Electronic Supplementary Material (ESI) for RSC Advances.


# Supporting information

# For

## Synthesis of Tetrasubstituted 1H-Indazolo[1,2-b] Phthalazinediones Derivatives bearing Three-Dimensional Turbine-Type by Domino Reaction of Phthalhydrazide and Vinylketones

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**CONTENTS**

**General information**

NMR spectra were recorded with tetramethylsilane as the internal standard. $^{1}$H NMR spectra were recorded at 400 MHz, and $^{13}$C NMR spectra were recorded at 100 MHz (Bruker Avance). Chemical shifts (δ) are reported in ppm downfield from $CDCl_3$ (δ = 7.26 ppm) for $^{1}$H NMR and relative to the central $CDCl_3$ resonance (δ = 76.0 ppm) for $^{13}$C NMR spectroscopy. The following abbreviations were used to describe peak patterns where appropriate: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants were reported in Hertz (Hz). Commercial reagents were used as received without further purification. Flash column chromatography was carried out using silica gel eluting with ethyl acetate and petroleum ether. Reactions were monitored by TLC and visualized with ultraviolet light. HRMS spectra for **3a-3d**, **3f-3m** were determined using Bruker MicrOTOF QII by prof. Zhi-Jun Wu of Chengdu Institute of Biology, Chinese Academy of Sciences. And HRMS spectra for **3e**, **3n-3s** and **5** were determined using Thermo Scientific LTQ Orbitrap XL by Yong Wang of Ji-Yun Shanghai Biotechnology Co., Ltd., Shanghai, China.

**General procedure for the Domino Reactions of Phthalhydrazide and Vinylketones**

The reactions were carried out with phthalhydrazide **1** (0.1 mmol), vinylketones **2** (0.20 mmol) and phosphotungstic acid (0.015 mmol) in cyanobenzene (1.0 mL) at 60 °C. After the phthalhydrazide was consumed as indicated monitored by TLC, the reaction solution was concentrated in-vacuo and the residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc) to afford the desired corresponding product **3a-3s** and **5**.

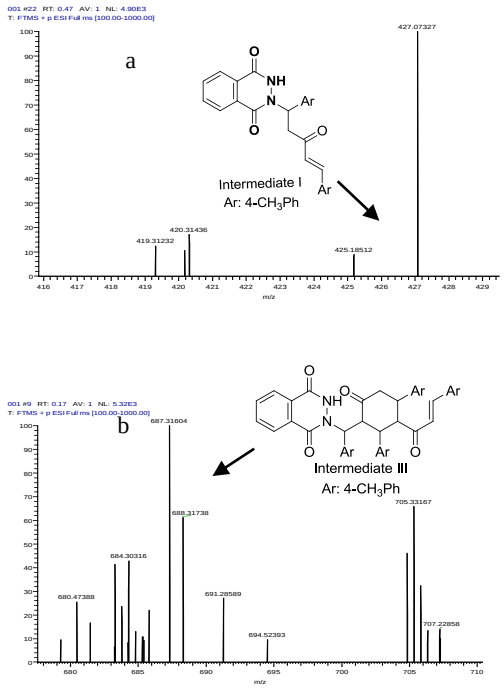
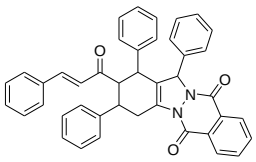



Figure S1. A) ESI-HRMS spectrum of the reaction of **1**, **2g** and phosphotungstic acid in 1.0 mL of

PhCN after 10 minutes; B) ESI-HRMS spectrum of the reaction of **1**, **2g** phosphotungstic acid in 1.0 mL of PhCN after 30 hours.

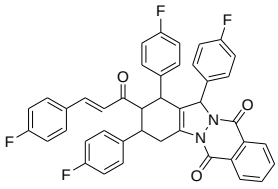
**2-cinnamoyl-1,3,13-triphenyl-1,2,3,4-tetrahydro-13H-indazolo[1,2-b]phthalazine-6,11-dione（3a）**



3a

Yellow solid, 92 % yield (56 mg), m.p. 264.1-265.3 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.44 – 8.30 (m, 1H), 8.29 – 8.15 (m, 1H), 7.91 – 7.67 (m, 2H), 7.32 (m, *J* = 18.1, 6.9, 3.7 Hz, 5H), 7.25 – 6.63 (m, 16H), 6.25 – 5.67 (m, 2H), 3.94 – 3.80 (m, 1H), 3.62 (m, *J* = 18.0, 17.2, 7.6 Hz, 2H), 3.51 – 3.29 (m, 2H).$^{13}$C NMR (100 MHz, $CDCl_3$) δ 200.44, 153.78, 153.34, 141.33, 140.04, 137.88, 134.65, 133.32, 132.37, 132.20, 129.24, 129.15, 127.99, 127.84, 127.73, 127.65, 127.61, 127.53, 127.37, 127.19, 127.11, 126.93, 126.85, 126.74, 126.54, 126.26, 126.14, 126.02, 121.21, 66.69, 57.49, 43.51, 43.33, 31.47. HRMS (ESI-TOF) calcd for $C_{42}$ $H_{32}$ $N_2$ Na $O_3$ ($[M+Na]^+$): 635.2305, found: 635.2301.

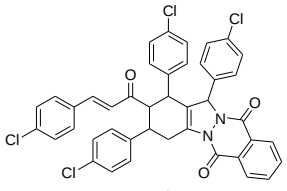
**(E)-1,3,13-tris(4-fluorophenyl)-2-(3-(4-fluorophenyl)acryloyl)-1,2,3,4-tetrahydro-13H-indazolo[1,2-b]phthalazine-6,11-dione（3b）**



3b

Yellow solid, 60 % yield (41 mg), m.p. 204.1-205.3 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.37 – 8.31 (m, 1H), 8.24 – 8.19 (m, *J* = 4.9, 2.2 Hz, 1H), 7.86 – 7.76 (m, *J* = 7.3, 1.5 Hz, 2H), 7.24 (dd, *J* = 8.6, 5.2 Hz, 2H), 7.18 – 7.09 (m, 2H), 7.06 – 6.90 (m, 12H), 6.86 (d, *J* = 15.9 Hz, 1H), 5.86 (d, *J* = 15.9 Hz, 1H), 5.80 (s, 1H), 3.85 (d, *J* = 16.9 Hz, 1H), 3.68 (d, *J* = 7.8 Hz, 1H), 3.52 – 3.27 (m, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 199.86, 163.64 (d, J = 94.6 Hz), 162,16 (d, J= 19.7 Hz), 161.14 (d, J = 91.4 Hz), 159.70 (d, J = 18.7 Hz), 153.58 (d, J = 38.55 Hz), 140.64, 135.38 (d, J = 2.4 Hz), 133.18 (d, J = 2.4 Hz ), 132.62, 132.52, 132.43, 130.05 (d, J = 2.3 Hz), 130.03, 129.13, 129.05, 129.01, 128.86, 128.34, 128.26, 128.24, 127.89, 127.90, 127.35, 126.55, 126.23, 125.12 (d, J = 1.5 Hz), 120.17, 115.03 (d, J = 15.8 Hz), 115.00 (d, J = 16.4 Hz), 114.96 (d, J =16.3 Hz), 114.60 (d, J = 15.9 Hz), 114.039 65.86, 57.77, 42.77, 42.40, 31.31. HRMS (ESI-TOF) calcd for $C_{42}$ $H_{28}$ $F_4$ $N_2$ Na $O_3$ ($[M+Na]^+$): 707.1928, found: 707.1929.

**(E)-1,3,13-tris(4-chlorophenyl)-2-(3-(4-chlorophenyl)acryloyl)-1,2,3,4-tetrahydro-13H-indazolo[1,2-b]phthalazine-6,11-dione(3c)**

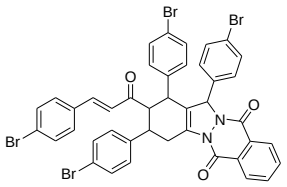


3c

Brown solid, 84 % yield (63 mg), m.p.181.5-182.9 °C. $^1$H NMR (400 MHz, CDCl3) δ 8.37 – 8.30 (m, 1H), 8.25 – 8.17 (m, 1H), 7.87 – 7.76 (m, 2H), 7.34 – 7.28 (m, 3H), 7.25 – 7.15 (m, 6H), 7.08 – 6.92 (m, 7H), 6.83 (d, J = 16.0 Hz, 1H), 5.87 (d, J = 15.9 Hz, 1H), 5.78 (s, 1H), 3.85 (d, J = 16.9 Hz, 1H), 3.64 (d, J = 8.3 Hz, 1H), 3.48 – 3.26 (m, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 200.45, 154.87, 154.39, 141.65, 139.14, 137.02, 136.68, 134.85, 133.91, 133.88, 133.83, 133.71, 133.52, 133.28, 132.37, 129.91, 129.81, 129.39, 129.27, 129.20, 129.15, 128.97, 128.55, 128.49, 128.38, 127.64, 127.32, 126.74, 120.67, 66.89, 58.69, 43.93, 43.54, 32.13. HRMS (ESI-TOF) calcd for $C_{42}$ $H_{28}$ $Cl_4$ $N_2$ Na $O_3$ ($[M+Na]^+$): 771.0746, found: 771.0750.

**(E)-1,3,13-tris(4-bromophenyl)-2-(3-(4-bromophenyl)acryloyl)-1,2,3,4-tetrahydro-13H-indazolo[1,2-b]phthalazine-6,11-dione(3d)**

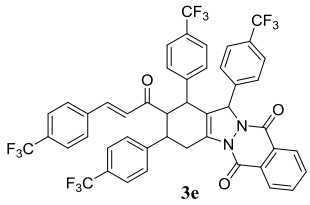
Brown solid, 89 % yield (83 mg), m.p.184.5-186.0 °C.$^1$H NMR (400 MHz, $CDCl_3$) δ 8.35 –



3d

8.30 (m, 1H), 8.23 – 8.17 (m, 1H), 7.84 – 7.75 (m, 2H), 7.46 – 7.35 (m, 8H), 7.16 – 7.10 (m, 2H), 6.98 – 6.90 (m, *J* = 17.4, 8.3 Hz, 6H), 6.80 (d, *J* = 15.9 Hz, 1H), 5.87 (d, *J* = 15.9 Hz, 1H), 5.76 (s, 1H), 3.84 (d, *J* = 17.1 Hz, 1H), 3.62 (d, *J* = 9.6 Hz, 1H), 3.48 – 3.26 (m, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 200.37, 154.87, 154.39, 141.76, 139.64, 137.53, 134.42, 133.86, 133.75, 133.55, 132.80, 132.36, 132.23, 132.12, 131.93, 130.16, 129.89, 129.62, 129.54, 128.76, 128.35, 127.66, 127.33, 126.81, 125.11, 123.10, 121.99, 121.41, 120.53, 66.95, 58.60, 43.96, 43.56, 32.05. HRMS (ESI-TOF) calcd for $C_{42}$ $H_{28}$ $Br_4$ $N_2$ Na $O_3$ ($[M+Na]^+$): 946.8726, found: 946.8716.

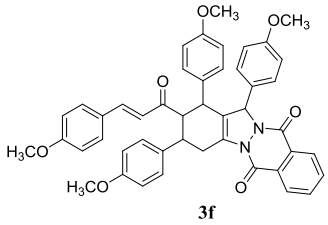
**(E)-1,3,13-tris(4-(trifluoromethyl)phenyl)-2-(3-(4-(trifluoromethyl)phenyl)acryloyl)-2,3,4,13-tetrahydro-1H-indazolo[1,2-b]phthalazine-6,11-dione (3e)**



3e

Yellow solid, 40 % yield (35 mg), m.p. 181.8-182.5°C. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.28 – 8.18 (m, 1H), 8.13 – 8.06 (m, 1H), 7.78 – 7.63 (m, 3H), 7.53 – 7.46 (m, 4H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 7.9 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.16 – 7.11 (m, 2H), 7.08 – 7.00 (m, 4H), 6.77 (d, *J* = 15.9 Hz, 1H), 5.86 – 5.70 (m, 2H), 3.90 – 3.78 (m, 1H), 3.71 – 3.61 (m, 1H), 3.51 – 3.39 (m, 2H), 3.39 – 3.26 (m, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 198.81, 153.93, 153.49, 143.55, 141.60, 140.37, 138.42, 135.98, 133.37, 132.84, 132.65, 131.32, 130.99, 130.36, 130.04, 129.76, 129.43, 129.11, 128.83, 128.69, 127.96, 127.28, 127.24, 127.20, 127.10, 126.70, 126.32, 125.28 (d, J = 2.7 Hz), 125.14 (d, J = 2.6 Hz), 124.84 (d, J = 2.6 Hz), 124.69 (d, J = 2.8 Hz), 124.01 (d, J = 5.2 Hz), 121.42, 121.30 (d, J = 5.4 Hz), 118.67, 65.90, 57.72, 43.27, 42.89, 30.89. HRMS (ESI-TOF) calcd for: $C_{46}$ $H_{29}$ $F_{12}$ $N_2$ $O_3$ ($[M+H]^+$): 885.19811, found: 885.19818 .

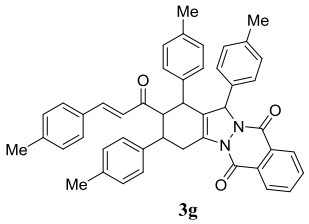
**(E)-1,3,13-tris(4-methoxyphenyl)-2-(3-(4-methoxyphenyl)acryloyl)-2,3,4,13-tetrahydro-1H-indazolo[1,2-b]phthalazine-6,11-dione (3f)**



3f

Pale yellow solid, 91 % yield (67 mg), m.p. 155.0-156.2 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 7.1 Hz, 1H), 8.20 (d, *J* = 7.1 Hz, 1H), 7.82 – 7.71 (m, 2H), 7.19 (d, *J* = 8.5 Hz, 2H), 7.09 (d, *J* = 8.6 Hz, 2H), 7.02 – 6.92 (m, *J* = 20.6, 8.2 Hz, 4H), 6.88 – 6.81 (m, *J* = 12.0, 9.0 Hz, 3H), 6.76 (t, *J* = 9.7 Hz, 6H), 5.88 (d, *J* = 15.9 Hz, 1H), 5.78 (s, 1H), 3.87 – 3.74 (m, *J* = 22.1, 14.0 Hz, 8H), 3.72 (s, 3H), 3.65 (s, 3H), 3.51 (t, *J* = 10.4 Hz, 1H), 3.45 – 3.26 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 201.62, 161.45, 159.75, 158.88, 158.53, 154.77, 154.28, 142.14, 133.34, 133.27, 133.18, 133.00, 130.90, 130.13, 129.96, 129.55, 128.86, 128.63, 128.57, 128.33, 127.48, 127.21, 127.02, 124.95, 122.77, 114.26, 114.23, 114.13, 114.01, 67.31, 58.69, 55.36, 55.28, 55.24, 55.16, 43.82, 43.47, 32.65. HRMS (ESI-TOF) calcd for $C_{46}$ $H_{40}$ $N_2$ Na $O_7$ ($[M+Na]^+$): 755.2728, found: 755.2732.

**(E)-1,3,13-trip-tolyl-2-(3-p-tolylacryloyl)-1,2,3,4-tetrahydro-13H-indazolo[1,2-b]phthalazine-6,11-dione(3g)**

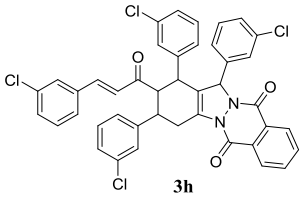


3g

Yellow solid, 90 % yield (60 mg), m.p. 295.0-296.5 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.37 – 8.30 (m, J = 7.6, 1.2 Hz, 1H), 8.24 – 8.17 (m, J = 7.5, 1.3 Hz, 1H), 7.83 – 7.71 (m, 2H), 7.14 (d, J = 8.0 Hz, 2H), 7.12 – 6.97 (m, J = 19.6, 15.2, 8.1 Hz, 10H), 6.92 (d, J = 8.0 Hz, 4H), 6.81 (d, J = 16.0 Hz, 1H), 5.91 (d, J = 16.0 Hz, 1H),

5.79 (s, 1H), 3.88 – 3.78 (m, 1H), 3.63 (d, J = 10.0 Hz, 1H), 3.54 (t, J = 10.3 Hz, 1H), 3.43 – 3.26 (m, 2H), 2.31 (s, 3H), 2.29 (s, 3H), 2.27 (s, 3H), 2.18 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 201.72, 154.71, 154.29, 142.23, 140.70, 138.46, 138.16, 137.24, 136.70, 135.95, 133.32, 133.16, 133.04, 132.68, 131.72, 130.17, 129.61, 129.56, 129.37, 129.31, 128.64, 128.42, 128.19, 127.70, 127.51, 127.27, 126.95, 126.26, 122.82, 67.49, 58.57, 44.12, 43.86, 32.61, 21.45, 21.26, 21.09, 20.97. HRMS (ESI-TOF) calcd for $C_{46}$ $H_{40}$ $N_2$ Na $O_3$ ($[M+Na]^+$): 691.2910, found: 691.2912.

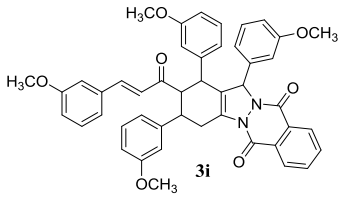
**(E)-1,3,13-tris(3-chlorophenyl)-2-(3-(3-chlorophenyl)acryloyl)-1,2,3,4-tetrahydro-13H-indazolo[1,2-b]phthalazine-6,11-dione(3h)**



**3h**

Pale yellow solid, 62 % yield (47 mg), m.p. 151.2-152.5 °C.$^1$H NMR (400 MHz, $CDCl_3$) δ 8.38 – 8.32 (m, 1H), 8.26 – 8.19 (m, 1H), 7.88 – 7.77 (m, *J* = 7.3, 1.5 Hz, 2H), 7.33 – 7.27 (m, *J* = 11.6, 6.5 Hz, 3H), 7.26 – 7.10 (m, 9H), 7.05 – 6.98 (m, *J* = 17.7, 4.6 Hz, 2H), 6.92 – 6.82 (m, *J* = 11.6, 8.8 Hz, 3H), 5.96 (d, *J* = 15.9 Hz, 1H), 5.78 (s, 1H), 3.87 (d, *J* = 13.1 Hz, 1H), 3.66 (d, *J* = 8.7 Hz, 1H), 3.55 – 3.46 (m, *J* = 13.0, 7.8 Hz, 1H), 3.44 – 3.29 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 200.21, 154.90, 154.42, 142.56, 141.46, 140.49, 137.63, 135.75, 135.22, 135.01, 134.81, 134.68, 133.76, 133.73, 133.56, 130.51, 130.47, 130.25, 130.12, 130.02, 129.96, 129.26, 128.43, 128.38, 128.20, 127.92, 127.83, 127.78, 127.71, 127.64, 127.37, 127.03, 126.84, 126.52, 126.31, 125.18, 120.38, 66.96, 58.26, 44.22, 43.66, 32.08. HRMS (ESI-TOF) calcd for $C_{42}$ $H_{28}$ $Cl_4$ $N_2$ Na $O_3$ ($[M+Na]^+$): 771.0746, found: 771.0749.

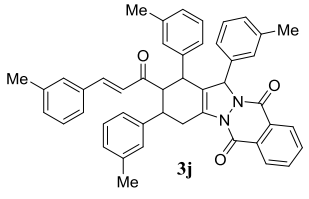
**(E)-1,3,13-tris(3-methoxyphenyl)-2-(3-(3-methoxyphenyl)acryloyl)-1,2,3,4-tetrahydro-13H-indazolo[1,2-b]phthalazine-6,11-dione(3i)**



**3i**

Yellow solid, 89 % yield (65 mg), m.p. 168.0-169.5 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 7.6 Hz, 1H), 8.22 (d, *J* = 7.2 Hz, 1H), 7.90 – 7.69 (m, 2H), 7.25 – 7.09 (m, 4H), 6.90 – 6.55 (m, 12H), 6.52 (d, *J* = 1.6 Hz, 1H), 5.98 (d, *J* = 16.0 Hz, 1H), 5.83 (s, 1H), 3.85 (d, *J* = 15.0 Hz, 1H), 3.79 – 3.56 (m, 14H), 3.43 – 3.30 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 201.26, 160.04, 159.82, 159.70, 154.77, 154.31, 142.66, 142.19, 140.61, 137.54, 135.78, 133.38, 133.22, 133.12, 130.17, 130.02, 129.89, 129.66, 129.60, 128.60, 128.57, 127.56, 127.48, 127.37, 127.29, 122.15, 120.93, 120.14, 118.99, 116.25, 114.66, 114.10, 113.95, 112.88, 112.84, 112.72, 112.57, 67.56, 58.07, 55.24, 55.21, 55.16, 44.54, 44.28, 32.44. HRMS (ESI-TOF) calcd for $C_{46}$ $H_{40}$ $N_2$ Na $O_7$ ($[M+Na]^+$): 755.2728, found: 755.2726.

**(E)-1,3,13-trim-tolyl-2-(3-m-tolylacryloyl)-1,2,3,4-tetrahydro-13H-indazolo[1,2-b]phthalazine-6,11-dione(3j)**

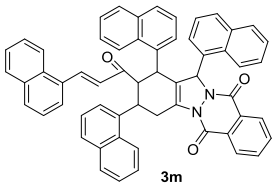


**3j**

Yellow solid, 86 % yield (57 mg), m.p. 212.8-213.9 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.37 – 8.33 (m, 1H), 8.25 – 8.18 (m, *J* = 7.5, 1.4 Hz, 1H), 7.83 – 7.72 (m, 2H), 7.19 – 7.13 (m, 2H), 7.12 – 7.00 (m, 7H), 6.91 (d, *J* = 5.9 Hz, 3H), 6.87 – 6.75 (m, 5H), 5.96 (d, *J* = 16.0 Hz, 1H), 5.78 (s, 1H), 3.85 (d, *J* = 13.4 Hz, 1H), 3.61 (d, *J* = 7.3 Hz, 2H), 3.45 – 3.28 (m, 2H), 2.30 (d, *J* = 6.7 Hz, 6H), 2.26 (s, 3H), 2.25 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 200.58, 153.73, 153.27, 141.40, 140.02, 137.80, 137.50, 137.36, 137.23, 137.10, 134.66, 133.33, 132.33, 132.18, 131.81, 130.06, 129.14, 128.49, 128.20,

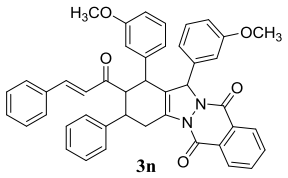
128.15, 127.73, 127.64, 127.61, 127.56, 127.48, 127.45, 127.42, 126.93, 126.48, 126.42, 126.25, 126.09, 124.74, 124.33, 123.88, 122.85, 121.75, 66.72, 56.99, 43.36, 43.10, 31.58, 28.67, 20.41, 20.39, 20.19. HRMS (ESI-TOF) calcd for $C_{46}$ $H_{40}$ $N_2$ Na $O_3$ ([M+Na]$^+$): 691.2931, found: 691.2934.

**(E)-1,3,13-tri(naphthalen-1-yl)-2-(3-(naphthalen-2-yl)acryloyl)-1,2,3,4-tetrahydro-13H-indazolo[1,2-b]phthalazine-6,11-dione(3m)**



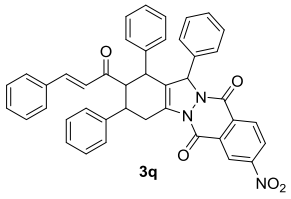

Brown solid, 99% yield (80 mg), m.p. 201.5-202.7 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.62 – 8.22 (m, 2H), 8.20 – 7.89 (m, 2H), 7.88 – 7.37 (m, 17H), 7.32 – 7.14 (m, 4H), 7.10 – 6.95 (m, 2H), 6.95 – 6.66 (m, 3H), 6.66 – 6.35 (m, 3H), 6.34 – 5.95 (m, 1H), 5.86 – 5.60 (m, 1H), 4.88 – 4.37 (m, 2H), 4.30 – 3.92 (m, 2H), 3.64 – 3.24 (m, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$, a mixture of two isomers) δ 200.66, 200.28, 153.53, 153.39, 138.69, 138.57, 137.12, 137.03, 135.61, 133.70, 132.98, 132.91, 132.39, 132.19, 132.16, 132.12, 131.35, 131.08, 130.73, 130.57, 130.49, 130.37, 130.00, 129.90, 129.84, 129.60, 129.53, 129.39, 129.24, 129.15, 128.79, 128.33, 128.15, 127.89, 127.52, 127.36, 127.33, 127.04, 126.89, 126.71, 126.69, 126.54, 126.47, 126.17, 125.61, 125.48, 125.36, 124.96, 124.92, 124.89, 124.82, 124.78, 124.53, 124.41, 124.26, 124.17, 124.04, 123.96, 123.91, 122.91, 122.75, 122.67, 122.40, 122.24, 121.97, 121.78, 121.59, 121.16, 120.48, 119.97, 61.65, 61.25, 57.74, 51.31, 45.88, 37.15, 36.88, 32.31, 32.13, 28.67. HRMS (ESI-TOF) calcd for $C_{58}$ $H_{40}$ $N_2$ Na $O_3$ ([M+Na]$^+$): 865.2931, found: 865.2935.

**2-cinnamoyl-1,13-bis(3-methoxyphenyl)-3-phenyl-2,3,4,13-tetrahydro-1H-indazolo[1,2-b]phthalazine-6,11-dione (3n)**




Brown solid, 85% yield (57 mg), m.p. 190.4-191.0 °C. $^1$H NMR (400 MHz, $CDCl_3$, a mixture of three isomers) δ 8.31 – 8.22 (m, 1H), 8.20 – 8.07 (m, 1H), 8.00 – 7.39 (m, 3H), 7.37 – 6.94 (m, 14H), 6.86 – 6.35 (m, 9H), 5.98 – 5.65 (m, 2H), 3.84 – 3.72 (m, 1H), 3.66 – 3.59 (m, 6H), 3.59 – 3.47 (m, 2H), 3.39 – 3.21 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$, a mixture of three isomers) δ 201.46, 201.39, 199.21, 160.02, 159.81, 159.65, 159.16, 154.75, 154.66, 154.27, 142.71, 142.40, 142.34, 141.07, 140.63, 140.50, 139.07, 138.93, 137.61, 135.82, 135.69, 134.73, 134.34, 134.31, 133.41, 133.35, 133.27, 131.76, 130.59, 130.32, 130.12, 130.06, 129.93, 129.70, 129.64, 129.03, 128.84, 128.76, 128.66, 128.57, 128.44, 128.16, 127.97, 127.91, 127.79, 127.54, 127.48, 127.30, 127.21, 127.14, 125.89, 122.15, 122.09, 120.95, 120.14, 118.99, 116.25, 114.72, 114.56, 114.11, 114.03, 112.86, 112.73, 112.51, 69.71, 67.69, 67.60, 60.38, 58.50, 58.22, 57.98, 55.29, 55.26, 55.24, 55.20, 55.15, 55.01, 54.95, 53.56, 44.64, 44.55, 44.36, 42.24, 37.58, 32.50. HRMS (ESI-TOF) calcd for $C_{44}H_{37}N_2O_5$ $(M+H)^+$ : 673.26970, found: 673.26971.

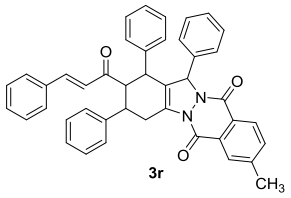
**2-cinnamoyl-8-nitro-1,3,13-triphenyl-2,3,4,13-tetrahydro-1H-indazolo[1,2-b]phthalazine-6,11-dione (3q)**




Brown solid, 87% yield (57 mg), m.p. 169.5-170.0 °C. The ratio of **3q**-A/**3q**-B was 1:0.13 as determined by $^1$H NMR. $^1$H NMR (400 MHz, $CDCl_3$, a mixture of two isomers) δ 9.05 – 8.89 (m, 1H, isomer A), 8.50 – 8.24 (m, 2H, for isomer A and isomer B, overlapped), 7.30 – 7.08 (m, 15H, for isomer A and isomer B, overlapped), 7.07 – 6.85 (m, 9H, for isomer A and isomer B, overlapped), 6.84 – 6.79 (m, 1H, for isomer A and isomer B, overlapped), 6.76 (d, *J* = 16.0 Hz, 1H, isomer A), 6.10 (s, 1H, isomer B), 6.03 (d, *J* = 15.9 Hz, 1H, isomer B), 5.84 (d, *J* = 16.0

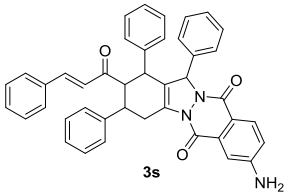
Hz, 1H, isomer A), 5.76 (s, 1H, isomer A), 4.06 – 3.99 (m, 1H, isomer B), 3.95 (s, 1H, isomer B), 3.80 – 3.75 (m, 1H, for isomer A and isomer B, overlapped), 3.64 – 3.62 (m, 1H, for isomer A and isomer B, overlapped), 3.56 (t, *J* = 10.3 Hz, 1H, isomer A), 3.43 – 3.21 (m, 2H, isomer A). $^{13}$C NMR (100 MHz, $CDCl_3$, a mixture of two isomers) δ 200.23, 200.21, 152.02, 151.95, 151.39, 151.33, 149.78, 149.71, 141.51, 139.75, 139.73, 137.52, 137.48, 133.73, 133.67, 133.33, 133.17, 132.21, 131.58, 130.62, 129.33, 128.91, 128.68, 128.40, 128.07, 128.05, 127.96, 127.73, 127.62, 127.46, 127.38, 127.36, 127.11, 126.90, 126.87, 126.82, 126.81, 126.39, 126.29, 126.13, 126.12, 125.98, 125.97, 124.87, 122.54, 122.21, 121.97, 67.14, 67.07, 57.26, 43.47, 43.28, 43.24, 31.27, 31.20. HRMS (ESI-TOF) calcd for $C_{42}H_{32}N_3O_5$ ($[M+H]^+$): 658.23365, found: 658.23364.

**2-cinnamoyl-8-methyl-1,3,13-triphenyl-2,3,4,13-tetrahydro-1H-indazolo[1,2-b]phthalazine-6,11-dione (3r)**




Yellow solid, 63% yield (39 mg), m.p. 255.0-255.4 °C. $^1$H NMR (400 MHz, $CDCl_3$) $^1$H NMR (400 MHz, $CDCl_3$, a mixture of four isomers) δ 8.14 – 7.85 (m, 2H), 7.52 – 7.41 (m, 1H), 7.24 – 7.08 (m, 12H), 7.06 – 6.88 (m, 7H), 6.88 – 6.81 (m, 1H), 6.74 (d, *J* = 16.0 Hz, 1H), 5.84 (d, *J* = 16.0 Hz, 1H), 5.75 (s, 1H), 3.84 – 3.71 (m, 1H), 3.64 – 3.47 (m, 2H), 3.44 – 3.19 (m, 2H), 2.44 – 2.31 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$, a mixture of four isomers) δ 201.59, 154.87, 154.43, 144.58, 144.34, 142.39, 141.14, 138.97, 135.88, 135.82, 134.54, 134.35, 134.31, 133.42, 130.30, 130.05, 129.02, 128.85, 128.69, 128.65, 128.59, 128.50, 128.42, 128.25, 128.16, 127.92, 127.90, 127.76, 127.66, 127.60, 127.51, 127.28, 127.25, 127.16, 127.04, 126.17, 125.89, 122.15, 121.89, 67.63, 67.57, 58.51, 44.57, 44.38, 32.52, 21.84. HRMS (ESI-TOF) calcd for $C_{43}H_{35}N_2O_3$ ($[M+H]^+$): 627.26422, found: 627.26416.

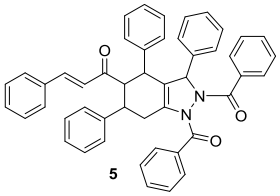
**8-amino-2-cinnamoyl-1,3,13-triphenyl-2,3,4,13-tetrahydro-1H-indazolo[1,2-b]phthalazine-6,11-dione (3s)**




Yellow solid, 69% yield (43 mg), m.p. 192.6-193.0 °C. The ratio of **3s**-A/**3s**-B was 1:0.44 as determined by $^1$H NMR. $^1$H NMR (400 MHz, $CDCl_3$, a mixture of two isomers ) δ 8.03 – 7.93 (m, 1H, isomer B), 7.87 – 7.78 (m, 1H, isomer B), 7.36 – 7.08 (m, 21H, for isomer A and isomer B, overlapped), 7.05 – 6.95 (m, 6H, for isomer A and isomer B, overlapped), 6.93 – 6.81 (m, 6H, for isomer A and isomer B, overlapped), 6.79 – 6.70 (m, 3H, for isomer A and isomer B, overlapped), 6.12 – 6.00 (m, 2H, isomer B), 5.84 (d, *J* = 16.0 Hz, 1H, isomer A), 5.72 (s, 1H, isomer A), 4.34 (brs, 3H, for isomer A and isomer B, overlapped), 3.97 – 3.69 (m, 2H, for isomer A and isomer B, overlapped), 3.64 – 3.44 (m, 3H, for isomer A and isomer B, overlapped), 3.39 – 3.21 (m, 2.7 H, for isomer A and isomer B, overlapped). $^{13}$C NMR (100 MHz, $CDCl_3$, a mixture of two isomers) δ 200.69, 200.64, 154.21, 154.04, 153.79, 153.44, 150.96, 150.56, 141.35, 140.17, 137.94, 135.38, 135.30, 133.25, 132.42, 132.26, 130.79, 129.23, 128.48, 128.09, 127.94, 127.74, 127.59, 127.38, 127.10, 127.00, 126.92, 126.83, 126.67, 126.09, 125.90, 124.85, 121.28, 119.51, 118.63, 118.32, 117.31, 109.27, 66.56, 66.23, 57.42, 43.47, 43.36, 43.28, 31.54. HRMS (ESI-TOF) calcd for $C_{42}H_{34}N_3O_3$ ($[M+H]^+$): 628.25947, found: 628.25928.

**(5-cinnamoyl-3,4,6-triphenyl-4,5,6,7-tetrahydro-1H-indazole-1,2(3H)-diyl)bis(phenylmethanone) (5)**

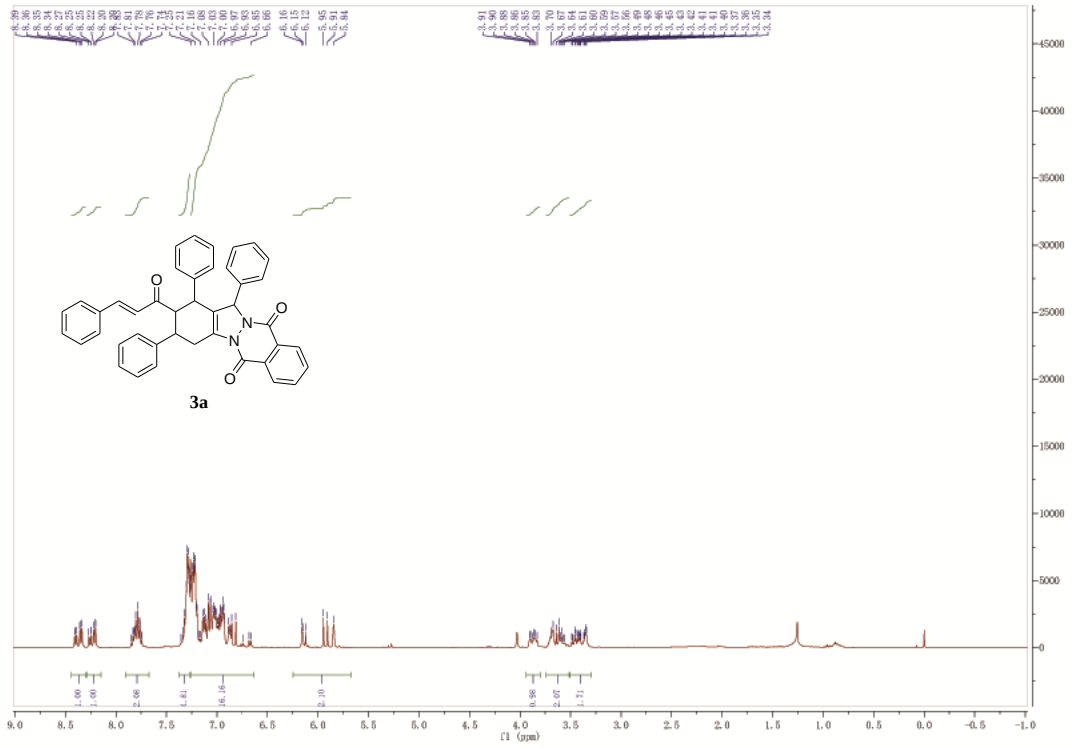
Yellow solid, 30% yield (21 mg), m.p. 155.5-156.2 °C. The ratio of **3s**-A/**3s**-B was 1:0.44 as determined by $^1$H NMR. $^1$H NMR (400 MHz, $CDCl_3$, a mixture of two isomers) δ 8.10 – 7.99 (m, 1H,

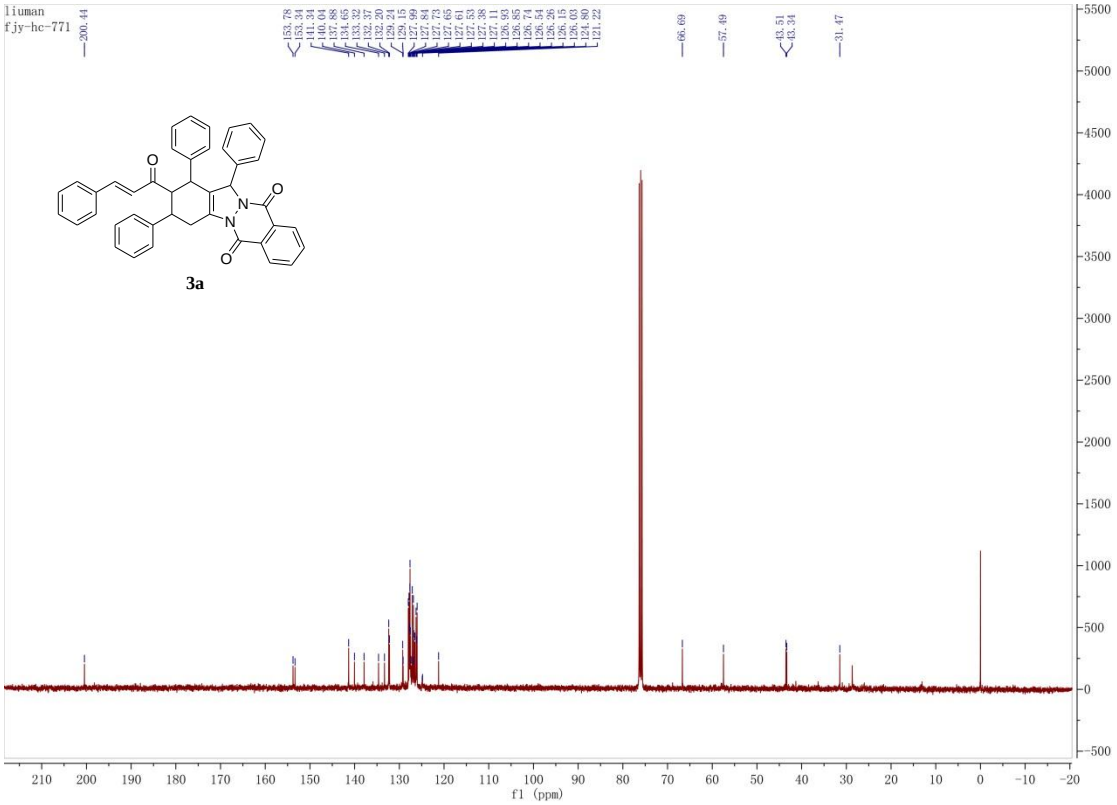


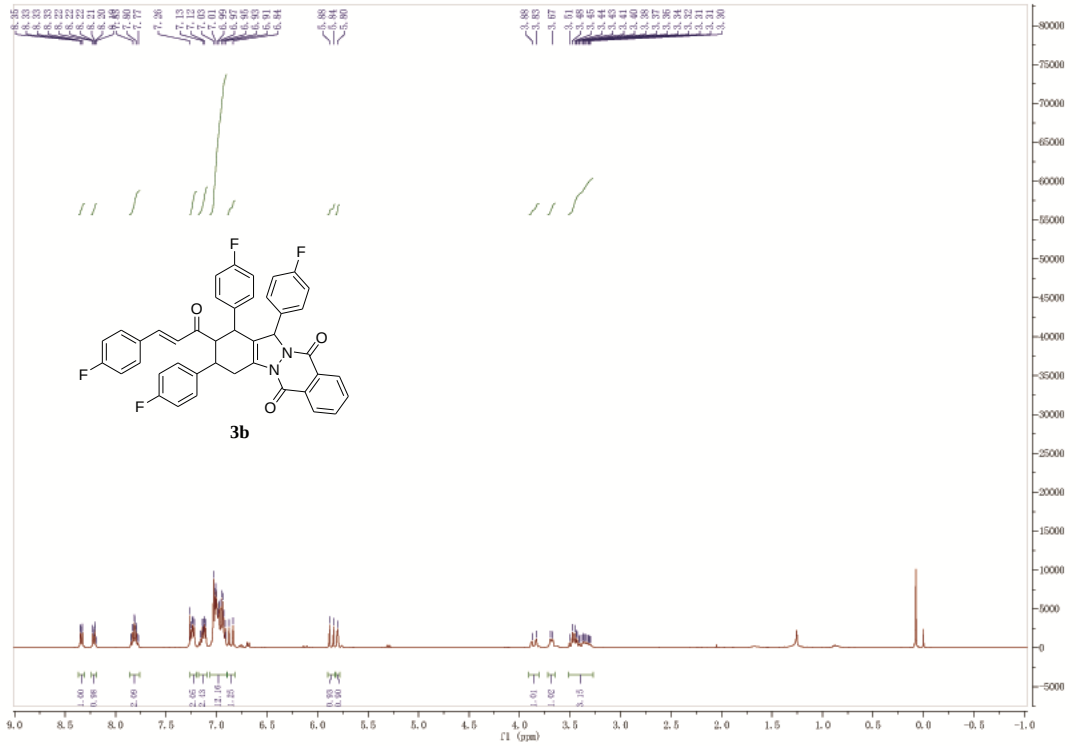
**5**

isomer A), 7.55 – 6.79 (m, 48H, for isomer A and isomer B, overlapped), 6.77 – 6.70 (m, 3H, for isomer A and isomer B, overlapped), 6.37 (d, *J* = 16.0 Hz, 1H, isomer A), 6.15 (d, *J* = 15.8 Hz, 1H, isomer A), 5.38 (d, *J* = 11.7 Hz, 1H, isomer A), 3.87 – 3.80 (m, 2H, isomer A), 3.67 – 3.60 (m, 1H, isomer A), 3.54 – 3.49 (m, 1H, isomer A), 3.49 – 3.42 (m, 1H, isomer A), 2.97 – 2.74 (m, 5H, isomer B). $^{13}$C NMR (100 MHz, $CDCl_3$, a mixture of two isomers) δ 199.01, 195.88, 167.01, 141.14, 140.98, 140.52, 140.16, 138.64, 137.04, 133.55, 133.53, 132.57, 131.83, 130.98, 129.32, 129.15, 128.94, 128.61, 127.80, 127.72, 127.65, 127.44, 127.39, 127.28, 127.26, 127.13, 126.43, 126.29, 125.92, 125.84, 125.14, 125.03, 124.90, 123.83, 105.35, 58.03, 56.72, 56.63, 47.07, 38.08, 28.81, 28.67. HRMS (ESI-TOF) calcd for $C_{48}H_{42}N_3O_3^+$ $(M+NH_4)^+$: 708.32207, found: 708.32172.

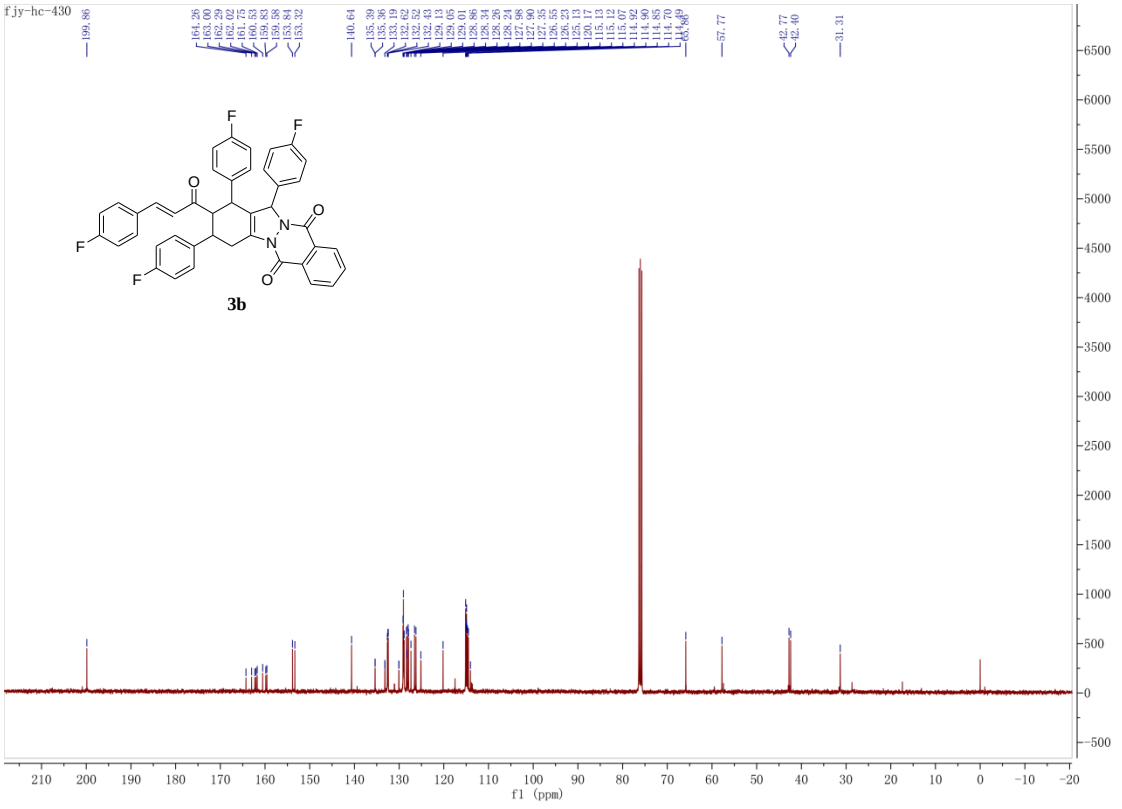
## 3. **NMR spectra of products**



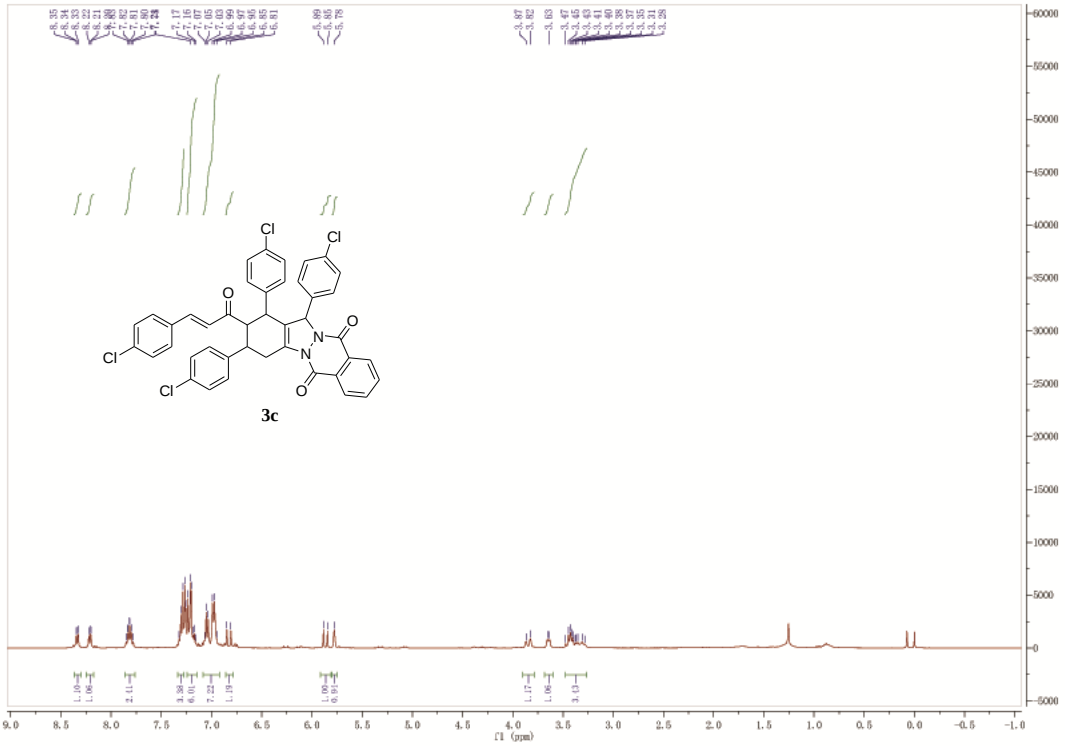





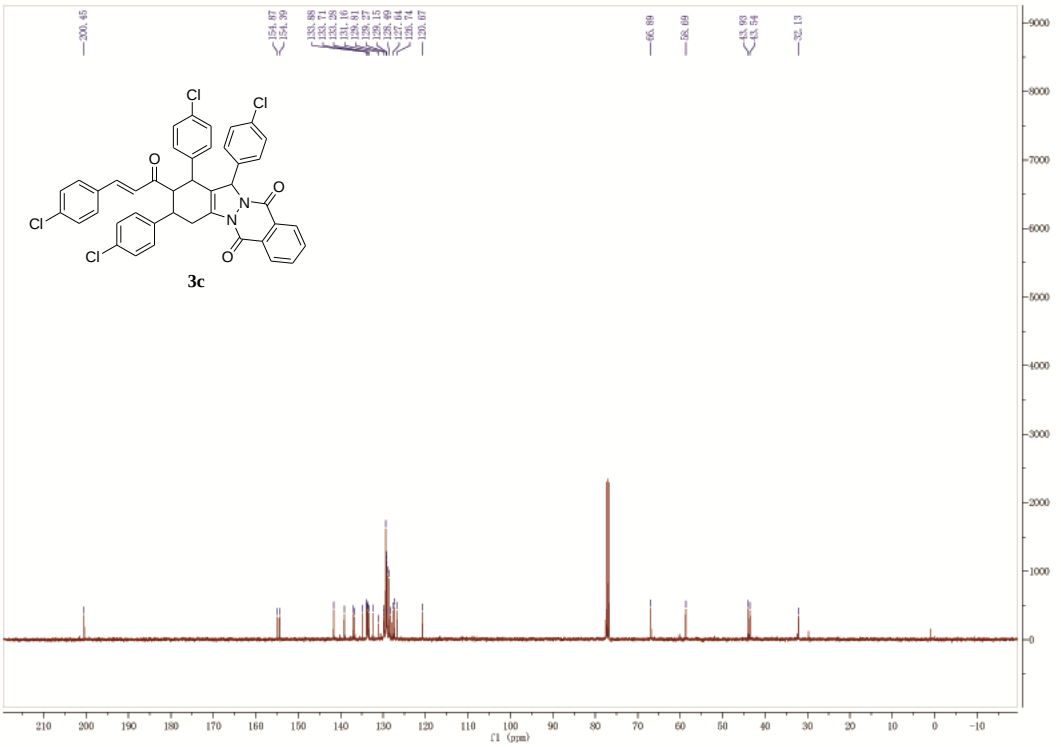

**3b**



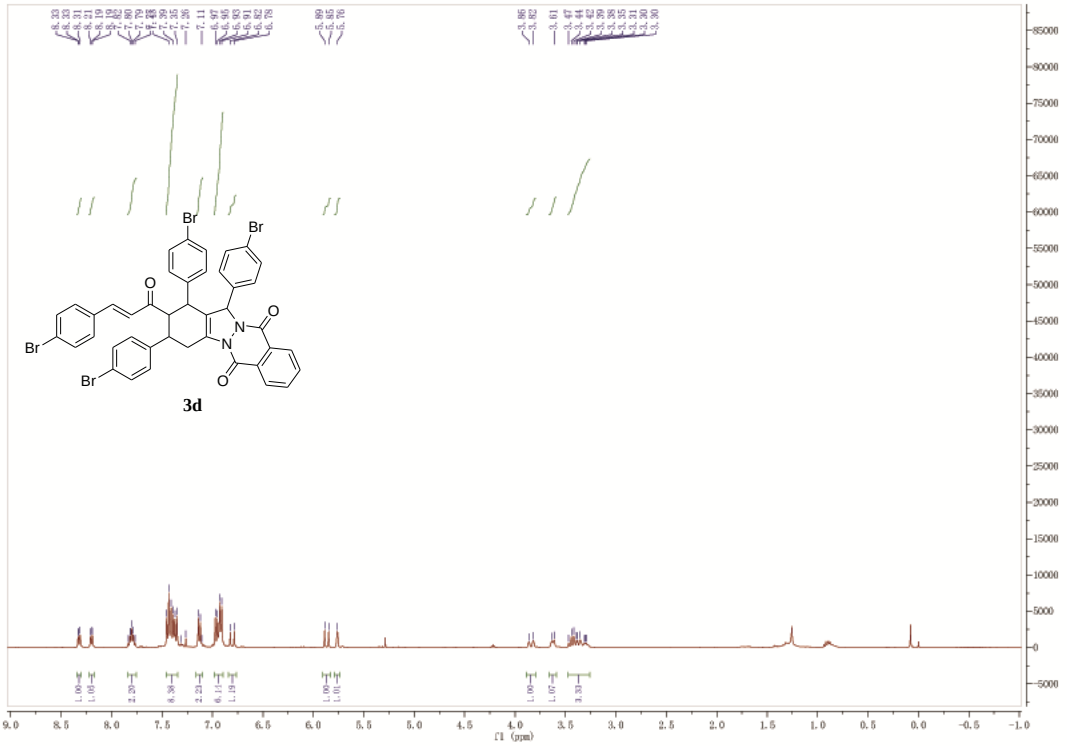

**3b**



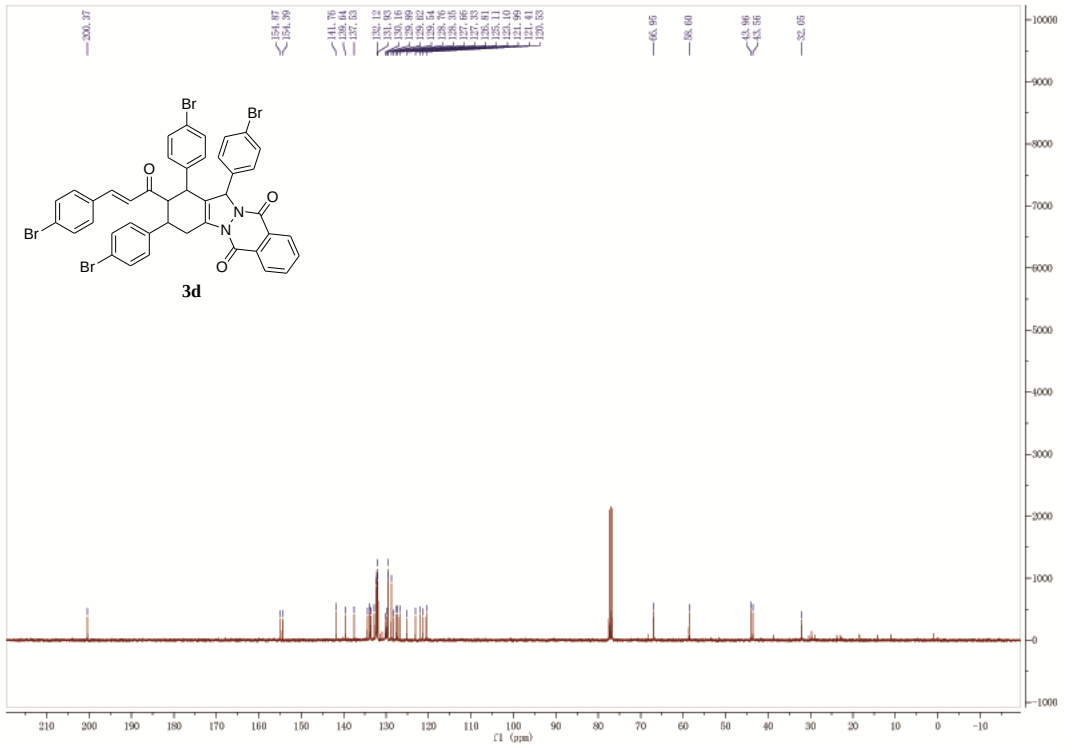

**3c**



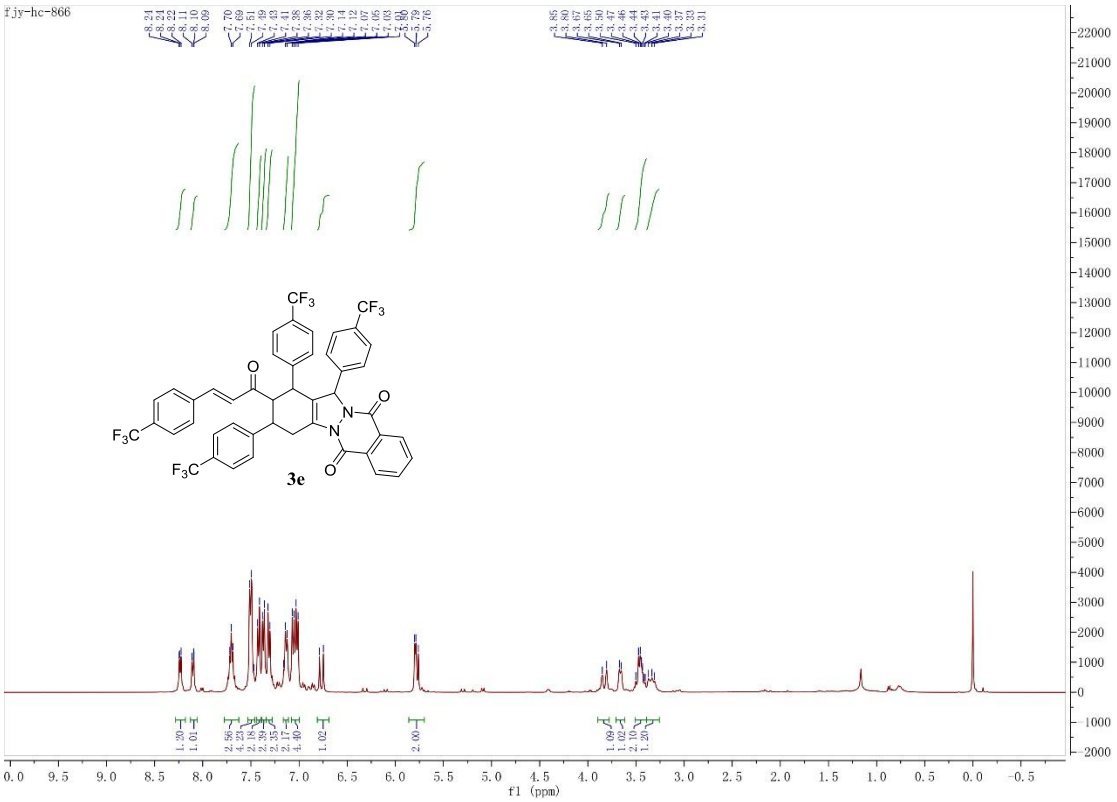

**3c**




**3d**




**3d**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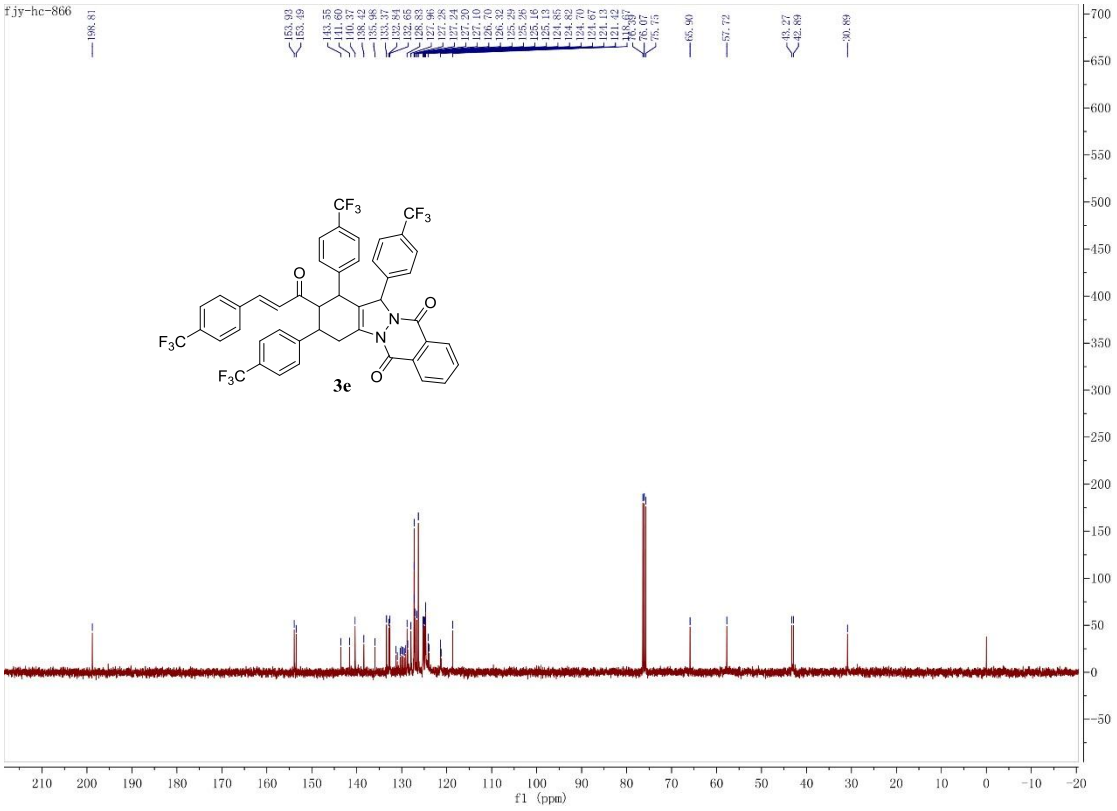
3e
f1 (ppm)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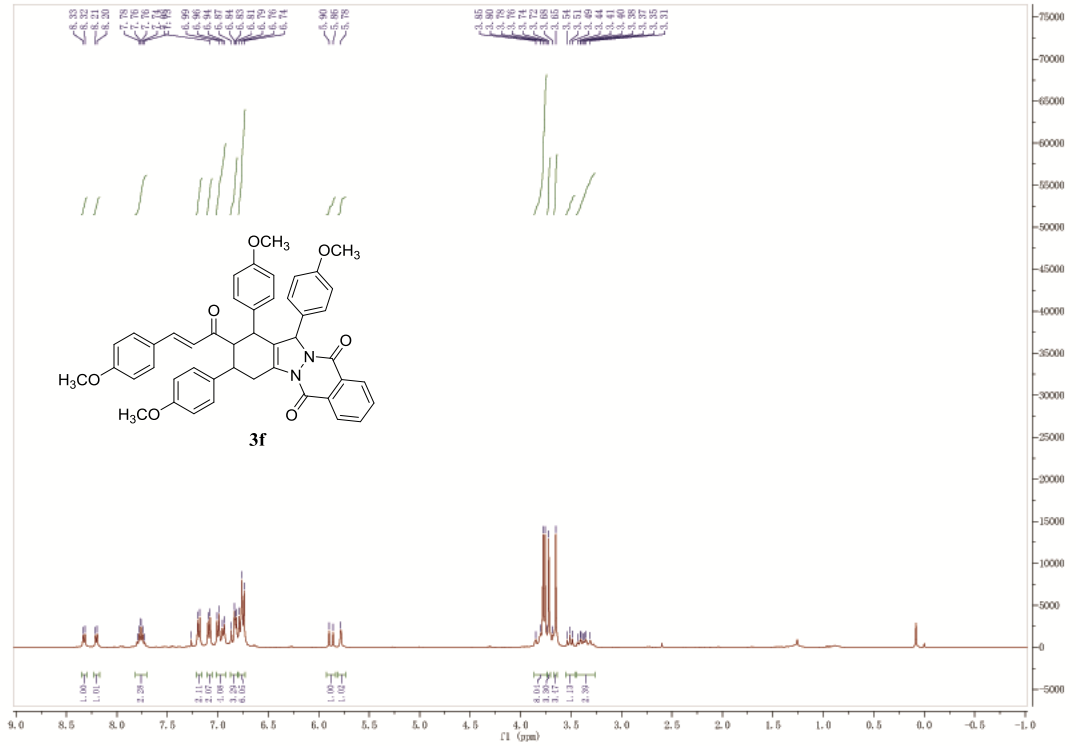
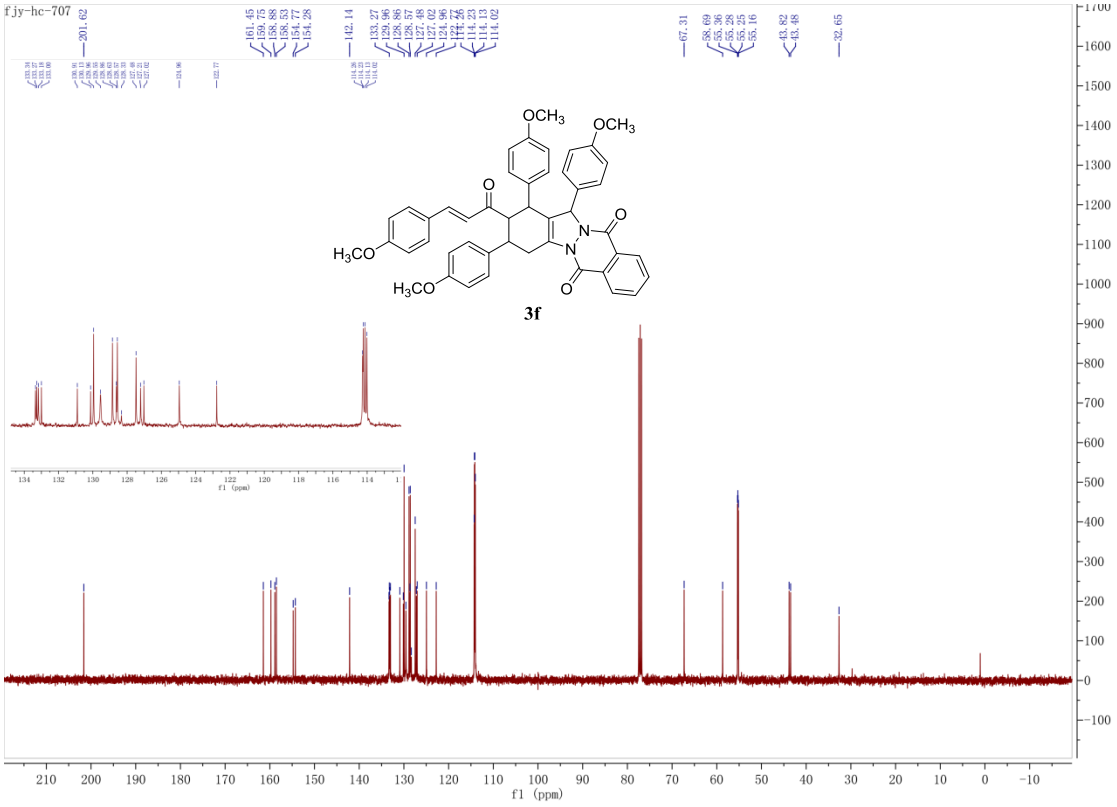
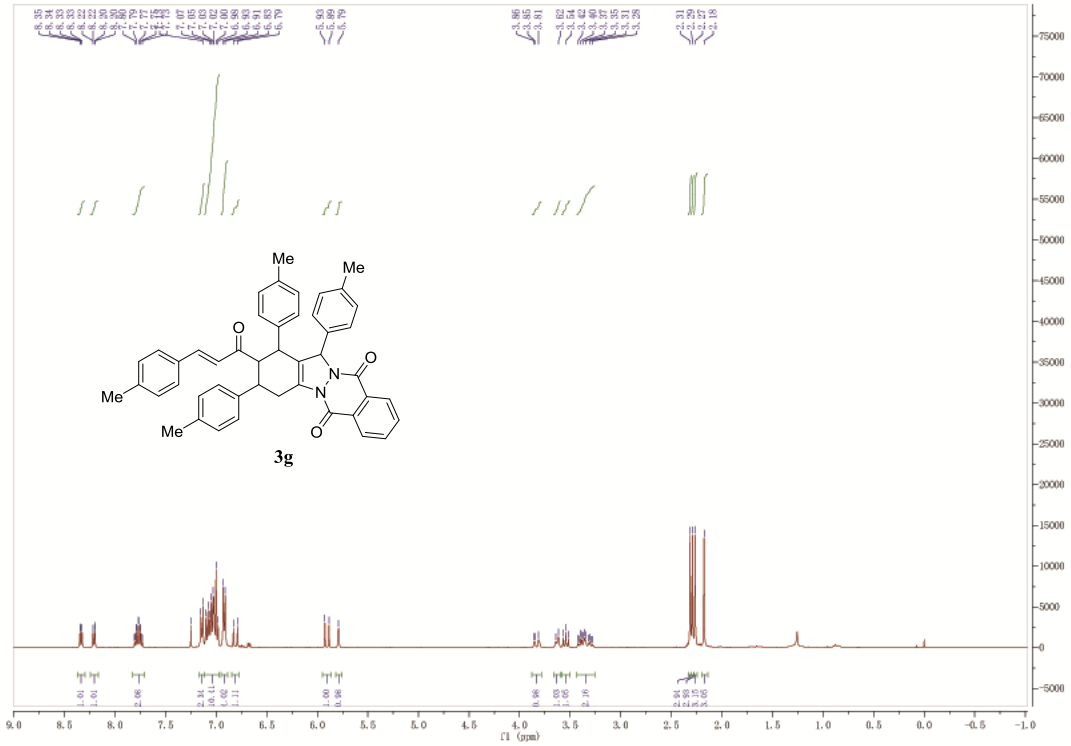
3e
f1 (ppm)


OCH3
OCH3
O
O
N
N
O
H3CO
H3CO
O
3f
f1 (ppm)


f jy-hc-707
OCH3
OCH3
O
O
N
N
O
H3CO
H3CO
O
3f
f1 (ppm)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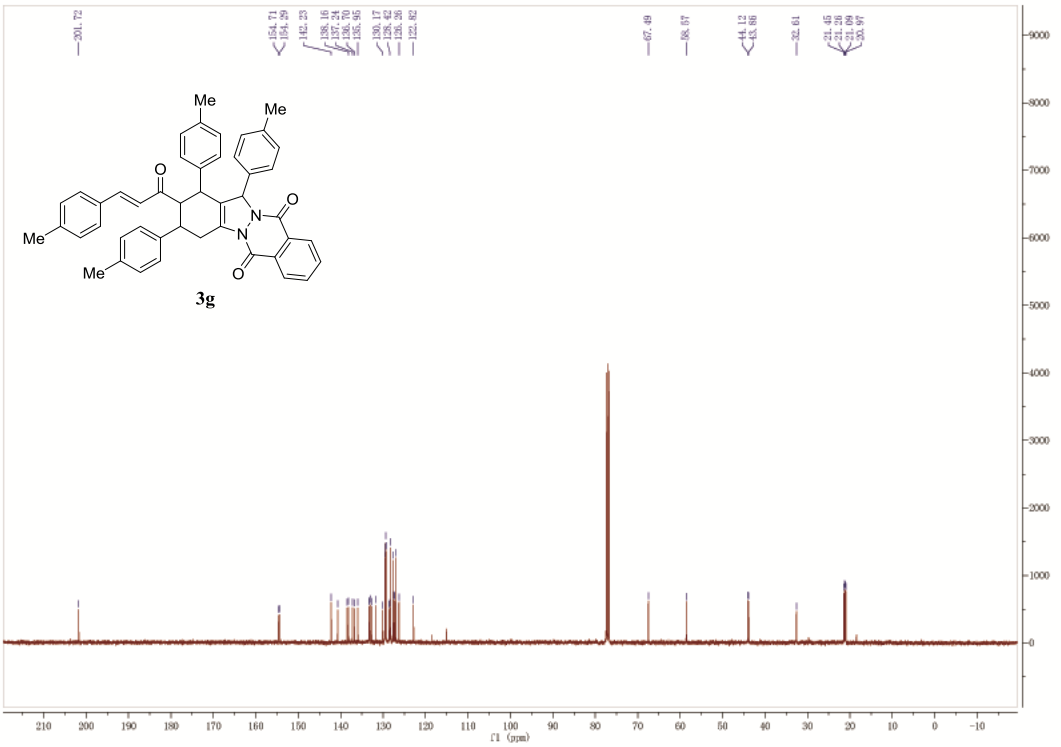
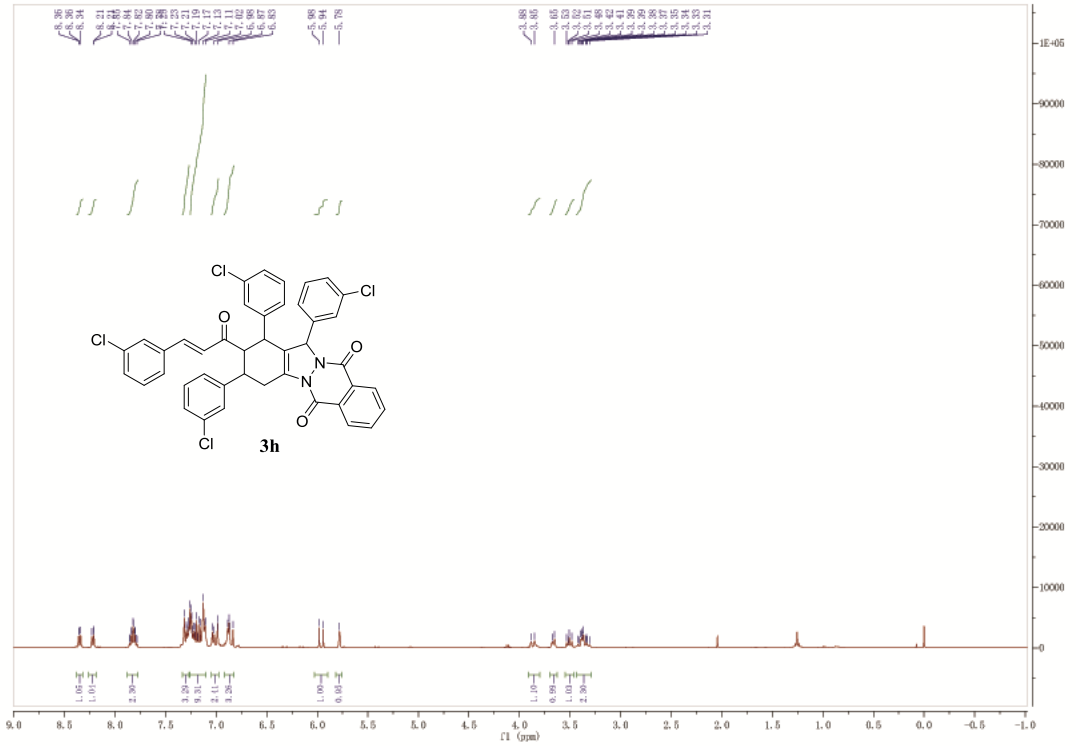
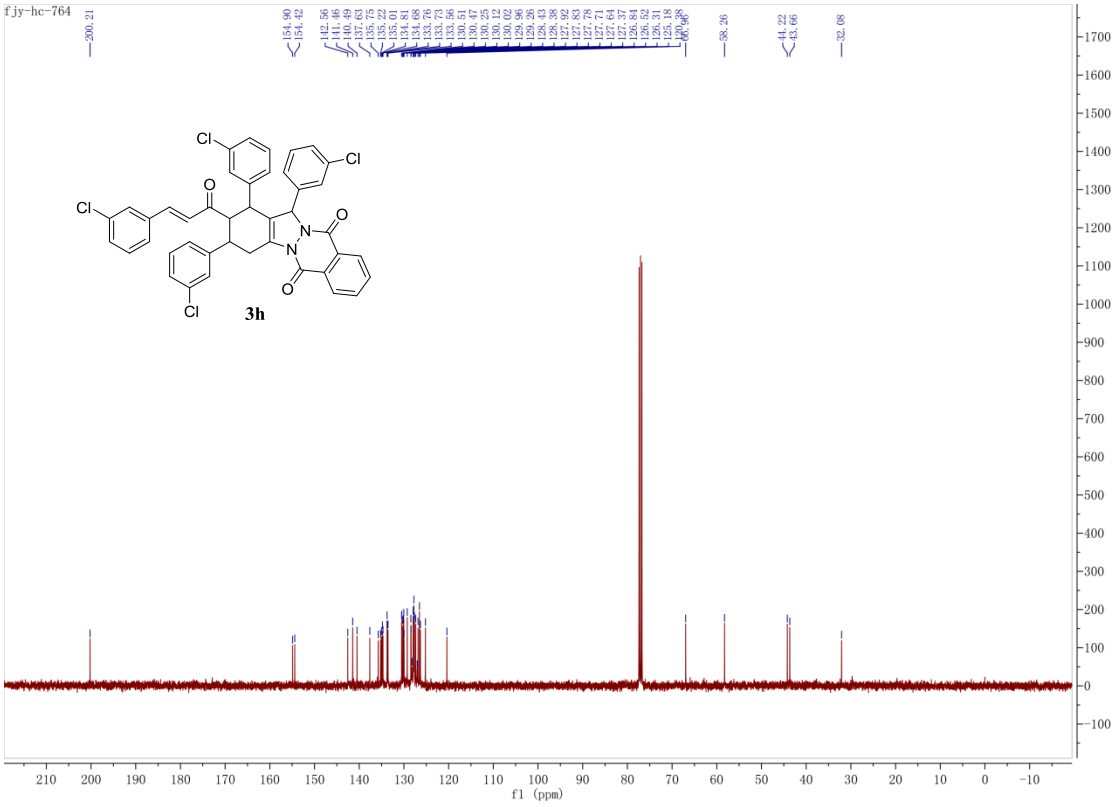
O
Me
N
N
O
O
Me
3g
f1 (ppm)


Me
Me
O
Me
N
N
O
O
Me
3g
f1 (ppm)


Cl
Cl
Cl
Cl
O
O
O
N
N
3h
f1 (ppm)


fjy-hc-764
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Cl
Cl
Cl
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O
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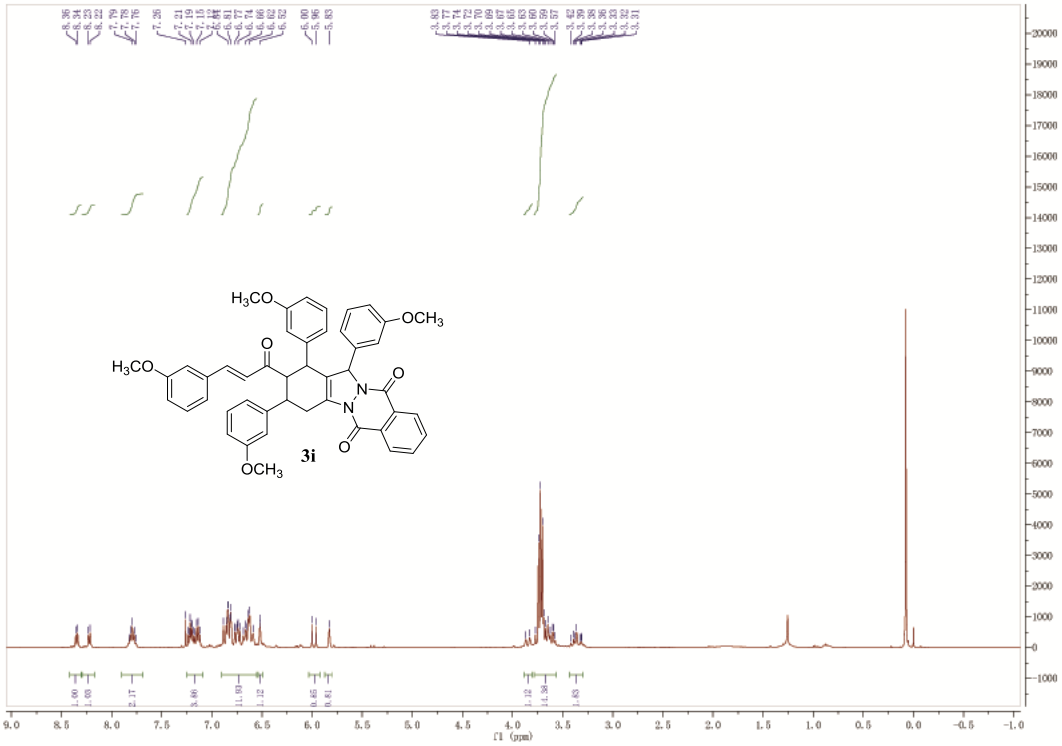
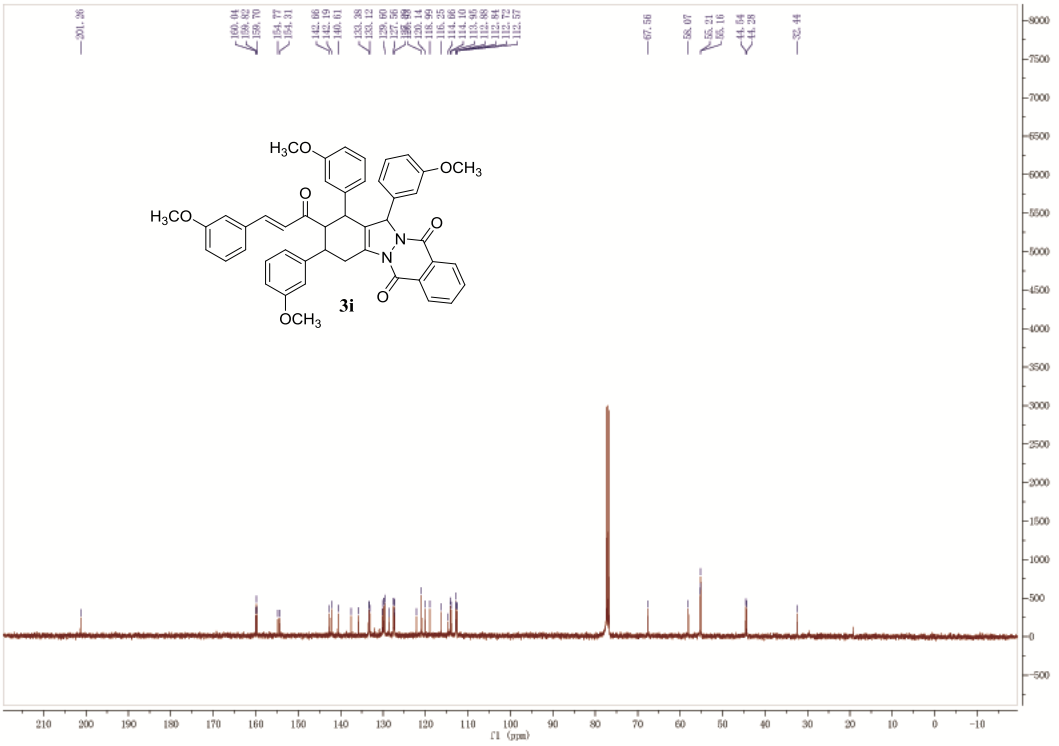
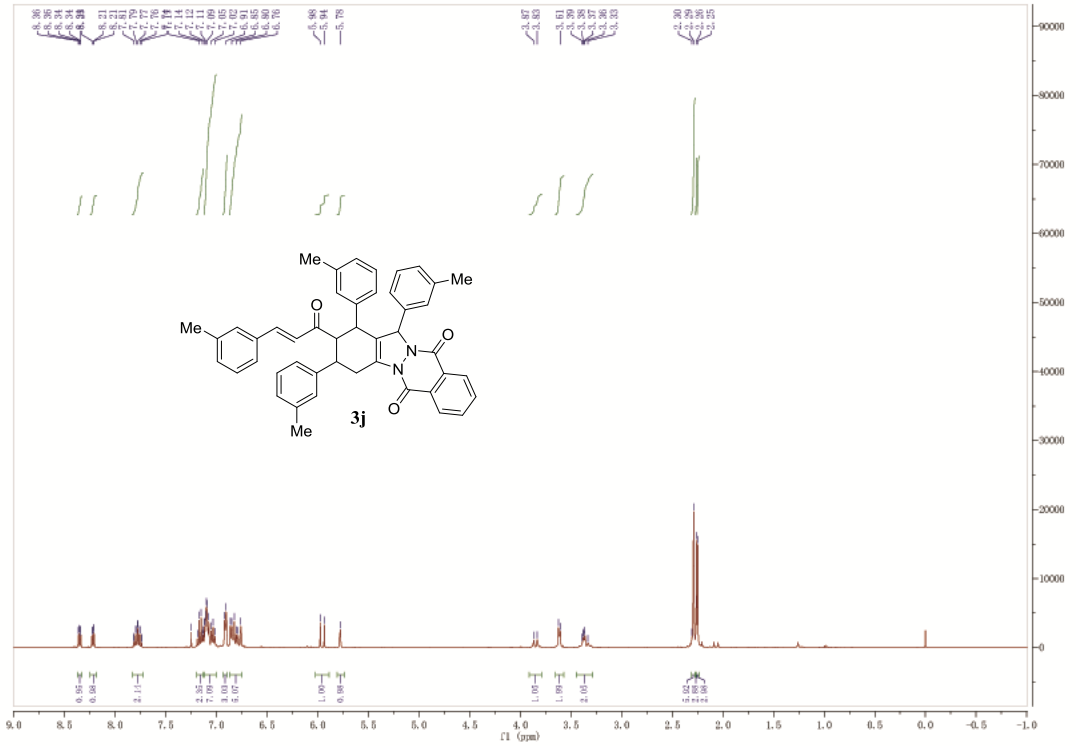
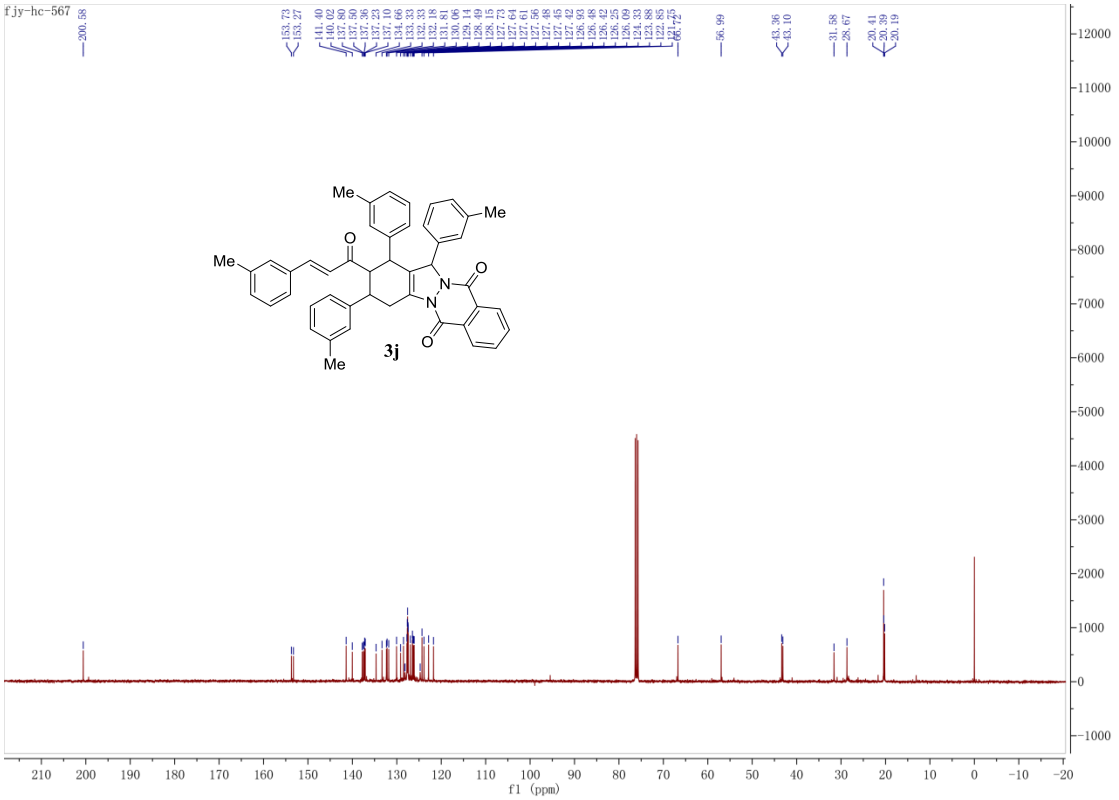
3h
f1 (ppm)


H3CO
OCH3
H3CO
O
O
N
N
O
OCH3
3i
f1 (ppm)


H3CO
OCH3
H3CO
O
O
N
N
O
OCH3
3i
f1 (ppm)


Me
Me
O
Me
N
N
O
O
Me
3j
f1 (ppm)


fjy-hc-567
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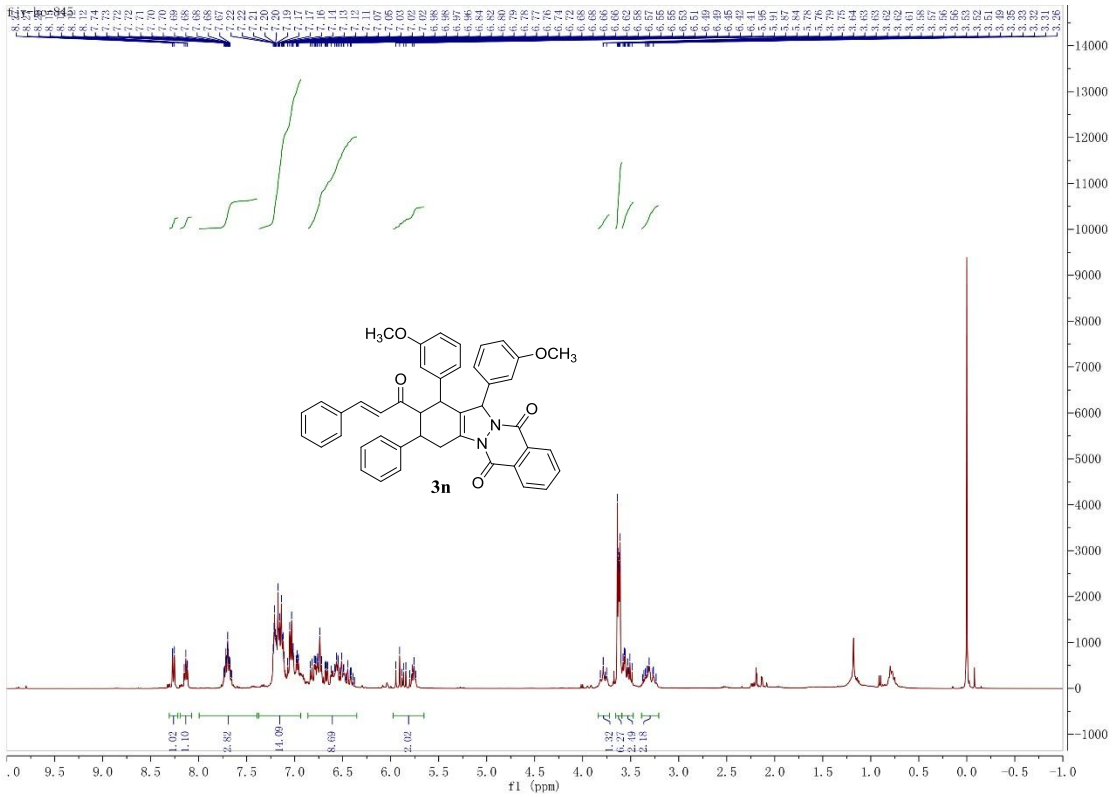
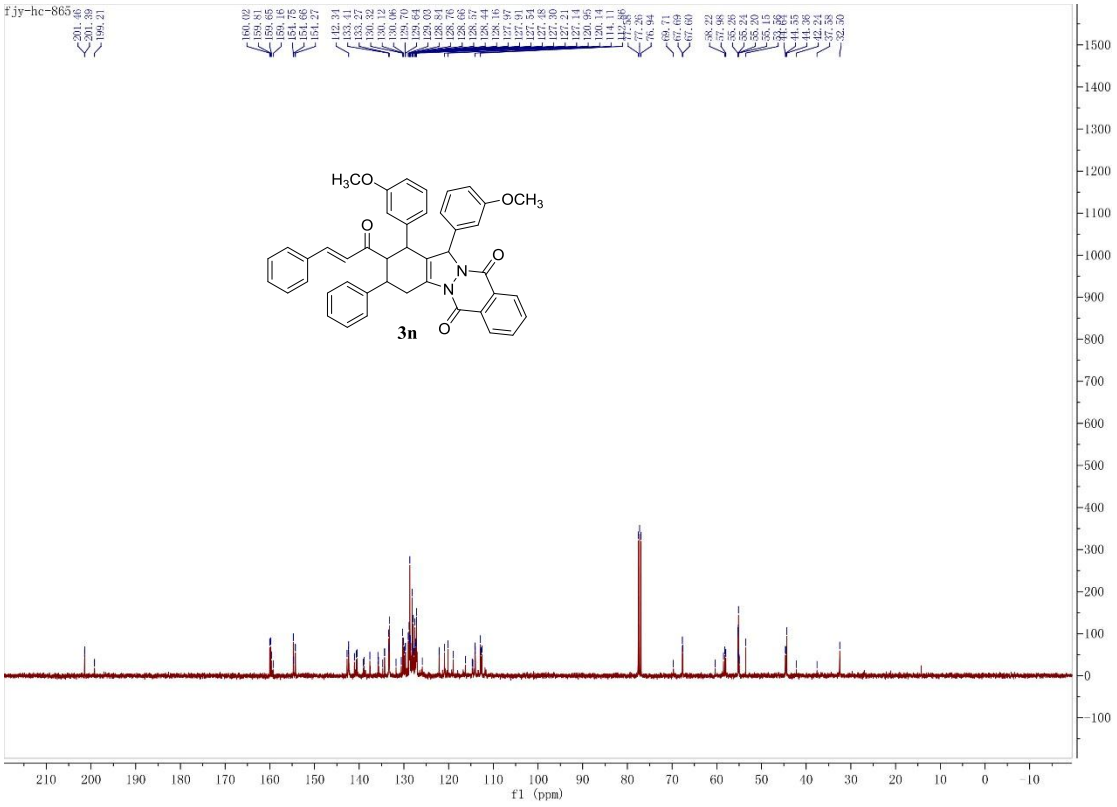
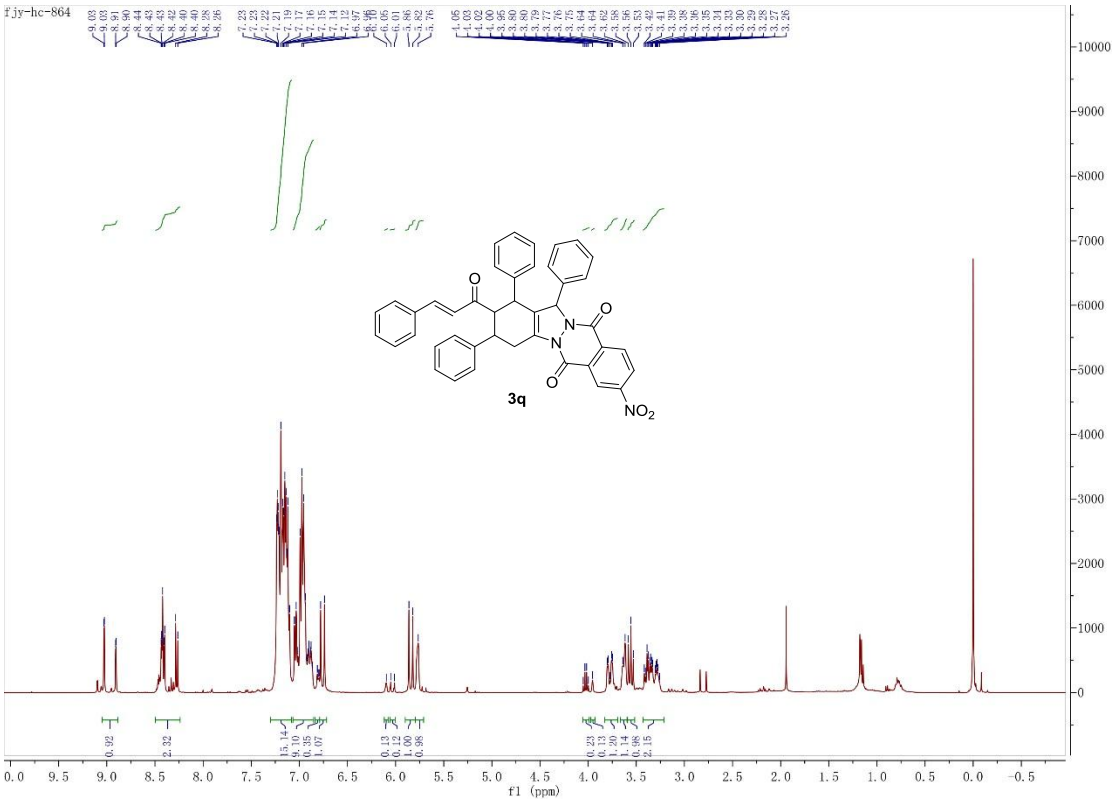
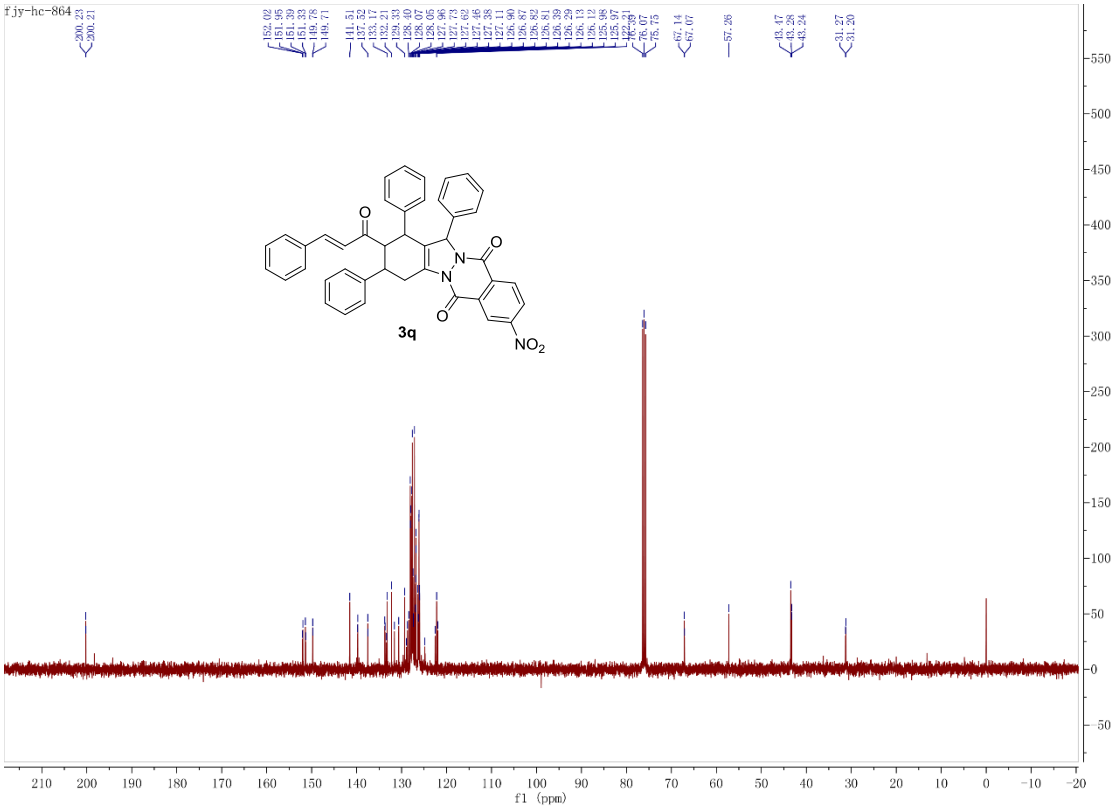
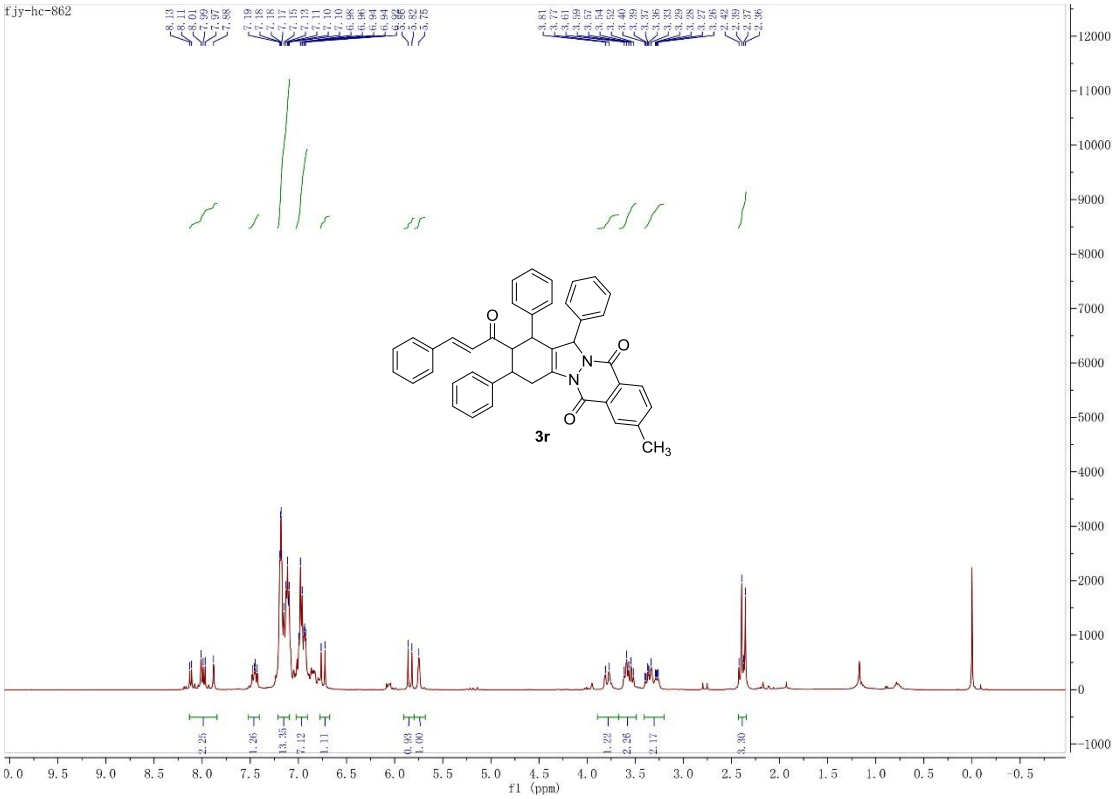
Me
N
N
O
O
Me
3j
f1 (ppm)

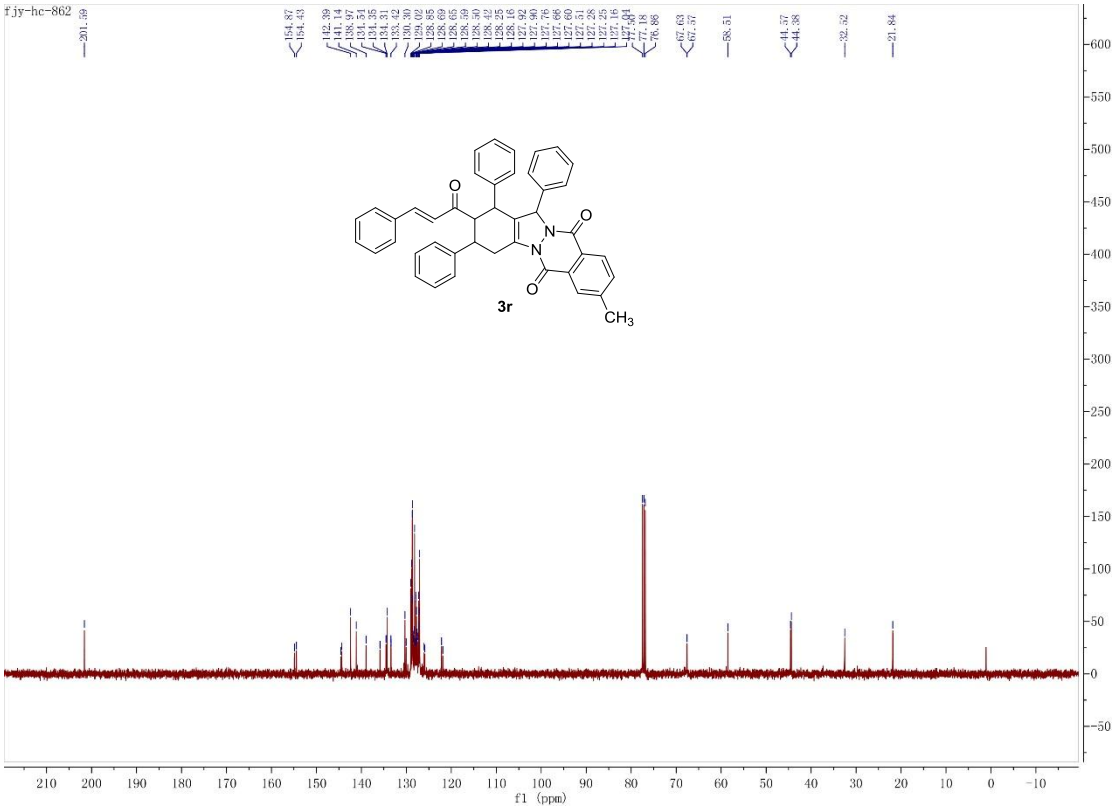

H3CO
OCH3
O
O
N
N
O
O
3n
1.02
1.10
2.82
14.09
8.69
2.02
1.32
6.27
2.19
2.18
f1 (ppm)

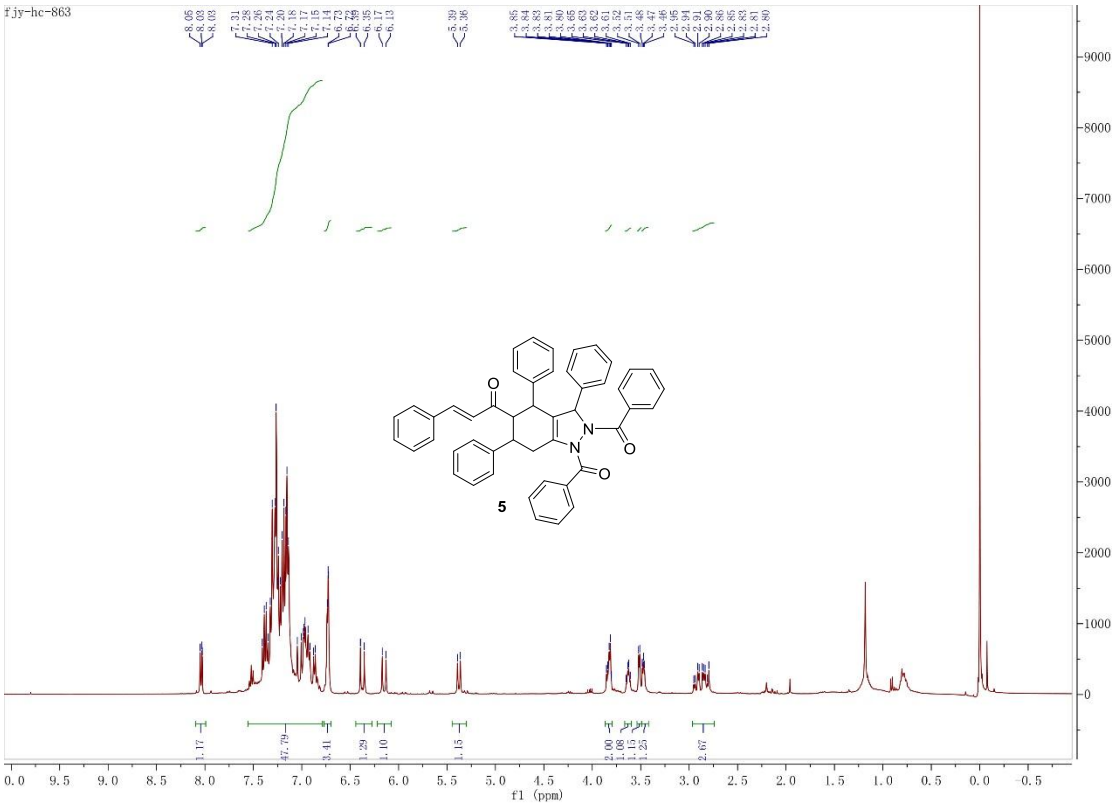

H3CO
OCH3
O
O
N
N
O
O
3n
f1 (ppm)

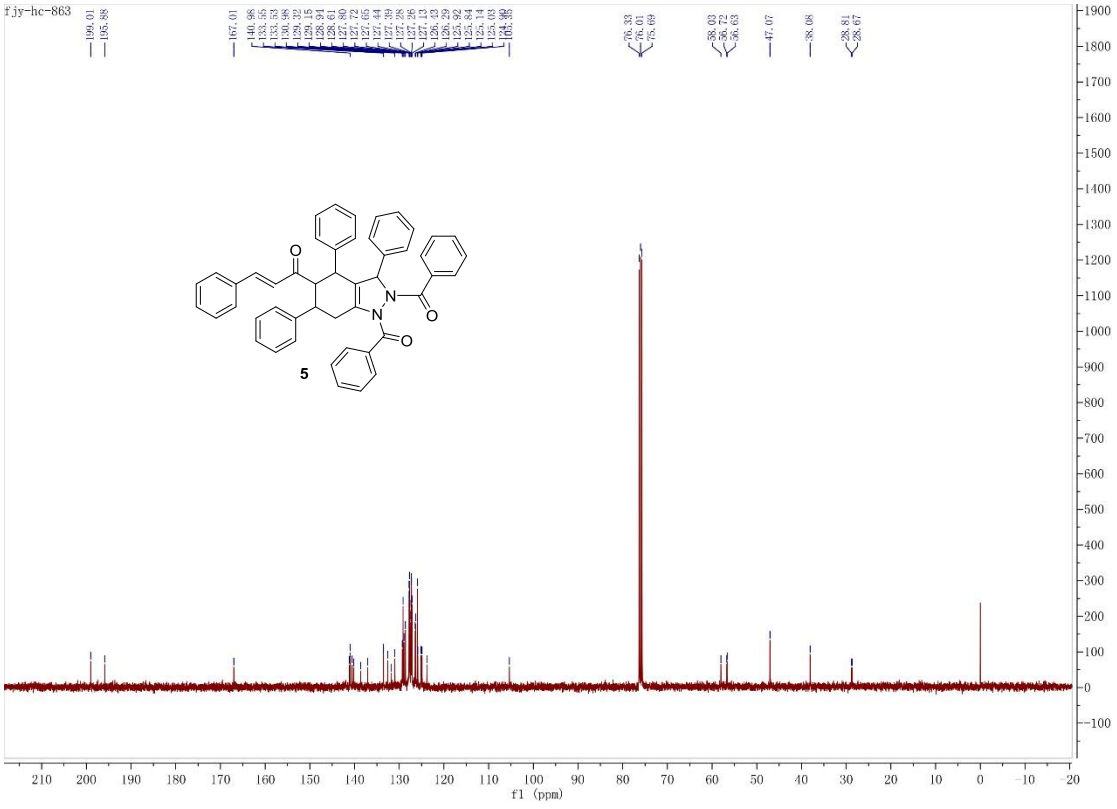

fjy-hc-864
3q
NO2
f1 (ppm)


fjy-hc-864
3q
NO2
f1 (ppm)


fjy-hc-862
3r
f1 (ppm)


fjy-hc-862
3r
f1 (ppm)


fjy-hc-863
5
f1 (ppm)


fjy-hc-863
5
f1 (ppm)