Electronic Supplementary Information

Trifunctionalization of C=C Bonds in Vinyl Azides to Access Densely Functionalized Phenanthridines Enabled by the NCS/$AgNO_2$ System

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1. General Information

Unless otherwise noted, all reactions were carried out in flame-dried reaction vessels with Teflon screw caps under nitrogen. Solvents were purified and dried according to standard methods prior to use. Unless otherwise stated, all reagents were purchased from commercial suppliers and used as received. Flash column chromatography was performed on silica gel (100-200 mesh) with the indicated eluent solvents. TLC analysis was performed on pre-coated, glass-backed silica gel plates and visualized with UV light.

Melting points are uncorrected. ^{1}H NMR spectra were recorded on a spectrometer at 25 ^{o}C in $CDCl_3$ at 500 MHz, with TMS as internal standard. ^{13}C NMR spectra were recorded on a spectrometer at 25 ^{o}C in $CDCl_3$ at 125 MHz. ^{19}F NMR spectra were recorded on a Bruker AVANCE III 500 at 25 °C in $CDCl_3$ at 470 MHz, with CF_3COOH as external standard. Chemical shifts (δ) are expressed in ppm and coupling constants *J* are given in Hz. Chemical shifts (δ) are expressed in ppm and coupling constants *J* are given in Hz. The following abbreviations were used to identify the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, br = broad and all combinations thereof can be explained by their integral parts. High resolution mass spectra (HRMS) were obtained on a Bruker micro TOF-Q II instrument with APCI source or Agilent 6200 series TOF/6500 series Q-TOF instrument with ESI source or Waters GCT Premier TOF MS with EI source.

2. Synthesis of the Starting Materials

The starting materials 2-(1-azidovinyl)-1,1'-biphenyls were prepared according previous work.[1,2]

3. Typical Procedure for the Synthesis of Target products 2

A mixture of vinyl azide **1** (0.3 mmol), NCS (89.4 mg, 0.66 mmol), $AgNO_2$ (101.6 mg, 0.66 mmol) and CH_3CN (3.0 mL) was sealed in a 10 mL round flask. Then the flask was stirred at 25 ℃ for 5 h. Upon completion of the reaction, the solution was evaporated in vacuo and the residue was purified by flash column chromatography on silica gel with petroleum ether/EtOAc as eluent to give pure product **2**.

3.1 Procedure for 1 mmol-Scale Synthesis of 2a

1a

(0.22 g, 1 mmol)

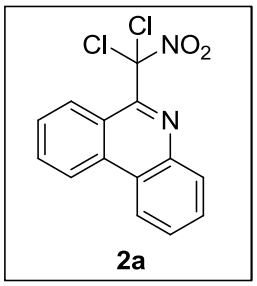
2a

(0.21 g, 68%)

A mixture of vinyl azide **1a** (0.22 g, 1.0 mmol), NCS (0.30 g, 2.2 mmol), $AgNO_2$ (0.34 g, 2.2 mmol) and CH_3CN (8.0 mL) was sealed in a 20 mL round flask. Then the flask was stirred at 25 ℃ for 10 h. Upon completion of the reaction, the solution was evaporated in vacuo and the residue was purified by flash column chromatography on silica gel with petroleum ether/EtOAc as eluent to give pure product **2a** (0.21 g, 68%).

4. Characterization Data

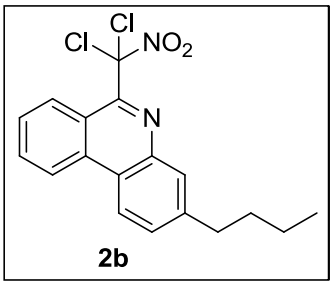
6-(dichloro(nitro)methyl)phenanthridine(2a)



2a

Purified by column chromatography (petroleum ether/EtOAC = 5/1 (V/V)) as a yellow solid (69.1 mg, 75%), m.p. 121–122 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.74 (d, *J* =8.5 Hz, 1H), 8.61–8.57 (m, 2H), 8.19–8.15 (m, 1H), 7.95–7.92 (m, 1H), 7.81–7.77 (m, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 149.9, 140.8, 134.7, 131.3, 131.3, 129.50, 129.49, 127.6, 126.2, 125.0, 123.17, 121.9, 120.8, 113.9; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_9Cl_2N_2O_2^+$ 307.0036; Found 307.0043.

3-butyl-6-(dichloro(nitro)methyl)phenanthridine (2b)

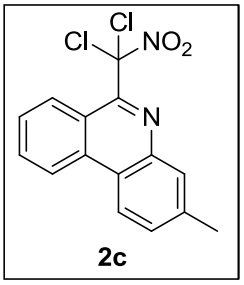


2b

Purified by column chromatography (petroleum ether/EtOAC = 5/1 (V/V)) as a yellow solid (69.7 mg, 64%), m.p. 69–70 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.69 (d, *J* = 8.5 Hz, 1H), 8.58 (d, *J* = 8.5 Hz, 1H), 8.48 (d, *J* = 8.5 Hz, 1H), 7.97 (d, *J* = 1.5 Hz, 1H), 7.92–7.88 (m, 1H), 7.75–7.72 (m, 1H), 7.62 (dd, J_1 =8.5

Hz, J_2= 1.5 Hz, 1H), 2.85 (t, J = 8.0 Hz, 2H), 1.77–1.71 (m, 2H), 1.46–1.38 (m, 2H), 0.98 (t, J = 8.0 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 149.8, 144.9, 141.0, 134.7, 131.1, 130.7, 130.1, 127.1, 126.2, 123.0, 122.9, 121.7, 120.5, 114.0, 35.4, 33.3, 22.4, 13.9; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{17}Cl_2N_2O_2^+$ 363.0662; Found 363.0657.

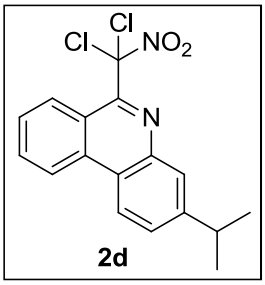
6-(dichloro(nitro)methyl)-3-methylphenanthridine (2c)



2c

Purified by column chromatography (petroleum ether/EtOAC = 5/1 (V/V)) as a yellow solid (63.5 mg, 66%), m.p. 136–137 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.66 (d, J = 8.5 Hz, 1H), 8.58 (d, J = 8.5 Hz, 1H), 8.44 (d, J = 8.5 Hz, 1H), 7.95 (s, 1H), 7.91–7.87 (m, 1H), 7.75 – 7.71 (m, 1H), 7.59 (dd, J_1 =8.5Hz , J_2= 1.5 Hz, 1H), 2.58 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 149.8, 140.9, 139.9, 134.7, 131.3, 131.1, 130.7, 127.0, 126.2, 123.0, 122.7, 121.7, 120.4, 114.0, 21.4; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{11}Cl_2N_2O_2^+$ 321.0192; Found 321.0188.

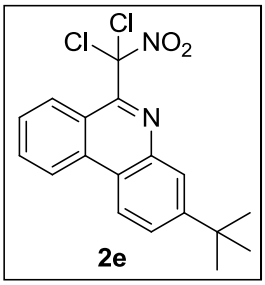
6-(dichloro(nitro)methyl)-3-isopropylphenanthridine (2d)



2d

Purified by column chromatography (petroleum ether/EtOAC = 5/1 (V/V)) as a yellow solid (74.5 mg, 71%), m.p. 107–108 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.70 (d, J = 8.5 Hz, 1H), 8.58 (d, J = 8.5 Hz, 1H), 8.51 (d, J = 8.5 Hz, 1H), 8.01 (d, J = 1.5 Hz, 1H), 7.92–7.89 (m, 1H), 7.76–7.72 (m, 1H), 7.69 (dd, J_1 =8.5 Hz, J_2= 2.0 Hz, 1H), 3.21–3.13 (m, 1H), 1.39 (t, J = 6.5 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 150.8, 149.8, 141.1, 134.7, 131.2, 129.1, 128.1, 127.1, 126.2, 123.1, 123.0, 121.9, 120.5, 114.0, 34.1, 23.8; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{15}Cl_2N_2O_2^+$ 349.0505; Found 349.0512.

3-tert-butyl-6-(dichloro(nitro)methyl)phenanthridine (2e)

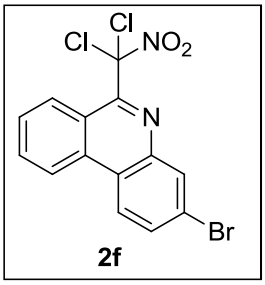


2e

Purified by column chromatography (petroleum ether/EtOAC =

5/1 (V/V)) as a yellow solid (65.3 mg, 60%), m.p. 145–146 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.71 (d, *J* = 8.5 Hz, 1H), 8.58 (d, *J* = 8.5 Hz, 1H), 8.53 (d, *J* = 9.0 Hz, 1H), 8.14 (d, *J* = 2.5 Hz, 1H), 7.93–7.87 (m, 2H), 7.76–7.73 (m, 1H), 1.47 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 153.2, 149.8, 140.9, 134.6, 131.1, 127.9, 127.14, 127.12, 126.2, 123.0, 122.7, 121.7, 120.6, 114.0, 35.1, 31.2; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{17}Cl_2N_2O_2^+$ 363.0662; Found 363.0668.

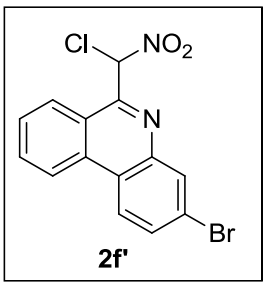
3-bromo-6-(dichloro(nitro)methyl)phenanthridine (2f)



2f

Purified by column chromatography (petroleum ether/EtOAC = 5/1 (V/V)) as a yellow solid (59.0 mg, 51%), m.p. 167–169 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.64 (d, *J* = 8.5 Hz, 1H), 8.57 (d, *J* = 8.5 Hz, 1H), 8.49 (d, *J* = 8.5 Hz, 1H), 8.32 (d, *J* = 2.0 Hz, 1H), 7.94–7.90 (m, 1H), 7.83 (dd, J_1 =9.0 Hz, J_2=2.0 Hz, 1H), 7.79–7.76 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 151.0, 141.6, 134.3, 133.6, 132.7, 131.7, 127.9, 126.4, 123.8, 123.4, 123.3, 123.1, 120.8, 113.6; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_8BrCl_2N_2O_2^+$ 384.9141; Found 384.9148.

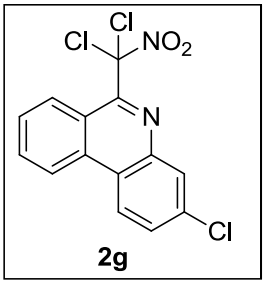
3-bromo-6-(chloro(nitro)methyl)phenanthridine (2f')



2f'

Purified by column chromatography (petroleum ether/EtOAC = 5/1 (V/V)) as a yellow solid (33.7 mg, 32%); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.86 (d, *J* = 8.5 Hz, 1H), 8.66 (d, *J* = 8.5 Hz, 1H), 8.44 (d, *J* = 9.0 Hz, 1H), 8.35 (d, *J* = 2.0 Hz, 1H), 7.84–7.82 (m, 3H), 7.28 (s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 155.8, 143.0, 134.0, 133.0, 131.6, 131.5, 127.6, 127.2, 123.8, 123.5, 122.9, 122.7, 121.8, 72.1; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_9BrClN_2O_2^+$ 350.9530; Found 350.9536.

3-chloro-6-(dichloro(nitro)methyl)phenanthridine (2g)

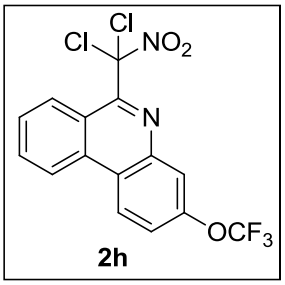


2g

Purified by column chromatography (petroleum ether/EtOAC =

5/1 (V/V)) as a yellow solid (48.2 mg, 47%), m.p. 132–133 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.63 (d, *J* = 8.5 Hz, 1H), 8.59 (d, *J* = 8.5 Hz, 1H), 8.46 (d, *J* = 9.0 Hz, 1H), 8.14 (d, *J* = 2.0 Hz, 1H), 7.95–7.92 (m, 1H), 7.80–7.77 (m, 1H), 7.70 (dd, J_1 =9.0 Hz, J_2= 2.5 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 151.1, 141.3, 135.3, 134.2, 131.7, 130.3, 130.0, 127.9, 126.4, 123.4, 123.3, 123.1, 120.7, 113.6; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_8Cl_3N_2O_2^+$ 340.9646; Found 340.9641.

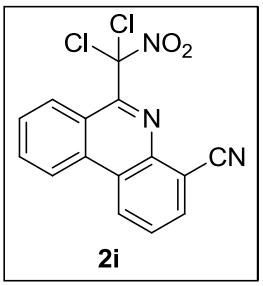
6-(dichloro(nitro)methyl)-3-(trifluoromethoxy)phenanthridine (2h)



2h

Purified by column chromatography (petroleum ether/EtOAC = 5/1 (V/V)) as a yellow solid (76.2 mg, 65%), m.p. 129–130 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.71 (d, *J* = 8.0 Hz, 1H), 8.64–8.60 (m, 2H), 8.46 (d, *J* = 9.0 Hz, 1H), 8.04–8.03 (m, 1H), 7.99–7.97 (m, 1H), 7.84–7.81 (m, 1H), 7.67–7.64 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 151.4, 149.64, 149.63, 141.5, 134.2, 131.8, 128.0, 126.4, 123.9, 123.5, 123.2, 122.8, 121.6, 120.5 (q, *J* = 256.3 Hz), 113.5; **^{19}F NMR** (470 MHz, $CDCl_3$): δ -57.72; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_8Cl_2F_3N_2O_3^+$ 390.9859; Found 390.9852.

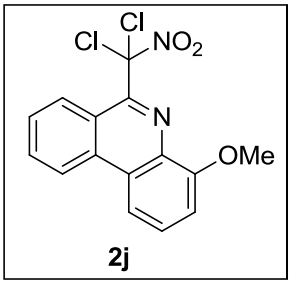
6-(dichloro(nitro)methyl)phenanthridine-4-carbonitrile (2i)



2i

Purified by column chromatography (petroleum ether/EtOAC = 5/1 (V/V)) as a yellow solid (67.6 mg, 70%), m.p. 198–200 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.94 (d, *J* = 1.5 Hz, 1H), 8.73 (d, *J* = 8.5 Hz, 1H), 8.66 (d, *J* = 8.0 Hz, 1H), 8.27 (d, *J* = 8.5 Hz, 1H), 8.07–8.04 (m, 1H), 7.98 (dd, J_1 = 8.5 Hz, J_2= 1.5 Hz, 1H), 7.92–7.88 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 152.8, 142.4, 133.7, 132.5, 134.0, 128.9, 127.7, 126.7, 125.2, 123.2, 121.2, 118.4, 113.3, 113.0; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_8Cl_2N_3O_2^+$ 331.9988; Found 331.9983.

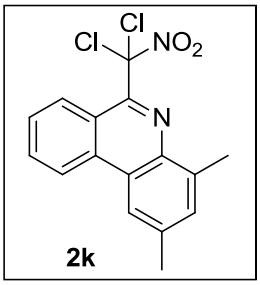
6-(dichloro(nitro)methyl)-4-methoxyphenanthridine (2j)



2j

Purified by column chromatography (petroleum ether/EtOAC = 5/1 (V/V)) as a yellow solid (63.7 mg, 63%), m.p. 126–128 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.66 (d, *J* = 8.5 Hz, 1H), 8.58 (d, *J* = 8.5 Hz, 1H), 8.09 (d, *J* = 9.0 Hz, 1H), 7.93–7.90 (m, 2H), 7.80–7.76 (m, 1H), 7.42 (dd, J_1 = 9.0 Hz, J_2= 2.0 Hz, 1H), 4.06 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 160.5, 147.3, 136.1, 134.0, 132.9, 130.7, 127.6, 126.5, 126.2, 123.2, 121.0, 119.5, 114.2, 102.8, 55.8; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{11}Cl_2N_2O_3^+$ 337.0141; Found 337.0145.

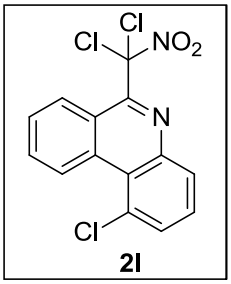
6-(dichloro(nitro)methyl)-2,4-dimethylphenanthridine (2k)



2k

Purified by column chromatography (petroleum ether/EtOAC = 5/1 (V/V)) as a yellow solid (83.4 mg, 83%), m.p. 161–162 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.68 (d, *J* = 8.5 Hz, 1H), 8.63 (d, *J* = 8.5 Hz, 1H), 8.17 (s, 1H), 7.89–7.86 (m, 1H), 7.76–7.73 (m, 1H), 7.45 (s, 1H), 2.71 (s, 3H), 2.58 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 147.6, 139.5, 139.1, 137.7, 134.6, 131.9, 130.74, 127.2, 126.1, 124.9, 123.3, 120.5, 119.3, 114.3, 22.2, 17.6; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{13}Cl_2N_2O_2^+$ 335.0349; Found 335.0356.

1-chloro-6-(dichloro(nitro)methyl)phenanthridine (2l)

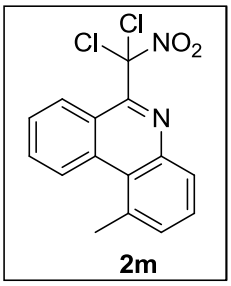


2l

Purified by column chromatography (petroleum ether/EtOAC = 5/1 (V/V)) as a yellow solid (58.4 mg, 57%), m.p. 120–121 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 10.03 (d, *J* = 9.0 Hz, 1H), 8.65 (dd, J_1 = 8.5 Hz, J_2= 1.0 Hz, 1H), 8.14–8.13 (dd, J_1 = 8.5 Hz, J_2= 1.5 Hz, 1H), 7.98–7.95 (m, 1H), 7.89–7.83 (m, 2H), 7.70–7.67 (t, *J* = 8.0 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 150.6, 142.0, 134.0, 133.4, 131.2, 130.8, 130.5, 128.7, 127.8, 127.3, 126.0, 122.7, 121.5, 113.7; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_8Cl_3N_2O_2^+$

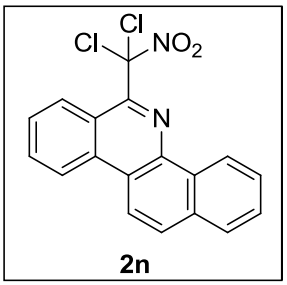
340.9646; Found 340.9642.

6-(dichloro(nitro)methyl)-1-methylphenanthridine (2m)



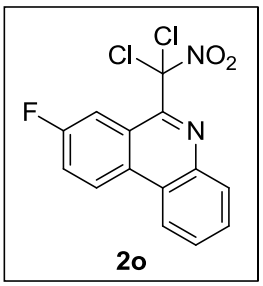
Purified by column chromatography (petroleum ether/EtOAC = 5/1 (V/V)) as a yellow solid (62.6 mg, 65%), m.p. 152–153 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.99 (d, J = 8.5 Hz, 1H), 8.65 (dd, J_1 = 8.5 Hz, J_2= 0.5 Hz, 1H), 8.07 (dd, J_1 = 8.5 Hz, J_2= 1.0 Hz, 1H), 7.94–7.90 (m, 1H), 7.80–7.77 (m, 1H), 7.69–7.62 (m, 2H), 3.13 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 149.5, 142.3, 135.9, 134.9, 133.8, 130.3, 130.3, 128.6, 127.5, 126.7, 126.1, 124.8, 121.6, 114.0, 26.6; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{11}Cl_2N_2O_2^+$ 321.0192; Found 321.0185.

6-(dichloro(nitro)methyl)benzo[c]phenanthridine (2n)



Purified by column chromatography (petroleum ether/EtOAC = 5/1 (V/V)) as a yellow solid (85.7 mg, 80%), m.p. 168–169 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$): 9.15 (d, J = 8.5 Hz, 1H), 8.82 (d, J = 8.5 Hz, 1H), 8.73 (d, J = 8.5 Hz, 1H), 8.55 (d, J = 9.0 Hz, 1H), 8.15 (d, J = 8.5 Hz, 1H), 8.00–7.97 (m, 2H), 7.85–7.78 (m, 2H), 7.75–7.71 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 148.6, 137.9, 134.9, 133.4, 131.8, 131.1, 130.6, 128.16, 128.0, 127.7, 127.5, 126.1, 124.9, 123.6, 122.9, 121.4, 119.2, 114.2; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{11}Cl_2N_2O_2^+$ 357.0192; Found 357.0187.

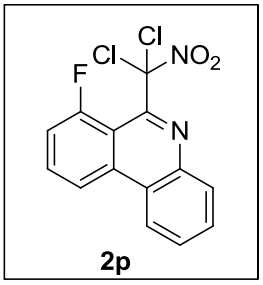
6-(dichloro(nitro)methyl)-8-fluorophenanthridine (2o)



Purified by column chromatography (petroleum ether/EtOAC = 5/1 (V/V)) as a yellow solid (70.2 mg, 72%), m.p. 181–182 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.74 (dd, J_1 = 9.5 Hz, J_2= 5.0 Hz, 1H), 8.54–8.52 (m, 1H), 8.28 (dd, J_1 = 8.5 Hz, J_2= 2.0 Hz, 1H), 8.17–8.15 (m, 1H), 7.82–7.77 (m, 2H), 7.72–7.68 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$):

δ 160.8 (d, *J* = 248.8 Hz), 149.1 (d, *J* = 3.0 Hz), 140.5, 131.5, 131.4 (d, *J* = 2.5 Hz), 130.0, 129.4, 125.8 (d, *J* = 8.8 Hz), 124.6, 122.9 (d, *J* = 8.8 Hz), 121.7, 120.8 (d, *J* = 23.8 Hz), 113.6, 111.4 (d, *J* = 23.8Hz); **^{19}F NMR** (470 MHz, $CDCl_3$): δ -109.15; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_8Cl_2FN_2O_2^+$ 324.9941; Found 324.9946.

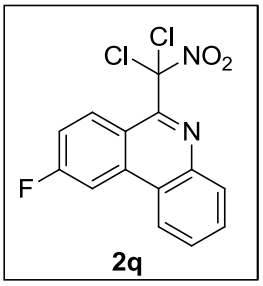
6-(dichloro(nitro)methyl)-7-fluorophenanthridine (2p)



2p

Purified by column chromatography (petroleum ether/EtOAC = 5/1 (V/V)) as a yellow solid (58.5 mg, 60%), m.p. 128–130 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.57–8.54 (m, 2H), 8.29–8.28 (m, 1H), 7.90–7.80 (m, 3H), 7.44–7.40 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 157.6 (d, *J* = 252.5 Hz), 146.4 (d, *J* = 3.8 Hz), 141.2, 136.7 (d, *J* = 2.5 Hz), 132.1 (d, *J* = 10.0 Hz), 131.3, 130.1, 123.9 (d, *J* = 2.5 Hz), 122.4, 119.3 (d, *J* = 3.8 Hz), 114.9, 114.7, 113.8, 111.6 (d, *J* = 13.8 Hz); **^{19}F NMR** (470 MHz, $CDCl_3$): δ -99.15; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_8Cl_2FN_2O_2^+$ 324.9941; Found 324.9943.

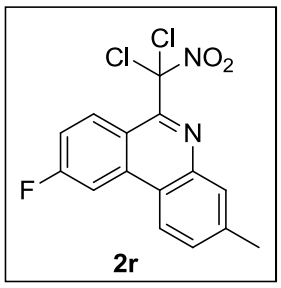
6-(dichloro(nitro)methyl)-9-fluorophenanthridine (2q)



2q

Purified by column chromatography (petroleum ether/EtOAC = 5/1 (V/V)) as a yellow solid (61.4 mg, 63%), m.p. 170–171 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.67 (dd, J_1 = 9.0 Hz, J_2= 5.0 Hz, 1H), 8.48–8.47 (m, 1H), 8.48 (dd, J_1 = 10.0 Hz, J_2= 2.5 Hz, 1H), 8.18–8.16 (m, 1H), 7.85–7.79 (m, 2H), 7.55–7.51 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 163.9 (d, *J* = 252.5 Hz), 149.6, 141.0, 137.5, 131.4, 130.2, 129.6, 129.4 (d, *J* = 8.8 Hz), 124.6 (d, *J* = 2.5 Hz), 122.1, 117.7, 116.9 (d, *J* = 23.8 Hz), 113.7, 108.4 (d, *J* = 22.5 Hz); **^{19}F NMR** (470 MHz, $CDCl_3$): δ -104.50; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_8Cl_2FN_2O_2^+$ 324.9941; Found 324.9938.

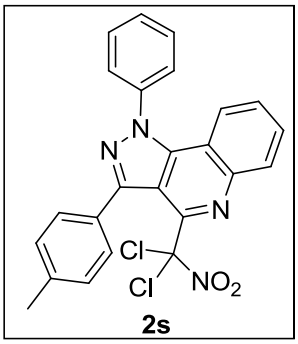
6-(dichloro(nitro)methyl)-9-fluoro-3-methylphenanthridine (2r)



2r

Purified by column chromatography (petroleum ether/EtOAC = 5/1 (V/V)) as a yellow solid (80.3 mg, 79%), m.p. 151–152 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.66 (d, J_1 = 9.0 Hz, J_2= 5.0 Hz, 1H), 8.37 (d, J = 8.5 Hz, 1H), 8.25 (d, J_1 = 7.5Hz, J_2= 2.5 Hz, 1H), 7.93 (s, 1H), 7.67–7.59 (m, 2H), 2.57 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 160.5 (d, J = 247.5 Hz), 149.0 (d, J = 4.3 Hz), 140.6, 139.9, 131.7, 131.5 (d, J = 2.5 Hz), 130.8, 125.6 (d, J = 8.8 Hz), 122.3, 121.6 (d, J = 8.8 Hz), 121.4, 120.7 (d, J = 23.8 Hz), 113.7, 111.2 (d, J = 23.8 Hz), 21.3; **^{19}F NMR** (470 MHz, $CDCl_3$): δ -109.95; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{10}Cl_2FN_2O_2^+$ 339.0098; Found 339.0095.

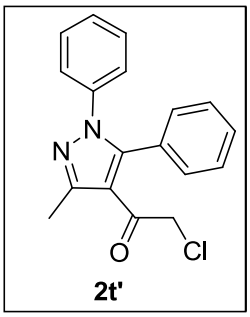
4-(dichloro(nitro)methyl)-1-phenyl-3-p-tolyl-1H-pyrazolo[4,3-c]quinoline (2s)



2s

Purified by column chromatography (petroleum ether/EtOAC = 5/1 (V/V)) as a yellow solid (76.4 mg, 55%). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.08–8.06 (m, 2H), 7.49–7.47 (m, 2H), 7.41–7.39 (m, 3H), 7.36–7.34 (m, 2H), 7.29–7.27 (m, 2H), 7.23–7.22 (m, 2H), 2.34 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 152.1, 149.7, 140.6, 138.7, 135.5, 129.7, 129.2, 129.1, 129.1, 128.7, 128.1, 125.3, 123.8, 115.1, 91.1, 21.4; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{17}Cl_2N_4O_2^+$ 463.0723; Found 463.0729.

2-chloro-1-(3-methyl-1,5-diphenyl-1H-pyrazol-4-yl)ethanone (2t')



2t'

Purified by column chromatography (petroleum ether/EtOAC = 5/1 (V/V)) as a yellow solid (62.4 mg, 67%). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.50 – 7.41 (m, 3H), 7.31 – 7.26 (m, 5H), 7.20 – 7.17 (m, 2H), 3.93 (s, 2H), 2.61 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 187.2, 152.2, 145.4, 138.8, 130.2, 130.1, 129.7, 129.1, 128.9, 128.1, 125.3, 118.8, 48.4, 14.5; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{16}ClN_2O^+$ 311.0946; Found 311.0940.

5. References

1. Y.-F. Wang, G. H. Lonca, M. L. Runigo and S. Chiba, *Org. Lett.*, 2014, **16**, 4272;
2. B. Zhou, L. Zheng, Z. Xu, H. Jin, Q. Wu, T. Li and Y. Liu, *ChemistrySelect*, 2018, **3**, 7354.

6. X-Ray Diffraction Analysis

The single crystals of compound **2m** were grown by slow diffusion of its hexane solution. Single-crystal X-ray diffraction data for analysis were collected at 293 K on a RAXIS-RAPID/ZJUG diffractometer with a MOKα radiation (λ = 0.71073 Å) by using an ω-2θ scan mode. Unit-cell dimensions were obtained with least-squares refinement. Data collection and reduction were performed using the SMART and SAINT software.[3] All structures were solved by direct methods and refined against F^2 by the full-matrix least squares techniques.[4] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in their calculated positions. CCDC 2348610 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +(44) 1223 336033; or deposit@ccdc.cam.ac.uk. Details of the X-ray experiments and crystal data are summarized in Table *S1*.

3. SMART-CCD Software, version 4.05; Siemens Analytical X-ray Instruments, Madison, WI, 1996.
4. G. K. Sheldrick, SHELXS-97 and SHELXL-97, Program for X-ray Crystal Structure Refinement; University of Göttingen: Göttingen, Germany 1997.

Table *S1*. Summary of X-ray Crystallographic Data for Compound **2m** (CCDC 2348610)

Crystal data	
$C_{15}H_{10}Cl_2N_2O_2$	F_{000} = 656
M_r = 321.15	D_x = 1.546 Mg m^{-3}
Orthohombic, Pnma	Mo Kα radiation
Hall symbol: -P 2ac 2n	Cell parameters from 3934 reflections
a = 11.0880(7) Å	λ= 0.71073 Å
b = 6.8830(4) Å	θ = 3.2-27.4 °
c = 18.0810(9) Å	μ = 0.301 mm^{-1}

α = 90.00 °

β = 90.00 °

γ = 90.00 °

V = 1379.92(14) Å^3

T = 296 (2) K

Chunk, colourless

0.48 x 0.28 x 0.20 mmm

Z = 4

Data collection

RAXIS-RAPID/ZJUG diffractometer
Detector resolution: 10.00 pixels mm-1
ω scans
Absorption correction: multi-scan
(ABSCOR; Higashi, 1995)
T_{min} = 0.7861, T_{max} = 0.9110
12881 measured reflections

1081 reflections with $I > 2\sigma(I)$
R_{int} = 0.0274
θ_{max} = 27.45 °
h = -14→14
k = -8→8
l = -23→22
1701 independent reflections

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)]$ = 0.0535

$wR(F^2)$ = 0.1242

S = 1.001

122 parameters

1701 reflections

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2)+(0.0661P)^2+1.2724P]$, $P=(F_o^2+2F_c^2)/3$

$(\triangle/\sigma)_{max} < 0.000$

$\Delta\ \rho_{max}$ = 0.390 e Å^{-3}

$\Delta\ \rho_{min}$ = -0.271 e Å^{-3}

Extinction correction: Larson (1970)

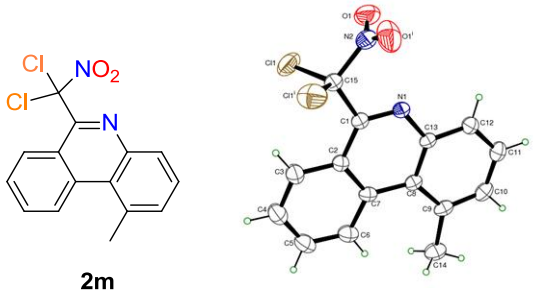
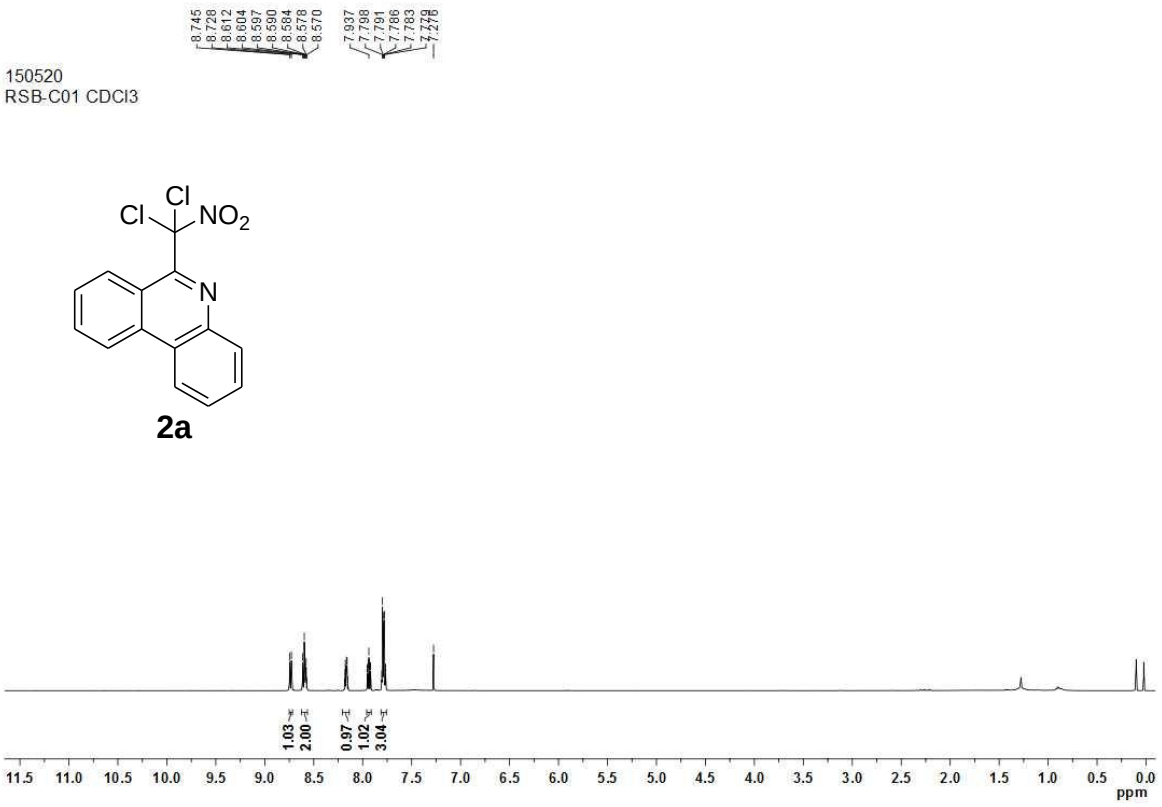
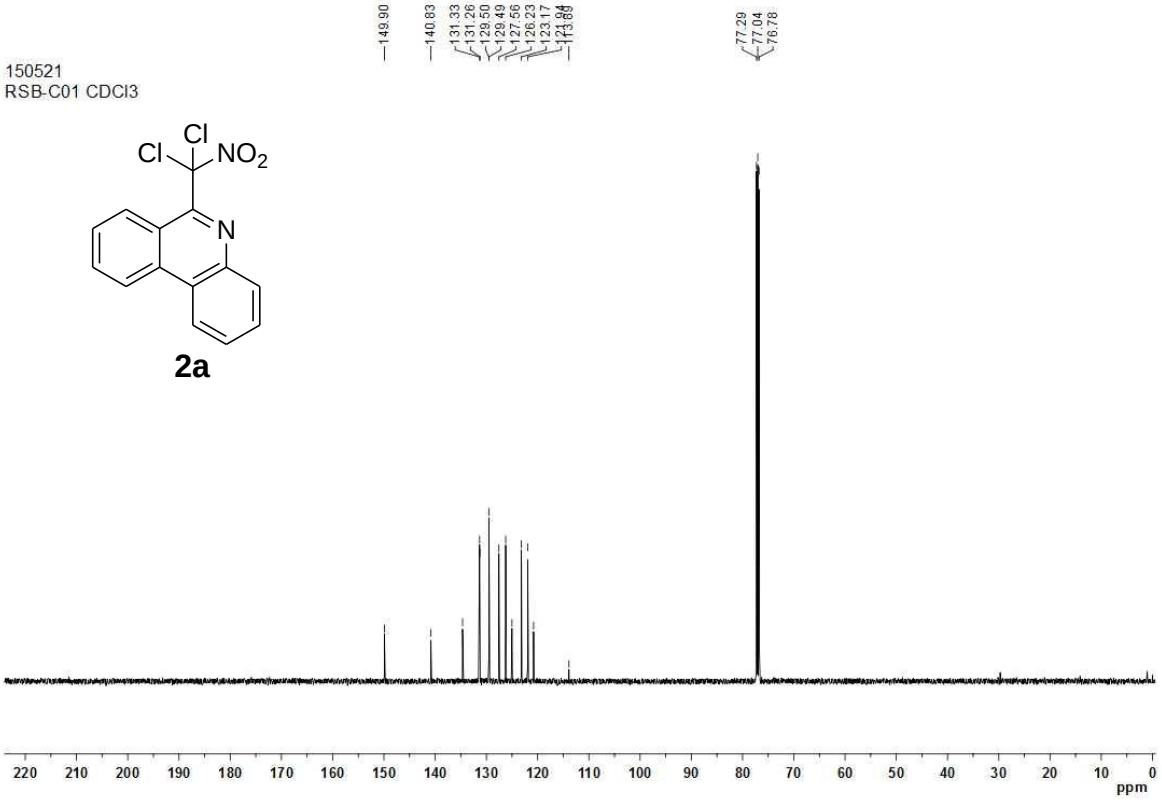


FIGURE *S1*. X-Ray crystal structure of **2m** (50% thermal ellipsoid)

7. ^{1}H NMR and ^{13}C NMR Spectra of All the Products





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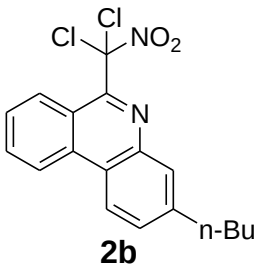
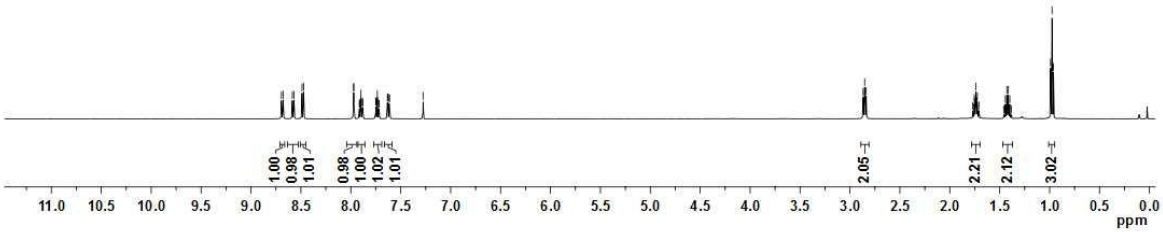


2b



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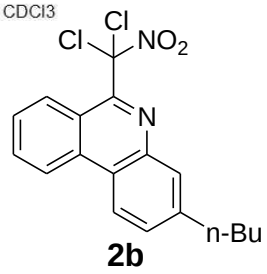

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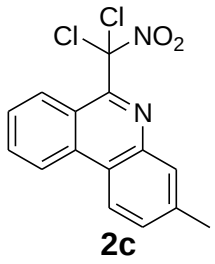

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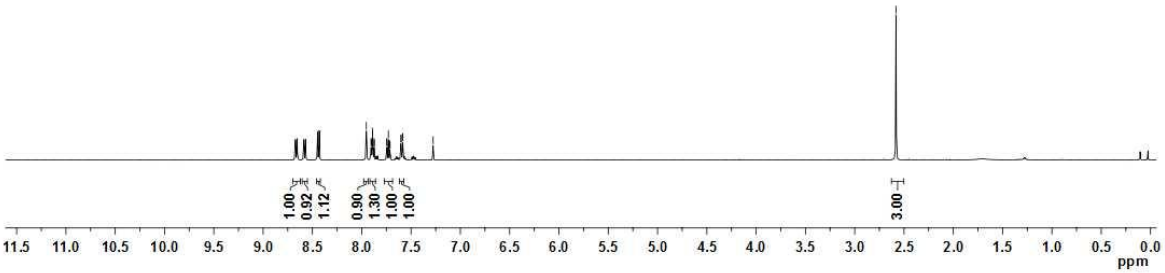

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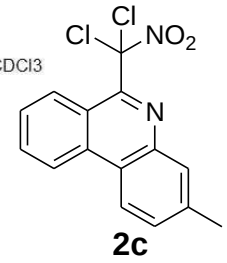

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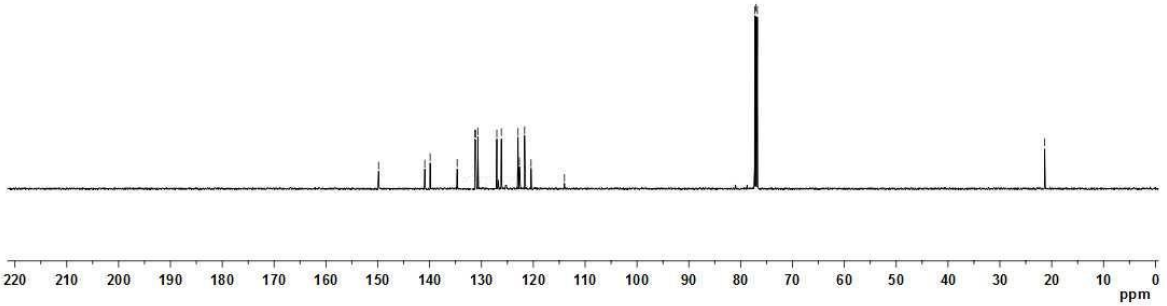

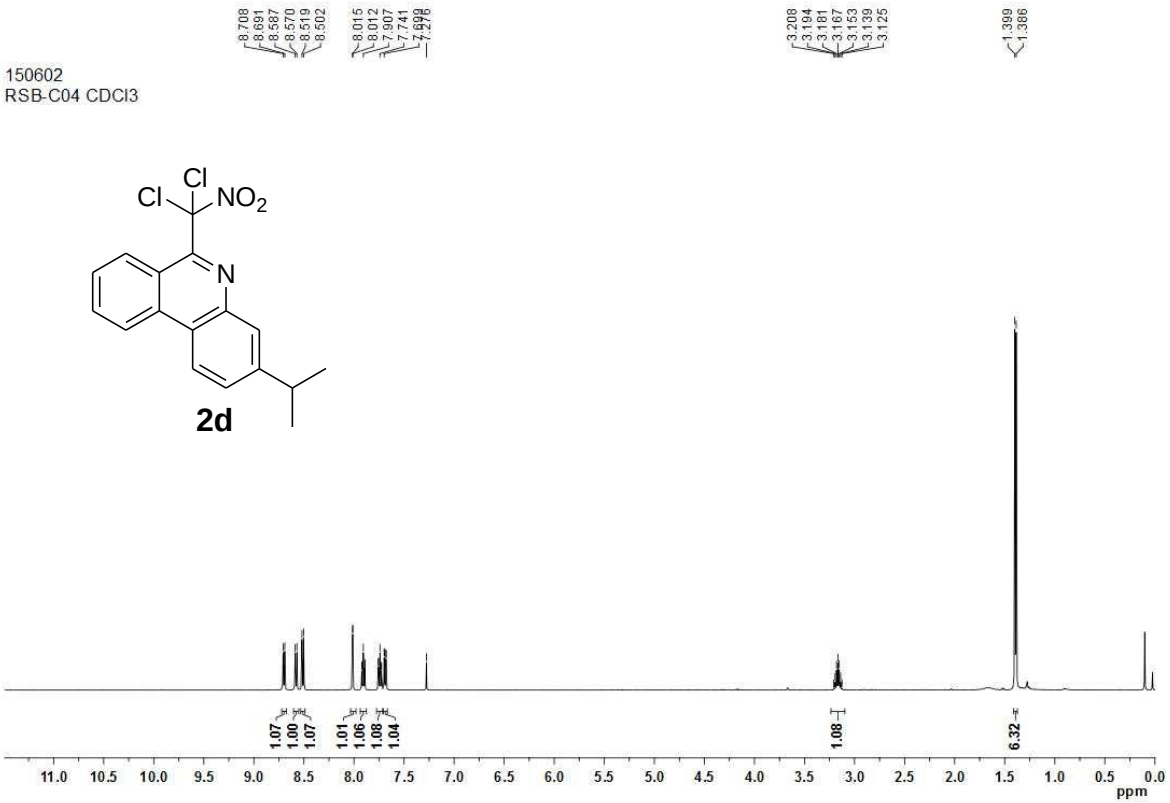
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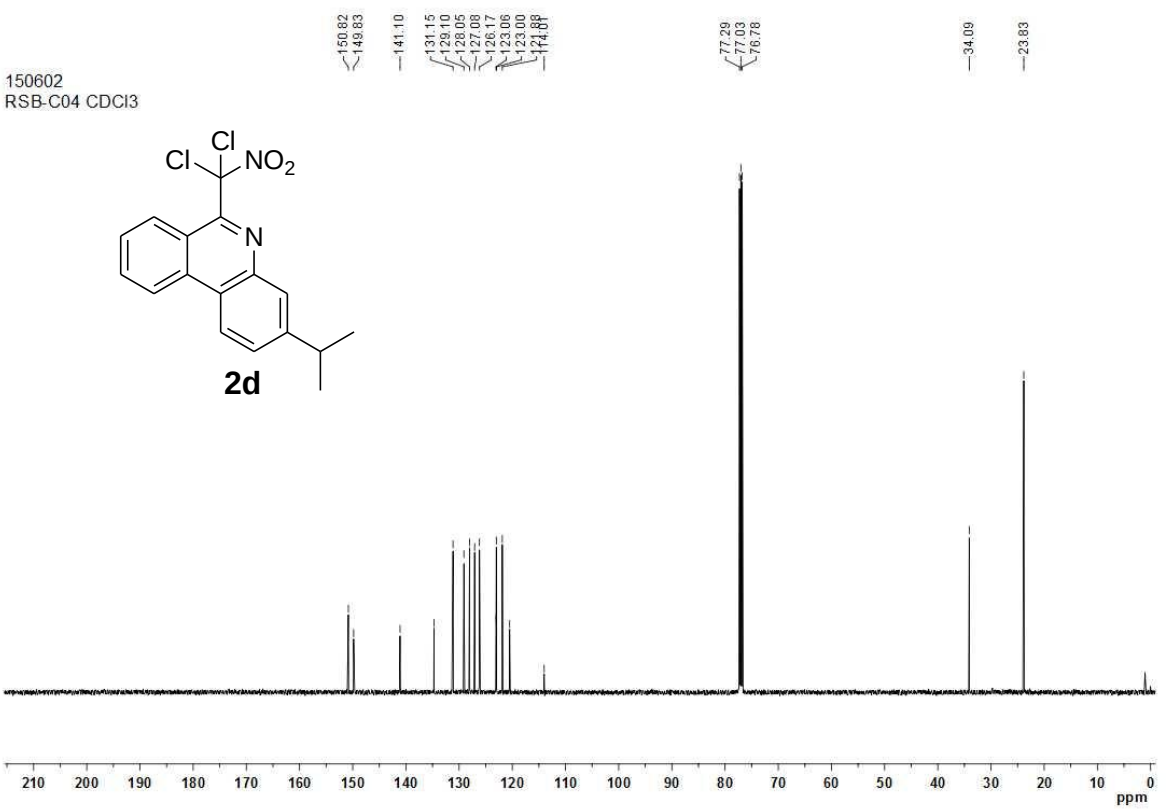
8.570
8.519
8.502
8.015
8.012
7.907
7.741
7.698
7.276
3.208
3.194
3.181
3.167
3.153
3.139
3.125
1.399
1.386
150602
RSB-C04 CDCl3
Cl
Cl
NO2
N
2d
1.07
1.00
1.07
1.01
1.06
1.08
1.04
1.08
6.32
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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141.10
131.15
129.10
128.05
127.08
126.17
123.06
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121.88
121.01
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77.03
76.78
34.09
23.83
150602
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Cl
Cl
NO2
N
2d
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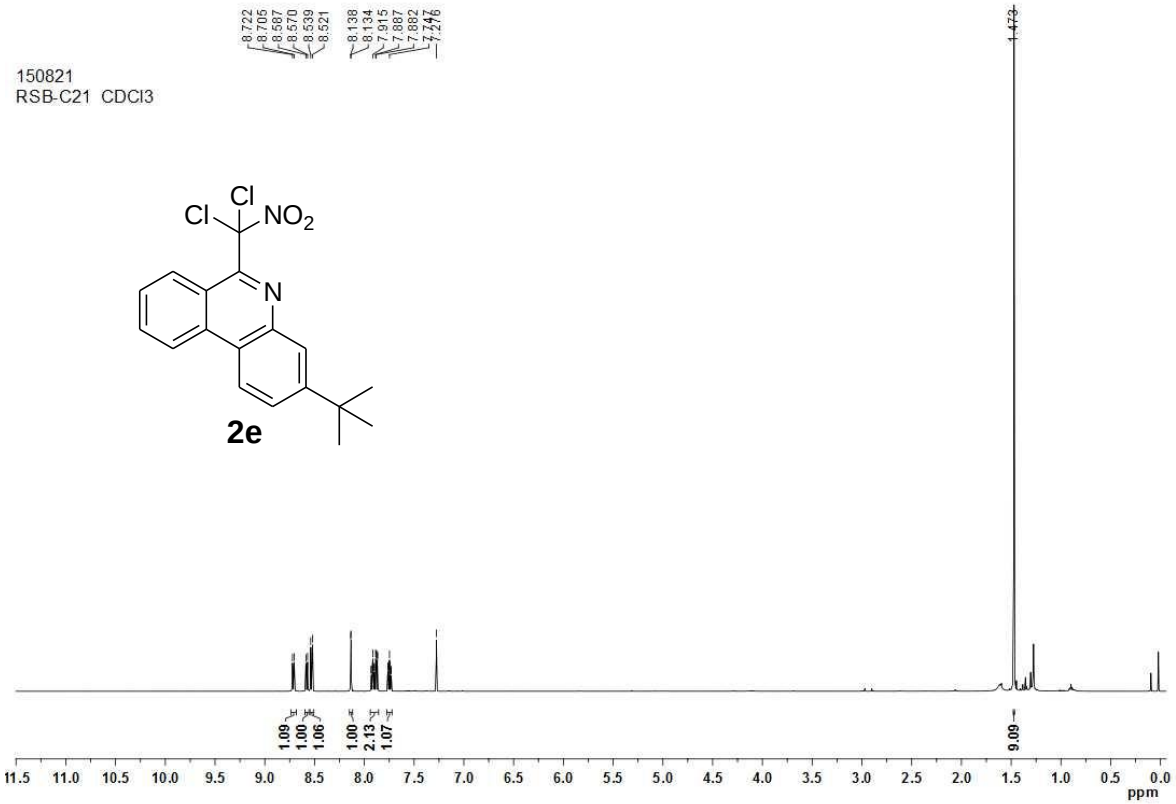
ppm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RSB-C21 CDCl3
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8.587
8.570
8.539
8.521
8.138
8.134
7.915
7.887
7.882
7.247
7.216
1.473
Cl
Cl
NO2
N
2e
1.09
1.00
1.06
1.00
2.13
1.07
9.09
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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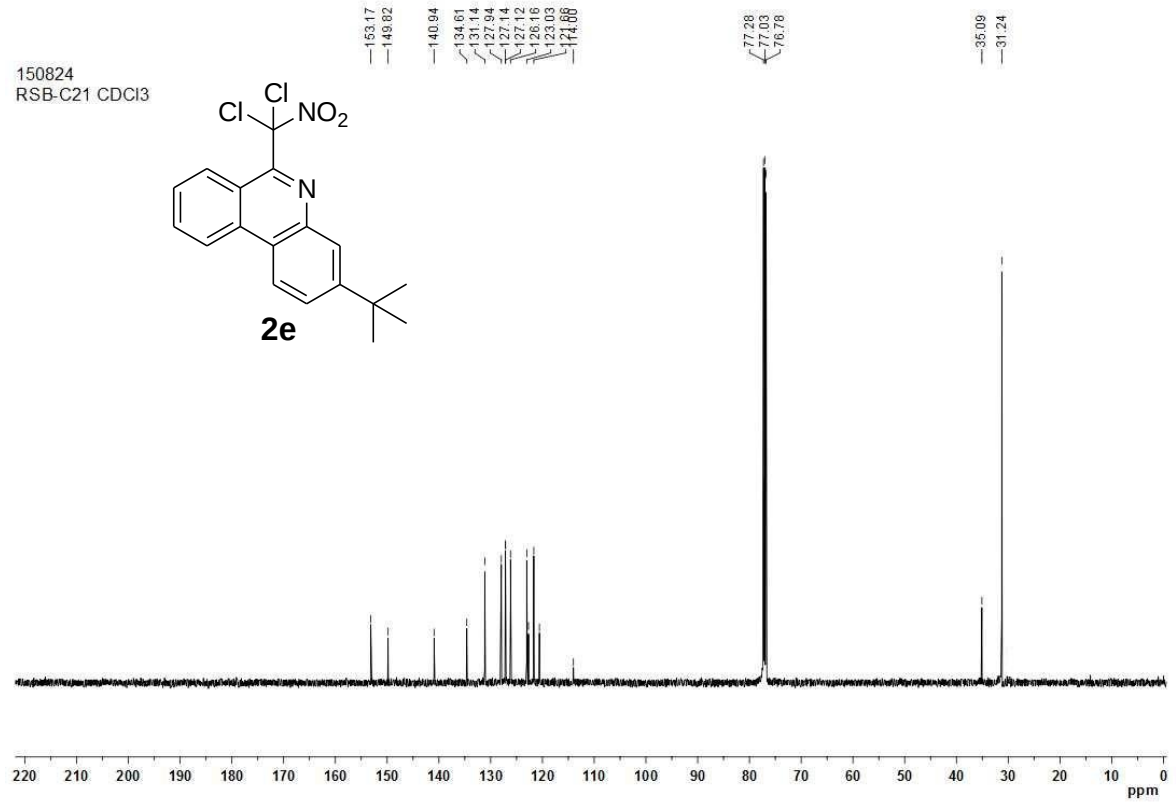
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RSB-C21 CDCl3
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127.94
127.14
127.12
126.16
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77.28
77.03
76.78
35.09
31.24
Cl
Cl
NO2
N
2e
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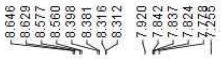
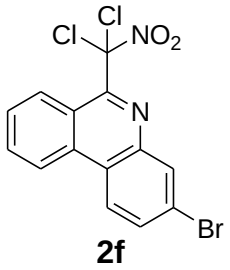
ppm



150818
RSB-C18-2 CDCl3



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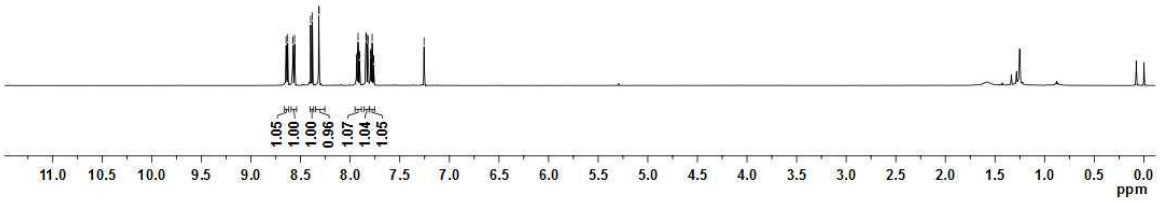

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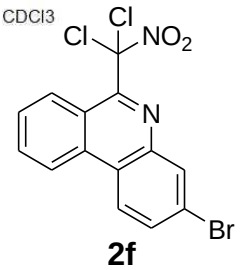
RSB-C18-2 CDCl3



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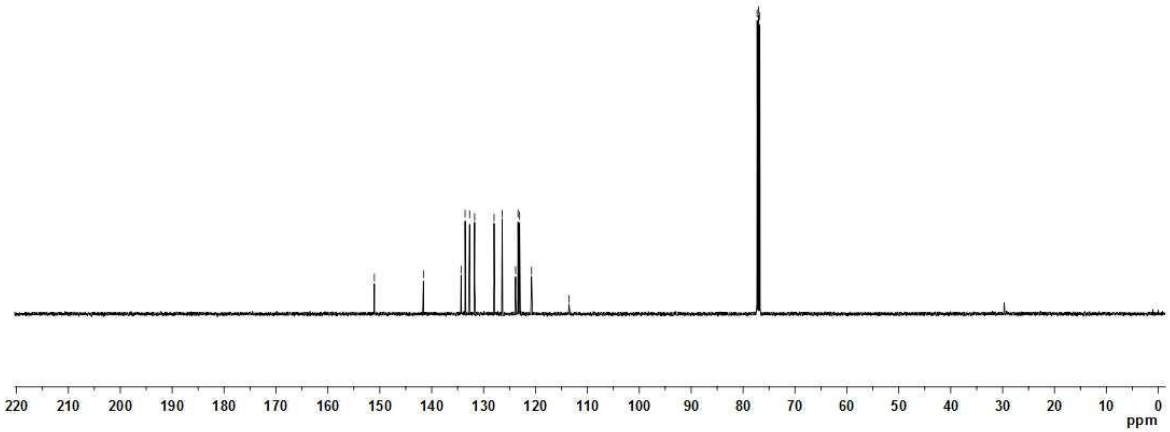

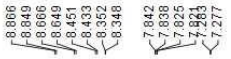

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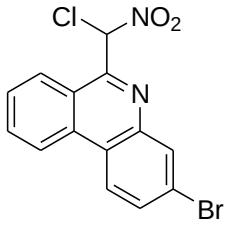

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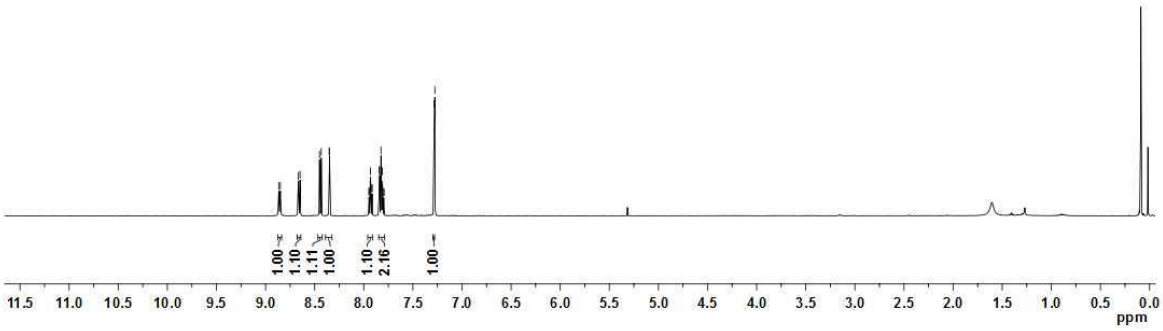
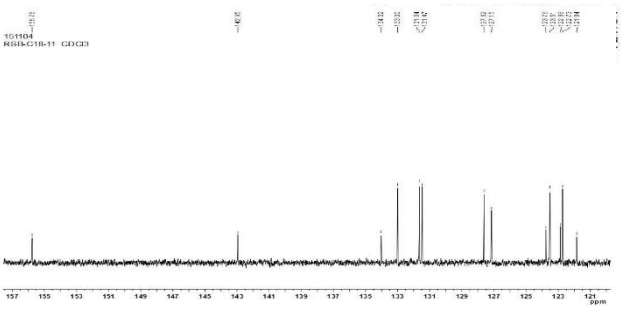
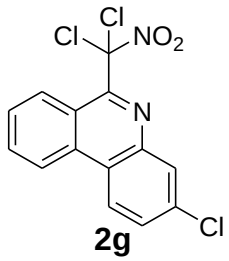


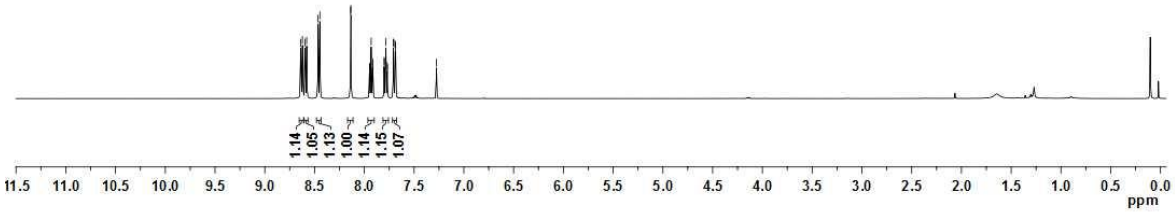


2f'

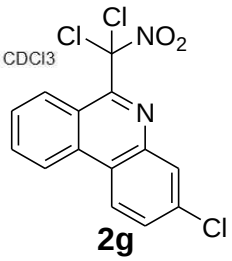
150709
RSB-C12 CDCl3



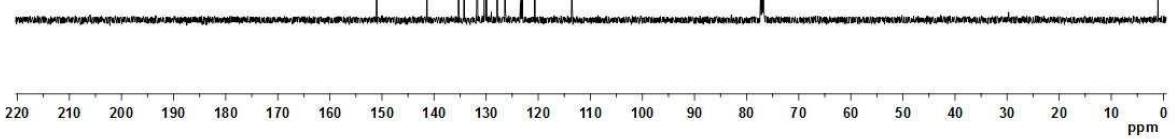
2g

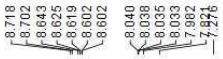


150710
RSB-C12 CDCl3

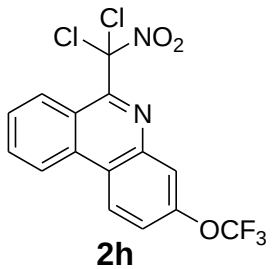


2g





150831
RSB-C22 CDCl3



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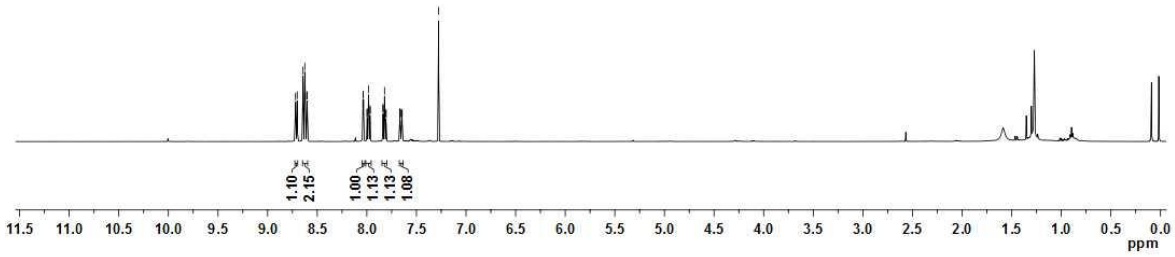
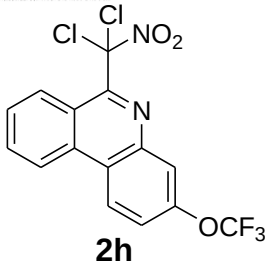


150831
RSB-C22 CDCl3



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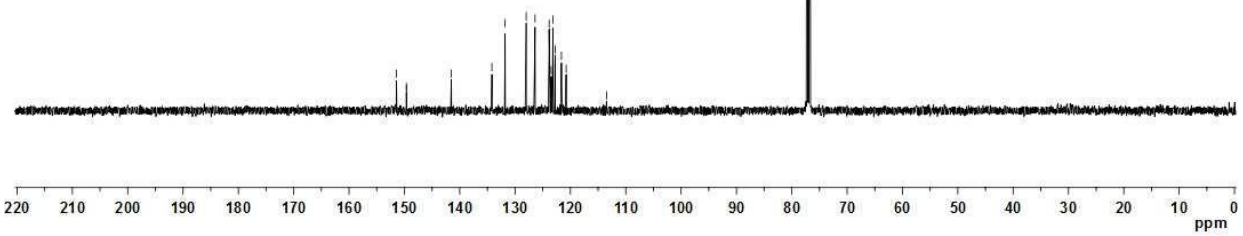
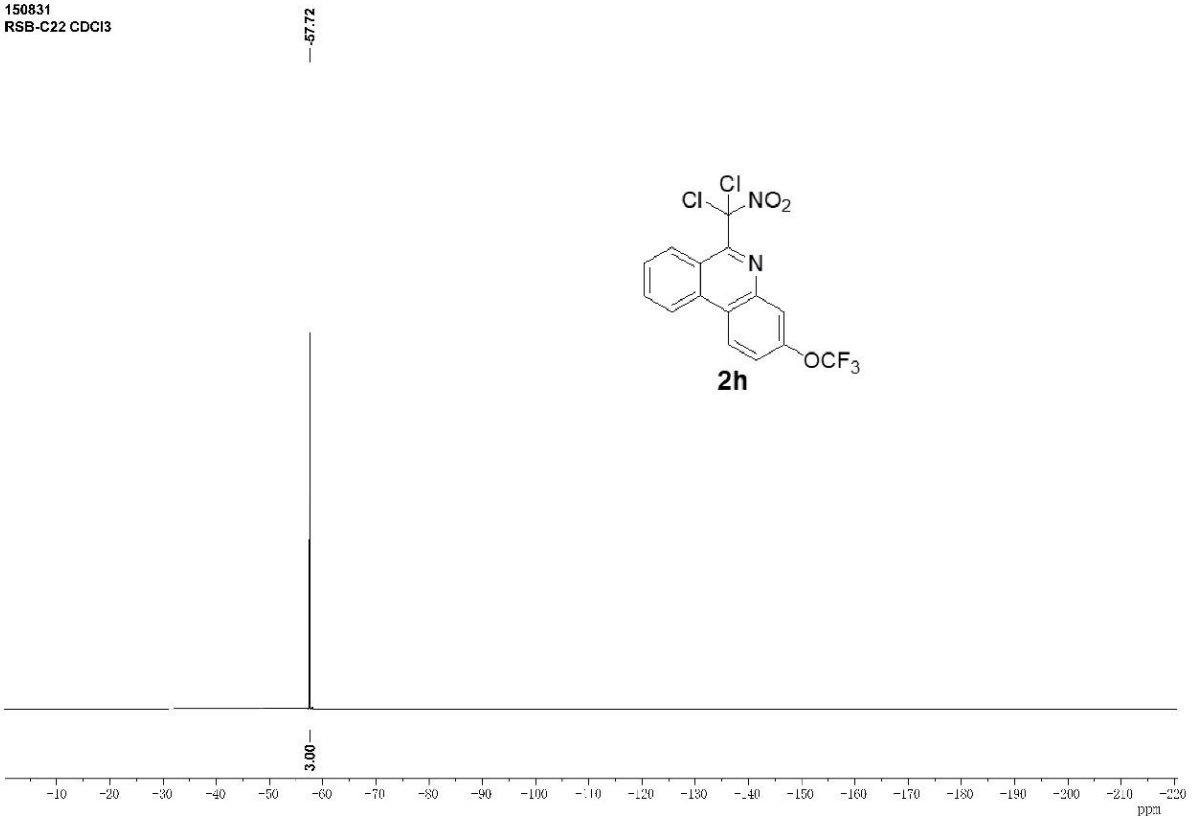
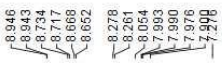


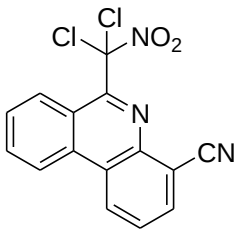
150831
RSB-C22 CDCl3



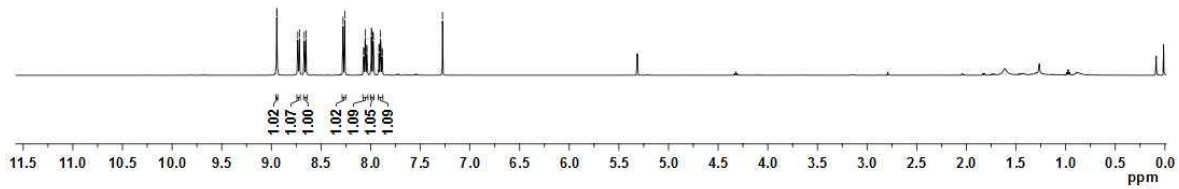
2h

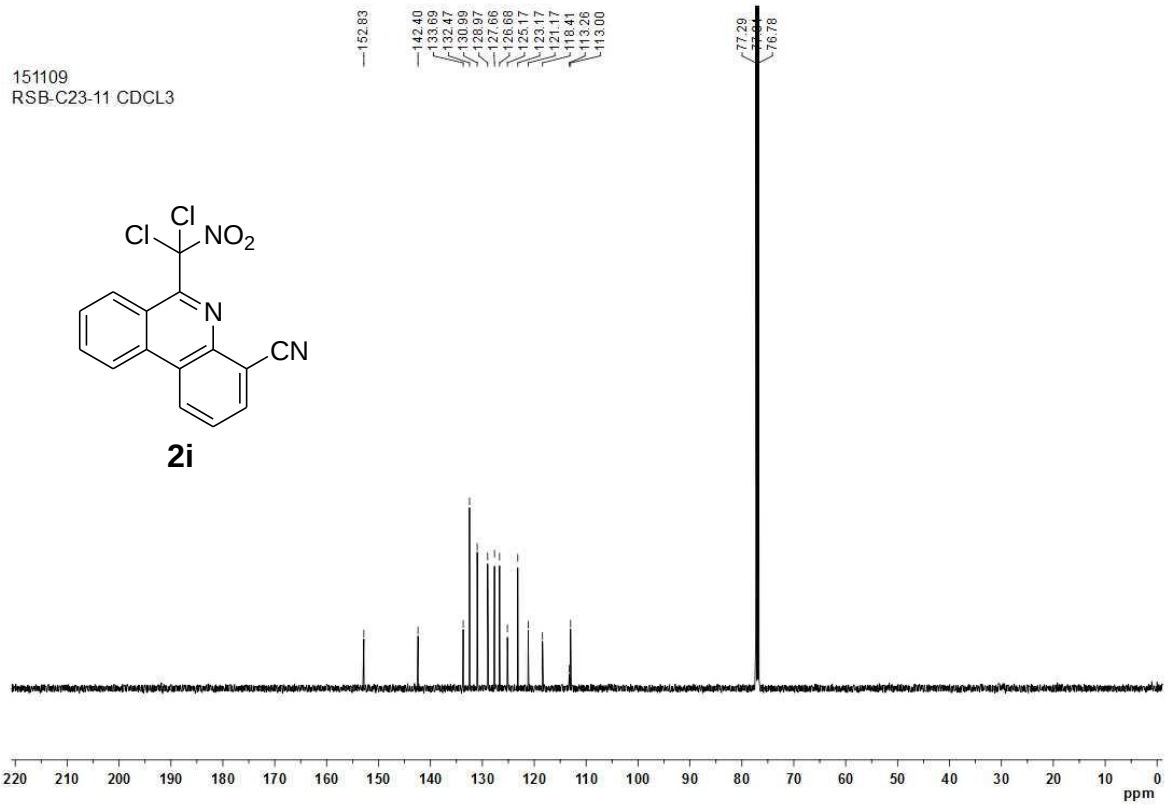


151109
RSB-C23-11 CDCL3

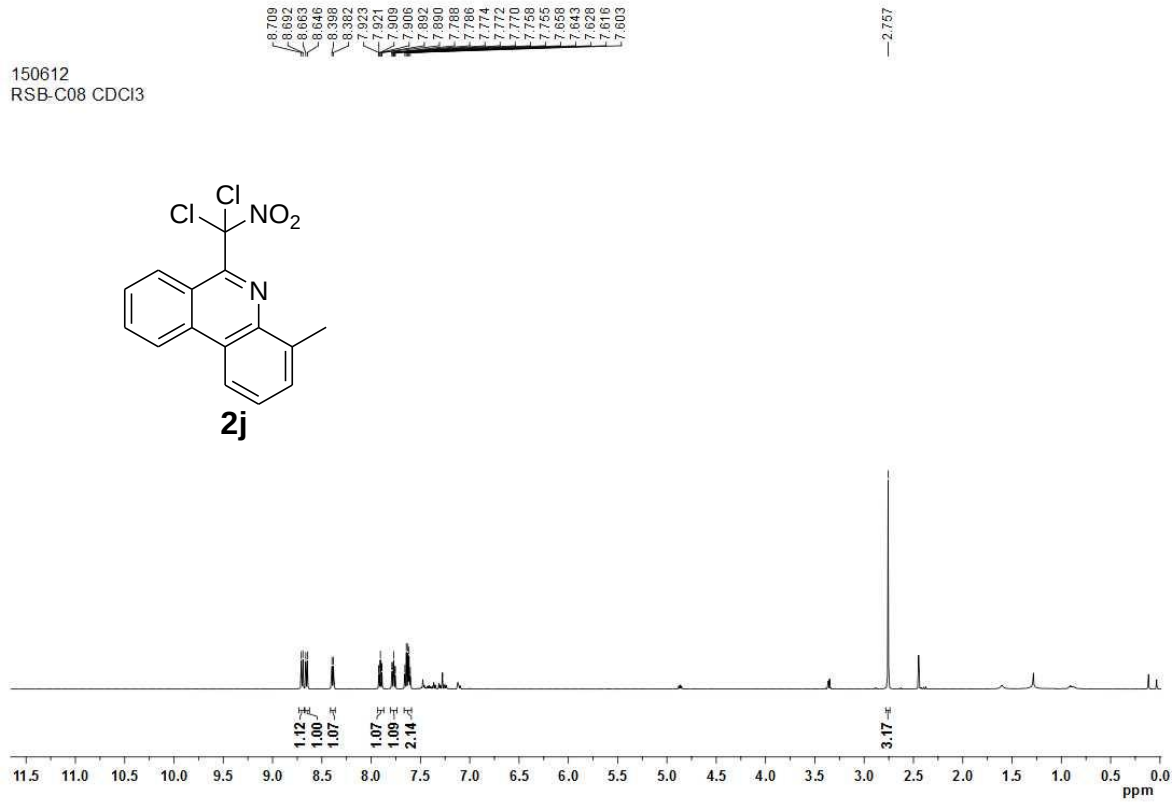


2i



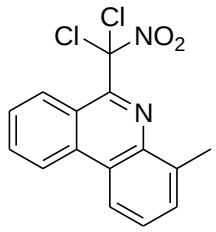

151109
RSB-C23-11 CDCL3
152.83
142.40
135.69
132.47
130.99
128.97
127.66
126.68
125.17
123.17
121.17
118.41
113.26
113.00
77.29
77.04
76.78
Cl
Cl
NO2
N
CN
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

2i


8.709
8.692
8.663
8.646
8.398
8.382
7.923
7.921
7.909
7.906
7.892
7.890
7.788
7.786
7.774
7.772
7.770
7.758
7.755
7.658
7.643
7.628
7.616
7.603
2.757
150612
RSB-C08 CDCl3
Cl
Cl
NO2
N
1.12
1.00
1.07
1.07
1.09
2.14
3.17
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

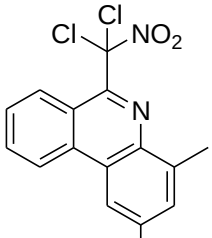
2j

150707
RSB-08 CDCl3

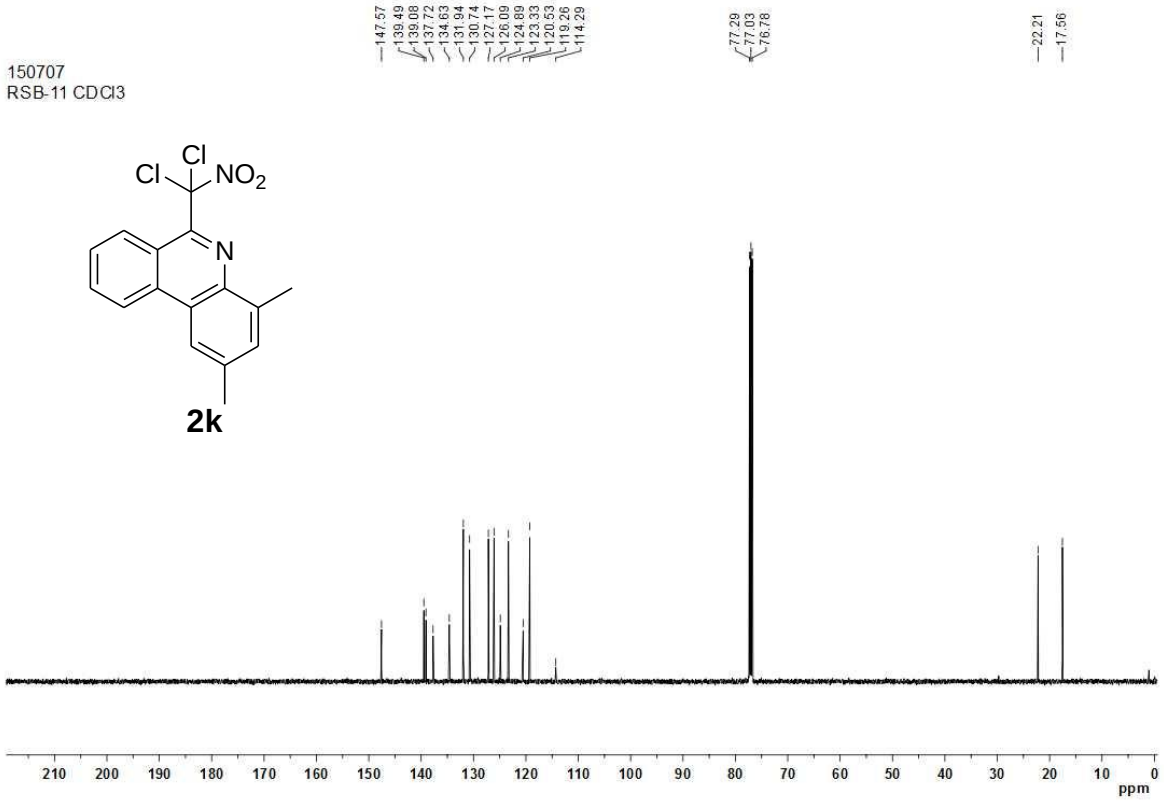


2j

150706
RSB-C11 CDCl3

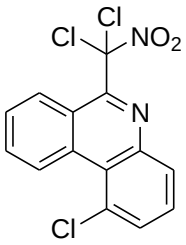


2k


147.57
139.49
139.08
137.72
134.63
131.94
130.74
127.17
126.09
124.89
123.33
120.53
119.26
114.29
77.29
77.03
76.78
22.21
17.56
150707
RSB-11 CDCl3
Cl
Cl
NO2
N
2k
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

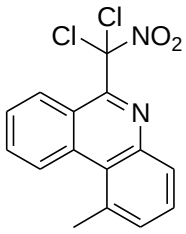

10.040
10.022
8.657
8.655
8.640
8.638
8.128
8.125
7.870
7.868
7.698
7.696
7.276
150710
RSB-C14 CDCl3
Cl
Cl
NO2
N
Cl
2l
1.00
1.00
1.14
1.09
2.10
1.11
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

150714
RSB-C14 CDCl3



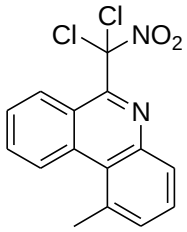
2l

150605
RSB-C06 CDCl3



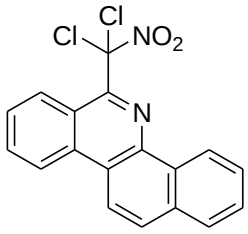
2m

150605
RSB-C06 CDCl3



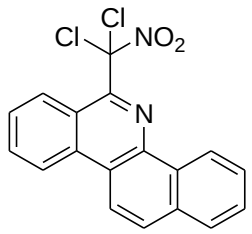
2m

150819
RSB-C19 CDCl3



2n

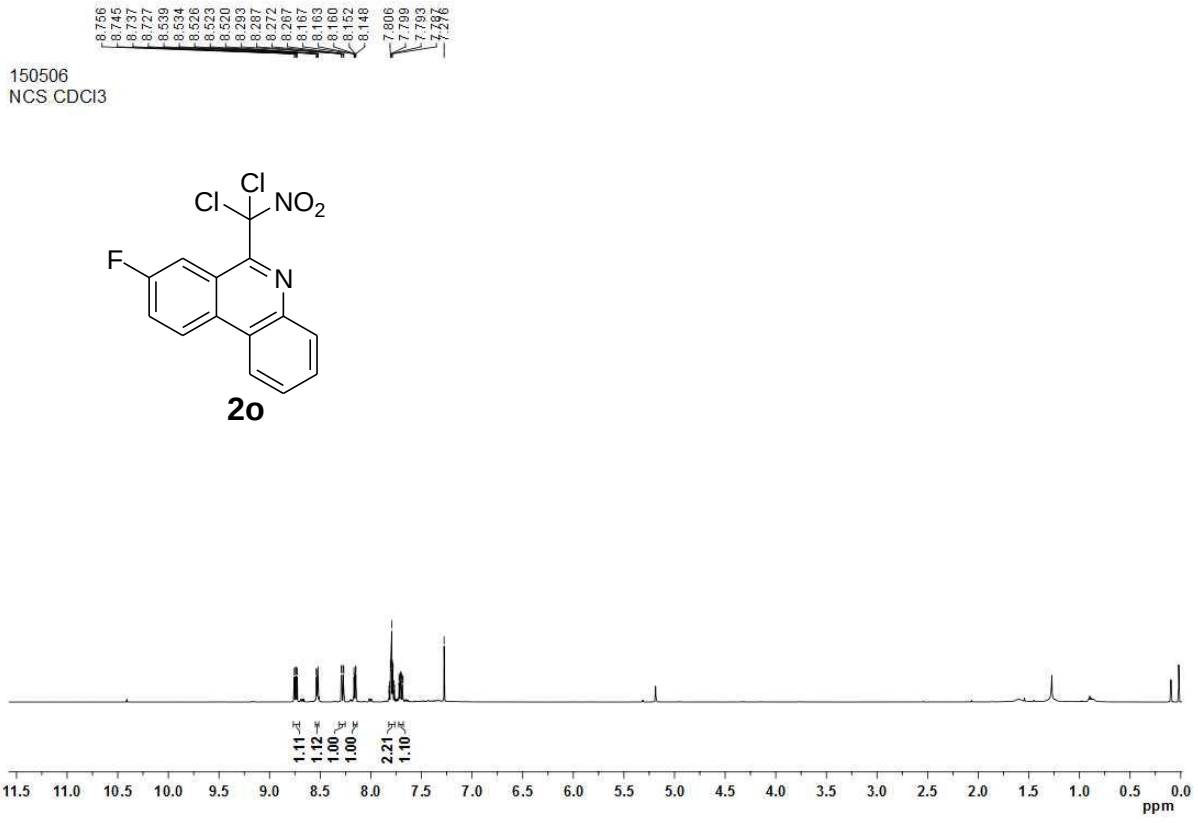
150821
RSB-C19 CDCl3

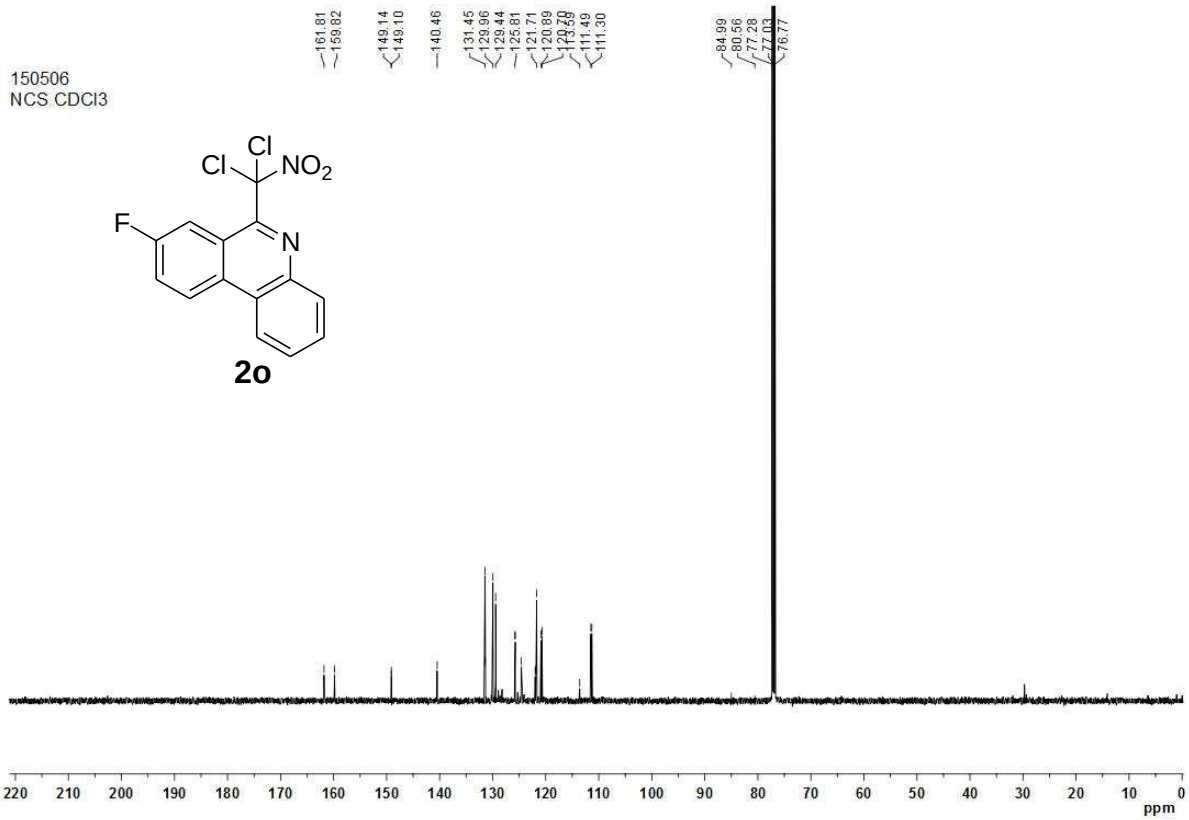


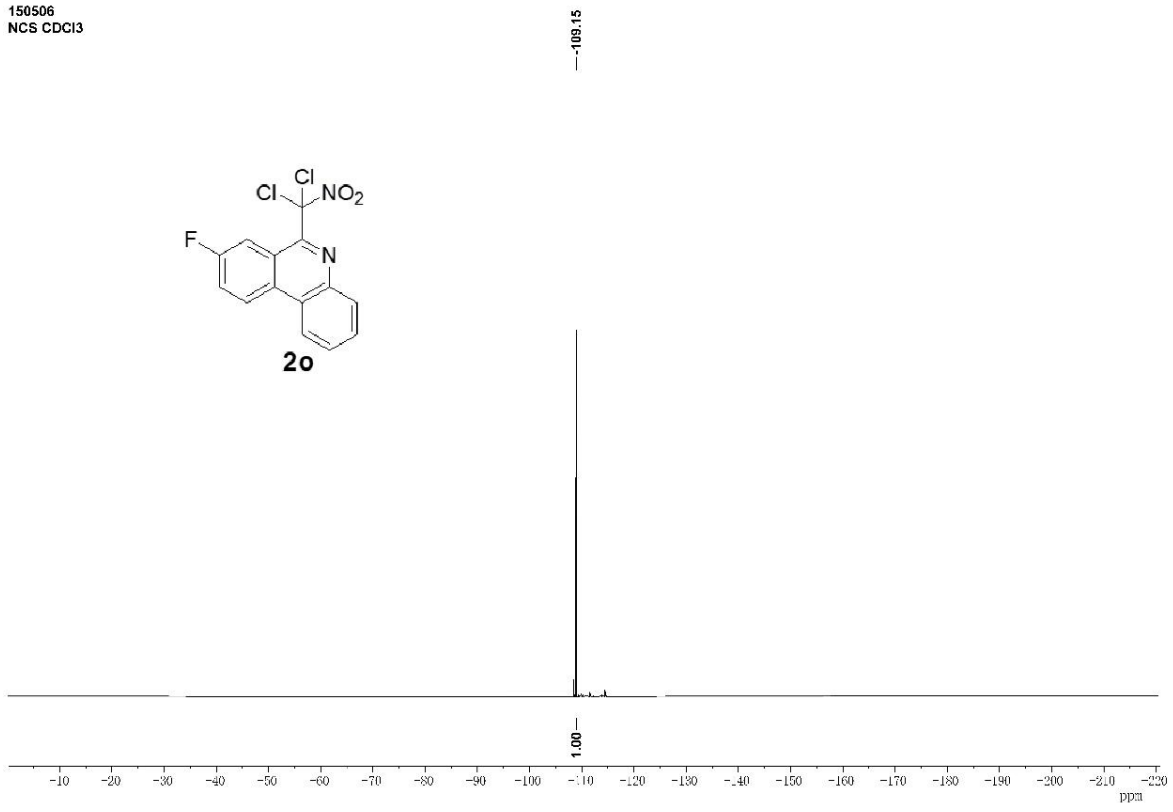
2n

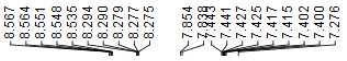
150506
NCS CDCl3

2o

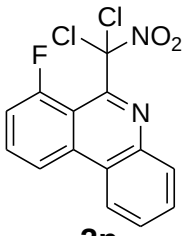



150506
NCS CDCl3
Cl
Cl
NO2
F
N
2o
161.81
159.82
149.14
149.10
140.46
131.45
129.96
129.44
125.81
121.71
120.89
111.49
111.30
84.99
80.56
77.28
77.03
76.77
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

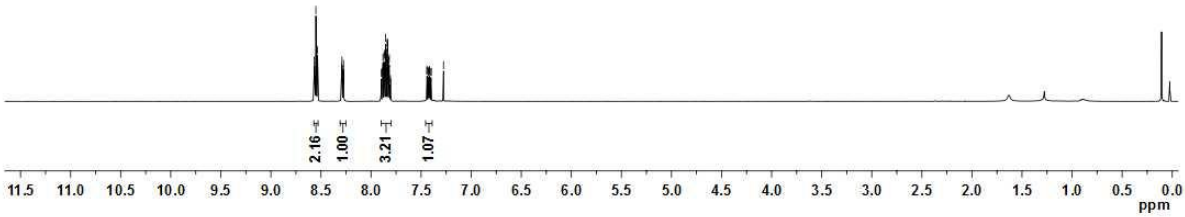

150506
NCS CDCl3
-109.15
Cl
Cl
NO2
F
N
2o
1.00
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
ppm



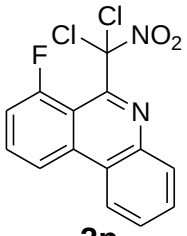
150821
RSB-C20 CDCl3



2p

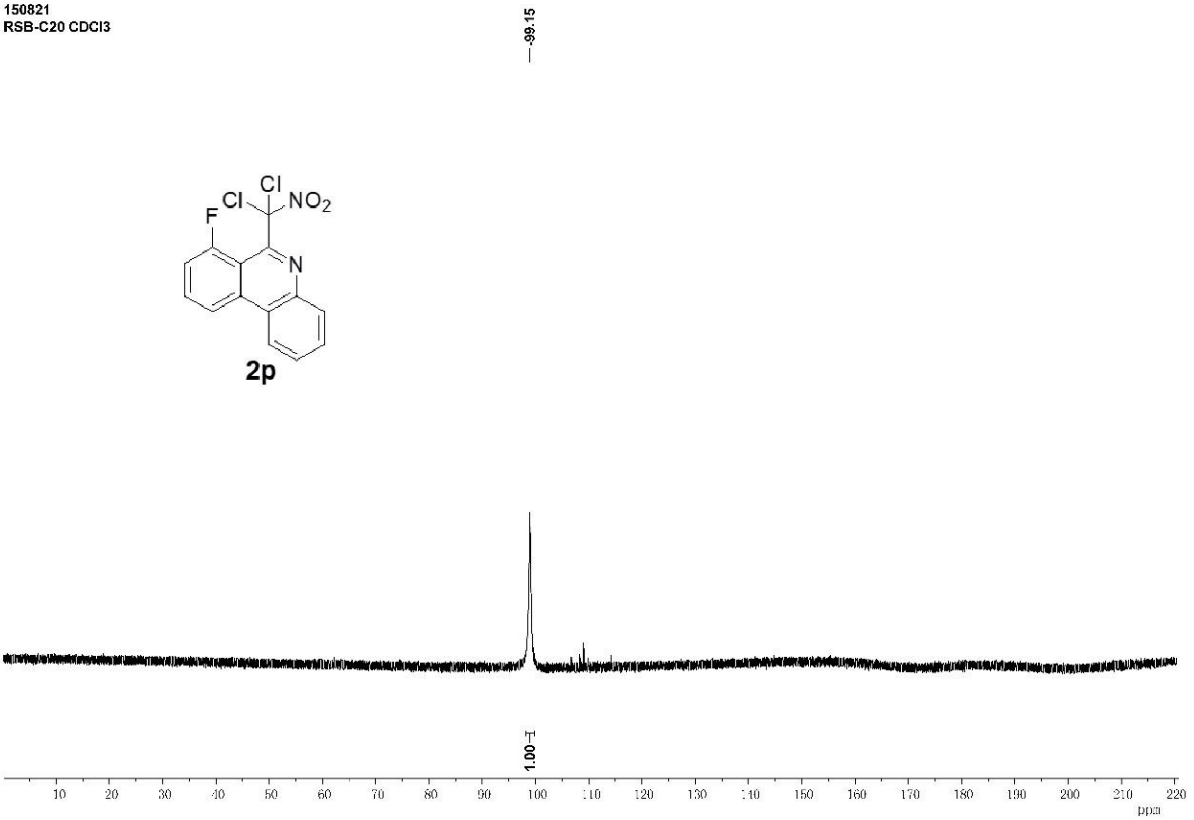


150824
RSB-C20 CDCl3



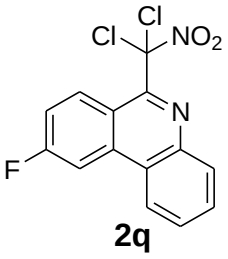
2p

150821
RSB-C20 CDCl3

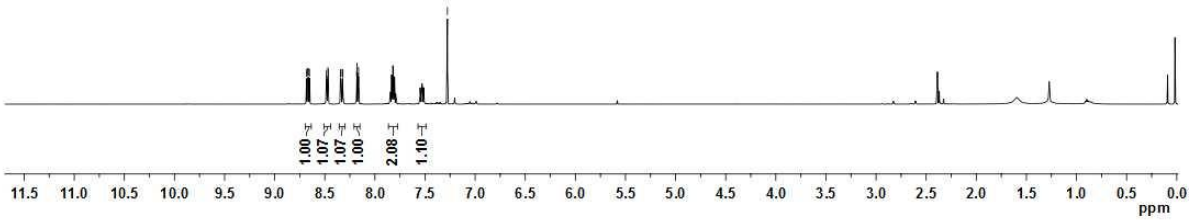


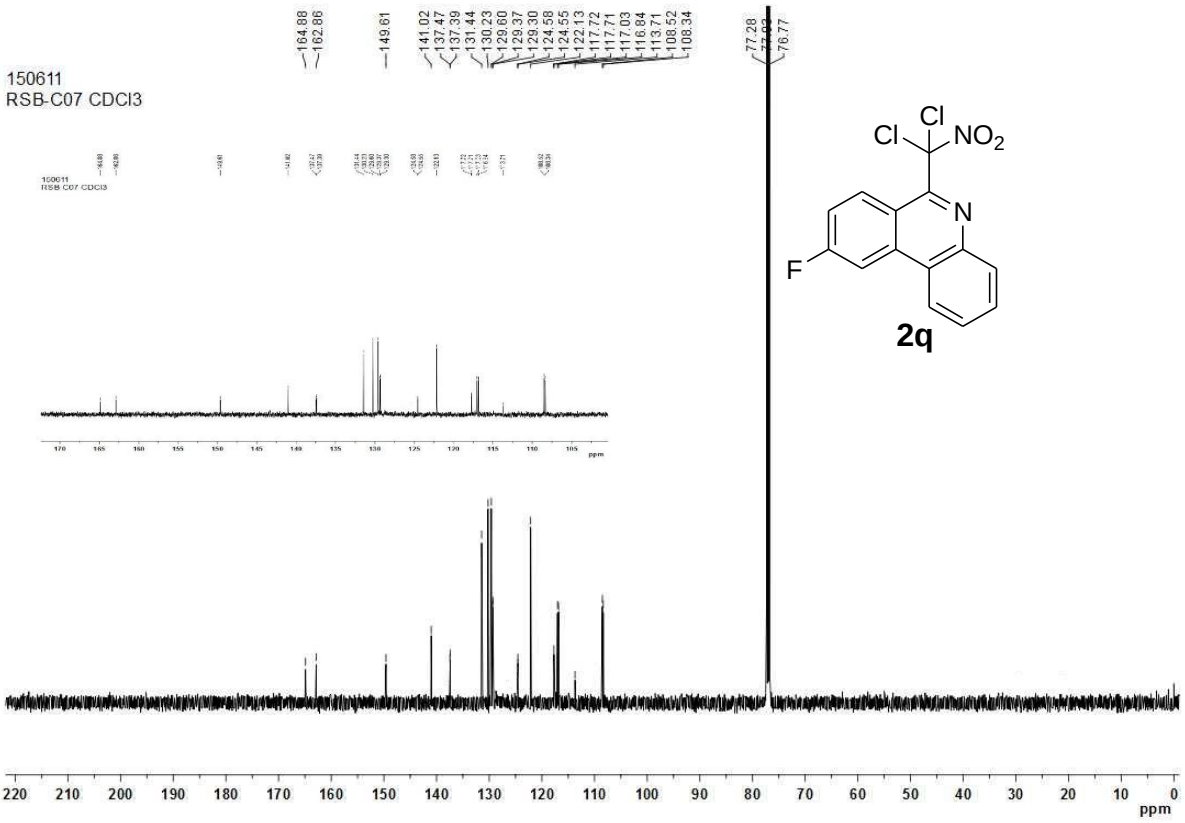
2p

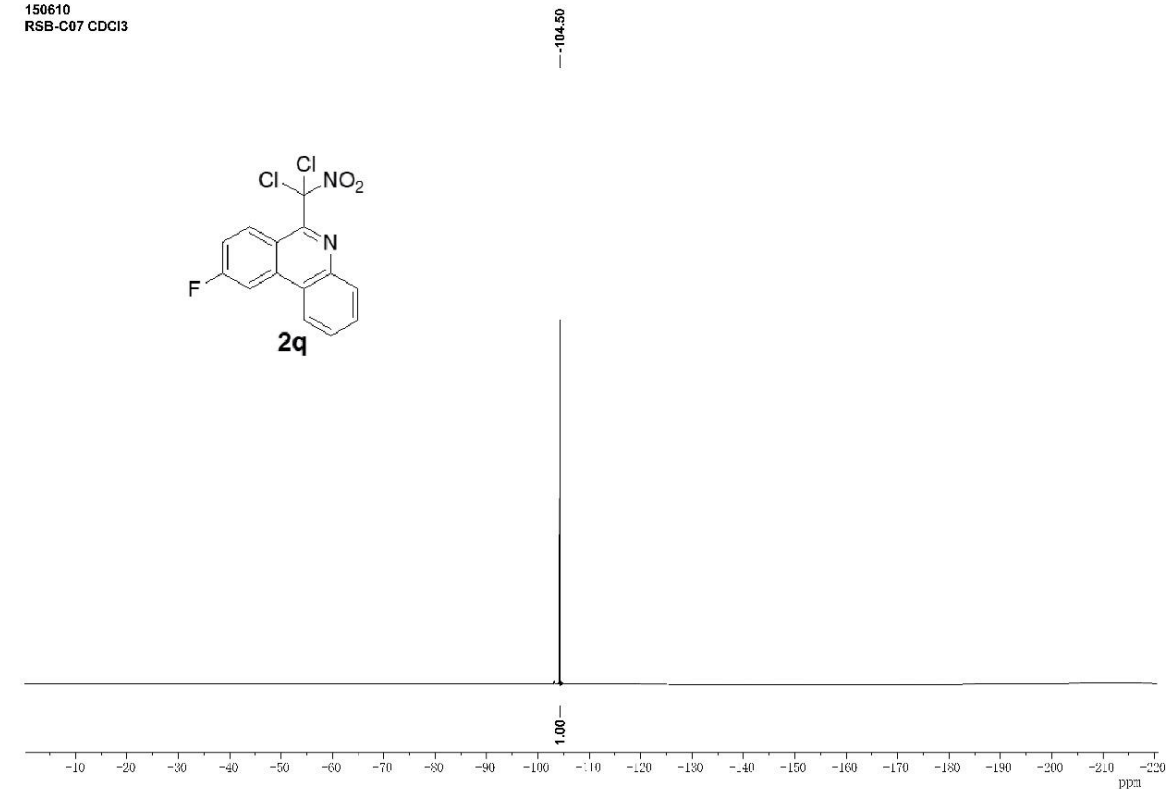
150610
RSB-07 CDCl3



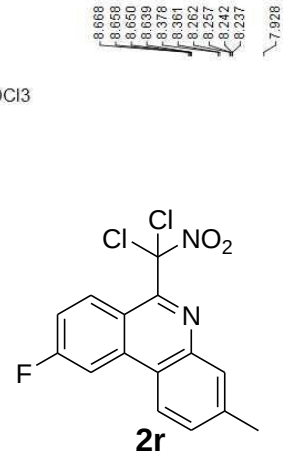
2q



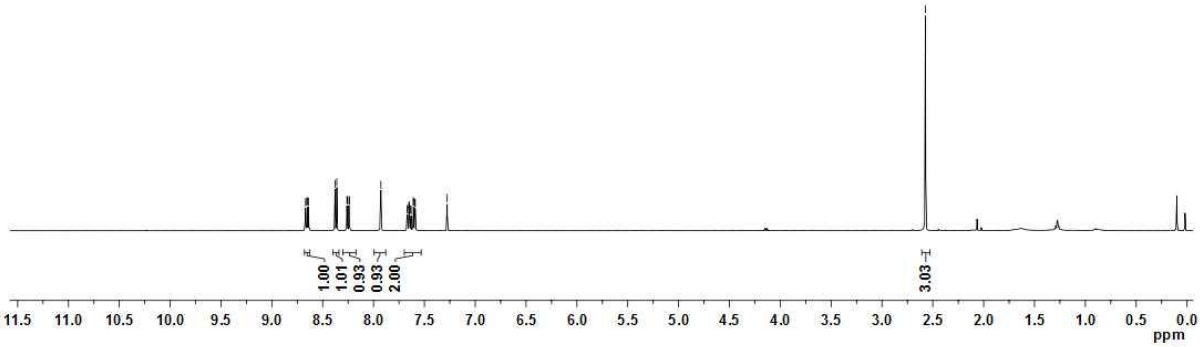

150611
RSB-C07 CDCl3
164.88
162.86
149.61
141.02
137.47
137.39
131.44
130.23
129.60
129.37
129.30
124.58
124.55
122.13
117.72
117.71
117.03
116.84
113.71
108.52
108.34
77.28
77.03
76.77
Cl
Cl
NO2
N
F
2q
ppm


150610
RSB-C07 CDCl3
-104.50
Cl
Cl
NO2
N
F
2q
1.00
ppm

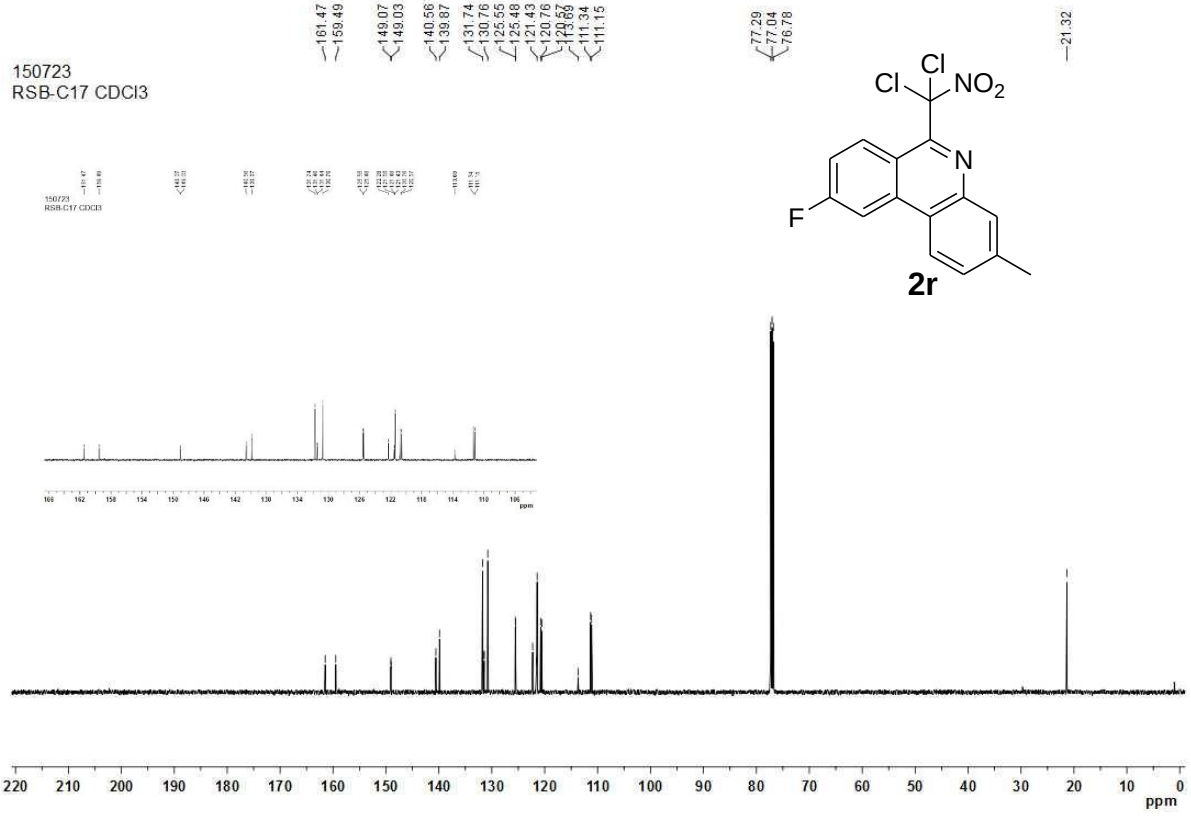
150722
RSB-C17 CDCl3



2r

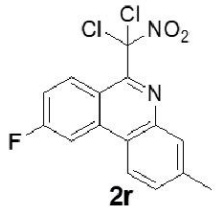


150723
RSB-C17 CDCl3



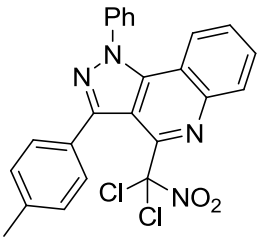
2r

150722
RSB-C17 CDCl3

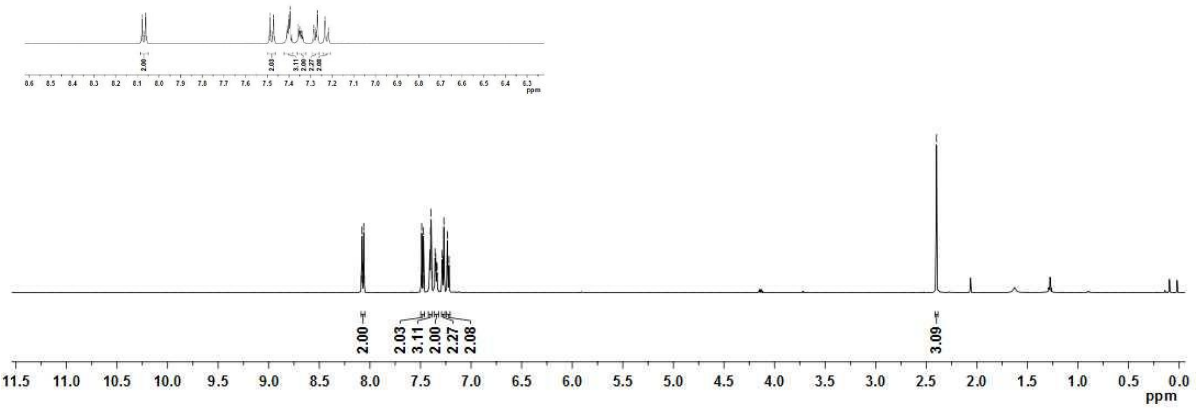


2r

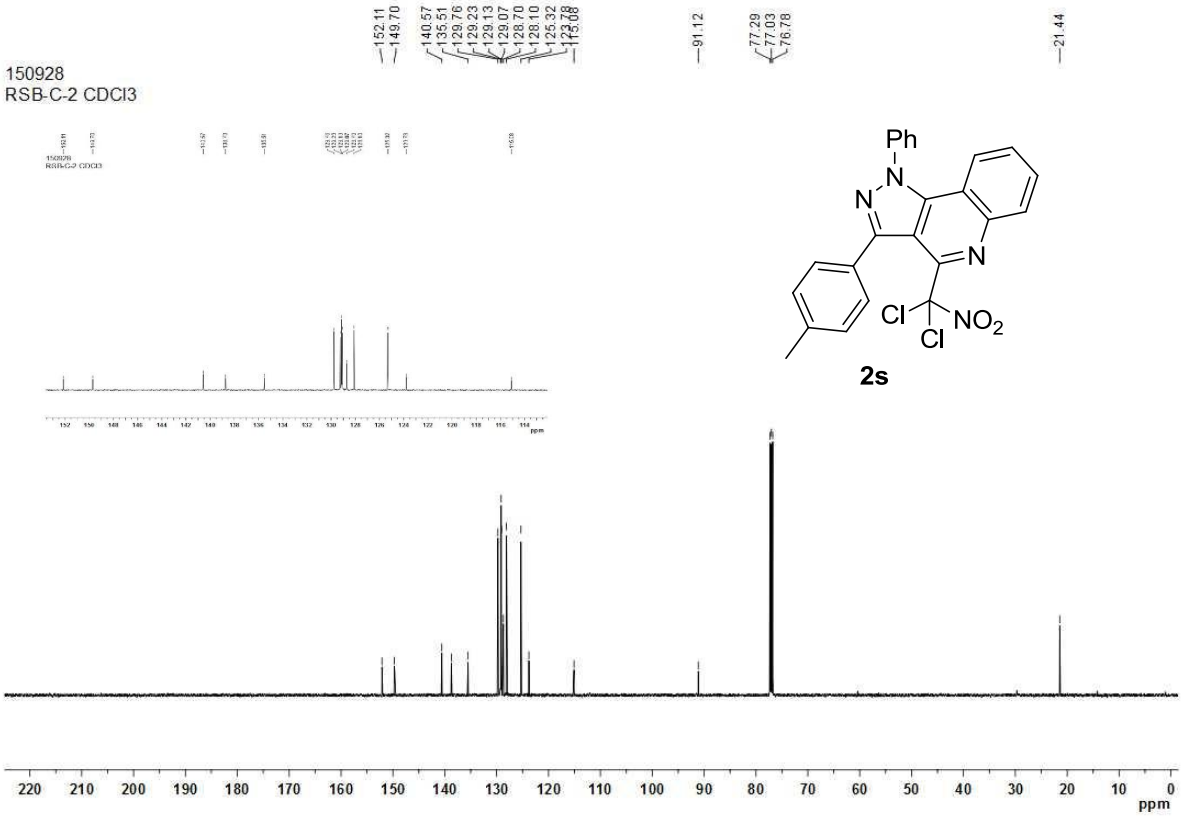
150925
RSB-C-2 CDCl3



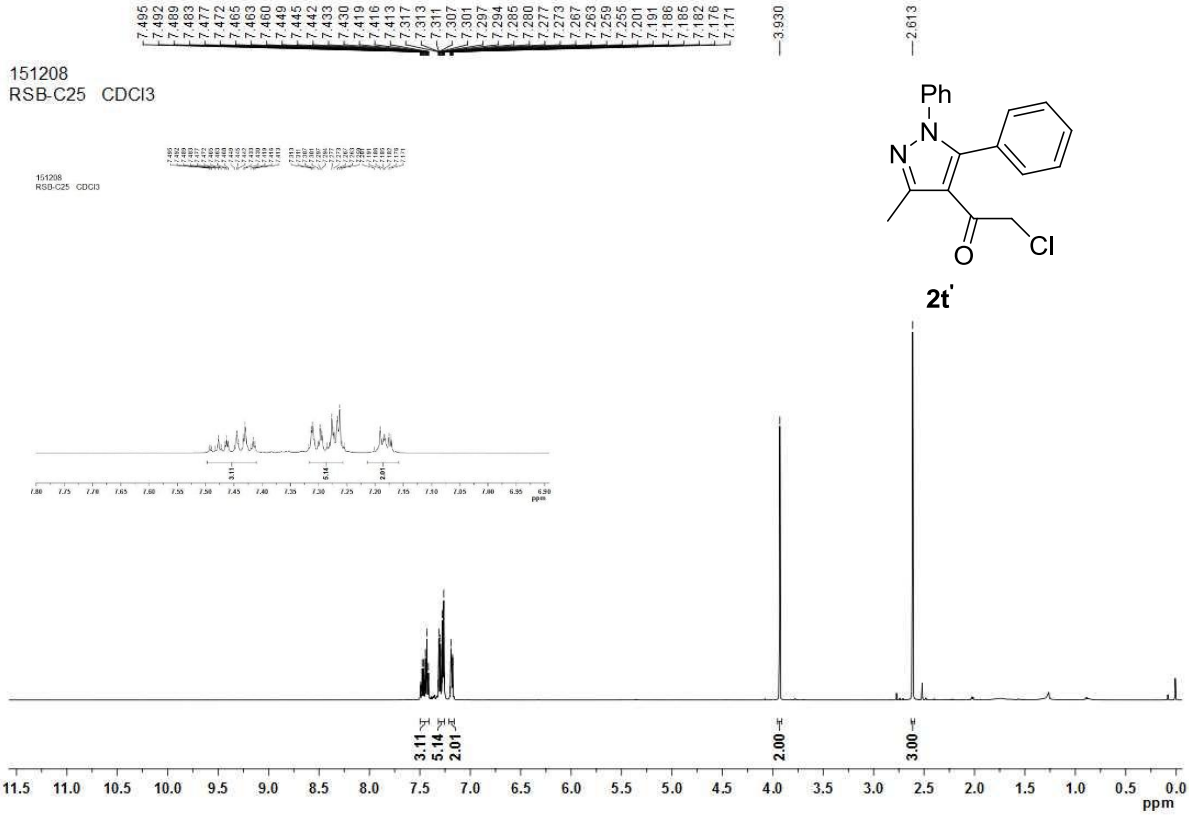
2s

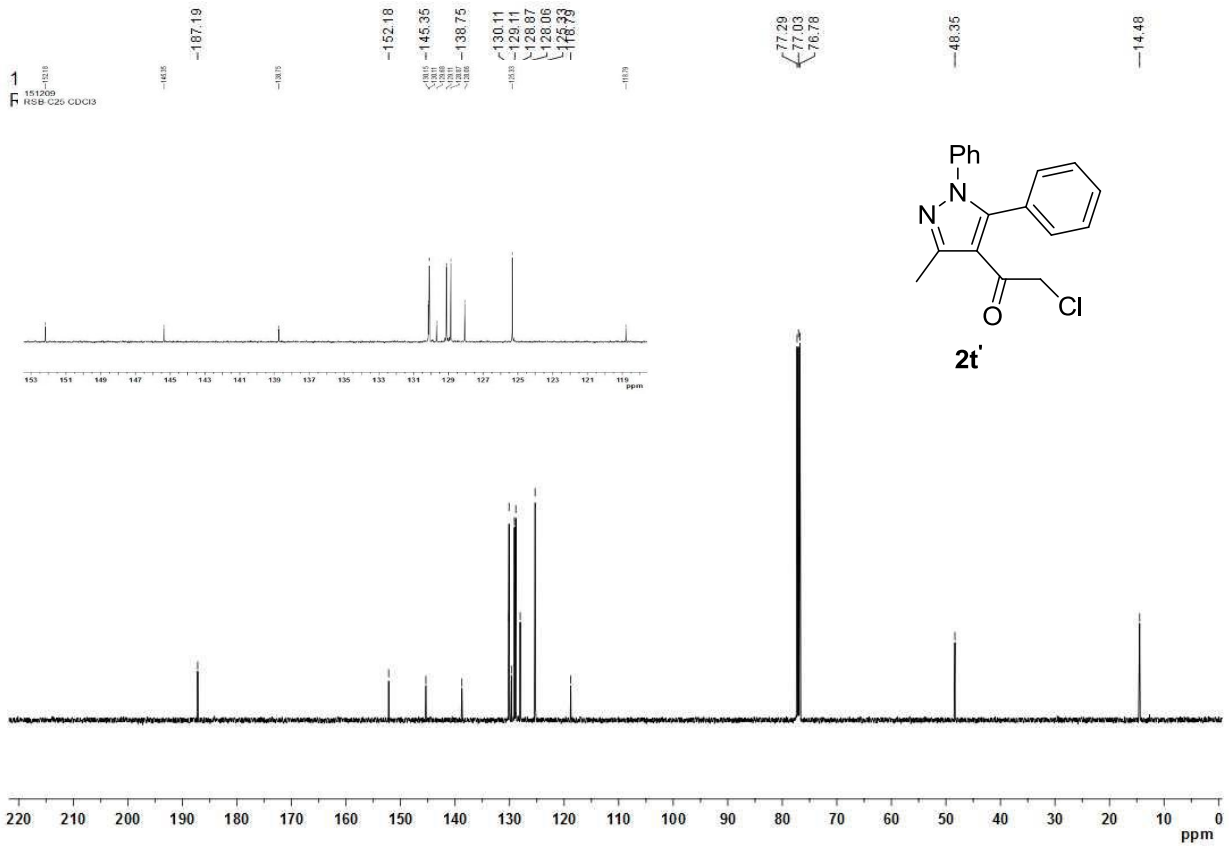


150928
RSB-C-2 CDCl3



151208
RSB-C25 CDCl3




187.19
152.18
145.35
138.75
130.11
129.11
128.87
128.06
125.33
118.79
77.29
77.03
76.78
48.35
14.48
151209
RSB-C25-CDCl3
Ph
N
N
O
Cl
2t'
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm