Supporting information

Base-Promoted Ring-pening/Recyclization of Naphthoquinones to Access Benzo[5,6][1,4]thiazino[4,3-*b*]isoquinoline-7,12-diones at Room Temperature

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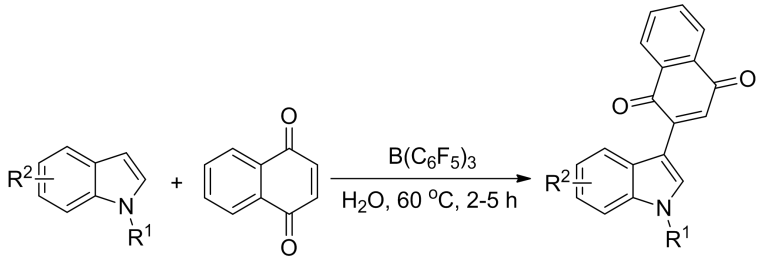
1. General information

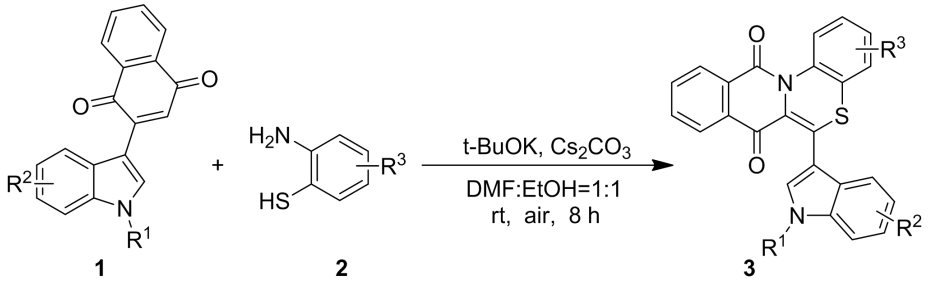
Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Column chromatography was performed using silica gel (200-300 mesh). ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on Bruker-AV (400, 100 and 376 MHz, respectively) instrument internally referenced solvent signals. Mass spectra were measured on Agilent 5977 GC-MS instrument (EI). High-resolution mass spectra (HRMS) were performed on FTMS ICR MS BRUKER 7T or Agilent 6230 TOF LC/MS. Melting points were measured on BÜCHI B-545 melting point instrument and were uncorrected. X-ray crystal structure data was using collected on a SuperNova, Dual, Cu at zero, AtlasS2 diffractometer. The structures were solved by direct methods using Olex2 software. The structures of known compounds were further corroborated by comparing their NMR and MS data with those of literature.

2. General procedure for synthesis of 2-(indol-3-yl)naphthoquinones



2-(indol-3-yl)naphthoquinones was prepared according to the previous literature.[1] indoles (0.4 mmol), naphthalene-1,4-dione (0.4 mmol, 1.0 equiv), $B(C_6F_5)_3$ (5 mol %) and H_2O (2.0 mL) was added to a 20 mL oven-dried reaction vessel and stirred at 60 °C for 2-5 h. The volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel to give 2-(indol-3-yl)naphthoquinones.

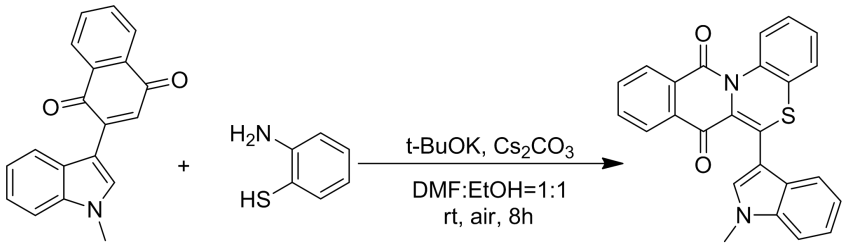
3. General procedure for the synthesis of products 3



A 10 mL oven-dried reaction vessel was added with 2-(1-methyl-1*H*-indol-3-yl)naphthalene-1,4-

diones (**1**, 0.2 mmol), 2-aminobenzenethiol (**2**, 0.5 mmol, 2.5 equiv), *t*-BuOK (0.18 mmol, 0.9 equiv), Cs_2CO_3 (0.12 mmol, 0.6 equiv), dry DMF (0.8 mL) and dry EtOH (0.8 mL). The sealed reaction vessel was stirred at room temperature for 8 hours under air atmosphere. The reaction mixture was diluted with ethyl acetate and filtered. The volatiles were removed under reduced pressure and the residue was purified by column chromatography on silica gel to give products **3**.

4. Procedure for the gram-scale synthesis of 3aa

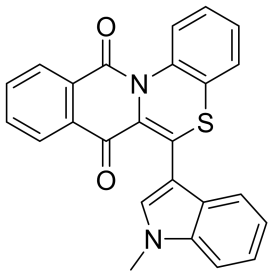


1a **2a** **3aa**

A 25 mL oven-dried reaction vessel was added with 2-(1-methyl-1*H*-indol-3-yl)naphthalene-1,4-dione (**1a**, 2.870 g, 10.0 mmol), 2-aminobenzenethiol (**2a**, 3.126 g, 25.0 mmol), *t*-BuOK (0.202 g, 1.8 mmol), Cs_2CO_3 (0.391 g, 1.2 mmol), dry DMF (8.0 mL) and dry EtOH (8.0 mL). The sealed reaction vessel was stirred at room temperature for 8 hour under air atmosphere. The reaction mixture was diluted with ethyl acetate and filtered. The volatiles were removed under reduced pressure and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5∶1) to give the product **3aa** (2.244 g, 55% yield).

5. Characterization data of products

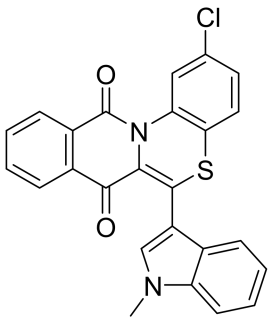
6-(1-Methyl-1*H*-indol-3-yl)benzo[5,6][1,4]thiazino[4,3-*b*]isoquinoline-7,12-dione (3aa)



The reaction was conducted with 2-(1-methyl-1*H*-indol-3-yl)naphthalene-1,4-dione (57.4 mg, 0.2 mmol) and 2-aminobenzenethiol (62.5 mg, 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) to yield the desired product **3aa** as red solid (62.1mg, 76% yield). mp: 258-260 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, J = 8.0 Hz, 1H), 8.06 (d, J = 7.6 Hz, 1H), 7.87 (t, J = 7.0 Hz, 1H), 7.79 (t, J = 7.4 Hz, 1H), 7.70 (d, J = 8.4 Hz, 1H), 7.61 (s, 1H), 7.38–7.34 (m, 2H), 7.30–7.24 (m, 3H), 7.14 (d, J = 8.0 Hz, 1H), 7.08 ((t, J = 7.6 Hz, 1H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.4, 159.9, 137.4, 136.2, 134.5, 134.3, 134.2, 133.3, 132.8, 131.2, 129.3, 129.2, 127.9, 127.3, 127.3, 127.0, 126.1, 125.7, 125.1, 122.8, 120.7, 120.5, 110.3, 109.1, 33.4. HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{25}H_{17}N_2O_2S$ 409.1005; found 409.1010.

2-Chloro-6-(1-methyl-1*H*-indol-3-yl)benzo[5,6][1,4]thiazino[4,3-*b*]isoquinoline-7,12-dione (3ab)

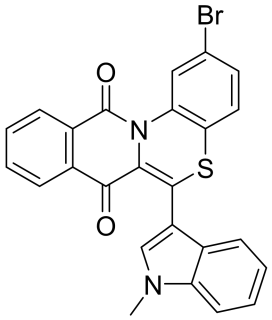


The reaction was conducted with 2-(1-methyl-1*H*-indol-3-yl)naphthalene-1,4-dione (57.4 mg, 0.2 mmol) and 2-amino-4-chlorobenzenethiol (79.5 mg, 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) to yield the desired product **3ab** as red solid (60.1 mg, 69% yield). mp: 272-274 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, J = 8.0 Hz, 1H), 8.05 (d, J = 8.0 Hz, 1H), 7.88 (t, J = 7.6 Hz,

1H), 7.80 (t, *J* = 7.4 Hz, 1H), 7.73 (s, 1H), 7.60 (s, 1H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.28–7.23 (m, 2H), 7.19 (d, *J* = 8.4 Hz, 1H), 7.12–7.06 (m, 2H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.2, 159.9, 137.5, 137.3, 134.5, 134.4, 134.3, 133.7, 133.6, 132.9, 130.9, 129.5, 128.9, 127.7, 127.6, 126.2, 125.9, 125.9, 125.1, 122.9, 120.7, 120.7, 110.4, 108.9, 33.4. HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{25}H_{16}ClN_2O_2S$ 443.0616; found 443.0596.

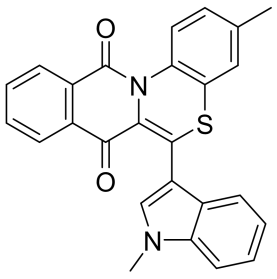
2-Bromo-6-(1-methyl-1*H*-indol-3-yl)benzo[5,6][1,4]thiazino[4,3-*b*]isoquinoline-7,12-dione (3ac)



The reaction was conducted with 2-(1-methyl-1*H*-indol-3-yl)naphthalene-1,4-dione (57.4 mg, 0.2 mmol) and 2-amino-4-bromobenzenethiol (102.0 mg, 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) to yield the desired product **3ac** as red solid (58.3 mg, 60% yield). mp: 270-272 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 7.6 Hz, 1H), 8.05 (d, *J* = 7.6 Hz, 1H), 7.87 (t, *J* = 7.4 Hz, 1H), 7.80 (t, *J* = 8.0 Hz, 1H), 7.59–7.56 (m, 2H), 7.46–7.42 (m, 2H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.28–724 (m, 1H), 7.12–7.08 (m, 2H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.3, 159.9, 137.5, 135.3, 134.4, 134.4, 133.6, 133.5, 132.8, 131.0, 130.9, 129.6, 129.4, 129.4, 129.2, 127.0, 126.2, 125.1, 122.9, 120.7, 120.7, 120.3, 110.4, 108.8, 33.5. HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{25}H_{16}BrN_2O_2S$ 487.0110; found 487.0090.

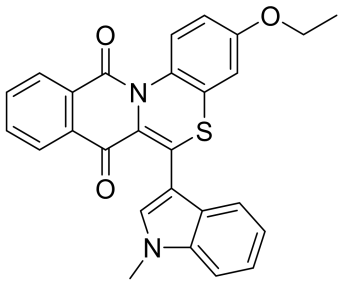
3-Methyl-6-(1-methyl-1*H*-indol-3-yl)benzo[5,6][1,4]thiazino[4,3-*b*]isoquinoline-7,12-dione (3ad)



The reaction was conducted with 2-(1-methyl-1*H*-indol-3-yl)naphthalene-1,4-dione (57.4 mg, 0.2 mmol) and 2-amino-5-methylbenzenethiol (69.5 mg, 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) to yield the desired product **3ad** as orange solid (54.9 mg, 65% yield). mp: 263-265℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, J = 7.6 Hz, 1H), 8.05 (d, J = 7.6 Hz, 1H), 7.86 (t, J = 7.6 Hz, 1H), 7.78 (t, J = 7.4 Hz, 1H), 7.59–7.57 (m, 2H), 7.34 (d, J = 8.4 Hz, 1H), 7.27–7.24 (m, 1H), 7.16–7.13 (m, 2H), 7.09–7.06 (m, 2H), 3.83 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.5, 159.8, 137.4, 137.4, 134.5, 134.2, 133.5, 133.2, 132.6, 131.3, 129.5, 129.3, 128.7, 127.1, 127.0, 126.1, 125.4, 125.2, 122.8, 120.7, 120.5, 110.3, 109.2, 33.4, 21.0. HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{26}H_{19}N_2O_2S$ 423.1162; found 423.1164.

3-Ethoxy-6-(1-methyl-1*H*-indol-3-yl)benzo[5,6][1,4]thiazino[4,3-*b*]isoquinoline-7,12-dione (3ae)

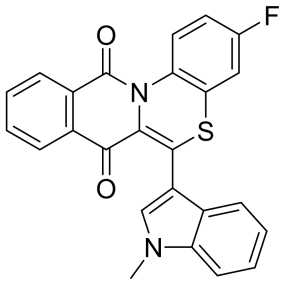


The reaction was conducted with 2-(1-methyl-1*H*-indol-3-yl)naphthalene-1,4-dione (57.4 mg, 0.2 mmol) and 2-amino-5-ethoxybenzenethiol (84.5 mg, 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) to yield the desired product **3ae** as red solid (65.1 mg, 72% yield). mp: 251-253 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, J = 7.6 Hz, 1H), 8.02 (d, J = 7.6 Hz, 1H), 7.84 (t, J = 7.6 Hz, 1H), 7.75 (t, J = 7.6 Hz, 1H), 7.61–7.58 (m, 2H), 7.33 (d, J = 8.4 Hz, 1H), 7.25–7.22 (m, 1H), 7.15 (d, J = 8.0 Hz, 1H), 7.06 (t, J = 7.4 Hz, 1H), 6.89-6.86 (m, 1H), 6.76 (s, 1H), 4.04 (q, J = 6.9 Hz, 2H), 3.82 (s, 3H), 1.42 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.6, 159.7, 157.7, 137.4, 134.4, 134.2, 133.6, 133.1, 132.7, 131.3, 129.7, 129.3, 128.5, 128.3, 126.6, 126.1, 125.3, 122.8, 120.7, 120.5, 114.5, 111.9, 110.3, 109.1, 64.1, 33.4, 14.9. HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{27}H_{20}N_2NaO_3S$ 475.1087; found 475.1083.

3-Fluoro-6-(1-methyl-1*H*-indol-3-yl)benzo[5,6][1,4]thiazino[4,3-*b*]isoquinoline-7,12-dione

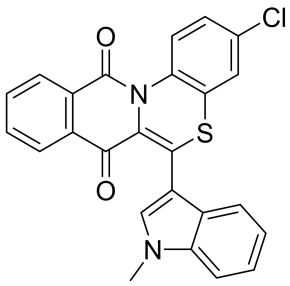
(3af)



The reaction was conducted with 2-(1-methyl-1*H*-indol-3-yl)naphthalene-1,4-dione (57.4 mg, 0.2 mmol) and 2-amino-5-fluorobenzenethiol (71.5 mg, 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) to yield the desired product **3af** as red solid (62.2 mg, 73% yield). mp: 212-214 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, J = 7.2 Hz, 1H), 8.05 (d, J = 7.6 Hz, 1H), 7.87 (t, J = 7.4 Hz, 1H), 7.79 (t, J = 7.4 Hz, 1H), 7.69–7.66 (m, 1H), 7.61 (s, 1H), 7.35 (d, J = 8.4 Hz, 1H), 7.26 (t, J = 7.4 Hz, 1H), 7.13 (d, J = 7.6 Hz, 1H), 7.09 (d, J = 6.8 Hz, 1H), 7.06-7.03 (m, 1H), 7.02-6.99 (m, 1H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.5, 160.8 (d, J = 248.0 Hz), 159.9, 137.5, 134.4, 134.3, 133.4, 133.3, 132.9, 132.0 (d, J = 3.2 Hz), 131.1, 129.4, 127.2 (d, J = 8.7 Hz), 126.1, 125.1, 122.9, 120.7 (d, J = 3.8 Hz), 115.0 (d, J = 22.9 Hz), 113.6 (d, J = 24.8 Hz), 110.4, 108.7, 33.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.1. HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{25}H_{15}FN_2NaO_2S$ 449.0730; found 449.0721.

3-Chloro-6-(1-methyl-1*H*-indol-3-yl)benzo[5,6][1,4]thiazino[4,3-*b*]isoquinoline-7,12-dione (3ag)

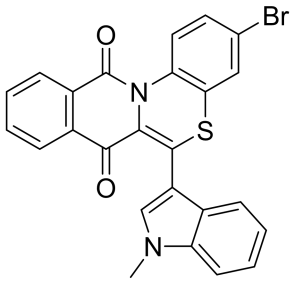


The reaction was conducted with 2-(1-methyl-1*H*-indol-3-yl)naphthalene-1,4-dione (57.4 mg, 0.2 mmol) and 2-amino-5-chlorobenzenethiol (79.5 mg, 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) to yield the desired product **3ag** as red solid (73.4 mg, 83% yield). mp: 278-280 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, J = 7.6 Hz, 1H), 8.05 (d, J = 7.6 Hz, 1H), 7.87 (t, J = 7.6 Hz,

1H), 7.79 (t, *J* = 7.4 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.59 (s, 1H), 7.36–7.26 (m, 4H), 7.12–7.06 (m, 2H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.3, 159.9, 137.5, 134.8, 134.4, 134.4, 133.5, 133.5, 132.8, 132.6, 131.0, 129.4, 129.2, 129.2, 128.0, 126.8, 126.6, 126.2, 125.1, 123.0, 120.7, 120.7, 110.4, 108.8, 33.5. HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{25}H_{15}ClN_2NaO_2S$ 465.0435; found 465.0436.

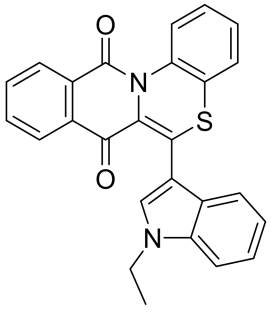
3-Bromo-6-(1-methyl-1H-indol-3-yl)benzo[5,6][1,4]thiazino[4,3-b]isoquinoline-7,12-dione (3ah)



The reaction was conducted with 2-(1-methyl-1*H*-indol-3-yl)naphthalene-1,4-dione (57.4 mg, 0.2 mmol) and 2-amino-5-bromobenzenethiol (102.0 mg, 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) to yield the desired product **3ah** as red solid (72.9 mg, 75% yield). mp: 274-276 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 8.0 Hz, 1H), 8.05 (d, *J* = 6.8 Hz, 1H), 7.87 (t, *J* = 7.4 Hz, 1H), 7.80 (t, *J* = 7.0 Hz, 1H), 7.59 ((s, 1H),) 7.57 (d, *J* = 8.8 Hz, 1H), 7.46–7.42 (m, 2H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.28-7.25 (m, 1H), 7.12–7.06 (m, 2H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.3, 159.9, 137.5, 135.3, 134.4, 134.4, 133.6, 133.5, 132.8, 131.0, 130.9, 129.6, 129.4, 129.4, 127.0, 126.2, 125.1, 125.1, 122.9, 120.7, 120.7, 120.2, 110.4, 108.8, 33.5. HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{25}H_{15}BrN_2NaO_2S$ 508.9930; found 508.9933.

6-(1-Ethyl-1*H*-indol-3-yl)benzo[5,6][1,4]thiazino[4,3-*b*]isoquinoline-7,12-dione (3ba)

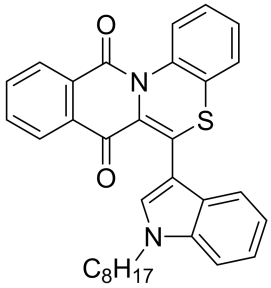


The reaction was conducted with 2-(1-ethyl-1H-indol-3-yl)naphthalene-1,4-dione (60.2 mg, 0.2

mmol) and 2-aminobenzenethiol (62.5 mg, 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) to yield the desired product **3ba** as orange solid (56.5 mg, 67% yield). mp: 275-277 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, J = 8.0 Hz, 1H), 8.07 (d, J = 7.6 Hz, 1H), 7.87 (t, J = 7.6 Hz, 1H), 7.79 (t, J = 7.4 Hz, 1H), 7.72–7.69 (m, 2H), 7.39–7.34 (m, 2H), 7.31–7.23 (m, 3H), 7.15 (d, J = 7.6 Hz, 1H), 7.08 (t, J = 7.6 Hz, 1H), 4.21 (q, J = 7.3 Hz, 2H), 1.54 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.4, 159.9, 136.6, 136.3, 134.5, 134.5, 134.2, 133.3, 131.2, 131.2, 129.3, 129.1, 127.8, 127.4, 127.2, 127.0, 126.1, 125.7, 125.3, 122.7, 120.9, 120.5, 110.4, 109.2, 41.5, 15.3. HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{26}H_{18}N_2NaO_2S$ 445.0981; found 445.0975.

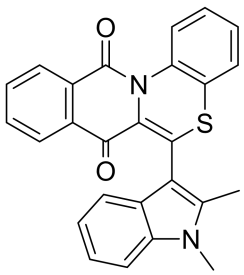
6-(1-Octyl-1*H*-indol-3-yl)benzo[5,6][1,4]thiazino[4,3-*b*]isoquinoline-7,12-dione (3ca)



The reaction was conducted with 2-(1-octyl-1*H*-indol-3-yl)naphthalene-1,4-dione (77.0 mg, 0.2 mmol) and 2-aminobenzenethiol (62.5 mg, 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) to yield the desired product **3ca** as orange solid (77.9 mg, 77% yield). mp: 194-196 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, J = 8.0 Hz, 1H), 8.06 (d, J = 7.6 Hz, 1H), 7.87 (t, J = 7.0 Hz, 1H), 7.79 (t, J = 7.4 Hz, 1H), 7.70 (d, J = 7.6 Hz, 1H), 7.66 (s, 1H), 7.38–7.33 (m, 2H), 7.31–7.28 (m, 2H), 7.23 (d, J = 8.0 Hz, 1H), 7.16 (d, J = 8.0 Hz, 1H), 7.07 (t, J = 7.6 Hz, 1H), 4.14 (t, J = 7.2 Hz, 2H), 1.93-1.86 (m, 2H), 1.41–1.25 (m, 10H), 0.92–0.86 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.3, 159.9, 136.8, 136.3, 134.6, 134.5, 134.2, 133.3, 131.9, 131.2, 129.4, 129.2, 127.8, 127.5, 127.3, 127.1, 126.1, 125.8, 125.3, 122.6, 120.9, 120.5, 110.5, 109.0, 47.0, 31.9, 30.1, 29.3, 29.3, 27.1, 22.7, 14.2. HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{32}H_{31}N_3O_2S$ 507.2101; found 507.2097.

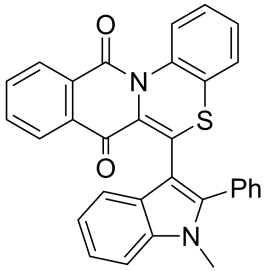
6-(1,2-Dimethyl-1*H*-indol-3-yl)benzo[5,6][1,4]thiazino[4,3-*b*]isoquinoline-7,12-dione (3ea)



The reaction was conducted with 2-(1,2-dimethyl-1*H*-indol-3-yl)naphthalene-1,4-dione (73.0 mg, 0.2 mmol) and 2-aminobenzenethiol (62.5 mg, 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) to yield the desired product **3ea** as red solid (46.4 mg, 55% yield). mp: 262-264 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, J = 7.6 Hz, 1H), 8.00 (d, J = 7.6 Hz, 1H), 7.85 (t, J = 7.2 Hz, 1H), 7.75 (d, J = 7.2 Hz, 1H), 7.71 (d, J = 8.8 Hz, 1H), 7.39–7.35 (m, 2H), 7.32–7.28 (m, 3H), 7.18 (t, J = 7.4 Hz, 1H), 7.05 (t, J = 7.4 Hz, 1H), 3.70 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.7, 159.7, 138.0, 137.0, 135.4, 134.4, 134.2, 133.3, 132.3, 131.1, 129.3, 127.8, 127.7, 127.5, 127.2, 126.3, 126.2, 126.0, 121.7, 120.3, 119.1, 109.4, 106.1, 30.0, 12.3. HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{26}H_{19}N_2O_2S$ 423.1162; found 423.1152.

6-(1-Methyl-2-phenyl-1*H*-indol-3-yl)benzo[5,6][1,4]thiazino[4,3-*b*]isoquinoline-7,12-dione (3fa)

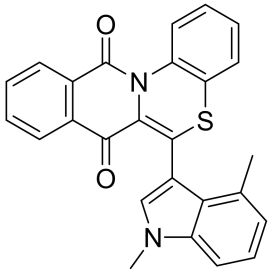


The reaction was conducted with 2-(1-methyl-2-phenyl-1*H*-indol-3-yl)naphthalene-1,4-dione (72.6 mg, 0.2 mmol) and 2-aminobenzenethiol (62.5 mg, 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) to yield the desired product **3fa** as red solid (62.9 mg, 65% yield). mp: 280-282 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, J = 7.6 Hz, 1H), 7.74-7.56 (m, 5H), 7.40 (d, J = 8.4 Hz, 1H), 7.34–7.30 (m, 4H), 7.28–7.17 (m, 3H), 7.13 (t, J = 7.8 Hz, 2H), 6.96 (t, J = 7.4 Hz, 1H), 3.70 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.5, 159.5, 140.1, 137.9, 135.5, 134.8, 133.8, 133.6, 132.5, 131.7, 130.8, 130.3, 130.1, 128.7, 128.6, 128.1, 127.8, 127.4, 127.3, 127.1, 126.7, 126.4, 125.7, 122.7, 120.9,

119.9, 110.3, 106.5, 31.5. HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{31}H_{21}N_2O_2S$ 485.1318; found 485.1316.

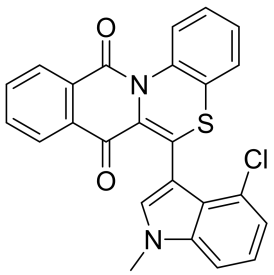
6-(1,4-Dimethyl-1*H*-indol-3-yl)benzo[5,6][1,4]thiazino[4,3-*b*]isoquinoline-7,12-dione (3ga)



The reaction was conducted with 2-(1,4-dimethyl-1*H*-indol-3-yl)naphthalene-1,4-dione (60.3 mg, 0.2 mmol) and 2-aminobenzenethiol (62.5 mg, 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) to yield the desired product **3ga** as red solid (40.5 mg, 48% yield). mp: 215-217 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, J = 7.2 Hz, 1H), 7.99 (d, J = 7.2 Hz, 1H), 7.83 (t, J = 7.0 Hz, 1H), 7.73 (d, J = 7.2 Hz, 2H), 7.69 (d, J = 8.4 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.28–7.22 (m, 1H), 7.19–7.13 (m, 2H), 7.06 (s, 1H), 6.86 (d, J = 6.4 Hz, 1H), 3.77 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.4, 159.8, 137.3, 135.6, 134.8, 134.3, 133.3, 132.2, 131.1, 131.0, 129.4, 128.7, 127.8, 127.6, 127.5, 126.8, 126.3, 126.0, 122.7, 121.9, 108.8, 107.7, 33.3, 19.4. HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{26}H_{19}N_2O_2S$ 423.1162; found 423.1155.

6-(4-Chloro-1-methyl-1*H*-indol-3-yl)benzo[5,6][1,4]thiazino[4,3-*b*]isoquinoline-7,12-dione (3ha)

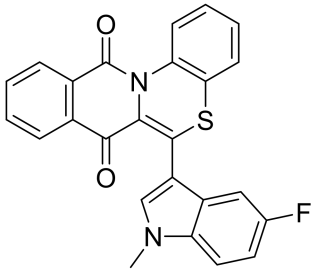


The reaction was conducted with 2-(4-chloro-1-methyl-1*H*-indol-3-yl)naphthalene-1,4-dione (64.4 mg, 0.2 mmol) and 2-aminobenzenethiol (62.5 mg, 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) to yield the desired product **3ha** as red solid (56.6 mg, 64% yield). mp: 254-256 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, J = 7.6 Hz, 1H), 8.08 (d, J = 7.6 Hz, 1H), 7.88 (t, J = 7.4 Hz,

1H), 7.81 (t, *J* = 7.4 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.57 (s, 1H), 7.38–7.34 (m, 1H), 7.29–7.23 (m, 3H), 7.19 (d, *J* = 8.8 Hz, 1H), 7.11 (d, *J* = 1.6 Hz, 1H), 3.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 177.9, 159.8, 136.1, 135.8, 134.5, 134.4, 133.6, 133.4, 133.2, 131.2, 129.6, 129.4, 128.0, 127.3, 127.1, 127.0, 126.6, 126.1, 126.1, 125.8, 123.1, 120.4, 111.3, 108.7, 33.5. HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{25}H_{15}ClN_2NaO_2S$ 465.0435; found 465.0435.

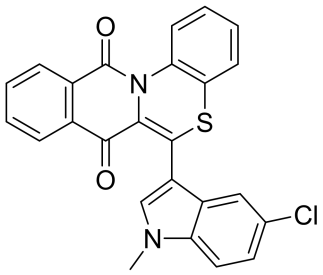
6-(5-Fluoro-1-methyl-1*H*-indol-3-yl)benzo[5,6][1,4]thiazino[4,3-*b*]isoquinoline-7,12-dione (3ia)



The reaction was conducted with 2-(5-fluoro-1-methyl-1*H*-indol-3-yl)naphthalene-1,4-dione (61.1mg, 0.2 mmol) and 2-aminobenzenethiol (62.5 mg, 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) to yield the desired product **3ia** as red solid (55.4mg, 65% yield). mp: 280-282 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.49 (d, *J* = 8.0 Hz, 1H), 8.08 (d, *J* = 7.6 Hz, 1H), 7.88 (t, *J* = 7.6 Hz, 1H), 7.80 (t, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.60 (s, 1H), 7.38–7.34 (m, 1H), 7.29–7.24 (m, 3H), 7.02-6.97 (m, 1H), 6.81-6.78 (m, 1H), 3.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 177.6, 159.9, 158.4 (d, *J* = 245.3 Hz), 136.2, 134.4, 134.4, 134.0, 134.0, 133.8, 133.5, 131,2, 129.4, 128.0, 127.3, 127.2, 127.1, 126.1, 125.8, 111.4, 111.1(d, *J* = 2.3 Hz), 111.0, 109.1 (d, *J* = 4.7 Hz), 106.1 (d, *J* = 24.7 Hz), 33.7. ^{19}F NMR (376 MHz, $CDCl_3$) *δ* -122.9. HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{25}H_{16}FN_2O_2S$ 427.0911; found 427.0903.

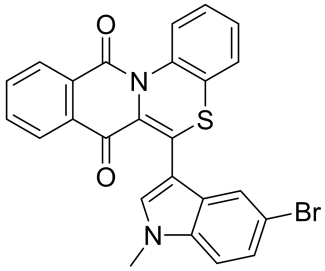
6-(5-Chloro-1-methyl-1*H*-indol-3-yl)benzo[5,6][1,4]thiazino[4,3-*b*]isoquinoline-7,12-dione (3ja)



The reaction was conducted with 2-(5-chloro-1-methyl-1*H*-indol-3-yl)naphthalene-1,4-dione (64.4 mg, 0.2 mmol) and 2-aminobenzenethiol (62.5 mg, 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) to yield the desired product **3ja** as red solid (48.6 mg, 55% yield). mp: 238-240 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 7.6 Hz, 1H), 8.08 (d, *J* = 7.6 Hz, 1H), 7.89 (t, *J* = 7.4 Hz, 1H), 7.82 (t, *J* = 8.2 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.56 (s, 1H), 7.38–7.34 (m, 1H), 7.28–7.23 (m, 3H), 7.21-7.18 (m, 1H), 7.11 (s, 1H), 3.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 177.9, 159.8, 136.1, 135.9, 134.5, 134.4, 133.6, 133.5, 133.3, 131.2, 129.6, 129.4, 128.0, 127.4, 127.1, 126.6, 126.2, 126.1, 125.8, 123.2, 120.4, 111.3, 108.7, 33.6. HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{25}H_{15}ClN_2NaO_2S$ 465.0435; found 465.0432.

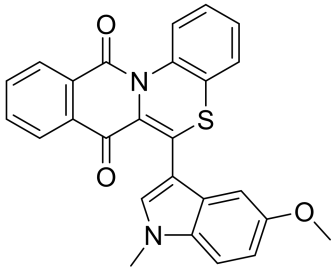
6-(5-Bromo-1-methyl-1*H*-indol-3-yl)benzo[5,6][1,4]thiazino[4,3-*b*]isoquinoline-7,12-dione (3ka)



The reaction was conducted with 2-(5-bromo-1-methyl-1H-indol-3-yl)naphthalene-1,4-dione (73.2 mg, 0.2 mmol) and 2-aminobenzenethiol (62.5 mg, 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) to yield the desired product **3ka** as red solid (41.8 mg, 43% yield). mp: 250-252 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.48 (d, *J* = 8.0 Hz, 1H), 8.08 (d, *J* = 7.6 Hz, 1H), 7.88 (t, *J* = 7.4 Hz, 1H), 7.82 (t, *J* = 7.6 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.55 (s, 1H), 7.38–7.31 (m, 2H), 7.28–7.25 (m, 3H), 7.20 (d, *J* = 8.8 Hz, 1H), 3.81 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 178.0, 159.8, 136.2, 136.1, 134.5, 134.5, 133.5, 133.0, 131.2, 129.7, 129.4, 128.0, 127.4, 127.1, 126.6, 126.2, 125.9, 125.7, 123.5, 114.2, 111.8, 108.7, 33.6. HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{25}H_{15}BrN_2NaO_2S$ 508.9930; found 508.9920.

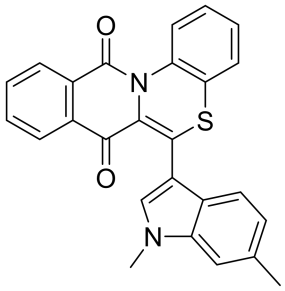
6-(5-Methoxy-1-methyl-1*H*-indol-3-yl)benzo[5,6][1,4]thiazino[4,3-*b*]isoquinoline-7,12-dione (3la)



The reaction was conducted with 2-(5-methoxy-1-methyl-1*H*-indol-3-yl)naphthalene-1,4-dione (63.4 mg, 0.2 mmol) and 2-aminobenzenethiol (62.5 mg, 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) to yield the desired product **3la** as red solid (40.3 mg, 46% yield). mp: 208-210 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, J = 7.6 Hz, 1H), 8.10 (d, J = 7.6 Hz, 1H), 7.86 (t, J = 7.4 Hz, 1H), 7.78 (t, J = 7.6 Hz, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.56 (s, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.30–7.25 (m, 2H), 7.22 (d, J = 9.2 Hz, 1H), 6.89 (d, J = 8.8 Hz, 1H), 6.46 (s, 1H), 3.80 (s, 3H), 3.51 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.4, 160.0, 155.0, 136.4, 134.9, 134.4, 134.3, 133.1, 133.0, 132.6, 131.3, 129.5, 128.7, 127.9, 127.3, 127.0, 126.2, 125.7, 125.6, 113.4, 111.2, 108.8, 102.2, 55.5, 33.6. HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{26}H_{18}N_2NaO_3S$ 461.0930; found 461.0932.

6-(1,6-Dimethyl-1*H*-indol-3-yl)benzo[5,6][1,4]thiazino[4,3-*b*]isoquinoline-7,12-dione (3ma)

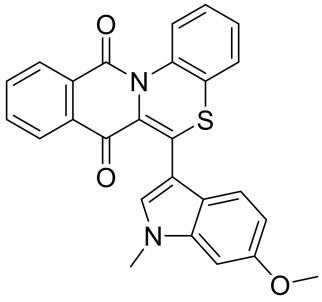


The reaction was conducted with 2-(1,6-dimethyl-1*H*-indol-3-yl)naphthalene-1,4-dione (60.2 mg, 0.2 mmol) and 2-aminobenzenethiol (62.5 mg, 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) to yield the desired product **3ma** as red solid (44.7 mg, 53% yield). mp: 268-270 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, J = 7.6 Hz, 1H), 8.03 (d, J = 7.6 Hz, 1H), 7.86 (t, J = 7.6 Hz, 1H), 7.77 (t, J = 7.6 Hz, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.46 (s, 1H), 7.37–7.33 (m, 1H), 7.28–7.23 (m, 2H), 6.97–6.89 (m, 3H), 4.09 (s, 3H), 2.75 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.4, 159.9, 136.2, 136.1, 134.5, 134.2, 134.1, 133.3, 131.2, 129.3, 127.8, 127.5, 127.3, 127.0, 126.3, 126.2, 125.8, 125.6, 122.3, 120.7, 118.8, 108.8, 37.5, 19.8. HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{26}H_{19}N_2O_2S$ 423.1162;

found 423.1161.

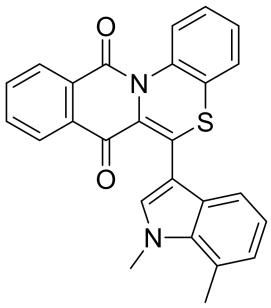
6-(6-Methoxy-1-methyl-1*H*-indol-3-yl)benzo[5,6][1,4]thiazino[4,3-*b*]isoquinoline-7,12-dione (3na)



The reaction was conducted with 2-(6-methoxy-1-methyl-1*H*-indol-3-yl)naphthalene-1,4-dione (63.4 mg, 0.2 mmol) and 2-aminobenzenethiol (62.5 mg, 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) to yield the desired product **3na** as orange solid (56.9 mg, 65% yield). mp: 235-237 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, J = 7.6 Hz, 1H), 8.06 (d, J = 7.6 Hz, 1H), 7.86 (t, J = 7.6 Hz, 1H), 7.79 (t, J = 7.4 Hz, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.51 (s, 1H), 7.35 (t, J = 7.4 Hz, 1H), 7.29–7.24 (m, 2H), 6.98 (d, J = 8.8 Hz, 1H), 6.78 (s, 1H), 6.73 (d, J = 8.8 Hz, 1H), 3.86 (s, 3H), 3.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.4, 160.0, 157.0, 138.4, 136.4, 134.6, 134.5, 134.2, 133.3, 131.9, 131.3, 129.4, 129.0, 127.9, 127.4, 127.2, 127.0, 126.1, 125.8, 121.5, 119.3, 110.3, 109.3, 93.9, 55.9, 33.4. HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{26}H_{19}N_2O_3S$ 439.1111; found 439.1117

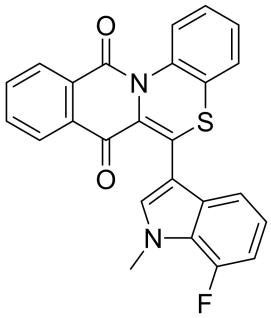
6-(1,7-Dimethyl-1*H*-indol-3-yl)benzo[5,6][1,4]thiazino[4,3-*b*]isoquinoline-7,12-dione (3pa)



The reaction was conducted with 2-(1,7-dimethyl-1*H*-indol-3-yl)naphthalene-1,4-dione (60.2mg, 0.2 mmol) and 2-aminobenzenethiol (62.5 mg, 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) to yield the desired product **3pa** as red solid (54.9 mg, 65% yield). mp: 244-246 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, J = 7.2 Hz, 1H), 8.04 (d, J = 7.6 Hz, 1H), 7.86 (t, J = 8.0 Hz, 1H), 7.78 (t, J = 8.0 Hz, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.46 (s, 1H), 7.35 (t, J = 7.4 Hz, 1H), 7.28–7.23 (m, 2H), 6.96-6.89 (m, 3H), 4.09 (s, 3H), 2.76 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.4, 159.9, 136.2, 136.1, 134.5, 134.2, 134.1, 133.3, 131.2, 129.4, 127.9, 127.5, 127.3, 127.0, 126.3, 126.2, 125.8, 125.6, 122.3, 120.7, 118.8, 108.8, 37.5, 19.8. HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{26}H_{19}N_2O_2S$ 423.1162; found 423.1165.

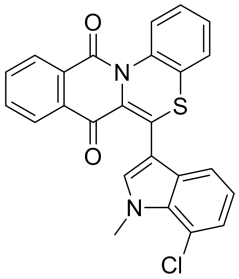
6-(7-Fluoro-1-methyl-1*H*-indol-3-yl)benzo[5,6][1,4]thiazino[4,3-*b*]isoquinoline-7,12-dione (3qa)



The reaction was conducted with 2-(7-fluoro-1-methyl-1*H*-indol-3-yl)naphthalene-1,4-dione (61.0 mg, 0.2 mmol) and 2-aminobenzenethiol (62.5 mg, 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) to yield the desired product **3qa** as red solid (59.6 mg, 70% yield). mp: 274-276 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, J = 7.6 Hz, 1H), 8.03 (d, J = 7.6 Hz, 1H), 7.87 (t, J = 7.6 Hz, 1H), 7.78 (t, J = 7.4 Hz, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.49 (s, 1H), 7.38–7.34 (m, 1H), 7.29–7.27 (m, 2H), 6.94–6.86 (m, 3H), 4.03 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.4, 159.9, 150.7 (d, J = 243.4 Hz), 136.0, 134.4, 134.3, 133.8, 133.4, 133.4, 131.2, 129.9, 129.4, 129.2 (d, J = 4.8 Hz), 128.0, 127.4, 127.2, 127.1, 126.2, 125.8, 125.4 (d, J = 10.3 Hz),120.9 (d, J = 6.6 Hz), 116.4 (d, J = 3.6 Hz), 109.8, 108.4 (d, J = 17.5 Hz), 36.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -122.9. HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{25}H_{16}FN_2O_2S$ 427.0911; found 427.0901.

6-(7-Chloro-1-methyl-1*H*-indol-3-yl)benzo[5,6][1,4]thiazino[4,3-*b*]isoquinoline-7,12-dione (3ra)



The reaction was conducted with 2-(7-chloro-1-methyl-1*H*-indol-3-yl)naphthalene-1,4-dione (31.5 mg, 0.2 mmol) and 2-aminobenzenethiol (62.5 mg, 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) to yield the desired product **3ra** as red solid (48.6 mg, 55% yield). mp: 285-288℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, J = 8.0 Hz, 1H), 8.01 (d, J = 8.0 Hz, 1H), 7.86 (t, J = 7.6 Hz, 1H), 7.77 (t, J = 7.6 Hz, 1H), 7.67 (d, J = 8.4 Hz, 1H), 7.46 (s, 1H), 7.37–7.33 (m, 1H), 7.28-7.25 (m, 2H), 7.15 (d, J = 8.0 Hz, 1H), 7.02 (d, J = 8.0 Hz, 1H), 6.91 (t, J = 7.8 Hz, 1H), 4.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.4, 159.9, 135.9, 134.7, 134.4, 134.3, 133.4, 133.1, 132.7, 131.2, 130.1, 129.4, 128.3, 128.0, 127.4, 127.2, 127.1, 126.2, 125.8, 124.4, 121.2, 119.3, 118.0, 109.2, 37.6. HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{25}H_{16}ClN_2O_2S$ 443.0616; found 443.0605.

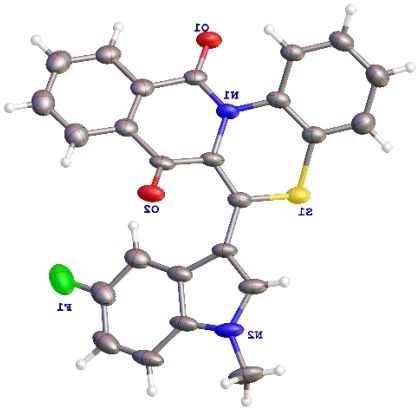
6. References

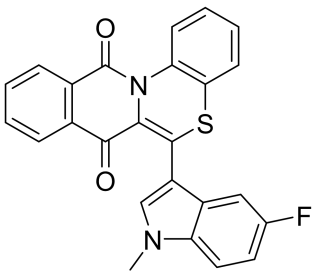
[1] Dong,Y.; Zhang, H.; Yang, J.; He, S.; Shi, Z.-C.; Zhang, X.-M.; Wang, J.-Y. $B(C_6F_5)_3$-Catalyzed C–C Coupling of 1,4-Naphthoquinones with the C-3 Position of Indole Derivatives in Water. *ACS Omega* **2019,** *4*, 21567−2157.

7. Crystal data and structure refinement for 3ia

The product **3ia** (20.0 mg) were complete dissolved in DCM (0.5 mL) in a test tube. Then *n*-hexane (2.0 mL) were added dropwise, slow volatilized at room temperature. A few days later, the crystal was grown at room temperature.

A suitable crystal was collected, on a SuperNova, Dual, Cu at zero, AtlasS2 diffractometer. The data were collected and processed using CrysAlisPro. The structures were solved by direct methods using Olex2 software. The crystal was kept at 150.0(10) K during data collection.





CCDC number: 2194045 **3ia**

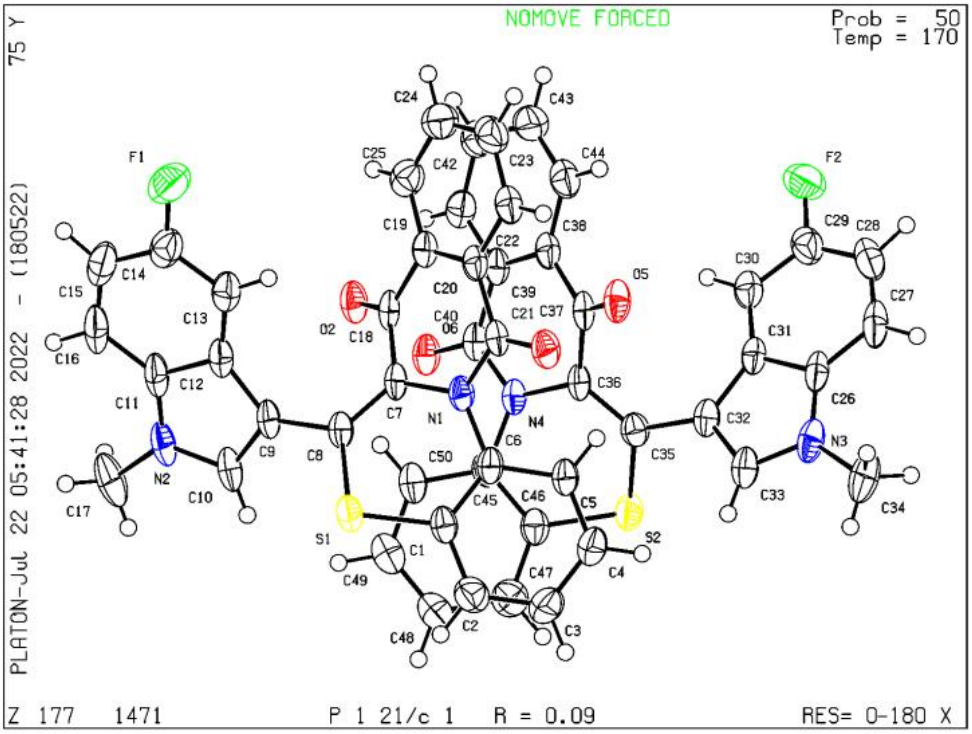


Figure S1. Ellipsoid plot of **3ia** (shown at 50% probability levels)

Table S1. Crystal data and structure refinement for **3ia**.

Identification code	**3ia**
Empirical formula	C25H15FN2O2S
Formula weight	426.45
Temperature/K	170.00(10)
Crystal system	monoclinic
Space group	P21/c
a/Å	7.8743(5)
b/Å	20.4362(15)
c/Å	24.2525(11)
α/°	90
β/°	93.218(4)
γ/°	90
Volume/Å3	3896.6(4)
Z	8
ρcalcg/cm3	1.454
μ/mm 1	1.782
F(000)	1760.0
Crystal size/mm3	0.15 × 0.13 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.658 to 149.362
Index ranges	-9 ≤ h ≤ 6, -23 ≤ k ≤ 25, -28 ≤ l ≤ 30
Reflections collected	15433
Independent reflections	7670 [Rint = 0.0545, Rsigma = 0.0609]
Data/restraints/parameters	7670/0/561
Goodness-of-fit on F2	1.065
Final R indexes [I>=2σ (I)]	R1 = 0.0865, wR2 = 0.2183
Final R indexes [all data]	R1 = 0.1154, wR2 = 0.2396

Crystal structure determination of **3ia**

Crystal Data for C25H15FN2O2S (M =426.45 g/mol): monoclinic, space group P21/c (no. 14), a = 7.8743(5) Å, b = 20.4362(15) Å, c = 24.2525(11) Å, β = 93.218(4)°, V = 3896.6(4) Å3, Z = 8, T = 170.00(10) K, μ(Cu Kα) = 1.782 mm-1, Dcalc = 1.454 g/cm3, 15433 reflections measured (5.658° ≤ 2Θ ≤ 149.362°), 7670 unique (Rint = 0.0545, Rsigma = 0.0609) which were used in all

calculations. The final R1 was 0.0865 ($I > 2\sigma(I)$) and wR2 was 0.2396 (all data).

Table S2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **3ia**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
S1	8638.4(15)	6294.7(6)	6911.6(4)	38.9(3)
O1	8747(4)	7691.3(17)	5263.5(12)	41.2(8)
O2	5456(4)	8197.5(18)	7082.2(12)	42.7(8)
F1	10037(5)	9348.2(17)	8104.5(15)	67.9(10)
N1	7645(5)	7328.0(19)	6056.7(13)	32.0(8)
N2	7083(5)	7002(2)	8516.8(14)	44.0(10)
C1	7917(5)	6153(2)	6223.2(16)	34.2(9)
C2	7788(7)	5509(3)	6039(2)	46.0(12)
C3	7230(7)	5379(3)	5495(2)	49.4(12)
C4	6725(6)	5893(3)	5150.4(19)	42.6(11)
C5	6803(5)	6528(2)	5333.5(16)	34.4(10)
C6	7470(5)	6666(2)	5870.2(16)	32.9(9)
C7	7238(5)	7463(2)	6616.4(15)	31.7(9)
C8	7674(5)	7050(2)	7036.4(16)	31.9(9)
C9	7556(6)	7179(2)	7622.2(16)	34.8(10)
C10	6986(6)	6743(3)	8002.8(17)	42.1(11)
C11	7759(6)	7625(3)	8485.3(17)	44.5(12)
C12	8089(6)	7753(2)	7931.2(16)	36.8(10)
C13	8850(6)	8347(3)	7795.8(19)	42.4(11)
C14	9260(7)	8766(3)	8224(2)	48.8(13)
C15	8935(8)	8651(3)	8774(2)	58.7(16)
C16	8203(7)	8065(3)	8910.3(19)	54.3(15)
C17	6460(7)	6699(4)	9009(2)	61.8(17)
C18	6433(5)	8108(2)	6715.5(15)	34.1(10)
C19	6993(6)	8643(2)	6354.0(17)	35.5(10)
C20	7829(6)	8497(2)	5881.6(17)	34.8(10)
C21	8144(5)	7812(2)	5705.8(16)	32.8(9)
C22	8329(6)	9007(2)	5542.7(18)	39.3(10)
C23	8012(7)	9647(3)	5685(2)	49.5(13)

C24	7195(7)	9789(3)	6165(2)	49.2(12)
C25	6677(6)	9291(3)	6498(2)	44.5(11)
S2	1567.5(15)	6184.5(6)	5307.9(4)	39.9(3)
F2	86(4)	9085.3(16)	3907.5(14)	62.3(9)
O5	4674(4)	8091.0(18)	5041.4(12)	43.7(8)
O6	1465(4)	7690.8(17)	6883.1(11)	40.1(8)
N3	3257(5)	6749(2)	3669.8(15)	44.6(10)
N4	2539(5)	7271.8(19)	6098.7(13)	32.9(8)
C26	2563(6)	7369(3)	3656.7(17)	40.3(11)
C27	2190(7)	7771(3)	3203.4(18)	51.8(14)
C28	1406(7)	8359(3)	3298(2)	52.7(14)
C29	963(7)	8508(3)	3832(2)	47.5(12)
C30	1329(6)	8135(2)	4286.5(18)	39.3(10)
C31	2158(5)	7538(2)	4195.1(16)	33.7(10)
C32	2687(6)	7000(2)	4548.2(16)	35.5(10)
C33	3320(6)	6535(3)	4202.9(17)	41.2(11)
C34	3881(7)	6399(3)	3199(2)	58.1(16)
C35	2529(5)	6924(2)	5142.5(17)	33.4(9)
C36	2930(5)	7376(2)	5536.3(15)	32.5(9)
C37	3683(6)	8018(2)	5403.8(16)	35.5(10)
C38	3074(6)	8575(2)	5724.7(17)	35.9(10)
C39	2263(5)	8455(2)	6213.3(17)	34.5(10)
C40	2040(5)	7786(2)	6431.6(16)	33.4(9)
C41	1740(6)	8988(3)	6525.6(19)	41.7(11)
C42	1977(7)	9616(3)	6342(2)	48.6(12)
C43	2712(7)	9732(3)	5844(2)	51.2(13)
C44	3285(7)	9215(3)	5540(2)	44.9(12)
C45	2788(6)	6630(2)	6324.1(17)	35.8(10)
C46	2356(6)	6091(2)	5998.3(17)	35.3(10)
C47	2567(7)	5460(3)	6207(2)	49.5(12)
C48	3184(7)	5368(3)	6751(2)	51.2(13)
C49	3656(7)	5913(3)	7069(2)	48.0(12)
C50	3493(6)	6540(3)	6858.3(17)	38.9(10)

Table S3. Anisotropic Displacement Parameters ($Å^2×10^3$) for **3ia** The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	43.6(6)	48.7(7)	24.1(5)	3.2(4)	-2.2(4)	3.6(5)
O1	48.0(19)	53(2)	23.6(15)	2.1(13)	8.4(13)	2.0(16)
O2	42.8(19)	63(2)	22.9(14)	-1.4(14)	4.0(12)	12.3(16)
F1	71(2)	56(2)	75(2)	-18.7(17)	-13.6(18)	0.8(17)
N1	33.6(19)	44(2)	18.8(16)	-0.1(14)	6.1(13)	3.8(16)
N2	44(2)	70(3)	18.4(17)	7.6(17)	3.8(15)	10(2)
C1	30(2)	49(3)	23.7(19)	1.5(17)	3.5(15)	3.8(19)
C2	51(3)	46(3)	41(3)	5(2)	5(2)	2(2)
C3	62(3)	45(3)	41(3)	-9(2)	6(2)	0(2)
C4	45(3)	52(3)	31(2)	-9(2)	1.2(18)	2(2)
C5	33(2)	48(3)	22.7(19)	-1.1(17)	3.4(16)	2.1(19)
C6	28(2)	48(3)	22.6(19)	-2.7(17)	3.4(15)	2.6(18)
C7	30(2)	49(3)	16.3(17)	-0.7(16)	1.7(14)	-2.3(18)
C8	28(2)	47(3)	20.7(19)	0.0(16)	2.4(15)	-1.2(18)
C9	34(2)	54(3)	16.7(18)	1.8(17)	2.4(15)	3(2)
C10	36(2)	70(3)	20(2)	7(2)	1.2(16)	1(2)
C11	45(3)	70(4)	18(2)	-3(2)	-0.3(17)	22(3)
C12	34(2)	55(3)	21(2)	-2.2(18)	-0.9(16)	11(2)
C13	37(3)	57(3)	32(2)	-5(2)	-4.8(18)	6(2)
C14	45(3)	54(3)	46(3)	-12(2)	-11(2)	11(2)
C15	64(4)	68(4)	41(3)	-22(3)	-19(2)	25(3)
C16	54(3)	86(4)	21(2)	-9(2)	-6(2)	30(3)
C17	52(3)	106(5)	29(2)	24(3)	13(2)	14(3)
C18	30(2)	56(3)	16.2(18)	-4.7(17)	-3.4(15)	2.1(19)
C19	33(2)	47(3)	26(2)	-1.4(18)	-6.4(16)	0.1(19)
C20	32(2)	45(3)	26(2)	1.5(17)	-7.8(16)	-2.3(19)
C21	30(2)	46(3)	21.1(19)	2.7(17)	-4.7(15)	0.9(18)
C22	36(2)	52(3)	29(2)	4.9(19)	-4.3(17)	-5(2)
C23	48(3)	51(3)	48(3)	9(2)	-13(2)	-7(2)
C24	45(3)	45(3)	56(3)	-2(2)	-9(2)	1(2)
C25	38(3)	49(3)	46(3)	-5(2)	-5(2)	1(2)

S2	46.4(7)	47.5(7)	25.9(5)	-3.0(4)	1.0(4)	-3.1(5)
F2	64(2)	47.3(19)	73(2)	13.0(16)	-15.8(16)	-3.2(16)
O5	43.5(19)	66(2)	21.8(14)	0.0(14)	4.3(13)	-10.8(17)
O6	40.1(18)	59(2)	21.7(14)	-3.0(13)	7.8(12)	1.7(15)
N3	44(2)	67(3)	22.9(18)	-9.8(18)	7.2(15)	-11(2)
N4	34(2)	45(2)	19.2(16)	-0.8(14)	0.7(13)	-1.2(16)
C26	43(3)	59(3)	19.1(19)	-3.0(19)	-0.9(17)	-16(2)
C27	52(3)	81(4)	21(2)	2(2)	-2.5(19)	-26(3)
C28	54(3)	65(4)	37(3)	18(2)	-12(2)	-21(3)
C29	48(3)	51(3)	42(3)	8(2)	-10(2)	-13(2)
C30	36(2)	51(3)	31(2)	0.9(19)	-3.9(17)	-6(2)
C31	29(2)	49(3)	22.4(19)	-2.4(17)	-2.5(15)	-7.9(19)
C32	33(2)	50(3)	23(2)	-3.5(18)	3.0(16)	-1(2)
C33	38(3)	61(3)	24(2)	-5.1(19)	2.8(17)	0(2)
C34	52(3)	93(5)	30(2)	-20(3)	12(2)	-10(3)
C35	32(2)	41(3)	27(2)	0.8(17)	4.1(16)	2.5(18)
C36	34(2)	47(3)	16.6(18)	-0.2(16)	1.7(15)	0.8(19)
C37	32(2)	55(3)	18.1(18)	0.6(17)	-5.9(15)	-1(2)
C38	33(2)	48(3)	25(2)	1.7(18)	-7.0(16)	-3.0(19)
C39	26(2)	49(3)	27(2)	-1.0(18)	-6.5(15)	2.0(19)
C40	27(2)	51(3)	22.1(19)	-1.5(17)	1.0(15)	-0.3(19)
C41	41(3)	50(3)	34(2)	-5(2)	-3.5(18)	2(2)
C42	47(3)	50(3)	47(3)	-4(2)	-11(2)	5(2)
C43	55(3)	44(3)	52(3)	3(2)	-12(2)	-1(2)
C44	45(3)	54(3)	35(2)	6(2)	-7.0(19)	-2(2)
C45	37(2)	45(3)	26(2)	2.8(18)	9.2(17)	-2(2)
C46	30(2)	48(3)	27(2)	0.7(18)	3.8(16)	-3.9(19)
C47	53(3)	50(3)	46(3)	1(2)	5(2)	-4(2)
C48	54(3)	53(3)	47(3)	15(2)	-1(2)	1(3)
C49	44(3)	59(3)	40(3)	12(2)	-1(2)	0(2)
C50	31(2)	59(3)	26(2)	2.4(19)	2.0(16)	0(2)

Table S4. Bond Lengths for **3ia.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	C1	1.757(4)	S2	C35	1.747(5)
S1	C8	1.754(5)	S2	C46	1.763(4)
O1	C21	1.222(5)	F2	C29	1.384(7)
O2	C18	1.222(5)	O5	C37	1.217(5)
F1	C14	1.377(7)	O6	C40	1.224(5)
N1	C6	1.431(6)	N3	C26	1.380(7)
N1	C7	1.439(5)	N3	C33	1.363(6)
N1	C21	1.377(6)	N3	C34	1.456(6)
N2	C10	1.353(6)	N4	C36	1.431(5)
N2	C11	1.383(7)	N4	C40	1.395(6)
N2	C17	1.455(6)	N4	C45	1.430(6)
C1	C2	1.392(7)	C26	C27	1.391(7)
C1	C6	1.386(6)	C26	C31	1.404(6)
C2	C3	1.392(7)	C27	C28	1.375(8)
C3	C4	1.386(7)	C28	C29	1.395(8)
C4	C5	1.372(7)	C29	C30	1.358(7)
C5	C6	1.404(6)	C30	C31	1.408(7)
C7	C8	1.353(6)	C31	C32	1.441(6)
C7	C18	1.487(6)	C32	C33	1.378(6)
C8	C9	1.453(5)	C32	C35	1.462(5)
C9	C10	1.377(6)	C35	C36	1.354(6)
C9	C12	1.441(7)	C36	C37	1.482(7)
C11	C12	1.408(6)	C37	C38	1.474(6)
C11	C16	1.398(7)	C38	C39	1.399(6)
C12	C13	1.401(7)	C38	C44	1.395(7)
C13	C14	1.370(7)	C39	C40	1.481(7)
C14	C15	1.391(8)	C39	C41	1.402(6)
C15	C16	1.377(9)	C41	C42	1.374(7)
C18	C19	1.485(6)	C42	C43	1.389(8)
C19	C20	1.385(6)	C43	C44	1.379(8)
C19	C25	1.395(7)	C45	C46	1.386(6)
C20	C21	1.489(6)	C45	C50	1.393(6)

C20	C22	1.397(6)	C46	C47	1.393(7)
C22	C23	1.378(7)	C47	C48	1.394(7)
C23	C24	1.393(8)	C48	C49	1.393(8)
C24	C25	1.375(7)	C49	C50	1.383(7)

Table S5. Bond Angles for **3ia.**

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
C8	S1	C1	100.9(2)	C35	S2	C46	100.2(2)
C6	N1	C7	117.2(4)	C26	N3	C34	125.7(4)
C21	N1	C6	120.7(3)	C33	N3	C26	108.1(4)
C21	N1	C7	122.1(4)	C33	N3	C34	126.1(5)
C10	N2	C11	108.2(4)	C40	N4	C36	121.5(4)
C10	N2	C17	125.8(5)	C40	N4	C45	120.4(3)
C11	N2	C17	125.9(5)	C45	N4	C36	118.0(4)
C2	C1	S1	118.3(4)	N3	C26	C27	128.8(5)
C6	C1	S1	121.3(4)	N3	C26	C31	108.3(4)
C6	C1	C2	120.3(4)	C27	C26	C31	122.8(5)
C1	C2	C3	119.9(5)	C28	C27	C26	117.5(5)
C4	C3	C2	119.4(5)	C27	C28	C29	118.9(5)
C5	C4	C3	121.0(4)	F2	C29	C28	117.5(5)
C4	C5	C6	119.8(4)	C30	C29	F2	117.1(5)
C1	C6	N1	120.2(4)	C30	C29	C28	125.4(6)
C1	C6	C5	119.3(4)	C29	C30	C31	116.0(5)
C5	C6	N1	120.5(4)	C26	C31	C30	119.4(4)
N1	C7	C18	116.2(4)	C26	C31	C32	107.0(4)
C8	C7	N1	122.0(4)	C30	C31	C32	133.6(4)
C8	C7	C18	121.6(4)	C31	C32	C35	129.0(4)
C7	C8	S1	120.9(3)	C33	C32	C31	105.5(4)
C7	C8	C9	126.5(4)	C33	C32	C35	125.4(4)
C9	C8	S1	112.4(3)	N3	C33	C32	111.1(5)
C10	C9	C8	125.3(5)	C32	C35	S2	112.4(3)
C10	C9	C12	106.0(4)	C36	C35	S2	121.0(3)
C12	C9	C8	128.6(4)	C36	C35	C32	126.4(4)
N2	C10	C9	111.1(5)	N4	C36	C37	116.7(4)

N2	C11	C12	108.5(4)	C35	C36	N4	121.1(4)
N2	C11	C16	129.2(5)	C35	C36	C37	122.1(4)
C16	C11	C12	122.1(6)	O5	C37	C36	123.1(4)
C11	C12	C9	106.3(4)	O5	C37	C38	121.8(4)
C13	C12	C9	134.4(4)	C38	C37	C36	115.1(4)
C13	C12	C11	119.3(4)	C39	C38	C37	119.3(4)
C14	C13	C12	116.6(5)	C44	C38	C37	120.4(4)
F1	C14	C15	117.1(5)	C44	C38	C39	120.3(5)
C13	C14	F1	117.9(5)	C38	C39	C40	122.3(4)
C13	C14	C15	125.0(6)	C38	C39	C41	118.9(5)
C16	C15	C14	118.6(5)	C41	C39	C40	118.7(4)
C15	C16	C11	118.3(5)	O6	C40	N4	121.9(4)
O2	C18	C7	122.8(4)	O6	C40	C39	121.6(4)
O2	C18	C19	122.7(4)	N4	C40	C39	116.5(4)
C19	C18	C7	114.4(4)	C42	C41	C39	120.1(5)
C20	C19	C18	120.0(4)	C41	C42	C43	120.8(5)
C20	C19	C25	120.8(5)	C44	C43	C42	119.9(5)
C25	C19	C18	119.2(4)	C43	C44	C38	119.8(5)
C19	C20	C21	122.3(4)	C46	C45	N4	119.1(4)
C19	C20	C22	119.3(5)	C46	C45	C50	119.9(4)
C22	C20	C21	118.4(4)	C50	C45	N4	121.0(4)
O1	C21	N1	122.4(4)	C45	C46	S2	121.2(4)
O1	C21	C20	121.4(4)	C45	C46	C47	120.6(4)
N1	C21	C20	116.2(4)	C47	C46	S2	118.2(4)
C23	C22	C20	119.9(5)	C48	C47	C46	119.8(5)
C22	C23	C24	120.4(5)	C49	C48	C47	119.0(5)
C25	C24	C23	120.2(5)	C50	C49	C48	121.3(5)
C24	C25	C19	119.5(5)	C49	C50	C45	119.3(5)

Table S6. Torsion Angles for **3ia.**

A	B	C	D	Angle/°	A	B	C	D	Angle/°
S1	C1	C2	C3	-179.7(4)	S2	C35	C36	N4	-1.7(6)
S1	C1	C6	N1	2.2(6)	S2	C35	C36	C37	-177.5(3)
S1	C1	C6	C5	-176.2(3)	S2	C46	C47	C48	-179.9(4)
S1	C8	C9	C10	-47.0(6)	F2	C29	C30	C31	177.4(4)
S1	C8	C9	C12	128.7(4)	O5	C37	C38	C39	-165.4(4)
O2	C18	C19	C20	-167.6(4)	O5	C37	C38	C44	15.5(6)
O2	C18	C19	C25	12.8(6)	N3	C26	C27	C28	176.3(5)
F1	C14	C15	C16	-178.2(5)	N3	C26	C31	C30	-176.0(4)
N1	C7	C8	S1	-4.4(6)	N3	C26	C31	C32	1.9(5)
N1	C7	C8	C9	170.3(4)	N4	C36	C37	O5	149.1(4)
N1	C7	C18	O2	150.9(4)	N4	C36	C37	C38	-33.9(5)
N1	C7	C18	C19	-32.6(5)	N4	C45	C46	S2	1.9(6)
N2	C11	C12	C9	0.8(5)	N4	C45	C46	C47	-179.4(4)
N2	C11	C12	C13	-177.4(4)	N4	C45	C50	C49	177.6(4)
N2	C11	C16	C15	177.0(5)	C26	N3	C33	C32	-0.2(6)
C1	S1	C8	C7	-24.9(4)	C26	C27	C28	C29	-2.7(7)
C1	S1	C8	C9	159.8(3)	C26	C31	C32	C33	-1.9(5)
C1	C2	C3	C4	-3.3(8)	C26	C31	C32	C35	-178.9(4)
C2	C1	C6	N1	-178.4(4)	C27	C26	C31	C30	0.4(7)
C2	C1	C6	C5	3.2(7)	C27	C26	C31	C32	178.3(4)
C2	C3	C4	C5	1.5(8)	C27	C28	C29	F2	-176.3(4)
C3	C4	C5	C6	2.7(7)	C27	C28	C29	C30	4.1(8)
C4	C5	C6	N1	176.6(4)	C28	C29	C30	C31	-2.9(8)
C4	C5	C6	C1	-5.0(7)	C29	C30	C31	C26	0.6(6)
C6	N1	C7	C8	39.8(6)	C29	C30	C31	C32	-176.6(5)
C6	N1	C7	C18	-144.8(4)	C30	C31	C32	C33	175.5(5)
C6	N1	C21	O1	-13.5(6)	C30	C31	C32	C35	-1.4(8)
C6	N1	C21	C20	163.5(4)	C31	C26	C27	C28	0.7(7)
C6	C1	C2	C3	0.9(7)	C31	C32	C33	N3	1.3(5)
C7	N1	C6	C1	-38.1(6)	C31	C32	C35	S2	128.0(4)
C7	N1	C6	C5	140.3(4)	C31	C32	C35	C36	-46.9(7)
C7	N1	C21	O1	168.1(4)	C32	C35	C36	N4	172.8(4)

C7	N1	C21	C20	-14.9(6)	C32	C35	C36	C37	-3.0(7)
C7	C8	C9	C10	138.0(5)	C33	N3	C26	C27	-177.3(5)
C7	C8	C9	C12	-46.3(7)	C33	N3	C26	C31	-1.1(5)
C7	C18	C19	C20	15.9(5)	C33	C32	C35	S2	-48.4(6)
C7	C18	C19	C25	-163.7(4)	C33	C32	C35	C36	136.7(5)
C8	S1	C1	C2	-153.4(4)	C34	N3	C26	C27	5.2(8)
C8	S1	C1	C6	25.9(4)	C34	N3	C26	C31	-178.6(4)
C8	C7	C18	O2	-33.7(7)	C34	N3	C33	C32	177.3(4)
C8	C7	C18	C19	142.7(4)	C35	S2	C46	C45	28.0(4)
C8	C9	C10	N2	177.9(4)	C35	S2	C46	C47	-150.8(4)
C8	C9	C12	C11	-177.7(4)	C35	C32	C33	N3	178.4(4)
C8	C9	C12	C13	0.1(9)	C35	C36	C37	O5	-34.9(7)
C9	C12	C13	C14	-176.2(5)	C35	C36	C37	C38	142.0(4)
C10	N2	C11	C12	0.1(5)	C36	N4	C40	O6	169.1(4)
C10	N2	C11	C16	-175.3(5)	C36	N4	C40	C39	-11.7(6)
C10	C9	C12	C11	-1.4(5)	C36	N4	C45	C46	-39.7(6)
C10	C9	C12	C13	176.4(5)	C36	N4	C45	C50	138.7(4)
C11	N2	C10	C9	-1.0(6)	C36	C37	C38	C39	17.6(5)
C11	C12	C13	C14	1.3(7)	C36	C37	C38	C44	-161.5(4)
C12	C9	C10	N2	1.5(5)	C37	C38	C39	C40	2.0(6)
C12	C11	C16	C15	2.2(7)	C37	C38	C39	C41	177.9(4)
C12	C13	C14	F1	178.9(4)	C37	C38	C44	C43	-179.9(4)
C12	C13	C14	C15	-1.9(8)	C38	C39	C40	O6	173.4(4)
C13	C14	C15	C16	2.6(8)	C38	C39	C40	N4	-5.8(6)
C14	C15	C16	C11	-2.6(8)	C38	C39	C41	C42	2.1(7)
C16	C11	C12	C9	176.6(4)	C39	C38	C44	C43	0.9(7)
C16	C11	C12	C13	-1.6(7)	C39	C41	C42	C43	0.9(7)
C17	N2	C10	C9	174.6(4)	C40	N4	C36	C35	-144.0(4)
C17	N2	C11	C12	-175.5(4)	C40	N4	C36	C37	32.0(6)
C17	N2	C11	C16	9.1(8)	C40	N4	C45	C46	144.5(4)
C18	C7	C8	S1	-179.5(3)	C40	N4	C45	C50	-37.1(6)
C18	C7	C8	C9	-4.9(7)	C40	C39	C41	C42	178.1(4)
C18	C19	C20	C21	2.2(6)	C41	C39	C40	O6	-2.4(6)
C18	C19	C20	C22	179.2(4)	C41	C39	C40	N4	178.4(4)
C18	C19	C25	C24	179.9(4)	C41	C42	C43	C44	-3.0(8)

C19	C20	C21	O1	173.4(4)	C42	C43	C44	C38	2.1(8)
C19	C20	C21	N1	-3.6(6)	C44	C38	C39	C40	-178.8(4)
C19	C20	C22	C23	1.0(6)	C44	C38	C39	C41	-3.0(6)
C20	C19	C25	C24	0.4(7)	C45	N4	C36	C35	40.3(6)
C20	C22	C23	C24	0.0(7)	C45	N4	C36	C37	-143.7(4)
C21	N1	C6	C1	143.4(4)	C45	N4	C40	O6	-15.3(6)
C21	N1	C6	C5	-38.2(6)	C45	N4	C40	C39	163.9(4)
C21	N1	C7	C8	-141.7(4)	C45	C46	C47	C48	1.3(8)
C21	N1	C7	C18	33.7(6)	C46	S2	C35	C32	156.6(3)
C21	C20	C22	C23	178.1(4)	C46	S2	C35	C36	-28.2(4)
C22	C20	C21	O1	-3.6(6)	C46	C45	C50	C49	-4.0(7)
C22	C20	C21	N1	179.3(4)	C46	C47	C48	C49	-3.0(8)
C22	C23	C24	C25	-0.8(8)	C47	C48	C49	C50	1.2(8)
C23	C24	C25	C19	0.6(7)	C48	C49	C50	C45	2.3(8)
C25	C19	C20	C21	-178.2(4)	C50	C45	C46	S2	-176.5(3)
C25	C19	C20	C22	-1.2(6)	C50	C45	C46	C47	2.2(7)

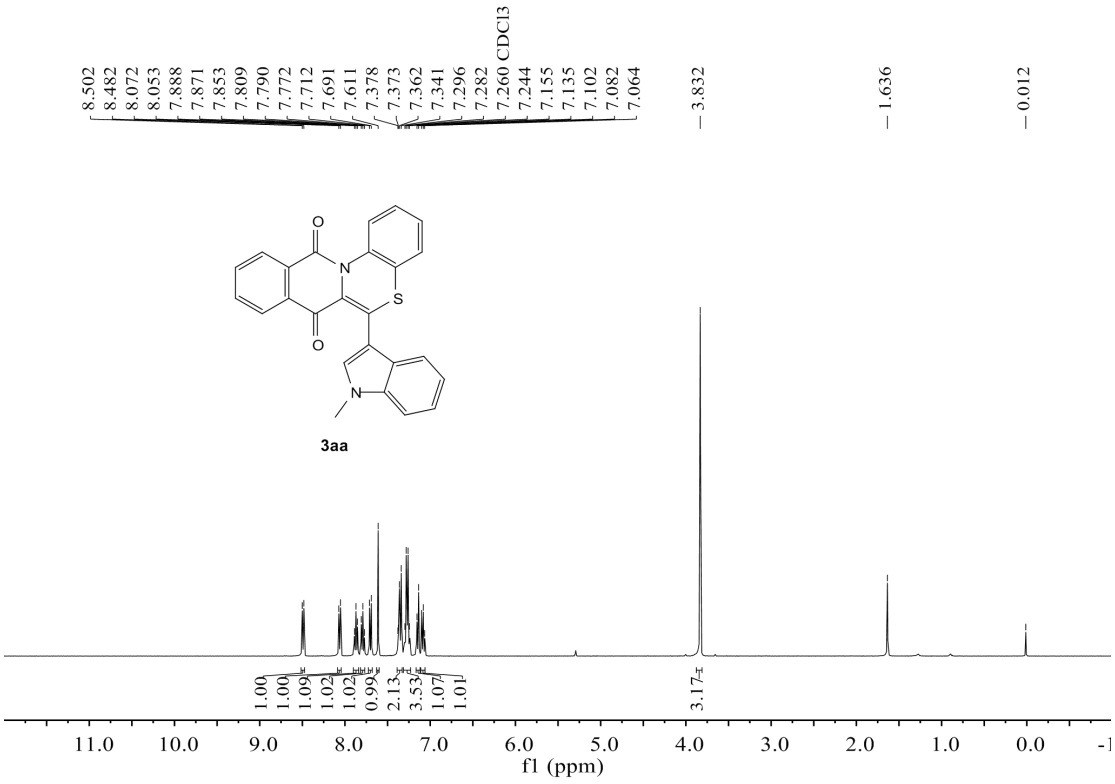
Table S7. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **3ia.**

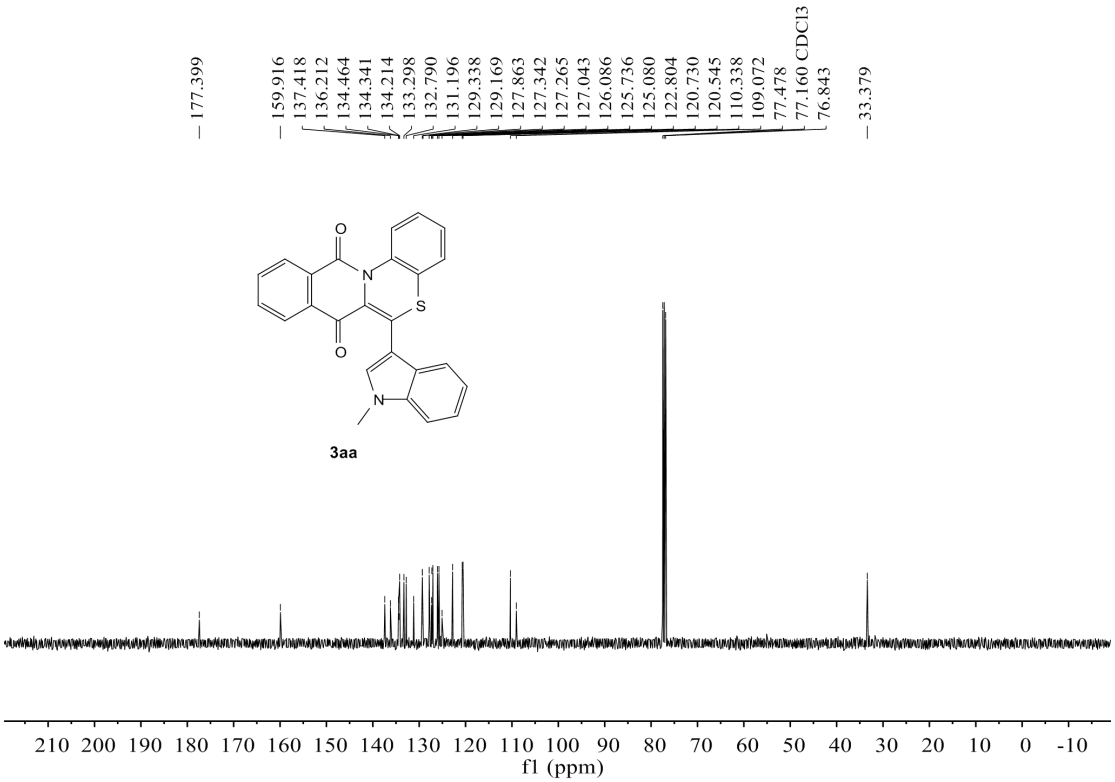
Atom	***x***	***y***	***z***	**U(eq)**
H2	8074.1	5166.35	6278.67	55
H3	7195.46	4950.89	5364.22	59
H4	6327.1	5805.49	4789.59	51
H5	6416.2	6866.17	5102.77	41
H10	6586.77	6324.29	7917.74	51
H13	9065.13	8452.52	7433.25	51
H15	9206.52	8963.24	9043.64	70
H16	8009.95	7964.74	9275.52	65
H17A	7358.87	6684.52	9293.29	93
H17B	6082.43	6262.17	8923.67	93
H17C	5527.99	6950.26	9135.71	93
H22	8875.05	8914.67	5221.46	47

Atom	*x*	*y*	*z*	U(eq)
H23	8345.94	9985.25	5458.82	59
H24	6998.04	10221.91	6260.79	59
H25	6120.86	9385.24	6817.07	53
H27	2460.26	7647.66	2849.87	62
H28	1174.64	8652.17	3009.92	63
H30	1048.46	8266.02	4637.13	47
H33	3735.31	6128.47	4318.31	49
H34A	3018.24	6396.54	2903.16	87
H34B	4154.05	5957.15	3304.88	87
H34C	4880.88	6612.62	3078.86	87
H41	1232.54	8917.17	6857.45	50
H42	1641.23	9967.29	6553.89	58
H43	2817.19	10157.96	5715.59	61
H44	3810.44	9292.15	5212.04	54
H47	2296.65	5100.45	5983.24	59
H48	3280.25	4949.31	6899.61	61
H49	4088.96	5853.88	7430.39	58
H50	3851.57	6898.31	7071	47

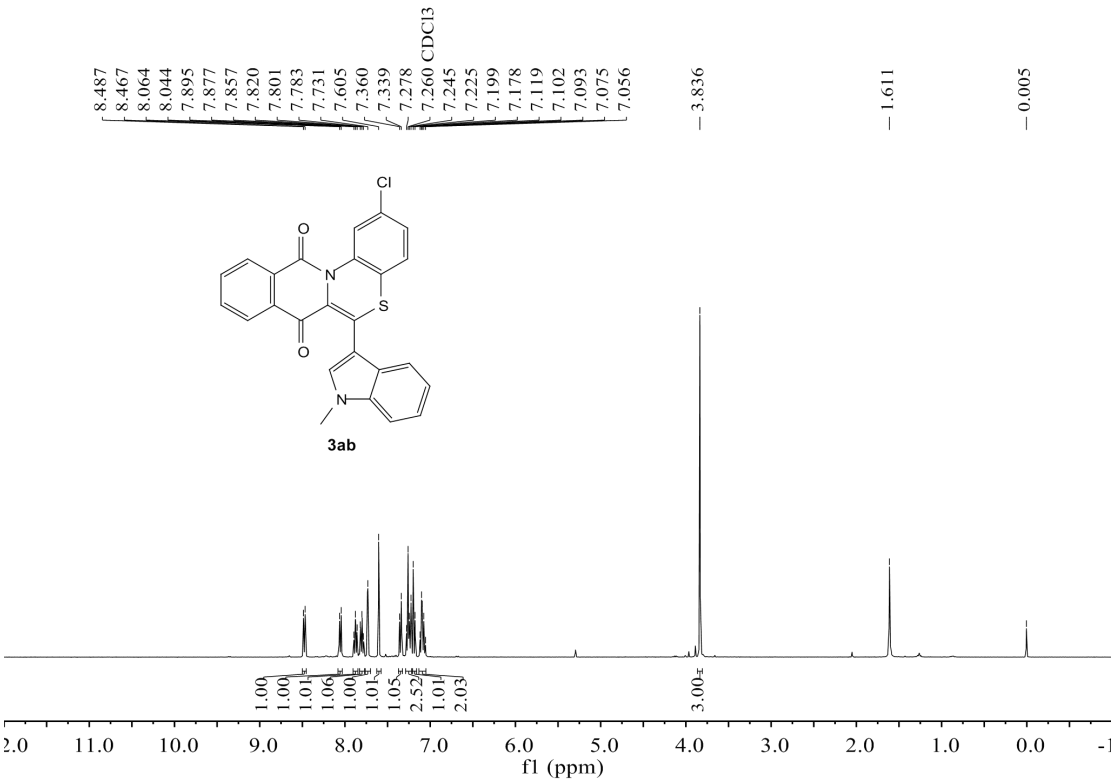
8. Copies of ^{1}H, ^{13}C and ^{19}F NMR spectra of all products

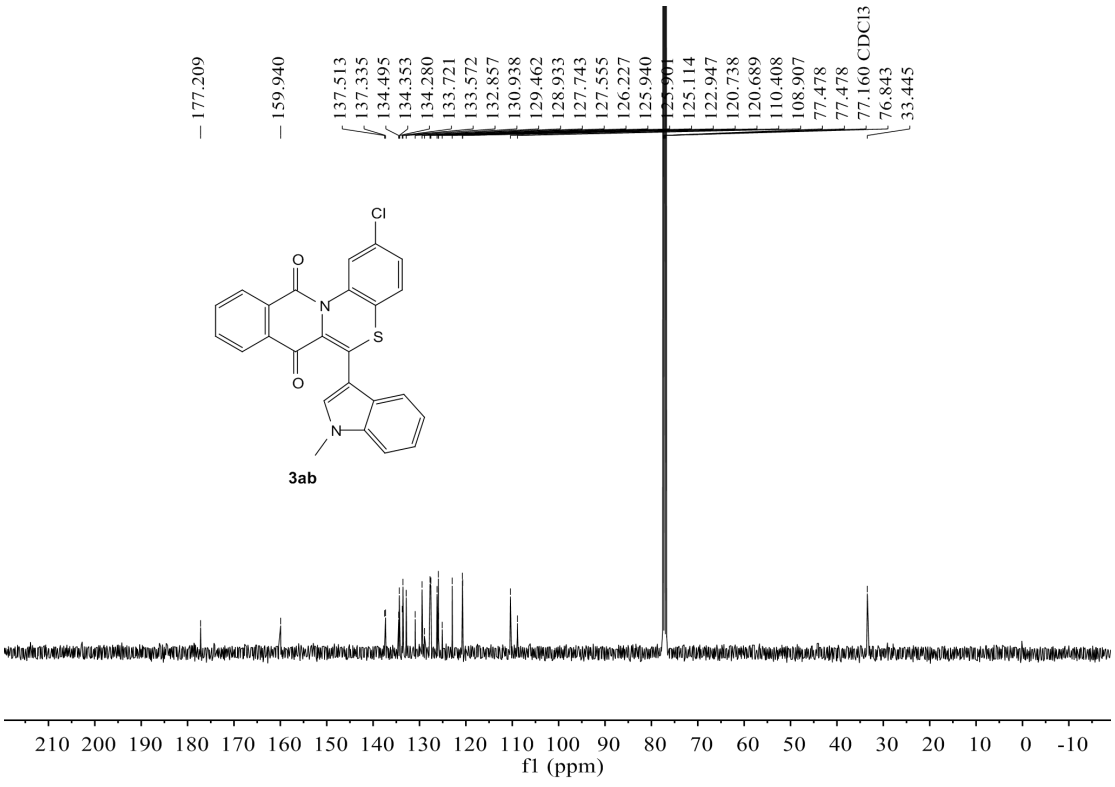
^{1}H NMR (400 MHz) and **^{13}C NMR** (100 MHz) spectra of **3aa** (**$CDCl_3$**)



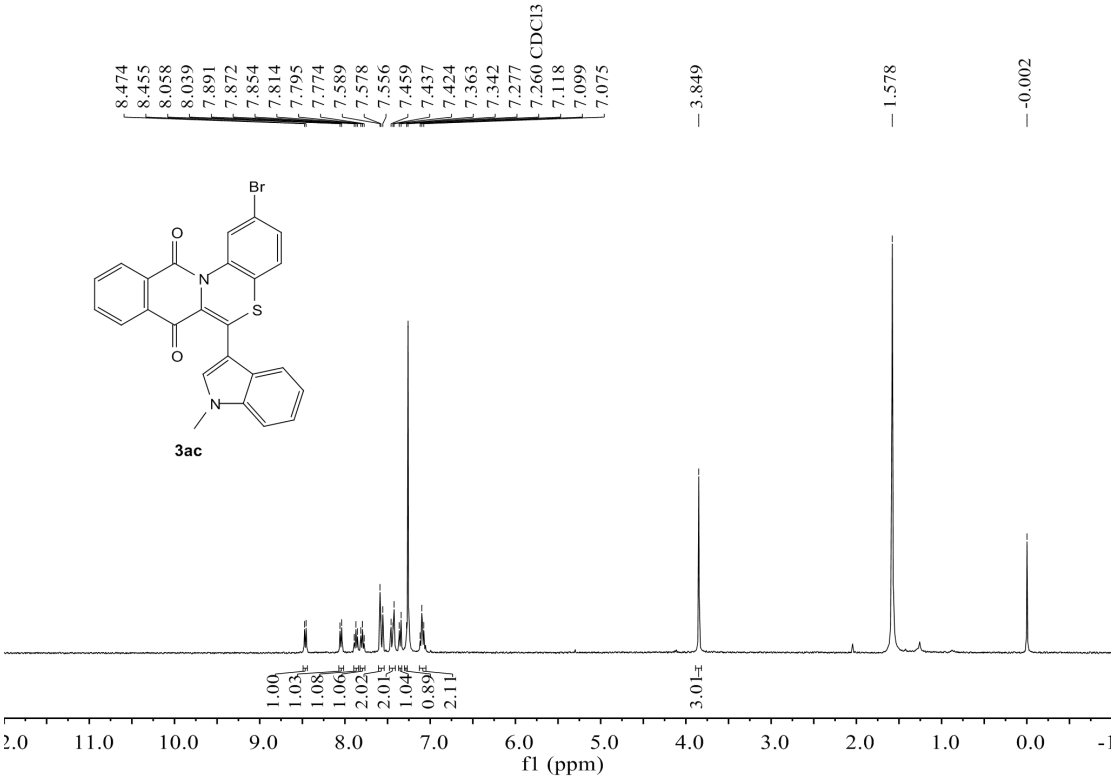


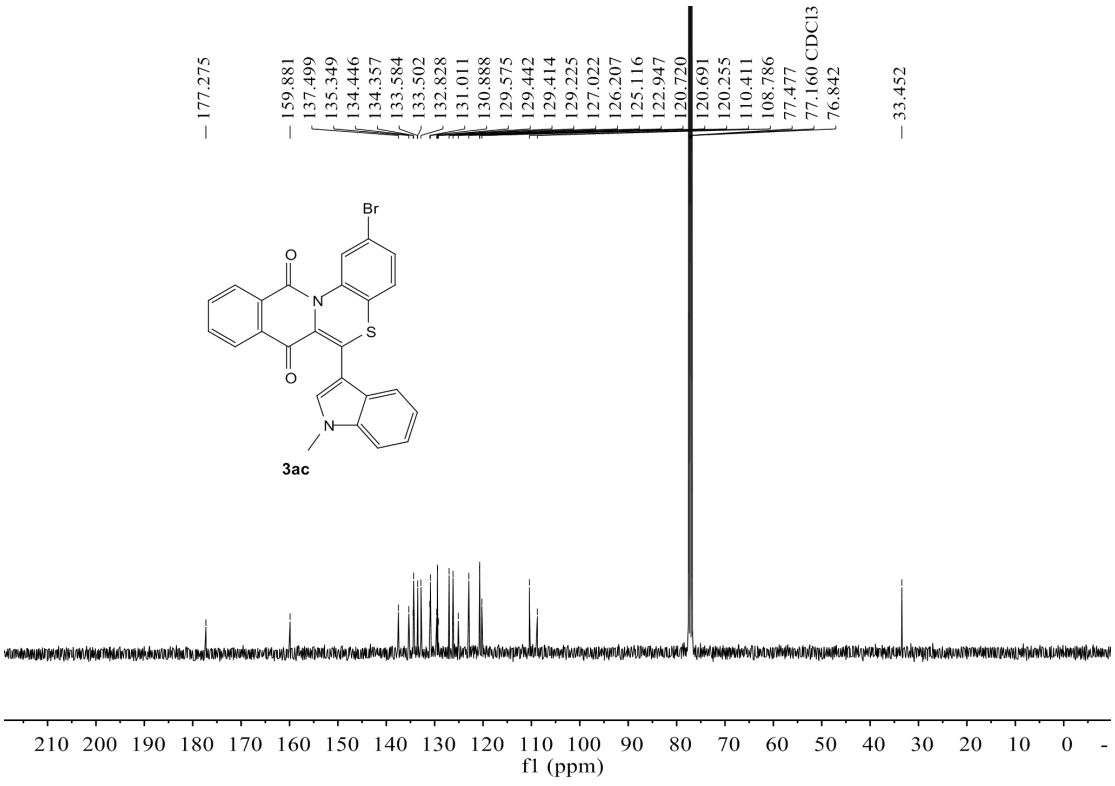
^{1}H NMR (400 MHz) and **^{13}C NMR** (100 MHz) spectra of **3ab** (**$CDCl_3$**)



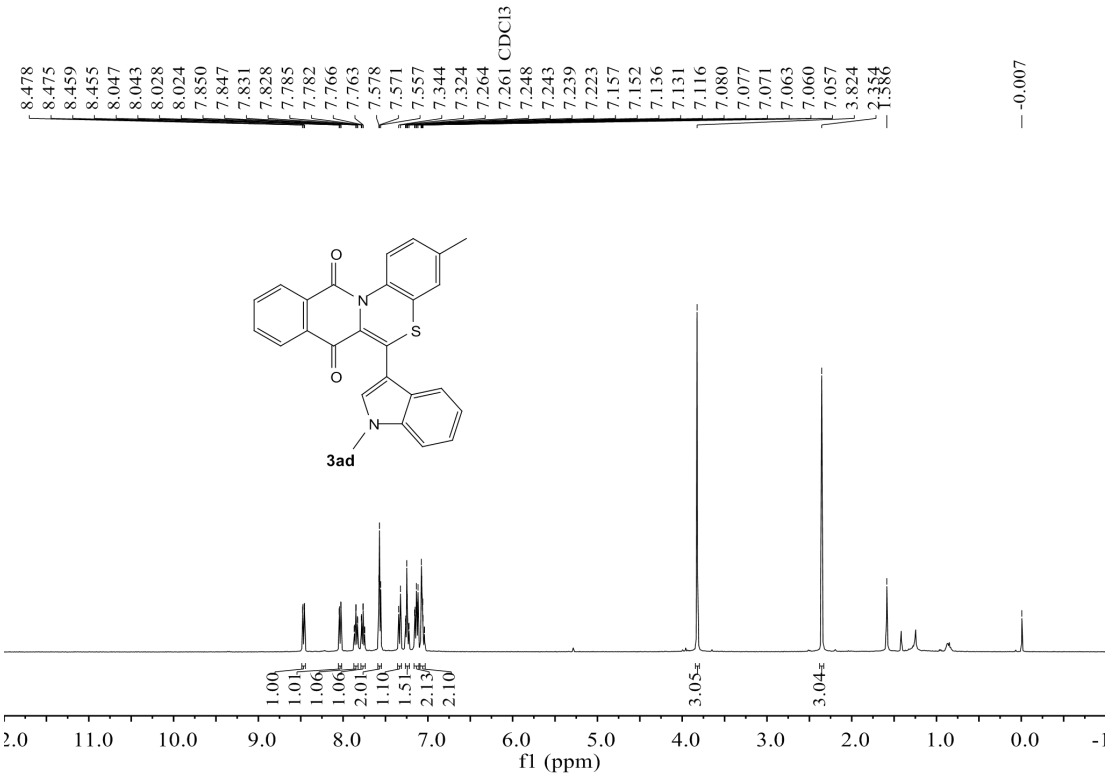


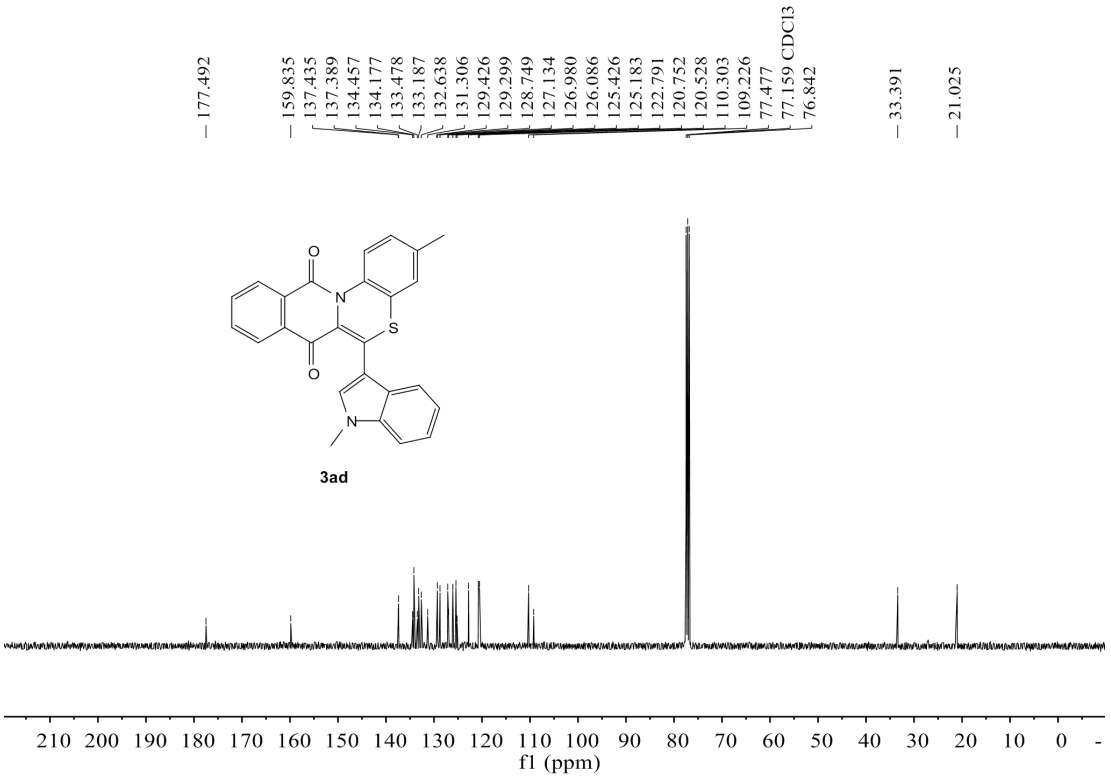
^{1}H NMR (400 MHz) and **^{13}C NMR** (100 MHz) spectra of **3ac** (**$CDCl_3$**)



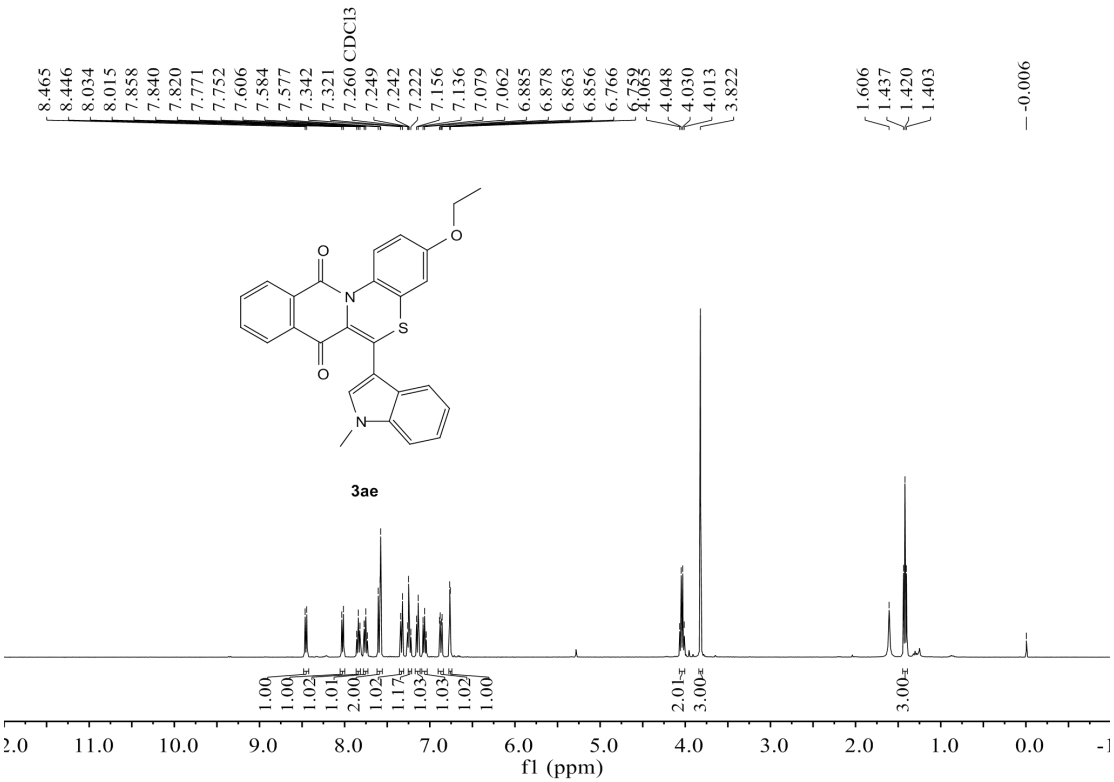


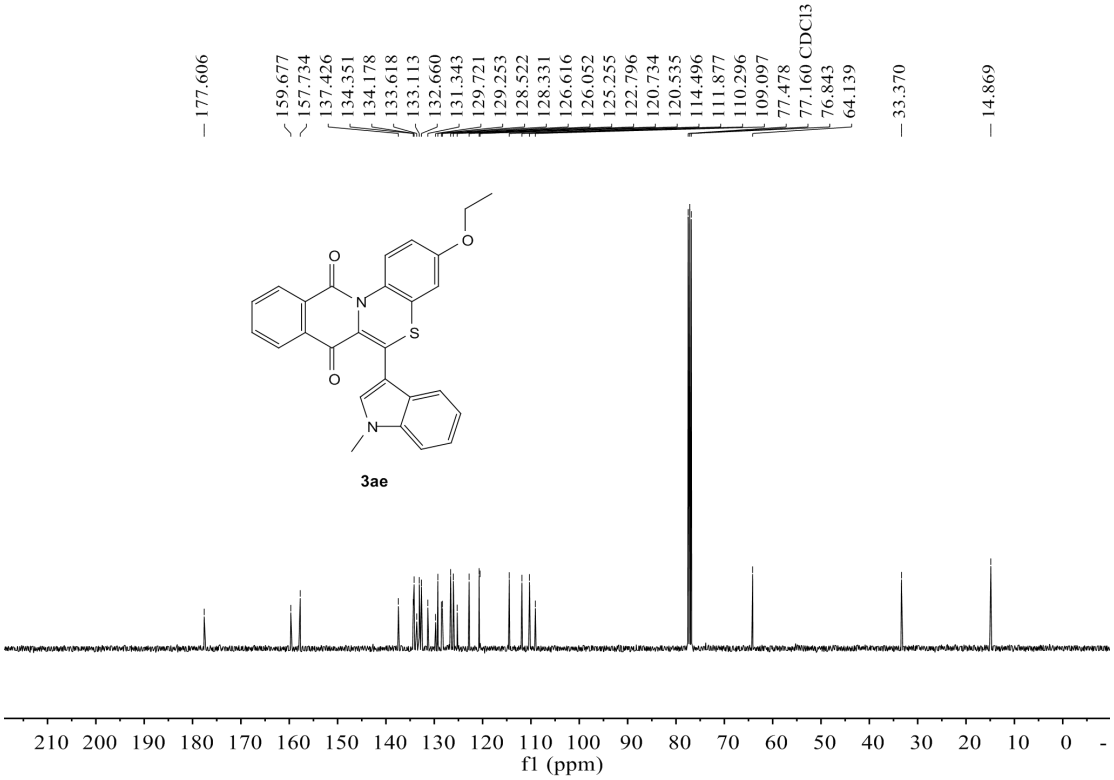
^{1}H NMR (400 MHz) and **^{13}C NMR** (100 MHz) spectra of **3ad** (**$CDCl_3$**)



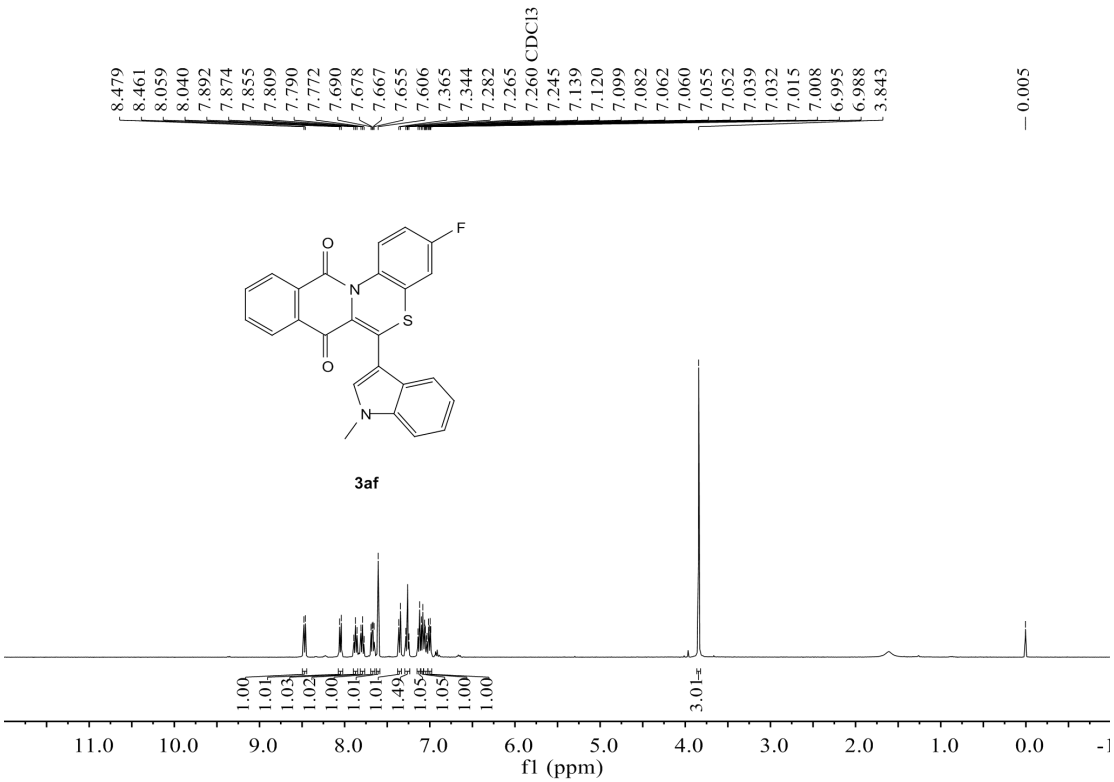


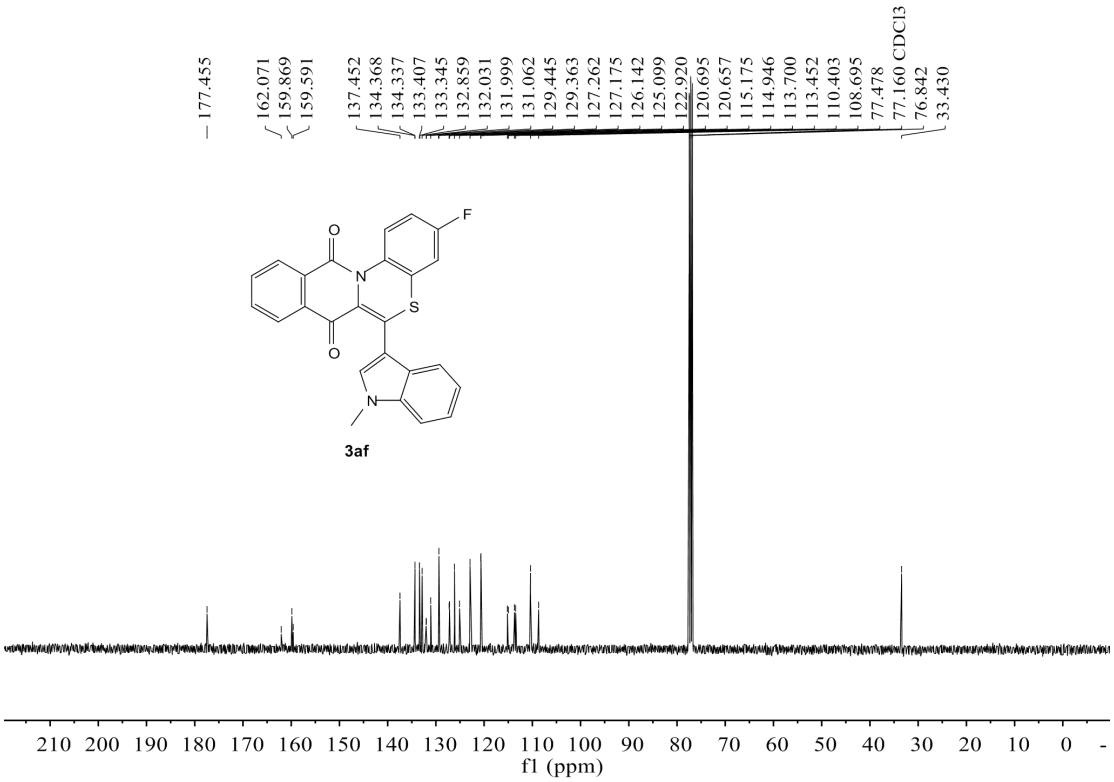
^{1}H NMR (400 MHz) and **^{13}C NMR** (100 MHz) spectra of **3ae** (**$CDCl_3$**)

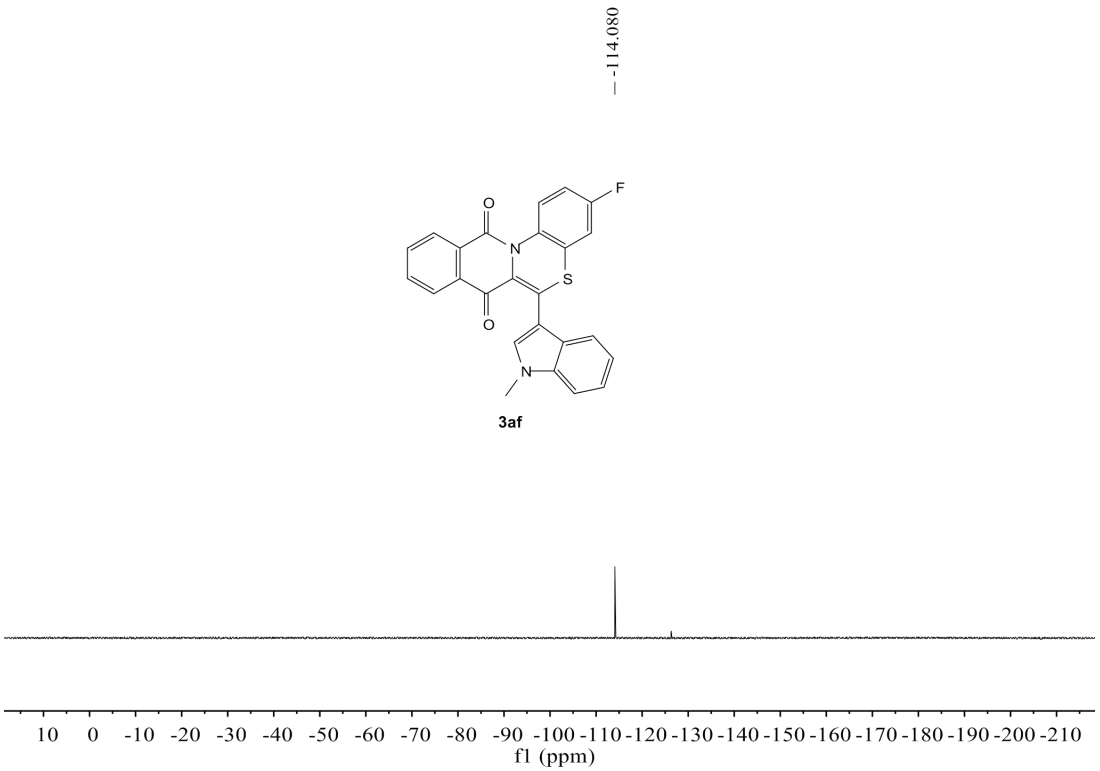




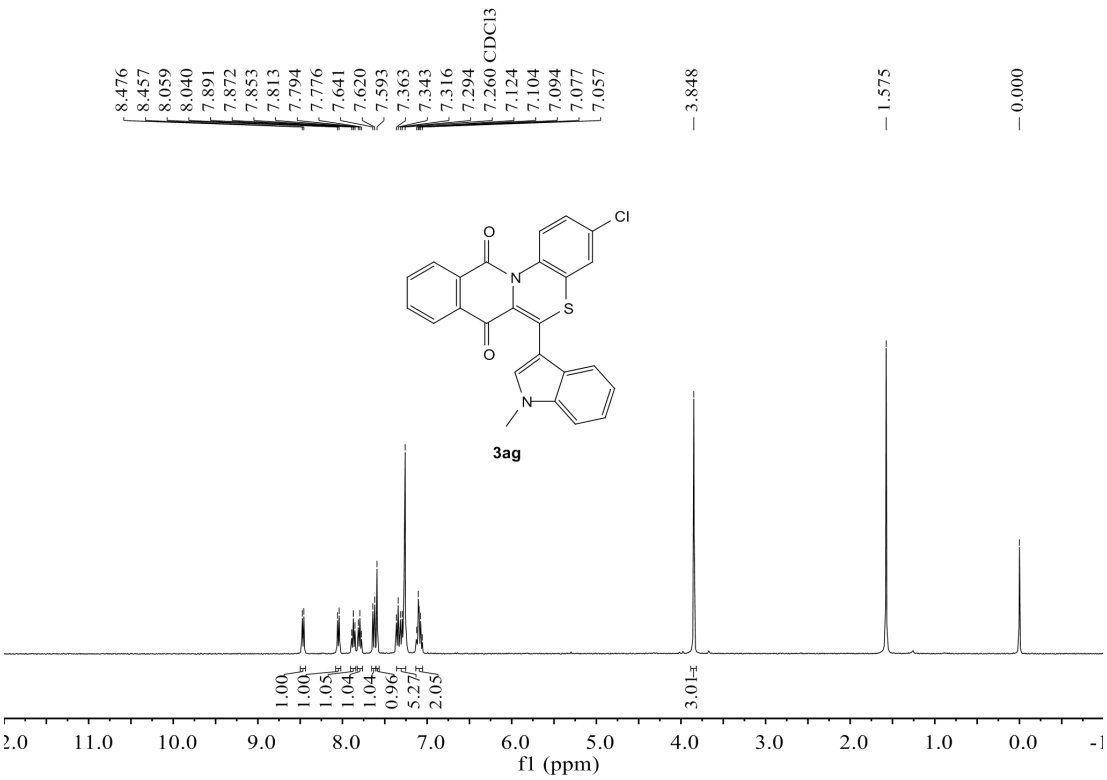
^{1}H NMR (400 MHz) and **^{13}C NMR** (100 MHz) spectra of **3af** (**$CDCl_3$**)

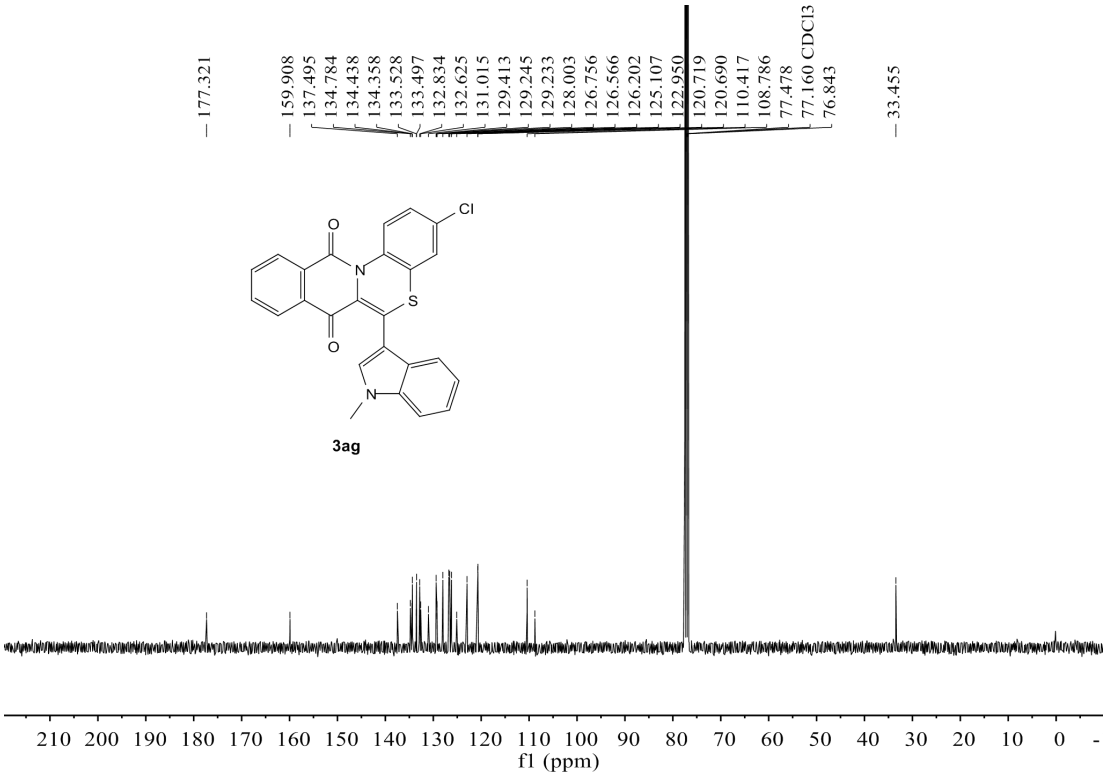




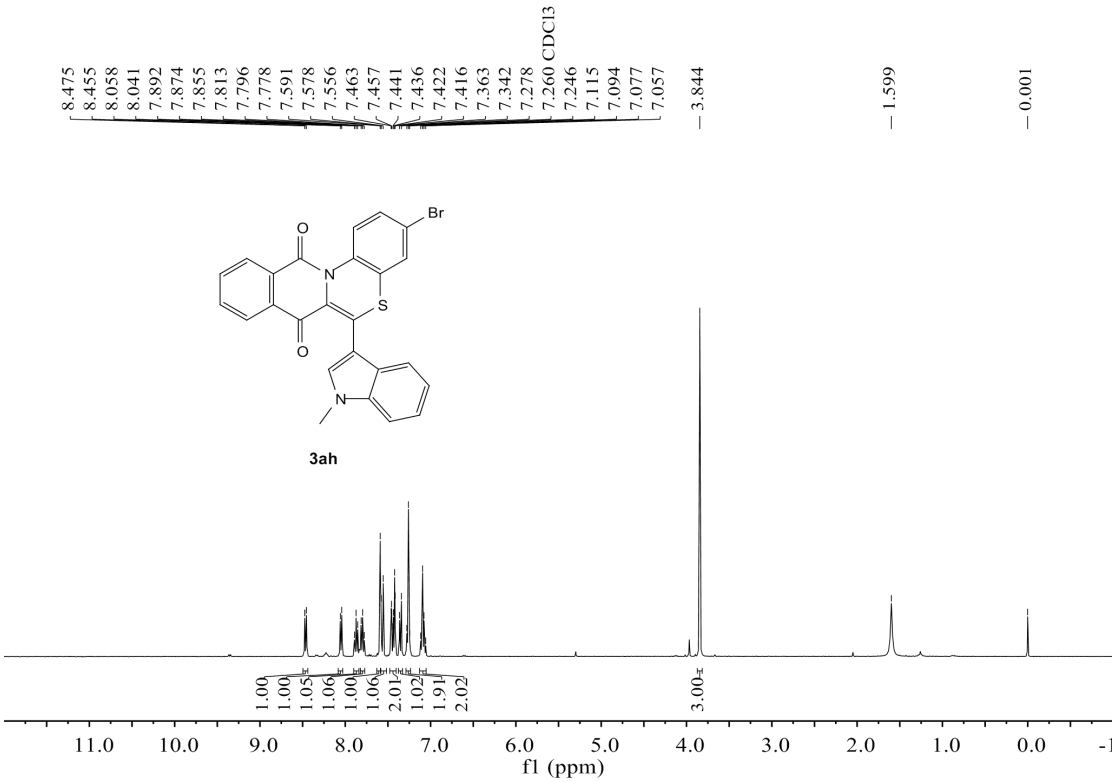

-114.080
F
O
N
S
O
N
3af
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

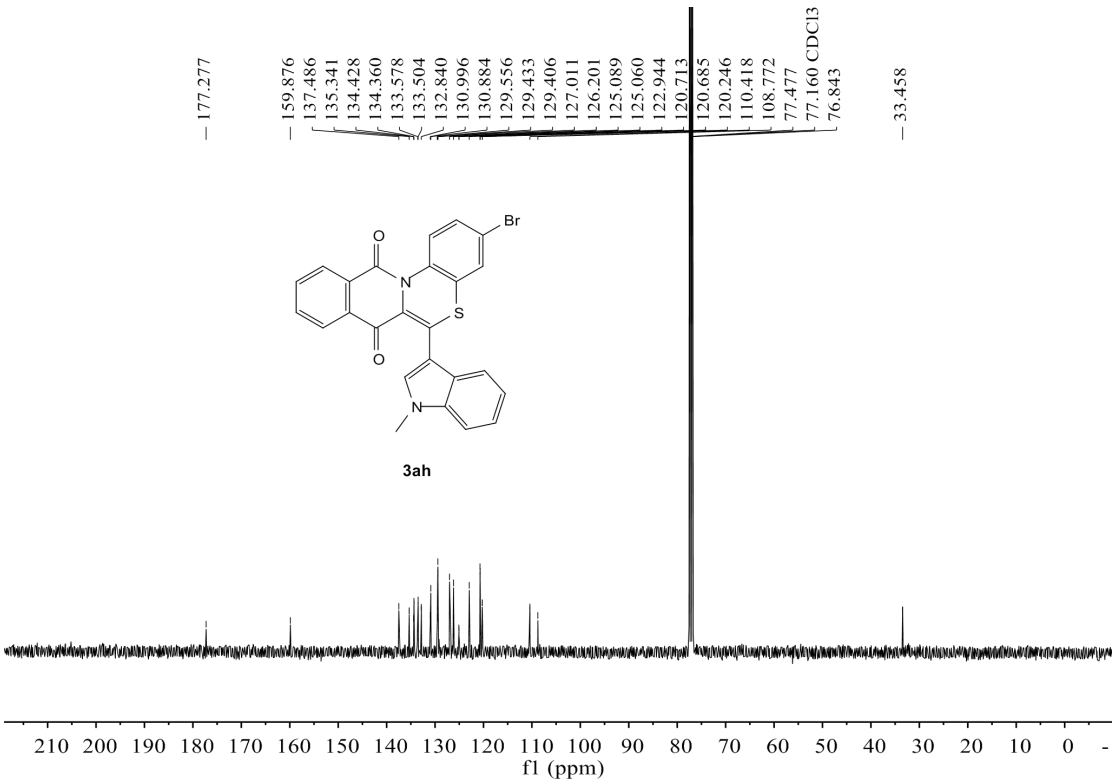
^{1}H NMR (400 MHz) and **^{13}C NMR** (100 MHz) spectra of **3ag** (**$CDCl_3$**)



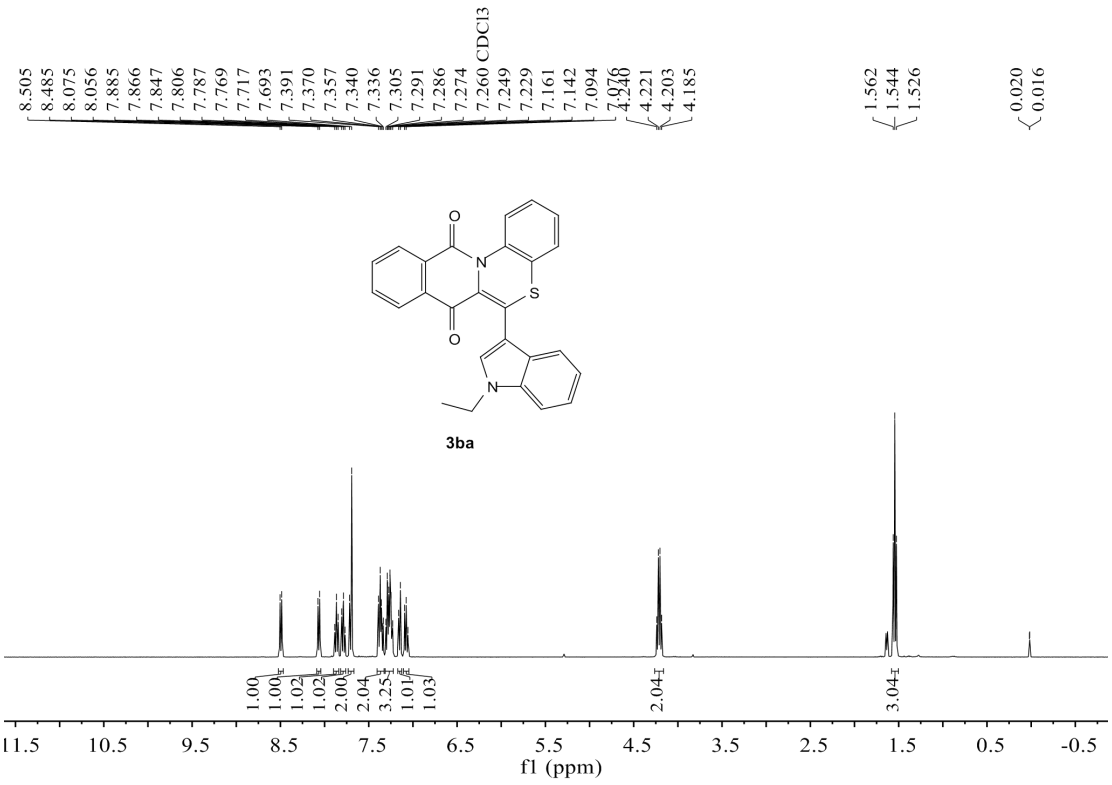


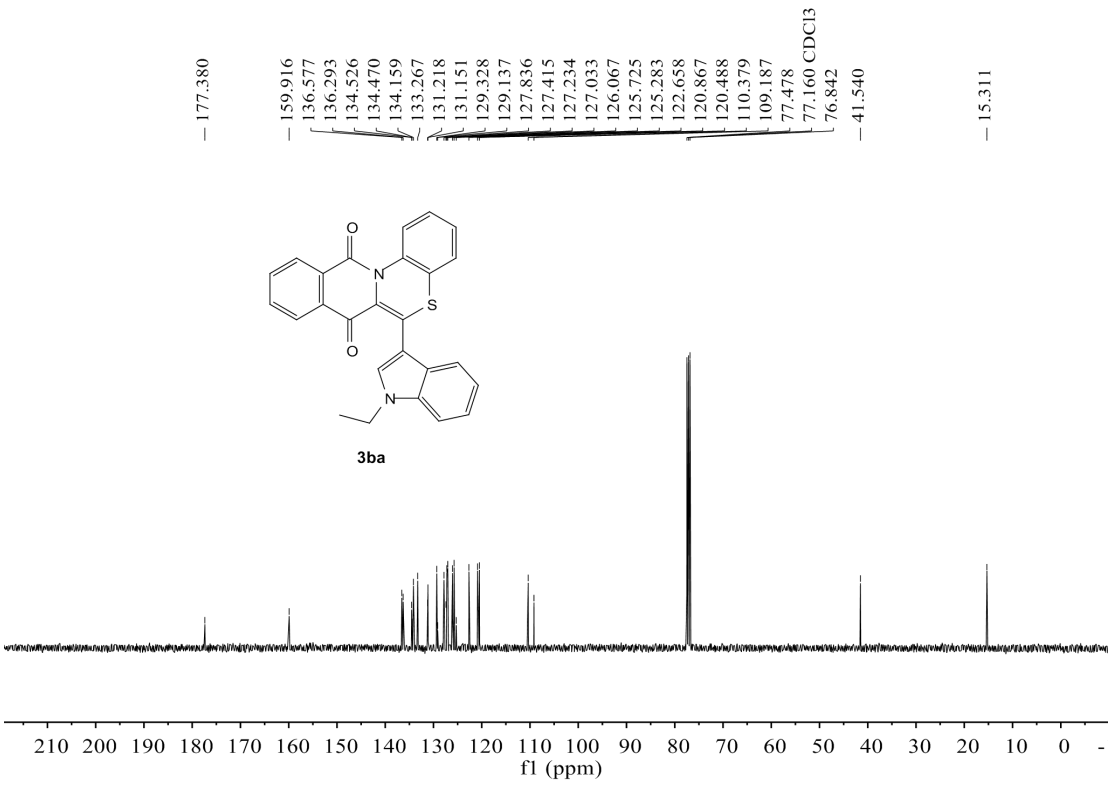
^{1}H NMR (400 MHz) and **^{13}C NMR** (100 MHz) spectra of **3ah** (**$CDCl_3$**)



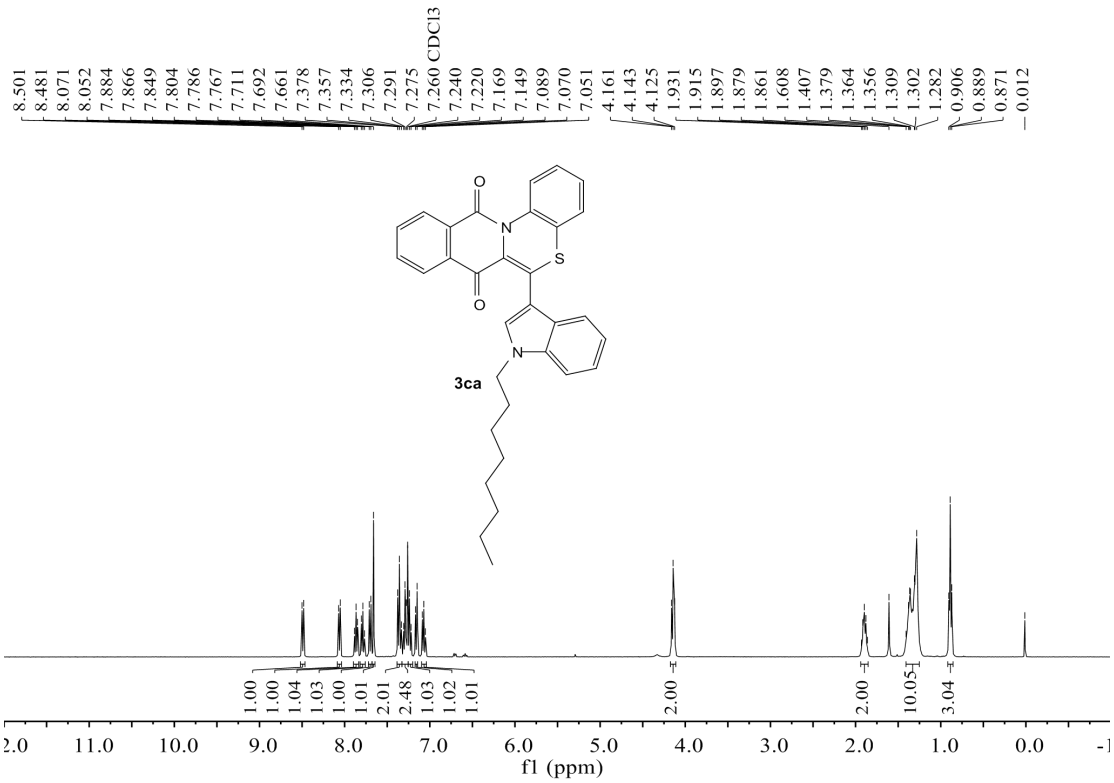


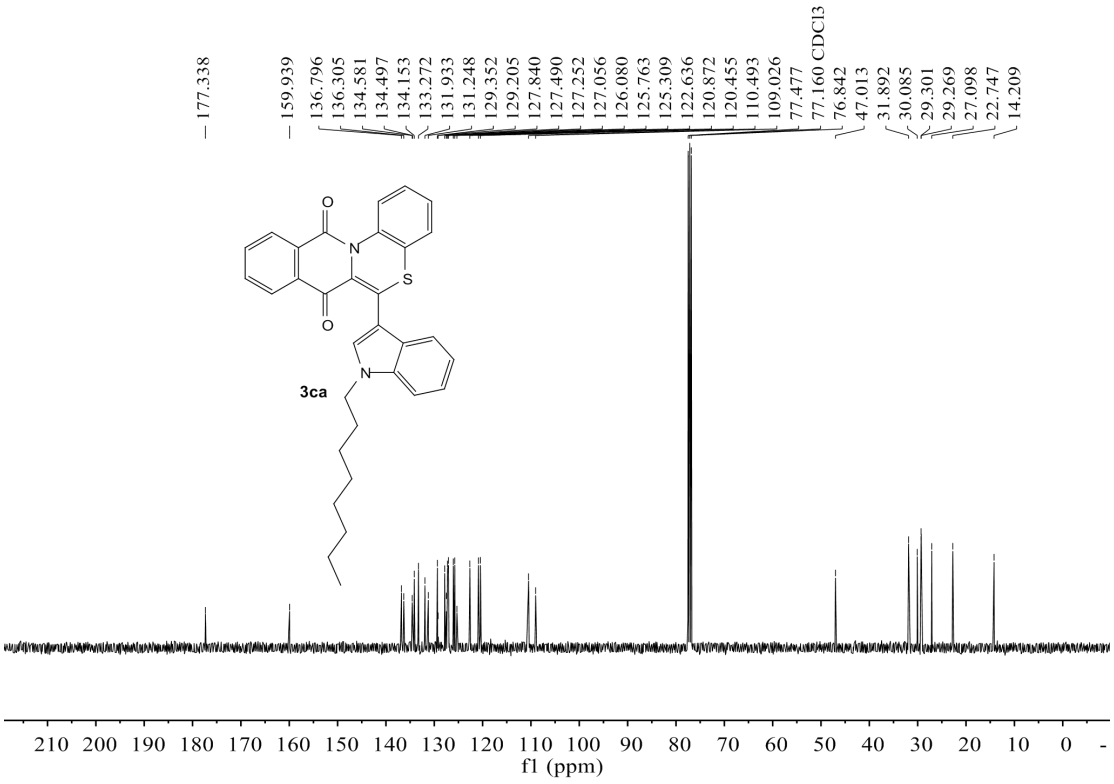
^{1}H NMR (400 MHz) and **^{13}C NMR** (100 MHz) spectra of **3ba** (**$CDCl_3$**)



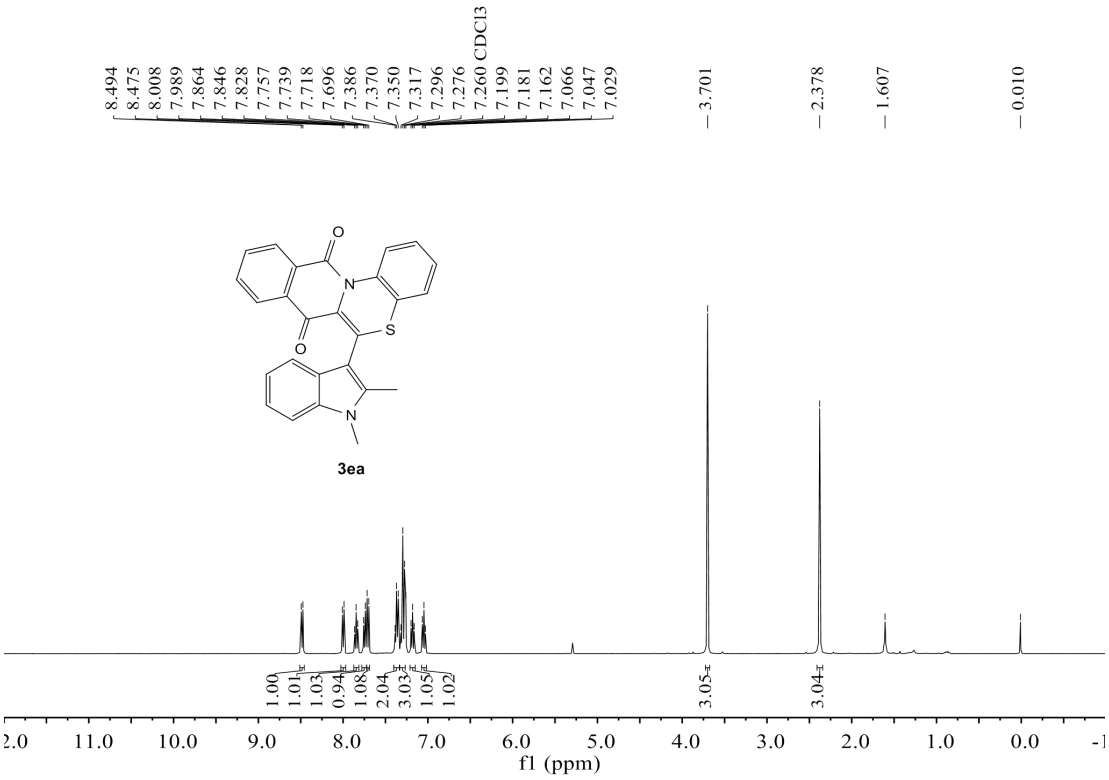


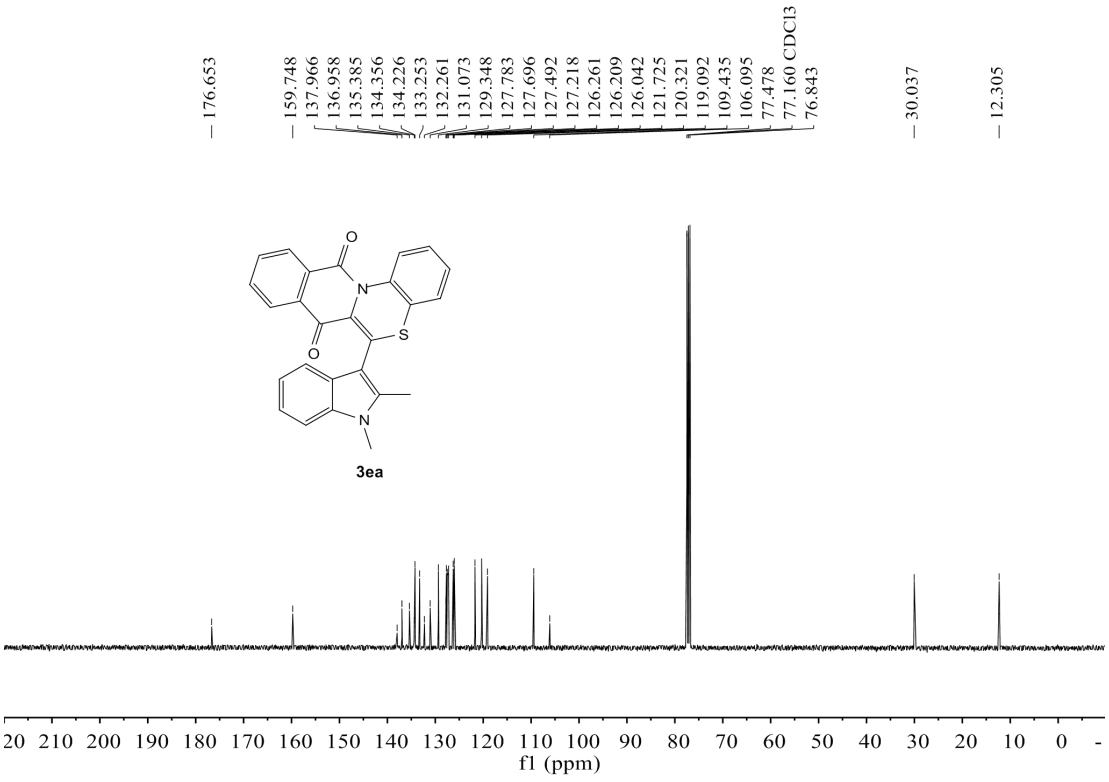
^{1}H NMR (400 MHz) and **^{13}C NMR** (100 MHz) spectra of **3ca** (**$CDCl_3$**)



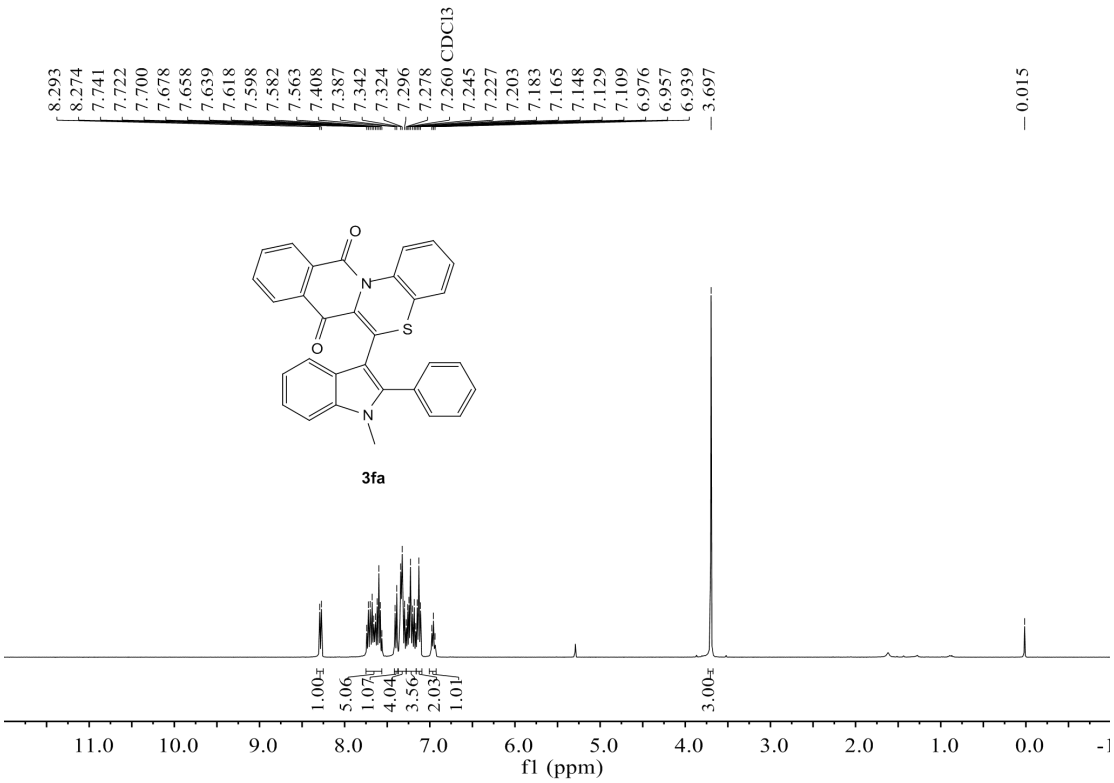


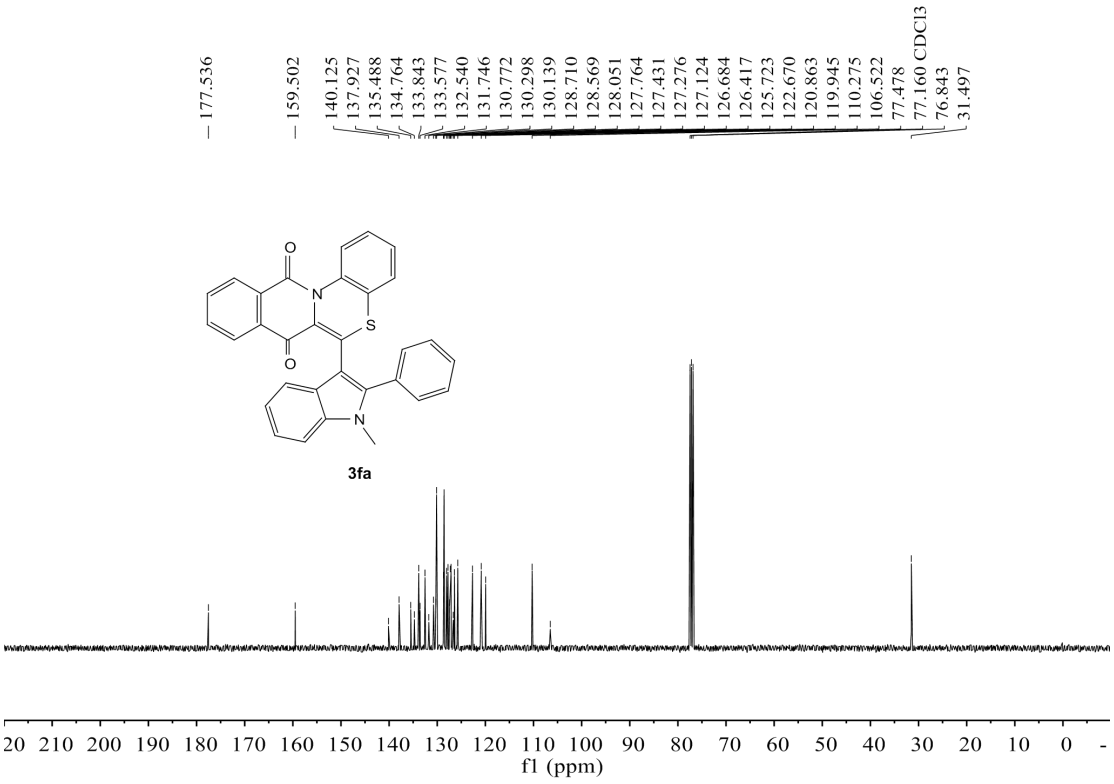
^{1}H NMR (400 MHz) and **^{13}C NMR** (100 MHz) spectra of **3ea** (**$CDCl_3$**)



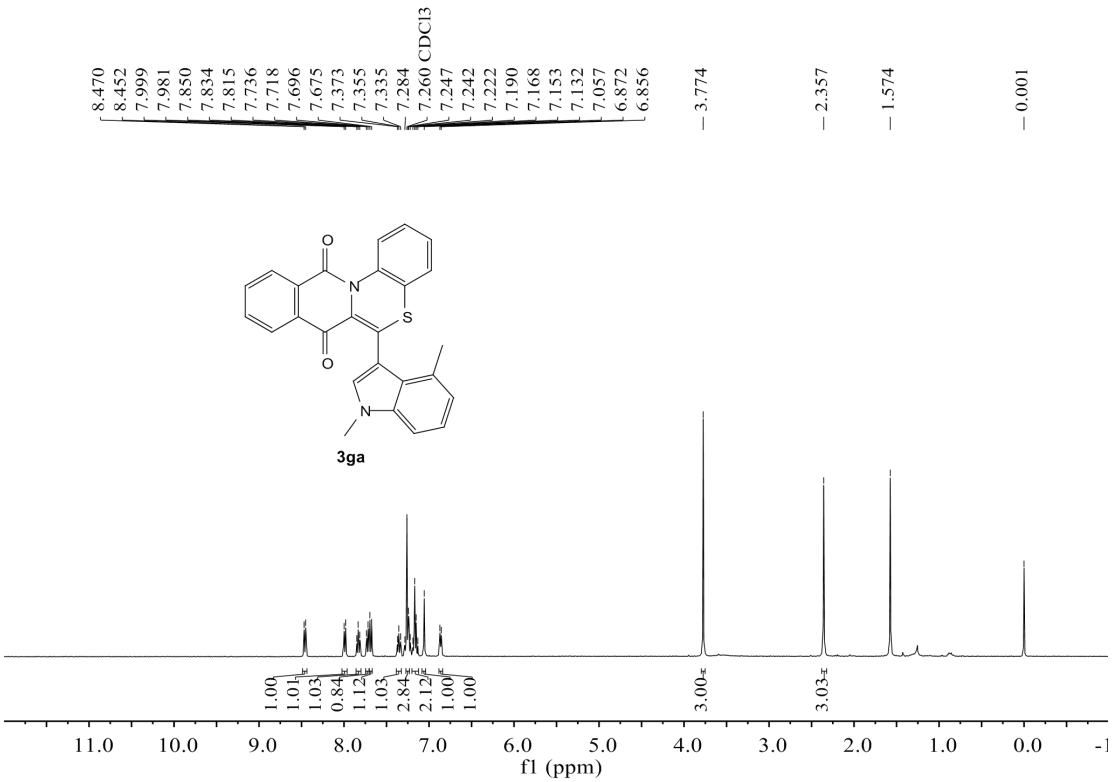


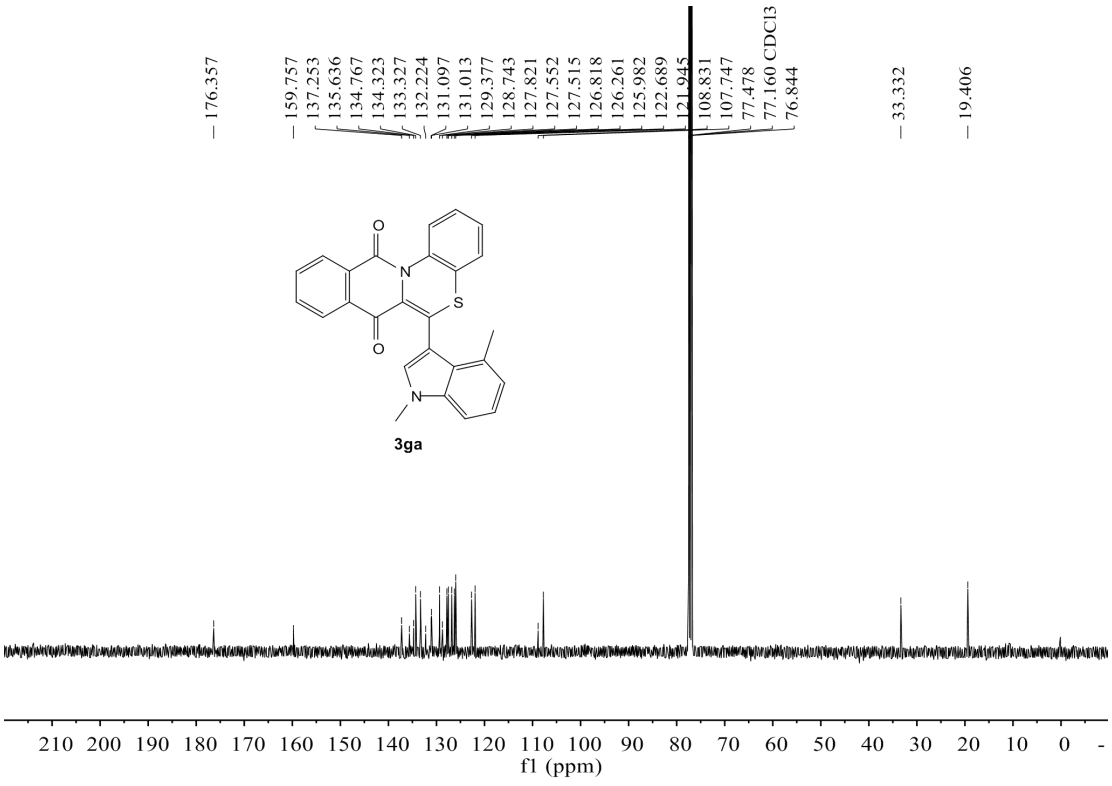
^{1}H NMR (400 MHz) and **^{13}C NMR** (100 MHz) spectra of **3fa** (**$CDCl_3$**)



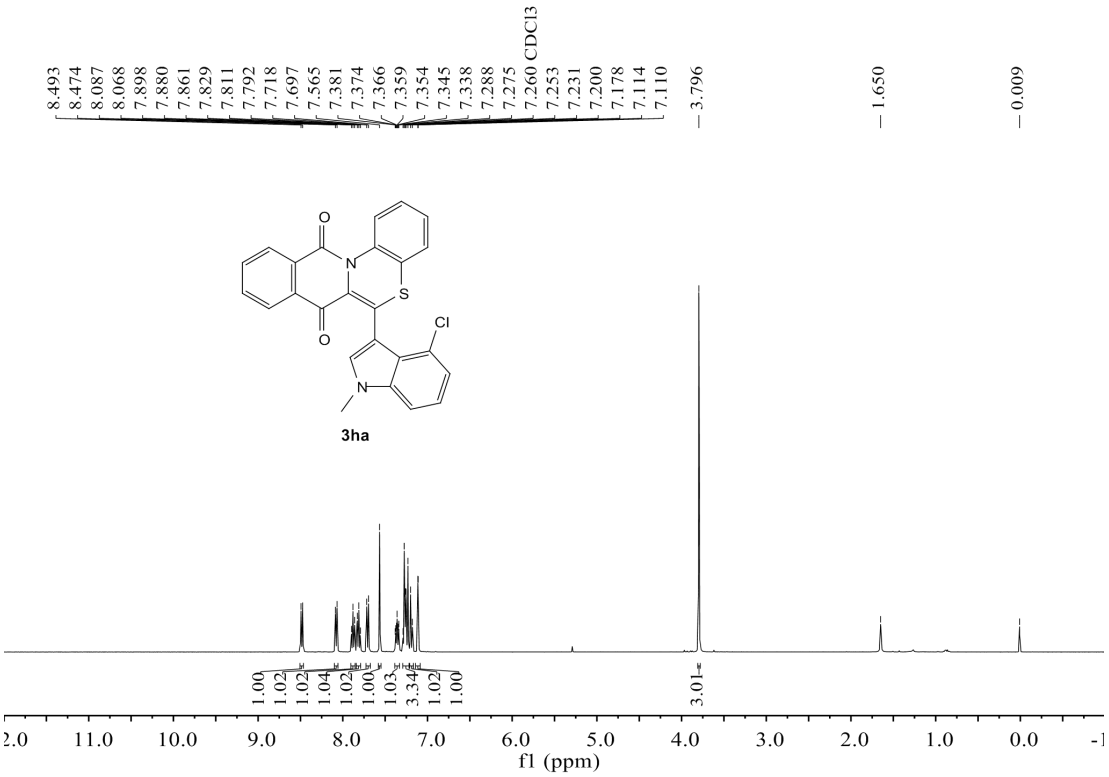


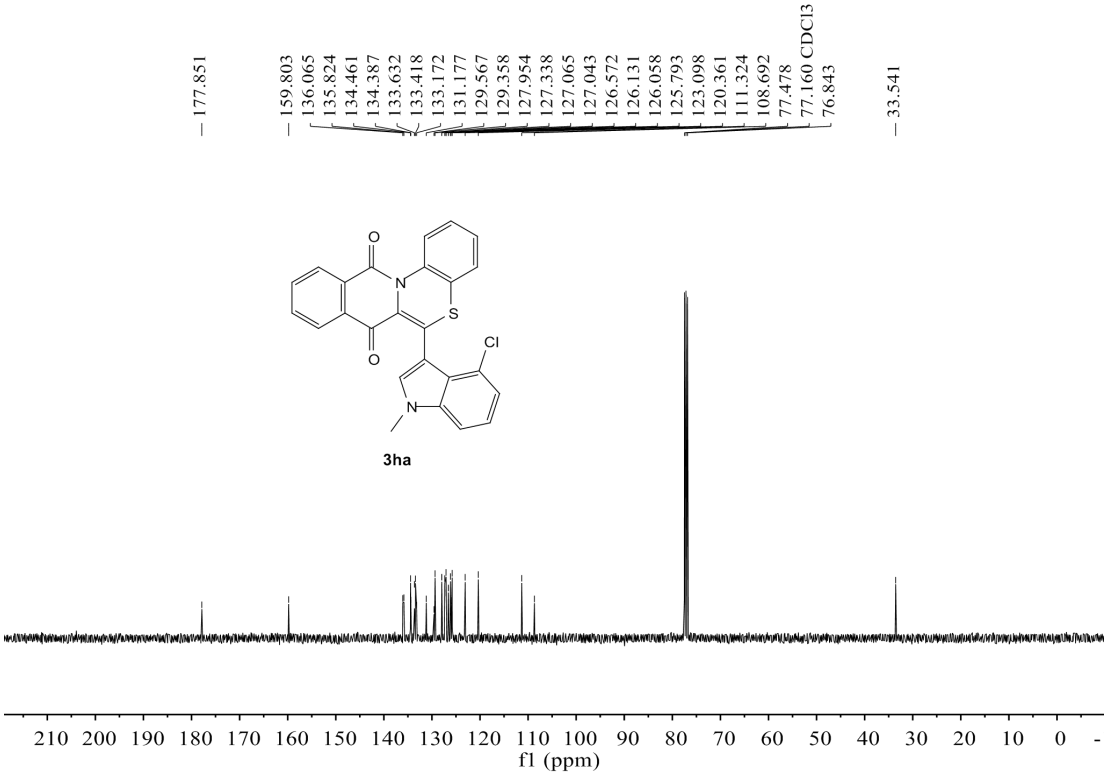
^{1}H NMR (400 MHz) and **^{13}C NMR** (100 MHz) spectra of **3ga** (**$CDCl_3$**)



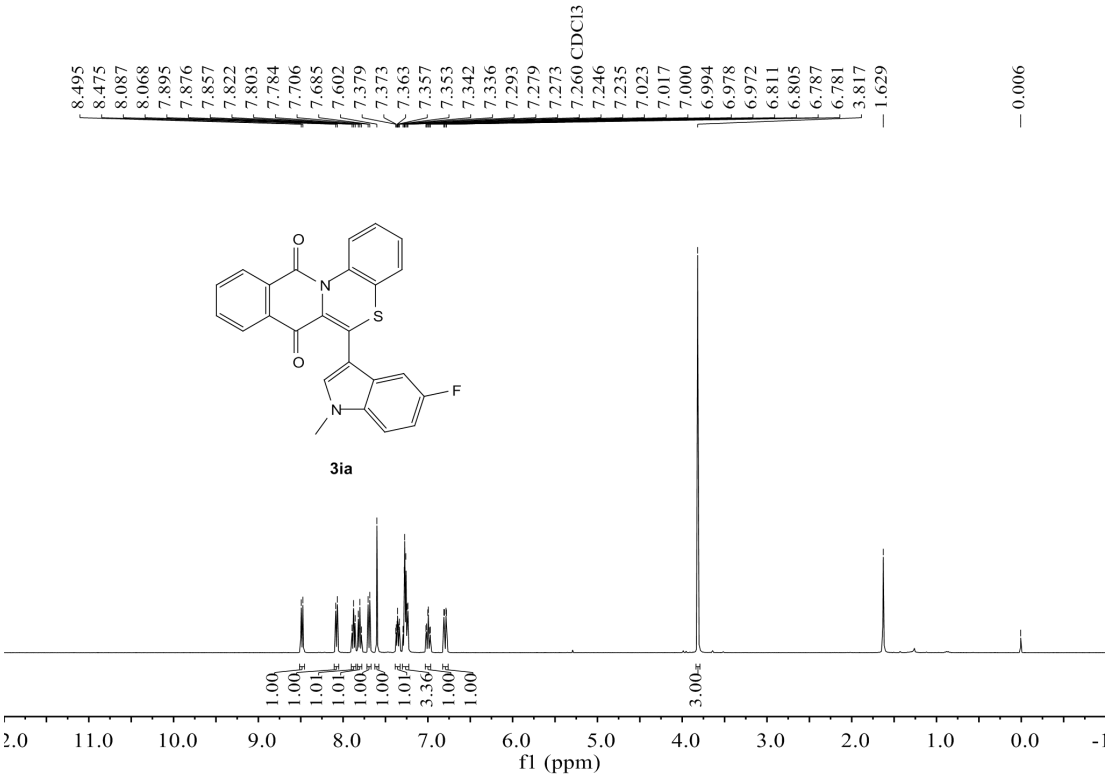


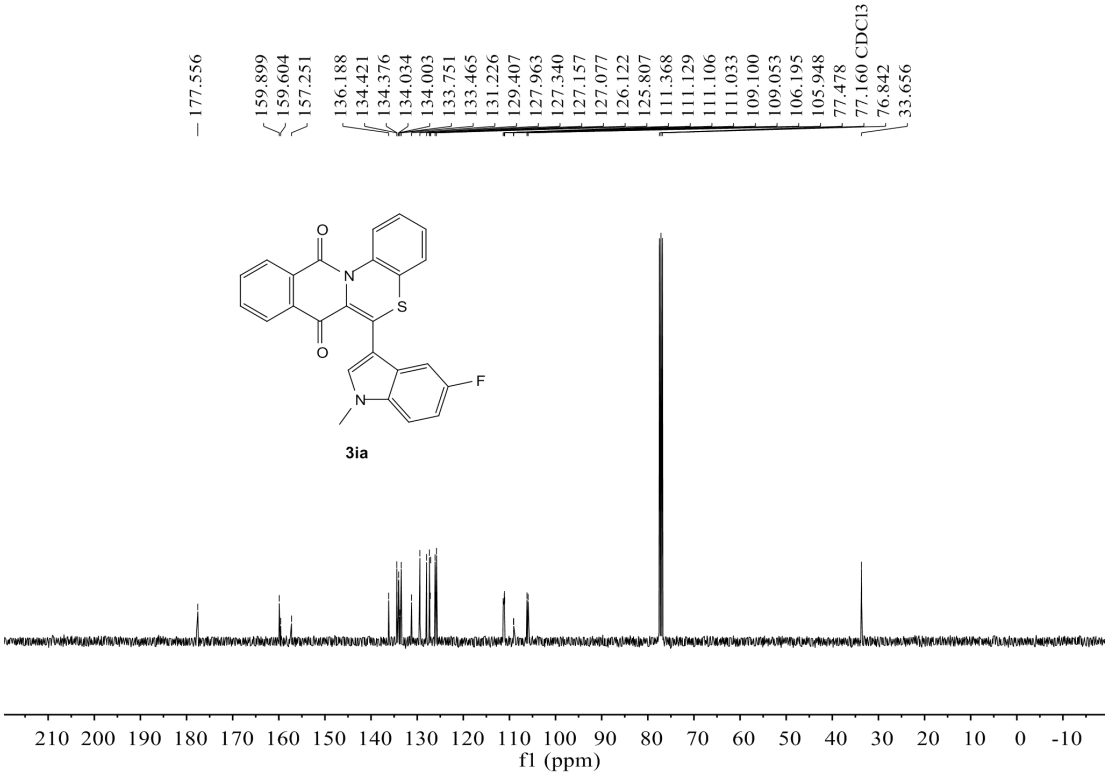
^{1}H NMR (400 MHz) and **^{13}C NMR** (100 MHz) spectra of **3ha** (**$CDCl_3$**)

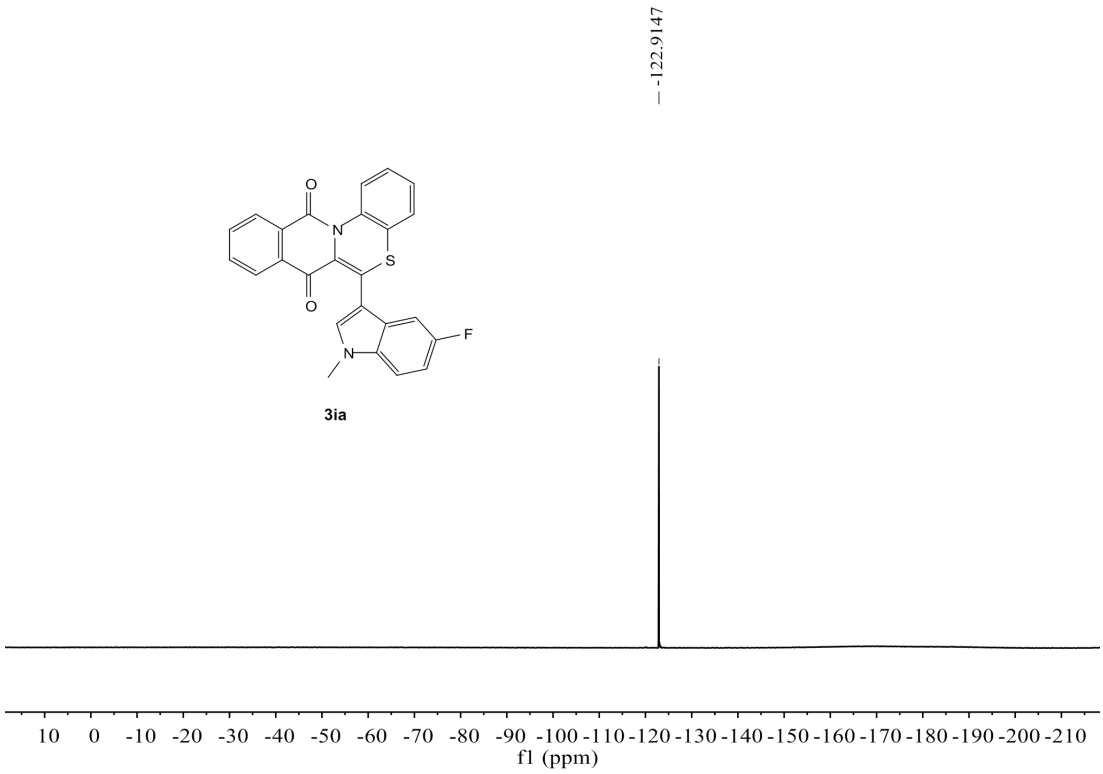




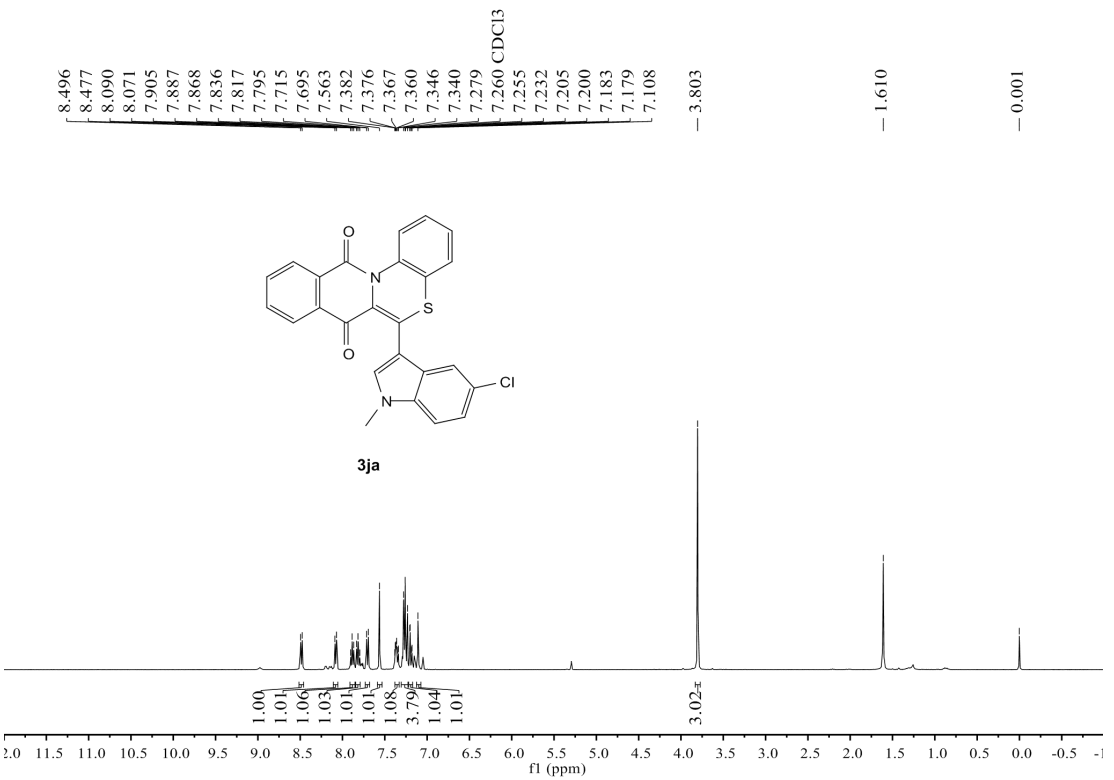
^{1}H NMR (400 MHz) and **^{13}C NMR** (100 MHz) spectra of **3ia** (**$CDCl_3$**)

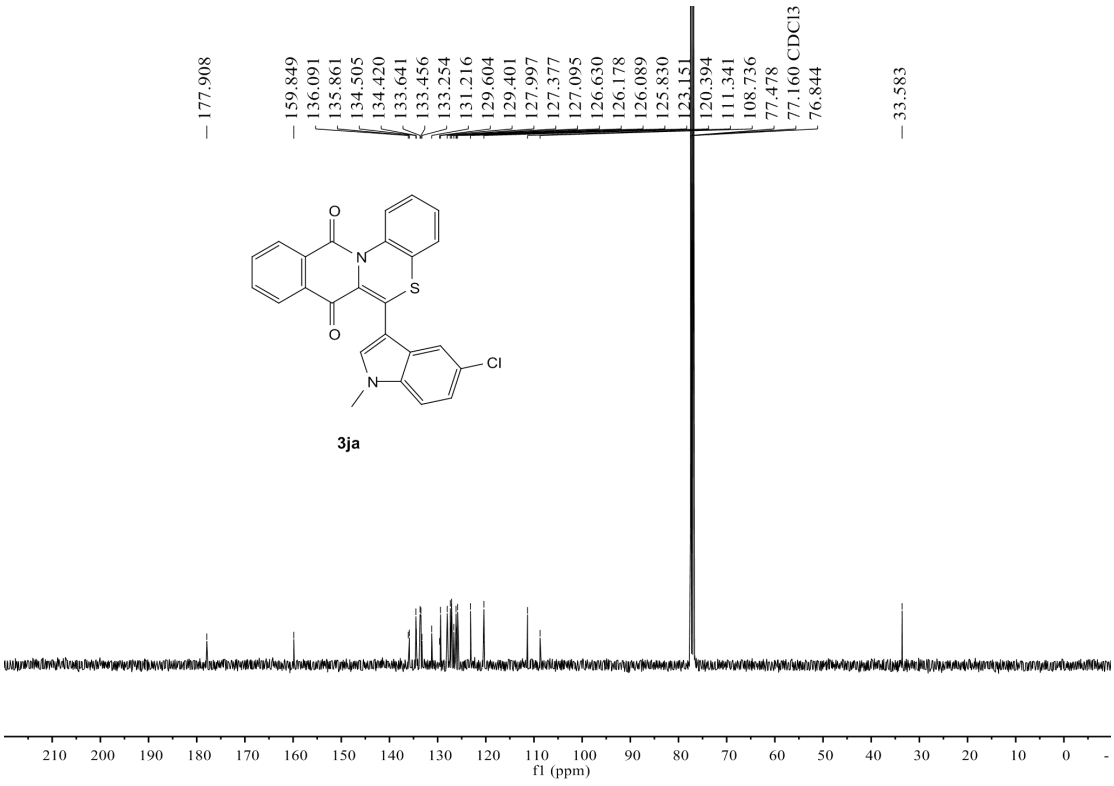




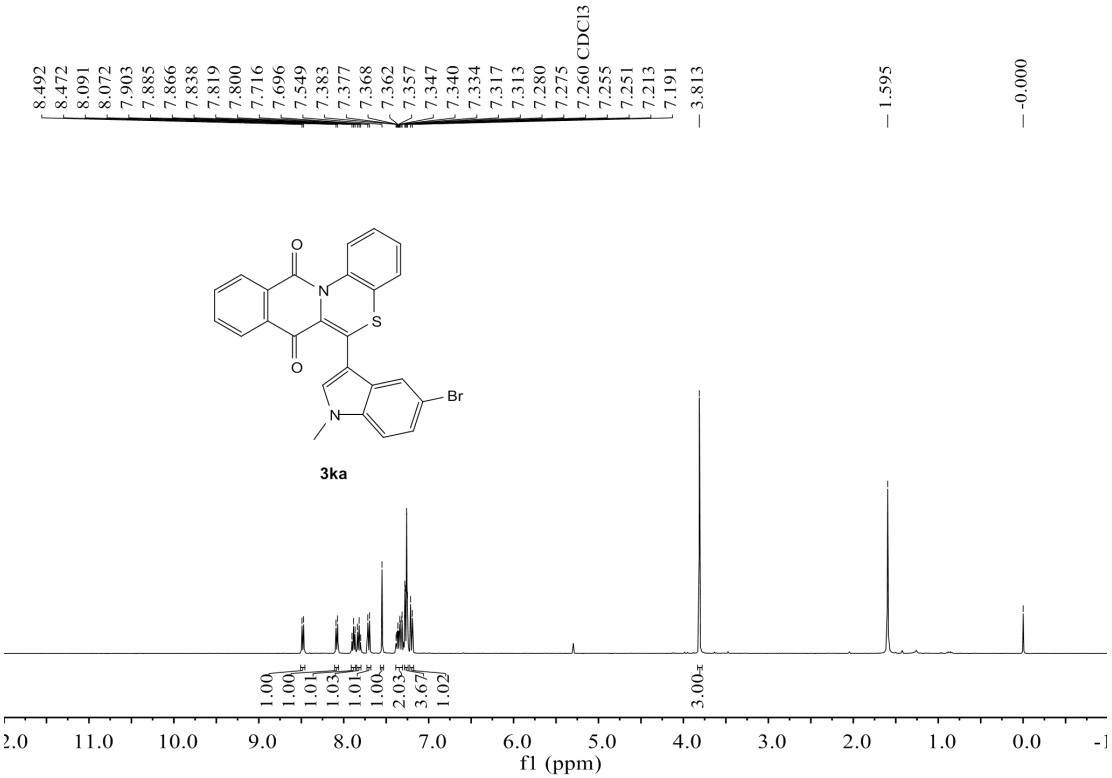

-122.9147
O
N
S
O
F
N
3ia
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

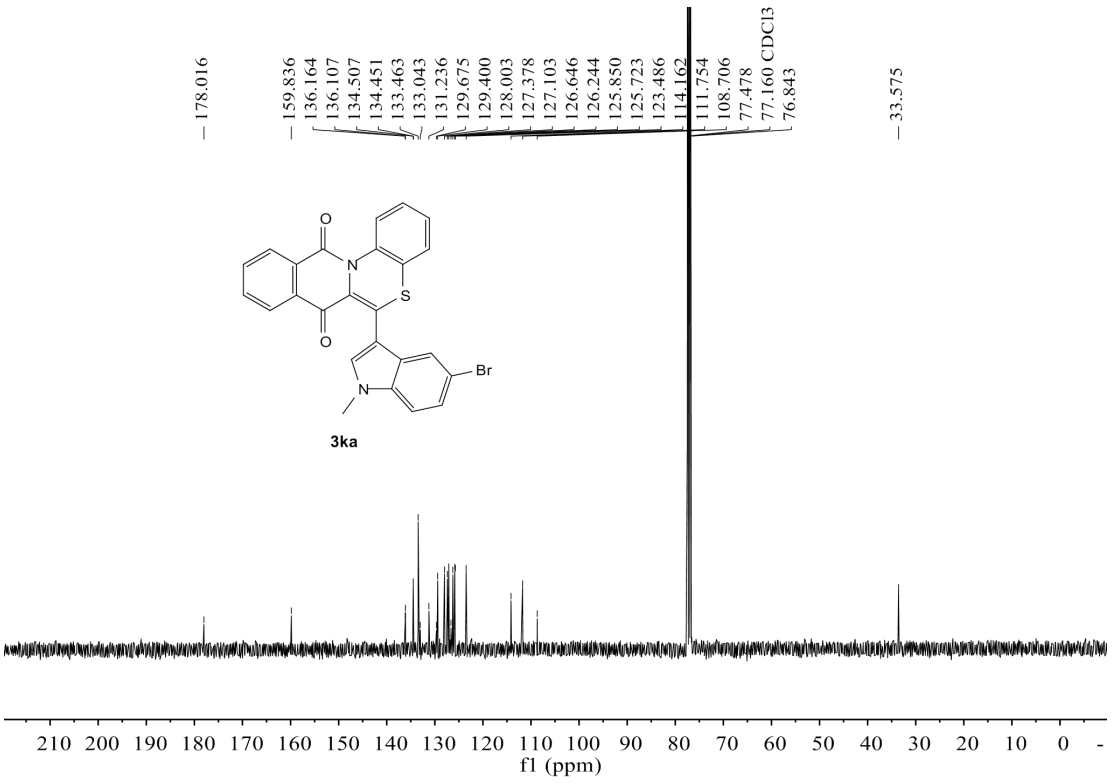
^{1}H NMR (400 MHz) and **^{13}C NMR** (100 MHz) spectra of **3ja** (**$CDCl_3$**)



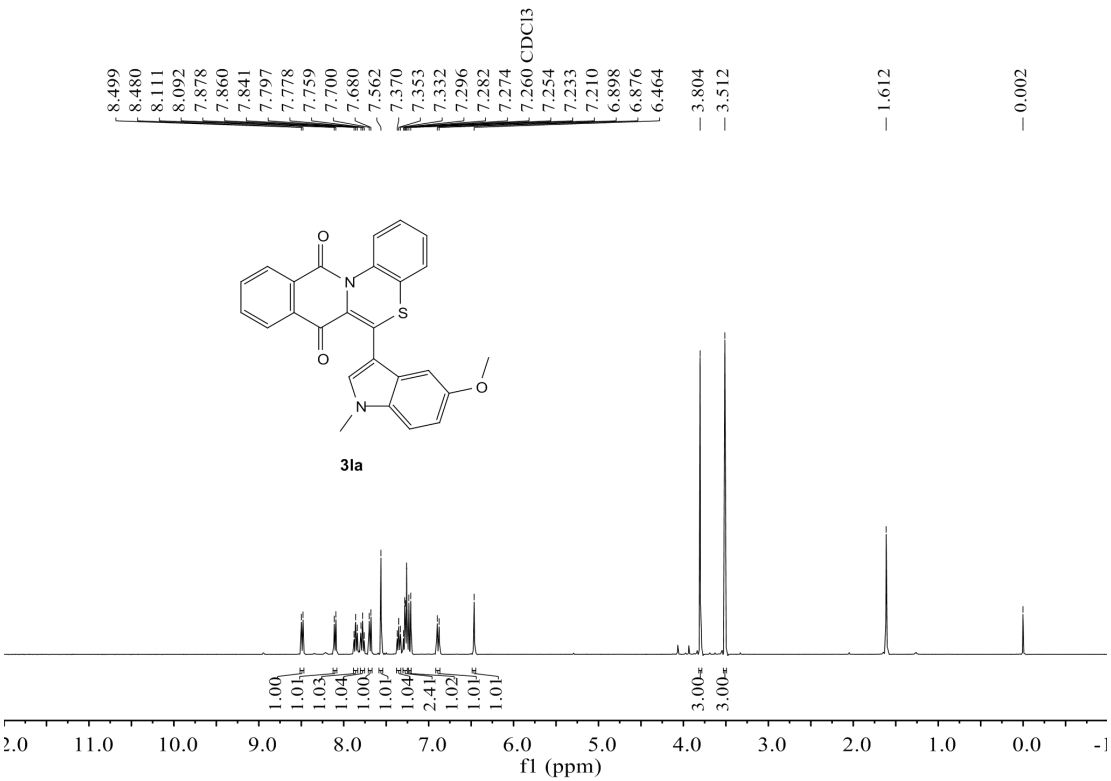


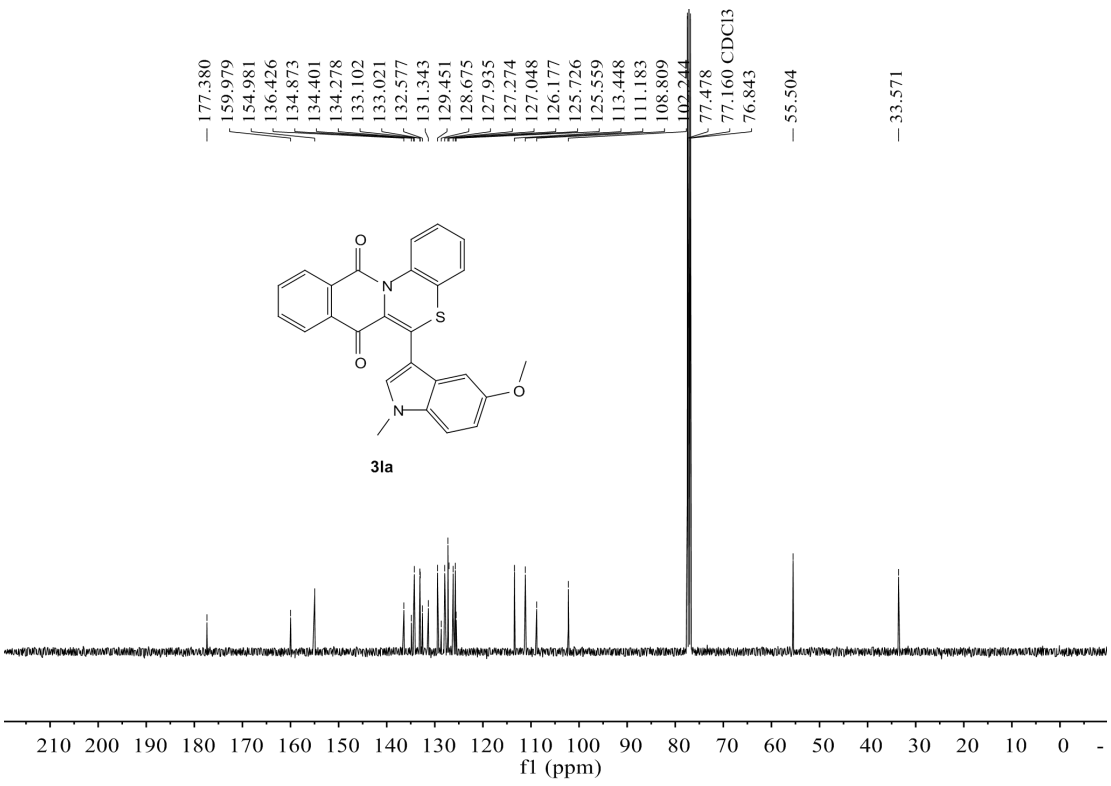
^{1}H NMR (400 MHz) and **^{13}C NMR** (100 MHz) spectra of **3ka** (**$CDCl_3$**)



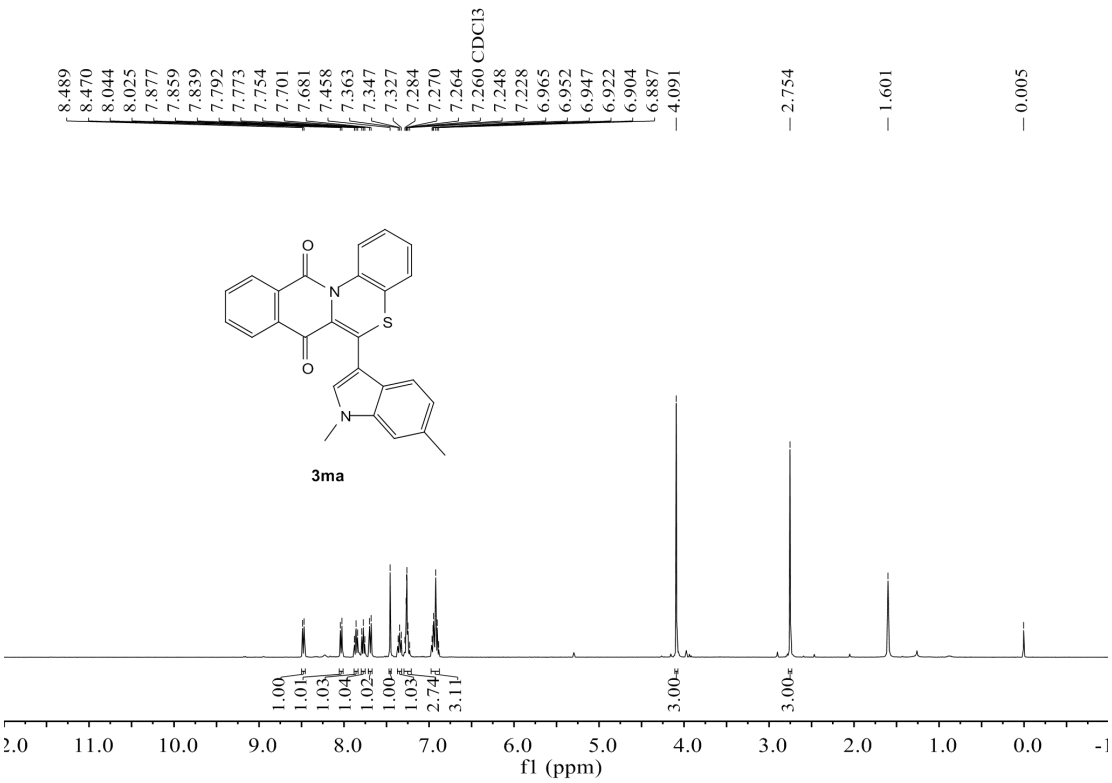


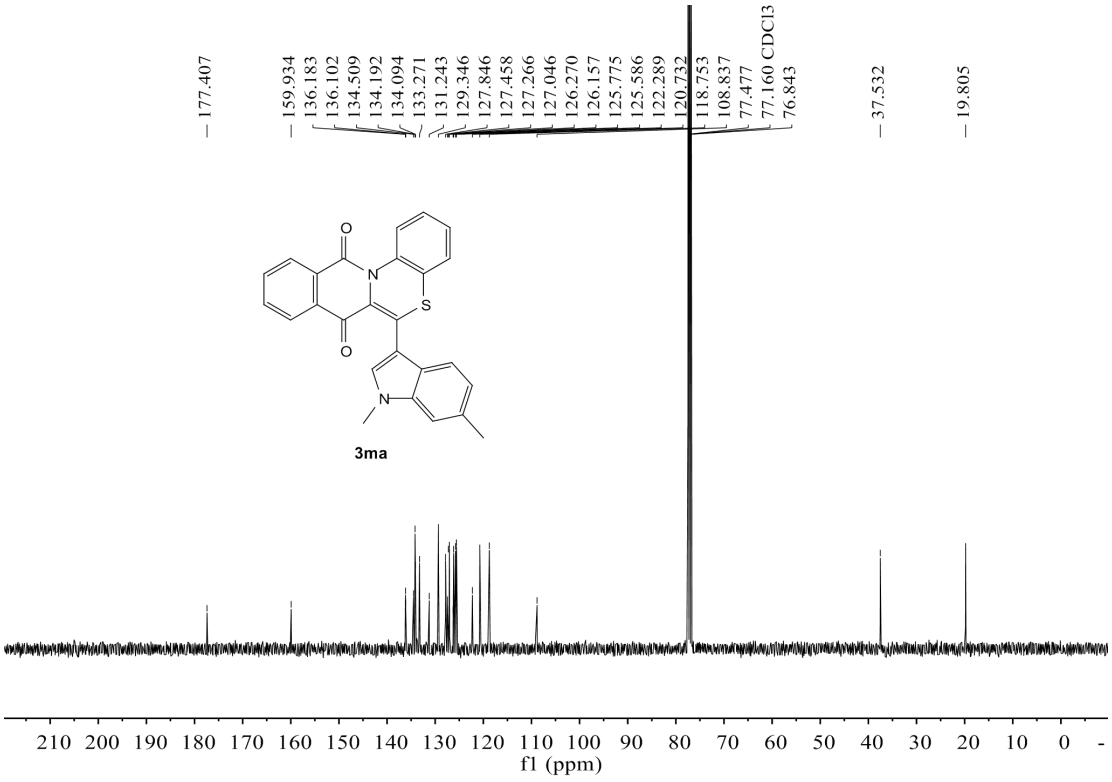
^{1}H NMR (400 MHz) and **^{13}C NMR** (100 MHz) spectra of **3la** (**$CDCl_3$**)



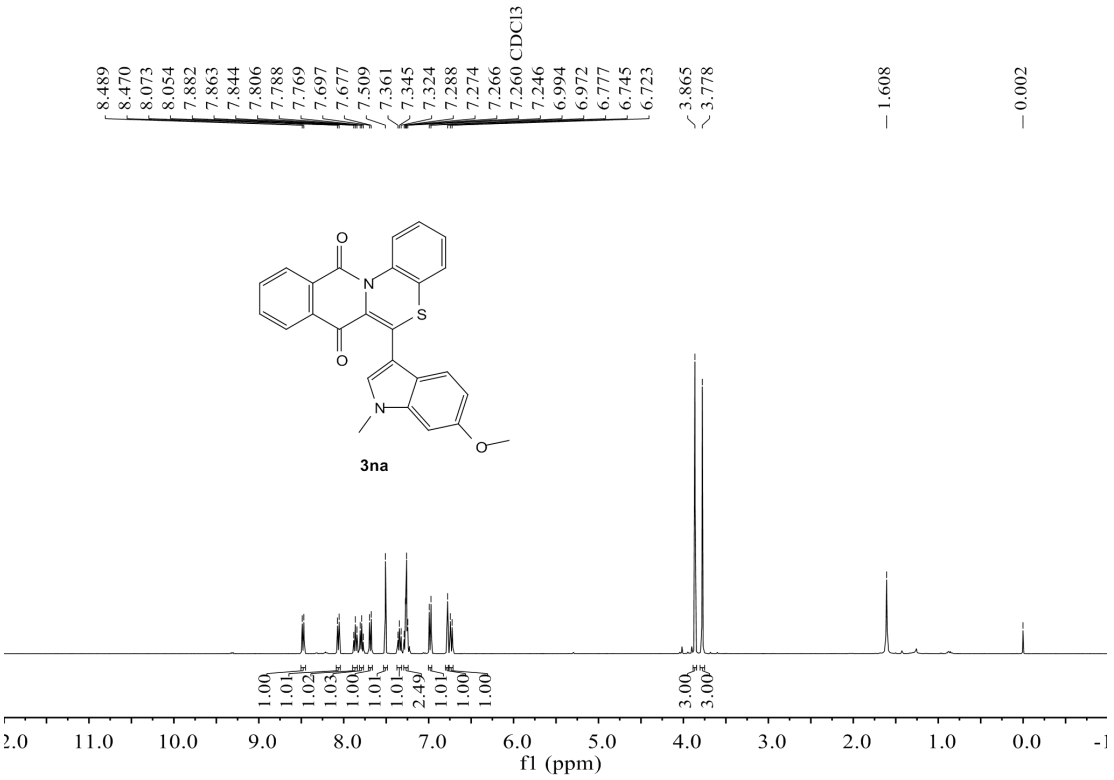


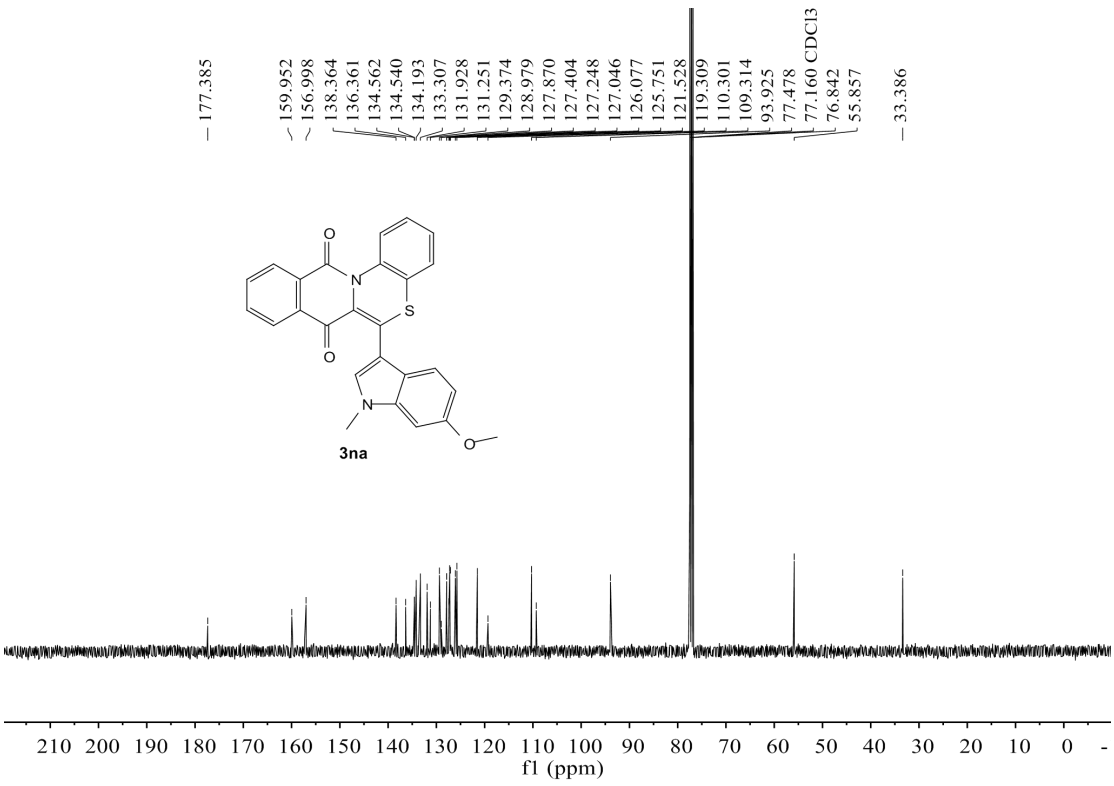
^{1}H NMR (400 MHz) and **^{13}C NMR** (100 MHz) spectra of **3ma** (**$CDCl_3$**)



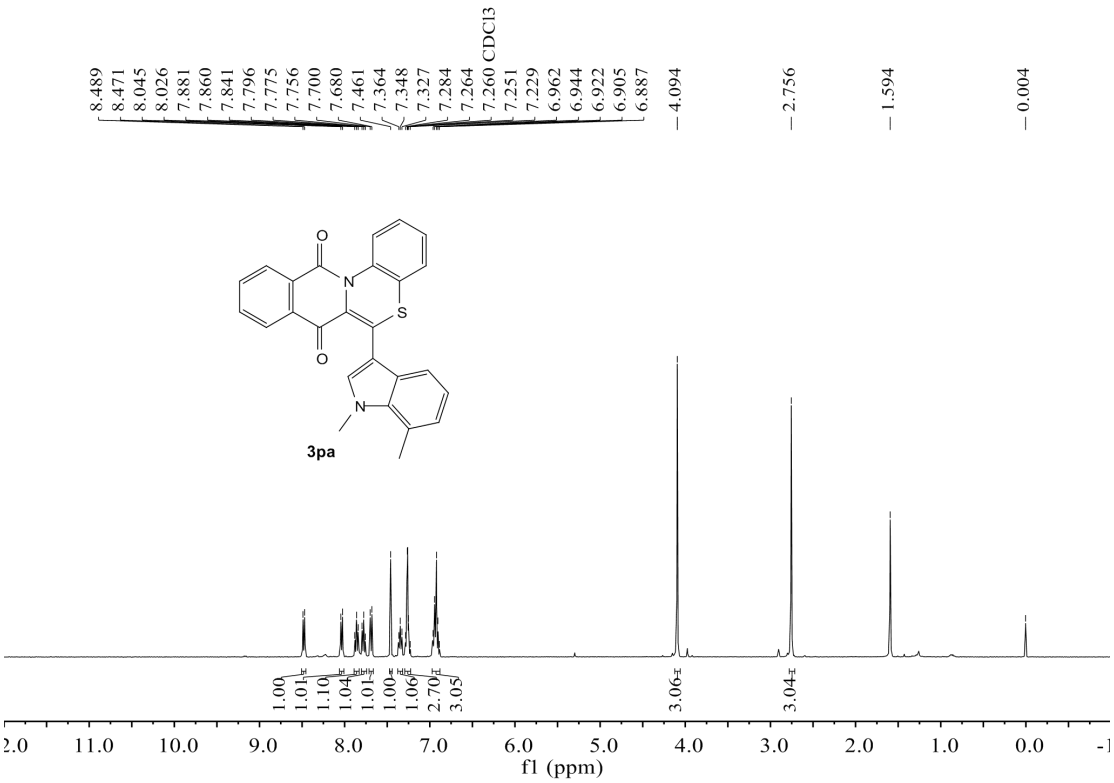


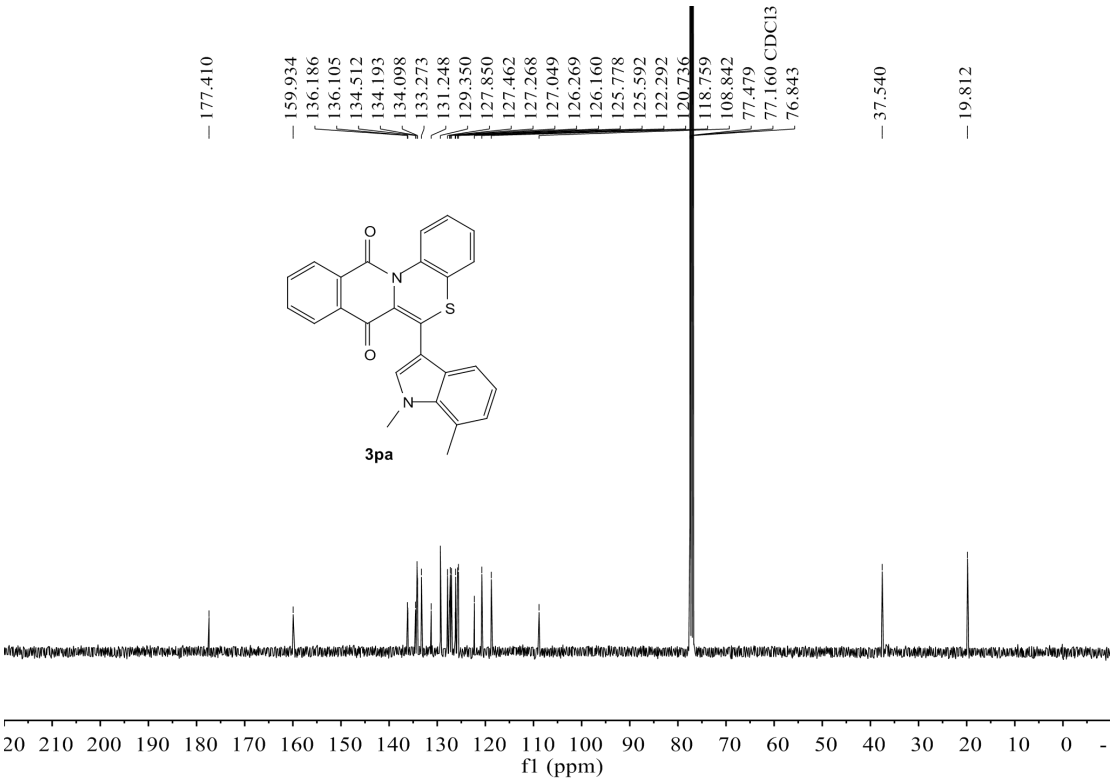
^{1}H NMR (400 MHz) and **^{13}C NMR** (100 MHz) spectra of **3na** (**$CDCl_3$**)



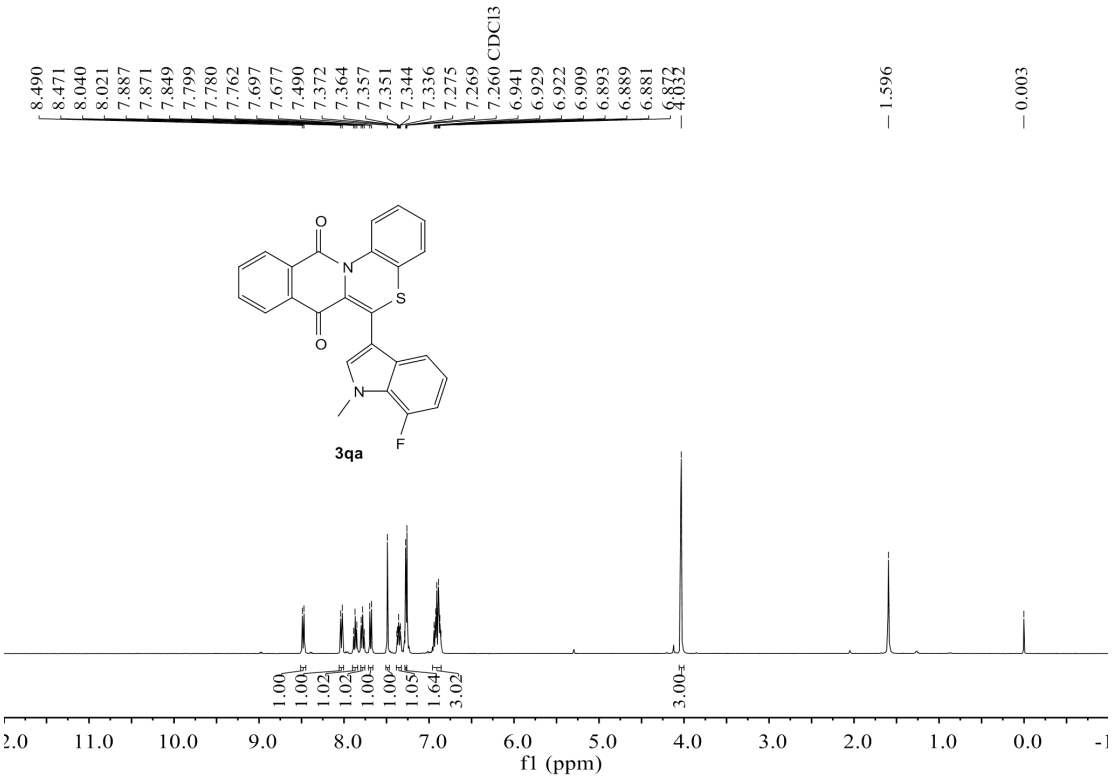


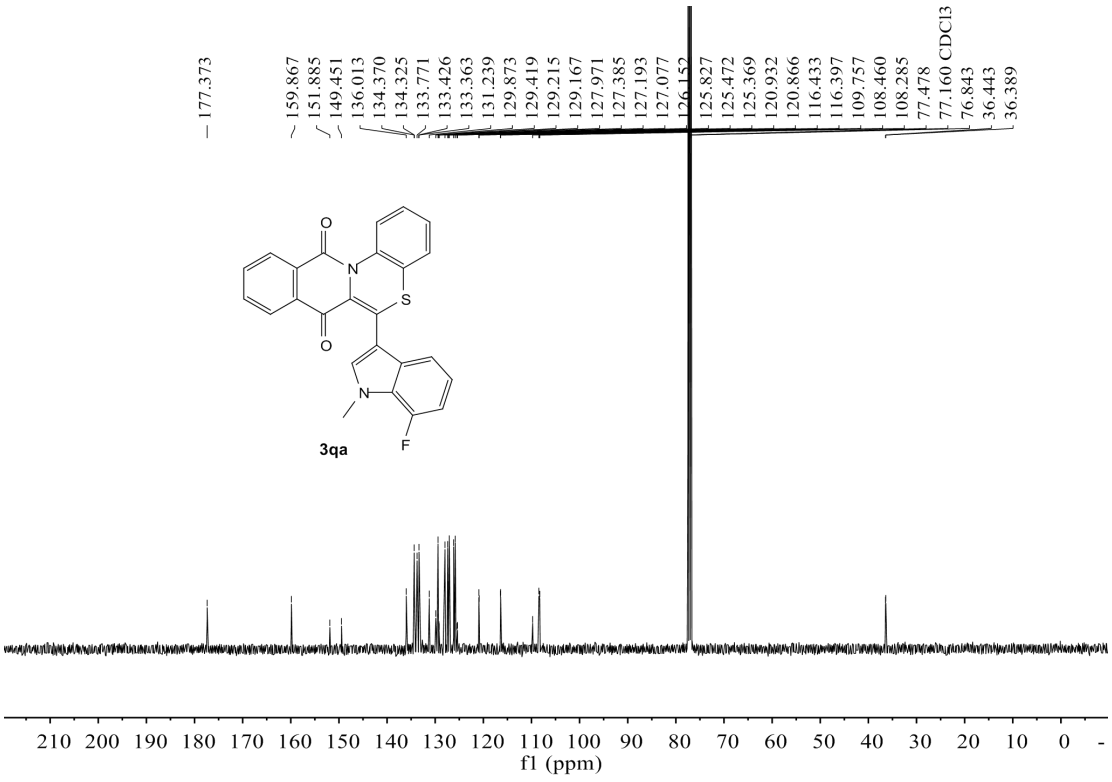
^{1}H NMR (400 MHz) and **^{13}C NMR** (100 MHz) spectra of **3pa** (**$CDCl_3$**)

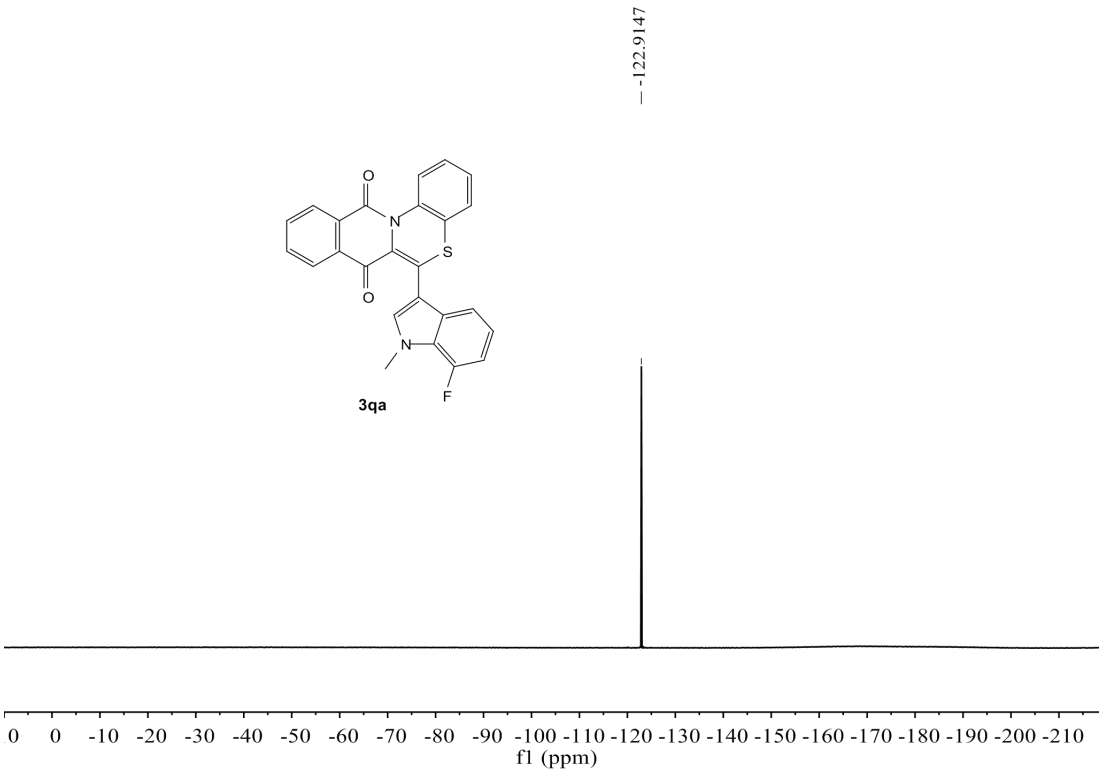




^{1}H NMR (400 MHz) and **^{13}C NMR** (100 MHz) spectra of **3qa** (**$CDCl_3$**)






-122.9147
O
N
S
O
N
F
3qa
0 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

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