

Cover Page for Supporting Information

Manuscript Title:

Palladium-catalyzed Synthesis of Benzosilolo[2,3-*b*]indoles via Cleavage of C(sp³)-Si Bond and Consequent Intramolecular C(sp²)-Si Coupling

Authors:

Yun Liang, Shaoguang Zhang, Zhenfeng Xi*

Affiliations:

Beijing National Laboratory for Molecular Science (BNLMS), Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, College of Chemistry, Peking University, Beijing 100871, China. Key Laboratory of Chemical Biology and Traditional Chinese Medicine Research, Ministry of Education, Hunan Normal University, Changsha Hunan 410081, China. State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai, 200032, China.

Contents:

1) General Information	S2
2) Synthesis of Starting Materials	S2–S10
3) Reaction Condition Optimization of the Pd-catalyzed Reaction of 4a	S10–S12
4) The Reaction of 3-(2-Chlorophenyl)- 2-(trimethylsilyl)-1 <i>H</i> -indole	S12
5) Typical Procedures	S12
6) Procedures and Characterization Data	S12–S18
7) X-ray Crystallographic Studies of 3a	S18–S20
8) GC Analyses of the Gas Composition of the Reactions	S20–S24
9) Scanned ¹ H NMR and ¹³ C NMR Spectra of All New Compounds	S25–S72

1) General Information

Unless otherwise noted, all starting materials were commercially available and were used without further purification. Solvents were purified by a Mbraun SPS-800 Solvent Purification System. *n*-BuLi and PhLi were obtained from Acros. All reactions were carried out under a dry and oxygen-free nitrogen atmosphere in slight positive pressure by using Schlenk techniques.

¹H and ¹³C NMR spectra were recorded on a JEOL JNM-AL300 spectrometer (FT, 300 MHz for ¹H; 75 MHz for ¹³C), or a Bruker ARX400 spectrometer (FT, 400 MHz for ¹H; 100 MHz for ¹³C) at room temperature, unless otherwise noted. High-resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS mass spectrometer using ESI (electrospray ionization). GC analyses were recorded on SHIMADZU GC-2010 spectrometer using FID.

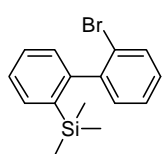
2) Synthesis of Starting Materials

Preparation of 4a-e:

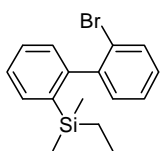
Compounds **4a-e** were prepared according the literature method.¹ To a solution of 4.72 g (20 mmol) of *o*-dibromobenzene in 50 mL of THF was added dropwise, under an atmosphere of nitrogen, 6.25 mL of a 1.6 M solution of *n*-BuLi (10 mmol) in *n*-hexane while the temperature was maintained -78 °C. After addition, the mixture was warmed to 0 °C and subsequently hydrolyzed with 10 mL of a 3 M HCl solution. The organic solvents were removed by rotary evaporation, and the residue was extracted with diethyl ether. The combined filtrates were concentrated under reduced pressure and the crude product was purified by using silicon gel column with petroleum ether as eluent to give the pure product of 2,2'-dibromobiphenyl 2.37 g (76%).

To a solution of 624 mg (2.0 mmol) of 2,2'-dibromobiphenyl in 10 mL of THF at -78 °C was added dropwise, under an atmosphere of argon, 1.3 mL of a 1.6 M solution of *n*-BuLi (2.1 mmol) in hexane. After addition, the mixture was stirred for 15 min and 325 mg (3 mmol) of chlorotrialkylsilane was added dropwise. The mixture was warmed to room temperature, a saturated solution of NH₄Cl in water added, and the mixture extracted with diethyl ether. The organic fractions were combined, washed (brine), dried

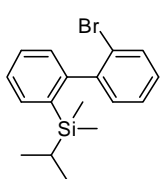
(Na₂SO₄), concentrated under reduced pressure and the crude product was purified by using SiO₂ column with petroleum ether as eluent to give the pure product of (2'-bromobiphenyl-2-yl)trialkylsilane.



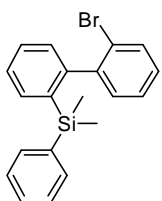
4a:¹ Colorless liquid, isolated yield 85% (518 mg); ¹H NMR (300 MHz, CDCl₃) δ: 7.65-7.61 (m, 2H), 7.40-7.37 (m, 2H), 7.33 (d, *J* = 6.6 Hz, 1H), 7.30-7.13 (m, 3H), -0.01 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ: 0.03, 124.32, 126.46, 126.84, 128.28, 128.92, 129.62, 131.56, 132.29, 134.51, 138.35, 144.21, 147.38.



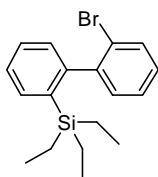
4b: Colorless liquid, isolated yield 87% (555 mg); ¹H NMR (400 MHz, CDCl₃) δ: 7.64-7.60 (m, 2H), 7.40-7.37 (m, 2H), 7.32 (t, *J* = 6.8 Hz, 1H), 7.25-7.20 (m, 2H), 7.14 (d, *J* = 8.8 Hz, 1H), 0.88-0.83 (m, 3H), 0.54-0.50 (m, 2H), -0.03 (s, 3H), -0.11 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ: -2.46, 7.54, 8.13, 124.34, 126.44, 126.74, 128.21, 128.88, 129.73, 131.52, 132.33, 134.83, 137.46, 144.38, 147.57.



4c: Colorless liquid, isolated yield 88% (586 mg); ¹H NMR (400 MHz, CDCl₃) δ: 7.69 (d, *J* = 8.8 Hz, 2H), 7.46-7.43 (m, 2H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.31-7.24 (m, 2H), 7.22 (d, *J* = 9.2 Hz, 1H), 0.96-0.93 (m, 7H), 0.07 (s, 3H), -0.13 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ: -4.49, -4.46, 13.99, 17.69, 17.73, 124.38, 126.40, 126.62, 128.16, 128.83, 129.77, 131.47, 132.30, 135.09, 136.91, 144.47, 147.60; HRMS (ESI, *m/z*) calcd for [C₁₇H₂₁BrSi]⁺Na⁺: 355.0488; found 355.0495.



4d: Colorless liquid, isolated yield 64% (470 mg); ¹H NMR (400 MHz, CDCl₃) δ: 7.66 (d, *J* = 8.8 Hz, 1H), 7.59 (d, *J* = 9.2 Hz, 1H), 7.45-7.30 (m, 7H), 7.22-7.14 (m, 3H), 6.99 (d, *J* = 9.2 Hz, 1H), 0.35 (s, 3H), 0.20 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ: -2.19, -0.99, 124.28, 126.39, 126.80, 127.56, 128.64, 128.72, 128.84, 129.94, 131.67, 132.24, 133.99, 135.61, 136.46, 139.21, 143.85, 147.80; HRMS (ESI, *m/z*) calcd for [C₂₀H₁₉BrSi]⁺Na⁺: 389.0332; found 389.0336.



4e: Colorless liquid, isolated yield 82% (569 mg); ¹H NMR (400 MHz,

CDCl₃) δ : 7.64-7.58 (m, 2H), 7.39-7.36 (m, 2H), 7.30 (t, J = 7.2 Hz, 1H), 7.23-7.19 (m, 2H), 7.14 (d, J = 8.8 Hz, 1H), 0.82 (t, J = 7.6 Hz, 9H), 0.54-0.39 (m, 6H); ¹³C NMR (75 MHz, CDCl₃) δ : 3.67, 7.47, 124.21, 126.40, 126.53, 128.06, 128.85, 130.01, 131.40, 132.35, 135.50, 135.56, 144.52, 147.95; HRMS (ESI, m/z) calcd for [C₁₄H₁₄Si]⁺: 211.0938; found 211.0936.

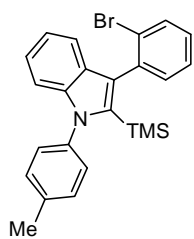
Preparation of 2a-t:

((2-Bromophenyl)ethynyl)trimethylsilane was prepared according the literature method.² Under the protection of nitrogen, 1-bromo-2-iodobenzene (5.66g, 20 mmol), ethynyltrimethylsilane (2.156 g, 22 mmol), PdCl₂(PPh₃)₂ (70 mg, 0.5 mol%), CuI (38 mg, 1 mol%) was added in 15 mL THF and 15 mL NEt₃. The reaction mixture was stirred at room temperature for the desired time until the complete consumption of the starting material as monitored by TLC. After the reaction was finished, diethyl ether was poured into the mixture. The mixture was then washed with brine, extracted with diethyl ether, dried by anhydrous Na₂SO₄, and evaporated under vacuum. The residue was purified by using SiO₂ column with petroleum ether as an eluent to afford ((2-bromophenyl)ethynyl)trimethylsilane (5 g, >99%).

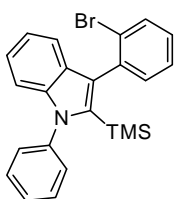
(*Z*)-(2-(2-Bromophenyl)-1-iodo-2-(2-iodophenyl)vinyl)trimethylsilane was prepared according literature.³ To a toluene (100 mL) solution of ZrCp₂Cl₂ (3212 mg, 11 mmol) was added an ether solution of PhLi (11 mL, 2 M, 22 mmol) at 0 °C. After stirring for 2 h, ((2-bromophenyl)ethynyl)trimethylsilane (2530 mg, 10 mmol) was added to the mixture at 0 °C. The mixture was warmed to 100 °C and stirred for 12 h. Then, iodine (10160 mg, 40 mmol) and CuCl (2079 mg, 21 mmol) was added at 0 °C, and the mixture stirred 12 h at room temperature. A saturated aqueous solution of Na₂S₂O₃ was added, and the mixture was extracted with hexane. The combined extract was washed with brine, dried over Na₂SO₄, filtered, and evaporated. The residue was purified by using SiO₂ column with petroleum ether as an eluent to afford product (*Z*)-(2-(2-bromophenyl)-1-iodo-2-(2-iodophenyl)vinyl)trimethylsilane (5432 mg, 93%).

Compounds **2a-t** were prepared by a modified procedure according the literature.⁴ Under the protection of nitrogen, Pd(OAc)₂ (5 mol%) and Xantphos (10 mol%) was added in 5 mL toluene. After this reaction mixture was stirred at room temperature for 15

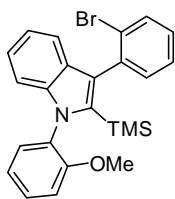
min, (Z)-(2-(2-bromophenyl)-1-iodo-2-(2-iodophenyl)vinyl)trimethylsilane (1 mmol), amine (1.2 mmol), Cs₂CO₃ (2 mmol) were added and this reaction mixture was stirred at 120 °C for 10 h. The reaction mixture was quenched with water and extracted with Et₂O. The extraction was washed with brine and dried over Na₂SO₄. The solvent was then evaporated in vacuo and the residue was purified by using SiO₂ column with petroleum ether and ethyl acetate as eluent (100:1) to afford the final products.



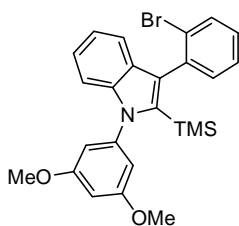
2a: Colorless solid, isolated yield 86% (373 mg); mp: 125.2-126.0 °C; ¹H NMR (300 MHz, CDCl₃) δ: 7.69 (d, *J* = 7.8 Hz, 1H), 7.43 (d, *J* = 7.5 Hz, 1H), 7.37-7.20 (m, 7H), 7.15-7.05 (m, 3H), 2.46 (s, 3H), -0.19 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ: 0.29, 21.27, 110.29, 119.65, 119.71, 122.61, 126.24, 126.73, 127.97, 128.02, 128.77, 129.71 (2C), 132.42, 133.50, 137.65, 138.05, 138.08, 138.10, 140.23; HRMS (ESI, *m/z*) calcd for [C₂₄H₂₄BrNSi]⁺: 434.0934; found 434.0943.



2b: Colorless solid, isolated yield 82% (349 mg); mp: 124.1-124.8 °C; ¹H NMR (400 MHz, CDCl₃) δ: 7.90 (d, *J* = 7.6 Hz, 1H), 7.72-7.63 (m, 6H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.49-7.36 (m, 2H), 7.34-7.27 (m, 3H), 0.01 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ: 0.25, 110.24, 119.73, 119.84, 122.75, 126.24, 126.76, 128.07, 128.20, 128.30, 128.35, 128.82, 129.07, 129.15, 132.47, 133.51, 138.03, 140.21, 140.37; HRMS (ESI, *m/z*) calcd for [C₂₃H₂₂BrNSi]⁺: 420.0778; found 420.0772.

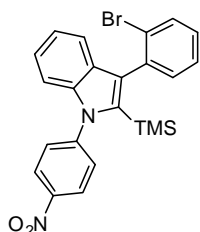


2c: Pale yellow oil, isolated yield 81% (365 mg); ¹H NMR (300 MHz, CDCl₃) δ: 7.69 (d, *J* = 8.1 Hz, 1H), 7.47-7.33 (m, 4H), 7.28-7.21 (m, 2H), 7.14-7.04 (m, 4H), 6.93 (t, *J* = 3.9 Hz, 1H), 3.71 (s, 3H), -0.21 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ: -0.13, 55.28, 110.17, 111.58, 119.41, 119.54, 120.38, 122.41, 126.41, 126.61, 126.66, 128.13, 128.60, 128.68, 129.90, 131.53, 132.30, 132.38, 133.65, 138.15, 140.13, 156.54; HRMS (ESI, *m/z*) calcd for [C₂₄H₂₄BrNOSi]⁺: 450.0883; found 450.0882.

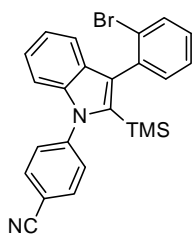


2d: Pale yellow solid, isolated yield 92% (442 mg); mp: 116.2-117.0 °C; ¹H NMR (300 MHz, CDCl₃) δ: 7.69 (d, *J* = 8.1 Hz, 1H), 7.45-7.33 (m, 2H), 7.29-7.14 (m, 4H), 7.08 (t, *J* = 7.05 Hz,

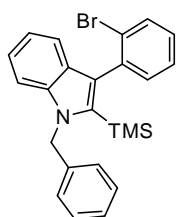
1H), 6.71 (s, 1H), 6.58 (s, 2H), 3.82 (s, 6H), -0.12 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3) δ : 0.30, 55.52, 100.46, 106.98, 107.17, 110.38, 119.75, 119.88, 122.79, 126.11, 126.76, 127.94, 128.37, 128.84, 132.46, 133.47, 137.76, 137.94, 139.75, 141.94, 160.94; HRMS (ESI, m/z) calcd for $[\text{C}_{25}\text{H}_{26}\text{BrNO}_2\text{Si}]\text{H}^+$: 480.0989; found 480.0990.



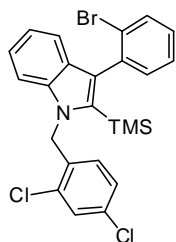
2e: Yellow solid, isolated yield 80% (371 mg); mp: 130.4-131.0 °C; ^1H NMR (300 MHz, CDCl_3) δ : 8.42 (d, J = 8.7 Hz, 2H), 8.10-8.07 (m, 1H), 7.85 (d, J = 7.8 Hz, 1H), 7.71 (d, J = 9.3 Hz, 2H), 7.61-7.58 (m, 1H), 7.52-7.43 (m, 2H), 7.32-7.29 (m, 2H), 7.24-7.17 (m, 1H), 0.42 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3) δ : 0.44, 109.68, 120.27, 120.75, 123.61, 124.75, 125.84, 126.94, 128.47, 129.19 (2C), 130.56, 132.63, 133.27, 137.21, 137.65, 139.55, 146.44, 146.71; HRMS (ESI, m/z) calcd for $[\text{C}_{23}\text{H}_{21}\text{BrN}_2\text{O}_2\text{Si}]\text{Na}^+$: 487.0448; found 487.0443.



2f: Pale yellow solid, isolated yield 84% (366 mg); mp: 62.5-63.2 °C; ^1H NMR (300 MHz, CDCl_3) δ : 7.86 (d, J = 7.5 Hz, 2H), 7.72 (d, J = 7.8 Hz, 1H), 7.63-7.60 (m, 2H), 7.43-7.36 (m, 2H), 7.31-7.29 (m, 2H), 7.26-7.10 (m, 3H), -0.17 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3) δ : 0.38, 100.46, 109.68, 111.65, 118.20, 120.19, 120.61, 123.48, 125.88, 126.91, 128.36, 129.15, 129.43, 130.18, 132.61, 133.28, 137.28, 137.63, 139.57, 144.69; HRMS (ESI, m/z) calcd for $[\text{C}_{24}\text{H}_{21}\text{BrN}_2\text{Si}]\text{H}^+$: 445.0730; found 445.0721.

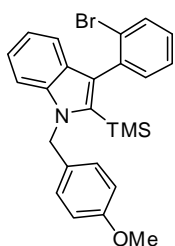


2g: Colorless solid, isolated yield 79% (343 mg); mp: 83.8-83.6 °C; ^1H NMR (400 MHz, CDCl_3) δ : 7.66 (d, J = 7.8 Hz, 1H), 7.40-7.29 (m, 2H), 7.26-7.17 (m, 5H), 7.10 (d, J = 3.6 Hz, 2H), 7.03-7.01 (m, 1H), 6.92 (d, J = 7.5 Hz, 2H), 5.55 (s, 2H), 0.01 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3) δ : 0.23, 49.68, 109.86, 119.56, 119.66, 122.62, 125.67, 126.68, 127.08, 128.63, 128.72, 128.78, 128.90, 132.25, 133.37, 137.05, 138.15, 138.25, 138.27, 138.75; HRMS (ESI, m/z) calcd for $[\text{C}_{24}\text{H}_{24}\text{BrNSi}]\text{H}^+$: 434.0934; found 434.0943.

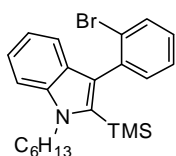


2h: Colorless solid, isolated yield 71% (357 mg); mp: 137.8-138.2 °C; ^1H NMR (400 MHz, CDCl_3) δ : 7.69 (d, J = 8.0 Hz, 1H), 7.44-7.34 (m, 3H), 7.27-7.16 (m, 3H), 7.12-7.06 (m, 2H), 7.02 (d, J = 8.4 Hz, 1H),

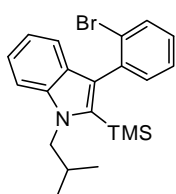
6.18 (d, $J = 8.4$ Hz, 1H), 5.60-5.48 (m, 2H), -0.01 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3) δ : 0.06, 47.21, 109.27, 119.87, 119.95, 123.02, 126.62, 126.77, 127.54, 127.70, 128.12, 128.87, 128.95, 128.99, 131.97, 132.27, 133.18, 133.45, 134.49, 136.80, 137.72, 138.57; HRMS (ESI, m/z) calcd for $[\text{C}_{24}\text{H}_{22}\text{BrCl}_2\text{NSi}]^{\text{H}^+}$: 502.0155; found 502.0150.



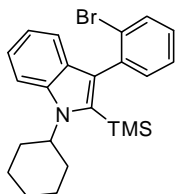
2i: Colorless solid, isolated yield 85% (394 mg); mp: 106.2-107.2 °C; ^1H NMR (400 MHz, CDCl_3) δ : 7.67 (d, $J = 8.0$ Hz, 1H), 7.39 (d, $J = 7.2$ Hz, 1H), 7.33 (t, $J = 6.8$ Hz, 1H), 7.23-7.17 (m, 2H), 7.12-7.09 (m, 2H), 7.03 (t, $J = 5.2$ Hz, 1H), 6.86 (d, $J = 8.8$ Hz, 2H), 6.79 (d, $J = 8.8$ Hz, 2H), 5.51 (s, 2H), 0.03 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3) δ : 0.25, 49.22, 55.18, 109.97, 114.03, 119.50, 119.63, 122.56, 126.69, 126.75, 126.80, 126.98, 128.77, 128.93, 130.24, 132.25, 133.39, 137.07, 138.21, 138.69, 158.64; HRMS (ESI, m/z) calcd for $[\text{C}_{25}\text{H}_{26}\text{BrNOSi}]^{\text{H}^+}$: 464.1040; found 464.1045.



2j: Colorless oil, isolated yield 78% (332 mg); ^1H NMR (400 MHz, CDCl_3) δ : 7.65 (d, $J = 8.4$ Hz, 1H), 7.36-7.30 (m, 3H), 7.24-7.19 (m, 2H), 7.16 (d, $J = 7.6$ Hz, 1H), 7.03 (t, $J = 7.4$ Hz, 1H), 4.24 (t, $J = 8.2$ Hz, 2H), 1.90-1.83 (m, 2H), 1.44-1.34 (m, 6H), 0.92 (t, $J = 6.8$ Hz, 3H), 0.13 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3) δ : 0.46, 14.03, 22.60, 26.78, 30.58, 31.54, 46.82, 109.44, 119.10, 119.73, 122.18, 126.37, 126.58, 126.64, 128.63, 128.68, 132.15, 133.43, 136.15, 138.03, 138.30; HRMS (ESI, m/z) calcd for $[\text{C}_{23}\text{H}_{30}\text{BrNSi}]^{\text{H}^+}$: 428.1404; found 428.1403.

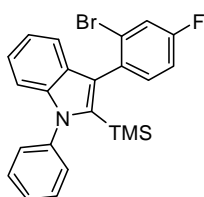


2k: Colorless solid, isolated yield 83% (332 mg); mp: 98.0-98.6 °C; ^1H NMR (300 MHz, CDCl_3) δ : 7.66 (d, $J = 8.1$ Hz, 1H), 7.39-7.28 (m, 3H), 7.22-7.17 (m, 3H), 7.03 (t, $J = 7.5$ Hz, 1H), 4.08 (t, $J = 8.4$ Hz, 2H), 2.39-2.30 (m, 1H), 0.94 (d, $J = 6.6$ Hz, 3H), 0.88 (d, $J = 6.6$ Hz, 3H), 0.13 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3) δ : 1.07, 20.05, 20.29, 29.74, 53.39, 110.27, 119.02, 119.64, 122.00, 126.59, 126.61, 126.97, 128.49, 128.66, 132.25, 133.48, 136.75, 138.24, 138.60; HRMS (ESI, m/z) calcd for $[\text{C}_{21}\text{H}_{26}\text{BrNSi}]^{\text{H}^+}$: 400.1091; found 400.1082.

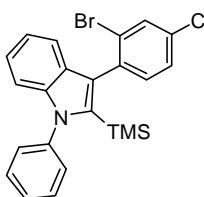


2l: Colorless solid, isolated yield 87% (373 mg); mp: 113.8-115.2 °C; ^1H NMR (400 MHz, CDCl_3) δ : 7.63 (t, $J = 9.0$ Hz, 2H), 7.34-7.28 (m,

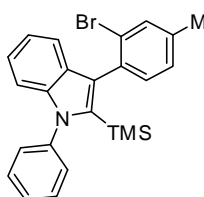
2H), 7.23-7.12 (m, 3H), 6.98 (t, $J = 7.4$ Hz, 1H), 4.33-4.27 (m, 1H), 2.50-2.42 (m, 2H), 2.02-1.81 (m, 5H), 1.49-1.32 (m, 3H), 0.12 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3) δ : 0.13, 25.53, 26.50, 31.38, 59.79, 112.38, 118.70, 119.96, 121.55, 125.60, 126.59, 126.83, 128.56, 130.12, 132.12, 133.39, 136.36, 137.10, 138.43; HRMS (ESI, m/z) calcd for $[\text{C}_{23}\text{H}_{28}\text{BrNSi}]\text{H}^+$: 426.1247; found 426.1247.



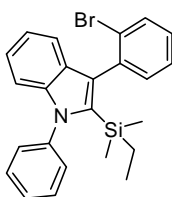
2m: Colorless solid, isolated yield 86% (377 mg); mp: 122.2-123.9 °C; ^1H NMR (300 MHz, CDCl_3) δ : 7.71-7.57 (m, 7H), 7.45 (d, $J = 7.5$ Hz, 1H), 7.36-7.27 (m, 4H), 0.19 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3) δ : 0.26, 110.30, 114.01 (d, $J = 21.0$ Hz), 119.49, 119.79, 119.92, 122.82, 126.26 (d, $J = 9.3$ Hz), 127.08, 127.99, 128.27, 128.98 (d, $J = 8.0$ Hz), 129.18, 133.99, 134.07 (d, $J = 3.75$ Hz), 138.32, 140.15 (d, $J = 5.55$ Hz), 160.08, 163.40; HRMS (ESI, m/z) calcd for $[\text{C}_{23}\text{H}_{21}\text{BrFNSi}]\text{H}^+$: 438.0683; found 438.0682.



2n: Colorless solid, isolated yield 83% (377 mg); mp: 116.8-118.2 °C; ^1H NMR (300 MHz, CDCl_3) δ : 7.73 (s, 1H), 7.53-7.45 (m, 4H), 7.24 (d, $J = 8.4$ Hz, 2H), 7.20-7.16 (m, 3H), 7.15-7.07 (m, 2H), -0.18 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3) δ : 0.32, 110.35, 119.49, 119.99, 122.87, 126.55, 126.99, 127.09, 127.83, 128.32, 128.96, 129.02, 129.20, 132.10, 133.72, 134.03, 136.72, 138.28, 140.17; HRMS (ESI, m/z) calcd for $[\text{C}_{23}\text{H}_{21}\text{BrClNSi}]\text{H}^+$: 454.0388; found 454.0382.

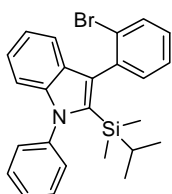


2o: Colorless solid, isolated yield 81% (352 mg); mp: 154.1-155.2 °C; ^1H NMR (300 MHz, CDCl_3) δ : 7.53-7.45 (m, 6H), 7.32-7.27 (m, 2H), 7.16-7.07 (m, 4H), 2.40 (s, 3H), -0.19 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3) δ : 0.30, 20.89, 110.19, 119.76, 122.68, 125.82, 127.64, 128.11, 128.14, 128.25, 128.94, 129.13, 132.89, 132.92, 133.14, 134.77, 138.04, 138.89, 140.09, 140.39; HRMS (ESI, m/z) calcd for $[\text{C}_{24}\text{H}_{24}\text{BrNSi}]\text{H}^+$: 434.0934; found 434.0932.

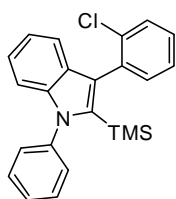


2p: Pale yellow oil, isolated yield 81% (362 mg); ^1H NMR (400 MHz, CDCl_3) δ : 7.67 (d, $J = 8.0$ Hz, 1H), 7.42 (d, $J = 7.6$ Hz, 1H), 7.36-7.25 (m, 6H), 7.19 (t, $J = 7.6$ Hz, 1H), 7.12 (t, $J = 7.0$ Hz, 1H), 7.08-7.04 (m, 2H), 2.43 (s, 3H), 0.73 (t, $J = 7.8$ Hz, 3H), 0.29-0.24 (m, 2H), -0.21 (s,

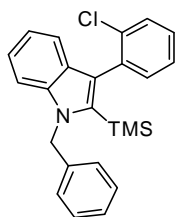
3H), -0.23 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ : -2.13, -2.11, 7.46, 8.00, 21.26, 110.28, 119.65, 119.68, 122.63, 126.26, 126.66, 128.03, 128.51, 128.72, 128.77, 128.85, 129.66, 132.38, 133.55, 137.16, 137.60, 138.07, 140.39; HRMS (ESI, m/z) calcd for $[\text{C}_{25}\text{H}_{27}\text{BrNSi}]^+\text{H}^+$: 448.1085; found 448.1091.



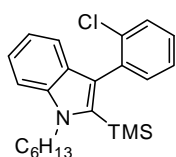
2q: Pale yellow oil, isolated yield 79% (365 mg); ^1H NMR (400 MHz, CDCl_3) δ : 7.68 (d, J = 6.8 Hz, 1H), 7.42 (d, J = 9.2 Hz, 1H), 7.35-7.28 (m, 5H), 7.23 (d, J = 8.0 Hz, 2H), 7.13 (t, J = 7.6 Hz, 1H), 7.07 (d, J = 6.8 Hz, 1H), 7.02 (t, J = 7.6 Hz, 1H), 2.45 (s, 3H), 0.77 (d, J = 7.2 Hz, 3H), 0.74 (d, J = 7.2 Hz, 3H), 0.50-0.43 (m, 1H), -0.25 (s, 3H), -0.27 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ : -4.34, -4.04, 13.19, 17.45, 17.56, 21.30, 110.31, 119.62, 119.63, 122.61, 126.38, 126.61, 128.11, 128.78, 128.87, 129.05, 129.63, 132.35, 133.62, 136.81, 137.54, 138.09, 138.19, 140.56; HRMS (ESI, m/z) calcd for $[\text{C}_{26}\text{H}_{29}\text{BrNSi}]^+\text{H}^+$: 462.1242; found 462.1247.



2r: Colorless solid, isolated yield 83% (312 mg); mp: 134.8-135.7 °C; ^1H NMR (400 MHz, CDCl_3) δ : 7.75-7.72 (m, 3H), 7.71-7.67 (m, 4H), 7.55-7.51 (m, 3H), 7.38-7.36 (m, 1H), 7.31 (t, J = 5.8 Hz, 2H), 0.07 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3) δ : 0.23, 110.26, 119.64, 119.91, 122.77, 125.59, 126.16, 126.42, 128.15, 128.64, 128.96, 129.15, 129.31, 133.57, 135.40, 135.91, 138.24, 140.20, 140.40; HRMS (ESI, m/z) calcd for $[\text{C}_{23}\text{H}_{22}\text{ClNSi}]^+\text{H}^+$: 376.1283; found 376.1277.



2s: Colorless solid, isolated yield 84% (328 mg); mp: 67.2-68.3 °C; ^1H NMR (400 MHz, CDCl_3) δ : 7.47 (d, J = 9.6 Hz, 1H), 7.39 (d, J = 9.6 Hz, 1H), 7.28-7.16 (m, 6H), 7.11-7.10 (m, 2H), 7.03-7.00 (m, 1H), 6.93 (d, J = 7.2 Hz, 2H), 5.56 (s, 2H), 0.02 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3) δ : 0.38, 49.70, 109.89, 119.59, 122.62, 124.86, 125.01, 125.66, 126.08, 127.09, 128.63, 128.72, 129.01, 129.13, 133.51, 135.73, 136.04, 137.32, 138.27, 138.83; HRMS (ESI, m/z) calcd for $[\text{C}_{24}\text{H}_{24}\text{ClNSi}]^+\text{H}^+$: 390.1439; found 390.1424.

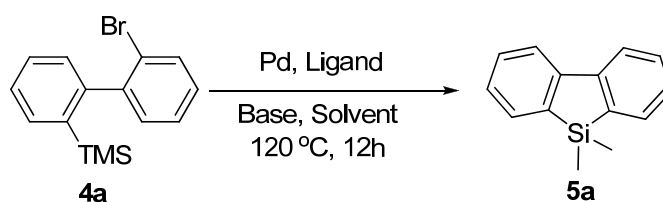


2t: Colorless oil, isolated yield 76% (292 mg); ^1H NMR (400 MHz, CDCl_3) δ : 7.46 (d, J = 9.2 Hz, 1H), 7.37-7.27 (m, 4H), 7.24-7.17 (m, 2H), 7.03 (t, J = 7.4 Hz, 1H), 4.24 (t, J = 8.4 Hz, 2H), 1.91-1.85 (m, 2H),

1.44-1.35 (m, 6H), 0.92 (t, $J = 6.8$ Hz, 3H), 0.13 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3) δ : 0.46, 14.00, 22.60, 26.80, 30.58, 31.55, 46.88, 109.47, 119.12, 119.67, 122.19, 124.31, 125.99, 128.44, 128.82, 129.06, 133.59, 135.69, 136.22, 136.46, 138.15; HRMS (ESI, m/z) calcd for $[\text{C}_{23}\text{H}_{30}\text{ClNSi}]\text{H}^+$: 384.1909; found 384.1903.

3) Reaction Condition Optimization of the Pd-catalyzed Reaction of **4a**

Table 1. Reaction Condition Optimization of the Pd-Catalyzed Reaction of **4a**^a



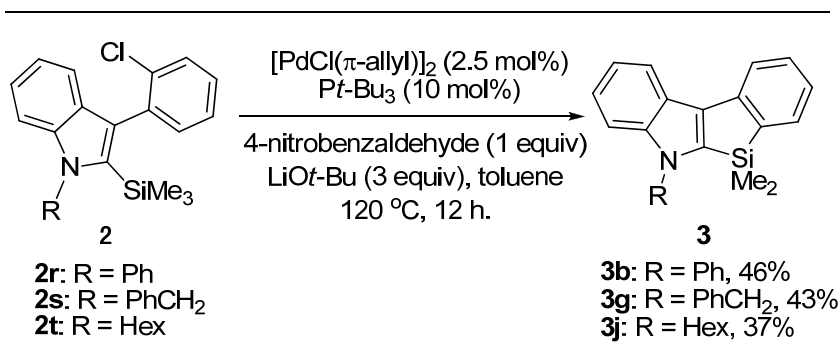
Entry	Pd (5%)	Ligand	Base	Solvent	Yield ^b
1	$\text{Pd}(\text{OAc})_2$	$Pt\text{-Bu}_3$	$\text{LiO}t\text{-Bu}$	Dioxane	19%
2	PdBr_2	$Pt\text{-Bu}_3$	$\text{LiO}t\text{-Bu}$	Dioxane	45%
3	PdCl_2	$Pt\text{-Bu}_3$	$\text{LiO}t\text{-Bu}$	Dioxane	24%
4	$\text{Pd}_2(\text{dba})_3$	$Pt\text{-Bu}_3$	$\text{LiO}t\text{-Bu}$	Dioxane	26%
5	$\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$	$Pt\text{-Bu}_3$	$\text{LiO}t\text{-Bu}$	Dioxane	43%
6	$[\text{PdCl}(\pi\text{-allyl})]_2$	$Pt\text{-Bu}_3$	LiO^tBu	Dioxane	46% (44%)
7	$[\text{PdCl}(\pi\text{-allyl})]_2$	no	$\text{LiO}t\text{-Bu}$	Dioxane	3%
8	$[\text{PdCl}(\pi\text{-allyl})]_2$	PCy_3	$\text{LiO}t\text{-Bu}$	Dioxane	14%
9	$[\text{PdCl}(\pi\text{-allyl})]_2$	Xantphos	LiO^tBu	Dioxane	0
10	$[\text{PdCl}(\pi\text{-allyl})]_2$	X-phos	$\text{LiO}t\text{-Bu}$	Dioxane	21%
11	$[\text{PdCl}(\pi\text{-allyl})]_2$	DPPF	$\text{LiO}t\text{-Bu}$	Dioxane	10%
12	$[\text{PdCl}(\pi\text{-allyl})]_2$	Davphos	LiO^tBu	Dioxane	44%

13	[PdCl(π -allyl)] ₂	PPh ₃	LiOt-Bu	Dioxane	23%
14	[PdCl(π -allyl)] ₂	Pt-Bu ₃	LiOt-Bu	Toluene	69% (69%)
15	[PdCl(π -allyl)] ₂	Pt-Bu ₃	LiOt-Bu	THF	23%
16	[PdCl(π -allyl)] ₂	Pt-Bu ₃	LiOt-Bu	DME	19%
17	[PdCl(π -allyl)] ₂	Pt-Bu ₃	Cs ₂ CO ₃	Dioxane	4%
18	[PdCl(π -allyl)] ₂	Pt-Bu ₃	CsF	Dioxane	0
19	[PdCl(π -allyl)] ₂	Pt-Bu ₃	K ₂ CO ₃	Dioxane	10%
20	[PdCl(π -allyl)] ₂	Pt-Bu ₃	NaOAc	Dioxane	9%
21 ^c	[PdCl(π -allyl)] ₂	Pt-Bu ₃	LiOt-Bu	Toluene	64%
22 ^d	[PdCl(π -allyl)] ₂	Pt-Bu ₃	LiOt-Bu	Toluene	77%
23 ^e	[PdCl(π -allyl)] ₂	Pt-Bu ₃	LiOt-Bu	Toluene	78% (73%)
24 ^f	[PdCl(π -allyl)] ₂	Pt-Bu ₃	LiOt-Bu	Toluene	79% (72%)
25 ^g	[PdCl(π -allyl)] ₂	Pt-Bu ₃	LiOt-Bu	Toluene	93% (82%)
27 ^h	[PdCl(π -allyl)] ₂	Pt-Bu ₃	LiOt-Bu	Toluene	83%

^a Conditions: **4a** (0.3 mmol), Pd catalyst (Pd 5 mol %), ligand (10 mol%), base (0.9 mmol), solvent (2 mL), 120 °C, 12 h. ^b GC yield (*n*-C₁₂H₂₆ as internal standard), isolated yield in parenthesis. ^c Added H₂O (1 equiv). ^d Added 4-methoxybenzaldehyde (1 equiv). ^e Added benzaldehyde (1 equiv). ^f Added biphenyl-4-carbaldehyde (1 equiv). ^g Added 4-nitrobenzaldehyde (1 equiv), tert-butyl 4-nitrobenzoate was isolated in 55% yield. ^h Added 4-nitrobenzaldehyde (0.5 equiv).

4) The Reaction of 3-(2-Chlorophenyl)- 2-(trimethylsilyl)-1*H*-indole

STable 2. The coupling reaction of 3-(2-chlorophenyl)- 2-(trimethylsilyl)-1*H*-indole ^{a, b}

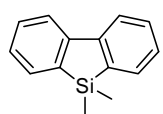


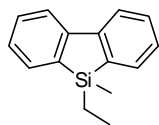
^a Conditions: 3-(2-bromophenyl)-2-(trimethylsilyl)-1*H*-indole (0.3 mmol), [PdCl(π-allyl)]₂ (2.5 mol%), Pt-Bu₃ (10 mol%), LiOt-Bu (0.9 mmol), 4-nitrobenzaldehyde (0.3 mmol), Toluene (2 mL), 120 °C, 12 h. ^b Isolated yield.

5) Typical Procedure

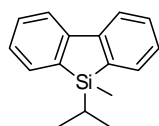
A typical procedure for the preparation of 3 or 5: Under the protection of nitrogen, [PdCl(π-allyl)]₂ (2.5 mol%) and Pt-Bu₃ (10 mol%) was added in 2 mL toluene. After this reaction mixture was stirred at room temperature for 15 min, **2** or **4** (0.3 mmol), LiOt-Bu (0.9 mmol), 4-nitrobenzaldehyde (0.3 mmol) were added and this reaction mixture was stirred at 120 °C for 10 h. The reaction mixture was quenched with water and extracted with Et₂O. The extraction was washed with brine and dried over MgSO₄. The solvent was then evaporated in vacuo and the residue was purified by using SiO₂ column with petroleum ether and ethyl acetate as eluent (100:1) to afford the final products.

6) Procedures and Characterization Data

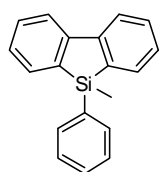
 **5a:**¹ Colorless solid, isolated yield 82% (52 mg); mp: 42.0-42.6 °C; ¹H NMR (300 MHz, CDCl₃) δ: 7.82 (d, *J* = 7.8 Hz, 2H), 7.63 (d, *J* = 6.9 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.27 (t, *J* = 7.35 Hz, 2H), 0.42 (s, 6H); ¹³C NMR (75 MHz, CDCl₃) δ: -3.32, 120.73, 127.26, 130.09, 132.64, 138.82, 147.70; HRMS (ESI, *m/z*) calcd for [C₁₄H₁₄Si]⁺: 211.0938; found 211.0936.



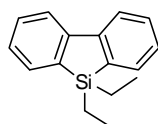
5b: Colorless solid, isolated yield 66% (44 mg); mp: 43.2-44.0 °C; ^1H NMR (300 MHz, CDCl_3) δ : 7.82 (d, J = 7.8 Hz, 2H), 7.62 (d, J = 6.9 Hz, 2H), 7.43 (t, J = 7.5 Hz, 2H), 7.27 (t, J = 7.2 Hz, 2H), 1.02 (t, J = 7.2 Hz, 3H), 0.94-0.87 (m, 2H), 0.42 (s, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ : -5.59, 5.68, 7.50, 120.77, 127.21, 130.09, 132.94, 138.09, 148.07; HRMS (ESI, m/z) calcd for $[\text{C}_{15}\text{H}_{16}\text{Si}]^+\text{H}^+$: 225.1094; found 225.1092.



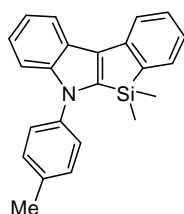
5c:⁵ Colorless solid, isolated yield 73% (52 mg); mp: 75.5-76.2 °C; ^1H NMR (400 MHz, CDCl_3) δ : 7.81 (d, J = 7.6 Hz, 2H), 7.61 (d, J = 7.2 Hz, 2H), 7.41 (t, J = 8.2 Hz, 2H), 7.25 (t, J = 7.8 Hz, 2H), 1.19-1.12 (m, 1H), 1.06 (d, J = 6.4 Hz, 6H), 0.39 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ : -7.46, 12.93, 17.59, 120.78, 127.18, 130.08, 133.14, 137.63, 148.30; HRMS (ESI, m/z) calcd for $[\text{C}_{16}\text{H}_{18}\text{Si}]^+\text{H}^+$: 239.1251; found 239.1247.



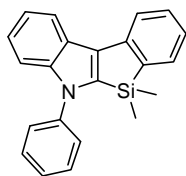
5d:⁶ Colorless solid, isolated yield 70% (57 mg); mp: 74.5-75.8 °C; ^1H NMR (300 MHz, CDCl_3) δ : 7.84 (d, J = 7.8 Hz, 2H), 7.64 (d, J = 6.9 Hz, 2H), 7.54 (d, J = 6.3 Hz, 2H), 7.43 (t, J = 7.5 Hz, 2H), 7.34-7.23 (m, 5H), 0.72 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ : -5.09, 120.93, 127.55, 128.01, 129.82, 130.46, 133.33, 134.41, 134.50, 137.27, 148.31; HRMS (ESI, m/z) calcd for $[\text{C}_{19}\text{H}_{16}\text{Si}]^+\text{H}^+$: 273.1094; found 273.1091.



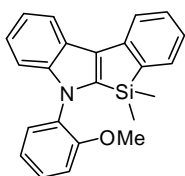
5e:⁷ Colorless solid, isolated yield 30% (21 mg); mp: 46.2-46.8 °C; ^1H NMR (300 MHz, CDCl_3) δ : 7.83 (d, J = 7.8 Hz, 2H), 7.62 (d, J = 6.9 Hz, 2H), 7.43 (t, J = 6.45 Hz, 2H), 7.26 (t, J = 7.2 Hz, 2H), 1.02-0.93 (m, 10H); ^{13}C NMR (75 MHz, CDCl_3) δ : 3.72, 7.54, 120.76, 127.10, 130.04, 133.18, 137.21, 148.42; HRMS (ESI, m/z) calcd for $[\text{C}_{16}\text{H}_{18}\text{Si}]^+\text{H}^+$: 239.1251; found 239.1249.



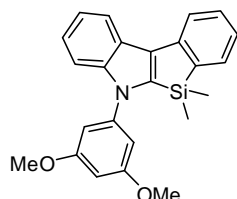
3a: Colorless solid, isolated yield 97% (99 mg); mp: 159.8-160.5 °C; ^1H NMR (300 MHz, CDCl_3) δ : 8.05 (d, J = 4.5 Hz, 1H), 7.82 (d, J = 7.5 Hz, 1H), 7.46-7.37 (m, 5H), 7.33-7.12 (m, 5H), 2.44 (s, 3H), 0.36 (s, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ : -3.18, 21.11, 111.36, 120.09, 120.49, 120.64, 122.77, 124.57, 124.91, 130.07, 130.22, 132.46, 133.26, 136.68, 138.11, 138.33, 142.49, 144.99, 145.18; HRMS (ESI, m/z) calcd for $[\text{C}_{23}\text{H}_{21}\text{NSi}]^+\text{H}^+$: 340.1516; found 340.1513.



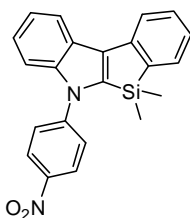
3b: Colorless solid, isolated yield 95% (93 mg); mp: 134.5-135.7 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.05 (d, J = 4.8 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.52-7.47 (m, 6H), 7.44-7.36 (m, 2H), 7.25-7.21 (m, 2H), 7.13 (t, J = 6.8 Hz, 1H), 0.36 (s, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ : -3.16, 111.33, 120.14, 120.53, 120.78, 122.90, 124.66, 124.82, 124.95, 126.81, 129.51, 130.23, 132.47, 133.57, 138.26, 140.65, 142.28, 144.88, 145.04; HRMS (ESI, m/z) calcd for $[\text{C}_{22}\text{H}_{19}\text{NSi}]\text{H}^+$: 326.1360; found 326.1357.



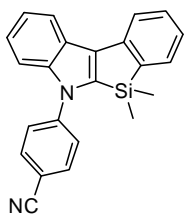
3c: Colorless solid, isolated yield 95% (101 mg); mp: 138.2-139.9 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.01 (d, J = 7.2 Hz, 1H), 7.79 (d, J = 7.6 Hz, 1H), 7.43-7.33 (m, 4H), 7.21-7.13 (m, 2H), 7.10-7.7.04 (m, 4H), 3.67 (s, 3H), 0.30 (s, 3H), 0.23 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ : -4.11, -3.22, 55.61, 111.62, 112.23, 119.89, 120.29, 120.44, 120.73, 122.44, 124.14, 124.32, 128.91, 128.97, 129.24, 130.14, 132.42, 132.77, 138.52, 143.50, 145.49, 145.96, 155.15; HRMS (ESI, m/z) calcd for $[\text{C}_{23}\text{H}_{21}\text{NOSi}]\text{H}^+$: 356.1465; found 356.1466.



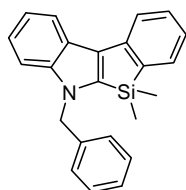
3d: Pale yellow solid, isolated yield 99% (114 mg); mp: 55.5-56.1 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.04 (d, J = 8.8 Hz, 1H), 7.81 (d, J = 7.6 Hz, 1H), 7.57 (t, J = 4.6 Hz, 1H), 7.47 (d, J = 7.2 Hz, 1H), 7.41 (t, J = 7.6 Hz, 1H), 7.24-7.22 (m, 2H), 7.12 (t, J = 7.8 Hz, 1H), 6.68 (s, 2H), 6.48 (s, 1H), 3.82 (s, 6H), 0.42 (s, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ : -3.07, 55.49, 98.76, 103.20, 111.64, 120.15, 120.55, 120.84, 122.95, 124.69, 124.89, 130.22, 132.46, 133.59, 138.35, 142.12, 142.36, 144.57, 144.93, 161.34; HRMS (ESI, m/z) calcd for $[\text{C}_{24}\text{H}_{23}\text{NO}_2\text{Si}]\text{H}^+$: 386.1571; found 386.1568.



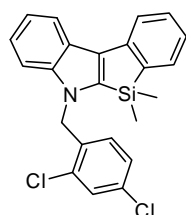
3e: Yellow solid, isolated yield 59% (65 mg); mp: 217.5-218.5 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.43 (d, J = 9.2 Hz, 2H), 8.09 (d, J = 8.8 Hz, 1H), 7.85 (d, J = 7.6 Hz, 1H), 7.72 (d, J = 8.8 Hz, 2H), 7.60 (d, J = 9.2 Hz, 1H), 7.51 (d, J = 6.8 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 7.33-7.30 (m, 2H), 7.20 (t, J = 7.2 Hz, 1H), 0.43 (s, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ : -2.98, 111.22, 120.64, 120.93, 121.94, 123.91, 124.06, 125.46, 125.49, 125.79, 130.41, 132.58, 136.07, 137.88, 141.56, 143.94, 144.06, 145.19, 146.32; HRMS (ESI, m/z) calcd for $[\text{C}_{22}\text{H}_{17}\text{N}_2\text{O}_2\text{Si}]\text{H}^+$: 370.1132; found 370.1129.



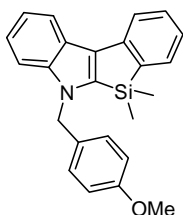
3f: Colorless solid, isolated yield 65% (68 mg); mp: 217.6-219.2 °C; ^1H NMR (300 MHz, CDCl_3) δ : 8.07 (d, J = 6.3 Hz, 1H), 7.84 (d, J = 8.7 Hz, 2H), 7.66 (d, J = 10.2 Hz, 2H), 7.56-7.42 (m, 4H), 7.31-7.18 (m, 3H), 0.41 (s, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ : -3.02, 102.23, 109.62, 111.10, 118.39, 120.55, 120.84, 121.73, 123.71, 124.56, 125.31, 125.56, 130.38, 132.56, 133.74, 135.61, 137.86, 141.51, 144.19, 144.58; HRMS (ESI, m/z) calcd for $[\text{C}_{23}\text{H}_{17}\text{N}_2\text{Si}]\text{Na}^+$: 373.1132; found 373.1123.



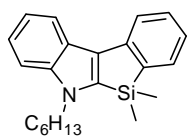
3g: Colorless oil, isolated yield 93% (95 mg); ^1H NMR (400 MHz, CDCl_3) δ : 8.01 (d, J = 9.2 Hz, 1H), 7.77 (d, J = 7.8 Hz, 1H), 7.43-7.36 (m, 2H), 7.31-7.24 (m, 4H), 7.224-7.18 (m, 2H), 7.08 (d, J = 7.2 Hz, 2H), 5.34 (s, 2H), 0.21 (s, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ : -3.99, 50.81, 110.22, 120.06, 120.12, 120.25, 122.42, 124.16, 124.27, 126.62, 127.66, 128.43, 128.77, 130.21, 132.40, 137.82, 138.33, 142.71, 144.78, 145.32; HRMS (ESI, m/z) calcd for $[\text{C}_{23}\text{H}_{21}\text{NSi}]\text{H}^+$: 340.1516; found 340.1514.



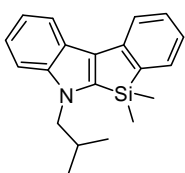
3h Colorless oil, isolated yield 88% (108 mg); ^1H NMR (300 MHz, CDCl_3) δ : 8.05 (d, J = 6.0 Hz, 1H), 7.80 (d, J = 7.2 Hz, 1H), 7.47-7.40 (m, 3H), 7.24-7.12 (m, 4H), 7.01 (d, J = 8.4 Hz, 1H), 6.39 (d, J = 8.4 Hz, 1H), 5.42 (s, 2H), 0.29 (s, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ : -3.82, 47.91, 110.01, 120.31, 120.40, 120.43, 122.77, 124.32, 124.53, 127.55, 128.44, 129.20, 130.34, 132.49, 132.53, 132.69, 133.87, 134.05, 138.08, 142.41, 144.67, 145.11; HRMS (ESI, m/z) calcd for $[\text{C}_{23}\text{H}_{19}\text{Cl}_2\text{NSi}]\text{H}^+$: 408.0737; found 408.0734.



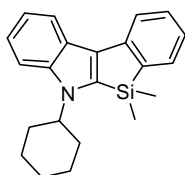
3i: Colorless solid, isolated yield 58% (64 mg); mp: 128.2-128.9 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.01 (d, J = 8.8 Hz, 1H), 7.77 (d, J = 7.2 Hz, 2H), 7.43-7.36 (m, 2H), 7.31 (t, J = 4.6 Hz, 1H), 7.22-7.18 (m, 2H), 7.10-7.02 (m, 3H), 6.81 (d, J = 8.8 Hz, 2H), 5.30 (s, 2H), 3.75 (s, 3H), 0.24 (s, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ : -3.89, 50.40, 55.28, 110.30, 114.11, 120.01, 120.11, 120.23, 122.36, 124.19, 124.23, 127.93, 129.80, 130.19, 132.04, 132.39, 138.39, 142.63, 144.75, 145.35, 159.08; HRMS (ESI, m/z) calcd for $[\text{C}_{24}\text{H}_{23}\text{NOSi}]\text{H}^+$: 370.1622; found 370.1619.



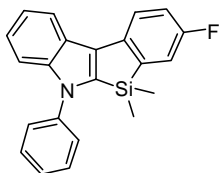
3j: Colorless oil, isolated yield 93% (93 mg); ^1H NMR (300 MHz, CDCl_3) δ : 7.98 (d, $J = 7.8$ Hz, 1H), 7.74 (d, $J = 7.8$ Hz, 1H), 7.46 (d, $J = 7.2$ Hz, 1H), 7.41-7.34 (m, 2H), 7.25-7.17 (m, 2H), 7.08 (t, $J = 6.3$ Hz, 1H), 4.13 (t, $J = 7.2$ Hz, 2H), 1.90-1.81 (m, 2H), 1.41-1.26 (m, 6H), 0.87 (t, $J = 6.9$ Hz, 3H), 0.50 (s, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ : -3.22, 13.98, 22.52, 26.87, 30.86, 31.56, 47.97, 110.21, 119.75, 120.13 (2C), 122.04, 124.08, 124.21, 130.26, 131.40, 132.38, 138.04, 142.12, 144.32, 145.60; HRMS (ESI, m/z) calcd for $[\text{C}_{22}\text{H}_{27}\text{NSi}]^+$: 334.1986; found 334.1986.



3k: Colorless oil, isolated yield 96% (88 mg); ^1H NMR (400 MHz, CDCl_3) δ : 7.98 (d, $J = 7.6$ Hz, 1H), 7.75 (d, $J = 7.6$ Hz, 1H), 7.46 (d, $J = 7.2$ Hz, 1H), 7.40-7.33 (m, 2H), 7.23-7.15 (m, 2H), 7.08 (t, $J = 7.4$ Hz, 1H), 3.92 (d, $J = 7.6$ Hz, 2H), 2.32-2.24 (m, 1H), 0.95 (d, $J = 6.8$ Hz, 6H), 0.49 (s, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ : -3.06, 20.44, 29.75, 55.73, 110.60, 119.75, 120.10, 120.15, 122.00, 124.11, 124.25, 130.27, 131.35, 132.37, 138.02, 142.39, 144.75, 145.55; HRMS (ESI, m/z) calcd for $[\text{C}_{20}\text{H}_{23}\text{NSi}]^+$: 306.1672; found 306.1666.

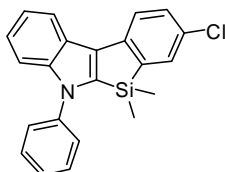


3l: Colorless solid, isolated yield 76% (75 mg); mp: 132.5-133.8 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ : 8.01 (d, $J = 7.6$ Hz, 1H), 7.77 (d, $J = 7.6$ Hz, 1H), 7.46 (d, $J = 7.2$ Hz, 1H), 7.41-7.36 (m, 2H), 7.25-7.16 (m, 2H), 7.09 (t, $J = 7.2$ Hz, 1H), 4.35-4.31 (m, 1H), 2.16-1.68 (m, 5H), 1.58-1.48 (m, 4H), 1.32-1.28 (m, 1H), 0.53 (s, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ : -2.02, 25.76, 26.03, 34.10, 56.07, 110.30, 119.90, 119.98, 120.14, 122.07, 124.04, 124.12, 130.16, 132.05, 132.15, 138.19, 140.89, 141.76, 145.21; HRMS (ESI, m/z) calcd for $[\text{C}_{22}\text{H}_{25}\text{NSi}]^+$: 332.1829; found 332.1830.

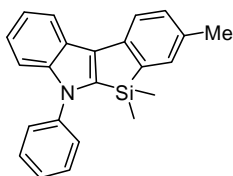


3m: Colorless solid, isolated yield 98% (101 mg); mp: 210.2-211.0 $^{\circ}\text{C}$; ^1H NMR (300 MHz, CDCl_3) δ : 8.12 (d, $J = 8.7$ Hz, 1H), 7.86 (t, $J = 6.45$ Hz, 1H), 7.65-7.49 (m, 6H), 7.37-7.27 (m, 3H), 7.20 (t, $J = 8.85$ Hz, 1H), 0.49 (s, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ : -3.24, 111.39, 116.22 (d, $J = 21.6$ Hz), 119.61 (d, $J = 20.4$ Hz), 119.89, 120.86, 121.29 (d, $J = 6.8$ Hz), 123.05, 124.46, 124.93, 126.91, 129.57, 140.58, 140.84 (d, $J = 3.1$

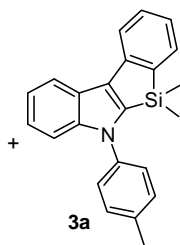
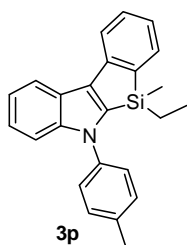
Hz), 141.26 (d, $J = 4.4$ Hz), 142.24, 144.01 (d, $J = 2.5$ Hz), 159.28, 162.53; HRMS (ESI, m/z) calcd for $[C_{22}H_{18}FNSi]H^+$: 344.1265; found 344.1262.



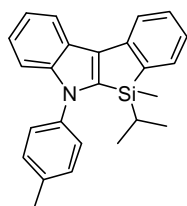
3n: Colorless solid, isolated yield 92% (99 mg); mp: 210.2-211.0 °C; 1H NMR (300 MHz, $CDCl_3$) δ : 7.99 (d, $J = 5.7$ Hz, 1H), 7.73 (t, $J = 6.3$ Hz, 1H), 7.53-7.47 (m, 5H), 7.41-7.37 (m, 1H), 7.25-7.15 (m, 3H), 7.07 (t, $J = 8.85$ Hz, 1H), 0.37 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ : -3.30, 111.45, 119.98, 120.99, 121.43, 123.16, 124.53, 124.98, 127.04, 129.60, 129.92, 130.23, 132.42, 132.71, 140.48, 140.88, 142.35, 143.27, 144.66; HRMS (ESI, m/z) calcd for $[C_{22}H_{18}ClNSi]H^+$: 360.0970; found 360.0965.



3o: Colorless solid, isolated yield 92% (92 mg); mp: 142.4-143.7 °C; 1H NMR (400 MHz, $CDCl_3$) δ : 8.03 (d, $J = 6.4$ Hz, 1H), 7.72 (d, $J = 7.6$ Hz, 1H), 7.51-7.47 (m, 5H), 7.38-7.35 (m, 1H), 7.31 (s, 1H), 7.23-7.21 (m, 3H), 2.36 (s, 3H), 0.36 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ : -3.06, 21.30, 111.29, 120.16, 120.33, 120.64, 122.81, 124.75, 124.89, 126.70, 129.13, 129.48, 130.64, 133.46, 133.66, 133.98, 138.38, 140.71, 142.16, 144.29; HRMS (ESI, m/z) calcd for $[C_{23}H_{21}NSi]H^+$: 340.1516; found 340.1514.

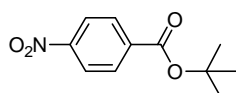


3p and 3a: 3p:3a = 2.7:1; Colorless solid, isolated yield 73% (77 mg); mp: 113.2-113.7 °C; 1H NMR (400 MHz, $CDCl_3$) δ : 8.06-8.04 (m, 1.3H), 7.82 (d, $J = 7.6$ Hz, 1.4H), 7.48-7.31 (m, 10.2H), 7.24-7.21 (m, 2.8H), 7.14-7.10 (m, 1.4H), 2.45 (s, 4.2H), 0.82-0.79 (m, 5H), 0.40 (s, 3H), 0.36 (s, 2.2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ : -5.00, -3.18, 5.60, 7.35, 21.12, 111.33, 120.04, 120.47, 120.57, 120.62, 122.69, 122.76, 124.46, 124.55, 124.67, 124.86, 125.02, 130.06, 130.17, 130.21, 132.46, 132.75, 133.65, 136.65, 136.73, 137.44, 138.05, 138.16, 138.30, 142.52, 144.38, 145.14, 145.52; HRMS (ESI, m/z) calcd for $[C_{24}H_{23}NSi]H^+$: 354.1667; found 354.1673.



3q: Colorless solid, isolated yield 72% (79 mg); mp: 120.9-122.1 °C; 1H NMR (400 MHz, $CDCl_3$) δ : 8.05 (d, $J = 8.4$ Hz, 1H), 7.82 (d, $J = 7.6$ Hz, 1H), 7.47-7.30 (m, 7H), 7.23-7.20 (m, 2H), 7.10 (t, $J = 7.0$ Hz, 1H), 2.44 (s, 3H), 1.05-0.97 (m, 1H), 0.82 (d, $J = 7.2$ Hz, 3H), 0.75 (d, $J =$

7.2 Hz, 3H), 0.46 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ : -6.09, 12.81, 17.49, 17.52, 21.15, 111.29, 120.02, 120.46, 120.53, 122.65, 124.39, 124.62, 125.35, 129.64, 130.05, 130.13, 133.01, 133.84, 136.86, 138.31, 142.62, 144.10, 145.73; HRMS (ESI, m/z) calcd for $[\text{C}_{25}\text{H}_{25}\text{NSi}]\text{H}^+$: 367.1755; found 367.1751.



8: Yellow solid, mp: 106.4-107.2 °C; ^1H NMR (300 MHz, CDCl_3) δ : 8.23 (d, J = 8.7 Hz, 2H), 8.11 (d, J = 8.7 Hz, 2H), 1.59 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3) δ : 28.01, 82.55, 123.31, 126.95, 130.46, 137.32, 163.68; HRMS (ESI, m/z) calcd for $[\text{C}_{11}\text{H}_{13}\text{NO}_4]\text{Na}^+$: 246.0737; found 246.0732.

7) X-ray Crystallographic Studies of **3a**

The single crystals of **3a** suitable for X-ray analysis were grown in solution of hexane, diethyl ether and ethyl acetate as co-solvent. Data collections for **3a** were performed at 20 °C on a Rigaku RAXIS RAPID IP diffractometer, using graphite-monochromated Mo $\text{K}\alpha$ radiation (λ = 0.71073 Å). The determination of crystal class and unit cell parameters was carried out by the Rapid-AUTO (Rigaku 2000) program package for **3a**. The raw frame data were processed using Crystal Structure (Rigaku/MSO 2000) for **3a** to yield the reflection data file. The structures of **3a** were solved by use of SHELXTL program. Refinement was performed on F^2 anisotropically for all the non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. Crystal data, data collection and processing parameters for compounds **3a** are summarized in **STable 3**. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-815222 (**3a**). Copies of these data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 3. Crystallographic data and structure refinement details for **3a**.⁸

Empirical formula	C ₂₃ H ₂₁ N Si	
Formula weight	339.50	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 19.804(4) Å	α = 90°
	b = 20.045(4) Å	β = 106.03(3) °
	c = 14.952(3) Å	γ = 90°
Volume	5705(2) Å ³	
Z	12	
Density (calculated)	1.186 Mg/m ³	
Absorption coefficient	0.128 mm ⁻¹	
F(000)	2160	
Crystal size	0.30 x 0.30 x 0.20 mm ³	
Theta range for data collection	1.07 to 27.48°.	
Index ranges	-25 ≤ h ≤ 24, -26 ≤ k ≤ 26, -19 ≤ l ≤ 19	
Reflections collected	13053	
Independent reflections	13053 [R(int) = 0.0917]	
Completeness to theta = 27.48°	99.7 %	
Absorption correction	Empirical	
Max. and min. transmission	0.9749 and 0.9627	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	13053 / 0 / 686	
Goodness-of-fit on F ²	0.529	
Final R indices [I > 2σ(I)]	R1 = 0.0472, wR2 = 0.0658	
R indices (all data)	R1 = 0.2289, wR2 = 0.0929	
Extinction coefficient	0.00162(5)	
Largest diff. peak and hole	0.243 and -0.258 e. Å ⁻³	

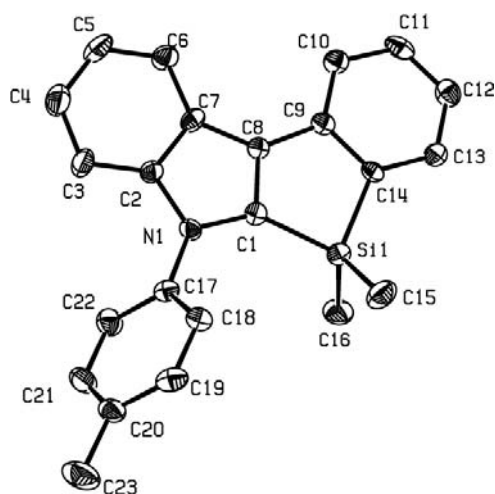


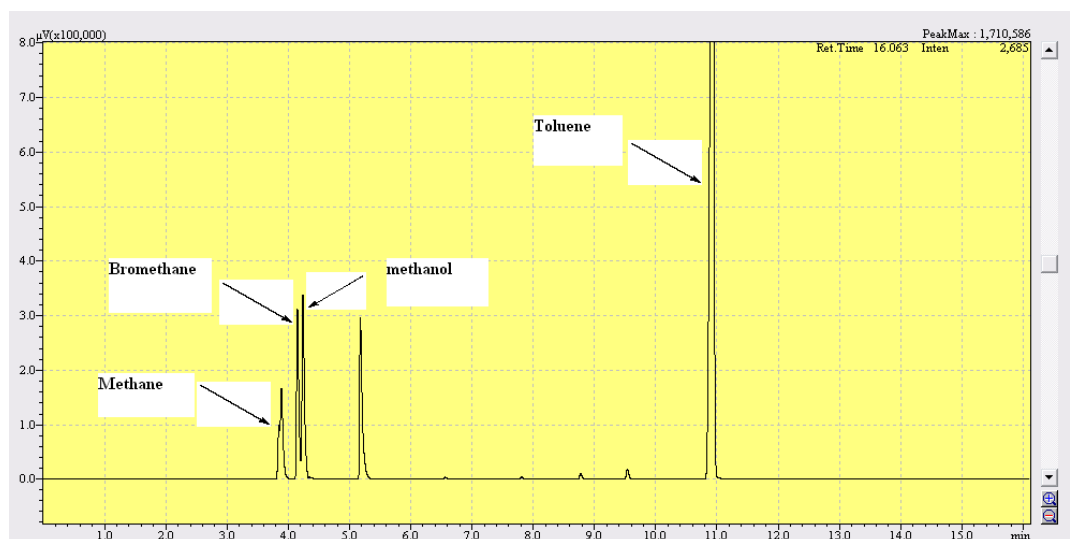
Figure 1. ORTEP drawing of **3a** with 30% probability thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

8) GC Analyses of the Gas Composition of the Reactions

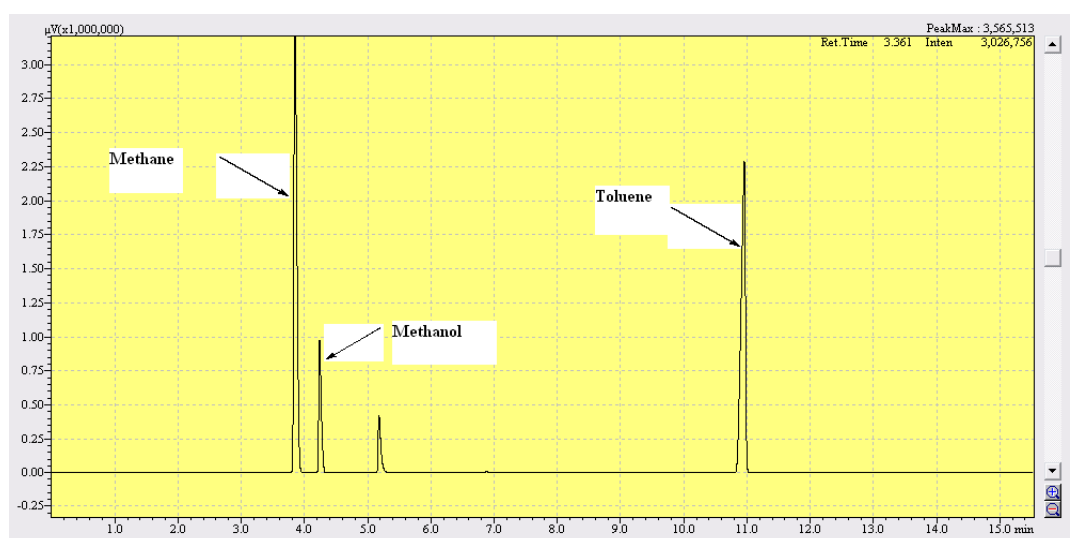
Experiment 1: Under the protection of nitrogen, $[\text{PdCl}(\pi\text{-allyl})]_2$ (2.5 mol%) and Pt-Bu_3 (10 mol%) was added in 5 mL toluene. After this reaction mixture was stirred at room temperature for 15 min, (2'-bromobiphenyl-2-yl)trimethylsilane (1.0 mmol), LiOt-Bu (3.0 mmol) were added and this reaction mixture was stirred at 120 °C for 10 h. Then, 250 μL of the mixed gas of the reaction was taken using a syringe and GC analyse of the gas composition was carried out.

Experiment 2: Under the protection of nitrogen, $[\text{PdCl}(\pi\text{-allyl})]_2$ (2.5 mol%) and Pt-Bu_3 (10 mol%) was added in 5 mL toluene. After this reaction mixture was stirred at room temperature for 15 min, (2'-bromobiphenyl-2-yl)trimethylsilane (1.0 mmol), LiOt-Bu (3.0 mmol), 4-nitrobenzaldehyde (1.0 mmol) were added and this reaction mixture was stirred at 120 °C for 10 h. Then, 250 μL of the mixed gas of the reaction was taken using a syringe and GC analyse of the gas composition was carried out.

GC analyse of experiment 1



GC analyse of experiment 2



GC analyse of standard sample methane (the mixture of CH₄ and H₂)



GC analyse of standard sample bromomethane (200 $\mu\text{g/mL}$ in methanol)



GC analyse of standard sample methanol (analytical-grade reagent)



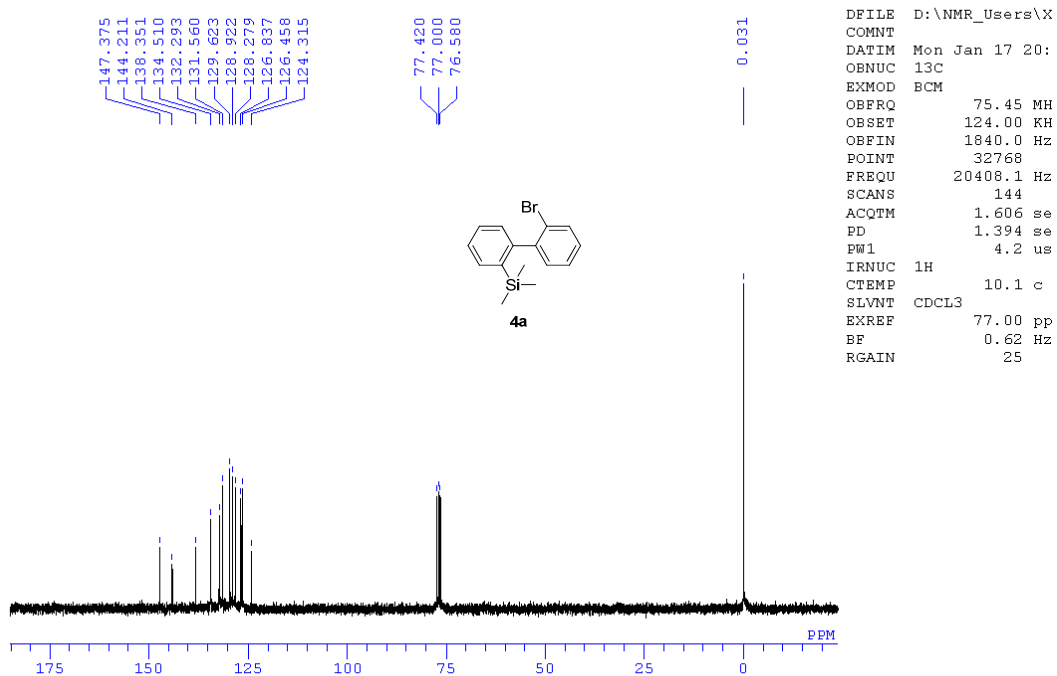
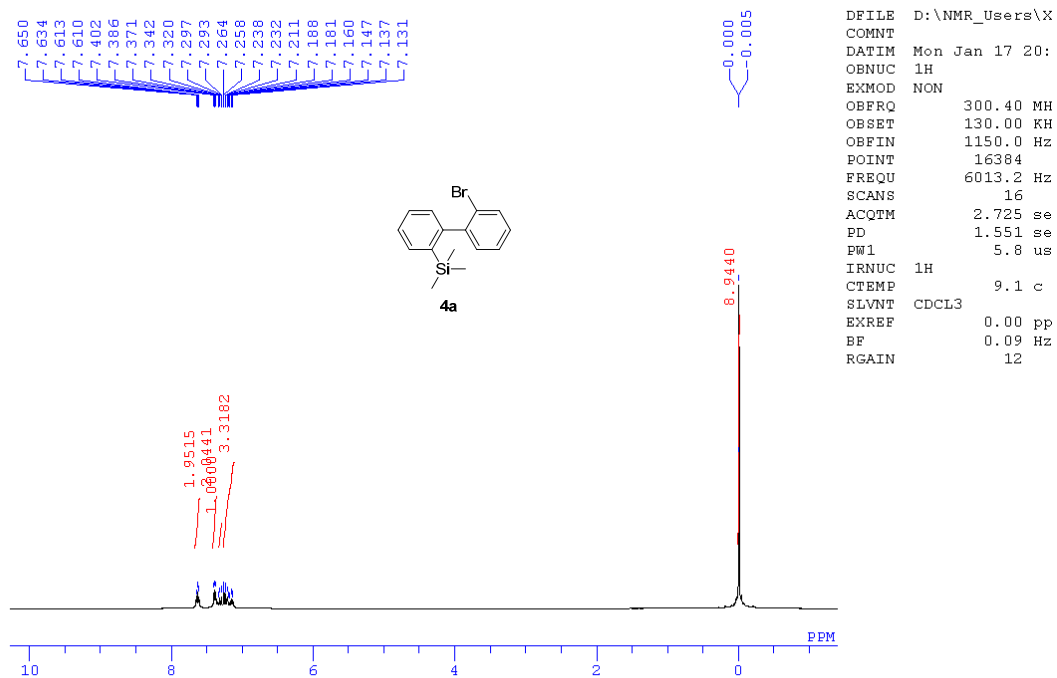
GC analyse of standard sample toluene (analytical-grade reagent)

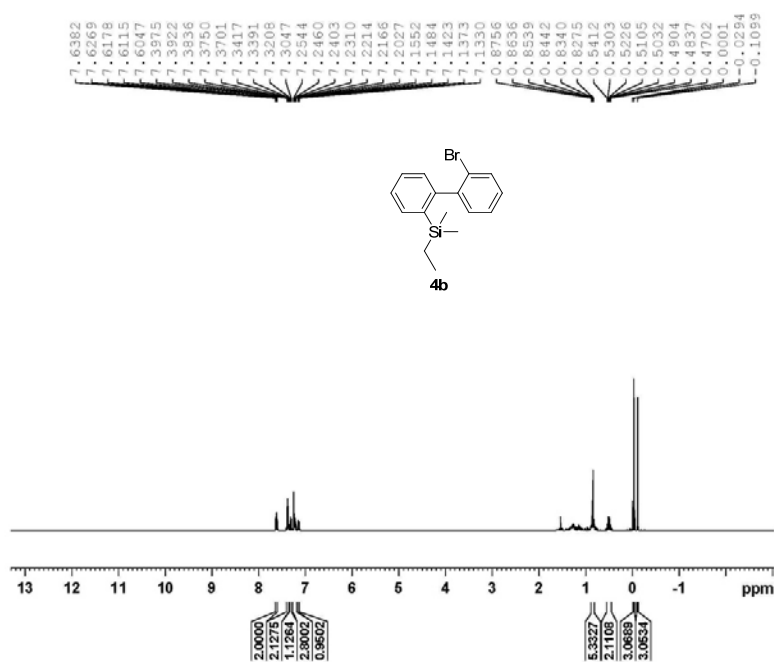


References:

1. van Klink, G. P. M.; de Boer, H. J. R.; Schat, G.; Akkerman, O. S. Bickelhaupt, F. Spek, A. L. *Organometallics* **2002**, *21*, 2119.
2. Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, *44*, 4467.
3. Zhang, H.-J.; Song, Z.; Wang, C.; Bruneau, C.; Xi, Z. *Tetrahedron Lett.* **2008**, *49*, 624.
4. (a) Willis, M. C.; Brace, G. N.; Holmes, I. P. *Angew. Chem., Int. Ed.* **2005**, *44*, 403.
(b) Willis, M. C.; Brace, G. N.; Findlay, T. J. K.; Holmes, I. P. *Adv. Synth. Catal.* **2006**, *348*, 851. (c) Fletcher, A. J.; Bax, M. N.; Willis, M. C. *Chem. Commun.* **2007**, 4764.
5. Wang, Z.; Fang, H.; Xi, Z. *Tetrahedron Lett.* **2005**, *46*, 499.
6. Hudrlik, P. F.; Dai, D.; Hudrlik, A. M. *J. Organomet. Chem.* **2006**, *691*, 1257.
7. Ureshino, T.; Yoshinda, T.; Kuninobu, Y.; Takai, K. *J. Am. Chem. Soc.* **2010**, *132*, 14324.
8. Sheldrick, G. M. SHELXTL 5.10 for Windows NT: *Structure Determination Software Programs*; Bruker Analytical X-ray Systems, Inc.: Madison, WI, **1997**.

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

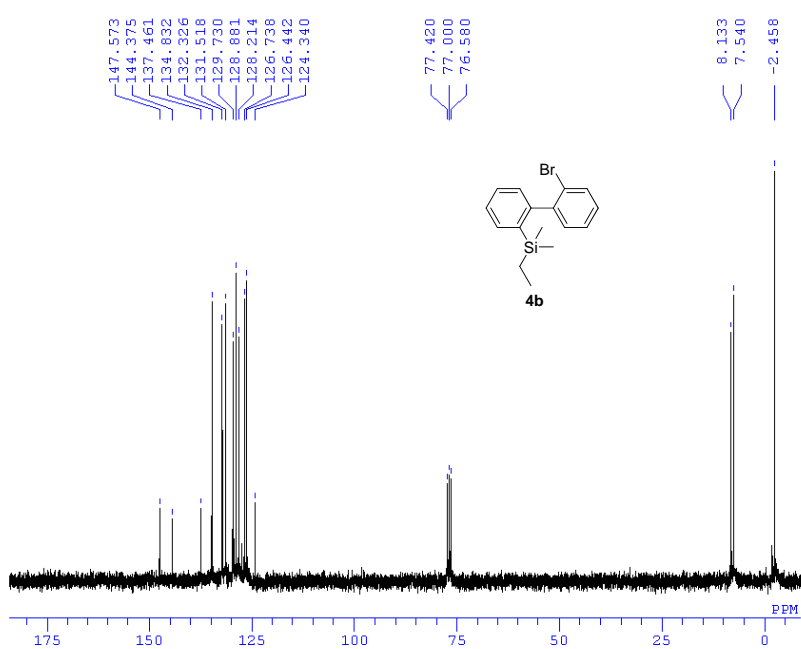




```

NAME      HMR11010956-3
EXPNO     1
PROCNO    1
Date_     20110115
Time      7.46
INSTRUM   ARX400
PROBHD    5 mm Multinu
PULPROG   zg
TD         32768
SOLVENT   CDCl3
NS         16
DS         0
SWH        8064.516 Hz
FIDRES     0.246119 Hz
AQ         2.0316660 sec
RG          715
DW         62.000 usec
DE         88.57 usec
TE         300.0 K
D1         2.00000000 sec
P1         3.00 usec
DE         88.57 usec
SFO1       400.1321971 MHz
NUC1       1H
SI         16384
SF         400.1300114 MHz
RGW        80
SSB        0
LB         0.00 Hz
GB         0
PC         4.00

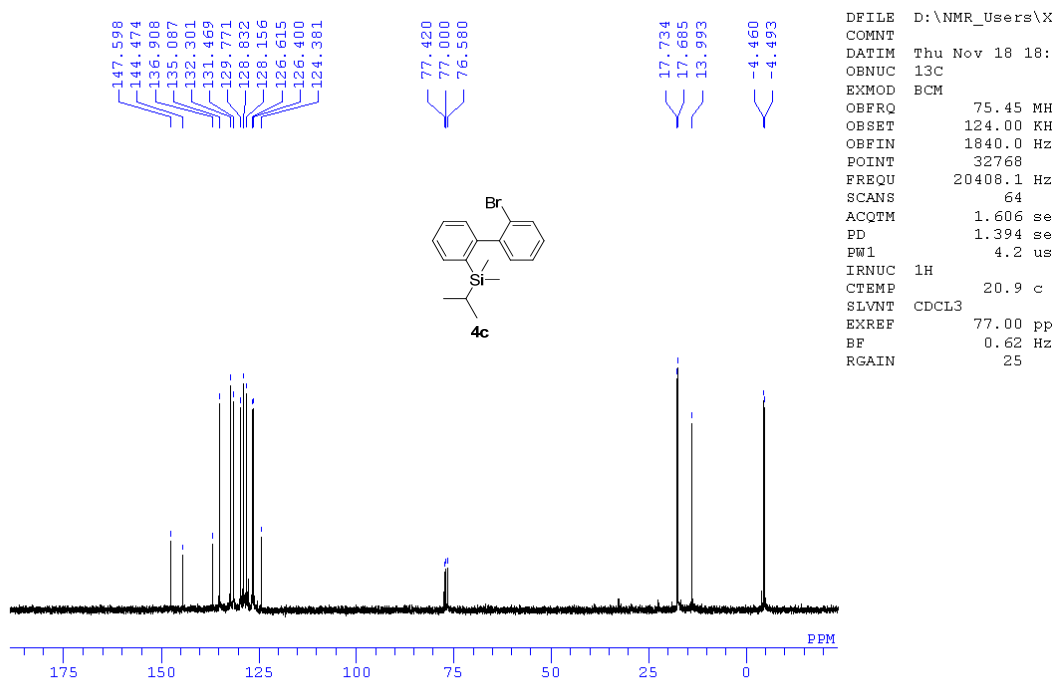
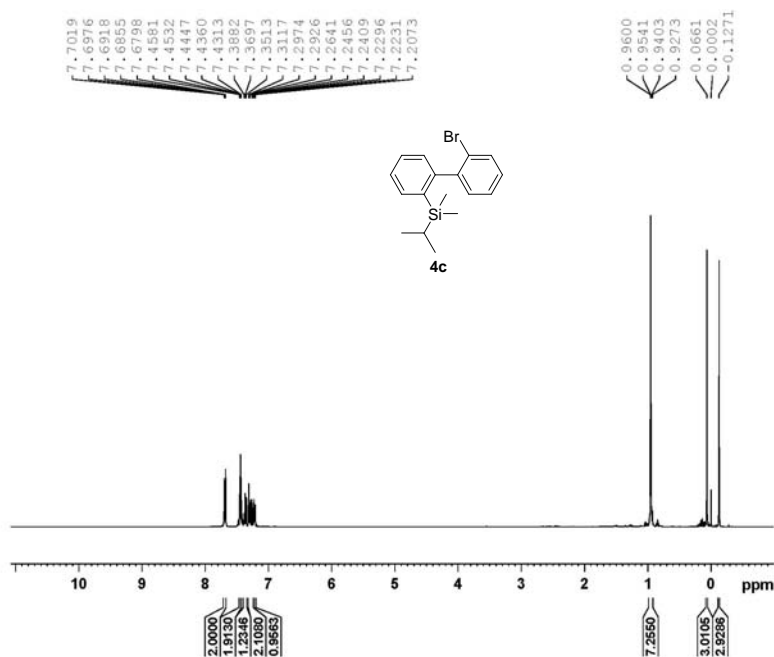
```

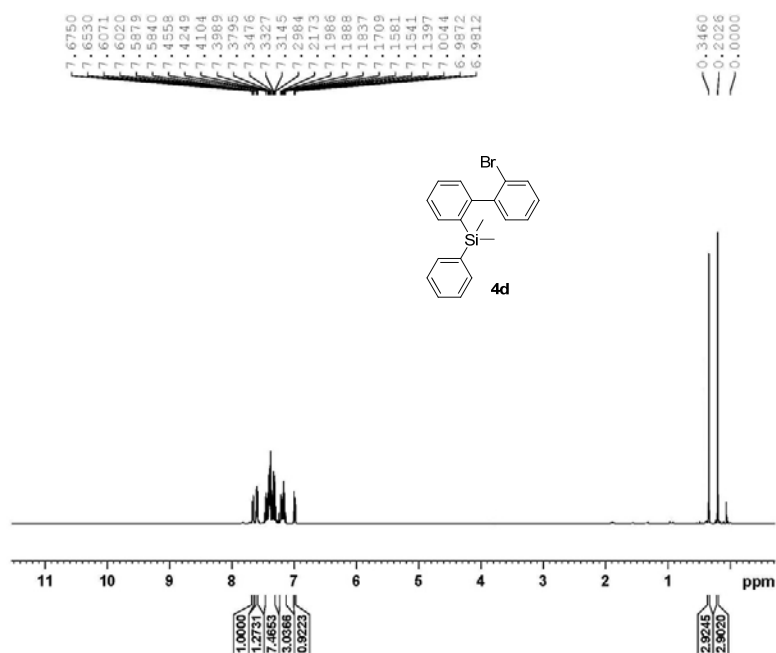


```

DFFILE    D:\NMR_Users\X
COMNT
DATIM     Thu Nov 18 19:
OBNUC     13C
EXMOD     BCM
OBFREQ    75.45 MH
OBSETE    124.00 KH
OBFIN     1840.0 Hz
POINT     32768
FREQU     20408.1 Hz
SCANS     80
ACQTM     1.606 se
PD         1.394 se
PWL       4.2 us
IRNUC     1H
CTEMP     20.7 c
SLVNT     CDCl3
EXREF     77.00 pp
BF         0.62 Hz
RGAIN     27

```

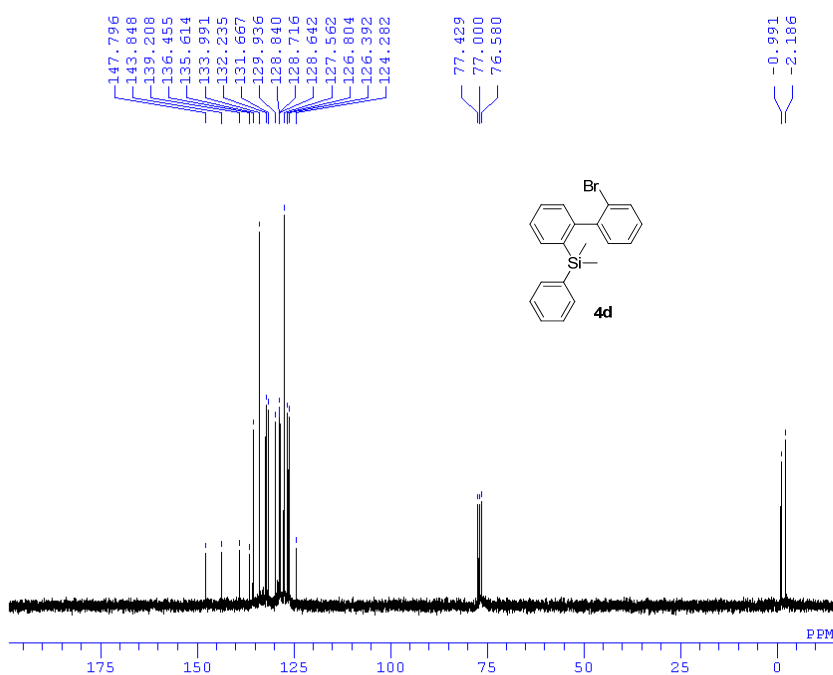




```

NAME      HMR11010556-7
EXPNO     1
PROCNO    1
Date_     20110115
Time      8.09
INSTRUM   ARX400
PROBHD    5 mm Multinu
PULPROG   zg
TD         32768
SOLVENT   CDCl3
NS         16
DS         0
SWH        8064.516 Hz
FIDRES     0.246119 Hz
AQ         2.0316660 sec
RG         180
DW         62.000 usec
DE         88.57 usec
TE         300.0 K
D1         2.00000000 sec
P1         3.00 usec
DE         88.57 usec
SFO1       400.1321971 MHz
NUC1       1H
SI         16384
SF         400.1300154 MHz
RGW        0
SSB        0
LB         0.00 Hz
GB         0
PC         4.00

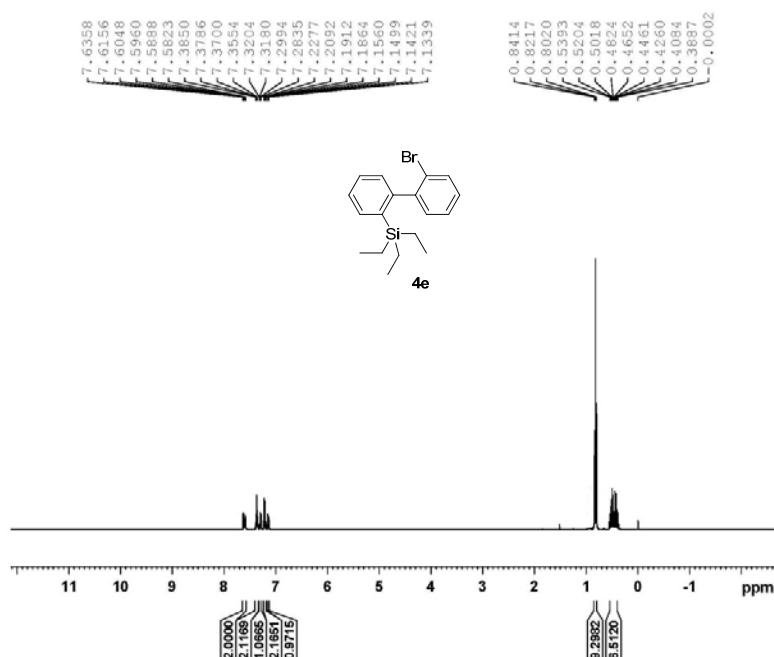
```



```

DFILE      D:\NMR_Users\X
COMNT
DATIM      Sat Nov 20 18:
OBNUC      13C
EXMOD      BCM
OBFREQ     75.45 MH
OBSET      124.00 KH
OBFIN      1840.0 Hz
POINT      32768
FREQU      20408.1 Hz
SCANS      128
AQCTM      1.606 se
PD         1.394 se
PW1        4.2 us
IRNUC      1H
CTEMP      23.9 c
SLVNT      CDCL3
EXREF      77.00 pp
BF         0.62 Hz
RGAIN      27

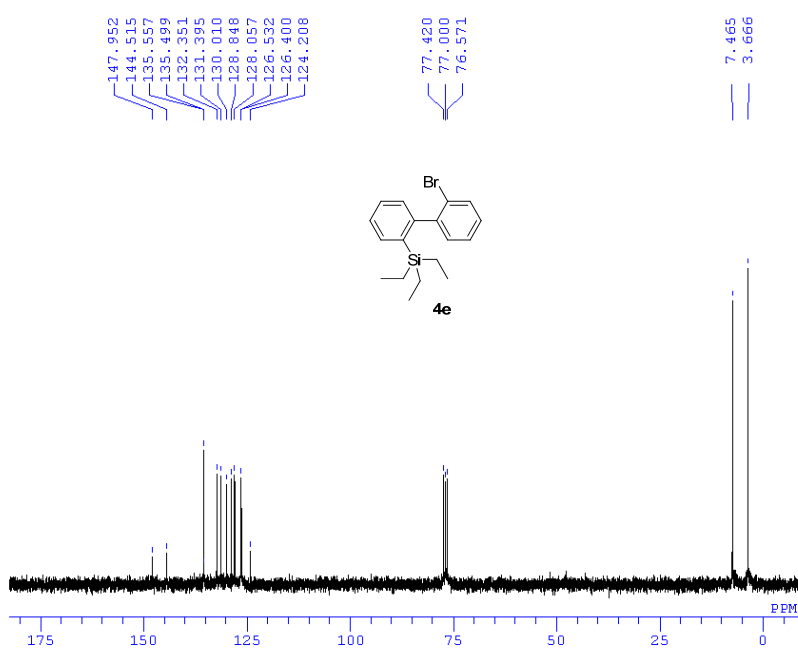
```



```

NAME      HMR11010956-5
EXPNO     1
PROCNO    1
Date_     20110115
Time      7.56
INSTRUM   ARX400
PROBHD    5 mm Multinu
PULPROG   zg
TD         32768
SOLVENT   CDCl3
NS         16
DS         0
SWH        8064.516 Hz
FIDRES     0.246119 Hz
AQ         2.0316660 sec
RG         256
DW         62.000 usec
DE         88.57 usec
TE         300.0 K
D1         2.00000000 sec
P1         3.00 usec
DE         88.57 usec
SFO1       400.1321971 MHz
NUC1       1H
SI         16384
SF         400.1300193 MHz
RGW        80
SSB        0
LB         0.00 Hz
GB         0
PC         4.00

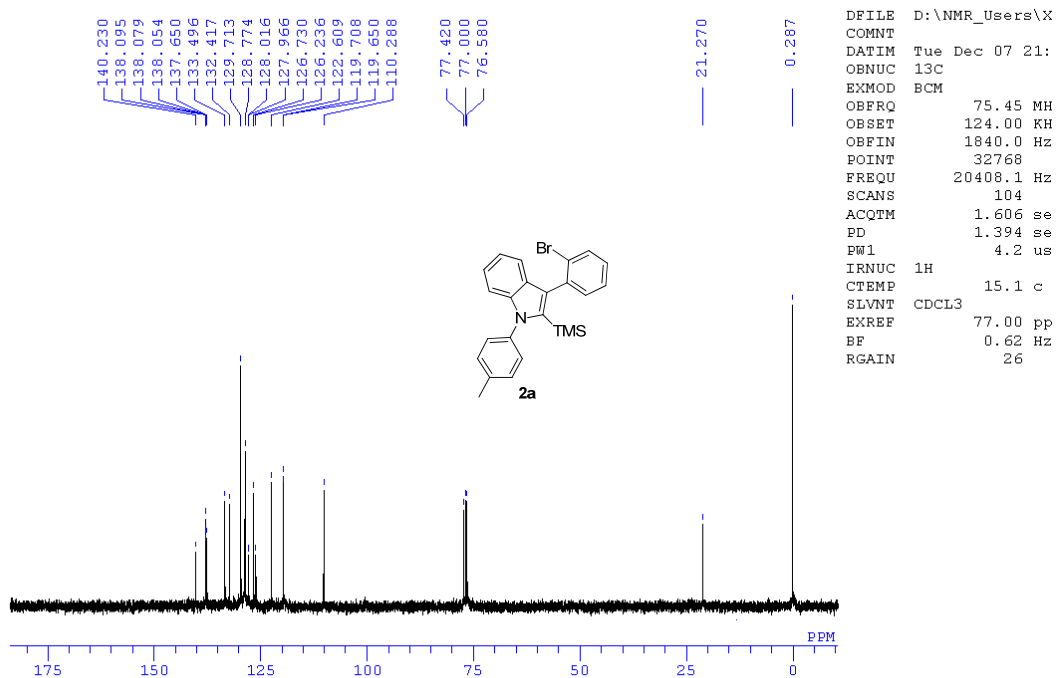
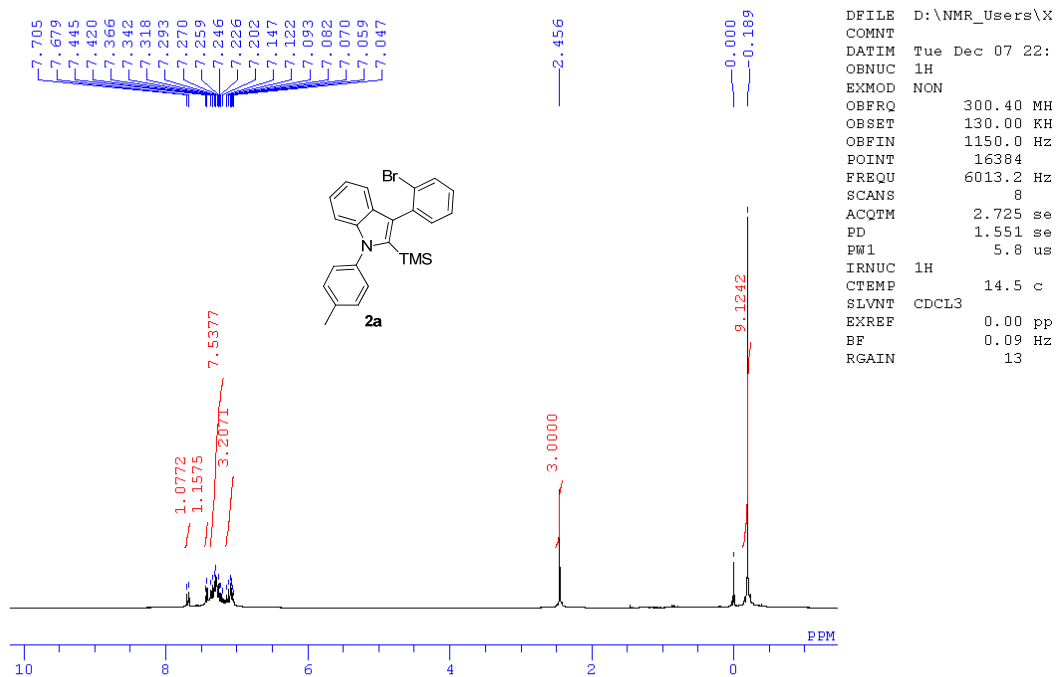
```

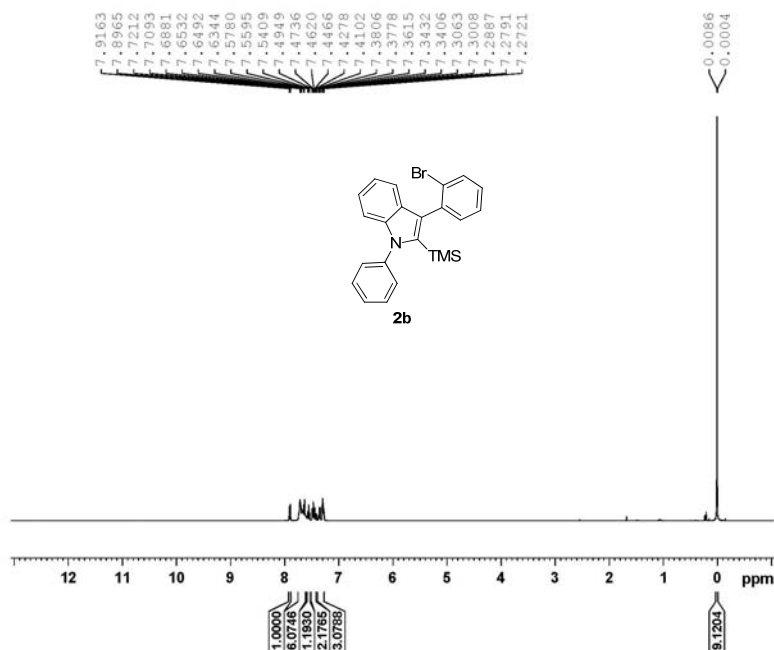


```

DFILE     C:\WINNMR95\CO
COMNT
DATIM     Fri Jan 14 19:
OBNUC     13C
EXMOD     BCM
OBFRQ     75.45 MH
OBSET     124.00 KH
OBFIN     1840.0 Hz
POINT     32768
FREQU     20408.1 Hz
SCANS     128
ACQTM     1.606 se
PD        1.394 se
PWL       4.2 us
IRNUC     1H
CTEMP     19.8 c
SLVNT     CDCL3
EXREF     77.00 pp
BF         0.62 Hz
RGAIN     26

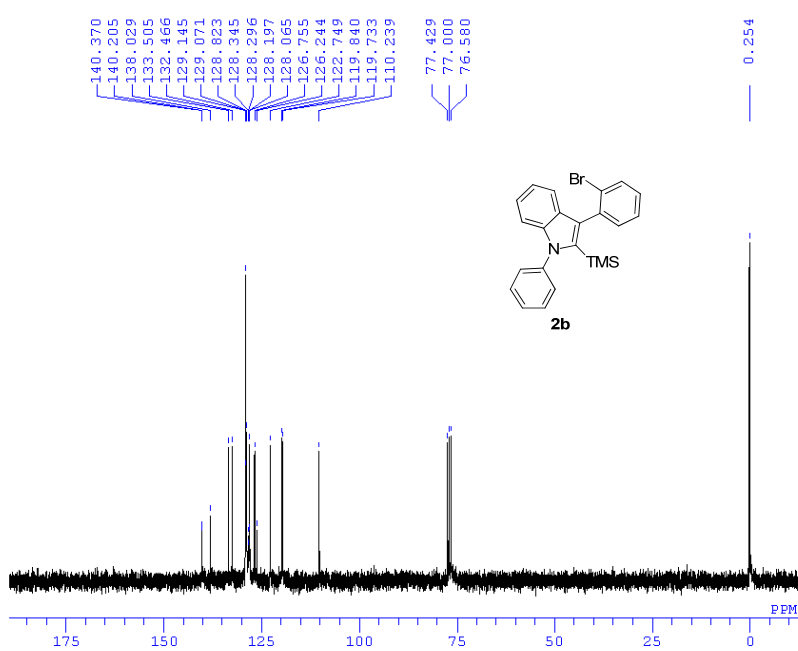
```





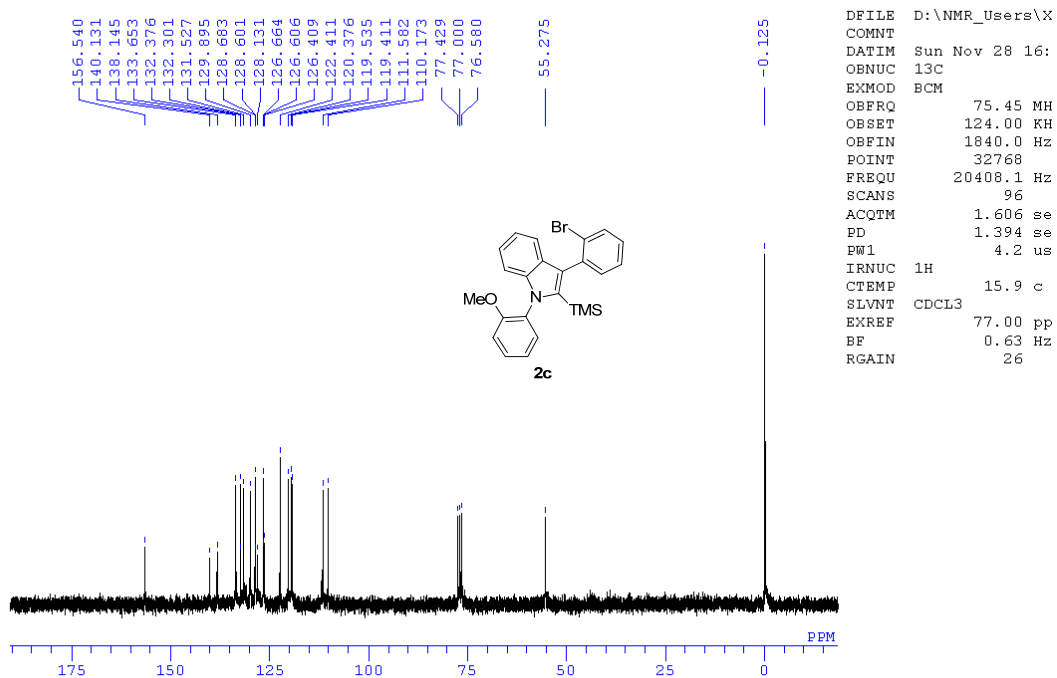
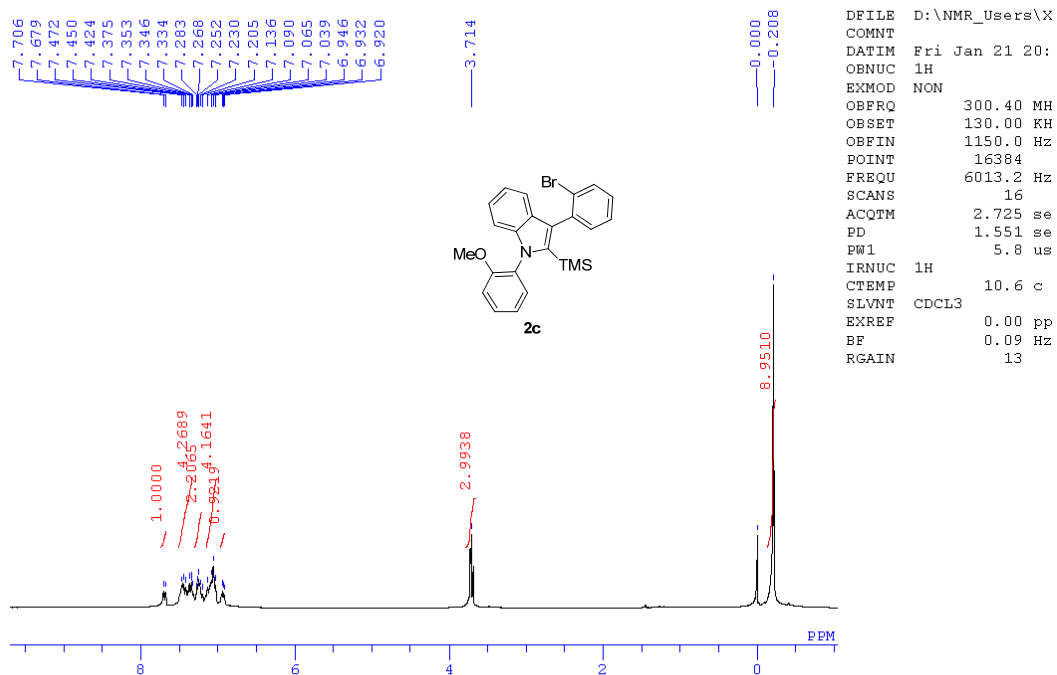
```

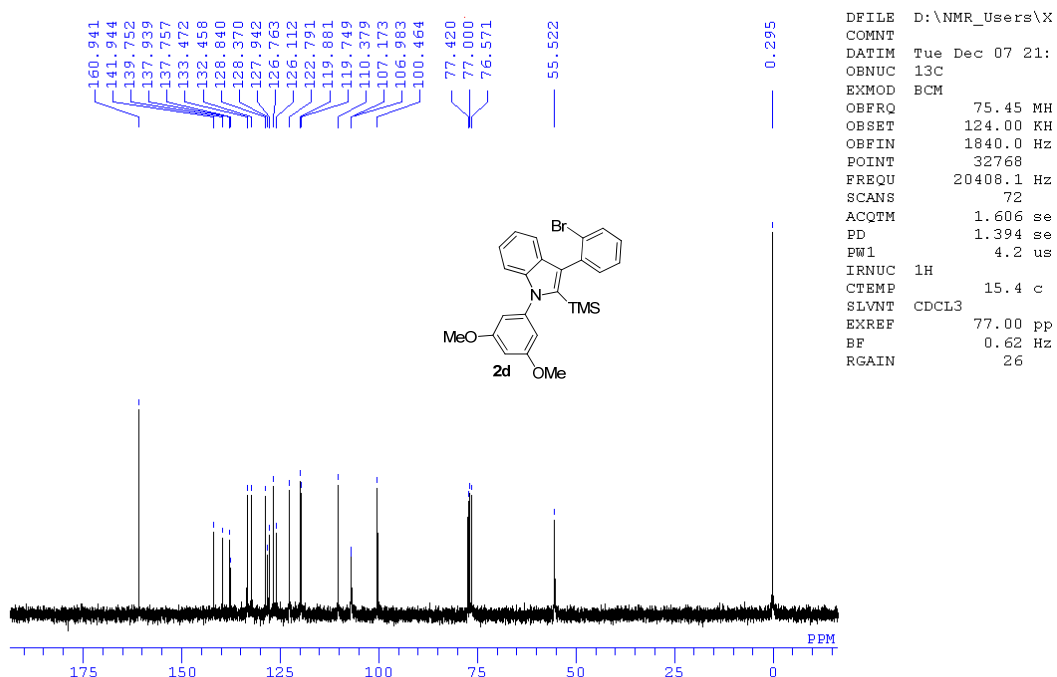
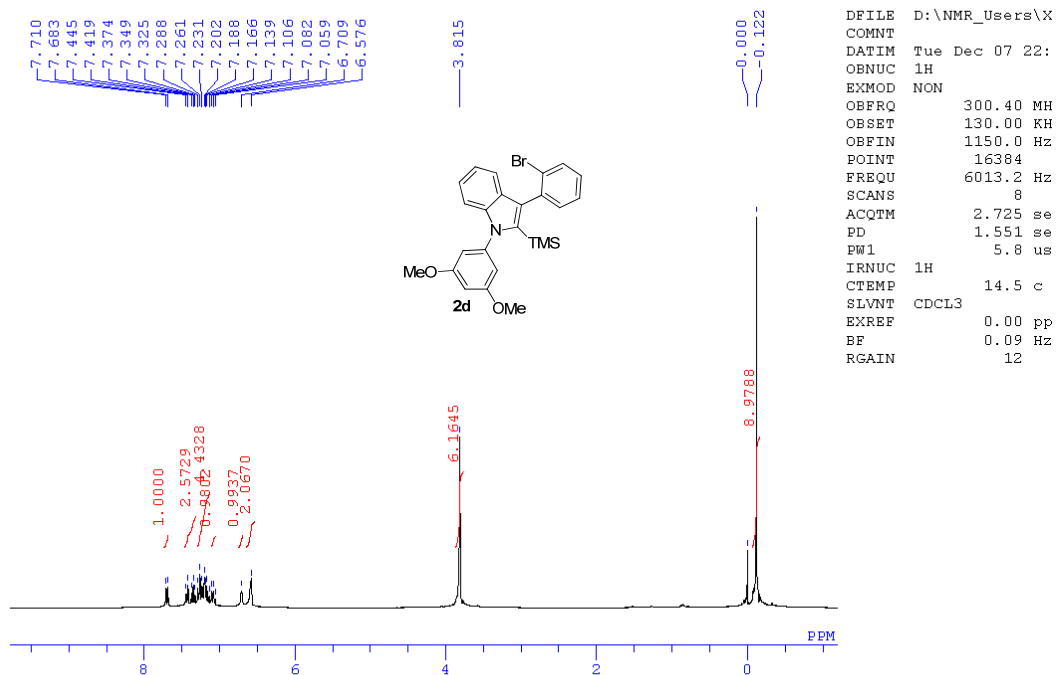
NAME      HNMRI1010556-2
EXPNO     1
PROCNO    1
Date_     20110115
Time      7.42
INSTRUM   ARX400
PROBHD    5 mm Multinu
PULPROG   zg
TD         32768
SOLVENT   CDCl3
NS         16
DS         0
SWH        8064.516 Hz
FIDRES     0.246110 Hz
AQ         2.0316660 sec
RG         256
DM         62.000 usec
DE         88.57 usec
TE         300.0 K
D1         2.00000000 sec
P1         3.00 usec
DE         88.57 usec
SFO1       400.1321971 MHz
NUC1       1H
SI         16384
SF         400.1299489 MHz
WDW        ho
SSB        0
LB         0.00 Hz
GB         0
PC         4.00
  
```

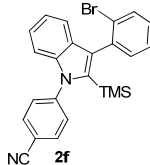
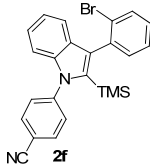


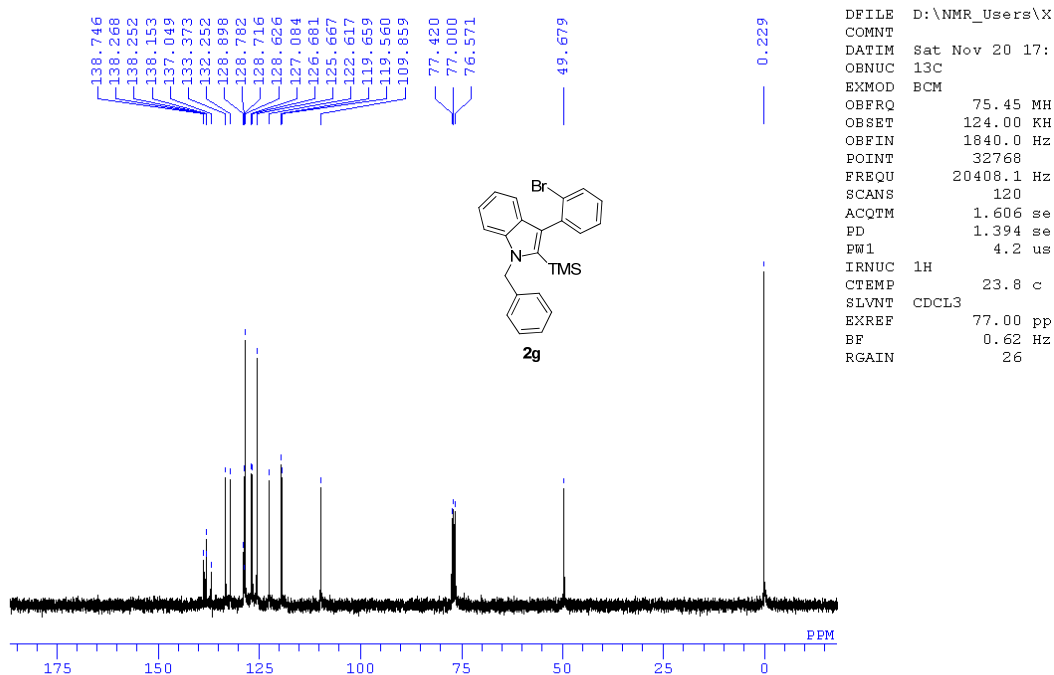
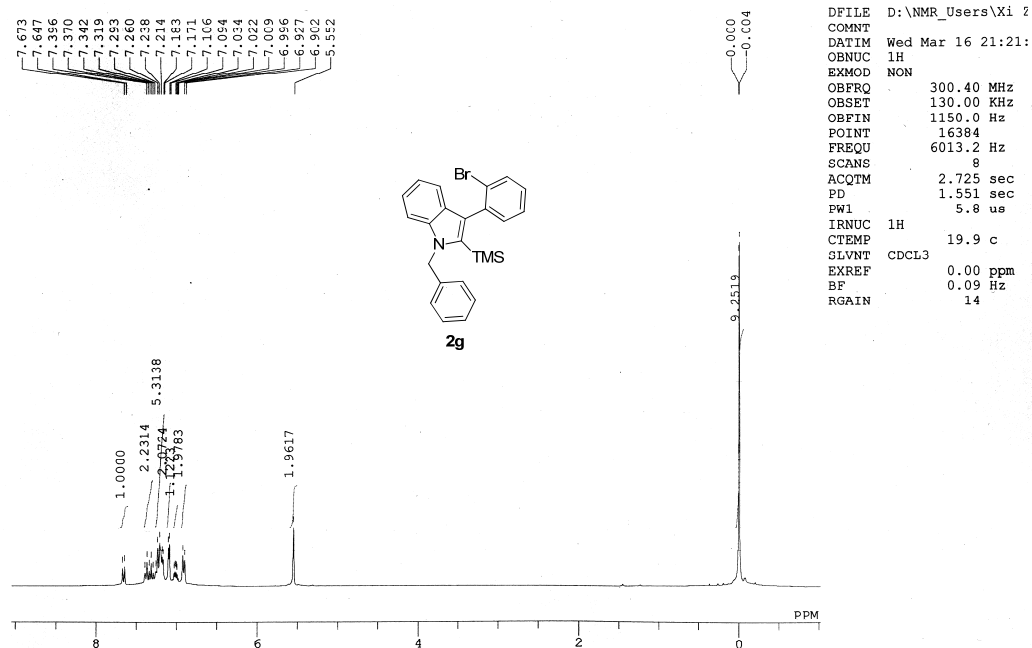
```

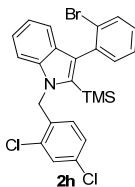
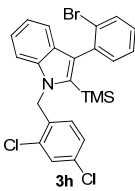
DFILE      D:\NMR_Users\X
COMNT
DATIM      Fri Jan 14 19:
OBNUC      13C
EXMOD      BCM
OBFRQ       75.45 MH
OBSET       124.00 KH
OBFIN       1840.0 Hz
POINT       32768
FREQU       20408.1 Hz
SCANS       160
ACQTM       1.606 se
PD          1.394 se
PWL         4.2 us
IRNUC      1H
CTEMP       19.7 c
SLVNT       CDCL3
EXREF       77.00 pp
BF          0.62 Hz
RGAIN       26
  
```

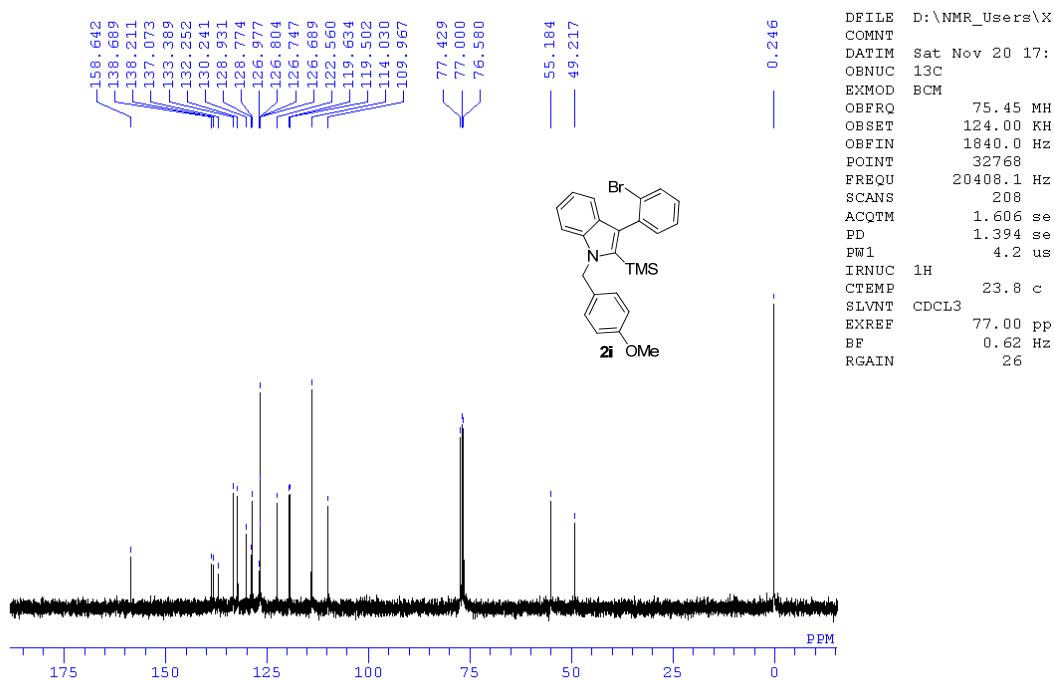
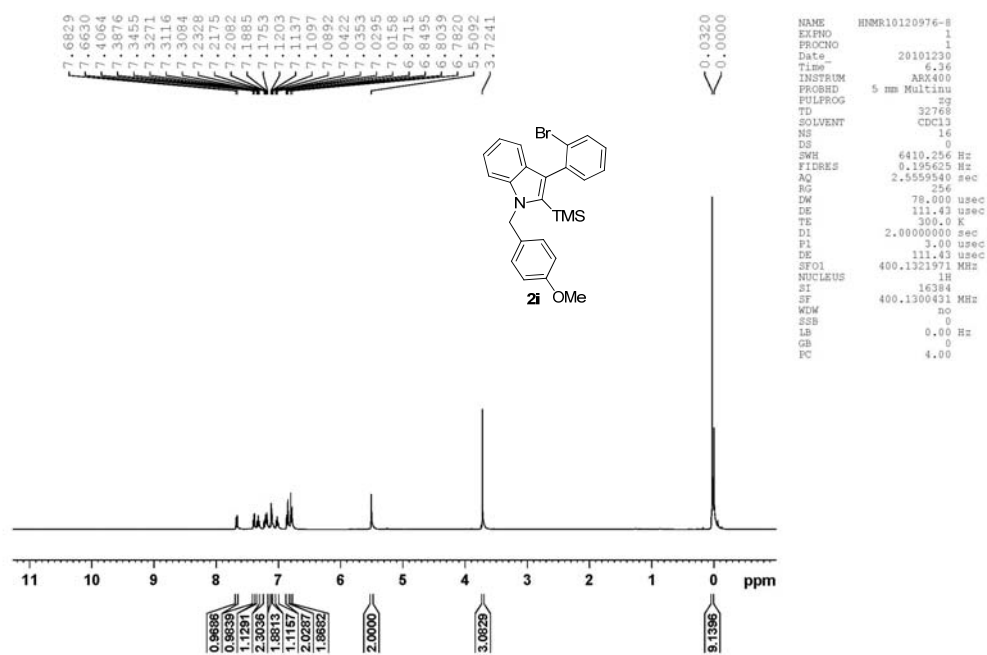


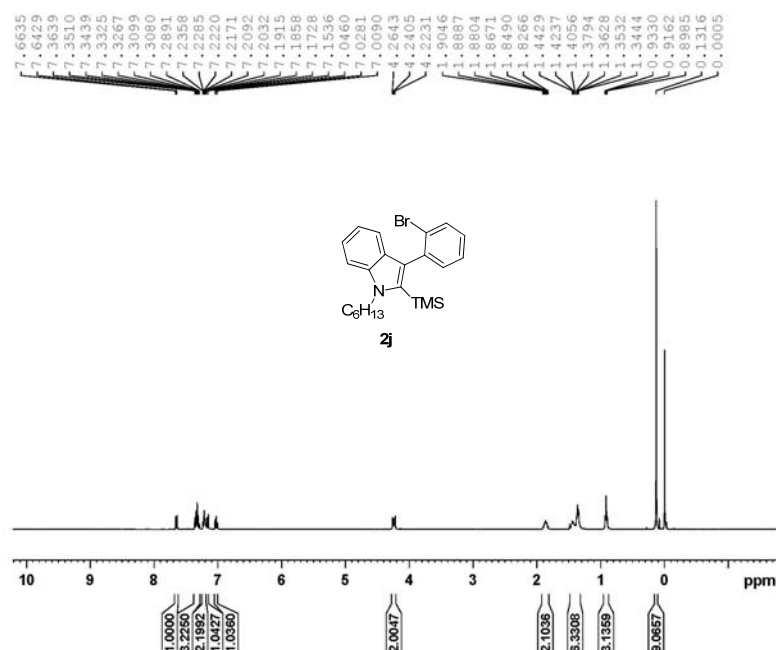






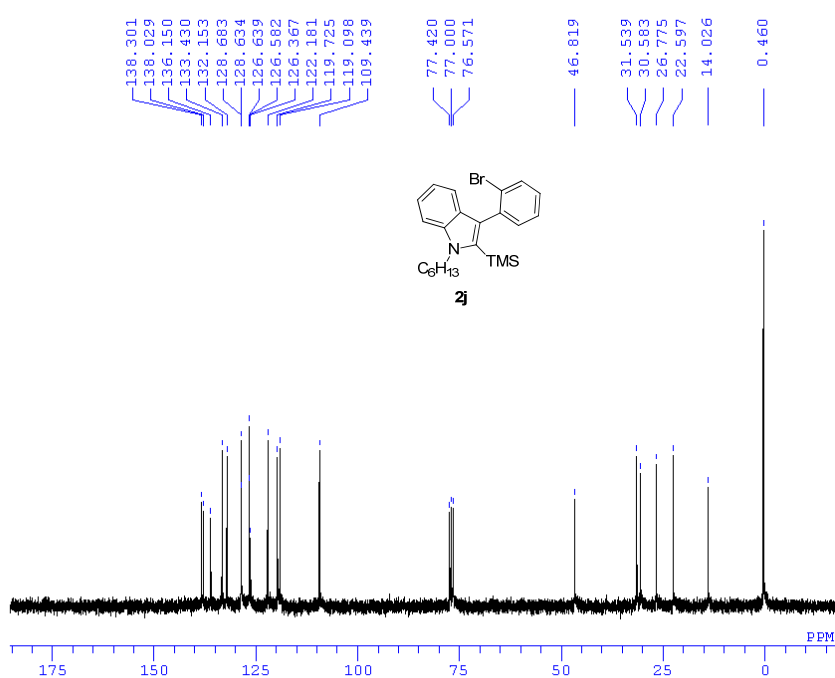






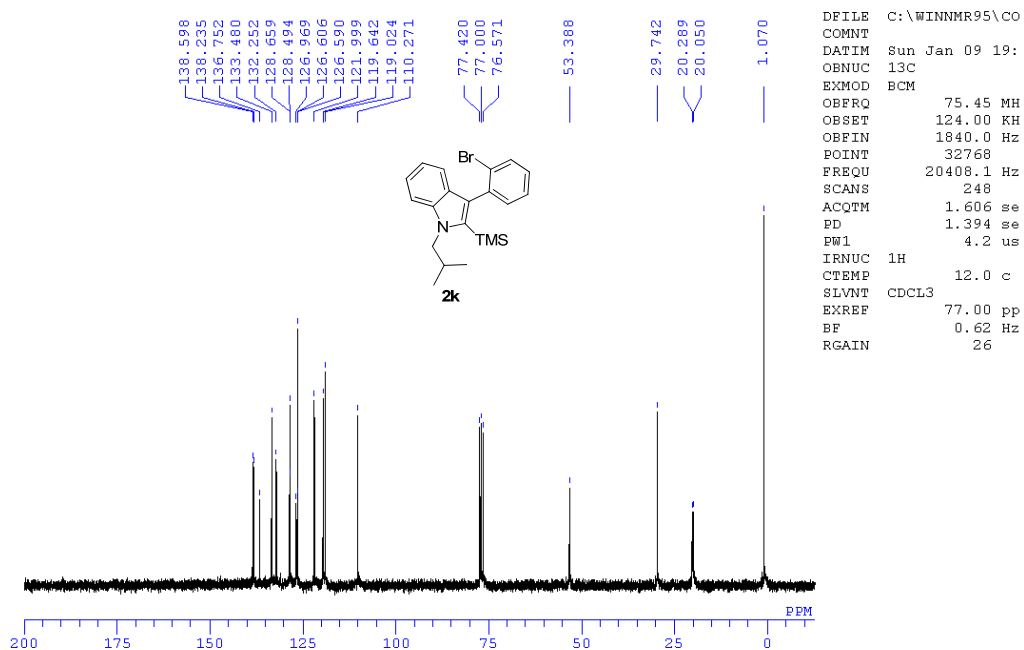
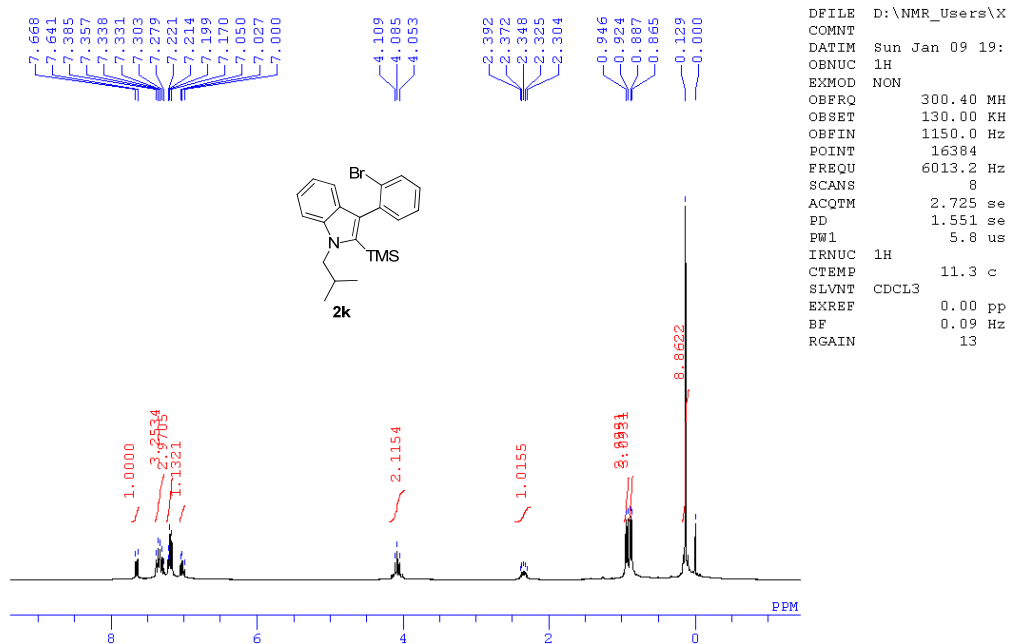
```

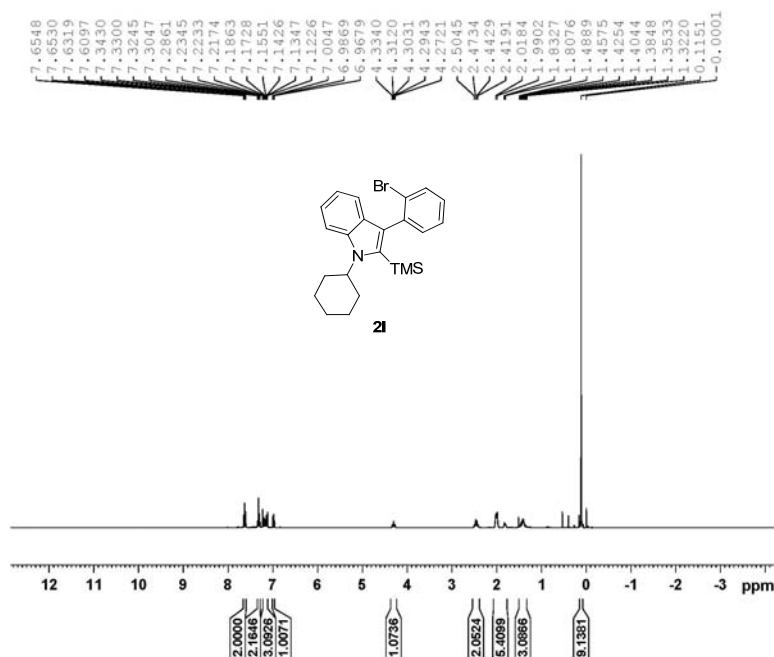
NAME      HMR10120976-6
EXPNO     1
PROCNO    1
Date_     20101230
Time      6.22
INSTRUM   ARX400
PROBHD    5 mm Multinu
PULPROG   zg
TD         32768
SOLVENT   CDCl3
NS         16
DS         0
SWH        6410.256 Hz
FIDRES     0.195625 Hz
AQ         2.5559540 sec
RG         256
DM         78.000 usec
DE         111.43 usec
TE         300.0 K
D1         2.00000000 sec
P1         3.00 usec
DE         111.43 usec
SFO1       400.1321971 MHz
NUC1       1H
SI         16384
SF         400.1300267 MHz
WCM        no
SSB        0
LB         0.00 Hz
GB         0
PC         4.00
  
```



```

DFILE      D:\NMR_Users\X
COMNT      Tue Nov 30 18:
OBNUC      13C
EXMOD      BCM
OBFRQ       75.45 MH
OBSET       124.00 KH
OBFIN       1840.0 Hz
POINT       32768
FREQU       20408.1 Hz
SCANS       88
ACQTM       1.606 se
PD          1.394 se
PW1         4.2 us
IRNUC      1H
CTEMP       13.9 c
SLVNT       CDCL3
EXREF       77.00 pp
BF          0.62 Hz
RGAIN       25
  
```

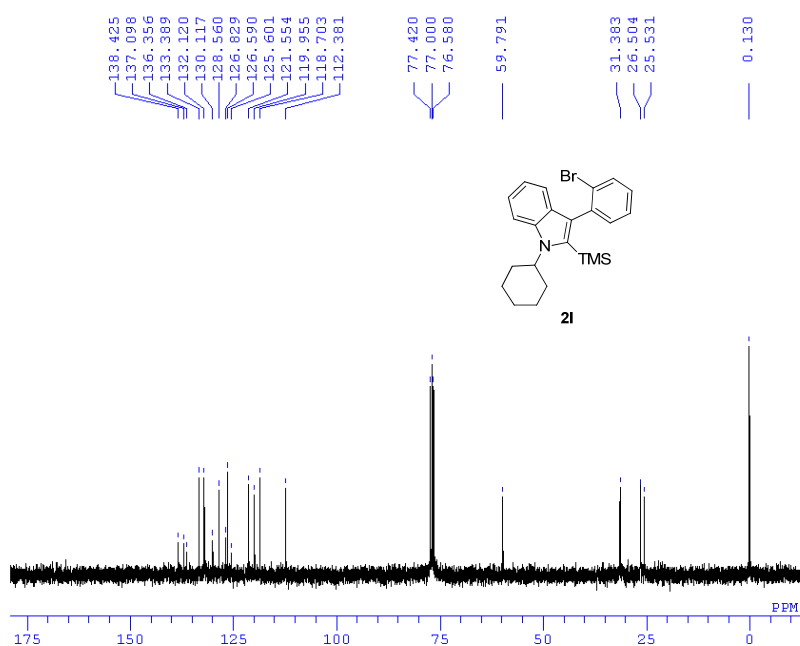




```

NAME      HNMR11010556-1
EXPNO     1
PROCNO    1
Date_     20110115
Time      7.37
INSTRUM   ARX400
PROBHD    5 mm Multinu
PULPROG   zg
TD         32768
SOLVENT   CDCl3
NS         16
DS         0
SWH        8064.516 Hz
FIDRES     0.346110 Hz
AQ         2.0316660 sec
RG         512
DM         62.000 usec
DE         88.57 usec
TE         300.0 K
D1         2.00000000 sec
P1         3.00 usec
DE         88.57 usec
SFO1       400.1321971 MHz
NUC1       1H
SI         16384
SF         400.1300193 MHz
WCM        no
SSB        0
LB         0.00 Hz
GB         0
PC         4.00

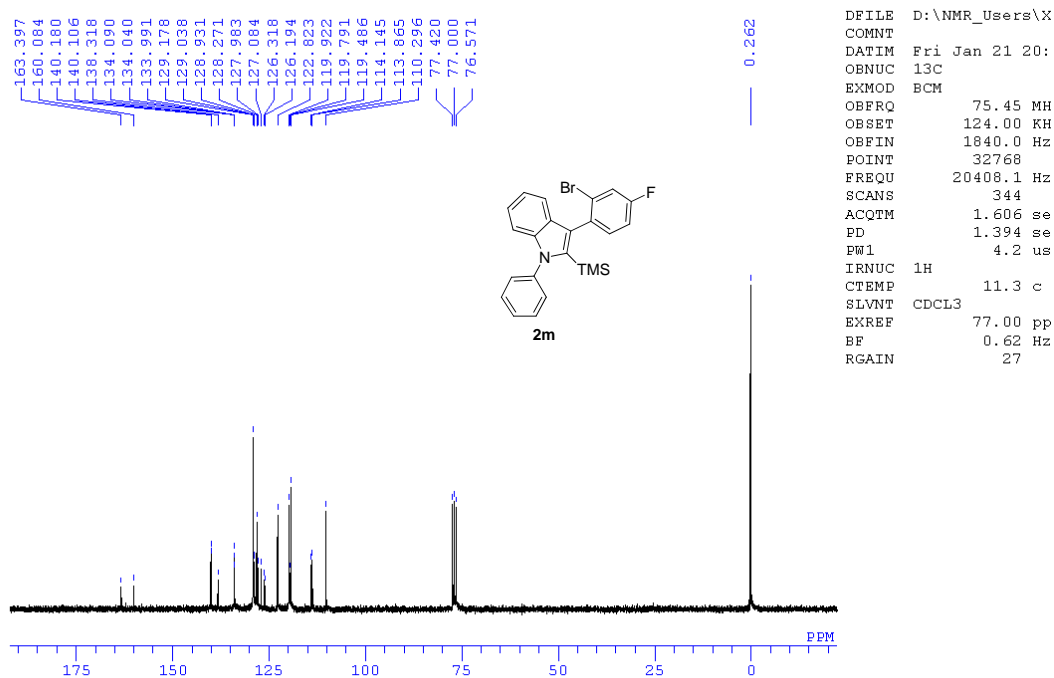
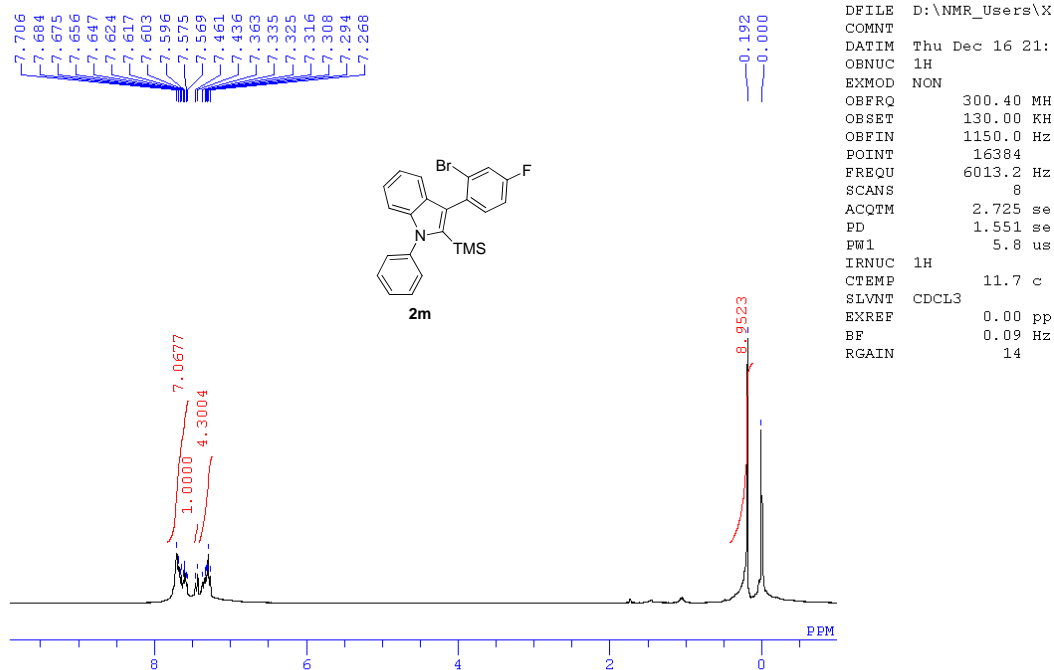
```

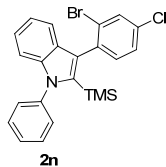
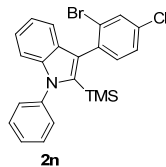


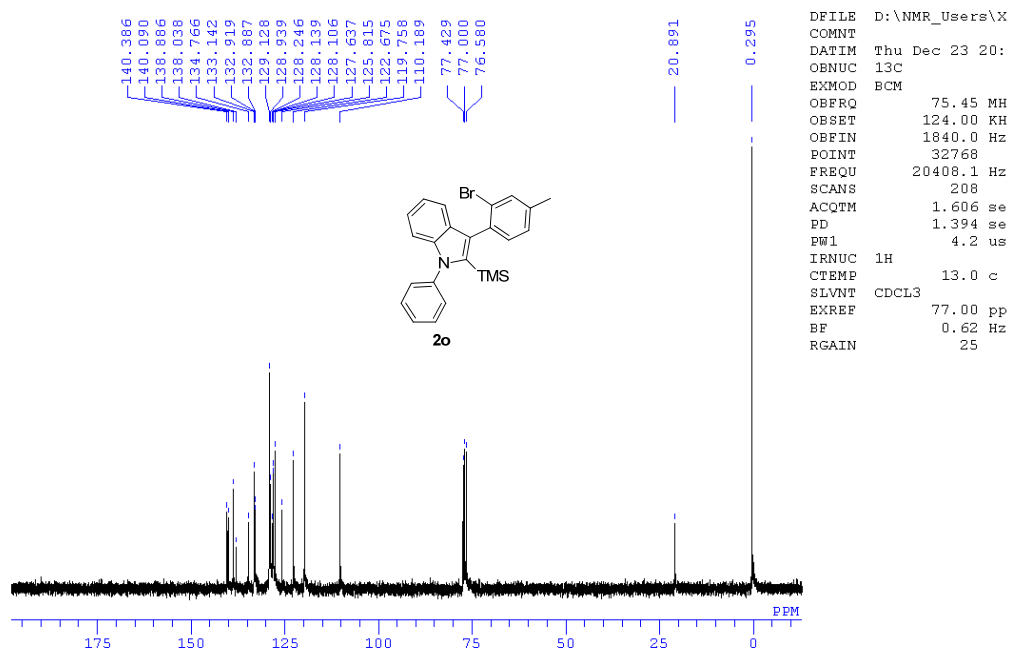
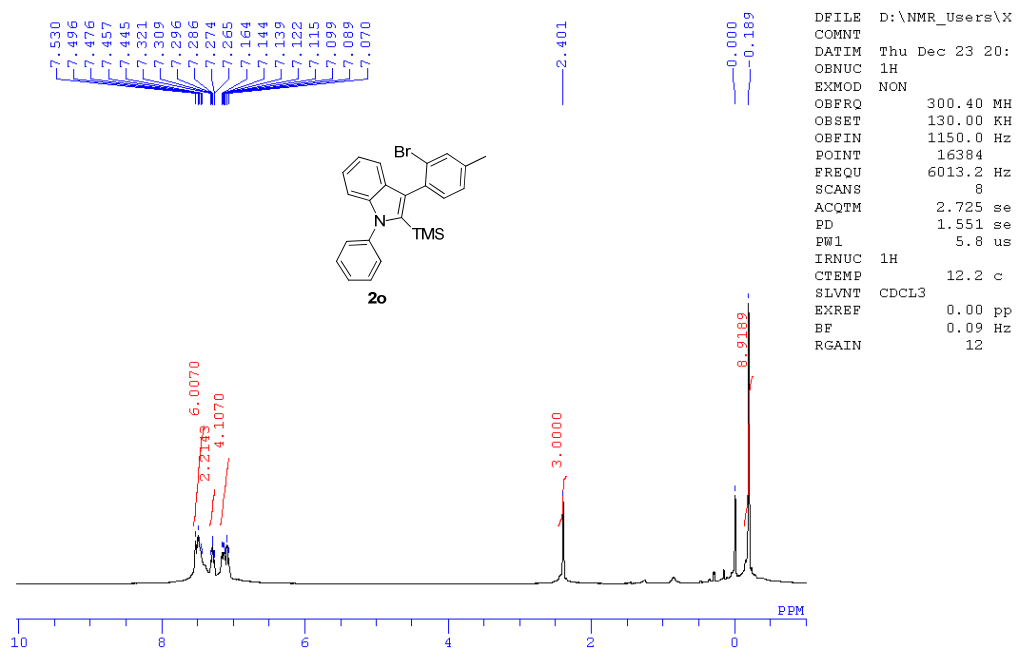
```

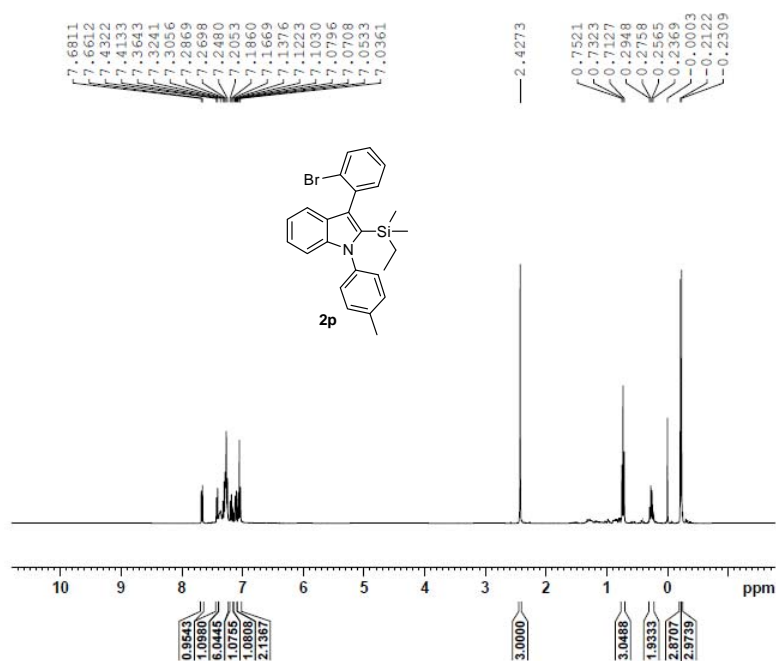
DFILE     D:\NMR_Users\X
COMNT
DATIM     Fri Jan 14 19:
OBNUC     13C
EXMOD     BCM
OBFRQ      75.45 MH
OBSET      124.00 KH
OBFIN      1840.0 Hz
POINT      32768
FREQU      20408.1 Hz
SCANS      160
ACQTM      1.606 se
PD         1.394 se
PW1        4.2 us
IRNUC      1H
CTEMP      19.9 c
SLVNT      CDCL3
EXREF      77.00 pp
BF         0.62 Hz
RGAIN      26

```



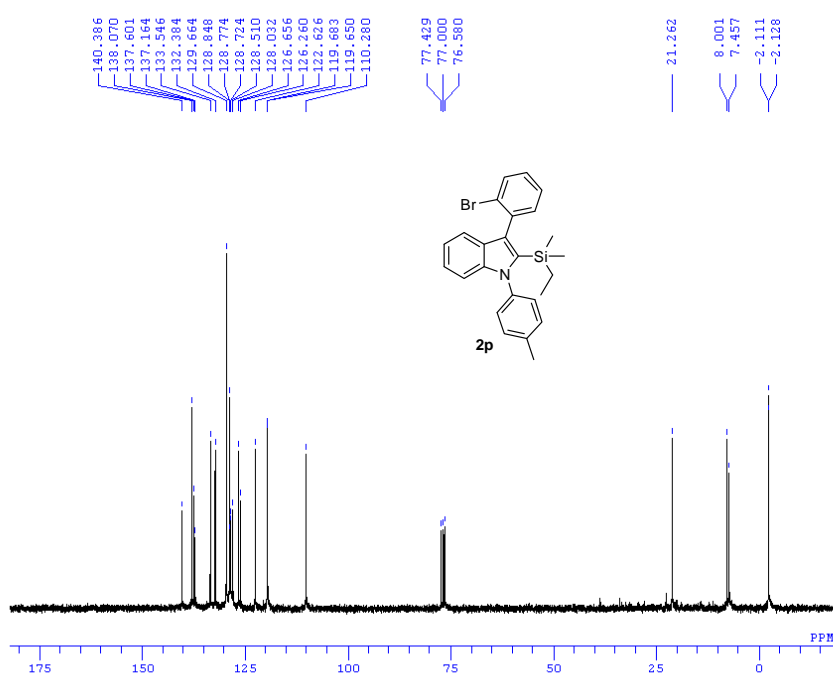






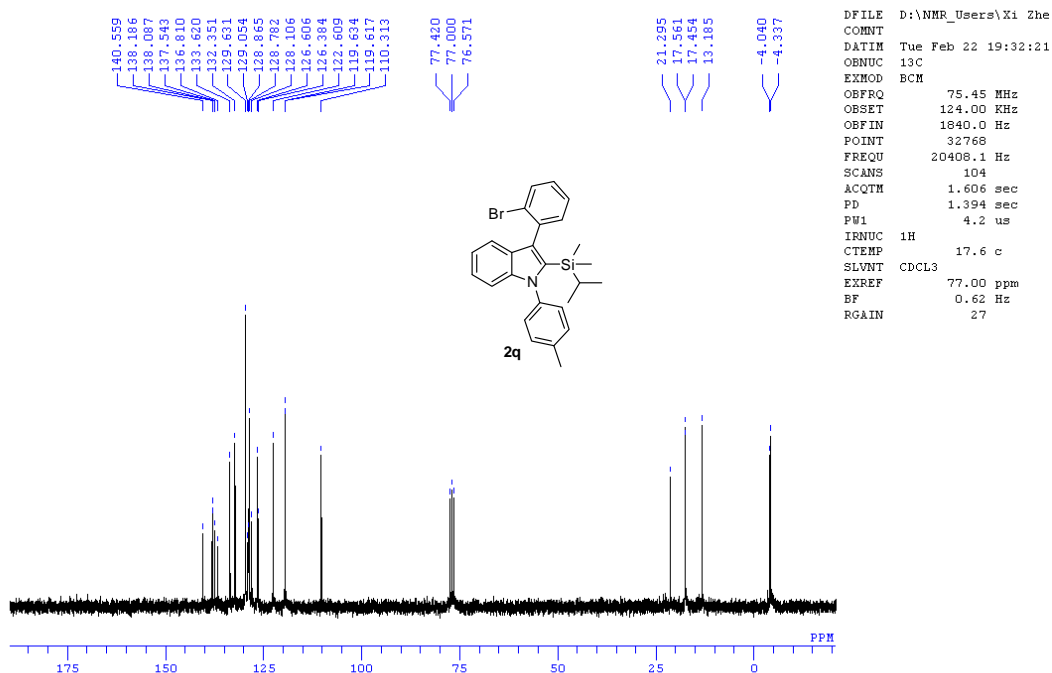
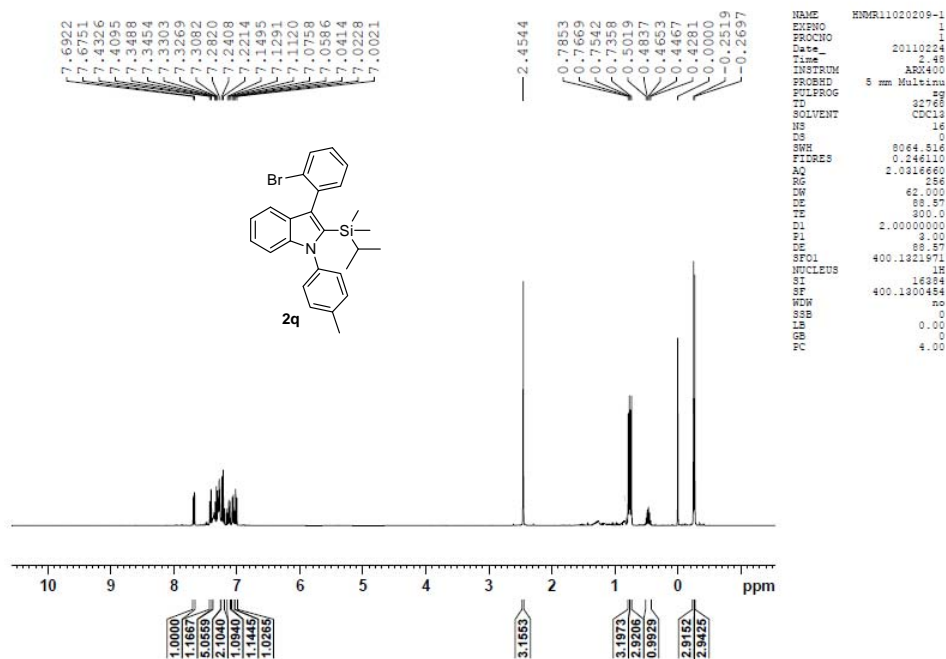
```

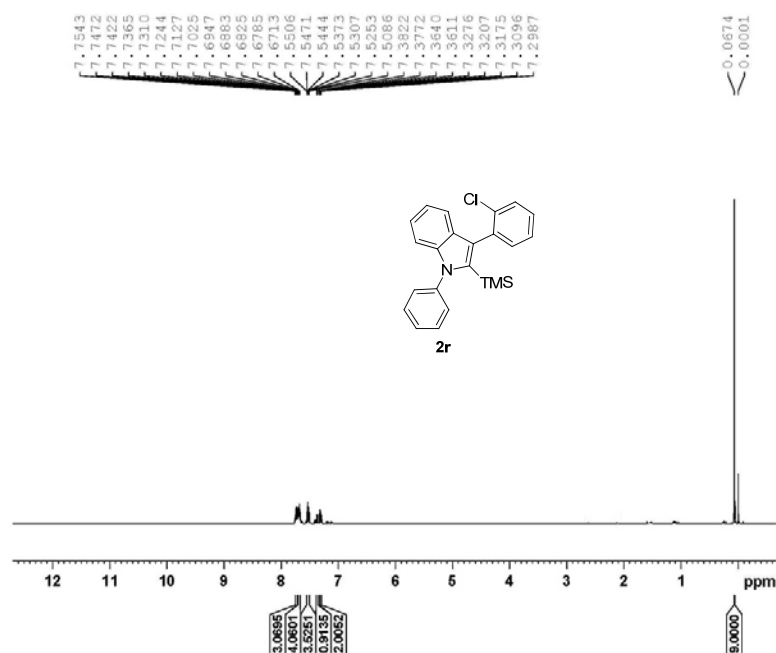
NAME      HMR11020260
EXPNO     1
PROCNO    1
Date_     20110221
Time      1.00
INSTRUM    ARX400
PROBHD     5 mm Multinu
PULPROG    zgpg30
TD          32768
SOLVENT    CDCl3
NS          22
DS          0
SWH         8064.816 Hz
FIDRES     0.246110 Hz
AQ          2.0316660 sec
RG          60
RG2         62.000 usec
RG3         68.57 usec
TE          300.0 K
D1          2.00000000 sec
d11         3.00 usec
DE          68.57 usec
SFO1       400.1321971 MHz
NUCLEUS    1H
SI          16384
SF          400.1300000 MHz
WDW         no
SSB         0
LB          0.00 Hz
GB          0
PC          4.00
  
```



```

DFILE      C:\WINNMR95\COMMON\
COMNT
DATIM      Wed Feb 23 21:05:56
OBNUC      13C
EXMOD      BCM
OBFRQ       75.45 MHz
OBSET       124.00 KHz
OBFIN       1840.0 Hz
POINT       32768
FREQU       20408.1 Hz
SCANS       168
AQTM        1.606 sec
PD           1.394 sec
PW1         4.2 us
IRNUC       1H
CTEMP       15.9 c
SLVNT       CDCL3
EXREF       77.00 ppm
BF           0.62 Hz
RGAIN       25
  
```

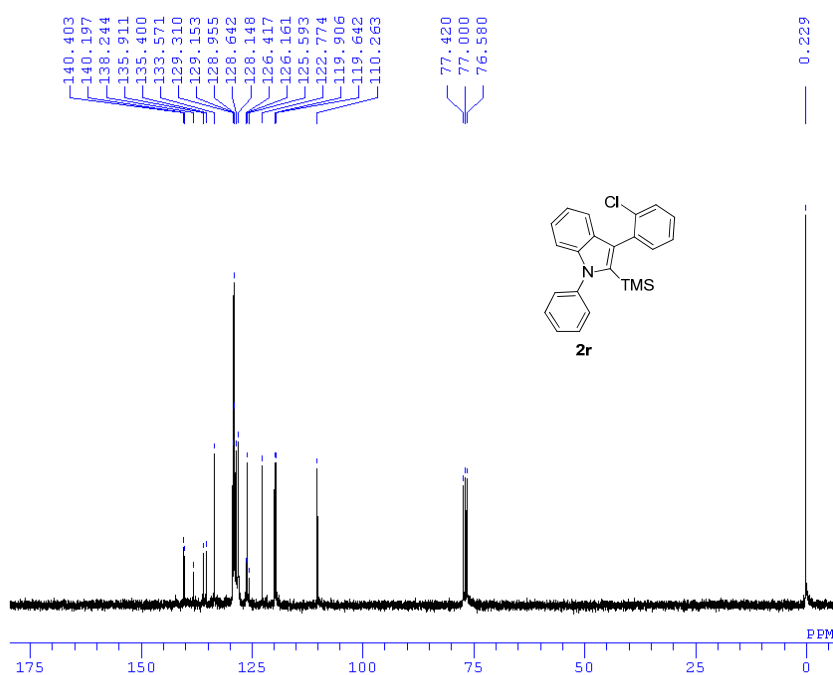




```

NAME      HMN11010484-2
EXPNO     1
PROCNO    1
Date_     20110114
Time      6.31
INSTRUM   ARX400
PROBHD    5 mm Multinu
PULPROG   zgpg30
TD         32768
SOLVENT   CDCl3
NS         32
DS         0
SWH        8064.516 Hz
FIDRES     0.246110 Hz
AQ         2.0316660 sec
RG         256
DM         62.000 usec
DE         88.57 usec
TE         300.0 K
D1         2.00000000 sec
P1         3.00 usec
DE         88.57 usec
SFO1       400.1321971 MHz
NUC1       1H
SI         16384
SF         400.1299460 MHz
WDW        no
SSB        0
LB         0.00 Hz
GB         0
PC         4.00

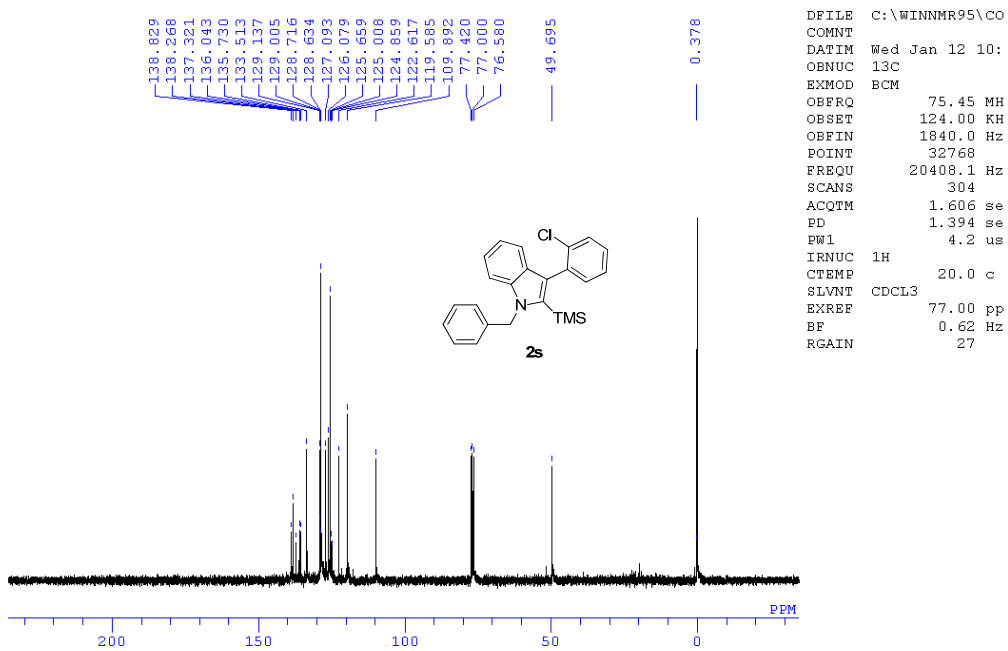
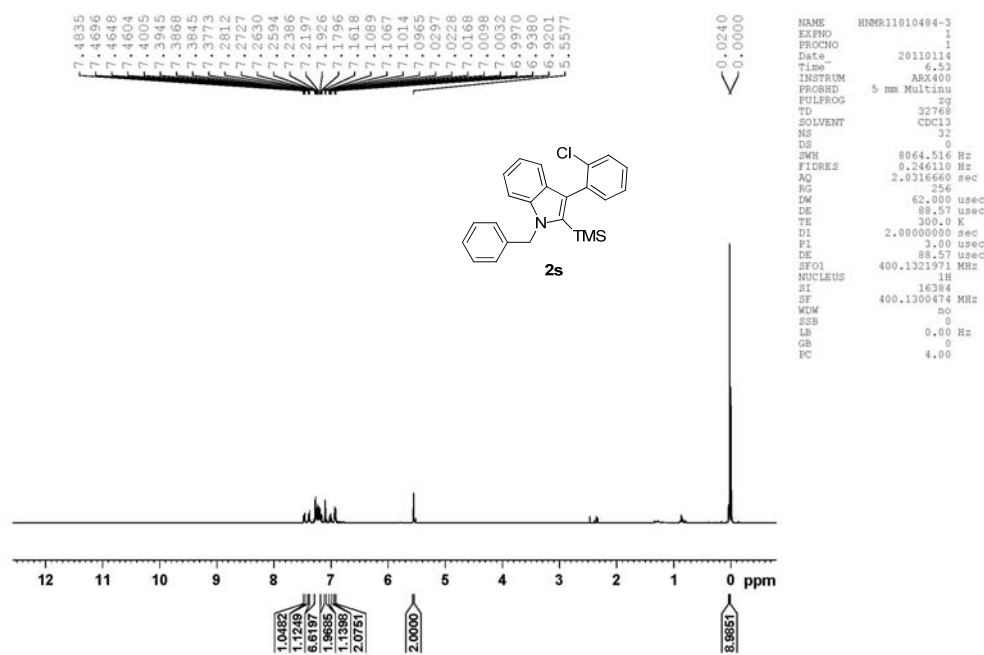
```

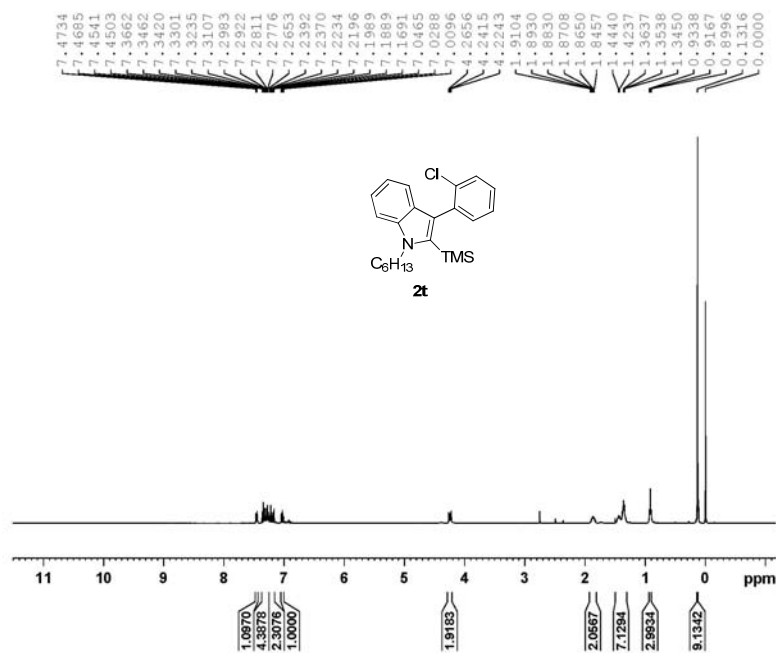


```

DFILE      D:\NMR_Users\X
COMNT      Wed Jan 12 09:
OBNUC      13C
EXMOD      BCM
OBFRQ       75.45 MH
OBSET       124.00 KH
OBFIN       1840.0 Hz
POINT       32768
FREQU       20408.1 Hz
SCANS       304
ACQTM       1.606 se
PD          1.394 se
PW1         4.2 us
IRNUC       1H
CTEMP       19.8 c
SLVNT       CDCL3
EXREF       77.00 pp
BF          0.62 Hz
RGAIN       27

```

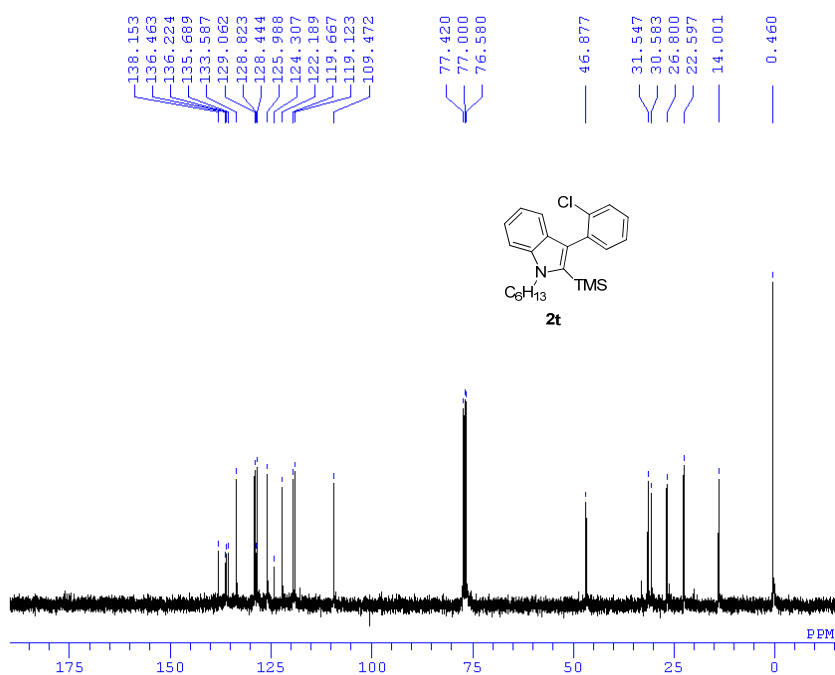




```

NAME      HNMR11010316-2
EXPNO     1
PROCNO    1
Date_     20110112
Time      1.35
INSTRUM   ARX400
PROBHD    5 mm Multinu
PULPROG   zg
TD         32768
SOLVENT   CDCl3
NS         64
DS         0
SWH        8064.516 Hz
FIDRES     0.246110 Hz
AQ         2.0316660 sec
RG         256
DM         62.000 usec
DE         88.57 usec
TE         300.0 K
D1         2.00000000 sec
P1         3.00 usec
DE         88.57 usec
SFO1       400.1321971 MHz
NUC1       1H
SI         16384
SF         400.1300237 MHz
WCM        no
SSB        0
LB         0.00 Hz
GB         0
PC         1.00

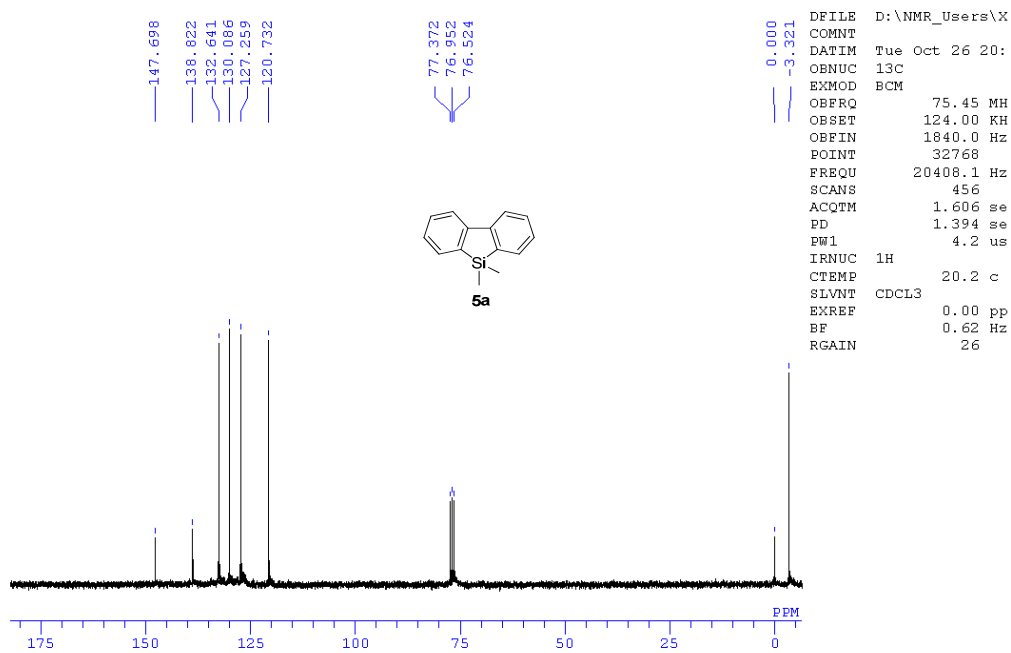
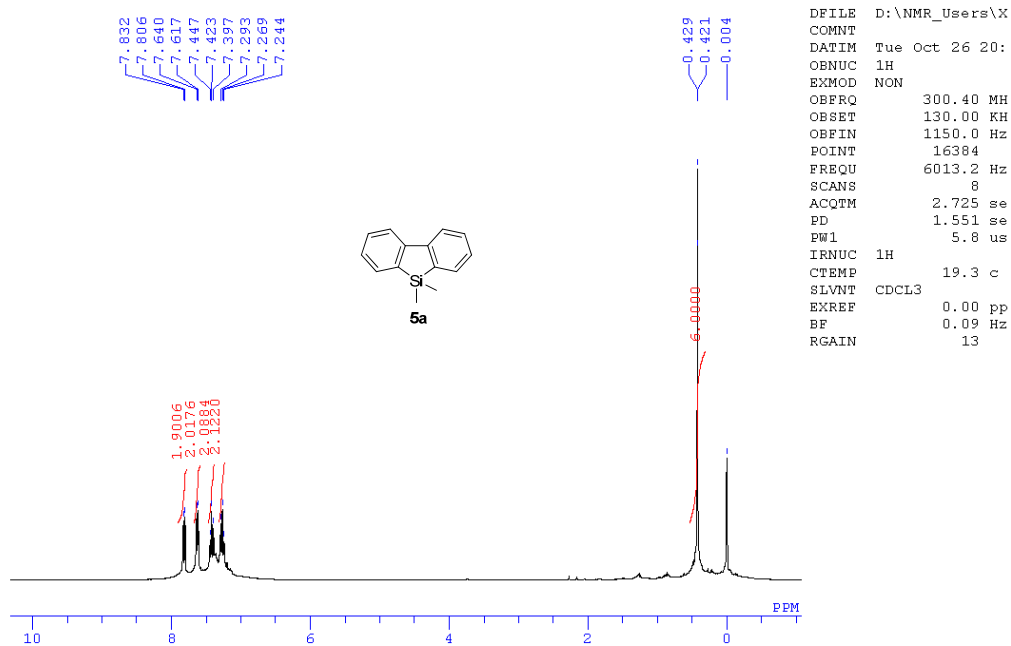
```

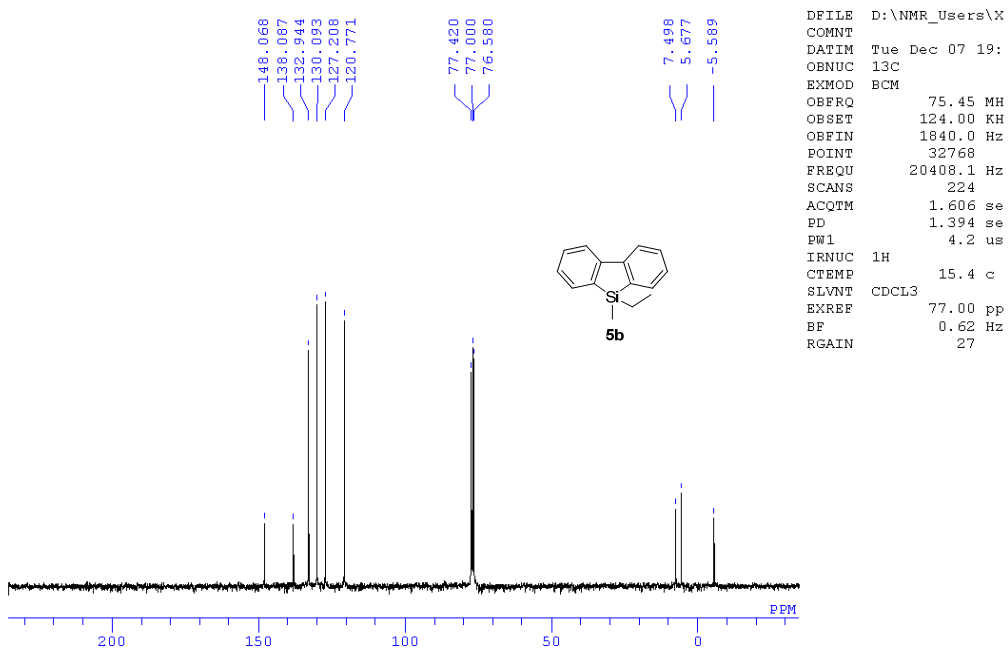
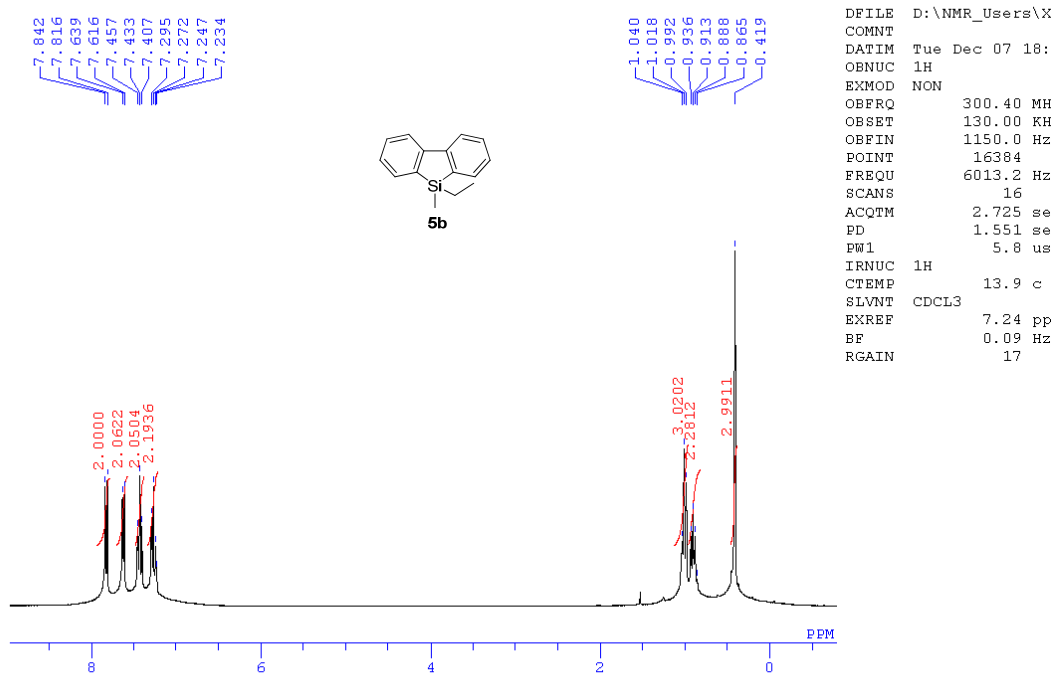


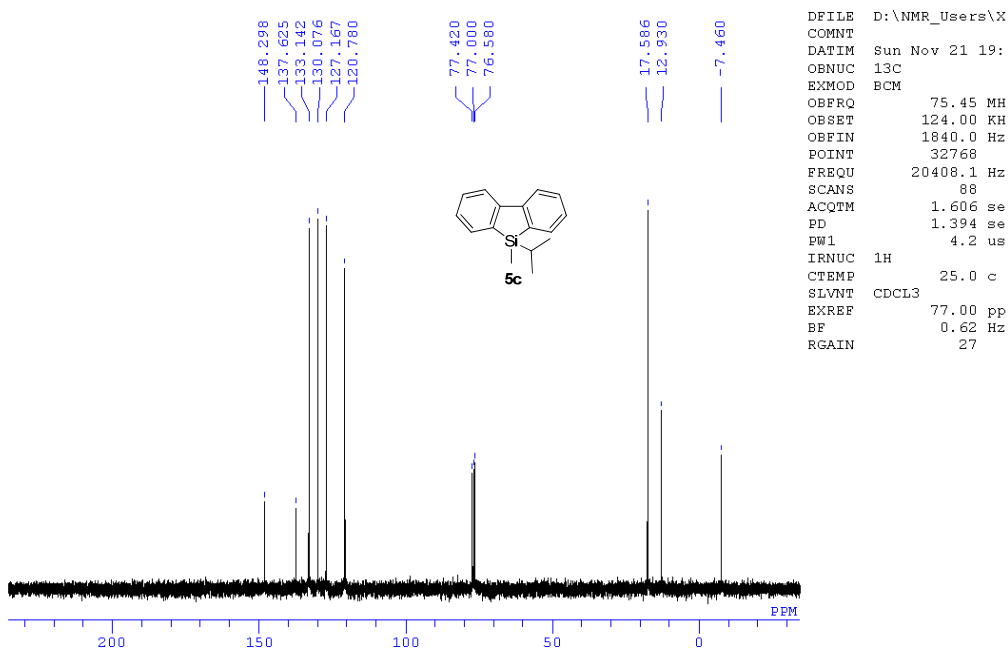
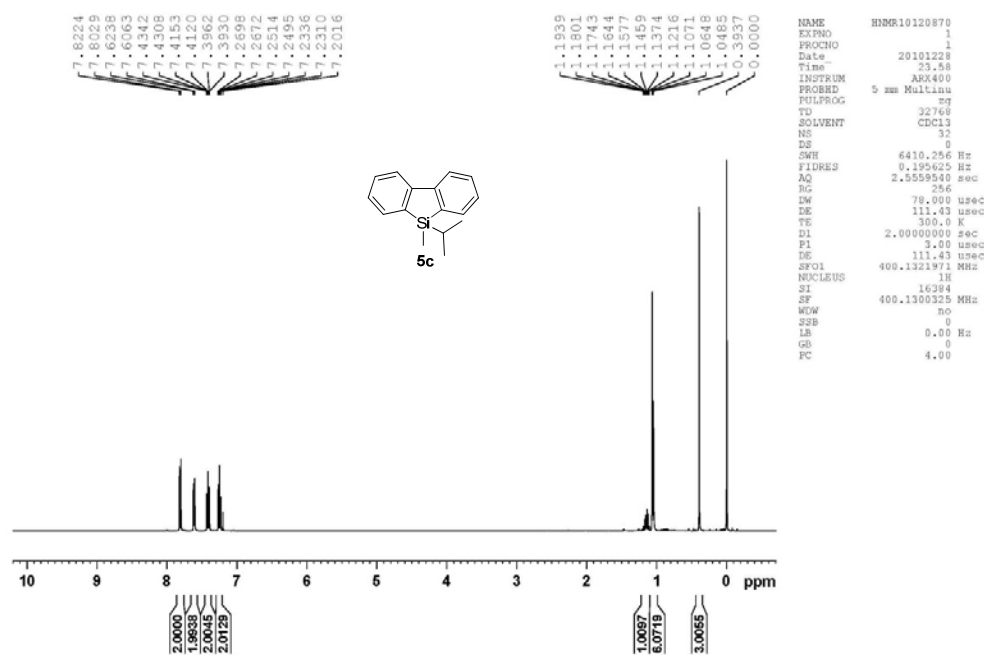
```

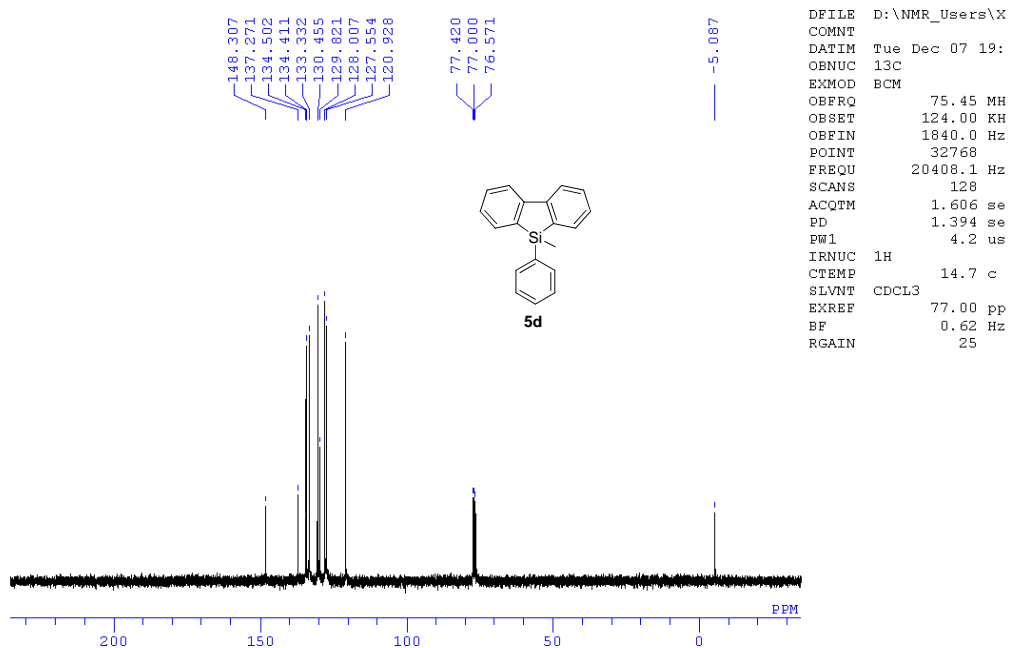
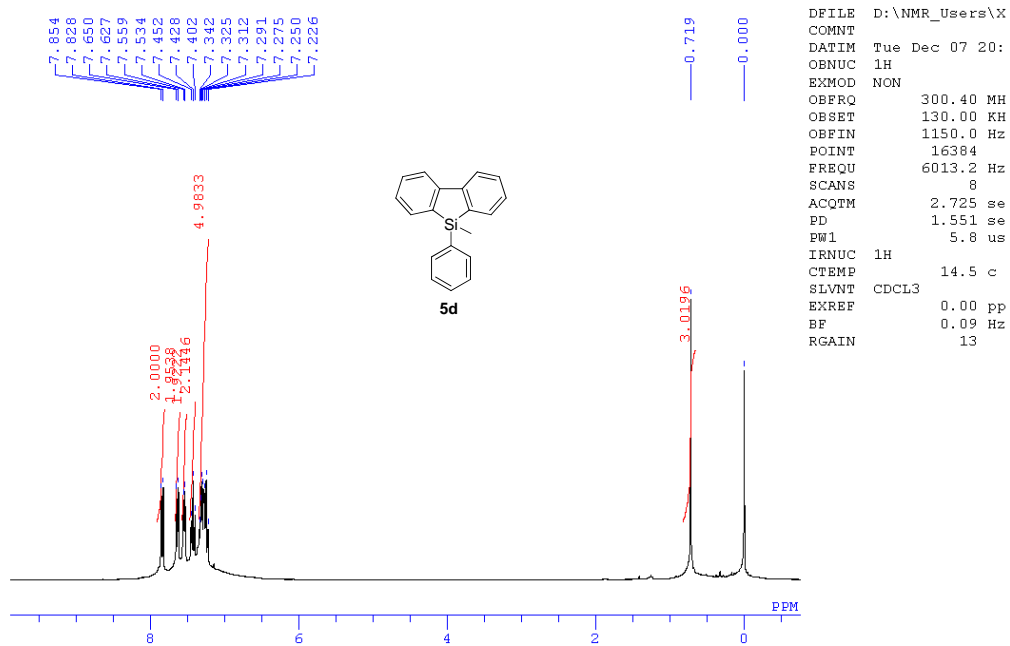
DFILE     D:\NMR_Users\X
COMNT     Mon Jan 10 21:
OBNUC     13C
EXMOD     BCM
OBFRQ      75.45 MH
OBSET      124.00 KH
OBFIN      1840.0 Hz
POINT      32768
FREQU      20408.1 Hz
SCANS      304
ACQTM      1.606 se
PD         1.394 se
PW1        4.2 us
IRNUC      1H
CTEMP      18.3 c
SLVNT      CDCL3
EXREF      77.00 pp
BF         0.62 Hz
RGAIN      26

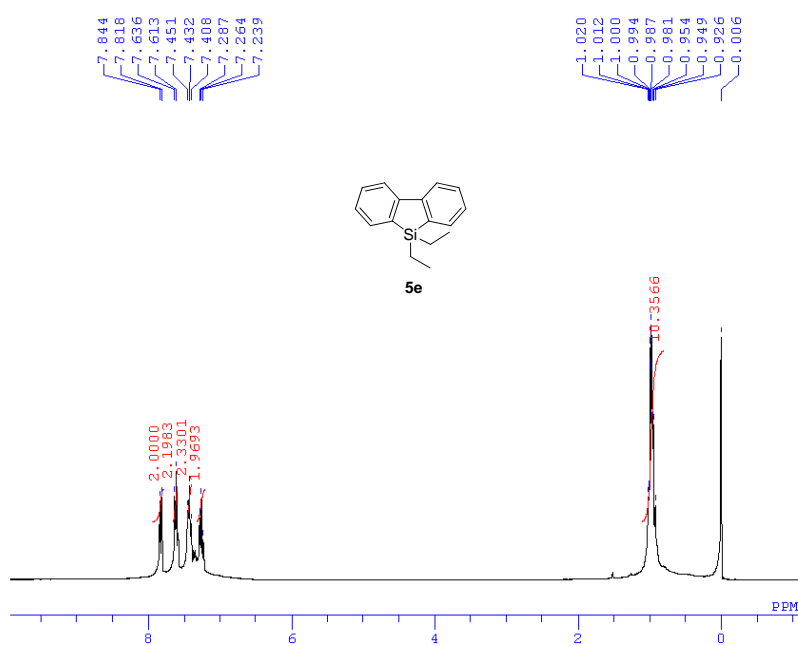
```



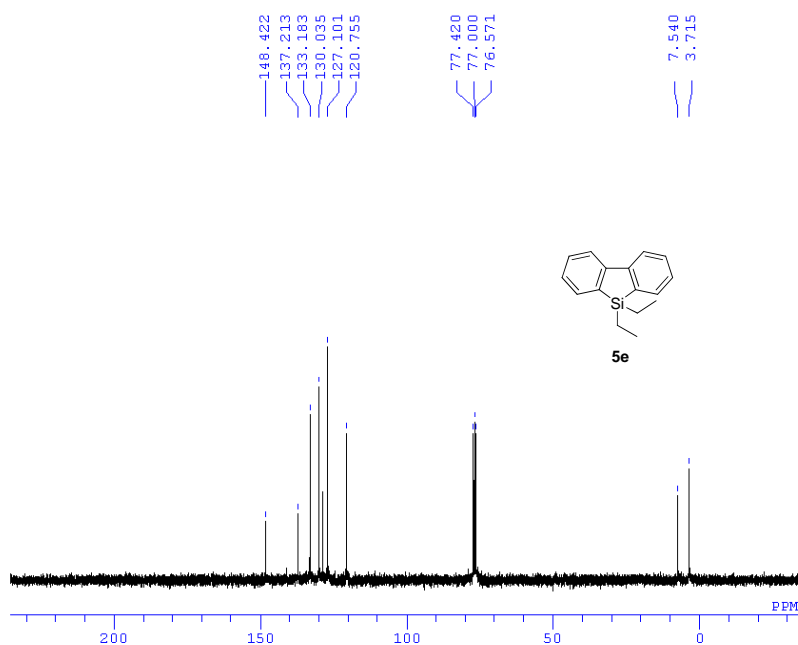




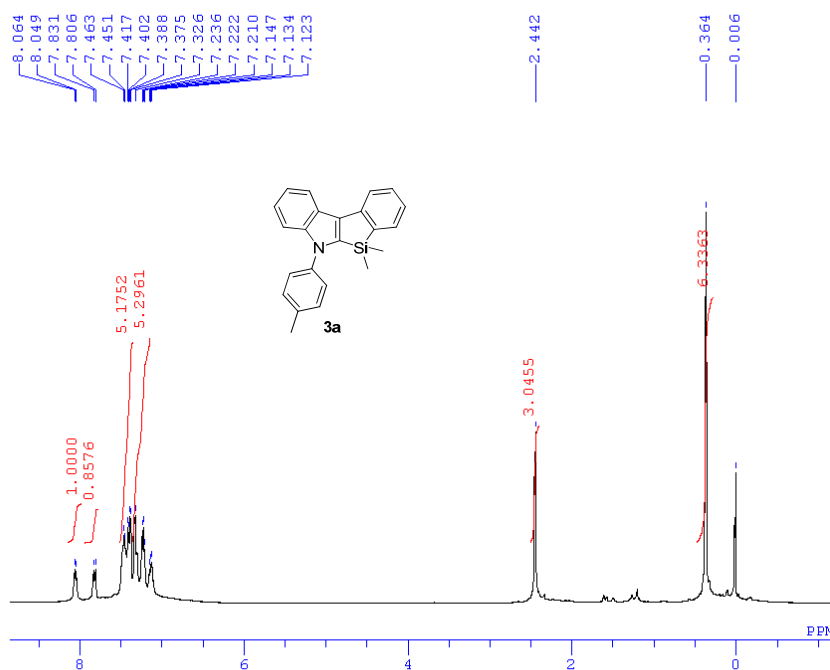




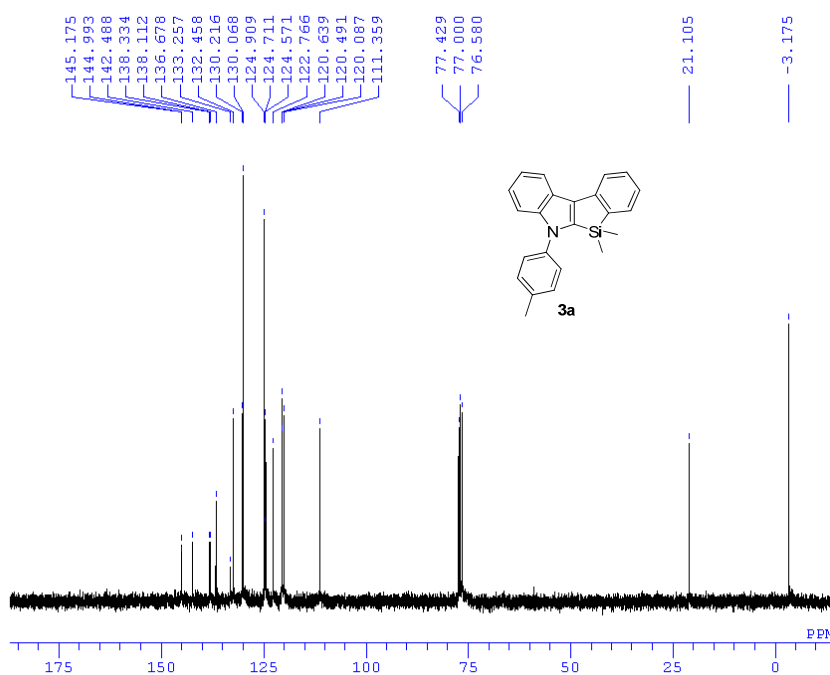
DFILE D:\NMR_Users\X
 COMNT
 DATIM Thu Dec 16 20:
 OBNUC ¹H
 EXMOD NON
 OBFRQ 300.40 MH
 OBSET 130.00 KH
 OBFIN 1150.0 Hz
 POINT 16384
 FREQU 6013.2 Hz
 SCANS 16
 ACQTM 2.725 se
 PD 1.551 se
 PW1 5.8 us
 IRNUC ¹H
 CTEMP 12.0 c
 SLVNT CDCL3
 EXREF 0.00 pp
 BF 0.09 Hz
 RGAIN 14



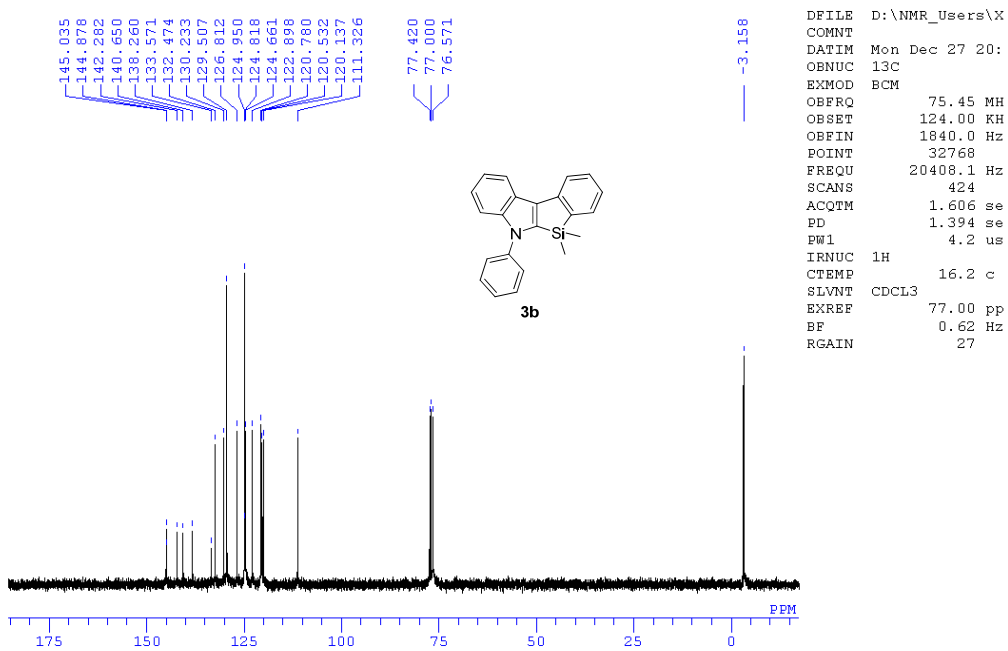
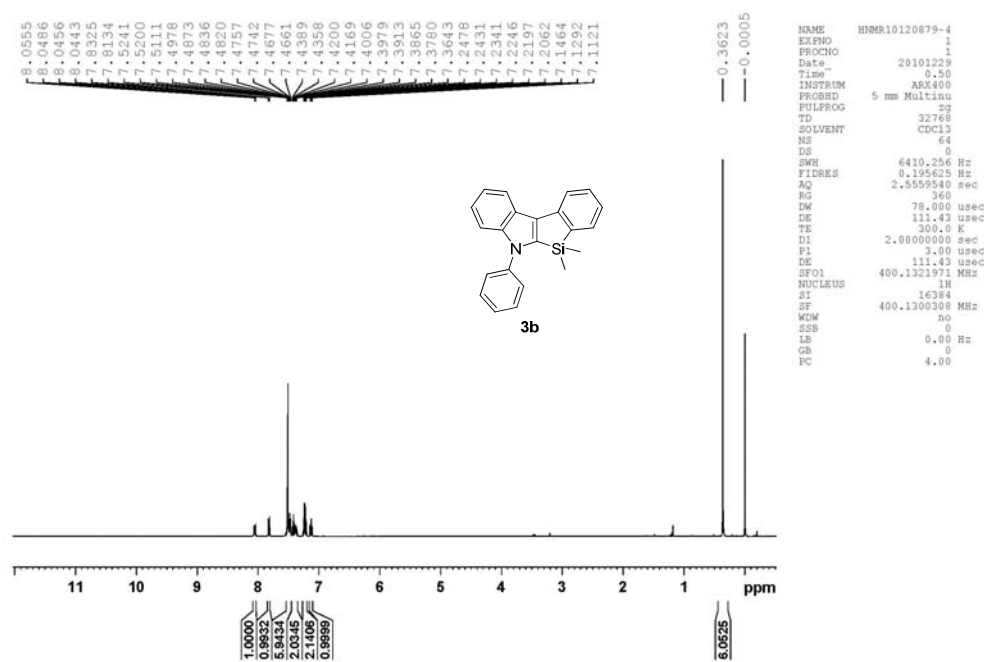
DFILE D:\NMR_Users\X
 COMNT
 DATIM Thu Dec 16 20:
 OBNUC ¹³C
 EXMOD BCM
 OBFRQ 75.45 MH
 OBSET 124.00 KH
 OBFIN 1840.0 Hz
 POINT 32768
 FREQU 20408.1 Hz
 SCANS 344
 ACQTM 1.606 se
 PD 1.394 se
 PW1 4.2 us
 IRNUC ¹H
 CTEMP 12.2 c
 SLVNT CDCL3
 EXREF 77.00 pp
 BF 0.62 Hz
 RGAIN 25

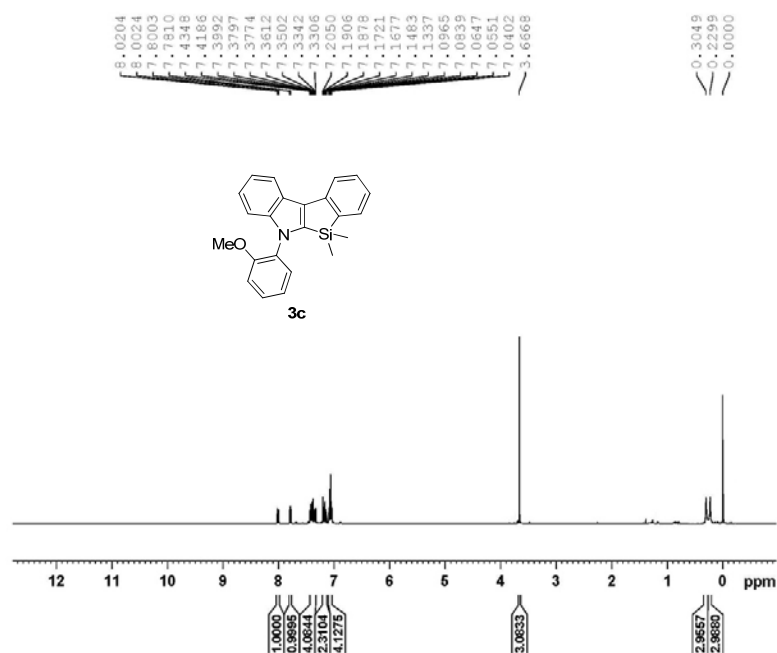


DFILE D:\NMR_Users\X
 COMNT
 DATIM Fri Dec 10 20:
 OBNUC ¹H
 EXMOD NON
 OBFRQ 300.40 MH
 OBSET 130.00 KH
 OBFIN 1150.0 Hz
 POINT 16384
 FREQU 6013.2 Hz
 SCANS 16
 ACQTM 2.725 se
 PD 1.551 se
 PW1 5.8 us
 IRNUC ¹H
 CTEMP 20.6 c
 SLVNT CDCL3
 EXREF 0.00 pp
 BF 0.09 Hz
 RGAIN 15



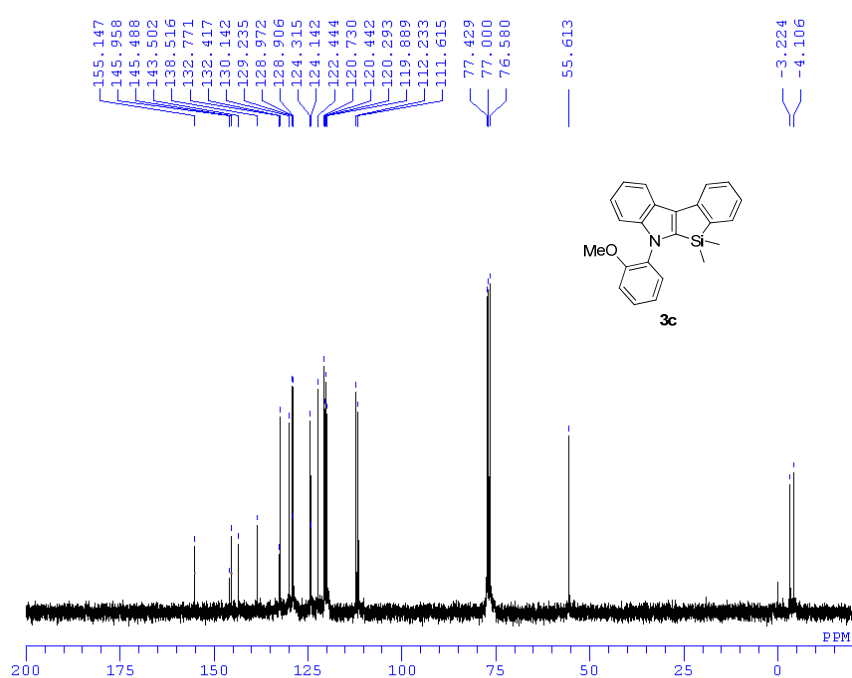
DFILE D:\NMR_Users\X
 COMNT
 DATIM Fri Dec 10 20:
 OBNUC ¹³C
 EXMOD BCM
 OBFRQ 75.45 MH
 OBSET 124.00 KH
 OBFIN 1840.0 Hz
 POINT 32768
 FREQU 20408.1 Hz
 SCANS 288
 ACQTM 1.606 se
 PD 1.394 se
 PW1 4.2 us
 IRNUC ¹H
 CTEMP 21.4 c
 SLVNT CDCL3
 EXREF 77.00 pp
 BF 0.62 Hz
 RGAIN 26





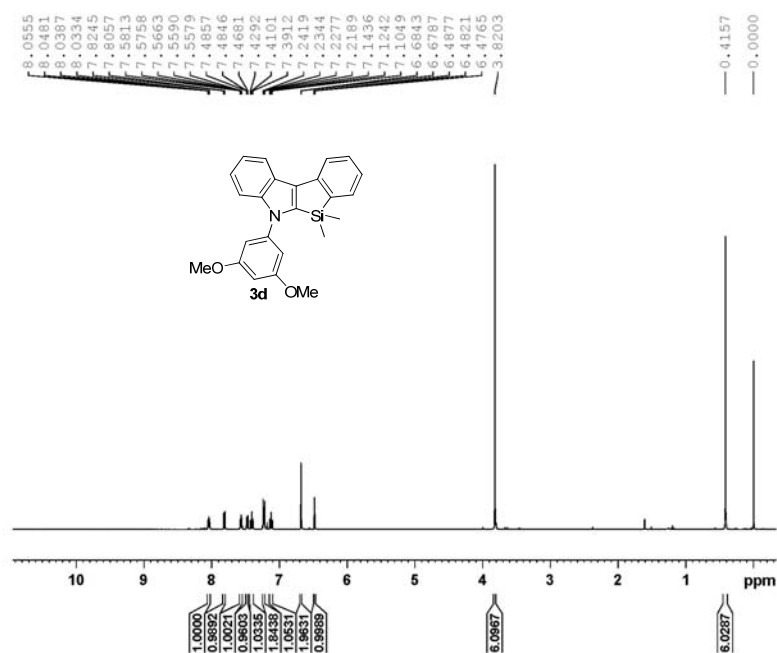
```

NAME  HMN11010484-1
EXPNO  1
PROCNO  1
Date_   20110114
Time    6.24
INSTRUM  ARX400
PROBHD  5 mm Multinu
PULPROG  zgpg
TD       32768
SOLVENT  CDCl3
NS       32
DS       0
SWH      8064.516 Hz
FIDRES   0.246110 Hz
AQ       2.0316660 sec
RG       512
DM       62.000 usec
DE       88.57 usec
TE       300.0 K
D1       2.00000000 sec
P1       3.00 usec
DE       88.57 usec
SFO1     400.1321971 MHz
NUC1     1H
SI       16394
SF       400.1300301 MHz
WDW      no
SSB      0
LB       0.00 Hz
GB       0
PC       4.00
  
```



```

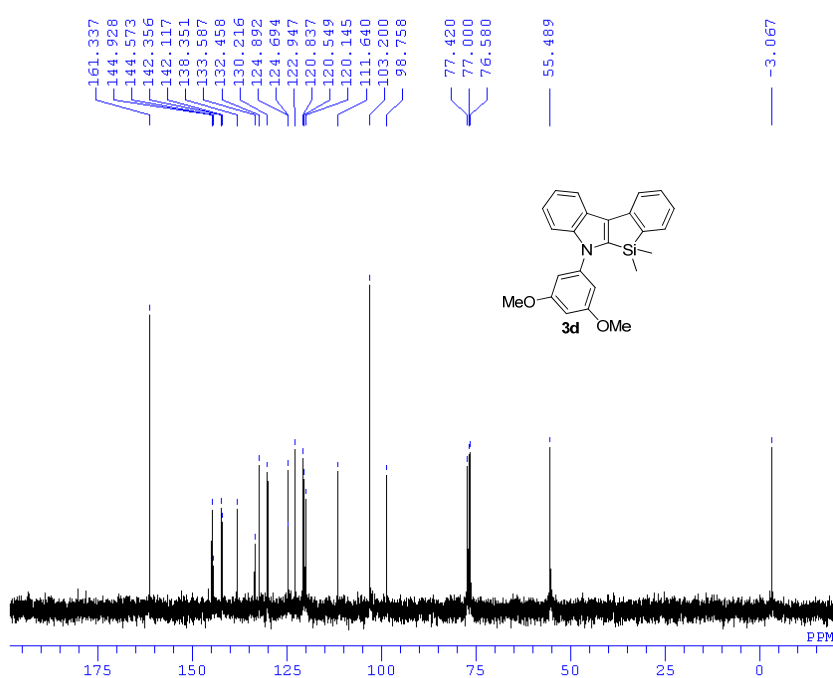
DFILE  C:\WINNMR95\CO
COMNT  Thu Jan 13 09:
OBNUC  13C
EXMOD  BCM
OBFRQ   75.45 MH
OBSET   124.00 KH
OBFIN   1840.0 Hz
POINT   32768
FREQU   20408.1 Hz
SCANS    640
ACQTM   1.606 se
PD       1.394 se
PWL      4.2 us
IRNUC   1H
CTEMP   20.3 c
SLVNT   CDCL3
EXREF   77.00 pp
BF       0.62 Hz
RGAIN    26
  
```



```

NAME      HNMR10120946-3
EXPNO     1
PROCNO    1
Date_     20101230
Time      0.58
INSTRUM   ARX400
PROBHD    5 mm Multinu
PULPROG   zg
TD         32768
SOLVENT   CDCl3
NS         16
DS         0
SWH        6410.256 Hz
FIDRES     0.195625 Hz
AQ         2.5559540 sec
RG         256
DM         78.000 usec
DE         111.43 usec
TE         300.0 K
D1         2.00000000 sec
P1         3.00 usec
DE         111.43 usec
SFO1       400.1321971 MHz
NUC1       1H
SI         16384
SF         400.1300408 MHz
WCM        no
SSB        0
LB         0.00 Hz
GB         0
PC         4.00

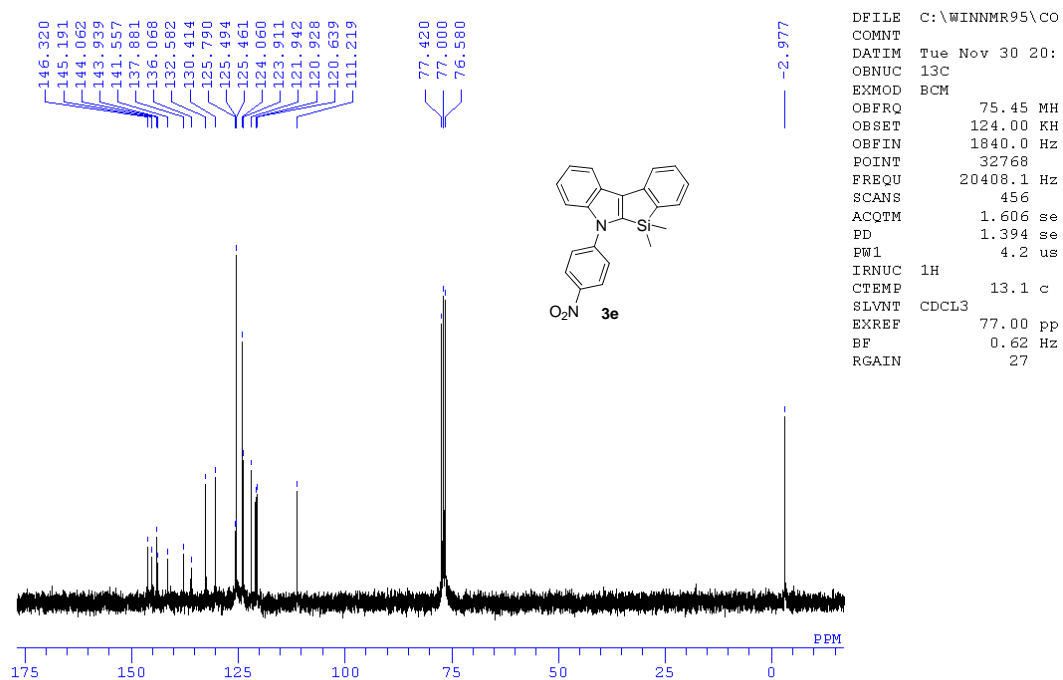
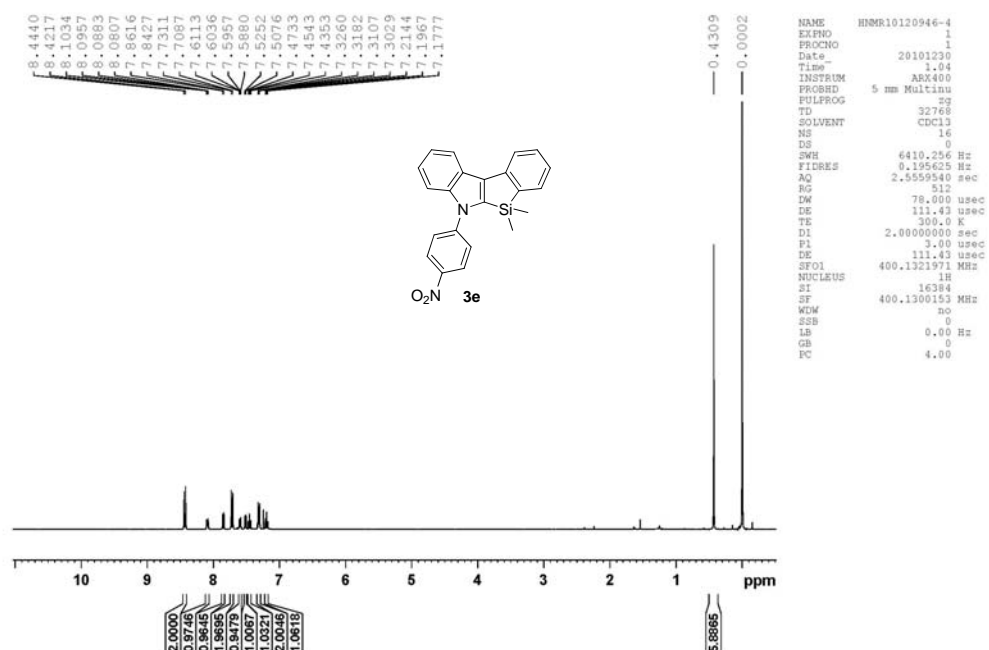
```

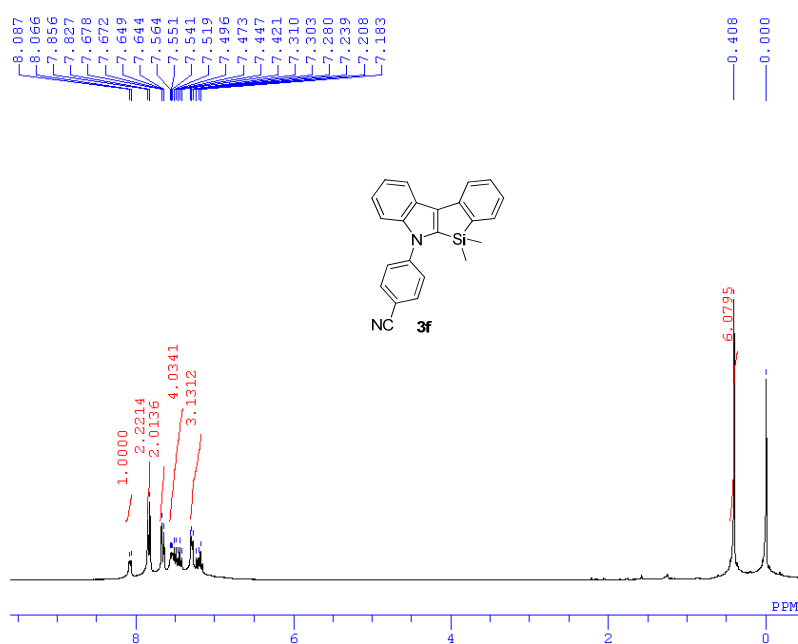


```

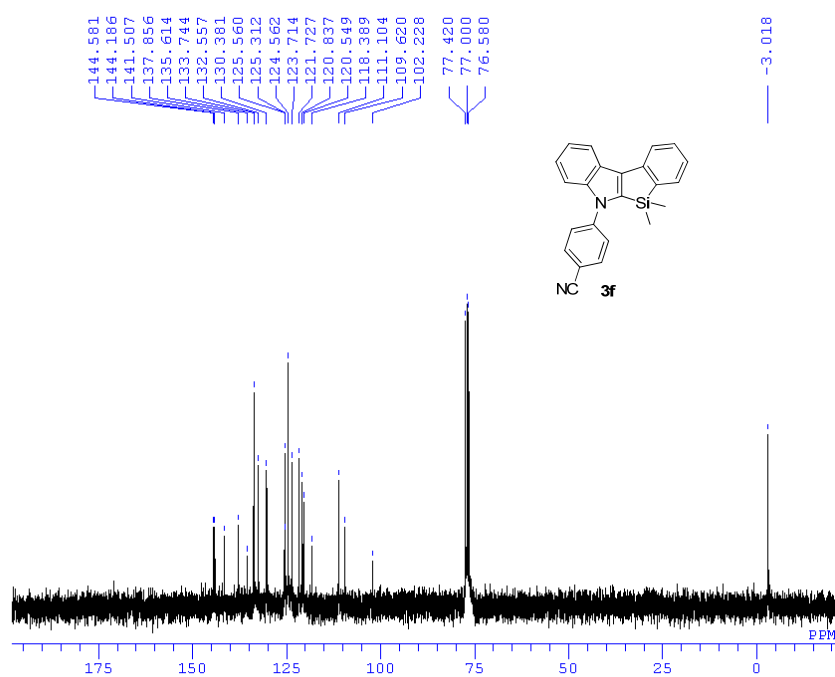
DFFILE    D:\NMR_Users\X
COMNT     Tue Dec 07 21:
OBNUC     13C
EXMOD     BCM
OBFRQ      75.45 MH
OBSET      124.00 KH
OBFIN      1840.0 Hz
POINT      32768
FREQU      20408.1 Hz
SCANS      56
ACQTM      1.606 se
PD         1.394 se
PW1        4.2 us
IRNUC      1H
CTEMP      15.4 c
SLVNT      CDCL3
EXREF      77.00 pp
BF         0.62 Hz
RGAIN      27

```

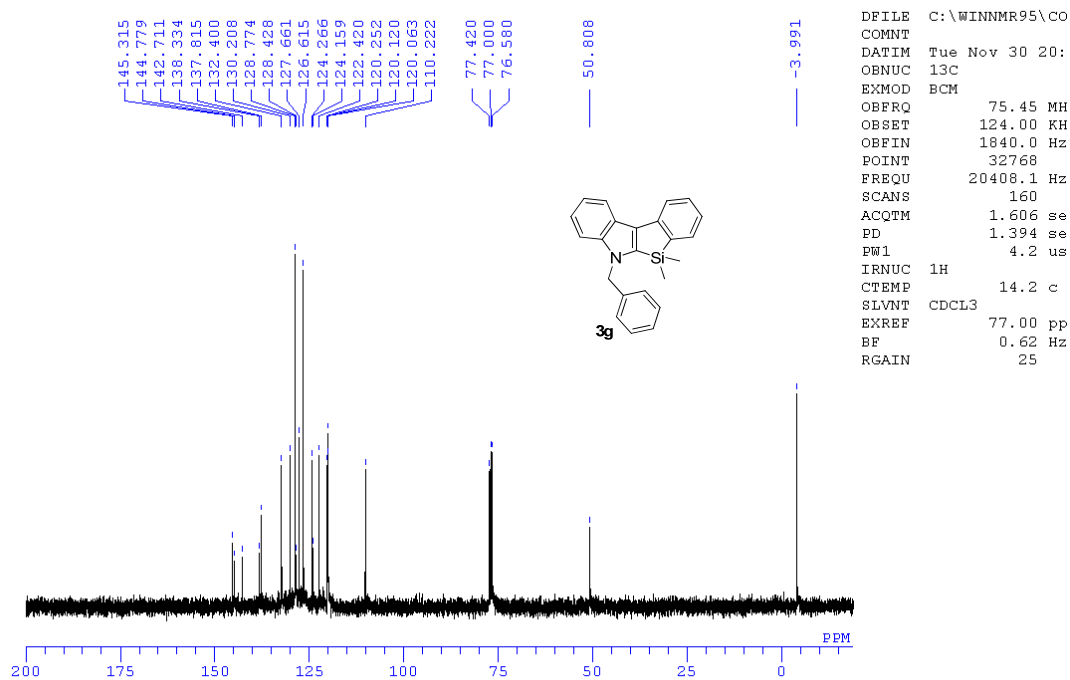
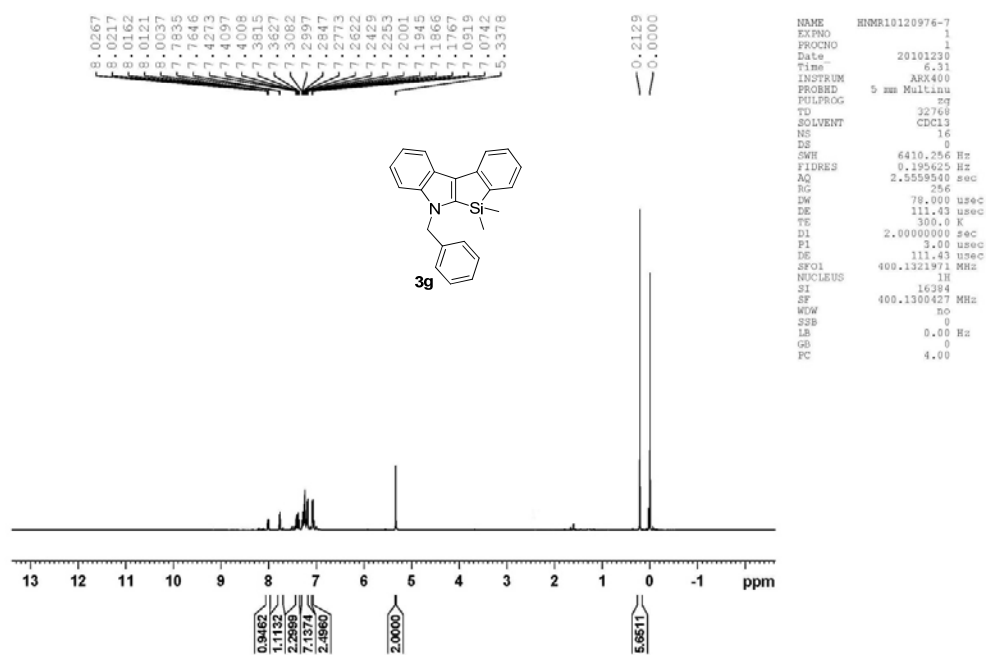


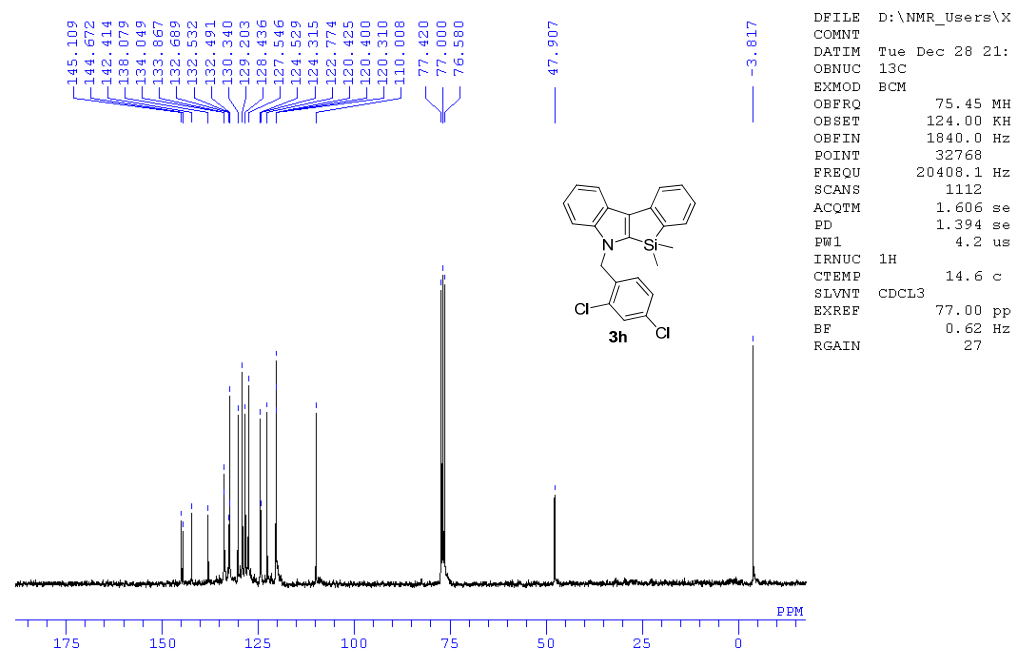
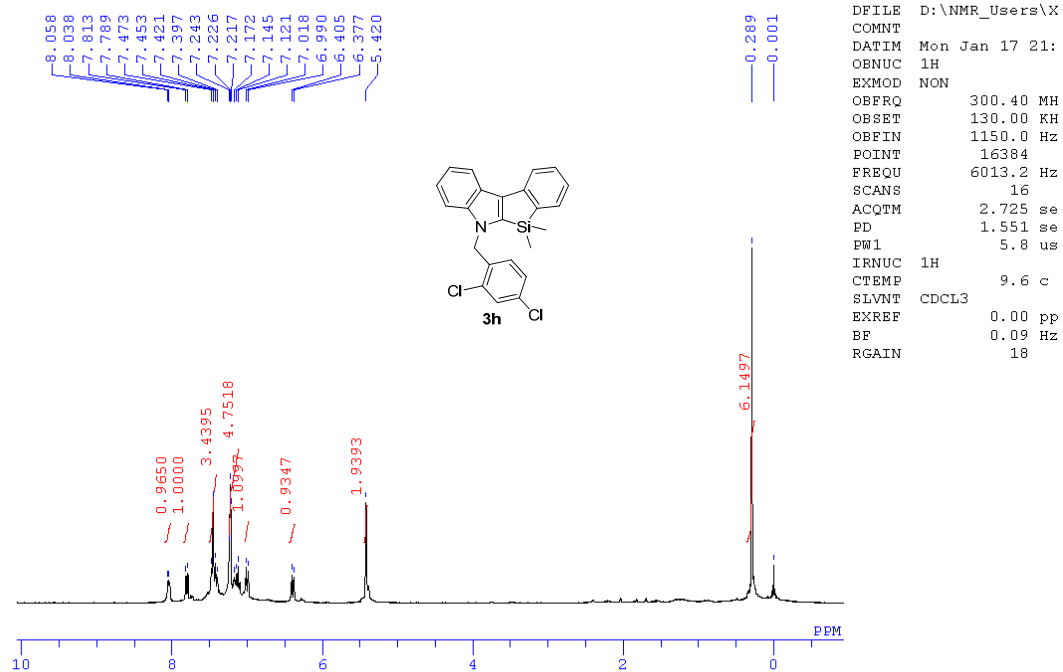


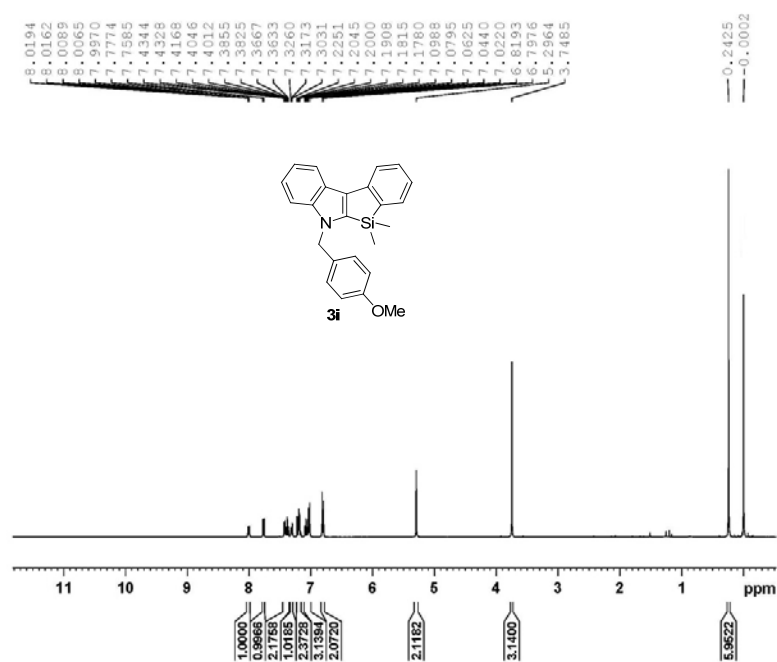
DFILE D:\NMR_Users\X
 COMNT
 DATIM Sun Jan 09 21:
 OBNUC 1H
 EXMOD NON
 OBFRQ 300.40 MH
 OBSET 130.00 KH
 OBFIN 1150.0 Hz
 POINT 16384
 FREQU 6013.2 Hz
 SCANS 16
 ACQTM 2.725 se
 PD 1.551 se
 PW1 5.8 us
 IRNUC 1H
 CTEMP 11.7 c
 SLVNT CDCL3
 EXREF 0.00 pp
 BF 0.09 Hz
 RGAIN 15



DFILE D:\NMR_Users\X
 COMNT
 DATIM Sun Jan 09 20:
 OBNUC 13C
 EXMOD BCM
 OBFRQ 75.45 MH
 OBSET 124.00 KH
 OBFIN 1840.0 Hz
 POINT 32768
 FREQU 20408.1 Hz
 SCANS 360
 ACQTM 1.606 se
 PD 1.394 se
 PW1 4.2 us
 IRNUC 1H
 CTEMP 11.7 c
 SLVNT CDCL3
 EXREF 77.00 pp
 BF 0.62 Hz
 RGAIN 26

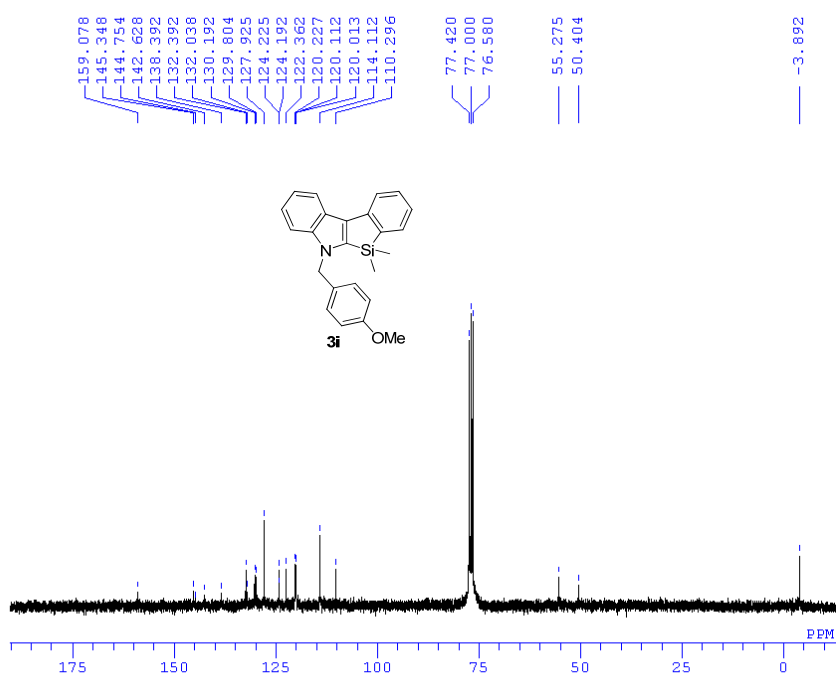






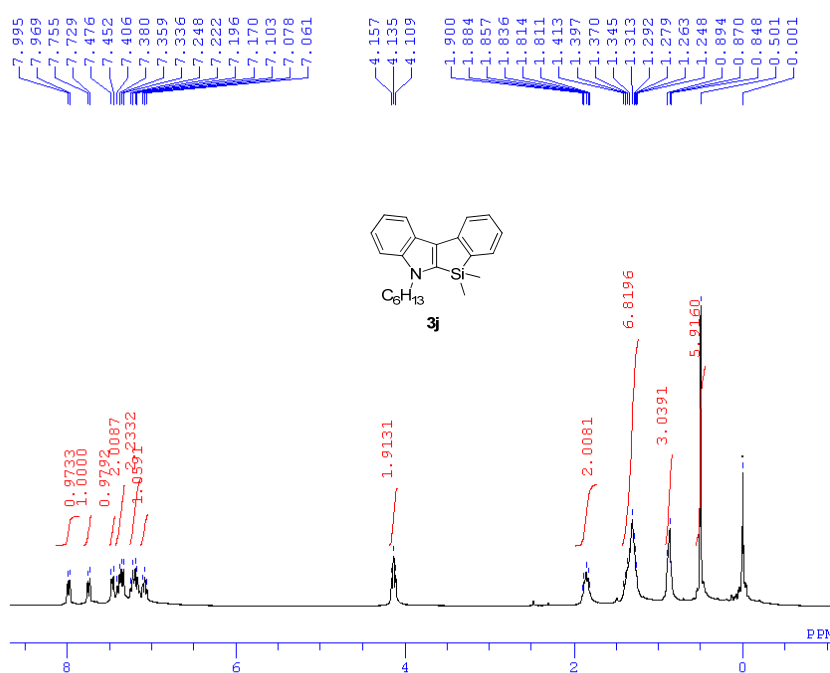
```

NAME      HMNMR10120879-3
EXPNO     1
PROCNO    1
Date_     20101229
Time      0.37
INSTRUM   ARX400
PROBHD    5 mm Multinu
PULPROG   zgpg30
TD         32768
SOLVENT   CDCl3
NS         64
DS         0
SWH        6410.256 Hz
FIDRES     0.195625 Hz
AQ         2.5559540 sec
RG          715
DM         78.000 usec
DE         111.43 usec
TE         300.0 K
D1         2.00000000 sec
P1         3.00 usec
DE         111.43 usec
SFO1       400.1321971 MHz
NUC1       1H
SI         16394
SF         400.1300231 MHz
WDW        no
SSB        0
LB         0.00 Hz
GB         0
PC         4.00
  
```

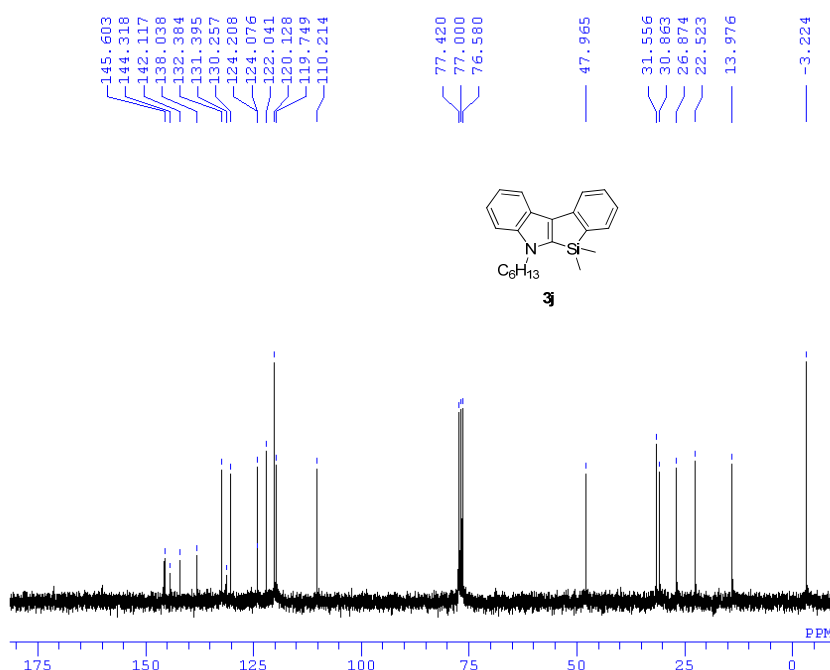


```

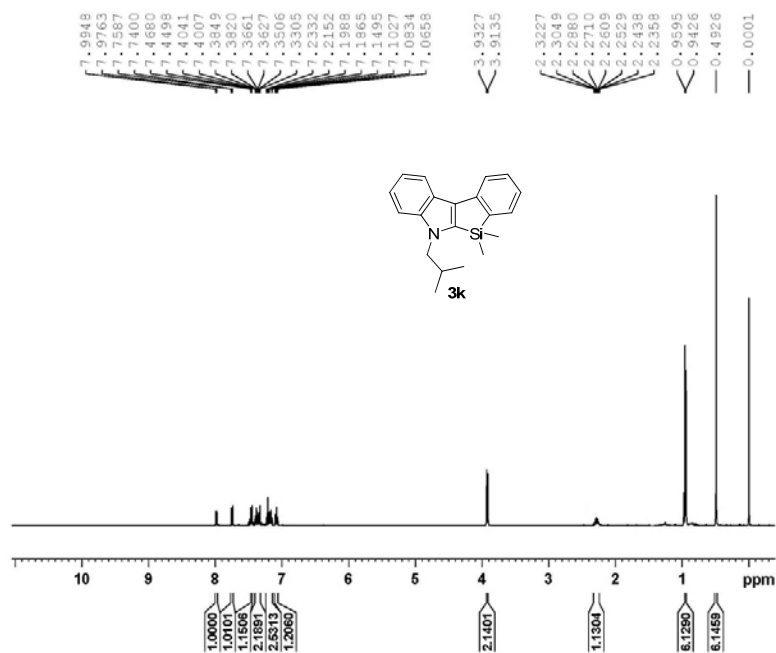
DFILE      C:\WINDOWS\Des
COMNT      Tue Nov 30 23:
OBNUC      13C
EXMOD      BCM
OBFRQ      75.45 MH
OBSET      124.00 KH
OBFIN      1840.0 Hz
POINT      32768
FREQU      20408.1 Hz
SCANS      2320
ACQTM      1.606 se
PD         1.394 se
PWL        4.2 us
IRNUC      1H
CTEMP      13.1 c
SLVNT      CDCL3
EXREF      77.00 pp
BF         0.62 Hz
RGAIN      25
  
```



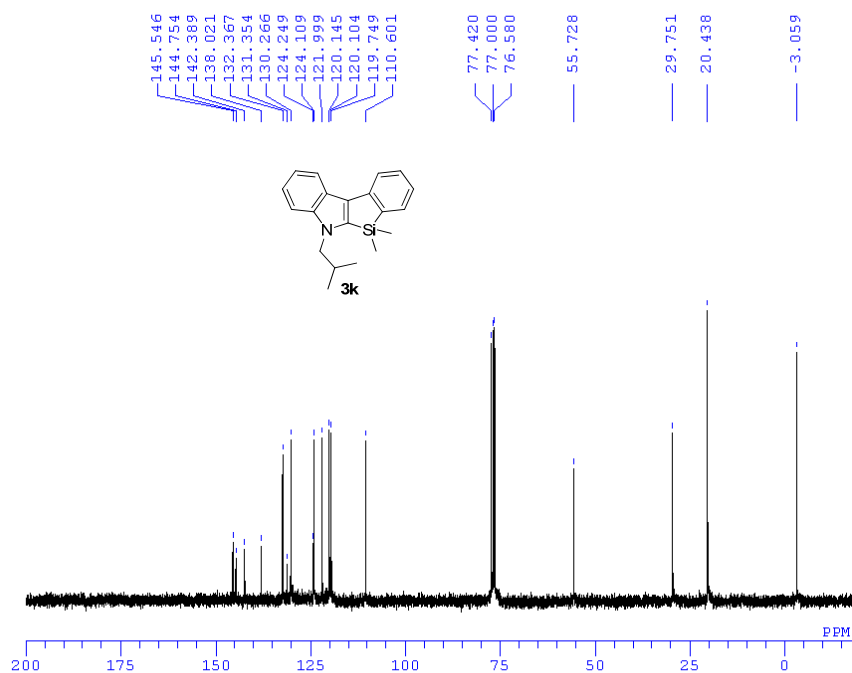
DFILE D:\NMR_Users\X
 COMNT
 DATIM Fri Dec 10 20:
 OBNUC 1H
 EXMOD NON
 OBFREQ 300.40 MH
 OBSET 130.00 KH
 OBFIN 1150.0 Hz
 POINT 16384
 FREQU 6013.2 Hz
 SCANS 16
 ACQTM 2.725 se
 PD 1.551 se
 PW1 5.8 us
 IRNUC 1H
 CTEMP 20.5 c
 SLVNT CDCL3
 EXREF 0.00 pp
 BF 0.09 Hz
 RGAIN 14



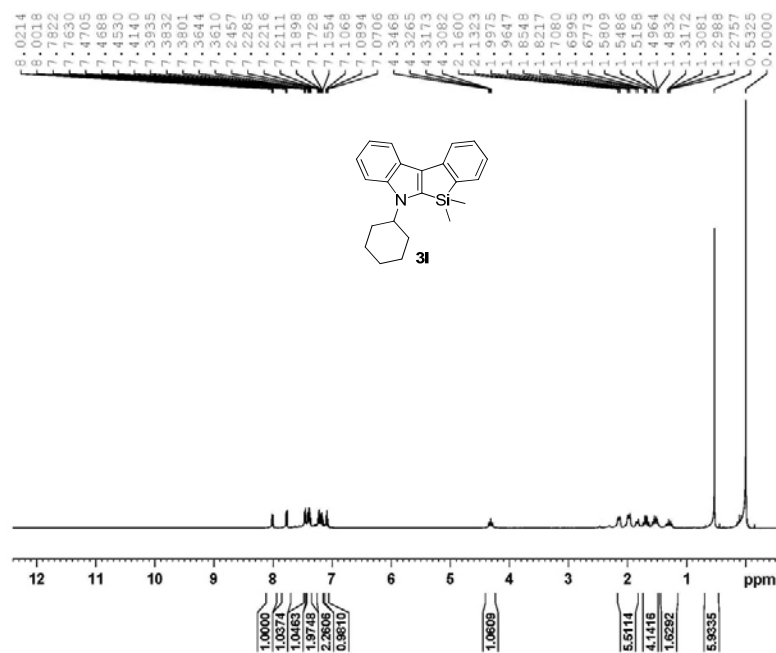
DFILE C:\WINNMR95\CO
 COMNT
 DATIM Fri Dec 10 20:
 OBNUC 13C
 EXMOD BCM
 OBFREQ 75.45 MH
 OBSET 124.00 KH
 OBFIN 1840.0 Hz
 POINT 32768
 FREQU 20408.1 Hz
 SCANS 192
 ACQTM 1.606 se
 PD 1.394 se
 PW1 4.2 us
 IRNUC 1H
 CTEMP 21.3 c
 SLVNT CDCL3
 EXREF 77.00 pp
 BF 0.62 Hz
 RGAIN 27



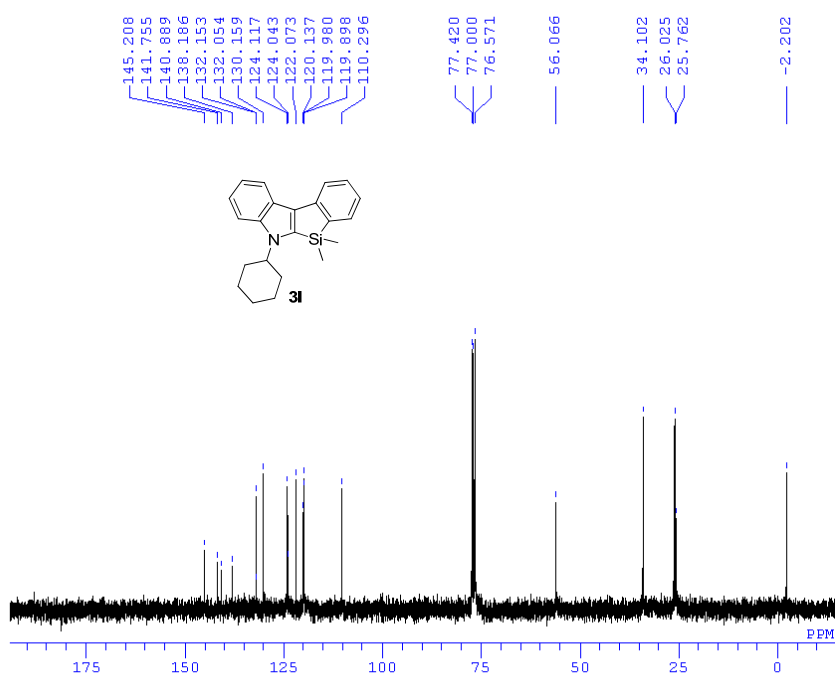
NAME HMR11010316-1
EXPNO 1
PROCNO 1
Date_ 20110112
Time 1.23
INSTRUM ARX400
PROBHD 5 mm Multinu
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 8064.516 Hz
FIDRES 0.246110 Hz
AQ 2.0316660 sec
RG 360
DM 62.000 usec
DE 88.57 usec
TE 300.0 K
D1 2.00000000 sec
P1 3.00 usec
DE 88.57 usec
SFO1 400.1321971 MHz
NUC1 1H
SI 16394
SF 400.1300272 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00



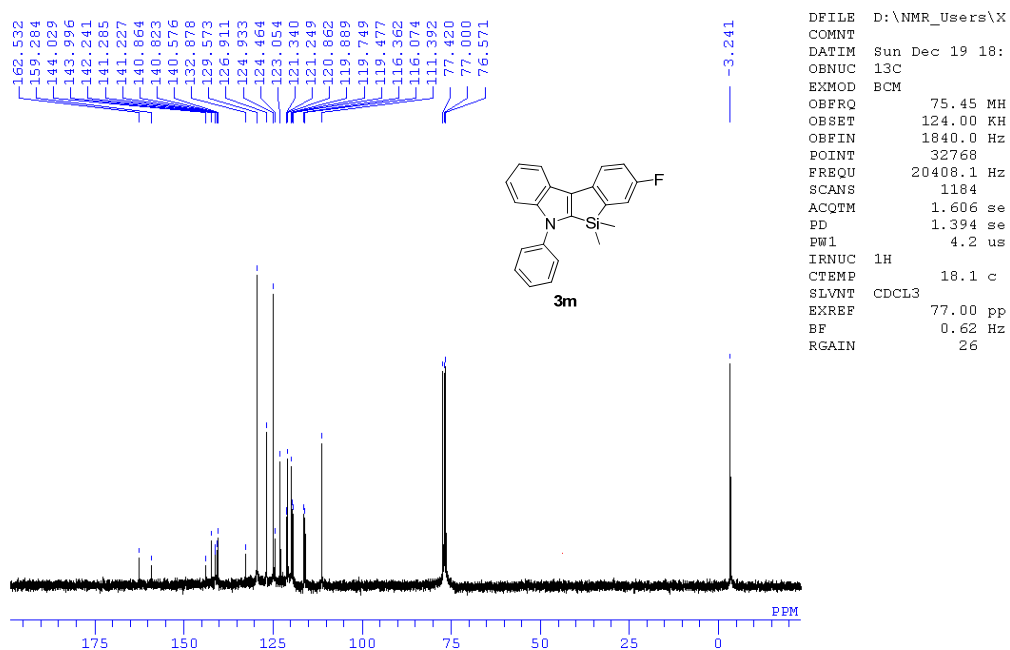
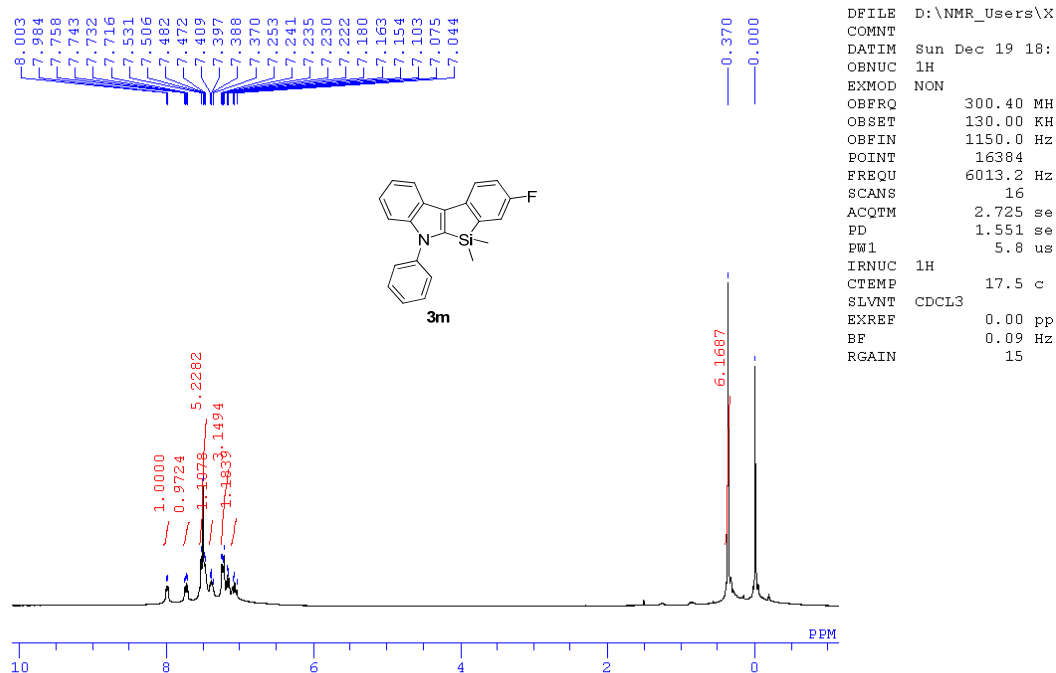
DFILE C:\WINNMR95\CO
COMNT
DATIM Mon Jan 10 20:
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MH
OBSET 124.00 KH
OBFIN 1840.0 Hz
POINT 32768
FREQU 20408.1 Hz
SCANS 576
ACQTM 1.606 se
PD 1.394 se
PW1 4.2 us
IRNUC 1H
CTEMP 18.1 c
SLVNT CDCL3
EXREF 77.00 pp
BF 0.62 Hz
RGAIN 27

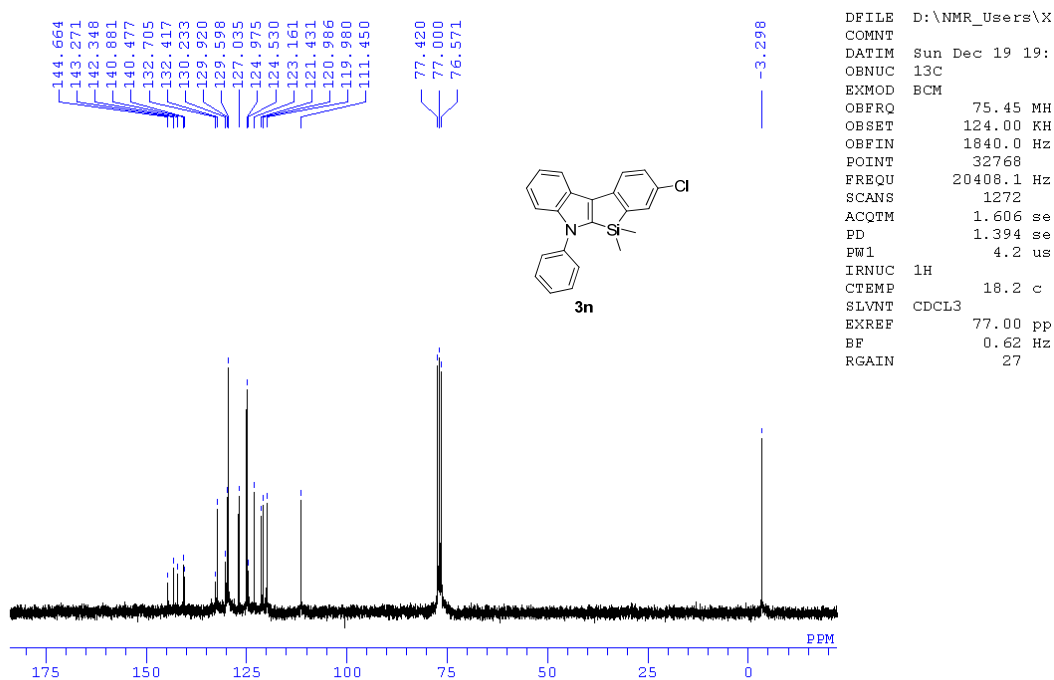
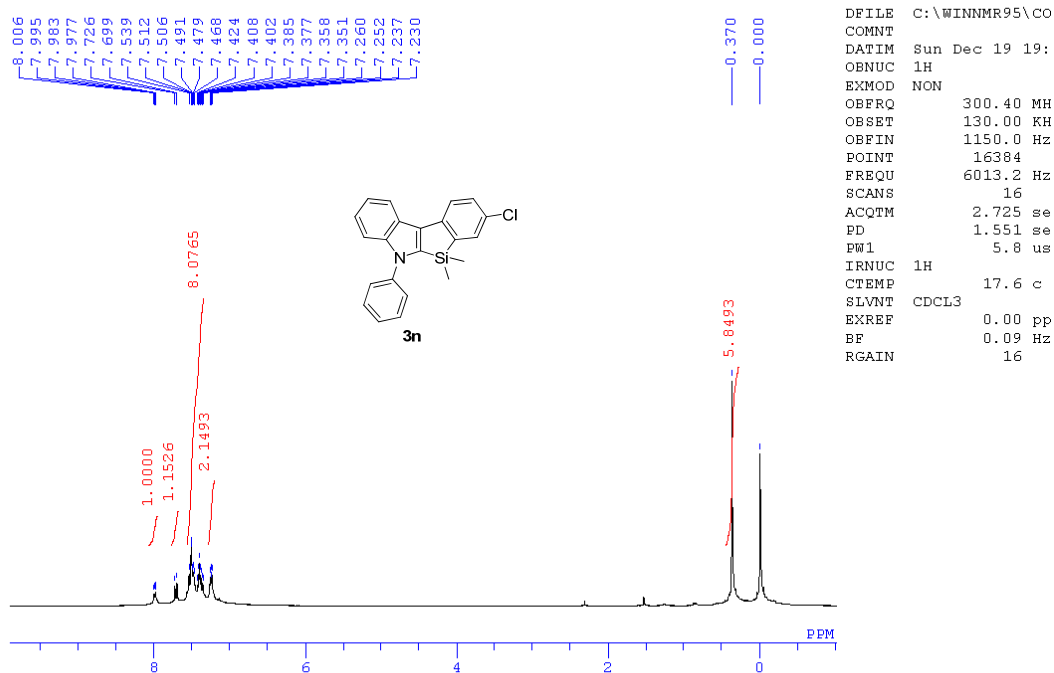


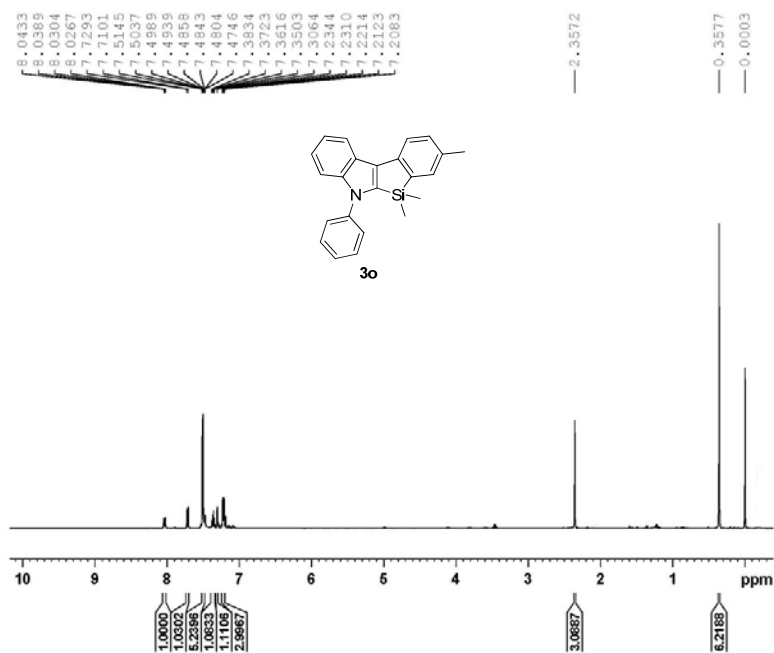
NAME HNMR10120946-1
 EXPNO 1
 PROCNO 1
 Date_ 20101230
 Time 0.41
 INSTRUM ARX400
 PROBRD 5 mm Multinu
 PULPROG zg
 TD 32768
 SOLVENT CDCl3
 NS 64
 DS 0
 SWH 6410.256 Hz
 FIDRES 0.195625 Hz
 AQ 2.5559540 sec
 RG 360
 DM 78.000 usec
 DE 111.43 usec
 TE 300.0 K
 D1 2.00000000 sec
 P1 3.00 usec
 DE 111.43 usec
 SFO1 400.1321971 MHz
 NUCLEUS 1H
 SI 16394
 SF 400.1300247 MHz
 WDW no
 SSB 0
 LB 0.00 Hz
 GB 0
 PC 4.00



DFILE C:\WINNMR95\CO
 COMNT Tue Nov 30 20:
 OBNUC 13C
 EXMOD BCM
 OBFRQ 75.45 MH
 OBSET 124.00 KH
 OBFIN 1840.0 Hz
 POINT 32768
 FREQU 20408.1 Hz
 SCANS 224
 ACQTM 1.606 se
 PD 1.394 se
 PW1 4.2 us
 IRNUC 1H
 CTEMP 13.8 c
 SLVNT CDCL3
 EXREF 77.00 pp
 BF 0.62 Hz
 RGAIN 26



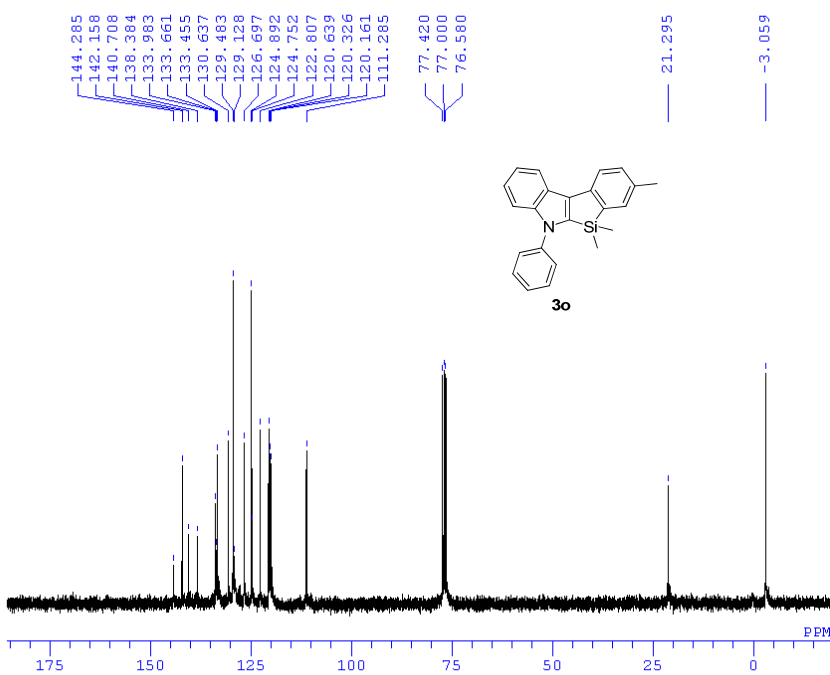




```

NAME      HMNMR10120946-5
EXPNO     1
PROCNO    1
Date_     20101230
Time      1.13
INSTRUM   ARX400
PROBHD    5 mm Multinu
PULPROG   zgpg
TD         32768
SOLVENT   CDCl3
NS         32
DS         0
SWH        6410.256 Hz
FIDRES     0.195625 Hz
AQ         2.5559540 sec
RG         256
DM         78.000 usec
DE         111.43 usec
TE         300.0 K
D1         2.00000000 sec
P1         3.00 usec
DE         111.43 usec
SFO1       400.1321971 MHz
NUC1       1H
SI         16384
SF         400.1300372 MHz
WDW        no
SSB        0
LB         0.00 Hz
GB         0
PC         4.00

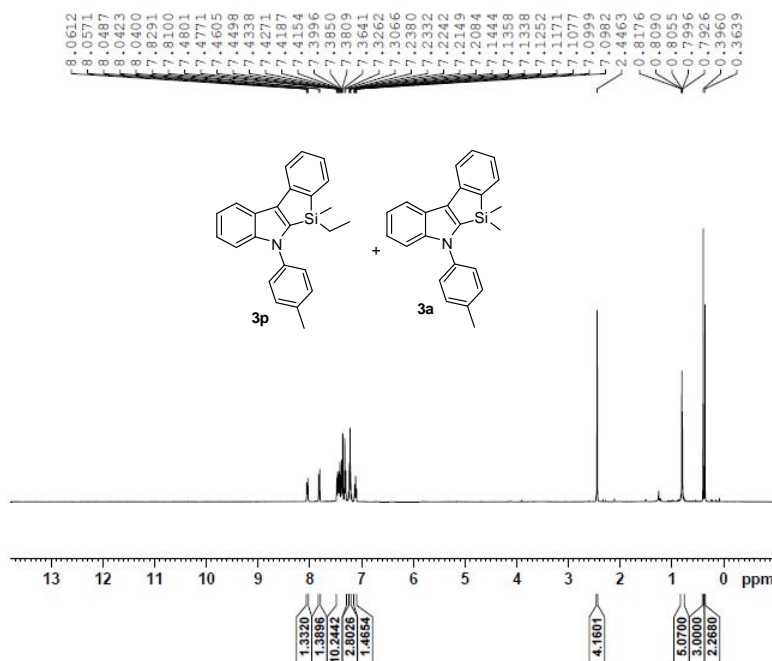
```



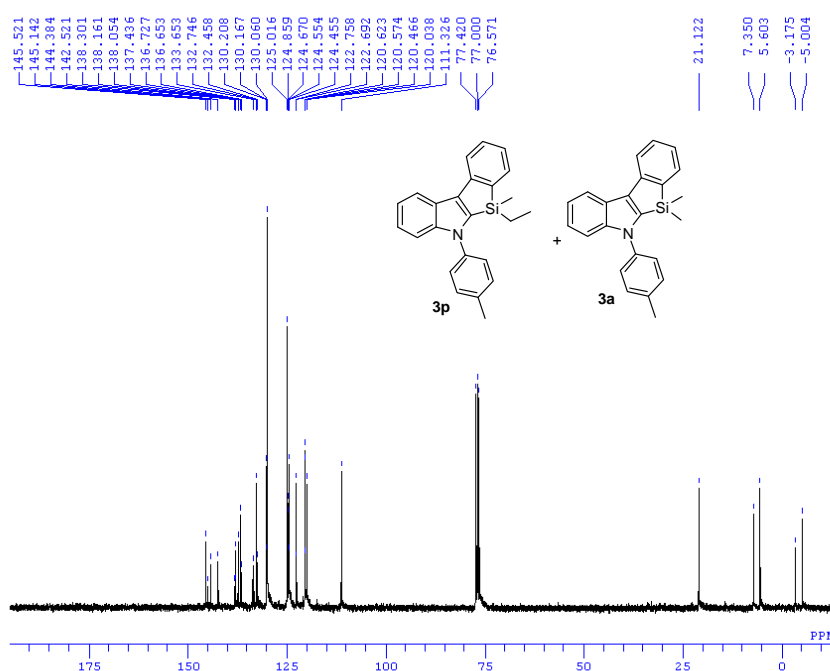
```

DFILE      D:\NMR_Users\X
COMNT      Tue Dec 28 22:
OBNUC      13C
EXMOD      BCM
OBFRQ       75.45 MH
OBSET       124.00 KH
OBFIN       1840.0 Hz
POINT       32768
FREQU       20408.1 Hz
SCANS       688
ACQTM       1.606 se
PD          1.394 se
PW1         4.2 us
IRNUC      1H
CTEMP       14.9 c
SLVNT       CDCL3
EXREF       77.00 pp
BF          0.62 Hz
RGAIN       25

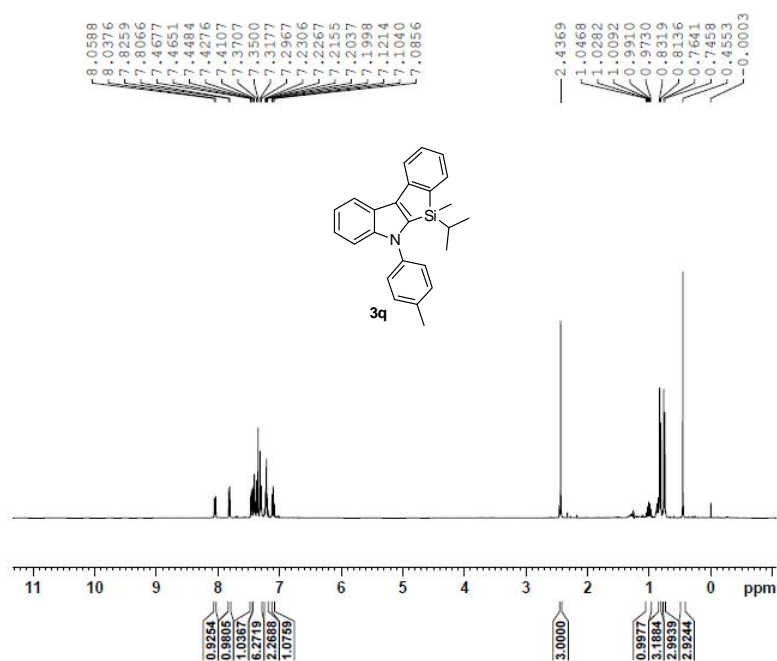
```



NAME HNMR11030006
 EXPNO 1
 PROCNO 1
 Date_ 20110901
 Time 1.48
 INSTRUM ARX400
 PROBRD 5 mm Multina
 PULPROG zg
 TD 32768
 SOLVENT CDCl3
 NS 32
 DS 0
 SWH 8064.516 Hz
 FIDRES 0.246110 Hz
 AQ 2.0316660 sec
 RG 718
 SFG 62.000 usec
 TMS 88.57 usec
 ZF 400.0 K
 DI 2.00000000 sec
 SI 3.00 usec
 SE 88.57 usec
 SFO1 400.1321971 MHz
 NUC1 1H
 SI 16284
 SF 400.1300238 MHz
 WCN no
 SSB 0
 LBS 0.00 Hz
 PC 4.00

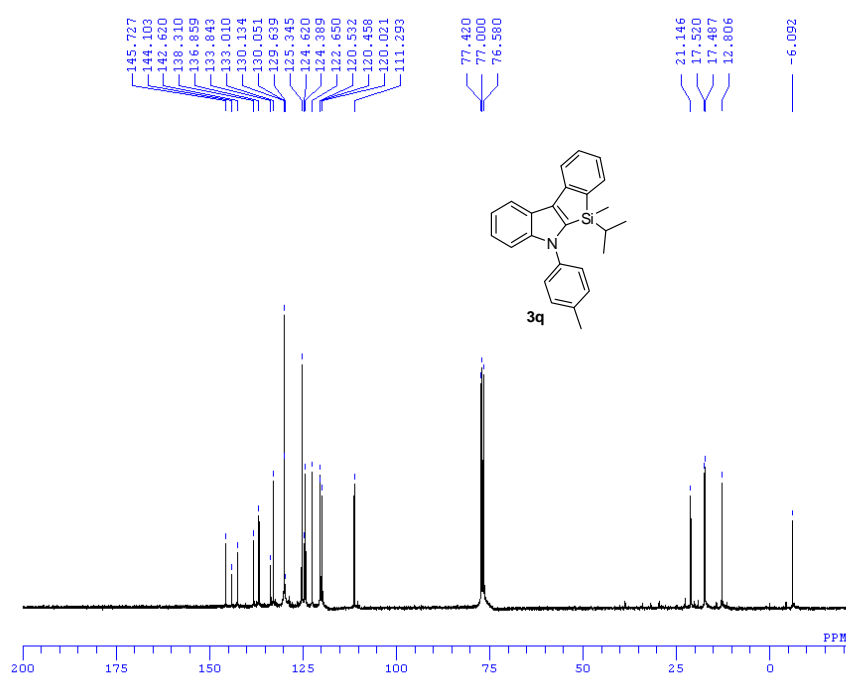


DFILE D:\NMR_Users\Xi Zhe
 COMNT
 DATIM Sun Feb 27 15:44:48
 OBNUC 13C
 EXMOD BCM
 OBFRQ 75.45 MHz
 OBSET 124.00 KHz
 OBFIN 1840.0 Hz
 POINT 32768
 FREQU 20408.1 Hz
 SCANS 1480
 ACQTM 1.606 sec
 PD 1.394 sec
 PW1 4.2 us
 IRNUC 1H
 CTEMP 14.1 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 0.62 Hz
 RGAIN 27



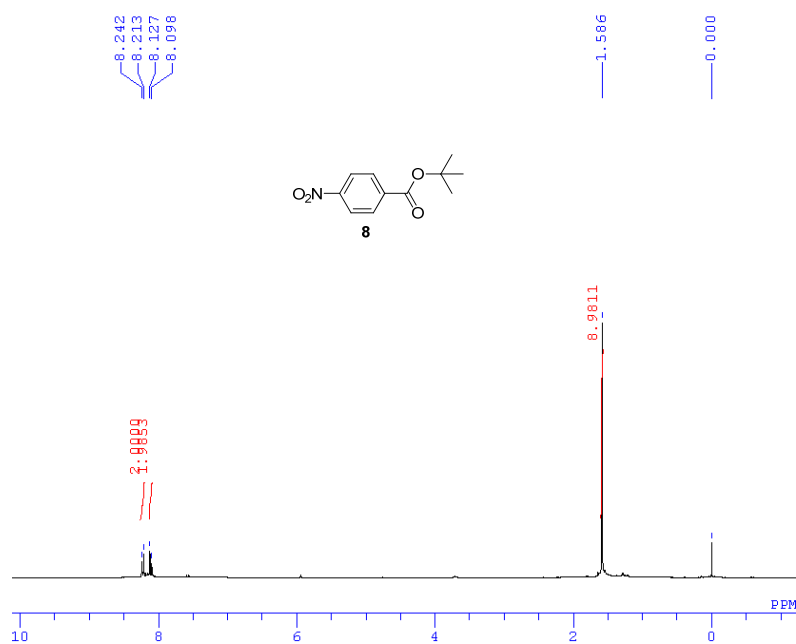
```

NAME      HMR11020920
EXPNO     1
PROCNO    1
Date_     20110226
Time      1.16
INSTRUM    ARX400
PROBHD     5 mm Multinu
PULPROG    zgpg30
TD         32768
SOLVENT    CDCl3
NS         16
DS         0
SWH        8064.816 Hz
FIDRES     0.346110 Hz
AQ         2.0816660 sec
RG         360
TSCG       62.000 usec
NUC1       13C
DE         88.57 usec
TE         300.0 K
D1         2.00000000 sec
DI         8.00 usec
DE         88.57 usec
SFO1       400.1821971 MHz
NUCLEUS    1H
SI         16384
SF         400.1800277 MHz
RG         na
WIDW       0
SSB        0
RGAIN      0.00 Hz
PC         4.00
  
```

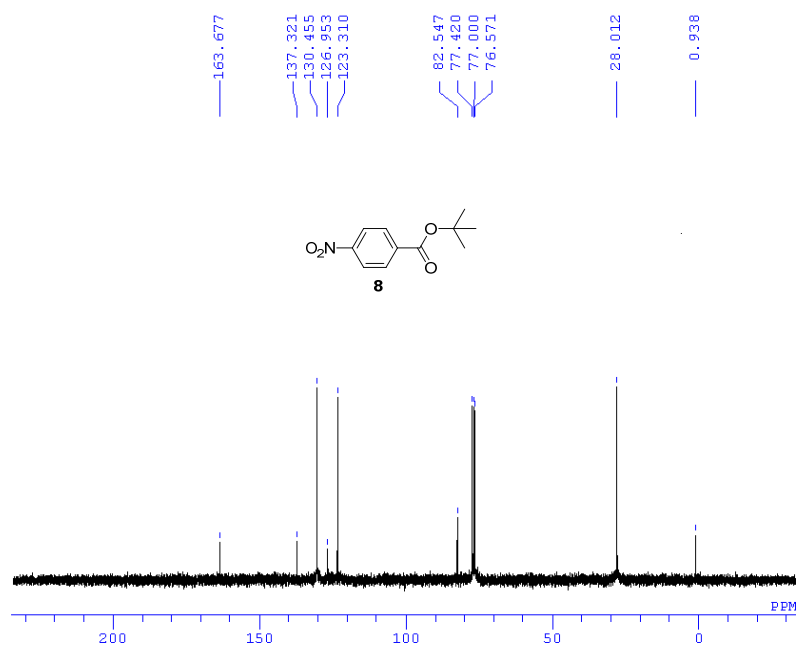


```

DFFILE C:\WINNMR95\COMMON\
COMENT
DATIM   Fri Feb 25 08:19:13
OBNUC   13C
EXMOD    BCM
OBFRQ    75.45 MHz
OBSET    124.00 KHz
OBFIN    1840.0 Hz
POINT    32768
FREQU    20408.1 Hz
SCANS    10641
AQTM     1.606 sec
PD       1.394 sec
PW1      4.2 us
IRNUC    1H
CTEMP    14.5 c
SLVNT    CDCL3
EXREF    77.00 ppm
BF       0.65 Hz
RGAIN    26
  
```



DFILE D:\NMR_Users\X
 COMNT
 DATIM Tue Nov 16 22:
 OBNUC 1H
 EXMOD NON
 OBFRQ 300.40 MH
 OBSST 130.00 KH
 OBFIN 1150.0 Hz
 POINT 16384
 FREQU 6013.2 Hz
 SCANS 16
 ACQTM 2.725 se
 PD 1.551 se
 PW1 5.8 us
 IRNUC 1H
 CTEMP 14.5 c
 SLVNT CDCL3
 EXREF 0.00 pp
 BF 0.09 Hz
 RGAIN 15



DFILE D:\NMR_Users\X
 COMNT
 DATIM Tue Nov 16 22:
 OBNUC 13C
 EXMOD BCM
 OBFRQ 75.45 MH
 OBSST 124.00 KH
 OBFIN 1840.0 Hz
 POINT 32768
 FREQU 20408.1 Hz
 SCANS 304
 ACQTM 1.606 se
 PD 1.394 se
 PW1 4.2 us
 IRNUC 1H
 CTEMP 14.3 c
 SLVNT CDCL3
 EXREF 77.00 pp
 BF 0.63 Hz
 RGAIN 26