

Supporting Information

Direct synthesis of indazole derivatives via Rh(III)-catalyzed C–H activation of phthalazinones and allenes

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1. General information

Unless otherwise noted, all reactions were carried out without exclusion of air or moisture. Commercial solvents and reagents were used without further purification. Analytical thin layer chromatography (TLC) was performed using silica gel GF254 plates. Column chromatography was performed using silica gel (200-300 mesh) eluting with petroleum ether and ethyl acetate. NMR spectra were recorded on 400 MHz or 600 MHz spectrometers in the solvent indicated. Chemical shifts are reported downfield from TMS (= 0) for ^1H NMR. For ^{13}C NMR, chemical shifts are reported in the scale relative to CDCl_3 (= 77.00). ^{19}F NMR were recorded on Bruker AscendTM (376 MHz). HR-MS spectra were recorded on an electrospray ionization quadrupole time-of-flight (ESI-Q-TOF) mass spectrometer. Melting points were determined using a Büchi B-540 capillary melting point apparatus. **1a-1w**,¹ **2a-2n**,² **2o**,³ **2p**⁴ and **2q**⁵ are known compounds and prepared according to the corresponding literature.

2. General procedure for the synthesis of products 3

A mixture of 2-phenyl-2,3-dihydrophthalazine-1,4-dione **1a** (47.6 mg, 0.20 mmol), buta-2,3-dien-1-ylbenzene **2a** (39.1 mg, 0.30 mmol), $[\text{Rh}^*\text{CpCl}_2]_2$ (3.1 mg, 2.5 mol %), NaOAc (16.4 mg, 0.20 mmol) and AgOAc (33.4 mg, 0.20 mmol) in MeCN (1.0 mL) was stirred at 120 °C under open air for 12 hours. The resulting mixture was cooled to room temperature, solvent was removed under vacuo and the crude reaction mixture was purified by silica gel (200-300 mesh) column chromatography using hexane/ethyl acetate (6:1) as the eluant to afford **3a** as a yellow solid.

3. Gram scale synthesis and derivatization

3.1 Gram scale synthesis

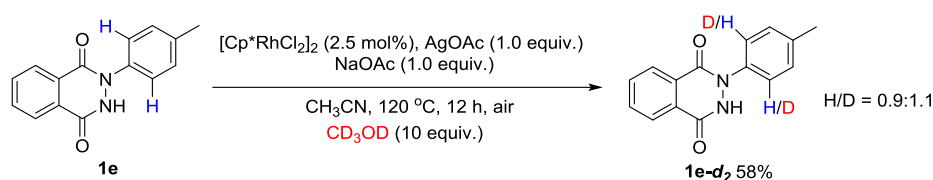
To a 50 mL oven-dried sealed tube, 2-phenyl-2,3-dihydrophthalazine-1,4-dione **1a** (1.2 g, 5.0 mmol), buta-2,3-dien-1-ylbenzene **2a** (1.0 g, 7.5 mmol), $[\text{Rh}^*\text{CpCl}_2]_2$ (77.5 mg, 2.5 mol %), NaOAc (0.41 g, 5.0 mmol) and AgOAc (0.84 g, 5.0 mmol) in MeCN (20.0 mL) were added sequentially under open air. The tube was sealed and placed in a preheated oil bath at 120 °C for 12 h. The reaction mixture was cooled to room temperature and concentrated under vacuo. The resulting mixture was purified by chromatography on silica gel with hexane/ethyl acetate (6:1) to give the corresponding product **3a** in 77 % yield (1.41 g).

3.2 Produce for the synthesis of compound 5

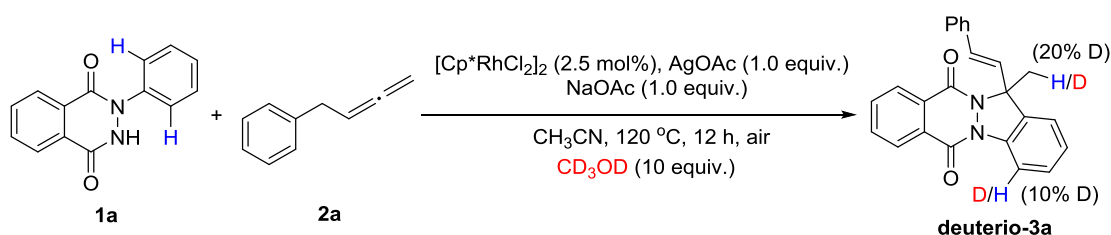
To a 10-mL round-bottomed flask containing **3a** (109.9 mg, 0.3 mmol, 1.0 equiv) and CH₂Cl₂/CH₃CN/H₂O (1:1:2) (4.0 mL) were added at room temperature. Then RuCl₃ (1.9 mg, 3.0 mol %) and NaIO₄ (321.0 mg, 5.0 equiv) were added and the resulting suspension was stirred at room temperature. After reaction, H₂O and EtOAc were added and the organic phase was washed with H₂O and brine, dried over anhydrous Na₂SO₄ and concentrated by rotary evaporation. Purification by silica column chromatography to afford corresponding product **5** (34.9 mg, 44%).

4. Isotope labeling experiments

4.1 H/D exchange experiment

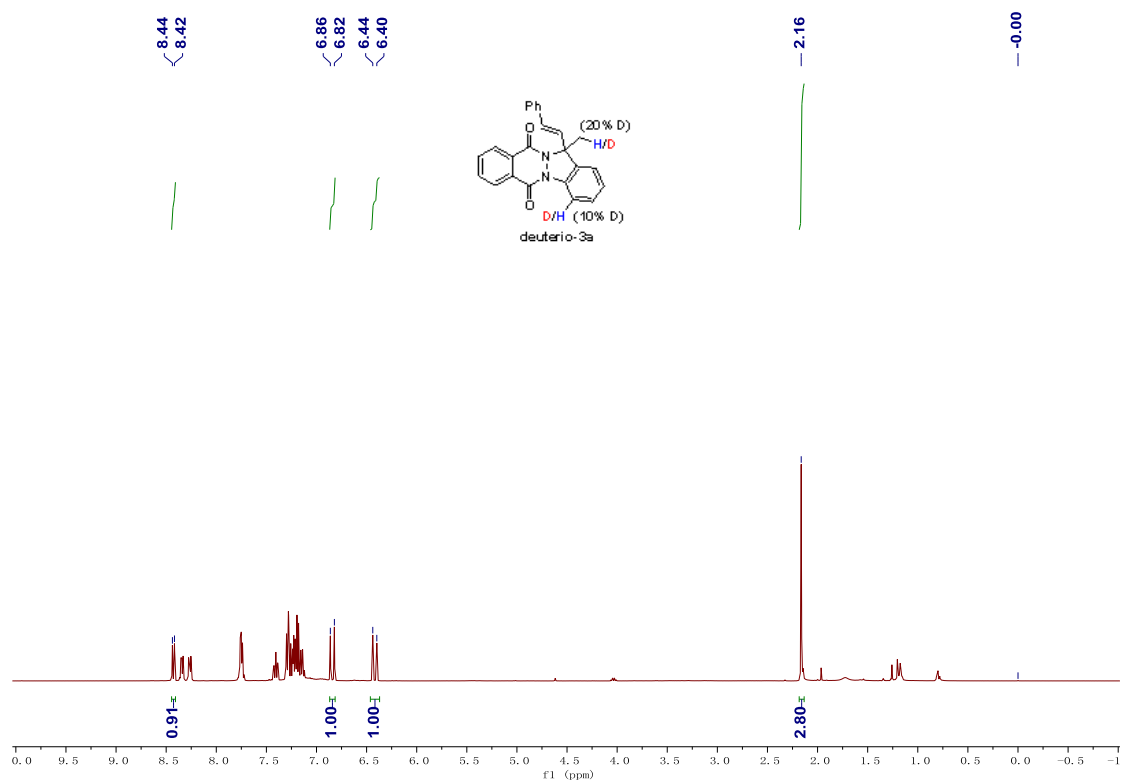
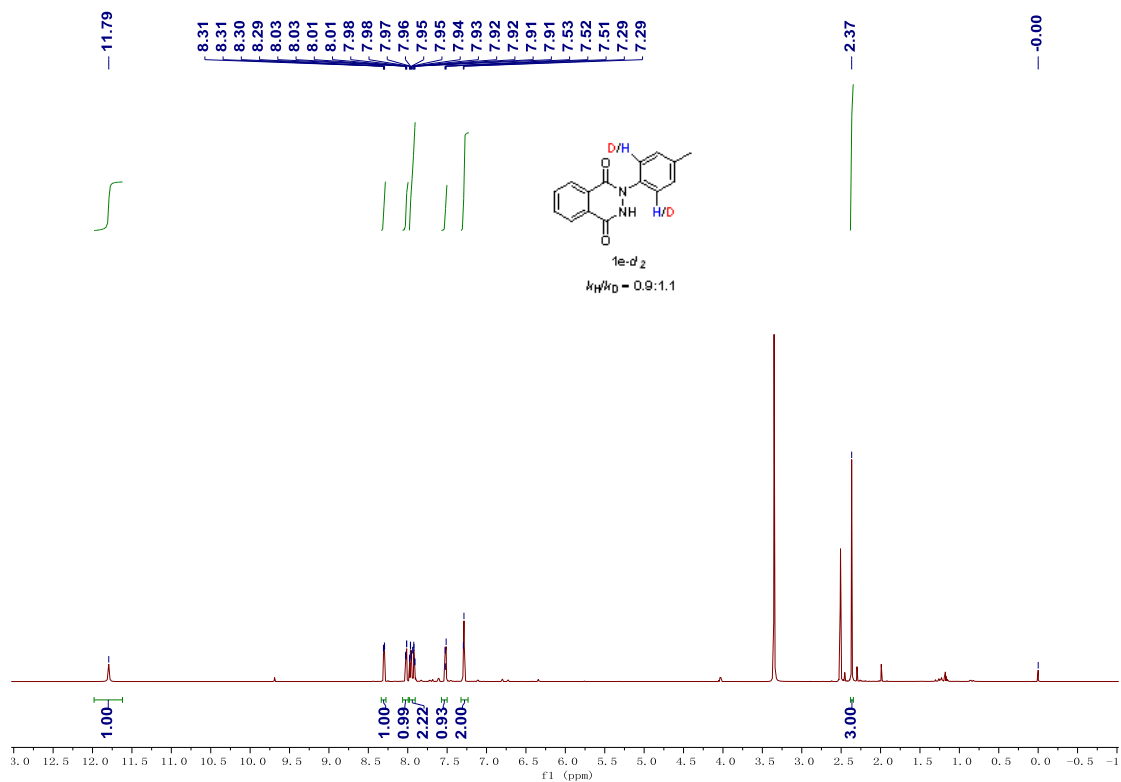


Compound **1e** (50.5 mg, 0.20 mmol), [Cp^{*}RhCl₂]₂ (3.1 mg, 2.5 mol %), AgOAc (33.4 mg, 0.20 mmol), NaOAc (16.4 mg, 0.20 mmol) and CD₃OD (72.1 mg, 2.0 mmol) were dissolved in MeCN (1.0 mL). The mixture was stirred at 120 °C under air for 12 hours. The resulting mixture was cooled to room temperature, solvent was removed under vacuo and the crude reaction mixture was purified by silica gel column chromatography (58% recovered) using hexane/ethyl acetate (2:1) as the eluant. The deuterated ratio was calculated from ¹H NMR analysis. (~55% D-incorporation was observed)

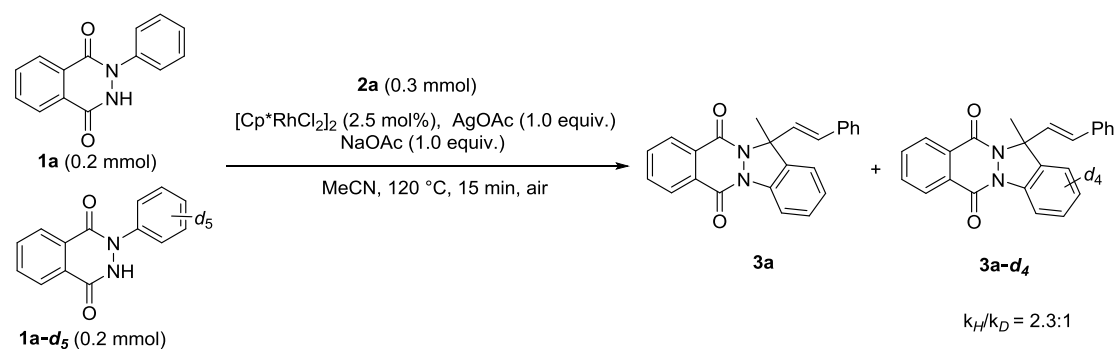


A mixture of 2-phenyl-2,3-dihydrophthalazine-1,4-dione **1a** (47.6 mg, 0.20 mmol), buta-2,3-dien-1-ylbenzene **2a** (39.1 mg, 0.30 mmol), [Cp^{*}RhCl₂]₂ (3.1 mg, 2.5 mol %), AgOAc (33.4 mg, 0.20 mmol), NaOAc (16.4 mg, 0.20 mmol) and CD₃OD (72.1 mg, 2.0 mmol) were dissolved in MeCN (1.0 mL). The mixture was stirred at 120 °C under open air for 12 hours. The resulting mixture was cooled to room temperature, solvent was removed under vacuo and the crude reaction mixture was purified by silica gel (200-300 mesh) column chromatography using hexane/ethyl acetate (6:1) as the eluant to afford **3a** as a yellow solid. The deuterated ratio was

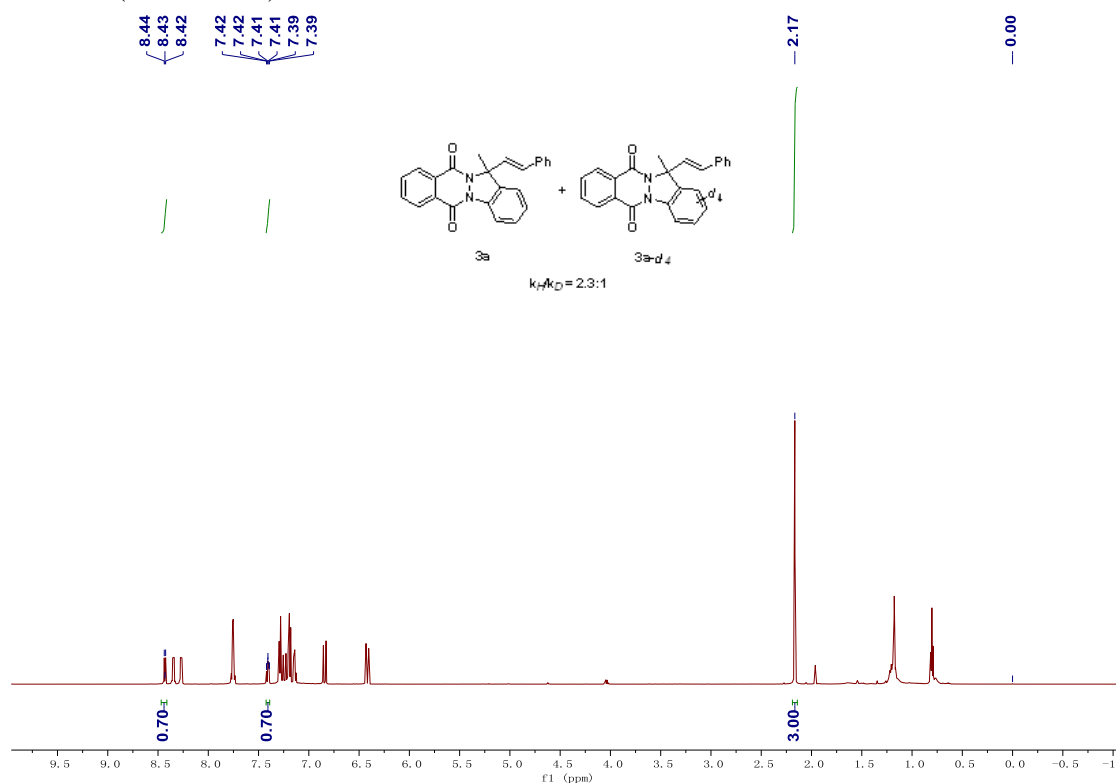
calculated from ^1H NMR analysis.

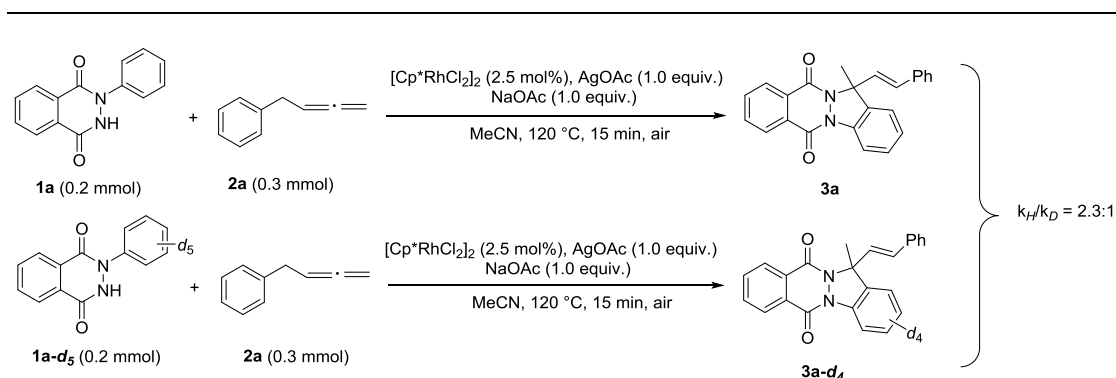


4.2 Kinetic isotope effect

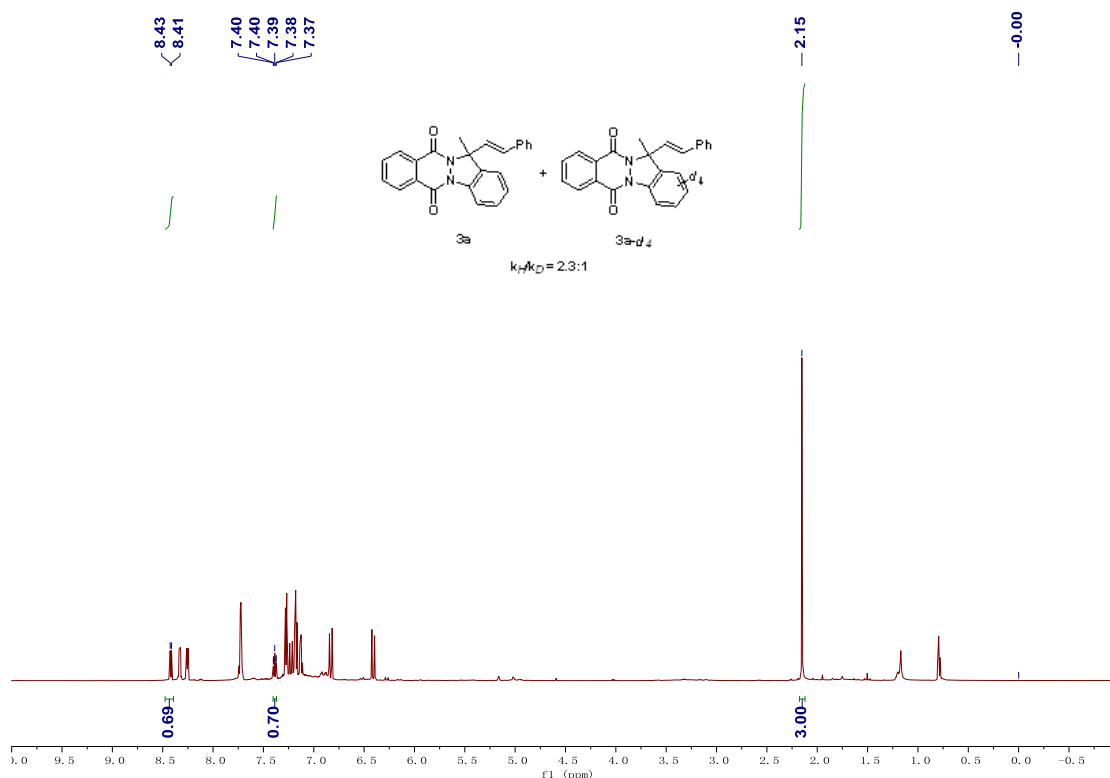


2-phenyl-2,3-dihydrophthalazine-1,4-dione **1a** (47.6 mg, 0.20 mmol) and [D_5]-2-phenyl-2,3-dihydrophthalazine-1,4-dione **1a-d₅** (48.7 mg, 0.20 mmol), buta-2,3-dien-1-ylbenzene **2a** (39.1 mg, 0.30 mmol), $[\text{Cp}^*\text{RhCl}_2]_2$ (3.1 mg, 2.5 mol %), AgOAc (33.4 mg, 0.20 mmol) and NaOAc (16.4 mg, 0.20 mmol) were dissolved in MeCN (1.0 mL). The mixture was stirred at 120 °C under air for 15 minutes. The resulting mixture was cooled to room temperature and solvent was removed under vacuo. Purification was performed by column chromatography on silica gel using hexane/ethyl acetate (6:1) as the eluant to provide a mixture of **3a** and **3a-d₄**. The ratio of **3a** and **3a-d₄** was determined to be 2.3:1 by ^1H NMR integration method ($k_H/k_D = 2.3$).

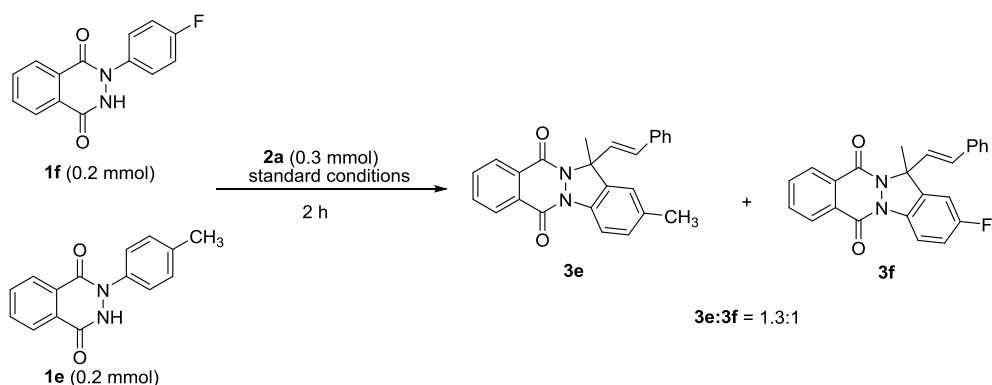




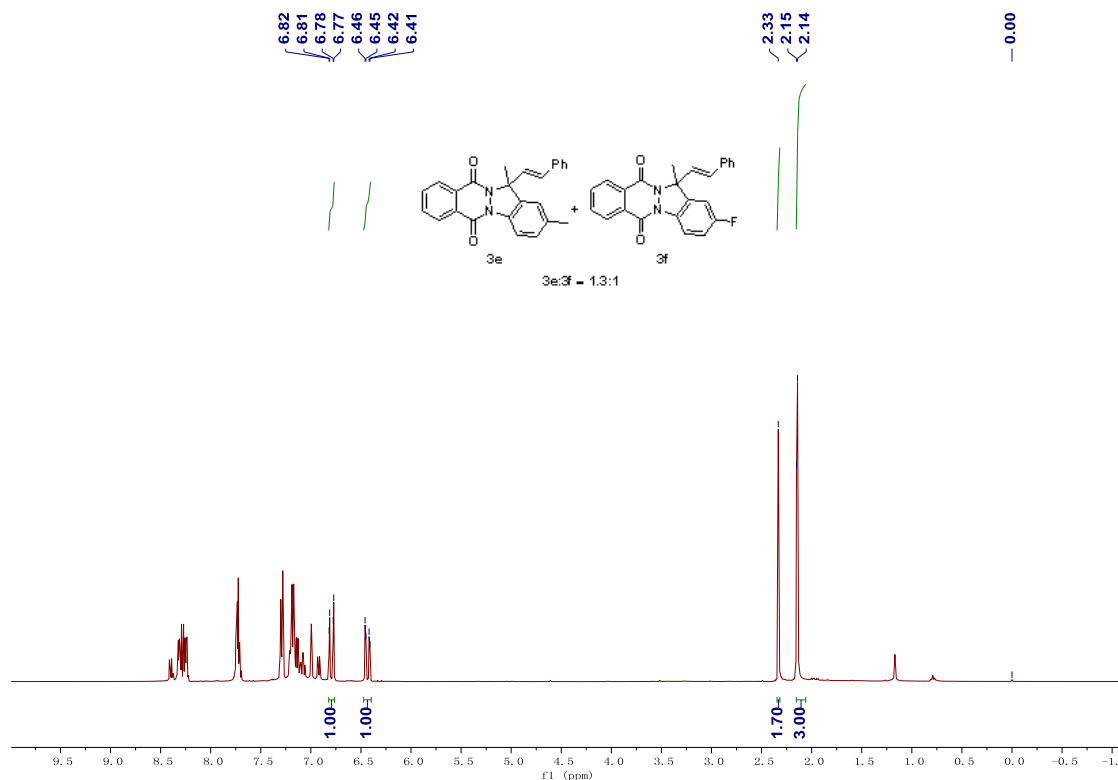
In a round bottom flask, a mixture of **1a** (47.6 mg, 0.20 mmol), allene **2a** (39.1 mg, 0.30 mmol), $[\text{Cp}^*\text{RhCl}_2]_2$ (3.1 mg, 2.5 mol %), AgOAc (33.4 mg, 0.20 mmol) and NaOAc (16.4 mg, 0.20 mmol) in MeCN (1.0 mL) was stirred at 120 °C under open air for 15 minutes. At the same time, in another round bottom flask, a solution of **1a-d₅** (48.7 mg, 0.20 mmol), allene **2a** (39.1 mg, 0.30 mmol), $[\text{Cp}^*\text{RhCl}_2]_2$ (3.1 mg, 2.5 mol %), AgOAc (33.4 mg, 0.20 mmol) and NaOAc (16.4 mg, 0.20 mmol) in MeCN (1.0 mL) was stirred at 120 °C under open air for 15 minutes. These two mixtures were rapidly combined, and all the volatiles were rapidly removed under a reduced pressure. The residue was purified by silica gel chromatography using hexane/ethyl acetate (6:1) as the eluant to provide a mixture of **3a** and **3a-d₄**. The ratio of **3a** and **3a-d₄** was determined to be 2.3:1 by ¹H NMR integration method ($k_H/k_D = 2.3$).



5. Competition experiments

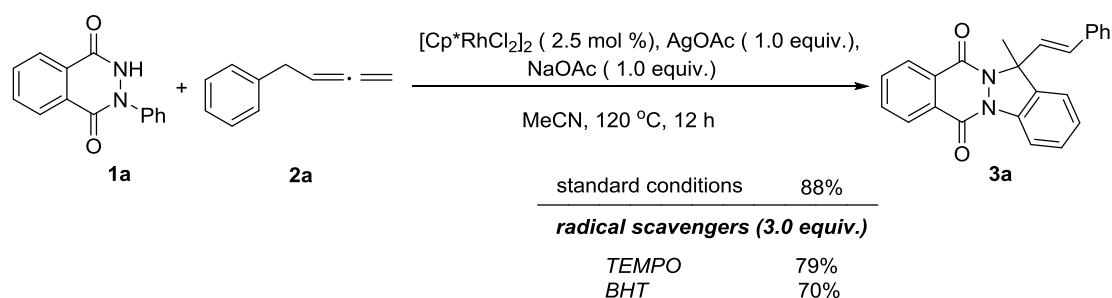


A solution of N-aryl phthalazinones **1e** (50.5 mg, 0.20 mmol) and **1f** (51.2 mg, 0.20 mmol), allene **2a** (39.1 mg, 0.30 mmol), [Cp**Rh*Cl₂]₂ (3.1 mg, 2.5 mol %), AgOAc (33.4 mg, 0.20 mmol) and NaOAc (16.4 mg, 0.20 mmol) in MeCN (1.0 mL) was stirred at 120 °C under open air for 2 hours. The solvent was removed under vacuo and the crude reaction mixture was directly loaded on silica gel column chromatography and purified using hexane/ethyl acetate (6:1) as the eluant to afford a mixture of compounds **3e** and **3f**. The ratio of **3e** and **3f** was determined to be 1.3:1 by ¹H NMR.

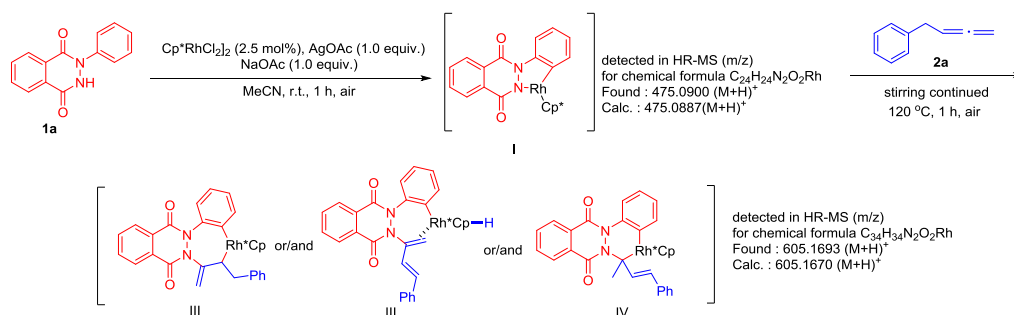


6. Radical inhibition studies

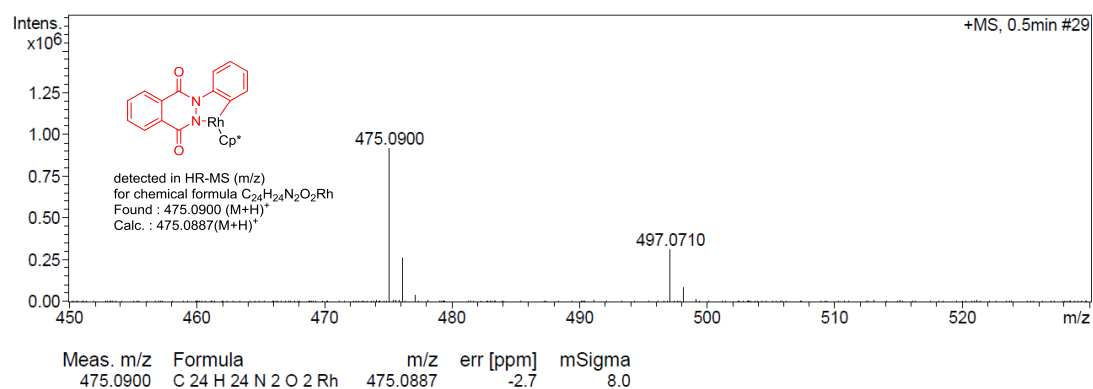
A mixture of **1a** (47.6 mg, 0.20 mmol), **2a** (39.1 mg, 0.30 mmol), [Cp*RhCl₂]₂ (3.1 mg, 2.5 mol %), AgOAc (33.4 mg, 0.20 mmol), NaOAc (16.4 mg, 0.20 mmol) and 2,2,6,6-tetramethylpiperidinoxy (93.8 mg, 6.00 mmol) or 2,6-di-tert-butyl-4-methylphenol (132.2 mg, 6.00 mmol) were dissolved in MeCN (1.0 mL). The mixture was stirred at 120 °C under open air for 12 hours. The resulting mixture was cooled to room temperature, solvent was removed under vacuo and the crude reaction mixture was purified by silica gel (200-300 mesh) column chromatography to afford **3a**.

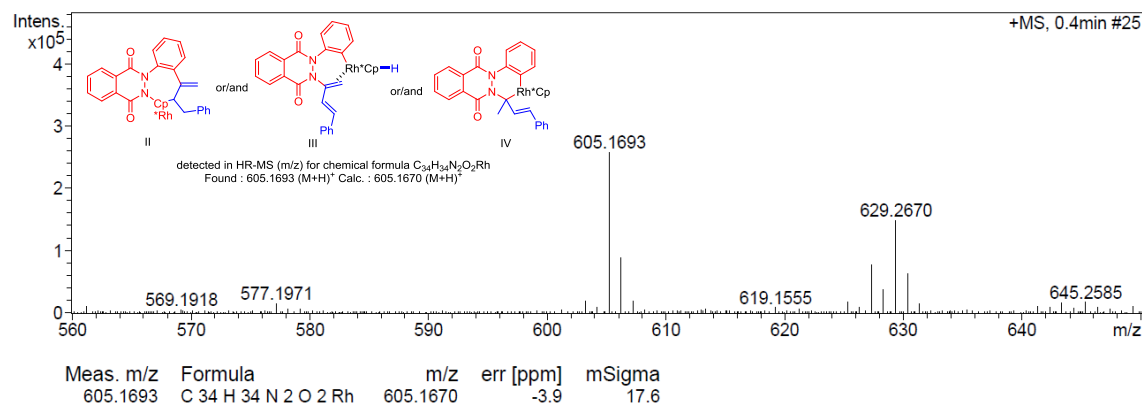


7. Intermediate capture experiments



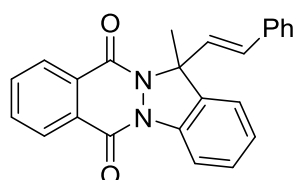
In an oven-dried 10 mL pressure tube, a mixture of **1a** (0.20 mmol), [Cp*RhCl₂]₂ (2.5 mol %), AgOAc (0.20 mmol) and NaOAc (0.20 mmol) in MeCN (1.0 mL) was stirred at room temperature under open air for 1 hours, and the reaction mixture characterized by HR-MS. To the reaction mixture was added **2a** (0.30 mmol), further stirring the reaction mixture for another 1 h at 120 °C and the reaction mixture characterized by HR-MS.





8. Analytical data and copies of NMR spectra

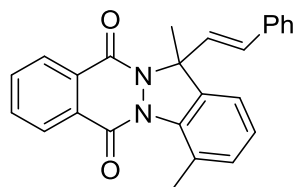
8.1 Analytical data for products



3a

(E)-13-methyl-13-styryl-13H-indazolo[1,2-*b*]phthalazine-6,11-dione

Compound **3a** was isolated as a yellow solid (64.6 mg, 88% yield). M.P.: 74-75 °C. ¹H NMR (600 MHz, CDCl₃, ppm) δ 8.49 (d, *J* = 7.8 Hz, 1H), 8.43 - 8.36 (m, 1H), 8.35 - 8.29 (m, 1H), 7.80 - 7.75 (m, 2H), 7.47 - 7.42 (m, 1H), 7.37 - 7.34 (m, 2H), 7.33 - 7.27 (m, 2H), 7.26 - 7.22 (m, 2H), 7.21 - 7.17 (m, 1H), 6.92 (d, *J* = 16.2 Hz, 1H), 6.50 (d, *J* = 16.2 Hz, 1H), 2.23 (s, 3H). ¹³C NMR (150 MHz, CDCl₃, ppm) δ 154.7, 154.6, 135.7, 135.4, 133.3, 133.1, 131.6, 131.5, 129.4, 129.4, 129.3, 128.9, 128.4, 128.0, 127.3, 127.2, 126.8, 126.1, 122.8, 115.9, 71.4, 24.6. HRMS (ESI) *m/z* calcd for C₂₄H₁₉N₂O₂⁺ [M + H⁺]: 367.1441; found: 367.1430.

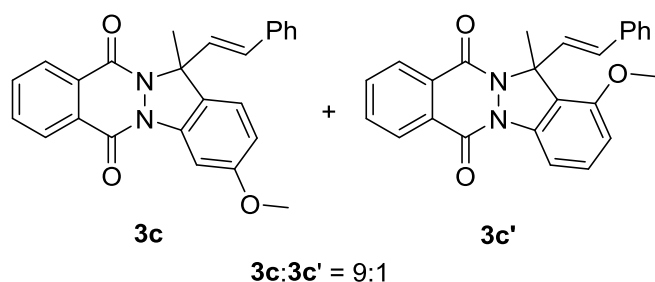


3b

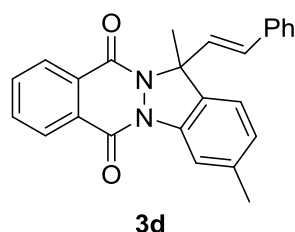
(E)-4,13-dimethyl-13-styryl-13H-indazolo[1,2-*b*]phthalazine-6,11-dione

Compound **3b** was isolated as a yellow solid (20.1mg, 26% yield). M.P.: 80-81 °C. ¹H NMR (400 MHz, CDCl₃, ppm) δ 8.30 - 8.19 (m, 2H), 7.77 - 7.71 (m, 2H), 7.30 - 7.26 (m, 1H), 7.23 - 7.10 (m, 6H), 7.05 - 7.01 (m, 1H), 6.78 (d, *J* = 16.0 Hz, 1H), 6.43 (d, *J* = 16.4 Hz, 1H), 2.51 (s, 3H), 2.13 (s, 3H). ¹³C NMR (100 MHz, CDCl₃, ppm) δ 156.4, 156.1, 135.8, 134.5, 134.0, 133.4, 133.2, 132.6, 131.4, 130.1, 129.8, 129.2,

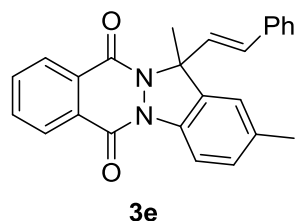
128.5, 128.1, 127.5, 127.2, 126.9, 120.3, 71.8, 25.2, 22.4. HRMS (ESI) m/z calcd for $C_{25}H_{21}N_2O_2^+$ $[M + H^+]$: 381.1598; found: 381.1603.



(E)-3-methoxy-13-methyl-13-styryl-13H-indazolo[1,2-*b*]phthalazine-6,11-dione (3c) and (E)-1-methoxy-13-methyl-13-styryl-13H-indazolo[1,2-*b*]phthalazine-6,11-dione (3c'). Compound 3c and 3c' were isolated as a yellow solid (55.5mg, 70% yield, 3c:3c' = 9:1). 1H NMR (400 MHz, $CDCl_3$, ppm) δ 8.44 - 8.38 (m, 1H), 8.37 - 8.30 (m, 1H), 8.21 - 8.11 (m, 1H), 7.89 - 7.79 (m, 2H), 7.47 - 7.34 (m, 2H), 7.32 - 7.14 (m, 4H), 6.97 - 6.82 (m, 2H), 6.54 - 6.37 (m, 1H), 3.92 (s, 2.7H), 3.86 (s, 0.3H), 2.33 (s, 0.3H), 2.21 (s, 2.7H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 160.7, 154.9, 154.8, 154.6, 154.4, 136.6, 136.5, 136.3, 135.8, 133.5, 133.4, 133.2, 133.1, 131.4, 131.0, 130.9, 129.5, 129.5, 129.4, 129.2, 128.5, 128.4, 128.2, 128.1, 127.8, 127.4, 127.4, 127.3, 126.9, 126.8, 123.4, 123.4, 113.4, 109.1, 108.7, 101.1, 72.1, 71.4, 55.8, 55.7, 24.9, 21.8. HRMS (ESI) m/z calcd for $C_{25}H_{21}N_2O_3^+$ $[M + H^+]$: 397.1547; found: 397.1554.

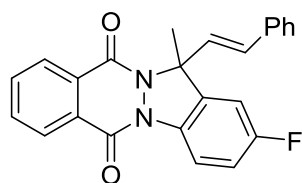


(E)-3,13-dimethyl-13-styryl-13H-indazolo[1,2-*b*]phthalazine-6,11-dione (3d). Compound 3d was isolated as a yellow solid (58.7mg, 77% yield). M.P.: 82-83 °C. 1H NMR (600 MHz, $CDCl_3$, ppm) δ 8.43 - 8.39 (m, 1H), 8.38 - 8.31 (m, 2H), 7.84 - 7.78 (m, 2H), 7.38 - 7.34 (m, 2H), 7.27 - 7.25 (m, 2H), 7.22 - 7.19 (m, 1H), 7.17 (d, $J = 7.2$ Hz, 1H), 7.15 - 7.12 (m, 1H), 6.92 (d, $J = 16.2$ Hz, 1H), 6.48 (d, $J = 16.2$ Hz, 1H), 2.47 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$, ppm) δ 154.8, 154.7, 139.9, 135.8, 135.7, 133.4, 133.1, 131.4, 129.6, 129.4, 129.2, 128.9, 128.5, 128.1, 127.3, 127.3, 127.0, 126.8, 122.5, 116.5, 71.5, 24.8, 21.7. HRMS (ESI) m/z calcd for $C_{25}H_{21}N_2O_2^+$ $[M + H^+]$: 381.1598; found: 381.1607.



(E)-2,13-dimethyl-13-styryl-13H-indazolo[1,2-b]phthalazine-6,11-dione

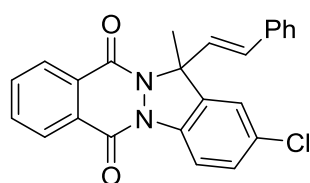
Compound **3e** was isolated as a yellow solid (54.5mg, 72% yield). M.P.: 84-85 °C. ¹H NMR (600 MHz, CDCl₃, ppm) δ 8.43 - 8.39 (m, 1H), 8.37 (d, *J* = 8.4 Hz, 1H), 8.35 - 8.30 (m, 1H), 7.82 - 7.78 (m, 2H), 7.39 - 7.36 (m, 2H), 7.29 - 7.25 (m, 3H), 7.23 - 7.19 (m, 1H), 7.08 (s, 1H), 6.88 (d, *J* = 16.2 Hz, 1H), 6.52 (d, *J* = 16.2 Hz, 1H), 2.42 (s, 3H), 2.22 (s, 3H). ¹³C NMR (150 MHz, CDCl₃, ppm) δ 154.8, 154.4, 136.4, 135.8, 133.3, 133.3, 133.2, 131.9, 131.5, 130.1, 129.6, 129.4, 129.1, 128.5, 128.1, 127.3, 127.3, 126.9, 123.2, 115.8, 71.5, 24.6, 21.3. HRMS (ESI) *m/z* calcd for C₂₅H₂₁N₂O₂⁺ [M + H⁺]: 381.1598; found: 381.1600.



3f

(E)-2-fluoro-13-methyl-13-styryl-13H-indazolo[1,2-b]phthalazine-6,11-dione

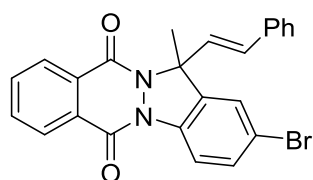
Compound **3f** was isolated as a yellow solid (51.5mg, 67% yield). M.P.: 82-83 °C. ¹H NMR (400 MHz, CDCl₃, ppm) δ 8.51 - 8.45 (m, 1H), 8.43 - 8.37 (m, 1H), 8.36 - 8.30 (m, 1H), 7.86 - 7.78 (m, 2H), 7.39 - 7.37 (m, 2H), 7.31 - 7.13 (m, 4H), 7.01 (dd, *J* = 7.6, 2.4 Hz, 1H), 6.88 (d, *J* = 16.0 Hz, 1H), 6.52 (d, *J* = 16.0 Hz, 1H), 2.24 (s, 3H). ¹³C NMR (100 MHz, CDCl₃, ppm) δ 160.7 (d, *J* = 246.8 Hz), 154.8, 154.5, 135.5, 133.8, 133.8, 133.5, 133.3, 131.2, 131.6 (d, *J* = 2.3 Hz), 129.3 (d, *J* = 11.4 Hz), 128.5, 128.4, 128.4, 127.4, 127.3, 126.9, 117.5 (d, *J* = 8.3 Hz), 116.4 (d, *J* = 23.4 Hz), 110.3 (d, *J* = 25.6 Hz), 71.3 (d, *J* = 2.5 Hz), 24.6. ¹⁹F NMR (376 MHz, CDCl₃, ppm) δ -114.11. HRMS (ESI) *m/z* calcd for C₂₄H₁₈FN₂O₂⁺ [M + H⁺]: 385.1347; found: 381.1353.



3g

(E)-2-chloro-13-methyl-13-styryl-13H-indazolo[1,2-b]phthalazine-6,11-dione

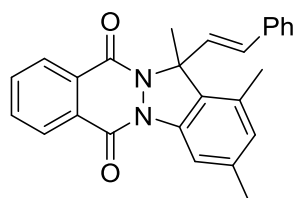
Compound **3g** was isolated as a yellow solid (54.2mg, 68% yield). M.P.: 103-104 °C. ¹H NMR (600 MHz, CDCl₃, ppm) δ 8.42 (d, *J* = 8.4 Hz, 1H), 8.41 - 8.37 (m, 1H), 8.36 - 8.30 (m, 1H), 7.84 - 7.79 (m, 2H), 7.42 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.40 - 7.36 (m, 2H), 7.31 - 7.21 (m, 4H), 6.86 (d, *J* = 16.2 Hz, 1H), 6.52 (d, *J* = 16.2 Hz, 1H), 2.23 (s, 3H). ¹³C NMR (150 MHz, CDCl₃, ppm) δ 154.7, 154.7, 135.5, 134.1, 133.6, 133.6, 133.3, 132.0, 131.5, 129.7, 129.4, 129.3, 128.5, 128.4, 128.4, 127.4, 127.4, 126.9, 123.1, 117.1, 71.3, 24.6. HRMS (ESI) *m/z* calcd for C₂₄H₁₈ClN₂O₂⁺ [M + H⁺]: 401.1051; found: 401.1055.



3h

(E)-2-bromo-13-methyl-13-styryl-13H-indazolo[1,2-*b*]phthalazine-6,11-dione

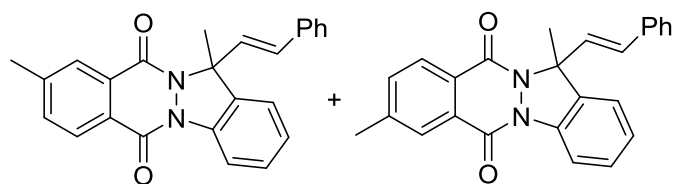
Compound **3h** was isolated as a yellow solid (33.0mg, 37% yield). M.P.: 138-139 °C. ¹H NMR (400 MHz, CDCl₃, ppm) δ 8.48 - 8.30 (m, 3H), 7.89 - 7.81 (m, 2H), 7.59 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.44 - 7.36 (m, 3H), 7.33 - 7.21 (m, 3H), 6.85 (d, *J* = 16.0 Hz, 1H), 6.52 (d, *J* = 16.4 Hz, 1H), 2.23 (s, 3H). ¹³C NMR (100 MHz, CDCl₃, ppm) δ 154.8, 154.7, 135.5, 134.6, 133.9, 133.7, 133.4, 132.6, 132.0, 129.4, 129.3, 128.6, 128.4, 128.4, 127.5, 127.5, 126.9, 126.0, 119.0, 117.5, 71.2, 24.7. HRMS (ESI) *m/z* calcd for C₂₄H₁₈BrN₂O₂⁺ [M + H⁺]: 445.0546; found: 445.0559.



3i

(E)-1,3,13-trimethyl-13-styryl-13H-indazolo[1,2-*b*]phthalazine-6,11-dione

Compound **3i** was isolated as a yellow solid (48.9mg, 62% yield). M.P.: 113-114 °C. ¹H NMR (400 MHz, CDCl₃, ppm) δ 8.43 - 8.38 (m, 1H), 8.36 - 8.26 (m, 2H), 7.86 - 7.78 (m, 2H), 7.39 (d, *J* = 7.2 Hz, 2H), 7.32 - 7.19 (m, 3H), 6.96 - 6.87 (m, 2H), 6.50 (d, *J* = 16.0 Hz, 1H), 2.44 (s, 3H), 2.32 (s, 3H), 2.27 (s, 3H). ¹³C NMR (100 MHz, CDCl₃, ppm) δ 154.5, 154.2, 139.6, 136.0, 135.7, 133.3, 133.1, 132.9, 132.6, 129.9, 129.5, 129.4, 128.5, 128.1, 127.6, 127.3, 127.1, 126.8, 126.3, 114.2, 71.5, 21.9, 21.5, 18.4. HRMS (ESI) *m/z* calcd for C₂₆H₂₃N₂O₂⁺ [M + H⁺]: 395.1754; found: 395.1773.



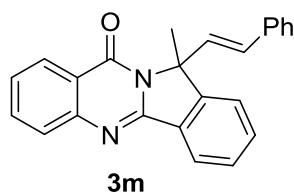
3j

3j'

3j:3j' = 1:1

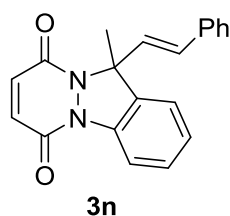
(E)-9,13-dimethyl-13-styryl-13H-indazolo[1,2-*b*]phthalazine-6,11-dione (3j) and (E)-8,13-dimethyl-13-styryl-13H-indazolo[1,2-*b*]phthalazine-6,11-dione(3j')

Compound **3j** and **3j'** were isolated as a yellow solid (66.4mg, 87% yield, **3j**: **3j'** = 1:1). ¹H NMR (400 MHz, CDCl₃, ppm) δ 8.55 - 8.46 (m, 1H), 8.34 - 8.11 (m, 2H), 7.66 - 7.60 (m, 1H), 7.51 - 7.45 (m, 1H), 7.41 - 7.18 (m, 7H), 6.92 (d, *J* = 16.0 Hz,



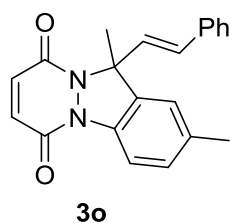
(E)-12-methyl-12-styrylisoindolo[1,2-*b*]quinazolin-10(12*H*)-one

Compound **3m** was isolated as a yellow solid (50.4mg, 72% yield). M.P.: 124-125 °C. ¹H NMR (600 MHz, CDCl₃, ppm) δ 8.33 (dd, *J* = 7.8, 0.6 Hz, 1H), 8.21 (d, *J* = 7.2 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.78 - 7.73 (m, 1H), 7.68 - 7.63 (m, 1H), 7.61 - 7.57 (m, 1H), 7.50 - 7.43 (m, 2H), 7.36 - 7.32 (m, 2H), 7.28 - 7.23 (m, 2H), 7.22 - 7.18 (m, 1H), 6.77 (d, *J* = 16.2 Hz, 1H), 6.54 (d, *J* = 16.2 Hz, 1H), 2.17 (s, 3H). ¹³C NMR (150 MHz, CDCl₃, ppm) δ 160.2, 153.9, 148.4, 135.9, 134.2, 132.7, 131.5, 130.8, 129.2, 128.5, 128.4, 128.1, 127.1, 126.8, 126.7, 126.4, 123.7, 123.0, 121.9, 71.1, 23.2. HRMS (ESI) *m/z* calcd for C₂₄H₁₉N₂O⁺ [M + H⁺]: 351.1492; found: 351.1494.



(E)-11-methyl-11-styryl-11*H*-pyridazino[1,2-*a*]indazole-6,9-dione

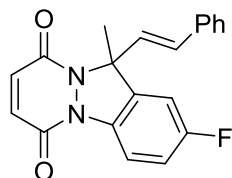
Compound **3n** was isolated as a yellow solid (39.2mg, 62% yield). M.P.: 112-113 °C. ¹H NMR (600 MHz, CDCl₃, ppm) δ 8.39 (d, *J* = 7.8 Hz, 1H), 7.48 - 7.44 (m, 1H), 7.37 - 7.32 (m, 3H), 7.30 - 7.26 (m, 3H), 7.25 - 7.21 (m, 1H), 6.95 (d, *J* = 10.2 Hz, 1H), 6.87 (d, *J* = 10.2 Hz, 1H), 6.83 (d, *J* = 15.6 Hz, 1H), 6.44 (d, *J* = 16.2 Hz, 1H), 2.16 (s, 3H). ¹³C NMR (150 MHz, CDCl₃, ppm) δ 154.0, 153.8, 135.6, 135.3, 135.1, 135.1, 132.0, 131.4, 129.5, 128.5, 128.3, 127.8, 126.8, 126.6, 122.8, 115.7, 72.0, 24.1. HRMS (ESI) *m/z* calcd for C₂₀H₁₇N₂O₂⁺ [M + H⁺]: 317.1285; found: 317.1291.



(E)-2,11-dimethyl-11-styryl-11*H*-pyridazino[1,2-*a*]indazole-6,9-dione

Compound **3o** was isolated as a yellow solid (40.4mg, 61% yield). M.P.: 163-164 °C. ¹H NMR (400 MHz, CDCl₃, ppm) δ 8.25 (d, *J* = 8.4 Hz, 1H), 7.41 - 7.34 (m, 2H), 7.32 - 7.18 (m, 4H), 7.07 (s, 1H), 6.97 (d, *J* = 10.4 Hz, 1H), 6.86 (d, *J* = 10.0 Hz, 1H),

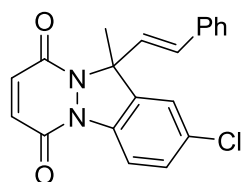
6.79 (d, $J = 16.0$ Hz, 1H), 6.46 (d, $J = 16.0$ Hz, 1H), 2.42 (s, 3H), 2.14 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3 , ppm) δ 154.1, 153.6, 137.0, 135.6, 135.2, 135.1, 133.0, 131.9, 131.6, 130.2, 128.5, 128.3, 127.9, 126.9, 123.2, 115.5, 72.0, 24.0, 21.4. HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{19}\text{N}_2\text{O}_2^+$ [$\text{M} + \text{H}^+$]: 331.1441; found: 331.1433.



3p

(E)-2-fluoro-11-methyl-11-styryl-11H-pyridazino[1,2-a]indazole-6,9-dione

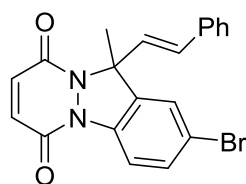
Compound **3p** was isolated as a yellow solid (43.5mg, 65% yield). M.P.: 128-129 °C. ^1H NMR (400 MHz, CDCl_3 , ppm) δ 8.43 - 8.32 (m, 1H), 7.39 - 7.34 (m, 2H), 7.33 - 7.23 (m, 3H), 7.16 (td, $J = 8.8, 2.4$ Hz, 1H), 7.02 - 6.93 (m, 2H), 6.87 (d, $J = 10.4$ Hz, 1H), 6.78 (d, $J = 16.0$ Hz, 1H), 6.46 (d, $J = 16.0$ Hz, 1H), 2.15 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3 , ppm) δ 161.0 (d, $J = 247.7$ Hz), 154.0, 153.6, 135.3, 135.1, 133.6, 133.6, 132.5, 131.3 (d, $J = 2.2$ Hz), 128.6, 128.5, 127.2, 126.9, 117.3 (d, $J = 8.3$ Hz), 116.6 (d, $J = 23.5$ Hz), 110.4 (d, $J = 25.7$ Hz), 71.9 (d, $J = 2.5$ Hz), 24.0. ^{19}F NMR (376 MHz, CDCl_3 , ppm) δ -113.12. HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{16}\text{FN}_2\text{O}_2^+$ [$\text{M} + \text{H}^+$]: 335.1190; found: 335.1195.



3q

(E)-2-chloro-11-methyl-11-styryl-11H-pyridazino[1,2-a]indazole-6,9-dione

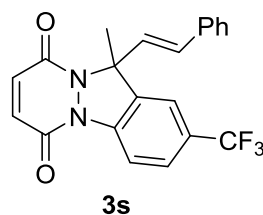
Compound **3q** was isolated as a yellow solid (44.2mg, 63% yield). M.P.: 153-154 °C. ^1H NMR (400 MHz, CDCl_3 , ppm) δ 8.32 (d, $J = 8.4$ Hz, 1H), 7.42 (dd, $J = 8.8, 2.0$ Hz, 1H), 7.40 - 7.35 (m, 2H), 7.34 - 7.21 (m, 4H), 6.95 (d, $J = 10.4$ Hz, 1H), 6.88 (d, $J = 10.4$ Hz, 1H), 6.76 (d, $J = 16.4$ Hz, 1H), 6.46 (d, $J = 16.0$ Hz, 1H), 2.15 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3 , ppm) δ 153.9, 153.7, 135.6, 135.3, 135.0, 133.6, 133.3, 132.5, 132.1, 129.8, 128.6, 128.5, 127.2, 126.9, 123.1, 116.8, 71.8, 24.0. HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{16}\text{ClN}_2\text{O}_2^+$ [$\text{M} + \text{H}^+$]: 351.0895; found: 351.0887



3r

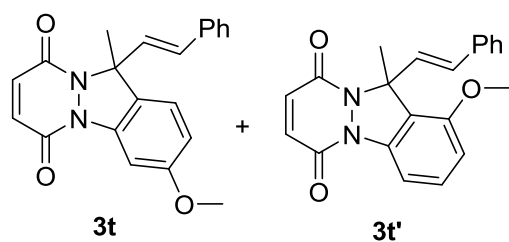
(E)-2-bromo-11-methyl-11-styryl-11H-pyridazino[1,2-a]indazole-6,9-dione

Compound **3r** was isolated as a yellow solid (46.6mg, 59% yield). M.P.: 191-192 °C. ¹H NMR (400 MHz, CDCl₃, ppm) δ 8.27 (d, *J* = 8.8 Hz, 1H), 7.58 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.43 - 7.36 (m, 3H), 7.34 - 7.22 (m, 3H), 6.97 (d, *J* = 10.0 Hz, 1H), 6.90 (d, *J* = 10.4 Hz, 1H), 6.76 (d, *J* = 16.4 Hz, 1H), 6.47 (d, *J* = 16.4 Hz, 1H), 2.15 (s, 3H). ¹³C NMR (100 MHz, CDCl₃, ppm) δ 153.9, 153.8, 135.7, 135.3, 135.0, 134.1, 133.6, 132.7, 132.5, 128.6, 128.5, 127.2, 126.9, 126.0, 119.6, 117.2, 71.7, 24.0. HRMS (ESI) *m/z* calcd for C₂₀H₁₆BrN₂O₂⁺ [M + H⁺]: 395.0390; found: 395.0385.



(E)-11-methyl-11-styryl-2-(trifluoromethyl)-11H-pyridazino[1,2-a]indazole-6,9-dione

Compound **3s** was isolated as a yellow solid (45.3mg, 59% yield). M.P.: 177-178 °C. ¹H NMR (400 MHz, CDCl₃, ppm) δ 8.48 (d, *J* = 8.4 Hz, 1H), 7.77 - 7.70 (m, 1H), 7.52 (s, 1H), 7.39 - 7.34 (m, 2H), 7.33 - 7.23 (m, 3H), 6.96 (d, *J* = 10.4 Hz, 1H), 6.90 (d, *J* = 10.4 Hz, 1H), 6.77 (d, *J* = 16.0 Hz, 1H), 6.45 (d, *J* = 16.4 Hz, 1H), 2.18 (s, 3H). ¹³C NMR (100 MHz, CDCl₃, ppm) δ 154.2, 153.9, 137.5, 136.1, 135.2, 134.8, 132.6, 132.3, 129.0, 128.6, 127.3 (q, *J* = 3.7 Hz), 127.0, 127.0, 124.9, 122.2, 120.1 (q, *J* = 3.7 Hz), 115.9, 72.0, 24.1. ¹⁹F NMR (376 MHz, CDCl₃, ppm) δ -61.94. HRMS (ESI) *m/z* calcd for C₂₁H₁₆F₃N₂O₂⁺ [M + H⁺]: 385.1158; found: 385.1160.



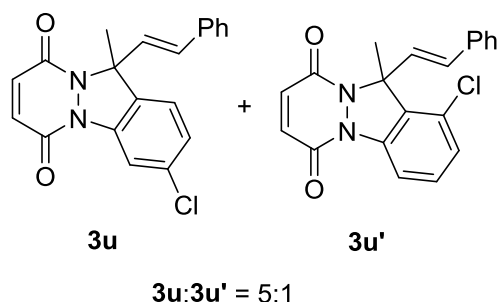
3t:3t' = 9:1

(E)-3-methoxy-11-methyl-11-styryl-11H-pyridazino[1,2-a]indazole-6,9-dione(3t)
and

(E)-1-methoxy-11-methyl-11-styryl-11H-pyridazino[1,2-a]indazole-6,9-dione(3t')

Compound **3t** and **3t'** were isolated as a yellow solid (38.2mg, 55% yield, **3t:3t'** = 9:1). ¹H NMR (400 MHz, CDCl₃, ppm) δ 8.07 - 7.97 (m, 1H), 7.39 - 7.33 (m, 2H), 7.32 - 7.20 (m, 3H), 7.16 (d, *J* = 8.4 Hz, 1H), 6.96 (d, *J* = 10.0 Hz, 1H), 6.92-6.75 (m, 3H), 6.50-6.30 (m, 1H), 3.90 (s, 2.7H), 3.86 (s, 0.3H), 2.24 (s, 0.3H), 2.12 (s, 2.7H). ¹³C NMR (100 MHz, CDCl₃, ppm) δ 160.7, 154.6, 154.0, 154.0, 153.9, 136.3, 136.1, 135.6, 135.5, 135.4, 135.0, 131.9, 131.3, 131.0, 128.5, 128.4, 128.3, 128.1, 128.0,

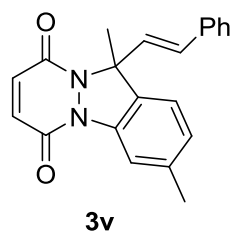
126.9, 126.8, 126.2, 123.4, 123.1, 113.7, 109.5, 108.4, 100.9, 72.7, 71.9, 55.9, 55.7, 24.3, 21.1. **HRMS (ESI)** m/z calcd for C₂₁H₁₉N₂O₃⁺ [M + H⁺]: 347.1390; found: 347.1392.



(E)-3-chloro-11-methyl-11-styryl-11H-pyridazino[1,2-a]indazole-6,9-dione(3u)
and

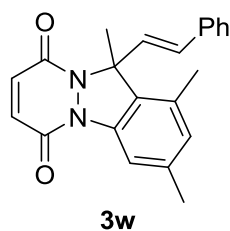
(E)-1-chloro-11-methyl-11-styryl-11H-pyridazino[1,2-a]indazole-6,9-dione(3u')

Compound **3u** and **3u'** were isolated as a yellow solid (40.6mg, 58% yield, **3u:3u'** = 5:1). ¹H NMR (400 MHz, CDCl₃, ppm) δ 8.47 - 8.34 (m, 1H), 7.39 - 7.22 (m, 6H), 7.20 (d, *J* = 8.0 Hz, 1H), 6.97 - 6.91 (m, 1H), 6.88 (d, *J* = 10.4 Hz, 1H), 6.85 - 6.72 (m, 1H), 6.48 - 6.36 (m, 1H), 2.30 (s, 0.5H), 2.13 (s, 2.5H). ¹³C NMR (100 MHz, CDCl₃, ppm) δ 153.9, 153.9, 153.4, 136.6, 135.8, 135.7, 135.5, 135.4, 135.2, 134.8, 133.2, 132.4, 130.9, 129.7, 129.4, 128.6, 128.5, 128.5, 128.4, 128.4, 128.3, 128.2, 128.2, 128.1, 127.2, 126.9, 124.9, 123.8, 116.0, 114.2, 72.9, 72.0, 24.1, 20.7. **HRMS (ESI)** m/z calcd for C₂₀H₁₆ClN₂O₂⁺ [M + H⁺]: 351.0895; found: 351.0896.



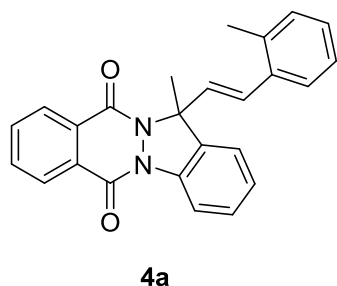
(E)-3,11-dimethyl-11-styryl-11H-pyridazino[1,2-a]indazole-6,9-dione

Compound **3v** was isolated as a yellow solid (44.9mg, 68% yield). M.P.: 184-185 °C. ¹H NMR (400 MHz, CDCl₃, ppm) δ 8.23 (s, 1H), 7.38 - 7.32 (m, 2H), 7.32 - 7.20 (m, 3H), 7.16 (d, *J* = 0.8 Hz, 2H), 6.95 (d, *J* = 10.0 Hz, 1H), 6.89 - 6.79 (m, 2H), 6.42 (d, *J* = 16.0 Hz, 1H), 2.46 (s, 3H), 2.13 (s, 3H). ¹³C NMR (100 MHz, CDCl₃, ppm) δ 154.1, 153.8, 140.0, 135.6, 135.3, 135.3, 135.1, 131.9, 128.6, 128.5, 128.3, 127.9, 127.5, 126.9, 122.5, 116.2, 72.0, 24.2, 21.6. **HRMS (ESI)** m/z calcd for C₂₁H₁₉N₂O₂⁺ [M + H⁺]: 331.1441; found: 331.1444.



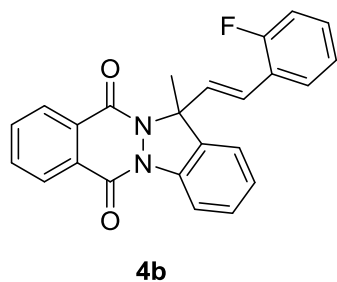
(E)-1,3,11-trimethyl-11-styryl-11H-pyridazino[1,2-a]indazole-6,9-dione

Compound **3w** was isolated as a yellow solid (35.9mg, 52% yield). M.P.: 190-191 °C. ¹H NMR (400 MHz, CDCl₃, ppm) δ 8.17 (s, 1H), 7.41 - 7.34 (m, 2H), 7.32 - 7.19 (m, 3H), 6.97 - 6.90 (m, 2H), 6.86 - 6.76 (m, 2H), 6.43 (d, *J* = 16.0 Hz, 1H), 2.42 (s, 3H), 2.30 (s, 3H), 2.18 (s, 3H). ¹³C NMR (100 MHz, CDCl₃, ppm) δ 153.7, 153.6, 139.8, 135.7, 135.7, 135.2, 135.1, 133.0, 130.3, 128.5, 128.3, 126.9, 126.5, 126.2, 113.9, 72.1, 21.4, 21.3, 18.3. HRMS (ESI) *m/z* calcd for C₂₂H₂₁N₂O₂⁺ [M + H⁺]: 345.1598; found: 345.1612.



(E)-13-methyl-13-(2-methylstyryl)-13H-indazolo[1,2-b]phthalazine-6,11-dione

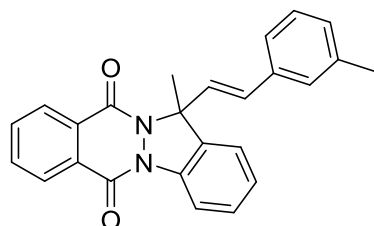
Compound **4a** was isolated as a yellow solid (68.5mg, 90% yield). M.P.: 146-147 °C. ¹H NMR (600 MHz, CDCl₃, ppm) δ 8.51 (d, *J* = 7.8 Hz, 1H), 8.46 - 8.40 (m, 1H), 8.39 - 8.33 (m, 1H), 7.86 - 7.80 (m, 2H), 7.51 - 7.46 (m, 1H), 7.45 - 7.42 (m, 1H), 7.36 - 7.29 (m, 2H), 7.16 - 7.07 (m, 3H), 6.78 (d, *J* = 16.2 Hz, 1H), 6.74 (d, *J* = 16.2 Hz, 1H), 2.24 (s, 6H). ¹³C NMR (150 MHz, CDCl₃, ppm) δ 154.8, 154.8, 135.8, 135.6, 135.0, 133.5, 133.2, 131.8, 130.4, 130.2, 129.6, 129.5, 129.5, 129.5, 128.0, 127.4, 127.3, 126.2, 126.1, 126.0, 122.8, 116.1, 71.7, 24.8, 19.6. HRMS (ESI) *m/z* calcd for C₂₅H₂₀NaN₂O₂⁺ [M + Na⁺]: 403.1417; found: 403.1417.



(E)-13-(2-fluorostyryl)-13-methyl-13H-indazolo[1,2-b]phthalazine-6,11-dione

Compound **4b** was isolated as a yellow solid (57.4mg, 75% yield). M.P.: 110-111 °C.

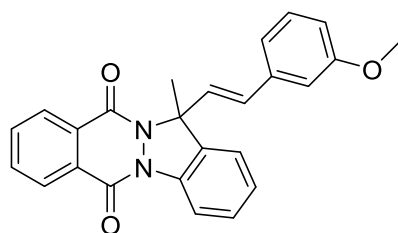
^1H NMR (400 MHz, CDCl_3 , ppm) δ 8.50 (d, $J = 8.0$ Hz, 1H), 8.46 - 8.40 (m, 1H), 8.39 - 8.32 (m, 1H), 7.86 - 7.79 (m, 2H), 7.52 - 7.43 (m, 2H), 7.37 - 7.28 (m, 2H), 7.23 - 7.16 (m, 1H), 7.08 - 6.93 (m, 3H), 6.72 (d, $J = 16.4$ Hz, 1H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3 , ppm) δ 160.3 (d, $J = 250.0$ Hz), 154.8, 154.8, 135.5, 133.3 (d, $J = 20.6$ Hz), 131.5, 131.4 (d, $J = 4.7$ Hz), 129.6, 129.5, 129.5, 129.4, 129.3, 127.6 (d, $J = 3.4$ Hz), 127.4 (d, $J = 6.1$ Hz), 126.3, 124.0 (d, $J = 3.5$ Hz), 123.8 (d, $J = 3.9$ Hz), 123.7 (d, $J = 12.0$ Hz), 122.8, 116.1, 115.8, 115.5, 71.6, 24.5. ^{19}F NMR (376 MHz, CDCl_3 , ppm) δ -117.42. HRMS (ESI) m/z calcd for $\text{C}_{24}\text{H}_{18}\text{FN}_2\text{O}_2^+$ [$\text{M} + \text{H}^+$]: 385.1347; found: 385.1349.



4c

(E)-13-methyl-13-(3-methylstyryl)-13H-indazolo[1,2-b]phthalazine-6,11-dione

Compound **4c** was isolated as a yellow solid (63.1mg, 83% yield). M.P.: 66-67 °C. ^1H NMR (400 MHz, CDCl_3 , ppm) δ 8.50 (d, $J = 8.0$ Hz, 1H), 8.46 - 8.38 (m, 1H), 8.38 - 8.29 (m, 1H), 7.87 - 7.75 (m, 2H), 7.51 - 7.43 (m, 1H), 7.37 - 7.27 (m, 2H), 7.20 (s, 1H), 7.19 - 7.11 (m, 2H), 7.06 - 7.00 (m, 1H), 6.92 (d, $J = 16.4$ Hz, 1H), 6.46 (d, $J = 16.4$ Hz, 1H), 2.29 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3 , ppm) δ 154.8, 154.8, 138.1, 135.6, 135.5, 133.4, 133.2, 131.7, 131.7, 129.5, 129.5, 129.4, 128.9, 128.7, 128.4, 127.4, 127.4, 127.3, 126.2, 124.1, 122.9, 116.0, 71.6, 24.8, 21.2. HRMS (ESI) m/z calcd for $\text{C}_{25}\text{H}_{21}\text{N}_2\text{O}_2^+$ [$\text{M} + \text{H}^+$]: 381.1598; found: 381.1616.

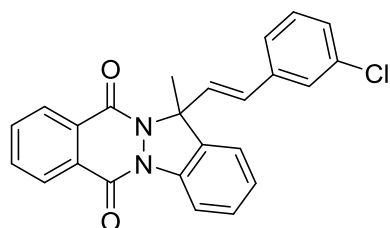


4d

(E)-13-(3-methoxystyryl)-13-methyl-13H-indazolo[1,2-b]phthalazine-6,11-dione

Compound **4d** was isolated as a yellow solid (52.3mg, 66% yield). M.P.: 70-71 °C. ^1H NMR (600 MHz, CDCl_3 , ppm) δ 8.50 (d, $J = 8.4$ Hz, 1H), 8.45 - 8.39 (m, 1H), 8.38 - 8.31 (m, 1H), 7.87 - 7.78 (m, 2H), 7.51 - 7.45 (m, 1H), 7.36 - 7.28 (m, 2H), 7.18 (t, $J = 7.8$ Hz, 1H), 6.96 (d, $J = 7.8$ Hz, 1H), 6.93 - 6.86 (m, 2H), 6.78 (dd, $J = 8.4, 2.4$ Hz, 1H), 6.47 (d, $J = 16.2$ Hz, 1H), 3.77 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (150 MHz, CDCl_3 , ppm) δ 159.7, 154.8, 154.8, 137.2, 135.5, 133.4, 133.2, 131.7, 131.6, 129.6, 129.5, 129.5, 129.4, 129.3, 127.4, 127.4, 126.2, 122.9, 119.6, 116.1, 114.2,

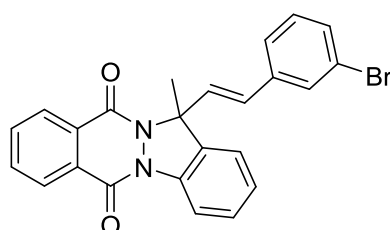
111.9, 71.5, 55.2, 24.7. **HRMS (ESI)** m/z calcd for $C_{25}H_{21}N_2O_3^+$ [$M + H^+$]: 397.1547; found: 397.1555.



4e

(E)-13-(3-chlorostyryl)-13-methyl-13H-indazolo[1,2-*b*]phthalazine-6,11-dione

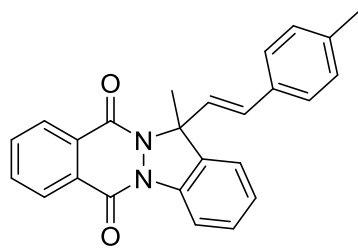
Compound **4e** was isolated as a yellow solid (61.7mg, 77% yield). M.P.: 94-95 °C. 1H NMR (400 MHz, $CDCl_3$, ppm) δ 8.50 (d, $J = 8.0$ Hz, 1H), 8.45 - 8.38 (m, 1H), 8.37 - 8.29 (m, 1H), 7.87 - 7.77 (m, 2H), 7.53 - 7.44 (m, 1H), 7.39 - 7.27 (m, 3H), 7.24 - 7.16 (m, 3H), 6.92 (d, $J = 16.4$ Hz, 1H), 6.45 (d, $J = 16.0$ Hz, 1H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 154.8, 154.7, 137.6, 135.5, 134.5, 133.5, 133.3, 131.3, 130.5, 130.2, 129.7, 129.6, 129.5, 129.3, 128.1, 127.4, 127.3, 126.7, 126.3, 125.1, 122.8, 116.1, 71.3, 24.6. **HRMS (ESI)** m/z calcd for $C_{24}H_{18}ClN_2O_2^+$ [$M + H^+$]: 401.1051; found: 401.1054.



4f

(E)-13-(3-bromostyryl)-13-methyl-13H-indazolo[1,2-*b*]phthalazine-6,11-dione

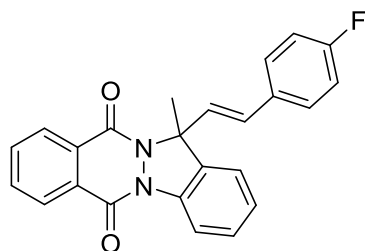
Compound **4f** was isolated as a yellow solid (57.0mg, 64% yield). M.P.: 163-164 °C. 1H NMR (600 MHz, $CDCl_3$, ppm) δ 8.50 (d, $J = 8.4$ Hz, 1H), 8.44 - 8.40 (m, 1H), 8.36 - 8.32 (m, 1H), 7.86 - 7.79 (m, 2H), 7.55 - 7.51 (m, 1H), 7.50 - 7.46 (m, 1H), 7.35 - 7.31 (m, 2H), 7.30 - 7.26 (m, 2H), 7.13 (t, $J = 7.8$ Hz, 1H), 6.91 (d, $J = 16.2$ Hz, 1H), 6.44 (d, $J = 15.6$ Hz, 1H), 2.23 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$, ppm) δ 154.8, 154.8, 137.9, 135.5, 133.5, 133.3, 131.4, 131.0, 130.6, 130.1, 130.0, 129.6, 129.6, 129.5, 129.3, 127.4, 127.4, 126.3, 125.6, 122.8, 122.7, 116.1, 71.3, 24.6. **HRMS (ESI)** m/z calcd for $C_{24}H_{18}BrN_2O_2^+$ [$M + H^+$]: 445.0546; found: 445.0556.



4g

(E)-13-methyl-13-(4-methylstyryl)-13H-indazolo[1,2-*b*]phthalazine-6,11-dione

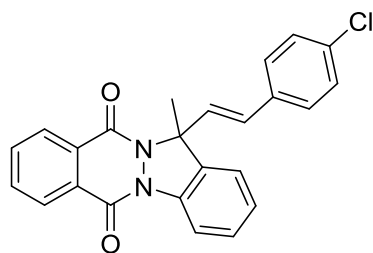
Compound **4g** was isolated as a yellow solid (60.9mg, 80% yield). M.P.: 126-127 °C. ¹H NMR (600 MHz, CDCl₃, ppm) δ 8.50 (d, *J* = 8.4 Hz, 1H), 8.44 - 8.38 (m, 1H), 8.37 - 8.31 (m, 1H), 7.84 - 7.78 (m, 2H), 7.50 - 7.44 (m, 1H), 7.34 - 7.27 (m, 2H), 7.27 - 7.23 (m, 2H), 7.07 (d, *J* = 7.8 Hz, 2H), 6.87 (d, *J* = 16.2 Hz, 1H), 6.45 (d, *J* = 16.2 Hz, 1H), 2.29 (s, 3H), 2.23 (s, 3H). ¹³C NMR (150 MHz, CDCl₃, ppm) δ 154.8, 138.1, 135.5, 133.4, 133.1, 133.0, 131.8, 131.5, 129.5, 129.5, 129.4, 129.2, 127.9, 127.4, 127.3, 126.8, 126.2, 122.9, 116.0, 71.7, 24.8, 21.1. HRMS (ESI) *m/z* calcd for C₂₅H₂₁N₂O₂⁺ [M + H⁺]: 381.1598; found: 381.1603.



4h

(E)-13-(4-fluorostyryl)-13-methyl-13H-indazolo[1,2-*b*]phthalazine-6,11-dione

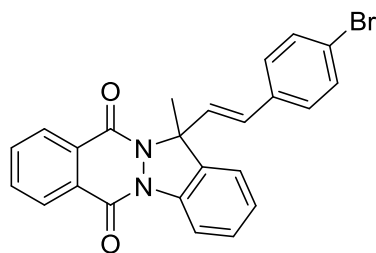
Compound **4h** was isolated as a yellow solid (56.9mg, 74% yield). M.P.: 118-119 °C. ¹H NMR (600 MHz, CDCl₃, ppm) δ 8.50 (d, *J* = 8.4 Hz, 1H), 8.44 - 8.39 (m, 1H), 8.37 - 8.31 (m, 1H), 7.85 - 7.79 (m, 2H), 7.50 - 7.45 (m, 1H), 7.36 - 7.31 (m, 3H), 7.31 - 7.27 (m, 1H), 6.98 - 6.92 (m, 2H), 6.84 (d, *J* = 16.2 Hz, 1H), 6.46 (d, *J* = 16.2 Hz, 1H), 2.23 (s, 3H). ¹³C NMR (150 MHz, CDCl₃, ppm) δ 162.6 (d, *J* = 247.8 Hz), 154.8, 154.8, 135.5, 133.5, 133.2, 132.0 (d, *J* = 3.3 Hz), 131.6, 130.4, 129.5, 129.4, 128.8 (d, *J* = 2.5 Hz), 128.5 (d, *J* = 8.2 Hz), 127.4, 127.3, 126.2, 122.8, 116.1, 115.5, 115.4, 71.5, 24.7. ¹⁹F NMR (376 MHz, CDCl₃, ppm) δ -113.35. HRMS (ESI) *m/z* calcd for C₂₄H₁₈FN₂O₂⁺ [M + H⁺]: 385.1347; found: 385.1357.



4i

(E)-13-(4-chlorostyryl)-13-methyl-13H-indazolo[1,2-*b*]phthalazine-6,11-dione

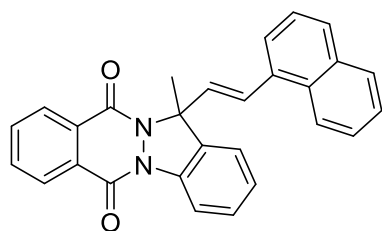
Compound **4i** was isolated as a yellow solid (55.3mg, 69% yield). M.P.: 131-132 °C. ¹H NMR (600 MHz, CDCl₃, ppm) δ 8.50 (d, *J* = 7.8 Hz, 1H), 8.45 - 8.39 (m, 1H), 8.37 - 8.31 (m, 1H), 7.86 - 7.79 (m, 2H), 7.51 - 7.46 (m, 1H), 7.35 - 7.31 (m, 1H), 7.31 - 7.27 (d, *J* = 8.4 Hz, 3H), 7.25 - 7.21 (m, 2H), 6.89 (d, *J* = 16.2 Hz, 1H), 6.45 (d, *J* = 16.2 Hz, 1H), 2.23 (s, 3H). ¹³C NMR (150 MHz, CDCl₃, ppm) δ 154.8, 154.8, 135.5, 134.3, 133.8, 133.5, 133.3, 131.5, 130.4, 129.7, 129.6, 129.5, 129.4, 128.7, 128.1, 127.4, 127.4, 126.2, 122.8, 116.1, 71.4, 24.7. HRMS (ESI) *m/z* calcd for C₂₄H₁₈ClN₂O₂⁺ [M + H⁺]: 401.1051; found: 401.1068.



4j

(E)-13-(4-bromostyryl)-13-methyl-13H-indazolo[1,2-*b*]phthalazine-6,11-dione

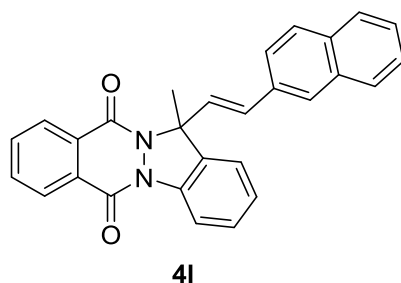
Compound **4j** was isolated as a yellow solid (54.4mg, 61% yield). M.P.: 164-165 °C. ¹H NMR (600 MHz, CDCl₃, ppm) δ 8.50 (d, *J* = 8.4 Hz, 1H), 8.45 - 8.39 (m, 1H), 8.37 - 8.30 (m, 1H), 7.88 - 7.80 (m, 2H), 7.51 - 7.46 (m, 1H), 7.42 - 7.37 (m, 2H), 7.33 (td, *J* = 7.8, 1.2 Hz, 1H), 7.31 - 7.27 (m, 1H), 7.25 - 7.20 (m, 2H), 6.91 (d, *J* = 16.2 Hz, 1H), 6.44 (d, *J* = 16.2 Hz, 1H), 2.23 (s, 3H). ¹³C NMR (150 MHz, CDCl₃, ppm) δ 154.8, 154.8, 135.6, 134.8, 133.5, 133.3, 131.6, 131.4, 130.4, 129.8, 129.6, 129.6, 129.4, 128.4, 127.4, 127.4, 126.2, 122.8, 122.0, 116.1, 71.4, 24.7. HRMS (ESI) *m/z* calcd for C₂₄H₁₈BrN₂O₂⁺ [M + H⁺]: 445.0546; found: 445.0563.



4k

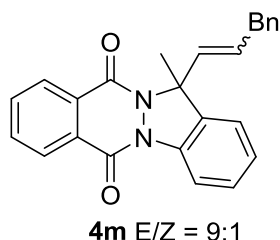
(E)-13-methyl-13-(2-(naphthalen-1-yl)vinyl)-13H-indazolo[1,2-b]phthalazine-6,11-dione

Compound **4k** was isolated as a yellow solid (43.3mg, 52% yield). M.P.: 133-134 °C. ¹H NMR (600 MHz, CDCl₃, ppm) δ 8.53 (d, *J* = 8.4 Hz, 1H), 8.45 - 8.39 (m, 1H), 8.38 - 8.32 (m, 1H), 7.84 - 7.79 (m, 2H), 7.77 - 7.69 (m, 4H), 7.58 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.52 - 7.47 (m, 1H), 7.44 - 7.38 (m, 2H), 7.36 - 7.32 (m, 2H), 7.05 (d, *J* = 15.6 Hz, 1H), 6.65 (d, *J* = 16.2 Hz, 1H), 2.28 (s, 3H). ¹³C NMR (150 MHz, CDCl₃, ppm) δ 154.9, 154.8, 135.6, 133.5, 133.4, 133.3, 133.2, 133.2, 131.8, 131.7, 129.6, 129.6, 129.5, 129.3, 128.2, 128.0, 127.6, 127.4, 127.4, 127.2, 126.2, 126.1, 123.7, 122.9, 116.1, 71.7, 24.9. HRMS (ESI) *m/z* calcd for C₂₈H₂₁N₂O₂⁺ [M + H⁺]: 417.1598; found: 417.1600.



(E)-13-methyl-13-(2-(naphthalen-2-yl)vinyl)-13H-indazolo[1,2-b]phthalazine-6,11-dione

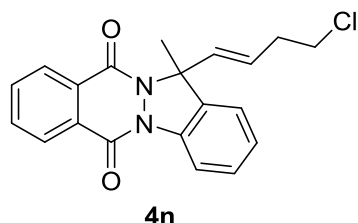
Compound **4l** was isolated as a yellow solid (60.9mg, 73% yield). M.P.: 145-146 °C. ¹H NMR (600 MHz, CDCl₃, ppm) δ 8.55 (d, *J* = 8.4 Hz, 1H), 8.47 - 8.42 (m, 1H), 8.40 - 8.36 (m, 1H), 7.92 (d, *J* = 7.8 Hz, 1H), 7.87 - 7.80 (m, 3H), 7.76 (d, *J* = 7.8 Hz, 1H), 7.61 (d, *J* = 7.2 Hz, 1H), 7.56 - 7.51 (m, 1H), 7.50 - 7.44 (m, 2H), 7.43 - 7.36 (m, 3H), 7.29 (d, *J* = 16.2 Hz, 1H), 6.94 (d, *J* = 15.6 Hz, 1H), 2.32 (s, 3H). ¹³C NMR (150 MHz, CDCl₃, ppm) δ 154.9, 154.9, 135.7, 133.6, 133.5, 133.3, 132.3, 131.8, 131.2, 129.6, 129.6, 129.5, 129.1, 128.5, 128.5, 127.5, 127.4, 126.3, 126.2, 125.8, 125.5, 124.4, 123.5, 122.8, 116.2, 71.8, 24.9. HRMS (ESI) *m/z* calcd for C₂₈H₂₁N₂O₂⁺ [M + H⁺]: 417.1598; found: 417.1593.



13-methyl-13-(3-phenylprop-1-en-1-yl)-13H-indazolo[1,2-b]phthalazine-6,11-dione

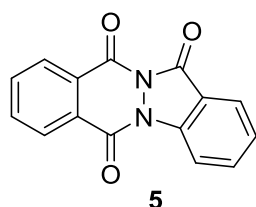
Compound **4m** was isolated as a colorless liquid (63.2mg, 83% yield). ¹H NMR (600 MHz, CDCl₃, ppm) δ 8.37 (d, *J* = 8.4 Hz, 1H), 8.35 - 8.31 (m, 1H), 8.30 - 8.25 (m, 1H), 7.78 - 7.68 (m, 2H), 7.38 - 7.31 (m, 1H), 7.26 - 7.14 (m, 3H), 7.12 (d, *J* = 7.8 Hz,

1H), 7.09 (t, $J = 7.8$ Hz, 1H), 7.07 - 6.98 (m, 2H), 6.28 (d, $J = 18.0$ Hz, 0.1H), 6.19 (d, $J = 15.6$ Hz, 0.9H), 5.78 - 5.57 (m, 1H), 3.44 - 3.22 (m, 2H), 2.04 (s, 2.7H), 2.02 (s, 0.3H). ^{13}C NMR (150 MHz, CDCl_3 , ppm) δ 155.3, 154.7, 154.6, 139.5, 136.8, 135.5, 135.4, 135.0, 133.4, 133.4, 133.1, 132.1, 132.1, 131.4, 131.4, 129.6, 129.5, 129.4, 129.3, 129.3, 128.5, 128.4, 128.3, 127.4, 127.3, 127.3, 127.3, 127.2, 126.2, 126.2, 126.1, 126.0, 122.7, 122.6, 121.3, 116.0, 115.9, 72.3, 71.4, 41.1, 38.4, 25.2, 24.6. **HRMS (ESI)** m/z calcd for $\text{C}_{25}\text{H}_{21}\text{N}_2\text{O}_2^+$ [$\text{M} + \text{H}^+$]: 381.1598; found: 381.1598.



(E)-13-(4-chlorobut-1-en-1-yl)-13-methyl-13H-indazolo[1,2-*b*]phthalazine-6,11-dione

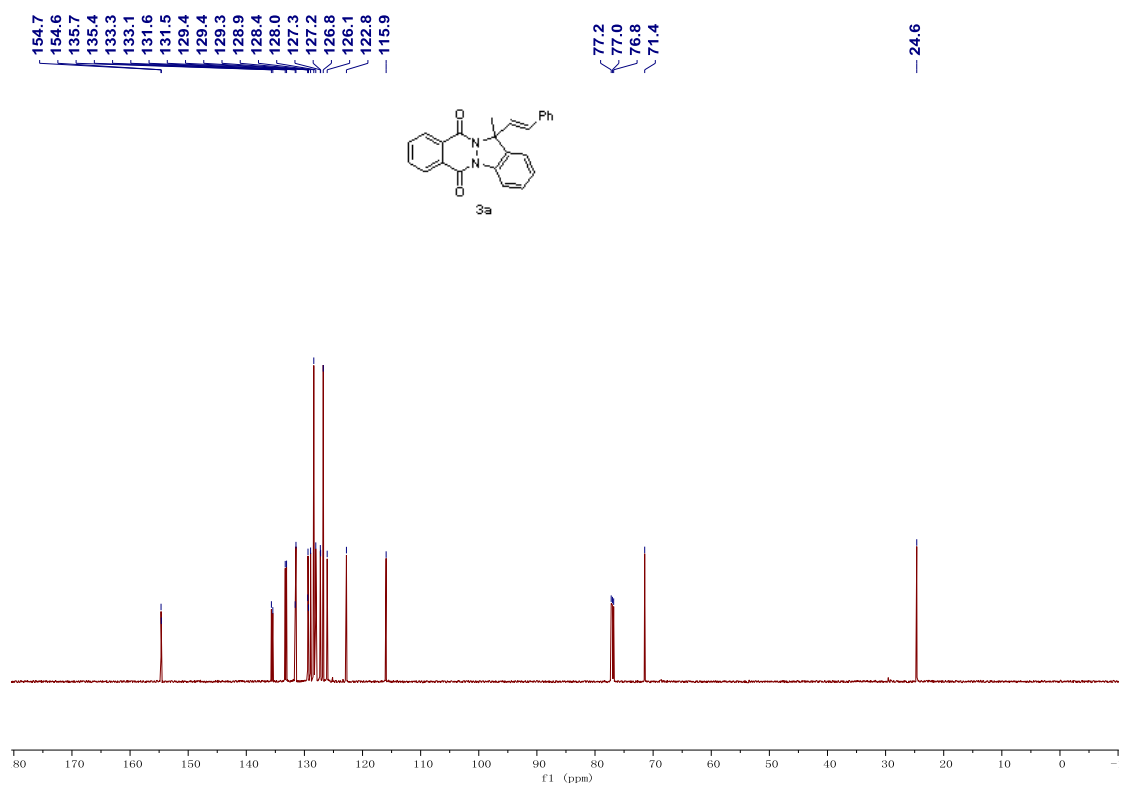
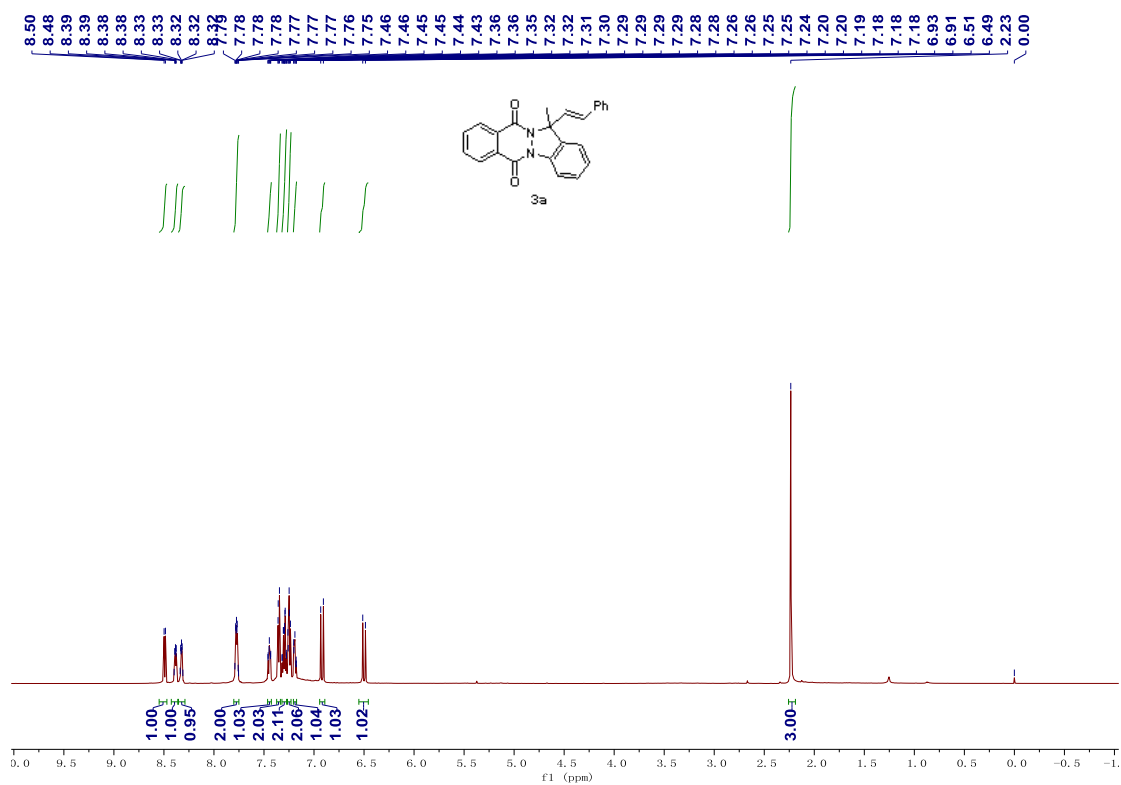
Compound **4n** was isolated as a colorless liquid (32.5mg, 46% yield). ^1H NMR (400 MHz, CDCl_3 , ppm) δ 8.38 (d, $J = 8.1$ Hz, 1H), 8.36 - 8.31 (m, 1H), 8.30 - 8.22 (m, 1H), 7.83 - 7.74 (m, 2H), 7.37 (t, $J = 7.6$ Hz, 1H), 7.24 (t, $J = 7.5$ Hz, 1H), 7.17 (t, $J = 8.0$ Hz, 1H), 6.21 (d, $J = 15.7$ Hz, 1H), 5.68 - 5.52 (m, 1H), 3.55 - 3.39 (m, 2H), 2.60 - 2.37 (m, 2H), 2.04 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3 , ppm) δ 154.7, 154.7, 135.3, 133.4, 133.2, 133.0, 131.7, 129.5, 129.4, 129.4, 128.4, 127.4, 127.2, 126.2, 122.7, 115.9, 71.2, 43.6, 35.1, 24.5. **HRMS (ESI)** m/z calcd for $\text{C}_{20}\text{H}_{18}\text{ClN}_2\text{O}_2^+$ [$\text{M} + \text{H}^+$]: 353.1051; found: 353.1059.

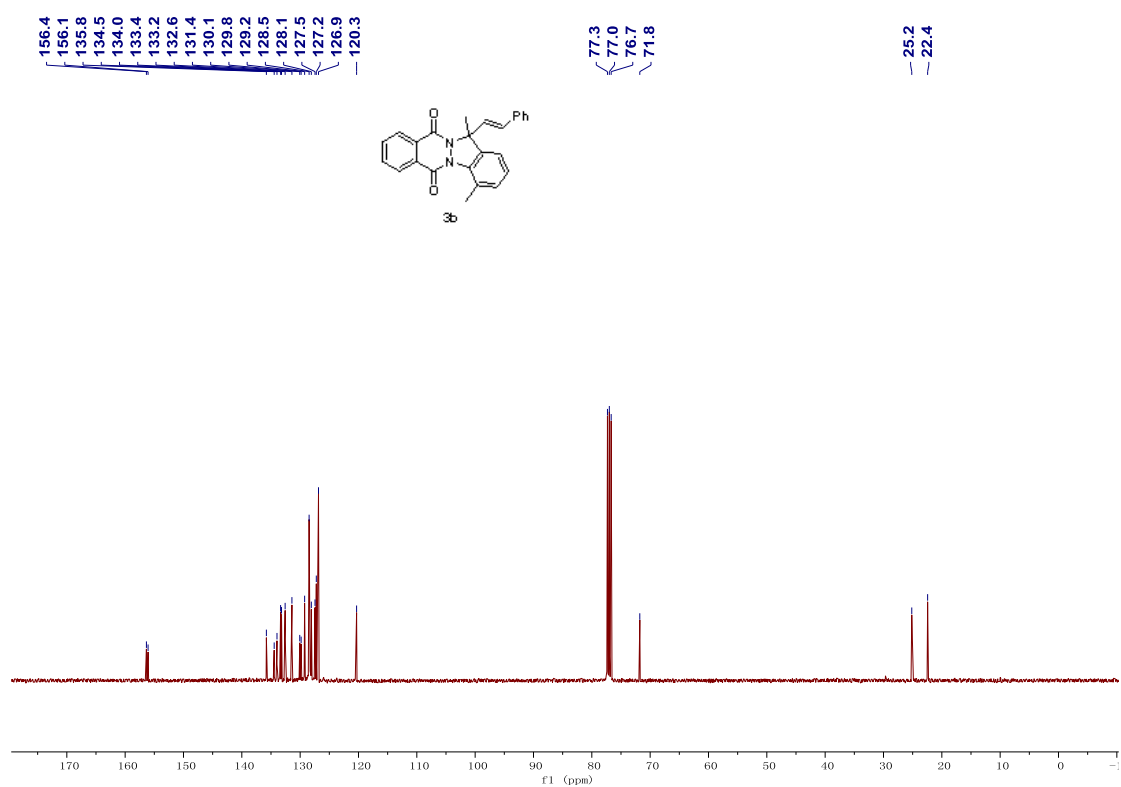
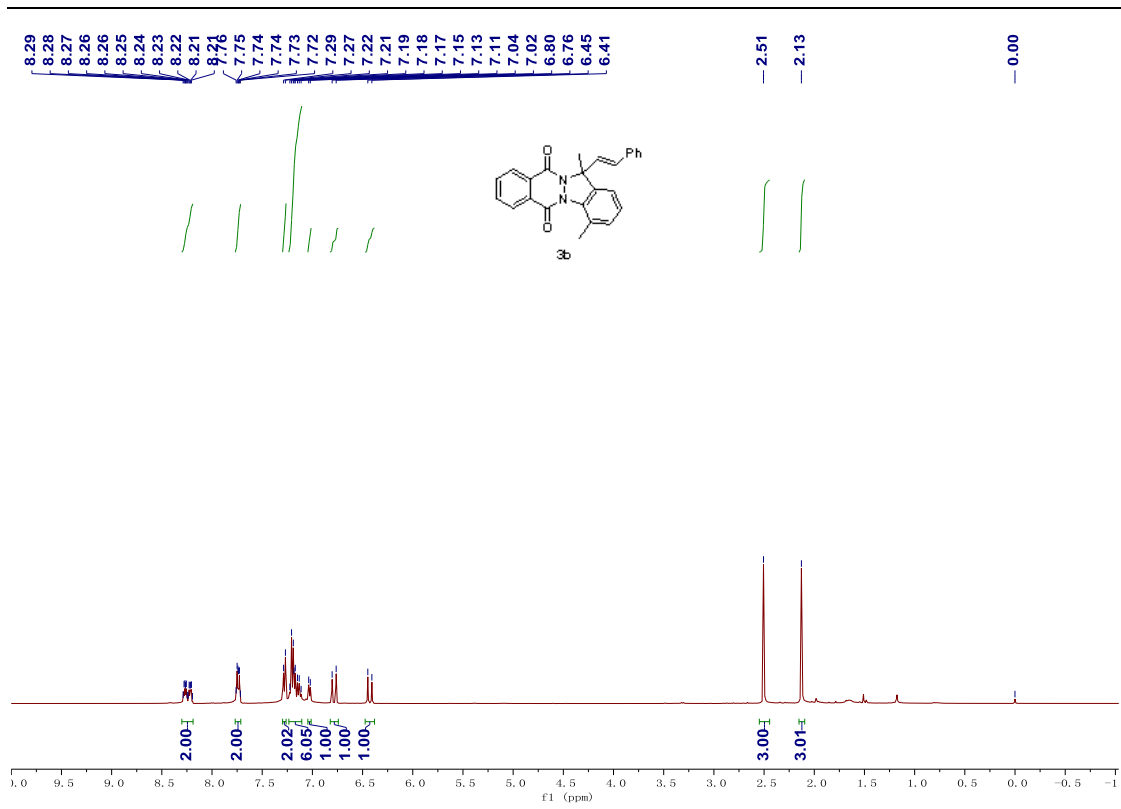


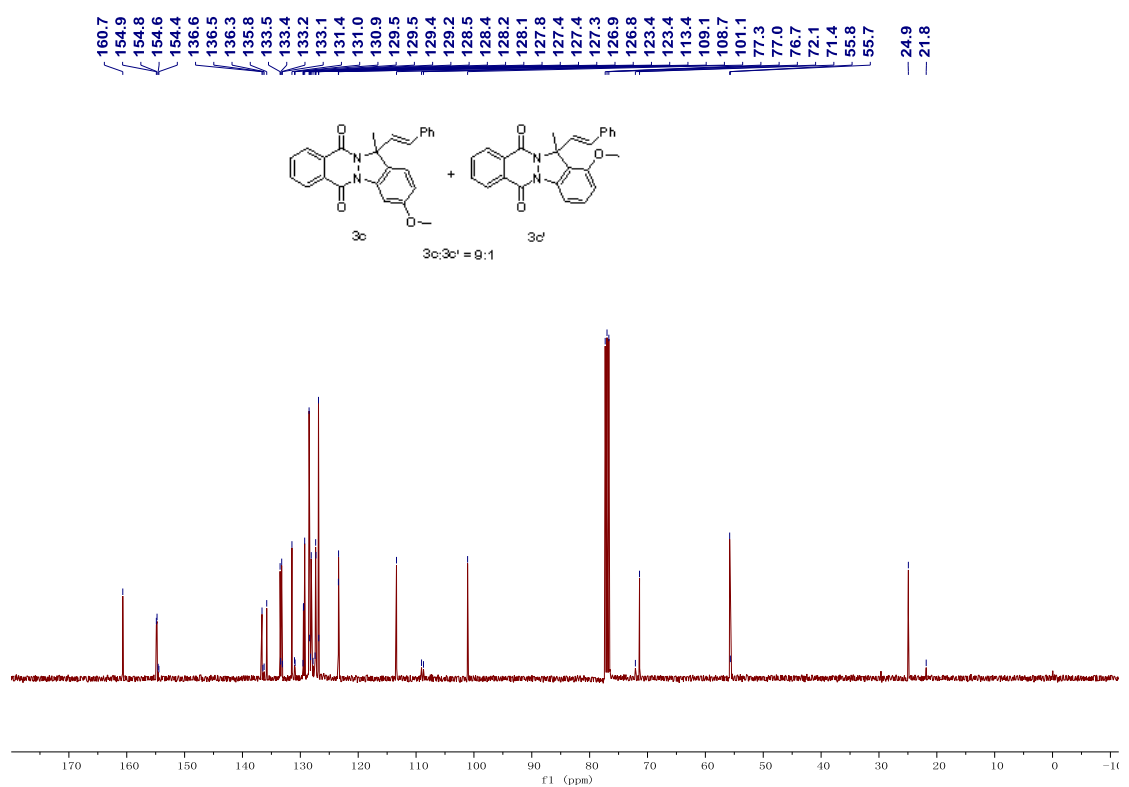
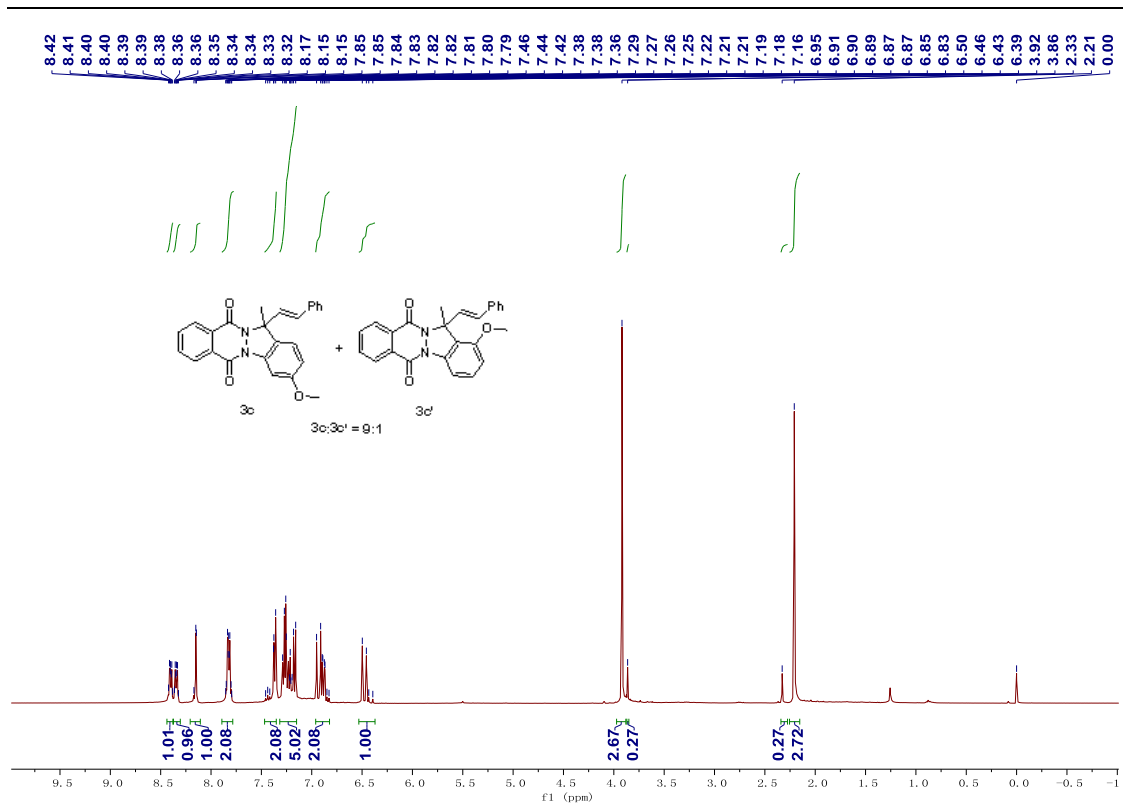
13H-indazolo[1,2-*b*]phthalazine-6,11,13-trione

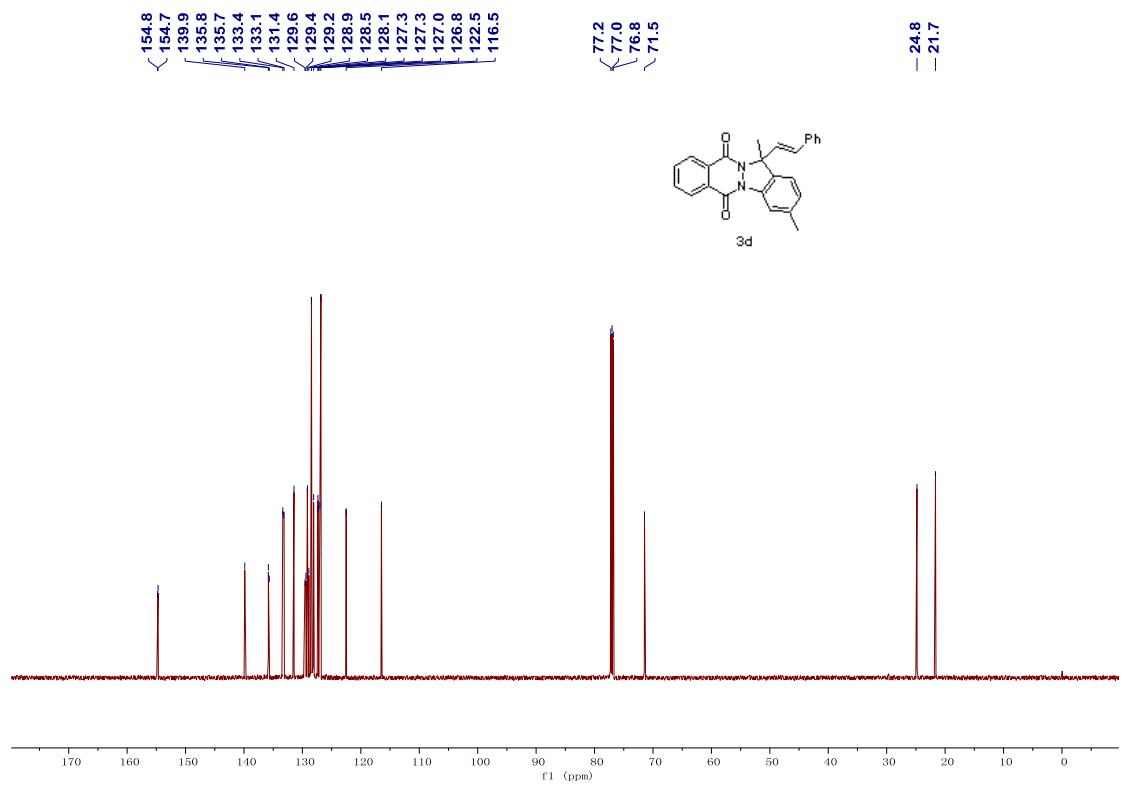
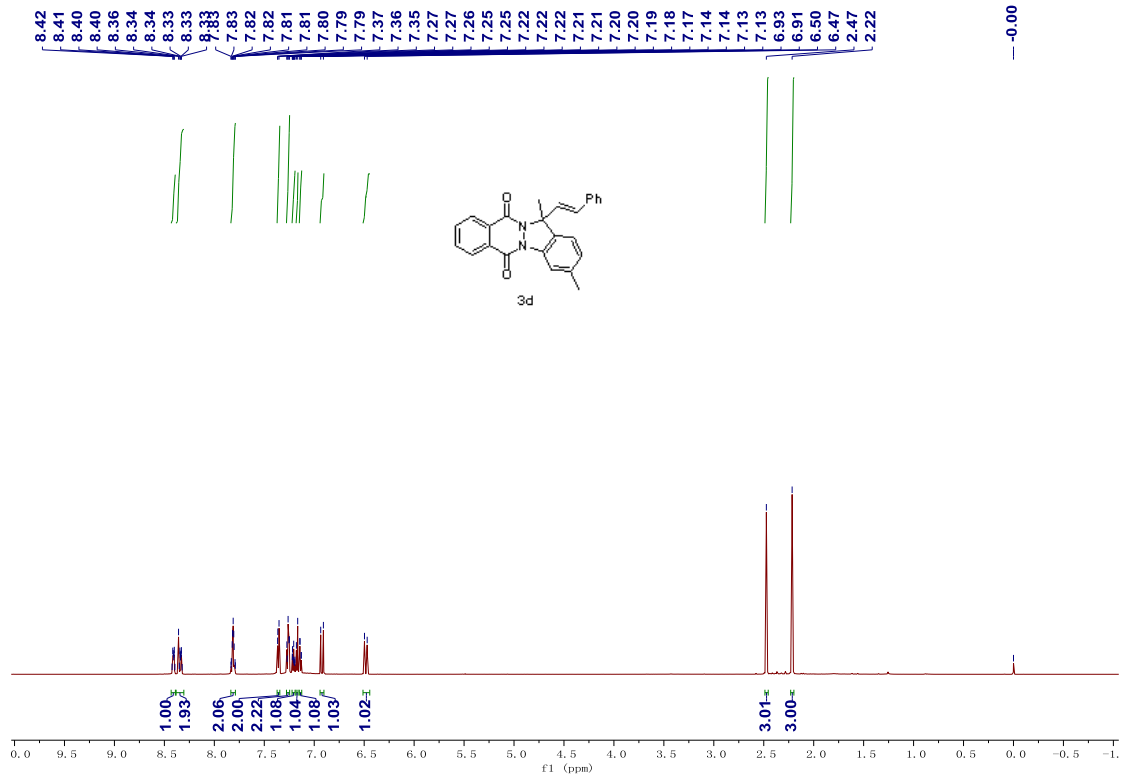
Compound **5** was isolated as a yellow solid (34.9mg, 44% yield). M.P.: 209-210 °C. ^1H NMR (400 MHz, CDCl_3 , ppm) δ 8.51 (d, $J = 8.3$ Hz, 1H), 8.46 - 8.40 (m, 1H), 8.39 - 8.31 (m, 1H), 8.00 (d, $J = 7.8$ Hz, 1H), 7.91 - 7.82 (m, 4H), 7.82 - 7.73 (m, 1H), 7.42 (t, $J = 7.5$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3 , ppm) δ 158.1, 154.8, 153.9, 139.1, 136.6, 135.2, 134.7, 129.2, 128.9, 128.8, 128.3, 126.4, 125.4, 116.5, 116.2. **HRMS (ESI)** m/z calcd for $\text{C}_{15}\text{H}_9\text{N}_2\text{O}_3^+$ [$\text{M} + \text{H}^+$]: 265.0608; found: 265.0611.

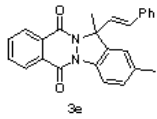
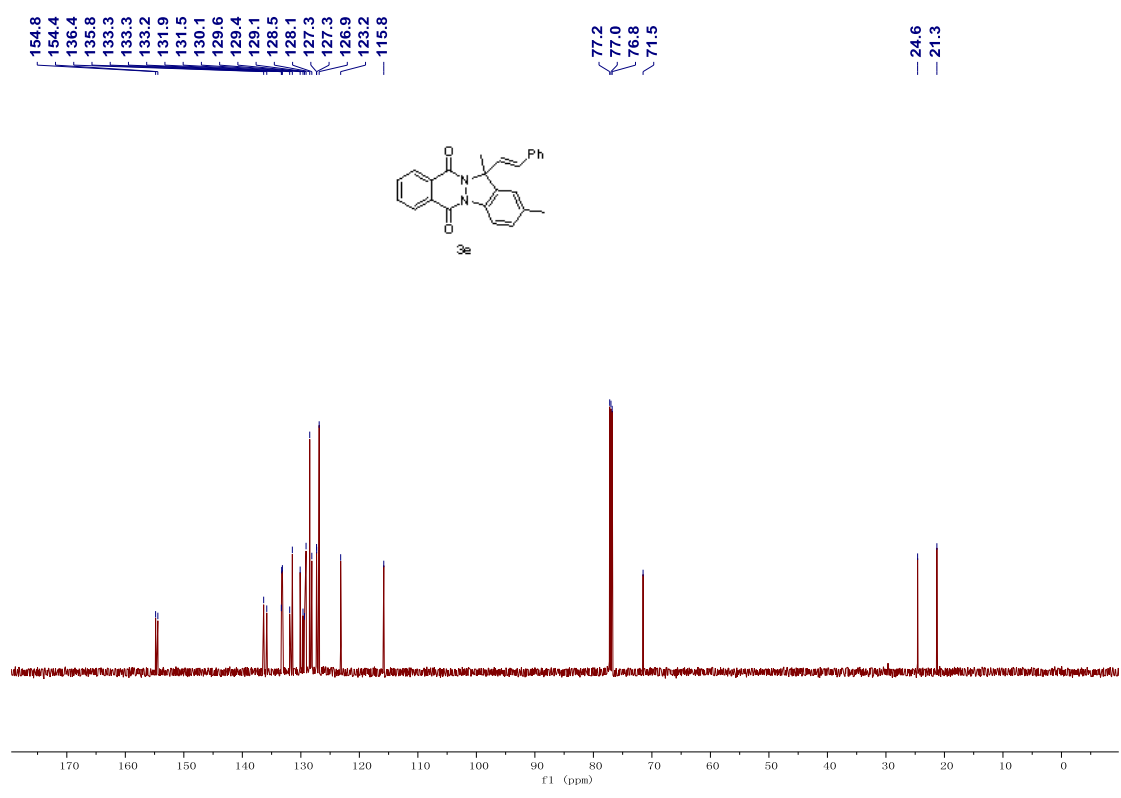
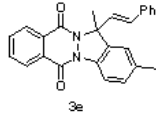
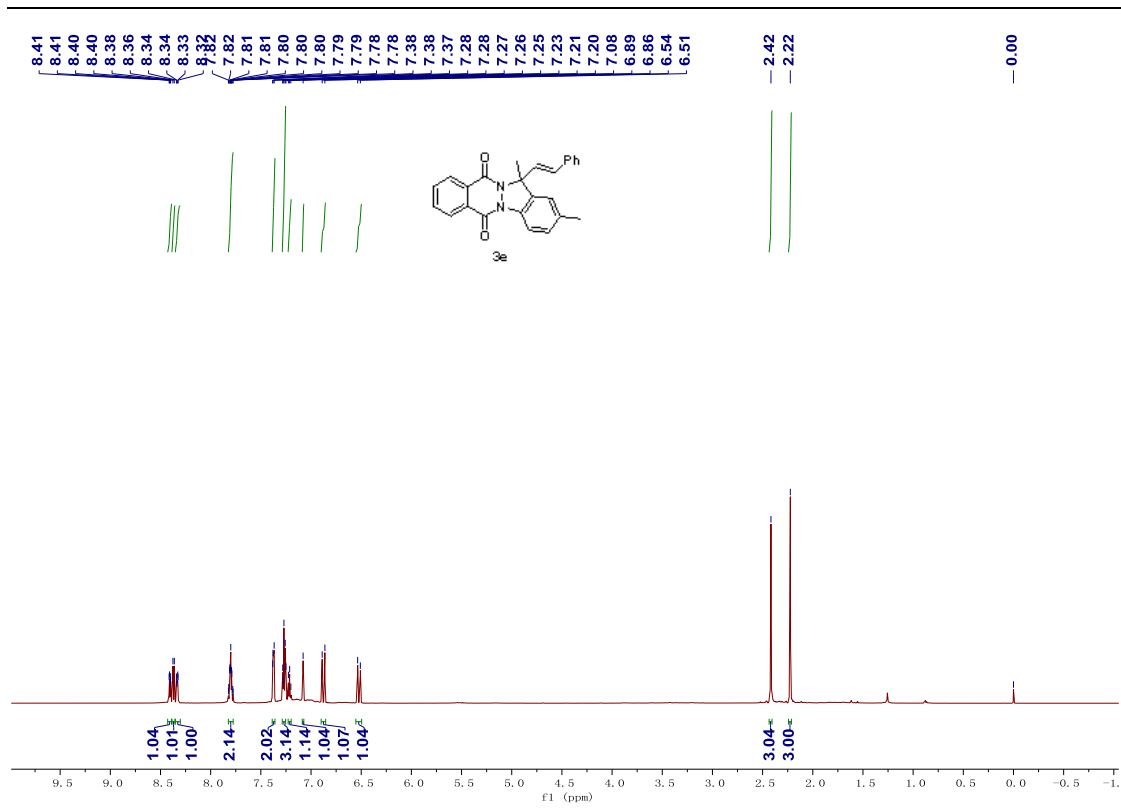
8.2 Copies of NMR spectra

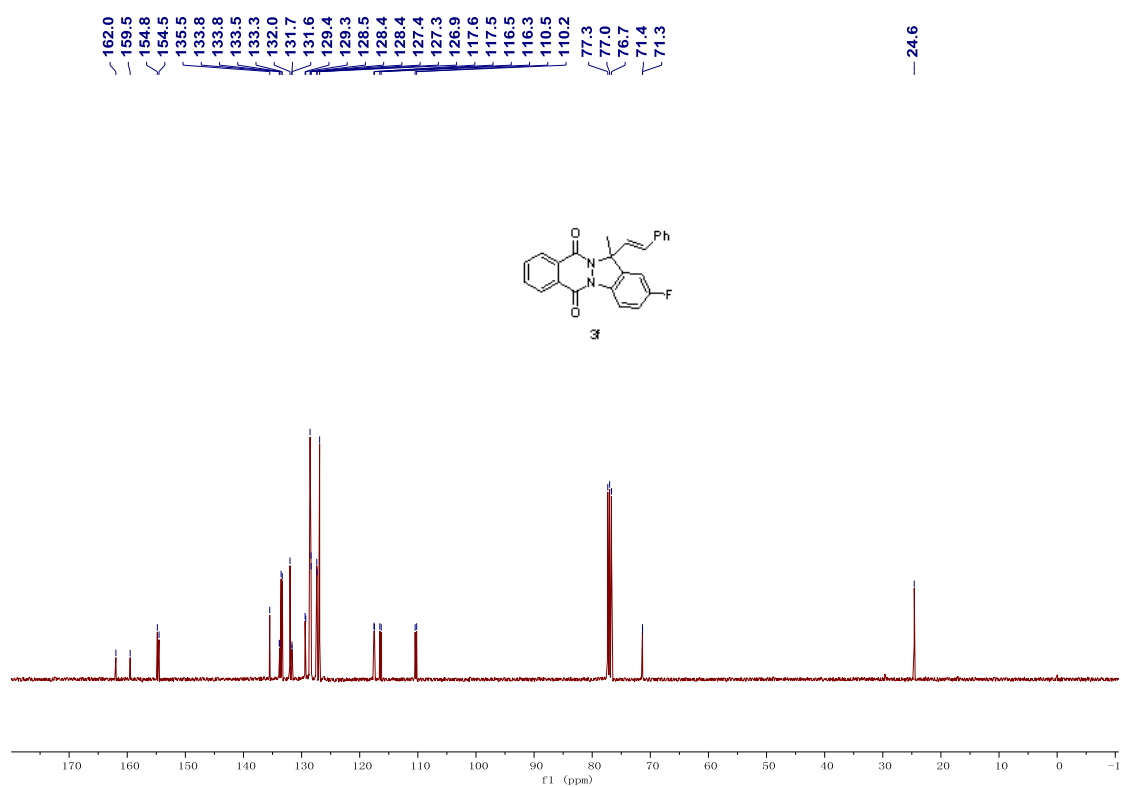
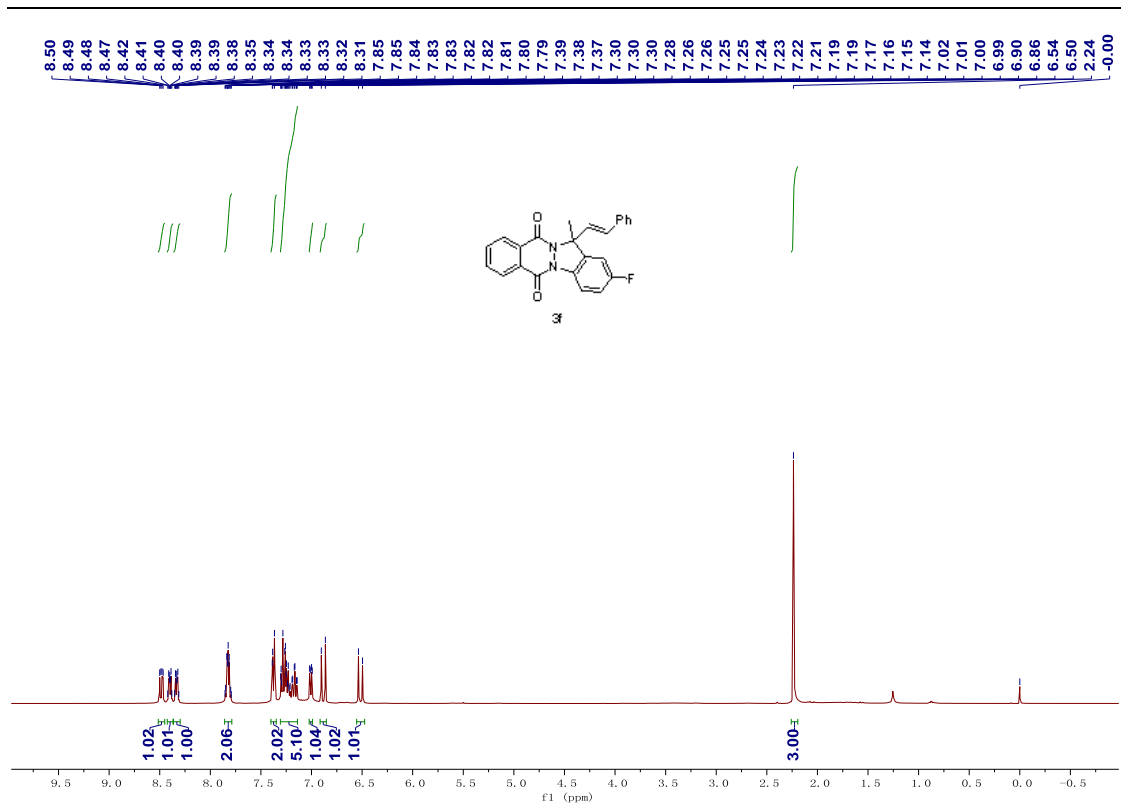


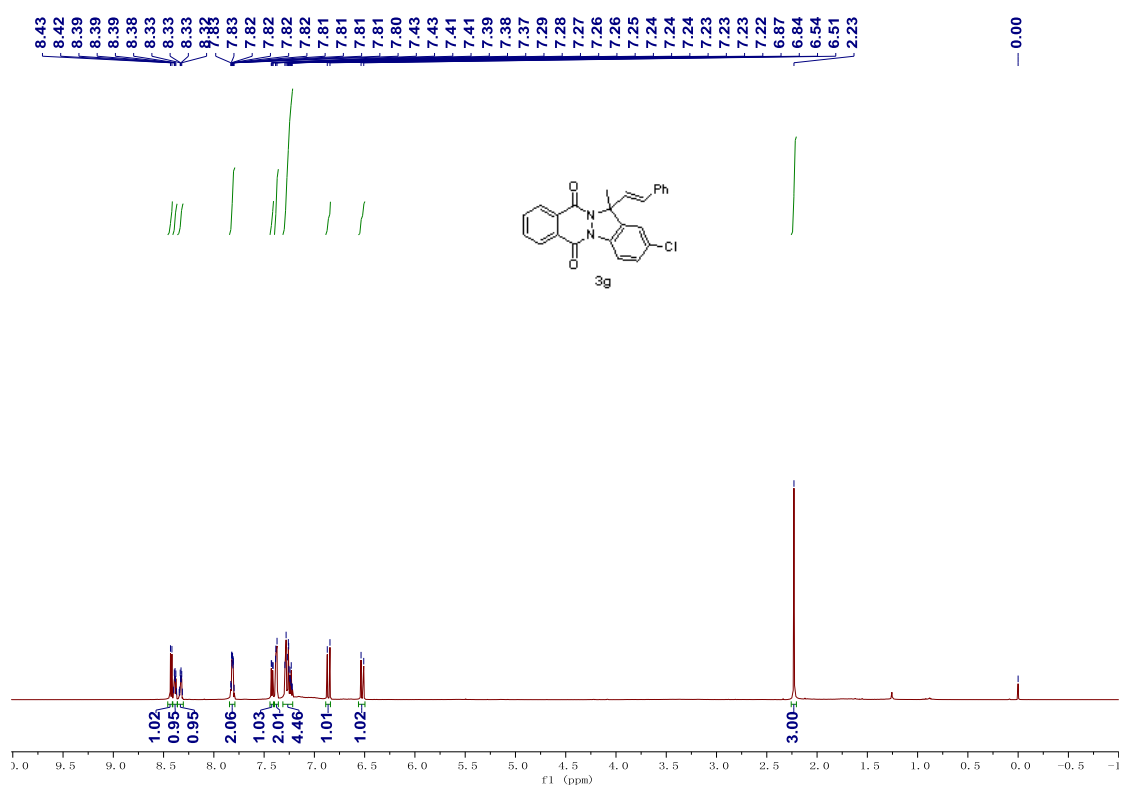
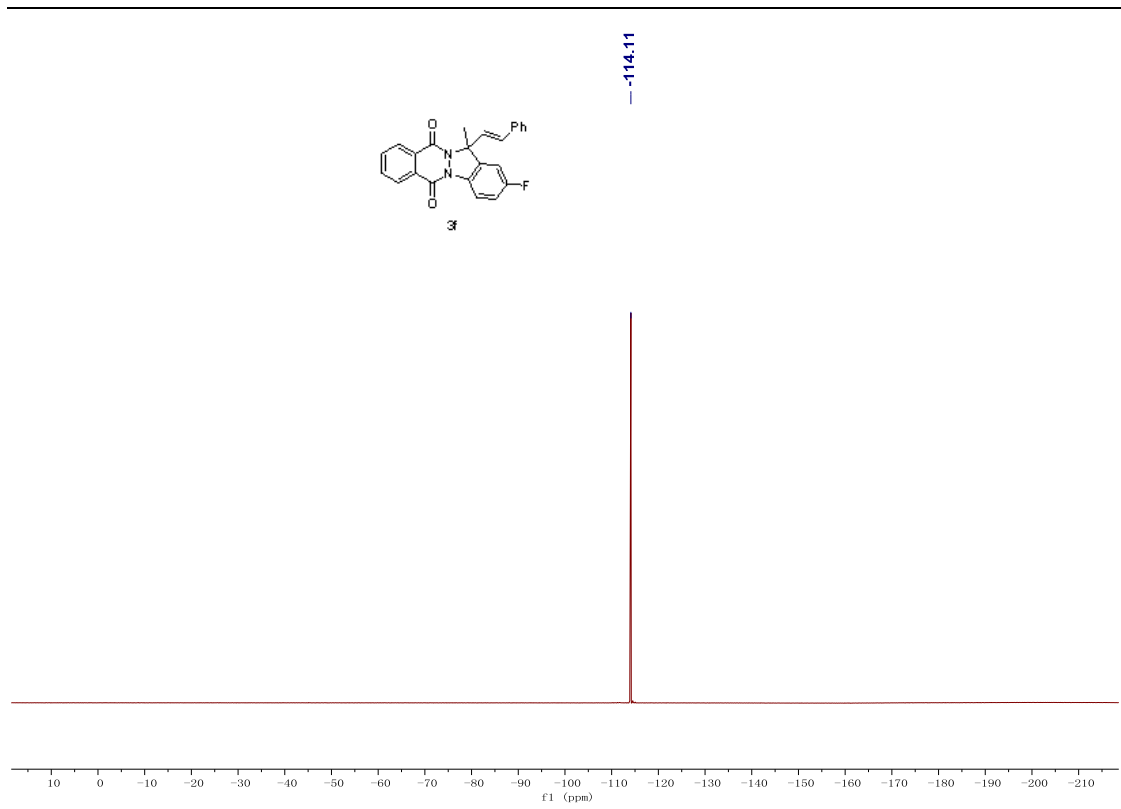


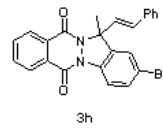
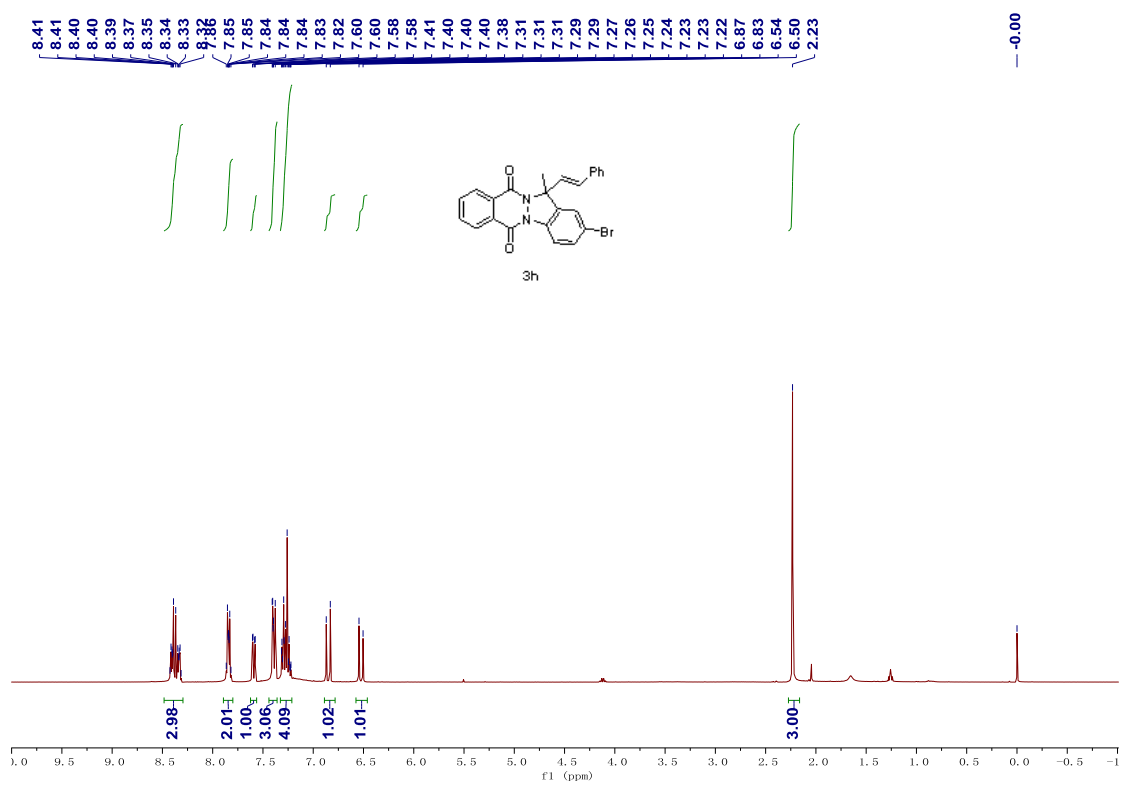
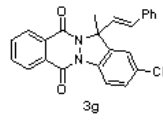
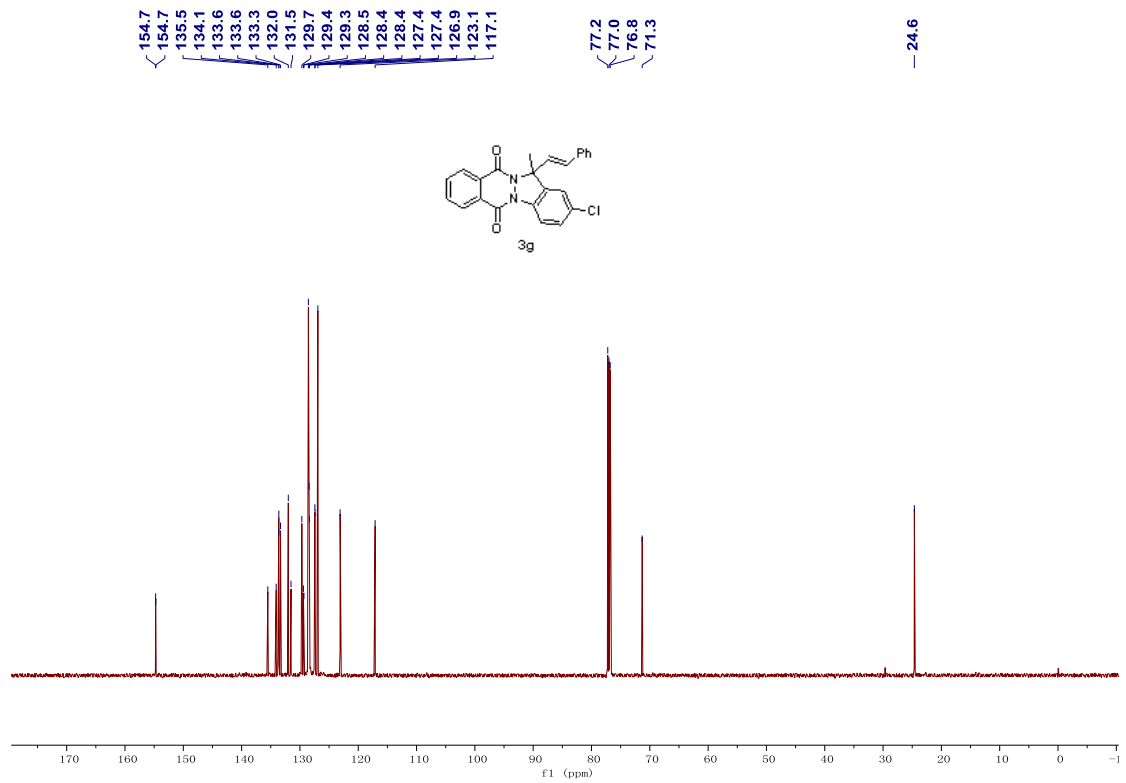


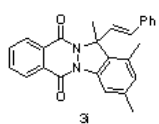
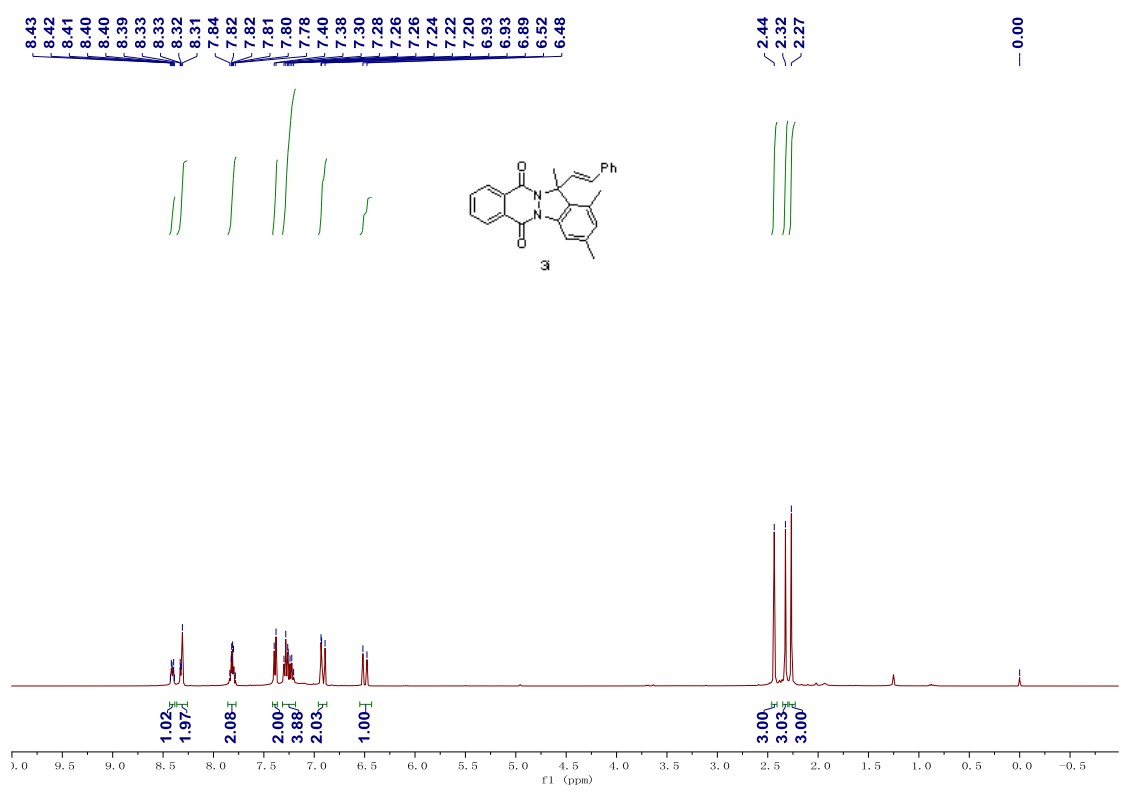
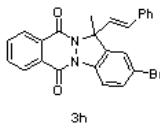
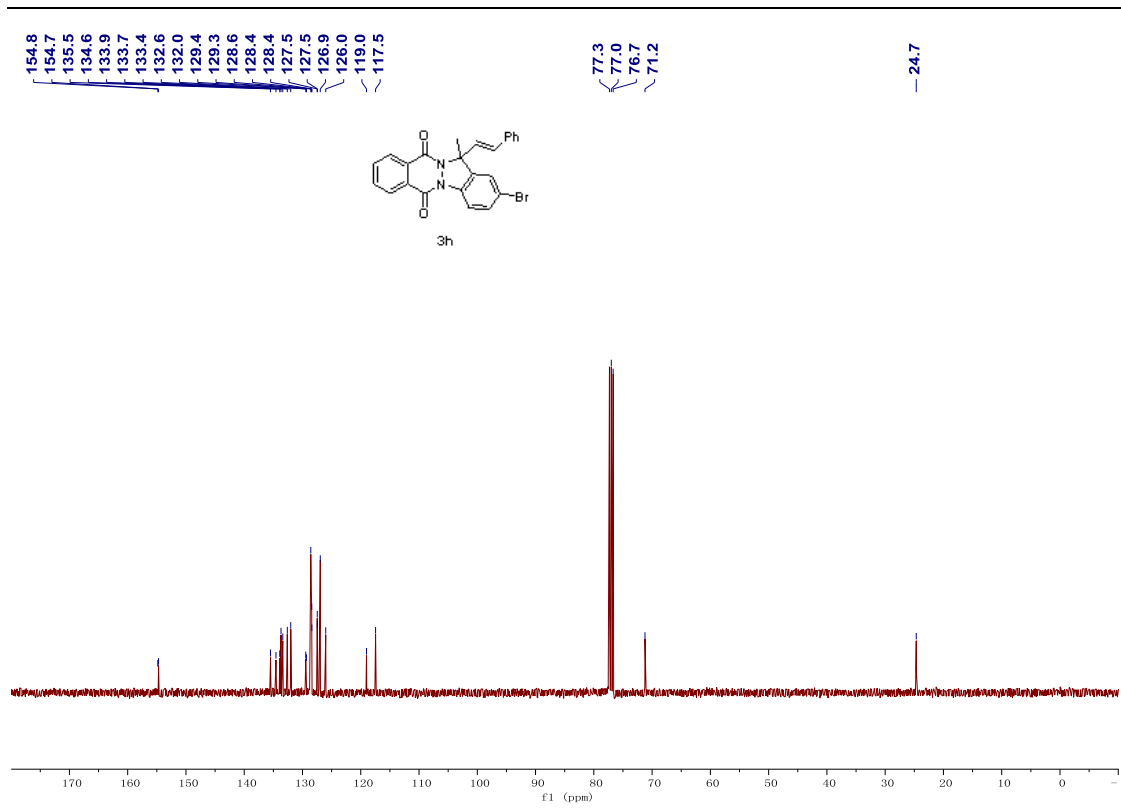


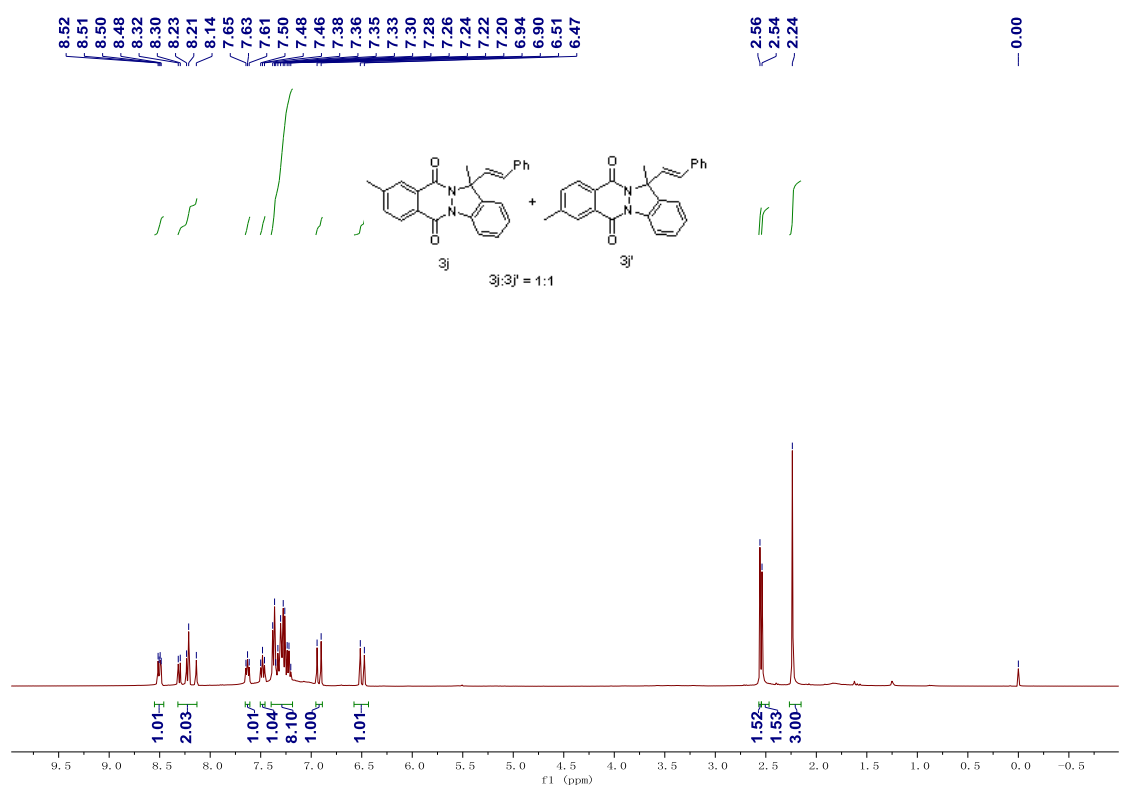
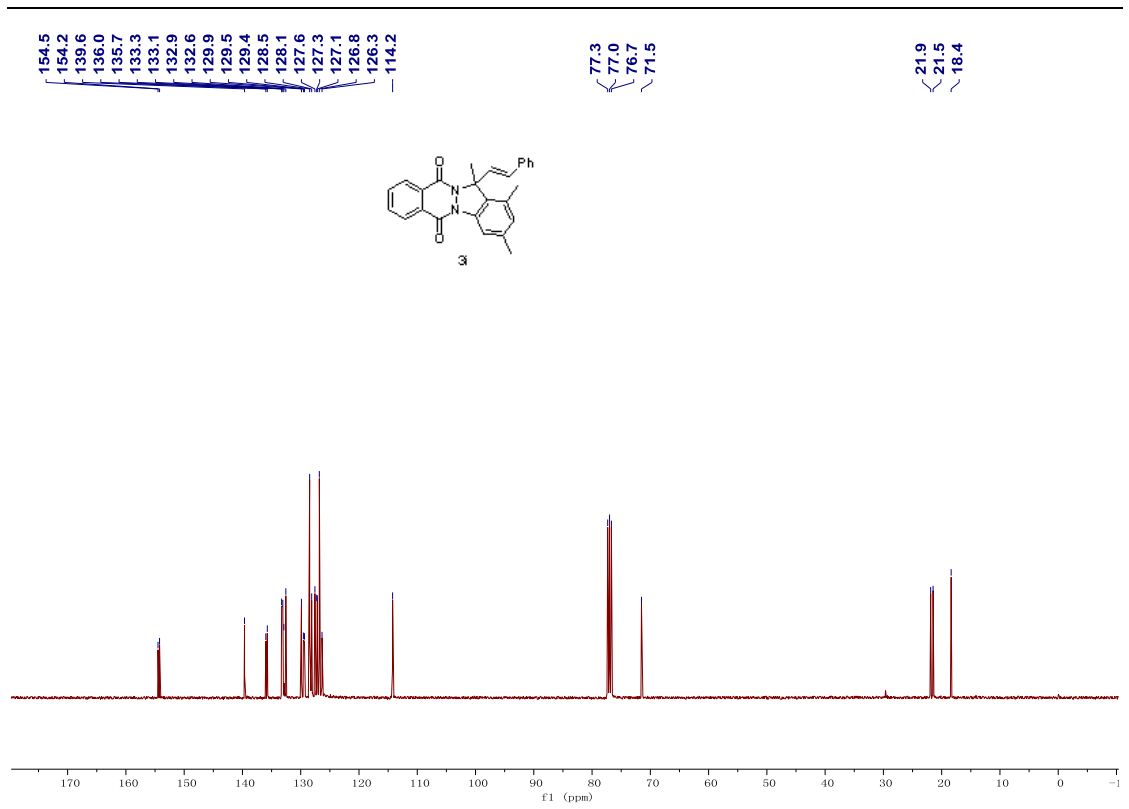


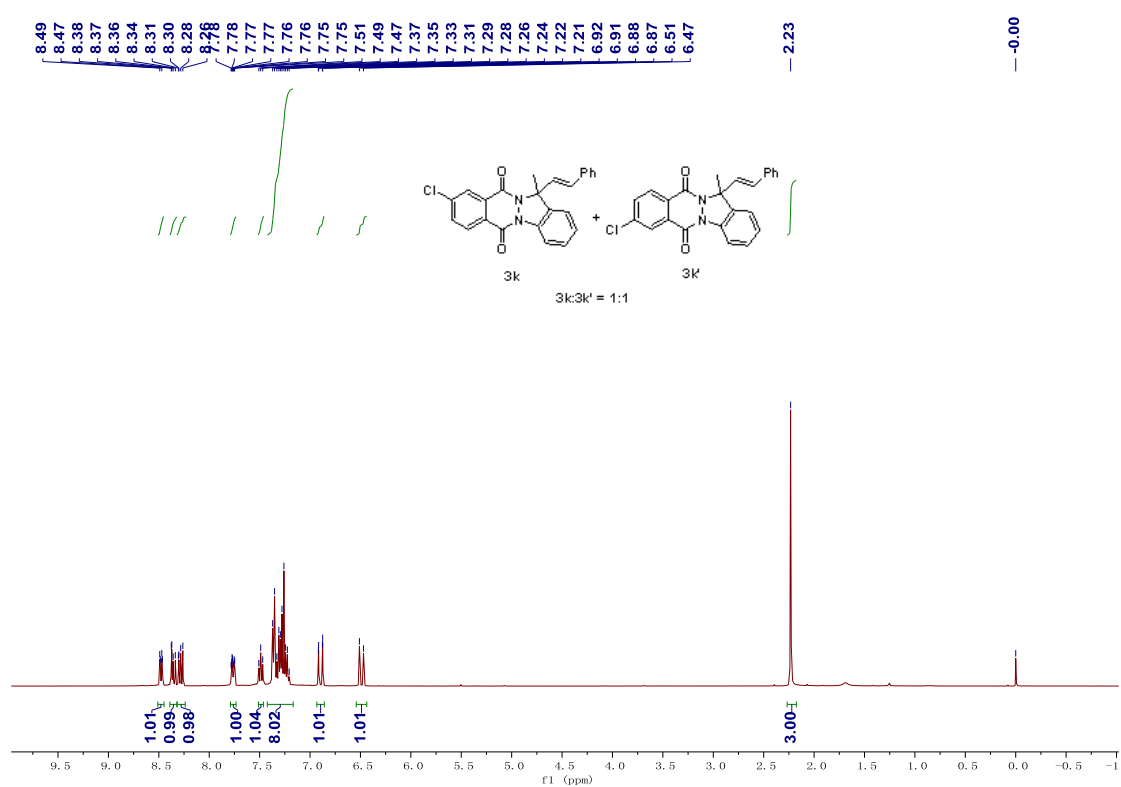
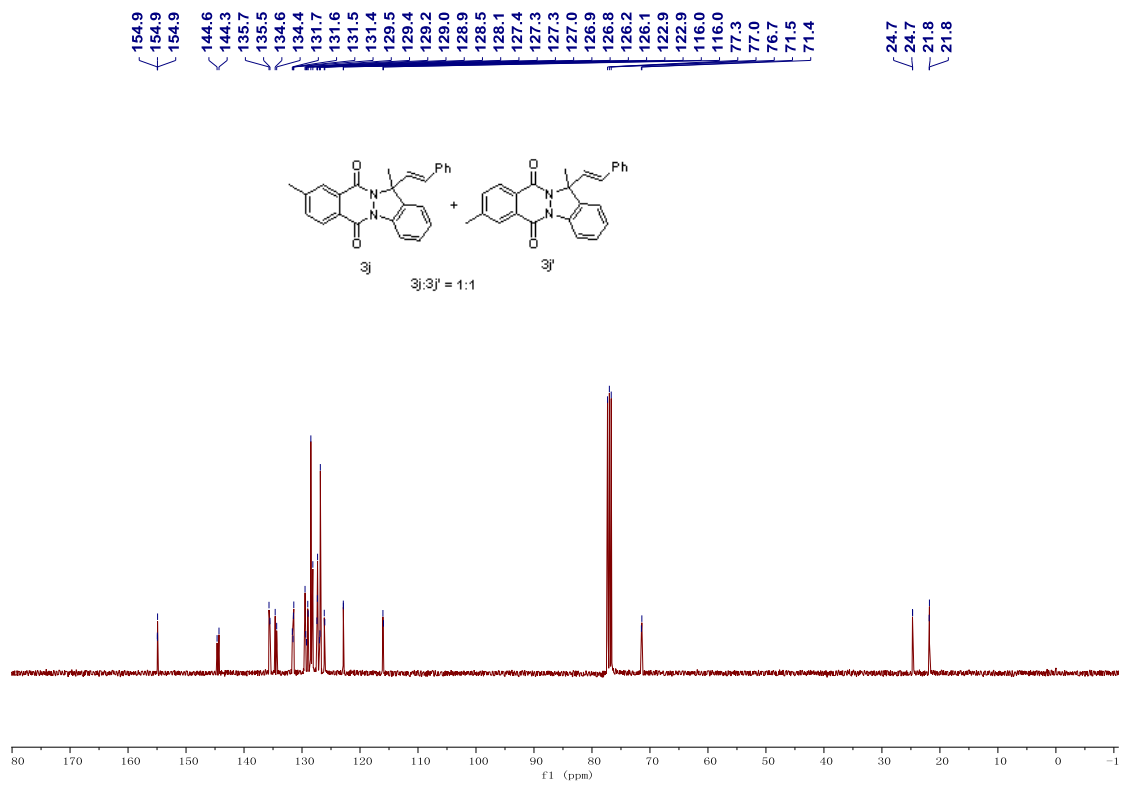


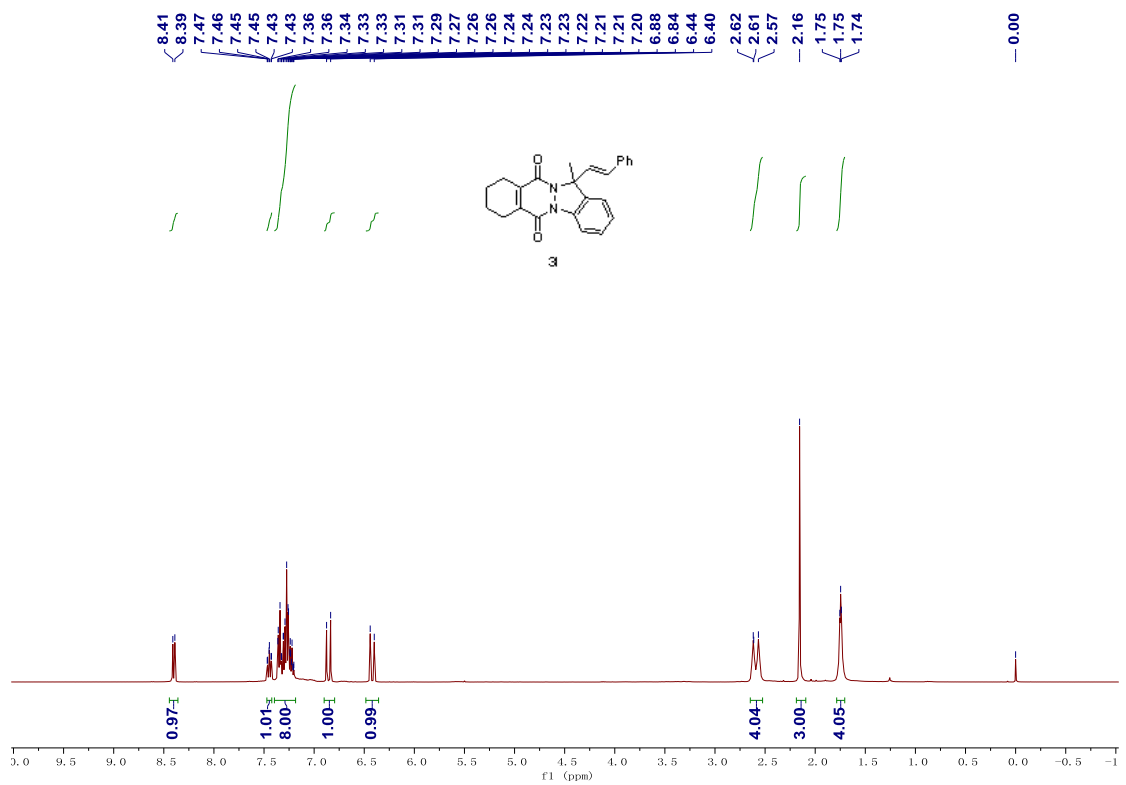
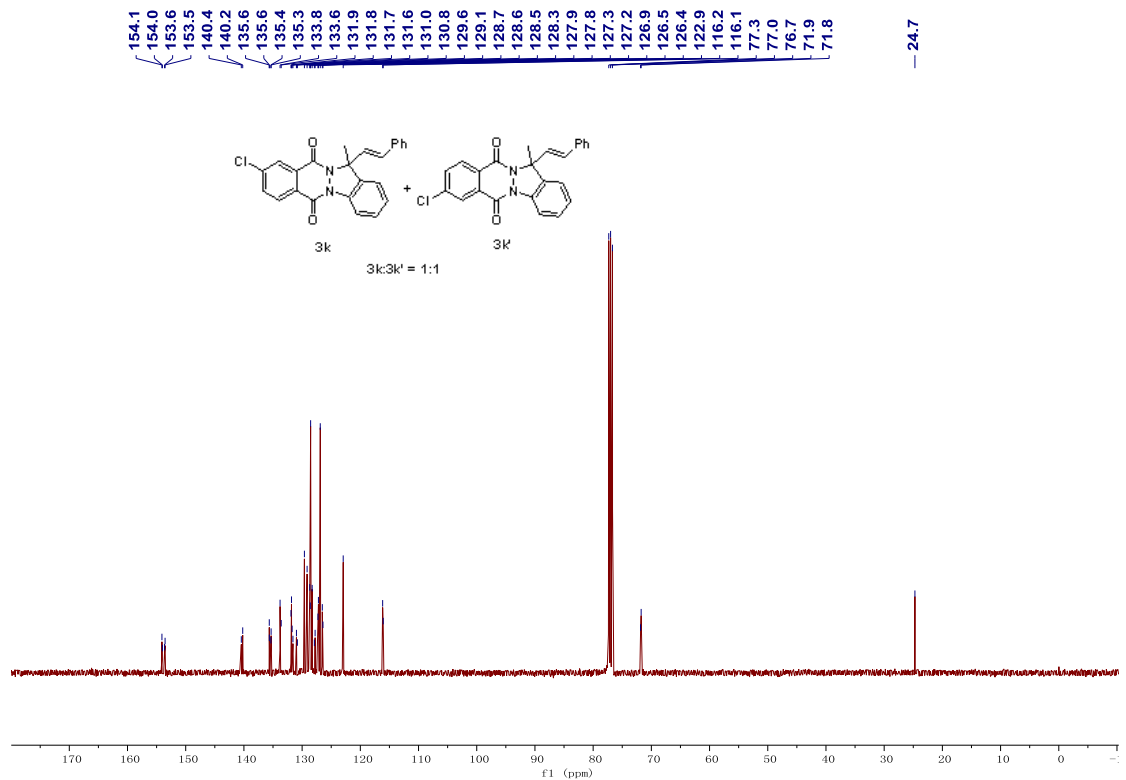


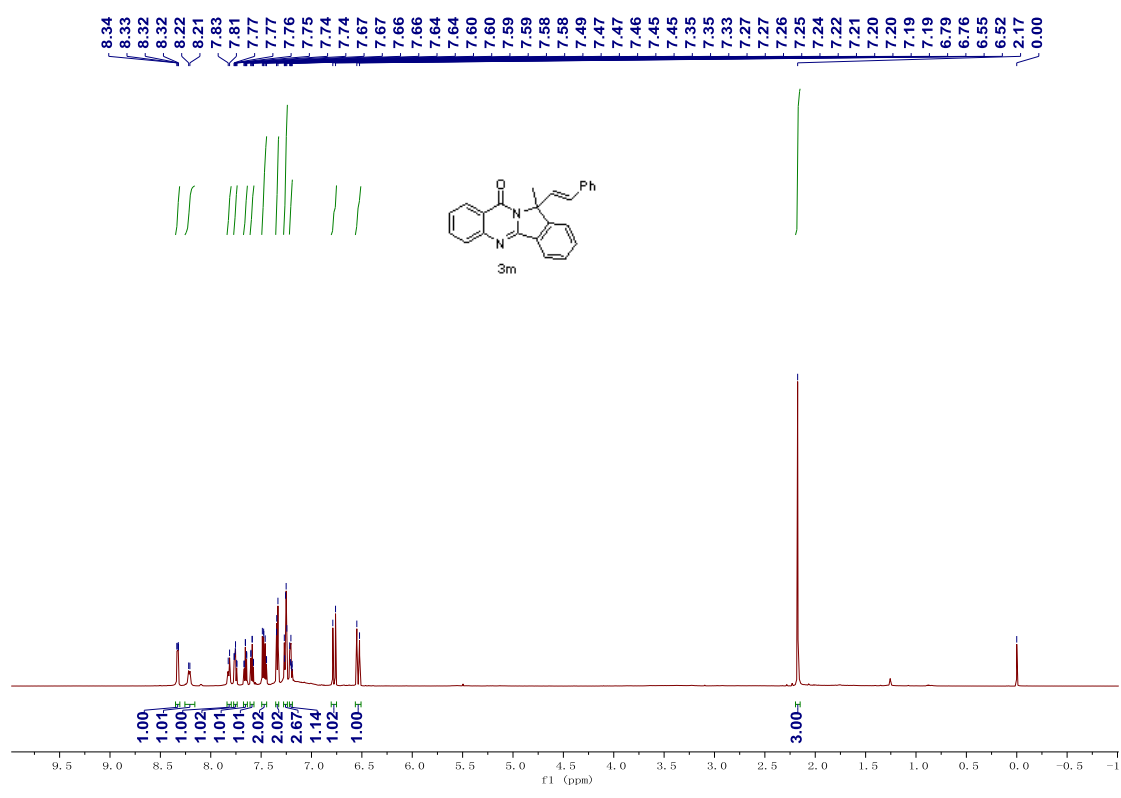
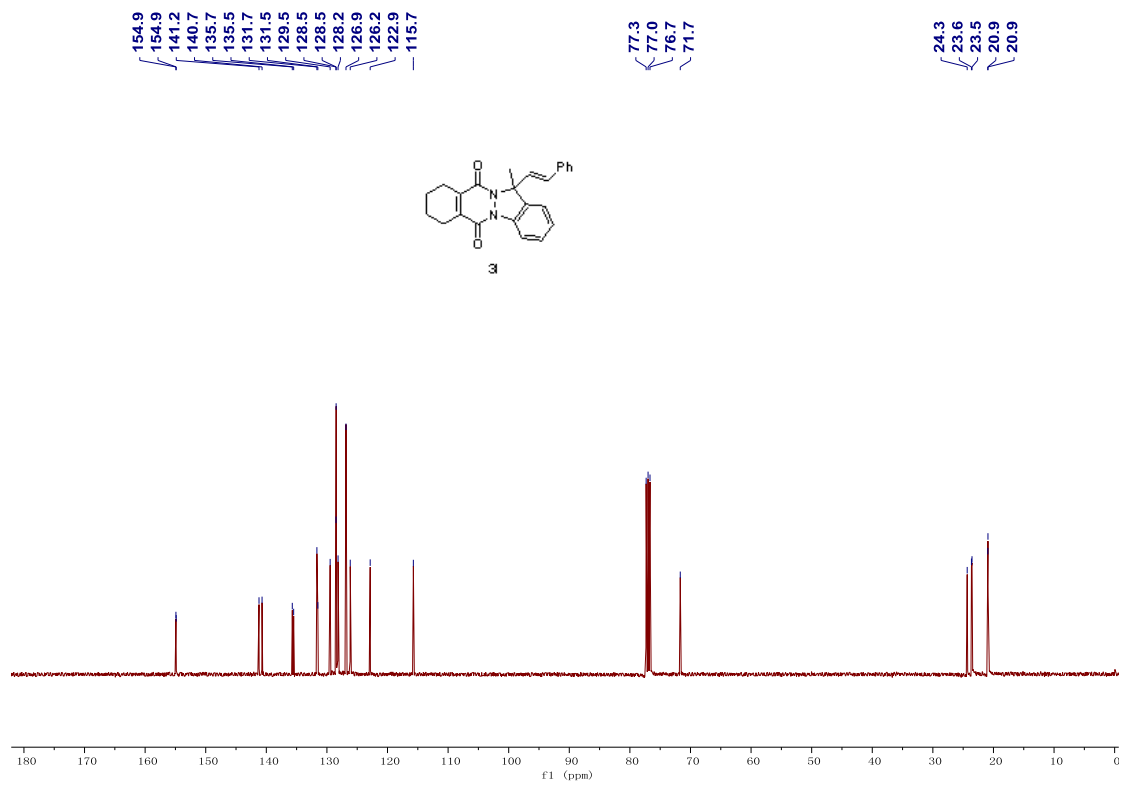


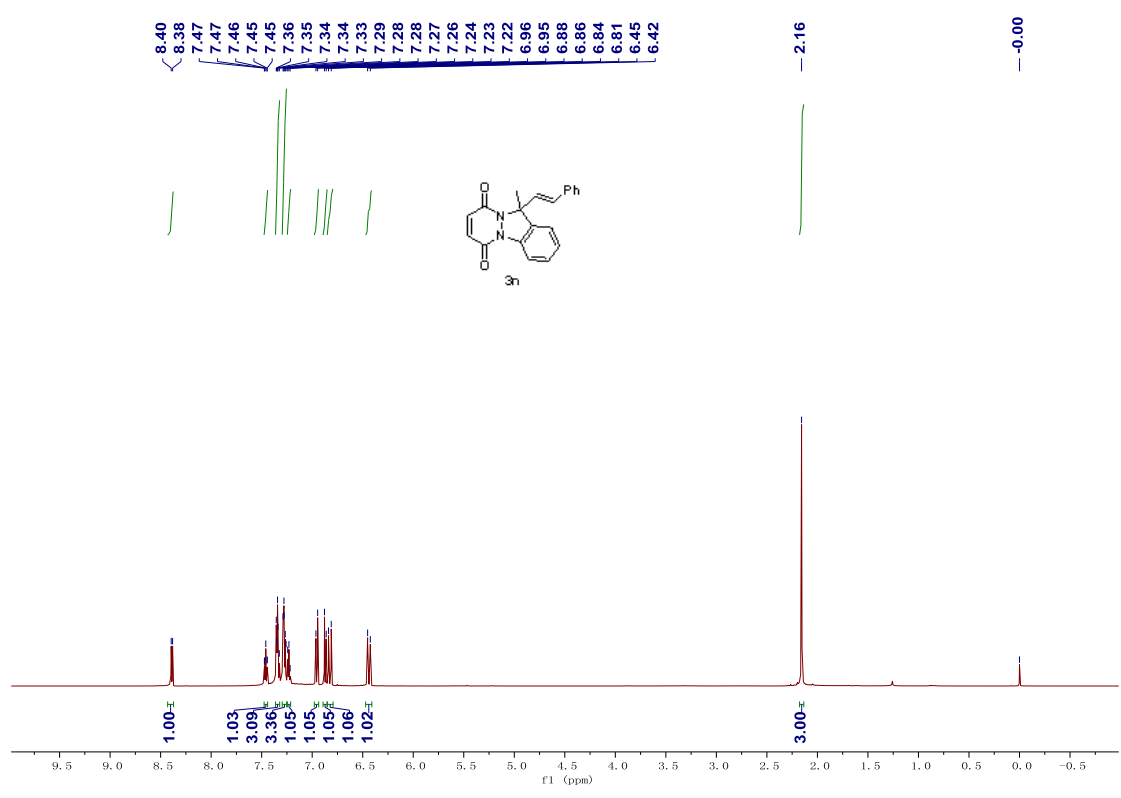
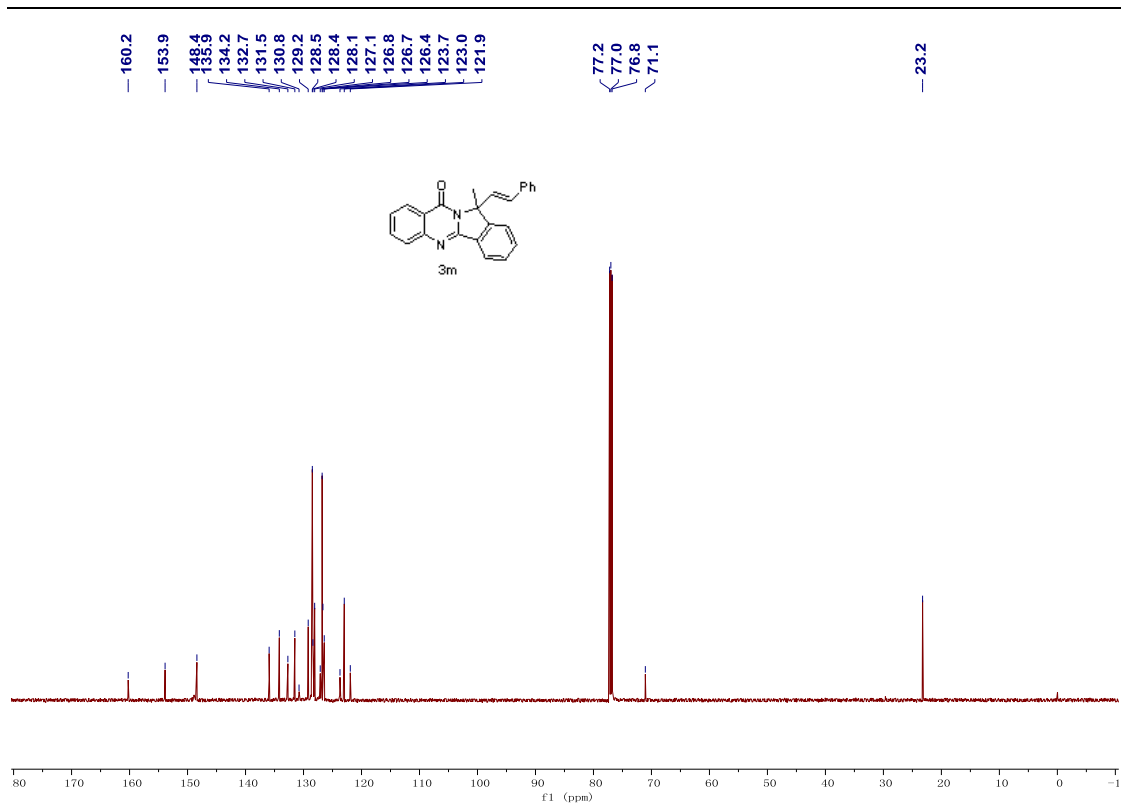


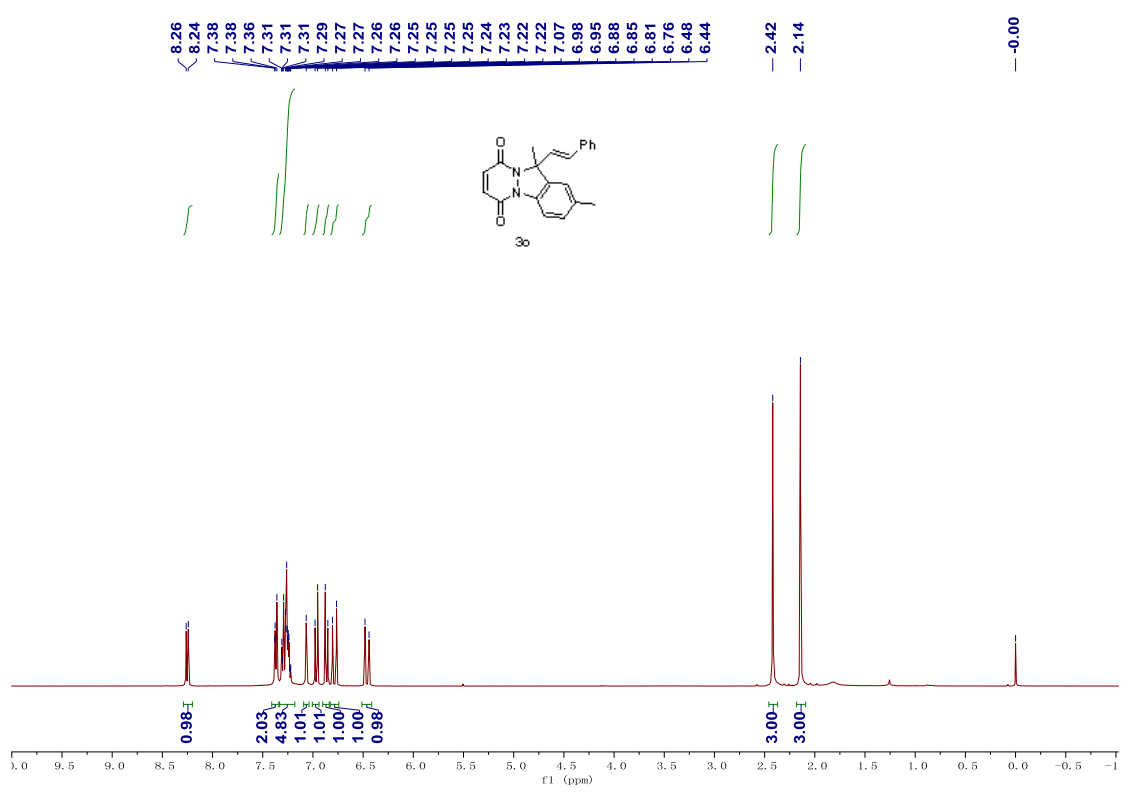
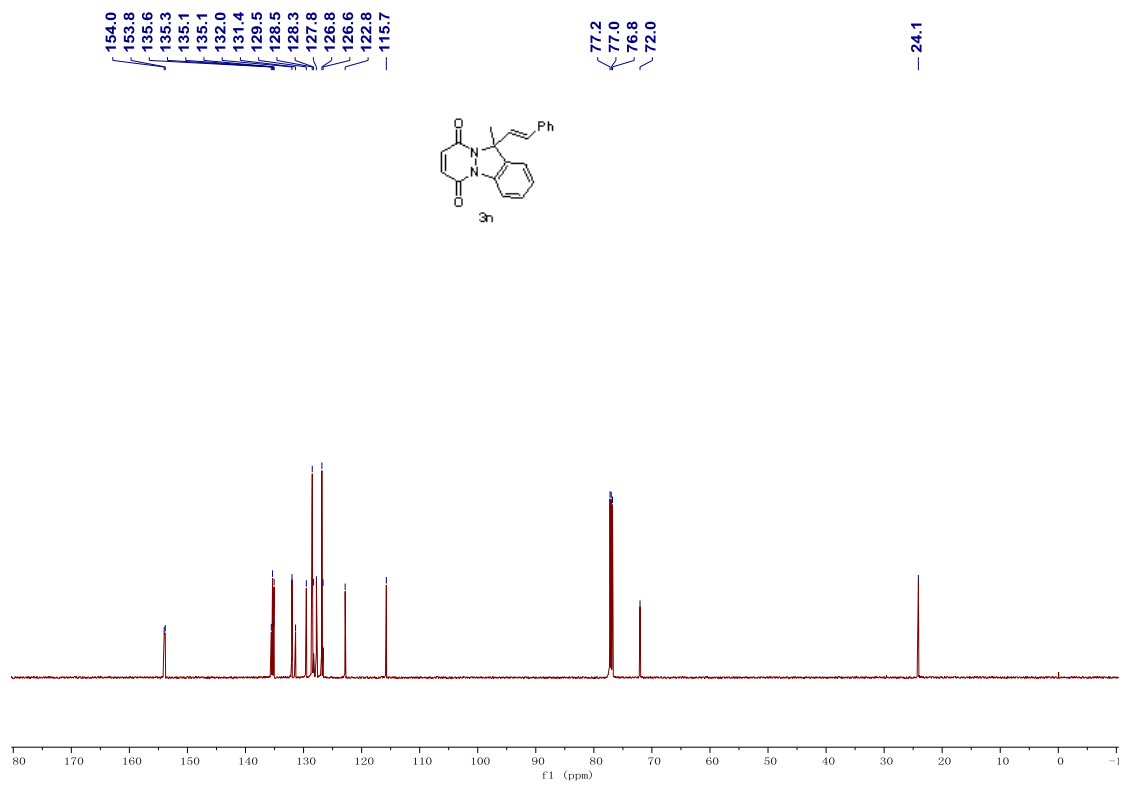


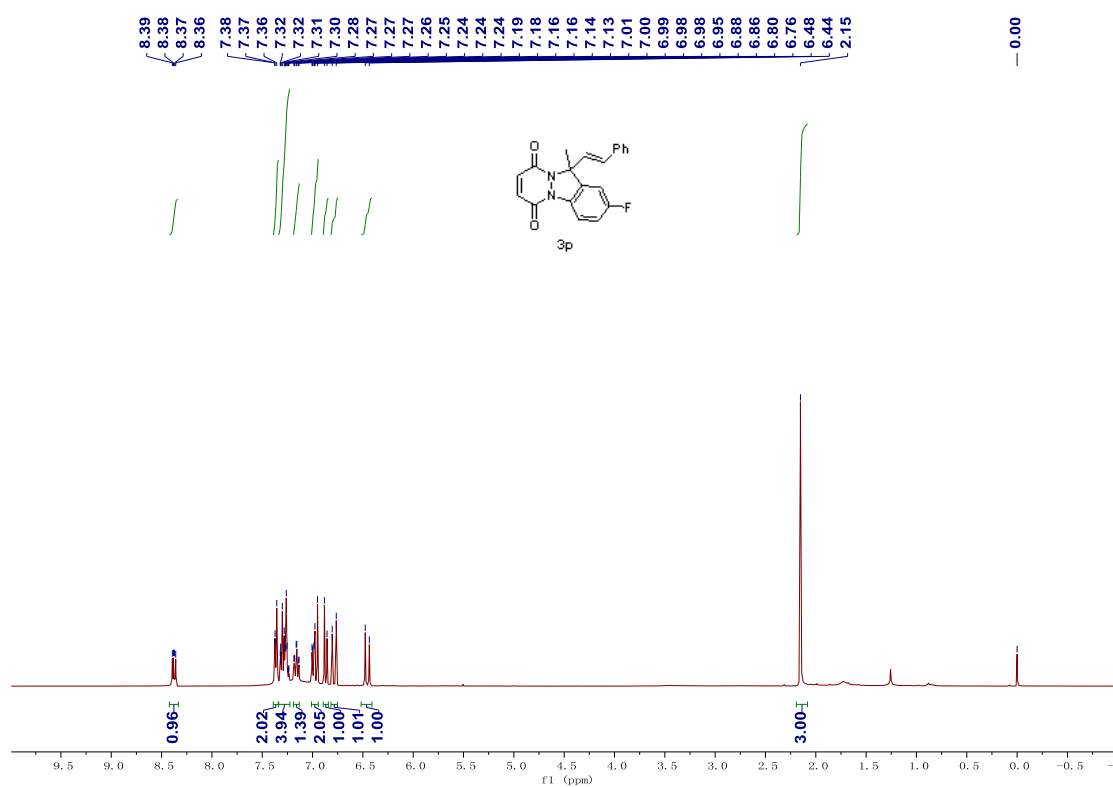
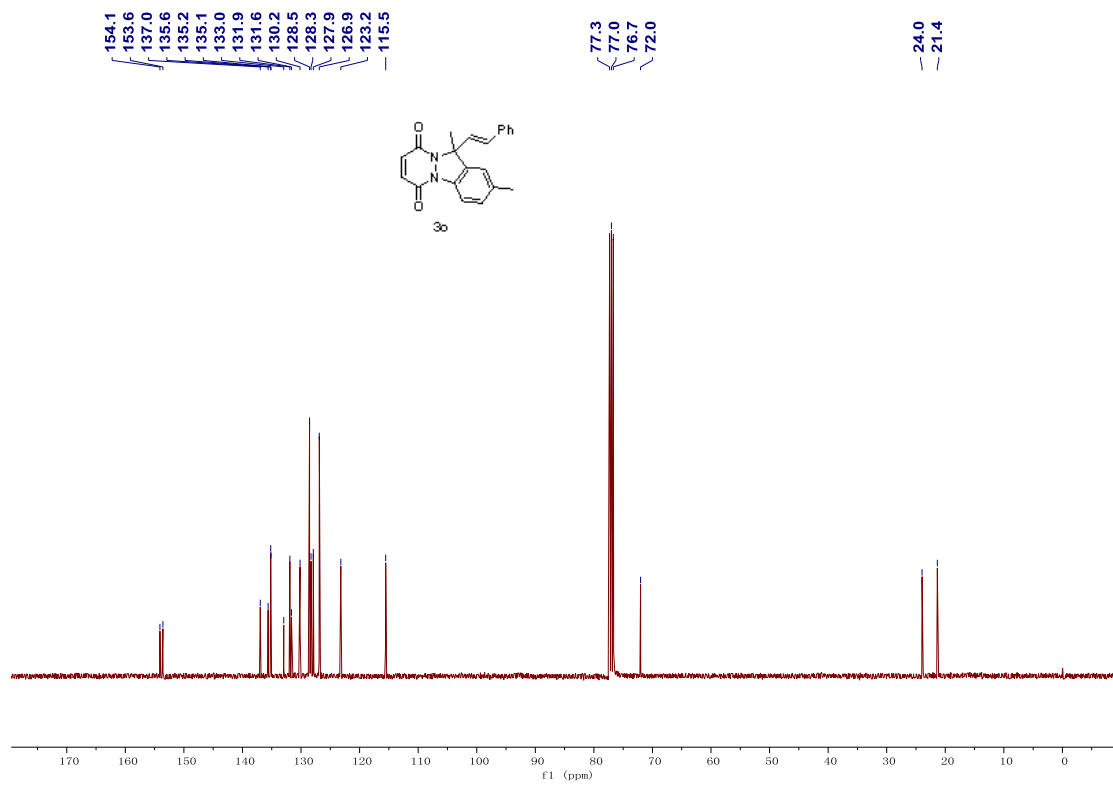


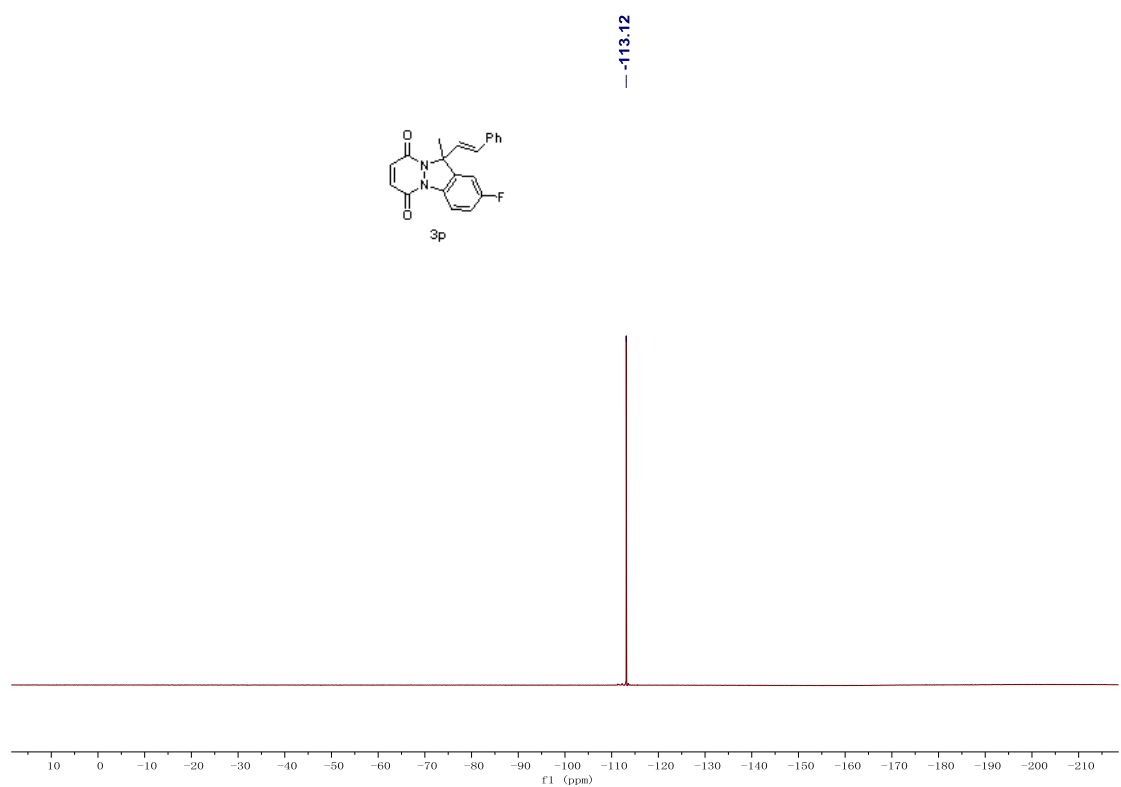
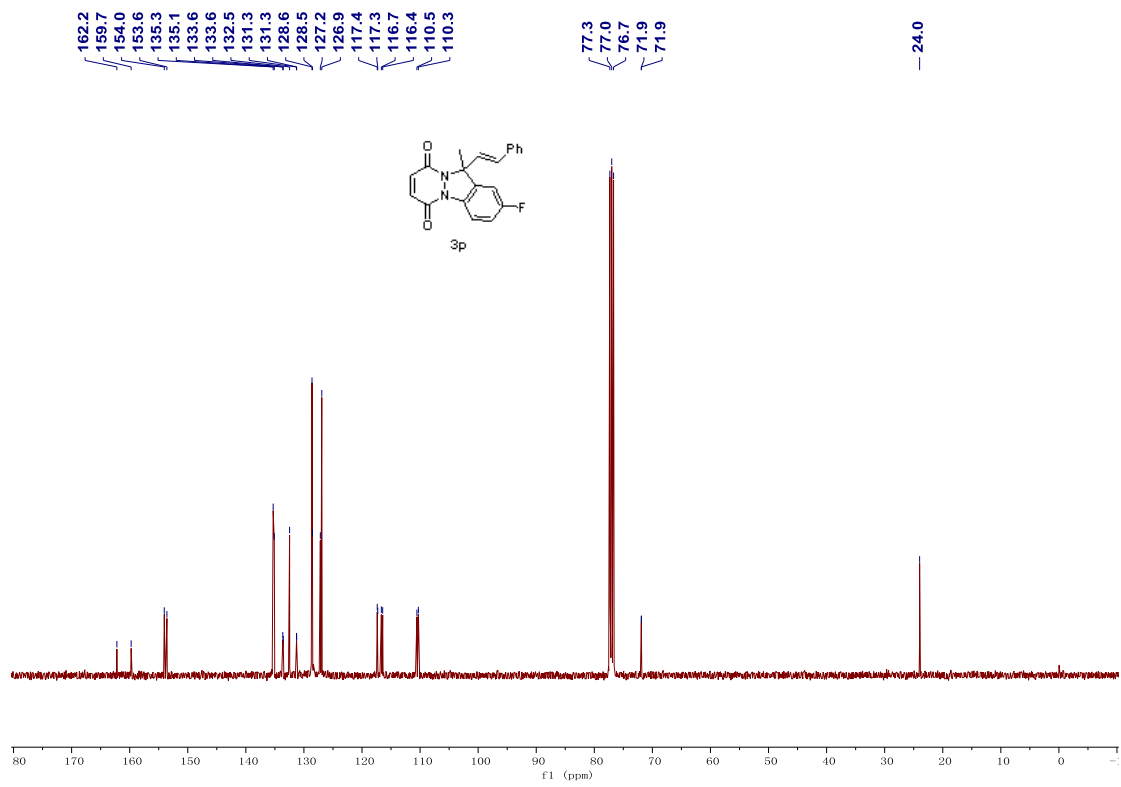


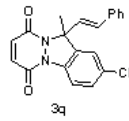
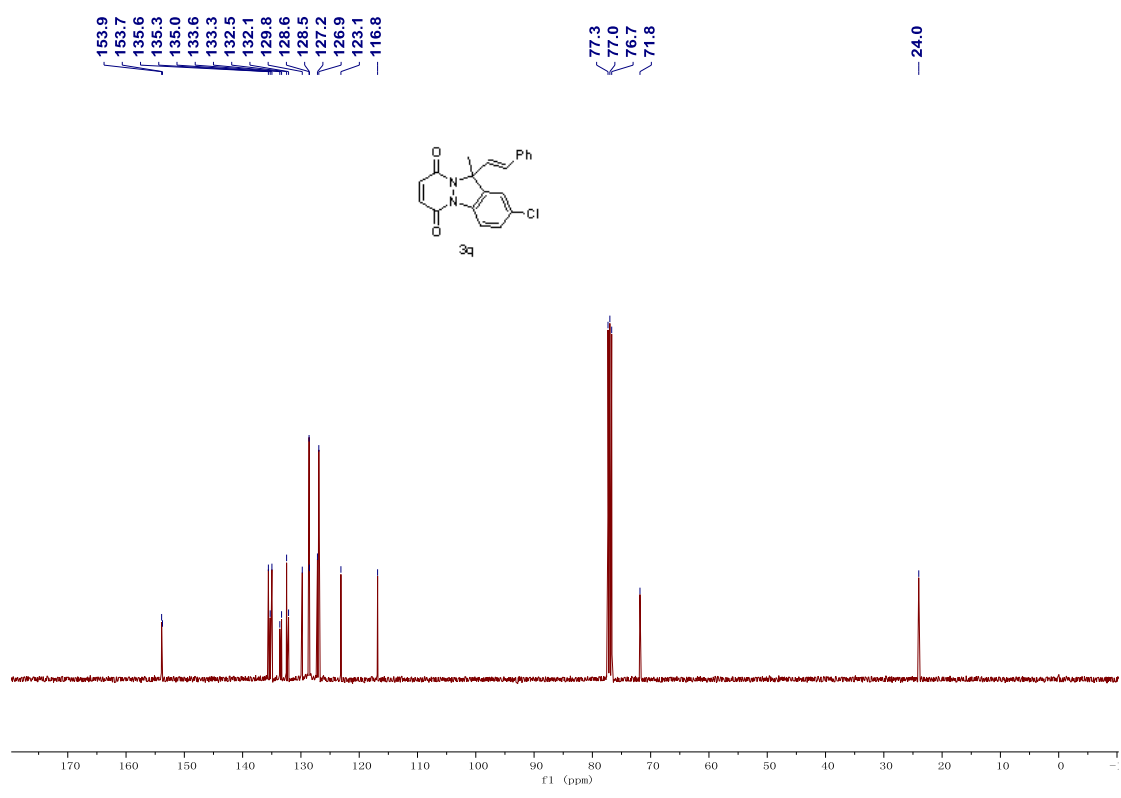
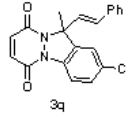
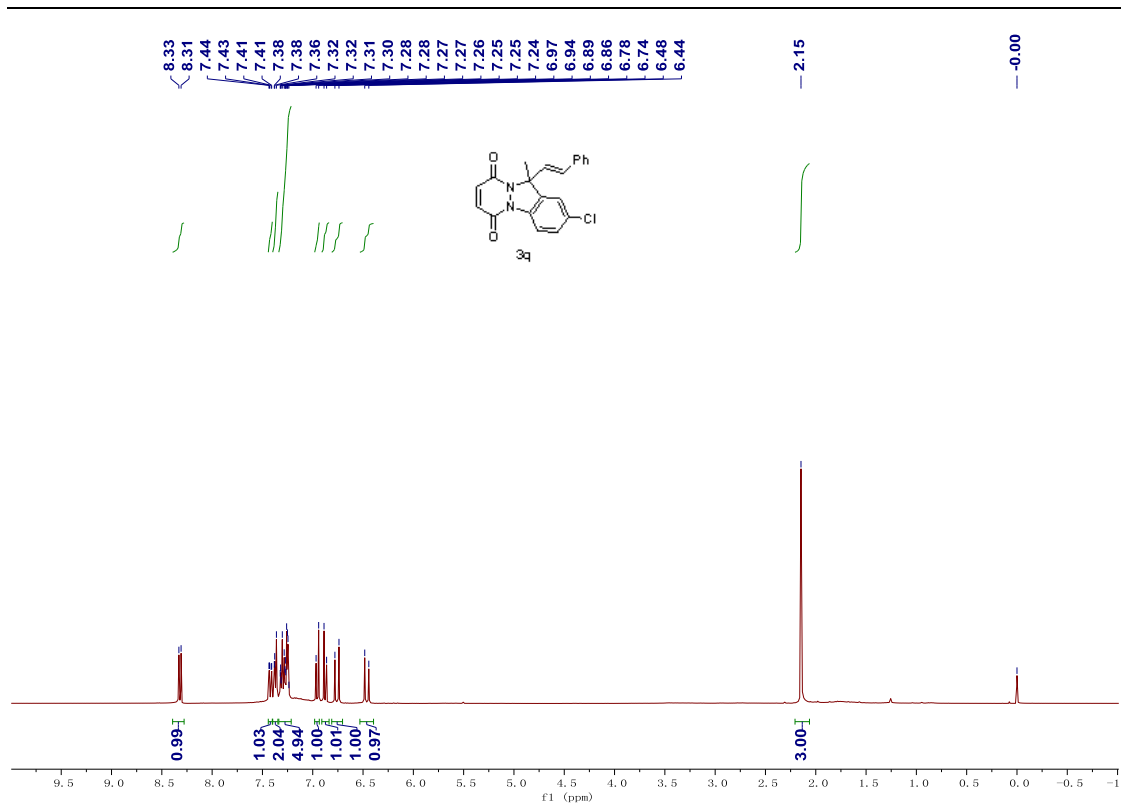


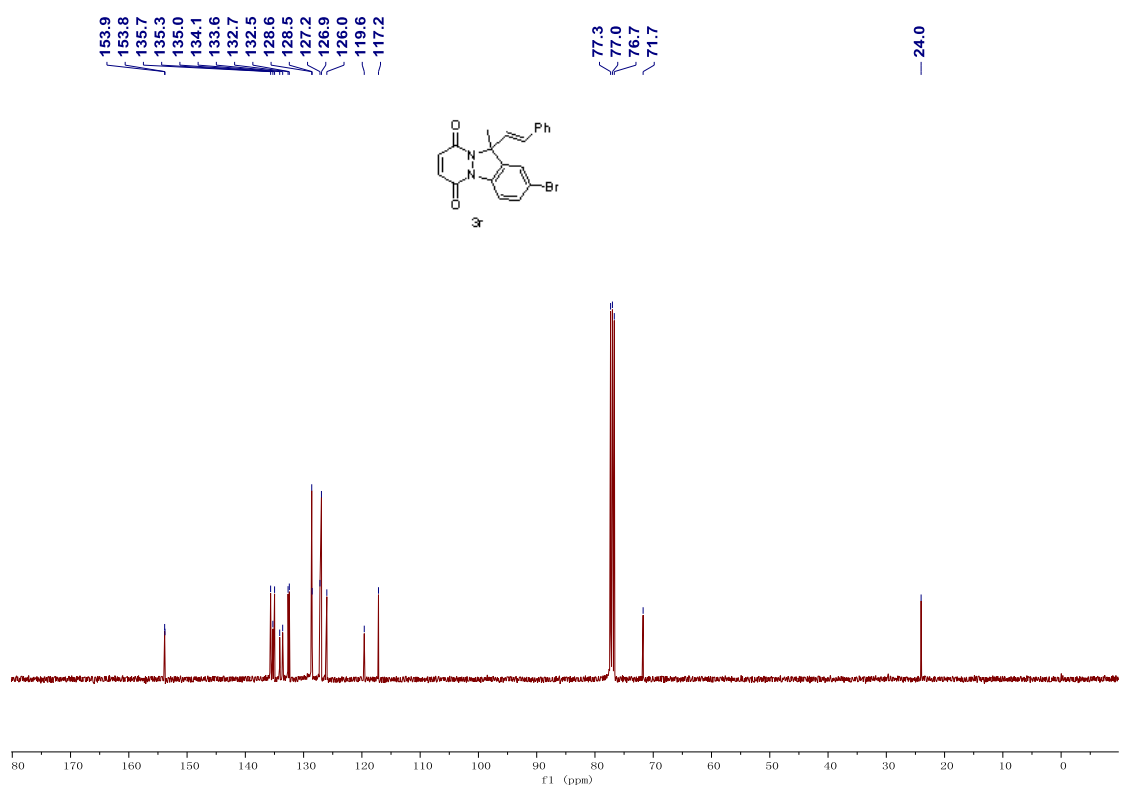
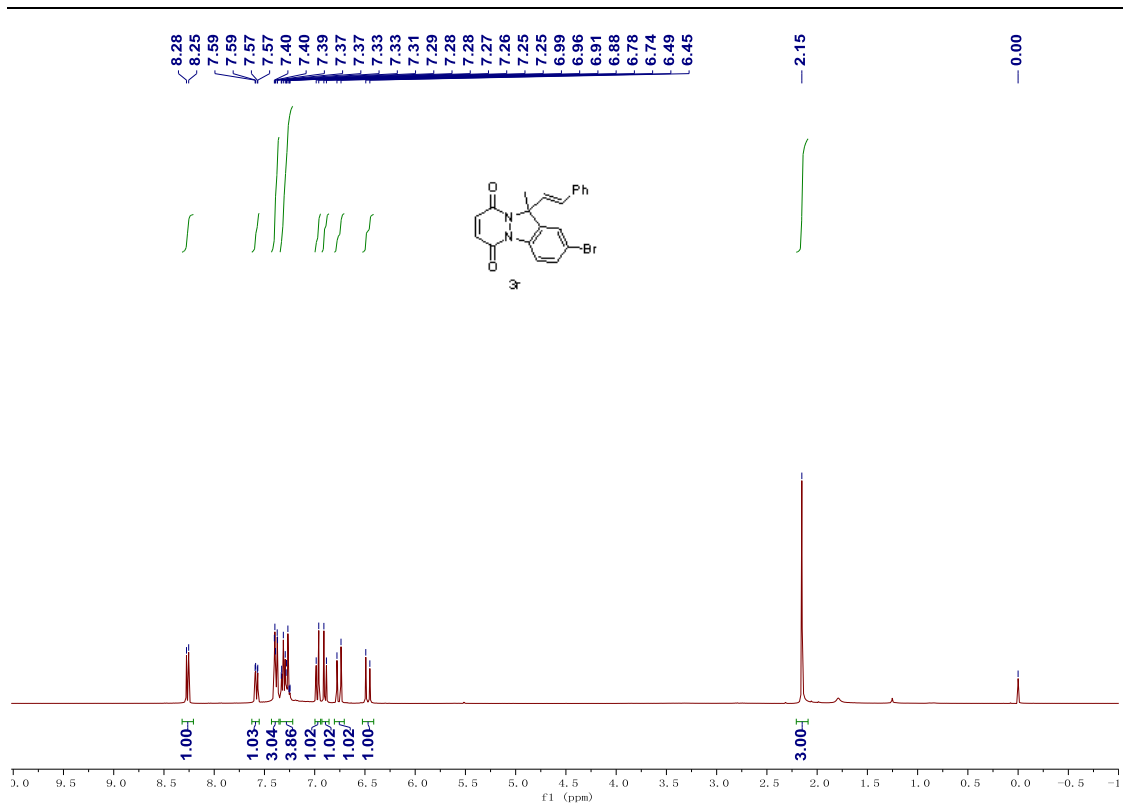


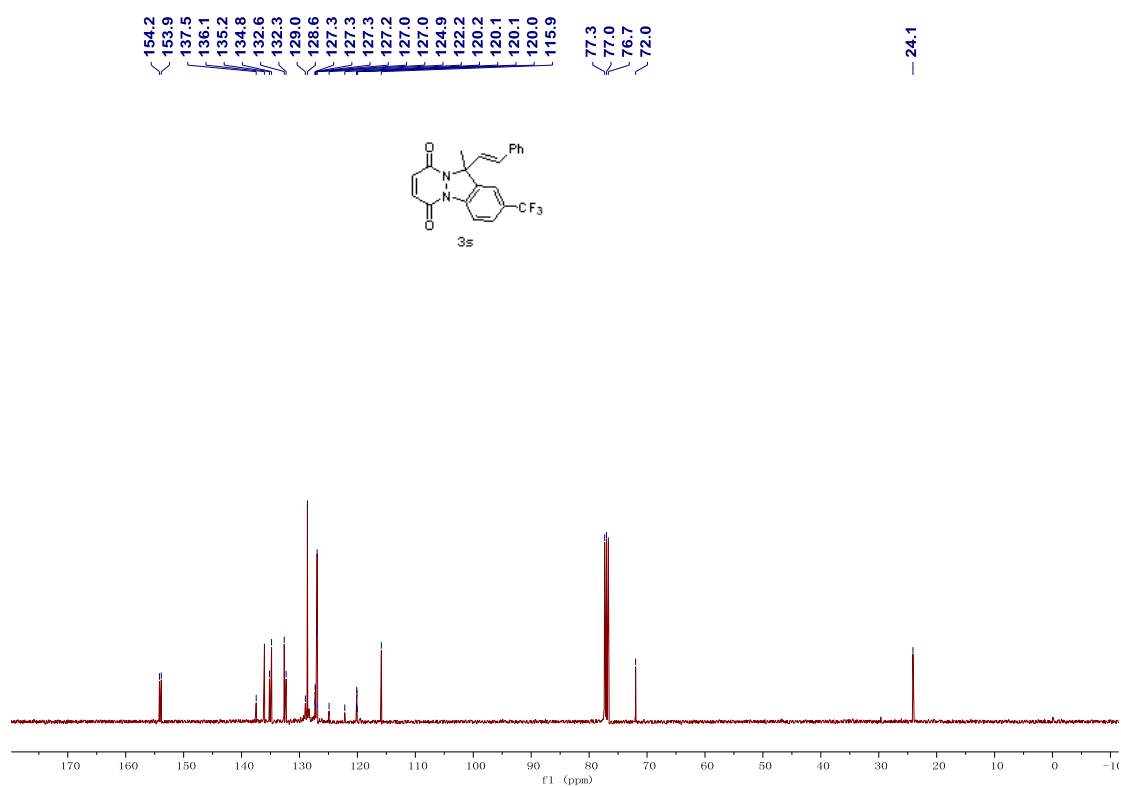
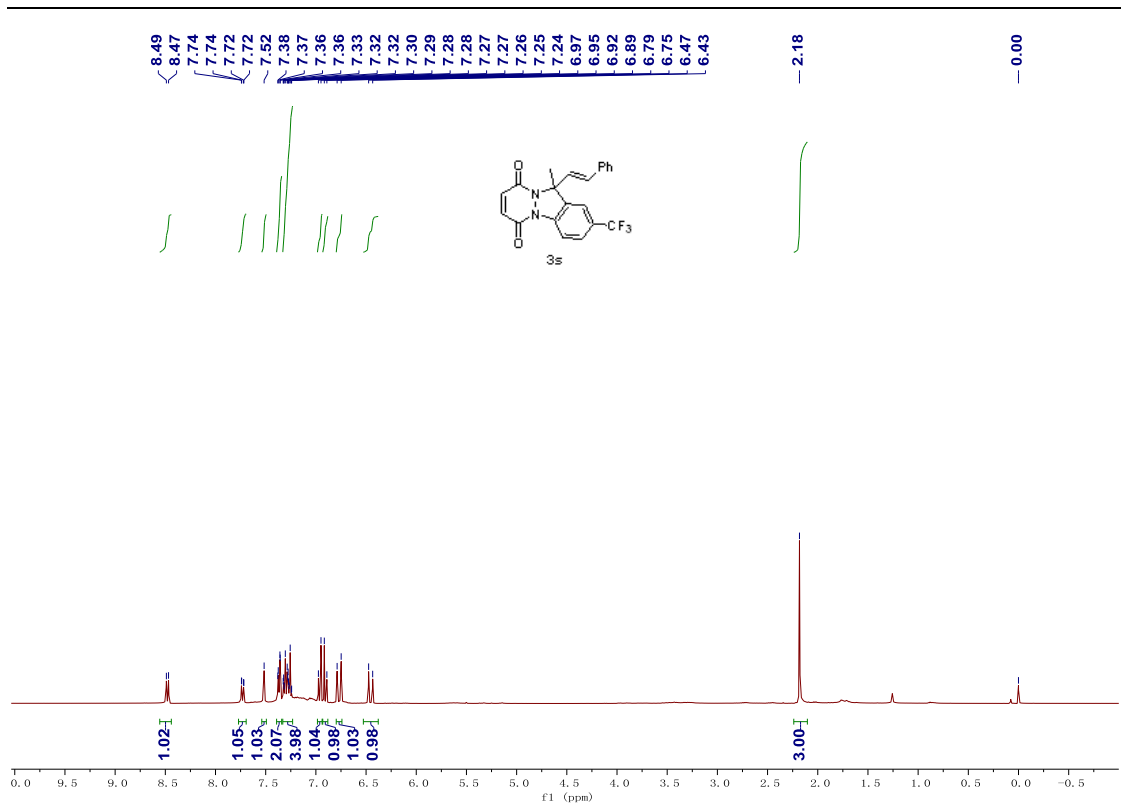


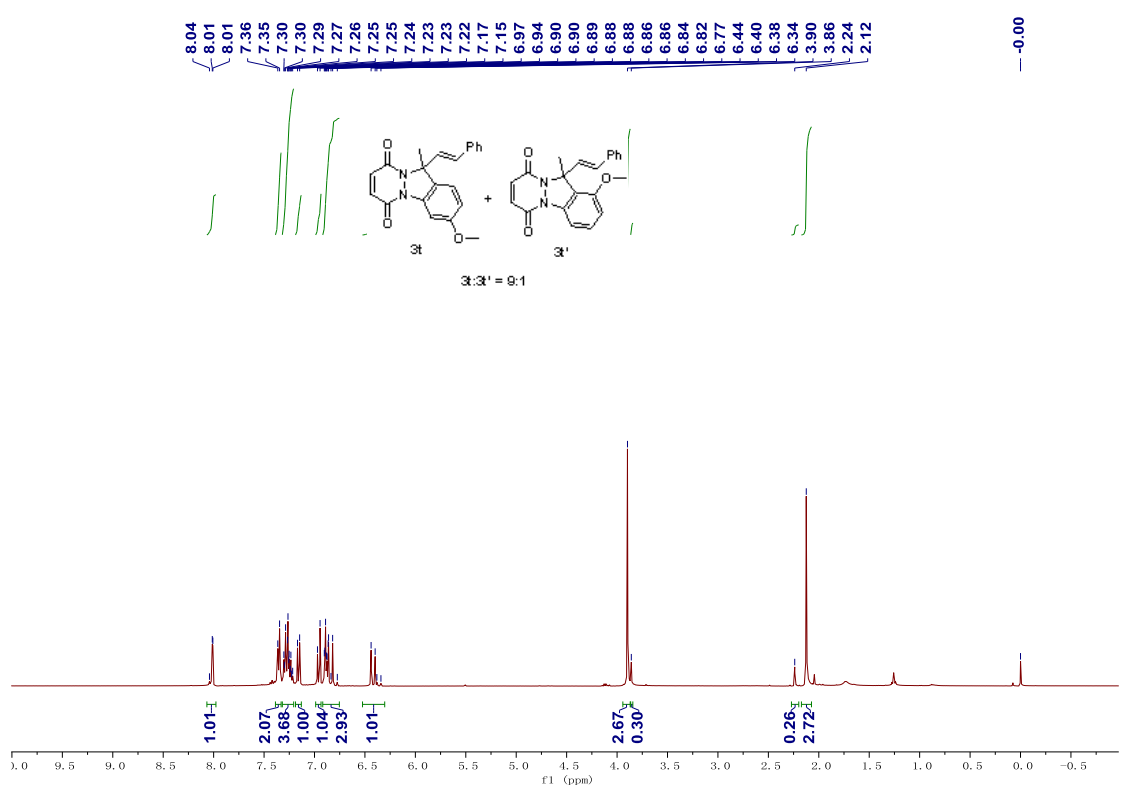
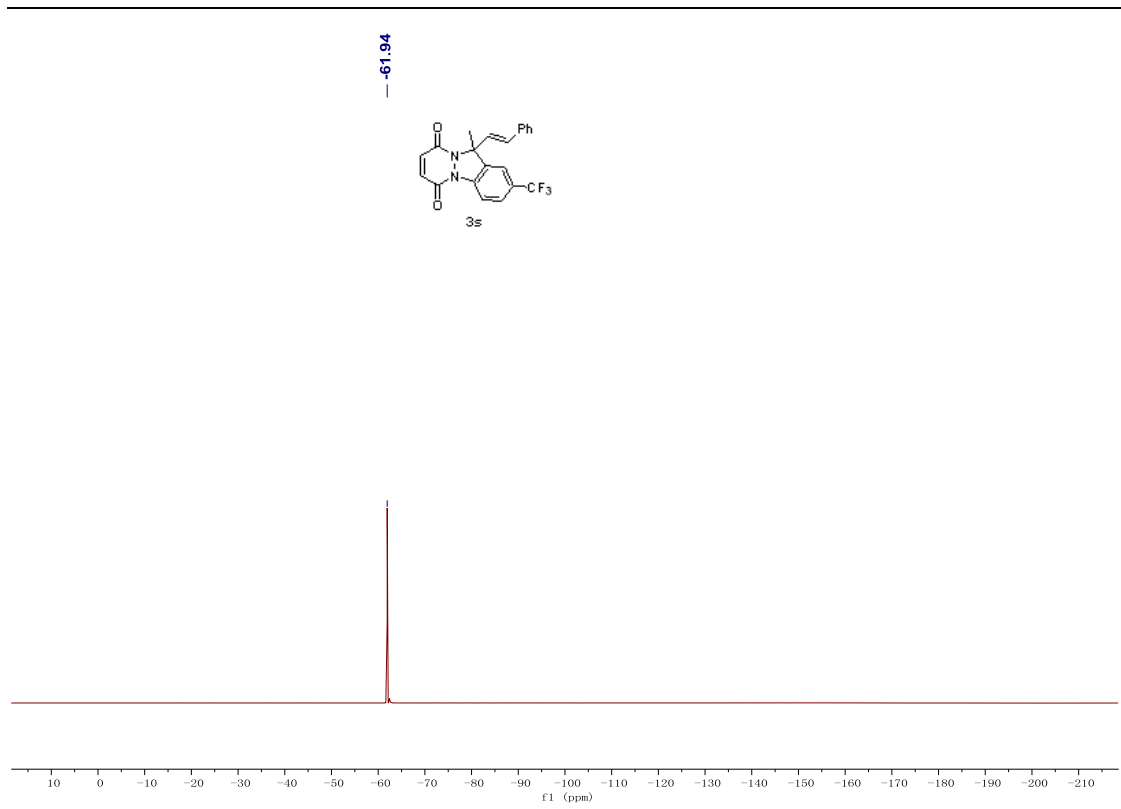


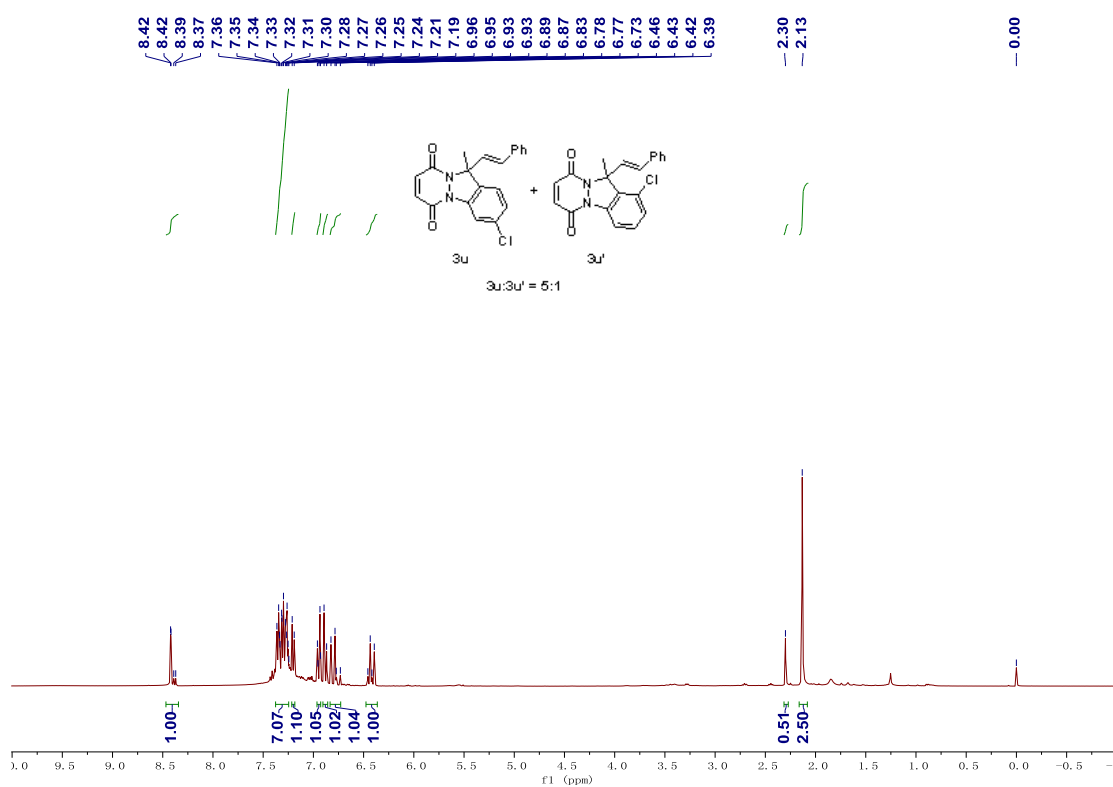
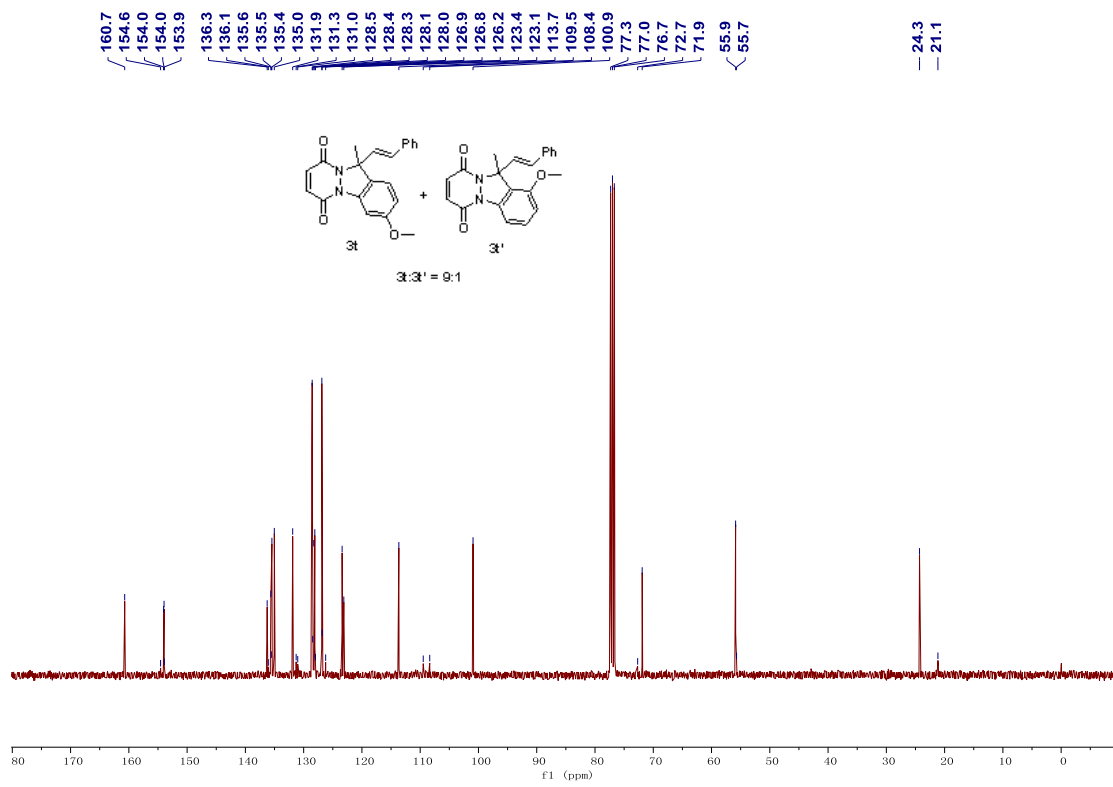


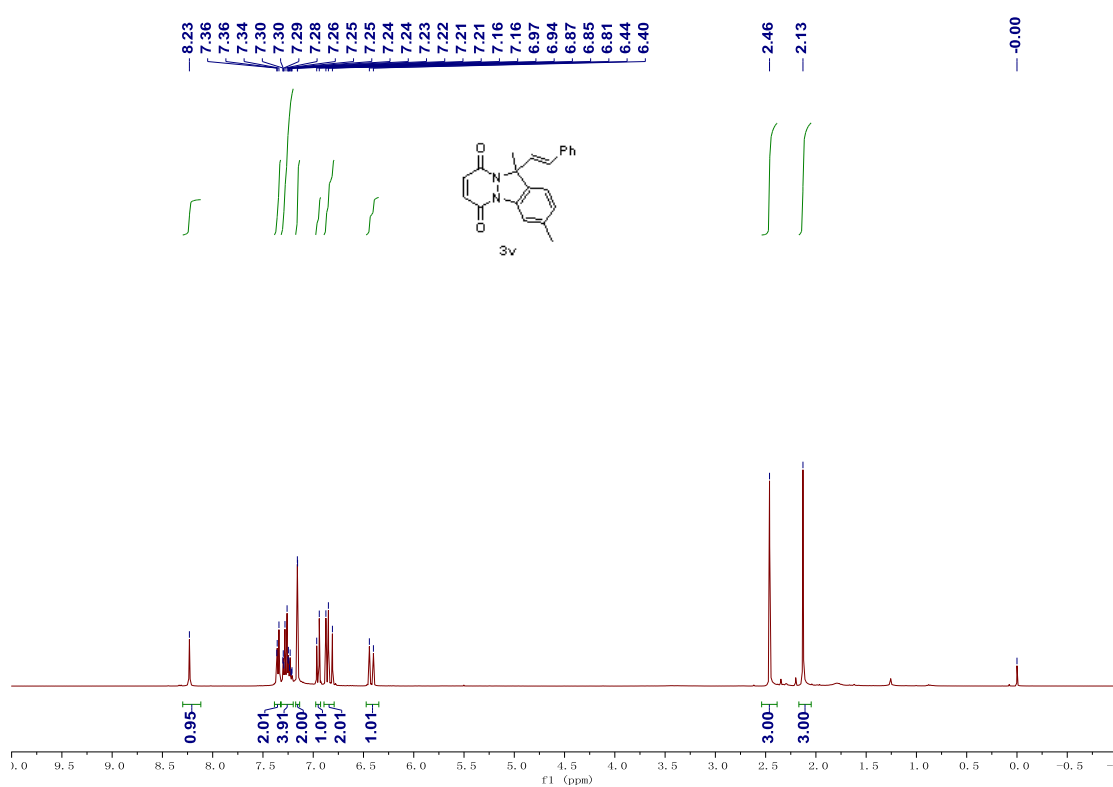
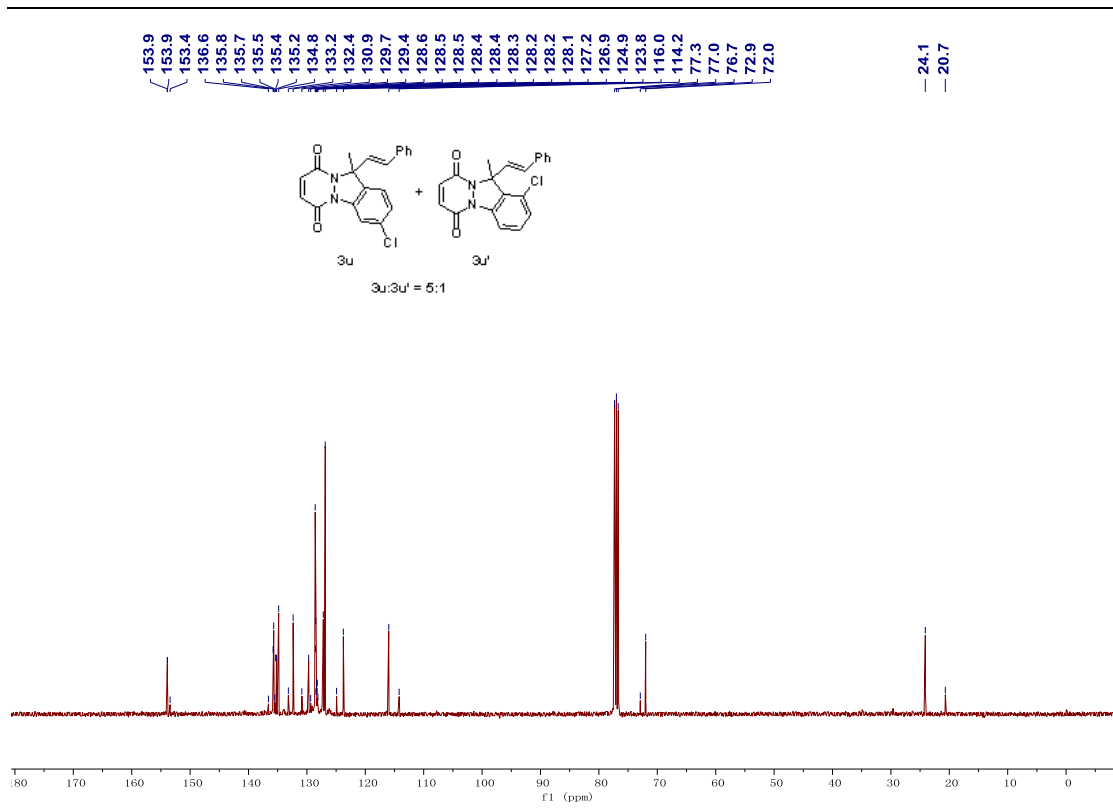


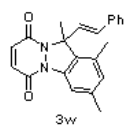
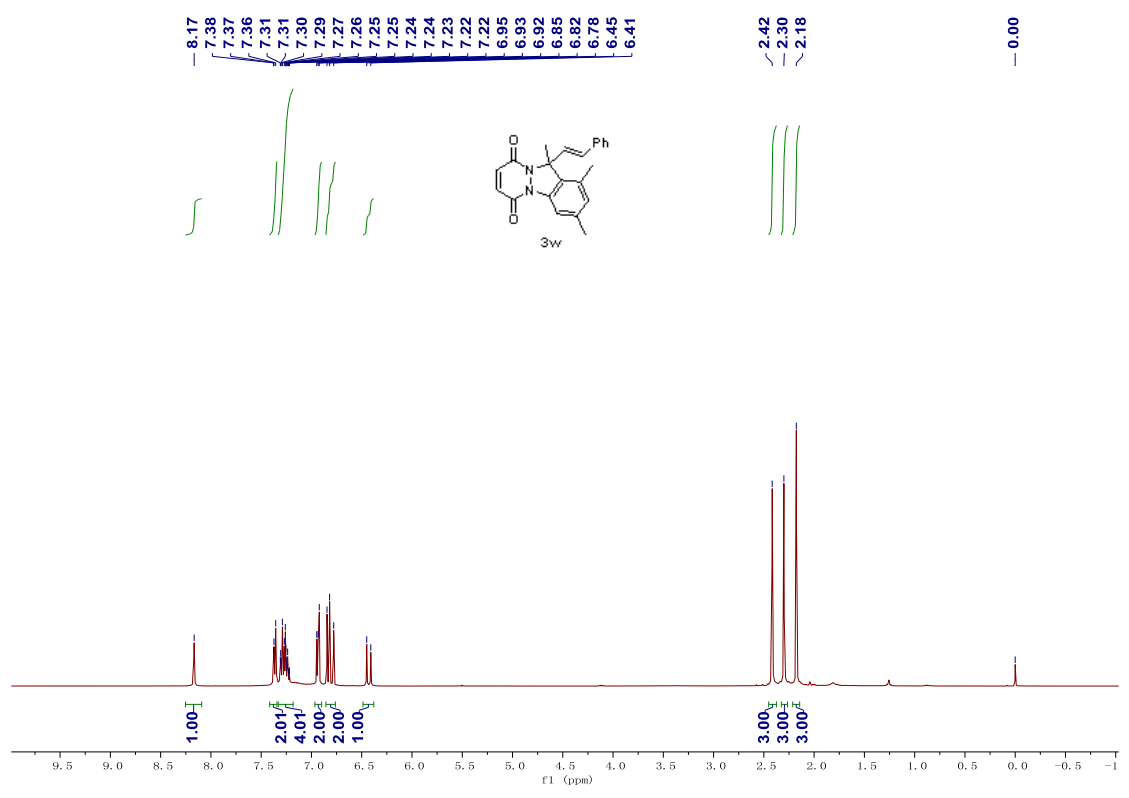
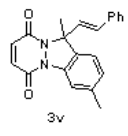
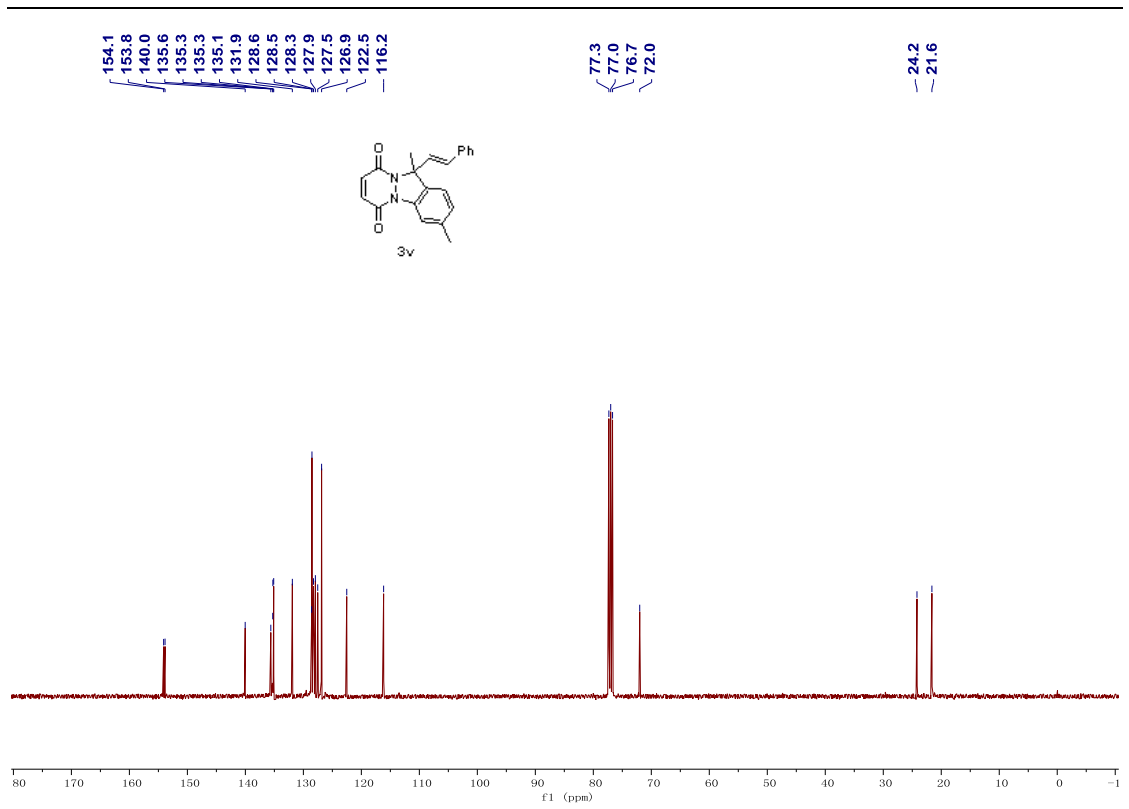


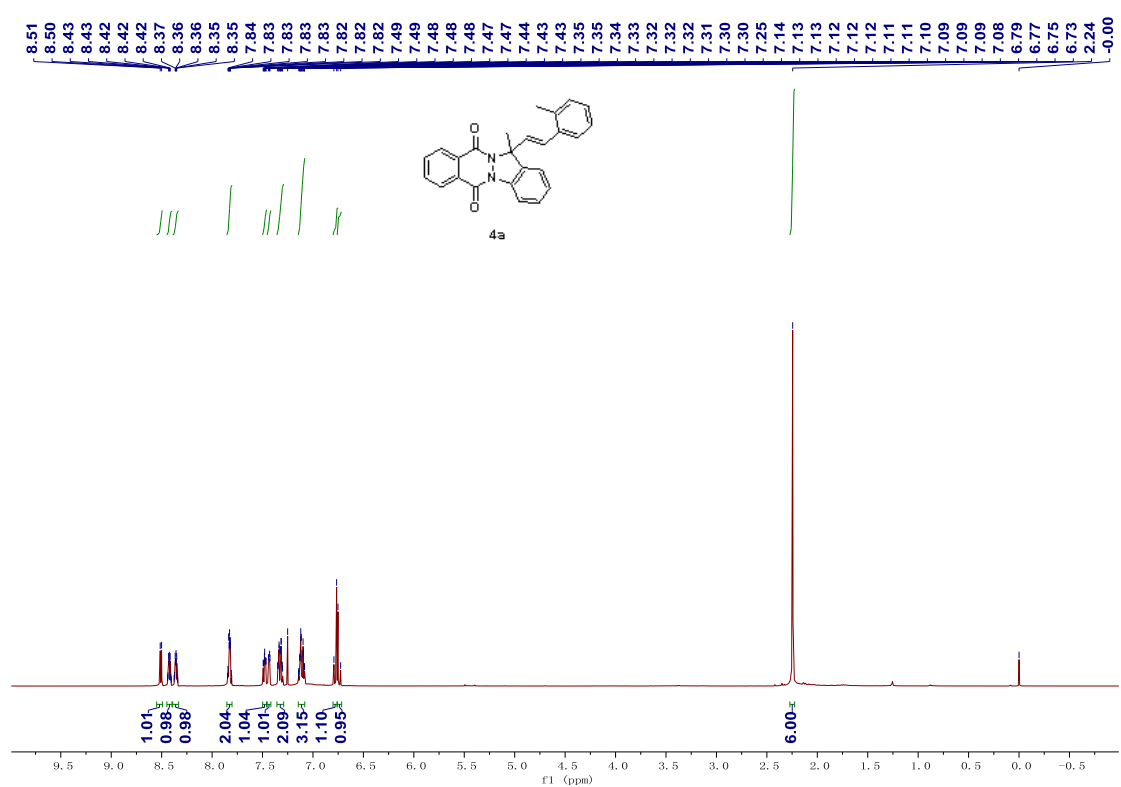
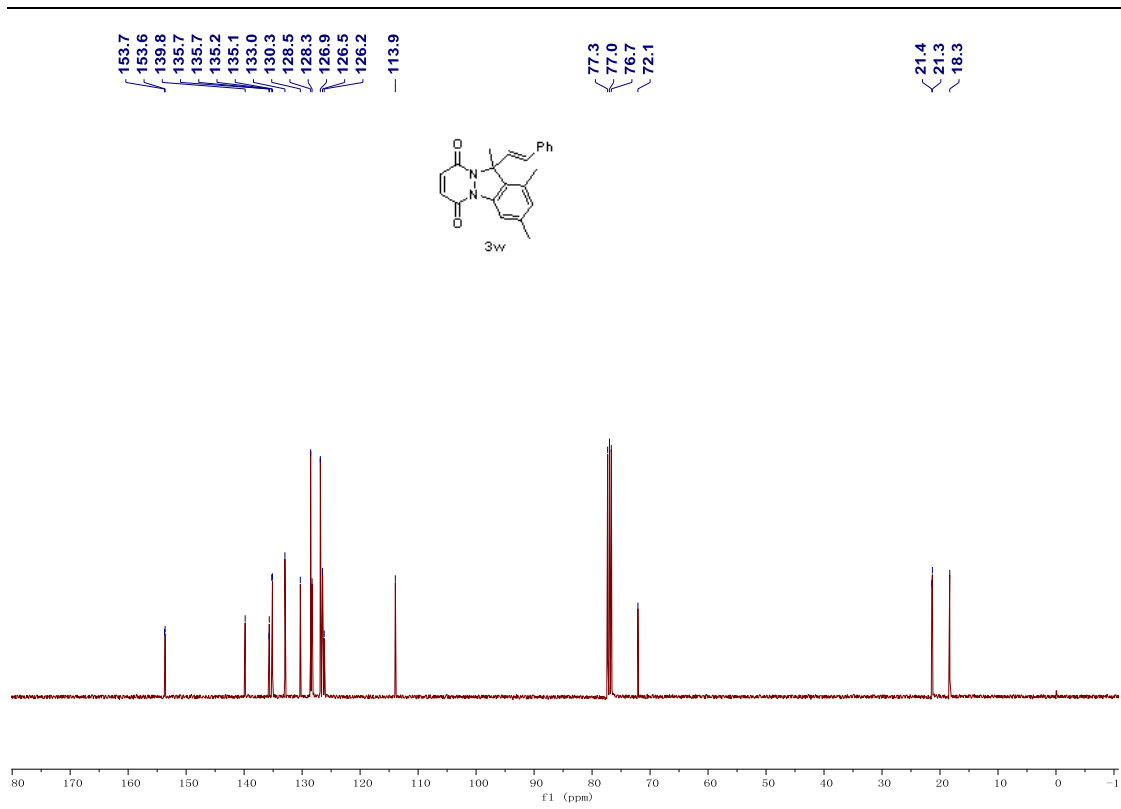


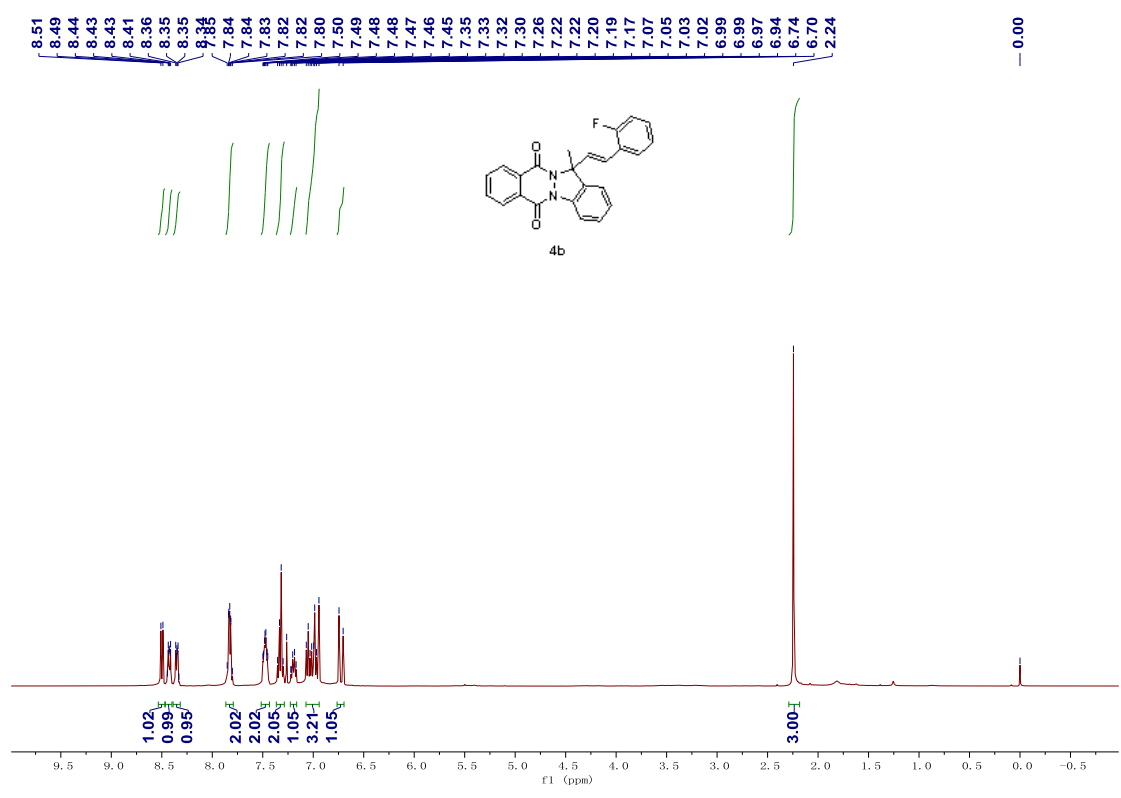
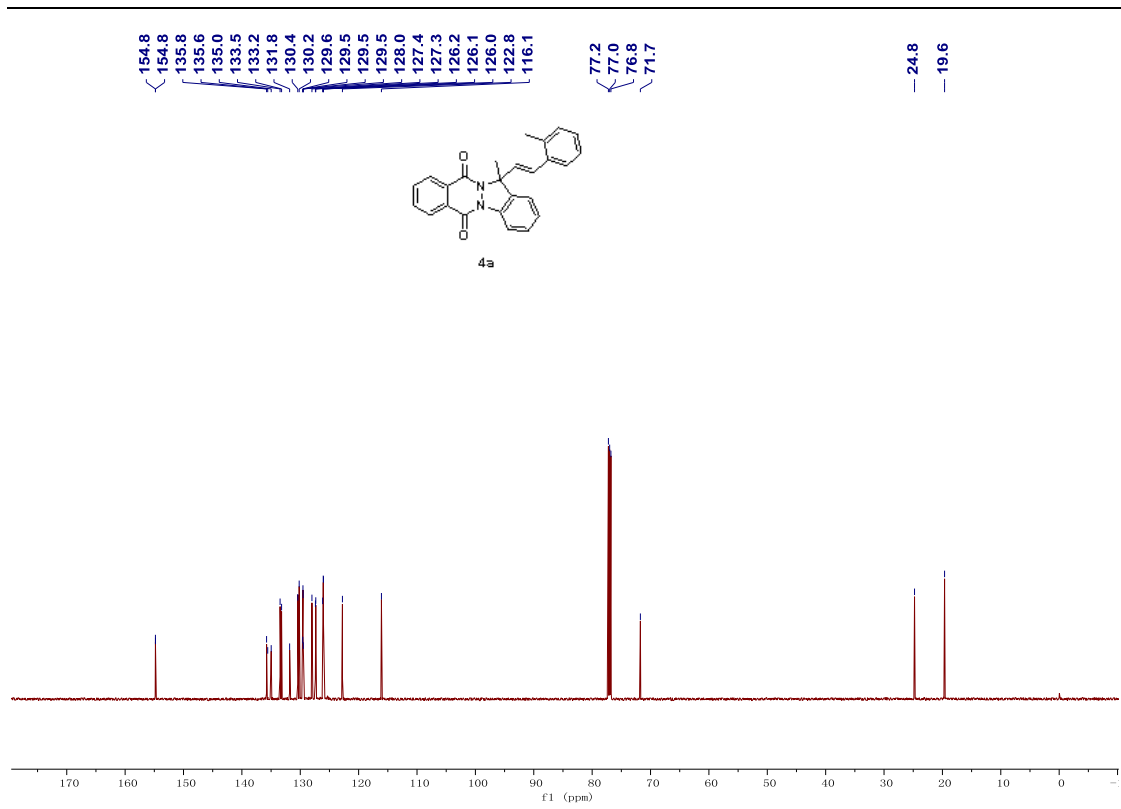


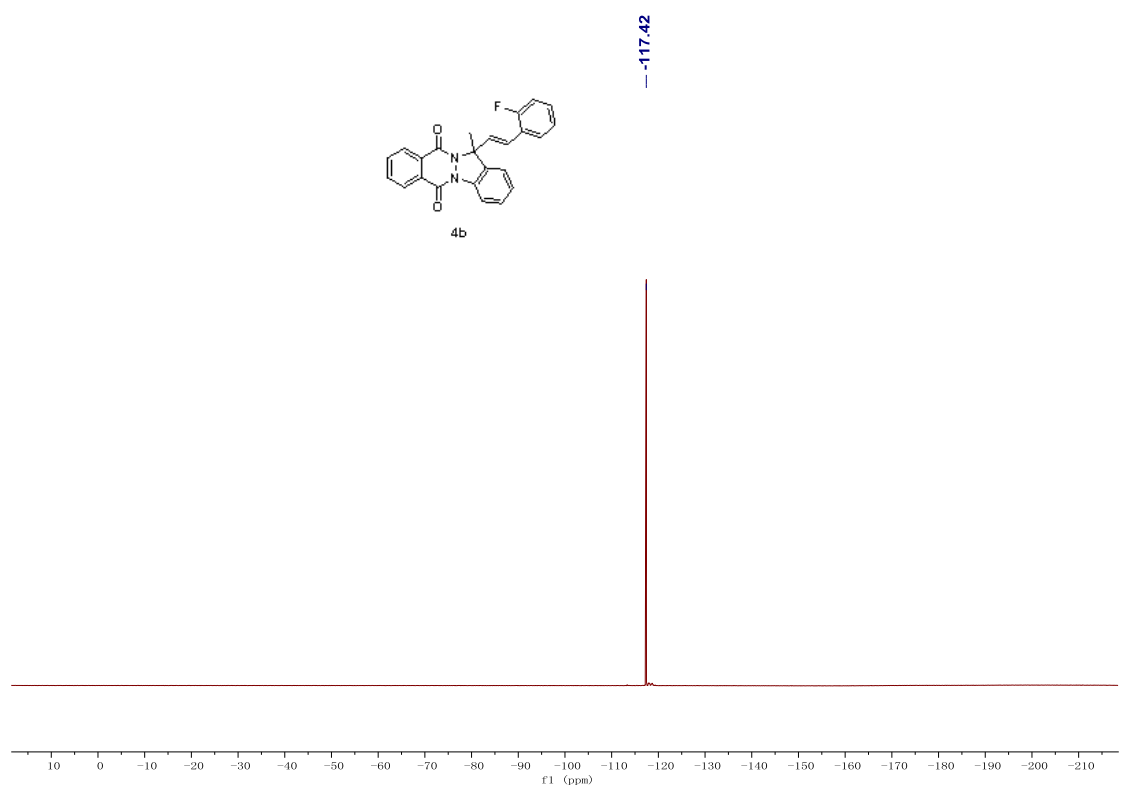
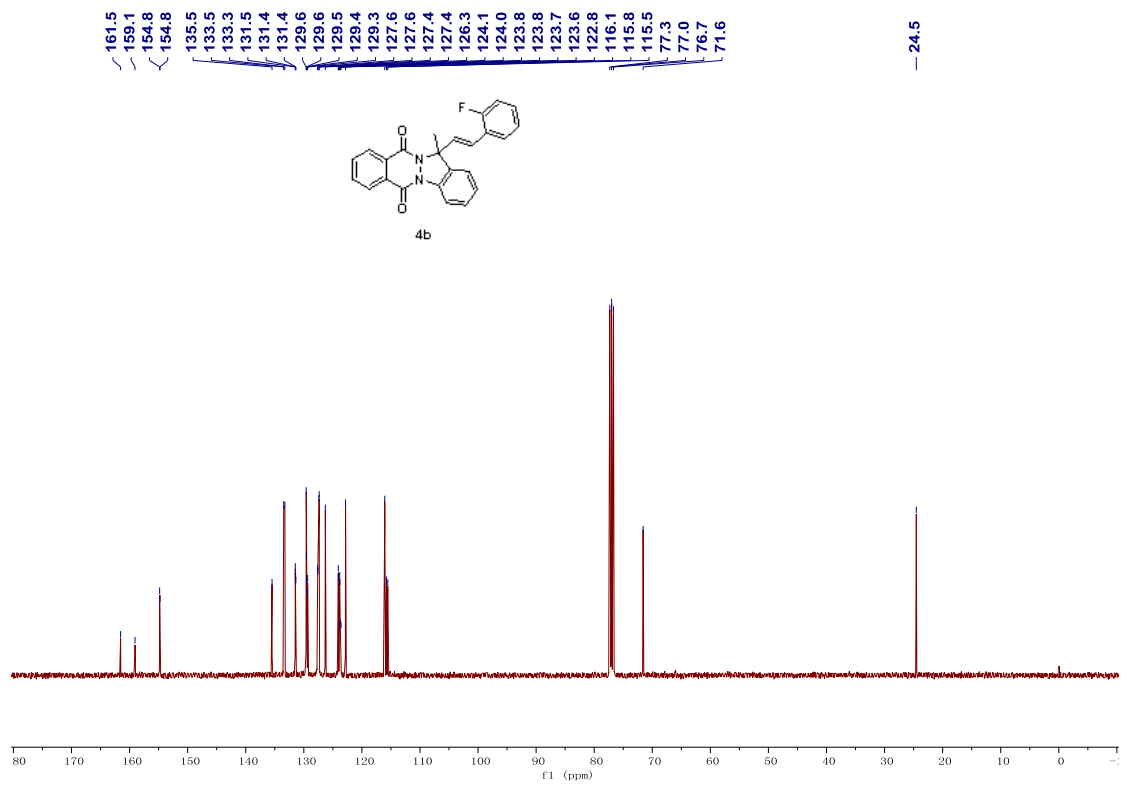


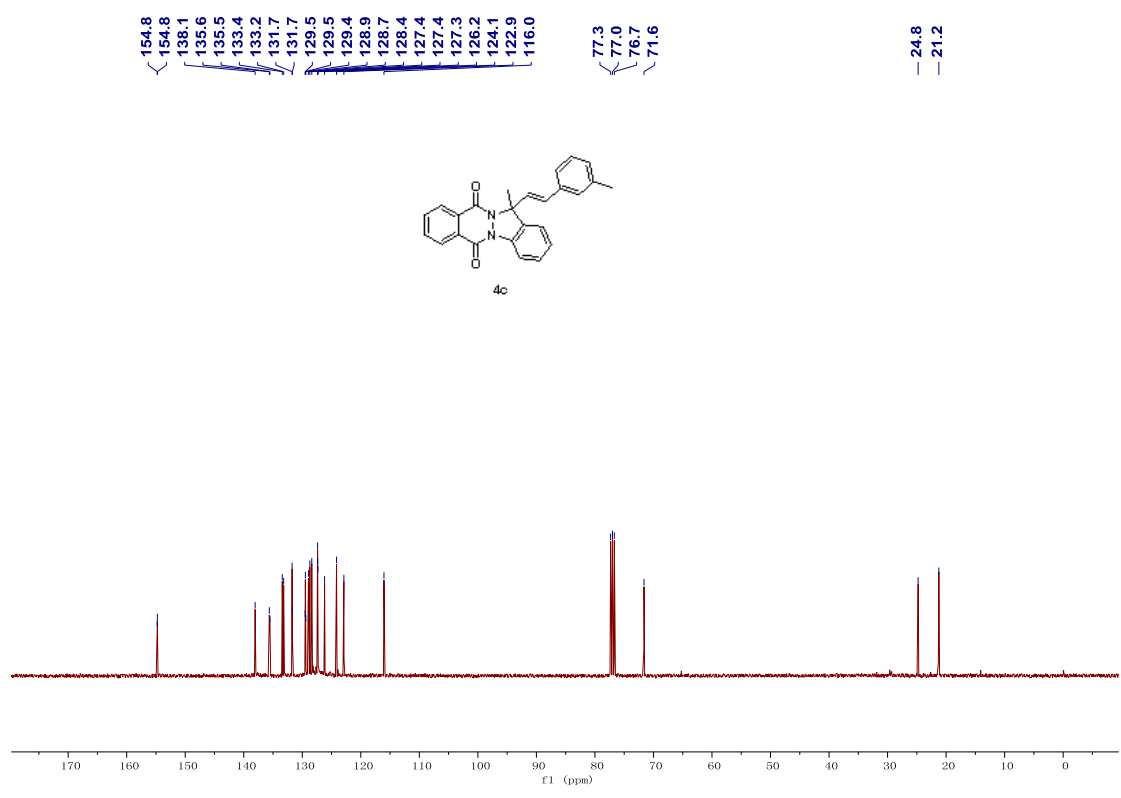
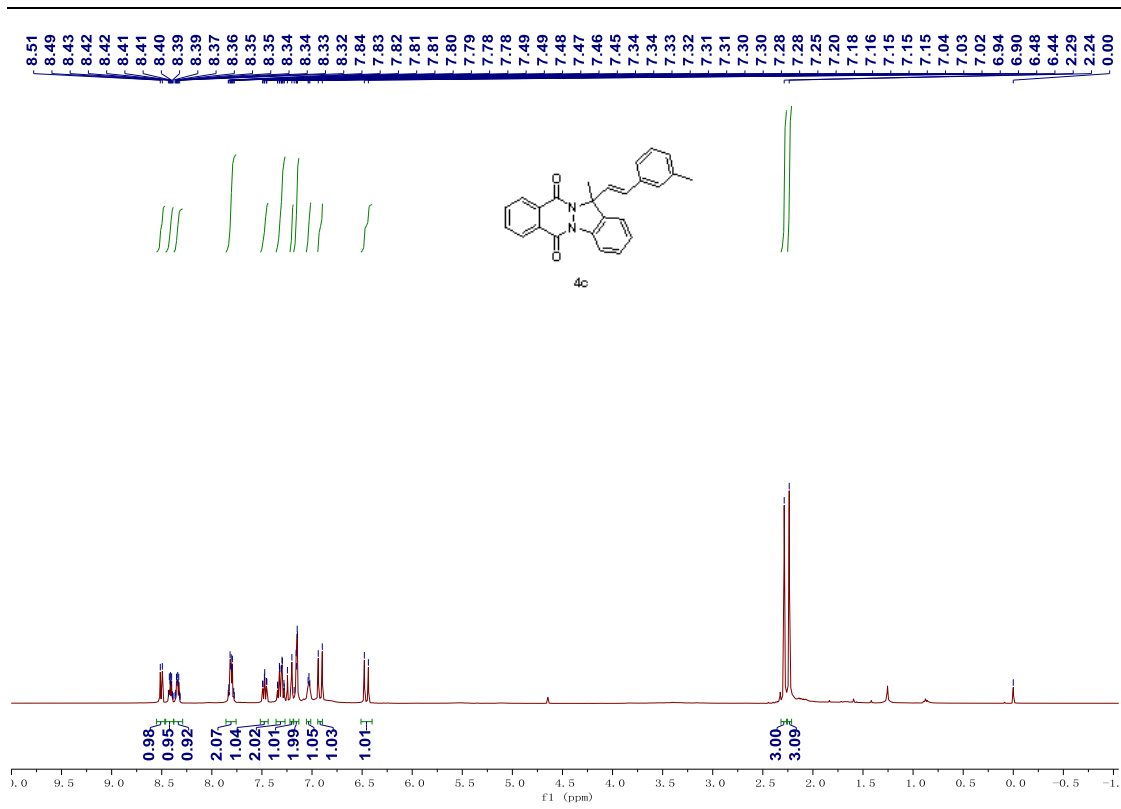


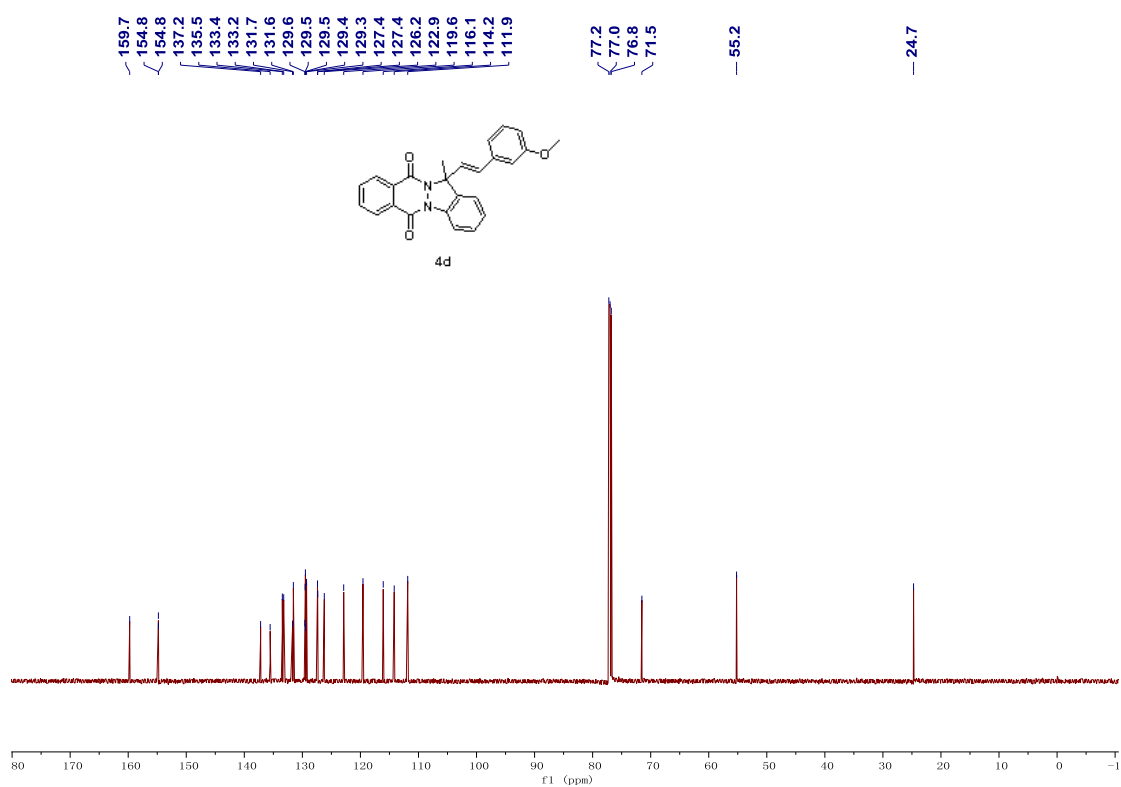
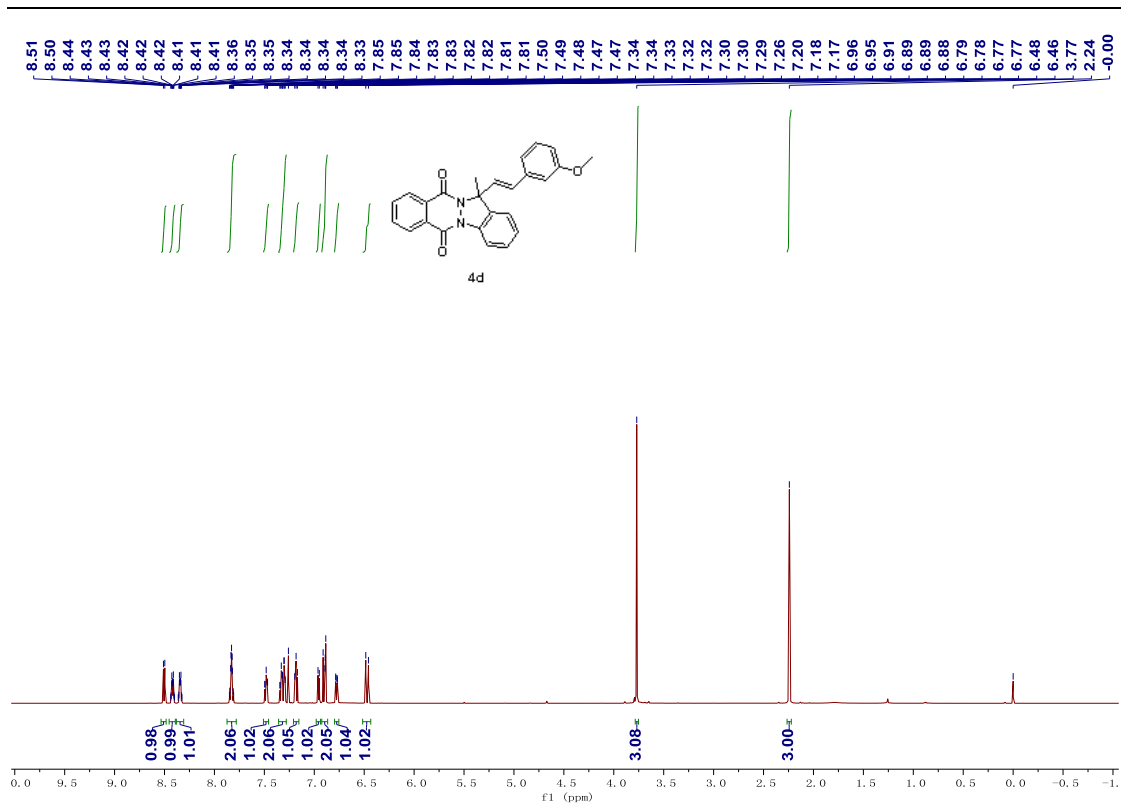


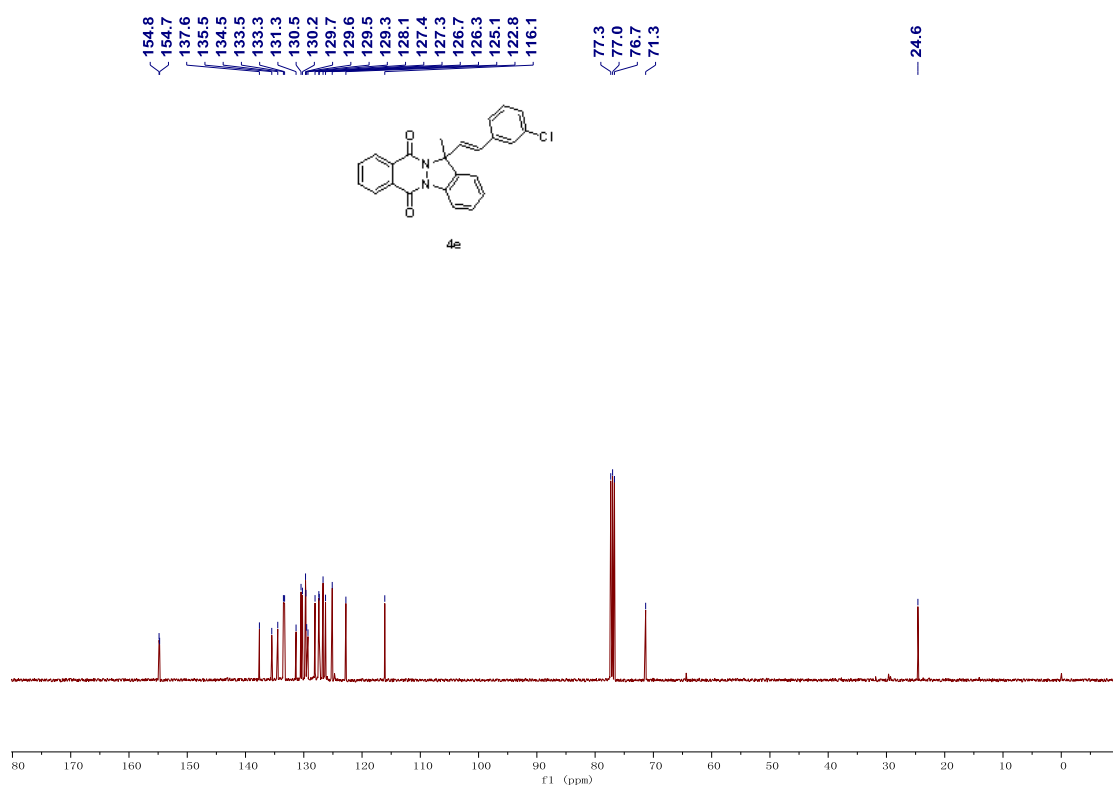
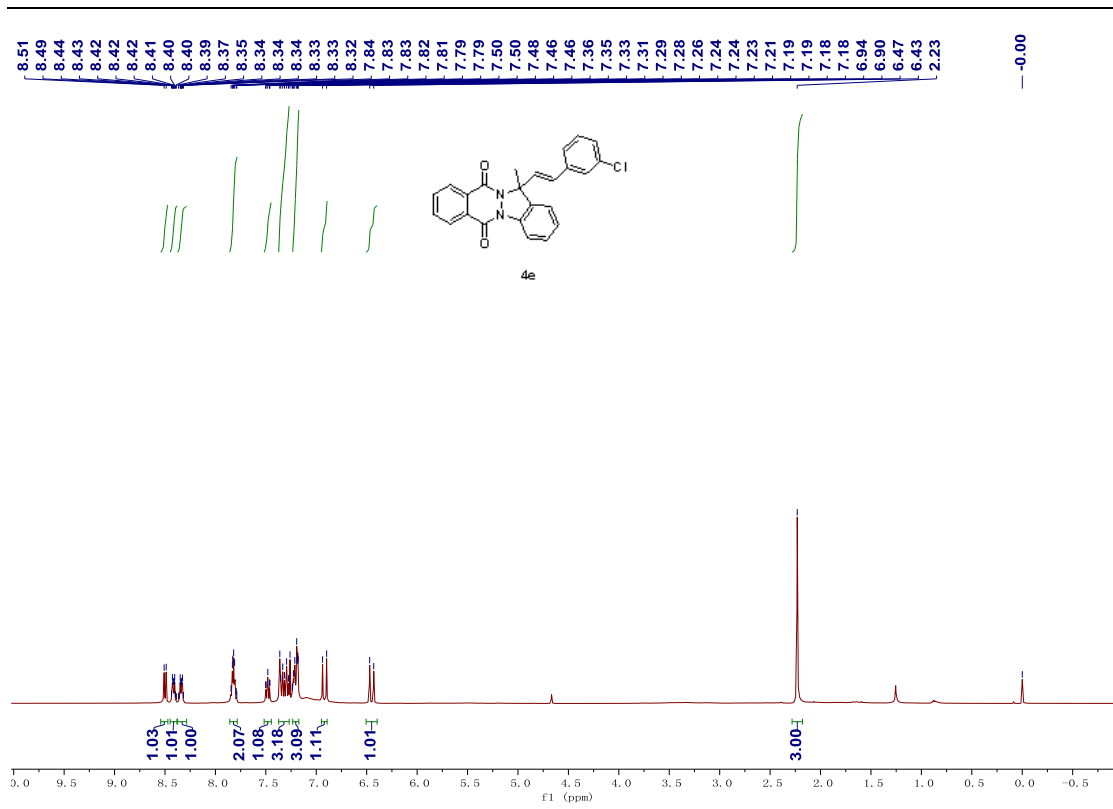


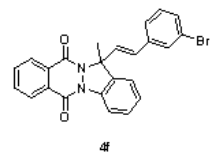
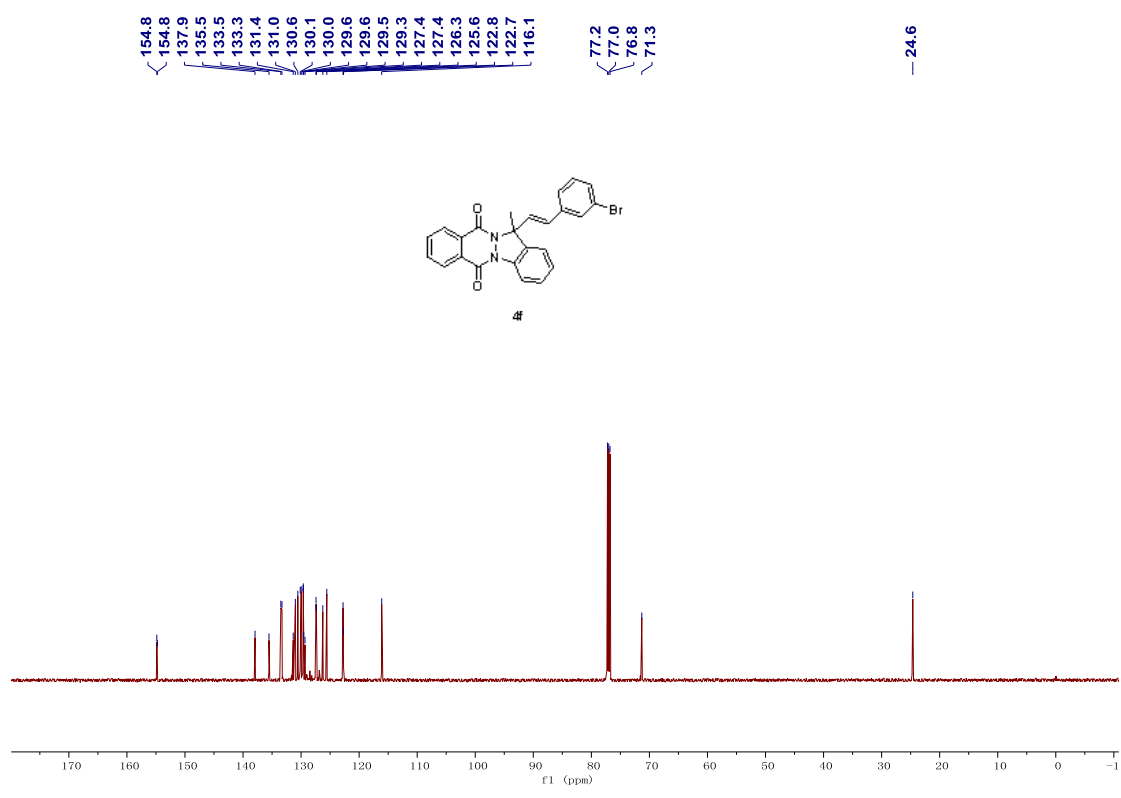
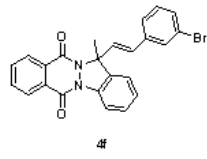
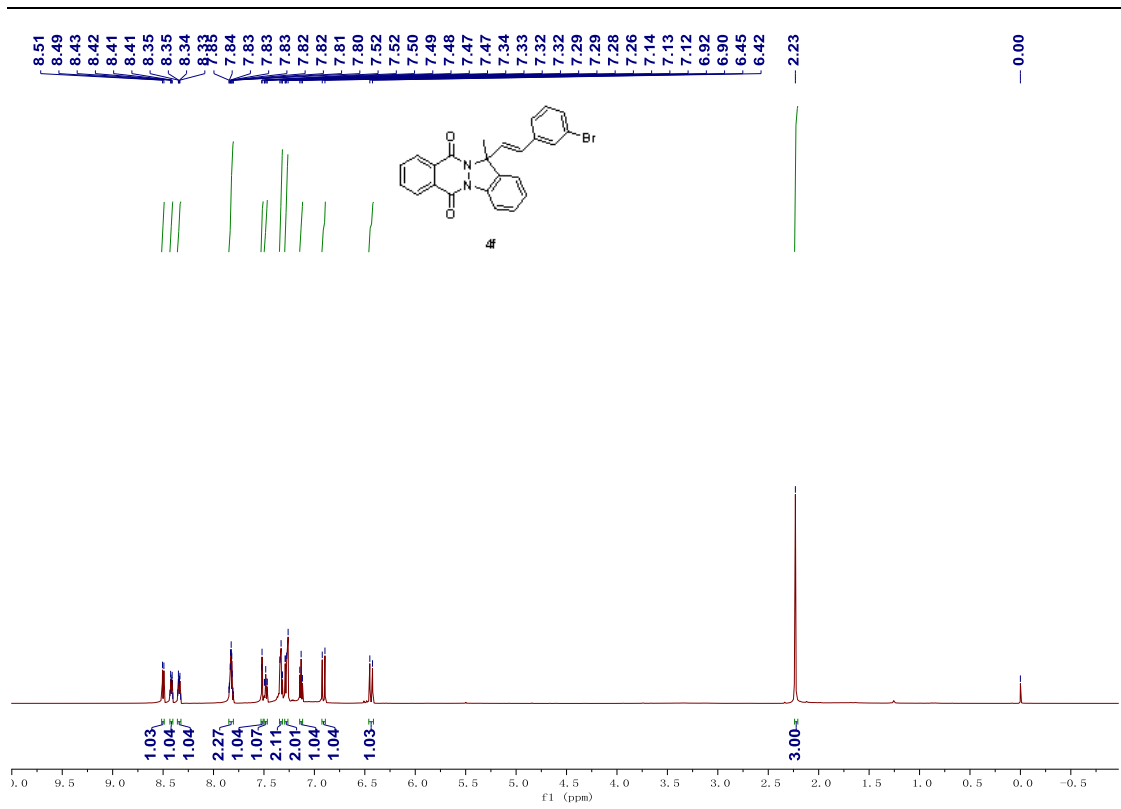


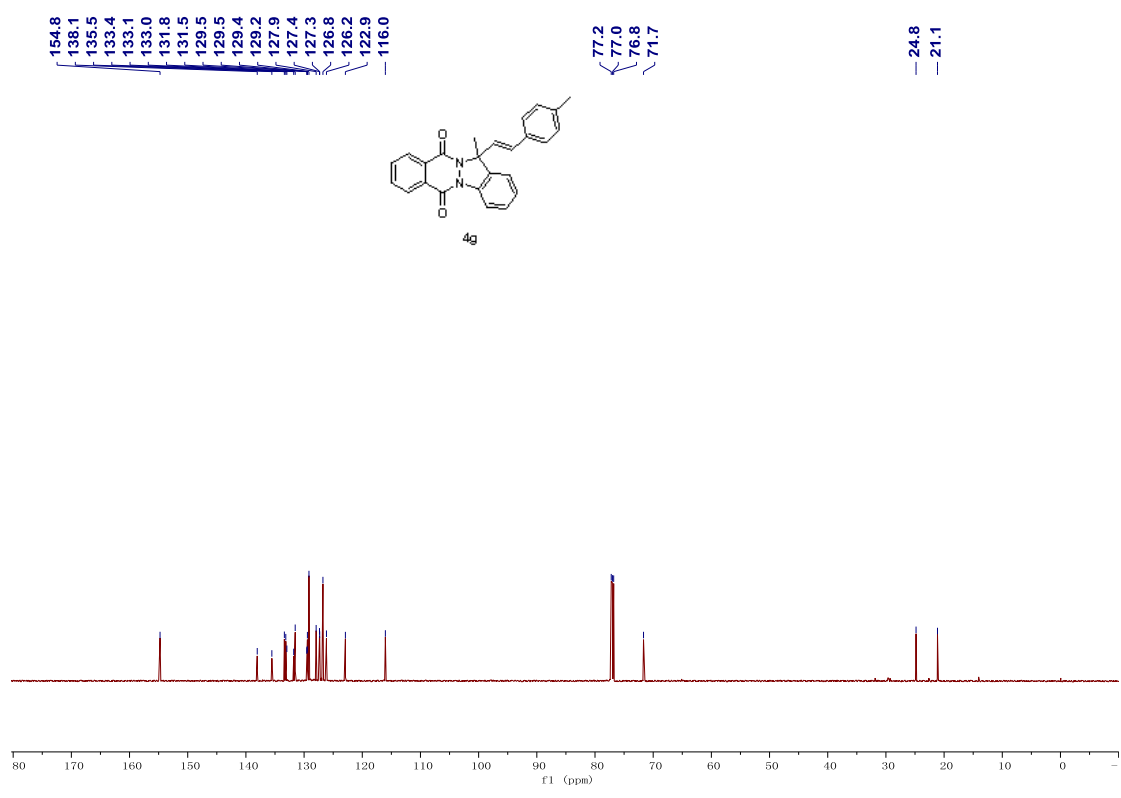
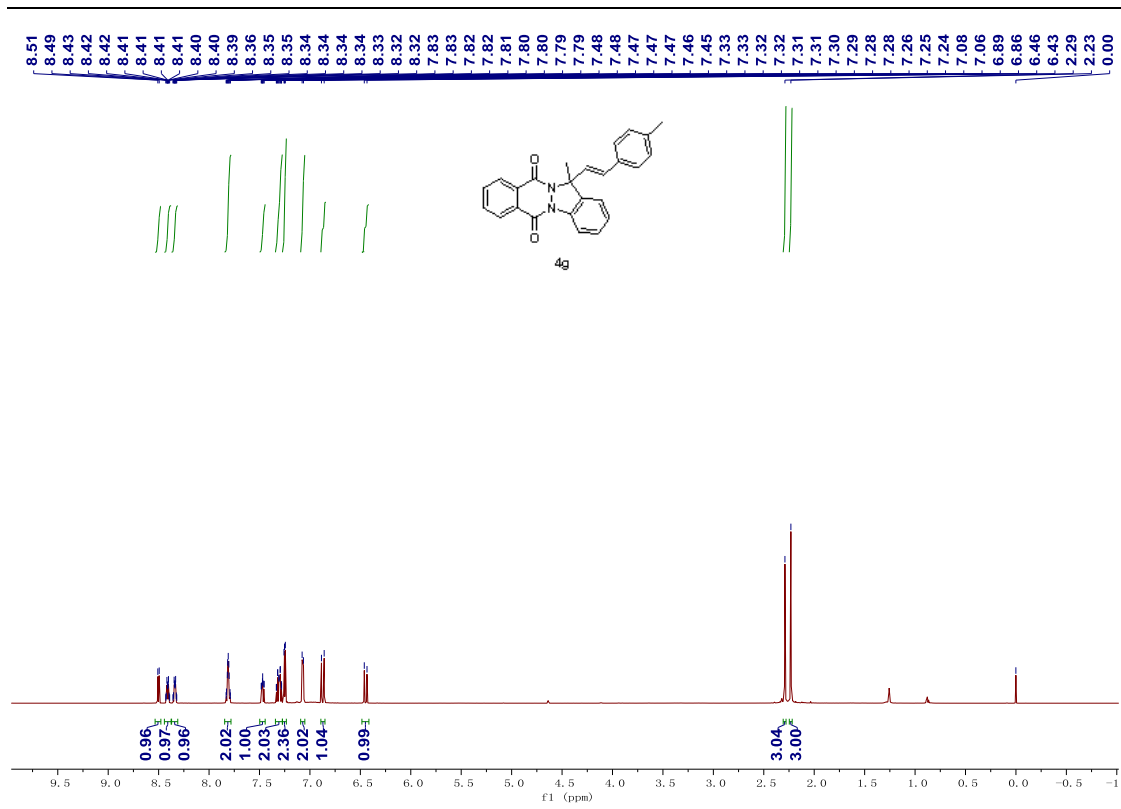


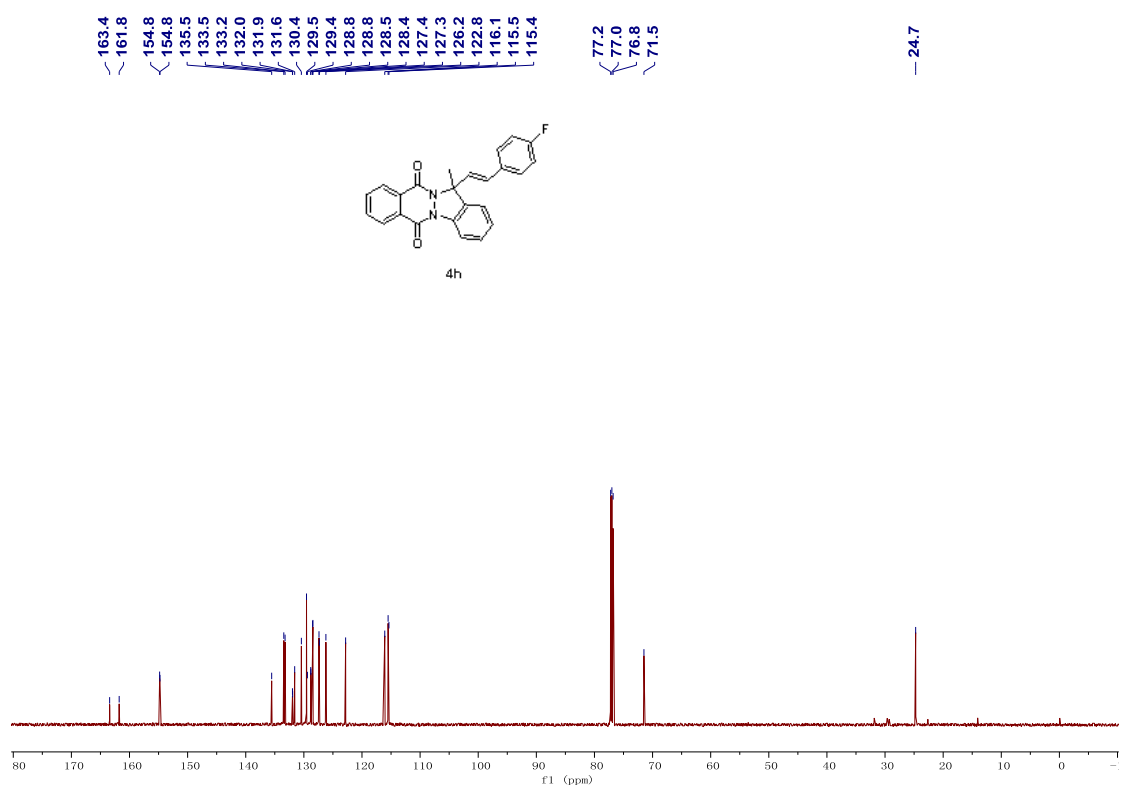
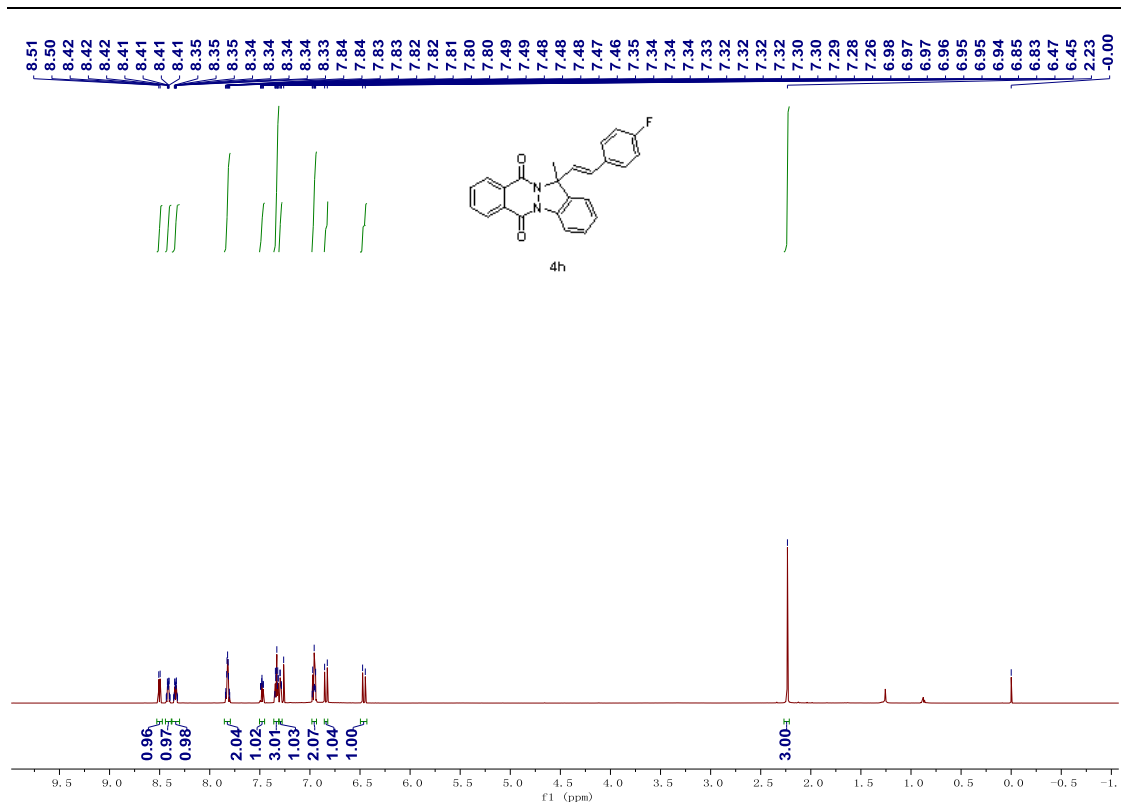


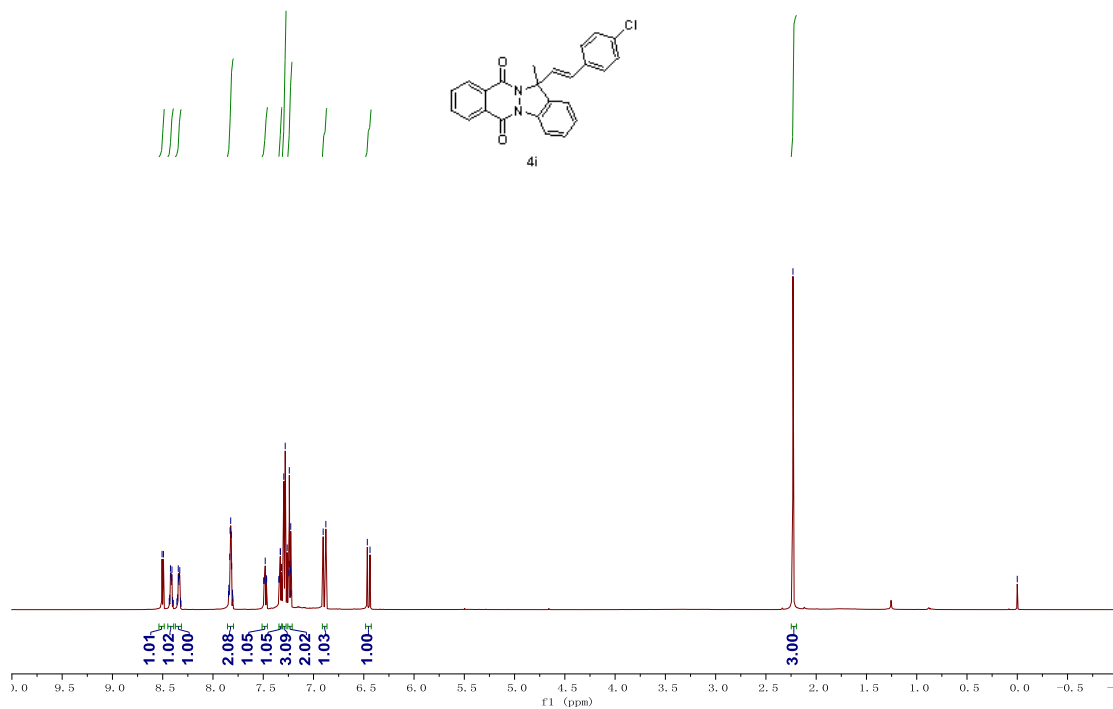
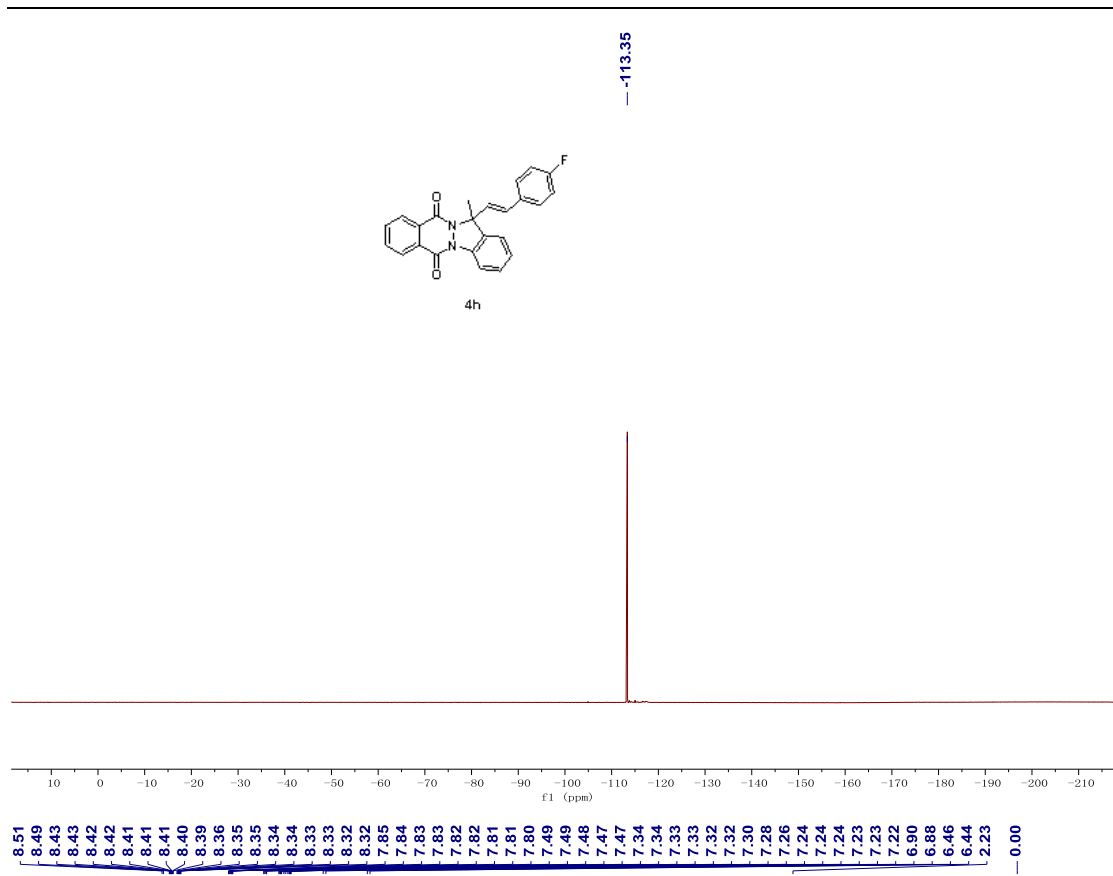


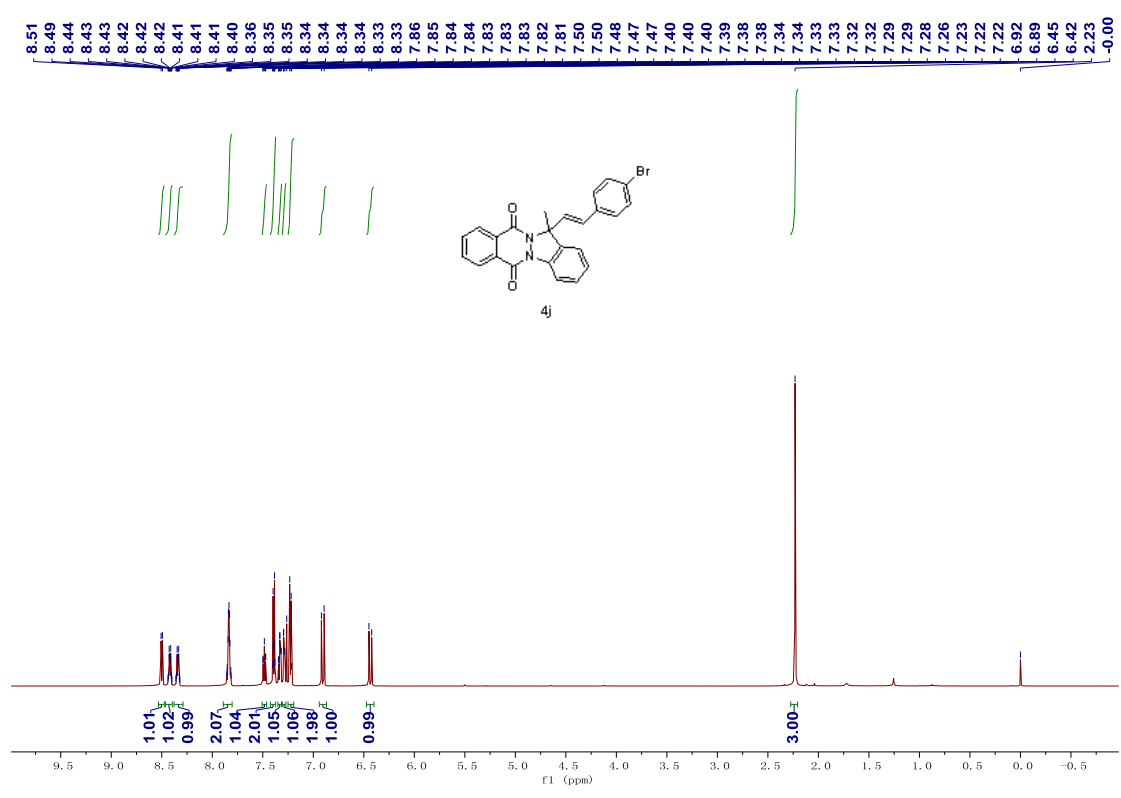
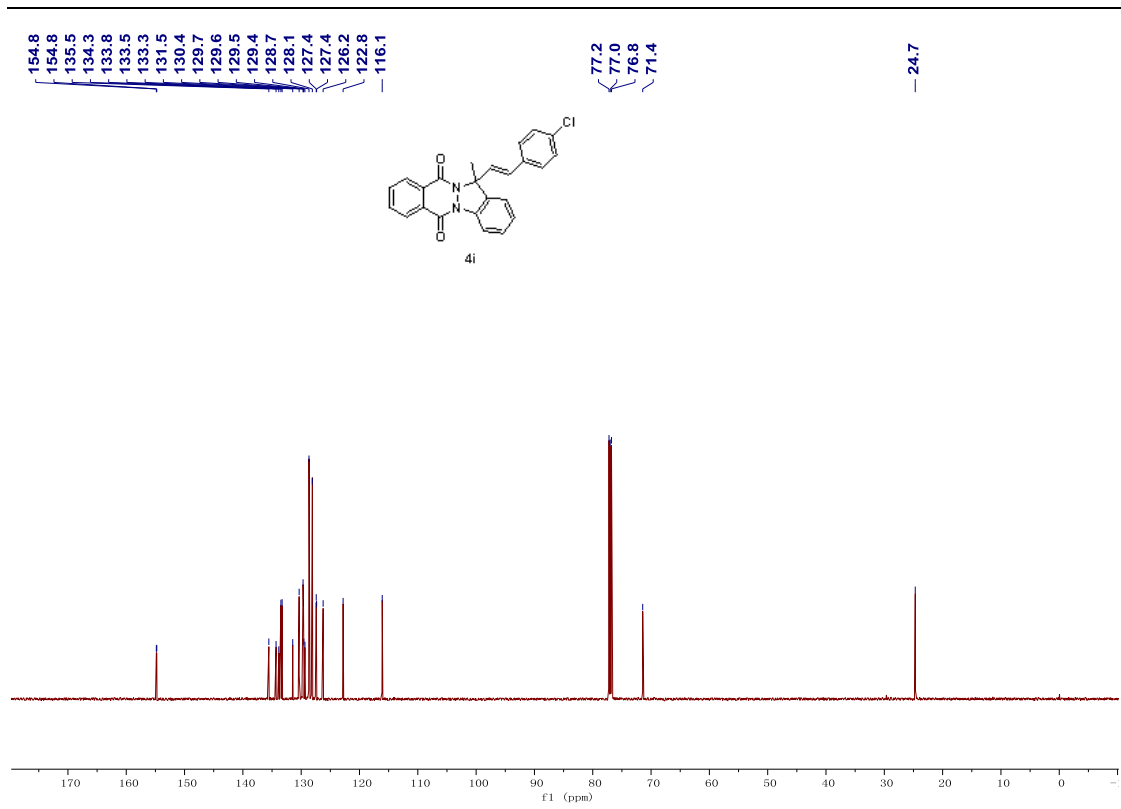


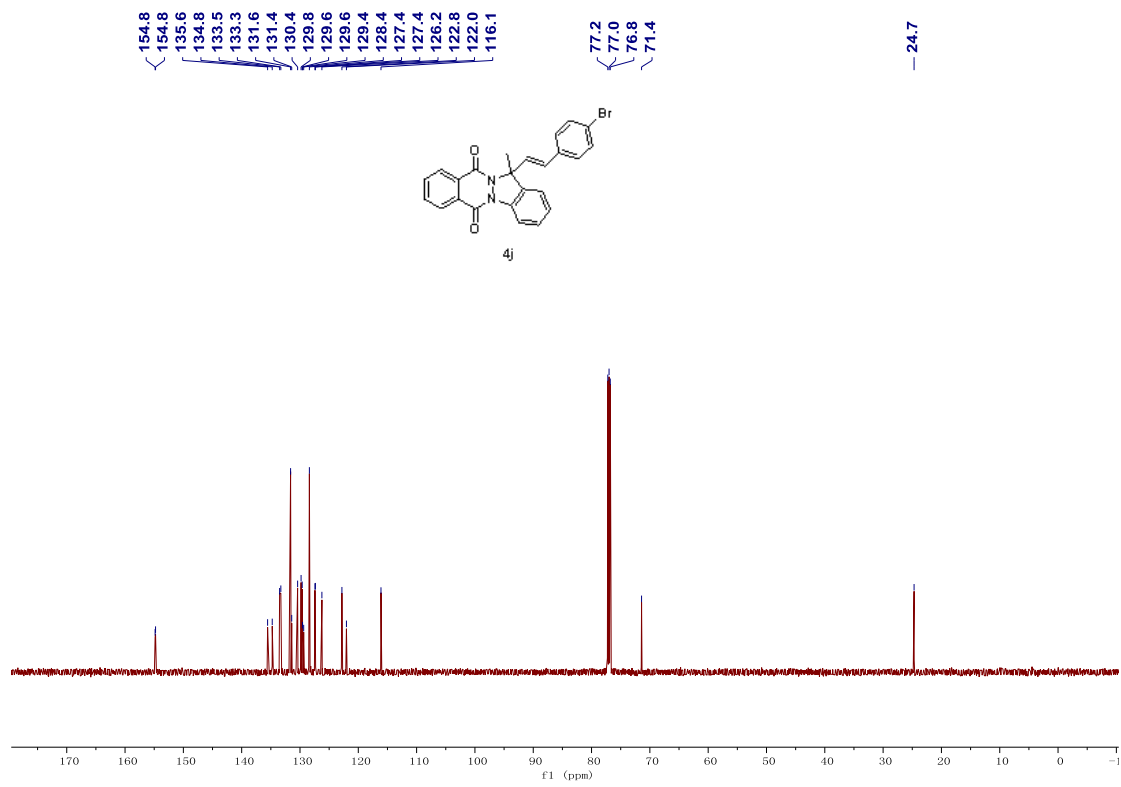




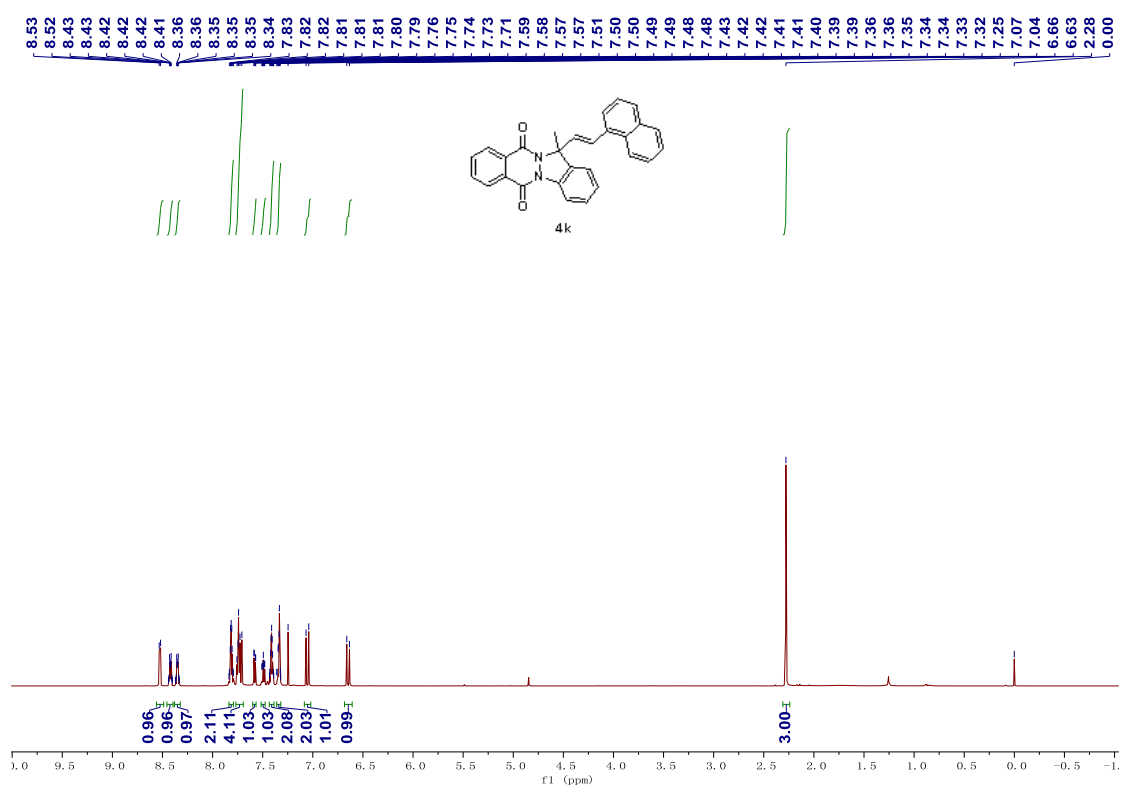


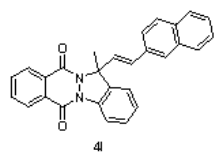
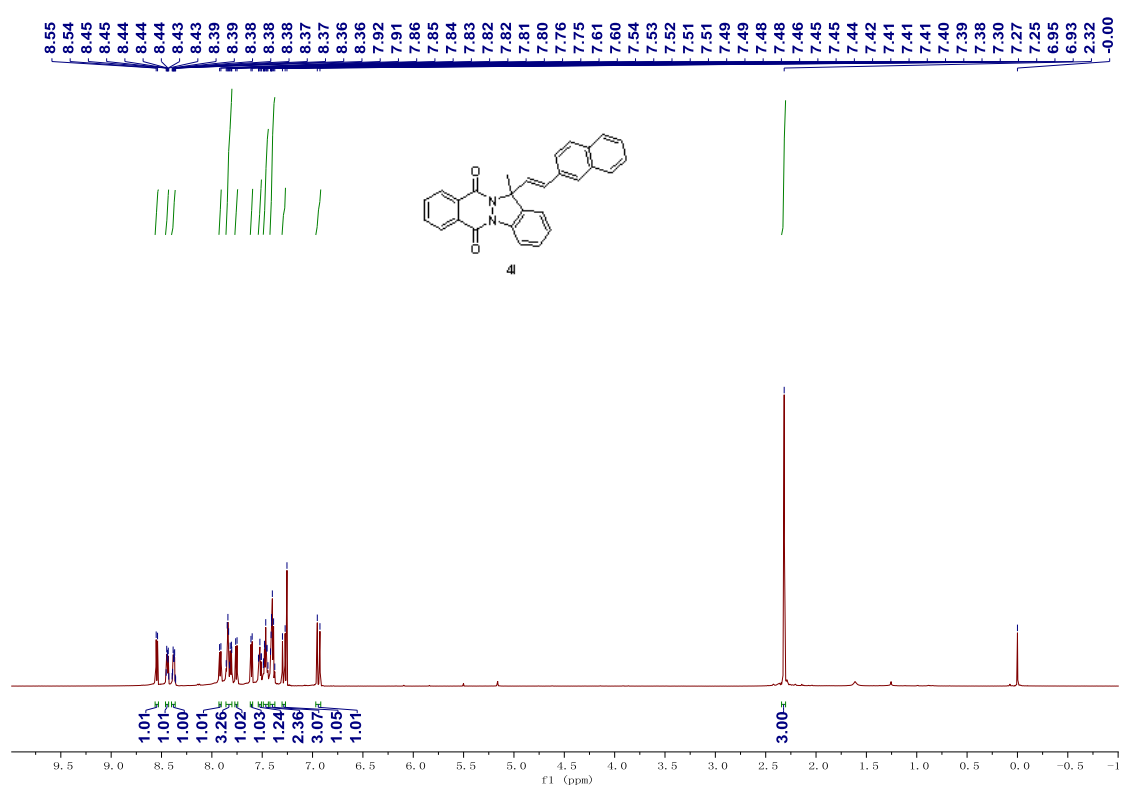
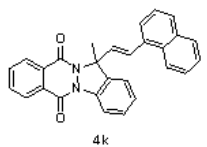
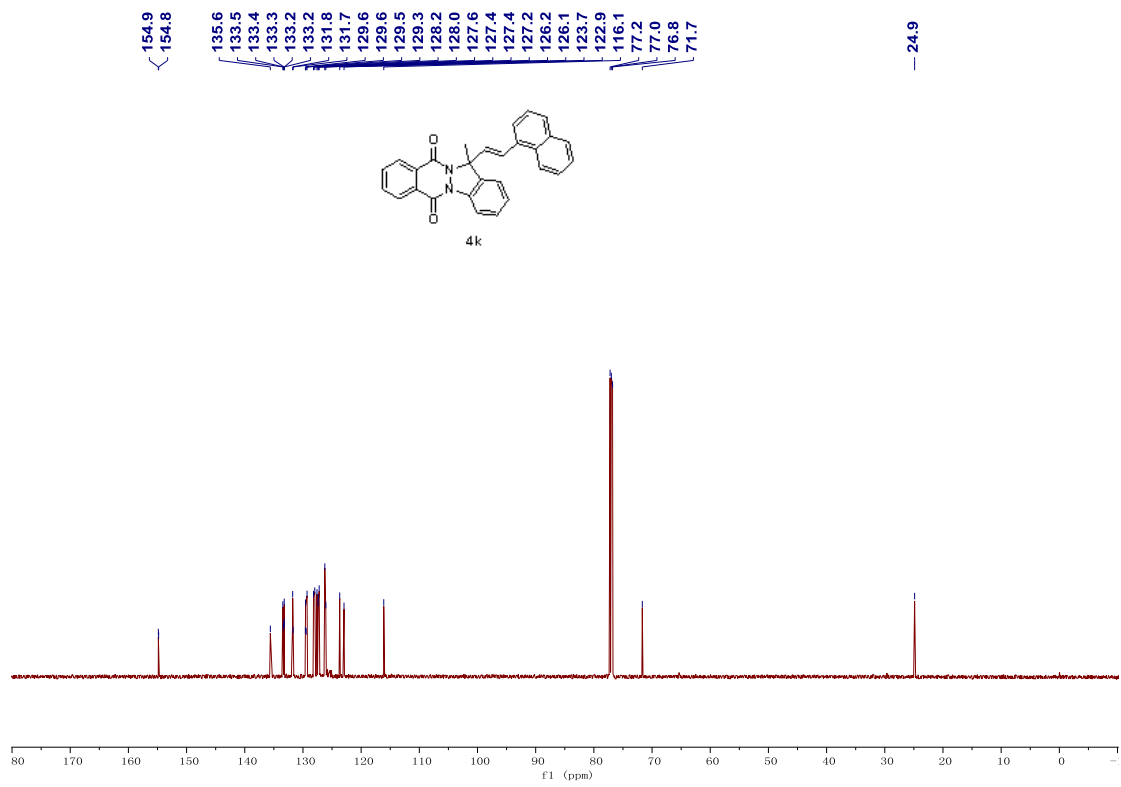


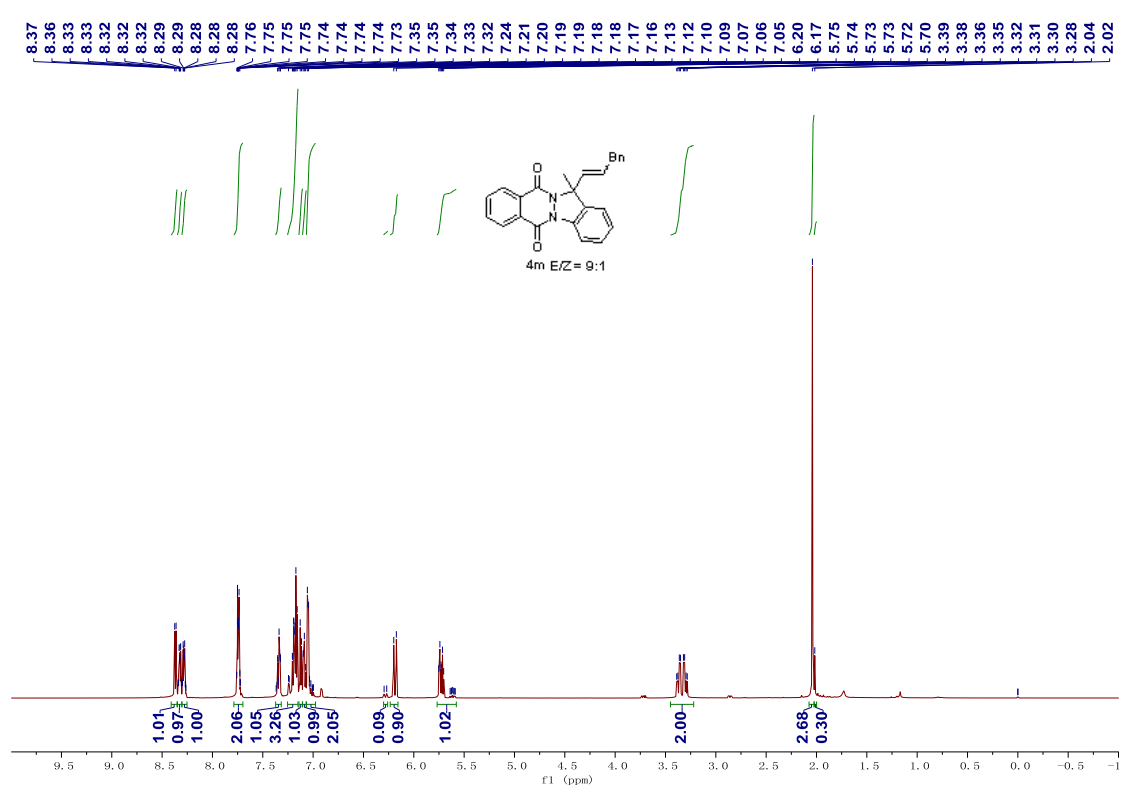
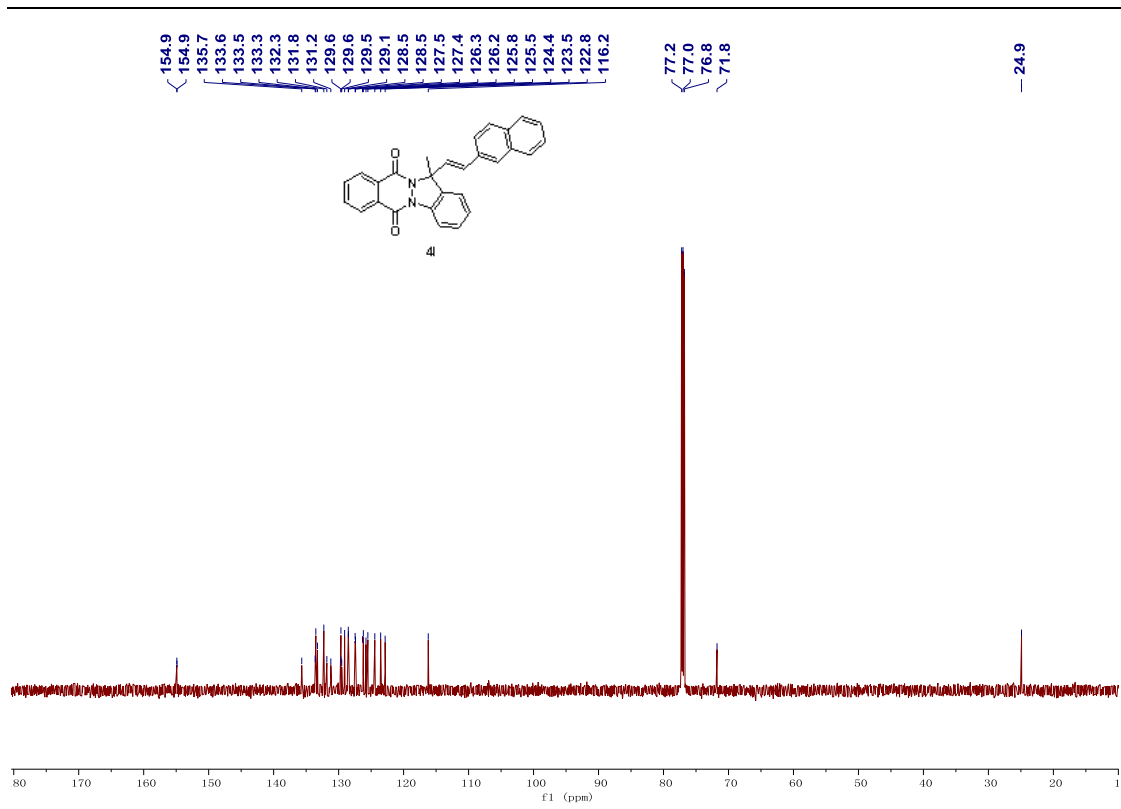


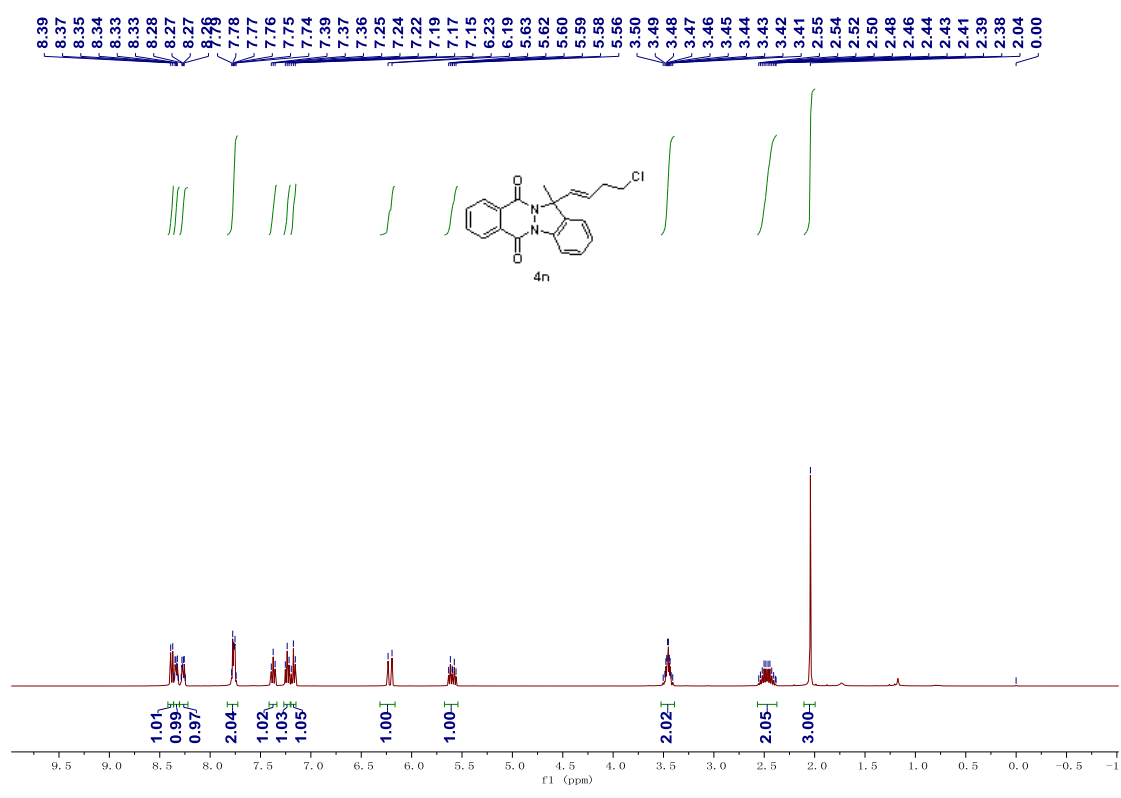
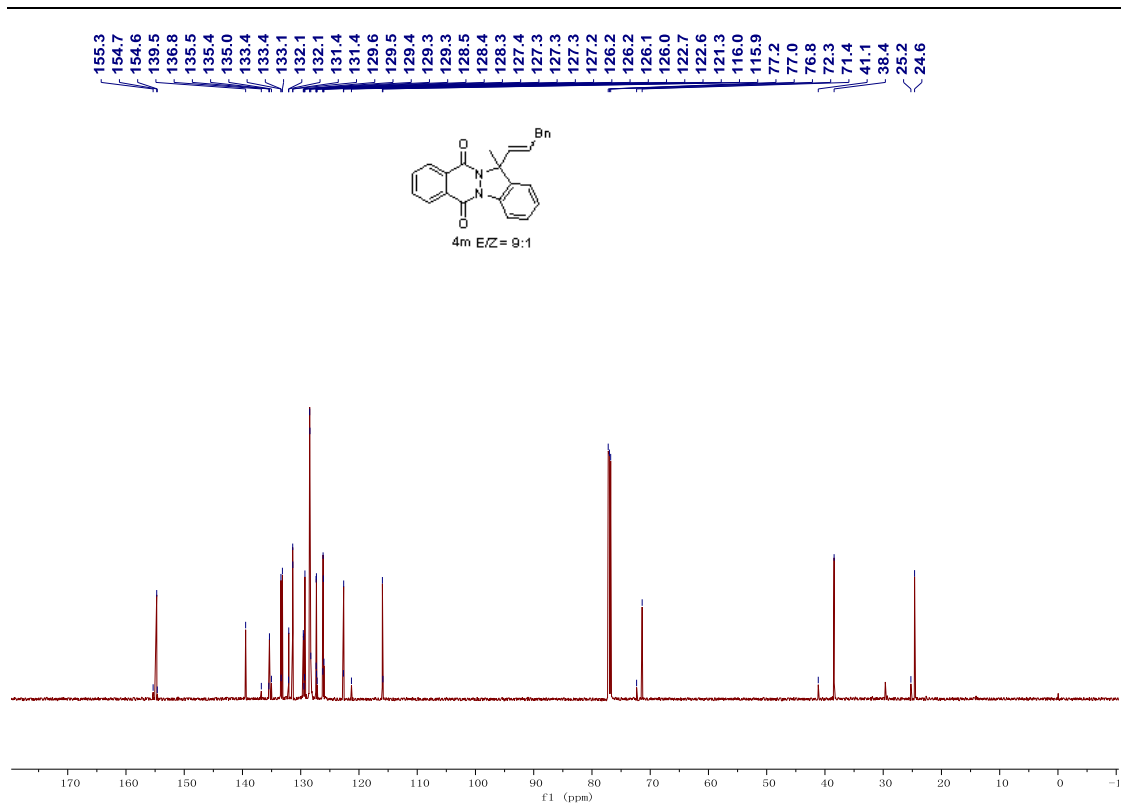


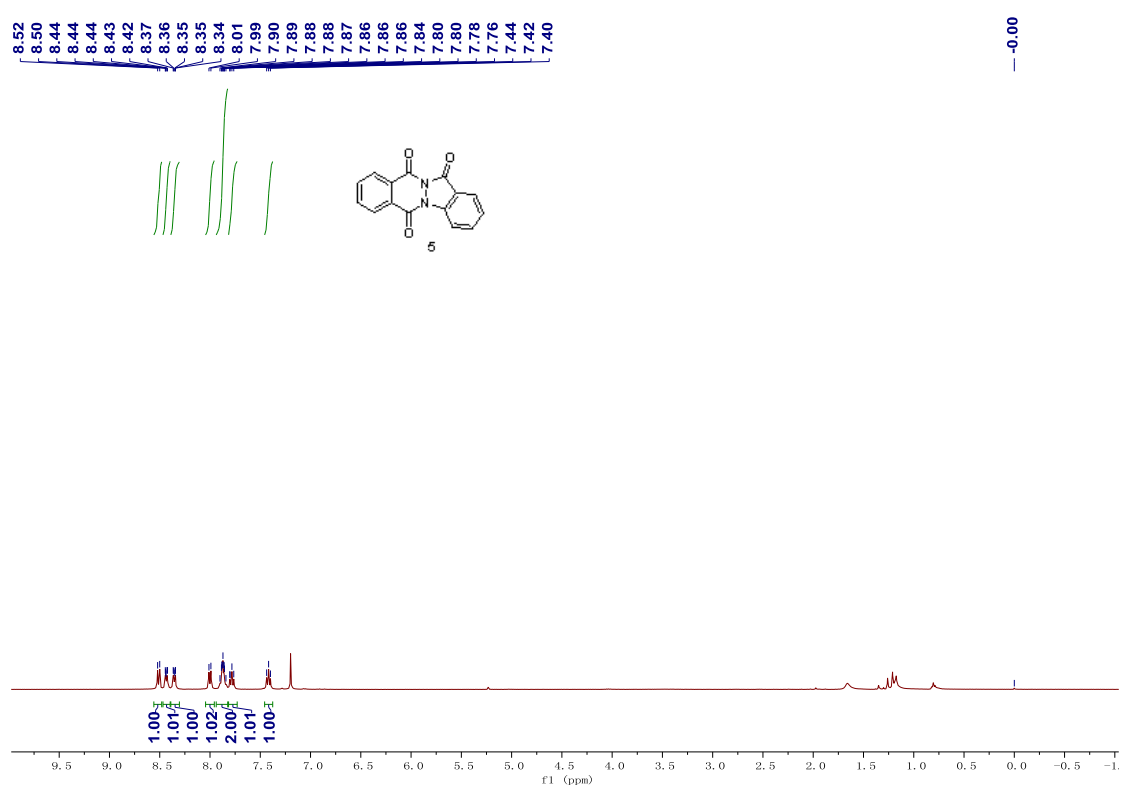
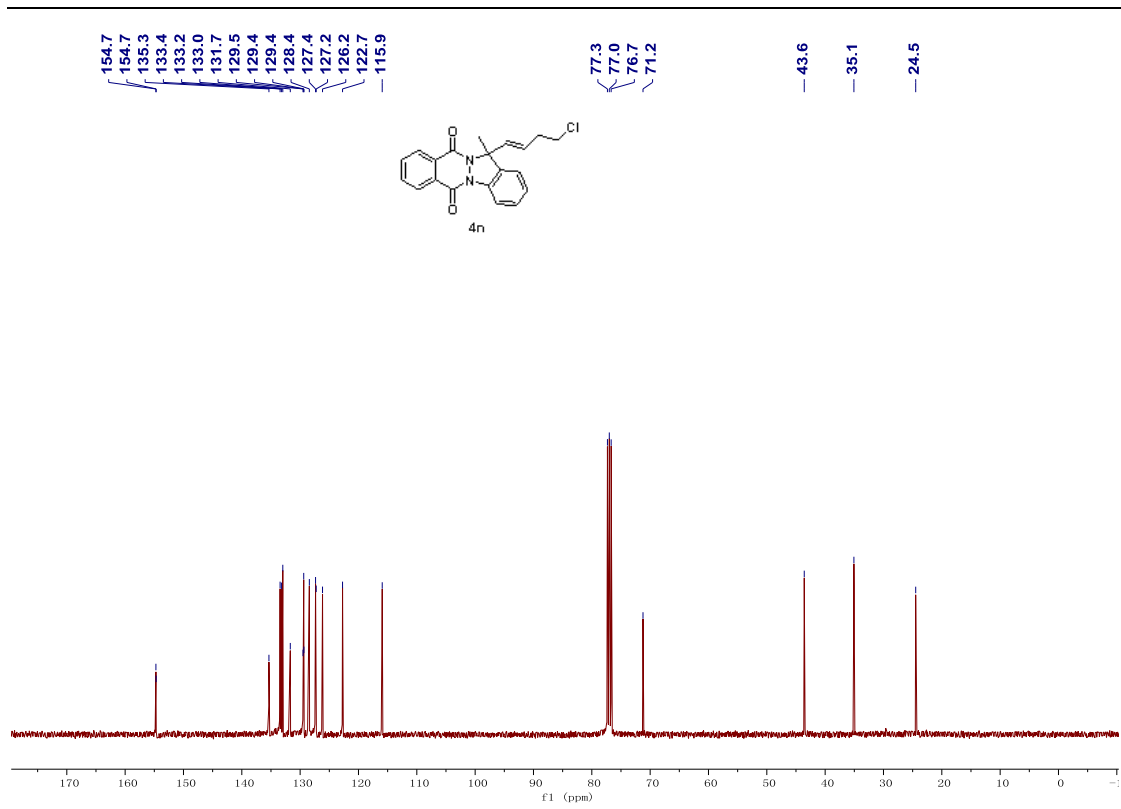
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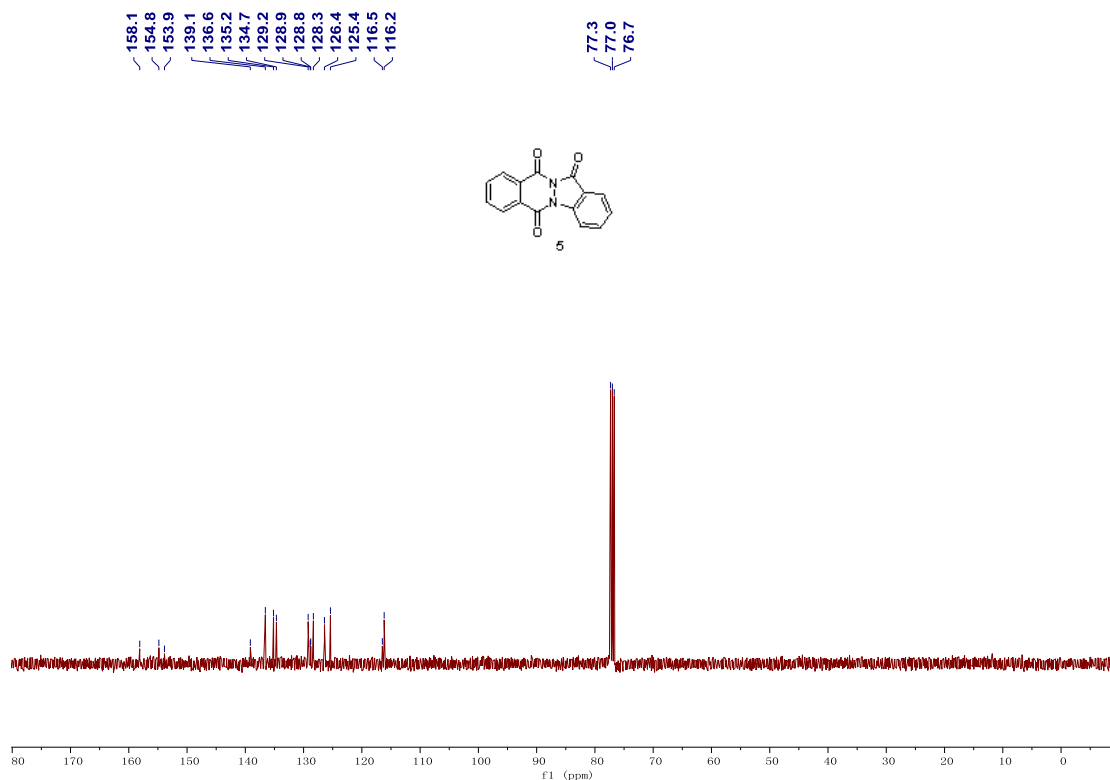












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