

Supporting Information

Synthesis of functionalized quinolines from the cascade reactions of *N*-aryl amidines with two CF₃-ynones via C–H/N–H/C–N/C–C bond cleavage

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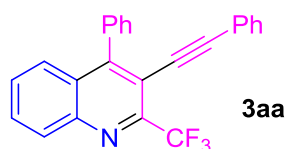
I. General experimental information

All reagents were purchased from commercial sources and were used without further purification. All solvents were purified and dried according to standard methods prior to use. *N*-Aryl amidine **1**^[1], trifluoromethyl ynones **2**^[2-3] and [RhCp*Cl₂]₂^[4] were prepared based on literature procedures. Melting points were recorded with a micro melting point apparatus and uncorrected. The ¹H NMR spectra were recorded at 400 MHz or 600 MHz. The ¹³C NMR spectra were recorded at 100 MHz or 150 MHz. The ¹⁹F NMR spectra were recorded at 376 MHz or 565 MHz. Chemical shifts were expressed in parts per million (δ), and were reported as s (singlet), d (doublet), t (triplet), dd (doublet of doublets), m (multiplet), etc. The coupling constants *J* were given in Hz. High resolution mass spectra (HRMS) were obtained *via* ESI mode by using a MicrOTOF mass spectrometer. All reactions were monitored by thin layer chromatography (TLC) using silica gel plates (silica gel 60 F254 0.25 mm), and components were visualized by observation under UV light (254 and 365 nm).

II. Experimental procedures and spectroscopic data

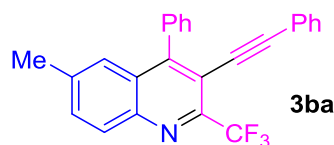
1. Typical procedure for the synthesis of 3aa and spectroscopic data of 3aa-3ra, 3ab-3as

To a reaction tube equipped with a stir bar were added *N*-phenylpivalimidamide (**1a**, 35.3 mg, 0.2 mmol), [RhCp*Cl₂]₂ (3.7 mg, 0.006 mmol), Cu(OAc)₂ · H₂O (40.0 mg, 0.2 mmol), PivOH (20.4 mg, 0.2 mmol), 1,1,1-trifluoro-4-phenylbut-3-yn-2-one (**2a**, 99.1 mg, 0.5 mmol) and MeOH (2 mL). The tube was then sealed, and the mixture was stirred at 70 °C (oil bath) under air for 12 h. Upon completion, it was cooled to room temperature, filtered through a pad of celite and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate (100:1) as eluent to afford **3aa**. Other products **3ba-3ra**, **3ab-3as** were obtained in a similar manner.



4-Phenyl-3-(phenylethynyl)-2-(trifluoromethyl)quinoline (**3aa**)

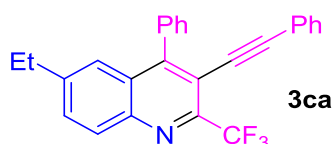
Eluent: petroleum ether/ethyl acetate (100:1). White solid (48.7 mg, 65%), mp 142.2-142.8 °C. ¹H NMR (600 MHz, CDCl₃): δ 8.25 (d, *J* = 8.4 Hz, 1H), 7.80-7.77 (m, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.61-7.57 (m, 4H), 7.50-7.49 (m, 2H), 7.29-7.25 (m, 3H), 7.21-7.19 (m, 2H). ¹³C{¹H} NMR (150 MHz, CDCl₃): δ 153.4, 147.2 (q, ²*J*_{C-F} = 33.5 Hz), 145.1, 135.8, 131.5, 130.8, 130.5, 130.0, 129.1, 128.93, 128.85, 128.4, 128.3, 127.5, 126.4, 122.6, 121.6 (q, ¹*J*_{C-F} = 274.1 Hz), 113.7, 100.0, 83.3. ¹⁹F NMR (565 MHz, CDCl₃): δ -66.14 (s). HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₂₄H₁₅F₃N 374.1151; Found 374.1141.



6-Methyl-4-phenyl-3-(phenylethynyl)-2-(trifluoromethyl)quinoline (**3ba**)

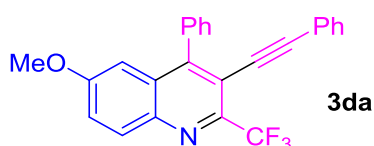
Eluent: petroleum ether/ethyl acetate (100:1). White solid (44.4 mg, 57%), mp 146.6-147.2 °C. ¹H NMR (600 MHz, CDCl₃): δ 8.14 (d, *J* = 9.0 Hz, 1H), 7.63-7.57 (m, 4H), 7.49-7.48 (m, 2H), 7.41 (s, 1H), 7.29-7.25 (m,

3H), 7.19-7.18 (m, 2H), 2.46 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ 152.7, 146.3 (q, $^2J_{\text{C-F}} = 33.5$ Hz), 143.7, 139.6, 136.0, 133.1, 131.5, 130.1, 130.0, 128.9, 128.7, 128.35, 128.31, 127.5, 125.1, 122.6, 121.6 (q, $^1J_{\text{C-F}} = 275.6$ Hz), 113.6, 99.8, 83.5, 22.0. ^{19}F NMR (565 MHz, CDCl_3): δ -66.01 (s). HRMS (ESI) m/z: $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{25}\text{H}_{17}\text{F}_3\text{N}$ 388.1308; Found 388.1290.



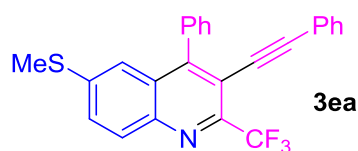
6-Ethyl-4-phenyl-3-(phenylethynyl)-2-(trifluoromethyl)quinoline (3ca)

Eluent: petroleum ether/ethyl acetate (100:1). White solid (48.3 mg, 60%), mp 112.6-113.3 °C. ^1H NMR (600 MHz, CDCl_3): δ 8.17 (d, $J = 9.0$ Hz, 1H), 7.67 (dd, $J_1 = 8.4$ Hz, $J_2 = 1.8$ Hz, 1H), 7.62-7.58 (m, 3H), 7.50-7.49 (m, 2H), 7.43 (d, $J = 1.2$ Hz, 1H), 7.30-7.25 (m, 3H), 7.20-7.18 (m, 2H), 2.75 (q, $J = 7.8$ Hz, 2H), 1.24 (t, $J = 7.8$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ 152.8, 146.4 (q, $^2J_{\text{C-F}} = 30.9$ Hz), 145.7, 143.9, 136.1, 132.0, 131.5, 130.3, 130.0, 128.8, 128.7, 128.33, 128.30, 127.5, 123.9, 122.6, 121.7 (q, $^1J_{\text{C-F}} = 273.9$ Hz), 113.6, 99.8, 83.5, 29.2, 15.4. ^{19}F NMR (565 MHz, CDCl_3): δ -66.00 (s). HRMS (ESI) m/z: $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{26}\text{H}_{19}\text{F}_3\text{N}$ 402.1464; Found 402.1469.



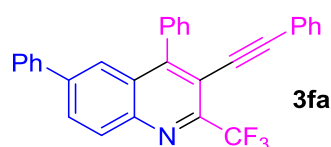
6-Methoxy-4-phenyl-3-(phenylethynyl)-2-(trifluoromethyl)quinoline (3da)

Eluent: petroleum ether/ethyl acetate (50:1). White solid (47.8 mg, 59%), mp 134.4-135.1 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.14 (d, $J = 9.2$ Hz, 1H), 7.62-7.56 (m, 3H), 7.51-7.49 (m, 2H), 7.43 (dd, $J_1 = 9.2$ Hz, $J_2 = 2.8$ Hz, 1H), 7.30-7.24 (m, 3H), 7.20-7.17 (m, 2H), 6.89 (d, $J = 2.8$ Hz, 1H), 3.75 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ 159.7, 151.7, 144.9 (q, $^2J_{\text{C-F}} = 32.1$ Hz), 141.2, 136.2, 131.9, 131.5, 129.8, 128.9, 128.8, 128.5, 128.3, 123.4, 122.6, 121.8 (q, $^1J_{\text{C-F}} = 274.8$ Hz), 114.0, 104.0, 100.0, 83.5, 55.6. ^{19}F NMR (565 MHz, CDCl_3): δ -65.82 (s). HRMS (ESI) m/z: $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{25}\text{H}_{17}\text{F}_3\text{NO}$ 404.1257; Found 404.1240.



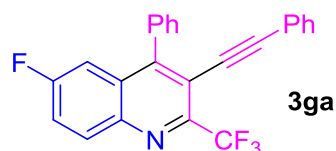
6-(Methylthio)-4-phenyl-3-(phenylethynyl)-2-(trifluoromethyl)quinoline (3ea)

Eluent: petroleum ether/ethyl acetate (50:1). White solid (38.7 mg, 46%), mp 132.7-133.6 °C. ^1H NMR (600 MHz, CDCl_3): δ 8.12 (d, $J = 9.0$ Hz, 1H), 7.64 (dd, $J_1 = 9.0$ Hz, $J_2 = 2.4$ Hz, 1H), 7.61-7.57 (m, 3H), 7.50-7.49 (m, 2H), 7.34 (d, $J = 1.8$ Hz, 1H), 7.31-7.25 (m, 3H), 7.19 (d, $J = 6.6$ Hz, 2H), 2.41 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ 151.7, 146.2 (q, $^2J_{\text{C-F}} = 33.2$ Hz), 143.2, 141.3, 135.7, 131.5, 130.4, 129.9, 129.7, 128.95, 128.92, 128.4, 128.3, 127.9, 122.5, 121.6 (q, $^1J_{\text{C-F}} = 274.7$ Hz), 120.3, 114.3, 100.2, 83.3, 15.2. ^{19}F NMR (565 MHz, CDCl_3): δ -65.98 (s). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{25}\text{H}_{17}\text{F}_3\text{NS}$ 420.1028; Found 420.1042.



4,6-Diphenyl-3-(phenylethynyl)-2-(trifluoromethyl)quinoline (3fa)

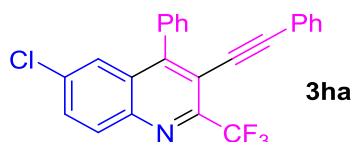
Eluent: petroleum ether/ethyl acetate (100:1). White solid (56.6 mg, 63%), mp 201.4-202.0 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.32 (d, $J = 8.8$ Hz, 1H), 8.06-8.03 (m, 1H), 7.84 (s, 1H), 7.61-7.53 (m, 7H), 7.46-7.36 (m, 3H), 7.29-7.20 (m, 5H). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ 153.5, 147.1 (q, $^2J_{\text{C-F}} = 33.6$ Hz), 144.4, 142.0, 139.9, 135.8, 131.6, 130.9, 130.6, 130.0, 129.1, 129.0, 128.9, 128.4, 128.3, 128.2, 127.6, 123.9, 122.5, 121.6 (q, $^1J_{\text{C-F}} = 276.5$ Hz), 114.1, 100.2, 83.4. ^{19}F NMR (565 MHz, CDCl_3): δ -66.06 (s). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{30}\text{H}_{19}\text{F}_3\text{N}$ 450.1464; Found 450.1460.



6-Fluoro-4-phenyl-3-(phenylethynyl)-2-(trifluoromethyl)quinoline (3ga)

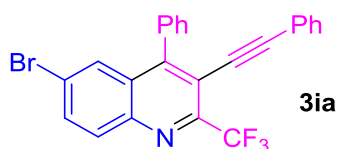
Eluent: petroleum ether/ethyl acetate (100:1). White solid (34.2 mg, 44%), mp 146.5-147.4 °C. ^1H NMR (600 MHz, CDCl_3): δ 8.26 (dd, $J_1 = 9.0$ Hz, $J_2 = 5.4$ Hz, 1H), 7.62-7.58 (m, 3H), 7.57-7.53 (m, 1H), 7.49-7.47 (m

2H), 7.32-7.26 (m, 4H), 7.21-7.19 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ 162.1 (d, $^1J_{\text{C-F}} = 250.2$ Hz), 152.7 (d, $^4J_{\text{C-F}} = 5.4$ Hz), 146.7 (qd, $^2J_{\text{C-F}} = 32.7$ Hz, $^6J_{\text{C-F}} = 2.4$ Hz), 142.1, 135.4, 133.2 (d, $^3J_{\text{C-F}} = 9.0$ Hz), 131.6, 129.8, 129.1, 128.7 (d, $^3J_{\text{C-F}} = 9.5$ Hz), 128.6, 128.3, 122.3, 121.5 (q, $^1J_{\text{C-F}} = 274.7$ Hz), 121.0 (d, $^2J_{\text{C-F}} = 26.4$ Hz), 114.5, 109.9 (d, $^2J_{\text{C-F}} = 24.6$ Hz), 100.7, 83.1. ^{19}F NMR (565 MHz, CDCl_3): δ -66.19 (s), -108.05 – -108.09 (m). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{24}\text{H}_{14}\text{F}_4\text{N}$ 392.1057; Found 392.1040.



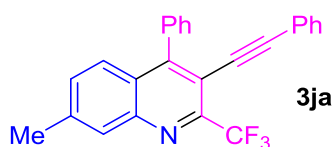
6-Chloro-4-phenyl-3-(phenylethynyl)-2-(trifluoromethyl)quinoline (3ha)

Eluent: petroleum ether/ethyl acetate (100:1). White solid (41.8 mg, 51%), mp 129.0-129.8 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.19 (d, $J = 8.8$ Hz, 1H), 7.72 (dd, $J_1 = 8.8$ Hz, $J_2 = 2.0$ Hz, 1H), 7.64 (d, $J = 2.0$ Hz, 1H), 7.63-7.60 (m, 3H), 7.49-7.47 (m, 2H), 7.31-7.25 (m, 3H), 7.20-7.18 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ 152.5, 147.4 (q, $^2J_{\text{C-F}} = 33.0$ Hz), 143.4, 135.4, 135.2, 132.0, 131.7, 131.6, 129.9, 129.2, 129.1, 128.6, 128.4, 128.3, 125.1, 122.3, 121.4 (q, $^1J_{\text{C-F}} = 274.2$ Hz), 114.7, 100.9, 83.0. ^{19}F NMR (565 MHz, CDCl_3): δ -66.28 (s). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{24}\text{H}_{14}\text{ClF}_3\text{N}$ 408.0761; Found 408.0756.



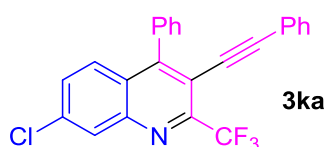
6-Bromo-4-phenyl-3-(phenylethynyl)-2-(trifluoromethyl)quinoline (3ia)

Eluent: petroleum ether/ethyl acetate (100:1). White solid (47.2 mg, 52%), mp 151.8-152.7 °C. ^1H NMR (600 MHz, CDCl_3): δ 8.11 (d, $J = 9.0$ Hz, 1H), 7.85 (dd, $J_1 = 8.4$ Hz, $J_2 = 1.8$ Hz, 1H), 7.82 (d, $J = 2.4$ Hz, 1H), 7.63-7.59 (m, 3H), 7.49-7.47 (m, 2H), 7.32-7.26 (m, 3H), 7.20-7.18 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ 152.4, 147.5 (q, $^2J_{\text{C-F}} = 32.9$ Hz), 143.6, 135.2, 134.3, 132.1, 131.6, 129.9, 129.2, 129.1, 128.7, 128.6, 128.42, 128.36, 123.8, 122.3, 121.4 (q, $^1J_{\text{C-F}} = 276.2$ Hz), 114.7, 100.9, 83.0. ^{19}F NMR (565 MHz, CDCl_3): δ -66.32 (s). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{24}\text{H}_{14}\text{BrF}_3\text{N}$ 452.0256; Found 452.0248.



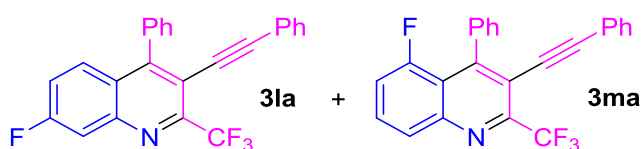
7-Methyl-4-phenyl-3-(phenylethynyl)-2-(trifluoromethyl)quinoline (3ja)

Eluent: petroleum ether/ethyl acetate (100:1). White solid (49.7 mg, 64%), mp 151.1-151.9 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.03 (s, 1H), 7.58-7.56 (m, 4H), 7.49-7.47 (m, 2H), 7.39 (d, $J = 8.8$ Hz, 1H), 7.27-7.23 (m, 3H), 7.20-7.18 (m, 2H), 2.57 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ 153.2, 147.2 (q, $^2J_{\text{C-F}} = 33.8$ Hz), 145.3, 141.6, 136.0, 131.5, 131.4, 130.0, 129.5, 128.81, 128.78, 128.3, 126.1, 125.5, 122.7, 121.6 (q, $^1J_{\text{C-F}} = 275.9$ Hz), 112.8, 99.6, 83.5, 21.8. ^{19}F NMR (376 MHz, CDCl_3): δ -66.06 (s). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{25}\text{H}_{17}\text{F}_3\text{N}$ 388.1308; Found 388.1293.



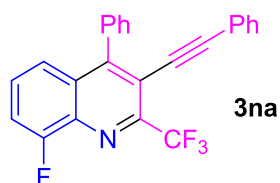
7-Chloro-4-phenyl-3-(phenylethynyl)-2-(trifluoromethyl)quinoline (3ka)

Eluent: petroleum ether/ethyl acetate (100:1). White solid (43.5 mg, 53%), mp 158.3-158.9 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.25 (d, $J = 2.0$ Hz, 1H), 7.64-7.58 (m, 4H), 7.51 (dd, $J_1 = 8.8$ Hz, $J_2 = 2.0$ Hz, 1H), 7.49-7.46 (m, 2H), 7.30-7.25 (m, 3H), 7.20-7.18 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ 153.4, 148.3 (q, $^2J_{\text{C-F}} = 32.4$ Hz), 145.4, 137.0, 135.4, 131.6, 130.1, 129.9, 129.4, 129.11, 129.08, 128.5, 128.4, 127.7, 126.0, 122.4, 121.3 (q, $^1J_{\text{C-F}} = 275.1$ Hz), 114.0, 100.5, 83.0. ^{19}F NMR (376 MHz, CDCl_3): δ -66.38 (s). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{24}\text{H}_{14}\text{ClF}_3\text{N}$ 408.0761; Found 408.0765.



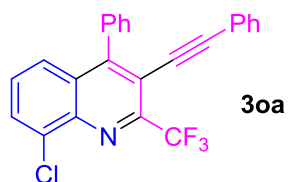
7-Fluoro-4-phenyl-3-(phenylethynyl)-2-(trifluoromethyl)quinoline and **5-Fluoro-4-phenyl-3-(phenylethynyl)-2-(trifluoromethyl)quinoline**

Eluent: petroleum ether/ethyl acetate (100:1). White solid (43.6 mg, 56%), mp 143.5-144.3 °C. ^1H NMR (600 MHz, CDCl_3): δ 8.09 (d, $J = 8.4$ Hz, 0.33H), 7.88 (dd, $J_1 = 9.6$ Hz, $J_2 = 2.4$ Hz, 1H), 7.75-7.72 (m, 0.33H), 7.70 (dd, $J_1 = 9.0$ Hz, $J_2 = 6.0$ Hz, 1H), 7.61-7.58 (m, 3H), 7.54-7.53 (m, 0.99H), 7.49-7.47 (m, 2H), 7.42-7.41 (m, 0.66H), 7.38-7.35 (m, 1H), 7.31-7.24 (m, 4.32H), 7.19-7.18 (m, 2H), 7.14-7.12 (m, 0.66H). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ 163.7 (d, $^1J_{\text{C-F}} = 252.3$ Hz), 157.7 (d, $^1J_{\text{C-F}} = 259.2$ Hz), 153.5, 150.8 (d, $^3J_{\text{C-F}} = 3.9$ Hz), 148.4 (q, $^2J_{\text{C-F}} = 32.4$ Hz), 147.8 (q, $^2J_{\text{C-F}} = 32.7$ Hz), 146.2 (d, $^3J_{\text{C-F}} = 13.5$ Hz), 146.0, 138.4 (d, $^4J_{\text{C-F}} = 3.6$ Hz), 135.6, 131.6, 131.5, 130.6 (d, $^3J_{\text{C-F}} = 8.0$ Hz), 129.9, 129.08, 129.06, 129.0, 128.9 (d, $^3J_{\text{C-F}} = 9.6$ Hz), 128.5 (d, $^4J_{\text{C-F}} = 3.5$ Hz), 128.5, 128.34, 128.32, 128.30, 127.8, 126.9 (d, $^3J_{\text{C-F}} = 4.2$ Hz), 124.7, 122.4, 121.4 (q, $^1J_{\text{C-F}} = 272.4$ Hz), 121.3 (q, $^1J_{\text{C-F}} = 275.0$ Hz), 119.7 (d, $^2J_{\text{C-F}} = 25.5$ Hz), 118.3 (d, $^2J_{\text{C-F}} = 9.6$ Hz), 115.7, 114.5 (d, $^2J_{\text{C-F}} = 21.3$ Hz), 114.2 (d, $^2J_{\text{C-F}} = 20.7$ Hz), 113.3 (d, $^4J_{\text{C-F}} = 3.8$ Hz), 101.5, 100.1, 83.0, 82.7. ^{19}F NMR (565 MHz, CDCl_3): δ -66.34 (s), -66.43 (s), -105.53 (dd, $J_1 = 9.6$ Hz, $J_2 = 6.8$ Hz), -106.97 – -107.01 (m). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{24}\text{H}_{14}\text{F}_4\text{N}$ 392.1057; Found 392.1065.



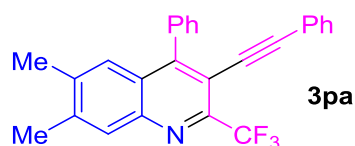
8-Fluoro-4-phenyl-3-(phenylethynyl)-2-(trifluoromethyl)quinoline (3na)

Eluent: petroleum ether/ethyl acetate (100:1). White solid (32.4 mg, 41%), mp 165.7-166.4 °C. ^1H NMR (600 MHz, CDCl_3): δ 7.60-7.58 (m, 3H), 7.53-7.46 (m, 5H), 7.31-7.26 (m, 3H), 7.21-7.19 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ 158.4 (d, $^1J_{\text{C-F}} = 258.9$ Hz), 153.3 (d, $^4J_{\text{C-F}} = 2.1$ Hz), 147.4 (q, $^2J_{\text{C-F}} = 31.5$ Hz), 135.5, 135.3 (d, $^3J_{\text{C-F}} = 10.7$ Hz), 131.6, 129.9, 129.2, 129.08, 129.07 (d, $^2J_{\text{C-F}} = 15.0$ Hz), 128.44, 128.37, 122.3, 122.1 (d, $^3J_{\text{C-F}} = 5.0$ Hz), 121.3 (q, $^1J_{\text{C-F}} = 273.8$ Hz), 114.93 (d, $^2J_{\text{C-F}} = 18.2$ Hz), 114.87, 100.9, 83.0. ^{19}F NMR (565 MHz, CDCl_3): δ -66.24 (s), -122.46 – -122.49 (m). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{24}\text{H}_{14}\text{F}_4\text{N}$ 392.1057; Found 392.1062.



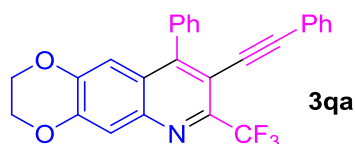
8-Chloro-4-phenyl-3-(phenylethynyl)-2-(trifluoromethyl)quinoline (3oa)

Eluent: petroleum ether/ethyl acetate (100:1). White solid (26.8 mg, 33%), mp 168.1-168.9 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.89 (dd, $J_1 = 7.2$ Hz, $J_2 = 1.2$ Hz, 1H), 7.61-7.58 (m, 4H), 7.50-7.46 (m, 3H), 7.31-7.25 (m, 3H), 7.21-7.18 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ 153.8, 147.5 (q, $^2J_{\text{C-F}} = 32.4$ Hz), 141.4, 135.6, 135.1, 131.6, 130.8, 129.9, 129.1, 129.04, 128.96, 128.9, 128.44, 128.36, 125.5, 122.3, 121.4 (q, $^1J_{\text{C-F}} = 277.7$ Hz), 114.8, 100.9, 83.0. ^{19}F NMR (376 MHz, CDCl_3): δ -66.26 (s). HRMS (ESI) m/z: $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{24}\text{H}_{14}\text{ClF}_3\text{N}$ 408.0761; Found 408.0747.



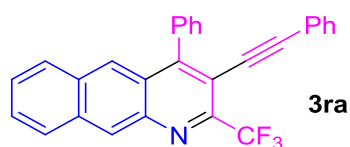
6,7-Dimethyl-4-phenyl-3-(phenylethynyl)-2-(trifluoromethyl)quinoline (3pa)

Eluent: petroleum ether/ethyl acetate (100:1). White solid (48.5 mg, 60%), mp 193.6-194.2 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.02 (s, 1H), 7.59-7.54 (m, 3H), 7.49-7.47 (m, 2H), 7.39 (s, 1H), 7.28-7.24 (m, 3H), 7.19-7.17 (m, 2H), 2.48 (s, 3H), 2.36 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ 152.4, 146.4 (q, $^2J_{\text{C-F}} = 31.4$ Hz), 144.2, 141.6, 139.6, 136.2, 131.5, 130.0, 129.8, 128.72, 128.65, 128.3, 126.0, 125.4, 122.7, 121.7 (q, $^1J_{\text{C-F}} = 275.0$ Hz), 112.7, 99.4, 83.6, 20.41, 20.37. ^{19}F NMR (565 MHz, CDCl_3): δ -65.92 (s). HRMS (ESI) m/z: $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{26}\text{H}_{19}\text{F}_3\text{N}$ 402.1464; Found 402.1448.



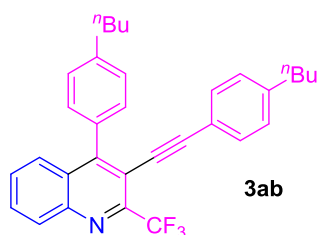
9-Phenyl-8-(phenylethynyl)-7-(trifluoromethyl)-2,3-dihydro-[1,4]dioxino[2,3-g]quinoline (3qa)

Eluent: petroleum ether/ethyl acetate (20:1). White solid (18.3 mg, 21%), mp 197.2-198.0 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.69 (s, 1H), 7.58-7.54 (m, 3H), 7.47-7.45 (m, 2H), 7.27-7.24 (m, 3H), 7.18-7.16 (m, 2H), 7.06 (s, 1H), 4.38-4.35 (m, 4H). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ 151.7, 148.0, 146.3, 145.8 (q, $^2J_{\text{C-F}} = 32.4$ Hz), 141.8, 136.2, 131.4, 129.8, 128.7, 128.6, 128.32, 128.26, 122.8, 121.7 (q, $^1J_{\text{C-F}} = 273.0$ Hz), 115.3, 111.0, 99.1, 83.6, 64.42, 64.39. ^{19}F NMR (376 MHz, CDCl_3): δ -65.87 (s). HRMS (ESI) m/z: $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{26}\text{H}_{17}\text{F}_3\text{NO}_2$ 432.1206; Found 432.1216.



4-Phenyl-3-(phenylethynyl)-2-(trifluoromethyl)benzo[g]quinoline (3ra)

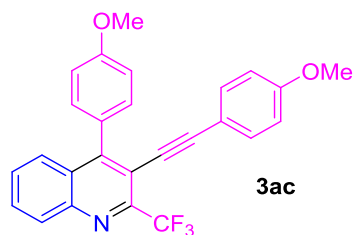
Eluent: petroleum ether/ethyl acetate (100:1). White solid (40.2 mg, 47%), mp 163.2-164.0 °C. ^1H NMR (600 MHz, CDCl_3): δ 8.87 (s, 1H), 8.22 (s, 1H), 8.11 (d, $J = 8.4$ Hz, 1H), 7.91 (d, $J = 8.4$ Hz, 1H), 7.67-7.63 (m, 3H), 7.60-7.57 (m, 3H), 7.53 (t, $J = 7.8$ Hz, 1H), 7.31-7.27 (m, 3H), 7.23-7.22 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ 153.7, 147.5 (q, $^2J_{\text{C-F}} = 33.5$ Hz), 141.1, 136.1, 134.3, 133.2, 131.5, 130.1, 129.3, 128.94, 128.86, 128.7, 128.6, 128.5, 128.3, 127.4, 127.3, 126.2, 125.4, 122.7, 121.5 (q, $^1J_{\text{C-F}} = 274.4$ Hz), 112.1, 99.8, 83.8. ^{19}F NMR (565 MHz, CDCl_3): δ -66.49 (s). HRMS (ESI) m/z: $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{28}\text{H}_{17}\text{F}_3\text{N}$ 424.1308; Found 424.1298.



4-(4-Butylphenyl)-3-((4-butylphenyl)ethynyl)-2-(trifluoromethyl)quinoline (3ab)

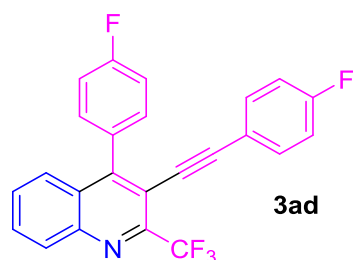
Eluent: petroleum ether/ethyl acetate (100:1). White solid (52.2 mg, 54%), mp 127.1-127.8 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.24 (d, $J = 8.0$ Hz, 1H), 7.79-7.75 (m, 1H), 7.73 (d, $J = 8.0$ Hz, 1H), 7.59-7.55 (m, 1H), 7.40 (s, 4H), 7.12-7.06 (m, 4H), 2.77 (t, $J = 7.6$ Hz, 2H), 2.58 (t, $J = 7.6$ Hz, 2H), 1.77-1.70 (m, 2H), 1.58-1.52 (m,

2H), 1.48-1.41 (m, 2H), 1.35-1.30 (m, 2H), 1.00 (t, $J = 7.2$ Hz, 3H), 0.91 (t, $J = 7.2$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ 153.5, 147.2 (q, $^2J_{\text{C-F}} = 33.0$ Hz), 145.0, 144.2, 143.6, 133.1, 131.5, 130.6, 130.4, 129.9, 128.9, 128.4, 128.3, 127.6, 126.5, 121.6 (q, $^1J_{\text{C-F}} = 274.5$ Hz), 119.8, 113.9, 100.2, 83.0, 35.7, 35.6, 33.8, 33.4, 22.4, 22.3, 14.1, 13.9. ^{19}F NMR (565 MHz, CDCl_3): δ -66.20 (s). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{32}\text{H}_{31}\text{F}_3\text{N}$ 486.2403; Found 486.2399.



4-(4-Methoxyphenyl)-3-((4-methoxyphenyl)ethynyl)-2-(trifluoromethyl)quinoline (3ac)

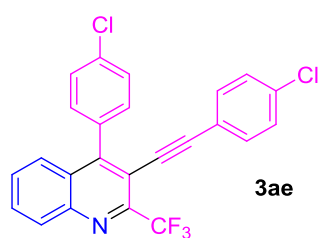
Eluent: petroleum ether/ethyl acetate (30:1). Yellow solid (38.1 mg, 44%), mp 132.8-133.6 °C. ^1H NMR (600 MHz, CDCl_3): δ 8.23 (d, $J = 8.4$ Hz, 1H), 7.77-7.73 (m, 2H), 7.57 (t, $J = 7.8$ Hz, 1H), 7.45 (d, $J = 9.0$ Hz, 2H), 7.21 (d, $J = 8.4$ Hz, 2H), 7.11 (d, $J = 8.4$ Hz, 2H), 6.81 (d, $J = 9.0$ Hz, 2H), 3.94 (s, 3H), 3.80 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ 160.2, 160.0, 152.5, 147.2 (q, $^2J_{\text{C-F}} = 31.5$ Hz), 144.9, 133.1, 131.5, 130.5, 130.4, 129.0, 128.0, 127.8, 126.4, 121.6 (q, $^1J_{\text{C-F}} = 273.9$ Hz), 114.8, 114.0, 113.7, 100.1, 82.5, 55.5, 55.3. ^{19}F NMR (565 MHz, CDCl_3): δ -66.23 (s). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{26}\text{H}_{19}\text{F}_3\text{NO}_2$ 434.1362; Found 434.1368.



4-(4-Fluorophenyl)-3-((4-fluorophenyl)ethynyl)-2-(trifluoromethyl)quinoline (3ad)

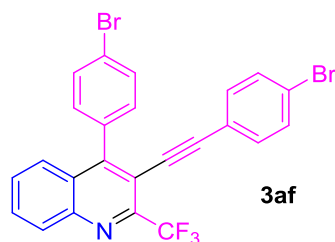
Eluent: petroleum ether/ethyl acetate (100:1). White solid (50.9 mg, 62%), mp 163.4-164.2 °C. ^1H NMR (600 MHz, CDCl_3): δ 8.26 (d, $J = 8.4$ Hz, 1H), 7.82-7.79 (m, 1H), 7.66 (d, $J = 7.8$ Hz, 1H), 7.61 (t, $J = 7.2$ Hz, 1H),

7.50-7.48 (m, 2H), 7.30 (t, $J = 8.4$ Hz, 2H), 7.23-7.20 (m, 2H), 7.00 (t, $J = 9.0$ Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ 163.1 (d, $^1J_{\text{C-F}} = 247.1$ Hz), 163.0 (d, $^1J_{\text{C-F}} = 249.2$ Hz), 152.1, 147.2 (q, $^2J_{\text{C-F}} = 33.8$ Hz), 145.1, 133.5 (d, $^3J_{\text{C-F}} = 8.3$ Hz), 131.9 (d, $^3J_{\text{C-F}} = 8.1$ Hz), 131.7 (d, $^4J_{\text{C-F}} = 3.0$ Hz), 130.9, 130.6, 129.4, 127.4, 126.1, 121.5 (q, $^1J_{\text{C-F}} = 274.1$ Hz), 118.5 (d, $^4J_{\text{C-F}} = 3.2$ Hz), 115.8 (d, $^2J_{\text{C-F}} = 21.9$ Hz), 115.5 (d, $^2J_{\text{C-F}} = 21.3$ Hz), 113.7, 99.1, 82.9. ^{19}F NMR (565 MHz, CDCl_3): δ -66.24 (s), -109.22 – -109.27 (m), -112.13 – -112.18 (m). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{24}\text{H}_{13}\text{F}_5\text{N}$ 410.0963; Found 410.0966.



4-(4-Chlorophenyl)-3-((4-chlorophenyl)ethynyl)-2-(trifluoromethyl)quinoline (3ae)

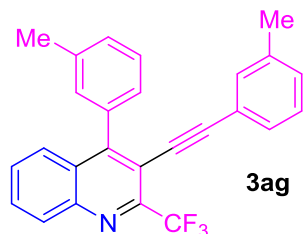
Eluent: petroleum ether/ethyl acetate (100:1). White solid (60.3 mg, 68%), mp 145.1-145.7 °C. ^1H NMR (600 MHz, CDCl_3): δ 8.26 (d, $J = 8.4$ Hz, 1H), 7.83-7.81 (m, 1H), 7.65-7.57 (m, 4H), 7.45-7.43 (m, 2H), 7.30-7.27 (m, 2H), 7.16-7.14 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ 152.0, 147.2 (q, $^2J_{\text{C-F}} = 32.9$ Hz), 145.1, 135.3, 135.2, 134.1, 132.7, 131.4, 131.1, 130.6, 129.5, 128.8, 128.7, 127.2, 126.0, 121.4 (q, $^1J_{\text{C-F}} = 275.0$ Hz), 120.8, 113.3, 99.1, 84.0. ^{19}F NMR (565 MHz, CDCl_3): δ -66.20 (s). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{24}\text{H}_{13}\text{Cl}_2\text{F}_3\text{N}$ 442.0372; Found 442.0387.



4-(4-Bromophenyl)-3-((4-bromophenyl)ethynyl)-2-(trifluoromethyl)quinoline (3af)

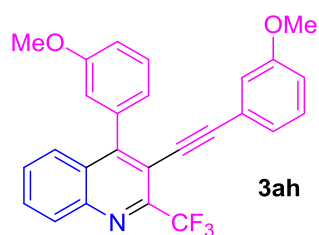
Eluent: petroleum ether/ethyl acetate (100:1). Yellowish solid (55.6 mg, 52%), mp 168.2-168.9 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.26 (d, $J = 8.4$ Hz, 1H), 7.84-7.80 (m, 1H), 7.74 (d, $J = 8.8$ Hz, 2H), 7.66-7.59 (m, 2H), 7.44 (d, $J = 8.4$ Hz, 2H), 7.38 (d, $J = 8.8$ Hz, 2H), 7.08 (d, $J = 8.4$ Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3):

δ 152.1, 147.1 (q, $^2J_{C-F} = 33.3$ Hz), 145.1, 134.6, 132.9, 131.8, 131.68, 131.65, 131.1, 130.6, 129.5, 127.1, 126.0, 123.6, 123.3, 121.4 (q, $^1J_{C-F} = 274.8$ Hz), 121.2, 113.3, 99.3, 84.1. ^{19}F NMR (565 MHz, CDCl_3): δ -66.19 (s). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{24}\text{H}_{13}\text{Br}_2\text{F}_3\text{N}$ 529.9361; Found 529.9371.



4-(*m*-Tolyl)-3-(*m*-tolylethynyl)-2-(trifluoromethyl)quinoline (3ag)

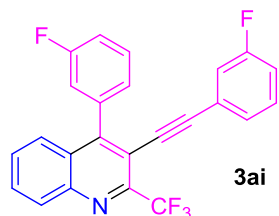
Eluent: petroleum ether/ethyl acetate (100:1). White solid (49.6 mg, 62%), mp 114.4-115.0 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.25 (d, $J = 8.4$ Hz, 1H), 7.80-7.76 (m, 1H), 7.72 (d, $J = 8.4$ Hz, 1H), 7.60-7.56 (m, 1H), 7.48 (t, $J = 7.6$ Hz, 1H), 7.38 (d, $J = 7.6$ Hz, 1H), 7.32 (s, 1H), 7.29 (d, $J = 7.6$ Hz, 1H), 7.16 (t, $J = 7.6$ Hz, 1H), 7.11 (d, $J = 7.6$ Hz, 1H), 7.03 (s, 1H), 7.00 (d, $J = 7.2$ Hz, 1H), 2.47 (s, 3H), 2.30 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ 153.6, 147.2 (q, $^2J_{C-F} = 32.1$ Hz), 145.0, 138.02, 137.97, 135.7, 132.1, 130.7, 130.6, 130.4, 129.8, 129.5, 129.0, 128.6, 128.23, 128.21, 127.5, 127.1, 126.5, 122.4, 121.6 (q, $^1J_{C-F} = 276.2$ Hz), 113.7, 100.3, 83.1, 21.6, 21.2. ^{19}F NMR (565 MHz, CDCl_3): δ -66.16 (s). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{26}\text{H}_{19}\text{F}_3\text{N}$ 402.1464; Found 402.1454.



4-(3-Methoxyphenyl)-3-((3-methoxyphenyl)ethynyl)-2-(trifluoromethyl)quinoline (3ah)

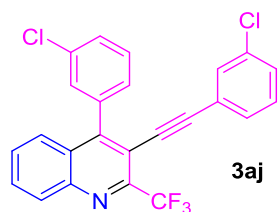
Eluent: petroleum ether/ethyl acetate (50:1). White solid (45.9 mg, 53%), mp 156.5-157.3 °C. ^1H NMR (600 MHz, CDCl_3): δ 8.25 (d, $J = 8.4$ Hz, 1H), 7.80-7.78 (m, 1H), 7.73 (d, $J = 8.4$ Hz, 1H), 7.60-7.57 (m, 1H), 7.50 (t, $J = 7.8$ Hz, 1H), 7.19 (t, $J = 7.8$ Hz, 1H), 7.11-7.09 (m, 1H), 7.07-7.04 (m, 2H), 6.87-6.84 (m, 2H), 6.712-6.706 (m, 1H), 3.85 (s, 3H), 3.77 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 159.6, 159.3, 153.4,

147.1 (q, $^2J_{C-F} = 32.5$ Hz), 145.1, 137.1, 130.8, 130.4, 129.5, 129.4, 129.2, 127.4, 126.4, 124.1, 123.5, 122.4, 121.5 (q, $^1J_{C-F} = 274.8$ Hz), 116.2, 115.7, 115.3, 114.7, 113.5, 100.1, 83.1, 55.4, 55.3. ^{19}F NMR (565 MHz, CDCl_3): δ -66.10 (s). HRMS (ESI) m/z: $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{26}\text{H}_{19}\text{F}_3\text{NO}_2$ 434.1362; Found 434.1376.



4-(3-Fluorophenyl)-3-((3-fluorophenyl)ethynyl)-2-(trifluoromethyl)quinoline (3ai)

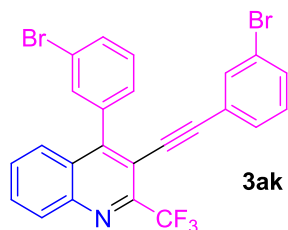
Eluent: petroleum ether/ethyl acetate (100:1). White solid (33.9 mg, 41%), mp 148.5-149.1 °C. ^1H NMR (600 MHz, CDCl_3): δ 8.27 (d, $J = 8.4$ Hz, 1H), 7.84-7.81 (m, 1H), 7.67 (d, $J = 7.8$ Hz, 1H), 7.64-7.61 (m, 1H), 7.58 (td, $J_1 = 7.8$ Hz, $J_2 = 6.0$ Hz, 1H), 7.32-7.22 (m, 4H), 7.04-7.02 (m, 2H), 6.91-6.89 (m, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ 162.7 (d, $^1J_{C-F} = 245.7$ Hz), 162.3 (d, $^1J_{C-F} = 245.4$ Hz), 152.0, 147.2 (q, $^2J_{C-F} = 32.7$ Hz), 145.2, 137.7 (d, $^3J_{C-F} = 9.3$ Hz), 131.2, 130.6, 130.2 (d, $^3J_{C-F} = 9.0$ Hz), 130.1 (d, $^3J_{C-F} = 8.7$ Hz), 129.5, 127.4 (d, $^4J_{C-F} = 3.0$ Hz), 127.1, 126.1, 125.8 (d, $^4J_{C-F} = 3.5$ Hz), 124.1 (d, $^3J_{C-F} = 9.2$ Hz), 121.4 (q, $^1J_{C-F} = 276.2$ Hz), 118.2 (d, $^2J_{C-F} = 22.7$ Hz), 117.1 (d, $^2J_{C-F} = 21.5$ Hz), 116.5 (d, $^2J_{C-F} = 22.4$ Hz), 116.0 (d, $^2J_{C-F} = 20.7$ Hz), 113.2, 98.9 (d, $^4J_{C-F} = 2.1$ Hz), 83.7. ^{19}F NMR (565 MHz, CDCl_3): δ -66.18 (s), -112.31 – -112.35 (m), -112.49 – -112.53 (m). HRMS (ESI) m/z: $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{24}\text{H}_{13}\text{F}_5\text{N}$ 410.0963; Found 410.0969.



4-(3-Chlorophenyl)-3-((3-chlorophenyl)ethynyl)-2-(trifluoromethyl)quinoline (3aj)

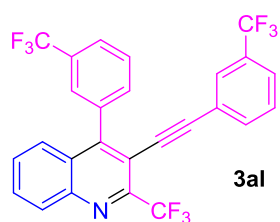
Eluent: petroleum ether/ethyl acetate (100:1). White solid (44.3 mg, 50%), mp 125.1-125.9 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.27 (d, $J = 8.8$ Hz, 1H), 7.85-7.81 (m, 1H), 7.69-7.61 (m, 2H), 7.60-7.53 (m, 3H), 7.39-7.36 (m, 1H), 7.32-7.29 (m, 1H), 7.26-7.22 (m, 2H), 7.14-7.12 (m, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ 151.8,

147.2 (q, $^2J_{C-F} = 32.7$ Hz), 145.2, 137.4, 134.5, 134.3, 131.3, 131.2, 130.6, 130.0, 129.8, 129.7, 129.6, 129.4, 129.2, 128.2, 127.0, 126.1, 123.9, 121.4 (q, $^1J_{C-F} = 276.6$ Hz), 113.1, 98.9, 84.0. ^{19}F NMR (376 MHz, CDCl_3): δ -66.17 (s). HRMS (ESI) m/z: $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{24}\text{H}_{13}\text{Cl}_2\text{F}_3\text{N}$ 442.0372; Found 442.0380.



4-(3-Bromophenyl)-3-((3-bromophenyl)ethynyl)-2-(trifluoromethyl)quinoline (3ak)

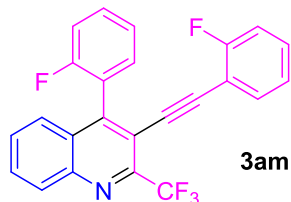
Eluent: petroleum ether/ethyl acetate (100:1). Yellow solid (44.5 mg, 42%), mp 140.1-140.7 °C. ^1H NMR (600 MHz, CDCl_3): δ 7.27 (d, $J = 8.4$ Hz, 1H), 7.84-7.82 (m, 1H), 7.74 (d, $J = 7.8$ Hz, 1H), 7.70 (t, $J = 1.8$ Hz, 1H), 7.68 (d, $J = 7.2$ Hz, 1H), 7.65-7.62 (m, 1H), 7.49 (t, $J = 7.8$ Hz, 1H), 7.46-7.44 (m, 1H), 7.42 (d, $J = 7.8$ Hz, 1H), 7.39 (s, 1H), 7.20-7.16 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ 151.7, 147.1 (q, $^2J_{C-F} = 32.6$ Hz), 145.2, 137.6, 134.2, 132.9, 132.3, 132.1, 131.2, 130.7, 130.1, 130.0, 129.9, 129.6, 128.7, 127.0, 126.1, 124.2, 122.5, 122.2, 121.4 (q, $^1J_{C-F} = 275.0$ Hz), 113.1, 98.9, 84.1. ^{19}F NMR (565 MHz, CDCl_3): δ -66.14 (s). HRMS (ESI) m/z: $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{24}\text{H}_{13}\text{Br}_2\text{F}_3\text{N}$ 529.9361; Found 529.9372.



2-(Trifluoromethyl)-4-(3-(trifluoromethyl)phenyl)-3-((3-(trifluoromethyl)phenyl)ethynyl)quinoline (3al)

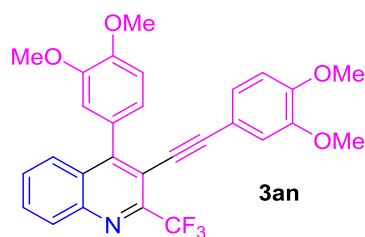
Eluent: petroleum ether/ethyl acetate (100:1). White solid (33.0 mg, 32%), mp 120.1-120.8 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.30 (d, $J = 8.4$ Hz, 1H), 7.89-7.84 (m, 3H), 7.76 (t, $J = 7.6$ Hz, 1H), 7.69 (d, $J = 8.0$ Hz, 1H), 7.66-7.61 (m, 2H), 7.56 (d, $J = 7.6$ Hz, 1H), 7.42 (t, $J = 8.0$ Hz, 1H), 7.39-7.36 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ 151.9, 147.2 (q, $^2J_{C-F} = 32.9$ Hz), 145.3, 136.5, 134.4, 133.3, 131.4, 131.3 (q, $^2J_{C-F} = 32.9$ Hz), 131.1 (q, $^2J_{C-F} = 32.7$ Hz), 130.8, 129.8, 129.1, 129.0, 128.2 (q, $^3J_{C-F} = 4.1$ Hz), 126.94, 126.93 (q, $^3J_{C-F} = 3.9$

Hz), 125.861, 125.862 (q, $^3J_{C-F} = 3.7$ Hz), 125.7 (q, $^3J_{C-F} = 3.6$ Hz), 123.9 (q, $^1J_{C-F} = 270.2$ Hz), 123.5 (q, $^1J_{C-F} = 270.9$ Hz), 123.0, 121.4 (q, $^1J_{C-F} = 274.8$ Hz), 113.1, 98.8, 84.1. ^{19}F NMR (565 MHz, CDCl_3): δ -62.61 (s), -63.18 (s), -66.18 (s). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{26}\text{H}_{13}\text{F}_9\text{N}$ 510.0899; Found 510.0889.



4-(2-Fluorophenyl)-3-((2-fluorophenyl)ethynyl)-2-(trifluoromethyl)quinoline (3am)

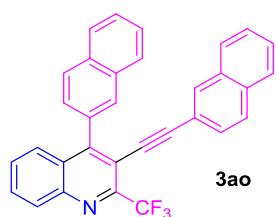
Eluent: petroleum ether/ethyl acetate (100:1). White solid (32.8 mg, 40%), mp 151.3-151.9 °C. ^1H NMR (600 MHz, CDCl_3): δ 8.28 (d, $J = 8.4$ Hz, 1H), 7.83-7.81 (m, 1H), 7.64-7.61 (m, 2H), 7.59-7.55 (m, 1H), 7.44 (td, $J_1 = 7.2$ Hz, $J_2 = 1.2$ Hz, 1H), 7.37 (td, $J_1 = 7.2$ Hz, $J_2 = 1.2$ Hz, 1H), 7.33-7.27 (m, 2H), 7.23-7.21 (m, 1H), 7.07-7.04 (m, 1H), 7.01 (t, $J = 7.8$ Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ 162.6 (d, $^1J_{C-F} = 252.6$ Hz), 159.7 (d, $^1J_{C-F} = 247.4$ Hz), 148.0, 147.1 (q, $^2J_{C-F} = 32.7$ Hz), 145.0, 133.5, 131.8 (d, $^4J_{C-F} = 2.7$ Hz), 131.2 (d, $^3J_{C-F} = 8.4$ Hz), 131.1, 130.8 (d, $^3J_{C-F} = 7.5$ Hz), 130.6, 129.5, 127.4, 126.0, 124.3 (d, $^3J_{C-F} = 3.5$ Hz), 123.9 (d, $^3J_{C-F} = 4.5$ Hz), 123.2 (d, $^2J_{C-F} = 15.9$ Hz), 121.4 (q, $^1J_{C-F} = 275.3$ Hz), 116.1 (d, $^2J_{C-F} = 21.5$ Hz), 115.6 (d, $^2J_{C-F} = 20.6$ Hz), 114.3, 111.1 (d, $^2J_{C-F} = 15.9$ Hz), 93.5, 87.5 (d, $^4J_{C-F} = 2.1$ Hz). ^{19}F NMR (565 MHz, CDCl_3): δ -66.16 (s), -108.80 – -108.84 (m), -112.85 – -112.88 (m). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{24}\text{H}_{13}\text{F}_5\text{N}$ 410.0963; Found 410.0961.



4-(3,4-Dimethoxyphenyl)-3-((3,4-dimethoxyphenyl)ethynyl)-2-(trifluoromethyl)quinoline (3an)

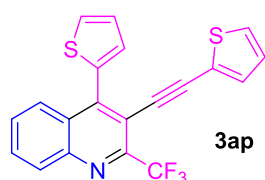
Eluent: petroleum ether/ethyl acetate (5:1). Yellow solid (36.4 mg, 37%), mp 163.5-164.2 °C. ^1H NMR (600 MHz, CDCl_3): δ 8.24 (d, $J = 8.4$ Hz, 1H), 7.80-7.77 (m, 2H), 7.59 (td, $J_1 = 8.4$ Hz, $J_2 = 0.6$ Hz, 1H), 7.11 (d, J

= 1.8 Hz, 1H), 7.09 (d, $J = 8.4$ Hz, 1H), 7.05 (dd, $J_1 = 7.8$ Hz, $J_2 = 1.8$ Hz, 1H), 6.89 (dd, $J_1 = 8.4$ Hz, $J_2 = 1.8$ Hz, 1H), 6.78 (d, $J = 8.4$ Hz, 1H), 6.67 (d, $J = 1.8$ Hz, 1H), 4.00 (s, 3H), 3.89 (s, 3H), 3.88 (s, 3H), 3.85 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ 152.7, 150.1, 149.4, 148.8, 148.7, 147.0 (q, $^2J_{\text{C-F}} = 32.3$ Hz), 145.0, 130.6, 130.5, 129.1, 128.3, 127.7, 126.4, 124.9, 122.9, 121.6 (q, $^1J_{\text{C-F}} = 275.1$ Hz), 114.7, 114.0, 113.9, 113.5, 111.0, 110.8, 100.5, 82.5, 56.1, 56.0, 55.9, 55.8. ^{19}F NMR (565 MHz, CDCl_3): δ -66.16 (s). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{28}\text{H}_{23}\text{F}_3\text{NO}_4$ 494.1574; Found 494.1578.



4-(Naphthalen-2-yl)-3-(naphthalen-2-ylethynyl)-2-(trifluoromethyl)quinoline (3ao)

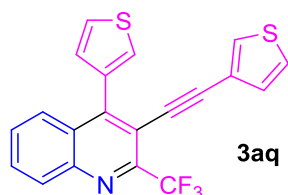
Eluent: petroleum ether/ethyl acetate (100:1). Yellow solid (43.8 mg, 46%), mp 203.9-204.8 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.29 (d, $J = 8.8$ Hz, 1H), 8.08 (d, $J = 8.4$ Hz, 1H), 8.06 (s, 1H), 8.03 (d, $J = 8.0$ Hz, 1H), 7.96 (d, $J = 8.0$ Hz, 1H), 7.82-7.78 (m, 1H), 7.75 (d, $J = 8.4$ Hz, 1H), 7.70-7.52 (m, 7H), 7.47 (s, 1H), 7.42-7.40 (m, 2H), 7.08 (dd, $J_1 = 8.4$ Hz, $J_2 = 1.6$ Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 153.4, 147.3 (q, $^2J_{\text{C-F}} = 32.3$ Hz), 145.1, 133.34, 133.30, 133.1, 133.0, 132.7, 131.8, 130.9, 130.6, 129.7, 129.3, 128.4, 128.1, 128.0, 127.95, 127.86, 127.73, 127.70, 127.6, 127.1, 127.0, 126.8, 126.6, 126.5, 121.7 (q, $^1J_{\text{C-F}} = 275.6$ Hz), 119.7, 113.9, 100.8, 83.9. ^{19}F NMR (376 MHz, CDCl_3): δ -65.99 (s). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{32}\text{H}_{19}\text{F}_3\text{N}$ 474.1464; Found 474.1447.



4-(Thiophen-2-yl)-3-(thiophen-2-ylethynyl)-2-(trifluoromethyl)quinoline (3ap)

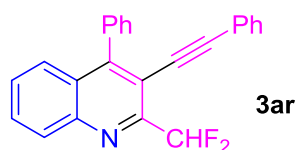
Eluent: petroleum ether/ethyl acetate (100:1). Yellow solid (42.7 mg, 55%), mp 128.6-129.2 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.22 (d, $J = 8.4$ Hz, 1H), 7.94 (d, $J = 8.4$ Hz, 1H), 7.81-7.77 (m, 1H), 7.66-7.60 (m, 2H),

7.32-7.27 (m, 3H), 7.17 (dd, $J_1 = 3.6$ Hz, $J_2 = 0.8$ Hz, 1H), 6.98 (dd, $J_1 = 5.2$ Hz, $J_2 = 3.6$ Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ 146.8 (q, $^2J_{\text{C-F}} = 32.6$ Hz), 145.9, 144.9, 135.0, 132.9, 131.0, 130.5, 130.3, 129.5, 128.8, 128.09, 128.06, 127.3, 127.2, 126.2, 122.4, 121.4 (q, $^1J_{\text{C-F}} = 274.2$ Hz), 114.5, 94.4, 87.1. ^{19}F NMR (565 MHz, CDCl_3): δ -66.27 (s). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{11}\text{F}_3\text{NS}_2$ 386.0280; Found 386.0284.



4-(Thiophen-3-yl)-3-(thiophen-3-ylethynyl)-2-(trifluoromethyl)quinoline (3aq)

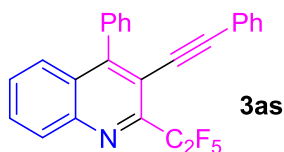
Eluent: petroleum ether/ethyl acetate (100:1). White solid (40.2 mg, 52%), mp 153.7-154.4 °C. ^1H NMR (600 MHz, CDCl_3): δ 8.23 (d, $J = 8.4$ Hz, 1H), 7.85 (d, $J = 8.4$ Hz, 1H), 7.80-7.78 (m, 1H), 7.62-7.59 (m, 2H), 7.56 (dd, $J_1 = 4.8$ Hz, $J_2 = 3.0$ Hz, 1H), 7.39 (dd, $J_1 = 3.0$ Hz, $J_2 = 1.2$ Hz, 1H), 7.34 (dd, $J_1 = 4.8$ Hz, $J_2 = 1.2$ Hz, 1H), 7.26 (dd, $J_1 = 4.8$ Hz, $J_2 = 2.4$ Hz, 1H), 7.01 (dd, $J_1 = 5.4$ Hz, $J_2 = 1.2$ Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ 148.4, 147.2 (q, $^2J_{\text{C-F}} = 32.1$ Hz), 145.0, 135.4, 130.8, 130.5, 129.7, 129.6, 129.2, 127.7, 126.7, 126.2, 125.61, 125.56, 121.7, 121.5 (q, $^1J_{\text{C-F}} = 275.7$ Hz), 113.8, 95.3, 83.0. ^{19}F NMR (565 MHz, CDCl_3): δ -66.27 (s). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{11}\text{F}_3\text{NS}_2$ 386.0280; Found 386.0266.



2-(Difluoromethyl)-4-phenyl-3-(phenylethynyl)quinoline (3ar)

Eluent: petroleum ether/ethyl acetate (100:1). Yellow solid (18.5 mg, 26%), mp 203.9-204.8 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.24 (d, $J = 8.4$ Hz, 1H), 7.79-7.75 (m, 1H), 7.69 (d, $J = 8.4$ Hz, 1H), 7.60-7.53 (m, 4H), 7.51-7.49 (m, 2H), 7.31-7.21 (m, 5H), 7.19 (t, $J = 54.4$ Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ 152.5, 151.2 (t, $^2J_{\text{C-F}} = 22.5$ Hz), 146.0, 135.9, 131.5, 130.5, 130.3, 130.0, 128.9, 128.8, 128.5, 128.4, 128.3, 127.3,

126.4, 122.5, 114.2, 113.6 (t, $^1J_{\text{C-F}} = 240.0$ Hz), 99.8, 83.5. ^{19}F NMR (565 MHz, CDCl_3): δ -116.64 (d, $J = 55.4$ Hz). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{24}\text{H}_{16}\text{F}_2\text{N}$ 356.1245; Found 356.1238.

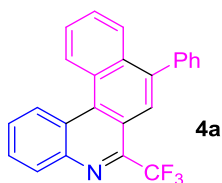


2-(Perfluoroethyl)-4-phenyl-3-(phenylethynyl)quinoline (3as)

Eluent: petroleum ether/ethyl acetate (100:1). Yellow solid (29.9 mg, 35%), mp 144.9-145.6 °C. ^1H NMR (600 MHz, CDCl_3): δ 8.24 (d, $J = 8.4$ Hz, 1H), 7.80-7.77 (m, 1H), 7.66 (d, $J = 7.8$ Hz, 1H), 7.61-7.57 (m, 4H), 7.49-7.47 (m, 2H), 7.31-7.25 (m, 3H), 7.17-7.15 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ 153.6, 146.8 (t, $^2J_{\text{C-F}} = 25.5$ Hz), 145.1, 135.9, 131.5, 130.7, 130.6, 130.0, 129.2, 128.85, 128.76, 128.33, 128.29, 127.2, 126.4, 122.6, 119.4 (qt, $^1J_{\text{C-F}} = 285.6$ Hz, $^2J_{\text{C-F}} = 36.5$ Hz), 114.6, 112.4 (tq, $^1J_{\text{C-F}} = 256.2$ Hz, $^2J_{\text{C-F}} = 35.4$ Hz), 100.1, 83.5. ^{19}F NMR (565 MHz, CDCl_3): δ -80.80 (s), -110.88 (s). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{25}\text{H}_{15}\text{F}_5\text{N}$ 424.1119; Found 424.1132.

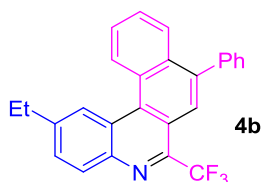
2. Typical procedure for the synthesis of 4a and spectroscopic data of 4a-4l^[5]

To a reaction tube equipped with a stir bar were added **3aa** (74.7 mg, 0.2 mmol), *p*-TsOH H_2O (1.14 g, 6.0 mmol). The tube was then sealed, and the mixture was stirred at 120 °C (oil bath) under air for 24 h. Upon completion, the resulting mixture was cooled to room temperature, neutralized with saturated aqueous solution of NaHCO_3 and extracted with ethyl acetate (10 mL \times 3). The combined organic phases were dried over Na_2SO_4 , filtered through a pad of celite and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 100:1) to give product **4a**. Other products **4b-4l** were obtained in a similar manner.



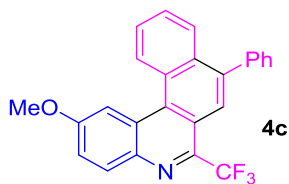
8-Phenyl-6-(trifluoromethyl)benzo[*k*]phenanthridine (4a)

Eluent: petroleum ether/ethyl acetate (100:1). White solid (66.7 mg, 89%), mp 180.0-180.6 °C. ¹H NMR (600 MHz, CDCl₃): δ 8.96 (d, *J* = 8.4 Hz, 1H), 8.86 (d, *J* = 7.8 Hz, 1H), 8.27 (dd, *J*₁ = 7.8 Hz, *J*₂ = 1.2 Hz, 1H), 8.06 (q, *J* = 1.8 Hz, 1H), 7.95 (dd, *J*₁ = 8.4 Hz, *J*₂ = 0.6 Hz, 1H), 7.71 (td, *J*₁ = 6.6 Hz, *J*₂ = 1.2 Hz, 1H), 7.67 (td, *J*₁ = 7.8 Hz, *J*₂ = 1.2 Hz, 1H), 7.60 (td, *J*₁ = 7.2 Hz, *J*₂ = 1.2 Hz, 1H), 7.56-7.54 (m, 1H), 7.48-7.43 (m, 4H), 7.40-7.37 (m, 1H). ¹³C{¹H} NMR (150 MHz, CDCl₃): δ 145.7 (q, ²*J*_{C-F} = 31.5 Hz), 143.8, 141.0, 139.7, 133.6, 133.2, 131.0, 130.0, 129.2, 129.0, 128.9, 128.8, 128.7, 128.1, 127.2, 127.07, 127.06, 125.1, 122.3 (q, ¹*J*_{C-F} = 275.9 Hz), 121.7 (q, ⁴*J*_{C-F} = 3.2 Hz), 120.6. ¹⁹F NMR (565 MHz, CDCl₃): δ -62.36 (s). HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₂₄H₁₅F₃N 374.1151; Found 374.1141.



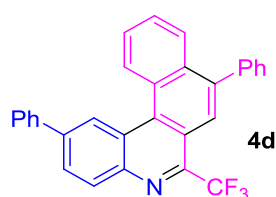
2-Ethyl-8-phenyl-6-(trifluoromethyl)benzo[*k*]phenanthridine (4b)

Eluent: petroleum ether/ethyl acetate (100:1). Colorless oil (69.6 mg, 87%). ¹H NMR (400 MHz, CDCl₃): δ 9.05 (d, *J* = 8.4 Hz, 1H), 8.75 (s, 1H), 8.24 (d, *J* = 8.4 Hz, 1H), 8.08 (q, *J* = 2.4 Hz, 1H), 8.00 (dd, *J*₁ = 8.0 Hz, *J*₂ = 0.4 Hz, 1H), 7.70-7.66 (m, 1H), 7.64-7.58 (m, 2H), 7.52-7.45 (m, 4H), 7.44-7.40 (m, 1H), 2.90 (q, *J* = 7.6 Hz, 2H), 1.33 (t, *J* = 7.6 Hz, 3H). ¹³C{¹H} NMR (150 MHz, CDCl₃): δ 144.3, 143.8 (q, ²*J*_{C-F} = 32.0 Hz), 141.4, 139.7, 138.7, 132.5, 131.9, 129.7, 128.9, 128.8, 128.3, 127.8, 127.6, 127.5, 127.0, 126.0, 125.9, 124.4, 124.1, 121.4 (q, ¹*J*_{C-F} = 275.4 Hz), 120.7 (q, ⁴*J*_{C-F} = 2.9 Hz), 119.6, 28.5, 14.6. ¹⁹F NMR (376 MHz, CDCl₃): δ -62.31 (d, *J* = 2.6 Hz). HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₂₆H₁₉F₃N 402.1464; Found 402.1478.



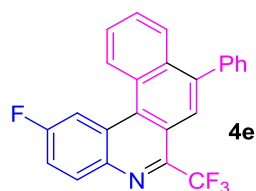
2-Methoxy-8-phenyl-6-(trifluoromethyl)benzo[*k*]phenanthridine (4c)

Eluent: petroleum ether/ethyl acetate (50:1). White solid (54.5 mg, 68%), mp 124.5-125.3 °C. ^1H NMR (400 MHz, CDCl_3): δ 9.22 (d, $J = 8.4$ Hz, 1H), 8.46 (d, $J = 2.8$ Hz, 1H), 8.33 (d, $J = 9.2$ Hz, 1H), 8.16 (q, $J = 2.0$ Hz, 1H), 8.10 (dd, $J_1 = 8.4$ Hz, $J_2 = 0.8$ Hz, 1H), 7.79-7.74 (m, 1H), 7.72-7.68 (m, 1H), 7.62-7.56 (m, 4H), 7.54-7.50 (m, 2H), 4.06 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ 160.0, 143.3 (q, $^2J_{\text{C-F}} = 30.8$ Hz), 141.0, 139.7, 139.4, 133.5, 132.5, 132.2, 130.0, 129.5, 128.7, 128.5, 128.05, 128.01, 127.2, 126.9, 126.5, 122.5 (q, $^1J_{\text{C-F}} = 274.2$ Hz), 121.8 (q, $^4J_{\text{C-F}} = 3.0$ Hz), 121.0, 119.4, 107.9, 55.9. ^{19}F NMR (376 MHz, CDCl_3): δ -62.21 (d, $J = 2.6$ Hz). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{25}\text{H}_{17}\text{F}_3\text{NO}$ 404.1257; Found 404.1266.



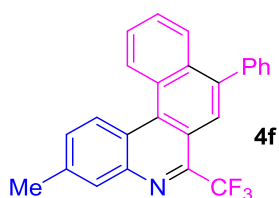
2,8-Diphenyl-6-(trifluoromethyl)benzo[*k*]phenanthridine (4d)

Eluent: petroleum ether/ethyl acetate (100:1). White solid (63.5 mg, 71%), mp 187.2-187.7 °C. ^1H NMR (400 MHz, CDCl_3): δ 9.23 (d, $J = 1.6$ Hz, 1H), 9.20 (d, $J = 8.4$ Hz, 1H), 8.48 (d, $J = 8.4$ Hz, 1H), 8.20 (q, $J = 2.0$ Hz, 1H), 8.11 (dd, $J_1 = 8.4$ Hz, $J_2 = 2.0$ Hz, 2H), 7.81-7.77 (m, 3H), 7.74-7.70 (m, 1H), 7.63-7.53 (m, 7H), 7.46 (t, $J = 7.2$ Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ 145.5 (q, $^2J_{\text{C-F}} = 33.2$ Hz), 143.1, 141.7, 141.1, 140.5, 139.7, 133.7, 133.3, 131.3, 130.0, 129.3, 129.2, 128.8, 128.73, 128.71, 128.5, 128.14, 128.09, 127.7, 127.24, 127.19, 125.43, 125.41, 122.3 (q, $^1J_{\text{C-F}} = 276.3$ Hz), 121.7 (q, $^4J_{\text{C-F}} = 2.6$ Hz), 120.9. ^{19}F NMR (376 MHz, CDCl_3): δ -62.40 (d, $J = 2.6$ Hz). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{30}\text{H}_{19}\text{F}_3\text{N}$ 450.1464; Found 450.1477.



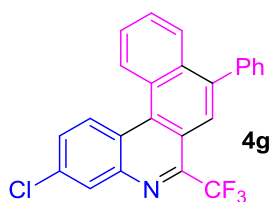
2-Fluoro-8-phenyl-6-(trifluoromethyl)benzo[*k*]phenanthridine (4e)

Eluent: petroleum ether/ethyl acetate (100:1). White solid (64.8 mg, 83%), mp 189.8-190.5 °C. ^1H NMR (400 MHz, CDCl_3): δ 9.05 (d, $J = 8.4$ Hz, 1H), 8.68 (dd, $J_1 = 10.8$ Hz, $J_2 = 2.8$ Hz, 1H), 8.39 (dd, $J_1 = 8.8$ Hz, $J_2 = 5.6$ Hz, 1H), 8.17 (q, $J = 2.0$ Hz, 1H), 8.09 (d, $J = 8.4$ Hz, 1H), 7.80-7.76 (m, 1H), 7.73-7.69 (m, 1H), 7.62-7.53 (m, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ 162.5 (d, $^1J_{\text{C-F}} = 274.7$ Hz), 145.1 (q, $^2J_{\text{C-F}} = 32.7$ Hz), 141.8, 140.7, 139.5, 133.5 (d, $^3J_{\text{C-F}} = 8.9$ Hz), 133.4, 132.5 (d, $^4J_{\text{C-F}} = 4.4$ Hz), 130.0, 129.2, 128.8, 128.7, 128.2, 128.1, 127.5, 127.3, 126.3 (d, $^3J_{\text{C-F}} = 10.2$ Hz), 122.2 (q, $^1J_{\text{C-F}} = 275.6$ Hz), 121.6 (q, $^4J_{\text{C-F}} = 3.3$ Hz), 120.9, 118.4 (d, $^2J_{\text{C-F}} = 24.8$ Hz), 111.8 (d, $^2J_{\text{C-F}} = 25.2$ Hz). ^{19}F NMR (376 MHz, CDCl_3): δ -62.50 (s), -109.38 – -109.45 (m). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{24}\text{H}_{14}\text{F}_4\text{N}$ 392.1057; Found 392.1060.



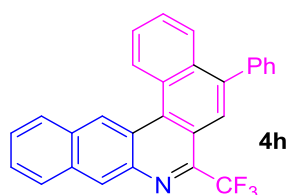
3-Methyl-8-phenyl-6-(trifluoromethyl)benzo[*k*]phenanthridine (4f)

Eluent: petroleum ether/ethyl acetate (100:1). White solid (42.6 mg, 55%), mp 199.2-199.9 °C. ^1H NMR (400 MHz, CDCl_3): δ 9.11 (d, $J = 8.4$ Hz, 1H), 8.91 (d, $J = 8.4$ Hz, 1H), 8.20 (s, 1H), 8.16 (q, $J = 2.0$ Hz, 1H), 8.08 (d, $J = 8.0$ Hz, 1H), 7.77-7.72 (m, 1H), 7.70-7.63 (m, 2H), 7.60-7.51 (m, 5H), 2.65 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ 145.6 (q, $^2J_{\text{C-F}} = 32.1$ Hz), 144.0, 140.5, 139.8, 139.5, 133.6, 133.3, 130.8, 130.3, 130.0, 129.2, 128.9, 128.7, 128.6, 128.0, 127.03, 126.96, 126.9, 123.0, 122.4 (q, $^1J_{\text{C-F}} = 275.9$ Hz), 121.8 (q, $^4J_{\text{C-F}} = 3.2$ Hz), 120.2, 21.4. ^{19}F NMR (376 MHz, CDCl_3): δ -62.42 (s). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{25}\text{H}_{17}\text{F}_3\text{N}$ 388.1308; Found 388.1300.



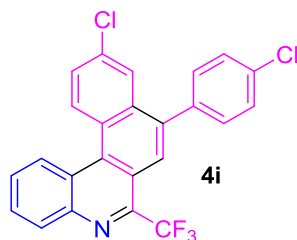
3-Chloro-8-phenyl-6-(trifluoromethyl)benzo[*k*]phenanthridine (4g)

Eluent: petroleum ether/ethyl acetate (100:1). Yellowish solid (69.1 mg, 85%), mp 216.9-217.5 °C. ^1H NMR (600 MHz, CDCl_3): δ 9.03 (d, $J = 8.4$ Hz, 1H), 8.96 (d, $J = 9.0$ Hz, 1H), 8.40 (d, $J = 2.4$ Hz, 1H), 8.16 (q, $J = 1.2$ Hz, 1H), 8.10 (d, $J = 8.4$ Hz, 1H), 7.80-7.76 (m, 2H), 7.74-7.71 (m, 1H), 7.59-7.56 (m, 4H), 7.54-7.51 (m, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ 146.8 (q, $^2J_{\text{C-F}} = 32.9$ Hz), 144.4, 141.4, 139.5, 134.8, 133.8, 133.1, 130.0, 129.9, 129.4, 129.01, 128.98, 128.7, 128.6, 128.5, 128.2, 127.35, 127.25, 123.6, 122.1 (q, $^1J_{\text{C-F}} = 275.3$ Hz), 121.6 (q, $^4J_{\text{C-F}} = 2.9$ Hz), 120.6. ^{19}F NMR (565 MHz, CDCl_3): δ -62.63 (s). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{24}\text{H}_{14}\text{ClF}_3\text{N}$ 408.0761; Found 408.0758.



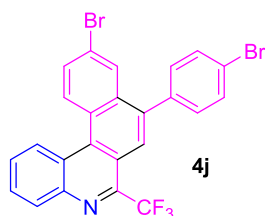
5-Phenyl-7-(trifluoromethyl)dibenzo[*b,k*]phenanthridine (4h)

Eluent: petroleum ether/ethyl acetate (100:1). Yellow solid (73.5 mg, 87%), mp 192.8-193.7 °C. ^1H NMR (400 MHz, CDCl_3): δ 9.50 (s, 1H), 9.28 (d, $J = 8.4$ Hz, 1H), 8.92 (s, 1H), 8.19-8.11 (m, 4H), 7.83-7.78 (m, 1H), 7.73-6.92 (m, 1H), 7.66-7.52 (m, 7H). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ 146.8 (q, $^2J_{\text{C-F}} = 31.2$ Hz), 140.9, 140.8, 139.8, 133.8, 133.0, 132.9, 132.8, 130.1, 129.6, 129.3, 128.7, 128.58, 128.56, 128.52, 128.47, 128.1, 127.3, 127.13, 127.11, 127.0, 123.0, 122.12 (q, $^1J_{\text{C-F}} = 275.7$ Hz), 122.08 (q, $^4J_{\text{C-F}} = 3.5$ Hz), 119.8. ^{19}F NMR (376 MHz, CDCl_3): δ -62.97 (s). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{28}\text{H}_{17}\text{F}_3\text{N}$ 424.1308; Found 424.1298.



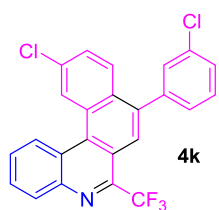
10-Chloro-8-(4-chlorophenyl)-6-(trifluoromethyl)benzo[*k*]phenanthridine (4i)

Eluent: petroleum ether/ethyl acetate (100:1). White solid (48.6 mg, 55%), mp 229.2-229.8 °C. ^1H NMR (600 MHz, CDCl_3): δ 9.05 (d, $J = 9.0$ Hz, 1H), 8.92 (d, $J = 8.4$ Hz, 1H), 8.41 (dd, $J_1 = 7.8$ Hz, $J_2 = 1.2$ Hz, 1H), 8.17 (q, $J = 1.2$ Hz, 1H), 7.99 (d, $J = 2.4$ Hz, 1H), 7.89 (td, $J_1 = 6.6$ Hz, $J_2 = 1.2$ Hz, 1H), 7.86-7.84 (m, 1H), 7.72 (dd, $J_1 = 9.0$ Hz, $J_2 = 2.4$ Hz, 1H), 7.57 (d, $J = 8.4$ Hz, 2H), 7.51 (d, $J = 7.8$ Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ 145.6 (q, $^2J_{\text{C-F}} = 33.2$ Hz), 144.0, 138.8, 137.4, 135.3, 134.6, 134.5, 133.1, 131.20, 131.16, 130.5, 129.5, 129.2, 127.8, 127.6, 127.0, 125.8, 124.7, 123.0 (q, $^4J_{\text{C-F}} = 3.0$ Hz), 122.1 (q, $^1J_{\text{C-F}} = 275.6$ Hz), 120.4. ^{19}F NMR (565 MHz, CDCl_3): δ -62.43 (s). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{24}\text{H}_{13}\text{Cl}_2\text{F}_3\text{N}$ 442.0372; Found 442.0366.



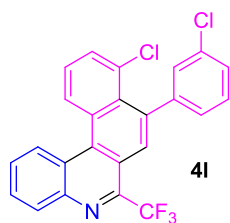
10-Bromo-8-(4-bromophenyl)-6-(trifluoromethyl)benzo[*k*]phenanthridine (4j)

Eluent: petroleum ether/ethyl acetate (100:1). Yellowish solid (60.5 mg, 57%), mp 241.3-242.0 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.97 (d, $J = 9.2$ Hz, 1H), 8.91 (d, $J = 8.0$ Hz, 1H), 8.40 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.2$ Hz, 1H), 8.151-8.147 (m, 2H), 7.90-7.82 (m, 3H), 7.73 (d, $J = 8.4$ Hz, 2H), 7.45 (d, $J = 8.4$ Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ 145.6 (q, $^2J_{\text{C-F}} = 33.2$ Hz), 144.0, 138.7, 137.8, 134.7, 133.2, 132.2, 131.5, 131.2, 130.6, 130.5, 129.5, 129.2, 129.0, 127.9, 126.9, 124.6, 123.7, 123.0 (q, $^4J_{\text{C-F}} = 3.2$ Hz), 122.8, 122.1 (q, $^1J_{\text{C-F}} = 276.3$ Hz), 120.4. ^{19}F NMR (376 MHz, CDCl_3): δ -62.42 (s). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{24}\text{H}_{13}\text{Br}_2\text{F}_3\text{N}$ 529.9361; Found 529.9374.



11-Chloro-8-(3-chlorophenyl)-6-(trifluoromethyl)benzo[*k*]phenanthridine (4k)

Eluent: petroleum ether/ethyl acetate (100:1). White solid (39.7 mg, 45%), mp 133.9-134.6 °C. ^1H NMR (400 MHz, CDCl_3): δ 9.12 (d, $J = 2.0$ Hz, 1H), 8.99-8.95 (m, 1H), 8.44-8.42 (m, 1H), 8.15 (q, $J = 2.0$ Hz, 1H), 7.98 (d, $J = 8.8$ Hz, 1H), 7.93-7.88 (m, 2H), 7.68 (dd, $J_1 = 9.2$ Hz, $J_2 = 2.4$ Hz, 1H), 7.56 (d, $J = 0.8$ Hz, 1H), 7.52-7.51 (m, 2H), 7.47-7.44 (m, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 145.6 (q, $^2J_{\text{C-F}} = 32.9$ Hz), 143.9, 141.0, 139.2, 134.8, 133.9, 132.4, 131.6, 131.2, 130.2, 130.1, 129.9, 129.5, 129.4, 128.5, 128.4, 128.13, 128.07, 126.7, 124.7, 122.14 (q, $^4J_{\text{C-F}} = 3.4$ Hz), 122.11 (q, $^1J_{\text{C-F}} = 275.5$ Hz), 120.9. ^{19}F NMR (376 MHz, CDCl_3): δ -62.47 (d, $J = 2.6$ Hz). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{24}\text{H}_{13}\text{Cl}_2\text{F}_3\text{N}$ 442.0372; Found 442.0376.

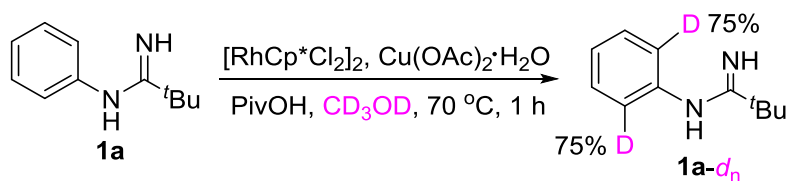


9-Chloro-8-(3-chlorophenyl)-6-(trifluoromethyl)benzo[k]phenanthridine (41)

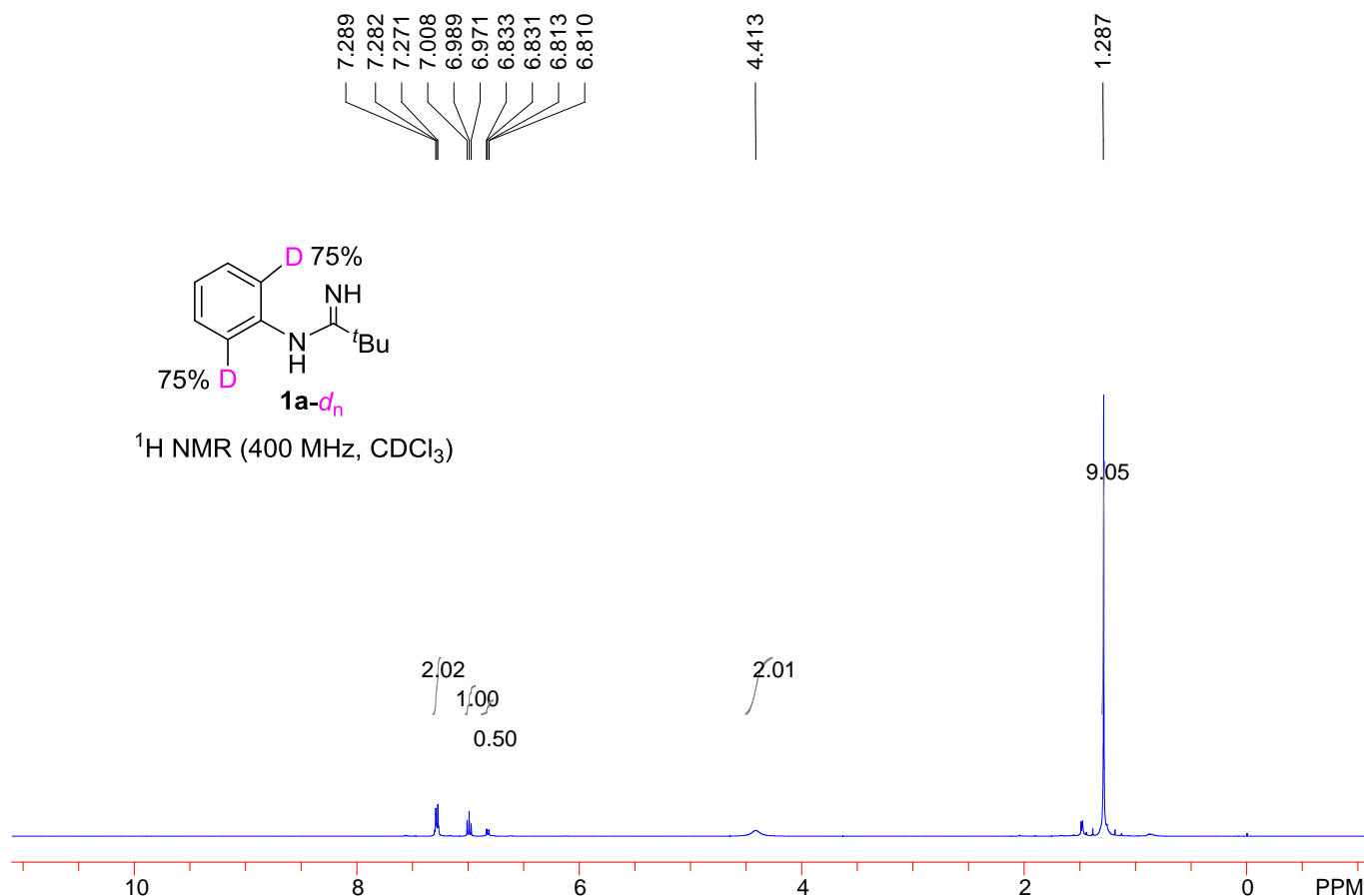
Eluent: petroleum ether/ethyl acetate (100:1). White solid (29.1 mg, 33%), mp 180.2-180.8 °C. ^1H NMR (400 MHz, CDCl_3): δ 9.04 (d, $J = 8.4$ Hz, 1H), 8.91 (d, $J = 7.6$ Hz, 1H), 8.42 (dd, $J_1 = 8.4$ Hz, $J_2 = 1.6$ Hz, 1H), 8.12 (q, $J = 1.6$ Hz, 1H), 7.91-7.83 (m, 2H), 7.80 (dd, $J_1 = 7.6$ Hz, $J_2 = 0.8$ Hz, 1H), 7.68 (t, $J = 8.0$ Hz, 1H), 7.43-7.38 (m, 3H), 7.35-7.32 (m, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 145.3 (q, $^2J_{\text{C-F}} = 32.8$ Hz), 144.3, 144.2, 137.8, 133.9, 133.8, 132.35, 132.31, 131.7, 131.1, 130.1, 129.5, 129.3, 129.24, 129.15, 128.5, 127.6, 127.4, 127.1, 125.8 (q, $^4J_{\text{C-F}} = 3.3$ Hz), 124.7, 122.0 (q, $^1J_{\text{C-F}} = 275.4$ Hz), 119.8. ^{19}F NMR (376 MHz, CDCl_3): δ -62.54 (s). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{24}\text{H}_{13}\text{Cl}_2\text{F}_3\text{N}$ 442.0372; Found 442.0364.

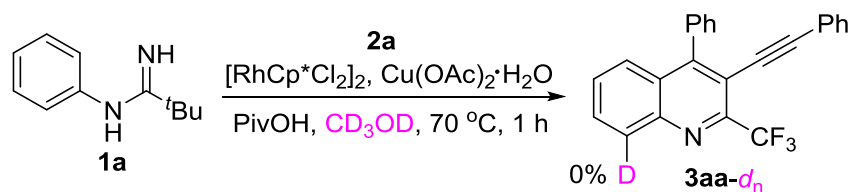
III. Mechanistic studies

1. Studies on the reversibility of C–H bond activation

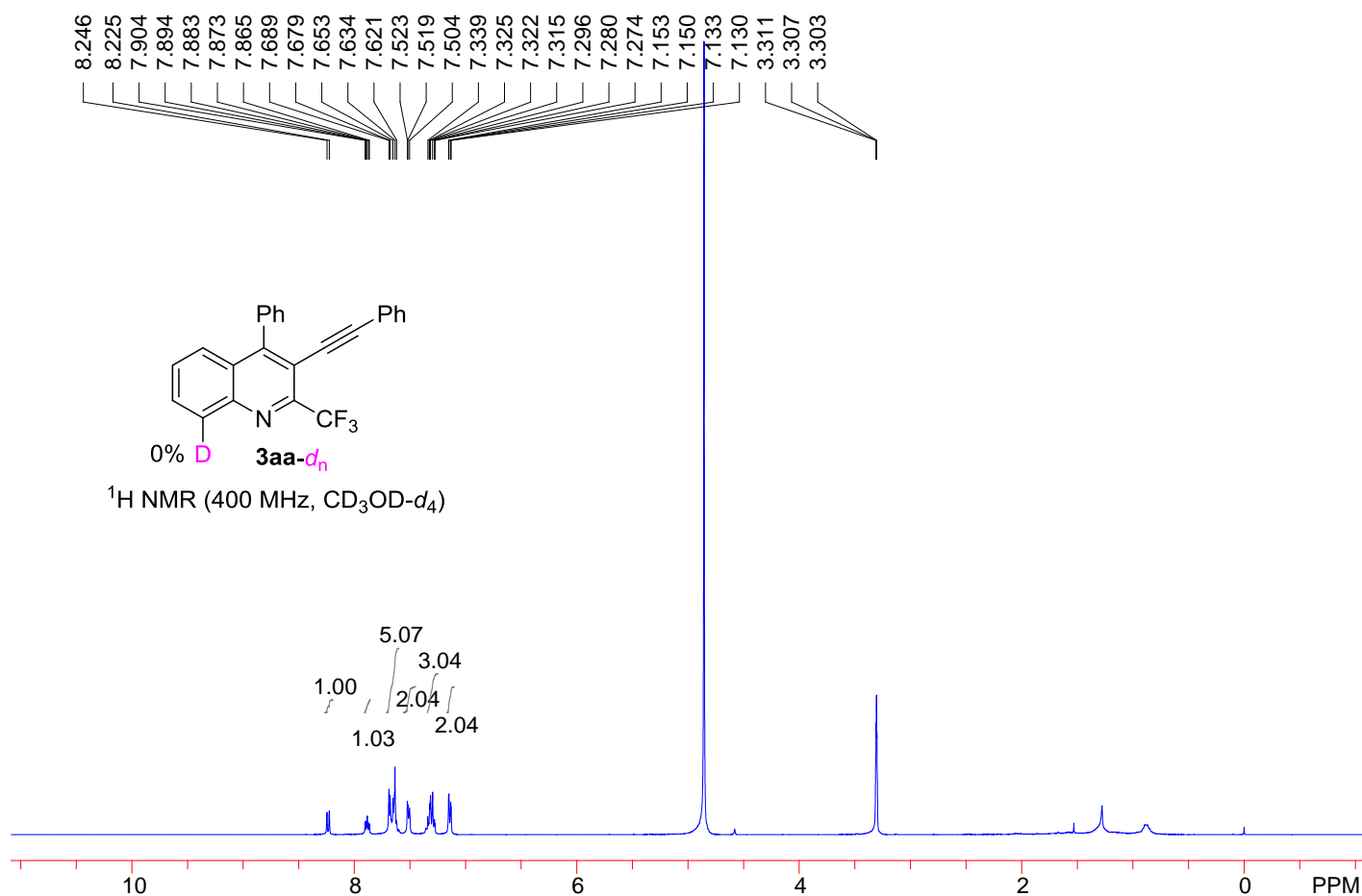


To a reaction tube equipped with a stir bar were added **1a** (35.3 mg, 0.2 mmol), $[\text{RhCp}^*\text{Cl}_2]_2$ (3.7 mg, 0.006 mmol), $\text{Cu(OAc)}_2\cdot\text{H}_2\text{O}$ (40.0 mg, 0.2 mmol), PivOH (20.4 mg, 0.2 mmol) and CD_3OD (2.2 mL). The tube was then sealed, and the mixture was stirred at 70 °C (oil bath) under air for 1 h. It was then cooled to room temperature, filtered through a pad of celite and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using dichloromethane/methanol (10:1) as eluent to afford **1a** and **1a-d_n**. Upon analyzing the ^1H NMR spectrum of the mixture, the deuteration percentage was determined as 75%.

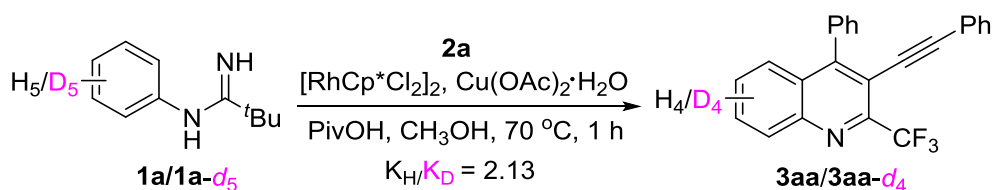




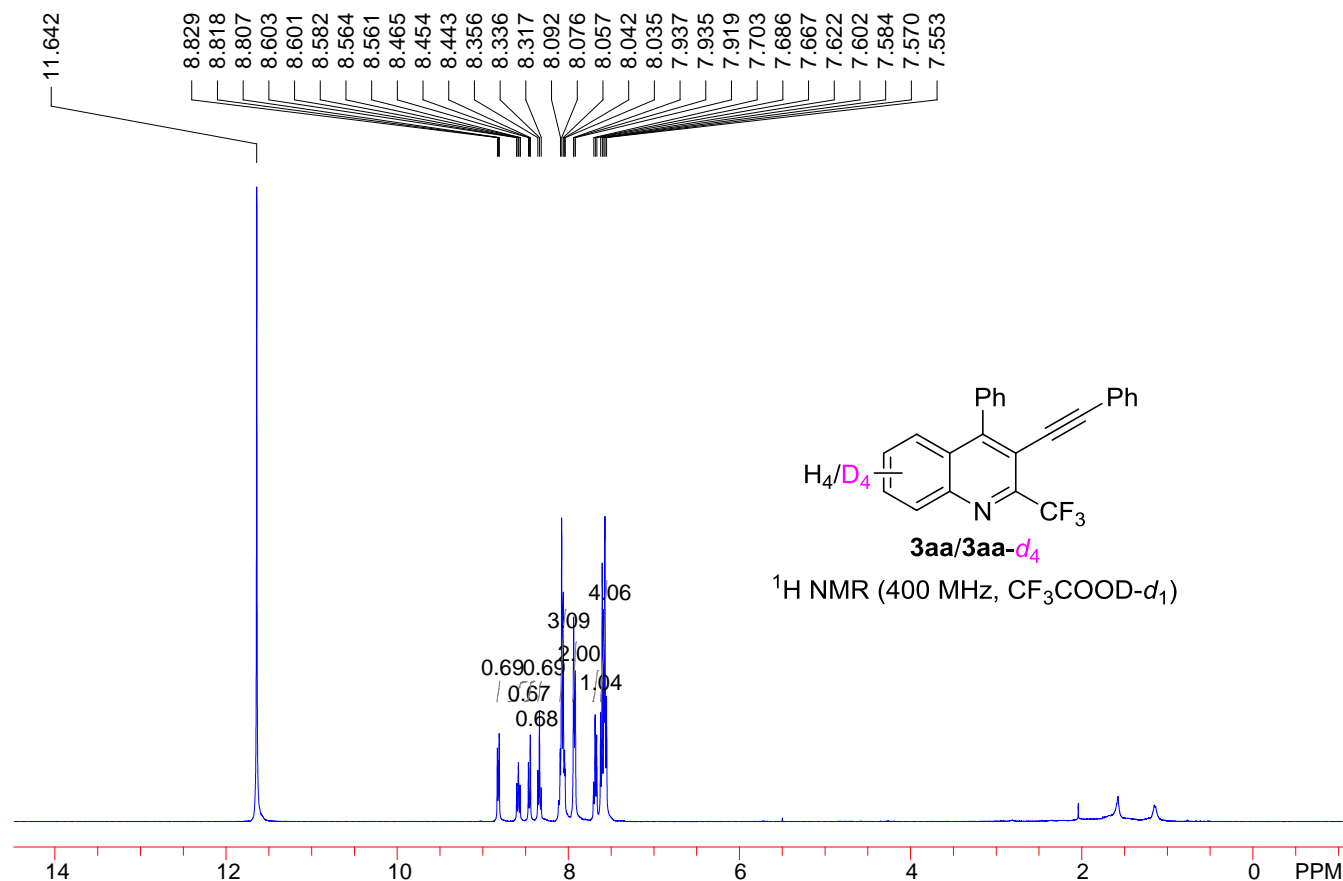
To a reaction tube equipped with a stir bar were added **1a** (35.3 mg, 0.2 mmol), $[\text{RhCp}^*\text{Cl}_2]_2$ (3.7 mg, 0.006 mmol), $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (40.0 mg, 0.2 mmol), PivOH (20.4 mg, 0.2 mmol), **2a** (99.1 mg, 0.5 mmol), and CD_3OD (2.2 mL). The tube was then sealed, and the mixture was stirred at 70 °C (oil bath) under air for 1 h. It was then cooled to room temperature, filtered through a pad of celite and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate (100:1) as eluent to afford **3aa-d_n**. No deuterium incorporation onto the unreacted *ortho*-position of the phenyl ring of product **3aa** was observed upon analyzing the ^1H NMR spectrum of the product.



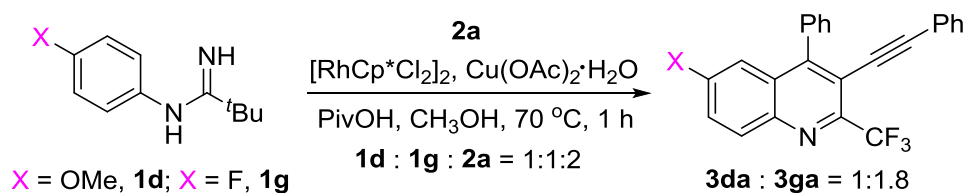
2. Kinetic isotope effect study



To a reaction tube equipped with a stir bar were added **1a** (35.3 mg, 0.2 mmol), **1a-d₅** (36.3 mg, 0.2 mmol), $[\text{RhCp}^*\text{Cl}_2]_2$ (3.7 mg, 0.006 mmol), $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (40.0 mg, 0.2 mmol), PivOH (20.4 mg, 0.2 mmol), **2a** (79.3 mg, 0.4 mmol) and MeOH (2 mL). The mixture was stirred at $70\text{ }^\circ\text{C}$ (oil bath) under air for 1 h. It was then cooled to room temperature, filtered through a pad of celite and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (100:1) as eluent to afford a mixture of **3aa** and **3aa-d₄**. Upon analyzing the ^1H NMR spectrum of the mixture, the ratio of **3aa** to **3aa-d₄** was determined to be 0.68:0.32. Accordingly, the intermolecular KIE value ($k_{\text{H}}/k_{\text{D}}$) was calculated to be about 2.13.

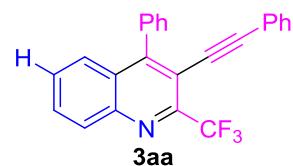
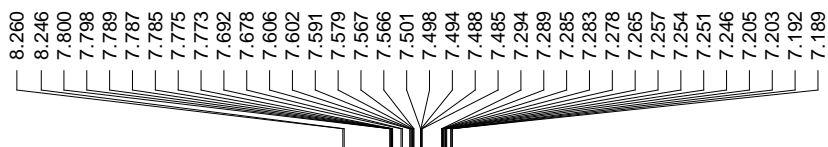


3. Electronic competition experiment

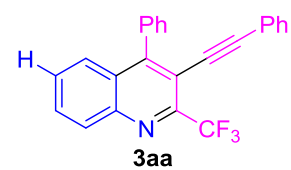
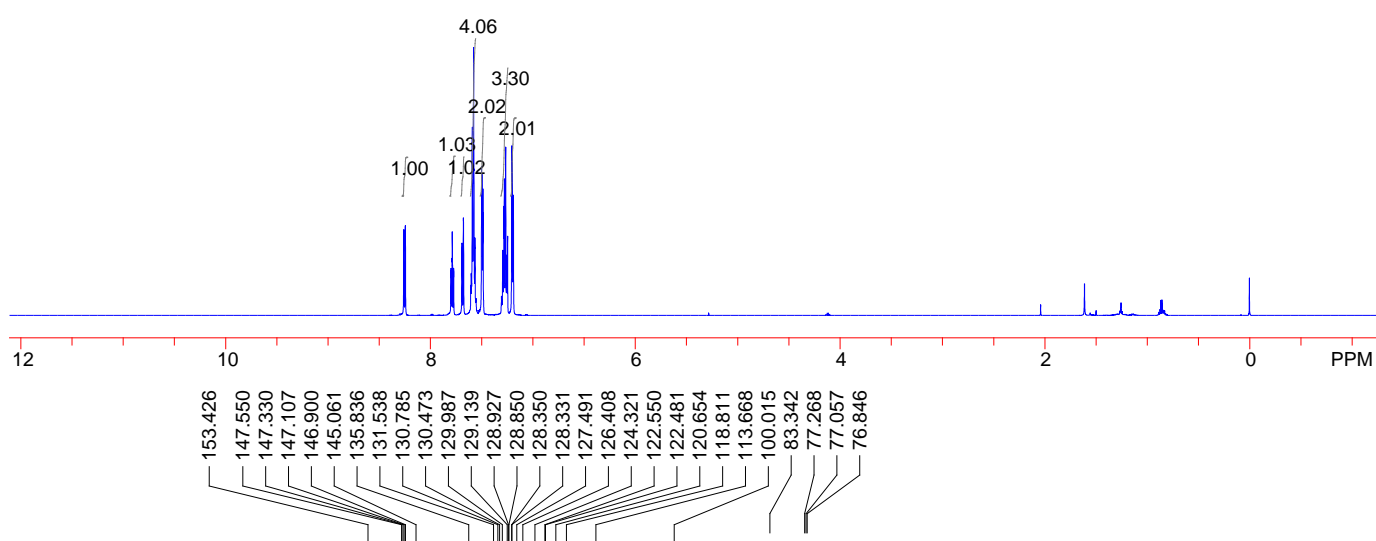


To a reaction tube equipped with a stir bar were added **1d** (41.3 mg, 0.2 mmol), **1g** (38.9 mg, 0.2 mmol), $[\text{RhCp}^*\text{Cl}_2]_2$ (3.7 mg, 0.006 mmol), $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (40.0 mg, 0.2 mmol), PivOH (20.4 mg, 0.2 mmol), **2a** (79.3 mg, 0.4 mmol) and MeOH (2 mL). The tube was then sealed, and the mixture was stirred at 70 °C (oil bath) under air for 1 h. It was then cooled to room temperature, filtered through a pad of celite and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate (100:1) as eluent to afford **3da** (8.1 mg, 10%) and **3ga** (14.1 mg, 18%).

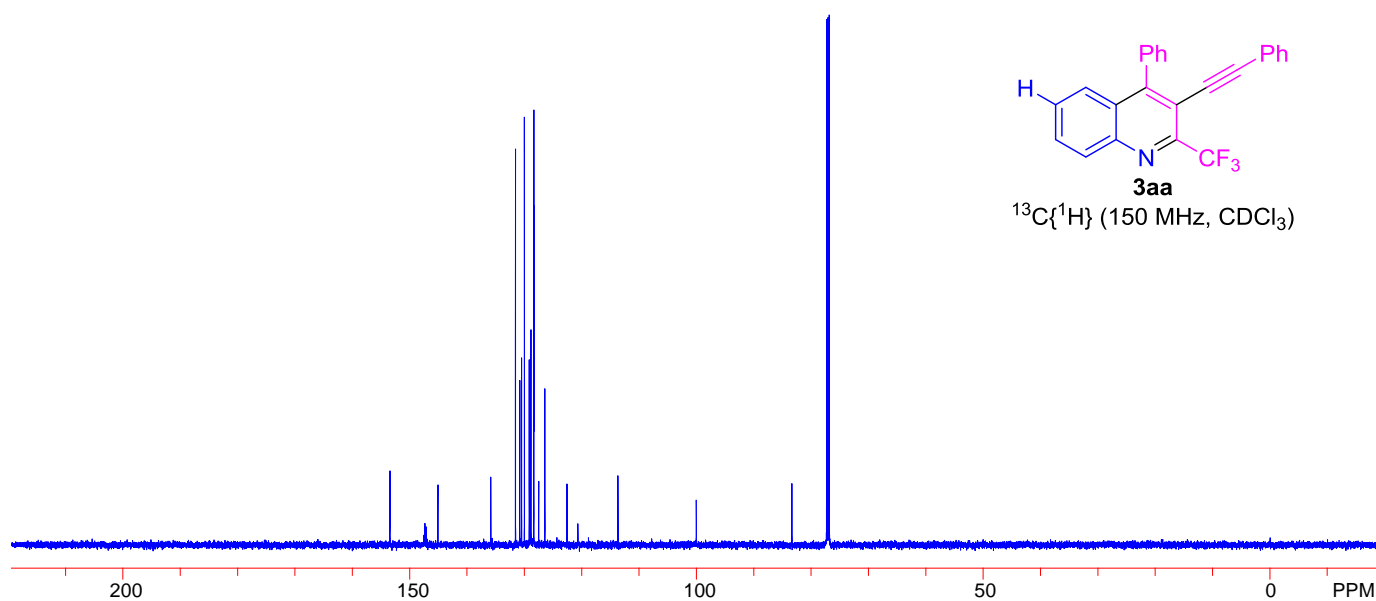
IV. NMR spectra of 3aa-3ra, 3ba-3sa



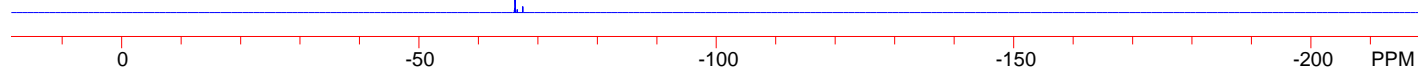
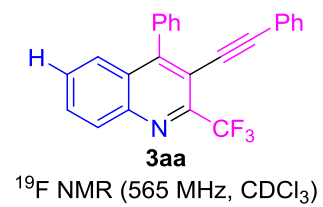
^1H NMR (600 MHz, CDCl_3)



$^{13}\text{C}\{^1\text{H}\}$ (150 MHz, CDCl_3)

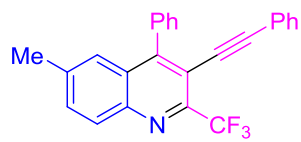


66.143

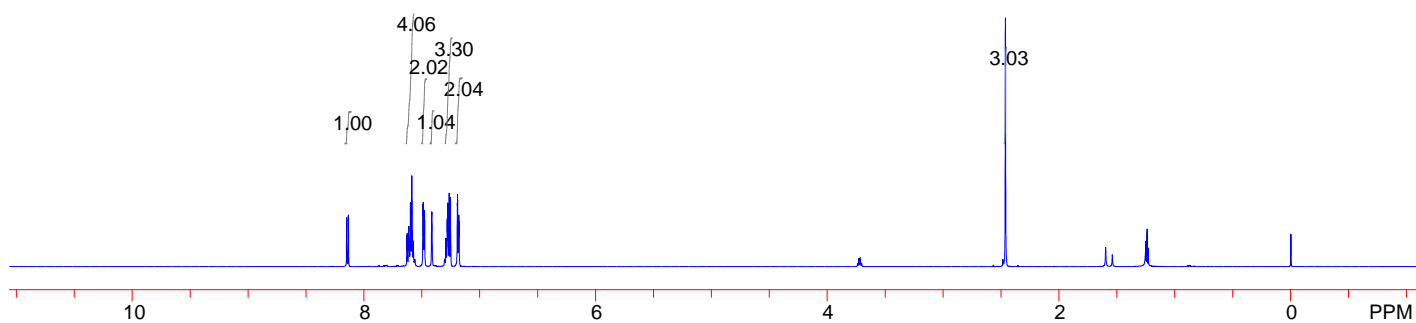


8.149
8.134
7.629
7.626
7.613
7.599
7.587
7.573
7.491
7.488
7.478
7.476
7.413
7.293
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7.253
7.250
7.193
7.191
7.180
7.178

2.462

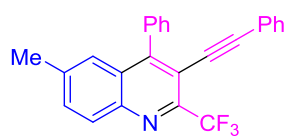


3ba
 $^1\text{H NMR}$ (600 MHz, CDCl_3)

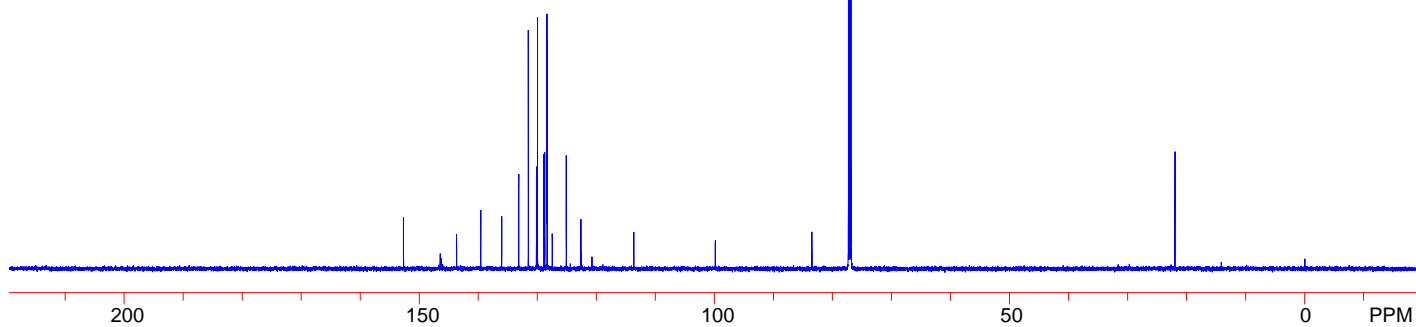


152.670
146.449
146.226
143.667
139.579
136.031
133.140
131.516
130.136
129.973
128.863
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128.346
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77.058
76.847

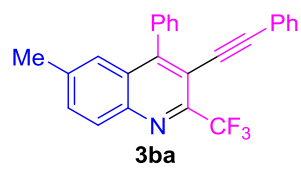
22.027



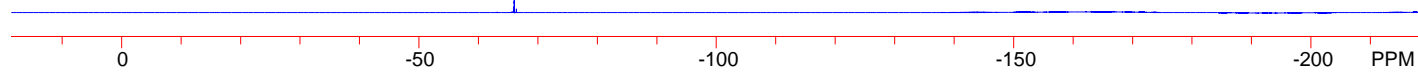
3ba
 $^{13}\text{C}\{^1\text{H}\}$ (150 MHz, CDCl_3)

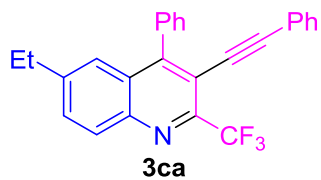
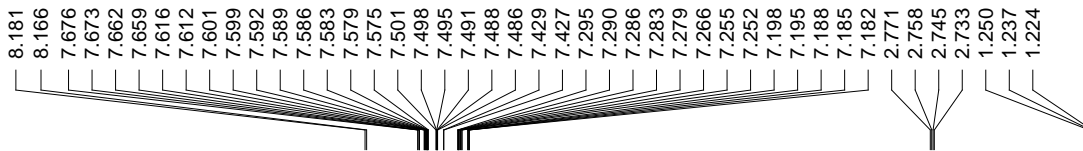


66.011

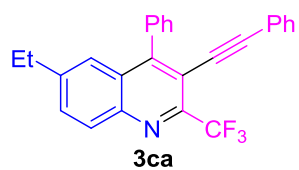
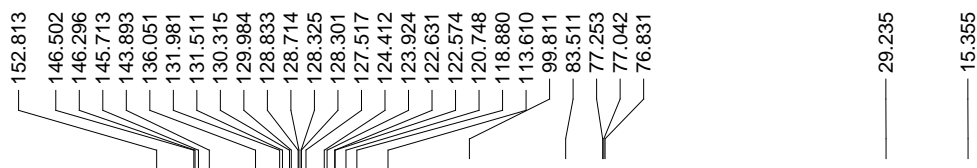
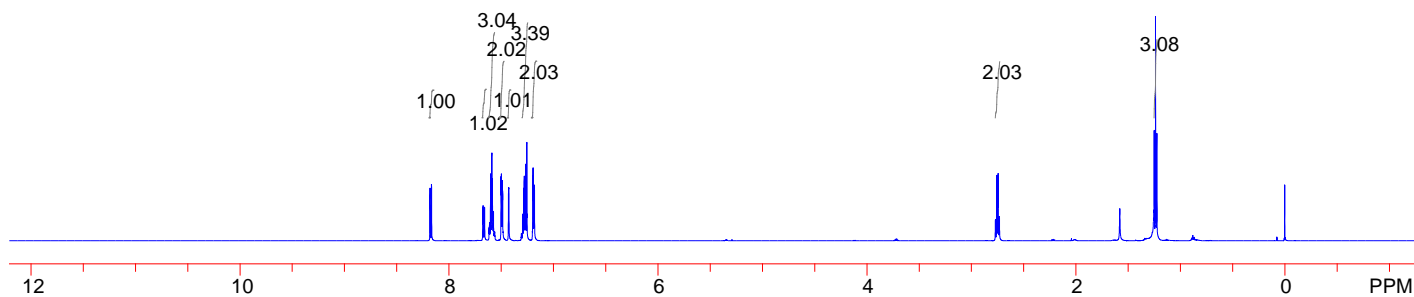


¹⁹F NMR (565 MHz, CDCl₃)

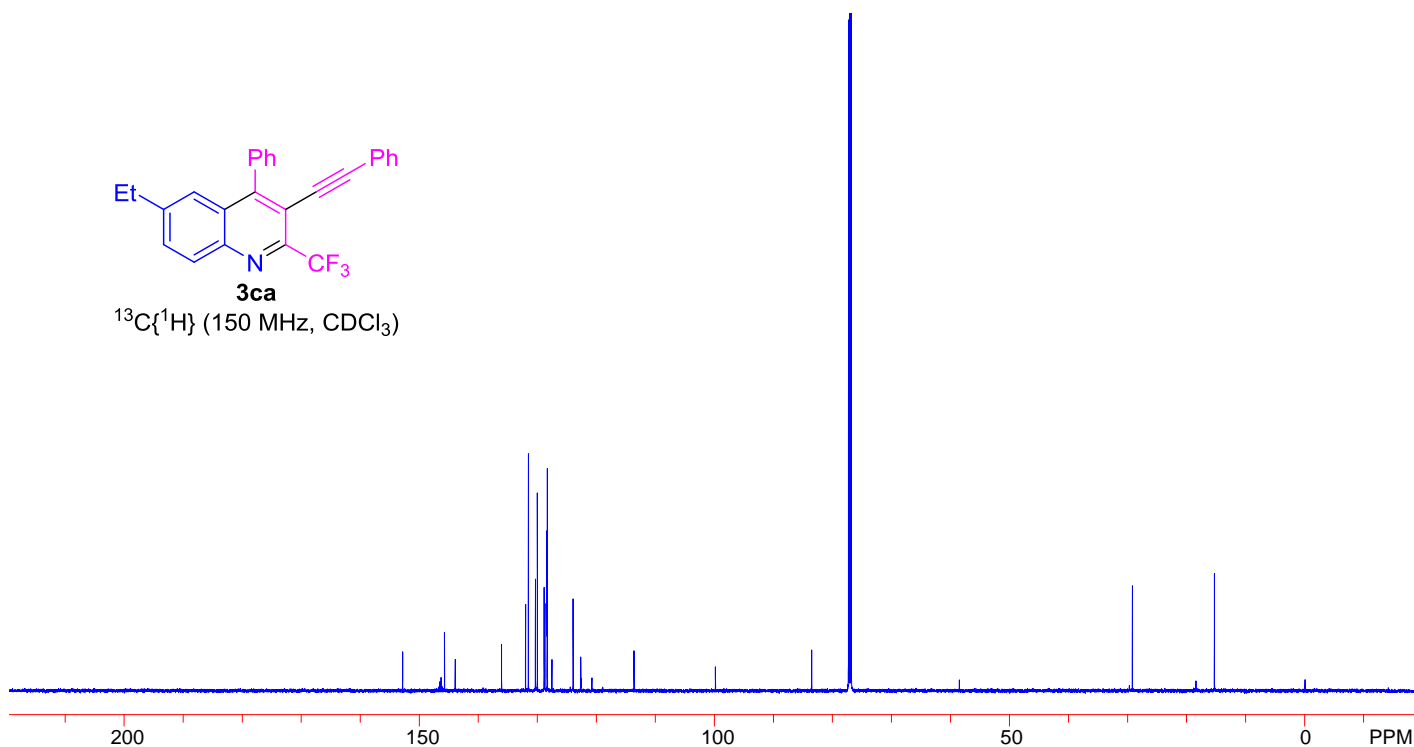




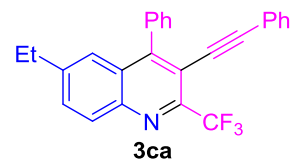
¹H NMR (600 MHz, CDCl₃)



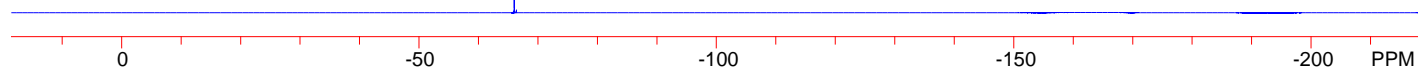
¹³C{¹H} (150 MHz, CDCl₃)

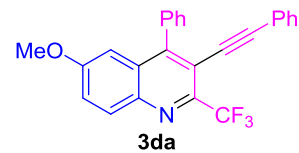
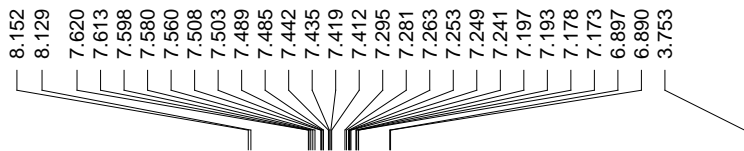


65.998

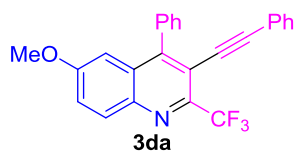
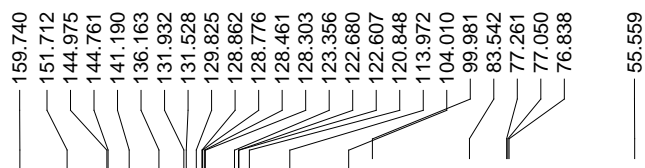
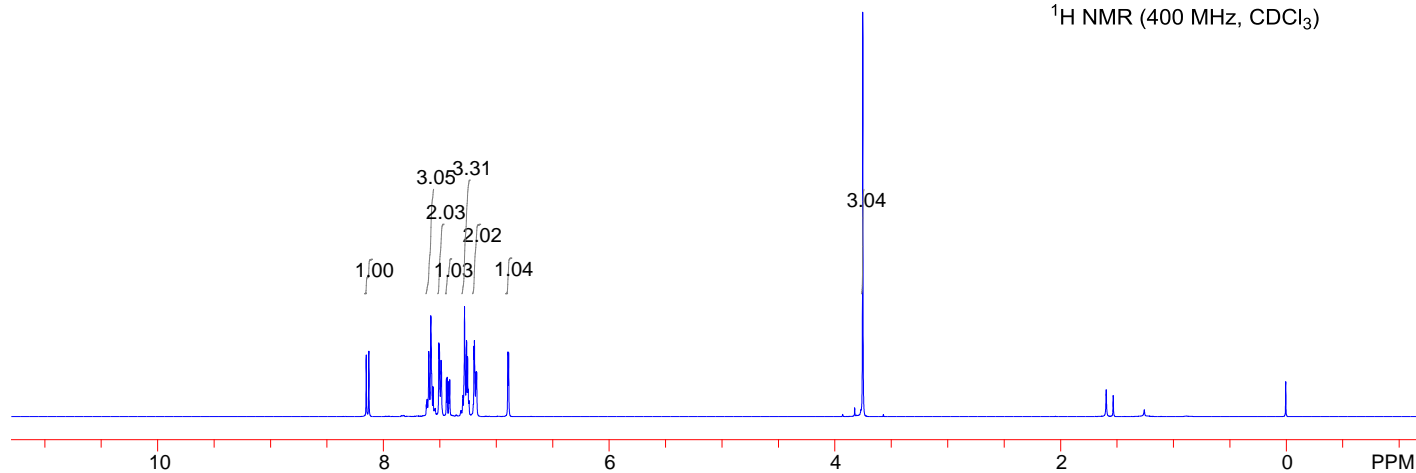


3ca
¹⁹F NMR (565 MHz, CDCl₃)

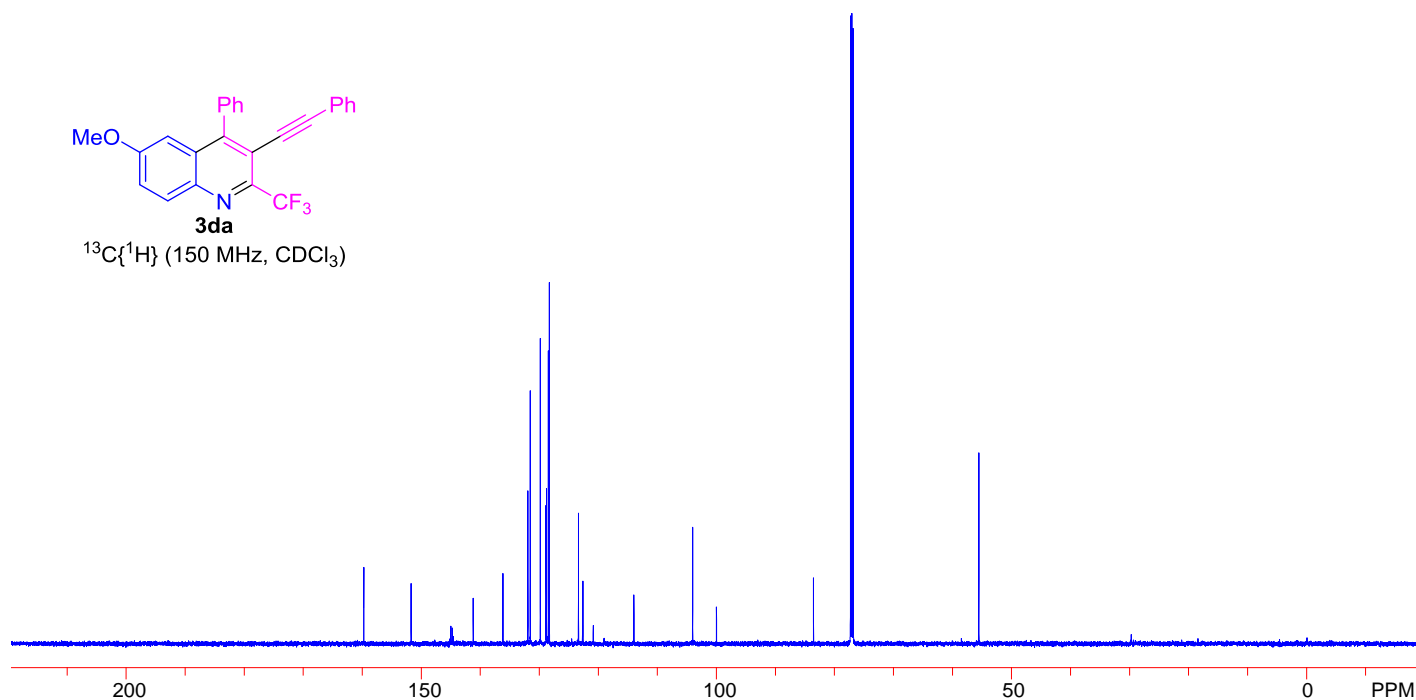




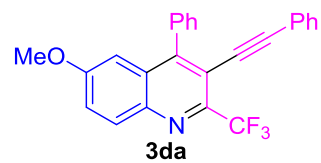
¹H NMR (400 MHz, CDCl₃)



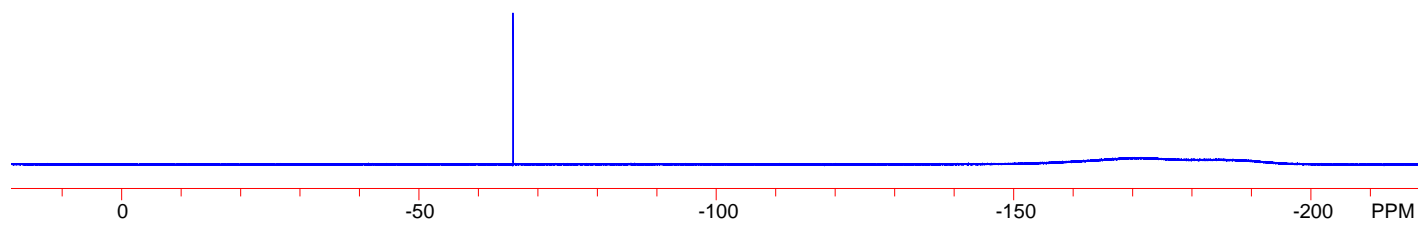
¹³C{¹H} (150 MHz, CDCl₃)

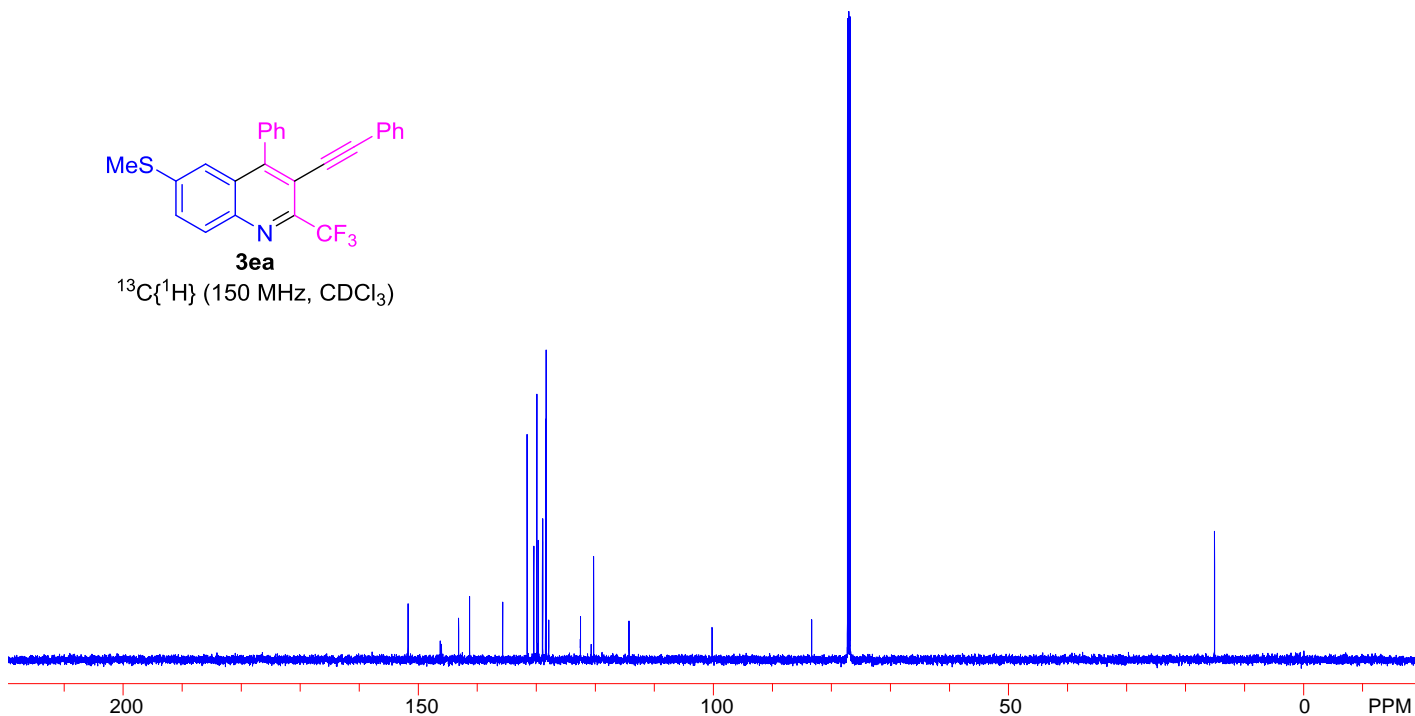
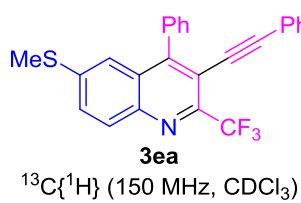
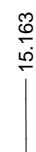
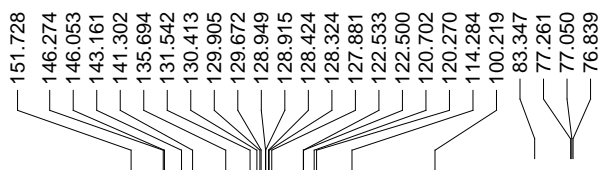
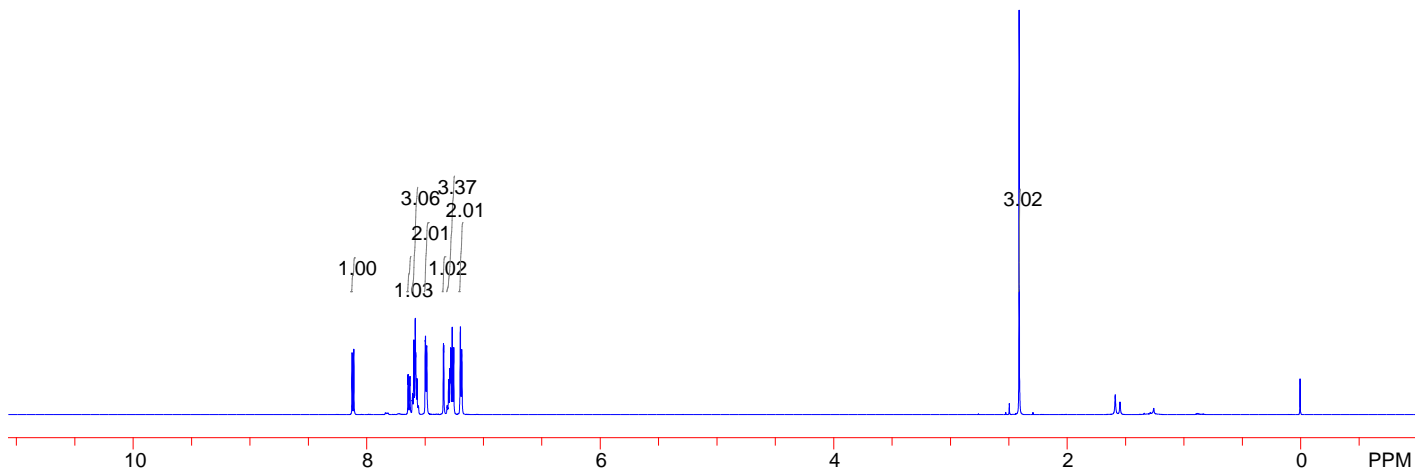
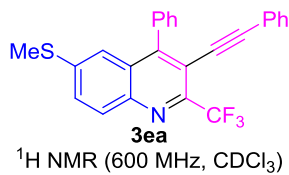
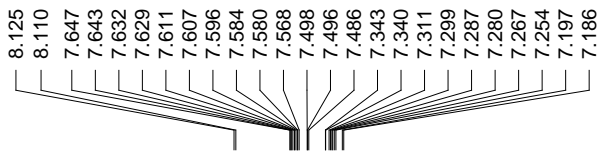


65.815

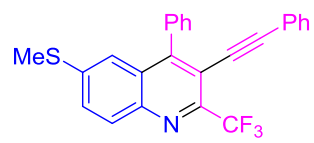


¹⁹F NMR (565 MHz, CDCl₃)

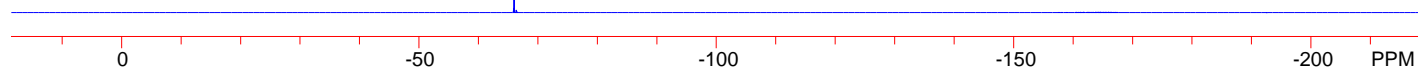


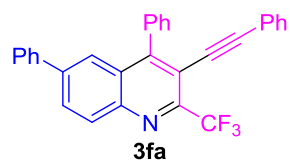
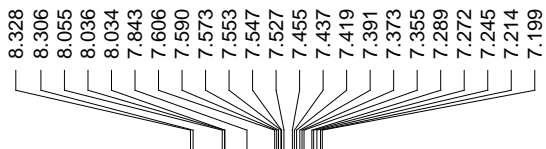


65.980

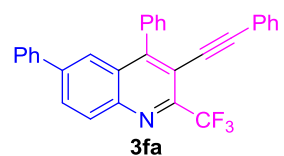
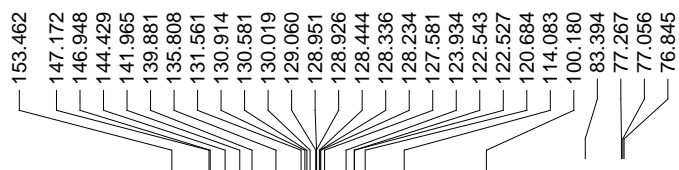
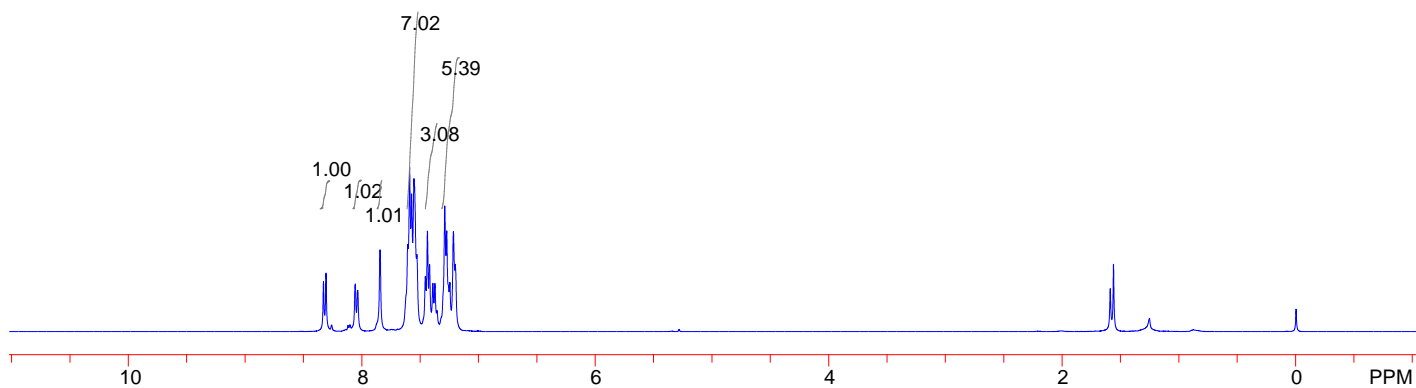


3a
¹⁹F NMR (565 MHz, CDCl₃)

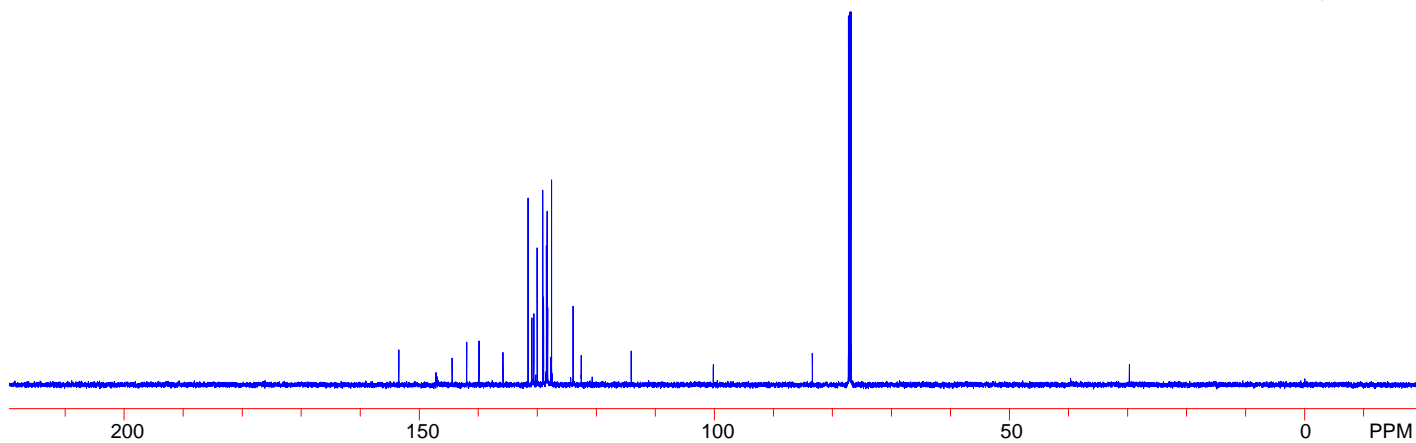




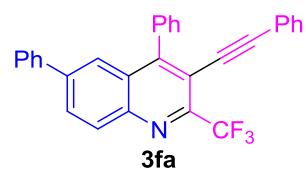
$^1\text{H NMR}$ (400 MHz, CDCl_3)



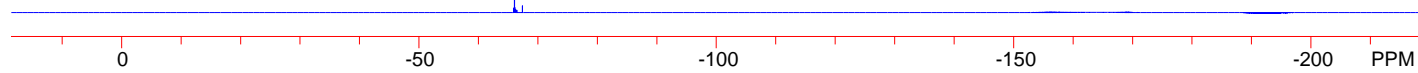
$^{13}\text{C}\{^1\text{H}\}$ (150 MHz, CDCl_3)

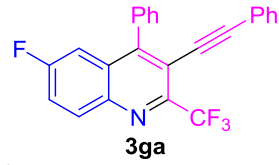
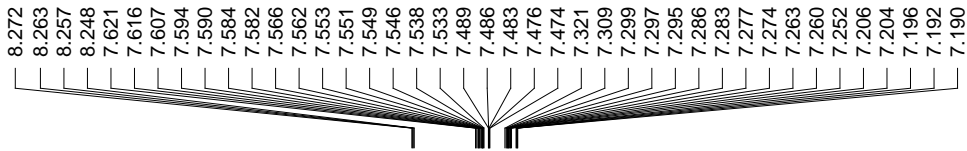


66.061

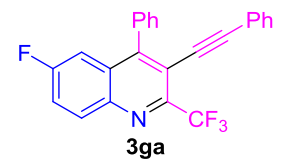
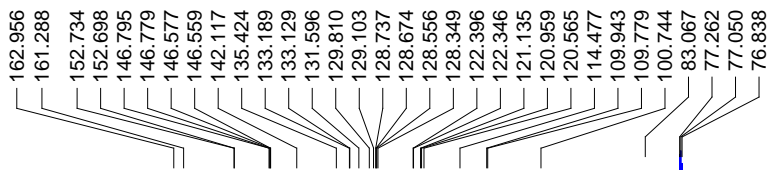
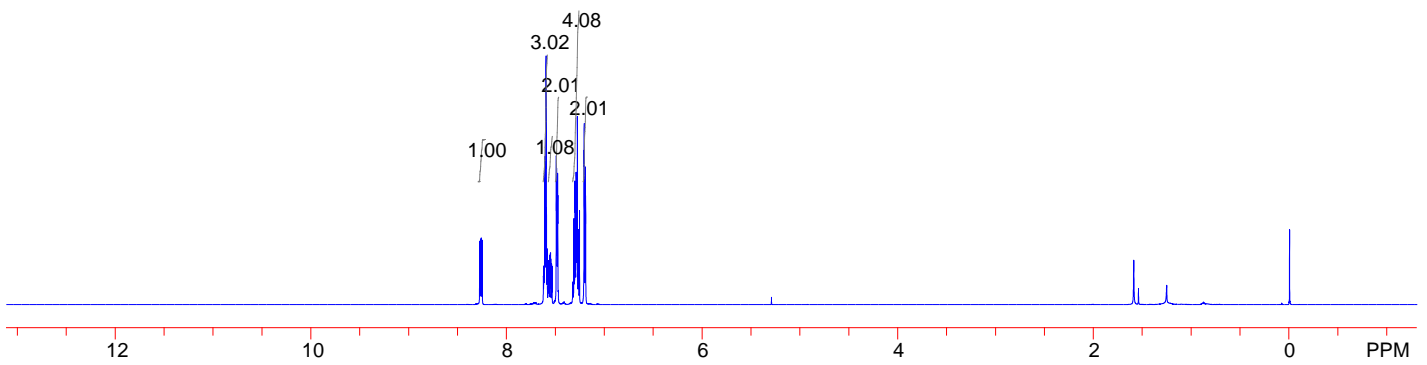


¹⁹F NMR (565 MHz, CDCl₃)

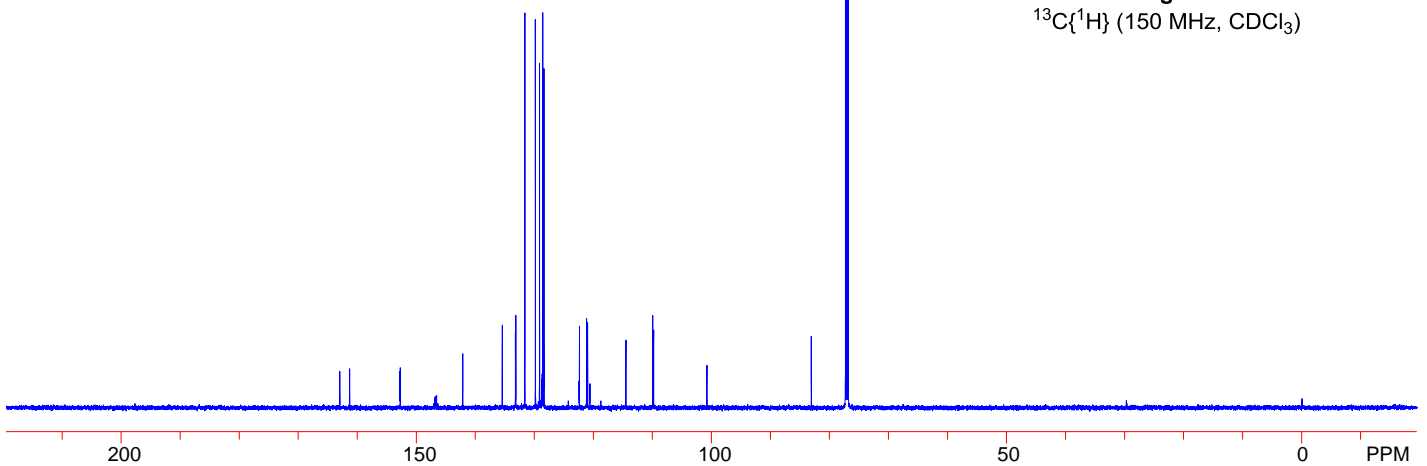


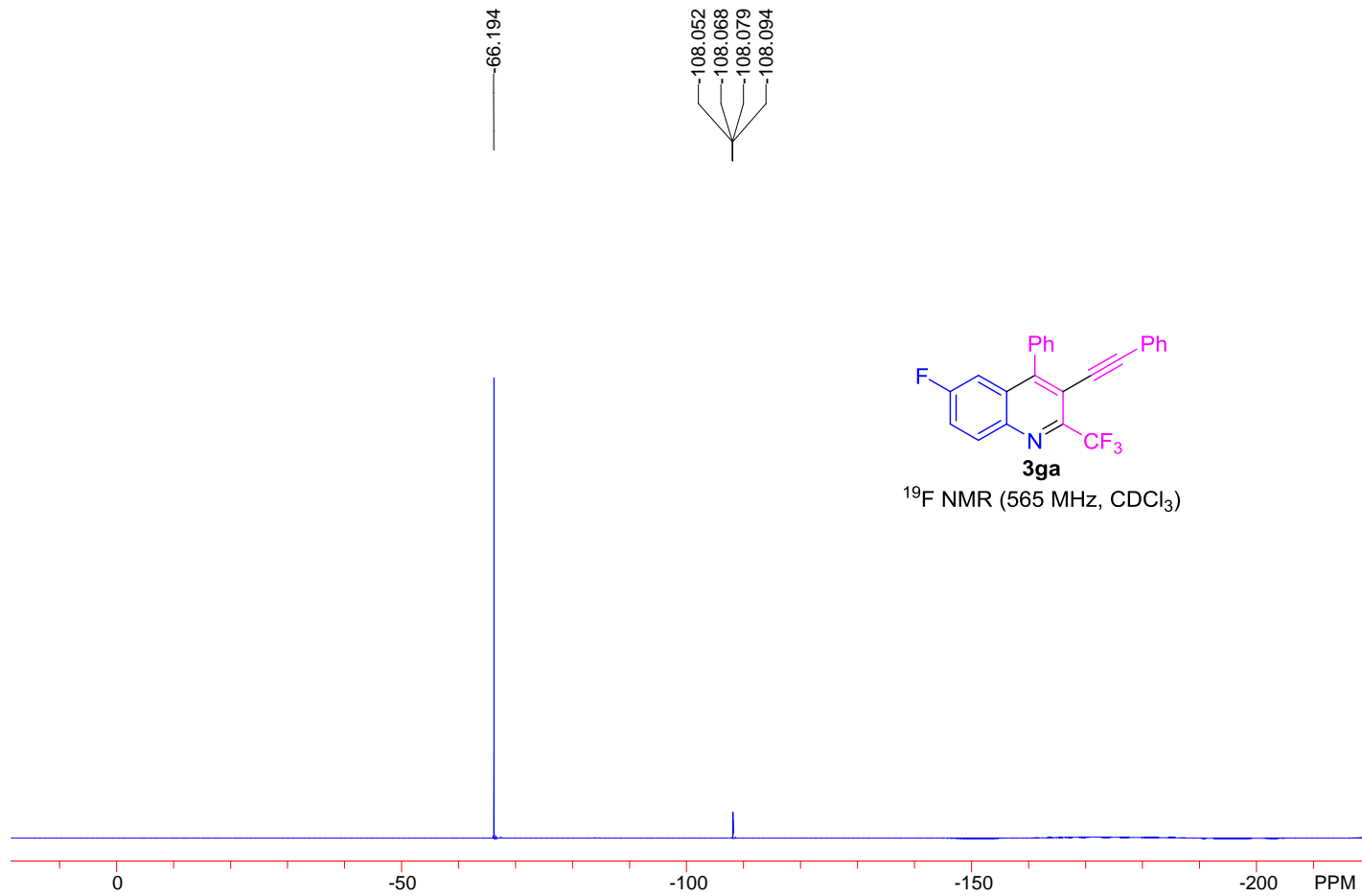


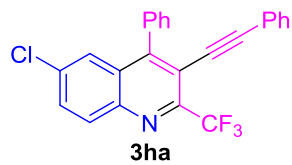
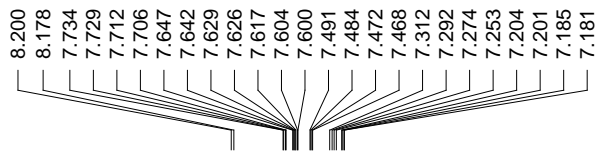
$^1\text{H NMR}$ (600 MHz, CDCl_3)



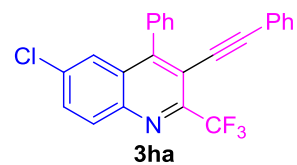
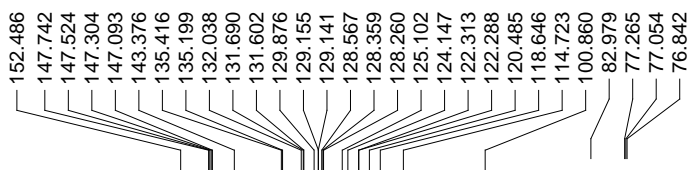
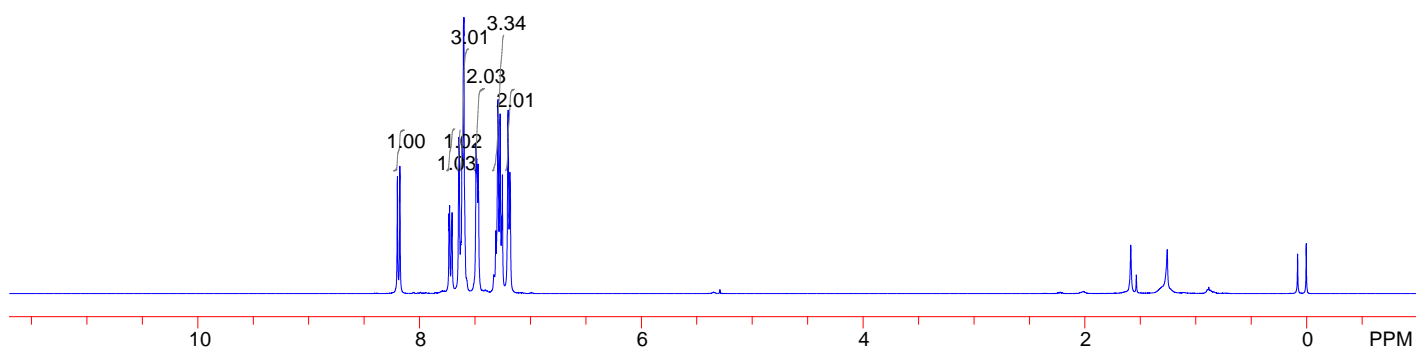
$^{13}\text{C}\{^1\text{H}\}$ (150 MHz, CDCl_3)



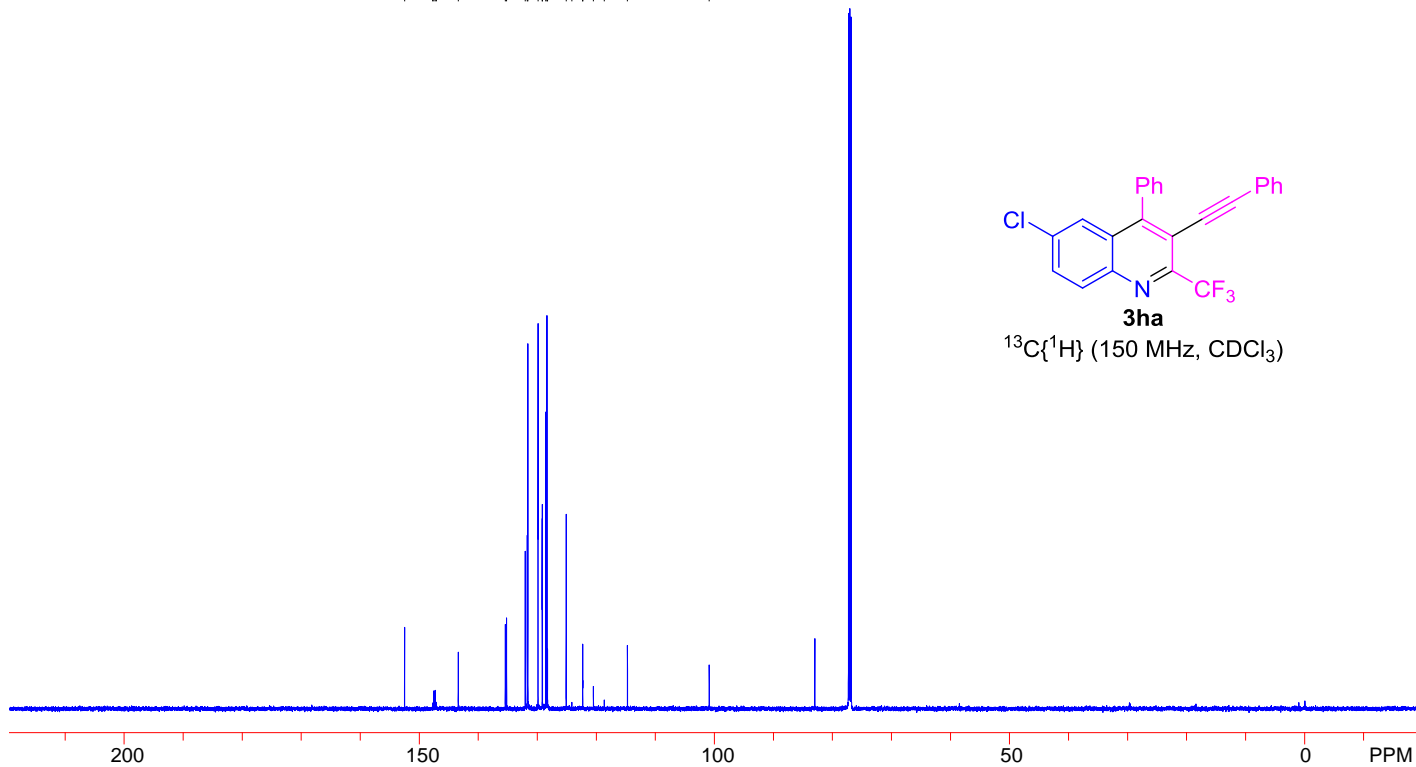




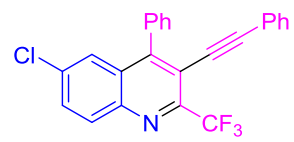
¹H NMR (400 MHz, CDCl₃)



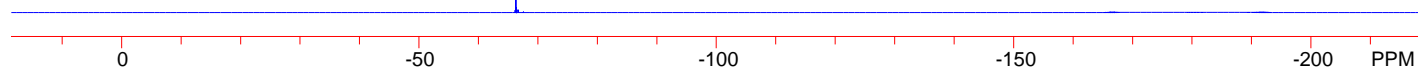
¹³C{¹H} (150 MHz, CDCl₃)

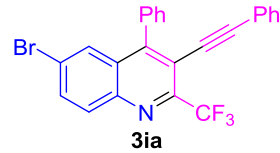
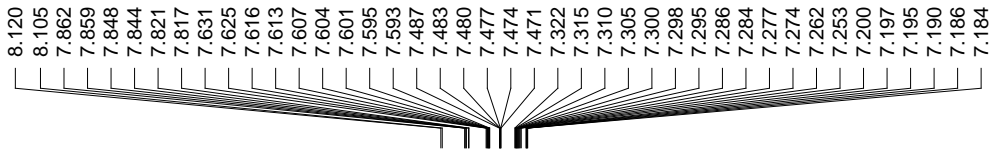


66.284

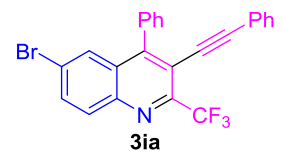
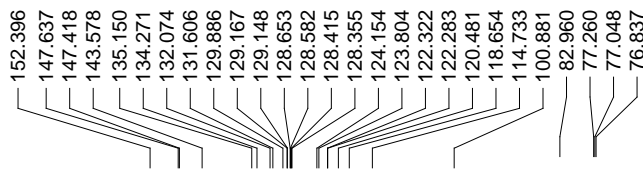
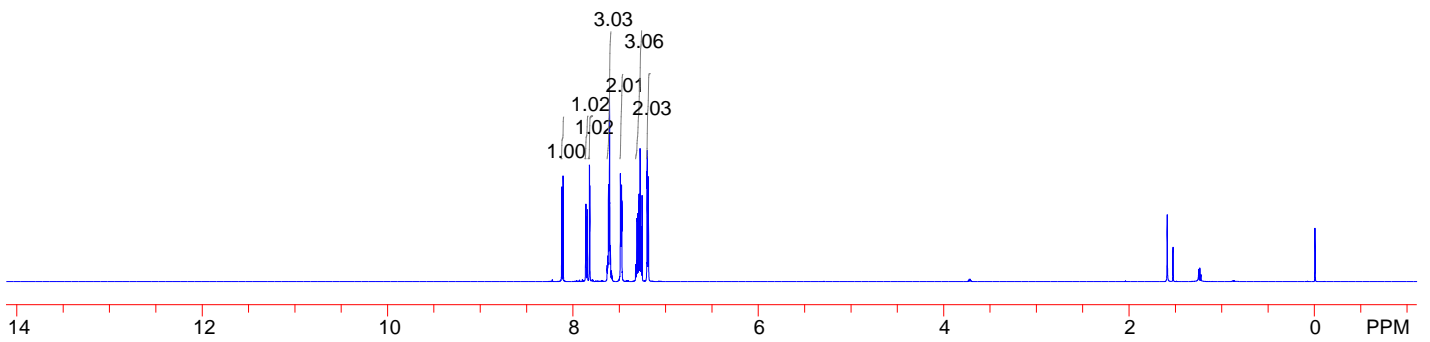


3ha
¹⁹F NMR (565 MHz, CDCl₃)

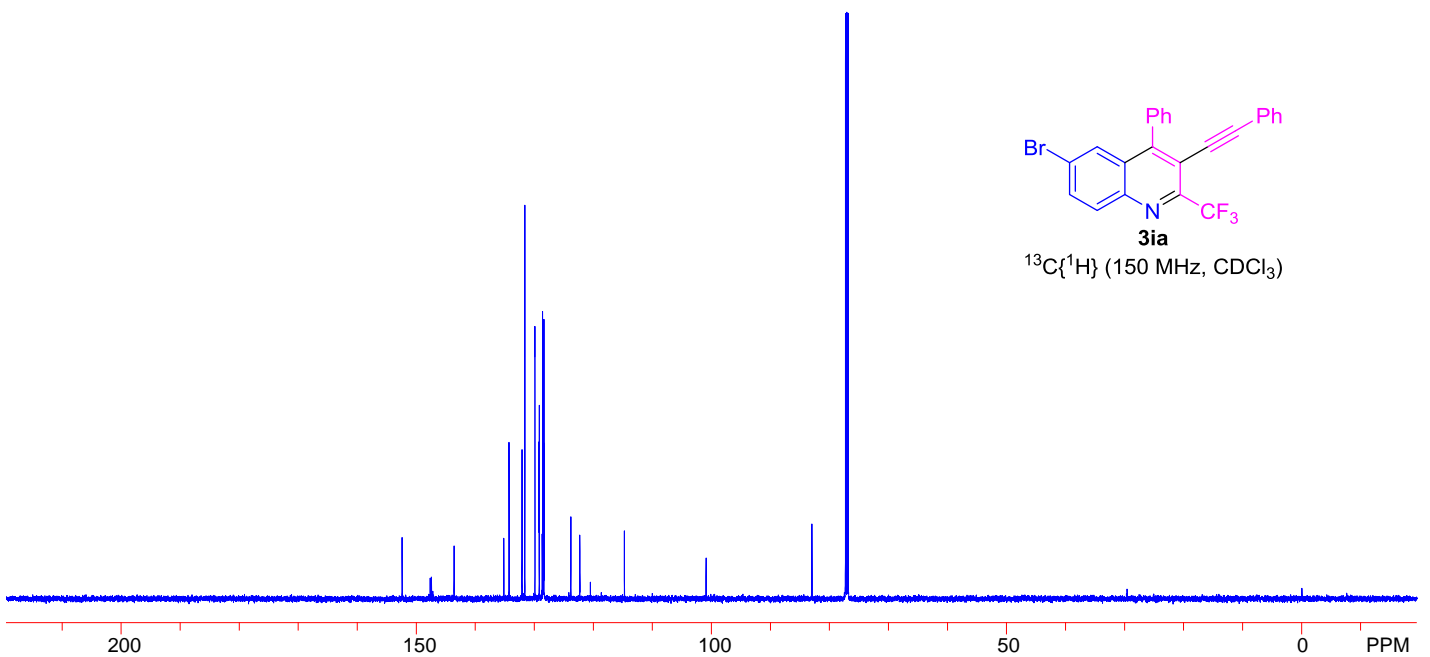




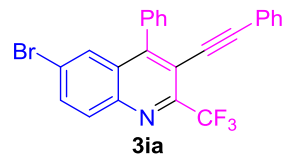
$^1\text{H NMR}$ (600 MHz, CDCl_3)



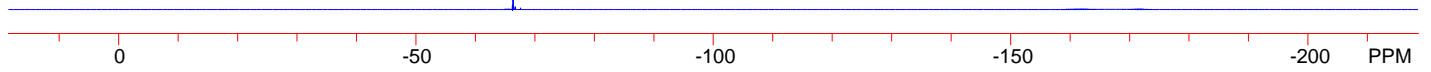
$^{13}\text{C}\{^1\text{H}\}$ (150 MHz, CDCl_3)



-66.317

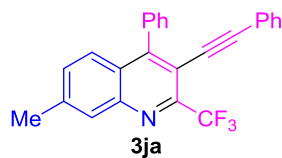


3ia
¹⁹F NMR (565 MHz, CDCl₃)

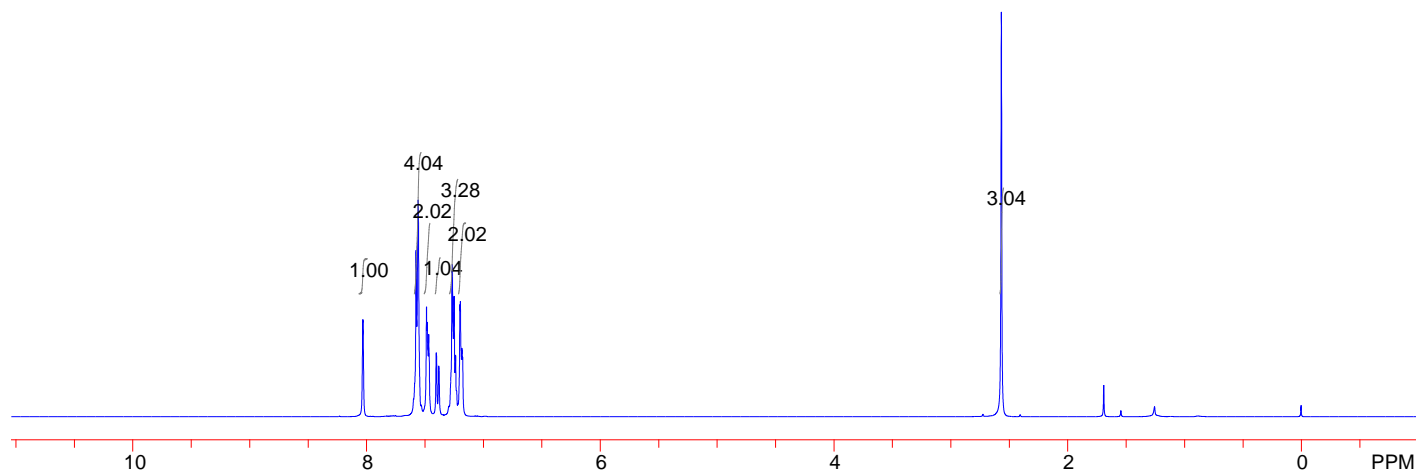


8.031
7.576
7.568
7.487
7.481
7.468
7.404
7.382
7.269
7.265
7.251
7.237
7.231
7.201
7.197
7.184
7.178

2.566

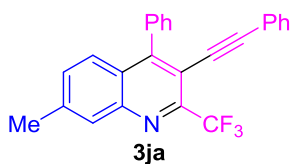


$^1\text{H NMR}$ (400 MHz, CDCl_3)

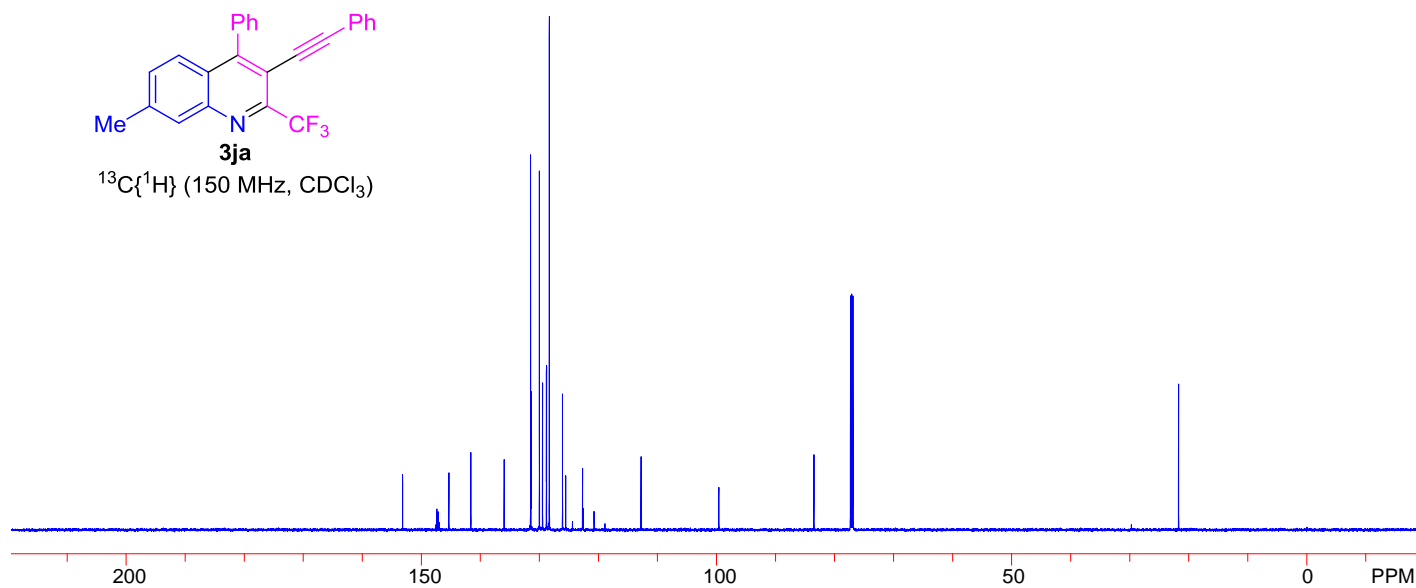


153.167
147.559
147.347
147.122
146.916
145.328
141.604
135.962
131.481
131.424
129.993
129.457
128.810
128.781
128.303
126.073
125.533
124.394
122.676
122.562
120.723
118.894
112.780
99.597
83.485
77.292
77.081
76.870

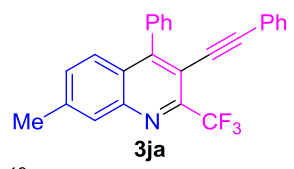
21.783



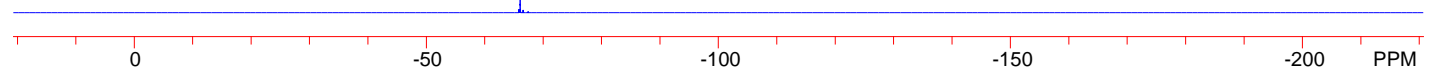
$^{13}\text{C}\{^1\text{H}\}$ (150 MHz, CDCl_3)

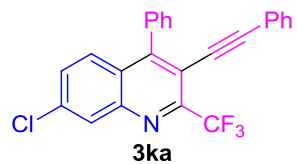
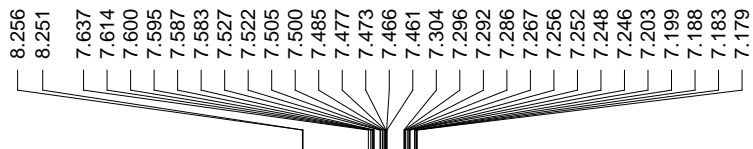


66.063

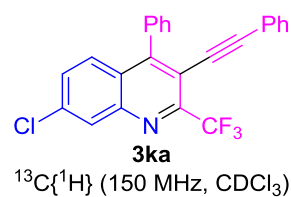
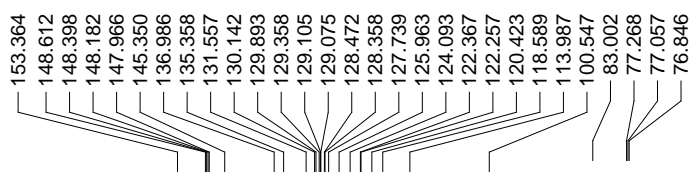
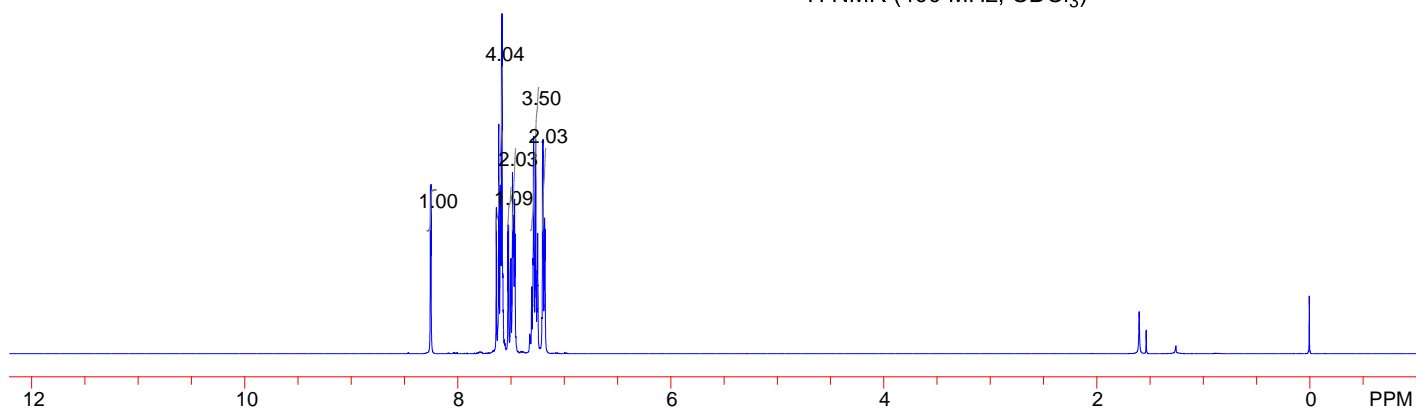


¹⁹F NMR (376 MHz, CDCl₃)

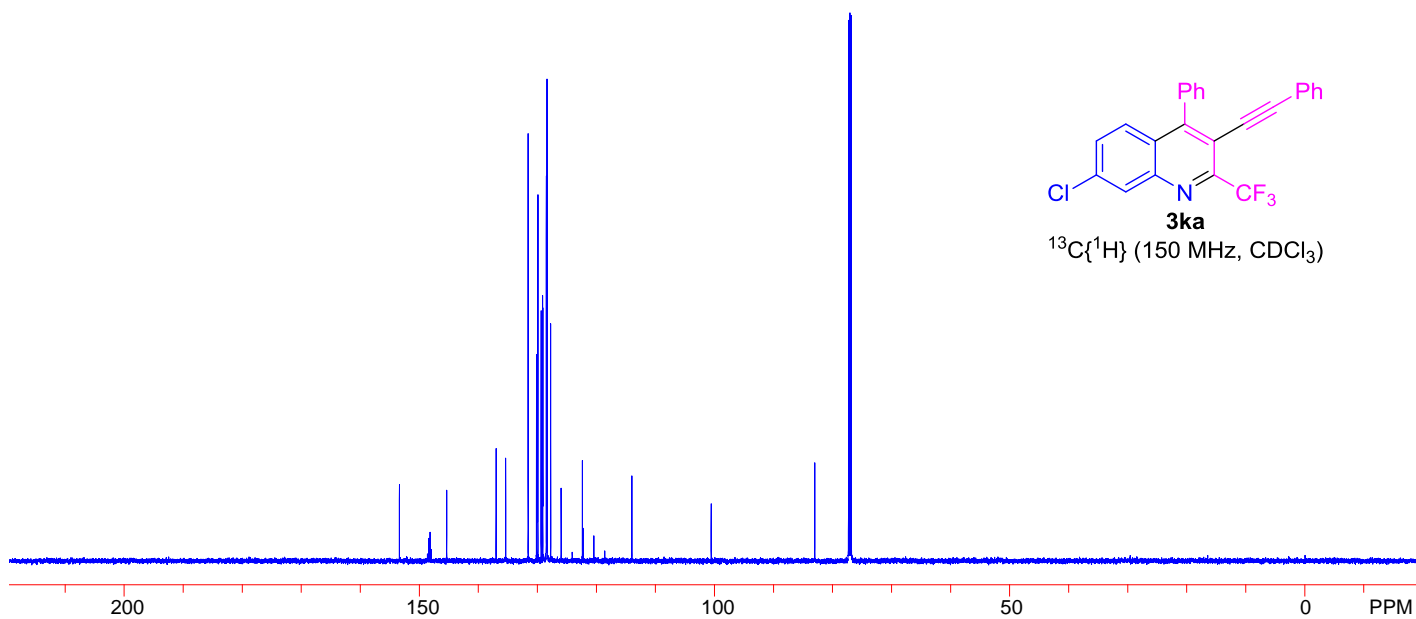




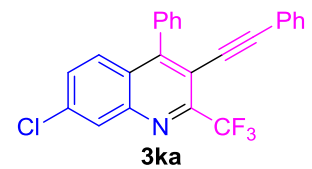
$^1\text{H NMR}$ (400 MHz, CDCl_3)



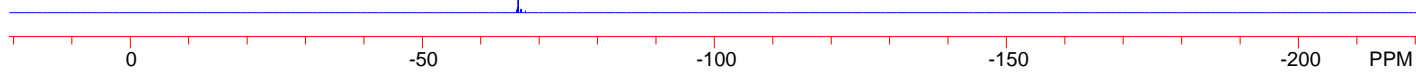
$^{13}\text{C}\{^1\text{H}\}$ (150 MHz, CDCl_3)

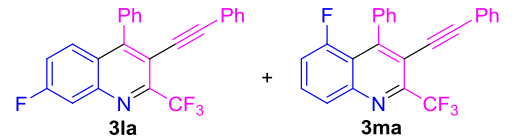
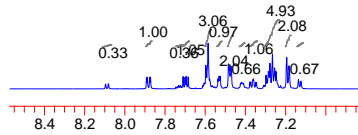
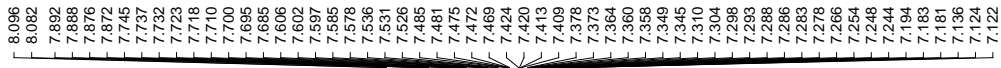
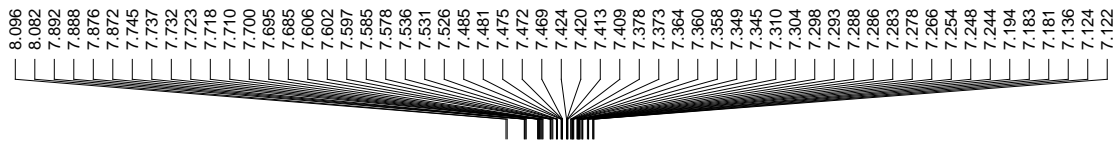


66.384

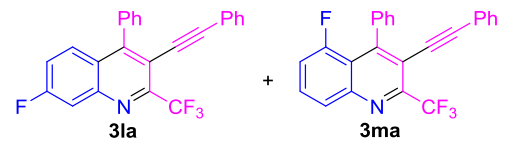
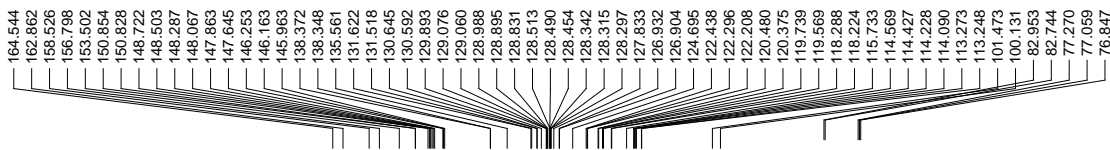
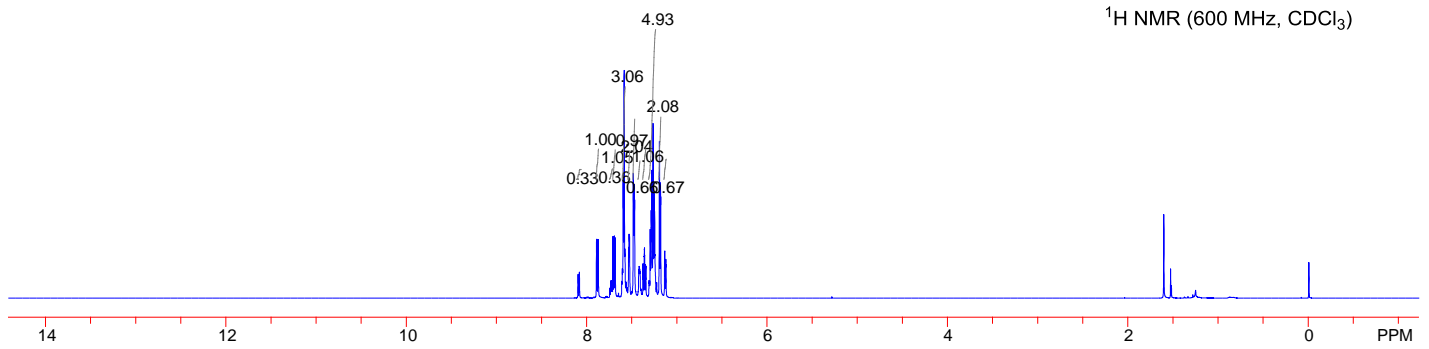


¹⁹F NMR (376 MHz, CDCl₃)

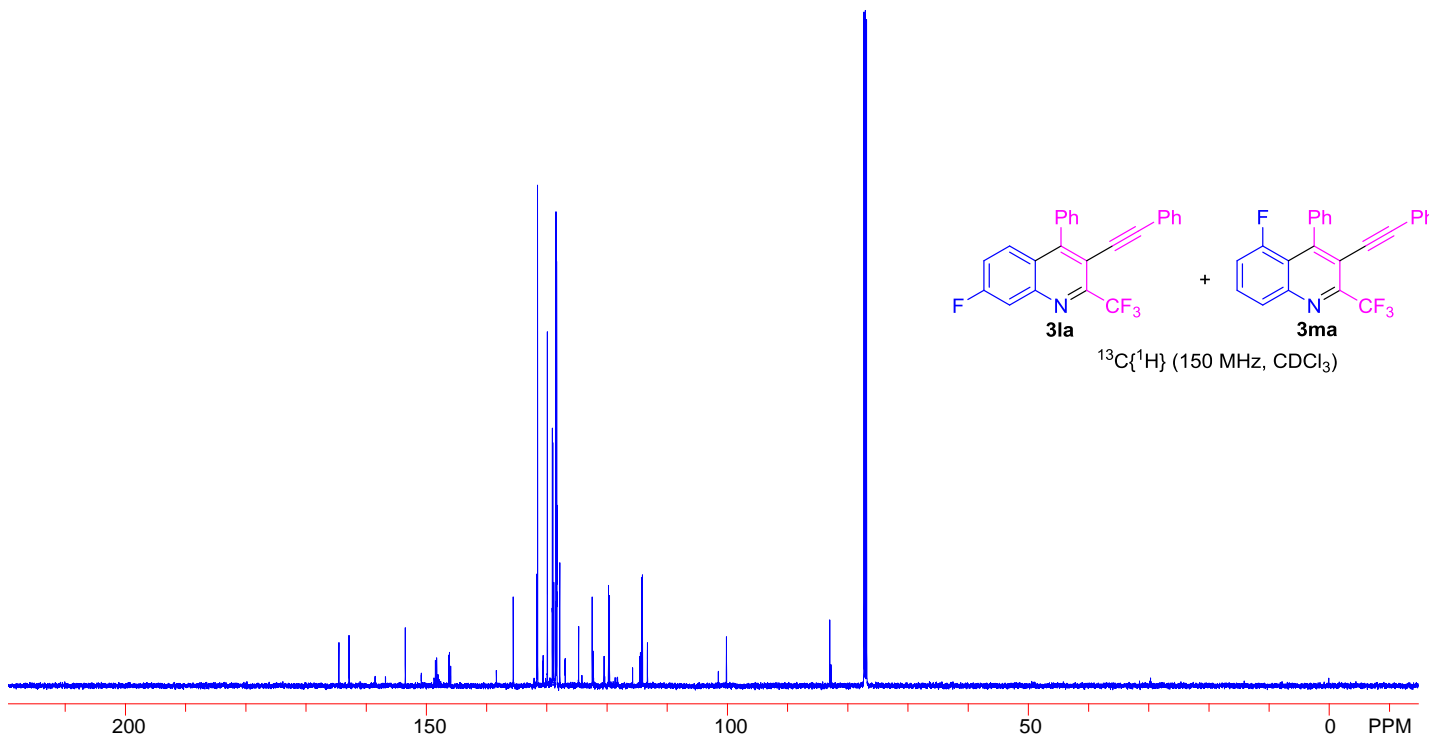


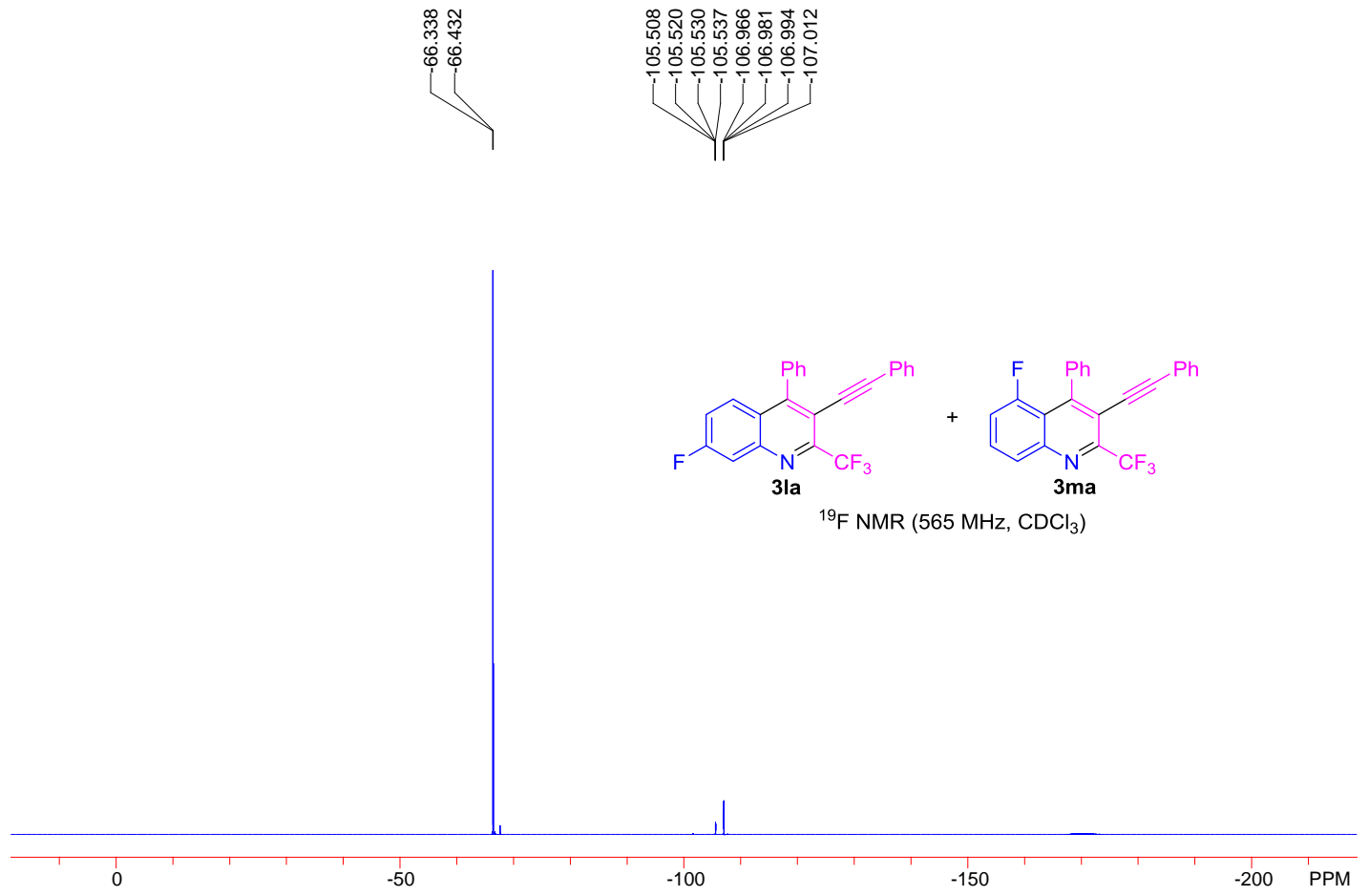


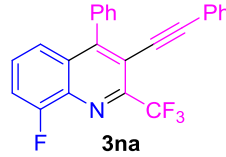
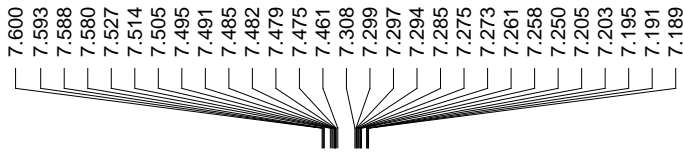
¹H NMR (600 MHz, CDCl₃)



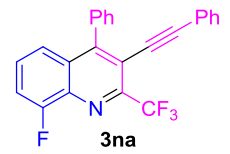
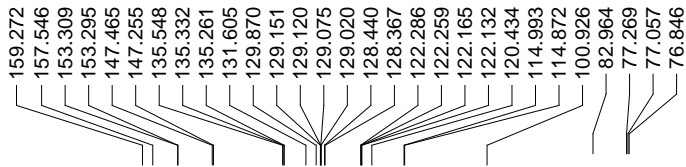
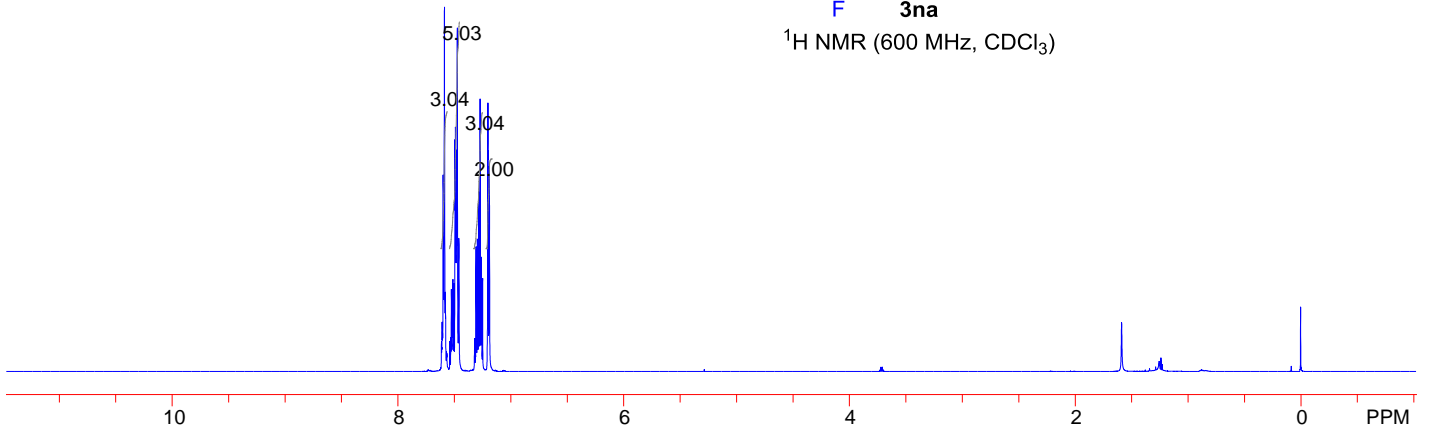
¹³C{¹H} (150 MHz, CDCl₃)



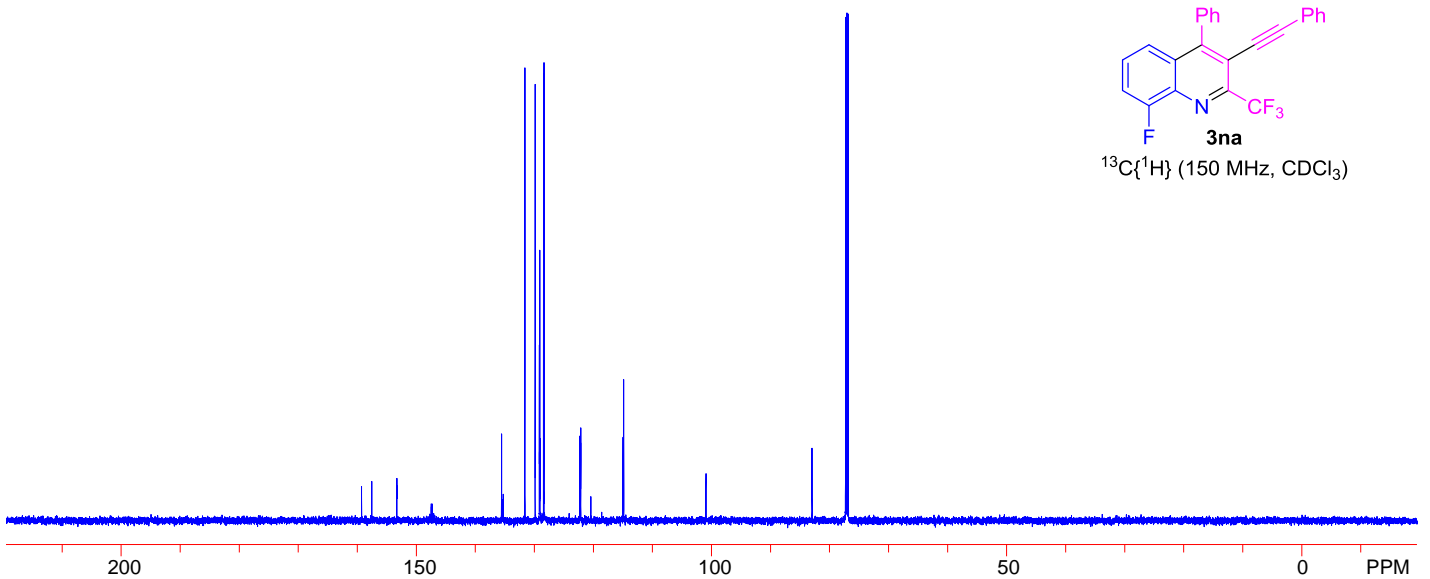


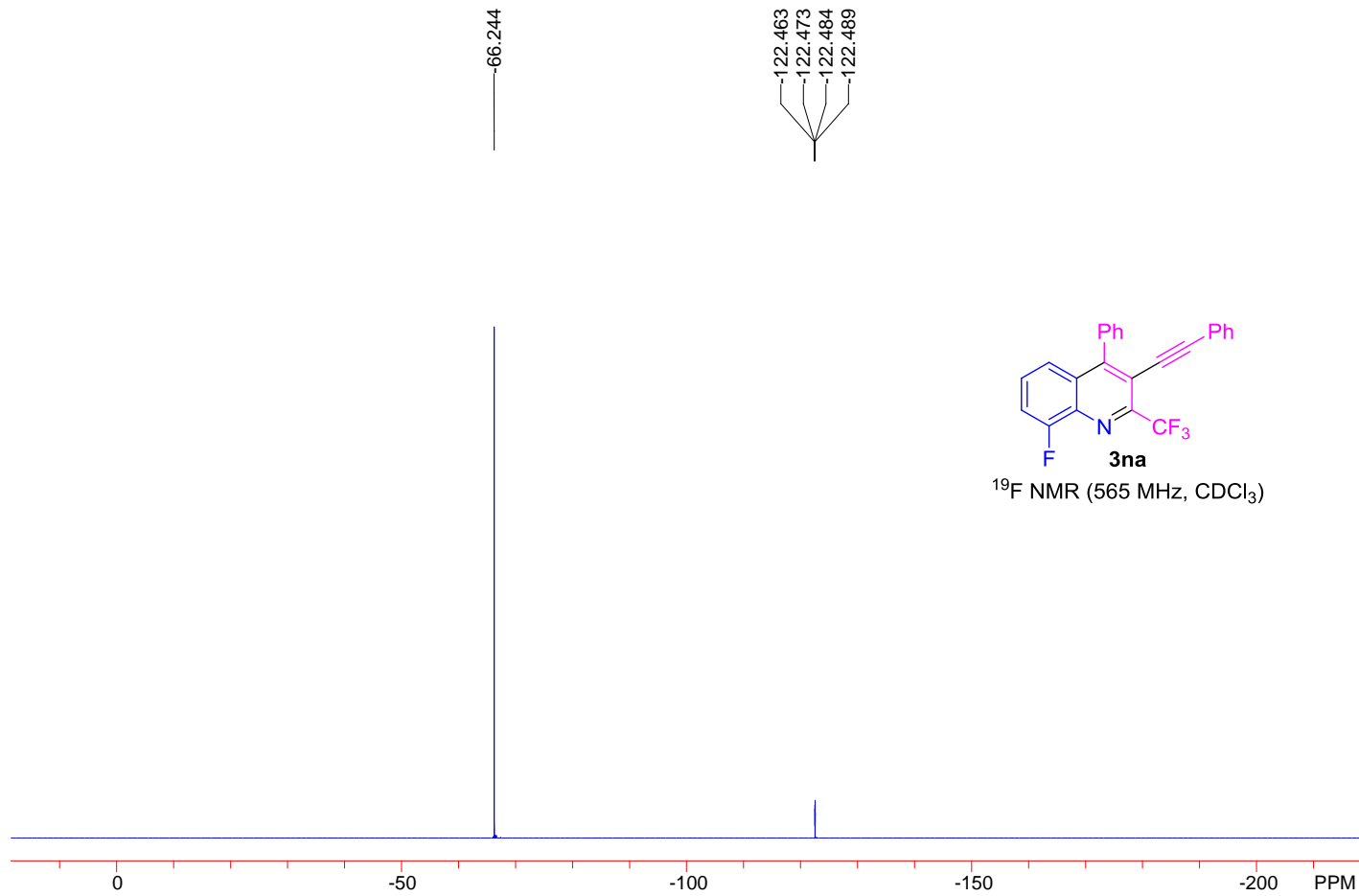


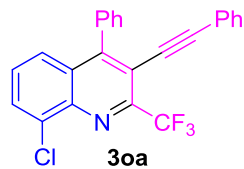
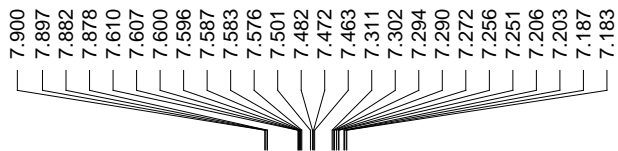
$^1\text{H NMR}$ (600 MHz, CDCl_3)



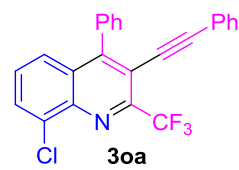
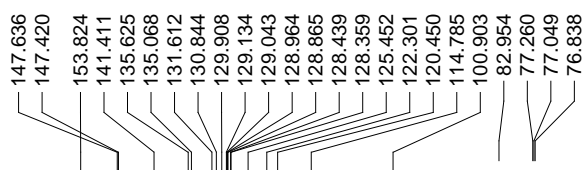
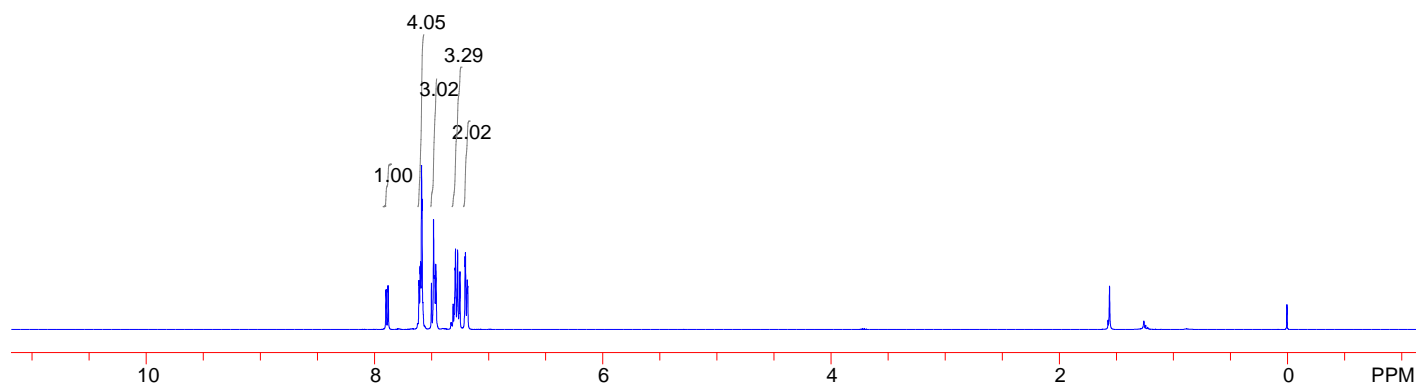
$^{13}\text{C}\{^1\text{H}\}$ (150 MHz, CDCl_3)



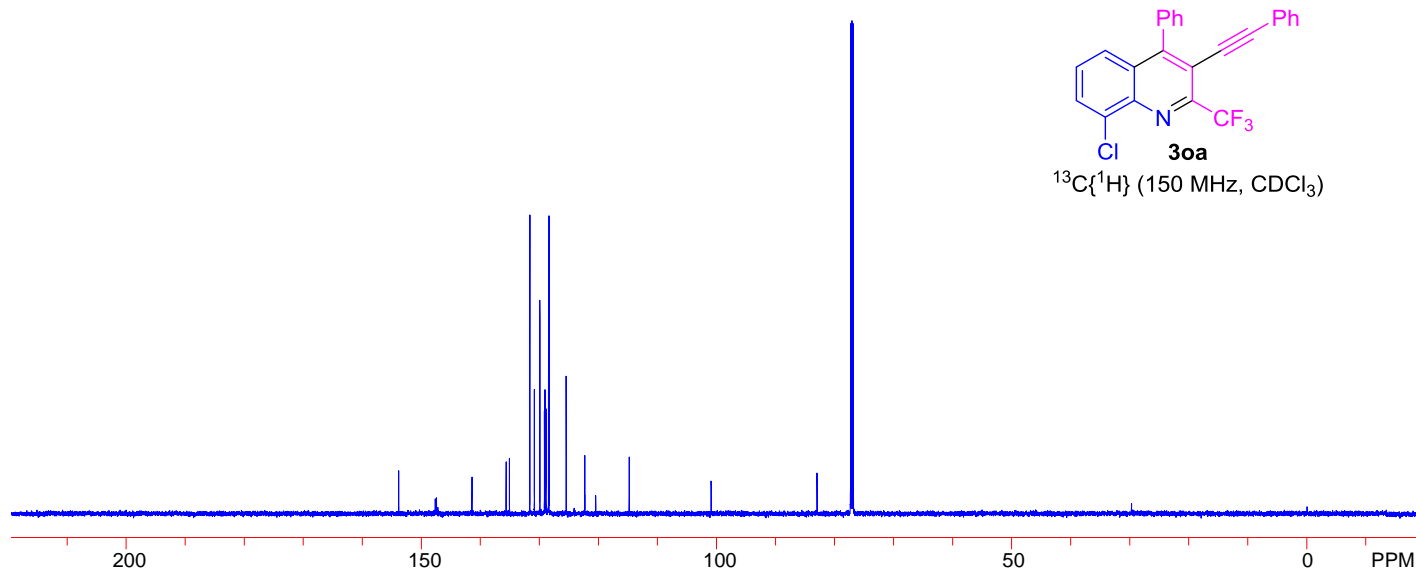




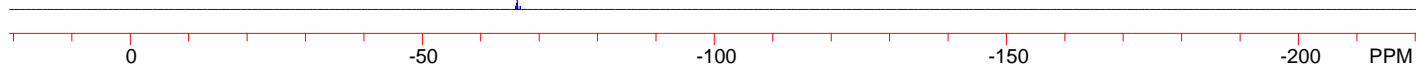
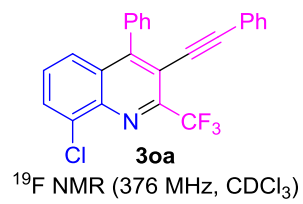
^1H NMR (400 MHz, CDCl_3)

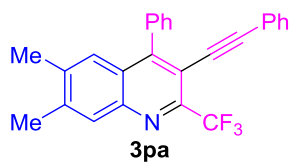
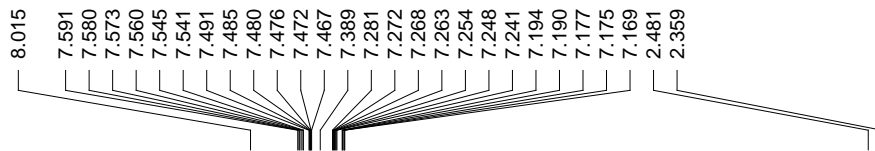


$^{13}\text{C}\{^1\text{H}\}$ (150 MHz, CDCl_3)

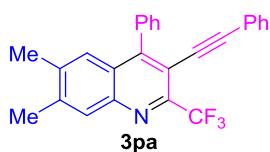
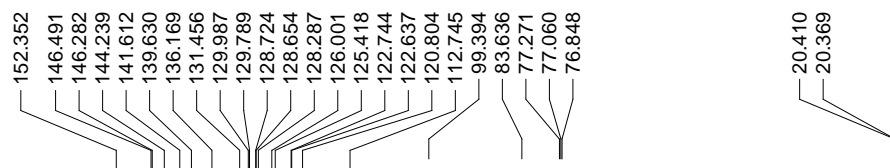
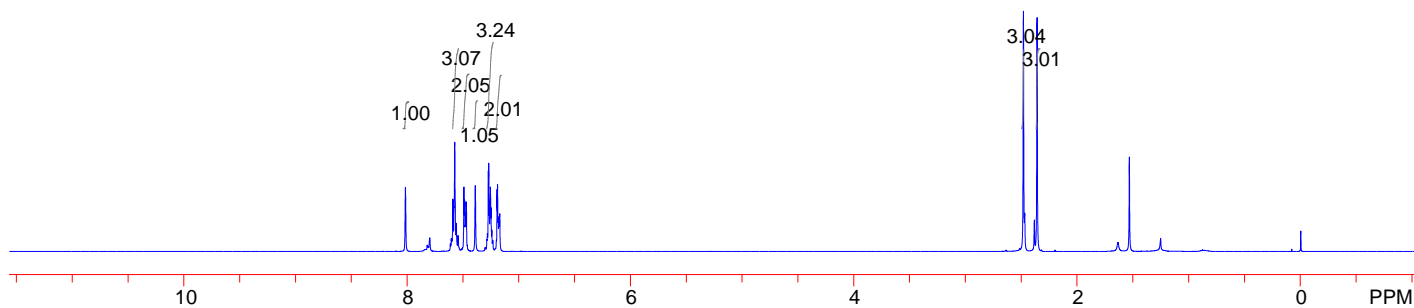


66.256

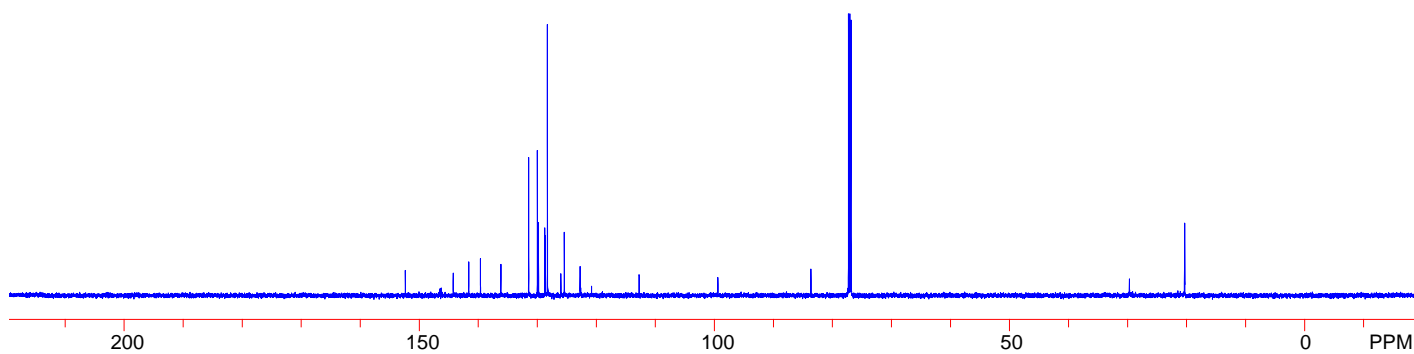




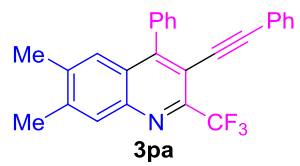
$^1\text{H NMR}$ (400 MHz, CDCl_3)



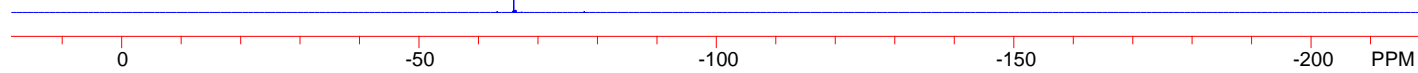
$^{13}\text{C}\{^1\text{H}\}$ (150 MHz, CDCl_3)

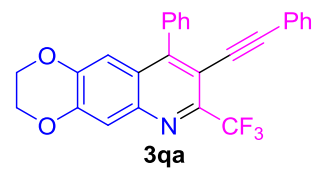
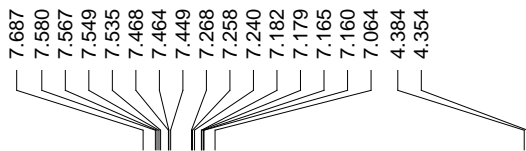


65.915

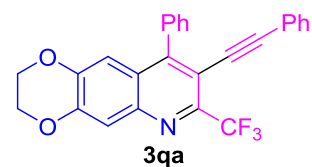
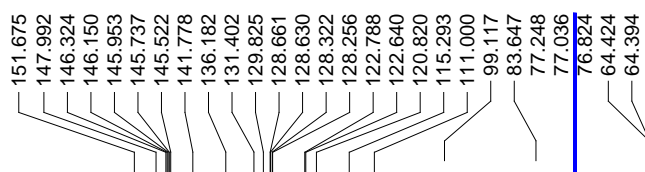
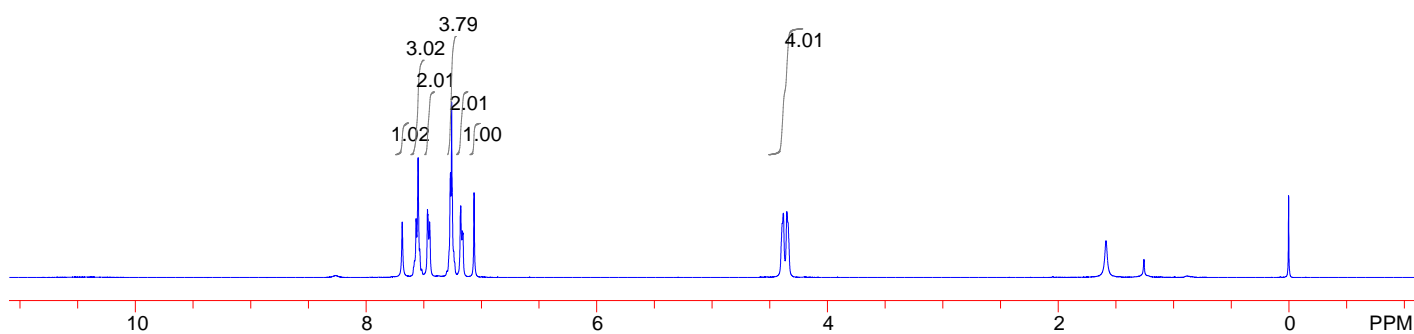


¹⁹F NMR (565 MHz, CDCl₃)

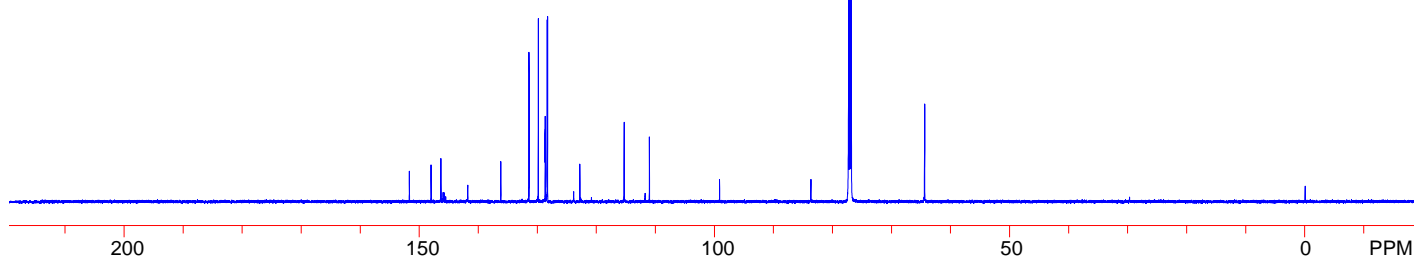




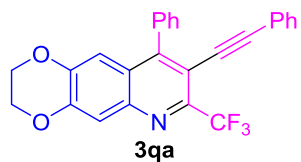
$^1\text{H NMR}$ (400 MHz, CDCl_3)



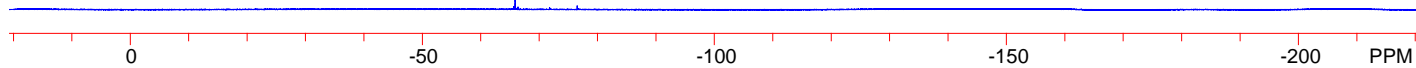
$^{13}\text{C}\{^1\text{H}\}$ (150 MHz, CDCl_3)

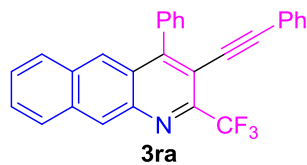
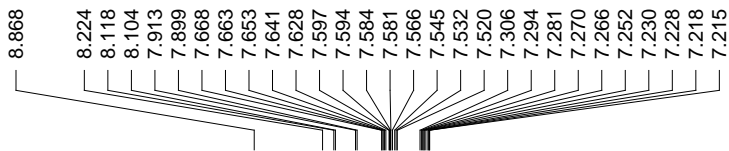


-65.870

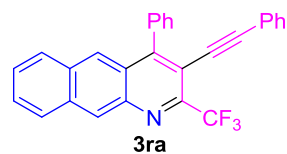
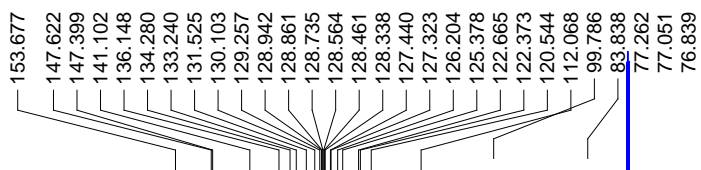
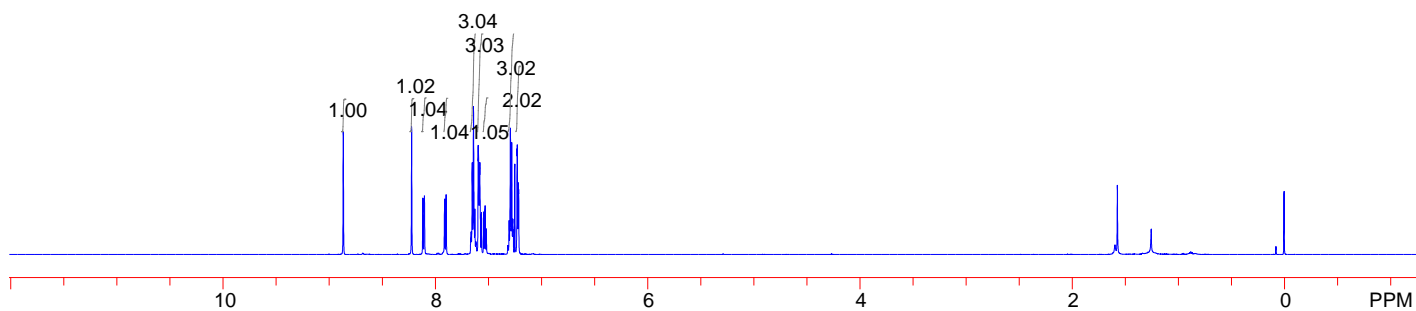


¹⁹F NMR (376 MHz, CDCl₃)

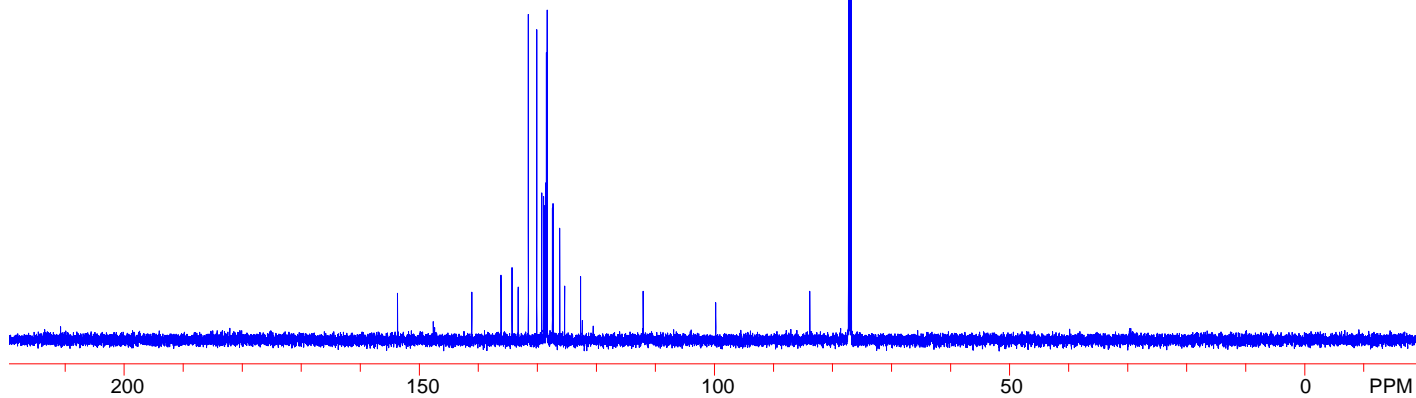




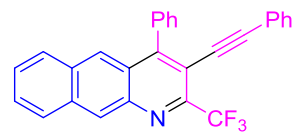
^1H NMR (600 MHz, CDCl_3)



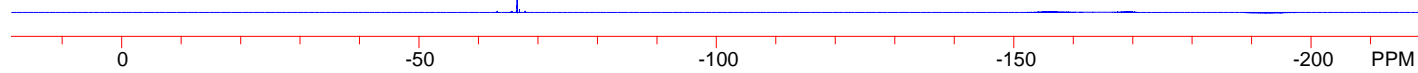
$^{13}\text{C}\{^1\text{H}\}$ (150 MHz, CDCl_3)

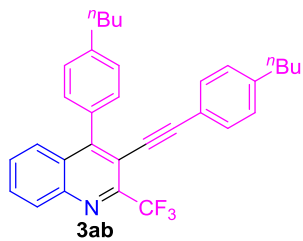
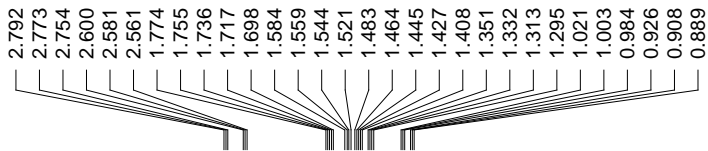
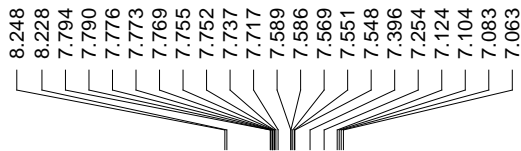


-66.494

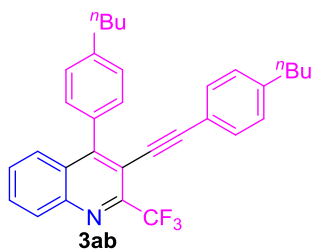
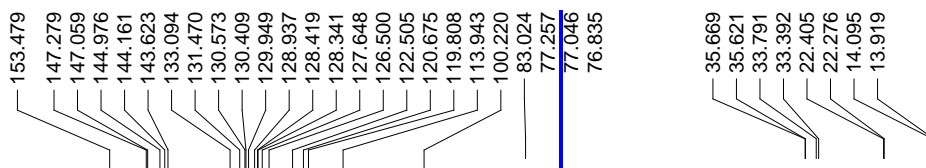
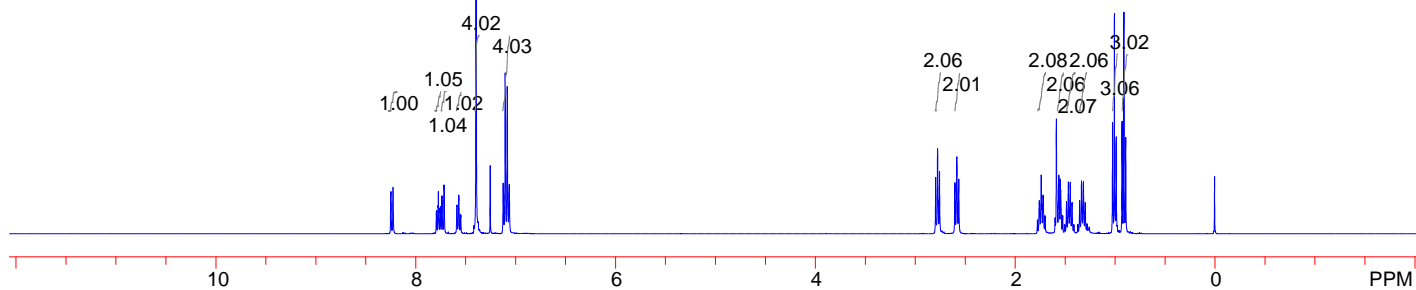


3ra
¹⁹F NMR (565 MHz, CDCl₃)

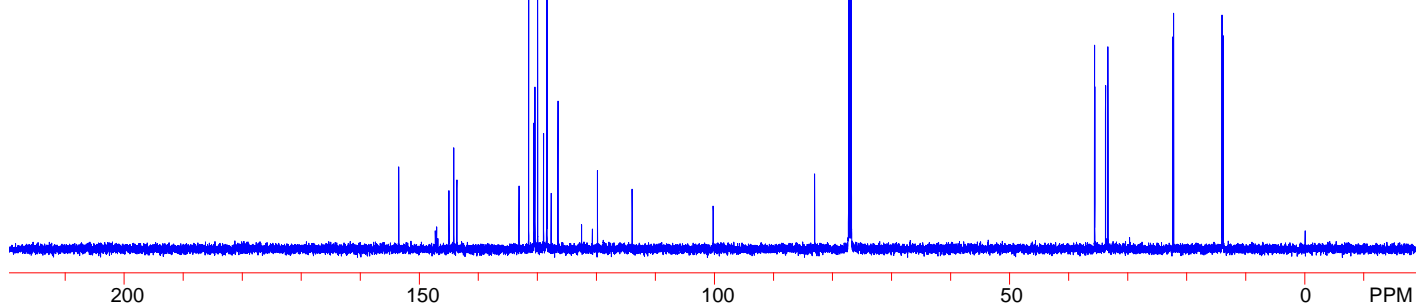




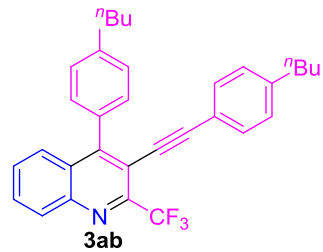
$^1\text{H NMR}$ (400 MHz, CDCl_3)



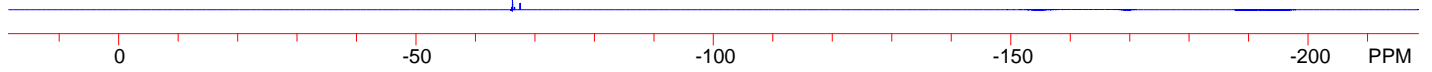
$^{13}\text{C}\{^1\text{H}\}$ (150 MHz, CDCl_3)

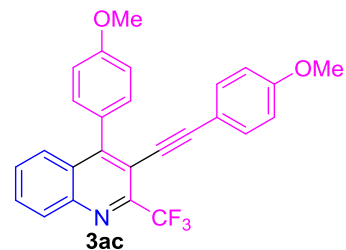
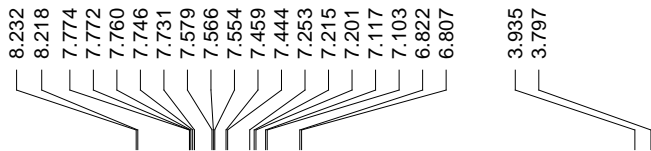


66.197

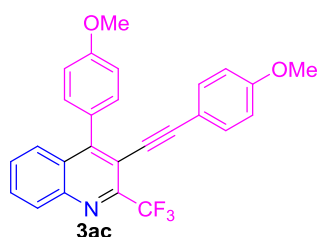
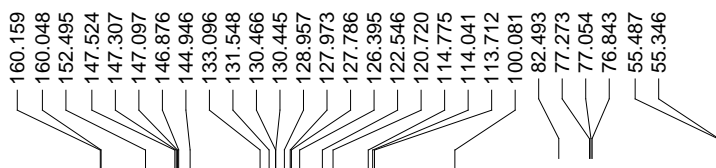
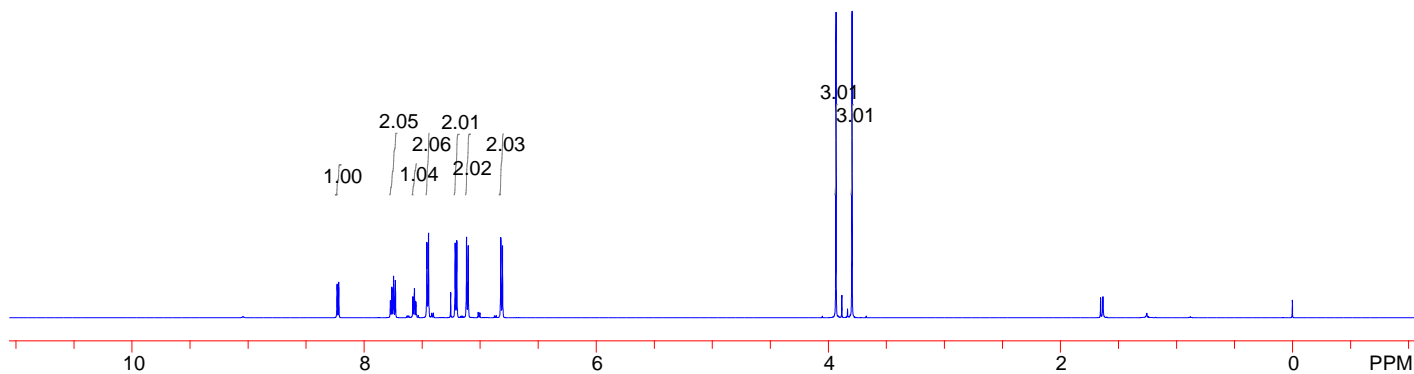


¹⁹F NMR (565 MHz, CDCl₃)

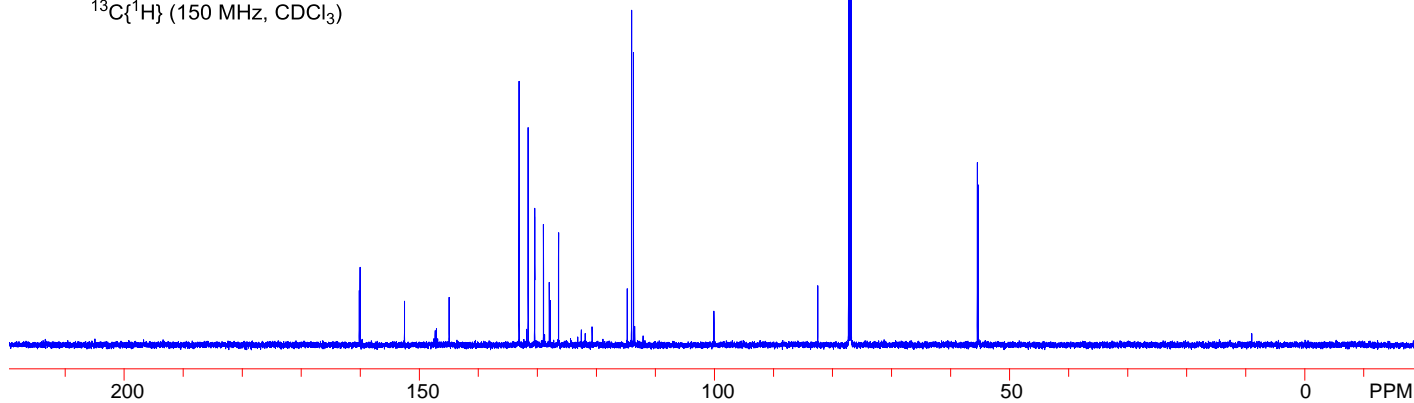




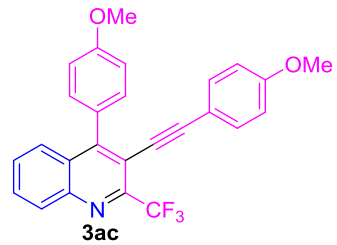
$^1\text{H NMR}$ (600 MHz, CDCl_3)



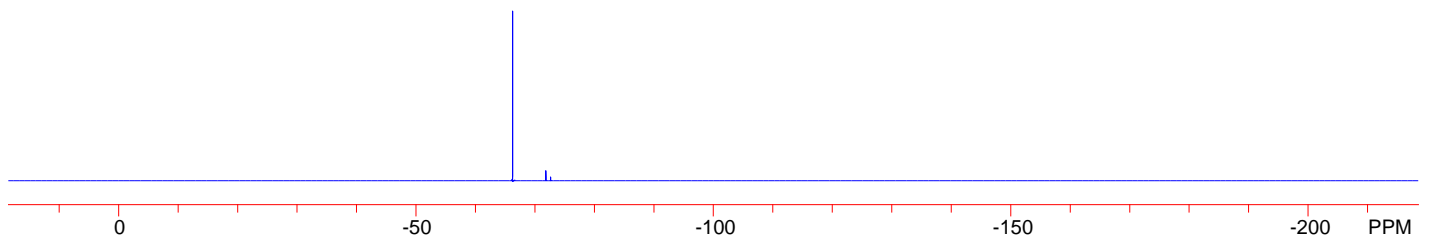
$^{13}\text{C}\{^1\text{H}\}$ (150 MHz, CDCl_3)



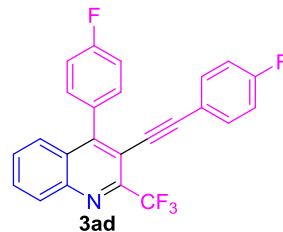
66.234



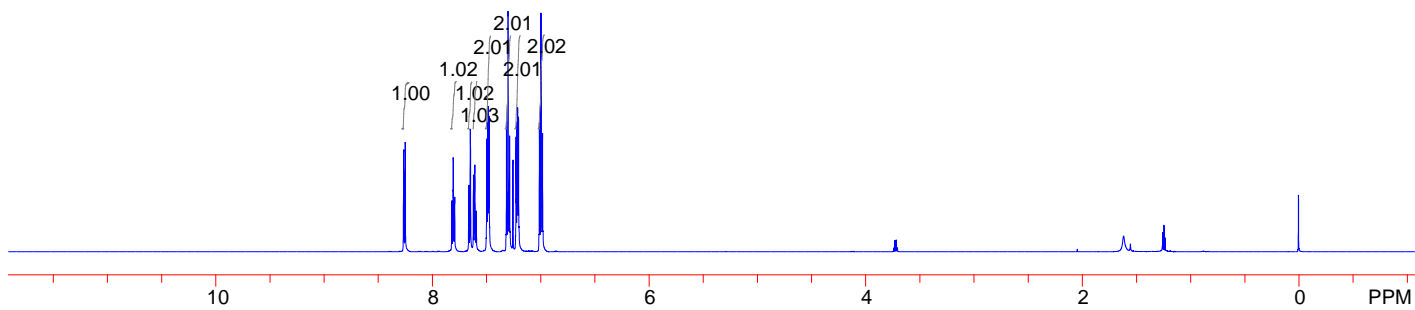
^{19}F NMR (565 MHz, CDCl_3)



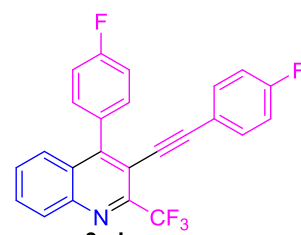
8.266
8.252
7.822
7.819
7.810
7.808
7.805
7.796
7.794
7.663
7.650
7.620
7.608
7.596
7.499
7.496
7.490
7.485
7.479
7.476
7.315
7.301
7.287
7.256
7.228
7.224
7.219
7.213
7.208
7.204
7.012
6.997
6.983



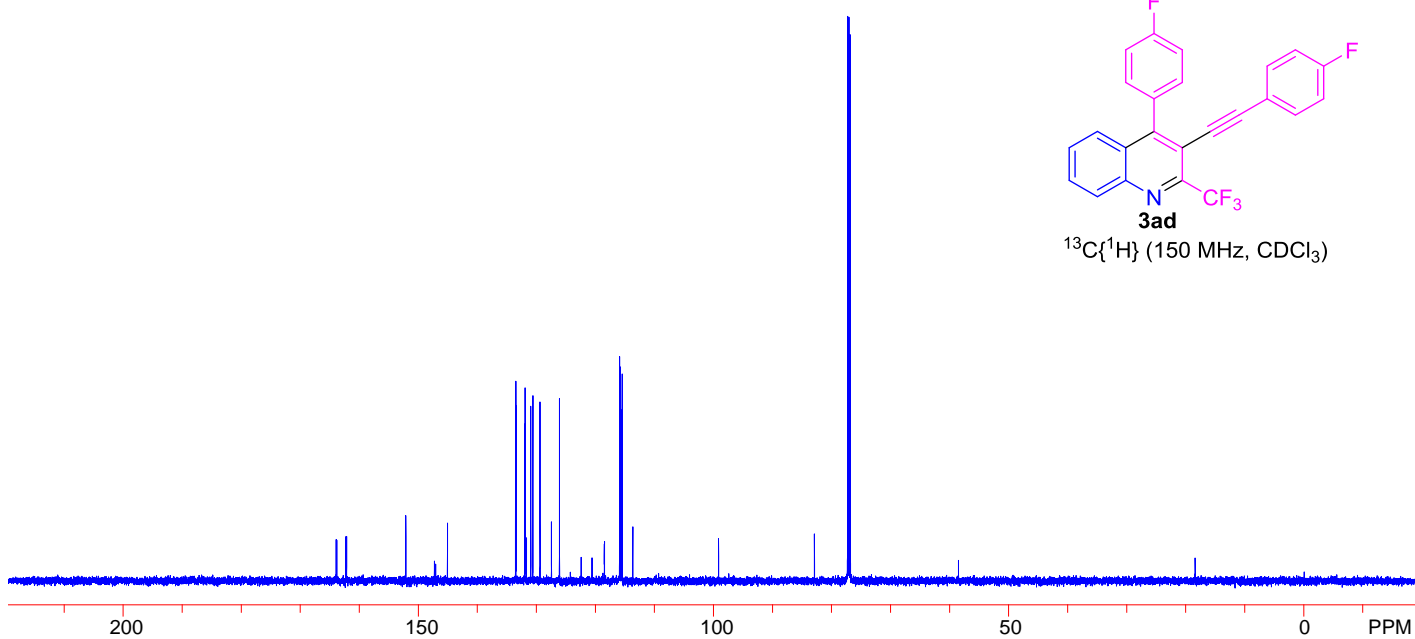
$^1\text{H NMR}$ (600 MHz, CDCl_3)

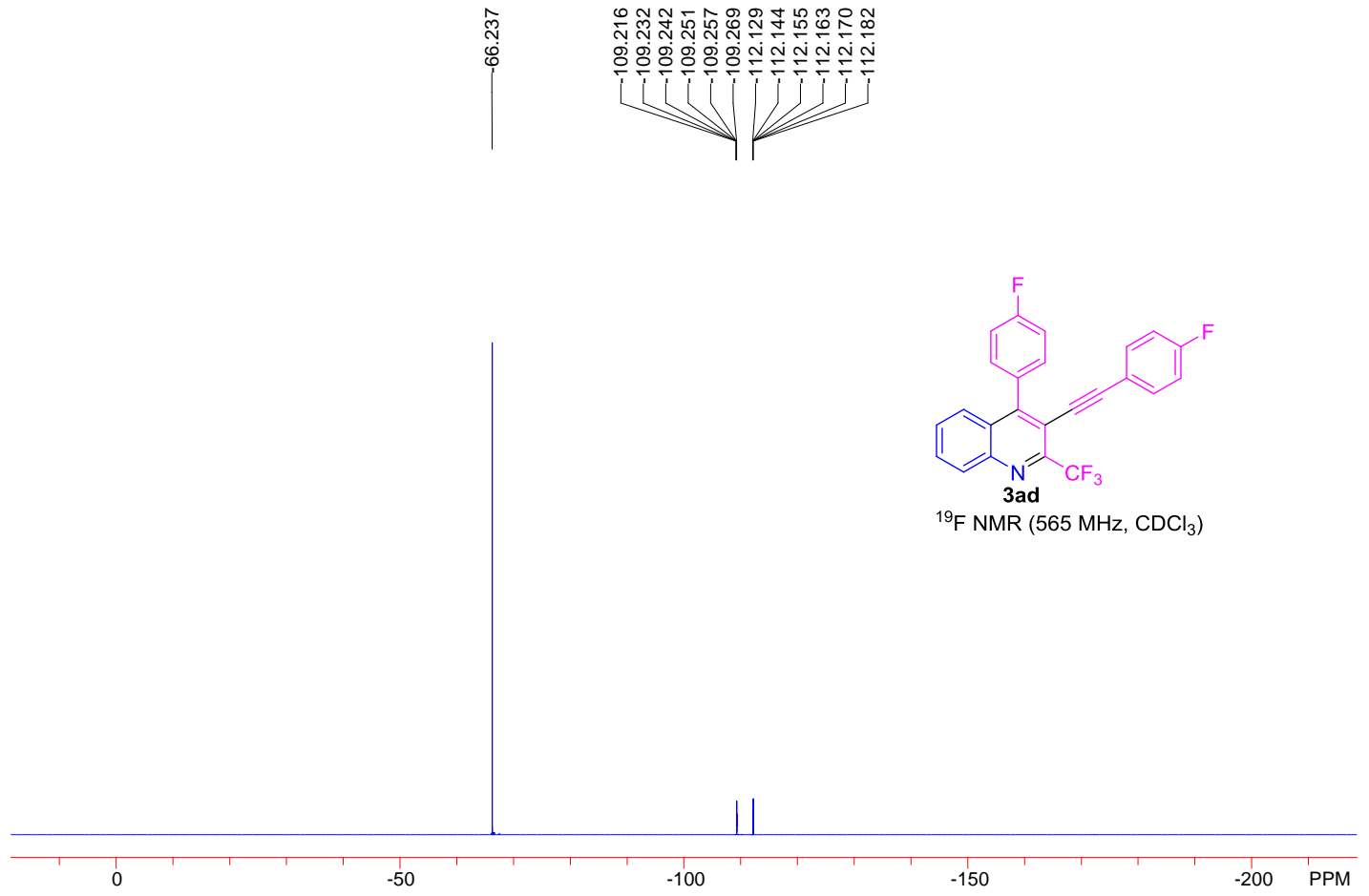


163.911
163.809
162.264
162.148
152.112
147.266
147.041
145.054
133.512
133.457
131.943
131.889
131.691
131.671
130.940
130.590
129.373
127.437
126.078
124.231
122.393
120.566
118.725
118.485
118.464
115.900
115.754
115.612
115.470
113.659
99.125
82.887
77.261
77.049
76.837

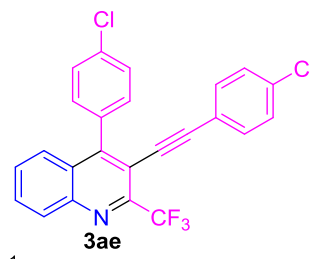


$^{13}\text{C}\{^1\text{H}\}$ (150 MHz, CDCl_3)

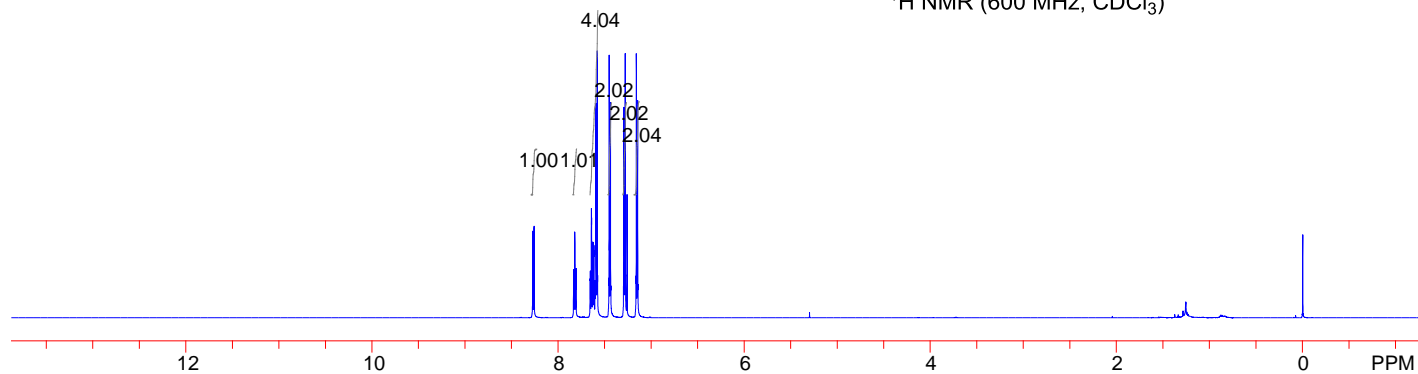




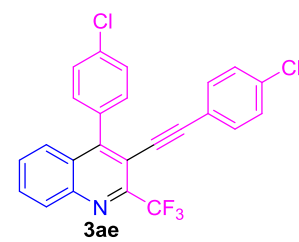
8.270
8.256
7.832
7.830
7.822
7.819
7.816
7.807
7.805
7.654
7.652
7.640
7.638
7.626
7.624
7.615
7.613
7.610
7.601
7.599
7.595
7.591
7.588
7.580
7.577
7.573
7.453
7.449
7.446
7.439
7.435
7.431
7.295
7.291
7.288
7.280
7.277
7.273
7.257
7.161
7.157
7.154
7.146
7.143
7.139



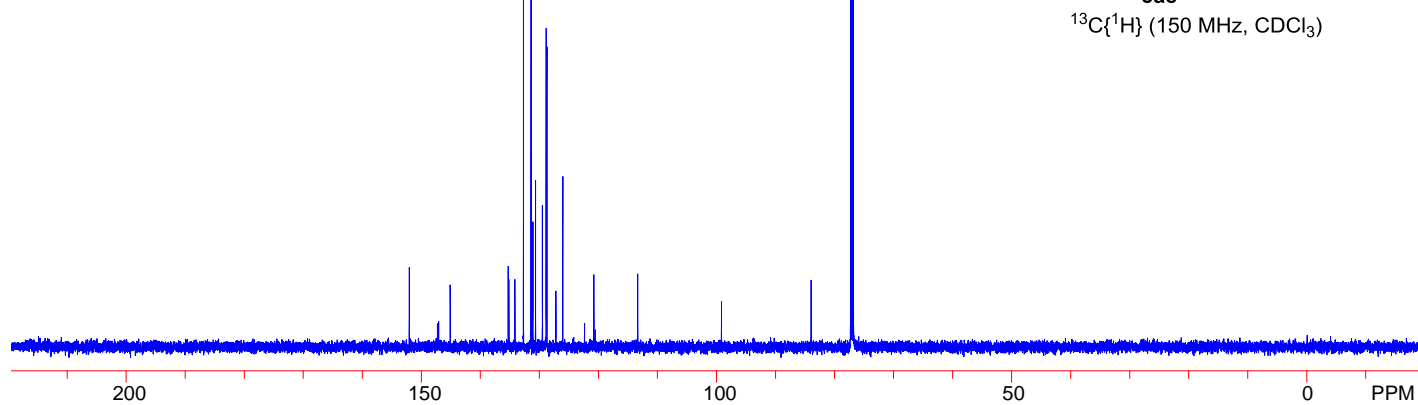
¹H NMR (600 MHz, CDCl₃)



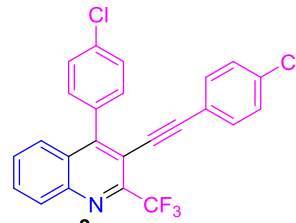
152.035
147.264
147.045
145.099
135.271
135.151
134.131
132.692
131.408
131.081
130.640
129.472
128.845
128.713
127.188
126.027
122.343
120.760
120.510
113.341
99.148
83.964
77.253
77.041
76.830



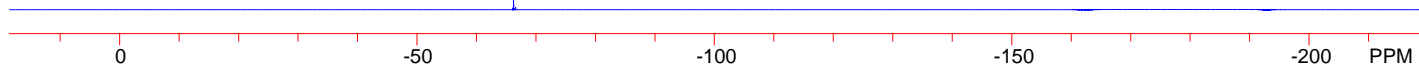
¹³C{¹H} (150 MHz, CDCl₃)



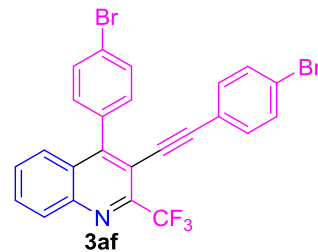
66.204



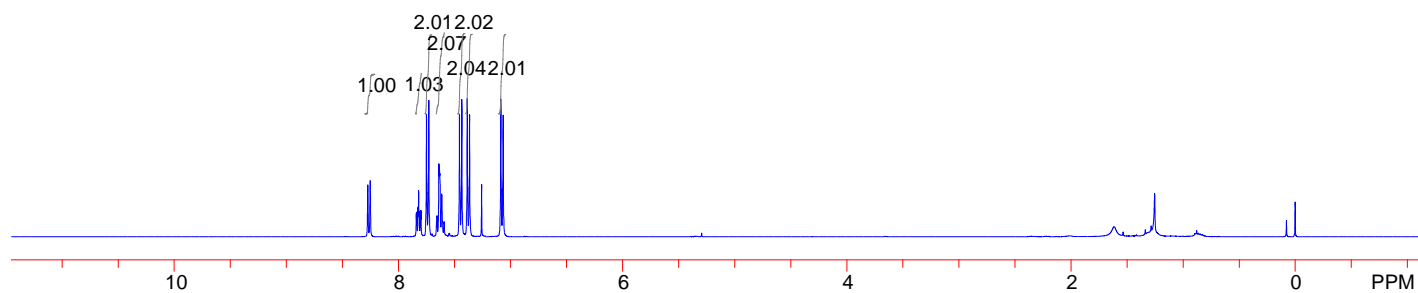
^{19}F NMR (565 MHz, CDCl_3)



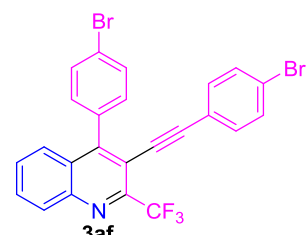
8.273
8.252
7.840
7.835
7.824
7.819
7.814
7.803
7.798
7.750
7.728
7.655
7.638
7.634
7.630
7.614
7.612
7.593
7.455
7.434
7.386
7.364
7.257
7.086
7.065



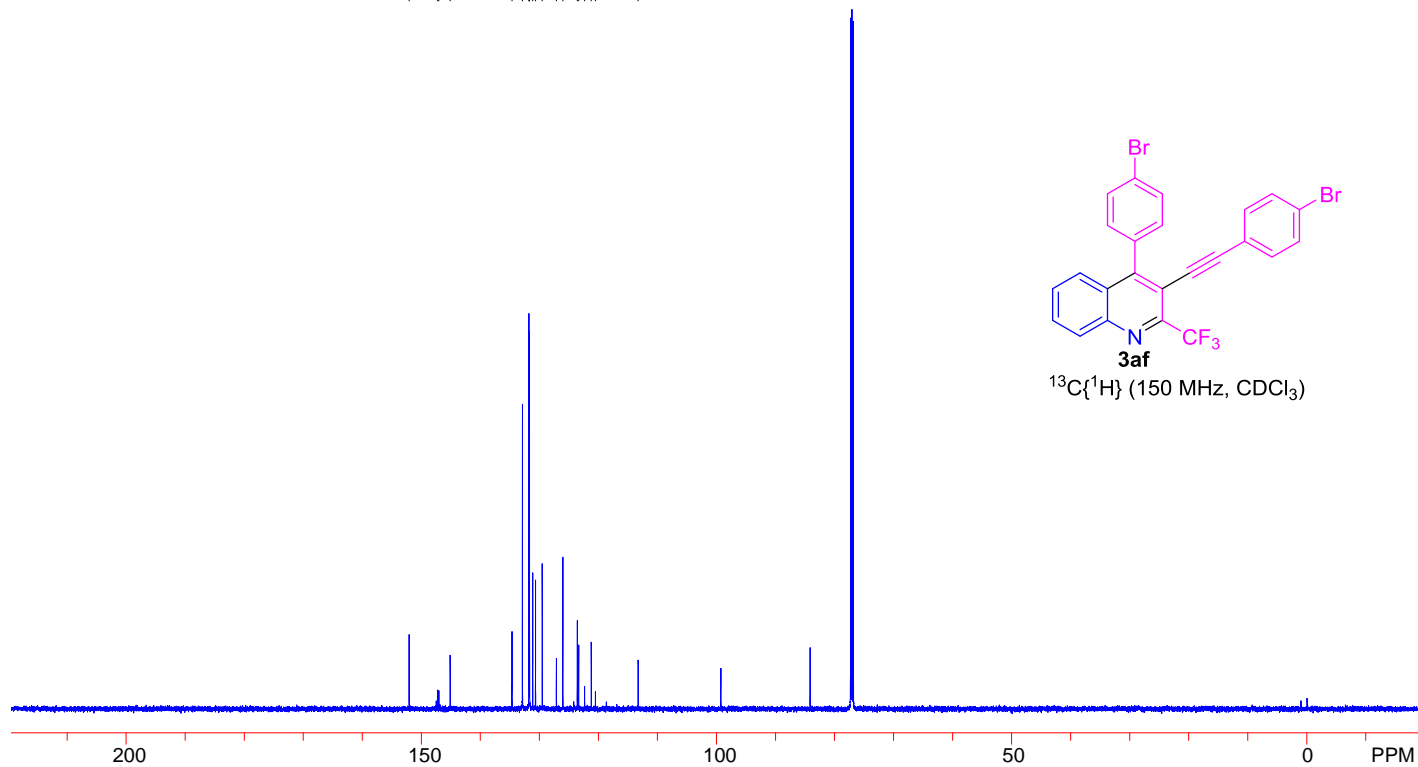
$^1\text{H NMR}$ (400 MHz, CDCl_3)



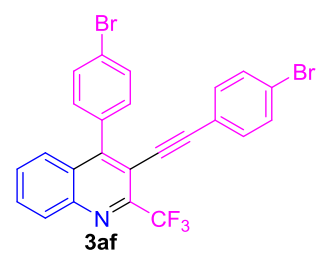
152.064
147.237
147.015
145.097
134.632
132.870
131.780
131.684
131.650
131.121
130.645
129.503
127.101
126.019
123.563
123.333
122.330
121.200
120.498
113.255
99.255
84.130
77.265
77.053
76.841



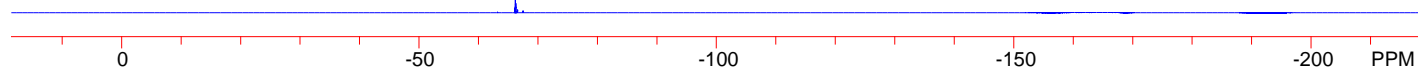
$^{13}\text{C}\{^1\text{H}\}$ (150 MHz, CDCl_3)

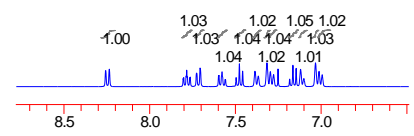
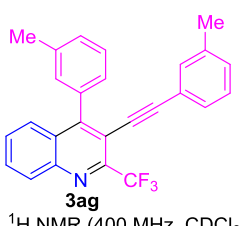
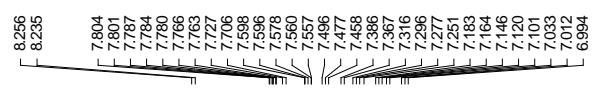
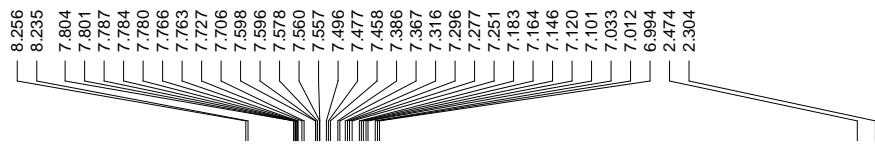


66.191

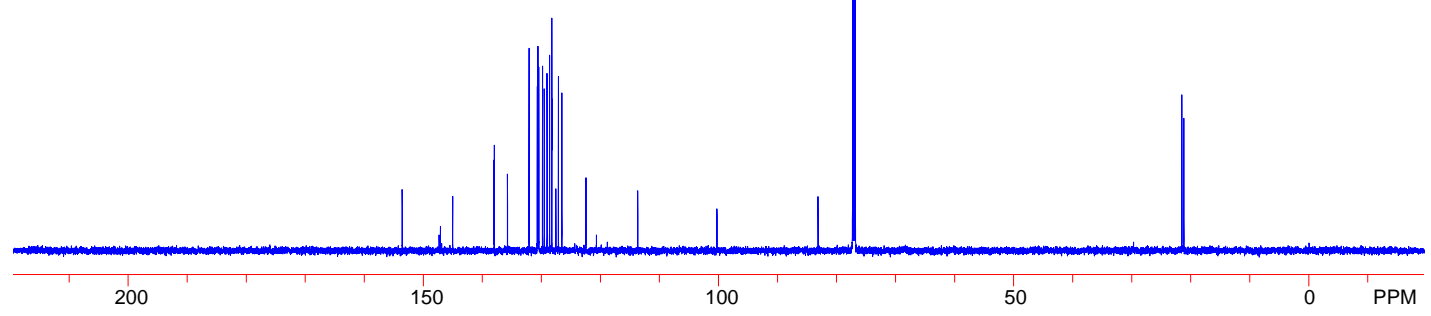
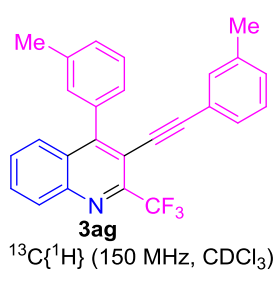
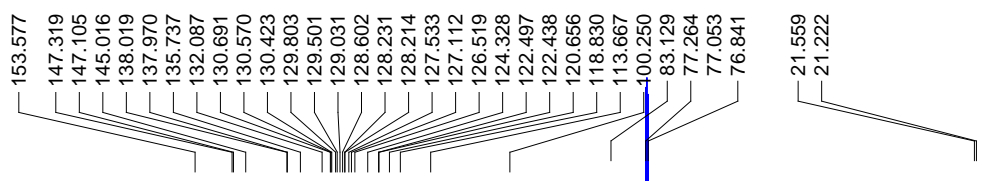
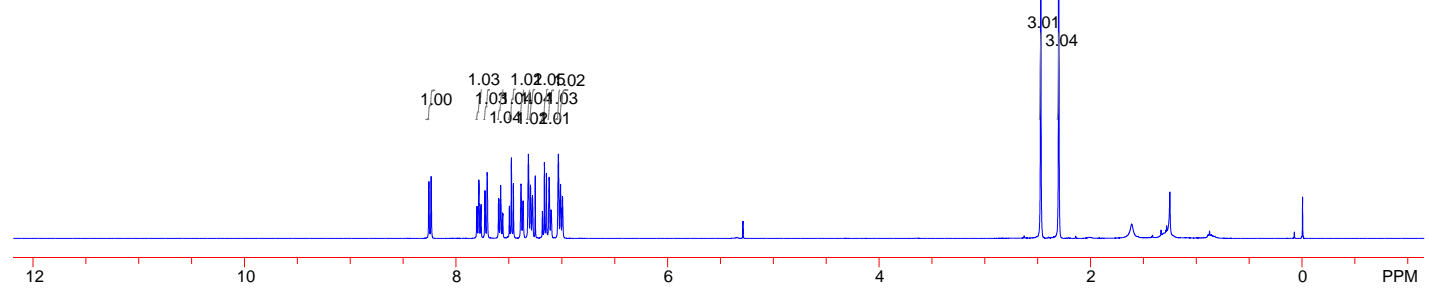


^{19}F NMR (565 MHz, CDCl_3)

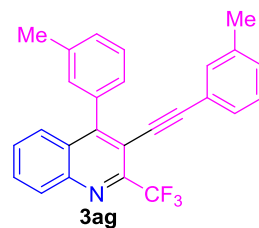




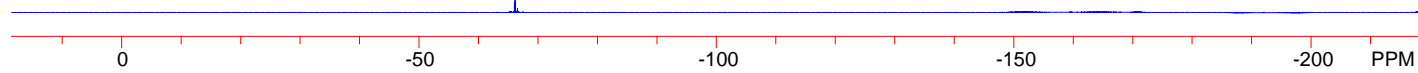
¹H NMR (400 MHz, CDCl₃)



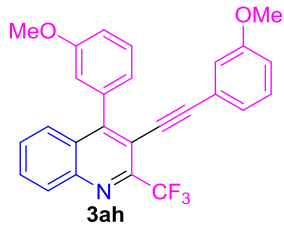
66.160



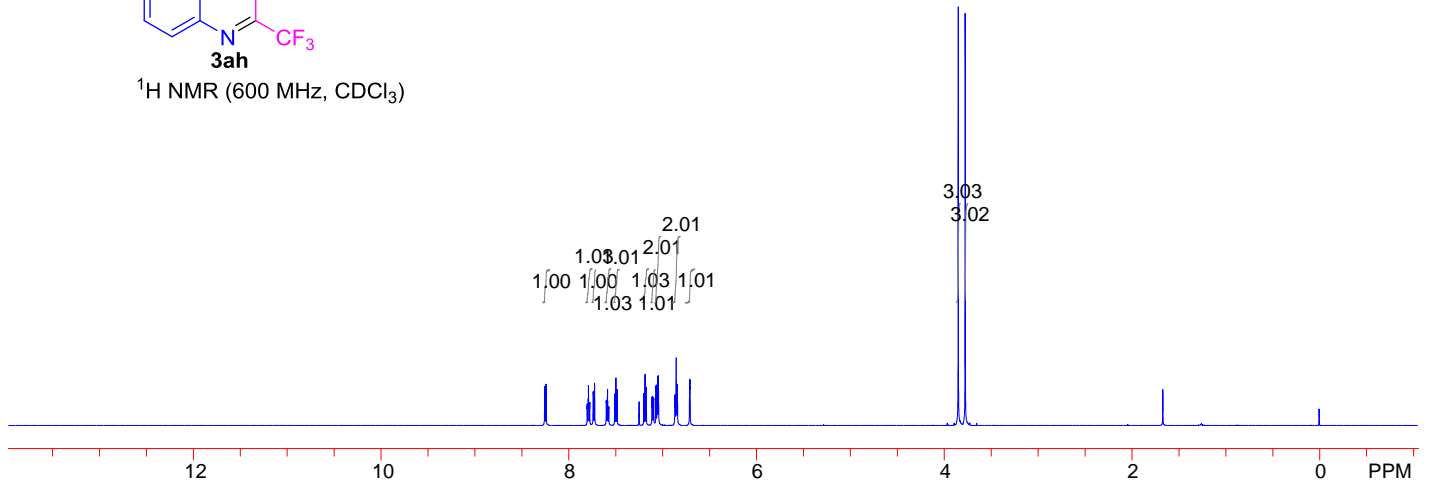
3ag
¹⁹F NMR (565 MHz, CDCl₃)



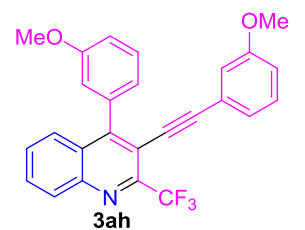
8.256
8.242
7.804
7.801
7.792
7.790
7.787
7.778
7.776
7.739
7.725
7.600
7.598
7.589
7.586
7.584
7.575
7.573
7.510
7.497
7.484
7.250
7.199
7.186
7.173
7.113
7.112
7.109
7.108
7.099
7.098
7.095
7.094
7.069
7.057
7.049
7.045
7.042
6.868
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6.855
6.844
6.842
6.712
6.709
6.708
6.706
3.847
3.773



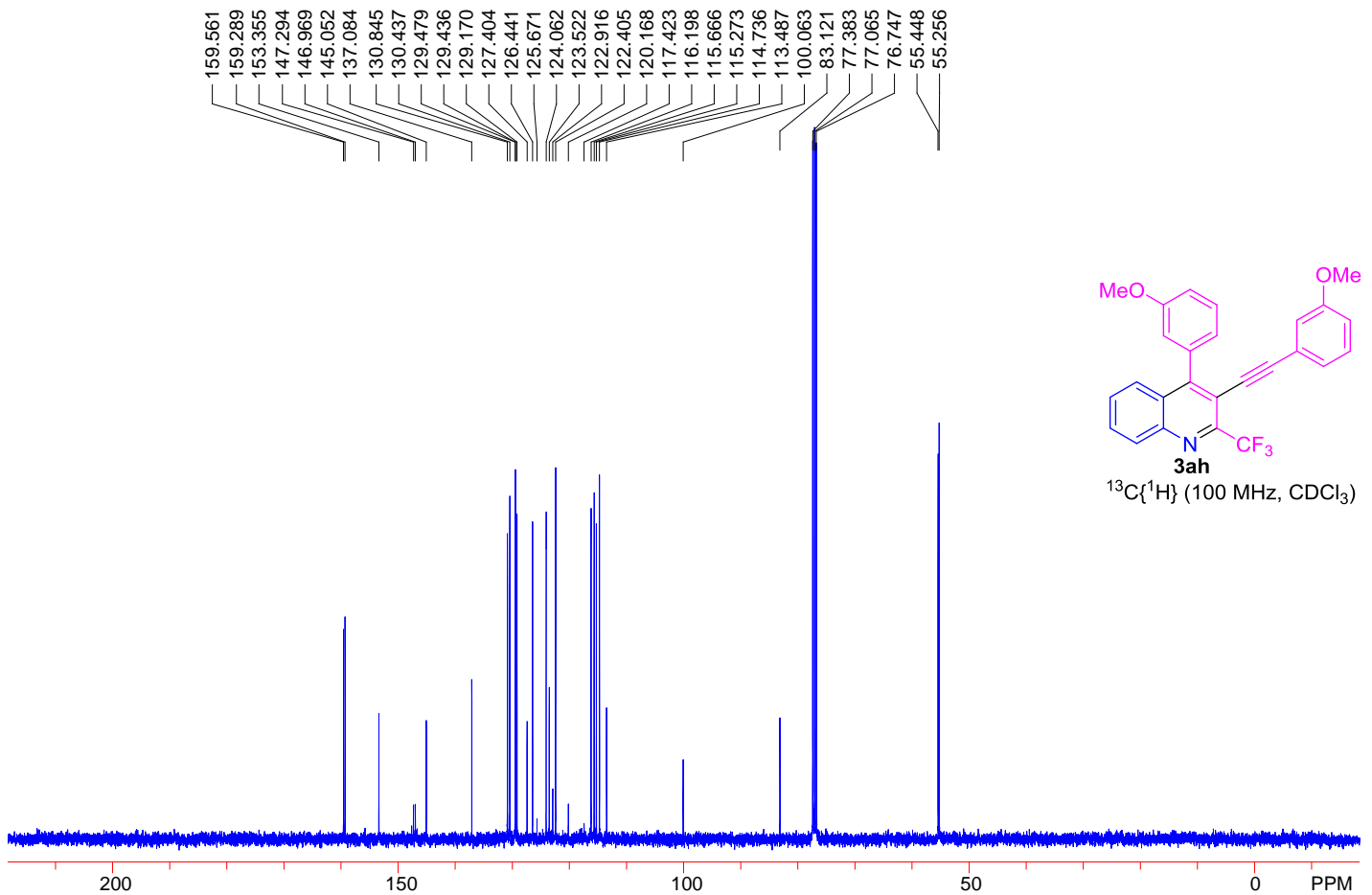
$^1\text{H NMR}$ (600 MHz, CDCl_3)



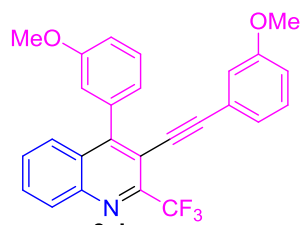
159.561
159.289
153.355
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146.969
145.052
137.084
130.845
130.437
129.479
129.436
129.170
127.404
126.441
125.671
124.062
123.522
122.916
122.405
120.168
117.423
116.198
115.666
115.273
114.736
113.487
100.063
83.121
77.383
77.065
76.747
55.448
55.256



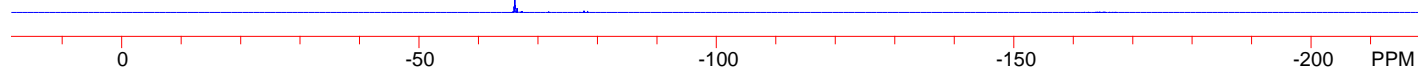
$^{13}\text{C}\{^1\text{H}\}$ (100 MHz, CDCl_3)

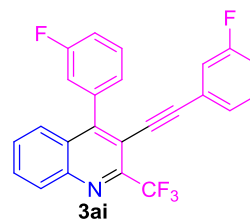
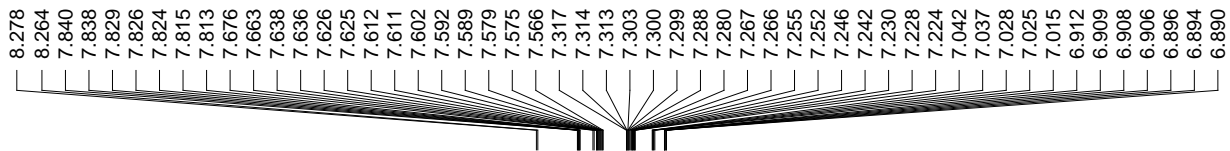


66.101

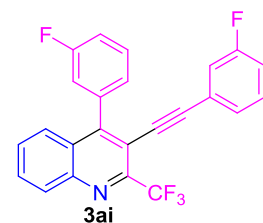
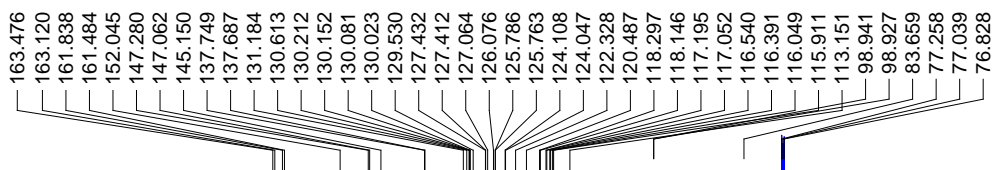
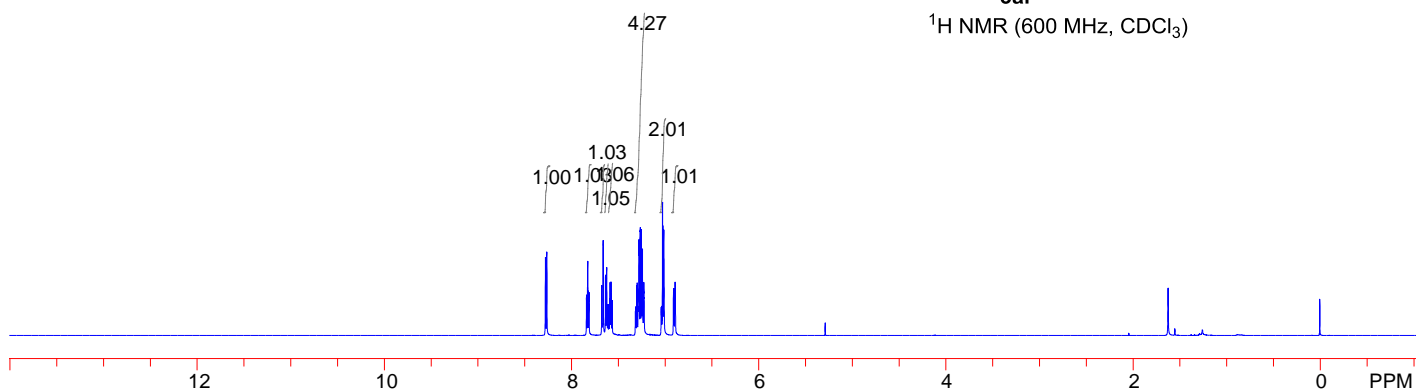


^{19}F NMR (565 MHz, CDCl_3)

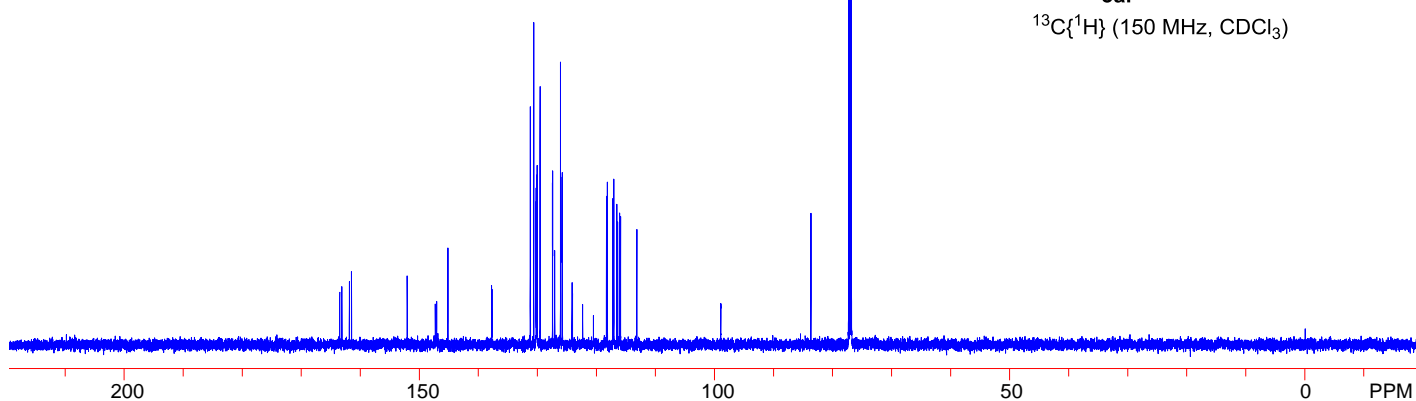


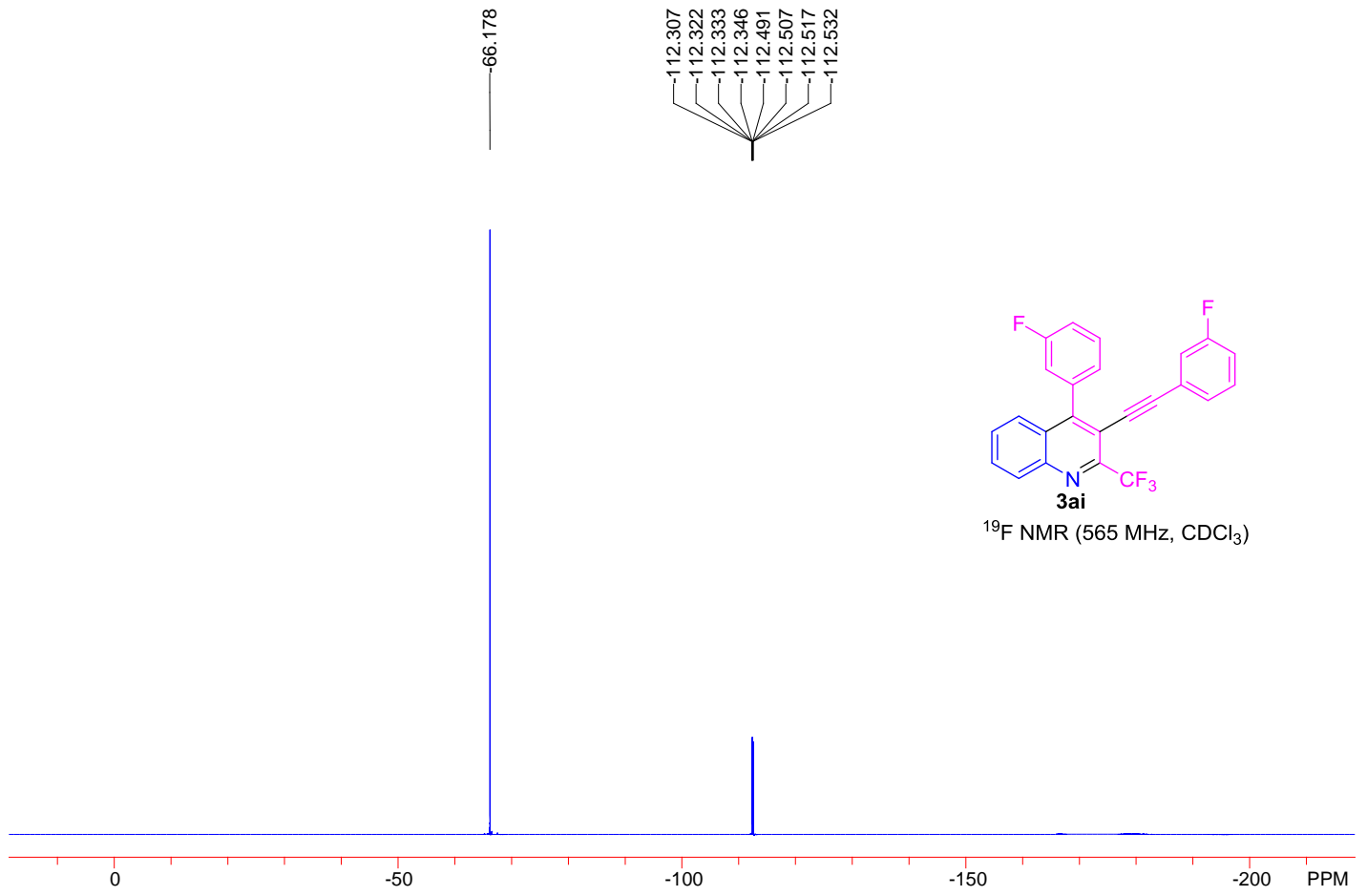


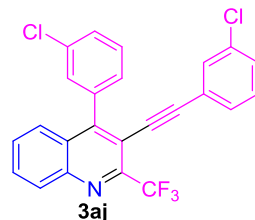
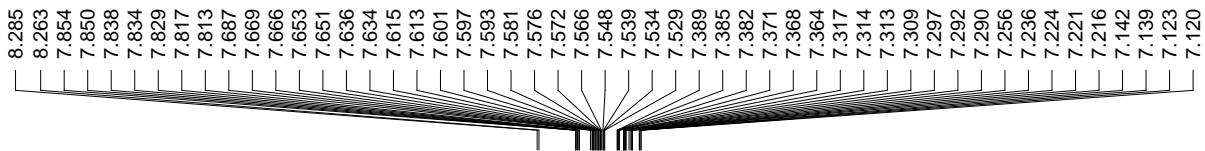
$^1\text{H NMR}$ (600 MHz, CDCl_3)



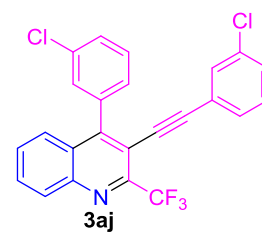
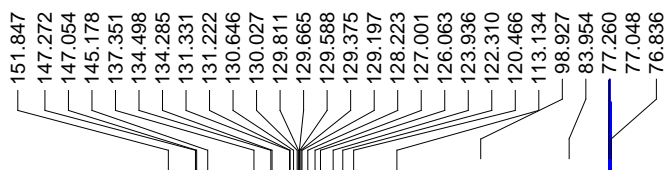
$^{13}\text{C}\{^1\text{H}\}$ (150 MHz, CDCl_3)







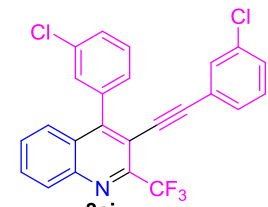
^1H NMR (400 MHz, CDCl_3)



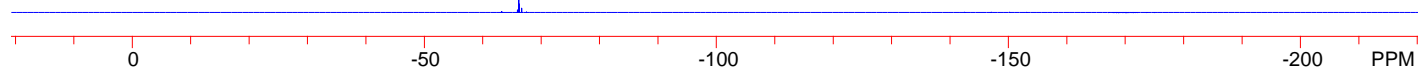
$^{13}\text{C}\{^1\text{H}\}$ (150 MHz, CDCl_3)

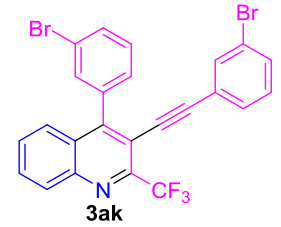
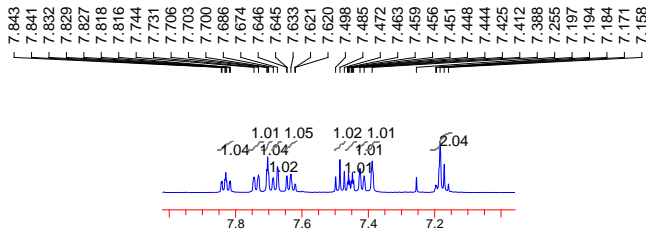
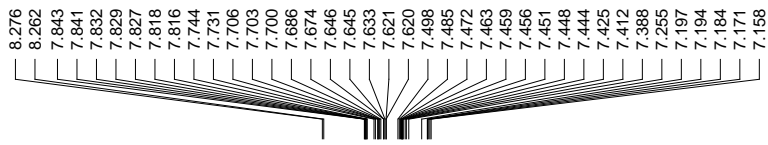


66.168

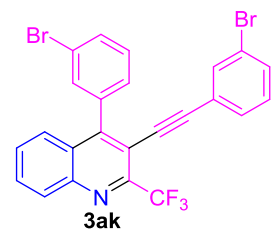
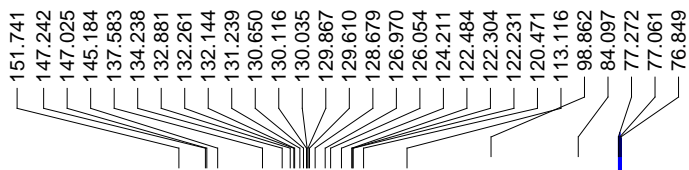
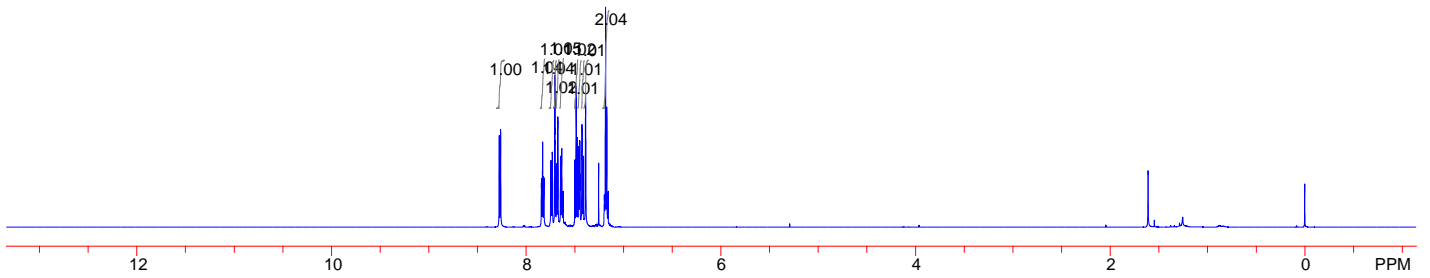


3aj
¹⁹F NMR (376 MHz, CDCl₃)

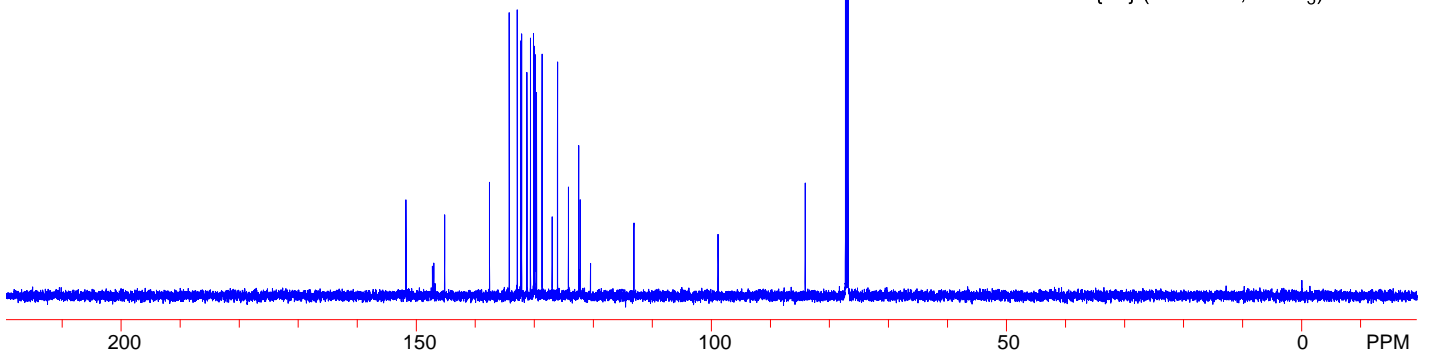


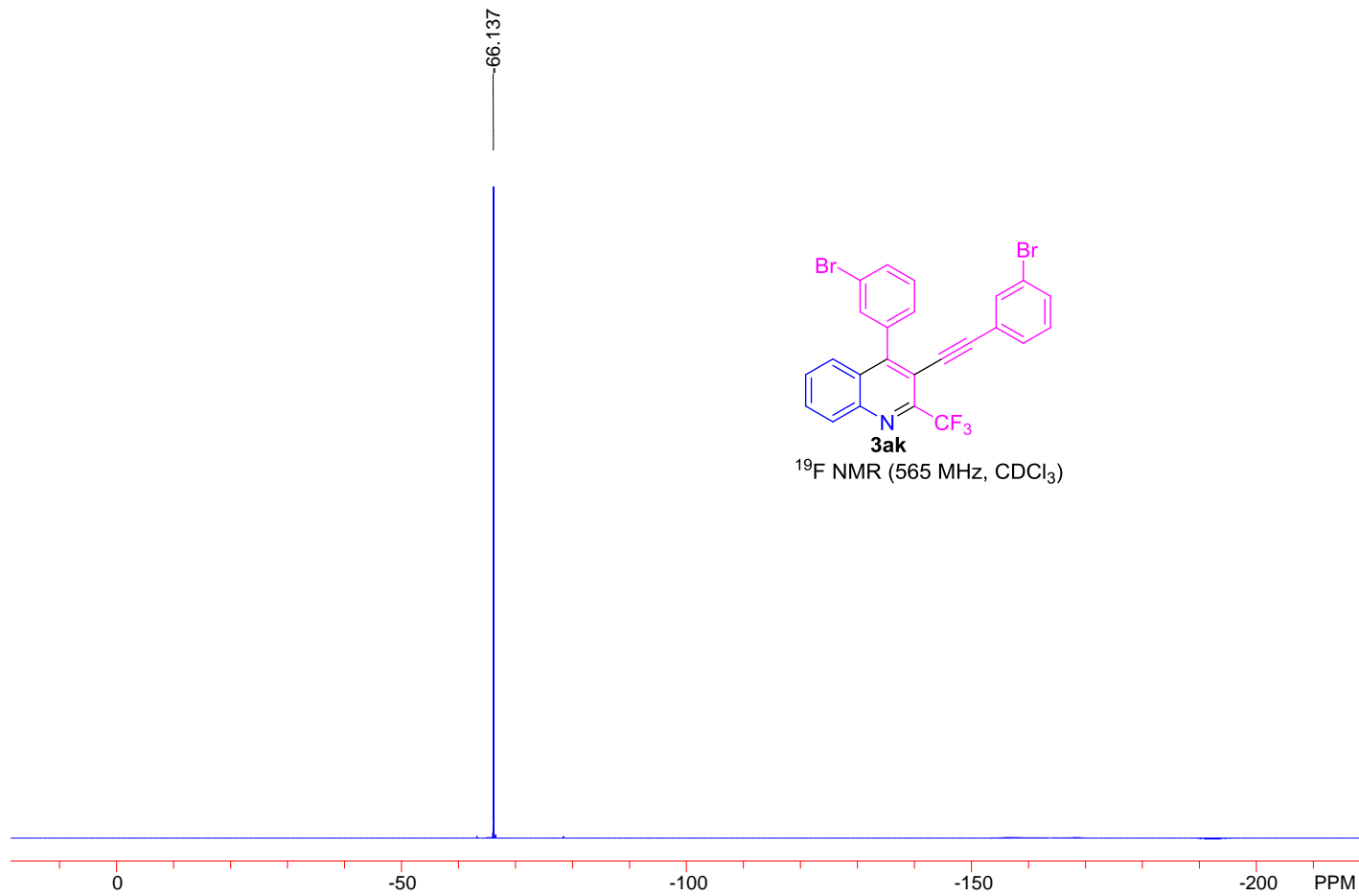


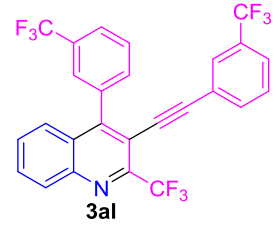
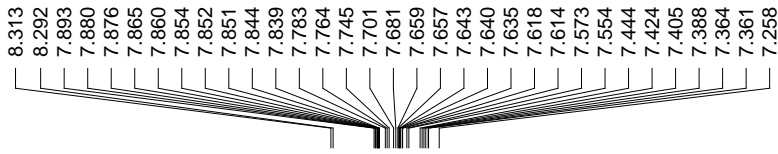
$^1\text{H NMR}$ (600 MHz, CDCl_3)



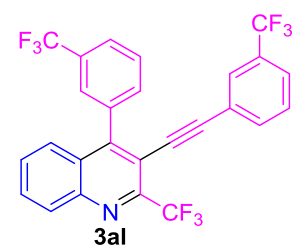
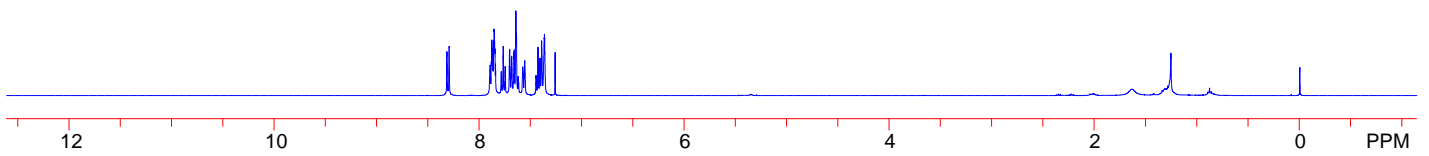
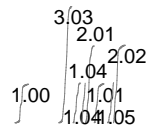
$^{13}\text{C}\{^1\text{H}\}$ (150 MHz, CDCl_3)



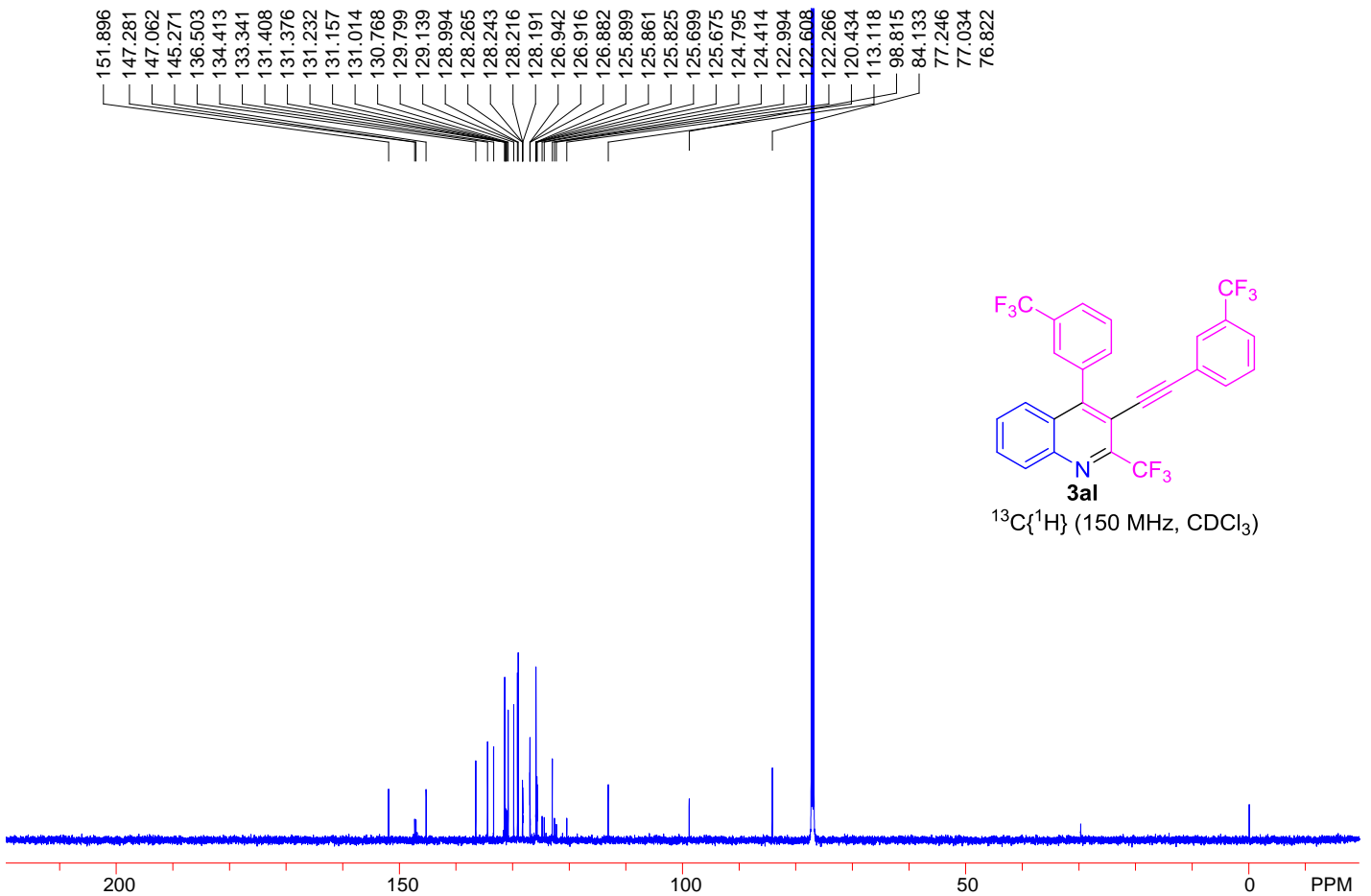




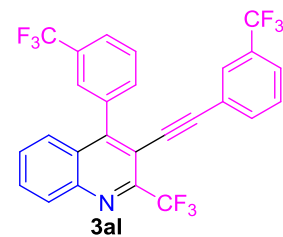
¹H NMR (400 MHz, CDCl₃)



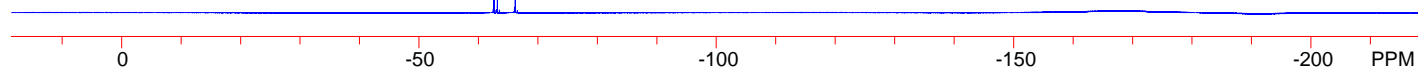
¹³C{¹H} (150 MHz, CDCl₃)

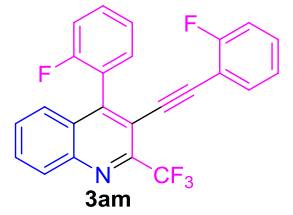
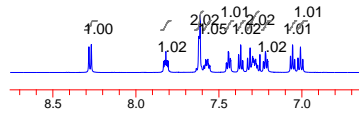
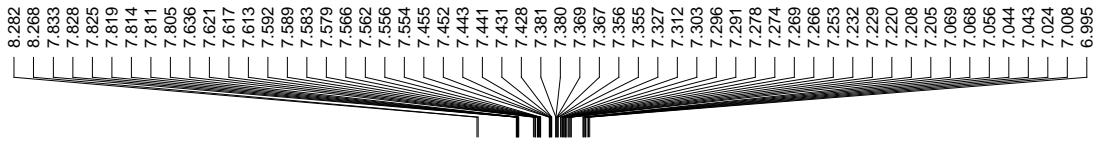


62.605
63.179
66.180

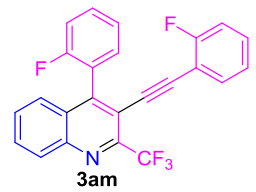
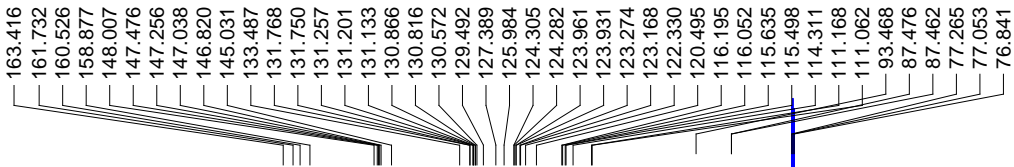
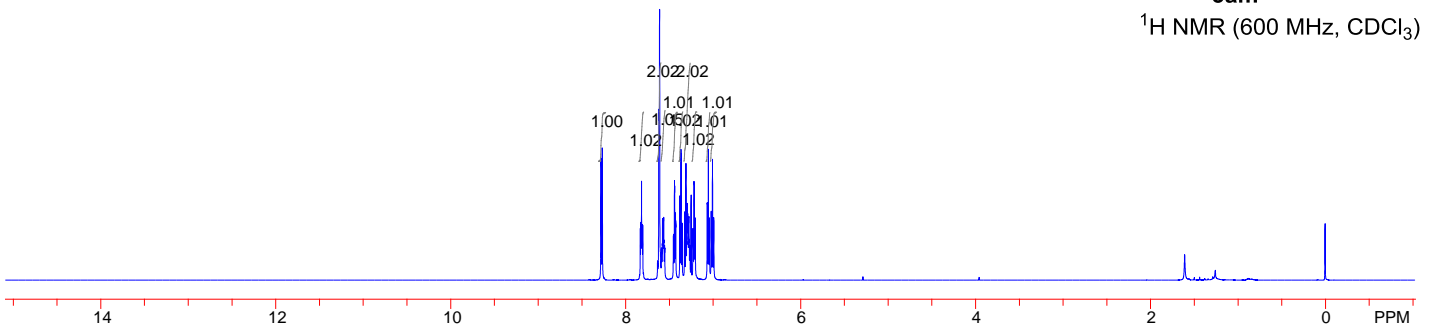


3al
¹⁹F NMR (565 MHz, CDCl₃)

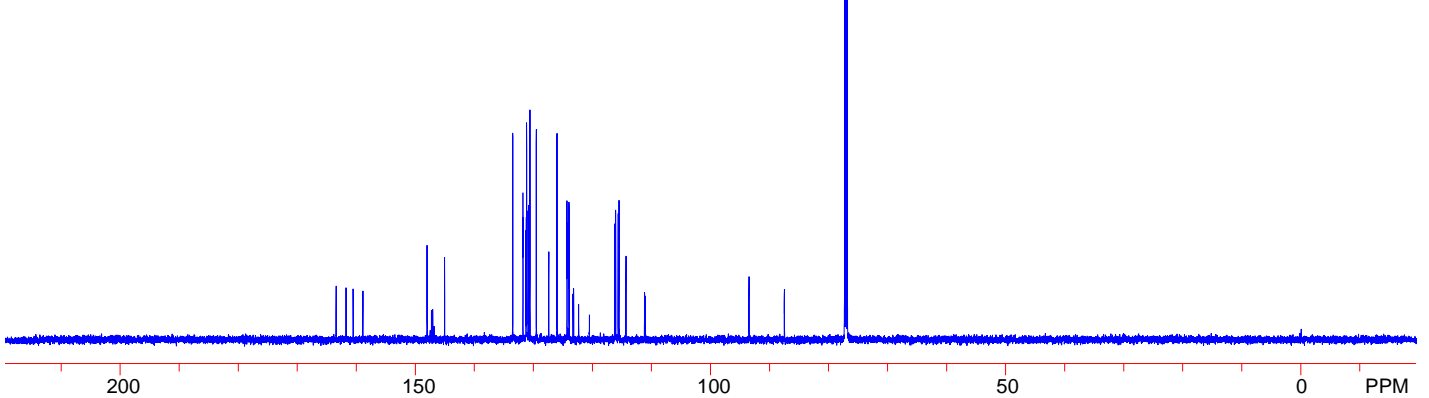


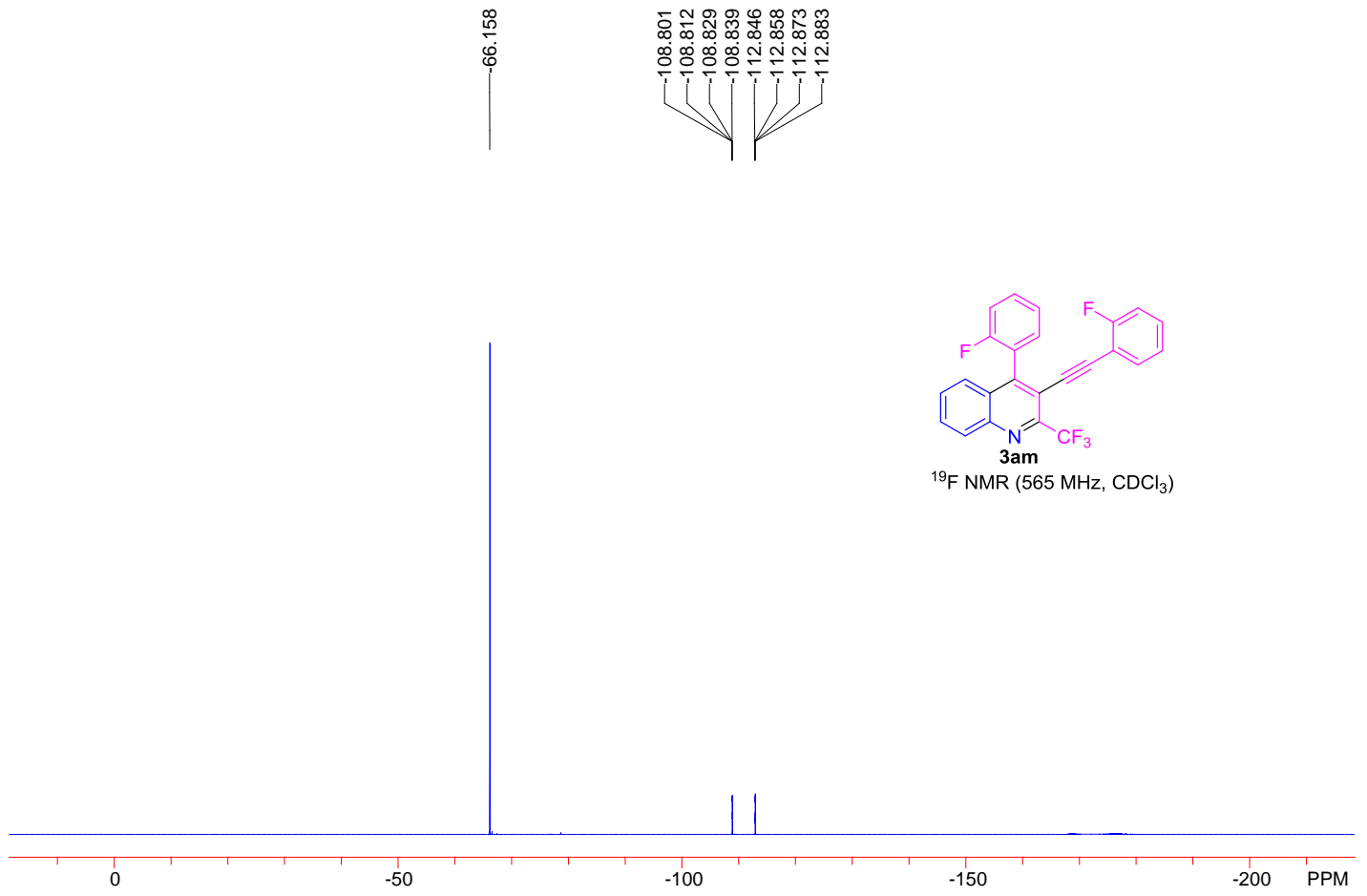


¹H NMR (600 MHz, CDCl₃)

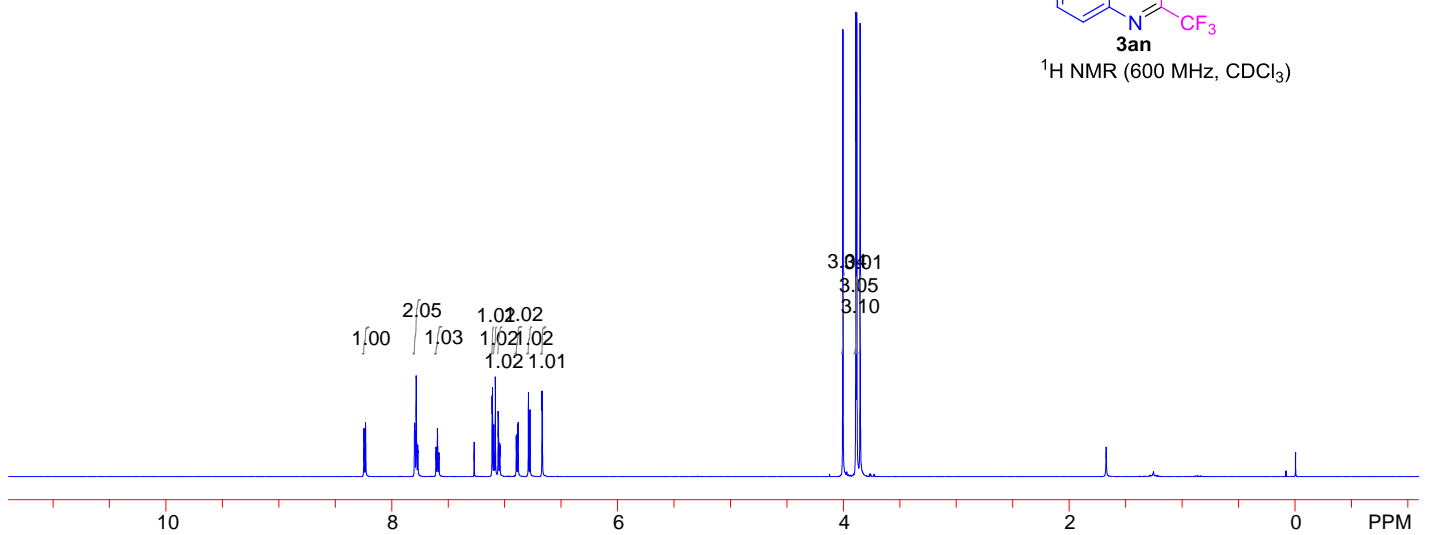
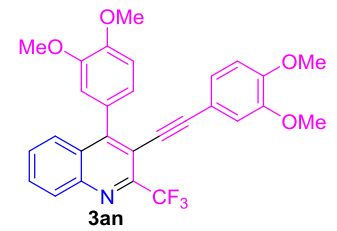


¹³C{¹H} (150 MHz, CDCl₃)

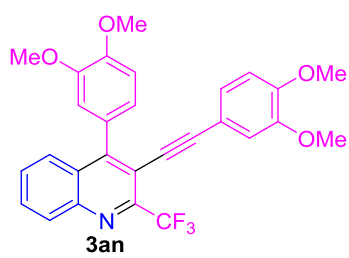




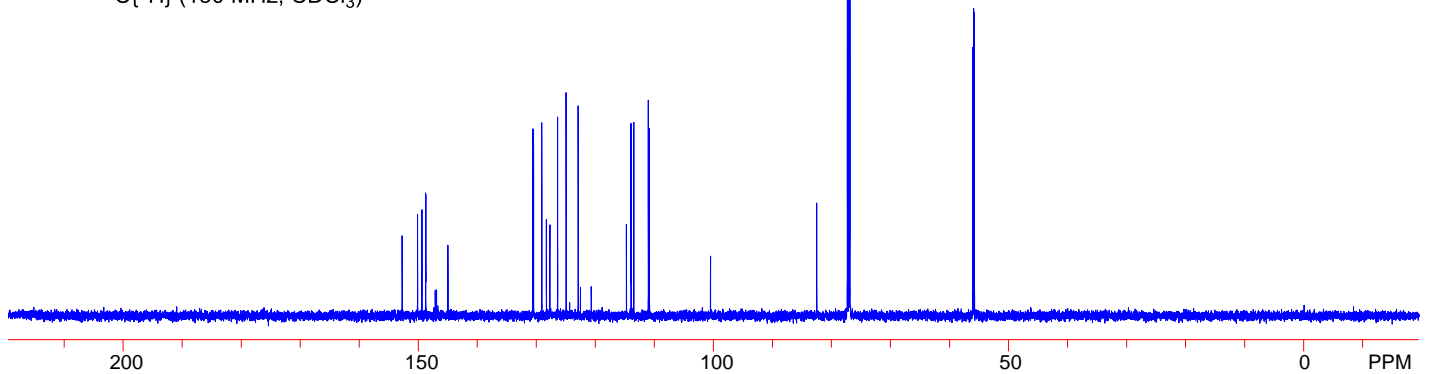
8.246
8.232
7.797
7.795
7.783
7.769
7.767
7.608
7.606
7.594
7.593
7.582
7.581
7.270
7.111
7.108
7.096
7.082
7.057
7.054
7.044
7.040
6.897
6.894
6.883
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6.789
6.775
6.666
6.666
4.004
3.889
3.881
3.851



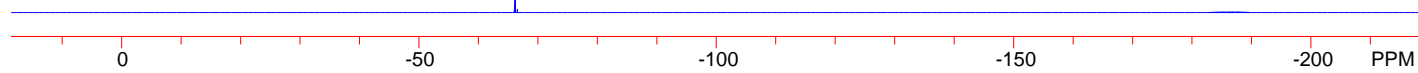
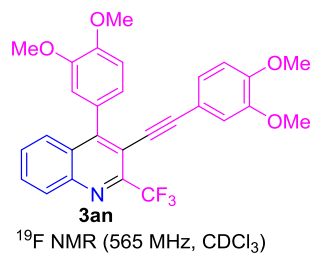
152.722
150.113
149.371
148.753
148.722
147.118
146.903
144.964
130.575
130.456
129.059
128.283
127.696
126.376
124.940
122.897
122.516
120.682
114.729
113.953
113.917
113.479
111.022
110.838
100.474
82.485
77.294
77.083
76.870
56.090
56.028
55.939
55.793

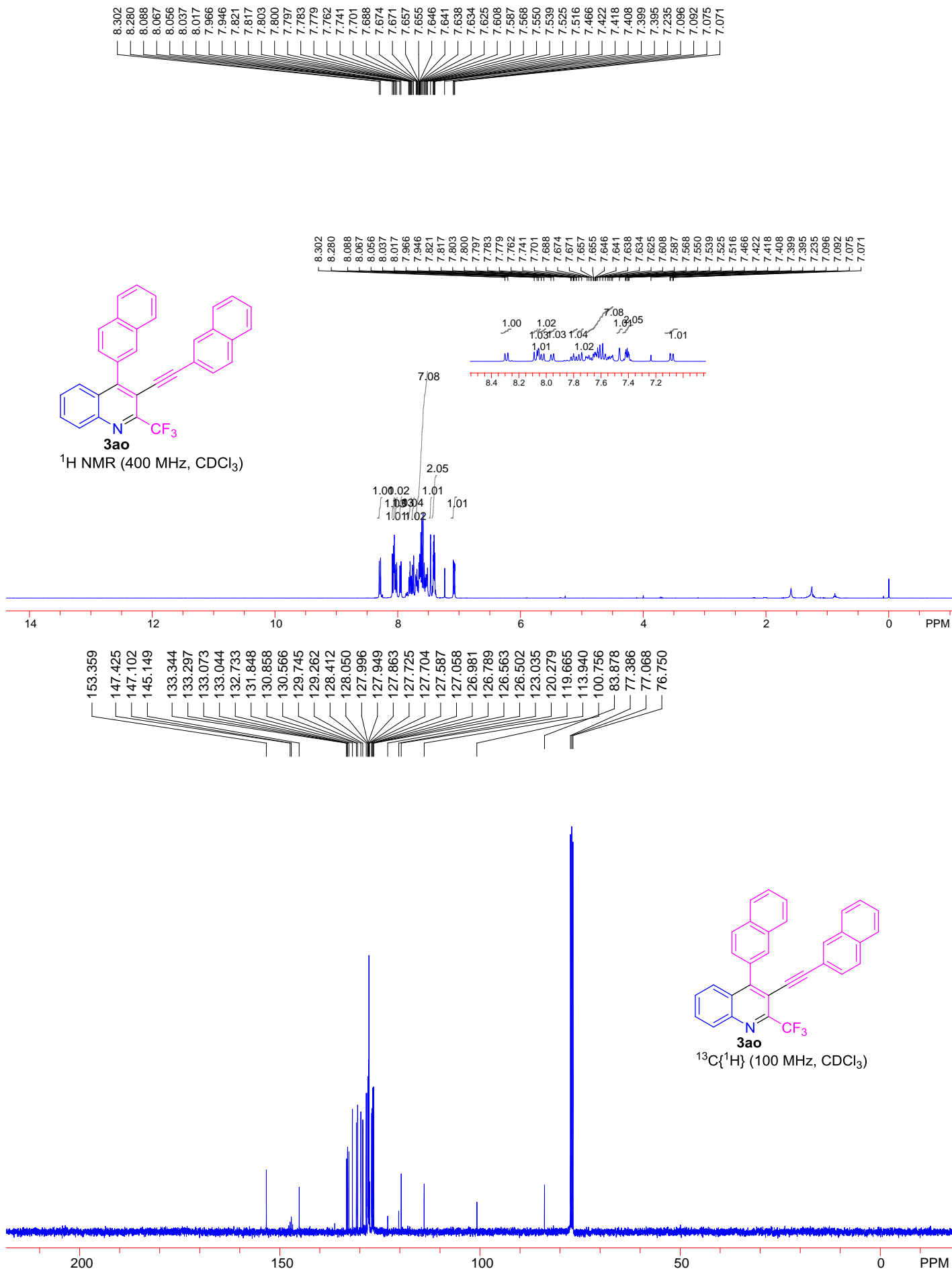


¹³C{¹H} (150 MHz, CDCl₃)

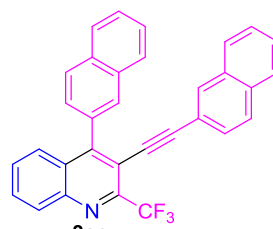


66.157

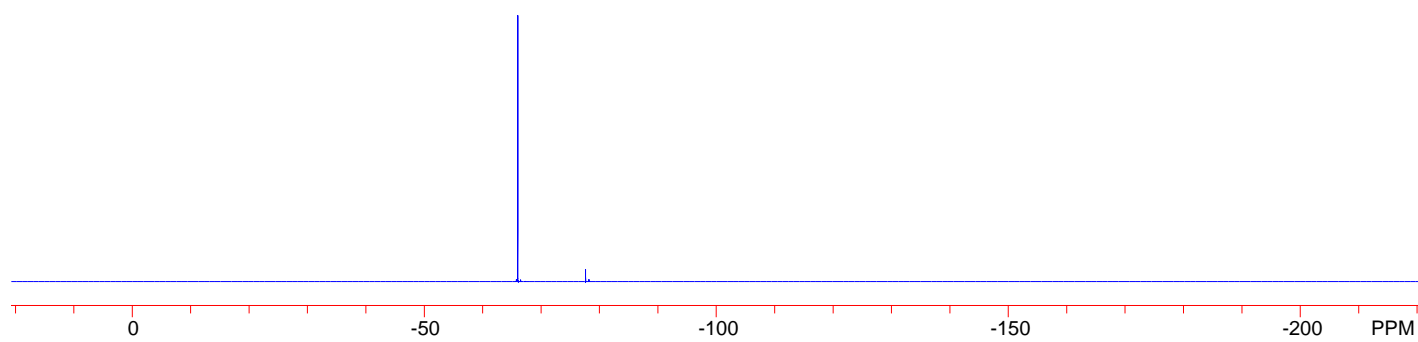


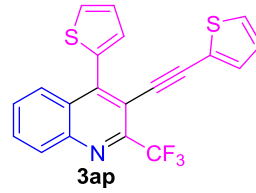
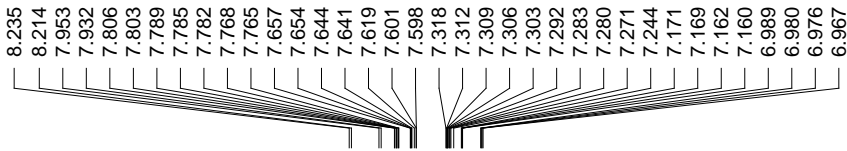


65.991

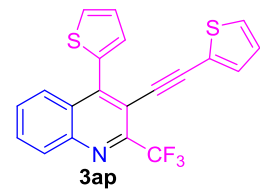
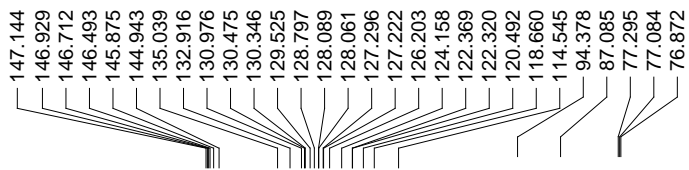
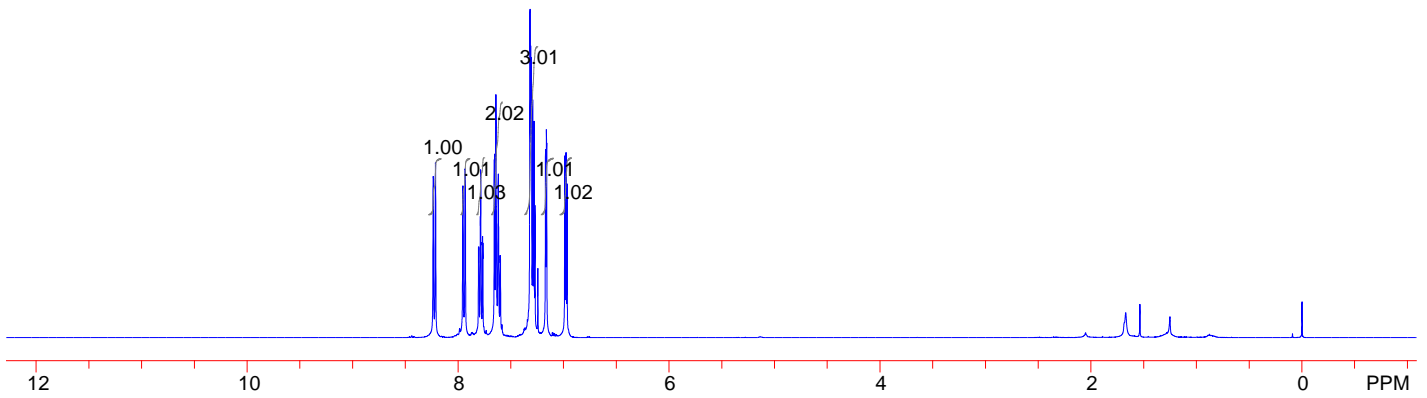


¹⁹F NMR (376 MHz, CDCl₃)

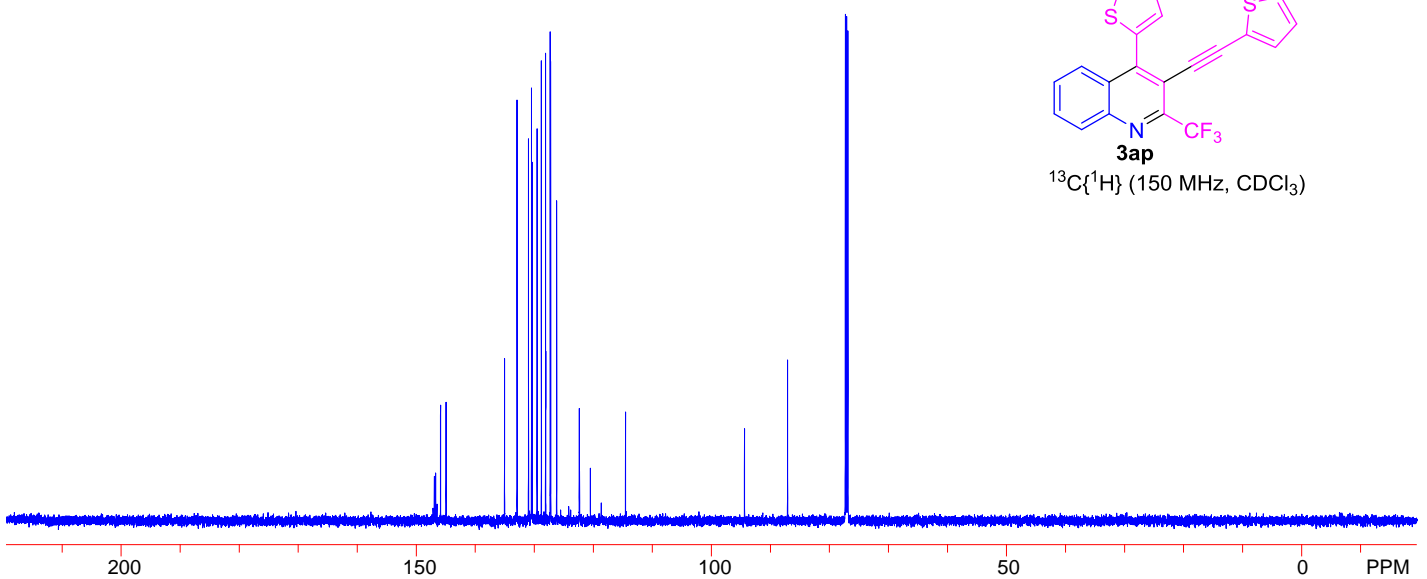




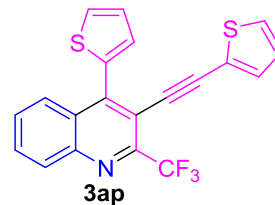
^1H NMR (400 MHz, CDCl_3)



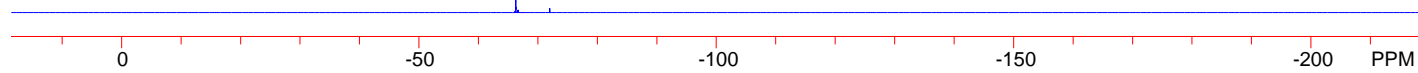
$^{13}\text{C}\{^1\text{H}\}$ (150 MHz, CDCl_3)

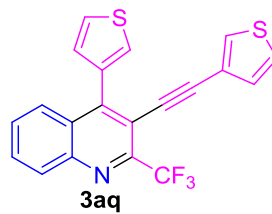
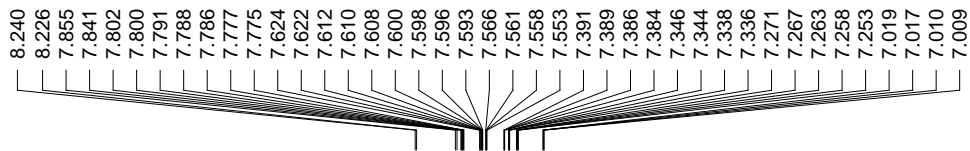


66.269

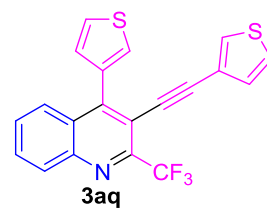
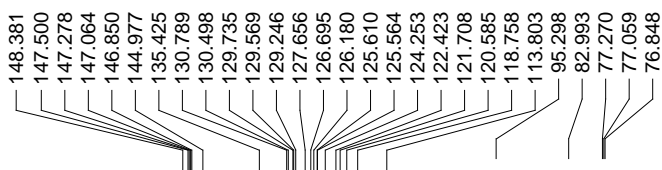
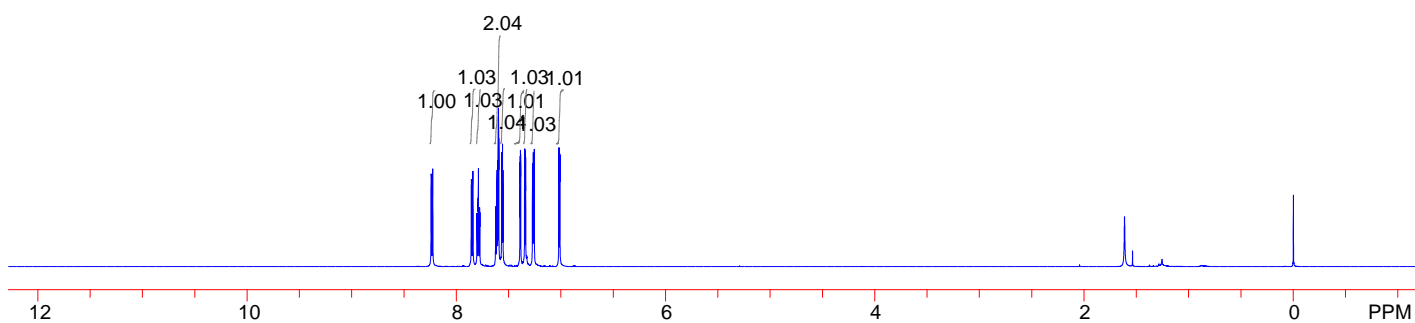


^{19}F NMR (565 MHz, CDCl_3)

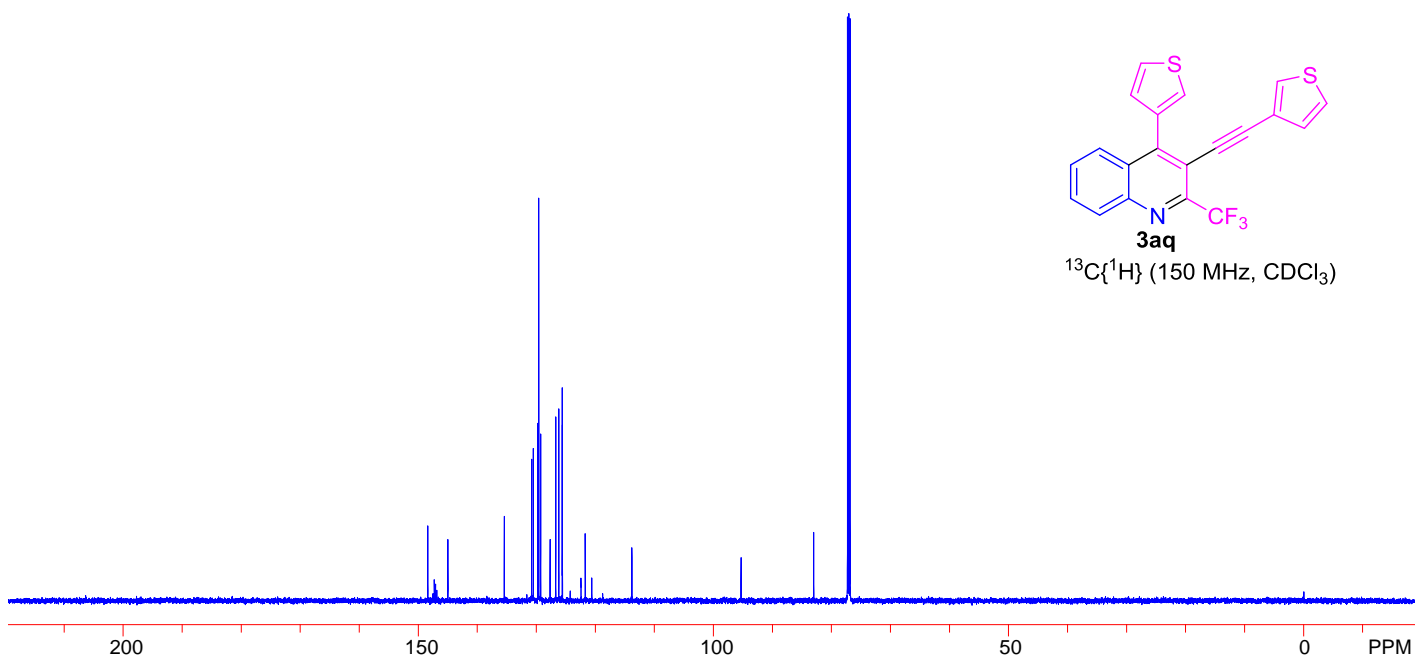




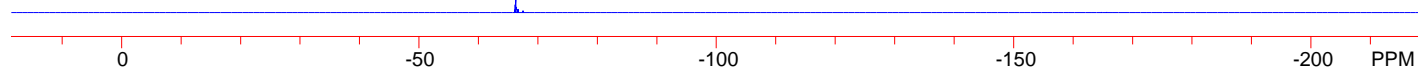
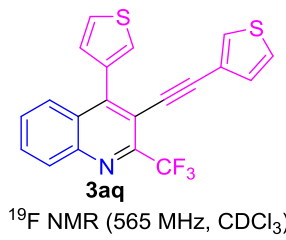
¹H NMR (600 MHz, CDCl₃)



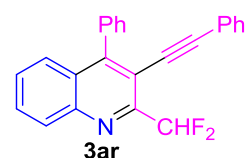
¹³C{¹H} (150 MHz, CDCl₃)



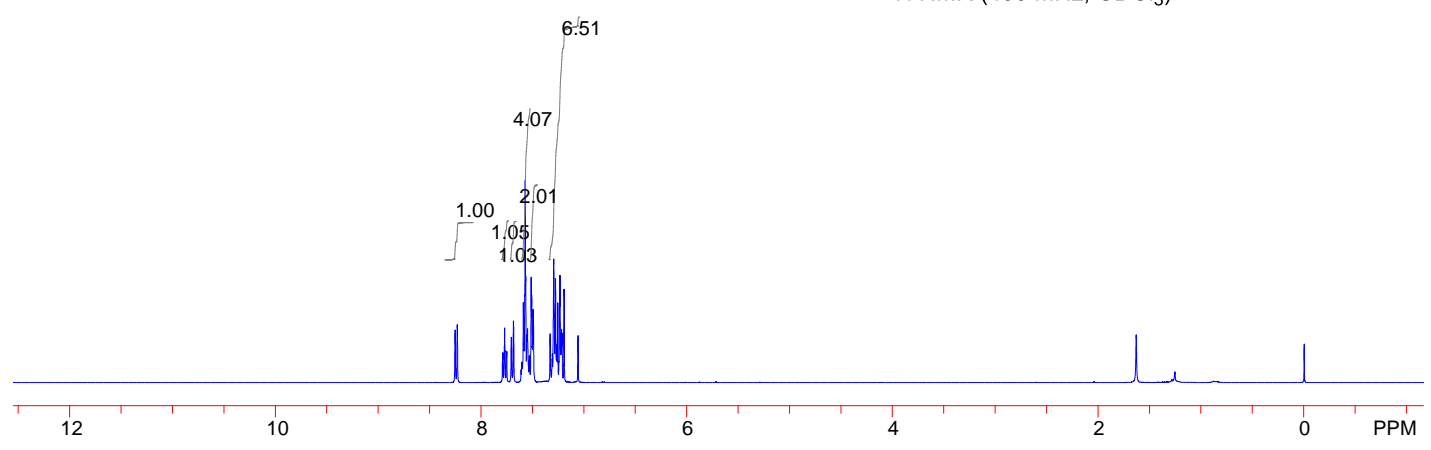
66.269



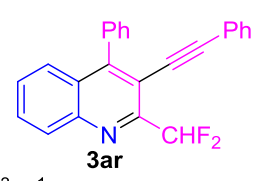
8.251
8.230
7.790
7.786
7.772
7.769
7.765
7.748
7.705
7.684
7.601
7.587
7.574
7.568
7.564
7.554
7.550
7.546
7.526
7.511
7.506
7.492
7.488
7.327
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7.252
7.234
7.230
7.215
7.210
7.191
7.055



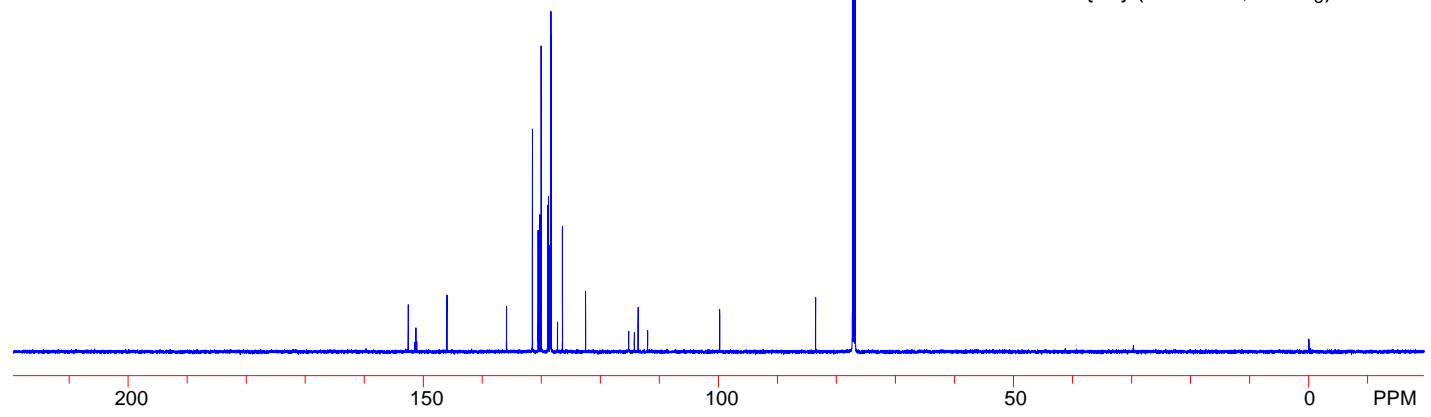
$^1\text{H NMR}$ (400 MHz, CDCl_3)

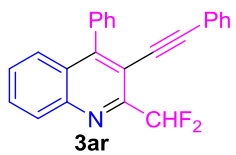


152.545
151.397
151.247
151.089
145.982
135.879
131.497
130.545
130.263
130.016
128.914
128.762
128.522
128.361
128.317
127.253
126.413
122.491
115.196
114.237
113.596
111.991
99.775
83.527
77.262
77.051
76.839

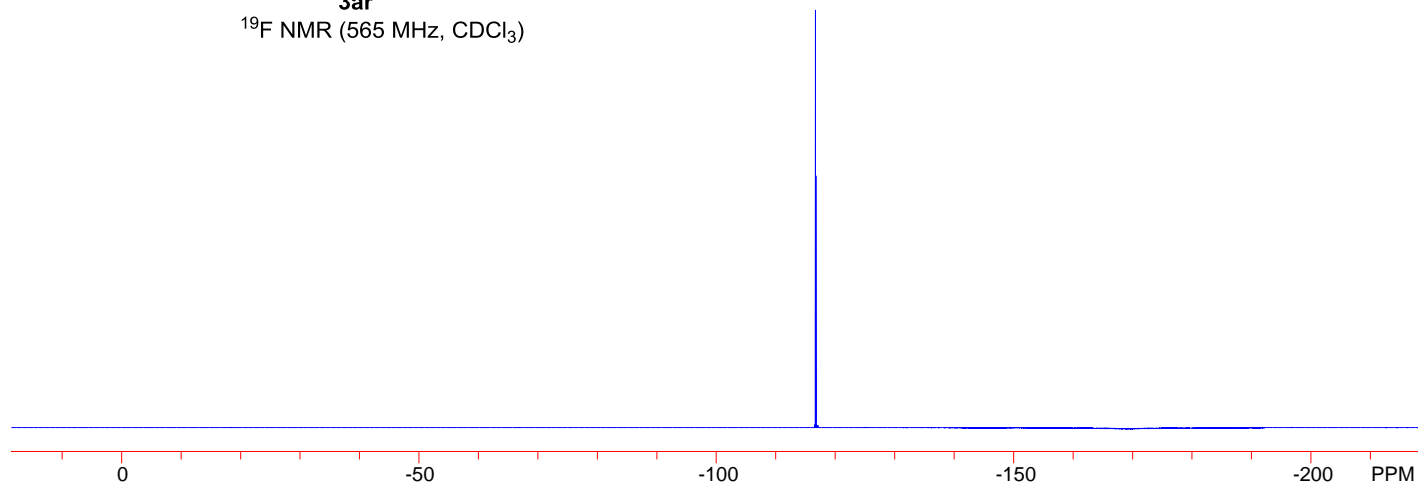


$^{13}\text{C}\{^1\text{H}\}$ (150 MHz, CDCl_3)

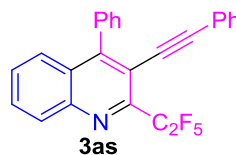




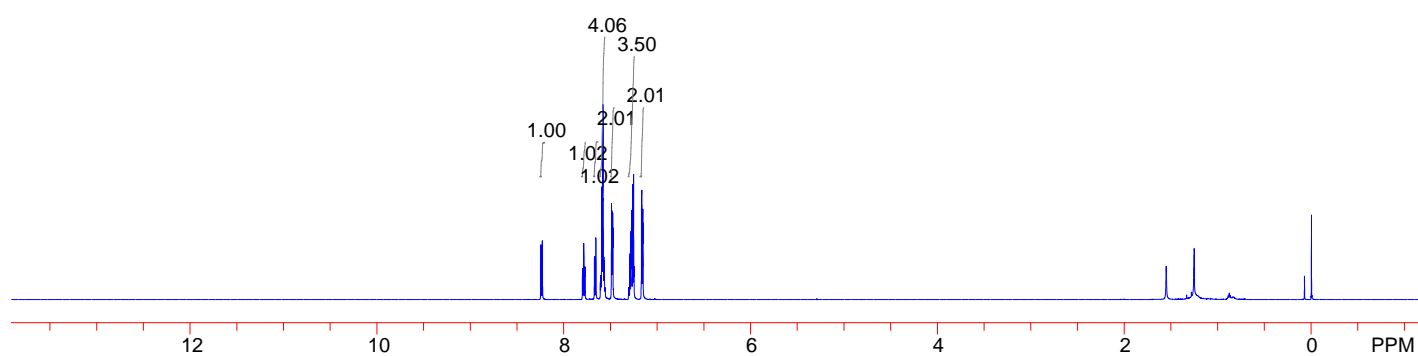
^{19}F NMR (565 MHz, CDCl_3)



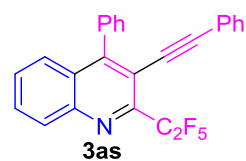
8.243
8.229
7.799
7.797
7.788
7.785
7.783
7.774
7.772
7.670
7.657
7.608
7.603
7.593
7.591
7.581
7.577
7.570
7.569
7.567
7.565
7.489
7.486
7.483
7.476
7.474
7.307
7.302
7.298
7.292
7.287
7.283
7.281
7.278
7.274
7.264
7.262
7.253
7.248
7.168
7.165
7.158
7.154
7.152



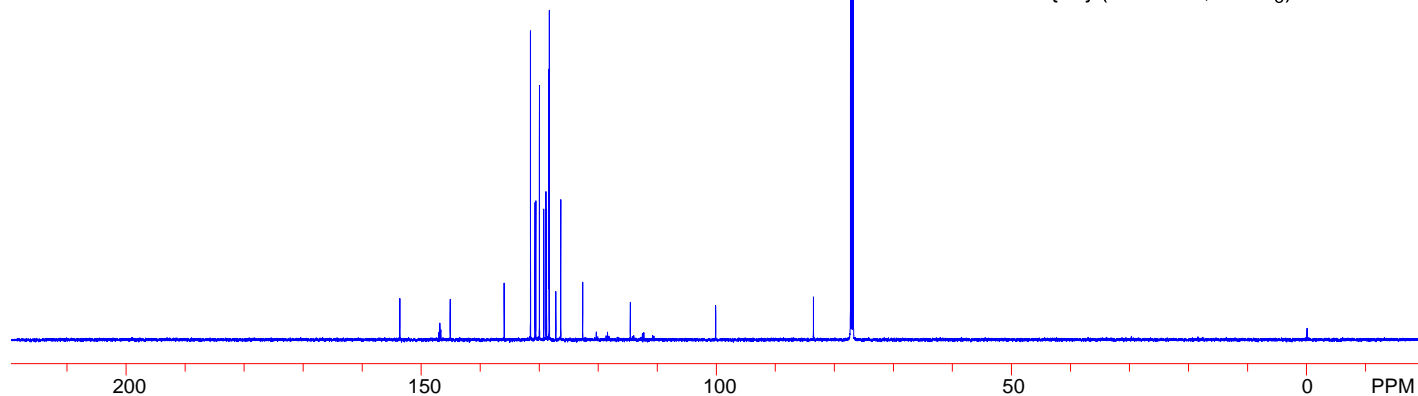
$^1\text{H NMR}$ (600 MHz, CDCl_3)

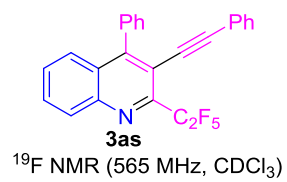


153.621
146.992
146.822
146.665
145.080
135.938
131.480
130.713
130.581
129.967
129.224
128.846
128.757
128.327
128.292
127.193
126.355
122.636
120.573
120.330
120.087
118.668
118.426
118.189
114.561
114.226
113.988
112.518
112.282
110.821
110.574
100.114
83.538
77.248
77.036
76.825



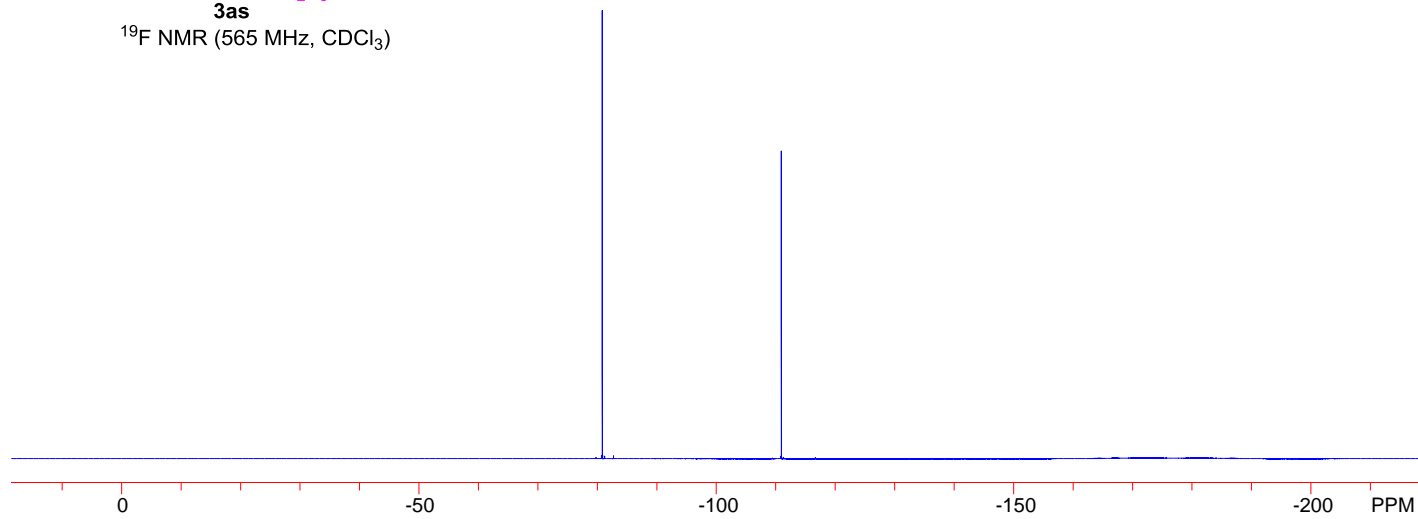
$^{13}\text{C}\{^1\text{H}\}$ (150 MHz, CDCl_3)



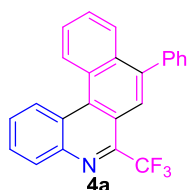
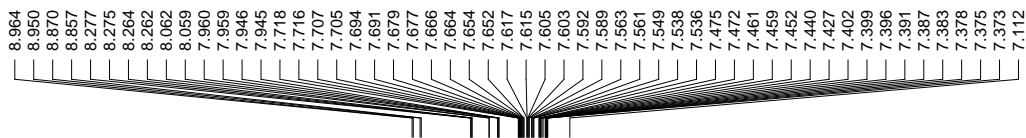


-80.804

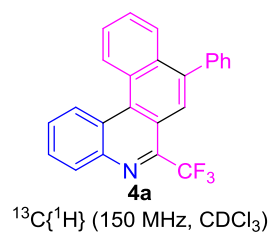
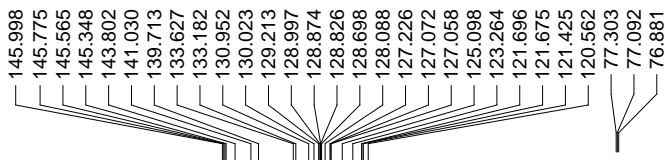
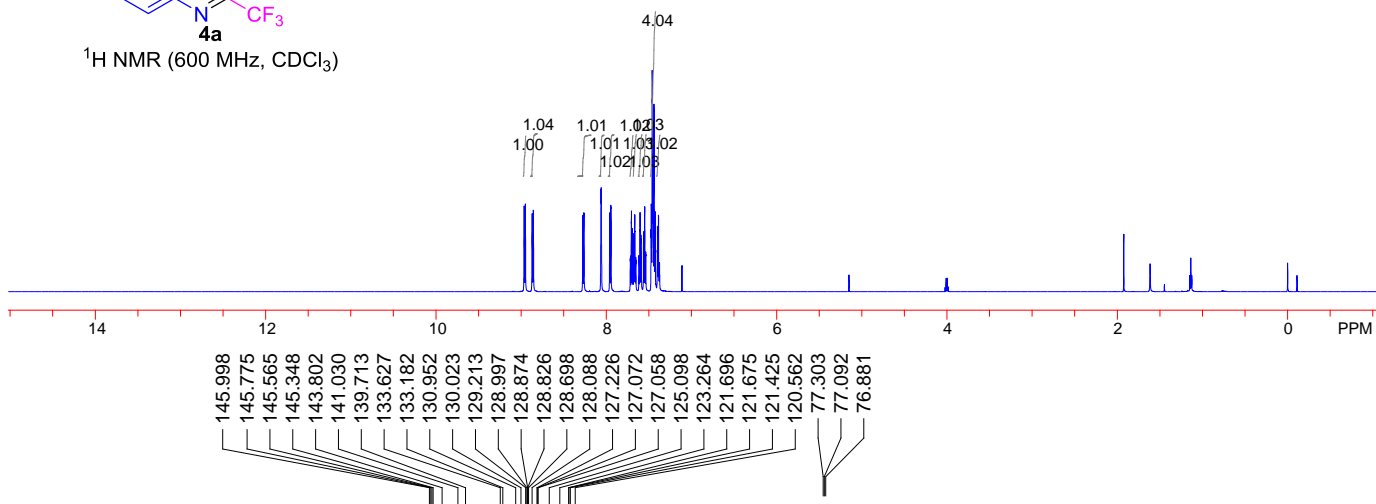
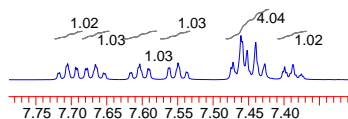
-110.882



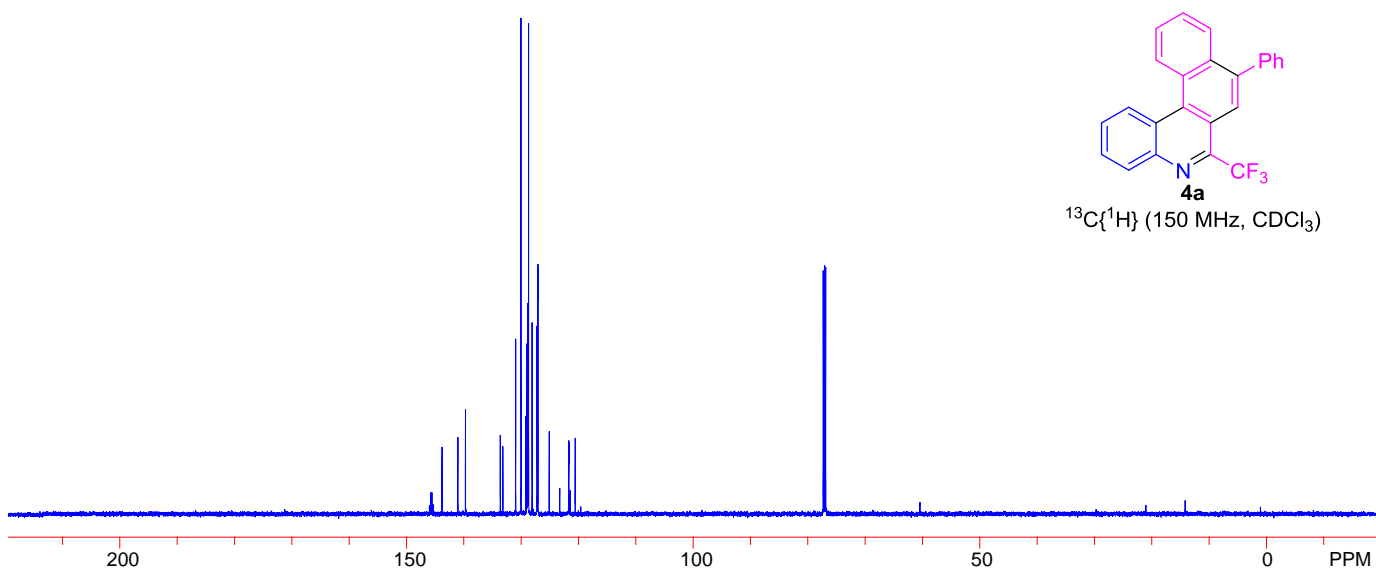
V. NMR spectra of 4a-4l



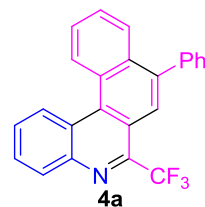
^1H NMR (600 MHz, CDCl_3)



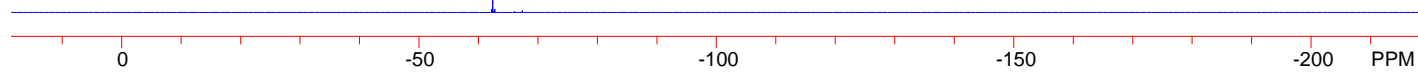
$^{13}\text{C}\{^1\text{H}\}$ (150 MHz, CDCl_3)

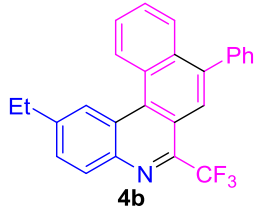
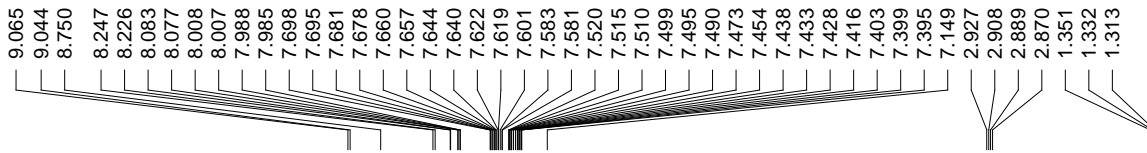


62.364

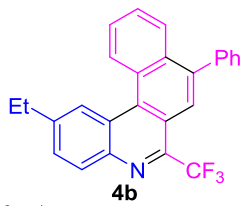
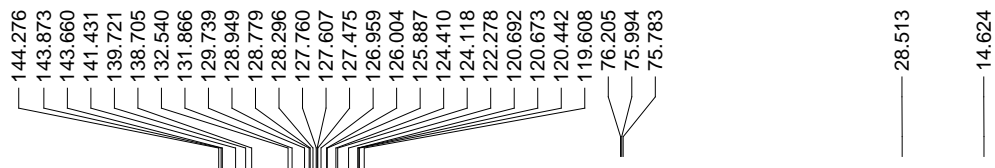
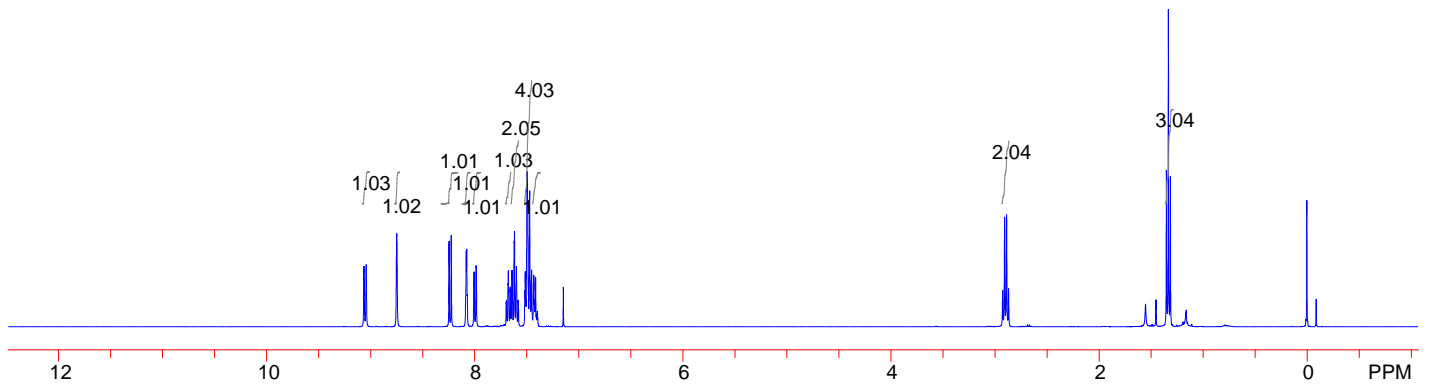


^{19}F NMR (565 MHz, CDCl_3)

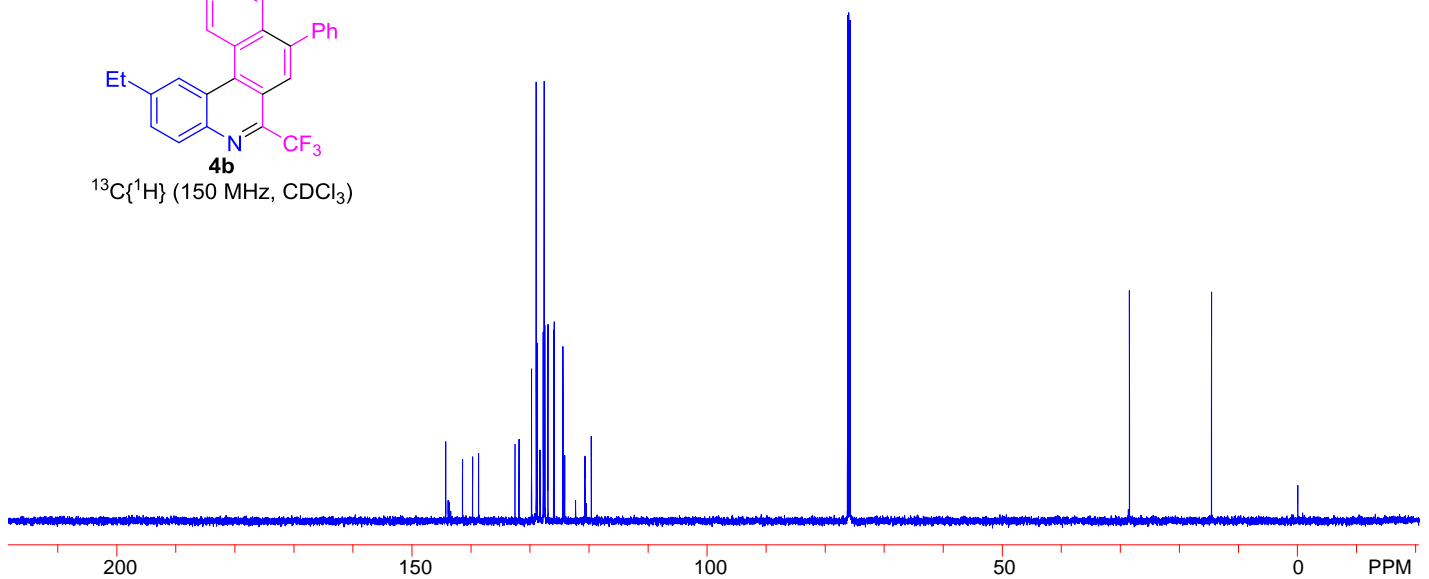




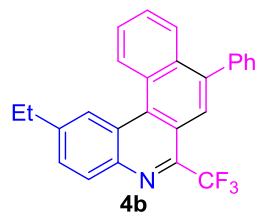
$^1\text{H NMR}$ (400 MHz, CDCl_3)



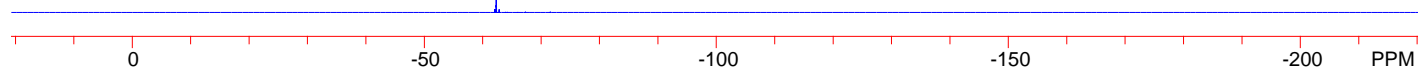
$^{13}\text{C}\{^1\text{H}\}$ (150 MHz, CDCl_3)

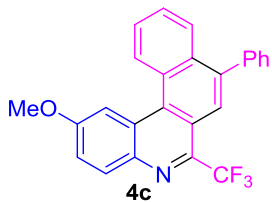
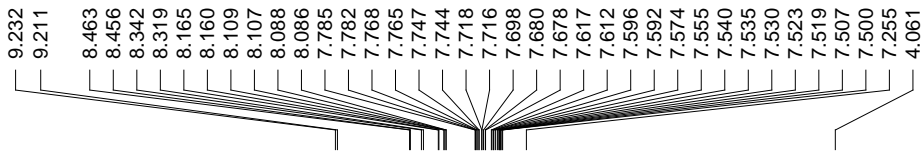


62.304
62.311

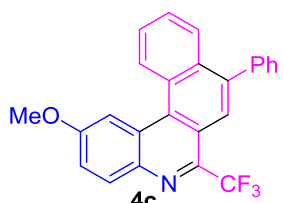
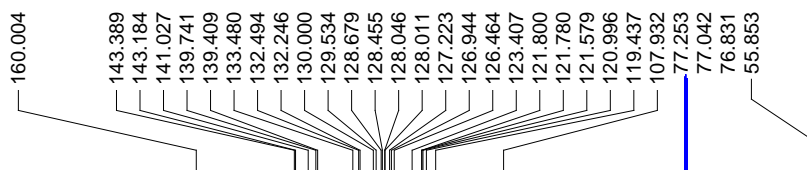
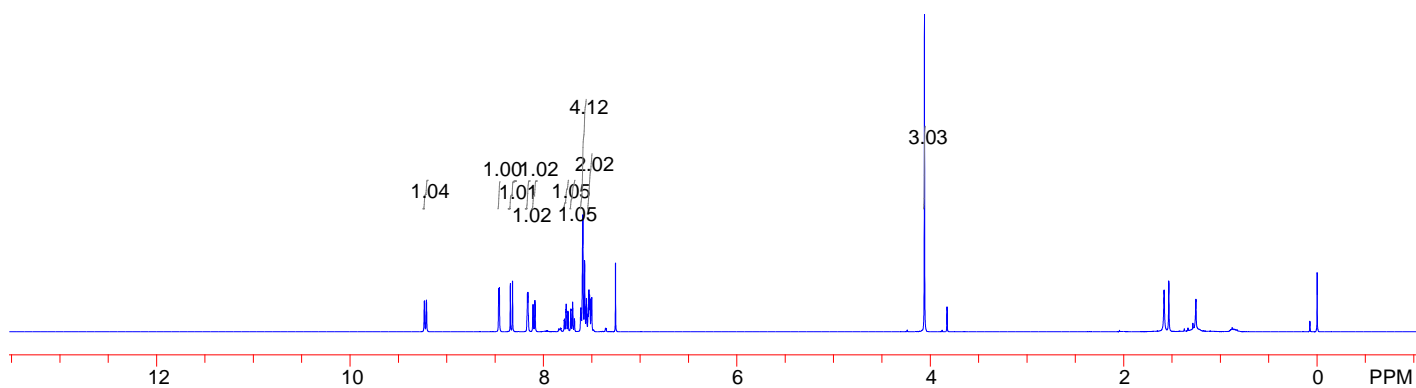


^{19}F NMR (376 MHz, CDCl_3)

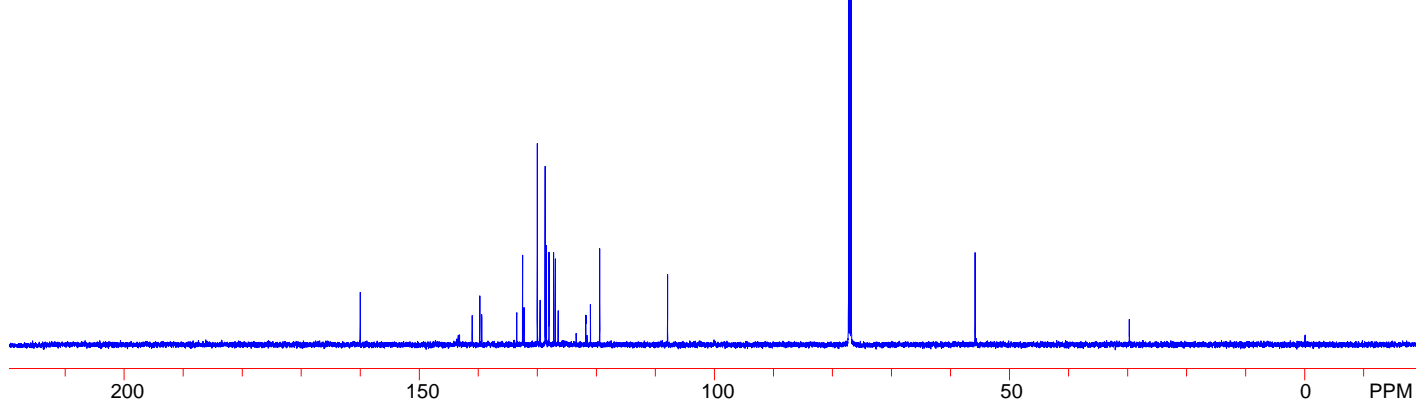




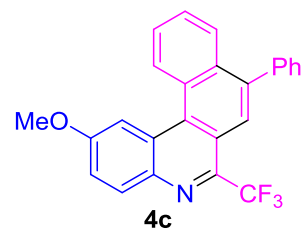
^1H NMR (400 MHz, CDCl_3)



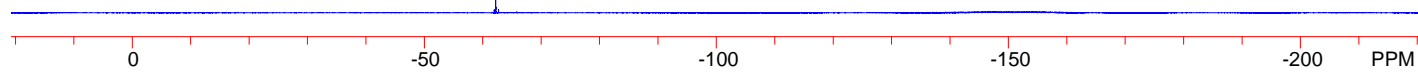
$^{13}\text{C}\{^1\text{H}\}$ (150 MHz, CDCl_3)

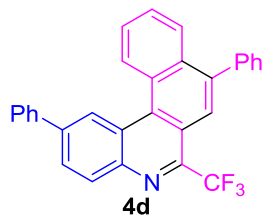
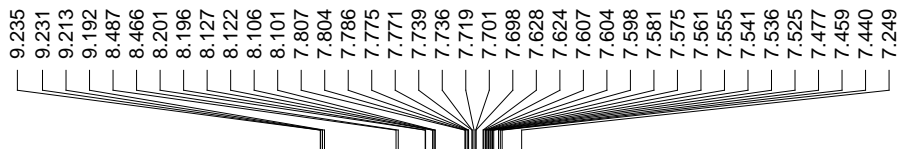


62.204
62.211

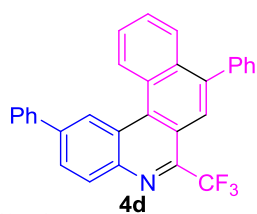
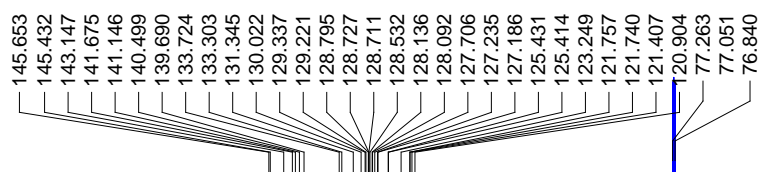
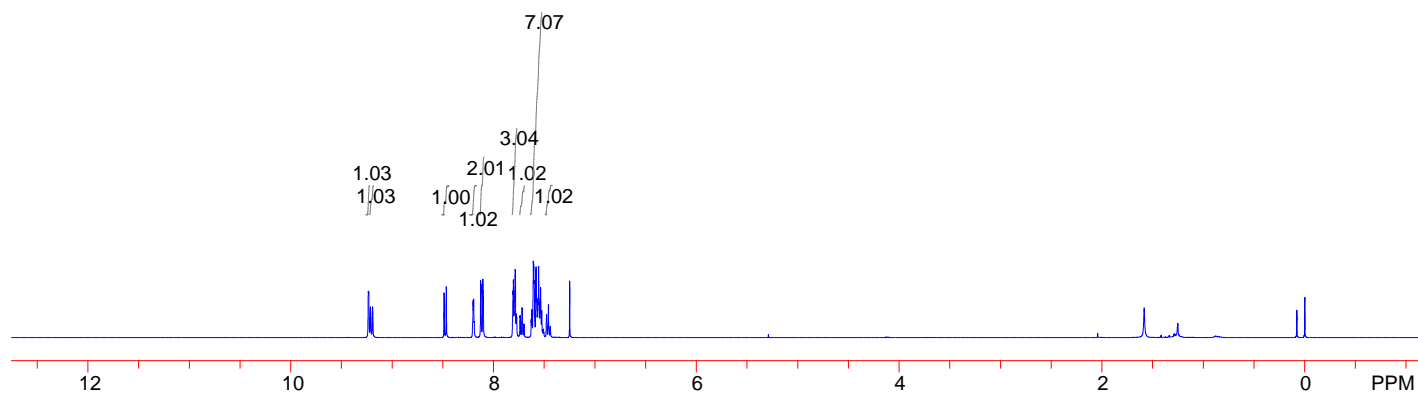


¹⁹F NMR (376 MHz, CDCl₃)

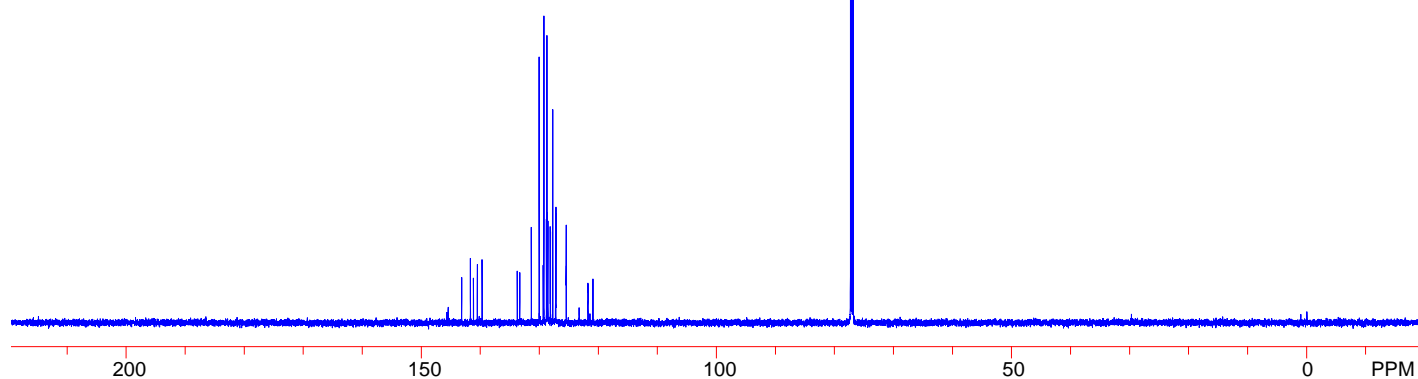




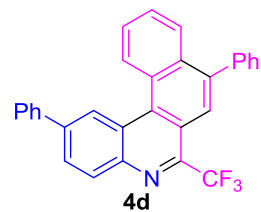
^1H NMR (400 MHz, CDCl_3)



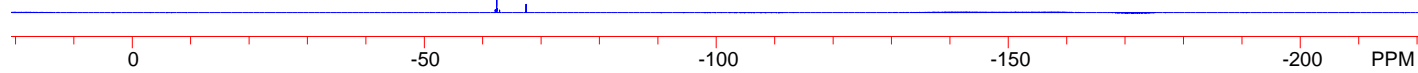
$^{13}\text{C}\{^1\text{H}\}$ (150 MHz, CDCl_3)

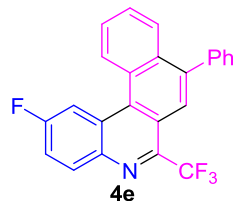
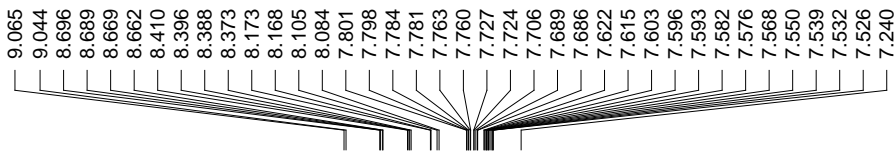


62.392
62.399

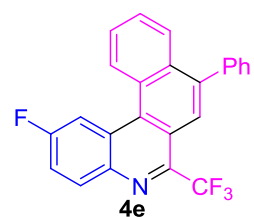
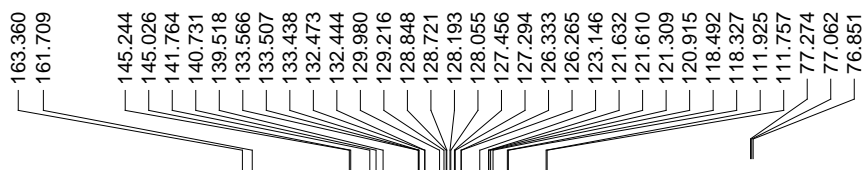
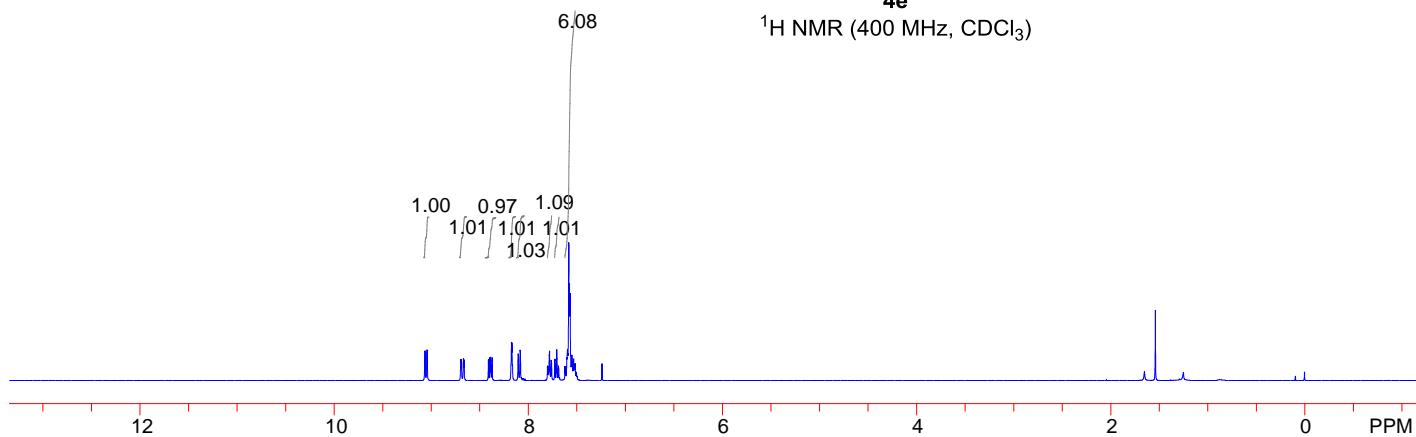


^{19}F NMR (376 MHz, CDCl_3)

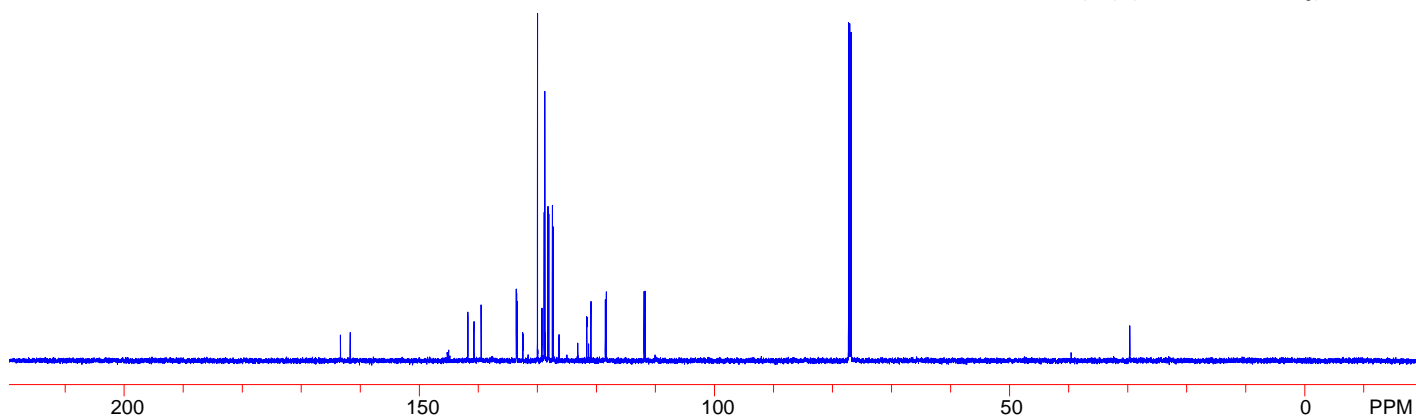


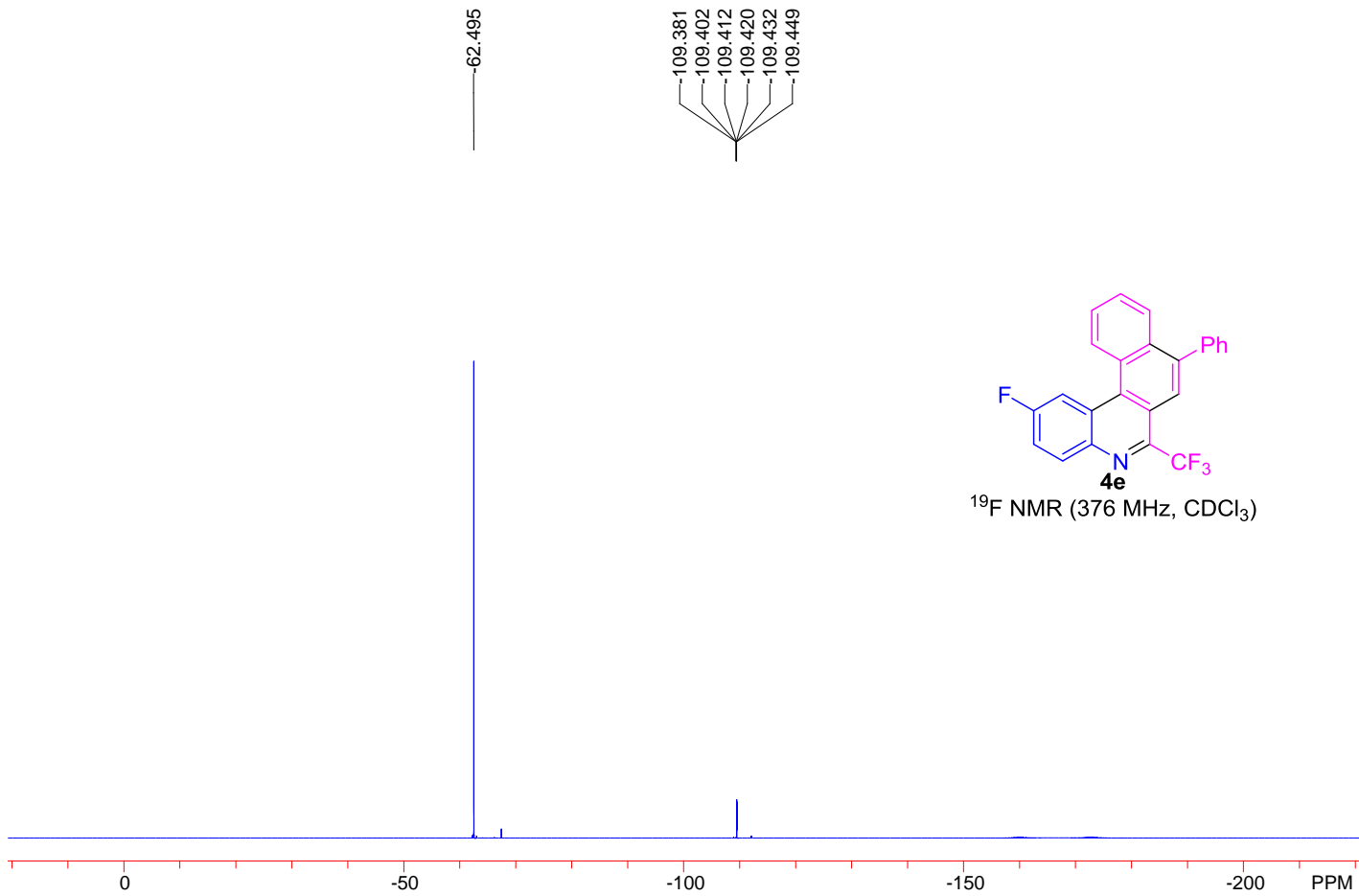


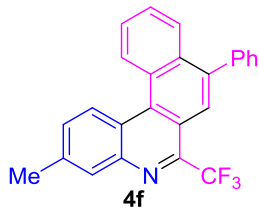
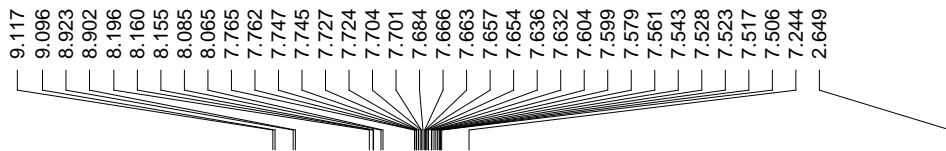
^1H NMR (400 MHz, CDCl_3)



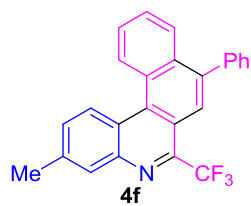
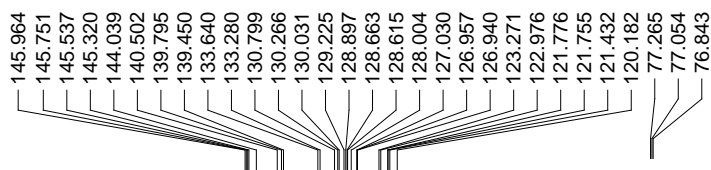
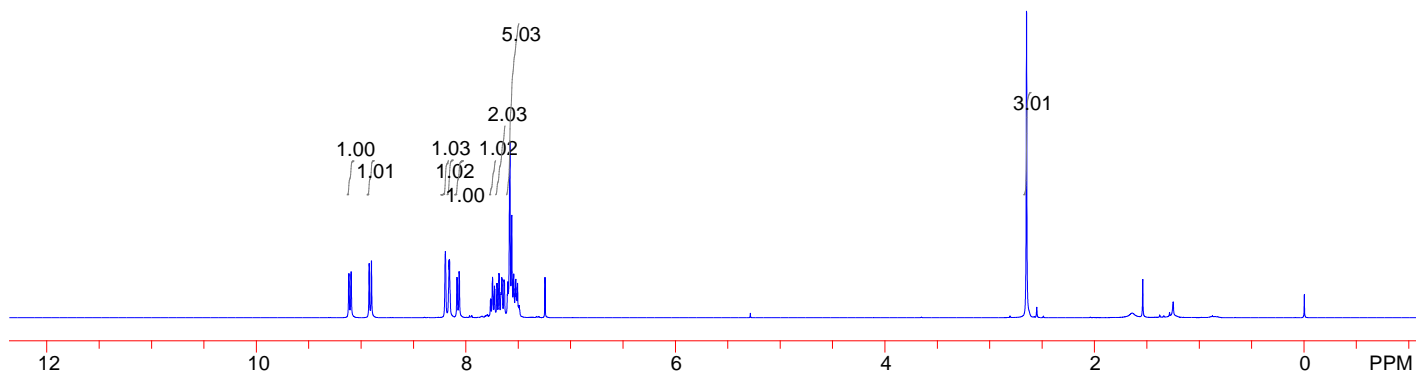
$^{13}\text{C}\{^1\text{H}\}$ (150 MHz, CDCl_3)



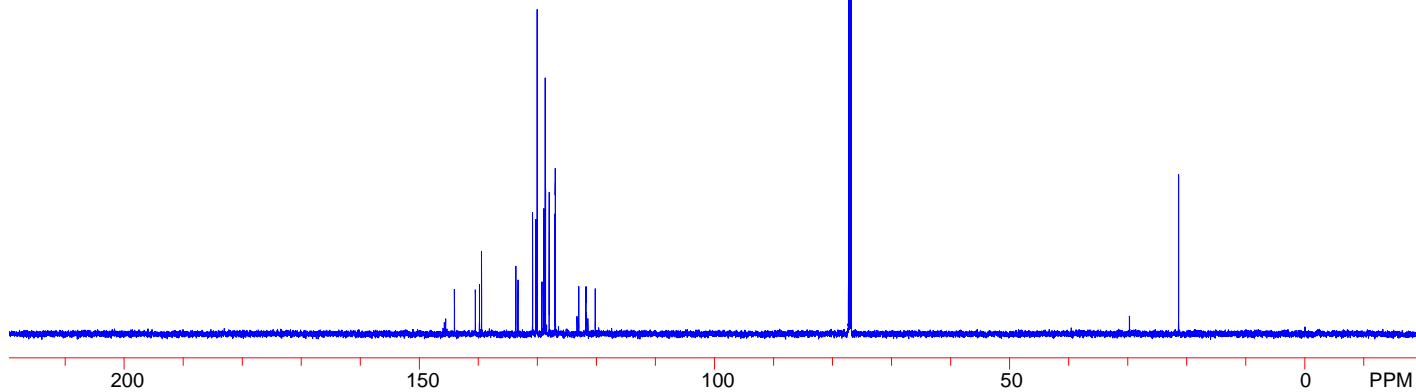




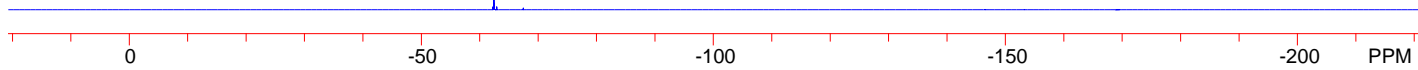
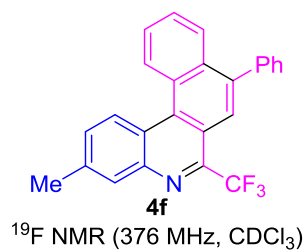
^1H NMR (400 MHz, CDCl_3)

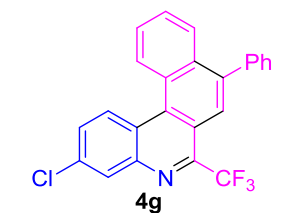
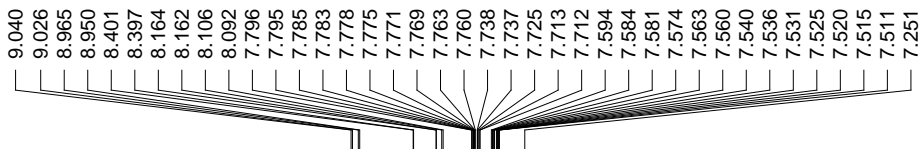


$^{13}\text{C}\{^1\text{H}\}$ (150 MHz, CDCl_3)

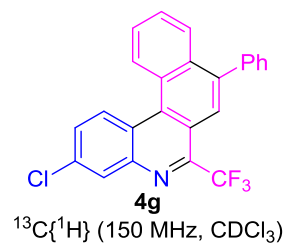
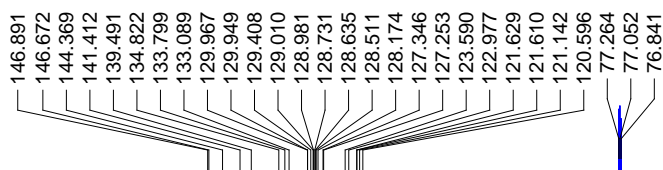
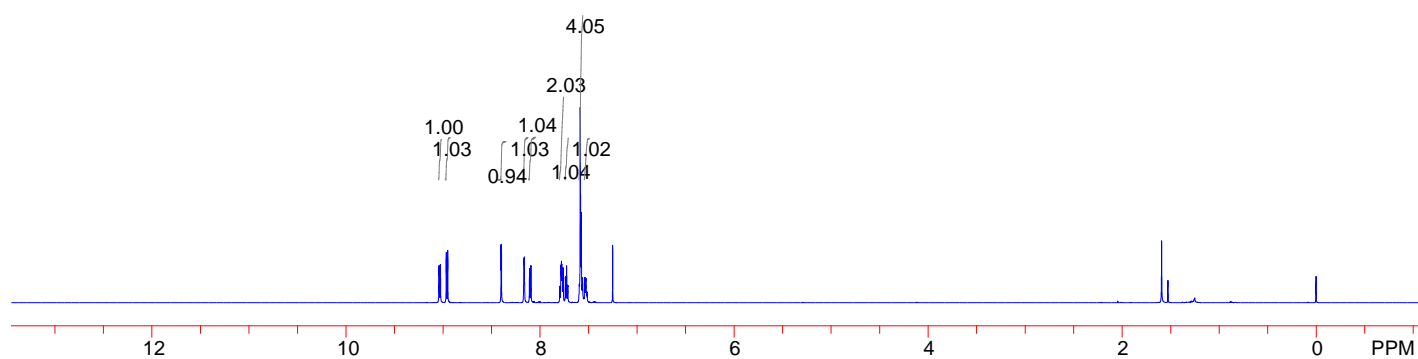


62.418

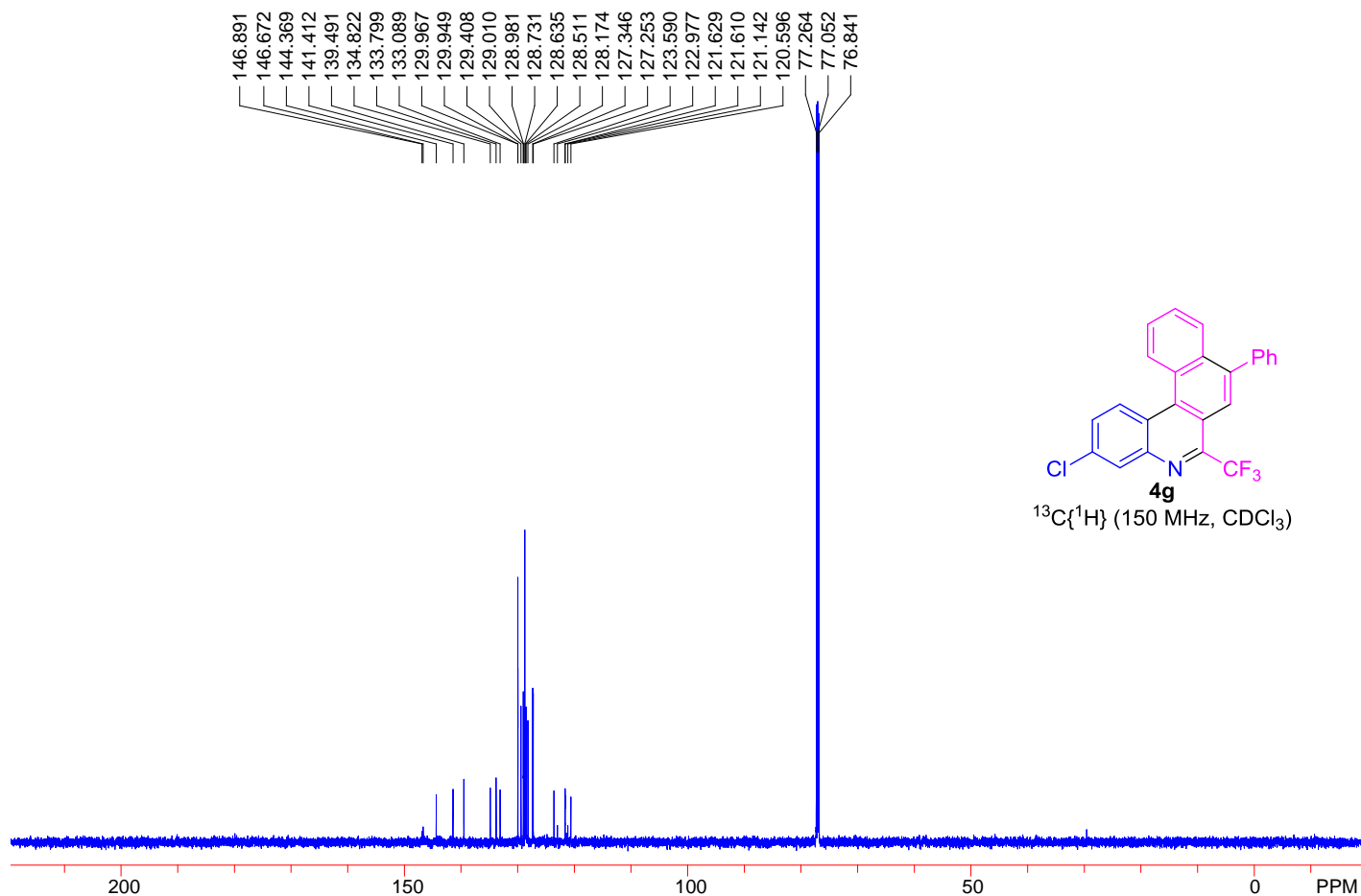




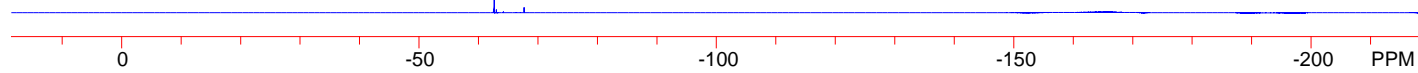
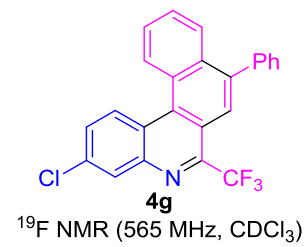
$^1\text{H NMR}$ (600 MHz, CDCl_3)



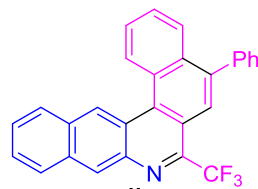
$^{13}\text{C}\{^1\text{H}\}$ (150 MHz, CDCl_3)



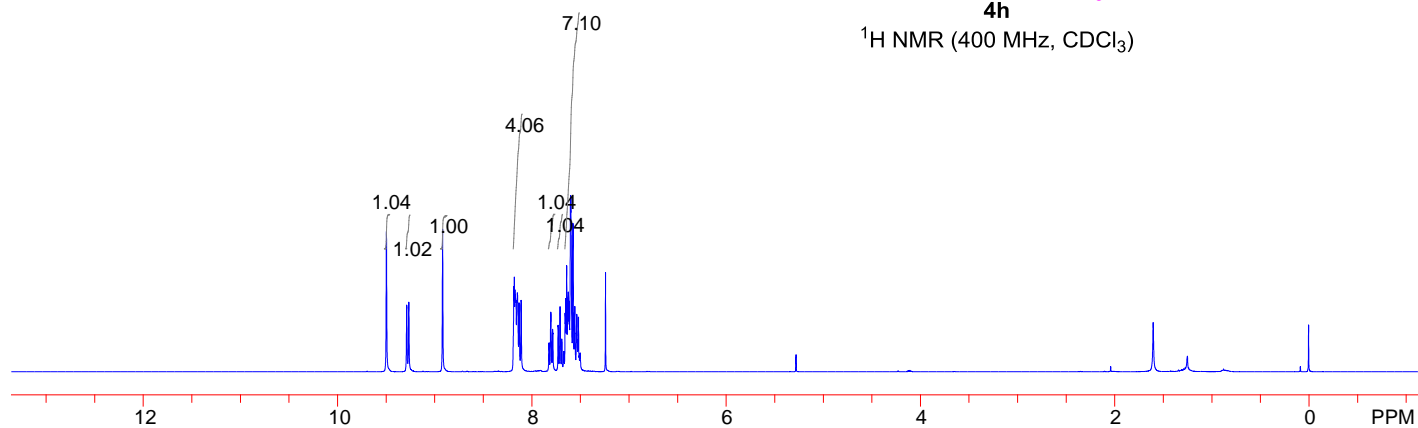
62.632



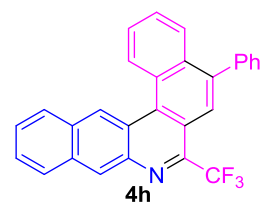
9.497
9.288
9.267
8.919
8.186
8.181
8.175
8.165
8.155
8.149
8.132
8.111
7.825
7.822
7.805
7.787
7.784
7.730
7.728
7.710
7.692
7.658
7.650
7.642
7.634
7.626
7.619
7.614
7.603
7.599
7.577
7.558
7.542
7.538
7.533
7.528
7.520
7.243



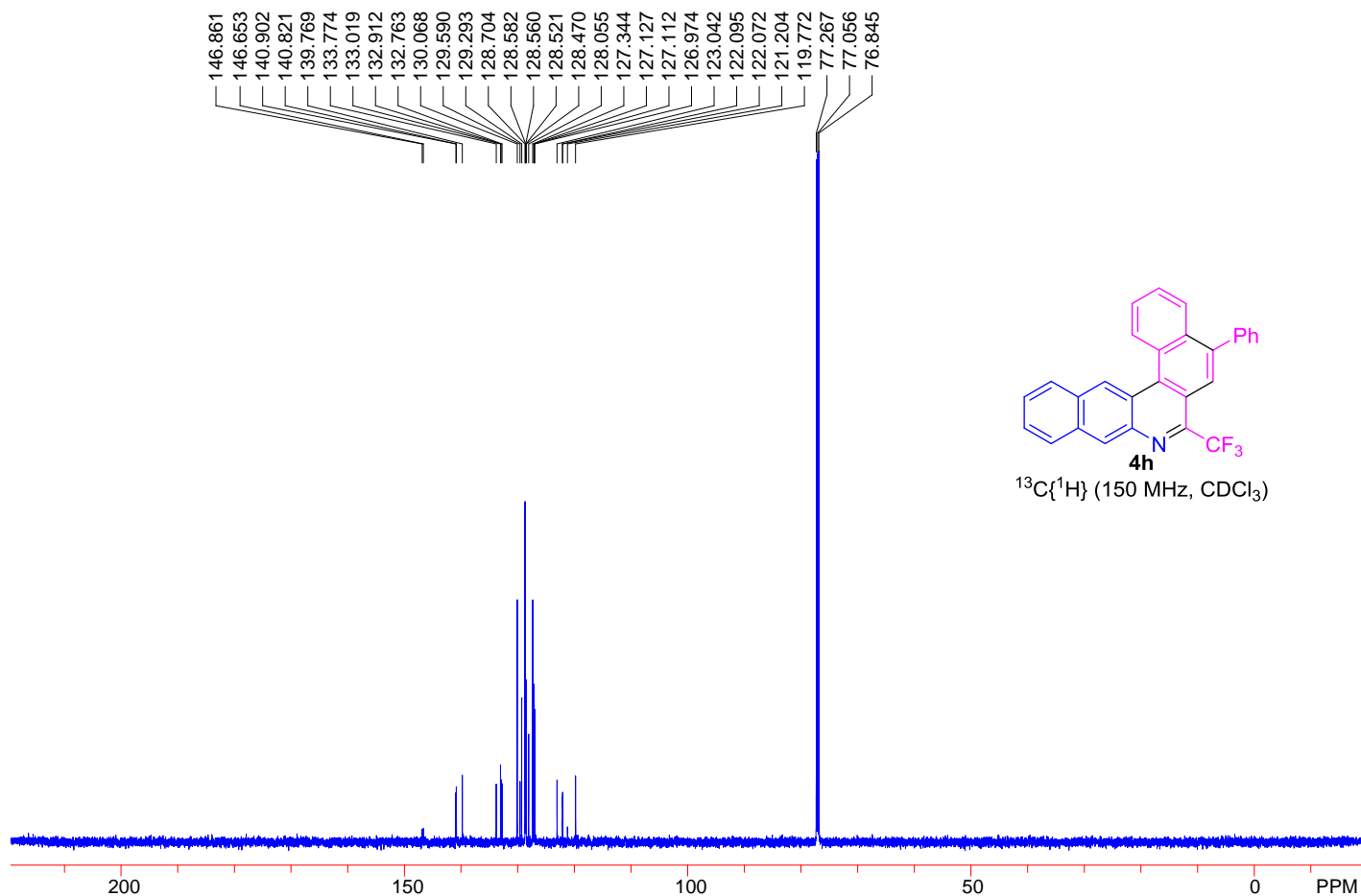
$^1\text{H NMR}$ (400 MHz, CDCl_3)



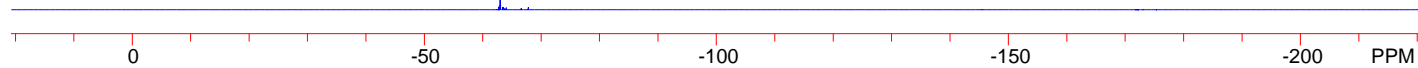
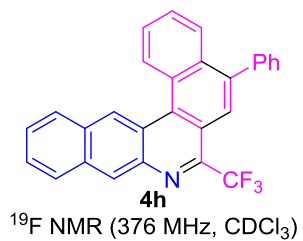
146.861
146.653
140.902
140.821
139.769
133.774
133.019
132.912
132.763
130.068
129.590
129.293
128.704
128.582
128.560
128.521
128.470
128.055
127.344
127.127
127.112
126.974
123.042
122.095
122.072
121.204
119.772
77.267
77.056
76.845



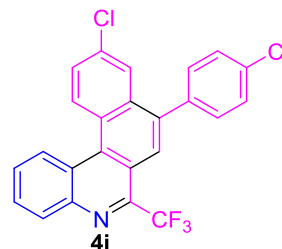
$^{13}\text{C}\{^1\text{H}\}$ (150 MHz, CDCl_3)



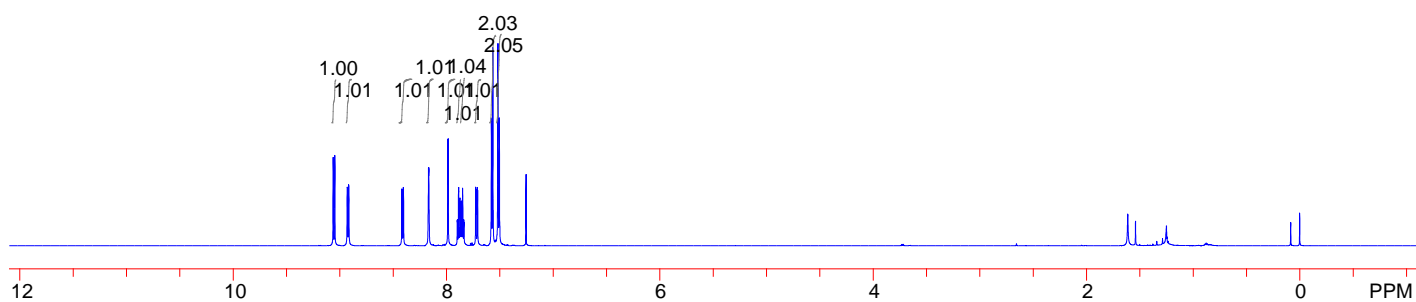
-62.971



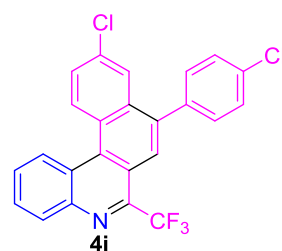
9.062
9.047
8.931
8.917
8.418
8.416
8.405
8.403
8.168
8.166
7.987
7.983
7.898
7.897
7.887
7.885
7.874
7.872
7.863
7.860
7.849
7.837
7.835
7.726
7.722
7.711
7.707
7.579
7.565
7.517
7.504
7.254



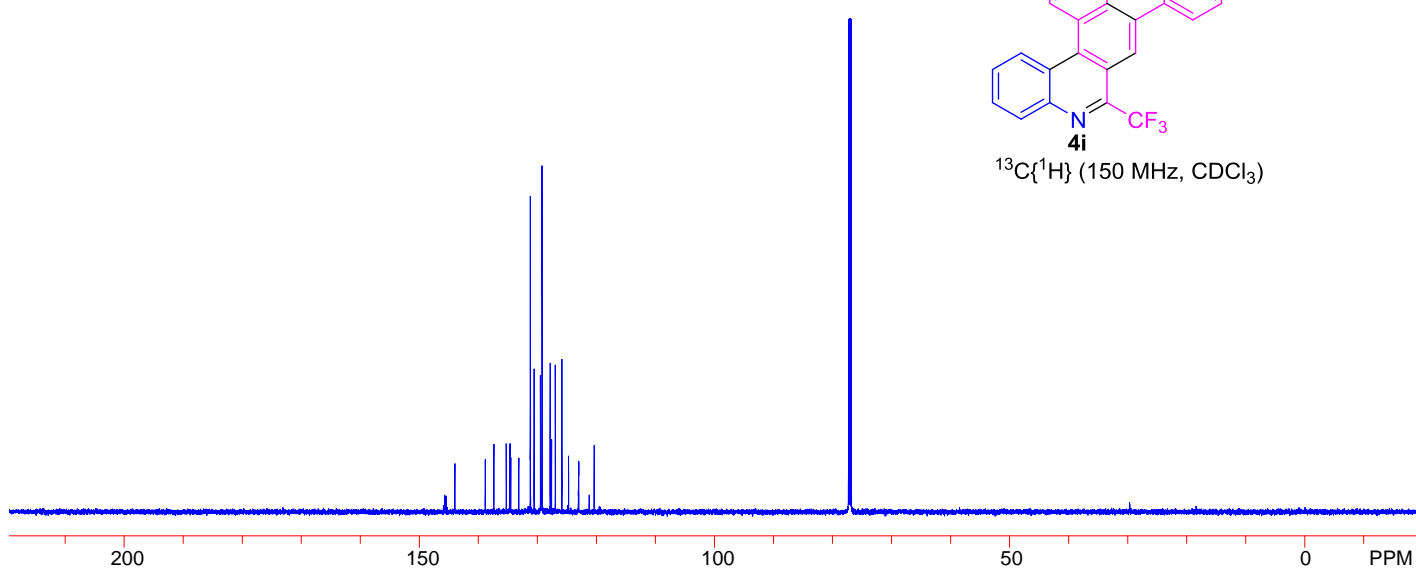
$^1\text{H NMR}$ (600 MHz, CDCl_3)



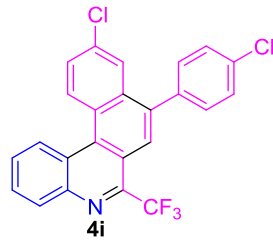
145.689
145.468
143.966
138.819
137.362
135.254
134.637
134.502
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131.195
131.159
130.547
129.467
129.200
127.827
127.594
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123.007
122.987
121.213
120.369
77.259
77.047
76.836



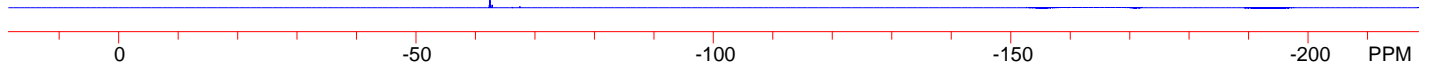
$^{13}\text{C}\{^1\text{H}\}$ (150 MHz, CDCl_3)



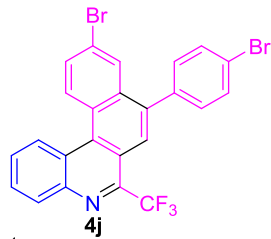
62.430



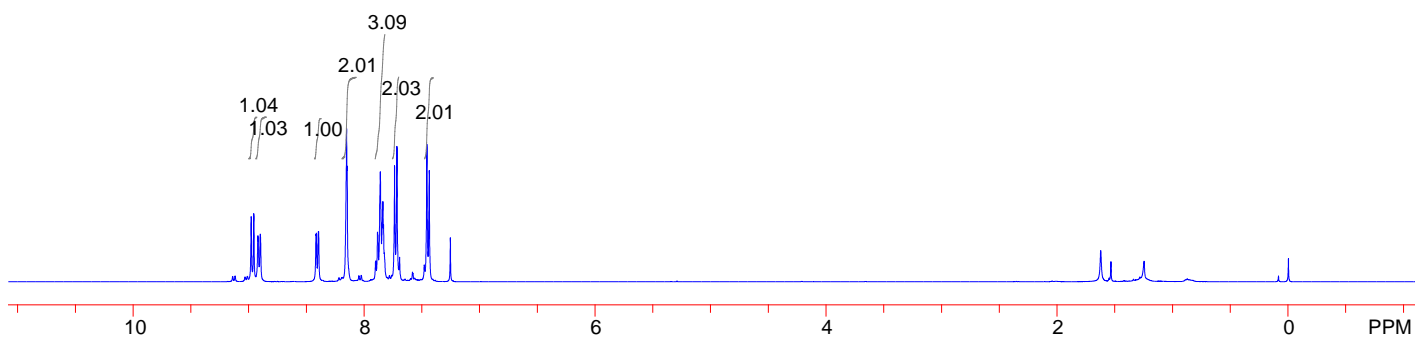
¹⁹F NMR (565 MHz, CDCl₃)



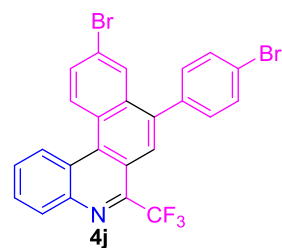
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8.955
8.919
8.899
8.816
8.413
8.396
8.394
8.151
8.147
7.901
7.898
7.884
7.859
7.837
7.831
7.824
7.736
7.715
7.456
7.435
7.252



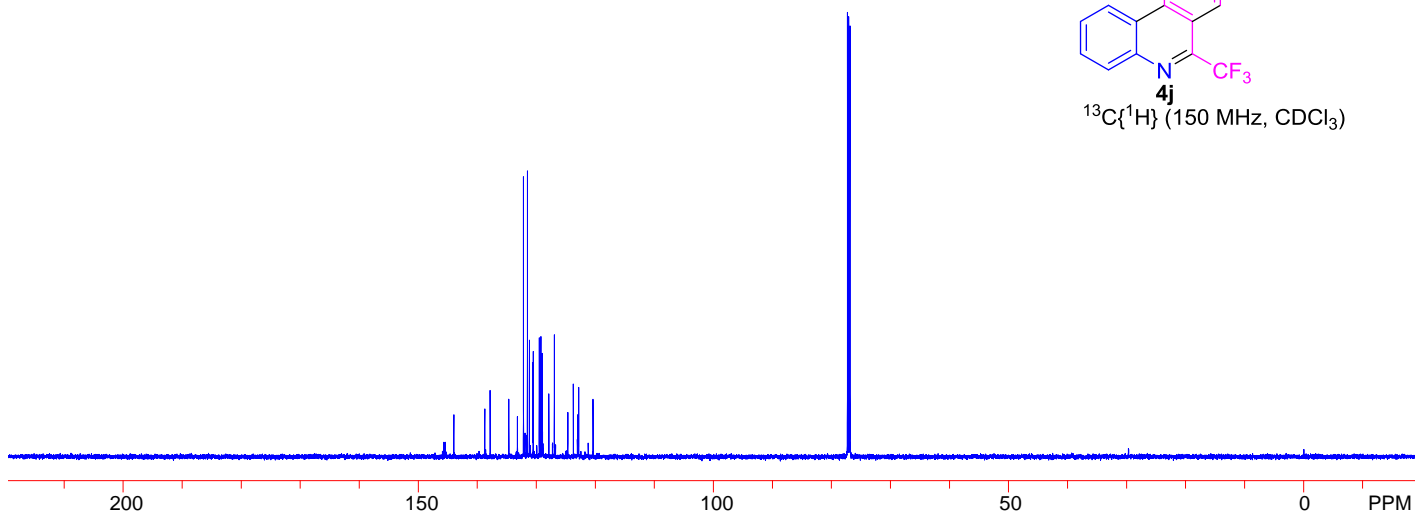
$^1\text{H NMR}$ (400 MHz, CDCl_3)



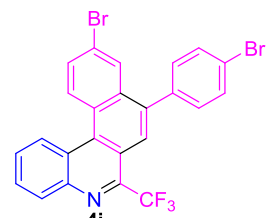
145.902
145.683
145.462
145.243
143.967
138.728
137.817
134.651
133.189
132.173
131.503
131.166
130.556
130.506
129.491
129.227
129.003
127.872
126.939
124.645
123.715
123.038
122.962
122.941
122.812
121.196
120.377
77.274
77.062
76.851



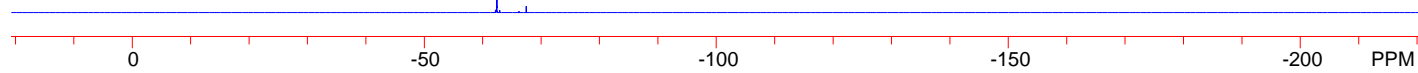
$^{13}\text{C}\{^1\text{H}\}$ (150 MHz, CDCl_3)

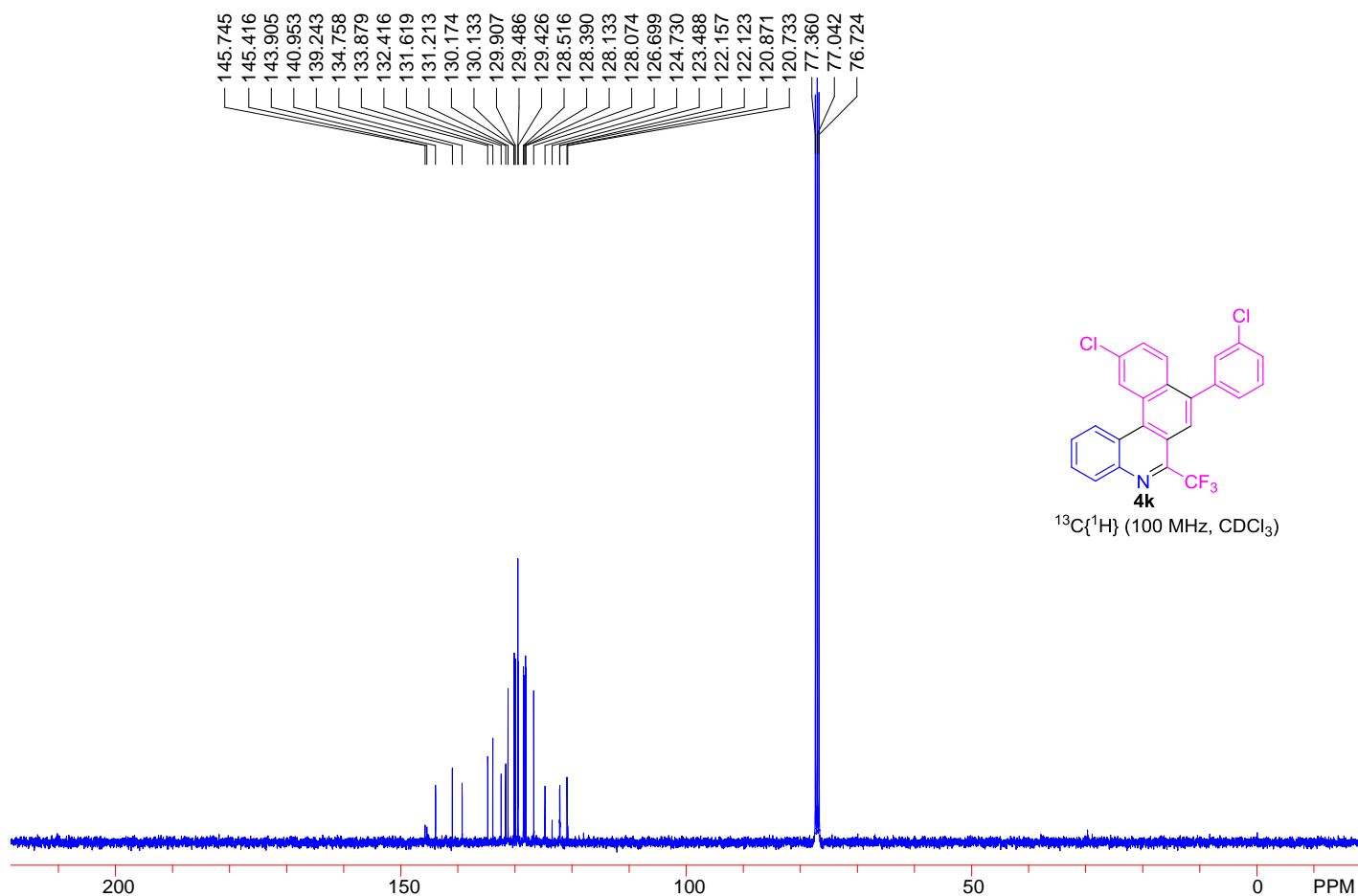
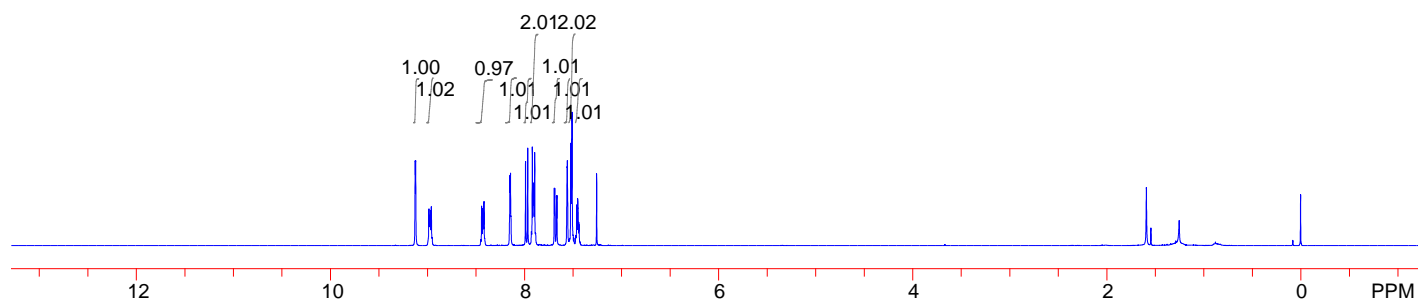
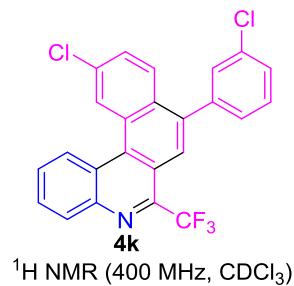
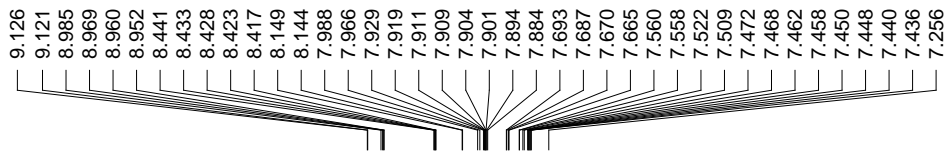


62.415

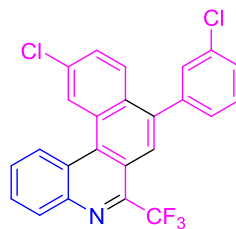


¹⁹F NMR (376 MHz, CDCl₃)

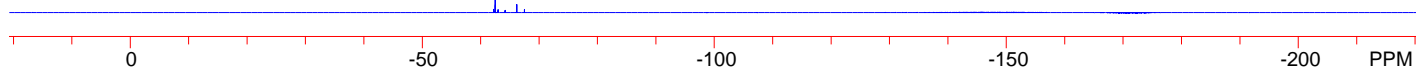




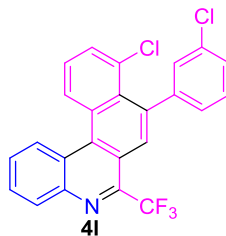
62.466
62.473



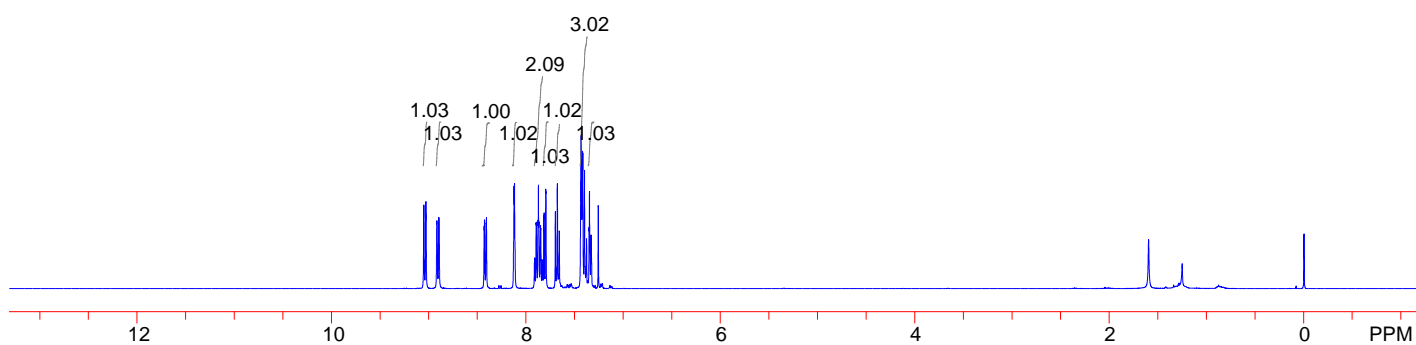
4k
¹⁹F NMR (376 MHz, CDCl₃)



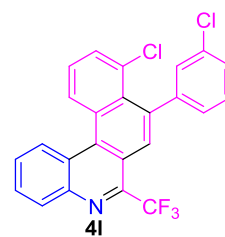
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9.029
8.915
8.896
8.829
8.425
8.408
8.406
8.121
8.117
7.912
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7.894
7.891
7.875
7.871
7.866
7.849
7.846
7.832
7.828
7.814
7.812
7.795
7.793
7.696
7.676
7.656
7.431
7.427
7.422
7.417
7.414
7.396
7.375
7.349
7.345
7.341
7.331
7.328
7.324
7.255



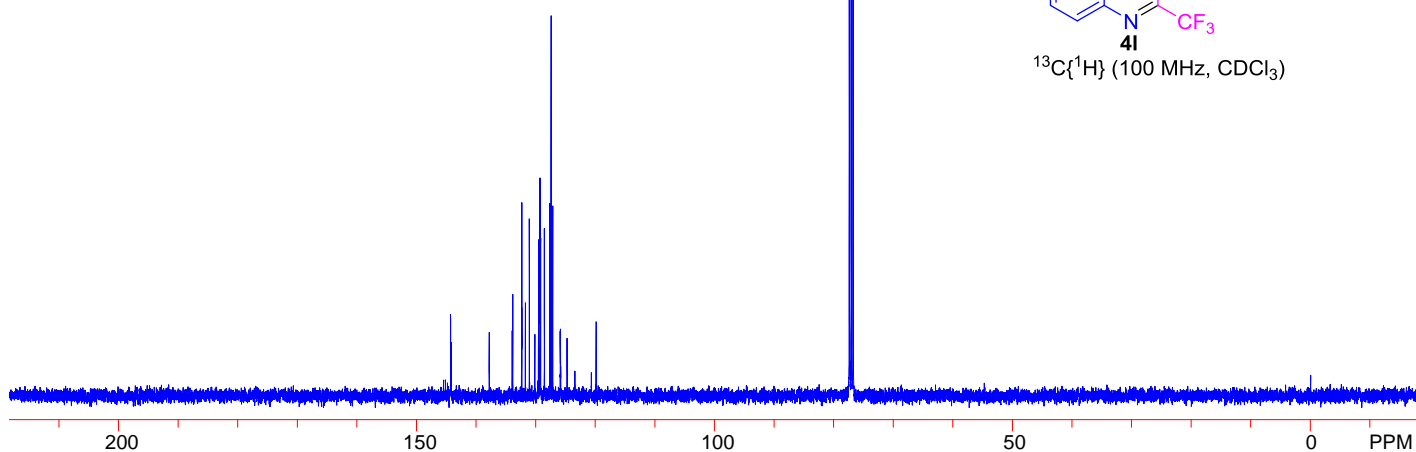
$^1\text{H NMR}$ (400 MHz, CDCl_3)



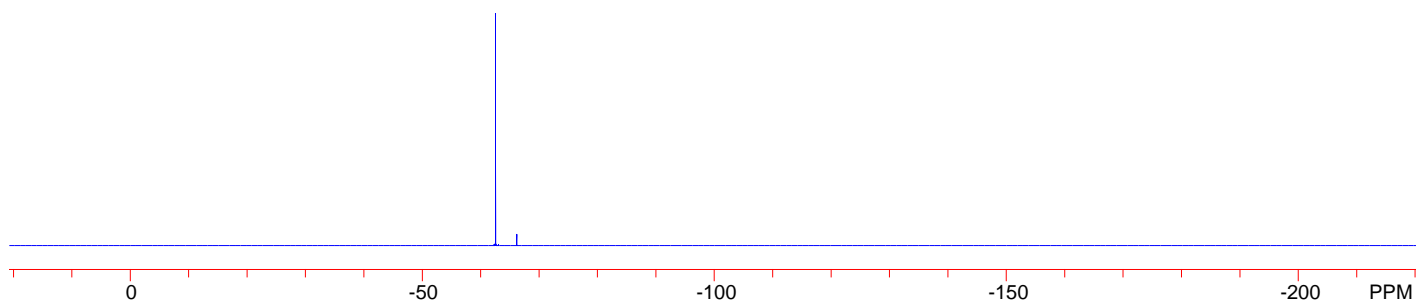
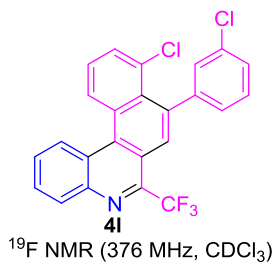
145.450
145.122
144.268
144.154
137.778
133.929
133.838
132.345
132.312
131.721
131.050
130.131
129.507
129.274
129.235
129.153
128.526
127.610
127.403
127.134
125.892
125.861
125.828
125.792
124.719
123.402
120.648
119.845
77.364
77.047
76.729



$^{13}\text{C}\{^1\text{H}\}$ (100 MHz, CDCl_3)



62.544



VI. X-ray crystal structure and data of 3aa

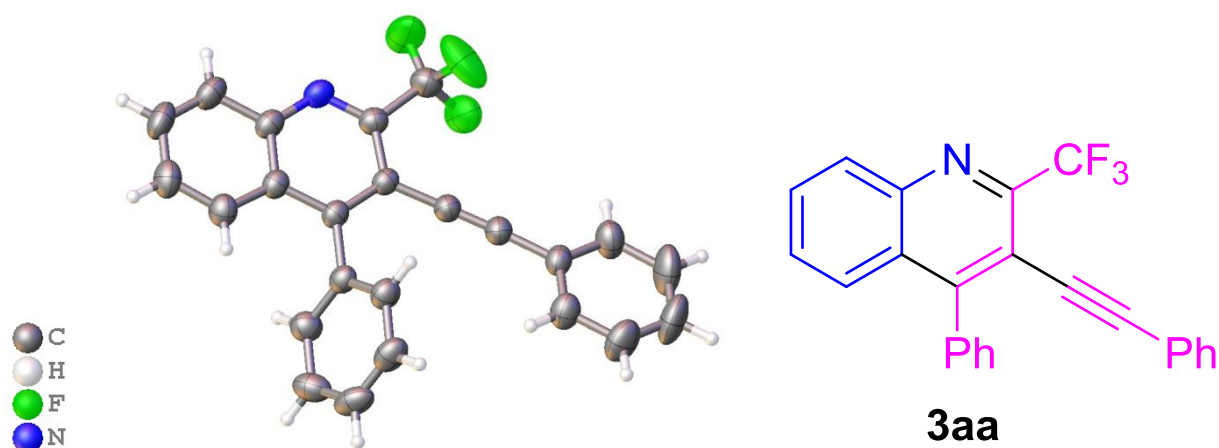


Fig. S1 X-ray crystal structure of **3aa** with 50% ellipsoid probability

X-ray structure determination. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent from a petroleum ether/ethyl acetate (4:1) solution of **3aa**. Crystal data collection and refinement parameters of **3aa** are summarized in Table S1. Intensity data were collected at 293 K on a SuperNova Dual diffractometer using mirror-monochromated Cu K α radiation, $\lambda = 1.54184 \text{ \AA}$. The data were corrected for decay, Lorentz, and polarization effects as well as absorption and beam corrections based on the multi-scan technique. Using Olex2, the structure was solved with the SHELXS structure solution program using Direct Methods and refined with the SHELXL refinement package using Least Squares minimisation. Nonhydrogen atoms were refined with anisotropic displacement parameters. The H-atoms were either located or calculated and subsequently treated with a riding model.

Table S1 Crystallographic data and structure refinement results of **3aa**

Empirical formula	C ₂₄ H ₁₄ F ₃ N
Formula weight	373.36
Temp, K	293(2)
Crystal system	monoclinic
Space group	P2 ₁ /c
<i>a</i> , Å	10.8004(3)
<i>b</i> , Å	7.5870(2)
<i>c</i> , Å	22.5090(5)

α (°)	90
β (°)	94.210(2)
γ (°)	90
Volume, Å ³	1839.47(8)
Z	4
ρ_{calc} , g cm ⁻³	1.348
λ , Å	1.54184
μ , mm ⁻¹	0.834
No. of data collected	7021
No. of unique data	3504
R_{int}	0.0225
Goodness-of-fit on F^2	1.042
R_1 , wR_2 ($I > 2\sigma(I)$)	0.0605, 0.1599
R_1 , wR_2 (all data)	0.0688, 0.1699

VII. Cell antiproliferative activity assay

Cell antiproliferative activity against A549 or HeLa cell was evaluated by the CCK-8 method. Dilute A549 or HeLa cell suspensions in growth medium to desired density and 100 μL were taken to 96-well plate. The test compounds with different concentration gradients were prepared. Add 100 μL culture medium containing compounds into 96-well plate according to the plate map. Final DMSO concentration in each well was below 0.1%. Then the cell was incubated at 37 $^{\circ}\text{C}$, 5% CO_2 for 72 h. Equilibrate the assay plate to room temperature before measurement. Add 20 μL of CCK-8 into each well. Mix contents for 2 minutes on an orbital shaker to induce cell lysis. Incubate at 37 $^{\circ}\text{C}$ and 5% CO_2 for 2 hours, and then the plates were recorded by measuring absorbance at 450 nm using an EnVision Multilabel Reader (PerkinElmer). The IC_{50} values were calculated using GraphPad Prism 6.0 software and determined by the concentration causing a half-maximal percent activity. All assays were conducted with two parallel samples and two repetitions, and 5-fluorouracil was used as the positive control.

Cell antiproliferative activity against Ramos cell was evaluated by the CellTiter-Glo (Promega, USA) assay. Dilute Ramos cell suspensions in growth medium to desired density and 100 μL were taken to 96-well plate. The test compounds with different concentration gradients were prepared. Add 100 μL culture medium containing compounds into 96-well plate according to the plate map. Final DMSO concentration in each well was below 0.1%. Then the cell was incubated at 37 $^{\circ}\text{C}$, 5% CO_2 for 72 h. Equilibrate the assay plate to room temperature before measurement. Add 20 μL of CellTiter-Glo[®] Reagent into each well. Mix contents for 2 minutes on an orbital shaker to induce cell lysis. Incubate at room temperature for 10 minutes to stabilize luminescent signal. Record luminescence using EnVision Multilabel Reader (PerkinElmer). Cell viability (CV%) was calculated relative to vehicle (DMSO) treated control wells using following formula: Cell viability(%) = $(\text{RLU compound} - \text{RLU blank}) / (\text{RLU control} - \text{RLU blank}) * 100\%$. The IC_{50} values were calculated using GraphPad Prism 6.0 software, fitting to a 4-parameter equation to generate concentration response curves. All assays were conducted with two parallel samples and two repetitions, and 5-fluorouracil was used as the positive control.

VIII. References

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