Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Copper halide mediated synthesis of mesoionic 6-halo-[1,2,3]triazolo[5,1-*a*]isoquinoliums: further transformation to polyheterocycles

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Table of Contents

1. General Information

^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz (100 MHz for ^{13}C NMR, 376 MHz for ^{19}F NMR) spectrometer. Chemical shift values are reported in ppm (parts per million) with tetramethylsilane (TMS) as an internal standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; dd, doublet of doublets; td, triplet of doublets. The coupling constants (*J*) are reported in Hertz (Hz). Melting points were determined on a XT4A micromelting point apparatus and are uncorrected. High-resolution mass spectra (HRMS) were obtained on a Q-TOF Mass Spectrometer equipped with an electrospray ion source (ESI), and operated in the positive mode. Flash column chromatography was performed over 200-300 mesh silica gel.

2. Synthesis and analytical data of compounds 1

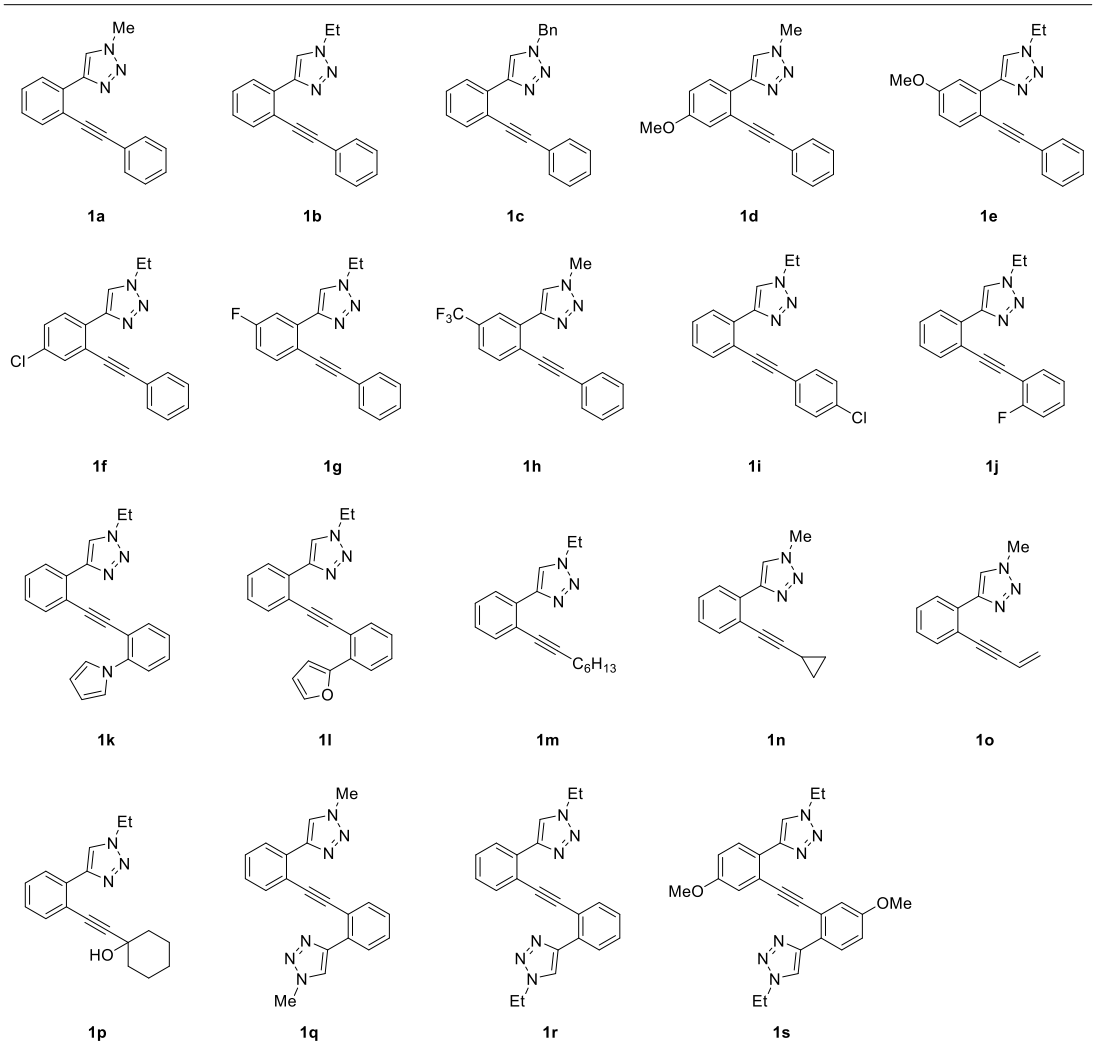


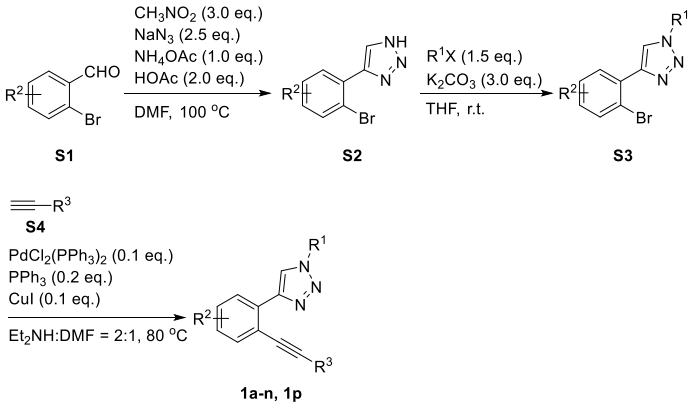
Figure S1. Substrates involved in the manuscript

Substrates 1a-n, 1p were prepared by the following procedure

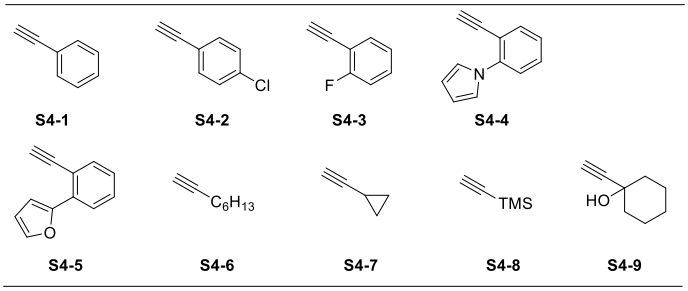
(i) Aldehydes **S1** (5.0 mmol), nitroalkanes (15.0 mmol), NaN_3 (12.5 mmol), HOAc (10.0 mmol), NH_4OAc (5.0 mmol) and DMF (30 mL) were charged in a 100 mL round bottom flask. Then, the reaction mixture was stirred at 100 ℃ for 0.5-2 h.[1] After the reaction was completed (detected by TLC), the mixture was cooled to room temperature. The reaction was quenched with H_2O (30 mL) and extracted with EtOAc (30 mL×3). The combined organic extracts were washed with brine (3 x 30 mL), then dried over anhydrous sodium sulfate and filtered. The filtrate was evaporated *in vacuo*. The corresponding triazoles **S2** were obtained after purification by flash chromatography on silica gel.

(ii) Triazoles **S2** (3.0 mmol), methyl iodide/ethyl iodide/benzyl bromide (4.5 mmol), K_2CO_3 (9.0 mmol) and THF (30 mL) were charged in a 100 mL round bottom flask. Then, the reaction mixture was stirred at room temperature overnight. After the reaction was completed (detected by TLC), the reaction was quenched with H_2O (30 mL) and extracted with EtOAc (30 mL×3). The filtrate was evaporated *in vacuo*. The corresponding triazoles **S3** were obtained after purification by flash chromatography on silica gel.

(iii) In a dry 100 mL round bottom flask, a reaction mixture of 4-(2-bromophenyl)-1,2,3-triazole **S3** (3.0 mmol), $PdCl_2(PPh_3)_2$ (0.3 mmol), CuI (0.3 mmol), triphenylphosphine (0.6 mmol) and terminal alkyne **S4** (15.0 mmol) in Et_2NH/DMF (30 mL, 2:1) was heated at 80 ℃ for 5-10 h until substrate **S3** consumed as indicated by TLC.[2] The cooled mixture was partitioned between H_2O (30 mL) and EtOAc (30 mL). The separated aqueous phase was extracted with EtOAc (3 x 30 mL). The combined organic extracts were washed with brine (3 x 30 mL), then dried over anhydrous sodium sulfate and filtered. The filtrate was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel to afford **1a-n, 1p**.



Terminal alkyne substrates S4

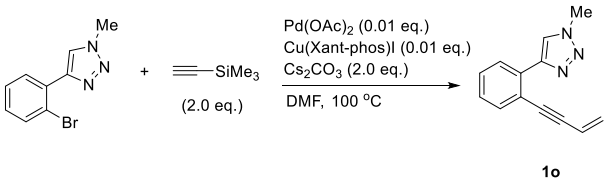


Compounds **S4** (**1**−**3), (6**−**9)** were purchased from commercial sources.

Compounds **S4** (**4**−**5)** were synthesized according to literature procedure method as described. [3]

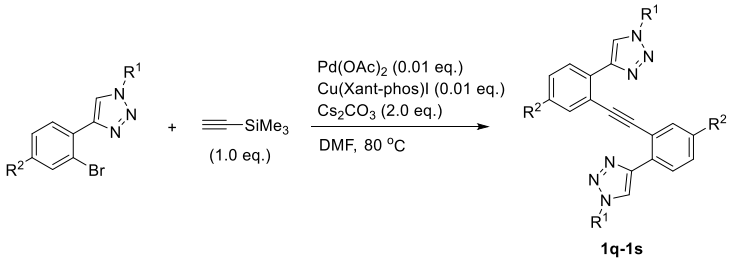
Substrate 1o was prepared by the following procedure

In a dry 35 mL glass tube, a reaction mixture of 4-(2-bromophenyl)-1,2,3-triazole **S3** (3.0 mmol), $Pd(OAc)_2$ (0.03 mmol), Cu(Xant-phos)I (0.03 mmol), Cs_2CO_3 (6.0 mmol) and trimethylsilylacetylene (6.0 mmol) in DMF (5 mL) was heated at 100 °C for 10 h. The cooled mixture was partitioned between H_2O (30 mL) and EtOAc (30 mL). The separated aqueous phase was extracted with EtOAc (3 x 30 mL). The combined organic extracts were washed with brine (3 x 30 mL), then dried over anhydrous sodium sulfate and filtered. The filtrate was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel to afford **1o**.



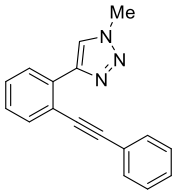
Substrates 1q-s were prepared by the following procedure

In a dry 35 mL glass tube, a reaction mixture of 4-(2-bromophenyl)-1,2,3-triazole **S3** (3.0 mmol), $Pd(OAc)_2$ (0.03 mmol), Cu(Xant-phos)I (0.03 mmol), Cs_2CO_3 (6.0 mmol) and trimethylsilylacetylene (3.0 mmol) in DMF (5 mL) was heated at 80 °C for 5-10 h until substrate consumed as indicated by TLC.[4] The cooled mixture was partitioned between H_2O (30 mL) and EtOAc (30 mL). The separated aqueous phase was extracted with EtOAc (3 x 30 mL). The combined organic extracts were washed with brine (3 x 30 mL), then dried over anhydrous sodium sulfate and filtered. The filtrate was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel to afford **1q**−**1s**.



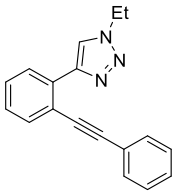
1q-1s

1-Methyl-4-(2-(phenylethynyl)phenyl)-1*H*-1,2,3-triazole 1a



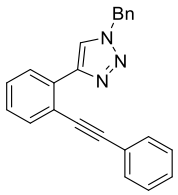
The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 6:1); 88% yield; light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.37 (s, 1H), 8.28 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.62 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.52−7.50 (m, 2H), 7.45 (td, *J* = 7.6, 1.4 Hz, 1H), 7.41−7.38 (m, 3H), 7.32 (td, *J* = 7.6, 1.4 Hz, 1H), 4.14 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 146.1, 133.4, 132.0, 131.5, 129.1, 128.8, 128.7, 127.8, 127.6, 123.6, 123.1, 119.7, 93.6, 89.6, 36.9 ppm.

1-Ethyl-4-(2-(phenylethynyl)phenyl)-1*H*-1,2,3-triazole 1b



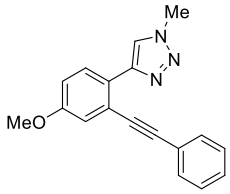
The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 8:1); 95% yield; light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.39 (s, 1H), 8.27 (dd, *J* = 8.0, 0.9 Hz, 1H), 7.62 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.51−7.48 (m, 2H), 7.44 (td, *J* = 7.8, 1.4 Hz, 1H), 7.40−7.36 (m, 3H), 7.31 (td, *J* = 7.6, 1.2 Hz, 1H), 4.46 (q, *J* = 7.4 Hz, 2H), 1.58 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 145.8, 133.3, 132.2, 131.4, 129.1, 128.7, 128.7, 127.7, 127.6, 123.1, 121.9, 119.6, 93.6, 89.6, 45.4, 15.6 ppm.

1-Benzyl-4-(2-(phenylethynyl)phenyl)-1*H*-1,2,3-triazole 1c



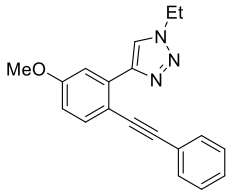
The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 6:1); 80% yield; yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.32 (s, 1H), 8.29 (dd, J = 8.0, 0.9 Hz, 1H), 7.60−7.58 (m, 1H), 7.46−7.42 (m, 1H), 7.37−7.33 (m, 5H), 7.31−7.29 (m, 4H), 7.21−7.18 (m, 2H), 7.59 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 146.3, 134.7, 133.4, 132.0, 131.4, 129.3, 129.1, 128.9, 128.61, 128.59, 128.4, 127.8, 127.6, 123.0, 122.5, 119.7, 89.5, 54.4 ppm.

4-(4-Methoxy-2-(phenylethynyl)phenyl)-1-methyl-1*H*-1,2,3-triazole 1d



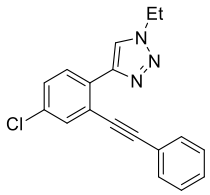
The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1); 90% yield; white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.26 (s, 1H), 8.17 (d, J = 8.7 Hz, 1H), 7.53−7.48 (m, 2H), 7.43−7.37 (m, 3H), 7.13 (d, J = 2.8 Hz, 1H), 7.02 (dd, J = 8.8, 2.8 Hz, 1H), 4.13 (s, 3H), 3.86 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 159.0, 146.0, 131.5, 129.1, 128.83, 128.75, 125.2, 123.1, 122.8, 120.8, 117.5, 116.0, 93.4, 89.51, 55.6, 36.9 ppm.

1-Ethyl-4-(5-methoxy-2-(phenylethynyl)phenyl)-1*H*-1,2,3-triazole 1e



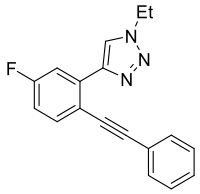
The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); 75% yield; light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.45 (s, 1H), 7.84 (d, J = 2.7 Hz, 1H), 7.53 (d, J = 8.6 Hz, 1H), 7.50−7.47 (m, 2H), 7.40−7.35 (m, 3H), 6.87 (dd, J = 8.6, 2.7 Hz, 1H), 4.47 (q, J = 7.4 Hz, 2H), 3.91 (s, 3H), 1.59 (t, J = 7.4 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.2, 145.8, 134.8, 133.8, 131.3, 128.7, 128.4, 123.5, 122.1, 115.2, 111.8, 111.3, 92.4, 89.8, 55.7, 45.5, 15.7 ppm.

4-(4-Chloro-2-(phenylethynyl)phenyl)-1-ethyl-1*H*-1,2,3-triazole 1f



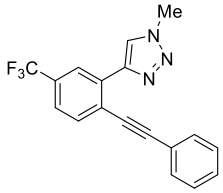
The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); 78% yield; light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.37 (s, 1H), 8.22 (d, J = 8.6 Hz, 1H), 7.59 (d, J = 2.2 Hz, 1H), 7.51−7.48 (m, 2H), 7.41−7.38 (m, 4H), 4.46 (q, J = 7.4 Hz, 2H), 1.58 (t, J = 7.4 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 145.0, 133.3, 132.8, 131.5, 130.7, 129.3, 129.1, 128.9, 128.8, 122.6, 121.9, 121.1, 94.6, 88.34, 45.5, 15.6 ppm.

1-Ethyl-4-(5-fluoro-2-(phenylethynyl)phenyl)-1*H*-1,2,3-triazole 1g



The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); 75% yield; light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.44 (s, 1H), 8.01 (dd, J = 10.2, 2.7 Hz, 1H), 7.58 (dd, J = 8.6, 5.7 Hz, 1H), 7.51−7.46 (m, 2H), 7.42−7.37 (m, 3H), 7.00 (td, J = 8.2, 2.7 Hz, 1H), 4.46 (q, J = 7.4 Hz, 2H), 1.58 (t, J = 7.4 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.8 (d, $J_{C–F}$ = 247.9 Hz), 144.8 (d, $J_{C–F}$ = 2.5 Hz), 135.3 (d, $J_{C–F}$ = 8.6 Hz), 134.5 (d, $J_{C–F}$ = 9.1 Hz), 131.3, 128.8, 128.7, 122.9, 122.1, 115.6 (d, $J_{C–F}$ = 3.2 Hz), 115.0 (d, $J_{C–F}$ = 22.2 Hz), 114.3 (d, $J_{C–F}$ = 24.0 Hz), 93.4, 88.7, 45.5, 15.6 ppm.

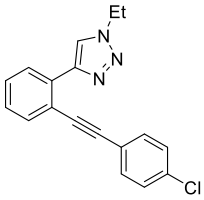
1-Methyl-4-(2-(phenylethynyl)-5-(trifluoromethyl)phenyl)-1*H*-1,2,3-triazole 1h



The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 8:1); 77% yield; brown solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.58 (s, 1H), 8.40 (s, 1H), 7.71−7.69 (m, 1H), 7.54−7.49 (m, 3H), 7.42−7.40 (m, 3H), 4.16 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 144.9, 133.9, 132.6, 131.5, 130.7

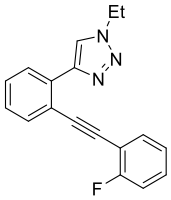
(q, $J_{C–F}$ = 32.7 Hz), 129.3, 128.8, 124.6 (q, $J_{C–F}$ = 3.7 Hz), 124.1 (q, $J_{C–F}$ = 3.6 Hz), 123.9, 123.8 (q, $J_{C–F}$ = 270.8 Hz), 123.0, 122.4, 95.9, 88.3, 37.0 ppm.

4-(2-((4-Chlorophenyl)ethynyl)phenyl)-1-ethyl-1*H*-1,2,3-triazole 1i



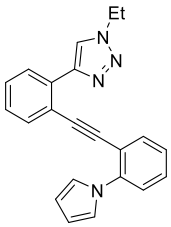
The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); 78% yield; yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.31 (s, 1H), 8.24 (dd, J = 8.0, 0.9 Hz, 1H), 7.60 (dd, J = 7.8, 1.4 Hz, 1H), 7.47−7.40 (m, 3H), 7.36−7.29 (m, 3H), 4.46 (q, J = 7.4 Hz, 2H), 1.57 (t, J = 7.4 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 145.8, 134.8, 133.3, 132.6, 132.3, 129.3, 129.0, 127.8, 127.7, 121.8, 121.6, 119.4, 92.3, 90.5 45.5, 15.7 ppm.

1-Ethyl-4-(2-((2-fluorophenyl)ethynyl)phenyl)-1*H*-1,2,3-triazole 1j



The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 6:1); 90% yield; light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.71 (s, 1H), 8.33 (dd, J = 8.0, 0.9 Hz, 1H), 7.64 (dd, J = 7.8, 1.4 Hz, 1H), 7.53 (td, J = 7.4, 1.7 Hz, 1H), 7.46 (td, J = 7.6, 1.3 Hz, 1H), 7.38−7.29 (m, 2H), 7.19−7.12 (m, 2H), 4.48 (q, J = 7.4 Hz, 2H), 1.61 (t, J = 7.4 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.8 (d, $J_{C–F}$ = 248.0 Hz), 145.4, 133.6, 133.5 (d, $J_{C–F}$ = 1.4 Hz), 132.2, 130.4 (d, $J_{C–F}$ = 8.1 Hz), 129.4, 127.6 (d, $J_{C–F}$ = 8.9 Hz), 124.5 (d, $J_{C–F}$ = 3.5 Hz), 122.4 (d, $J_{C–F}$ = 5.8 Hz), 119.1, 115.8, 115.6, 111.8 (d, $J_{C–F}$ = 15.3 Hz), 94.6, 87.5, 45.5, 15.6 ppm.

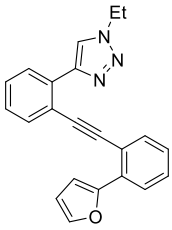
4-(2-((2-(1*H*-pyrrol-1-yl)phenyl)ethynyl)phenyl)-1-ethyl-1*H*-1,2,3-triazole 1k



The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 6:1); 80% yield; brown liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ =

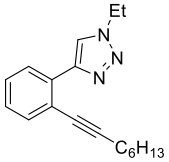
8.22 (dd, *J* = 8.0, 0.9 Hz, 1H), 7.66 (s, 1H), 7.64−7.58 (m, 2H), 7.46−7.40 (m, 2H), 7.36−7.28 (m, 3H), 7.20 (t, *J* = 2.2 Hz, 2H), 6.34 (t, *J* = 2.2 Hz, 2H), 4.30 (q, *J* = 7.4 Hz, 2H), 1.48 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 145.2, 141.6, 133.9, 133.7, 132.0, 129.7, 129.2, 127.6, 127.5, 126.5, 125.1, 122.1, 121.7, 119.2, 117.8 109.9, 93.7, 90.3, 45.3, 15.8 ppm.

1-Ethyl-4-(2-((2-(furan-2-yl)phenyl)ethynyl)phenyl)-1*H*-1,2,3-triazole 1l



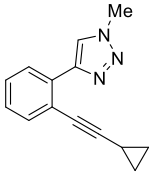
The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 6:1); 86% yield; light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.32 (s, 1H), 8.27 (dd, *J* = 7.9, 0.9 Hz, 1H), 7.87 (dd, *J* = 8.0, 0.7 Hz, 1H), 7.65 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.55 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.50−7.46 (m, 2H), 7.42 (td, *J* = 7.8, 1.3 Hz, 1H), 7.35 (td, *J* = 7.6, 1.3 Hz, 1H), 7.29−7.24 (m, 2H), 6.43 (dd, *J* = 3.4, 1.8 Hz, 1H), 4.32 (q, *J* = 7.4 Hz, 2H), 1.44 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 151.9, 145.6, 142.2, 133.6, 133.3, 132.3, 131.9, 129.3, 129.1, 127.81, 127.80, 127.1, 126.0, 122.1, 119.8, 118.2, 111.9, 109.8, 93.7, 93.4, 45.4, 15.4 ppm.

1-Ethyl-4-(2-(oct-1-yn-1-yl)phenyl)-1*H*-1,2,3-triazole 1m



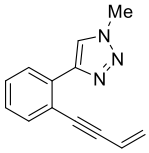
The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); 83% yield; brown liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.38 (s, 1H), 8.22 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.48 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.37 (td, *J* = 7.6, 1.4 Hz, 1H), 7.26−7.22 (m, 1H), 4.46 (q, *J* = 7.4 Hz, 2H), 2.48 (t, *J* = 7.4 Hz, 3H), 1.67−1.58 (m, 5H), 1.49−1.42 (m, 2H), 1.34−1.27 (m, 4H), 0.91−0.87 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 146.0, 133.6, 131.8, 128.3, 127.6, 127.4, 121.7, 120.5, 95.0, 80.9, 45.4, 31.5, 28.9, 28.8, 22.7, 19.9, 15.7, 14.2 ppm.

4-(2-(Cyclopropylethynyl)phenyl)-1-methyl-1*H*-1,2,3-triazole 1n



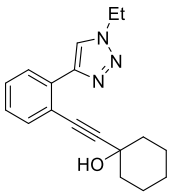
The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 6:1); 77% yield; light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.32 (s, 1H), 8.20 (dd, J = 8.0, 0.9 Hz, 1H), 7.45 (dd, J = 7.7, 1.1 Hz, 1H), 7.36 (td, J = 7.5, 1.4 Hz, 1H), 7.23 (td, J = 7.6, 1.4 Hz, 1H), 4.16 (s, 3H), 1.55−1.48(m, 1H), 0.95−0.90 (m, 2H), 0.83−0.79 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 146.2, 133.6, 131.9, 128.3, 127.6, 127.4, 123.3, 120.4, 97.9, 76.0, 36.9, 8.5, 0.6 ppm.

4-(2-(But-3-en-1-yn-1-yl)phenyl)-1-methyl-1*H*-1,2,3-triazole 1o



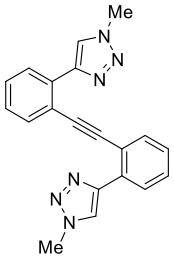
The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 15:1); 61% yield; light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.28 (s, 1H), 8.25 (dd, J = 8.0, 0.9 Hz, 1H), 7.53 (dd, J = 7.8, 1.0 Hz, 1H), 7.43 (td, J = 7.6, 1.4 Hz, 1H), 7.29 (td, J = 7.6, 1.3 Hz, 1H), 6.08 (dd, J = 17.6, 11.2 Hz, 1H), 5.73 (dd, J = 17.6, 1.9 Hz, 1H), 5.61 (dd, J = 11.2, 1.9 Hz, 1H), 4.16 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 146.0, 133.4, 132.0, 129.1, 127.7, 127.6, 127.4, 123.5, 119.5, 117.2, 92.5, 90.2, 36.9 ppm.

1-((2-(1-Ethyl-1*H*-1,2,3-triazol-4-yl)phenyl)ethynyl)cyclohexan-1-ol 1p



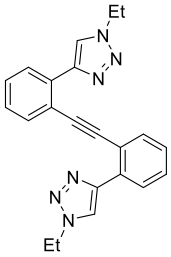
The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1); 87% yield; light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.46 (s, 1H), 8.07 (dd, J = 8.0, 1.0 Hz, 1H), 7.36 (dd, J = 7.7, 1.2 Hz, 1H), 7.23 (td, J = 7.7, 1.4 Hz, 1H), 7.11 (td, J = 7.6, 1.3 Hz, 1H), 4.24 (q. J = 7.4 Hz, 2H), 1.98−1.94 (m, 2H), 1.66−1.60 (m, 4H), 1.53−1.43 (m, 3H), 1.39 (t, J = 7.4 Hz, 3H), 1.23−1.14 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 145.2, 133.2, 131.6, 128.4, 127.3, 127.1, 122.3, 119.5, 97.9, 83.5, 68.9, 45.2, 39. 8, 25.1, 23.2, 15.2 ppm.

1,2-Bis(2-(1-methyl-1*H*-1,2,3-triazol-4-yl)phenyl)ethyne 1q



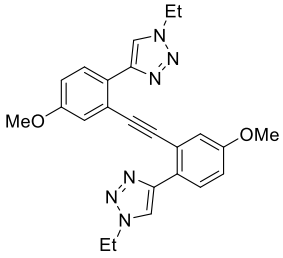
The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1); 55% yield; light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.11 (dd, *J* = 7.9, 0.8 Hz, 2H), 7.99 (s, 2H), 7.62 (dd, *J* = 8.6, 0.9 Hz, 2H), 7.47 (td, *J* = 7.6, 1.4 Hz, 2H), 7.36 (td, *J* = 7.6, 1.4 Hz, 2H), 3.92 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 145.7, 133.1, 132.4, 129.5, 128.3, 128.1, 123.9, 120.0, 92.8, 36.8 ppm.

1,2-Bis(2-(1-ethyl-1*H*-1,2,3-triazol-4-yl)phenyl)ethyne 1r



The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1); 60% yield; light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.12 (d, *J* = 7.9 Hz, 2H), 8.08 (s, 2H), 7.56 (d, *J* = 7.24, 2H), 7.44−7.40 (m, 2H), 7.31 (td, *J* = 7.6, 0.9 Hz, 2H), 4.22 (q, *J* = 7.4 Hz, 4H), 1.34 (t, *J* = 7.4 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 145.2, 133.0, 132.3, 129.3, 127.9, 127.8, 122.1, 119.6, 92.9, 45.3, 15.3 ppm.

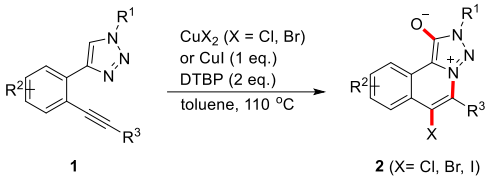
1,2-bis(2-(1-ethyl-1*H*-1,2,3-triazol-4-yl)-5-methoxyphenyl)ethyne 1s



The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1); white solid; 45% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.08

(d, *J* = 8.8 Hz, 2H), 7.95 (s, 2H), 7.13 (d, *J* = 2.8 Hz, 2H), 7.04 (dd, *J* = 8.8, 2.8 Hz, 2H), 4.22 (q, *J* = 7.4 Hz, 4H), 3.87 (s, 6H), 1.36 (t, *J* = 7.4 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 159.1, 145.3, 129.6, 125.6, 121.5, 120.6, 117.5, 116.1, 92.7, 55.7, 45.4, 15.4 ppm.

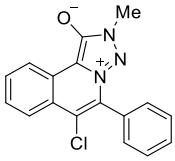
3. Synthesis and analytical data of compounds 2



1 **2** (X= Cl, Br, I)

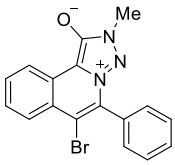
A solution of **1** (0.2 mmol), CuX_2 (X = Cl, Br) or CuI (0.2 mmol), and DTBP (0.4 mmol) in toluene (3 mL) in a sealed tube was stirred at 110 °C for 8-40 h until substrate **1** consumed as indicated by TLC. The cooled mixture was partitioned between H_2O (30 mL) and EtOAc (30 mL). The separated aqueous phase was extracted with EtOAc (3 x 30 mL). The combined organic extracts were dried over anhydrous sodium sulfate and filtered. The filtrate was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel to afford **2**.

6-Chloro-2-methyl-5-phenyl-2*H*-[1,2,3]triazolo[5,1-*a*]isoquinolin-4-ium-1-olate 2aa



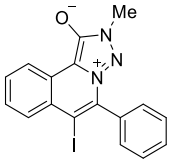
The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 1:1); 75% yield; yellow solid; mp: 205−206 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.88 (dd, *J* = 8.0, 0.6 Hz, 1H), 8.14 (dd, *J* = 8.3, 0.7 Hz, 1H), 7.75 (ddd, *J* = 8.2, 7.2, 1.2 Hz, 1H), 7.62−7.53 (m, 6H), 3.80 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.9, 131.8, 130.7, 130.54, 130.53, 129.2, 129.1, 127.5, 127.3, 125.9, 124.9, 124.8, 121.8, 114.6, 31.4 ppm; IR (neat): ν_{max} 1648, 1606, 1449 cm^{-1}; ESI-HRMS: *m/z* $[M + H]^+$ calcd for $C_{17}H_{13}{}^{35}ClN_3O$: 310.0742, found: 310.0740.

6-Bromo-2-methyl-5-phenyl-2*H*-[1,2,3]triazolo[5,1-*a*]isoquinolin-4-ium-1-olate 2ab



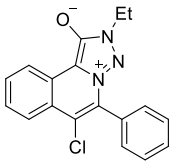
The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 1:1); 70% yield; yellow solid; mp: 238−240 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ = 8.67 (d, J = 7.9 Hz, 1H), 8.09 (d, J = 8.1 Hz, 1H), 7.80 (t, J = 7.2 Hz, 1H), 7.67−7.63 (m, 1H), 7.67−7.51 (m, 5H), 3.65 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ = 152.9, 133.6, 131.2, 130.6, 130.4, 130.1, 129.0, 127.5, 127.2, 125.5, 125.1, 120.2, 118.3, 113.4, 30.8 ppm; IR (neat): ν_{max} 1648, 1251 cm^{-1}; ESI-HRMS: *m/z* [M + H]$^{+}$ calcd for $C_{17}H_{13}{}^{79}BrN_3O$: 354.0237, found: 354.0236.

6-Iodo-2-methyl-5-phenyl-2*H*-[1,2,3]triazolo[5,1-*a*]isoquinolin-4-ium-1-olate 2ac



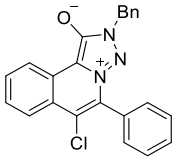
The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 1:1); 72% yield; yellow solid; mp: 227−229 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.84 (dd, J = 8.0, 0.8 Hz, 1H), 8.08 (d, J = 8.1 Hz, 1H), 7.73−7.69 (m, 1H), 7.64−7.59 (m, 3H), 7.58−7.53 (m, 1H), 7.46−7.41 (m, 2H), 3.78 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.7, 136.7, 135.0, 132.8, 130.6, 130.5, 130.4, 129.3, 128.0, 127.9, 125.5, 121.8, 115.3, 99.7, 31.4 ppm; IR (neat): ν_{max} 1643, 1408 cm^{-1}; ESI-HRMS: *m/z* [M + H]$^{+}$ calcd for $C_{17}H_{13}IN_3O$: 402.0098, found: 402.0096.

6-Chloro-2-ethyl-5-phenyl-2*H*-[1,2,3]triazolo[5,1-*a*]isoquinolin-4-ium-1-olate 2ba



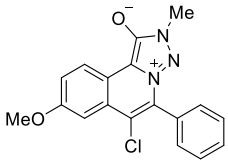
The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 1:1); 72% yield; yellow solid; mp: 211−212 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.88 (d, J = 8.6 Hz, 1H), 8.13 (d, J = 7.9 Hz, 1H), 7.73 (td, J = 7.4, 1.1 Hz, 1H), 7.62−7.57 (m, 4H), 7.56−7.53 (m, 2H), 4.25 (q, J = 7.3 Hz, 2H), 1.42 (t, J = 7.3 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.3, 131.8, 130.6, 130.6, 130.4, 129.2, 129.0, 127.4, 127.2, 126.0, 124.8, 124.8, 121.7, 114.6, 39.9, 14.5 ppm; IR (neat): ν_{max} 1648, 1448 cm^{-1}; ESI-HRMS: *m/z* [M + H]$^{+}$ calcd for $C_{18}H_{15}{}^{35}ClN_3O$: 324.0898, found: 324.0898.

2-Benzyl-6-chloro-5-phenyl-2*H*-[1,2,3]triazolo[5,1-*a*]isoquinolin-4-ium-1-olate 2ca



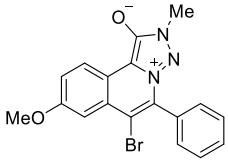
The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 1:1); 50% yield; yellow solid; mp: 53−55 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ = 8.68 (d, J = 7.4 Hz, 1H), 8.08 (d, J = 7.9 Hz, 1H), 7.82−7.78 (m, 1H), 7.66−7.62 (m, 3H), 7.61−7.56 (m, 3H), 7.33−7.29 (m, 2H), 7.27−7.25 (m, 3H), 5.33 (s, 2H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ = 152.8, 136.0, 132.1, 130.6, 130.5, 130.3, 129.0, 128.9, 128.6, 127.7, 127.5, 127.4, 126.0, 125.5, 124.4, 124.1, 120.2, 113.5, 47.0 ppm; IR (neat): ν_{max} 1648, 1606, 1448 cm^{-1}; ESI-HRMS: *m/z* [M + H]$^{+}$ calcd for $C_{23}H_{17}{}^{35}ClN_3O$: 386.1055, found: 386.1057.

6-Chloro-8-methoxy-2-methyl-5-phenyl-2*H*-[1,2,3]triazolo[5,1-*a*]isoquinolin-4-ium-1-olate 2da



The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1); 75% yield; yellow solid; mp: 225−226 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.83 (d, J = 8.9 Hz, 1H), 7.62−7.59 (m, 3H), 7.56−7.53 (m, 3H), 7.37 (dd, J = 8.9, 2.5 Hz, 1H), 3.97 (s, 3H), 3.80 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 159.3, 153.4, 132.2, 130.5, 129.3, 129.1, 126.7, 126.6, 123.6, 120.1, 120.0, 115.0, 106.9, 55.8, 31.4 ppm; IR (neat): ν_{max} 1654, 1462 cm^{-1}; ESI-HRMS: *m/z* [M + H]$^{+}$ calcd for $C_{18}H_{15}{}^{35}ClN_3O_2$: 340.0847, found: 340.0848.

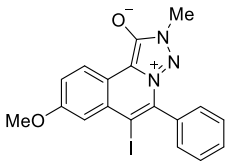
6-Bromo-8-methoxy-2-methyl-5-phenyl-2*H*-[1,2,3]triazolo[5,1-*a*]isoquinolin-4-ium-1-olate 2db



The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 1:1); 83% yield; yellow solid; mp: 253−255 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ = 8.62 (d, J = 8.7 Hz, 1H), 7.63−7.55 (m, 5H), 7.51−7.46 (m, 2H), 3.93 (s, 3H), 3.64 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ = 158.6, 152.4, 134.0,

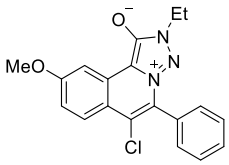
131.4, 130.3, 130.1, 128.9, 126.9, 122.2, 119.6, 119.5, 117.7, 113.8, 109.4, 55.6, 30.7 ppm; IR (neat): ν_{max} 1444, 1260 cm^{-1}; ESI-HRMS: *m/z* $[M + H]^+$ calcd for $C_{18}H_{15}{}^{79}BrN_3O_2$: 384.0342, found: 384.0341.

6-Iodo-8-methoxy-2-methyl-5-phenyl-2*H*-[1,2,3]triazolo[5,1-*a*]isoquinolin-4-ium-1-olate 2dc



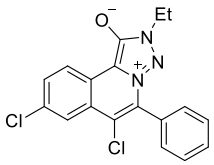
The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1); 87% yield; yellow solid; mp: 281−283 °C; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.81 (d, *J* = 8.8 Hz, 1H), 7.63−7.59 (m, 3H), 7.55 (d, *J* = 2.5 Hz, 1H), 7.44−7.42 (m, 2H), 7.32 (dd, *J* = 8.8, 2.5 Hz, 1H), 3.97 (s, 3H), 3.76 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 159.6, 137.1, 135.2, 130.4, 130.3, 129.7, 129.3, 128.7, 123.7, 119.59, 119.57, 115.4, 100.1, 99.0, 55.8, 31.4 ppm; IR (neat): ν_{max} 1632, 1614, 1458 cm^{-1}; ESI-HRMS: *m/z* $[M + H]^+$ calcd for $C_{18}H_{15}IN_3O_2$: 432.0203, found: 432.0203.

6-Chloro-2-ethyl-9-methoxy-5-phenyl-2H-[1,2,3]triazolo[5,1-*a*]isoquinolin-4-ium-1-olate 2ea



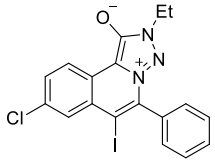
The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 1:1); 71% yield; yellow solid; mp: 191−192 °C; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.34 (s, 1H), 8.02 (d, *J* = 9.0 Hz, 1H), 7.60−7.53 (m, 5H), 7.12 (d, *J* = 9.0 Hz, 1H), 4.27 (br, 2H), 4.02 (s, 3H), 1.42 (t, *J* = 6.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.3, 130.8, 130.2, 129.5, 129.3, 128.9, 126.9, 126.4, 119.0, 118.1, 102.2, 56.0, 39.7, 14.6 ppm; IR (neat): ν_{max} 1483, 1221 cm^{-1}; ESI-HRMS: *m/z* $[M + H]^+$ calcd for $C_{19}H_{17}{}^{35}ClN_3O_2$: 354.1004, found: 354.1005.

6,8-Dichloro-2-ethyl-5-phenyl-2*H*-[1,2,3]triazolo[5,1-*a*]isoquinolin-4-ium-1-olate 2fa



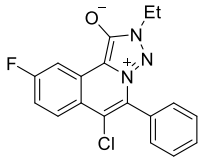
The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 1:1); 73% yield; yellow solid; mp: 205−206 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.81 (d, J = 8.6 Hz, 1H), 8.11 (d, J = 2.0 Hz, 1H), 7.68 (dd, J = 8.6, 2.0 Hz, 1H), 7.62−7.58 (m, 3H), 7.57−7.53 (m, 2H), 4.25 (q, J = 7.3 Hz, 2H), 1.42 (t, J = 7.3 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.3, 133.4, 133.0, 131.1, 130.7, 130.5, 129.1, 128.8, 126.2, 126.0, 124.5, 124.4, 123.2, 114.3, 40.1, 14.4 ppm; IR (neat): ν_{max} 1650, 1491, 1415 cm^{-1}; ESI-HRMS: *m/z* [M + H]$^{+}$ calcd for $C_{18}H_{14}{}^{35}Cl_2N_3O$: 358.0508, found: 358.0507.

8-Chloro-2-ethyl-6-iodo-5-phenyl-2*H*-[1,2,3]triazolo[5,1-*a*]isoquinolin-4-ium-1-olate 2fc



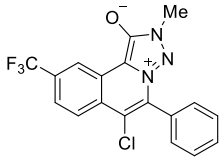
The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 1:1); 85% yield; yellow solid; mp: 243−244 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.78 (d, J = 8.6 Hz, 1H), 8.08 (d, J = 2.0 Hz, 1H), 7.65−7.59 (m, 4H), 7.44−7.41 (m, 2H), 4.23 (q, J = 7.2 Hz, 2H), 1.40 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 137.9, 134.7, 133.7, 132.4, 130.9, 130.6, 130.3, 129.2, 124.0, 123.2, 97.6, 40.0, 14.4 ppm; IR (neat): ν_{max} 1644, 1408 cm^{-1}; ESI-HRMS: *m/z* [M + H]$^{+}$ calcd for $C_{18}H_{14}{}^{35}ClIN_3O$: 449.9865, found: 449.9863.

6-Chloro-2-ethyl-9-fluoro-5-phenyl-2*H*-[1,2,3]triazolo[5,1-*a*]isoquinolin-4-ium-1-olate 2ga



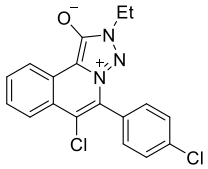
The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1); 69% yield; yellow solid; mp: 184−185 °C; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -107.2 ppm; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.52 (dd, J = 9.2, 2.6 Hz, 1H), 8.11 (dd, J = 9.0, 5.2 Hz, 1H), 7.61−7.58 (m, 3H), 7.56−7.51 (m, 2H), 7.27 (td, J = 8.1, 2.6 Hz, 1H), 4.24 (q, J = 7.3 Hz, 2H), 1.41 (t, J = 7.3 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.8 (d, $J_{C–F}$ = 250.8 Hz), 153.4, 131.2 (d, $J_{C–F}$ = 2.9 Hz), 130.6, 130.5, 129.0, 128.9, 127.6 (d, $J_{C–F}$ = 11.5 Hz), 127.5 (d, $J_{C–F}$ = 9.5 Hz), 126.7 (d, $J_{C–F}$ = 1.0 Hz), 121.4 (d, $J_{C–F}$ = 2.1 Hz), 115.8 (d, $J_{C–F}$ = 23.9 Hz), 114.0 (d, $J_{C–F}$ = 4.5 Hz), 107.3 (d, $J_{C–F}$ = 25.0 Hz), 40.0, 14.4 ppm; IR (neat): ν_{max} 1648, 1253, 1030 cm^{-1}; ESI-HRMS: *m/z* [M + H]$^{+}$ calcd for $C_{18}H_{14}{}^{35}ClFN_3O$: 342.0804, found: 342.0802.

6-Chloro-2-methyl-5-phenyl-9-(trifluoromethyl)-2*H*-[1,2,3]triazolo[5,1-*a*]isoquinolin-4-ium-1-olate 2ha



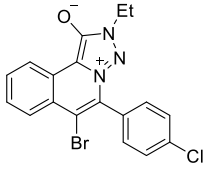
The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 1:1); 56% yield; yellow solid; mp: 260−262 °C; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.6 ppm; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.12 (br, 1H), 8.24 (d, J = 8.6 Hz, 1H), 7.77 (dd, J = 8.6, 1.5 Hz, 1H), 7.64−7.61 (m, 3H), 7.57−7.54 (m, 2H), 3.81 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.9, 133.7, 132.5 (q, $J_{C–F}$ = 33.0 Hz), 130.9, 130.3, 129.2, 128.5, 126.9, 126.6, 125.9, 125.8, 123.7 (q, $J_{C–F}$ = 271.3 Hz), 123.4 (q, $J_{C–F}$ = 3.5 Hz), 118.9 (q, $J_{C–F}$ = 4.1 Hz), 114.0, 31.6 ppm; IR (neat): ν_{max} 1645, 1466 cm^{-1}; ESI-HRMS: *m/z* $[M + H]^+$ calcd for $C_{18}H_{12}{}^{35}ClF_3N_3O$: 378.0616, found: 378.0615.

6-Chloro-5-(4-chlorophenyl)-2-ethyl-2*H*-[1,2,3]triazolo[5,1-*a*]isoquinolin-4-ium-1-olate 2ia



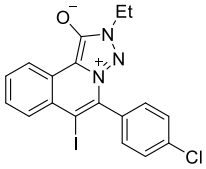
The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1); 70% yield; yellow solid; mp: 185−187 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.85 (d, J = 7.8 Hz, 1H), 8.11 (d, J = 8.2 Hz, 1H), 7.75−7.71 (m, 1H), 7.59−7.55 (m, 3H), 7.51−7.48 (m, 2H), 4.25 (q, J = 7.3 Hz, 2H), 1.42 (t, J = 7.3 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.3, 136.6, 132.1, 130.8, 130.7, 129.4, 127.5, 127.5, 127.4, 126.0, 124.8, 124.7, 121.7, 114.7, 39.9, 14.4 ppm; IR (neat): ν_{max} 1646, 1482 cm^{-1}; ESI-HRMS: *m/z* $[M + H]^+$ calcd for $C_{18}H_{14}{}^{35}Cl_2N_3O$: 358.0508, found: 358.0508.

6-Bromo-5-(4-chlorophenyl)-2-ethyl-2*H*-[1,2,3]triazolo[5,1-*a*]isoquinolin-4-ium-1-olate 2ib



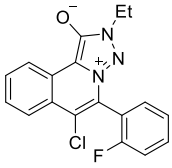
The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 1:1); 71% yield; yellow solid; mp: 245−246 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.86 (d, J = 7.9 Hz, 1H), 8.13 (d, J = 8.8 Hz, 1H), 7.75−7.71 (m, 1H), 7.58−7.55 (m, 3H), 7.47−7.44 (m, 2H), 4.24 (q, J = 7.2 Hz, 2H), 1.41 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.3, 136.5, 132.3, 132.0, 130.8, 129.6, 129.5, 127.64, 127.63, 126.1, 125.7, 121.8, 119.8, 115.0, 39.9, 14.5 ppm; IR (neat): ν_{max} 2851, 1648 cm^{-1}; ESI-HRMS: *m/z* $[M + H]^+$ calcd for $C_{18}H_{14}{}^{79}Br^{35}ClN_3O$: 402.0003, found: 402.0007.

5-(4-Chlorophenyl)-2-ethyl-6-iodo-2*H*-[1,2,3]triazolo[5,1-*a*]isoquinolin-4-ium-1-olate 2ic



The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 1:1); 70% yield; yellow solid; mp: 246−247 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.83−8.81 (m, 1H), 8.05 (d, J = 8.0 Hz, 1H), 7.71−7.69 (m, 1H), 7.59−7.57 (m, 2H), 7.53 (t, J = 7.8 Hz, 1H), 7.40−7.37 (m, 2H), 4.25−4.24 (m, 2H), 1.42−1.39 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 136.5, 135.7, 133.3, 132.8, 132.0, 130.7, 129.6, 128.0, 127.7, 125.5, 121.8, 99.7, 39.8, 14.5 ppm; IR (neat): ν_{max} 1630, 1484 cm^{-1}; ESI-HRMS: *m/z* $[M + H]^+$ calcd for $C_{18}H_{14}{}^{35}ClIN_3O$: 449.9865, found: 449.9867.

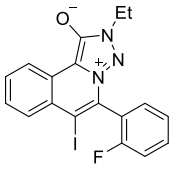
6-Chloro-2-ethyl-5-(2-fluorophenyl)-2*H*-[1,2,3]triazolo[5,1-*a*]isoquinolin-4-ium-1-olate 2ja



The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1); 75% yield; yellow solid; mp: 193−194 °C; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -111.2 ppm; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.88−8.86 (m, 1H), 8.14−8.12 (m, 1H), 7.77−7.73 (m, 1H), 7.64−7.56 (m, 2H), 7.53−7.49 (m, 1H), 7.38 (td, J = 7.6, 1.1 Hz, 1H), 7.32−7.27 (m, 1H), 4.32−4.18 (m, 2H), 1.42 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.6 (d, $J_{C–F}$ = 249.8 Hz), 153.4, 132.8 (d, $J_{C–F}$ = 8.3 Hz), 132.3 (d, $J_{C–F}$ = 2.3 Hz), 134.0, 128.8, 127.4, 126.9, 126.3, 124.9, 124.7 (d, $J_{C–F}$ = 3.6 Hz), 124.5, 121.8, 117.3 (d, $J_{C–F}$ = 15.6 Hz), 116.5 (d, $J_{C–F}$ = 21.0 Hz),

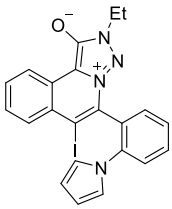
114.5, 39.9, 14.4 ppm; IR (neat): ν_{max} 1657, 1487 cm^{-1}; ESI-HRMS: *m/z* $[M + H]^+$ calcd for $C_{18}H_{14}{}^{35}ClFN_3O$: 342.0804, found: 342.0802.

2-Ethyl-5-(2-fluorophenyl)-6-iodo-2*H*-[1,2,3]triazolo[5,1-*a*]isoquinolin-4-ium-1-olate 2jc



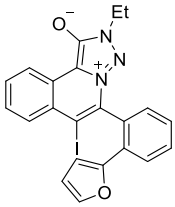
The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 1:1); 85% yield; yellow solid; mp: 250−252 °C; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -112.3 ppm; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.82 (d, *J* = 7.9 Hz, 1H), 8.04 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.72−7.67 (m, 1H), 7.64−7.58 (m, 1H), 7.55−7.51 (m, 1H), 7.44−7.36 (m, 2H), 7.31−7.26 (m, 1H), 4.24 (br, 2H), 1.40 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.1 (d, $J_{C–F}$ = 249.1 Hz), 153.2, 132.8, 132.7, 132.4 (d, $J_{C–F}$ = 2.2 Hz), 132.1, 130.9, 127.9, 127.5, 125.8, 124.9 (d, $J_{C–F}$ = 3.5 Hz), 123.0 (d, $J_{C–F}$ = 15.8 Hz), 121.8, 116.5 (d, $J_{C–F}$ = 20.8 Hz), 115.2, 100.8, 39.9, 14.4 ppm; IR (neat): ν_{max} 1639, 1607, 1481 cm^{-1}; ESI-HRMS: *m/z* $[M + H]^+$ calcd for $C_{18}H_{14}FIN_3O$: 434.0160, found: 434.0161.

5-(2-(1*H*-pyrrol-1-yl)phenyl)-2-ethyl-6-iodo-2*H*-[1,2,3]triazolo[5,1-*a*]isoquinolin-4-ium-1-olate 2kc



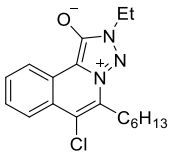
The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 1:1); 88 % yield; yellow solid; mp: 150−151 °C; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.76 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.99 (d, *J* = 8.2 Hz, 1H), 7.71−7.65 (m, 2H), 7.58−7.47 (m, 4H), 6.60 (t, *J* = 2.1 Hz, 2H), 5.97 (t, *J* = 2.1 Hz, 2H), 4.31−4.22 (m, 1H), 4.12−4.04 (m, 1H), 1.36 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.1, 140.9, 134.9, 132.7, 131.8, 130.8, 130.2, 127.8, 127.6, 127.4, 126.3, 125.5, 121.7, 121.2, 114.9, 110.0, 100.8, 39.7, 14.4 ppm; IR (neat): ν_{max} 1648, 1495 cm^{-1}; ESI-HRMS: *m/z* $[M + H]^+$ calcd for $C_{22}H_{18}IN_4O$: 481.0520, found: 481.0524.

2-Ethyl-5-(2-(furan-2-yl)phenyl)-6-iodo-2*H*-[1,2,3]triazolo[5,1-*a*]isoquinolin-4-ium-1-olate 2lc



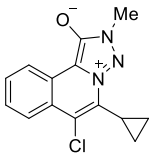
The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1); 75 % yield; yellow solid; mp: 230−231 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.84 (d, *J* = 8.0 Hz, 1H), 8.05 (dd, *J* = 8.3, 1.1 Hz, 1H), 7.94 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.72 (t, *J* = 7.3 Hz, 1H), 7.64 (td, *J* = 7.6, 1.4 Hz, 1H), 7.56−7.49 (m, 2H), 7.39 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.17 (d, *J* = 1.2 Hz, 1H), 6.17 (dd, *J* = 3.4, 1.8 Hz, 1H), 5.92 (d, *J* = 3.4 Hz, 1H), 4.24−4.08 (m, 2H), 1.27 (t, *J* = 7.2 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.2, 151. 6, 142.8, 137.0, 132.6, 131.9, 130.9, 130.8, 130.7, 130.6, 128.2, 127.8, 127.7, 127.0, 125.5, 121.8, 111.8, 107.4, 99.6, 39.7, 14.4 ppm; IR (neat): ν_{max} 1650, 1288 cm^{-1}; ESI-HRMS: *m/z* $[M + H]^+$ calcd for $C_{22}H_{17}IN_3O_2$: 482.0360, found: 482.0362.

6-Chloro-2-ethyl-5-hexyl-2*H*-[1,2,3]triazolo[5,1-*a*]isoquinolin-4-ium-1-olate 2ma



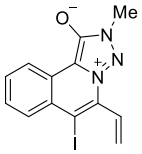
The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 3:1); 58% yield; yellow solid; mp: 93−95 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.81(d, *J* = 7.5 Hz, 1H), 8.04 (d, *J* = 8.2 Hz, 1H), 7.68−7.64 (m, 1H), 7.55−7.51 (m, 1H), 4.35 (q, *J* = 7.3 Hz, 2H), 3.29−3.25 (m, 2H), 1.78−1.70 (m, 2H), 1.53 (t, *J* = 7.3 Hz, 3H), 1.49−1.43 (m, 2H), 1.39−1.30 (m, 4H), 0.89 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.5, 133.7, 129.8, 127.2, 125.8, 125.2, 124.6, 124.2, 121.6, 114.1, 39.8, 31.5, 29.2, 27.5, 25.9, 22.6, 14.5, 14.2 ppm; IR (neat): ν_{max} 1642, 1300 cm^{-1}; ESI-HRMS: *m/z* $[M + H]^+$ calcd for $C_{18}H_{23}{}^{35}ClN_3O$: 332.1524, found: 332.1524.

6-Chloro-5-cyclopropyl-2-methyl-2*H*-[1,2,3]triazolo[5,1-*a*]isoquinolin-4-ium-1-olate 2na



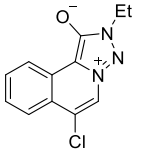
The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1); 60% yield; yellow solid; mp: 124−126 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.79 (d, *J* = 8.0 Hz, 1H), 8.05 (d, *J* = 8.2 Hz, 1H), 7.65 (t, *J* = 7.2 Hz, 1H), 7.51 (t, *J* = 7.3 Hz, 1H), 3.91 (s, 3H), 2.11−2.04 (m, 1H), 1.34−1.28 (m, 2H), 1.21−1.13 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.9, 132.3, 130.0, 128.5, 127.2, 125.2, 124.8, 124.2, 121.5, 114.1, 31.4, 9.6, 8.9 ppm; IR (neat): ν_{max} 1636, 1253 cm^{-1}; ESI-HRMS: *m/z* $[M + H]^+$ calcd for $C_{14}H_{13}{}^{35}ClN_3O$: 274.0742, found: 274.0744.

6-Iodo-2-methyl-5-vinyl-2*H*-[1,2,3]triazolo[5,1-*a*]isoquinolin-4-ium-1-olate 2oc



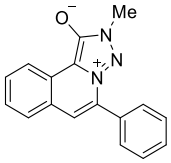
The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 1:1); 88 % yield; yellow solid; mp: 115−116 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.81 (d, *J* = 7.9 Hz, 1H), 8.07 (d, *J* = 8.3 Hz, 1H), 7.66 (t, *J* = 7.9 Hz, 1H), 7.52 (t, *J* = 8.2 Hz, 1H), 7.06 (dd, *J* = 17.7, 12.2 Hz, 1H), 6.51 (dd, *J* = 17.7, 0.9 Hz, 1H), 6.01 (dd, *J* = 12.2, 0.9 Hz, 1H), 3.91 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.5, 133.1, 132.3, 131.0, 130.5, 128.0, 127.7, 127.6, 124.8, 121.6, 115.1, 99.6, 31.4 ppm; IR (neat): ν_{max} 1637, 1260 cm^{-1}; ESI-HRMS: *m/z* $[M + H]^+$ calcd for $C_{13}H_{11}IN_3O$: 351.9941, found: 351.9942.

6-Chloro-2-ethyl-2*H*-[1,2,3]triazolo[5,1-*a*]isoquinolin-4-ium-1-olate 2pa



The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 1:2); 73% yield; yellow solid; mp: 164−165 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.76 (d, *J* = 8.0 Hz, 1H), 8.08 (s, 1H), 8.03 (d, *J* = 8.1 Hz, 1H), 7.73−7.69 (m, 1H), 7.58−7.54 (m, 1H), 4.31 (q, *J* = 7.3 Hz, 2H), 1.51 (t, *J* = 7.3 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.1, 132.2, 131.0, 128.7, 127.5, 126.6,124.3, 122.0, 120.5, 114.2, 39.8, 14.5 ppm; IR (neat): ν_{max} 1642 cm^{-1}; ESI-HRMS: *m/z* $[M + H]^+$ calcd for $C_{12}H_{11}{}^{35}ClN_3O$: 248.0585, found: 248.0587.

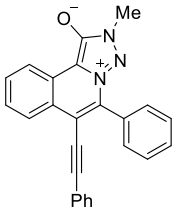
4. Analytical data of compound 3aa



Yellow solid; mp: 186−187 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.85 (d, J = 8.0 Hz, 1H), 7.83−7.80 (m, 2H), 7.71−7.65 (m, 2H), 7.57−7.53 (m, 3H), 7.52−7.47 (m, 1H), 7.33 (s, 1H), 3.89 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 154.1, 134.3, 131.0, 130.4, 129.8, 129.3, 128.9, 127.2, 127.0, 126.4, 126.1, 121.8, 121.3, 115.9, 31.5 ppm; IR (neat): ν_{max} 1648, 1495 cm^{-1}; ESI-HRMS: *m/z* [M + H]$^{+}$ calcd for $C_{17}H_{14}N_3O$: 276.1131, found: 276.1133.

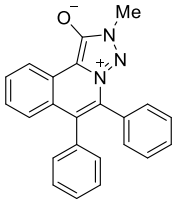
5. Synthesis and analytical data of compounds 4

2-Methyl-5-phenyl-6-(phenylethynyl)-2*H*-[1,2,3]triazolo[5,1-*a*]isoquinolin-4-ium-1-olate 4a



A mixture of 6-iodo-2-methyl-5-phenyl-2*H*-[1,2,3]triazolo[5,1-*a*]isoquinolin-4-ium-1-olate **2ac** (80.2 mg, 0.2 mmol), phenylacetylene (102.1 mg, 1.0 mmol), $Pd(PPh_3)_2Cl_2$ (14.0 mg, 0.02 mmol), CuI (3.8 mg, 0.02 mmol) and PPh_3 (10.5 mg, 0.04 mmol) in DMF/Et_2NH (5 mL, 1:1) was stirred at 80 °C for 12 h. The cooled mixture was partitioned between H_2O (30 mL) and EtOAc (30 mL). The separated aqueous phase was extracted with EtOAc (3 x 30 mL). The combined organic extracts were washed with brine (3 x 30 mL), then dried over anhydrous sodium sulfate and filtered. The filtrate was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 1:2) to afford **4a** as yellow solid; 71.4 mg, 95 % yield; mp: 227−228 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.87 (d, J = 8.0 Hz, 1H), 8.27 (d, J = 8.0 Hz, 1H), 7.78−7.76 (m, 2H), 7.72 (t, J = 7.1 Hz, 1H), 7.61−7.54 (m, 4H), 7.36−7.31 (m, 5H), 3.86 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 136.5, 131.7, 130.9, 130.5, 130.1, 129.3, 128.8, 128.6, 128.5, 127.3, 126.1, 126.0, 125.5, 122.2, 121.8, 115.6, 99.7, 83.5, 31.4 ppm; IR (neat): ν_{max} 2920, 2000, 1511 cm^{-1}; ESI-HRMS: *m/z* [M + H]$^{+}$ calcd for $C_{25}H_{18}N_3O$: 376.1444, found: 376.1446.

2-Methyl-5,6-diphenyl-2*H*-[1,2,3]triazolo[5,1-*a*]isoquinolin-4-ium-1-olate 4b

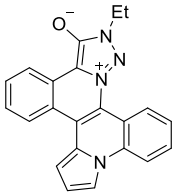


A mixture of 6-iodo-2-methyl-5-phenyl-2*H*-[1,2,3]triazolo[5,1-*a*]isoquinolin-4-ium-1-olate **2ac** (80.2 mg, 0.2 mmol), phenylboronic acid (36.6 mg, 0.3 mmol) $Pd(PPh_3)_4$ (2.9 mg, 0.0025 mmol) and K_2CO_3 (110.6, 0.8 mmol) in EtOH:toluene:H_2O (7 mL, 1:4:2) was stirred at 100 °C for 10 h. The cooled mixture was partitioned between H_2O (30 mL) and EtOAc (30 mL). The separated aqueous phase was extracted with EtOAc (3 x 30 mL). The combined organic extracts were dried over anhydrous sodium sulfate and filtered. The filtrate was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 1:1) to afford **4b** as yellow solid; 68.9 mg, 98 % yield; mp: 270−272 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.94 (d, J = 7.9 Hz, 1H), 7.69−7.65 (m, 1H), 7.40−7.36 (m, 1H), 7.34−7.28 (m, 9H), 7.20−7.17 (m, 2H), 3.84 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 154.1, 134.8, 132.9, 132.1, 131.1, 130.9, 130.3, 129.6, 129.3, 128.4, 128.3, 128.0, 127.4, 126.8, 126.6, 126.2, 121.7, 115.2, 31.4 ppm; IR (neat): ν_{max} 1648, 1438 cm^{-1}; ESI-HRMS: *m/z* $[M + H]^+$ calcd for $C_{23}H_{18}N_3O$: 352.1444, found: 352.1443.

6. Synthesis and analytical data of compounds 5 and 6

A mixture of **2jc/2kc** (0.2 mmol), $Pd(OAc)_2$ (0.02 mmol), and ^{t}BuOLi (0.4 mmol) in DMF (5 mL) was stirred at 120 °C for 2 h until substrate **2jc/2kc** consumed as indicated by TLC. The cooled mixture was partitioned between H_2O (30 mL) and EtOAc (30 mL). The separated aqueous phase was extracted with EtOAc (3 x 30 mL). The combined organic extracts were washed with brine (3 x 30 mL), then dried over anhydrous sodium sulfate and filtered. The filtrate was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel to afford **5**/**6**.

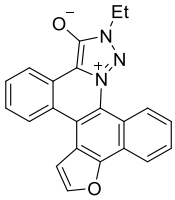
2-Ethyl-2*H*-dibenzo[*c*,*h*]pyrrolo[2,1-*f*][1,2,3]triazolo[1,5-*a*][1,6]naphthyridin-4-ium-1-olate 5



The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 1:1); 95 % yield; yellow solid; mp: 233−235 °C; ^{1}H NMR (400

MHz, $CDCl_3$) δ = 9.75 (dd, *J* = 8.6, 1.0 Hz, 1H), 9.05 (dd, *J* = 8.0, 0.9 Hz, 1H), 8.74 (d, *J* = 8.4 Hz, 1H), 7.95−7.92 (m, 2H), 7.74−7.70 (m, 1H), 7.68−7.64 (m, 1H), 7.59−7.54 (m, 1H), 7.50−7.44 (m, 2H), 6.89 (dd, *J* = 4.1, 2.9 Hz, 1H), 4.48 (q, *J* = 7.3 Hz, 2H), 1.65 (t, *J* = 7.3 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.7, 133.1, 130.1, 129.7, 128.0, 127.1, 126.1, 125.9, 125.8, 124.4, 122.9, 121.9, 120.9, 119.5, 116.1, 114.9, 114. 8, 114.6, 114.2, 109.6, 39.9, 14.7 ppm; IR (neat): ν_{max} 1643, 1408 cm^{-1}; ESI-HRMS: *m/z* $[M + H]^+$ calcd for $C_{22}H_{17}N_4O$: 353.1397, found: 353.1398.

9-Ethyl-9*H*-benzo[c]furo[3,2-*a*][1,2,3]triazolo[1,5-*f*]phenanthridin-11-ium-8-olate 6

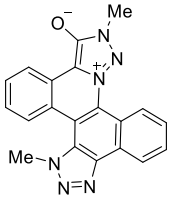


The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1); 78 % yield; yellow solid; mp: 227−229 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.96 (d, *J* = 8.5 Hz, 1H), 9.10 (d, *J* = 7.9 Hz, 1H), 8.57 (d, *J* = 8.4 Hz, 1H), 8.40 (d, *J* = 7.4 Hz, 1H), 7.87 (d, *J* = 1.8 Hz, 1H), 7.76−7.68 (m, 3H), 7.62 (d, *J* = 1.8 Hz, 1H), 7.60−7.56 (m, 1H), 4.50 (q, *J* = 7.2 Hz, 2H), 1.68 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.9, 150.9, 145.0, 129.3, 127.9, 127.4, 127.3, 126.8, 125.4, 125.2, 124.7, 123.6, 122.5, 122.0, 121.9, 120.9, 120.5, 117.9, 114.8, 109. 6, 40.0, 14.7 ppm; IR (neat): ν_{max} 1634, 1457 cm^{-1}; ESI-HRMS: *m/z* $[M + H]^+$ calcd for $C_{22}H_{16}N_3O_2$: 354.1237, found: 354.1236.

7. Synthesis and analytical data of compounds 7a–7c

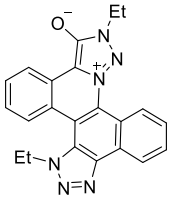
A mixture of **1p**–**1r** (0.2 mmol), CuI (0.2 mmol) and DTBP (0.4 mmol) in toluene (3 mL) was stirred at 110 °C for 14-18 h until substrate **1p**–**1r** consumed as indicated by TLC. The cooled mixture was evaporated *in vacuo*, $Pd(OAc)_2$ (0.02 mmol), ^{t}BuOLi (0.4 mmol) and DMF (5 mL) were then added. The mixture was heated to 120 °C for 2-3 h until the intermediate consumed as indicated by TLC. The cooled mixture was partitioned between H_2O (30 mL) and EtOAc (30 mL). The separated aqueous phase was extracted with EtOAc (3 x 30 mL). The combined organic extracts were washed with brine (3 x 30 mL), then dried over anhydrous sodium sulfate and filtered. The filtrate was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel to afford **7a−7c**.

3,9-Dimethyl-3,9-dihydrobenzo[*c*]bis([1,2,3]triazolo)[4,5-*a*:1',5'-*f*]phenanthridin-11-ium-8-olate 7a



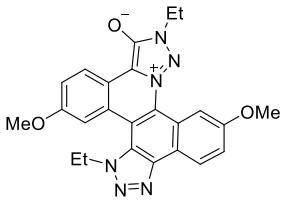
The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 1:2); 77 % yield; yellow solid; mp: 266−267 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.95 (d, *J* = 8.7 Hz, 1H), 9.06 (dd, *J* = 8.0, 0.7 Hz, 1H), 8.99 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.98 (d, *J* = 8.1 Hz, 1H), 7.92−7.88 (m, 1H), 7.84−7.76 (m, 2H), 7.67−7.62 (m, 1H), 4.43 (s, 3H), 4.10 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.3, 143.1, 130.1, 129.7, 128.7, 128.1, 127.33, 127.25, 127.0, 126.4, 125.6, 125.3, 123.0, 122.6, 121.8, 121.3, 115.3, 114. 5, 40.3, 31.8 ppm; IR (neat): ν_{max} 1654, 1259 cm^{-1}; ESI-HRMS: *m/z* $[M + H]^+$ calcd for $C_{20}H_{15}N_6O$: 355.1302, found: 355.1305.

3,9-Diethyl-3,9-dihydrobenzo[*c*]bis([1,2,3]triazolo)[4,5-*a*:1',5'-*f*]phenanthridin-11-ium-8-olate 7b



The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 1:2); 72 % yield; yellow solid; mp: 238−240 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.98 (d, *J* = 8.7 Hz, 1H), 9.07 (dd, *J* = 8.0, 0.7 Hz, 1H), 9.02 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.98 (d, *J* = 8.1 Hz, 1H), 7.93−7.90 (m, 1H), 7.86−7.81 (m, 1H), 7.80−7.76 (m, 1H), 7.65−7.61 (m, 1H), 4.91 (q, *J* = 7.2 Hz, 2H), 4.55 (q, *J* = 7.3 Hz, 2H), 1.69 (t, *J* = 7.3 Hz, 3H), 1.38 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.9, 143.5, 130.2, 129.7, 128.2, 127.8, 127.5, 127.0, 126.6, 126.3, 125.8, 125.4, 123.1, 122.9, 122.0, 121.6, 115.4, 114.7, 47.8, 40.3, 15.3, 14.7 ppm; IR (neat): ν_{max} 1654, 1259 cm^{-1}; ESI-HRMS: *m/z* $[M + H]^+$ calcd for $C_{20}H_{15}N_6O$: 383.1615, found: 383.1614.

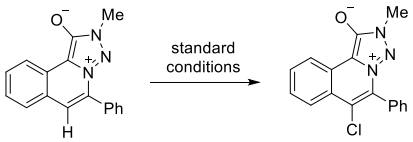
3,9-Diethyl-5,13-dimethoxy-3,9-dihydrobenzo[*c*]bis([1,2,3]triazolo)[4,5-*a*:1',5'-*f*]phenanthridin-11-ium-8-olate 7c



The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 1:2); 74 % yield; red solid; mp: 226−227 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.60 (d, J = 2.4 Hz, 1H), 9.04 (d, J = 8.9 Hz, 1H), 8.94 (d, J = 8.9 Hz, 1H),7.57 (dd, J = 8.9, 2.4 Hz, 1H), 7.49 (d, J = 2.4 Hz, 1H), 7.41 (dd, J = 8.8, 2.4 Hz, 1H), 4.97 (q, J = 7.3 Hz, 2H), 4.52 (q, J = 7.3 Hz, 2H), 4.06 (s, 3H), 4.00 (s, 3H), 1.70 (t, J = 7.3 Hz, 3H), 1.33 (t, J = 7.3 Hz, 3H) ppm; IR (neat): ν_{max} 1631, 1458 cm^{-1}; ESI-HRMS: *m/z* $[M + H]^+$ calcd for $C_{24}H_{23}N_6O_3$: 443.1826, found: 443.1828.

8. Control experiment to elucidate the reaction mechanism

To elucidate the reaction mechanism for the formation of 6-halo-[1,2,3]triazolo[5,1-*a*]isoquinoliums **2**, the control experiment was conducted as follows. The reaction of [1,2,3]triazolo[5,1-*a*]isoquinolin-4-ium-1-olate **3aa** under the standard reaction conditions did not afforded 6-chloro-[1,2,3]triazolo[5,1-*a*]isoquinolin-4-ium-1-olate **2aa**. This suggested that vinylic C−H bromination of **3aa** did not proceed under the present reaction conditions.



3aa **2aa**, 0%

9. Crystallographic Data

6-Chloro-5-(4-chlorophenyl)-2-ethyl-2*H*-[1,2,3]triazolo[5,1-*a*]isoquinolin-4-ium-1-olate (2ia)

The structure of **2ia** was determined by X-ray diffraction. The X-ray data have been deposited at the Cambridge Crystallographic Data Center (CCDC 2202803).

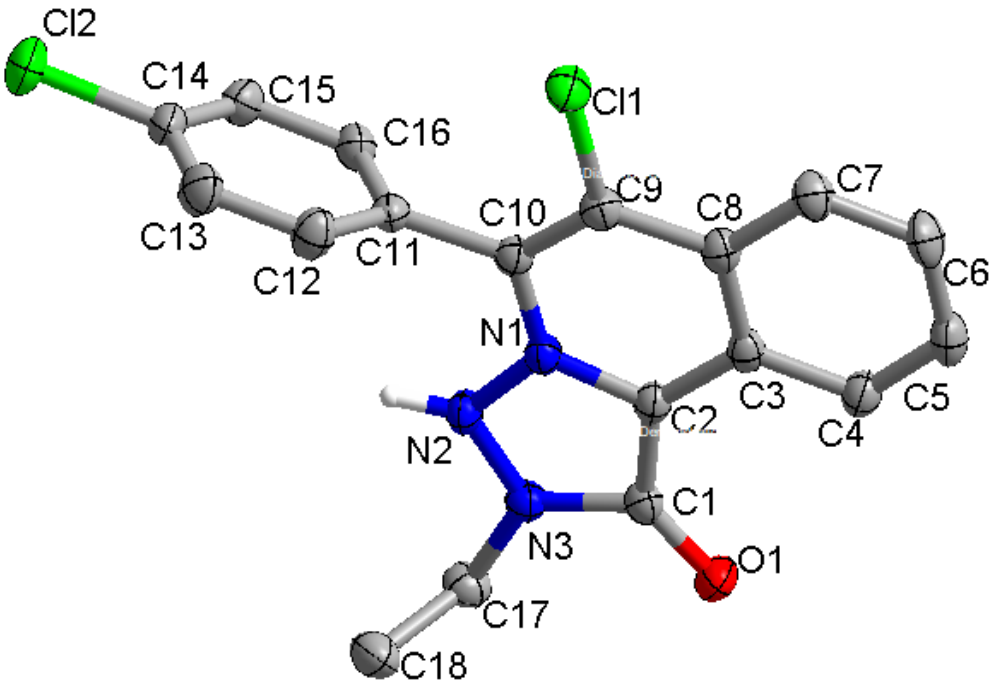


Table 1. Crystal data and structure refinement for 2ia

Empirical formula	$C_{18}H_{14}Cl_2N_3O$
Formula weight	359.22
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	9.4903(6)
b/Å	9.7844(8)
c/Å	10.1573(9)
α/°	117.682(9)
β/°	100.666(7)
γ/°	93.883(6)
Volume/Å^3	807.88(13)
Z	2
ρ_{calc}g/cm^3	1.477
μ/mm^{-1}	3.696
F(000)	370.0

Crystal size/mm^3	0.16 × 0.12 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	9.634 to 134.168
Index ranges	-11 ≤ h ≤ 11, -11 ≤ k ≤ 9, -12 ≤ l ≤ 11
Reflections collected	5805
Independent reflections	2881 [R_{int} = 0.0252, R_{sigma} = 0.0406]
Data/restraints/parameters	2881/0/219
Goodness-of-fit on F^2	0.977
Final R indexes [I>=2σ (I)]	R_1 = 0.0420, wR_2 = 0.1015
Final R indexes [all data]	R_1 = 0.0559, wR_2 = 0.1147
Largest diff. peak/hole / e Å^{-3}	0.23/-0.33

Table 2. Fractional Atomic Coordinates (×104) and Equivalent Isotropic Displacement Parameters (Å2×103) for 2ia. Ueq is defined as 1/3 of of the trace of the orthogonalised UIJ tensor.

Atom	*x*	*y*	*z*	U(eq)
C1	5756(3)	8266(3)	-1550(3)	40.3(5)
C2	6130(2)	8612(3)	3(3)	38.1(5)
C3	7393(2)	9456(3)	1236(3)	38.9(5)
C4	8592(3)	10246(3)	1090(3)	47.4(6)
C5	9771(3)	11077(3)	2324(3)	54.1(7)
C6	9779(3)	11157(3)	3720(3)	53.1(7)
C7	8621(3)	10375(3)	3886(3)	47.5(6)
C8	7412(2)	9501(3)	2647(3)	39.3(5)
C9	6148(3)	8672(3)	2751(3)	40.0(5)
C10	4933(2)	7920(3)	1598(3)	37.7(5)
C11	3578(3)	7127(3)	1664(3)	38.5(5)
C12	3514(3)	5677(3)	1586(3)	53.4(7)
C13	2271(3)	4969(3)	1705(3)	58.1(7)
C14	1108(3)	5729(3)	1916(3)	50.6(7)
C15	1145(3)	7168(3)	1988(3)	51.4(7)
C16	2391(3)	7868(3)	1860(3)	45.4(6)
C17	3425(3)	6715(3)	-3613(3)	49.8(7)
C18	3153(4)	4949(3)	-4428(3)	66.8(9)
Cl1	6188.0(7)	8659.5(8)	4469.1(7)	50.0(2)
Cl2	-452.7(9)	4862.4(10)	2097.4(10)	79.1(3)
N1	4963(2)	7918(2)	225(2)	37.5(5)
N2	3859(2)	7162(2)	-1017(2)	41.9(5)
N3	4357(2)	7396(2)	-2069(2)	41.3(5)
O1	6422(2)	8601(2)	-2335(2)	54.7(5)

Table 3. Anisotropic Displacement Parameters (Å2×103) for 202010226. The Anisotropic displacement factor exponent takes the form: -2π2[h2a*2U11+2hka*b*U12+…]

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	41.4(13)	35.3(12)	42.7(13)	18.2(10)	10.4(11)	3.7(10)
C2	34.8(12)	35.9(12)	43.2(13)	19.0(10)	10.6(10)	3.4(9)
C3	32.7(12)	34.1(12)	47.7(14)	18.1(10)	9.8(10)	6.0(9)
C4	42.1(14)	48.4(14)	53.0(15)	25.8(12)	13.3(12)	2.7(11)
C5	38.3(14)	49.6(15)	71.5(19)	29.9(14)	9.5(13)	-2.0(12)
C6	35.9(14)	49.9(15)	62.9(18)	26.6(13)	-5.0(12)	-3.6(11)
C7	39.4(14)	49.3(15)	50.7(15)	25.6(12)	2.4(12)	3.9(11)
C8	34.0(12)	36.7(12)	46.1(14)	20.6(10)	6.0(10)	6.6(10)
C9	39.9(13)	40.1(13)	40.7(13)	21.1(11)	7.6(10)	7.2(10)
C10	37.2(13)	36.5(12)	39.6(13)	18.8(10)	10.0(10)	4.7(10)
C11	38.6(13)	39.5(12)	34.2(12)	16.6(10)	7.8(10)	0.2(10)
C12	50.2(16)	48.8(15)	69.4(18)	33.1(14)	20.0(14)	10.7(12)
C13	65.5(19)	46.0(15)	70.6(19)	32.3(14)	25.1(16)	4.4(14)
C14	48.5(15)	53.3(16)	43.6(14)	19.5(12)	14.2(12)	-9.2(12)
C15	43.2(14)	54.4(16)	51.8(16)	21.7(13)	13.6(12)	5.0(12)
C16	44.1(14)	41.9(13)	49.9(15)	23.2(12)	10.4(12)	2.2(11)
C17	51.5(16)	53.6(16)	41.7(14)	23.7(12)	5.2(12)	6.6(12)
C18	81(2)	54.0(17)	49.6(17)	15.1(14)	15.3(16)	-3.9(15)
Cl1	46.5(4)	59.0(4)	45.1(4)	29.0(3)	4.3(3)	2.5(3)
Cl2	66.8(5)	81.8(6)	85.6(6)	37.3(5)	31.7(4)	-15.5(4)
N1	32.6(10)	37.9(10)	39.3(11)	18.0(9)	6.2(8)	1.6(8)
N2	36.7(11)	45.4(11)	40.6(11)	20.9(9)	5.1(9)	0.8(9)
N3	43.1(11)	42.1(11)	37.2(11)	19.8(9)	6.4(9)	3.2(9)
O1	58.0(12)	58.5(11)	49.9(11)	28.4(9)	17.6(9)	-4.1(9)

Table 4. Bond Lengths for 2ia

Atom	Atom	Length/Å
C1	C2	1.417(3)
C1	N3	1.392(3)
C1	O1	1.243(3)
C2	C3	1.427(3)
C2	N1	1.368(3)
C3	C4	1.402(3)
C3	C8	1.410(3)
C4	C5	1.376(3)
C5	C6	1.382(4)
C6	C7	1.376(4)
C7	C8	1.401(3)
C8	C9	1.450(3)
C9	C10	1.351(3)

Atom	Atom	Length/Å
C10	C11	1.485(3)
C10	N1	1.399(3)
C11	C12	1.380(3)
C11	C16	1.376(3)
C12	C13	1.381(4)
C13	C14	1.366(4)
C14	C15	1.373(4)
C14	Cl2	1.739(3)
C15	C16	1.383(3)
C17	C18	1.506(4)
C17	N3	1.457(3)
N1	N2	1.332(2)
N2	N3	1.347(3)

C9	Cl1	1.745(2)

Table 5. Bond Angles for 2ia

Atom	Atom	Atom	Angle/˚
N3	C1	C2	102.0(2)
O1	C1	C2	132.6(2)
O1	C1	N3	125.4(2)
C1	C2	C3	133.8(2)
N1	C2	C1	106.35(19)
N1	C2	C3	119.9(2)
C4	C3	C2	122.2(2)
C4	C3	C8	119.5(2)
C8	C3	C2	118.2(2)
C5	C4	C3	120.1(3)
C4	C5	C6	120.5(2)
C7	C6	C5	120.4(2)
C6	C7	C8	120.5(3)
C3	C8	C9	117.8(2)
C7	C8	C3	118.8(2)
C7	C8	C9	123.3(2)
C8	C9	Cl1	118.15(17)
C10	C9	C8	123.8(2)
C10	C9	Cl1	118.00(19)
C9	C10	C11	126.3(2)

Atom	Atom	Atom	Angle/˚
C9	C10	N1	116.2(2)
N1	C10	C11	117.57(19)
C12	C11	C10	120.6(2)
C16	C11	C10	119.7(2)
C16	C11	C12	119.6(2)
C11	C12	C13	120.5(3)
C14	C13	C12	119.1(3)
C13	C14	C15	121.3(2)
C13	C14	Cl2	119.5(2)
C15	C14	Cl2	119.1(2)
C14	C15	C16	119.3(3)
C11	C16	C15	120.2(2)
N3	C17	C18	112.4(2)
C2	N1	C10	124.01(19)
N2	N1	C2	113.90(19)
N2	N1	C10	122.02(18)
N1	N2	N3	102.68(17)
C1	N3	C17	126.4(2)
N2	N3	C1	115.03(19)
N2	N3	C17	118.61(19)

Table 6. Torsion Angles for 2ia

A	B	C	D	Angle/˚
C1	C2	C3	C4	3.9(4)
C1	C2	C3	C8	-176.9(3)
C1	C2	N1	C10	176.5(2)
C1	C2	N1	N2	-0.4(3)
C2	C1	N3	C17	-179.8(2)
C2	C1	N3	N2	-0.9(3)
C2	C3	C4	C5	178.4(2)
C2	C3	C8	C7	-177.6(2)
C2	C3	C8	C9	0.6(3)
C2	N1	N2	N3	-0.2(3)
C3	C2	N1	C10	-2.7(3)
C3	C2	N1	N2	-179.7(2)
C3	C4	C5	C6	-0.8(4)
C3	C8	C9	C10	-3.0(4)
C3	C8	C9	Cl1	177.62(18)
C4	C3	C8	C7	1.6(3)
C4	C3	C8	C9	179.8(2)

A	B	C	D	Angle/˚
C10	C11	C12	C13	177.5(2)
C10	C11	C16	C15	-177.2(2)
C10	N1	N2	N3	-177.2(2)
C11	C10	N1	C2	179.5(2)
C11	C10	N1	N2	-3.8(3)
C11	C12	C13	C14	-0.6(4)
C12	C11	C16	C15	0.4(4)
C12	C13	C14	C15	1.0(4)
C12	C13	C14	Cl2	-179.0(2)
C13	C14	C15	C16	-0.7(4)
C14	C15	C16	C11	0.0(4)
C16	C11	C12	C13	-0.1(4)
C18	C17	N3	C1	113.7(3)
C18	C17	N3	N2	-65.2(3)
Cl1	C9	C10	C11	2.9(3)
Cl1	C9	C10	N1	-178.13(16)
Cl2	C14	C15	C16	179.3(2)

C4	C5	C6	C7	1.5(4)
C5	C6	C7	C8	-0.6(4)
C6	C7	C8	C3	-0.9(4)
C6	C7	C8	C9	-179.0(2)
C7	C8	C9	C10	175.0(2)
C7	C8	C9	Cl1	-4.3(3)
C8	C3	C4	C5	-0.8(4)
C8	C9	C10	C11	-176.5(2)
C8	C9	C10	N1	2.5(4)
C9	C10	C11	C12	-76.7(3)
C9	C10	C11	C16	101.0(3)
C9	C10	N1	C2	0.4(3)
C9	C10	N1	N2	177.1(2)

N1	C2	C3	C4	-177.1(2)
N1	C2	C3	C8	2.1(3)
N1	C10	C11	C12	104.3(3)
N1	C10	C11	C16	-78.0(3)
N1	N2	N3	C1	0.7(3)
N1	N2	N3	C17	179.7(2)
N3	C1	C2	C3	179.8(3)
N3	C1	C2	N1	0.7(2)
O1	C1	C2	C3	-0.4(5)
O1	C1	C2	N1	-179.5(3)
O1	C1	N3	C17	0.4(4)
O1	C1	N3	N2	179.3(2)

Table 7. Hydrogen Atom Coordinates (Å×104) and Isotropic Displacement Parameters (Å2×103) for 2ia

Atom	x	y	z	U(eq)
H4	8590.81	10209.71	158.81	57
H5	10568.23	11589.21	2217.56	65
H6	10571.02	11741.72	4552.64	64
H7	8641.74	10427.92	4827.18	57
H12	4313.87	5173.08	1451.33	64
H13	2225.66	3987.84	1642.83	70
H15	341.7	7666.11	2121.22	62
H16	2426	8842.27	1906.95	55
H17A	3878.59	7077.75	-4202.12	60
H17B	2499.91	7076.57	-3557.27	60
H18A	2680.6	4583.27	-3864.43	100
H18B	4064.5	4584.64	-4500.83	100
H18C	2541.33	4554.44	-5439.68	100

10. References

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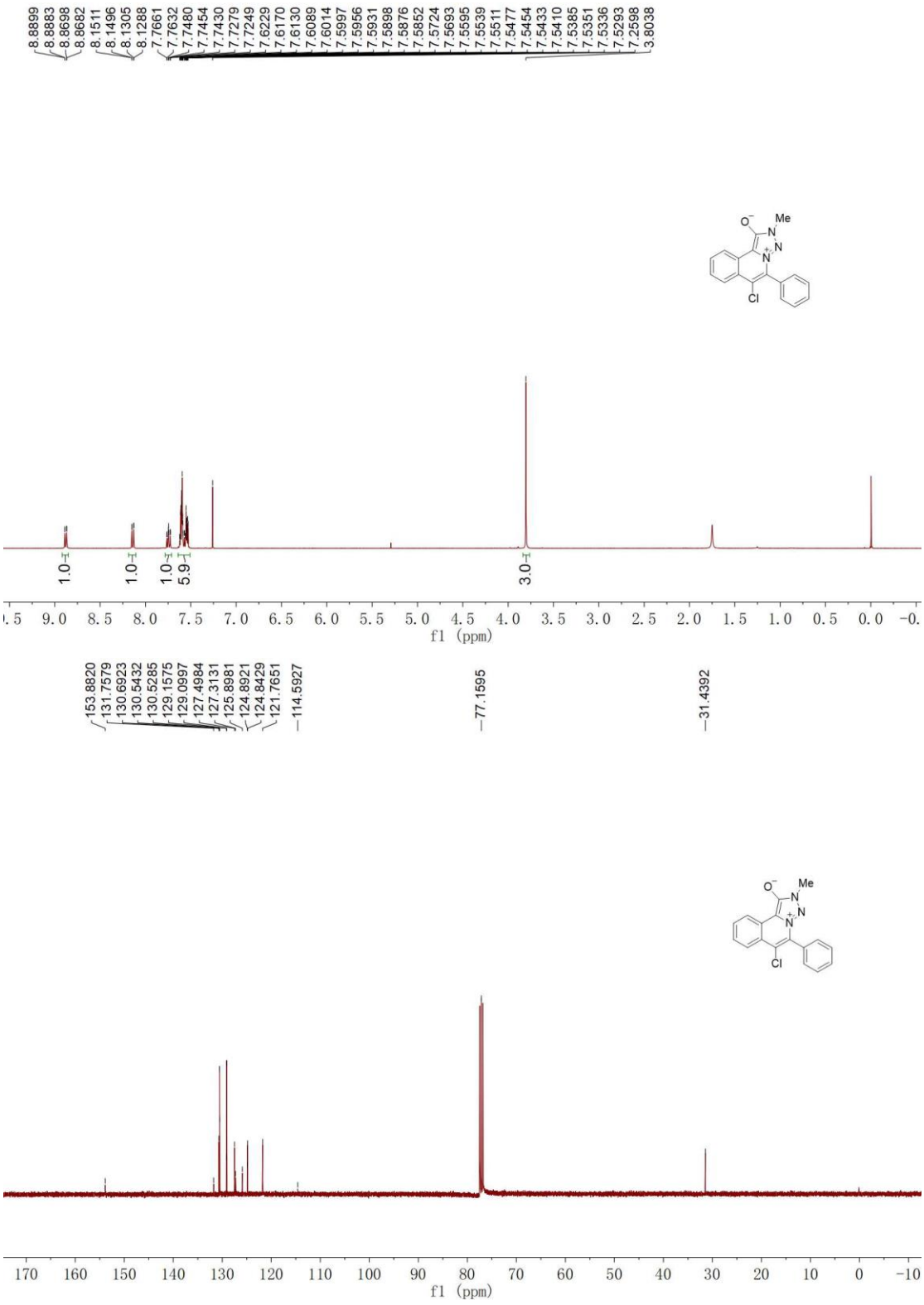
(2) P. Pierrat, S. Hesse, C. Cebrián and P. C. Gros, Controlling charge-transfer properties through a microwave-assisted mono-or bis-annulation of dialkynyl-N-(het) arylpyrroles. *Org. Biomol. Chem*., 2017, **15**, 8568−8575.

(3) K. Naveen, S. A. Nikson and P. T. Perumal, Palladium-Catalyzed Synthesis of Tetrasubstituted Olefins by Triple Domino Process. *Adv. Synth. Catal*., 2017, **359**, 2407−2413.

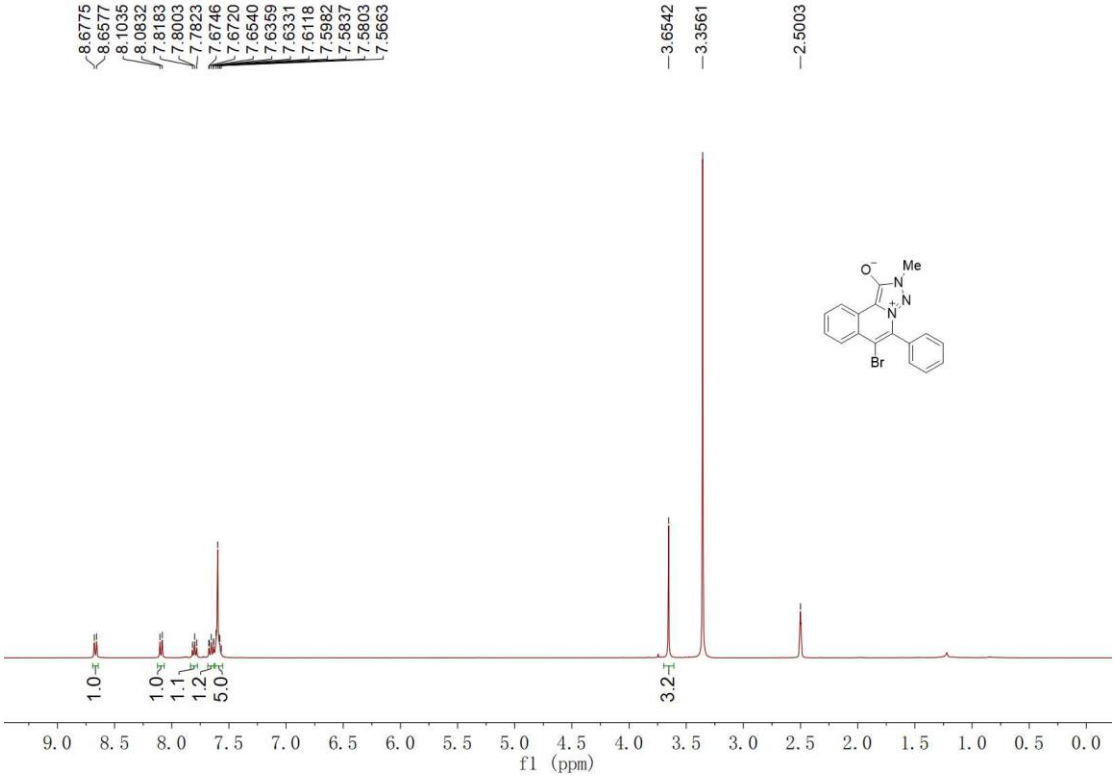
(4) S. Qiu, C. Zhang, R. Qiu, G. Yin and J. Huang, One-Pot Domino Synthesis of Diarylalkynes/1,4-Diaryl-1,3-diynes by [9,9-Dimethyl-4,5-bis(diphenylphosphino) xanthene](Xantphos)–Copper(I) Iodide–Palladium(II) Acetate-Catalyzed Double Sonogashira-Type Reaction. *Adv. Synth. Catal*., 2018, **360**, 313−321.

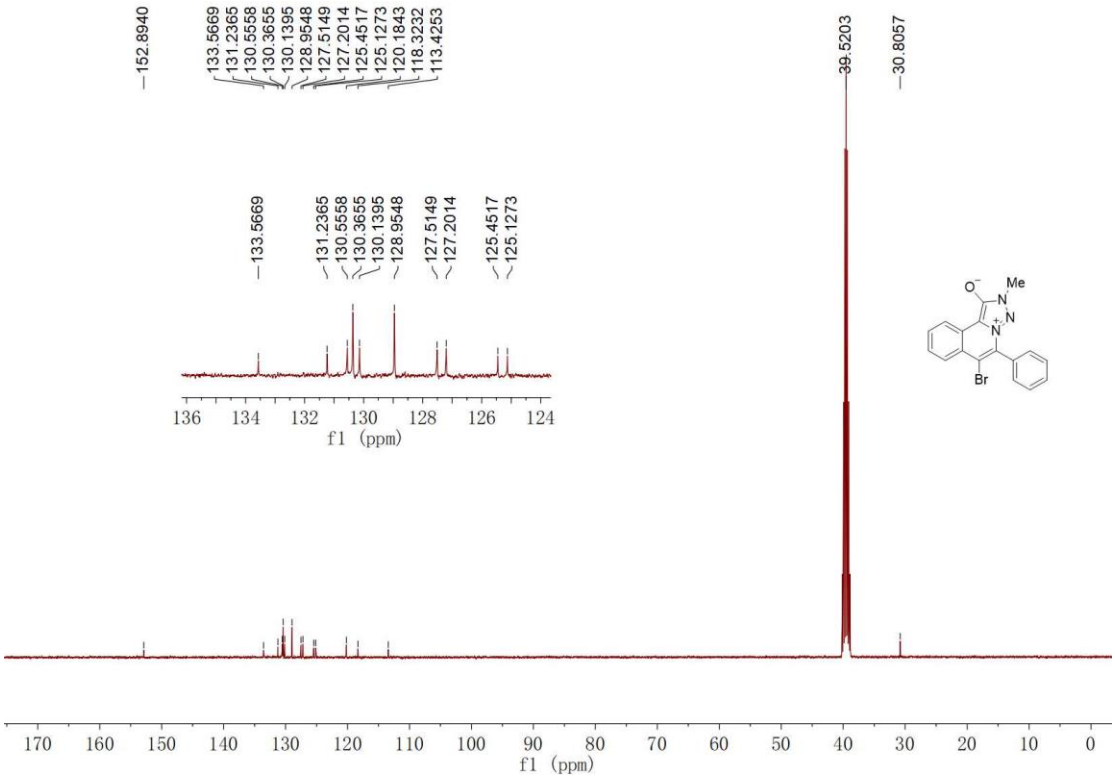
11. NMR spectra

^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectra of **2aa**

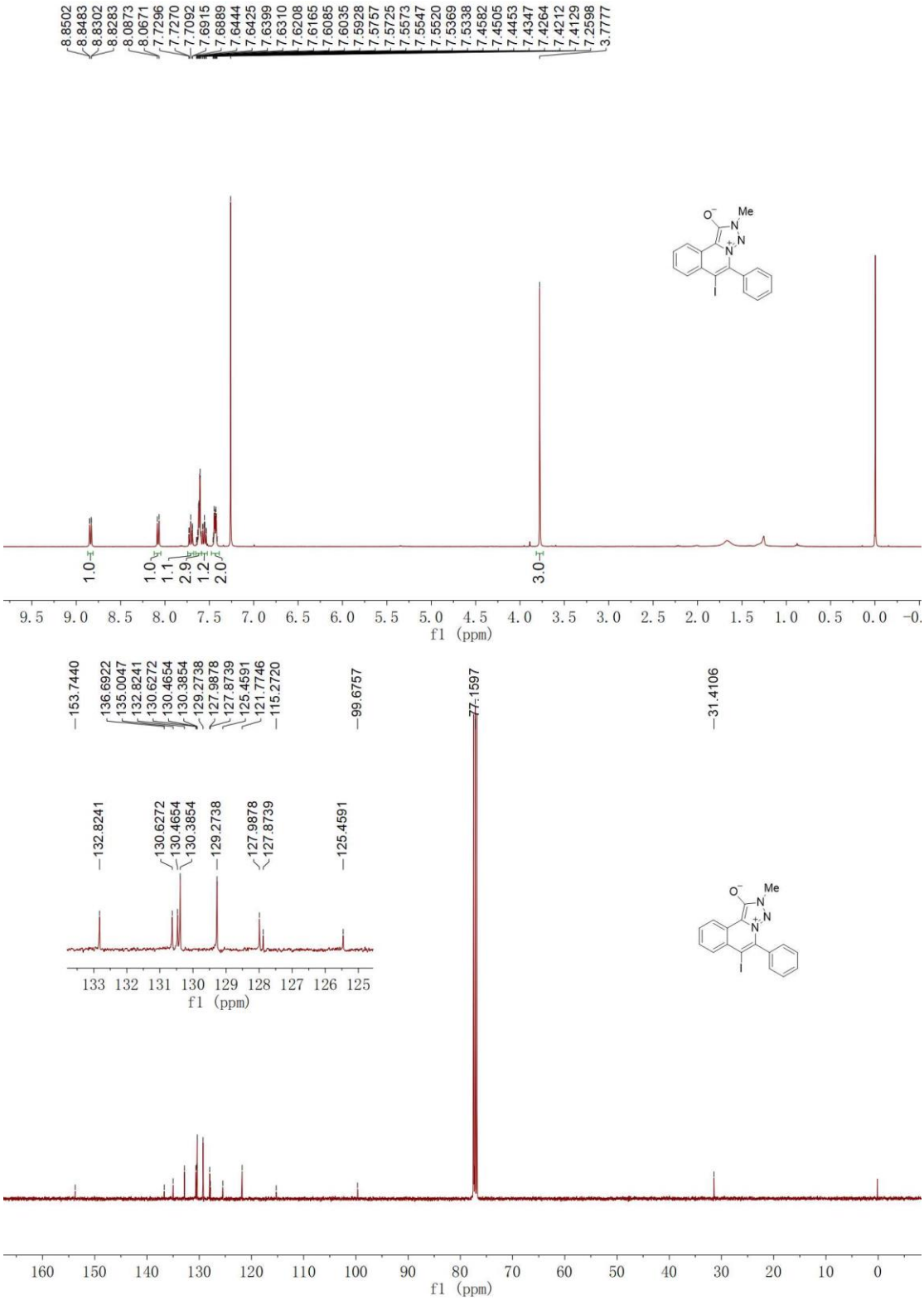


^{1}H NMR (DMSO-d_6, 400 MHz) and ^{13}C NMR (DMSO-d_6, 100 MHz) spectra of **2ab**

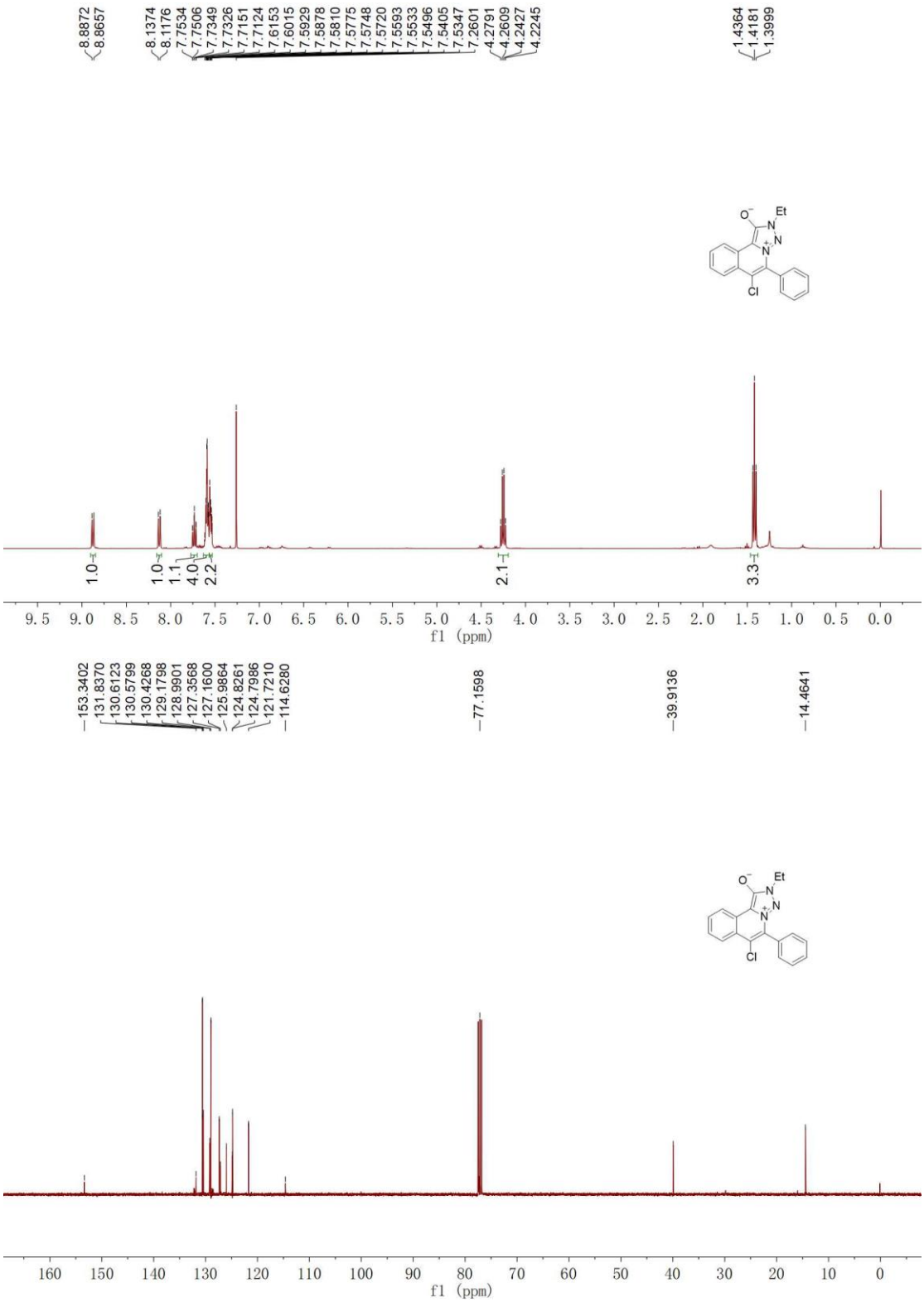




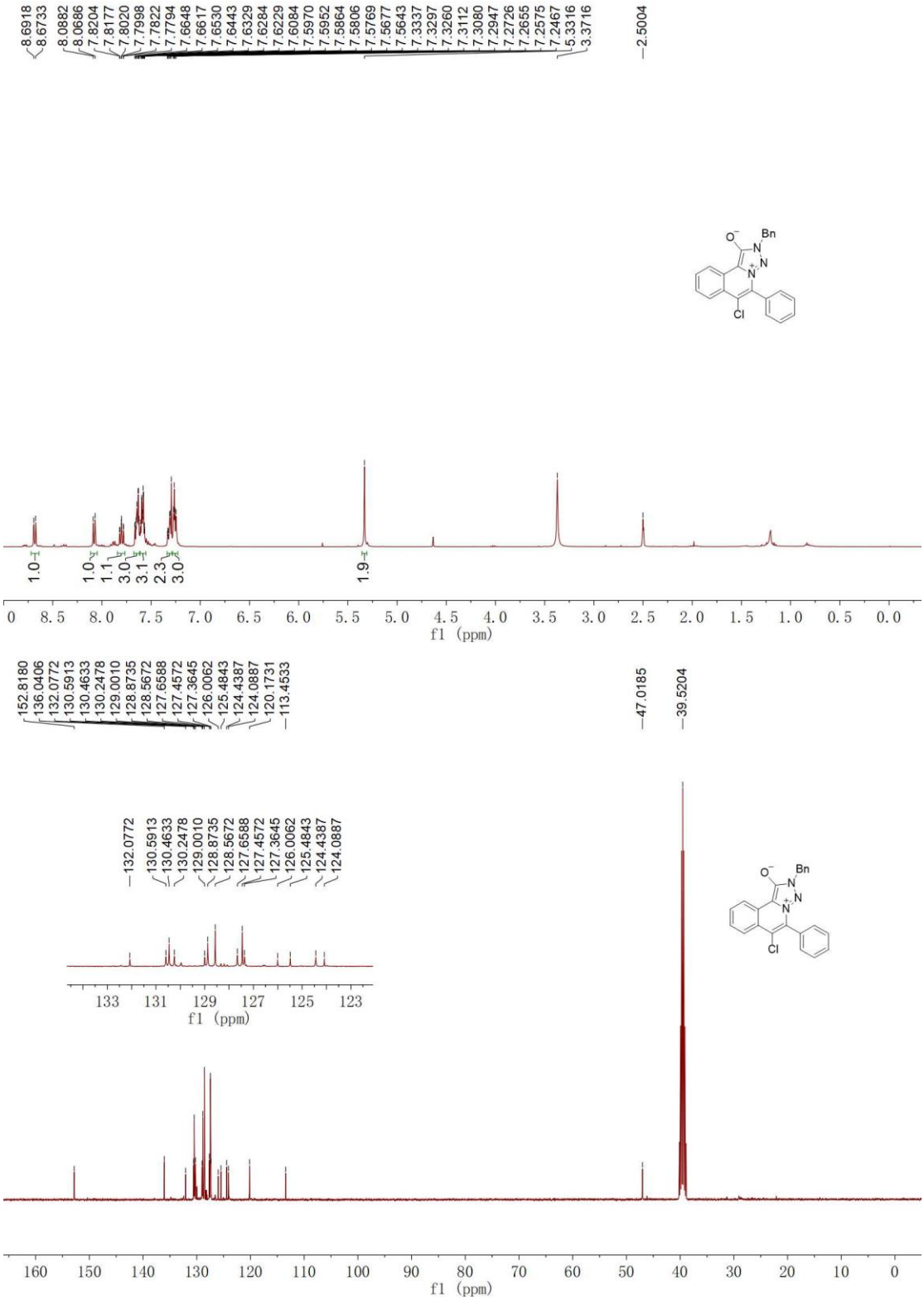
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectra of **2ac**



^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectra of **2ba**



^{1}H NMR (DMSO-d_6, 400 MHz) and ^{13}C NMR (DMSO-d_6, 100 MHz) spectra of **2ca**



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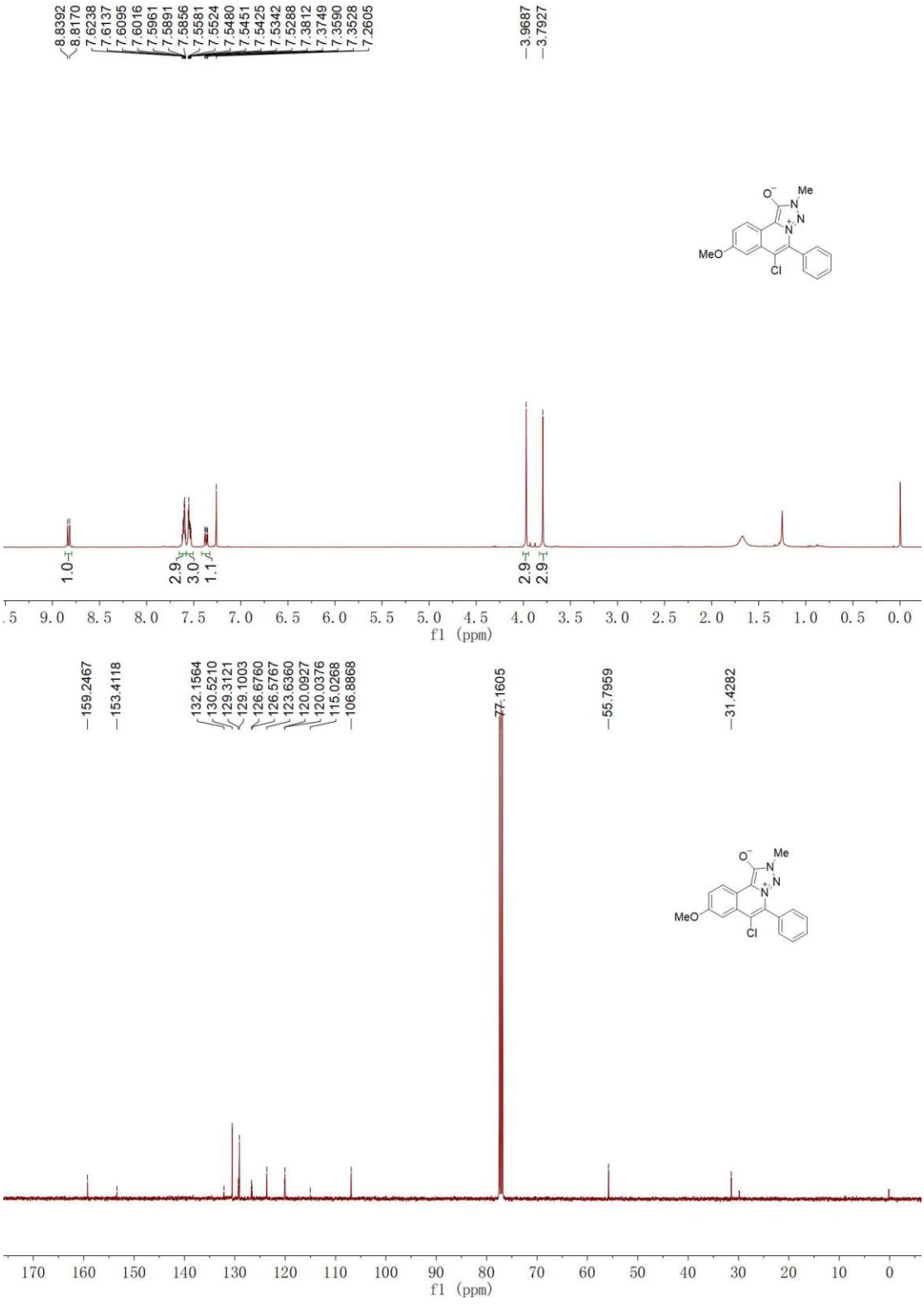

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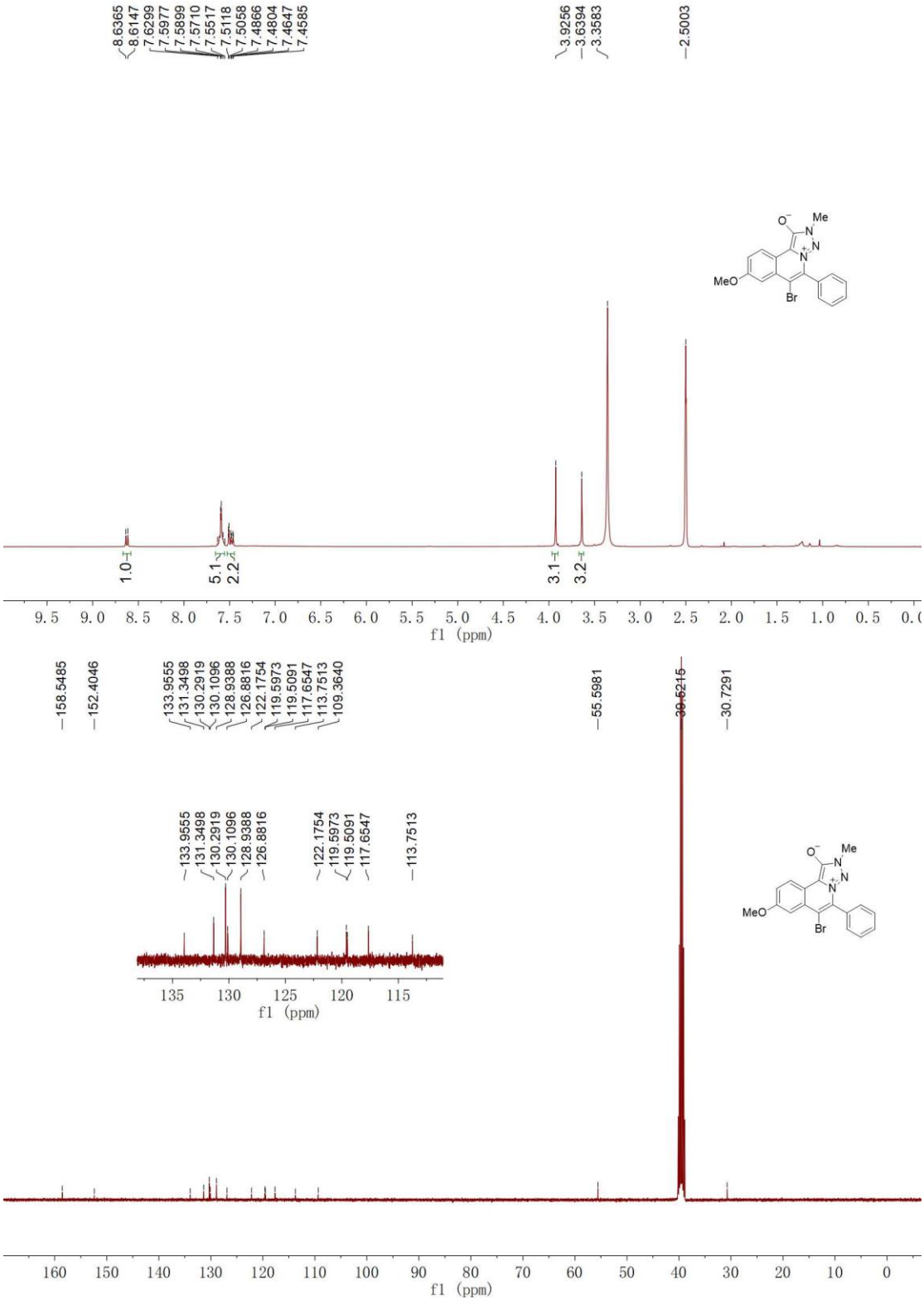
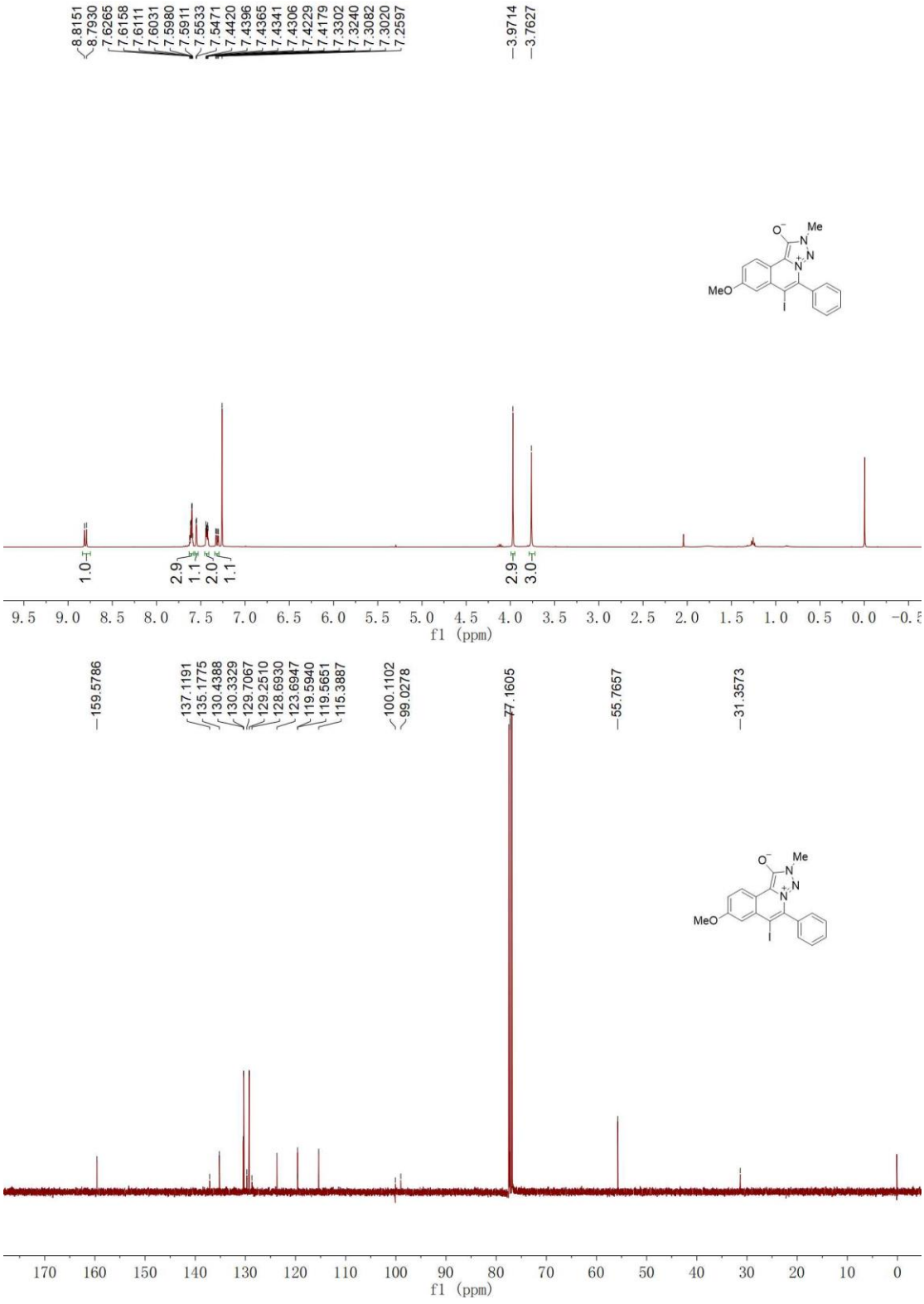


^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectra of **2dc**



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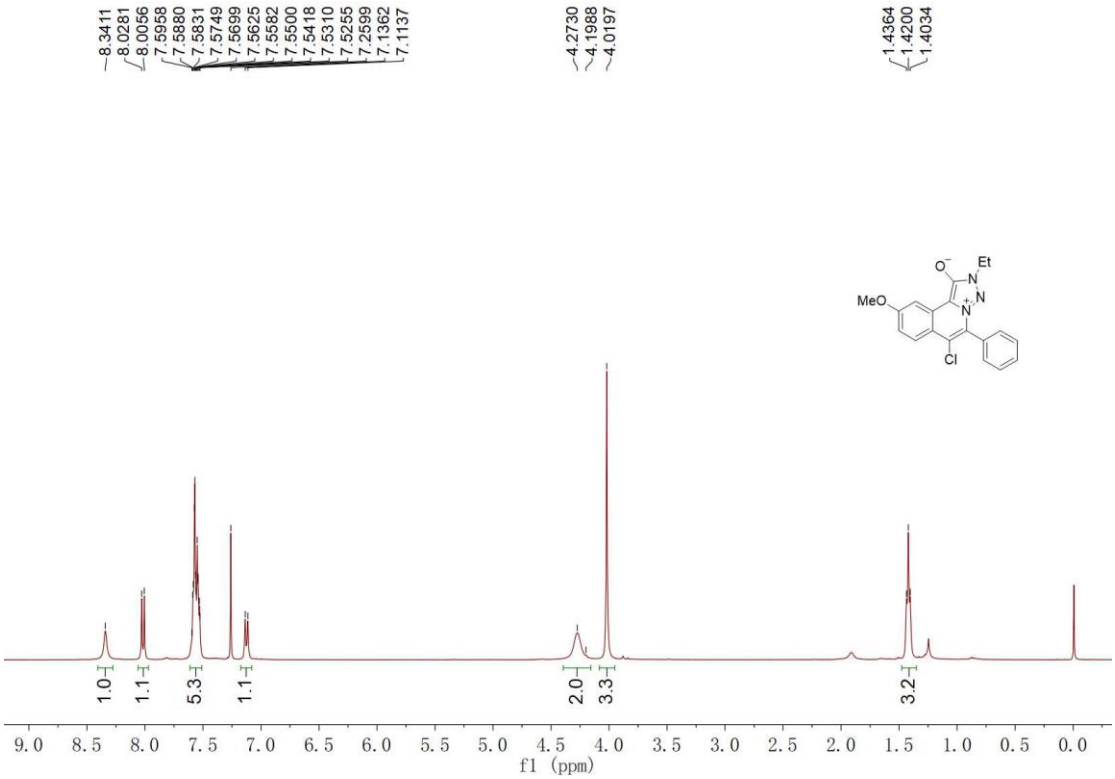
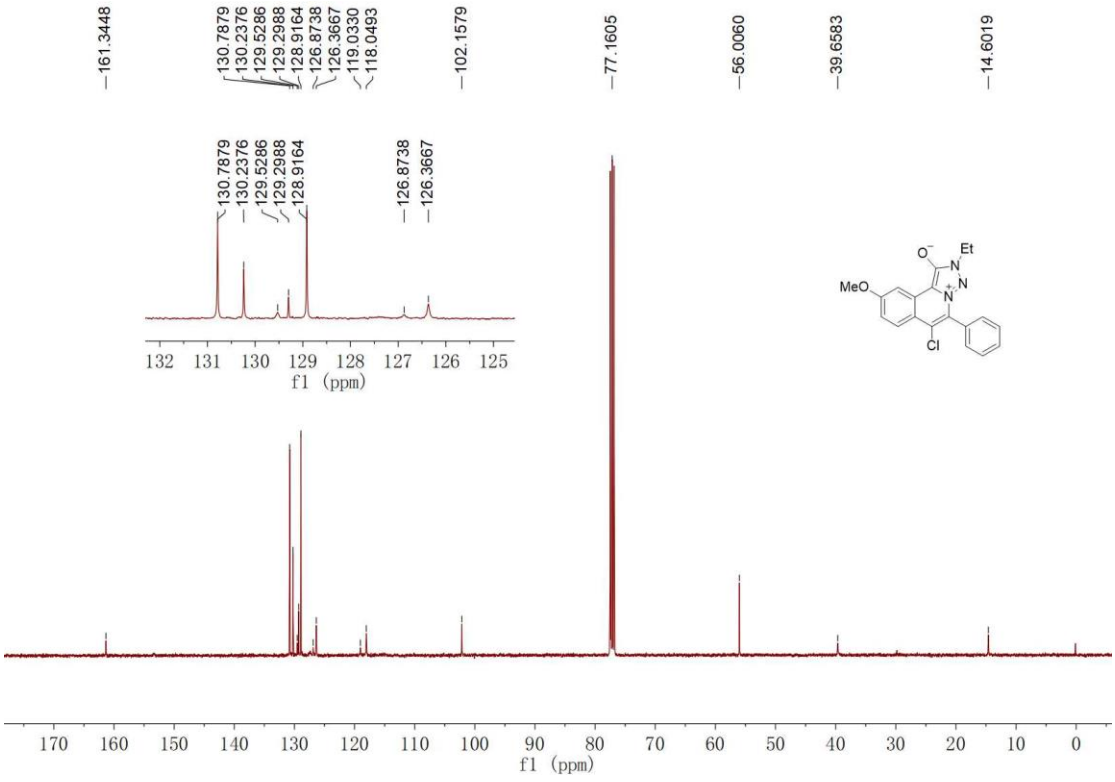
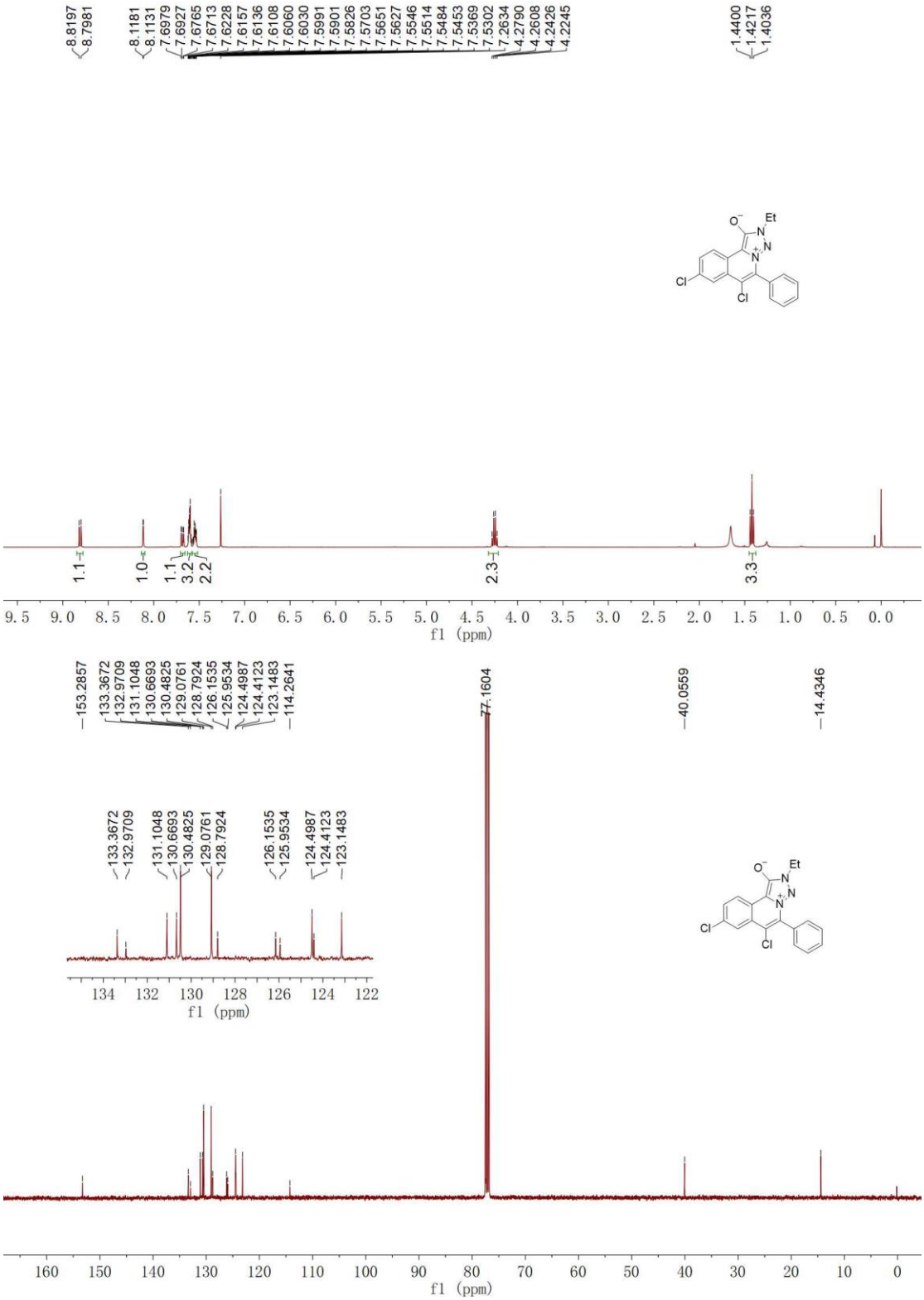
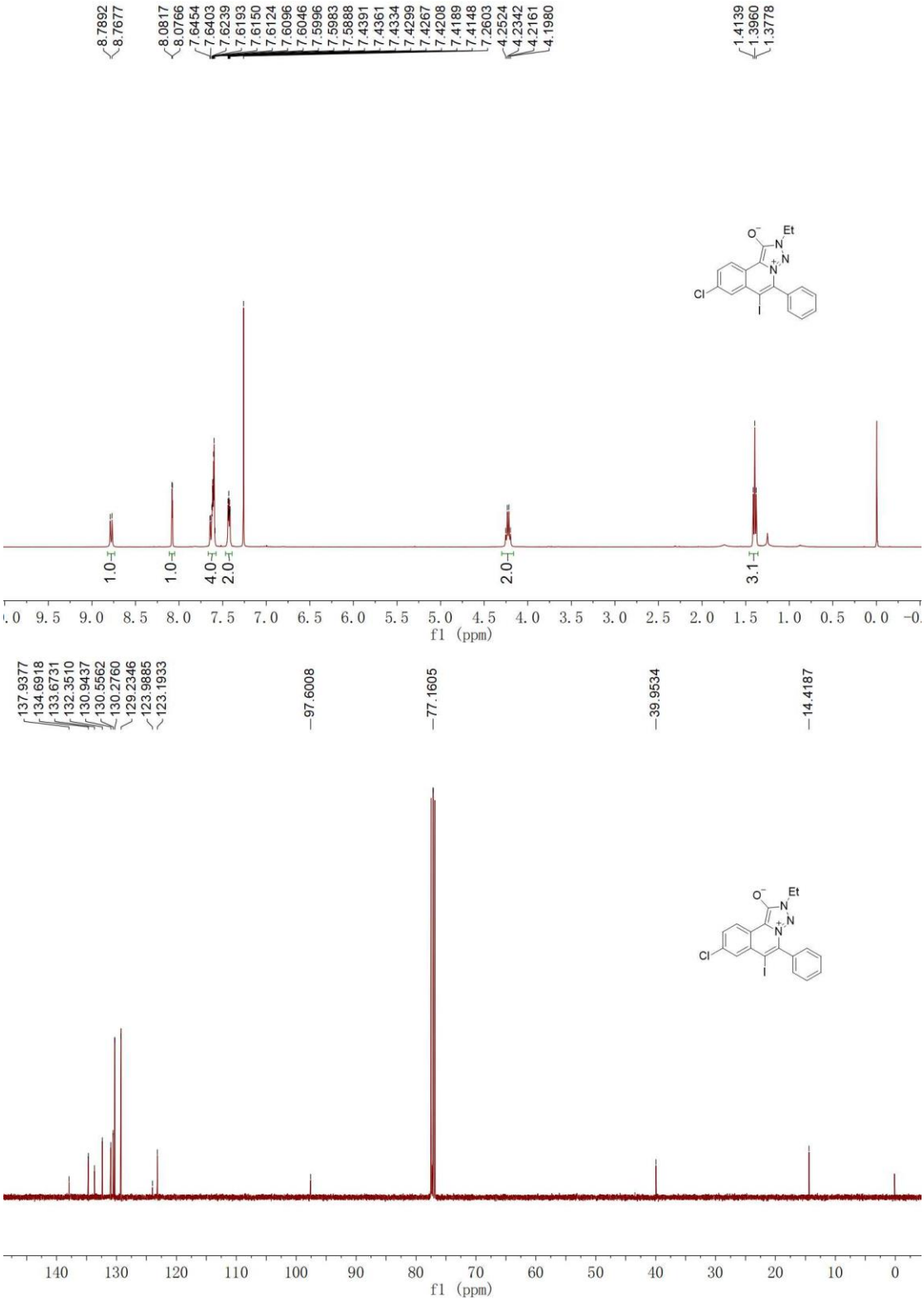




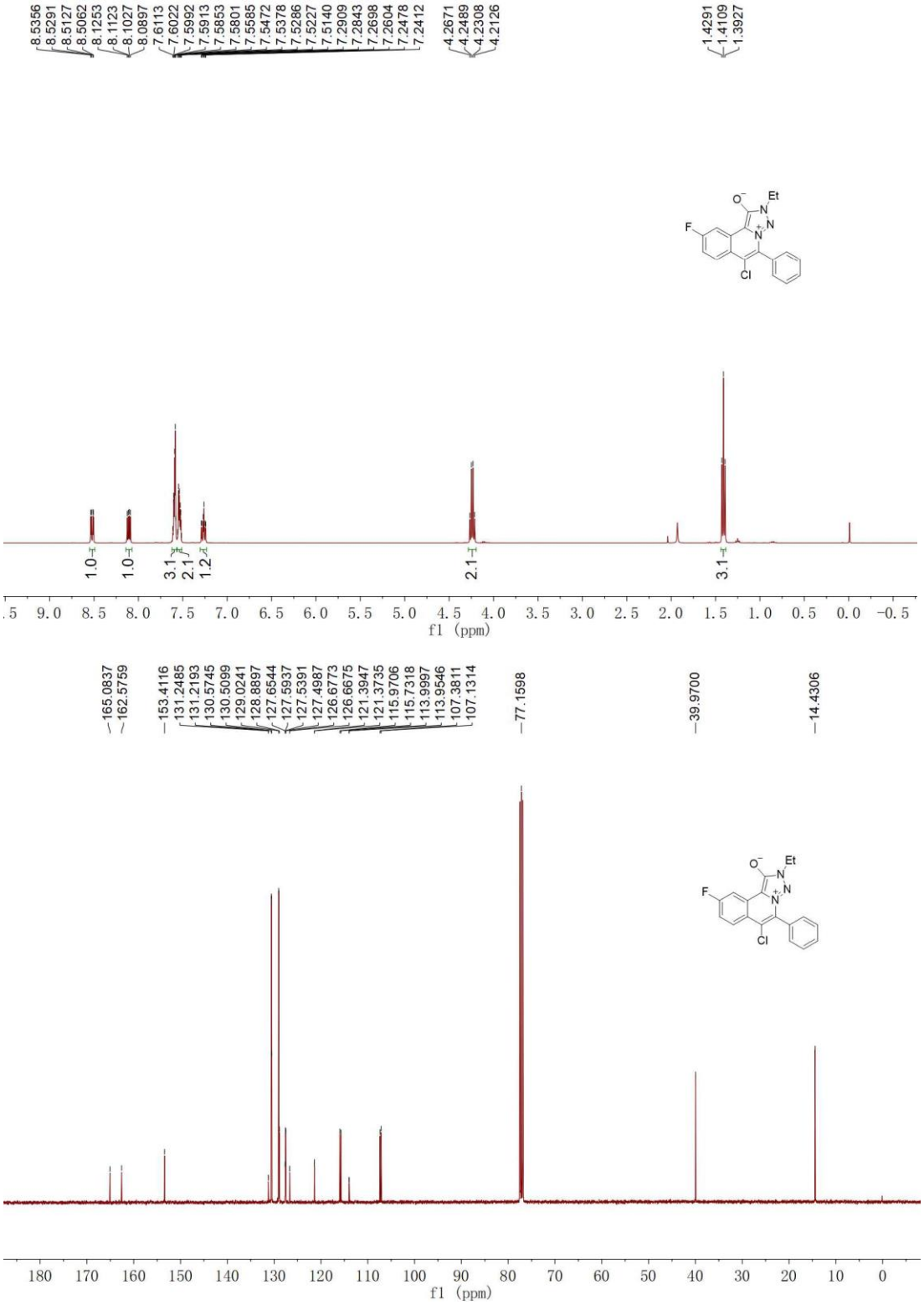
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectra of **2fa**

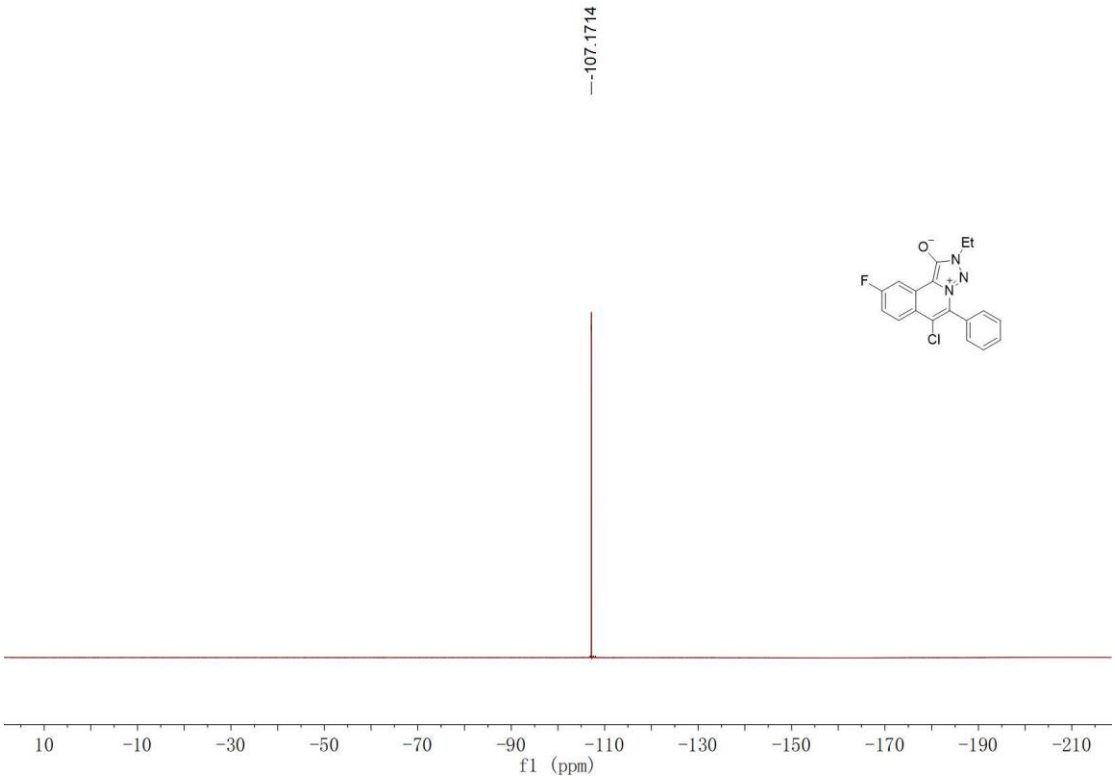


^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectra of **2fc**



^{1}H NMR ($CDCl_3$, 400 MHz), ^{13}C NMR ($CDCl_3$, 100 MHz) and ^{19}F NMR ($CDCl_3$, 376 MHz) spectra of **2ga**

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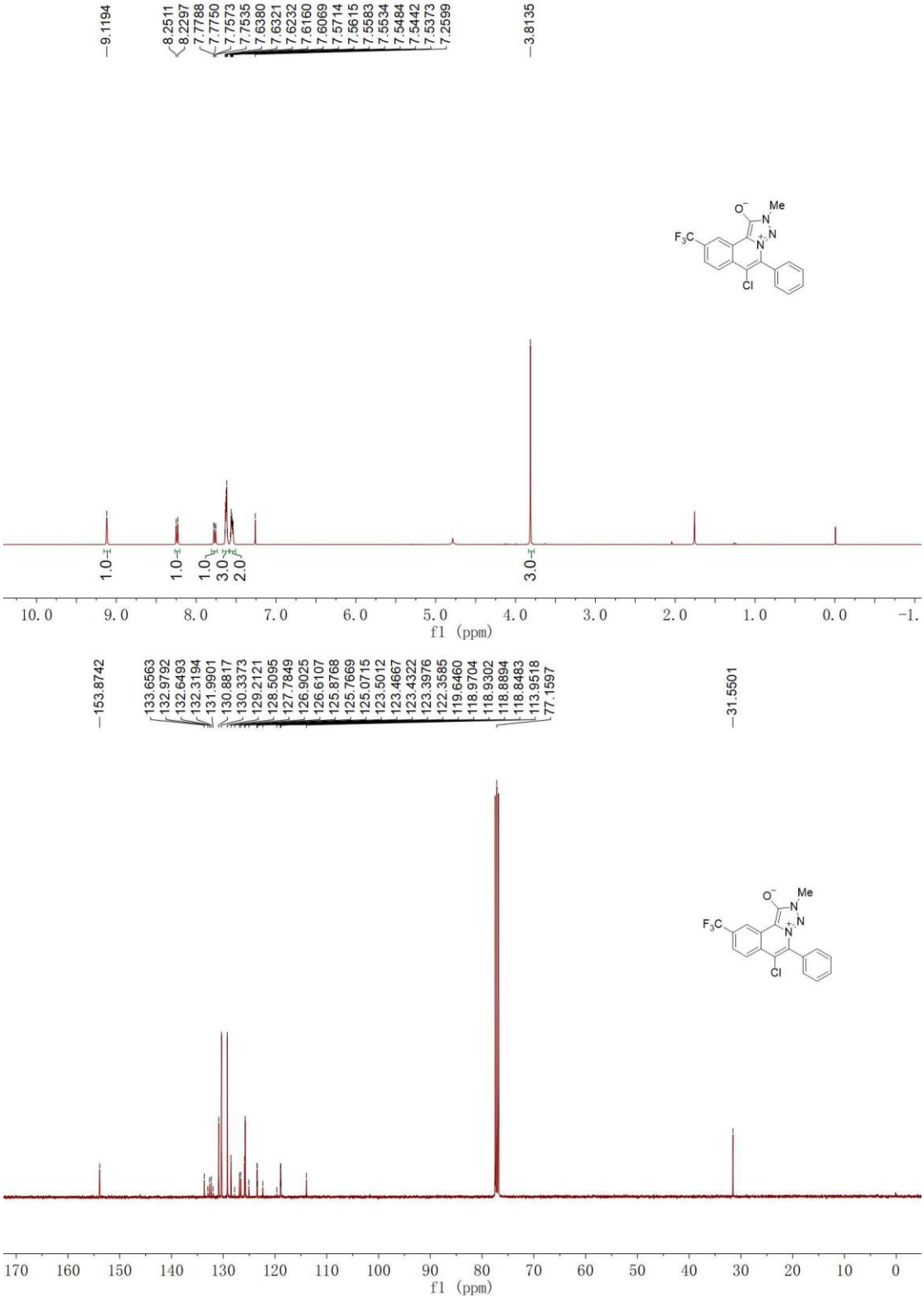
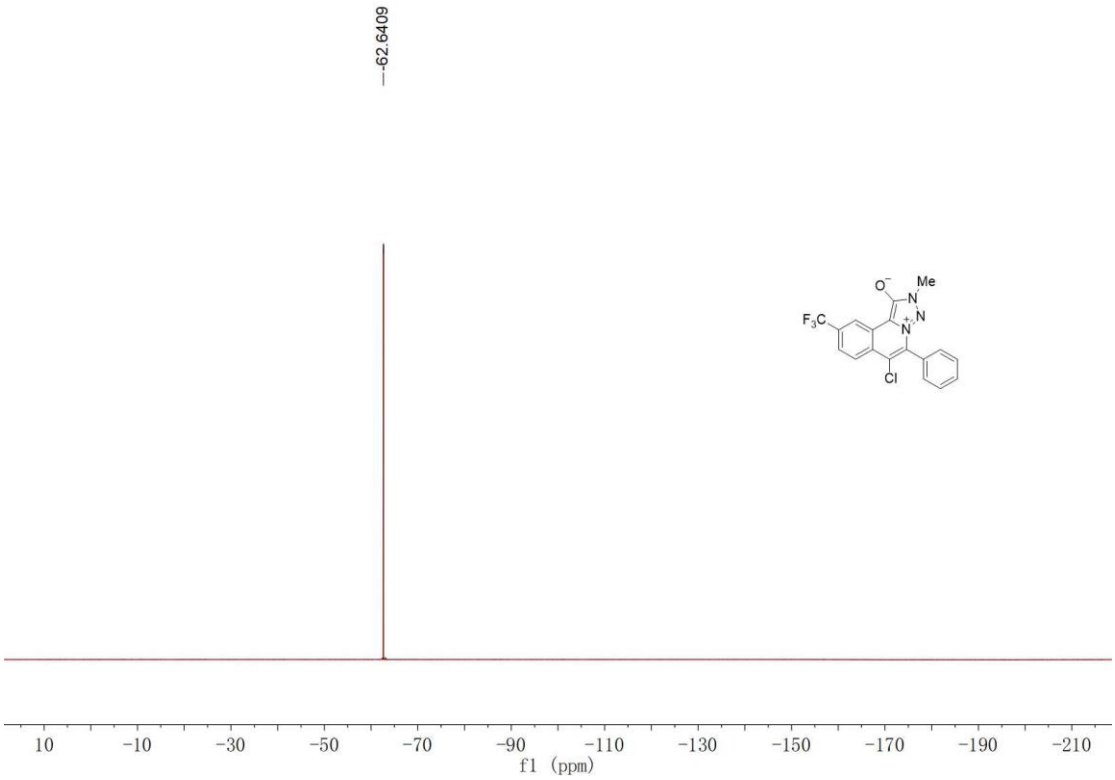
f1 (ppm)

^{1}H NMR ($CDCl_3$, 400 MHz), ^{13}C NMR ($CDCl_3$, 100 MHz) and ^{19}F NMR ($CDCl_3$, 376 MHz) spectra of **2ha**

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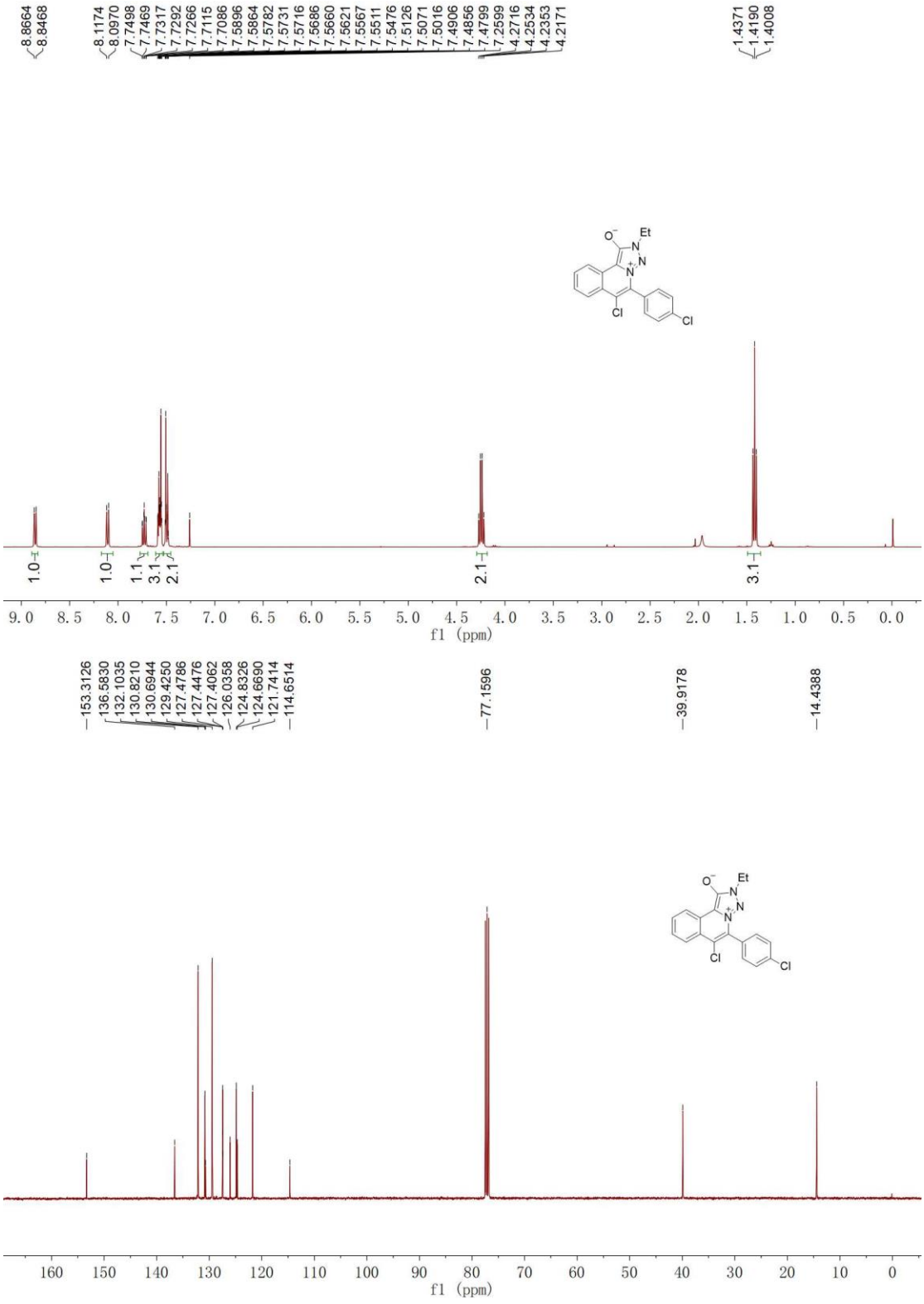
f1 (ppm)

^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectra of **2ia**



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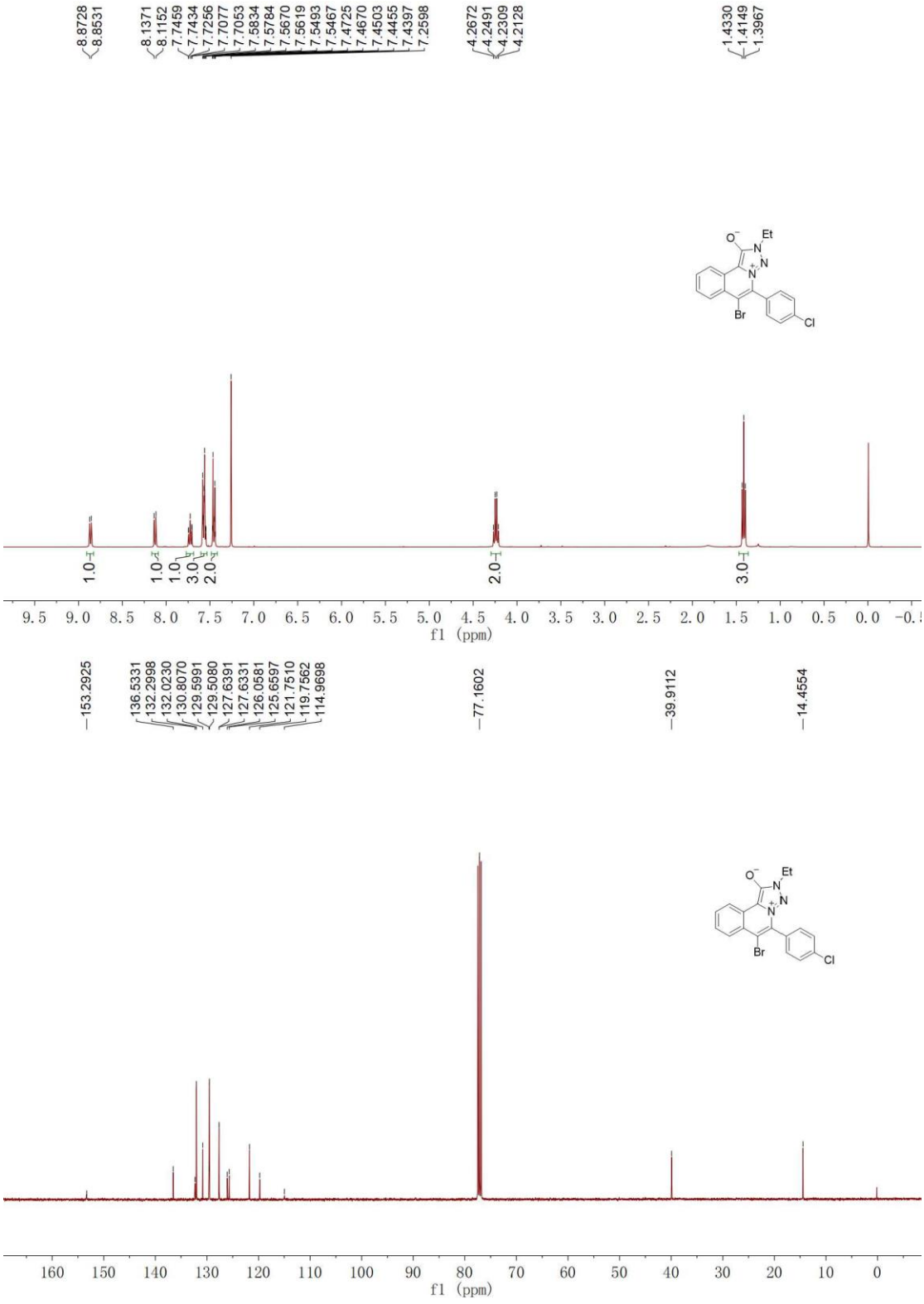

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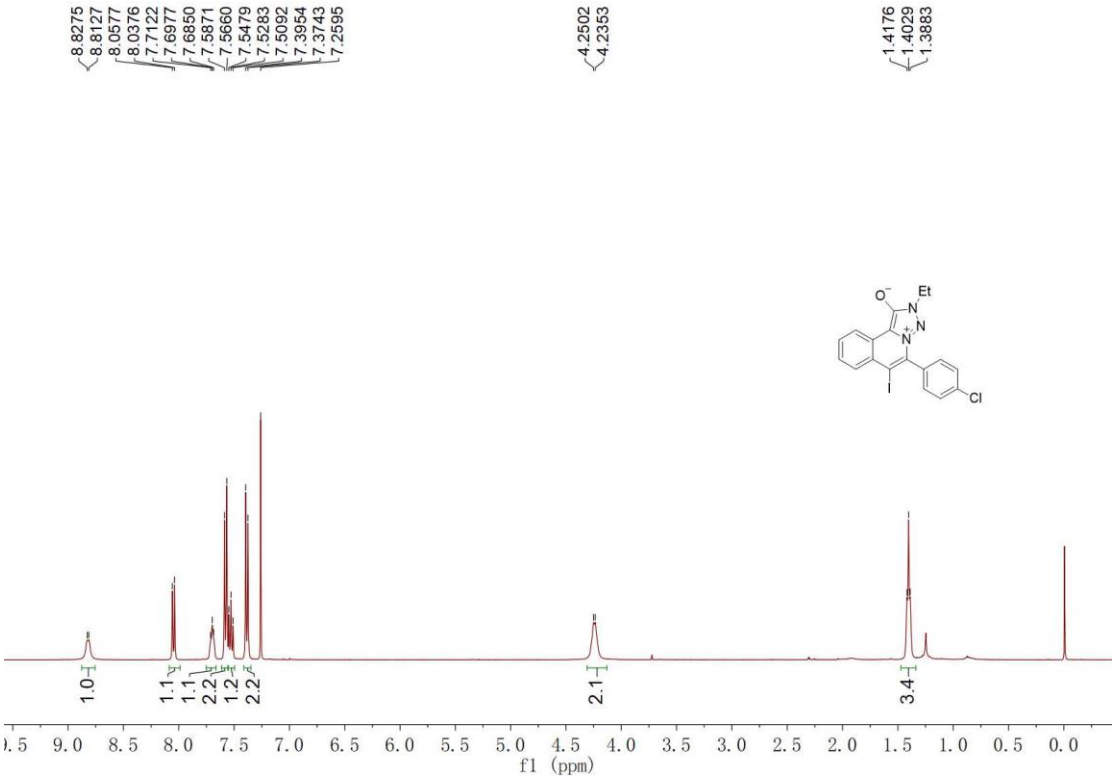
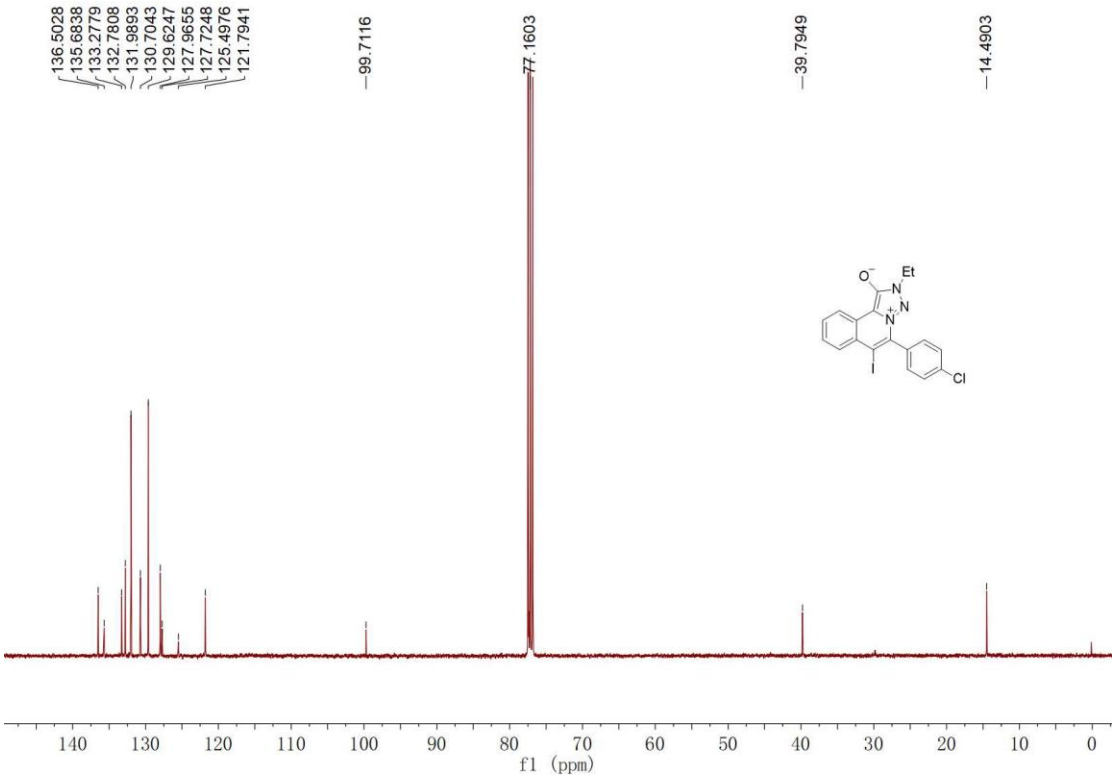
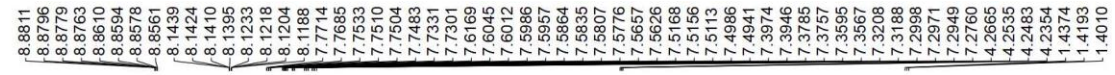
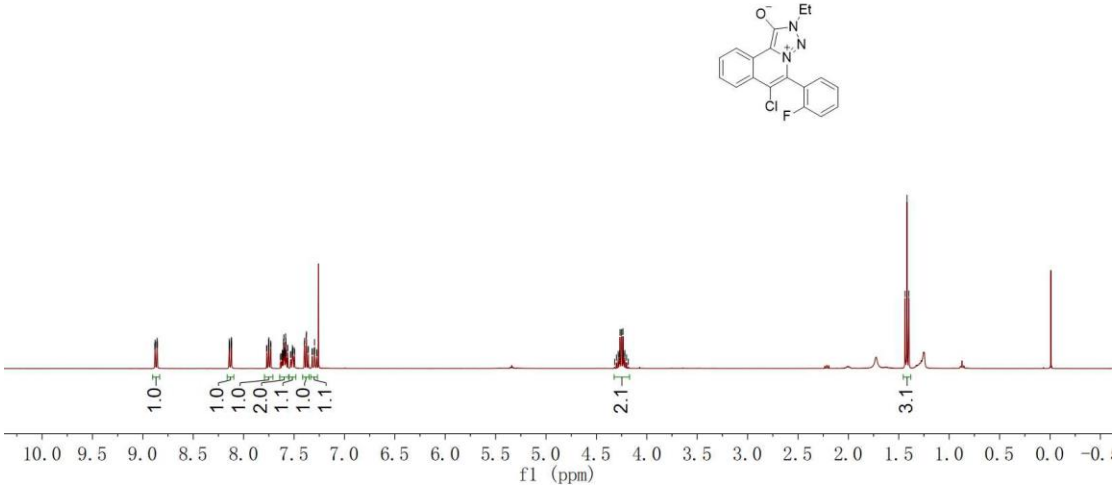
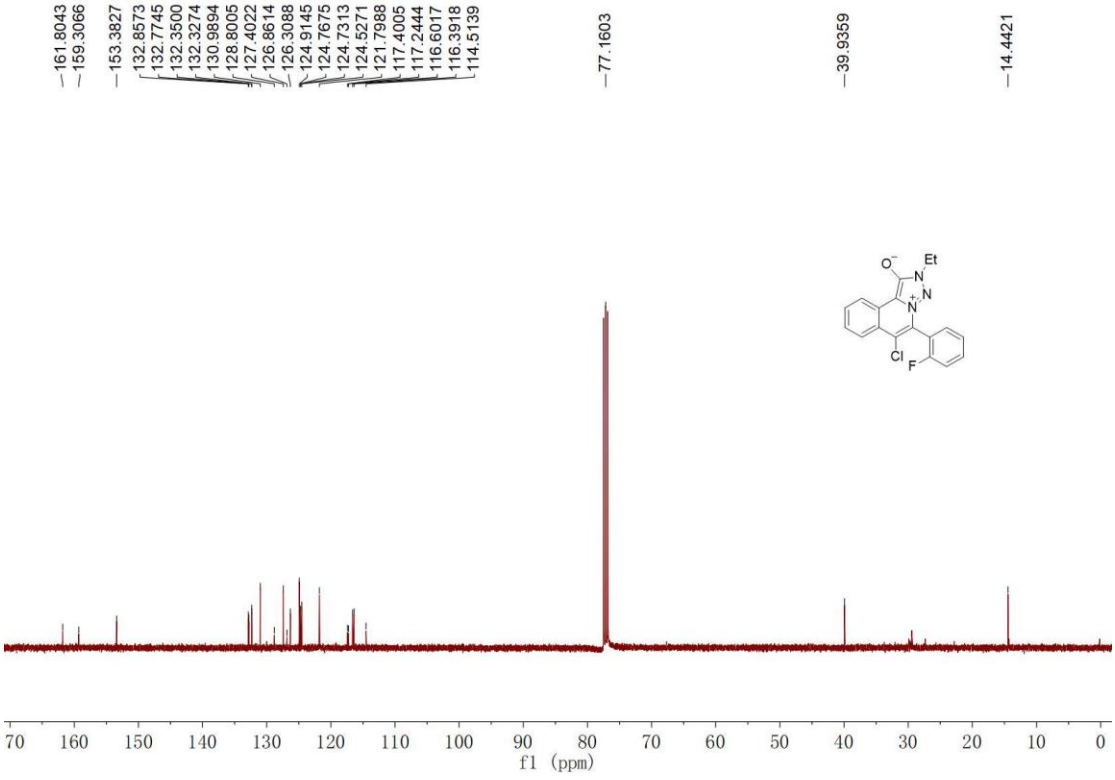


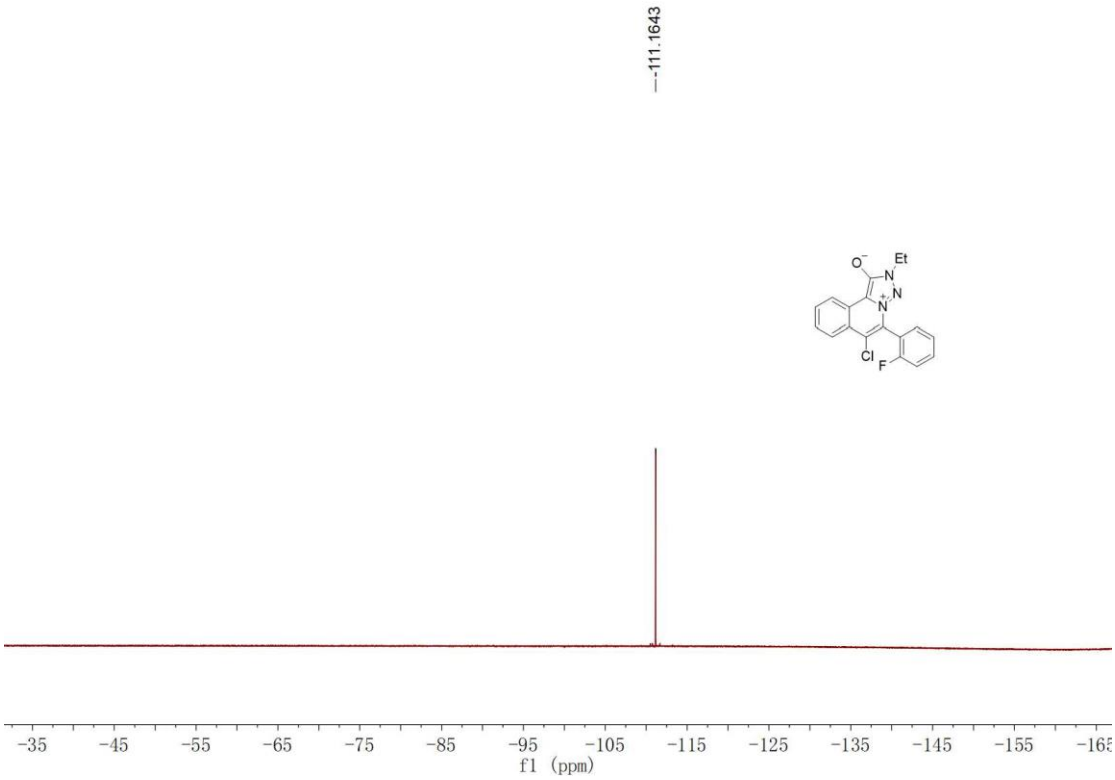


^{1}H NMR ($CDCl_3$, 400 MHz), ^{13}C NMR ($CDCl_3$, 100 MHz) and ^{19}F NMR ($CDCl_3$, 376 MHz) spectra of **2ja**





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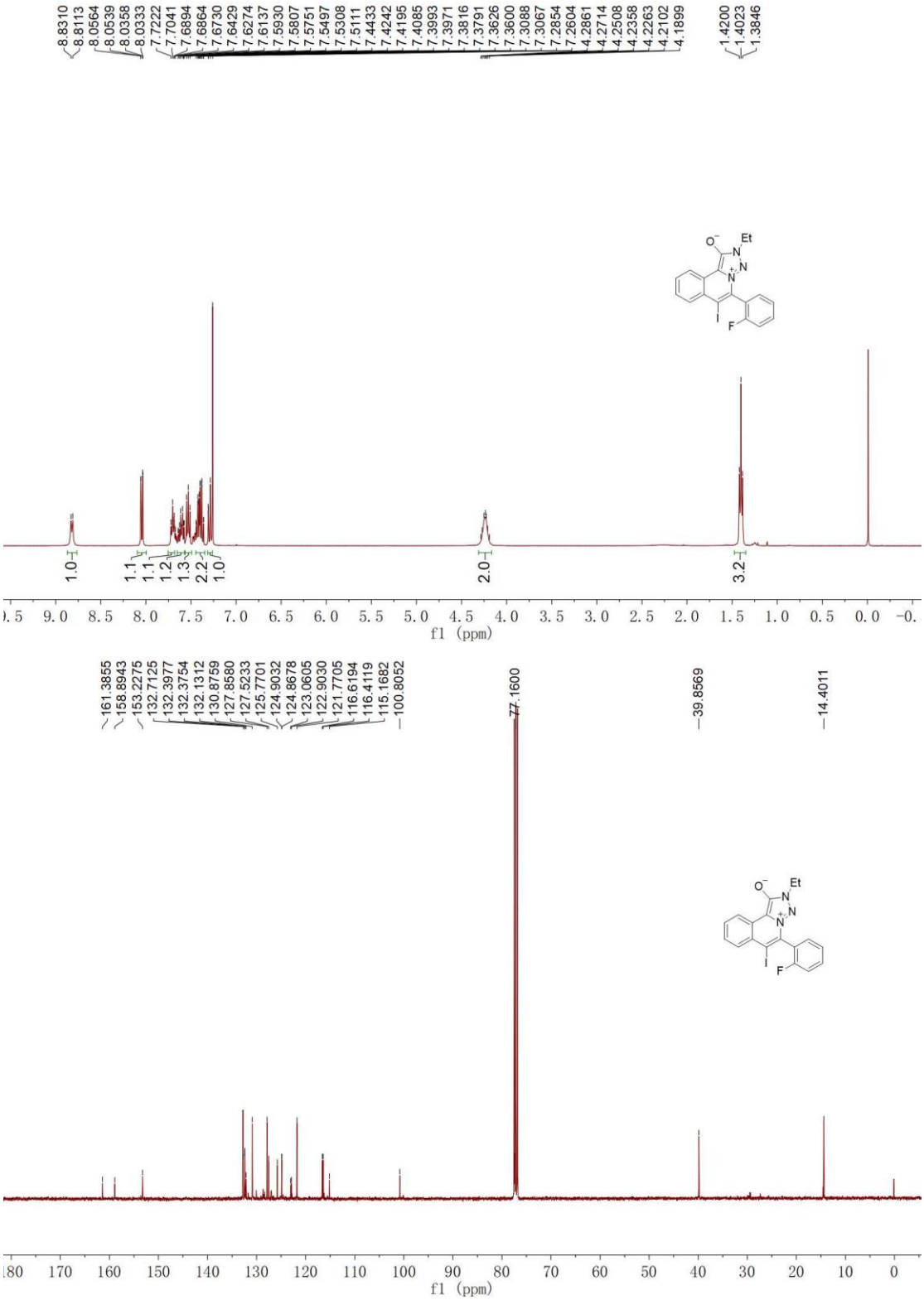
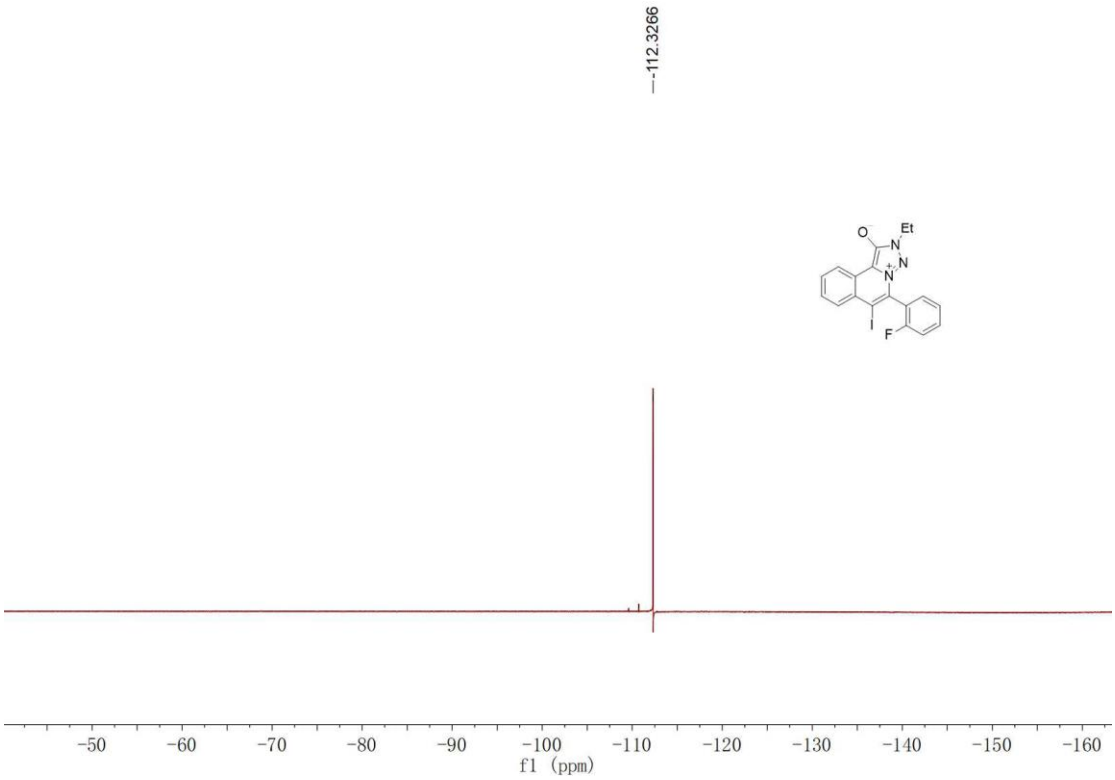
^{1}H NMR ($CDCl_3$, 400 MHz), ^{13}C NMR ($CDCl_3$, 100 MHz) and ^{19}F NMR ($CDCl_3$, 376 MHz) spectra of **2jc**

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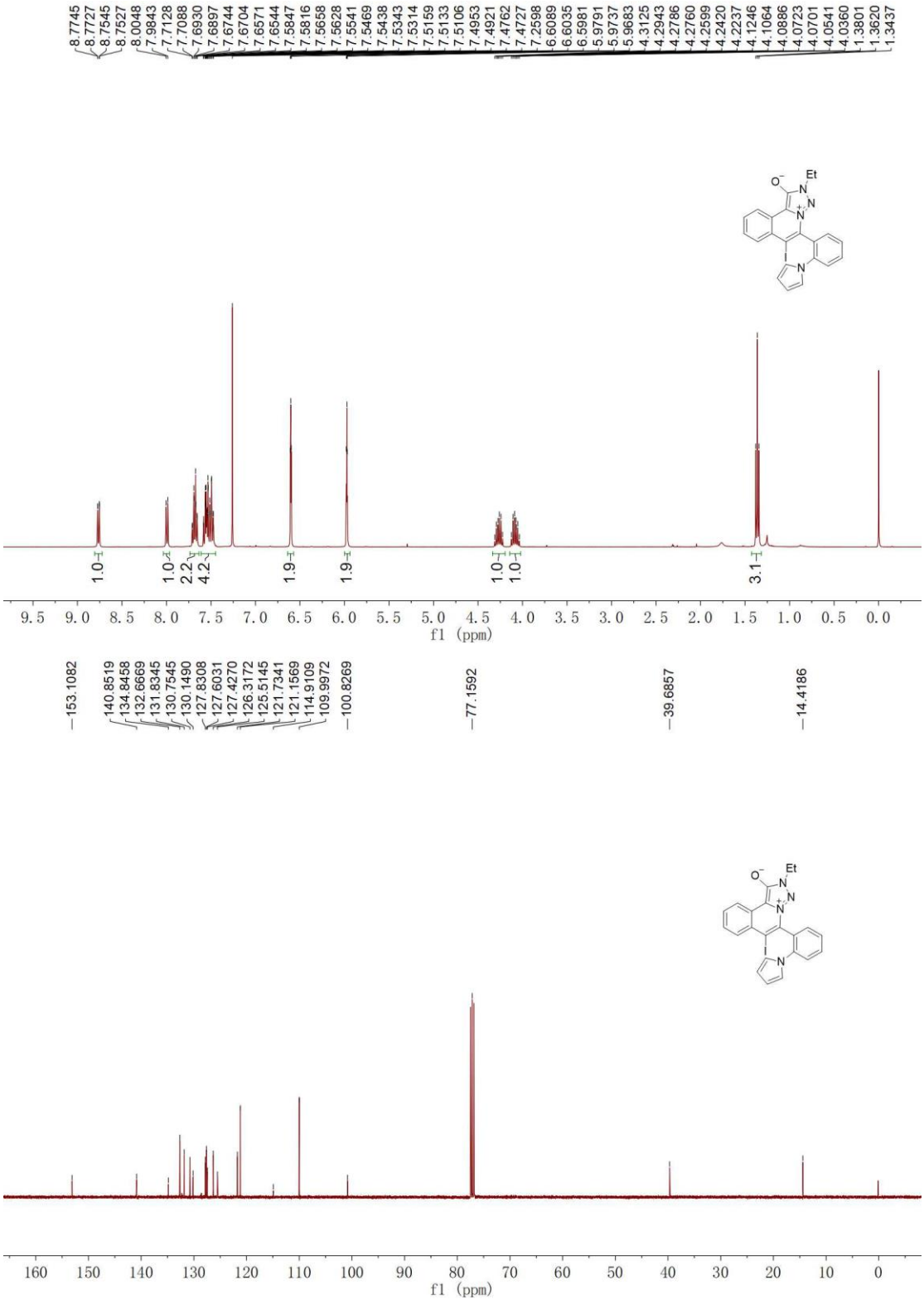
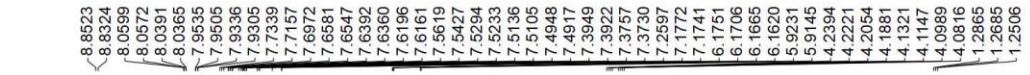
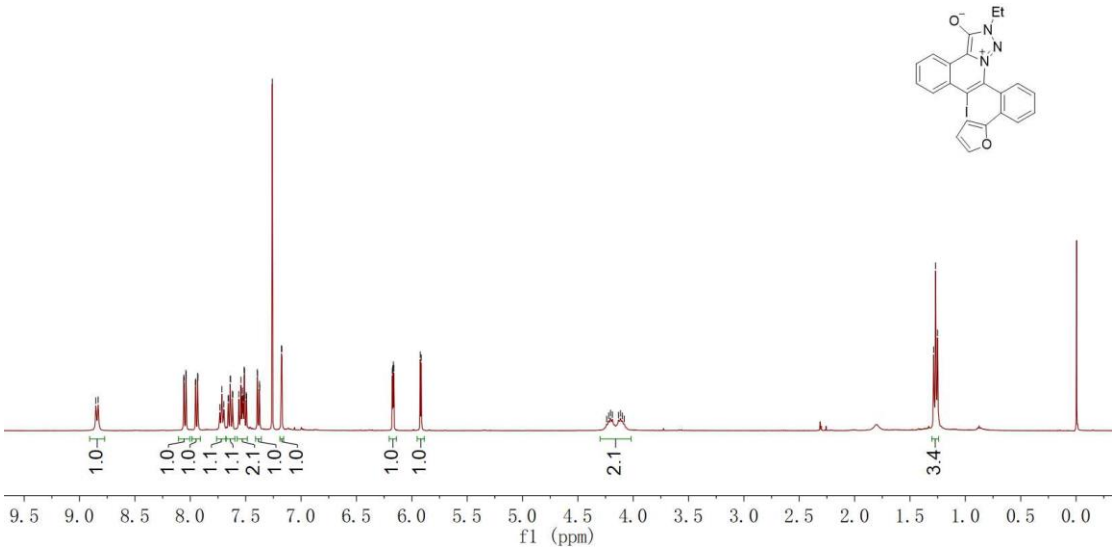
f1 (ppm)

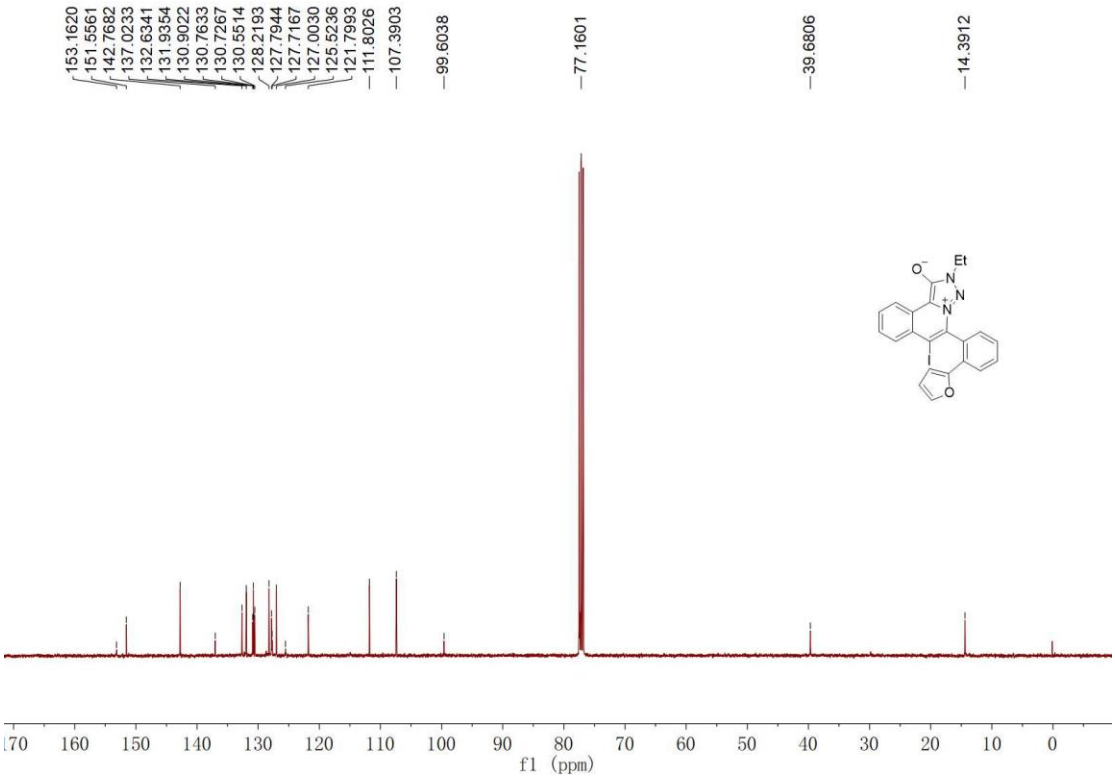
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectra of **2kc**



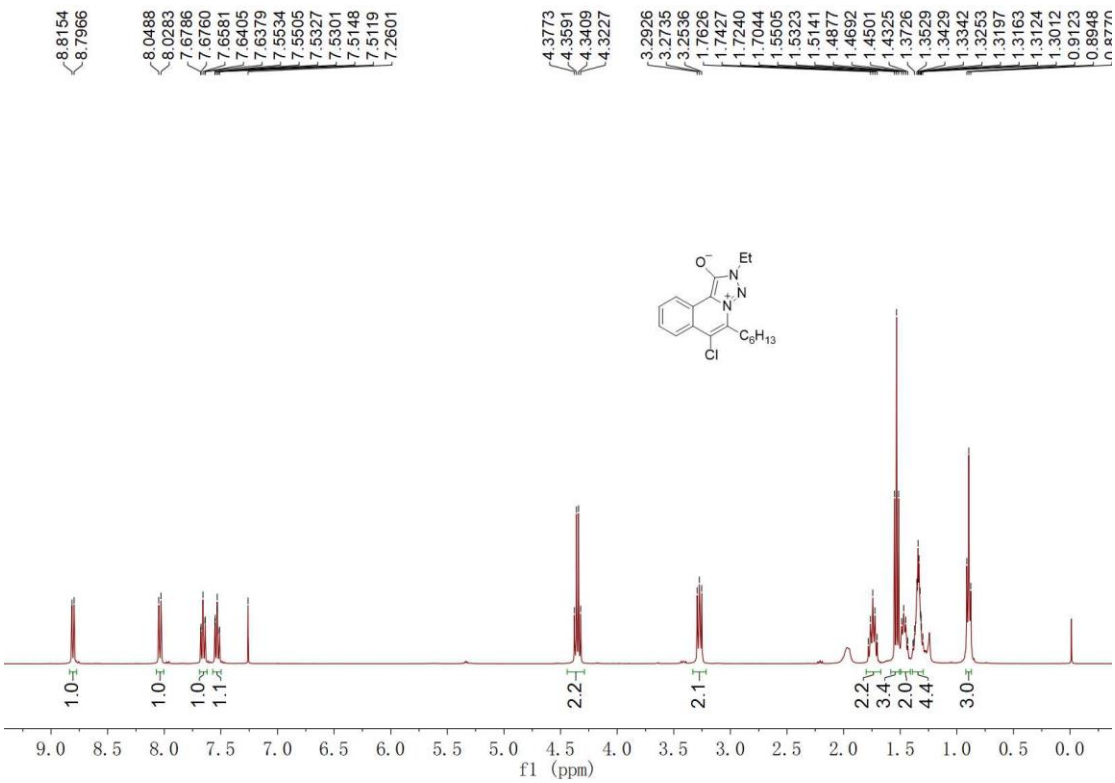
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectra of **2lc**

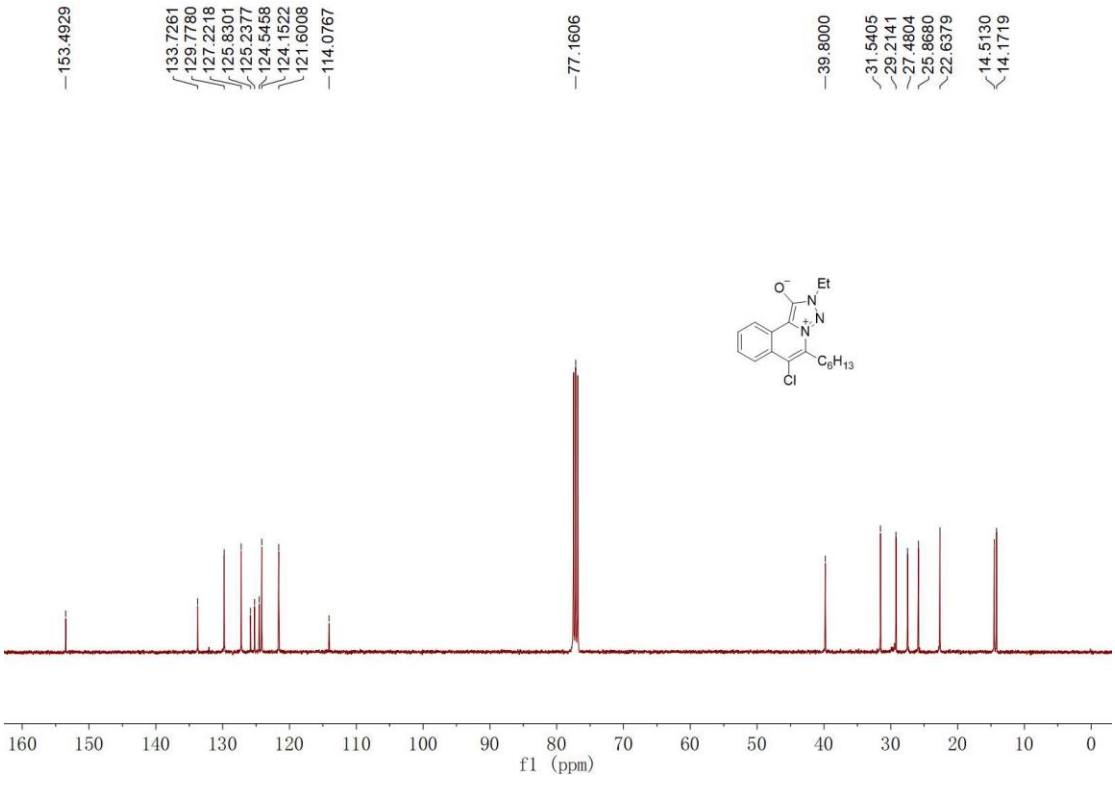




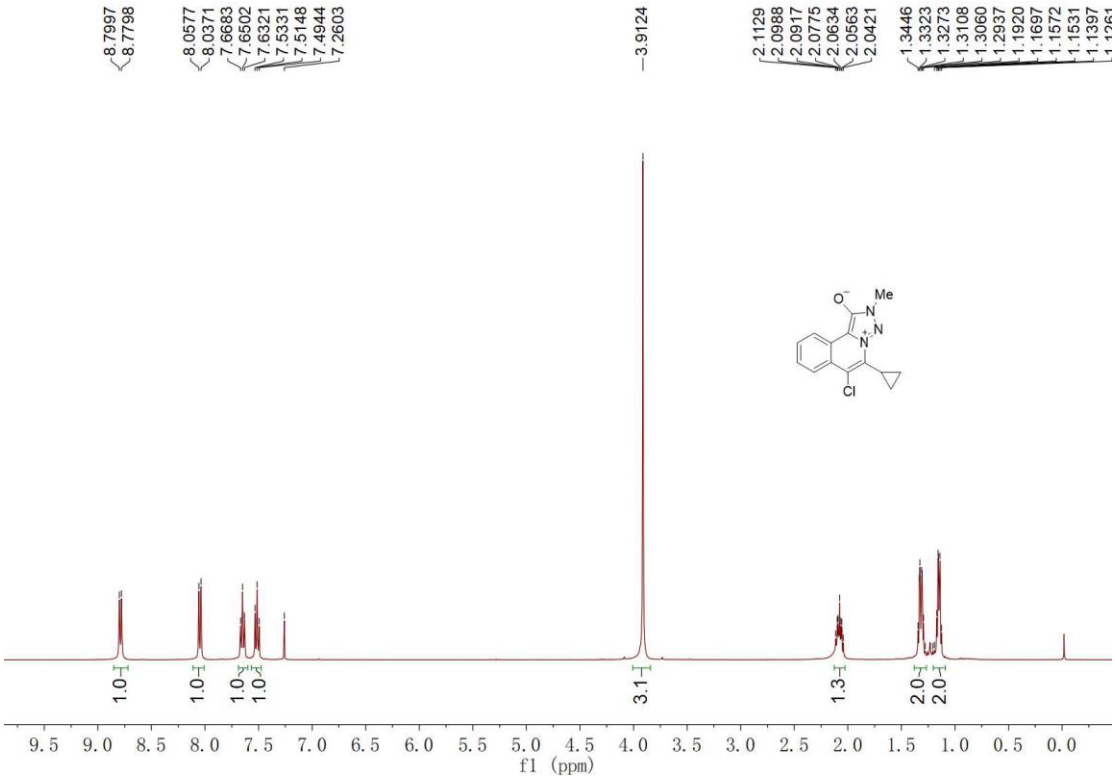


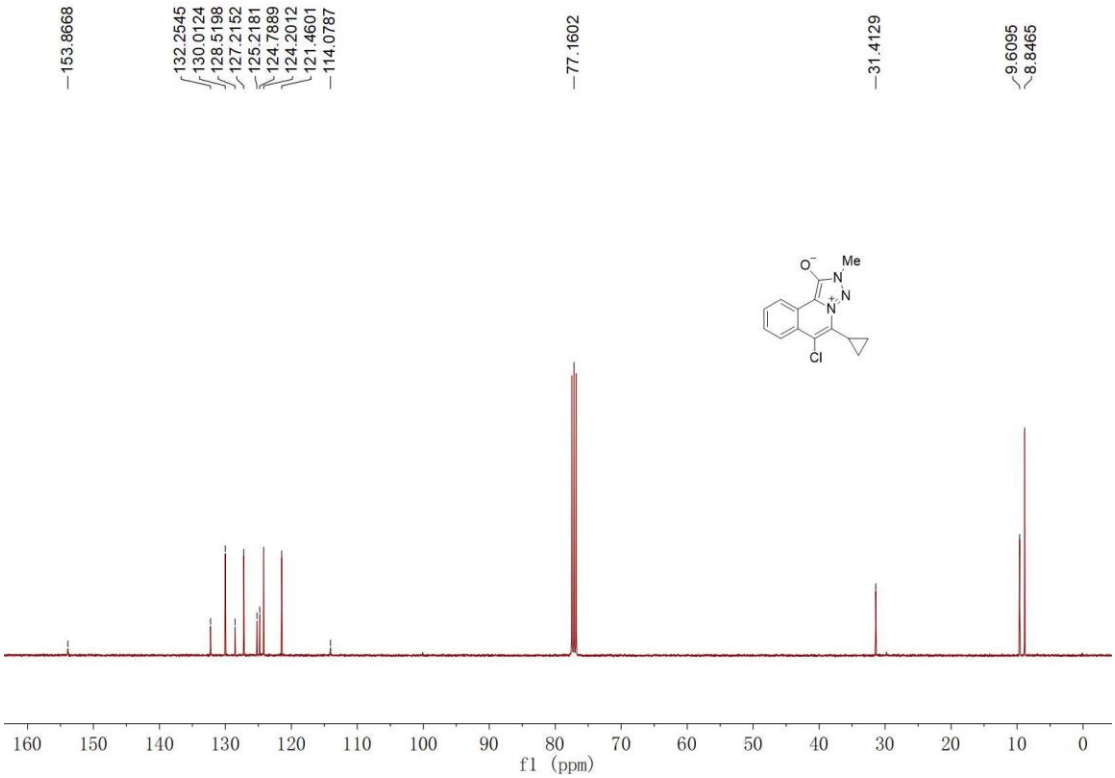
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectra of **2ma**



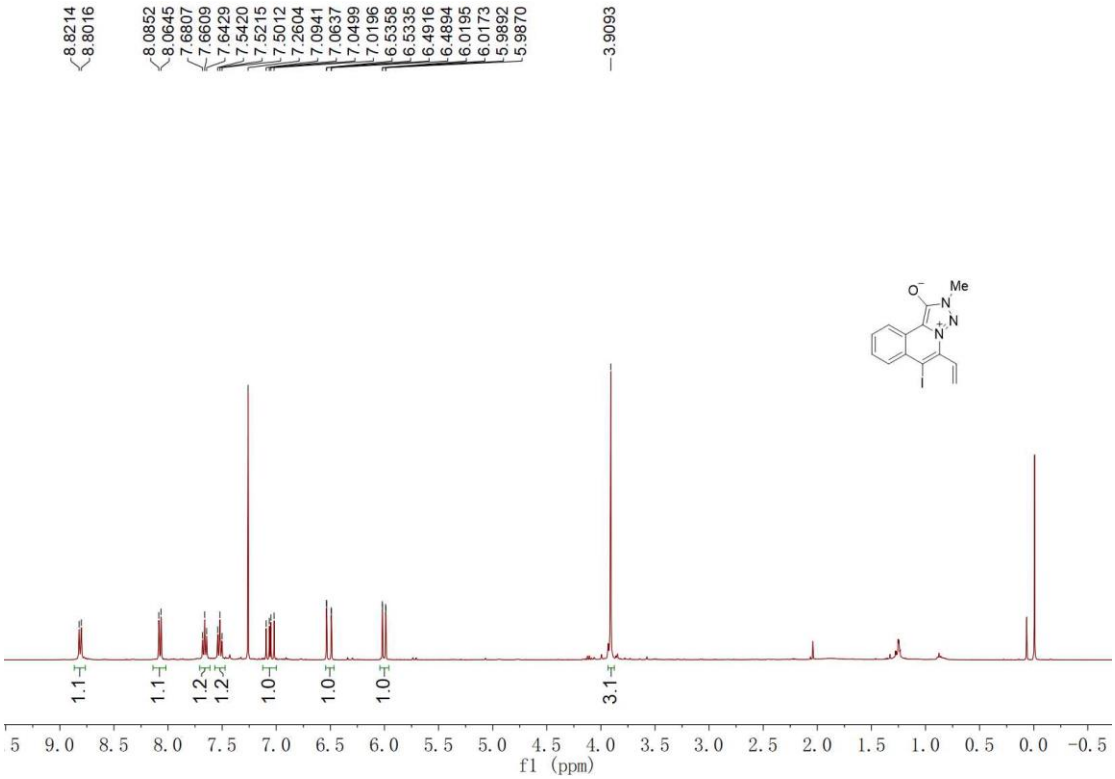


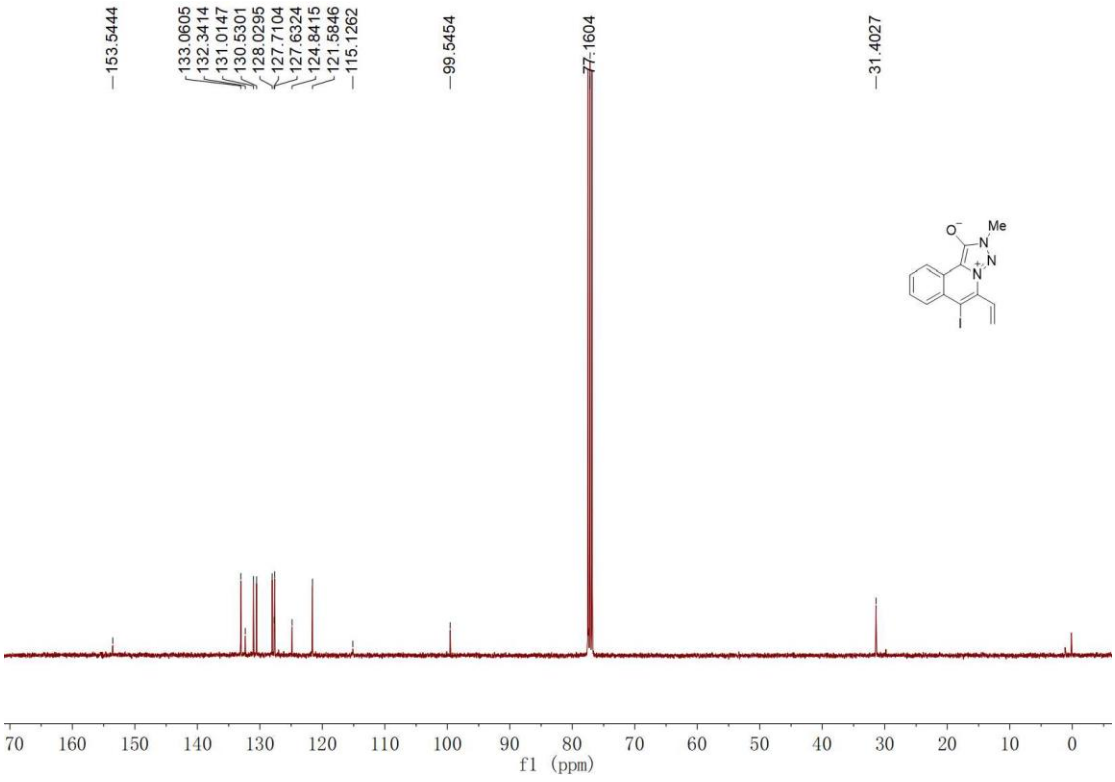
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectra of **2na**



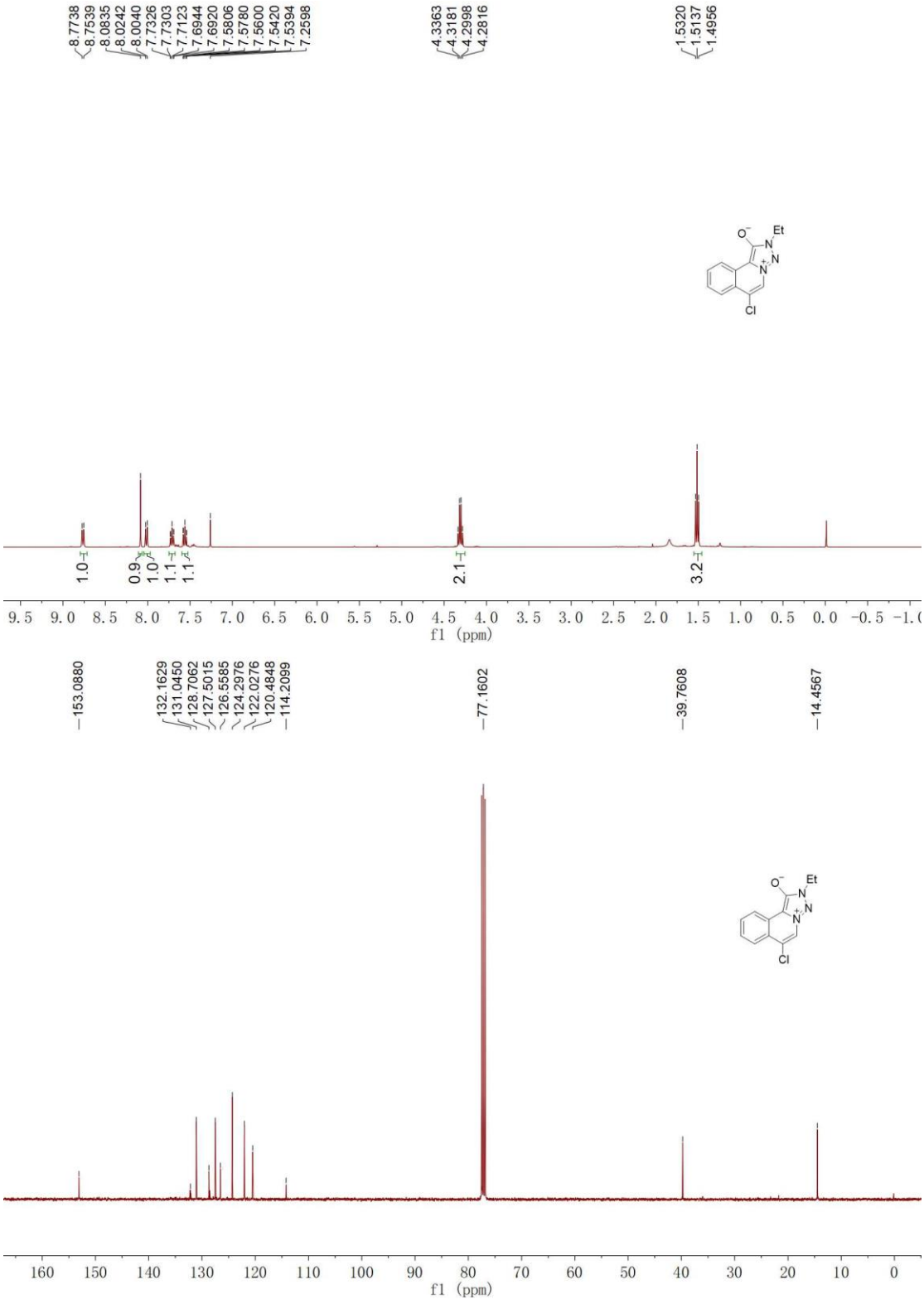


^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectra of **2oc**

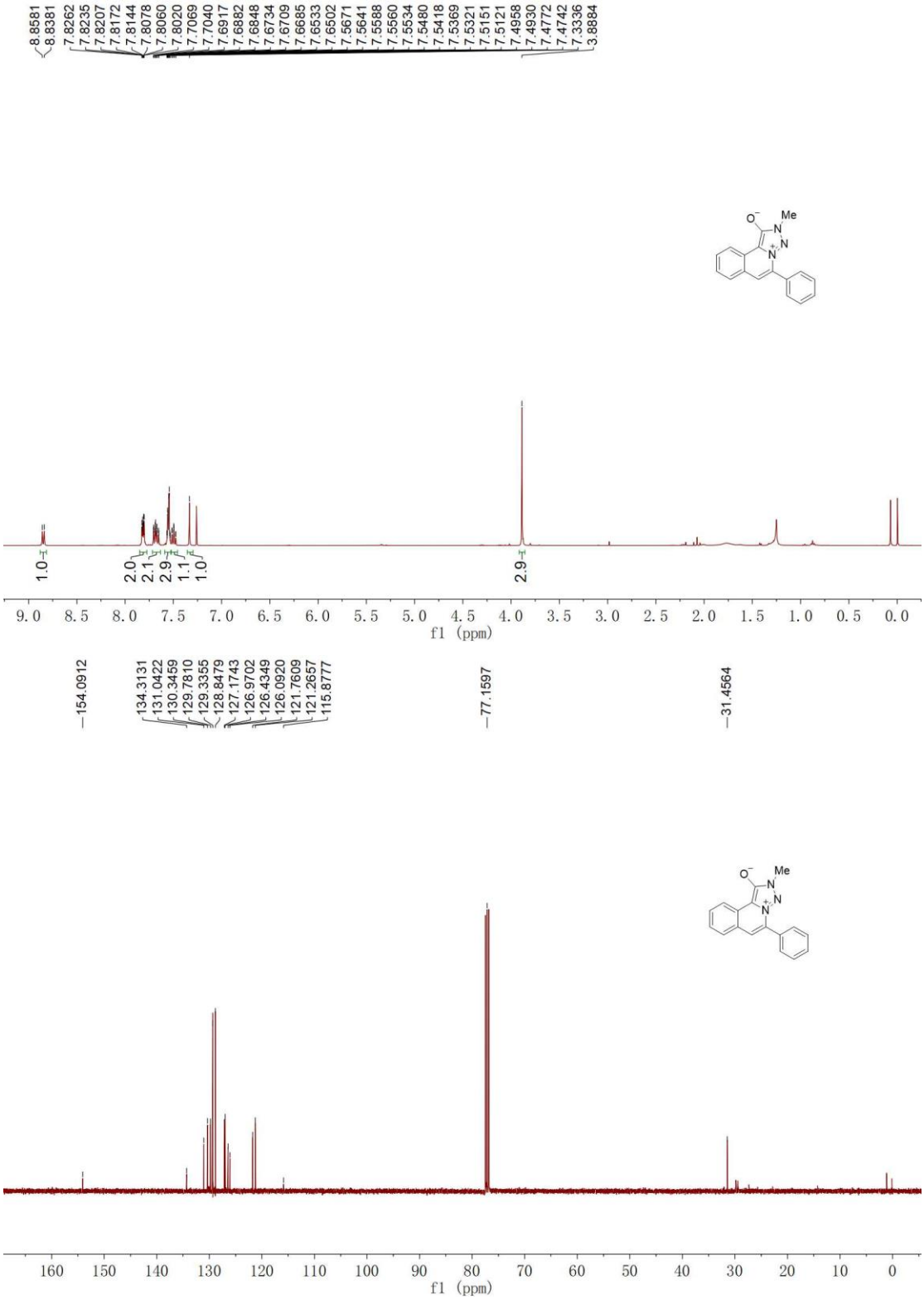




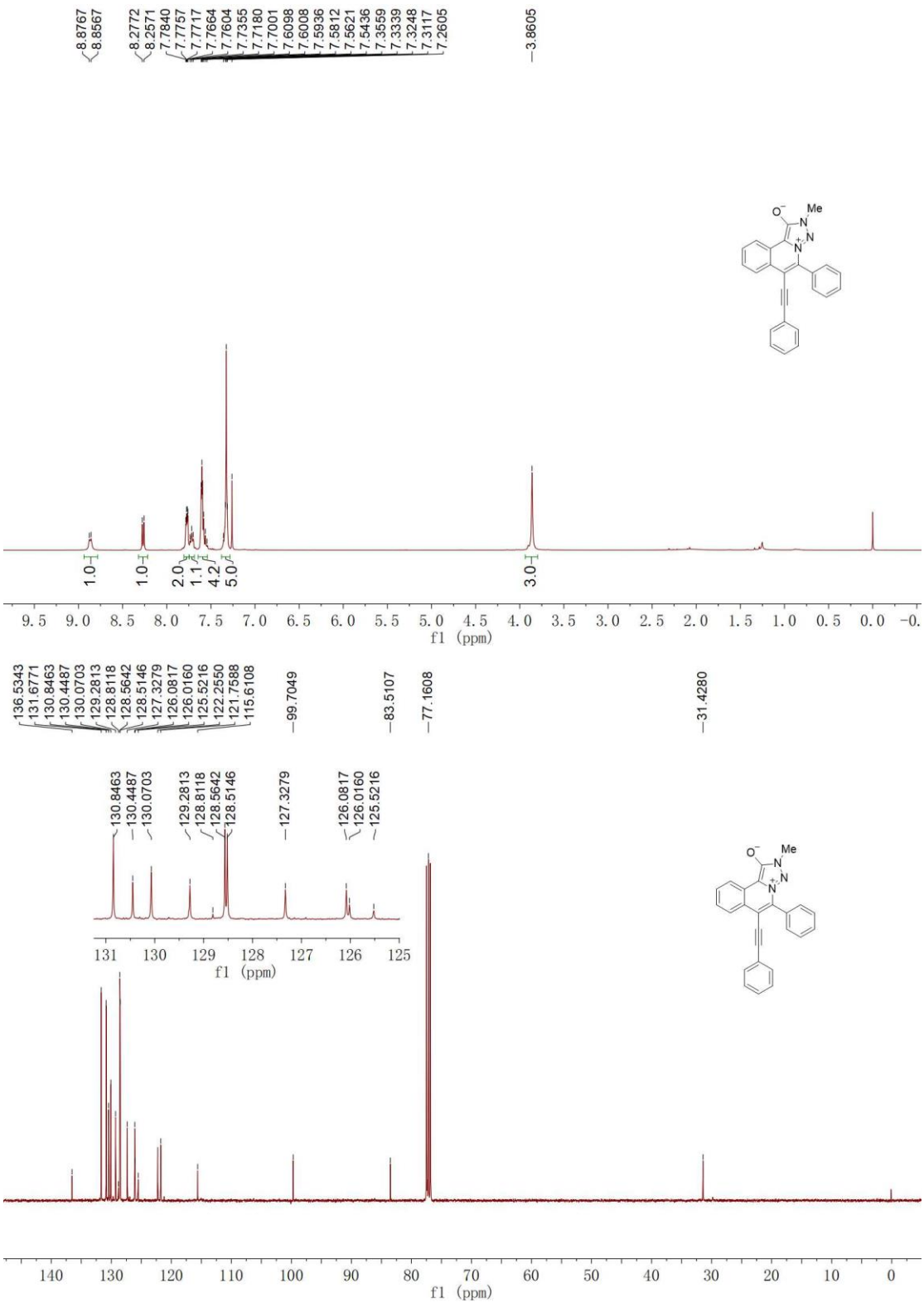
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectra of **2pa**



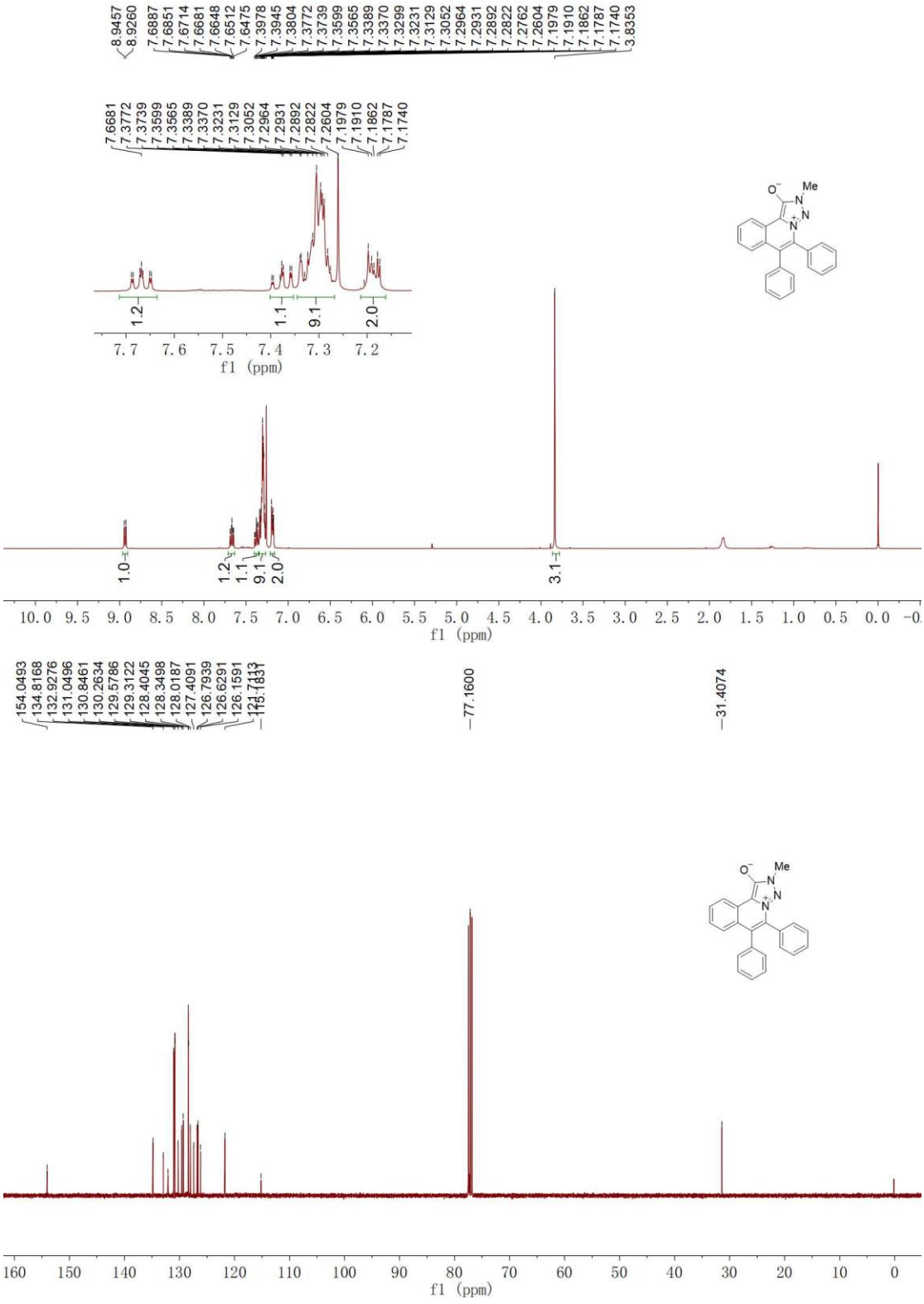
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectra of **3aa**



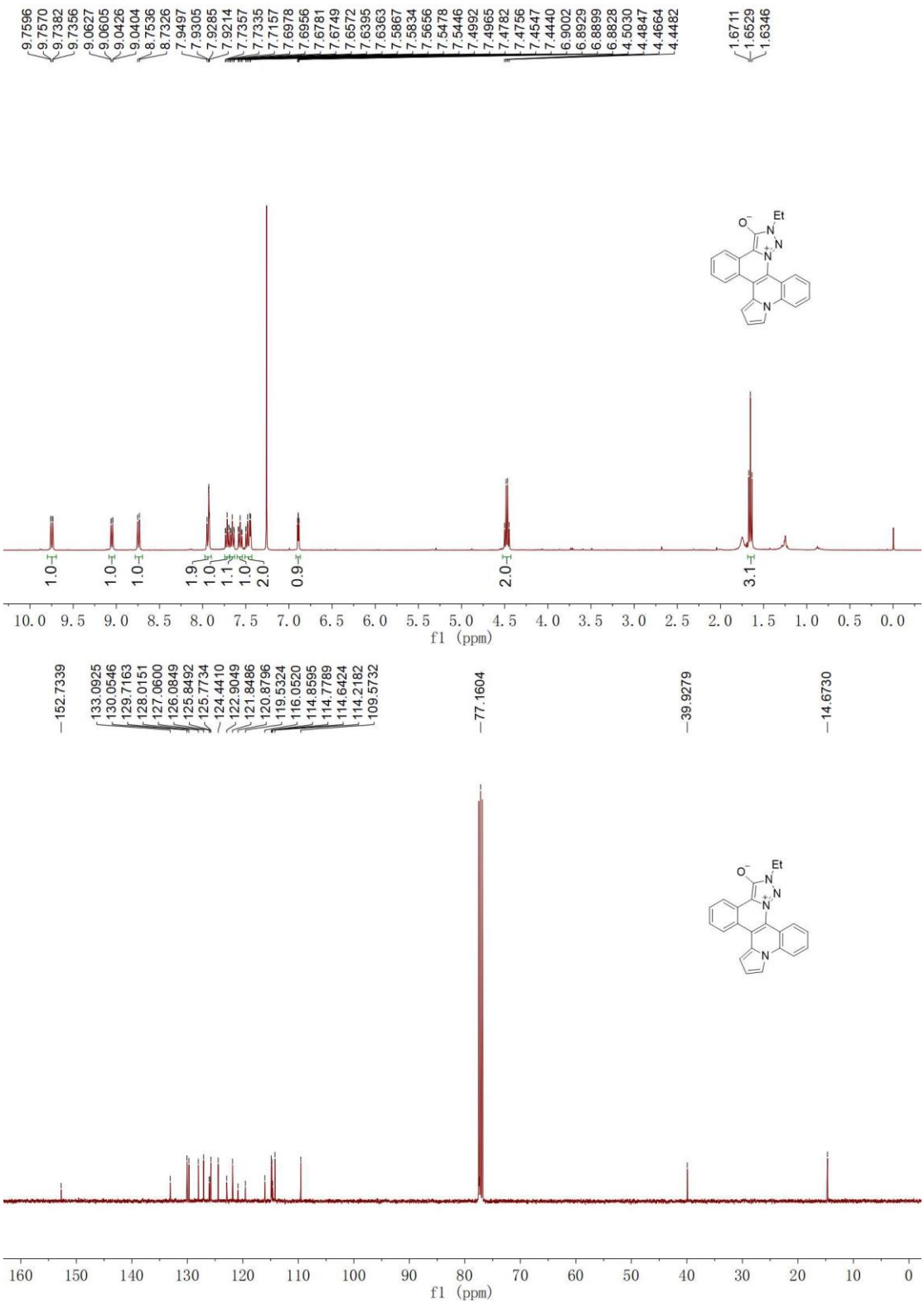
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectra of **4a**



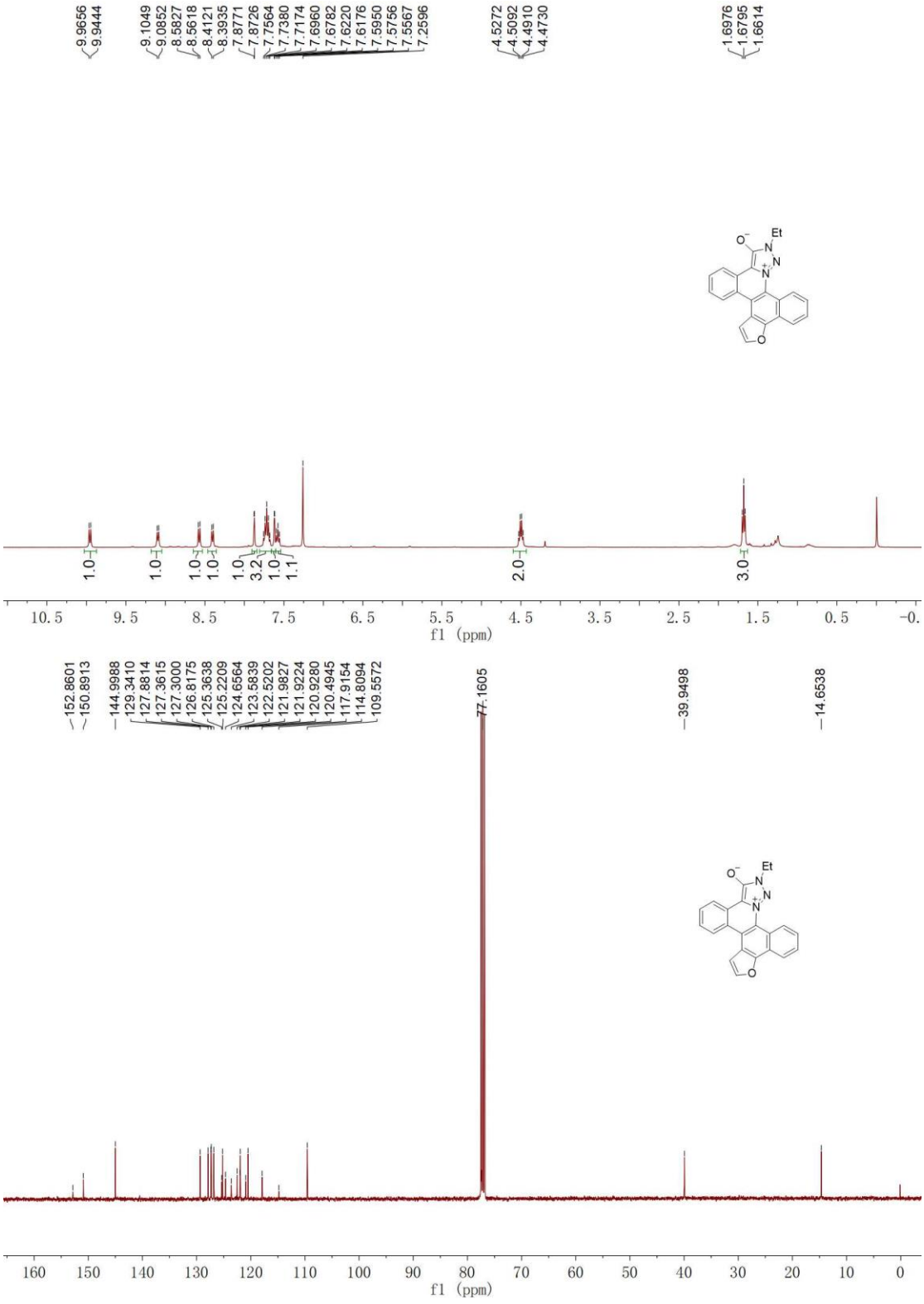
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectra of **4b**



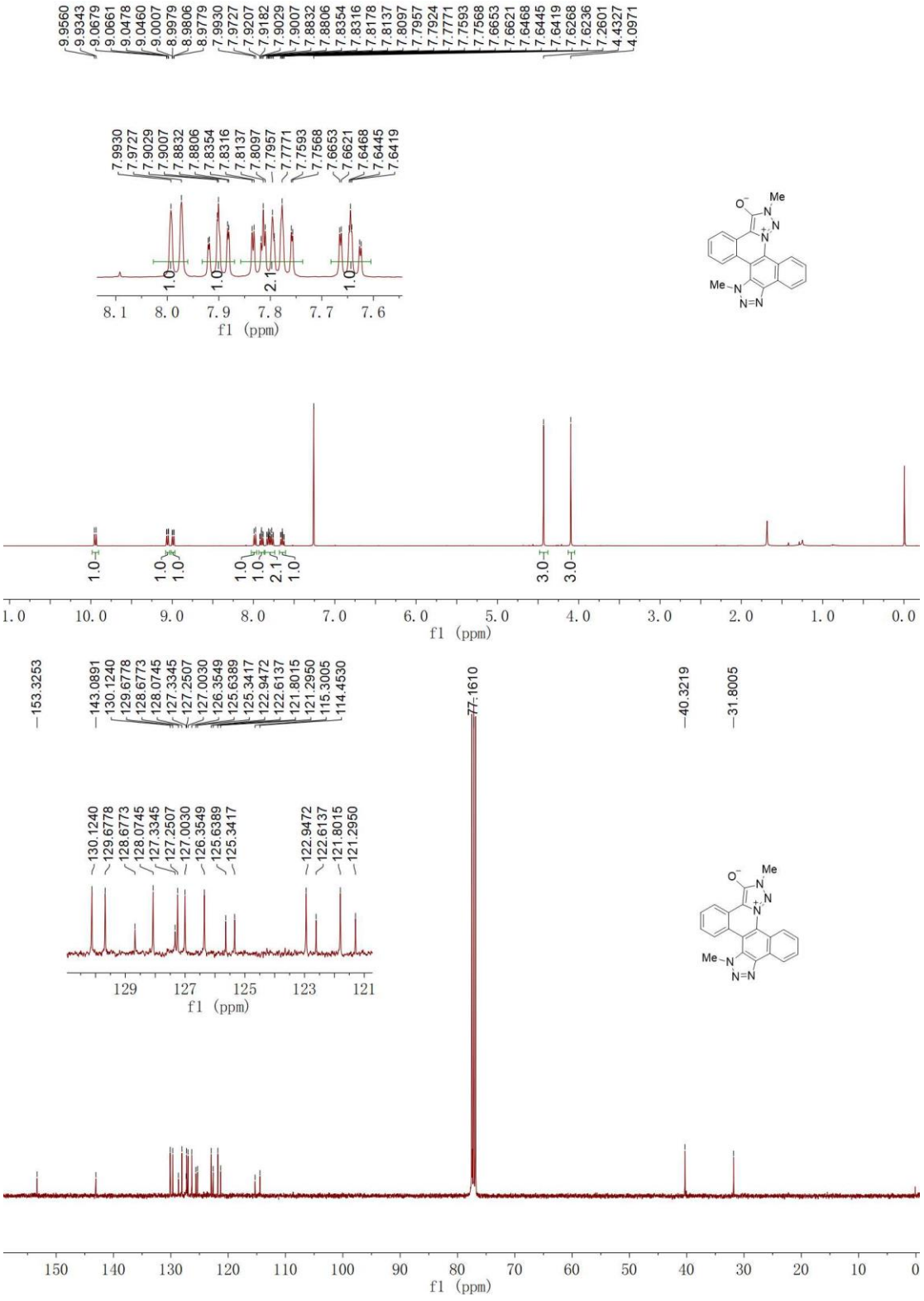
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectra of **5**



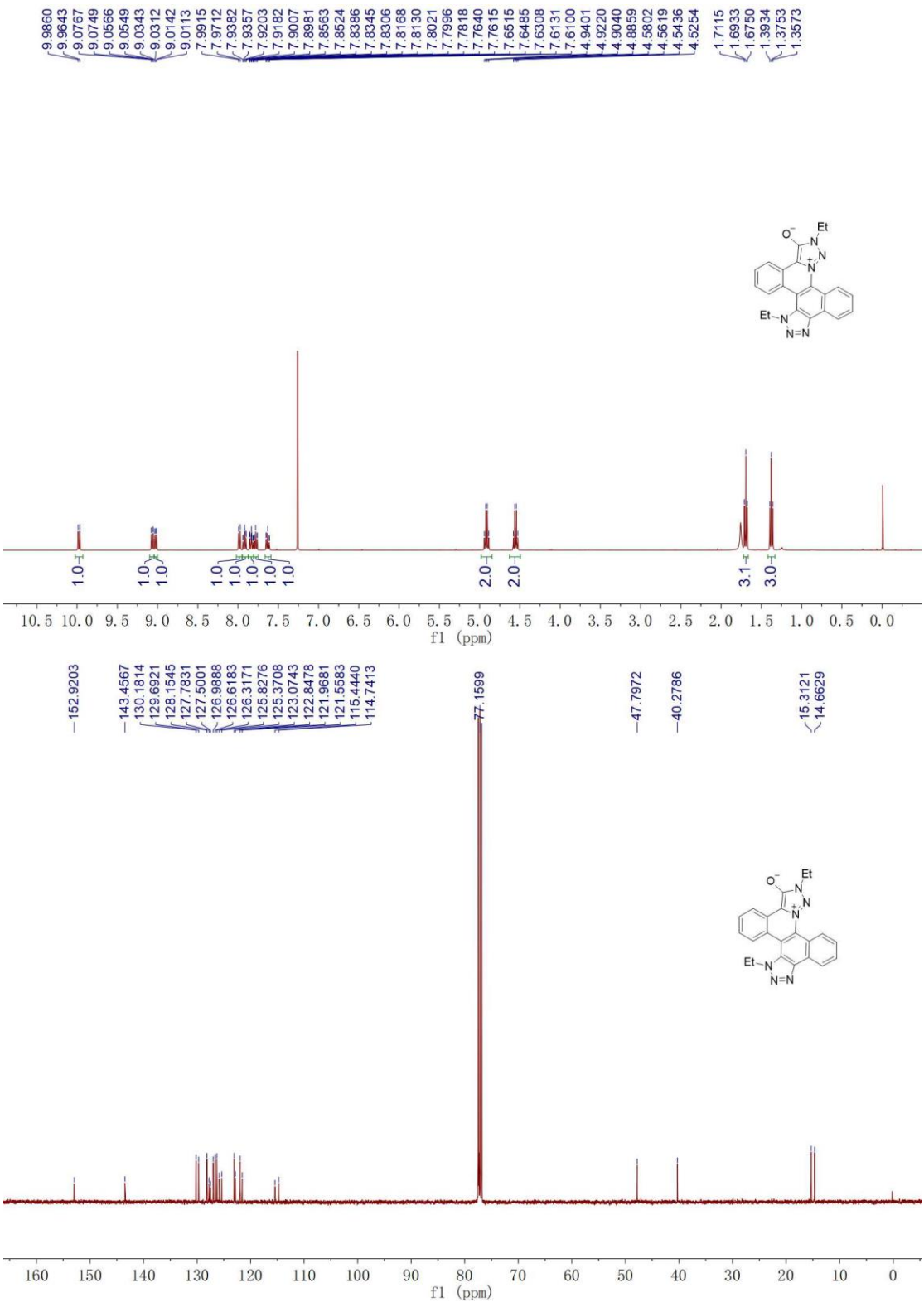
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectra of **6**



^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectra of **7a**



^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectra of **7b**



^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectra of **7c**