Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Rhodium-catalyzed intramolecular carbo-silylation of alkynes via C(sp^3)-Si bond cleavage

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Contents:

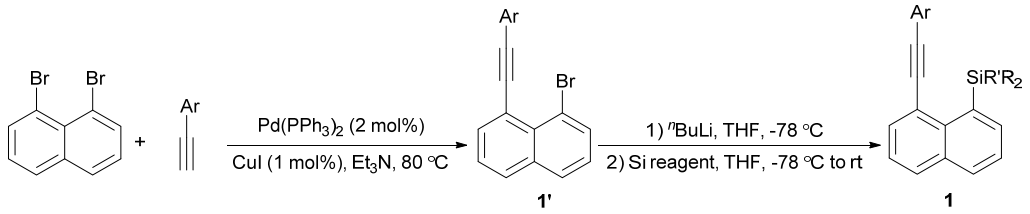
1) Experimental Details and Characterization Data

General information: Unless otherwise noted, all starting materials were commercially available and were used without further purification. Solvents were purified by an Mbraun SPS-800 Solvent Purification System and dried over fresh Na chips in the glovebox. All reactions were carried out under N_2 atmosphere.

^1H and ^{13}C NMR spectra were recorded on a Bruker ARX400 spectrometer (FT, 400 MHz for ^1H; 100 MHz for ^{13}C) or a Bruker ARX500 spectrometer (FT, 500 MHz for ^1H; 125 MHz for ^{13}C) at room temperature, unless otherwise noted. High-resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS mass spectrometer using EI (electronic ionization).

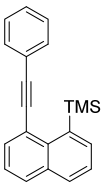
Procedures and Characterization Data

A Typical Procedure for the Preparation of 1-Trimethylsilyl-8-alkynyl Naphthalene derivatives 1.



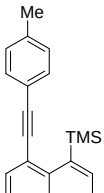
Compounds **1'** were prepared according the literature method.[1]

Compounds **1** were prepared according the literature method.[2]



1a1

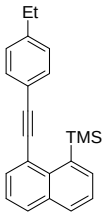
Yellow oil, isolated yield 59% (885 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 0.61 (s, 9H, $SiCH_3$), 7.38-7.42 (m, 3H, CH), 7.45-7.50 (m, 2H, CH), 7.61-7.64 (m, 2H, CH), 7.87-7.90 (m, 2H, CH), 7.93-7.96 (m, 2H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 3.5, 93.8, 96.2, 122.0, 124.1, 124.9, 125.3, 128.6, 130.9, 131.1, 131.8, 132.7, 134.5, 135.8, 136.5 137.0, 138.3; HRMS calcd. for $C_{21}H_{20}Si$ $[M]^+$: 300.1329, found 300.1326.



1a2

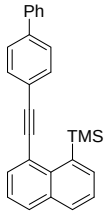
Yellow solid, isolated yield 78% (1.2 g); mp: 102.2-102.6 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 0.57 (s, 9H, $SiCH_3$), 2.40 (s, 3H, CH_3), 7.19-7.21 (m, 2H, CH), 7.43-7.50 (m, 4H, CH) 7.84-7.92 (m, 4H, CH); ^{13}C NMR (100

MHz, $CDCl_3$): δ 3.5, 21.7, 93.1, 96.5, 121.0, 122.2, 124.9, 125.2, 129.3, 130.7, 131.0, 131.7, 134.5, 135.7, 136.5, 137.1, 138.4, 138.7; HRMS calcd. for $C_{22}H_{22}Si$ $[M]^+$: 314.1485, found 314.1487.



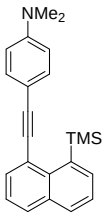
1a3

Yellow oil, isolated yield 80% (1.3 g); ^1H NMR (400 MHz, $CDCl_3$): δ 0.57 (s, 9H, $SiCH_3$), 1.25 (t, J = 7.6 Hz, 3H, CH_3), 2.67 (q, J = 7.6 Hz, 2H, CH_2), 7.20-7.22 (m, 2H, CH), 7.40-7.45 (m, 2H, CH), 7.50-7.52 (m, 2H, CH), 7.82-7.86 (m, 2H, CH), 7.82-7.89 (m, 2H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 3.6, 15.4, 29.0, 93.1, 96.5, 121.2, 122.3, 124.9, 125.2, 128.1, 130.7, 131.0, 131.7, 134.5, 135.7, 136.4, 137.1, 138.4, 144.9; HRMS calcd. for $C_{23}H_{24}Si$ $[M]^+$: 328.1647, found 328.1642.



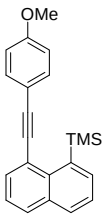
1a4

Yellow solid, isolated yield 55% (1.0 g); mp: 112.2-112.9 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 0.62 (s, 9H, $SiCH_3$), 7.37-7.41 (m, 1H, CH), 7.46-7.50 (m, 4H, CH), 7.43-7.69 (m, 6H, CH), 7.87-7.90 (m, 2H, CH), 7.94-7.96 (m, 2H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 3.6, 94.5, 96.2, 122.1, 122.9, 124.9, 125.3, 127.20, 127.24, 127.8, 129.0, 130.9, 131.1, 132.2, 134.6, 135.8, 136.5, 137.1, 138.3, 140.5, 141.2; HRMS calcd. for $C_{27}H_{24}Si$ $[M]^+$: 376.1642, found 376.1641.



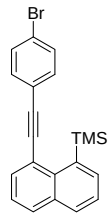
1a5

Brown solid, isolated yield 50% (858 mg); mp: 136.3-136.8 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 0.59 (s, 9H, $SiCH_3$), 3.02 (s, 6H, CH_3), 6.70-6.72 (m, 2H, CH), 7.44-7.49 (m, 4H, CH), 7.81-7.93 (m, 4H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 3.6, 40.3, 91.6, 97.7, 111.0, 112.0, 123.0, 124.9, 125.1, 130.1, 131.0, 132.9, 134.6, 135.4, 136.3, 137.2, 138.5, 150.2; HRMS calcd. for $C_{23}H_{25}SiN$ $[M]^+$: 343.1751, found 343.1758.



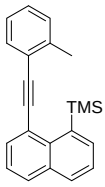
1a6

Yellow solid, isolated yield 70% (1.2 g); mp: 103.1-103.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.59 (s, 9H, $SiCH_3$), 3.86 (s, 3H, CH_3), 6.93-6.95 (m, 2H, CH), 7.43-7.48 (m, 2H, CH), 7.54-7.56 (m, 2H, CH), 7.85-7.94 (m, 4H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 3.5, 55.5, 92.4, 96.3, 114.2, 116.2, 122.4, 124.9, 125.2, 130.6, 131.0, 133.2, 134.5, 135.6, 136.4, 137.1, 138.3, 159.8; HRMS calcd. for $C_{22}H_{22}OSi$ $[M]^+$: 330.1434, found 330.1432.



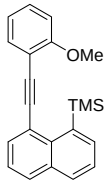
1a7

Yellow oil, isolated yield 60% (1.1 g); ^{1}H NMR (400 MHz, $CDCl_3$): 0.63 (s, 9H, $SiCH_3$), 7.28-7.32 (m, 2H, CH), 7.46-7.51 (m, 3H, CH), 7.63-7.65 (m, 1H, CH), 7.88-7.92 (m, 2H, CH), 7.95-7.97 (m, 1H, CH), 8.04-8.06 (m, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 3.5, 93.2, 98.9, 121.7, 123.8, 124.9, 125.3, 126.6, 129.4, 129.6, 131.1, 131.3, 132.6, 134.5, 136.3, 136.6, 138.2; HRMS calcd. for $C_{21}H_{19}SiBr$ $[M]^+$: 378.0434, found 378.0440.



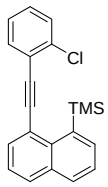
1a8

Yellow oil, isolated yield 59% (926 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.57 (s, 9H, $SiCH_3$), 2.57 (s, 3H, CH_3), 7.19-7.23 (m, 1H, CH), 7.27-7.28 (m, 2H, CH), 7.44-7.47 (m, 2H, CH), 7.54-7.56 (m, 1H, CH), 7.86-7.89 (m, 2H, CH), 7.91-7.93 (m, 2H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 3.5, 21.1, 95.4, 97.6, 122.4, 123.7, 124.9, 125.3, 125.8, 128.5, 129.8, 130.8, 131.0, 131.4, 134.6, 135.6, 136.5, 137.0, 138.4, 141.1; HRMS calcd. for $C_{22}H_{22}Si$ $[M]^+$: 314.1485, found 314.1487.



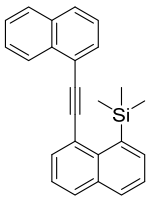
1a9

Brown oil, isolated yield 45% (743 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.61 (s, 9H, $SiCH_3$), 3.86 (s, 3H, CH_3), 6.94-6.96 (m, 1H, CH), 7.15-7.16 (m, 1H, CH), 7.21-7.23 (m, 1H, CH), 7.30-7.34 (m, 1H, CH), 7.45-7.49 (m, 2H, CH), 7.87-7.90 (m, 2H, CH), 7.93-7.95 (m, 2H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 3.5, 55.5, 93.6, 96.1, 114.9, 116.8, 122.0, 124.3, 124.8, 125.1, 125.3, 129.6, 130.9, 131.1, 134.5, 135.8, 136.5, 137.0, 138.3, 159.6; HRMS calcd. for $C_{22}H_{22}SiO$ $[M]^+$: 330.1434, found 330.1432.



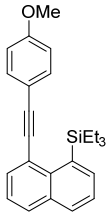
1a10

Yellow oil, isolated yield 53% (832 mg); ^{1}H NMR (400 MHz, $CDCl_3$): 0.63 (s, 9H, $SiCH_3$), 7.29-7.32 (m, 2H, CH), 7.47-7.51 (m, 3H, CH), 7.62-7.65 (m, 1H, CH), 7.89-7.92 (m, 2H, CH), 7.95-7.97 (m, 1H, CH), 8.03-8.06 (m, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 3.5, 93.2, 98.9, 121.7, 123.8, 124.9, 125.3, 126.6, 129.4, 129.6, 131.1, 131.3, 132.7, 134.5, 136.3, 136.6, 136.89, 136.91, 138.2; HRMS calcd. for $C_{21}H_{19}SiCl$ $[M]^+$: 334.0939, found 334.0934.



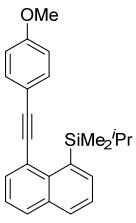
1a11

Yellow oil, isolated yield 60% (1.1 g); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.58 (s, 9H, $SiCH_3$), 7.41-7.47 (m, 3H, CH), 7.49-7.51 (m, 1H, CH), 7.53-7.57 (m, 1H, CH), 7.80-7.85 (m, 5H, CH), 7.92-7.94 (m, 1H, CH), 8.02-8.05 (m, 1H, CH), 8.47-8.49 (m, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 3.6, 94.6, 98.6, 121.6, 122.2, 124.9, 125.3, 125.4, 126.5, 126.6, 127.0, 128.5, 129.0, 130.1, 131.0, 131.1, 133.5, 134.0, 134.6, 135.8, 136.6, 137.1, 138.4; HRMS calcd. for $C_{25}H_{22}Si$ $[M]^+$: 350.1491, found 350.1493.



1b

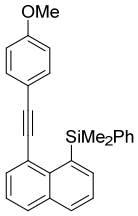
Yellow oil, isolated yield 35% (651 mg); ^{1}H NMR (400 MHz, $CDCl_3$): 0.71-0.77 (m, 6H, $SiCH_2$), 0.90 (t, J = 7.6 Hz, 9H, CH_3), 3.91 (s, 3H, CH_3), 6.99-7.01 (m, 2H, CH), 7.41-7.43 (m, 3H, CH), 7.51-7.59 (m, 2H, CH), 7.78-7.84 (m, 3H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 5.2, 8.3, 55.5, 92.3, 96.1, 113.4, 114.2, 123.1, 124.7, 125.0, 126.3, 130.7, 130.9, 132.7, 133.1, 135.7, 137.8, 153.9, 159.8; HRMS calcd. for $C_{25}H_{28}OSi$ $[M]^+$: 372.1906, found 372.1904.



1c

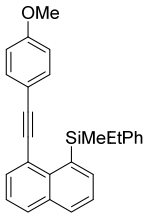
Yellow oil, isolated yield 42% (752 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.52 (s, 6H, $SiCH_3$), 0.93 (d, J = 7.6 Hz, 6H, CH_3), 2.02 (hept, J = 7.2 Hz, 1H, SiCH), 3.86 (s, 3H, CH_3), 6.94 (d, J = 8.8 Hz, 2H, CH), 7.43-7.48 (m, 2H, CH), 7.54 (d, J = 8.8 Hz, 2H, CH), 7.85-7.89 (m, 2H, CH), 7.91-7.93 (m, 2H, CH). ^{13}C NMR (100 MHz, $CDCl_3$): δ -0.9, 14.8, 18.3, 55.4, 92.4, 96.3, 113.5, 114.2, 116.2, 122.3, 124.7, 125.1, 130.7, 130.9, 133.2,

134.6, 135.7, 136.7, 137.3, 159.8; HRMS calcd. for $C_{24}H_{26}SiO$ $[M]^+$: 358.1747, found 358.1747.



1d

Yellow oil, isolated yield 35% (686 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.76 (s, 6H, $SiCH_3$), 3.73 (s, 3H, CH_3), 6.70-6.72 (m, 2H, CH), 6.90-6.93 (m, 2H, CH), 7.16-7.24 (m, 3H, CH), 7.37-7.42 (m, 4H, CH), 7.81-7.89 (m, 4H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 3.0, 55.3, 91.9, 97.6, 113.7, 115.9, 122.7, 125.0, 125.3, 127.5, 128.2, 130.4, 131.5, 133.2, 134.1, 134.5, 135.3, 135.5, 138.4, 138.4, 142.1, 159.7; HRMS calcd. for $C_{27}H_{24}OSi$ $[M]^+$: 392.1591, found 392.1595.

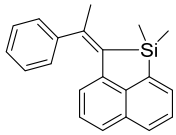


1e

Yellow oil, isolated yield 30% (609 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.24 (s, 3H, $SiCH_3$), 0.86-0.90 (m, 2H, $SiCH_2$), 1.21 (t, J = 7.6 Hz, 3H, CH_3), 3.83 (s, 3H, CH_3), 6.70-6.72 (m, 2H, CH), 6.99-7.01 (m, 2H, CH), 7.07-7.09 (m, 2H, CH), 7.13-7.17 (m, 2H, CH), 7.46-7.50 (m, 2H, CH), 7.55-7.57 (m, 2H, CH), 7.71-7.75 (m, 2H, CH), 7.84-7.86 (m, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ -2.1, 7.5, 10.8, 55.4, 91.9, 96.7, 114.2, 114.4, 121.1, 124.9, 125.3, 127.9, 129.7, 131.0, 131.5, 133.3, 133.4, 134.1, 134.4, 135.6, 136.2, 136.4, 136.6, 160.2. HRMS calcd. for $C_{28}H_{26}OSi$ $[M]^+$: 406.1744, found 406.1747.

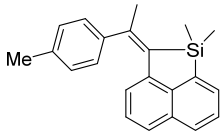
Typical Procedure for the Preparation of Silacyclic Compounds 2:

In a 25 mL of flask, $[RhCl(cod)]_2$ catalyst (0.025 mmol, 12.3 mg), LiO^{t}Bu (1.5 mmol, 120 mg), **1** (0.50 mmol) was added to octanol (0.8 mL) in 1,2-dioxane (4.0 mL). The mixture was stirred at 100 °C for 12 h. The black solution was diluted with ethyl acetate (EA). After then the solvent of the reaction mixture was evaporated under vacuum. The residue was purified by chromatography with petroleum ether (PE) and EA to give products **2**.



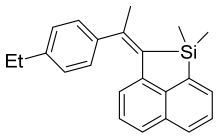
2a1

Yellow crastal, isolated yield 58% (87 mg); mp: 206.7-207.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.60 (s, 6H, $SiCH_3$), 2.43 (s, 3H, CH_3), 6.52-6.54 (m, 1H, CH), 7.03-7.07 (m, 1H, CH), 7.27-7.28 (m, 2H, CH), 7.35-7.38 (m, 1H, CH), 7.42-7.44 (m, 2H, CH), 7.51-7.53 (m, 2H, CH), 7.72-7.73 (m, 1H, CH), 7.78-7.80 (m, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ -1.0, 29.7, 122.1, 125.0, 126.26, 126.31, 127.2, 127.3, 128.1, 129.2, 129.4, 132.4, 133.7, 138.2, 141.0, 143.0, 145.7, 148.7; HRMS calcd. for $C_{21}H_{20}Si$ $[M]^+$: 300.1329, found 300.1311.



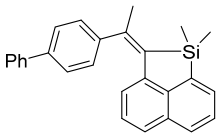
2a2

Yellow soild, isolated yield 65% (102 mg); mp: 100.4-101.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.47 (s, 6H, $SiCH_3$), 2.30 (s, 3H, CH_3), 2.51 (s, 3H, CH_3), 6.39-6.41 (m, 1H, CH), 6.91-6.94 (m, 1H, CH), 7.12-7.15 (m, 1H, CH), 7.36-7.40 (m, 2H, CH), 7.42-7.44 (m, 1H, CH), 7.47-7.49 (m, 1H, CH), 7.56-7.67 (m, 3H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ -1.0, 24.1, 29.7, 122.1, 122.8, 125.0, 125.4, 127.2, 127.8, 128.3, 129.4, 133.7, 138.2, 139.6, 141.0, 145.7, 148.3, 148.7, 150.4; HRMS calcd. for $C_{22}H_{22}Si$ $[M]^+$: 314.1485, found 314.1489.



2a3

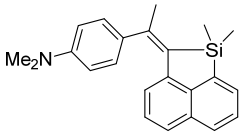
Yellow solid, isolated yield 73% (120 mg); mp: 103.3-103.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.25 (s, 6H, $SiCH_3$), 1.09 (t, J = 7.6 Hz, 3H, CH_3), 2.24 (s, 3H, CH_3), 2.44 (q, J = 7.6 Hz, 2H, CH_2), 7.01-7.03 (m, 2H, CH), 7.12-7.15 (m, 2H, CH), 7.42-7.50 (m, 4H, CH), 7.87-7.89 (m, 2H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ -0.2, 15.7, 28.9, 29.0, 123.5, 124.9, 125.1, 125.2, 126.4, 127.5, 127.8, 128.1, 129.8, 130.7, 131.0, 131.7, 135.7, 136.4, 143.8, 144.3; HRMS calcd. for $C_{23}H_{24}Si$ $[M]^+$: 328.1642, found 328.1639.



2a4

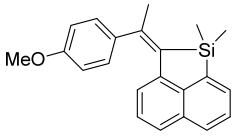
Yellow solid, isolated yield 50% (94 mg); mp: 110.4-111.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.05 (s, 6H, $SiCH_3$), 2.67 (s, 3H, CH_3),

7.38-7.40 (m, 1H, CH), 7.45-7.50 (m, 4H, CH), 7.52-7.54 (m, 1H, CH), 7.56-7.58 (m, 1H, CH), 7.61-7.62 (m, 1H, CH), 7.65-7.72 (m, 5H, CH), 7.75-7.72 (m, 1H, CH), 7.82-7.84 (m, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ -0.2, 24.0, 122.9, 125.4, 126.4, 126.6, 126.9, 127.2, 127.6, 127.8, 128.8, 129.0, 129.2, 132.3, 138.5, 139.6, 140.5, 140.8, 142.7, 143.1, 147.2, 150.0; HRMS calcd. for $C_{27}H_{24}Si$ $[M]^+$: 376.1642, found 376.1644.



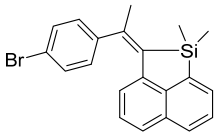
2a5

Yellow solid, isolated yield 65% (111 mg); mp: 141.2-141.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.59 (s, 6H, $SiCH_3$), 2.42 (s, 3H, CH_3), 3.03 (s, 6H, CH_3), 6.78-6.80 (m, 2H, CH), 7.11-7.20 (m, 1H, CH), 7.30-7.32 (m, 1H, CH), 7.48-7.54 (m, 2H, CH) 7.62-7.63 (m, 2H, CH), 7.67-7.69 (m, 1H, CH), 7.82-7.84 (m, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ -0.9, 23.8, 40.9, 112.3, 122.0, 122.5, 124.6, 124.8, 126.4, 126.5, 127.6, 128.3, 129.0, 129.1, 130.3, 130.5, 140.1, 142.7, 143.5; HRMS calcd. for $C_{23}H_{25}NSi$ $[M]^+$: 343.1751, found 343.1753.



2a6

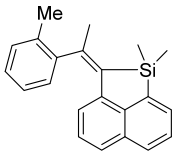
Yellow soild, isolated yield 82% (135 mg); mp: 130.3-130.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.59 (s, 6H, $SiCH_3$), 2.41 (s, 3H, CH_3), 3.88 (s, 3H, CH_3), 6.65-6.66 (m, 1H, CH), 7.08-7.11 (m, 1H, CH), 7.28-7.33 (m, 2H, CH), 7.51-7.54 (m, 2H, CH), 7.68-7.74 (m, 2H, CH), 7.78-7.82 (m, 2H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ -1.0, 29.7, 55.4, 113.6, 114.6, 122.0, 122.6, 124.9, 128.1, 128.5, 129.4, 129.5, 137.8, 140.9, 141.2, 148.3, 150.2, 158.8, 159.3; HRMS calcd. for $C_{22}H_{22}OSi$ $[M]^+$: 330.1434, found 330.1437.



2a7

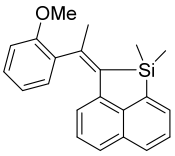
Yellow crastal, isolated yield 50% (95 mg); mp: 208.6-209.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.50 (s, 6H, $SiCH_3$), 2.32 (s, 3H, CH_3), 6.42-6.44 (m, 1H, CH), 6.93-6.97 (m, 1H, CH), 7.16-7.18 (m, 2H, CH), 7.30-7.35 (m, 2H, CH), 7.38-7.42 (m, 2H, CH), 7.61-7.63 (m, 1H, CH), 7.66-7.68 (m, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ -1.0,

29.7, 122.1, 125.0, 126.2, 126.3, 127.2, 127.3, 128.1, 129.2, 129.4, 132.4, 133.7, 138.2, 141.0, 143.0, 145.7, 148.7; HRMS calcd. for $C_{21}H_{19}SiBr$ $[M]^+$: 378.0434, found 378.0440.



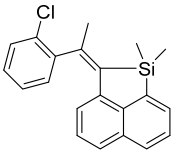
2a8

Yellow solid, isolated yield 60% (94 mg); mp: 105.6-106.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.58 (d, J = 2.0 Hz, 6H, $SiCH_3$), 2.15 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 6.37-6.38 (m, 1H, CH), 7.03-7.07 (m, 1H, CH), 7.12-7.14 (m, 1H, CH), 7.48-7.52 (m, 3H, CH), 7.71-7.78 (m, 4H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ -1.0, -0.9, 18.9, 28.8, 120.9, 125.2, 126.2, 126.8, 126.9, 127.1, 127.2, 128.1, 129.2, 130.8, 132.3, 133.9, 134.0, 138.2, 141.3, 142.8, 145.0, 147.8; HRMS calcd. for $C_{22}H_{22}Si$ $[M]^+$: 314.1485, found 314.1488.



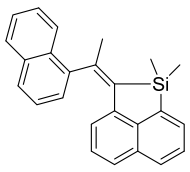
2a9

Yellow solid, isolated yield 60% (99 mg); mp: 132.9-133.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.63 (d, J = 12.0 Hz, 6H, $SiCH_3$), 2.41 (s, 3H, CH_3), 3.79 (s, 3H, CH_3), 6.58-6.59 (m, 1H, CH), 7.00-7.13 (m, 4H, CH), 7.35-7.39 (m, 1H, CH), 7.49-7.53 (m, 2H, CH), 7.72-7.74 (m, 1H, CH), 7.77-7.79 (m, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ -1.0, -0.9, 28.8, 55.9, 111.9, 121.5, 121.7, 124.9, 126.2, 126.5, 128.0, 128.6, 128.9, 129.1, 132.3, 134.2, 134.4, 138.4, 141.5, 143.0, 146.2, 156.0; HRMS calcd. for $C_{22}H_{22}OSi$ $[M]^+$: 330.1433, found 330.1434.



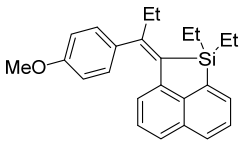
2a10

Yellow oil, isolated yield 55% (92 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.47 (d, J = 7.6 Hz, 6H, $SiCH_3$), 2.25 (s, 3H, CH_3), 6.23-6.25 (m, 1H, CH), 6.91-6.95 (m, 1H, CH), 7.05-7.07 (m, 1H, CH), 7.15-7.18 (m, 2H, CH), 7.34-7.40 (m, 3H, CH), 7.57-7.58 (m, 1H, CH), 7.62-7.64 (m, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ -1.2, -1.1, 27.9, 121.2, 125.5, 126.3, 126.6, 128.0, 128.2, 128.6, 129.0, 129.3, 130.3, 131.6, 132.4, 135.5, 138.0, 140.8, 142.9, 144.1, 144.7; HRMS calcd. for $C_{21}H_{19}SiCl$ $[M]^+$: 334.0939, found 334.0941.



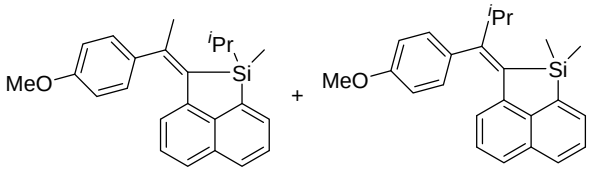
2a11

Yellow oil, isolated yield 40% (70 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.69-0.73 (m, 6H, $SiCH_3$), 2.53 (s, 3H, CH_3), 6.16-6.18 (m, 1H, CH), 6.82-6.86 (m, 1H, CH), 7.34-7.38 (m, 2H, CH), 7.51-7.54 (m, 4H, CH), 7.75-7.77 (m, 2H, CH), 7.87-7.89 (m, 2H, CH), 7.92-7.94 (m, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ -0.9, -0.8, 29.8, 121.6, 121.9, 122.2, 124.9, 125.3, 125.4, 126.5, 126.6, 127.0, 128.5, 129.0, 129.3, 130.1, 131.0, 131.1, 133.5, 134.0, 134.6, 135.8, 136.6, 137.1, 138.5; HRMS calcd. for $C_{25}H_{22}Si$ $[M]^+$: 350.1491, found 350.1493.



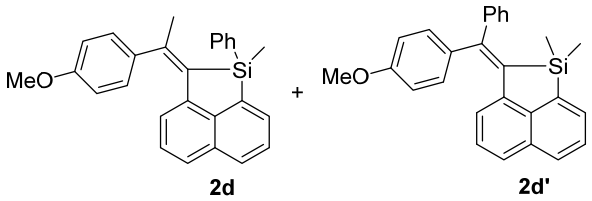
2b

Yellow oil, isolated yield 40% (74 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.47 (brs, 4H, $SiCH_2$), 0.87-0.93 (m, 9H, CH_3), 1.15 (q, J = 8.0 Hz, 2H, CH_2), 3.85 (s, 3H, CH_3), 6.91-6.93 (m, 2H, CH), 7.40-7.46 (m, 2H, CH), 7.50-7.53 (m, 2H, CH), 7.83-7.89 (m, 4H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ -0.9, 6.7, 8.3, 18.3, 55.5, 114.2, 122.3, 124.6, 124.7, 125.1, 130.1, 130.3, 130.7, 130.9, 133.2, 135.7, 136.7, 137.0, 137.3, 156.1, 159.8; HRMS calcd. for $C_{25}H_{28}OSi$ $[M]^+$: 372.1906, found 372.1904.



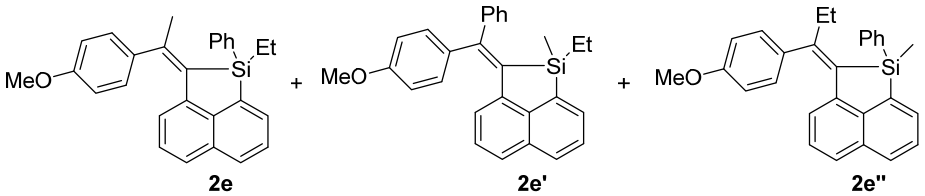
2c **2c'**

Yellow oil, combined isolated yield 90% (161 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.11 (s, 3H, $SiCH_3$), 0.61 (s, 3H, $SiCH_3$), 0.86-0.94 (m, 3H, CH_3), 1.00 (d, J = 6.4 Hz, 6H, CH_3), 2.39 (s, 1H, SiCH), 2.62 (s, 3H, CH), 3.88 (s, 3H, CH_3), 3.90 (s, 1.5H, CH_3), 6.93-6.95 (m, 2H, CH), 6.99-7.01 (m, 1H, CH), 7.31-7.32 (m, 1H, CH), 7.39-7.44 (m, 2H, CH), 7.48-7.64 (m, 3H, CH), 7.67-7.73 (m, 3H, CH), 7.78-7.84 (m, 3H, CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ -3.2, -2.9, 14.7, 15.2, 17.0, 17.8, 18.0, 24.1, 55.4, 55.5, 113.4, 113.6, 114.7, 122.0, 122.5, 123.2, 124.9, 125.1, 125.3, 126.3, 127.5, 127.71, 127.73, 128.1, 128.5, 128.6, 129.3, 129.8, 130.1, 130.2, 131.0, 132.2, 135.7, 136.4, 137.4, 140.9, 142.6, 143.6, 143.8, 150.0, 153.4, 159.3, 159.4; HRMS calcd. for $C_{24}H_{26}OSi$ $[M]^+$: 358.1747, found 358.1751.



2d **2d'**

Yellow oil, combined isolated yield 75% (147 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86-0.89 (m, 5H, $SiCH_3$), 2.27 (s, 3H, CH_3), 3.83 (s, 1H, CH_3), 3.88 (s, 3H, CH_3), 6.71-6.73 (m, 1H, CH), 6.96-6.99 (m, 3H, CH), 7.04-7.06 (m, 1H, CH), 7.11-7.16 (m, 3H, CH), 7.21-7.23 (m, 2H, CH), 7.34-7.37 (m, 3H, CH), 7.46-7.50 (m, 1.5H, CH), 7.54-7.56 (m, 1.5H, CH), 7.63-7.69 (m, 3H, CH), 7.90-7.81 (m, 1H, CH); ^{13}C NMR (100 MHz, C_6D_6): δ -3.1, -2.7, 24.1, 54.9, 113.8, 113.9, 115.0, 123.0, 125.4, 125.6, 126.6, 127.8, 127.9, 128.1, 128.3, 128.9, 129.6, 130.5, 131.3, 132.7, 137.6, 138.1, 138.2, 140.9, 141.2, 148.0, 148.5, 148.7, 149.0, 149.1, 150.3, 159.9, 160.0; HRMS calcd. for $C_{27}H_{24}OSi$ $[M]^+$: 392.1591, found 392.1595.



2e **2e'** **2e''**

Yellow oil, combined isolated yield 60% (147 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.81-0.85 (m, CH_3), 0.88-0.89 (m, $SiCH_3$), 1.24-1.31 (m, CH_3), 1.47-1.51 (m, CH_2), 2.37 (s, CH_3), 3.82 (brs, CH_3), 3.88 (s, CH_3), 6.72-6.75 (m, CH), 6.85-6.87 (m, CH), 6.96-6.98 (m, CH), 7.13-7.23 (m, CH), 7.35-7.41 (m, CH), 7.43-7.47 (m, CH), 7.51-7.60 (m, CH), 7.70-7.73 (m, CH), 7.78-7.80 (m, CH), 7.86-7.91 (m, CH), 7.96-7.98 (m, CH), 8.26-8.28 (m, CH); HRMS calcd. for $C_{28}H_{26}OSi$ $[M]^+$: 406.1747, found 406.1744.

2) X-ray Crystallographic Studies for 2a1 and 1a2

The single crystals of **2a1** and **1a2** suitable for X-ray analysis were grown in DCM at rt. Data collections for **2a1** and **1a2** were performed at 180 K on a SuperNova diffractometer, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structures of **2a1** and **1a2** were solved with the olex2 solve structure solution program using Charge Flipping and refined with the ShelXL refinement package using Least Squares minimization. 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 **2a1** and **1a2** are summarized in Table S1–Table S2. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 1560337 (**2a1**), and CCDC 1560336 (**1a2**). 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.

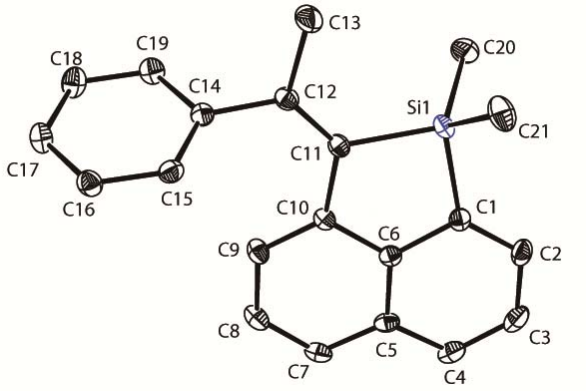


Figure S1. ORTEP drawing of **2a1** with 30% thermal ellipsoids.

Table S1. Crystal data and structure refinement for **2a1**

Identification code	**2a1**
Empirical formula	$C_{21}H_{20}Si$
Formula weight	300.46
Temperature/K	180.00(10)
Crystal system	monoclinic

Space group	$P2_1/n$
a/Å	12.2864(7)
b/Å	9.5206(6)
c/Å	14.4288(8)
α/°	90
β/°	96.731(6)
γ/°	90
Volume/Å^3	1676.15(17)
Z	4
ρ_{calc}g/cm^3	1.191
μ/mm^{-1}	0.135
F(000)	640.0
Crystal size/mm^3	0.05 × 0.05 × 0.05
Radiation	Mo K^{α} (λ = 0.71073)
2Θ range for data collection/°	5.68 to 52.04
Index ranges	$-15 \leq h \leq 15$, $-11 \leq k \leq 11$, $-17 \leq l \leq 17$
Reflections collected	19569
Independent reflections	3304 [R_{int} = 0.0502, R_{sigma} = 0.0344]
Data/restraints/parameters	3304/0/202
Goodness-of-fit on F^2	1.074
Final R indexes [I>=2σ (I)]	R_1 = 0.0407, wR_2 = 0.0958
Final R indexes [all data]	R_1 = 0.0575, wR_2 = 0.1070
Largest diff. peak/hole / e Å^{-3}	0.24/-0.27

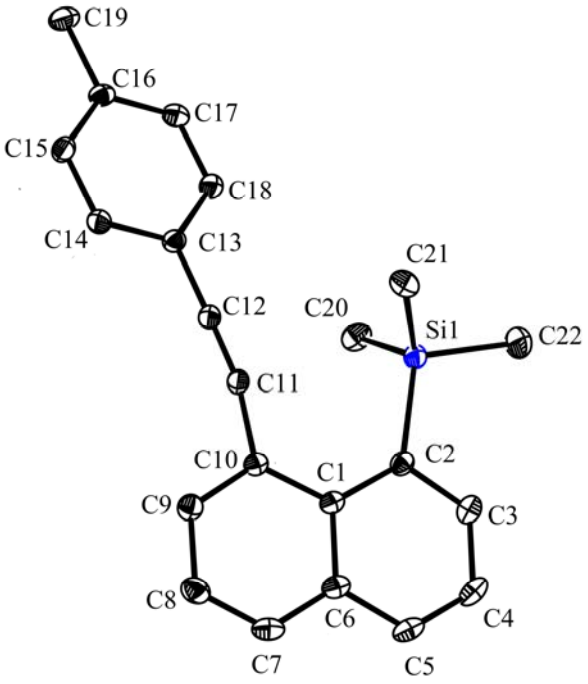


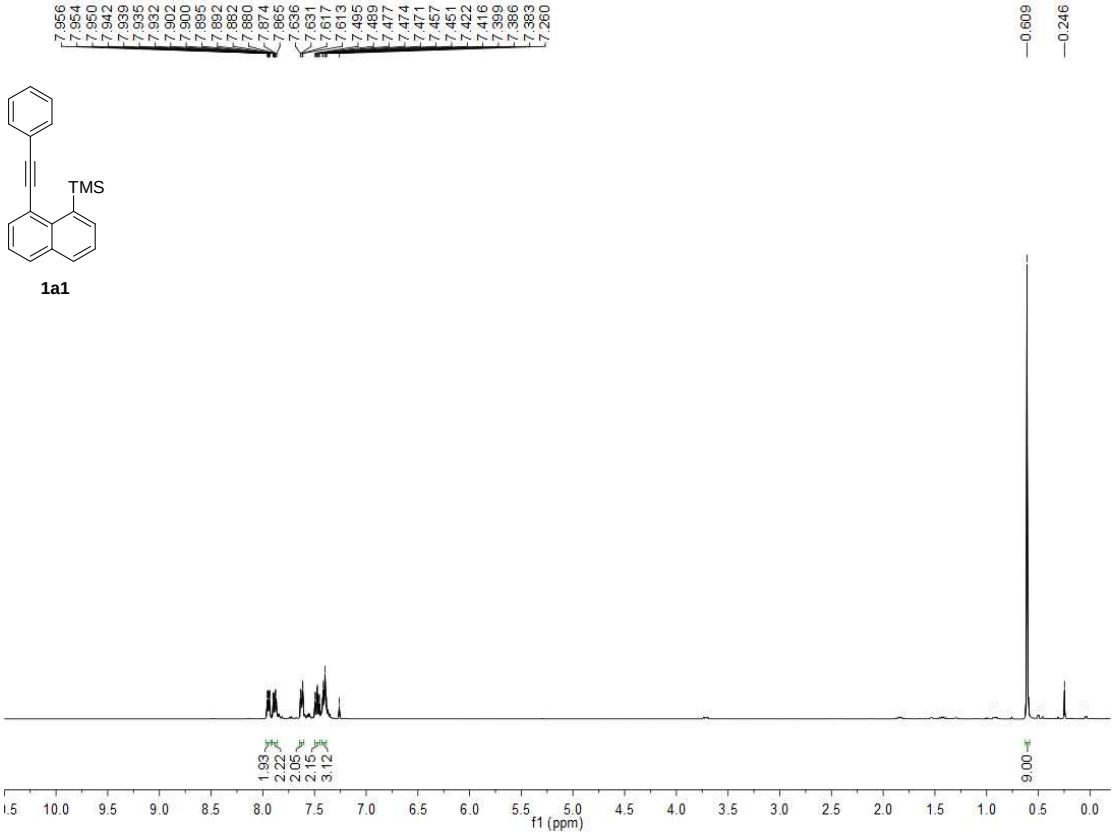
Figure S2. ORTEP drawing of **1a2** with 30% thermal ellipsoids.

Table S2. Crystal data and structure refinement for **1a2**

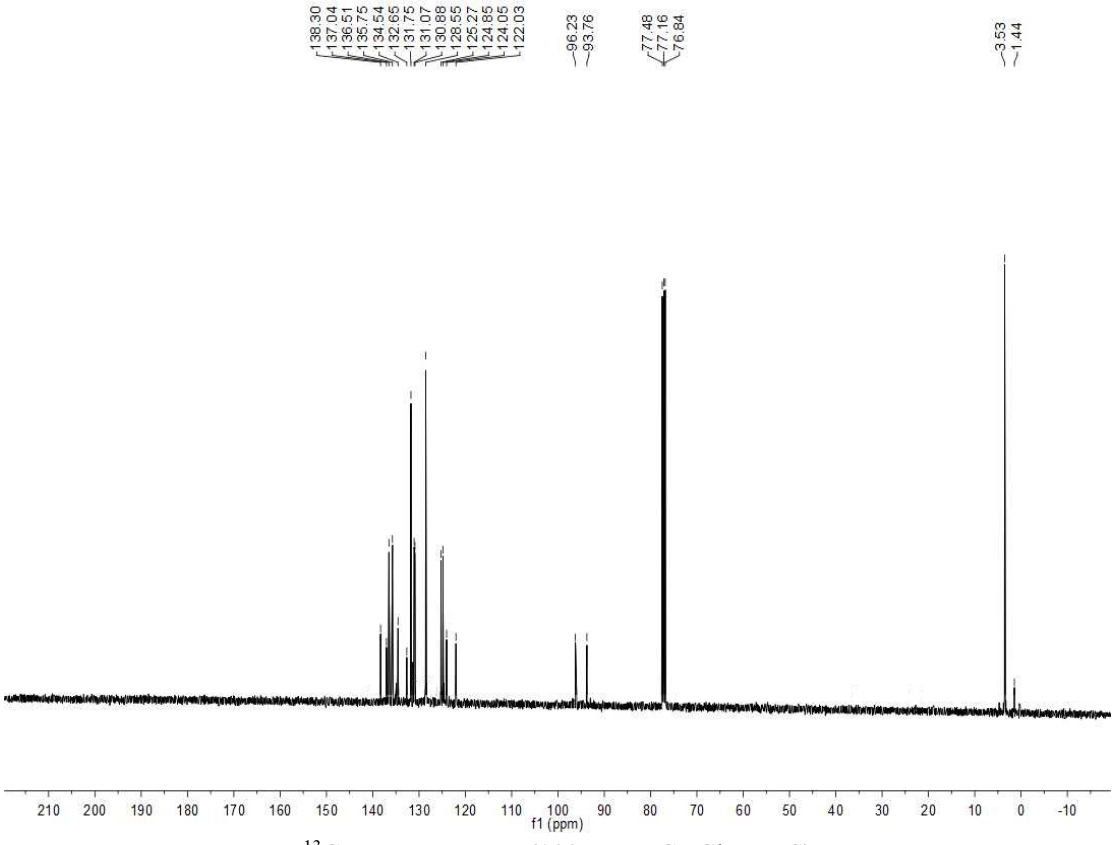
Identification code	**1a2**
Empirical formula	$C_{22}H_{22}Si$
Formula weight	314.48
Temperature/K	180.00(10)
Crystal system	orthorhombic
Space group	Pbca
a/Å	8.8464(4)
b/Å	13.6195(6)
c/Å	30.1026(12)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3626.9(3)
Z	8
ρ_{calc}g/cm^3	1.152
μ/mm^{-1}	0.127
F(000)	1344.0
Crystal size/mm^3	0.1 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)

2Θ range for data collection/°	7.108 to 52.03
Index ranges	$-10 \leq h \leq 10$, $-16 \leq k \leq 16$, $-37 \leq l \leq 37$
Reflections collected	60476
Independent reflections	3555 [R_{int} = 0.0442, R_{sigma} = 0.0170]
Data/restraints/parameters	3555/0/212
Goodness-of-fit on F^2	1.034
Final R indexes [I>=2σ (I)]	R_1 = 0.0365, wR_2 = 0.0977
Final R indexes [all data]	R1 = 0.0400, wR2 = 0.1005
Largest diff. peak/hole / e Å-3	0.24/-0.21

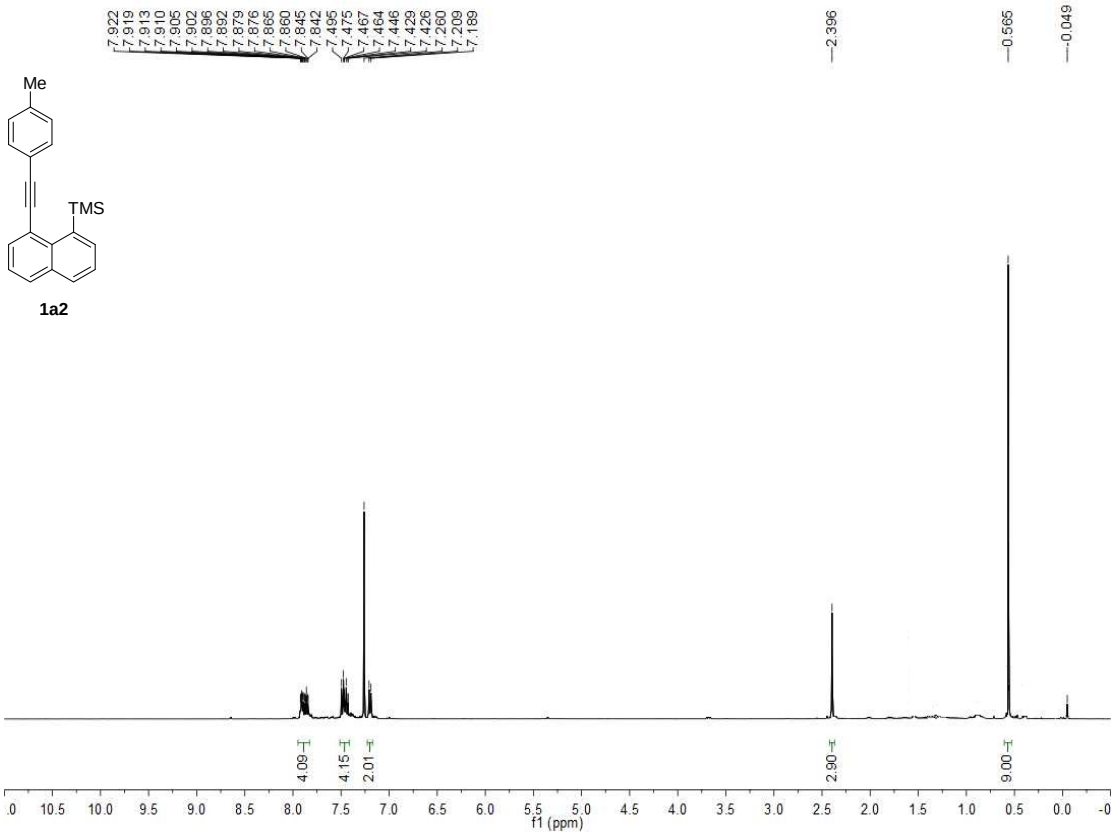
3) Copies of ^{1}H NMR and ^{13}C NMR Spectra of All New Compounds



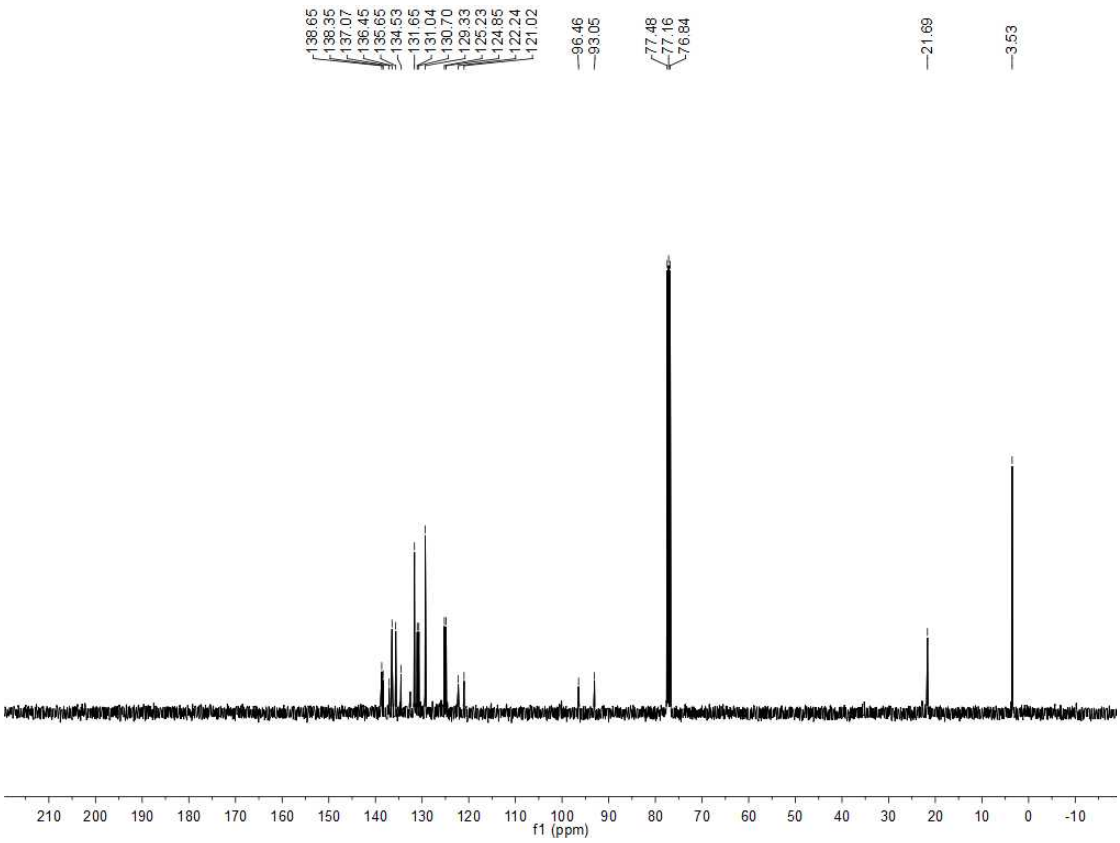
^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS)



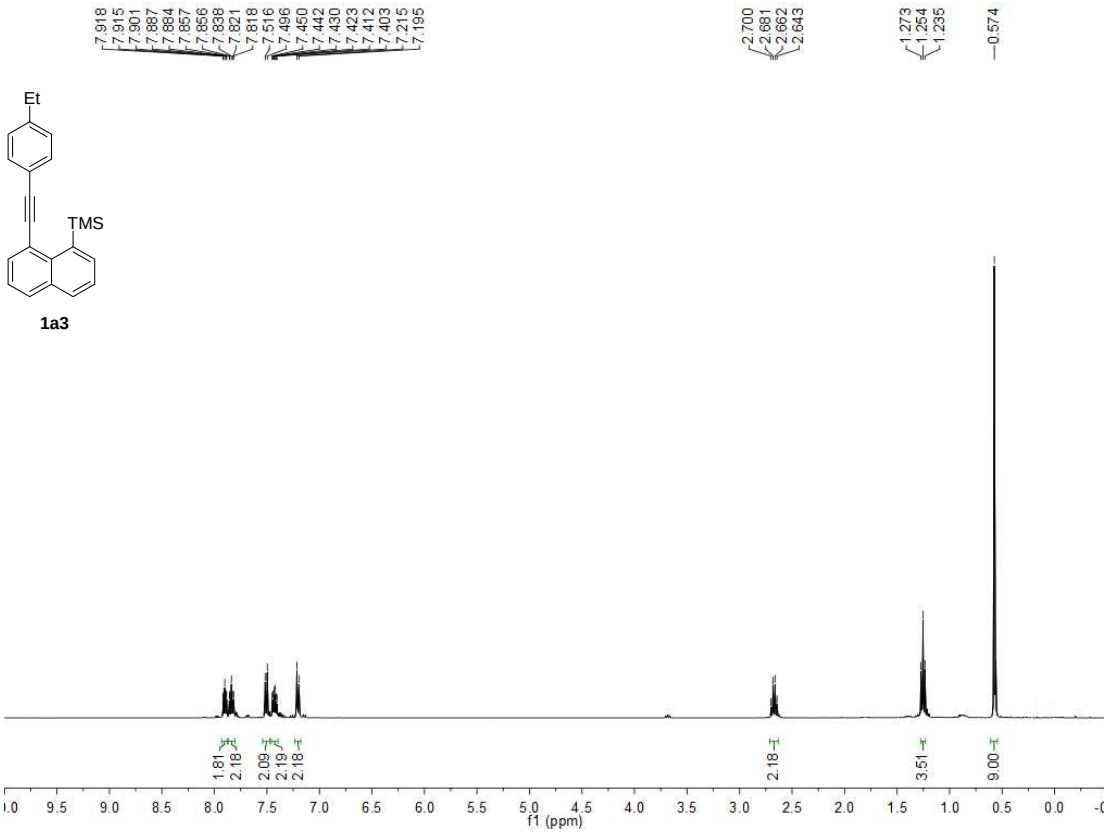
^{13}C NMR spectrum (100 MHz, $CDCl_3$, TMS)



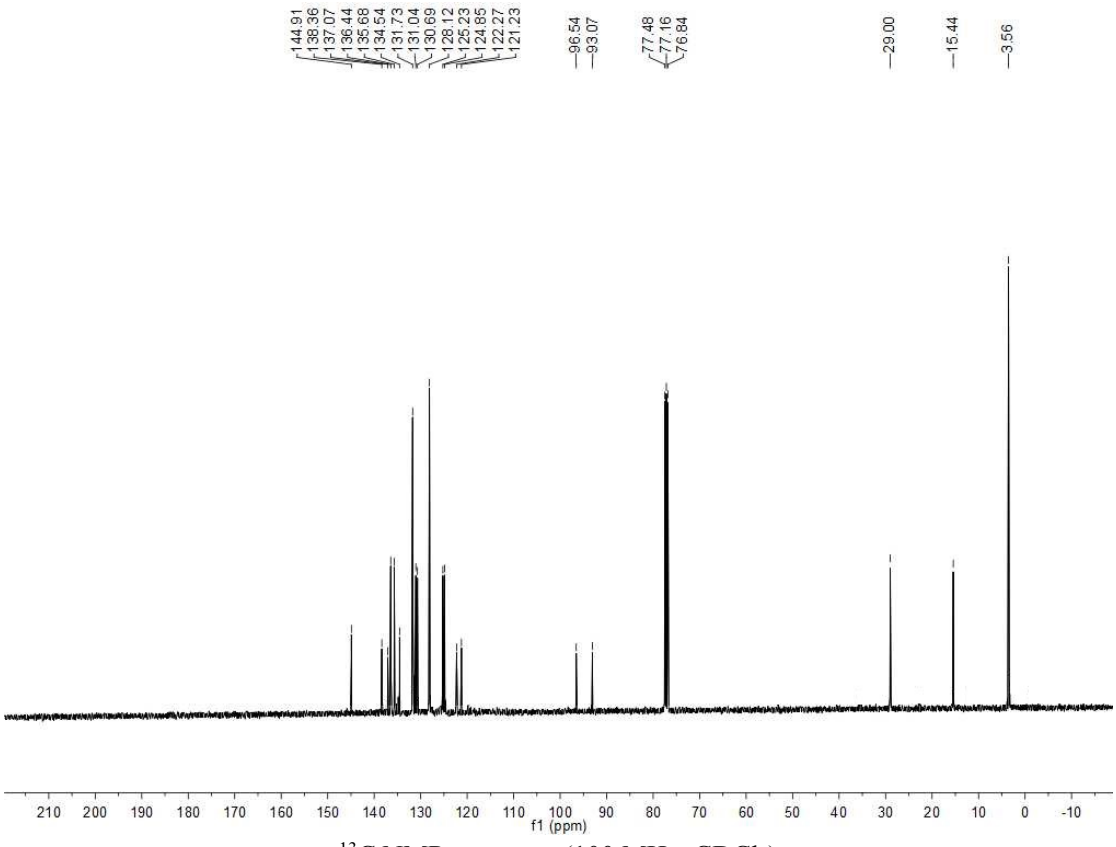
^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS)



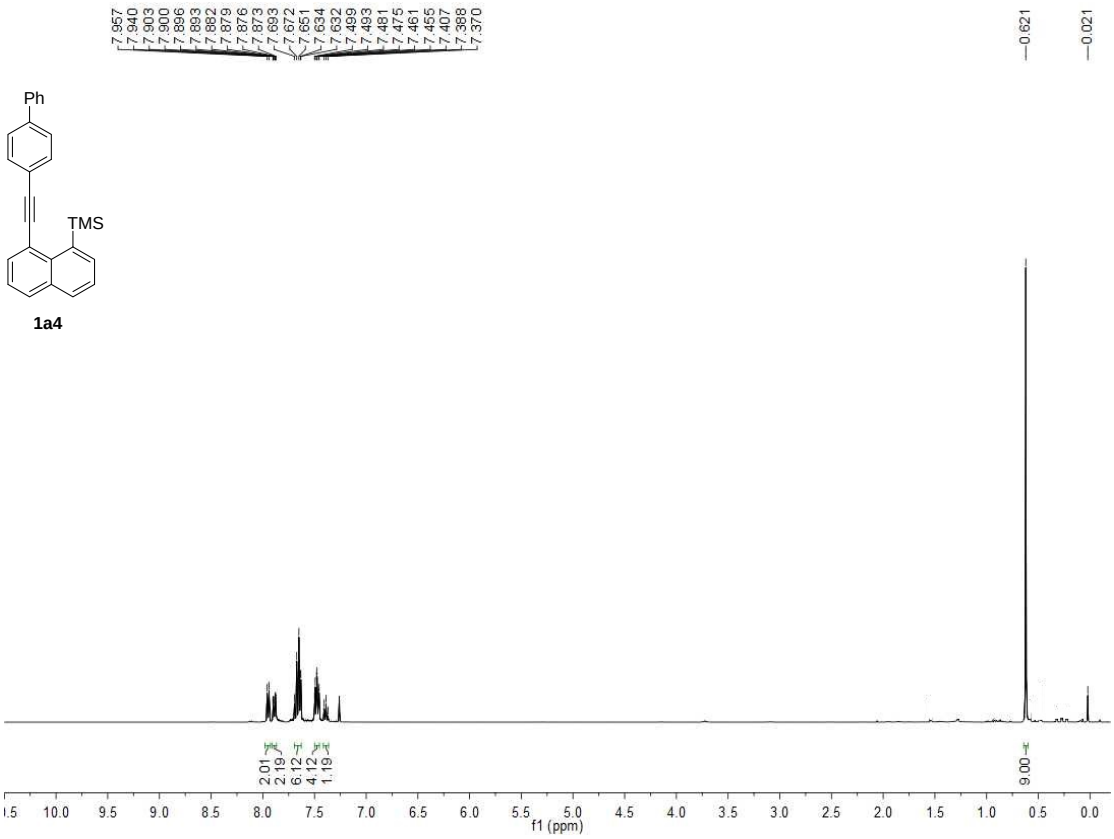
^{13}C NMR spectrum (100 MHz, $CDCl_3$)



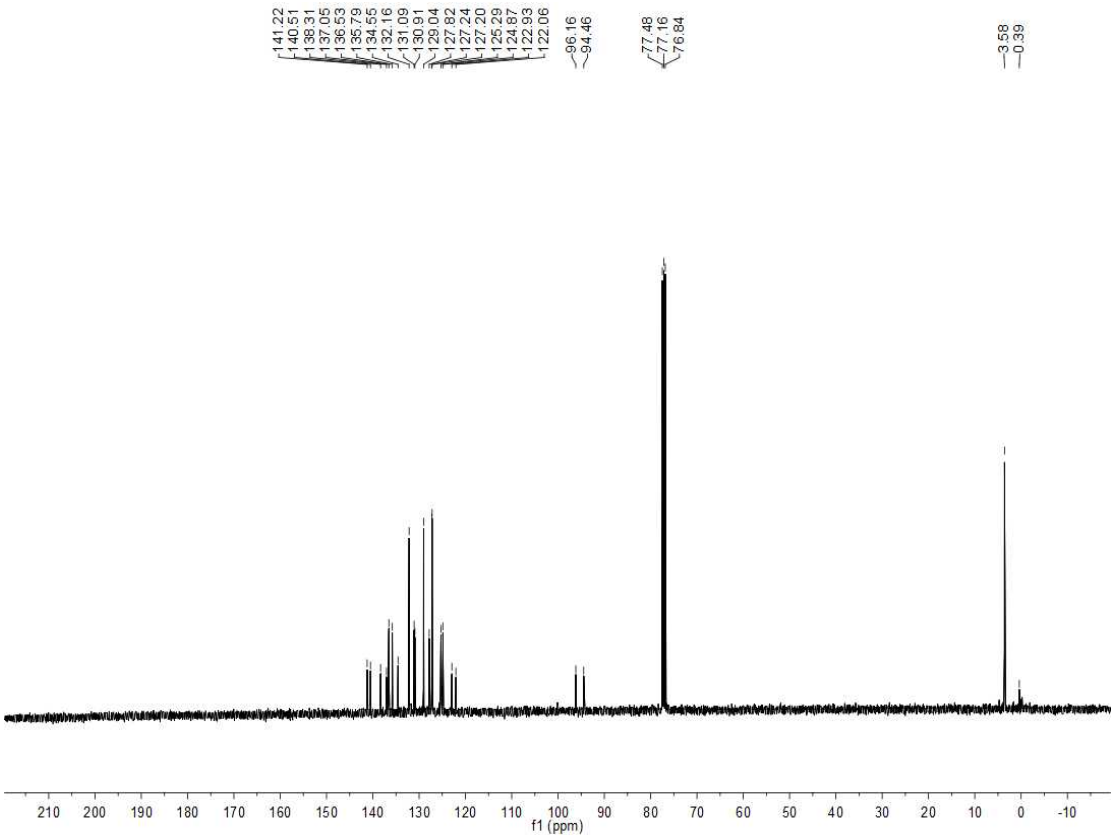
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



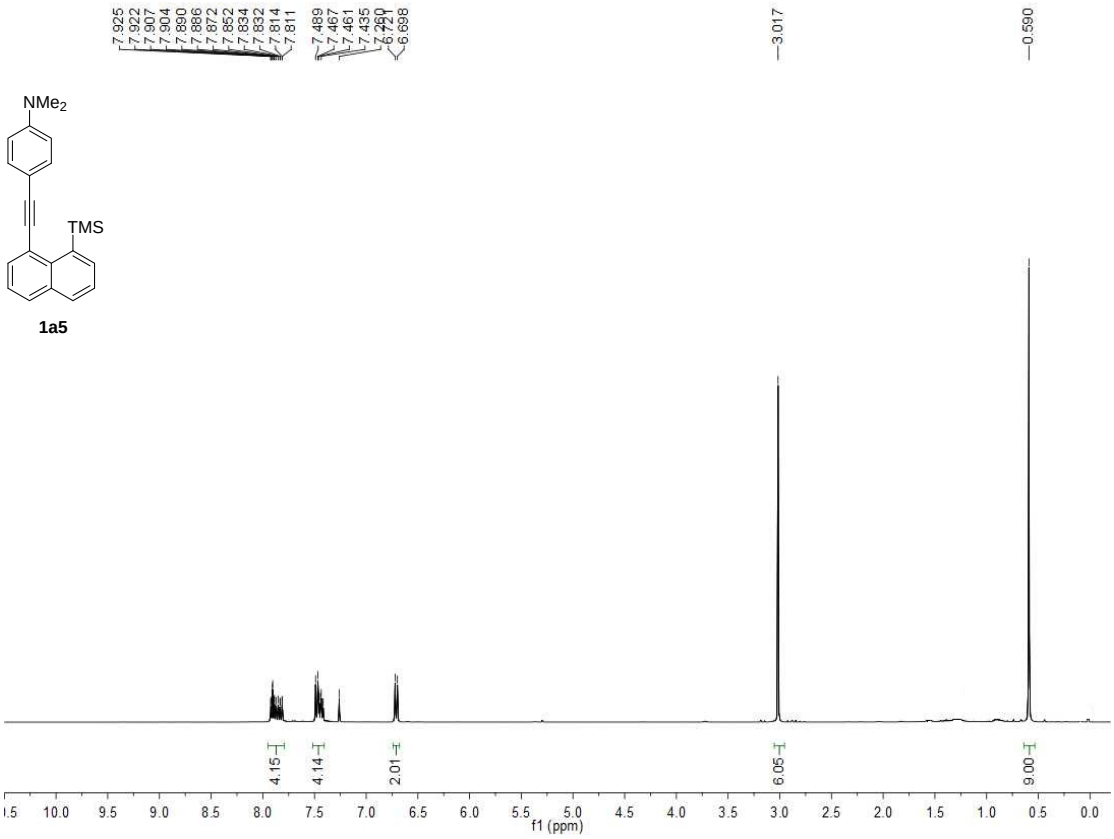
^{13}C NMR spectrum (100 MHz, $CDCl_3$)



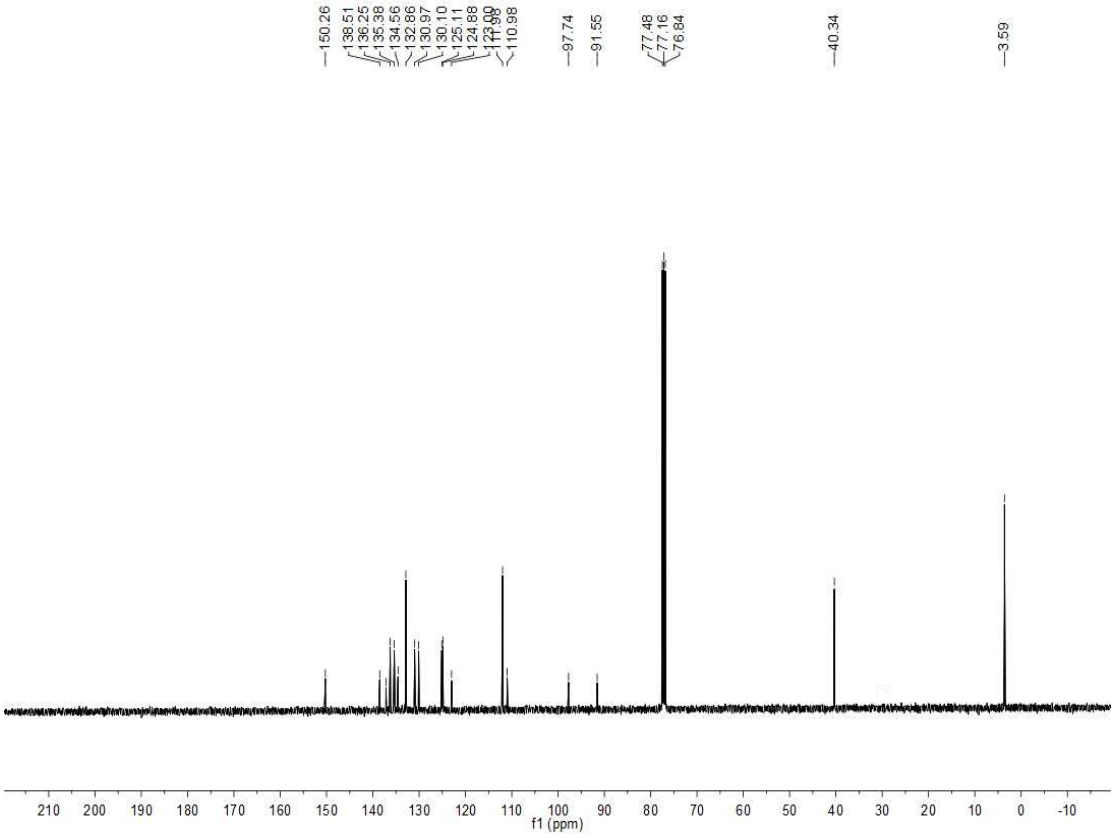
^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS)



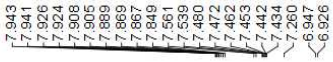
^{13}C NMR spectrum (100 MHz, $CDCl_3$, TMS)

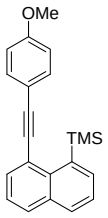


^{1}H NMR spectrum (400 MHz, $CDCl_3$)



^{13}C NMR spectrum (100 MHz, $CDCl_3$)





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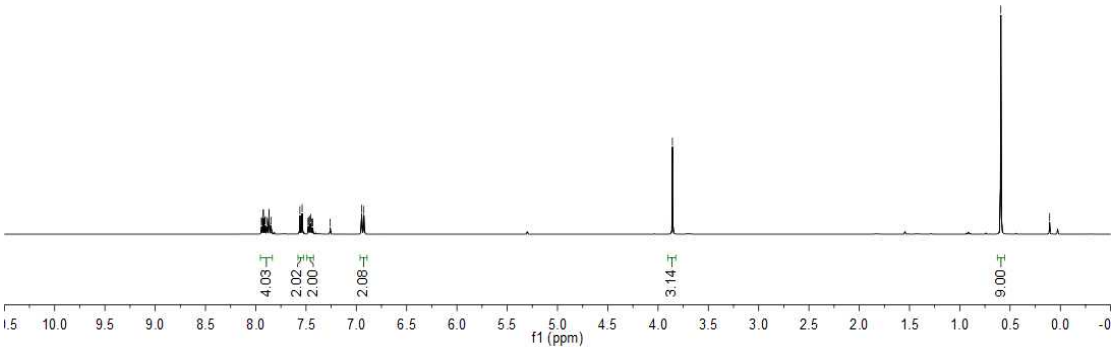
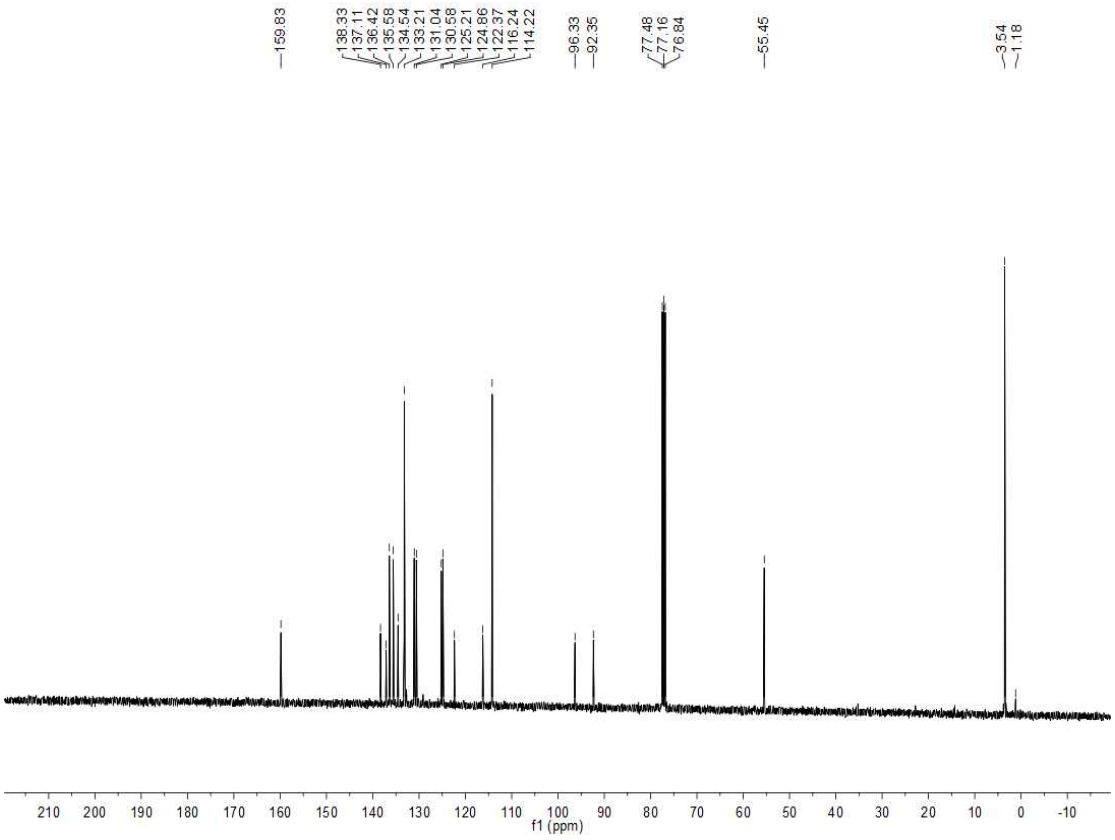
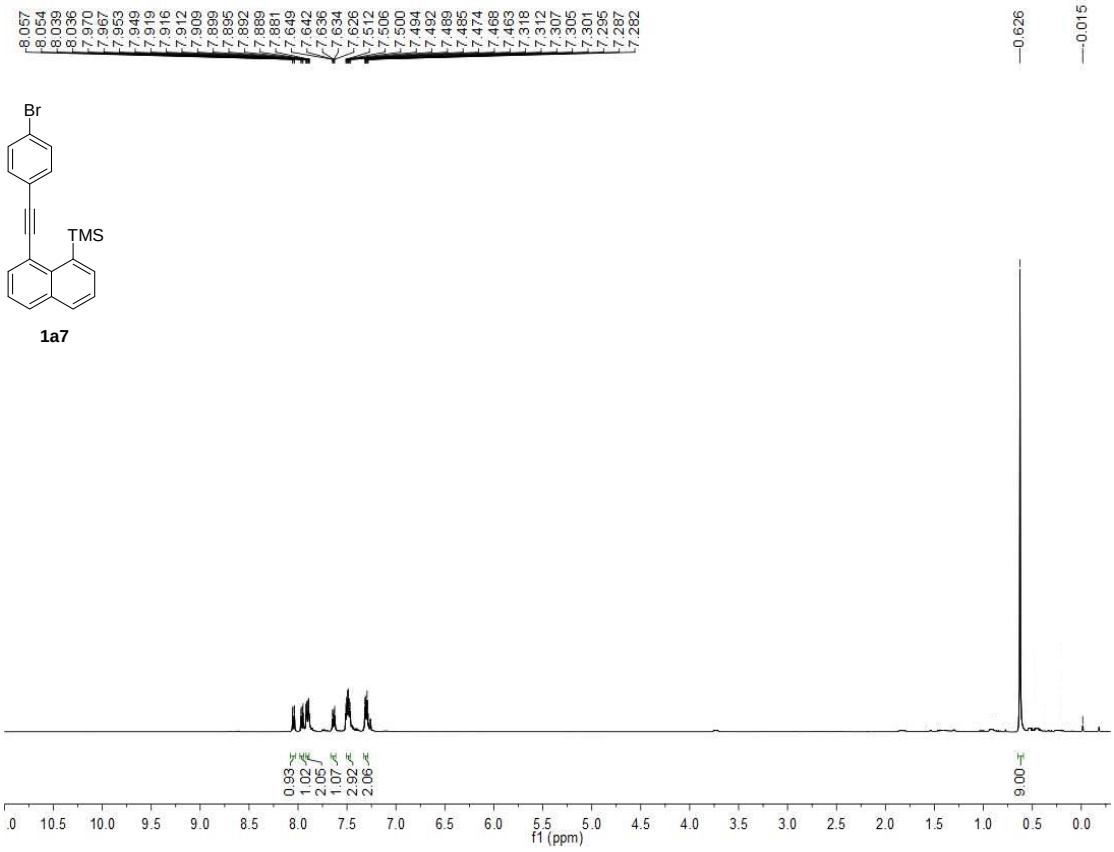


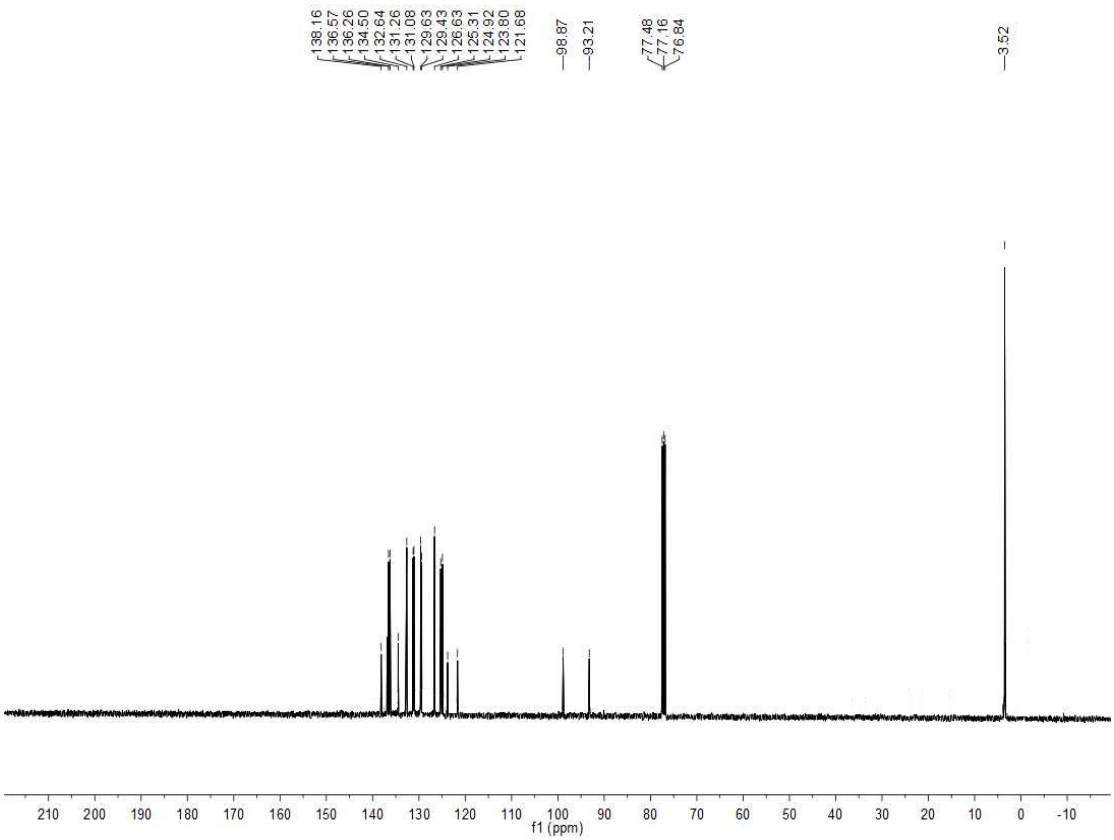
^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS)



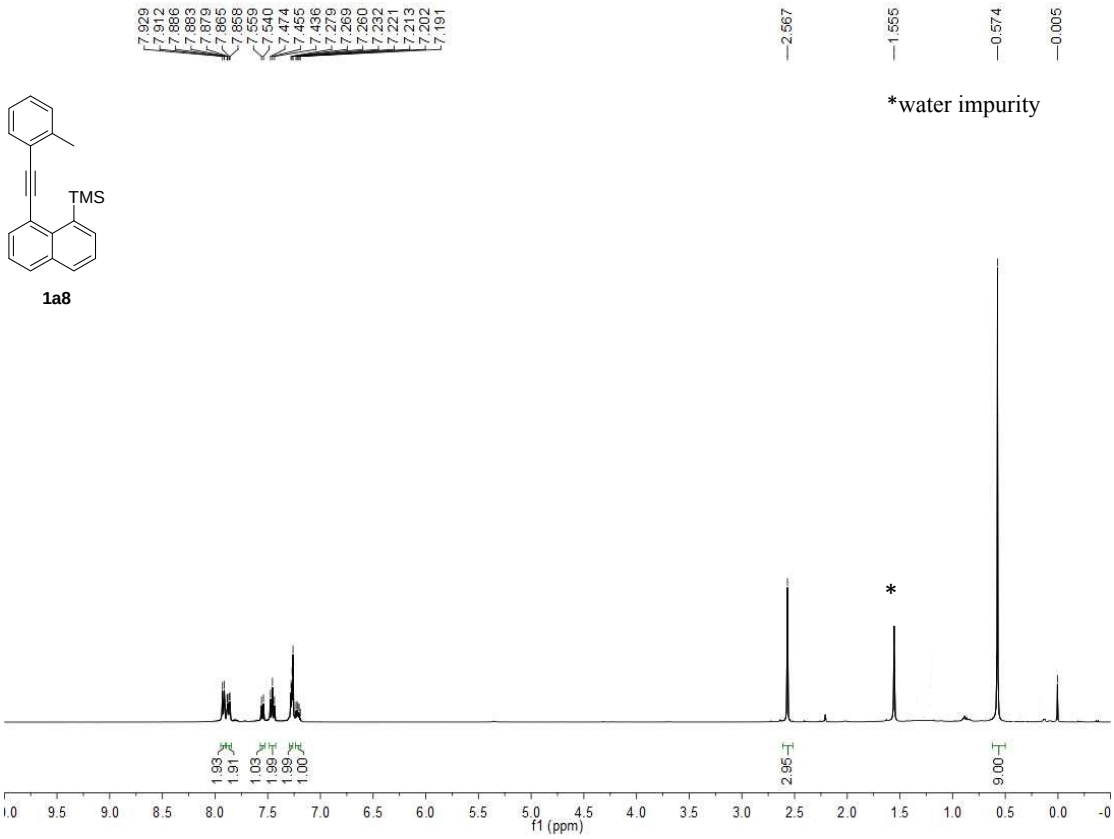
^{13}C NMR spectrum (100 MHz, $CDCl_3$, TMS)



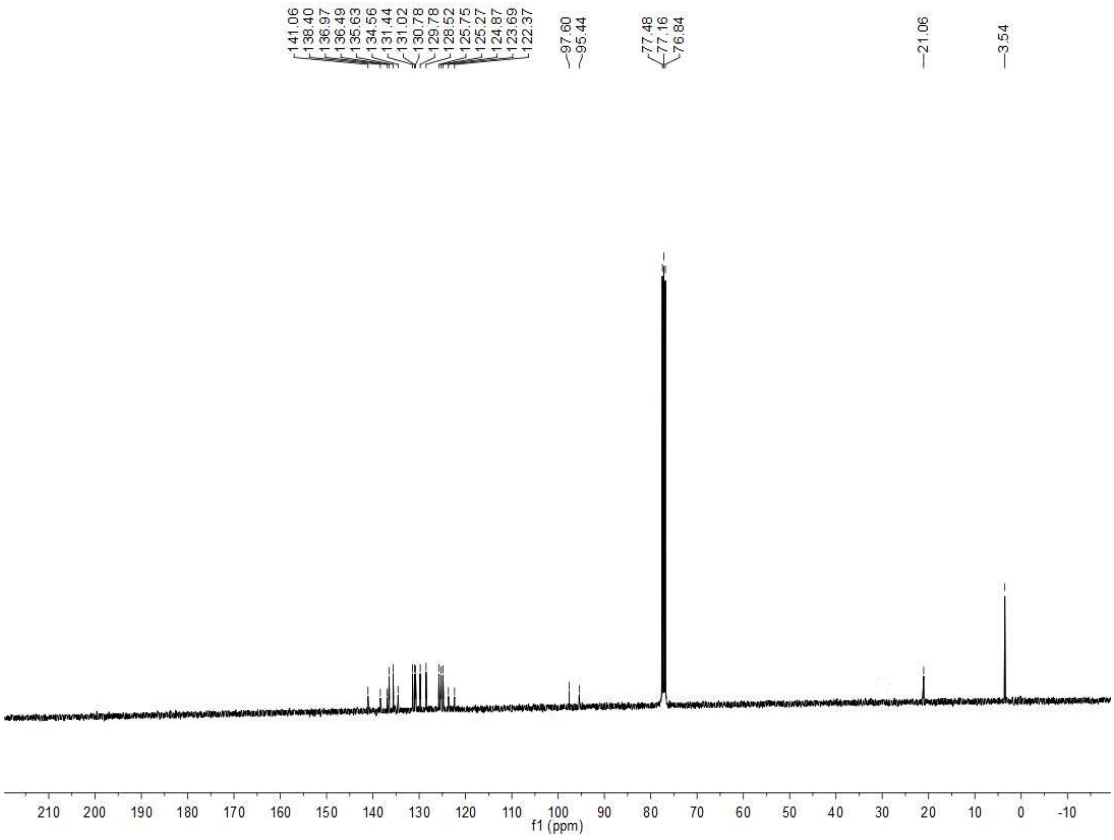
^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS)



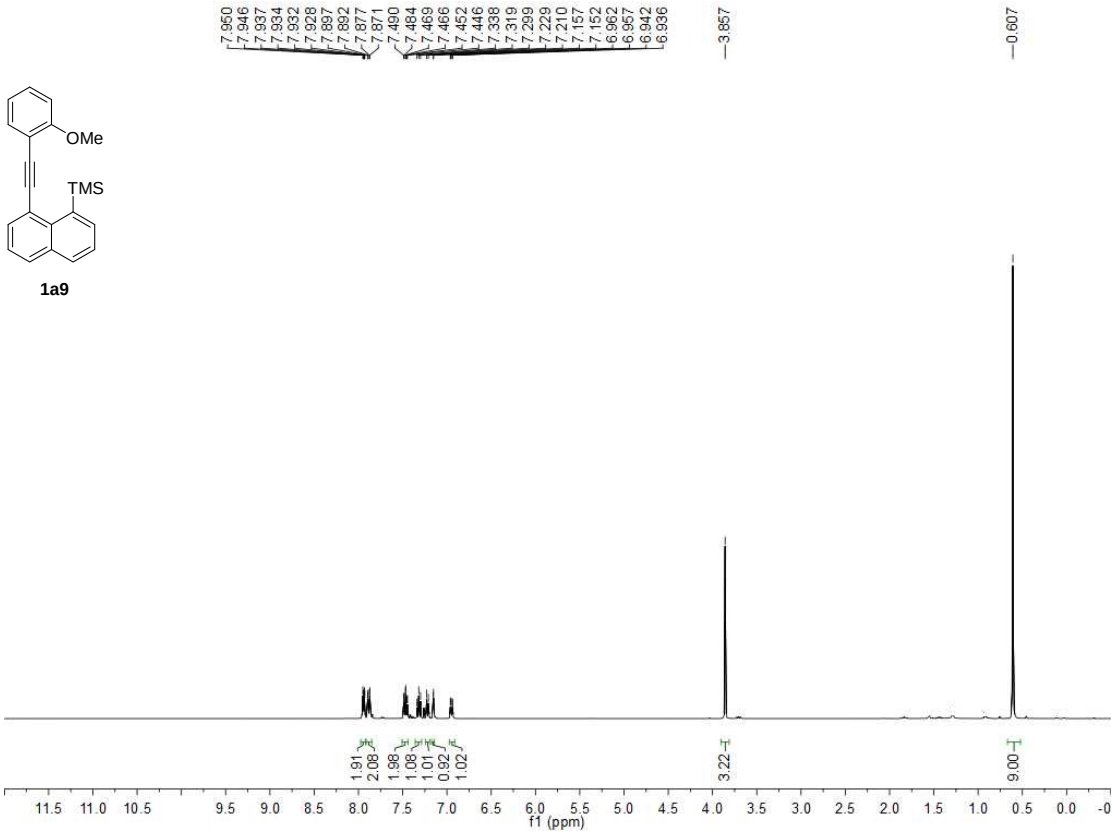
^{13}C NMR spectrum (100 MHz, $CDCl_3$)



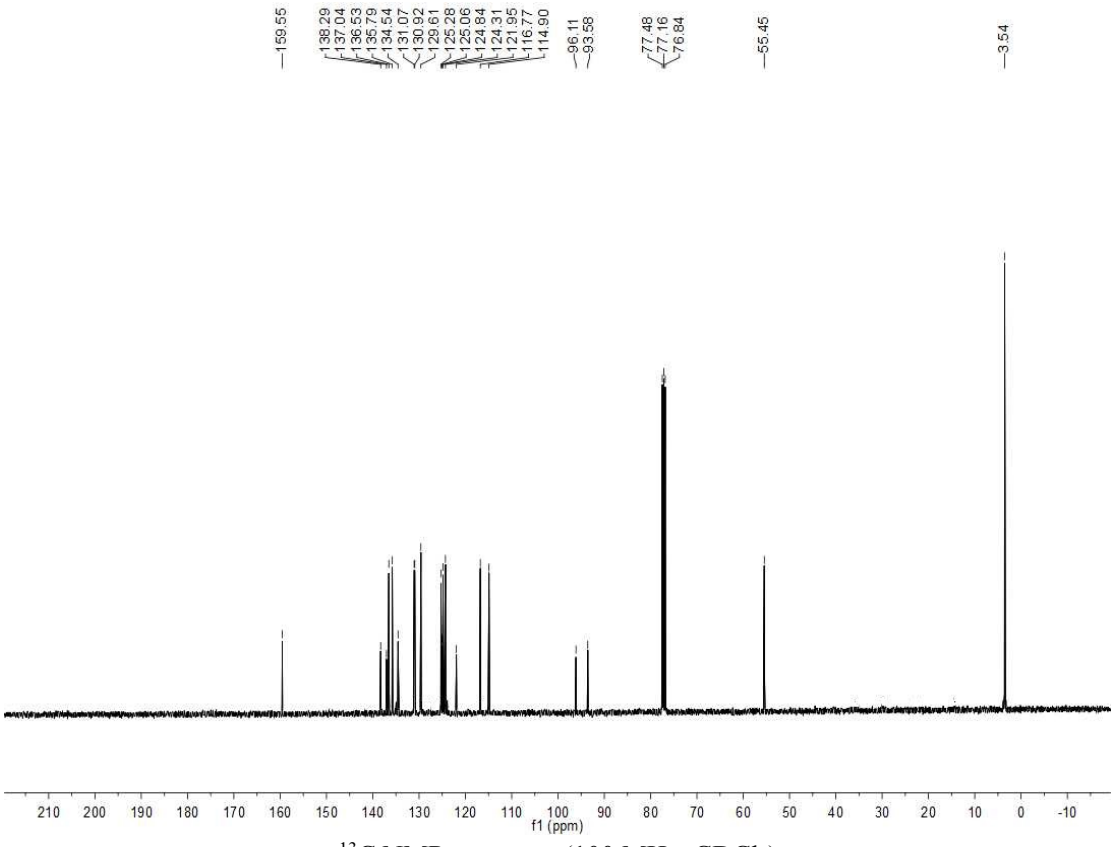
^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS)



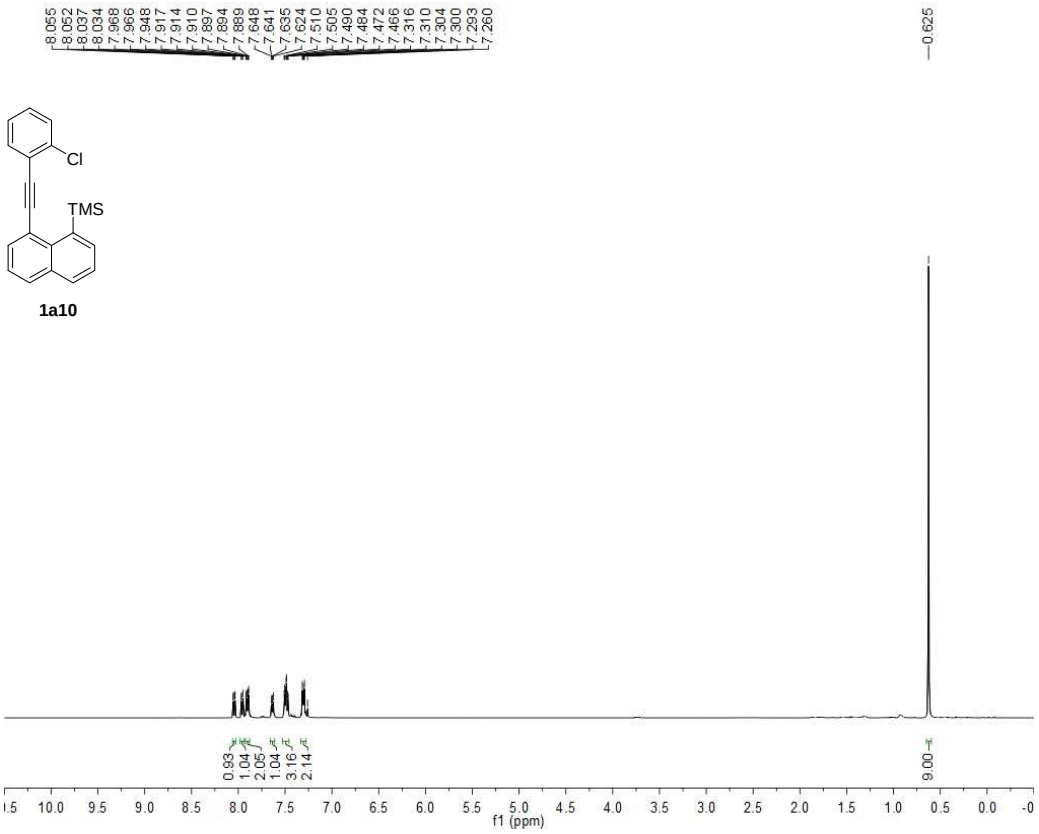
^{13}C NMR spectrum (100 MHz, $CDCl_3$)



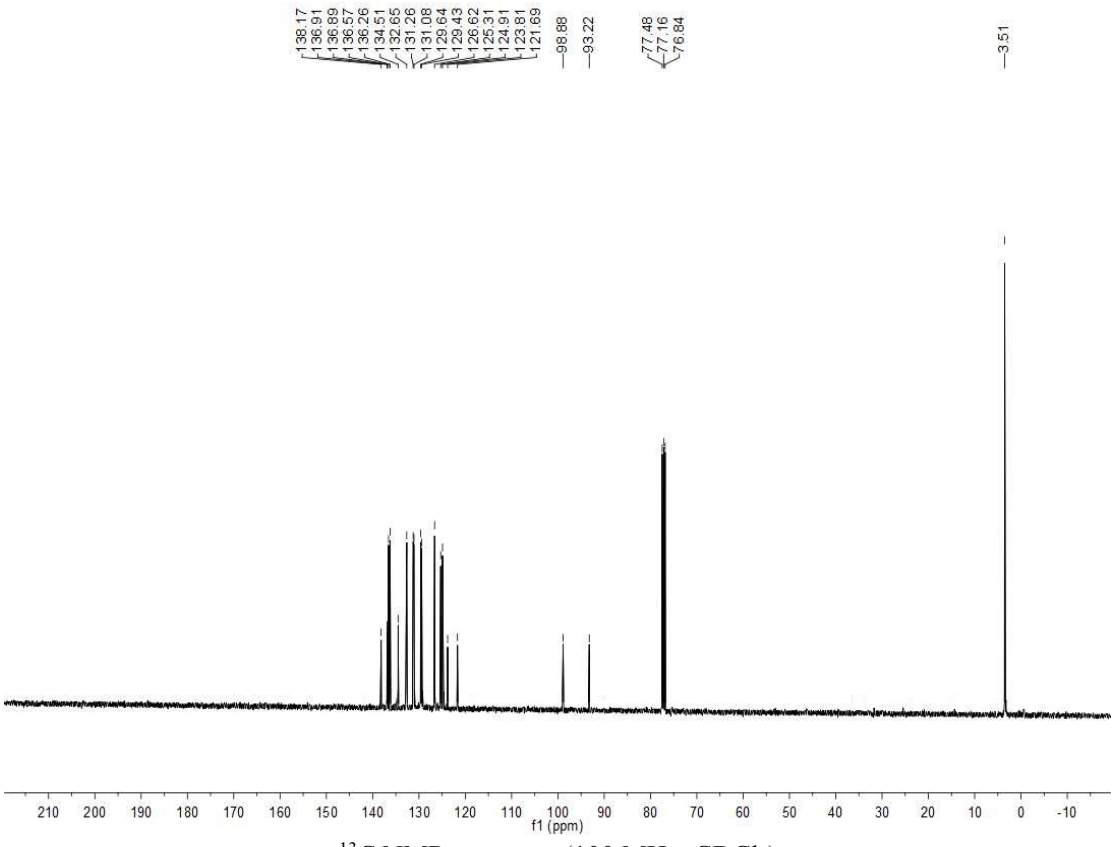
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



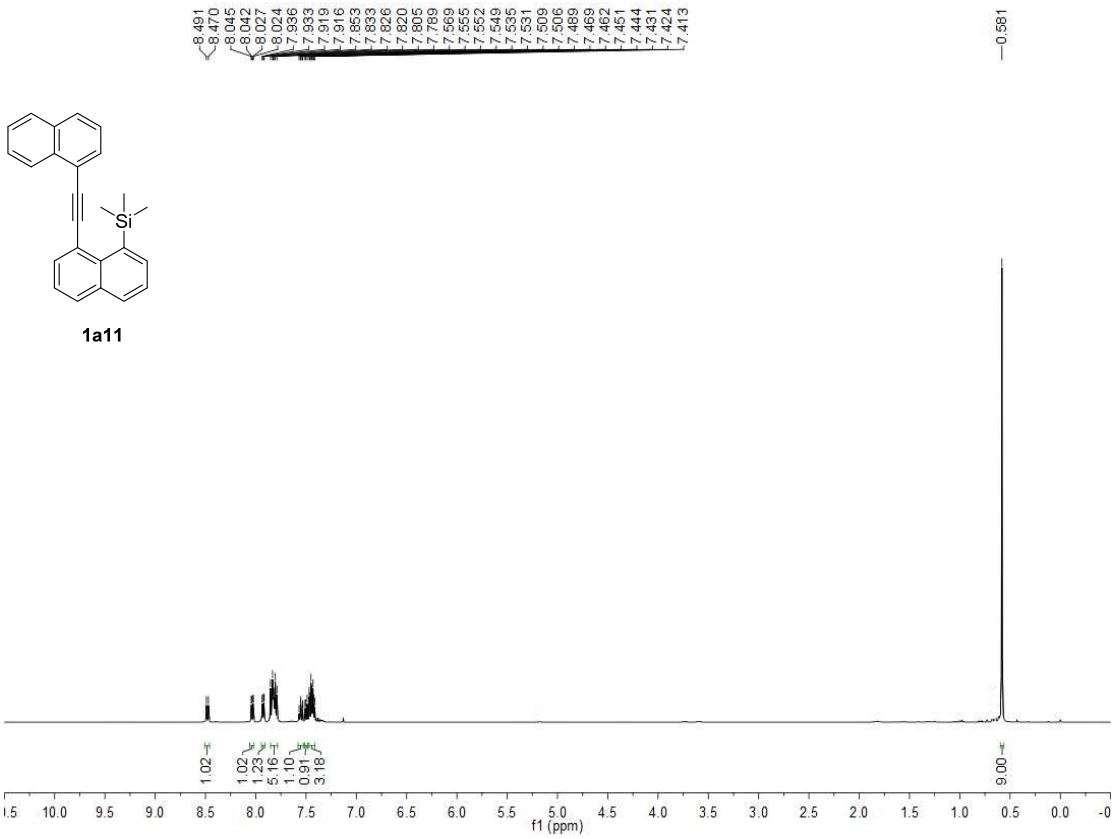
^{13}C NMR spectrum (100 MHz, $CDCl_3$)



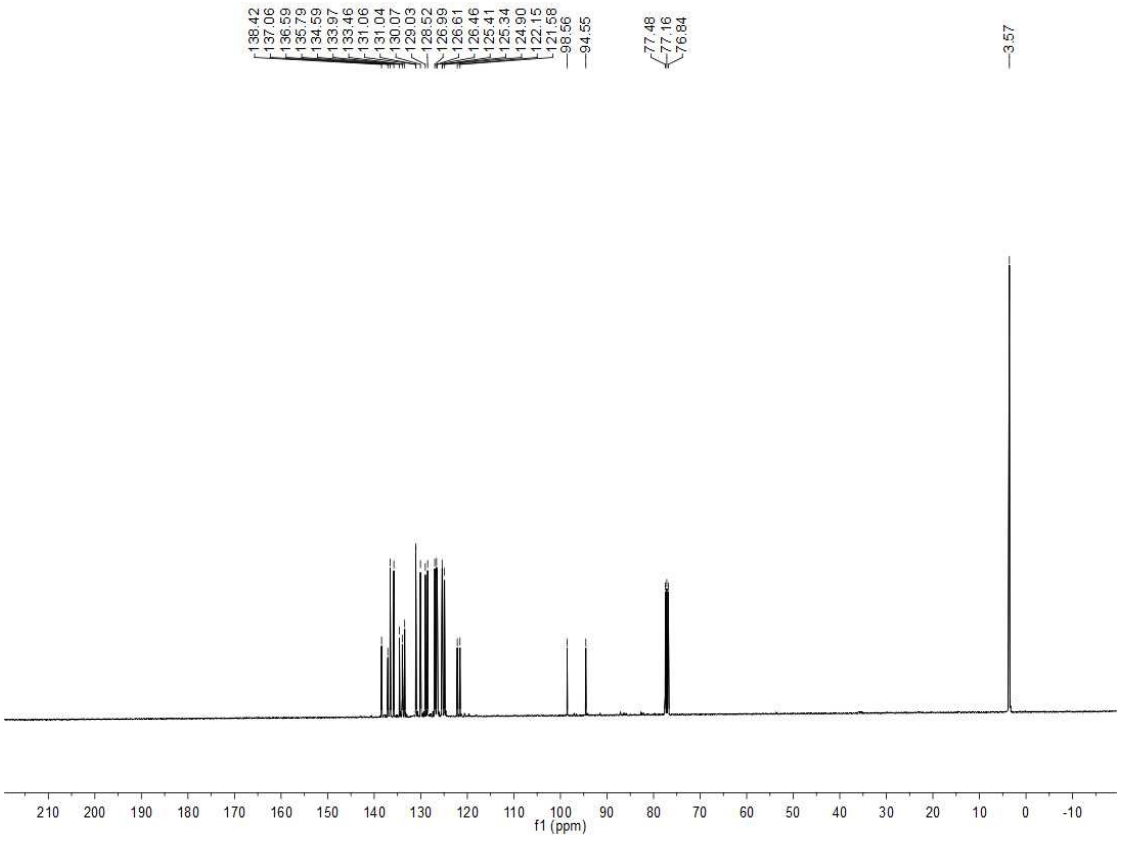
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



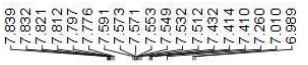
^{13}C NMR spectrum (100 MHz, $CDCl_3$)

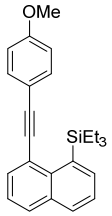


^{1}H NMR spectrum (400 MHz, $CDCl_3$)

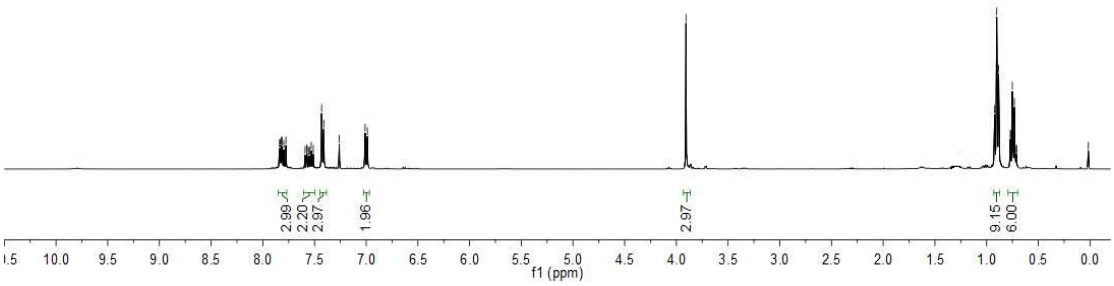


^{13}C NMR spectrum (100 MHz, $CDCl_3$)

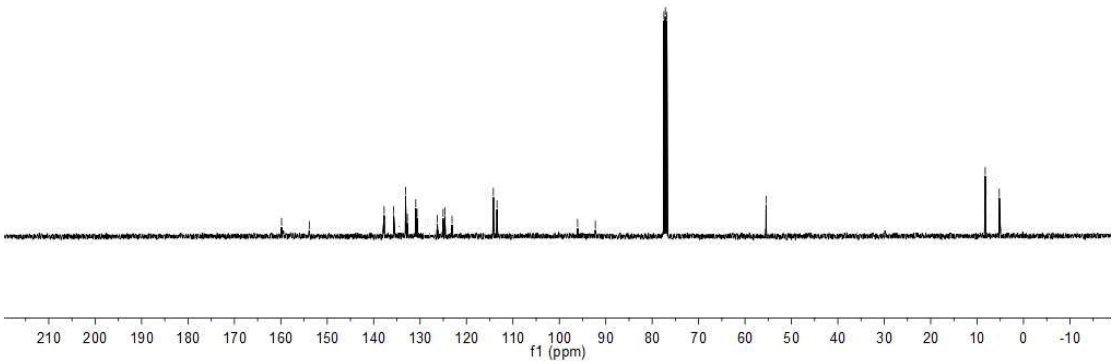




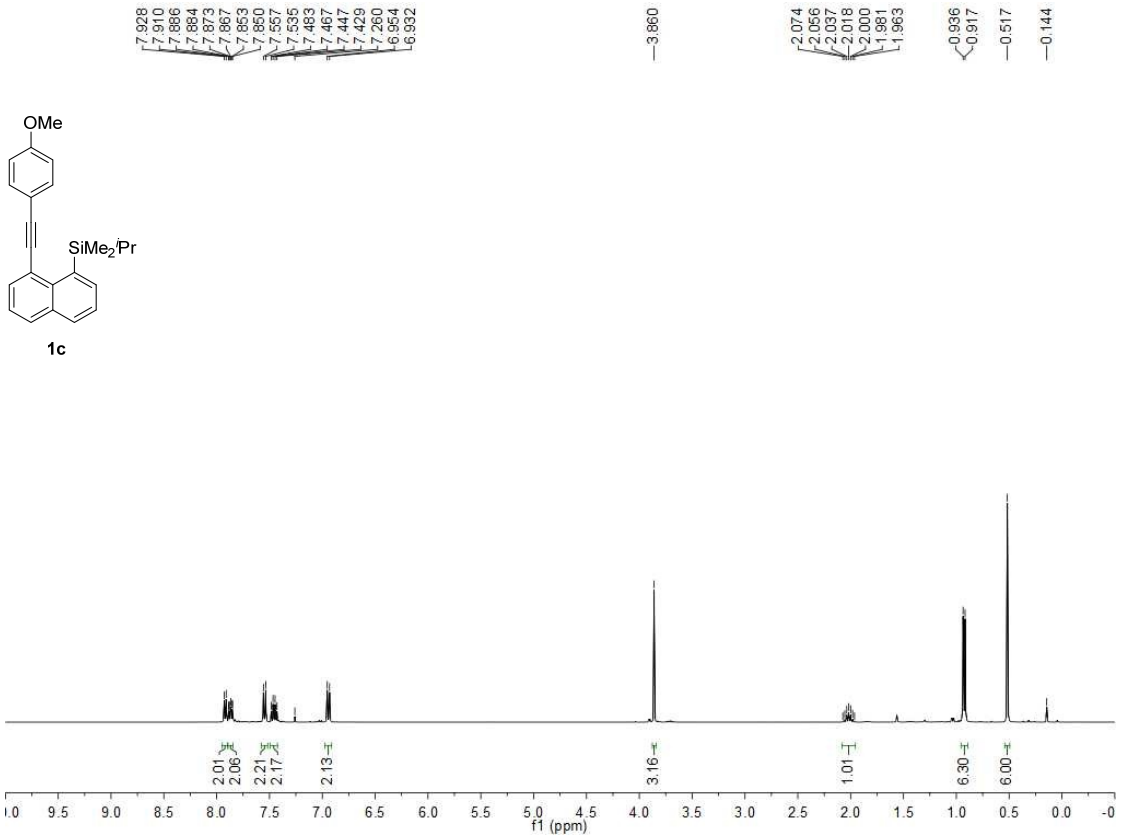
1b



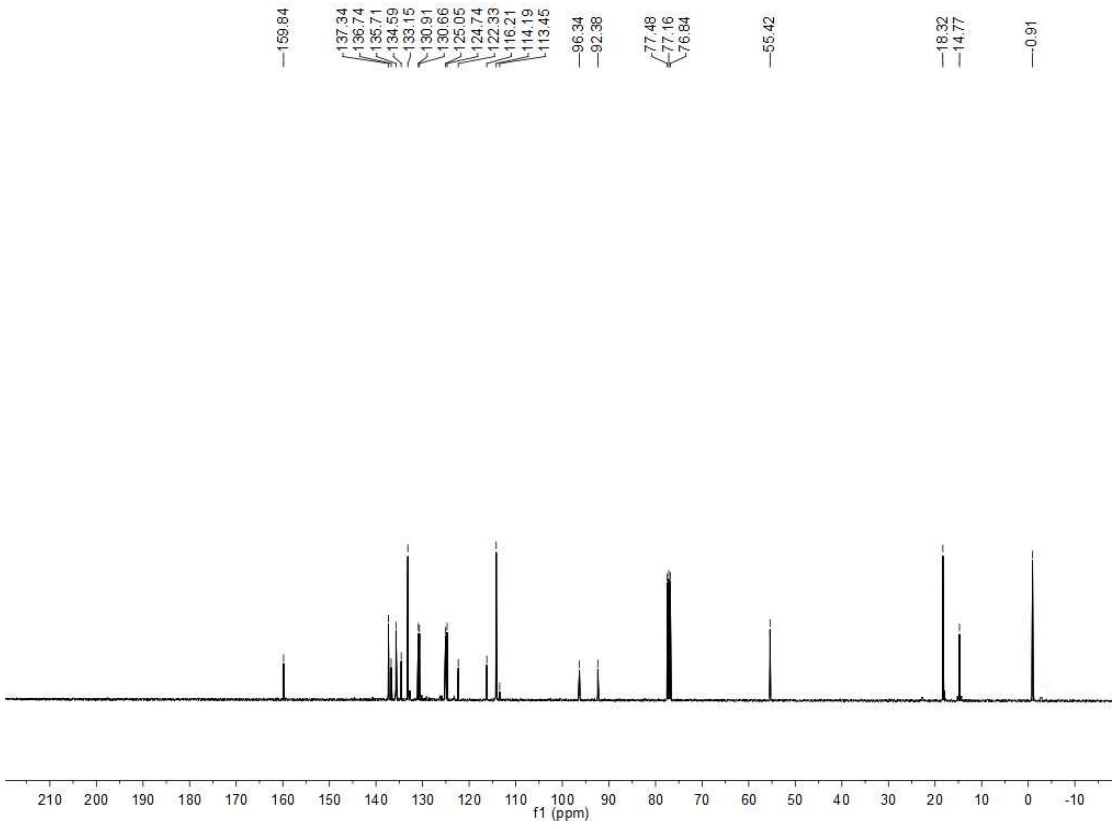
^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS)



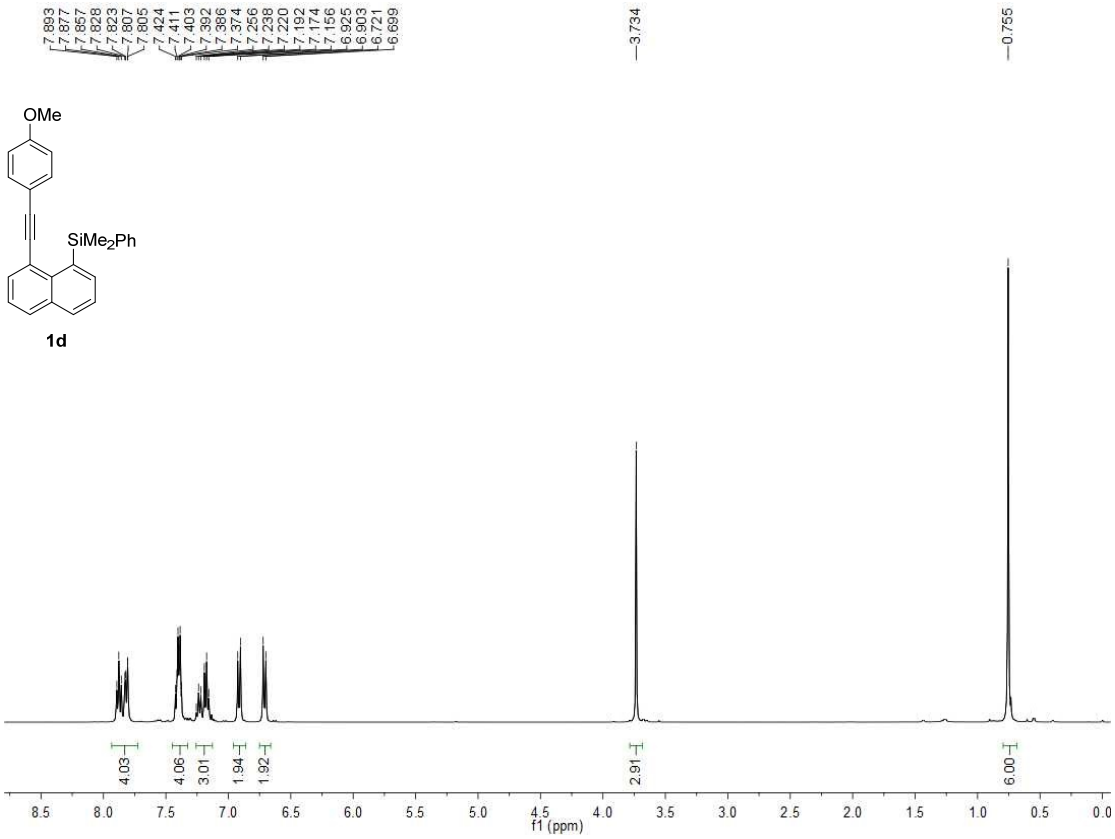
^{13}C NMR spectrum (100 MHz, $CDCl_3$)



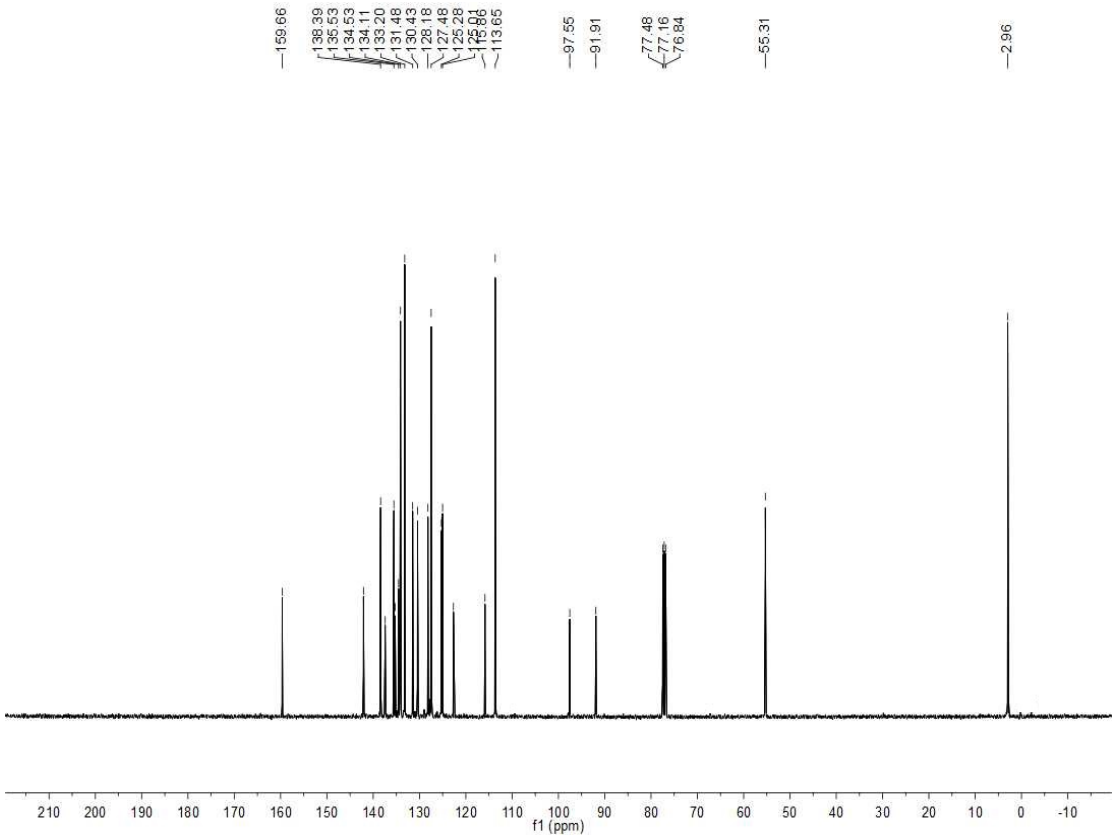
^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS)



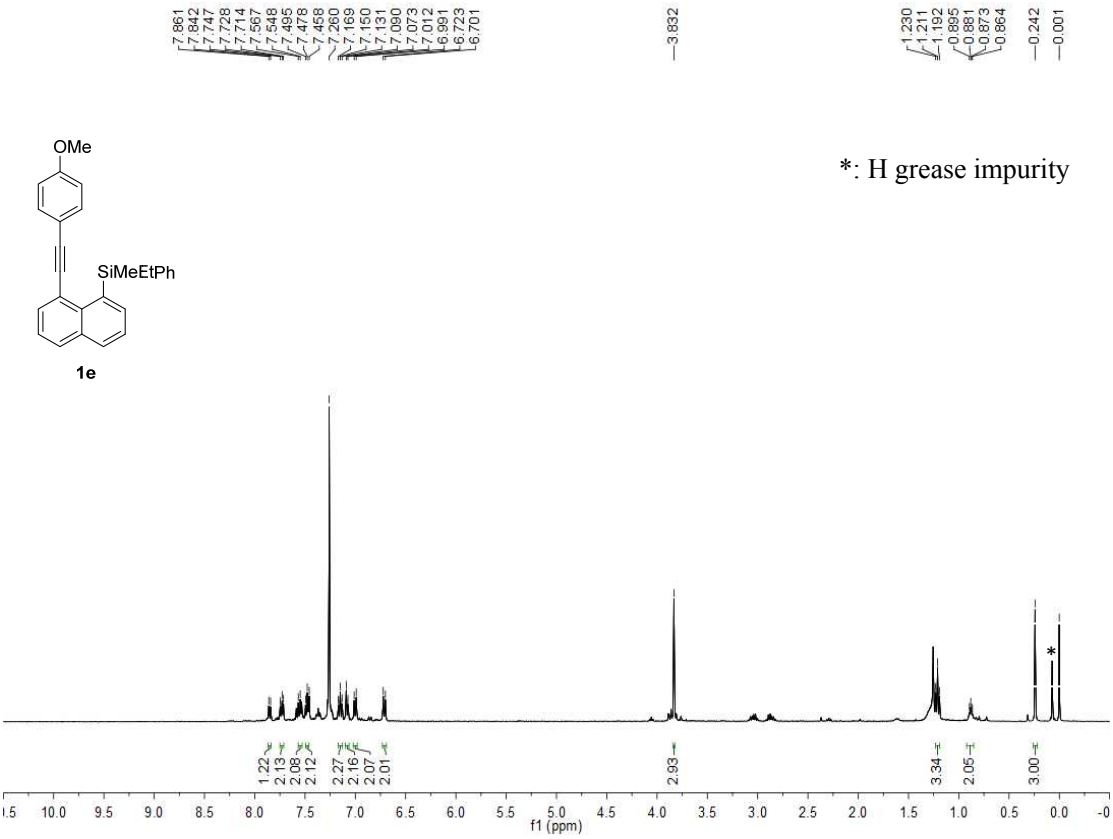
^{13}C NMR spectrum (100 MHz, $CDCl_3$)



^{1}H NMR spectrum (400 MHz, $CDCl_3$)

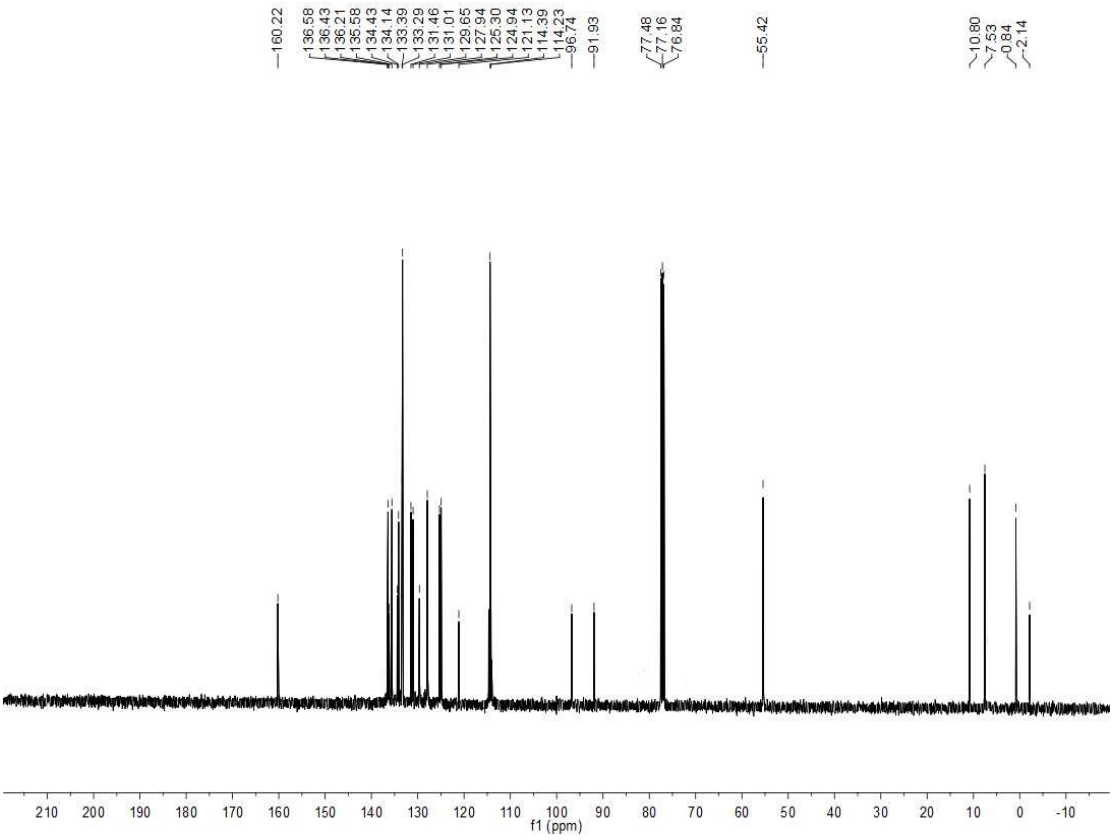


13C NMR spectrum (100 MHz, $CDCl_3$)

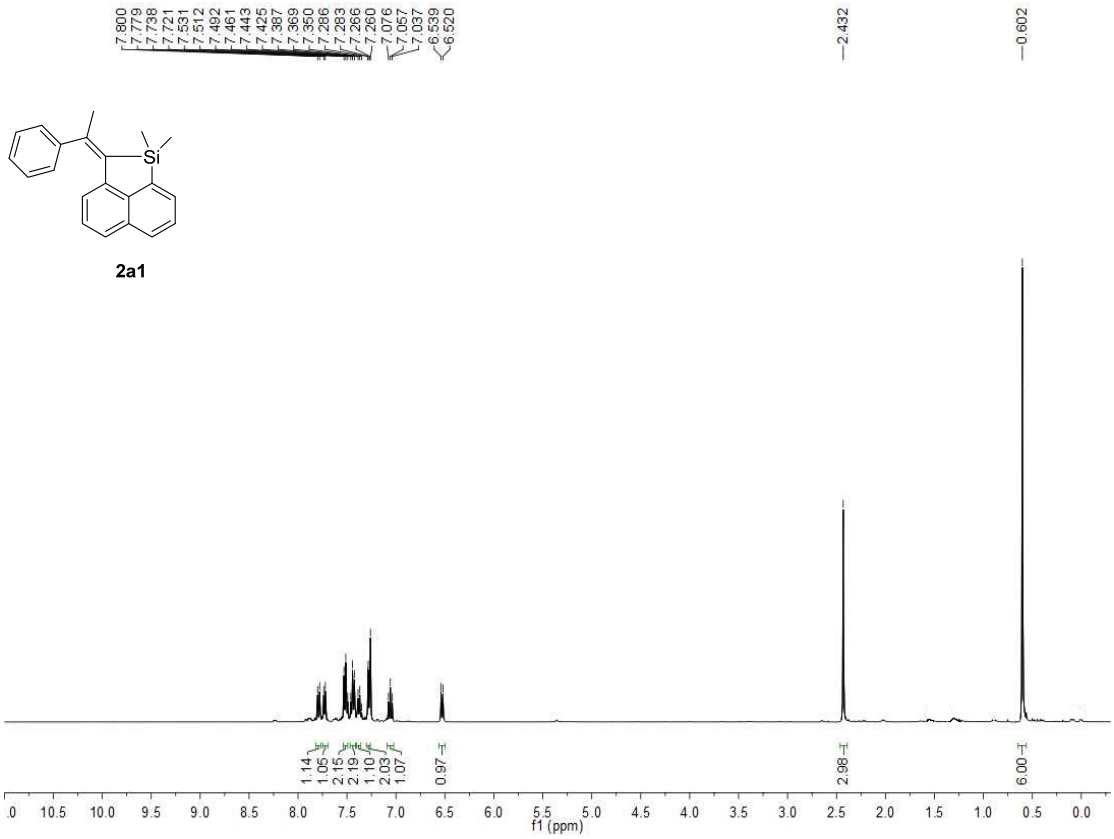


*: H grease impurity

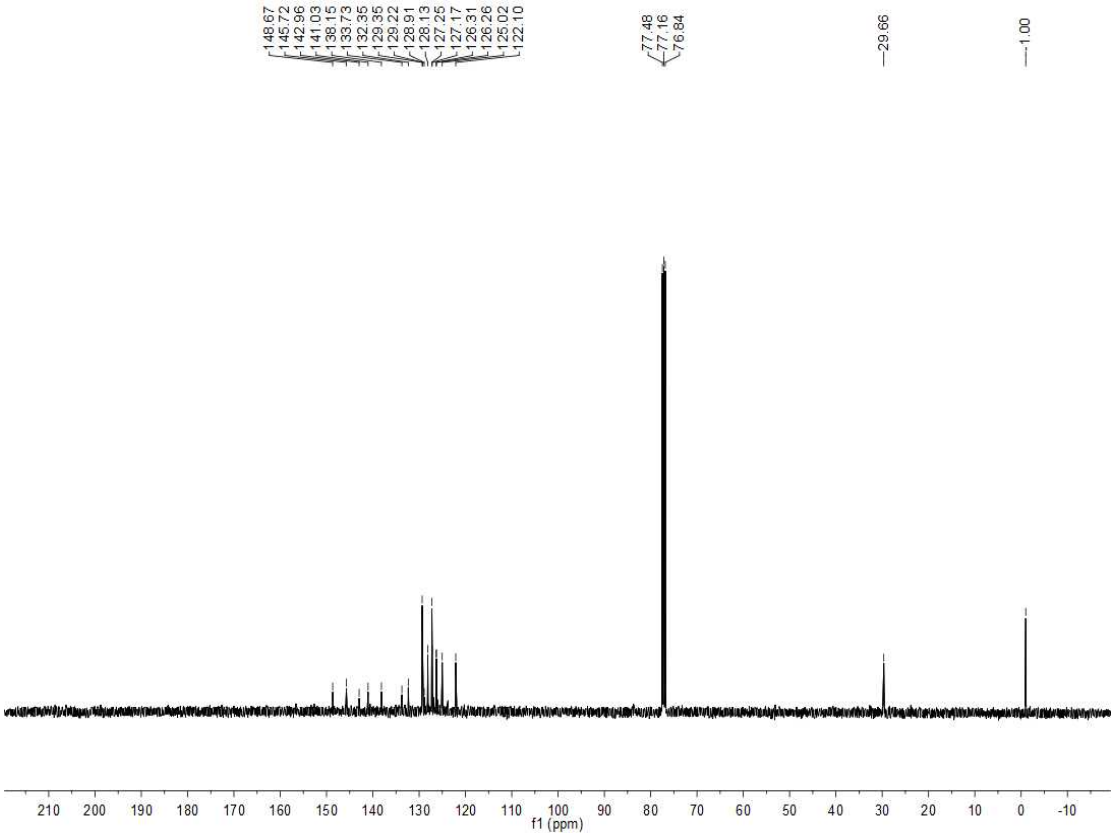
^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS)



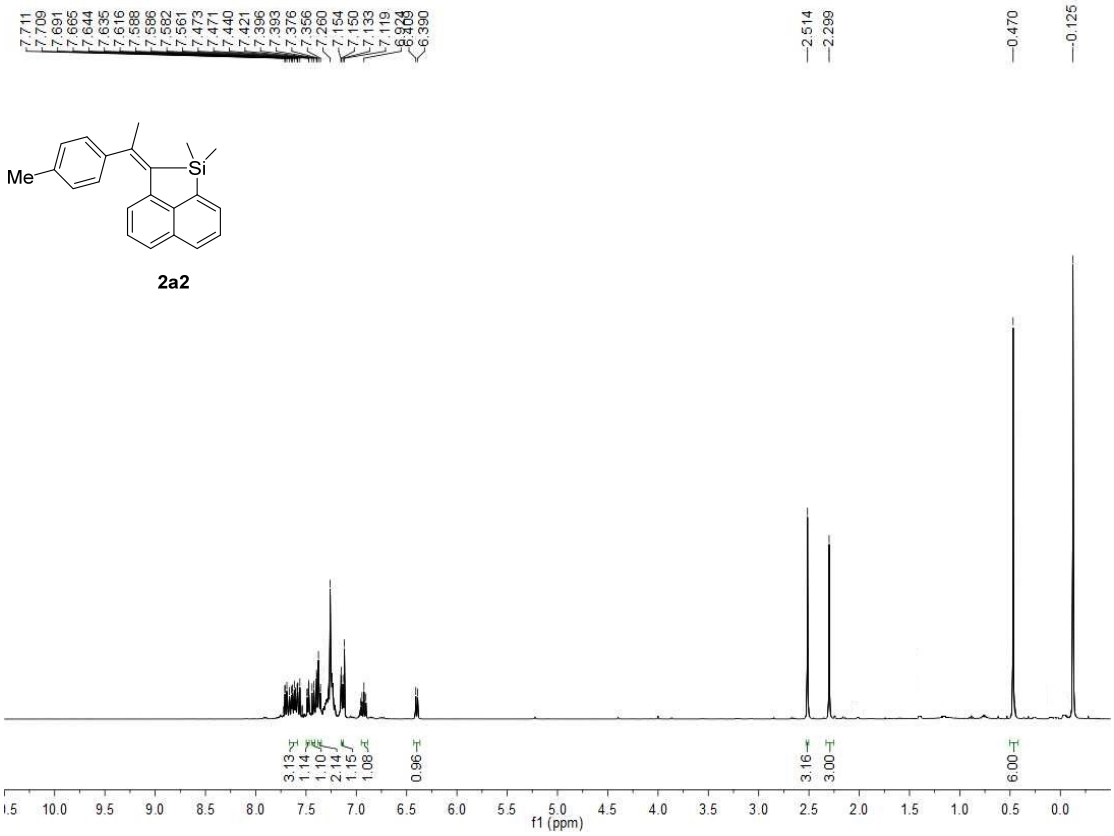
^{13}C NMR spectrum (100 MHz, $CDCl_3$, TMS)



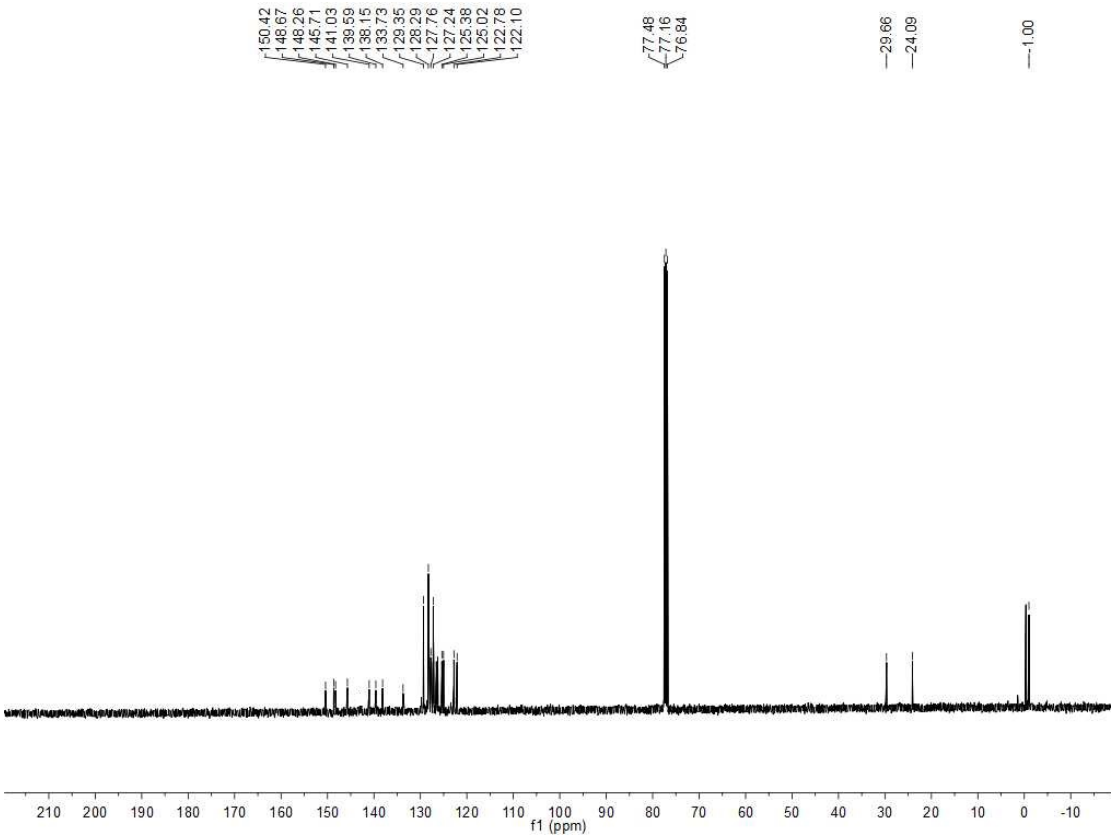
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



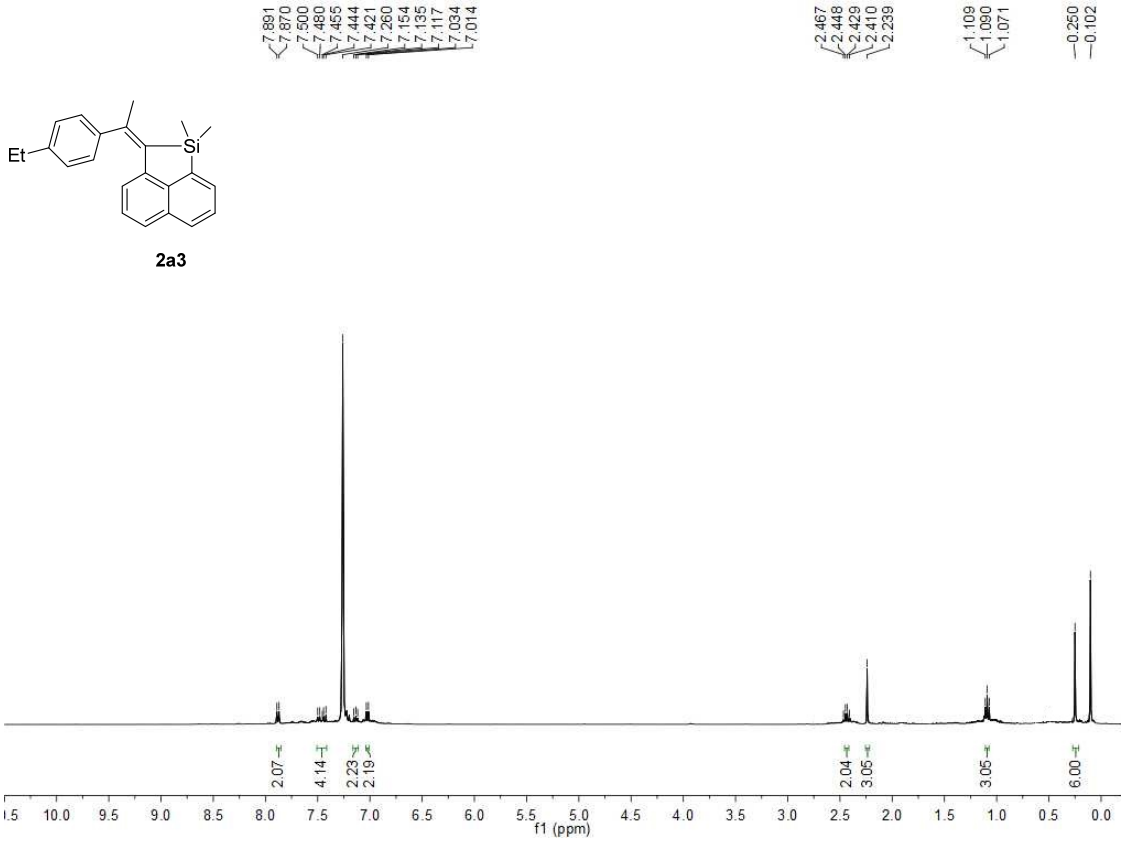
^{13}C NMR spectrum (100 MHz, $CDCl_3$)



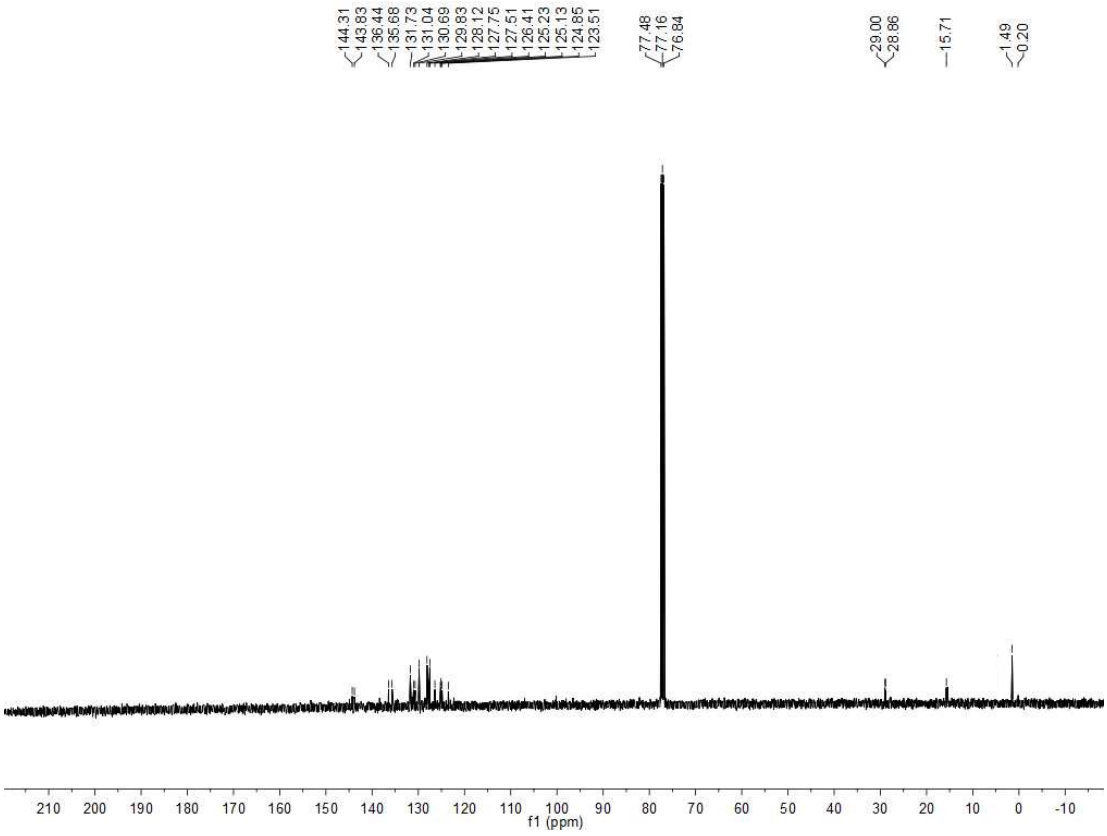
^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS)



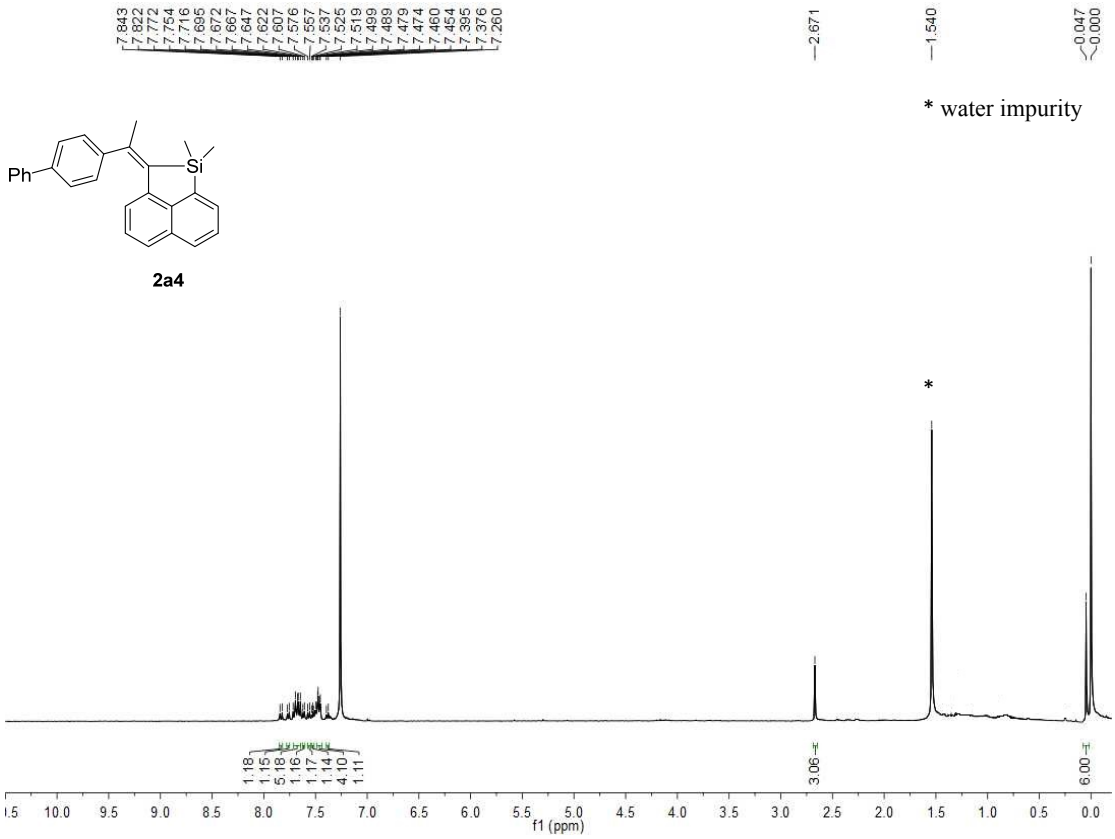
^{13}C NMR spectrum (100 MHz, $CDCl_3$, TMS)



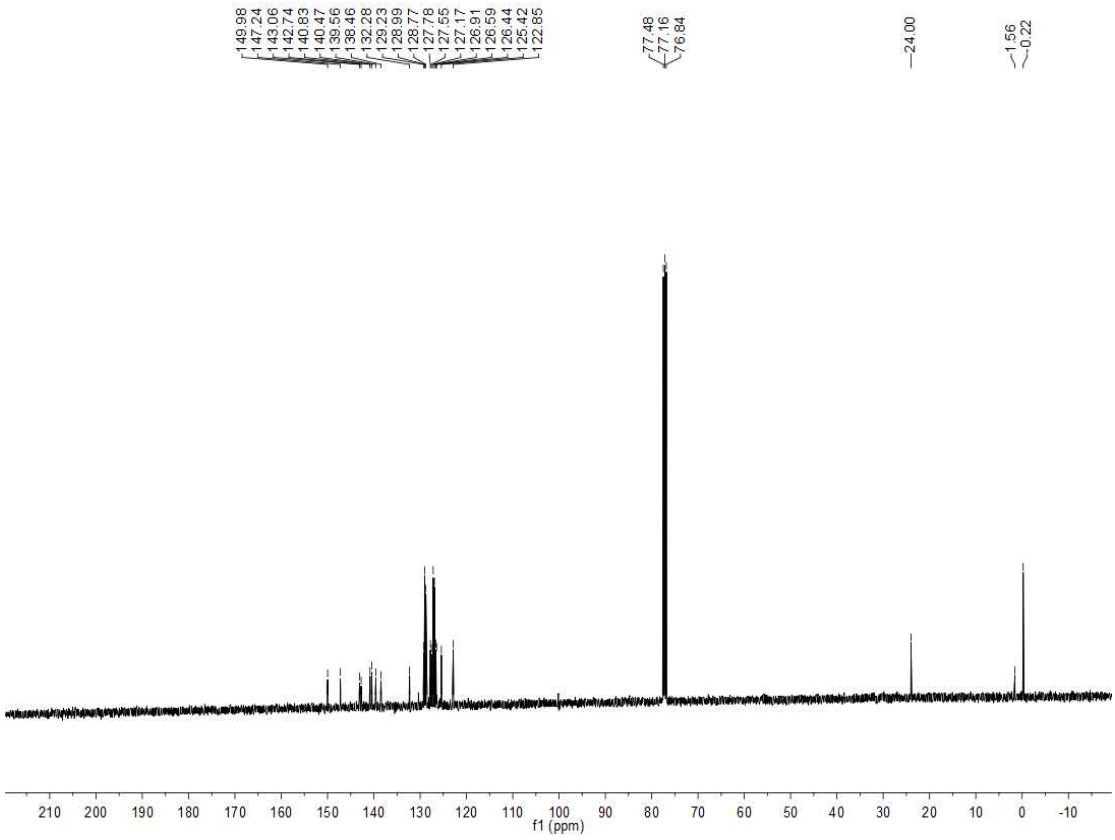
^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS)



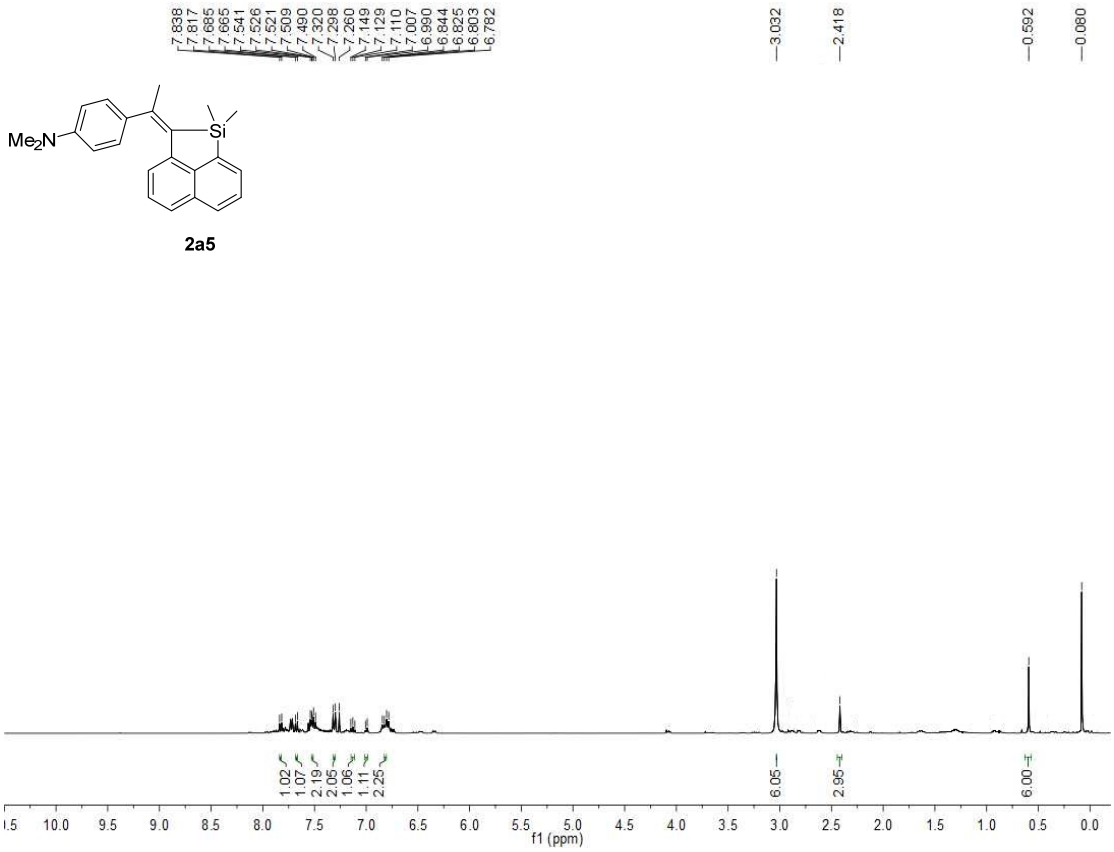
^{13}C NMR spectrum (100 MHz, $CDCl_3$)



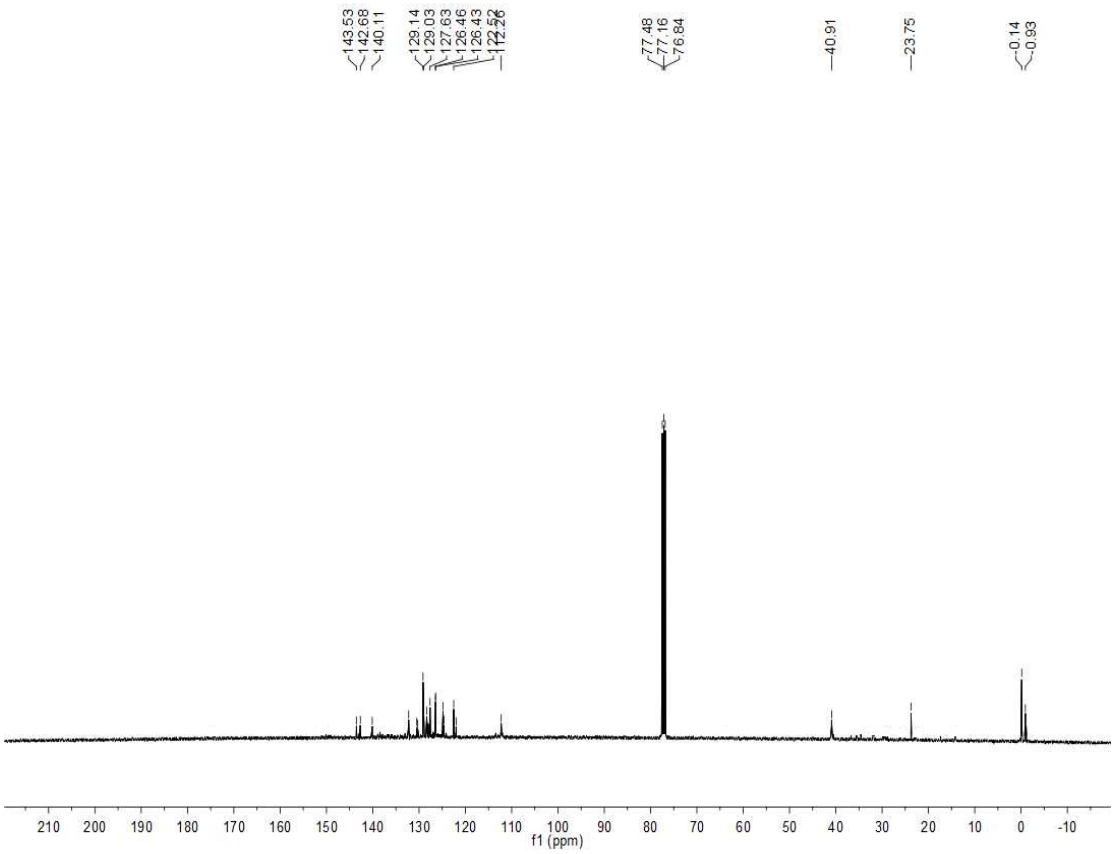
^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS)



^{13}C NMR spectrum (100 MHz, $CDCl_3$, TMS)

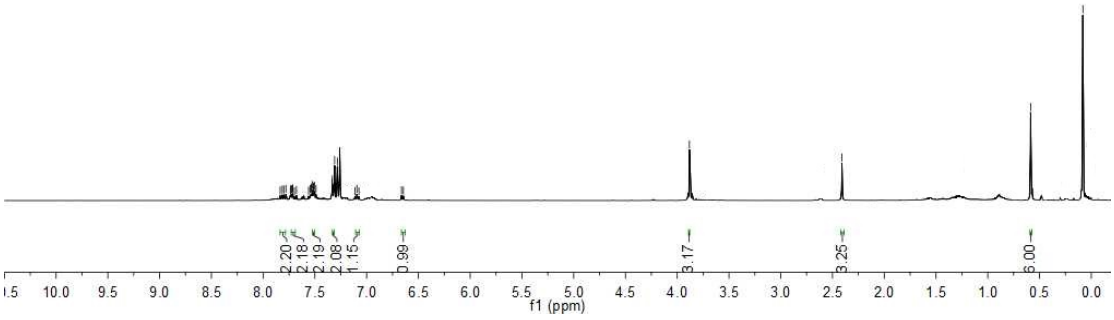


^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS)

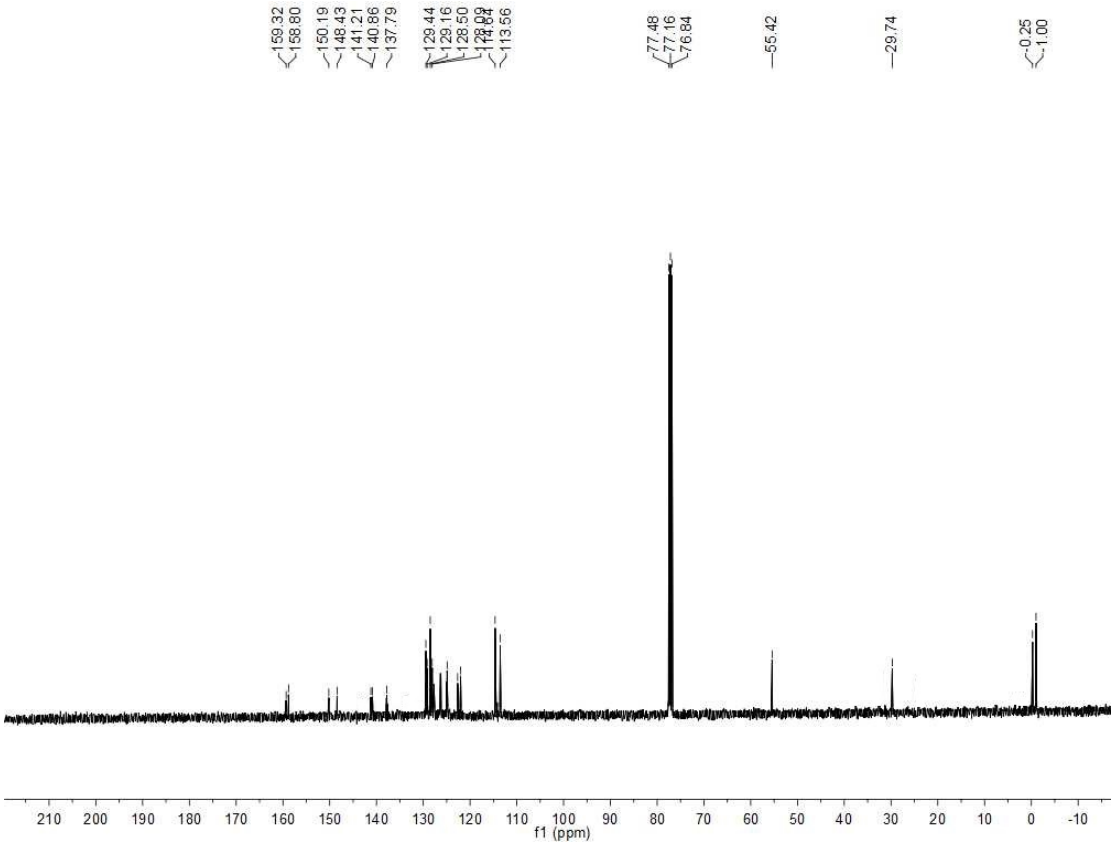


^{13}C NMR spectrum (100 MHz, $CDCl_3$, TMS)

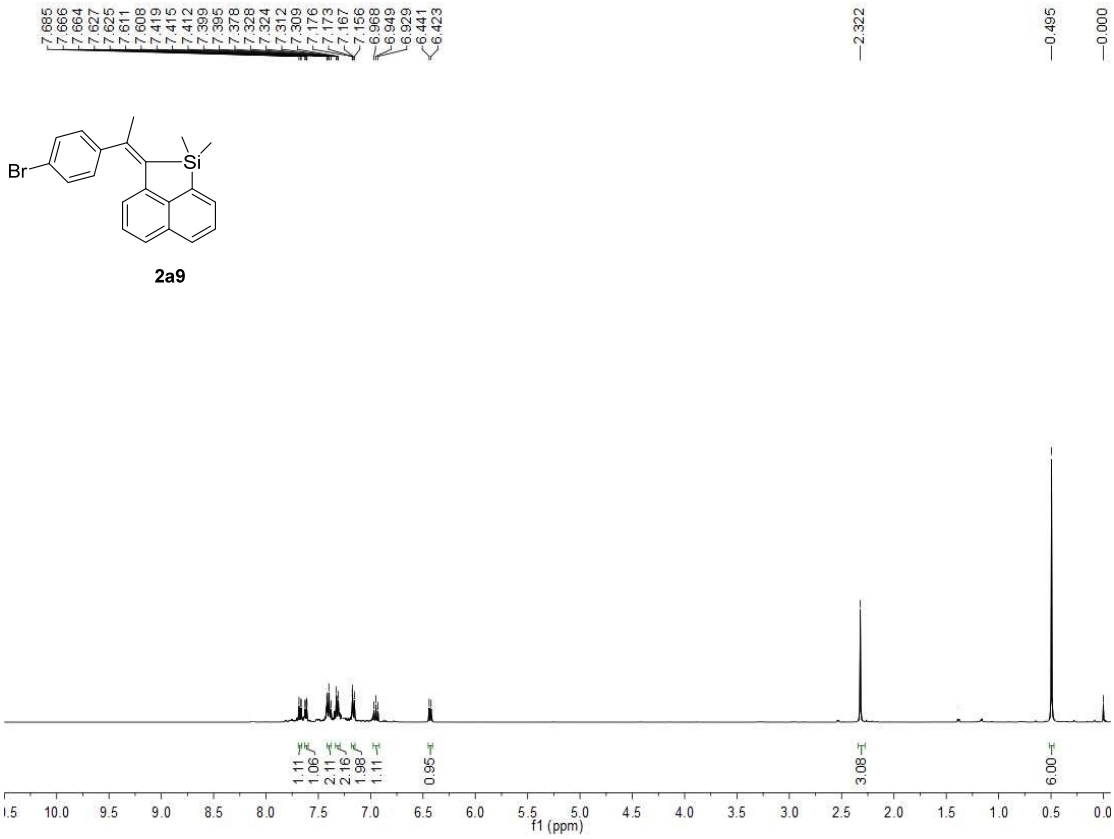
2a6



^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS)



^{13}C NMR spectrum (100 MHz, $CDCl_3$, TMS)



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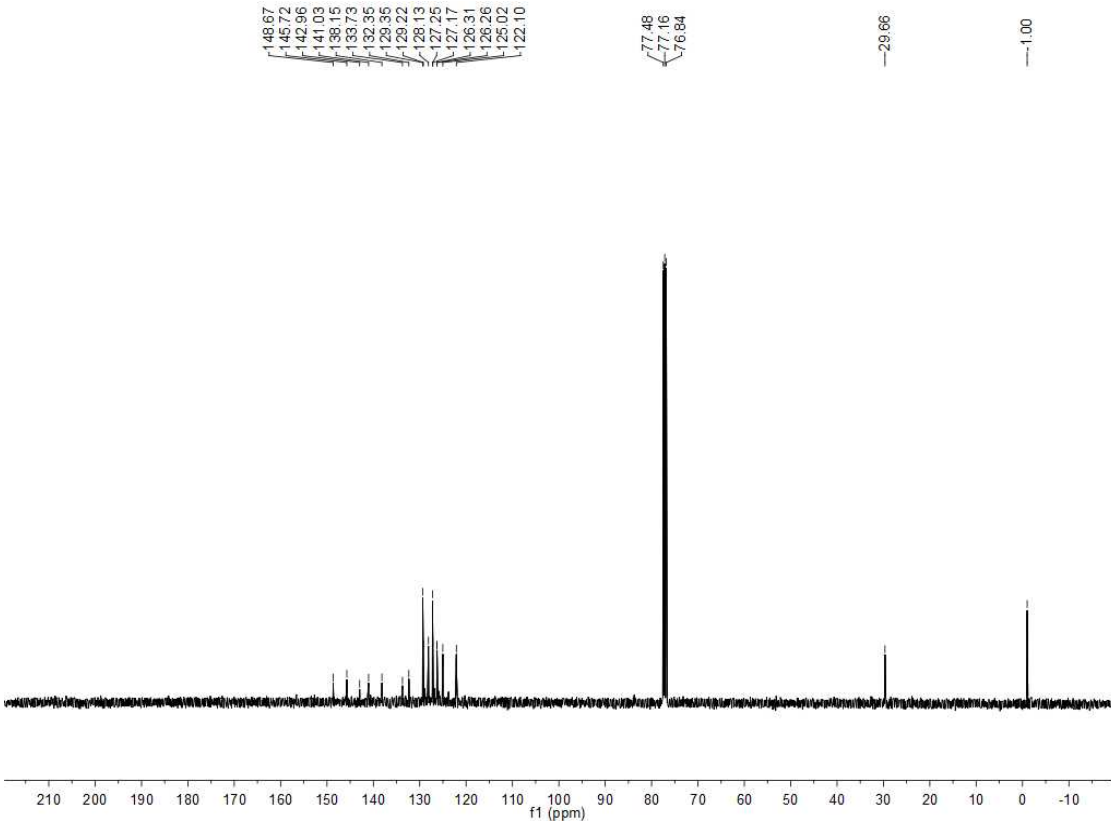
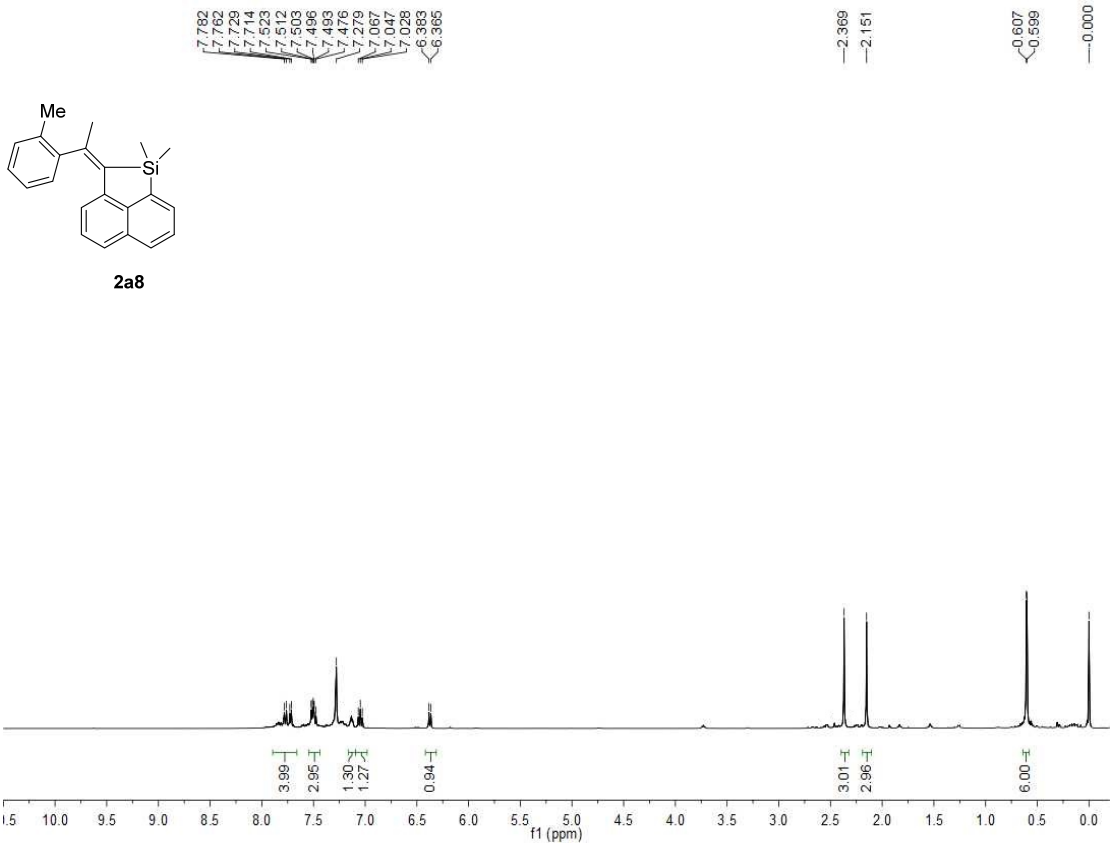
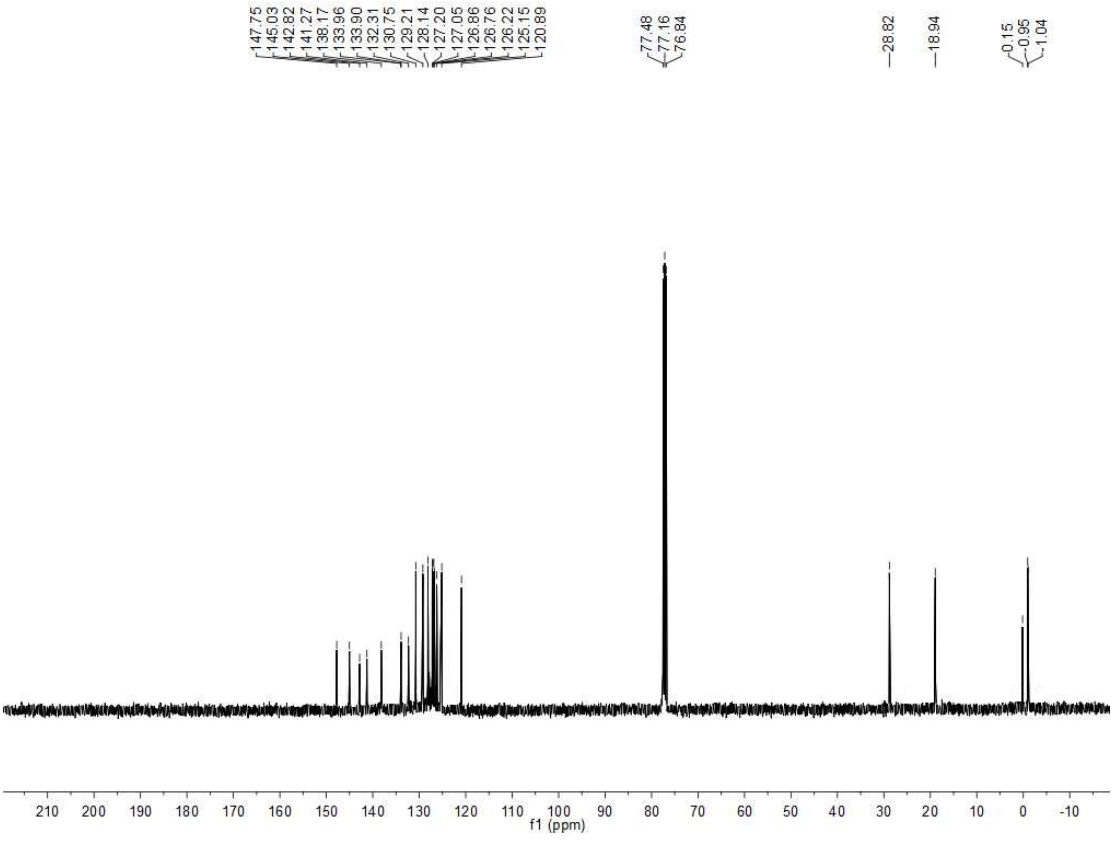
^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS)



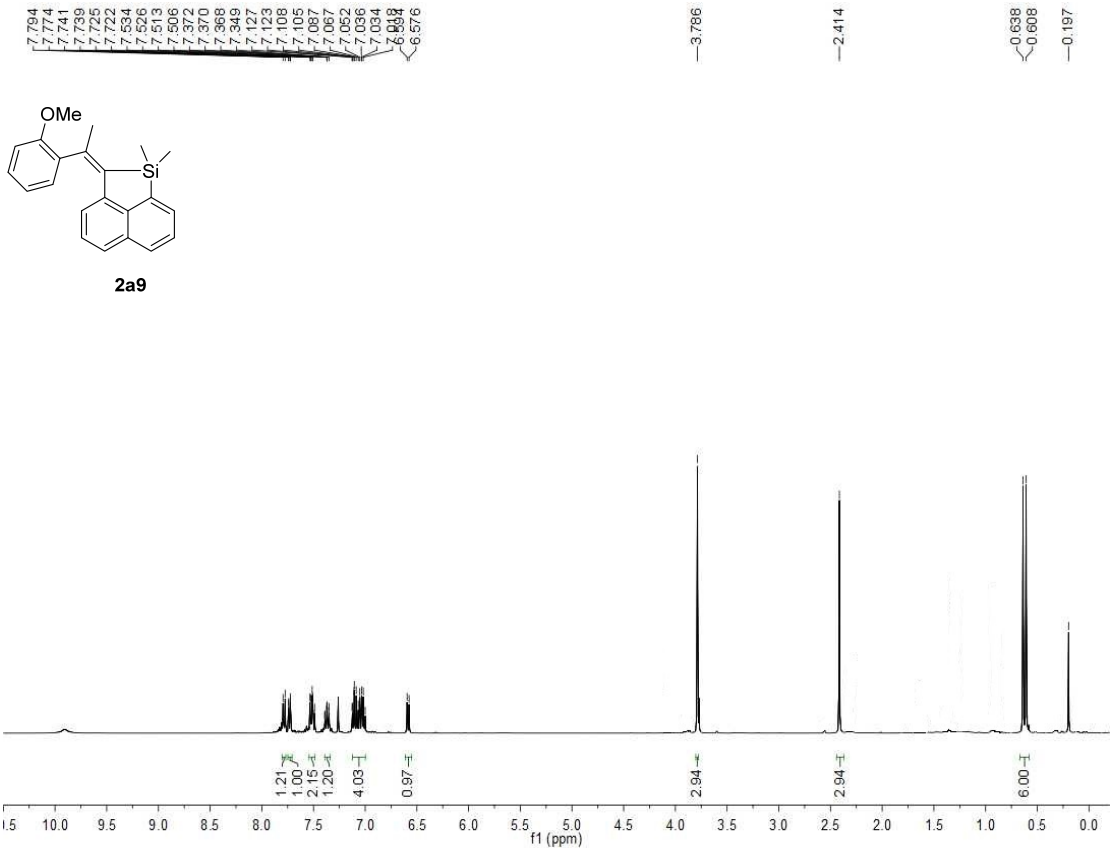
^{13}C NMR spectrum (100 MHz, $CDCl_3$)



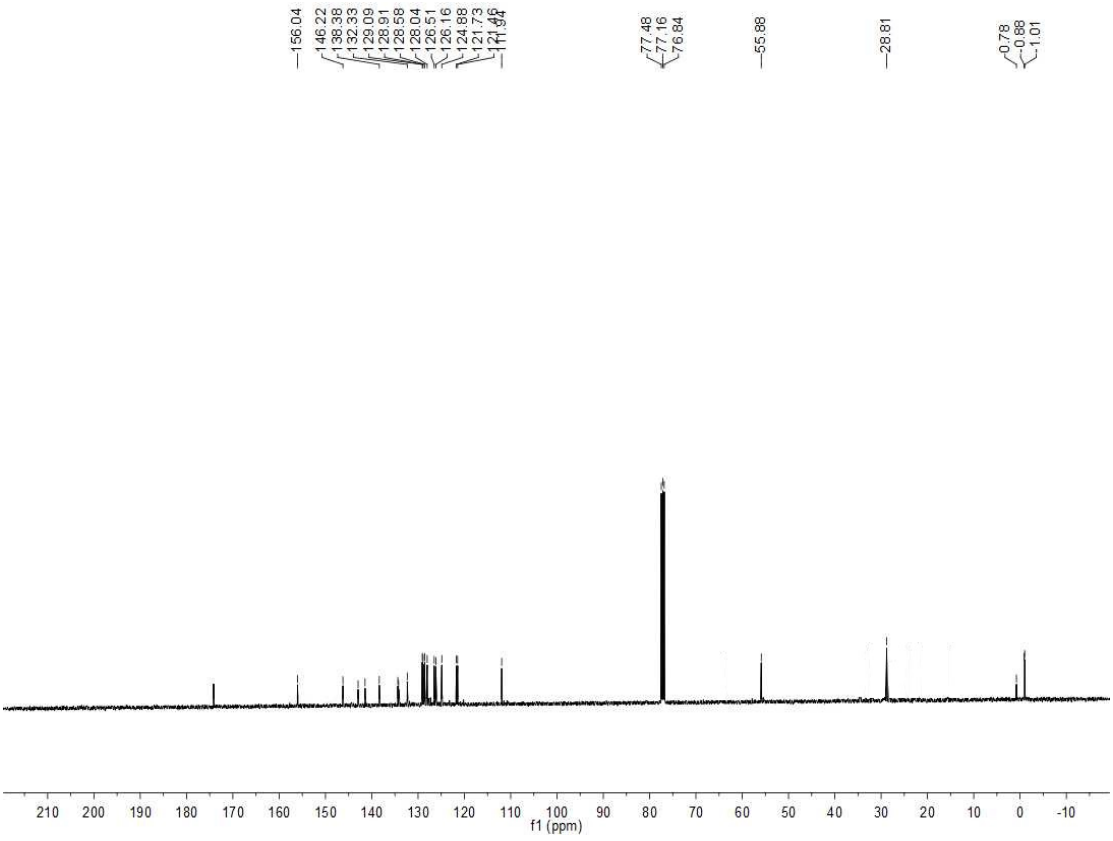
^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS)



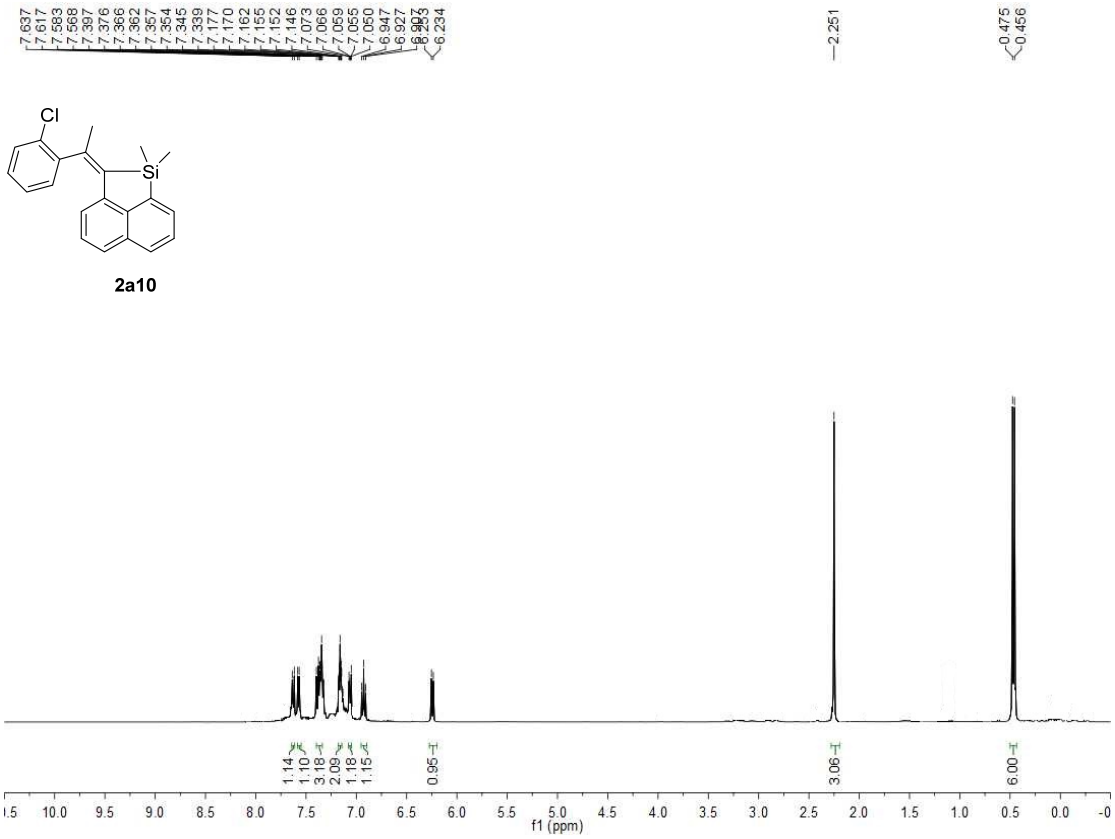
^{13}C NMR spectrum (100 MHz, $CDCl_3$, TMS)



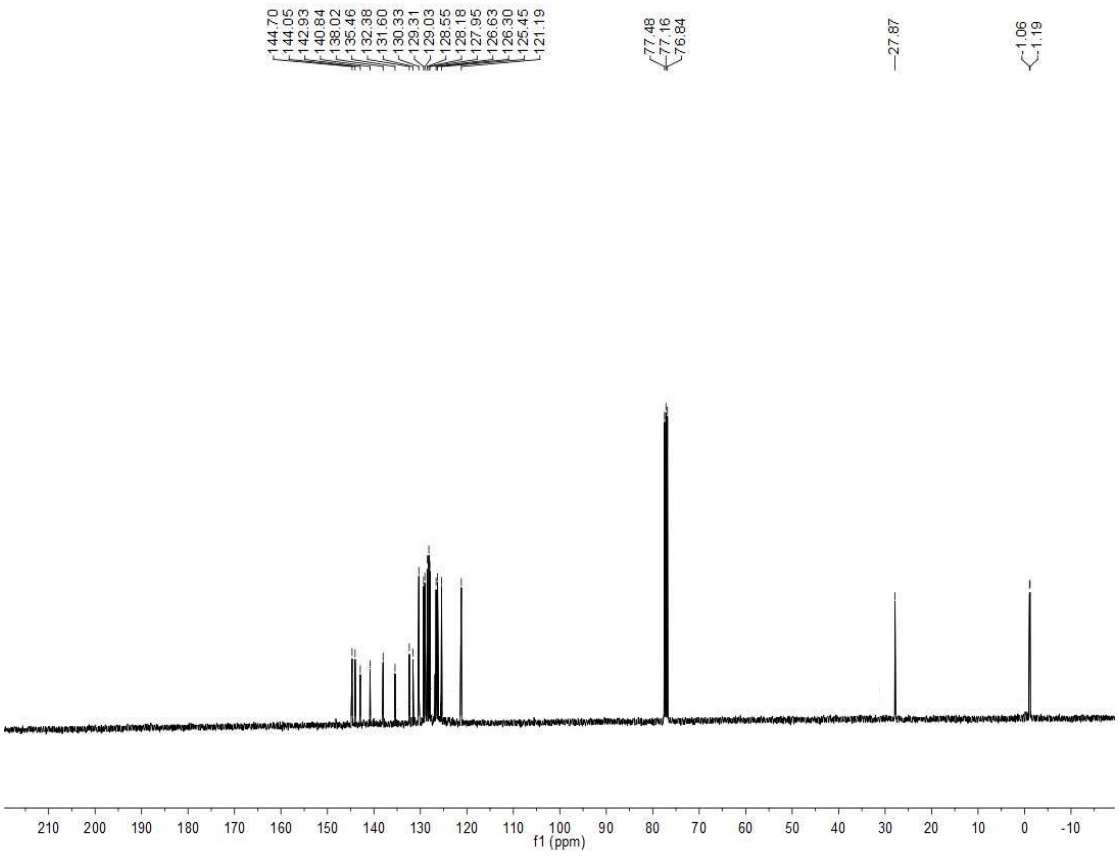
^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS)



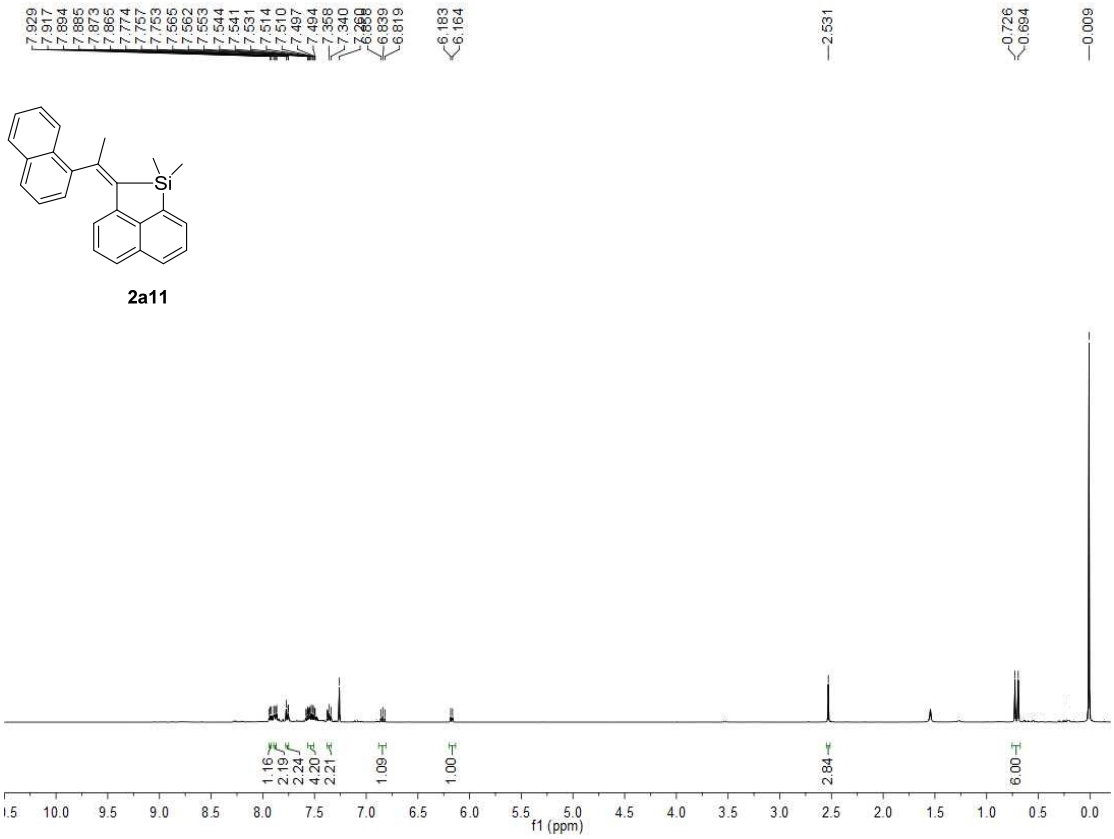
^{13}C NMR spectrum (100 MHz, $CDCl_3$, TMS)



^{1}H NMR spectrum (400 MHz, $CDCl_3$)

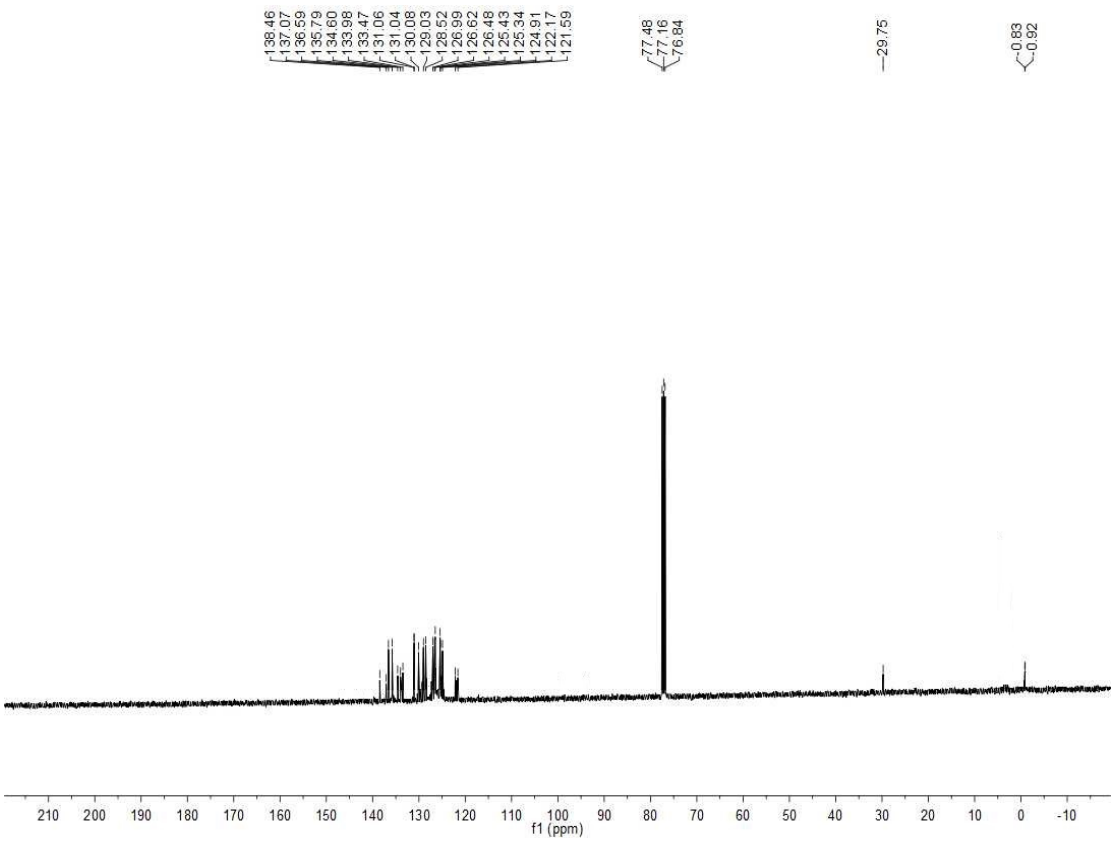


^{13}C NMR spectrum (100 MHz, $CDCl_3$)

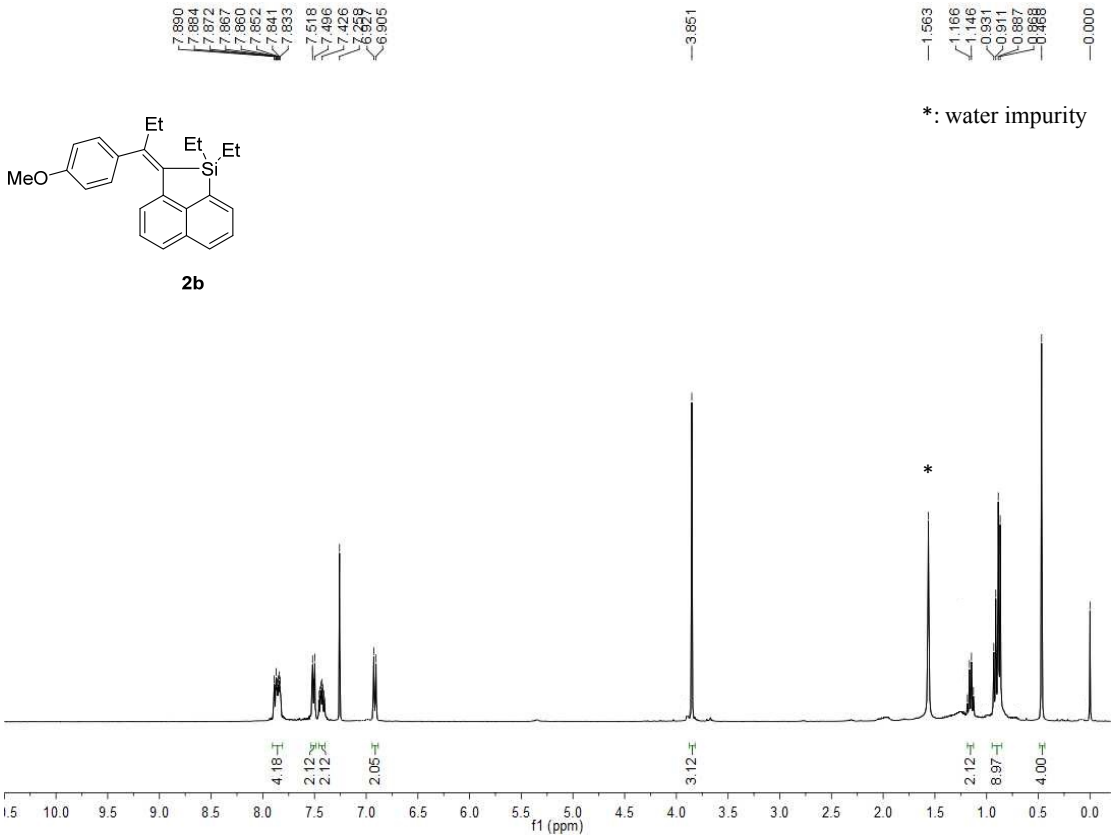


2a11

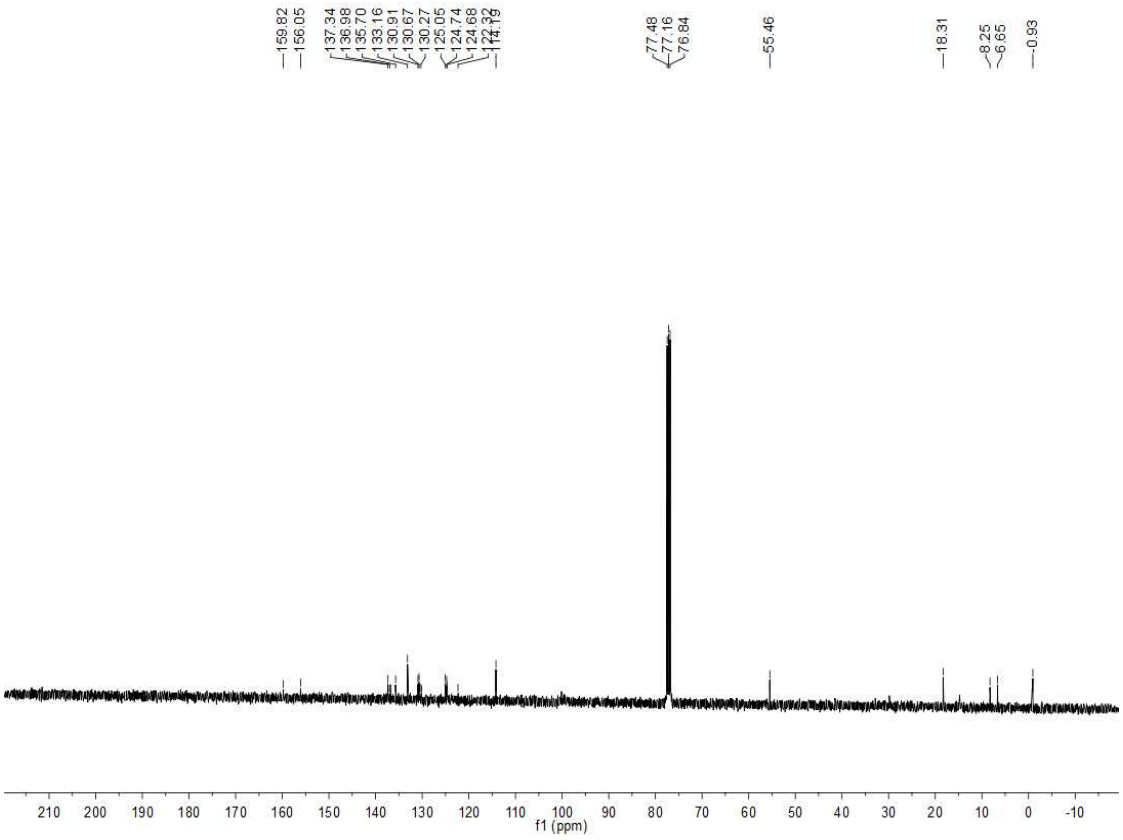
^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS)



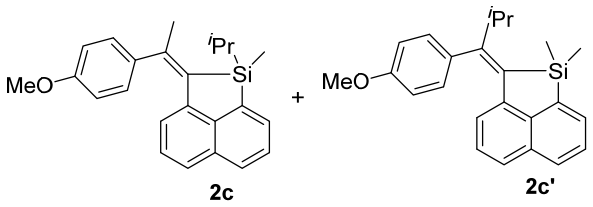
^{13}C NMR spectrum (100 MHz, $CDCl_3$)



^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS)

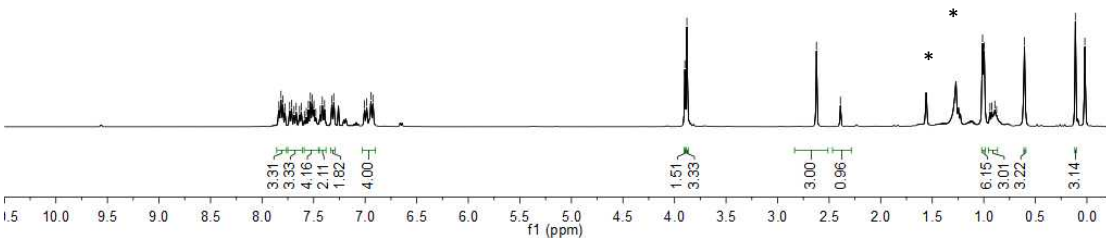


^{13}C NMR spectrum (100 MHz, $CDCl_3$)

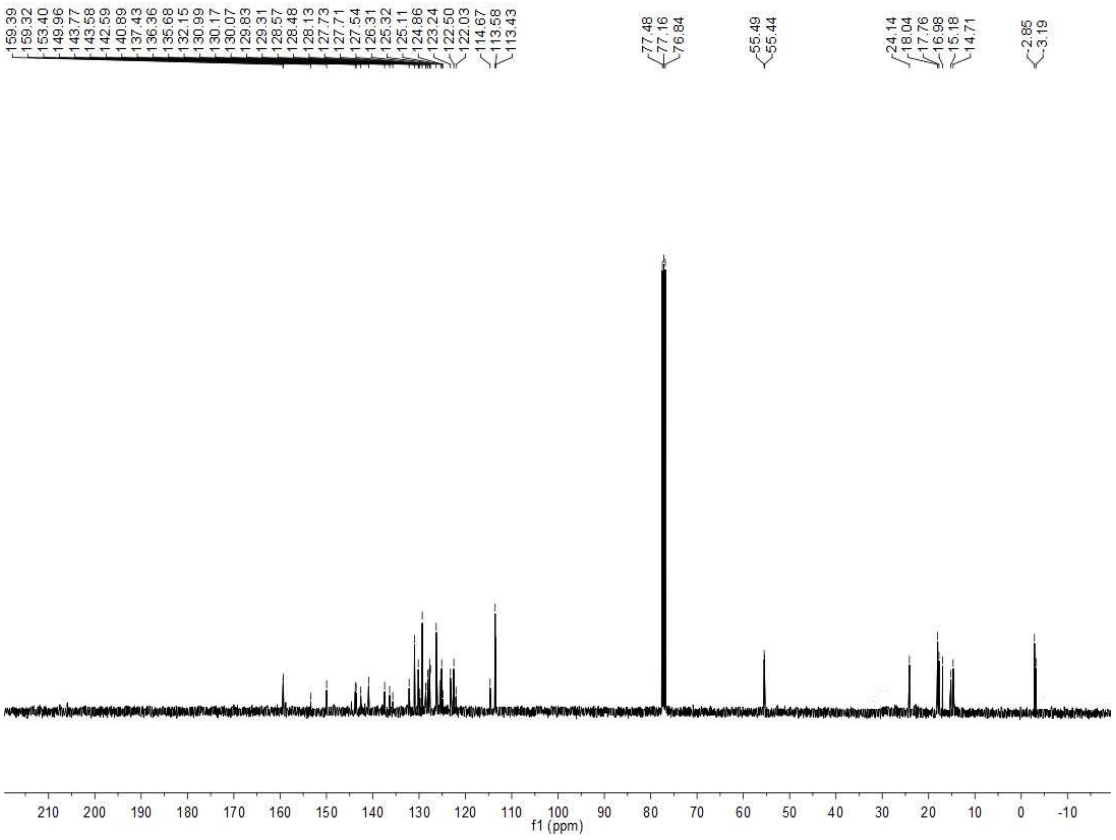


2c 2c'

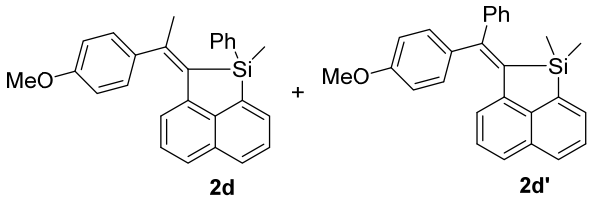
*: water and H grease impurity



^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS)

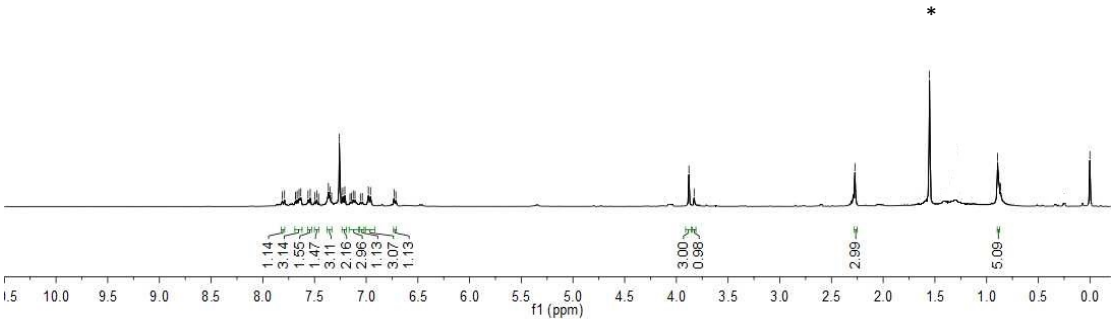


^{13}C NMR spectrum (100 MHz, $CDCl_3$)

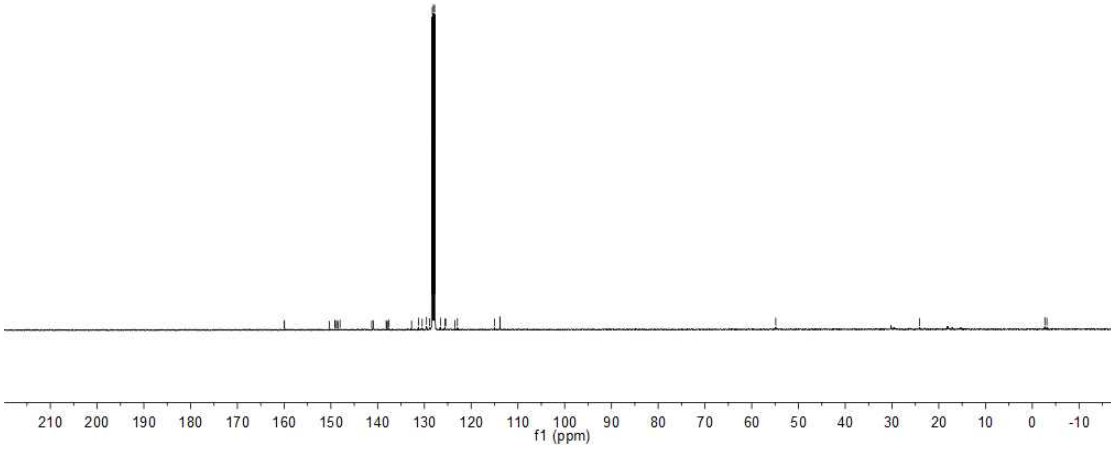


2d 2d'

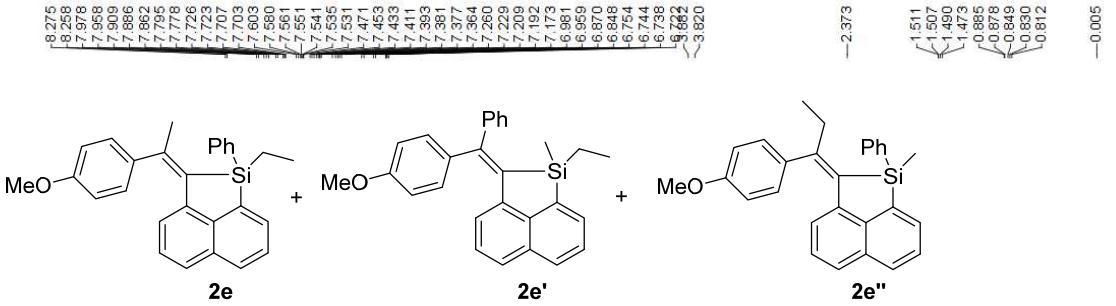
*: water impurity



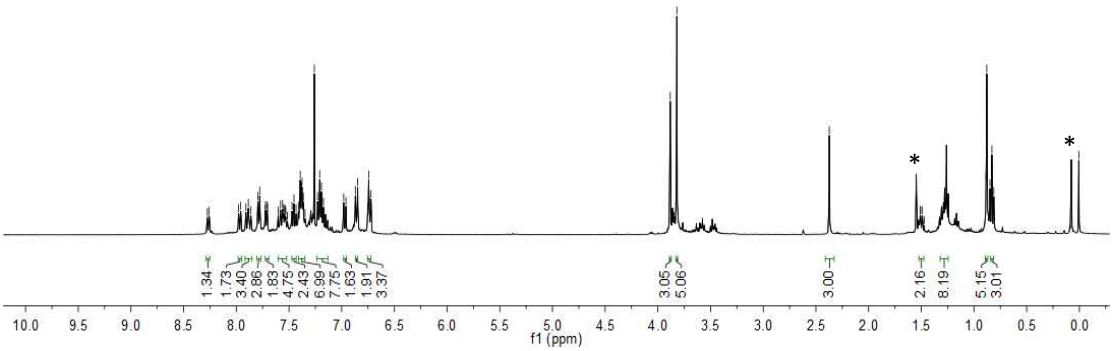
^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS)



^{13}C NMR spectrum (100 MHz, C_6D_6)



*: water and H grease impurity



^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS)

References:

(1) F.-G. Sun and Z.-H. Gu, *Org. Lett.,* 2015, **17**, 2222.

(2) Y. Liang, S. Zhang and Z. Xi, *J. Am. Chem. Soc.*, 2011, **133**, 9204.