Cover Page for Supporting Information

Manuscript Title:

Palladium-Catalyzed Cleavage of the Me-Si Bond in *ortho*-Trimethylsilyl Aryltriflates: Synthesis of Benzosilole Derivatives from *ortho*-Trimethylsilyl Aryltriflates and Alkynes

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Contents:

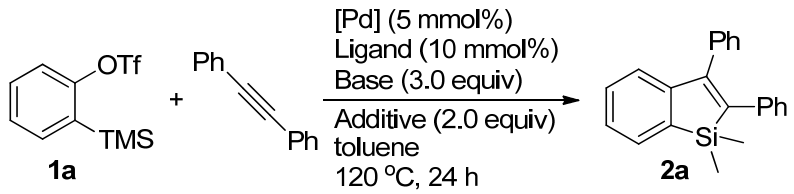
1) General Information

Unless otherwise noted, all starting materials were commercially available and were used without further purification. All reactions were carried out using standard Schlenk techniques or under a nitrogen atmosphere in a Glovebox. The nitrogen in the glovebox was constantly circulated through a copper/molecular sieve catalyst unit. The oxygen and moisture concentrations in the glovebox atmosphere were monitored by an O_2/H_2O Combi-Analyzer to ensure both were always below 1 ppm. Solvents were purified by a Mbraun SPS-800 Solvent Purification System and dried over fresh Na chips in the glovebox.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker ARX 400 spectrometer (FT, 400 MHz for 1H; 100MHz for ^{13}C) or a Bruker AVANCE III 500 spectrometer (FT, 500 MHz for 1H; 125MHz for ^{13}C) at room temperature in $CDCl_3$ solutions and with tetramethylsilane (0.00 ppm) as internal standard, unless otherwise noted. High-resolution mass spectra (HRMS) were recorded on a on a Bruker Apex IV FTMS mass spectrometer using ESI (electrospray ionization) and FT-ICR mass analyser. GC/MS analyses were recorded on Agilent 7890A/5975C using EI MSD.

2) Reaction Condition Optimization of Reaction of 1a with Diphenylacetylene

STable 1. Optimization of Reaction Conditions for the Reaction of **1a** with Diphenylacetylene[a]



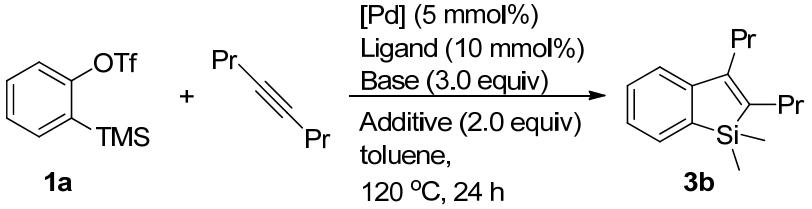
Entry	[Pd]	Base	Ligand	Additive	GC Yield[b]
1	$Pd(PPh_3)_4$	K_2CO_3	-	KBr	19
2	$PdCl_2$	LiOEt	P*t*-Bu_3	KBr	NR
3	$[Pd(\pi\text{-allyl})Cl]_2$	LiO*t*-Bu	P*t*-Bu_3	-	15
4	$[Pd(\pi\text{-allyl})Cl]_2$	LiO*t*-Bu	P*t*-Bu_3	KBr	32

5[c]	[Pd(π-allyl)Cl]$_2$	LiO*t*-Bu	P*t*-Bu$_3$	KBr	13
6[c]	[Pd(π-allyl)Cl]$_2$	LiO*t*-Bu	P*t*-Bu$_3$	-	NR
7	[Pd(π-allyl)Cl]$_2$	LiO*t*-Bu	P*t*-Bu$_3$	KI	trace
8	[Pd(π-allyl)Cl]$_2$	LiO*t*-Bu	P*t*-Bu$_3$	NaI	NR
9	[Pd(π-allyl)Cl]$_2$	LiO*t*-Bu	P*t*-Bu$_3$	LiI	NR
10	[Pd(π-allyl)Cl]$_2$	Li_2CO_3	P*t*-Bu$_3$	KBr	NR
11	[Pd(π-allyl)Cl]$_2$	Na_2CO_3	P*t*-Bu$_3$	KBr	10
12	[Pd(π-allyl)Cl]$_2$	K_2CO_3	P*t*-Bu$_3$	KBr	41
13	[Pd(π-allyl)Cl]$_2$	Cs_2CO_3	P*t*-Bu$_3$	KBr	12
14	[Pd(π-allyl)Cl]$_2$	LiOEt	P*t*-Bu$_3$	-	16
15	***[Pd(π-allyl)Cl]$_2$***	***LiOEt***	***Pt-Bu$_3$***	***KBr***	***84***
16	[Pd(π-allyl)Cl]$_2$	NaOEt	P*t*-Bu$_3$	KBr	decompose
17	[Pd(π-allyl)Cl]$_2$	LiOAc	P*t*-Bu$_3$	KBr	NR
18	[Pd(π-allyl)Cl]$_2$	NaOAc	P*t*-Bu$_3$	KBr	22
19	[Pd(π-allyl)Cl]$_2$	KOAc	P*t*-Bu$_3$	KBr	18
20	[Pd(π-allyl)Cl]$_2$	NaO*t*-Bu	P*t*-Bu$_3$	KBr	decompose
21	[Pd(π-allyl)Cl]$_2$	KO*t*-Bu	P*t*-Bu$_3$	KBr	decompose
22	[Pd(π-allyl)Cl]$_2$	LiOEt	P*t*-Bu$_3$H·BF$_4$	KBr	NR
23	[Pd(π-allyl)Cl]$_2$	LiOEt	PMe*t*-Bu$_2$H·BF$_4$	KBr	11

[a] Conditions: **1a** (0.1 mmol), diphenylacetylene (0.12 mmol), [Pd] (5 mol %), ligand (10 mol%), base (0.3 mmol), additive (0.2 mmol), toluene (1.5 ml), 120 C, 24 h. [b] GC yield (*n*-$C_{12}H_{26}$ as internal standard). [c] 0.1 mmol of *p*-nitrobenzaldehyde was added into the reaction.

3) Reaction Condition Optimization of Reaction of 1a with 4-Octyne

STable 2. Optimization of Reaction Conditions for the Reaction of **1a** with 4-Octyne[a]



Entry	[Pd]	Base	Ligand	Additive	GC Yield[b]
1	$Pd(PPh_3)_4$	K_2CO_3	-	-	32
2	$Pd(PPh_3)_4$	K_2CO_3	-	KBr	50
3	$Pd(PPh_3)_4$	-	-	KBr	18
4	$Pd(PPh_3)_4$	K_2CO_3	-	KBr	27
5	$Pd(OAc)_2$	K_2CO_3	-	KBr	NR
6	$Pd_2(dba)_3$	K_2CO_3	-	KBr	NR
7	$PdCl_2$	K_2CO_3	-	KBr	NR
8	$Pd(PPh_3)Cl_2$	K_2CO_3	-	KBr	NR
9	$Pd(PPh_3)_4$	K_2CO_3	-	NaI	9
10	$Pd(PPh_3)_4$	K_2CO_3	-	KI	15
11	$Pd(PPh_3)_4$	K_2CO_3	-	LiI	NR
12	$Pd(PPh_3)_4$	Li_2CO_3	-	KBr	15
13	$Pd(PPh_3)_4$	Na_2CO_3	-	KBr	23
14	$Pd(PPh_3)_4$	Cs_2CO_3	-	KBr	trace
15	$Pd(PPh_3)_4$	LiOEt	-	KBr	61
16	$Pd(PPh_3)_4$	NaOEt	-	KBr	-
17[c]	$Pd(PPh_3)_4$	LiOAc	-	KBr	27
18	$Pd(PPh_3)_4$	NaOAc	-	KBr	41
19	$Pd(PPh_3)_4$	KOAc	-	KBr	23
20	$Pd(PPh_3)_4$	LiO*t*-Bu	-	KBr	37
21	$Pd(PPh_3)_4$	NaO*t*-Bu	-	KBr	NR
22	$Pd(PPh_3)_4$	KO*t*-Bu	-	KBr	decompose
23	$Pd(PPh_3)_4$	$LiOH \cdot H_2O$	-	KBr	40
24	$Pd(PPh_3)_4$	NaOH	-	KBr	14
25	$Pd(PPh_3)_4$	KOH	-	KBr	decompose
26	$Pd(PPh_3)_4$	K_3PO_4	-	KBr	25
27	$Pd(PPh_3)_4$	$K_2HPO_4 \cdot 3H_2O$	-	KBr	17
28	$Pd(PPh_3)_4$	$NaH_2PO_4 \cdot 2H_2O$	-	KBr	16
29	$Pd(PPh_3)_4$	LiOEt	-	-	31

30	$Pd(OAc)_2$	LiOEt	PPh_3	KBr	trace
31	$PdCl_2$	LiOEt	PPh_3	KBr	18
32	$[Pd(\pi\text{-allyl})Cl]_2$	LiOEt	PPh_3	KBr	41
33	***$Pd(PPh_3)Cl_2$***	***LiOEt***	***PPh_3***	***KBr***	***79***
34	$Pd_2(dba)_3$	LiOEt	PPh_3	KBr	60
35	$Pd(PPh_3)Cl_2$	LiOEt	PCy_3	KBr	NR
36	$Pd(PPh_3)Cl_2$	LiOEt	P-(2-Furyl)$_3$	KBr	NR
37	$Pd(PPh_3)Cl_2$	LiOEt	XantPhos	KBr	61
38	$Pd(PPh_3)Cl_2$	LiOEt	DPEPhos	KBr	36
39	$Pd(PPh_3)Cl_2$	LiOEt	DPPF	KBr	23
40	$Pd(PPh_3)Cl_2$	LiOEt	DPPP	KBr	39

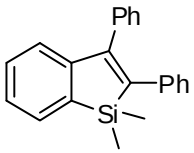
[a] Conditions: **1a** (0.1 mmol), 4-Octyne (0.2 mmol), [Pd] (5 mol %), ligand (10 mol%), base (0.3 mmol), additive (0.2 mmol), toluene (1.5 ml), 120 C, 24 h. [b] GC yield (n-$C_{12}H_{26}$ as internal standard). [c] 0.1 mmol of Bu_4NBr was added into the reaction.

4) Typical Procedures and Characterization Data

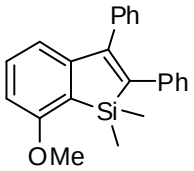
A typical procedure for the preparation of 2: Under nitrogen, $[PdCl(\pi\text{-allyl})]_2$ (2.5 mol%) and P*t*-Bu_3 (10 mol%) were added in 1.5 ml toluene. After this reaction mixture was stirred at room temperature for 15 min, *ortho*-trimethylsilyl aryltriflates **1** (0.3 mmol), arylalkynyl (0.36 mmol), LiOEt (0.9 mmol), KBr (0.6 mmol) were added and this reaction mixture was stirred at 120 °C for 24 h. The reaction mixture was extracted with EtOAc. The solvent was then evaporated in vacuo and the residue was purified by using SiO_2 column with petroleum ether and ethyl acetate as eluent to afford the final products.

A typical procedure for the preparation of 3: Under nitrogen, $Pd(PPh_3)_2Cl_2$ (5 mol%), PPh_3 (10 mol%), *ortho*-trimethylsilyl aryltriflates **1** (0.3 mmol), aliphatic alkyne (0.6 mmol), LiOEt (0.9 mmol) and KBr (0.6 mmol) were added in 1.5 ml toluene. and this reaction mixture was stirred at 120 °C for 24 h. The reaction mixture was extracted with EtOAc. The solvent was then evaporated in vacuo and the residue was purified by using SiO_2 column with petroleum ether and ethyl acetate as eluent to afford

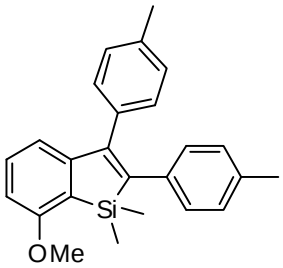
the final products.



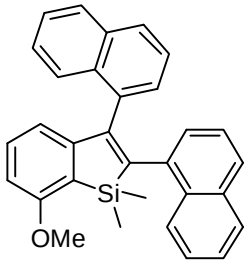
2a:[1] Colorless solid, isolated yield 80% (75 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.47 (s, 6H, CH_3), 6.96-6.99 (m, 2H, CH), 7.04-7.07 (m, 2H, CH), 7.11-7.14 (m, 2H, CH), 7.18-7.21 (m, 2H, CH), 7.26-7.34 (m, 5H, CH), 7.60-7.62 (m, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: -3.51 ($2CH_3$), 123.98, 125.66, 126.65, 127.05, 127.93 (2CH), 128.34 (2CH), 128.59 (2CH), 129.66 (2CH), 129.76, 131.62, 138.13, 138.16, 139.96, 142.99, 150.71, 153.12.



2b: Colorless solid, isolated yield 86% (88 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.49 (s, 6H, CH_3), 3.85 (s, 3H, CH_3), 6.69 (d, J = 7.5 Hz, 1H, CH), 6.76 (d, J = 8.2 Hz, 1H, CH), 6.96-6.98 (m, 2H, CH), 7.04-7.32 (m, 9H, CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: -4.03 ($2CH_3$), 55.41, 109.03, 117.41, 123.60, 125.57, 126.93, 127.87 (2CH), 128.22 (2CH), 128.57 (2CH), 129.68 (2CH), 131.87, 138.32, 140.07, 143.85, 152.32, 152.35, 162.96; HRMS (ESI, m/z) calcd. for $[C_{23}H_{22}OSi]H^+$: 343.1513; found 343.1515.

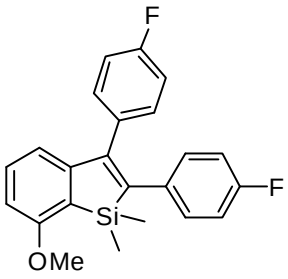


2c: Colorless solid, isolated yield 64% (71 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.48 (s, 6H, CH_3), 2.24 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 3.85 (s, 3H, CH_3), 6.68 (d, J = 7.5 Hz, 1H, CH), 6.74 (d, J = 8.2 Hz, 1H, CH), 6.87-6.94 (m, 4H, CH), 7.06-7.14 (m, 4H, CH), 7.23-7.25 (m, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: -3.90 ($2CH_3$), 21.11, 21.32, 55.41, 108.85, 117.33, 123.56, 128.57 (2CH), 128.66 (2CH), 129.03 (2CH), 129.53 (2CH), 131.78, 135.12, 135.55, 136.39, 137.08, 143.18, 151.73, 152.76, 162.92; HRMS (ESI, m/z) calcd. for $[C_{25}H_{26}OSi]H^+$: 371.1826; found 371.1817.

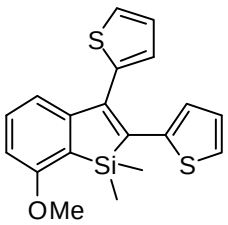


2d: Pale yellow solid, isolated yield 67% (89 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.46 (s, 3H, CH_3), 0.49 (s, 3H, CH_3), 3.88 (s, 3H, CH_3), 6.27 (d, J = 7.5 Hz, 1H, CH), 6.77 (d, J = 8.2 Hz, 1H, CH), 6.92 (br, 1H, CH), 7.11-7.17 (m, 4H, CH), 7.31-7.36 (m, 4H, CH), 7.45 (d, J = 8.2 Hz, 1H, CH), 7.54 (dd, J = 7.6, 1.3 Hz, 1H, CH),

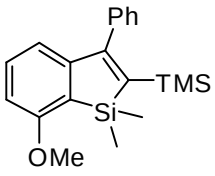
7.65-7.70 (m, 2H, CH), 7.88 (d, J = 7.6 Hz, 1H, CH), 8.01 (d, J = 7.3 Hz, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: -4.13, -3.69, 55.43, 109.11, 117.97, 123.72, 124.86, 125.23, 125.27, 125.35 (2CH), 125.42 (3CH), 125.63, 126.58, 126.67, 127.26, 127.94, 128.05, 131.58, 131.84, 132.09, 133.20, 133.35, 135.93, 138.56, 146.97, 152.40, 153.34, 162.99; HRMS (ESI, m/z) calcd. for $[C_{31}H_{26}OSi]H^+$: 443.1826; found 443.1824.



2e: Colorless solid, isolated yield 59% (67 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.47 (s, 6H, CH_3), 3.86 (s, 3H, CH_3), 6.66 (d, J = 7.5 Hz, 1H, CH), 6.77-6.91 (m, 5H, CH), 7.01 (t, J = 8.8 Hz, 2H, CH), 7.11-7.15 (m, 2H, CH), 7.28 (t, J = 7.9 Hz, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: -4.18 ($2CH_3$), 55.43, 109.22, 114.96 (d, J = 21.0 Hz, 2CH), 115.37 (d, J = 21.1 Hz, 2CH), 117.19, 123.38, 129.93 (d, $J_{C\text{-}F}$ = 7.8 Hz, 2CH), 131.35 (d, $J_{C\text{-}F}$ = 7.8 Hz, 2CH), 132.02, 133.85 (d, $J_{C\text{-}F}$ = 3.4 Hz), 135.88 (d, $J_{C\text{-}F}$ = 3.5 Hz), 143.41, 151.39, 151.95, 160.24 (d, $J_{C\text{-}F}$ = 88.1 Hz), 162.69 (d, $J_{C\text{-}F}$ = 88.9 Hz), 163.05; HRMS (ESI, m/z) calcd. for $[C_{23}H_{20}F_2OSi]H^+$: 379.1324; found 379.1319.

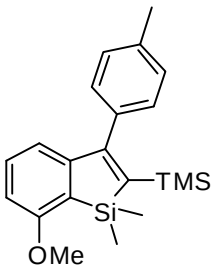


2f: White solid, isolated yield 73% (78 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.57 (s, 6H, CH_3), 3.85 (s, 3H, CH_3), 6.63 (d, J = 7.5 Hz, 1H, CH), 6.75 (d, J = 8.2 Hz, 1H, CH), 6.93-7.02 (m, 3H, CH), 7.16-7.22 (m, 2H, CH), 7.28 (t, J = 7.9 Hz, 1H, CH), 7.54 (dd, J = 5.1, 0.9 Hz, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: -3.30 ($2CH_3$), 55.43, 109.01, 117.07, 121.78, 126.14, 127.07 (2CH), 127.87, 127.93, 128.06, 132.36, 138.10, 139.90, 141.57, 142.54, 153.06, 162.85; HRMS (ESI, m/z) calcd. for $[C_{19}H_{18}OS_2Si]H^+$: 355.0641; found 355.0642.

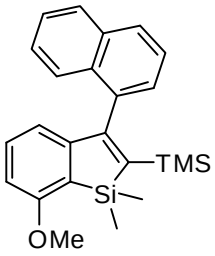


2g: Colorless oil, isolated yield 65% (66 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ: -0.13 (s, 9H, CH_3), 0.43 (s, 6H, CH_3), 3.83 (s, 3H, CH_3), 6.44 (d, J = 7.5 Hz, 1H, CH), 6.73 (d, J = 8.2 Hz, 1H, CH), 7.17-7.22 (m, 3H, CH), 7.33-7.39 (m, 3H, CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: -3.43 ($2CH_3$), 0.73 ($3CH_3$), 55.39, 109.08, 117.20, 126.13, 126.94, 127.87 (2CH), 128.63

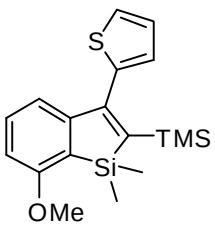
(2CH), 131.69, 141.88, 143.05, 153.49, 162.77, 166.35; HRMS (ESI, m/z) calcd. for $[C_{20}H_{26}OSi_2]H^+$: 339.1595; found 339.1601.



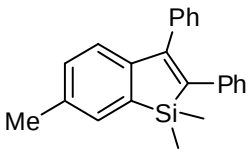
2h: Colorless oil, isolated yield 53% (56 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ: -0.12 (s, 9H, CH_3), 0.42 (s, 6H, CH_3), 2.40 (s, 3H, CH_3), 3.83 (s, 3H, CH_3), 6.46 (d, *J* = 7.5 Hz, 1H, CH), 6.72 (d, *J* = 8.2 Hz, 1H, CH), 7.06-7.08 (m, 2H, CH), 7.17-7.22 (m, 3H, CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: -3.41 ($2CH_3$), 0.81 ($3CH_3$), 21.30, 55.39, 109.03, 117.21, 126.17, 128.52 (4CH), 131.64, 136.46, 138.86, 142.88, 153.65, 162.75, 166.55; HRMS (ESI, m/z) calcd. for $[C_{21}H_{28}OSi_2]H^+$: 353.1752; found 353.1744.



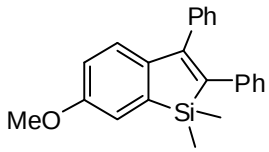
2i: Colorless solid, isolated yield 56% (65 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ: -0.30 (s, 9H, CH_3), 0.51 (s, 3H, CH_3), 0.53 (s, 3H, CH_3), 3.85 (s, 3H, CH_3), 6.17 (d, *J* = 7.5 Hz, 1H, CH), 6.71 (d, *J* = 8.2 Hz, 1H, CH), 7.08 (t, *J* = 7.8 Hz, 1H, CH), 7.27-7.34 (m, 2H, CH), 7.42-7.51 (m, 2H, CH), 7.64 (d, *J* = 8.4 Hz, 1H, CH), 7.85 (t, *J* = 7.7 Hz, 2H, CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: -3.52, -3.01, 0.32 ($3CH_3$), 55.37, 109.08, 117.39, 125.26, 125.72, 125.76, 125.89, 125.99, 126.46, 127.39, 128.02, 131.85, 132.09, 133.33, 139.73, 145.27, 153.68, 162.76, 164.85; HRMS (ESI, m/z) calcd. for $[C_{24}H_{28}OSi_2]H^+$: 389.1752; found 389.1753.



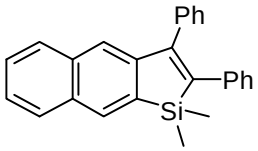
2j: Colorless oil, isolated yield 51% (53 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ: -0.04 (s, 9H, CH_3), 0.42 (s, 6H, CH_3), 3.83 (s, 3H, CH_3), 6.68 (d, *J* = 7.5 Hz, 1H, CH), 6.74 (d, *J* = 8.2 Hz, 1H, CH), 6.89 (dd, *J* = 3.4, 1.0 Hz, 1H, CH), 7.04-7.07 (m, 1H, CH), 7.23-7.27 (m, 1H, CH), 7.33 (dd, *J* = 5.1, 1.0 Hz, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: -3.57 ($2CH_3$), 0.48 ($3CH_3$), 55.41, 109.23, 116.92, 124.67, 125.72, 126.52, 126.54, 131.90, 141.81, 149.17, 153.40, 158.02, 162.78; HRMS (ESI, m/z) calcd. for $[C_{18}H_{24}OSSi_2]H^+$: 345.1159; found 345.1156.



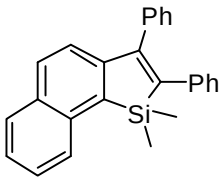
2k:, Pale yellow solid, isolated yield 56% (55 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.46 (s, 6H, CH_3), 2.37 (s, 3H, CH_3), 6.93-6.98 (m, 3H, CH), 7.03-7.13 (m, 4H, CH), 7.18-7.20 (m, 2H, CH), 7.26-7.33 (m, 3H, CH), 7.44 (s, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: -3.42 ($2CH_3$), 21.21, 123.80, 125.51, 126.96, 127.89 (2CH), 128.29 (2CH), 128.59 (2CH), 129.59 (2CH), 130.26, 132.60, 136.30, 138.21, 138.32, 140.04, 141.71, 148.14, 153.02; HRMS (ESI, m/z) calcd. for $[C_{23}H_{22}Si]H^{+}$: 327.1564; found 327.1565.



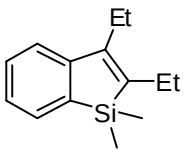
2l:[2] Colorless solid, isolated yield 63% (62 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.46 (s, 6H, CH_3), 3.83 (s, 3H, CH_3), 6.77 (dd, *J* = 8.5, 2.6 Hz, 1H, CH), 6.96 (t, *J* = 7.8 Hz, 3H, CH), 7.02-7.05 (m, 1H, CH), 7.09-7.12 (m, 2H, CH), 7.17-7.20 (m, 3H, CH), 7.27-7.33 (m, 3H, CH); ^{13}C NMR (125 MHz, $CDCl_3$) δ: -3.37 ($2CH_3$), 55.42, 113.81, 118.17, 124.94, 125.41, 127.00, 127.89 (2CH), 128.31 (2CH), 128.59 (2CH), 129.59 (2CH), 138.45, 140.12, 140.27, 140.39, 143.60, 152.86, 158.91.



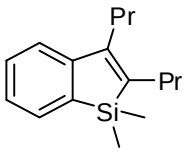
2m:[1] White solid, isolated yield 58% (63 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.52 (s, 6H, CH_3), 7.00-7.16 (m, 6H, CH), 7.23-7.27 (m, 1H, CH), 7.33-7.42 (m, 6H, CH), 7.64-7.67 (m, 1H, CH), 7.81-7.83 (m, 1H, CH), 8.06 (m, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: -2.87 ($2CH_3$), 122.43, 125.75, 125.79, 126.47, 127.15, 127.82, 127.95 (2CH), 128.39 (2CH), 128.45, 128.58 (2CH), 129.77 (2CH), 132.37, 132.69, 134.59, 136.45, 138.20, 140.07, 144.72, 147.55, 153.65.



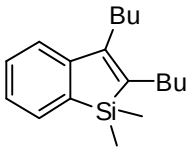
2n: White solid, isolated yield 84% (91 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.63 (s, 6H, CH_3), 7.02-7.17 (m, 5H, CH), 7.22-7.53 (m, 8H, CH), 7.76-7.87 (m, 3H, CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: -2.90 ($2CH_3$), 122.78, 125.26, 125.70, 126.55, 127.13, 127.98 (2CH), 128.16, 128.45 (2CH), 128.65 (2CH), 128.84, 129.69 (2CH), 130.14, 132.41, 135.92, 135.97, 138.28, 139.82, 142.74, 149.35, 153.06; HRMS (ESI, m/z) calcd. for $[C_{26}H_{22}Si]H^{+}$: 363.1564; found 363.1571.



3a:[1] Colorless oil, isolated yield 70% (45 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.30 (s, 6H, CH_3), 1.09-1.13 (m, 6H, CH_3), 2.42 (q, J = 7.6 Hz, 2H, CH_2), 2.54 (q, J = 7.6 Hz, 2H, CH_2), 7.15 (td, J = 7.0, 1.2 Hz, 1H, CH), 7.27-7.35 (m, 2H, CH), 7.48 (d, J = 6.8 Hz, 1H, CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ: -3.47 ($2CH_3$), 13.53, 15.07, 19.82, 22.26, 120.81, 125.57, 129.59, 131.29, 138.47, 142.64, 150.00, 152.44.



3b:[1] Colorless oil, isolated yield 76% (56 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.29 (s, 6H, CH_3), 0.94-1.00 (m, 6H, CH_3), 1.49-1.56 (m, 4H, CH_2), 2.38 (t, J = 7.9 Hz, 2H, CH_2), 2.51 (t, J = 7.8 Hz, 2H, CH_2), 7.14 (t, J = 7.6 Hz, 1H, CH), 7.23-7.34 (m, 2H, CH), 7.47 (d, J = 6.8 Hz, 1H, CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ: -3.41 ($2CH_3$), 14.40, 14.57, 22.00, 23.69, 28.98, 31.96, 120.97, 125.54, 129.56, 131.21, 138.45, 142.03, 150.33, 151.17.



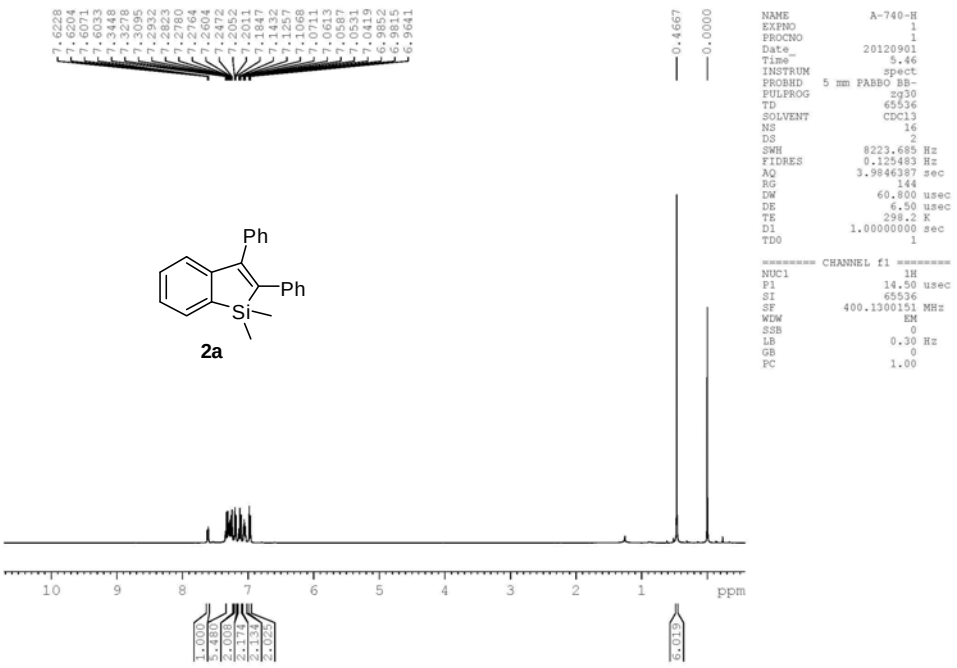
3c:[1] Colorless oil, isolated yield 53% (43 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.28 (s, 6H, CH_3), 0.92-0.96 (m, 6H, CH_3), 1.36-1.48 (m, 8H, CH_2), 2.39 (t, J = 7.8 Hz, 2H, CH_2) 2.52 (t, J = 7.6 Hz, 2H, CH_2), 7.15 (t, J = 7.1 Hz, 1H, CH), 7.25-7.34 (m, 2H, CH), 7.47 (d, J = 6.9 Hz, 1H, CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ: -3.42 ($2CH_3$), 14.05, 14.09, 23.11, 23.14, 26.73, 29.39, 31.04, 32.70, 120.91, 125.51, 129.55, 131.21, 138.47, 141.87, 150.34, 151.29.

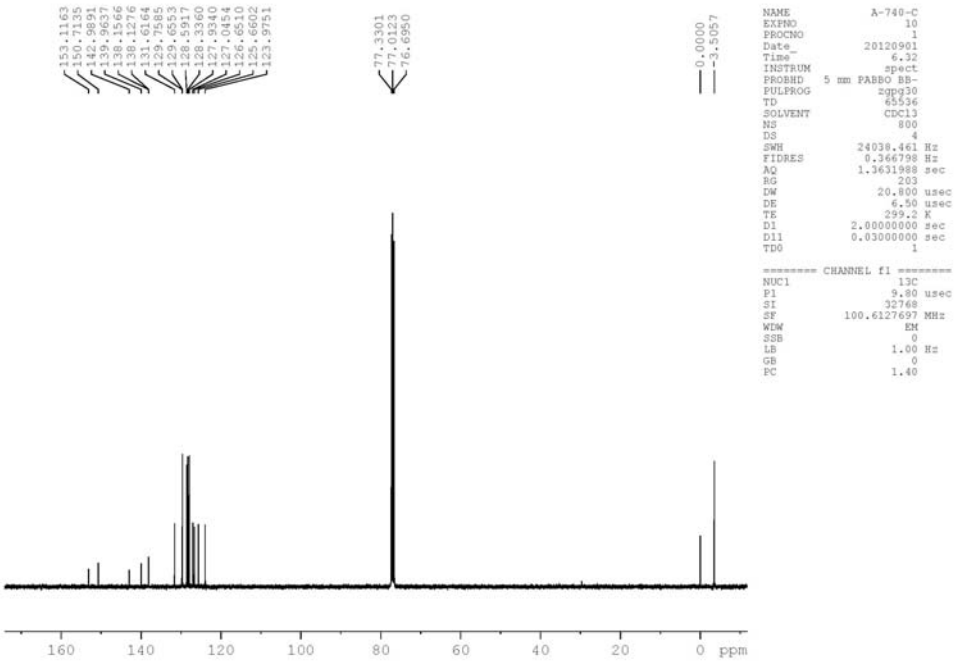
References:

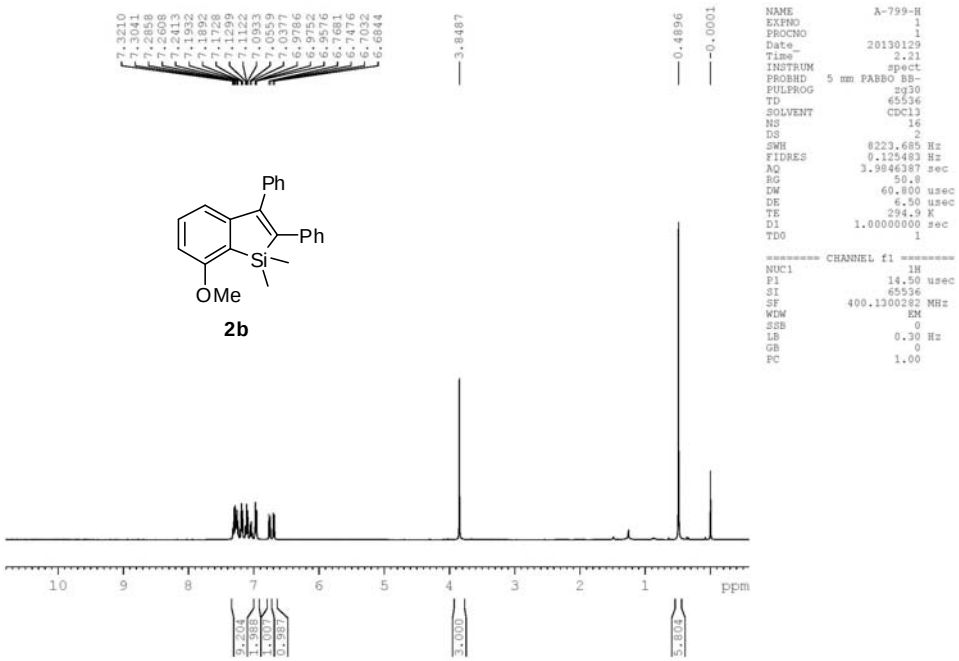
[1] (*a*) M. Onoe, K. Baba, Y. Kim, Y. Kita, M. Tobisu and N. Chatani, *J. Am. Chem. Soc.*, 2012, **134**, 19477; (*b*) M. Tobisu, M. Onoe, Y. Kita and N. Chatani, *J. Am. Chem. Soc.*, 2009, **131**, 7506. (*c*) A. Kawachi, A. Tani, K. Machida and Y. Yamamoto, *Organometallics,* 2007, **26**, 4697.

[2] Y. Liang, W. Geng, J. Wei and Z. Xi, *Angew. Chem., Int. Ed.*, 2012, **51**, 1934.

5) Scanned ^{1}H NMR and ^{13}C NMR Spectra of All New Compounds



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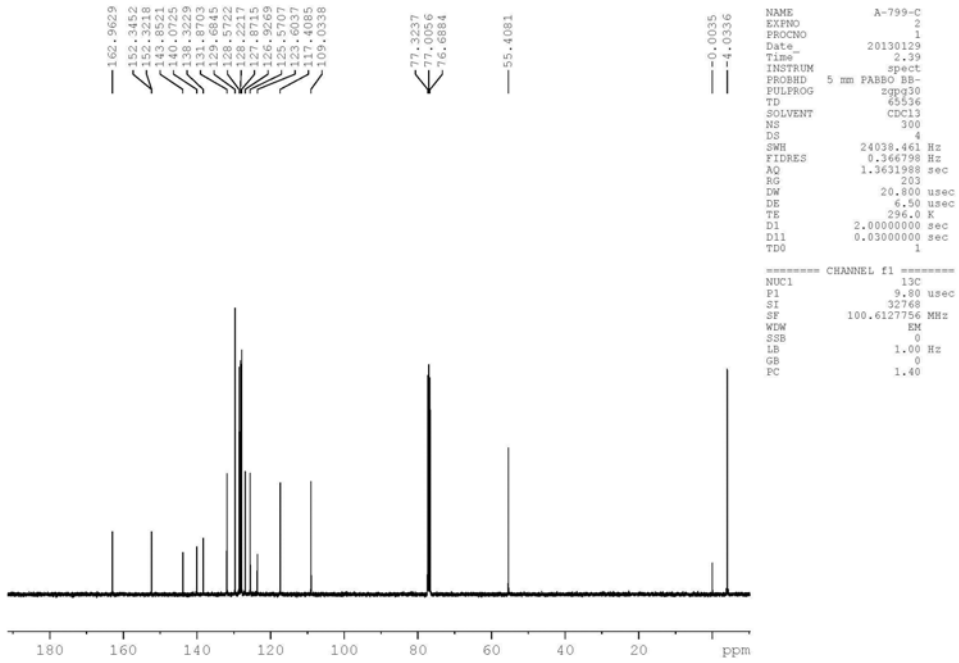
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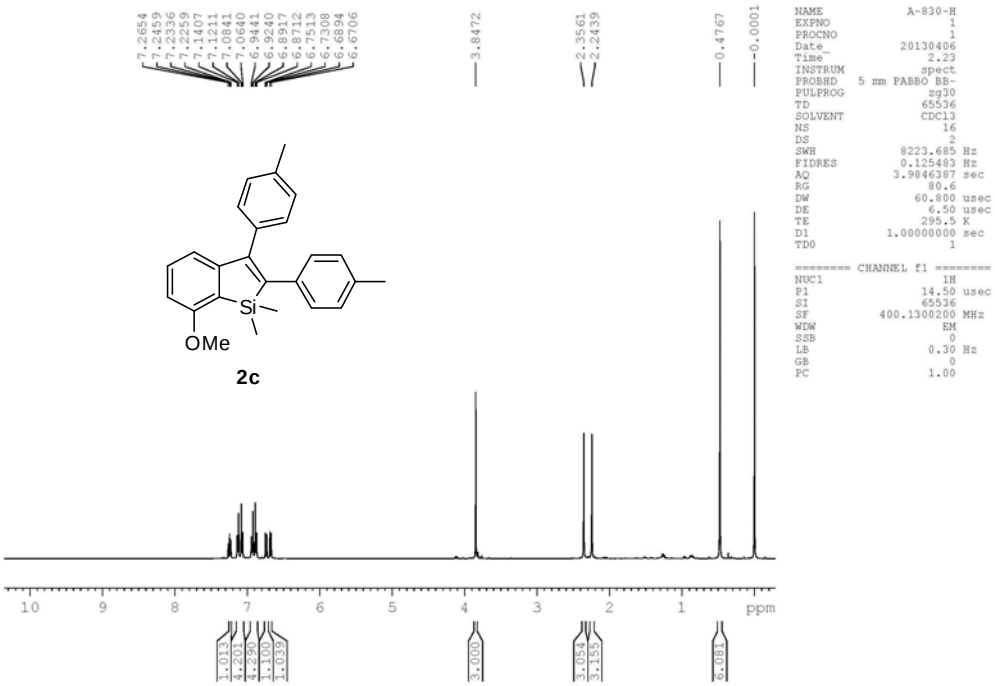
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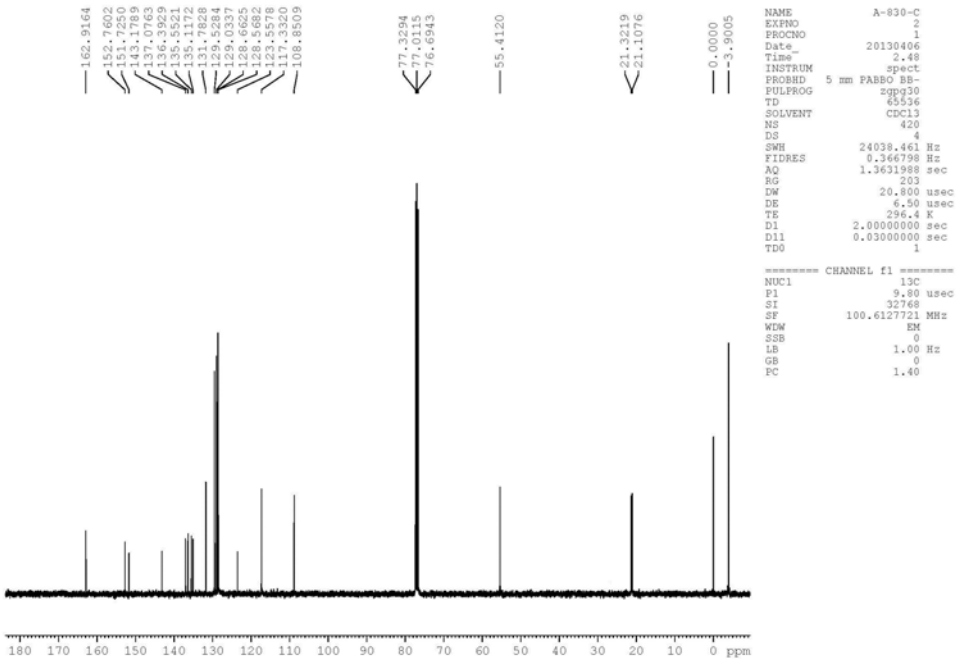
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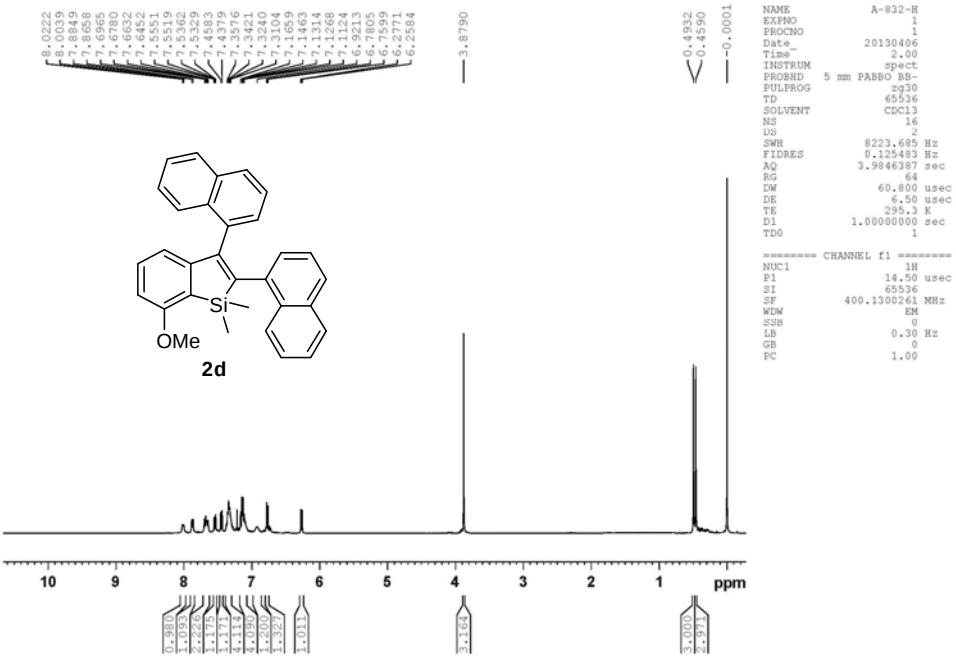
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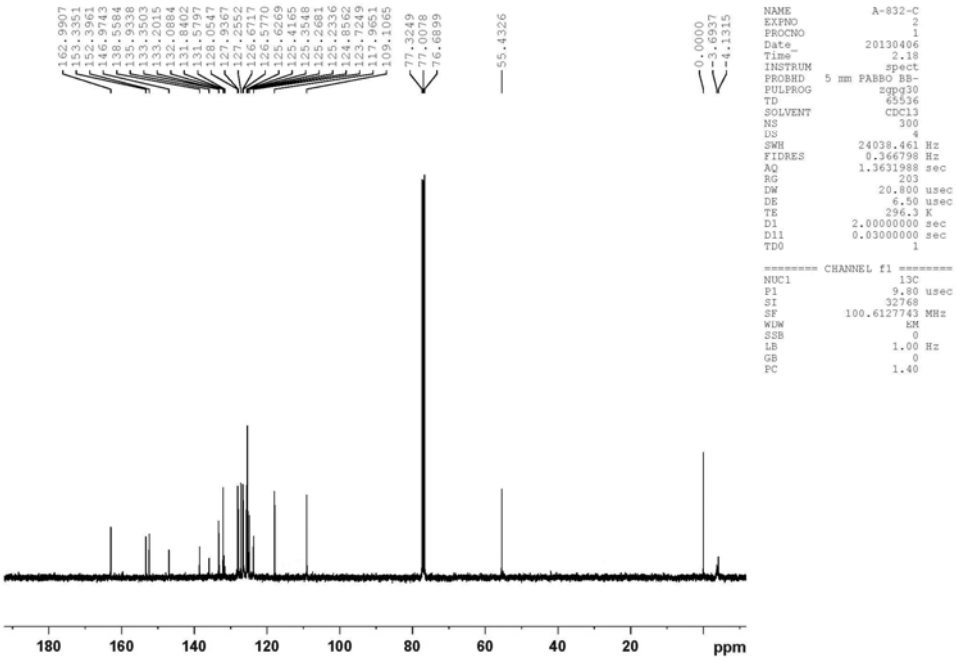
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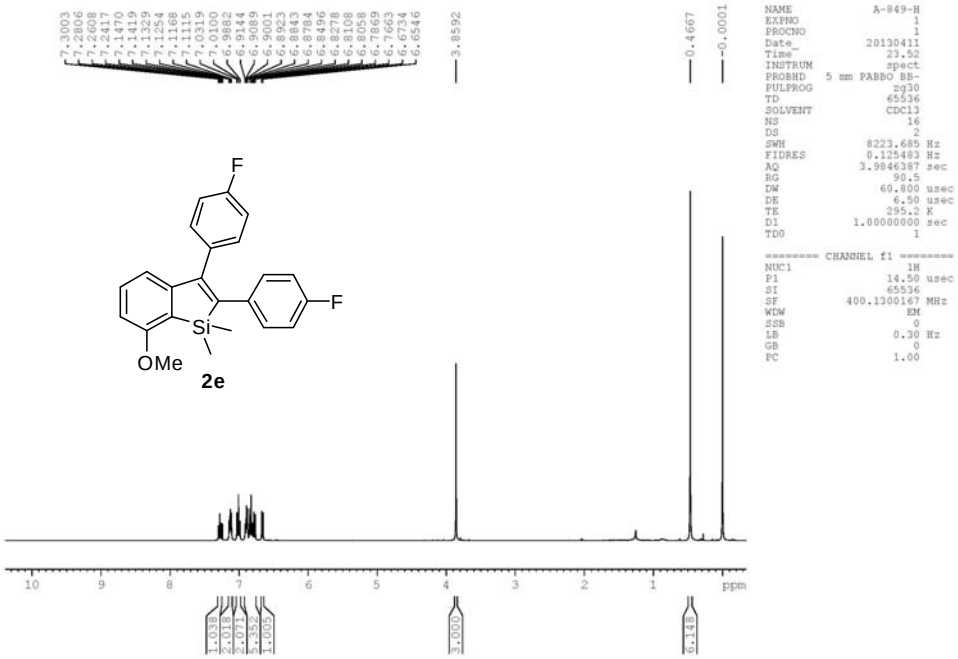
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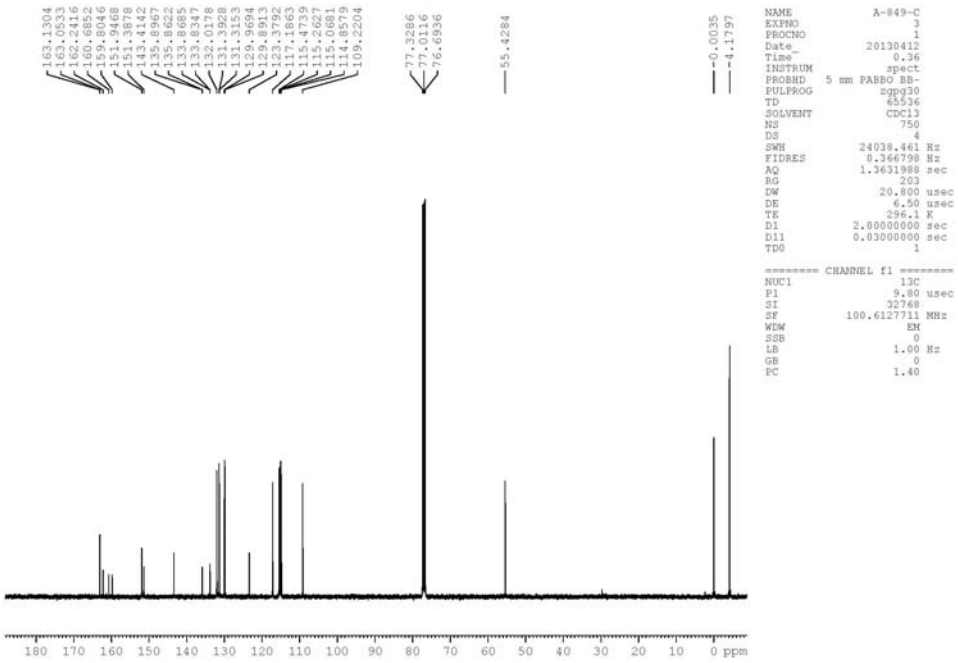
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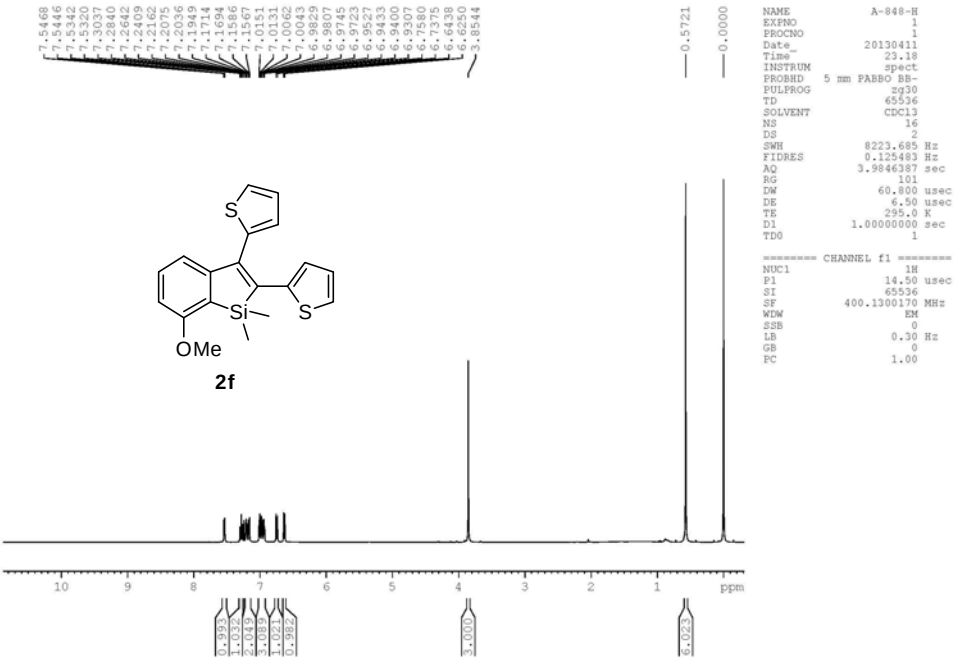
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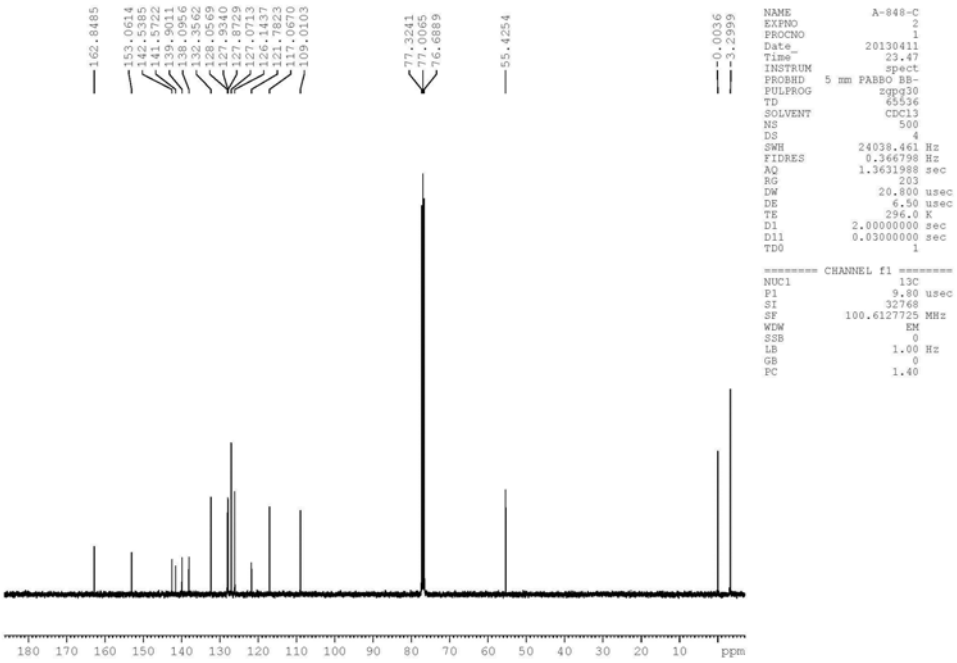
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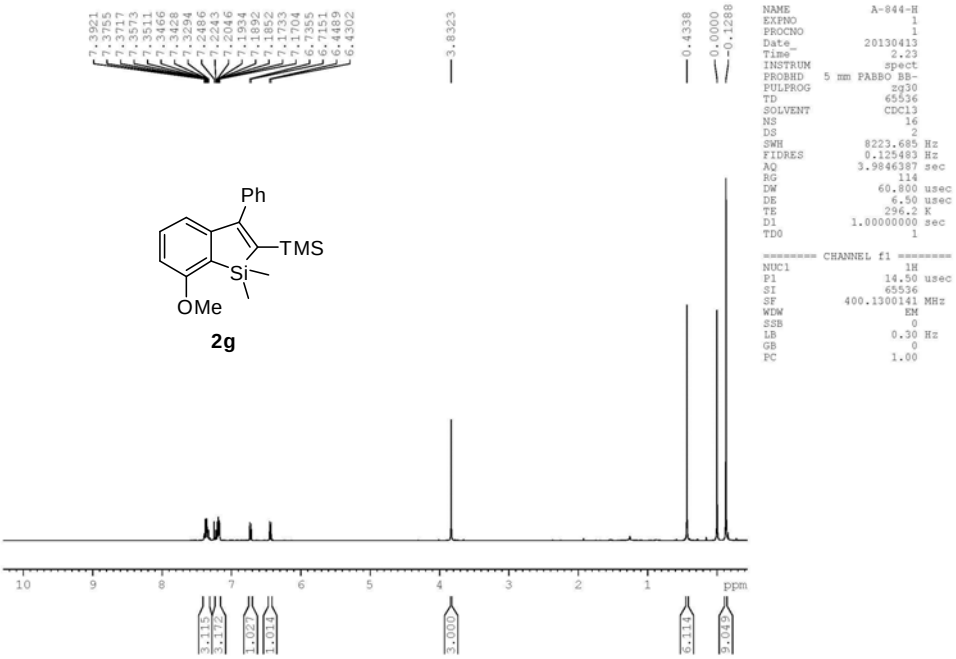

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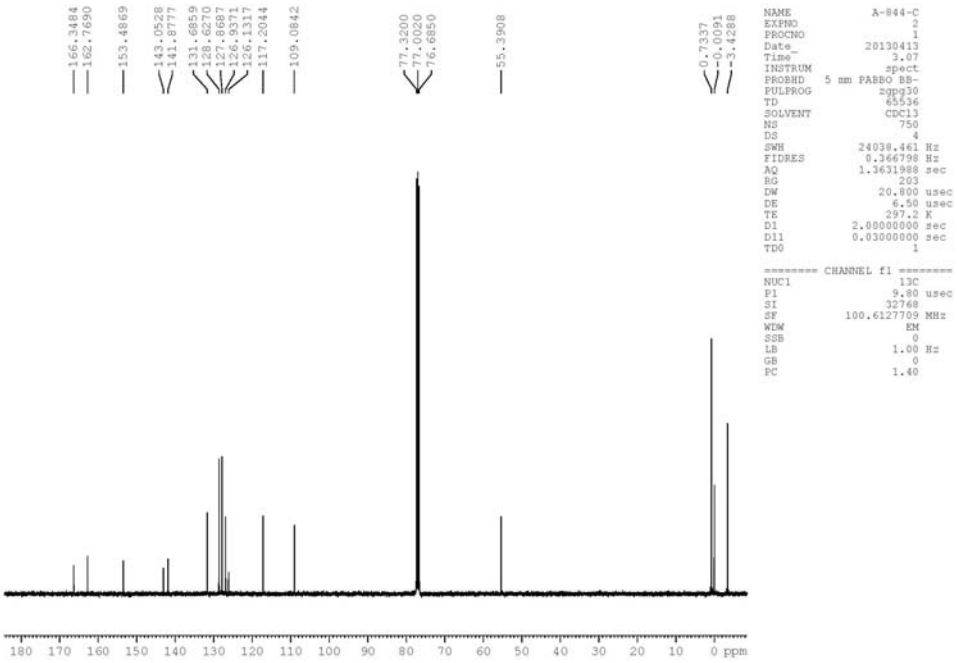

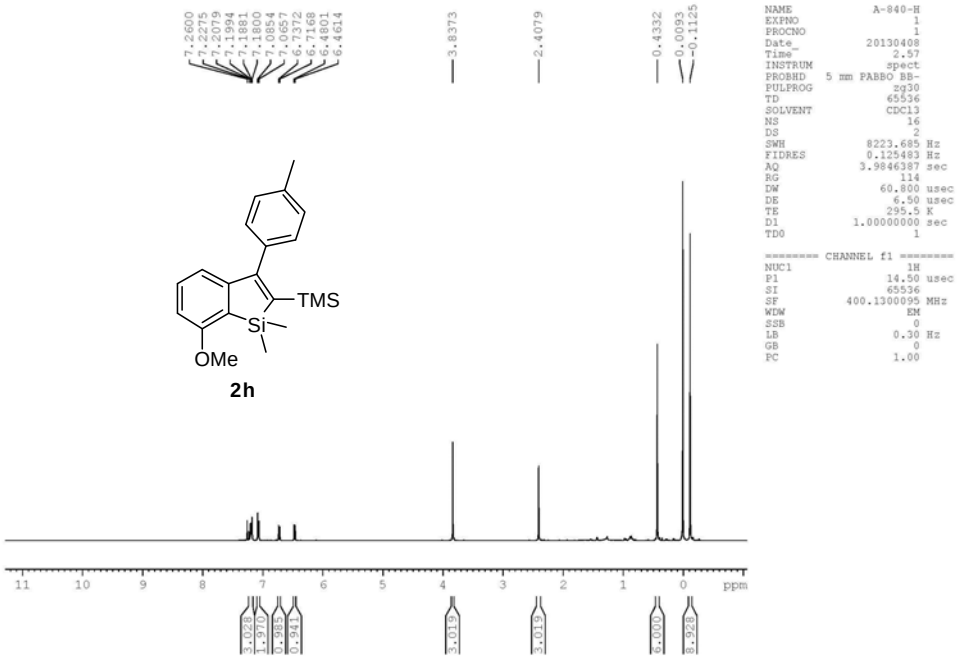
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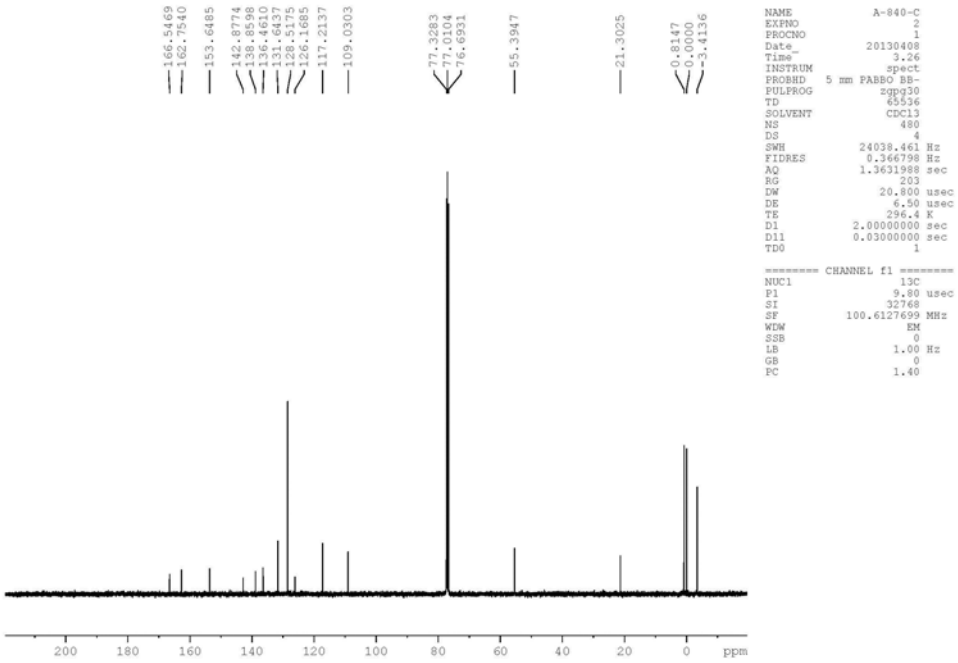
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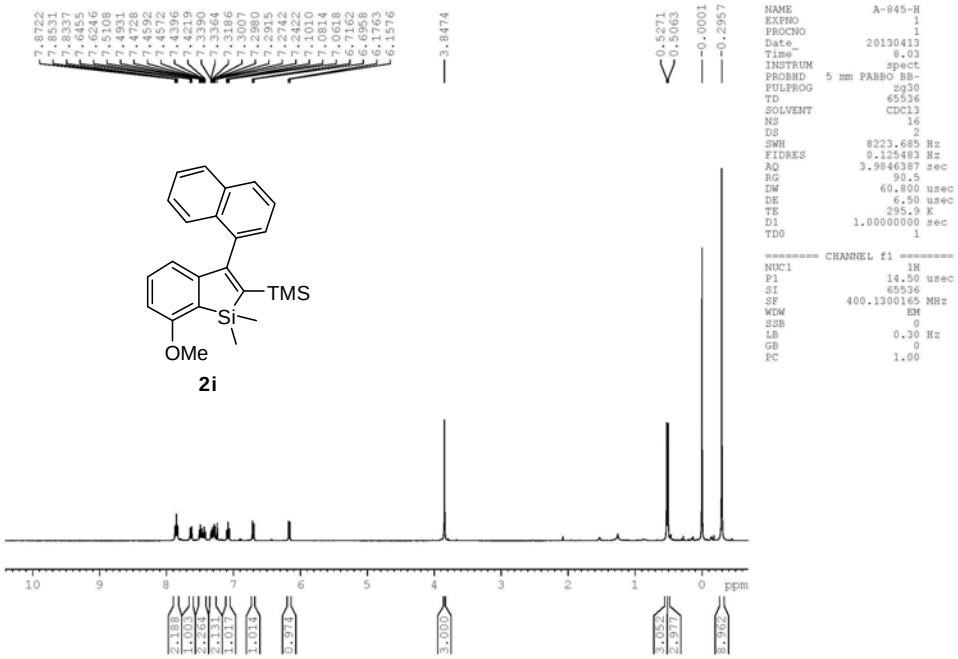
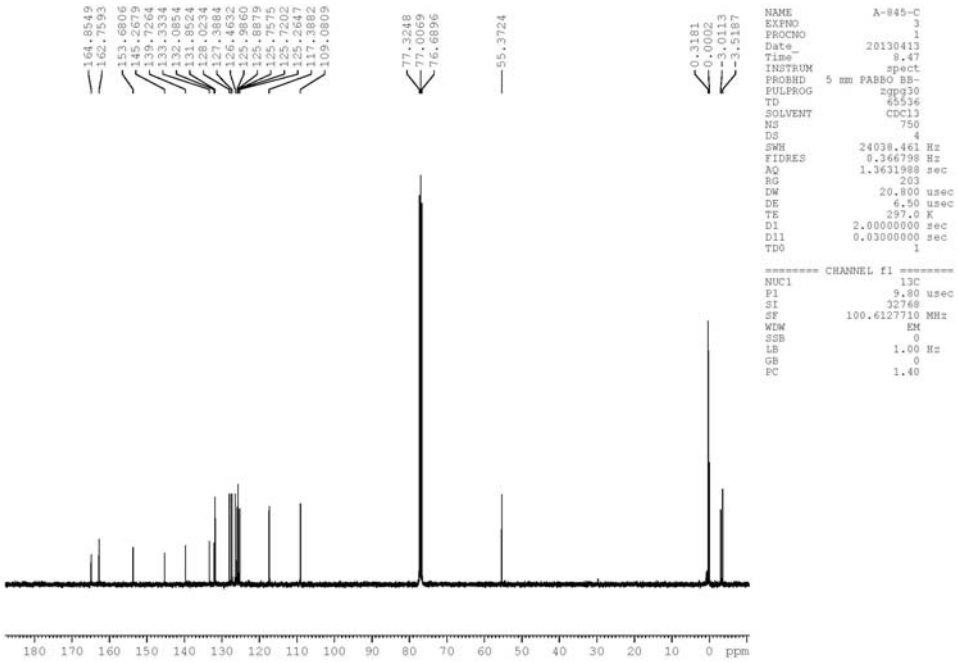
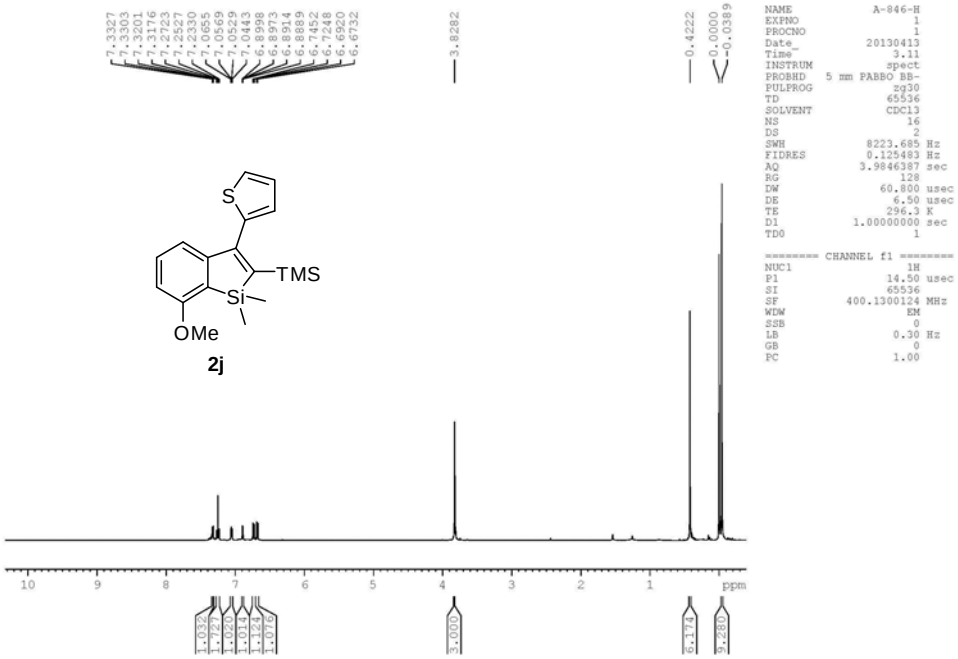
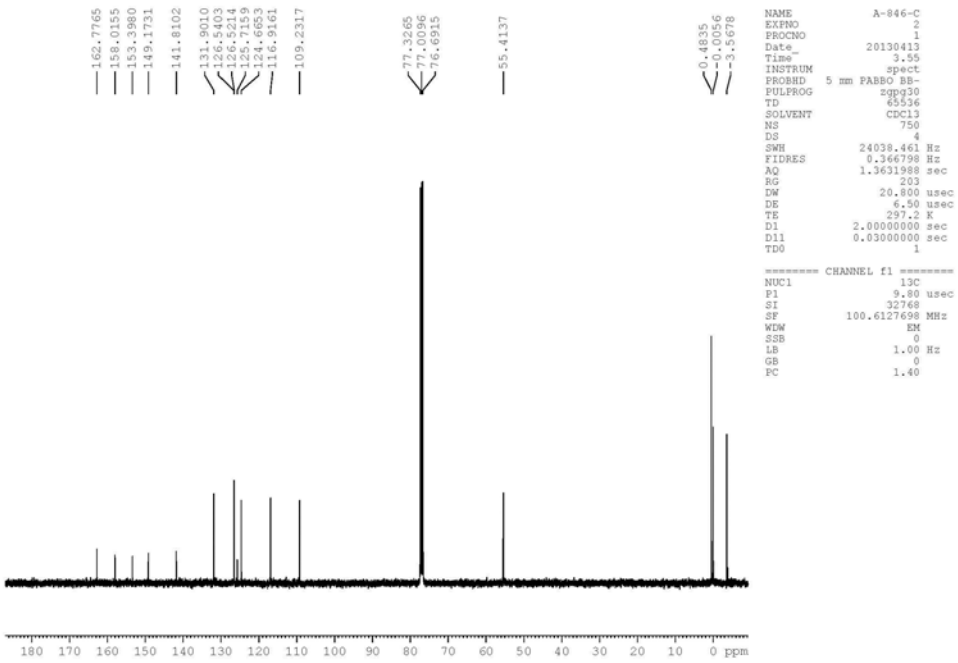
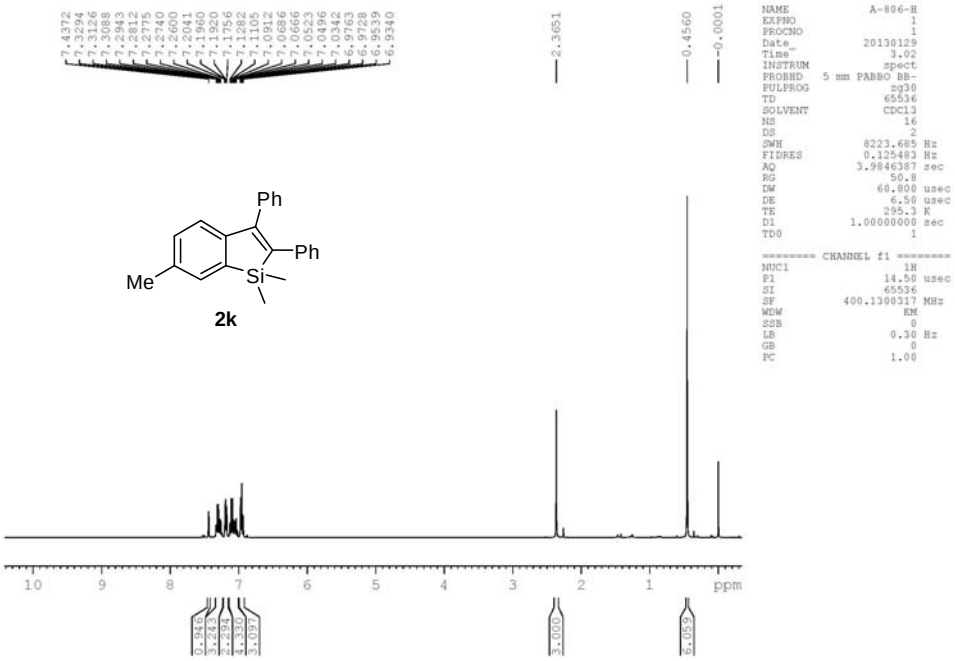
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 480
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 296.4 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.80 usec
SI 32768
SF 100.6127699 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

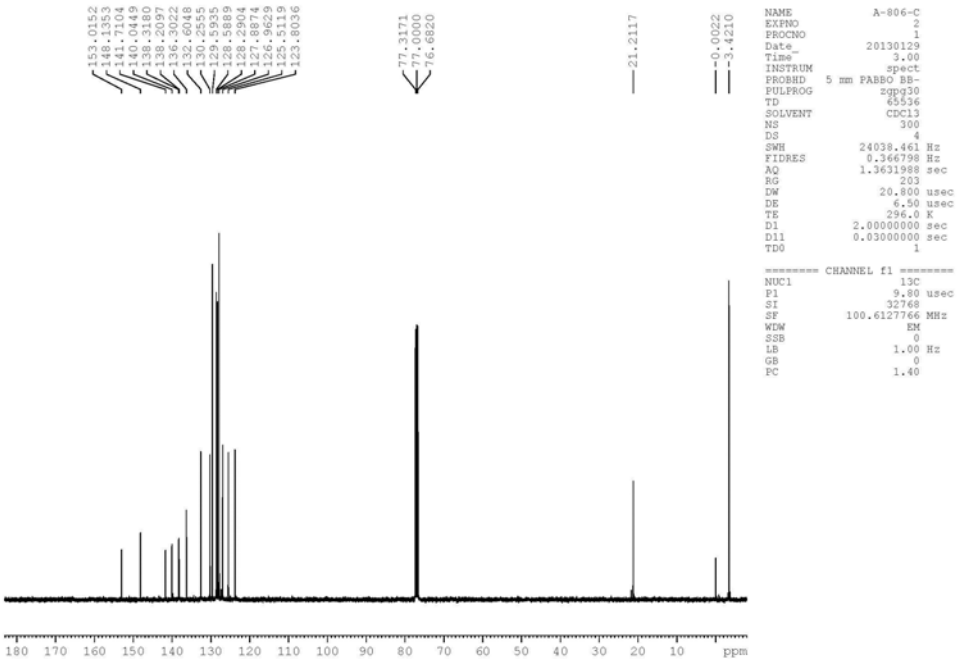

TMS
Si
OMe
2i
ppm

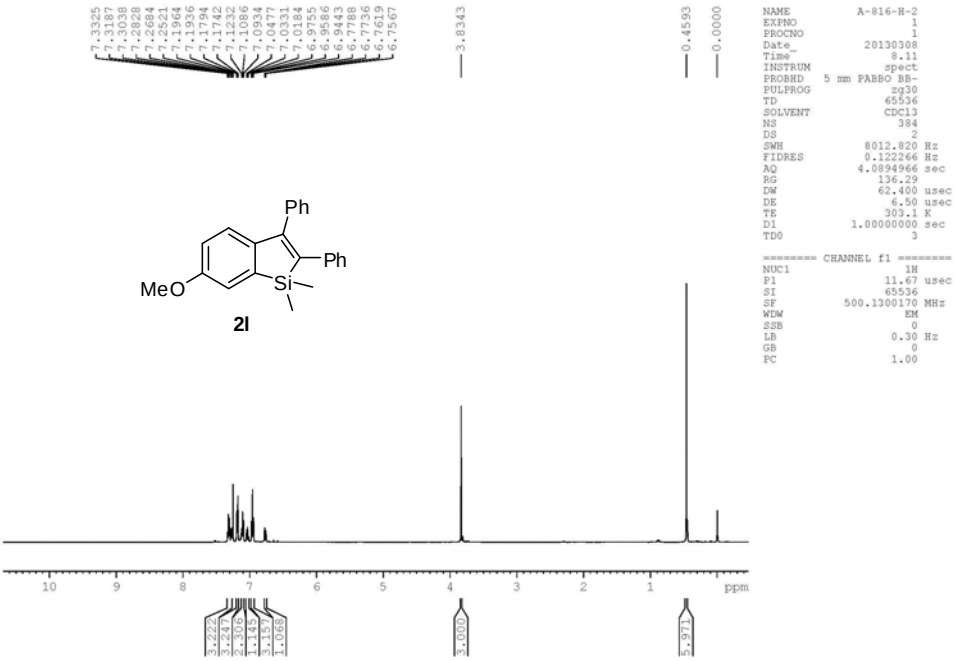

ppm

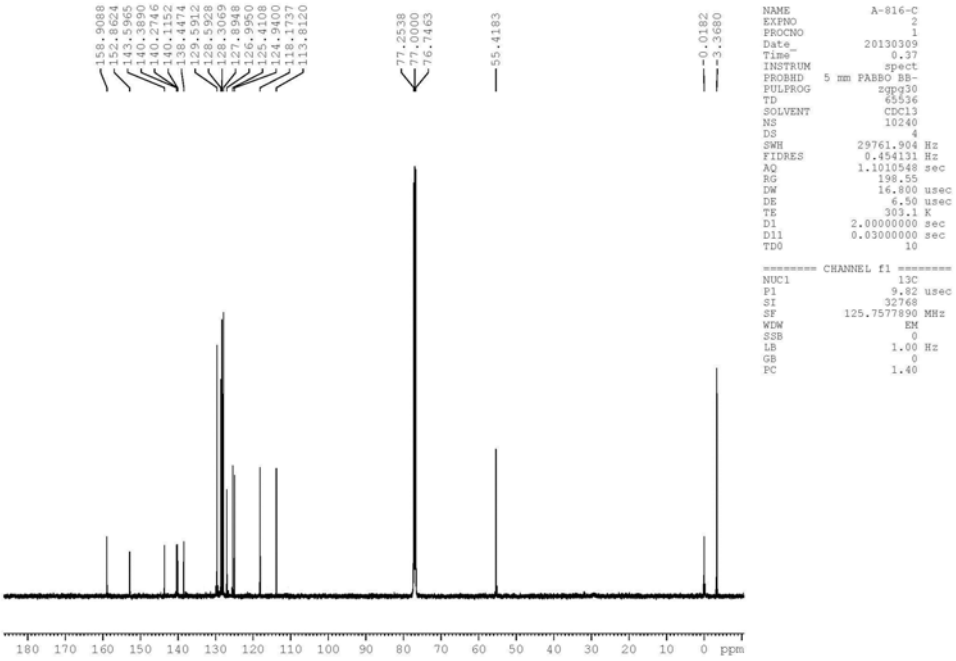

7.3327
7.3303
7.3201
7.3176
7.2723
7.2527
7.2330
7.0655
7.0569
7.0529
7.0443
6.8998
6.8973
6.8914
6.8889
6.7452
6.7248
6.6920
6.6732
3.8282
0.4222
0.0000
-0.0389
S
TMS
Si
OMe
2j
NAME A-846-H
EXPNO 1
PROCNO 1
Date_ 20130413
Time 3.11
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 128
DW 60.800 usec
DE 6.50 usec
TE 296.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.50 usec
SI 65536
SF 400.1300124 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
10 9 8 7 6 5 4 3 2 1 ppm
1.033
1.721
1.020
1.014
1.124
1.076
3.000
5.174
5.280

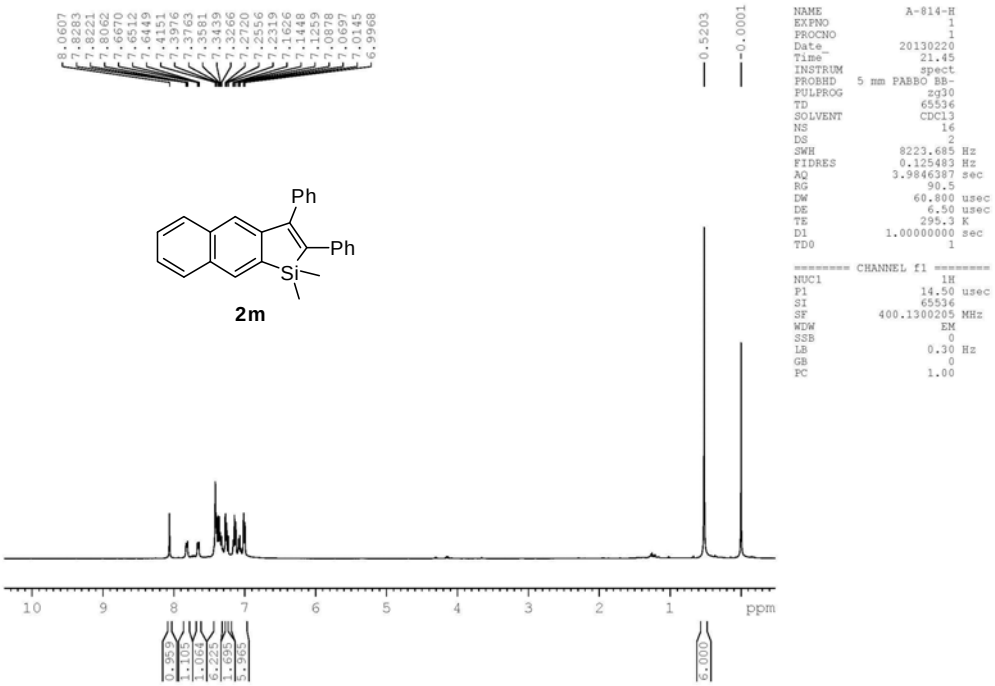

162.7765
158.0155
153.3980
149.1731
141.8102
131.9010
126.5403
126.5214
125.7159
124.6653
116.9161
109.2317
77.3265
77.0096
76.6915
55.4137
0.4835
0.0056
-3.5678
NAME A-846-C
EXPNO 2
PROCNO 1
Date_ 20130413
Time 3.55
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 750
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 297.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.80 usec
SI 32768
SF 100.6127698 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

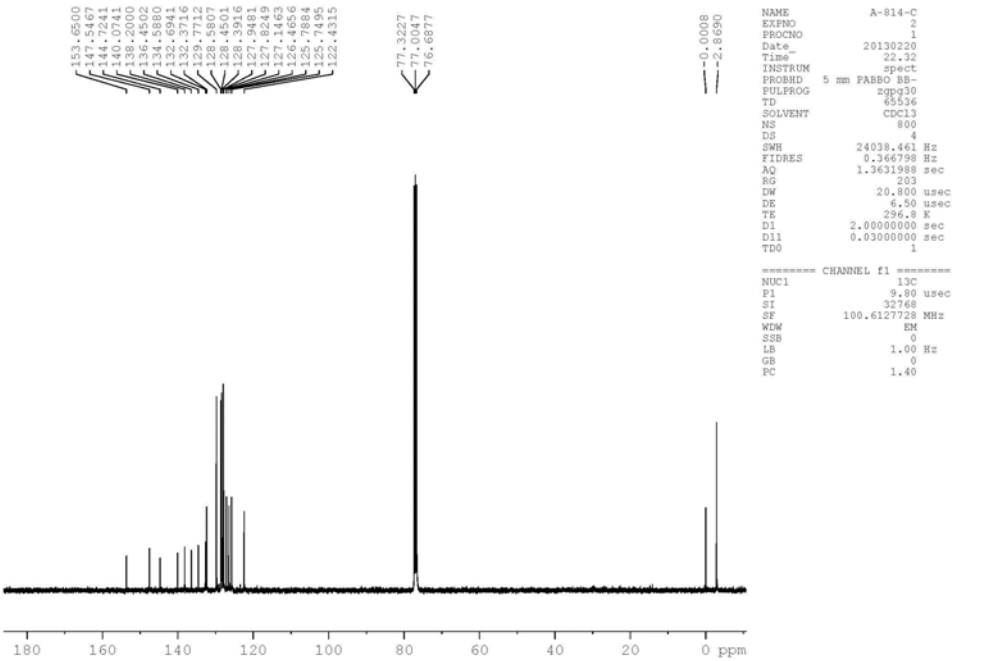

Ph
Ph
Me
Si
2k
ppm

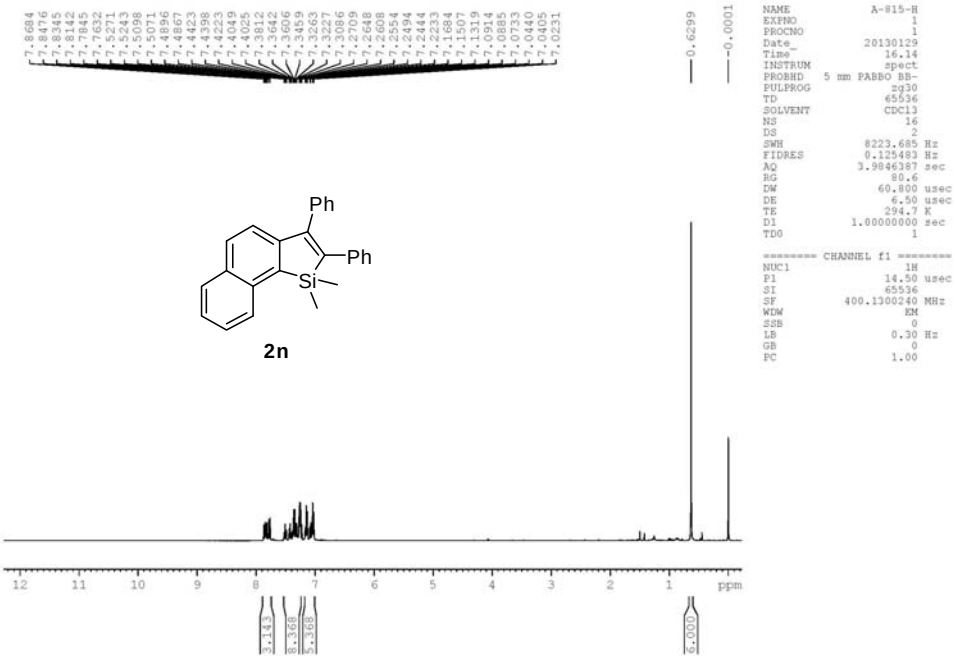

ppm

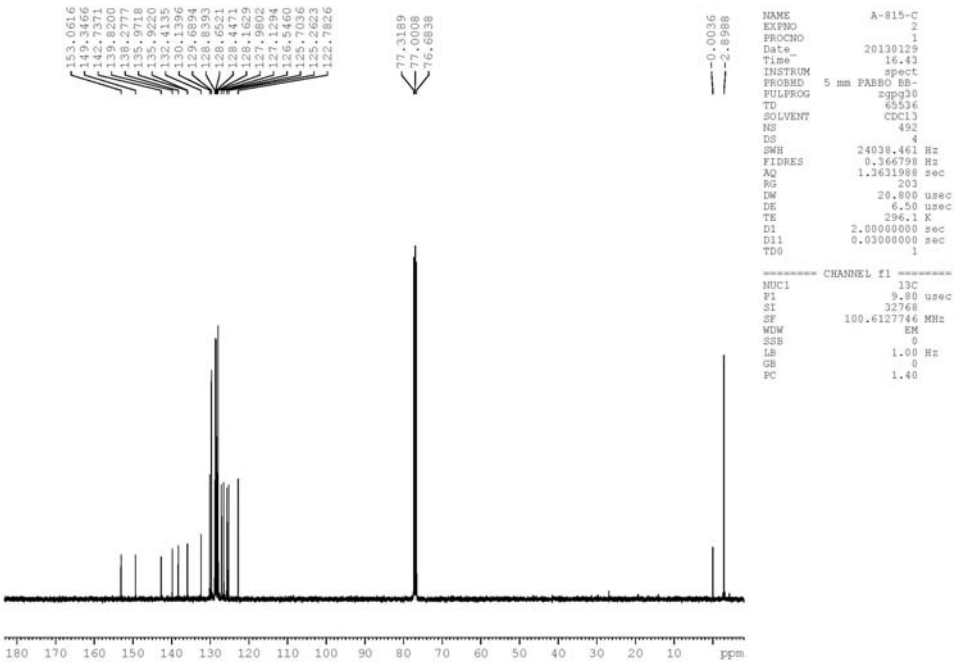

7.3325
7.3187
7.3038
7.2828
7.2684
7.2521
7.1964
7.1936
7.1794
7.1742
7.1232
7.1086
7.0934
7.0477
7.0331
7.0184
6.9755
6.9586
6.9443
6.7788
6.7736
6.7619
6.7567
3.8343
0.4593
0.0000
Ph
Ph
MeO
Si
2l
NAME A-816-H-2
EXPNO 1
PROCNO 1
Date_ 20130308
Time_ 8.11
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDC13
NS 384
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 136.29
DW 62.400 usec
DE 6.50 usec
TE 303.1 K
D1 1.00000000 sec
TD0 3
======== CHANNEL f1 ========
NUC1 1H
P1 11.67 usec
SI 65536
SF 500.1300170 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
10 9 8 7 6 5 4 3 2 1 ppm
3.22
3.24
3.30
1.14
3.15
1.06
3.00
5.97

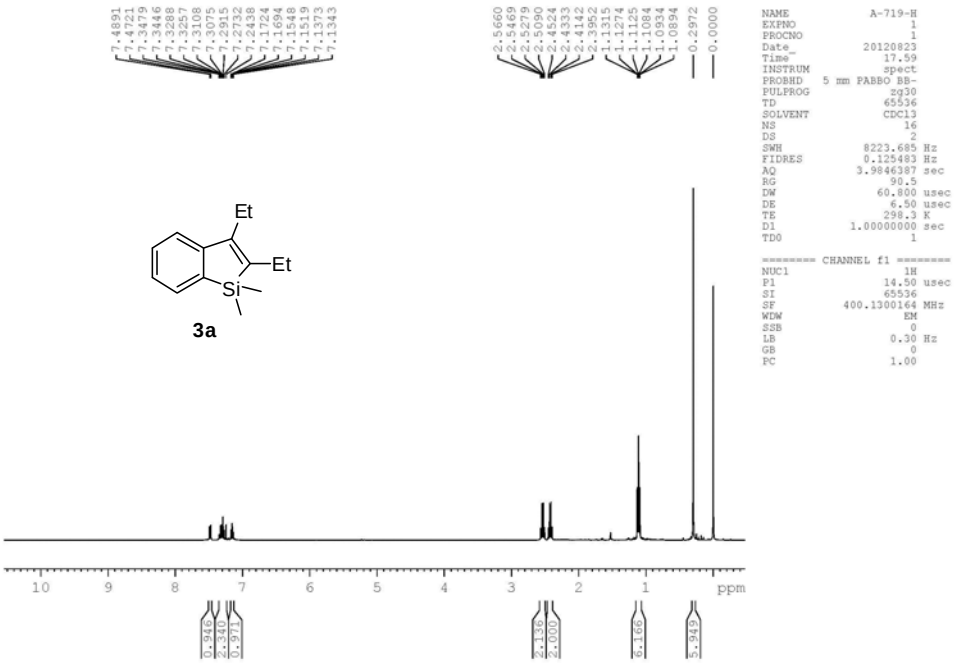

158.9088
152.8624
143.5965
140.3890
140.2746
140.1152
138.4414
129.5912
128.9288
128.3069
127.8948
126.9950
125.4108
124.9400
118.1737
113.8120
77.2538
77.0000
76.7463
55.4183
-0.0182
-3.3680
NAME A-816-C
EXPNO 2
PROCNO 1
Date_ 20130309
Time_ 0.37
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDC13
NS 10240
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010548 sec
RG 198.55
DW 16.800 usec
DE 6.50 usec
TE 303.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 10
======== CHANNEL f1 ========
NUC1 13C
P1 9.82 usec
SI 32768
SF 125.7577890 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

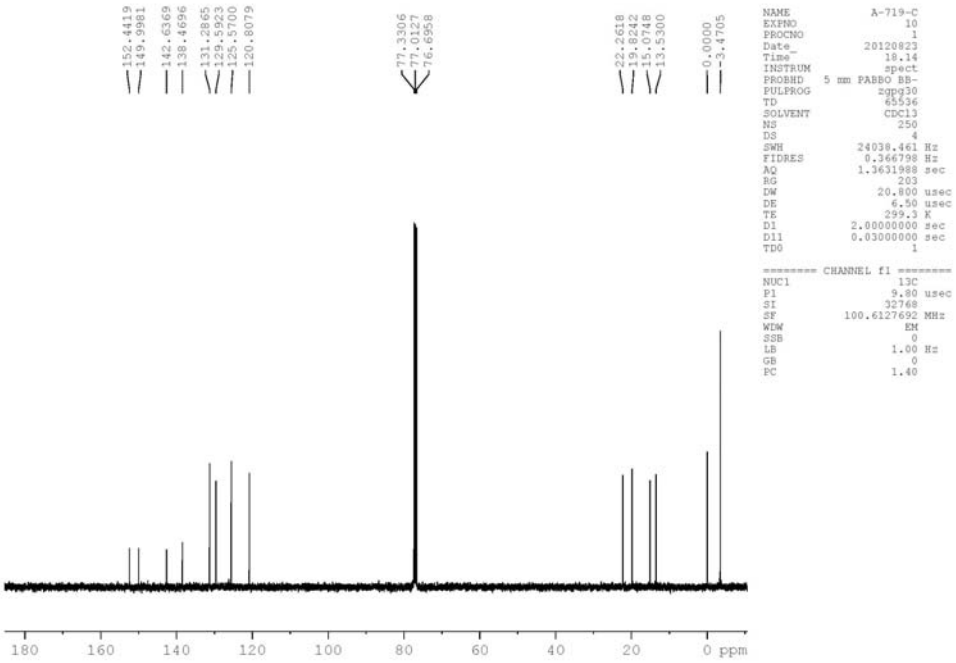

8.0607
7.8283
7.8221
7.8062
7.6670
7.6512
7.6449
7.4151
7.3976
7.3763
7.3581
7.3439
7.3266
7.2720
7.2556
7.2319
7.1626
7.1448
7.1259
7.0878
7.0697
7.0145
6.9968
0.5203
0.0001
Ph
Ph
Si
2m
NAME A-814-H
EXPNO 1
PROCNO 1
Date_ 20130220
Time_ 21.45
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 90.5
DW 60.800 usec
DE 6.50 usec
TE 295.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.50 usec
SI 65536
SF 400.1300205 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
10
9
8
7
6
5
4
3
2
1
ppm
0.953
1.105
1.064
6.225
1.695
5.965
6.000

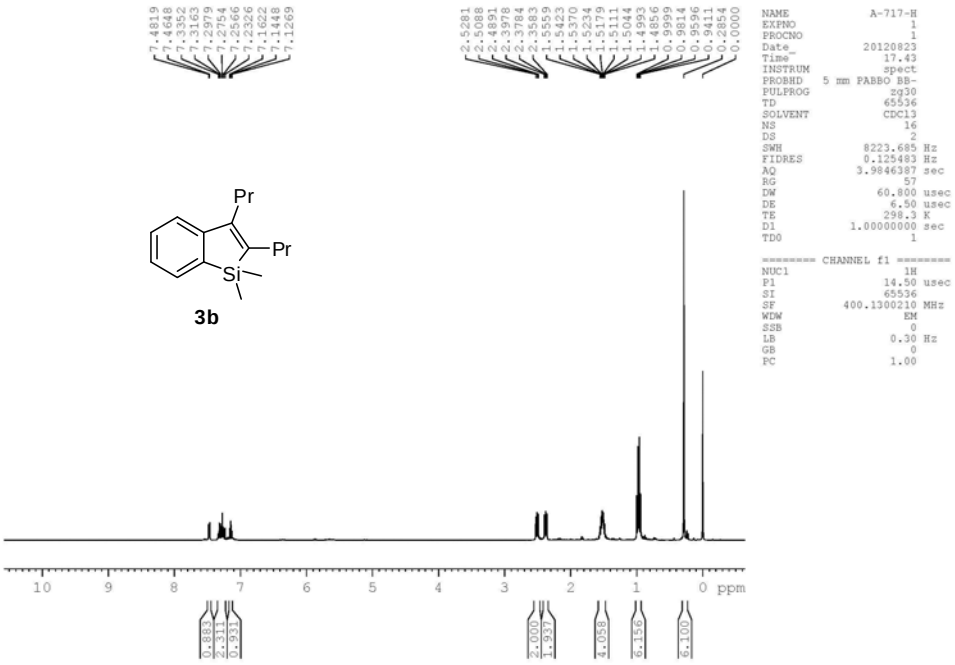

153.6500
147.5467
144.7241
140.0741
138.2000
136.4502
134.5880
132.6941
132.3716
129.7712
128.5807
128.4501
128.3916
127.9481
127.8249
127.1463
126.7866
126.7684
125.7495
122.4315
77.3227
77.0047
76.6877
0.0008
2.8690
NAME A-814-C
EXPNO 2
PROCNO 1
Date_ 20130220
Time_ 22.32
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 800
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 296.8 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.80 usec
SI 32768
SF 100.6127728 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
180
160
140
120
100
80
60
40
20
0 ppm

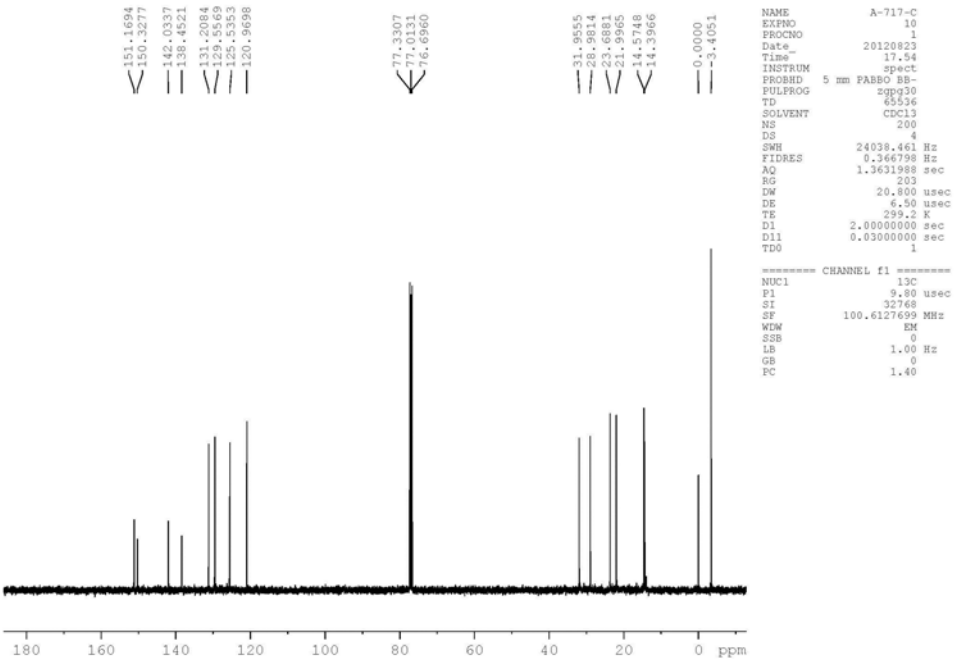

Ph
Ph
Si
2n

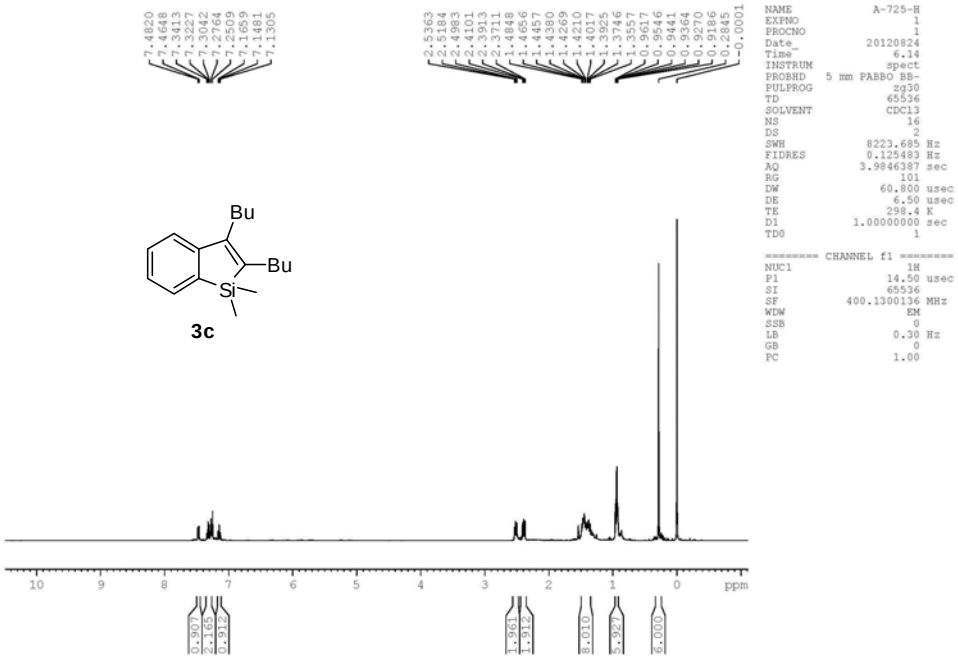


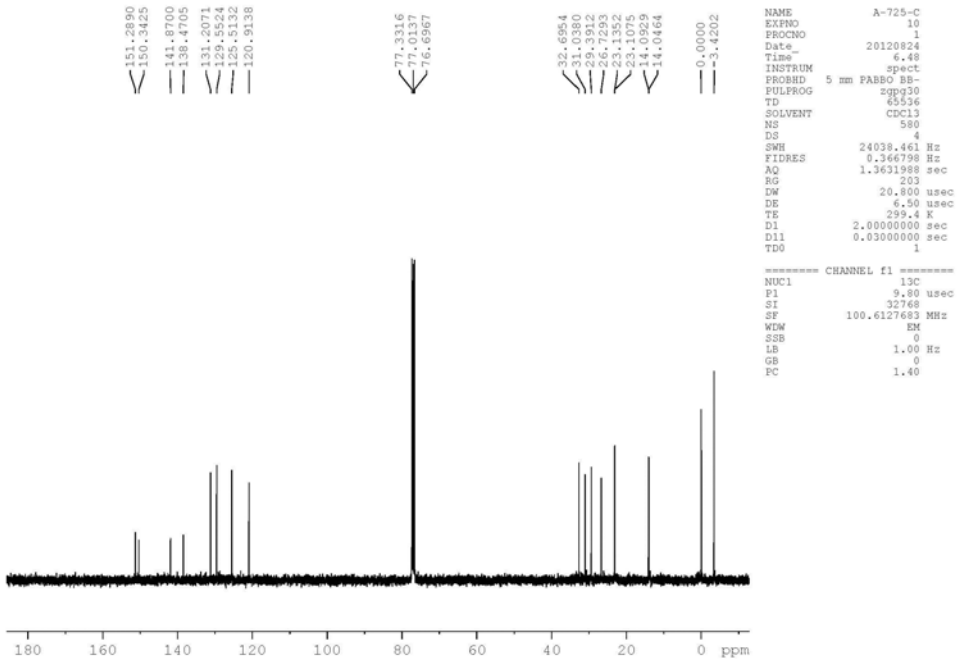

7.4891
7.4721
7.3479
7.3446
7.3288
7.3257
7.3108
7.3075
7.2915
7.2732
7.2438
7.1724
7.1694
7.1548
7.1519
7.1373
7.1343
2.5660
2.5469
2.5279
2.5090
2.4524
2.4333
2.4142
2.3952
1.1315
1.1274
1.1125
1.1084
1.0934
1.0894
0.2972
0.0000
Et
Et
Si
3a
NAME A-719-H
EXPNO 1
PROCNO 1
Date_ 20120823
Time_ 17.59
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 90.5
DW 60.800 usec
DE 6.50 usec
TE 298.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.50 usec
SI 65536
SF 400.1300164 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
10 9 8 7 6 5 4 3 2 1 ppm
0.946
0.940
0.971
2.136
2.000
6.166
5.949


152.4419
149.9981
142.6369
138.4696
131.2865
129.5923
125.5700
120.8079
77.3306
77.0127
76.6958
22.2618
19.8242
15.0748
13.5300
0.0000
-3.4705
NAME A-719-C
EXPNO 10
PROCNO 1
Date_ 20120823
Time_ 18.14
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 250
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 299.3 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.80 usec
SI 32768
SF 100.6127692 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
180 160 140 120 100 80 60 40 20 0 ppm


Pr
Pr
Si
3b
ppm


ppm


7.4820
7.4648
7.3413
7.3227
7.3042
7.2764
7.2509
7.1659
7.1481
7.1305
2.5363
2.5184
2.4983
2.4101
2.3913
2.3711
1.4848
1.4656
1.4457
1.4380
1.4269
1.4210
1.4017
1.3925
1.3746
1.3557
1.3367
0.9546
0.9441
0.9364
0.9270
0.9186
0.2845
-0.0001
Bu
Bu
Si
3c
NAME A-725-H
EXPNO 1
PROCNO 1
Date_ 20120824
Time 6.14
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 101
DW 60.800 usec
DE 6.50 usec
TE 298.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.50 usec
SI 65536
SF 400.1300136 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
10 9 8 7 6 5 4 3 2 1 0 ppm
0.907
2.165
0.913
1.961
1.918
5.010
5.925
6.000


151.2890
150.3425
141.8700
138.4705
131.2071
129.5524
125.5132
120.9138
77.3316
77.0137
76.6967
32.6954
31.0380
29.3912
26.7293
23.1075
14.0929
14.0464
0.0000
-3.4202
NAME A-725-C
EXPNO 10
PROCNO 1
Date_ 20120824
Time 6.48
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 580
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 299.4 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.80 usec
SI 32768
SF 100.6127683 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
180 160 140 120 100 80 60 40 20 0 ppm