Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

For

Transition-metal-free radical fluoroalkylation of isocyanides for the synthesis of tri-/di-/monofluoromethylated phenanthridines

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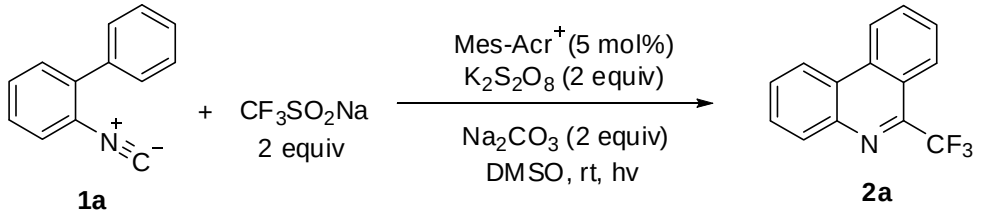
1. General remarks

^{1}H NMR spectra were recorded on 400 or 600 MHz (100 or 150 MHz for ^{13}C NMR, 376 or 564 MHz for ^{19}F NMR) agilent NMR spectrometer with $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the internal standard. Chemical shifts were reported in parts per million (ppm, δ scale) downfield from TMS at 0.00 ppm and referenced to the $CDCl_3$ at 7.26 ppm (for ^{1}H NMR) or 77.16 ppm (for ^{13}C NMR). Mass spectroscopy data of the products were collected on a GCT PremierTM (CI) Mass Spectrometer. Infrared (FT-IR) spectra were recorded on a Varian 1000FT-IR, ν_{max} in cm^{-1}. Melting points were measured using SGW, X-4B and values are uncorrected. All commercially available reagents and solvents were used as received unless otherwise specified. The substrates were readily prepared according to known methods (*Org. Lett*., **2013**, 15, 4846; *Org. Lett*., **2015**, 17, 4401; *Angew. Chem., Int. Ed.*, **2016**, 55, 2743).

2. Typical experimental procedure



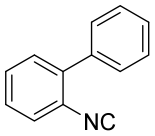
1a **2a**

To a suspension of **1a** (35.8 mg, 0.2 mmol), CF_3SO_2Na (62.4 mg, 0.4 mmol) and *N*-Methyl-9-mesityl acridinium perchlorate (4 mg, 0.01 mmol) in DMSO (2 mL) was added $K_2S_2O_8$ (108.1 mg, 0.4 mmol) and Na_2CO_3 (42.4 mg, 0.4 mmol) at rt. The resulting mixture was stirred upon 5W white LEDs irradiation under argon balloon. After the reaction was finished, the resulting mixture was purified by flash column chromatography on silica gel to give **2a** as a yellow solid (42.0 mg, 85% yield).

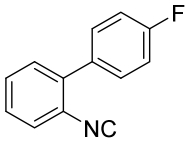
3. References for known products

Entry	References	Compounds
1	Q. Wang; L.Zhou. *Org. Lett*., **2013**, 15, 4846.	**2a, 2c, 2d, 2f, 2j, 2k, 2o, 2o'**
2	Y. Z. Cheng; S. Y. Yu. *Org. Lett*., **2013**, 15, 5520.	**2h, 2p**
3	X. Y. Tang; B. Zhang. *RSC Adv*., **2015**, 5, 76363.	**2b, 2e, 2n**
4	Z. X. Zhang; D. Jr. *Org. Lett*., **2015**, 17, 4401.	**3c, 4e**
5	J. Rong; J. B. Hu. *Angew. Chem., Int. Ed.* **2016**, 55, 2743.	**3a, 3b**
6	X. Y. Sun; S. Y. Yu. *Org. Lett.,* **2014**, 16, 2938.	**3c, 5a**
7	W. Y. Wang; X. G. Zhang. *J. Org. Chem*., **2013**, 78, 6025.	**2i**

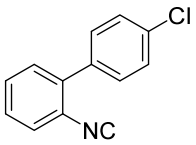
4. Characterization of the substrates and products



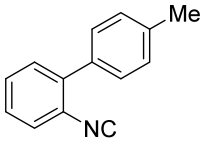
2-Isocyano-1,1'-bipheny (1a): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.41 (m, 8H), 7.38 (t, *J* = 7.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.5, 138.9, 137.1, 130.6, 129.6, 129.0, 128.6, 128.4, 128.2, 127.9, 124.6.



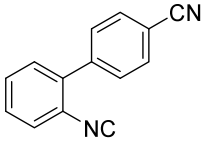
4'-Fluoro-2-isocyano-1,1'-biphenyl (1b): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.43 (m, 4H), 7.43 – 7.33 (m, 2H), 7.18 (t, *J* = 8.6 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.9, 162.9 (d, J_{C-F} = 248.2 Hz), 137.9, 133.1 (d, J_{C-F} = 3.1 Hz), 130.9 (d, J_{C-F} = 8.5 Hz), 130.6, 129.7, 128.4, 128.0, 124.7, 115.7 (d, J_{C-F} = 21.7 Hz).



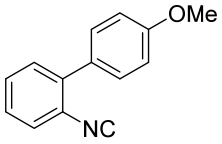
4'-Chloro-2-isocyano-1,1'-biphenyl (1c): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.43 (m, 6H), 7.43 – 7.35 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 137.7, 135.5, 134.7, 130.5, 130.4, 129.8, 129.0, 128.6, 128.0, 124.6.



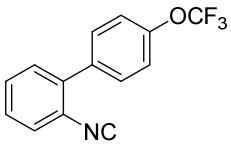
2-Isocyano-4'-methyl-1,1'-biphenyl (1d): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.9 Hz, 1H), 7.46 – 7.40 (m, 4H), 7.36 (t, *J* = 7.3 Hz, 1H), 7.30 (d, *J* = 7.7 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.5, 138.9, 138.4, 134.2, 130.6, 129.6, 129.4, 128.9, 128.0, 127.9, 124.7, 21.4.



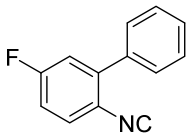
2'-Isocyano-[1,1'-biphenyl]-4-carbonitrile (1e): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.9 Hz, 2H), 7.63 (d, *J* = 7.9 Hz, 2H), 7.57 – 7.36 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.9, 141.7, 136.9, 132.5, 130.4, 130.0, 129.9, 129.5, 128.2, 124.6, 118.6, 112.5.



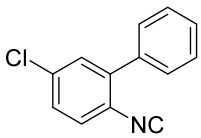
2-Isocyano-4'-methoxy-1,1'-biphenyl (1f): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.38 (m, 5H), 7.33 (t, J = 7.2 Hz, 1H), 7.01 (d, J = 8.4 Hz, 2H), 3.87 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.4, 159.8, 138.6, 130.6, 130.3, 129.6, 129.4, 128.0, 127.8, 124.7, 114.2, 55.5.



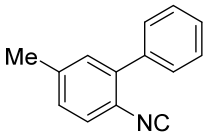
2-Isocyano-4'-(trifluoromethoxy)-1,1'-biphenyl (1g): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 8.2 Hz, 2H), 7.52 – 7.45 (m, 2H), 7.45 – 7.37 (m, 2H), 7.34 (d, J = 8.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 149.4 (q, $J_{C\text{-}F}$ = 1.8 Hz), 137.5, 135.7, 130.64, 130.56, 129.8, 128.7, 128.0, 124.7, 121.1, 120.6 (q, $J_{C\text{-}F}$ = 257.6 Hz).



5-Fluoro-2-isocyano-1,1'-biphenyl (1h): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.37 (m, 6H), 7.14 (dd, J = 8.9, 2.4 Hz, 1H), 7.11 – 7.02 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.9, 162.3 (d, $J_{C\text{-}F}$ = 252.0 Hz), 141.4 (d, $J_{C\text{-}F}$ = 8.6 Hz), 136.1, 129.9 (d, $J_{C\text{-}F}$ = 9.2 Hz), 129.0, 128.9, 128.8, 121.0, 117.6 (d, $J_{C\text{-}F}$ = 23.5 Hz), 115.4 (d, $J_{C\text{-}F}$ = 23.3 Hz).

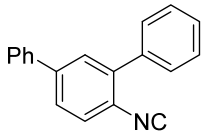


5-Chloro-2-isocyano-1,1'-biphenyl (1i): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.39 (m, 7H), 7.35 (d, J = 8.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 140.5, 135.9, 135.49, 130.7, 129.1, 129.0, 128.9, 128.8, 128.4, 123.2.

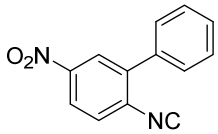


2-Isocyano-5-methyl-1,1'-biphenyl (1j): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.34 (m, 6H), 7.23 (s, 1H), 7.17 (d, J = 8.0 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.8, 140.0, 138.7, 137.3, 131.2, 129.0, 128.9, 128.6, 128.4, 127.8, 122.2,

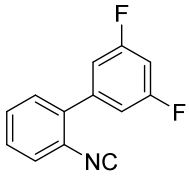
21.5.



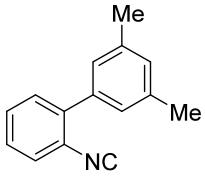
2-Isocyano-5-phenyl-1,1'-biphenyl (1k): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.63 – 7.54 (m, 6H), 7.54 – 7.37 (m, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.2, 142.7, 139.4, 139.3, 137.2, 129.3, 129.2, 129.1, 128.7, 128.6, 128.40, 128.36, 127.3, 126.8, 123.7.



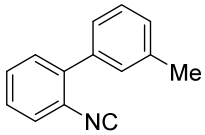
2-Isocyano-5-nitro-1,1'-biphenyl (1l): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, J = 1.9 Hz, 1H), 8.25 (dd, J = 8.6, 2.0 Hz, 1H), 7.67 (d, J = 8.7 Hz, 1H), 7.61 – 7.47 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 147.7, 140.6, 134.9, 129.7, 129.13, 129.11, 129.0, 125.9, 123.3.



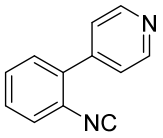
3',5'-Difluoro-2-isocyano-1,1'-biphenyl (1m): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.30 (m, 4H), 7.04 (d, J = 6.1 Hz, 2H), 6.88 (t, J = 8.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.8, 162.9 (dd, $J_{C\text{-}F}$ = 249.4, 12.9 Hz), 140.1 (t, $J_{C\text{-}F}$ = 9.9 Hz), 136.5, 130.3, 129.8, 129.3, 128.1, 124.5, 112.3 (dd, $J_{C\text{-}F}$ = 20.6, 5.6 Hz), 103.9 (t, $J_{C\text{-}F}$ = 25.2 Hz).



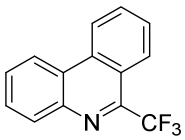
2-Isocyano-3',5'-dimethyl-1,1'-biphenyl (1n): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.39 (m, 3H), 7.40 – 7.30 (m, 1H), 7.14 (s, 2H), 7.08 (s, 1H), 2.40 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.4, 139.2, 138.1, 137.0, 130.6, 130.1, 129.5, 128.0, 127.9, 126.9, 124.7, 21.4.



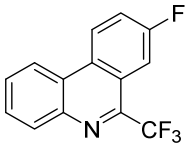
2-Isocyano-3'-methyl-1,1'-biphenyl (1o): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.28 (m, 7H), 7.23 (d, *J* = 6.9 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.5, 139.1, 138.3, 137.0, 130.6, 129.7, 129.5, 129.2, 128.5, 128.1, 127.9, 126.1, 124.7, 21.5.



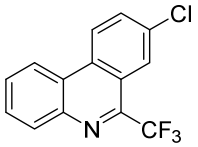
4-(2-Isocyanophenyl)pyridine (1p): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 5.0 Hz, 2H), 7.66 – 7.35 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 150.2, 144.8, 136.0, 130.2, 130.0, 129.7, 128.2, 124.5, 123.7.



6-(Trifluoromethyl)phenanthridine (2a): Yellow solid; m.p. 77-79 ℃; 85% yield (42 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 8.3 Hz, 1H), 8.54 (d, *J* = 7.6 Hz, 1H), 8.36 (d, *J* = 8.0 Hz, 1H), 8.27 (d, *J* = 7.7 Hz, 1H), 7.88 (t, *J* = 7.6 Hz, 1H), 7.84 – 7.68 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 146.6 (q, J_{C-F} = 32.9 Hz), 141.8, 134.0, 131.4, 131.2, 129.4, 129.3, 128.1, 126.0, 125.2, 122.6, 122.1, 122.1 (q, J_{C-F} = 277.1 Hz), 121.8; ^{19}F NMR (564 MHz, $CDCl_3$) δ -63.44 (d, *J* = 1.6 Hz, 3F).

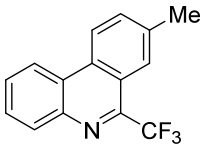


8-Fluoro-6-(trifluoromethyl)phenanthridine (2b): Yellow solid; m.p. 107-109 ℃; 81% yield (43 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (dd, *J* = 9.0, 5.3 Hz, 1H), 8.58 – 8.49 (m, 1H), 8.33 – 8.24 (m, 1H), 8.00 (d, *J* = 9.5 Hz, 1H), 7.85 – 7.75 (m, 2H), 7.72 – 7.63 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.6 (d, J_{C-F} = 250.1 Hz), 145.9 (qd, J_{C-F} =32.7, 3.9 Hz), 141.6, 131.4, 130.8, 129.8, 129.4, 125.3 (d, J_{C-F} = 8.7 Hz), 124.9, 123.0 (d, J_{C-F} = 8.6 Hz), 122.0, 121.9 (q, J_{C-F} = 276.9 Hz), 121.0 (d, J_{C-F} = 24.1 Hz), 110.9 (dq, J_{C-F} = 23.2, 3.2 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ -64.06 (s, 3F), -109.93 – -110.00 (m, 1F).

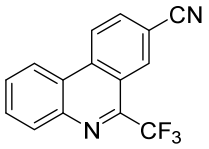


8-Chloro-6-(trifluoromethyl)phenanthridine (2c): Yellow solid; m.p. 126-128 ℃; 83% yield (42 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 8.9 Hz, 1H), 8.46 (d, *J* = 7.6 Hz, 1H), 8.28 (s, 1H), 8.24 (d, *J* = 7.6 Hz, 1H), 7.85 – 7.72 (m, 3H); ^{13}C NMR

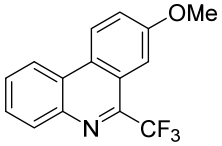
(150 MHz, $CDCl_3$) δ 145.5 (q, J_{C-F} = 33.4 Hz), 141.7, 134.4, 132.3, 132.1, 131.3, 129.8, 129.7, 125.3, 124.7, 124.3, 122.6, 122.0, 121.8 (q, J_{C-F} = 277.1 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ -63.63 (d, J = 1.3 Hz, 3F).



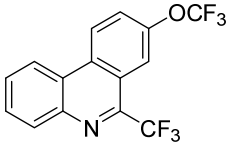
8-Methyl-6-(trifluoromethyl)phenanthridine (2d): White solid; m.p. 108-110 ℃; 77% yield (40 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 8.58 – 8.49 (m, 2H), 8.30 – 8.22 (m, 1H), 8.12 (s, 1H), 7.81 – 7.68 (m, 3H), 2.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, overlapping peaks) δ 146.3 (q, J_{C-F} = 32.8 Hz), 141.6, 138.4, 133.3, 132.0, 131.2, 129.2, 129.0, 125.3 (q, J_{C-F} = 3.3 Hz), 122.5, 122.1 (q, J_{C-F} = 277.1 Hz), 122.1, 122.0, 22.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.45 (d, J = 2.4 Hz, 3F).



6-(Trifluoromethyl)phenanthridine-8-carbonitrile (2e): White solid; m.p. 185-187 ℃; 81% yield (44 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 8.81 (d, J = 8.6 Hz, 1H), 8.70 (s, 1H), 8.62 (d, J = 7.9 Hz, 1H), 8.34 (d, J = 7.9 Hz, 1H), 8.10 (d, J = 8.5 Hz, 1H), 7.98 – 7.85 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.9 (q, J_{C-F} = 33.9 Hz), 142.8, 136.4, 132.7, 131.7, 131.4, 131.3, 130.4, 124.2, 124.0, 122.8, 121.6 (q, J_{C-F} = 277.2 Hz), 121.3, 118.1, 112.1; ^{19}F NMR (564 MHz, $CDCl_3$) δ -63.30 (d, J = 1.4 Hz, 3F).

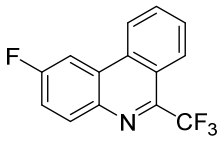


8-Methoxy-6-(trifluoromethyl)phenanthridine (2f): White solid; m.p. 105-107 ℃; 78% yield (43 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, J = 9.1 Hz, 1H), 8.51 – 8.43 (m, 1H), 8.28 – 8.20 (m, 1H), 7.78 – 7.69 (m, 2H), 7.65 (s, 1H), 7.52 (d, J = 8.8 Hz, 1H), 3.99 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.1, 145.6 (q, J_{C-F} = 32.8 Hz), 141.1, 131.2, 129.4, 128.6, 128.4, 125.4, 124.2, 123.3, 122.6, 122.2 (q, J_{C-F} = 277.0 Hz), 121.7, 105.6, 55.7; ^{19}F NMR (564 MHz, $CDCl_3$) δ -64.12 (s, 3F).

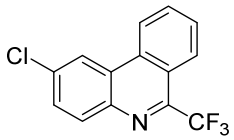


8-(Trifluoromethoxy)-6-(trifluoromethyl)phenanthridine (2g): Yellow solid; m.p. 101-103 ℃; 48% yield (32 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, J = 9.1 Hz,

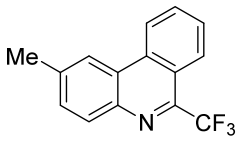
1H), 8.56 (d, J = 7.3 Hz, 1H), 8.30 (d, J = 7.4 Hz, 1H), 8.19 (s, 1H), 7.89 – 7.75 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, overlapping peaks) δ 148.4, 146.0 (q, J_{C-F} = 33.6 Hz), 141.9, 132.5, 131.5, 130.0 125.1, 125.0, 124.5, 122.6, 122.2, 121.8 (q, J_{C-F} = 277.0 Hz), 120.7 (q, J_{C-F} = 258.9 Hz), 117.4; ^{19}F NMR (564 MHz, $CDCl_3$) δ -57.85 (s, 3F), -63.82 (d, J = 1.4 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 2921, 1485, 1254, 1119, 761; HRMS (CI) calcd $C_{15}H_8NOF_6$ $[M + H]^+$: 332.0510, found: 332.0504.



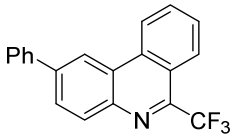
2-Fluoro-6-(trifluoromethyl)phenanthridine (2h): Yellow solid; m.p. 123-125 ℃; 78% yield (41 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, J = 8.3 Hz, 1H), 8.37 (d, J = 7.9 Hz, 1H), 8.27 (dd, J = 8.6, 5.8 Hz, 1H), 8.16 (d, J = 8.8 Hz, 1H), 7.92 (t, J = 7.6 Hz, 1H), 7.80 (t, J = 7.6 Hz, 1H), 7.58 – 7.47 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.8 (d, J_{C-F} = 250.7 Hz), 146.0 (qd, J_{C-F} = 33.2, 2.6 Hz), 138.7, 133.7 (d, J_{C-F} = 9.5 Hz), 133.5 (d, J_{C-F} = 4.2 Hz), 131.6, 128.9, 126.9 (d, J_{C-F} = 9.5 Hz), 126.1 (d, J_{C-F} = 3.0 Hz), 122.8, 122.0 (q, J_{C-F} = 276.9 Hz), 121.9, 118.6 (d, J_{C-F} = 24.6 Hz), 107.3 (d, J_{C-F} = 23.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.49 (s, 3F), -108.76 (s, 1F).



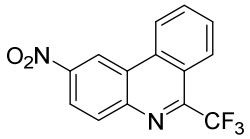
2-Chloro-6-(trifluoromethyl)phenanthridine (2i): Yellow solid; m.p. 104-106 ℃; 74% yield (42 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, J = 8.3 Hz, 1H), 8.52 (s, 1H), 8.37 (d, J = 7.9 Hz, 1H), 8.20 (d, J = 8.7 Hz, 1H), 7.93 (t, J = 7.5 Hz, 1H), 7.80 (t, J = 7.6 Hz, 1H), 7.73 (d, J = 8.6 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 146.9 (q, J_{C-F} = 33.1 Hz), 140.3, 135.6, 133.1, 132.7, 131.8, 130.1, 128.9, 126.3, 126.2, 122.7, 122.1, 121.9, 121.9 (q, J_{C-F} = 277.1 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.52 (d, J = 2.1 Hz, 3F).



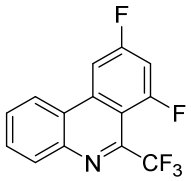
2-Methyl-6-(trifluoromethyl)phenanthridine (2j): White solid; m.p. 113-115 ℃; 81% yield (42 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, J = 8.3 Hz, 1H), 8.33 (d, J = 8.2 Hz, 1H), 8.30 (s, 1H), 8.14 (d, J = 8.3 Hz, 1H), 7.85 (t, J = 7.6 Hz, 1H), 7.71 (t, J = 7.7 Hz, 1H), 7.59 (d, J = 8.3 Hz, 1H), 2.63 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.6 (q, J_{C-F} = 32.8 Hz), 140.2, 139.6, 133.7, 131.2, 131.1, 130.9, 128.0, 125.9 (q, J_{C-F} = 3.2 Hz), 125.0, 122.5, 122.2 (q, J_{C-F} = 276.9 Hz), 121.9, 121.7, 22.2; ^{19}F NMR (564 MHz, $CDCl_3$) δ -63.35 (d, J = 2.1 Hz, 3F).



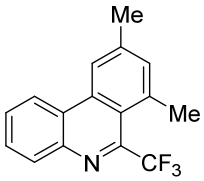
2-Phenyl-6-(trifluoromethyl)phenanthridine (2k): White solid; m.p. 114-116 ℃; 64% yield (41 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 – 8.70 (m, 2H), 8.39 (d, *J* = 8.0 Hz, 1H), 8.34 (d, *J* = 8.5 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 1H), 7.93 (t, *J* = 7.6 Hz, 1H), 7.83 – 7.73 (m, 3H), 7.55 (t, *J* = 7.4 Hz, 2H), 7.46 (t, *J* = 7.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 146.4 (q, J_{C-F} = 33.0 Hz), 142.2, 141.2, 140.5, 134.1, 131.6, 131.5, 129.2, 128.9, 128.3, 128.3, 127.8, 126.1, 125.4, 122.7, 122.1, 122.1 (q, J_{C-F} = 277.0 Hz), 120.4; ^{19}F NMR (564 MHz, $CDCl_3$) δ -63.38 (s, 3F).



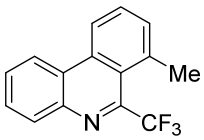
2-Nitro-6-(trifluoromethyl)phenanthridine (2l): White solid; m.p. 187-189 ℃; 64% yield (37 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.51 (d, *J* = 1.4 Hz, 1H), 8.79 (d, *J* = 8.3 Hz, 1H), 8.58 (dd, *J* = 8.9, 1.8 Hz, 1H), 8.51 – 8.39 (m, 2H), 8.08 (t, *J* = 7.7 Hz, 1H), 7.92 (t, *J* = 7.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.0 (q, J_{C-F} = 33.7 Hz), 147.5, 144.6, 134.1, 132.9, 132.9, 129.8 , 126.7 (q, J_{C-F} = 3.4 Hz), 125.3, 123.2, 123.0, 122.2, 121.6 (q, J_{C-F} = 277.6 Hz), 118.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.76 (d, *J* = 2.5 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 1511, 1344, 1128, 774, 720; HRMS (CI) calcd $C_{14}H_8N_2F_3O_2$ $[M + H]^+$: 293.0538, found: 293.0542.



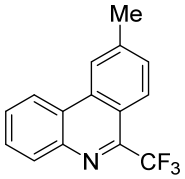
7,9-Difluoro-6-(trifluoromethyl)phenanthridine (2m): White solid; m.p. 112-114 ℃; 62% yield (35 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 8.0 Hz, 1H), 8.28 (d, *J* = 7.9 Hz, 1H), 8.14 (d, *J* = 9.3 Hz, 1H), 7.91 – 7.78 (m, 2H), 7.25 (t, *J* = 9.6 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.0 (dd, J_{C-F} = 255.3, 13.3 Hz), 159.5 (dd, J_{C-F} = 262.7, 13.3 Hz), 142.6 (q, J_{C-F} = 37.3 Hz), 141.8, 137.8 (dd, J_{C-F} = 10.8, 4.5 Hz), 131.5, 130.8, 130.0, 123.7, 122.6, 121.4 (q, J_{C-F} = 275.2 Hz), 109.5 (dd, J_{C-F} = 15.4, 1.8 Hz), 105.1 (t, J_{C-F} = 27.5 Hz), 104.5 (dd, J_{C-F} = 22.3, 4.2 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ -65.81 (d, *J* = 44.5 Hz, 3F), -100.20 (qt, *J* = 44.5, 12.1 Hz, 1F), -101.85 (dt, *J* = 12.3, 9.1 Hz, 1F); FT-IR (thin film, KBr): ν (cm^{-1}) 2920, 2850, 1632, 1122, 767; HRMS (CI) calcd $C_{14}H_7NF_5$ $[M + H]^+$: 284.0499, found: 284.0506.



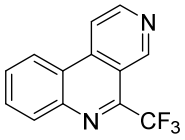
7,9-Dimethyl-6-(trifluoromethyl)phenanthridine (2n): Yellowish solid; m.p. 57-59 ℃; 58% yield (32 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 7.7 Hz, 1H), 8.35 (s, 1H), 8.20 (d, *J* = 7.6 Hz, 1H), 7.80 – 7.68 (m, 2H), 7.41 (s, 1H), 2.88 (s, 3H), 2.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.06 (q, J_{C-F} = 33.5 Hz), 141.0, 140.9, 135.9, 135.6, 134.6, 130.7, 129.1, 129.0, 125.4, 122.4, 122.2 (q, J_{C-F} = 275.4 Hz), 120.6, 120.5, 23.4 (q, J_{C-F} = 8.9 Hz), 21.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.81 (s, 3F).



7-Methyl-6-(trifluoromethyl)phenanthridine (2o): White solid; m.p. 53-55 ℃; 45% yield (23 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 8.4 Hz, 1H), 8.59 (d, *J* = 8.8 Hz, 1H), 8.24 (d, *J* = 7.2 Hz, 1H), 7.83 – 7.72 (m, 3H), 7.61 (d, *J* = 7.2 Hz, 1H), 2.93 (s, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2 (q, J_{C-F} = 33.7 Hz), 140.8, 136.1, 135.7, 132.8, 130.8, 130.7, 129.4, 129.3, 125.5, 122.5, 122.4, 122.2 (q, J_{C-F} = 275.5 Hz), 120.9, 23.6 (q, J_{C-F} = 8.9 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.78 (s, 3F).

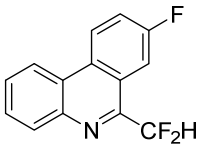


9-Methyl-6-(trifluoromethyl)phenanthridine (2o'): White solid; m.p. 82-84 ℃; 36% yield (19 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 7.4 Hz, 1H), 8.48 (s, 1H), 8.27 (d, *J* = 7.6 Hz, 2H), 7.84 – 7.74 (m, 2H), 7.59 (d, *J* = 8.5 Hz, 1H), 2.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.6 (q, J_{C-F} = 32.8 Hz), 142.2, 142.1, 134.3, 131.2, 130.0, 129.3, 129.1, 125.9 (q, J_{C-F} = 3.2 Hz), 125.1, 122.3, 122.2, 122.1 (q, J_{C-F} = 277.1 Hz), 120.0, 22.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.51 (d, *J* = 2.6 Hz, 3F).

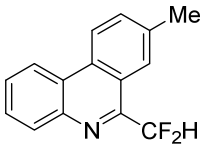


5-(Trifluoromethyl)benzo[c][2,7]naphthyridine (2p): White solid; m.p. 139-141 ℃; 60% yield (30 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.74 (s, 1H), 9.03 (d, *J* = 5.5 Hz, 1H), 8.62 (d, *J* = 8.1 Hz, 1H), 8.47 (d, *J* = 5.5 Hz, 1H), 8.35 (d, *J* = 8.1 Hz, 1H), 7.96 (t, *J* = 7.5 Hz, 1H), 7.88 (t, *J* = 7.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8 (q,

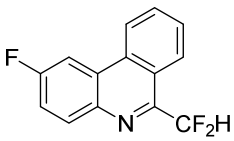
$J_{C\text{-}F}$ = 4.3 Hz), 149.2, 146.4 (q, $J_{C\text{-}F}$ = 34.6 Hz), 143.1, 138.8, 131.8, 131.5, 130.1, 123.2, 122.8, 121.5 (q, $J_{C\text{-}F}$ = 276.9 Hz), 117.3, 115.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.98 (d, J = 1.2 Hz, 3F).



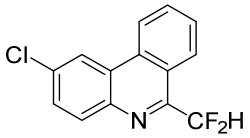
6-(Difluoromethyl)-8-fluorophenanthridine (3a): White solid; m.p. 118-120 ℃; 47% yield (23 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 – 8.60 (m, 1H), 8.59 – 8.45 (m, 1H), 8.27 – 8.13 (m, 2H), 7.85 – 7.71 (m, 2H), 7.65 (t, J = 7.6 Hz, 1H), 6.99 (t, J = 54.3 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.5 (d, $J_{C\text{-}F}$ = 249.4 Hz), 150.7 (td, $J_{C\text{-}F}$ = 26.8, 4.1 Hz), 142.3, 130.9, 130.7, 129.2, 129.1, 125.1 (d, $J_{C\text{-}F}$ = 8.6 Hz), 124.7, 123.6 (d, $J_{C\text{-}F}$ = 8.6 Hz), 122.1, 120.8 (d, $J_{C\text{-}F}$ = 24.1 Hz), 118.4 (t, $J_{C\text{-}F}$ = 243.3 Hz), 111.4 (dt, $J_{C\text{-}F}$ = 22.6, 4.4 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ -110.70 (ddd, J = 9.5, 8.2, 5.2 Hz, 1F), -111.03 (dd, J = 54.3, 1.2 Hz, 2F);



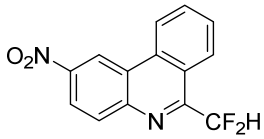
6-(Difluoromethyl)-8-methylphenanthridine (3b): White solid; m.p. 111-113 ℃; 52% yield (25 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, J = 8.1 Hz, 2H), 8.34 (s, 1H), 8.17 (d, J = 8.0 Hz, 1H), 7.83 – 7.68 (m, 3H), 7.01 (t, J = 54.4 Hz, 1H), 2.62 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.2 (t, $J_{C\text{-}F}$ = 26.3 Hz), 142.3, 138.0, 133.2, 131.8, 130.7, 128.8, 128.7, 125.9 (t, $J_{C\text{-}F}$ = 3.8 Hz), 125.2, 122.7, 122.4, 122.1, 118.6 (t, $J_{C\text{-}F}$ = 243.5 Hz), 22.0; ^{19}F NMR (564 MHz, $CDCl_3$) δ -110.80 (dd, J = 54.6, 1.4 Hz, 2F).



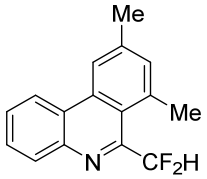
6-(Difluoromethyl)-2-fluorophenanthridine (3c): White solid; m.p. 131-133 ℃; 52% yield (26 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, J = 8.1 Hz, 1H), 8.50 (d, J = 8.3 Hz, 1H), 8.25 – 8.08 (m, 2H), 7.88 (t, J = 7.6 Hz, 1H), 7.77 (t, J = 7.6 Hz, 1H), 7.49 (td, J = 8.8, 2.3 Hz, 1H), 6.99 (t, J = 54.3 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.4 (d, $J_{C\text{-}F}$ = 249.6 Hz), 150.8 (td, $J_{C\text{-}F}$ = 26.6, 2.6 Hz), 139.3, 133.3 (d, $J_{C\text{-}F}$ = 4.1 Hz), 133.1 (d, $J_{C\text{-}F}$ = 9.4 Hz), 131.3, 128.5, 126.6, 122.6, 122.5, 118.4 (t, $J_{C\text{-}F}$ = 243.3 Hz), 118.3, 118.1, 107.3 (d, $J_{C\text{-}F}$ = 23.5 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ -109.93 (dd, J = 14.7, 8.6 Hz, 1F), -110.64 (d, J = 54.3 Hz, 2F).



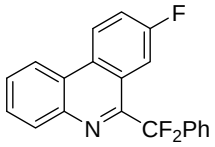
2-Chloro-6-(difluoromethyl)phenanthridine (3d): White solid; m.p. 127-129 ℃; 48% yield (26 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 – 8.51 (m, 2H), 8.50 (d, *J* = 1.9 Hz, 1H), 8.10 (d, *J* = 8.7 Hz, 1H), 7.89 (t, *J* = 7.7 Hz, 1H), 7.77 (t, *J* = 7.7 Hz, 1H), 7.69 (dd, *J* = 8.7, 2.1 Hz, 1H), 6.99 (t, *J* = 54.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.7 (t, J_{C-F} = 26.5 Hz), 140.9, 134.9, 132.8, 132.2, 131.6, 129.8, 128.6, 126.6 (t, J_{C-F} = 4.3 Hz), 126.1, 122.7, 122.5, 122.0, 118.3 (t, J_{C-F} = 243.6 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.71 (dd, *J* = 54.4, 2.6 Hz, 2F).



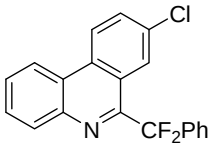
6-(Difluoromethyl)-2-nitrophenanthridine (3e): White solid; m.p. 175-177 ℃; 50% yield (27 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.49 (s, 1H), 8.75 (d, *J* = 8.3 Hz, 1H), 8.64 (d, *J* = 8.1 Hz, 1H), 8.55 (d, *J* = 8.8 Hz, 1H), 8.32 (d, *J* = 8.9 Hz, 1H), 8.04 (t, *J* = 7.6 Hz, 1H), 7.88 (t, *J* = 7.6 Hz, 1H), 7.02 (t, *J* = 54.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.9 (t, J_{C-F} = 26.8 Hz), 147.1, 145.4, 133.9, 132.6, 132.3, 129.5, 127.1 (t, J_{C-F} = 4.4 Hz), 125.1, 123.0, 122.8, 122.8 (t, J_{C-F} = 1.9 Hz), 118.9, 117.8 (t, J_{C-F} = 244.4 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ -111.16 (dd, *J* = 54.2, 1.9 Hz, 2F); FT-IR (thin film, KBr): ν (cm^{-1}) 1506, 1345, 1128, 1017, 774; HRMS (CI) calcd $C_{14}H_9N_2F_2O_2$ $[M + H]^+$: 275.0632, found: 275.0629.



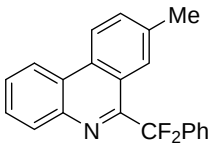
6-(Difluoromethyl)-7,9-dimethylphenanthridine (3f): White solid; m.p. 116-119 ℃; 45% yield (23 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 8.0 Hz, 1H), 8.36 (s, 1H), 8.20 (d, *J* = 7.9 Hz, 1H), 7.79 – 7.65 (m, 2H), 7.40 (s, 1H), 7.34 (t, *J* = 55.1 Hz, 1H), 2.94 (s, 3H), 2.58 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 150.4 (t, J_{C-F} = 23.3 Hz), 142.0, 140.9, 135.6, 134.1, 130.5, 128.9, 128.4, 127.0, 125.1, 122.4, 121.6, 120.7, 115.6 (t, J_{C-F} = 244.1 Hz), 24.3 (t, J_{C-F} = 7.4 Hz), 22.0; ^{19}F NMR (564 MHz, $CDCl_3$) δ -112.14 (d, *J* = 55.1 Hz, 2F); FT-IR (thin film, KBr): ν (cm^{-1}) 2921, 2850, 1447, 1016, 769; HRMS (CI) calcd $C_{16}H_{14}NF_2$ $[M + H]^+$: 258.1094, found: 258.1089.



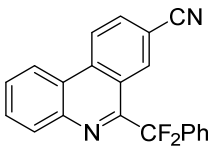
6-(Difluoro(phenyl)methyl)-8-fluorophenanthridine (4a): White solid; m.p. 140-142 ℃; 70% yield (45 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (dd, *J* = 9.0, 5.4 Hz, 1H), 8.54 – 8.42 (m, 1H), 8.27 – 8.16 (m, 1H), 8.05 (d, *J* = 10.1 Hz, 1H), 7.80 – 7.70 (m, 2H), 7.66 (d, *J* = 6.7 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.51 – 7.40 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.2 (d, J_{C-F} = 248.5 Hz), 152.5 (td, J_{C-F} = 29.1, 4.0 Hz), 141.9, 136.3 (t, J_{C-F} = 26.1 Hz), 131.3, 130.8, 130.4, 129.0 (d, J_{C-F} = 3.2 Hz), 128.5, 126.3 (t, J_{C-F} = 5.6 Hz), 125.0 (d, J_{C-F} = 8.6 Hz), 124.4, 124.2 (d, J_{C-F} = 8.6 Hz), 121.8, 120.4 (t, J_{C-F} = 244.0 Hz), 120.3, 120.2, 112.2 (dt, J_{C-F} = 23.0, 5.3 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ -88.52 (s, 2F), -110.76 – -110.88 (m, 1F); FT-IR (thin film, KBr): ν (cm^{-1}) 2921, 2851, 1452, 1197, 763; HRMS (CI) calcd $C_{20}H_{13}NF_3$ $[M + H]^+$: 324.1000, found: 324.1014.



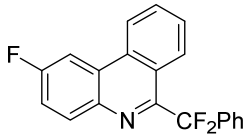
8-Chloro-6-(difluoro(phenyl)methyl)phenanthridine (4b): White solid; m.p. 152-154 ℃; 62% yield (42 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 8.9 Hz, 1H), 8.49 (d, *J* = 7.6 Hz, 1H), 8.41 (s, 1H), 8.18 (d, *J* = 7.7 Hz, 1H), 7.80 – 7.71 (m, 3H), 7.67 (d, *J* = 6.5 Hz, 2H), 7.52 – 7.42 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 152.2 (t, J_{C-F} = 29.3 Hz), 142.1, 136.3 (t, J_{C-F} = 26.0 Hz), 133.6, 132.4, 131.4, 131.3, 130.4, 129.3, 129.0, 128.5, 126.7 (t, J_{C-F} = 5.6 Hz), 126.31 (t, J_{C-F} = 5.6 Hz), 124.2, 124.1, 123.8, 121.9, 120.5 (t, J_{C-F} = 244.1 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ -88.01 (s, 2F); FT-IR (thin film, KBr): ν (cm^{-1}) 2919, 1616, 1335, 1140, 758; HRMS (CI) calcd $C_{20}H_{13}NF_2{}^{35}Cl$ $[M + H]^+$: 340.0705, found: 340.0701.



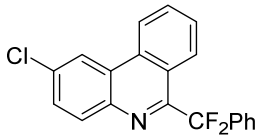
6-(Difluoro(phenyl)methyl)-8-methylphenanthridine (4c): White solid; m.p. 127-129 ℃; 65% yield (41 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 7.7 Hz, 2H), 8.20 (d, *J* = 5.4 Hz, 1H), 8.17 (s, 1H), 7.77 – 7.70 (m, 2H), 7.70 – 7.60 (m, 3H), 7.50 – 7.39 (m, 3H), 2.52 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 152.9 (t, J_{C-F} = 28.3 Hz), 141.9, 137.5, 136.9 (t, J_{C-F} = 26.2 Hz), 132.6, 132.0, 131.2, 130.2, 128.6, 128.44, 128.42, 126.8 (t, J_{C-F} = 4.9 Hz), 126.3 (t, J_{C-F} = 5.6 Hz), 124.9, 123.2, 122.4, 121.9, 120.5 (t, J_{C-F} = 243.9 Hz), 22.1; ^{19}F NMR (564 MHz, $CDCl_3$) δ -87.93 (s, 2F); FT-IR (thin film, KBr): ν (cm^{-1}) 2920, 2850, 1454, 1100, 791; HRMS (CI) calcd $C_{20}H_{16}NF_2$ $[M + H]^+$: 320.1251, found: 320.1264.



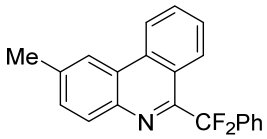
6-(Difluoro(phenyl)methyl)phenanthridine-8-carbonitrile (4d): White solid; m.p. 226-228 ℃; 68% yield (45 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (s, 1H), 8.75 (d, *J* = 8.7 Hz, 1H), 8.57 (d, *J* = 7.9 Hz, 1H), 8.21 (d, *J* = 7.9 Hz, 1H), 8.00 (d, *J* = 8.6 Hz, 1H), 7.90 – 7.78 (m, 2H), 7.65 (d, *J* = 7.0 Hz, 2H), 7.54 – 7.44 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 152.6 (t, J_{C-F} = 29.9 Hz), 143.1, 136.5, 135.8 (t, J_{C-F} = 25.9 Hz), 132.9 (t, J_{C-F} = 5.6 Hz), 132.0, 131.6, 130.9, 130.6, 129.5, 128.6, 126.3 (t, J_{C-F} = 5.6 Hz), 123.9, 123.5, 122.6, 122.4, 120.5 (t, J_{C-F} = 244.2 Hz), 118.5, 111.3; ^{19}F NMR (564 MHz, $CDCl_3$) δ -87.40 (s, 2F); FT-IR (thin film, KBr): ν (cm^{-1}) 2117, 1540, 1344, 1064, 705; HRMS (CI) calcd $C_{21}H_{13}N_2F_2$ $[M + H]^+$: 331.1047, found: 331.1044.



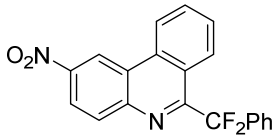
6-(Difluoro(phenyl)methyl)-2-fluorophenanthridine (4e): White solid; m.p. 131-133 ℃; 64% yield (41 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 8.3 Hz, 1H), 8.40 (d, *J* = 8.3 Hz, 1H), 8.26 – 8.09 (m, 2H), 7.84 (t, *J* = 7.6 Hz, 1H), 7.70 – 7.57 (m, 3H), 7.56 – 7.35 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.4 (d, J_{C-F} = 249.2 Hz), 152.6 (td, J_{C-F} = 28.6, 2.5 Hz), 139.1 (s), 136.6 (t, J_{C-F} = 26.1 Hz), 133.6 (d, J_{C-F} = 9.4 Hz), 133.5 (d, J_{C-F} = 4.2 Hz), 130.9, 130.3, 128.5, 128.2, 127.6 (t, J_{C-F} = 4.8 Hz), 126.4, 126.3 (t, J_{C-F} = 5.5 Hz), 123.1, 122.7, 120.4 (t, J_{C-F} = 243.9 Hz), 118.1 (d, J_{C-F} = 24.4 Hz), 107.1 (d, J_{C-F} = 23.5 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ -87.92 (s, 2F), -110.33 – -110.43 (m, 1F).



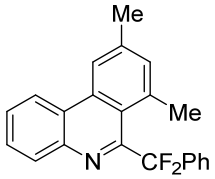
2-Chloro-6-(difluoro(phenyl)methyl)phenanthridine (4f): White solid; m.p. 152-154 ℃; 60% yield (41 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 8.9 Hz, 1H), 8.50 (d, *J* = 7.5 Hz, 1H), 8.41 (s, 1H), 8.18 (d, *J* = 7.4 Hz, 1H), 7.82 – 7.69 (m, 3H), 7.67 (d, *J* = 6.5 Hz, 2H), 7.50 – 7.36 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 152.2 (t, J_{C-F} = 29.4 Hz), 142.1, 136.3 (t, J_{C-F} = 26.0 Hz), 133.6, 132.4, 131.5, 131.3, 130.4, 129.4, 129.0, 128.5, 126.7 (t, J_{C-F} = 5.5 Hz), 126.3 (t, J_{C-F} = 5.6 Hz), 124.2, 124.2, 123.8, 121.9, 120.5 (t, J_{C-F} = 244.1 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ -88.03 (s, 2F); FT-IR (thin film, KBr): ν (cm^{-1}) 1452, 1246, 1136, 941, 727; HRMS (CI) calcd $C_{20}H_{13}NF_2$ $[M + H]^+$: 340.0705, found: 340.0712.



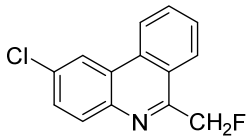
6-(Difluoro(phenyl)methyl)-2-methylphenanthridine (4g): White solid; m.p. 162-164 ℃; 65% yield (41 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, J = 8.2 Hz, 1H), 8.38 (s, 1H), 8.33 (d, J = 8.0 Hz, 1H), 8.13 (d, J = 8.2 Hz, 1H), 7.81 (t, J = 7.4 Hz, 1H), 7.65 (d, J = 6.3 Hz, 2H), 7.63 – 7.56 (m, 2H), 7.49 – 7.34 (m, 3H), 2.65 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 152.2 (t, J_{C-F} = 28.2 Hz), 140.6, 138.7, 136.9 (t, J_{C-F} = 26.2 Hz), 133.8, 131.0, 130.8, 130.6, 130.2, 128.5, 127.5, 127.4, 126.3 (t, J_{C-F} = 5.4 Hz), 124.7, 123.2, 122.5, 121.7, 120.4 (t, J_{C-F} = 243.8 Hz), 22.3; ^{19}F NMR (564 MHz, $CDCl_3$) δ -88.06 (s, 2F); FT-IR (thin film, KBr): ν (cm^{-1}) 2919, 2850, 1633, 1259, 701; HRMS (CI) calcd $C_{21}H_{16}NF_2$ $[M + H]^+$: 320.1251, found: 320.1263.



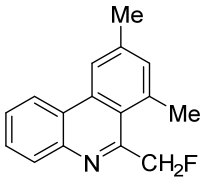
6-(Difluoro(phenyl)methyl)-2-nitrophenanthridine (4h): White solid; m.p. 198-200 ℃; 62% yield (43 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.49 (s, 1H), 8.74 (d, J = 8.2 Hz, 1H), 8.50 (t, J = 9.8 Hz, 2H), 8.31 (d, J = 9.0 Hz, 1H), 7.96 (t, J = 7.5 Hz, 1H), 7.76 (t, J = 7.6 Hz, 1H), 7.66 (d, J = 6.4 Hz, 2H), 7.53 – 7.41 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9 (t, J_{C-F} = 29.1 Hz), 147.0, 145.1, 136.1 (t, J_{C-F} = 25.9 Hz), 134.0, 132.7, 132.1, 130.6, 129.1, 129.0, 128.6, 128.0 (t, J_{C-F} = 5.3 Hz), 126.3 (t, J_{C-F} = 5.7 Hz), 124.8, 123.3, 122.8, 120.2 (t, J_{C-F} = 244.9 Hz), 118.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -88.29 (s, 2F); FT-IR (thin film, KBr): ν (cm^{-1}) 1519, 1244, 1105, 756, 705; HRMS (CI) calcd $C_{20}H_{13}N_2O_2F_2$ $[M + H]^+$: 351.0945, found: 351.0948.



6-(Difluoro(phenyl)methyl)-7,9-dimethylphenanthridine (4i): White solid; m.p. 140-142 ℃; 57% yield (38 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 – 8.52 (m, 1H), 8.38 (s, 1H), 8.08 – 8.01 (m, 1H), 7.73 – 7.62 (m, 4H), 7.53 – 7.42 (m, 3H), 7.36 (s, 1H), 2.67 (s, 3H), 2.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, overlapping peaks) δ 152.2 (t, J_{C-F} = 30.0 Hz), 141.1, 140.3, 138.1 (t, J_{C-F} = 27.0 Hz), 136.5, 135.7, 134.1, 130.5, 129.9, 128.6, 128.2, 126.8 (t, J_{C-F} = 5.2 Hz), 124.7, 122.3, 122.0, 121.1 (t, J_{C-F} = 243.4 Hz), 120.3, 25.1 (t, J_{C-F} = 10.6 Hz), 21.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.17 (s, 2F); FT-IR (thin film, KBr): ν (cm^{-1}) 2920, 2851, 1456, 1062, 762; HRMS (CI) calcd $C_{22}H_{18}NF_2$ $[M + H]^+$: 334.1407, found: 334.1400.



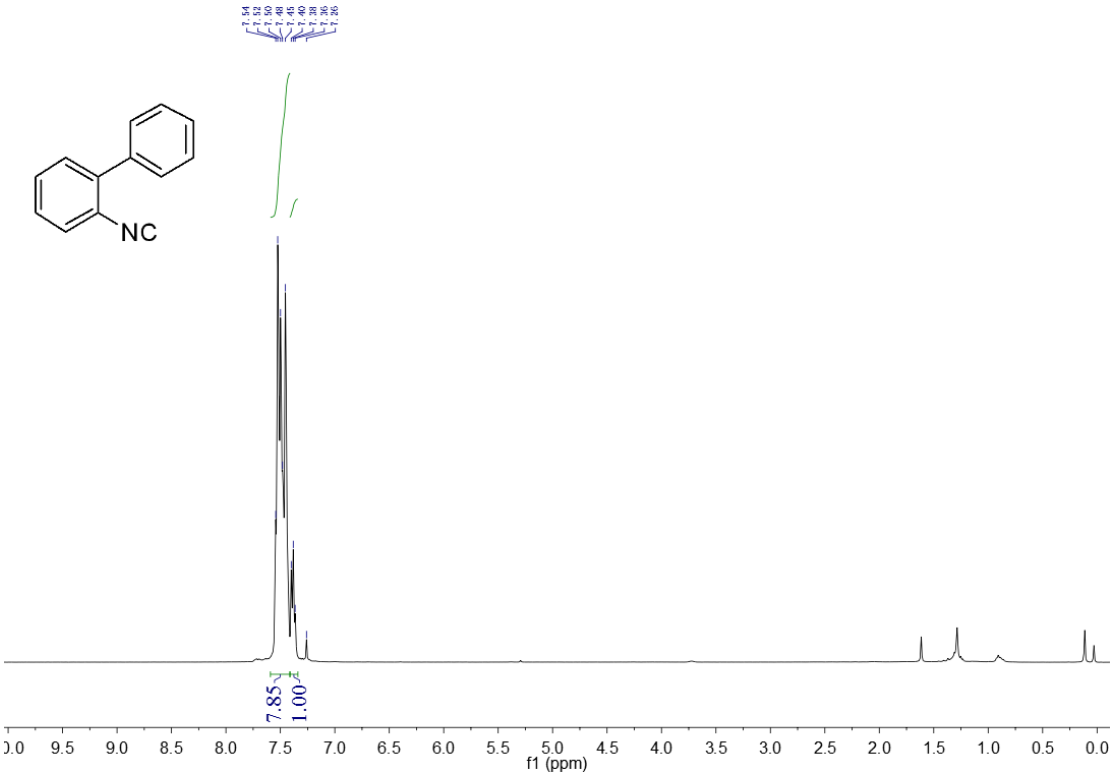
2-Chloro-6-(fluoromethyl)phenanthridine (5a): Yellow solid; m.p. 127-129 ℃; 21% yield (10 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 8.2 Hz, 1H), 8.52 (s, 1H), 8.35 (d, *J* = 8.0 Hz, 1H), 8.11 (d, *J* = 8.7 Hz, 1H), 7.90 (t, *J* = 7.5 Hz, 1H), 7.78 (t, *J* = 7.5 Hz, 1H), 7.69 (d, *J* = 8.5 Hz, 1H), 5.99 (d, *J* = 47.3 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 155.2 (d, J_{C-F} = 17.0 Hz), 141.7, 133.9, 132.3, 131.9, 131.4, 129.6, 128.5, 126.4 (d, J_{C-F} = 4.0 Hz), 125.8, 124.9, 122.6, 121.9, 85.4 (d, J_{C-F} = 169.8 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ -213.38 (t, *J* = 47.3 Hz, 1F).



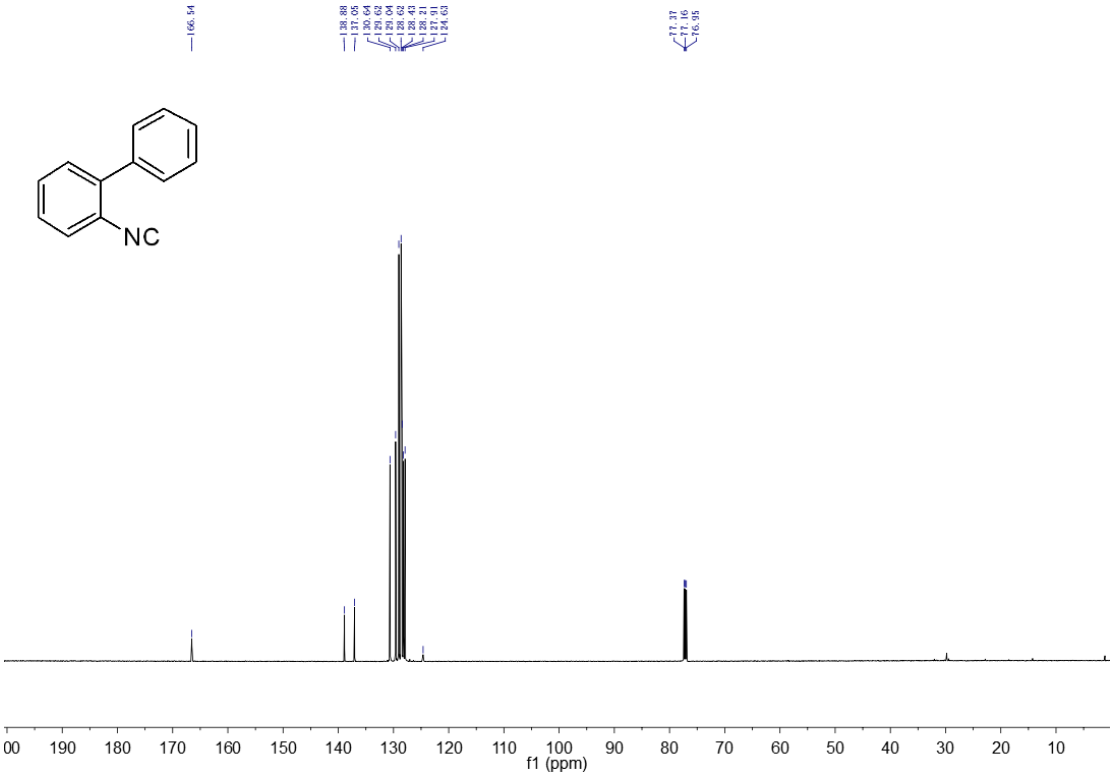
6-(Fluoromethyl)-7,9-dimethylphenanthridine (5b): Yellow solid; m.p. 116-119 ℃; 24% yield (11 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 8.1 Hz, 1H), 8.36 (s, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 7.79 – 7.60 (m, 2H), 7.38 (s, 1H), 6.05 (d, *J* = 47.2 Hz, 2H), 2.99 (s, 3H), 2.59 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.3 (d, J_{C-F} = 16.1 Hz), 142.8, 140.6, 136.2, 135.3, 133.7, 130.1, 128.7, 127.7, 124.8 (d, J_{C-F} = 1.1 Hz), 123.2, 122.5, 120.7, 87.8 (d, J_{C-F} = 170.4 Hz), 23.8 (d, J_{C-F} = 7.7 Hz), 22.0; ^{19}F NMR (564 MHz, $CDCl_3$) δ -205.15 (t, *J* = 47.3 Hz, 1F); FT-IR (thin film, KBr): ν (cm^{-1}) 2924, 2853, 1616, 1459, 756; HRMS (CI) calcd $C_{16}H_{15}NF$ $[M + H]^+$: 240.1189, found: 240.1180.

5. NMR Spectra for the substrates and products

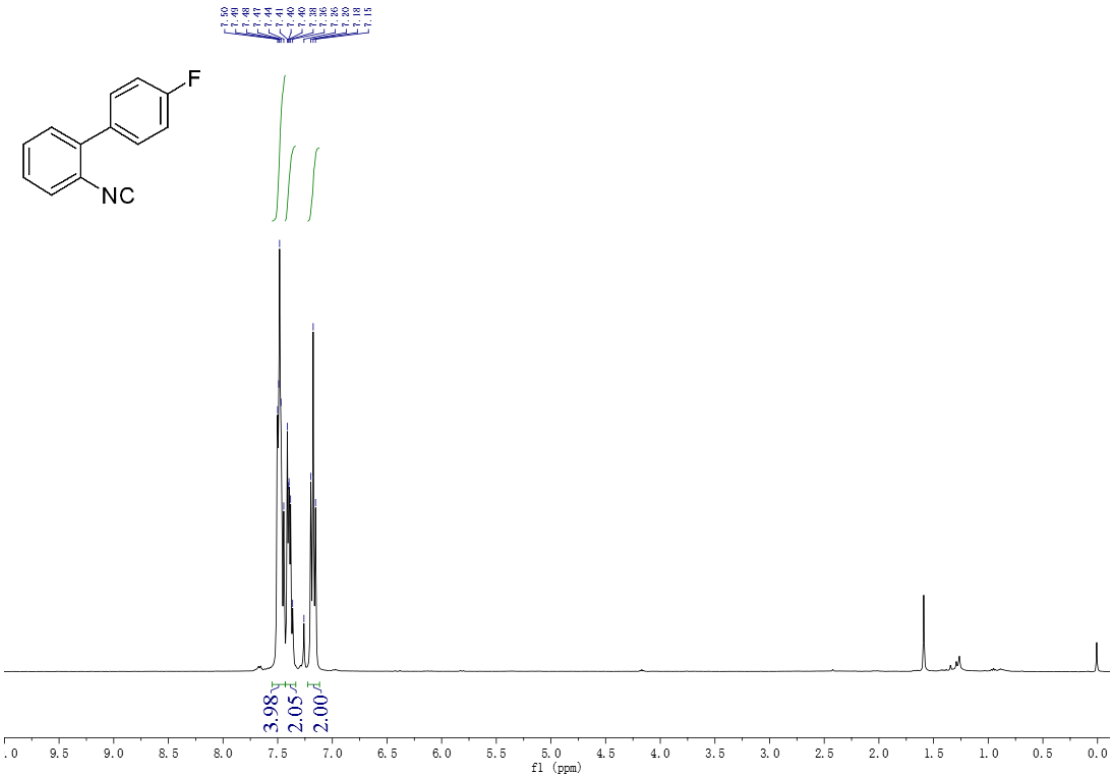
^{1}H NMR of **1a**



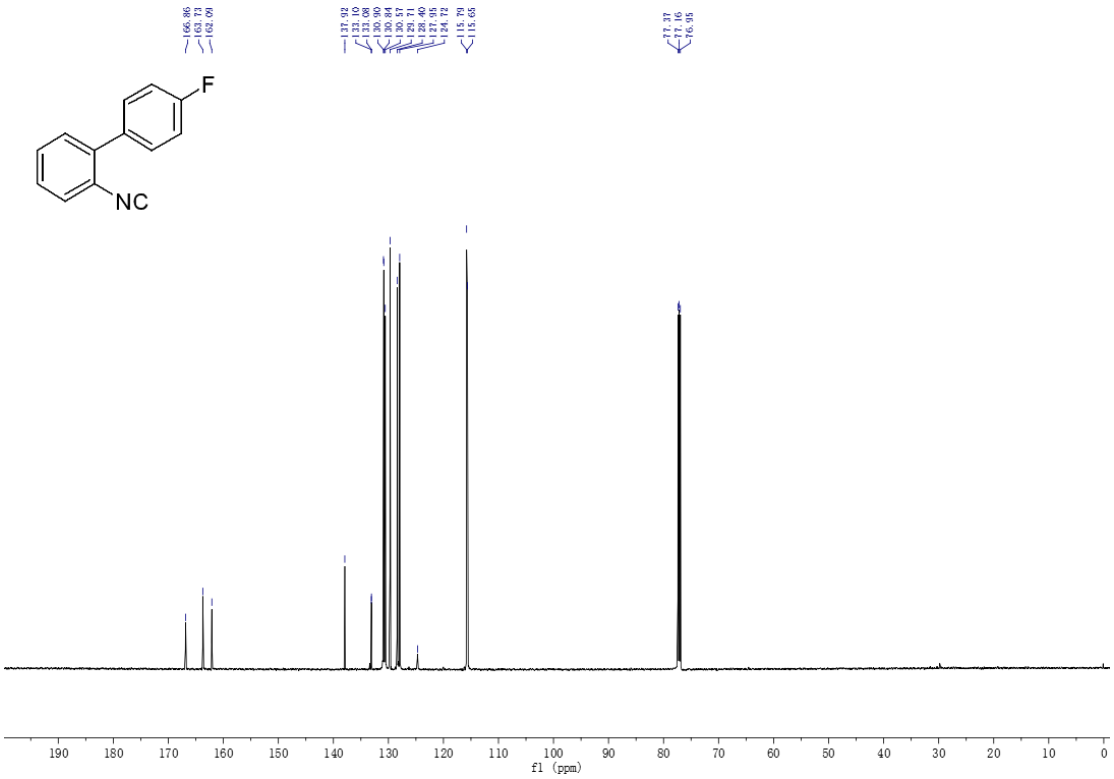
^{13}C NMR of **1a**



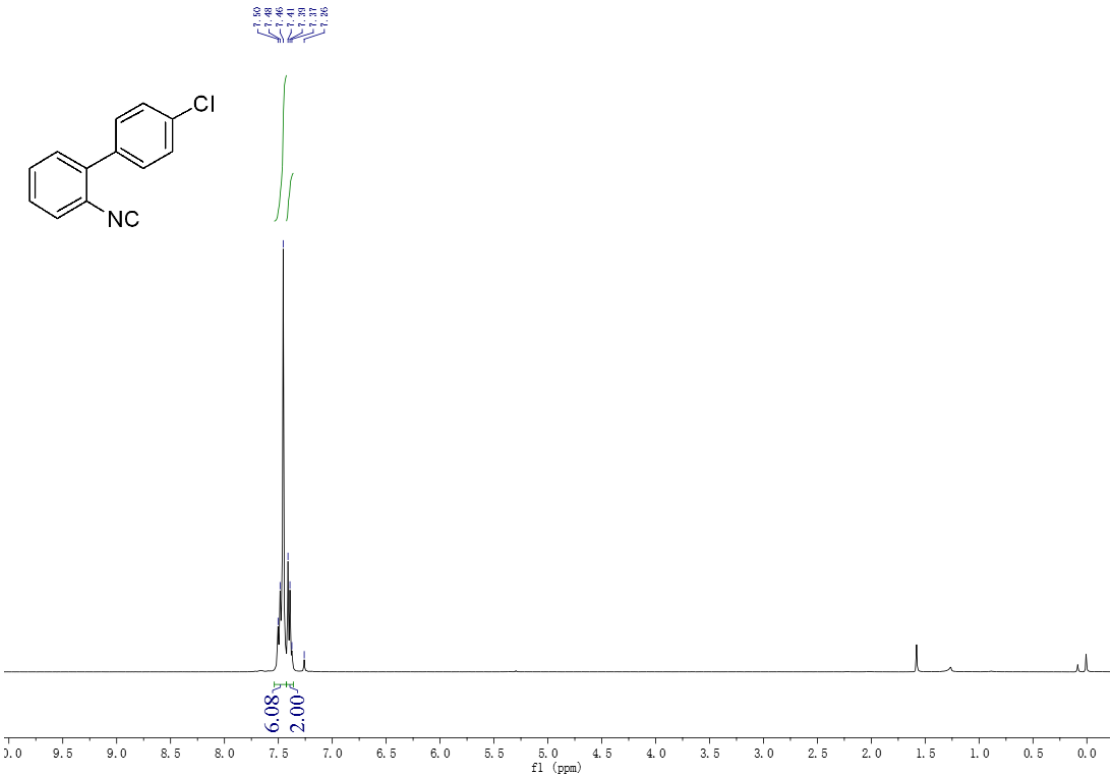
^{1}H NMR of **1b**



^{13}C NMR of **1b**



^{1}H NMR of **1c**



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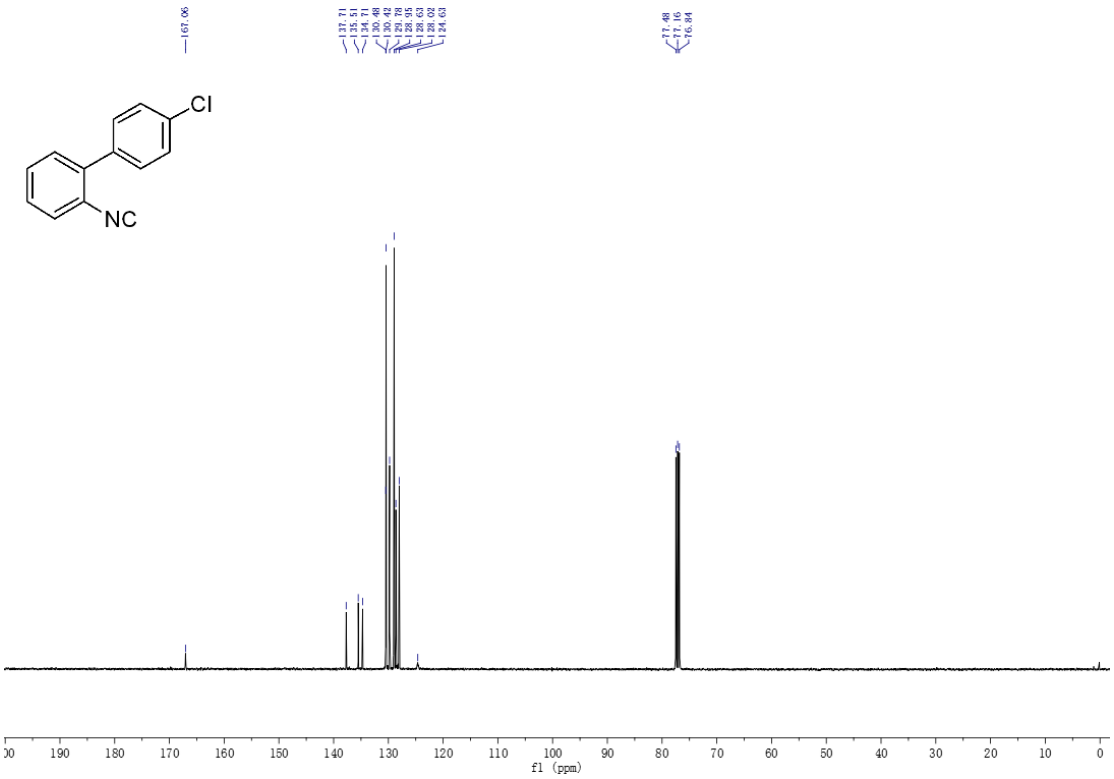

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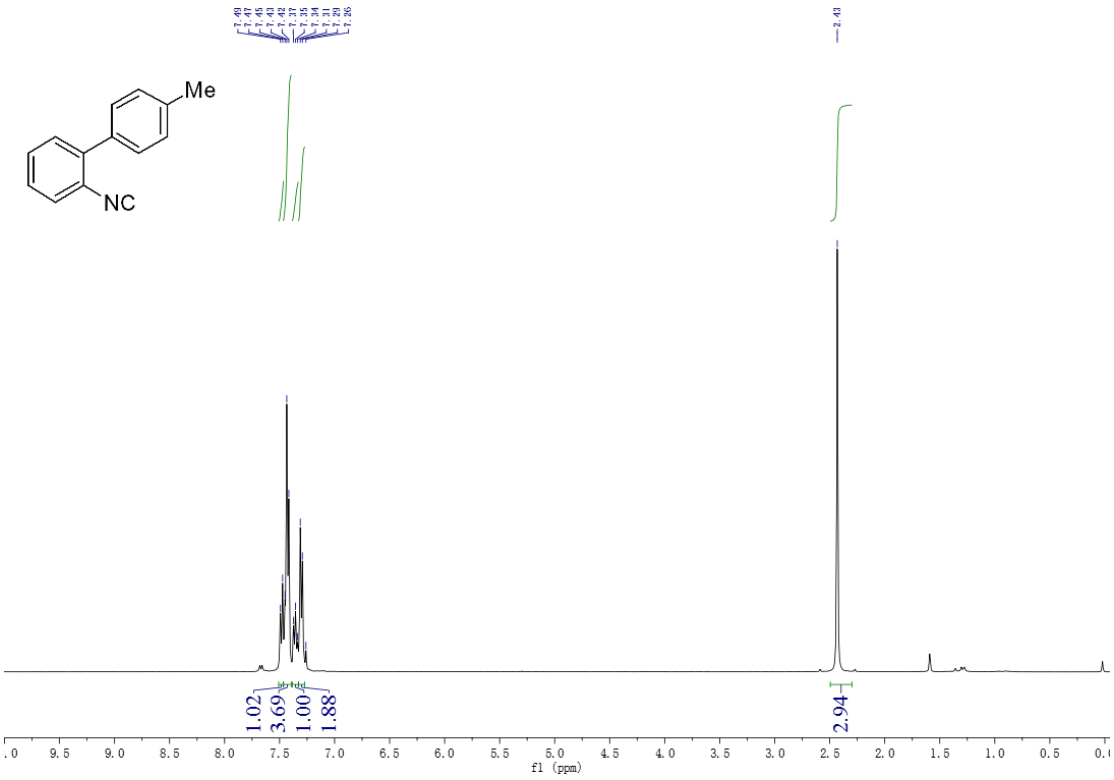

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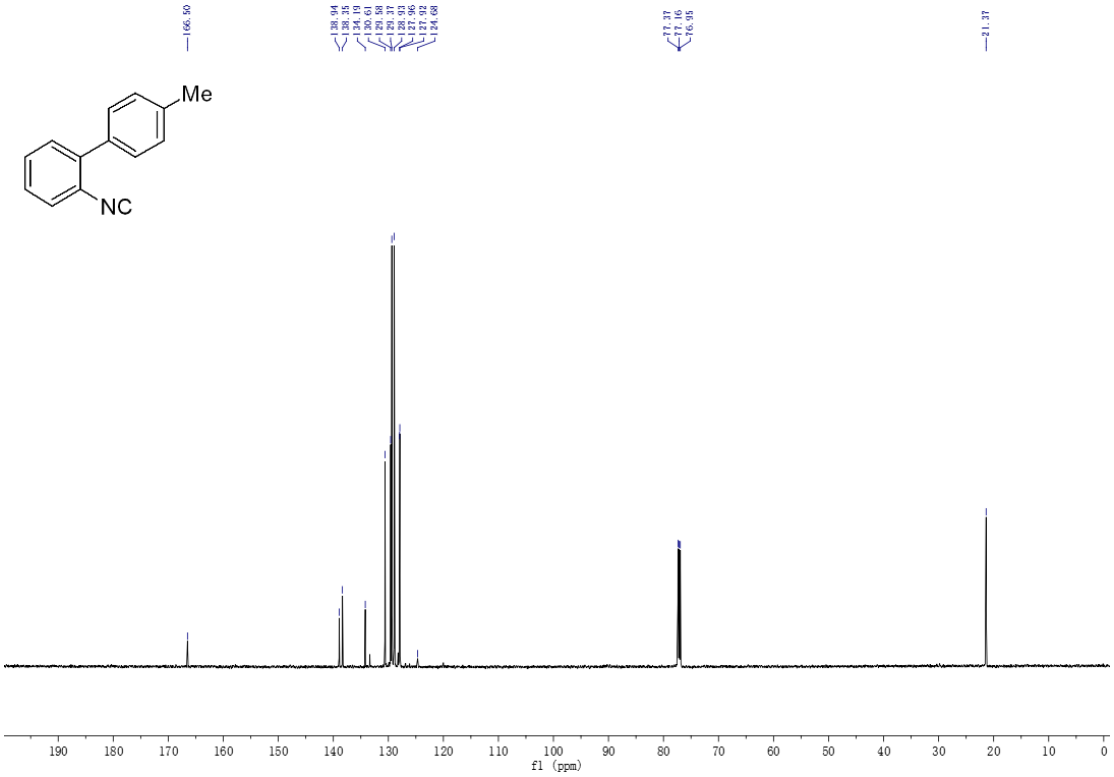

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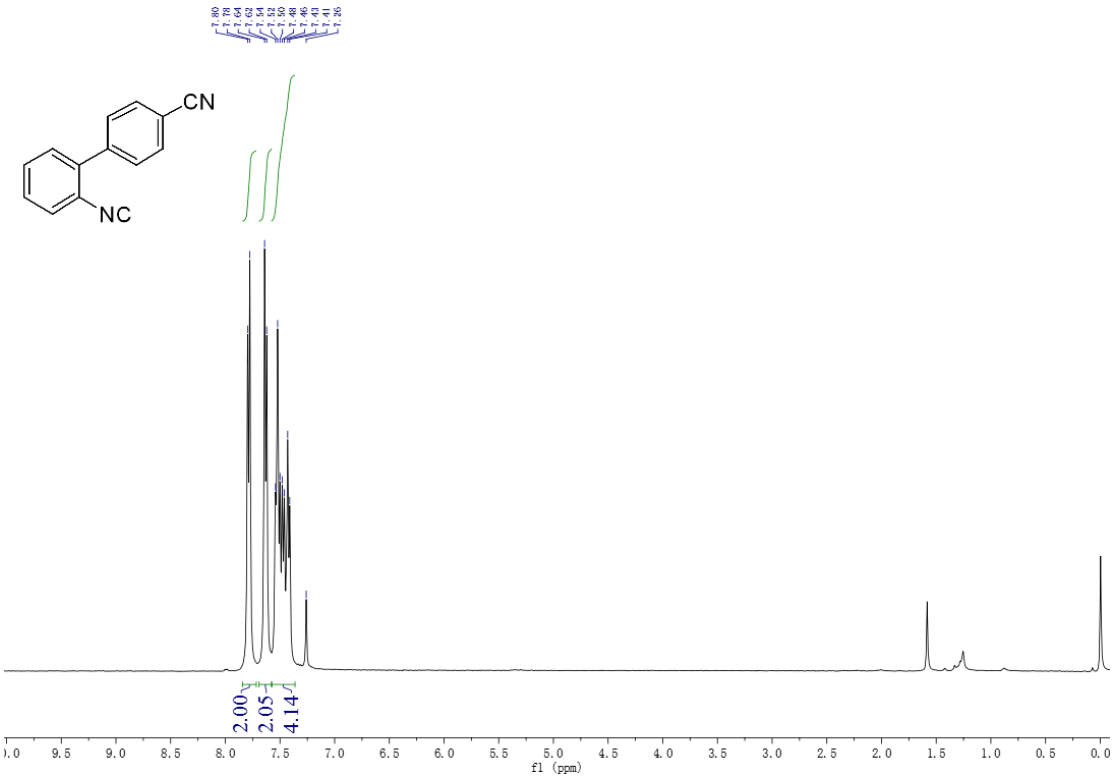

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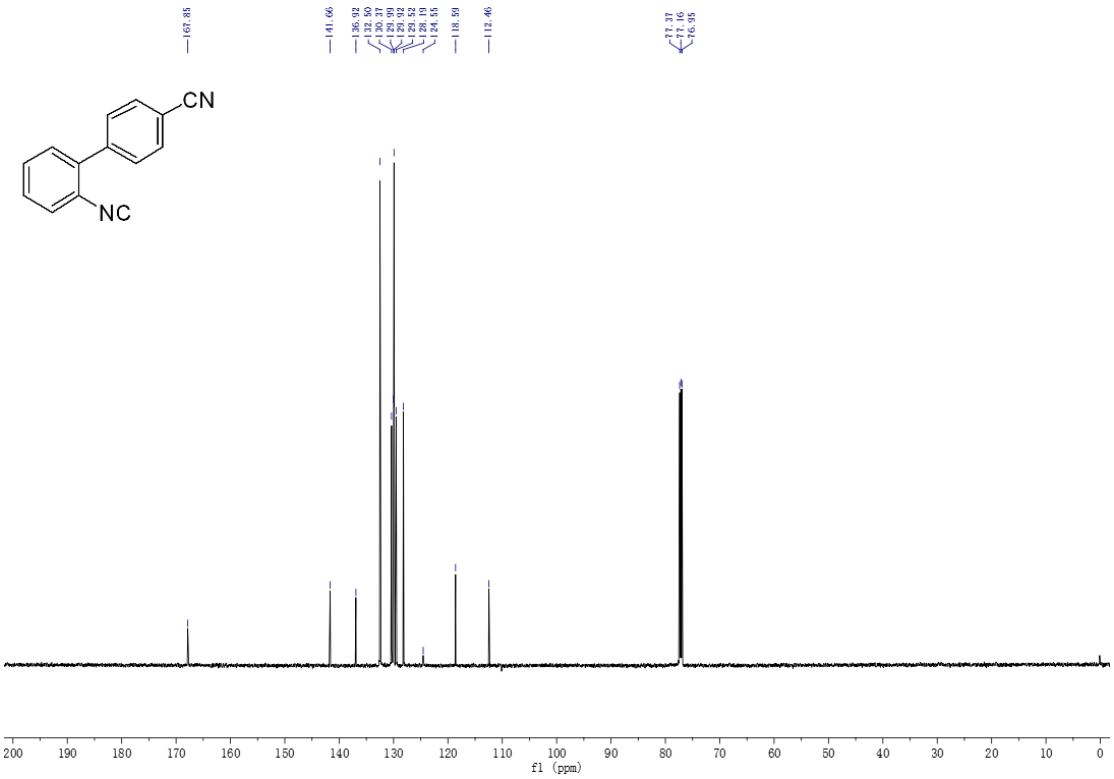
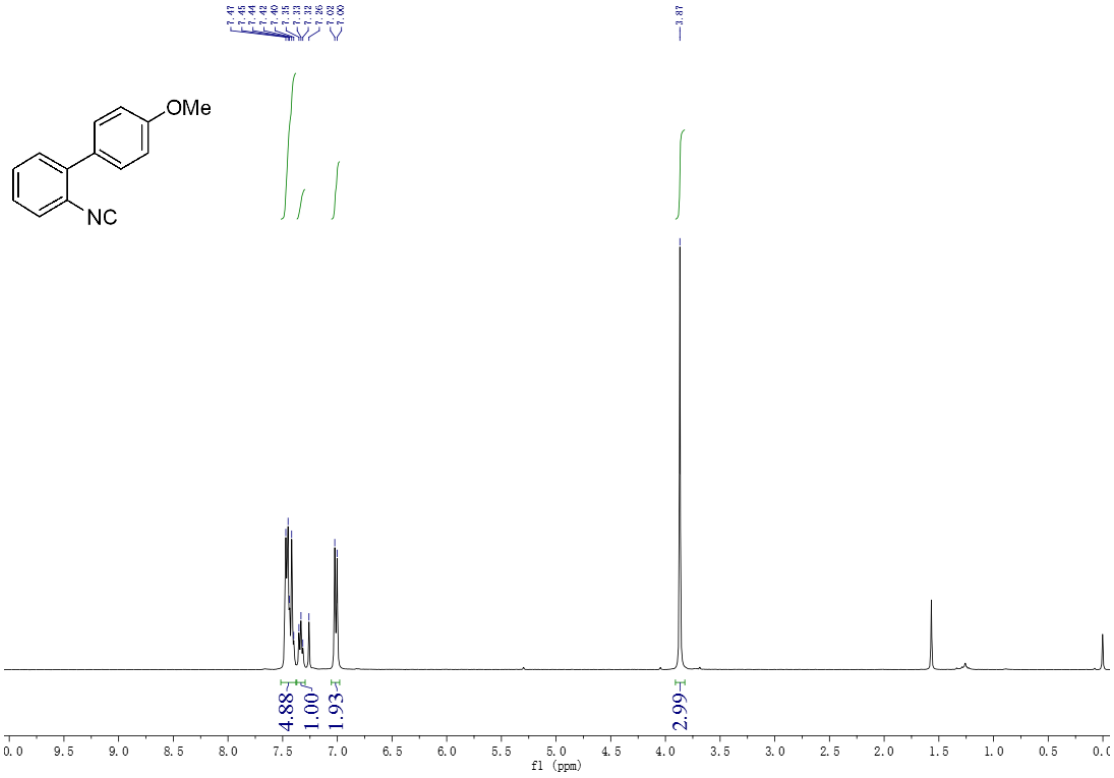
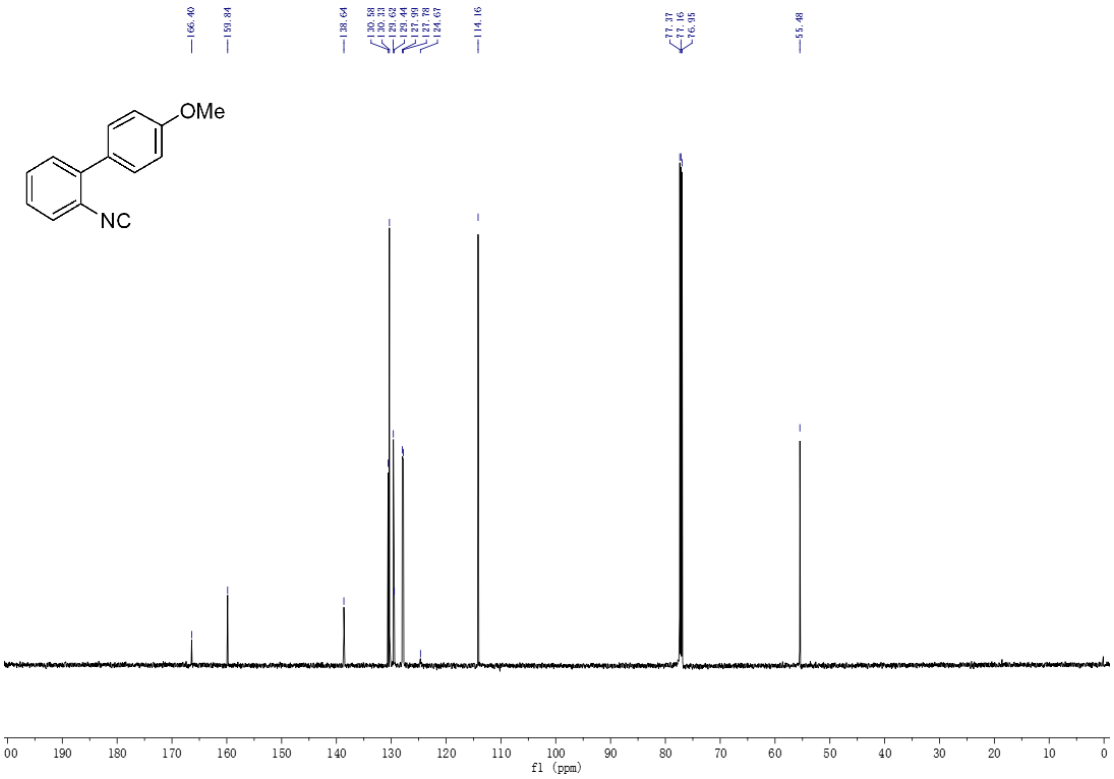


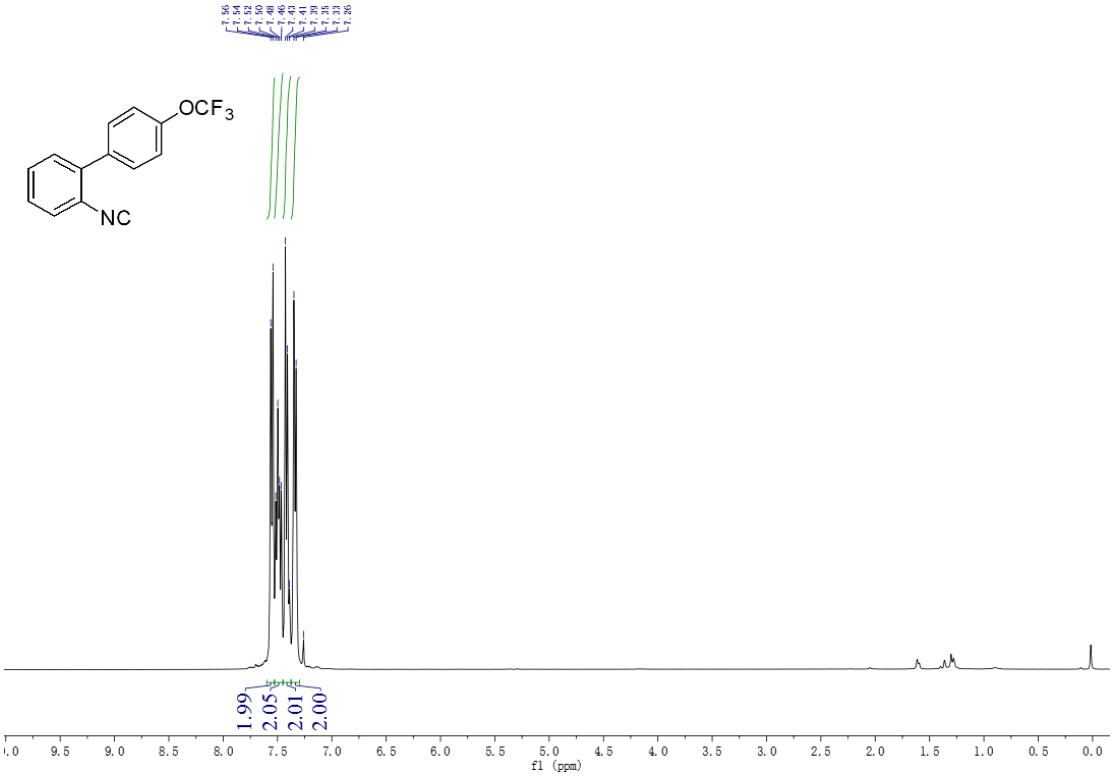
^{1}H NMR of **1f**



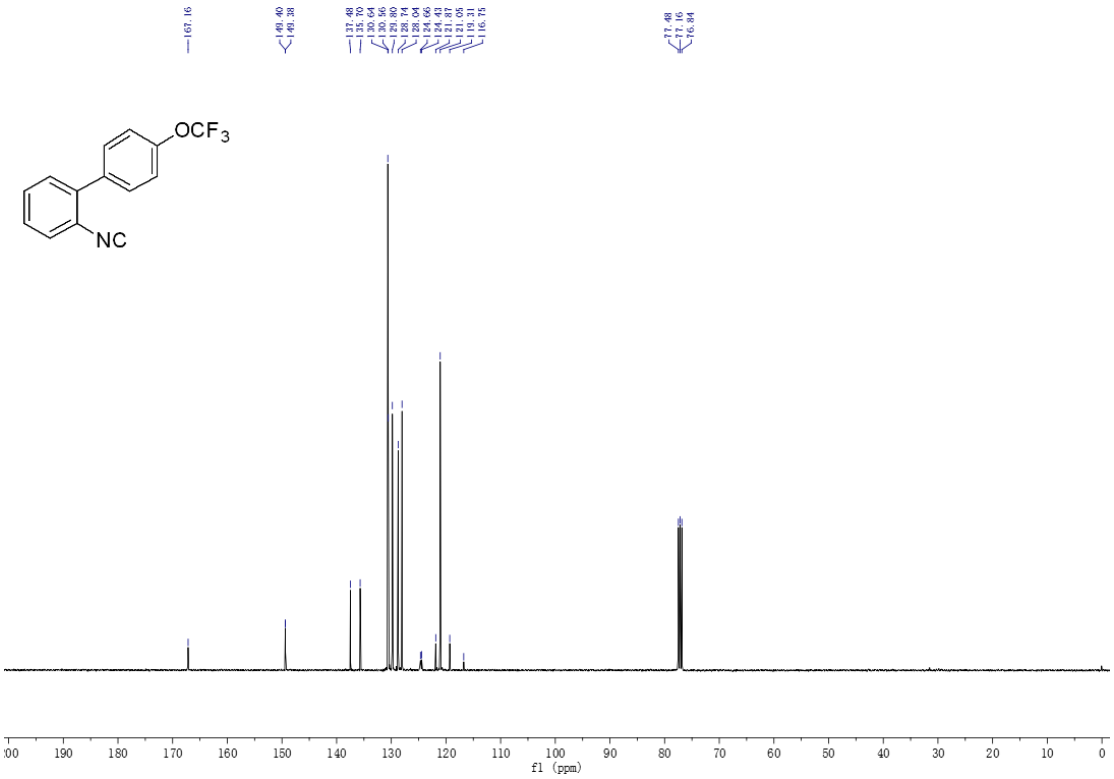
^{13}C NMR of **1f**



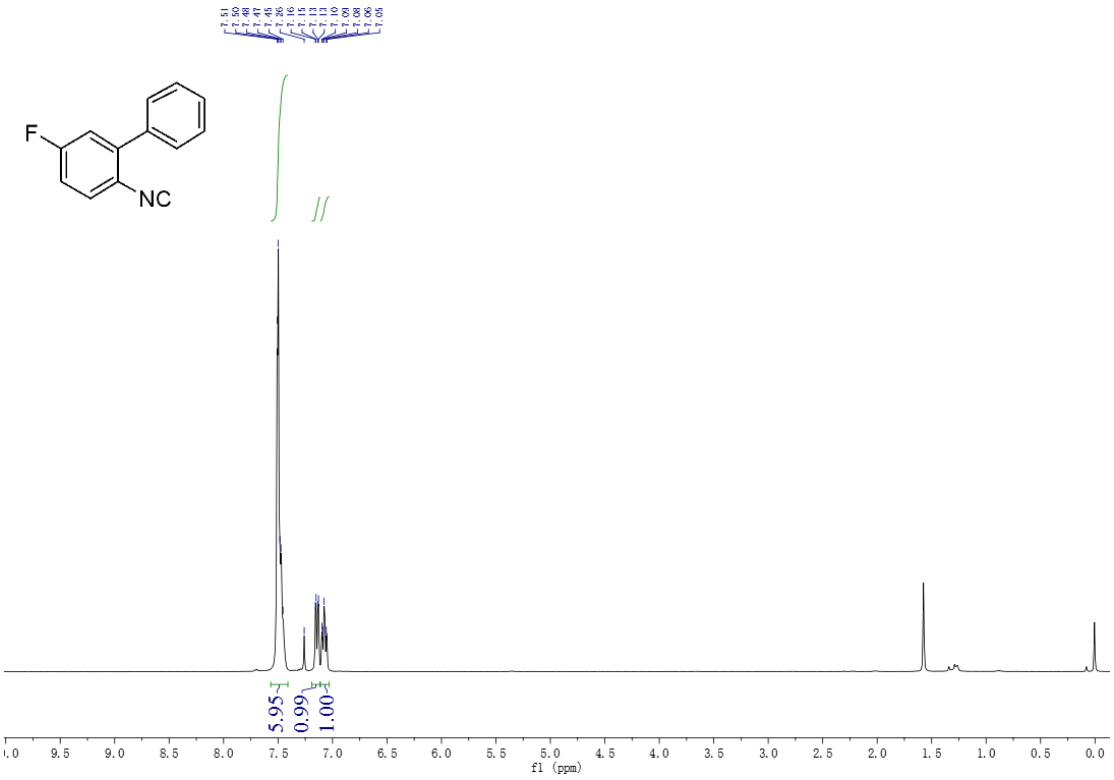
^{1}H NMR of **1g**



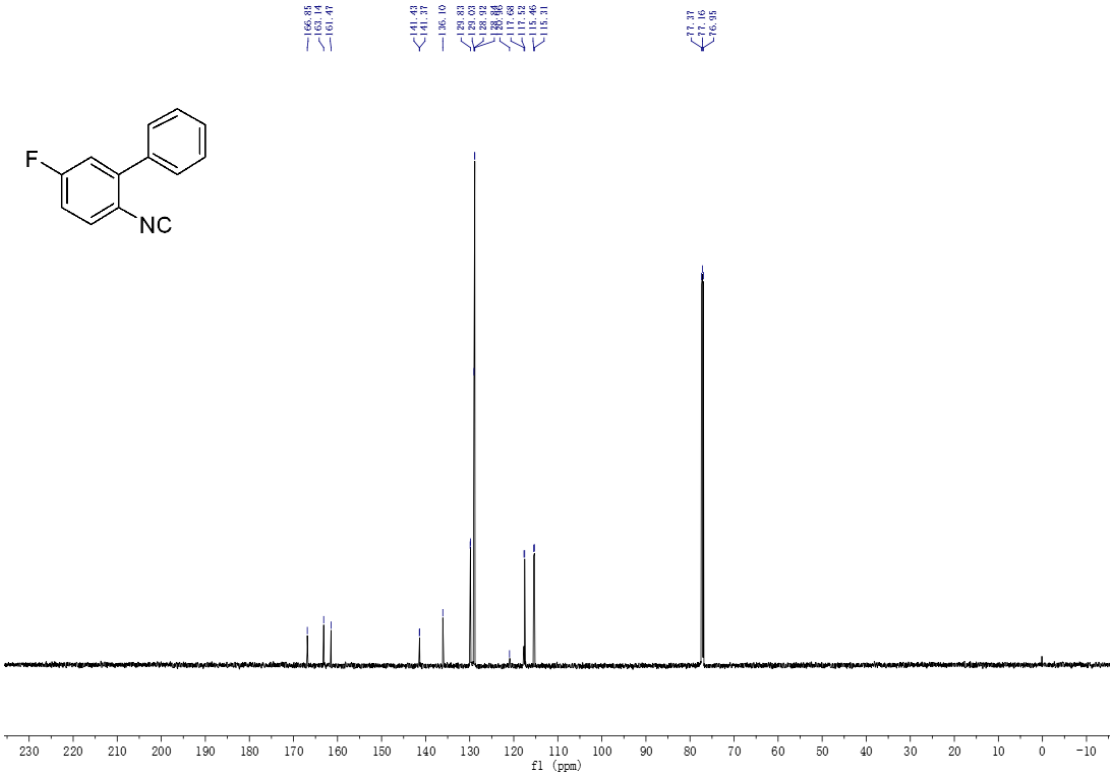
^{13}C NMR of **1g**



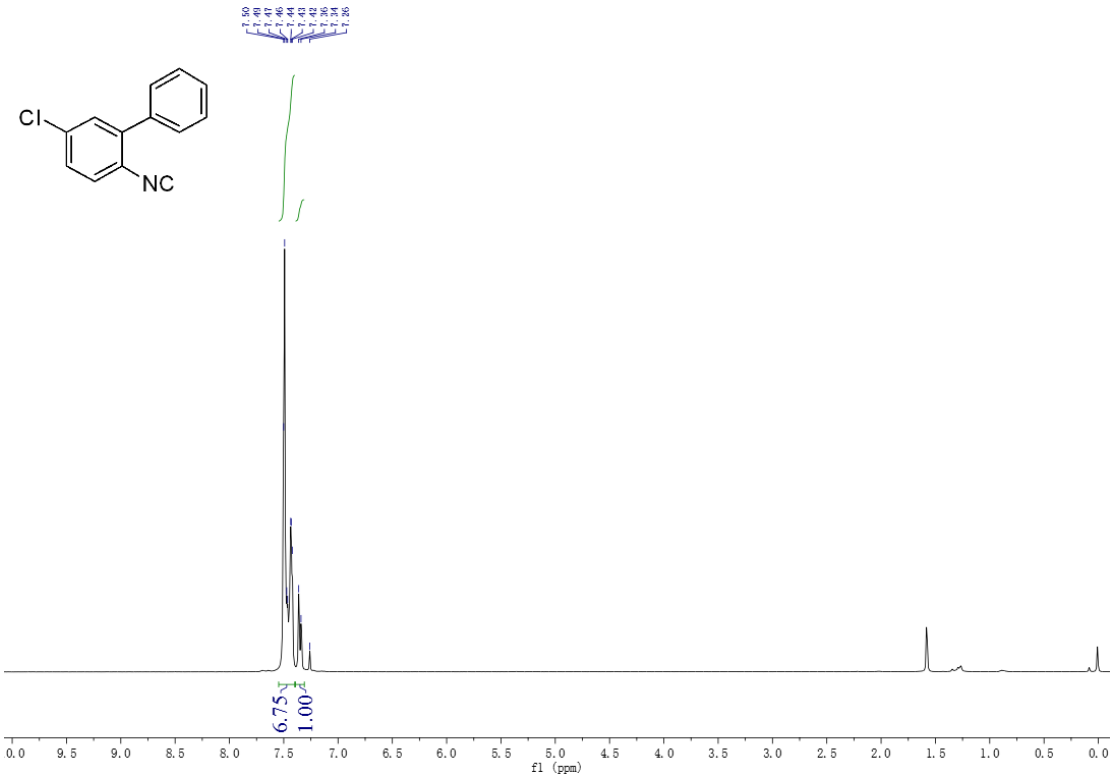
^{1}H NMR of **1h**



^{13}C NMR of **1h**



^{1}H NMR of **1i**



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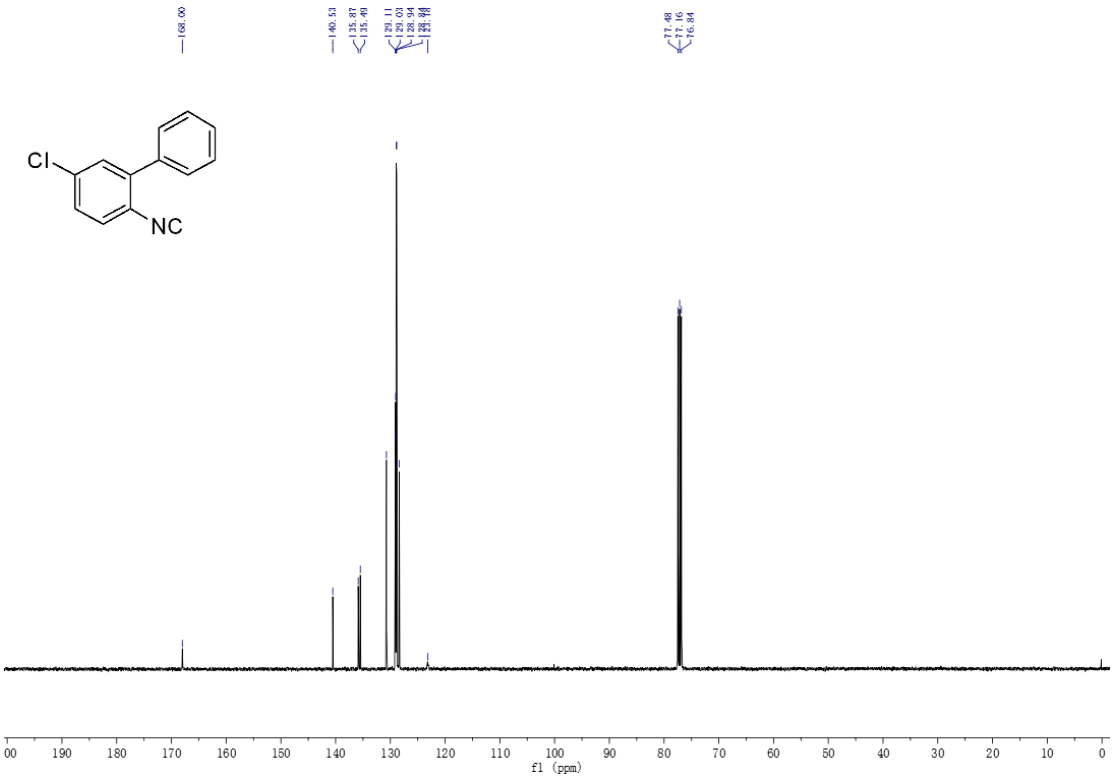

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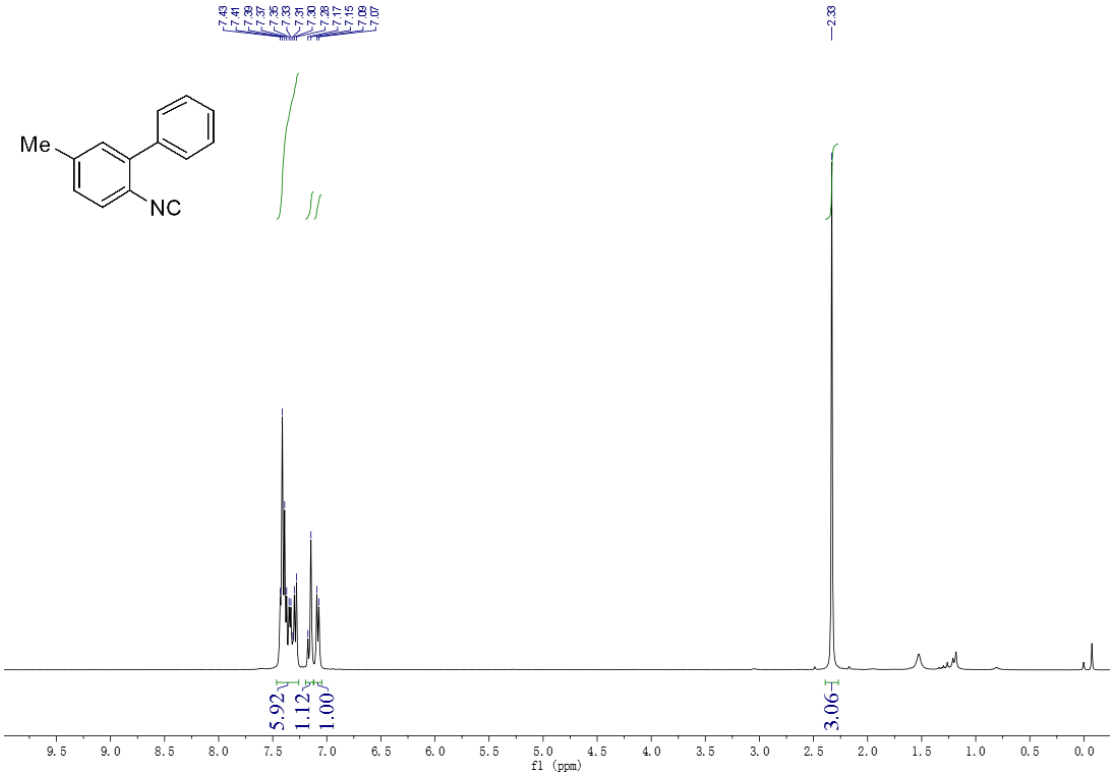

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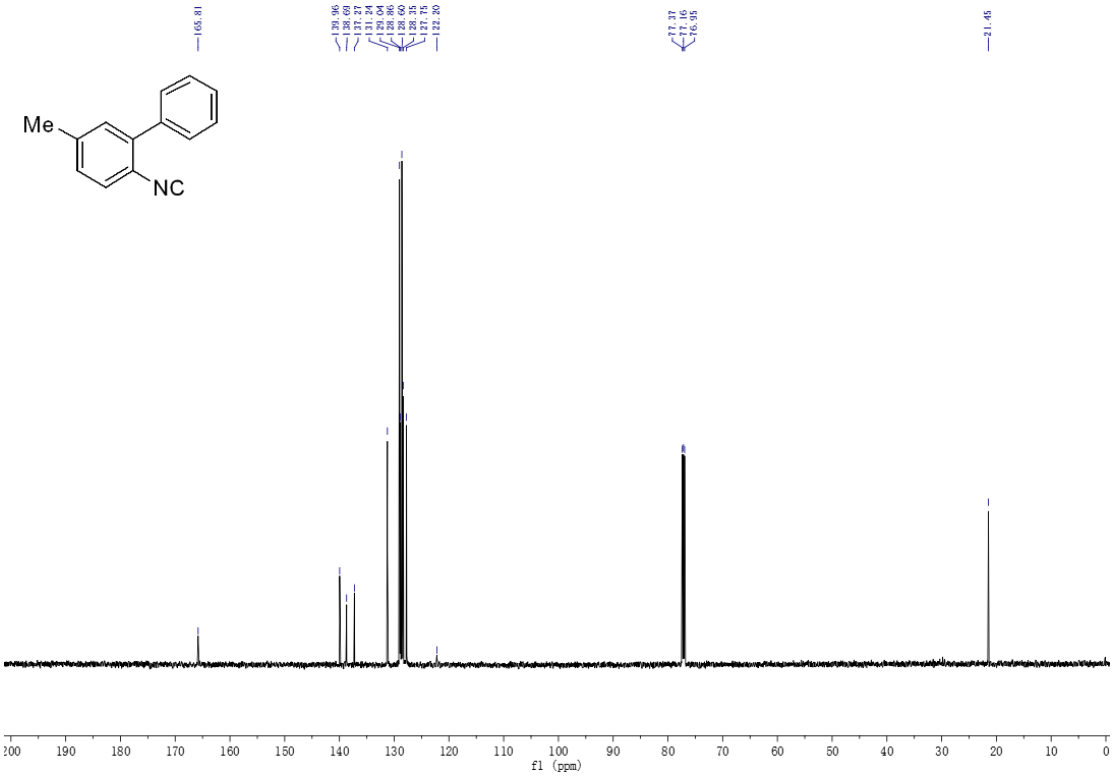

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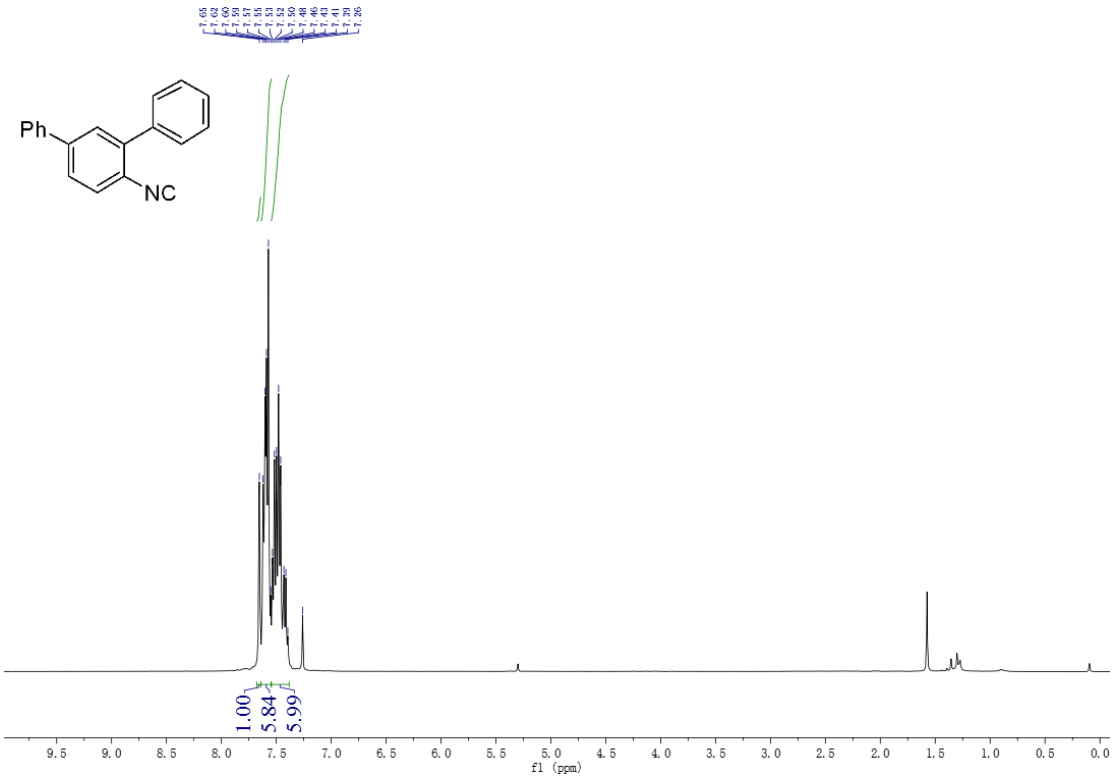

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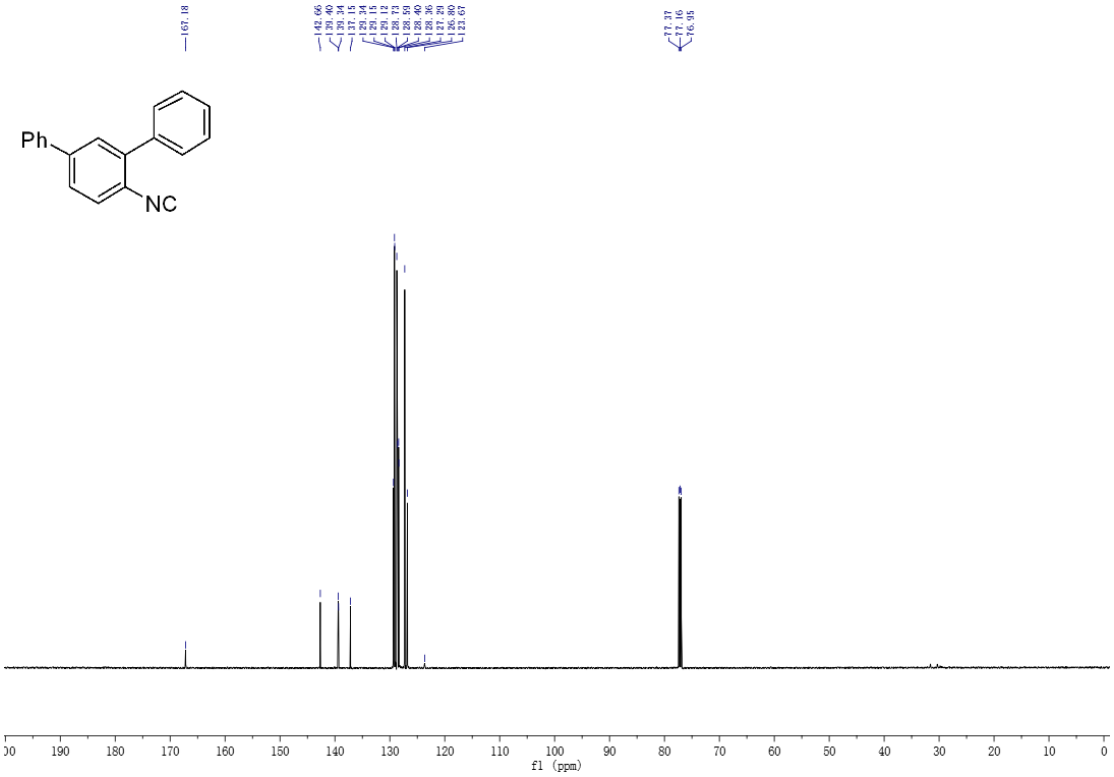
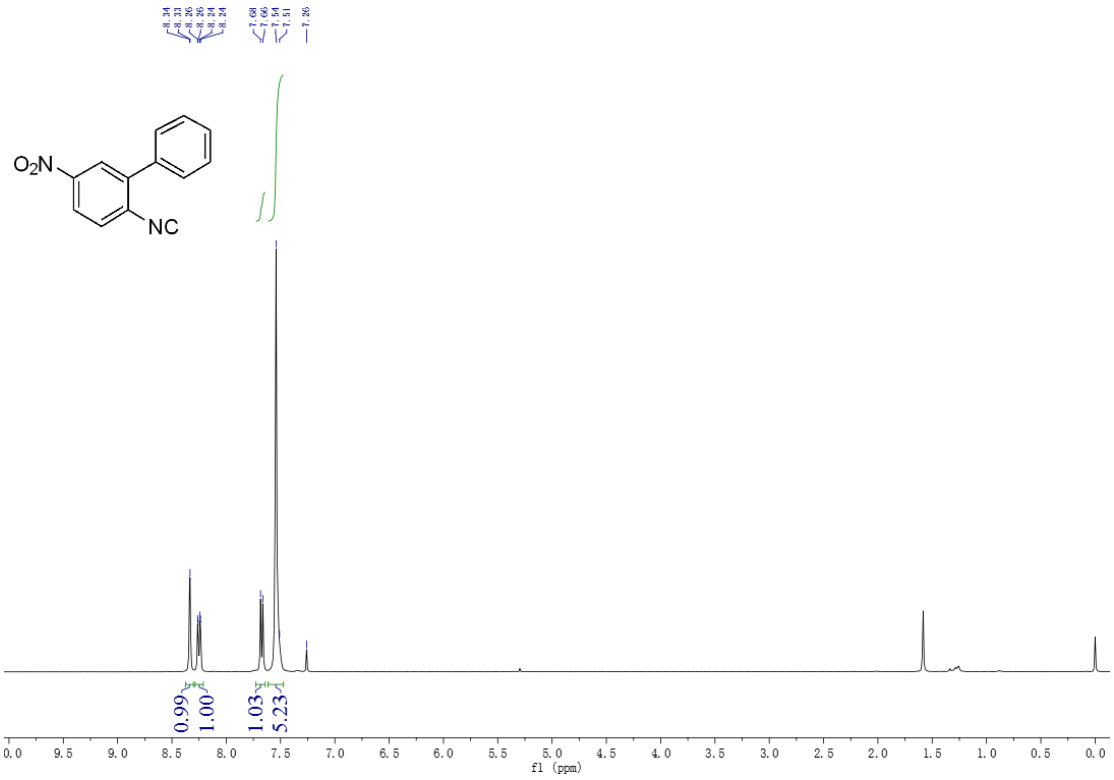
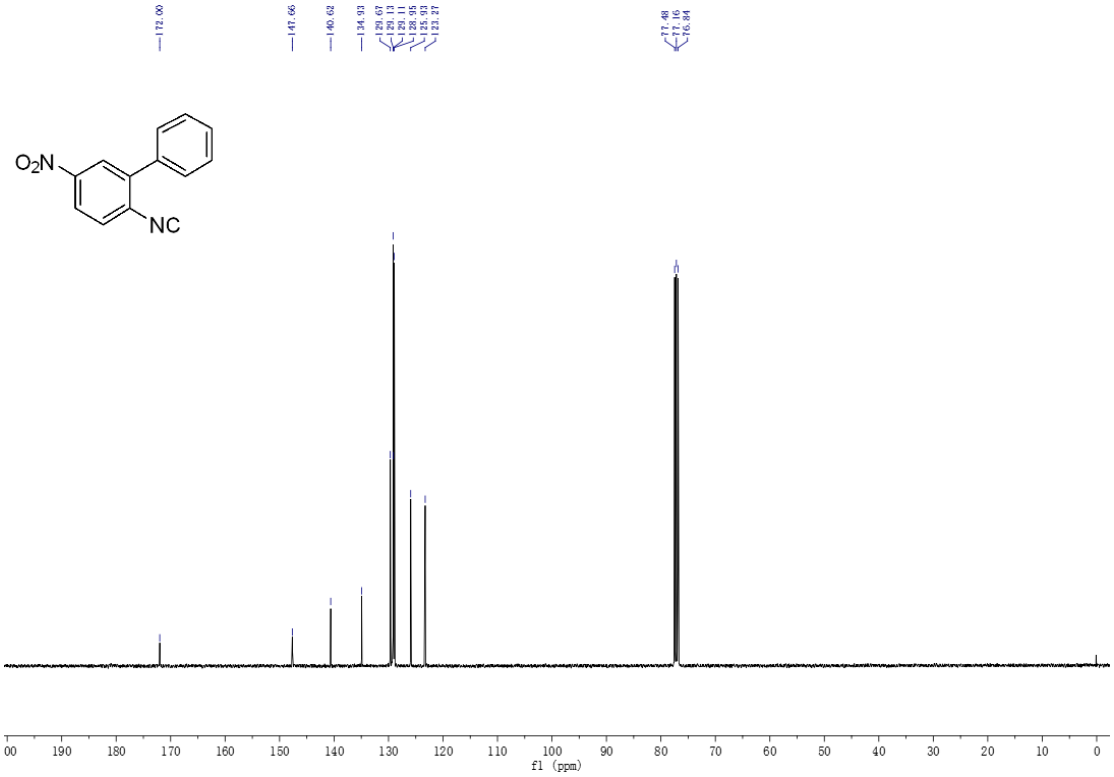


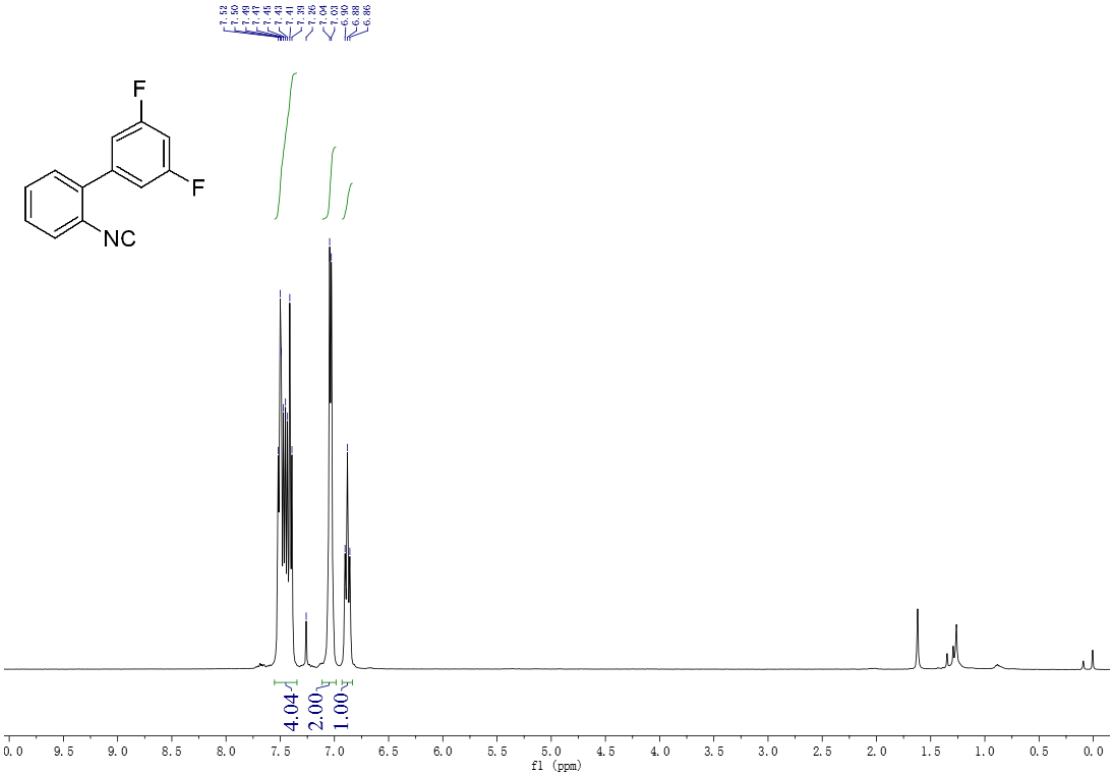
^{1}H NMR of **1l**



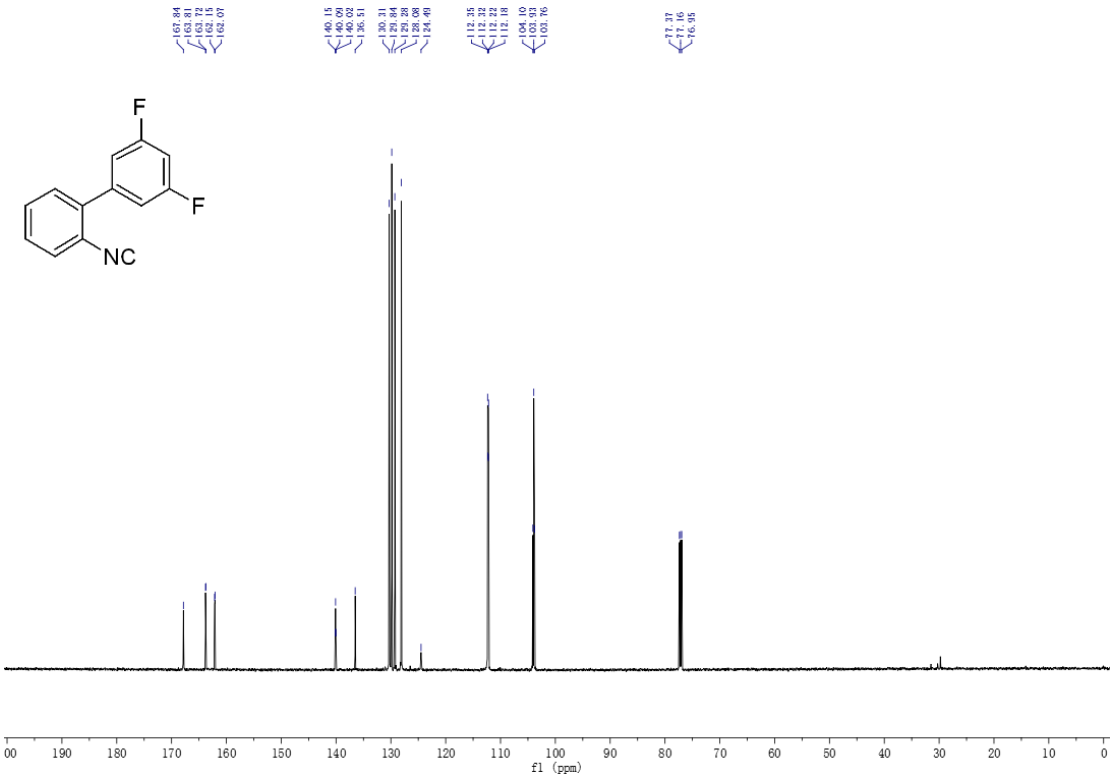
^{13}C NMR of **1l**



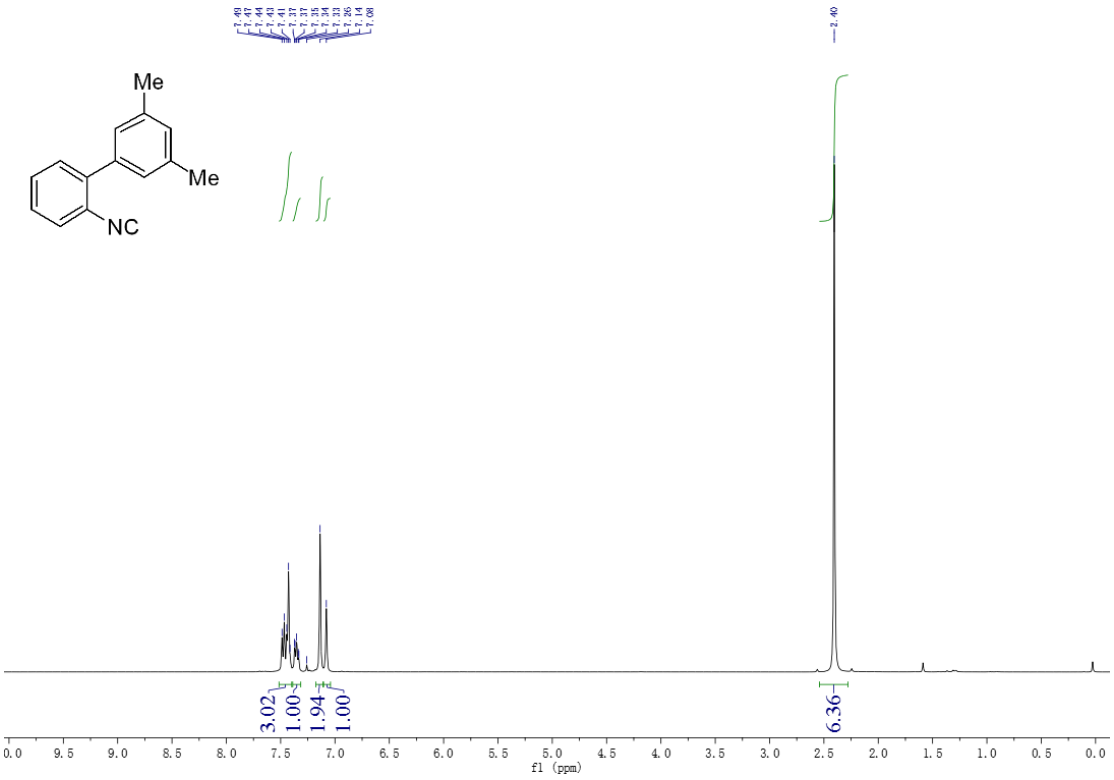
^{1}H NMR of **1m**



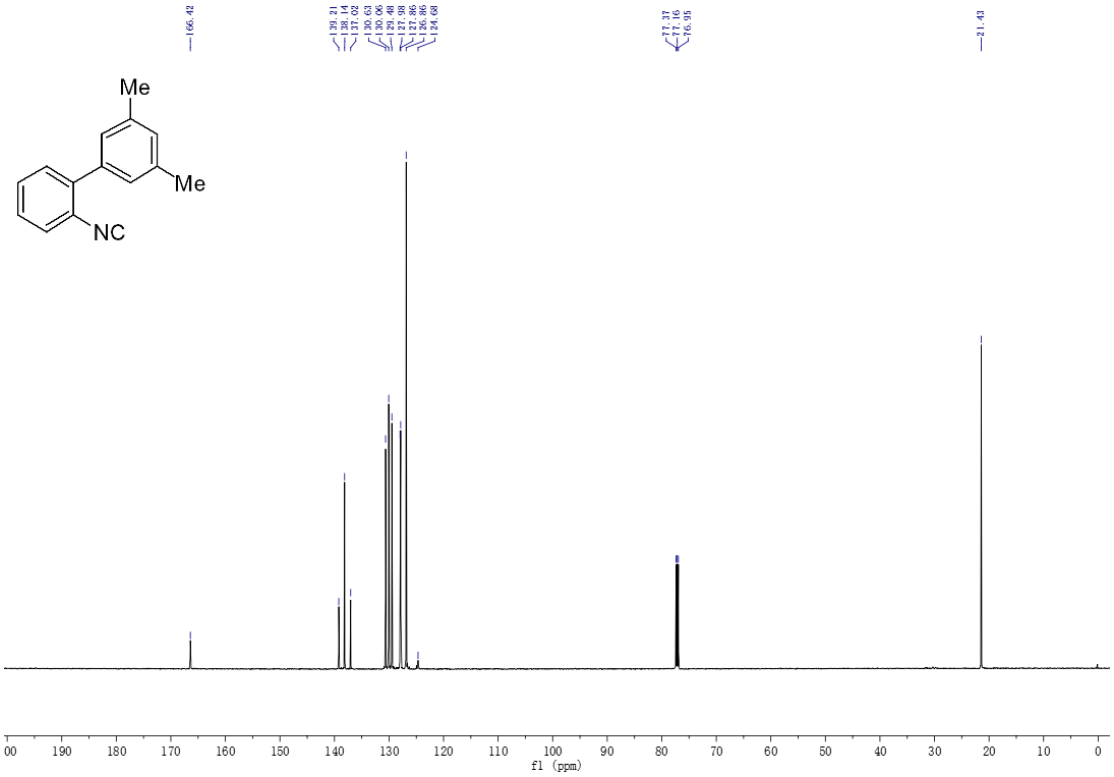
^{13}C NMR of **1m**



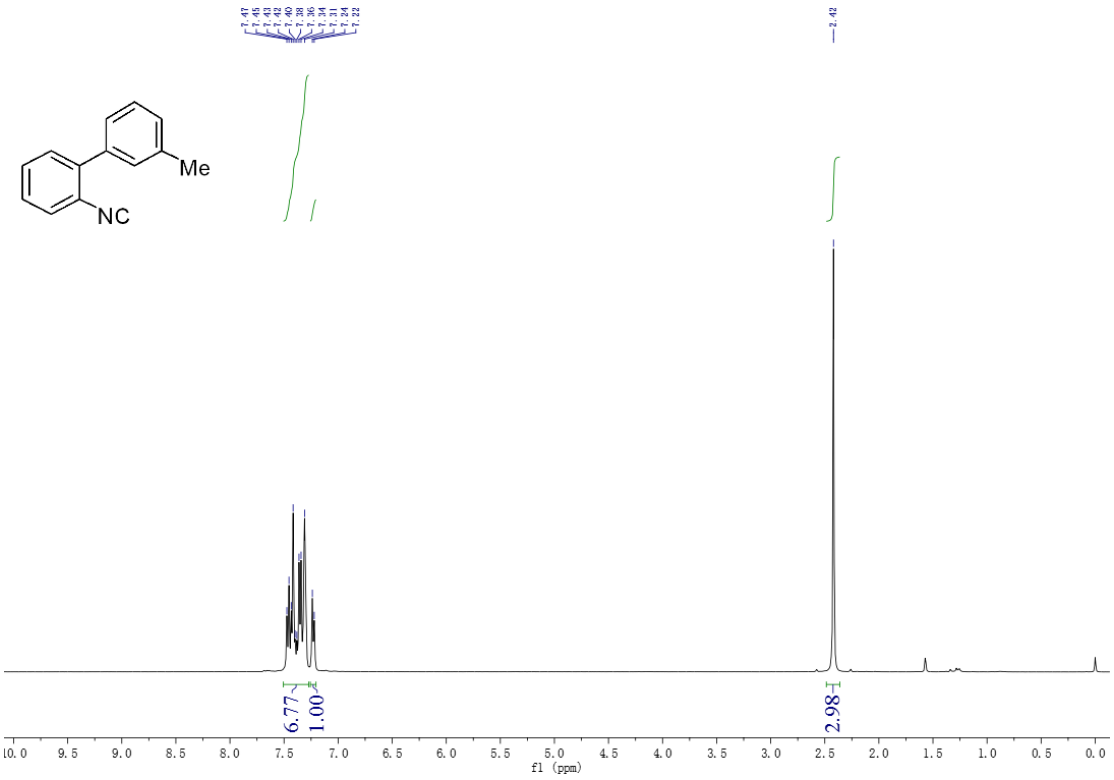
^{1}H NMR of **1n**



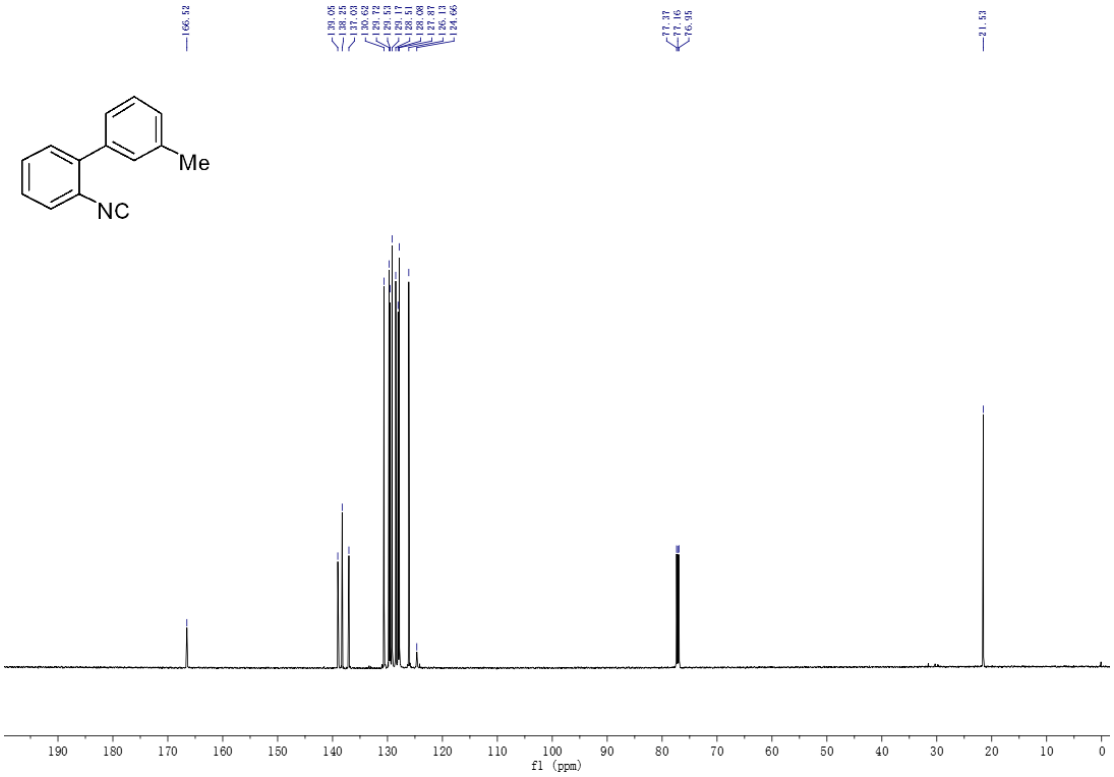
^{13}C NMR of **1n**



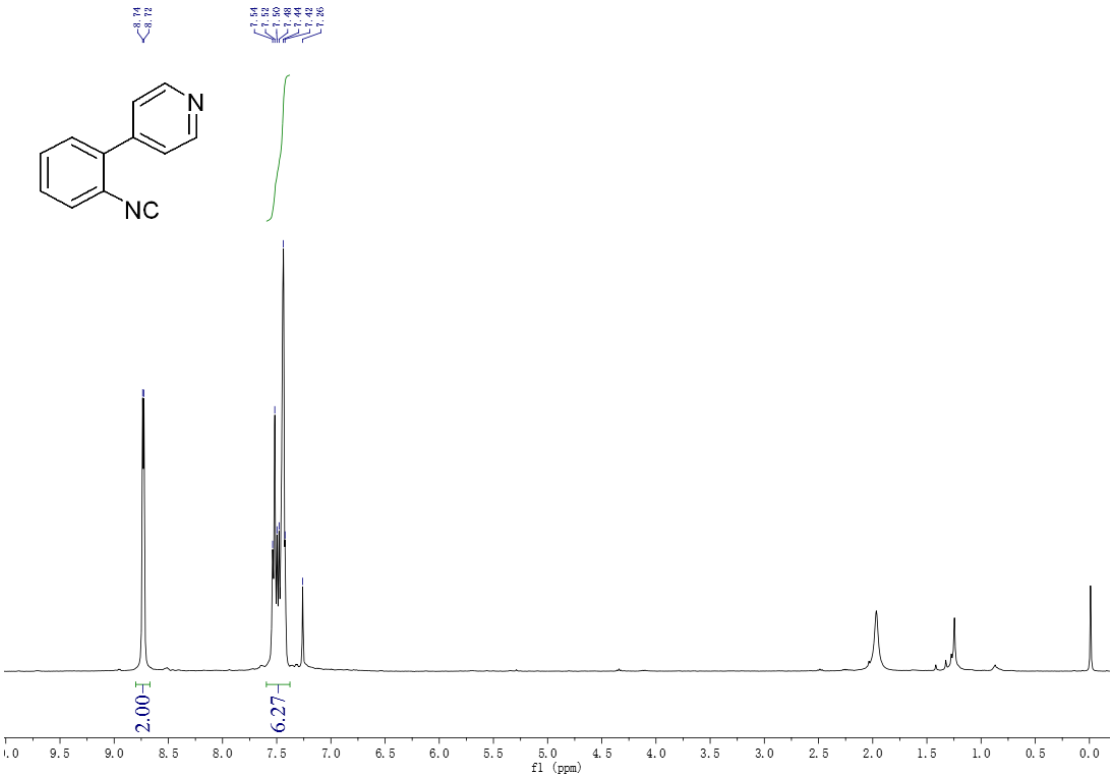
^{1}H NMR of **1o**



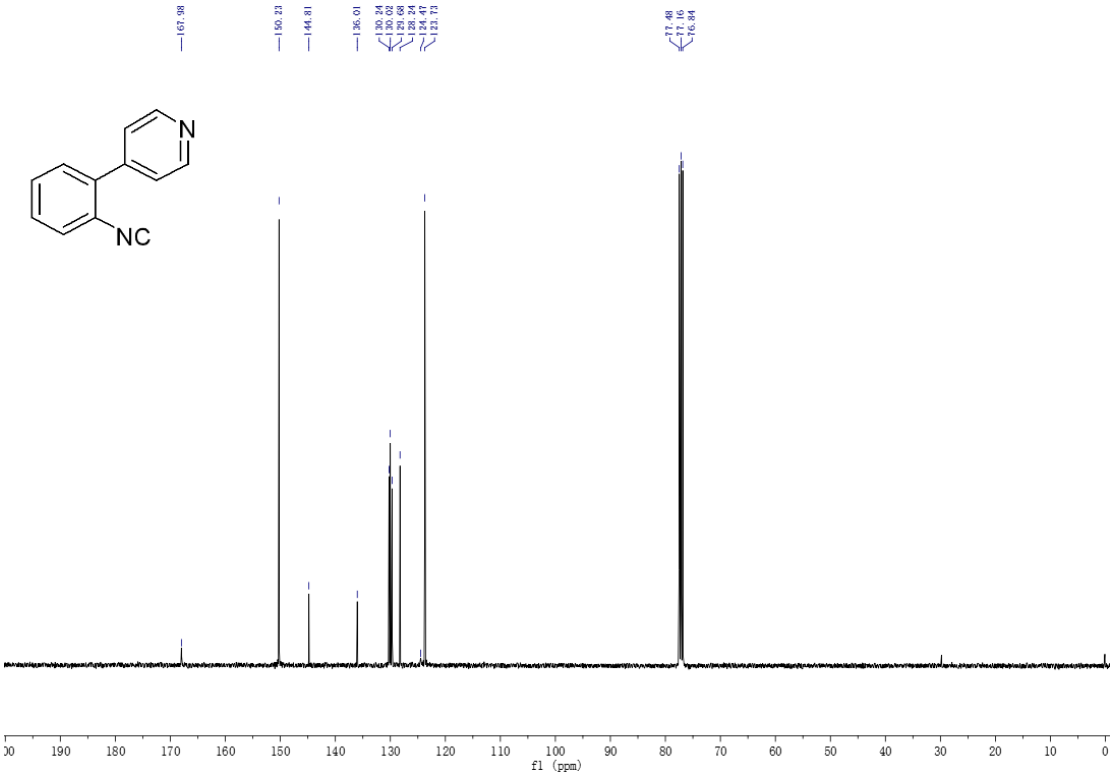
^{13}C NMR of **1o**



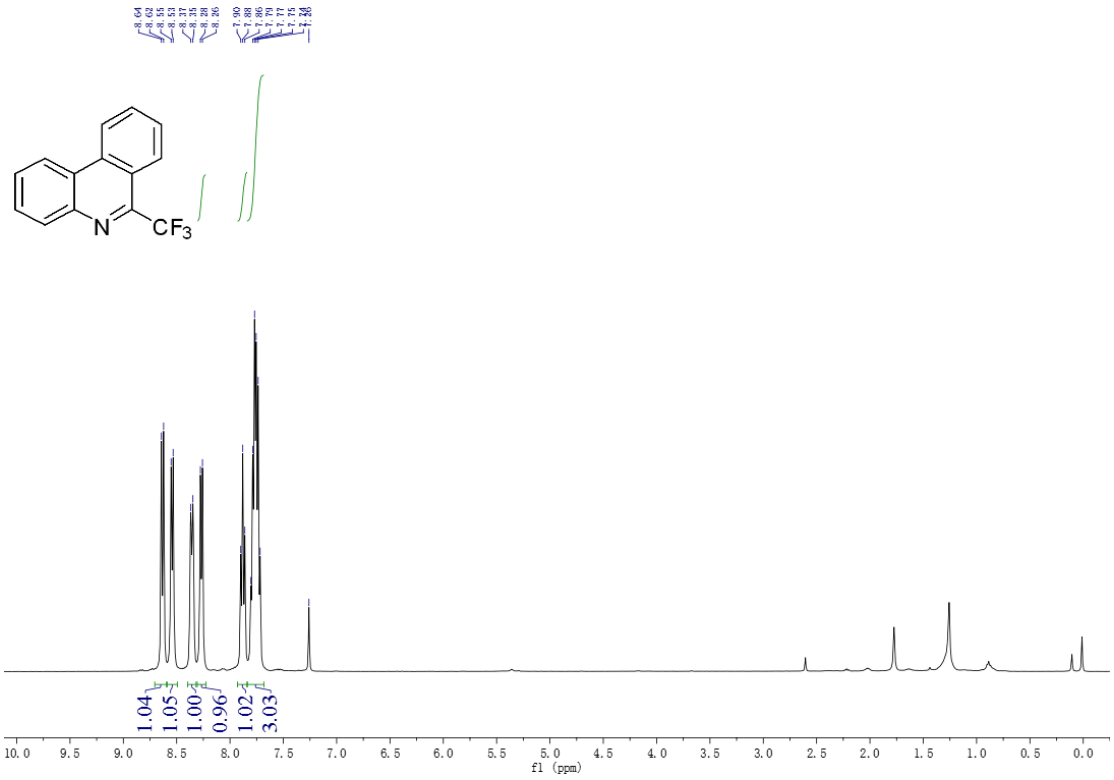
^{1}H NMR of **1p**



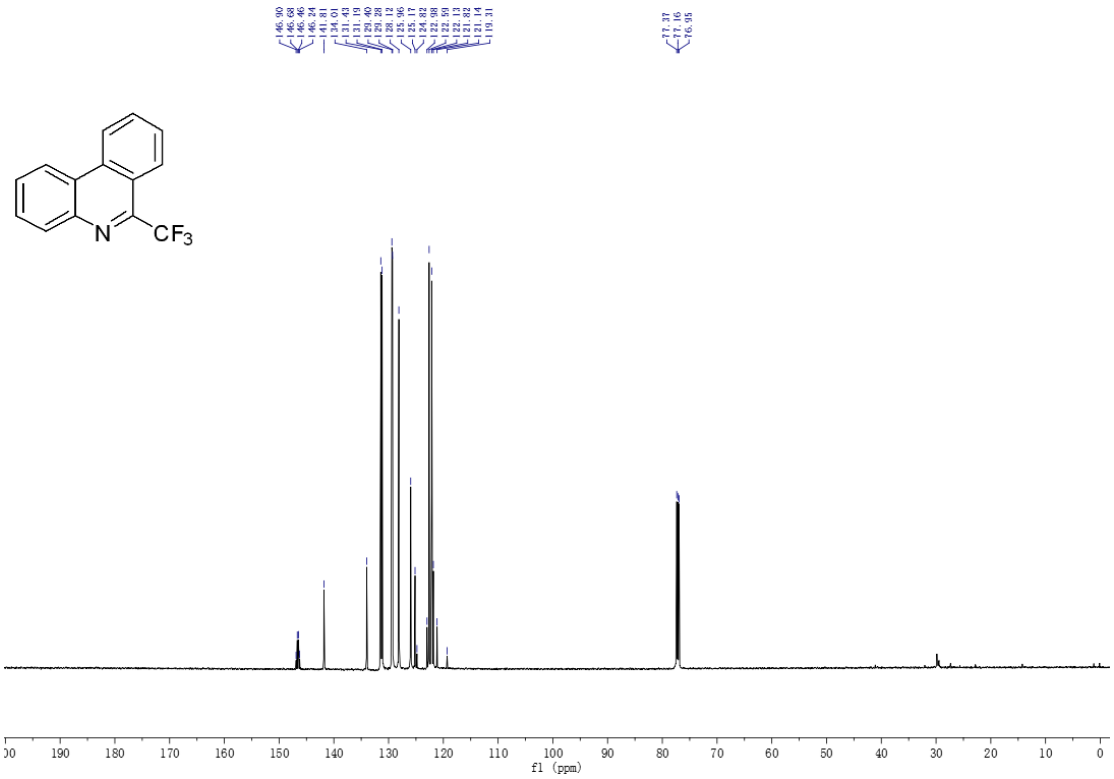
^{13}C NMR of **1p**



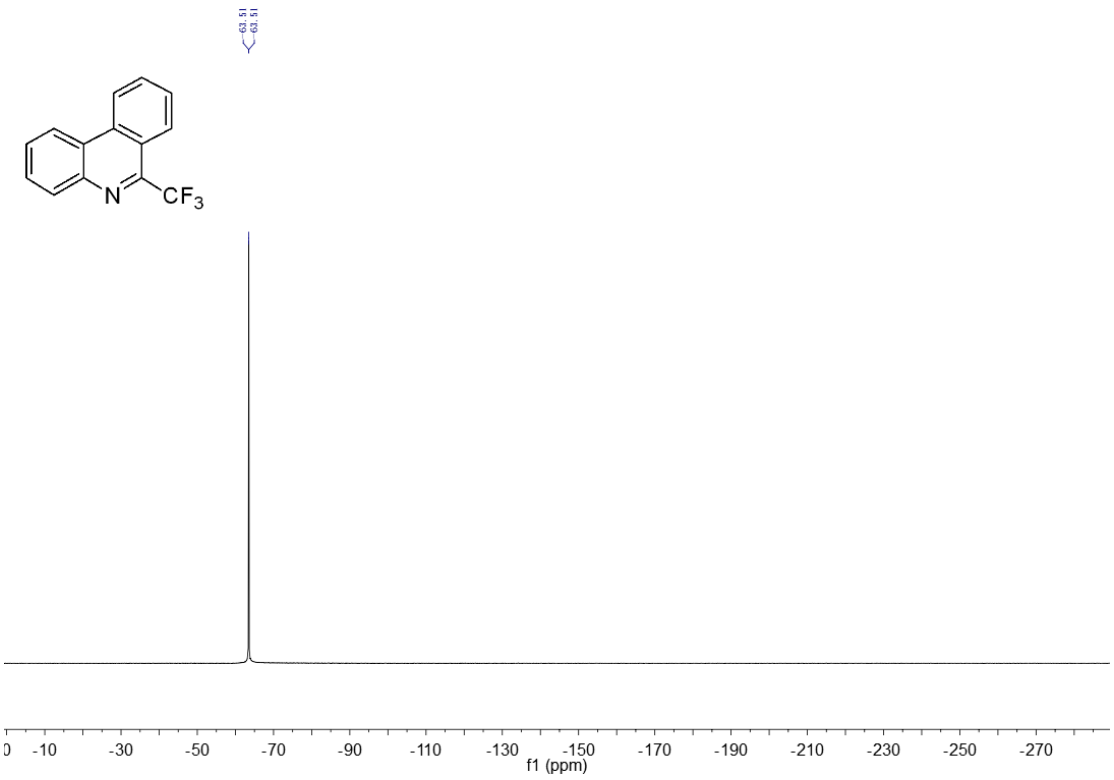
^{1}H NMR of **2a**



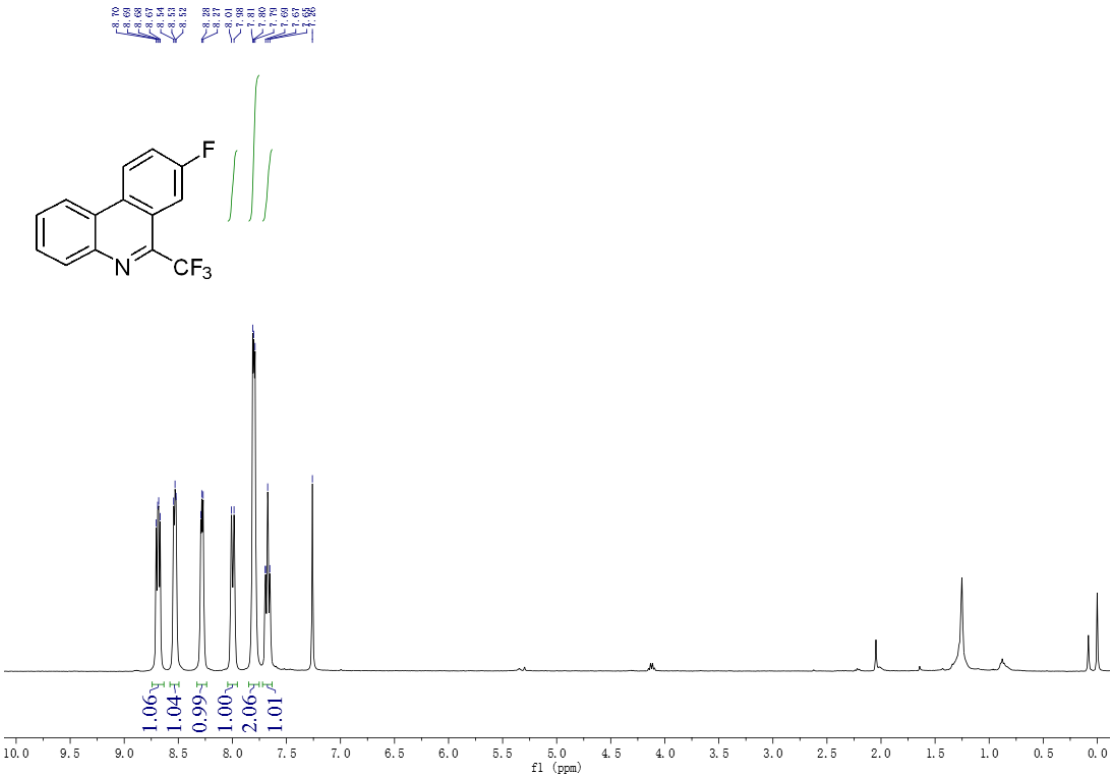
^{13}C NMR of **2a**



^{19}F NMR of **2a**



^{1}H NMR of **2b**



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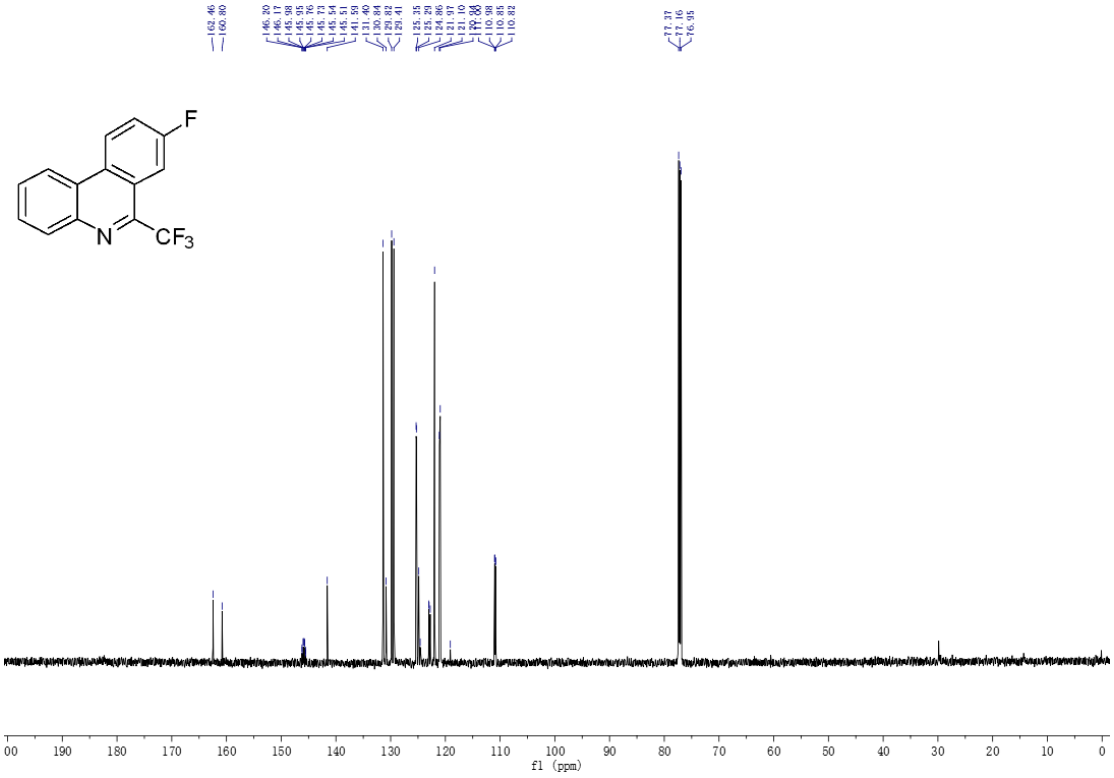
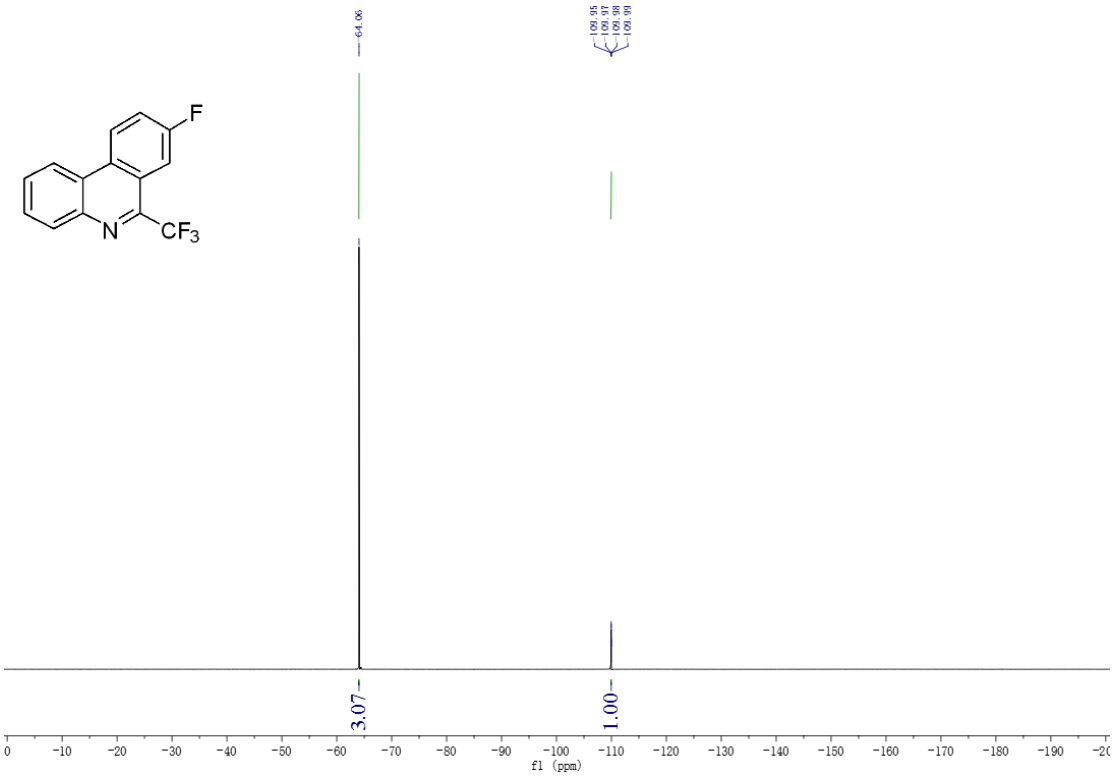
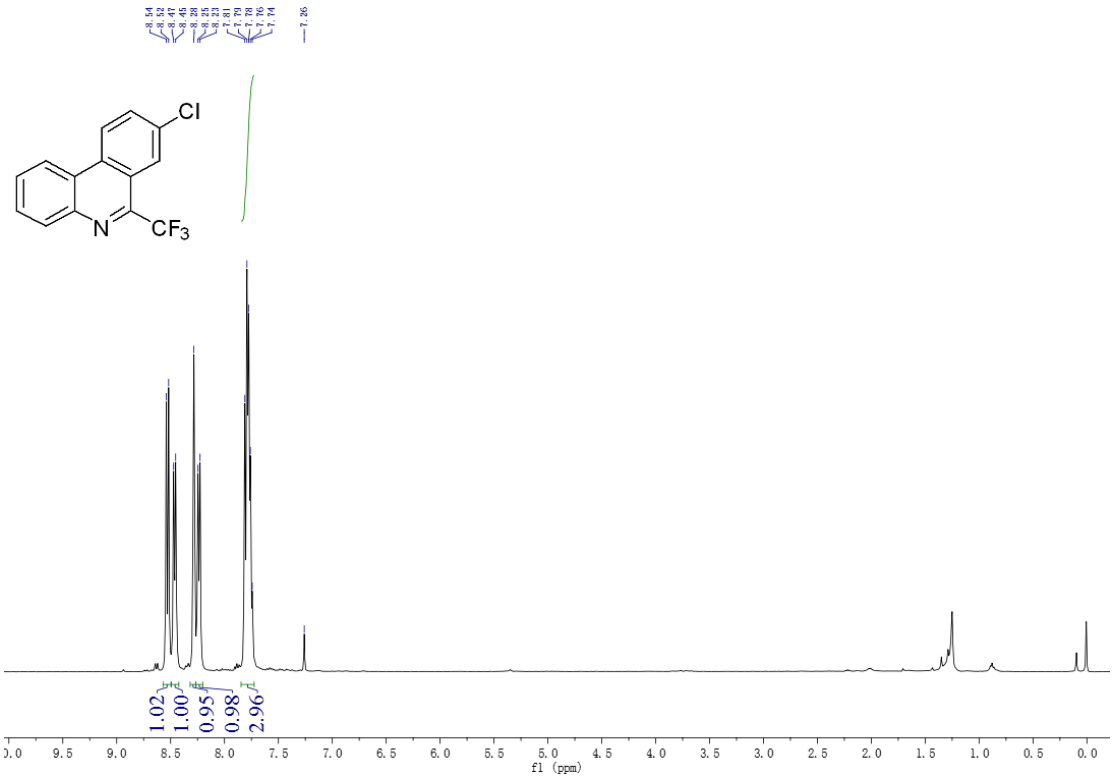


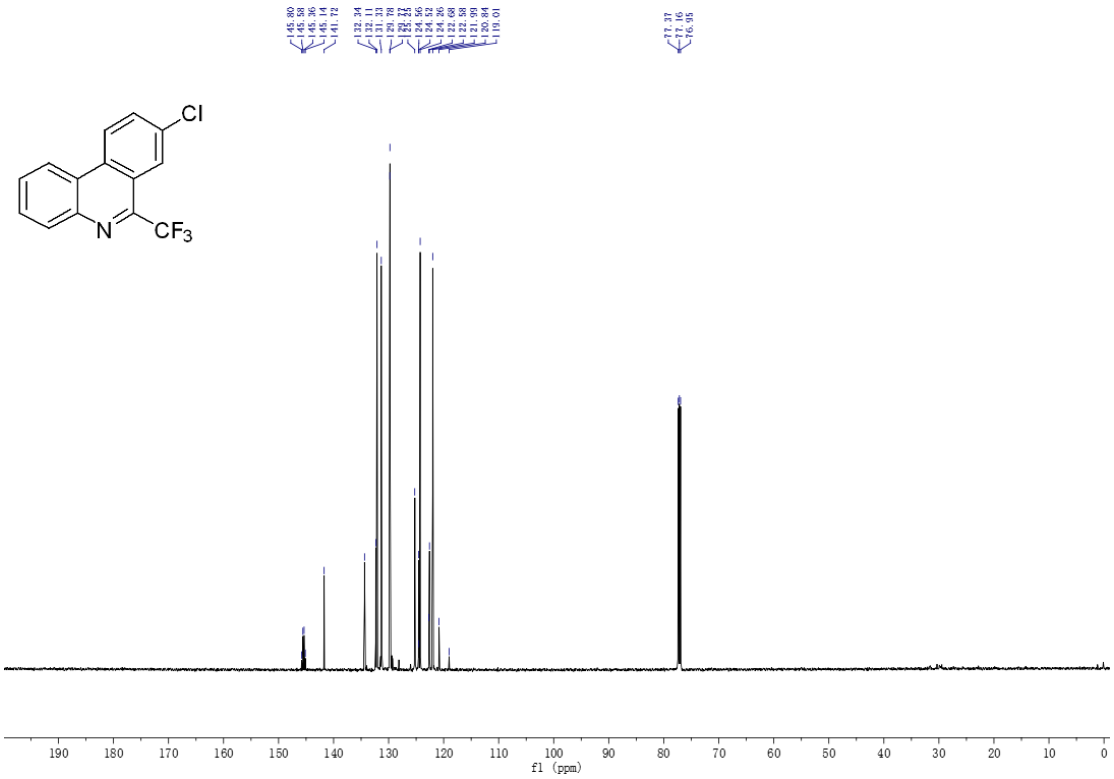
^{19}F NMR of **2b**



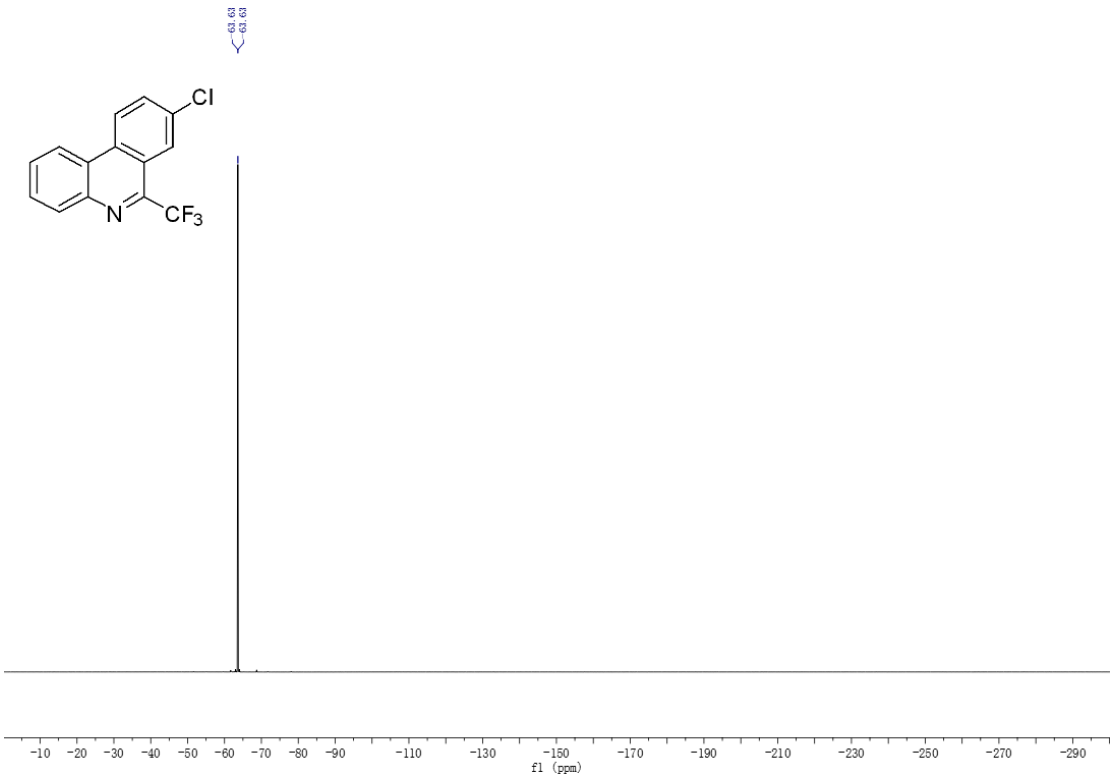
^{1}H NMR of **2c**



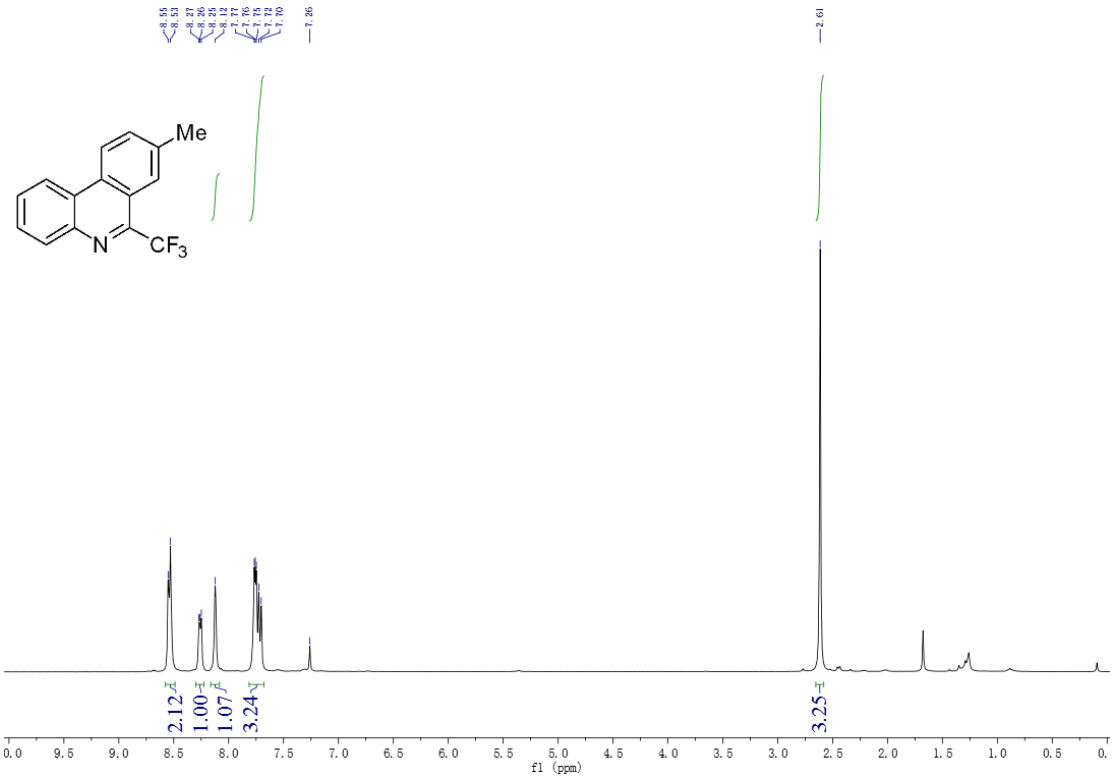
^{13}C NMR of **2c**



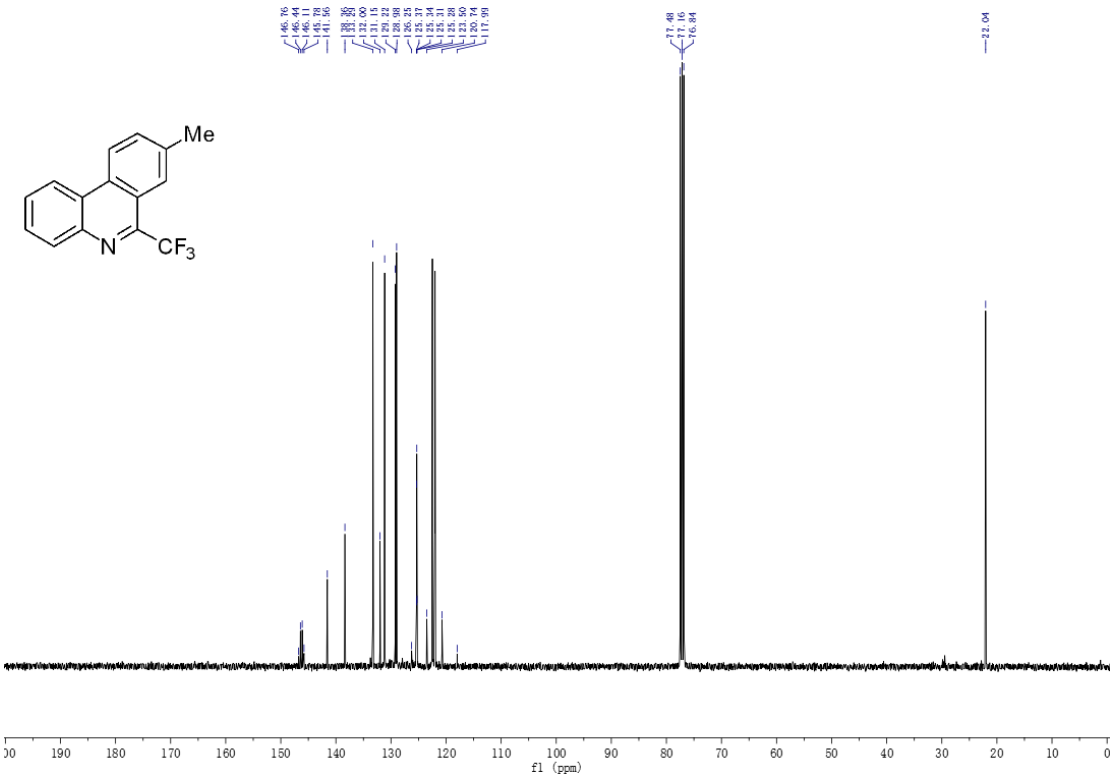
^{19}F NMR of **2c**



^{1}H NMR of **2d**



^{13}C NMR of **2d**



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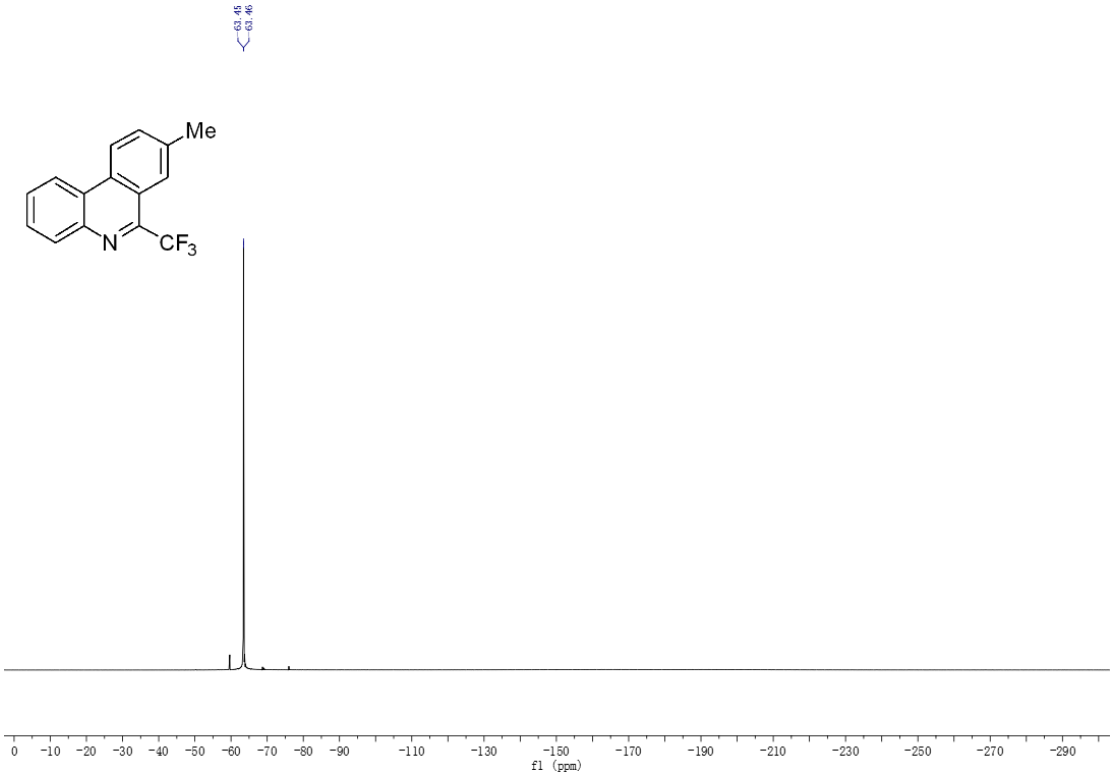

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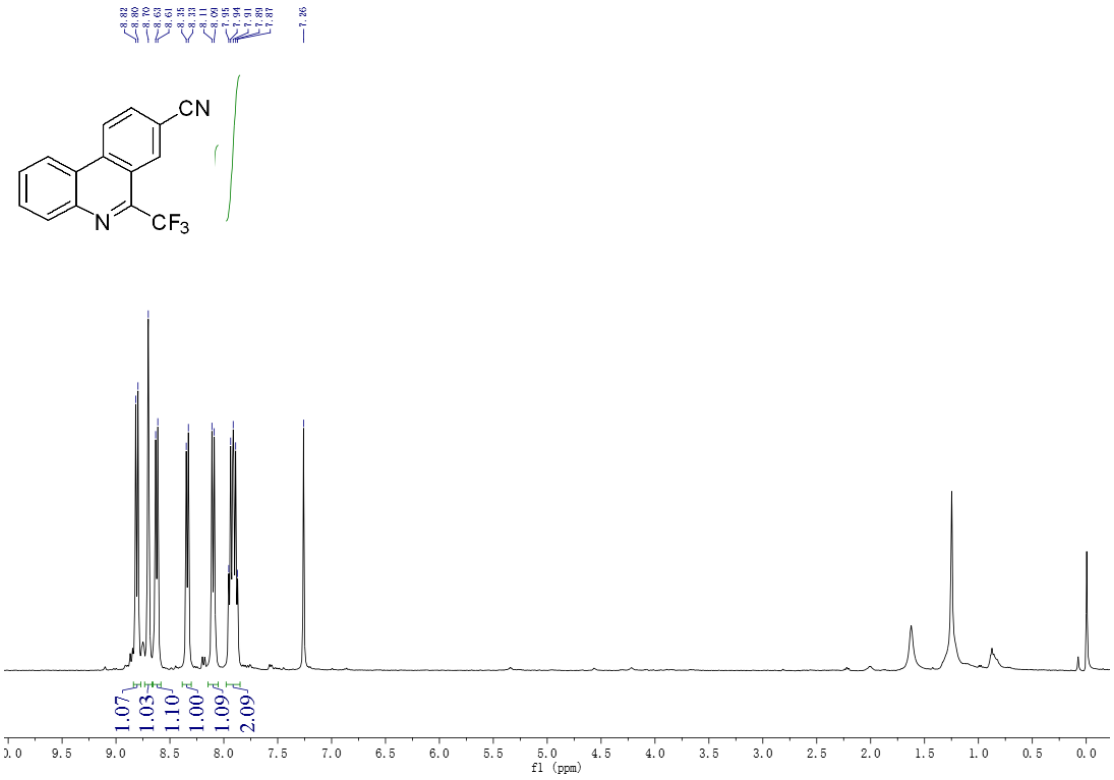
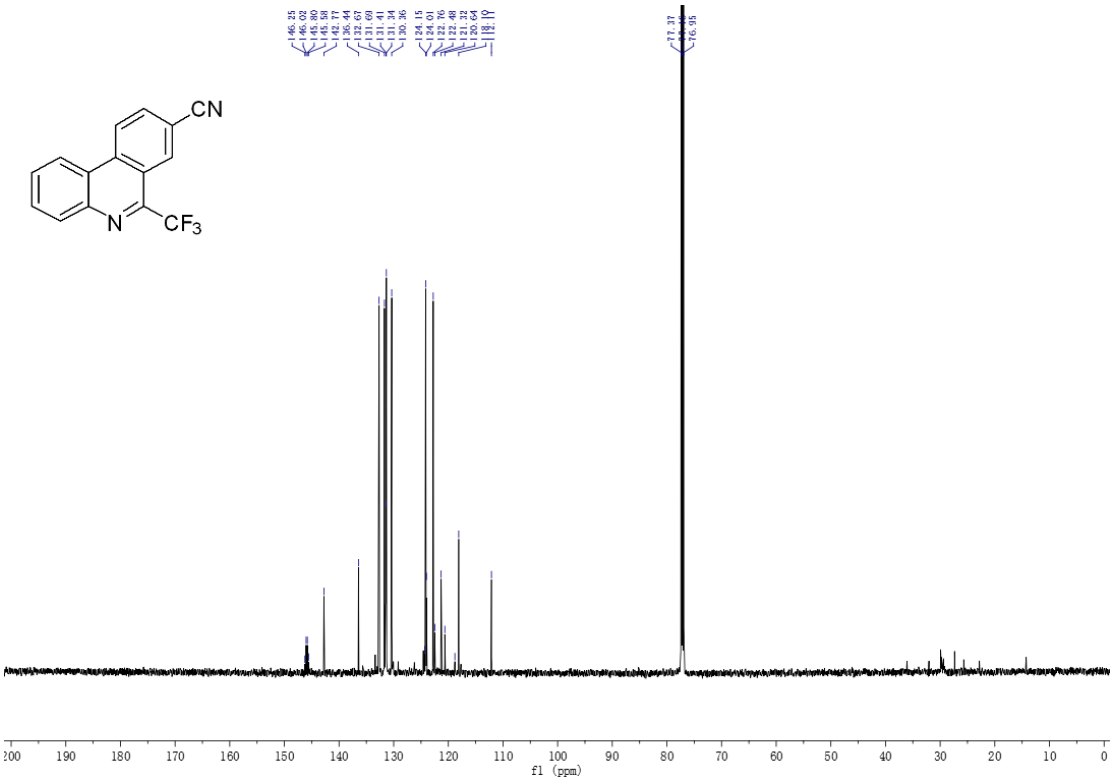


^{13}C NMR of **2e**



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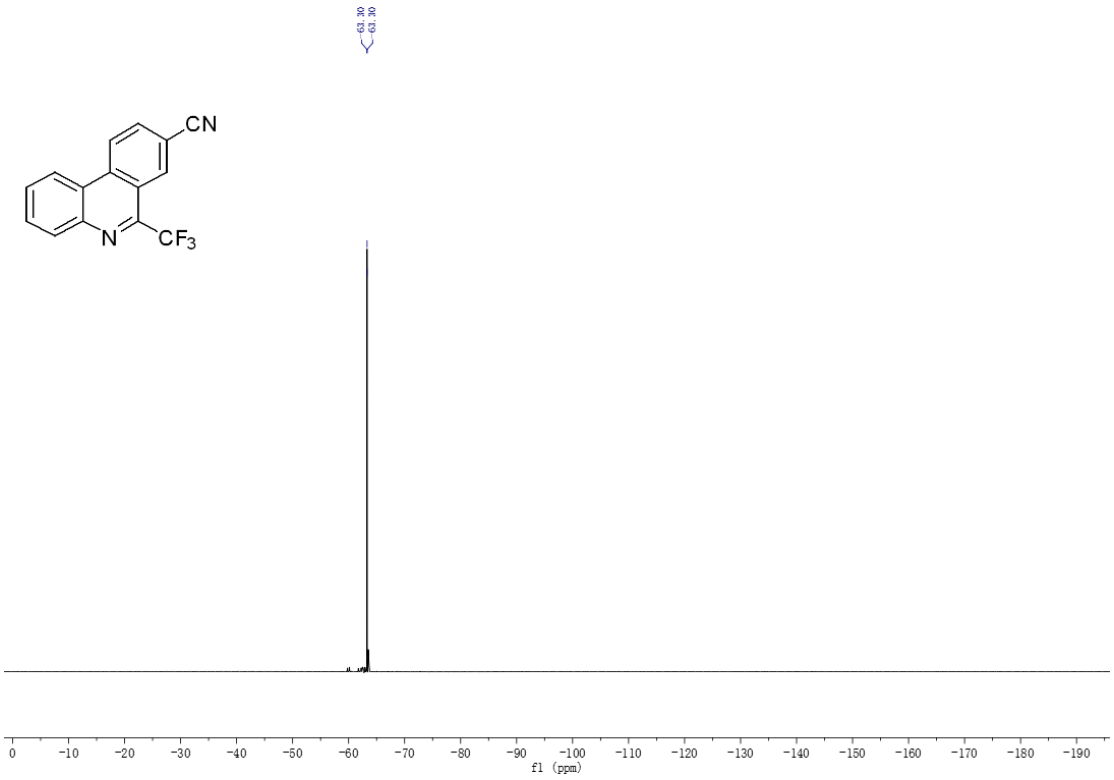
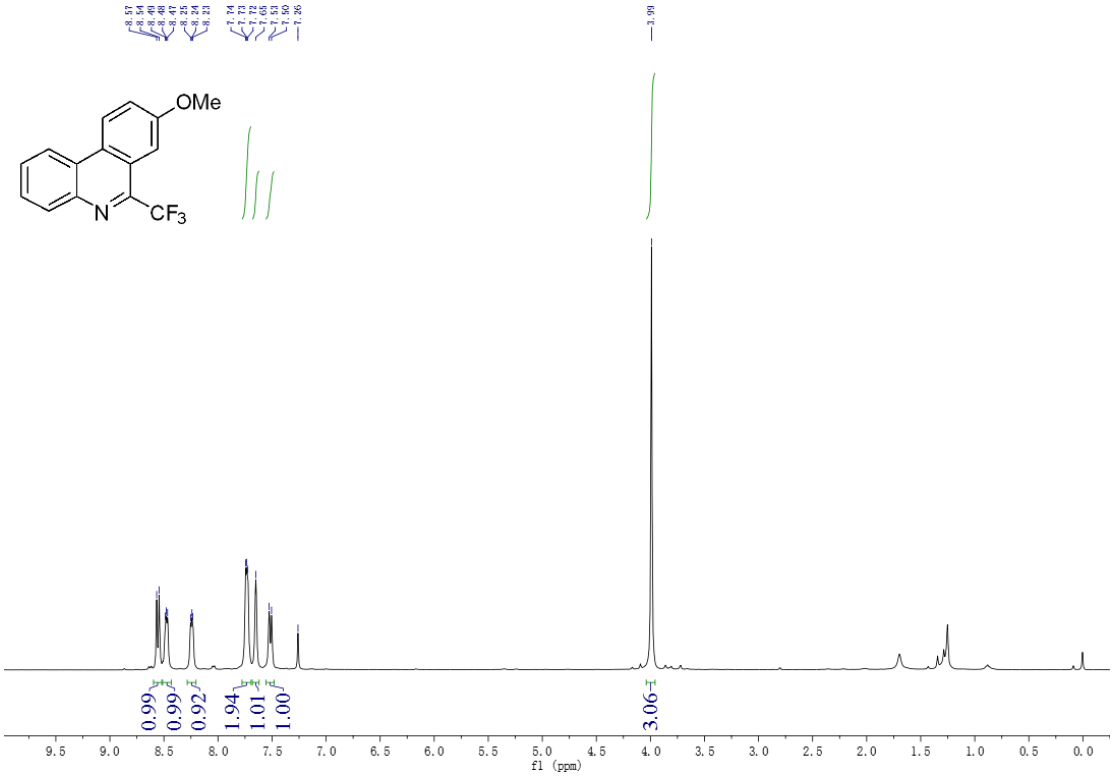
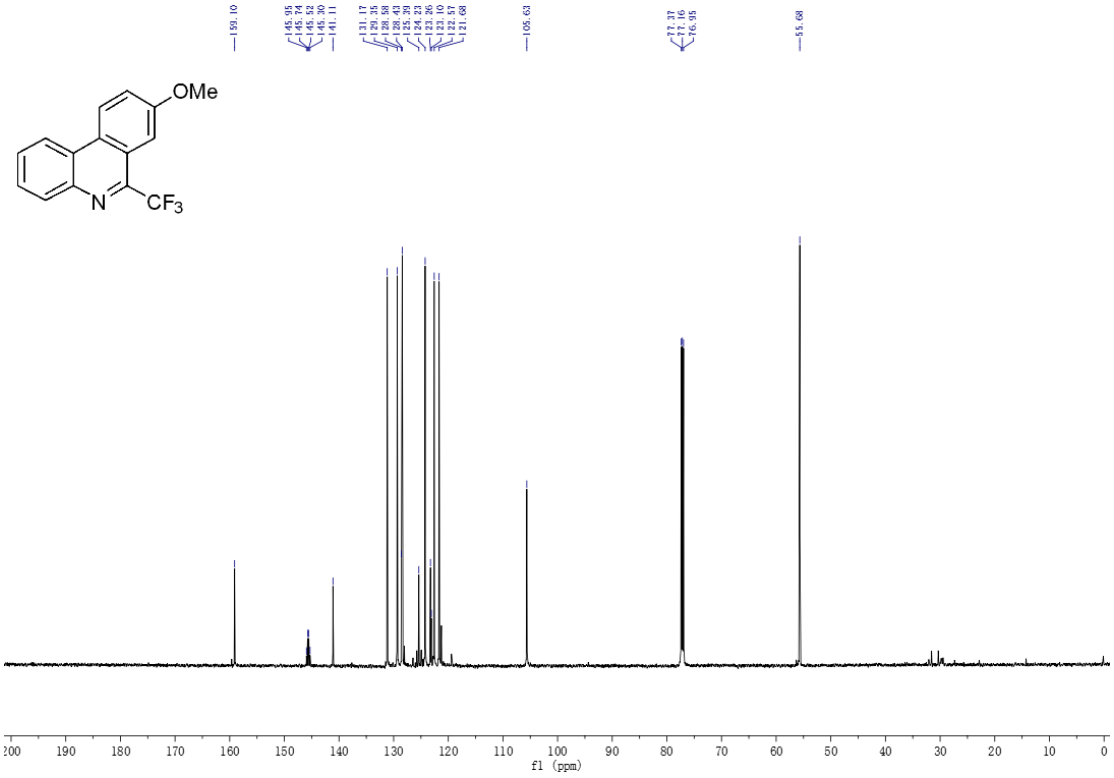


^{1}H NMR of **2f**



^{13}C NMR of **2f**



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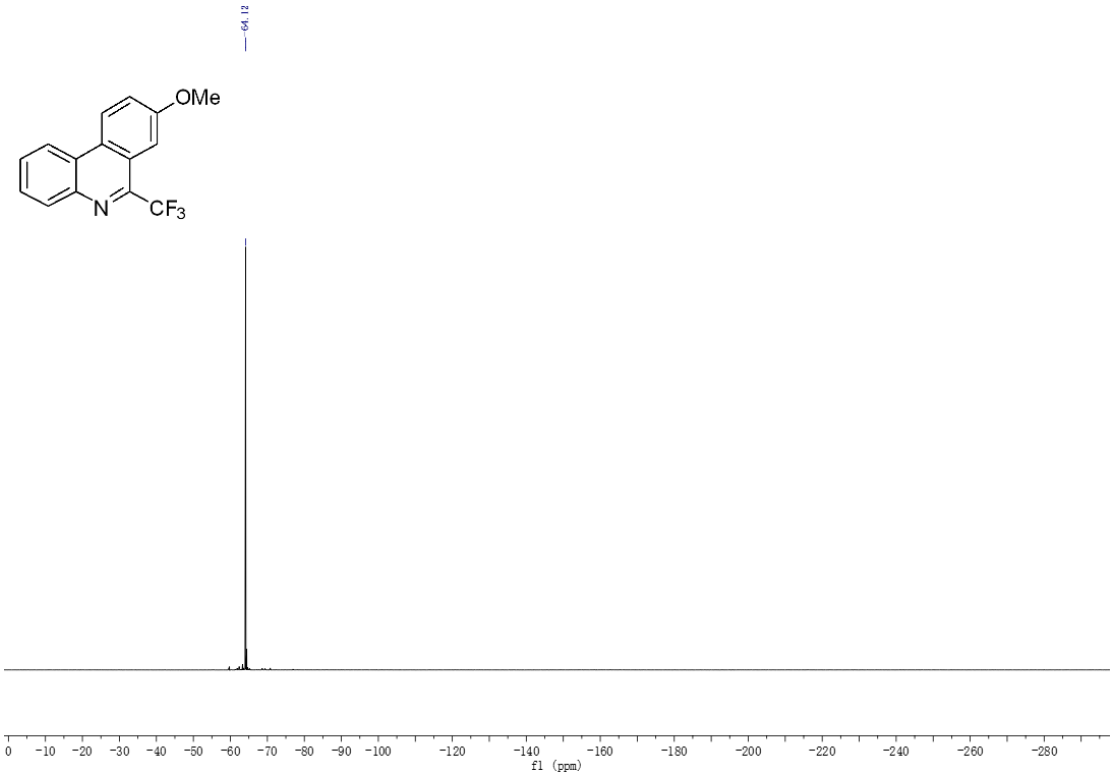

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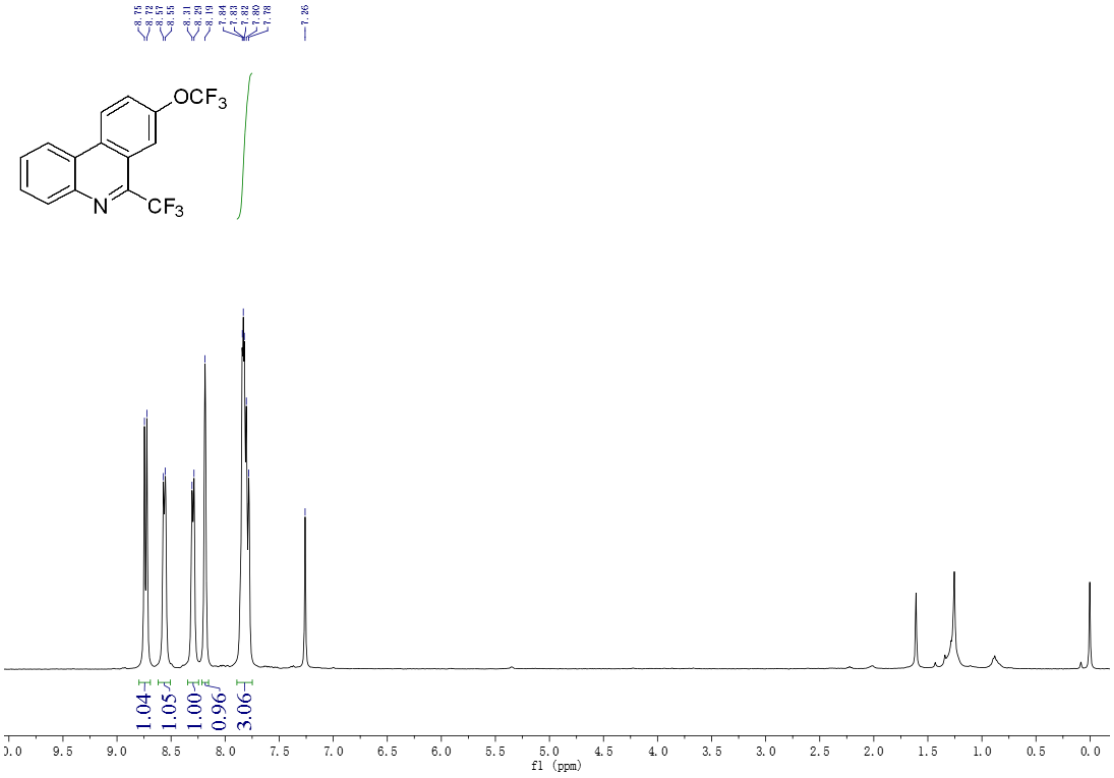
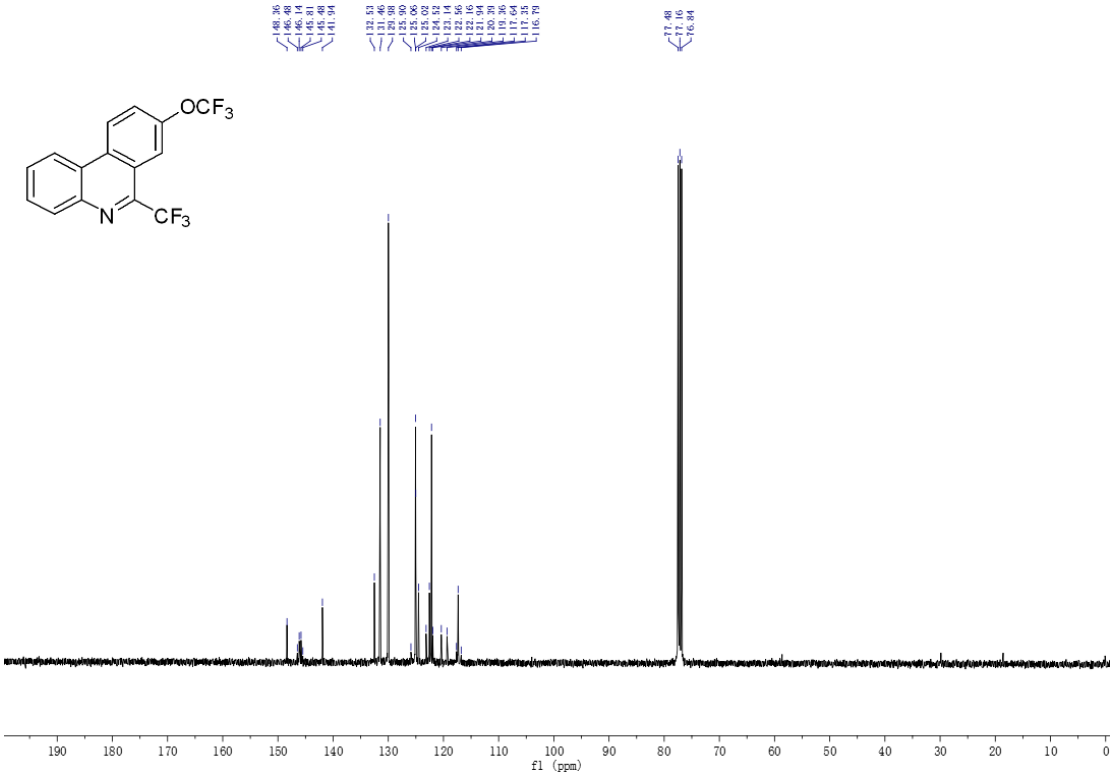
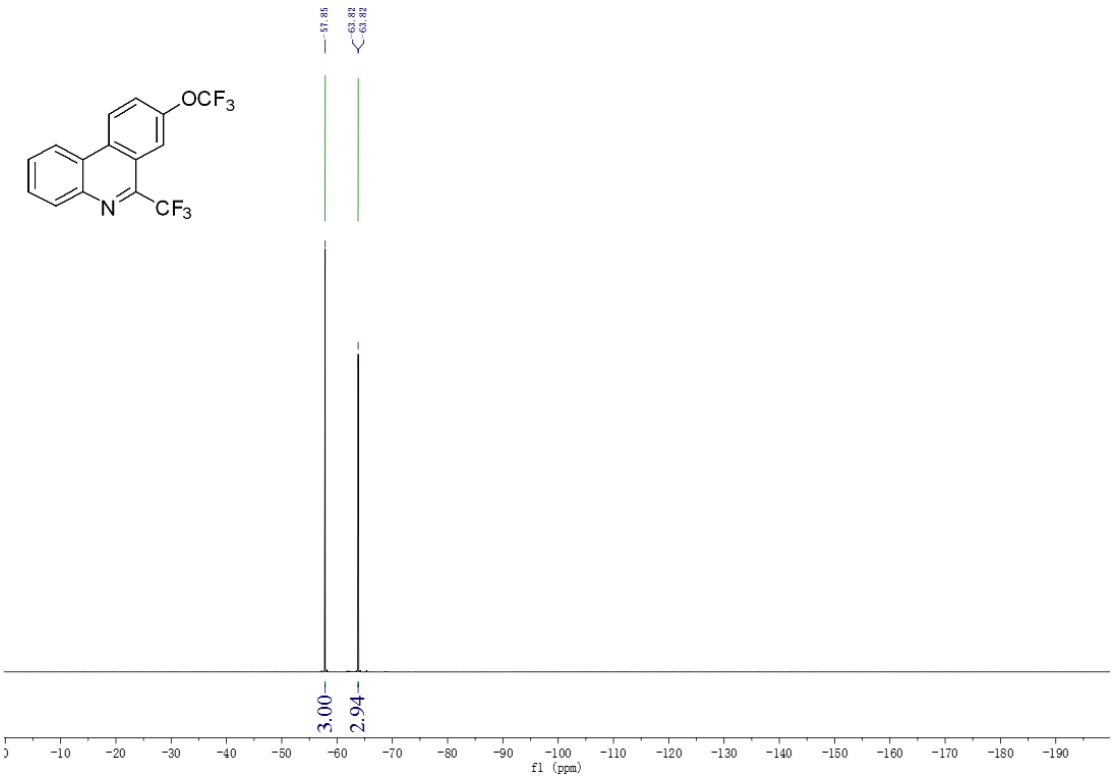


^{13}C NMR of **2g**



^{19}F NMR of **2g**



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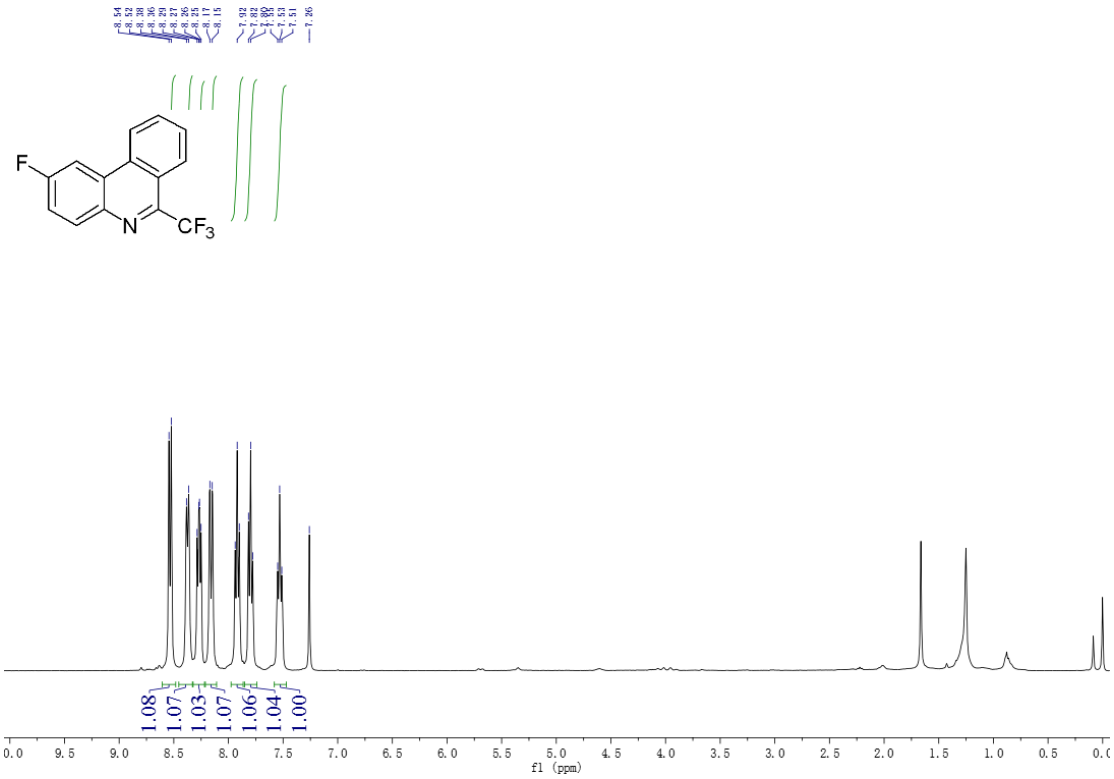

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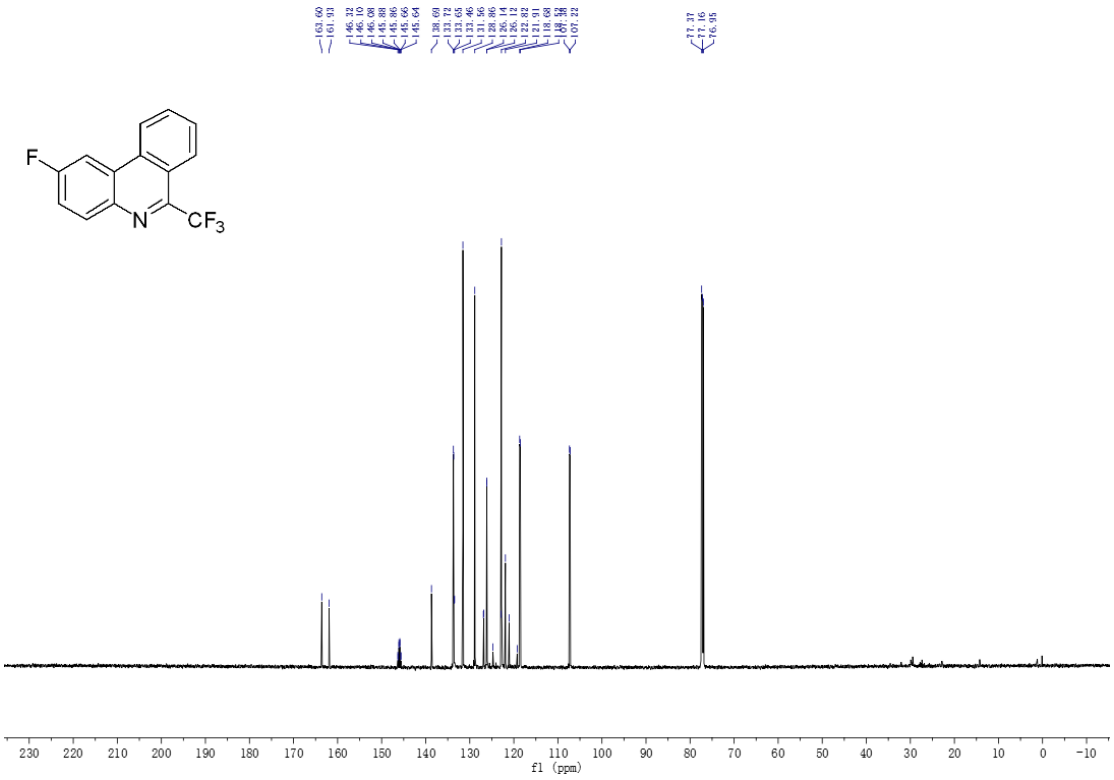

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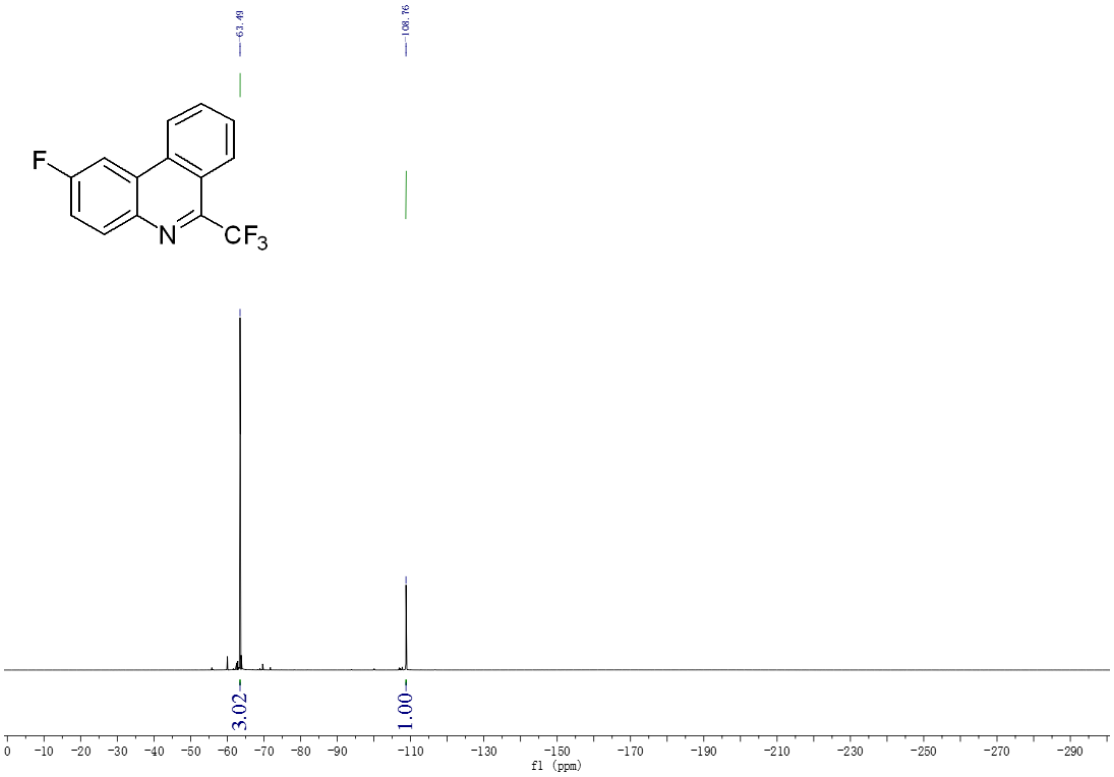

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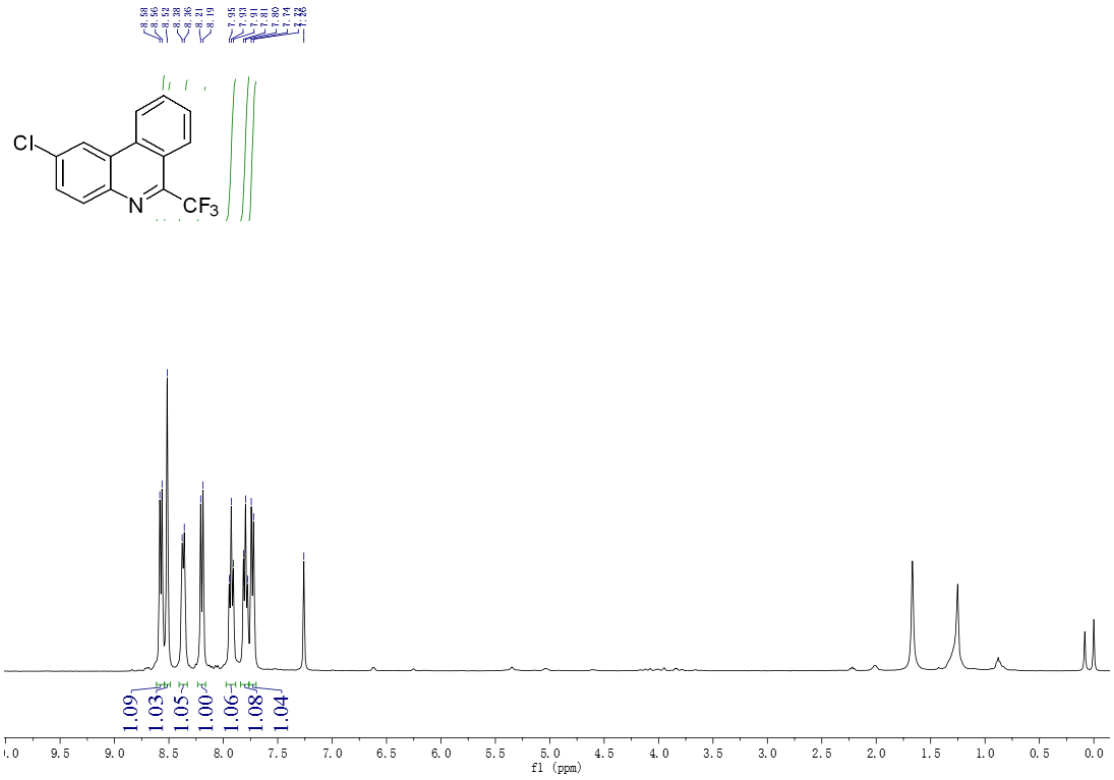

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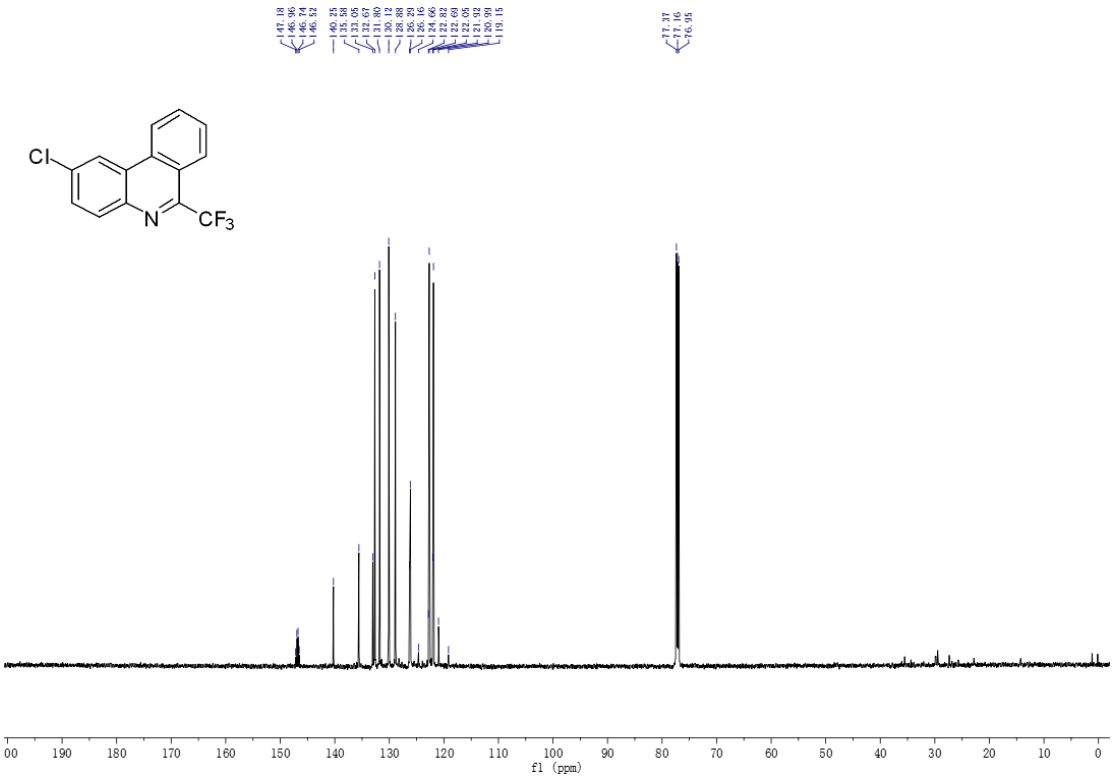

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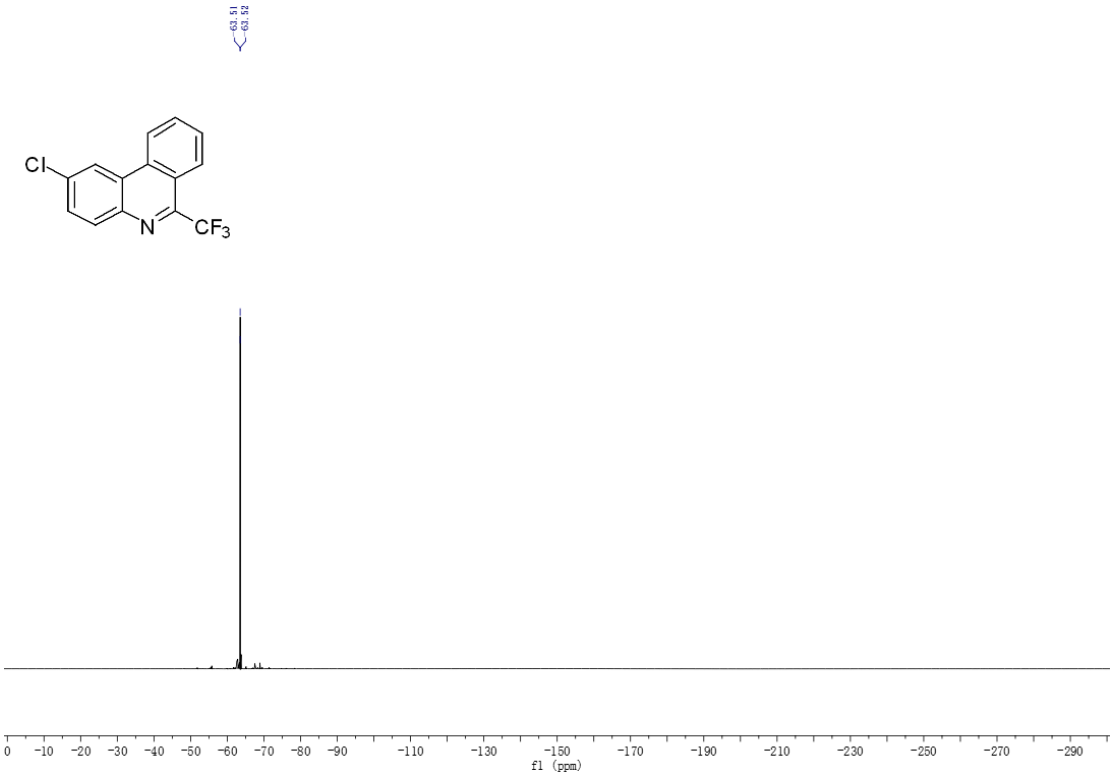

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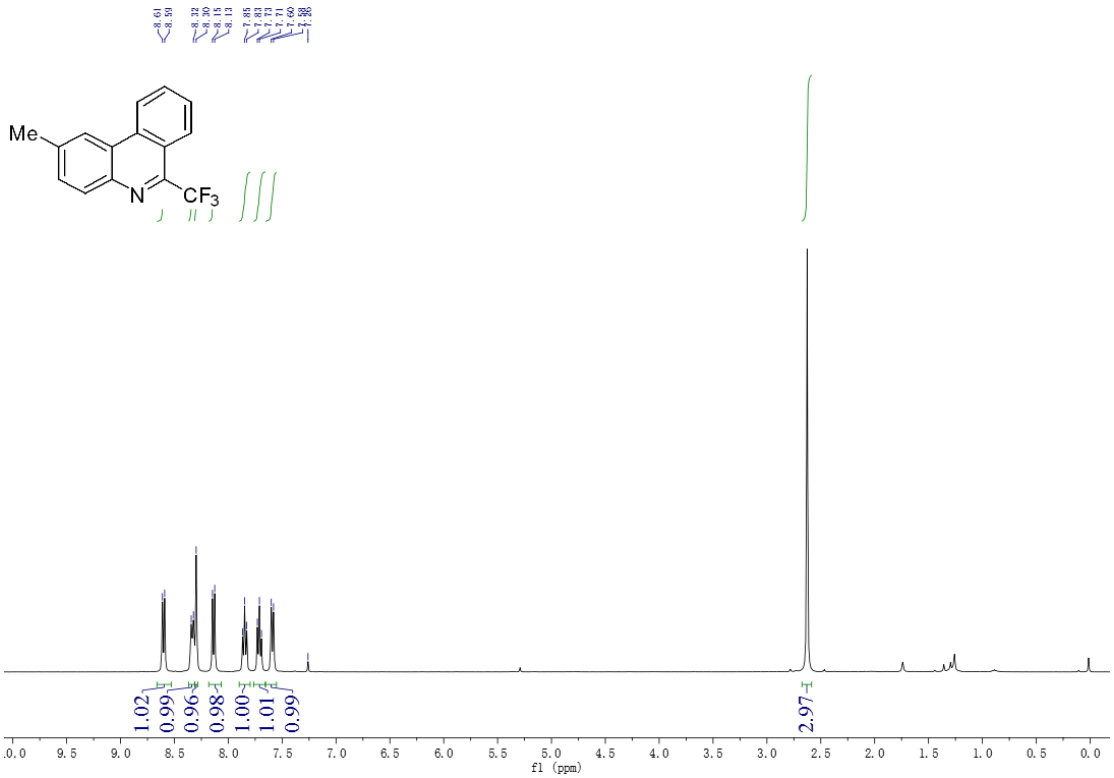

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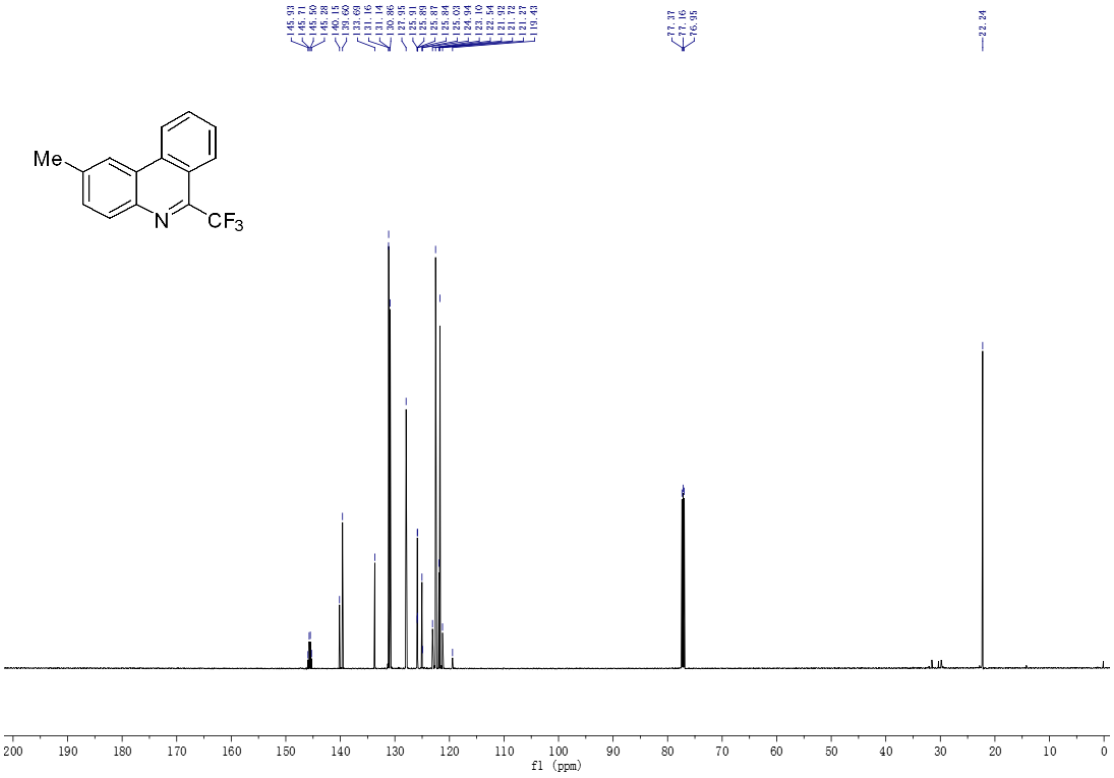
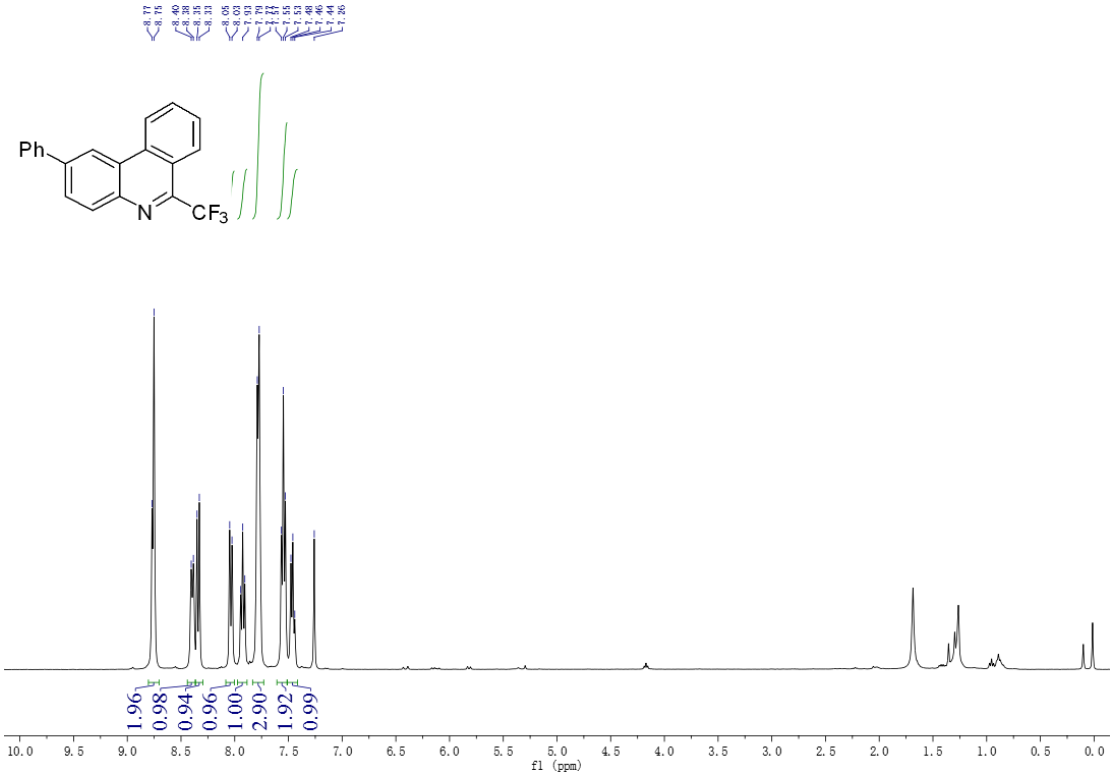
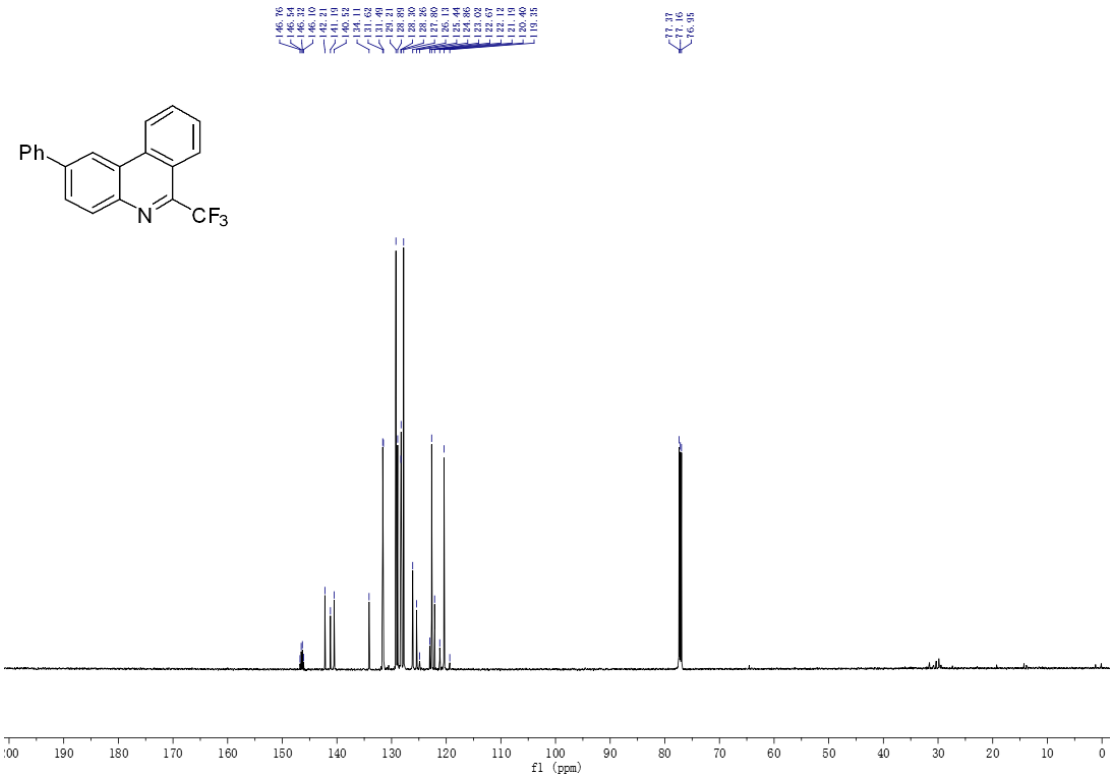


^{19}F NMR of **2j**

^{1}H NMR of **2k**



^{13}C NMR of **2k**



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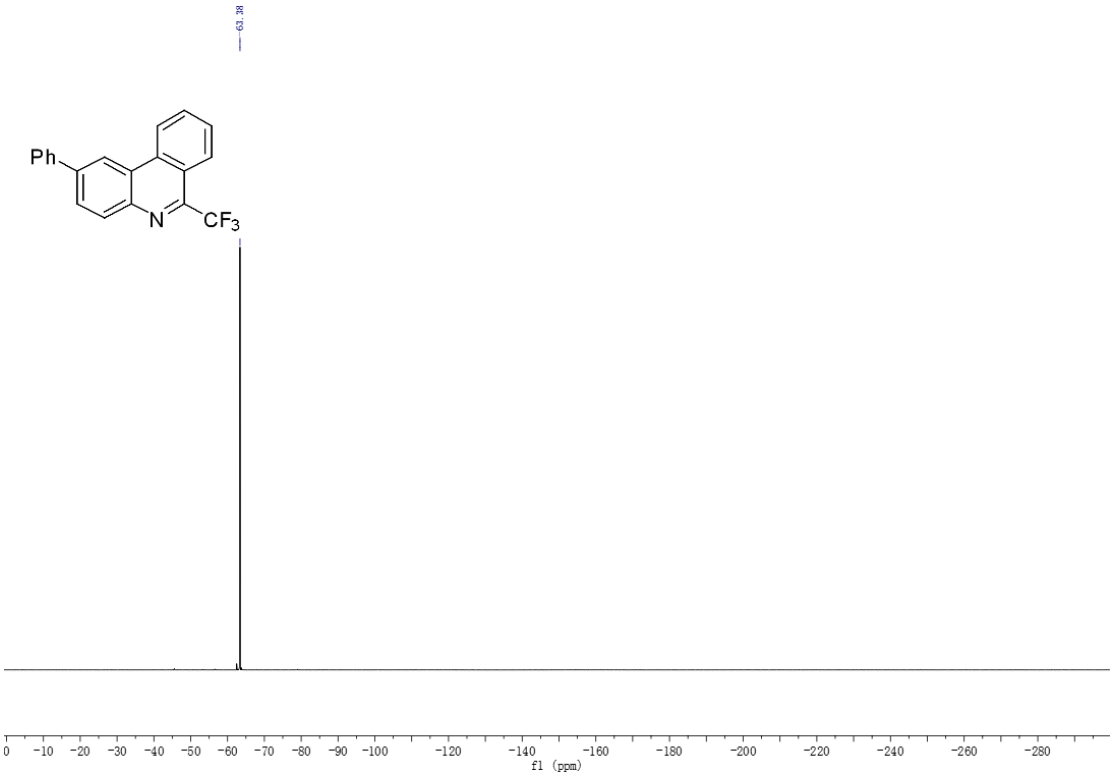

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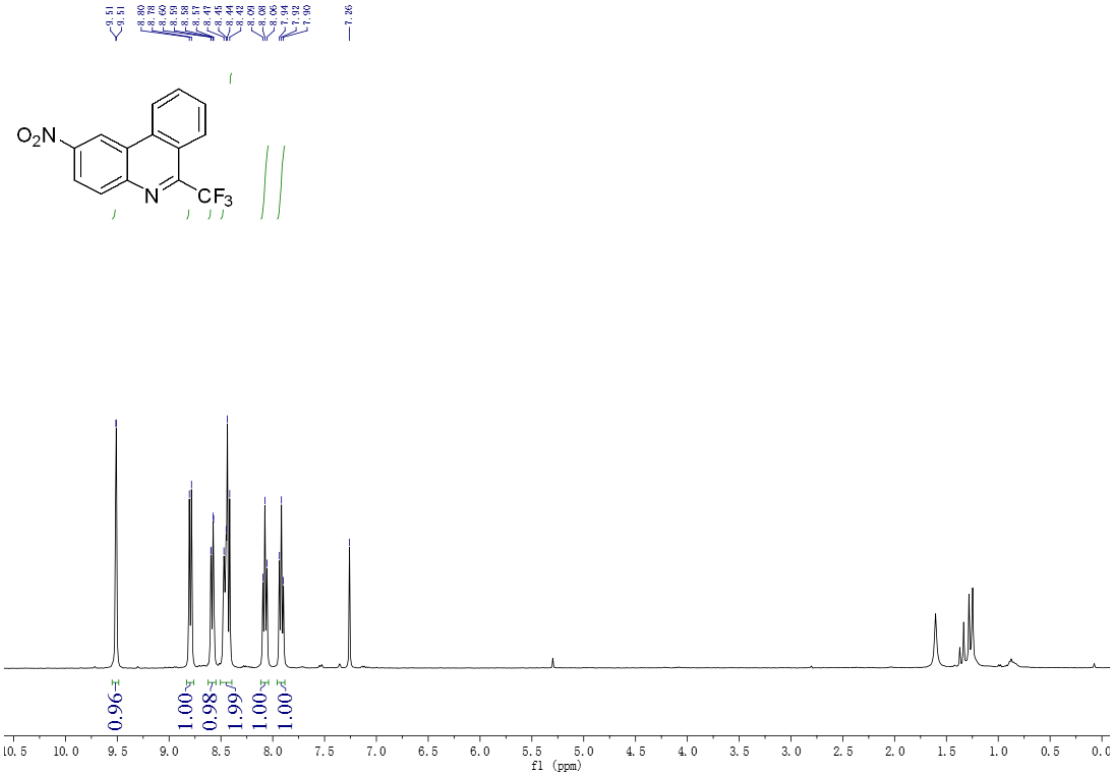

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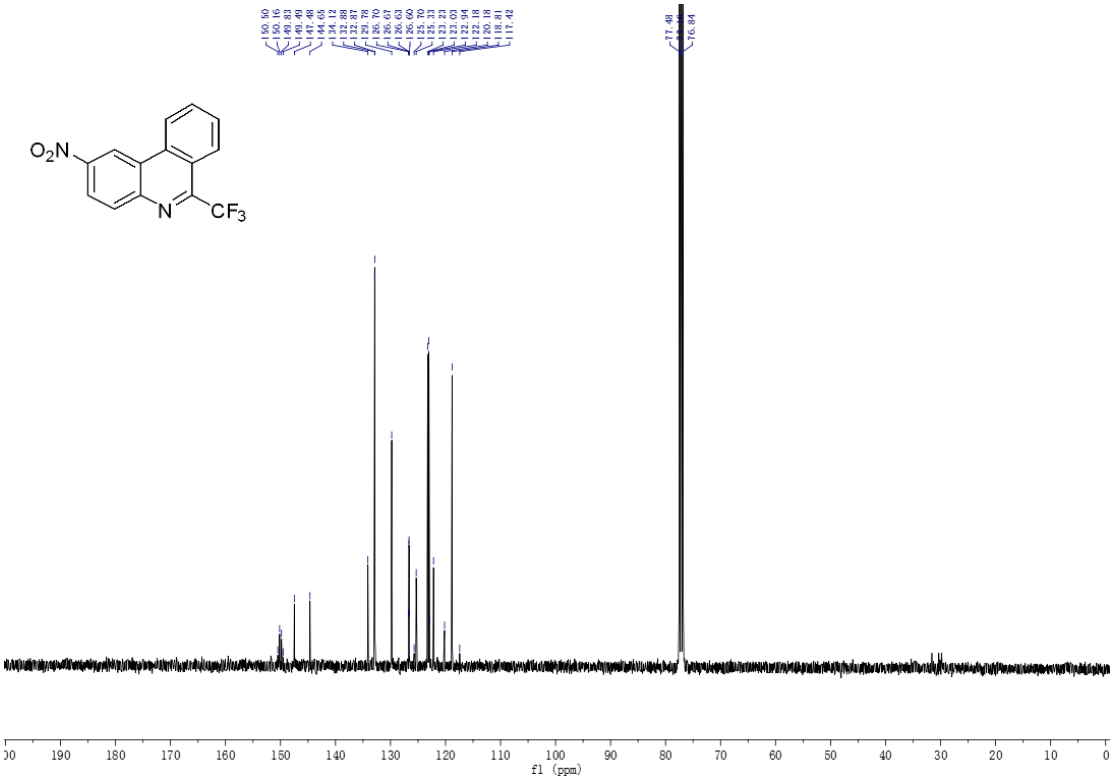

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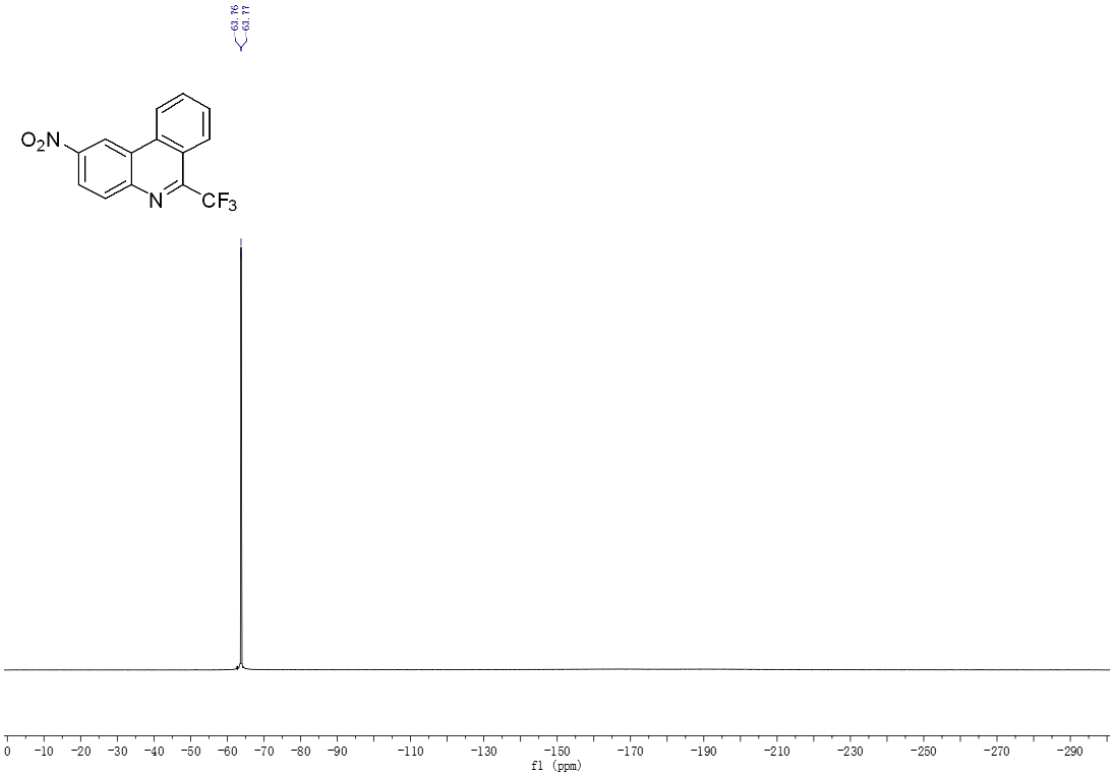

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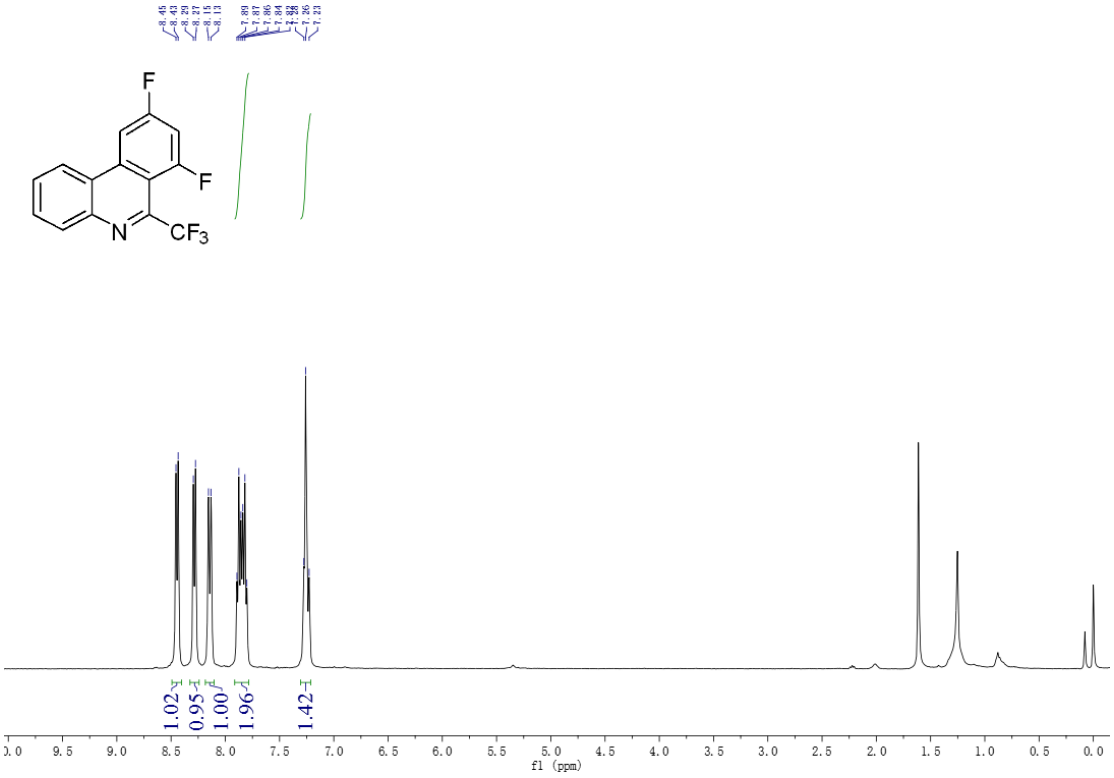

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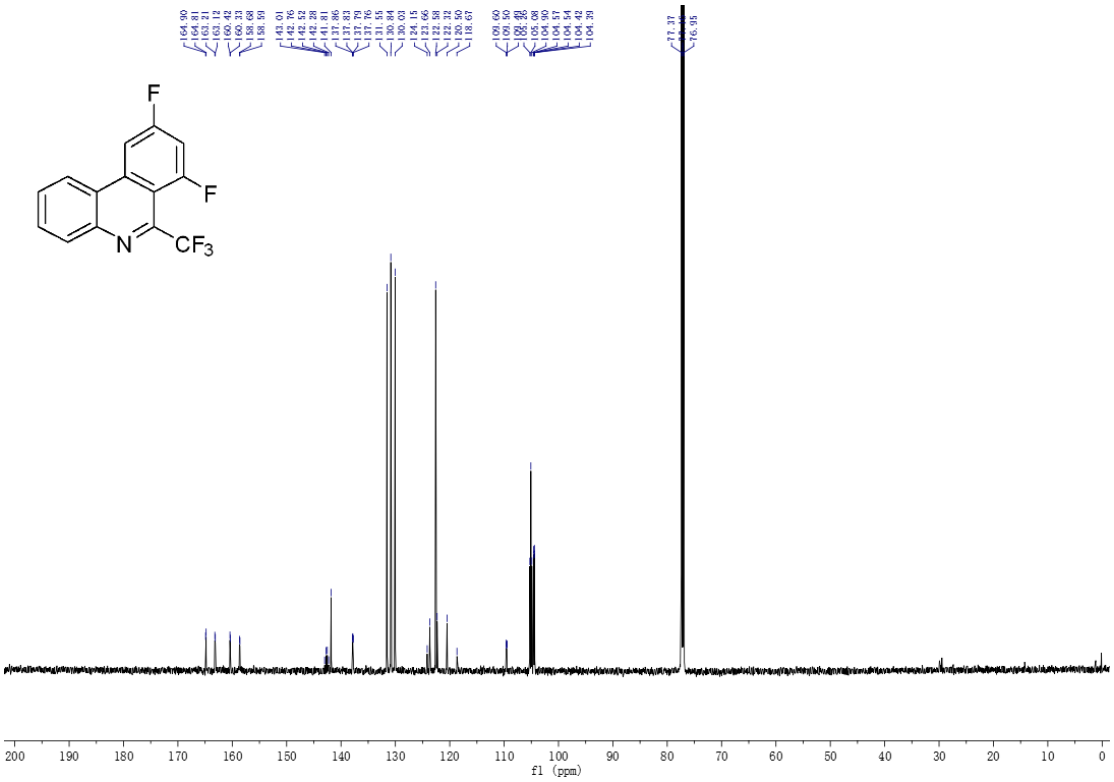

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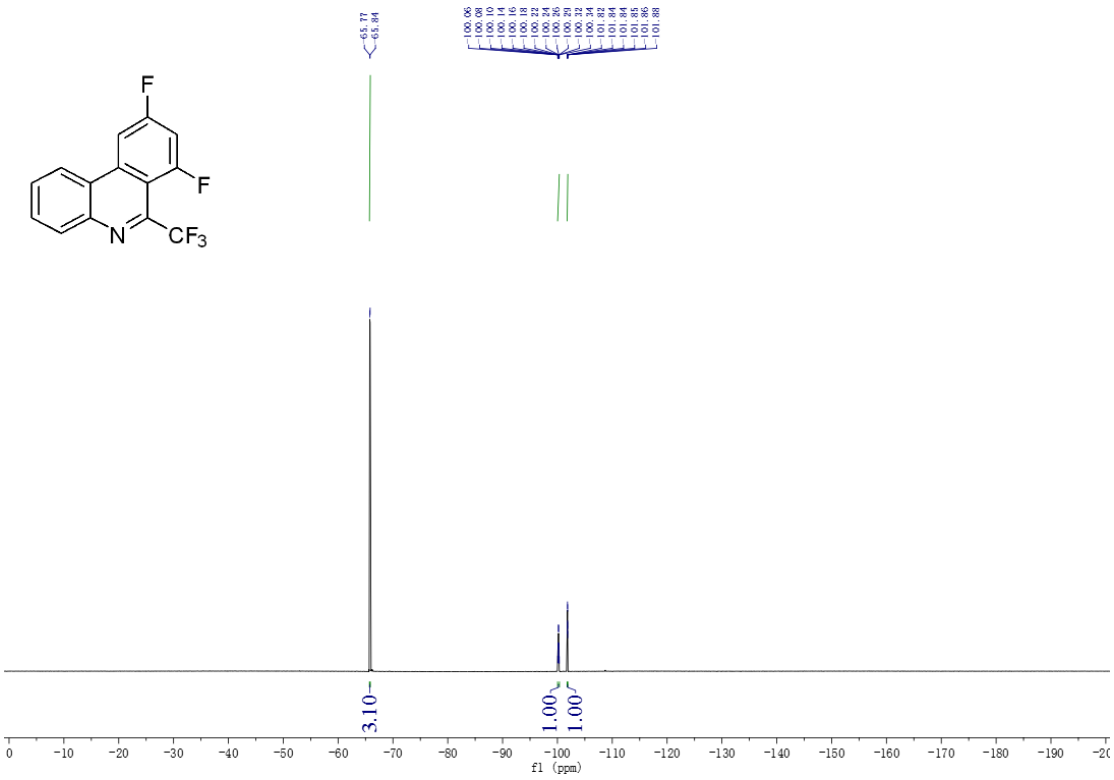

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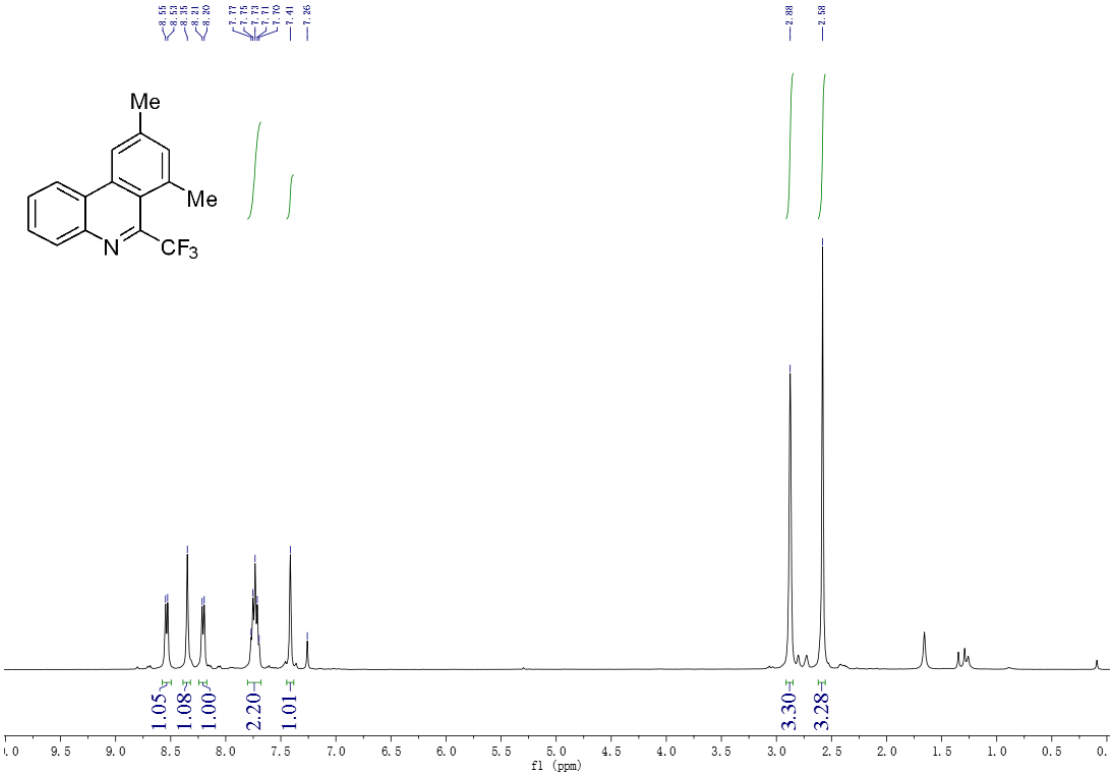

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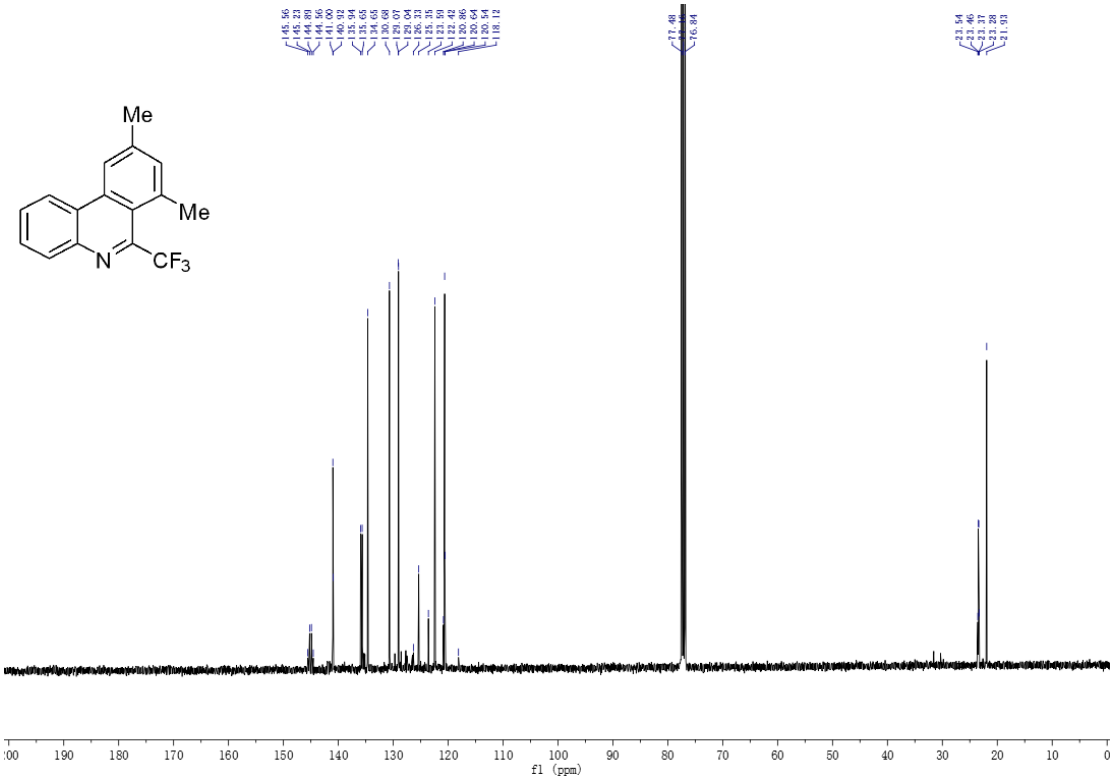

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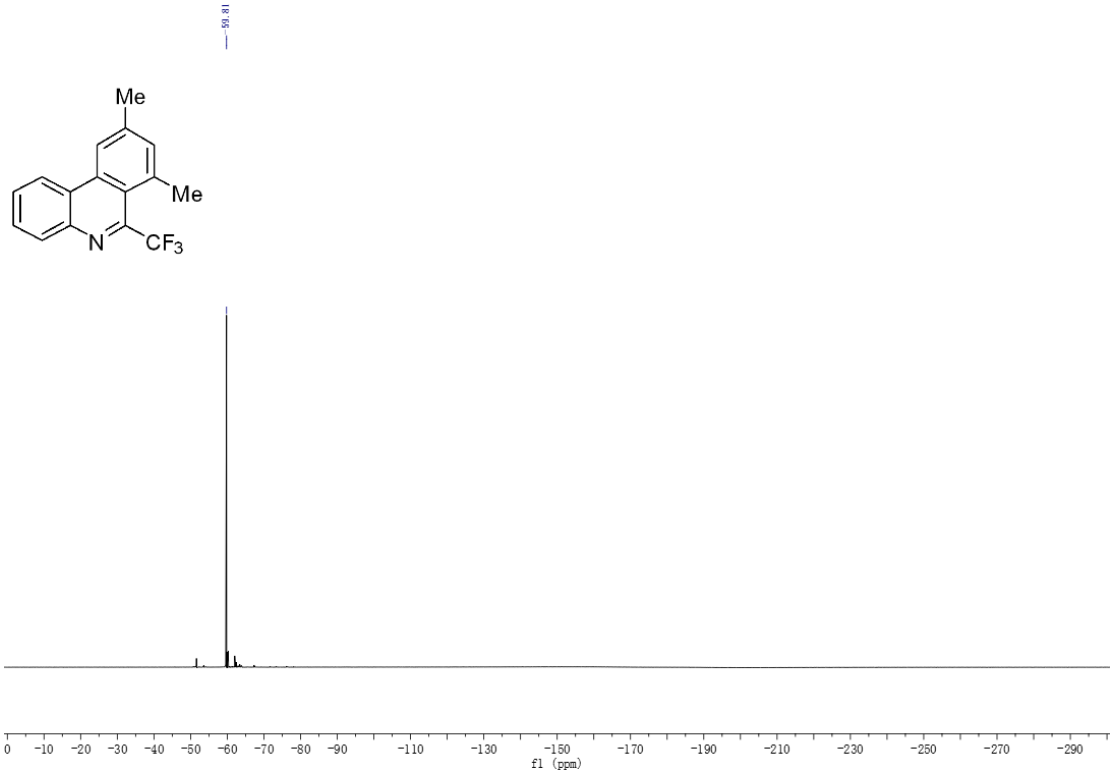

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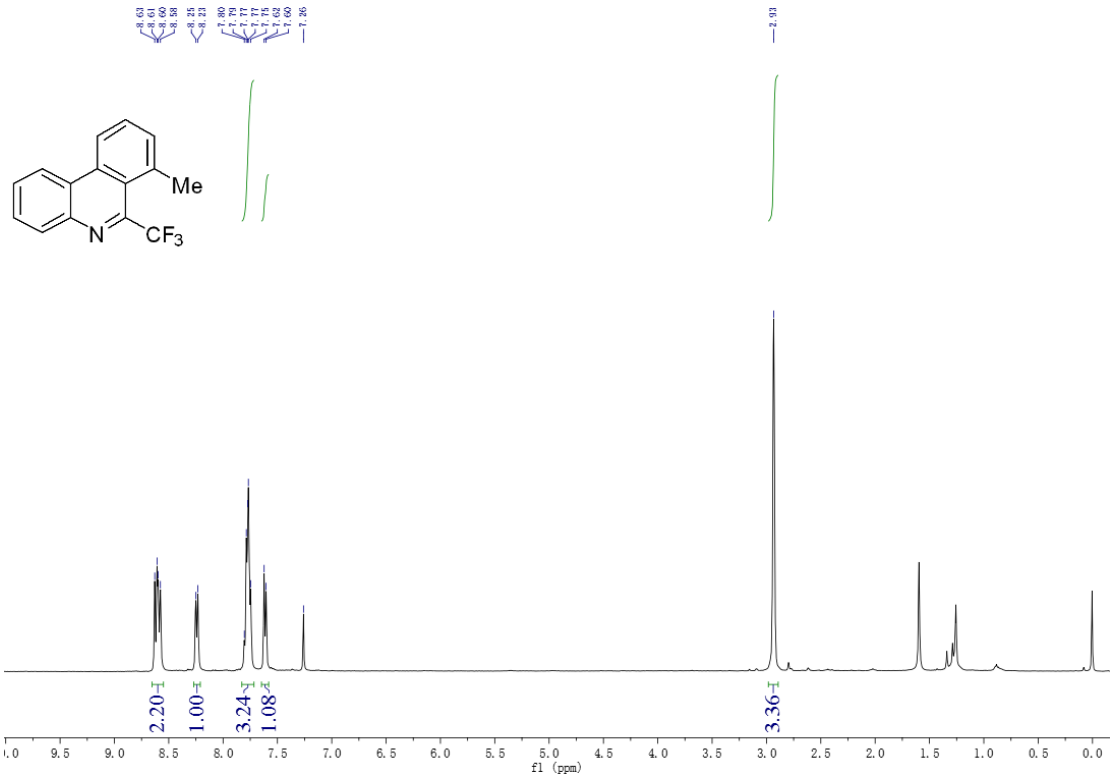

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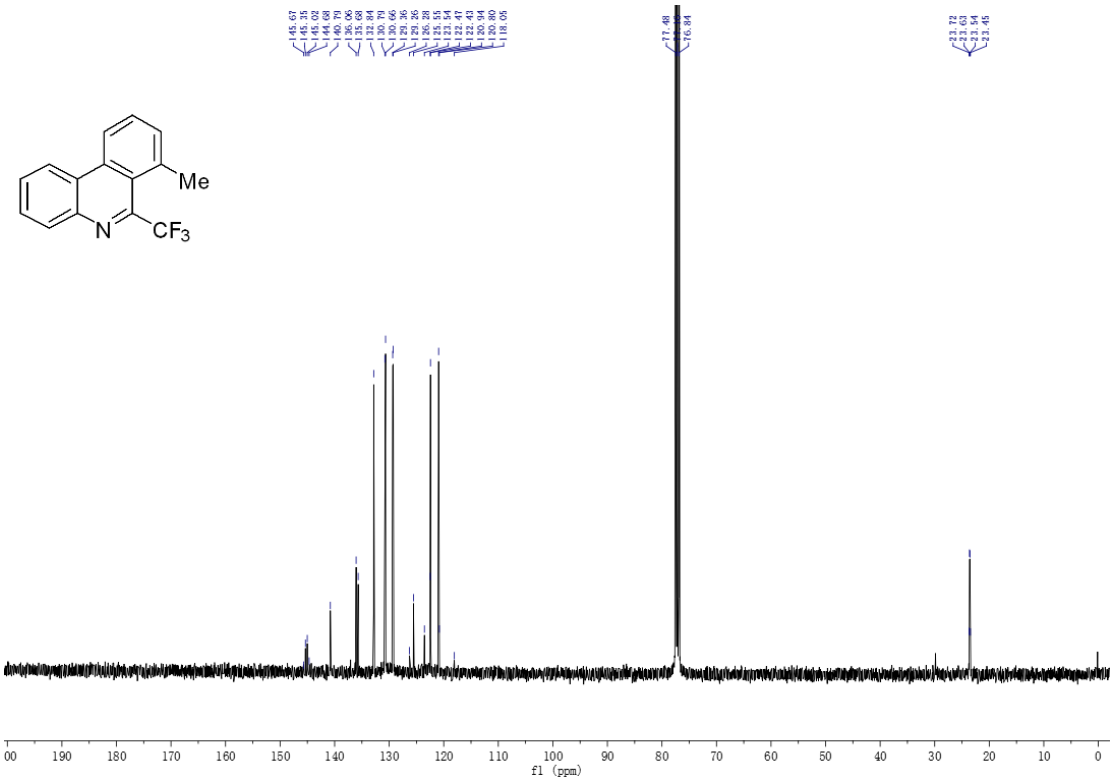

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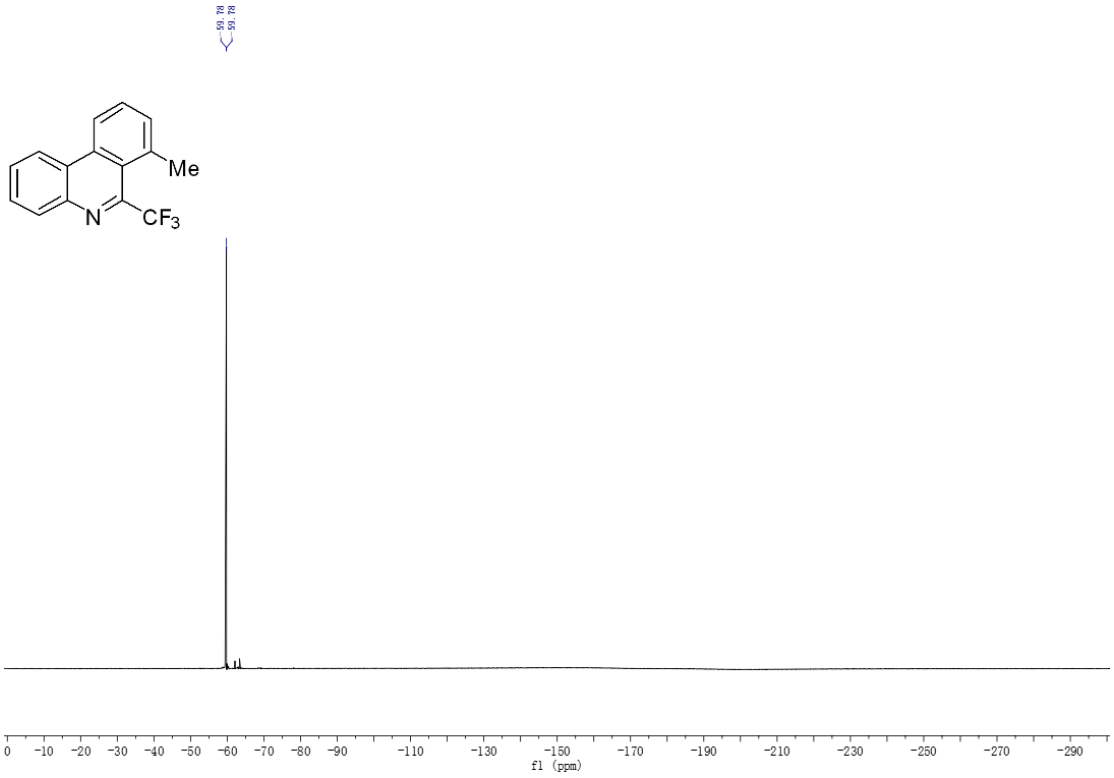

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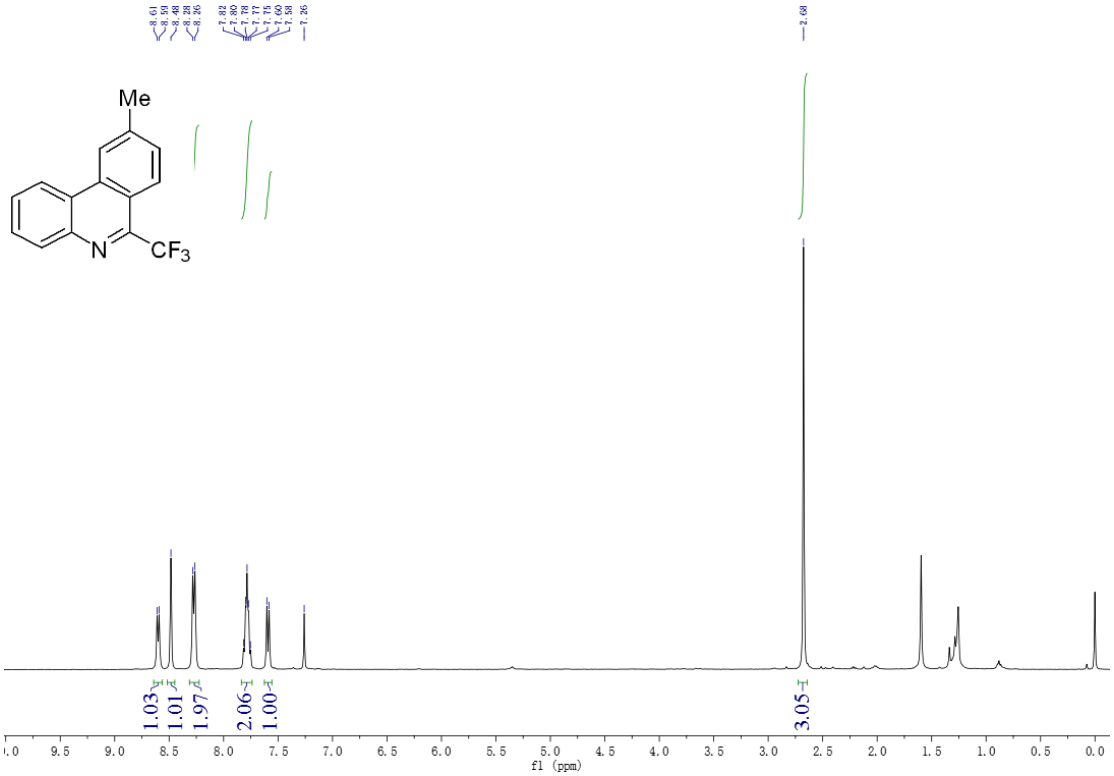

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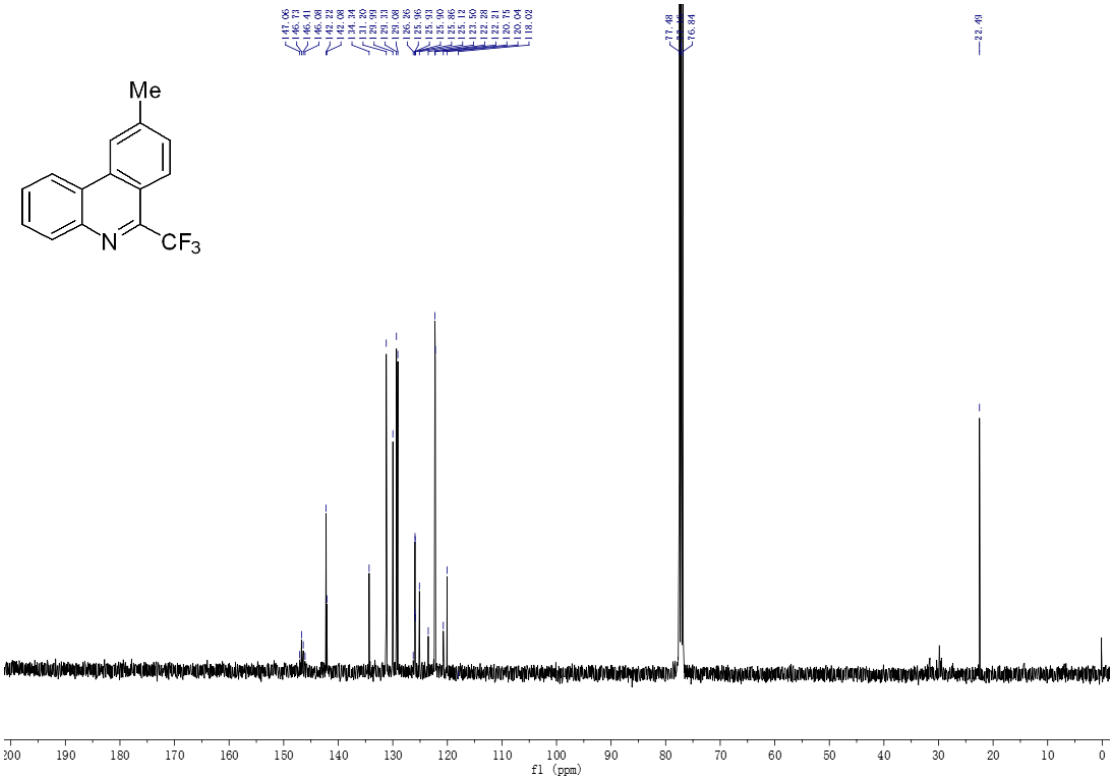
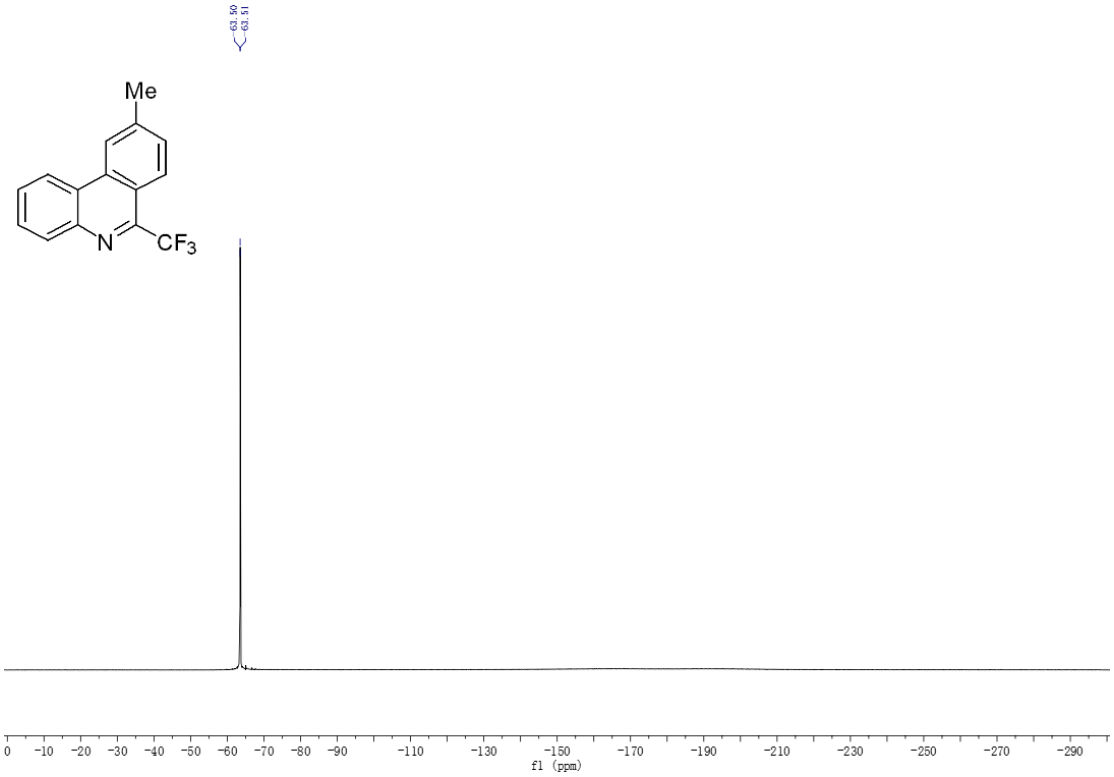
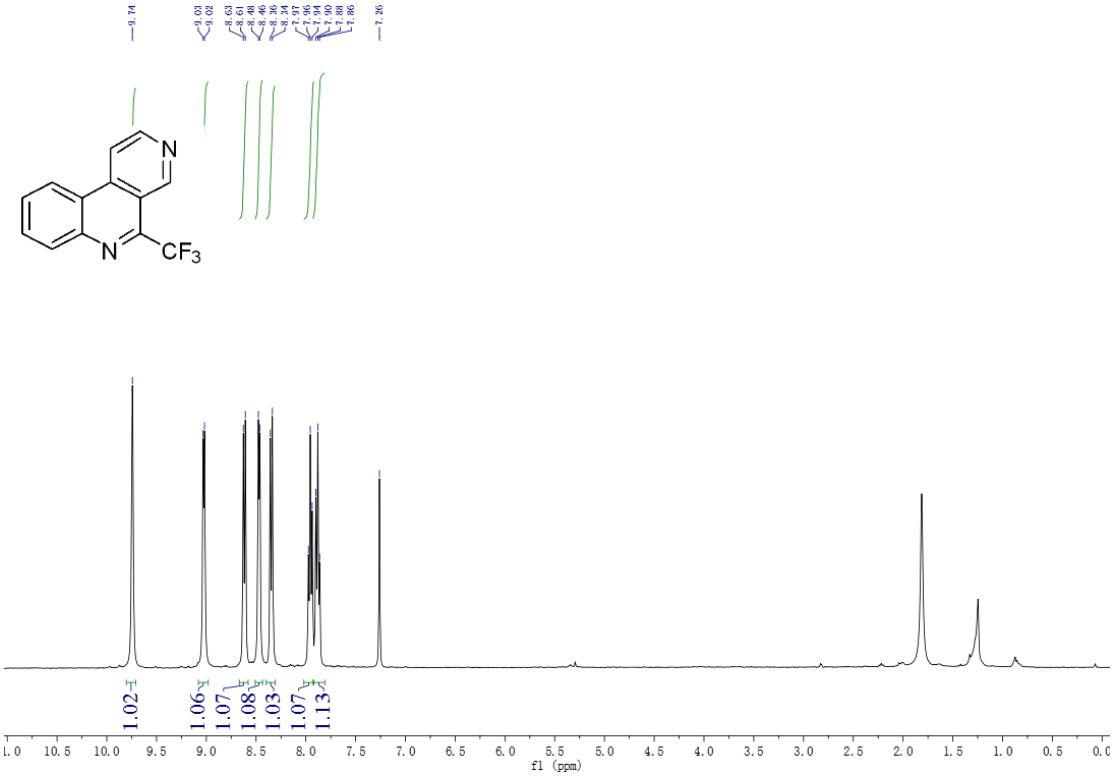


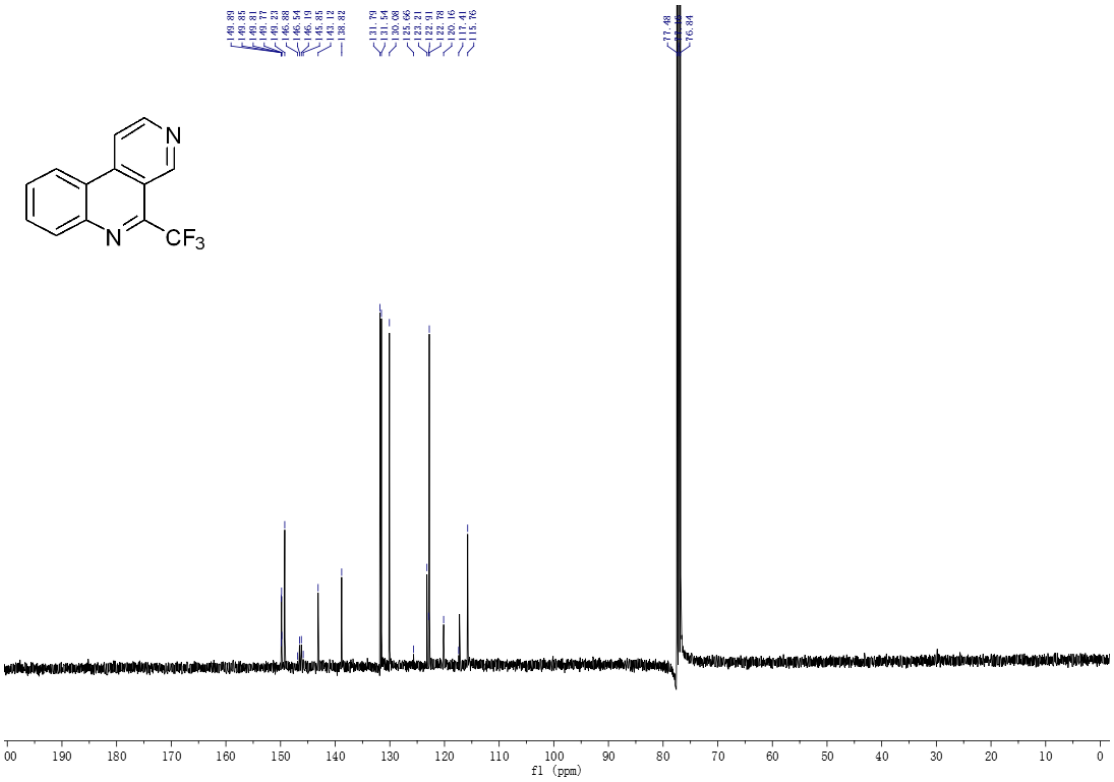
^{19}F NMR of **2o'**



^{1}H NMR of **2p**



^{13}C NMR of **2p**



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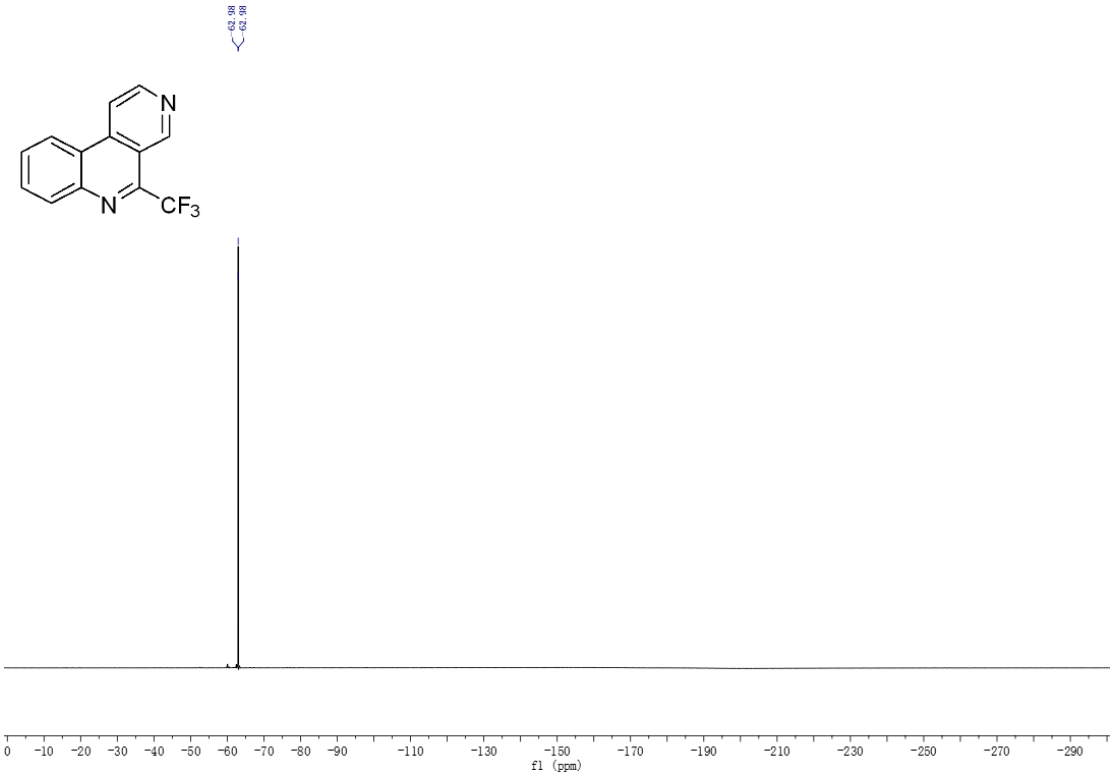
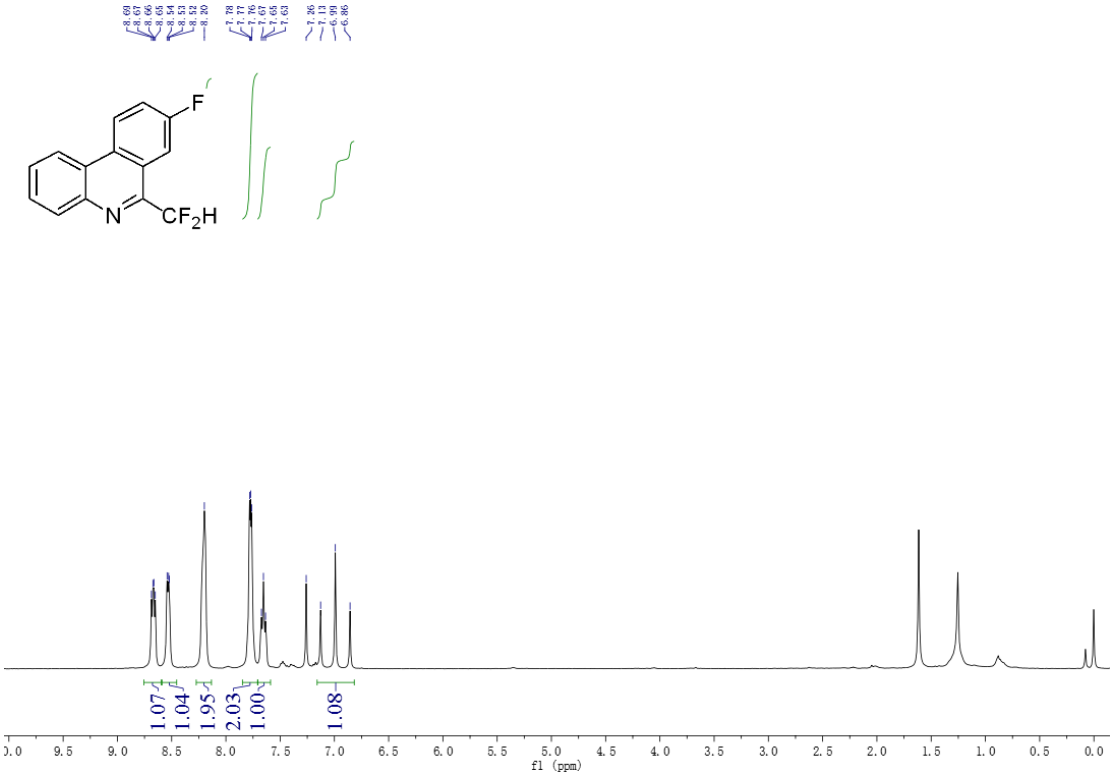


^{1}H NMR of **3a**



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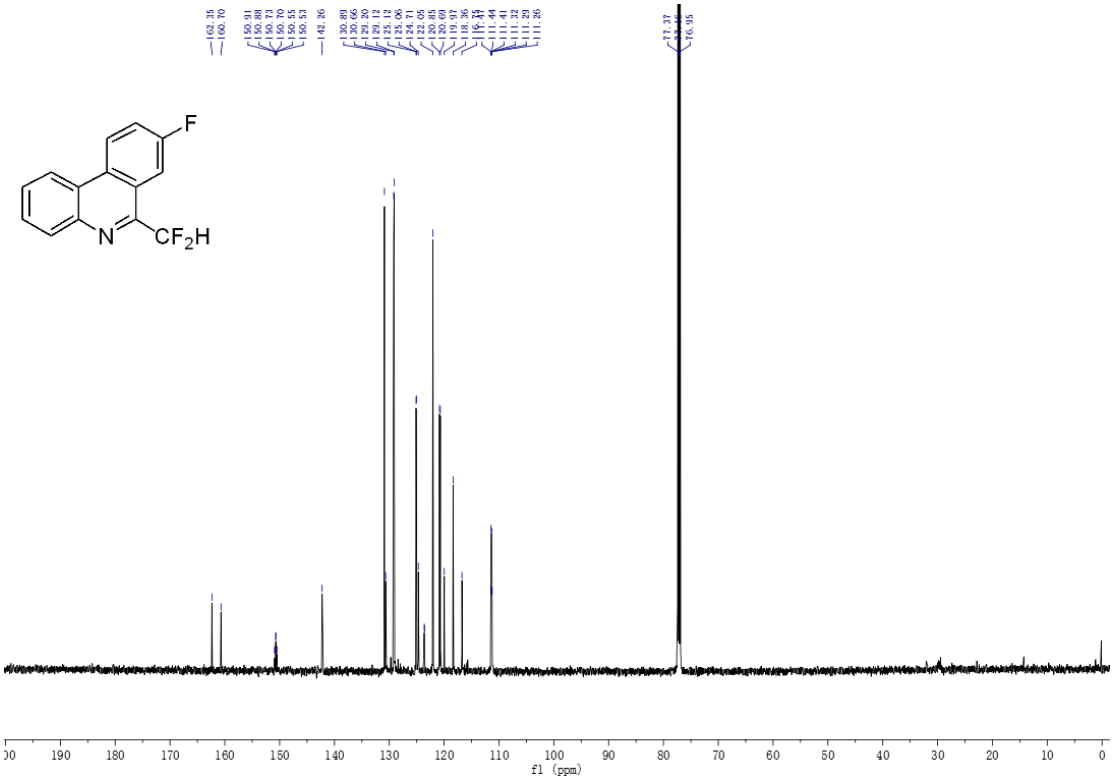

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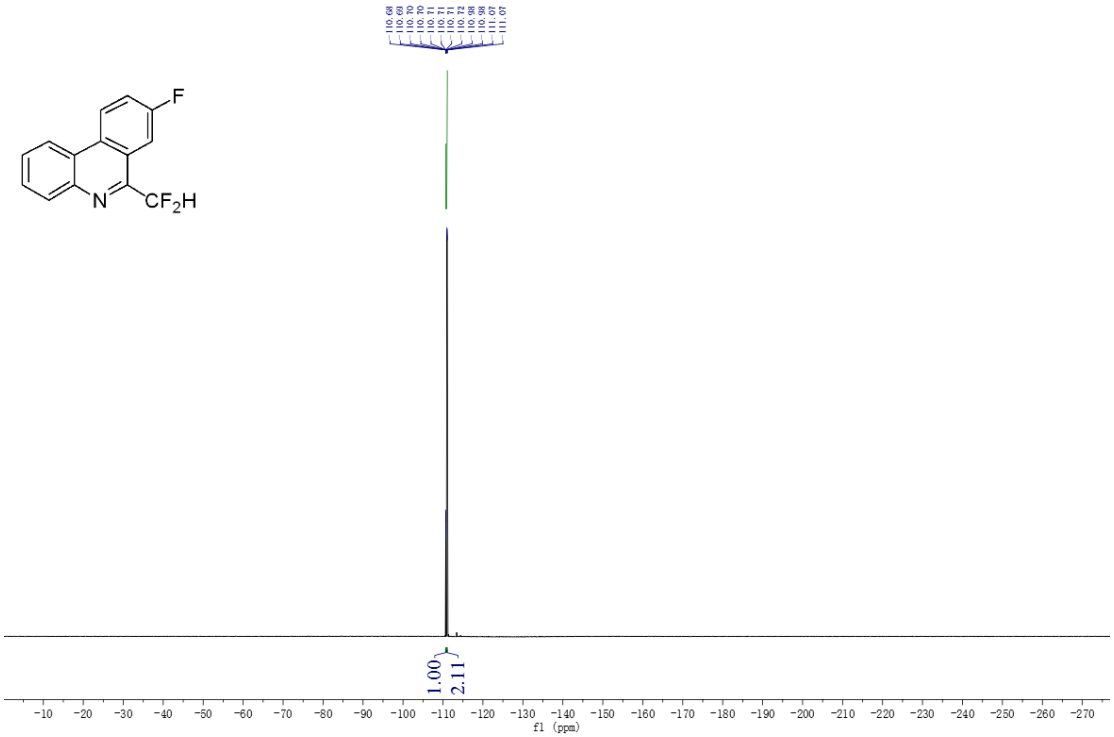

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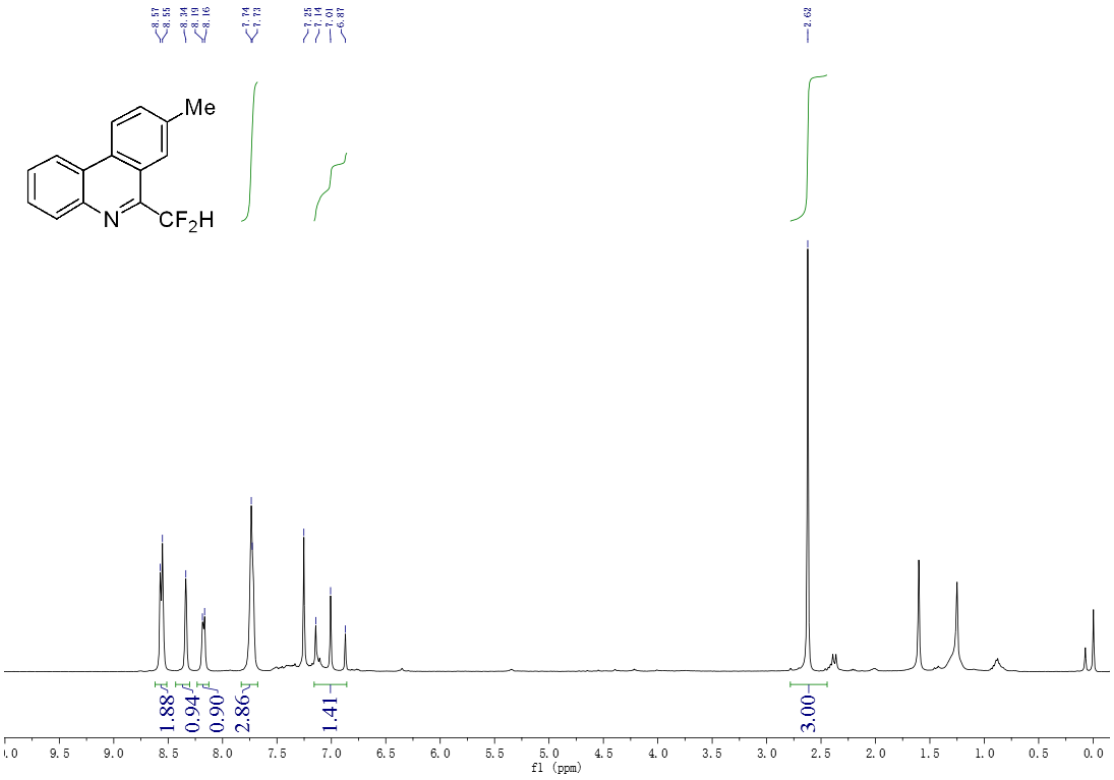

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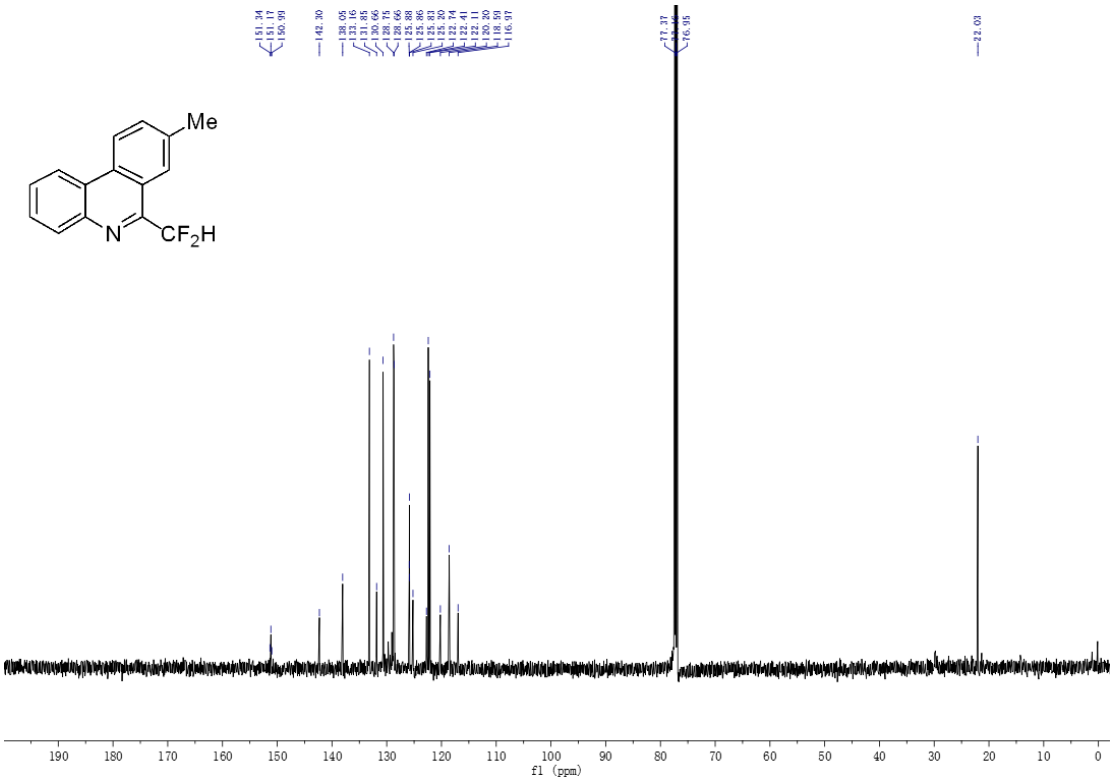

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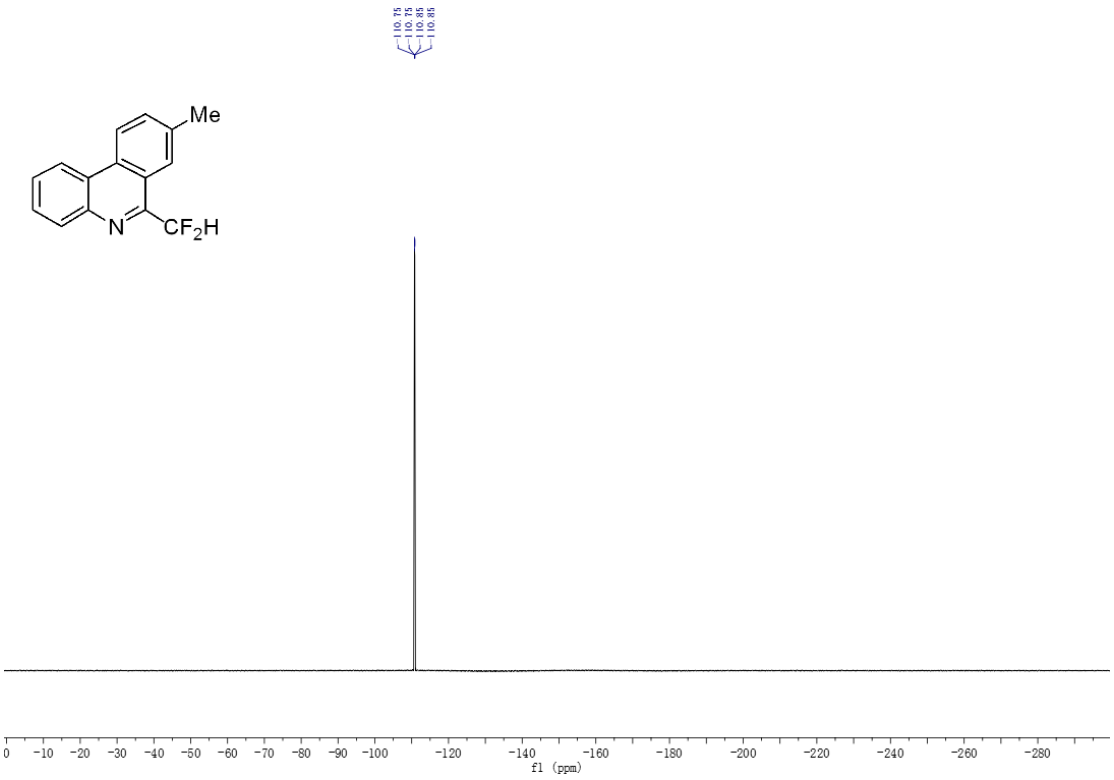

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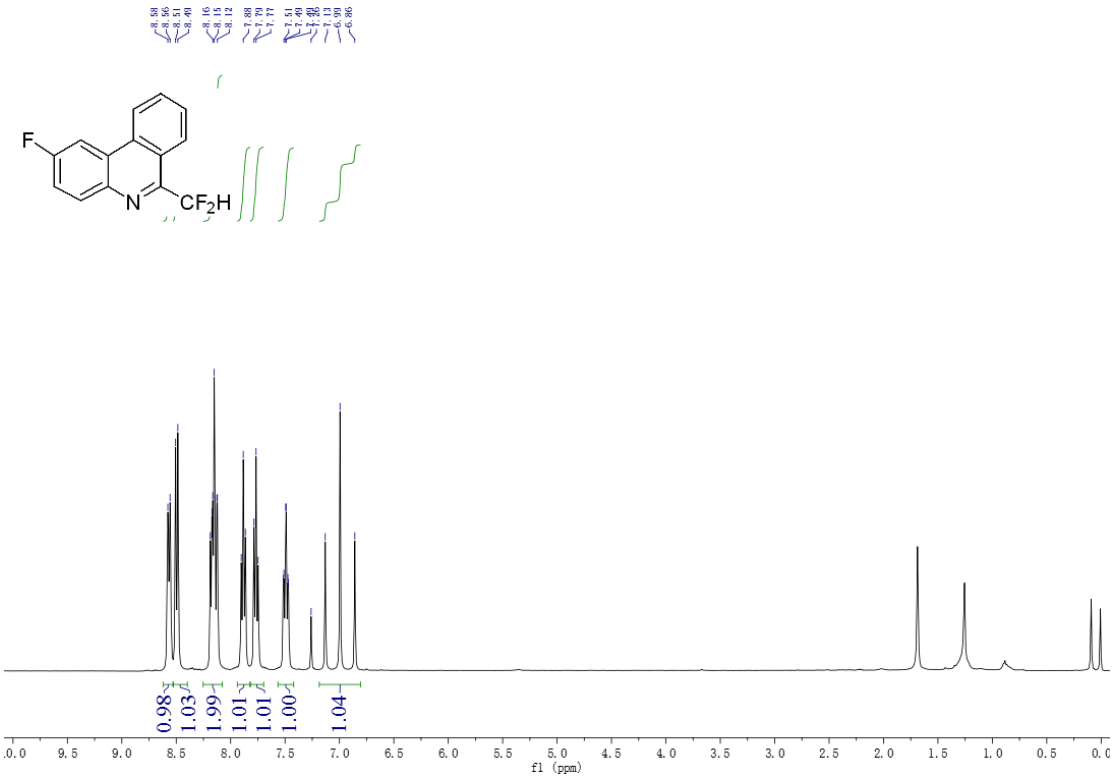

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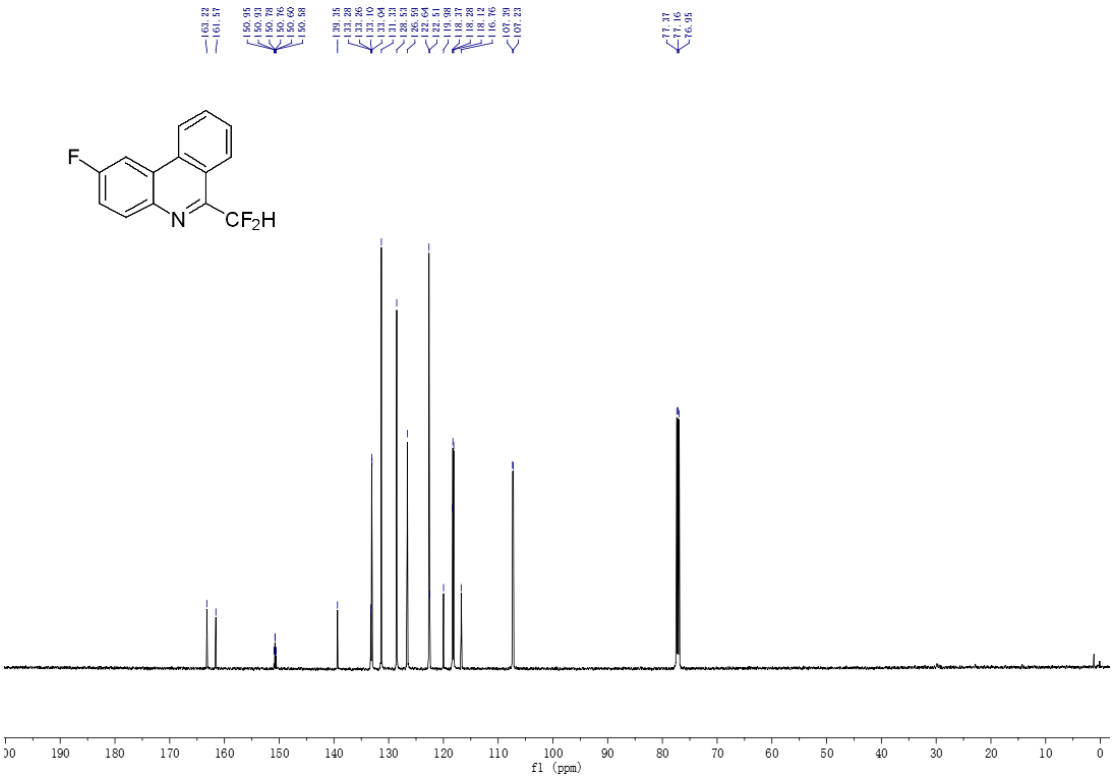
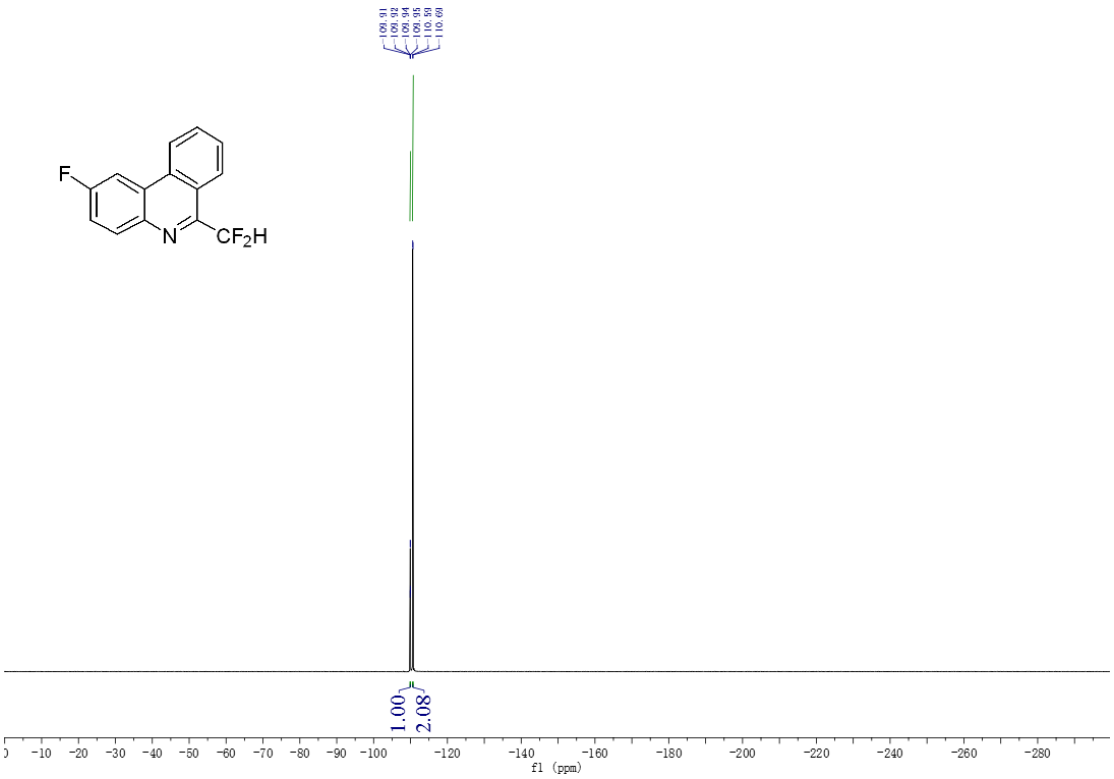


^{19}F NMR of **3c**



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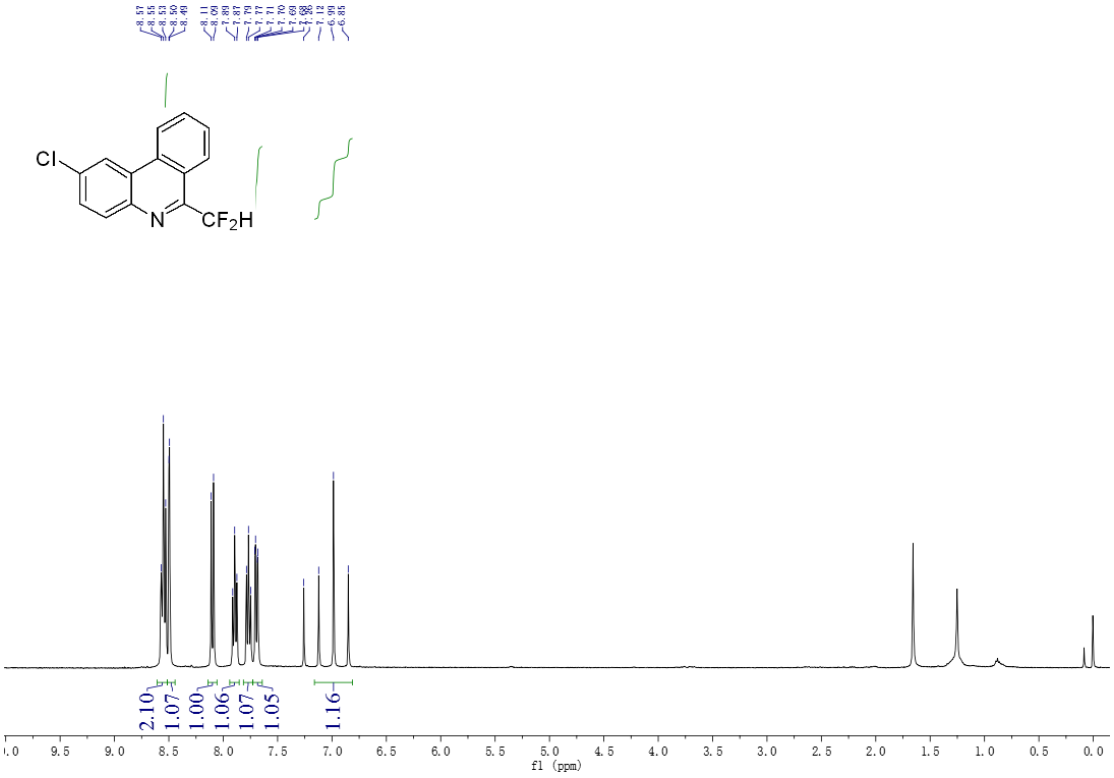

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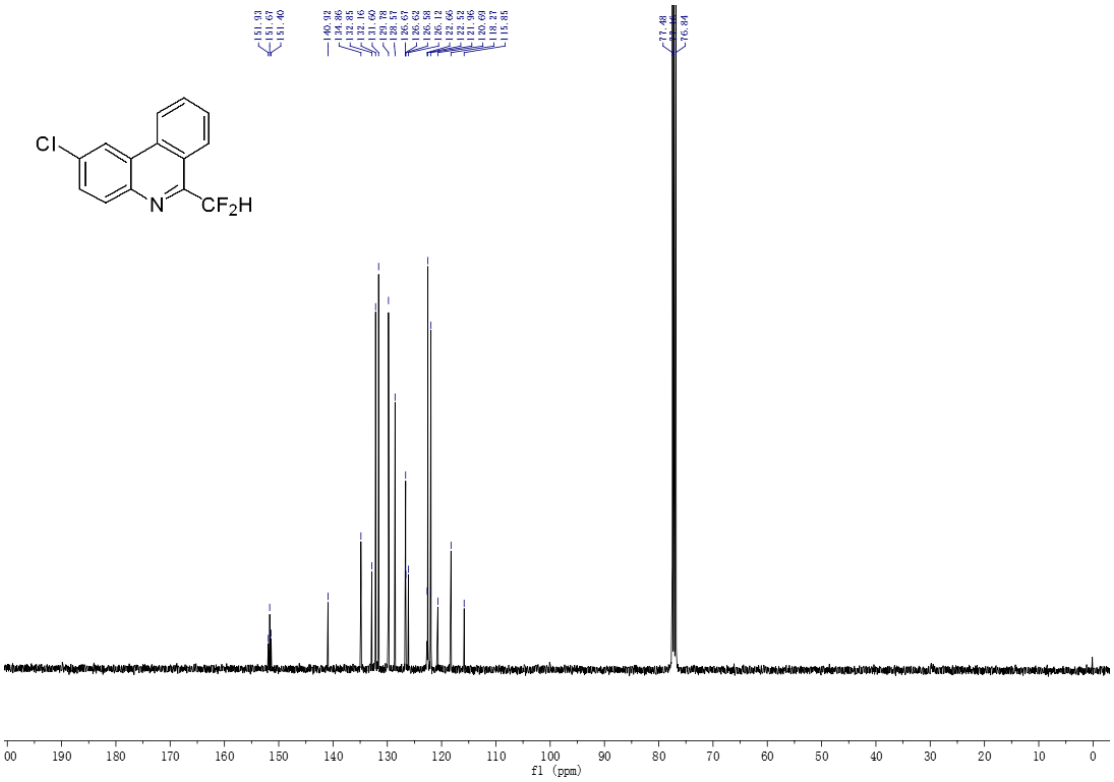

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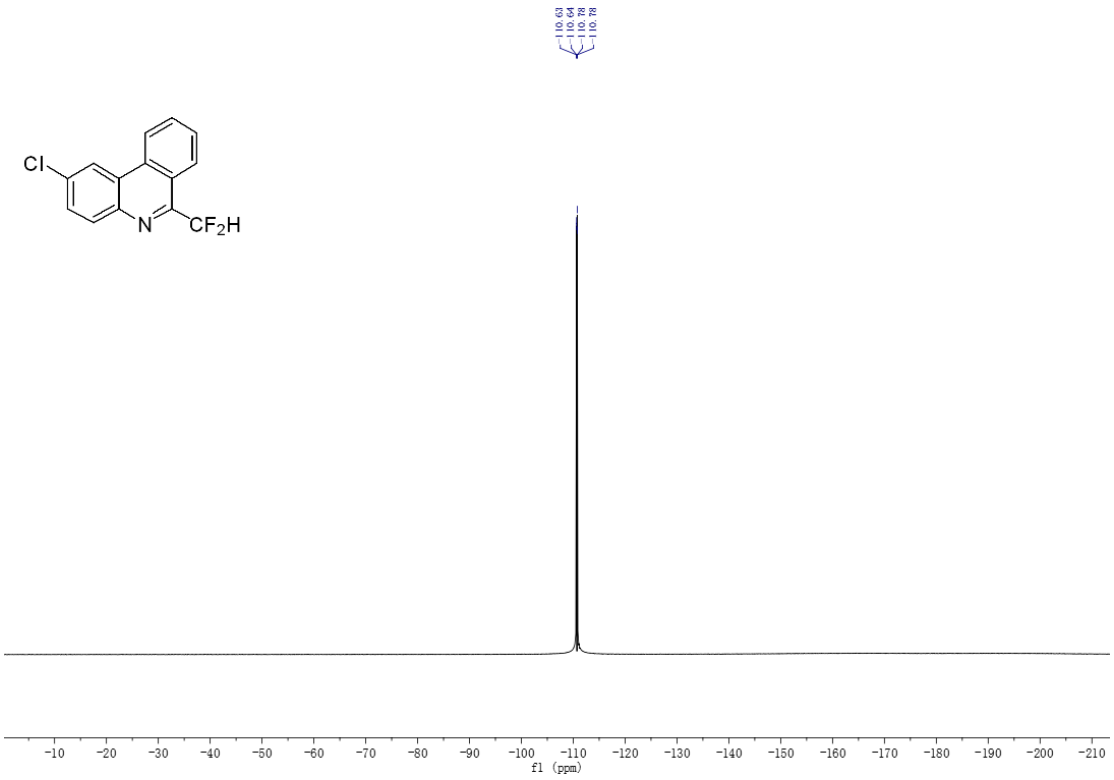

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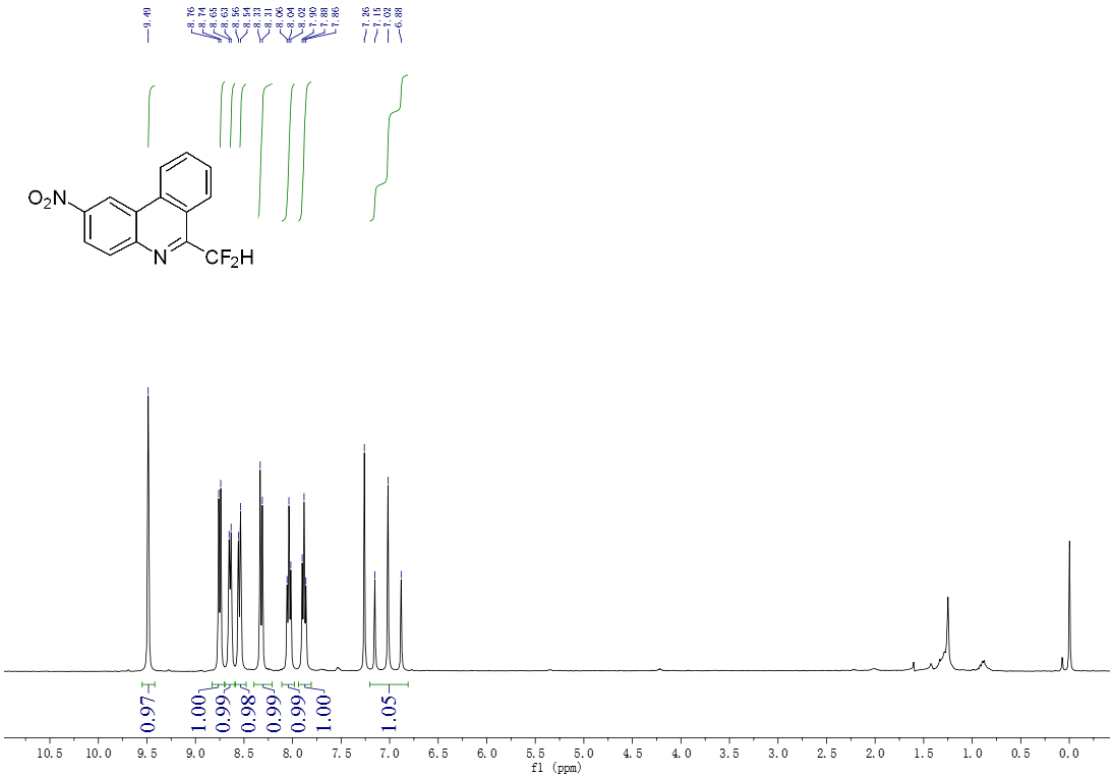

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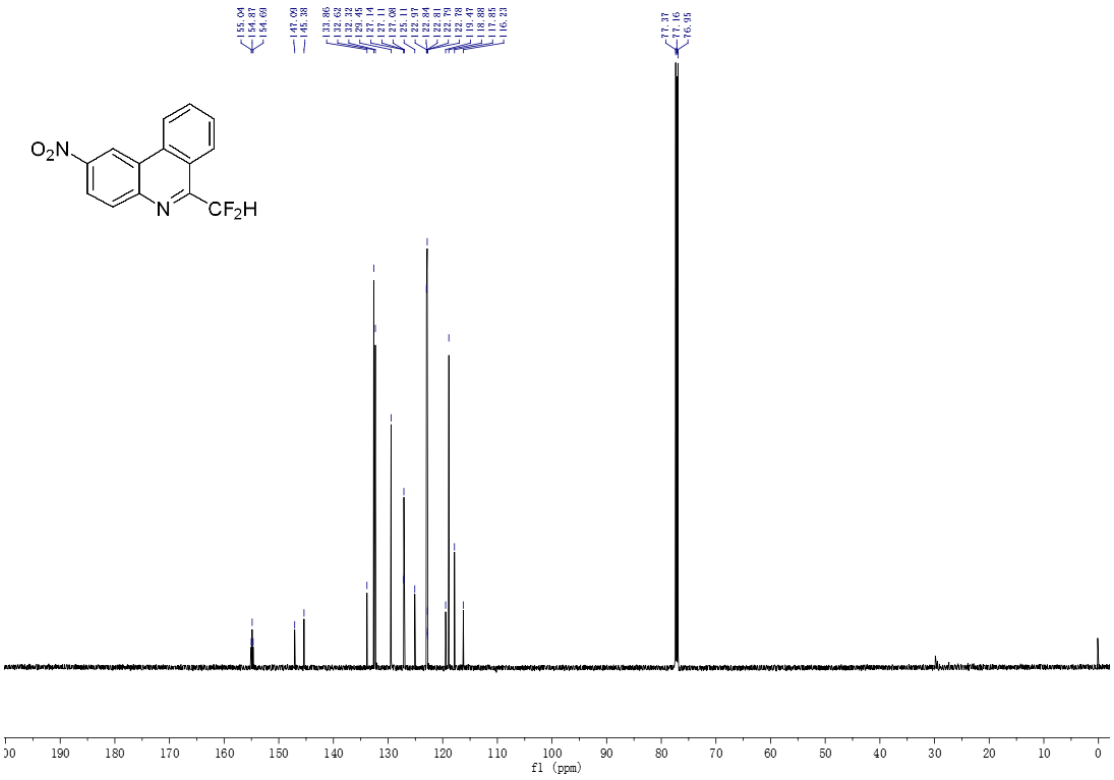
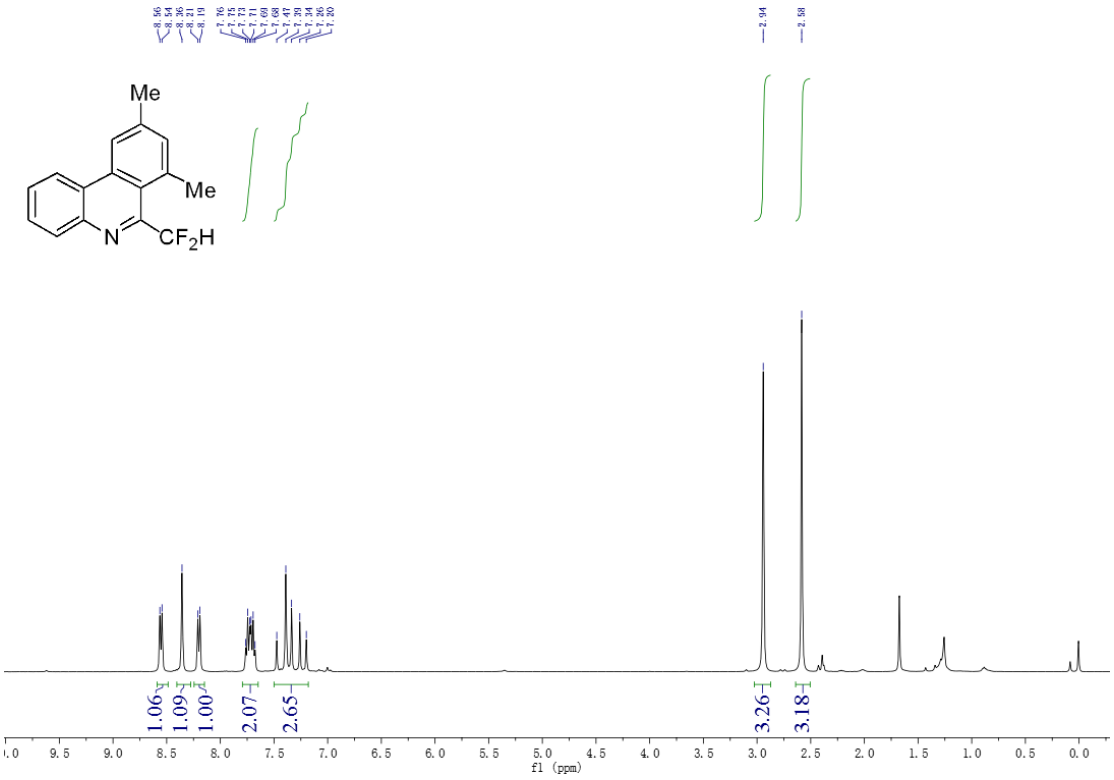


^{19}F NMR of **3e**

^{1}H NMR of **3f**



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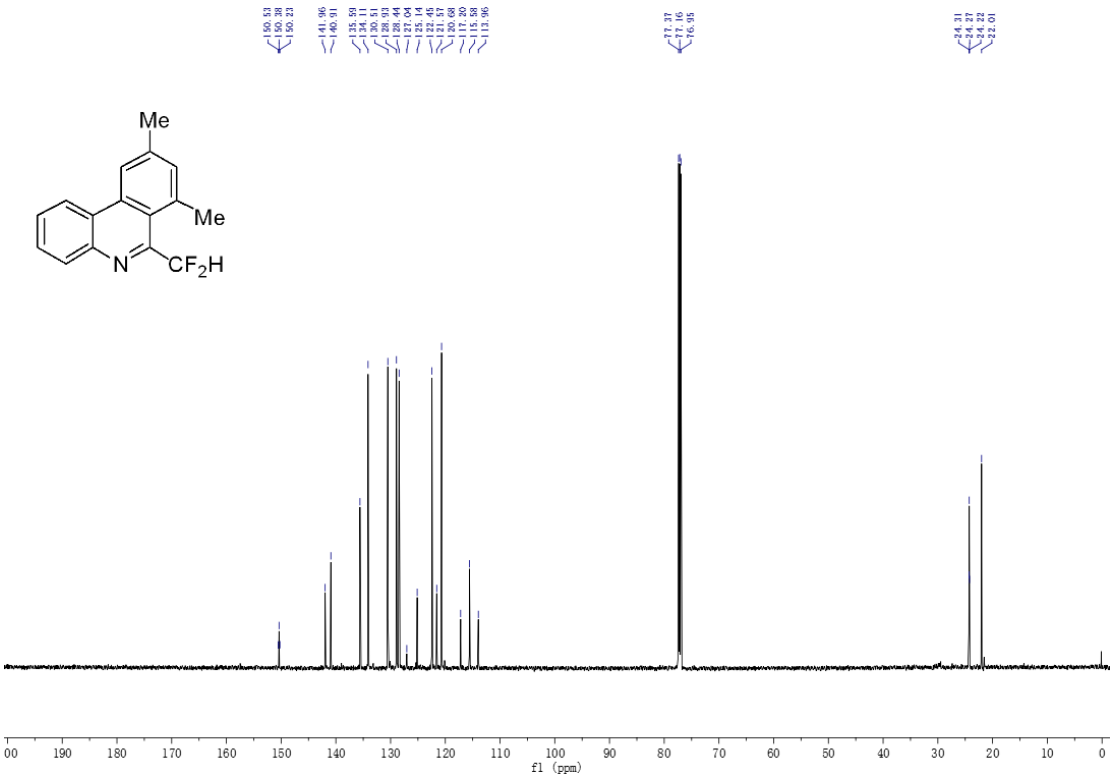

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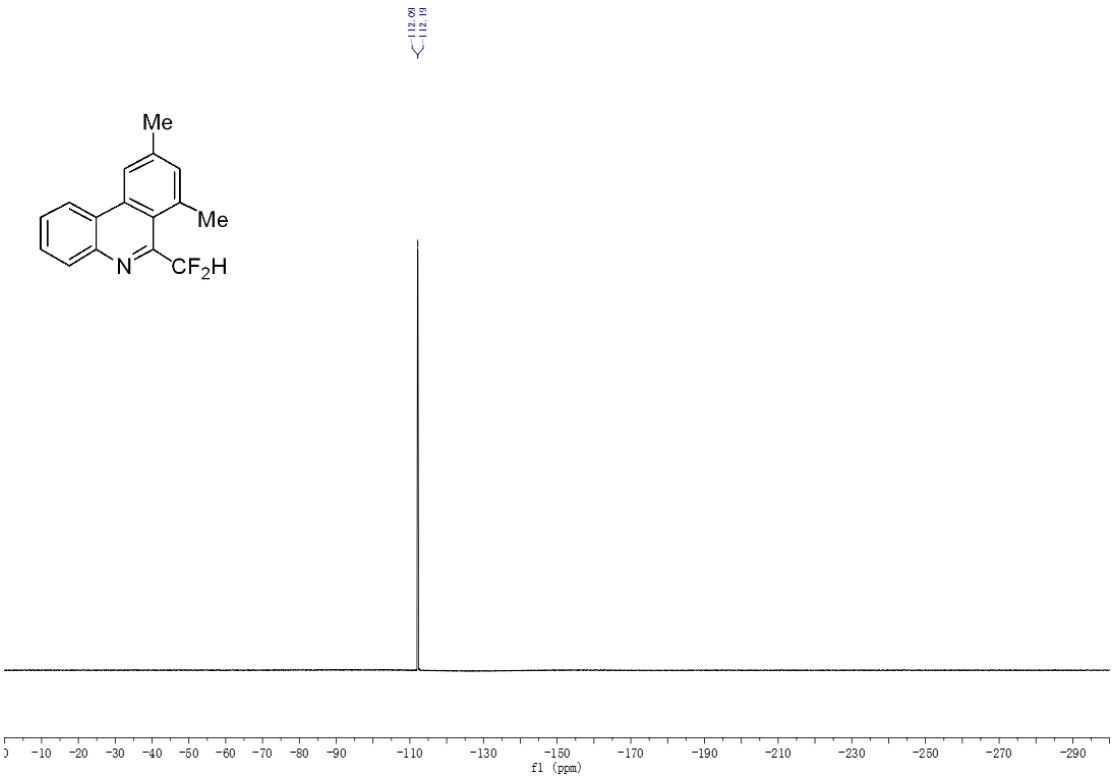
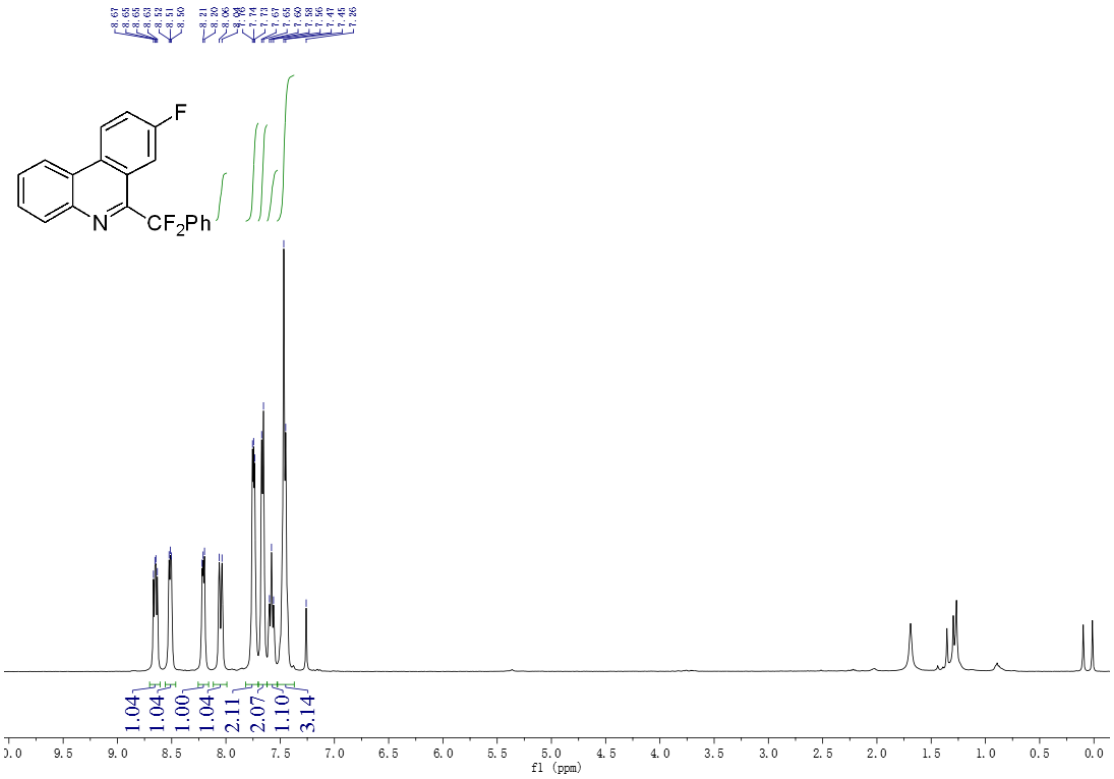
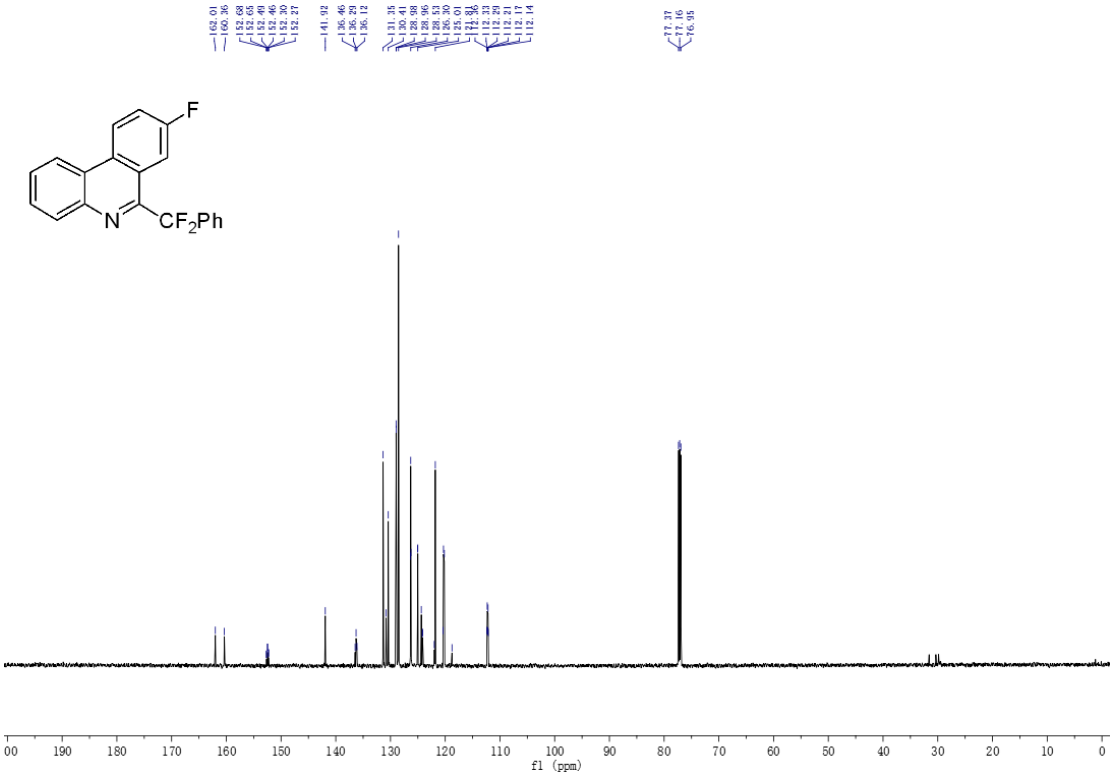


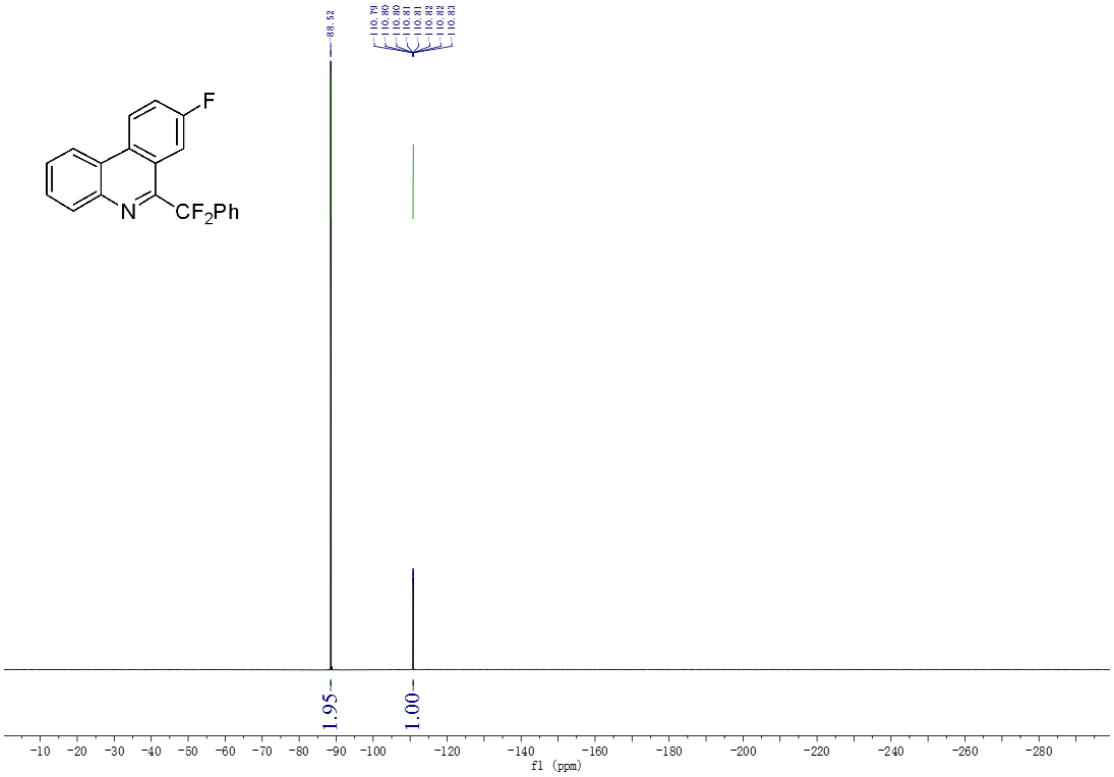
^{1}H NMR of **4a**



^{13}C NMR of **4a**



^{19}F NMR of **4a**



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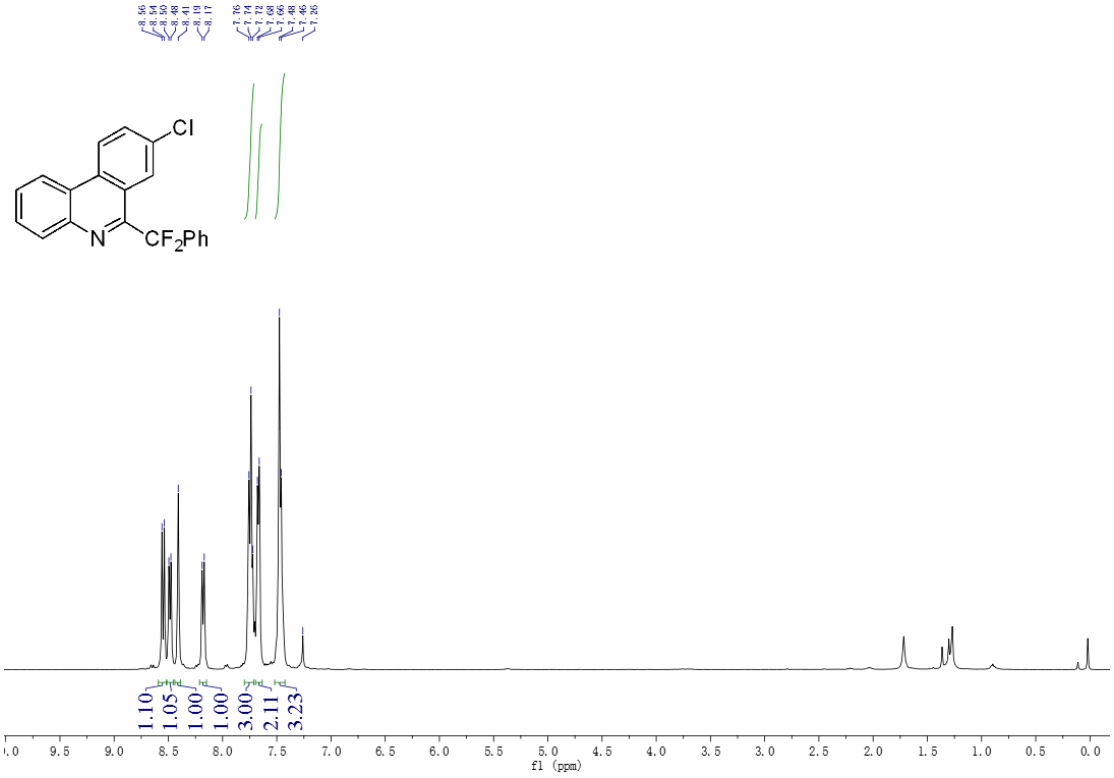
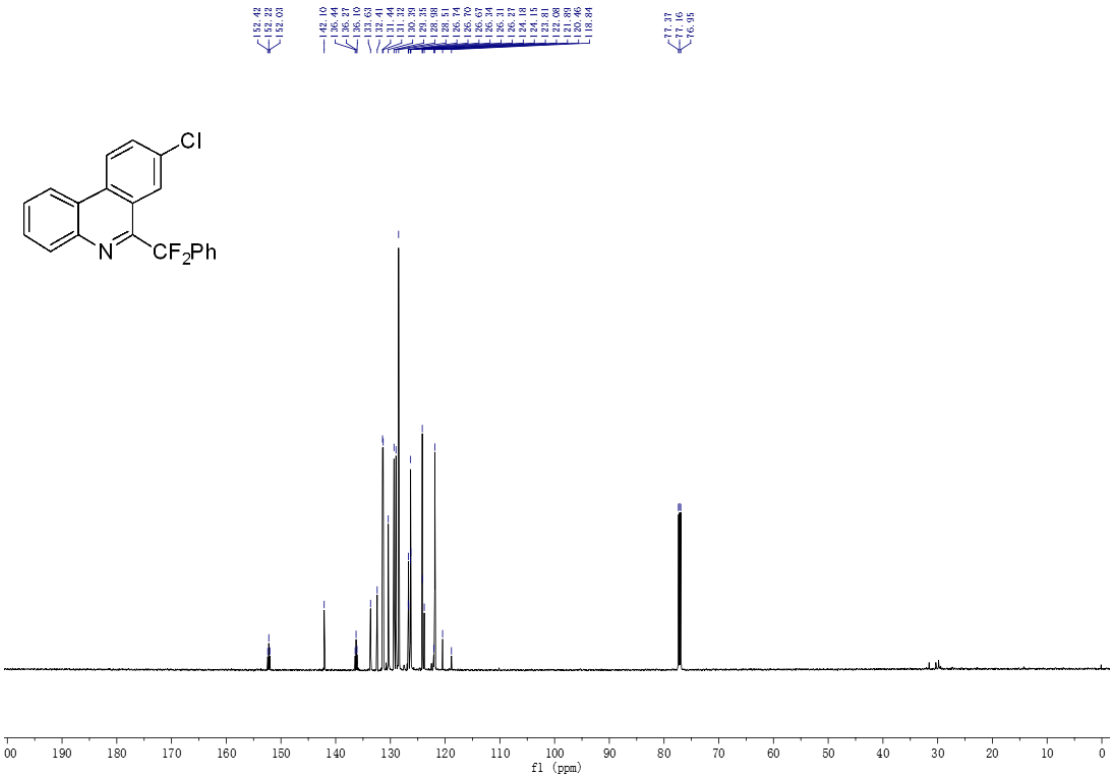
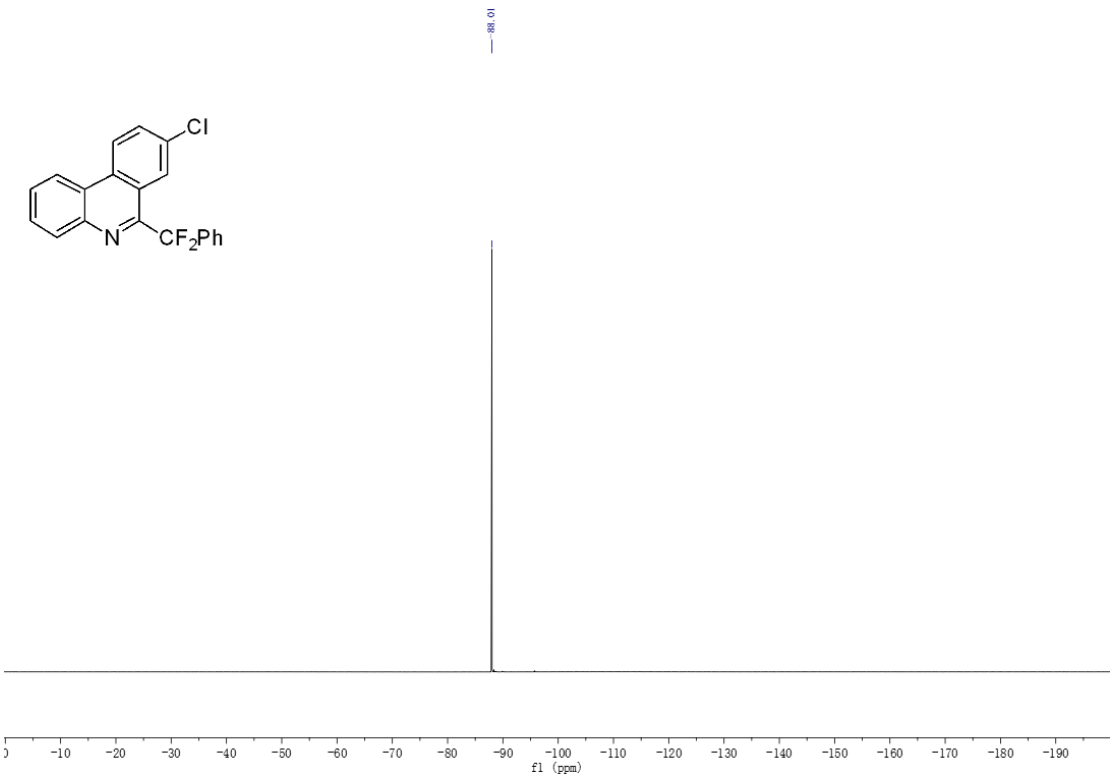


^{13}C NMR of **4b**



^{19}F NMR of **4b**



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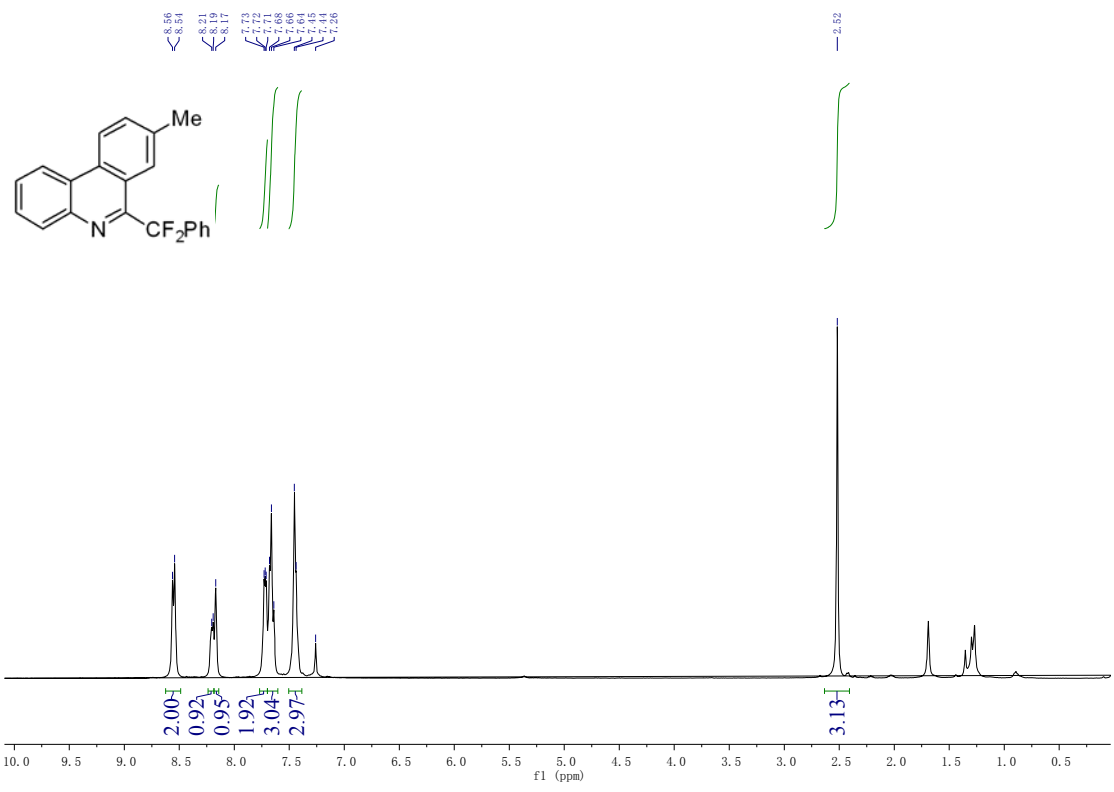
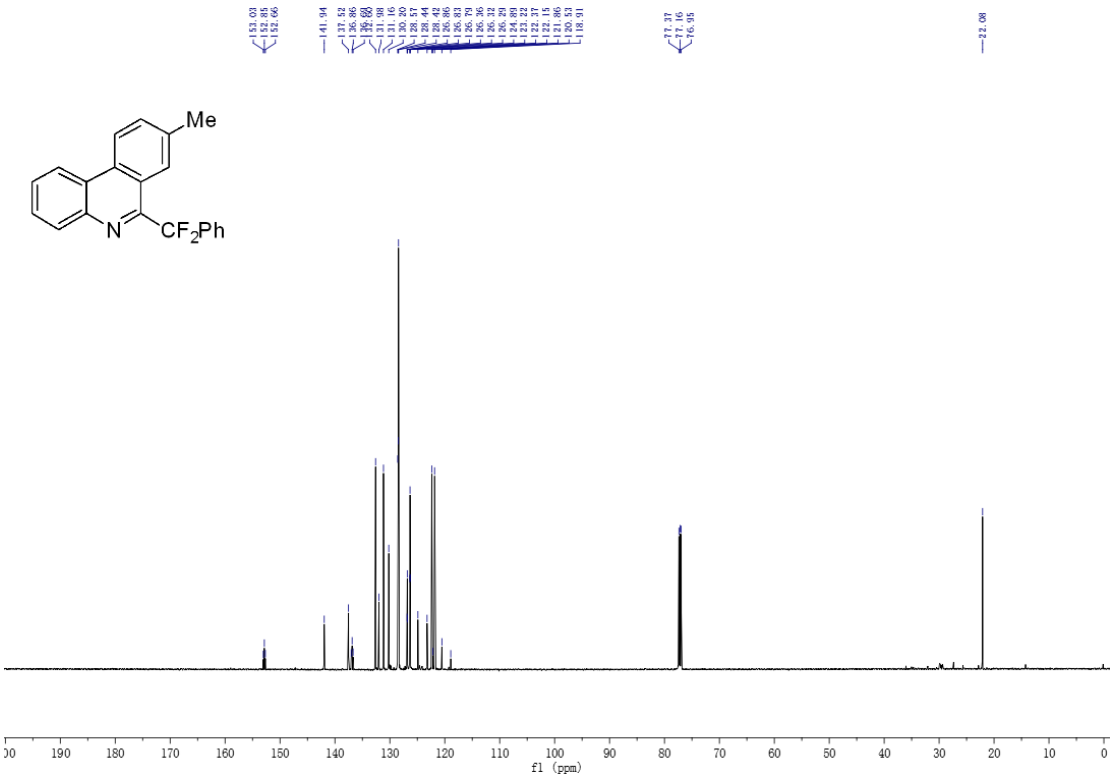


^{13}C NMR of **4c**



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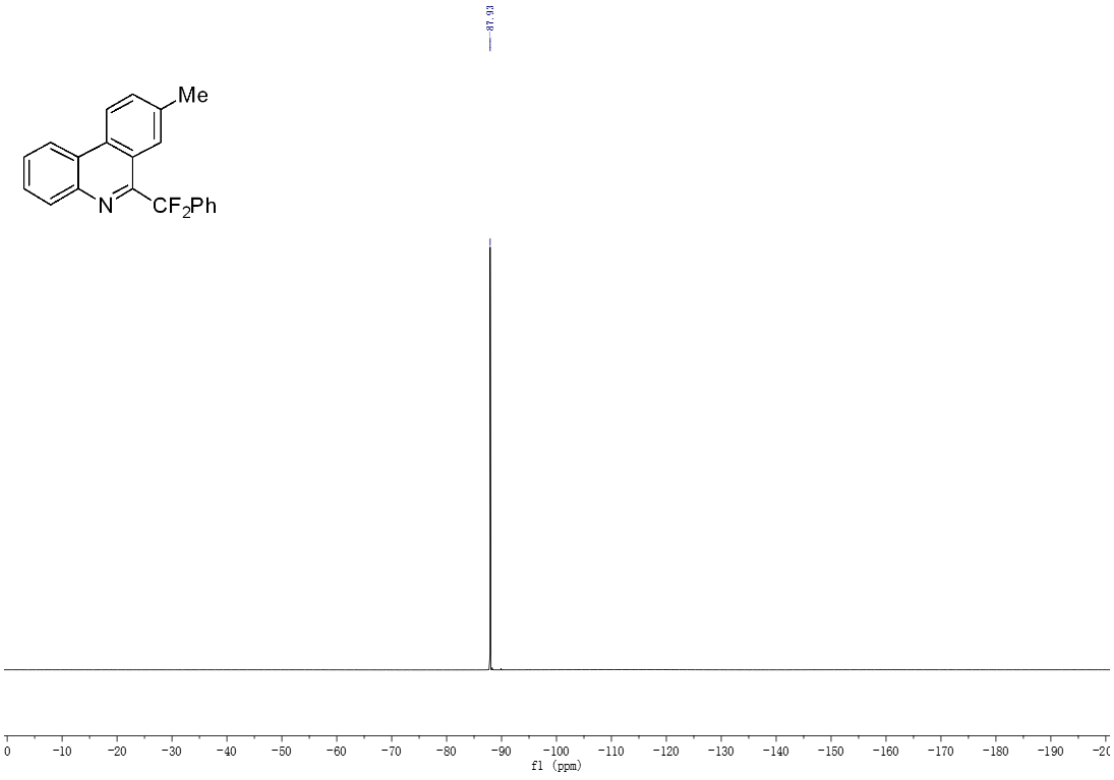

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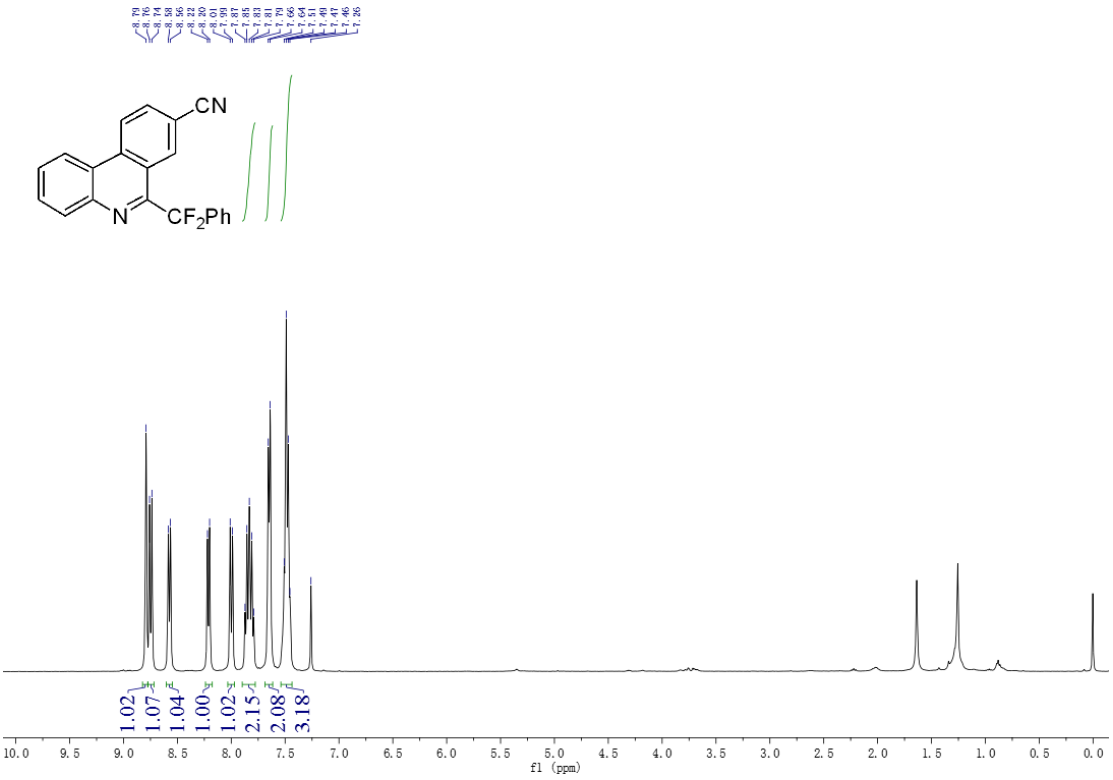

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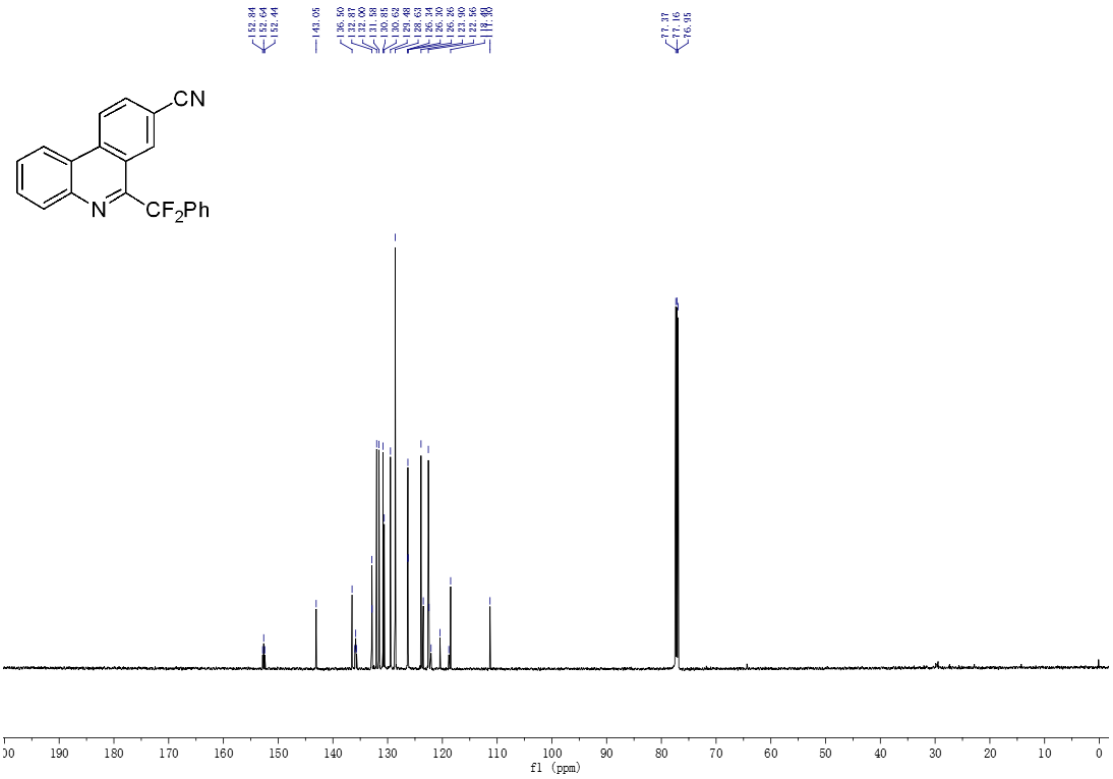

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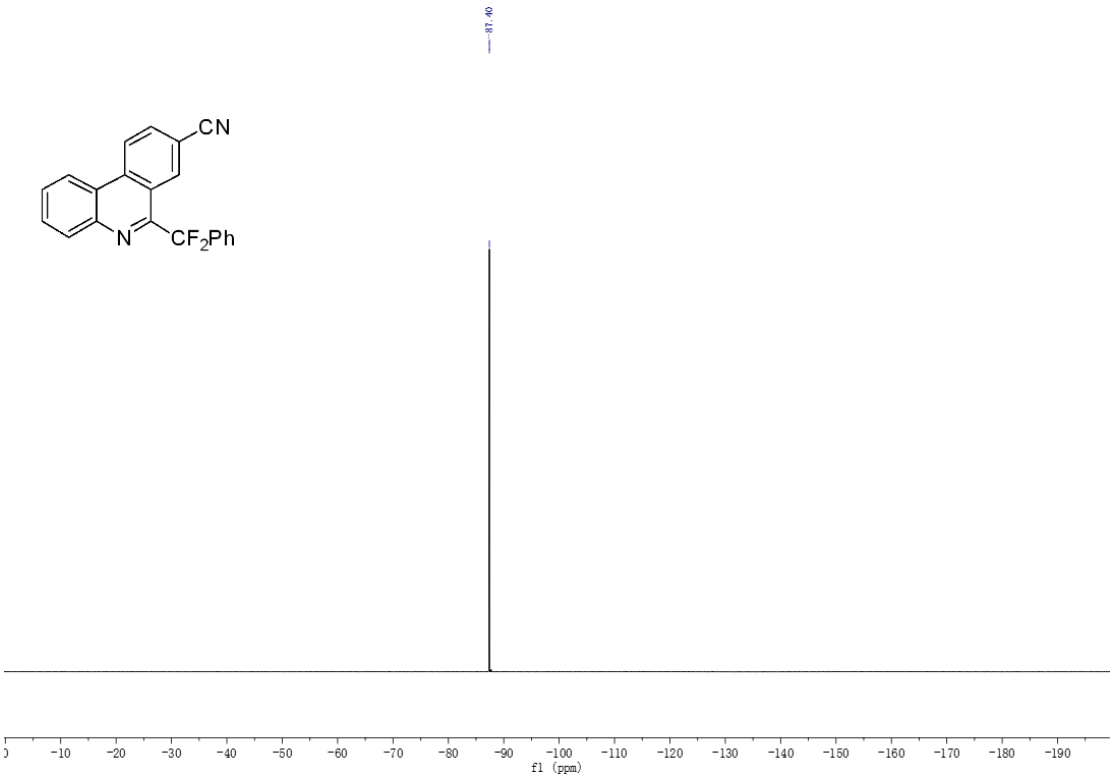

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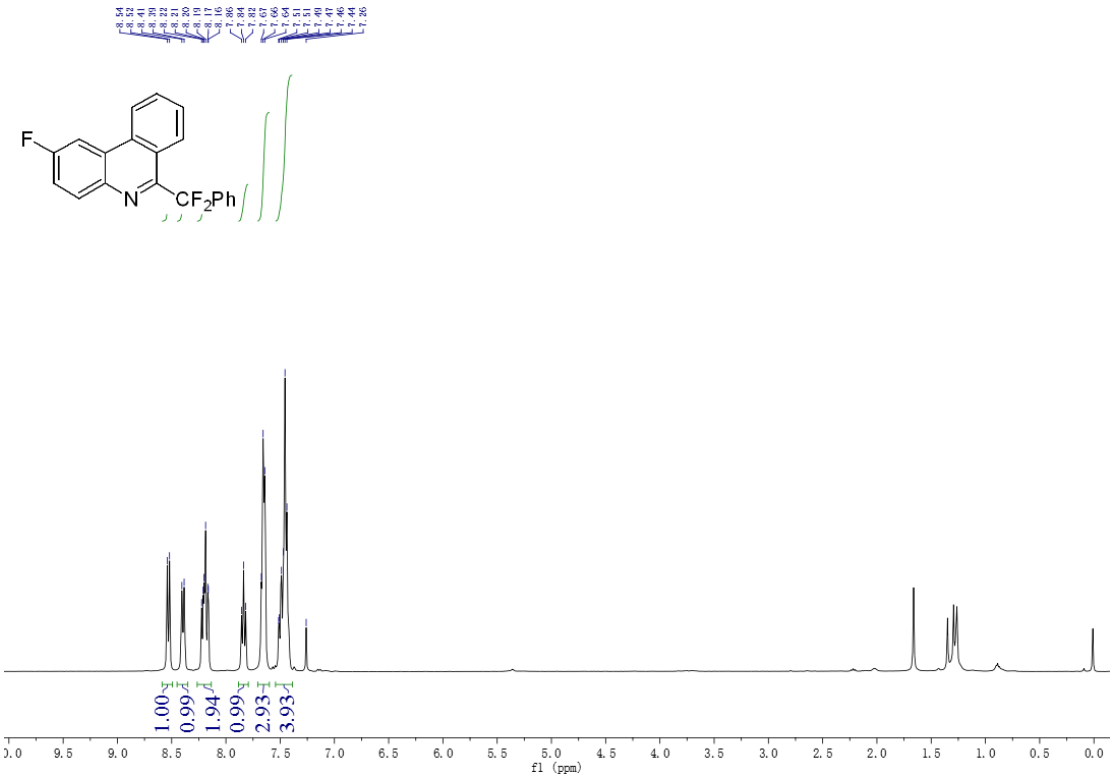

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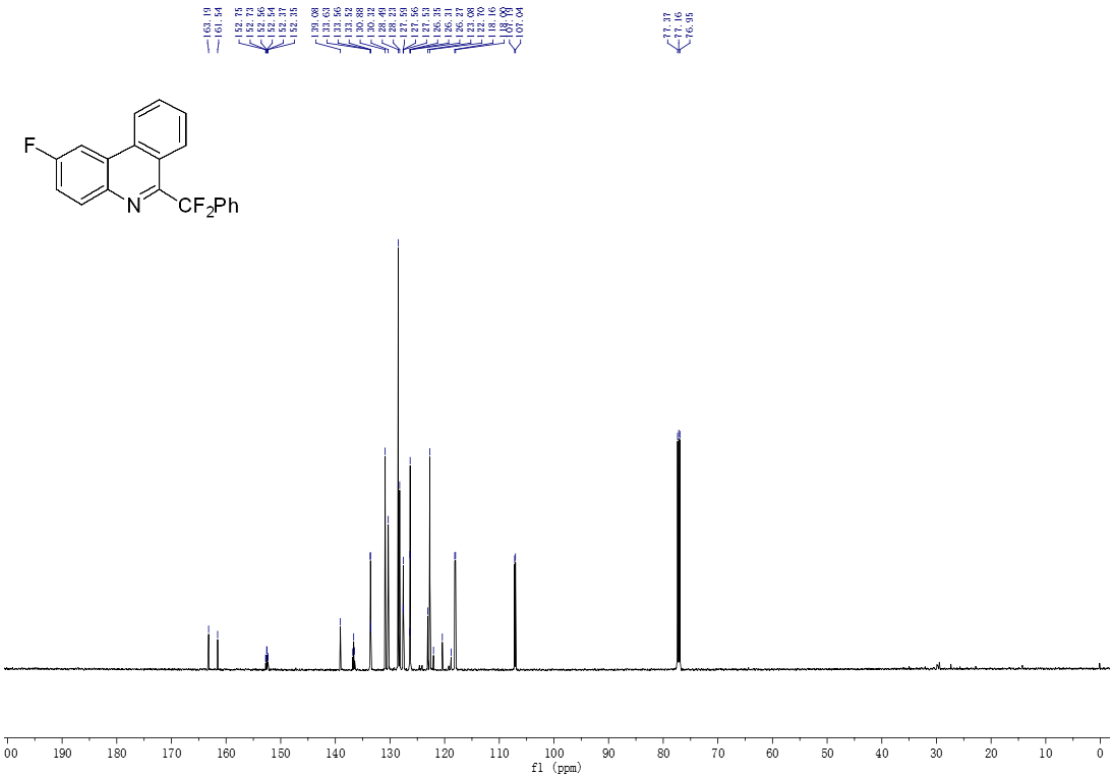

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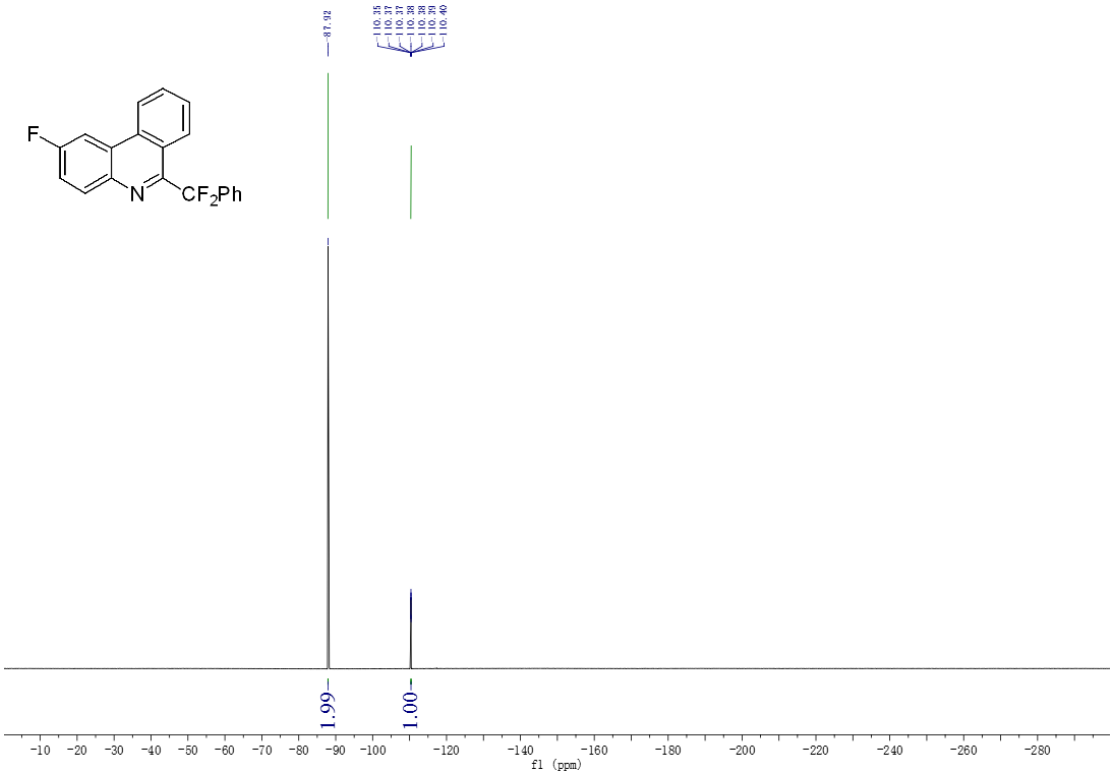

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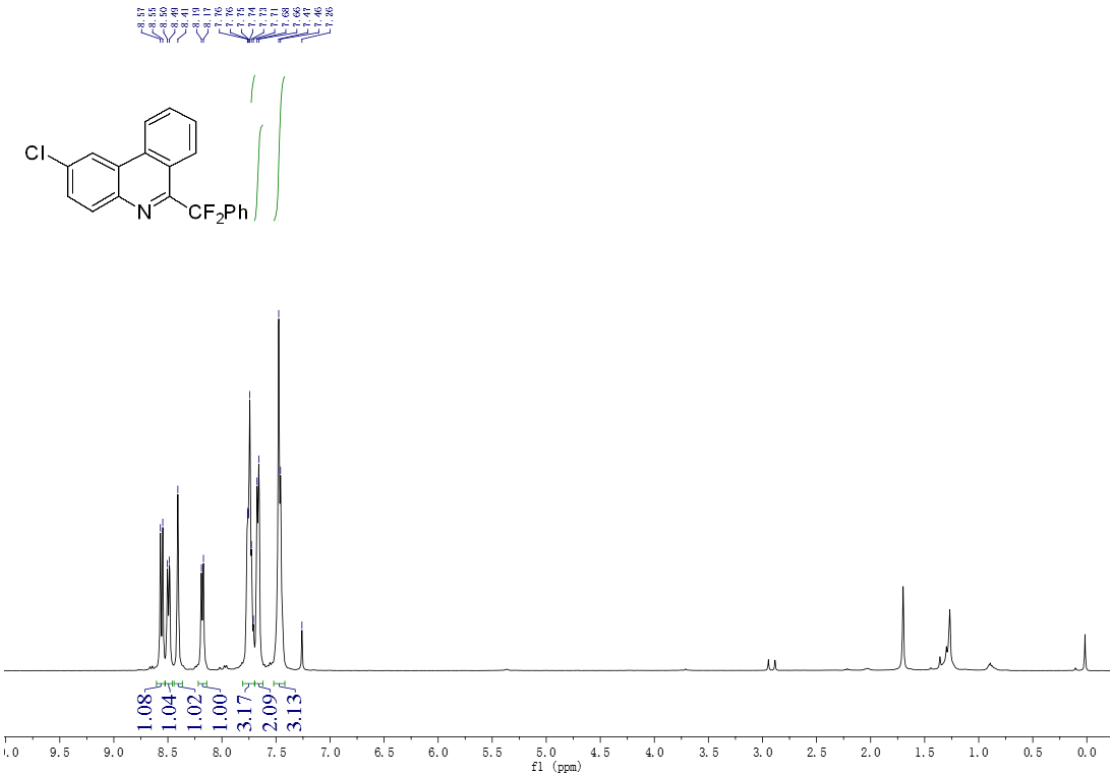

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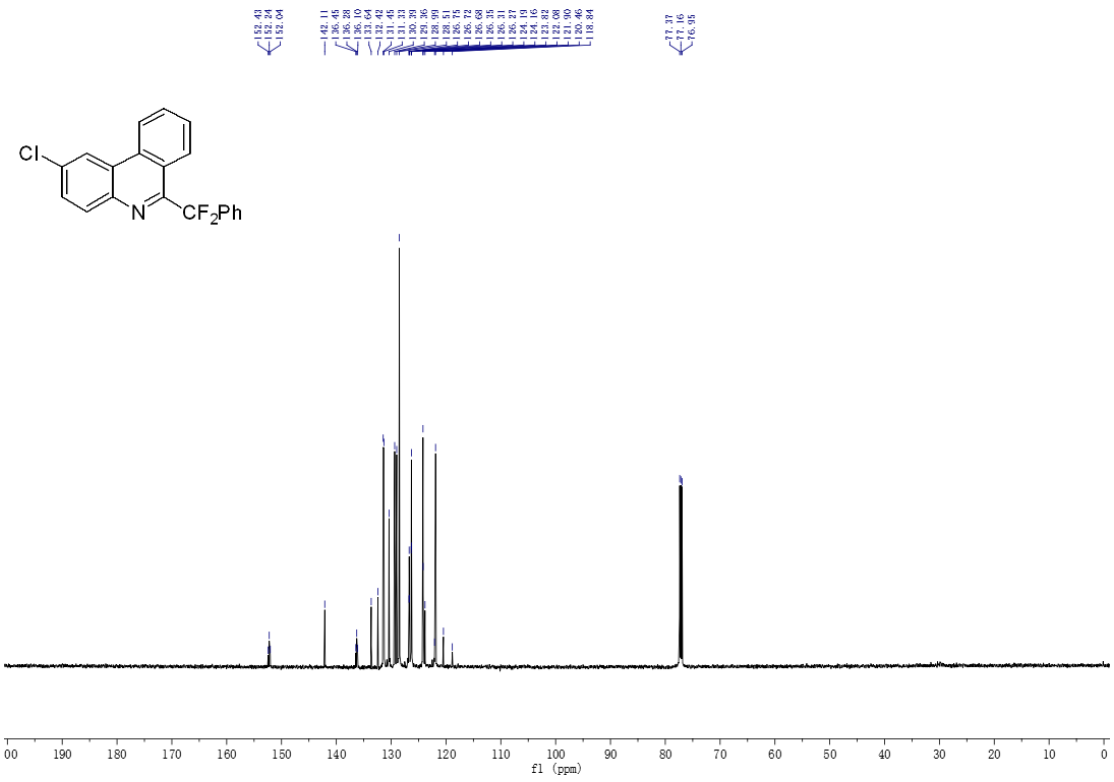

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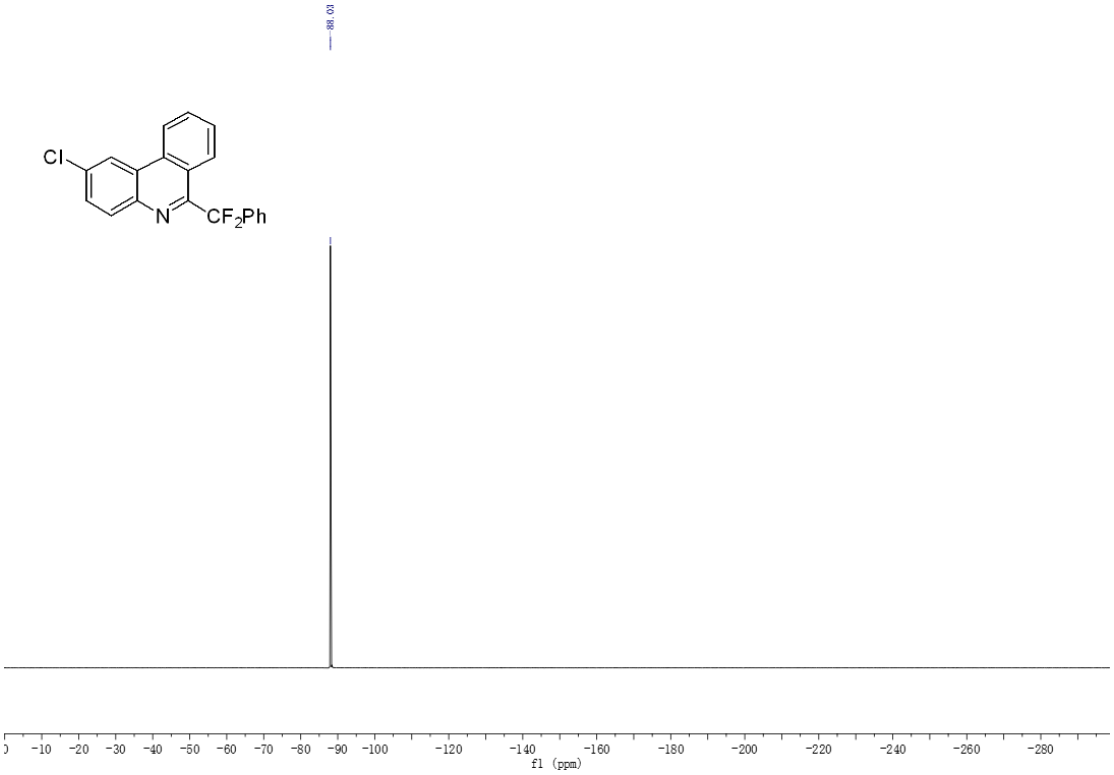

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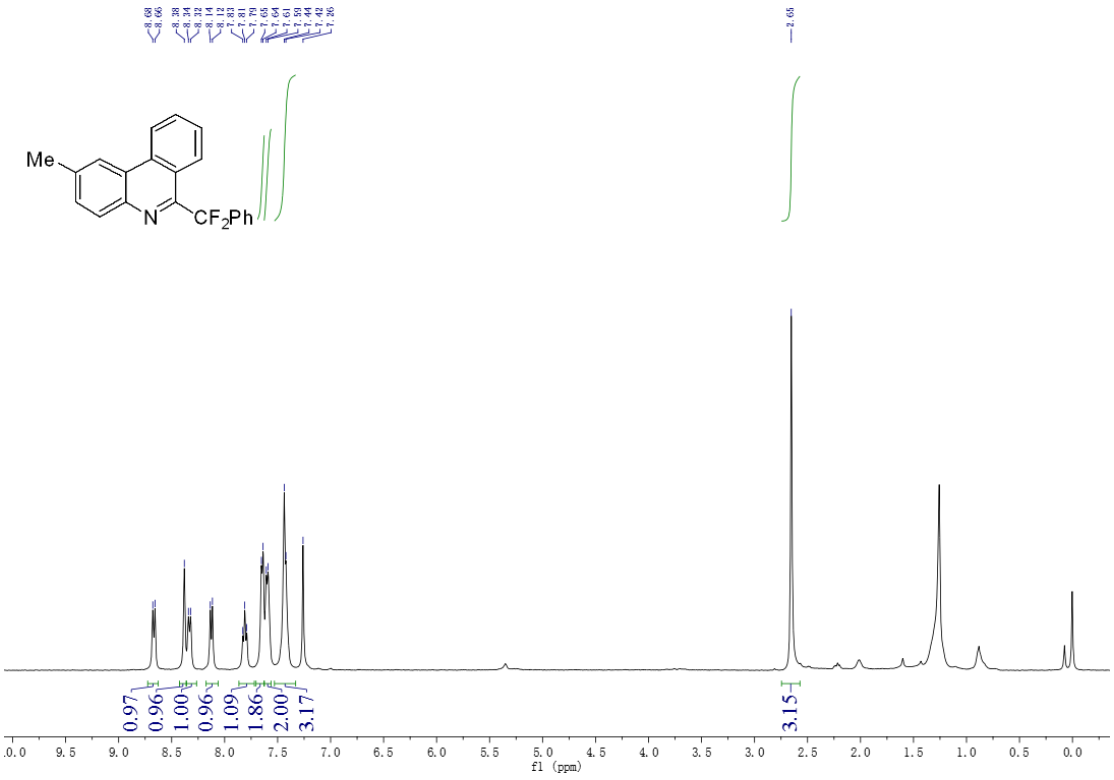
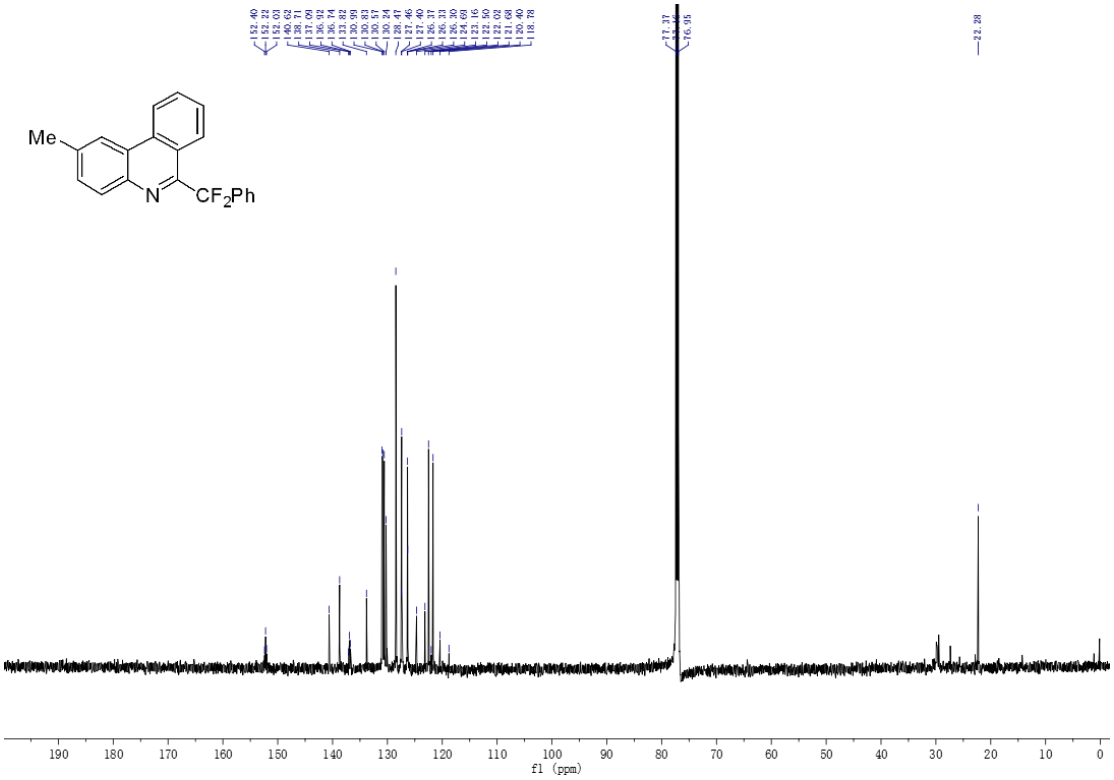
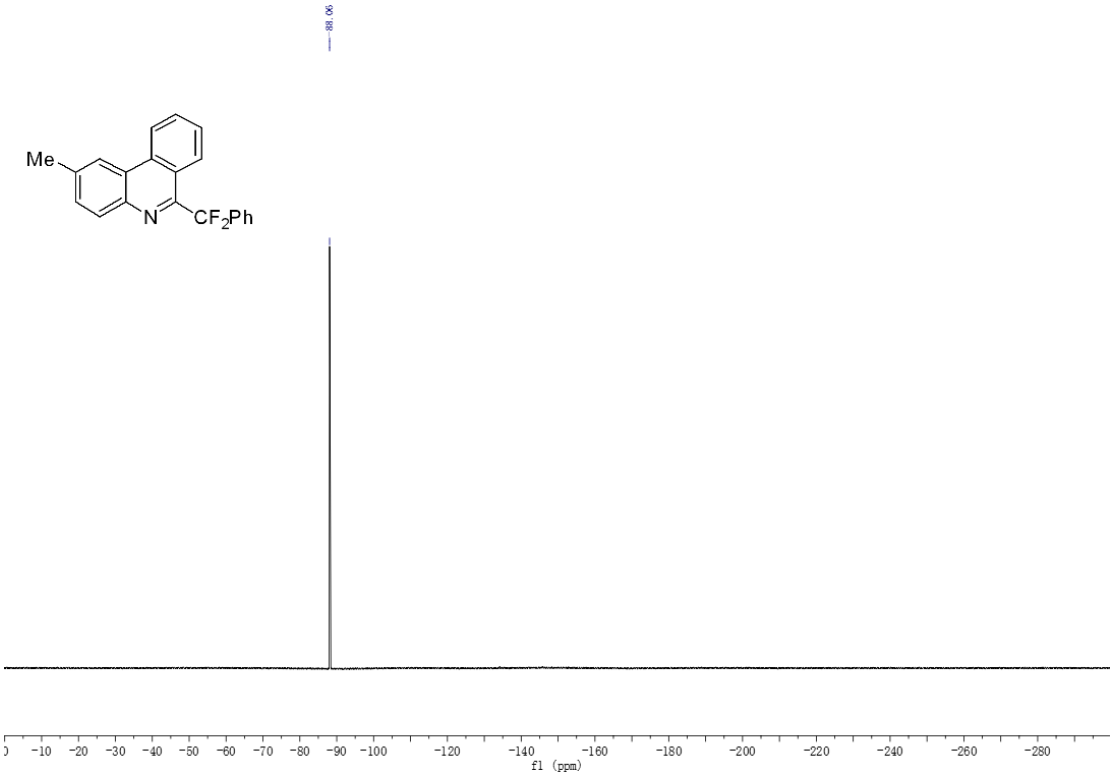


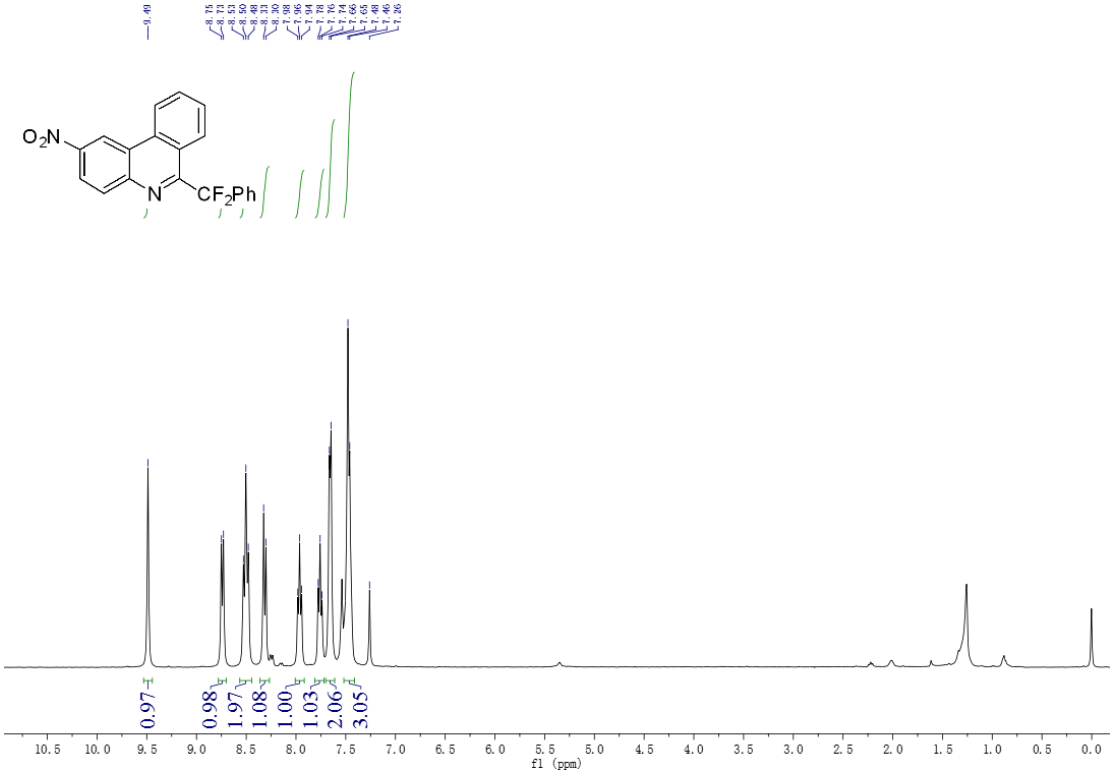
^{13}C NMR of **4g**



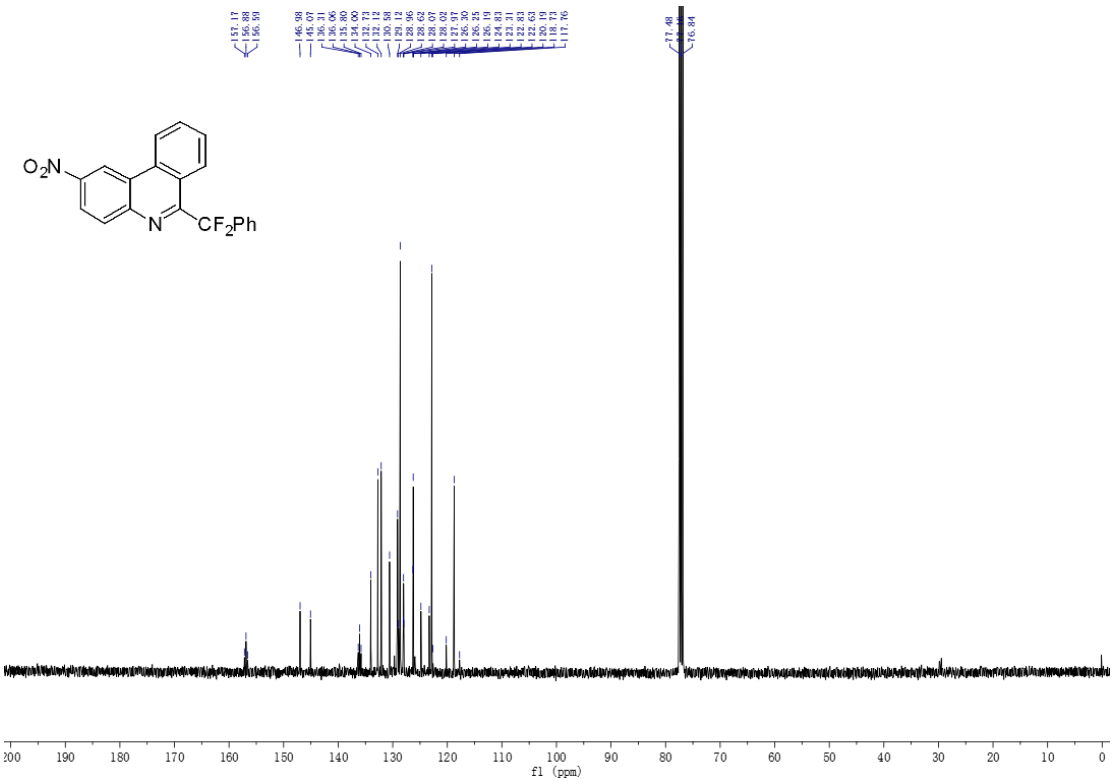
^{19}F NMR of **4g**



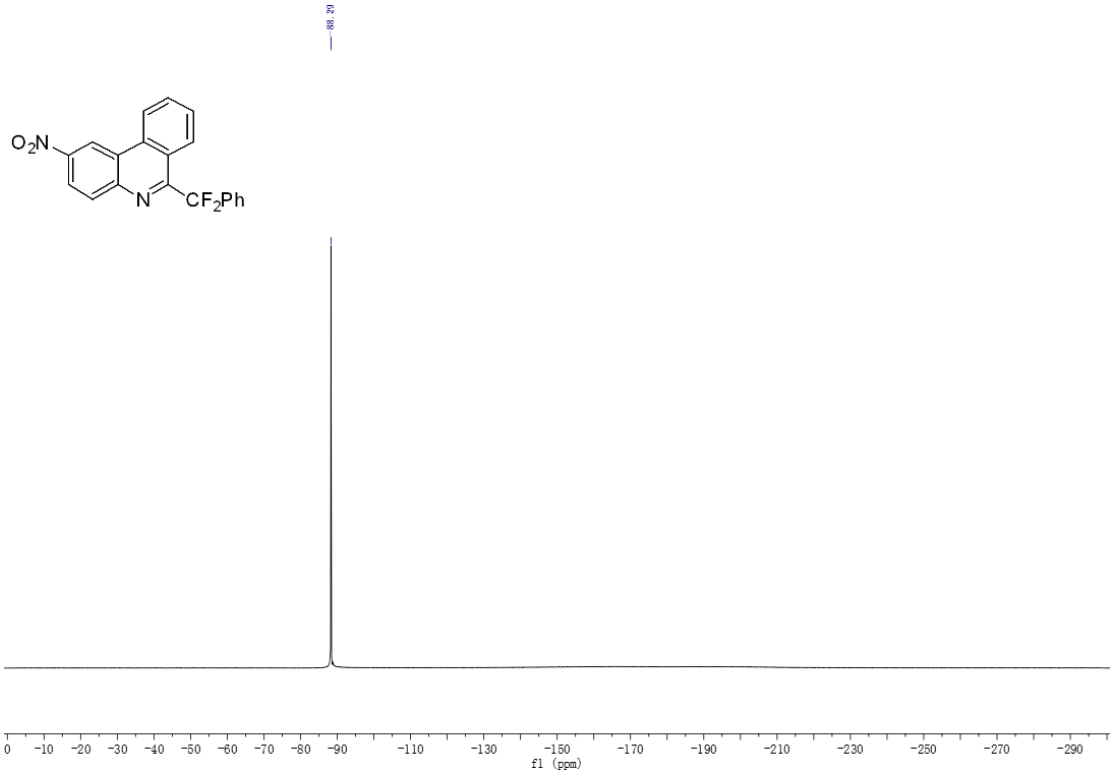
^{1}H NMR of **4h**



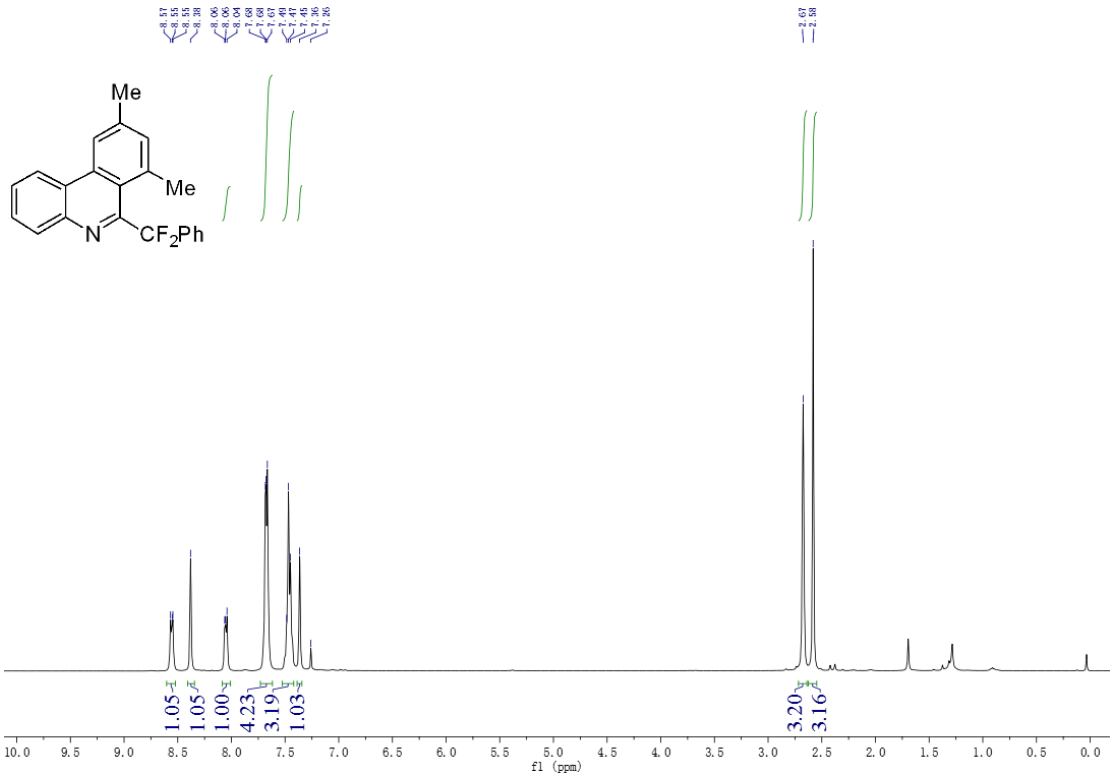
^{13}C NMR of **4h**



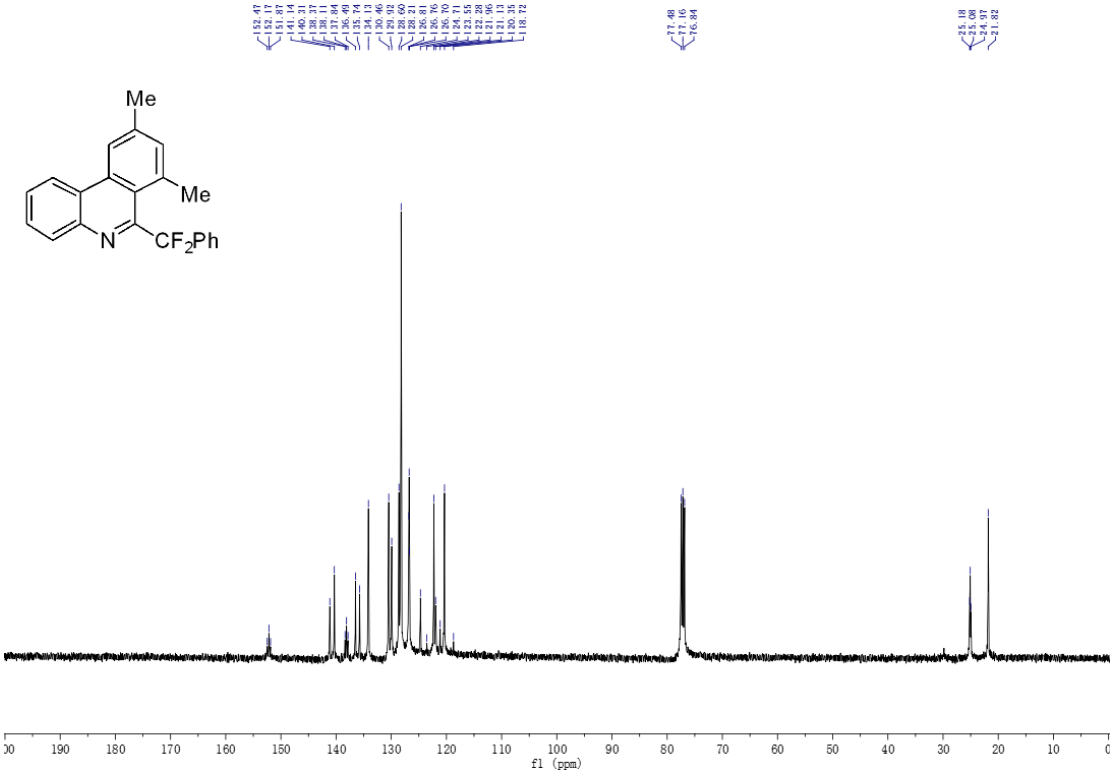
^{19}F NMR of **4h**



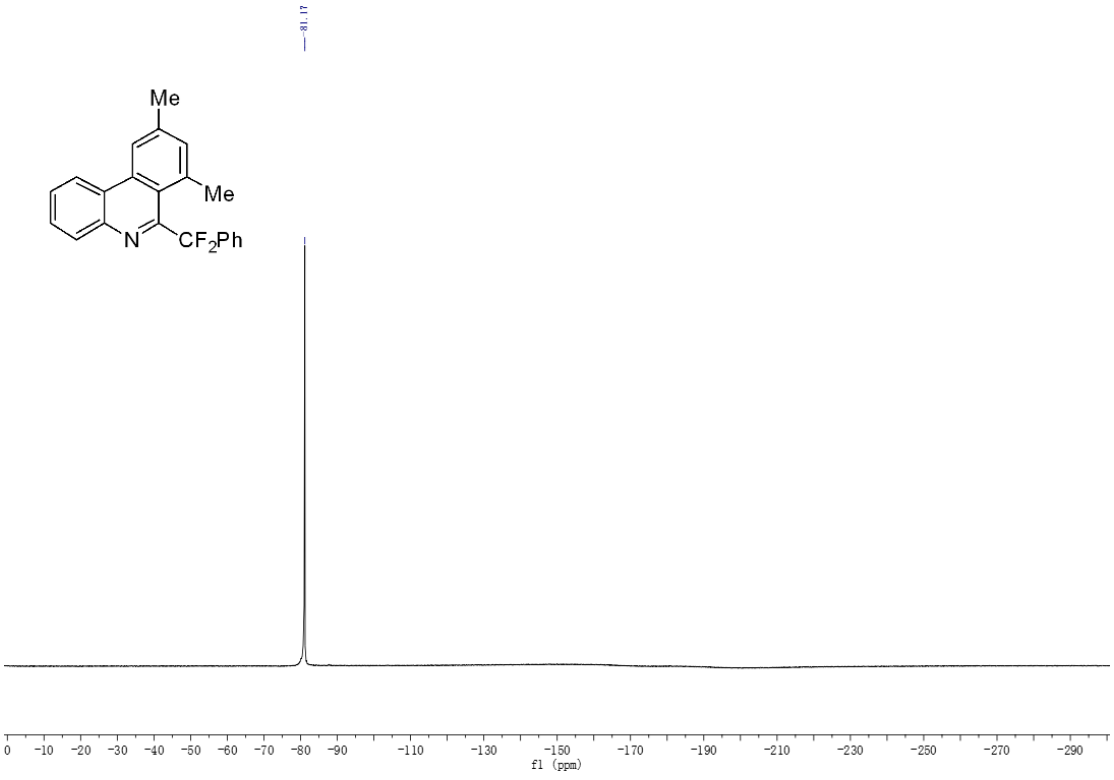
^{1}H NMR of **4i**



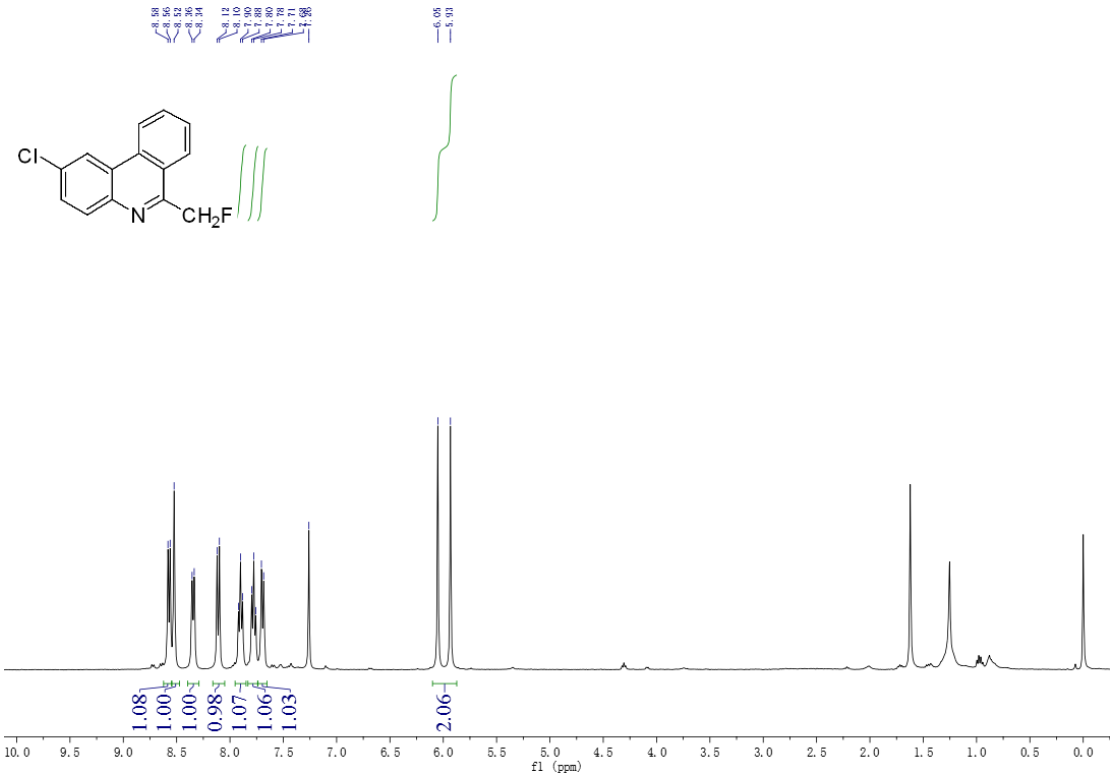
^{13}C NMR of **4i**



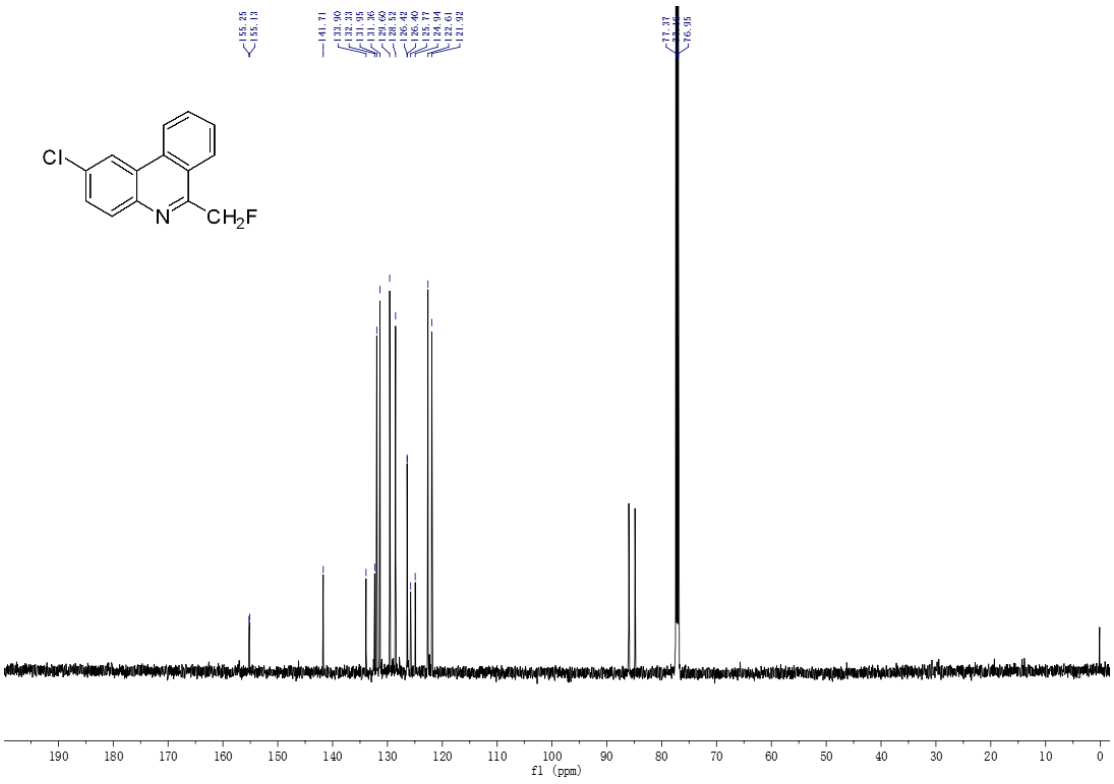
^{19}F NMR of **4i**



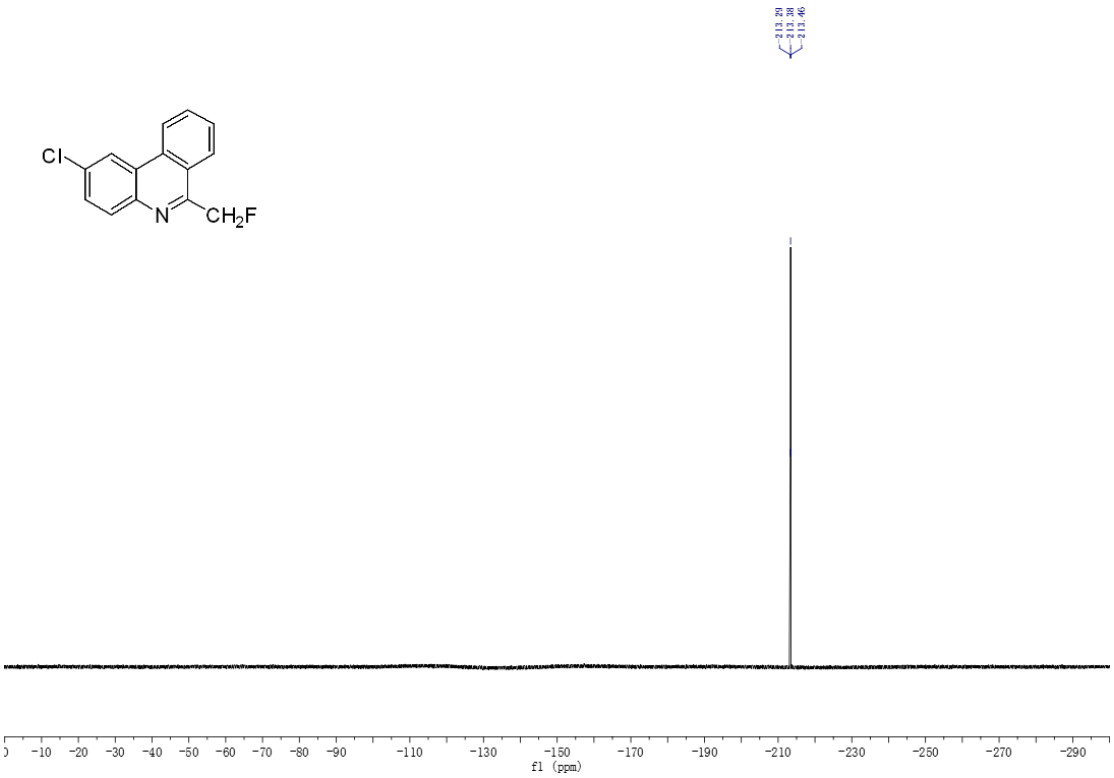
^{1}H NMR of **5a**



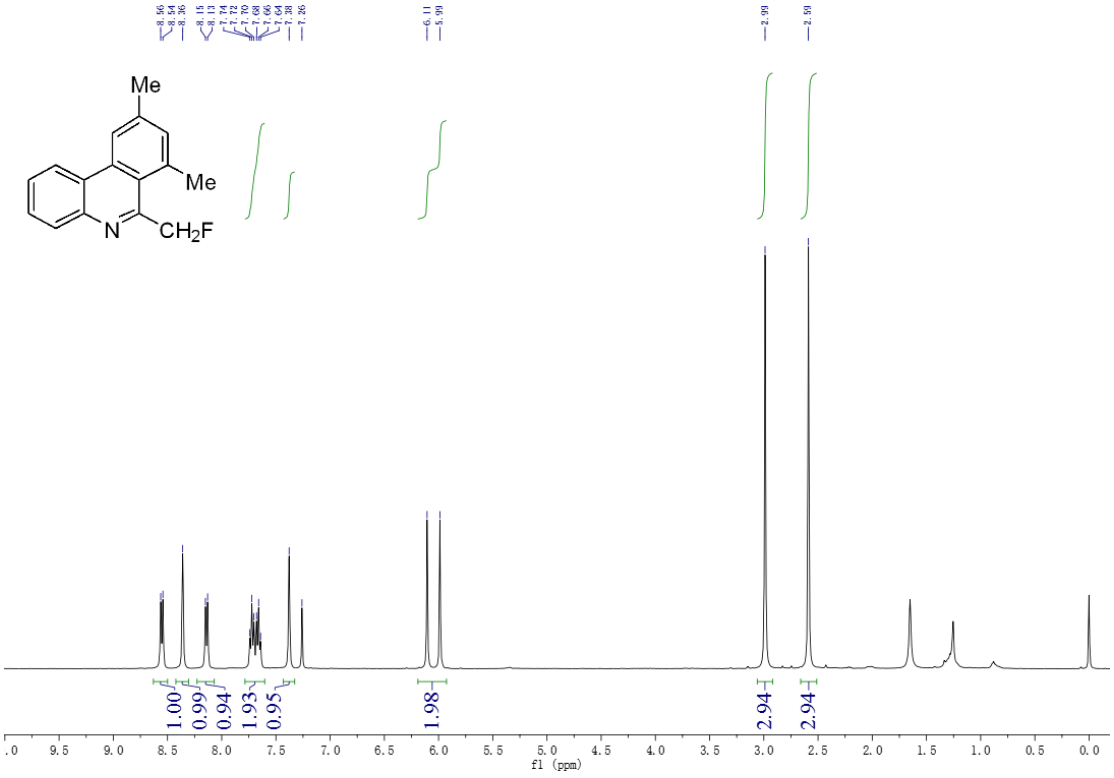
^{13}C NMR of **5a**



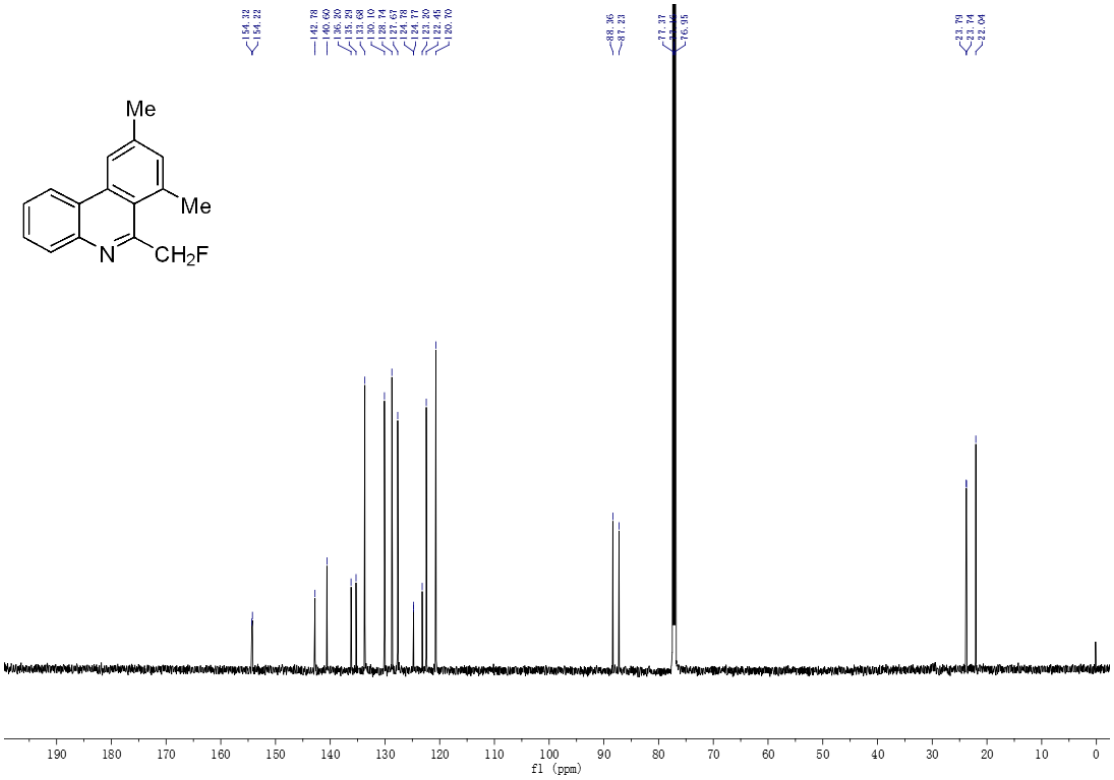
^{19}F NMR of **5a**



^{1}H NMR of **5b**



^{13}C NMR of **5b**



^{19}F NMR of **5b**