Electronic Supplementary Information

Light Triggered Radical Addition/Annulation of 2-Isocyanobiphenyls toward 6-Trifluoromethyl-Phenanthridines under Photocatalysts-free Conditions

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1. General Information:

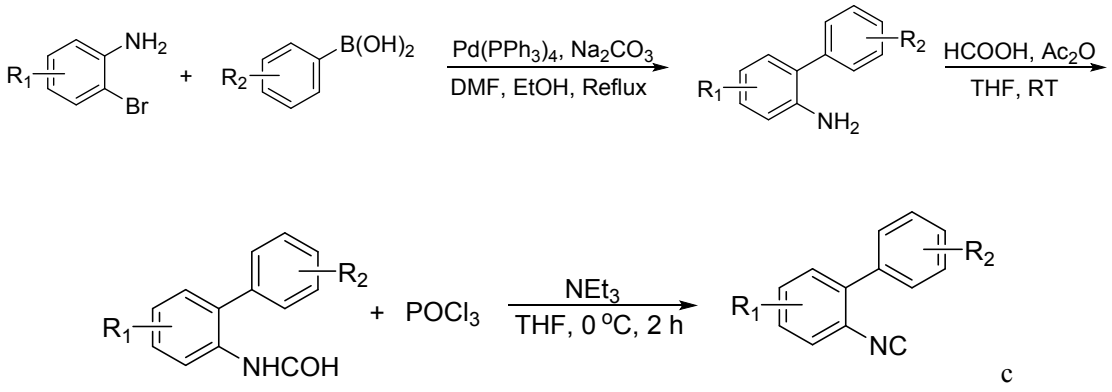
Materials

All purchased reagents were used without further purification. Analytical thin layer chromatography was performed on 0.20 mm Qingdao Haiyang silica gel plates. Silica gel (200-300 mesh) (from Qingdao Haiyang Chem. Company, Ltd.) was used for flash chromatography.

Characterization

The reaction was irradiated with 300WXe arclamp (280-780 nm, CEL-HXF300/CEL-HXUV300, Beijing 10 Aulight Co. Ltd.). ^{1}H, ^{13}C, ^{19}F NMR were recorded on Varian Mercury Plus 400 instruments at 400 MHz (^{1}H NMR), 100 MHz (^{13}C NMR), as well as 376 MHz (^{19}F NMR). Chemical shifts were reported in parts per million (ppm) down field from internal Me_4Si and external CCl_3F, respectively. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), br (broad). Coupling constants were reported in hertz (Hz). HRMS were recorded on an Agilent Q-TOF spectrometer using the ESI method. IR spectras were recorded on an AVATAR 360 FT-IR spectrometer.

2. Typical procedure for the synthesis of substrates[1-2]



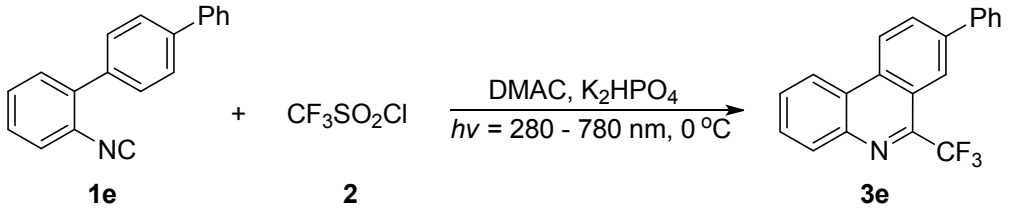
c

Reference:

1. B. Zhang, C. Mück-Lichtenfeld, C. G. Daniliuc and A. Studer, *Angew. Chem. Int. Ed.*, 2013, **52**, 10792.

2. Q. L. Wang, X. C. Dong, T. B. Xiao and L. Zhou, *Org. Lett.*, 2013, **15**, 4846.

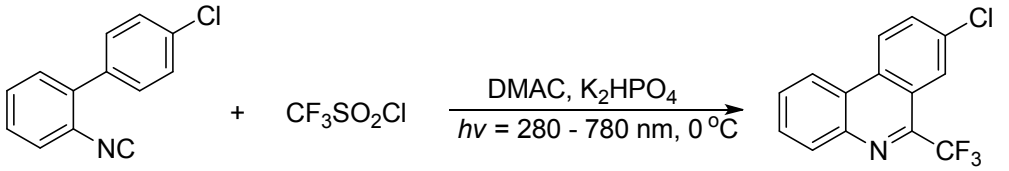
3. General procedure for light triggered radical addition/annulation of 2-isocyanobiphenyls (the synthesis of 3e as example)



1e **2** **3e**

Compound **1e** (0.2 mmol, 51.1 mg), K_2HPO_4 (98%, 0.6 mmol, 106.6 mg), and DMAC (1.0 mL) were added to a dried 10 mL schlenk flask under air. Then, the schlenk tube was sealed well, and immersed in an ice bath maintaining for 5 min. After that, CF_3SO_2Cl (98%, 0.6 mmol, 103.2 mg) was added to the mixture via the microinjector. The schlenk tube was immediately moved to a distance of ca. 30 cm from the light source and the resulting solution was stirred at 0 °C under light irradiation for 6 h. After the completion of the reaction (by TLC), water (5.0 mL) was added to the reaction media and extracted with CH_2Cl_2 (3×10.0 mL). The combined organic layers were washed with brine, and dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was purified by flash column chromatography on silica gel to give the desired product **3e**.

4. Procedure for the amplifying experiments

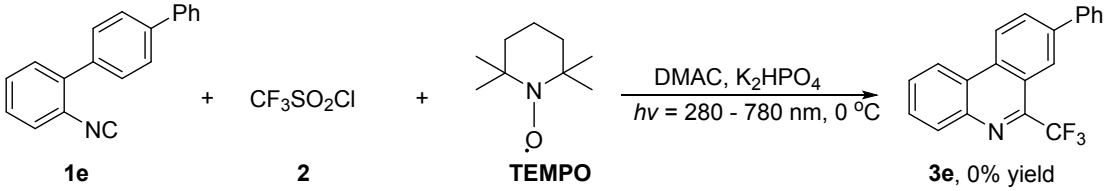


1g (1.2 mmol) **2** (3.6 mmol) **3g** (219.2 mg, 65%)

Compound **1g** (1.2 mmol, 256.4 mg), K_2HPO_4 (98%, 3.6 mmol, 639.6 mg), and DMAC (6.0 mL) were added to a dried 25 mL schlenk flask under air. Then, the schlenk tube was sealed well, and immersed in an ice bath maintaining for 5 min. After that, CF_3SO_2Cl (98%, 3.6 mmol, 619.2 mg) was added to the mixture via the microinjector. The schlenk tube was immediately moved to a distance of ca. 30 cm from the light source and the resulting solution was stirred at 0 °C under light irradiation for 6 h. After the completion of the reaction (by TLC), water (30.0 mL) was added to the reaction media and extracted with CH_2Cl_2 (3×30.0 mL). The combined organic layers were washed with brine, and dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was purified by flash column chromatography on silica gel to give the desired product **3g** in 65% yields.

5. Procedure for the control experiments

The addition of TEMPO to the reaction system under standard conditions



1e **2** **TEMPO** **3e**, 0% yield

Compound **1e** (0.2 mmol, 51.1 mg), K_2HPO_4 (98%, 0.6 mmol, 106.6 mg), TEMPO (0.4mmol, 62.5mg), and DMAC (1.0 mL) were added to a dried 10 mL schlenk flask under air. Then, the schlenk tube was sealed well, and immersed in an ice bath maintaining for 5 min. After that, CF_3SO_2Cl (98%, 0.6 mmol, 103.2 mg) was added to the mixture via the microinjector. The schlenk tube was immediately moved to a distance of ca. 30 cm from the light source and the resulting solution was stirred at 0 °C under light irradiation for 6 h. ^{19}F NMR analysis of this reaction mixture showed that the product **3e** was not detected, which supported that a radical pathway was involved in this arylation/trifluoromethylation of 2-aryl isonitriles.

6. UV−visible absorption spectrum of CF_3SO_2Cl in DMAC

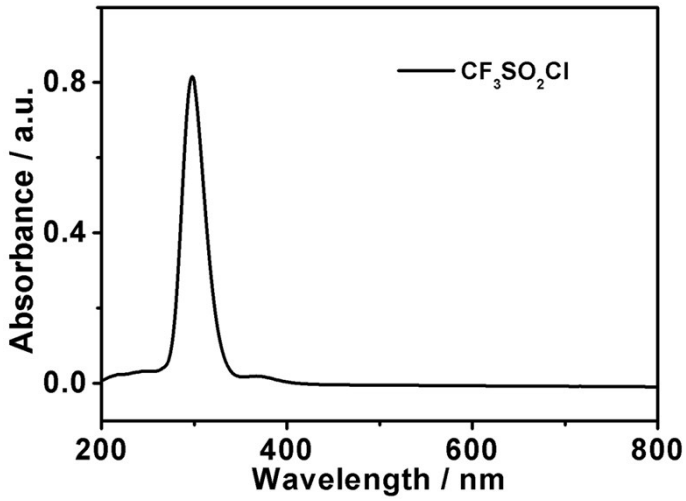
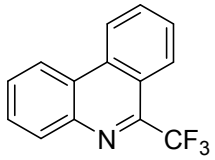


Fig. S1 UV−visible absorption spectrum of CF_3SO_2Cl in DMAC

In order to determine the effective wavelength range, the UV-visible absorption spectrum of CF_3SO_2Cl in DMAC was conducted (Fig. S1). This result revealed that the optimal wavelength absorption range of CF_3SO_2Cl was approximately between 270-350 nm, and the rest section of 350-780 nm that our light source generated was useless.

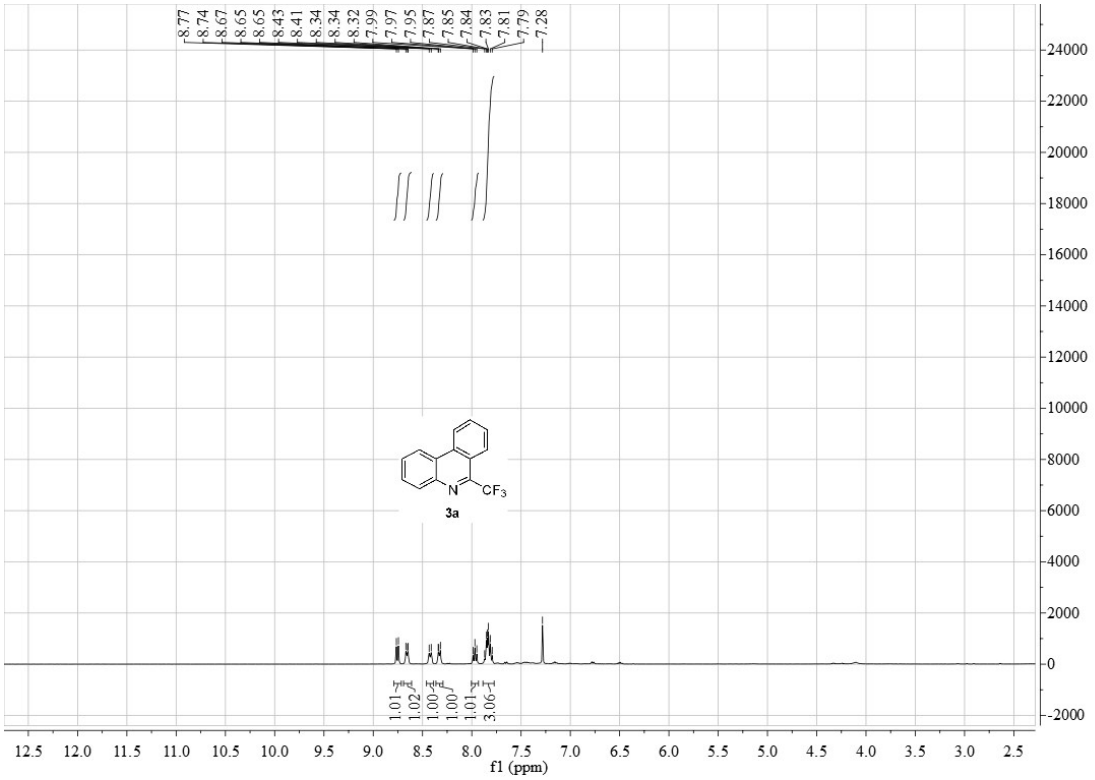
7. Copies of NMR Spectra

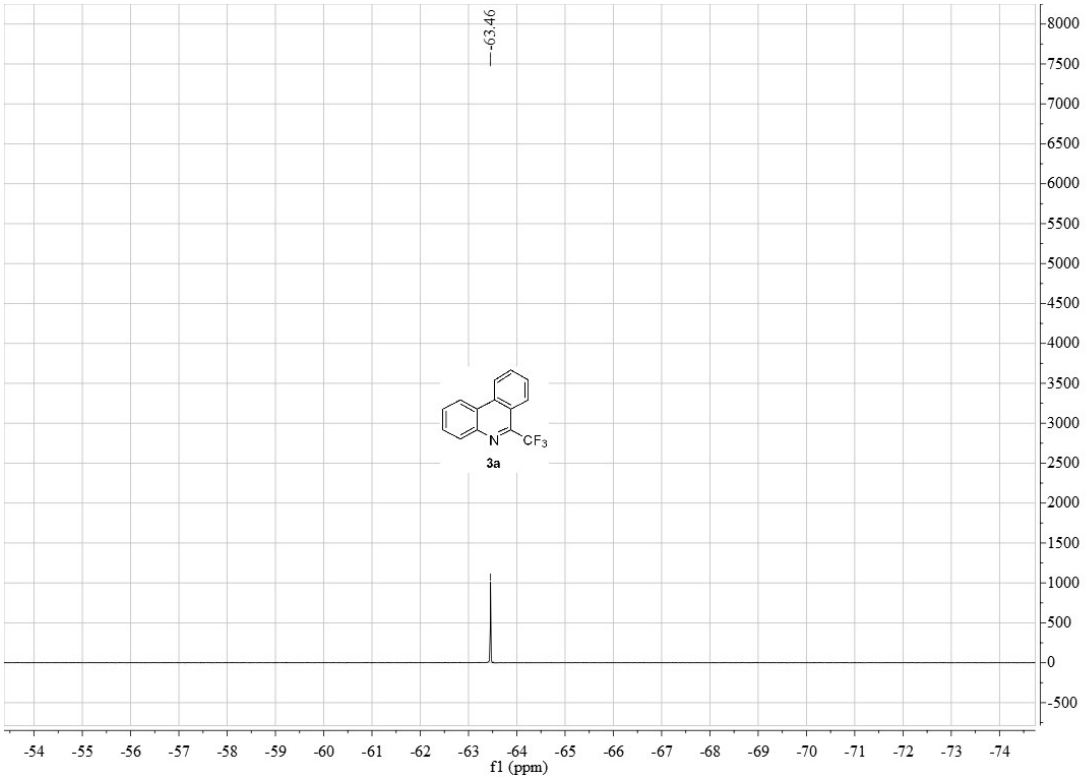


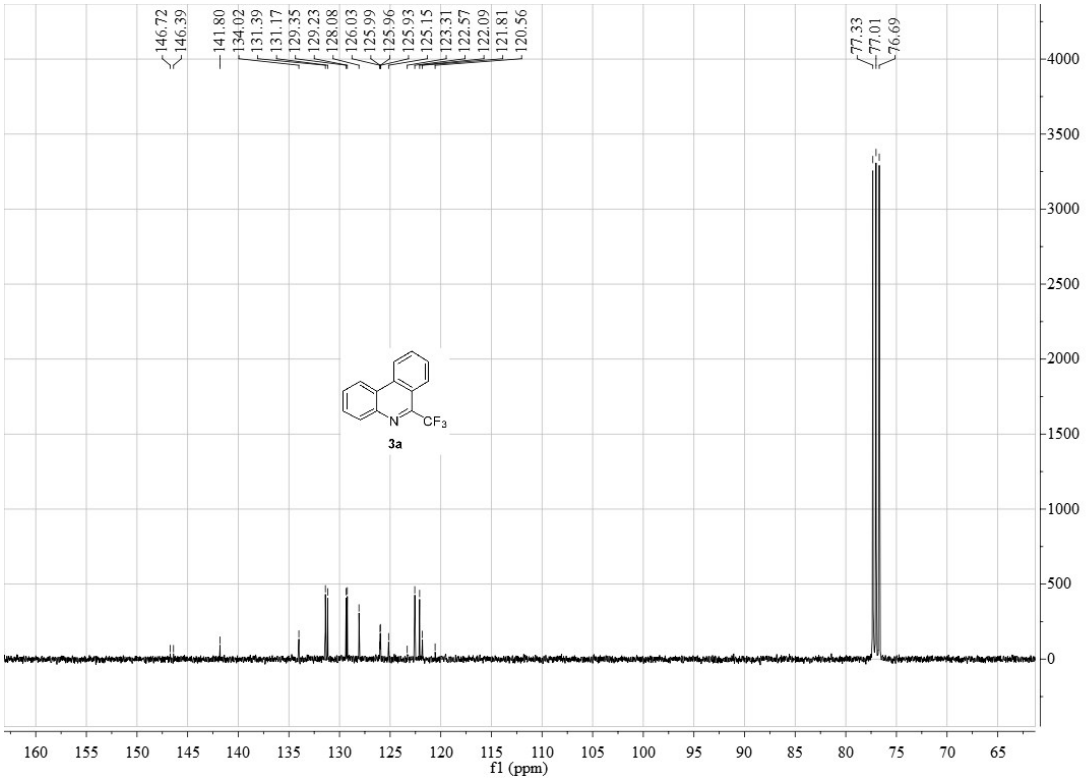
3a

6-(trifluoromethyl)phenanthridine (3a)

^{1}H NMR (400 MHz, $CDCl_3$) [ppm] δ 8.75 (d, J = 8.3 Hz, 1H), 8.69 – 8.61 (m, 1H), 8.42 (d, J = 8.4 Hz, 1H), 8.36 – 8.29 (m, 1H), 7.97 (t, J = 7.6 Hz, 1H), 7.83 (dq, J = 15.5, 7.6 Hz, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ -63.46 (s, 3F); **^{13}C NMR** (100 MHz, $CDCl_3$) [ppm] δ 146.6 (q, J = 33.0 Hz), 141.8 (s), 134.0 (s), 131.4 (s), 131.2 (s), 129.4 (s), 129.2 (s), 128.1 (s), 126.0 (q, J = 3.0 Hz), 125.2 (s), 122.6 (s), 122.1 (s), 121.9 (q, J = 275.0 Hz), 121.8; **IR** (KBr) ν (cm^{-1}): 3077, 1728, 1525, 1378, 1251, 1171, 1118, 1020, 969, 797, 757, 718; **HRMS** (ESI) found: *m/z* 248.0679 $[M+H]^+$; calcd. for $C_{14}H_8F_3N$+H 248.0687.




-63.46
3a
f1 (ppm)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126.03
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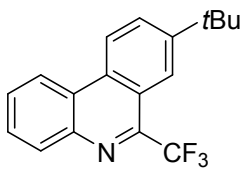
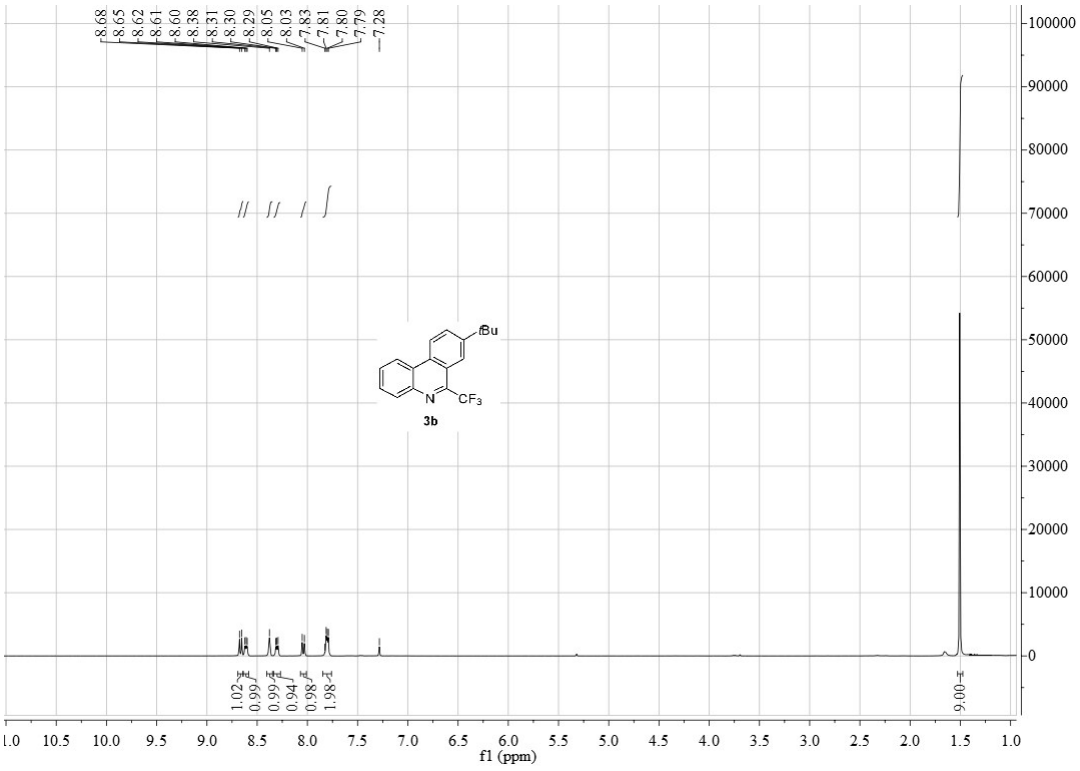
77.33
77.01
76.69
3a
f1 (ppm)

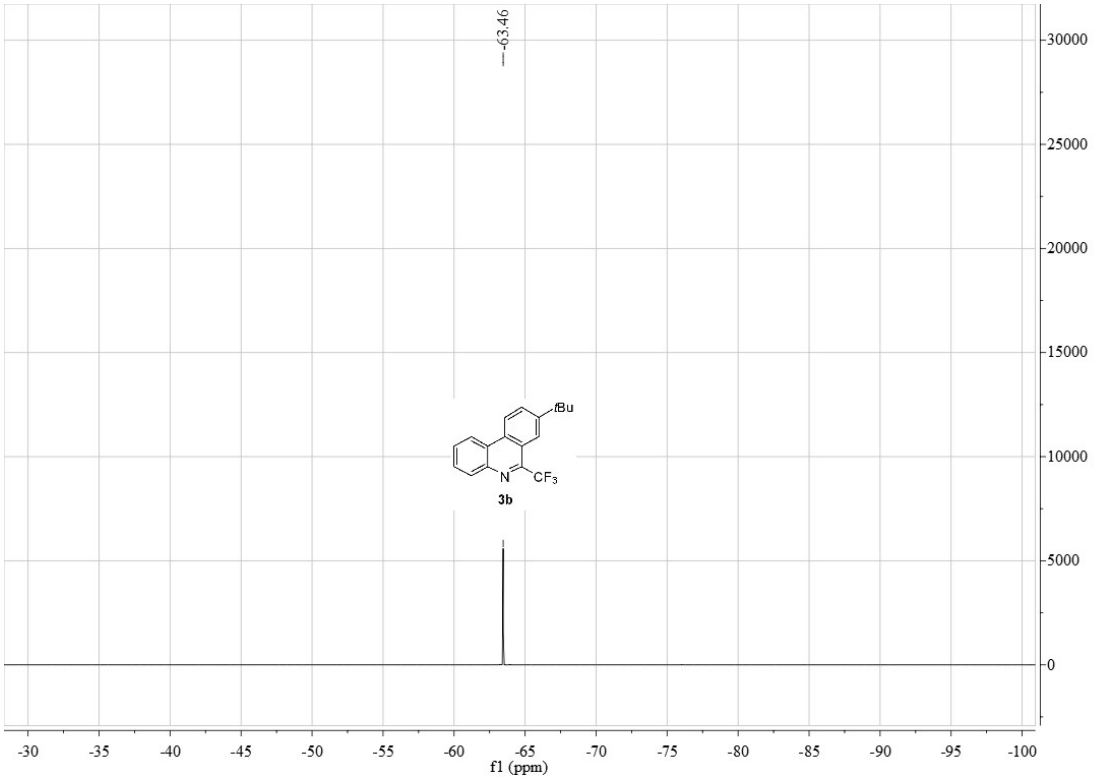

tBu
N
CF3

3b

8-(tert-butyl)-6-(trifluoromethyl)phenanthridine (3b)

^{1}H NMR (400 MHz, $CDCl_3$) [ppm] δ 8.66 (d, J = 8.8 Hz, 1H), 8.64 – 8.58 (m, 1H), 8.38 (s, 1H), 8.33 – 8.27 (m, 1H), 8.04 (d, J = 8.8 Hz, 1H), 7.81 (dd, J = 9.1, 4.8 Hz, 2H), 1.51 (s, 9H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ -63.46 (s, 3F); **^{13}C NMR** (100 MHz, $CDCl_3$) [ppm] δ 151.3 (s), 146.6 (q, J = 32.0 Hz), 141.6 (s), 131.9 (s), 131.0 (s), 129.9 (s), 129.1 (s), 128.9 (s), 125.1 (s), 122.3 (s), 122.1 (q, J = 276.0 Hz), 122.0 (s), 121.9 (s), 121.4 (q, J = 3.0 Hz), 35.2 (s), 31.2 (s); **IR** (KBr) ν (cm^{-1}): 3064, 2966, 1727, 1619, 1580, 1465, 1365, 1335, 1183, 1132, 986, 836; **HRMS** (ESI) found: *m/z* 304.1305 $[M+H]^+$; calcd. for $C_{18}H_{16}F_3N$+H 304.1313.

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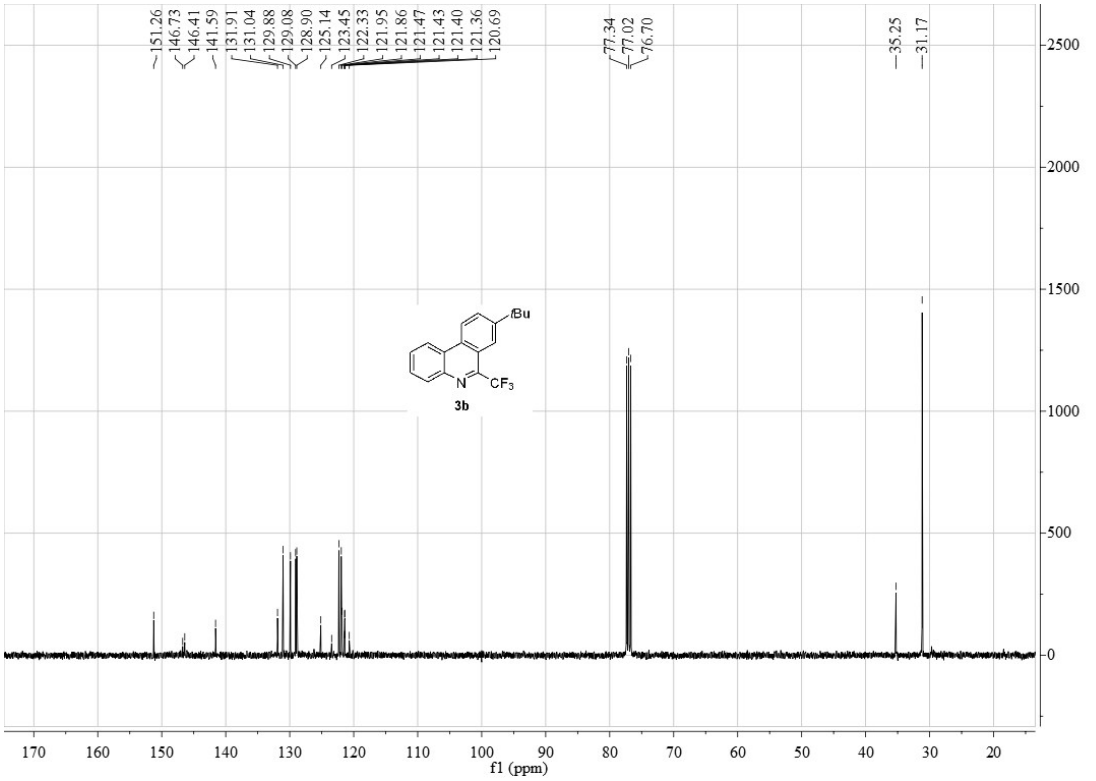
N
CF3
3b
f1 (ppm)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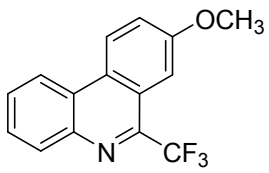
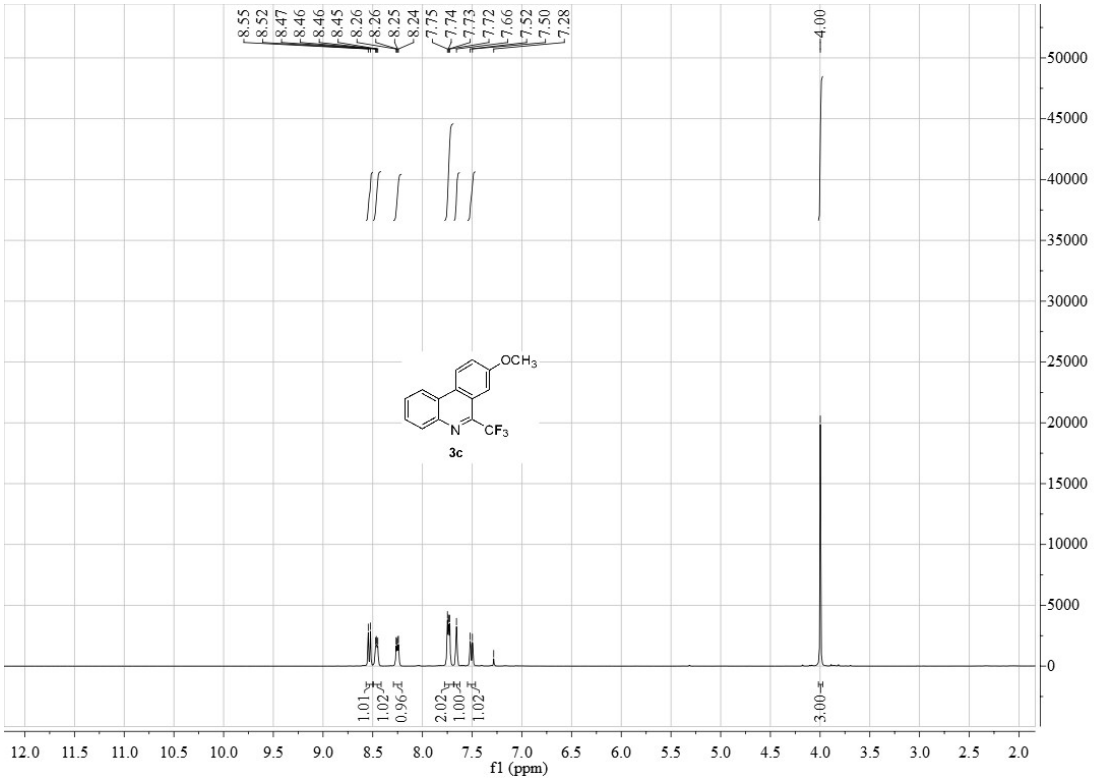
3b
f1 (ppm)

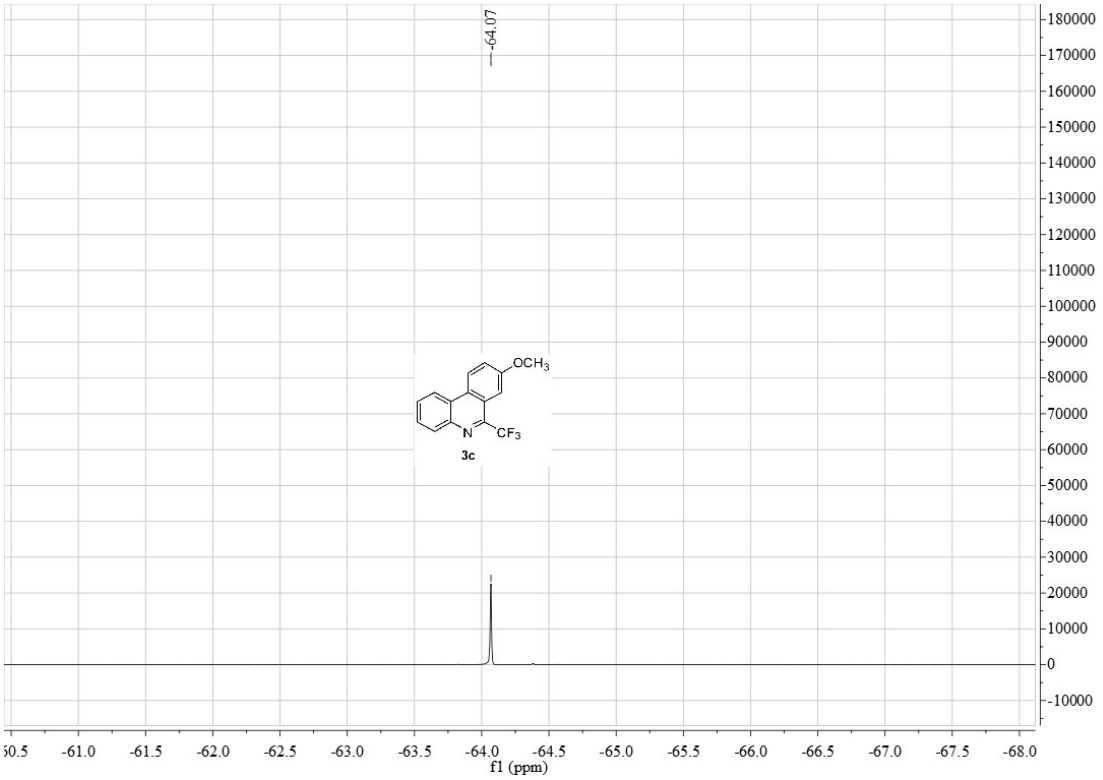

OCH3
N
CF3

3c

8-methoxy-6-(trifluoromethyl)phenanthridine (3c)

^{1}H NMR (400 MHz, $CDCl_3$) [ppm] δ 8.53 (d, J = 9.1 Hz, 1H), 8.46 (dd, J = 5.9, 3.4 Hz, 1H), 8.25 (dd, J = 5.9, 3.6 Hz, 1H), 7.74 (dd, J = 6.2, 3.4 Hz, 2H), 7.66 (s, 1H), 7.51 (d, J = 9.1 Hz, 1H), 4.00 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ -64.07 (s, 3F); **^{13}C NMR** (100 MHz, $CDCl_3$) [ppm] δ 159.0 (s), 145.5 (q, J = 33.0 Hz), 141.0 (s), 131.0 (s), 129.2 (s), 128.4 (s), 128.3 (s), 125.2 (s), 124.1 (s), 123.1 (s), 122.4 (s), 122.1 (q, J = 275.0 Hz), 121.5 (s), 105.5 (q, J = 3.0 Hz), 55.5 (s); **IR** (KBr) ν (cm^{-1}): 3072, 2922, 2852, 1726, 1619, 1580, 1487, 1461, 1390, 1335, 1258, 1224, 1172, 1134, 1036, 988, 893, 834, 764, 734; **HRMS** (ESI) found: *m/z* 278.0789 $[M+H]^+$; calcd. for $C_{15}H_{10}F_3NO$+H 278.0792.

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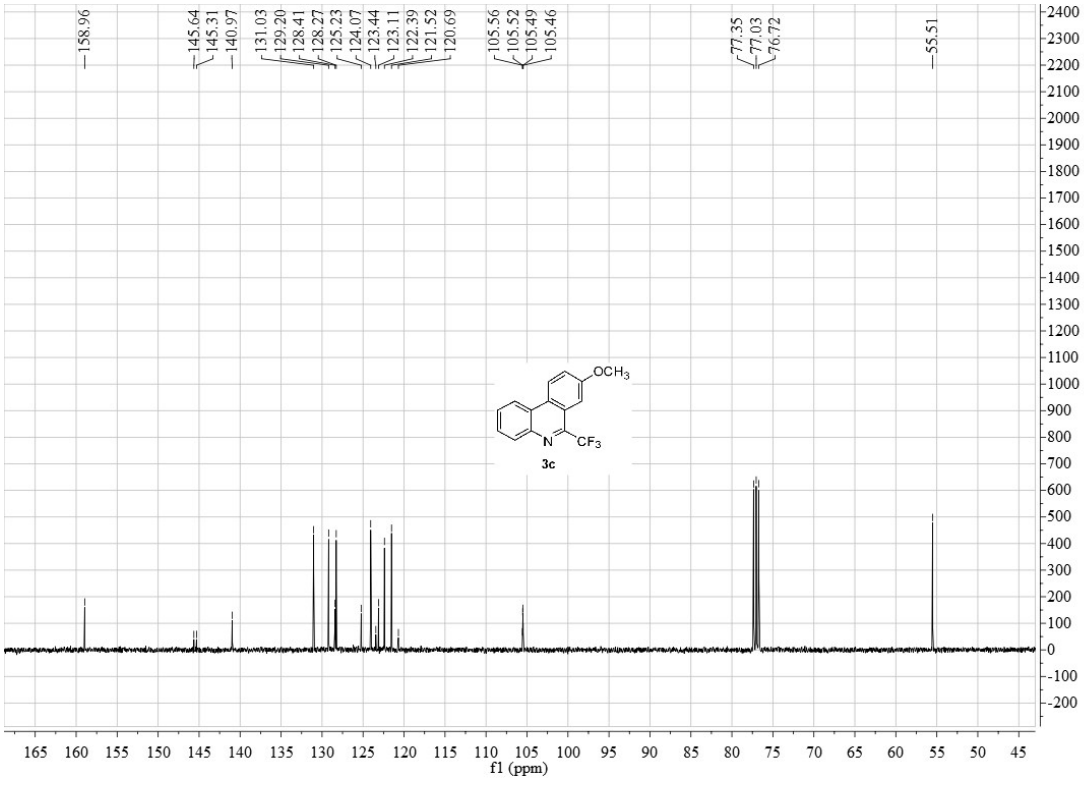
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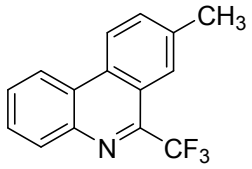
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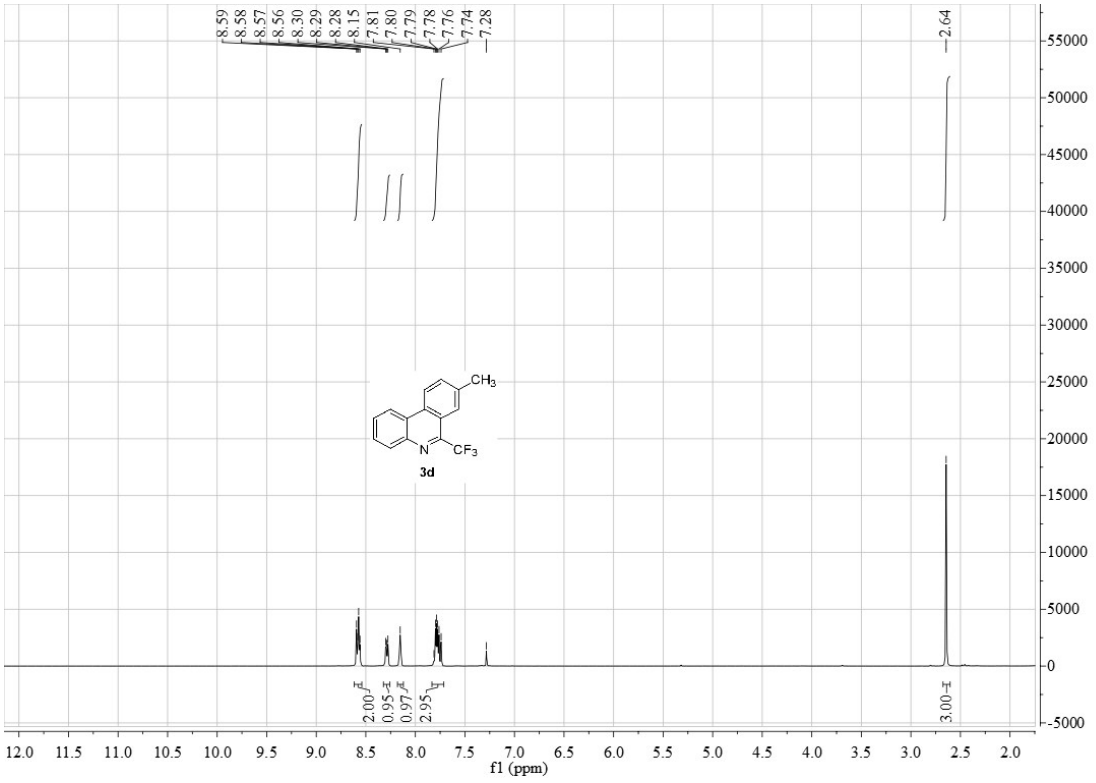
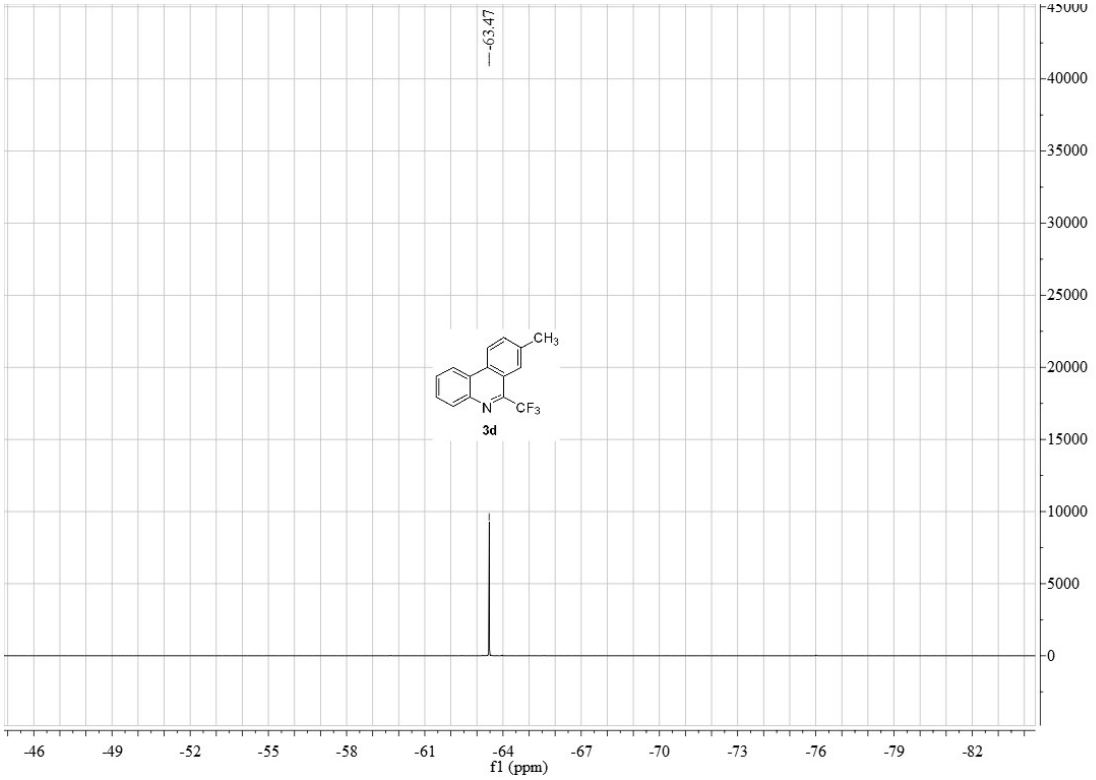
N
CF3

3d

8-methyl-6-(trifluoromethyl)phenanthridine (3d)

^{1}H NMR (400 MHz, $CDCl_3$) [ppm] δ 8.58 (dd, J = 9.1, 5.0 Hz, 2H), 8.32 – 8.26 (m, 1H), 8.15 (s, 1H), 7.83 – 7.71 (m, 3H), 2.64 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ -63.47 (s, 3F); **^{13}C NMR** (100 MHz, $CDCl_3$) [ppm] δ 146.2 (q, J = 33.0 Hz), 141.5 (s), 138.2 (s), 133.2 (s), 131.9 (s), 131.0 (s), 129.1 (s), 128.9 (s), 125.2 (q, J = 3.0 Hz), 125.2 (s), 122.4 (s), 122.0 (q, J = 275.0 Hz), 122.0 (s), 121.9 (s), 21.9 (s); **IR** (KBr) ν (cm^{-1}): 3029, 2921, 2852, 1729, 1576, 1532, 1461, 1385, 1332, 1259, 1166, 1133, 985, 791; **HRMS** (ESI) found: *m/z* 262.0843 $[M+H]^+$; calcd. for $C_{15}H_{10}F_3N$+H 262.0843.

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CF3
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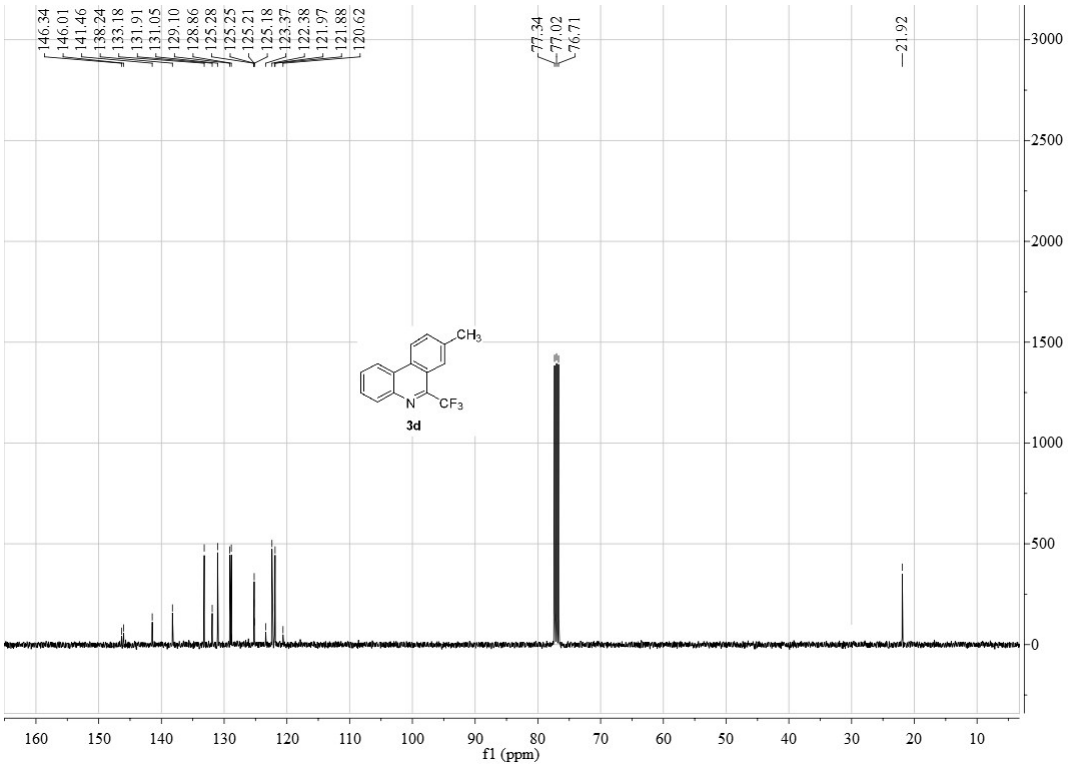
f1 (ppm)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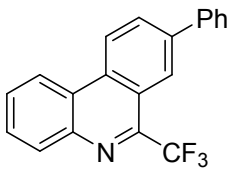
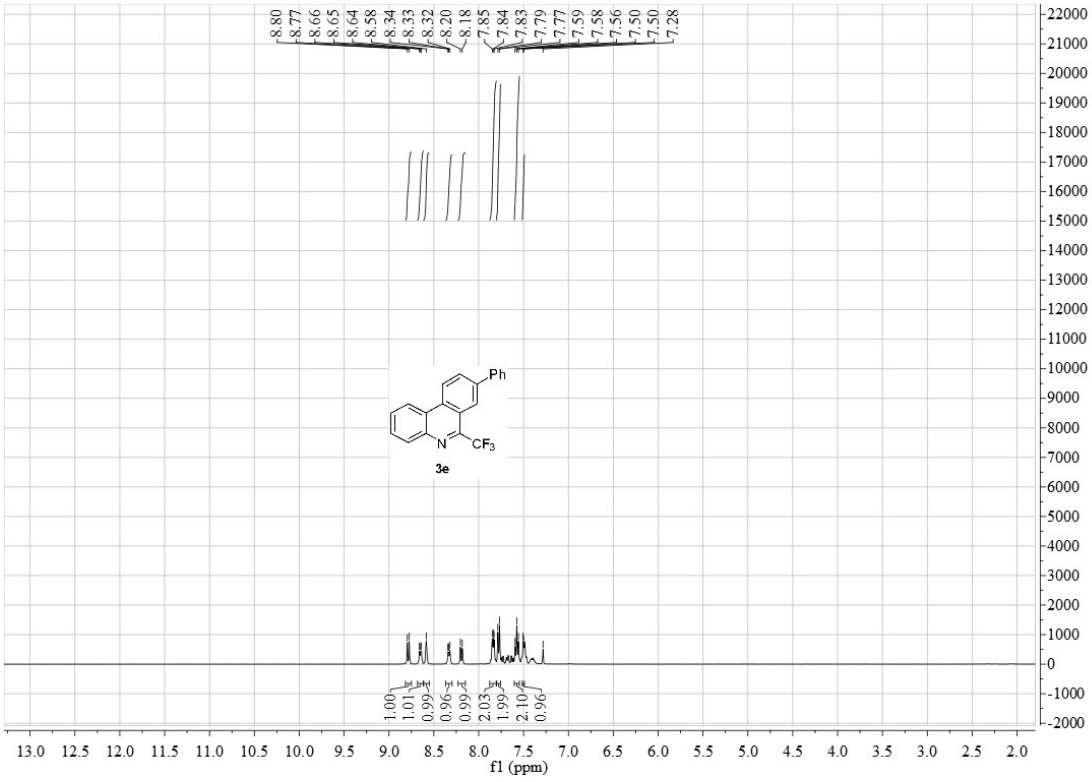
3d
f1 (ppm)

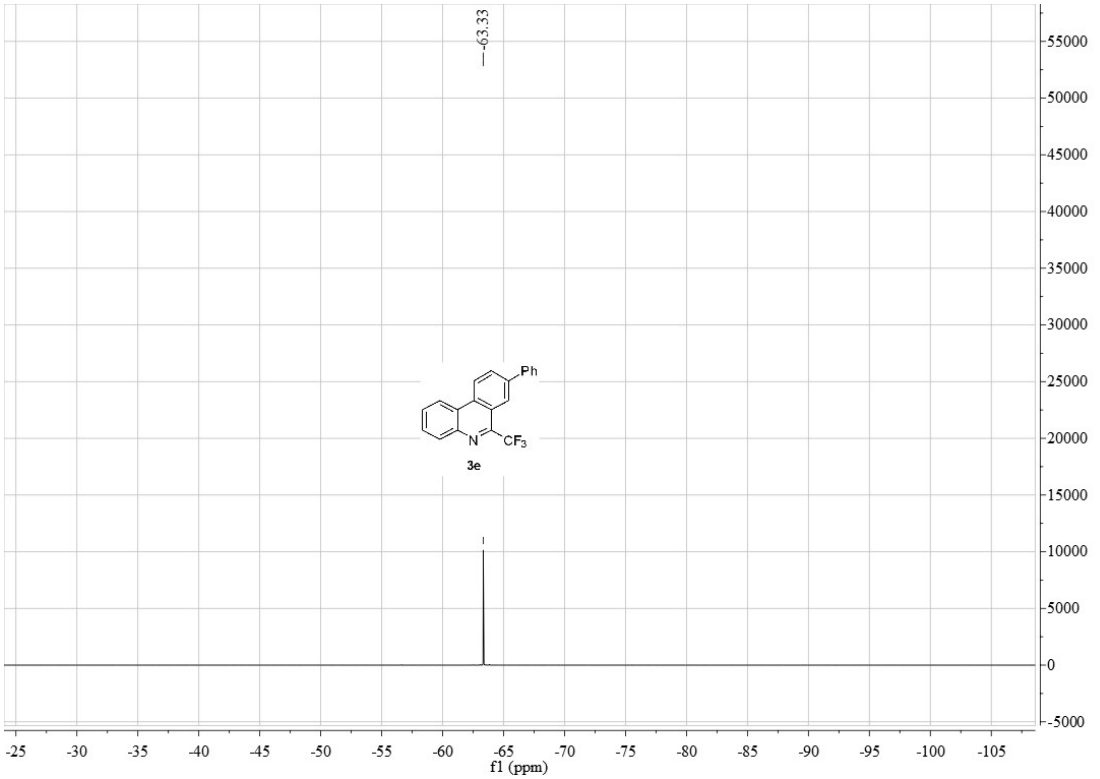

Ph
N
CF3

3e

8-phenyl-6-(trifluoromethyl)phenanthridine (3e)

^{1}H NMR (400 MHz, $CDCl_3$) [ppm] δ 8.78 (d, J = 8.7 Hz, 1H), 8.68 – 8.61 (m, 1H), 8.58 (s, 1H), 8.37 – 8.30 (m, 1H), 8.19 (d, J = 8.5 Hz, 1H), 7.88 – 7.80 (m, 2H), 7.78 (d, J = 7.6 Hz, 2H), 7.58 (t, J = 7.5 Hz, 2H), 7.50 (d, J = 2.7 Hz, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ -63.33 (s, 3F); **^{13}C NMR** (100 MHz, $CDCl_3$) [ppm] δ 146.6 (q, J = 33.5 Hz), 141.7 (s), 141.0 (s), 139.8 (s), 133.0 (s), 131.2 (s), 130.7 (s), 129.3 (s), 129.3 (s), 129.2 (s), 128.2 (s), 127.5 (s), 125.0 (s), 123.8 (q, J = 3.0 Hz), 123.1 (s), 122.2 (s), 122.10 (s), 122.0 (q, J = 275.0 Hz); **IR** (KBr) ν (cm^{-1}): 3036, 1728, 1579, 1465, 1386, 1277, 1181, 1125, 1075, 1032, 977, 864, 799, 760, 734; **HRMS** (ESI) found: *m/z* 324.0998 $[M+H]^+$; calcd. for $C_{20}H_{12}F_3N$+H 324.1000.

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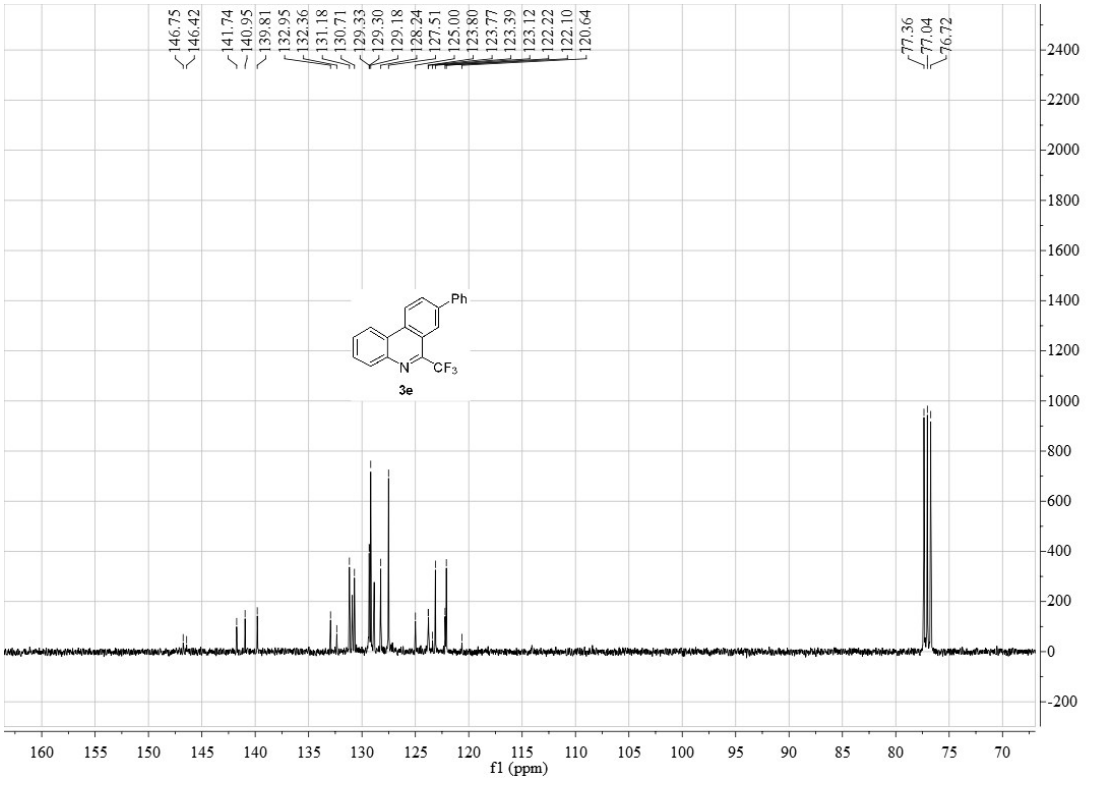
Ph
N
CF3
3e
f1 (ppm)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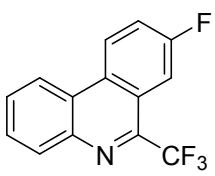
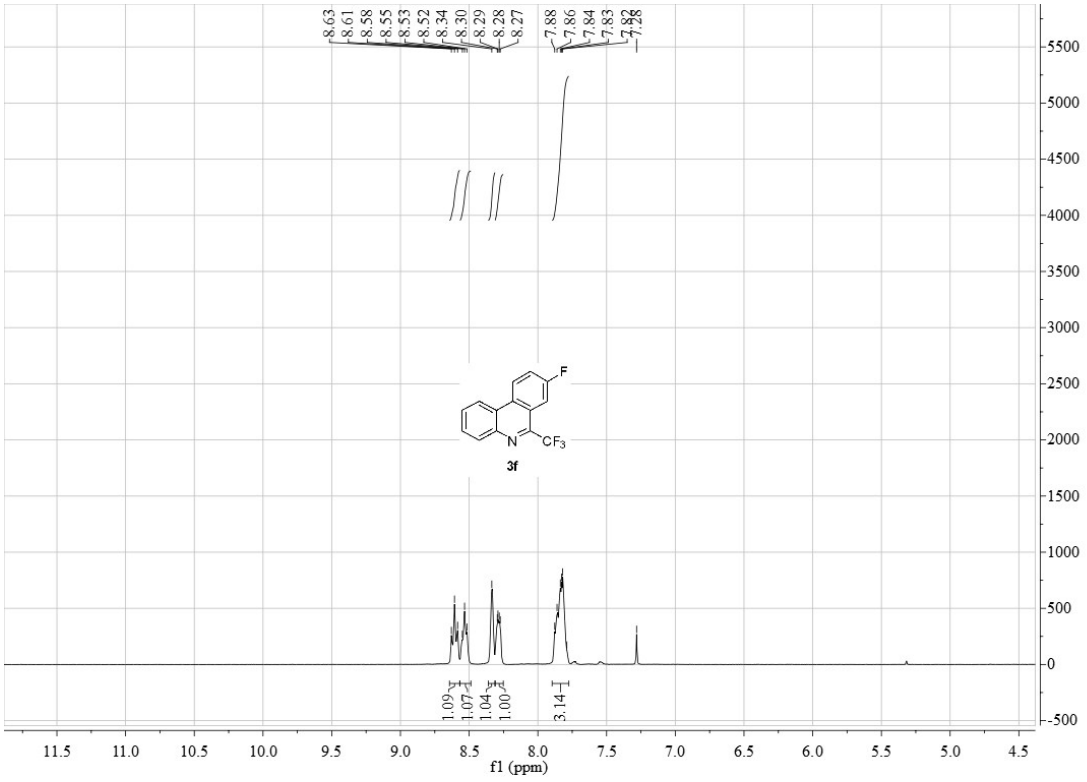
77.36
77.04
76.72
Ph
N
CF3
3e
f1 (ppm)

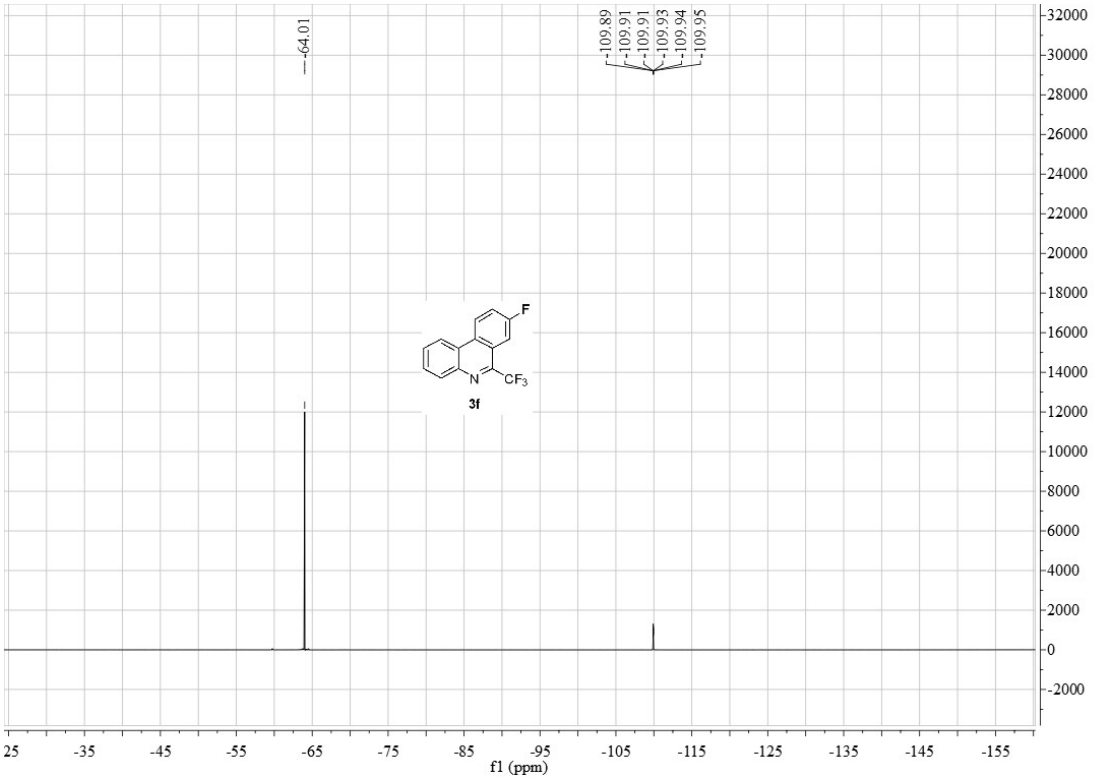

F
N
CF3

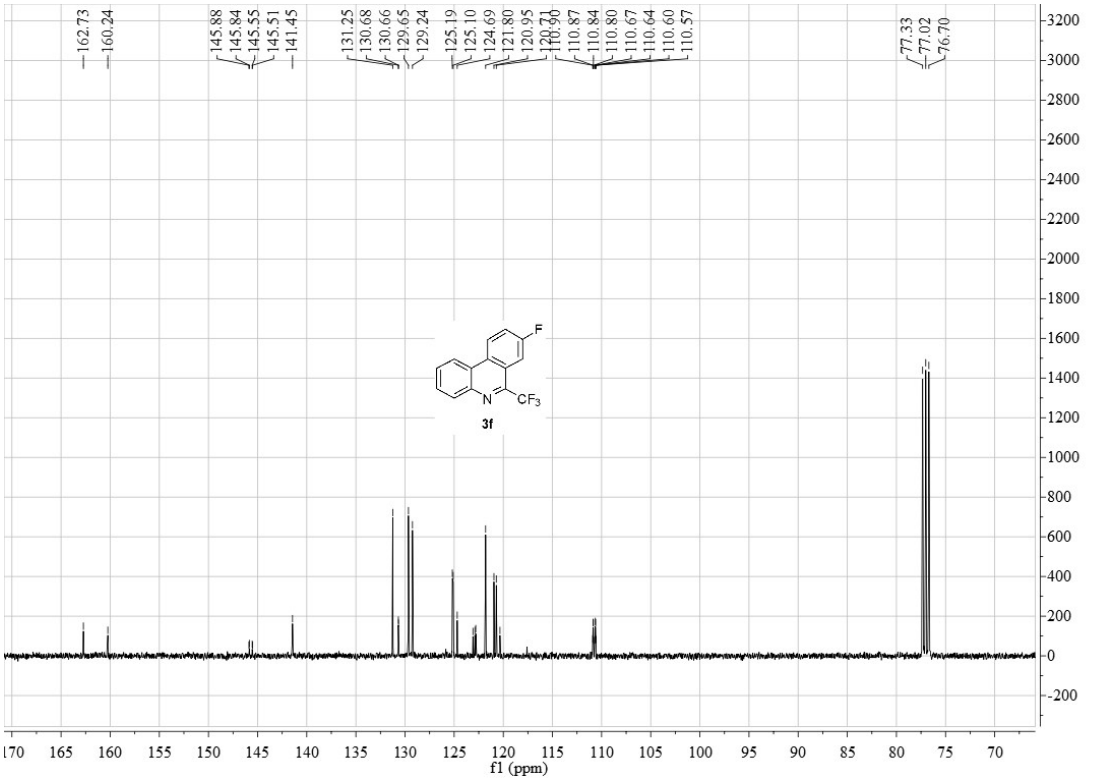
3f

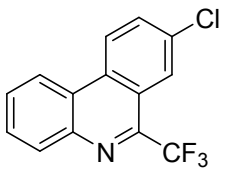
8-fluoro-6-(trifluoromethyl)phenanthridine (3f)

^{1}H NMR (400 MHz, $CDCl_3$) [ppm] δ 8.61 (t, J = 9.1 Hz, 1H), 8.53 (t, J = 6.5 Hz, 1H), 8.34 (s, 1H), 8.29 (dd, J = 6.2, 2.4 Hz, 1H), 7.90 – 7.77 (m, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ -64.01 (s, 3F), -109.89 to -109.95 (m, 1F); **^{13}C NMR** (100 MHz, $CDCl_3$) [ppm] δ 161.5 (d, J = 249.0 Hz), 145.7 (q, J = 33.0 Hz), 141.4 (s), 131.2 (s), 130.7 (d, J = 2.0 Hz), 129.6 (s), 129.2 (s), 125.1 (d, J = 9.0 Hz), 124.7 (s), 122.8 (d, J = 9.0 Hz), 121.8 (s), 121.7 (q, J = 275.0 Hz), 120.8 (d, J = 24.0 Hz), 110.7 (dq, J = 23.2 Hz, 3.5 Hz); **IR** (KBr) ν (cm^{-1}): 1623, 1574, 1533, 1483, 1431, 1385, 1336, 1285, 1209, 1180, 1123, 998, 901, 876, 826, 734; **HRMS** (ESI) found: *m/z* 266.0588 $[M+H]^+$; calcd. for $C_{14}H_7F_4N$+H 266.0593.




-64.01
-109.89
-109.91
-109.91
-109.93
-109.94
-109.95
F
N
CF3
3f
f1 (ppm)

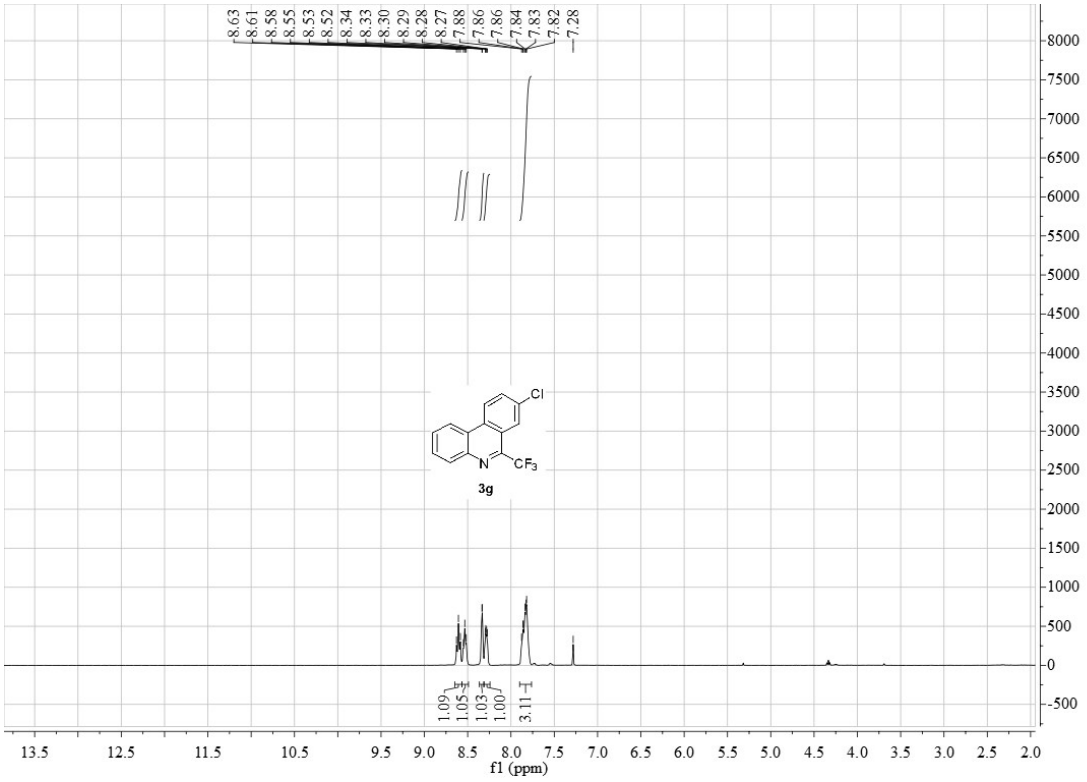

162.73
160.24
145.88
145.84
145.55
145.51
141.45
131.25
130.68
130.66
129.65
129.24
125.19
125.10
124.69
121.80
120.95
120.71
110.87
110.84
110.80
110.67
110.64
110.60
110.57
77.33
77.02
76.70
F
N
CF3
3f
f1 (ppm)

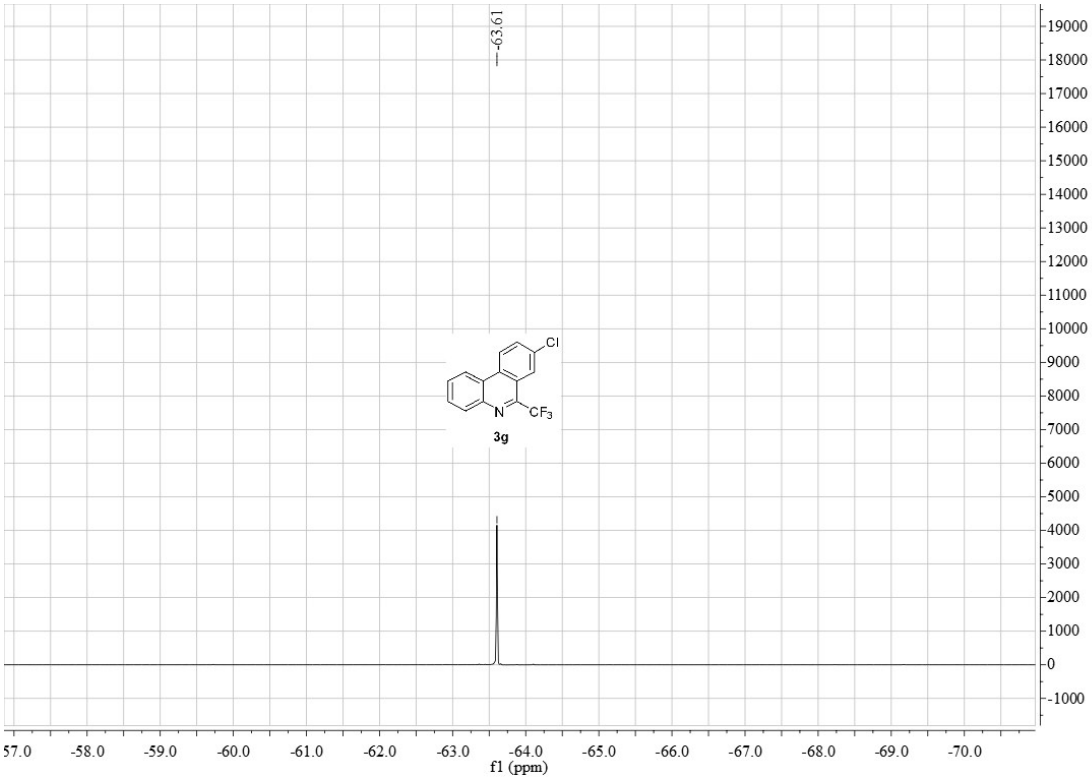

Cl
N
CF3

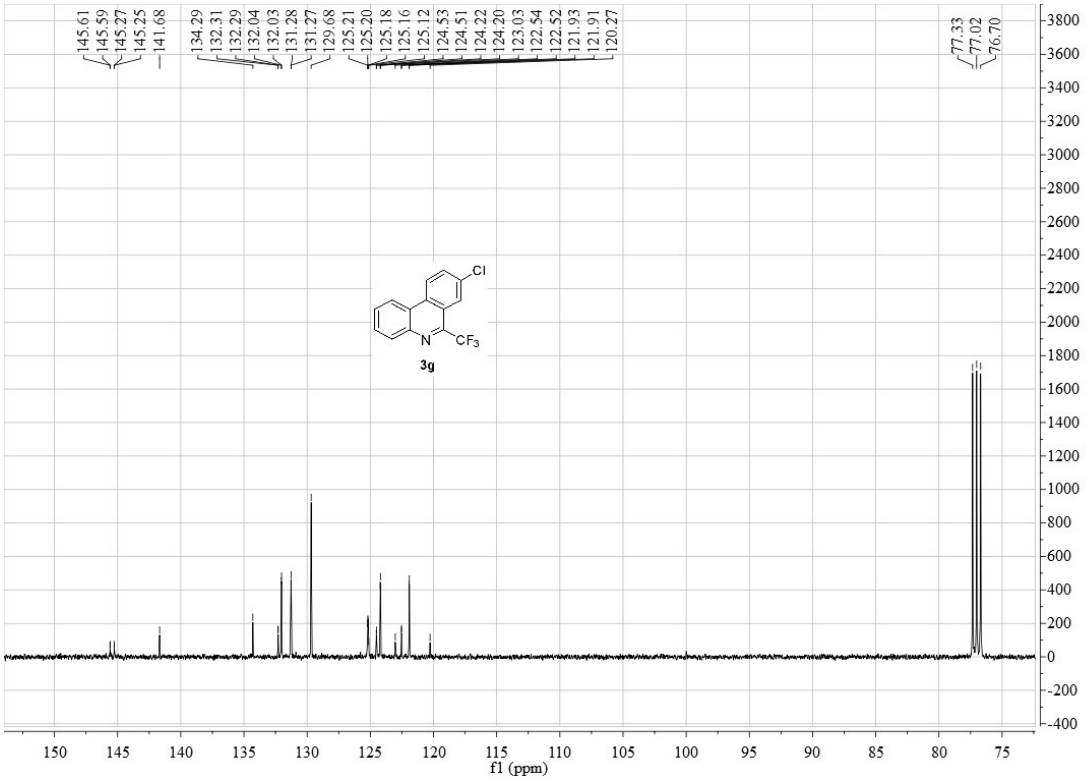
3g

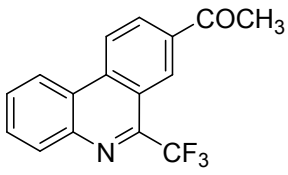
8-chloro-6-(trifluoromethyl)phenanthridine (3g)

^{1}H NMR (400 MHz, $CDCl_3$) [ppm] δ 8.61 (t, J = 9.1 Hz, 1H), 8.53 (t, J = 6.5 Hz, 1H), 8.33 (d, J = 1.2 Hz, 1H), 8.29 (dd, J = 6.2, 2.4 Hz, 1H), 7.90 – 7.76 (m, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ -63.61 (s, 3F); **^{13}C NMR** (100 MHz, $CDCl_3$) [ppm] δ 145.4 (q, J = 34.0 Hz), 141.7 (s), 134.3 (s), 132.3 (d, J = 2.0 Hz), 132.0 (d, J = 1.0 Hz), 131.3 (d, J = 1.0 Hz), 129.7 (s), 125.2 (d, J = 2.0 Hz), 125.2 (q, J = 4.0 Hz), 124.5 (d, J = 2.0 Hz), 124.2 (d, J = 2.0 Hz), 122.5 (d, J = 2.0 Hz), 121.9, (d, J = 2.0 Hz), 121.6 (q, J = 276.0 Hz); **IR** (KBr) ν (cm^{-1}): 3062, 1726, 1574, 1521, 1470, 1409, 1378, 1336, 1252, 1180, 982, 864; **HRMS** (ESI) found: *m/z* 282.0287 $[M+H]^+$; calcd. for $C_{14}H_7ClF_3N$+H 282.0297.




-63.61
Cl
N
CF3
3g
f1 (ppm)

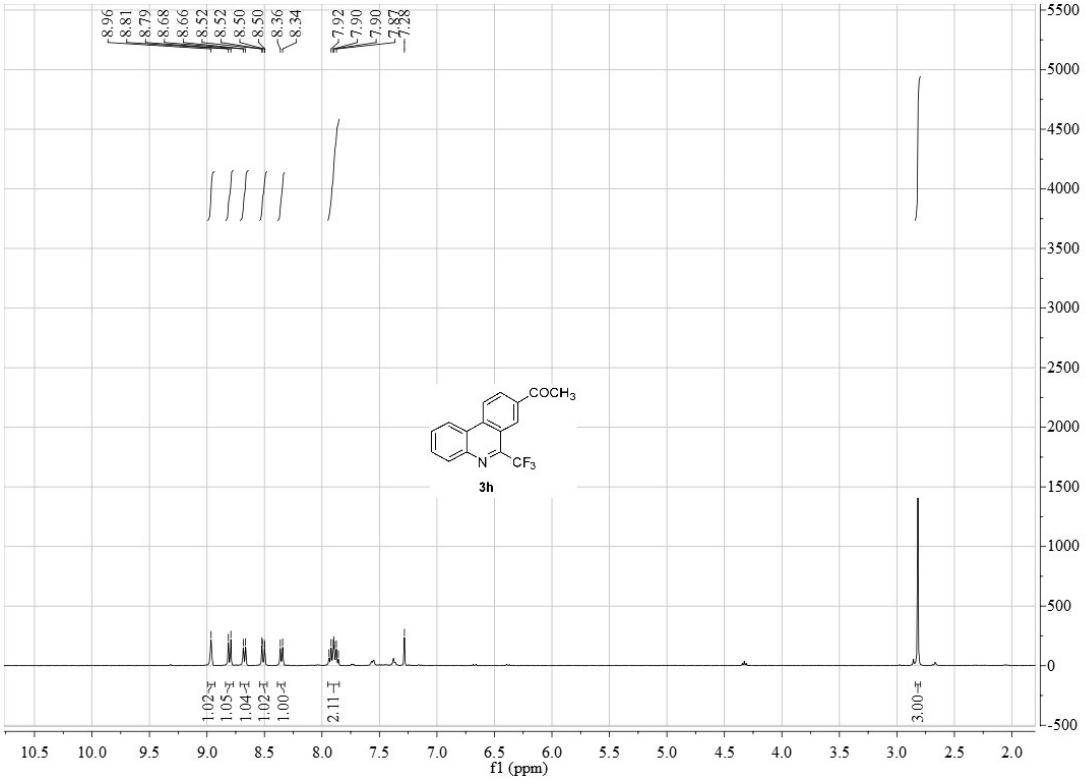

145.61
145.59
145.27
145.25
141.68
134.29
132.31
132.29
132.04
132.03
131.28
131.27
129.68
125.21
125.20
125.18
125.16
125.12
124.53
124.51
124.22
124.20
123.03
122.54
122.52
121.93
121.91
120.27
77.33
77.02
76.70
Cl
N
CF3
3g
f1 (ppm)

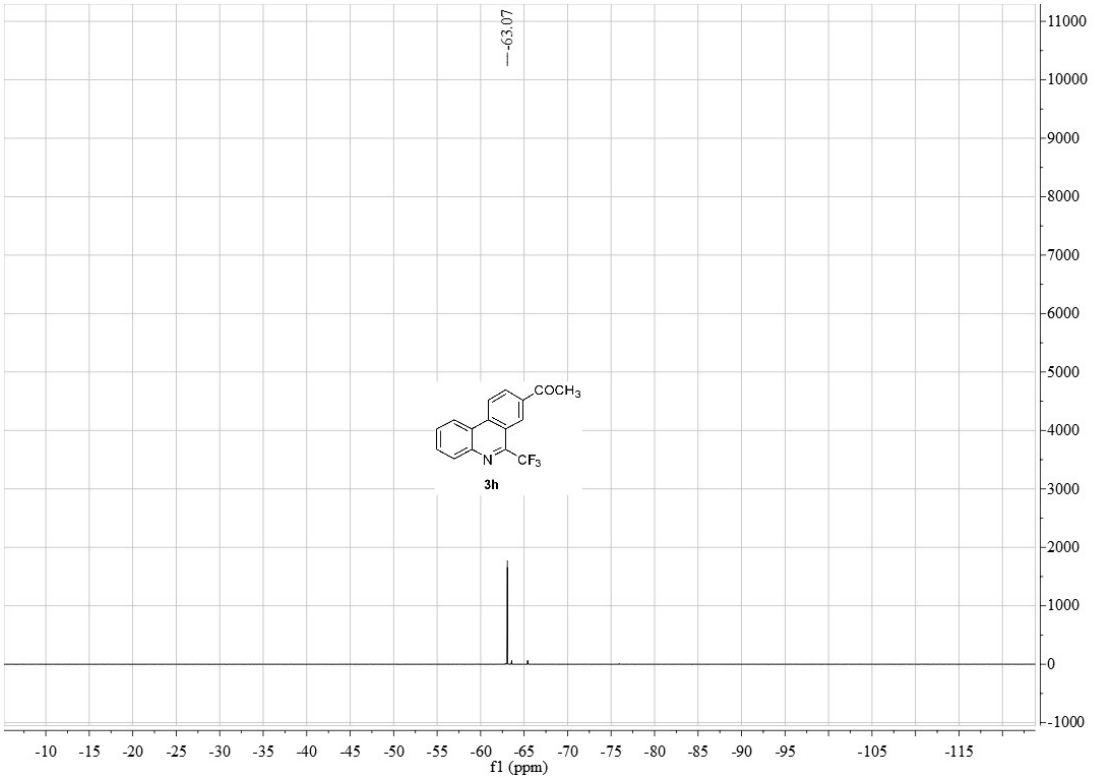

COCH3
N
CF3

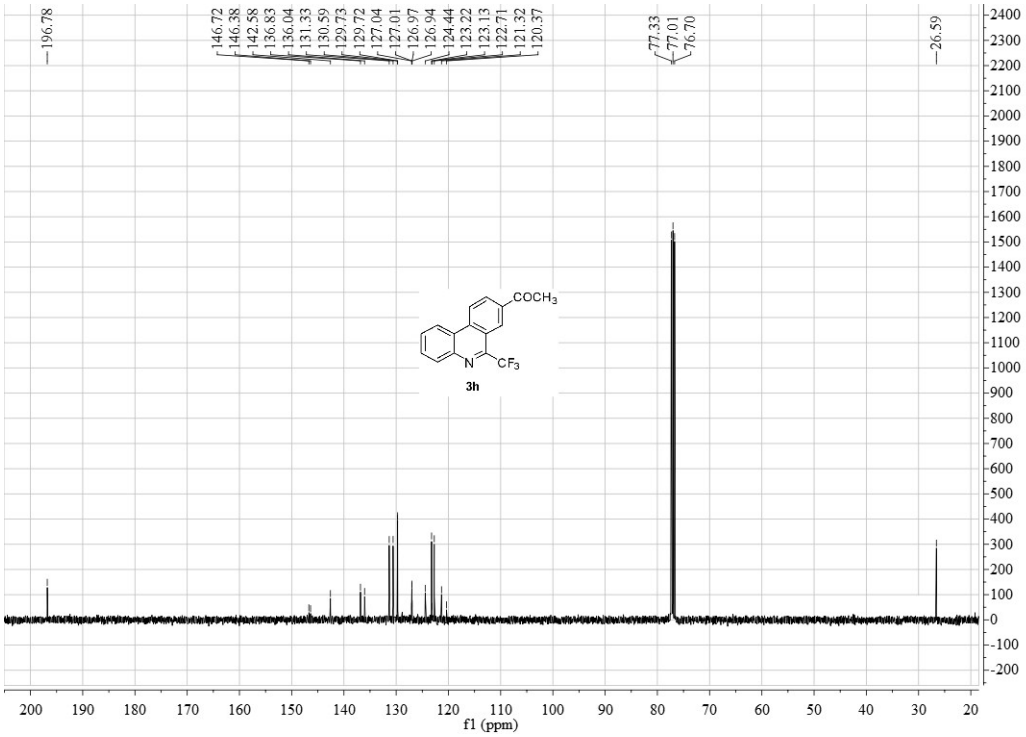
3h

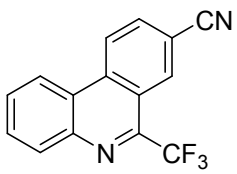
1-(6-(trifluoromethyl)phenanthridin-8-yl)ethan-1-one (3h)

^{1}H NMR (400 MHz, $CDCl_3$) [ppm] δ 8.96 (s, 1H), 8.80 (d, J = 8.8 Hz, 1H), 8.67 (d, J = 7.9 Hz, 1H), 8.51 (dd, J = 8.7, 1.2 Hz, 1H), 8.35 (d, J = 8.1 Hz, 1H), 7.90 (tt, J = 13.8, 7.1 Hz, 2H), 2.82 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ -63.07 (s, 3F); **^{13}C NMR** (100 MHz, $CDCl_3$) [ppm] δ 196.8 (s), 146.6 (q, J = 34.0 Hz), 142.6 (s), 136.8 (s), 136.0 (s), 131.3 (s), 130.6 (s), 129.7 (d, J = 1.0 Hz), 127.0 (q, J = 4.0 Hz), 124.4 (s), 123.2(s), 122.7 (s), 121.8 (q, J = 276.0 Hz), 121.3 (s), 26.6 (s); **IR** (KBr) ν (cm^{-1}): 1728, 1685, 1609, 1415, 1358, 1296, 1254, 1174, 1124, 968, 836, 732; **HRMS** (ESI) found: *m/z* 290.0782 $[M+H]^+$; calcd. for $C_{16}H_{10}F_3NO$+H 290.0792.




-63.07
COCH3
CF3
N
3h
f1 (ppm)

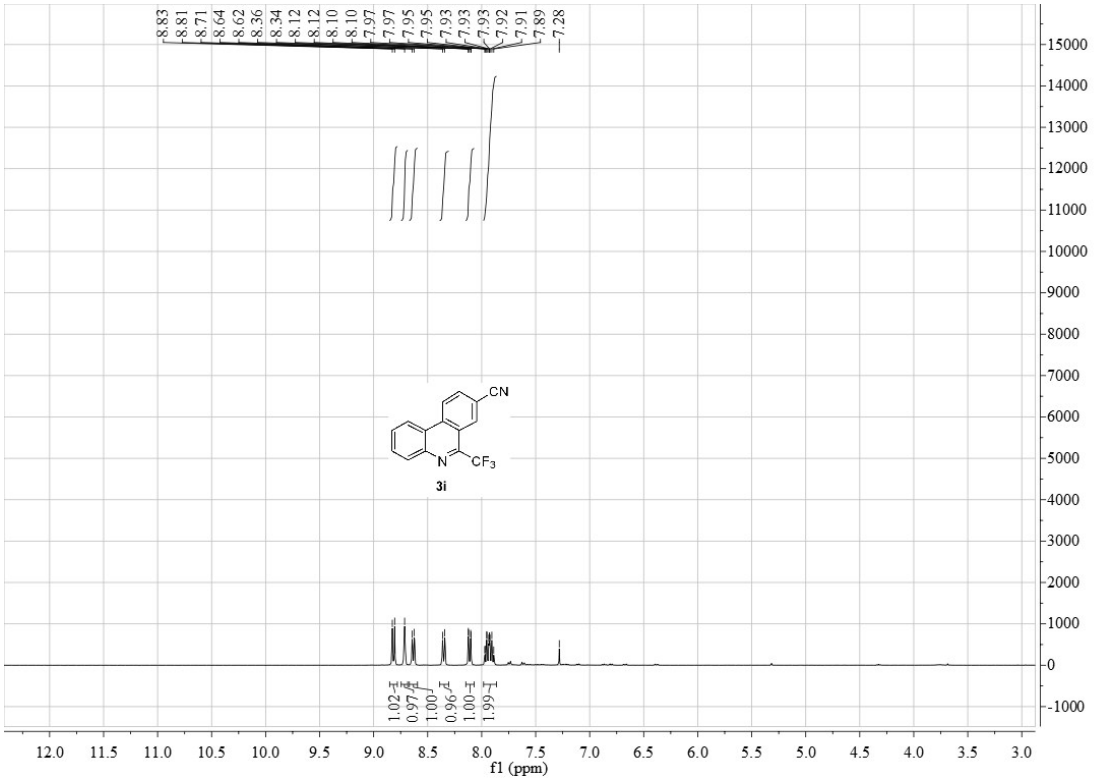

196.78
146.72
146.38
142.58
136.83
136.04
131.33
130.59
129.73
129.72
127.04
127.01
126.97
126.94
124.44
123.22
123.13
122.71
121.32
120.37
77.33
77.01
76.70
26.59
COCH3
CF3
N
3h
f1 (ppm)

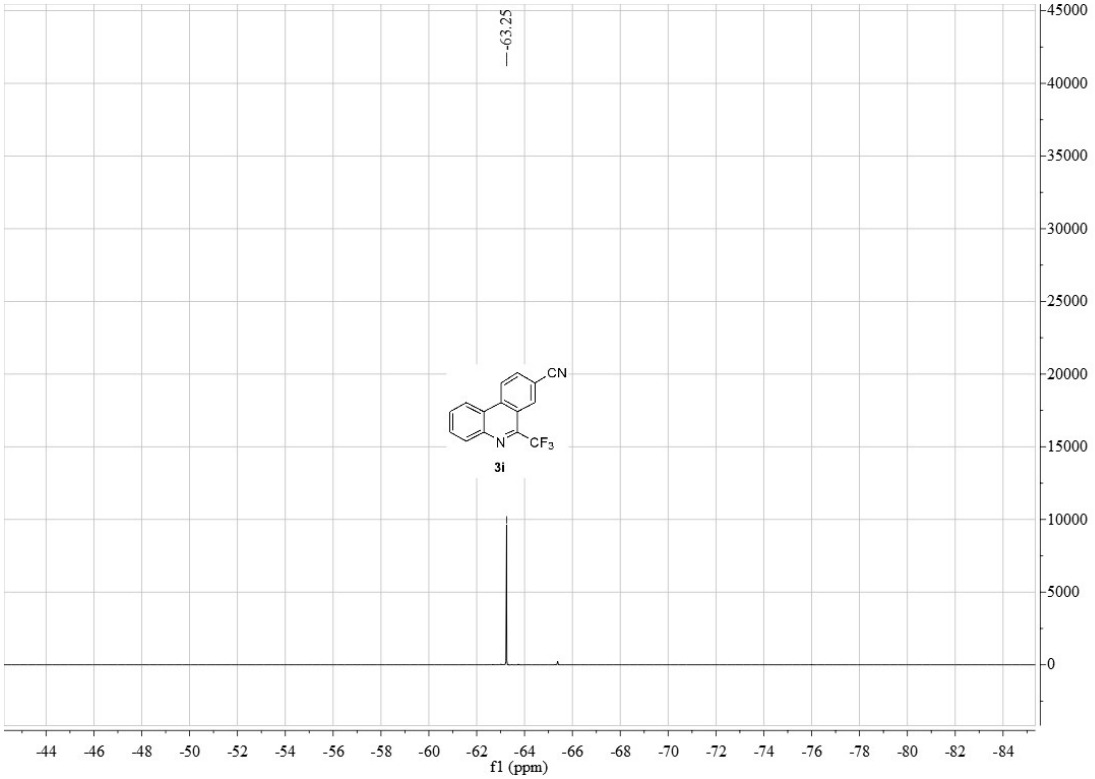

CN
N
CF3

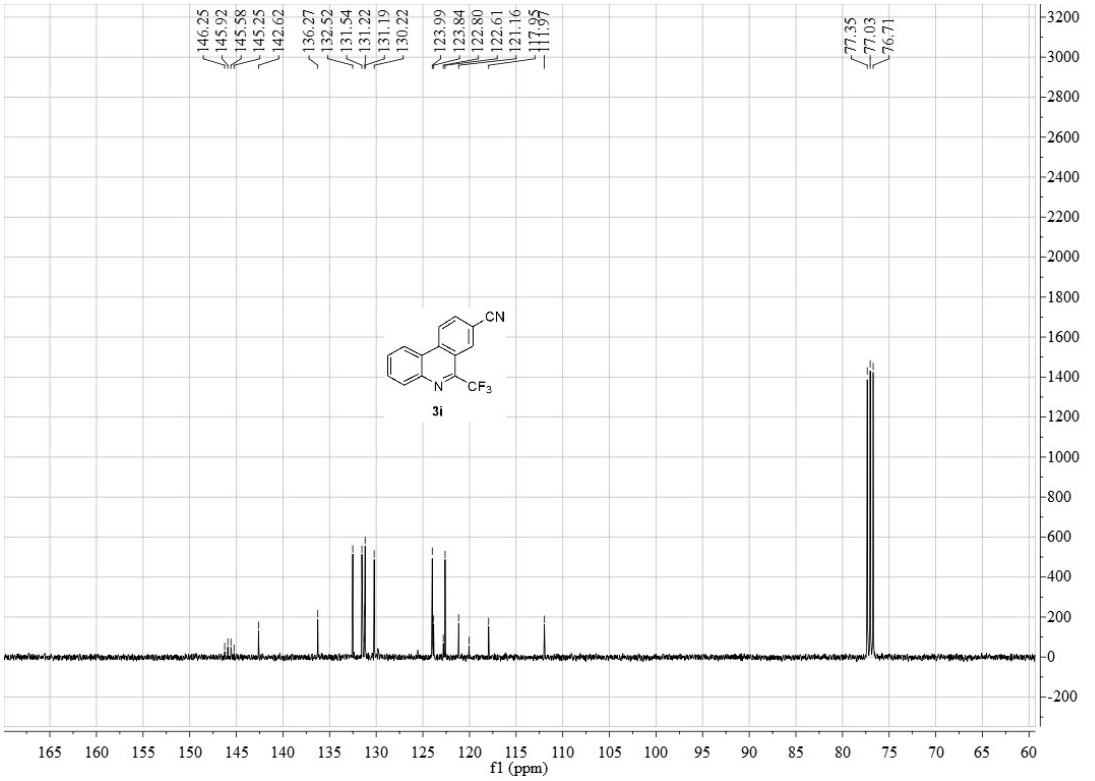
3i

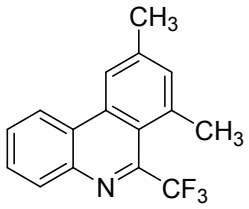
6-(trifluoromethyl)phenanthridine-8-carbonitrile (3i)

^{1}H NMR (400 MHz, $CDCl_3$) [ppm] δ 8.82 (d, J = 8.7 Hz, 1H), 8.71 (s, 1H), 8.63 (d, J = 7.9 Hz, 1H), 8.35 (d, J = 7.7 Hz, 1H), 8.11 (dd, J = 8.7, 1.1 Hz, 1H), 7.98 – 7.86 (m, 2H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ -63.25 (s, 3F); **^{13}C NMR** (100 MHz, $CDCl_3$) [ppm] δ 145.8 (q, J = 34.0 Hz), 142.6 (s), 136.3 (s), 132.5 (s), 131.5 (s), 131.2 (q, J = 4.0 Hz), 131.2 (s), 130.2 (s), 124.0 (s), 123.8 (s), 122.6 (s), 121.4 (q, J = 275.0 Hz), 121.2 (s), 118.0 (s), 112.0 (s); **IR** (KBr) ν (cm^{-1}): 3085, 2229, 1729, 1613, 1527, 1466, 1414, 1378, 1335, 1258, 1176, 1130, 992, 838; **HRMS** (ESI) found: *m/z* 273.0636 $[M+H]^+$; calcd. for $C_{15}H_7F_3N_2$+H 273.0639.




-63.25
CN
N
CF3
3i
f1 (ppm)

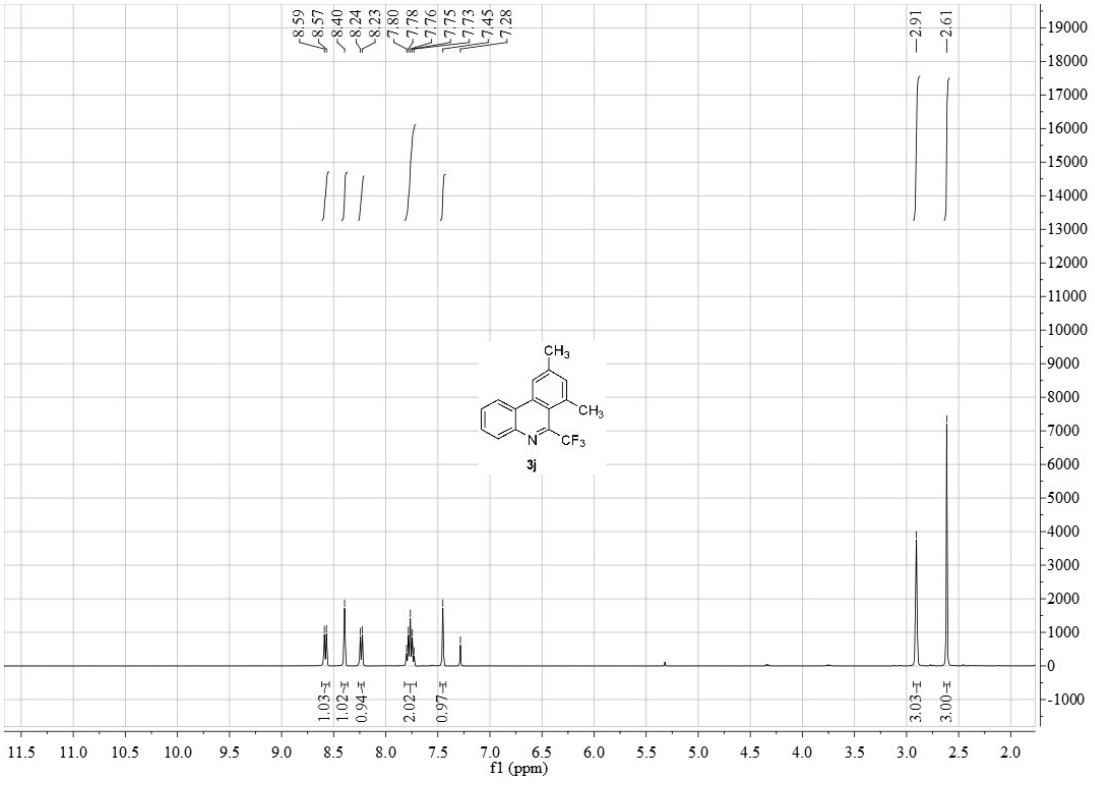

146.25
145.92
145.58
145.25
142.62
136.27
132.52
131.54
131.22
131.19
130.22
123.99
123.84
122.80
122.61
121.16
117.95
111.97
77.35
77.03
76.71
CN
N
CF3
3i
f1 (ppm)

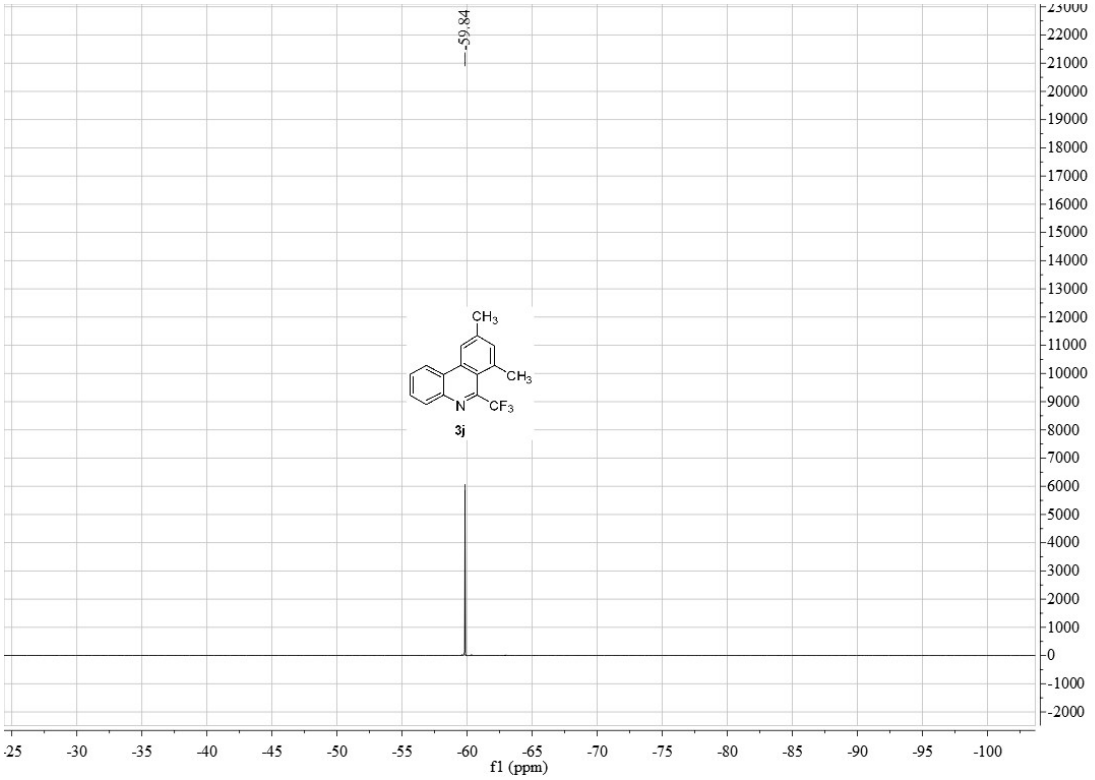


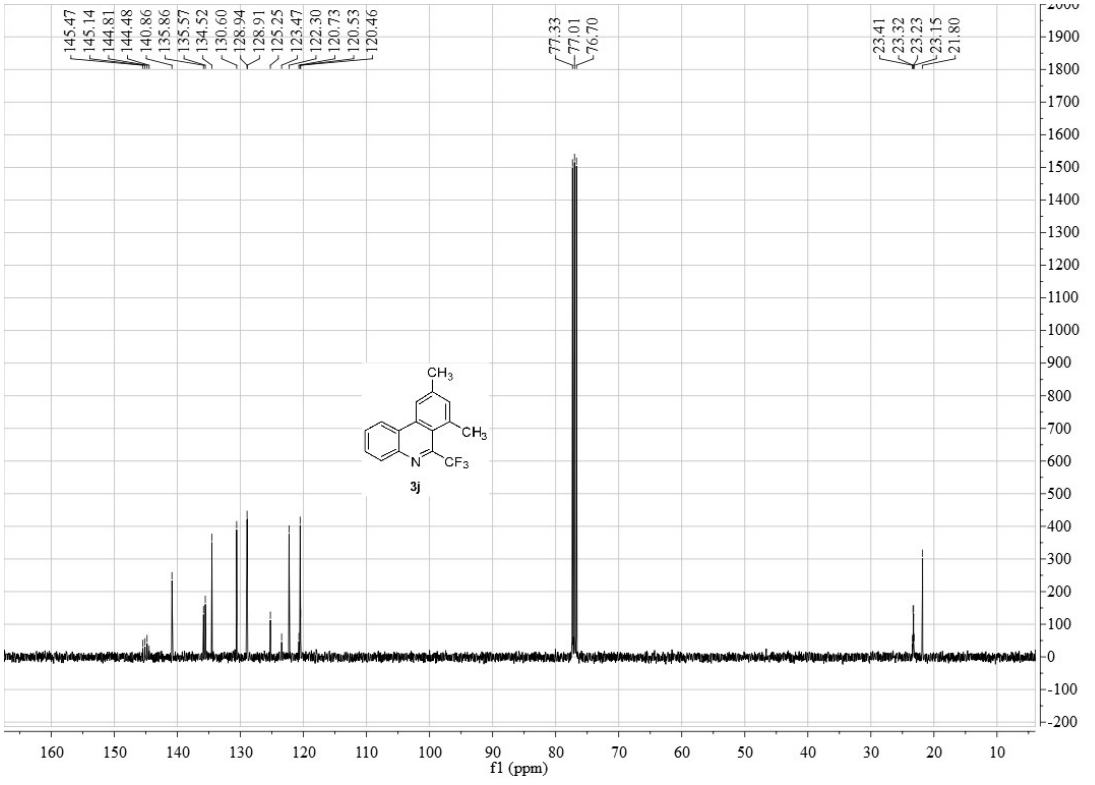
3j

7,9-dimethyl-6-(trifluoromethyl)phenanthridine (3j)

^{1}H NMR (400 MHz, $CDCl_3$) [ppm] δ 8.58 (d, J = 8.1 Hz, 1H), 8.40 (s, 1H), 8.23 (d, J = 7.7 Hz, 1H), 7.82 – 7.71 (m, 2H), 7.45 (s, 1H), 2.91 (s, 3H), 2.61 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ -59.84 (s, 3F); **^{13}C NMR** (100 MHz, $CDCl_3$) [ppm] δ 145.0 (q, J = 33.0 Hz), 140.9 (s), 140.8 (s), 135.9 (s), 135.6 (s), 134.5 (s), 130.6 (s), 128.9 (s), 128.9 (s), 125.2 (s), 122.3 (s), 122.1 (q, J = 275.0 Hz), 120.5 (s), 120.5 (s), 23.3 (q, J = 9.0 Hz), 21.8 (s); **IR** (KBr) ν (cm^{-1}): 2917, 1725, 1615, 1576, 1513, 1466, 1379, 1350, 1241, 1160, 1119, 960, 849, 768; **HRMS** (ESI) found: *m/z* 276.0998 $[M+H]^+$; calcd. for $C_{16}H_{12}F_3N$+H 276.1000.




-59.84
CH3
CH3
N
CF3
3j
f1 (ppm)


145.47
145.14
144.81
144.48
140.86
135.86
135.57
134.52
130.60
128.94
128.91
125.25
123.47
122.30
120.73
120.53
120.46
77.33
77.01
76.70
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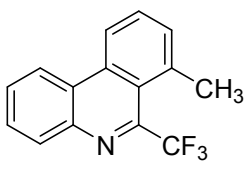
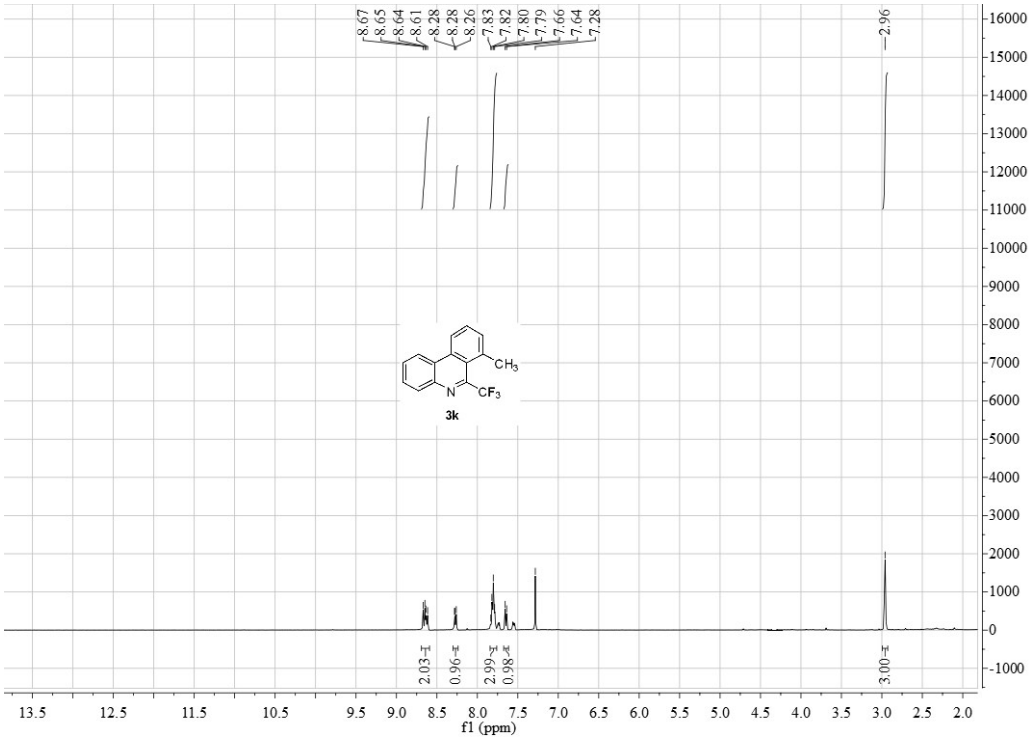
23.32
23.23
23.15
21.80
CH3
CH3
N
CF3
3j
f1 (ppm)

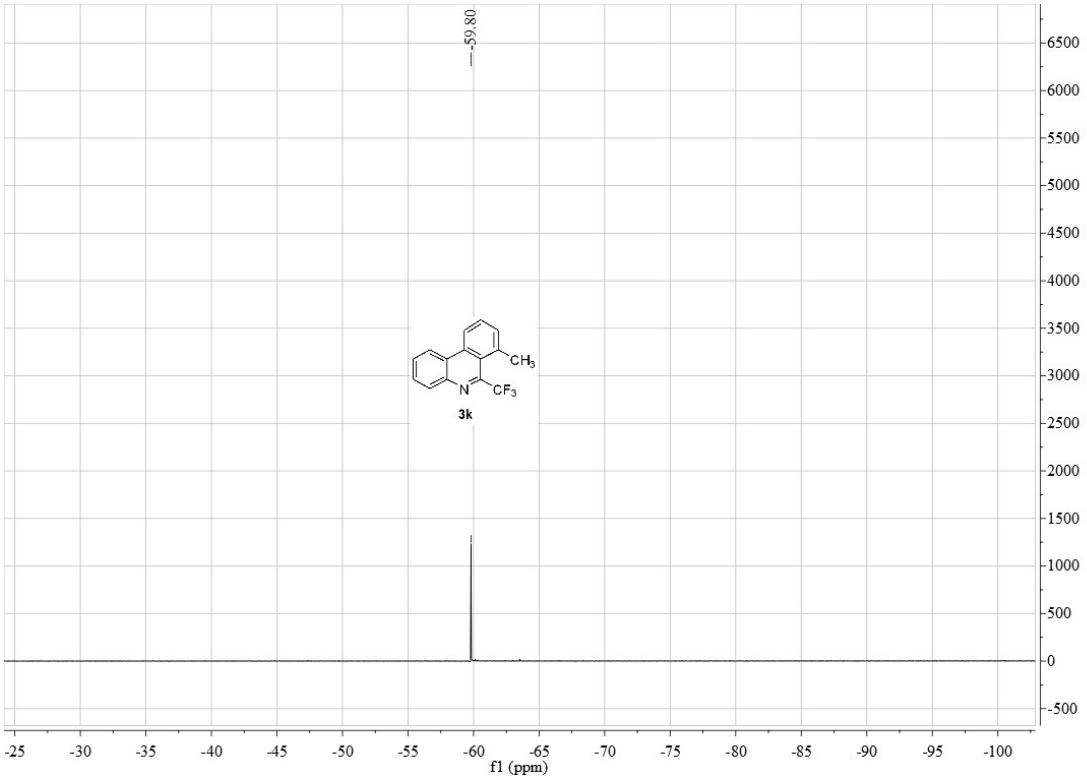

CH3
N
CF3

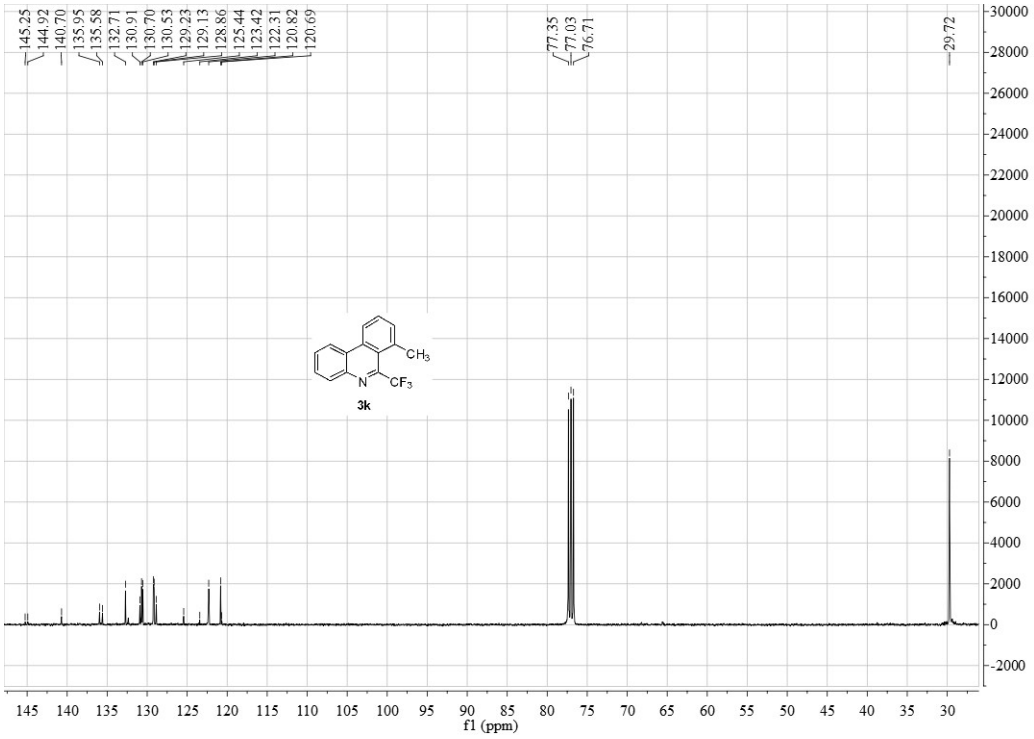
3k

7-methyl-6-(trifluoromethyl)phenanthridine (3k)

^{1}H NMR (400 MHz, $CDCl_3$) [ppm] δ 8.64 (dd, J = 13.3, 8.7 Hz, 2H), 8.30 – 8.24 (m, 1H), 7.84 – 7.76 (m, 3H), 7.65 (d, J = 7.2 Hz, 1H), 2.96 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ -59.80 (s, 3F); **^{13}C NMR** (100 MHz, $CDCl_3$) [ppm] δ 144.8 (q, J = 33.0 Hz), 140.7 (s), 136.0 (s), 135.6 (s), 132.7 (s), 130.9 (s), 130.7 (s), 130.5 (s), 129.2 (s), 129.1 (s), 128.9 (s), 122.3 (s), 122.0 (q, J = 273.0 Hz), 120.8 (s), 29.72 (s); **IR** (KBr) ν (cm^{-1}): 2958, 2920, 1726, 1600, 1524, 1460, 1381, 1346, 1260, 1176, 1130, 964, 803; **HRMS** (ESI) found: *m/z* 262.0838 $[M+H]^+$; calcd. for $C_{15}H_{10}F_3N$+H 262.0843.




-59.80
CH3
N
CF3
3k
f1 (ppm)


145.25
144.92
140.70
135.95
135.58
132.71
130.91
130.70
130.53
129.23
129.13
128.86
125.44
123.42
122.31
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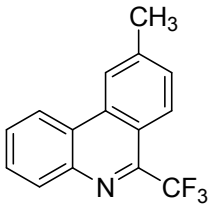
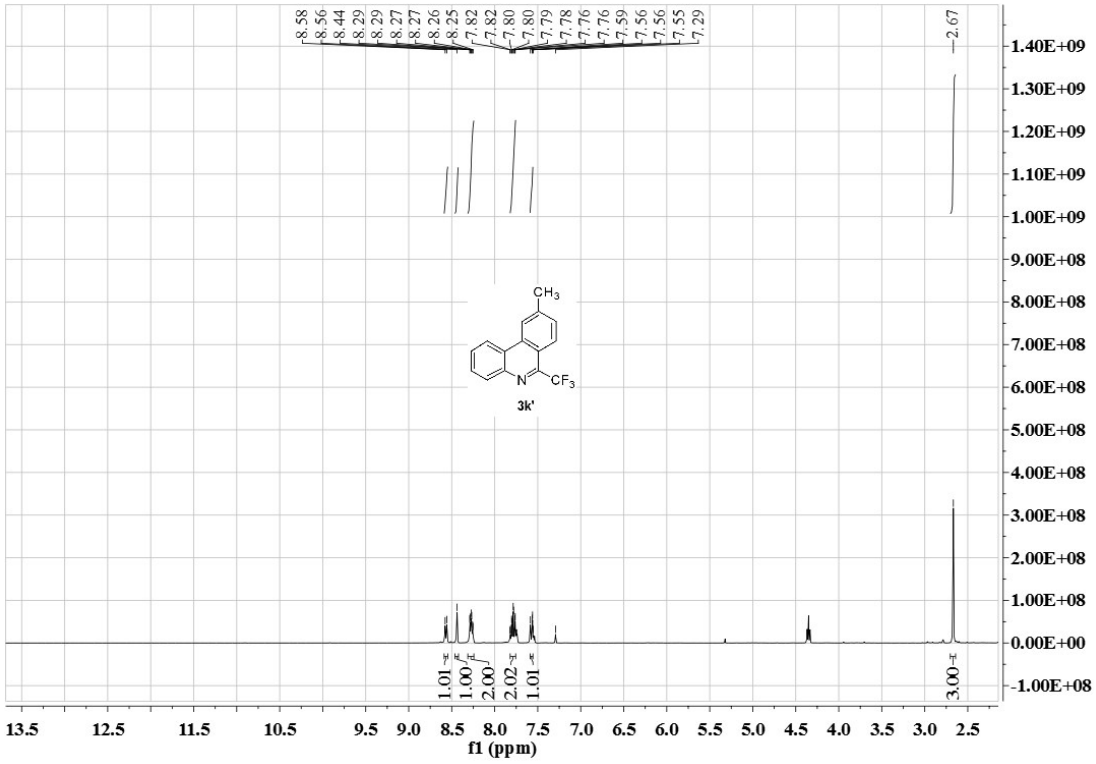
120.69
77.35
77.03
76.71
29.72
CH3
N
CF3
3k
f1 (ppm)

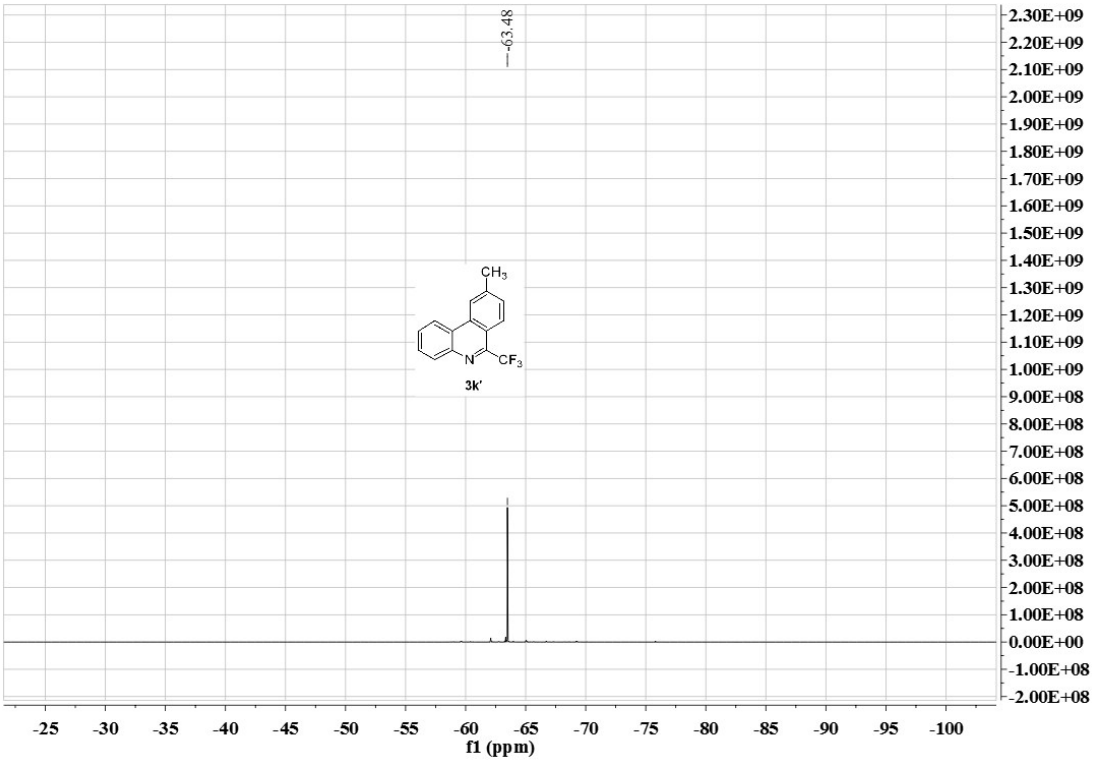

CH3
N
CF3

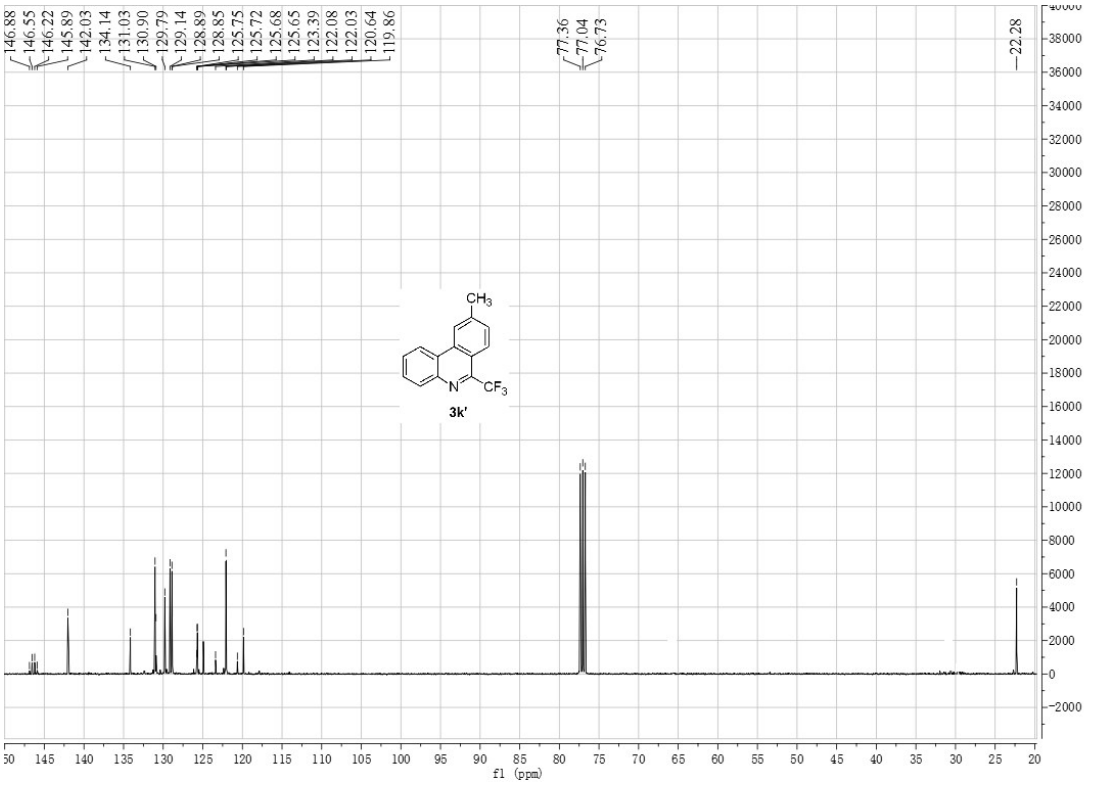
3k'

9-methyl-6-(trifluoromethyl)phenanthridine(3k')

^{1}H NMR (400 MHz, $CDCl_3$) [ppm] δ 8.57 (d, J = 7.7 Hz, 1H), 8.44 (s, 1H), 8.31 – 8.24 (m, 2H), 7.82 – 7.76 (m, 2H), 7.59 – 7.56 (m, 1H), 2.67 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ -63.48 (s, 3F); **^{13}C NMR** (100 MHz, $CDCl_3$) [ppm] δ 146.4 (q, J = 33.0 Hz), 142.03 (s), 134.1 (s), 131.0 (s), 130.9 (s), 129.8 (s), 129.1 (s), 128.9 (s), 128.8 (s), 125.7 (q, J = 4.0 Hz), 122.1 (s), 122.0 (q, J = 275.0 Hz), 122.0 (s), 119.9 (s), 22.3 (s); **IR** (KBr) ν (cm^{-1}): 2960, 2927, 1726, 1620, 1518, 1463, 1379, 1285, 1249, 1119, 968, 874, 757, 731; **HRMS** (ESI) found: *m/z* 262.0838 $[M+H]^+$; calcd. for $C_{15}H_{10}F_3N$+H 262.0843.




-63.48
CH3
CF3
N
3k'
f1 (ppm)


146.88
146.55
146.22
145.89
142.03
134.14
131.03
130.90
129.79
129.14
128.89
128.85
125.75
125.72
125.68
125.65
123.39
122.08
122.03
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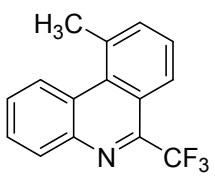
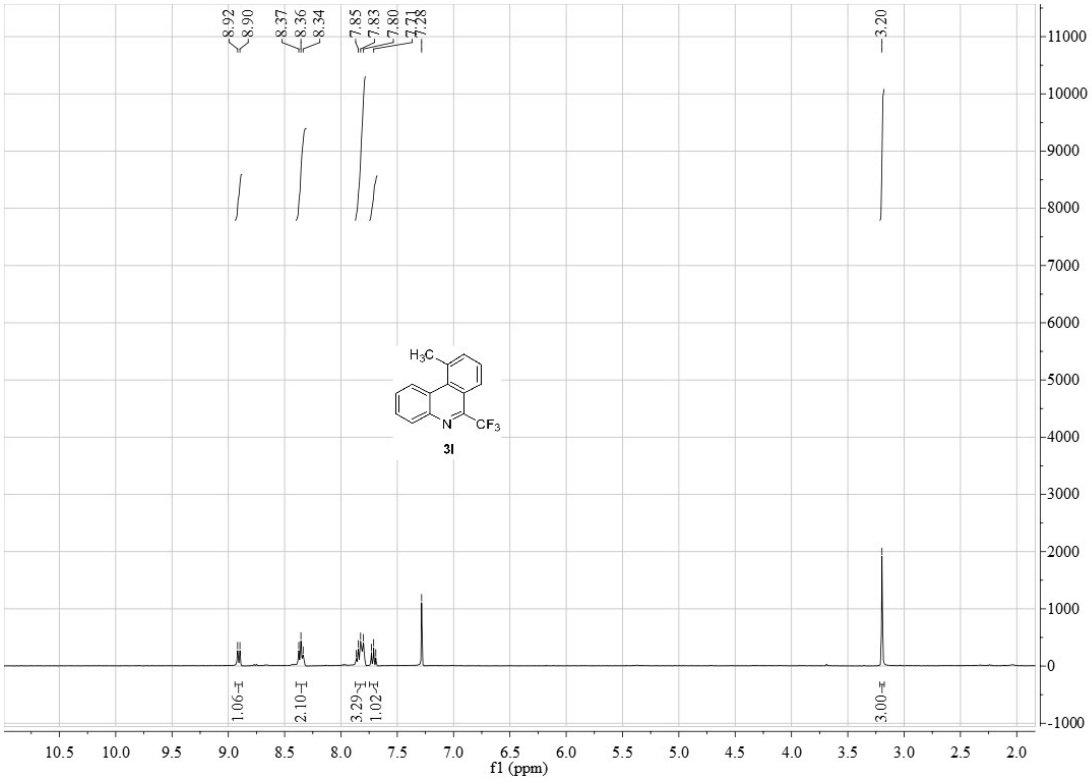
119.86
77.36
77.04
76.73
22.28
CH3
CF3
N
3k'
f1 (ppm)

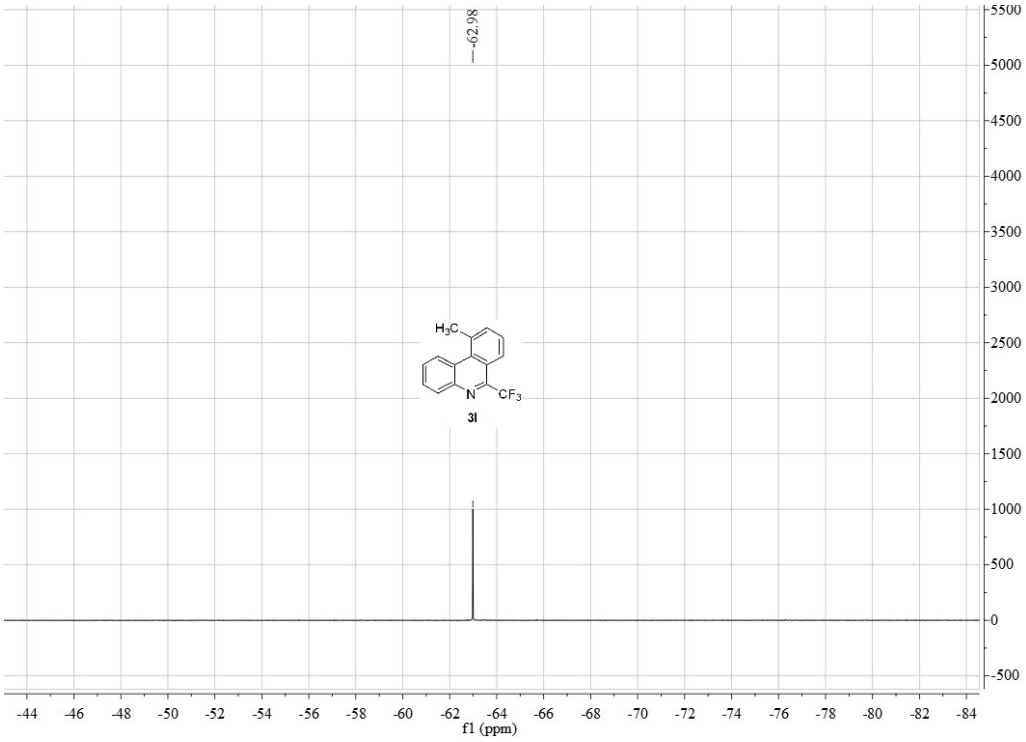

H3C
N
CF3

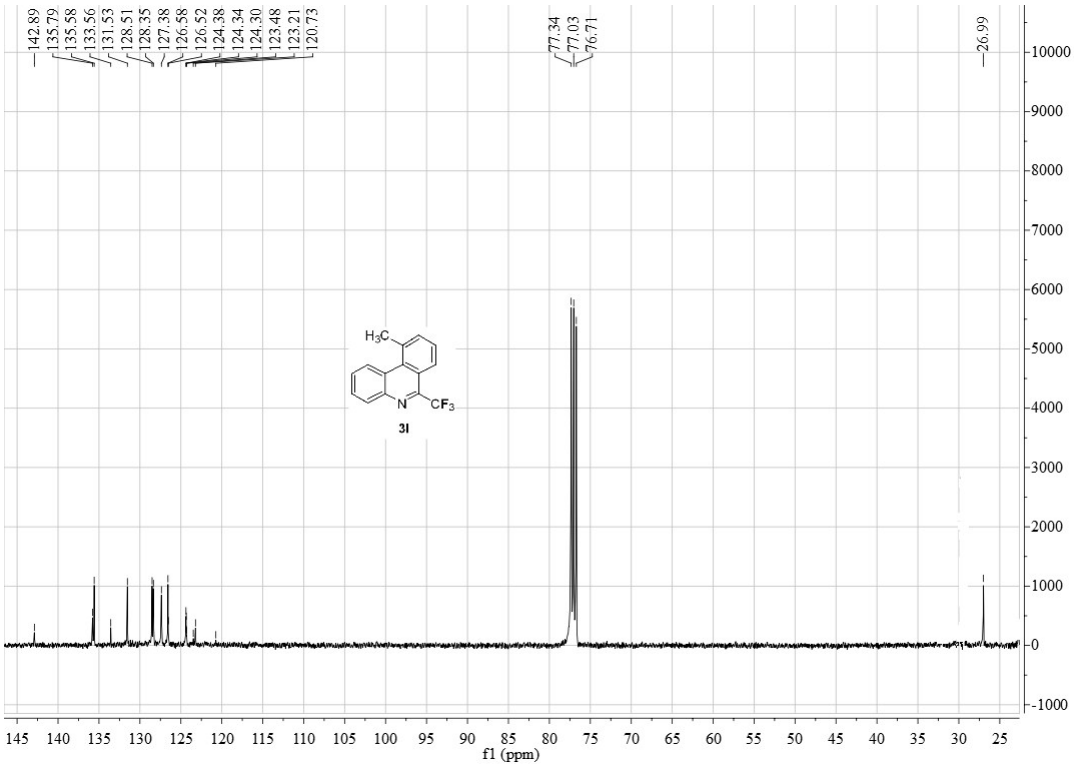
3l

10-methyl-6-(trifluoromethyl)phenanthridine (3l)

^{1}H NMR (400 MHz, $CDCl_3$) [ppm] δ 8.91 (d, J = 8.2 Hz, 1H), 8.36 (t, J = 7.7 Hz, 2H), 7.83 (dd, J = 16.6, 8.6 Hz, 3H), 7.71 (t, J = 7.8 Hz, 1H), 3.20 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ -62.98 (s, 3F); **^{13}C NMR** (100 MHz, $CDCl_3$) [ppm] δ 147.1 (q, J = 32.5 Hz), 142.9 (s), 135.8 (s), 135.6 (s), 133.6 (s), 131.5 (s), 128.5 (s), 128.4 (s), 127.4 (s), 126.6 (s), 126.5 (s), 124.4 (q, J = 4.0 Hz), 123.2 (s), 122.1 (q, J = 275.0 Hz), 27.0 (s); **IR** (KBr) ν (cm^{-1}): 2920, 2852, 1729, 1587, 1529, 1459, 1376, 1260, 1180, 1114, 1052, 802, 759, 722; **HRMS** (ESI) found: *m/z* 262.0838 $[M+H]^+$; calcd. for $C_{15}H_{10}F_3N$+H 262.0843.




-62.98
H3C
N
CF3
3l
f1 (ppm)


142.89
135.79
135.58
133.56
131.53
128.51
128.35
127.38
126.58
126.52
124.38
124.34
124.30
123.48
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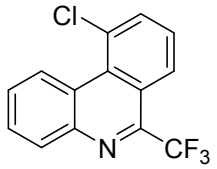
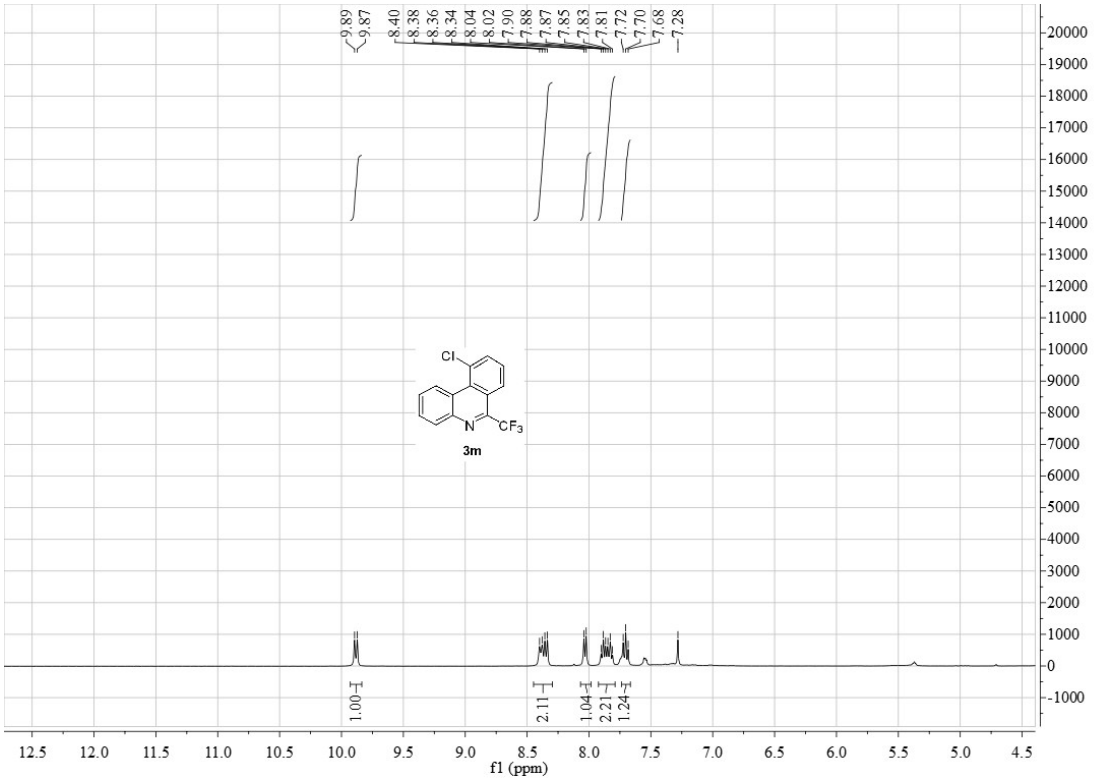
120.73
77.34
77.03
76.71
26.99
H3C
N
CF3
3l
f1 (ppm)

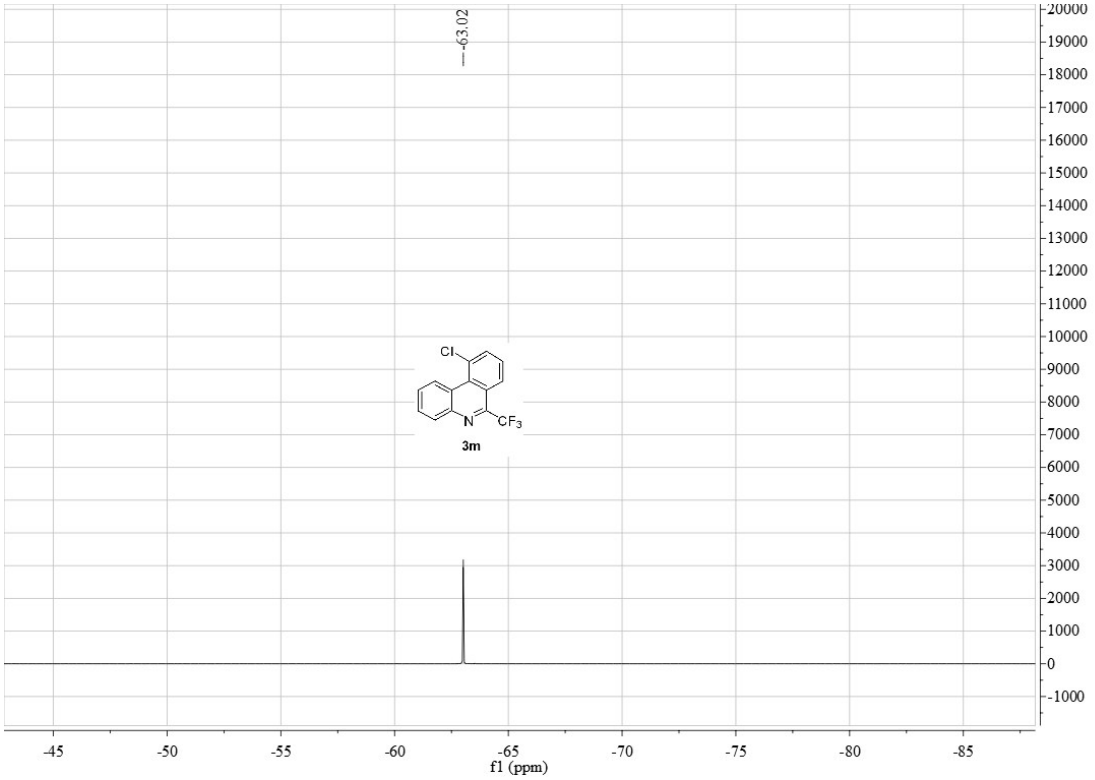

Cl
N
CF3

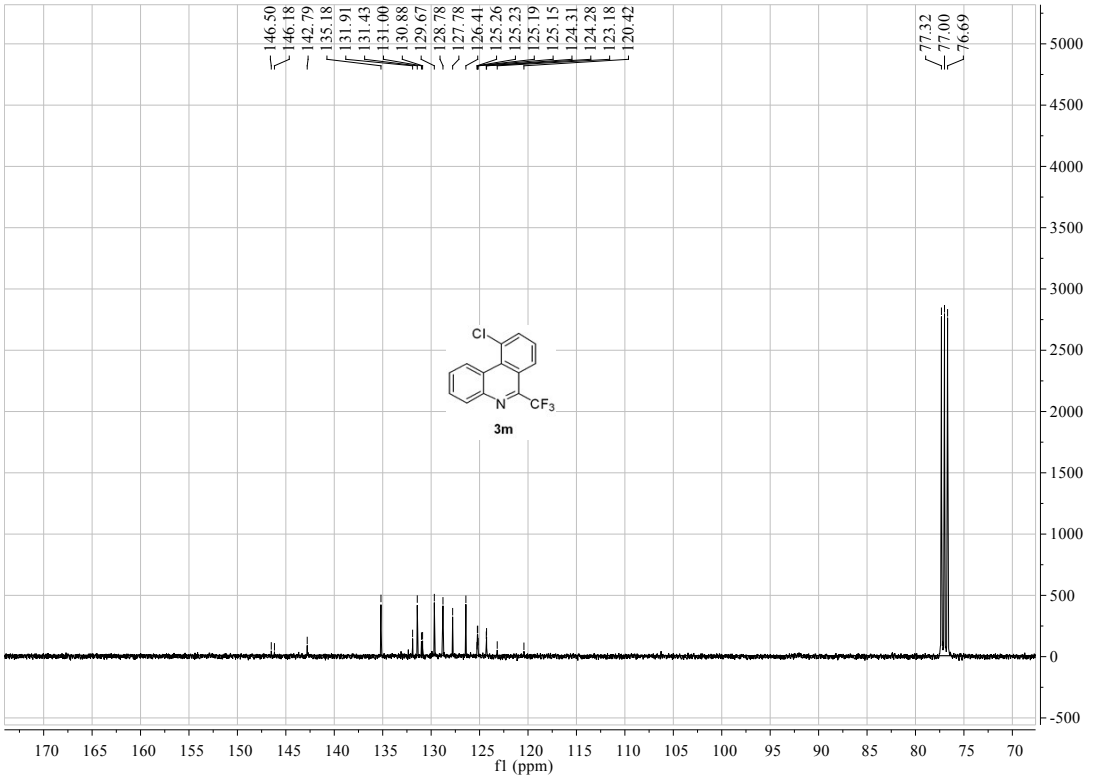
3m

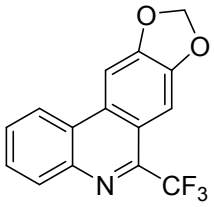
10-chloro-6-(trifluoromethyl)phenanthridine (3m)

^{1}H NMR (400 MHz, $CDCl_3$) [ppm] δ 9.88 (d, J = 8.4 Hz, 1H), 8.37 (dd, J = 17.0, 8.0 Hz, 2H), 8.03 (d, J = 7.6 Hz, 1H), 7.86 (dt, J = 14.5, 7.0 Hz, 2H), 7.70 (t, J = 8.1 Hz, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ -63.02 (s, 3F); **^{13}C NMR** (100 MHz, $CDCl_3$) [ppm] δ 146.3 (q, J = 32.0 Hz), 142.8 (s), 135.2 (s), 131.9 (s), 131.4 (s), 131.0 (s), 130.9 (s), 129.7 (s), 128.8 (s), 127.8 (s), 126.4 (s), 125.2 (q, J = 4.0 Hz), 124.3 (s), 121.8 (q, J = 276.0 Hz); **IR** (KBr) ν (cm^{-1}): 2921, 2853, 1726, 1593, 1523, 1465, 1373, 1258, 1181, 1108, 804, 755, 720; **HRMS** (ESI) found: *m/z* 282.0295 $[M+H]^+$; calcd. for $C_{14}H_7ClF_3N$+H 282.0297.




-63.02
Cl
N
CF3
3m
f1 (ppm)

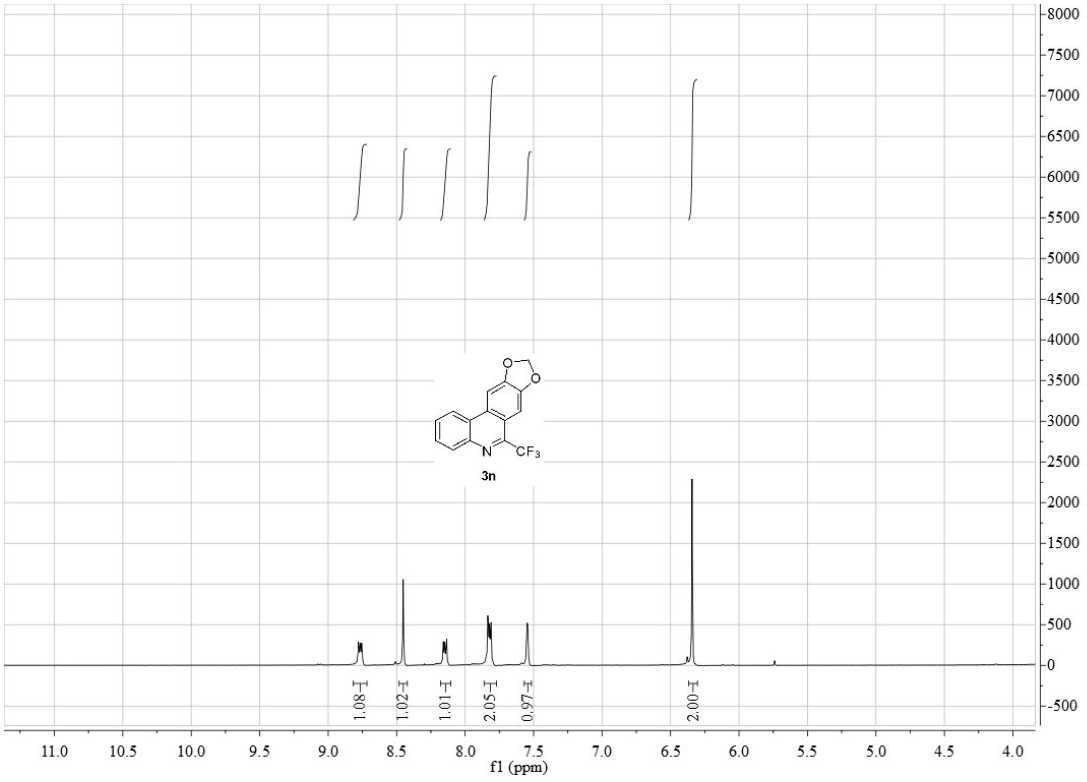

146.50
146.18
142.79
135.18
131.91
131.43
131.00
130.88
129.67
128.78
127.78
126.41
125.26
125.23
125.19
125.15
124.31
124.28
123.18
120.42
77.32
77.00
76.69
Cl
N
CF3
3m
f1 (ppm)

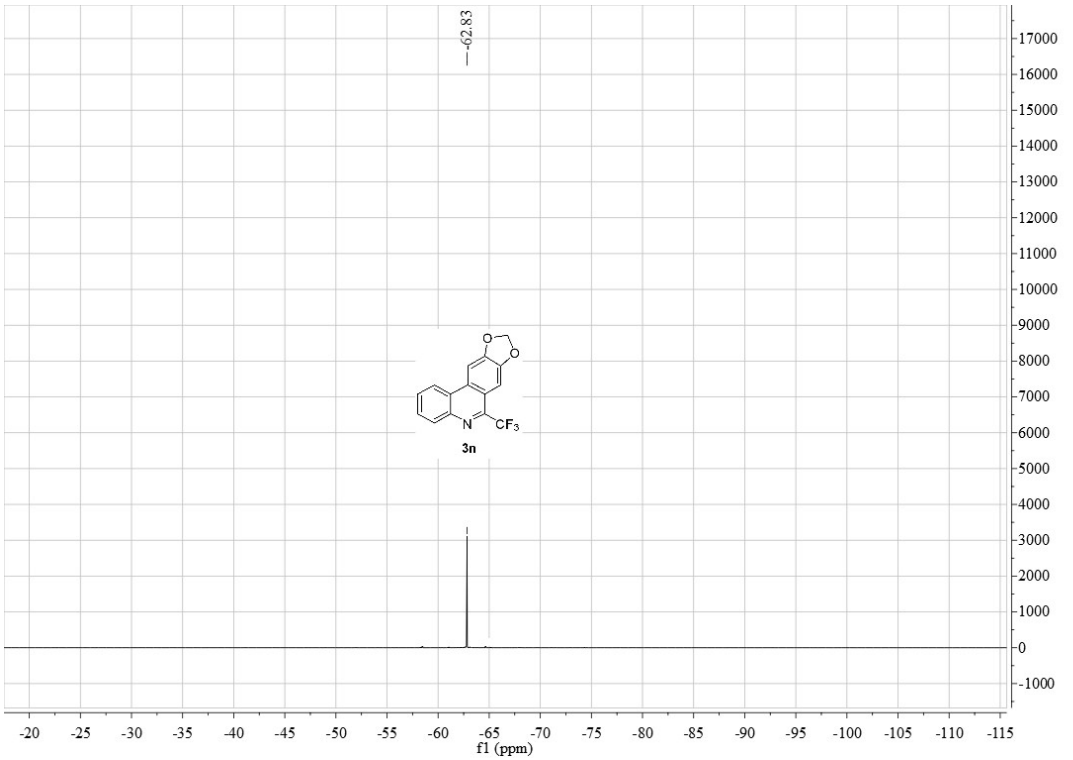


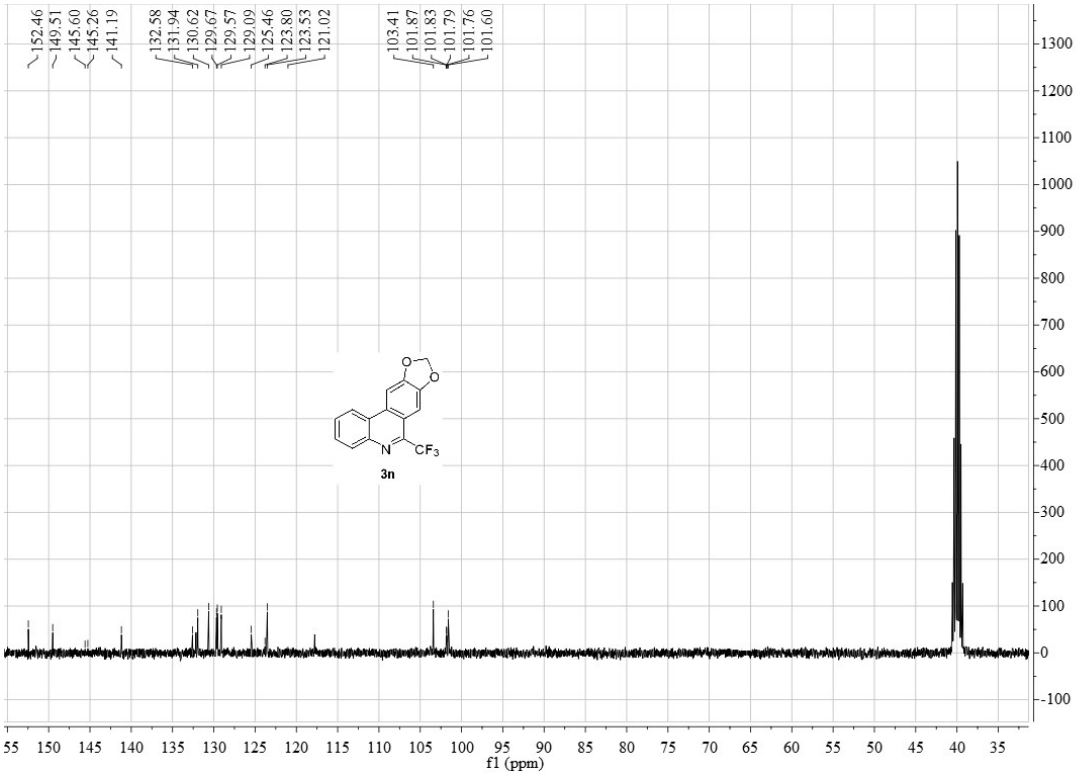
3n

6-(trifluoromethyl)-[1,3]dioxolo[4,5-j]phenanthridine (3n)

^{1}H NMR (400 MHz, DMSO) [ppm] δ 8.82 – 8.72 (m, 1H), 8.45 (s, 1H), 8.15 (dd, J = 6.3, 3.2 Hz, 1H), 7.86 – 7.77 (m, 2H), 7.55 (d, J = 1.7 Hz, 1H), 6.34 (s, 2H); **^{19}F NMR** (376 MHz, DMSO) [ppm] δ -62.83 (s, 3F); **^{13}C NMR** (100 MHz, DMSO) [ppm] δ 152.5 (s), 149.5 (s), 145.4 (q, J = 34.0 Hz), 141.2 (s), 132.6 (s), 131.9 (s), 130.6 (s), 129.7 (s), 129.6 (s), 129.1 (s), 125.5 (s), 123.5 (s), 103.4 (s), 101.8 (q, J = 4.0 Hz), 101.6 (s); **IR** (KBr) ν (cm^{-1}): 2926, 1651, 1507, 1464, 1264, 1188, 1111, 1028, 1003, 824, 763, 732, 615; **HRMS** (ESI) found: *m/z* 292.0579 $[M+H]^{+}$; calcd. for $C_{15}H_8F_3NO_2$+H 292.0585.




-62.83
3n
f1 (ppm)


152.46
149.51
145.60
145.26
141.19
132.58
131.94
130.62
129.67
129.57
129.09
125.46
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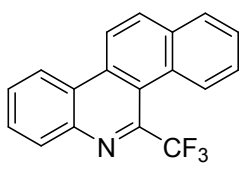
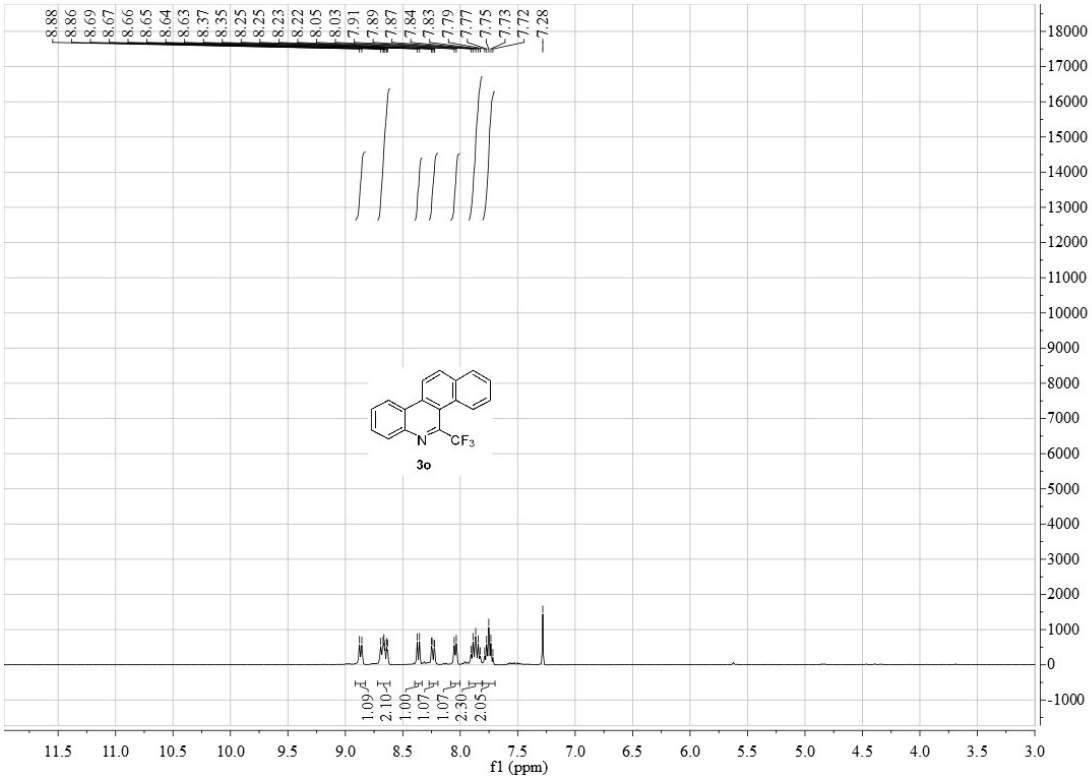
121.02
103.41
101.87
101.83
101.79
101.76
101.60
3n
f1 (ppm)

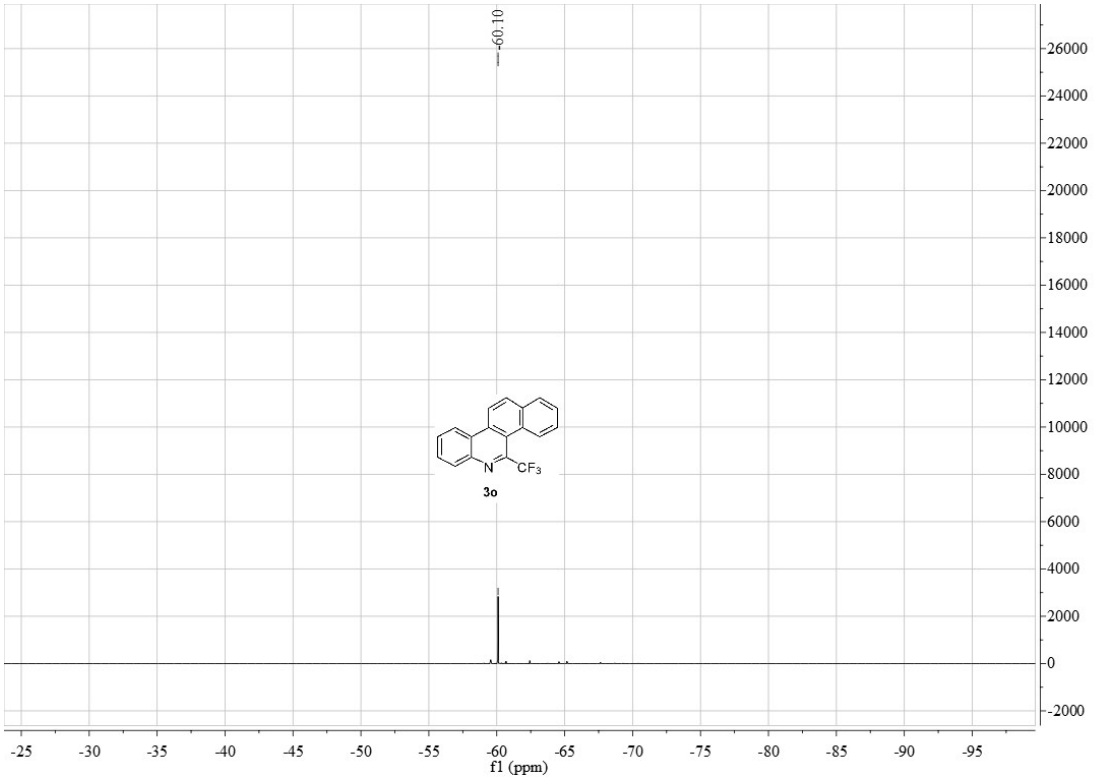


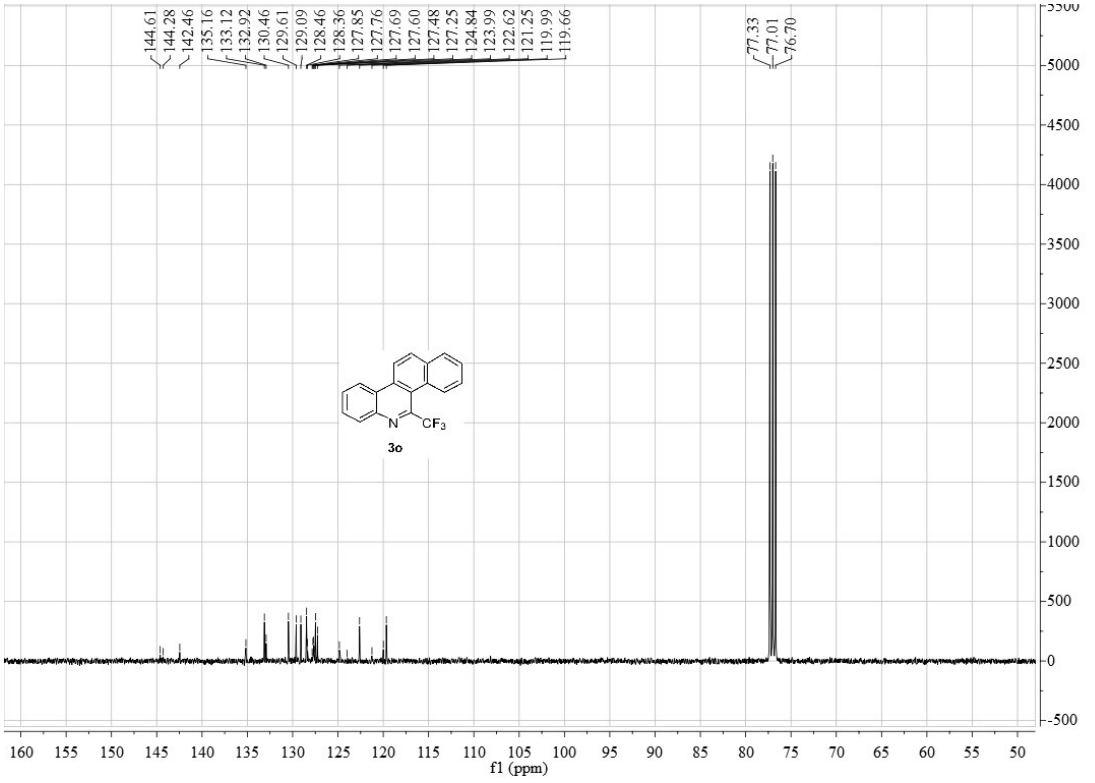
3o

5-(trifluoromethyl)benzo[i]phenanthridine (3o)

^{1}H NMR (400 MHz, $CDCl_3$) [ppm] δ 8.87 (d, J = 8.2 Hz, 1H), 8.72 – 8.61 (m, 2H), 8.36 (d, J = 8.1 Hz, 1H), 8.24 (dd, J = 9.0, 2.0 Hz, 1H), 8.04 (d, J = 7.3 Hz, 1H), 7.93 – 7.81 (m, 2H), 7.75 (p, J = 6.8 Hz, 2H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ -60.10 (s, 3F); **^{13}C NMR** (100 MHz, $CDCl_3$) [ppm] δ 144.4 (q, J = 33.0 Hz), 142.5 (s), 135.2 (s), 133.1 (s), 132.9 (s), 130.5 (s), 129.6 (s), 129.1 (s), 128.5 (s), 128.4 (s), 127.7 (q, J = 8.0 Hz), 127.5 (s), 127.3 (s), 124.8 (s), 122.6 (q, J = 274.0 Hz), 122.6 (s), 120.0 (s), 119.7 (s); **IR** (KBr) ν (cm^{-1}): 3060, 1724, 1615, 1574, 1517, 1465, 1386, 1277, 1180, 1124, 1086, 945, 828, 801, 760; **HRMS** (ESI) found: *m/z* 298.0838 $[M+H]^+$; calcd. for $C_{18}H_{10}F_3N$+H 298.0843.




-60.10
N
CF3
3o
f1 (ppm)


144.61
144.28
142.46
135.16
133.12
132.92
130.46
129.61
129.09
128.46
128.36
127.85
127.76
127.69
127.60
127.48
127.25
124.84
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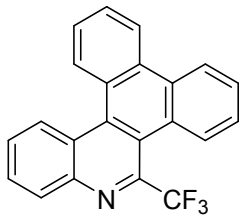
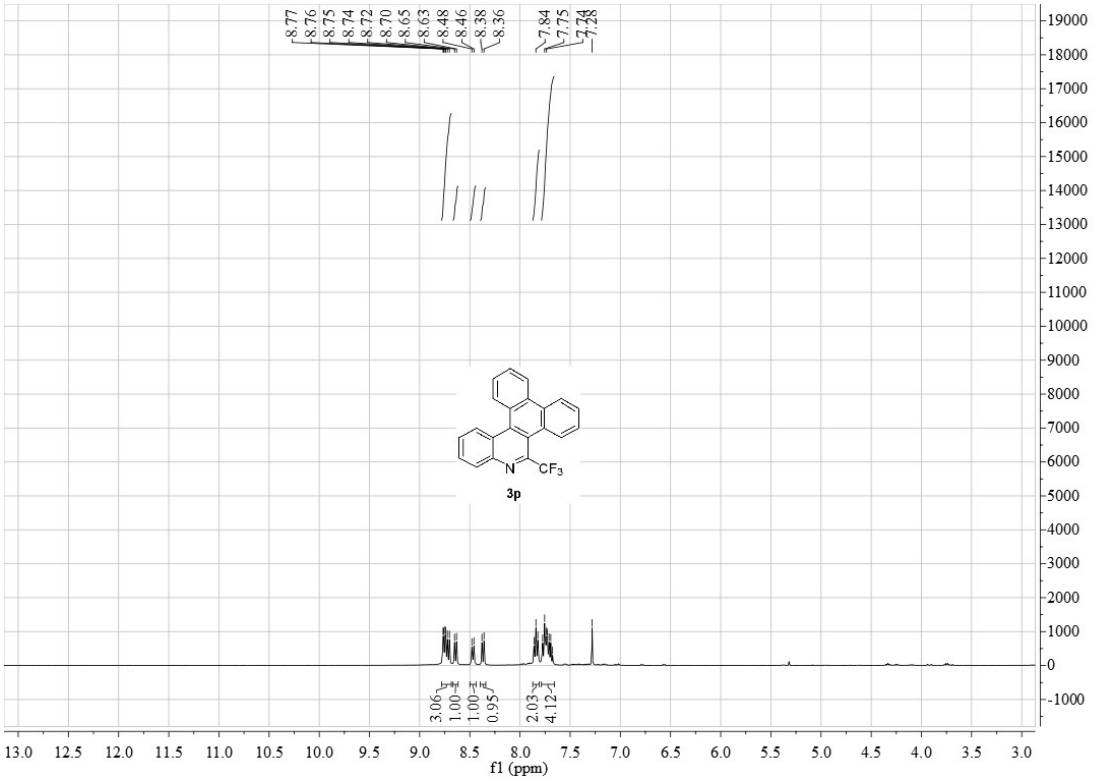
119.99
119.66
77.33
77.01
76.70
N
CF3
3o
f1 (ppm)

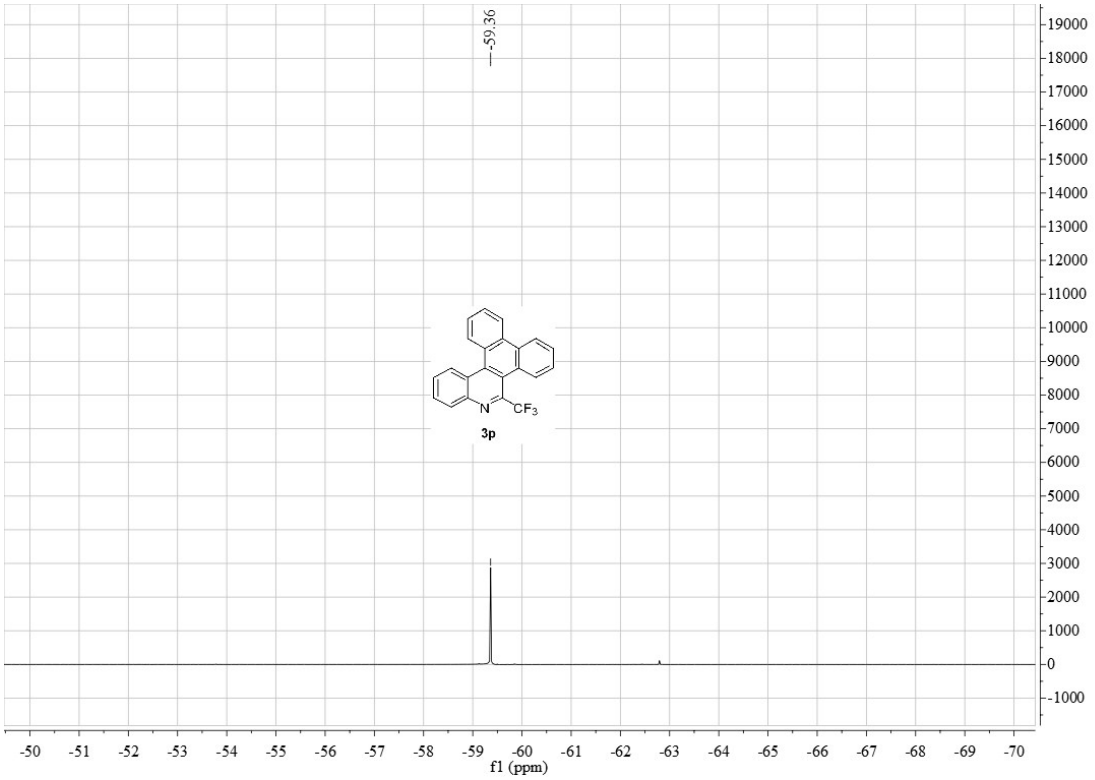


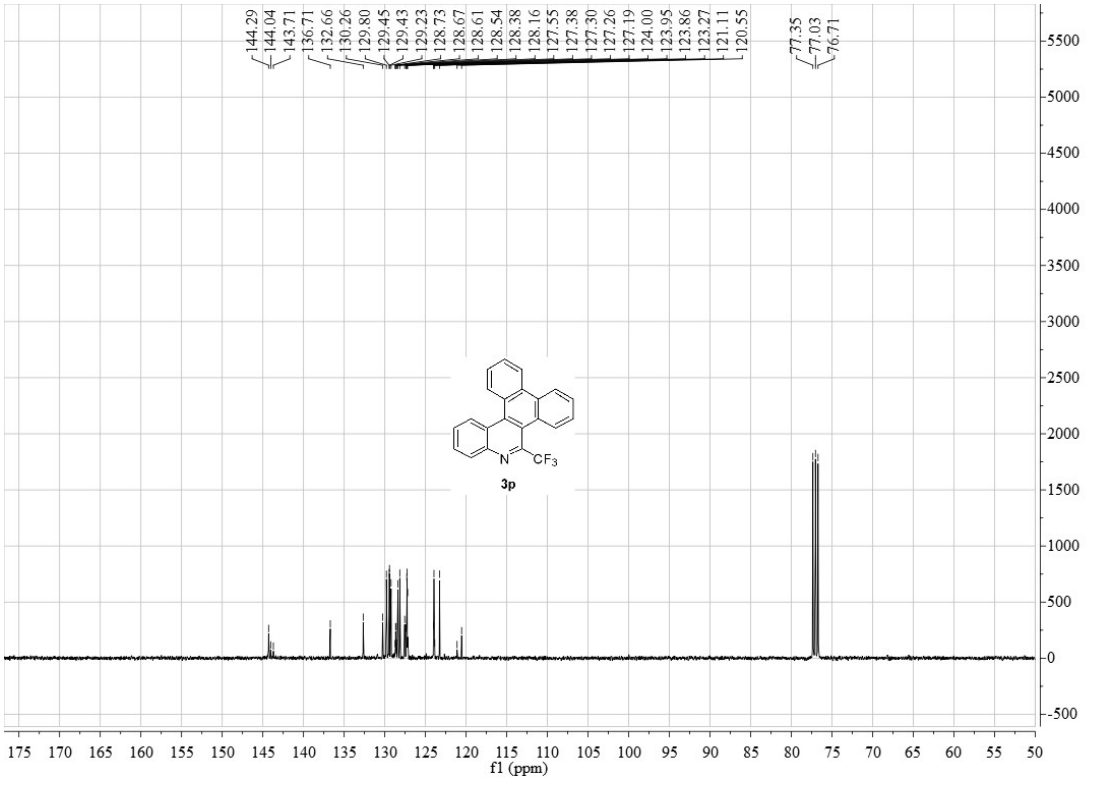
3p

5-(trifluoromethyl)dibenzo[i,k]phenanthridine (3p)

^{1}H NMR (400 MHz, $CDCl_3$) [ppm] δ 8.78 – 8.68 (m, 3H), 8.64 (d, J = 8.0 Hz, 1H), 8.47 (d, J = 8.1 Hz, 1H), 8.37 (d, J = 8.3 Hz, 1H), 7.84 (t, J = 7.6 Hz, 2H), 7.79 – 7.66 (m, 4H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ -59.36 (s, 3F); **^{13}C NMR** (100 MHz, $CDCl_3$) [ppm] δ 144.3 (s), 143.9 (q, J = 33.0 Hz), 136.7 (s), 132.7 (s), 130.3 (s), 129.8 (s), 129.5 (s), 129.4 (s), 129.2 (s), 128.7 (q, J = 6.0 Hz), 128.4 (s), 128.2 (s), 127.6 (s), 127.4 (s), 127.3 (s), 127.3 (s), 127.2 (s), 124.0 (s), 124.0 (s), 123.3 (s), 122.5 (q, J = 275.0 Hz), 120.6 (s); **IR** (KBr) ν (cm^{-1}): 3072, 1726, 1607, 1562, 1490, 1459, 1357, 1286, 1183, 1129, 1080, 763, 729; **HRMS** (ESI) found: *m/z* 348.0995 $[M+H]^+$; calcd. for $C_{22}H_{12}F_3N$+H 348.1000.




-59.36
3p
f1 (ppm)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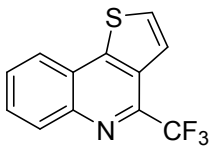
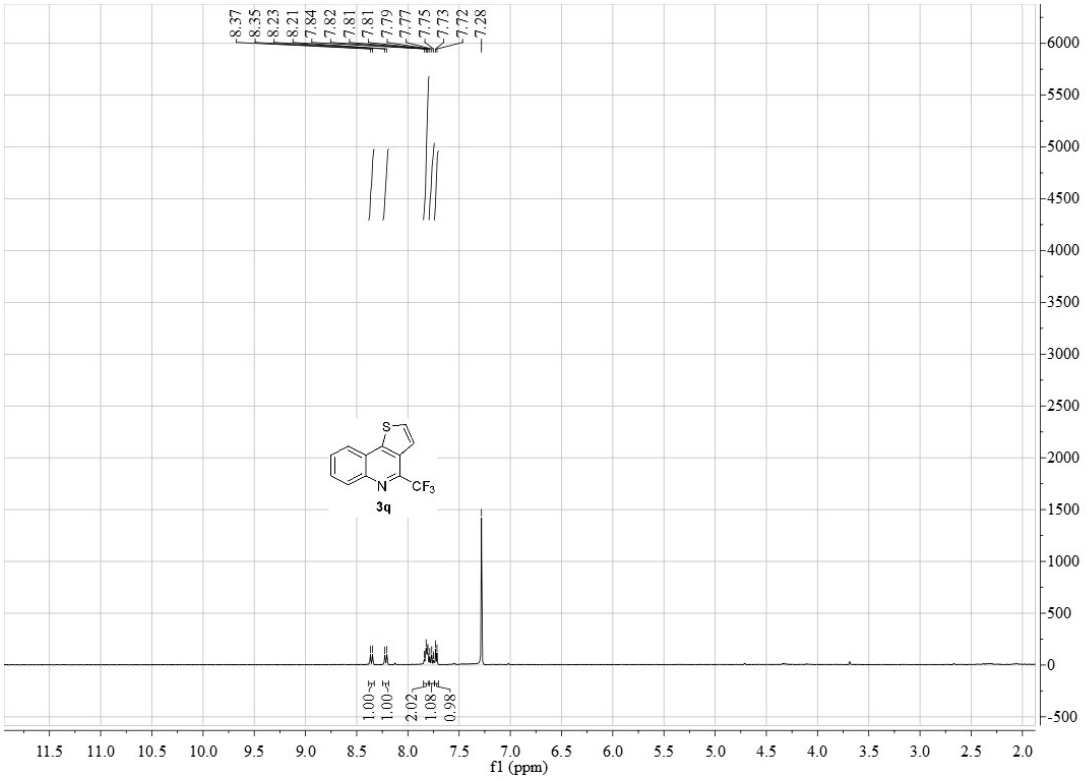
144.04
143.71
136.71
132.66
130.26
129.80
129.45
129.43
129.23
128.73
128.67
128.61
128.54
128.38
128.16
127.55
127.38
127.30
127.26
127.19
124.00
123.95
123.86
123.27
121.11
120.55
77.35
77.03
76.71
3p
f1 (ppm)

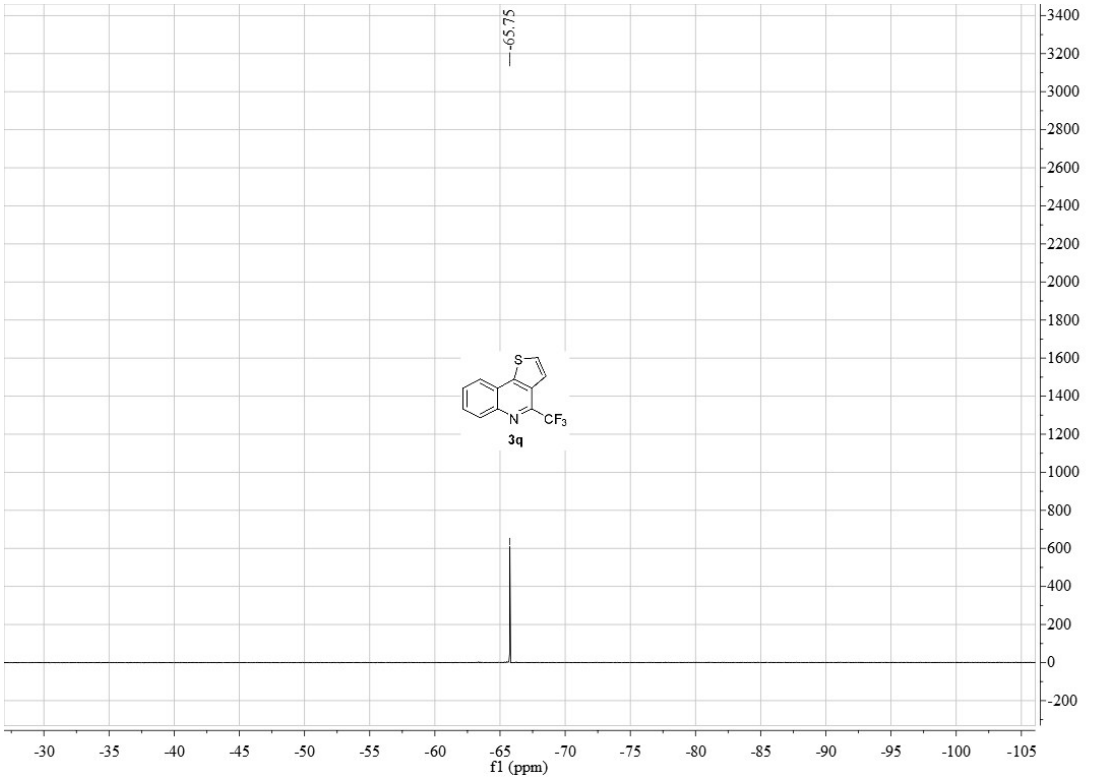

S
N
CF3

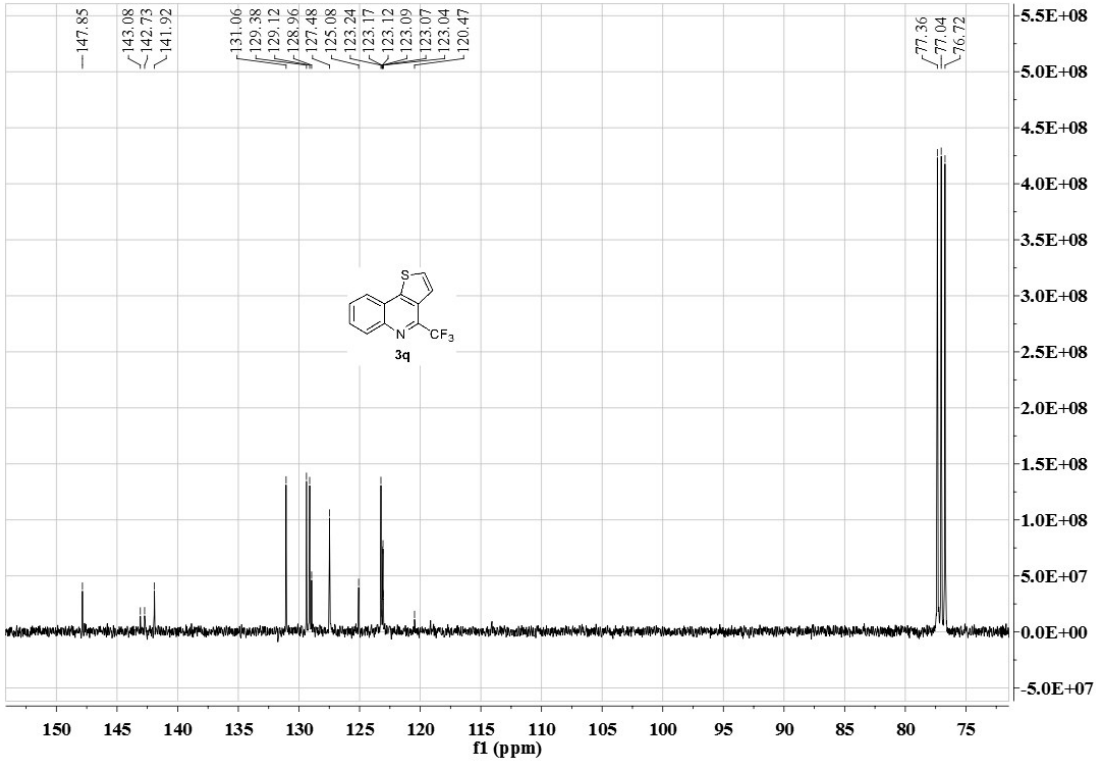
3q

4-(trifluoromethyl)thieno[3,2-c]quinoline (3q)

^{1}H NMR (400 MHz, $CDCl_3$) [ppm] δ 8.36 (d, J = 8.0 Hz, 1H), 8.22 (d, J = 8.1 Hz, 1H), 7.82 (dd, J = 8.9, 5.3 Hz, 2H), 7.77 (t, J = 7.3 Hz, 1H), 7.72 (d, J = 5.5 Hz, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ -65.75 (s, 3F); **^{13}C NMR** (100 MHz, $CDCl_3$) [ppm] δ 147.8 (s), 142.9 (q, J = 35.0 Hz), 141.9 (s), 131.1 (s), 129.4 (s), 129.1 (s), 129.0 (s), 127.5 (s), 125.1 (s), 123.2 (s), 123.1 (q, J = 2.0 Hz), 121.8 (q, J = 273.0 Hz); **IR** (KBr) ν (cm^{-1}): 3758, 3654, 1721, 1556, 1462, 1376, 1337, 1276, 1185, 1129, 1059, 946, 874, 758; **HRMS** (ESI) found: *m/z* 254.0245 $[M+H]^+$; calcd. for $C_{12}H_6F_3NS$+H 254.0251.




-65.75
3q
f1 (ppm)


147.85
143.08
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141.92
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129.38
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128.96
127.48
125.08
123.24
123.17
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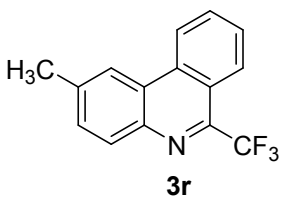
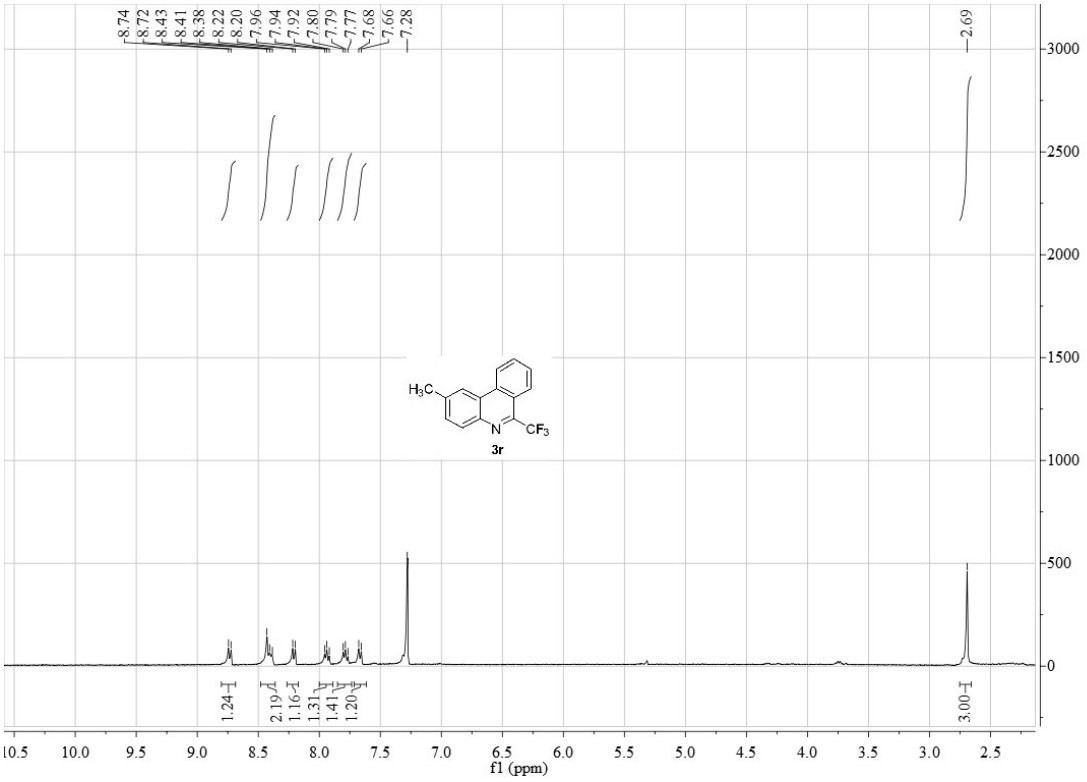
123.07
123.04
120.47
77.36
77.04
76.72
3q
f1 (ppm)

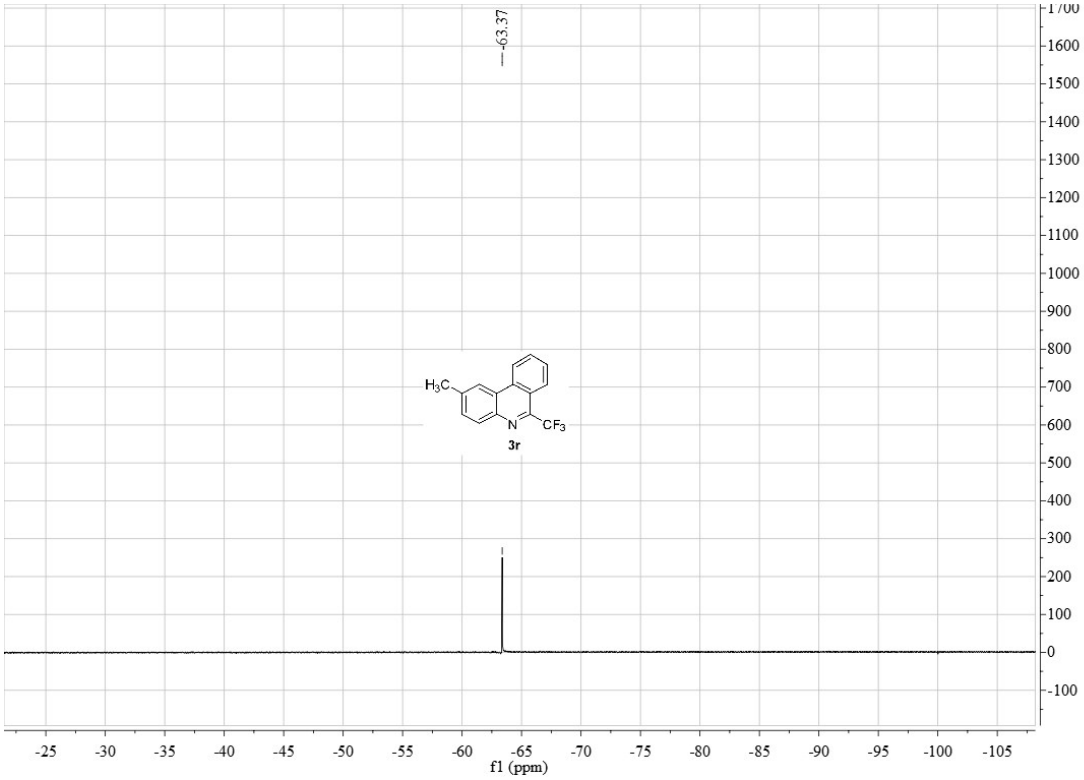


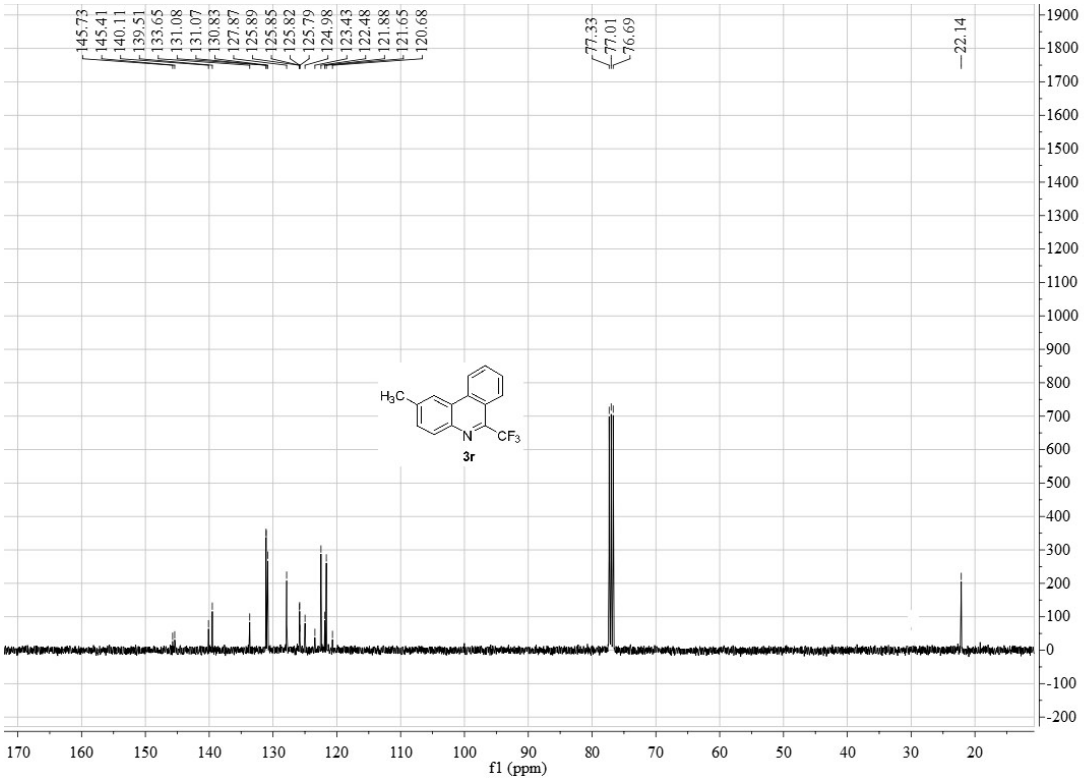
3r

2-methyl-6-(trifluoromethyl)phenanthridine (3r)

^{1}H NMR (400 MHz, $CDCl_3$) [ppm] δ 8.73 (d, J = 8.3 Hz, 1H), 8.48 – 8.36 (m, 2H), 8.21 (d, J = 8.4 Hz, 1H), 8.00 – 7.89 (m, 1H), 7.85 – 7.73 (m, 1H), 7.67 (d, J = 8.2 Hz, 1H), 2.69 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ -63.37 (s, 3F); **^{13}C NMR** (100 MHz, $CDCl_3$) [ppm] δ 145.6 (q, J = 32.0 Hz), 140.1 (s), 139.5 (s), 133.6 (s), 131.1 (s), 131.1 (s), 130.8 (s), 127.9 (s), 125.8 (q, J = 4.0 Hz), 125.0 (s), 122.5 (s), 122.0 (q, J = 275.0 Hz), 121.9 (s), 121.6 (s), 22.1 (s); **IR** (KBr) ν (cm^{-1}): 3074, 2923, 2854, 1752, 1617, 1575, 1451, 1382, 1303, 1255, 1170, 1123, 972, 824, 770, 724, 682; **HRMS** (ESI) found: *m/z* 262.0838 $[M+H]^+$; calcd. for $C_{15}H_{10}F_3N$+H 262.0843.




-63.37
H3C
N
CF3
3r
f1 (ppm)


145.73
145.41
140.11
139.51
133.65
131.08
131.07
130.83
127.87
125.89
125.85
125.82
125.79
124.98
123.43
122.48
121.88
121.65
120.68
77.33
77.01
76.69
22.14
H3C
N
CF3
3r
f1 (ppm)