

Metal-free tandem carbene N–H insertions and C–C bond cleavages

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Supporting Information

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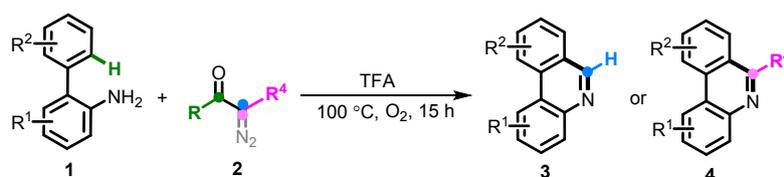
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A. General information:

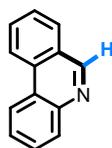
All reagents were used as received unless otherwise noted. DMF, DME and CH₃CN was dried over CaH₂. Toluene, 1,4-dioxane and THF were dried over sodium. Analytical thin-layer chromatography was performed with 0.25 mm coated commercial silica gel plates (TLC Silica Gel 60 F₂₅₄); visualization of the developed chromatogram was performed by fluorescence. Flash Chromatography was performed with silica gel (200-300 mesh). Proton-1 nuclear magnetic resonance (¹H NMR) data were acquired at 400 MHz on a Bruker Ascend 400 (400 MHz) spectrometer, and chemical shifts are reported in delta (δ) units, in parts per million (ppm) downfield from tetramethylsilane. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet, coupling constants *J* are quoted in Hz. Carbon-13 nuclear magnetic resonance (¹³C NMR) data were acquired at 100 MHz on a Bruker Ascend 400 spectrometer, chemical shifts are reported in ppm relative to the center line of a triplet at 77.0 ppm for CDCl₃. Infrared spectra (IR) data were recorded on a TENSOR 27 FT-IR spectrometer and recorded in wave numbers (cm⁻¹). High resolution mass spectra were acquired on a Bruker Daltonics MicroTof-Q II mass spectrometer. (**1a-c**, **i**, **s**, **u**)¹, (**1d-e**, **t**, **r**)², (**1f**, **k-m**, **p**, **v**)³, **1g**⁴, **1h**⁵, **1j**⁶, **1n**⁷, **1o**⁸, **1q**⁹, **1w**¹⁰, **2a**¹¹, **2b**¹², (**2c-e**)¹³, **2f**¹⁴, (**3f**)¹⁵ were prepared according to literature methods.

B. Reaction results:

1)

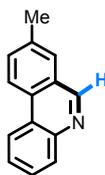


A pressure tube (capacity: 15.0 mL, outside diameter: 26.0 mm, length: 70.0 mm) was charged with 2-arylaniline **1** (0.2 mmol), diazo compound **2** (0.3 mmol) and TFA (1.2 mL). The reaction mixture was stirred at 100 °C for 15 h under O₂ condition. After cooling to room temperature, a saturated aqueous solution (30 mL) of NaHCO₃ was added, followed by an extraction with EtOAc (3 × 10 mL). The combined organic extracts were dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure to yield the crude product, which was further purified by silica gel chromatography to afford the desired product **3** or **4**.



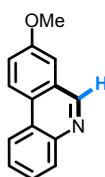
Phenanthridine (**3a**):

White solid (23.3 mg, 65% yield). PE/EA = 10:1, R_f = 0.25. ¹H NMR (400 MHz, CDCl₃): δ 9.33 (s, 1H), 8.67-8.57 (m, 2H), 8.25 (d, *J* = 8.1 Hz, 1H), 8.07 (d, *J* = 7.9 Hz, 1H), 7.89 (t, *J* = 7.7 Hz, 1H), 7.79 (t, *J* = 7.5 Hz, 1H), 7.73 (q, *J* = 7.4 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 153.5, 144.5, 132.6, 131.0, 130.2, 128.7, 128.7, 127.5, 127.1, 126.4, 124.1, 122.2, 121.9. IR (KBr): 3059, 2922, 1630, 1580, 1522, 1449, 1235, 747 cm⁻¹. HRMS (ESI) *m/z* calculated for C₁₃H₁₀N [M+H]⁺ 180.0808, found 180.0808.



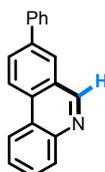
8-Methylphenanthridine (3b):

Pale yellow solid (27.4 mg, 71% yield). PE/EA = 10:1, $R_f = 0.32$. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 9.27 (s, 1H), 8.55 (dd, $J = 19.1, 8.2$ Hz, 2H), 8.22 (d, $J = 8.1$ Hz, 1H), 7.85 (s, 1H), 7.81-7.66 (m, 3H), 2.64 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 153.4, 144.3, 137.5, 132.8, 130.5, 130.1, 128.2, 128.1, 127.0, 126.6, 124.2, 122.0, 121.8, 21.5. IR (KBr): 3063, 2921, 2854, 1628, 1580, 1454, 1236, 750 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{14}\text{H}_{12}\text{N}$ $[\text{M}+\text{H}]^+$ 194.0964, found 194.0958.



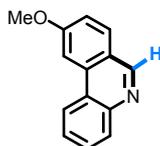
8-Methoxyphenanthridine (3c):

White solid (27.6 mg, 66% yield). PE/EA = 5:1, $R_f = 0.30$. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 9.27 (s, 1H), 8.56 (t, $J = 8.7$ Hz, 2H), 8.25-8.17 (m, 1H), 7.76-7.65 (m, 2H), 7.54 (dd, $J = 9.0, 2.6$ Hz, 1H), 7.43 (d, $J = 2.6$ Hz, 1H), 4.04 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 158.9, 152.8, 143.7, 130.1, 127.8, 127.6, 127.1, 127.0, 124.3, 123.6, 122.0, 121.7, 108.1, 55.6. IR (KBr): 3063, 2933, 2840, 1675, 1619, 1470, 1248, 761 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{14}\text{H}_{12}\text{NO}$ $[\text{M}+\text{H}]^+$ 210.0913, found 210.0913.



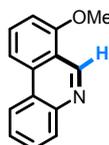
8-Phenylphenanthridine (3d):

Pale yellow solid (26.0 mg, 51% yield). PE/EA = 10:1, $R_f = 0.35$. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 9.38 (s, 1H), 8.68 (d, $J = 8.6$ Hz, 1H), 8.61 (d, $J = 8.0$ Hz, 1H), 8.30-8.22 (m, 2H), 8.13 (dd, $J = 8.6, 1.9$ Hz, 1H), 7.89-7.76 (m, 3H), 7.76-7.69 (m, 1H), 7.57 (t, $J = 7.5$ Hz, 2H), 7.48 (t, $J = 7.4$ Hz, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 153.7, 144.5, 140.4, 140.0, 131.6, 130.2, 129.1, 128.7, 127.9, 127.3, 127.2, 126.8, 126.6, 124.0, 122.5, 122.3. IR (KBr): 3060, 2926, 1580, 1477, 1233, 760, 686 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{19}\text{H}_{14}\text{N}$ $[\text{M}+\text{H}]^+$ 256.1121, found 256.1119.



9-Methoxyphenanthridine (3e):

Yellow solid (20.1 mg, 48% yield). PE/EA = 5:1, $R_f = 0.22$. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 9.20 (s, 1H), 8.52 (d, $J = 7.9$ Hz, 1H), 8.21 (d, $J = 8.2$ Hz, 1H), 7.98 (d, $J = 8.7$ Hz, 1H), 7.94 (d, $J = 2.4$ Hz, 1H), 7.77 (t, $J = 7.6$ Hz, 1H), 7.68 (t, $J = 7.6$ Hz, 1H), 7.33 (d, $J = 6.9$ Hz, 1H), 4.07 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 161.8, 152.7, 144.8, 134.6, 130.5, 130.1, 128.7, 126.5, 123.9, 122.2, 121.5, 117.9, 102.6, 55.6. IR (KBr): 3067, 3008, 2943, 1620, 1457, 1231, 761 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{14}\text{H}_{12}\text{NO}$ $[\text{M}+\text{H}]^+$ 210.0913, found 210.0913.



7-Methoxyphenanthridine (3e'):

Pale yellow solid (10.0 mg, 24% yield). PE/EA = 5:1, $R_f = 0.35$. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 9.79 (s, 1H), 8.59 (d, $J = 8.2$ Hz, 1H), 8.22 (dd, $J = 17.3, 8.2$ Hz, 2H), 7.84-7.75 (m, 2H), 7.70 (t, $J = 7.6$ Hz, 1H), 7.10 (d, $J = 8.0$ Hz, 1H), 4.11 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 157.5, 148.3, 144.7, 134.0, 131.6, 130.1, 128.7, 126.8, 123.8, 122.7, 117.5, 113.8, 106.7, 55.8. IR (KBr): 3060, 2929, 2840, 1614, 1459, 1257, 1017, 756 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{14}\text{H}_{12}\text{NO}$ $[\text{M}+\text{H}]^+$ 210.0913, found 210.0913.



[1,3]Dioxolo[4,5-j]phenanthridine (3f):

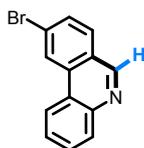
Yellow solid (37.1 mg, 83% yield). PE/EA = 5:1, $R_f = 0.20$. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 9.09 (s, 1H), 8.36 (dd, $J = 8.2, 1.4$ Hz, 1H), 8.17 (dd, $J = 8.2, 1.4$ Hz, 1H), 7.87 (s, 1H), 7.78-7.59 (m, 2H), 6.16 (s, 2H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 151.7, 151.4, 148.1, 144.1, 130.2, 130.0, 127.9, 126.6, 124.2, 123.1, 121.9, 105.4, 101.9, 99.8. IR (KBr): 3066, 2914, 1625, 1493, 1467, 1256, 1035, 755 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{14}\text{H}_{10}\text{NO}_2$ $[\text{M}+\text{H}]^+$ 224.0706, found 224.0706.



9-Fluorophenanthridine (3g):

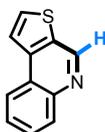
Pale yellow solid (24.5 mg, 62% yield). PE/EA = 10:1, $R_f = 0.23$. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 9.28 (s, 1H), 8.47 (d, $J = 8.1$ Hz, 1H), 8.23 (t, $J = 8.0$ Hz, 2H), 8.09 (dd, $J = 8.7, 5.7$ Hz, 1H), 7.82 (t, $J = 7.0$ Hz, 1H), 7.72 (t, $J = 8.0$ Hz, 1H), 7.47 (td, $J = 8.5, 2.3$ Hz, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 165.4 (d, $J = 250.5$ Hz), 152.6, 144.5, 134.8 (d, $J = 9.6$ Hz), 131.5 (d, $J = 9.7$ Hz), 130.3, 129.4, 127.1, 123.6 (d, $J = 4.0$ Hz), 123.4, 122.4, 116.9 (d, $J = 24.1$ Hz), 107.3 (d, $J = 22.4$ Hz). $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ -105.63 to -105.80 (m, 1F). IR (KBr): 3051, 1622, 1493, 1233, 1186, 900, 750 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{13}\text{H}_9\text{FN}$ $[\text{M}+\text{H}]^+$ 198.0714,

found 198.0714.



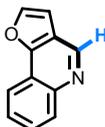
9-Bromophenanthridine (3h):

Pale yellow solid (26.3 mg, 51% yield). PE/EA = 10:1, R_f = 0.22. ^1H NMR (400 MHz, CDCl_3): δ 9.28 (s, 1H), 8.79 (s, 1H), 8.58-8.48 (m, 1H), 8.24 (d, J = 8.2 Hz, 1H), 7.95 (d, J = 8.4 Hz, 1H), 7.88-7.78 (m, 2H), 7.74 (t, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 152.7, 144.6, 133.9, 130.9, 130.2, 129.4, 127.4, 126.0, 124.9, 124.8, 122.8, 122.2. IR (KBr): 3055, 2921, 1612, 1516, 1451, 1269, 816, 766 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{13}\text{H}_9\text{BrN}$ $[\text{M}+\text{H}]^+$ 257.9913, found 257.9912.



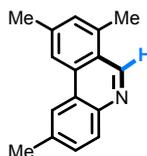
Thieno[2,3-c]quinoline (3i):

Yellow solid (28.2 mg, 76% yield). PE/EA = 10:1, R_f = 0.35. ^1H NMR (400 MHz, CDCl_3): δ 9.35 (s, 1H), 8.30 (dd, J = 15.3, 8.2 Hz, 2H), 8.01 (d, J = 5.3 Hz, 1H), 7.88 (d, J = 5.3 Hz, 1H), 7.72 (dt, J = 30.4, 7.6 Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 145.1, 144.4, 141.6, 133.2, 131.6, 129.9, 128.0, 126.9, 124.4, 123.3, 121.5. IR (KBr): 3060, 1726, 1674, 1562, 1457, 954, 761, 731 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{11}\text{H}_8\text{NS}$ $[\text{M}+\text{H}]^+$ 186.0372, found 186.0372.



Furo[3,2-c]quinoline (3j):

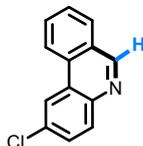
Yellow oil (15.9 mg, 47% yield). PE/EA = 10:1, R_f = 0.15. ^1H NMR (400 MHz, CDCl_3): δ 9.23 (s, 1H), 8.34 (d, J = 8.1 Hz, 1H), 8.27 (d, J = 8.4 Hz, 1H), 7.84 (d, J = 2.0 Hz, 1H), 7.72 (dt, J = 28.0, 7.1 Hz, 2H), 7.04 (d, J = 2.0 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 155.6, 145.8, 145.5, 144.9, 129.7, 128.2, 126.9, 120.1, 120.0, 117.4, 106.1. IR (KBr): 3063, 2925, 1673, 1571, 1504, 1333, 1010, 870, 733 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{11}\text{H}_8\text{NO}$ $[\text{M}+\text{H}]^+$ 170.0600, found 170.0600.



2,7,9-Trimethylphenanthridine (3k):

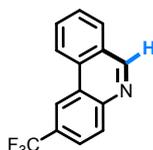
Yellow solid (35.9 mg, 81% yield). PE/EA = 10:1, R_f = 0.26. ^1H NMR (400 MHz, CDCl_3): δ 9.45 (s, 1H), 8.35 (s, 1H), 8.24 (s, 1H), 8.10 (d, J = 8.3 Hz, 1H), 7.57 (d, J = 8.3 Hz, 1H), 7.31 (s,

1H), 2.83 (s, 3H), 2.66 (s, 3H), 2.61 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 149.1, 142.6, 140.7, 136.5, 136.2, 132.7, 130.4, 130.1, 129.6, 124.0, 123.2, 121.9, 119.5, 22.3, 21.9, 18.7. IR (KBr): 3060, 2920, 2857, 1620, 1508, 1449, 1250, 1032, 824, 748 cm⁻¹. HRMS (ESI) m/z calculated for C₁₆H₁₆N [M+H]⁺ 222.1277, found 222.1275.



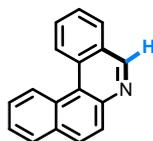
2-Chlorophenanthridine (3l):

Yellow solid (28.2 mg, 66% yield). PE/EA = 10:1, R_f = 0.30. ¹H NMR (400 MHz, CDCl₃): δ 9.28 (s, 1H), 8.52 (dd, *J* = 5.4, 3.0 Hz, 2H), 8.14 (d, *J* = 8.8 Hz, 1H), 8.07 (d, *J* = 7.8 Hz, 1H), 7.90 (t, *J* = 7.9 Hz, 1H), 7.77 (t, *J* = 7.5 Hz, 1H), 7.71 (dd, *J* = 8.7, 2.3 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 153.7, 142.9, 133.0, 131.6, 131.5, 131.3, 129.2, 128.8, 128.2, 126.5, 125.2, 121.9, 121.9. IR (KBr): 3047, 1617, 1484, 1237, 1084, 822, 750 cm⁻¹. HRMS (ESI) m/z calculated for C₁₃H₉ClN [M+H]⁺ 214.0418, found 214.0417.



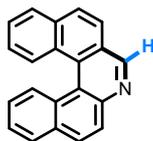
2-(Trifluoromethyl)phenanthridine (3m):

White solid (24.7 mg, 50% yield). PE/EA = 10:1, R_f = 0.33. ¹H NMR (400 MHz, CDCl₃): δ 9.42 (s, 1H), 8.89 (s, 1H), 8.68 (d, *J* = 8.3 Hz, 1H), 8.34 (d, *J* = 8.5 Hz, 1H), 8.15 (d, *J* = 7.9 Hz, 1H), 8.02-7.94 (m, 2H), 7.84 (t, *J* = 7.5 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 155.7, 146.0, 132.3, 131.8, 131.2, 129.1, 128.8, 128.5, 126.7, 124.7 (q, *J* = 3.1 Hz), 123.9, 123.0 (q, *J* = 270.4 Hz), 122.0, 120.1 (q, *J* = 4.2 Hz). ¹⁹F NMR (376 MHz, CDCl₃): δ -61.83 (s, 3F). IR (KBr): 3050, 1621, 1431, 1313, 1165, 1110, 749 cm⁻¹. HRMS (ESI) m/z calculated for C₁₄H₉F₃N [M+H]⁺ 248.0682, found 248.0681.



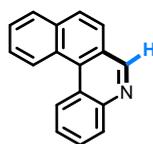
Benzo[a]phenanthridine (3n):

Yellow solid (34.4 mg, 75% yield). PE/EA = 10:1, R_f = 0.30. ¹H NMR (400 MHz, CDCl₃): δ 9.42 (s, 1H), 9.14 (dd, *J* = 8.6, 3.8 Hz, 2H), 8.19 (dd, *J* = 8.4, 6.2 Hz, 2H), 8.12-8.05 (m, 2H), 7.93 (t, *J* = 7.8 Hz, 1H), 7.73 (dt, *J* = 23.0, 7.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 152.9, 144.4, 133.3, 132.7, 130.7, 129.8, 129.6, 128.8, 128.7, 128.4, 127.7, 127.5, 126.7, 126.6, 126.5, 126.4, 120.7. IR (KBr): 3053, 1613, 1573, 1507, 1229, 829, 770 cm⁻¹. HRMS (ESI) m/z calculated for C₁₇H₁₂N [M+H]⁺ 230.0964, found 230.0963.



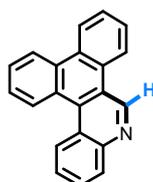
Dibenzo[a,k]phenanthridine (3o):

Yellow solid (34.5 mg, 62% yield). PE/EA = 10:1, $R_f = 0.29$. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 9.37 (s, 1H), 8.69 (d, $J = 8.5$ Hz, 1H), 8.62 (d, $J = 8.5$ Hz, 1H), 8.21 (d, $J = 8.8$ Hz, 1H), 8.13 (d, $J = 8.8$ Hz, 1H), 8.01 (dd, $J = 13.9, 7.6$ Hz, 4H), 7.65 (dt, $J = 24.5, 7.4$ Hz, 2H), 7.44-7.34 (m, 2H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 151.7, 146.2, 134.5, 132.6, 131.2, 130.0, 129.9, 129.1, 129.0, 128.7, 128.7, 128.4, 128.2, 128.0, 127.8, 126.9, 126.4, 125.0, 124.7, 124.4, 121.0. IR (KBr): 3051, 1629, 1569, 1480, 1266, 808, 745 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{21}\text{H}_{14}\text{N}$ $[\text{M}+\text{H}]^+$ 280.1121, found 280.1120.



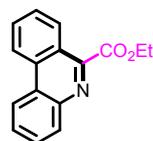
Benzo[k]phenanthridine (3p):

Yellow solid (33.5 mg, 73% yield). PE/EA = 10:1, $R_f = 0.29$. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 9.37 (s, 1H), 9.20 (d, $J = 8.7$ Hz, 1H), 9.10 (d, $J = 8.4$ Hz, 1H), 8.37 (d, $J = 8.1$ Hz, 1H), 8.07 (dd, $J = 7.4, 2.0$ Hz, 1H), 8.01 (d, $J = 8.5$ Hz, 1H), 7.93 (d, $J = 8.5$ Hz, 1H), 7.86-7.81 (m, 1H), 7.81-7.71 (m, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 152.6, 146.7, 135.2, 131.1, 130.3, 129.0, 128.9, 128.7, 128.2, 128.1, 127.8, 127.0, 126.9, 126.8, 125.2, 125.0, 124.6. IR (KBr): 3053, 1590, 1490, 1384, 1221, 943, 814, 755 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{17}\text{H}_{12}\text{N}$ $[\text{M}+\text{H}]^+$ 230.0964, found 230.0963.



Dibenzo[i,k]phenanthridine (3q):

Pale yellow solid (44.1 mg, 79% yield). PE/EA = 10:1, $R_f = 0.29$. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 10.12 (s, 1H), 8.92 (dd, $J = 24.5, 8.3$ Hz, 2H), 8.81-8.67 (m, 3H), 8.41-8.28 (m, 1H), 7.91-7.61 (m, 6H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 147.1, 146.9, 132.3, 132.0, 130.0, 129.8, 129.5, 128.5, 128.3, 128.2, 127.9, 127.7, 127.6, 127.4, 126.6, 126.6, 124.0, 123.6, 123.2, 122.8, 121.8. IR (KBr): 3068, 1639, 1575, 1379, 1262, 750, 723 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{21}\text{H}_{14}\text{N}$ $[\text{M}+\text{H}]^+$ 280.1121, found 280.1120.



Ethyl phenanthridine-6-carboxylate (4a):

Pale yellow oil (38.2 mg, 76% yield). PE/EA = 20:1, $R_f = 0.21$. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.64 (d, $J = 8.3$ Hz, 1H), 8.59-8.51 (m, 2H), 8.29 (d, $J = 7.6$ Hz, 1H), 7.86 (t, $J = 7.2$ Hz, 1H), 7.80-7.67 (m, 3H), 4.64 (q, $J = 7.1$ Hz, 2H), 1.53 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 166.3, 151.1, 142.6, 133.3, 131.1, 130.8, 128.9, 128.5, 127.8, 127.2, 124.7, 123.3, 122.1, 121.1, 62.3, 14.3. IR (KBr): 3071, 2982, 2850, 1726, 1244, 1192, 1027, 760, 727 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{16}\text{H}_{14}\text{NO}_2$ $[\text{M}+\text{H}]^+$ 252.1019, found 252.1019.



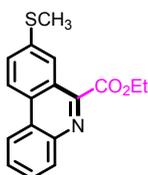
Ethyl 8-methylphenanthridine-6-carboxylate (4b):

White solid (38.2 mg, 72% yield). PE/EA = 20:1, $R_f = 0.22$. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.55 (d, $J = 8.5$ Hz, 2H), 8.30 (s, 1H), 8.29-8.24 (m, 1H), 7.82-7.64 (m, 3H), 4.64 (q, $J = 7.1$ Hz, 2H), 2.60 (s, 3H), 1.54 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 166.4, 150.8, 142.3, 137.9, 132.9, 131.2, 130.7, 128.5, 128.4, 126.4, 124.8, 123.4, 122.0, 121.8, 62.2, 21.8, 14.3. IR (KBr): 3051, 2981, 2851, 1725, 1247, 1171, 1035, 763, 725 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{17}\text{H}_{16}\text{NO}_2$ $[\text{M}+\text{H}]^+$ 266.1176, found 266.1174.



Ethyl 8-methoxyphenanthridine-6-carboxylate (4c):

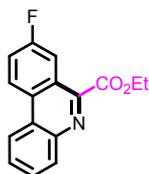
White solid (37.7 mg, 67% yield). PE/EA = 20:1, $R_f = 0.20$. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.56 (d, $J = 9.1$ Hz, 1H), 8.51-8.47 (m, 1H), 8.29-8.24 (m, 1H), 8.03 (d, $J = 2.6$ Hz, 1H), 7.73-7.70 (m, 2H), 7.50 (dd, $J = 9.1, 2.6$ Hz, 1H), 4.64 (q, $J = 7.1$ Hz, 2H), 3.99 (s, 3H), 1.55 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 166.3, 159.0, 149.5, 141.8, 130.9, 128.7, 128.0, 128.0, 125.1, 124.9, 123.7, 122.3, 121.5, 106.7, 62.2, 55.5, 14.3. IR (KBr): 3060, 2980, 2838, 1722, 1617, 1247, 1175, 1105, 763 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{17}\text{H}_{16}\text{NO}_3$ $[\text{M}+\text{H}]^+$ 282.1125, found 282.1124.



Ethyl 8-(methylthio)phenanthridine-6-carboxylate (4d):

Yellow solid (31.5 mg, 53% yield). PE/EA = 10:1, $R_f = 0.20$. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.42 (d, $J = 8.4$ Hz, 2H), 8.34 (s, 1H), 8.25 (d, $J = 8.0$ Hz, 1H), 7.80-7.58 (m, 3H), 4.65 (q, $J = 7.1$ Hz, 2H), 2.61 (s, 3H), 1.55 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 166.2, 149.5, 142.2, 139.4, 130.9, 130.6, 129.8, 128.8, 128.7, 124.8, 124.0, 122.4, 122.2, 121.7, 62.4, 15.4, 14.4.

IR (KBr): 3068, 2982, 2925, 1723, 1465, 1243, 1180, 1096, 763 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{17}\text{H}_{16}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$ 298.0896, found 298.0897.



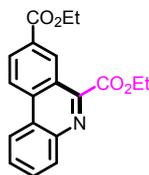
Ethyl 8-fluorophenanthridine-6-carboxylate (4e):

Pale red solid (24.8 mg, 46% yield). PE/EA = 20:1, R_f = 0.30. ^1H NMR (400 MHz, CDCl_3): δ 8.63 (dd, J = 9.2, 5.3 Hz, 1H), 8.57-8.47 (m, 1H), 8.43-8.24 (m, 2H), 7.79-7.73 (m, 2H), 7.65-7.60 (m, 1H), 4.65 (q, J = 7.1 Hz, 2H), 1.55 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 165.9, 160.3 (d, J = 247.4 Hz), 149.5 (d, J = 4.3 Hz), 142.3, 131.2, 130.2 (d, J = 1.7 Hz), 129.0 (d, J = 20.4 Hz), 124.8 (d, J = 8.9 Hz), 124.7 (d, J = 8.5 Hz), 124.6, 121.8, 120.4 (d, J = 20.4 Hz), 112.0 (d, J = 23.0 Hz), 62.6, 14.4. ^{19}F NMR (376 MHz, CDCl_3): δ -110.58 to -110.84 (m, 1F). IR (KBr): 3068, 2984, 2902, 1723, 1243, 1169, 1032, 764 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{16}\text{H}_{12}\text{FNNO}_2$ $[\text{M}+\text{Na}]^+$ 292.0744, found 292.0742.



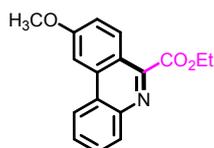
Ethyl 8-bromophenanthridine-6-carboxylate (4f):

White solid (21.8 mg, 33% yield). PE/EA = 20:1, R_f = 0.31. ^1H NMR (400 MHz, CDCl_3): δ 8.75 (d, J = 2.0 Hz, 1H), 8.51-8.36 (m, 2H), 8.35-8.20 (m, 1H), 7.89 (dd, J = 8.8, 2.1 Hz, 1H), 7.80-7.69 (m, 2H), 4.65 (q, J = 7.2 Hz, 2H), 1.55 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 165.7, 149.3, 142.5, 134.3, 132.0, 131.1, 129.8, 129.4, 129.1, 124.6, 124.3, 123.9, 122.1, 121.8, 62.6, 14.4. IR (KBr): 3071, 2982, 1721, 1244, 1179, 1033, 762 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{16}\text{H}_{12}\text{BrNNaO}_2$ $[\text{M}+\text{Na}]^+$ 351.9944, found 351.9942.



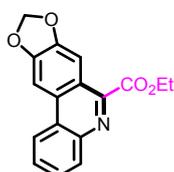
Diethyl phenanthridine-6,8-dicarboxylate (4g):

White solid (26.5 mg, 41% yield). PE/EA = 10:1, R_f = 0.20. ^1H NMR (400 MHz, CDCl_3): δ 9.28 (d, J = 1.6 Hz, 1H), 8.72 (d, J = 8.7 Hz, 1H), 8.63 (d, J = 8.1 Hz, 1H), 8.50 (dd, J = 8.7, 1.7 Hz, 1H), 8.33 (d, J = 8.0 Hz, 1H), 7.88-7.76 (m, 2H), 4.70 (q, J = 7.1 Hz, 2H), 4.51 (q, J = 7.1 Hz, 2H), 1.59 (t, J = 7.1 Hz, 3H), 1.49 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 165.9, 165.8, 151.4, 143.5, 136.2, 131.1, 130.9, 130.1, 129.6, 129.0, 124.2, 122.9, 122.6, 122.5, 62.6, 61.6, 14.4, 14.4. IR (KBr): 3061, 2983, 1721, 1262, 1180, 1031, 751 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{19}\text{H}_{17}\text{NNaO}_4$ $[\text{M}+\text{Na}]^+$ 346.1050, found 346.1049.



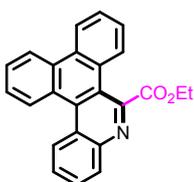
Ethyl 9-methoxyphenanthridine-6-carboxylate (4h):

Yellow solid (32.1 mg, 57% yield). PE/EA = 5:1, $R_f = 0.26$. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.49 (d, $J = 9.2$ Hz, 2H), 8.27 (d, $J = 8.1$ Hz, 1H), 7.93 (d, $J = 2.5$ Hz, 1H), 7.85-7.67 (m, 2H), 7.32 (dd, $J = 9.2, 2.5$ Hz, 1H), 4.64 (q, $J = 7.1$ Hz, 2H), 4.05 (s, 3H), 1.54 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 166.5, 161.6, 150.5, 143.1, 135.8, 130.9, 129.3, 129.1, 128.0, 124.6, 122.0, 118.5, 118.3, 102.7, 62.3, 55.6, 14.4. IR (KBr): 3069, 2980, 2839, 1726, 1615, 1243, 1192, 1022, 764 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{17}\text{H}_{15}\text{NNaO}_3$ $[\text{M}+\text{Na}]^+$ 304.0944, found 304.0943.



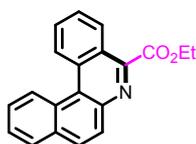
Ethyl [1,3]dioxolo[4,5-j]phenanthridine-6-carboxylate (4i):

Yellow solid (29.5 mg, 50% yield). PE/EA = 5:1, $R_f = 0.26$. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.38 (d, $J = 7.9$ Hz, 1H), 8.25 (d, $J = 8.4$ Hz, 1H), 7.94 (d, $J = 9.6$ Hz, 2H), 7.80-7.63 (m, 2H), 6.19 (s, 2H), 4.64 (q, $J = 7.1$ Hz, 2H), 1.55 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 166.5, 151.5, 149.2, 148.6, 142.4, 131.7, 130.8, 128.4, 128.2, 125.0, 121.9, 120.3, 104.4, 102.2, 100.0, 62.4, 14.4. IR (KBr): 3068, 2982, 1721, 1497, 1254, 1033, 764 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{17}\text{H}_{13}\text{NNaO}_4$ $[\text{M}+\text{Na}]^+$ 318.0737, found 318.0736.



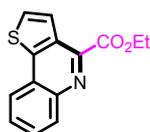
Ethyl dibenzo[i,k]phenanthridine-5-carboxylate (4j):

Yellow solid (51.3 mg, 73% yield). PE/EA = 10:1, $R_f = 0.19$. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.82-8.57 (m, 4H), 8.34 (d, $J = 8.3$ Hz, 1H), 8.22 (d, $J = 8.2$ Hz, 1H), 7.85-7.69 (m, 2H), 7.72-7.55 (m, 4H), 4.55 (q, $J = 7.2$ Hz, 2H), 1.36 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 169.0, 149.6, 145.1, 135.1, 132.5, 130.3, 129.8, 129.7, 129.0, 128.9, 127.7, 127.7, 127.6, 127.6, 127.3, 127.3, 127.0, 126.5, 123.8, 123.4, 120.1, 62.5, 13.9. IR (KBr): 3071, 2981, 1732, 1233, 1190, 1134, 1093, 765, 730 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{24}\text{H}_{17}\text{NNaO}_2$ $[\text{M}+\text{Na}]^+$ 374.1151, found 374.1149.



Ethyl benzo[a]phenanthridine-5-carboxylate (4k):

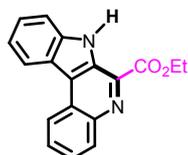
Yellow oil (39.8 mg, 66% yield). PE/EA = 20:1, $R_f = 0.31$. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 9.04 (d, $J = 8.8$ Hz, 1H), 8.97 (d, $J = 7.6$ Hz, 1H), 8.67 (d, $J = 7.6$ Hz, 1H), 8.17 (d, $J = 8.8$ Hz, 1H), 8.09-7.96 (m, 2H), 7.86 (t, $J = 8.5$ Hz, 1H), 7.75-7.70 (m, 1H), 7.70-7.62 (m, 2H), 4.67 (q, $J = 7.1$ Hz, 2H), 1.55 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 166.3, 149.7, 142.4, 133.8, 133.4, 130.6, 129.9, 129.0, 128.7, 128.3, 127.9, 127.2, 127.0, 126.8, 126.8, 126.7, 124.8, 122.1, 62.3, 14.3. IR (KBr): 3071, 2981, 1732, 1233, 1190, 1134, 1093, 765. 730 cm^{-1} . IR (KBr): 3057, 2983, 2931, 1724, 1265, 1193, 1031, 869, 749 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{20}\text{H}_{15}\text{NNaO}_2$ $[\text{M}+\text{Na}]^+$ 324.0995, found 324.0994.

**Ethyl thieno[3,2-c]quinoline-4-carboxylate (4l):**

Yellow solid (21.6 mg, 42% yield). PE/EA = 10:1, $R_f = 0.20$. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.39 (dd, $J = 8.4, 1.3$ Hz, 1H), 8.31 (d, $J = 5.4$ Hz, 1H), 8.13 (dd, $J = 8.1, 1.5$ Hz, 1H), 7.82-7.58 (m, 3H), 4.64 (q, $J = 7.2$ Hz, 2H), 1.56 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 165.5, 147.5, 143.9, 142.7, 132.1, 131.4, 129.0, 129.0, 126.8, 125.6, 125.3, 123.2, 62.4, 14.4. IR (KBr): 3064, 2987, 2923, 1713, 1301, 1241, 815, 754 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{14}\text{H}_{11}\text{NNaSO}_2$ $[\text{M}+\text{Na}]^+$ 280.0403, found 280.0401.

**Ethyl thieno[2,3-c]quinoline-4-carboxylate (4m):**

Yellow solid (30.9 mg, 60% yield). PE/EA = 10:1, $R_f = 0.22$. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.42 (d, $J = 7.6$ Hz, 1H), 8.30 (d, $J = 8.0$ Hz, 1H), 8.02-7.94 (m, 2H), 7.80-7.70 (m, 2H), 4.67 (q, $J = 8.0$ Hz, 2H), 1.57 (t, $J = 7.2$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 165.3, 143.9, 143.8, 142.2, 134.9, 131.7, 131.1, 128.8, 128.5, 125.2, 123.2, 120.7, 62.8, 14.3. IR (KBr): 3060, 2983, 1708, 1412, 1242, 1139, 770, 732 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{14}\text{H}_{11}\text{NNaSO}_2$ $[\text{M}+\text{Na}]^+$ 280.0403, found 280.0402.

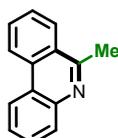
**Ethyl 7H-indolo[2,3-c]quinoline-6-carboxylate (4n):**

Yellow solid (31.9 mg, 55% yield). PE/EA = 5:1, $R_f = 0.23$. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 10.23 (s, 1H), 8.59 (d, $J = 8.2$ Hz, 1H), 8.42 (t, $J = 8.0$ Hz, 2H), 7.78-7.49 (m, 4H), 7.38-7.33 (m, 1H), 4.66 (q, $J = 7.1$ Hz, 2H), 1.56 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 166.6, 141.9, 139.3, 133.3, 132.5, 131.7, 128.9, 127.6, 126.1, 123.7, 123.1, 122.9, 121.5, 120.8, 112.2, 62.4, 14.4. IR (KBr): 3057, 2981, 2931, 1699, 1317, 1192, 1095, 698 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{18}\text{H}_{14}\text{N}_2\text{NaO}_2$ $[\text{M}+\text{Na}]^+$ 313.0947, found 313.0947.



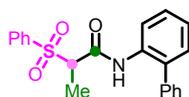
Methyl phenanthridine-6-carboxylate (4o):

White solid (31.8 mg, 67% yield). PE/EA = 10:1, $R_f = 0.21$. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.72-8.48 (m, 3H), 8.36-8.19 (m, 1H), 7.88 (t, $J = 8.3$ Hz, 1H), 7.80-7.70 (m, 3H), 4.15 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 166.5, 150.4, 142.6, 133.5, 131.2, 131.0, 129.1, 128.7, 128.0, 127.4, 125.0, 123.6, 122.2, 122.1, 53.2. IR (KBr): 3063, 3032, 2955, 1715, 1442, 1250, 1200, 741, 715 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{15}\text{H}_{11}\text{NNaO}_2$ $[\text{M}+\text{Na}]^+$ 260.0682, found 260.0682.



6-Methylphenanthridine (5):

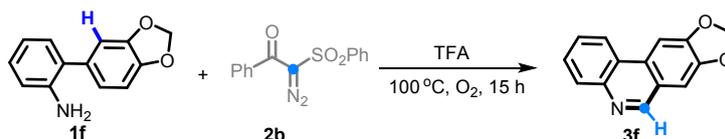
Pale yellow oil (7.2 mg, 18% yield). PE/EA = 10:1, $R_f = 0.21$. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.67 (d, $J = 8.3$ Hz, 1H), 8.58 (d, $J = 8.1$ Hz, 1H), 8.26 (d, $J = 8.2$ Hz, 1H), 8.16 (d, $J = 8.1$ Hz, 1H), 7.88 (t, $J = 7.6$ Hz, 1H), 7.75 (q, $J = 7.2$ Hz, 2H), 7.66 (t, $J = 7.6$ Hz, 1H), 3.09 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 158.8, 143.7, 132.6, 130.5, 129.4, 128.6, 127.3, 126.5, 126.3, 125.9, 123.8, 122.3, 121.9, 23.3. IR (KBr): 3067, 2920, 1580, 1484, 1376, 1034, 755, 720 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{14}\text{H}_{12}\text{N}$ $[\text{M}+\text{H}]^+$ 194.0964, found 194.0964.



N-([1,1'-biphenyl]-2-yl)-2-(phenylsulfonyl)propanamide (6):

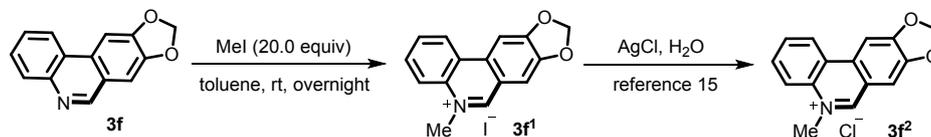
Yellow oil. PE/EA = 5:1, $R_f = 0.32$. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.29 (s, 1H), 8.16 (d, $J = 8.2$ Hz, 1H), 7.79 (d, $J = 7.6$ Hz, 2H), 7.71 (t, $J = 7.4$ Hz, 1H), 7.57 (q, $J = 7.1$ Hz, 4H), 7.51 (d, $J = 7.3$ Hz, 1H), 7.49-7.44 (m, 2H), 7.40 (t, $J = 7.8$ Hz, 1H), 7.35 (d, $J = 7.5$ Hz, 1H), 7.27 (t, $J = 7.4$ Hz, 1H), 3.88 (q, $J = 7.1$ Hz, 1H), 1.52 (d, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 162.5, 137.7, 136.2, 134.4, 134.2, 133.4, 130.3, 129.4, 129.2, 129.2, 129.1, 128.4, 128.2, 125.1, 121.6, 66.9, 11.9. IR (KBr): 3059, 1689, 1525, 1445, 1314, 1267, 1144, 741, 725 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{21}\text{H}_{20}\text{NO}_3\text{S}$ $[\text{M}+\text{H}]^+$ 366.1158, found 366.1159.

C. Synthetic transformation of products:

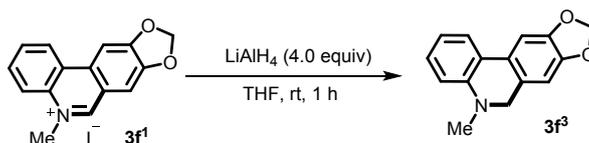


A pressure tube (capacity: 75.0 mL, outside diameter: 46.0 mm, length: 90.0 mm) was charged with 2-arylaniline **1f** (426.5 mg, 2.0 mmol), diazo compound **2b** (858.9 mg, 3.0 mmol) and TFA (12.0 mL). The reaction mixture was stirred at 100 °C for 15 h under O_2 condition. After cooling to room temperature, a saturated aqueous solution of NaHCO_3 was added, followed by an

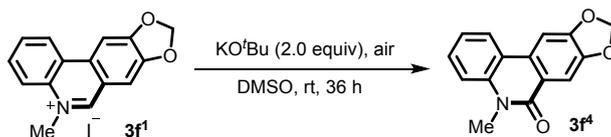
extraction with EtOAc (3 × 20 mL). The combined organic extracts were dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure to yield the crude product, which was further purified by silica gel chromatography to afford the desired product **3f** (334.7 mg, 75% yield).



A 50 mL reaction flask was charged with Trisphaeridine **3f** (223.2 mg, 1.0 mmol), MeI (methyl iodide, 2838.8 mg, 20.0 mmol) and toluene (20.0 mL). The reaction mixture was stirred at room temperature for 18 h, then filtered by funnel, and the solid residue was washed by CH₂Cl₂ to afford **3f¹** as a yellow solid (193.5 mg, 81% yield). ¹H NMR (400 MHz, DMSO-*d*₆): δ 9.92 (s, 1H), 9.07 (d, *J* = 8.3 Hz, 1H), 8.66 (s, 1H), 8.48 (d, *J* = 8.6 Hz, 1H), 8.13 (t, *J* = 7.8 Hz, 1H), 8.06 (t, *J* = 7.6 Hz, 1H), 7.92 (s, 1H), 6.52 (s, 2H), 4.62 (s, 3H). ¹³C NMR (100 MHz, DMSO-*d*₆): δ 157.7, 152.3, 150.5, 134.9, 134.1, 132.0, 130.0, 125.4, 125.3, 120.9, 120.1, 107.6, 104.7, 101.8, 45.8. IR (KBr): 3065, 2921, 2851, 1638, 1465, 1267, 1195, 742, 626 cm⁻¹. HRMS (ESI) *m/z* calculated for C₁₅H₁₂NO₂ [M-I]⁺ 238.0863, found 238.0862.



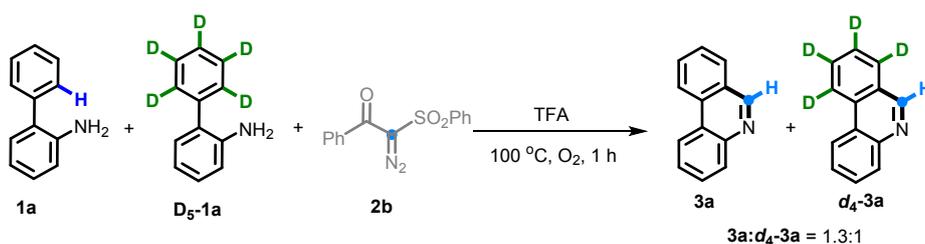
A pressure tube (capacity: 15.0 mL, outside diameter: 26.0 mm, length: 70.0 mm) was charged with 5-methyl-[1,3]dioxolo[4,5-j]phenanthridin-5-ium iodide **3f¹** (73.0 mg, 0.2 mmol) and THF (2.0 mL), LiAlH₄ (30.4 mg, 0.8 mmol) was then slowly added into the solution. The reaction mixture was stirred at room temperature for 1 h, then added ethyl acetate to quench the excess LiAlH₄, filtered through a thin Celite pad, and concentrated under reduced pressure to yield the crude product, which was further purified by silica gel chromatography to afford the desired product **3f³** as a yellow solid (37.3 mg, 78% yield). PE/EA = 50:1, R_f = 0.35. ¹H NMR (400 MHz, CDCl₃): δ 7.60 (d, *J* = 8.5 Hz, 1H), 7.30-7.21 (m, 2H), 6.92 (t, *J* = 7.5 Hz, 1H), 6.79 (d, *J* = 8.1 Hz, 1H), 6.68 (s, 1H), 6.01 (s, 2H), 4.14 (s, 2H), 2.96 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 147.6, 146.8, 146.5, 128.4, 127.2, 126.3, 123.7, 123.0, 118.7, 112.2, 106.1, 103.2, 101.0, 55.1, 38.6. IR (KBr): 3060, 2961, 2855, 1635, 1589, 1459, 1394, 1061, 1028, 740 cm⁻¹. HRMS (ESI) *m/z* calculated for C₁₅H₁₄NO₂ [M+H]⁺ 240.1019, found 240.1016.



A 10 mL reaction flask was charged with 5-methyl-[1,3]dioxolo[4,5-j]phenanthridin-5-ium iodide **3f¹** (73.0 mg, 0.2 mmol), *t*-BuOK (44.9 mg, 0.4 mmol) and DMSO (1.0 mL). The reaction mixture was stirred at room temperature for 38 h under air. Then it was diluted with EtOAc (10.0 mL) and water (10.0 mL) and extracted with EtOAc (10 mL × 3). The combined organic extracts

were dried over anhydrous MgSO_4 , filtered and concentrated under reduced pressure to yield the crude product, which was further purified by silica gel chromatography to afford the desired product **3f** as a white solid (40.5 mg, 80% yield). PE/EA = 10:1, $R_f = 0.28$. ^1H NMR (400 MHz, CDCl_3): δ 8.11 (d, $J = 8.0$ Hz, 1H), 7.94 (s, 1H), 7.63 (s, 1H), 7.54 (t, $J = 7.7$ Hz, 1H), 7.42 (d, $J = 8.4$ Hz, 1H), 7.37-7.30 (m, 1H), 6.16 (s, 2H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 161.0, 152.2, 148.4, 137.5, 130.4, 128.9, 122.9, 122.3, 121.3, 119.2, 115.0, 107.0, 101.9, 100.4, 30.0. IR (KBr): 3065, 2911, 1640, 1459, 1397, 1250, 1031, 931, 741 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{15}\text{H}_{12}\text{NO}_3$ $[\text{M}+\text{H}]^+$ 254.0812, found 254.0810.

D. Mechanistic studies:



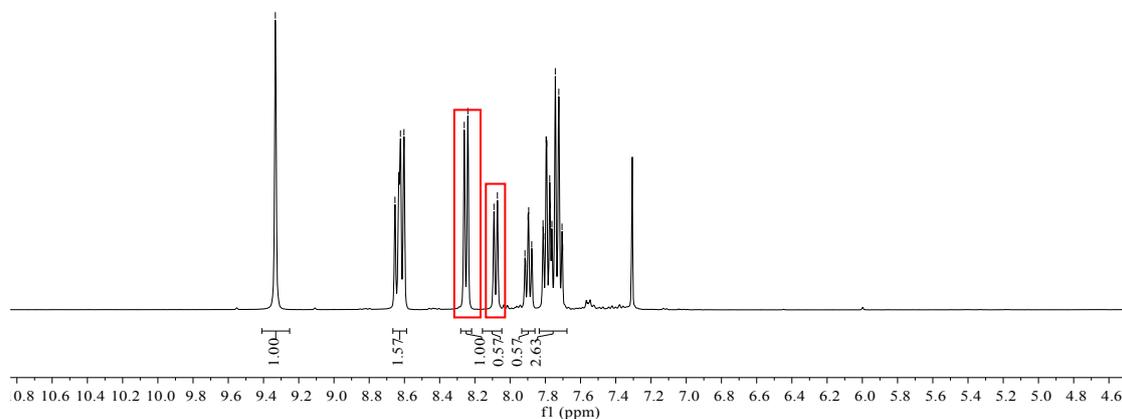
A pressure tube (capacity: 15.0 mL, outside diameter: 26.0 mm, length: 70.0 mm) was charged with 2-arylaniline **1a** (16.9 mg, 0.1 mmol), **D₅-1a** (17.4 mg, 0.1 mmol), diazo compound **2b** (85.9 mg, 0.3 mmol) and TFA (1.2 mL). The reaction mixture was stirred at 100 °C for 1 h under O_2 condition. After cooling to room temperature, a saturated aqueous solution (30 mL) of NaHCO_3 was added, followed by an extraction with EtOAc (3×10 mL). The combined organic extracts were dried over anhydrous MgSO_4 , filtered and concentrated under reduced pressure to yield the crude product, which was further purified by silica gel chromatography to afford the desired product **3a** and **d₄-3a** (15.0 mg, 41% yield).

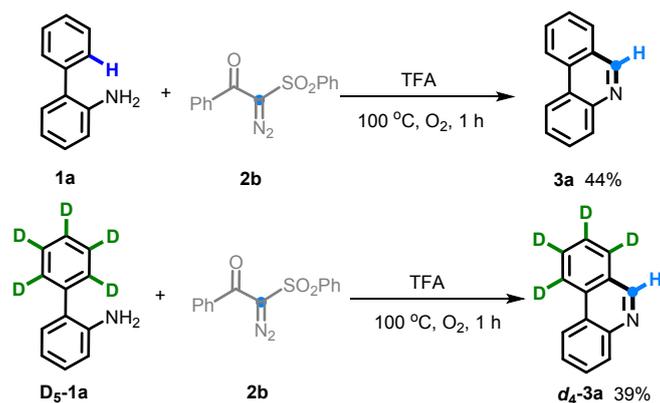


$$n(\text{H}) = 0.57$$

$$n(\text{D}) = 0.43$$

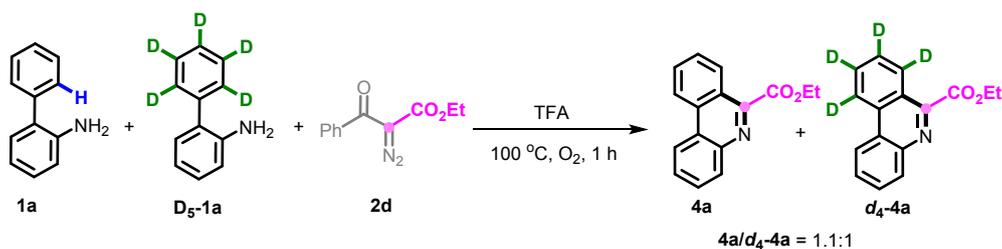
$$\text{KIE} = k_{\text{H}}/k_{\text{D}} = 1.3$$



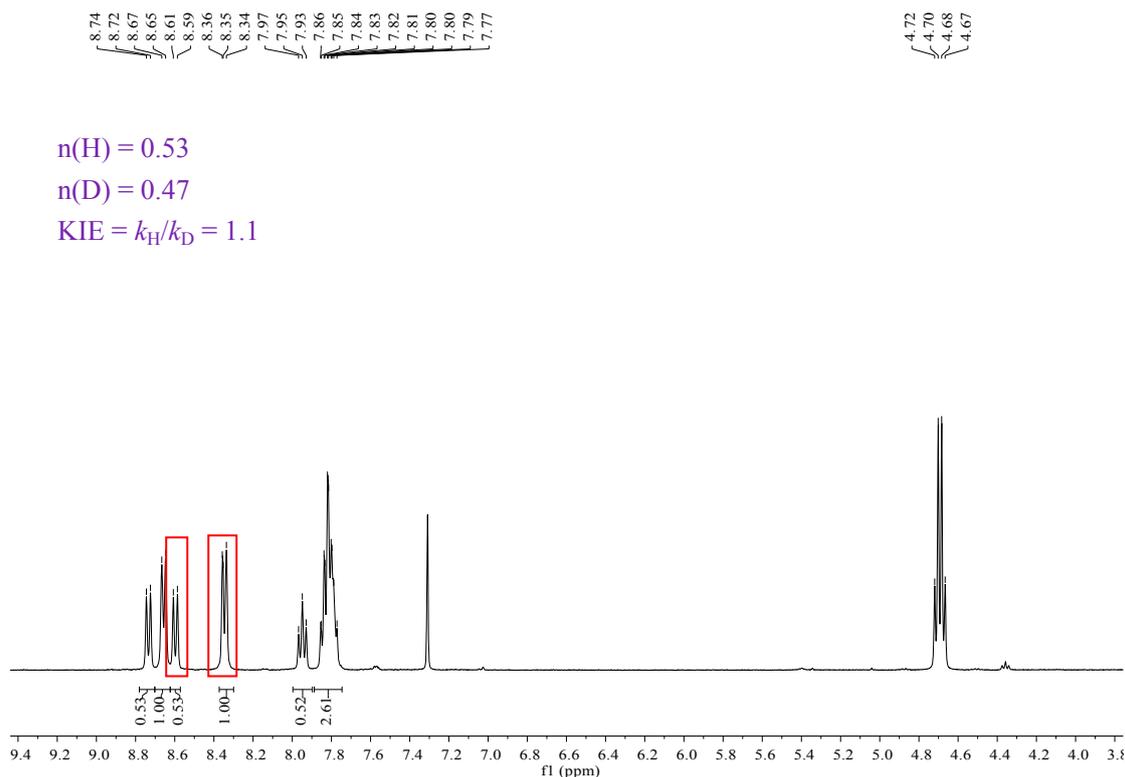


A pressure tube (capacity: 15.0 mL, outside diameter: 26.0 mm, length: 70.0 mm) was charged with 2-arylaniline **1a** (33.8 mg, 0.2 mmol), diazo compound **2b** (85.9 mg, 0.3 mmol) and TFA (1.2 mL). The reaction mixture was stirred at 100 °C for 1 h under O₂ condition. After cooling to room temperature, a saturated aqueous solution (30 mL) of NaHCO₃ was added, followed by an extraction with EtOAc (3 × 10 mL). The combined organic extracts were dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure to yield the crude product, which was further purified by silica gel chromatography to afford the desired product **3a** (15.7 mg, 44% yield).

A pressure tube (capacity: 15.0 mL, outside diameter: 26.0 mm, length: 70.0 mm) was charged with 2-arylaniline **D₅-1a** (34.9 mg, 0.2 mmol), diazo compound **2b** (85.9 mg, 0.3 mmol) and TFA (1.2 mL). The reaction mixture was stirred at 100 °C for 1 h under O₂ condition. After cooling to room temperature, a saturated aqueous solution (30 mL) of NaHCO₃ was added, followed by an extraction with EtOAc (3 × 10 mL). The combined organic extracts were dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure to yield the crude product, which was further purified by silica gel chromatography to afford the desired product **d₄-3a** (14.3 mg, 39% yield).



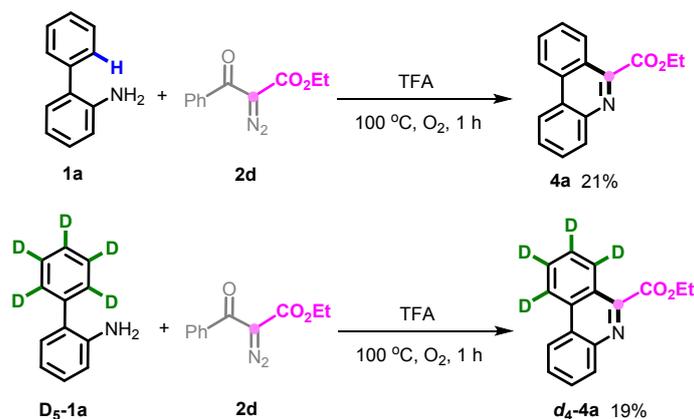
A pressure tube (capacity: 15.0 mL, outside diameter: 26.0 mm, length: 70.0 mm) was charged with 2-arylaniline **1a** (16.9 mg, 0.1 mmol), **D₅-1a** (17.4 mg, 0.1 mmol), diazo compound **2d** (65.5 mg, 0.3 mmol) and TFA (1.2 mL). The reaction mixture was stirred at 100 °C for 1 h under O₂ condition. After cooling to room temperature, a saturated aqueous solution (30 mL) of NaHCO₃ was added, followed by an extraction with EtOAc (3 × 10 mL). The combined organic extracts were dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure to yield the crude product, which was further purified by silica gel chromatography to afford the desired product **4a** and **d₄-4a** (9.9 mg, 20% yield).



$$n(\text{H}) = 0.53$$

$$n(\text{D}) = 0.47$$

$$\text{KIE} = k_{\text{H}}/k_{\text{D}} = 1.1$$

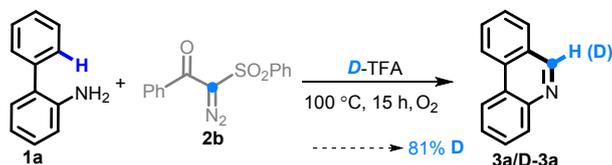


$$\text{KIE} = k_{\text{H}}/k_{\text{D}} = 0.21/0.19 = 1.1$$

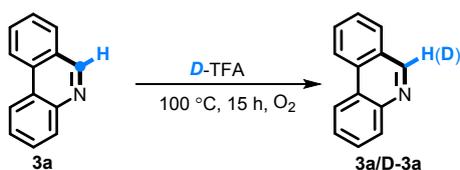
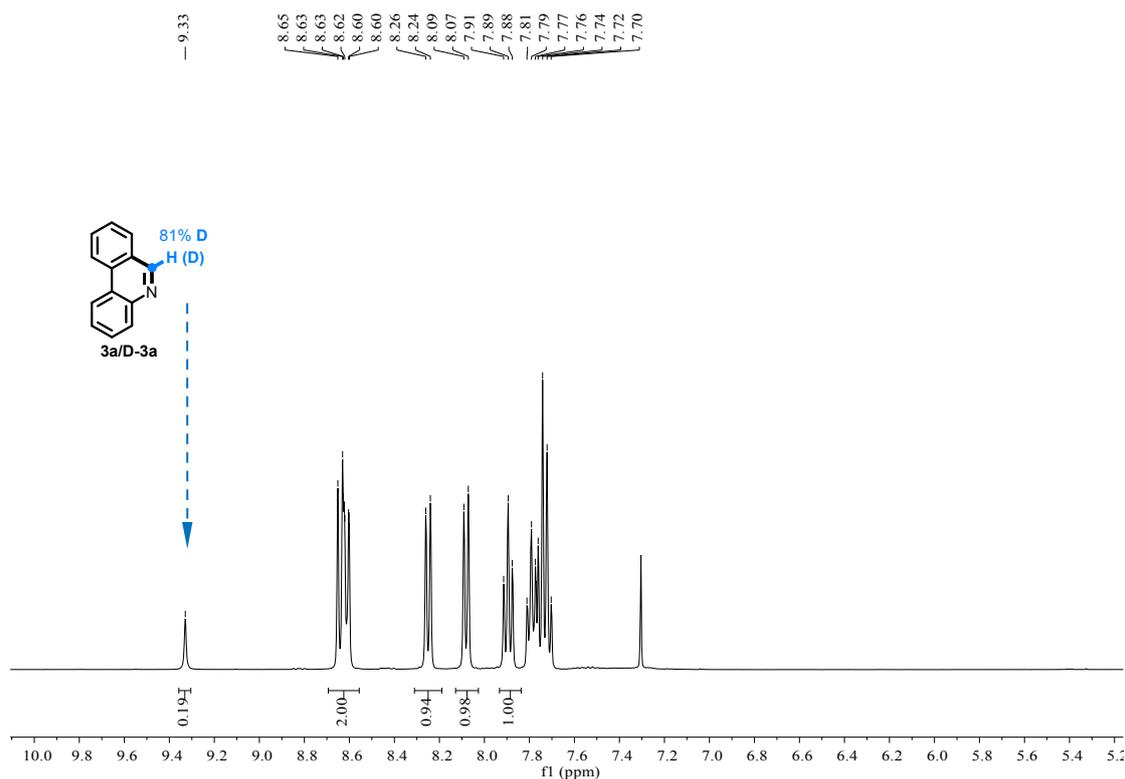
A pressure tube (capacity: 15.0 mL, outside diameter: 26.0 mm, length: 70.0 mm) was charged with 2-arylaniline **1a** (33.8 mg, 0.1 mmol), diazo compound **2d** (65.5 mg, 0.3 mmol) and TFA (1.2 mL). The reaction mixture was stirred at 100 °C for 1 h under O₂ condition. After cooling to room temperature, a saturated aqueous solution (30 mL) of NaHCO₃ was added, followed by an extraction with EtOAc (3 × 10 mL). The combined organic extracts were dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure to yield the crude product, which was further purified by silica gel chromatography to afford the desired product **4a** (10.5 mg, 21% yield).

A pressure tube (capacity: 15.0 mL, outside diameter: 26.0 mm, length: 70.0 mm) was charged with 2-arylaniline **D₅-1a** (34.9 mg, 0.1 mmol), diazo compound **2d** (65.5 mg, 0.3 mmol) and TFA (1.2 mL). The reaction mixture was stirred at 100 °C for 1 h under O₂ condition. After cooling to room temperature, a saturated aqueous solution (30 mL) of NaHCO₃ was added,

followed by an extraction with EtOAc (3 × 10 mL). The combined organic extracts were dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure to yield the crude product, which was further purified by silica gel chromatography to afford the desired product **d**₄-**4a** (9.7 mg, 19% yield).

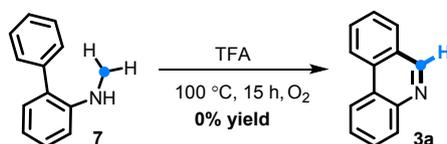
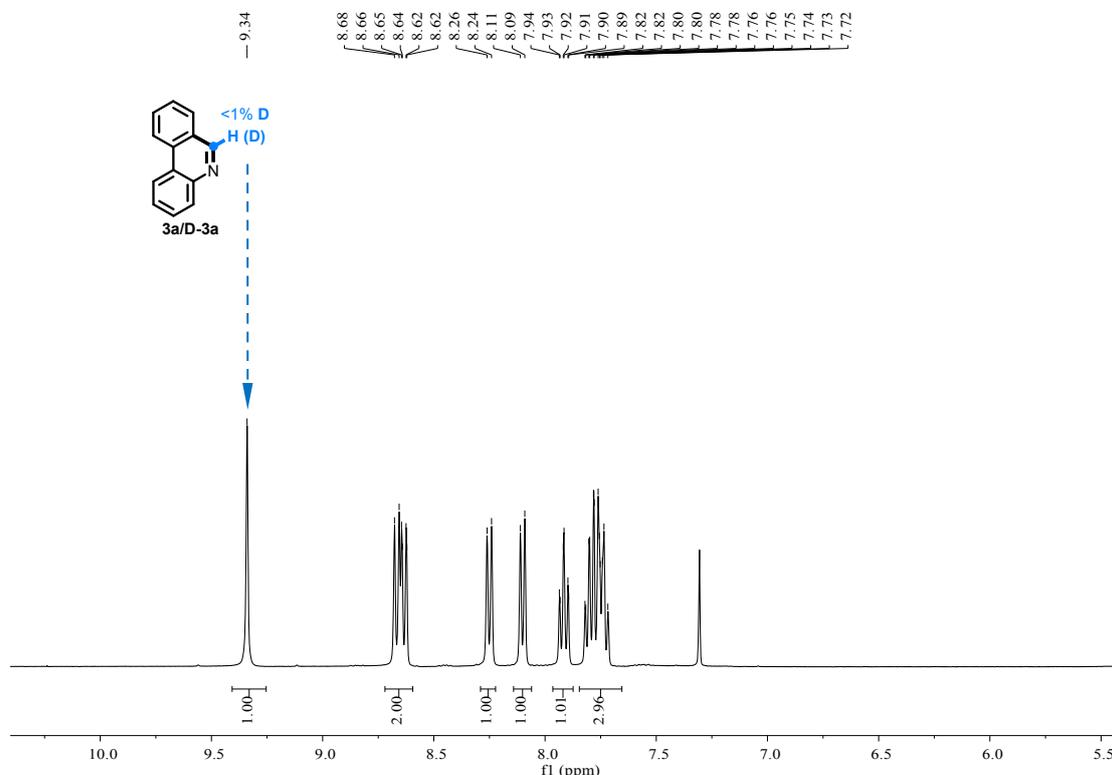


A pressure tube (capacity: 15.0 mL, outside diameter: 26.0 mm, length: 70.0 mm) was charged with 2-arylaniline **1a** (33.8 mg, 0.2 mmol), diazo compound **2b** (85.9 mg, 0.3 mmol) and *D*-TFA (1.2 mL). The reaction mixture was stirred at 100 °C for 15 h under O₂ condition. After cooling to room temperature, a saturated aqueous solution (30 mL) of NaHCO₃ was added, followed by an extraction with EtOAc (3 × 10 mL). The combined organic extracts were dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure to yield the crude product, which was further purified by silica gel chromatography to afford the desired product **3a** and **D-3a** (23.4 mg, 65% yield).

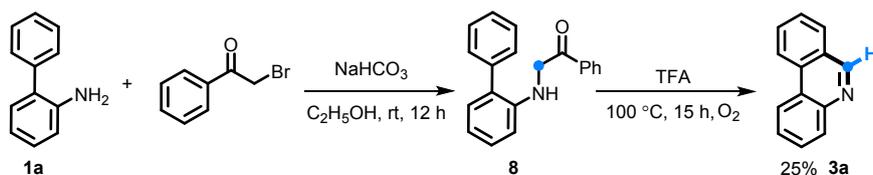


A pressure tube (capacity: 15.0 mL, outside diameter: 26.0 mm, length: 70.0 mm) was charged with Phenanthridine **3a** (17.9 mg, 0.1 mmol) and *D*-TFA (0.6 mL). The reaction mixture

was stirred at 100 °C for 15 h under O₂ condition. After cooling to room temperature, a saturated aqueous solution (30 mL) of NaHCO₃ was added, followed by an extraction with EtOAc (3 × 10 mL). The combined organic extracts were dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure to yield the crude product, which was further purified by silica gel chromatography to afford the desired product (16.1 mg, 90% yield).



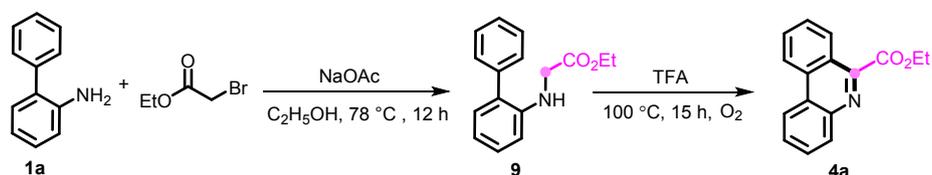
A pressure tube (capacity: 15.0 mL, outside diameter: 26.0 mm, length: 70.0 mm) was charged with N-methyl-[1,1'-biphenyl]-2-amine **7** (36.7 mg, 0.2 mmol) and TFA (1.2 mL). The reaction mixture was stirred at 100 °C for 15 h under O₂ condition. After cooling to room temperature, a saturated aqueous solution (30 mL) of NaHCO₃ was added, followed by an extraction with EtOAc (3 × 10 mL). The combined organic extracts were dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure to yield the crude product, which was further purified by silica gel chromatography to afford the desired product **3a** (0 mg, 0% yield).



A 10 mL reaction flask was charged with 2-arylaniline **1a** (169.2 mg, 1.0 mmol), 2-bromo-1-phenylethan-1-one (199.0 mg, 1.0 mmol), NaHCO₃ (84.0 mg, 1.0 mmol) and C₂H₅OH (2.0 mL). The reaction mixture was stirred at room temperature for 12 h under air, then filtered by funnel,

and the solid residue was washed by C₂H₅OH to afford **8** as a white solid (206.7 mg, 72% yield). PE/EA = 20:1, R_f = 0.33. ¹H NMR (400 MHz, CDCl₃): δ 8.06-7.99 (m, 2H), 7.65 (d, *J* = 7.5 Hz, 1H), 7.59-7.51 (m, 6H), 7.48-7.42 (m, 1H), 7.34 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.22 (dd, *J* = 7.4, 1.6 Hz, 1H), 6.88 (td, *J* = 7.4, 1.1 Hz, 1H), 6.75 (d, *J* = 8.1 Hz, 1H), 5.31 (s, 1H), 4.66 (d, *J* = 4.5 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 194.9, 144.1, 139.2, 135.0, 133.8, 130.5, 129.3, 129.0, 128.9, 128.7, 128.2, 127.7, 127.4, 117.5, 110.7, 50.5. IR (KBr): 3057, 1686, 1641, 1508, 1439, 1350, 1211, 990, 743, 696 cm⁻¹. HRMS (ESI) *m/z* calculated for C₂₀H₁₈NO [M+H]⁺ 288.1383, found 288.1382.

A pressure tube (capacity: 15.0 mL, outside diameter: 26.0 mm, length: 70.0 mm) was charged with 2-([1,1'-biphenyl]-2-ylamino)-1-phenylethan-1-one **8** (57.5 mg, 0.2 mmol) and TFA (1.2 mL). The reaction mixture was stirred at 100 °C for 15 h under O₂ condition. After cooling to room temperature, a saturated aqueous solution (30 mL) of NaHCO₃ was added, followed by an extraction with EtOAc (3 × 10 mL). The combined organic extracts were dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure to yield the crude product, which was further purified by silica gel chromatography to afford the desired product **3a** (9.0 mg, 25% yield).



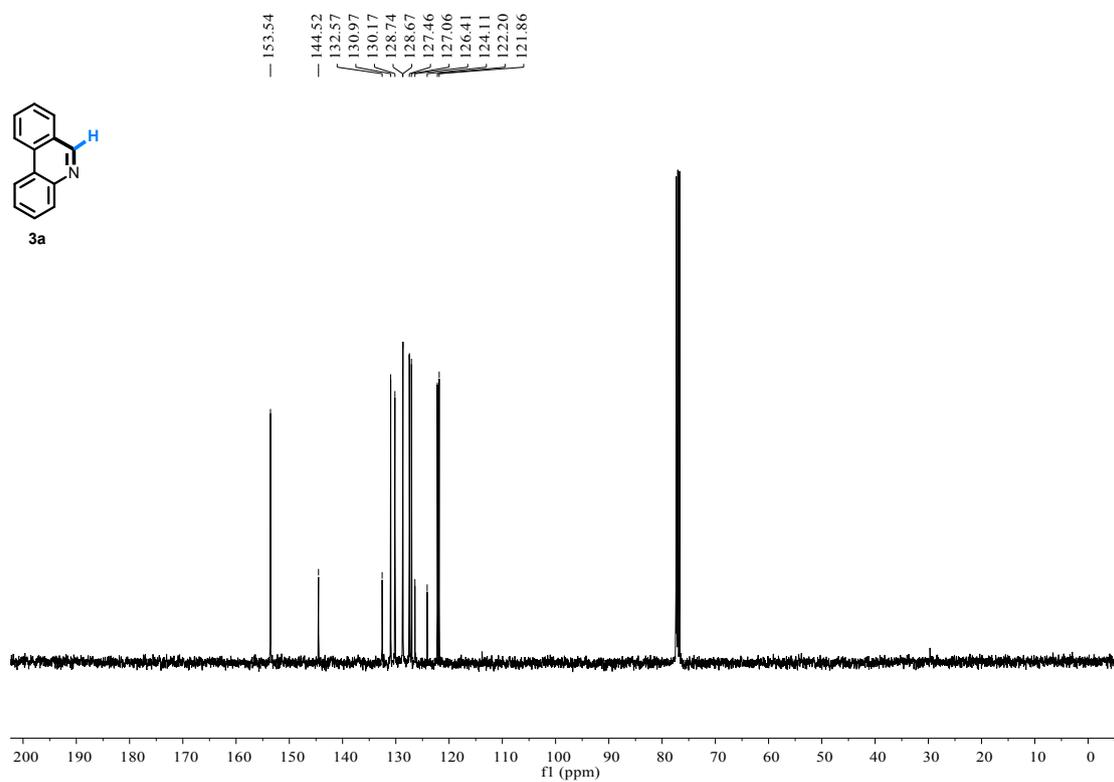
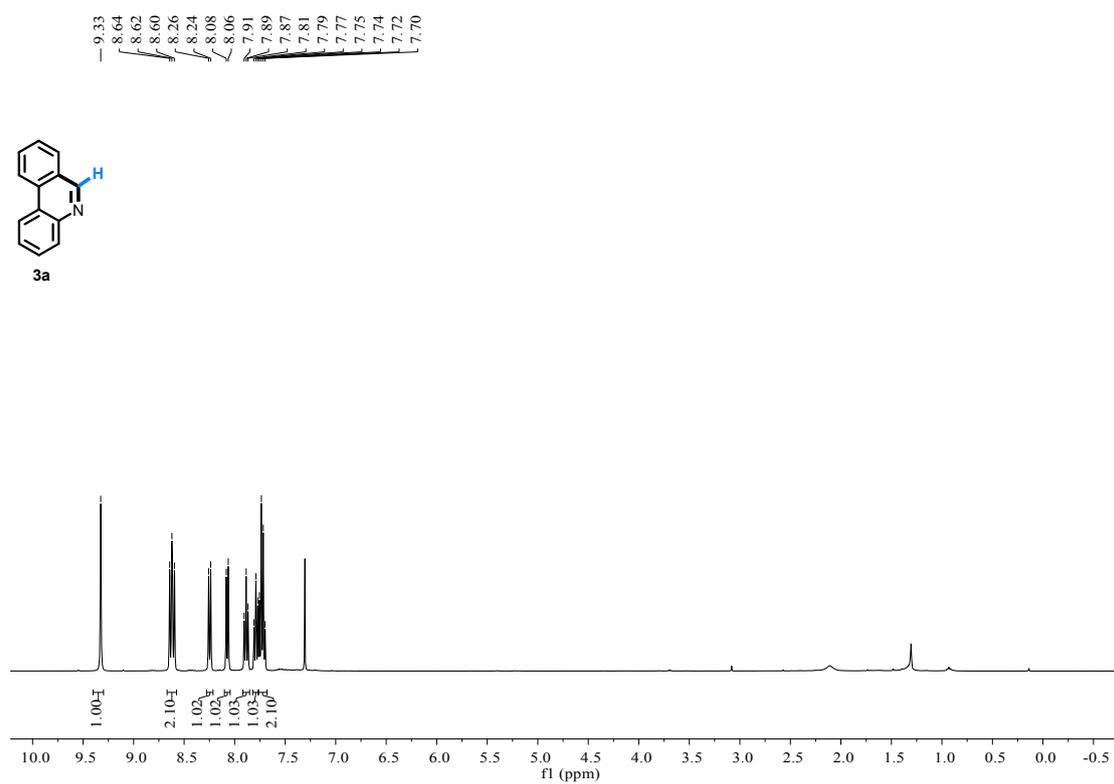
A pressure tube (capacity: 15.0 mL, outside diameter: 26.0 mm, length: 70.0 mm) was charged with 2-arylaniline **1a** (169.2 mg, 1.0 mmol), ethyl 2-bromoacetate (167.0 mg, 1.0 mmol), sodium acetate (98.4 mg, 1.2 mmol) and C₂H₅OH (3.0 mL). The reaction mixture was stirred at 78 °C for 12 h under N₂ condition. Ethanol was removed under reduced pressure, Water (10 mL) was added, followed by an extraction with CH₂Cl₂ (3 × 10 mL). The combined organic layer was washed with aqueous NaHCO₃ and brine, dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure to yield the crude product, which was further purified by silica gel chromatography to afford the desired product **9** as a Colorless oil (140.5 mg, 55% yield). PE/EA = 20:1, R_f = 0.35. ¹H NMR (400 MHz, CDCl₃): δ 7.51 (d, *J* = 4.3 Hz, 4H), 7.41 (q, *J* = 4.3 Hz, 1H), 7.27 (d, *J* = 8.4 Hz, 1H), 7.18 (d, *J* = 8.8 Hz, 1H), 6.87 (t, *J* = 7.4 Hz, 1H), 6.63 (d, *J* = 8.1 Hz, 1H), 4.63 (s, 1H), 4.24 (q, *J* = 7.2 Hz, 2H), 3.94 (d, *J* = 5.7 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 171.0, 144.0, 139.2, 130.4, 129.3, 128.9, 128.7, 128.2, 127.3, 117.8, 110.4, 61.2, 45.9, 14.1. IR (KBr): 3063, 2983, 1733, 1641, 1590, 1513, 1442, 1204, 1022, 744, 703 cm⁻¹. HRMS (ESI) *m/z* calculated for C₁₆H₁₈NO₂ [M+H]⁺ 256.1332, found 256.1330.

A pressure tube (capacity: 15.0 mL, outside diameter: 26.0 mm, length: 70.0 mm) was charged with ethyl [1,1'-biphenyl]-2-ylglycinate **9** (51.1 mg, 0.2 mmol) and TFA (1.2 mL). The reaction mixture was stirred at 100 °C for 15 h under O₂ condition. After cooling to room temperature, a saturated aqueous solution (30 mL) of NaHCO₃ was added, followed by an extraction with EtOAc (3 × 10 mL). The combined organic extracts were dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure to yield the crude product, which was further purified by silica gel chromatography to afford the desired product **4a** (11.6 mg, 23% yield).

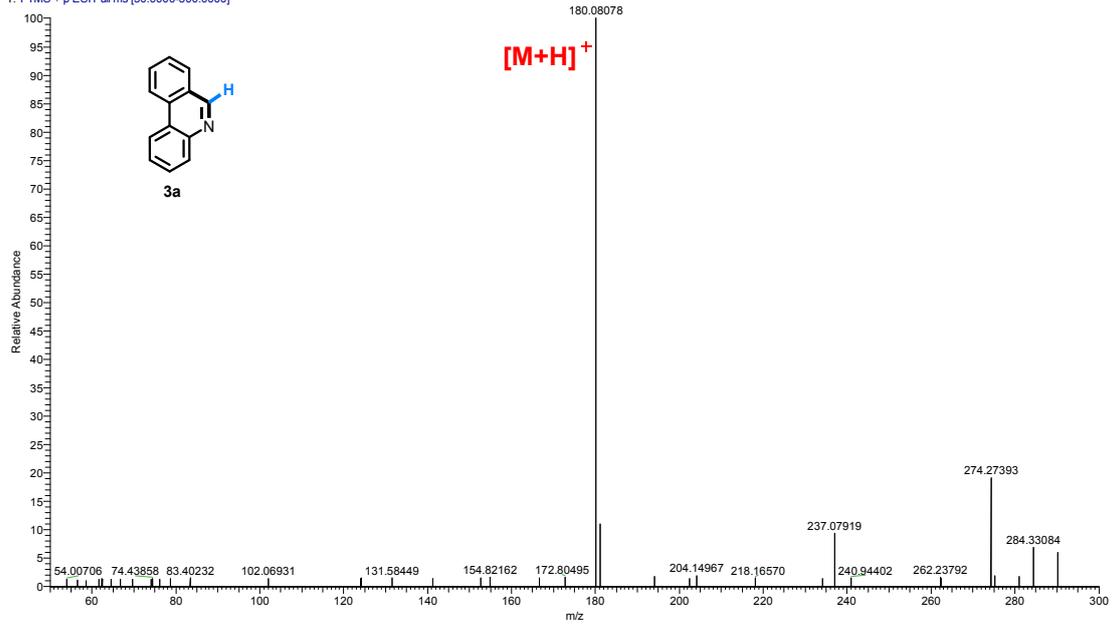
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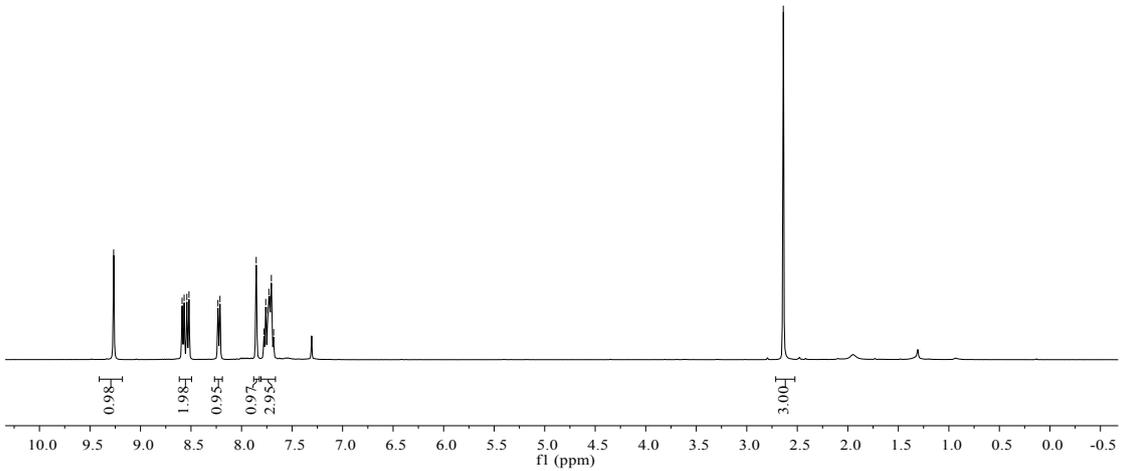
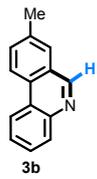
F. NMR spectra and ESI-MS spectrum:

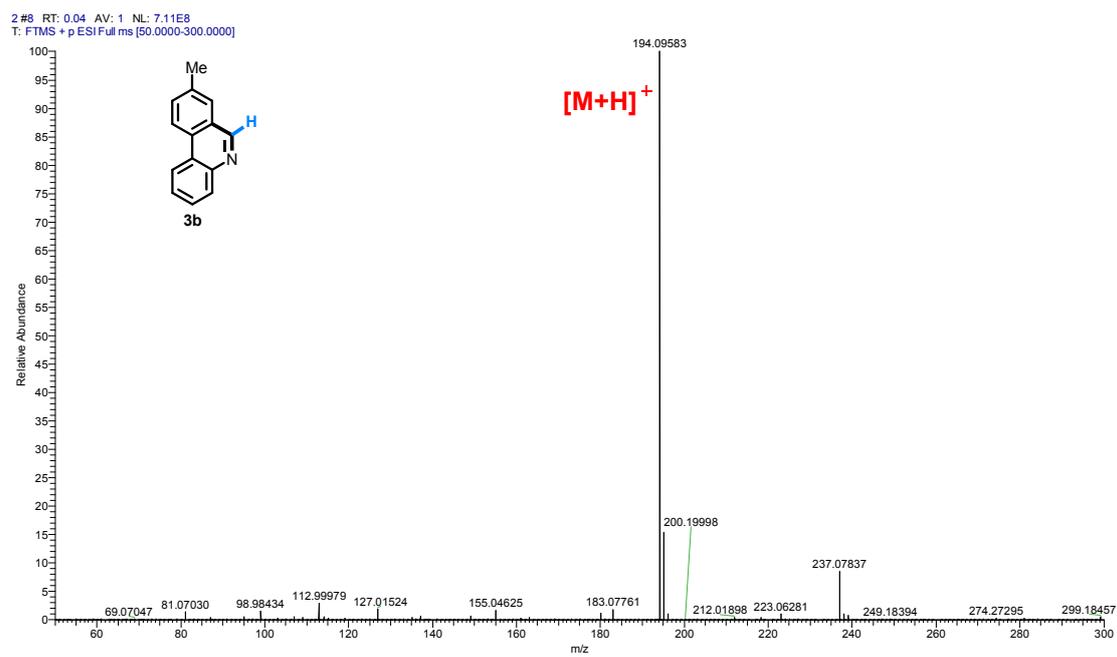
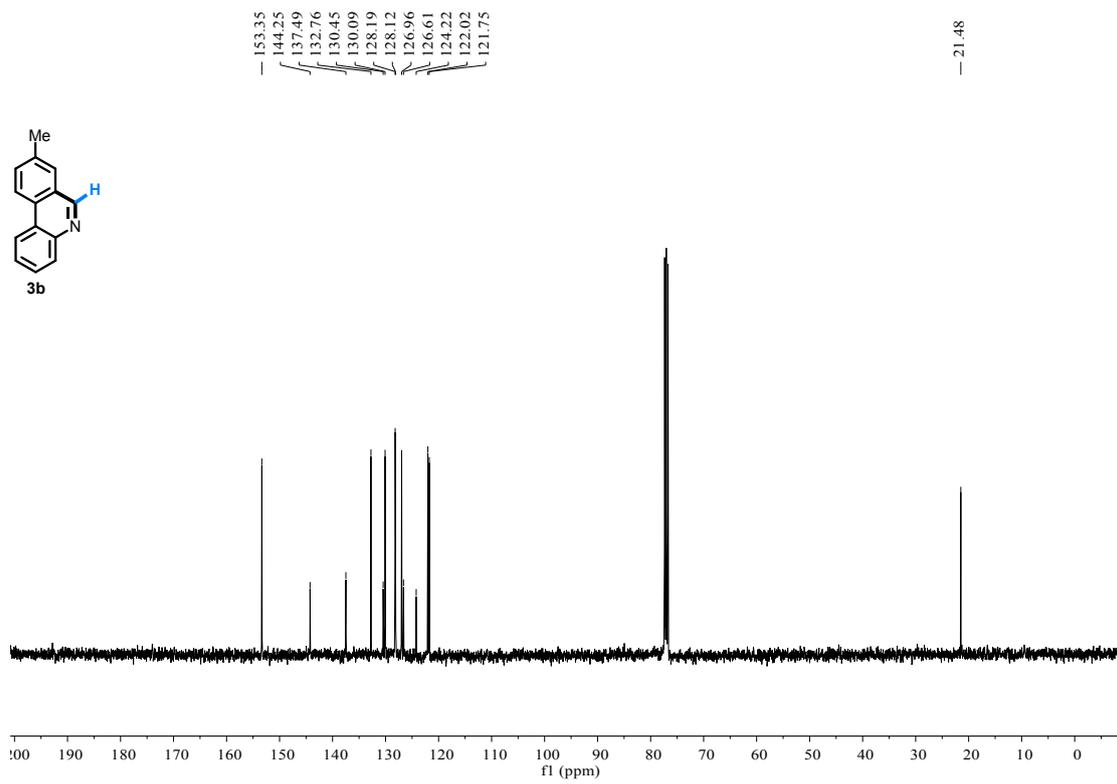


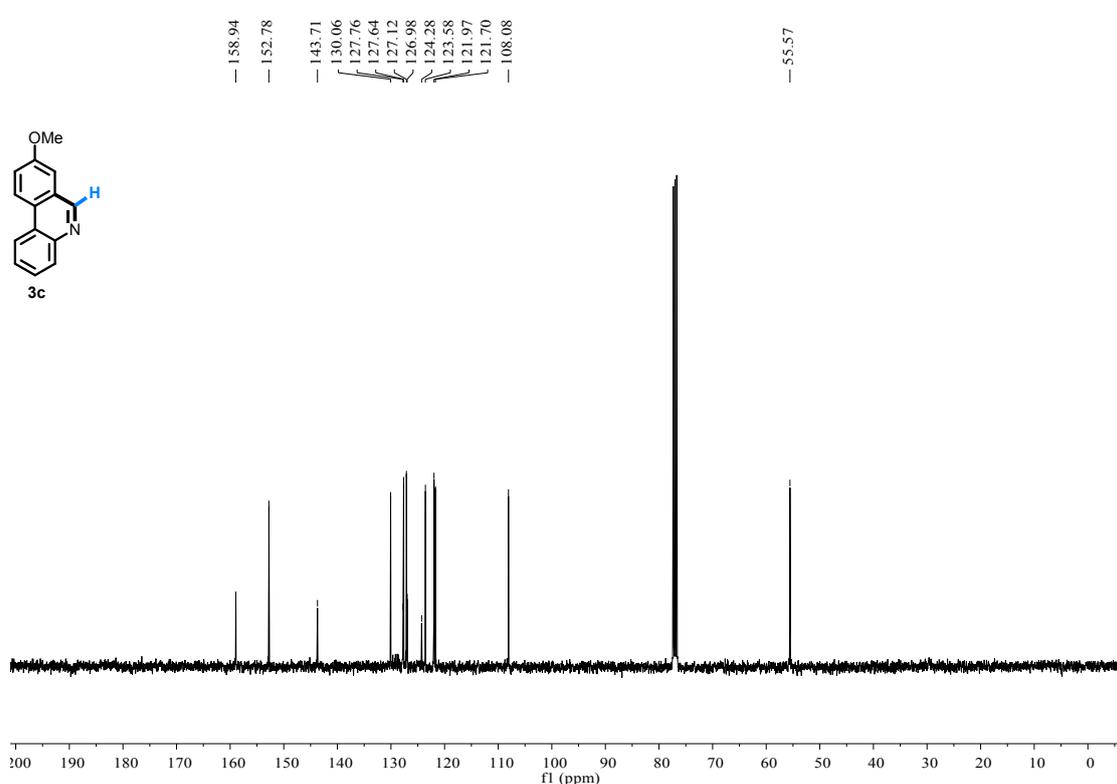
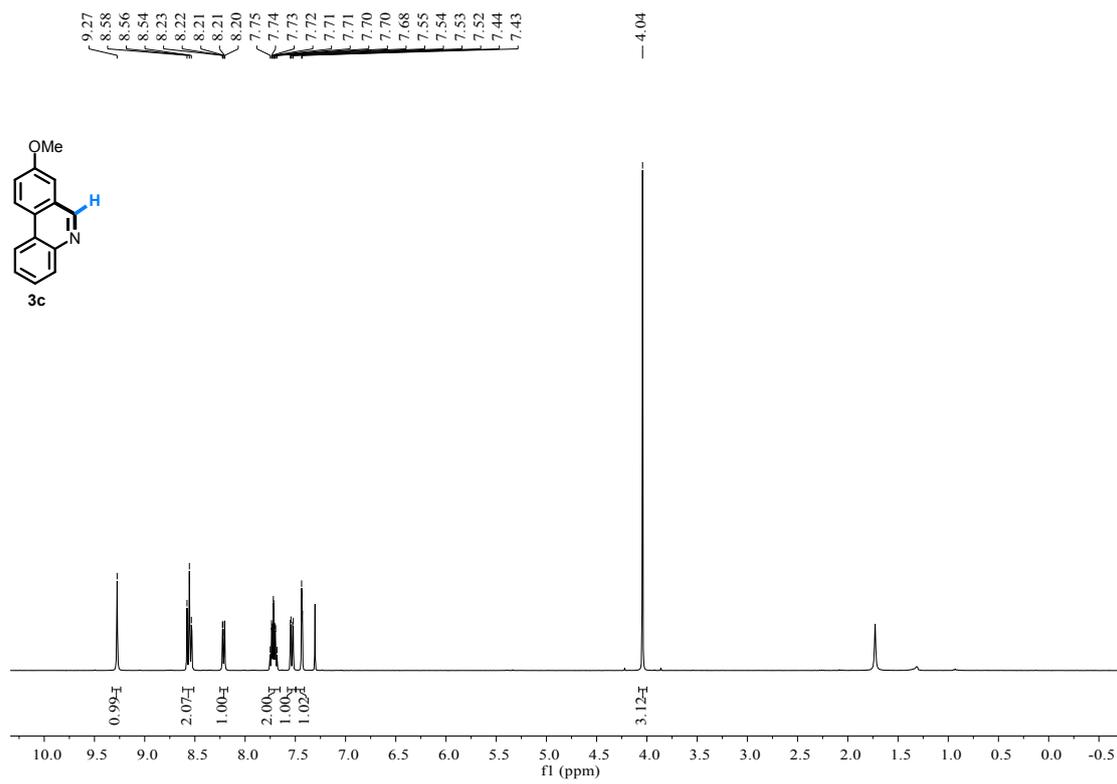
1 #5 RT: 0.03 AV: 1 NL: 7.01E4
T: FTMS + p ESI Full ms [50.0000-300.0000]



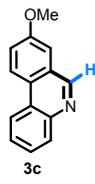
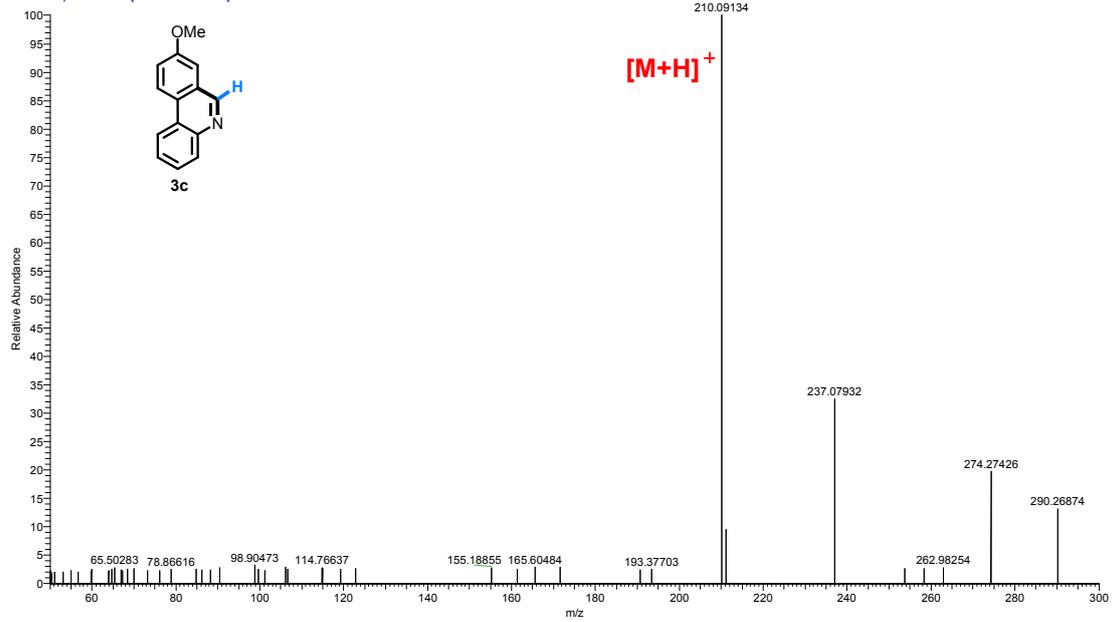
9.27
8.59
8.57
8.54
8.52
8.23
8.21
7.85
7.78
7.76
7.74
7.73
7.72
7.70
7.68
-2.64



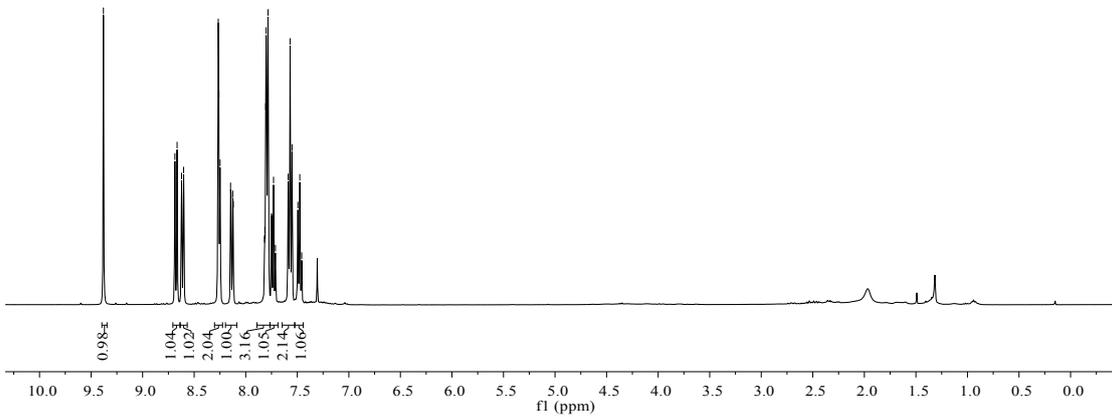
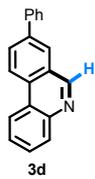


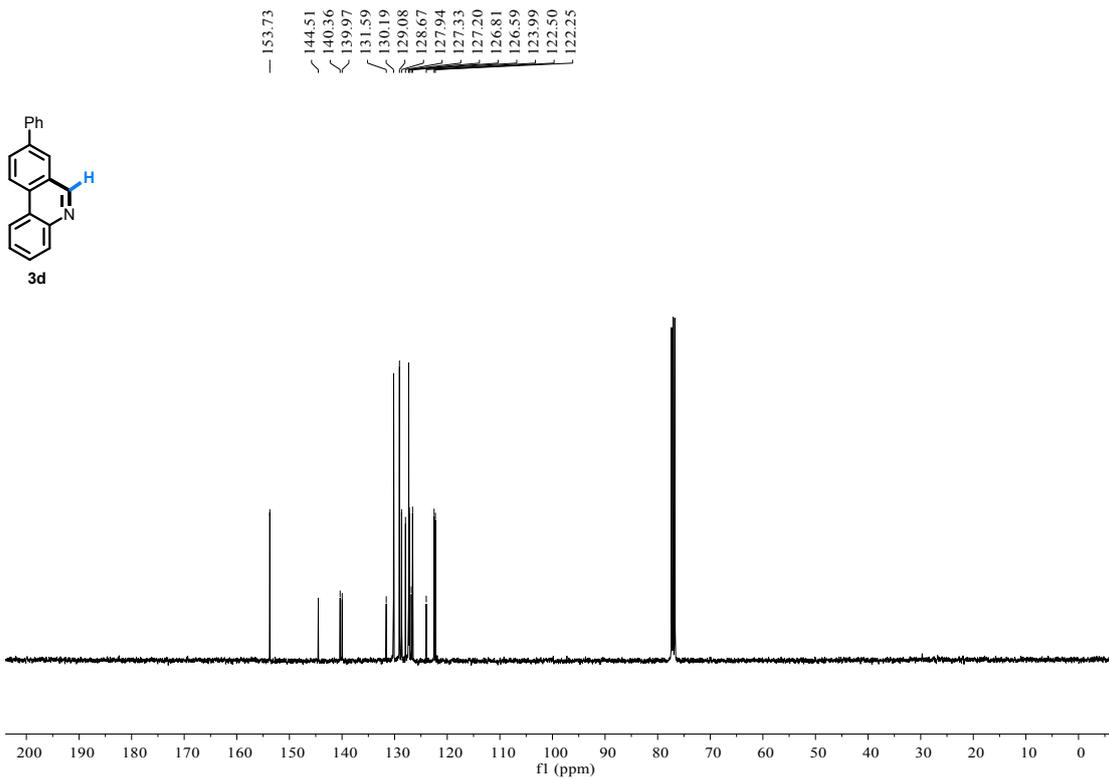


3 #9 RT: 0.05 AV: 1 NL: 3.92E4
T: FTMS + p ESI Full ms [50,0000-300,0000]

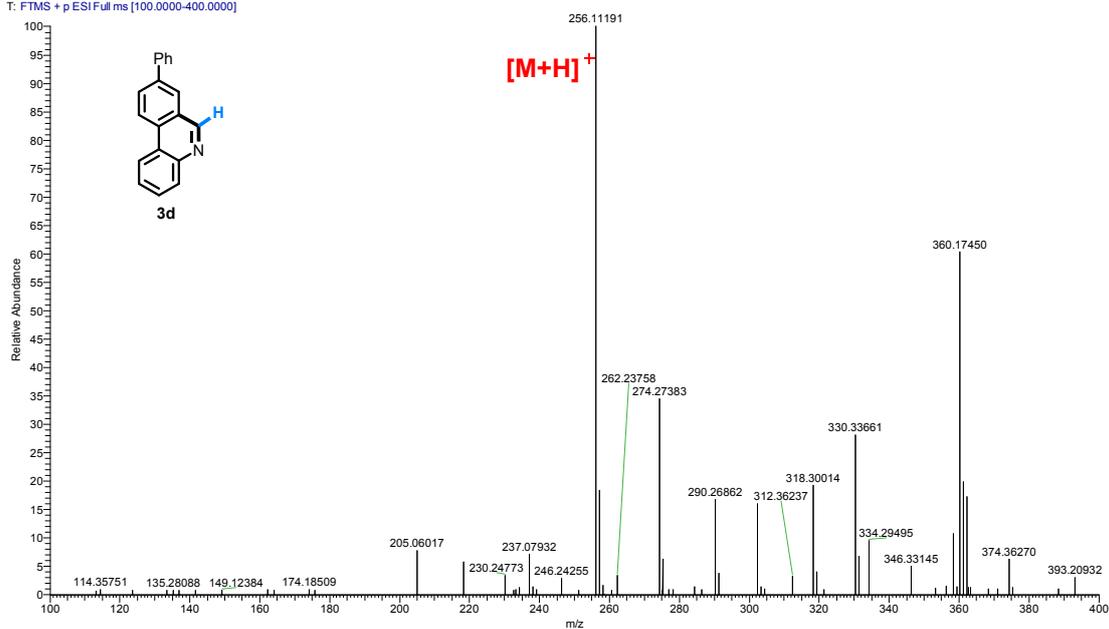


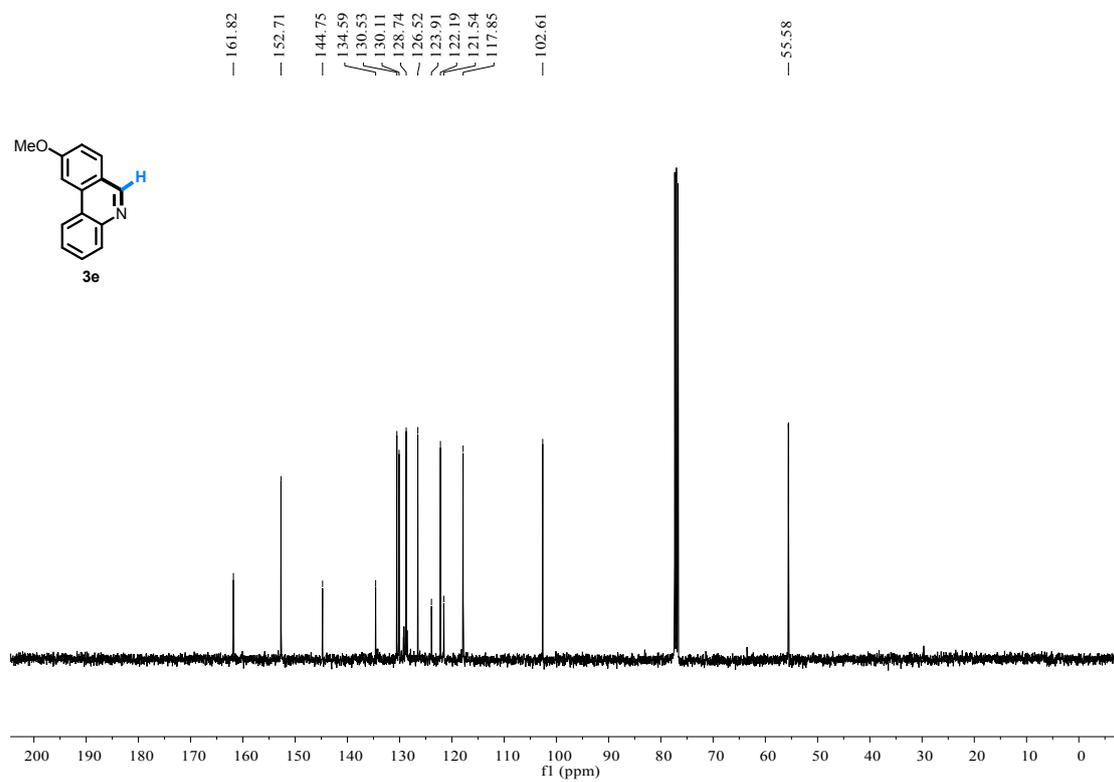
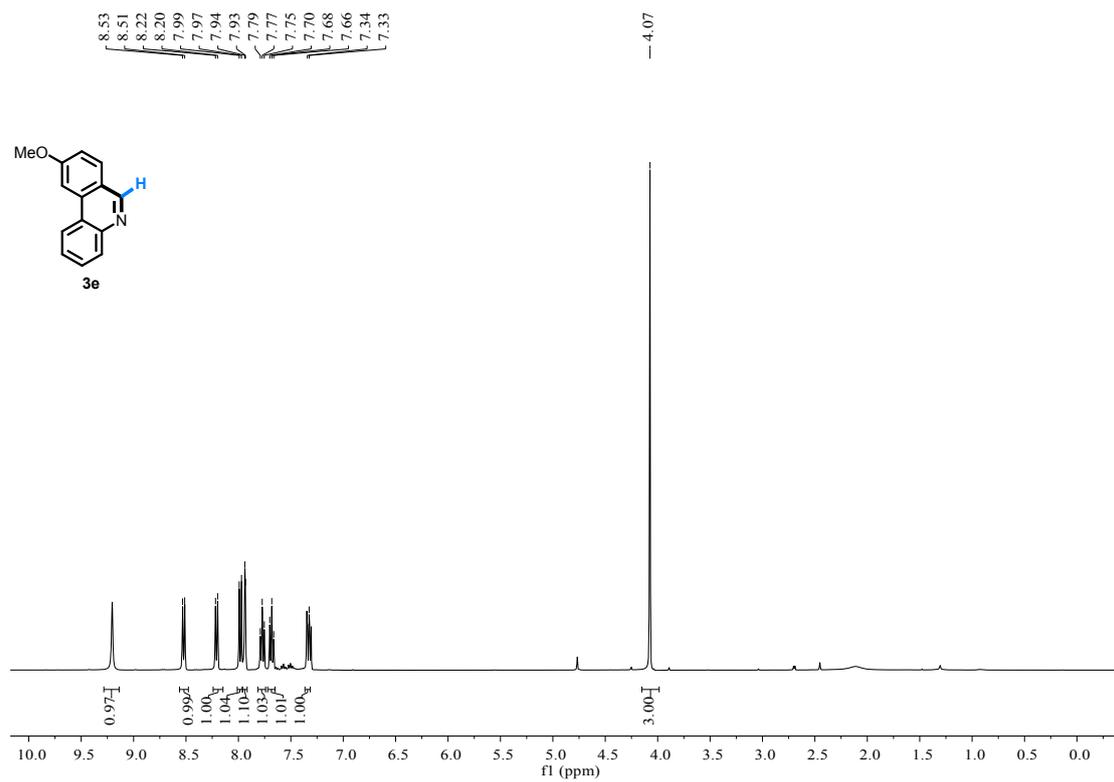
9.38
8.69
8.67
8.62
8.60
8.27
8.26
8.25
8.15
8.14
8.13
8.12
7.82
7.81
7.81
7.80
7.80
7.78
7.75
7.75
7.73
7.71
7.59
7.57
7.55
7.49
7.48
7.46



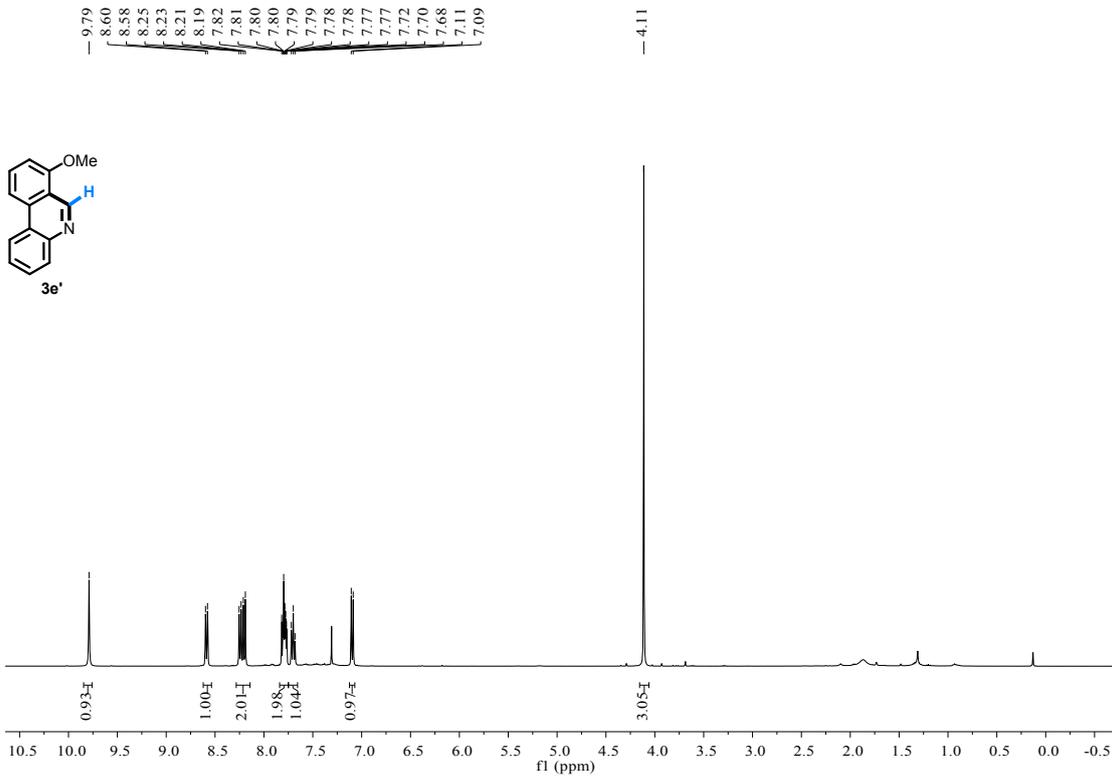
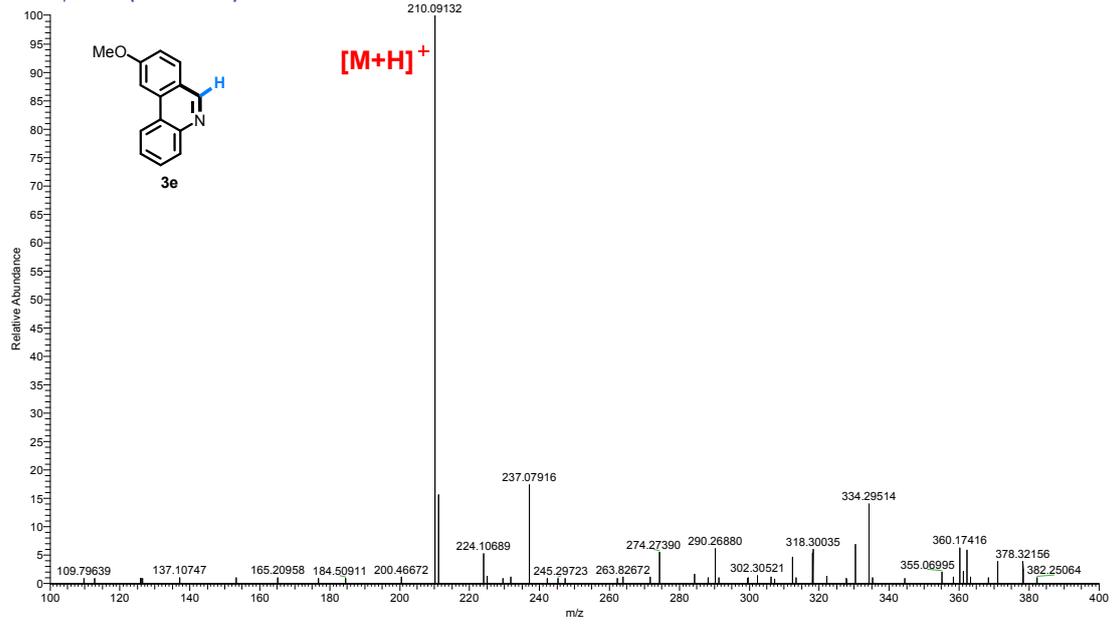


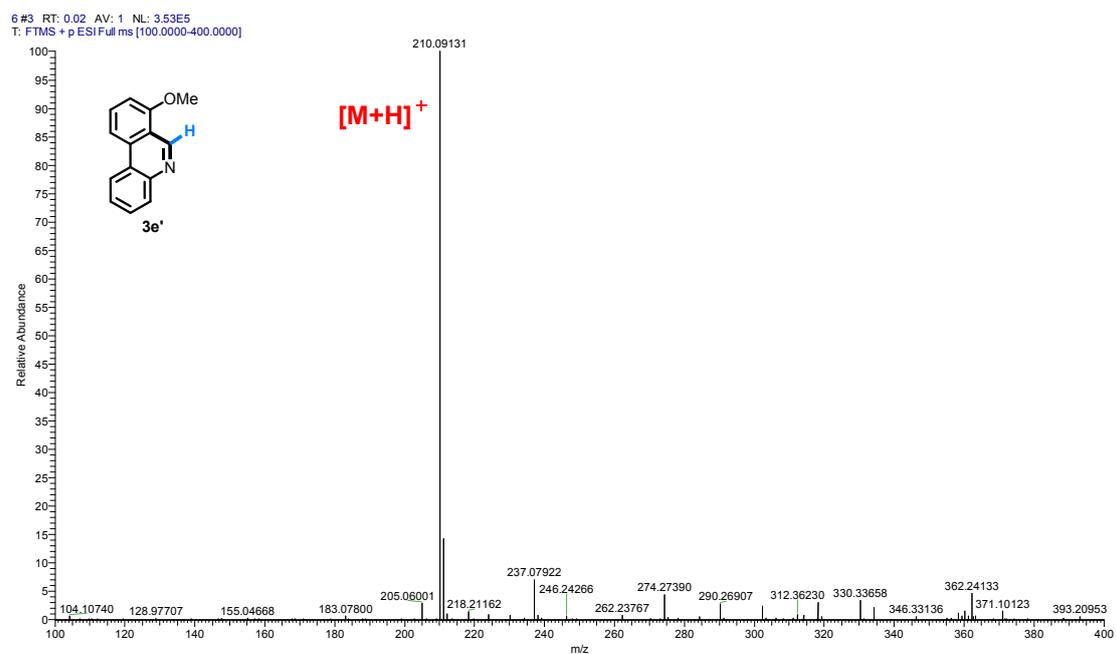
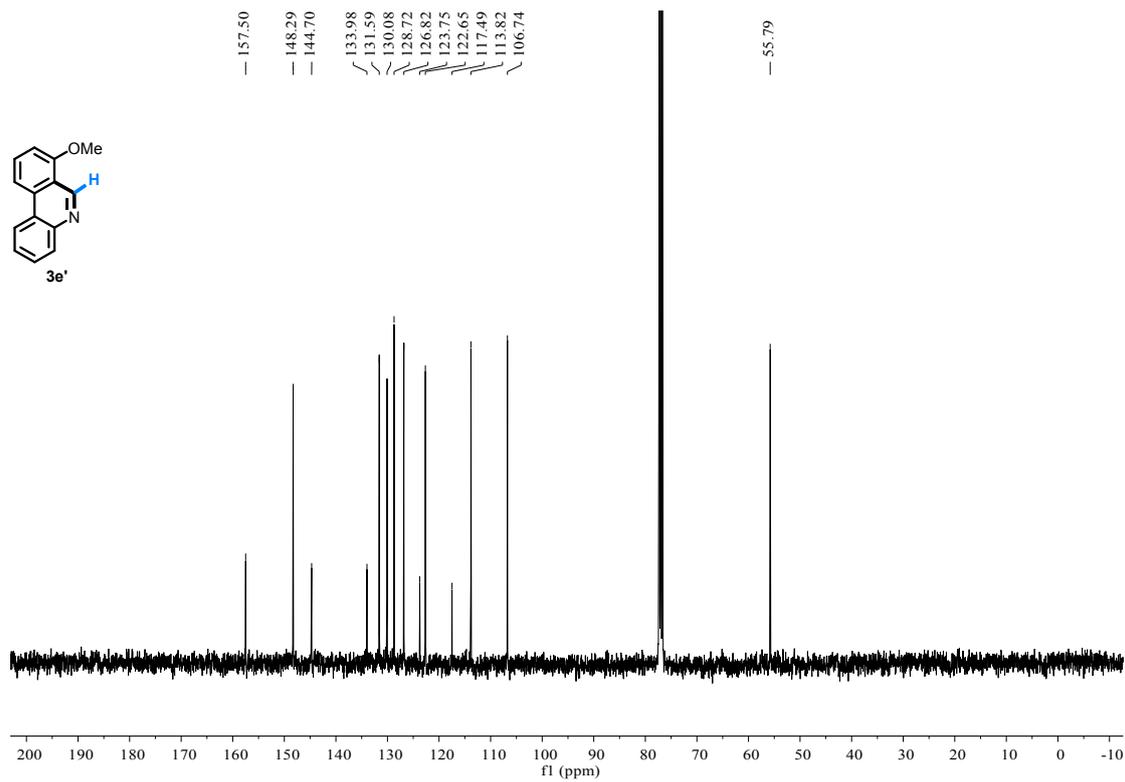
4 #4 RT: 0.02 AV: 1 NL: 6.76E4
T: FTMS + p ESI Full ms [100.0000-400.0000]

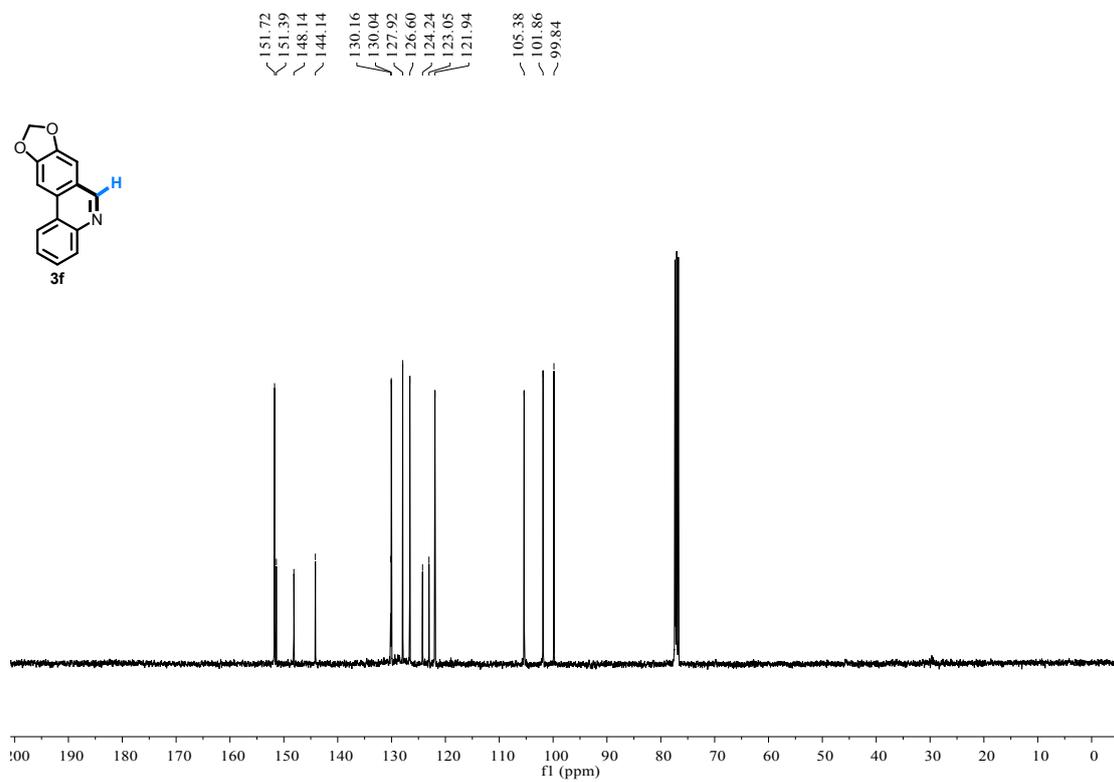
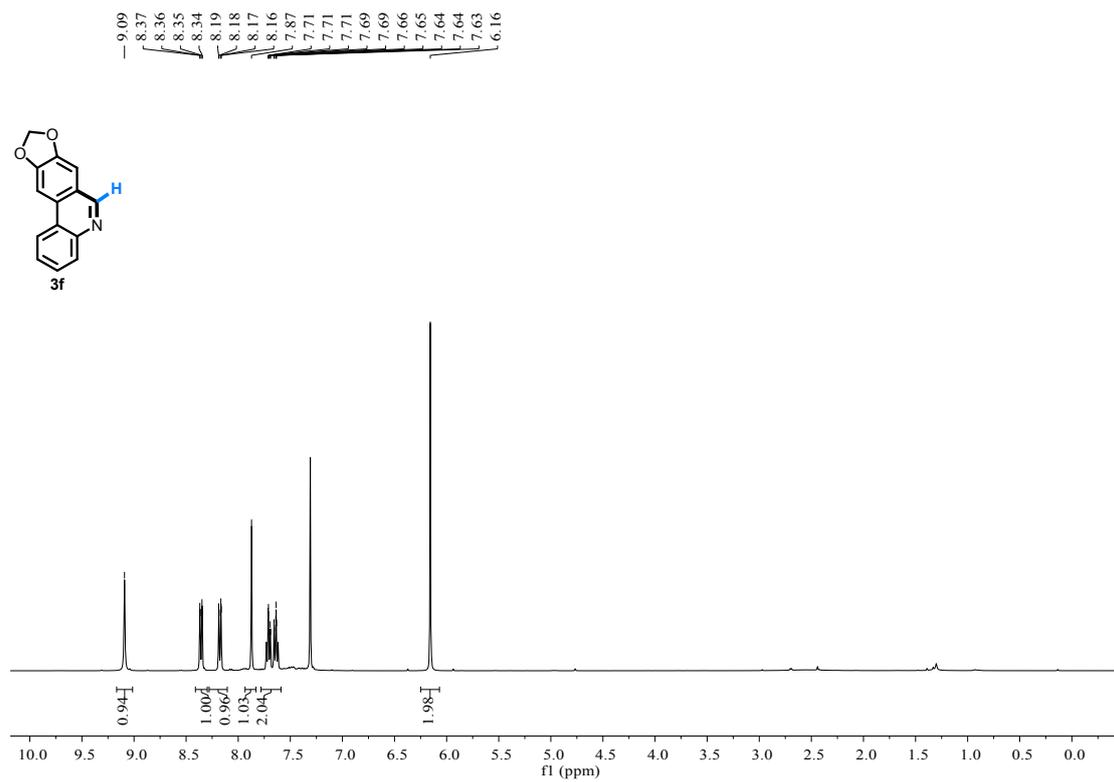




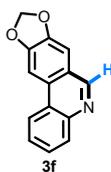
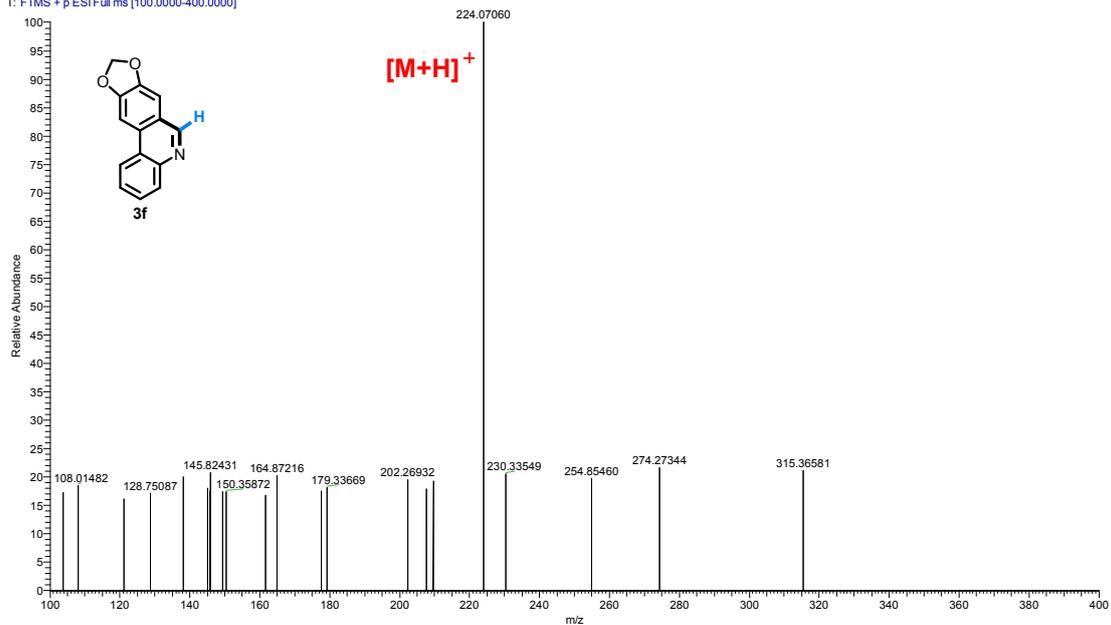
5 #2 RT: 0.01 AV: 1 NL: 5.73E4
T: FTMS + p ESI Full ms [100.0000-400.0000]



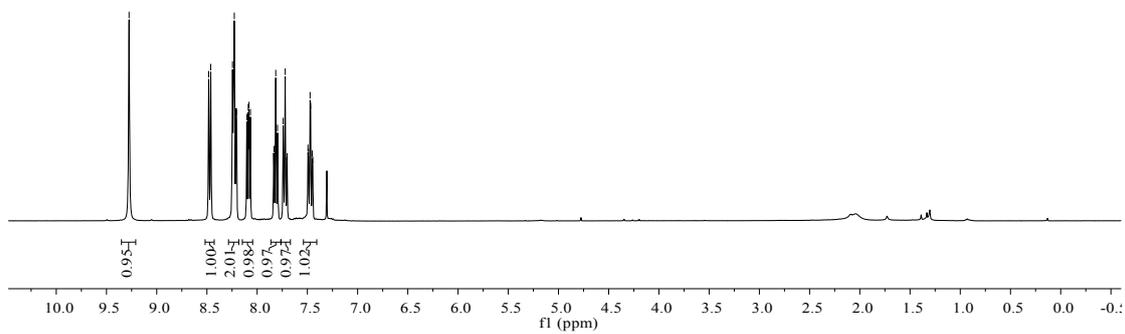
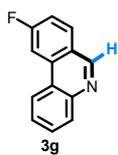


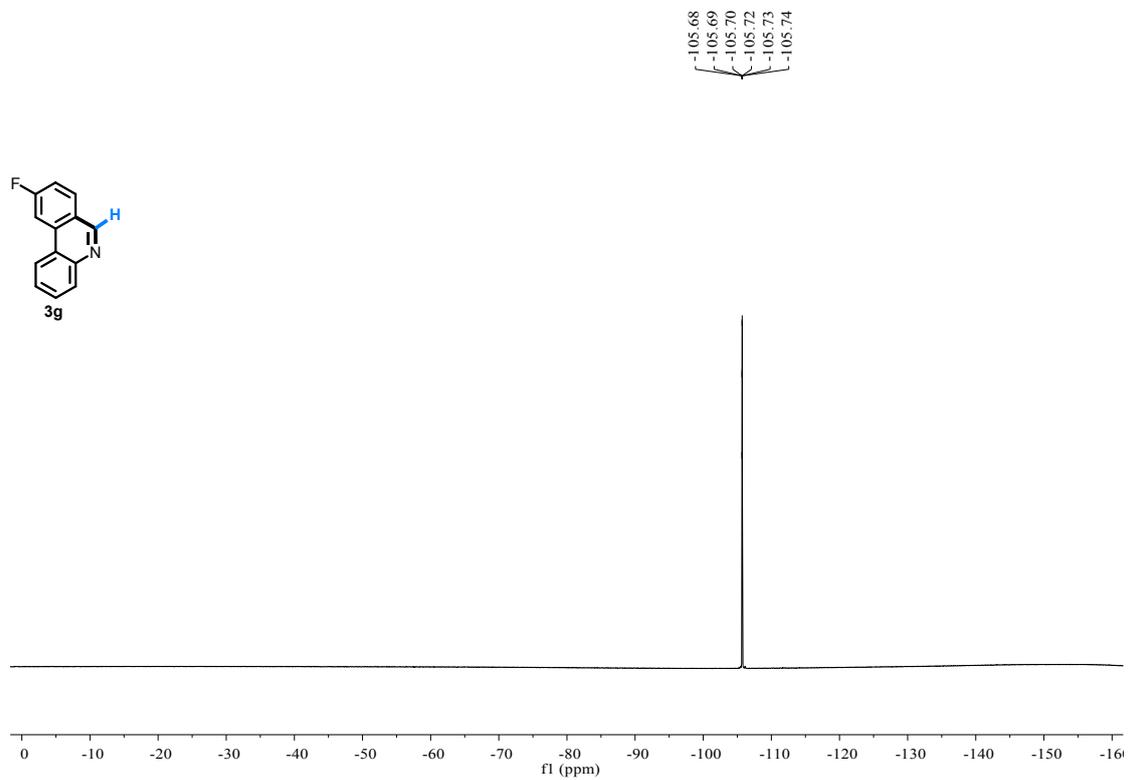
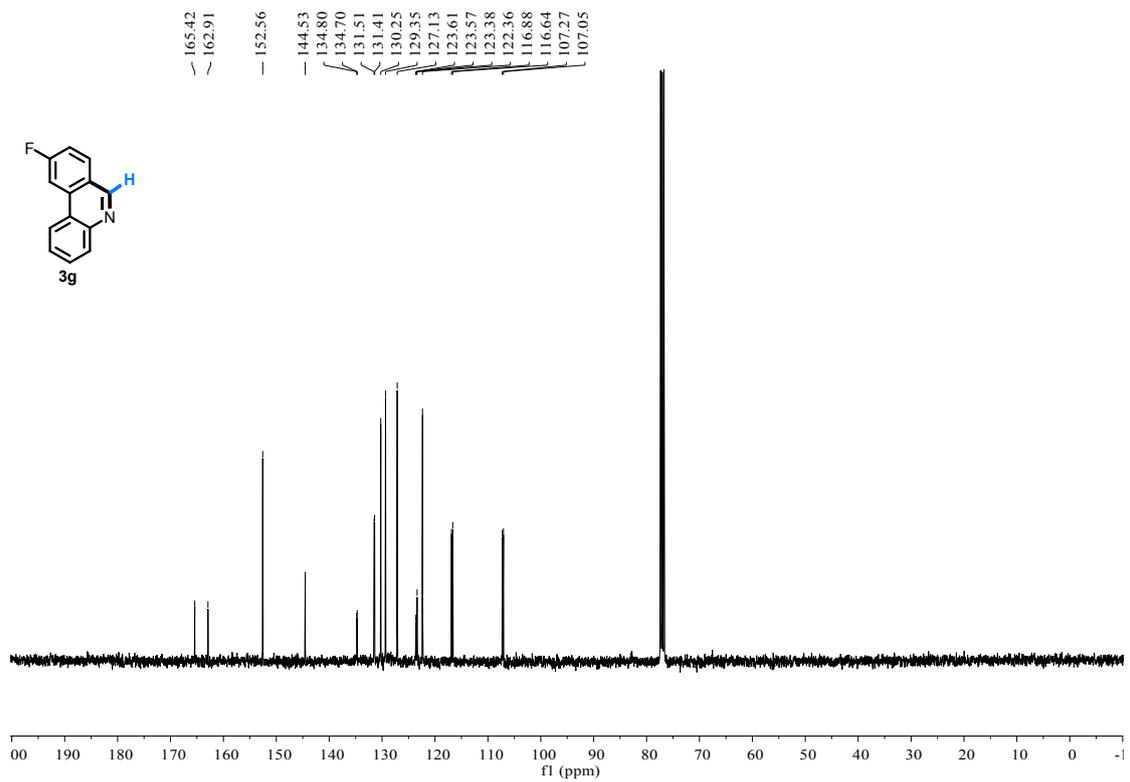


7 #5 RT: 0.03 AV: 1 NL: 3.01E3
T: FTMS + p ESI Full ms [100.0000-400.0000]

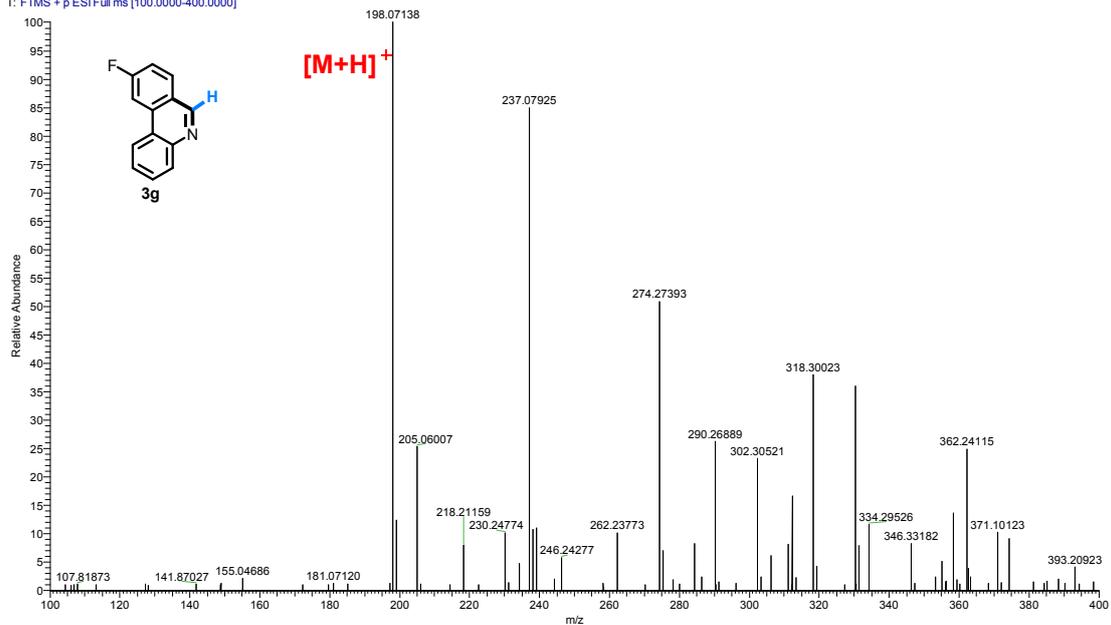


9.28
8.48
8.46
8.25
8.23
8.21
8.10
8.09
8.08
8.07
7.83
7.82
7.80
7.74
7.72
7.70
7.49
7.49
7.47
7.47
7.45
7.45

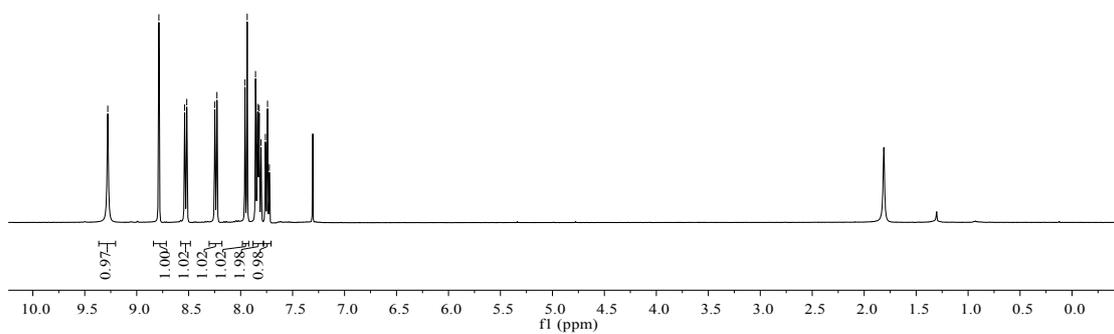
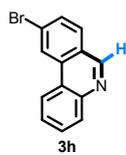


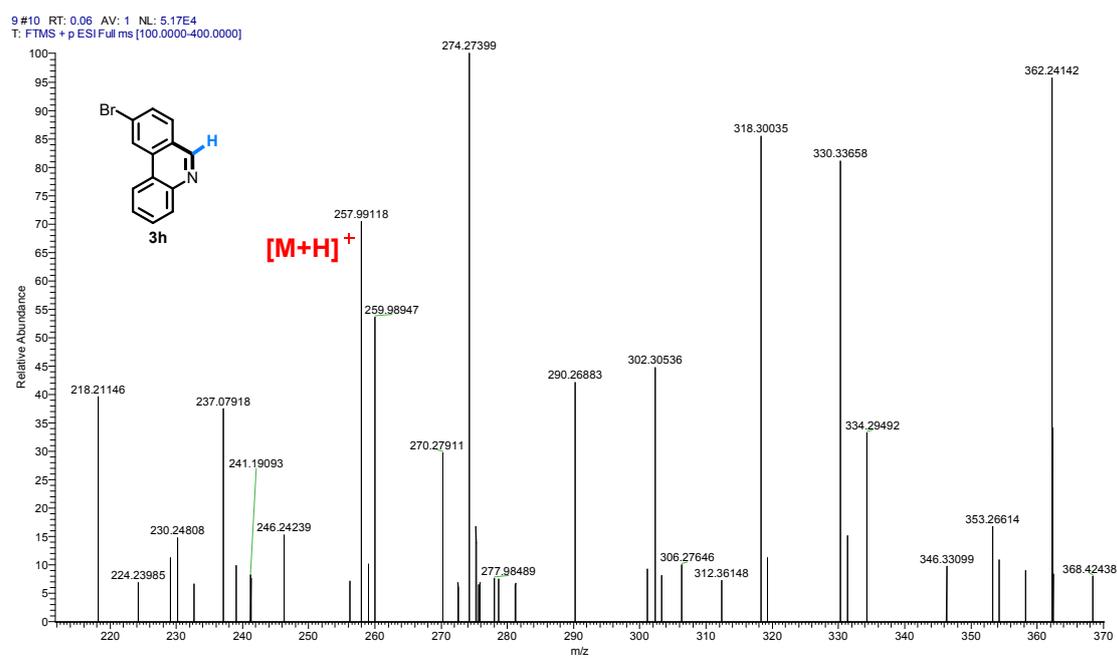
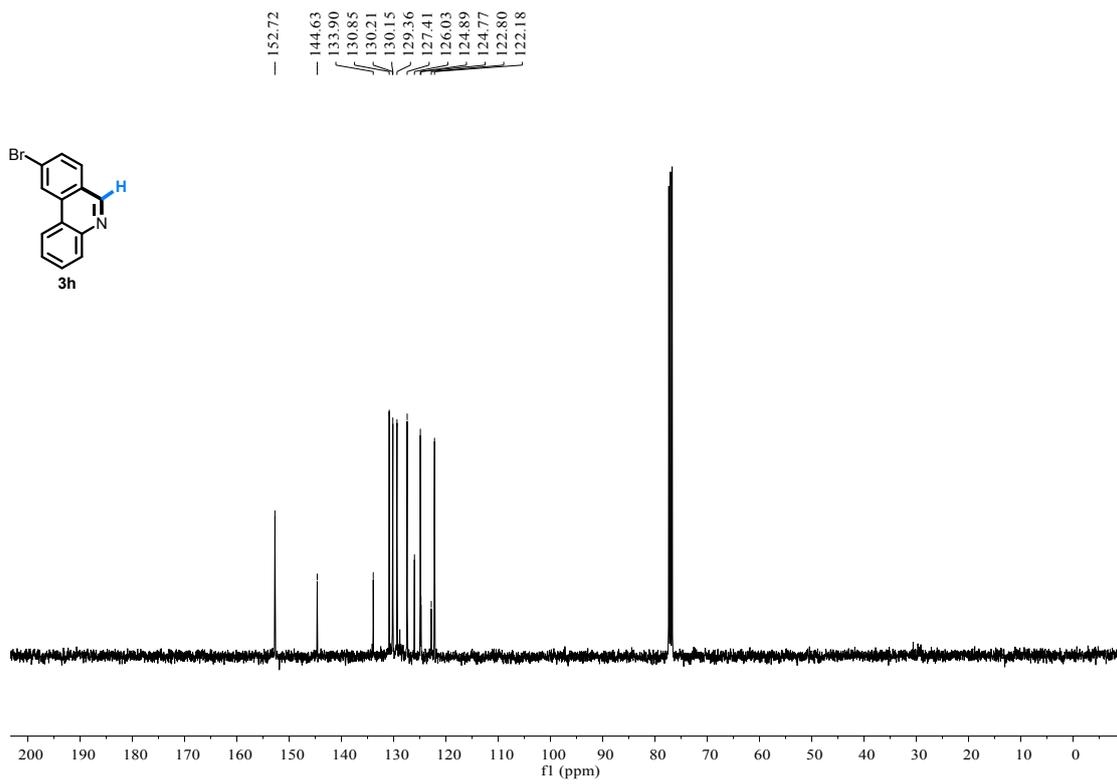


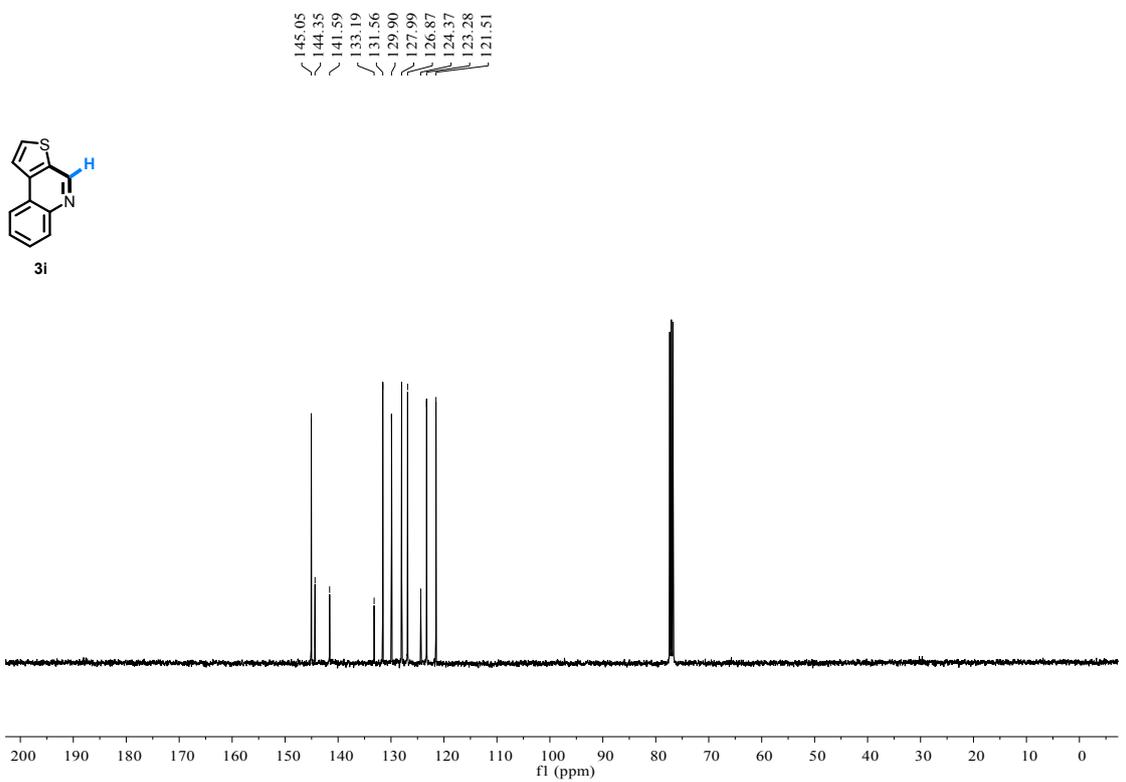
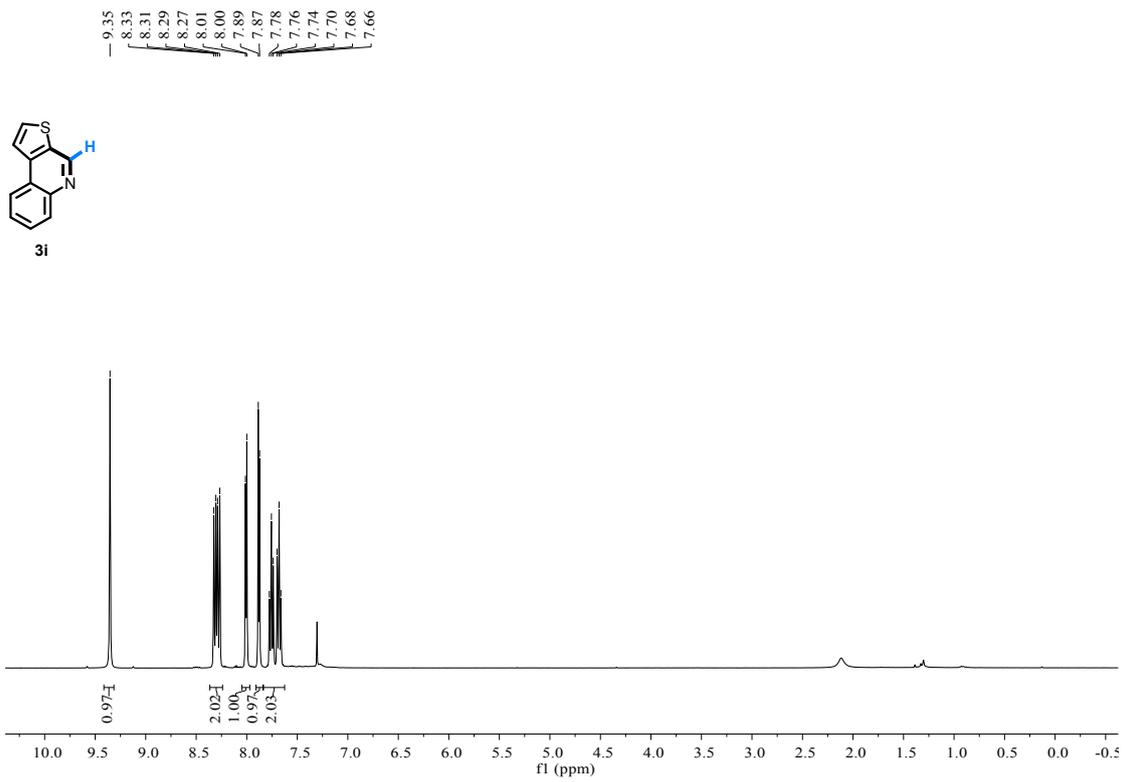
8 #8 RT: 0.05 AV: 1 NL: 5.39E4
T: FTMS + p ESI Full ms [100.0000-400.0000]



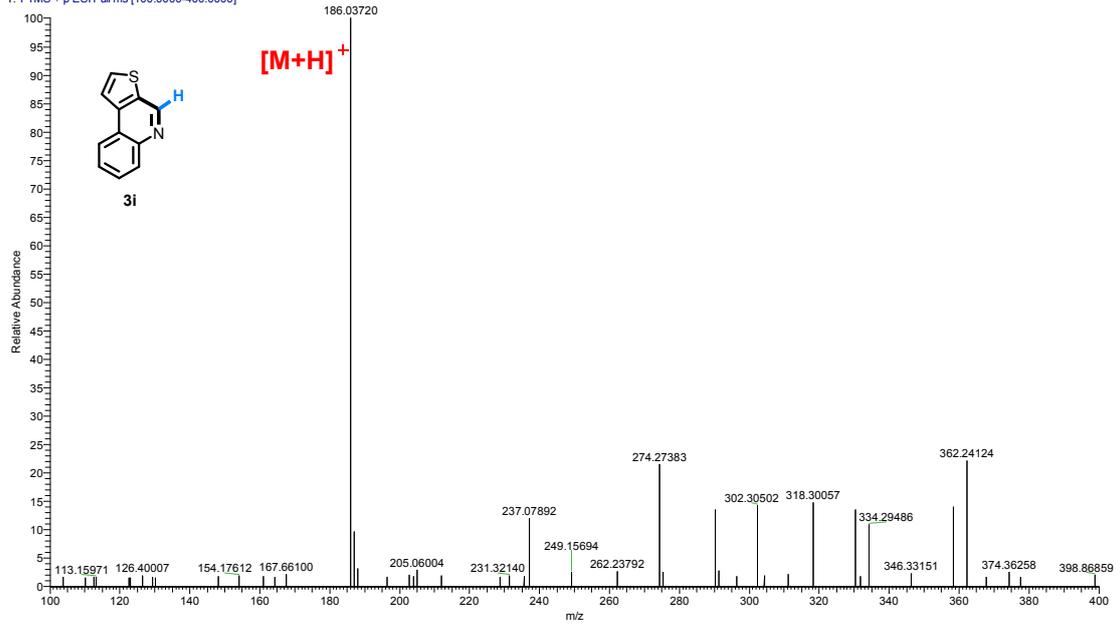
9.28
8.79
8.54
8.52
8.25
8.23
7.96
7.94
7.86
7.85
7.84
7.83
7.82
7.80
7.76
7.74
7.72



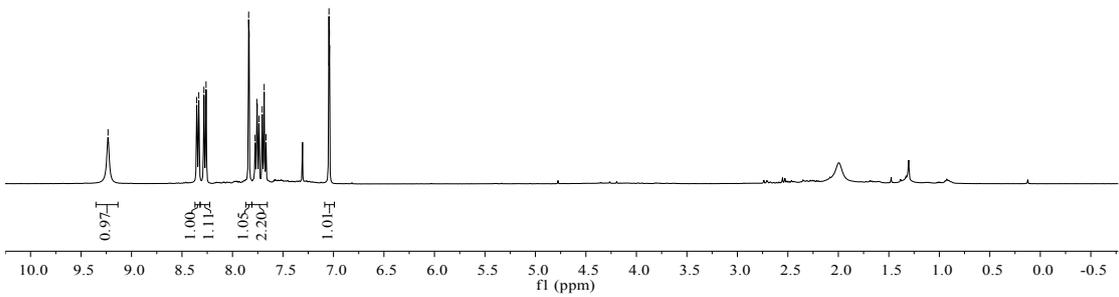
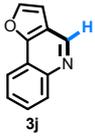


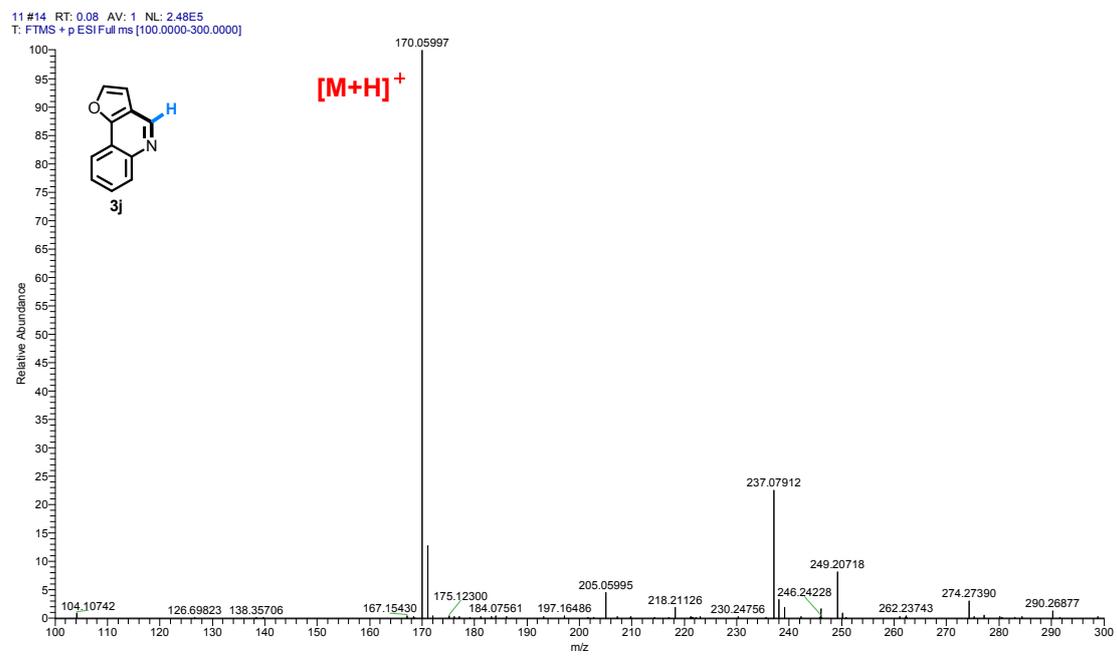
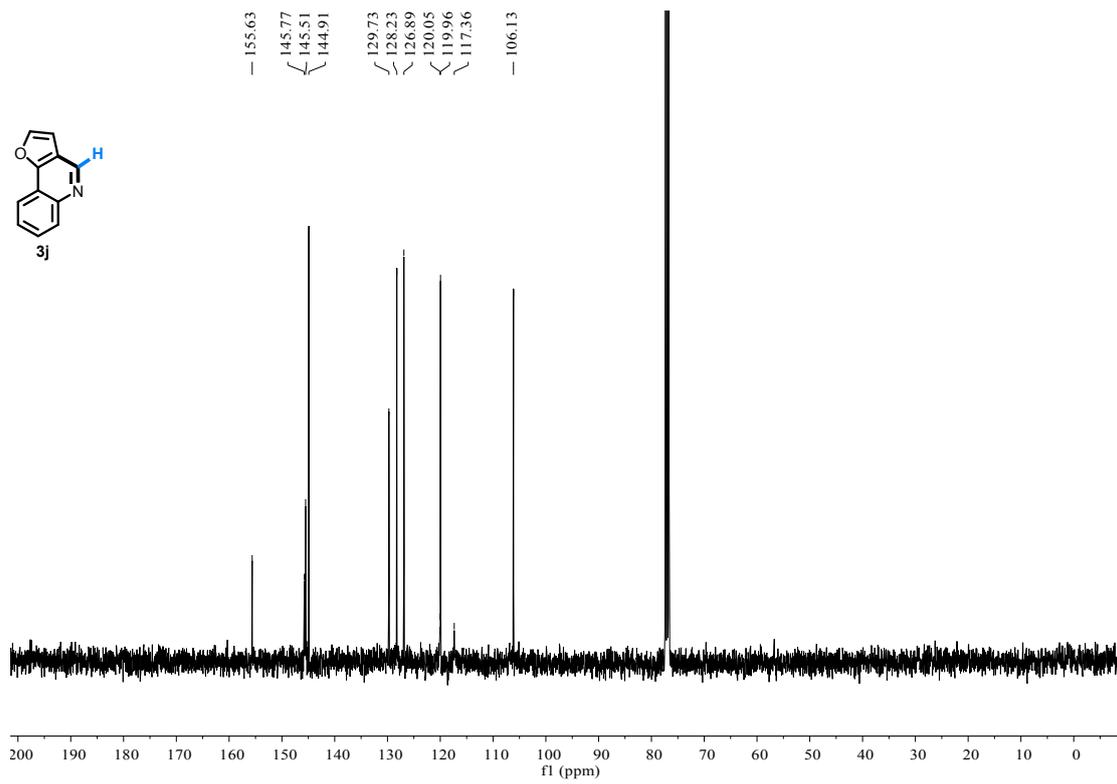


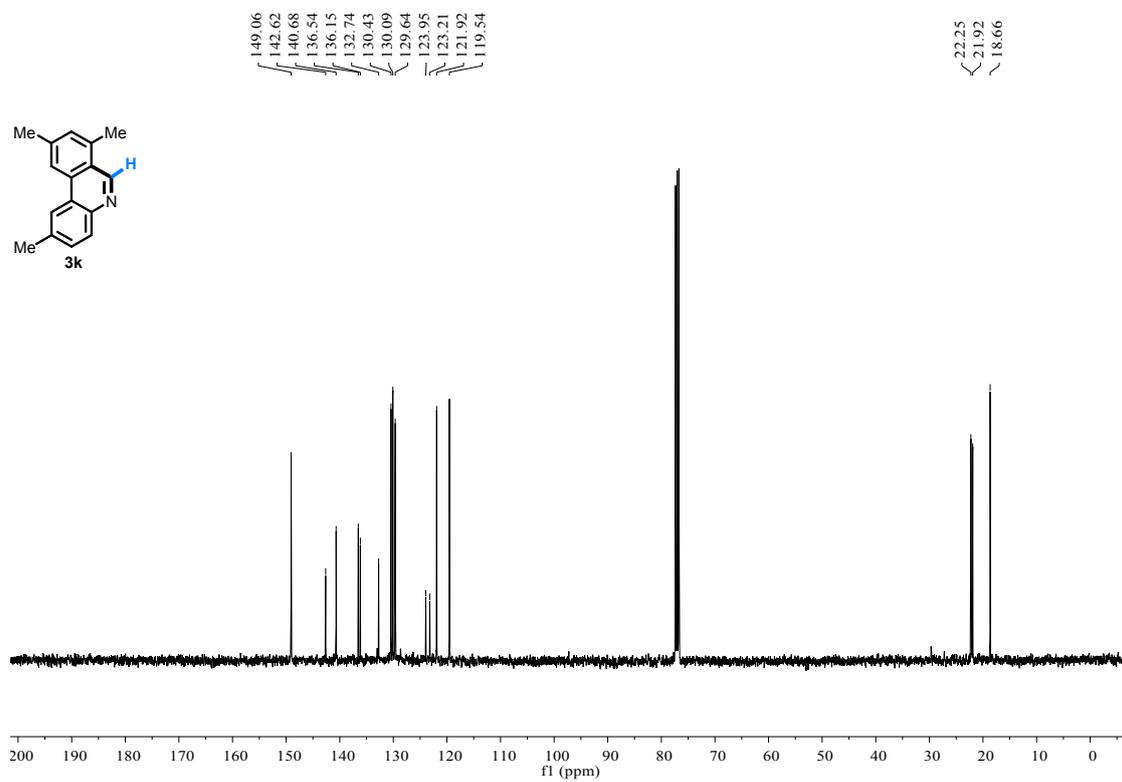
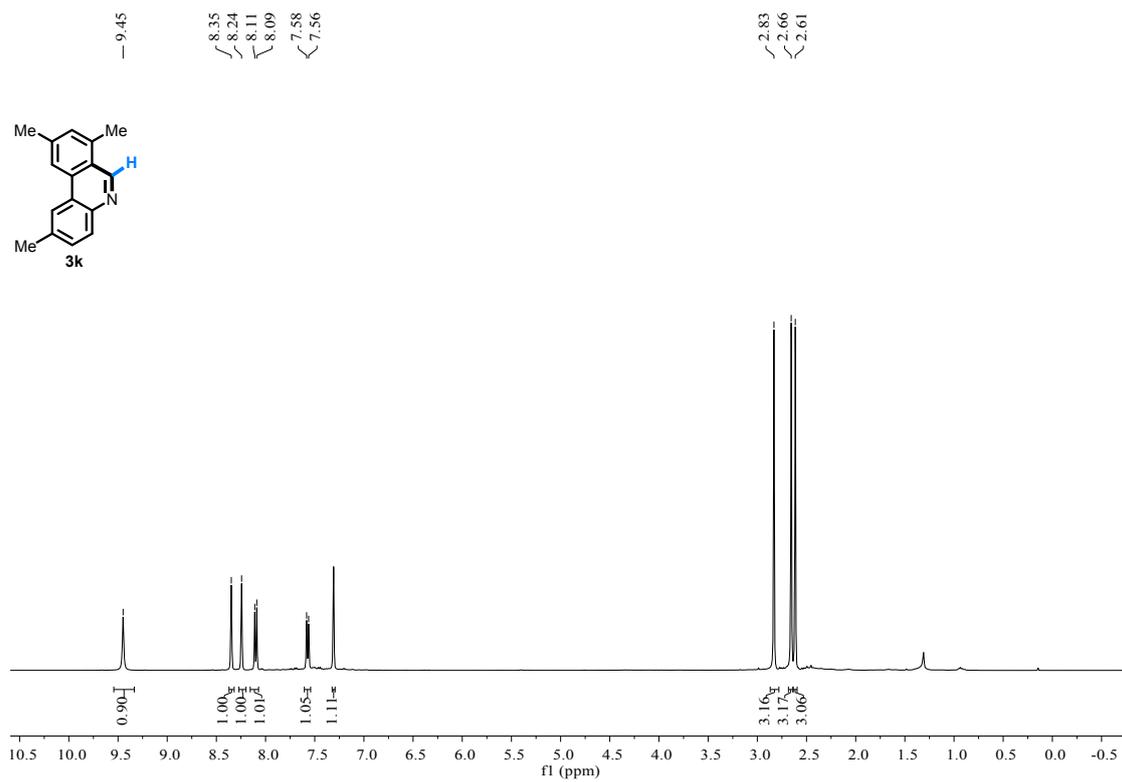
10 #4 RT: 0.02 AV: 1 NL: 3.09E4
T: FTMS + p ESI Full ms [100.0000-400.0000]



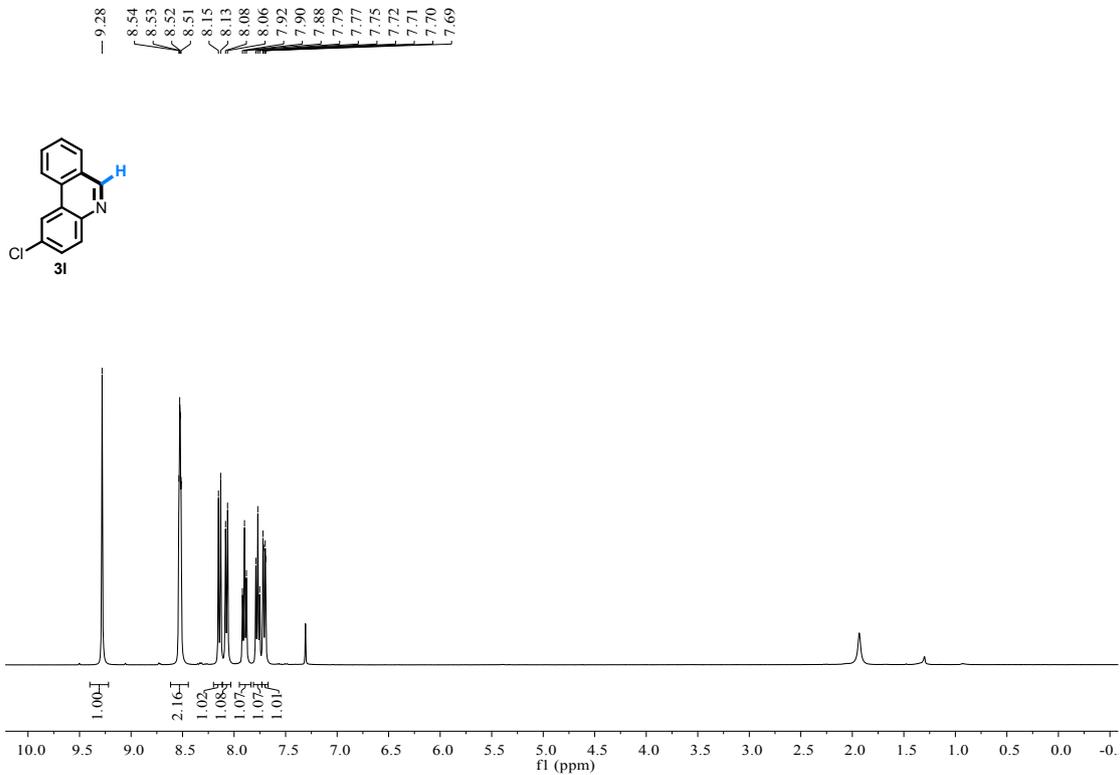
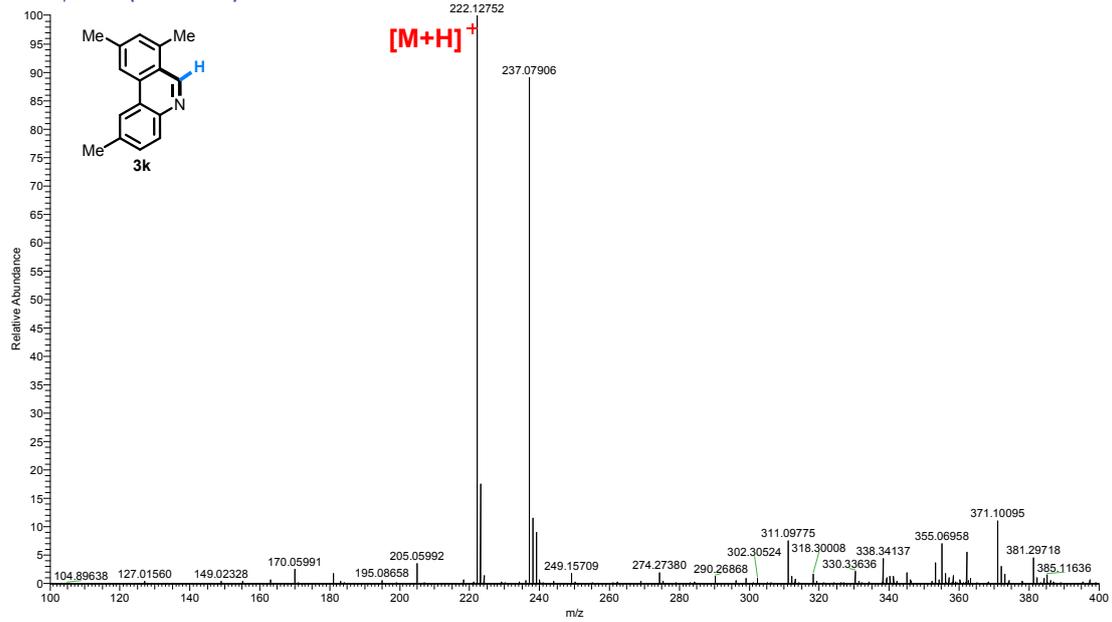
9.23
8.35
8.33
8.28
8.26
7.84
7.78
7.76
7.74
7.71
7.69
7.67
7.04
7.04

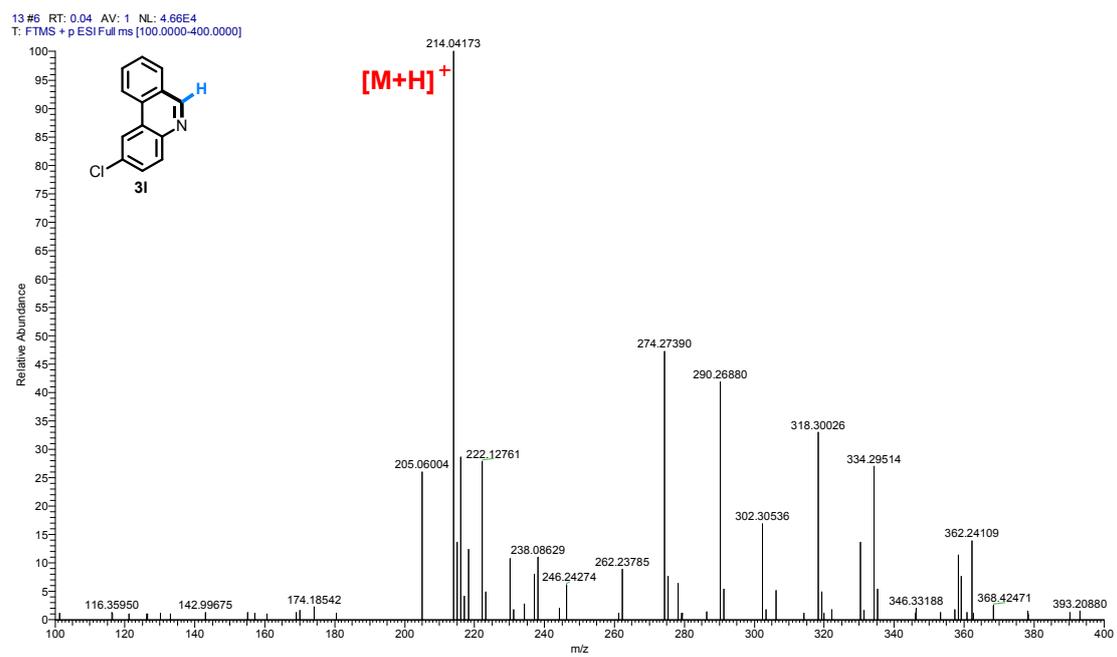
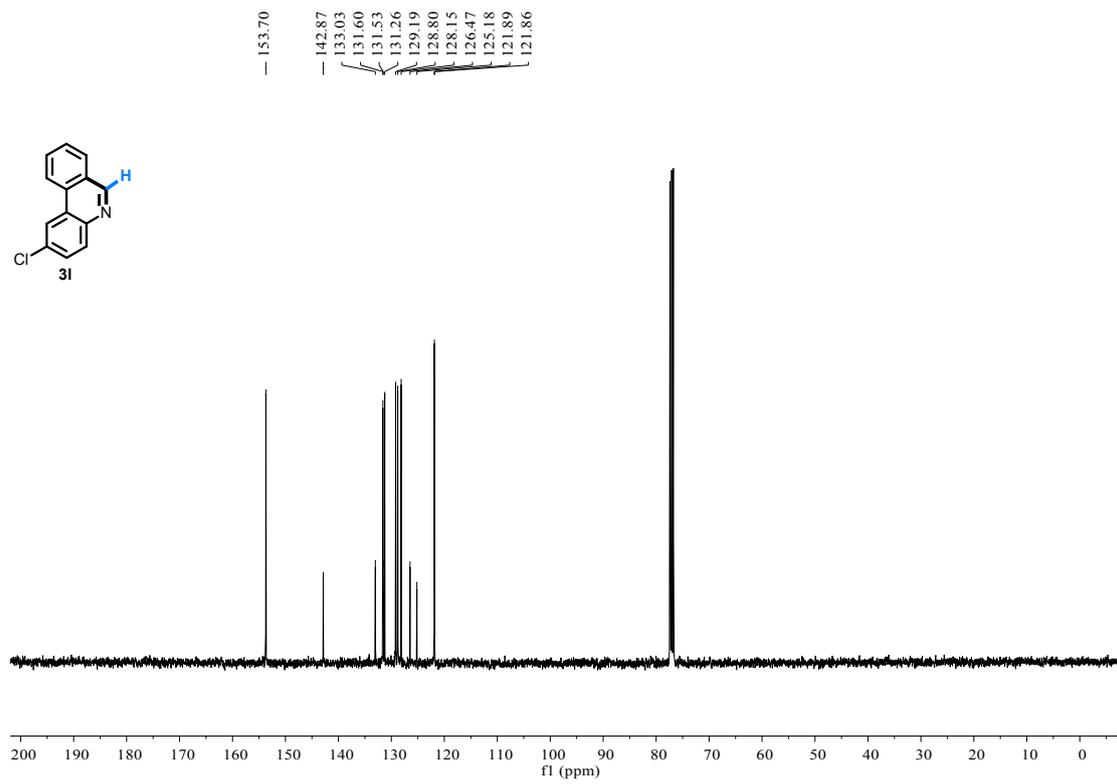


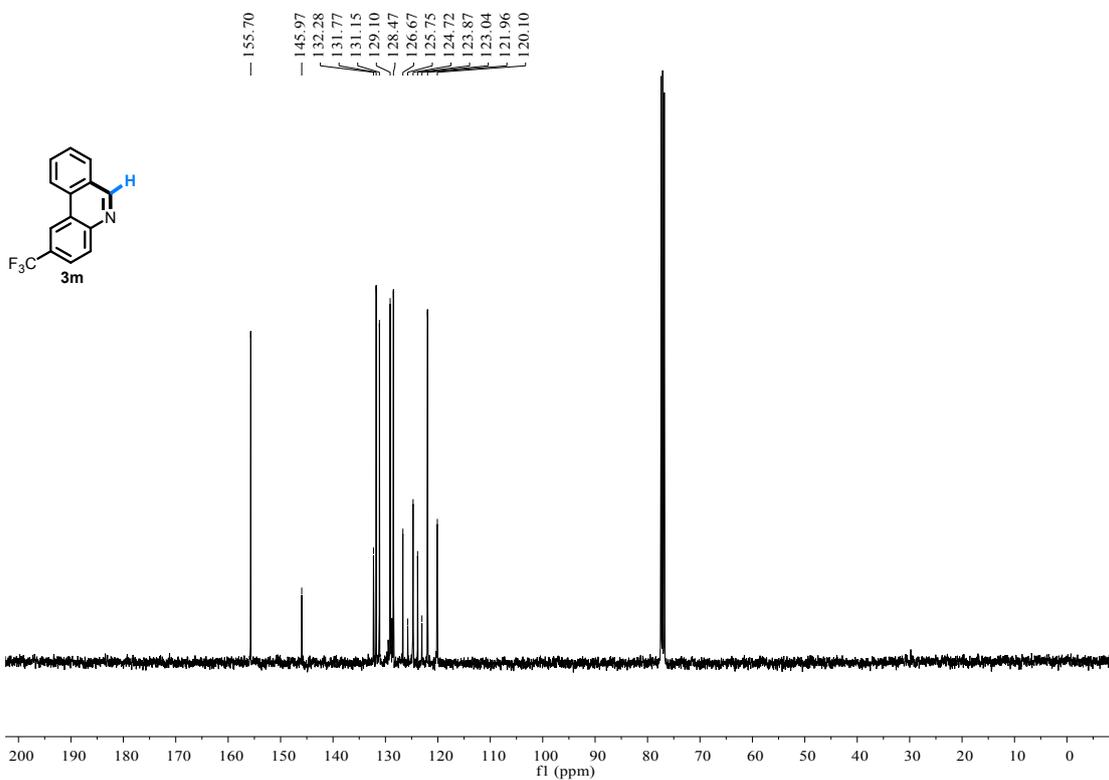
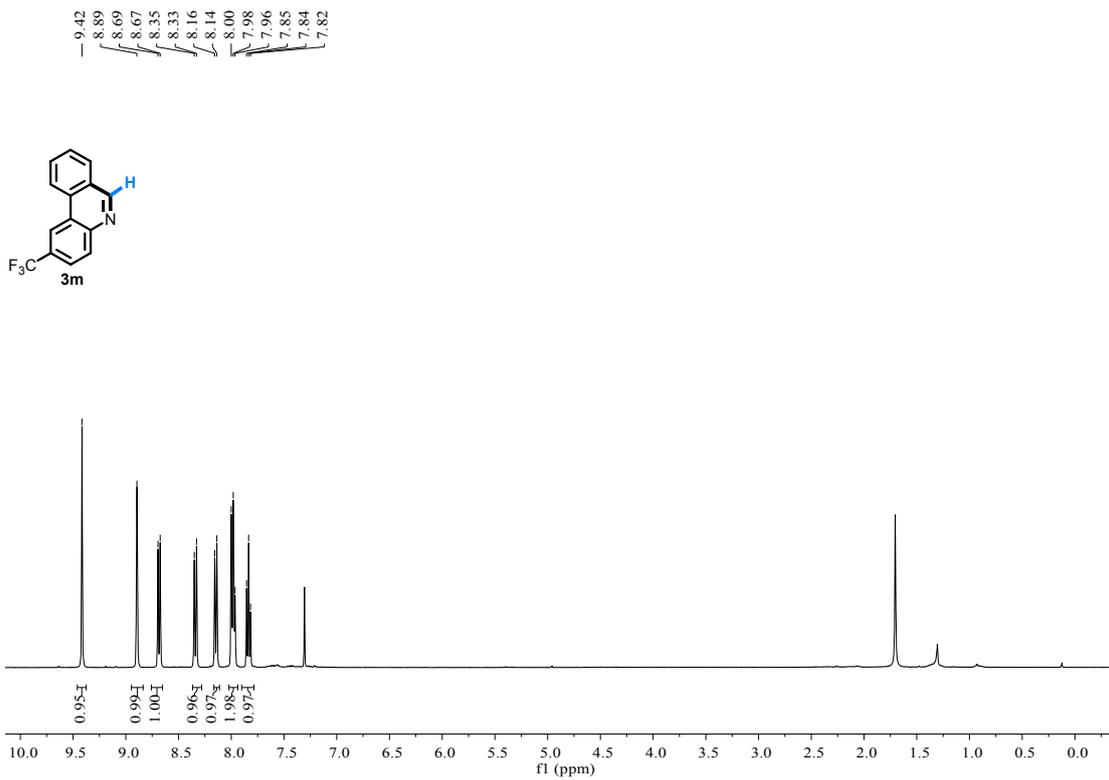




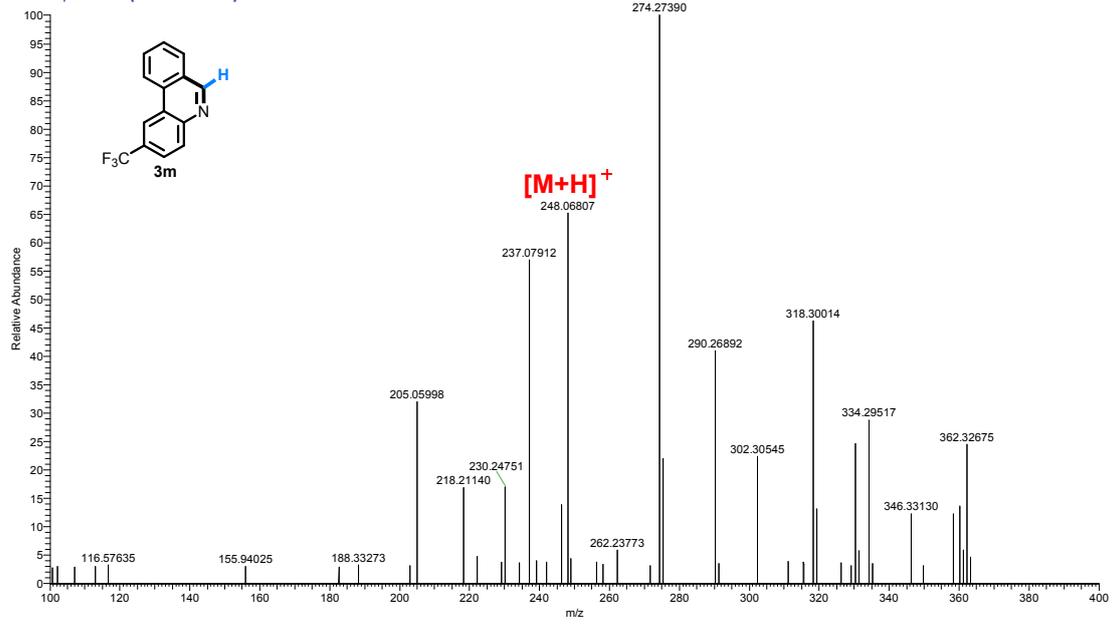
12#8 RT: 0.05 AV: 1 NL: 9.26E5
T: FTMS + p ESI Full ms [100.0000-400.0000]



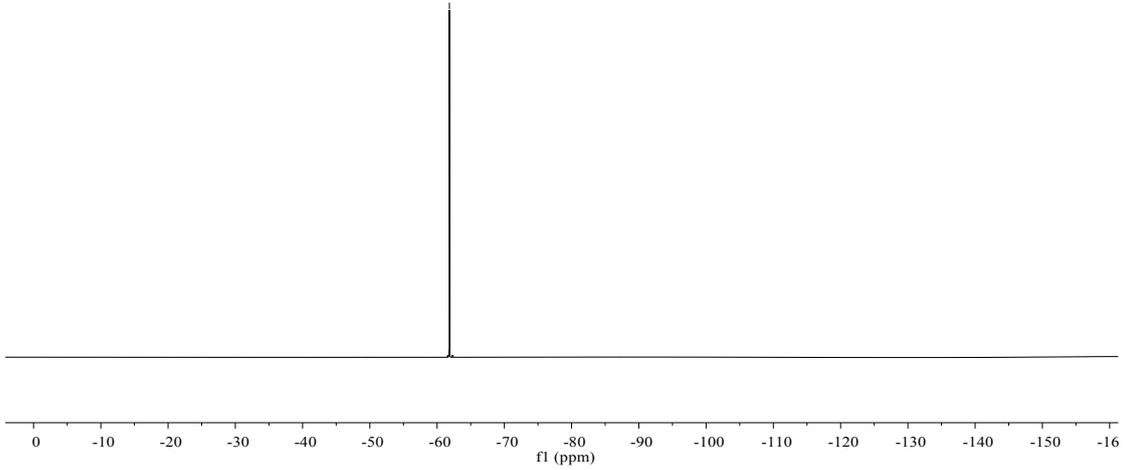


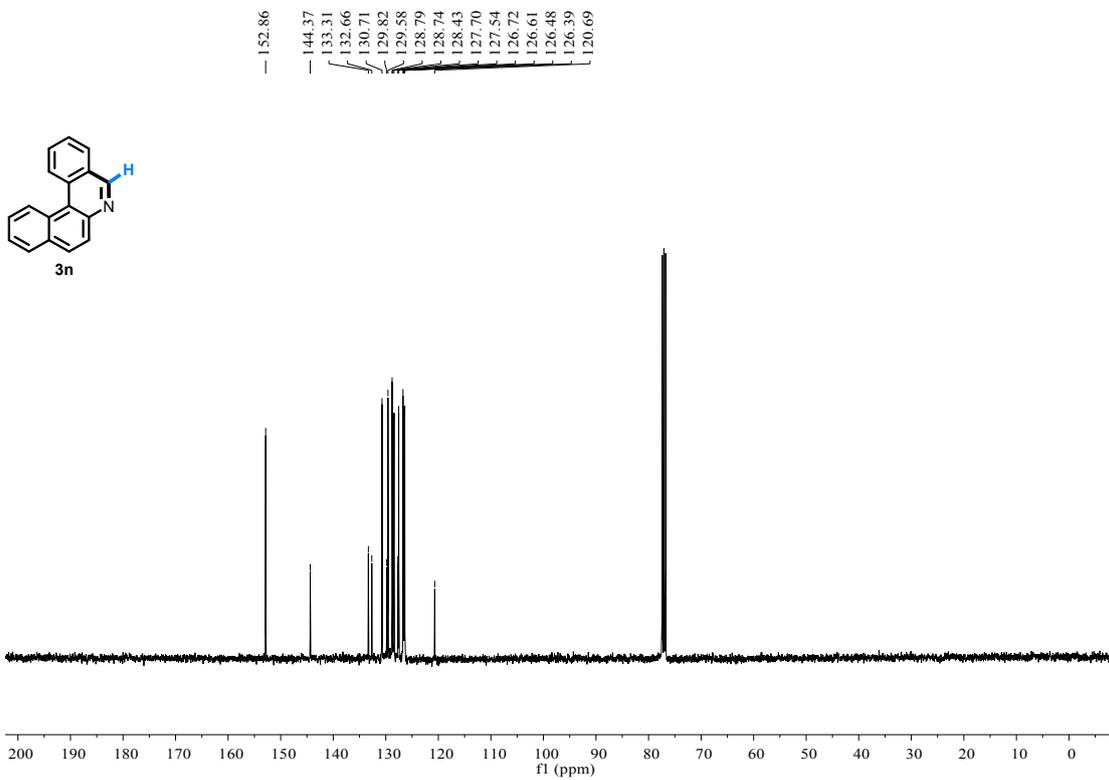
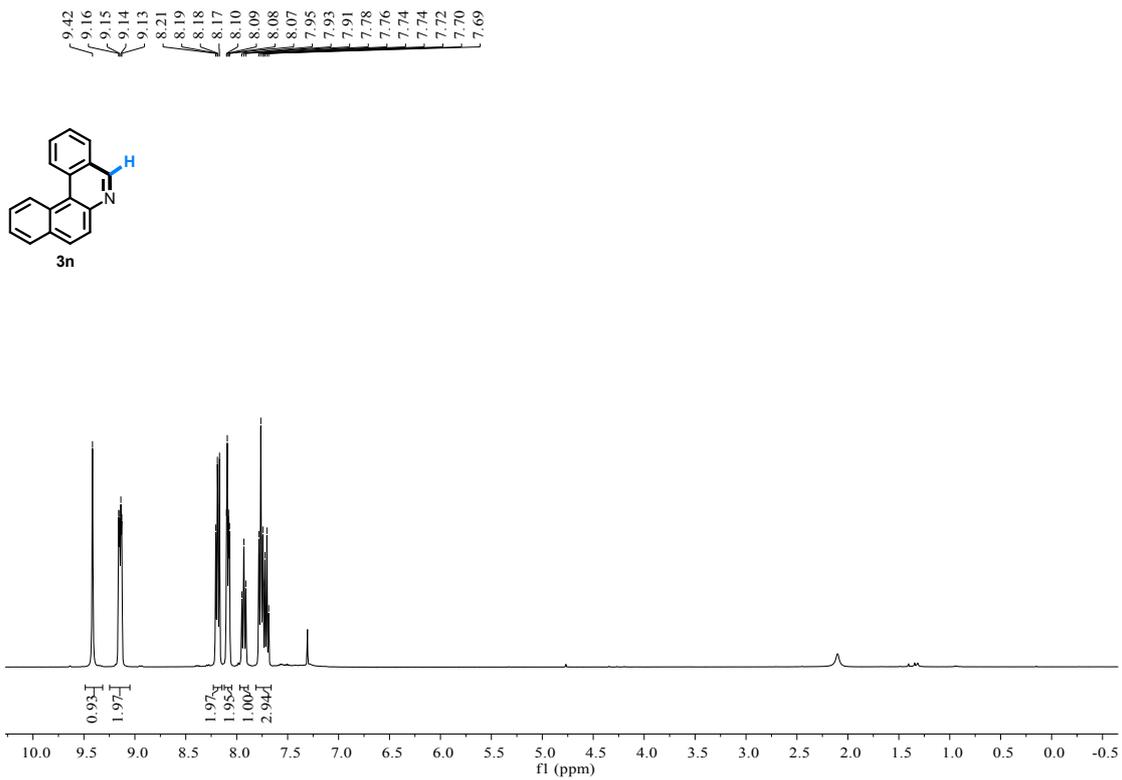


14#1 RT: 0.01 AV: 1 NL: 1.73E4
T: FTMS + p ESI Full ms [100.0000-400.0000]

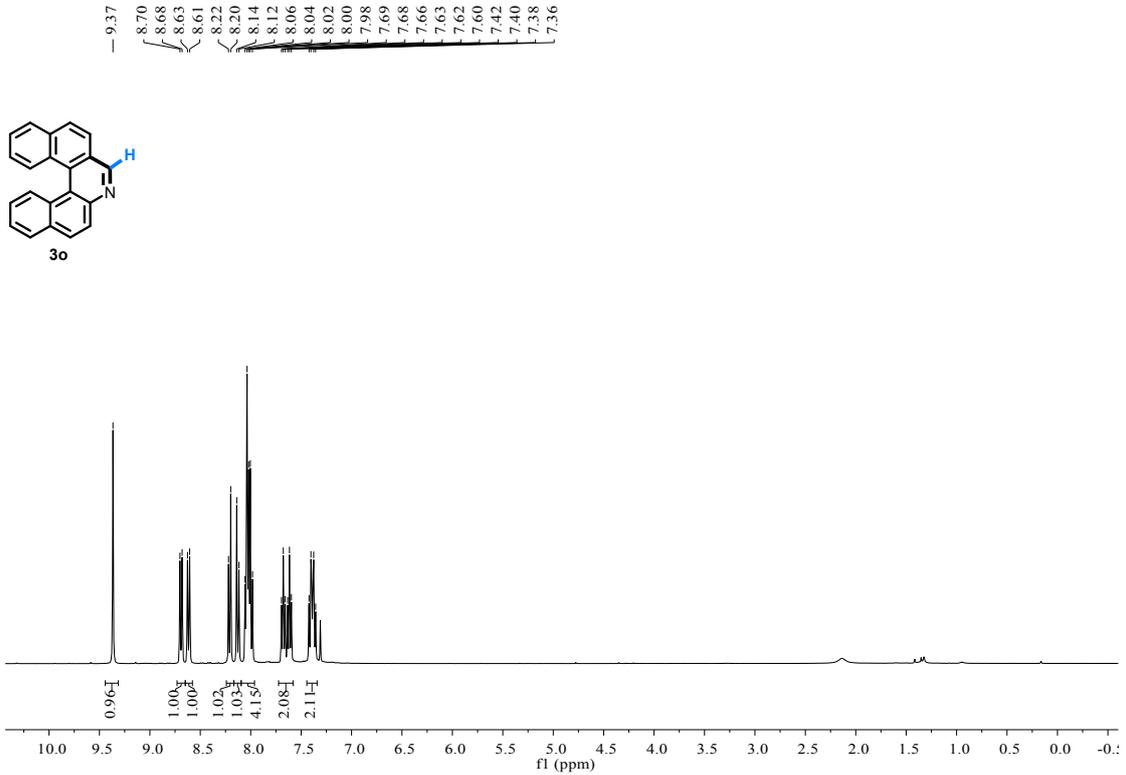
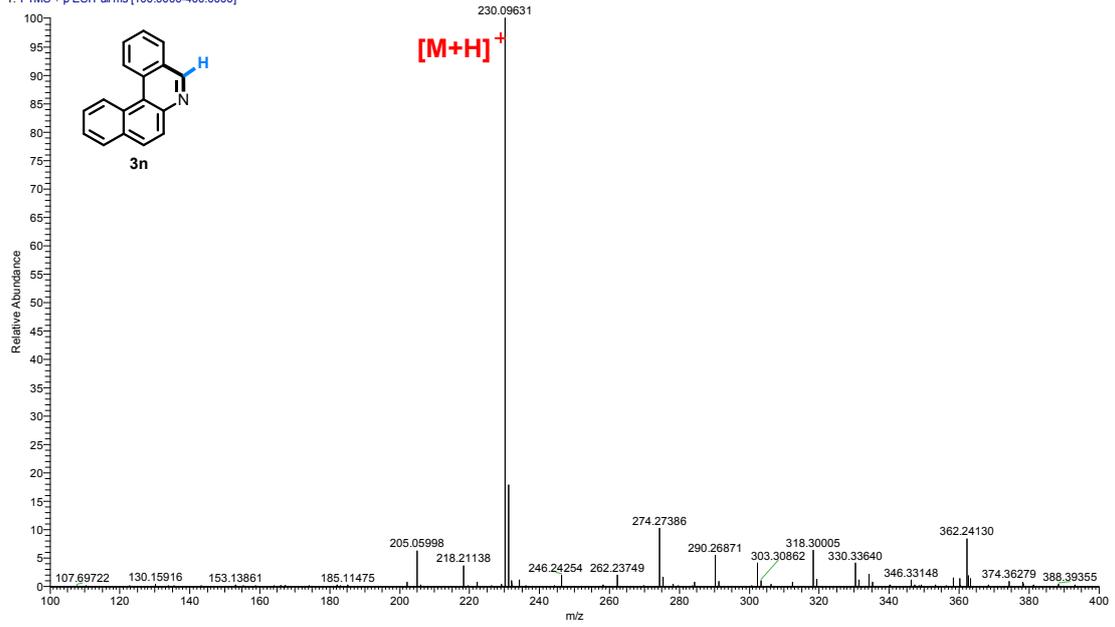


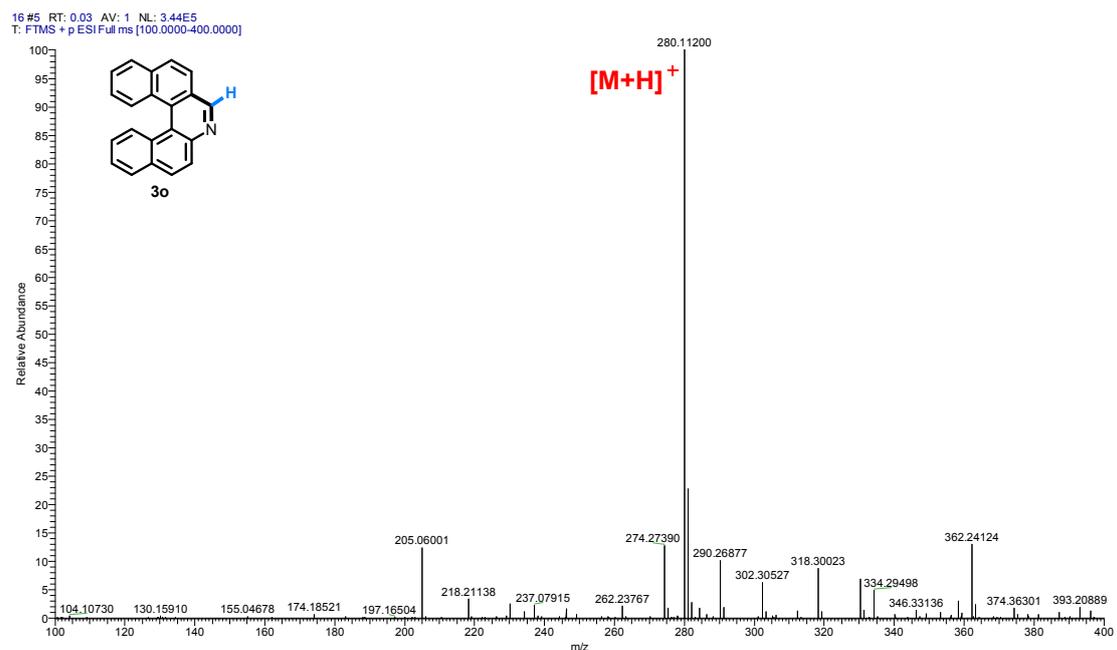
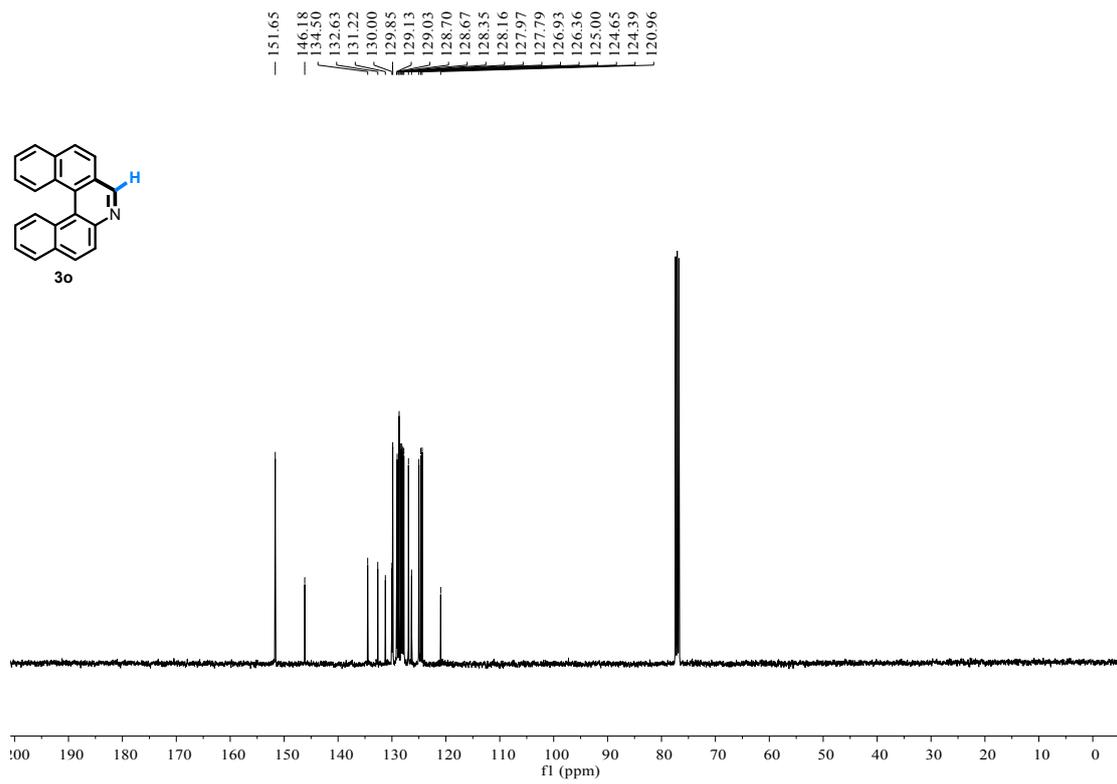
-61.83

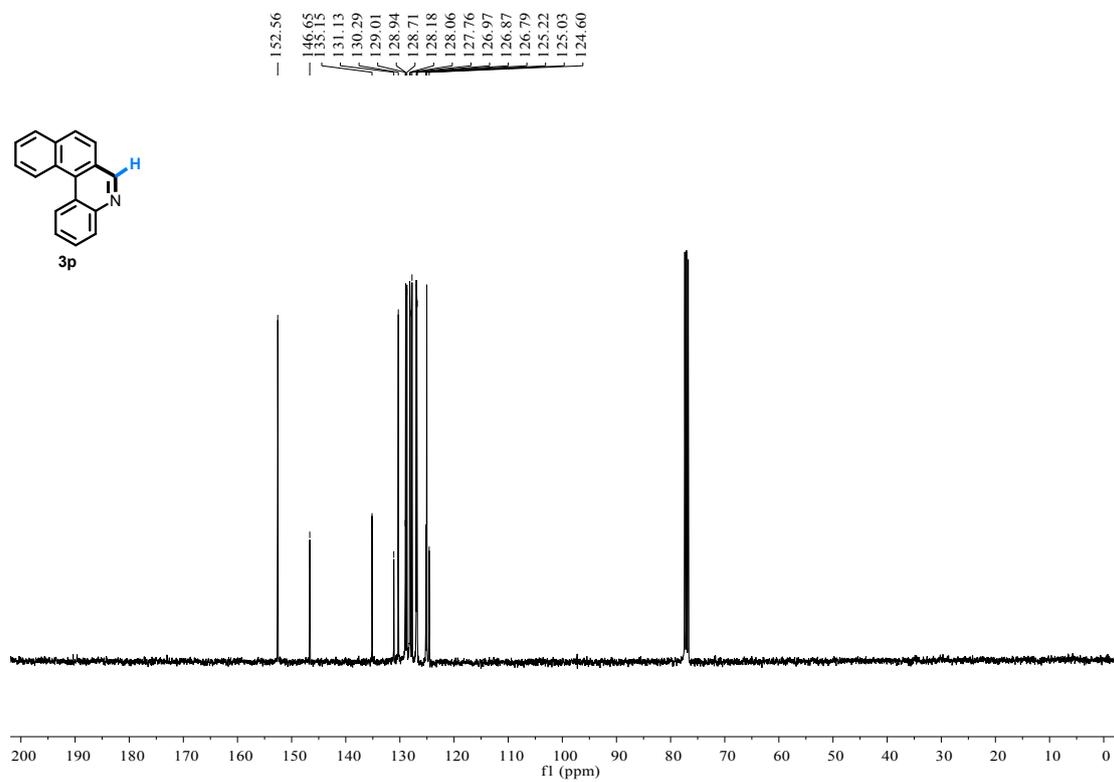
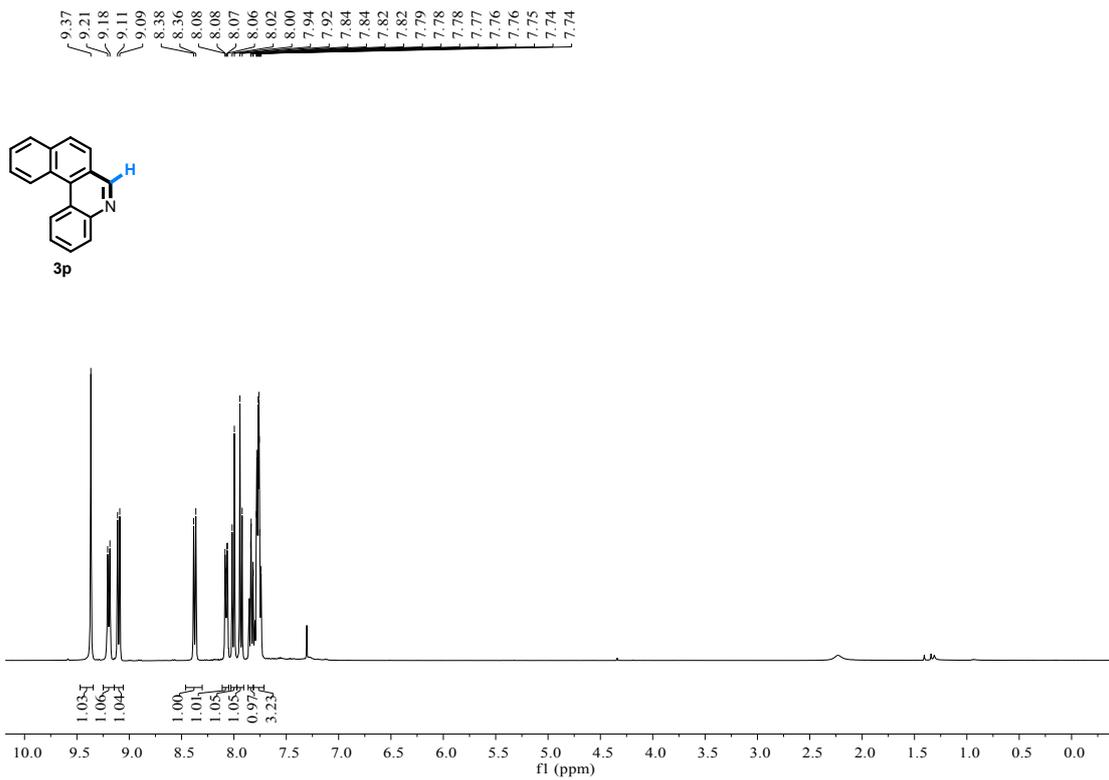




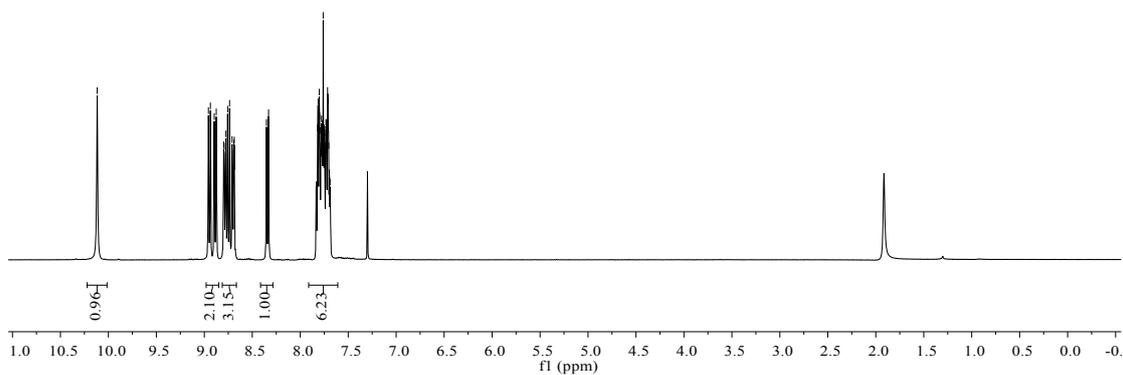
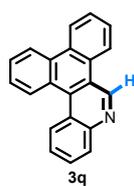
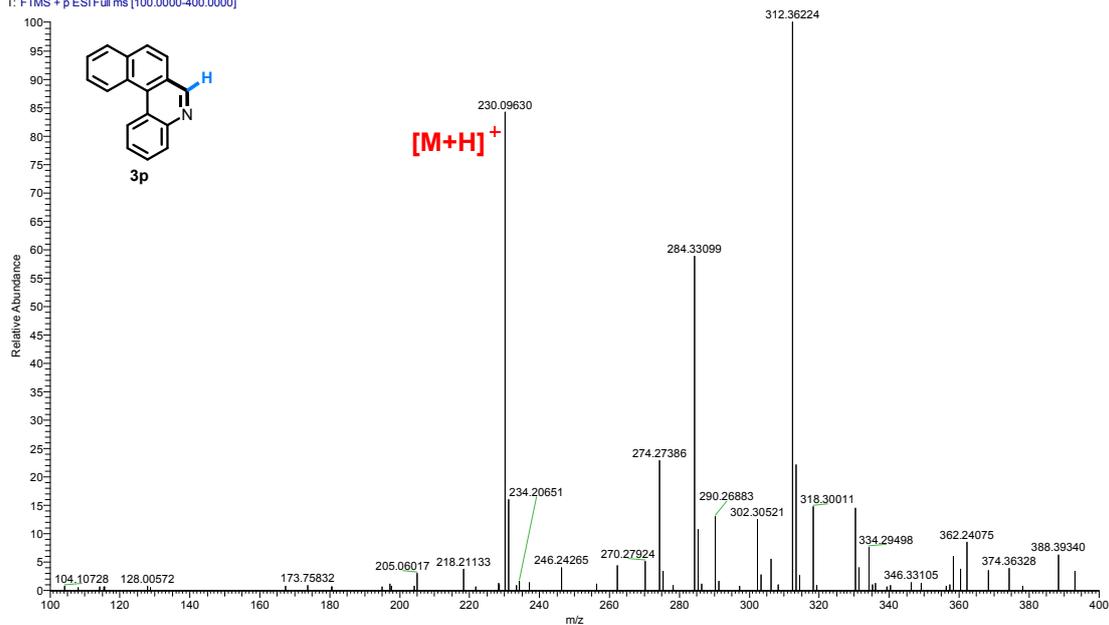
15#3 RT: 0.02 AV: 1 NL: 3.15E5
T: FTMS + p ESI Full ms [100.0000-400.0000]

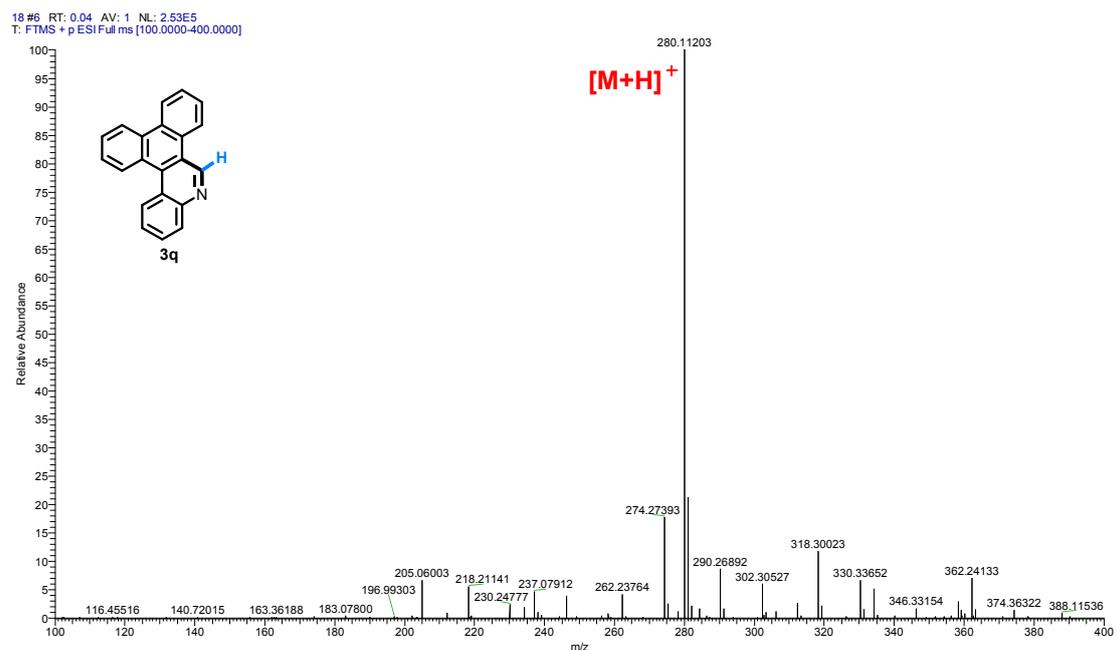
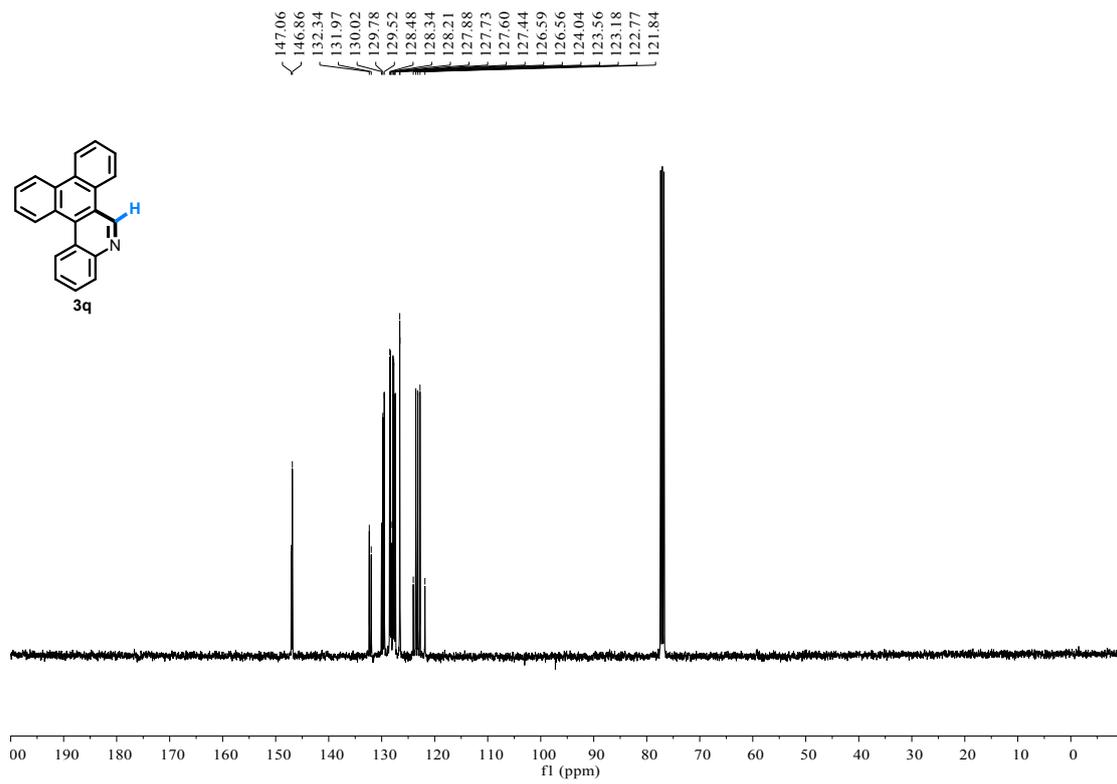




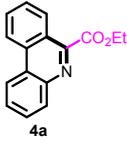
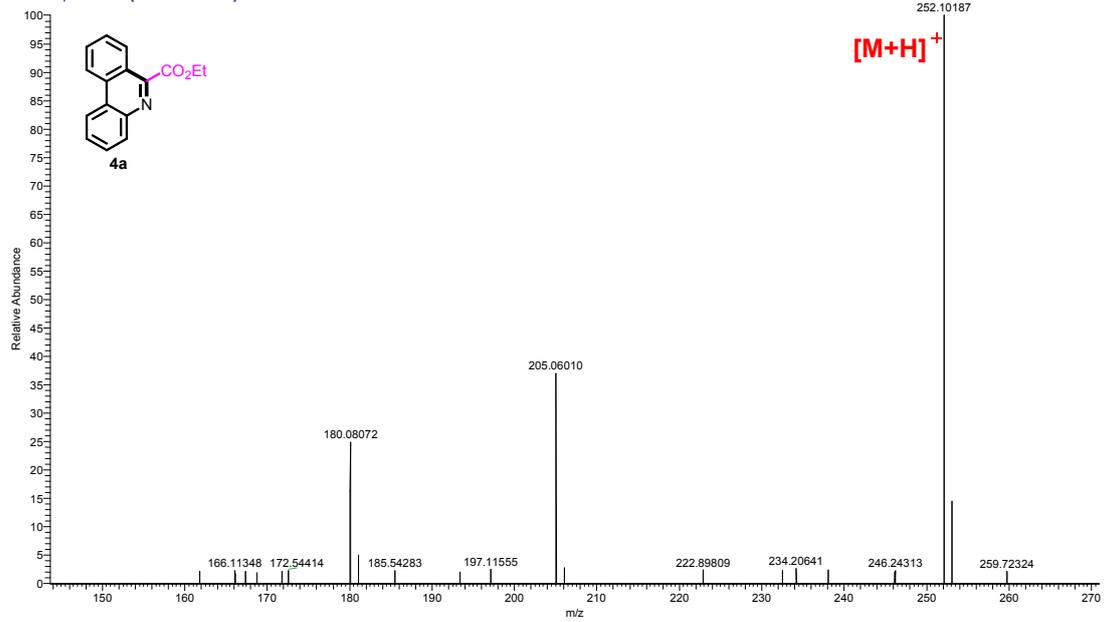


17#3 RT: 0.02 AV: 1 NL: 7.62E4
T: FTMS + p ESI Full ms [100.0000-400.0000]

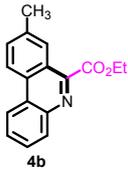
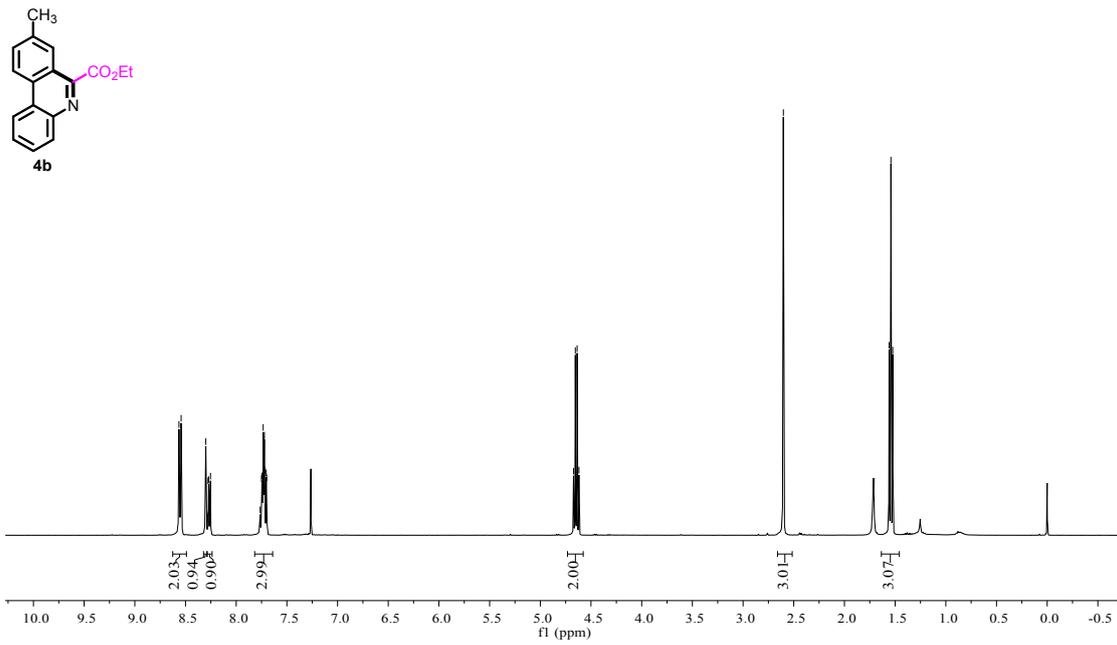


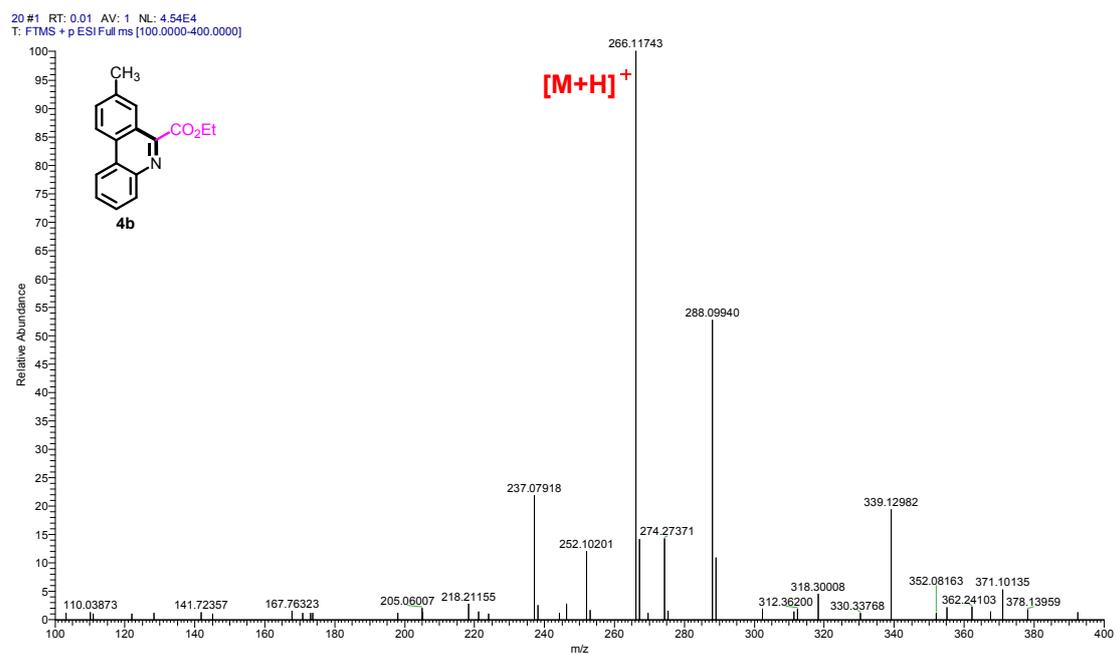
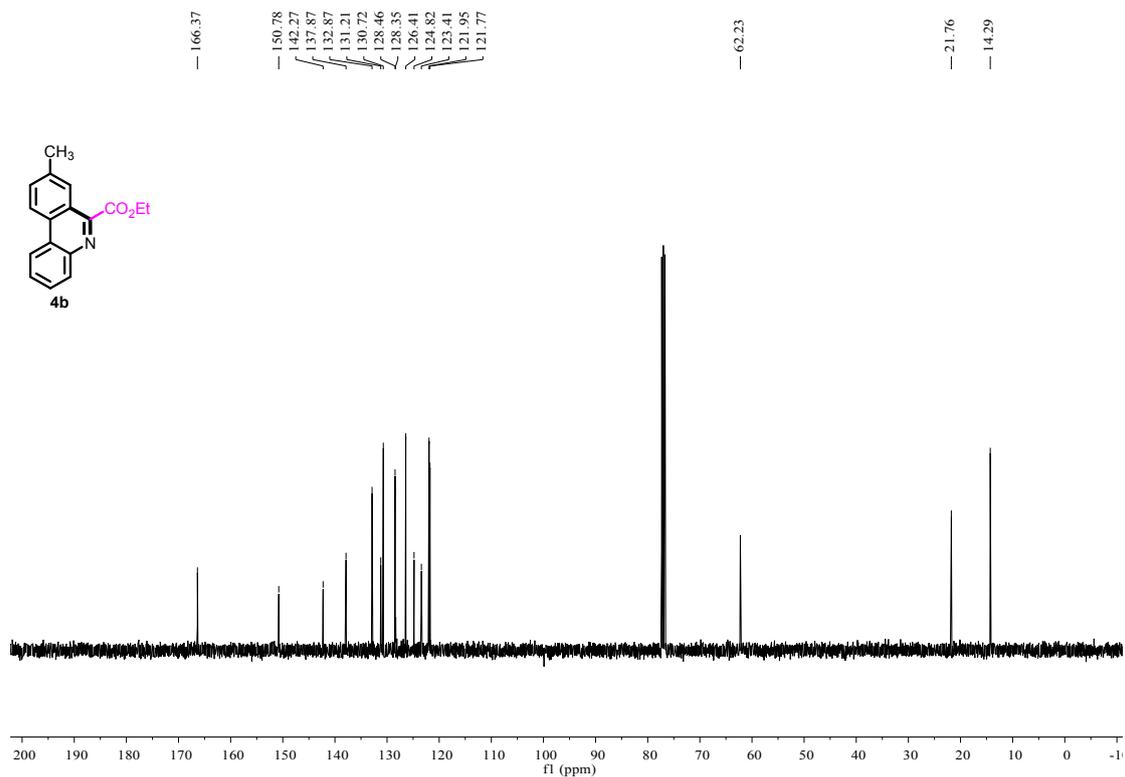


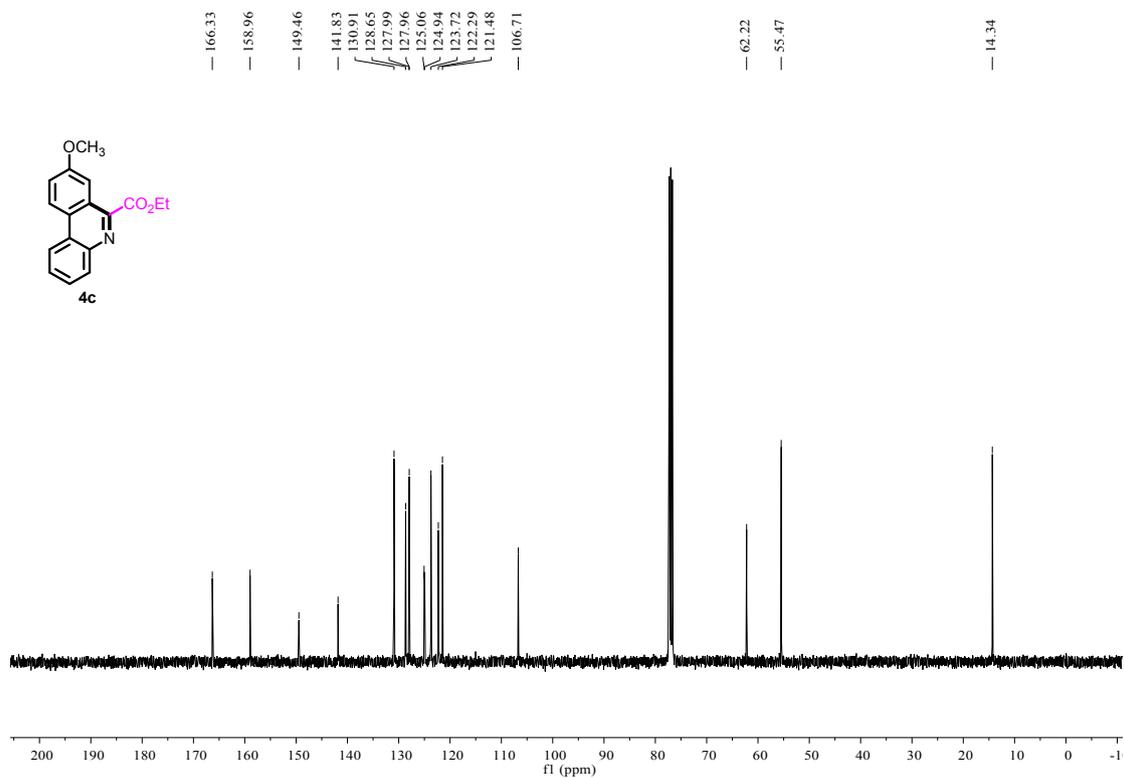
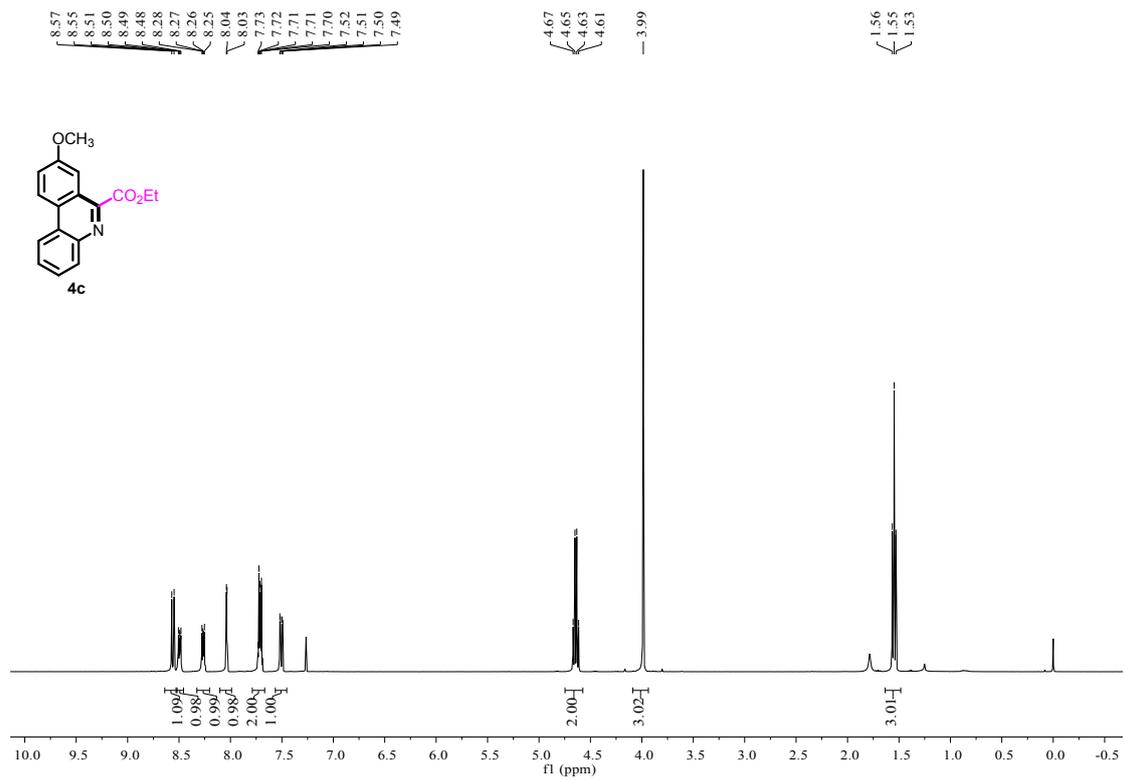
19#14 RT: 0.08 AV: 1 NL: 1.59E5
T: FTMS + p ESI Full ms [100.0000-400.0000]



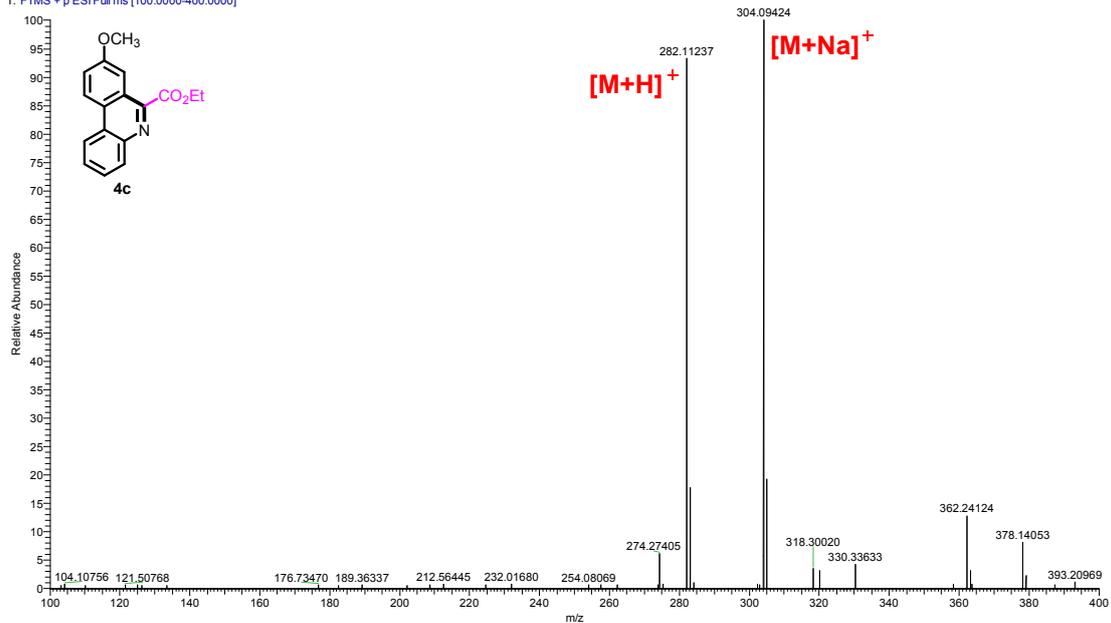
8.56, 8.55, 8.54, 8.30, 8.28, 8.27, 8.26, 8.25, 7.76, 7.75, 7.74, 7.73, 7.72, 7.70, 4.67, 4.65, 4.64, 4.62, -2.60, 1.56, 1.54, 1.52



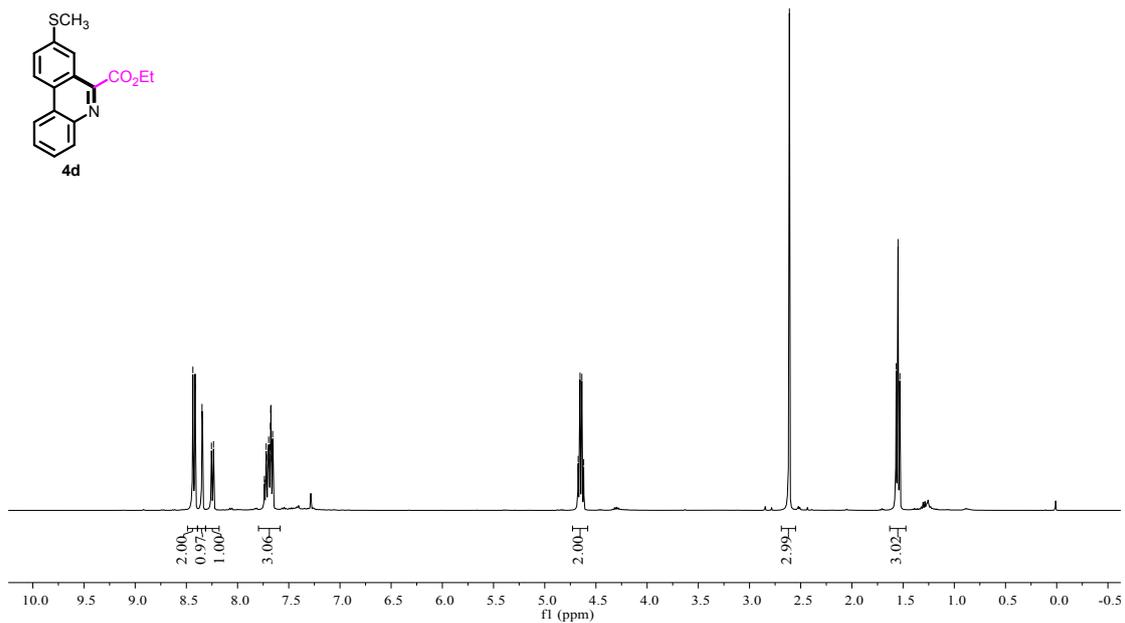


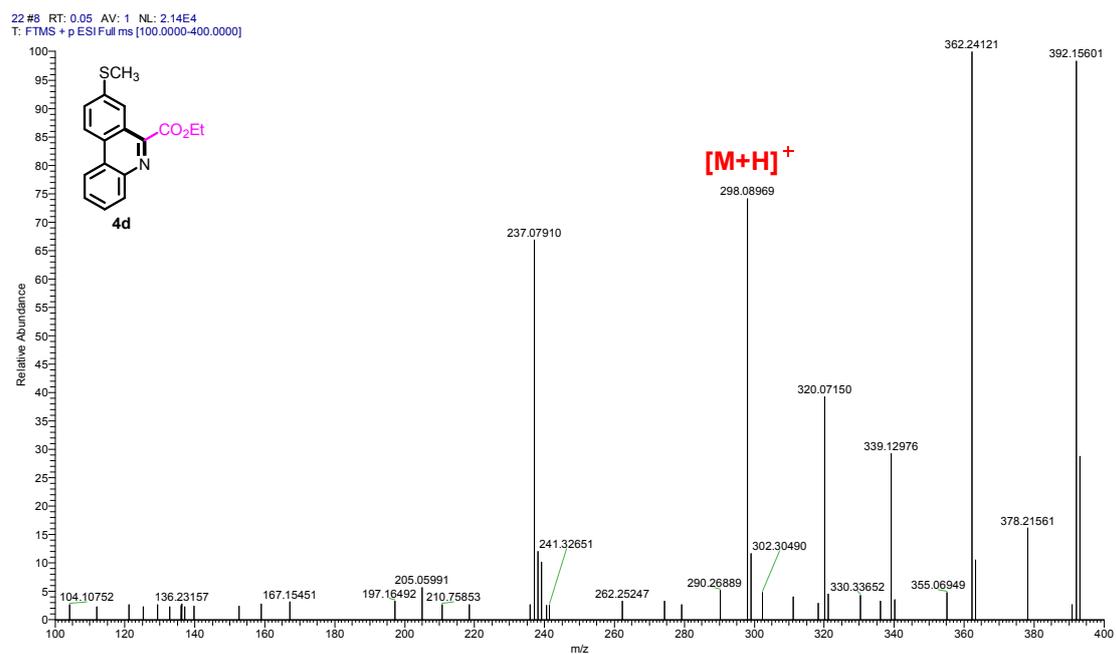
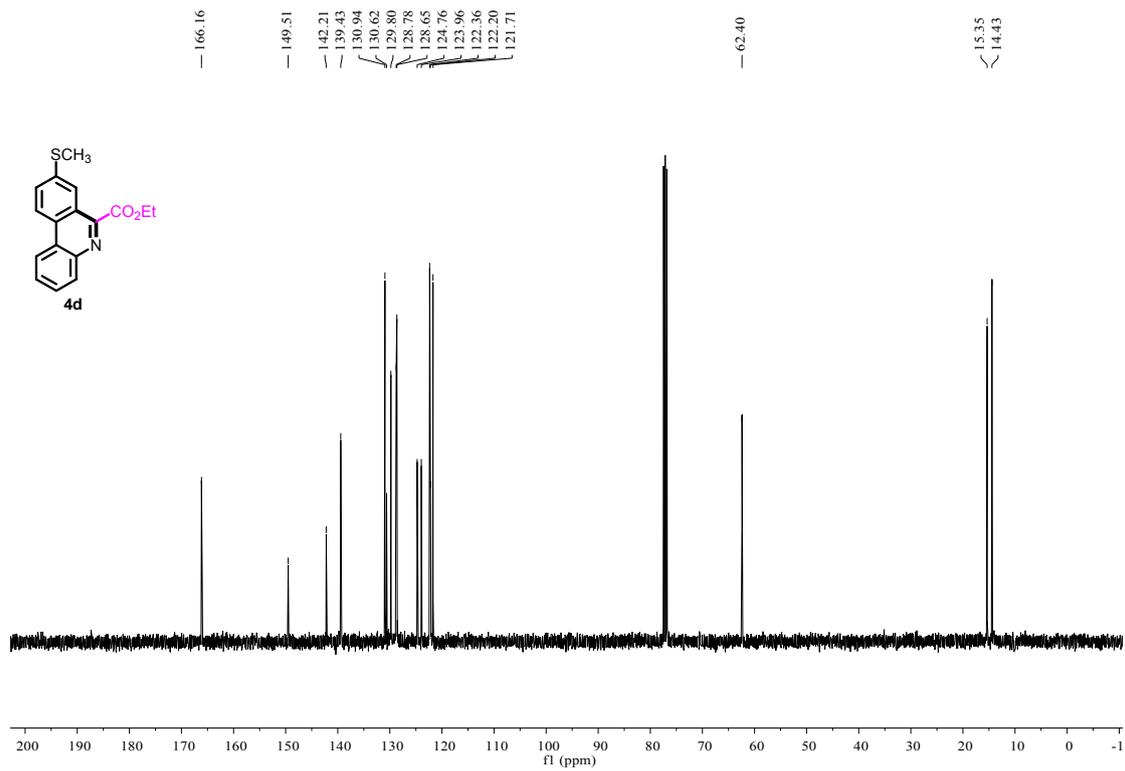


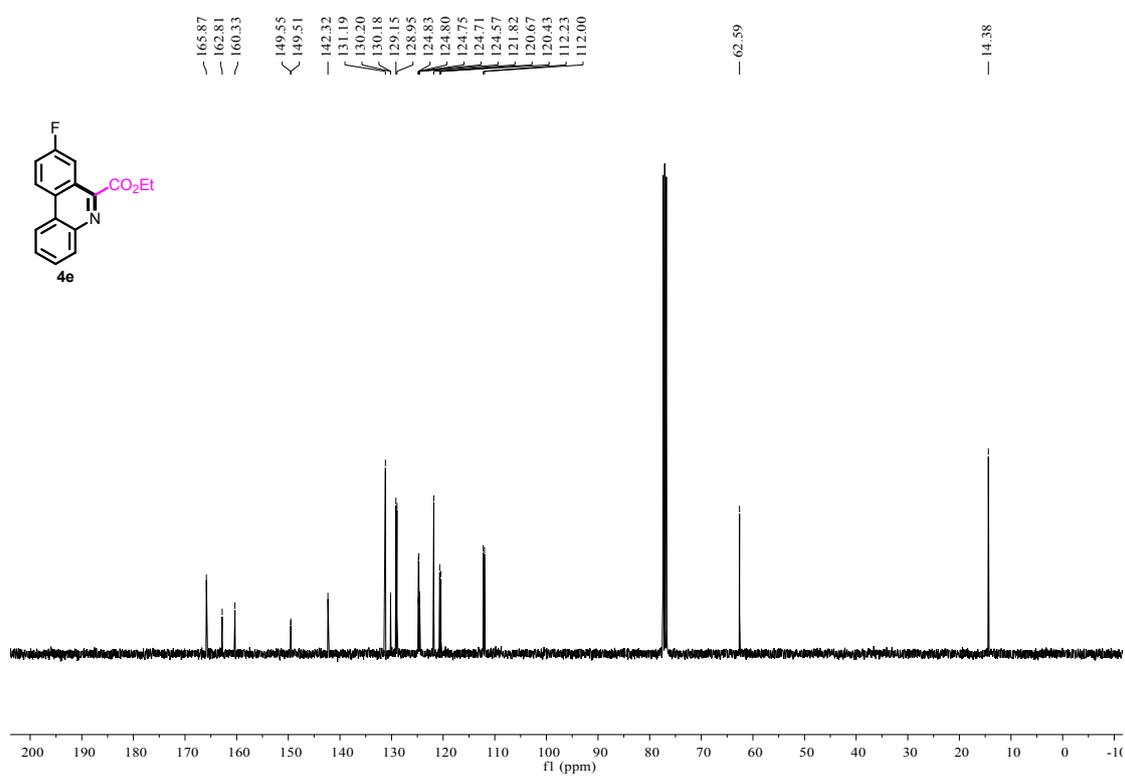
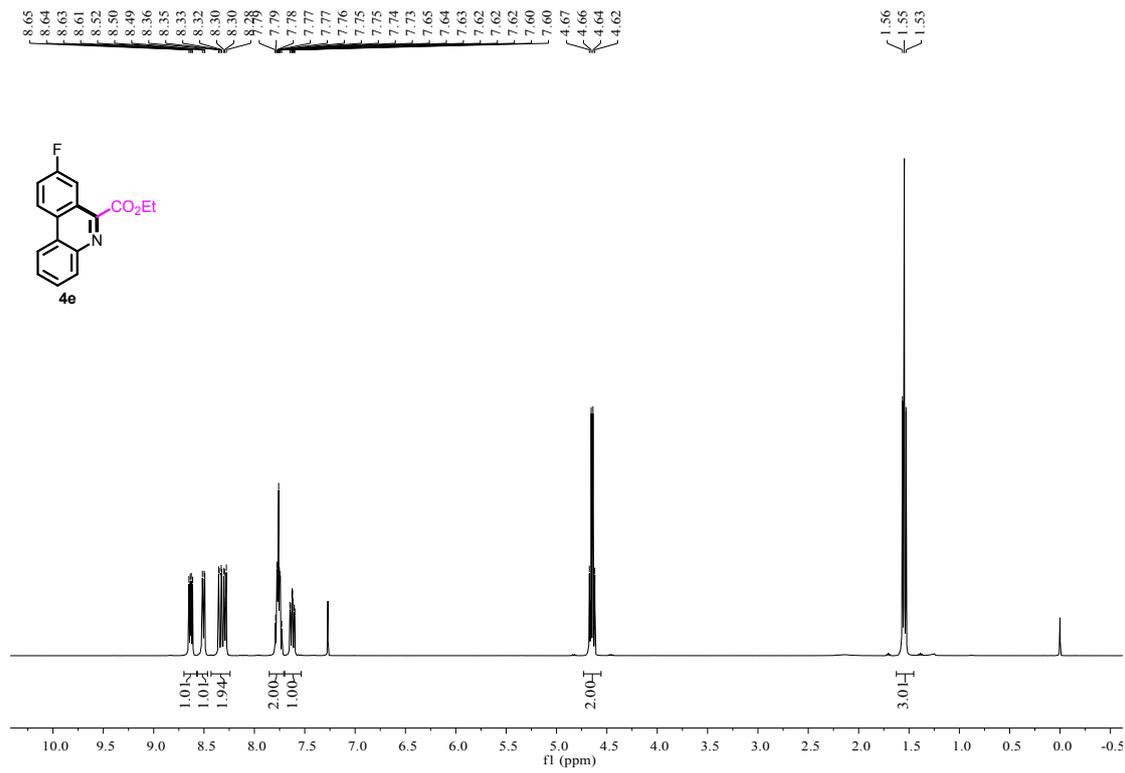
21 #11 RT: 0.07 AV: 1 NL: 8.33E4
 T: FTMS + p ESI Full ms [100.0000-400.0000]

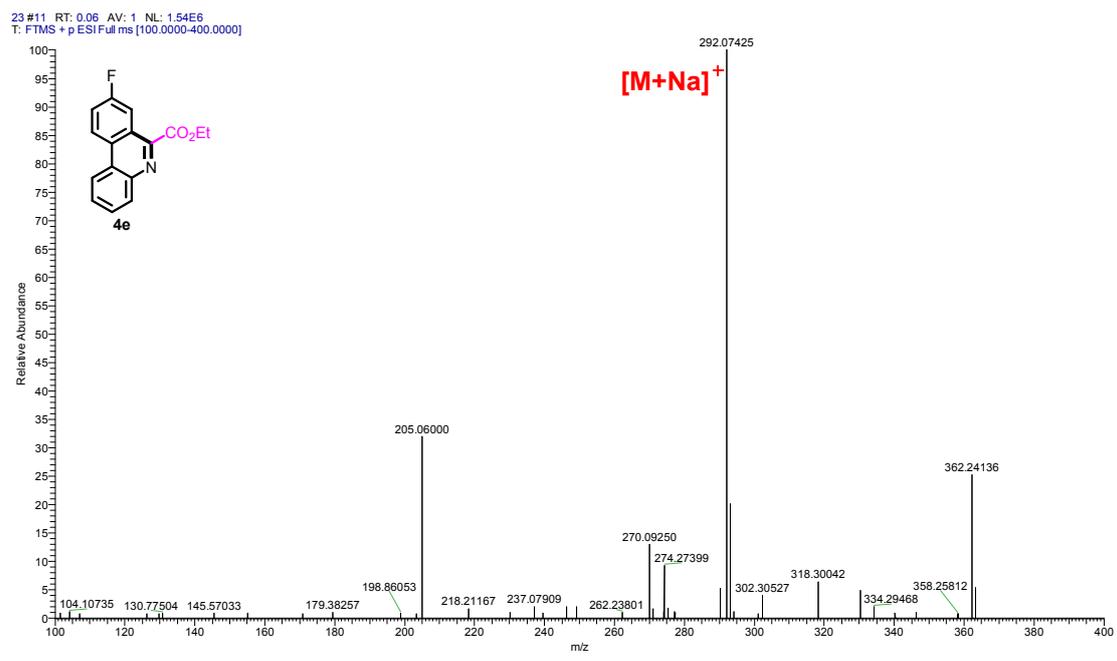
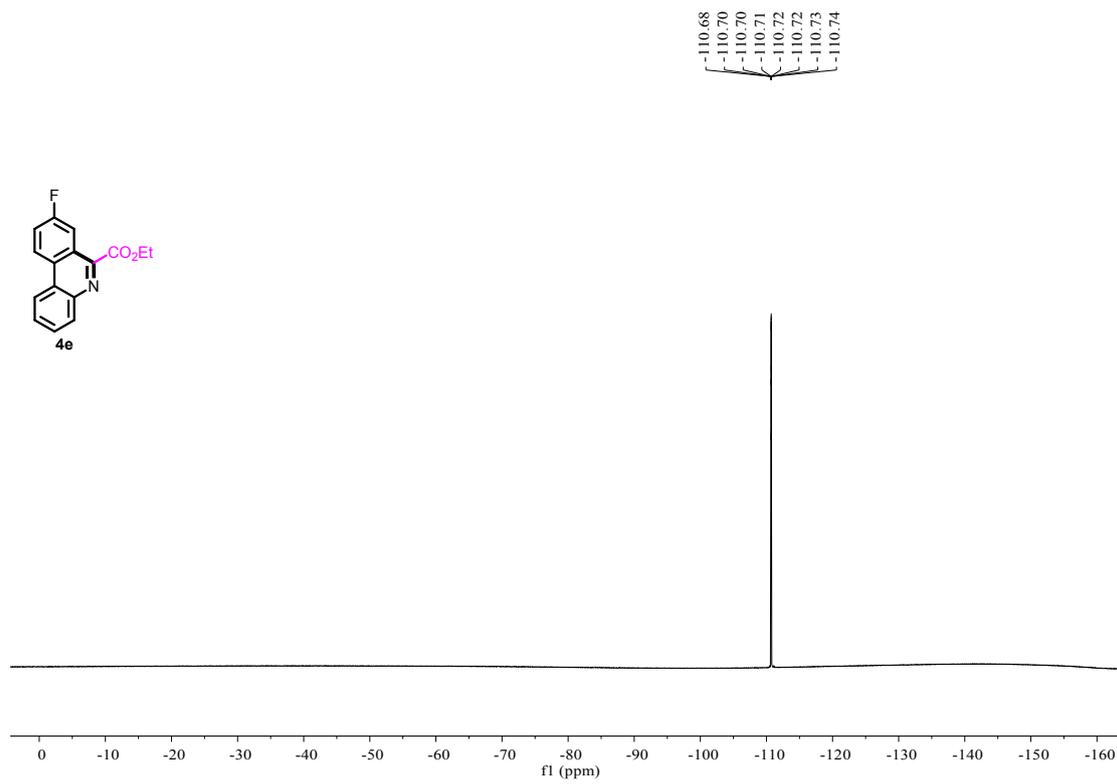


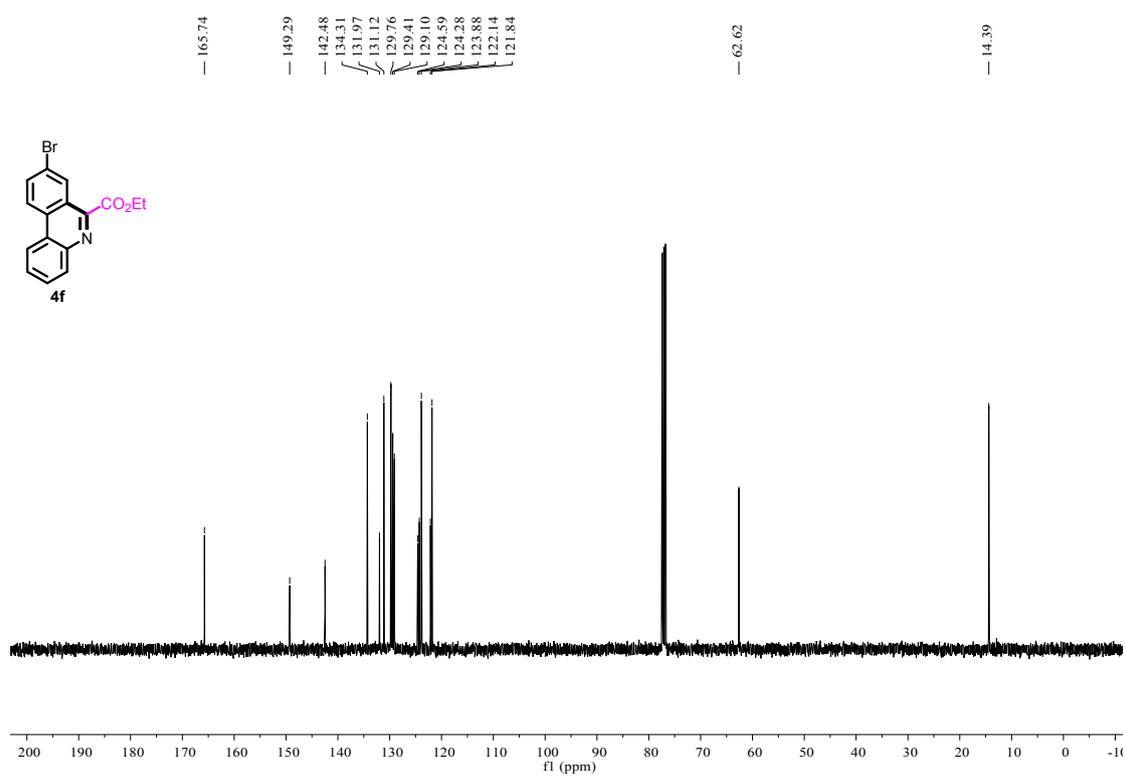
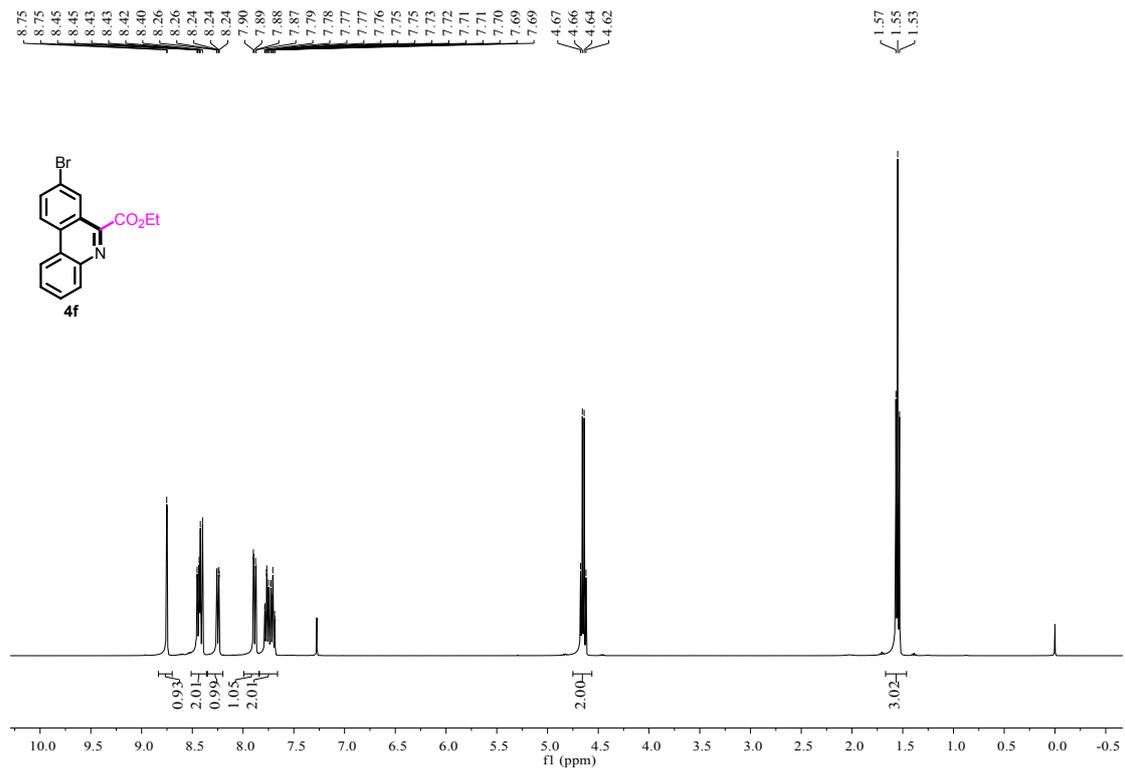
8.44
 8.41
 8.35
 8.26
 8.23
 7.74
 7.73
 7.72
 7.72
 7.72
 7.70
 7.70
 7.70
 7.69
 7.69
 7.68
 7.68
 7.68
 7.67
 7.67
 7.66
 7.66
 7.65
 7.65
 4.67
 4.66
 4.64
 4.62
 -2.61
 1.57
 1.55
 1.53



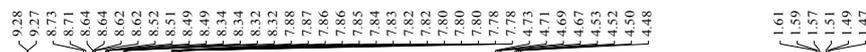
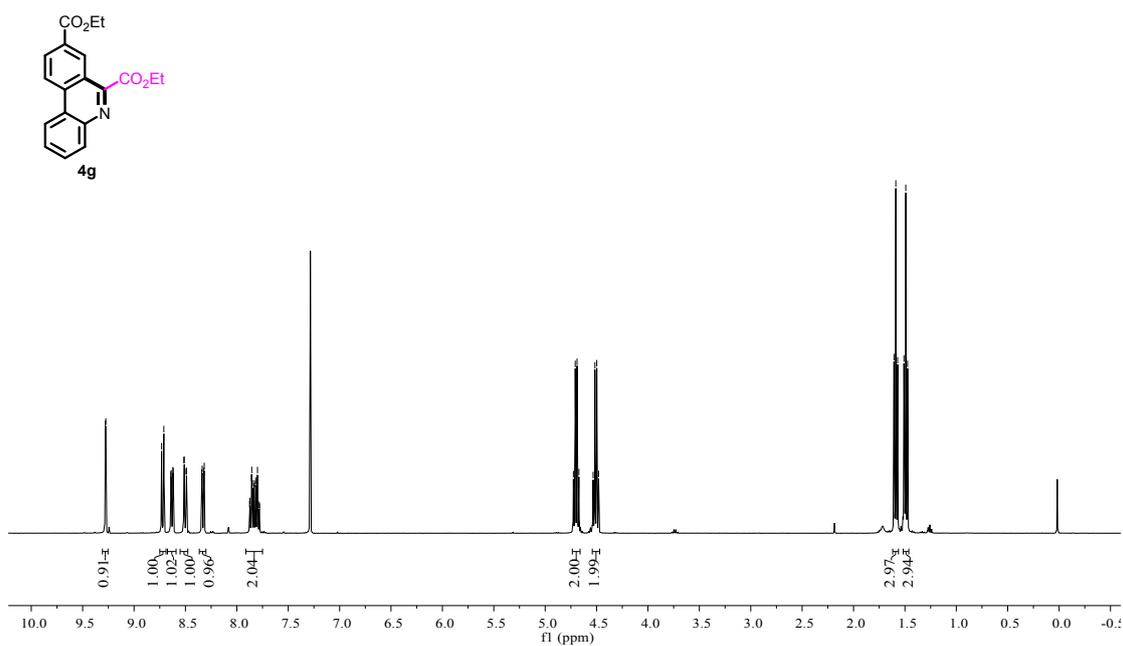
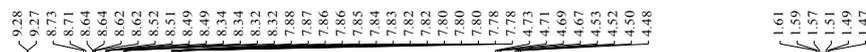
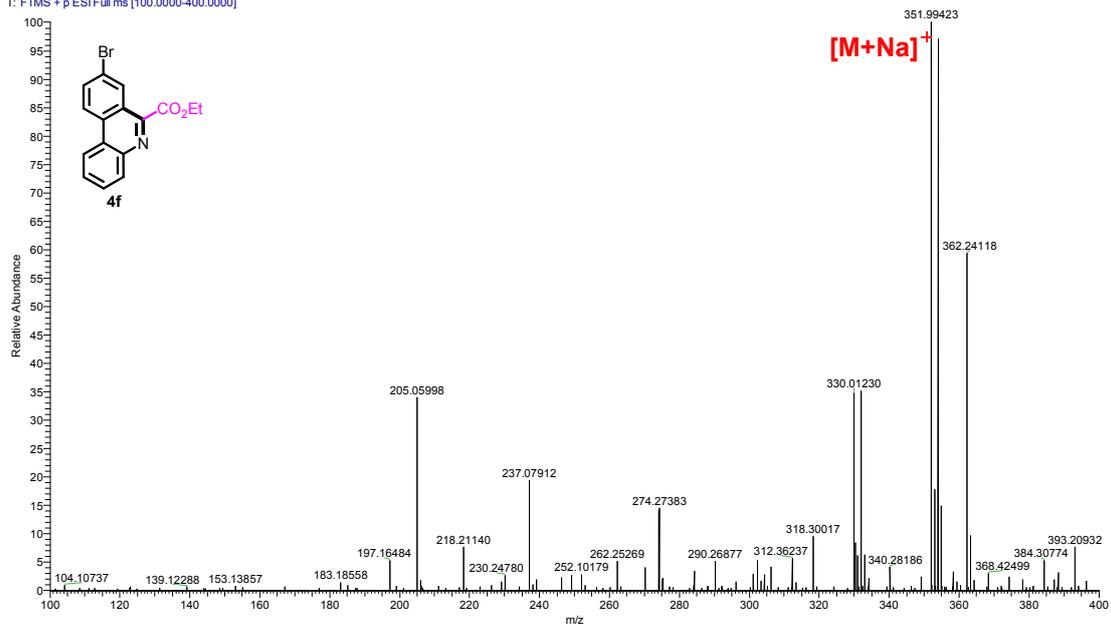


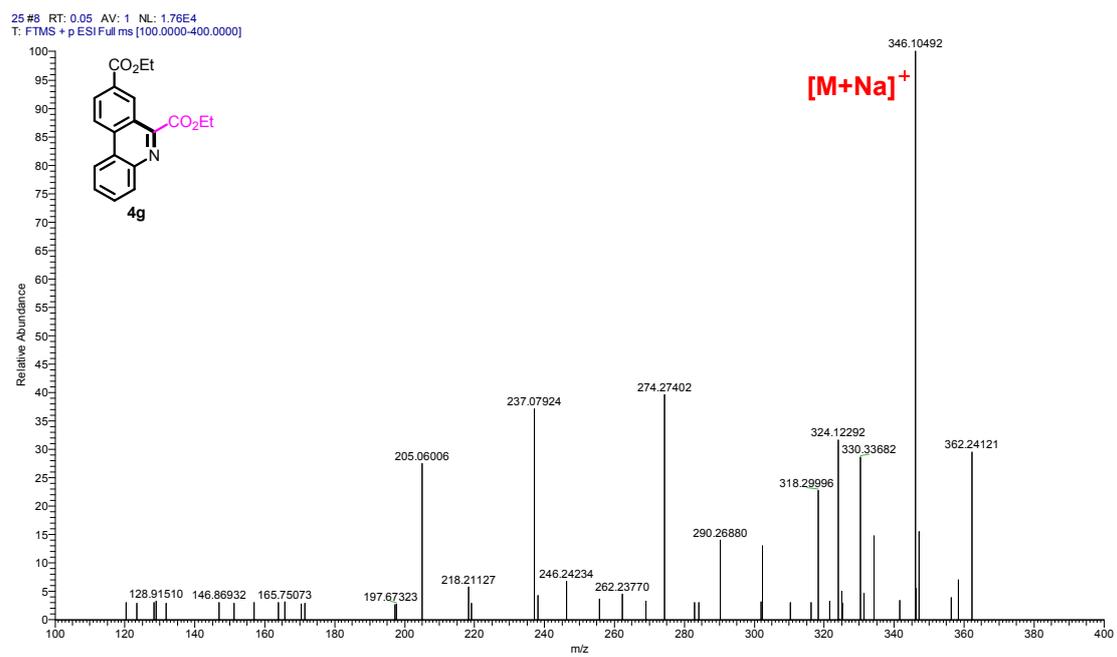
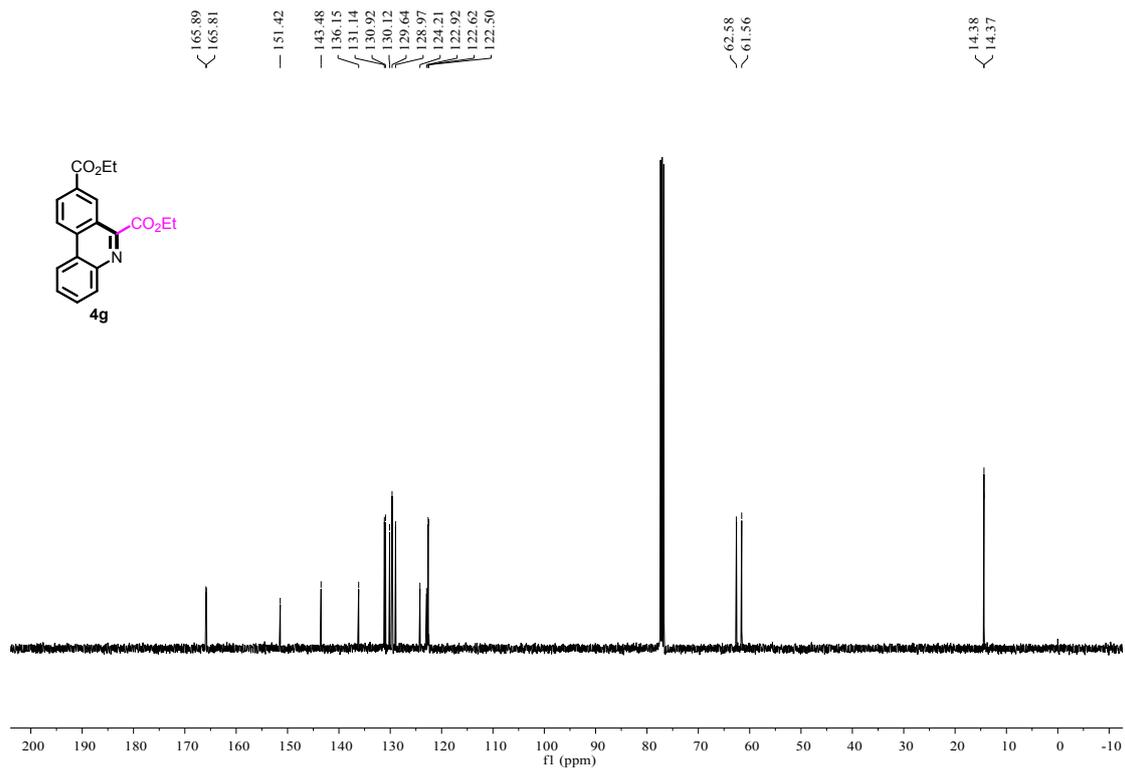


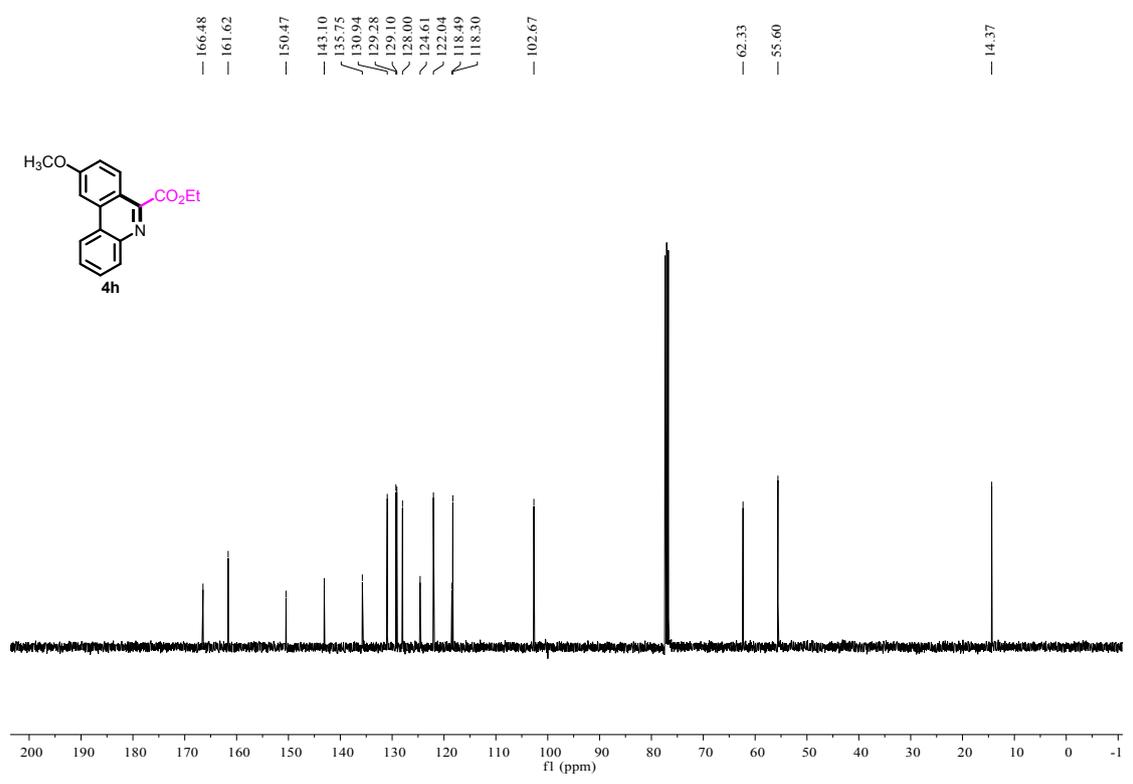
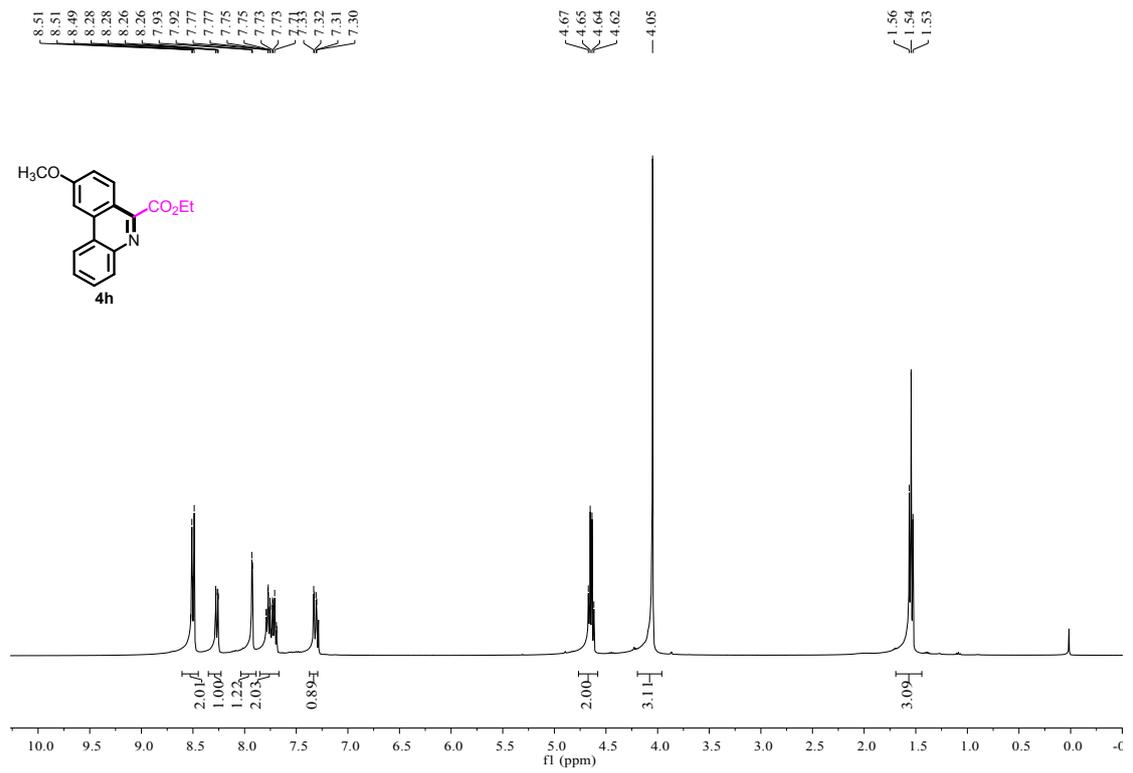




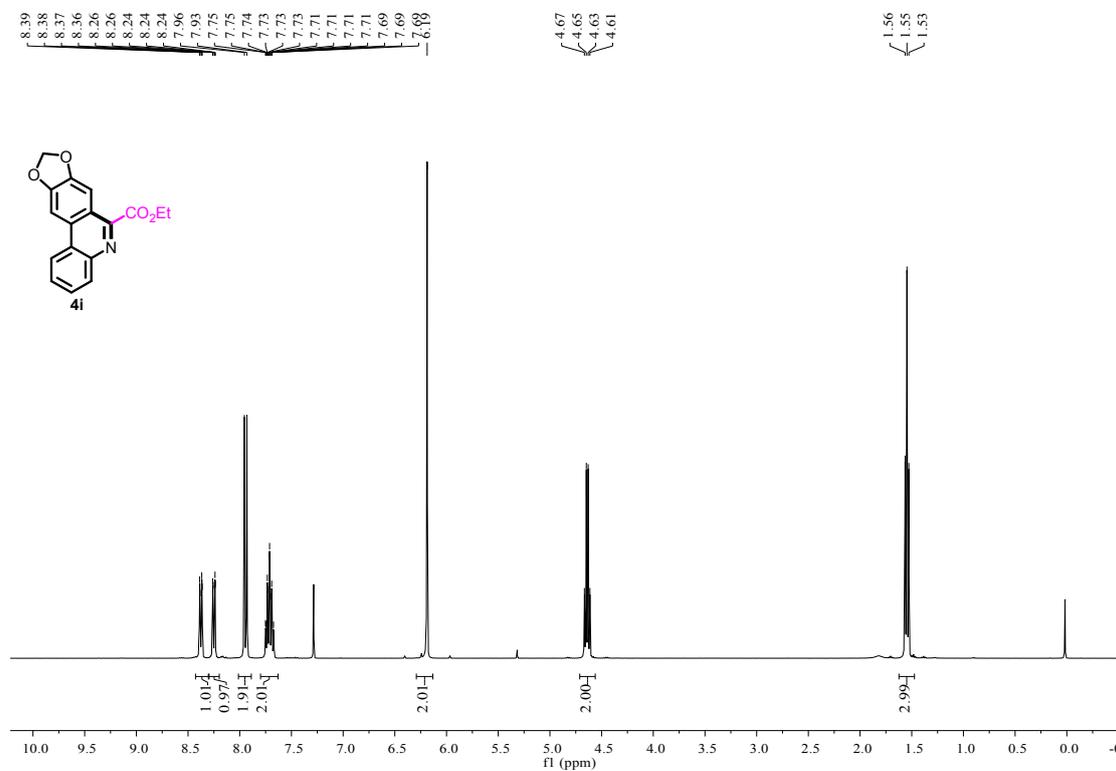
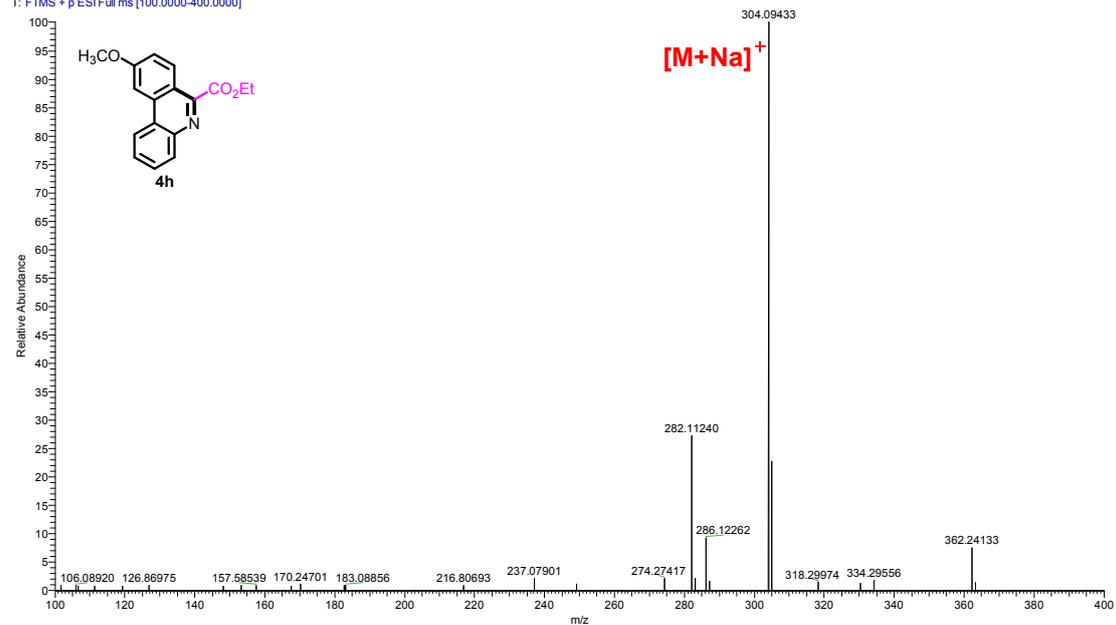
24 #2 RT: 0.01 AV: 1 NL: 1.51E5
T: FTMS + p ESI Full ms [100.0000-400.0000]

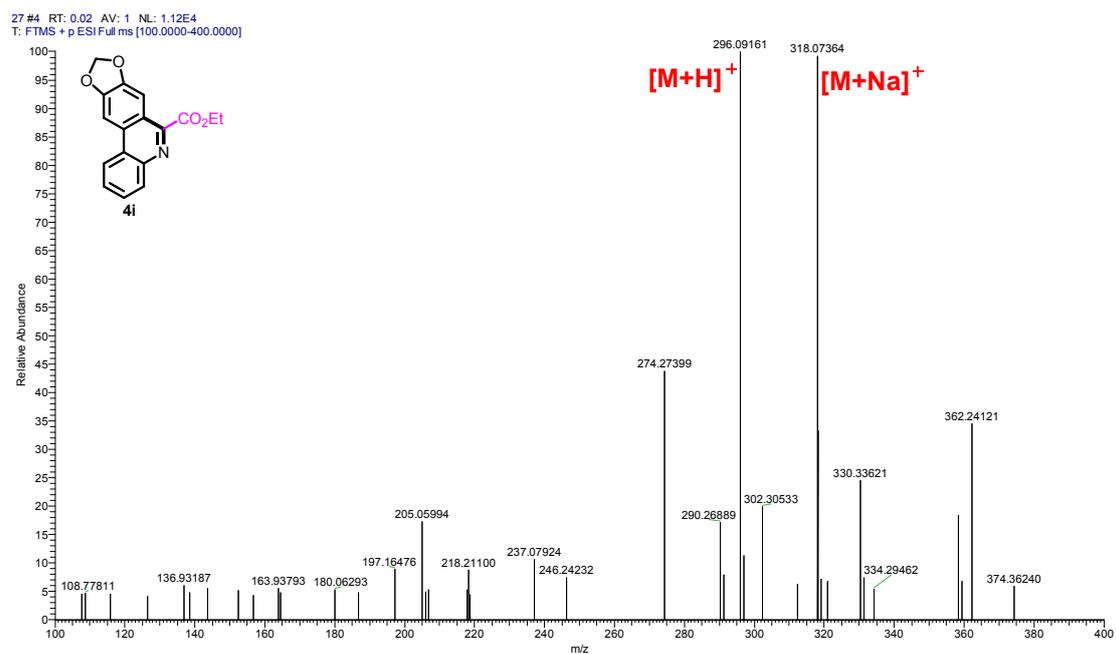
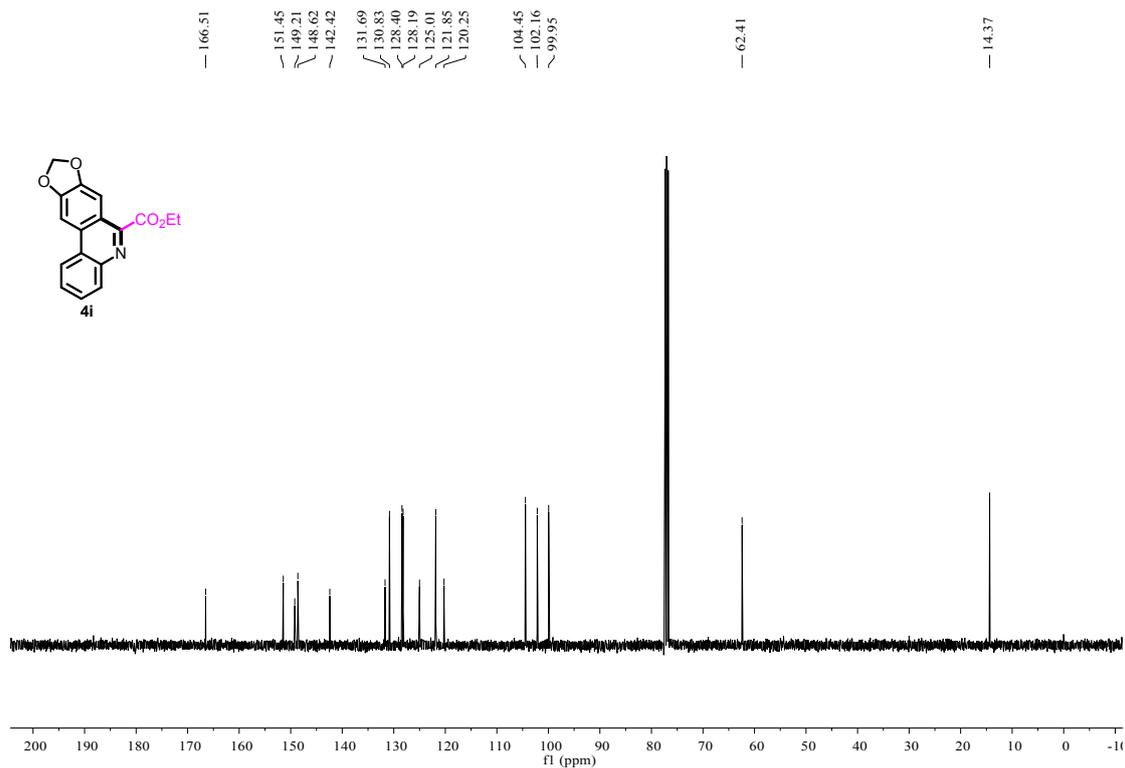


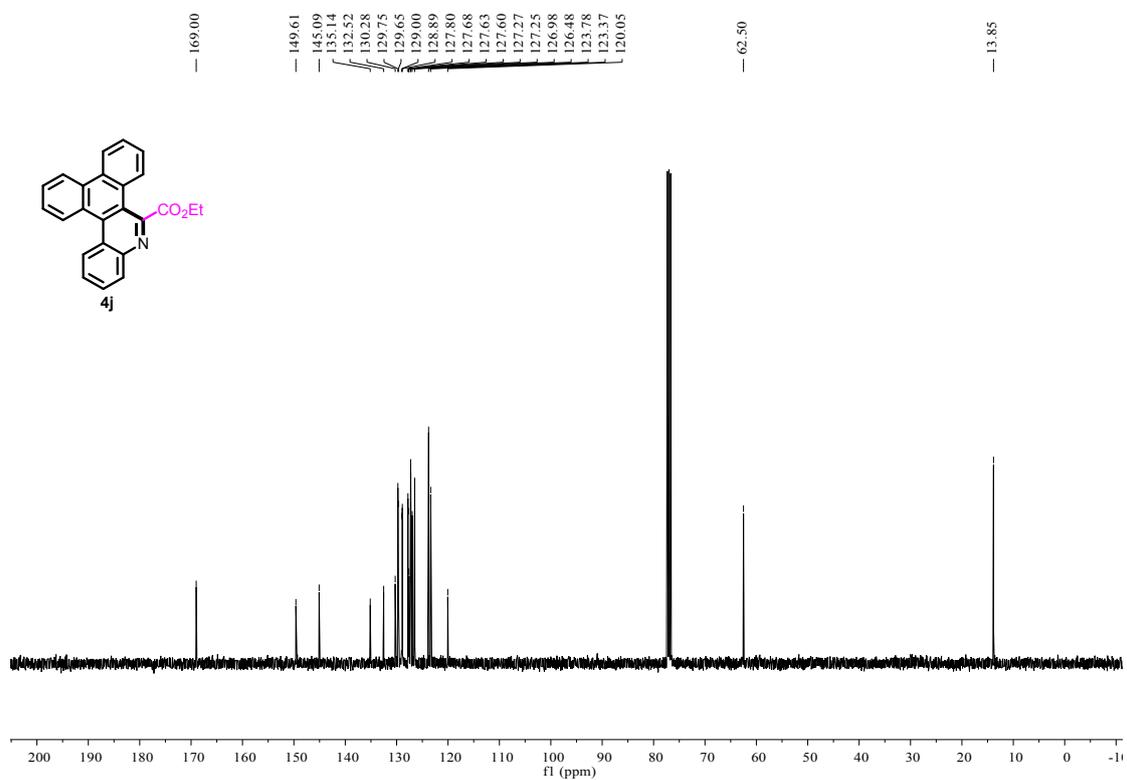
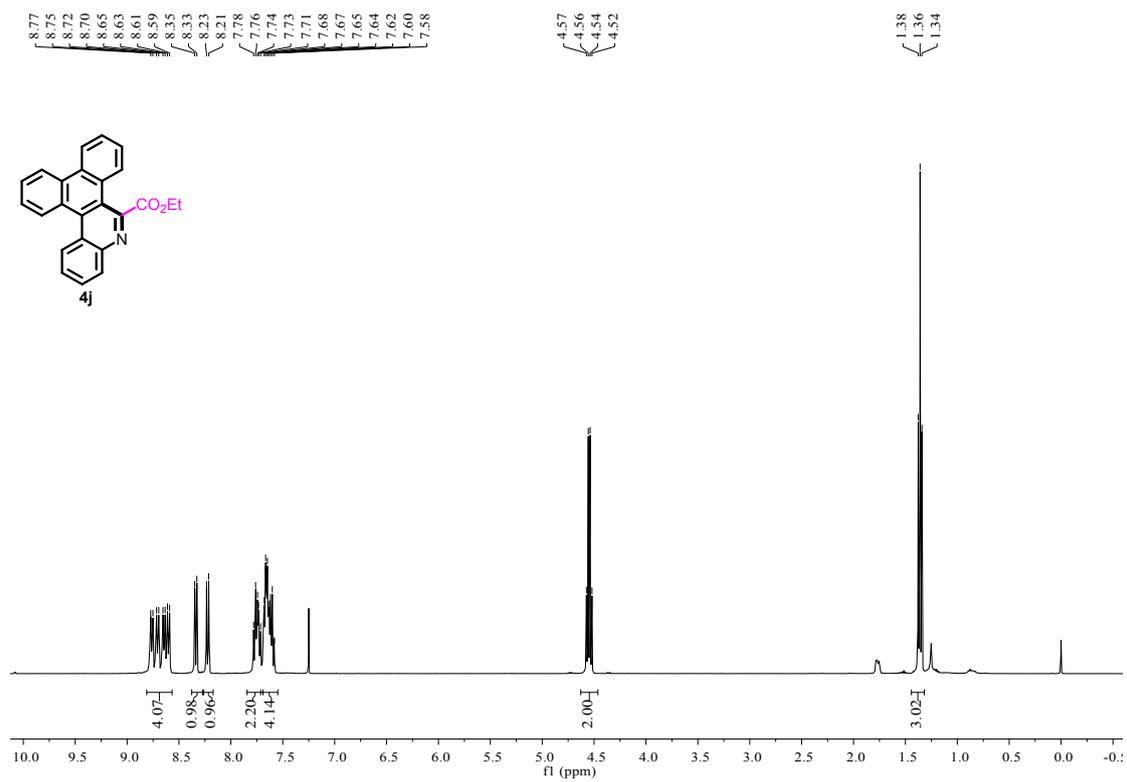




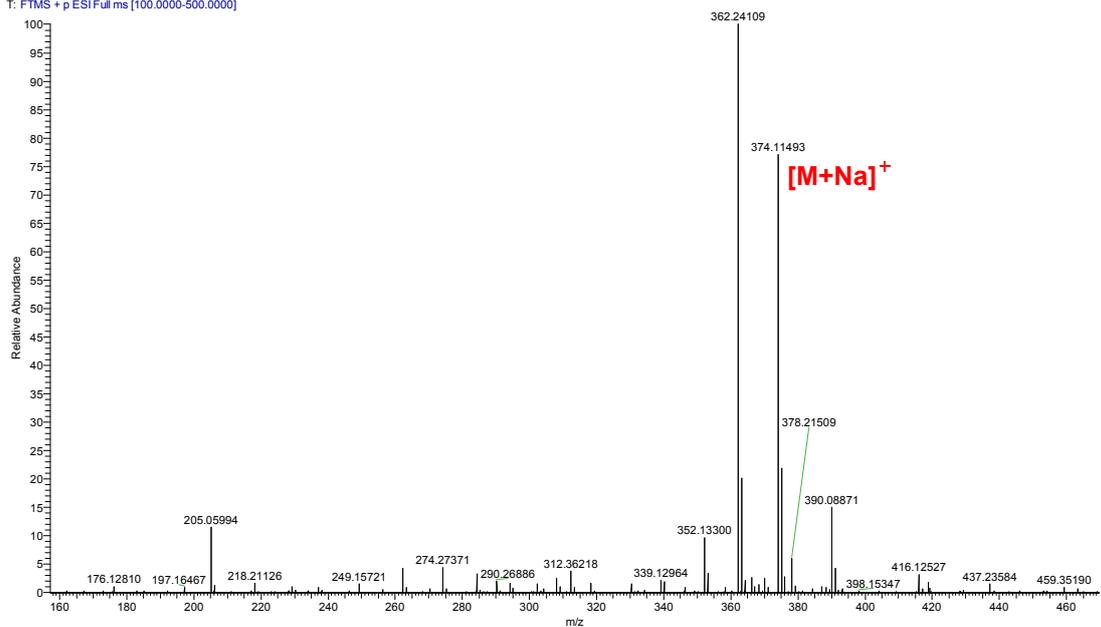
26 #4 RT: 0.02 AV: 1 NL: 5.88E4
T: FTMS + p ESI Full ms [100.0000-400.0000]



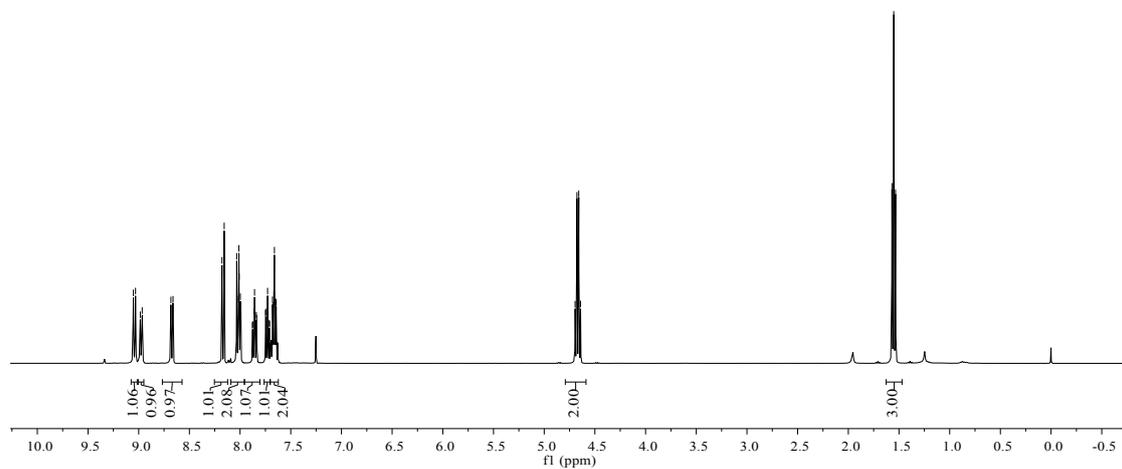
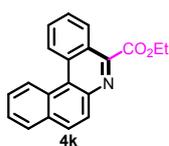


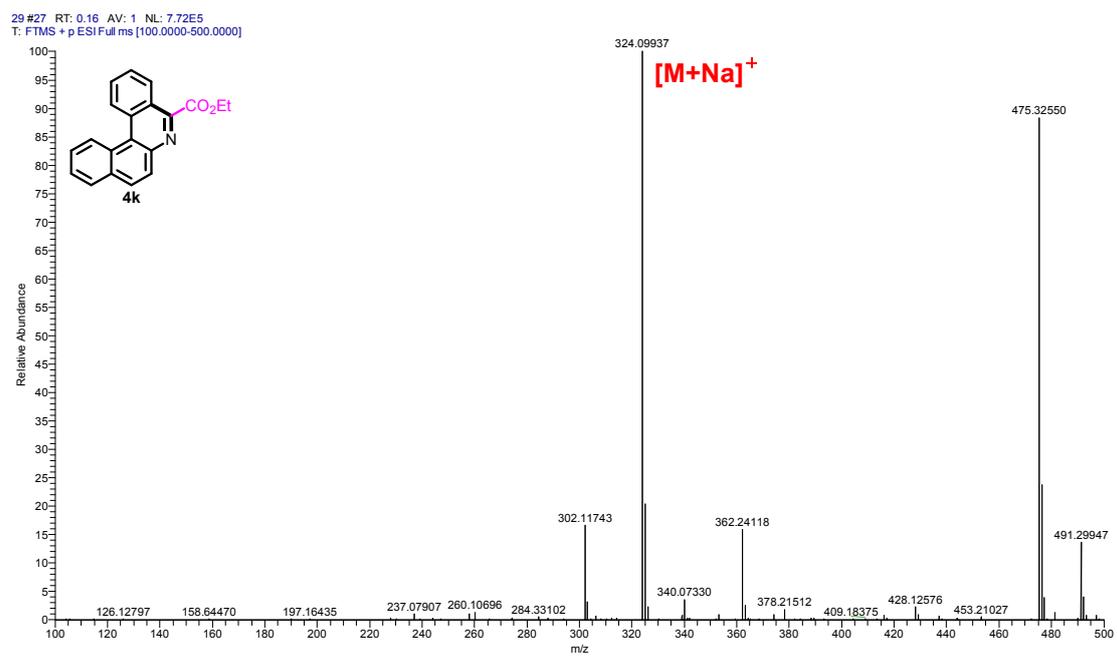
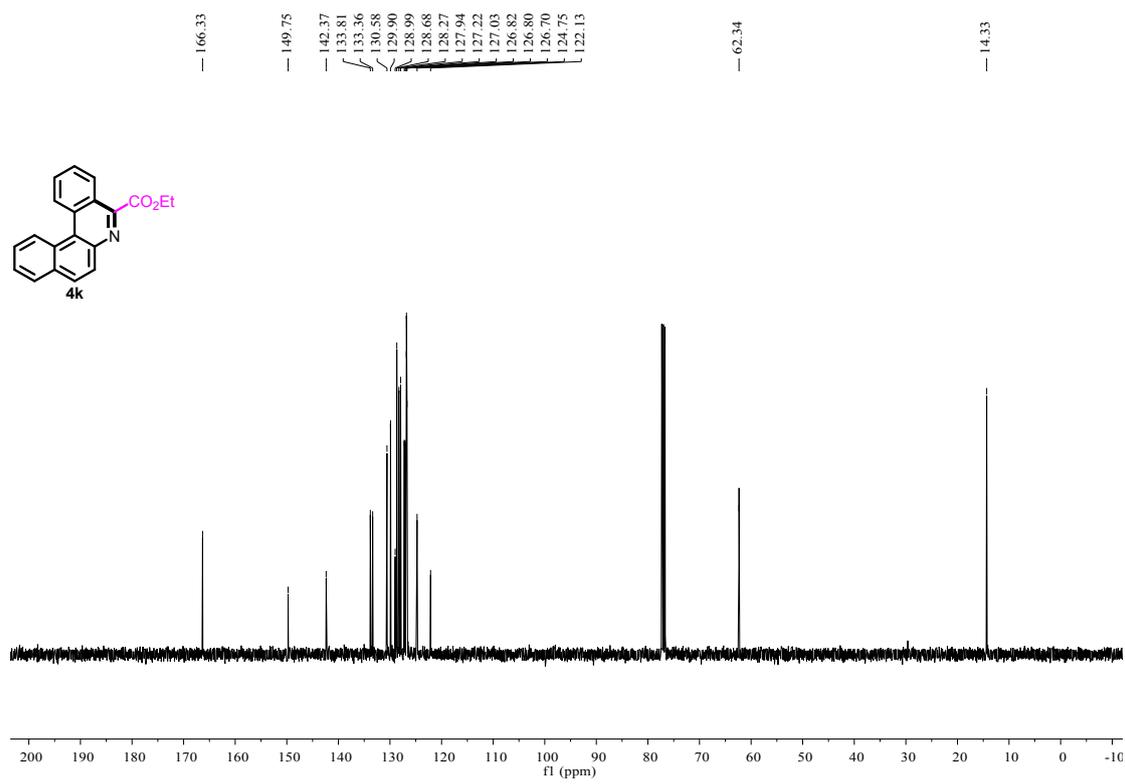


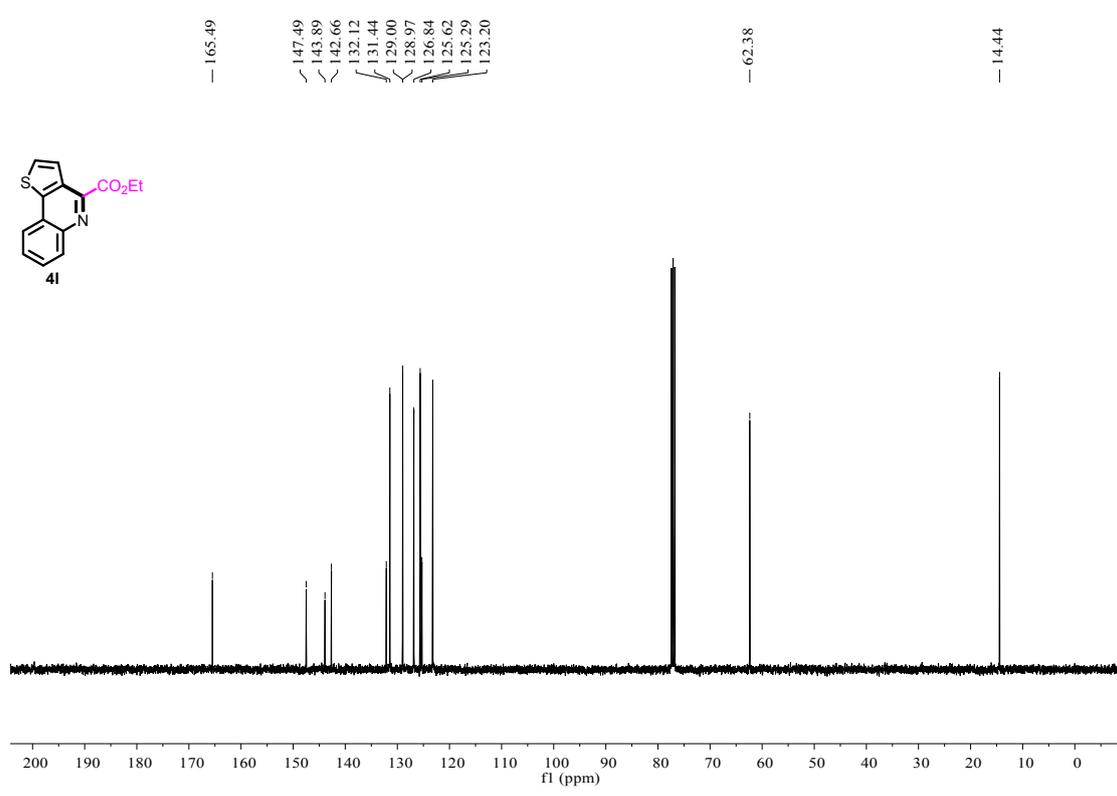
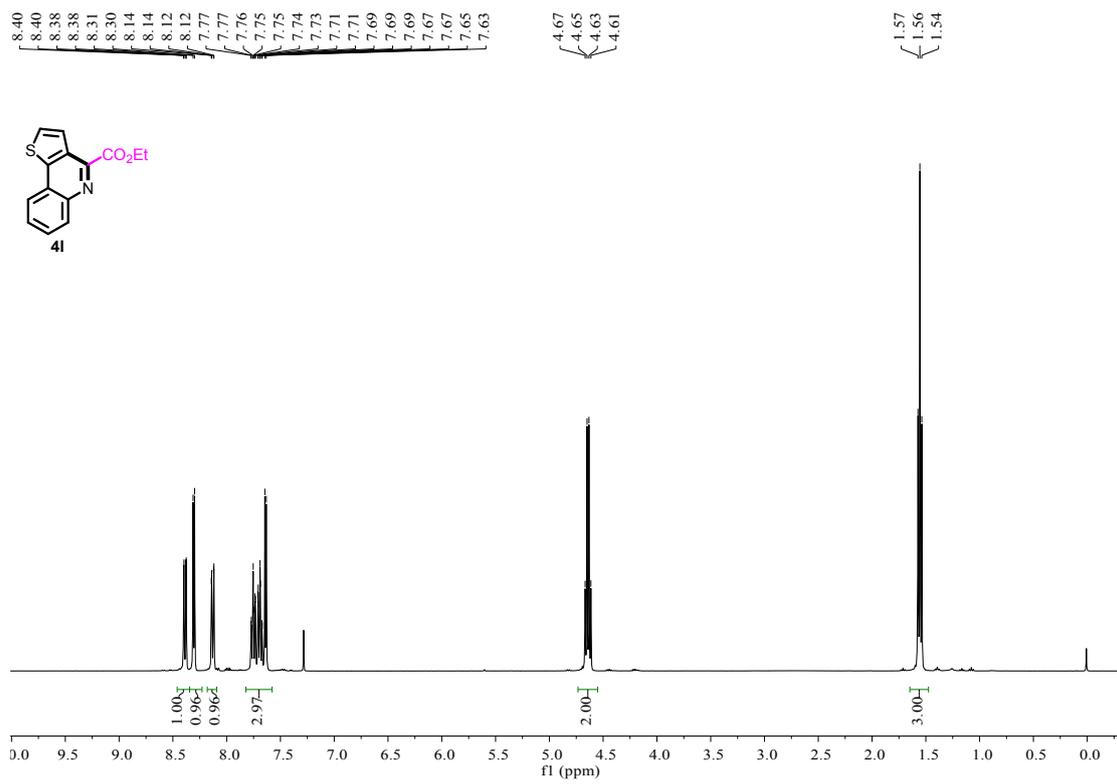
28 #7 RT: 0.04 AV: 1 NL: 3.55E6
T: FTMS + p ESI Full ms [100.0000-500.0000]



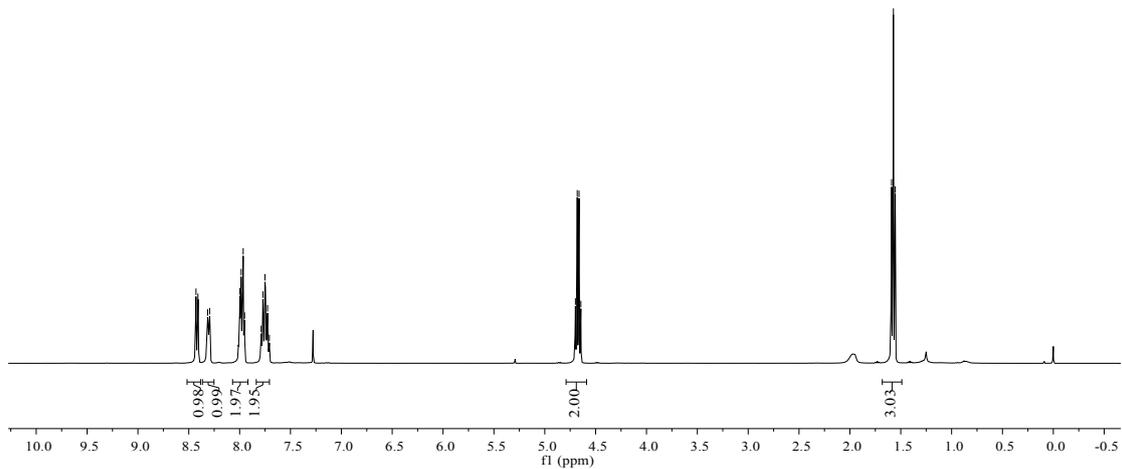
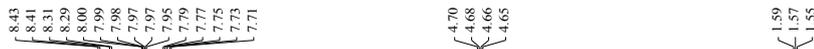
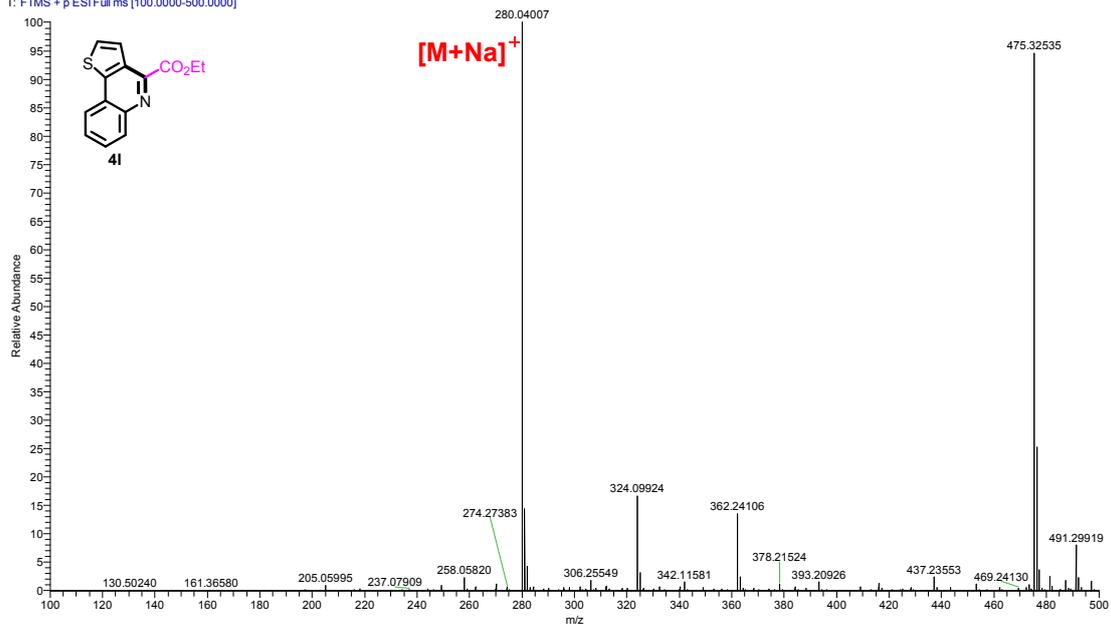
9.05
9.03
8.98
8.97
8.68
8.66
8.18
8.16
8.03
8.02
8.01
8.00
7.99
7.88
7.88
7.86
7.86
7.84
7.84
7.75
7.75
7.73
7.71
7.71
7.68
7.68
7.67
7.66
7.66
7.65
7.64
7.64
4.69
4.68
4.66
4.64
1.57
1.55
1.53

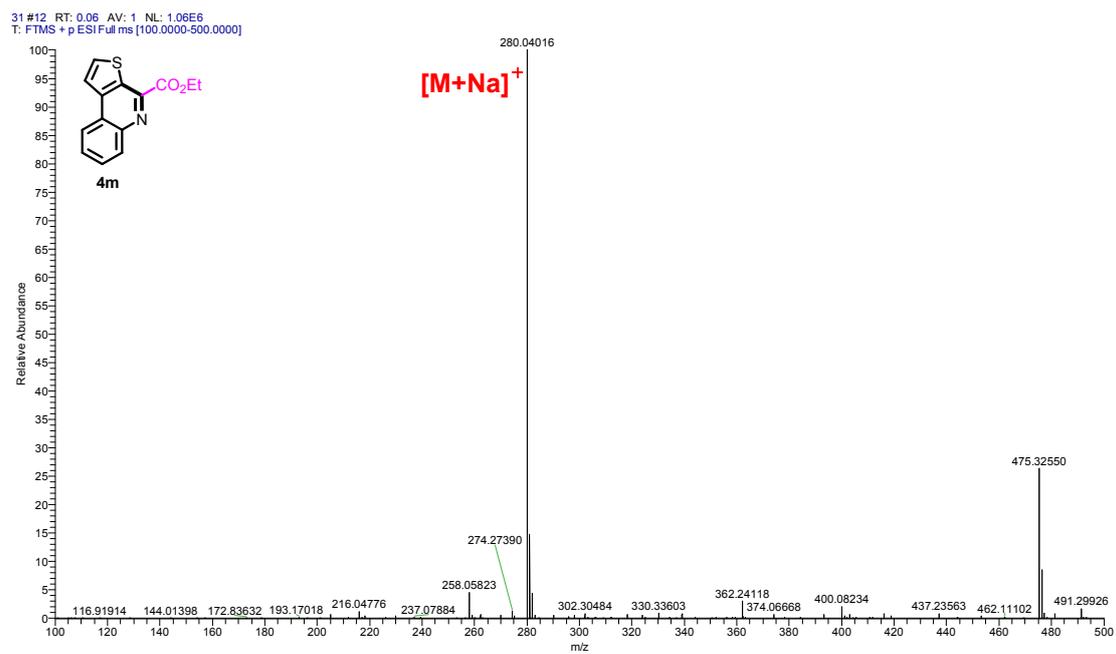
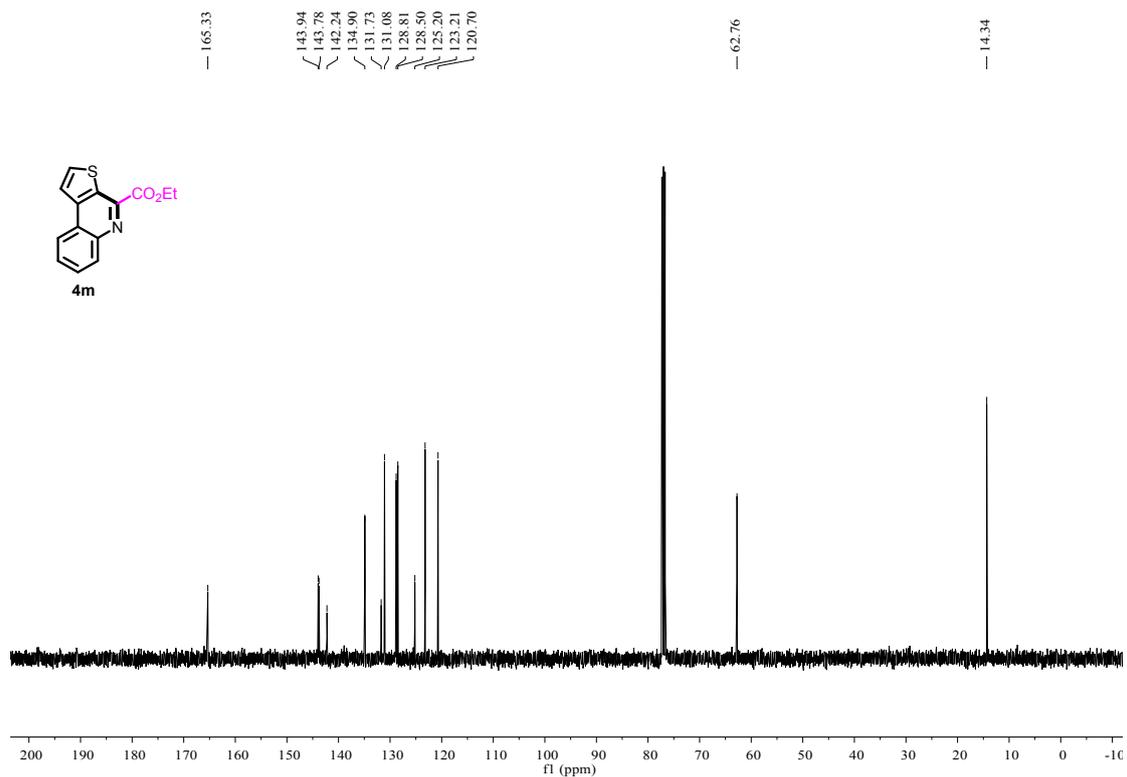


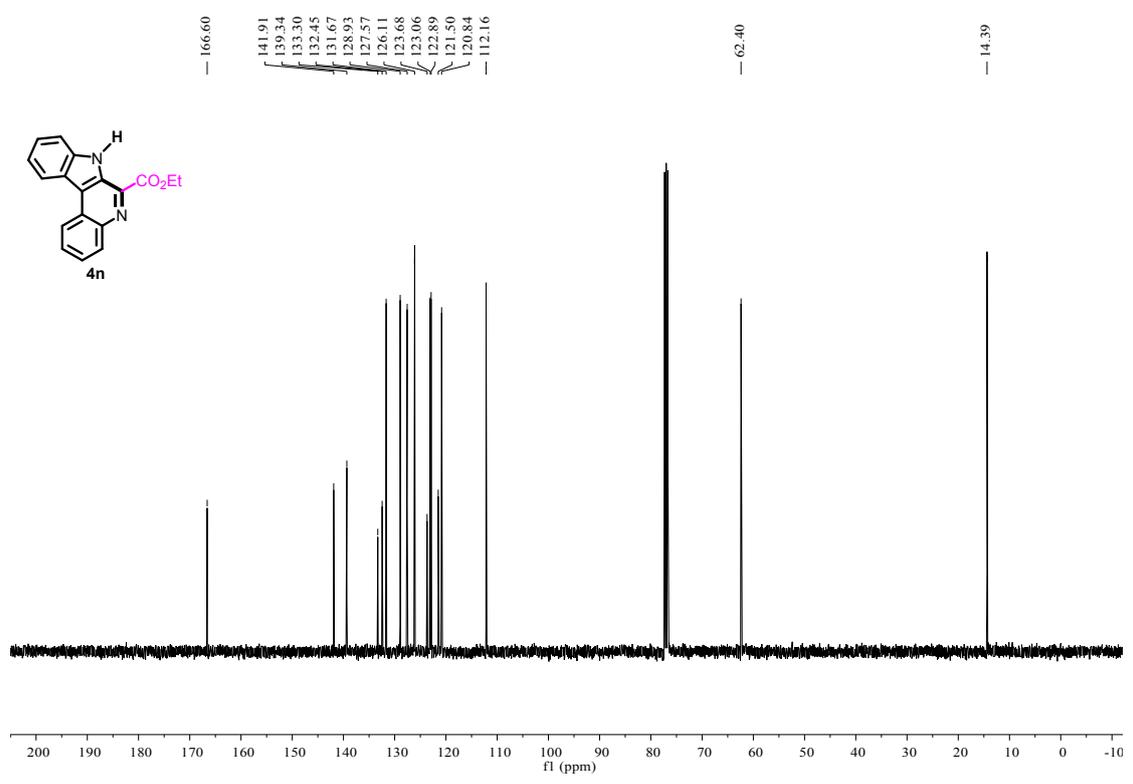
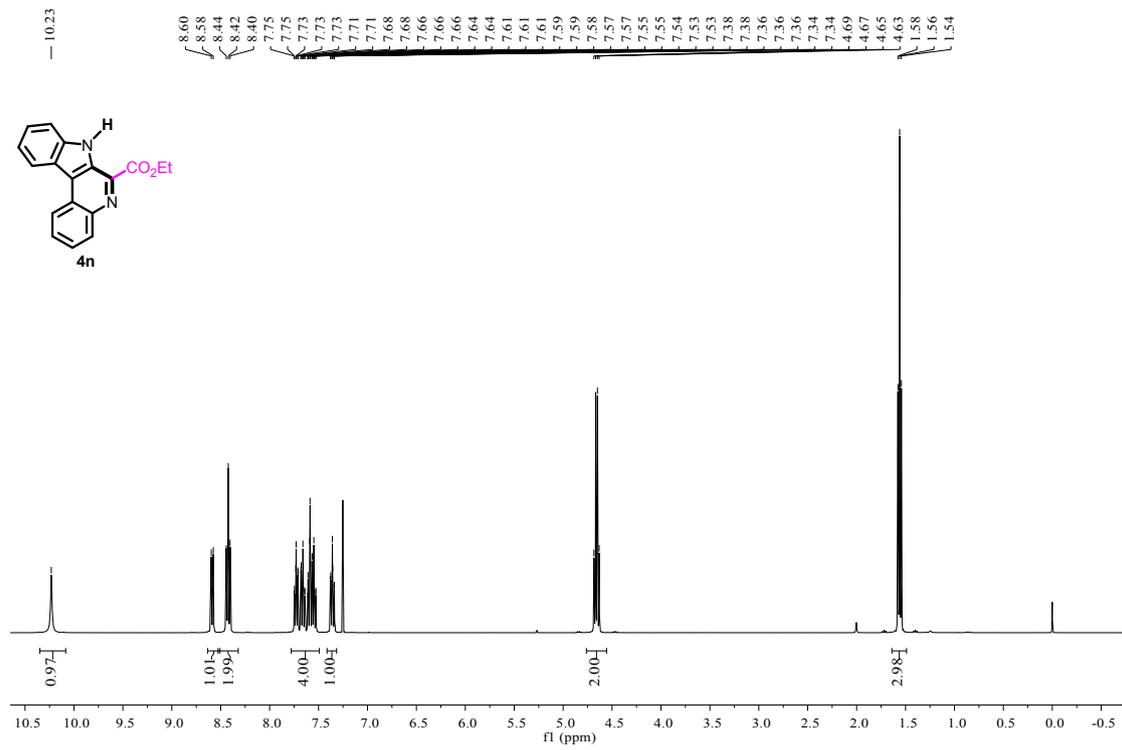




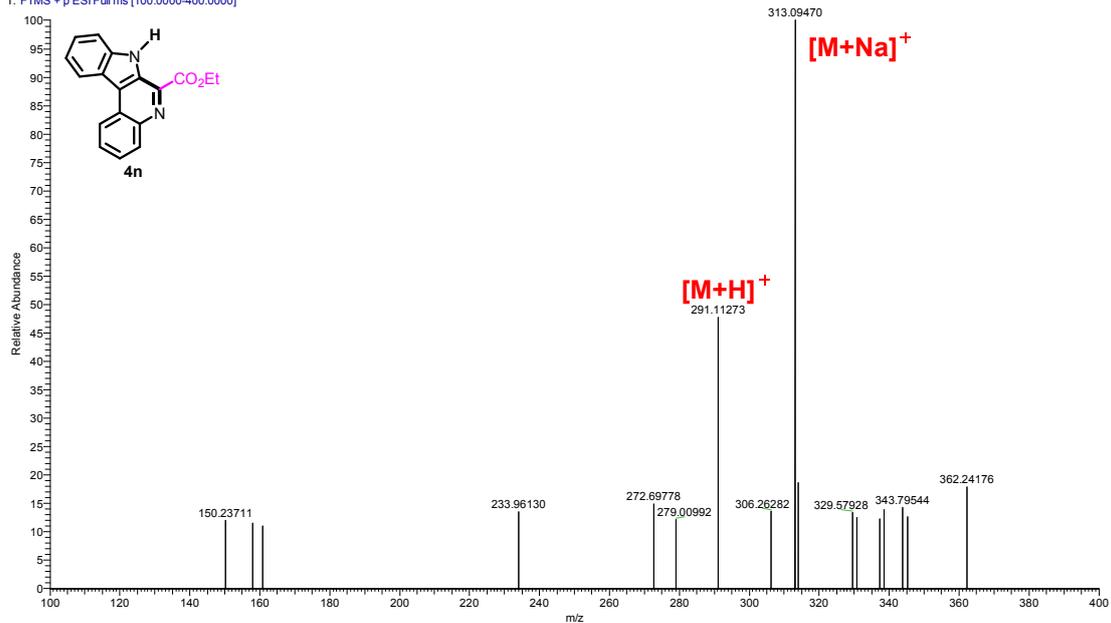
30 #12 RT: 0.07 AV: 1 NL: 3.73E6
T: FTMS + p ESI Full ms [100.0000-500.0000]



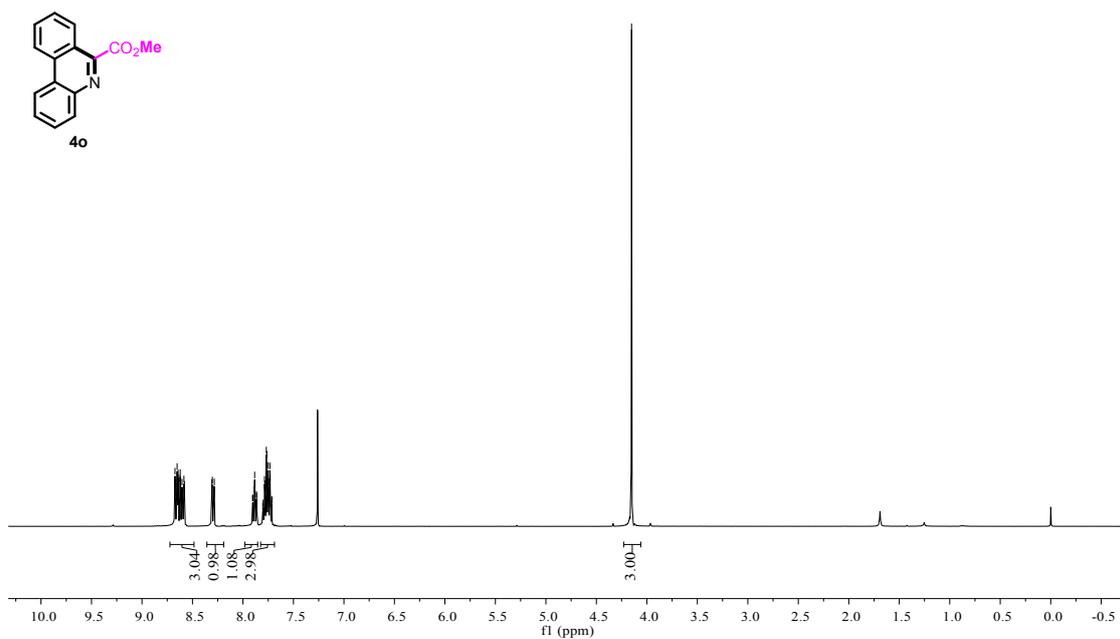


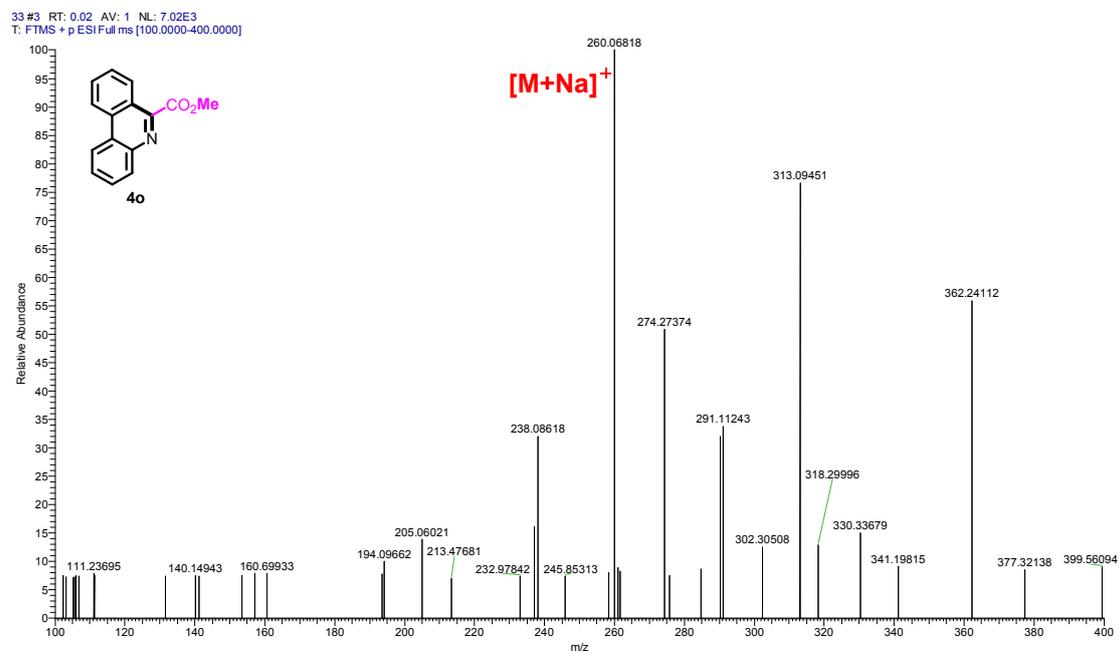
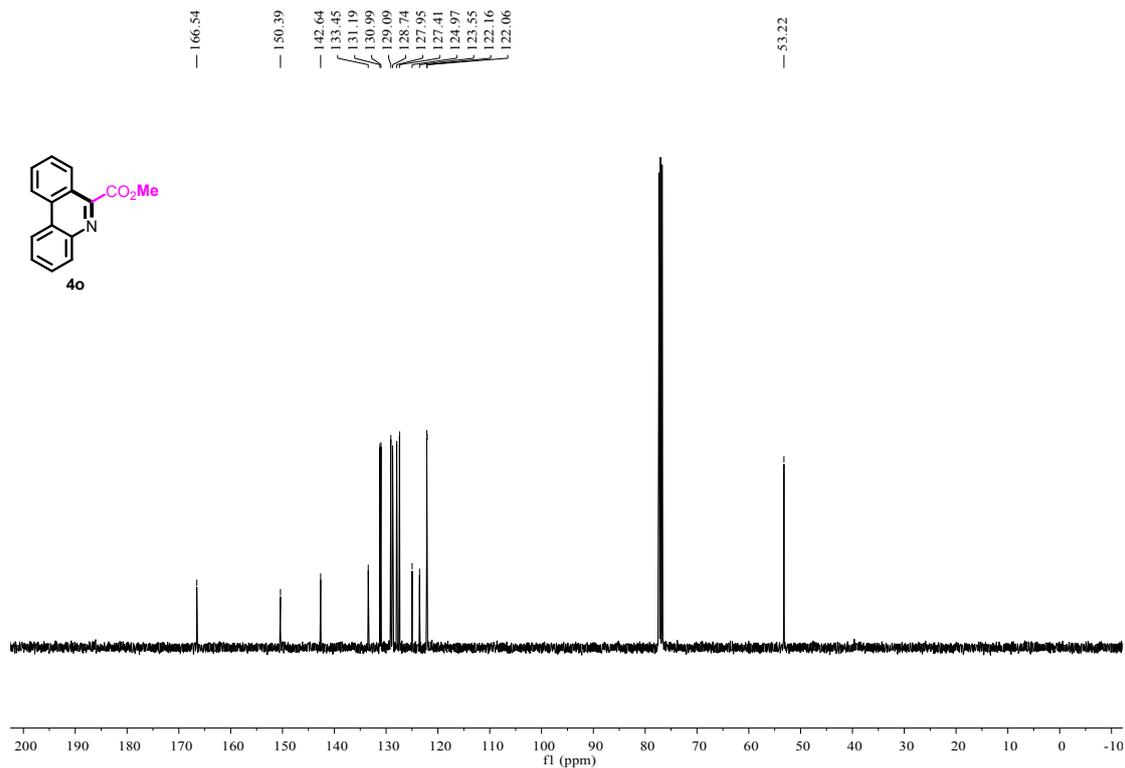


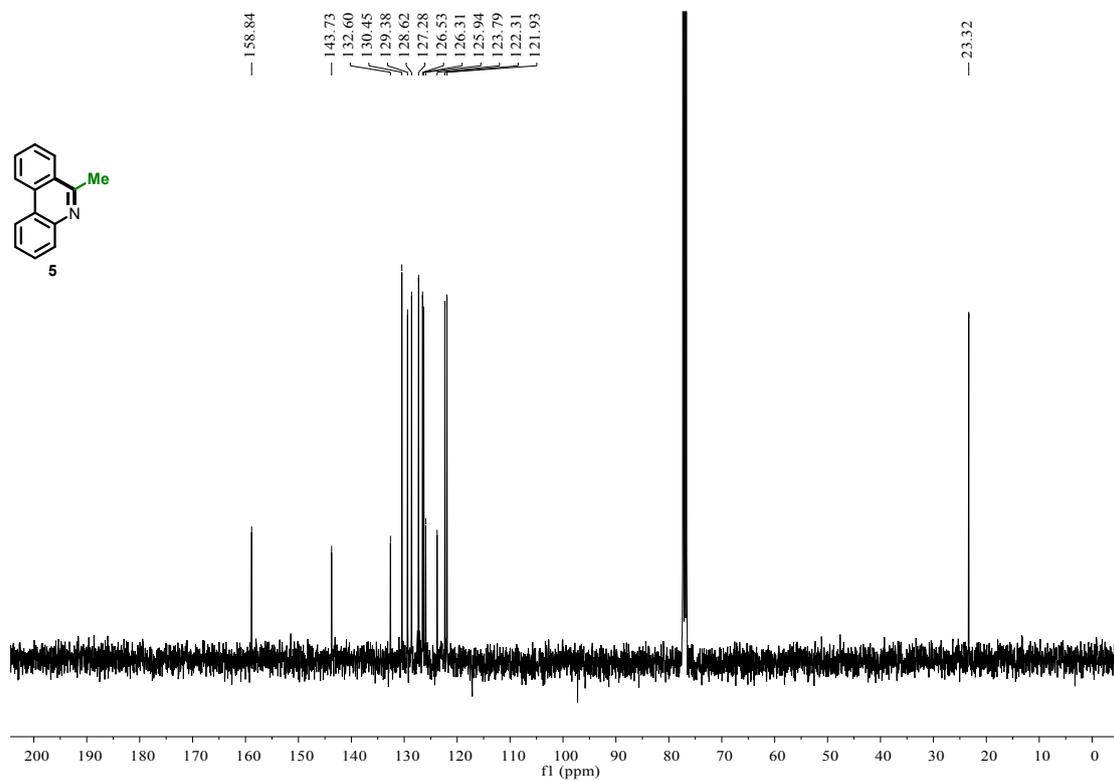
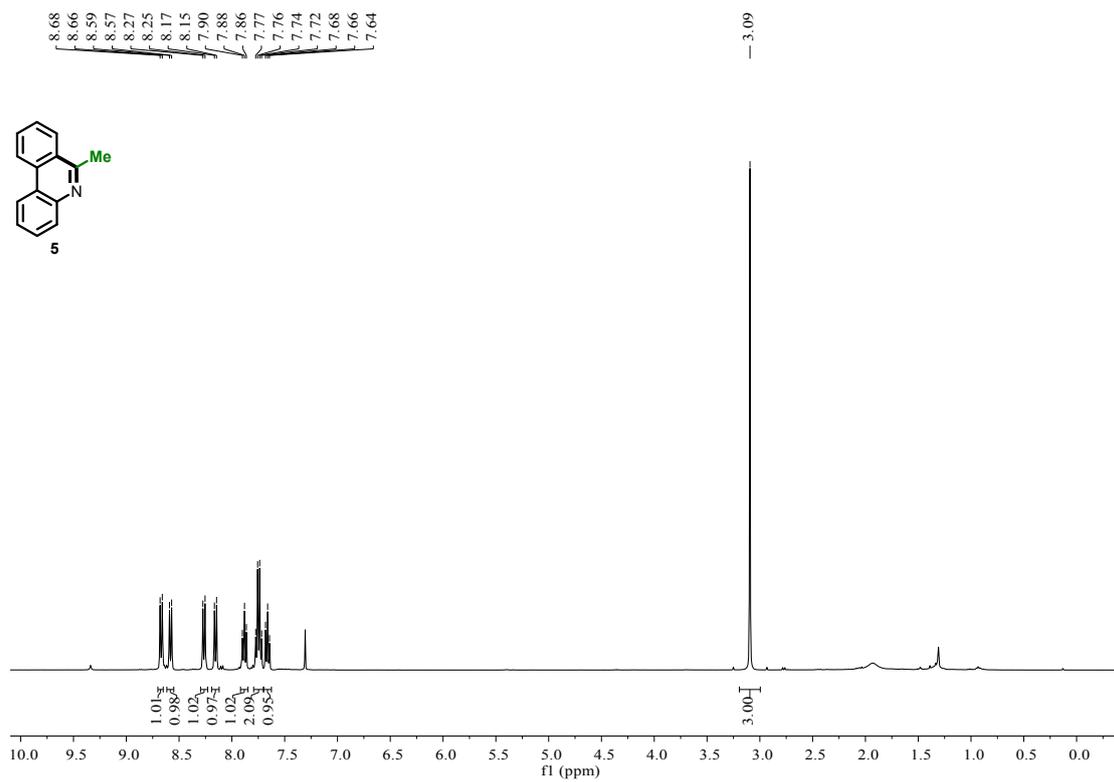
32 #1 RT: 0.01 AV: 1 NL: 4.55E3
T: FTMS + p ESI Full ms [100.0000-400.0000]



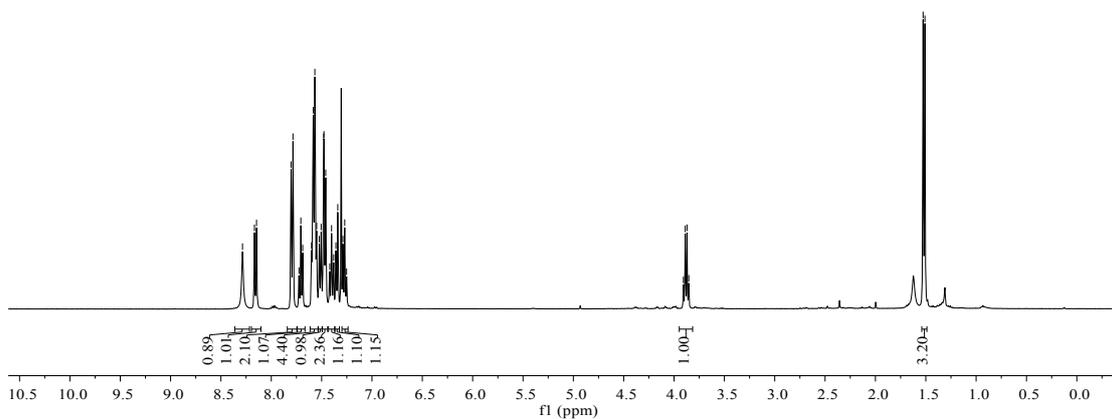
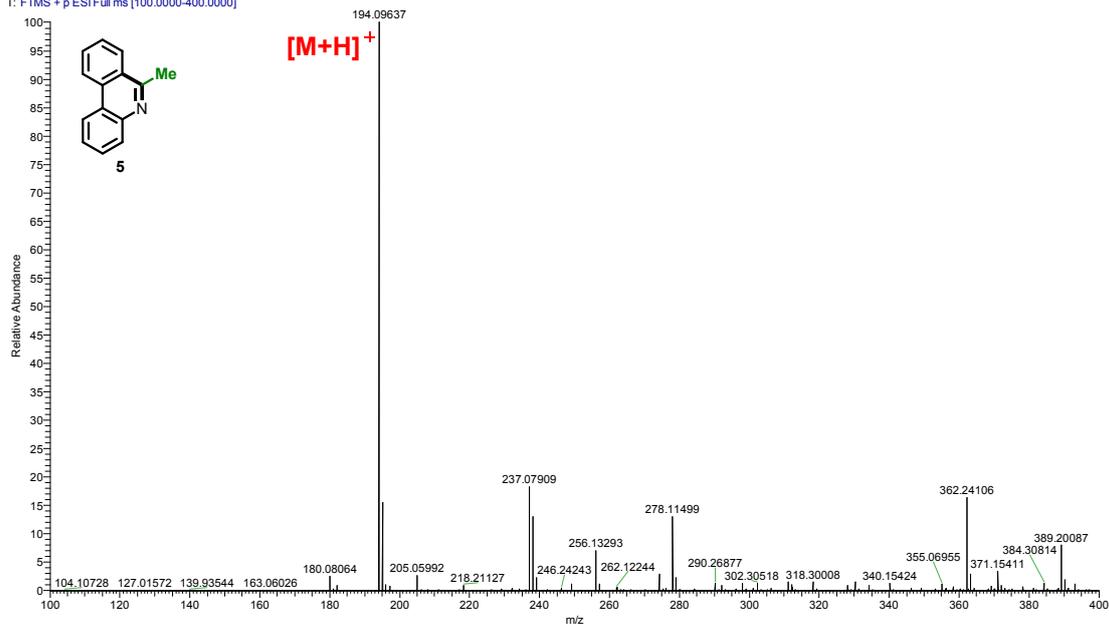
8.67
8.65
8.64
8.64
8.64
8.62
8.62
8.60
8.58
8.31
8.30
8.29
7.90
7.89
7.88
7.87
7.86
7.80
7.79
7.78
7.77
7.76
7.75
7.75
7.74
7.73
7.73
7.72
7.71
-4.15

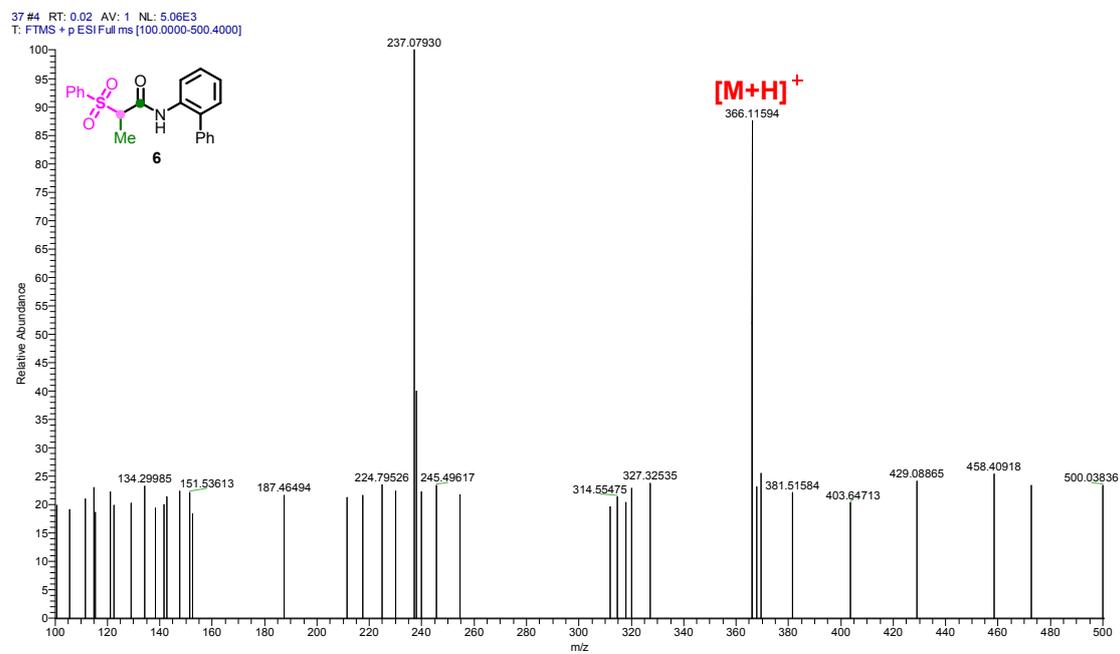
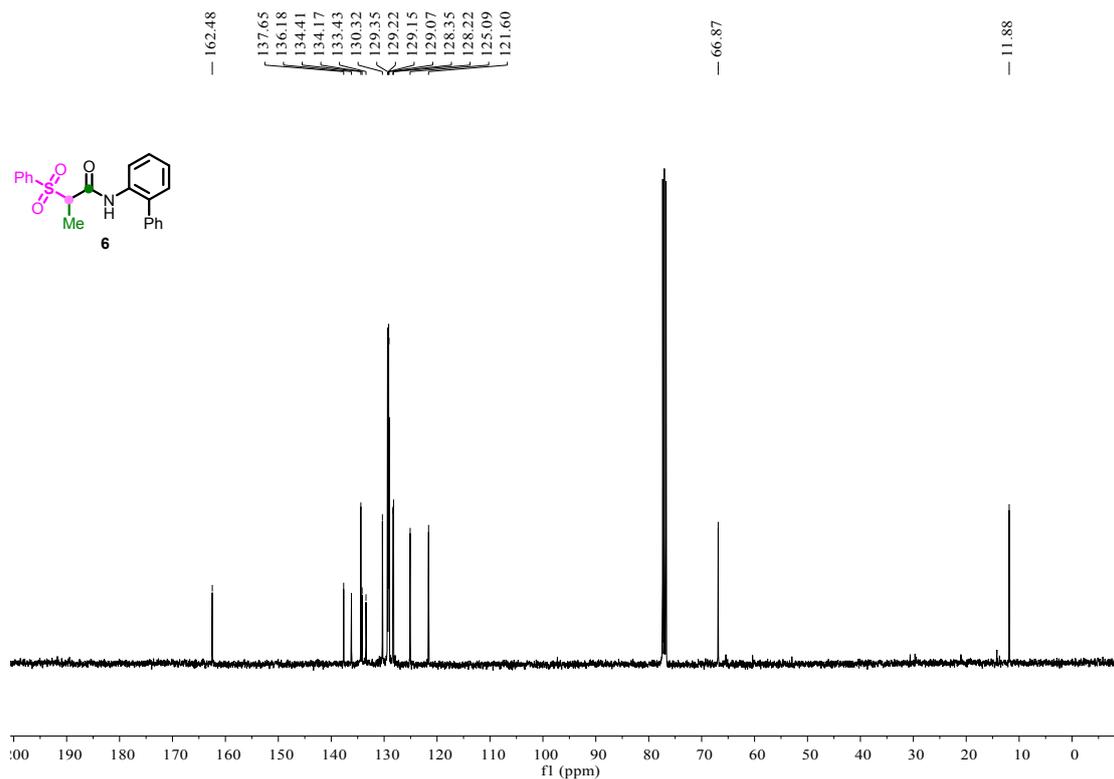


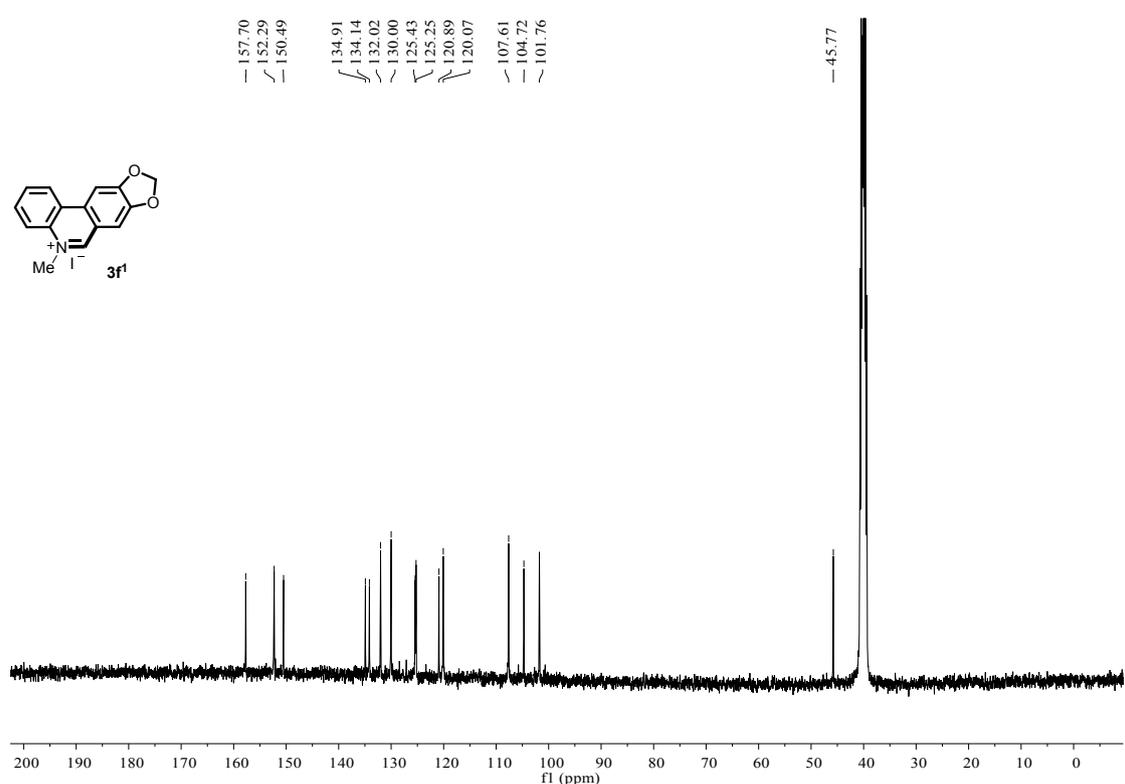
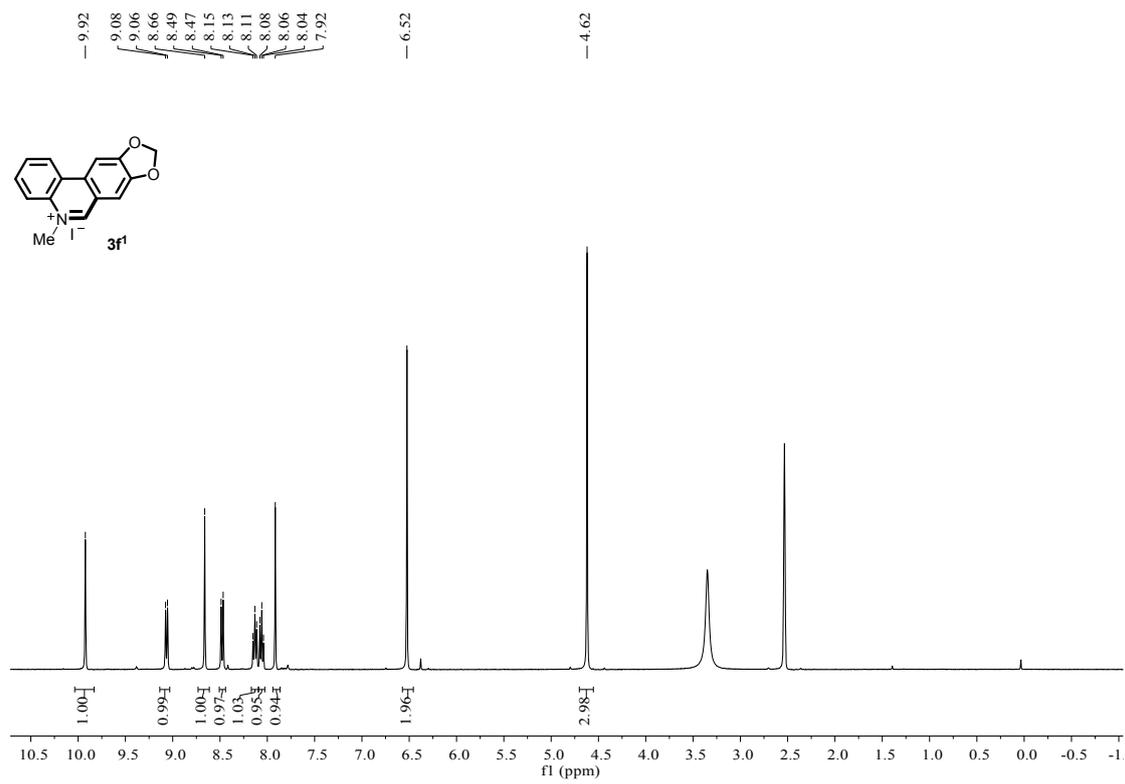




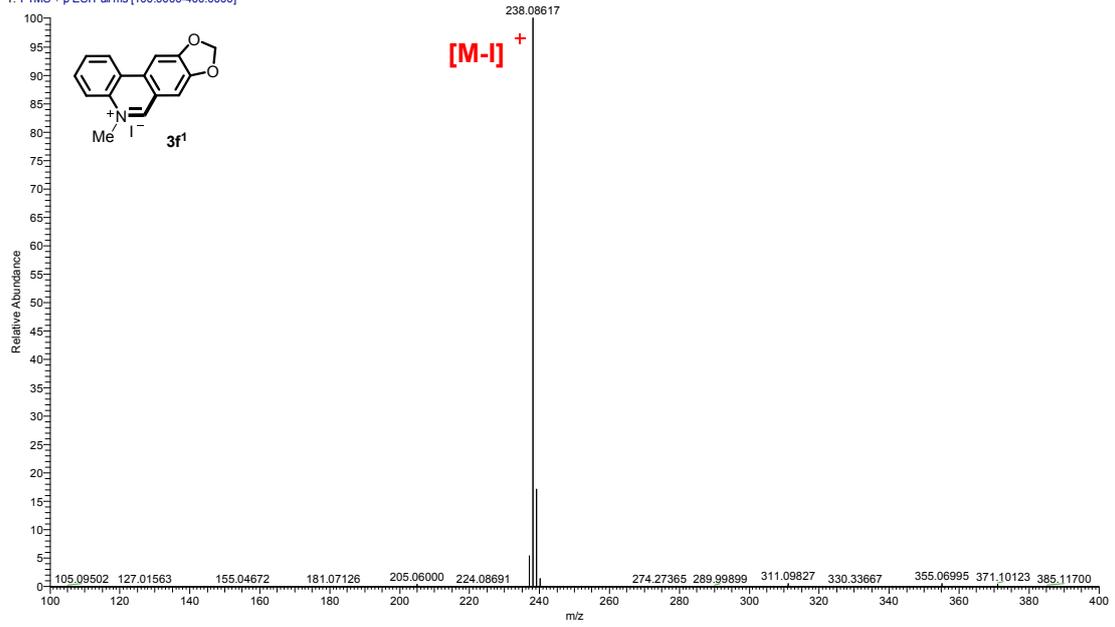
40 #3 RT: 0.02 AV: 1 NL: 1.78E6
T: FTMS + p ESI Full ms [100.0000-400.0000]



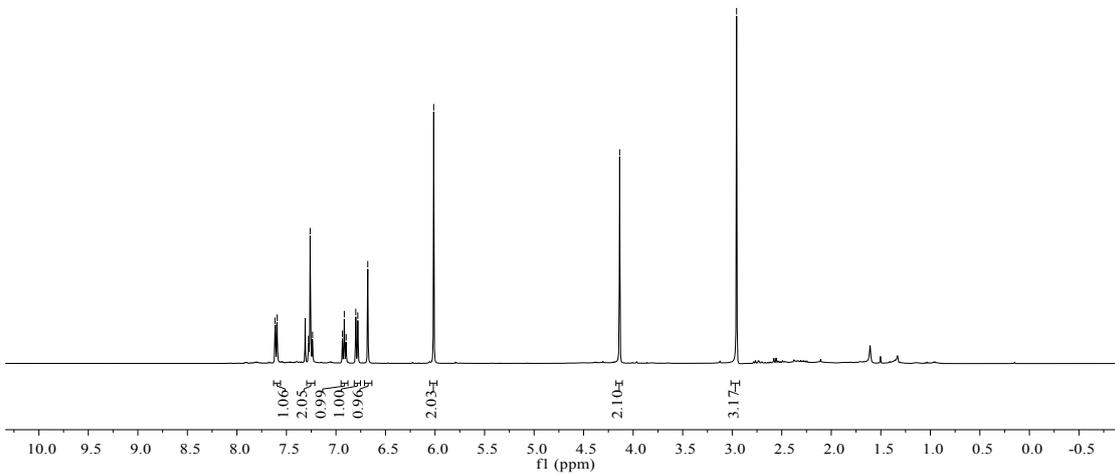
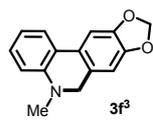


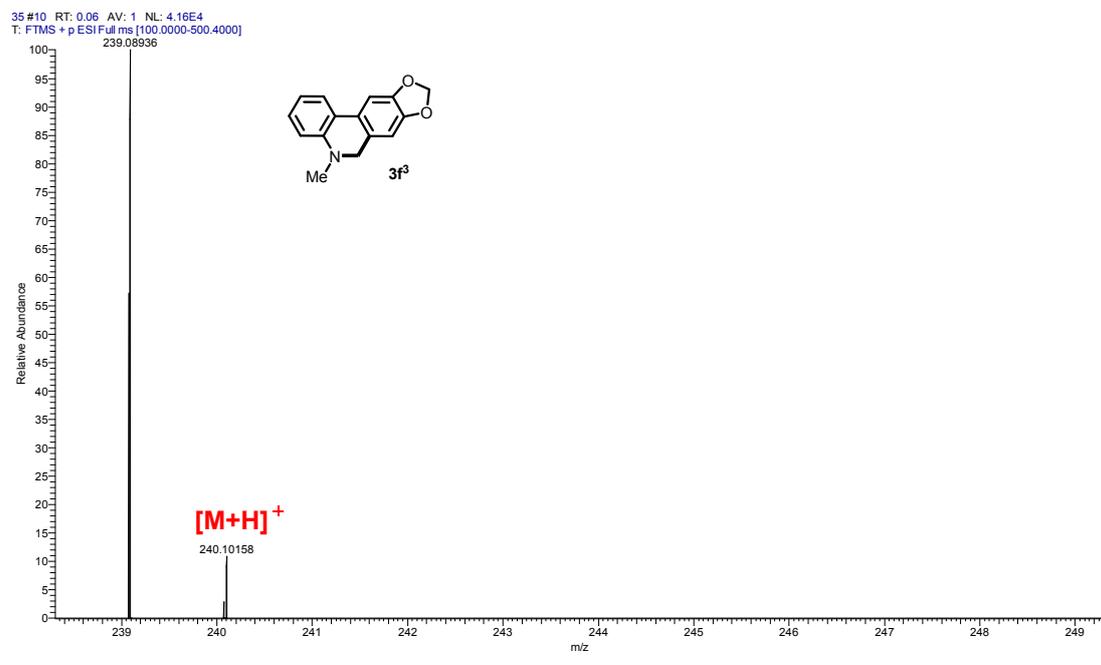
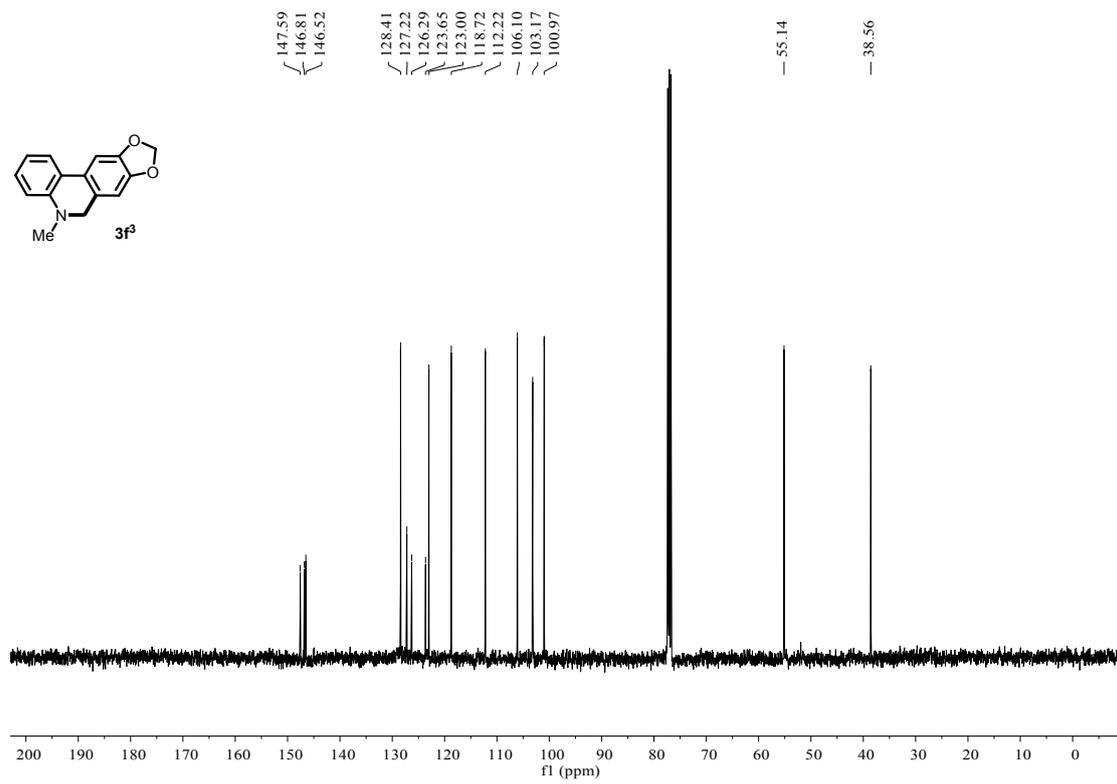


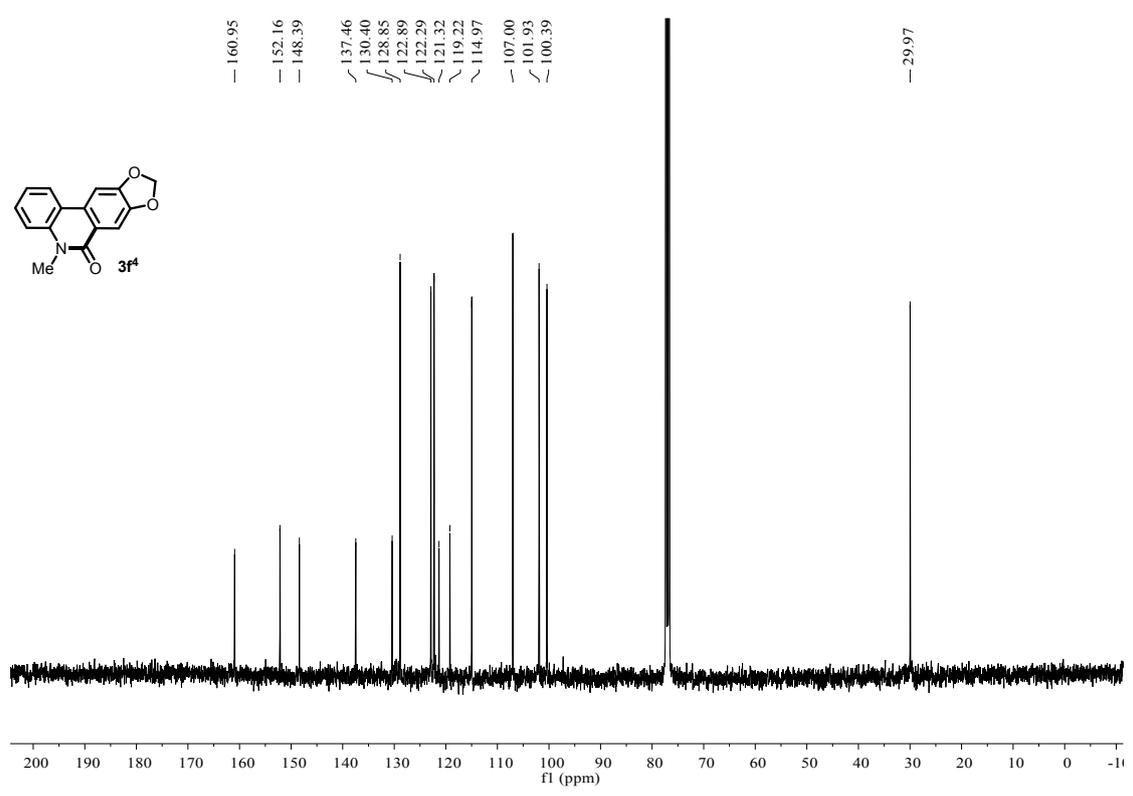
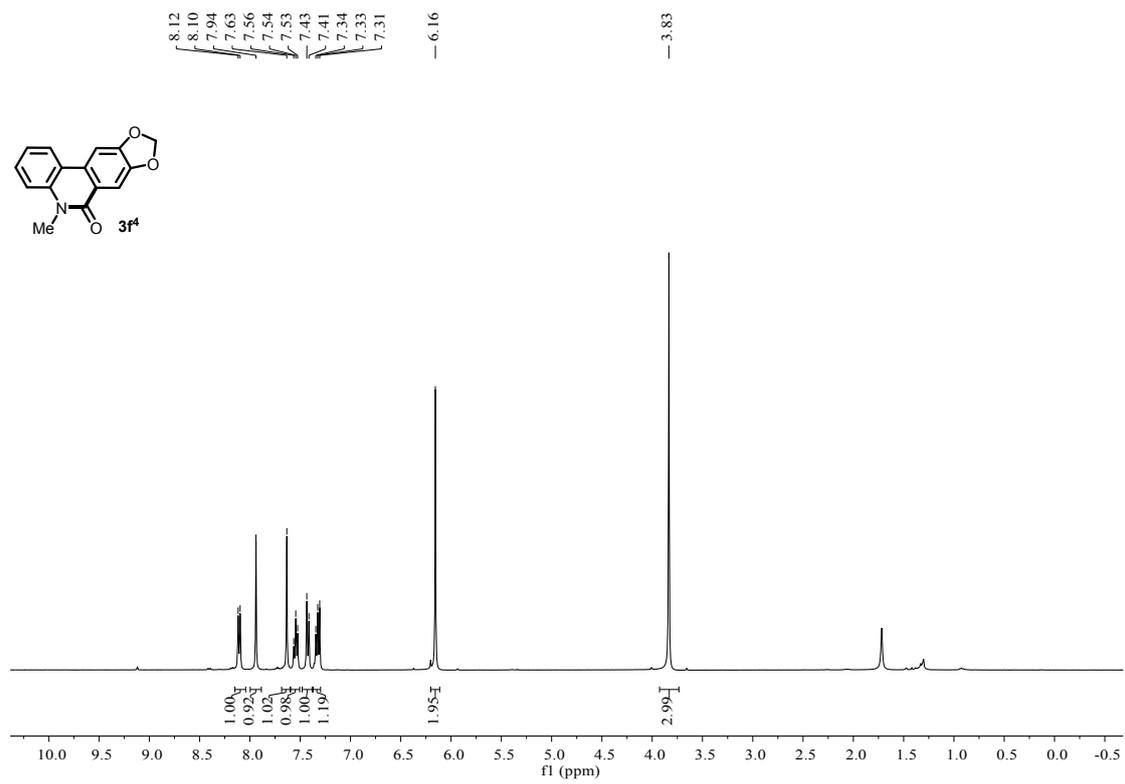
34 #6 RT: 0.04 AV: 1 NL: 9.60E5
T: FTMS + p ESI Full ms [100.0000-400.0000]



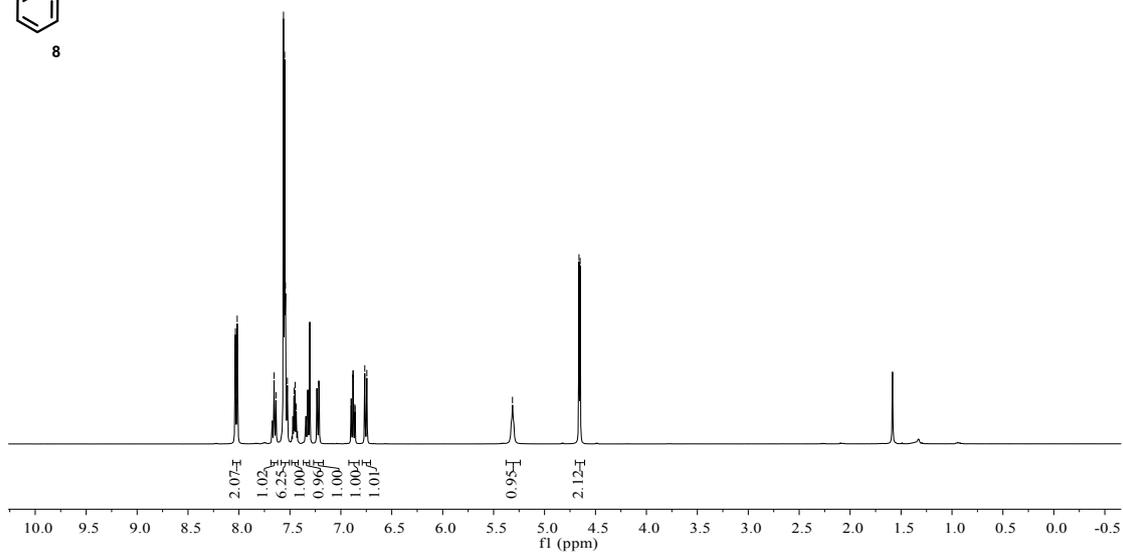
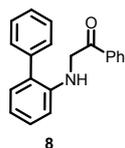
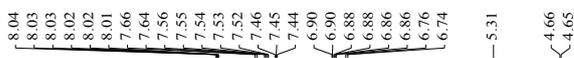
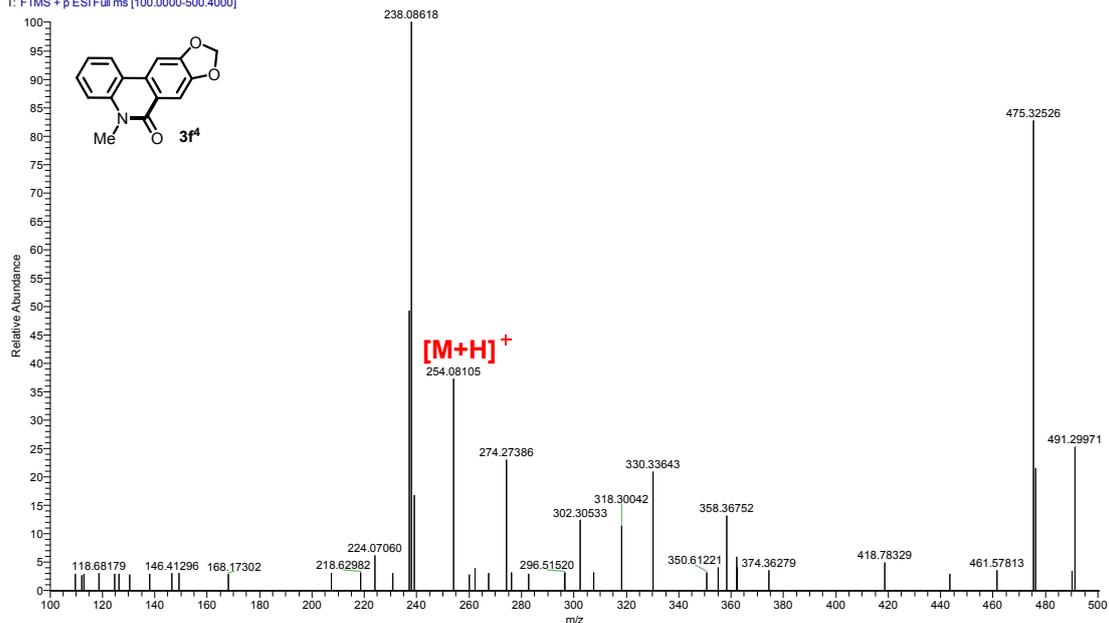
7.61
7.59
7.28
7.26
7.24
6.93
6.92
6.90
6.80
6.78
6.68
6.01
4.14
2.96

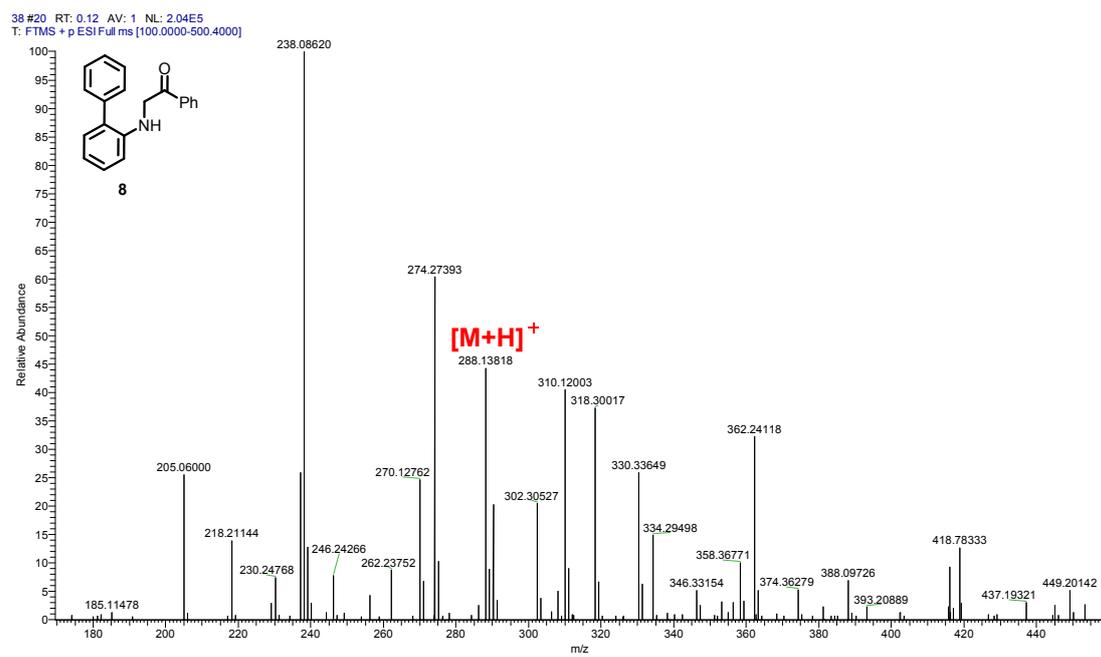
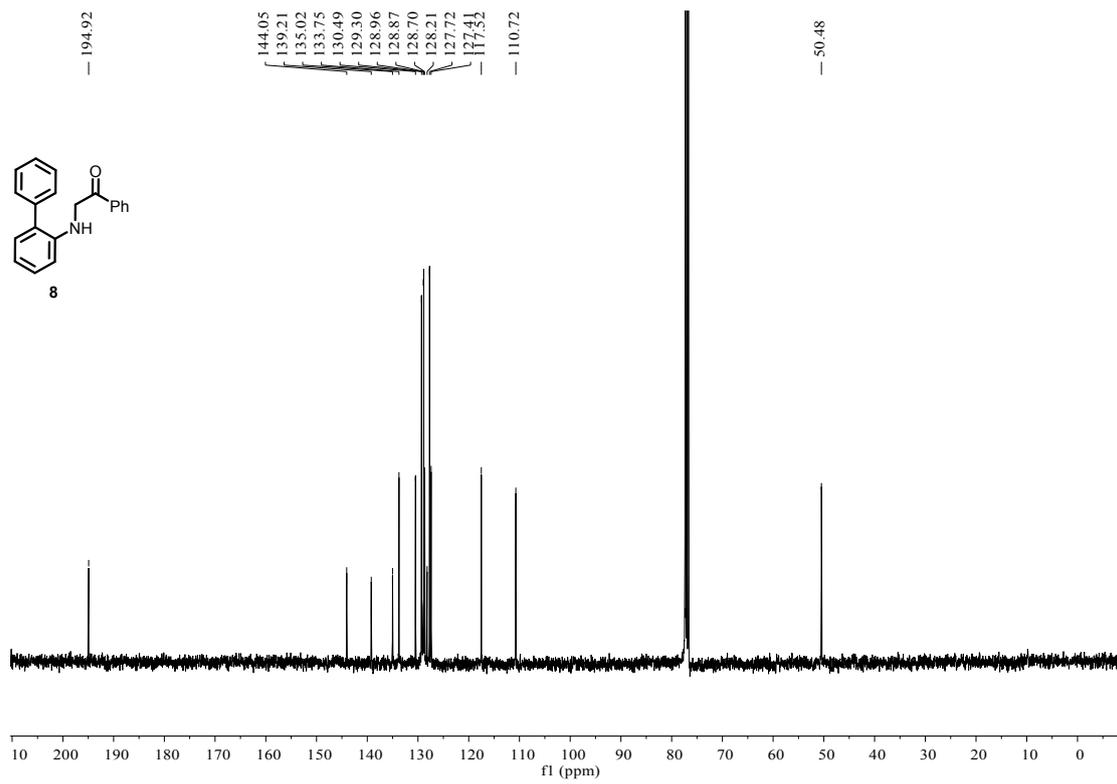


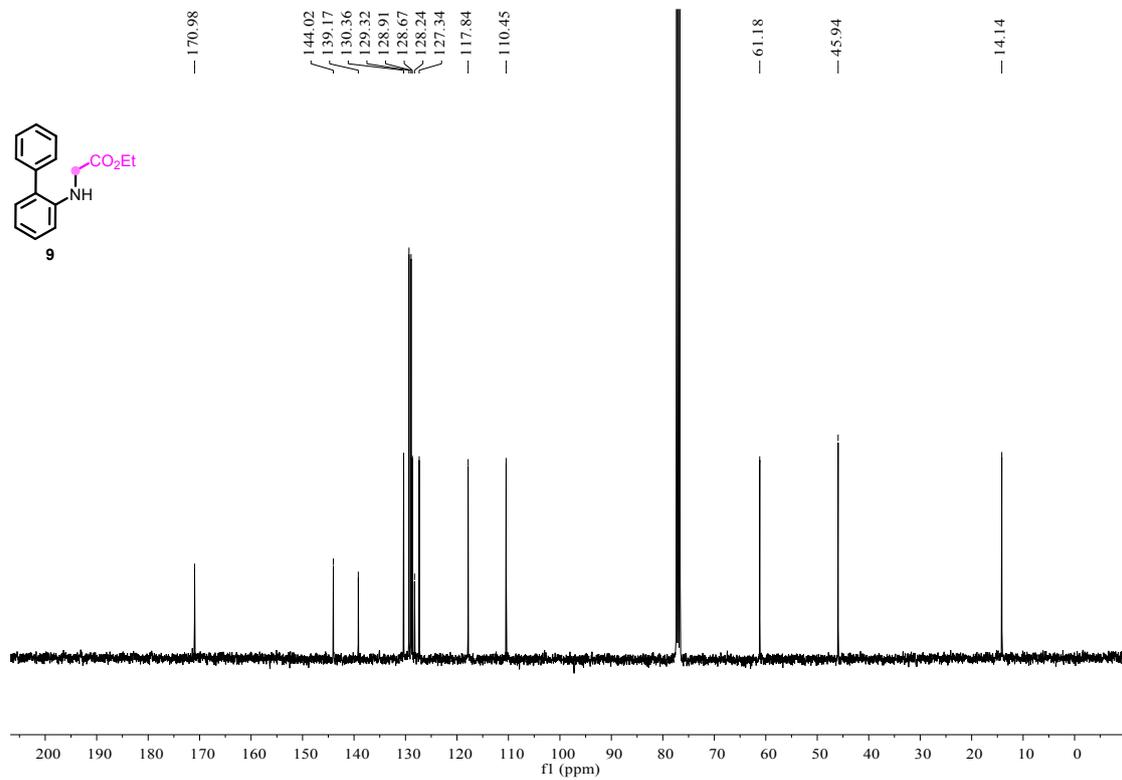
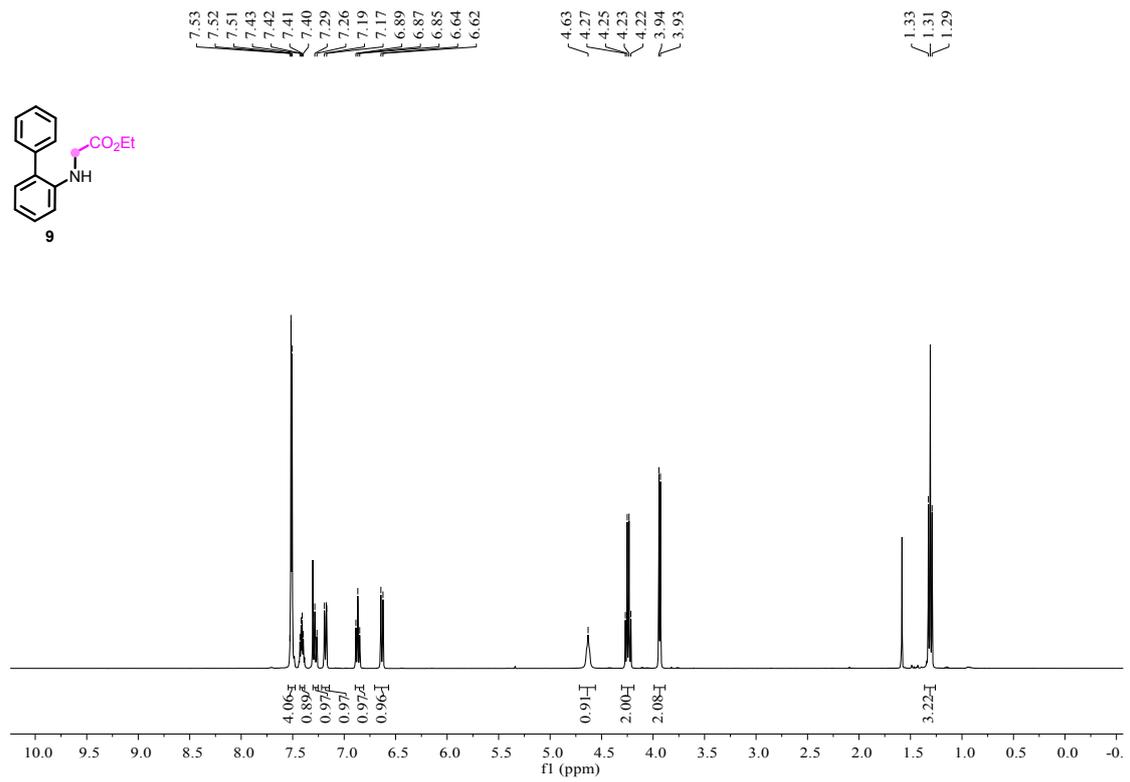
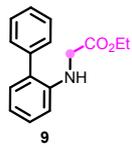




36 #20 RT: 0.12 AV: 1 NL: 3.57E4
T: FTMS + p ESI Full ms [100.0000-500.4000]







39#2 RT: 0.01 AV: 1 NL: 5.44E5
T: FTMS + p ESI Full ms [100.0000-400.0000]

