Supporting Information for

tert-Butyl benzoperoxoate (TBPB) mediated 2-isocyanobiaryls insertion with 1,4-dioxane: efficient synthesis of 6-alkyl phenanthridines via C(sp^3)-H/C(sp^2)-H bond functionalization

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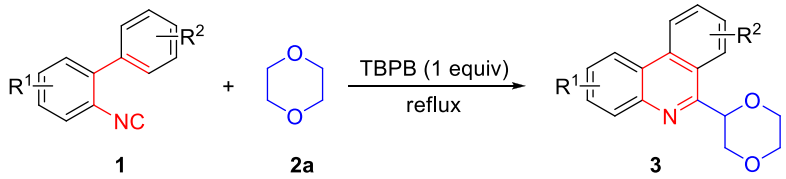
Experimental Section

General

Melting points were recorded on an Electrothermal digital melting point apparatus and were uncorrected. IR spectra were recorded on a Varian FT-1000 spectrophotometer using KBr optics. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian INOVA 400 or 600 MHz (^{1}H NMR) ,101 or 151 MHz (^{13}C NMR) spectrumeter using $CDCl_3$ as solvent and TMS as internal standard. High resolution mass spectra were obtained using GCT-TOF instrument with CI source.

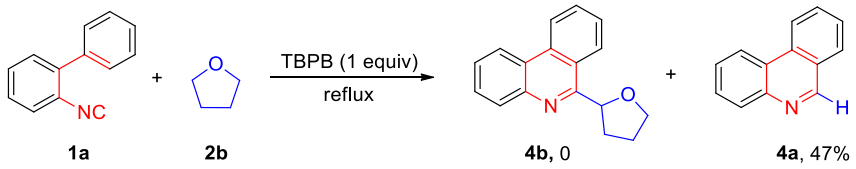
Typical procedure for products 3a-o:



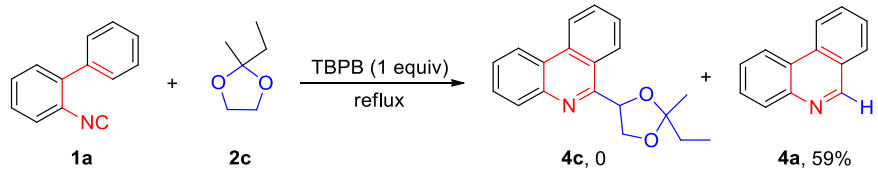
1 **2a** **3**

A mixture of isocyanide **1** (0.5mmol) and 1,4-dioxane (**2a**) (3 mL), TBHP (1 equiv) were added into a flask under Ar. Then the mixture was vigorously stirred under at 100 ^{o}C for 3 h (monitored by TLC). After removing the solvents in vacuo, the residue was directly purified by flash column chromatography by using ethyl acetate and petroleum ether as eluents to afford pure product **3**.

Typical procedure for products 4a:



1a **2b** **4b**, 0 **4a**, 47%



1a **2c** **4c**, 0 **4a**, 59%

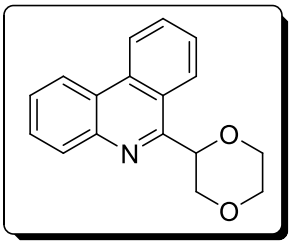
A mixture of isocyanide **1a** (0.5mmol) and **2b** or **2c** (3 mL), TBHP (1 equiv) were added into a flask under Ar. Then the mixture was vigorously stirred under at 100 ^{o}C for 3 h (monitored by TLC). After removing the solvents in vacuo, the residue was directly purified by flash column chromatography by using ethyl acetate and petroleum ether as eluents to afford pure product **4a**.

Preparation of isonitriles:

All isonitriles were prepared according to a reported method.[1]

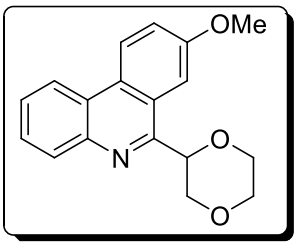
Analytical data of **1a**, **1b**, **1f**, **1g**, **1h**, **1j**, **1l**, **1m** are in agreement with those reported in the literature.

Compound characterizations:



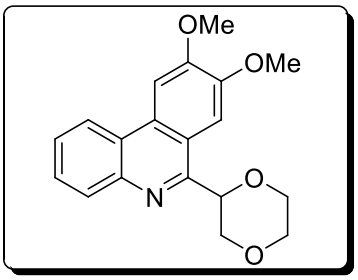
6-(1,4-dioxan-2-yl)phenanthridine (3a)

Yield=89%. White solid. M.p. 163.6-164.3℃.IR (KBr) 3056, 2955, 2915, 2855, 1614, 1574, 1448, 1252, 759 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.50 (d, *J*= 8.3 Hz, 1H, Ar-H), 8.41 (d, *J*= 8.0 Hz, 1H, Ar-H), 8.31 (d, *J*= 8.2 Hz, 1H, Ar-H), 8.10 (d, *J*= 8.1 Hz, 1H, Ar-H), 7.70 (t, *J*= 7.6 Hz, 1H, Ar-H), 7.66 – 7.47 (m, 3H, Ar-H), 5.36 (dd, *J*= 7.7, 4.6 Hz, 1H, CH), 4.33 – 4.12 (m, 2H, CH_2), 4.11 – 3.93 (m, 2H, CH_2), 3.89 – 3.70 (m, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 156.14, 143.17, 133.20, 130.53, 130.50, 128.63, 127.38, 127.33, 126.07, 124.52, 124.04, 122.44, 121.89, 76.19, 70.08, 67.75, 66.59. HRMS (CI) m/z calculated for $C_{17}H_{15}NO_2$, $[M+H]^+$ 266.1181; found 266.1179.



6-(1,4-dioxan-2-yl)-8-methoxyphenanthridine (3b)

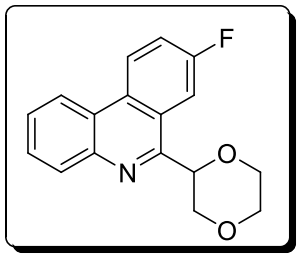
Yield=81%. White solid. M.p. 168.7-170.3℃. IR (KBr) 2971, 2919, 2859, 1623, 1238, 1108, 750 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.45 (d, *J*= 9.1 Hz, 1H, Ar-H), 8.38 – 8.32 (m, 1H, Ar-H), 8.15 – 8.03 (m, 1H, Ar-H), 7.69 (d, *J*= 2.4 Hz, 1H, Ar-H), 7.56 (pd, *J*= 7.0, 1.4 Hz, 2H, Ar-H), 7.38 (dd, *J*= 9.1, 2.5 Hz, 1H, Ar-H), 5.33 (dd, *J*= 8.2, 4.2 Hz, 1H, CH), 4.35 – 4.15 (m, 2H, CH_2), 4.12 – 3.96 (m, 2H, CH_2), 3.91 (s, 3H, CH_3), 3.87 – 3.77 (m, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 158.59, 155.21, 142.34, 130.46, 127.64, 127.39, 125.84, 124.15, 124.10, 121.40, 120.83, 106.52, 76.45, 69.97, 67.68, 66.60, 55.50. HRMS (CI^+) m/z calculated for $C_{18}H_{17}NO_3$, $[M+H]^+$ 296.1287; found 296.1284.



6-(1,4-dioxan-2-yl)-8,9-dimethoxyphenanthridine (3c)

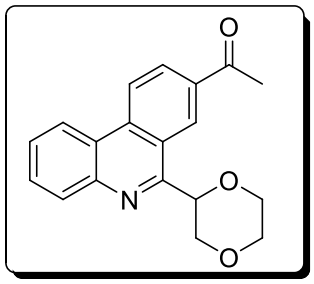
Yield=49%. White solid. M.p. 189.1-192.7℃. IR (KBr) 2954, 2850, 1614, 1506, 1260, 1091,754 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.33 (d, *J*= 8.1 Hz, 1H, Ar-H), 8.09 (d, *J*= 7.8 Hz, 1H, Ar-H), 7.83 (s, 1H, Ar-H),

7.70 (s, 1H, Ar-H), 7.57 (ddd, *J*= 15.1, 13.6, 6.9 Hz, 1H, Ar-H), 5.31 (dd, *J*= 8.7, 3.7 Hz, 1H, CH), 4.25 – 4.20 (m, 2H, CH_2), 4.05 (s, 3H, CH_2, CH_3), 4.05 – 4.02 (m, 2H, CH_2), 4.01 (s, 3H, CH_3), 3.84 (dd, *J*= 7.6, 3.3 Hz, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 154.46, 152.39, 149.50, 142.85, 130.52, 129.26, 127.78, 126.85, 123.77, 121.42, 119.88, 105.75, 102.19, 76.87, 69.99, 67.64, 66.61, 56.08, 55.98. HRMS (CI^+) m/z calculated for $C_{19}H_{19}NO_4$, $[M+H]^+$ 326.1392; found 326.1395.



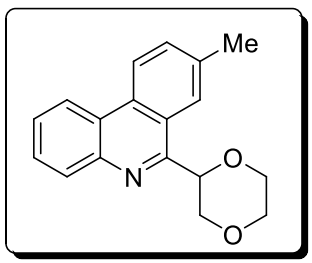
6-(1,4-dioxan-2-yl)-8-fluorophenanthridine (3d)

Yield=73%. White solid. M.p. 205.3-207.0℃.IR (KBr) 2971, 2863, 1536, 1484, 1117, 763 cm^{-1}.^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.57 (dd, *J*= 9.1, 5.4 Hz, 1H, Ar-H), 8.42 (d, *J*= 7.8 Hz, 1H, Ar-H), 8.20 – 8.07 (m, 1H, Ar-H), 8.03 (dd, *J*= 10.0, 2.5 Hz, 1H, Ar-H), 7.69 – 7.57 (m, 2H, Ar-H), 7.52 (td, *J*= 9.0, 2.6 Hz, 1H, Ar-H), 5.27 (dd, *J*= 8.2, 4.2 Hz, 1H, CH), 4.31 – 4.20 (m, 2H, CH_2), 4.12 – 3.96 (m, 2H, CH_2), 3.84 (dd, *J*= 7.7, 2.1 Hz, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 162.56, 160.09, 155.44, 142.77, 130.63, 128.54, 127.77, 125.92, 124.99, 123.65, 121.67, 119.92, 110.98, 76.37, 69.76, 67.70, 66.57. HRMS (CI^+) m/z calculated for $C_{17}H_{14}FNO_2$, $[M+H]^+$ 284.1087; found 284.1084.



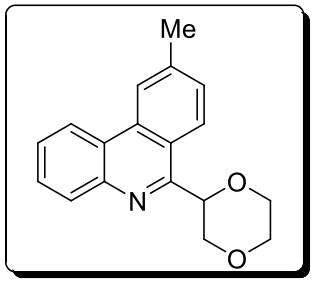
1-(6-(1,4-dioxan-2-yl)phenanthridin-8-yl)ethanone (3e)

Yield=47%. White solid. M.p. 212.5-214.8℃.IR (KBr) 2972, 2928, 2854, 1684, 1611, 1370, 1264, 1109, 762 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.00 (d, *J*= 1.5 Hz, 1H, Ar-H), 8.59 (t, *J*= 11.6 Hz, 1H, Ar-H), 8.49 (d, *J*= 7.7 Hz, 1H, Ar-H), 8.29 (dd, *J*= 8.7, 1.7 Hz, 1H, Ar-H), 8.13 (dd, *J*= 8.1, 0.8 Hz, 1H, Ar-H), 7.75 – 7.67 (m, 1H, Ar-H), 7.67 – 7.58 (m, 1H, Ar-H), 5.48 – 5.37 (m, 1H, CH), 4.33 – 4.22 (m, 2H, CH_2), 4.16 – 4.00 (m, 2H, CH_2), 3.91 – 3.76 (m, 2H, CH_2), 2.71 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 197.23, 156.76, 143.95, 136.30, 135.40, 130.66, 129.90, 128.98, 127.82, 127.62, 124.13, 123.35, 122.98, 122.54, 76.19, 69.89, 67.69, 66.61, 26.71. HRMS (CI^+) m/z calculated for $C_{19}H_{17}NO_3$, $[M+H]^+$ 308.1287; found 308.1290.



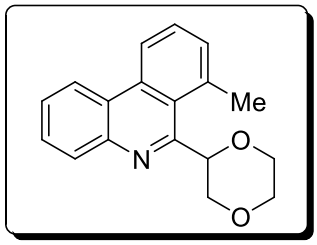
6-(1,4-dioxan-2-yl)-8-methylphenanthridine (3f)

Yield=86%. White solid. M.p. 177.7-178.6℃. IR (KBr) 2954, 2846, 1584, 1454, 1247, 907, 767 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.43 (dd, *J*= 13.0, 4.8 Hz, 2H, Ar-H), 8.12 (dd, *J*= 8.1, 1.1 Hz, 1H, Ar-H), 8.07 (s, 1H, Ar-H), 7.66 – 7.51 (m, 3H, Ar-H), 5.46 – 5.36 (m, 1H, CH), 4.21 (d, *J*= 6.4 Hz, 2H, CH_2), 4.11 – 3.98 (m, 2H, CH_2), 3.91 – 3.79 (m, 2H, CH_2), 2.54 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 155.72, 142.89, 137.38, 132.32, 131.10, 130.48, 128.18, 127.25, 125.24, 124.61, 124.12, 122.40, 121.70, 76.01, 70.20, 67.76, 66.59, 22.00. HRMS (CI^+) m/z calculated for $C_{18}H_{17}NO_2$, $[M+H]^+$ 280.1338; found 280.1344.



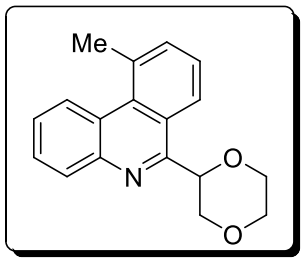
6-(1,4-dioxan-2-yl)-9-methylphenanthridine (3g)

Yield=51%. White solid. M.p. 161.5-162.9℃. IR (KBr) 2956, 2915, 2858, 1631, 1611, 1370, 1264, 1109, 762 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.48 (d, *J*= 8.0 Hz, 1H, Ar-H), 8.37 (s, 1H, Ar-H), 8.26 (d, *J*= 8.4 Hz, 1H, Ar-H), 8.14 (d, *J*= 8.0 Hz, 1H, Ar-H), 7.64 (t, *J*= 7.0 Hz, 1H, Ar-H), 7.58 (t, *J*= 7.1 Hz, 1H, Ar-H), 7.47 (d, *J*= 7.9 Hz, 1H, Ar-H), 5.41 (t, *J*= 6.0 Hz, 1H, CH), 4.21 (d, *J*= 6.3 Hz, 2H, CH_2), 4.12 – 3.99 (m, 2H, CH_2), 3.90 – 3.77 (m, 2H, CH_2), 2.58 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 155.97, 133.46, 130.39, 129.17, 128.55, 127.13, 125.93, 123.93, 122.59, 122.12, 121.87, 76.30, 70.16, 67.73, 66.57, 22.30. HRMS (CI^+) m/z calculated for $C_{18}H_{17}NO_2$, $[M+H]^+$ 280.1338; found 280.1336.



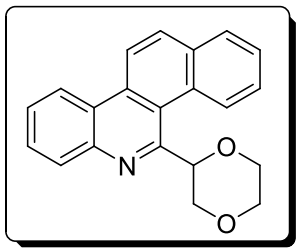
6-(1,4-dioxan-2-yl)-7-methylphenanthridine (3g')

Yield=24%. White solid. M.p. 131.8-134.4℃. IR (KBr) 2968, 2928, 2850, 1439, 1264, 1076, 750 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.52 – 8.42 (m, 2H, Ar-H), 8.05 (dd, *J*= 8.0, 1.1 Hz, 1H, Ar-H), 7.65 – 7.59 (m, 2H), 7.59 – 7.53 (m, 1H, Ar-H), 7.46 (d, *J*= 7.2 Hz, 1H, Ar-H), 5.42 (dd, *J*= 9.3, 2.4 Hz, 1H, CH), 4.51 (dd, *J*= 12.0, 9.3 Hz, 1H,CH_2), 4.16 (dd, *J*= 12.0, 2.4 Hz, 1H, CH_2), 4.03 – 3.88 (m, 2H, CH_2), 3.86 – 3.75 (m, 2H, CH_2), 3.02 (s, 3H,CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 155.86, 142.20, 136.32, 134.87, 131.89, 130.16, 129.77, 128.41, 127.39, 125.25, 124.32, 122.15, 120.81, 70.58, 67.59, 66.46, 23.58, 1.03. HRMS (ESI) m/z calculated for $C_{18}H_{17}NO_2$, $[M+H]^+$ 280.1338; found 280.1335.



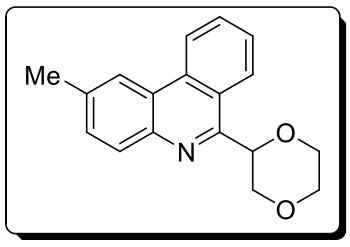
6-(1,4-dioxan-2-yl)-10-methylphenanthridine (3h)

Yield=45%. White solid. M.p. 167.0-168.4℃. IR (KBr) 2971, 2923, 2876, 1575, 1441, 1359, 1130, 866 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.72 (d, *J*= 8.4 Hz, 1H, Ar-H), 8.27 (d, *J*= 8.1 Hz, 1H, Ar-H), 8.18 (d, *J*= 7.9 Hz, 1H, Ar-H), 7.69 – 7.50 (m, 4H, Ar-H), 5.39 (dd, *J*= 9.1, 3.2 Hz, 1H, CH), 4.34 – 4.19 (m, 2H, CH_2), 4.13 – 3.97 (m, 2H, CH_2), 3.89 – 3.80 (m, 2H, CH_2), 3.03 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 156.45, 135.61, 134.74, 132.78, 130.84, 128.65, 127.85, 126.80, 126.50, 126.46, 126.00, 125.46, 124.46, 76.14, 70.15, 67.78, 66.59, 26.98. HRMS (CI^+) m/z calculated for $C_{18}H_{17}NO_2$, $[M+H]^+$ 280.1338; found 280.1333.



5-(1,4-dioxan-2-yl)benzo[i]phenanthridine (3i)

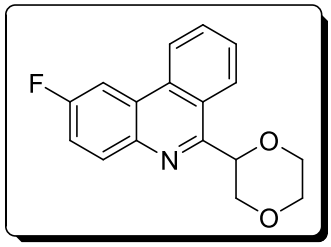
Yield=38%. White solid. M.p. 166.1-168.2℃. IR (KBr) 2952, 2838, 1570, 1435, 1366, 1129, 926, 750 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.84 (d, *J*= 8.5 Hz, 1H, Ar-H), 8.52 (t, *J*= 8.2 Hz, 2H, Ar-H), 8.19 (dd, *J*= 8.2, 0.7 Hz, 1H, Ar-H), 8.07 (d, *J*= 8.9 Hz, 1H, Ar-H), 7.95 (dd, *J*= 7.9, 0.9 Hz, 1H, Ar-H), 7.75 – 7.67 (m, 2H, Ar-H), 7.67 – 7.56 (m, 2H, Ar-H), 5.49 (dd, *J*= 9.5, 2.4 Hz, 1H, CH), 4.66 (dd, *J*= 11.8, 9.6 Hz, 1H, CH_2), 4.14 (dtd, *J*= 14.2, 11.5, 2.8 Hz, 2H, CH_2), 4.00 (td, *J*= 11.5, 2.9 Hz, 1H, CH_2), 3.86 (dd, *J*= 11.7, 2.6 Hz, 1H, CH_2), 3.75 (dd, *J*= 11.8, 2.2 Hz, 1H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 154.19, 143.70, 134.01, 133.05, 132.05, 130.17, 129.61, 128.88, 128.69, 127.52, 127.37, 127.35, 126.89, 123.75, 122.78, 122.40, 119.99, 70.22, 67.21, 66.42. HRMS (CI^+) m/z calculated for $C_{21}H_{17}NO_2$, $[M+H]^+$ 316.1338; found 316.1335.



6-(1,4-dioxan-2-yl)-2-methylphenanthridine (3k)

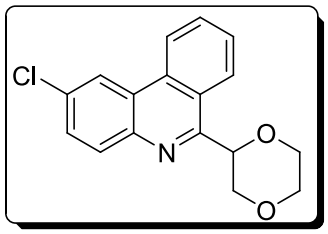
Yield=86%. White solid. M.p. 153.8-155.1℃. IR (KBr) 2981, 2956, 2858, 1574, 1443, 1121, 815, 913, 652 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.55 (d, *J*= 8.3 Hz, 1H, Ar-H), 8.33 (d, *J*= 8.2 Hz, 1H, Ar-H), 8.24 (s, 1H, Ar-H), 8.02 (d, *J*= 8.3 Hz, 1H, Ar-H), 7.74 (t, *J*= 7.6 Hz, 1H, Ar-H), 7.61 (t, *J*= 7.6 Hz, 1H, Ar-H), 7.47 (dd, *J*= 8.3, 1.2 Hz, 1H, Ar-H), 5.46 – 5.32 (m, 1H, CH), 4.28 – 4.17 (m, 2H, CH_2), 4.12 – 3.97 (m, 2H, CH_2), 3.91 – 3.79 (m, 2H, CH_2), 2.61 – 2.48 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 155.10, 141.48, 137.27,

132.99, 130.37, 130.30, 130.24, 127.24, 125.98, 124.58, 123.87, 122.43, 121.52, 76.20, 70.11, 67.75, 66.58, 22.03. HRMS (CI^+) m/z calculated for $C_{18}H_{17}NO_2$, $[M+H]^+$ 280.1338; found 280.1330.



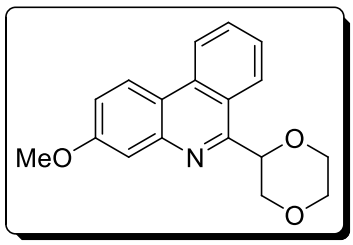
6-(1,4-dioxan-2-yl)-2-fluorophenanthridine (3l)

Yield=61%. White solid. M.p. 199.5-201.1℃. IR (KBr) 2968, 2928, 2866, 1586, 1496, 1125, 913, 763 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.42 (d, *J*= 8.2 Hz, 1H, Ar- H), 8.35 (d, *J*= 8.2 Hz, 1H, Ar- H), 8.11 (dd, *J*= 9.0, 5.7 Hz, 1H, Ar- H), 8.05 (dd, *J*= 10.1, 2.6 Hz, 1H, Ar- H), 7.77 (t, *J*= 7.5 Hz, 1H, Ar- H), 7.67 (t, *J*= 7.5 Hz, 1H, Ar- H), 7.37 (td, *J*= 8.7, 2.7 Hz, 1H, Ar- H), 5.43 – 5.32 (m, 1H, CH), 4.28 – 4.18 (m, 2H, CH_2), 4.12 – 3.97 (m, 2H,CH_2), 3.89 – 3.79 (m, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 162.79, 160.33, 155.40, 139.99, 132.81, 130.59, 128.05, 126.17, 125.50, 124.56, 122.62, 117.67, 107.00, 75.98, 69.99, 67.75, 66.58. HRMS (CI^+) m/z calculated for $C_{17}H_{14}FNO_2$, $[M+H]^+$ 284.1087; found 284.1083.



2-chloro-6-(1,4-dioxan-2-yl)phenanthridine (3m)

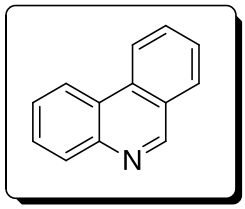
Yield=70%. White solid. M.p. 200.6-203.4℃. IR (KBr) 2972, 2928, 2866, 1492, 1439, 1129, 913, 762 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.48 (d, *J*= 8.3 Hz, 1H, Ar-H), 8.42 (d, *J*= 2.1 Hz, 1H, Ar-H), 8.36 (d, *J*= 8.2 Hz, 1H, Ar-H), 8.05 (d, *J*= 8.7 Hz, 1H, Ar-H), 7.78 (t, *J*= 7.4 Hz, 1H, Ar-H), 7.68 (t, *J*= 7.5 Hz, 1H, Ar-H), 7.58 (dd, *J*= 8.7, 2.1 Hz, 1H, Ar-H), 5.38 (t, *J*= 6.2 Hz, 1H, CH), 4.22 (d, *J*= 6.3 Hz, 2H, CH_2), 4.11 – 3.98 (m, 2H, CH_2), 3.88 – 3.80 (m, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 156.45, 141.55, 133.29, 132.22, 131.99, 130.84, 129.19, 128.08, 126.19, 125.14, 124.67, 122.49, 121.60, 75.99, 69.97, 67.76, 66.57. HRMS (CI^+) m/z calculated for $C_{17}H_{14}ClNO_2$, [M] 300.0791; found 300.0785.



6-(1,4-dioxan-2-yl)-3-methoxyphenanthridine (3o)

Yield=66%. White solid. M.p. 175.4-177.8℃. IR (KBr) 2976, 2915, 2854, 1623, 1439, 1121, 917, 758 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.47 (d, *J*= 8.3 Hz, 1H, Ar-H), 8.36 (d, *J*= 9.1 Hz, 1H, Ar-H), 8.31 (d, *J*= 8.3 Hz, 1H, Ar-H), 7.78 – 7.70 (m, 1H, Ar-H), 7.61 – 7.51 (m, 2H, Ar-H), 7.23 (dd, *J*= 9.0, 2.7 Hz, 1H, Ar-H), 5.43

(dd, *J*= 9.2, 3.1 Hz, 1H, CH), 4.18 (qd, *J*= 11.9, 6.3 Hz, 2H, CH_2), 4.09 – 4.03 (m, 2H, CH_2), 3.91 (s, 3H, CH_3), 3.89 – 3.80 (m, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 160.11, 156.55, 133.46, 130.63, 126.33, 125.89, 123.48, 123.10, 122.03, 118.61, 118.09, 110.14, 76.35, 70.29, 67.80, 66.57, 55.67. HRMS (CI^+) m/z calculated for $C_{18}H_{17}NO_3$, [M] 296.1287; found 296.1291.



phenanthridine (4a)

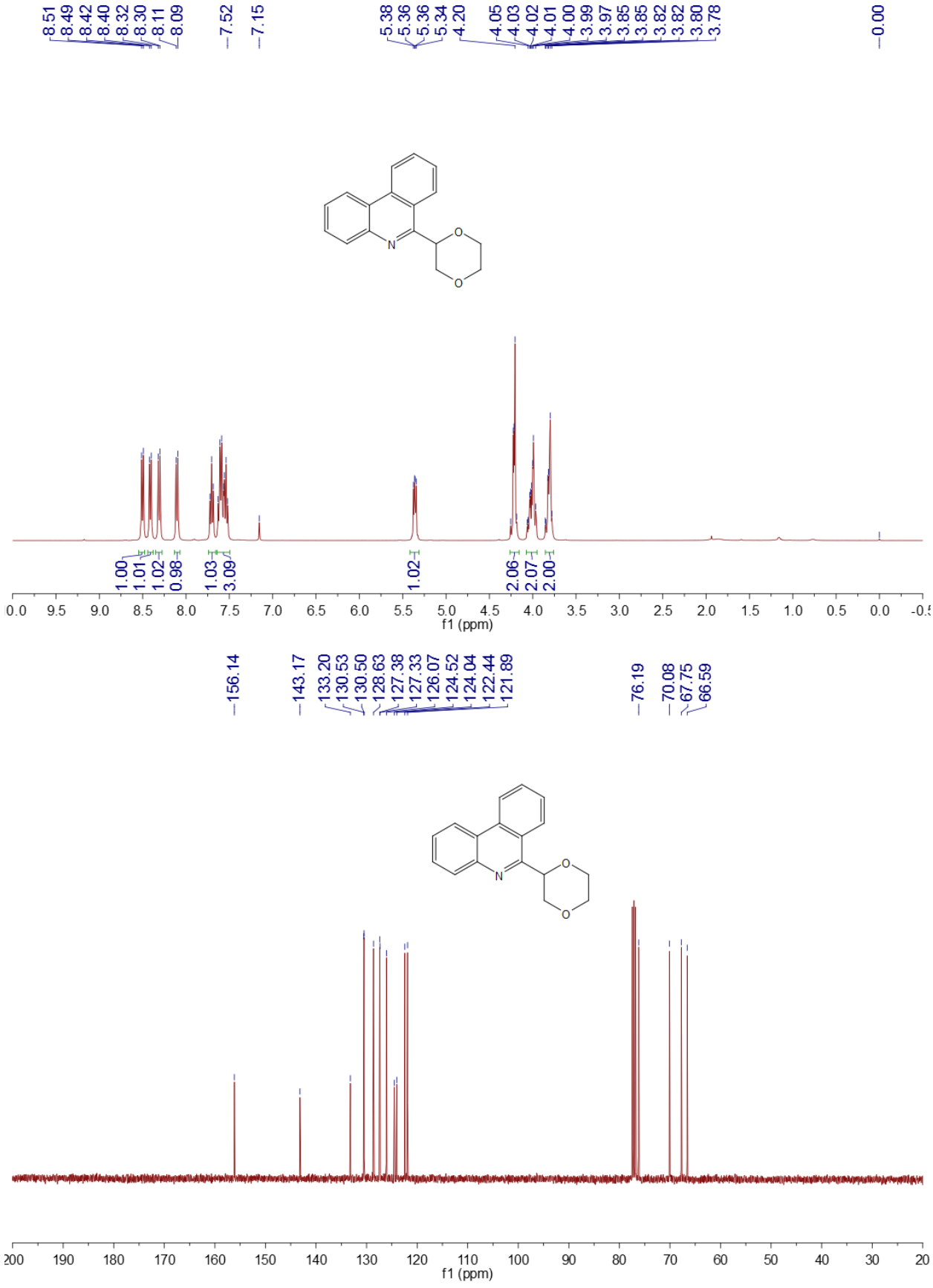
Yield=47%. White solid. 85.3-88.4℃. IR (KBr) 2923, 2850, 1458, 1247, 888, 745 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 9.23 (s, 1H, Ar-H), 8.56 (d, *J*= 8.3 Hz, 1H, Ar-H), 8.53 (dd, *J*= 8.1, 1.2 Hz, 1H, Ar-H), 8.18 – 8.11 (m, 1H, Ar-H), 8.00 (d, *J*= 7.9 Hz, 1H, Ar-H), 7.85 – 7.77 (m, 1H, Ar-H), 7.72 – 7.59 (m, 3H, Ar-H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 153.50, 144.32, 132.64, 131.14, 130.07, 128.85, 128.76, 127.56, 127.17, 126.38, 124.14, 122.25, 121.92. HRMS (CI^+) m/z calculated for $C_{13}H_9N$, $[M+H]^+$ 180.0813; found 180.0809.

References

[1] (a)Tobisu, M.; Koh, K.; Furukawa, T.; Chatani, N. *Angew. Chem. Int. Ed.* **2012**, *51*,11363. (b)Zhang, B.; Muck-Lichtenfeld, C.; Daniliuc, C. G.; Studer, A. *Angew. Chem. Int. Ed.* **2012**, *52*, 1. (c)Wang, Q.-L.; Dong, X.-C.; Xiao, T.-B.; Zhou, L. *Org. Lett.*, **2013**, *15*, 4846.

NMR Spectra

6-(1,4-dioxan-2-yl)phenanthridine (3a):



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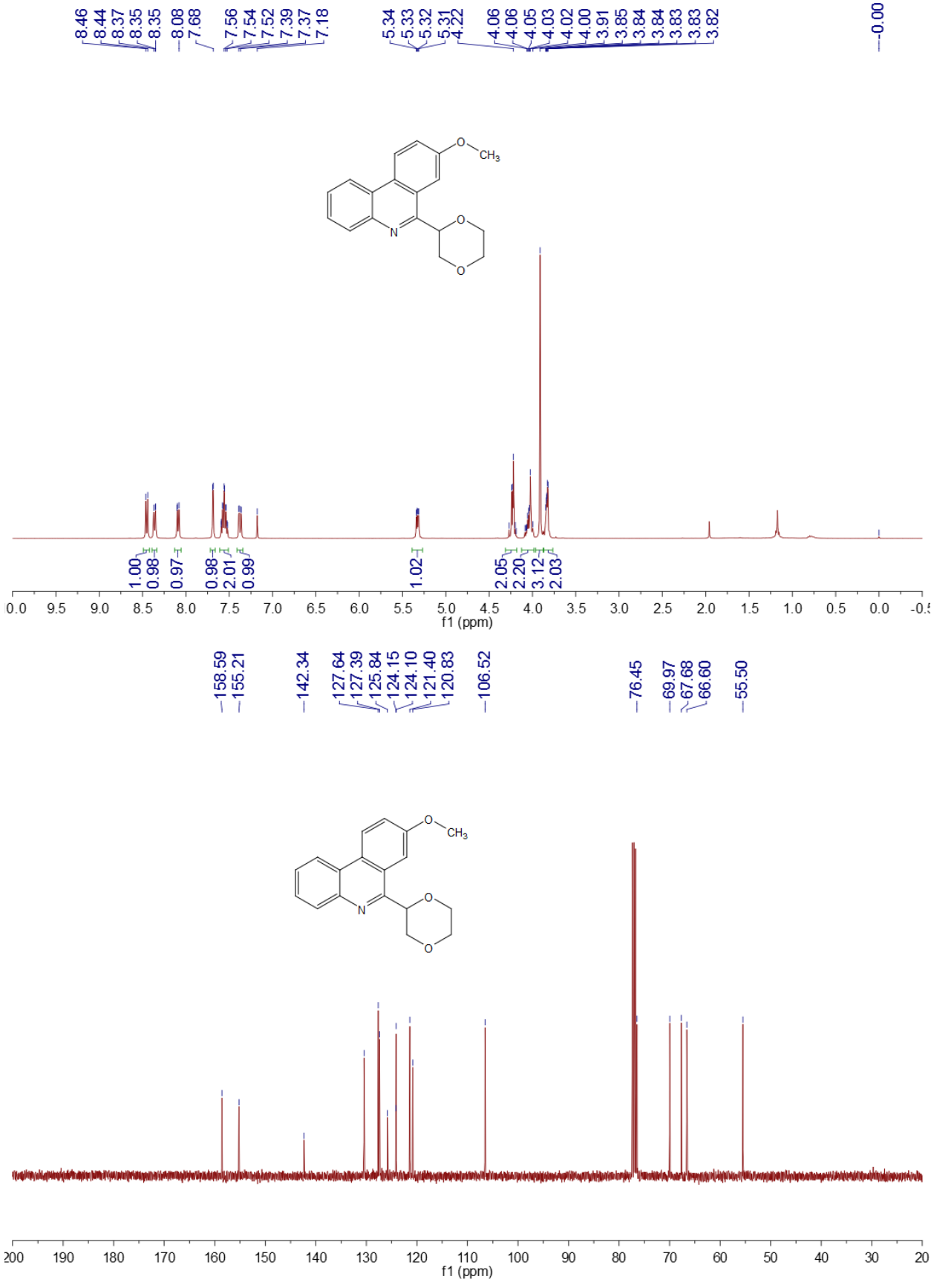

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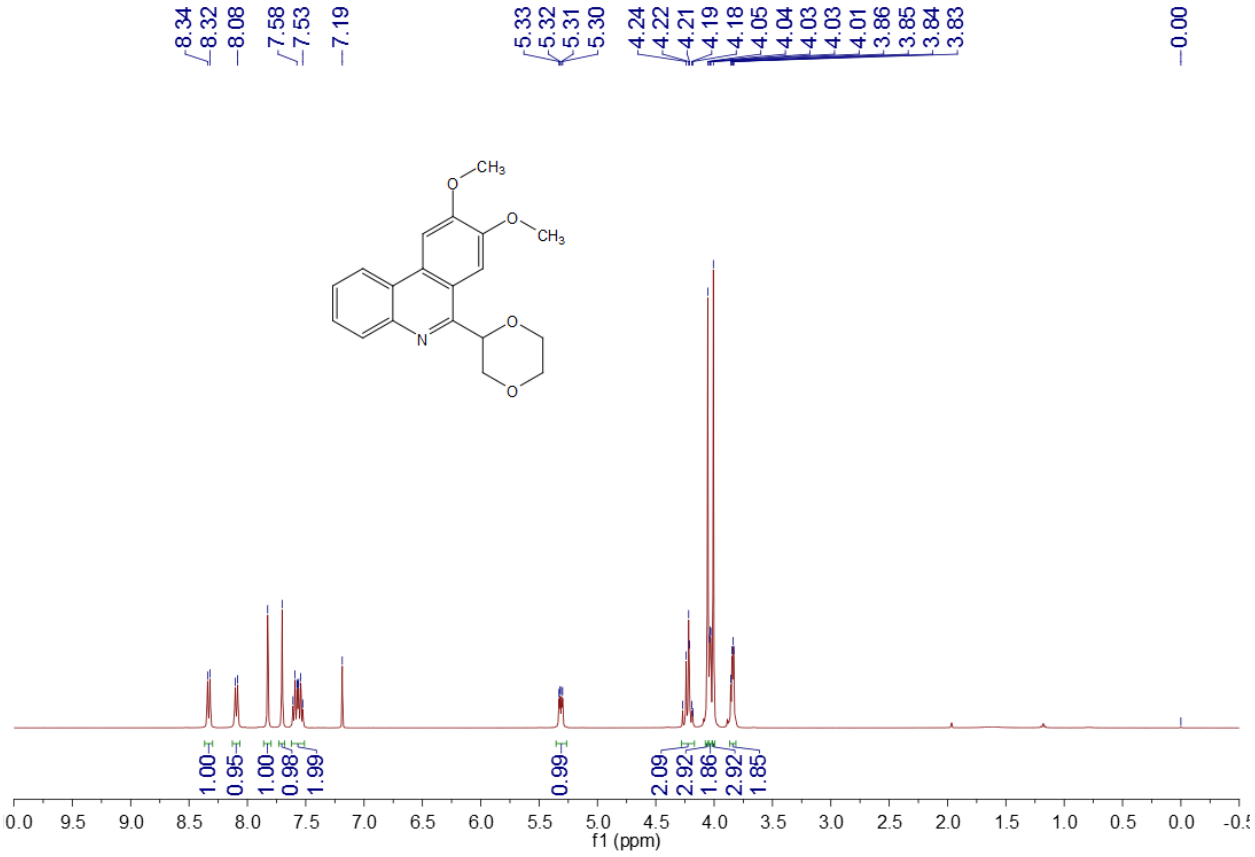

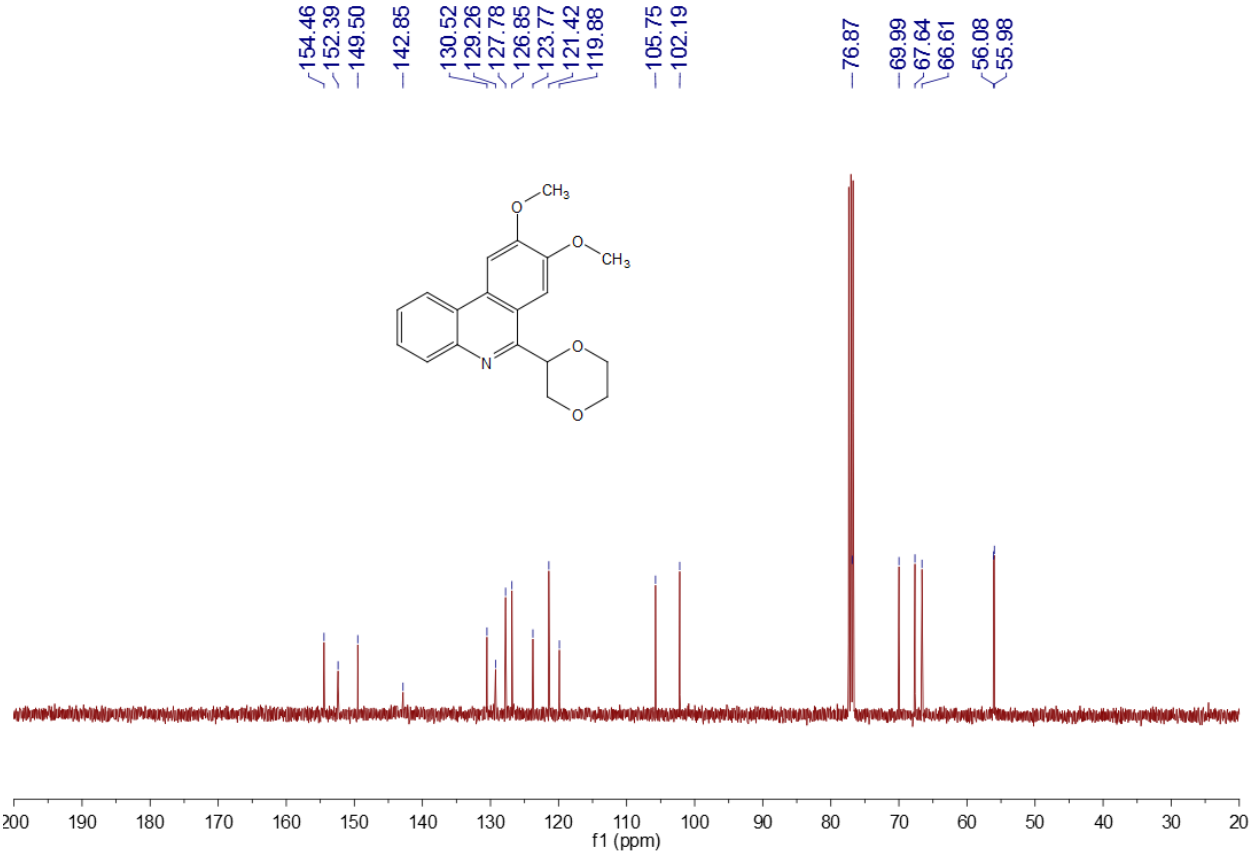

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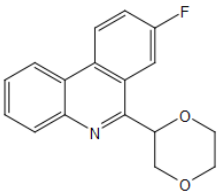
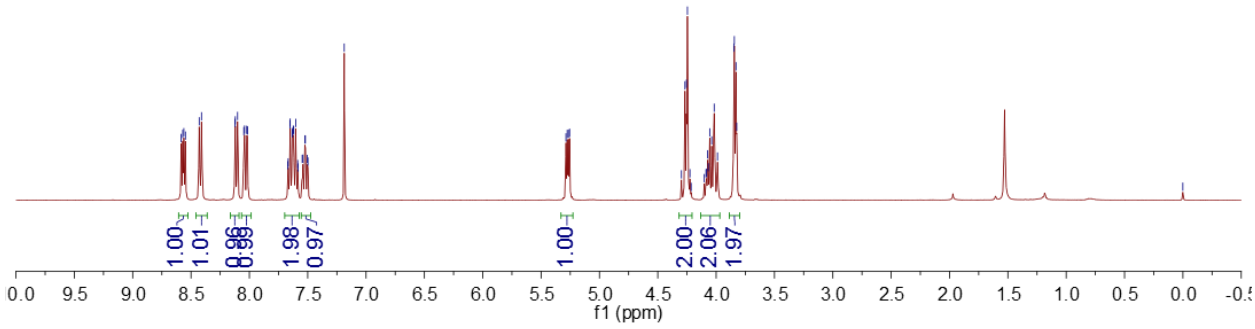
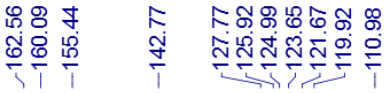
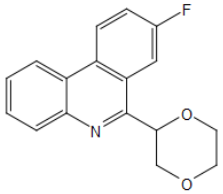
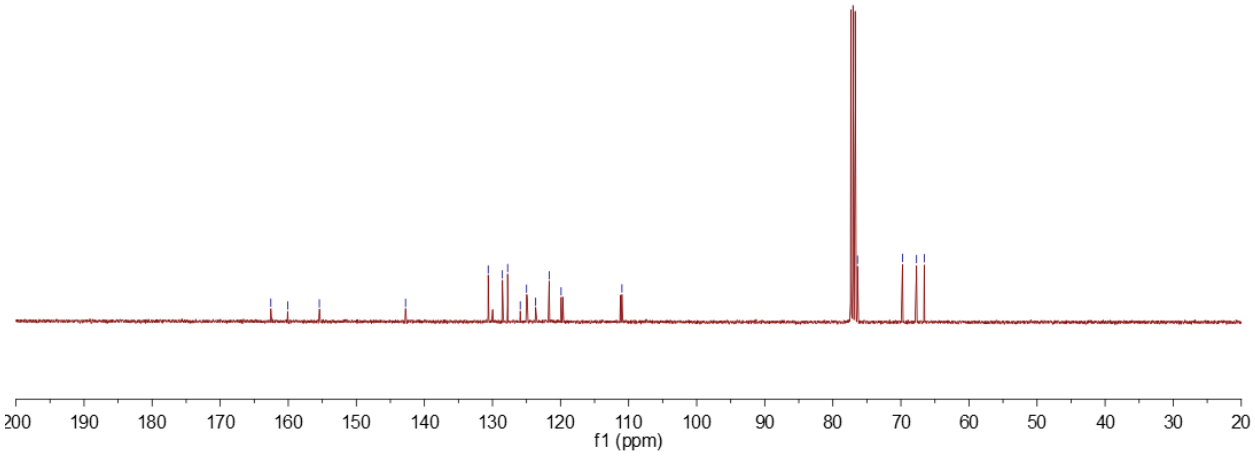


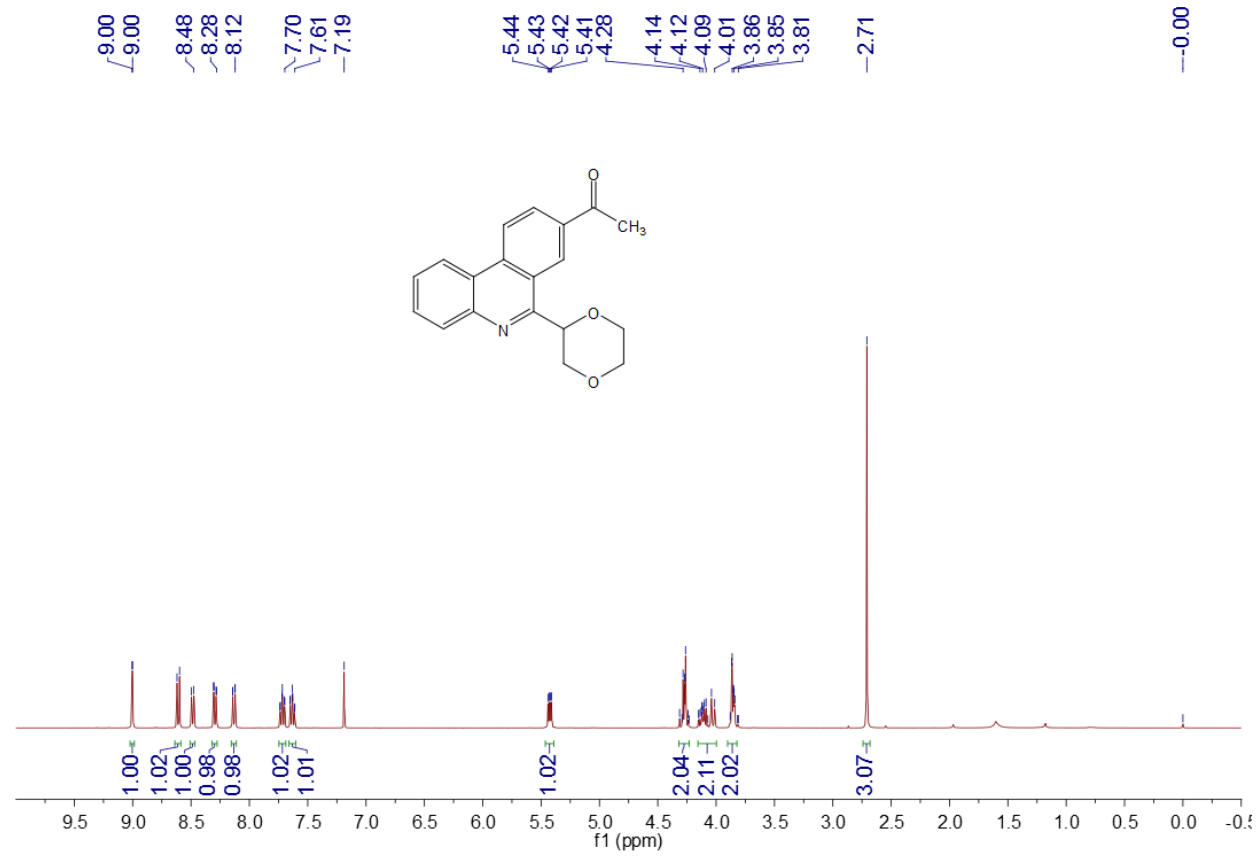


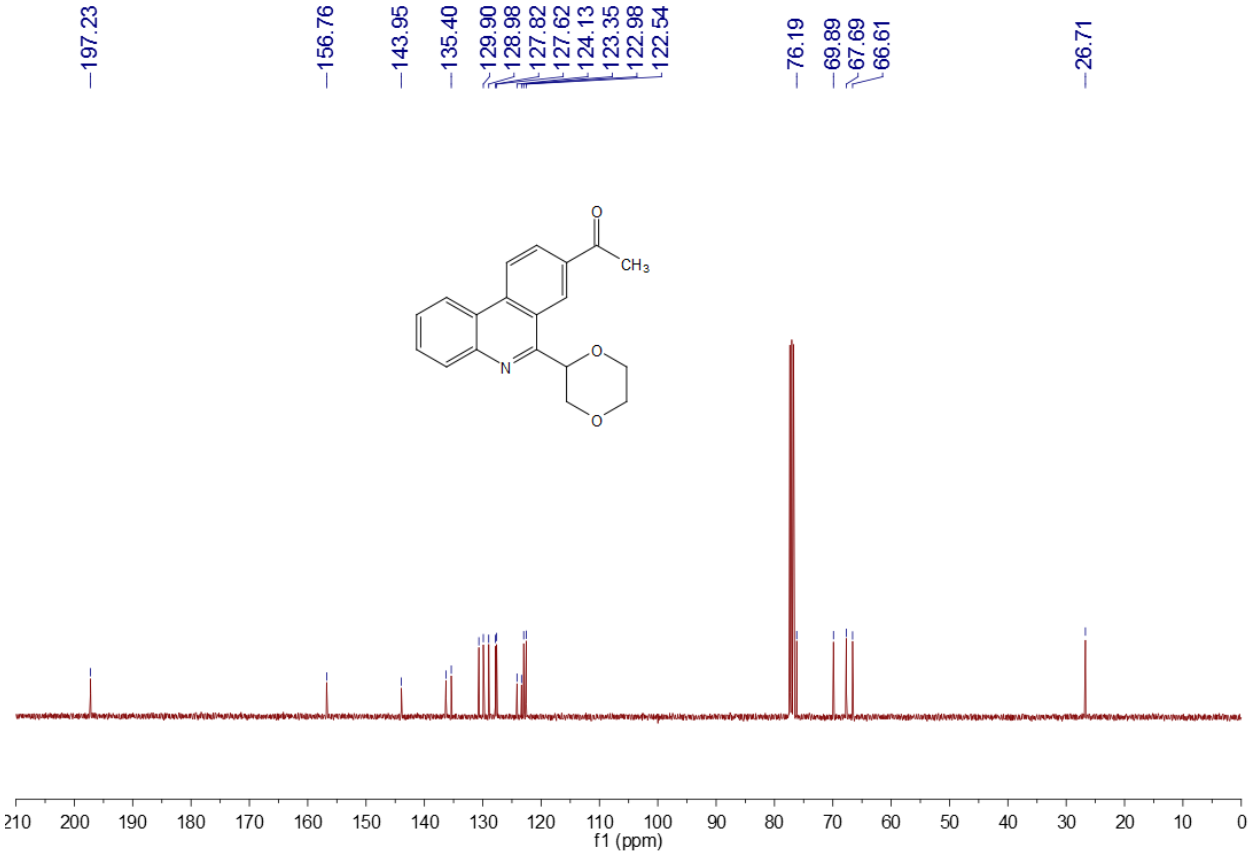




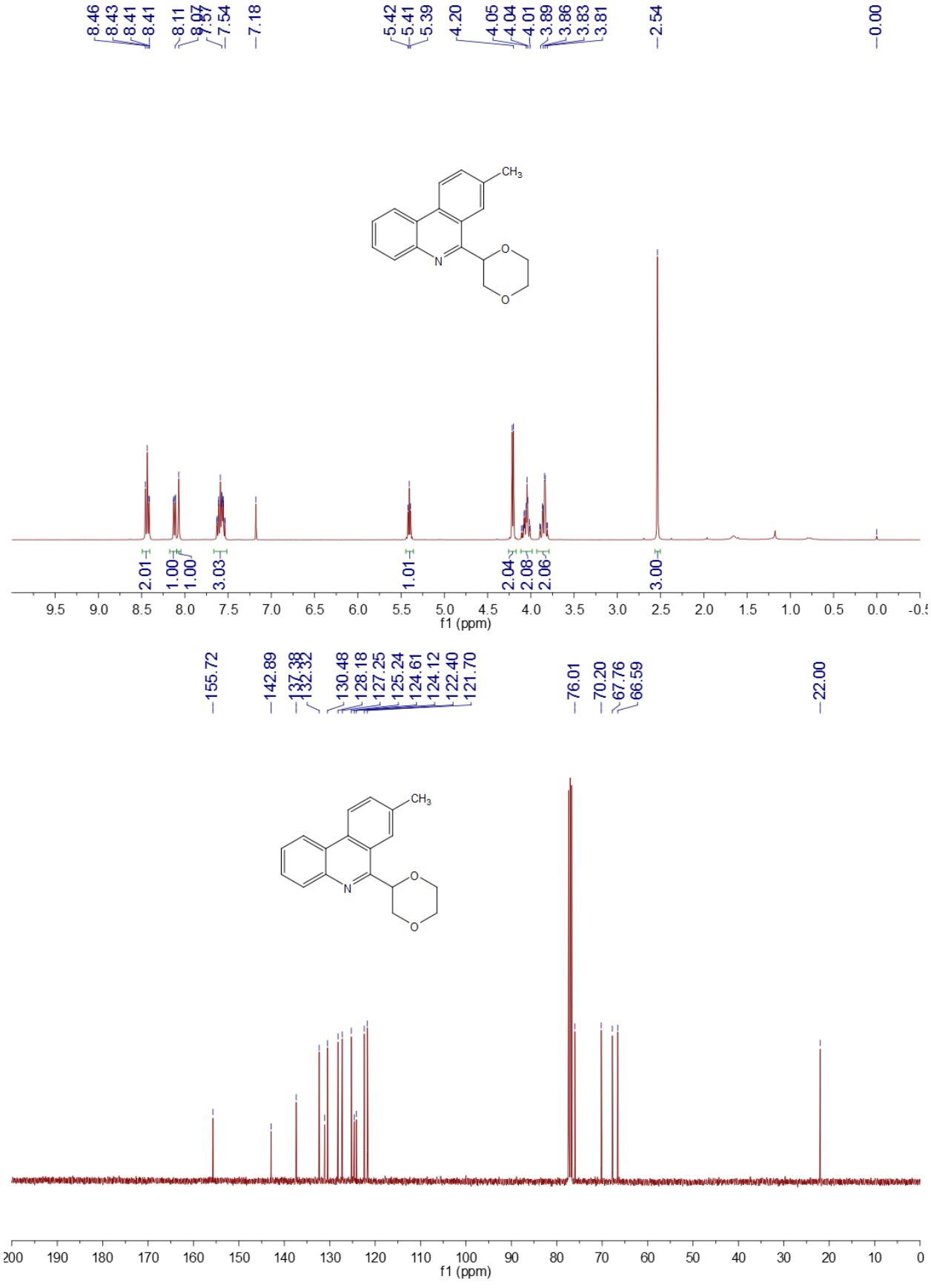


1-(6-(1,4-dioxan-2-yl)phenanthridin-8-yl)ethanone (3e):

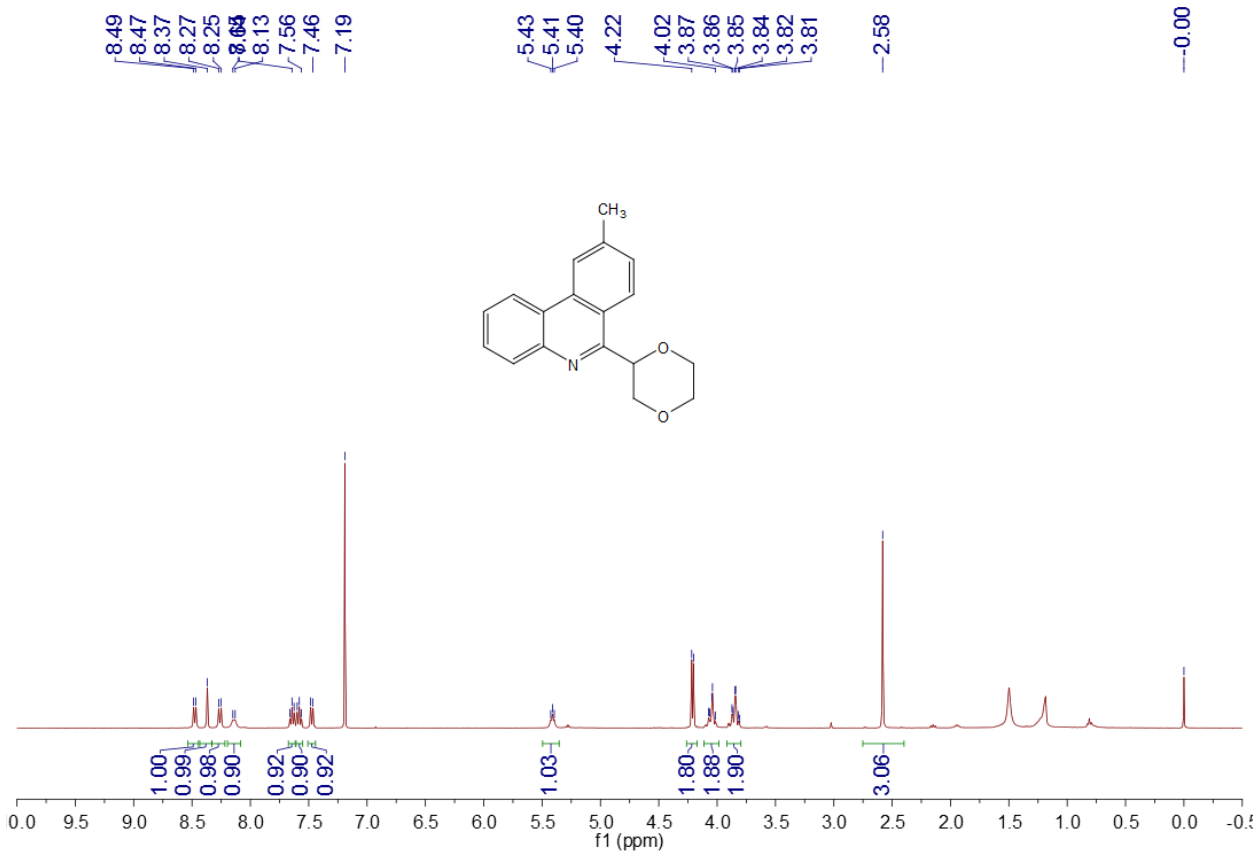


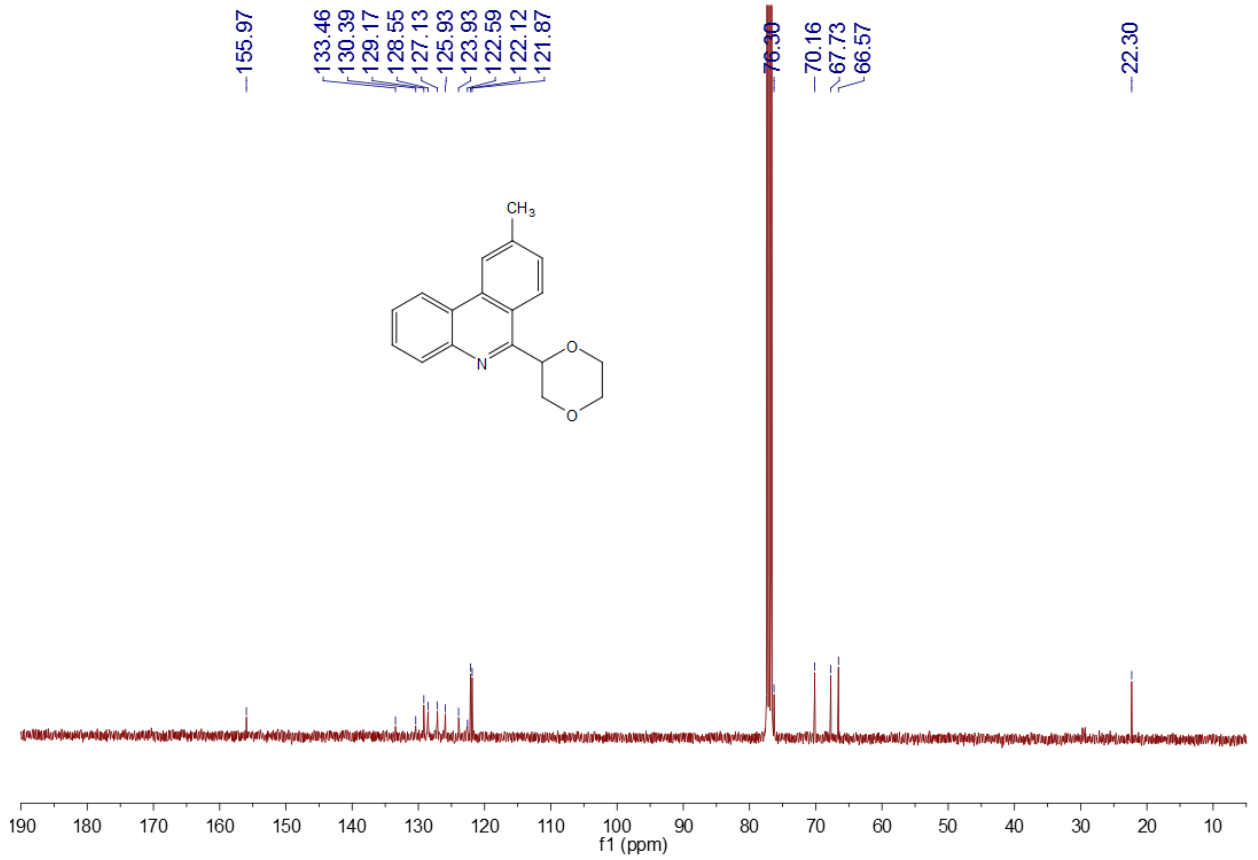


6-(1,4-dioxan-2-yl)-8-methylphenanthridine (3f):



6-(1,4-dioxan-2-yl)-9-methylphenanthridine (3g):





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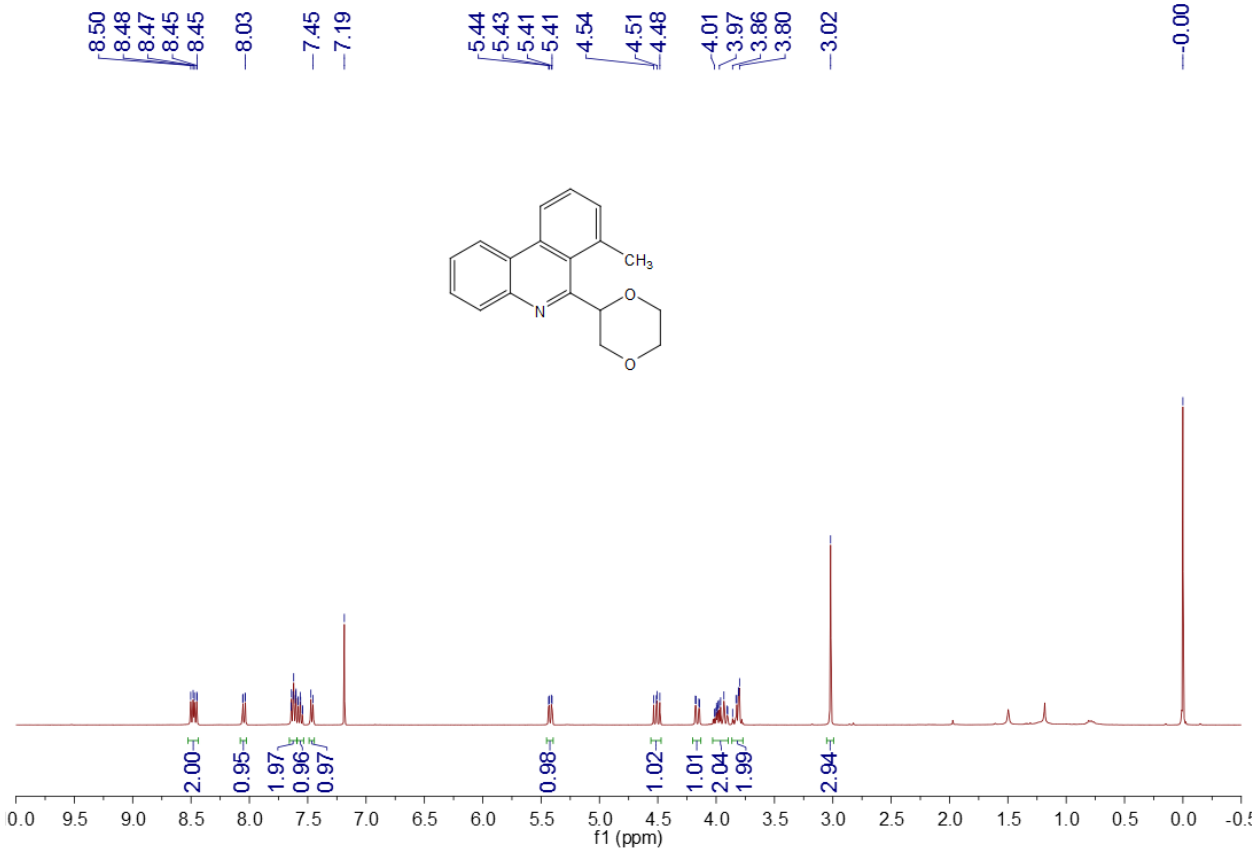

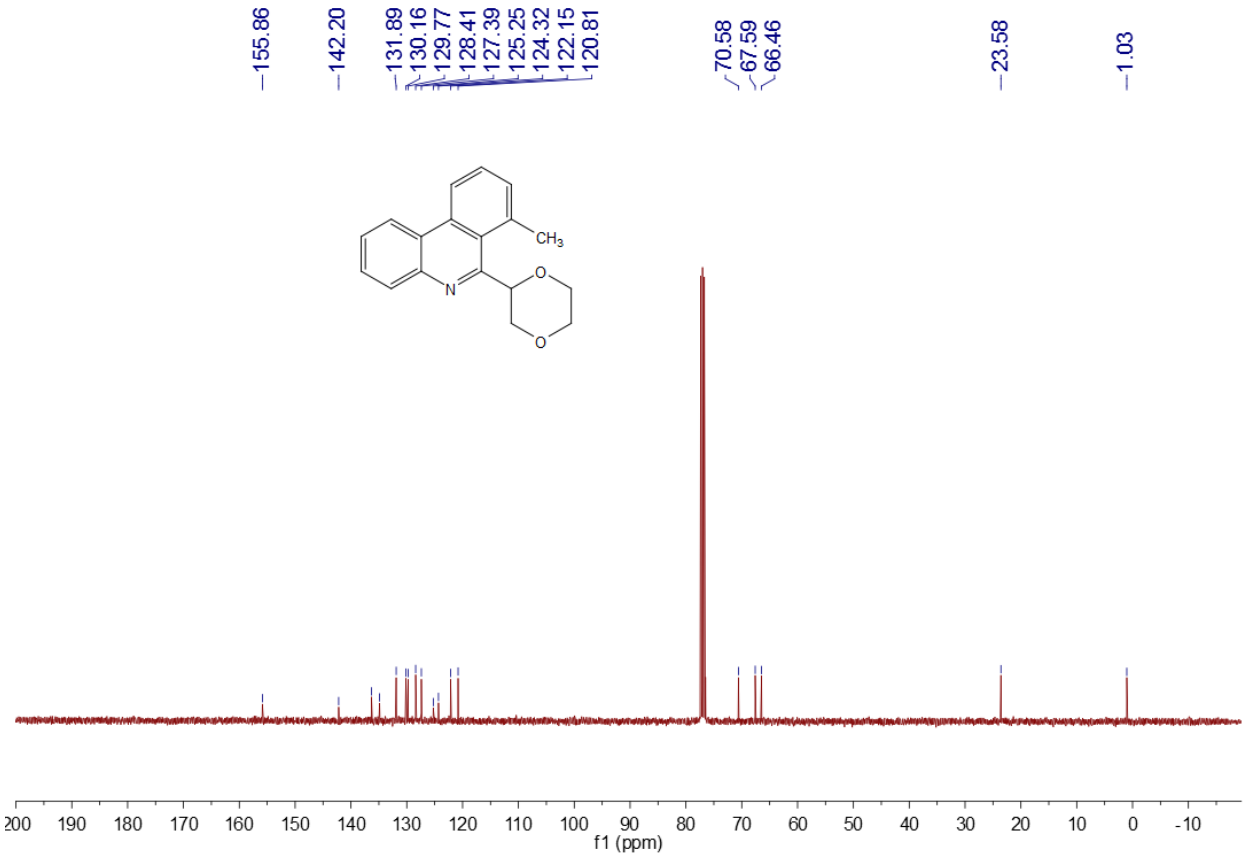

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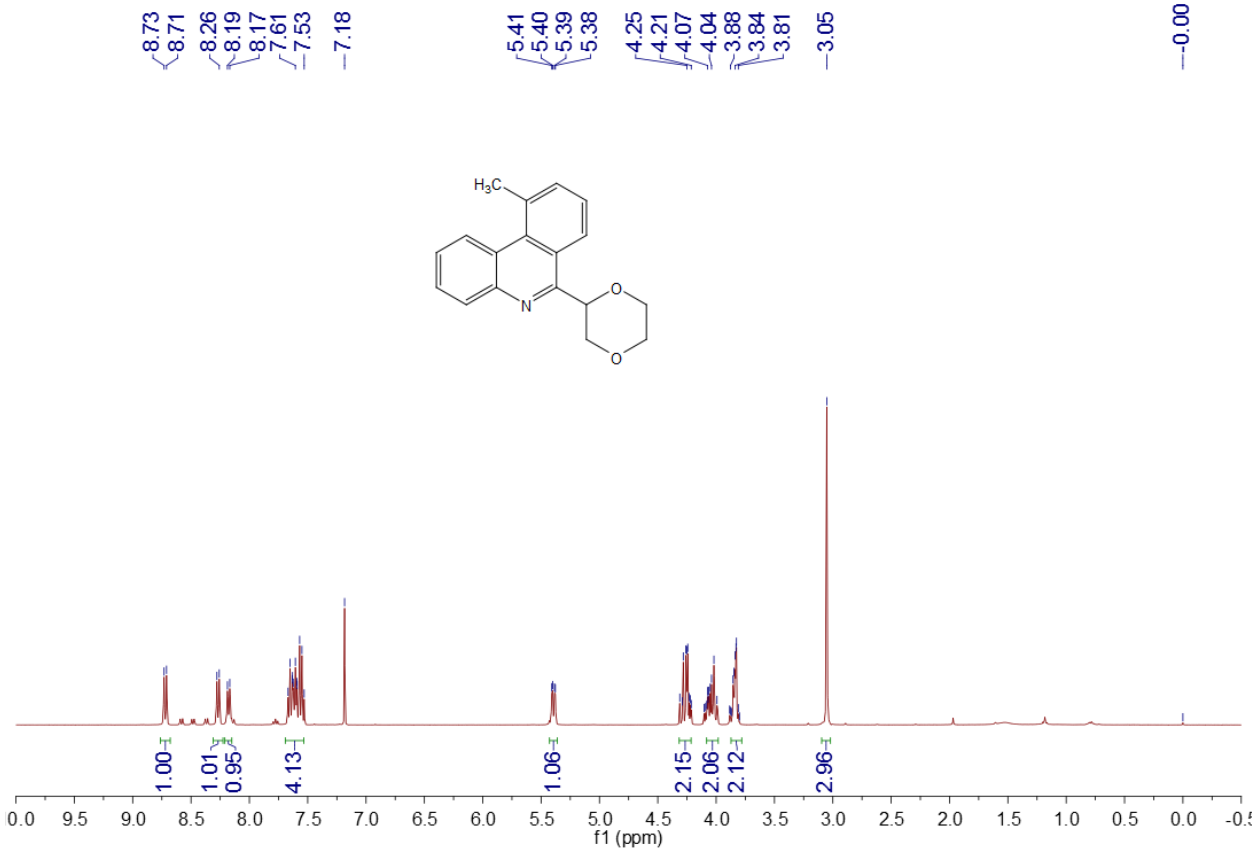
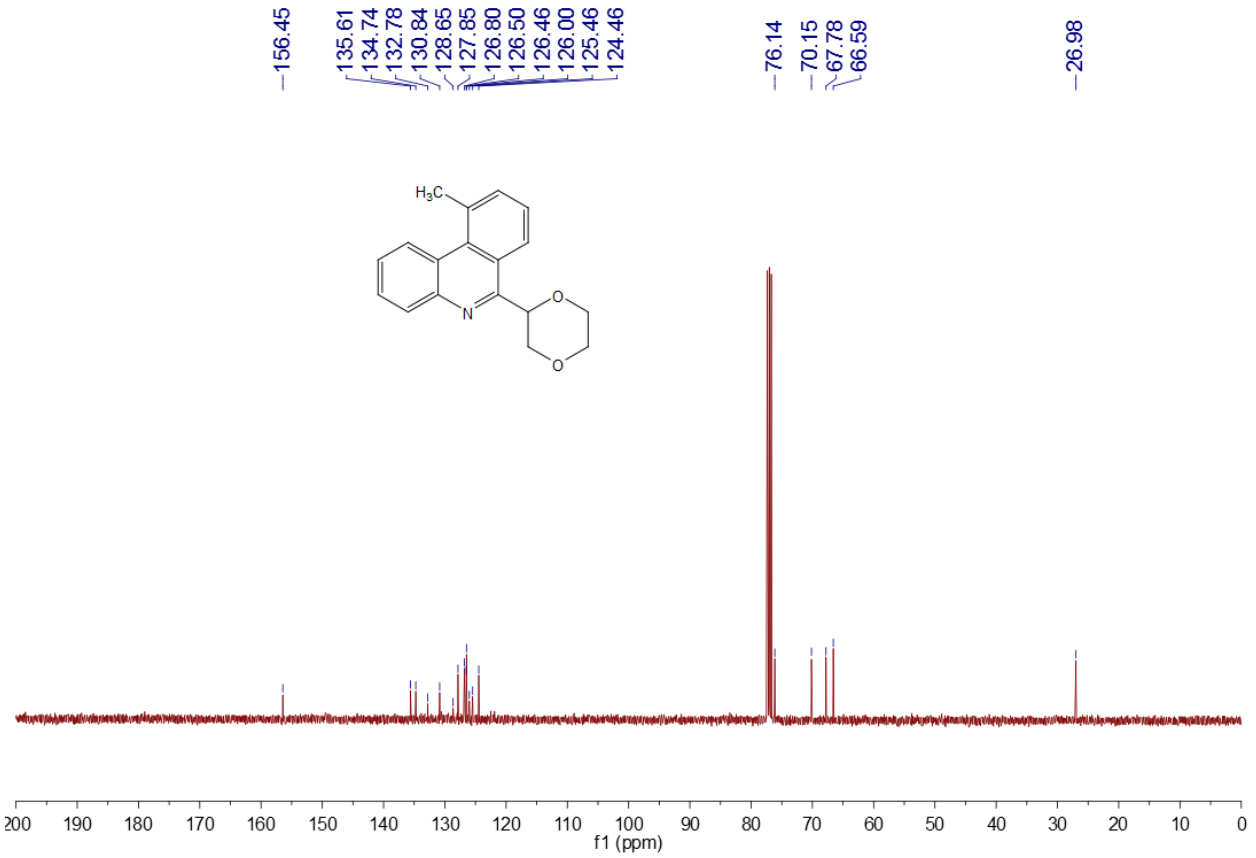
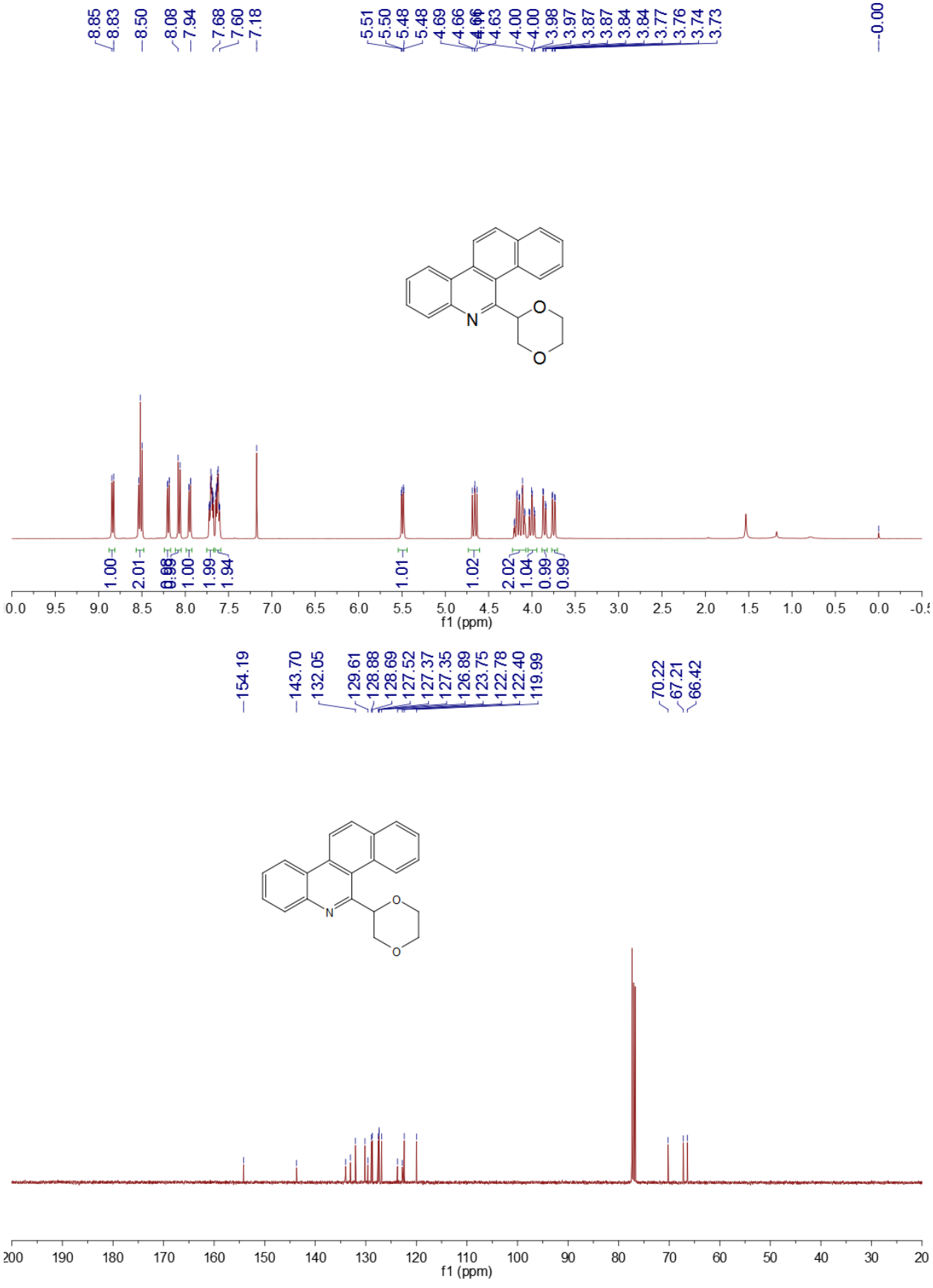
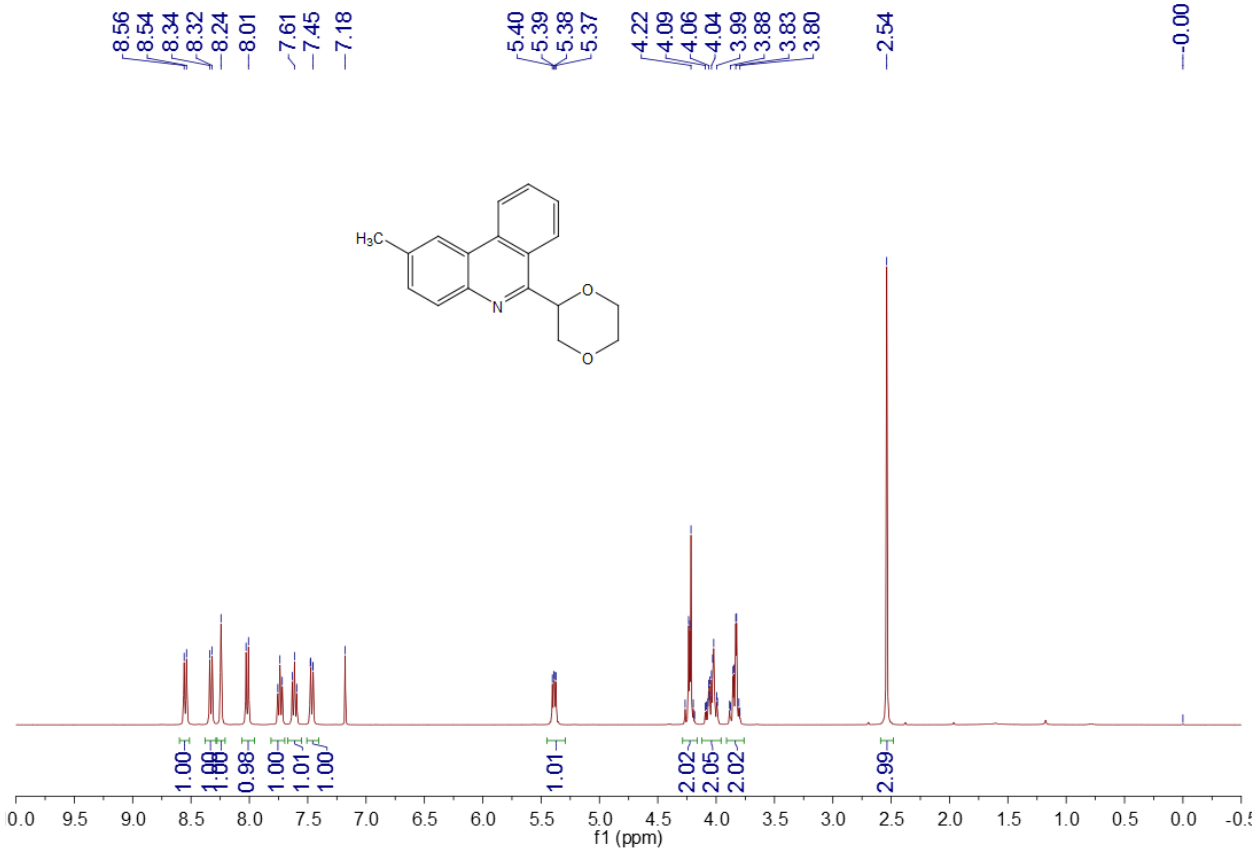


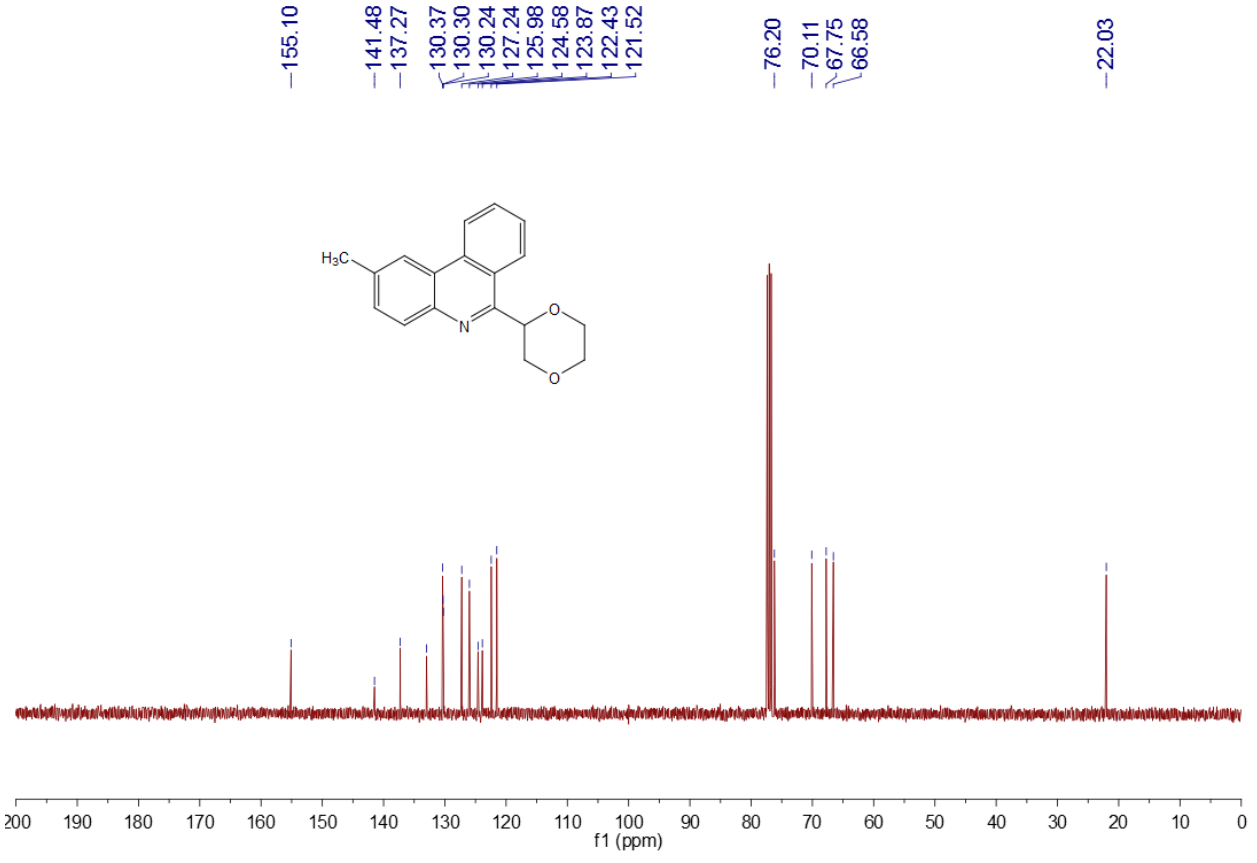


5-(1,4-dioxan-2-yl)benzo[i]phenanthridine (3i):



6-(1,4-dioxan-2-yl)-2-methylphenanthridine (3k):





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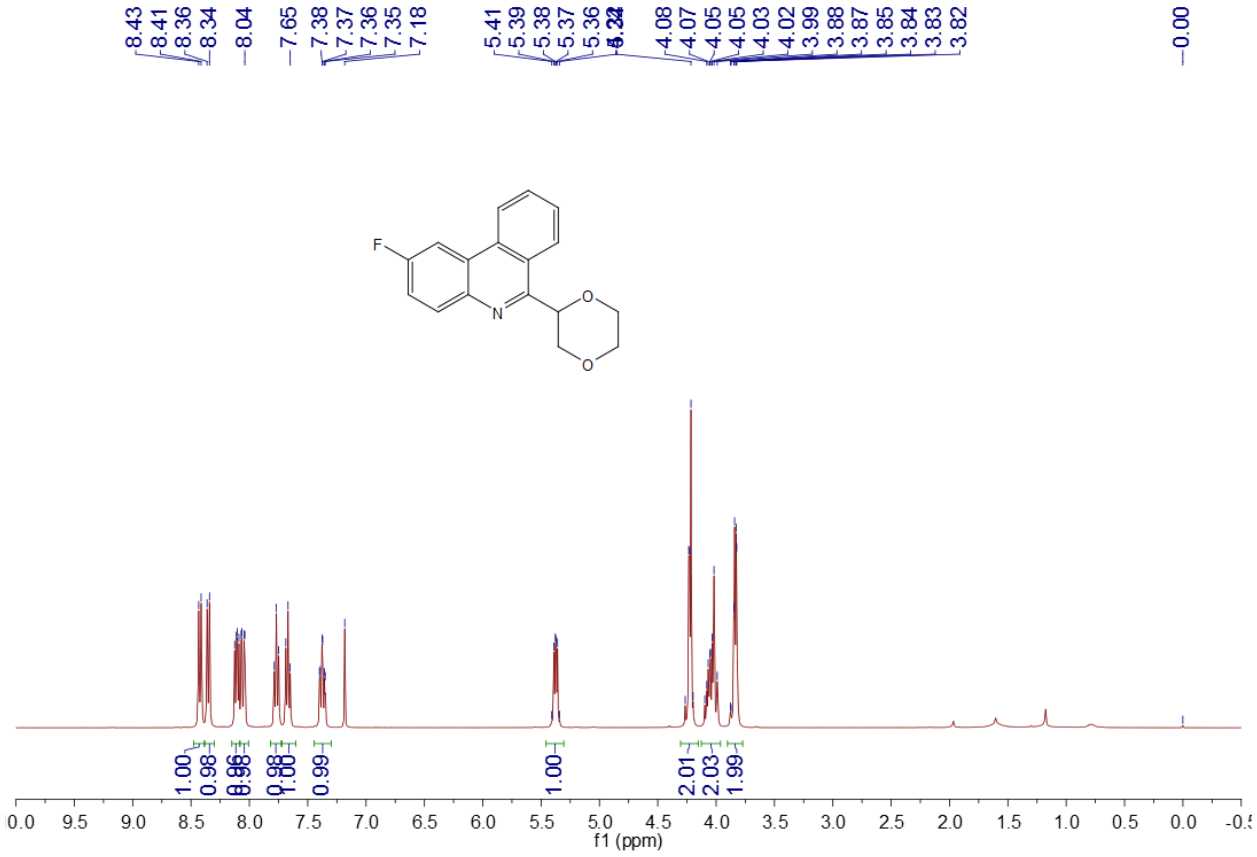
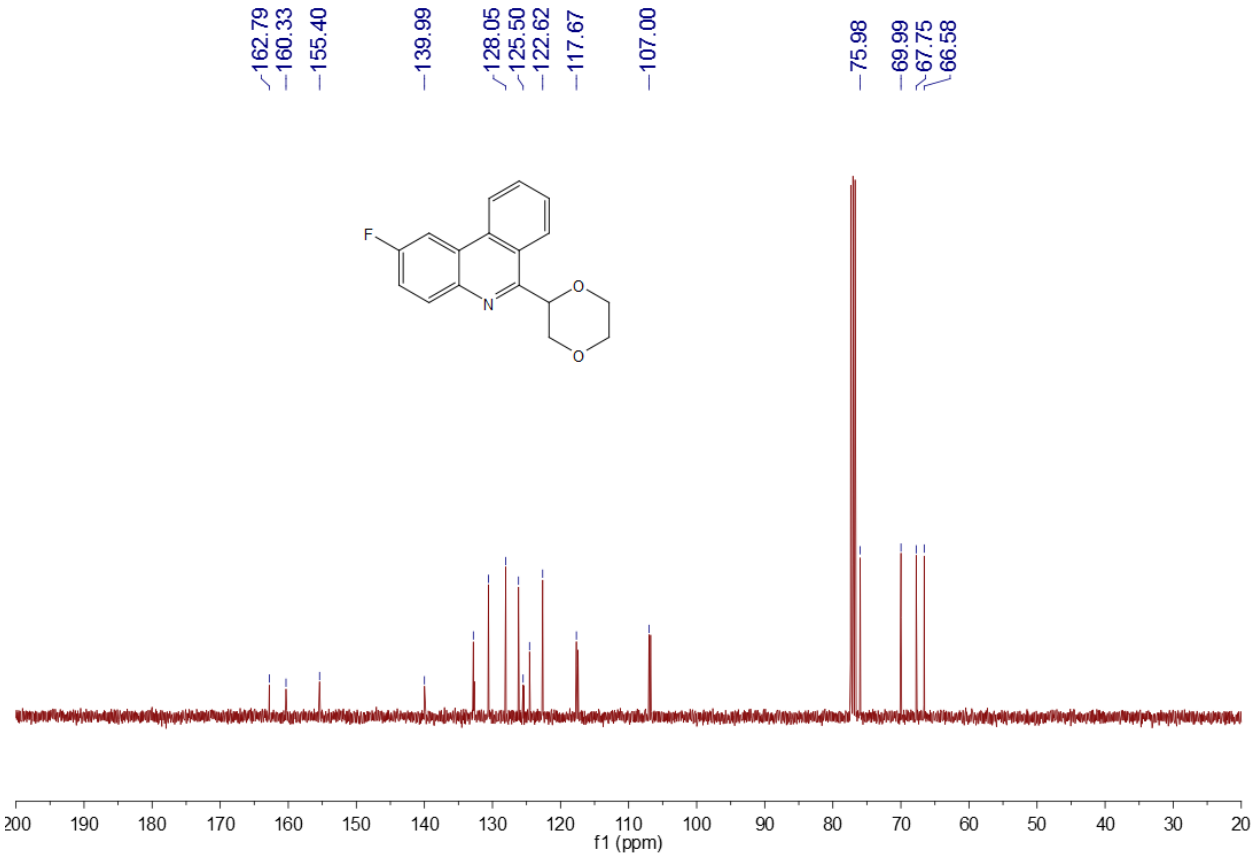
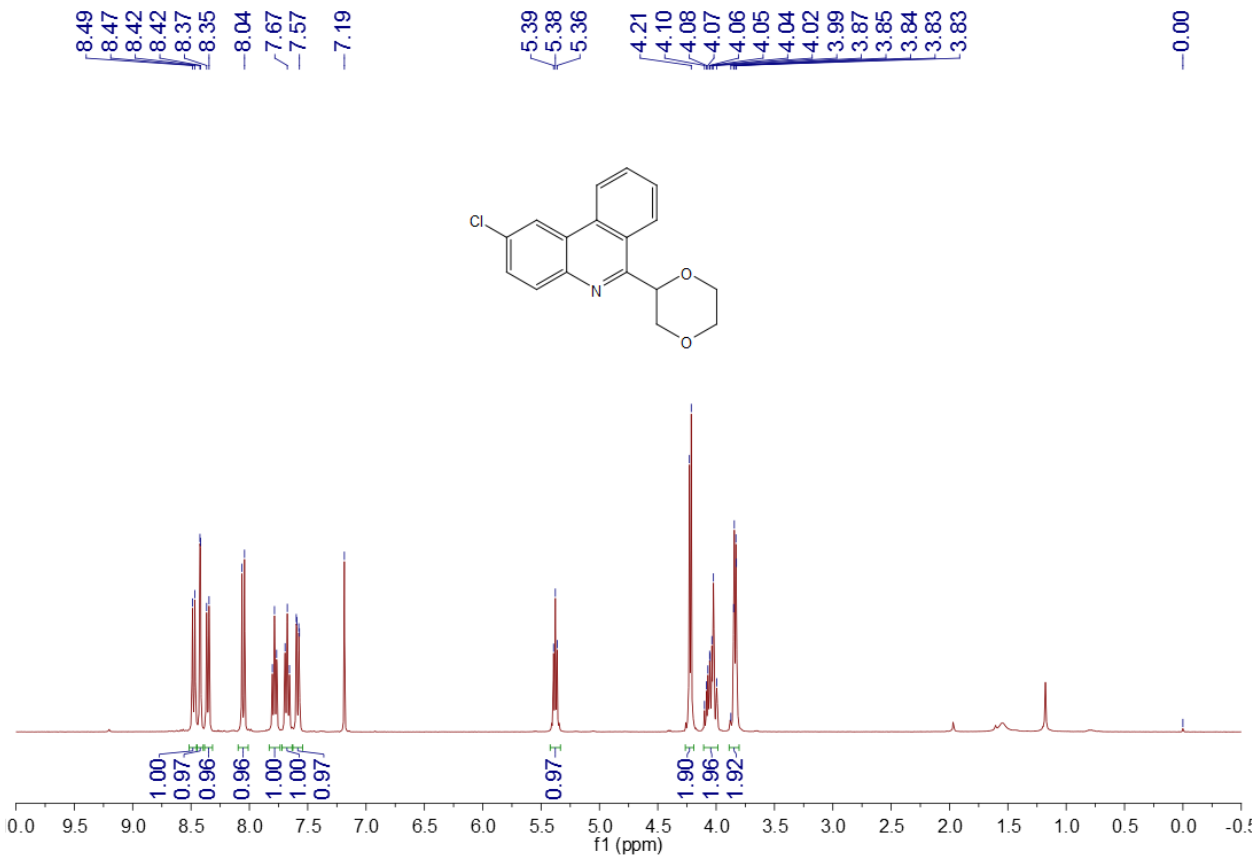
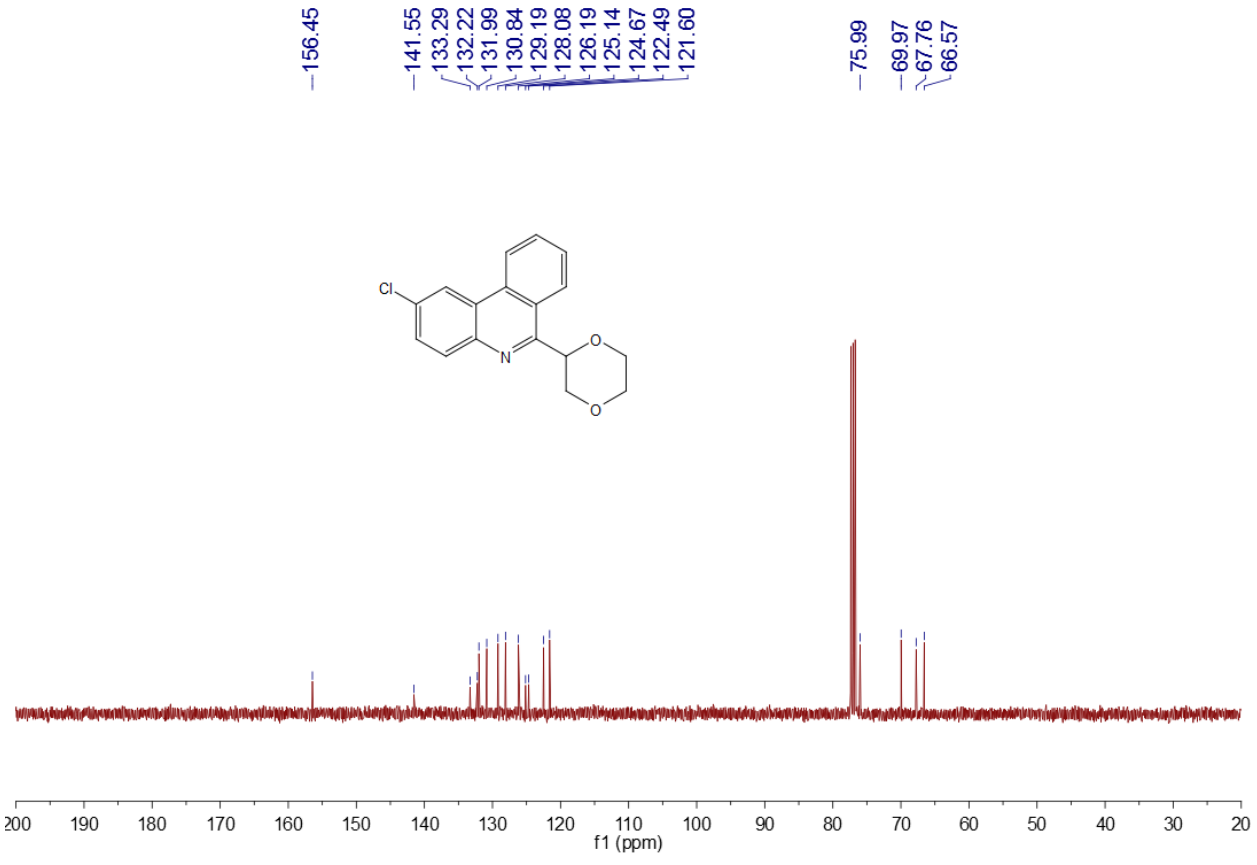


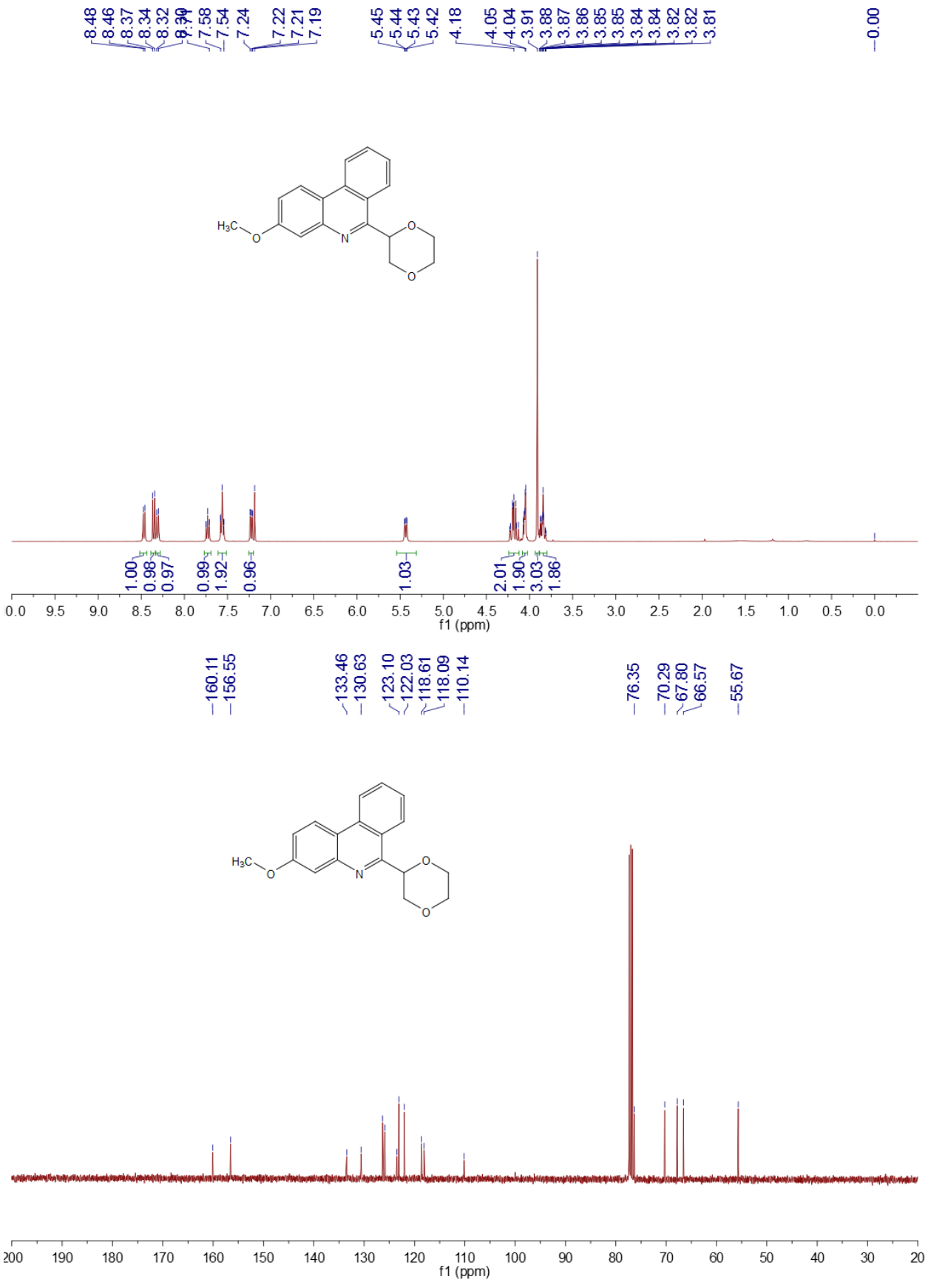


2-chloro-6-(1,4-dioxan-2-yl)phenanthridine (3m):





6-(1,4-dioxan-2-yl)-3-methoxyphenanthridine (3o):



phenanthridine (4a):