_f = 0.7 (petroleum ether). Yield = 47%, m = 18.0 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.50-7.47 (m, 2.7 H), 7.14-7.10 (m, 4H).

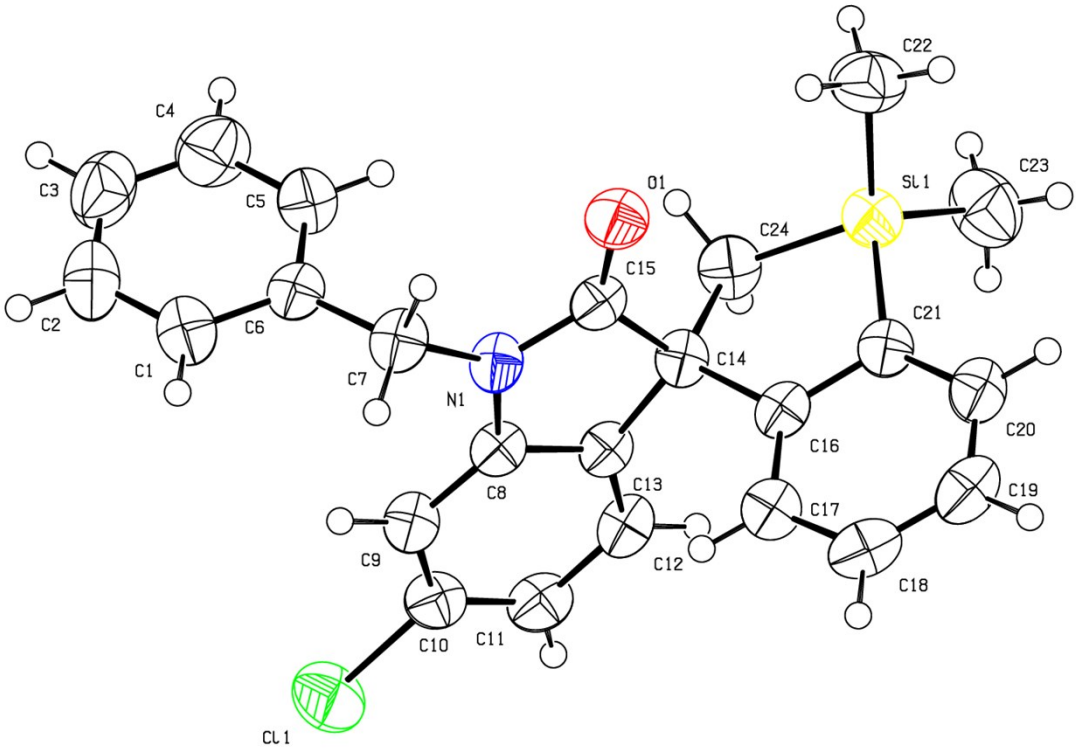
palladacycle B[6]



Yellow soild, R_f = 0.45 (petroleum ether : EtOAc = 4 :1). Yield = 50%, m = 86.6 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.59 (t, *J* = 8.5 Hz, 7H), 7.32-7.26 (m, 6H), 7.24-7.18 (m, 7H), 7.12 (t, *J* = 7.5 Hz, 6H), 7.06-6.98 (s, 7H), 6.84-6.79 (m, 2H), 6.63 (t, *J* = 7.5 Hz, 1H), 6.41 (d, *J* = 7.5 Hz, 1H), 6.35 (t, *J* = 7.5 Hz, 1H), 3.25 (s, 3H), 2.15-2.06 (m, 2H).

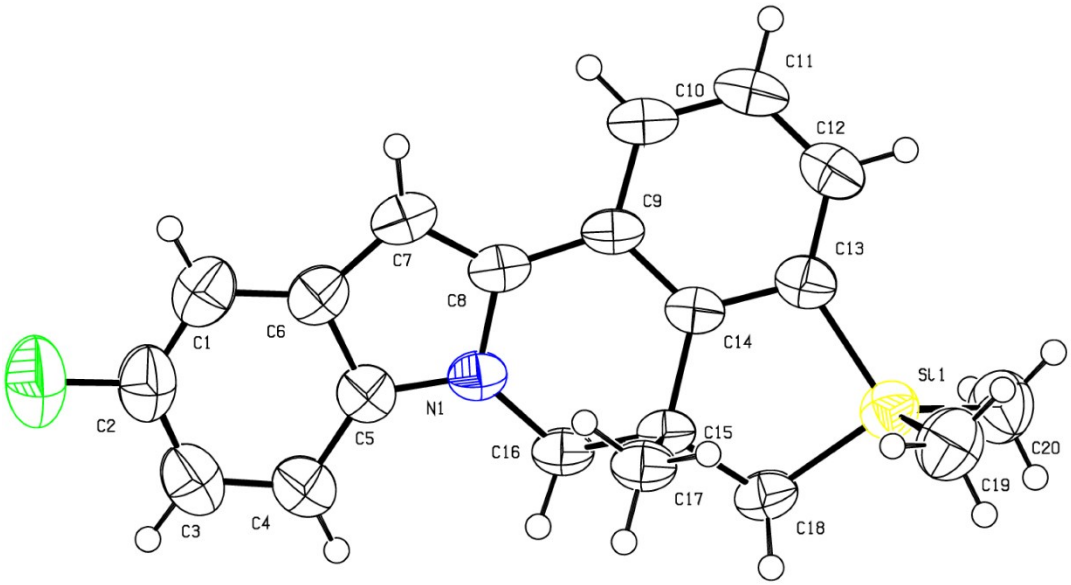
10. The X-ray Single-Crystal Diffraction Analysis of 3g, 5d and 8a.

10.1 Crystallographic Data Details for 3g (CCDC: 2040658)



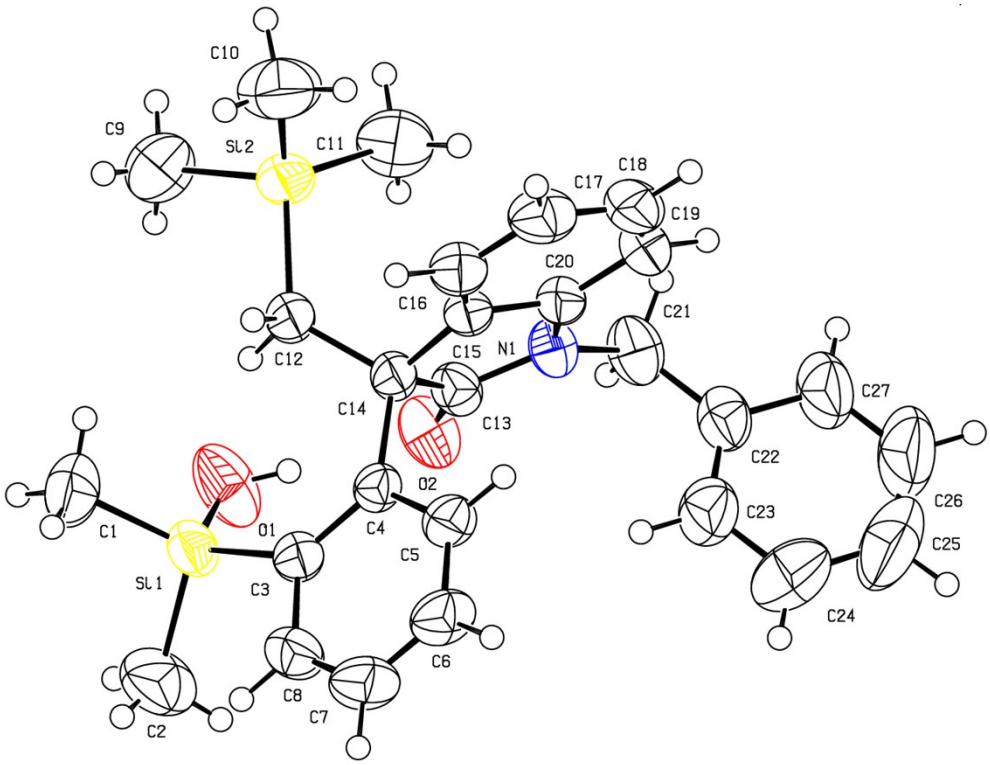
Empirical formula	C24 H22 Cl N O Si
Formula weight	403.96
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 8.468(7) A alpha = 112.361(10) deg. b = 10.762(9) A beta = 99.502(11) deg. C = 13.404(11) A gamma = 100.767(11) deg.
Volume	1071.6(15) A^3
Z, Calculated density	2, 1.252 Mg/m^3
Absorption coefficient	0.248 mm^-1
F(000)	424
Crystal size	0.260 x 0.220 x 0.190 mm
Theta range for data collection	2.535 to 25.008 deg.
Limiting indices	-10<=h<=9, -12<=k<=12, -14<=l<=15
Reflections collected / unique	7693 / 3587 [R(int) = 0.0415]
Completeness to theta = 25.242	92.8 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3587 / 0 / 253
Goodness-of-fit on F^2	1.037
Final R indices [I>2sigma(I)]	R1 = 0.0535, wR2 = 0.1406
R indices (all data)	R1 = 0.0754, wR2 = 0.1552
Extinction coefficient	n/a
Largest diff. peak and hole	0.273 and -0.433 e.A^-3

10.2 Crystallographic Data Details for 5d (CCDC: 2040659)



Empirical formula	C20 H20 F N Si
Formula weight	321.46
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P b c a
Unit cell dimensions	a = 12.1901(7) A alpha = 90 deg. b = 10.4424(6) A beta = 90 deg. c = 26.4680(16) A gamma = 90 deg.
Volume	3369.2(3) A^3
Z, Calculated density	8, 1.267 Mg/m^3
Absorption coefficient	0.148 mm^-1
F(000)	1360
Crystal size	0.230 x 0.220 x 0.190 mm
Theta range for data collection	2.271 to 25.008 deg.
Limiting indices	-14<=h<=14, -12<=k<=12, -31<=l<=31
Reflections collected / unique	33084 / 2973 [R(int) = 0.0351]
Completeness to theta = 25.242	97.4 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2973 / 0 / 208
Goodness-of-fit on F^2	1.051
Final R indices [I>2sigma(I)]	R1 = 0.0409, wR2 = 0.1054
R indices (all data)	R1 = 0.0552, wR2 = 0.1122
Extinction coefficient	n/a
Largest diff. peak and hole	0.208 and -0.223 e.A^-3

10.3 Crystallographic Data Details for8a (CCDC: 2040657)

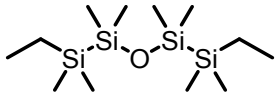


Empirical formula	C27 H33 N O2 Si2
Formula weight	459.72
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 21/c
Unit cell dimensions	a = 9.5504(9) A alpha = 90 deg. b = 25.159(3) A beta = 93.6710(10) deg. c = 10.9734(11) A gamma = 90 deg.
Volume	2631.3(4) A^3
Z, Calculated density	4, 1.160 Mg/m^3
Absorption coefficient	0.157 mm^-1
F(000)	984
Crystal size	0.230 x 0.220 x 0.190 mm
Theta range for data collection	2.137 to 25.006 deg.
Limiting indices	-11<=h<=11, -29<=k<=29, -13<=l<=13
Reflections collected / unique	25209 / 4633 [R(int) = 0.0264]
Completeness to theta = 25.242	97.4 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4633 / 0 / 295
Goodness-of-fit on F^2	1.041
Final R indices [I>2sigma(I)]	R1 = 0.0549, wR2 = 0.1404
R indices (all data)	R1 = 0.0684, wR2 = 0.1468
Extinction coefficient	n/a
Largest diff. peak and hole	0.302 and -0.247 e.A^-3

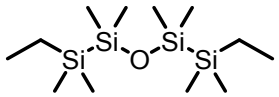
11. References

1. W. Kong, Q. Wang and J. Zhu, *Angew. Chem. Int. Ed.*, 2016, **55**, 9714.
2. S. P. Chavan, A. B. Pathak, A.Pandey and U. R. Kalkote, *Synth. Commun.*, 2007, **37,** 4253.
3. H. Lu, X.Yang, L. Zhou, W. Li, G. Deng, Y. Yang and Y. Liang, *Org. Chem. Front.*, 2020, **7**, 2016.
4. G. Shi, D. Chen, H. Jiang, Y. Zhang and Y. Zhang, *Org. Lett.,* 2016*,* **18**, 2958.
5. S. Dekeukeleire, M. D'hooghe and N. D. Kimpe, *J. Org. Chem.*, 2009, **74**, 1644.
6. H. Yoon, A. Lossouarn, F. Landau and M. Lautens, *Org. Lett.* 2016, **18**, 6324.
7. G. P. M. van Klink, H. J. R. de Boer, G. Schat, O. S. Akkerman, F. Bickelhaupt and A. L. Spek, *Organometallics,* 2020*,* **21**, 2119.
8. L. Omann and M. Oestreich, *Angew. Chem. Int. Ed.,* 2015, **54**, 10276.
9. T. Ureshino, T. Yoshida, Y. Kuninobu and K. Takai, *J. Am. Chem. Soc.,* 2010, **132**, 14324.
10. F. Mareš, and V. Chvalovský, *Collect. Czech. Chem. Commun.,* 1967*,* **32**, 382.
11. R.-F. Chen, Q.-L. Fan, S.-J. Liu, R. Zhu and K.-Y. Pu, *Synthetic Metals,* 2006*,* **156**, 1161.
12. B. Kar, S. Bardhan, P. Ghosh, B. Ganguly, K. Kundu, S. Sarkar, B. K. Paul and S. Das. *ChemistrySelect,* 2017, **2**, 1079.

12. NMR Spectra



2i



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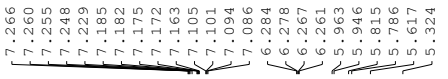
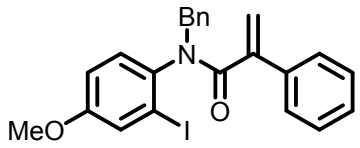


500 MHz, $CDCl_3$



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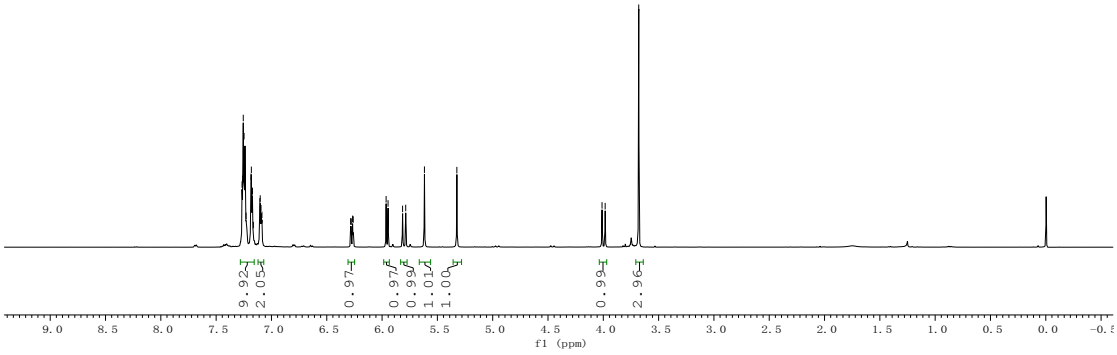
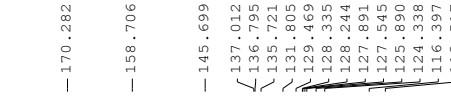
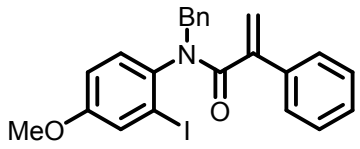
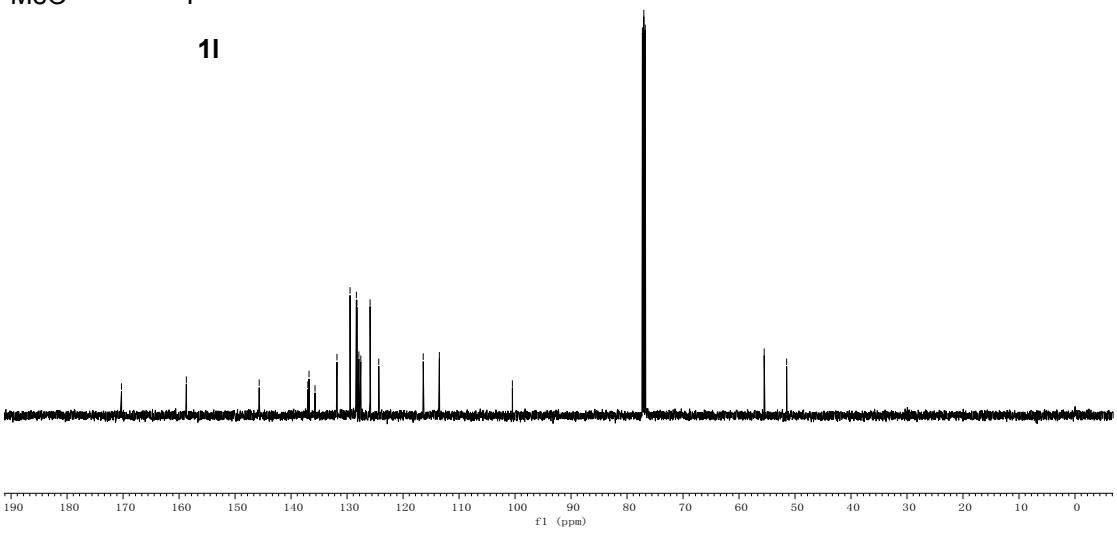


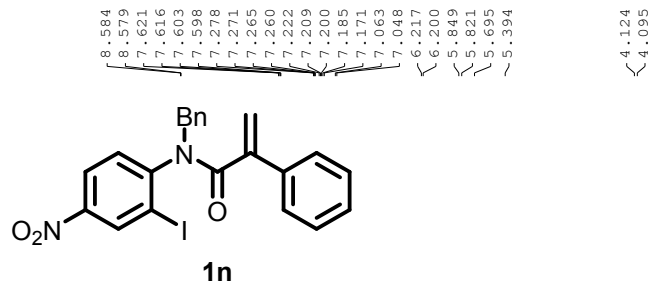


125 MHz, $CDCl_3$



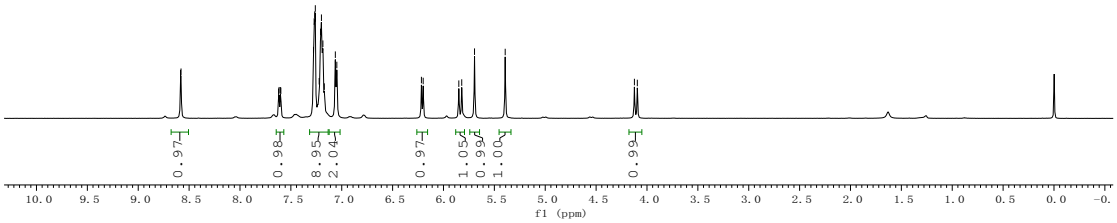
1l

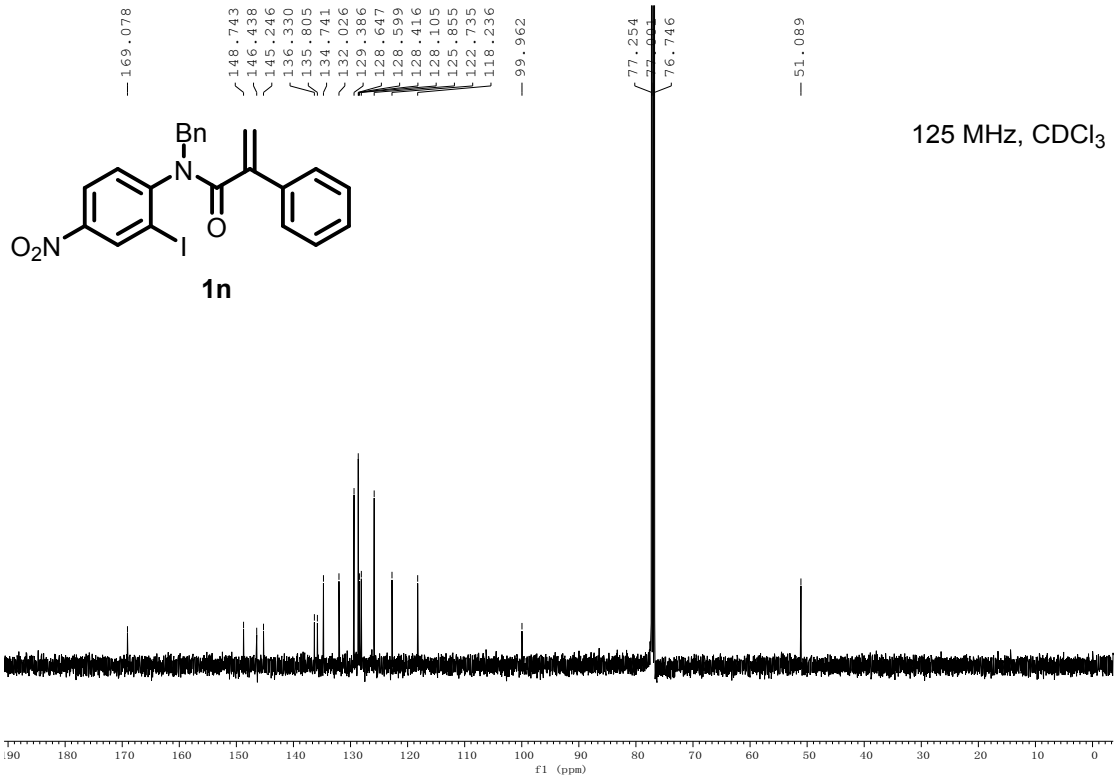




500 MHz, $CDCl_3$

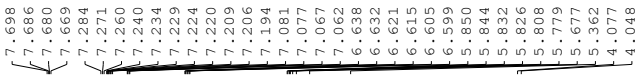
1n



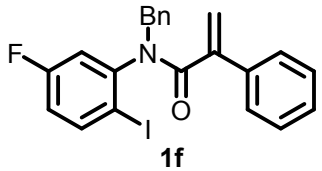


125 MHz, $CDCl_3$

1n



500 MHz, $CDCl_3$



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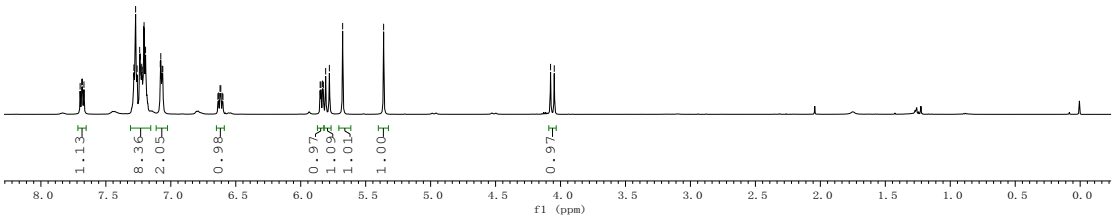
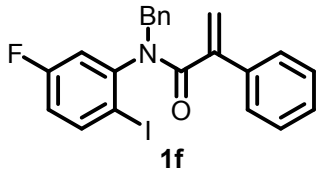


125 MHz, $CDCl_3$



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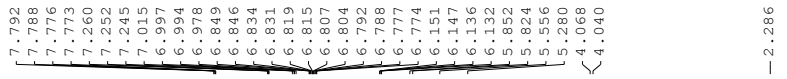
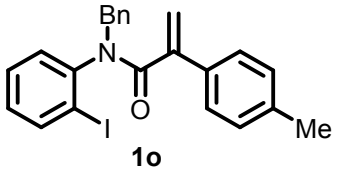
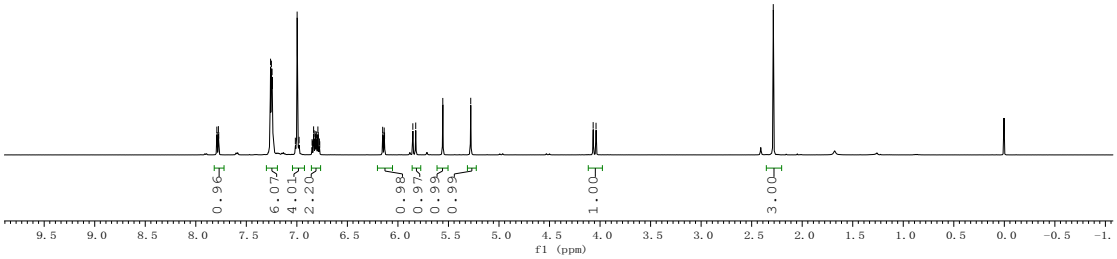
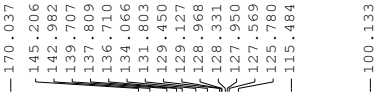


500 MHz, $CDCl_3$

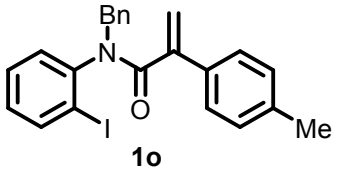


1o

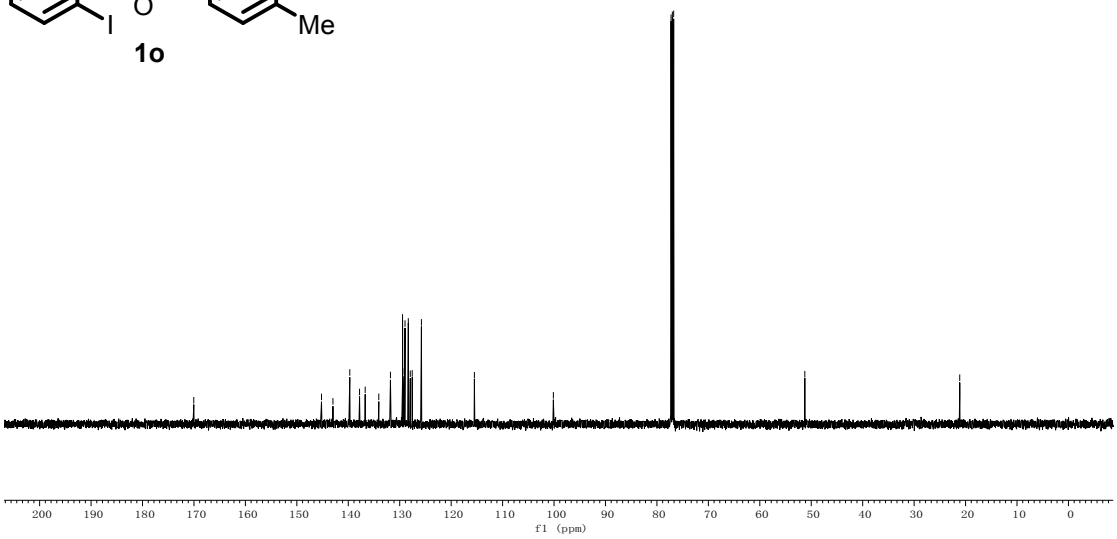


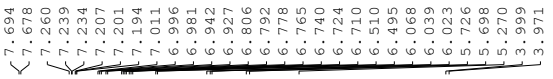


125 MHz, $CDCl_3$

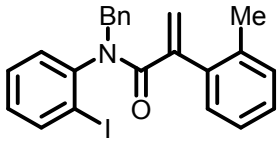


1o

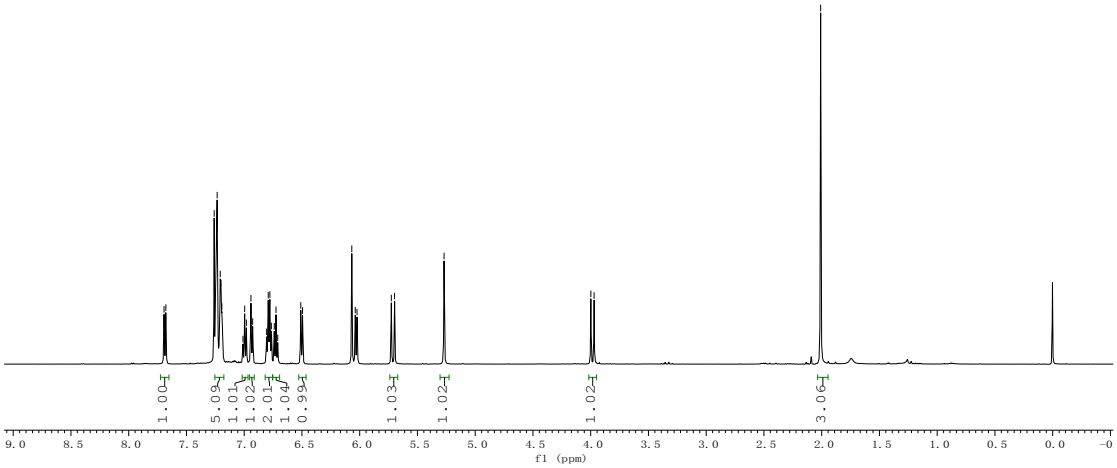


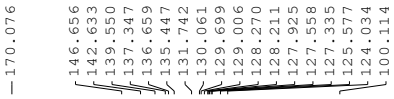


500 MHz, $CDCl_3$

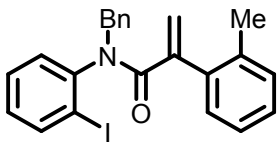


1r

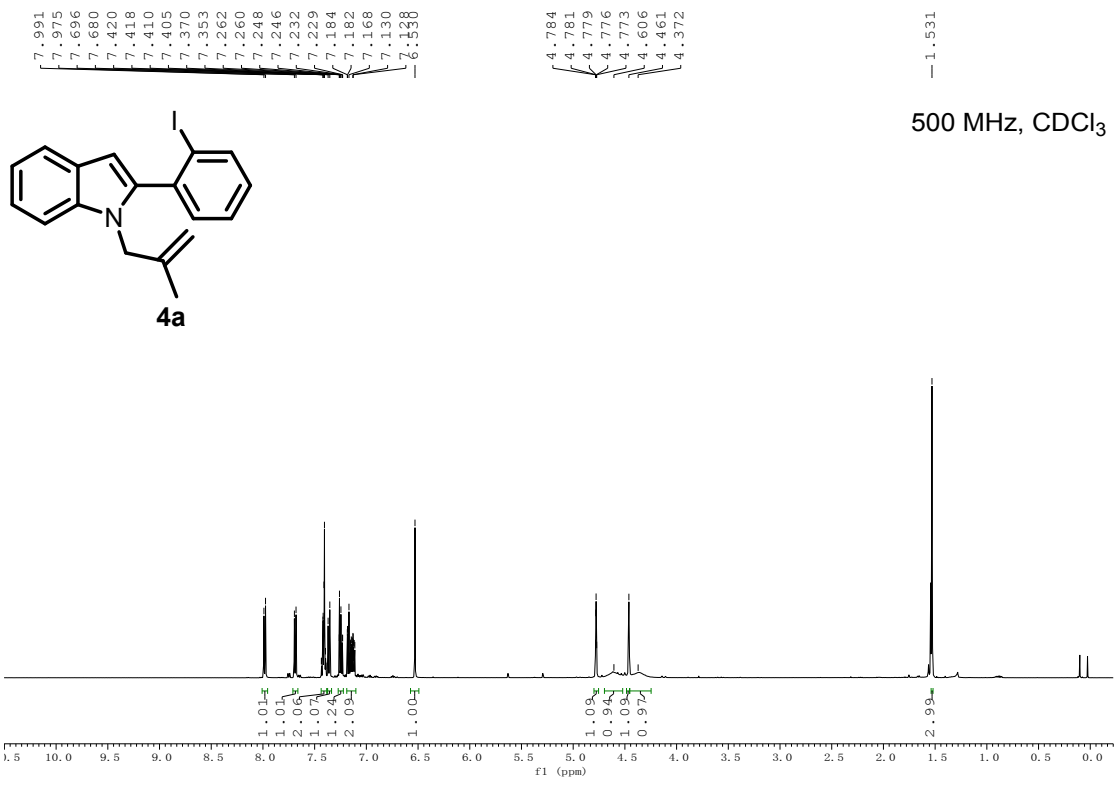


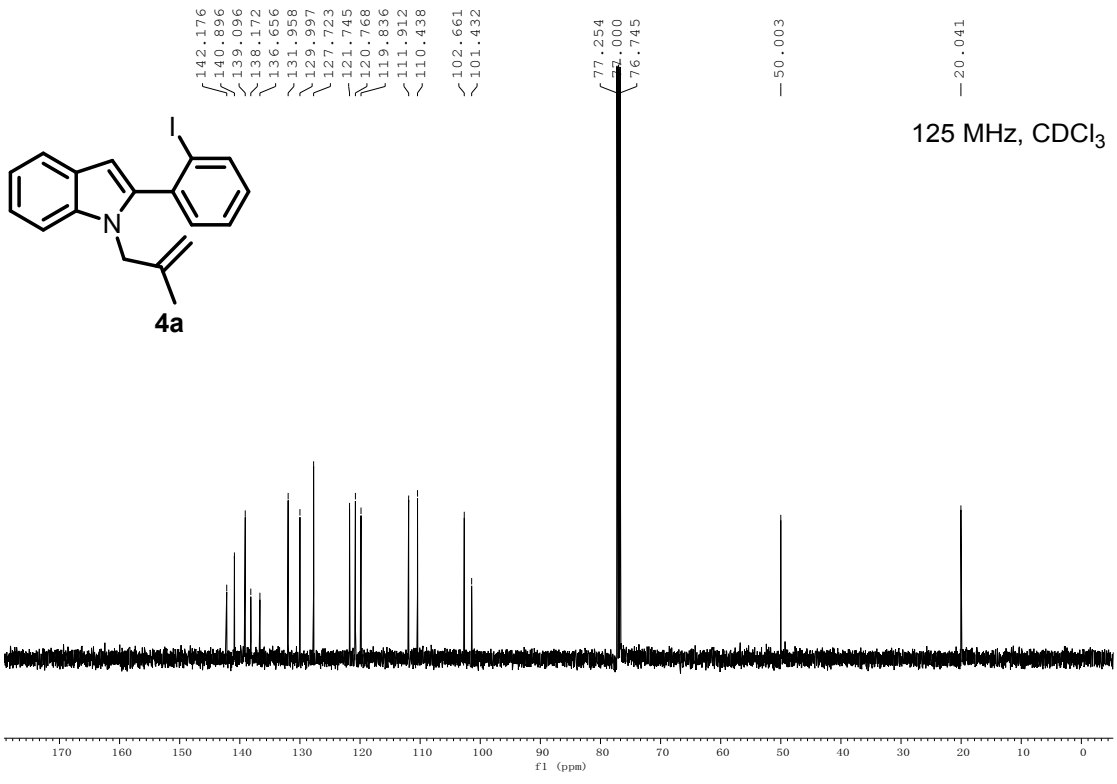


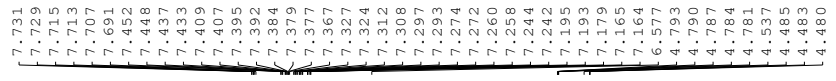
125 MHz, $CDCl_3$

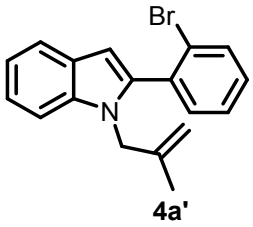


1r


7.991
7.975
7.696
7.680
7.420
7.418
7.410
7.405
7.370
7.353
7.262
7.260
7.248
7.246
7.232
7.229
7.184
7.182
7.168
7.130
6.530
4.784
4.781
4.779
4.776
4.773
4.606
4.461
4.372
1.531
I
N
4a
500 MHz, CDCl3
1.01
1.01
2.05
1.07
1.24
2.00
1.00
1.09
0.94
1.03
0.97
2.99
f1 (ppm)

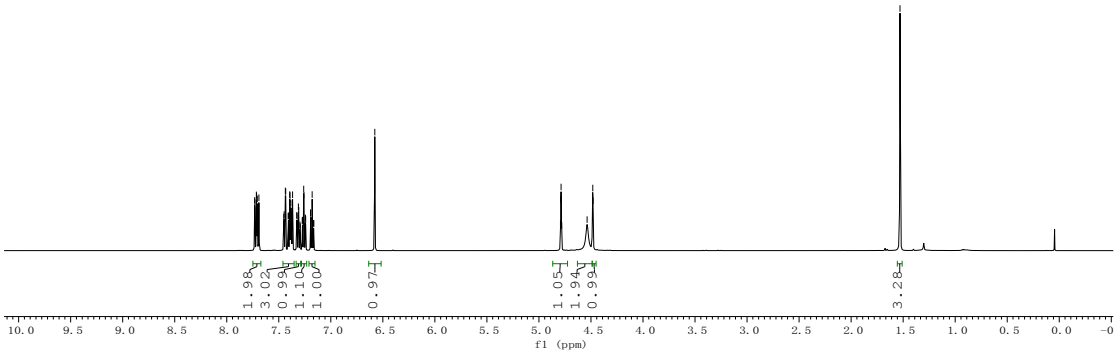

142.176
140.896
139.096
138.172
136.656
131.958
129.997
127.723
121.745
120.768
119.836
111.912
110.438
102.661
101.432
77.254
77.000
76.745
50.003
20.041
I
N
4a
125 MHz, CDCl3
f1 (ppm)

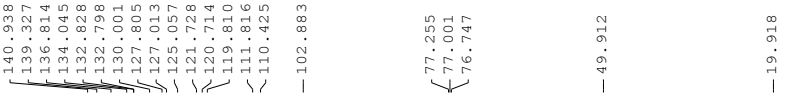


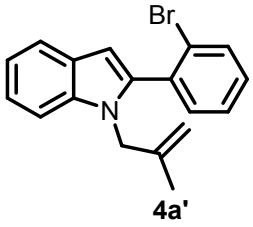


4a'

500 MHz, $CDCl_3$

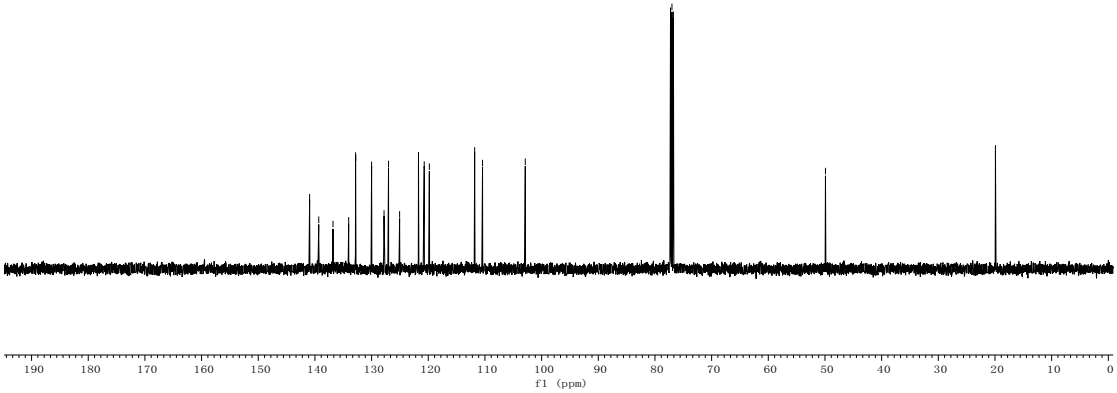


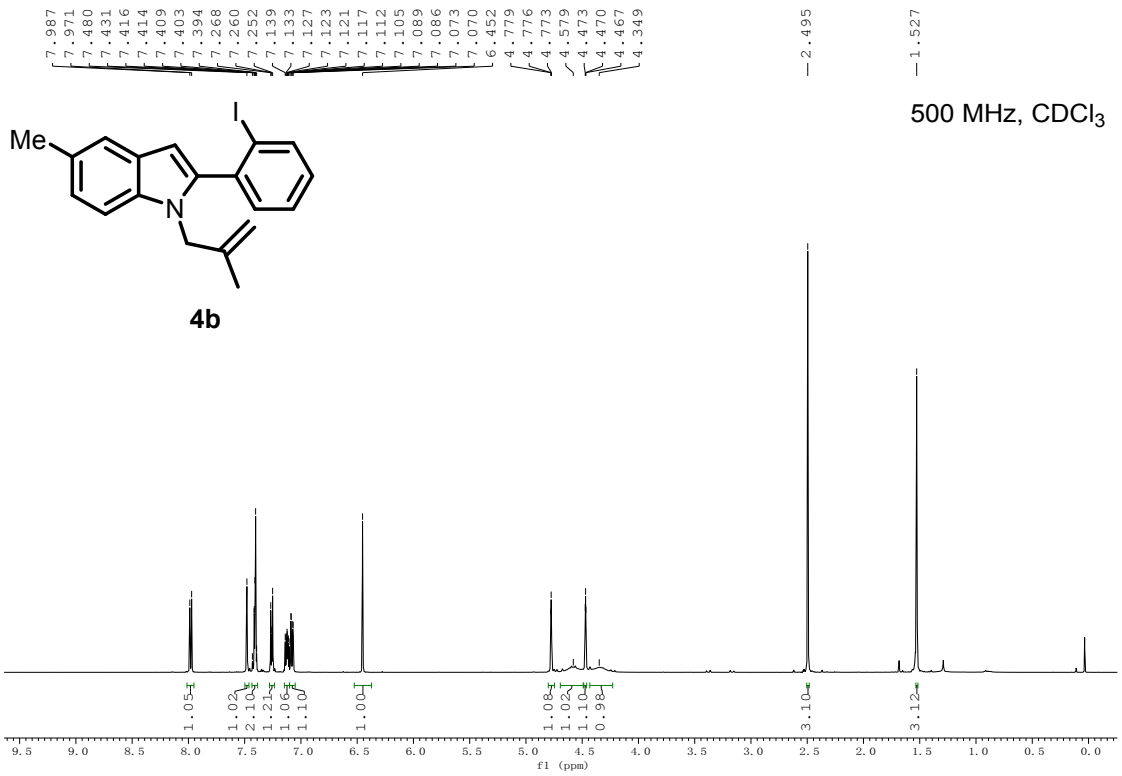


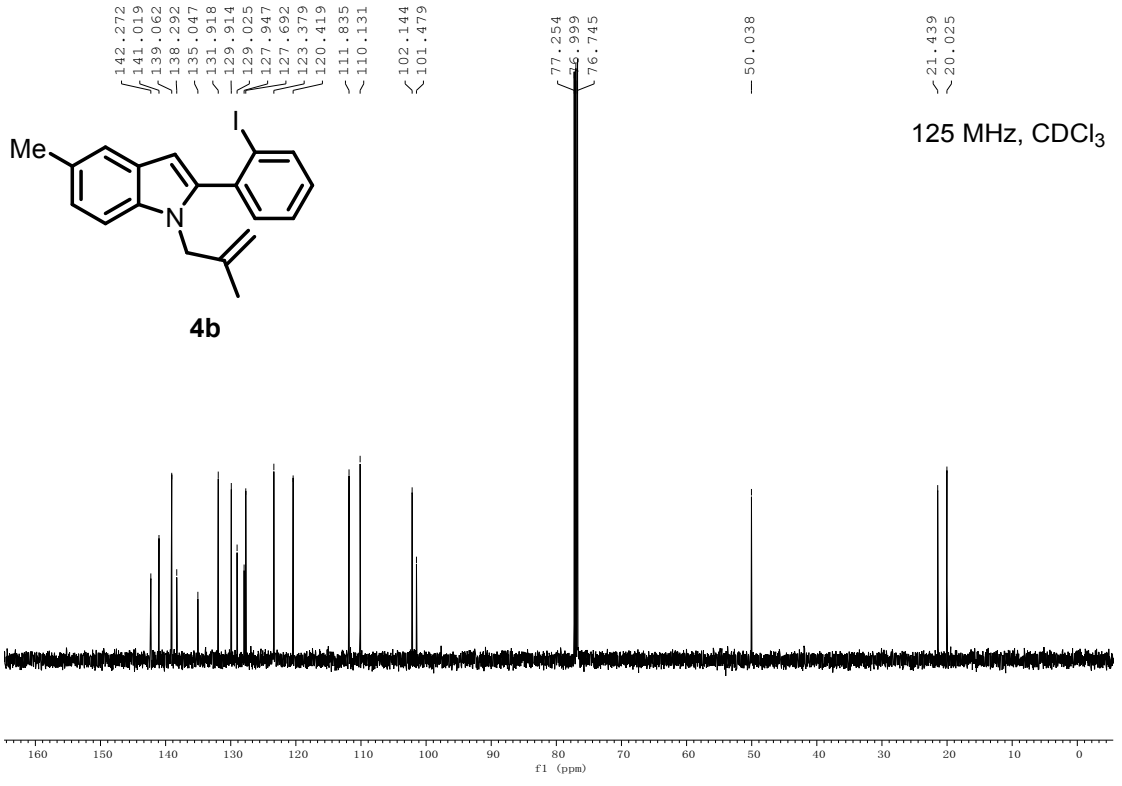


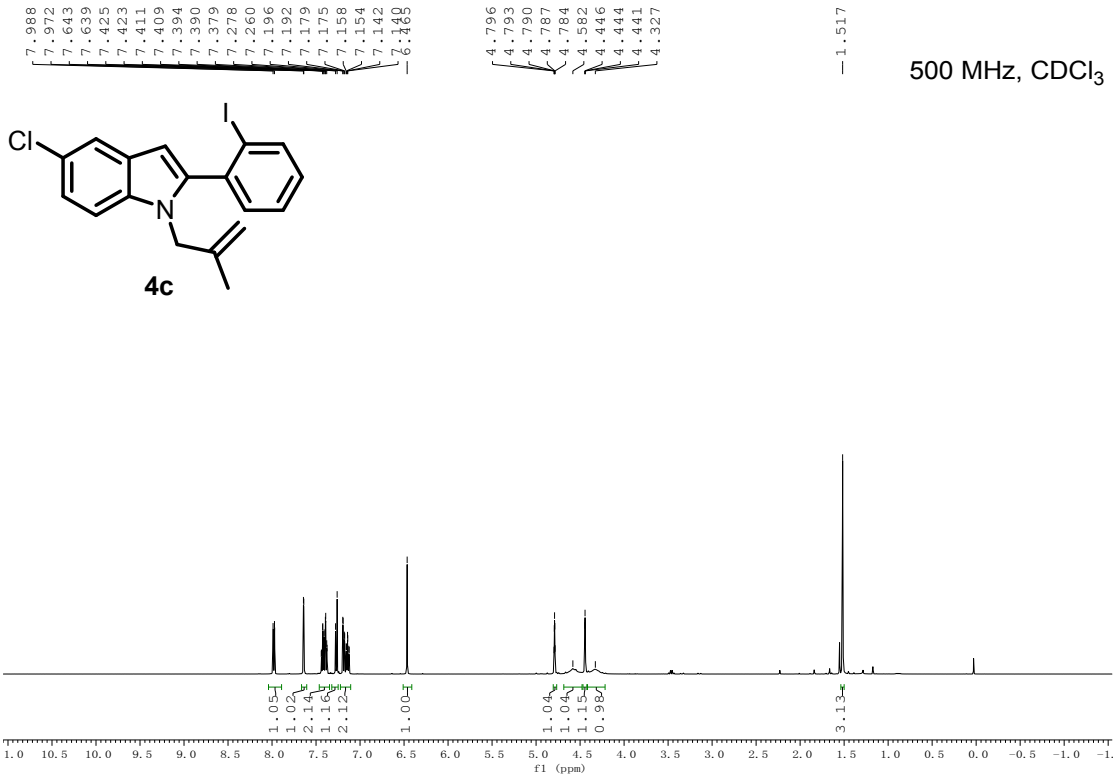
4a'

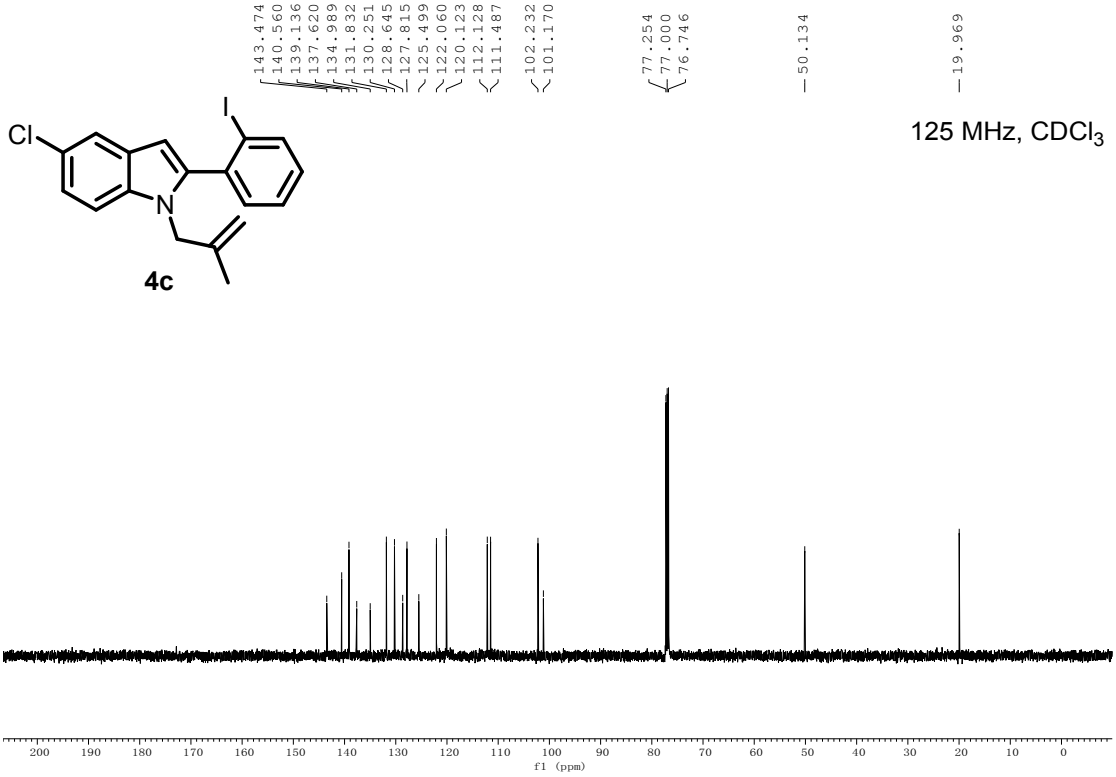
125 MHz, $CDCl_3$

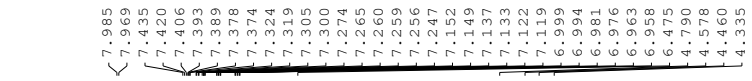



7.987
7.971
7.480
7.431
7.416
7.414
7.409
7.403
7.394
7.268
7.260
7.252
7.139
7.133
7.127
7.123
7.121
7.117
7.112
7.105
7.089
7.086
7.073
7.070
6.452
4.779
4.776
4.773
4.579
4.473
4.470
4.467
4.349
2.495
1.527
500 MHz, CDCl3
Me
I
N
4b
1.05
1.02
2.05
1.21
1.06
1.10
1.00
1.08
1.02
1.10
0.98
3.10
3.12
f1 (ppm)

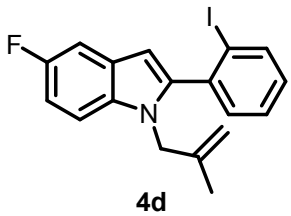

142.272
141.019
139.062
138.292
135.047
131.918
129.914
129.025
127.947
127.692
123.379
120.419
111.835
110.131
102.144
101.479
77.254
76.999
76.745
50.038
21.439
20.025
125 MHz, CDCl3
Me
I
N
4b
f1 (ppm)


7.988
7.972
7.643
7.639
7.425
7.423
7.411
7.409
7.394
7.390
7.379
7.278
7.260
7.196
7.192
7.179
7.175
7.158
7.154
7.142
7.140
6.465
4.796
4.793
4.790
4.787
4.784
4.582
4.446
4.444
4.441
4.327
1.517
500 MHz, CDCl3
Cl
I
N
4c
1.05
1.02
2.14
1.16
2.12
1.00
1.04
1.04
1.15
0.98
3.13
f1 (ppm)

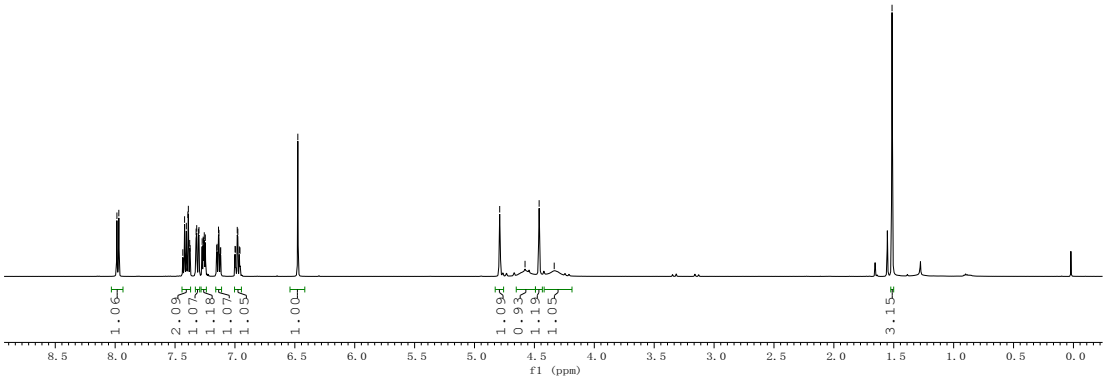

143.474
140.560
139.136
137.620
134.989
131.832
130.251
128.645
127.815
125.499
122.060
120.123
112.128
111.487
102.232
101.170
77.254
77.000
76.746
50.134
19.969
125 MHz, CDCl3
Cl
I
N
4c
f1 (ppm)

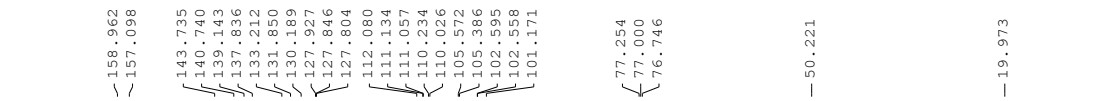


500 MHz, $CDCl_3$

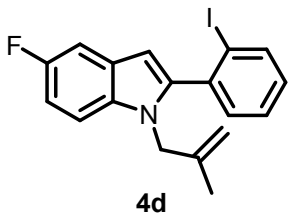


4d

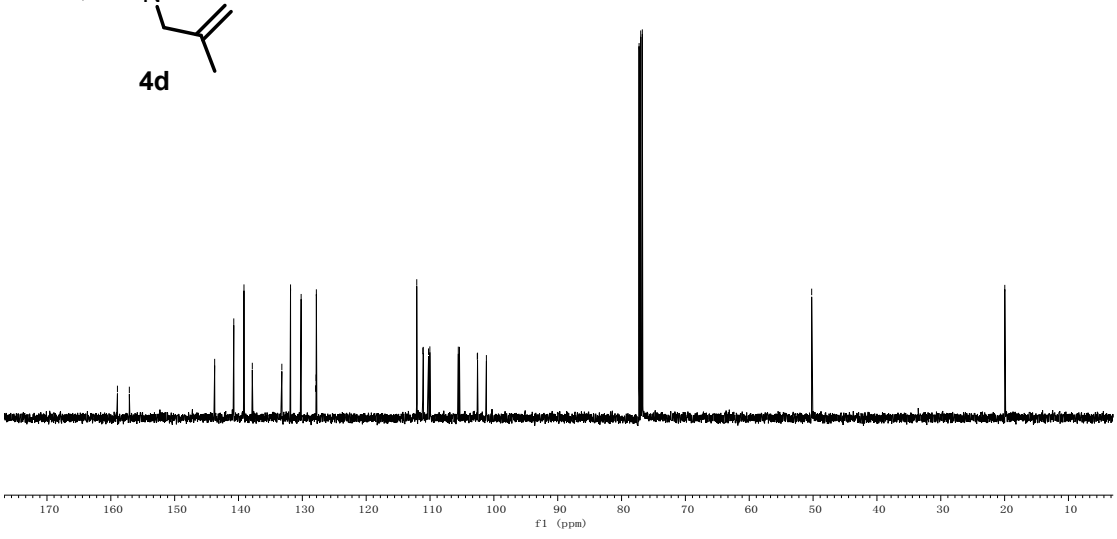




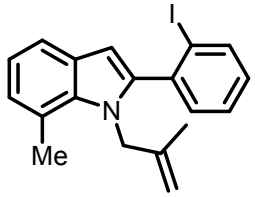
125 MHz, $CDCl_3$



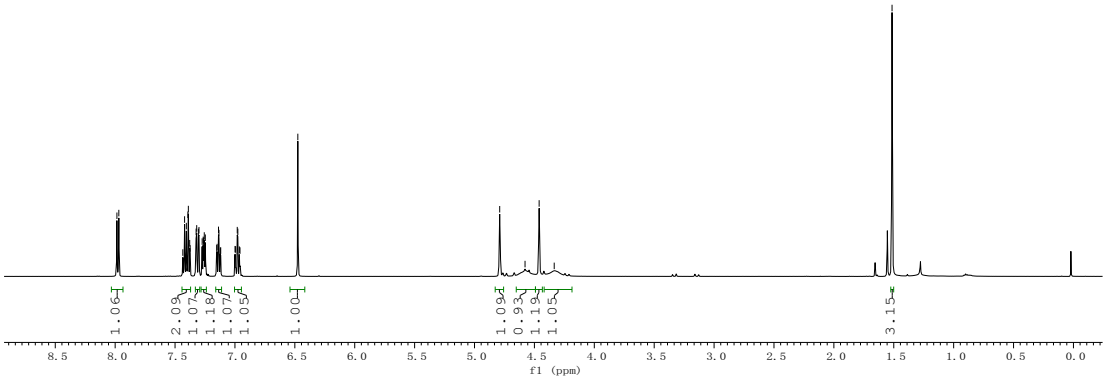
4d

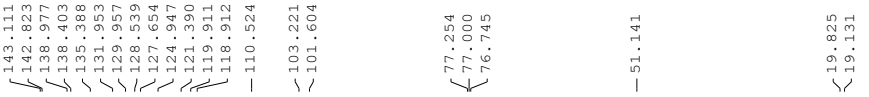


500 MHz, $CDCl_3$

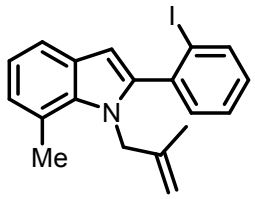


4e

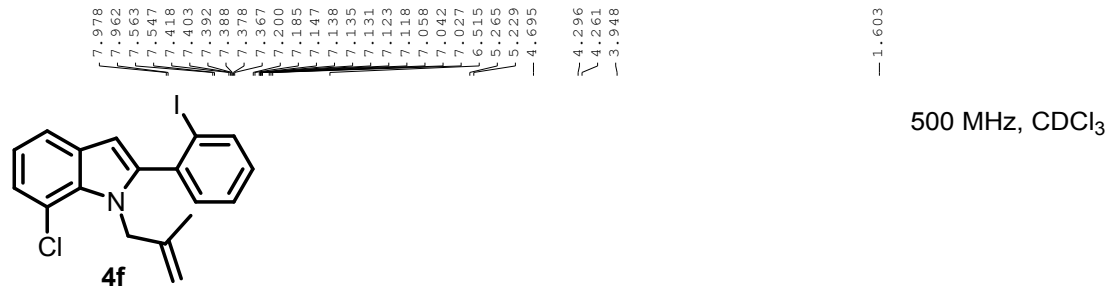




125 MHz, $CDCl_3$

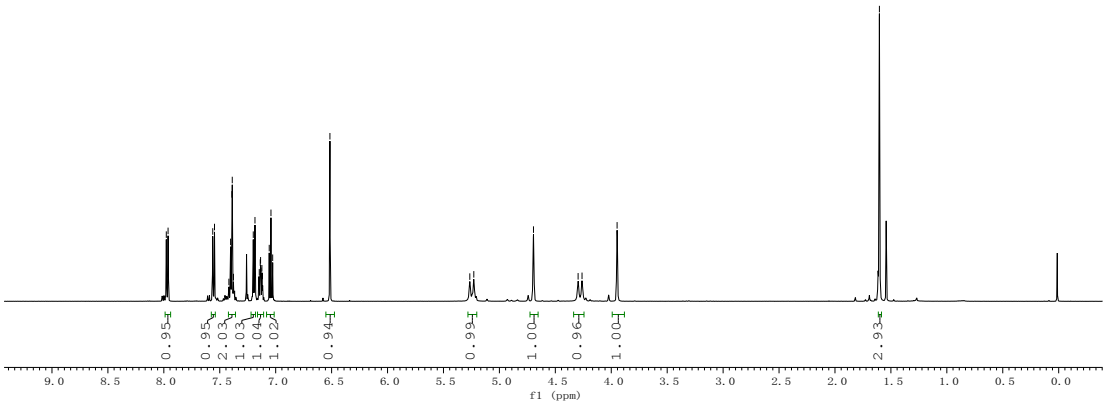


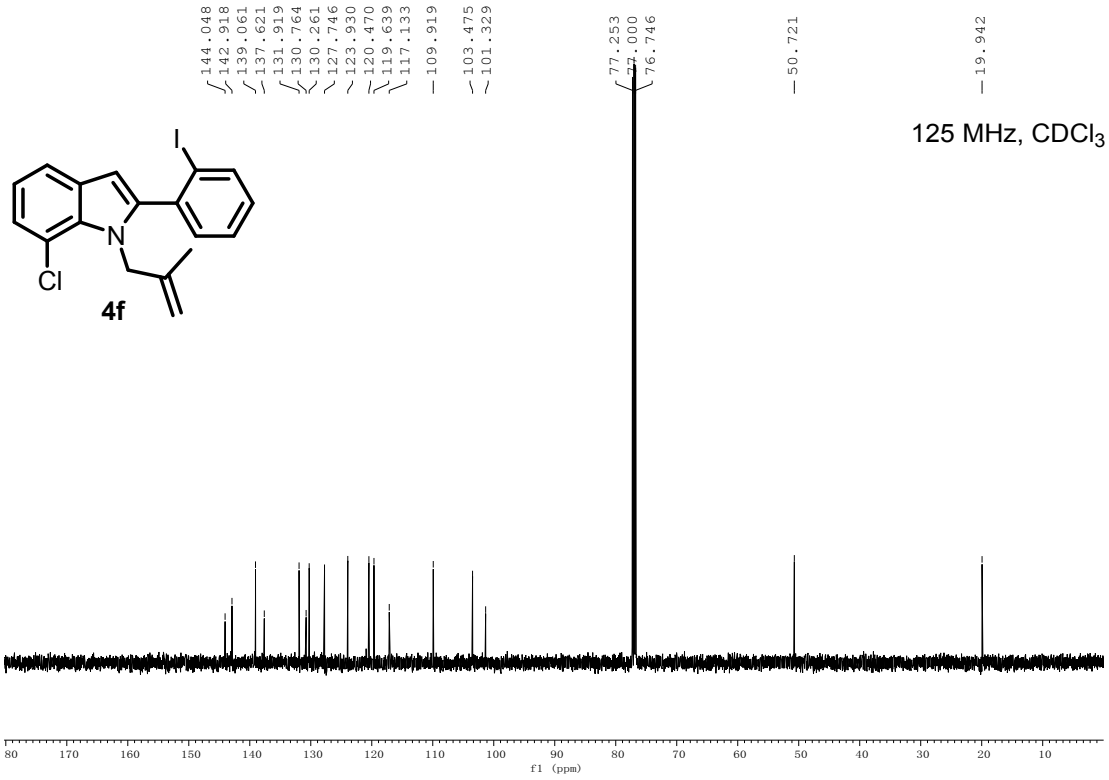
4e



500 MHz, $CDCl_3$

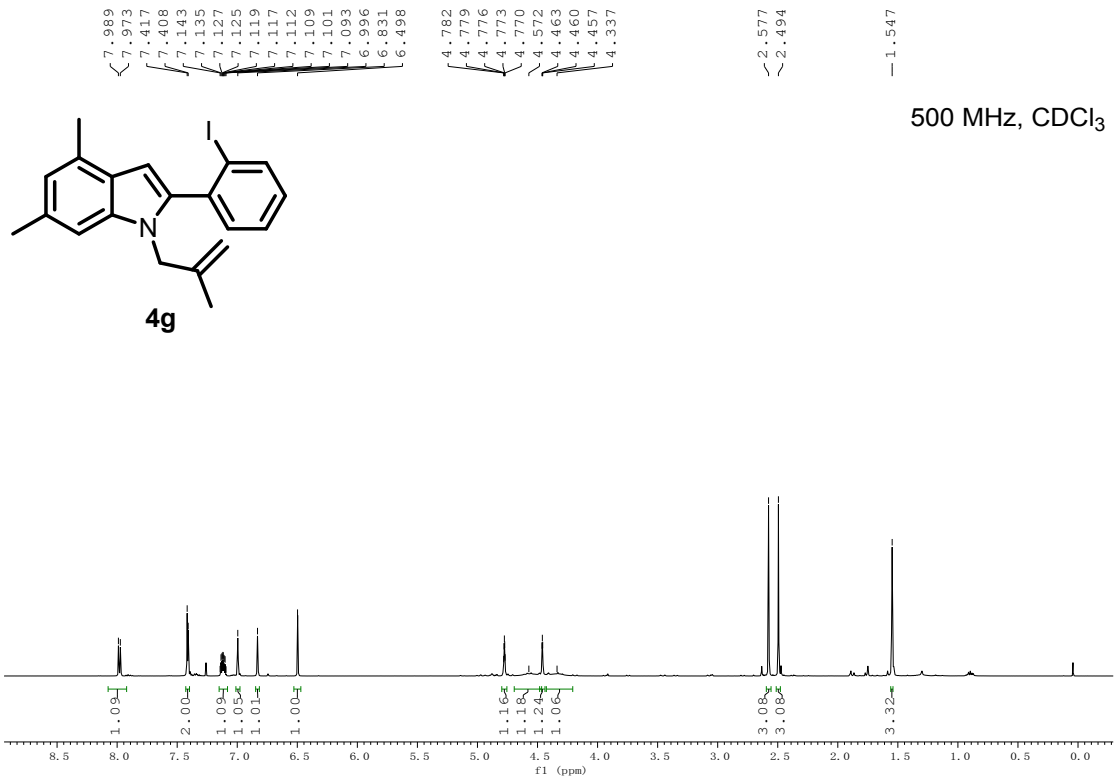
4f

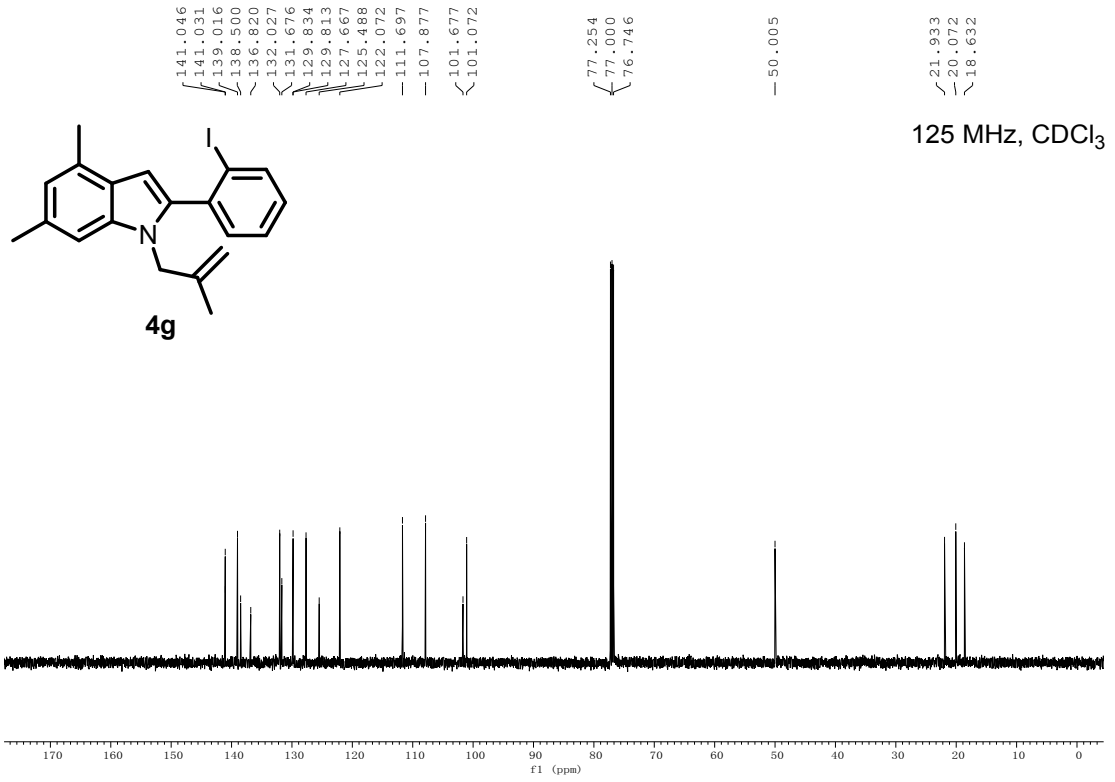


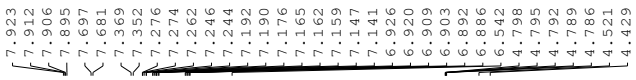


125 MHz, $CDCl_3$

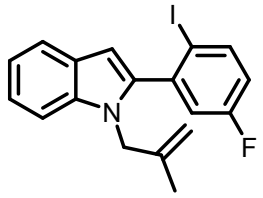
4f


7.989
7.973
7.417
7.408
7.143
7.135
7.127
7.125
7.119
7.117
7.112
7.109
7.101
7.093
6.996
6.831
6.498
4.782
4.779
4.776
4.773
4.770
4.572
4.463
4.460
4.457
4.337
2.577
2.494
1.547
500 MHz, CDCl3
I
N
4g
1.09
2.00
1.09
1.05
1.01
1.00
1.16
1.18
1.24
1.06
3.08
3.08
3.32
f1 (ppm)

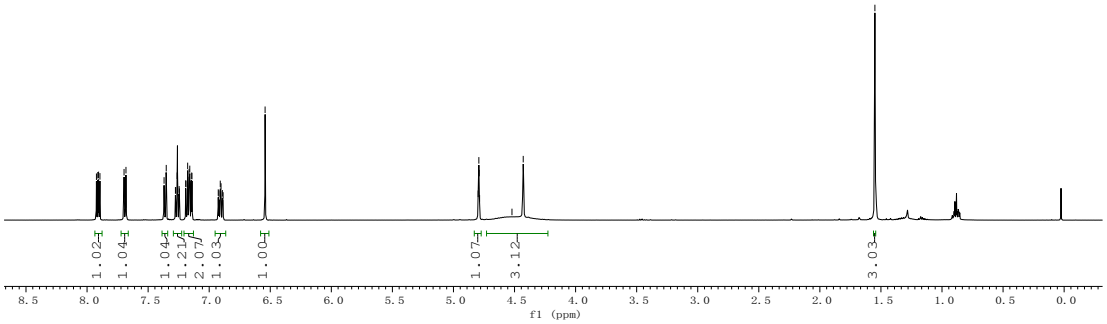

141.046
141.031
139.016
138.500
136.820
132.027
131.676
129.834
129.813
127.667
125.488
122.072
111.697
107.877
101.677
101.072
77.254
77.000
76.746
50.005
21.933
20.072
18.632
125 MHz, CDCl3
I
N
4g
f1 (ppm)

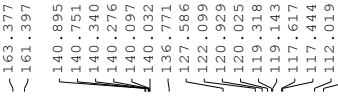


500 MHz, $CDCl_3$

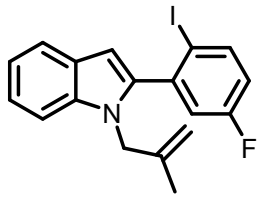


4h

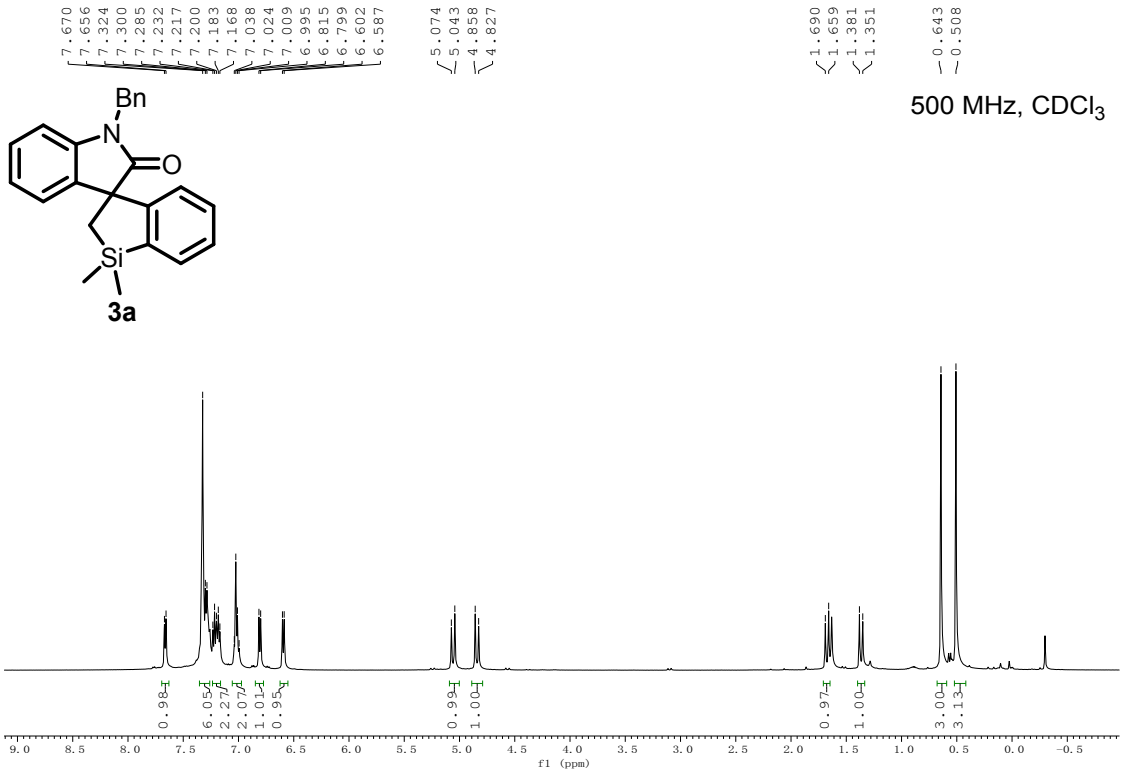


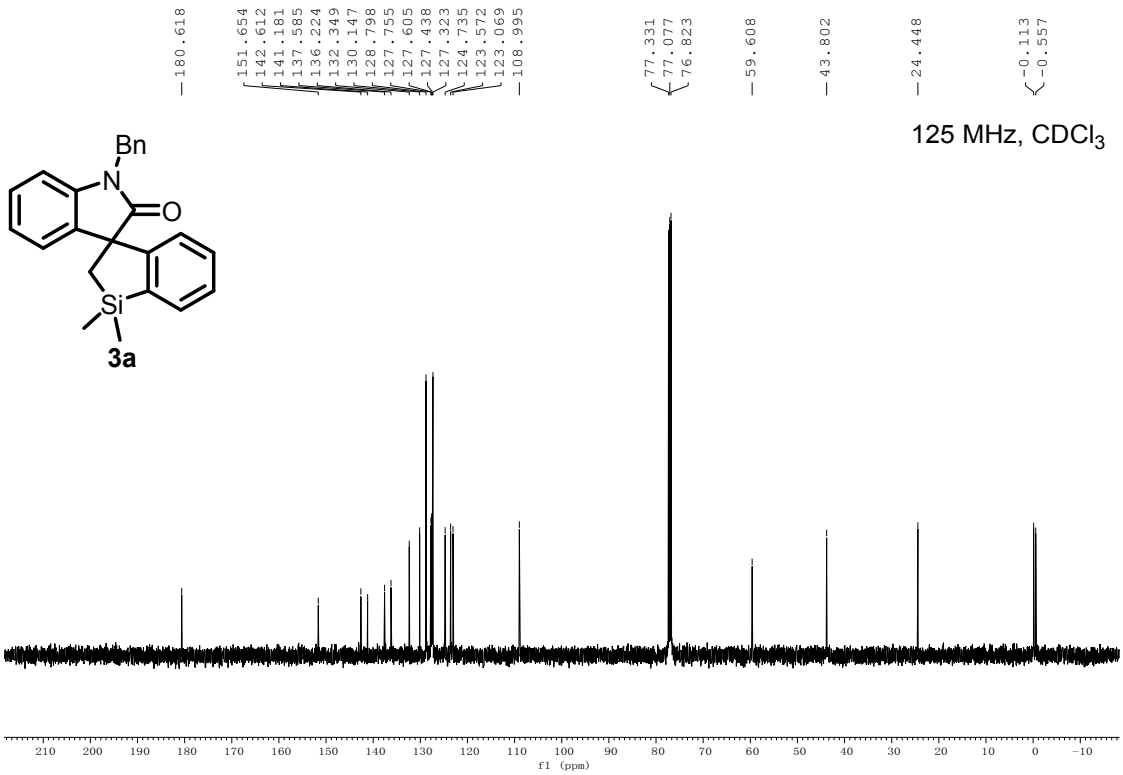


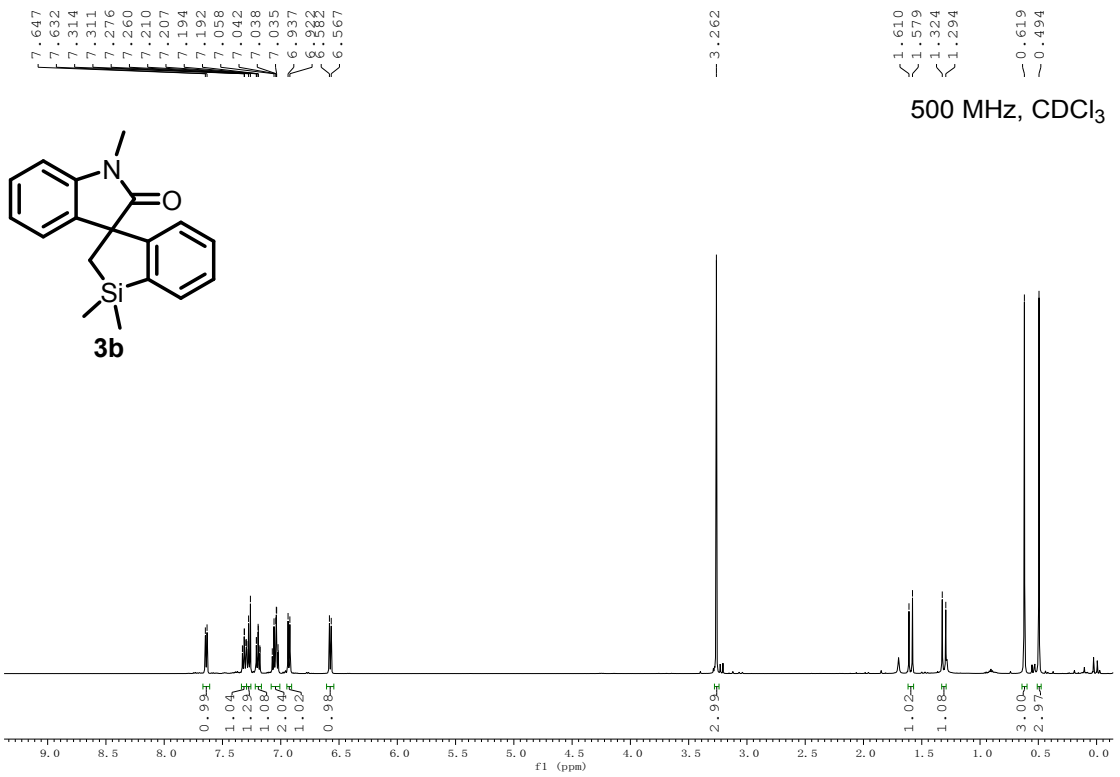
125 MHz, $CDCl_3$

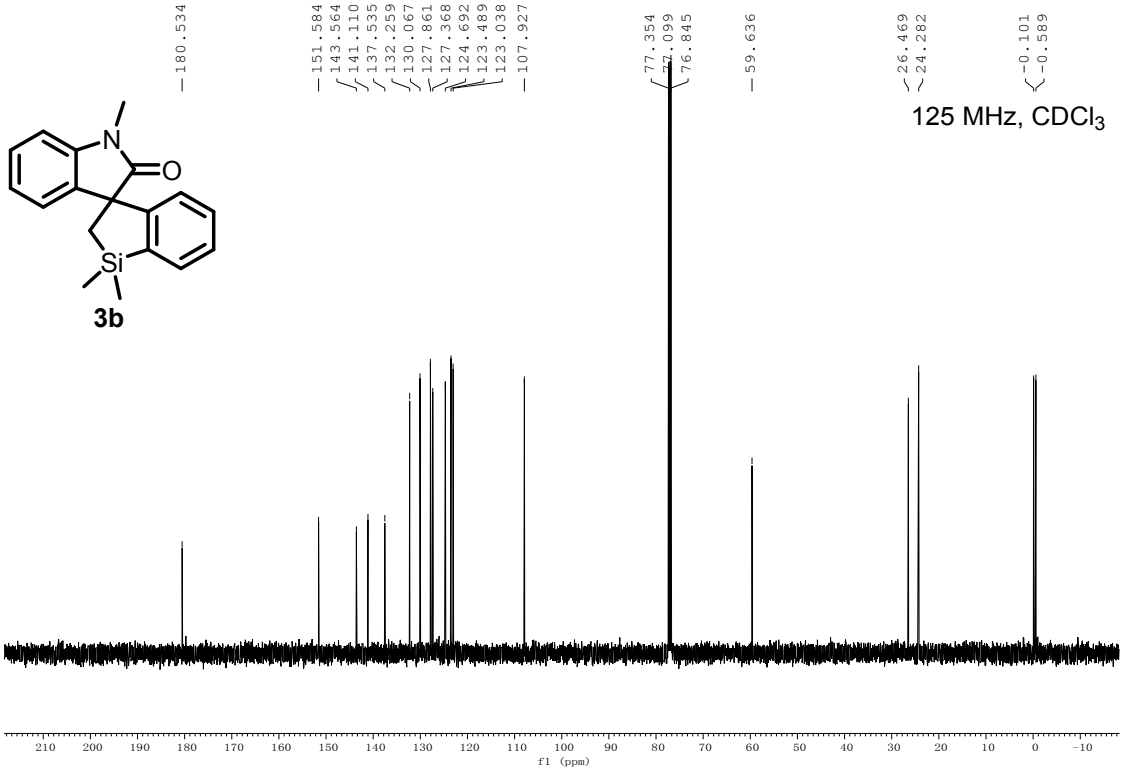


4h


7.670
7.656
7.324
7.300
7.285
7.232
7.217
7.200
7.183
7.168
7.038
7.024
7.009
6.995
6.815
6.799
6.602
6.587
5.074
5.043
4.858
4.827
1.690
1.659
1.381
1.351
0.643
0.508
Bn
N
O
Si
3a
500 MHz, CDCl3
0.98
6.05
2.27
2.07
1.01
0.95
0.99
1.00
0.97
1.00
3.00
3.13
f1 (ppm)


180.618
151.654
142.612
141.181
137.585
136.224
132.349
130.147
128.798
127.755
127.605
127.438
127.323
124.735
123.572
123.069
108.995
77.331
77.077
76.823
59.608
43.802
24.448
0.113
-0.557
Bn
N
O
Si
3a
125 MHz, CDCl3
f1 (ppm)


7.647
7.632
7.314
7.311
7.276
7.260
7.210
7.207
7.194
7.192
7.058
7.042
7.038
7.035
6.937
6.922
6.567
3.262
1.610
1.579
1.324
1.294
0.619
0.494
500 MHz, CDCl3
N
O
Si
3b
0.99
1.04
1.29
1.08
2.04
1.02
0.98
2.99
1.02
1.08
3.00
2.97
f1 (ppm)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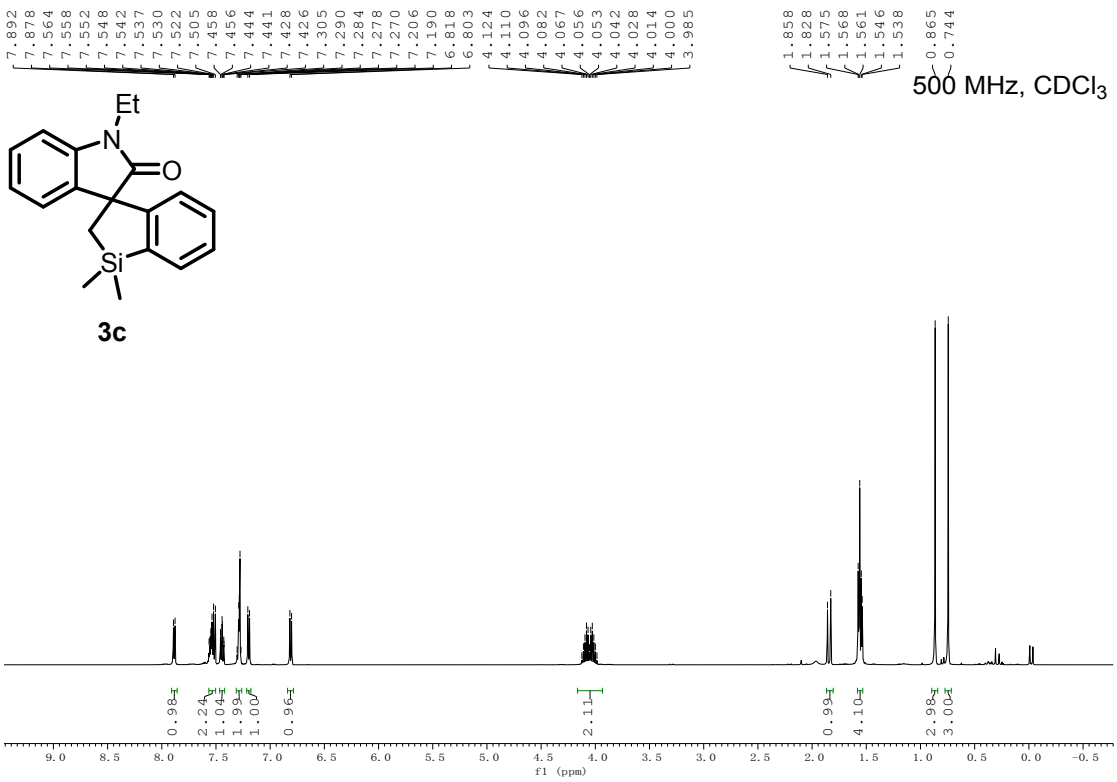
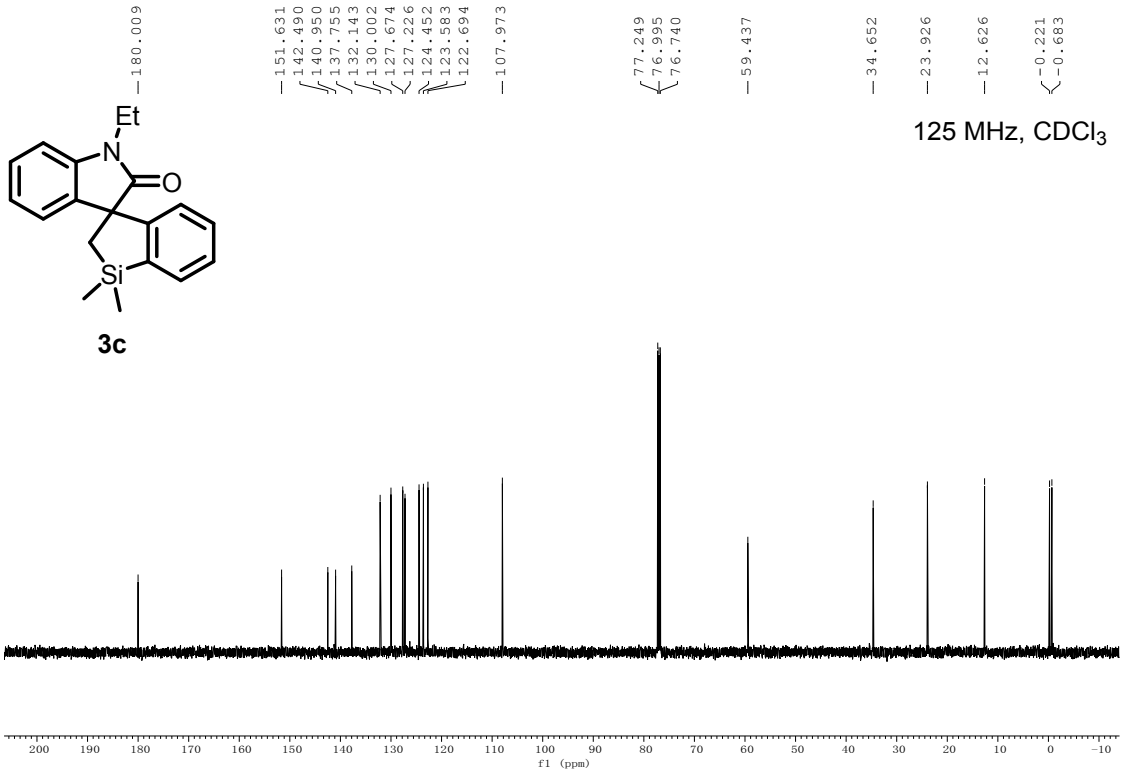
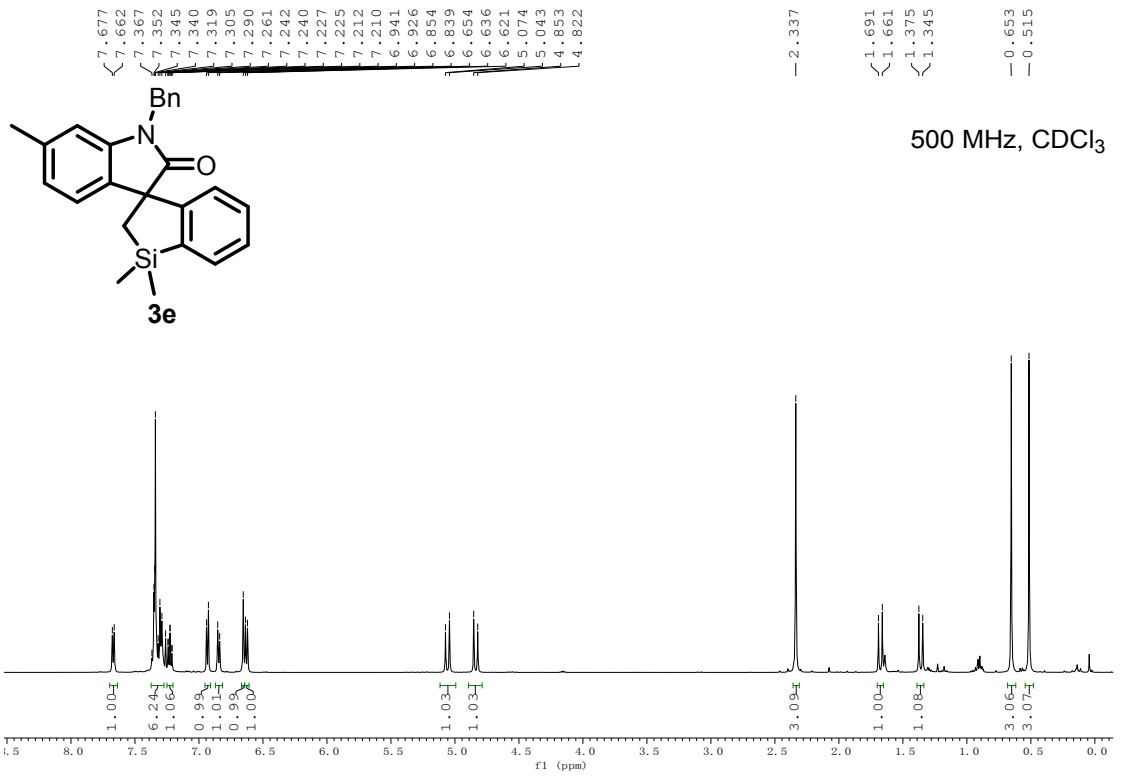
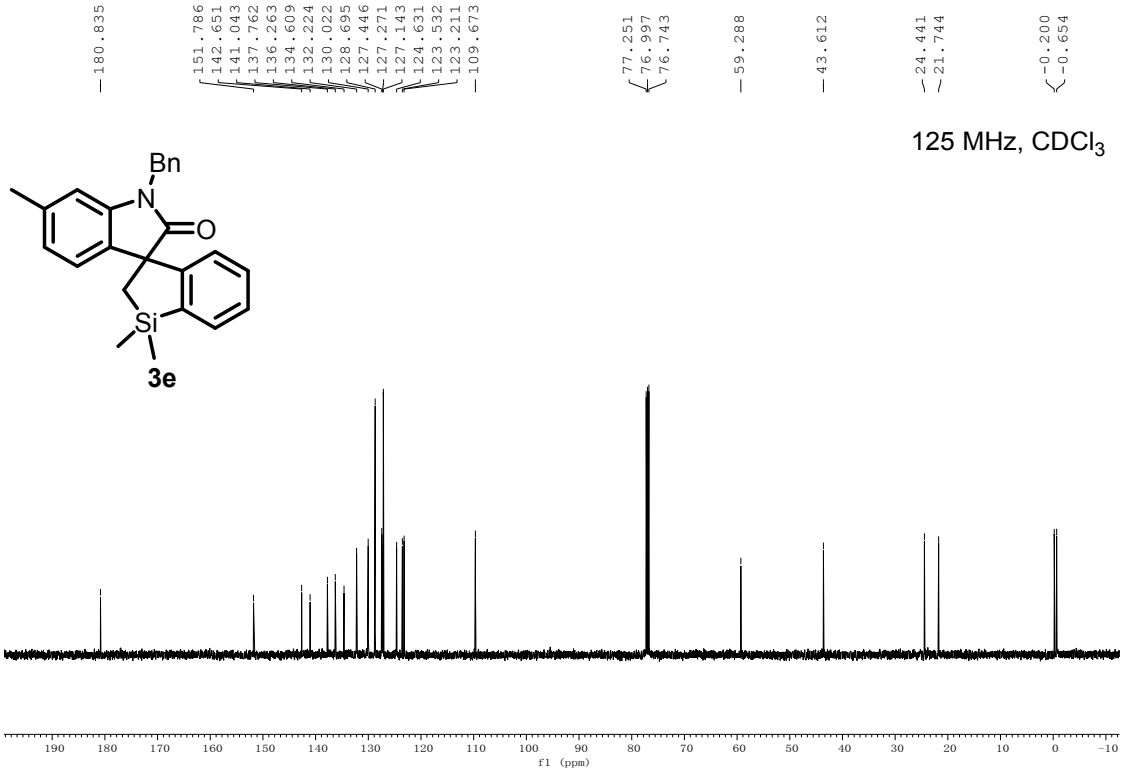
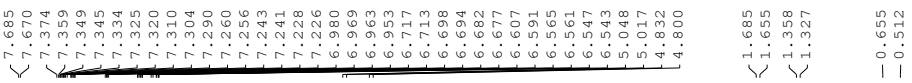
151.584
143.564
141.110
137.535
132.259
130.067
127.861
127.368
124.692
123.489
123.038
107.927
77.354
77.099
76.845
59.636
26.469
24.282
-0.101
-0.589
125 MHz, CDCl3
N
O
Si
3b
f1 (ppm)


7.892
7.878
7.564
7.558
7.552
7.548
7.542
7.537
7.530
7.522
7.505
7.458
7.456
7.444
7.441
7.428
7.426
7.305
7.290
7.284
7.278
7.270
7.206
7.190
6.818
6.803
4.124
4.110
4.096
4.082
4.067
4.056
4.053
4.042
4.028
4.014
4.000
3.985
1.858
1.828
1.575
1.568
1.561
1.546
1.538
0.865
0.744
500 MHz, CDCl3
Et
N
O
Si
3c
0.98
2.24
1.04
1.93
1.00
0.96
2.11
0.99
4.10
2.98
3.00
f1 (ppm)

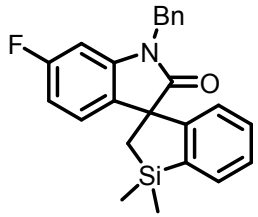

180.009
151.631
142.490
140.950
137.755
132.143
130.002
127.674
127.226
124.452
123.583
122.694
107.973
77.249
76.995
76.740
59.437
34.652
23.926
12.626
0.221
-0.683
125 MHz, CDCl3
Et
N
O
Si
3c
f1 (ppm)


7.677
7.662
7.367
7.352
7.345
7.340
7.319
7.305
7.290
7.261
7.242
7.240
7.227
7.225
7.212
7.210
6.941
6.926
6.854
6.839
6.654
6.636
6.621
5.074
5.043
4.853
4.822
2.337
1.691
1.661
1.375
1.345
0.653
0.515
Bn
N
O
Si
3e
500 MHz, CDCl3
1.00
6.24
1.08
0.99
1.01
0.99
1.00
1.03
1.03
3.09
1.00
1.08
3.06
3.07
f1 (ppm)

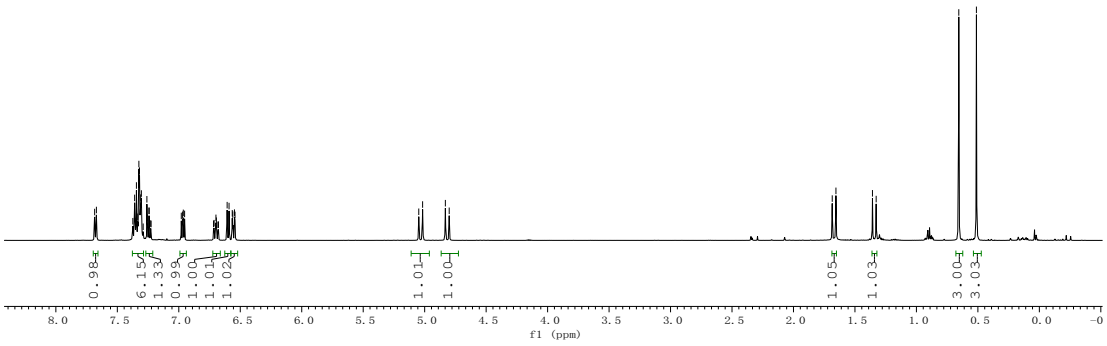

180.835
151.786
142.651
141.043
137.762
136.263
134.609
132.224
130.022
128.695
127.446
127.271
127.143
124.631
123.532
123.211
109.673
77.251
76.997
76.743
59.288
43.612
24.441
21.744
0.200
0.654
Bn
N
O
Si
3e
125 MHz, CDCl3
f1 (ppm)

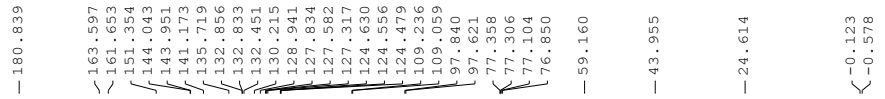


500 MHz, $CDCl_3$

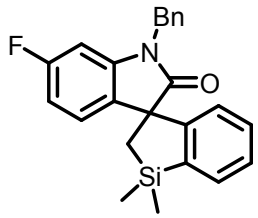


3f

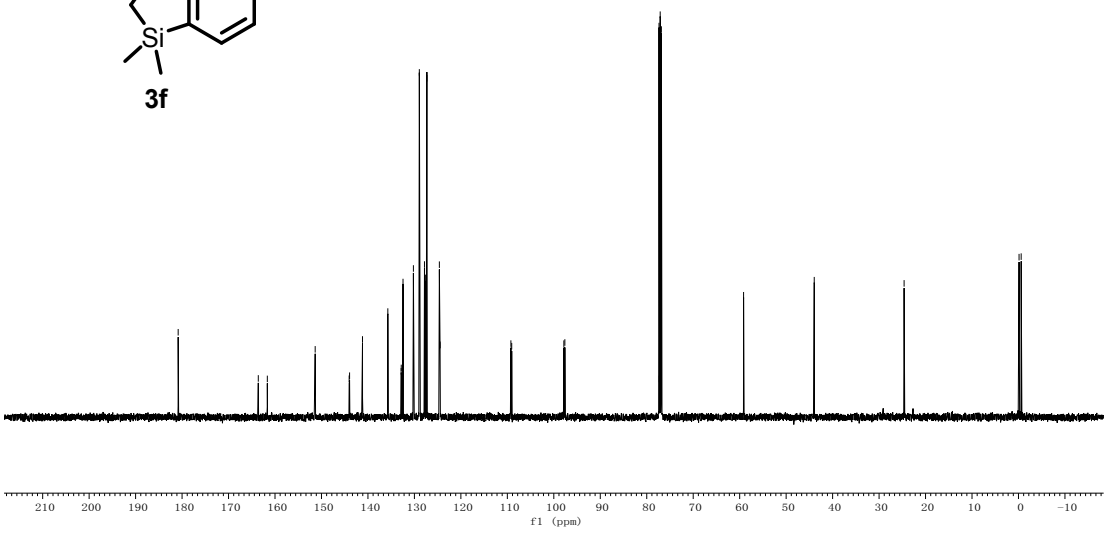


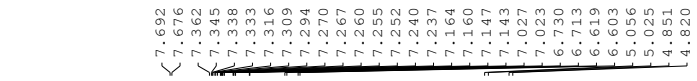


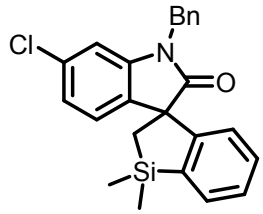
125 MHz, $CDCl_3$



3f

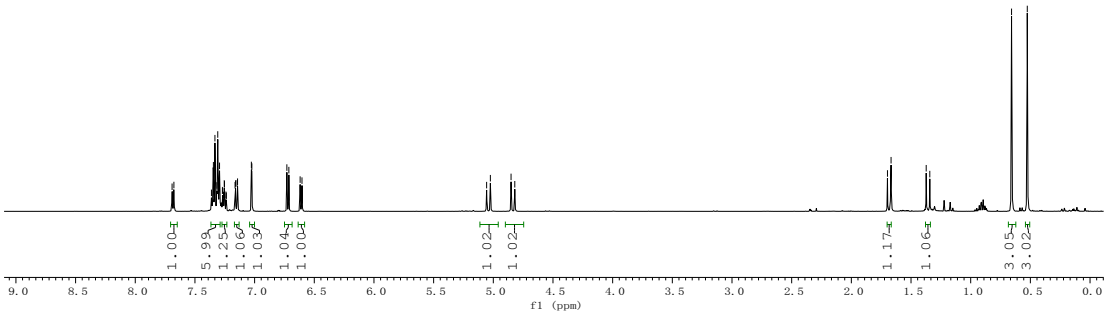


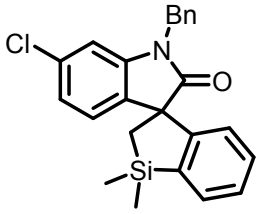




3g

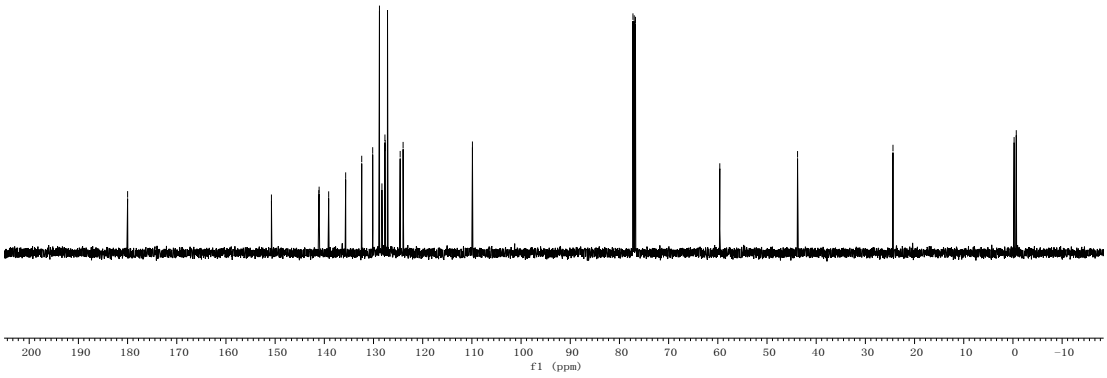
500 MHz, $CDCl_3$

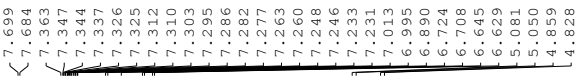


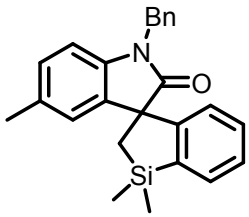


3g

125 MHz, $CDCl_3$

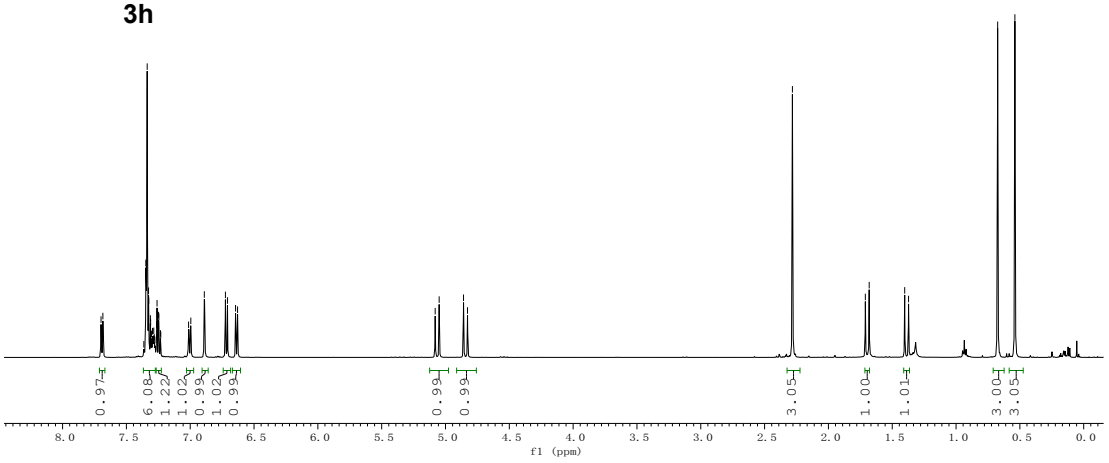


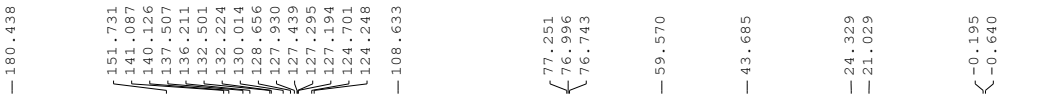


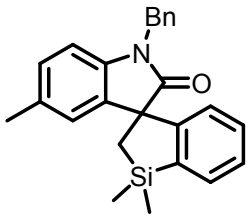


3h

500 MHz, $CDCl_3$

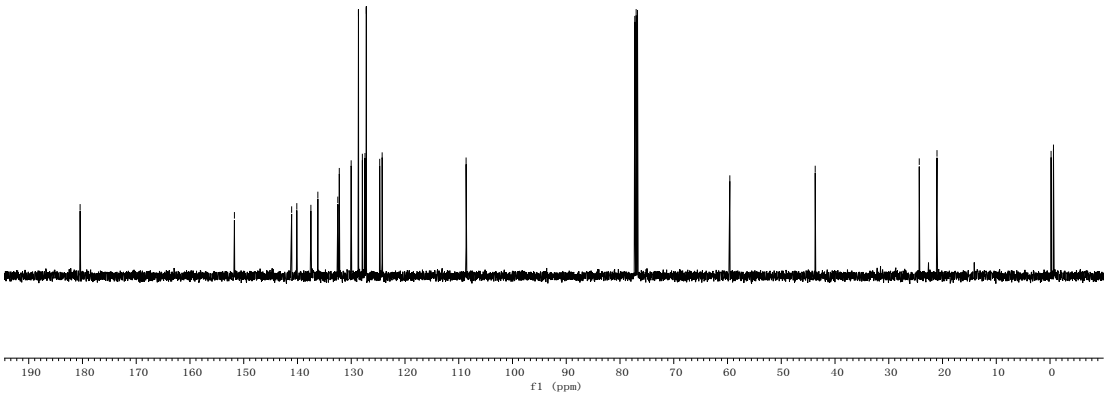


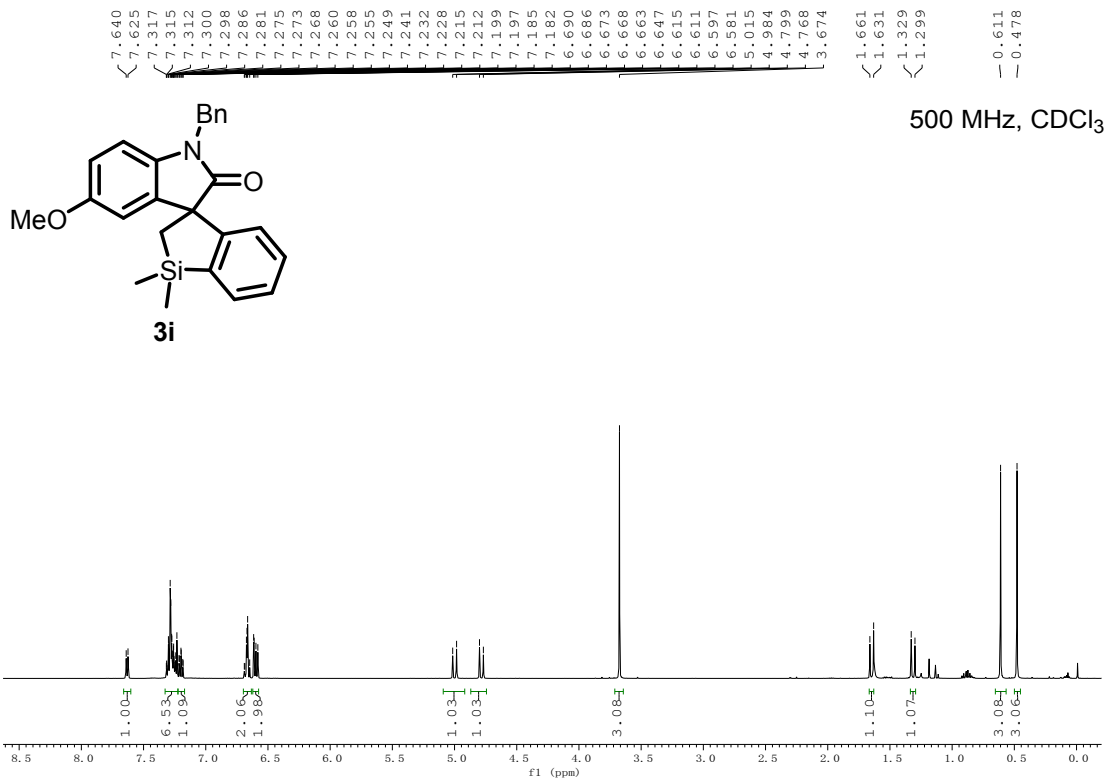




3h

125 MHz, $CDCl_3$




7.640
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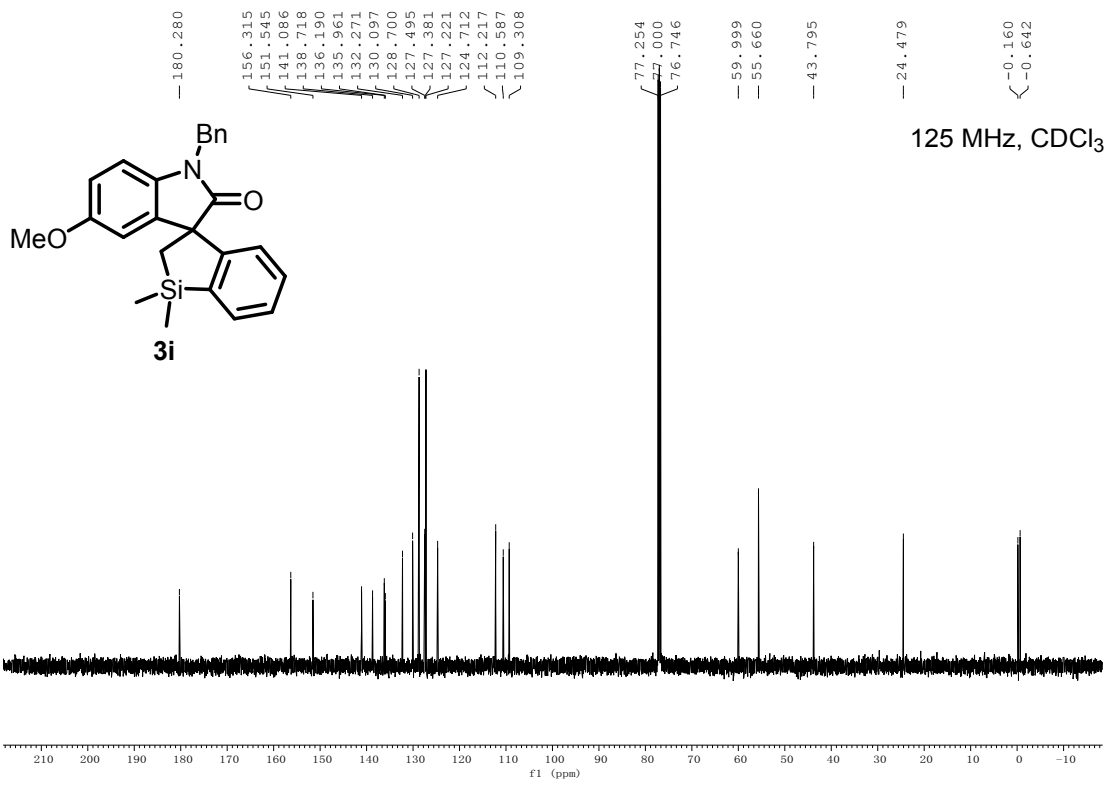
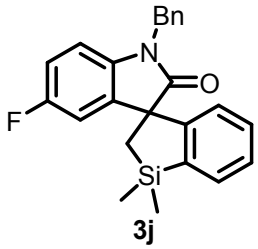
7.317
7.315
7.312
7.300
7.298
7.286
7.281
7.275
7.273
7.268
7.260
7.258
7.255
7.249
7.241
7.232
7.228
7.215
7.212
7.199
7.197
7.185
7.182
6.690
6.686
6.673
6.668
6.663
6.647
6.615
6.611
6.597
6.581
5.015
4.984
4.799
4.768
3.674
1.661
1.631
1.329
1.299
0.611
0.478
Bn
N
O
MeO
Si
500 MHz, CDCl3
1.00
6.53
1.09
2.06
1.98
1.03
1.03
3.08
1.10
1.07
3.08
3.06
f1 (ppm)

3i

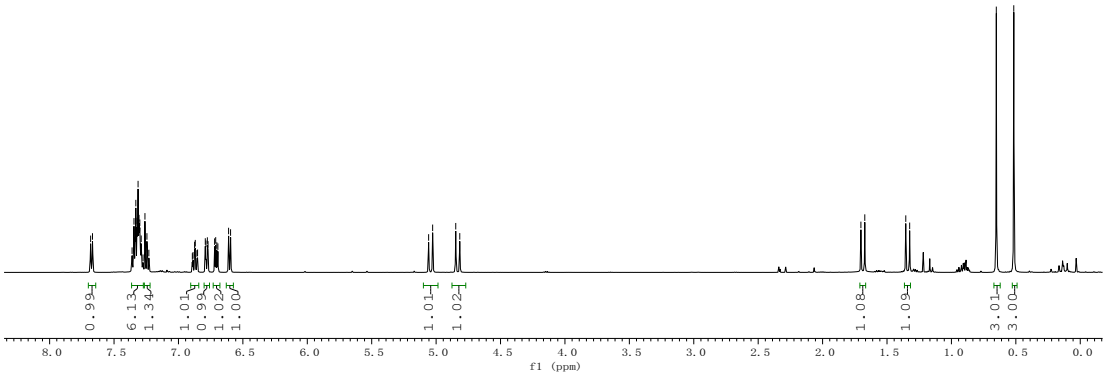

180.280
156.315
151.545
141.086
138.718
136.190
135.961
132.271
130.097
128.700
127.495
127.381
127.221
124.712
112.217
110.587
109.308
77.254
77.000
76.746
59.999
55.660
43.795
24.479
0.160
0.642
Bn
N
O
MeO
Si
125 MHz, CDCl3
f1 (ppm)

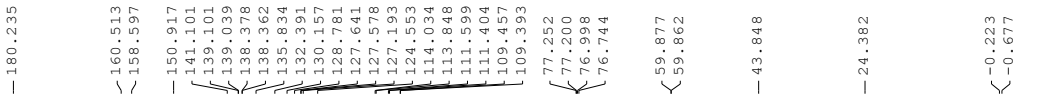
3i

500 MHz, $CDCl_3$

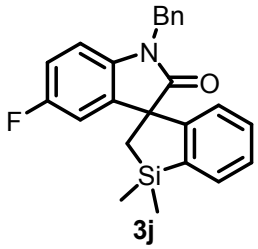


3j

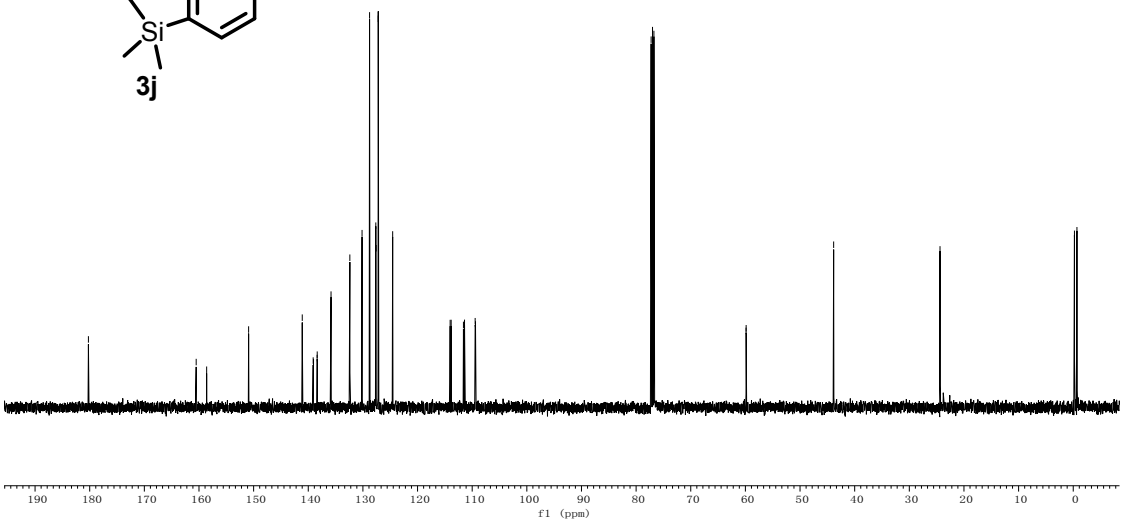


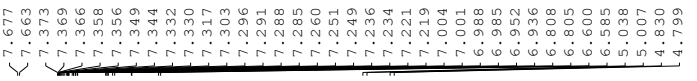


125 MHz, $CDCl_3$

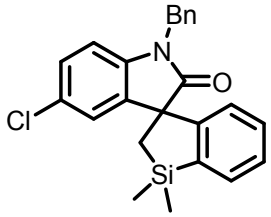


3j

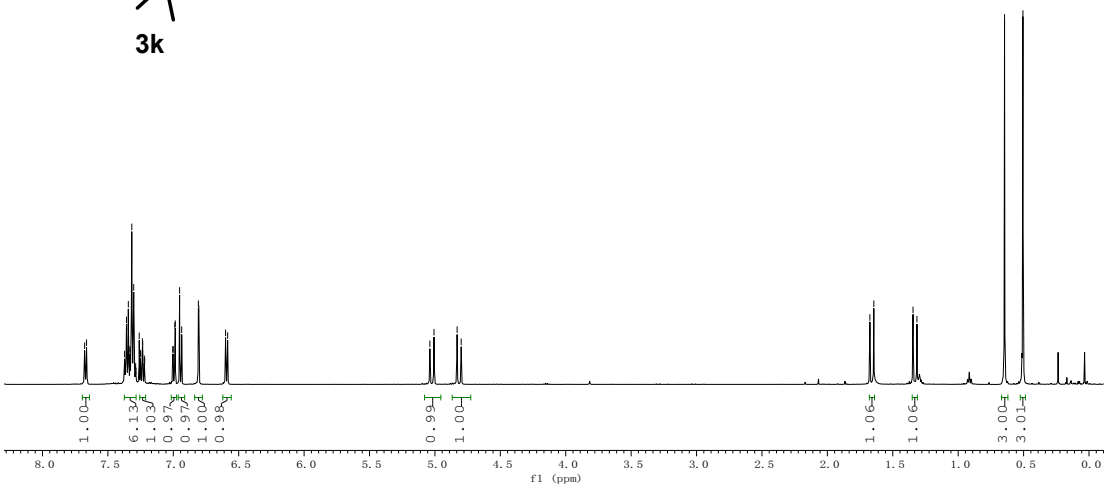


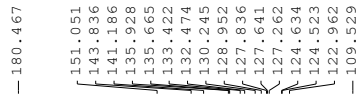


500 MHz, $CDCl_3$

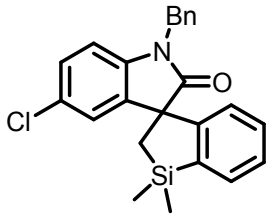


3k

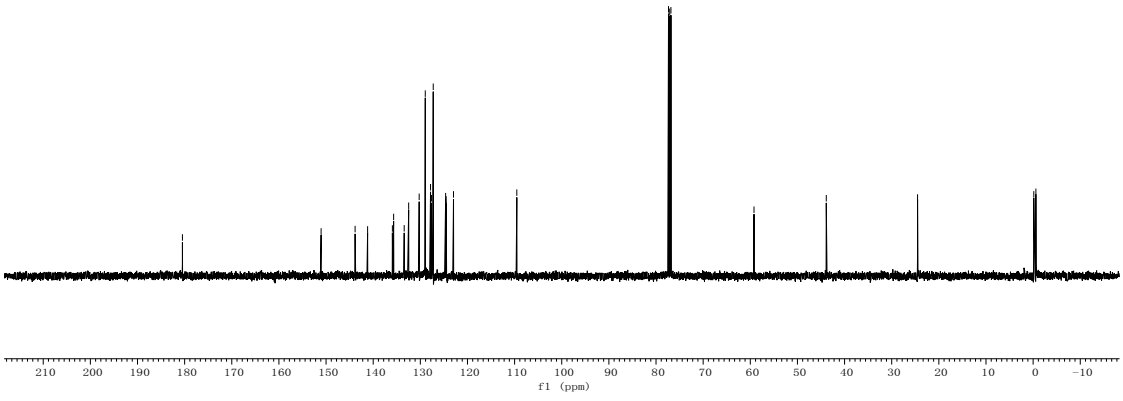


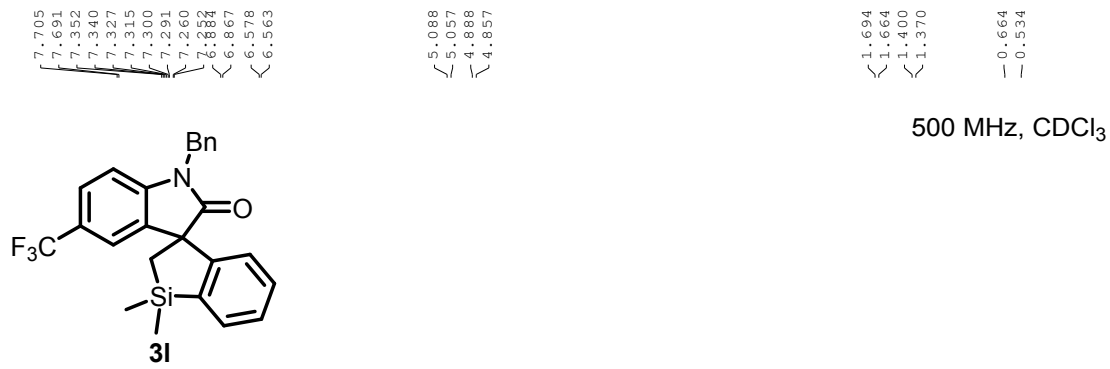


125 MHz, $CDCl_3$

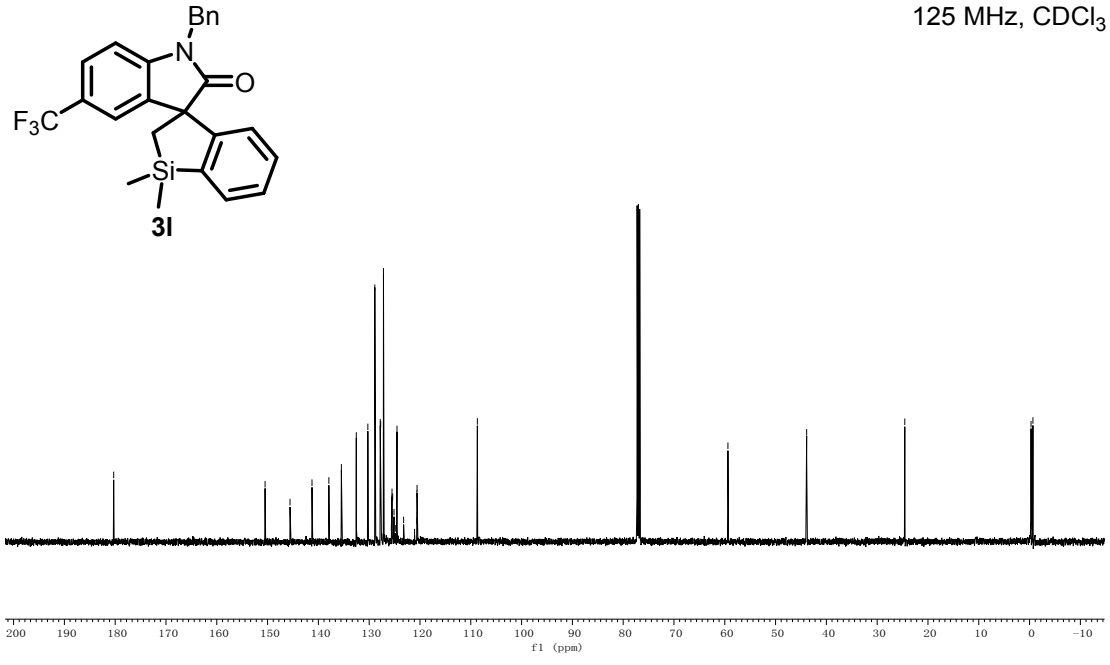


3k

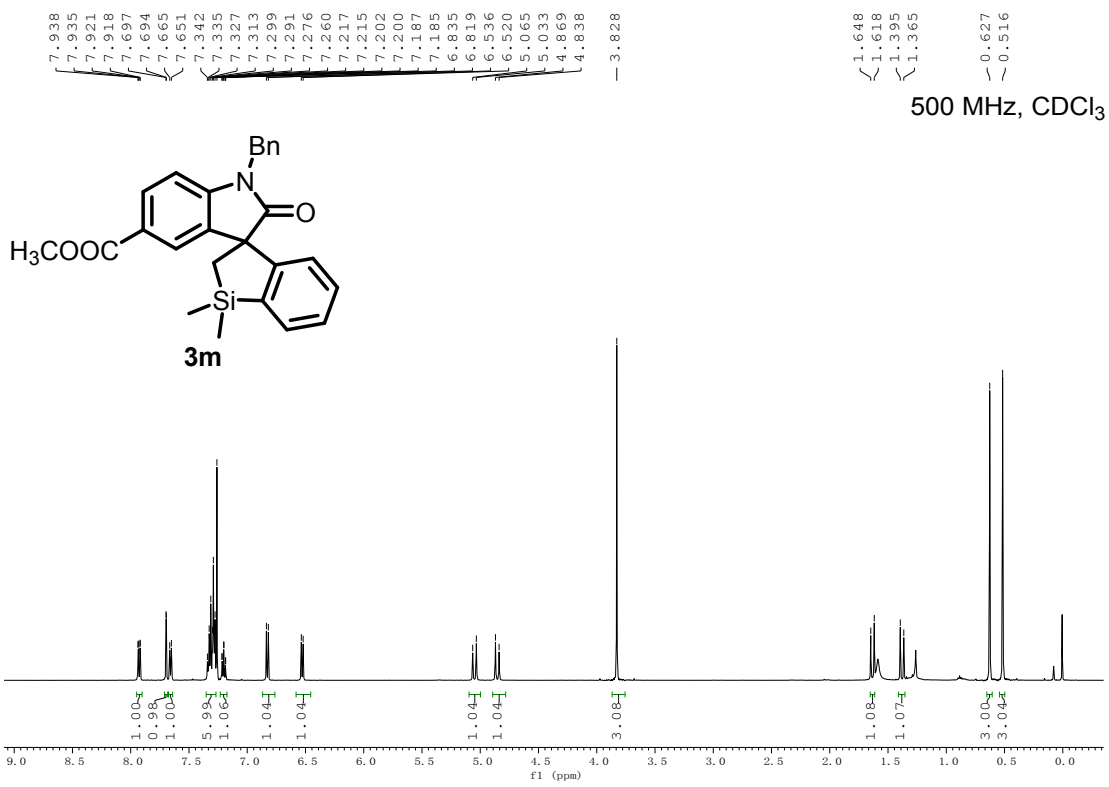




500 MHz, $CDCl_3$



125 MHz, $CDCl_3$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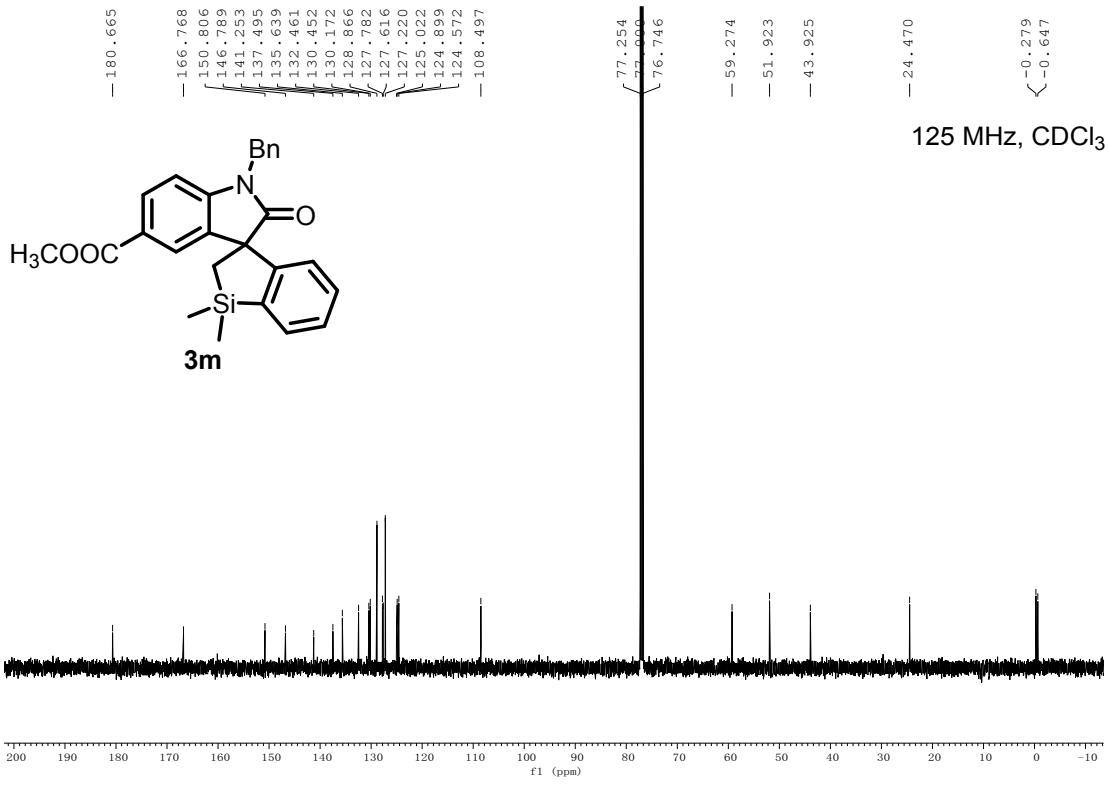
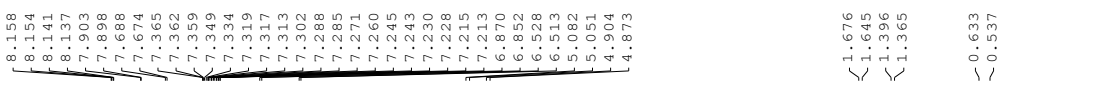
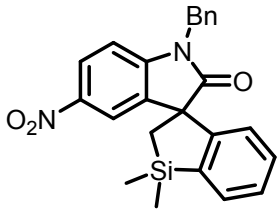
7.921
7.918
7.697
7.694
7.665
7.651
7.342
7.335
7.327
7.313
7.299
7.291
7.276
7.260
7.217
7.215
7.202
7.200
7.187
7.185
6.835
6.819
6.536
6.520
5.065
5.033
4.869
4.838
3.828
1.648
1.618
1.395
1.365
0.627
0.516
500 MHz, CDCl3
Bn
N
O
H3COOC
Si
3m
1.00
0.98
1.00
5.99
1.06
1.04
1.04
1.04
1.04
3.08
1.08
1.07
3.00
3.04
f1 (ppm)

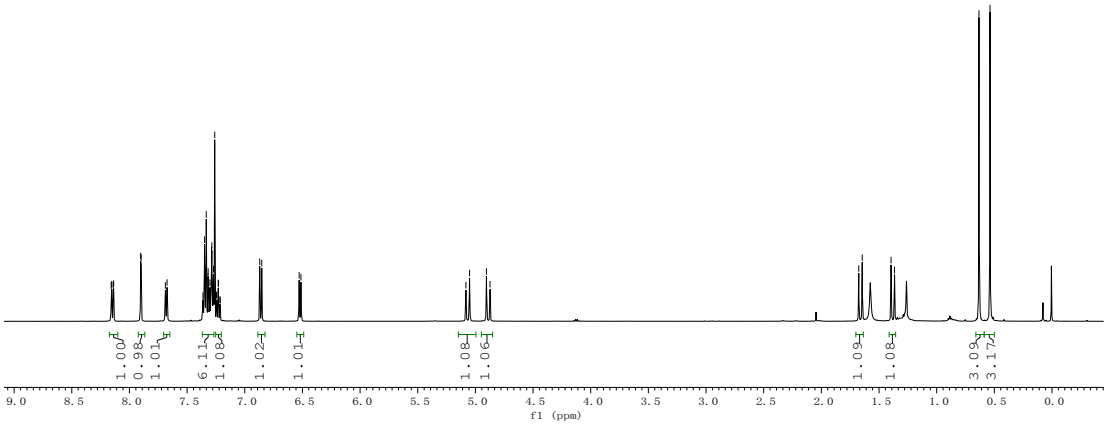

180.665
166.768
150.806
146.789
141.253
137.495
135.639
132.461
130.452
130.172
128.866
127.782
127.616
127.220
125.022
124.899
124.572
108.497
77.254
77.000
76.746
59.274
51.923
43.925
24.470
0.279
0.647
125 MHz, CDCl3
Bn
N
O
H3COOC
Si
3m
f1 (ppm)

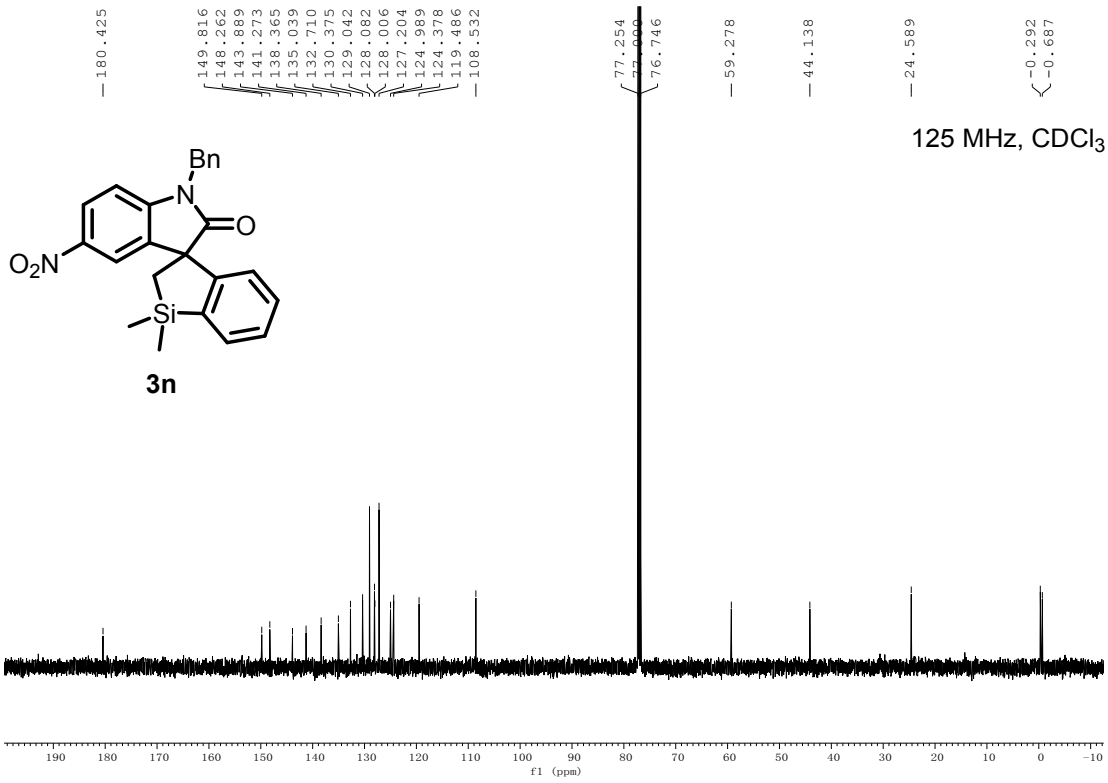


500 MHz, $CDCl_3$



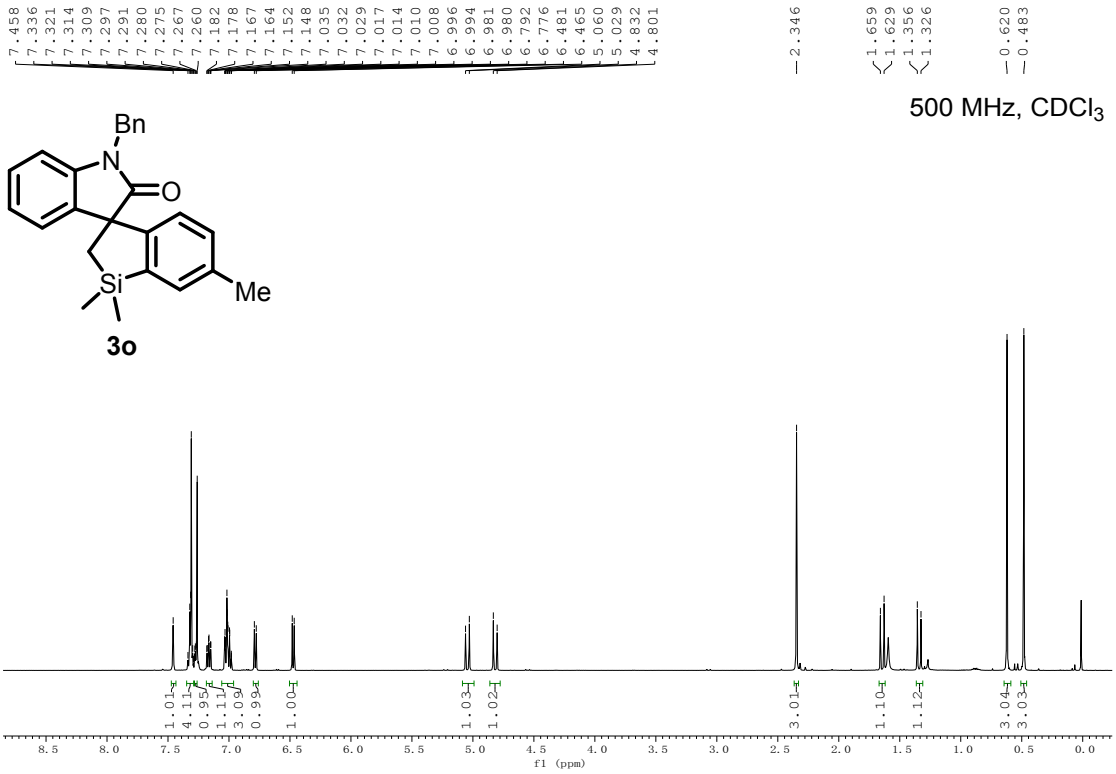
3n

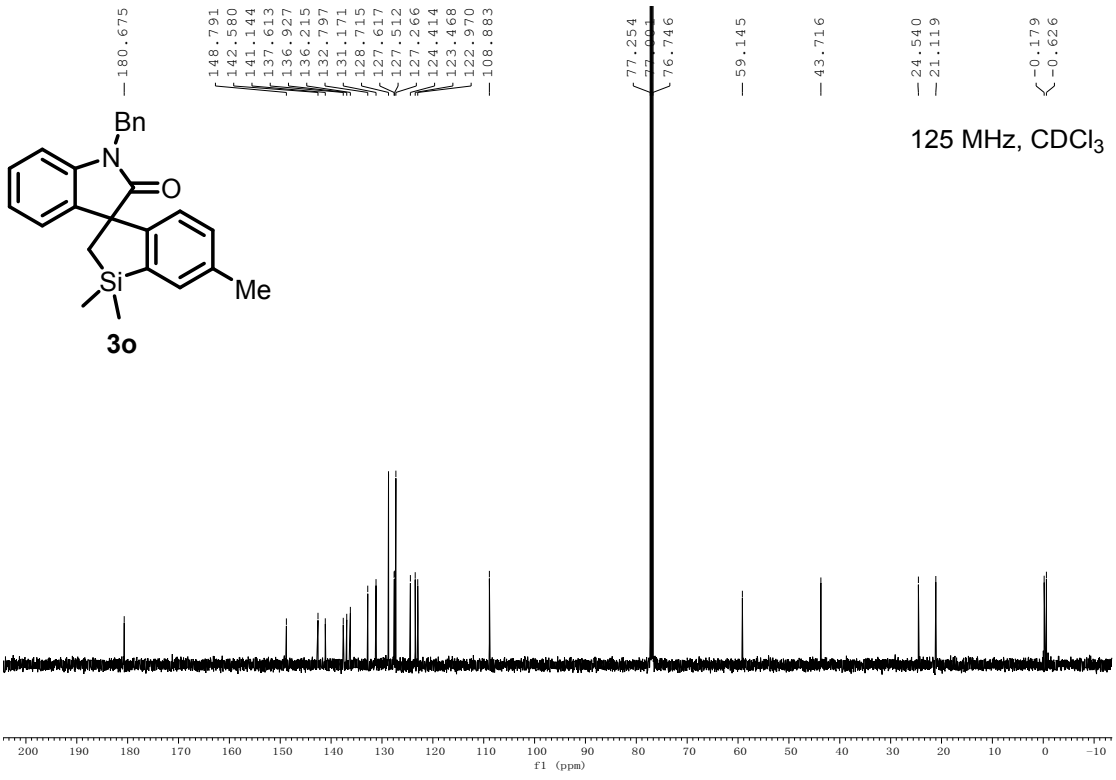




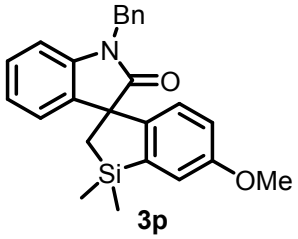
125 MHz, $CDCl_3$

3n

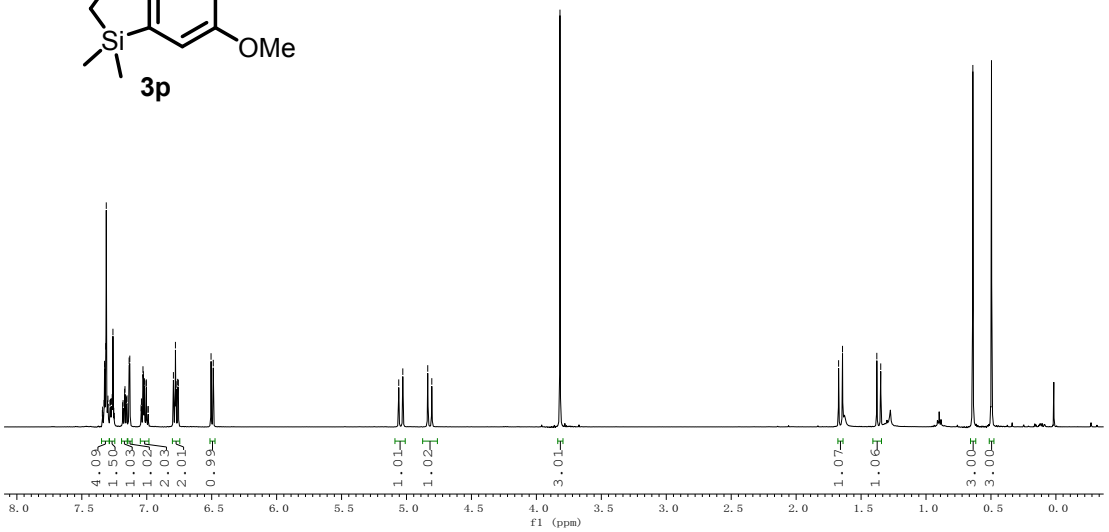

7.458
7.336
7.321
7.314
7.309
7.297
7.291
7.280
7.275
7.267
7.260
7.182
7.178
7.167
7.164
7.152
7.148
7.035
7.032
7.029
7.017
7.014
7.010
7.008
6.996
6.994
6.981
6.980
6.792
6.776
6.481
6.465
5.060
5.029
4.832
4.801
2.346
1.659
1.629
1.356
1.326
0.620
0.483
500 MHz, CDCl3
Bn
N
O
Si
Me
3o
1.01
4.11
0.95
1.11
3.09
0.99
1.00
1.03
1.02
3.01
1.10
1.12
3.04
3.03
f1 (ppm)

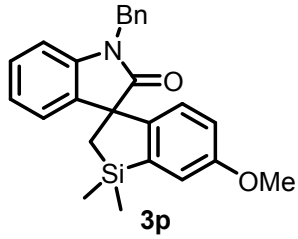

180.675
148.791
142.580
141.144
137.613
136.927
136.215
132.797
131.171
128.715
127.617
127.512
127.266
124.414
123.468
122.970
108.883
77.254
77.001
76.746
59.145
43.716
24.540
21.119
0.179
0.626
125 MHz, CDCl3
Bn
N
O
Si
Me
3o
f1 (ppm)

500 MHz, $CDCl_3$



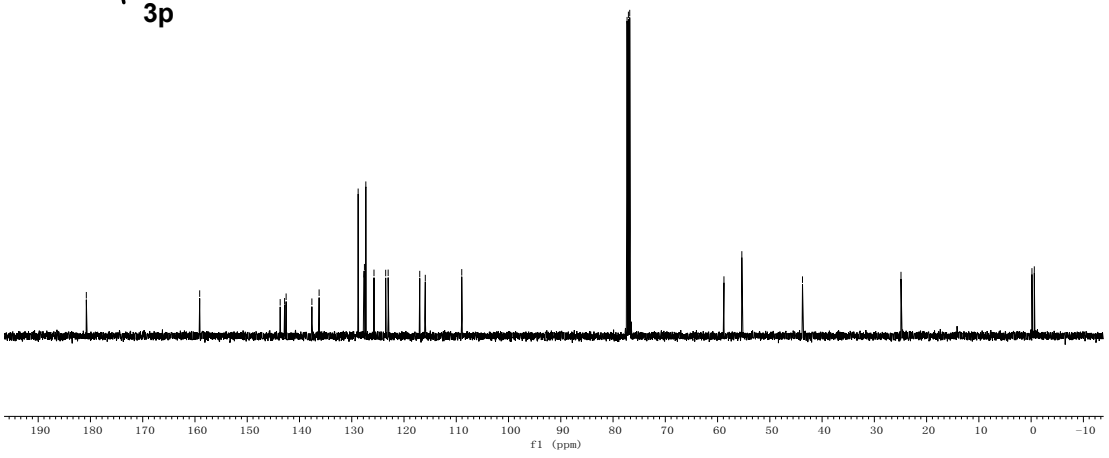
3p

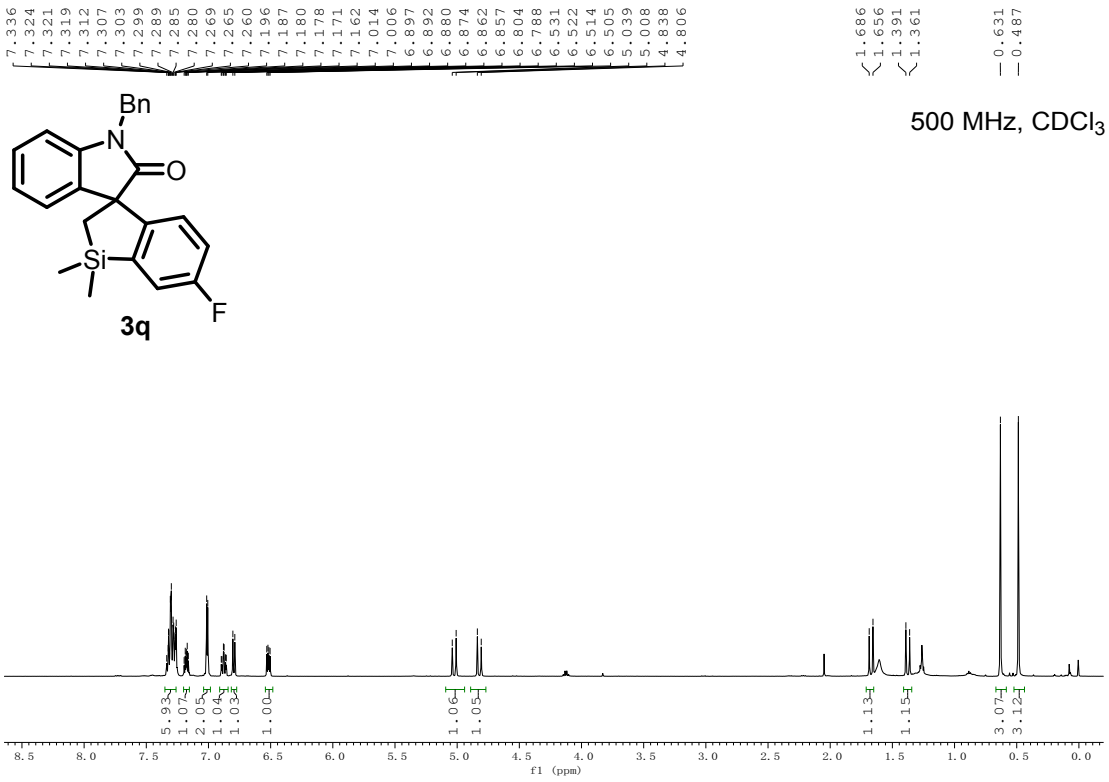


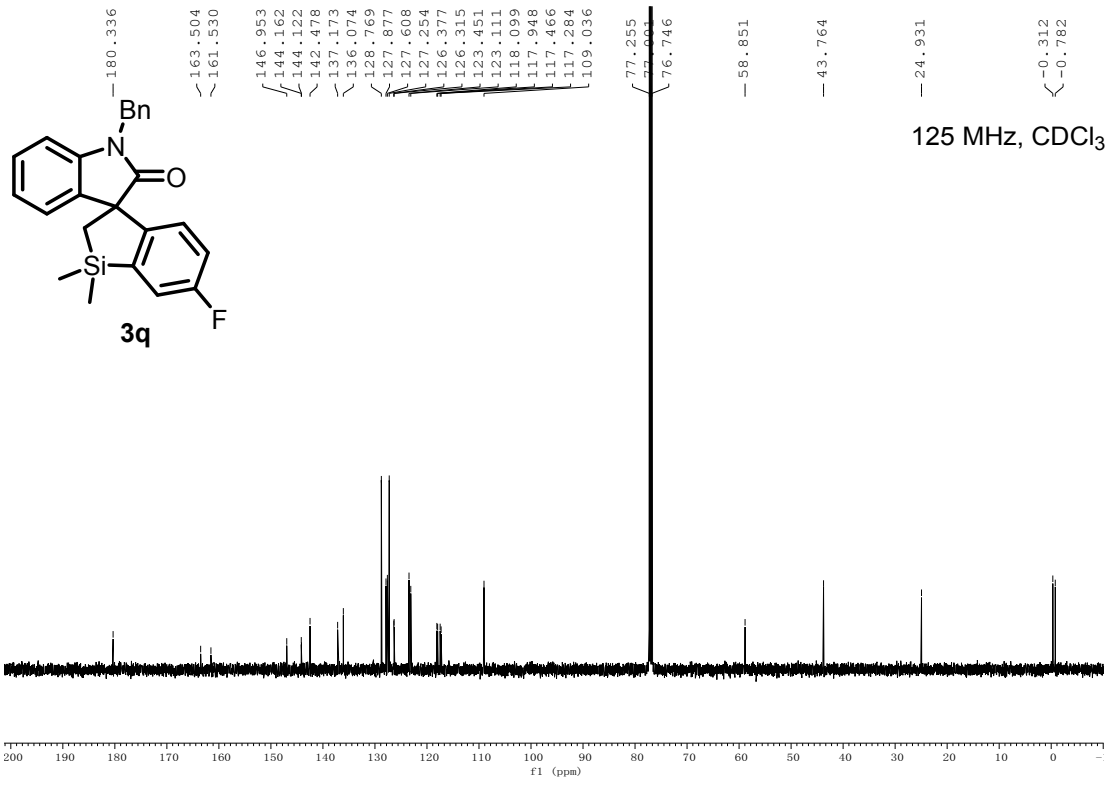


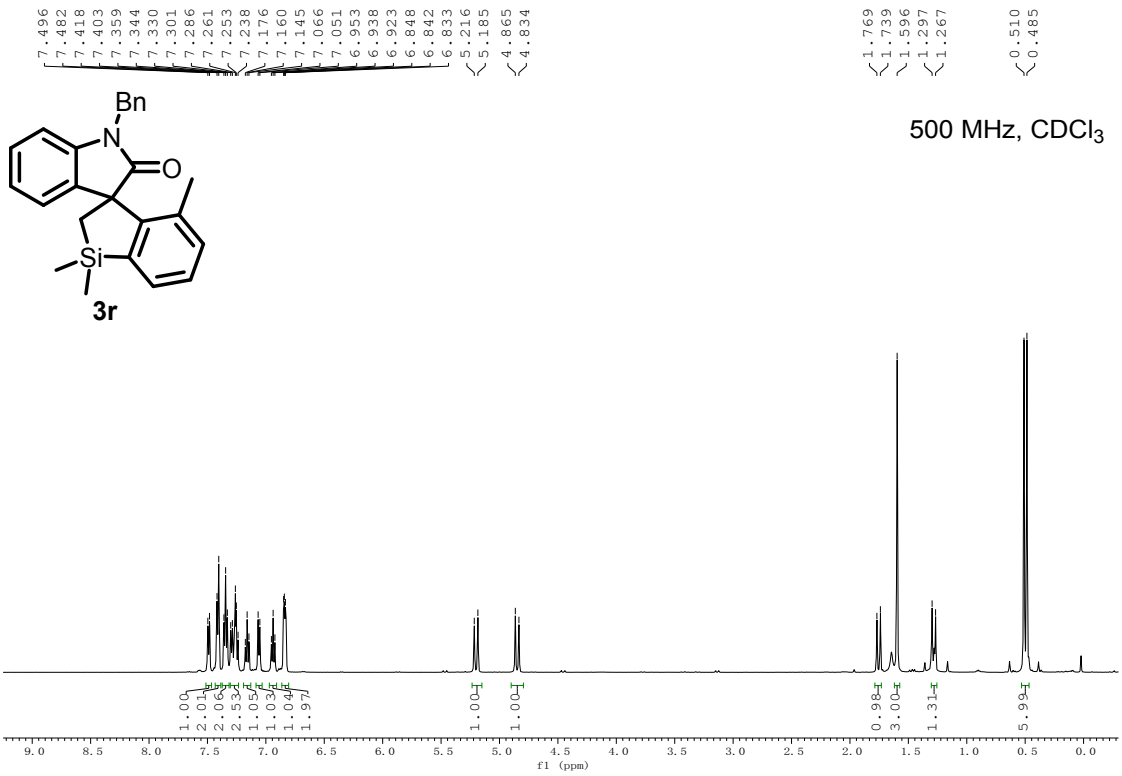
3p

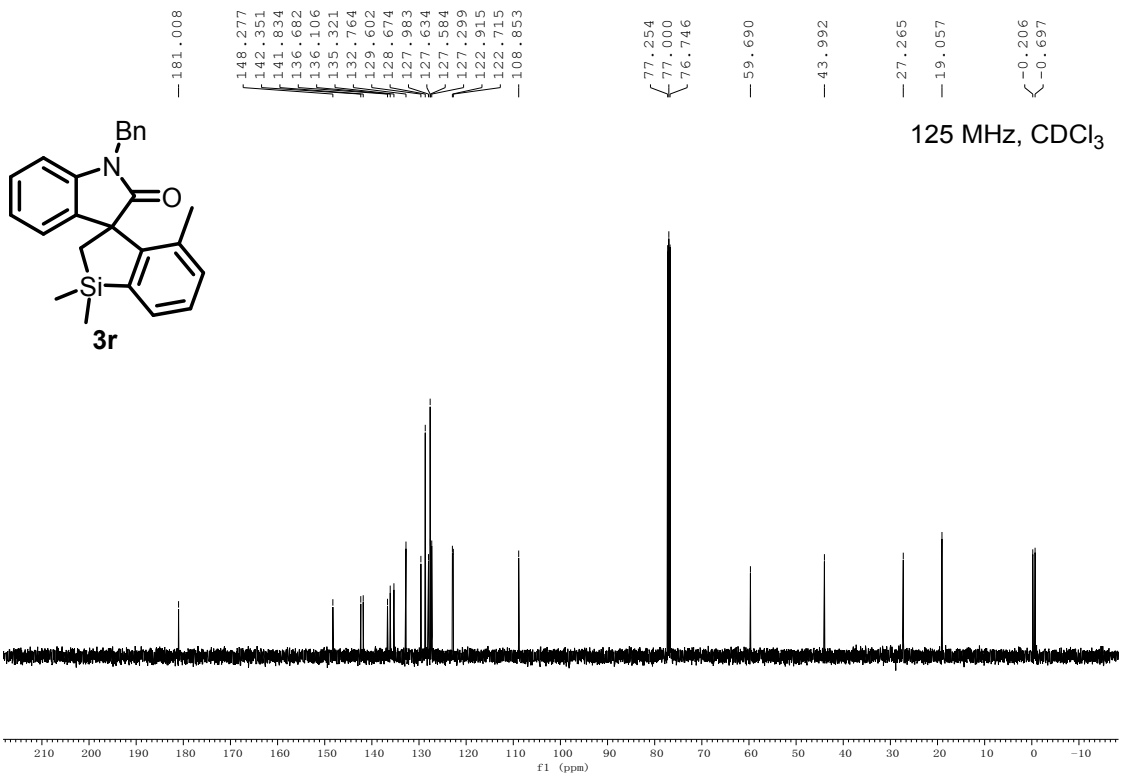
125 MHz, $CDCl_3$

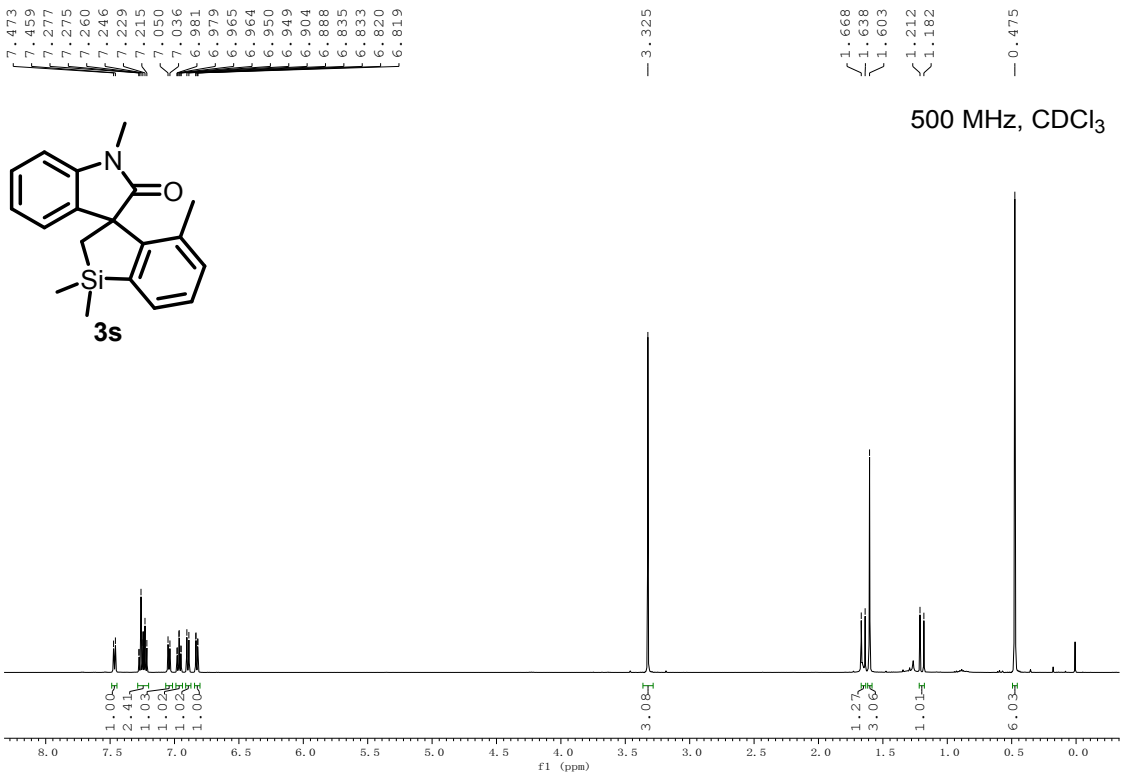


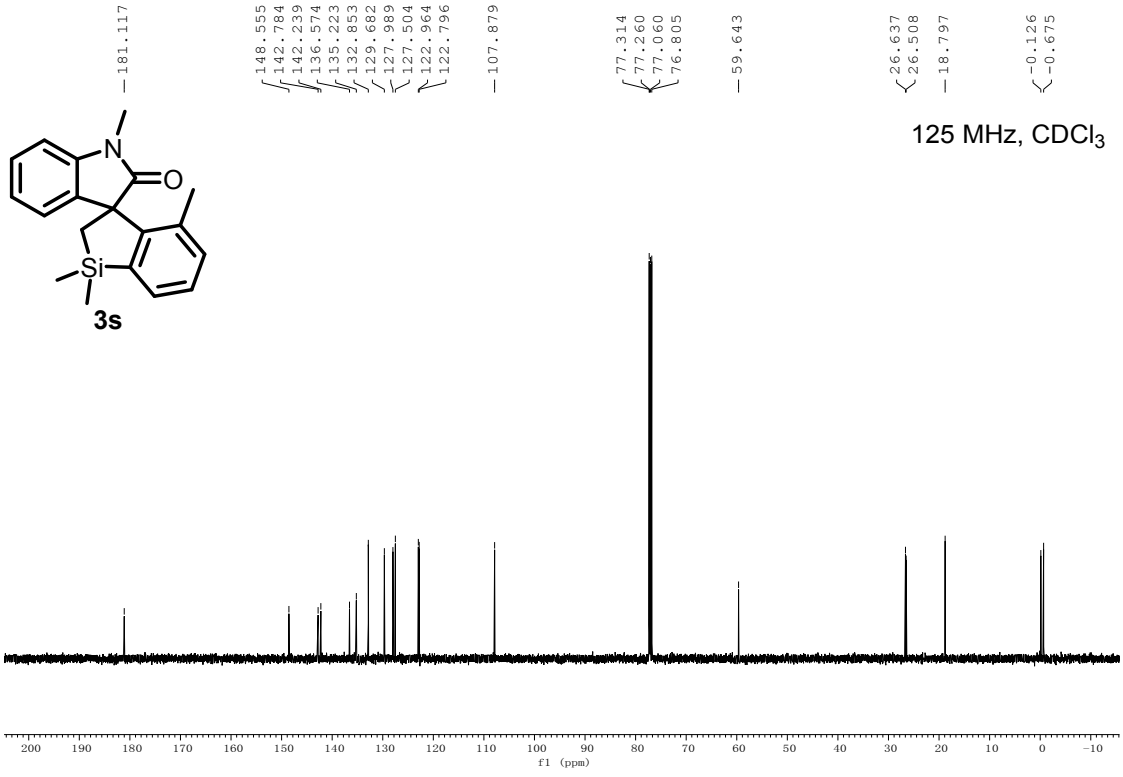

7.336
7.324
7.321
7.319
7.312
7.307
7.303
7.299
7.289
7.285
7.280
7.269
7.265
7.260
7.196
7.187
7.180
7.178
7.171
7.162
7.014
7.006
6.897
6.892
6.880
6.874
6.862
6.857
6.804
6.788
6.531
6.522
6.514
6.505
5.039
5.008
4.838
4.806
1.686
1.656
1.391
1.361
0.631
0.487
Bn
N
O
Si
F
3q
500 MHz, CDCl3
5.93
1.07
2.05
1.04
1.03
1.00
1.06
1.05
1.13
1.15
3.07
3.12
f1 (ppm)


180.336
163.504
161.530
146.953
144.162
144.122
142.478
137.173
136.074
128.769
127.877
127.608
127.254
126.377
126.315
123.451
123.111
118.099
117.948
117.466
117.284
109.036
77.255
76.746
58.851
43.764
24.931
0.312
0.782
Bn
N
O
Si
F
3q
125 MHz, CDCl3
f1 (ppm)

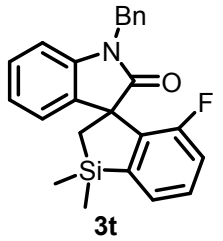

7.496
7.482
7.418
7.403
7.359
7.344
7.330
7.301
7.286
7.261
7.253
7.238
7.176
7.160
7.145
7.066
7.051
6.953
6.938
6.923
6.848
6.842
6.833
5.216
5.185
4.865
4.834
1.769
1.739
1.596
1.297
1.267
0.510
0.485
Bn
N
O
Si
3r
500 MHz, CDCl3
f1 (ppm)


181.008
148.277
142.351
141.834
136.682
136.106
135.321
132.764
129.602
128.674
127.983
127.634
127.584
127.299
122.915
122.715
108.853
77.254
77.000
76.746
59.690
43.992
27.265
19.057
-0.206
-0.697
Bn
N
O
Si
3r
125 MHz, CDCl3
f1 (ppm)

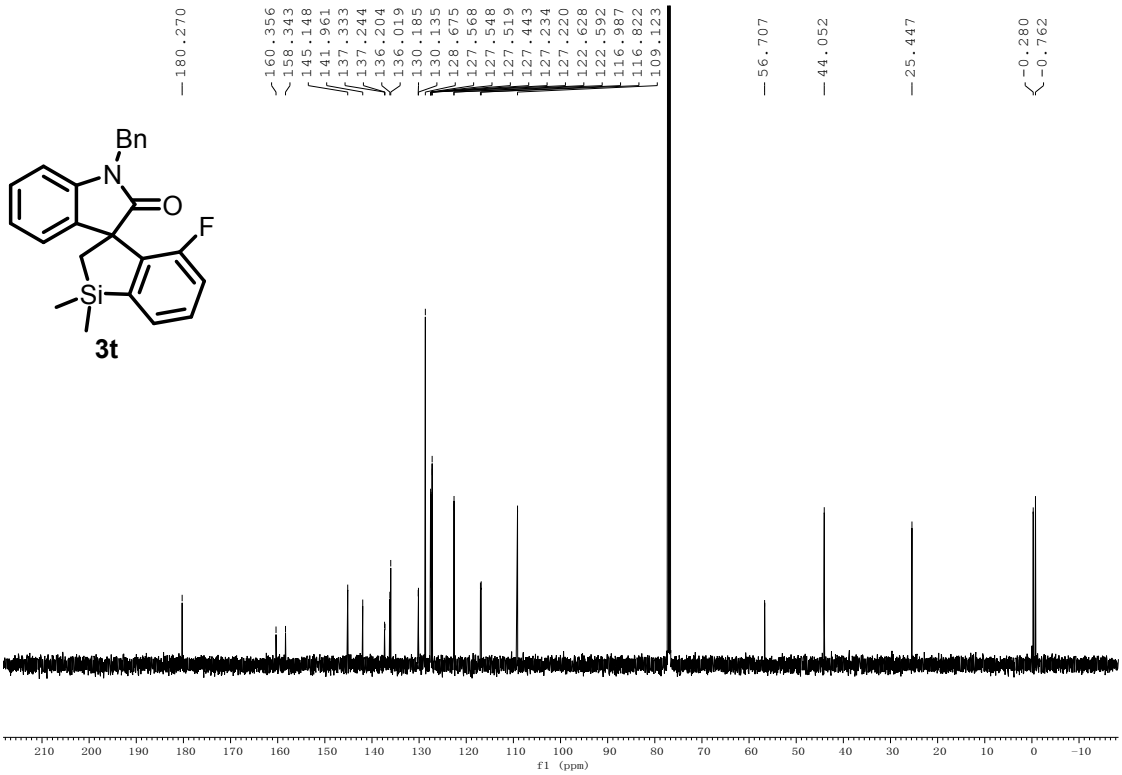

7.473
7.459
7.277
7.275
7.260
7.246
7.229
7.215
7.050
7.036
6.981
6.979
6.965
6.964
6.950
6.949
6.904
6.888
6.835
6.833
6.820
6.819
3.325
1.668
1.638
1.603
1.212
1.182
0.475
500 MHz, CDCl3
N
O
Si
3s
1.00
2.41
1.03
1.02
1.02
1.00
3.08
1.27
3.06
1.01
6.03
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


181.117
148.555
142.784
142.239
136.574
135.223
132.853
129.682
127.989
127.504
122.964
122.796
107.879
77.314
77.260
77.060
76.805
59.643
26.637
26.508
18.797
-0.126
-0.675
125 MHz, CDCl3
N
O
Si
3s
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

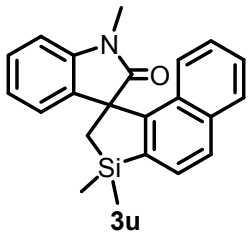
500 MHz, $CDCl_3$



3t

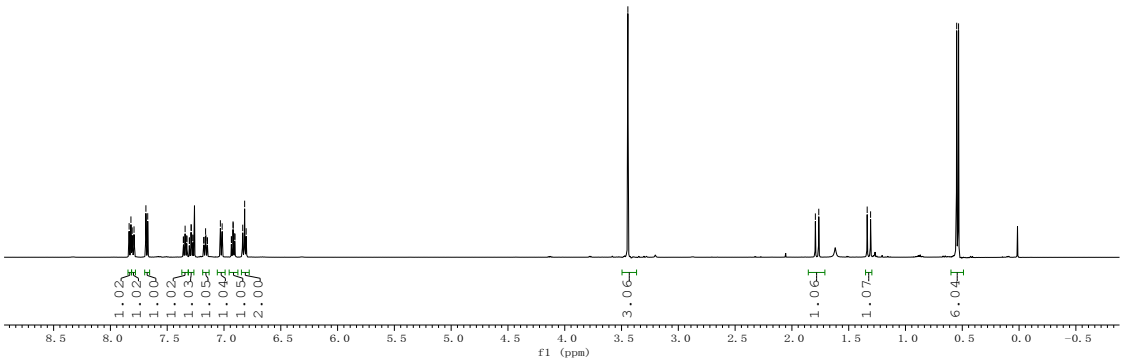


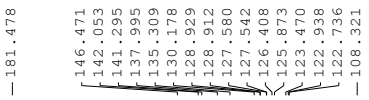
3t

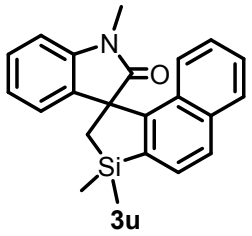


3u

500 MHz, $CDCl_3$

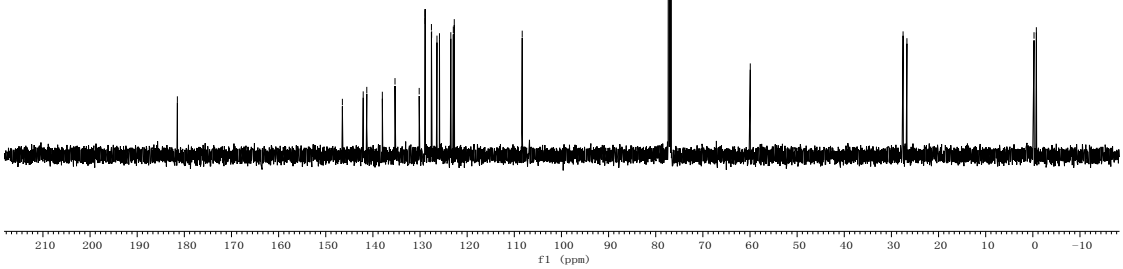


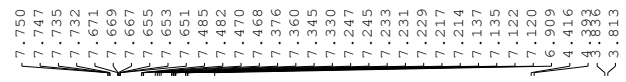




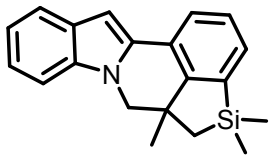
3u

125 MHz, $CDCl_3$

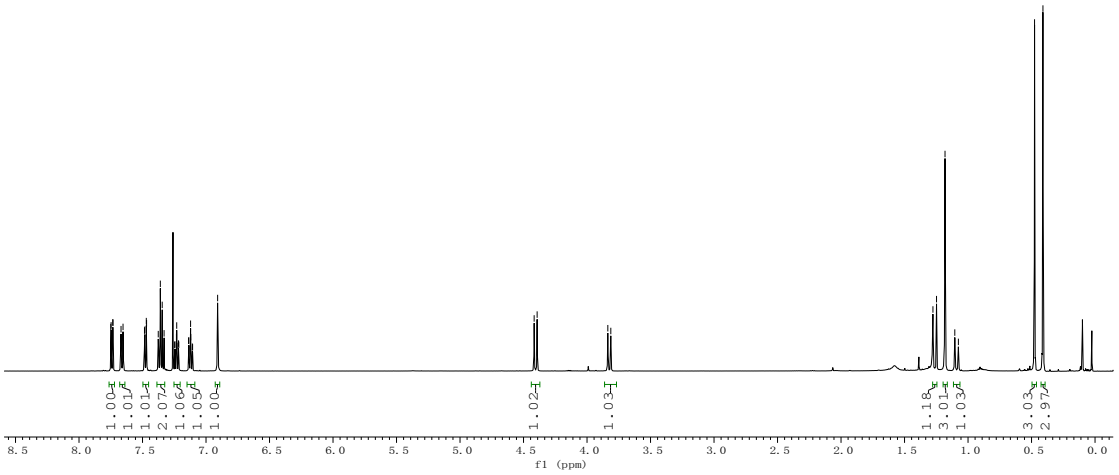


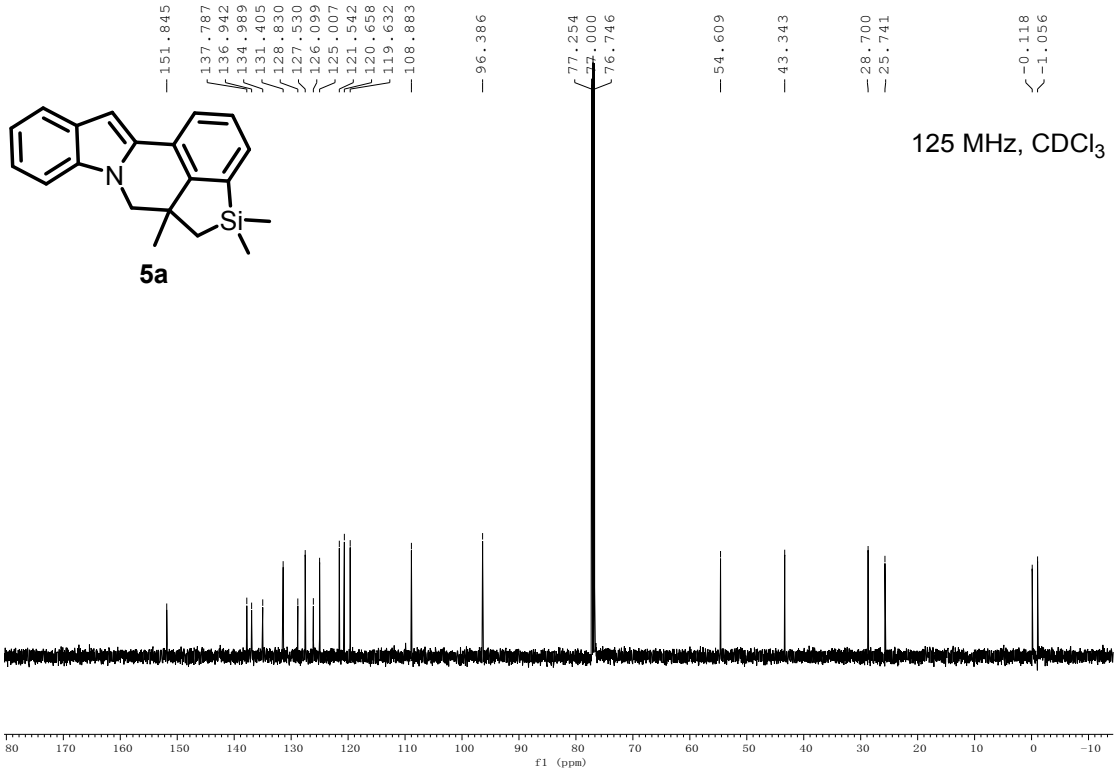


500 MHz, $CDCl_3$



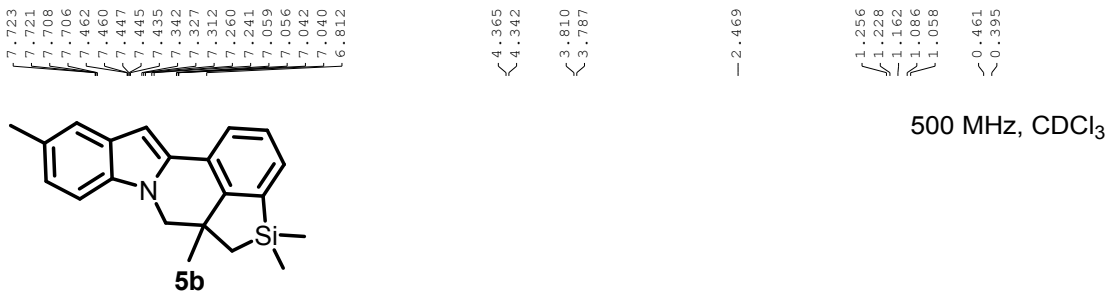
5a





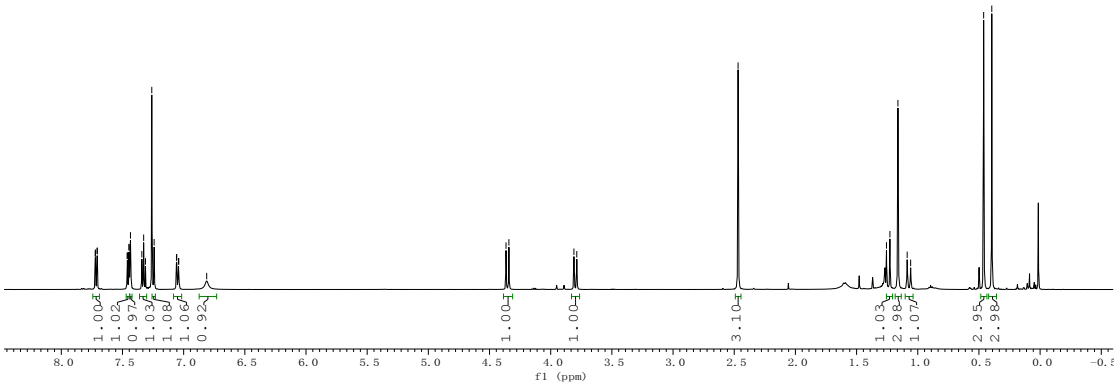
125 MHz, $CDCl_3$

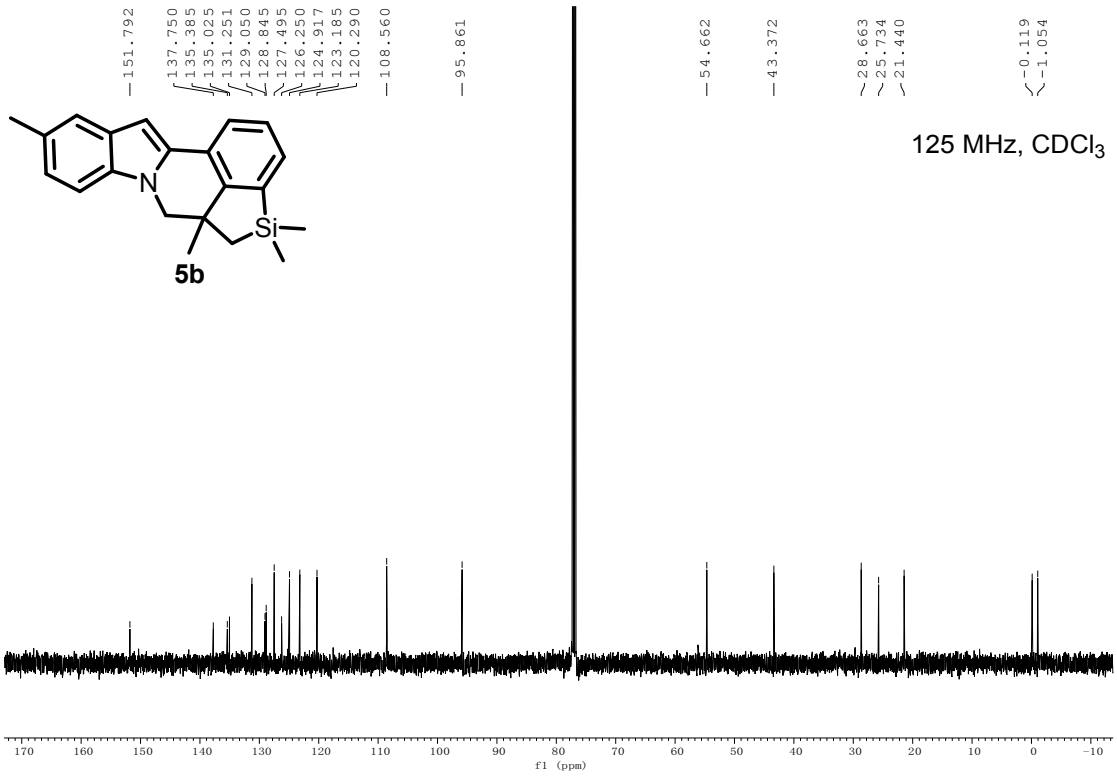
5a



500 MHz, $CDCl_3$

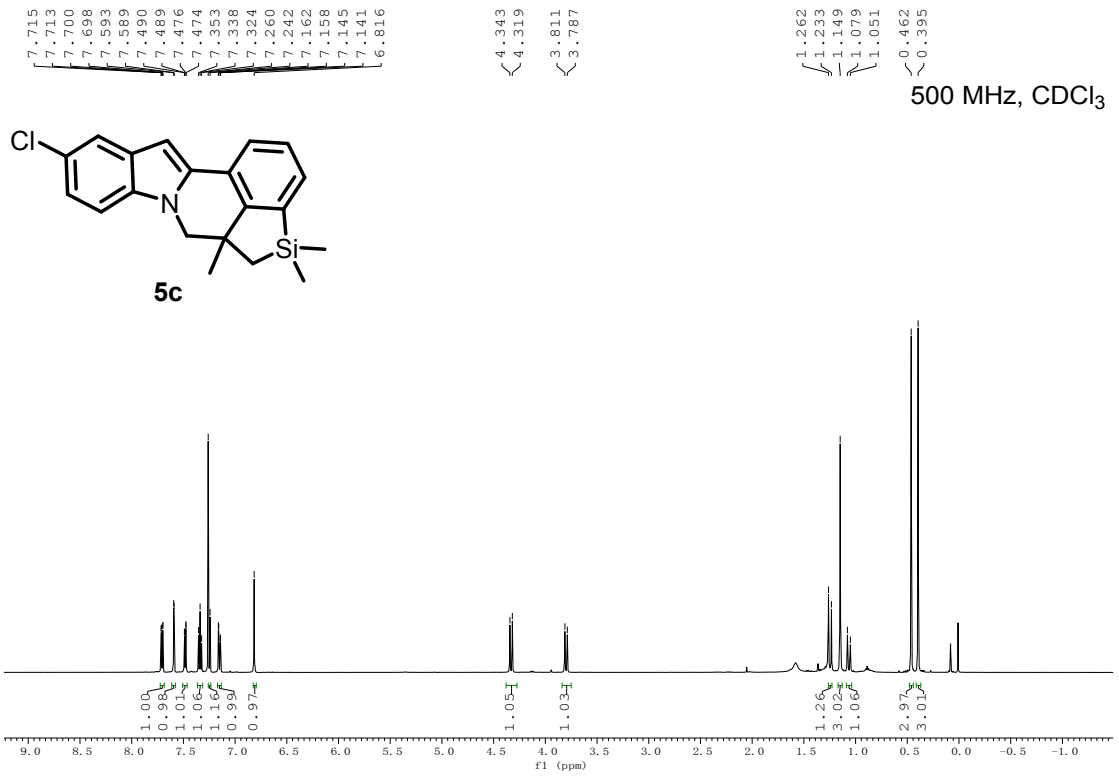
5b

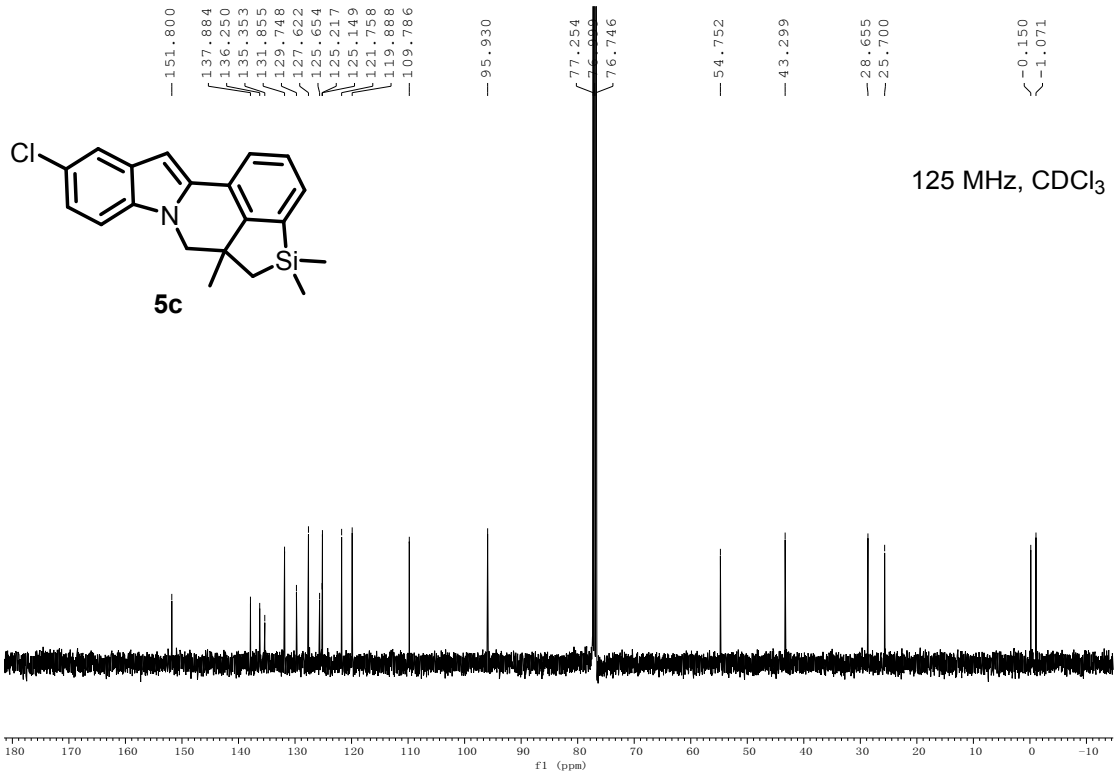


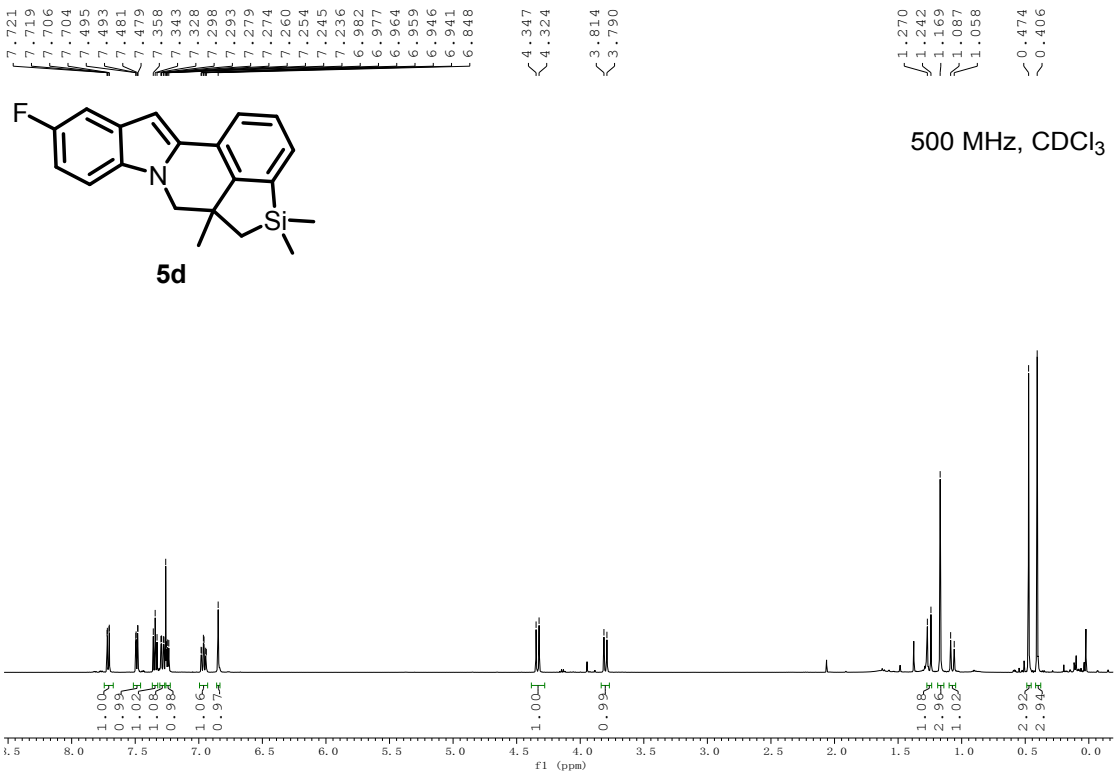


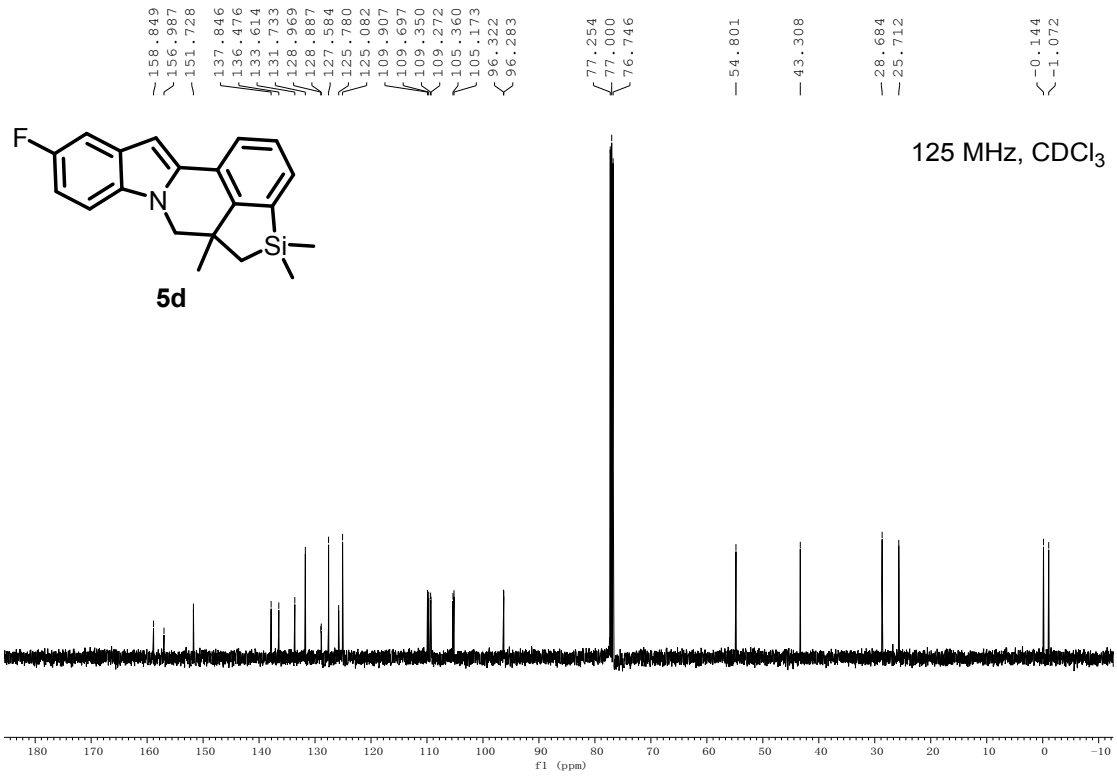
125 MHz, $CDCl_3$

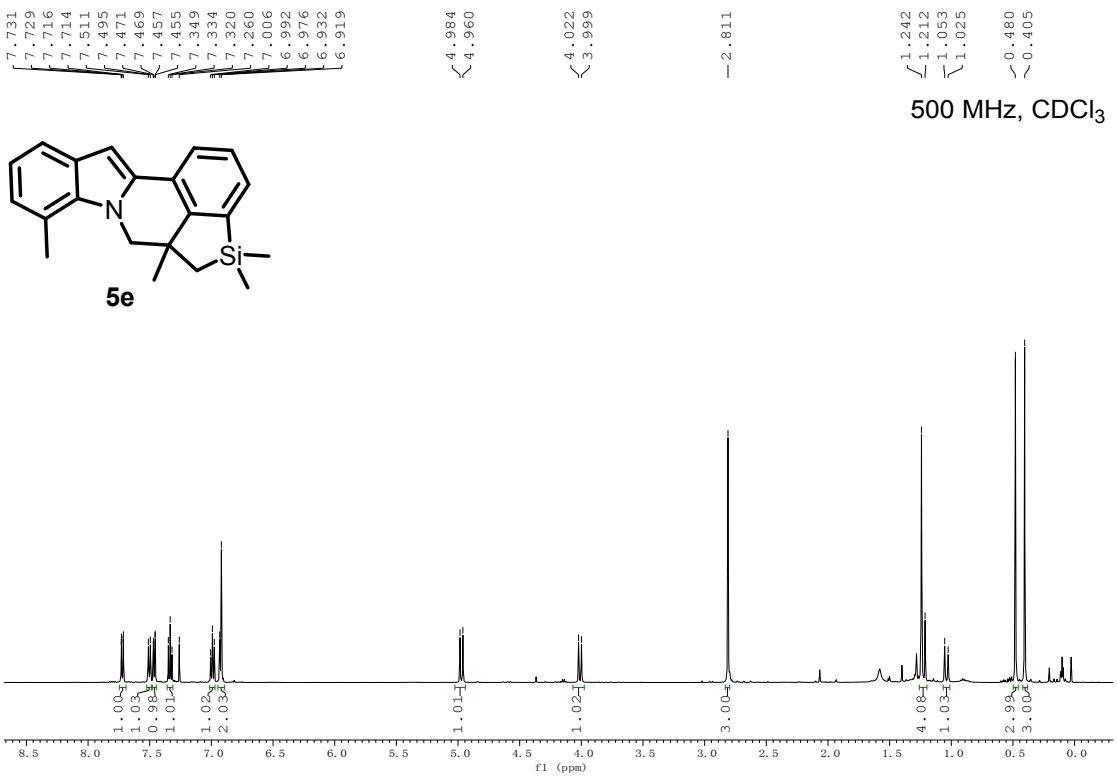
5b

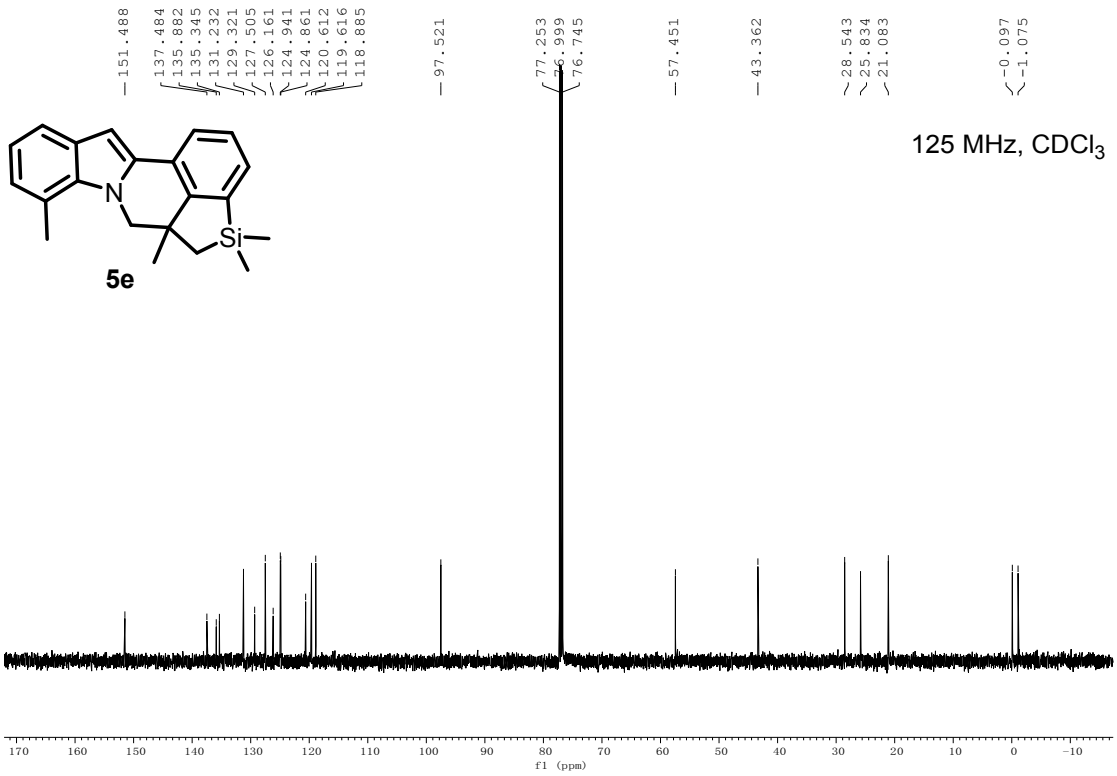

7.715
7.713
7.700
7.698
7.593
7.589
7.490
7.489
7.476
7.474
7.353
7.338
7.324
7.260
7.242
7.162
7.158
7.145
7.141
6.816
4.343
4.319
3.811
3.787
1.262
1.233
1.149
1.079
1.051
0.462
0.395
500 MHz, CDCl3
Cl
N
Si
5c
1.00
0.98
1.01
1.05
1.16
0.99
0.97
1.05
1.03
1.26
3.02
1.06
2.97
3.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

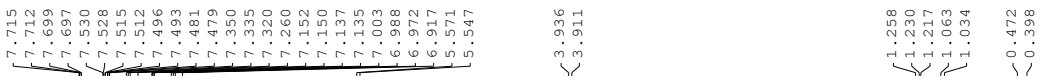

151.800
137.884
136.250
135.353
131.855
129.748
127.622
125.654
125.217
125.149
121.758
119.888
109.786
95.930
77.254
77.000
76.746
54.752
43.299
28.655
25.700
0.150
-1.071
Cl
N
Si
5c
125 MHz, CDCl3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.721
7.719
7.706
7.704
7.495
7.493
7.481
7.479
7.358
7.343
7.328
7.298
7.293
7.279
7.274
7.260
7.254
7.245
7.236
6.982
6.977
6.964
6.959
6.946
6.941
6.848
4.347
4.324
3.814
3.790
1.270
1.242
1.169
1.087
1.058
0.474
0.406
F
N
Si
5d
500 MHz, CDCl3
1.00
0.99
1.02
1.08
0.98
1.06
0.97
1.00
0.99
1.08
2.96
1.02
2.92
2.94
f1 (ppm)

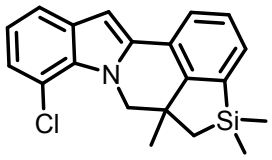

158.849
156.987
151.728
137.846
136.476
133.614
131.733
128.969
128.887
127.584
125.780
125.082
109.907
109.697
109.350
109.272
105.360
105.173
96.322
96.283
77.254
77.000
76.746
54.801
43.308
28.684
25.712
-0.144
-1.072
F
N
Si
5d
125 MHz, CDCl3
f1 (ppm)


7.731
7.729
7.716
7.714
7.511
7.495
7.471
7.469
7.457
7.455
7.349
7.334
7.320
7.260
7.006
6.992
6.976
6.932
6.919
4.984
4.960
4.022
3.999
2.811
1.242
1.212
1.053
1.025
0.480
0.405
500 MHz, CDCl3
N
Si
5e
f1 (ppm)

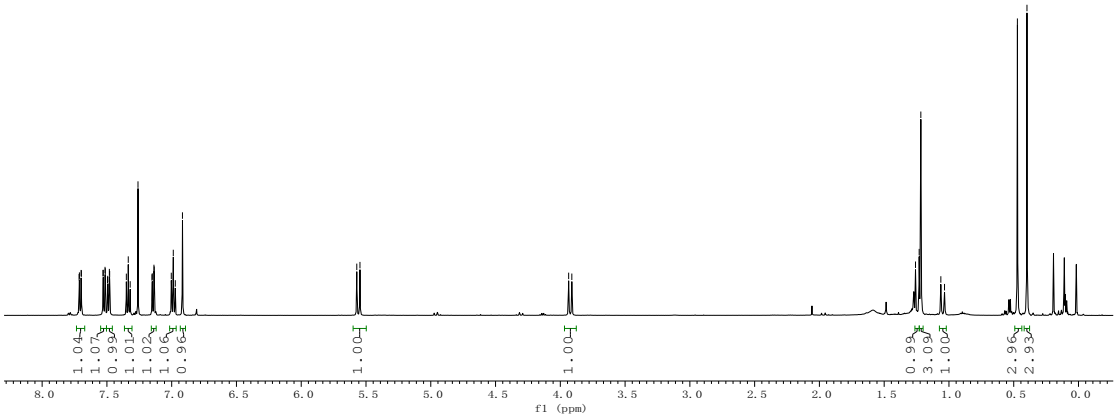

151.488
137.484
135.882
135.345
131.232
129.321
127.505
126.161
124.941
124.861
120.612
119.616
118.885
97.521
77.253
76.999
76.745
57.451
43.362
28.543
25.834
21.083
-0.097
-1.075
125 MHz, CDCl3
N
Si
5e
f1 (ppm)

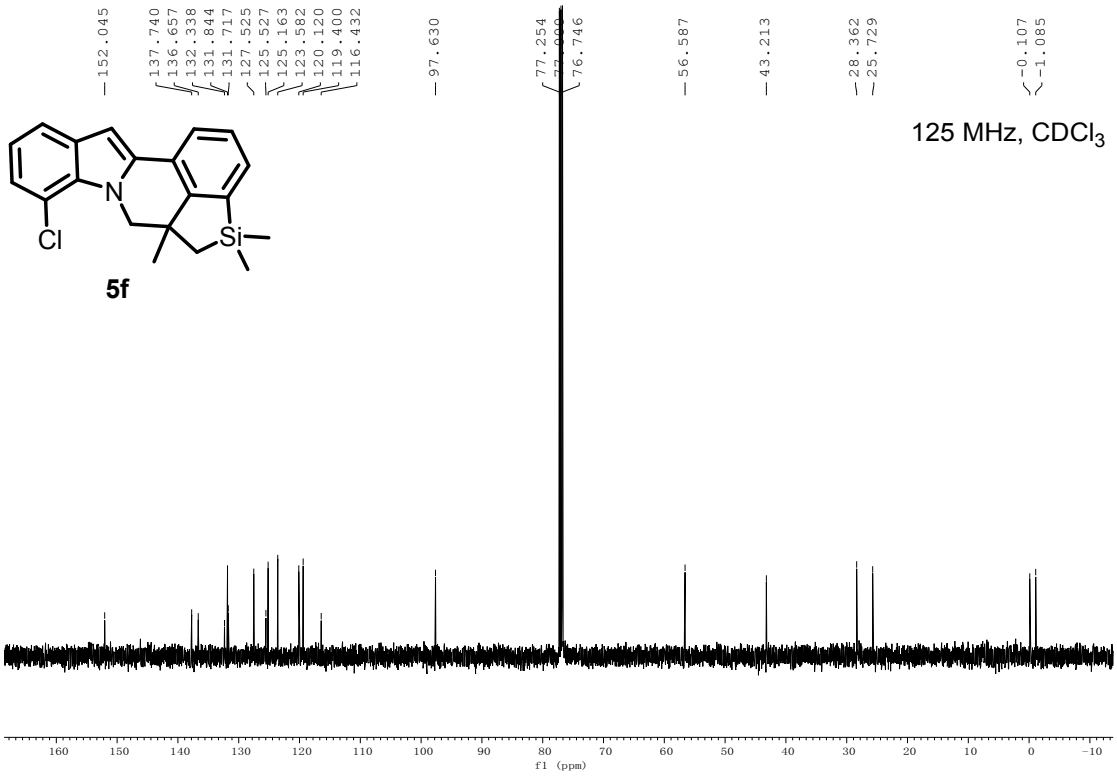


500 MHz, $CDCl_3$



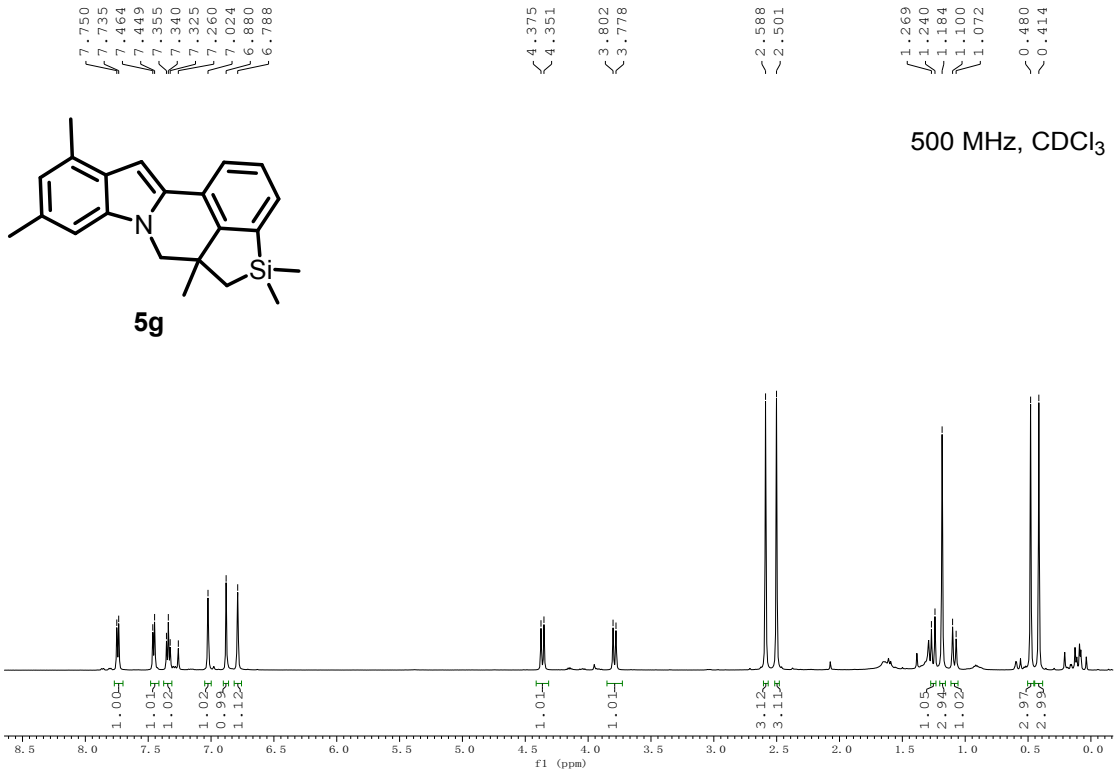
5f

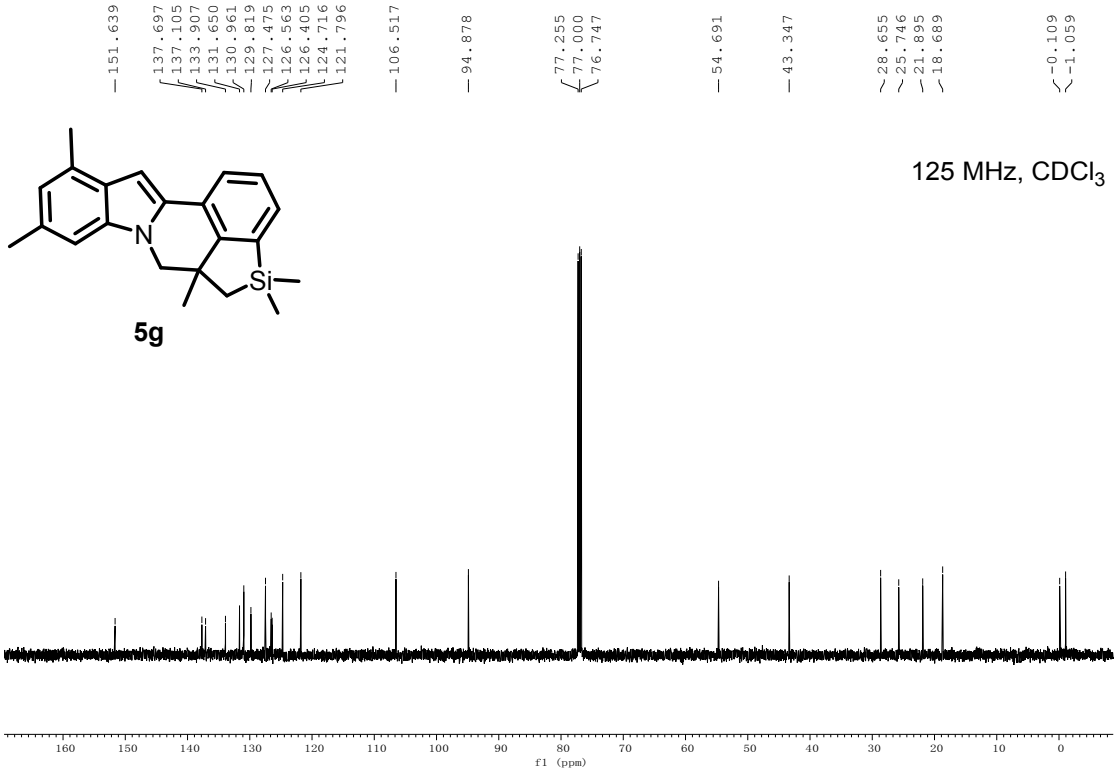


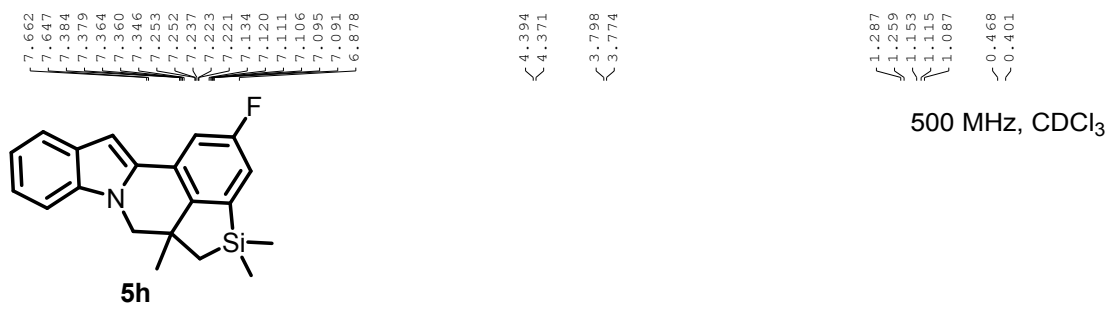


125 MHz, $CDCl_3$

5f

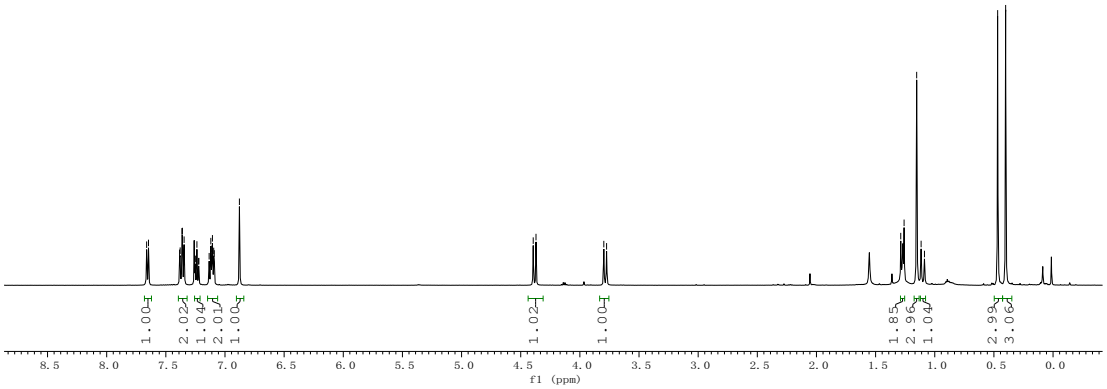

7.750
7.735
7.464
7.449
7.355
7.340
7.325
7.260
7.024
6.880
6.788
4.375
4.351
3.802
3.778
2.588
2.501
1.269
1.240
1.184
1.100
1.072
0.480
0.414
500 MHz, CDCl3
N
Si
5g
1.00
1.01
1.02
1.02
0.99
1.12
1.01
1.01
3.12
3.11
1.05
2.94
1.02
2.97
2.93
f1 (ppm)

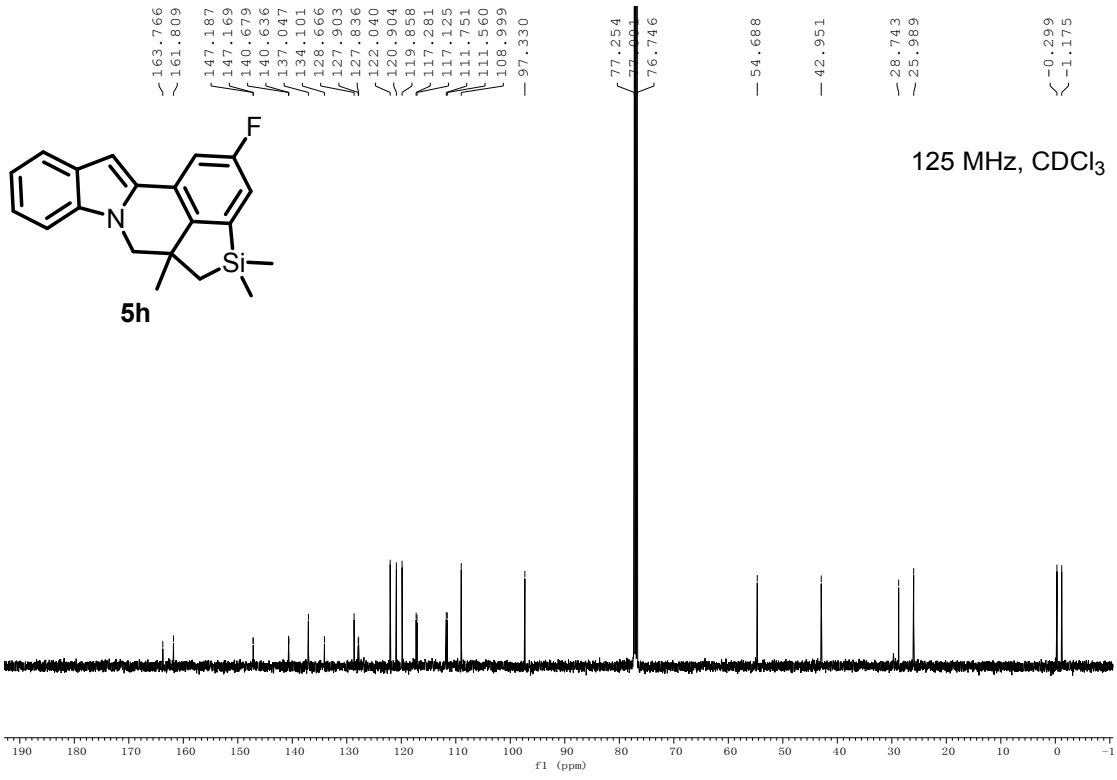

151.639
137.697
137.105
133.907
131.650
130.961
129.819
127.475
126.563
126.405
124.716
121.796
106.517
94.878
77.255
77.000
76.747
54.691
43.347
28.655
25.746
21.895
18.689
0.109
-1.059
125 MHz, CDCl3
N
Si
5g
f1 (ppm)



500 MHz, $CDCl_3$

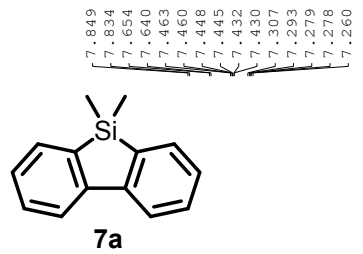
5h





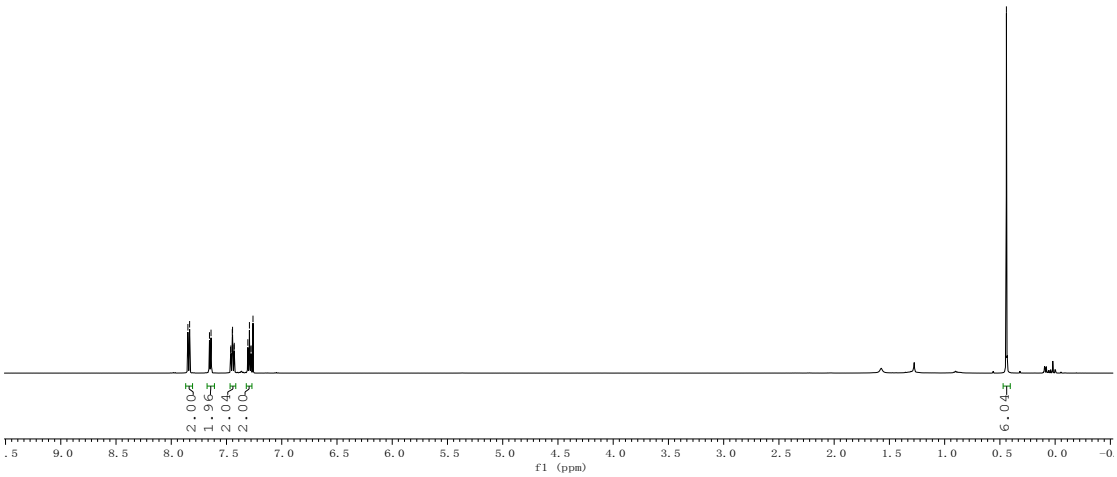
125 MHz, $CDCl_3$

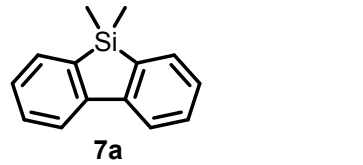
5h



7a

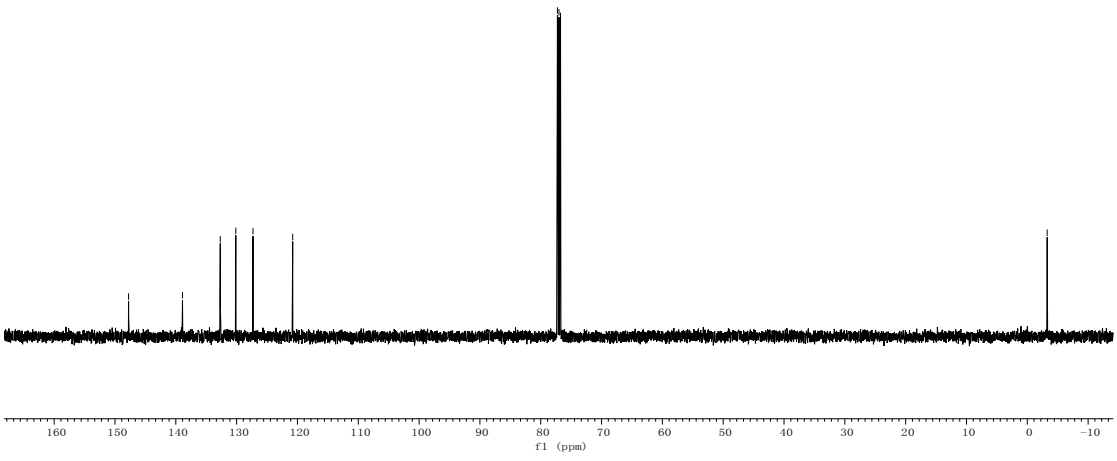
500 MHz, $CDCl_3$

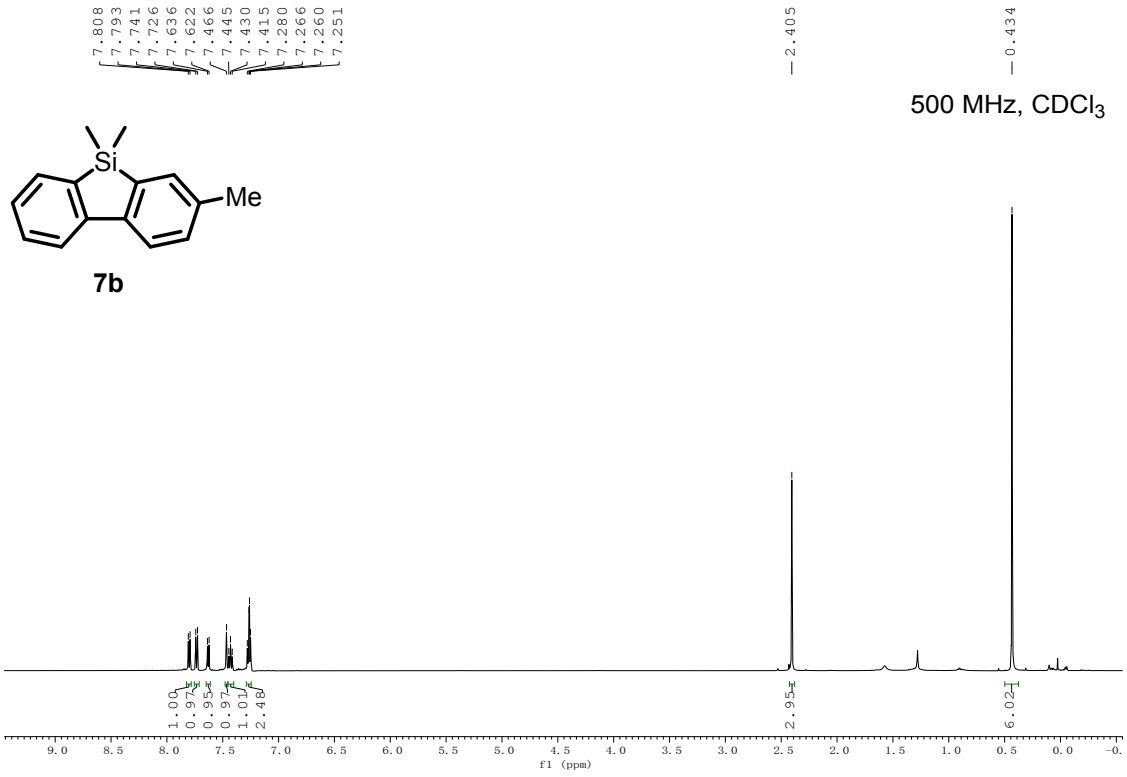




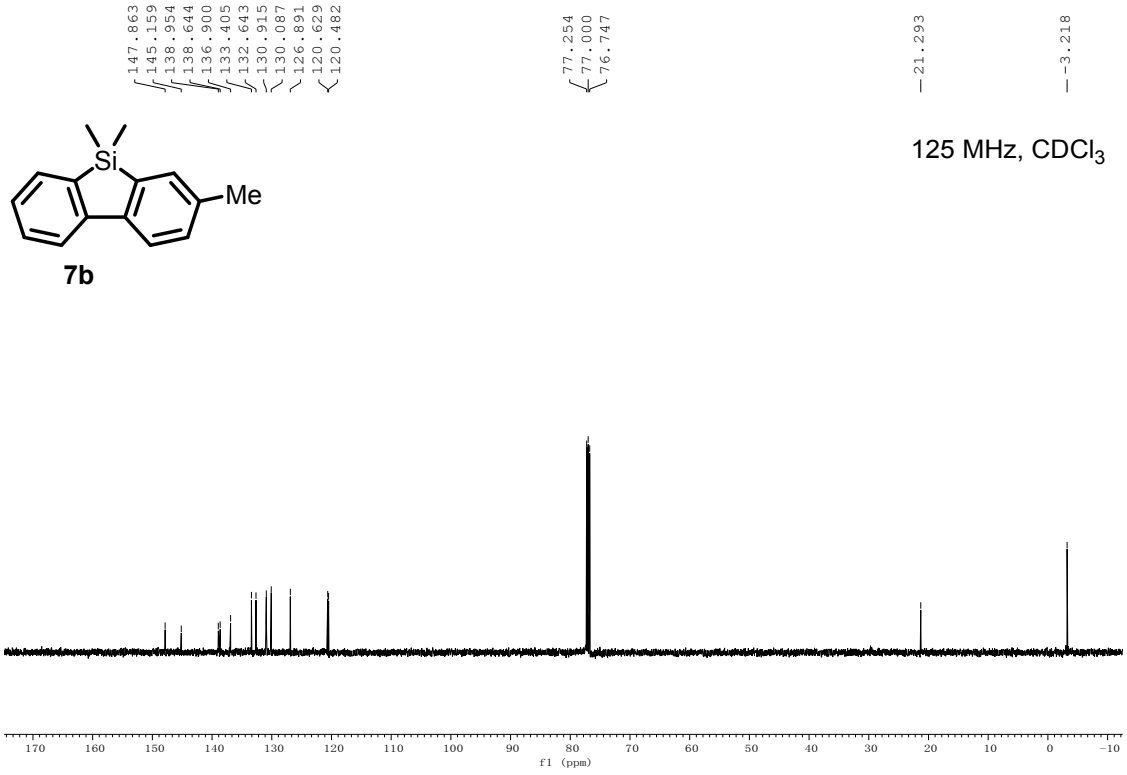
7a

125 MHz, $CDCl_3$

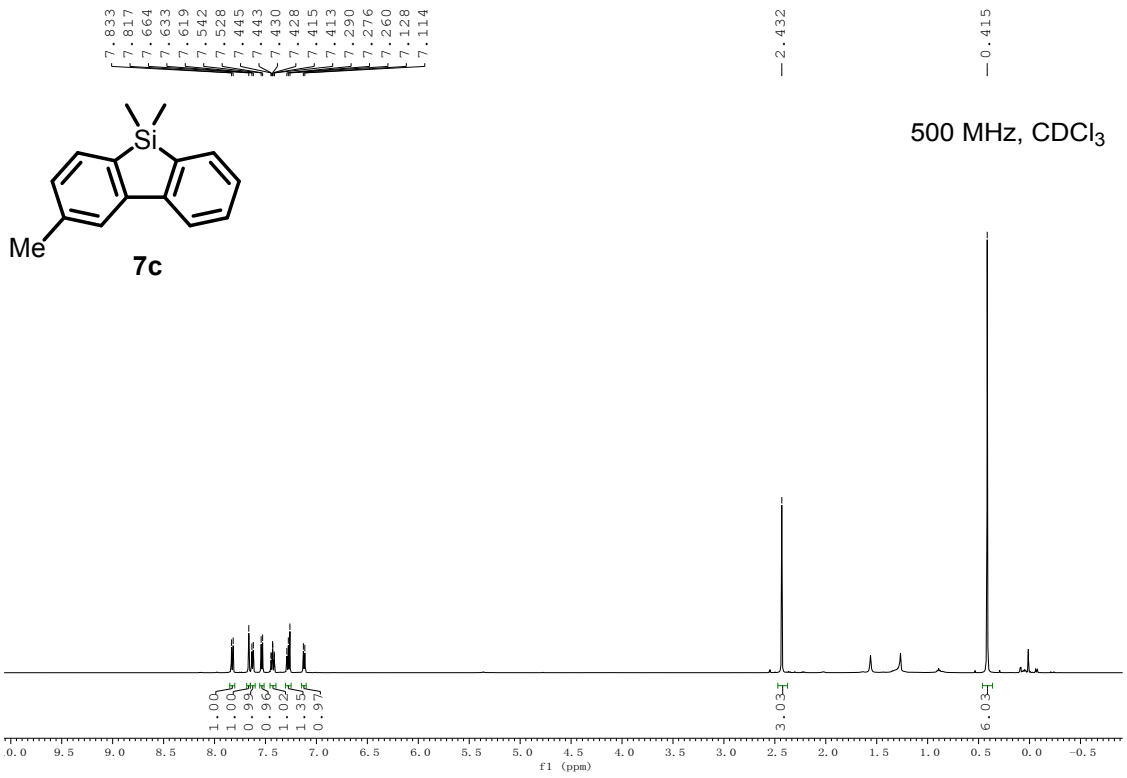


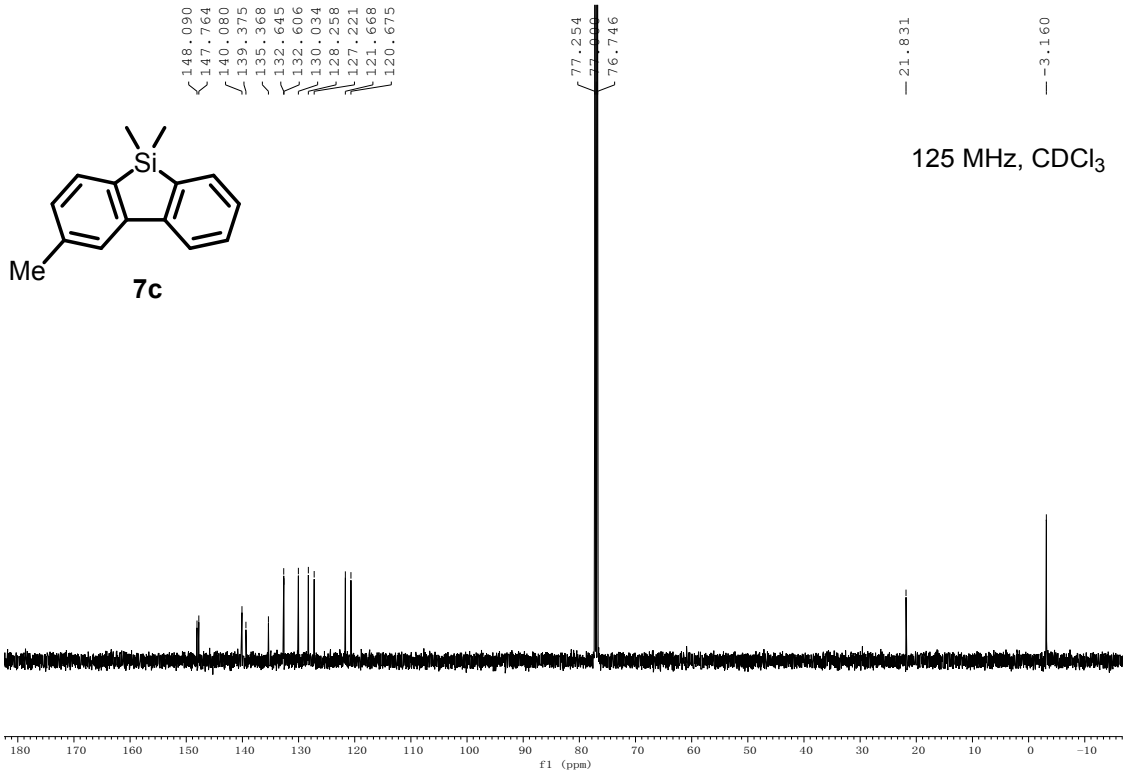

7.808
7.793
7.741
7.726
7.636
7.622
7.466
7.445
7.430
7.415
7.280
7.260
7.251
2.405
0.434
500 MHz, CDCl3
Si
Me
1.00
0.97
0.95
0.97
1.05
2.48
2.95
6.02
f1 (ppm)

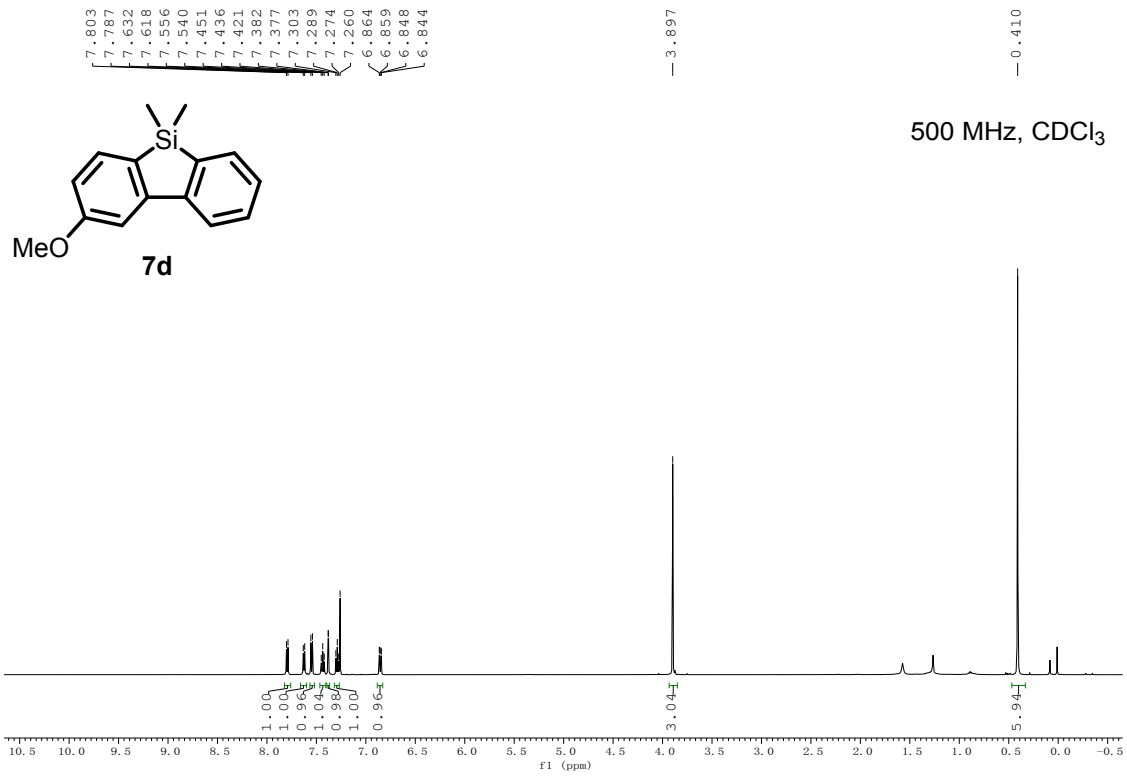
7b


147.863
145.159
138.954
138.644
136.900
133.405
132.643
130.915
130.087
126.891
120.629
120.482
77.254
77.000
76.747
21.293
3.218
125 MHz, CDCl3
Si
Me
f1 (ppm)

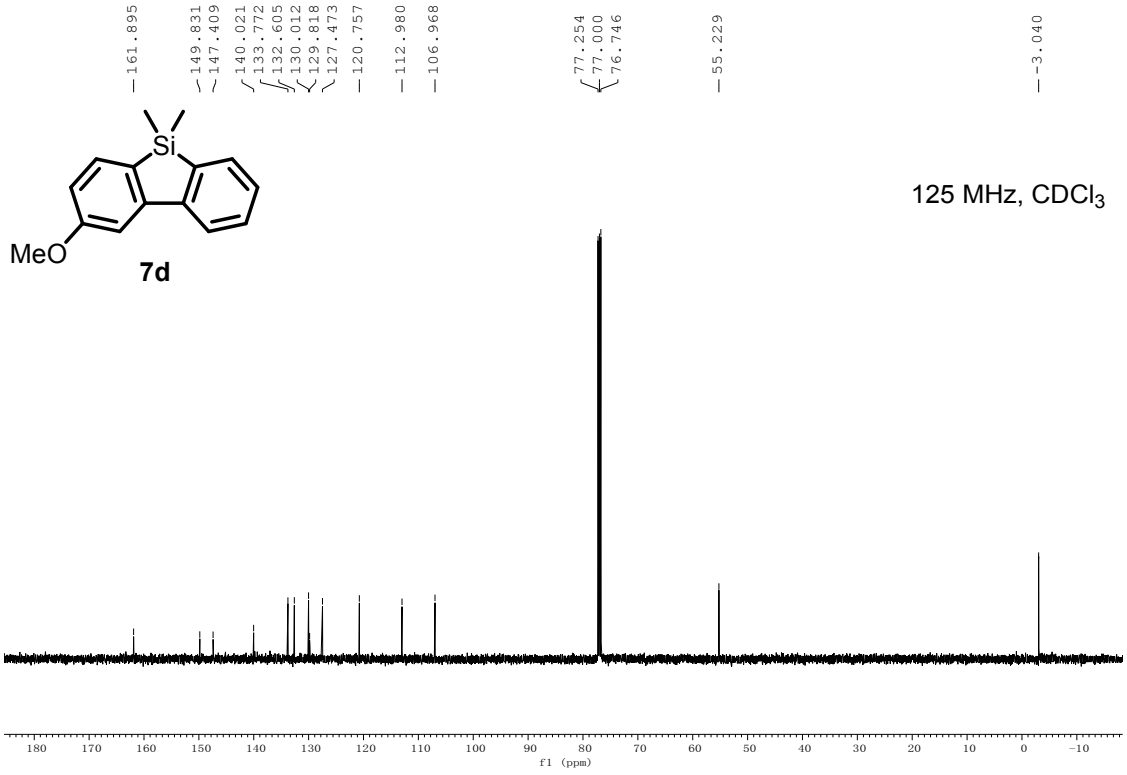
7b


7.833
7.817
7.664
7.633
7.619
7.542
7.528
7.445
7.443
7.430
7.428
7.415
7.413
7.290
7.276
7.260
7.128
7.114
2.432
0.415
Si
Me
7c
500 MHz, CDCl3
1.00
1.00
0.99
0.96
1.02
1.35
0.97
3.03
6.03
f1 (ppm)

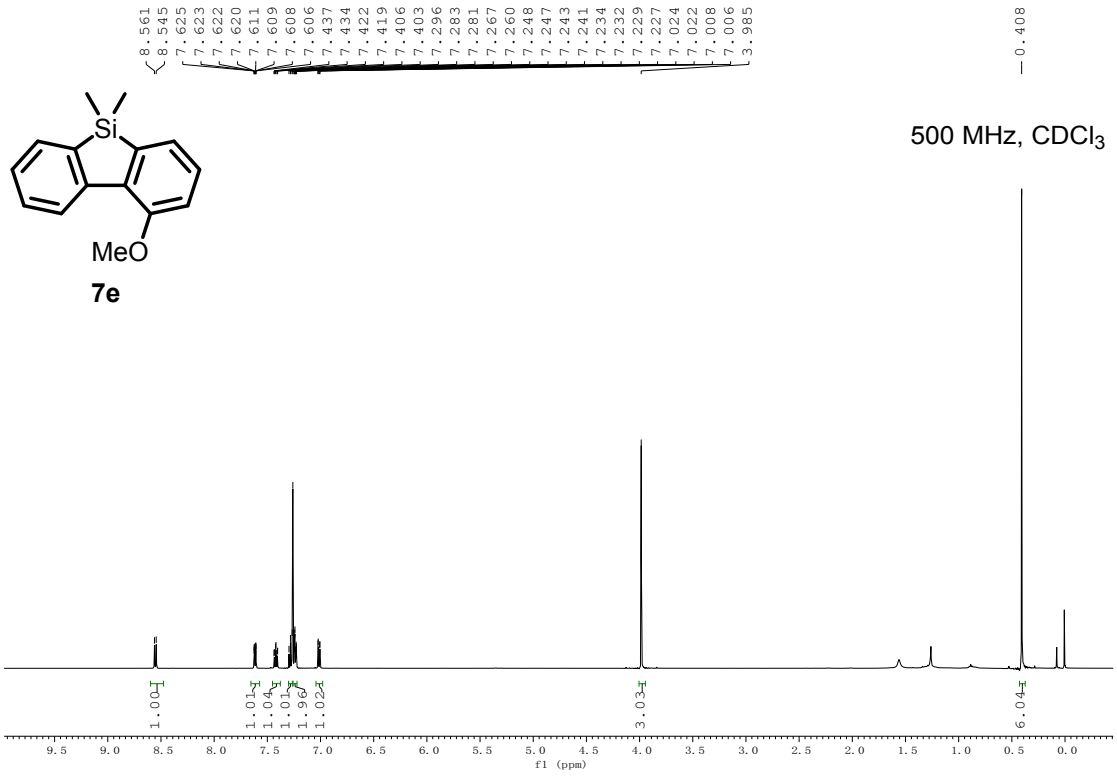

148.090
147.764
140.080
139.375
135.368
132.645
132.606
130.034
128.258
127.221
121.668
120.675
77.254
77.000
76.746
21.831
3.160
Si
Me
7c
125 MHz, CDCl3
f1 (ppm)


7.803
7.787
7.632
7.618
7.556
7.540
7.451
7.436
7.421
7.382
7.377
7.303
7.289
7.274
7.260
6.864
6.859
6.848
6.844
3.897
0.410
Si
MeO
500 MHz, CDCl3
1.00
1.00
0.96
1.04
0.98
1.00
0.96
3.04
5.94
f1 (ppm)

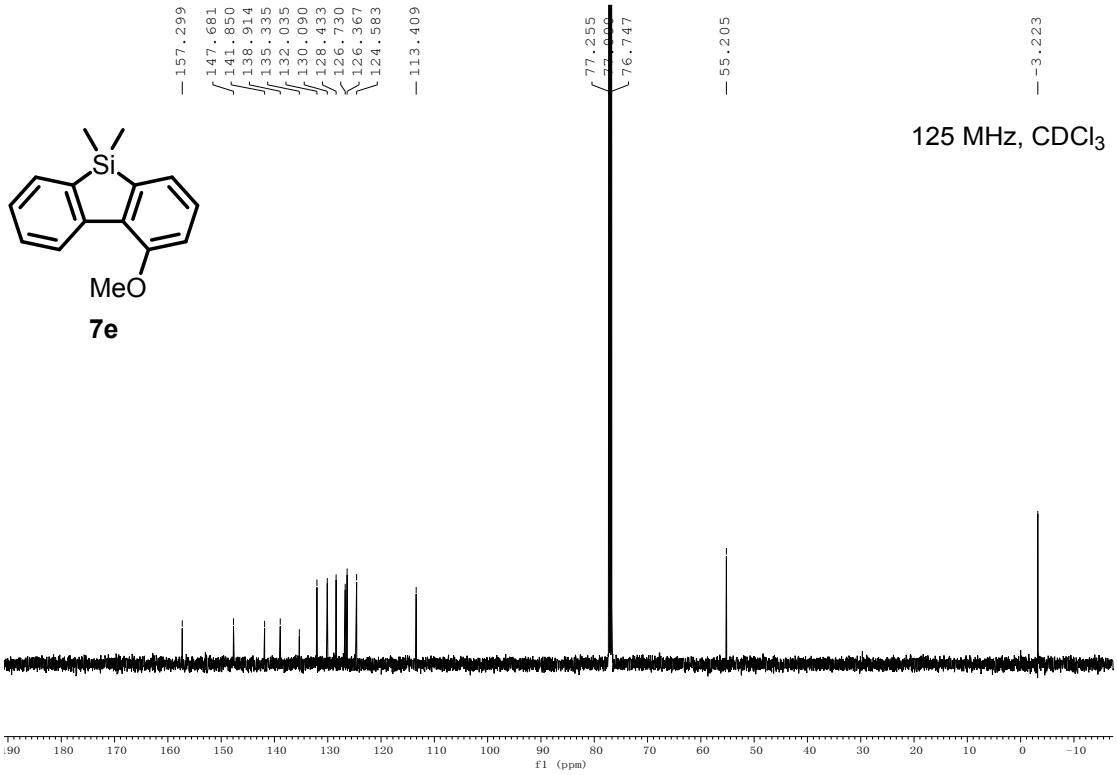
7d


161.895
149.831
147.409
140.021
133.772
132.605
130.012
129.818
127.473
120.757
112.980
106.968
77.254
77.000
76.746
55.229
3.040
Si
MeO
125 MHz, CDCl3
f1 (ppm)

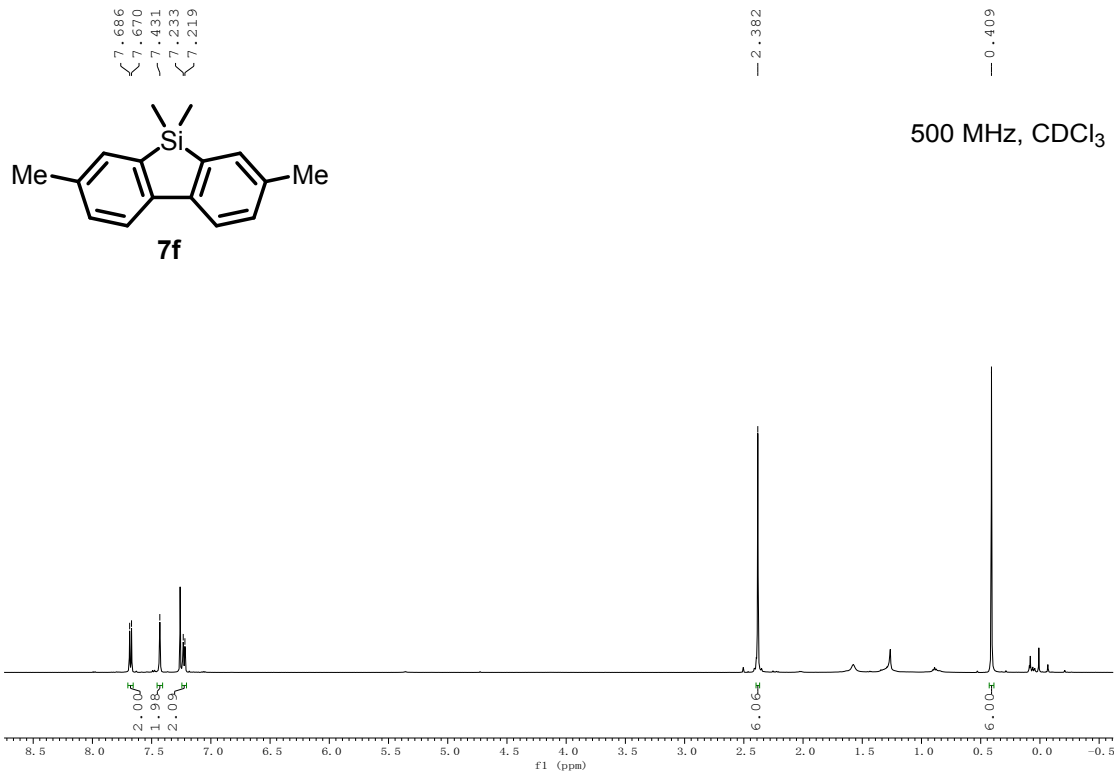
7d

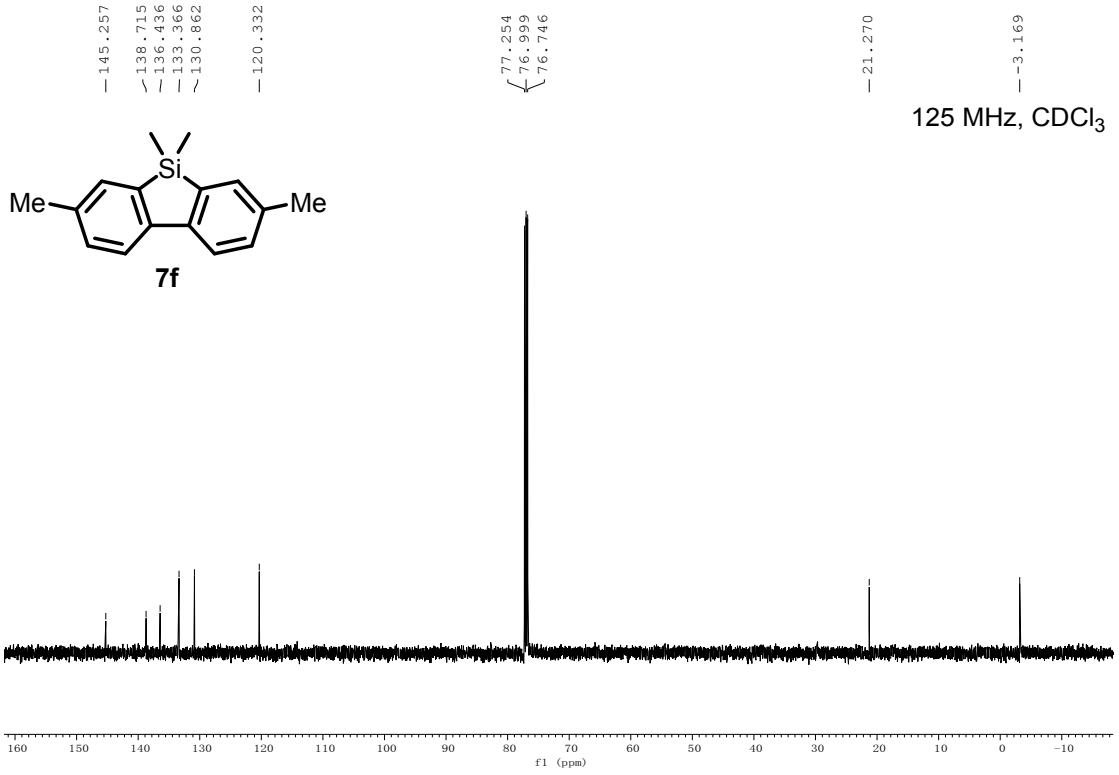

8.561
8.545
7.625
7.623
7.622
7.620
7.611
7.609
7.608
7.606
7.437
7.434
7.422
7.419
7.406
7.403
7.296
7.283
7.281
7.267
7.260
7.248
7.247
7.243
7.241
7.234
7.232
7.229
7.227
7.024
7.022
7.008
7.006
3.985
0.408
Si
MeO
500 MHz, CDCl3
1.00
1.01
1.04
1.01
1.96
1.02
3.03
6.04
f1 (ppm)

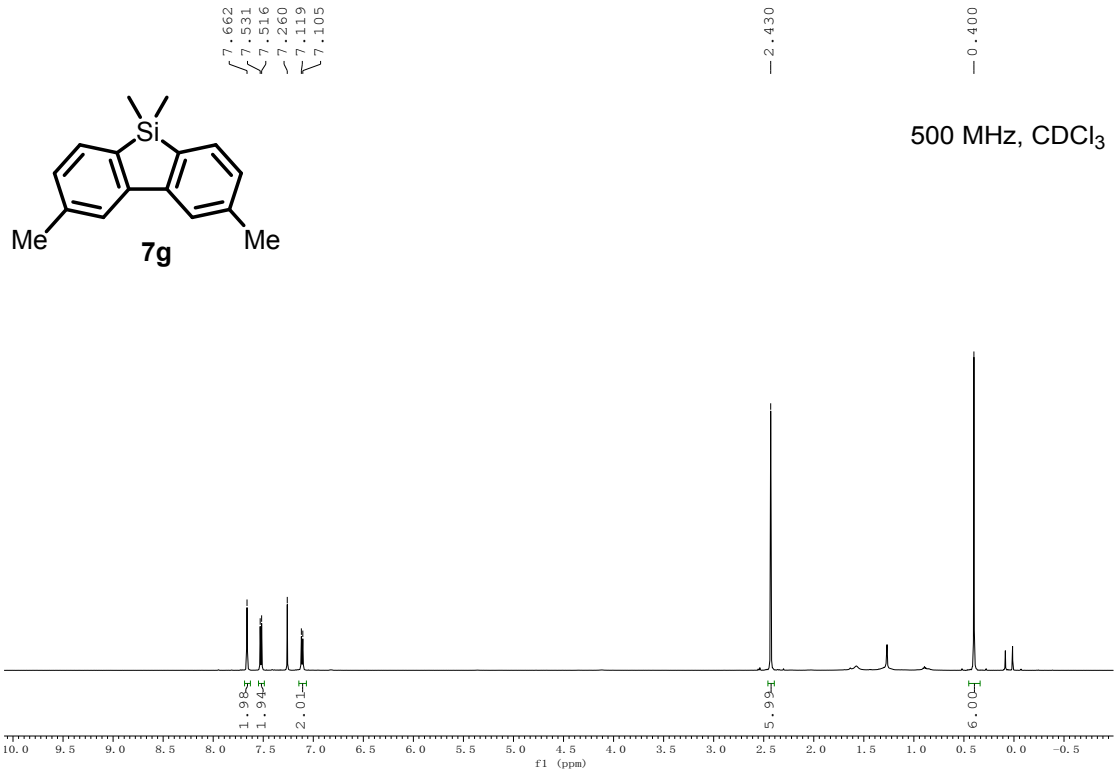
7e

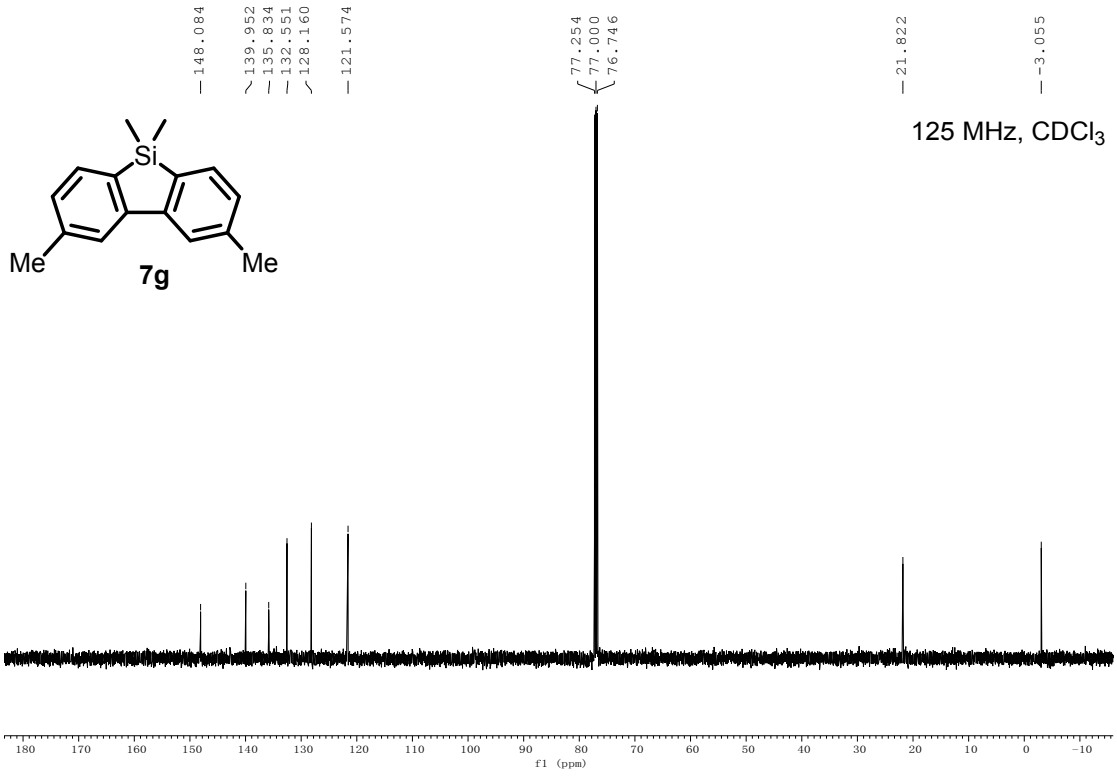

157.299
147.681
141.850
138.914
135.335
132.035
130.090
128.433
126.730
126.367
124.583
113.409
77.255
77.000
76.747
55.205
-3.223
Si
MeO
125 MHz, CDCl3
f1 (ppm)

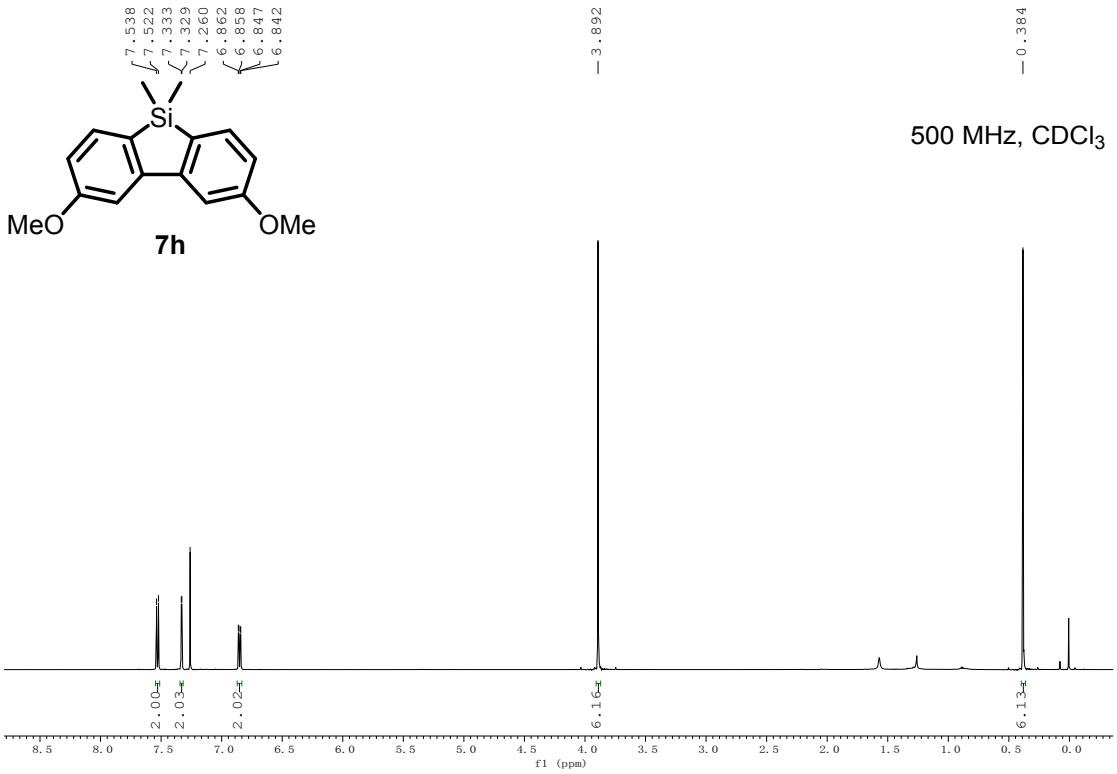
7e

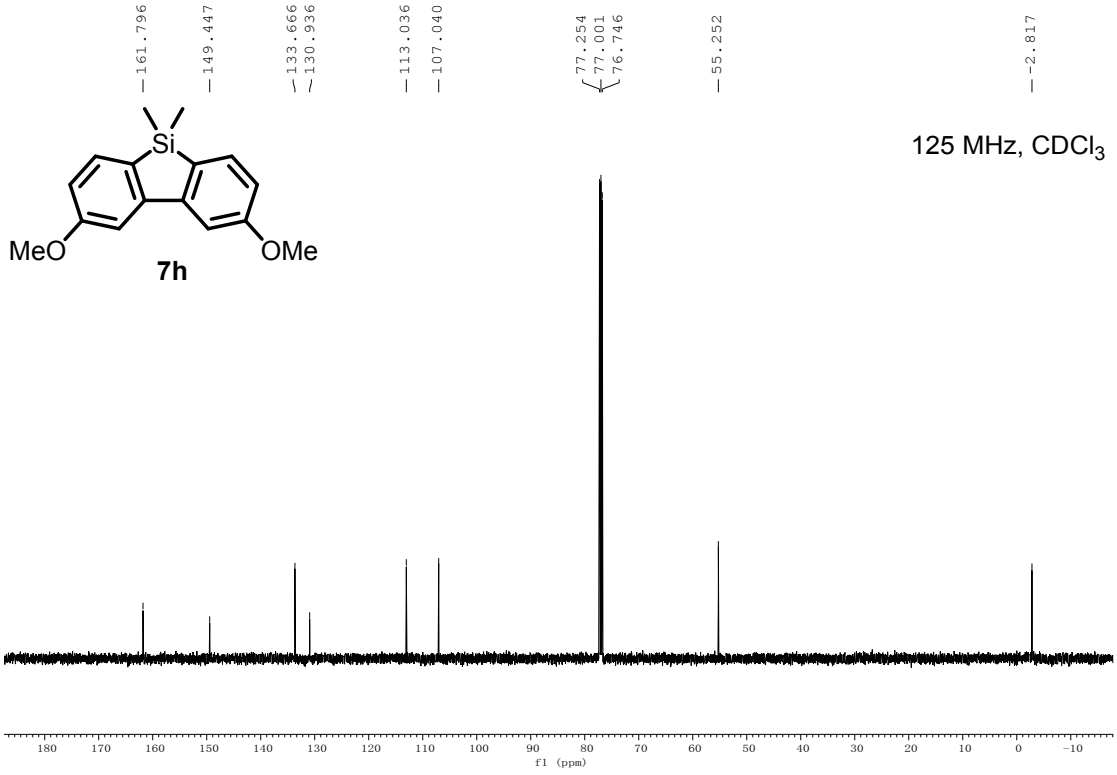

7.686
7.670
7.431
7.233
7.219
2.382
0.409
Si
Me
Me
500 MHz, CDCl3
7f
2.00
1.98
2.03
6.06
6.00
f1 (ppm)

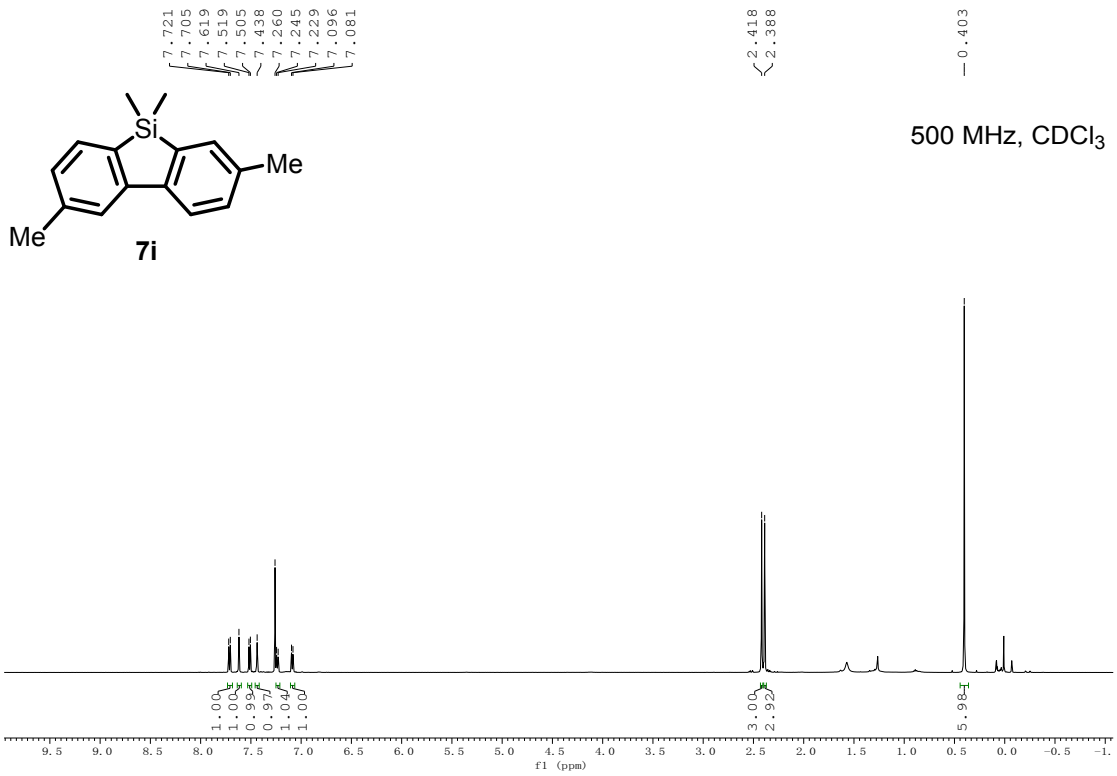

145.257
138.715
136.436
133.366
130.862
120.332
77.254
76.999
76.746
21.270
3.169
Si
Me
Me
125 MHz, CDCl3
7f
f1 (ppm)

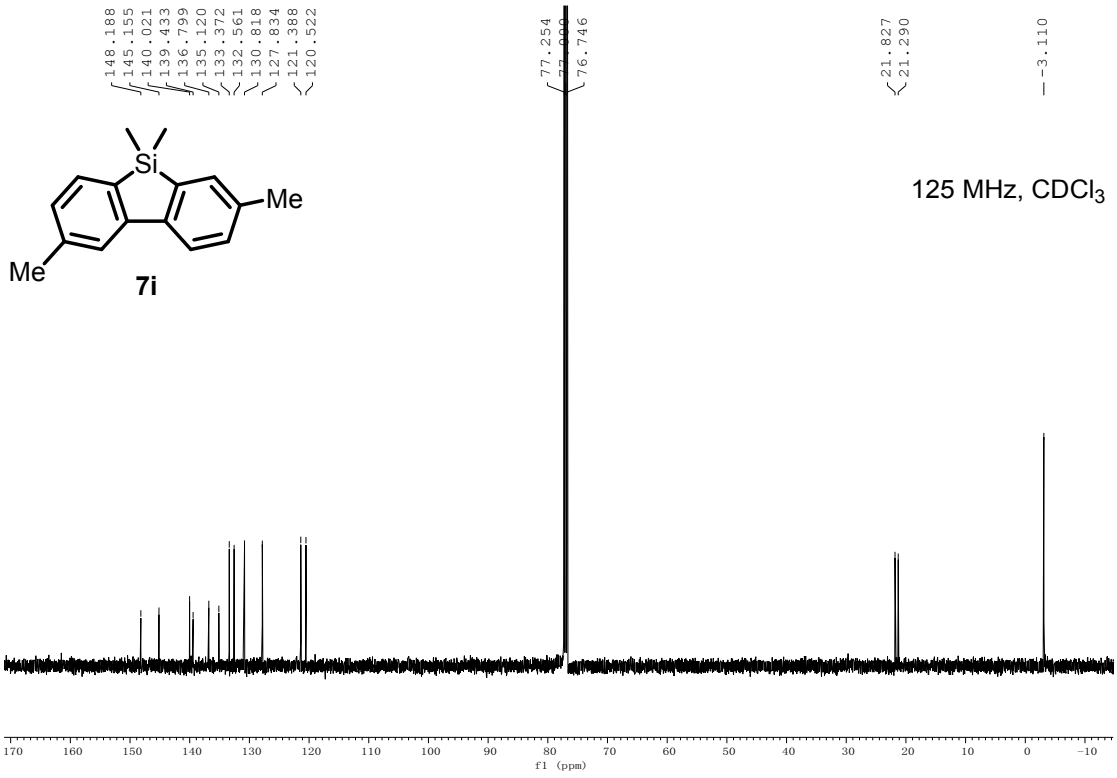

7.662
7.531
7.516
7.260
7.119
7.105
2.430
0.400
Si
Me
Me
7g
500 MHz, CDCl3
1.98
1.94
2.01
5.99
6.00
f1 (ppm)

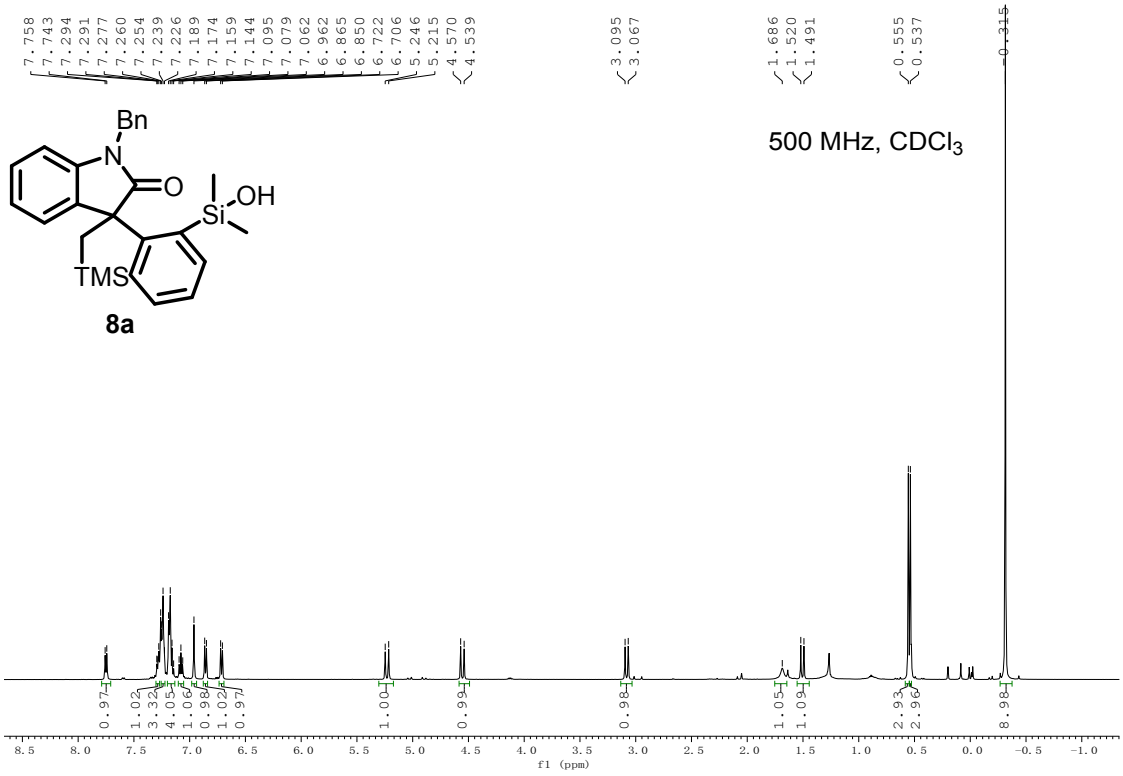

148.084
139.952
135.834
132.551
128.160
121.574
77.254
77.000
76.746
21.822
3.055
Si
Me
Me
7g
125 MHz, CDCl3
f1 (ppm)

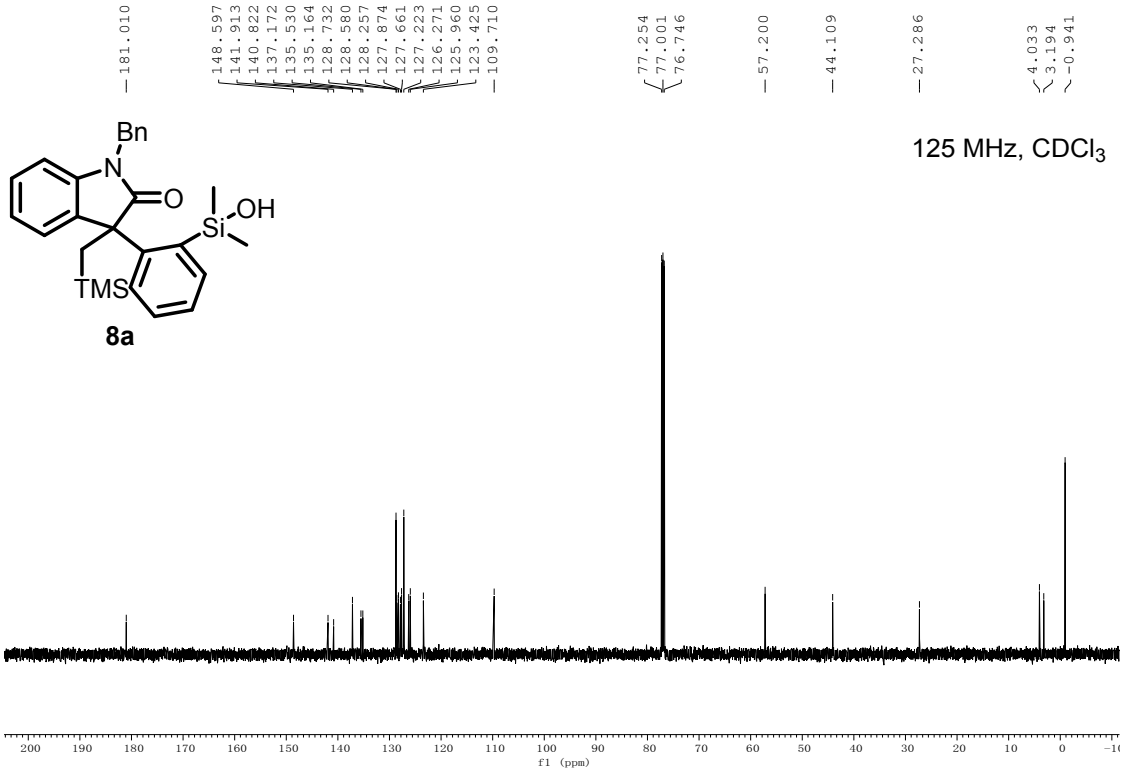

7.538
7.522
7.333
7.329
7.260
6.862
6.858
6.847
6.842
3.892
0.384
Si
MeO
OMe
7h
500 MHz, CDCl3
2.00
2.03
2.02
6.16
6.13
f1 (ppm)

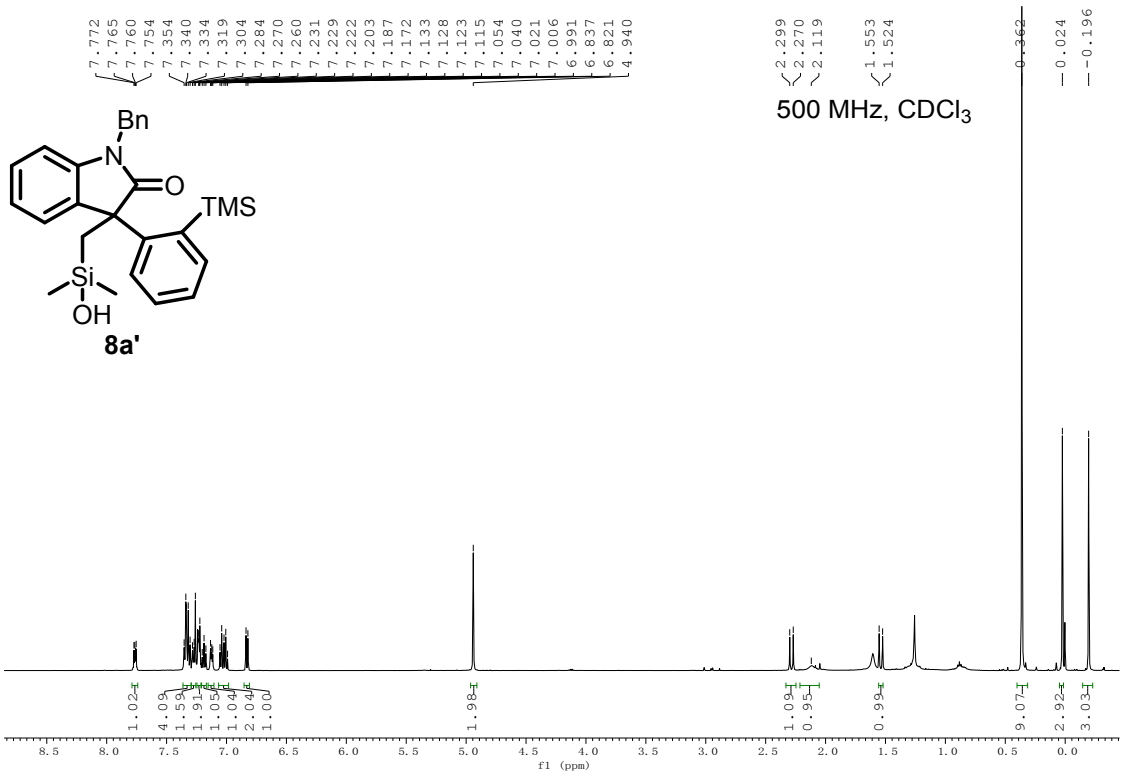

161.796
149.447
133.666
130.936
113.036
107.040
77.254
77.001
76.746
55.252
2.817
Si
MeO
OMe
7h
125 MHz, CDCl3
f1 (ppm)

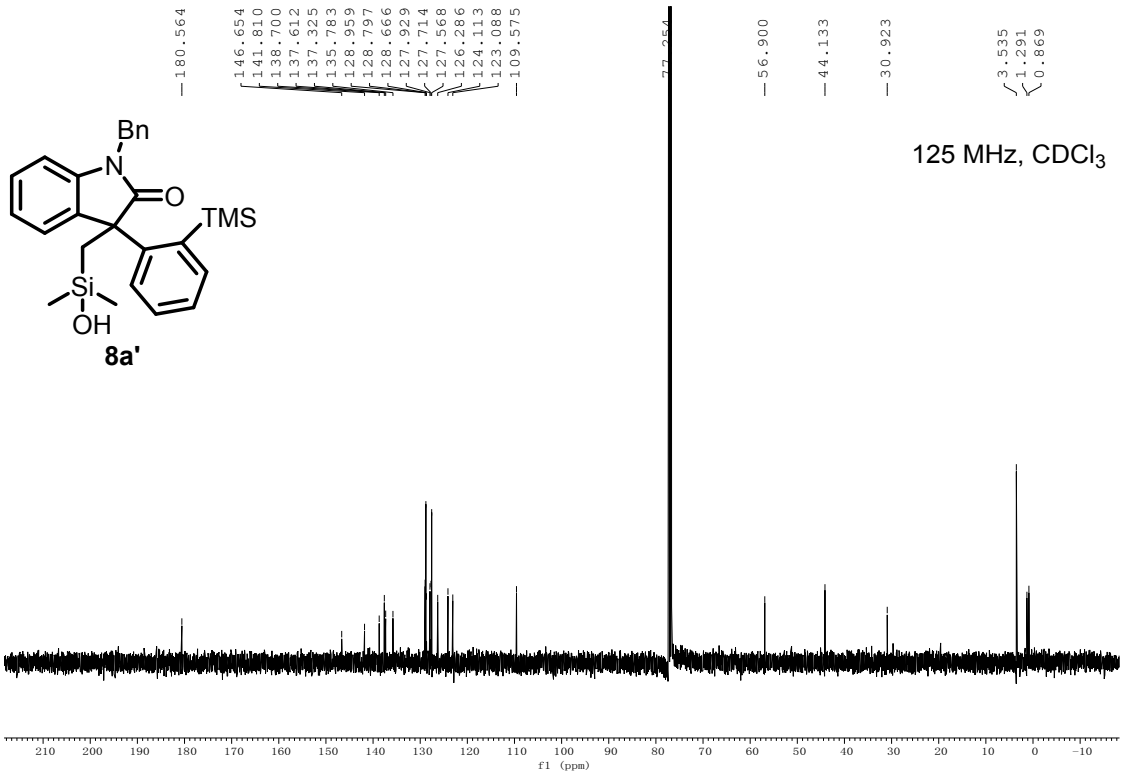

7.721
7.705
7.619
7.519
7.505
7.438
7.260
7.245
7.229
7.096
7.081
2.418
2.388
0.403
Si
Me
Me
7i
500 MHz, CDCl3
1.00
1.00
0.97
0.97
1.04
1.00
3.00
2.92
5.98
f1 (ppm)


148.188
145.155
140.021
139.433
136.799
135.120
133.372
132.561
130.818
127.834
121.388
120.522
77.254
77.000
76.746
21.827
21.290
3.110
Si
Me
Me
7i
125 MHz, CDCl3
f1 (ppm)

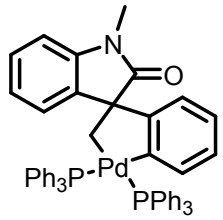

7.758
7.743
7.294
7.291
7.277
7.260
7.254
7.239
7.226
7.189
7.174
7.159
7.144
7.095
7.079
7.062
6.962
6.865
6.850
6.722
6.706
5.246
5.215
4.570
4.539
3.095
3.067
1.686
1.520
1.491
0.555
0.537
0.315
Bn
N
O
Si
OH
TMS
8a
500 MHz, CDCl3
0.97
1.02
3.32
4.05
1.08
0.98
1.02
0.97
1.00
0.91
0.98
1.05
1.03
2.93
2.96
8.98
f1 (ppm)


181.010
148.597
141.913
140.822
137.172
135.530
135.164
128.732
128.580
128.257
127.874
127.661
127.223
126.271
125.960
123.425
109.710
77.254
77.001
76.746
57.200
44.109
27.286
4.033
3.194
0.941
Bn
N
O
Si
OH
TMS
8a
125 MHz, CDCl3
f1 (ppm)

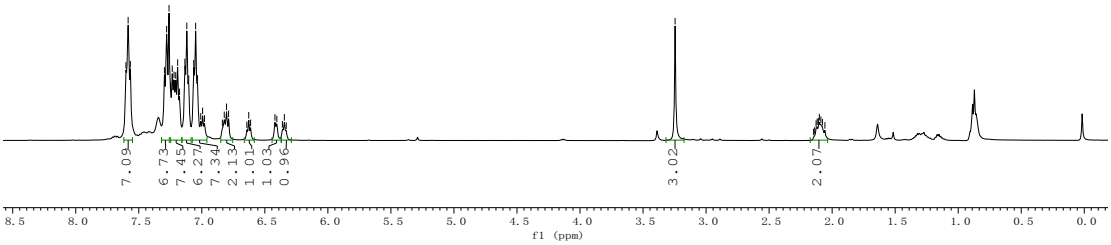

Bn
N
O
TMS
Si
OH
8a'
500 MHz, CDCl3


Bn
N
O
TMS
Si
OH
8a'
125 MHz, CDCl3

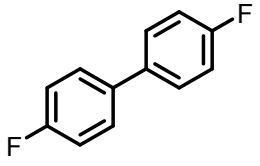
500 MHz, $CDCl_3$



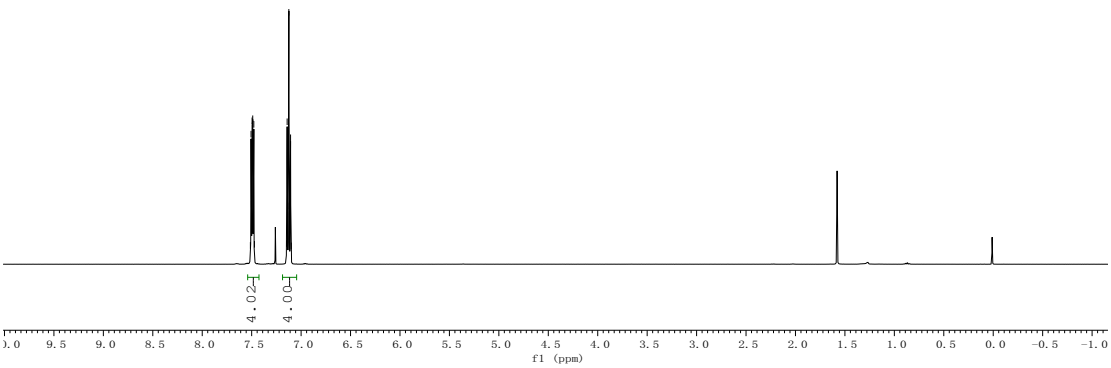
B

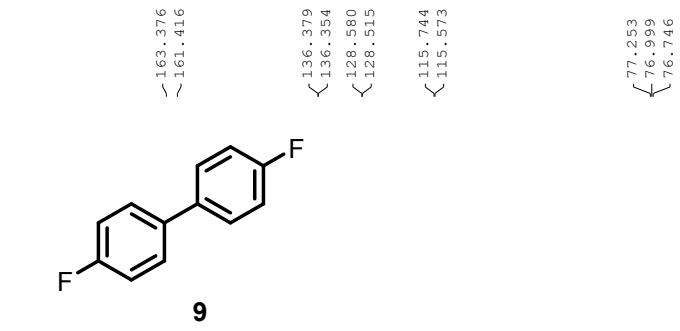


500 MHz, $CDCl_3$



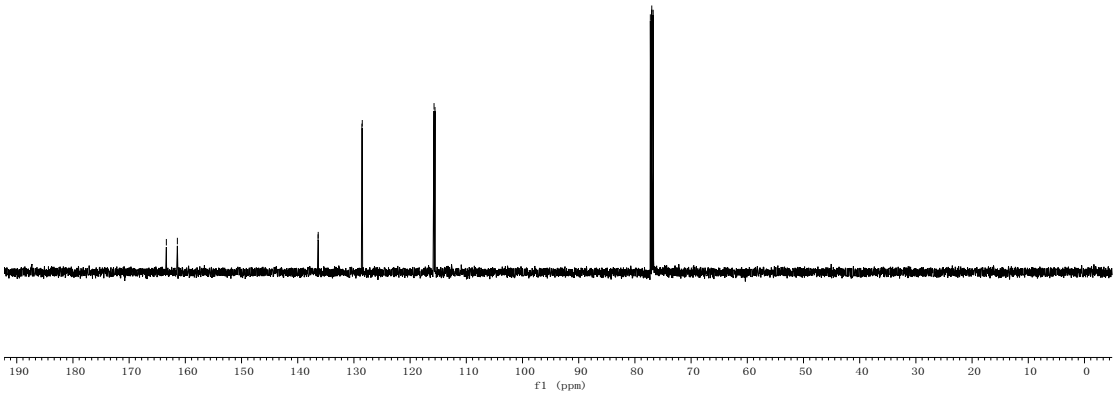
9

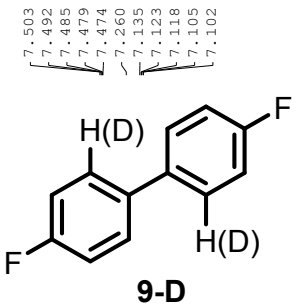




9

125 MHz, $CDCl_3$





9-D

500 MHz, $CDCl_3$