Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

TBHP promoted sequential radical silylation and aromatisation of aryl isonitriles with silanes

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1 General experimental details:

Chemicals were used as received without special purification unless stated otherwise. ^{1}H and ^{13}C NMR spectra were recorded at ambient temperature on a 300 or 400 MHz NMR spectrometer (75 or 100 MHz for ^{13}C NMR). NMR results were reported in δ units, parts per million (ppm), and were referenced to $CDCl_3$ (δ 7.26 or 77.0 ppm) as the internal standard. The coupling constants *J* are given in Hz. Melting points were taken on an electrothermal melting point apparatus and without correction. IR spectra were recorded on a FT-IR-480 spectrometer using KBr discs.

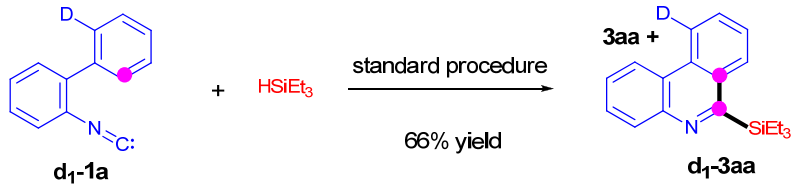
General synthetic procedure:

A sealed tube was charged with isocyanide (0.2 mmol), triethylsilane (1.0 mmol), TBHP (70% in water, 1.4 mmol), Cs_2CO_3 (0.6 mmol), BQ (0.06 mmol), CH_3CN + benzene (2:1) 3 mL. The mixture was purged with nitrogen and kept stirring under nitrogen at 95 ^{o}C for 12 h. The mixture was concentrated in vacuum and the residue was purified by preparative TLC on GF254 (petroleum/ethyl acetate) to afford the desired product.

2 KIE experiments:

2.1 Intramolecular KIE experiment:

In a sealed tube, substrate **d_1-1a** (0.2 mmol) was treated by standard procedures. The resulted mixture was concentrated in vacuum and the residue was purified by preparative TLC on GF254 (petroleum/ethyl acetate) to afford the desired product **3aa** and **d_1-3aa** in 66% total yield. The mixture was analyzed using ^{1}H NMR spectrometer. As shown in Figure S1, the ratio of **3aa** and **d_1-3aa** is nearly 1 : 1.



Scheme S1 Intramolecular KIE experiment of **d_1-1a**

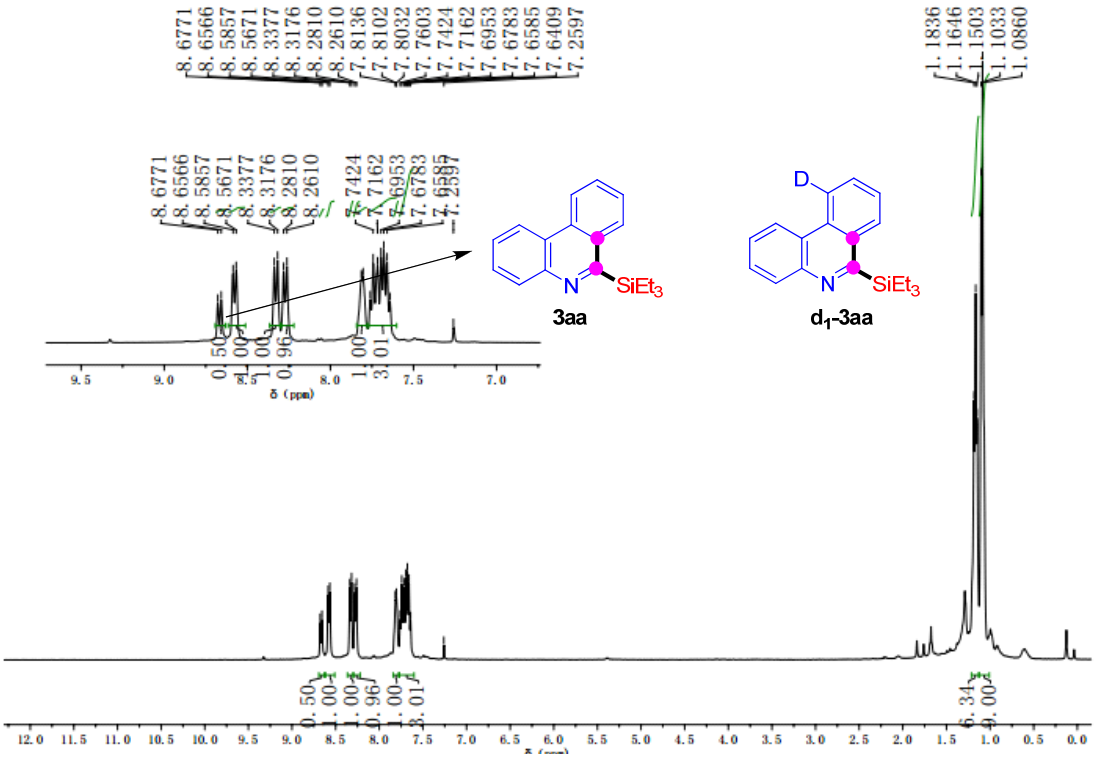
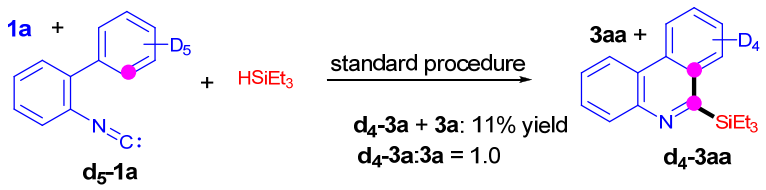


Figure S1 The ^{1}H NMR spectrum of the intramolecular KIE results

2.2 Intermolecular KIE experiment:

In a sealed tube, the mixture of **1a** (0.1 mmol) and **d_5-1a** (0.1 mmol) was treated by standard procedures and heated for 15 min. The mixture was concentrated in vacuum and the residue was purified by preparative TLC on GF254 (petroleum/ethyl acetate) to afford the desired product **3aa** and **d_4-3aa** in 11% total yield. The mixture was analyzed using ^{1}H NMR spectrometer. As shown in Figure S2, the ratio of **3aa** and **d_4-3aa** is nearly 1 : 1.



Scheme S2 Intermolecular KIE experiment of **1a** and **d_5-la**

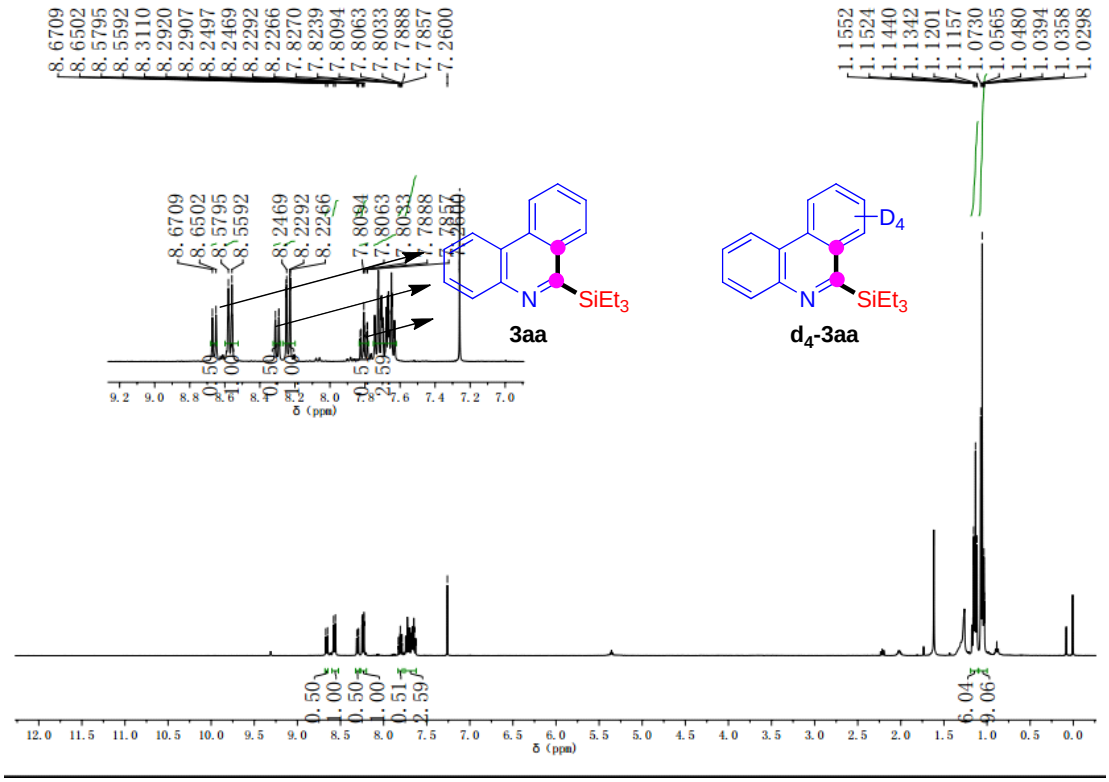
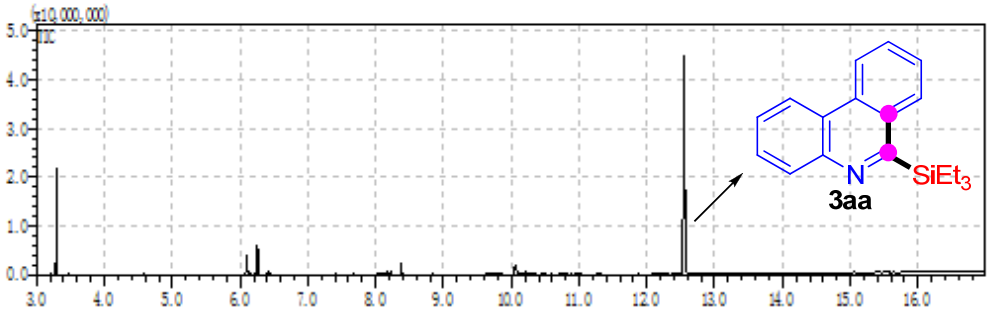


Figure S2 The ^{1}H NMR spectrum of the intermolecular KIE results

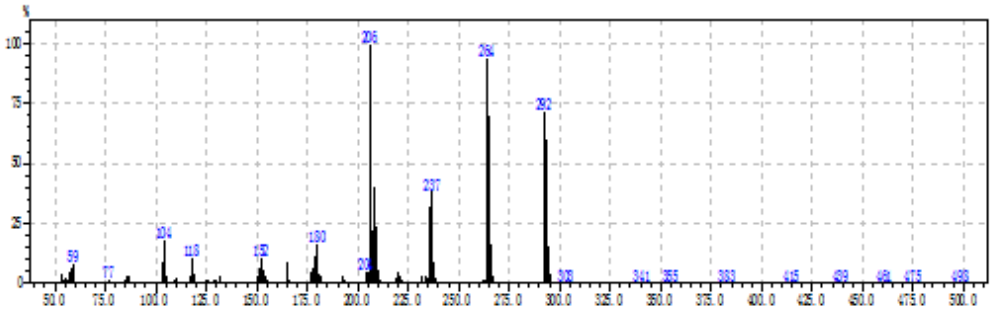
3 Free radical capture experiment

Under standard procedure, a Schlenk tube was charged with **1a** (0.2 mmol), **2a** (1.0 mmol), TBHP (70% in water, 1.4 mmol), Cs_2CO_3 (0.6 mmol), BQ (0.06 mmol), TEMPO (1 mmol), CH_3CN + benzene (2:1) 3 mL. The reaction was conducted under nitrogen at 95 ^oC for 12 h. The reaction mixture was analyzed using GCMS spectrometer, as shown in Figure S3, no products were detected.

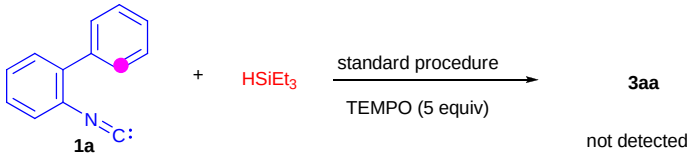
3.1 Standard procedure



Time: 12.533



3.2 Standard procedure + TEMPO (5 equiv)



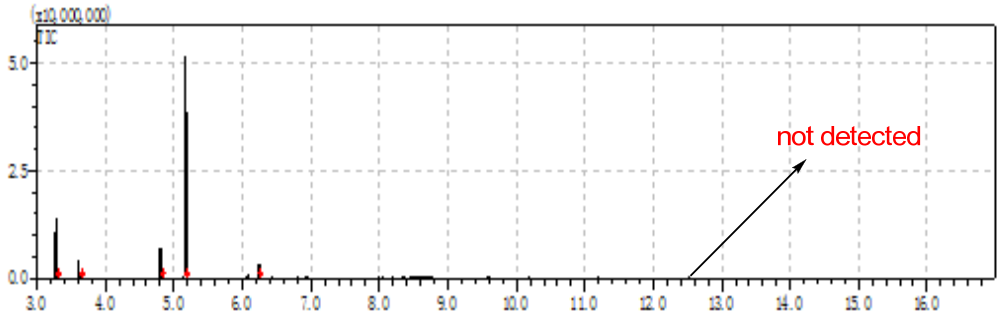
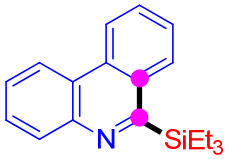


Figure S3 Free radical capture experiment results

4 Characterization data for the products

6-(Triethylsilyl)phenanthridine (3aa)



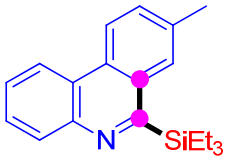
The product was purified by preparative TLC on GF254 (ethyl acetate: petroleum ether, 1 : 30) gave **3aa** (44.0 mg, 75% yield) as colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.66 (d, J = 8.2 Hz, 1H), 8.58 (d, J = 8.1 Hz, 1H), 8.31 (d, J = 8.1 Hz 1H), 8.25 (d, J = 8.1 Hz 1H), 7.81 (t, J = 7.6 Hz, 1H), 7.75-7.63 (m, 3H), 1.19-1.13 (m, 6H), 1.09-1.04 (m, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.5, 144.3, 130.9, 130.7, 130.5, 129.7, 128.5, 128.1, 126.9, 126.8, 123.1, 122.3, 121.8, 7.8, 4.9.

IR (KBr): 3070, 2957, 2871, 1457, 1237, 1004, 756, 722 cm^{-1}.

MS (EI): 293 (M^+); HRMS (ESI): Calcd. for $C_{19}H_{24}NSi$ $(M+H)^+$ 294.1673, found 294.1661.

8-Methyl-6-(triethylsilyl)phenanthridine (3ba)



The product was purified by preparative TLC on GF254 (ethyl acetate: petroleum ether, 1 : 30) gave **3ba** (37.0 mg, 60% yield) as colorless oil.

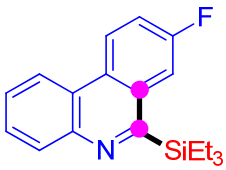
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.56-8.53 (m, 2H), 8.25 (d, J = 8.0 Hz, 1H), 8.10 (s, 1H), 7.71 (t, J = 7.4 Hz 1H), 7.65-7.62 (m, 2H), 2.63 (s, 3H), 1.18-1.14 (m, 6H), 1.11-1.07 (m, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.1, 144.1, 136.5, 131.3, 130.8, 130.7, 128.5, 128.1, 127.7, 126.8, 123.2, 122.2, 121.6, 21.8, 7.8, 4.9.

IR (KBr): 3062, 2958, 2875, 1461, 1239, 1012, 762, 734, 720 cm^{-1}.

MS (EI): 307 (M^+); HRMS (ESI): Calcd. for $C_{20}H_{26}NSi$ $(M+H)^+$ 308.1829, found

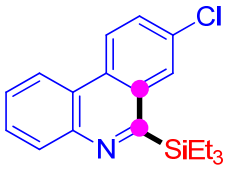
308.1833.

8-Fluoro-6-(triethylsilyl)phenanthridine (3ca)



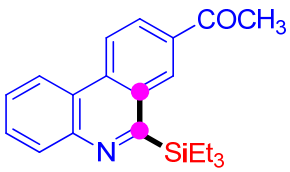
The product was purified by preparative TLC on GF254 (ethyl acetate: petroleum ether, 1 : 30) gave **3ca** (43.5mg, 70% yield) as colorless oil.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.66-8.63 (m, 1H), 8.50 (d, J = 8.1 Hz, 1H), 8.24 (d, J = 8.0 Hz, 1H), 7.92 (d, J = 9.7 Hz, 1H), 7.72 (t, J = 7.6 Hz, 1H), 7.65 (t, J = 7.5 Hz, 1H), 7.55 (t, J = 8.5 Hz, 1H), 1.17-1.11 (m, 6H), 1.08-1.03 (m, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.6, 161.1 (d, J_{C-F} = 245.9 Hz), 144.0, 131.5, (d, J_{C-F} = 7.4 Hz), 130.0, 128.0, 127.4, 127.3, 124.8 (d, J_{C-F} = 8.4 Hz), 122.7, 121.6, 118.8 (d, J_{C-F} = 23.5 Hz), 112.7 (d, J_{C-F} = 20.1 Hz), 7.7, 4.7.
IR (KBr): 3062, 2954, 2877, 1616, 1527, 1476, 1234, 1196, 1001, 755, 739, 719 cm^{-1}.
MS (EI): 311 (M^+); HRMS (APCI): Calcd. for $C_{19}H_{23}FNSi$ $(M+H)^+$ 312.1578, found 312.1566.

8-Chloro-6-(triethylsilyl)phenanthridine (3da)



The product was purified by preparative TLC on GF254 (ethyl acetate: petroleum ether, 1 : 30) gave **3da** (43.5 mg, 66% yield) as colorless oil.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.58 (d, J = 8.8 Hz, 1H), 8.51 (d, J = 8.2 Hz, 1H), 8.25-8.22 (m, 2H), 7.76-7.72 (m, 2H), 7.66 (t, J = 7.5 Hz, 1H), 1.17-1.11 (m, 6H), 1.08-1.03 (m, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.5, 144.3, 132.6, 131.3, 131.0, 130.2, 129.1, 128.5, 127.7, 127.4, 124.2, 122.5, 121.7, 7.7, 4.8.
IR (KBr): 3065, 2956, 2874, 1468, 1233, 1093, 1008, 813, 758 737, 718 cm^{-1}.
MS (EI): 327 (M^+); HRMS (ESI): Calcd. for $C_{19}H_{23}ClNSi$ $(M+H)^+$ 328.1283, found 328.1287.

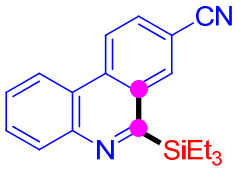
1-(6-(Triethylsilyl)phenanthridin-8-yl)ethanone（3ea）



The product was purified by preparative TLC on GF254 (ethyl acetate: petroleum ether, 1 : 10) gave **3ea** (34.2 mg, 51% yield) as colorless oil.

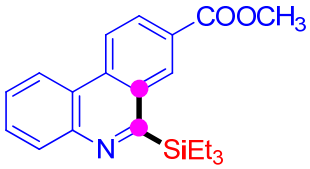
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.94 (s, 1H), 8.70 (d, J = 8.6 Hz, 1H), 8.58 (d, J = 8.1 Hz, 1H), 8.36 (d, J = 8.6 Hz, 1H), 8.26 (d, J = 8.1 Hz, 1H), 7.79 (t, J = 7.5 Hz, 1H), 7.68 (t, J = 7.6 Hz, 1H), 2.78 (s, 3H), 1.21-1.15 (m, 6H), 1.10-1.06 (m, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 197.2, 172.4, 145.2, 135.0, 134.0, 131.0, 130.0, 129.8, 129.4, 128.1, 127.4, 122.9, 122.4, 122.4, 26.7, 7.8, 5.0.
IR (KBr): 3061, 2958, 2865, 1692, 1618, 1359, 1248, 1018, 762, 735, 720 cm^{-1}.
MS (EI): 335 (M^+); HRMS (ESI): Calcd. for $C_{21}H_{26}NOSi$ $(M+H)^+$ 336.1778, found 336.1768.

6-(Triethylsilyl)phenanthridine-8-carbonitrile (3fa)



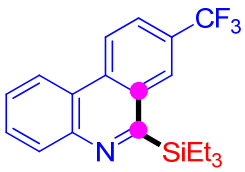
The product was purified by preparative TLC on GF254 (ethyl acetate: petroleum ether, 1 : 30) gave **3fa** (36.2 mg, 57% yield) as a white solid. Mp: 78-81 ^{o}C.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.74 (d, J = 8.6 Hz, 1H), 8.60 (s, 1H), 8.55 (d, J = 8.1 Hz, 1H), 8.27 (d, J = 8.1 Hz, 1H), 7.98 (d, J = 8.6 Hz, 1H), 7.83 (t, J = 7.1 Hz, 1H), 7.72 (t, J = 7.2 Hz, 1H), 1.17-1.11 (m, 6H), 1.07-1.02 (m, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.2, 145.1, 133.7, 133.5, 131.2, 131.0, 130.0, 129.5, 127.8, 123.8, 122.3, 121.7, 118.8, 110.2, 7.7, 4.8.
IR (KBr): 3080, 2931, 2226, 1608, 1469, 1452, 1236, 766, 737, 689 cm^{-1}.
MS (EI): 318 (M^+); HRMS (ESI): Calcd. for $C_{20}H_{23}N_2Si$ $(M+H)^+$ 319.1625, found 319.1635.

Methyl 6-(triethylsilyl)phenanthridine-8-carboxylate（3ga）



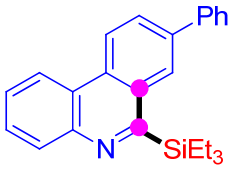
The product was purified by preparative TLC on GF254 (ethyl acetate: petroleum ether, 1 : 30) gave **3ga** (39.3 mg, 56% yield) as colorless oil.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.06 (s, 1H), 8.69 (d, J = 8.6 Hz, 1H), 8.58 (d, J = 8.1 Hz, 1H), 8.40 (d, J = 8.6 Hz, 1H), 8.26 (d, J = 8.2 Hz, 1H), 7.78 (t, J = 8.0 Hz, 1H), 7.68 (t, J = 8.1 Hz, 1H), 4.04 (s, 3H), 1.20-1.14 (m, 6H), 1.08-1.04 (m, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 172.4, 166.7, 145.1, 133.8, 131.1, 131.0, 129.7, 129.4, 129.3, 128.1, 127.3, 122.6, 122.5, 122.4, 52.4, 7.7, 4.8.
IR (KBr): 3070, 2950, 2867, 1721, 1610, 1359, 1314, 1249, 757, 737 cm^{-1}.
MS (EI): 351 (M^+); HRMS (ESI): Calcd. for $C_{20}H_{26}N_2OSi$ $(M+H)^+$ 352.1727, found 352.1727.

6-(Triethylsilyl)-8-(trifluoromethyl)phenanthridine (3ha)



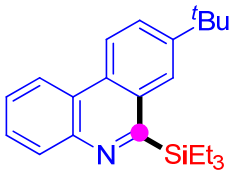
The product was purified by preparative TLC on GF254 (ethyl acetate: petroleum ether, 1 : 30) gave **3ha** (39.7mg, 55% yield) as colorless oil.
^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.76 (d, J = 8.7 Hz, 1H), 8.61-8.56 (m, 2H), 8.28 (d, J = 8.1 Hz, 1H), 8.00 (d, J = 8.7 Hz, 1H), 7.81 (t, J = 6.4 Hz, 1H), 7.70 (d, J = 7.6 Hz, 1H), 1.17-1.12 (m, 6H), 1.09-1.03 (m, 9H); ($CDCl_3$, 75 MHz): δ 171.8, 145.0, 133.0, 131.1, 129.5, 129.4, 128.5 (q, $J_{C\text{-}F}$ = 32.4 Hz), 127.5, 126.0 (q, $J_{C\text{-}F}$ = 4.1 Hz), 125.6 (q, $J_{C\text{-}F}$ = 3.1 Hz), 124.2 (q, $J_{C\text{-}F}$ = 272.0 Hz), 123.5, 122.2, 7.7, 4.8.
IR (KBr): 3070, 2950, 2876, 1619, 1324, 1258, 1129, 1083, 761, 734, 697 cm^{-1}.
MS (EI): 361 (M^+); HRMS (ESI): Calcd. for $C_{20}H_{23}F_3NSi$ $(M+H)^+$ 362.1546, found 362.1532.

8-Phenyl-6-(triethylsilyl)phenanthridine (3ia)



The product was purified by preparative TLC on GF254 (ethyl acetate: petroleum ether, 1 : 30) gave **3ia** (49.1 mg, 66% yield) as a white solid. Mp: 56-58 ^{o}C.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.71 (d, J = 8.6 Hz, 1H), 8.59 (d, J = 8.1 Hz, 1H), 8.53 (s, 1H), 8.26 (d, J = 8.1 Hz, 1H), 8.07 (d, J = 8.5 Hz, 1H), 7.78-7.71 (m, 3H), 7.67 (t, J = 7.5 Hz, 1H), 7.56 (t, J = 7.5 Hz, 2H), 7.45 (t, J = 7.4 Hz, 1H), 1.22-1.16 (m, 6H), 1.11-1.06 (m, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.7, 144.4, 140.6, 139.4, 130.9, 129.8, 129.1, 128.9, 128.2, 127.7, 127.3, 127.0, 126.6, 123.0, 123.0, 121.9, 7.8, 5.0.
IR (KBr): 3058, 2952, 1580, 1471, 1238, 758, 739, 669 cm^{-1}.
MS (EI): 369 (M^+); HRMS (ESI): Calcd. for $C_{25}H_{28}NSi$ $(M+H)^+$ 370.1986, found 370.1975.

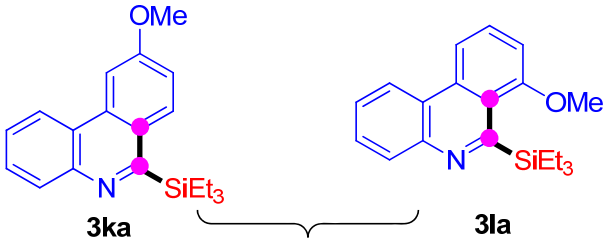
8-(Tert-butyl)-6-(triethylsilyl)phenanthridine (3ja)



The product was purified by preparative TLC on GF254 (ethyl acetate: petroleum ether, 1 : 30) gave **3ja** (36.0 mg, 51% yield) as colorless oil.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.59 (d, J = 8.7 Hz, 1H), 8.55 (d, J = 8.0 Hz, 1H), 8.31 (s, 1H), 8.24 (d, J = 8.1 Hz 1H), 7.89 (d, J = 8.7 Hz, 1H), 7.70 (t, J = 8.0 Hz, 1H), 7.64 (t, J = 8.1 Hz, 1H), 1.50 (s, 9H) 1.18-1.15 (m, 6H), 1.11-1.07 (m, 9H); ^{13}C NMR

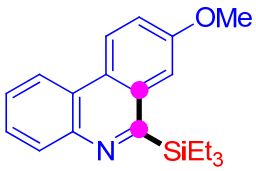
($CDCl_3$, 100 MHz): δ 171.6, 149.7, 144.3, 130.8, 130.6, 128.4, 127.9, 127.7, 126.8, 124.5, 123.2, 122.0, 121.7, 35.1, 31.4, 7.8, 5.0.
IR (KBr): 3065, 2958, 2870, 1480, 1460, 1243, 1009, 767, 722, 698 cm^{-1}.
MS (EI): 349 (M^+); HRMS (ESI): Calcd. for $C_{23}H_{32}NSi$ $(M+H)^+$ 350.2299, found 350.2283.

9-Methoxy-6-(triethylsilyl)phenanthridine (3ka)
7-Methoxy-6-(triethylsilyl)phenanthridine (3la)



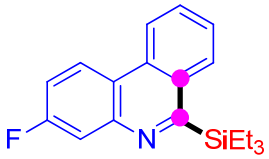
The product was purified by preparative TLC on GF254 (ethyl acetate: petroleum ether, 1 : 30) gave **3ka** and **3la** (41.5 mg, 64% yield) as colorless oil.
^1H NMR ($CDCl_3$, 400 MHz): δ 8.55-8.51 (m, $1H_{la}$, $1H_{ka}$), 8.28-8.22 (m, $2H_{la}$, $2H_{ka}$), 7.99(s, $1H_{ka}$), 7.76-7.69 (m, $2H_{la}$, 1 H_{ka}), 7.66-7.62 (m, $1H_{la}$, $1H_{ka}$), 7.32 (d, J = 8.9 Hz $1H_{ka}$), 7.05 (d, J = 7.9 Hz $1H_{la}$), 4,05 (m, $3H_{la}$, $3H_{ka}$), 1.18-1.14 (m, 6 H_{ka}), 1.11-1.06(m, $6H_{la}$), 1.06-1.01 (m, $9H_{la}$, $9H_{ka}$); $^{13}C_{la}$ NMR ($CDCl_3$, 100 MHz): δ 167.6, 157.5, 144.1, 132.6, 130.8, 130.1, 128.2, 126.8, 122.4, 122.2, 116.8, 114.3, 106.3, 54.4, 8.3, 5.3. $^{13}C_{ka}$ NMR ($CDCl_3$, 100 MHz): δ 170.4, 160.4, 144.6, 132.8, 130.8, 130.3, 128.2, 126.4, 125.9, 123.1, 122.0, 121.8, 102.9, 55.4, 7.8, 4.9.
IR (KBr): 3072, 2956, 2874, 1613, 1552, 1456, 1259, 1089, 1019, 756, 686 cm^{-1}.
MS (EI): 323 (M^+); HRMS (ESI): Calcd. for $C_{20}H_{26}NOSi$ $(M+H)^+$ 324.1778, found 324.1759.

8-Methoxy-6-(triethylsilyl)phenanthridine (3ma)



The product was purified by preparative TLC on GF254 (ethyl acetate: petroleum ether, 1 : 30) gave **3ma** (46.5 mg, 72% yield) as colorless oil.
^1H NMR ($CDCl_3$, 400 MHz): δ 8.56 (d, J = 9.0 Hz, 1H), 8.48 (d, J = 7.8 Hz, 1H), 8.23 (d, J = 7.8 Hz, 1H), 7.70-7.60 (m, 3H), 7.44 (d, J = 9.0 Hz, 1H), 4.00 (s, 3H), 1.18-1.14 (m, 6H), 1.11-1.07 (m, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.4, 158.2, 143.7, 131.8, 130.8, 127.1, 127.0, 124.9, 123.9, 123.3, 121.4, 120.1, 108.7, 55.4, 7.7, 4.8.
IR (KBr): 3061, 2956, 2872, 1616, 1525, 1459, 1208, 1042, 761, 737, 716 cm^{-1}.
MS (EI): 323 (M^+); HRMS (ESI): Calcd. for $C_{20}H_{26}NOSi$ $(M+H)^+$ 324.1778, found 324.1762.

3-Fluoro-6-(triethylsilyl)phenanthridine (3na)



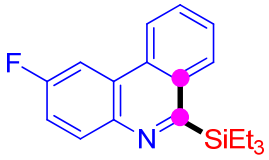
The product was purified by preparative TLC on GF254 (ethyl acetate: petroleumether, 1 : 30) gave **3na** (37.2 mg, 60% yield) as colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.58 (d, J = 8.2 Hz, 1H), 8.53 (t, J = 7.4 Hz, 1H), 8.31 (d, J = 8.1 Hz, 1H), 7.89 (d, J = 9.8 Hz, 1H), 7.81 (t, J = 7.9 Hz, 1H), 7.67 (t, J = 7.9 Hz, 1H), 7.40 (t, J = 8.3 Hz, 1H), 1.16-1.12 (m, 6H), 1.08-1.04 (m, 9H); ($CDCl_3$, 100 MHz): δ 173.3, 162.4 (d, $J_{C\text{-}F}$ = 246.0 Hz), 145.5 (d, $J_{C\text{-}F}$ = 11.3 Hz), 130.4, 130.2, 130.1, 128.7, 126.6, 123.8 (d, $J_{C\text{-}F}$ = 9.3 Hz), 122.1, 119.8 (d, $J_{C\text{-}F}$ = 1.9 Hz), 115.9 (d, $J_{C\text{-}F}$ = 23.7 Hz),, 115.1 (d, $J_{C\text{-}F}$ = 19.6 Hz), 7.7, 4.8.

IR (KBr): 3072, 2952, 2875, 1618, 1481, 1453, 1008, 956, 869, 763, 736, 717 cm^{-1}.

MS (EI): 311 (M^+); HRMS (ESI): Calcd. for $C_{19}H_{23}FNSi$ $(M+H)^+$ 312.1578, found 312.1577.

2-Fluoro-6-(triethylsilyl)phenanthridine (3oa)



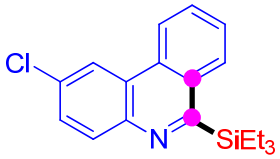
The product was purified by preparative TLC on GF254 (ethyl acetate: petroleum ether, 1 : 30) gave **3oa** (39.8 mg, 64% yield) as colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.52 (d, J = 8.2 Hz, 1H), 8.31 (d, J = 8.1 Hz, 1H), 8.23 (t, J = 7.4 Hz,, 1H), 8.16 (d, J = 10.2 Hz 1H), 7.81 (t, J = 7.2 Hz, 1H), 7.72 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 8.6 Hz, 1H), 1.15-1.12 (m, 6H), 1.11-1.04 (m, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.5, 161.3 (d, $J_{C\text{-}F}$ = 245.1 Hz), 141.4, 133.1 (d, $J_{C\text{-}F}$ = 9.0 Hz), 130.4, 130.2 (d, $J_{C\text{-}F}$ = 4.1 Hz), 129.7, 128.6, 127.4, 124.5 (d, $J_{C\text{-}F}$ = 9.0 Hz), 122.5, 117.0 (d, $J_{C\text{-}F}$ = 24.1 Hz), 106.6 (d, $J_{C\text{-}F}$ = 23.0 Hz), 7.8, 4.8.

IR (KBr): 3068, 2949, 2875, 1621, 1557, 1487, 1440, 1203, 1174, 979, 953 cm^{-1}.

MS (EI): 311 (M^+); HRMS (ESI): Calcd. for $C_{19}H_{23}FNSi$ $(M+H)^+$ 312.1578, found 312.1567.

2-Chloro-6-(triethylsilyl)phenanthridine (3pa)

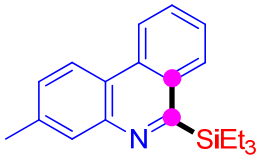


The product was purified by preparative TLC on GF254 (ethyl acetate: petroleum ether, 1 : 30) gave **3pa** (35.8 mg, 70% yield) as colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.56 (d, J = 8.2 Hz, 1H), 8.52 (s, 1H), 8.30 (d, J = 8.2 Hz, 1H), 8.16 (d, J = 8.7 Hz, 1H), 7.81 (t, J = 7.6 Hz, 1H), 7.71 (t, J = 7.6 Hz, 1H), 7.66 (d, J = 8.7 Hz, 1H), 1.17-1.11 (m, 6H), 1.07-1.02 (m, 9H); ^{13}C NMR ($CDCl_3$,

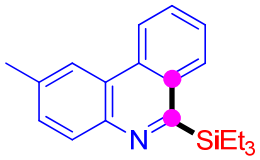
100 MHz): δ 172.0, 142.7, 132.7, 132.4, 130.6, 130.0, 129.7, 128.7, 128.6, 127.4, 124.3, 122.4, 121.5, 7.7, 4.8.
IR (KBr): 3070, 2952, 2873, 1602, 1479, 1436, 1238, 1085, 1014, 761, 738, 698 cm^{-1}.
MS (EI): 327 (M^+); HRMS (ESI): Calcd. for $C_{19}H_{23}NSi$ $(M+H)^+$ 328.1283, found 328.1282.

3-Methyl-6-(triethylsilyl)phenanthridine (3qa)



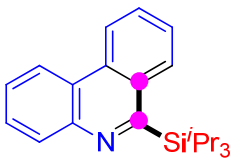
The product was purified by preparative TLC on GF254 (ethyl acetate: petroleum ether, 1 : 30) gave **3qa** (28.4mg, 46% yield) as colorless oil.
^1H NMR ($CDCl_3$, 400 MHz): δ 8.62 (d, J = 8.2 Hz, 1H), 8.46 (d, J = 8.3 Hz, 1H), 8.30 (d, J = 8.1 Hz 1H), 8.06 (s, 1H), 7.78 (t, J = 8.0 Hz, 1H), 7.65 (t, J = 7.9 Hz, 1H), 7.48 (d, J = 8.3 Hz, 1H), 2.61 (s, 3H) 1.16-1.12 (m, 6H), 1.08-1.05 (m, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.4, 144.5, 138.2, 130.8, 130.4, 130.3, 129.6, 128.7, 128.5, 126.3, 122.2, 121.6, 120.8, 21.4, 7.8, 5.0.
IR (KBr): 3068, 2958, 2873, 1617, 1480, 1454, 1239, 1012, 762, 739, 723 cm^{-1}.
MS (EI): 307 (M^+); HRMS (ESI): Calcd. for $C_{20}H_{26}NSi$ $(M+H)^+$ 308.1829, found 308.1822.

2-Methyl-6-(triethylsilyl)phenanthridine (3ra)



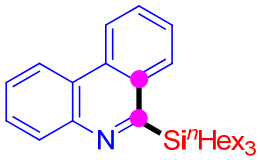
The product was purified by preparative TLC on GF254 (ethyl acetate: petroleum ether, 1 : 30) gave **3ra** (32.2 mg, 52% yield) as colorless oil.
^1H NMR ($CDCl_3$, 400 MHz): δ 8.65 (d, J = 8.2 Hz, 1H), 8.35 (s, 1H), 8.29 (d, J = 8.1 Hz, 1H), 8.14 (d, J = 8.3 Hz 1H), 7.79 (t, J = 7.8 Hz, 1H), 7.67 (t, J = 7.8 Hz, 1H), 7.56 (d, J = 8.3 Hz, 1H), 2.63 (s, 3H), 1.16-1.13 (m, 6H), 1.08-1.05 (m, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.1, 142.8, 136.8, 130.7, 130.6, 130.4, 129.8, 129.4, 128.4, 126.6, 123.0, 122.3, 121.4, 22.0, 7.8, 4.8.
IR (KBr): 3070, 2953, 2872, 1612, 1558, 1457, 1414, 1238, 1008, 825, 763, 735, 697cm^{-1}.
MS (EI): 307 (M^+); HRMS (ESI): Calcd. for $C_{20}H_{26}NSi$ $(M+H)^+$ 308.1829, found 308.1825.

6-(Triisopropylsilyl)phenanthridine (3ab)



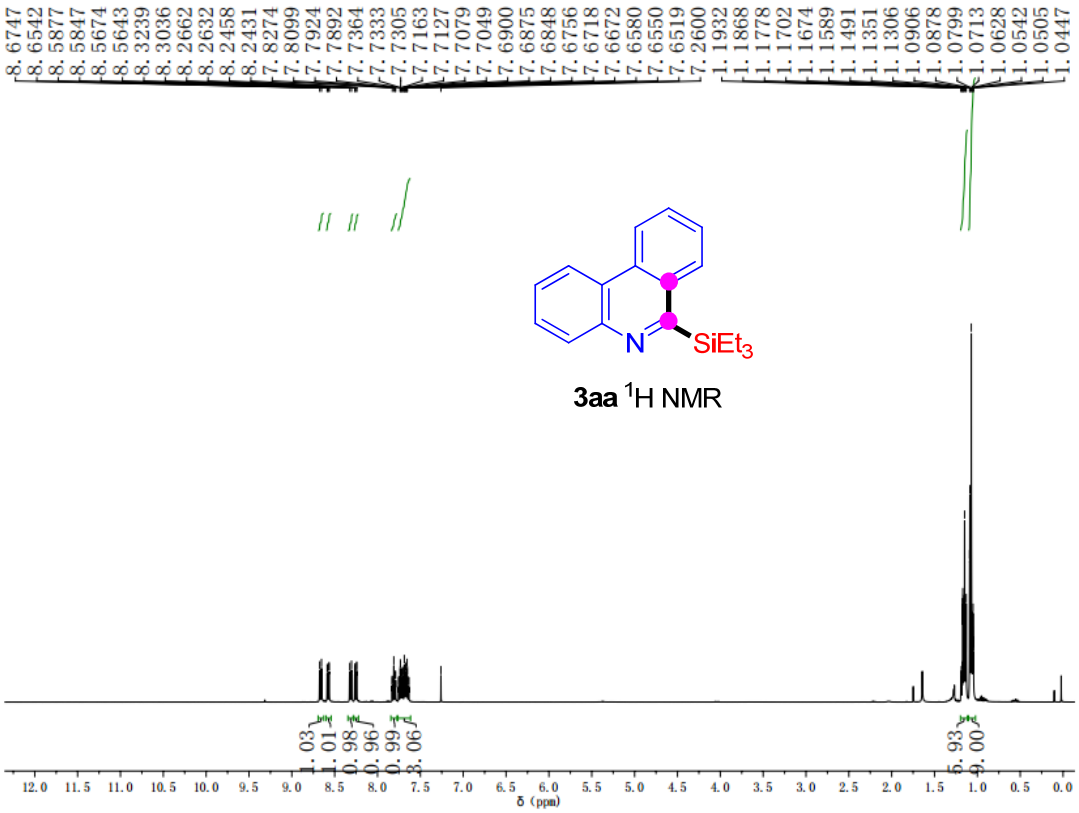
The product was purified by preparative TLC on GF254 (ethyl acetate: petroleum ether, 1 : 30) gave **3ab** (36.9mg, 55% yield) as a white solid. Mp: 89-92 ^{o}C.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.67 (d, J = 8.2 Hz, 1H), 8.58 (d, J = 8.0 Hz, 1H), 8.25 (d, J = 8.1 Hz 2H), 7.80 (d, J = 7.8 Hz 1H), 7.73 (t, J = 7.7 Hz, 1H), 7.70-7.64 (m, 2H), 1.81-1.73 (m, 3H), 1.28-1.18 (m, 18H), ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.0, 144.2, 130.9, 130.8, 130.8, 129.5, 129.1, 128.1, 126.9, 126.6, 122.9, 122.3, 121.8 19.2, 13.4.
IR (KBr): 3057, 2947, 1552, 1465, 1452, 1381, 1375, 1251, 754, 725, 679 cm^{-1}.
MS (EI): 335 (M^+); HRMS (ESI): Calcd. for $C_{31}H_{48}NSi$ $(M+H)^+$ 336.2142, found 336.2127.

6-(Trihexylsilyl)phenanthridine (3ac)

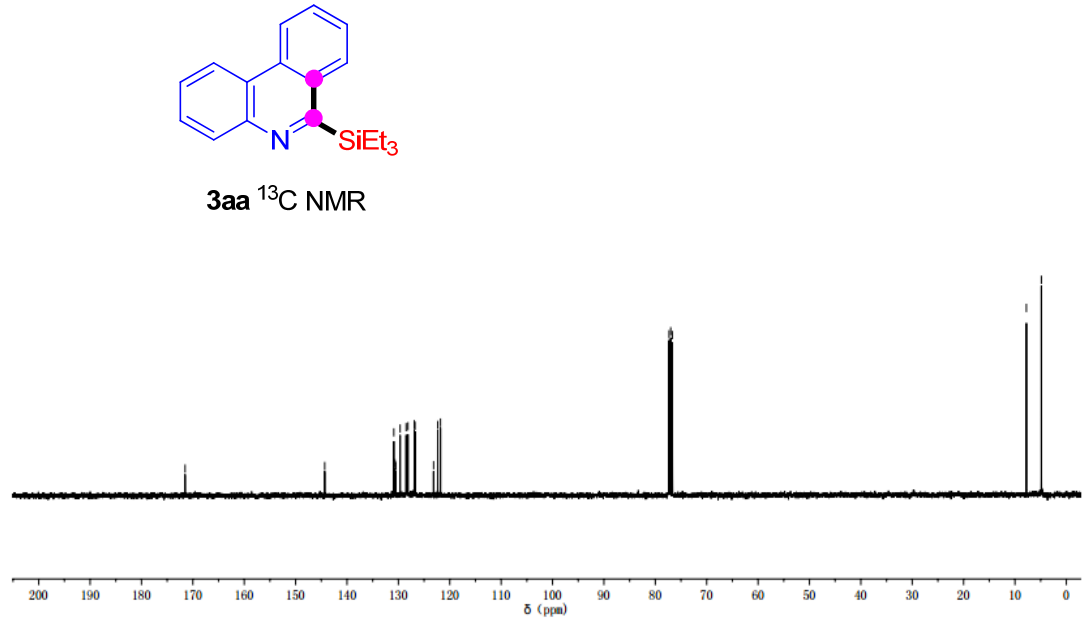


The product was purified by preparative TLC on GF254 (ethyl acetate: petroleum ether, 1 : 30) gave **3ac** (55.7 mg, 60 % yield) as colorless oil.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.66 (d, J = 8.2 Hz, 1H), 8.57 (d, J = 8.1 Hz, 1H), 8.31 (d, J = 8.1 Hz 1H), 8.24 (d, J = 8.0 Hz 1H), 7.81 (t, J = 7.6 Hz, 1H), 7.75-7.63 (m, 3H), 1.39-1.25 (m, 24H), 1.15-1.11 (m, 6H), 0.87-0.83 (m, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 172.1, 144.3, 130.9, 130.7, 130.4, 129.6, 128.6, 128.1, 126.8, 126.7, 123.2, 122.4, 121.8, 33.4, 31.4, 24.0, 22.6, 14.1, 13.8.
IR (KBr): 3072, 2960, 2927, 2858, 2098, 1457, 1251, 1180, 1099, 1032, 845, 755, 719 cm^{-1}.
MS (EI): 461 (M^+); HRMS (ESI): Calcd. for $C_{31}H_{48}NSi$ $(M+H)^+$ 462.3551, found 462.3530.

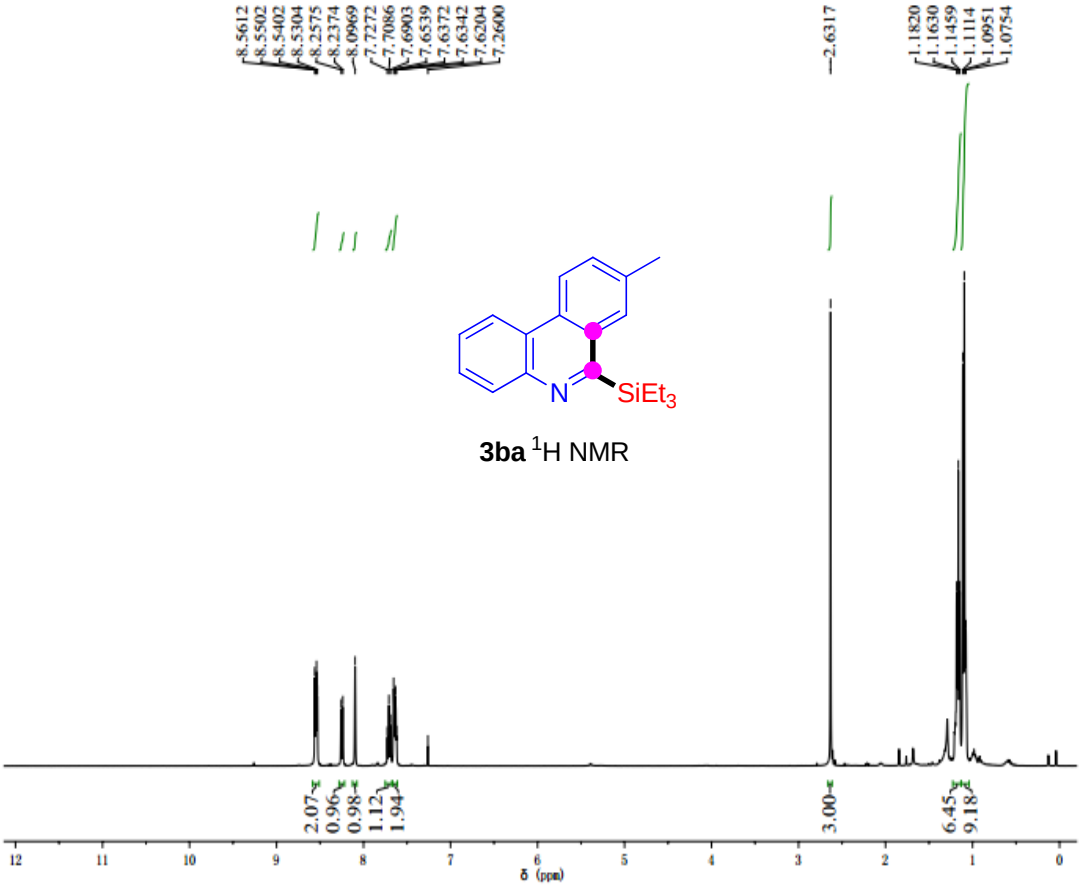
5 Copies of ^{1}H NMR and ^{13}C NMR spectra



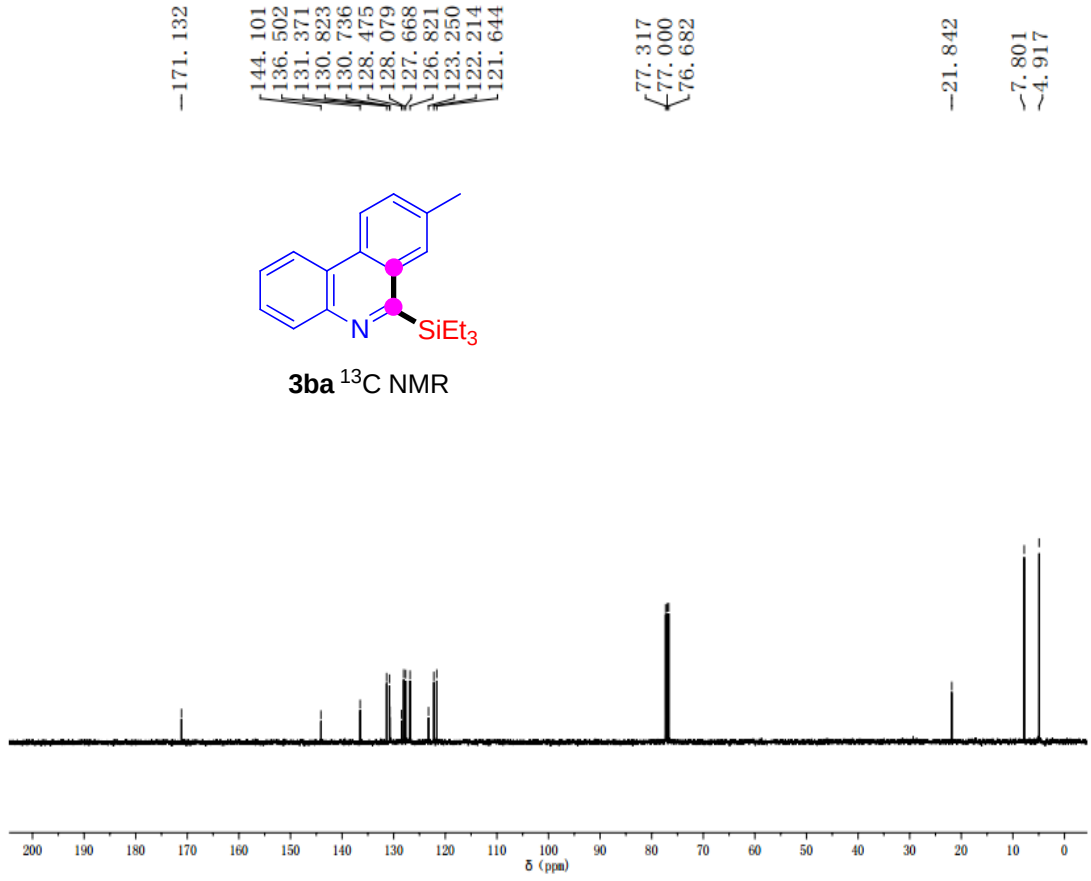
3aa ^{1}H NMR



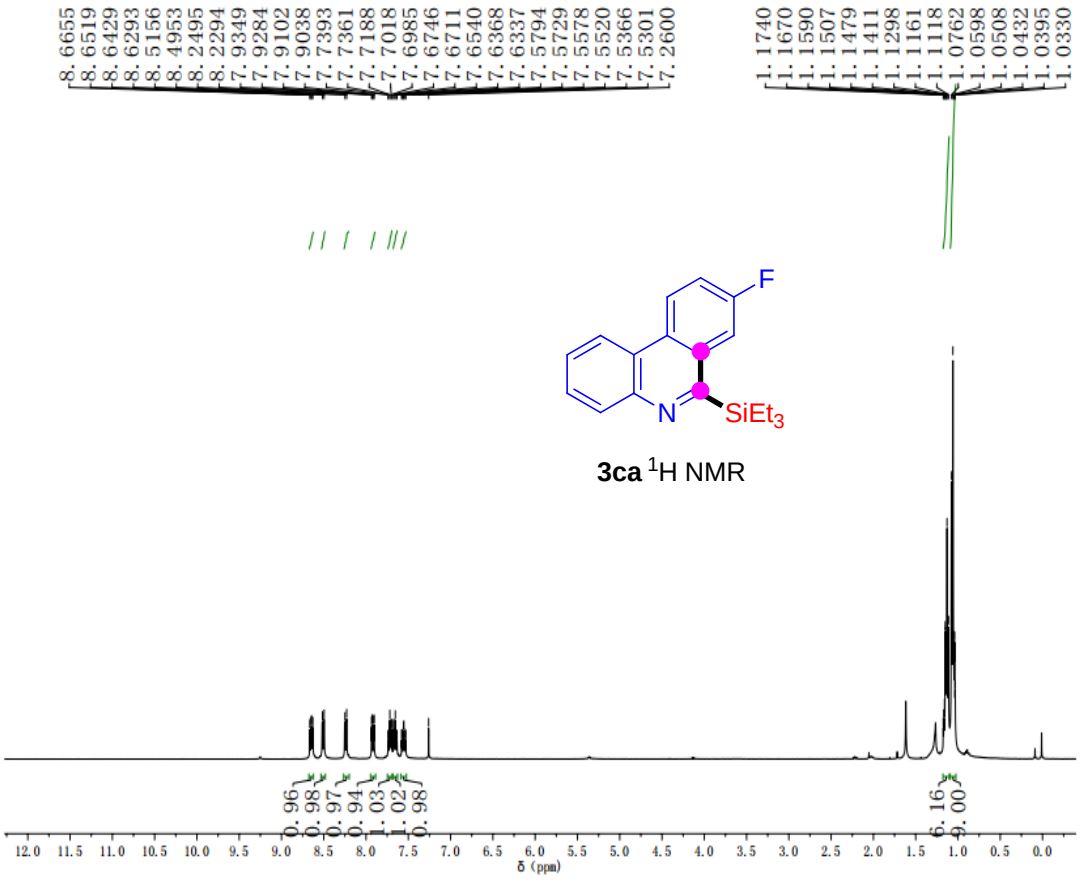
3aa ^{13}C NMR



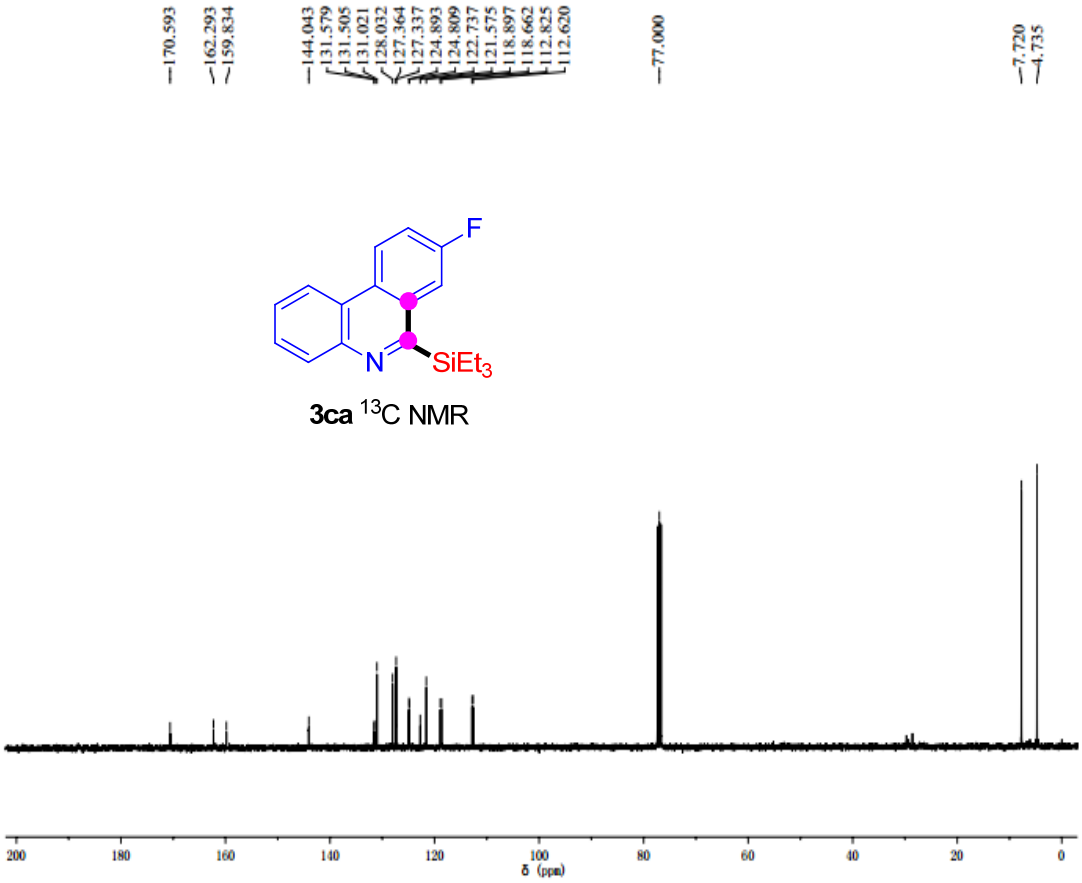
3ba ^{1}H NMR



3ba ^{13}C NMR



3ca ^{1}H NMR



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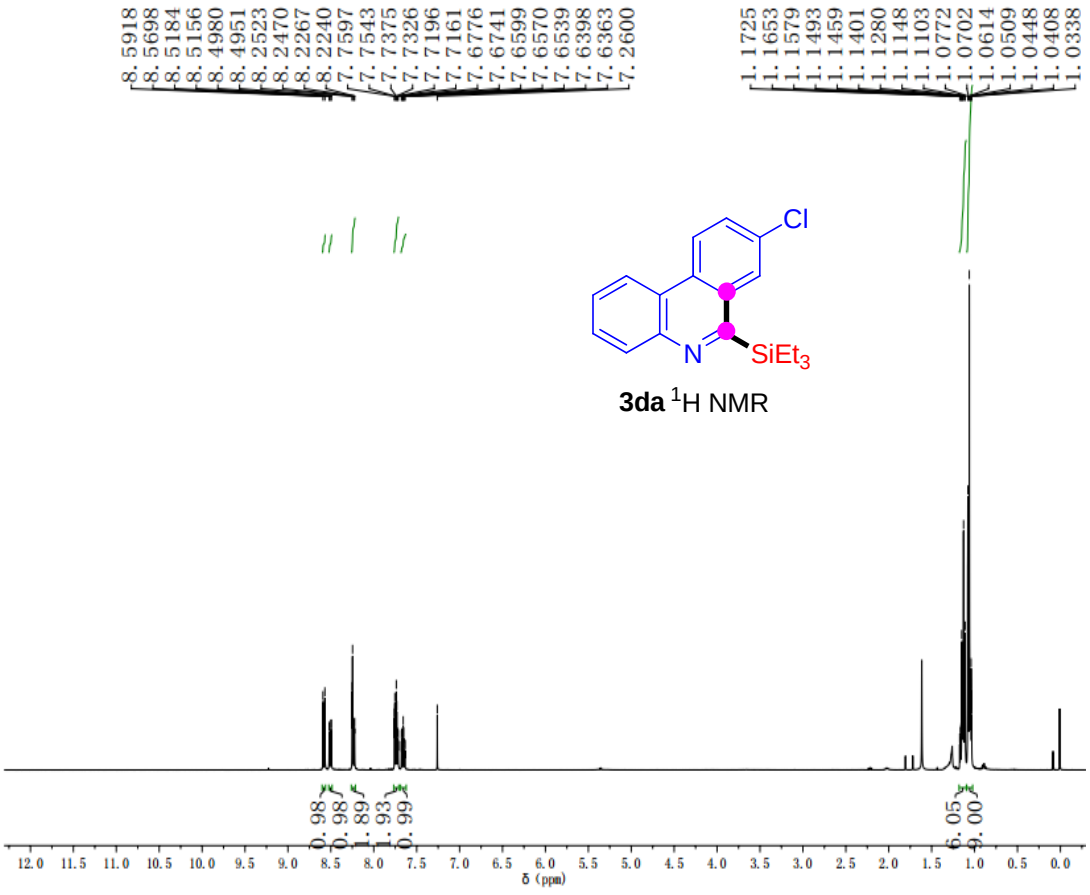

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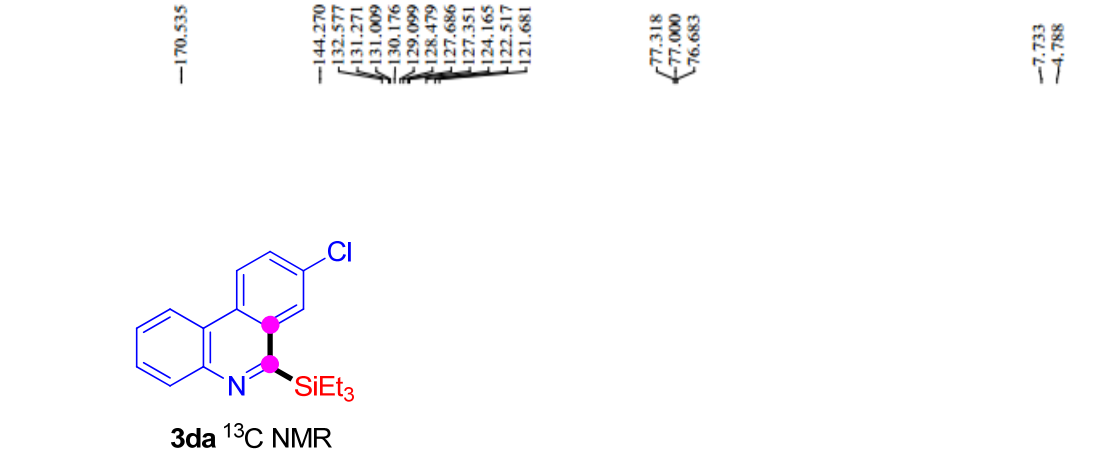

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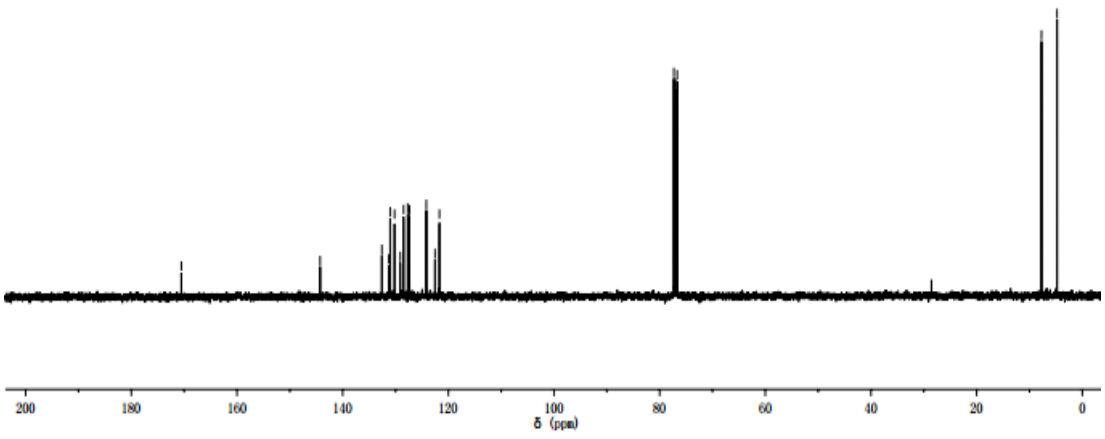

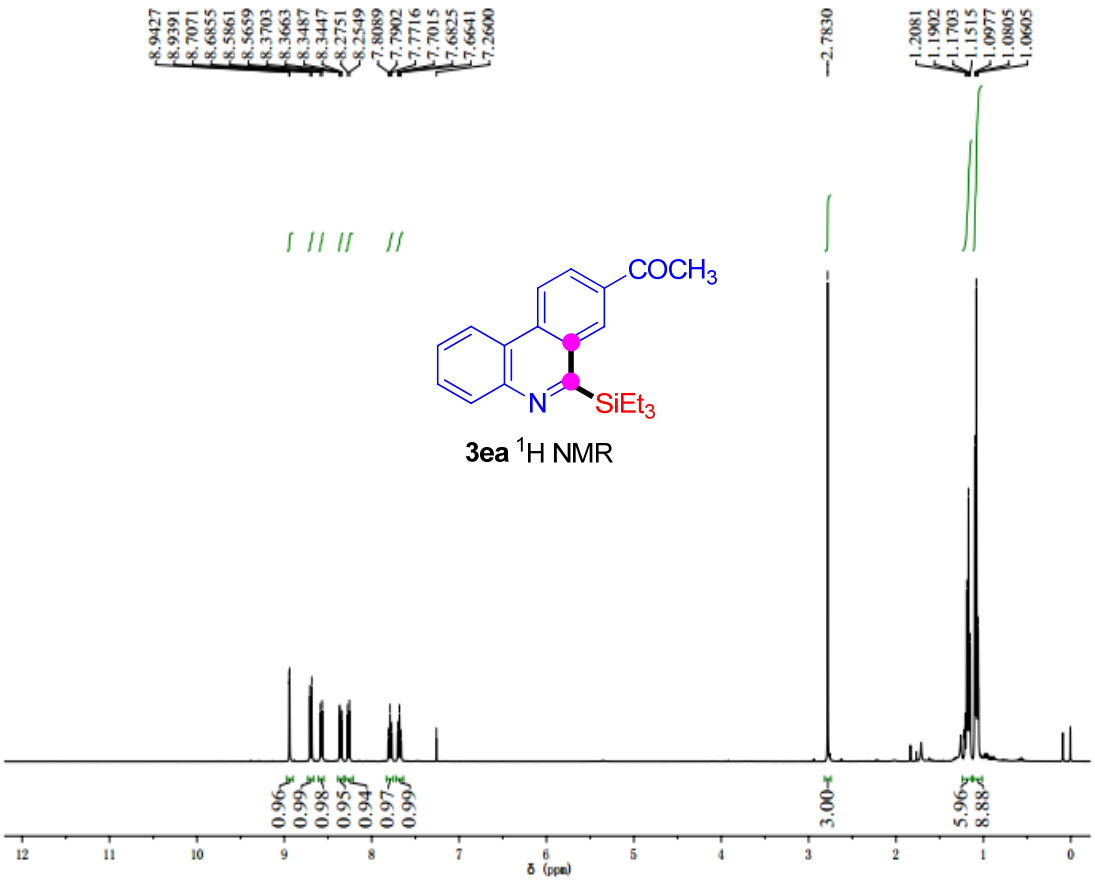

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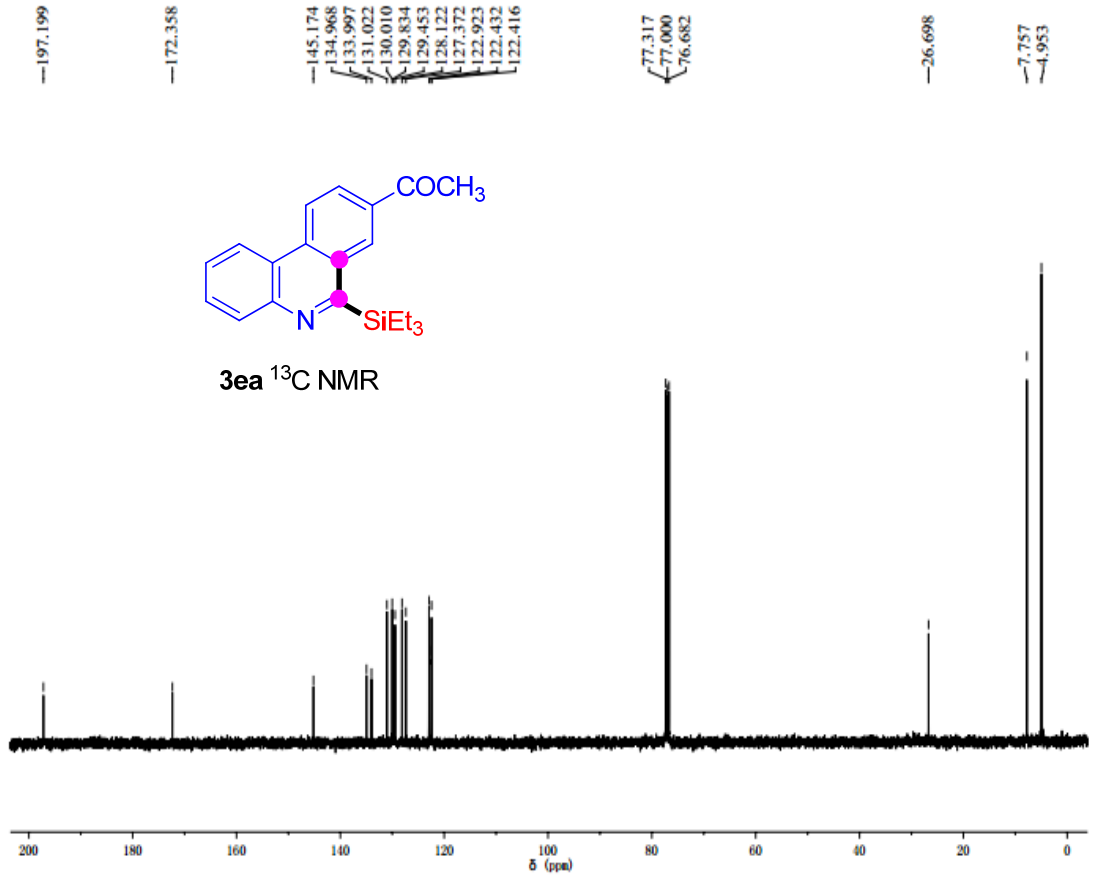

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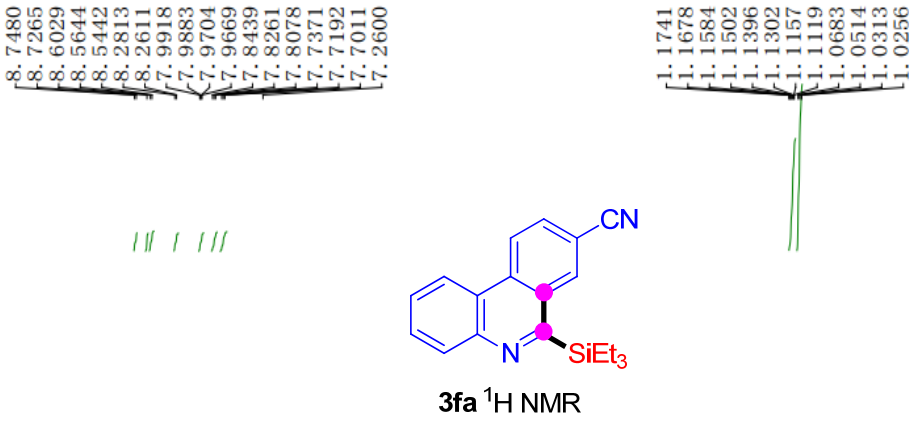

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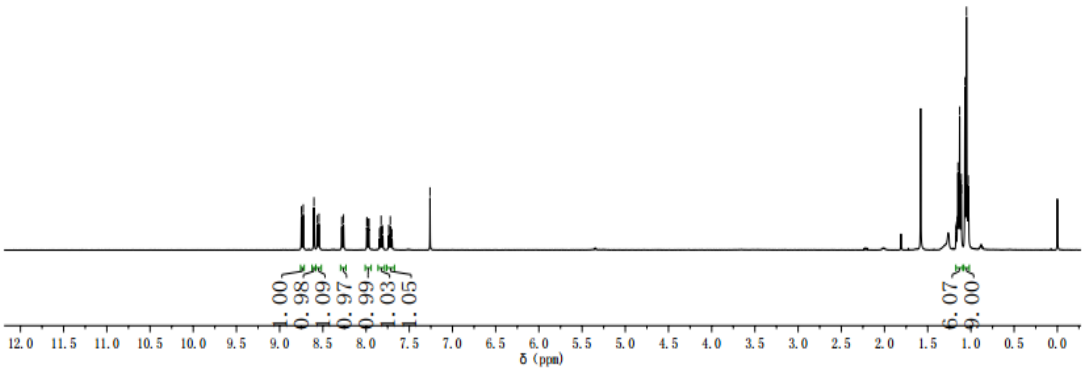

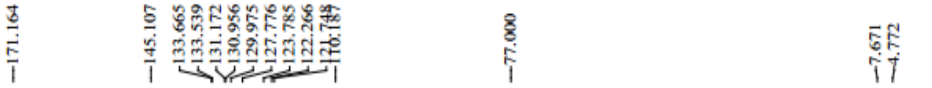

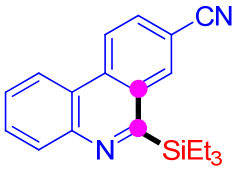

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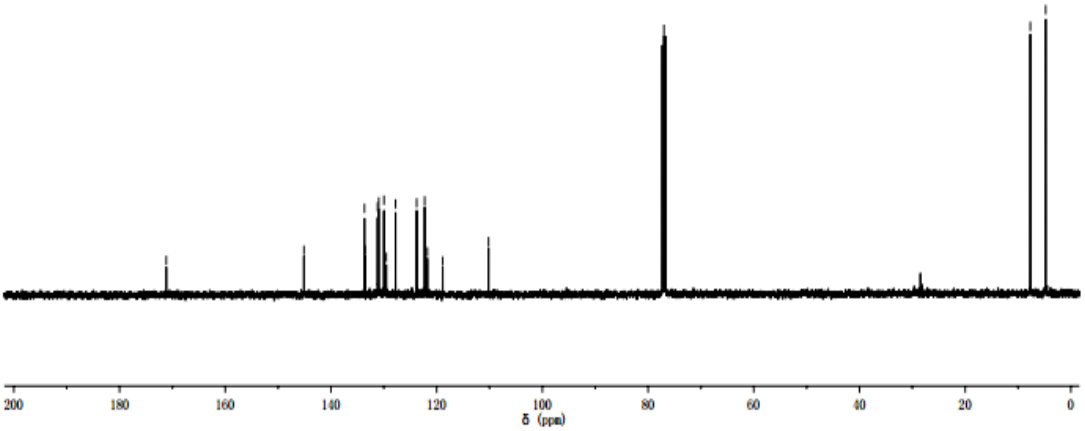
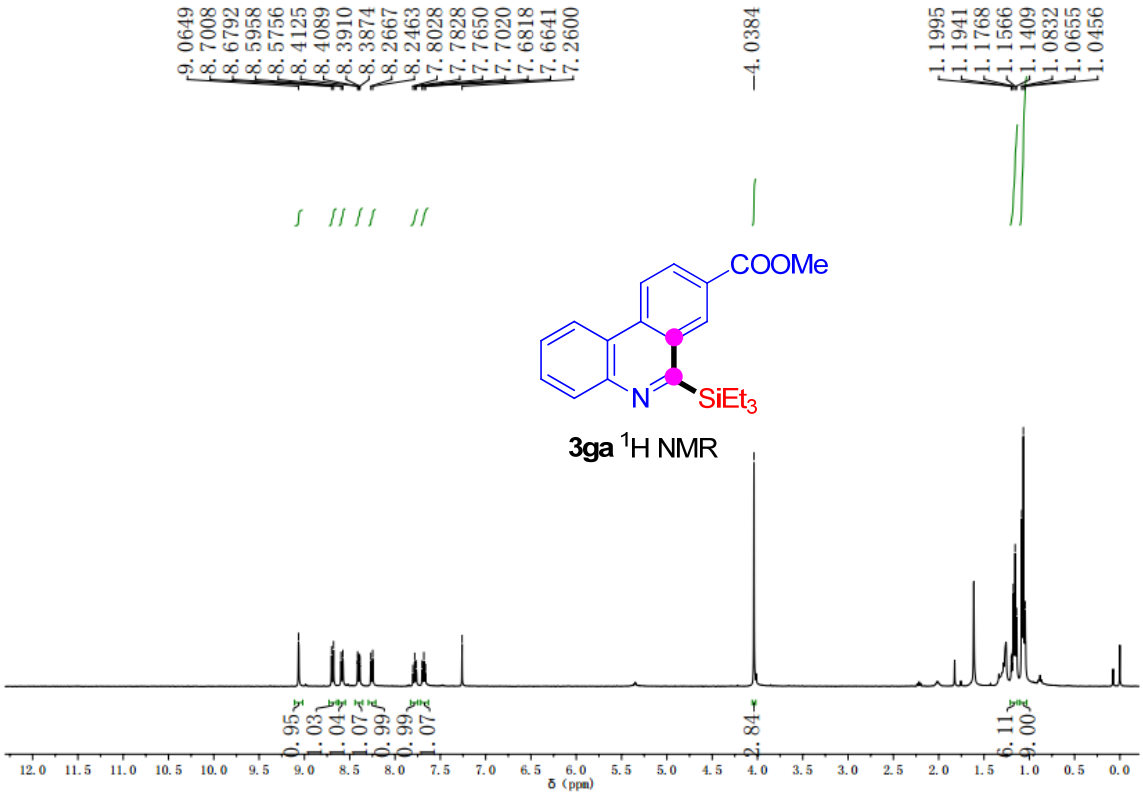
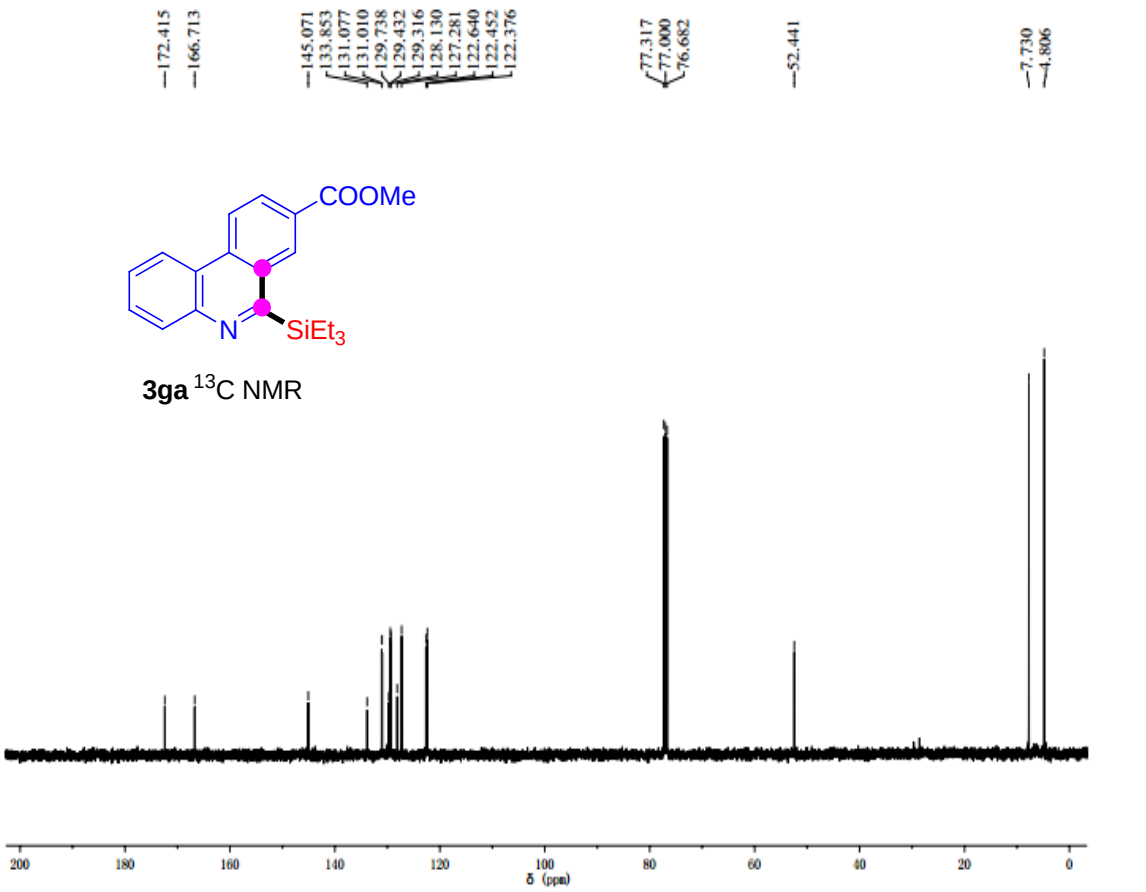




3ga ^{1}H NMR



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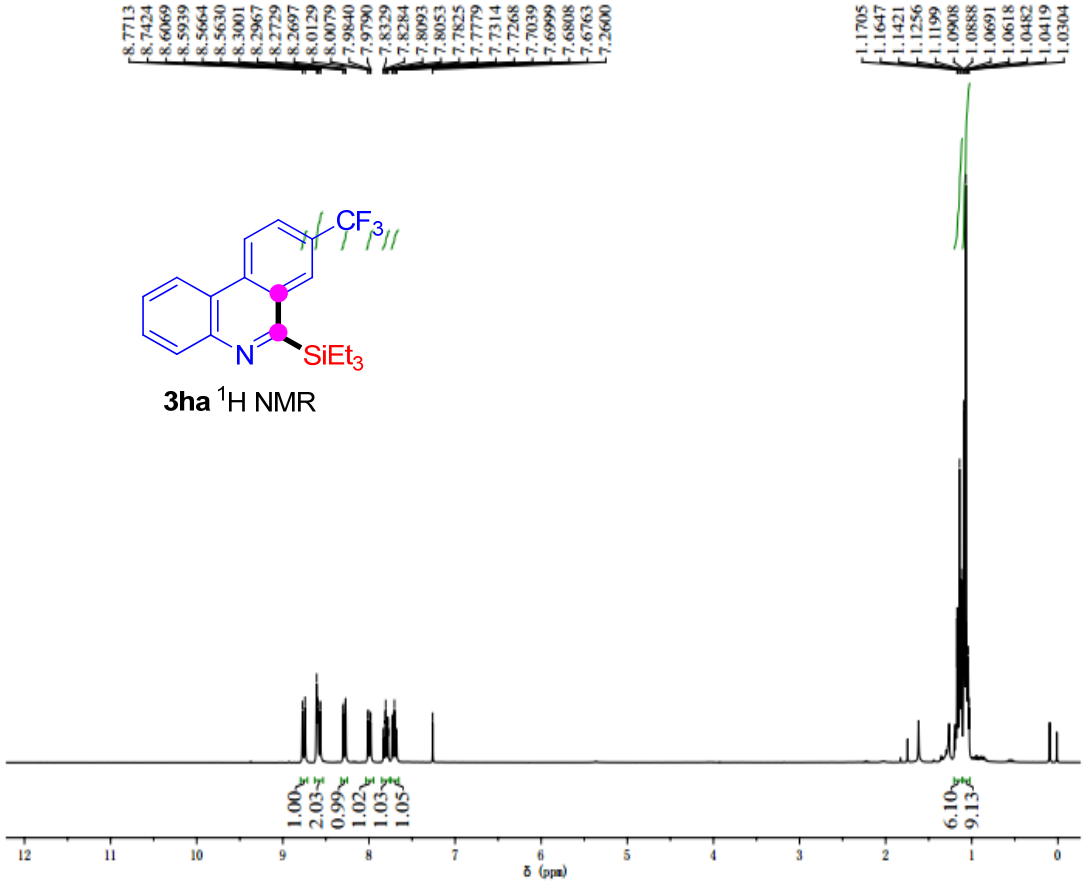
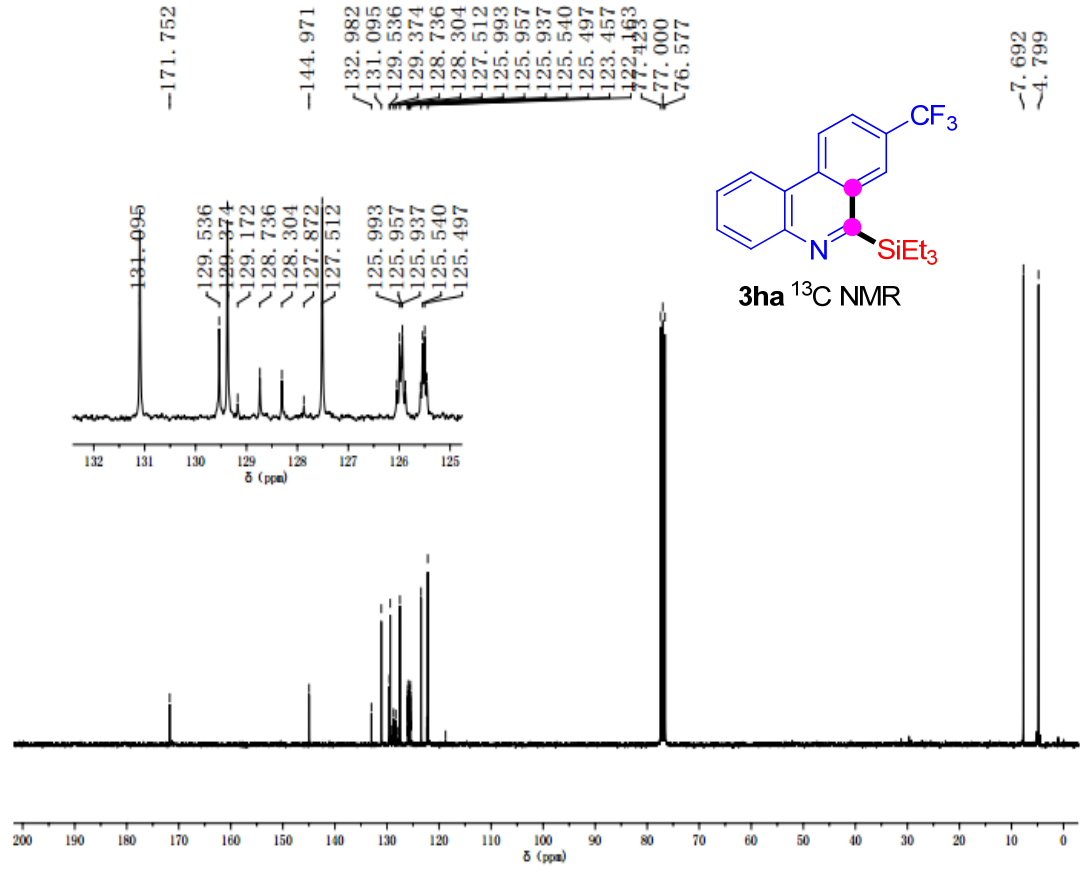
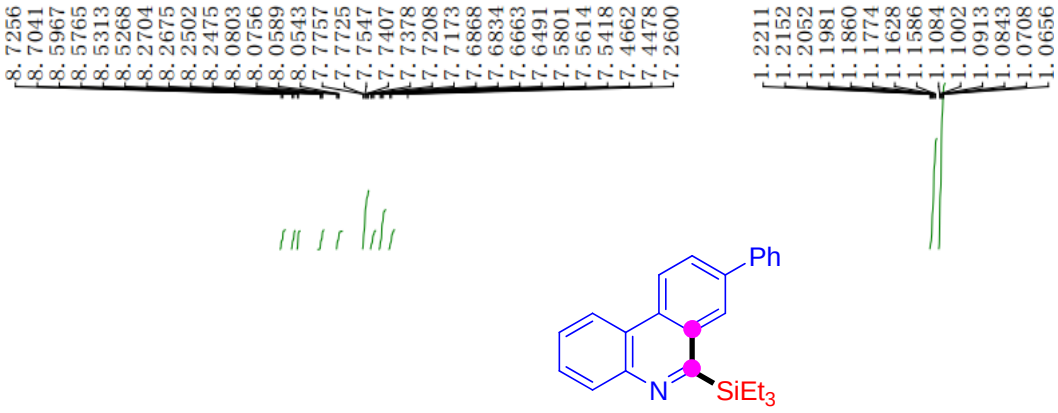


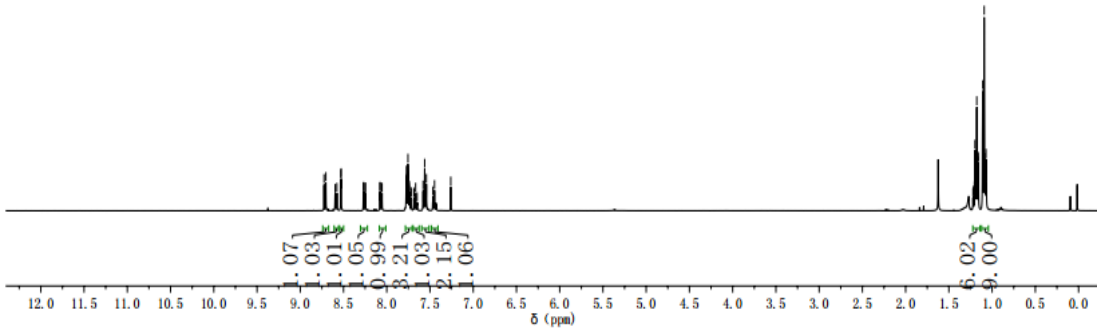
3ha ^{1}H NMR

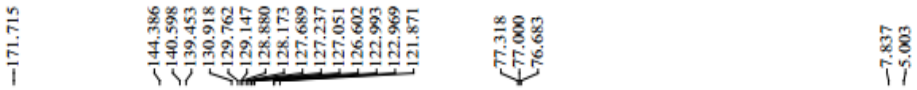


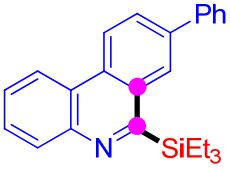
3ha ^{13}C NMR



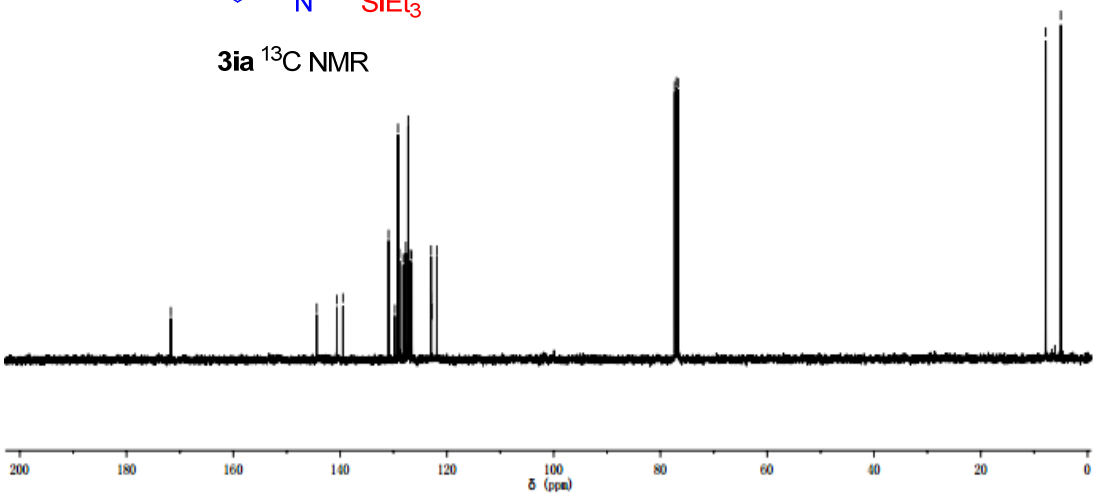
3ia ^{1}H NMR

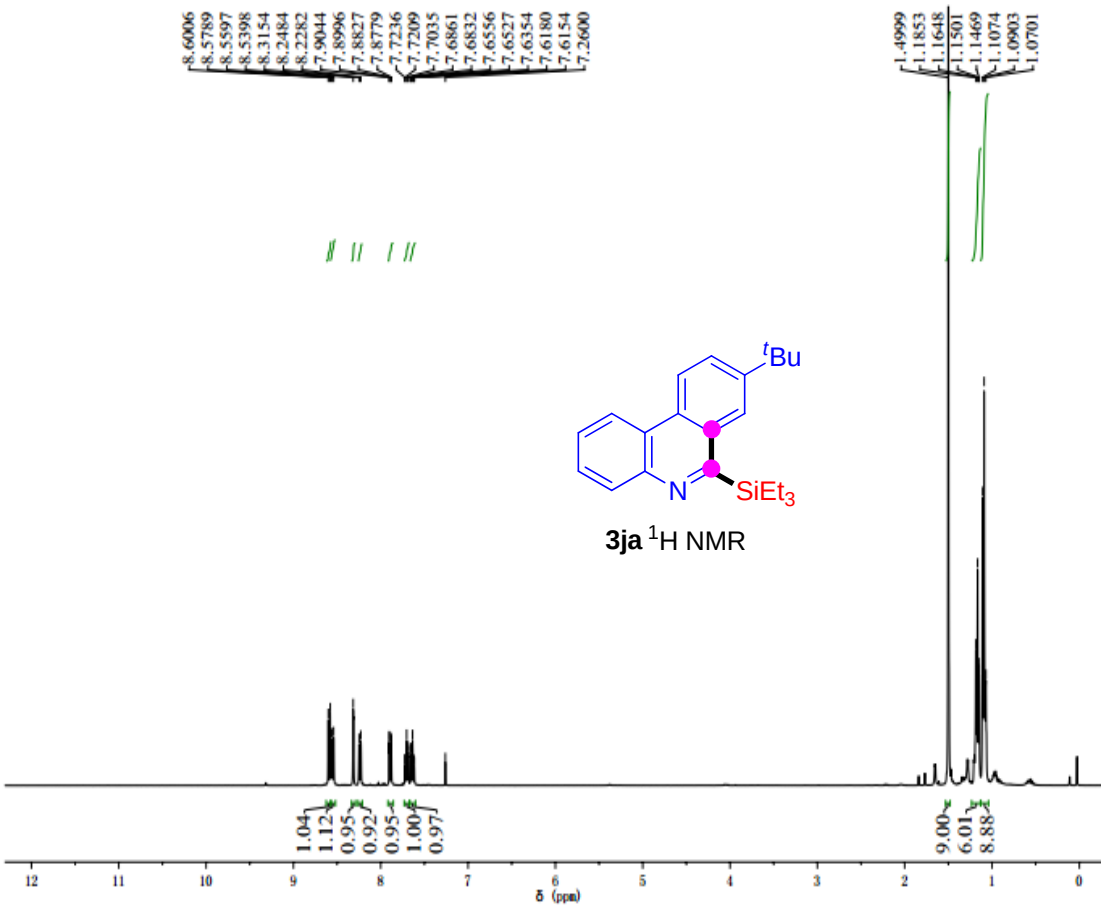




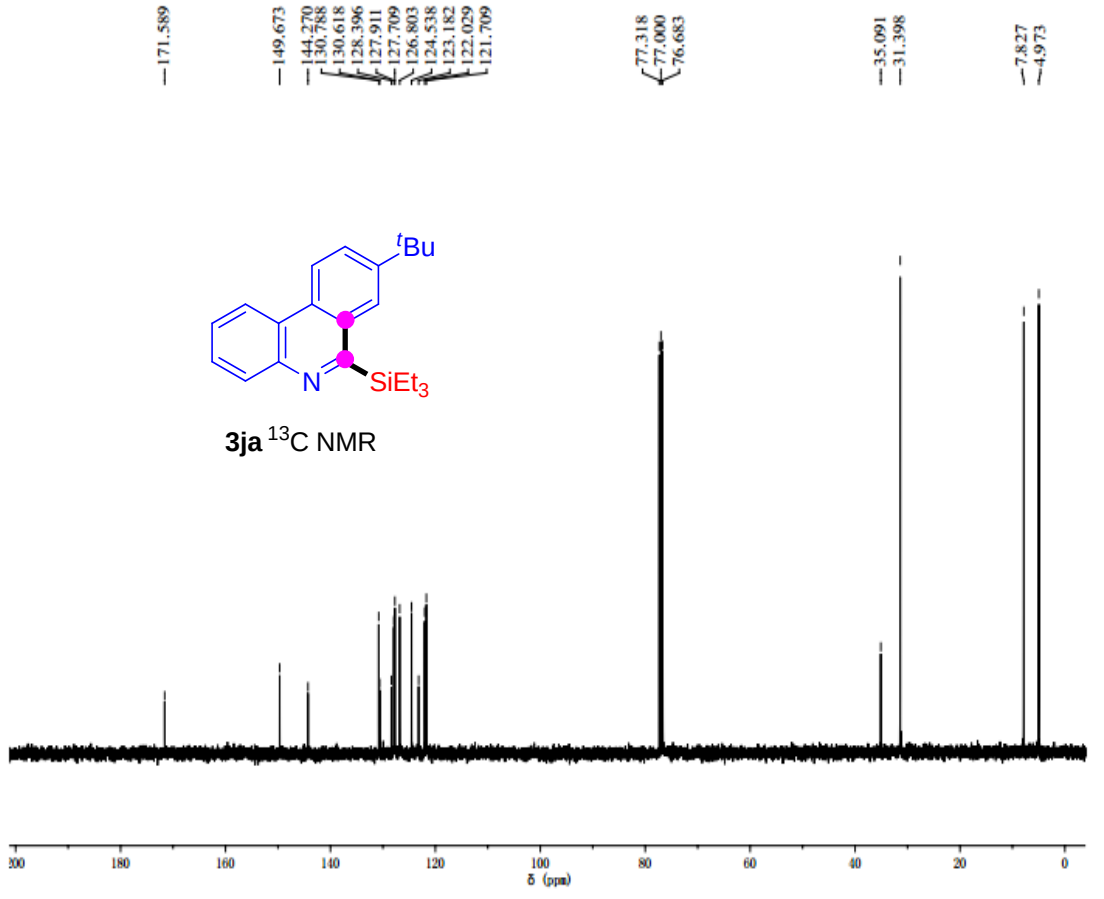


3ia ^{13}C NMR

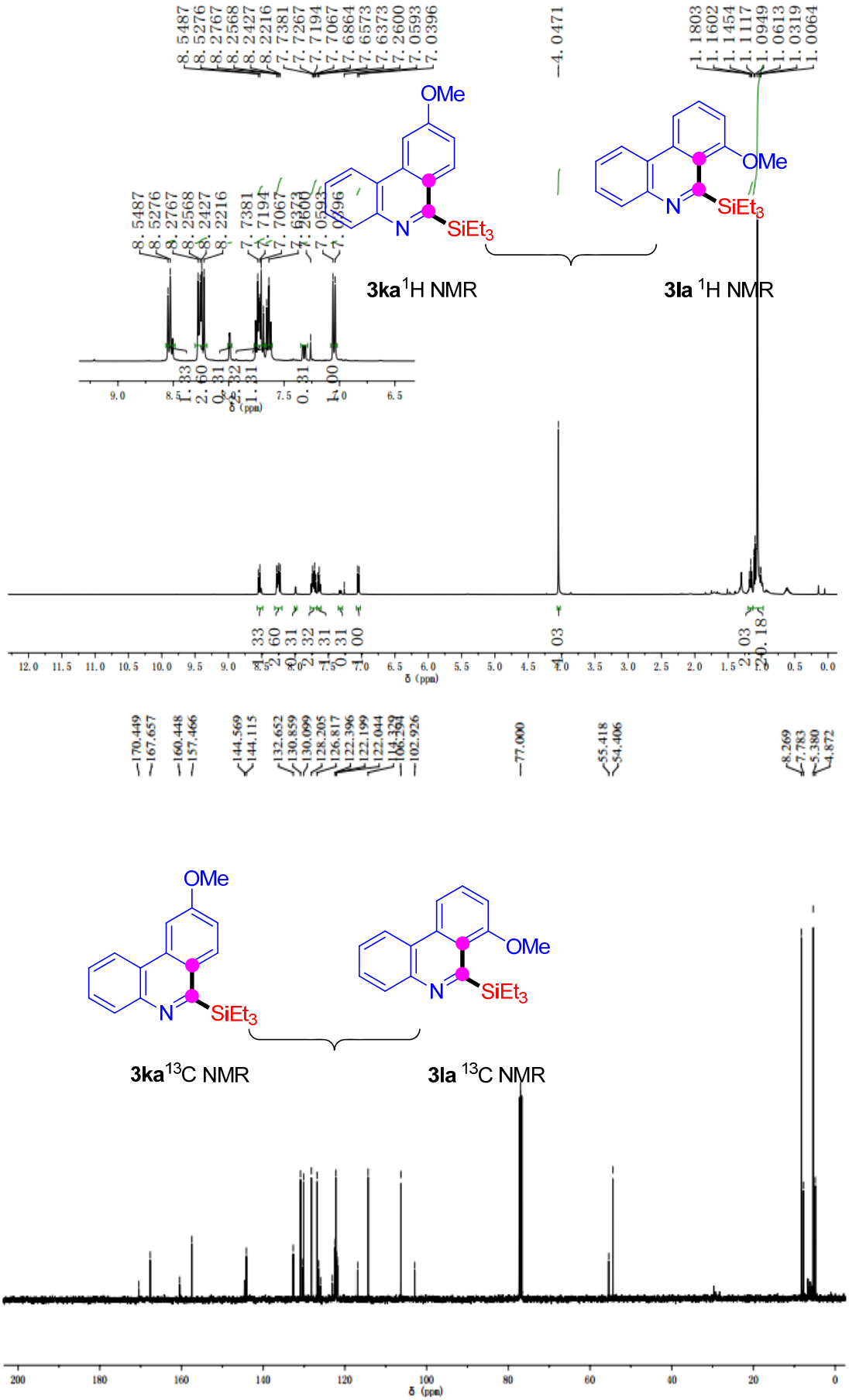


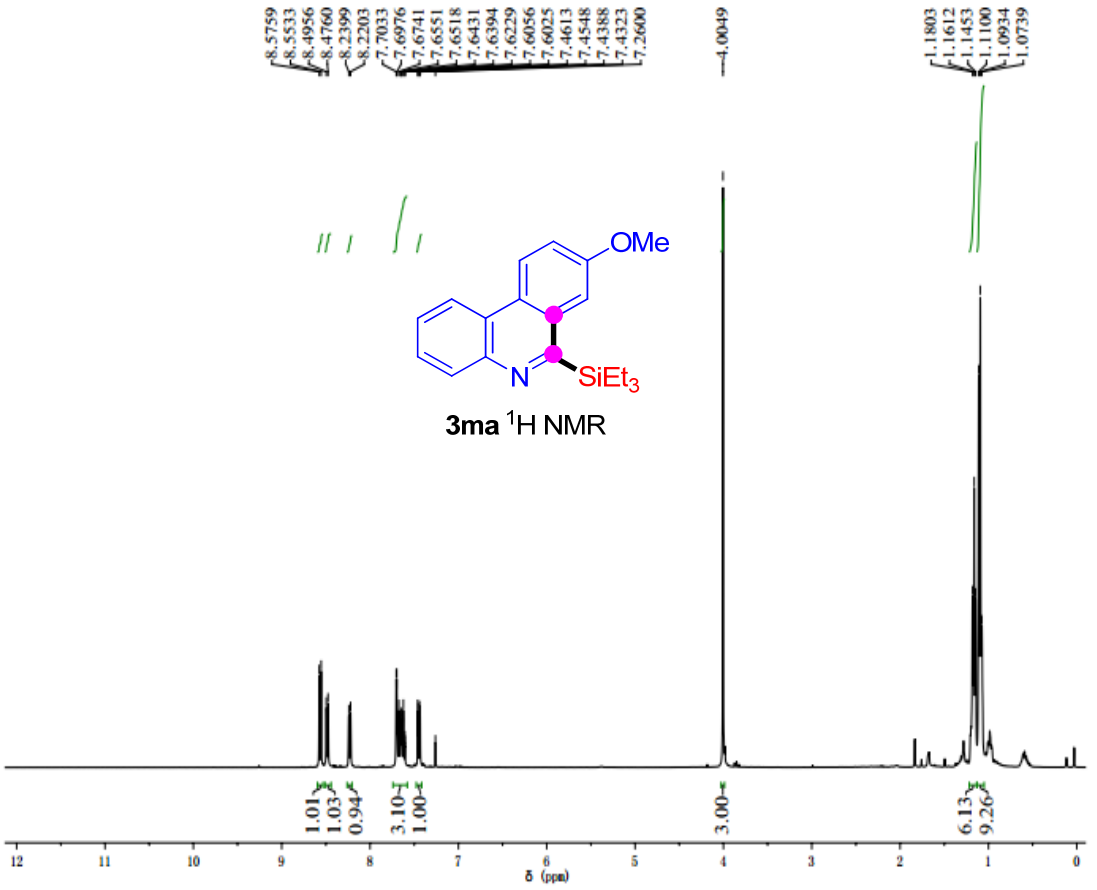


3ja ^{1}H NMR

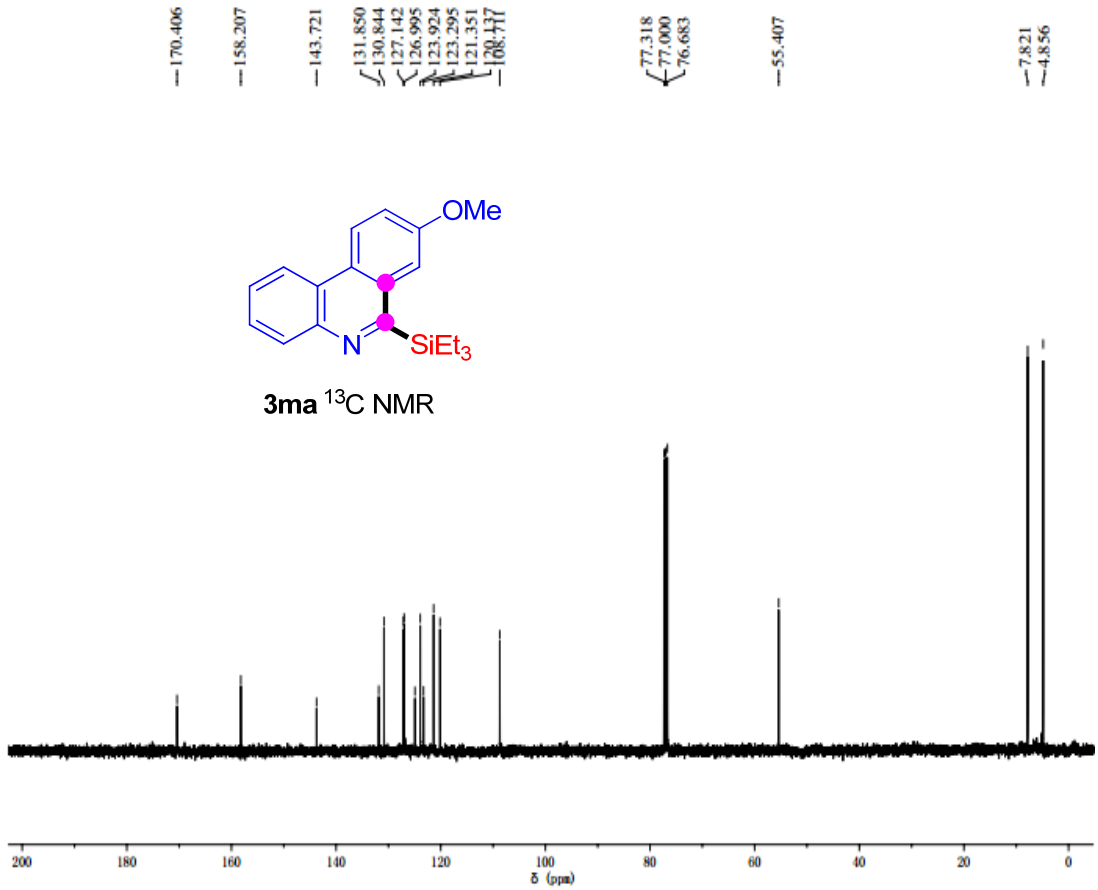


3ja ^{13}C NMR

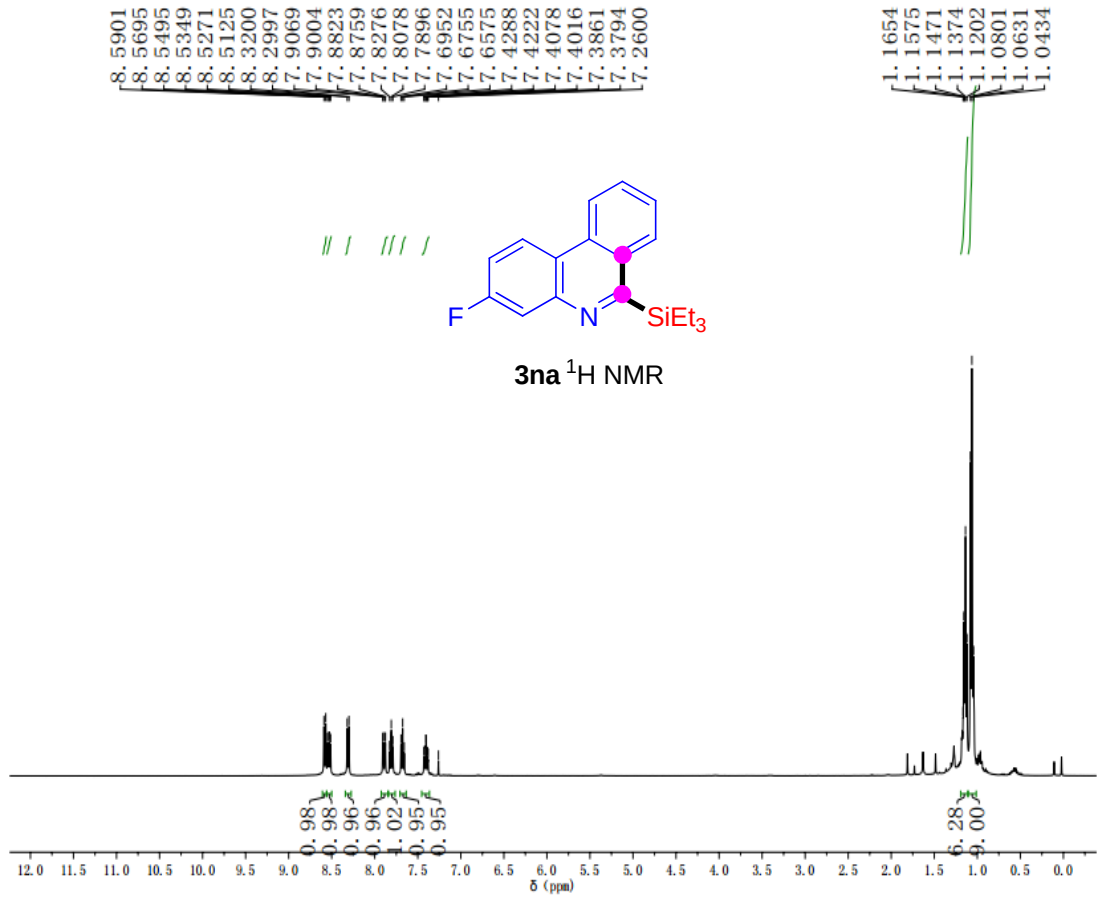

OMe
SiEt3
N
3ka 1H NMR
3la 1H NMR
δ (ppm)
3ka 13C NMR
3la 13C NMR



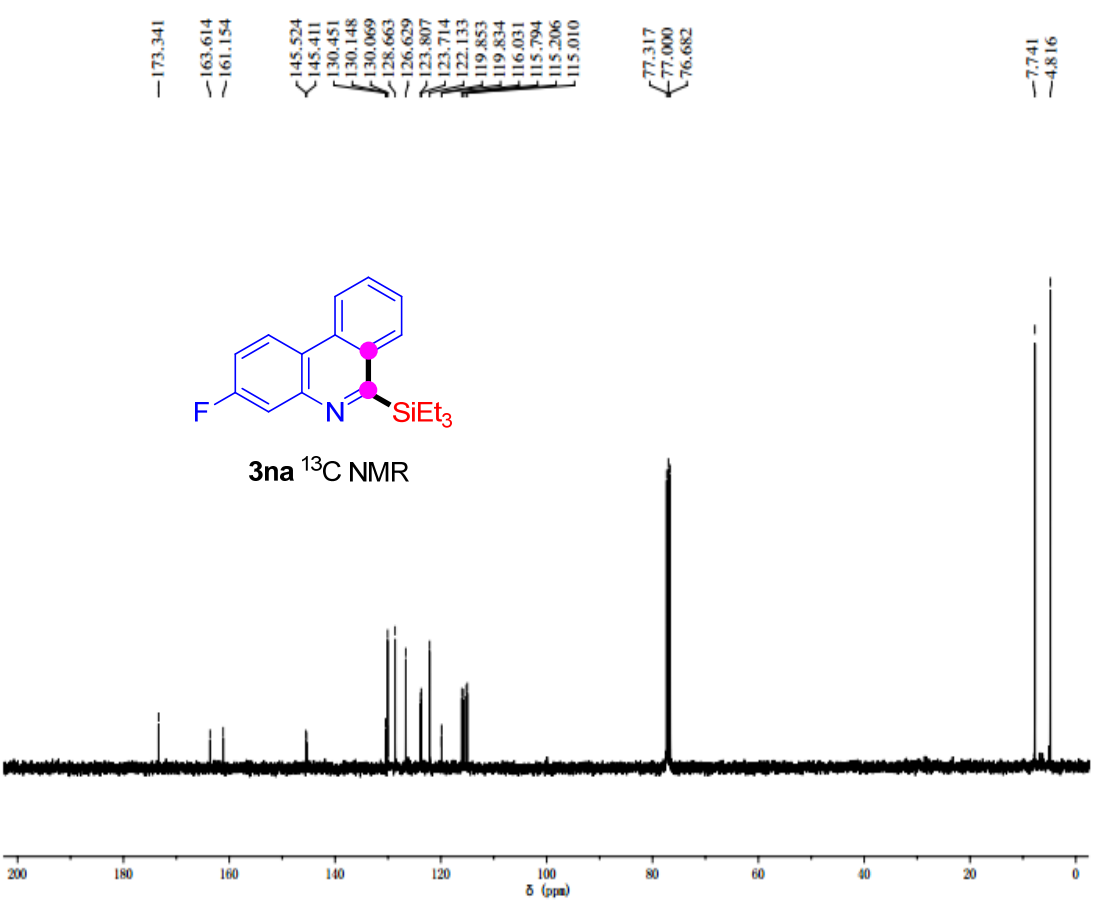
3ma ^{1}H NMR



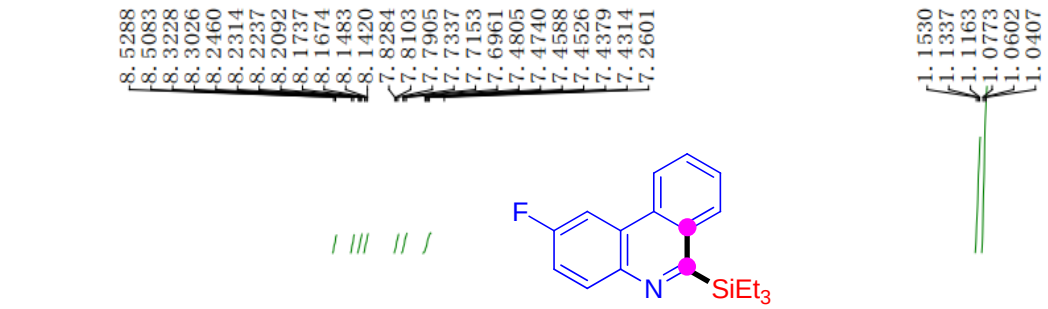
3ma ^{13}C NMR



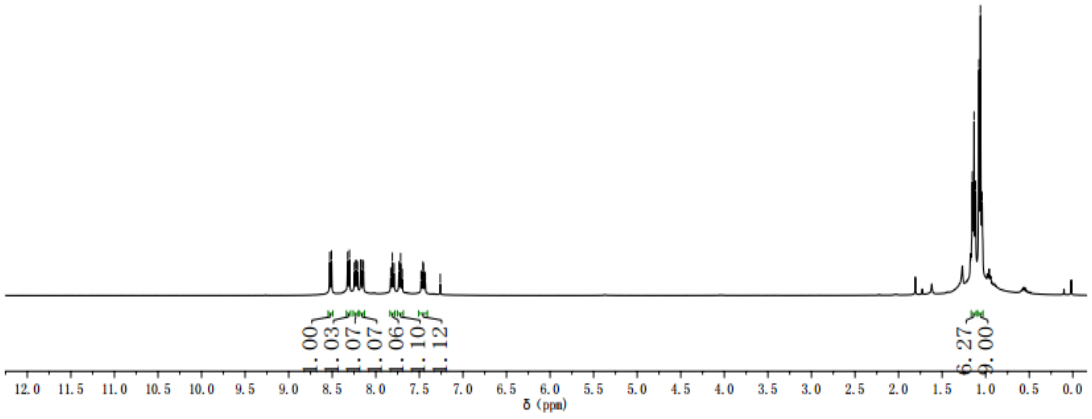
3na ^{1}H NMR

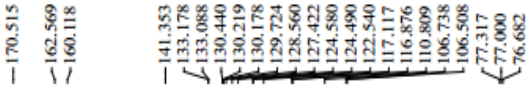


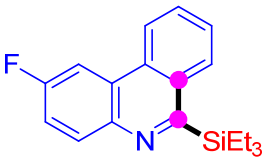
3na ^{13}C NMR



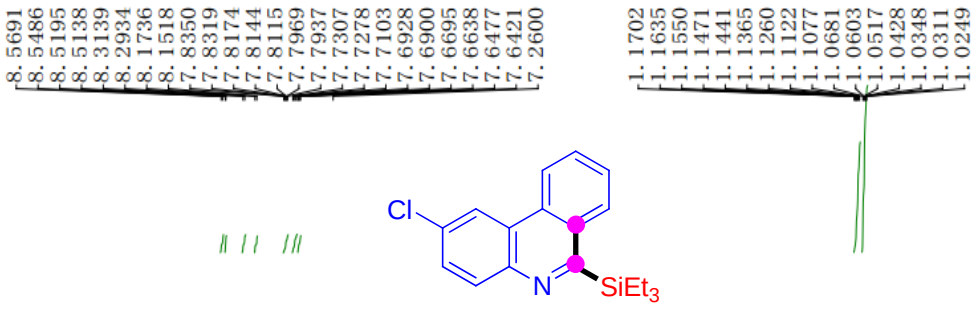
3oa ^{1}H NMR



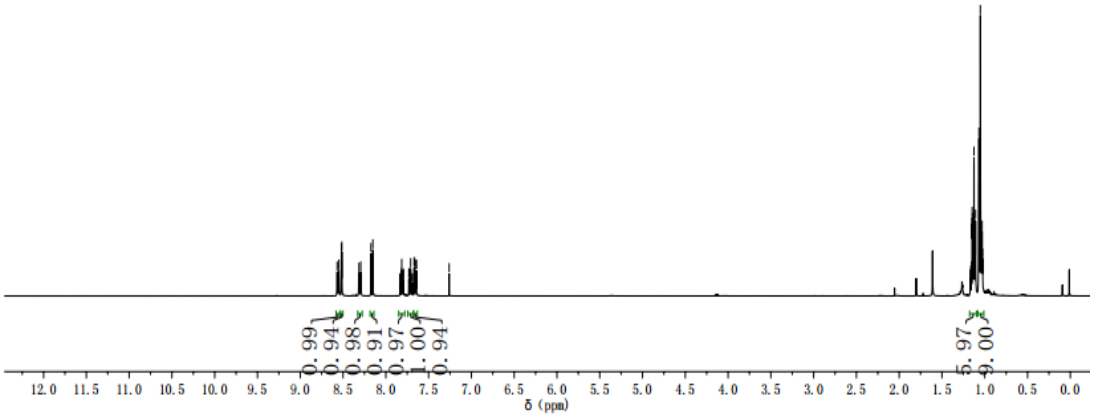


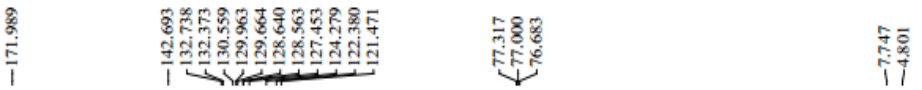


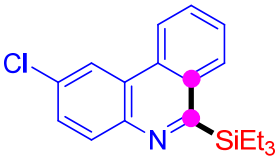
3oa ^{13}C NMR



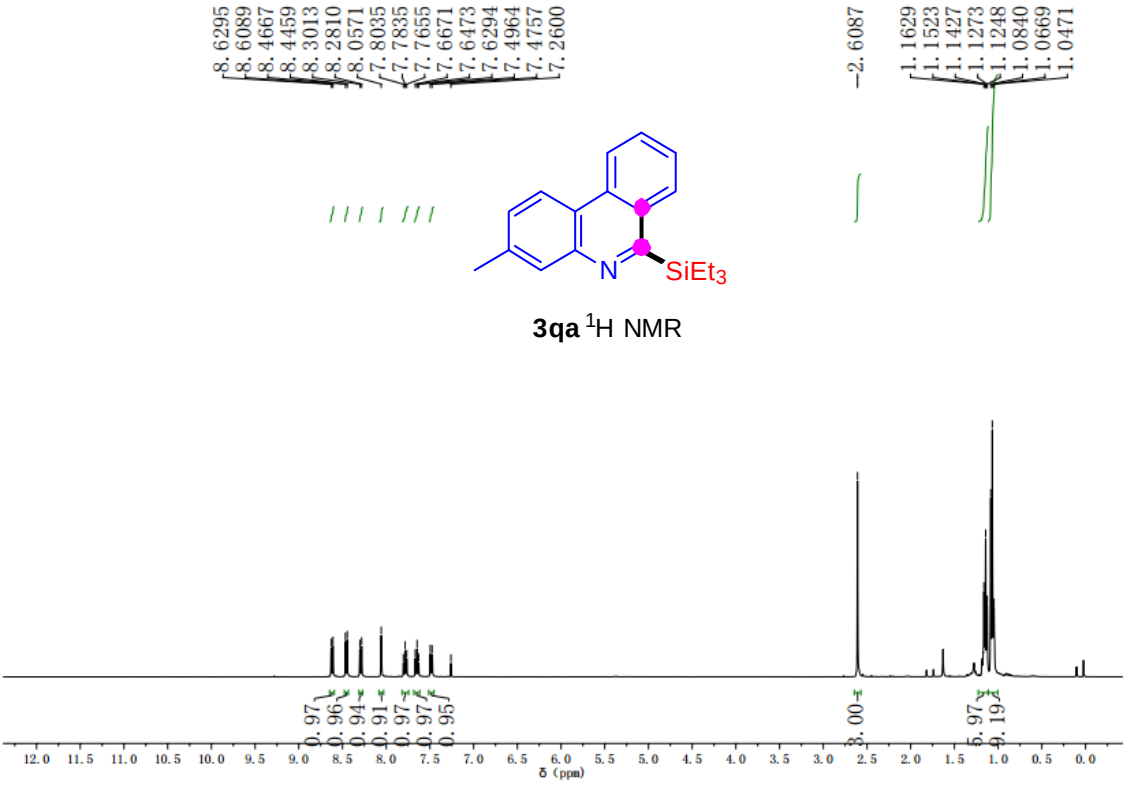
3pa ^{1}H NMR



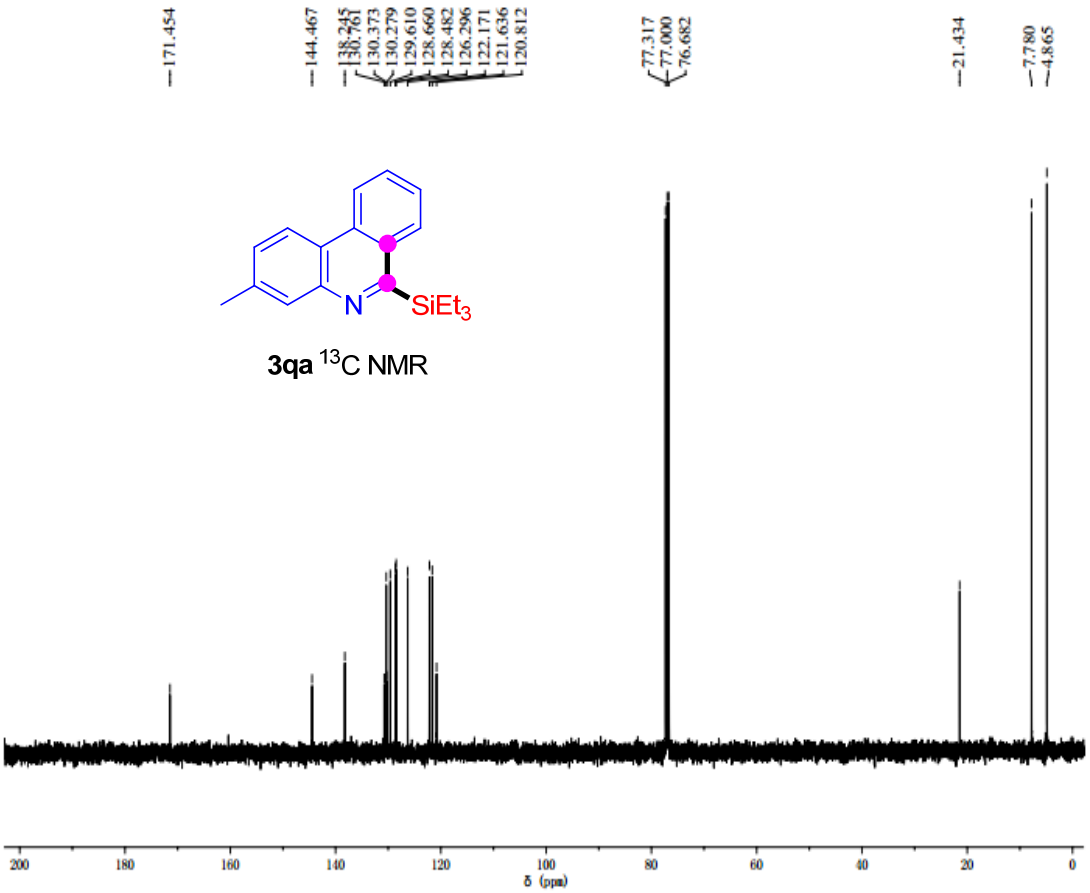




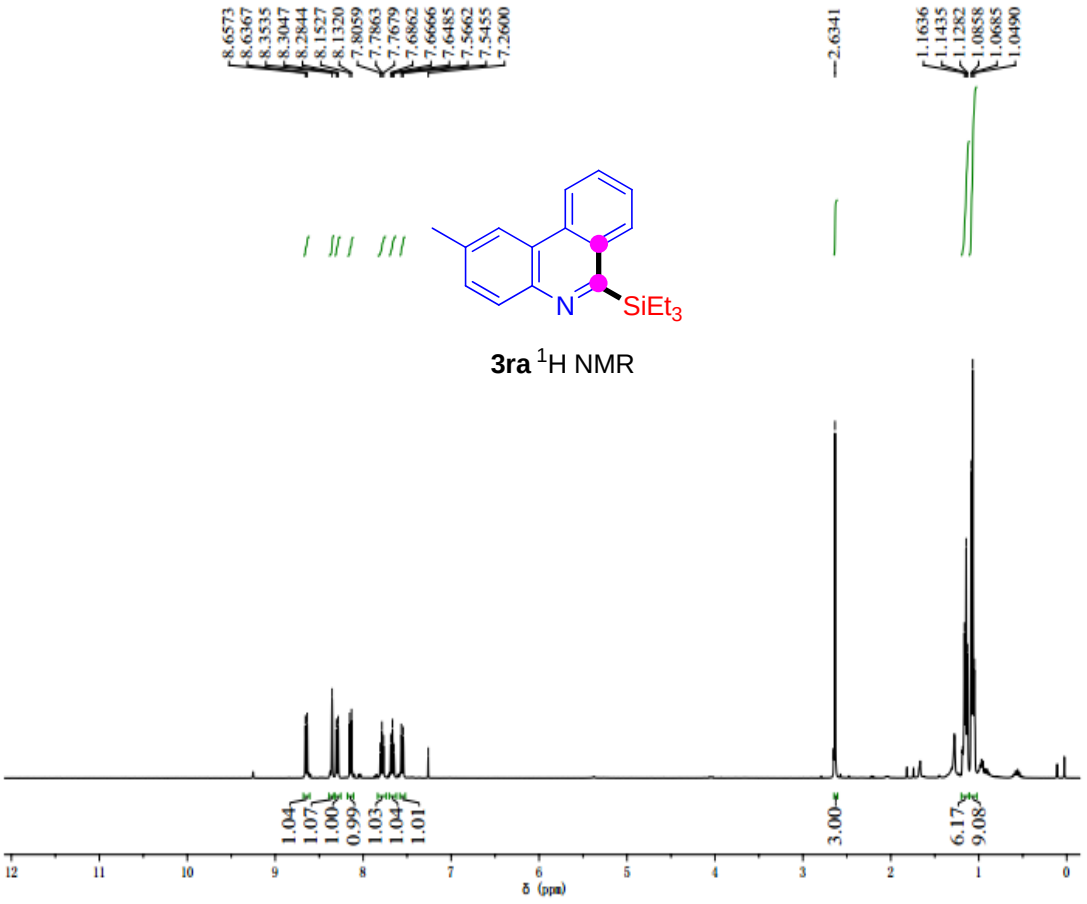
3pa ^{13}C NMR



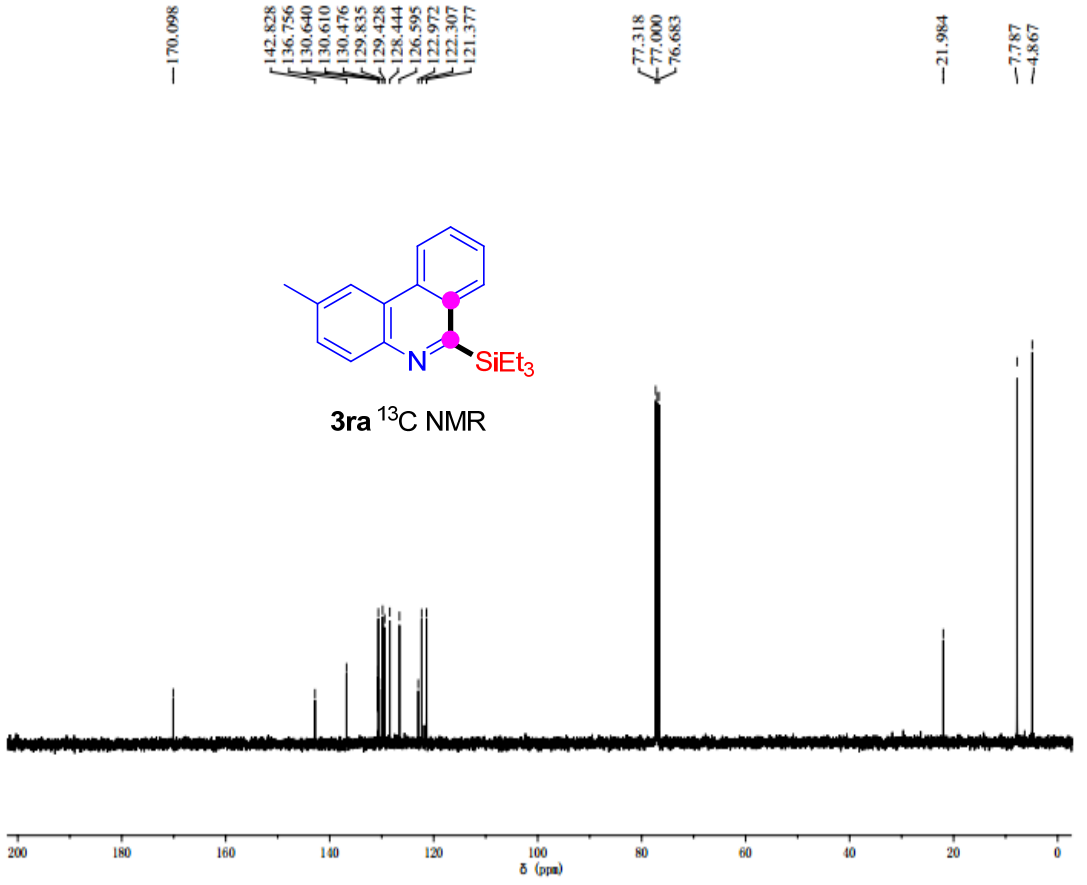
3qa ^{1}H NMR



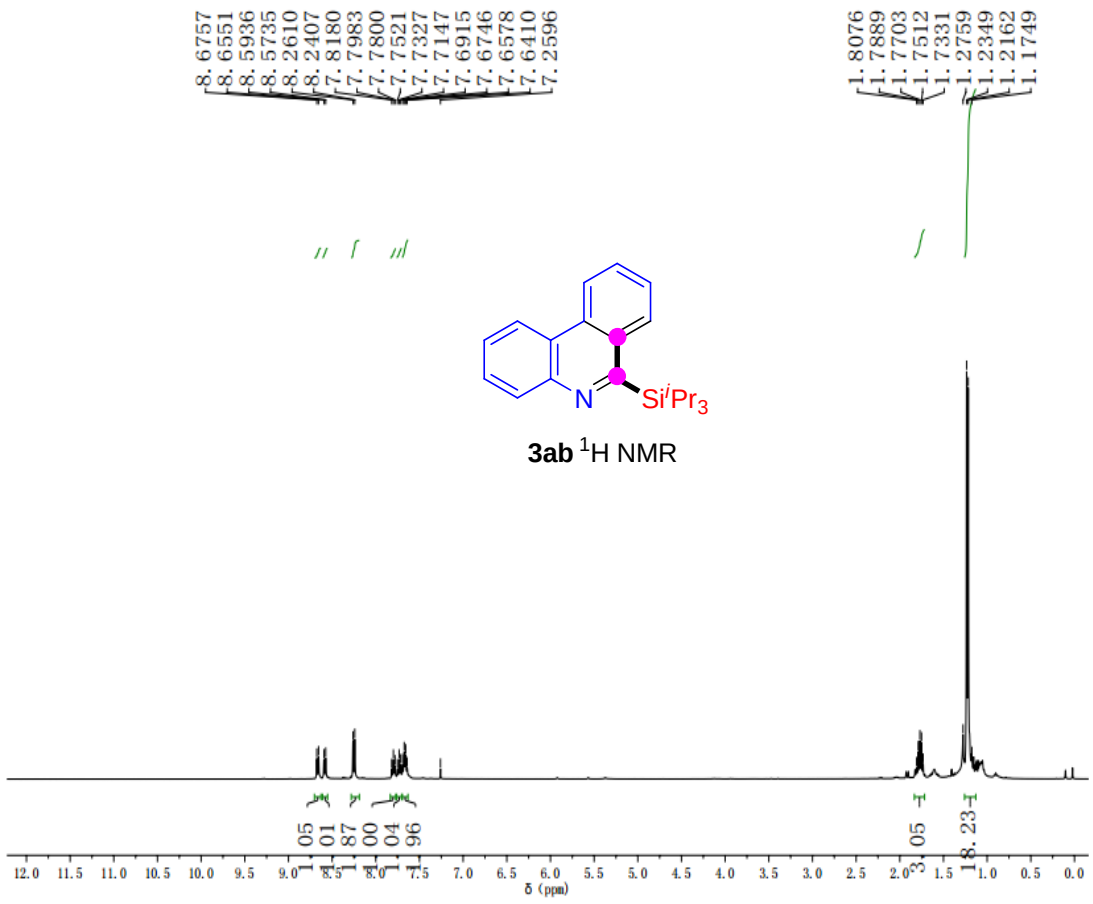
3qa ^{13}C NMR



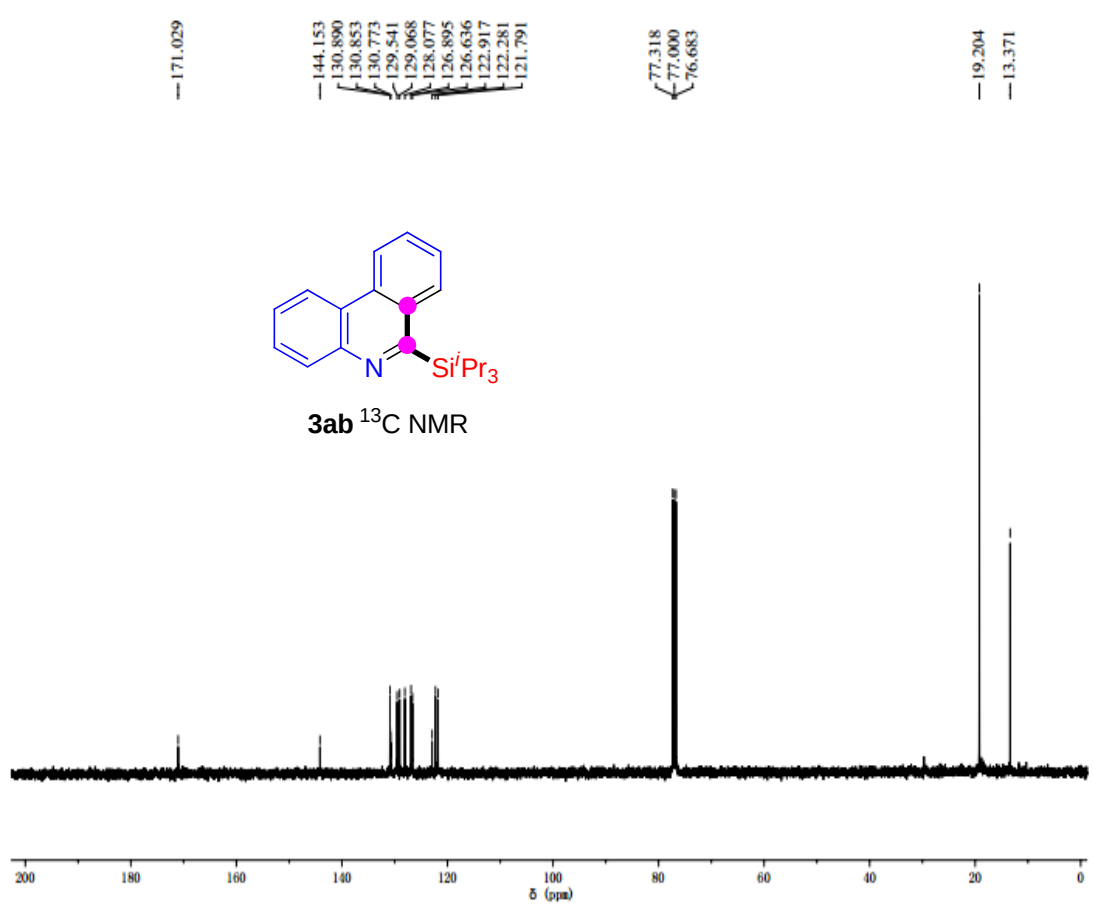
3ra ^{1}H NMR



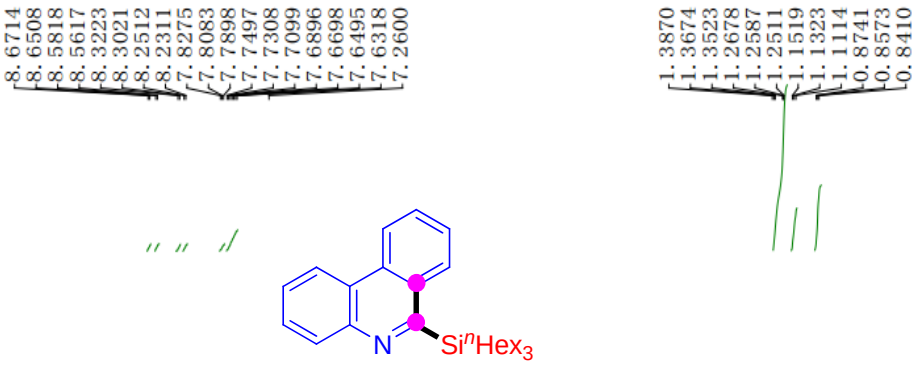
3ra ^{13}C NMR



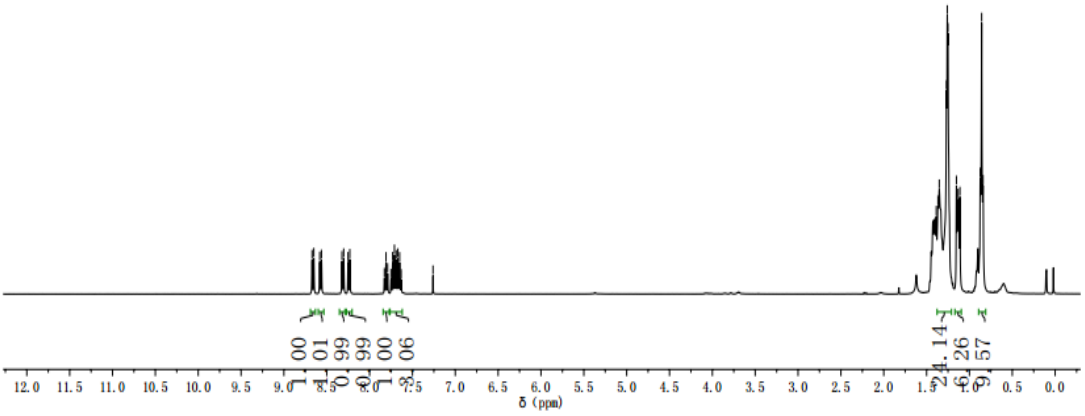
3ab ^{1}H NMR

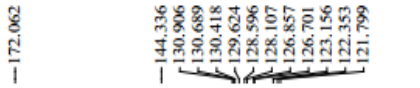


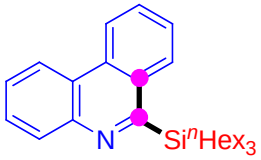
3ab ^{13}C NMR



3ac ^{1}H NMR







3ac ^{13}C NMR