Supporting Information for

Visible light-induced synthesis of benzofuro[3,2-b]pyridines from aurone-derived 1-azadienes

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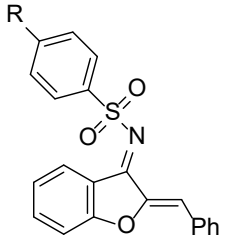
Content

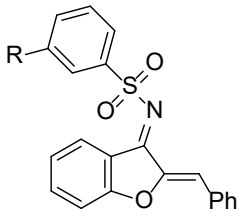
1. General information

NMR spectral data were recorded at 500 MHz for ^{1}H NMR, 125 MHz for ^{13}C NMR. Chemical shift values for ^{1}H NMR were expressed in parts per million (ppm) relative to tetramethylsilane (TMS) at 0.0 ppm. $^{13}C\{^{1}H\}$ NMR spectra were obtained using the same NMR spectrometers, and chemical shifts were reported in ppm relative to the center line of the $CDCl_3$ triplet at 77.00 ppm. Coupling constants (*J* values) are provided in Hz. All high-resolution mass spectra (HRMS) were acquired using ESI on a quadrupole time-of-flight (Q-TOF) mass spectrometer. Flash column chromatography was performed using prepacked flash chromatography columns (300-400 mesh silica gel). Reactions driven by visible light were conducted in a parraller light reactor, enabling simultaneous processing.

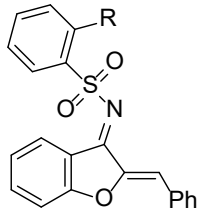
All chemicals, solvents, and reagents were purchased from commercial suppliers and used without further purification. Aurone-derived azadienes **1a-r** were synthesized according to the published procedure. [1]



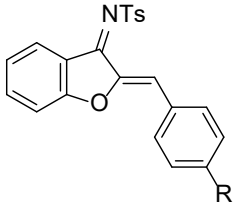
1a, R = Me
1d, R = MeO
1e, R = Br
1h, R = NO_2



1c, R = H
1f, R = Br
1i, R = NO_2



1b, R = Me
1g, R = Cl
1j, R = NO_2



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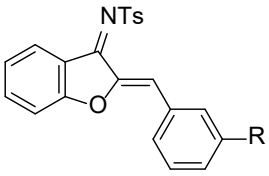
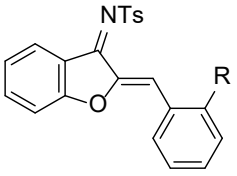
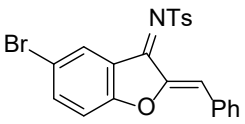
1l, R = MeO



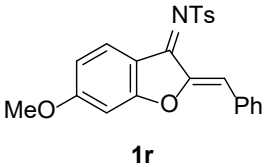
1m, R = Br
1n, R = MeO



1o, R =Br
1p, R = MeO



1q



1r

2. General Procedure for the synthesis of compounds 2 and 3

Method A: 1-Azadiene **1** (0.1 mmol) was dissolved in dichloromethane (DCM, 0.5 mL). The solution was then irradiated with a 10 W blue LED (450-455 nm) at room

temperature for 26 hours. Following solvent removal under vacuum, K_2CO_3 (2 equiv) and methanol (2 mL) were introduced to the mixture. The resulting solution was heated at 90 °C for an additional 40 hours. Upon cooling to room temperatur, 1 mL of aqueous HCl (0.1M) was added, and the product was extracted with DCM (2 × 5 mL). The organic layers were combined and dried over anhydrous magnesium sulfate. After removing the solvent under vacuum, the resedue was purified via silic gel colum chromatography (petroleum ether/AcOEt/DCM = 10:1:2, v/v) to afford pure product.

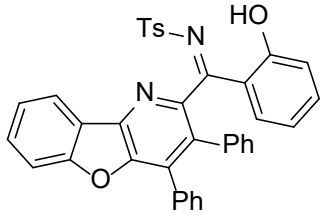
Method B: 1-Azadiene **1** (0.1 mmol) was dissolved in DCM (0.5 mL). The solution was irradiated with a 10 W blue LED (450-455 nm) at room temperature for 26 hours. After removing the solvent under vacuum, the resedue was subjected to silic gel colum chromatography (petroleum ether/AcOEt /DCM = 10:1:2, v/v) to give pure product.

3. Procedure for the synthesis of compound 4

To a solution of **2a** (0.1 mmol) in MeOH (2 mL) was added $NaBH_4$ (0.1 mol). The resulting mixture was stirred at room temperature for 12 hours. Then 1 mL of water was added to quench the reaction. After removed the solvent in vacuo, the resedue was extracted with dichloromethane (2 × 10 mL), and dried over with anhydrous sodium sulfate. The solvent was removed and the crude product was purified by silic gel colum chromatography (petroleum ether/AcOEt = 10:1, v/v) to give pure **4** (42 mg, 71% yield).

4. Analytic data for all products 2, 3 and 4

N-((3,4-Diphenylbenzofuro[3,2-b]pyridin-2-yl)(2-hydroxyphenyl)methylene)-4-methylbenzenesulfonamide (**2a**)



White solid (12 mg, 40% yield); mp = 234-235 ℃;

^{1}H NMR(500 MHz, $CDCl_3$): δ 12.0 (s, 1H), 8.19 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 8.0

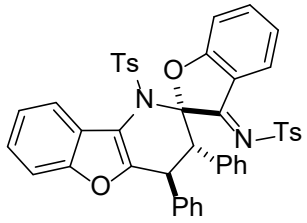
Hz, 2H), 7.68-7.61 (m, 2H), 7.51 (td, *J* = 7.0, 1.0 Hz, 1H), 7.42-7.38 (m, 2H), 7.35-7.30 (m, 5H), 7.27 (t, *J* = 8.0 Hz, 2H), 7.20-6.99 (m, 4H), 6.89 (dd, *J* = 8.0, 1.0 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.61 (td, *J* = 7.0, 1.0 Hz, 1H), 2.44 (s, 3H);

^{13}C NMR(125 MHz, $CDCl_3$): δ178.1, 162.7, 158.3, 148.4, 148.1, 144.5, 142.8, 137.3, 136.3, 134.8, 133.6, 133.4, 132.8, 131.9, 131.0, 130.6, 129.7, 129.7, 128.5, 128.1, 128.0, 127.8, 123.9, 123.0, 121.5, 118.9, 118.6, 118.2, 112.6, 21.7;

IR (KBr): 3069, 2923, 1676, 1654, 1618, 1586, 1560, 1438, 1370, 1333, 1227, 1203, 1162, 1086, 822, 746 cm^{-1};

HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{37}H_{27}N_2O_4S$ 595.1686, found 595.1684.

(±)-*N*-((2S,3'S,4'S,E)-3',4'-Diphenyl-1'-tosyl-3',4'-dihydro-1'H,3H-spiro[benzofuran-2,2'-benzofuro[3,2-b]pyridin]-3-ylidene)-4-methylbenzenesulfonamide (**3a**)



White solid (8 mg, 21% yield); mp = 123-124 ℃.

^{1}H NMR(500 MHz, $CDCl_3$): δ 8.52 (d, *J* = 8.0 Hz, 1H), 8.09 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.43-7.39 (m, 3H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.19-7.10 (m, 4H), 7.04-6.91 (m, 9H), 6.89-6.85 (m, 2H), 6.81 (d, *J* = 8.0 Hz, 1H), 6.57 (t, *J* = 7.5 Hz, 1H), 6.41 (t, *J* = 8.5 Hz, 1H), 4.76 (d, *J* = 14.5 Hz, 1H), 4.63 (d, *J* = 14.5 Hz, 1H), 2.57 (s, 3H), 2.29 (s, 3H).

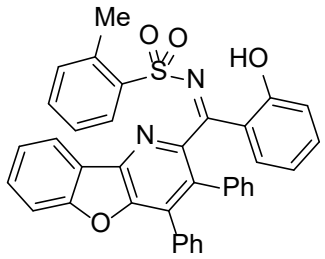
^{13}C NMR(125 MHz, $CDCl_3$): δ 175.4, 174.9, 167.8, 152.4, 144.4, 143.7, 139.0, 138.6, 136.0, 130.6, 130.5, 130.4, 130.0, 129.5, 129.0, 128.9, 128.9, 128.4, 128.3, 128.2, 128.2, 128.1, 127.3, 125.5, 123.8, 122.6, 117.7, 111.6, 110.9, 102.3, 59.4, 56.0, 21.7, 21.5.

IR (KBr): 3031, 2924, 1814, 1602, 1496, 1477, 1461, 1323, 1305, 1186, 1157, 1089, 1018, 871, 834, 755 cm^{-1};

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{44}H_{34}N_2NaO_6S_2$ 773.1750, found

773.1751.

N-((3,4-Diphenylbenzofuro[3,2-b]pyridin-2-yl)(2-hydroxyphenyl)methylene)-2-methylbenzenesulfonamide (**2b**)



Red solid (9 mg, 30% yield); mp = 92-93 ℃;

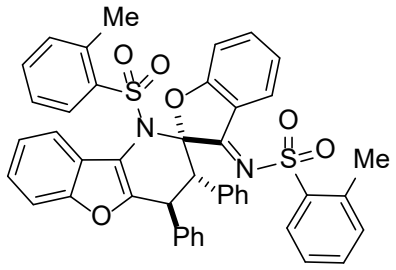
^{1}H NMR(500 MHz, $CDCl_3$): δ 12.07 (s, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 7.75 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.67-7.60 (m, 2H), 7.52-7.45 (m, 2H), 7.42-7.39 (m, 2H), 7.36 (d, *J* = 7.5 Hz, 1H), 7.34-7.31 (m, 3H), 7.30-7.27 (m, 2H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.19-6.92 (m, 4H), 6.89 (dd, *J* = 8.0, 1.0 Hz, 1H), 6.81 (dd, *J* = 8.0, 1.0 Hz, 1H), 6.61 (td, *J* = 8.0, 1.0 Hz, 1H), 2.84 (s, 3H);

^{13}C NMR(125 MHz, $CDCl_3$): δ 179.3, 162.6, 158.3, 148.4, 148.1, 142.7, 138.9, 138.4, 136.5, 134.8, 133.7, 133.5, 133.4, 132.8, 132.6, 132.0, 131.0, 130.7, 129.7, 129.5, 128.5, 128.1, 127.8, 125.1, 123.8, 122.9, 121.6, 118.9, 118.7, 118.2, 112.5, 20.7;

IR (KBr): 3058, 2924, 1654, 1625, 1560, 1474, 1420, 1382, 1325, 1194, 1159, 1131, 1064, 874, 747, 696 cm^{-1};

HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{37}H_{27}N_2O_4S$ 595.1686, found 595.1688.

(±)-*N*-((2S,3'S,4'S)-3',4'-Diphenyl-1'-(*o*-tolylsulfonyl)-3',4'-dihydro-1'*H*,3*H*-spiro-[benzofuran-2,2'-benzofuro[3,2-b]pyridin]-3-ylidene)-2-methylbenzenesulfonamide (**3b**)



White solid. (15 mg, 40% yield); mp = 159-160 ℃;

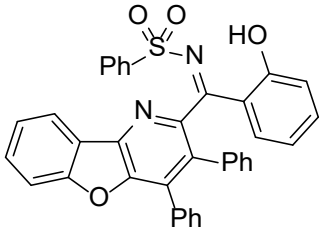
^{1}H NMR(500 MHz, $CDCl_3$): δ 8.16 (d, *J* = 8.5 Hz, 1H), 7.80 (t, *J* = 8.0 Hz, 2H), 7.49-7.44 (m, 2H), 7.28-7.26 (m, 2H), 7.23-7.14 (m, 7H), 7.11 (t, *J* = 8.0 Hz, 2H), 7.07 (dd, *J* = 7.5, 1.0 Hz, 2H), 7.00-6.95 (m, 3H), 6.92-6.88 (m, 3H), 6.84 (t, *J* = 8.0 Hz, 1H), 6.46 (t, *J* = 7.5 Hz, 1H), 5.08 (d, *J* = 12.0 Hz, 1H), 3.86 (d, *J* = 12.0 Hz, 1H), 2.69 (s, 3H), 2.63 (s, 3H);

^{13}C NMR(125 MHz, $CDCl_3$): δ 178.7, 168.6, 153.6, 140.3, 139.4, 139.1, 138.1, 138.0, 136.6, 136.5, 132.7, 132.4, 132.3, 132.1, 131.3, 130.1, 129.1, 128.7, 128.6, 128.5, 128.4, 127.9, 127.6, 127.4, 125.0, 125.9, 125.4, 124.1, 123.0, 122.5, 122.4, 122.0, 121.3, 119.7, 118.3, 112.9, 111.5, 99.8, 58.5, 42.4, 20.8, 20.6;

IR (KBr): 3061, 2925, 1602, 1497, 1460, 1351, 1316, 1159, 1130, 1064, 1017, 967, 871, 828, 754 cm^{-1};

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{44}H_{34}N_2NaO_6S_2$ 773.1750, found 773.1749.

N-((3,4-Diphenylbenzofuro[3,2-b]pyridin-2-yl)(2-hydroxyphenyl)methylene)-benzenesulfonamide (**2c**)



White solid (10 mg, 35% yield); mp = 204-205 ℃;

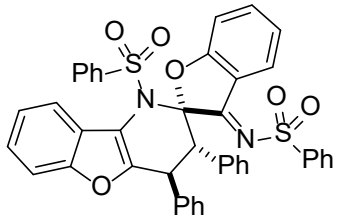
^{1}H NMR(500 MHz, $CDCl_3$): δ 11.96 (s, 1H), 8.19 (d, *J* = 8.0 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 2H), 7.68-7.62 (m, 3H), 7.54 (t, *J* = 8.0 Hz, 2H), 7.50 (td, *J* = 8.0, 1.0 Hz, 1H), 7.42-7.39 (m, 2H), 7.35-7.31 (m, 3H), 7.30-7.27 (m, 1H), 7.21-6.99 (m, 5H), 6.90 (dd, *J* = 8.0, 1.0 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 6.63 (t, *J* = 8.0 Hz, 1H);

^{13}C NMR(125 MHz, $CDCl_3$): δ 178.7, 162.8, 158.3, 148.4, 148.1, 142.9, 140.3, 136.5, 134.8, 133.7, 133.5, 133.4, 132.9, 131.9, 130.7, 129.8, 129.1, 128.5, 128.1, 128.0, 127.9, 125.4, 123.9, 123.0, 121.5, 119.0, 118.6, 118.2, 112.6, 110.0;

IR (KBr): 3060, 1618, 1586, 1537, 1459, 1370, 1327, 1238, 1225, 1202, 1158, 1087, 978, 874, 749 cm^{-1};

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{36}H_{24}N_2NaO_4S$ 603.1349, found 603.1351.

(±)-*N*-((2S,3'S,4'S,E)-3',4'-Diphenyl-1'-(phenylsulfonyl)-3',4'-dihydro-1'H,3H-spiro[benzofuran-2,2'-benzofuro[3,2-b]pyridin]-3-ylidene)benzenesulfonamide (**3c**)



White solid (11 mg, 30% yield); mp = 132-133 ℃;

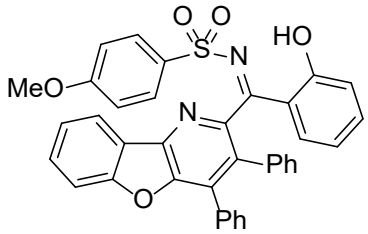
^{1}H NMR(500 MHz, $CDCl_3$): δ 8.06 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 7.5 Hz, 2H), 7.64 (t, *J* = 7.5 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 2H), 7.54-7.49 (m, 2H), 7.44 (t, *J* = 8.0 Hz, 1H), 7.32-7.27 (m, 3H), 7.25-7.22 (m, 2H), 7.17 (t, *J* = 8.0 Hz, 1H), 7.10-7.06 (m, 3H), 6.97-6.92 (m, 3H), 6.89 (s, 3H), 6.82 (d, *J* = 7.5 Hz, 2H), 4.78 (d, *J* = 12.0 Hz, 1H), 3.57 (d, *J* = 12.0 Hz, 1H);

^{13}C NMR(125 MHz, $CDCl_3$): δ 178.2, 174.5, 157.6, 153.9, 141.0, 139.0, 137.9, 136.2, 133.2, 132.9, 132.1, 129.0, 128.8, 128.7, 128.6, 128.5, 128.2, 127.9, 127.8, 127.8, 127.3, 125.9, 125.8, 124.5, 123.0, 122.7, 122.6, 117.8, 111.5, 111.2, 100.1, 43.0, 29.7;

IR (KBr): 3063, 2925, 1603, 1497, 1477, 1448, 1370, 1324, 1257, 1160, 1089, 1016, 966, 874, 753 cm^{-1};

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{42}H_{30}N_2NaO_6S_2$ 745.1437, found 745.1439.

N-((3,4-Diphenylbenzofuro[3,2-b]pyridin-2-yl)(2-hydroxyphenyl)methylene)-4-methoxybenzenesulfonamide (**2d**)



Red solid (17 mg, 56% yield); mp = 131-132 ℃;

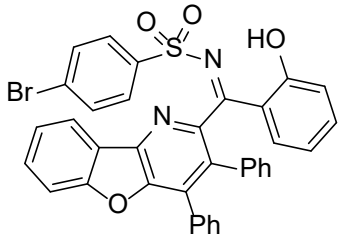
^{1}H NMR(500 MHz, $CDCl_3$): δ 12.03 (s, 1H), 8.20 (d, *J* = 7.5 Hz, 1H), 7.91 (d, *J* = 8.5 Hz, 2H), 7.68-7.61 (m, 2H), 7.50 (td, *J* =8.0, 1.0 Hz, 1H), 7.42-7.39 (m, 2H), 7.35-7.31 (m, 5H), 7.26 (td, *J* = 7.5, 1.5 Hz, 2H), 7.23-7.04 (m, 3H), 6.98 (d, *J* = 8.5 Hz, 3H), 6.88 (dd, *J* = 8.5, 1.5 Hz, 1H), 6.80 (dd, *J* = 8.0, 1.0 Hz, 1H), 6.61 (td, *J* =8.0, 1.0 Hz, 1H), 3.88 (s, 3H);

^{13}C NMR(125 MHz, $CDCl_3$): δ 177.6, 163.6, 162.7, 158.3, 148.5, 148.1, 142.8, 136.2, 134.8, 133.6, 133.4, 132.9, 132.0, 131.8, 131.0, 130.7, 130.3, 129.7, 128.5, 128.1, 127.8, 123.9, 123.0, 121.4, 118.9, 118.6, 118.2, 114.3, 112.6, 55.7;

IR (KBr): 3059, 2922, 1654, 1596, 1577, 1497, 1459, 1370, 1330, 1254, 1157, 1089, 1025, 979, 874, 751 cm^{-1};

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{37}H_{26}N_2NaO_5S$ 633.1455, found 633.1459.

N-((3,4-Diphenylbenzofuro[3,2-b]pyridin-2-yl)(2-hydroxyphenyl)methylene)-4-bromobenzenesulfonamide (**2e**)



White solid (20 mg, 60% yield); mp = 253-254 ℃;

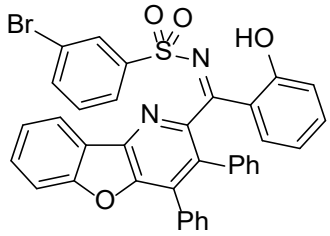
^{1}H NMR(500 MHz, $CDCl_3$): δ 11.90 (s, 1H), 8.14 (d, *J* = 7.5 Hz, 1H), 7.84 (d, *J* = 8.5 Hz, 2H), 7.69-7.64 (m, 4H), 7.53 (t, *J* = 8.0 Hz, 1H), 7.42-7.39 (m, 2H), 7.35-7.32 (m, 3H), 7.29 (t, *J* = 8.0 Hz, 1H), 7.22-7.13 (m, 1H), 7.12-6.92 (m, 4H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.63 (t, *J* = 8.0 Hz, 1H)

^{13}C NMR(125 MHz, $CDCl_3$): δ 179.3, 162.9, 158.4, 148.2, 148.2, 142.8, 139.4, 136.8, 134.7, 133.7, 133.5, 133.0, 132.3, 131.8, 130.9, 130.6, 129.9, 129.5, 128.8, 128.5, 128.1, 127.9, 124.1, 122.9, 121.4, 119.1, 118.5, 118.3, 112.7;

IR (KBr): 3059, 1654, 1617, 1585, 1483, 1459, 1389, 1343, 1225, 1201, 1157, 1087, 1069, 1010, 977, 750, 696 cm^{-1};

HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{36}H_{24}BrN_2O_4S$ 659.0635, found 659.0635.

N-((3,4-Diphenylbenzofuro[3,2-b]pyridin-2-yl)(2-hydroxyphenyl)methylene)-3-bromobenzenesulfonamide (**2f**)



White solid (16 mg, 49% yield); mp = 188-189 ℃;

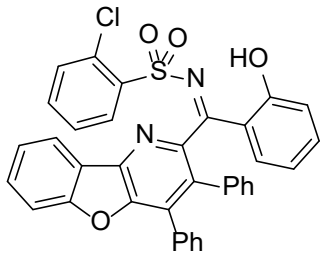
^{1}H NMR(500 MHz, $CDCl_3$): δ 11.85 (s, 1H), 8.26 (d, *J* = 7.5 Hz, 1H), 8.19 (s, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7,67-7.62 (m, 2H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.44-7.39 (m, 3H), 7.35-7.27 (m, 5H), 7.24-7.13 (m, 1H), 7.13-6.93 (m, 3H), 6.91 (d, *J* = 8.5 Hz, 1H), 6.83 (d, *J* = 8.5 Hz, 1H), 6.65 (t, *J* = 7.5 Hz, 1H);

^{13}C NMR(125 MHz, $CDCl_3$): δ 179.7, 163.0, 158.5, 148.4, 148.3, 143.1, 142.2, 137.0, 136.7, 134.9, 134.0, 133.6, 133.1, 132.0, 131.1, 131.0, 130.8, 130.7, 130.0, 128.7, 128.3, 128.1, 125.7, 124.2, 123.1, 123.0, 121.9, 119.3, 118.8, 118.5, 112.7;

IR (KBr): 3063, 1654, 1618, 1586, 1459, 1438, 1370, 1331, 1294, 1203, 1165, 1078, 978, 820, 747, 656 cm^{-1};

HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{36}H_{24}BrN_2O_4S$ 659.0635, found 659.0631.

N-((3,4-Diphenylbenzofuro[3,2-b]pyridin-2-yl)(2-hydroxyphenyl)methylene)-2-chlorobenzenesulfonamide (**2g**)



White solid (17 mg, 55% yield); mp = 113-114 ℃;

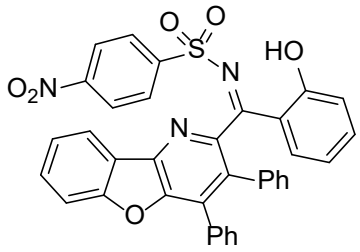
^{1}H NMR(500 MHz, $CDCl_3$): δ 12.12 (s, 1H), 8.04 (d, *J* = 7.5 Hz, 1H), 7.84 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.67-7.62 (m, 2H), 7.61-7.58 (m, 1H), 7.55 (td, *J* = 8.0, 1.5 Hz, 1H), 7.47 (td, *J* = 8.0, 1.0 Hz, 1H), 7.42-7.38 (m, 2H), 7.36-7.28 (m, 6H), 7.22-7.11 (m, 2H), 7.10-7.05 (m, 2H), 6.92 (dd, *J* = 8.0, 1.0 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 6.62 (t, *J* = 8.0 Hz, 1H);

^{13}C NMR(125 MHz, $CDCl_3$): δ 180.2, 163.0, 158.3, 148.4, 148.1, 142.8, 138.4, 136.9, 134.7, 134.4, 134.0, 133.4, 133.1, 132.9, 132.0, 131.9, 131.1, 130.7, 129.8, 128.5, 128.1, 127.9, 126.8, 123.9, 122.9, 121.6, 118.9, 118.4, 112.6;

IR (KBr): 3059, 1618, 1583, 1535, 1483, 1455, 1368, 1333, 1238, 1165, 1107, 1041, 978, 819, 749 cm^{-1};

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{36}H_{23}ClN_2NaO_4S$ 637.0959, found 637.0959.

N-((3,4-Diphenylbenzofuro[3,2-b]pyridin-2-yl)(2-hydroxyphenyl)methylene)-4-nitrobenzenesulfonamide (**2h**)



White solid (8 mg, 26% yield); mp = 256-257 ℃;

^{1}H NMR(500 MHz, $CDCl_3$): δ 11.79 (s, 1H), 8.36 (d, *J* = 8.5 Hz, 2H), 8.17 (d, *J* = 8.5 Hz, 2H), 8.07 (d, *J* = 8.0 Hz, 1H), 7.69- 7.65 (m, 2H), 7.58-7.50 (m, 2H), 7.42-7.38 (m, 2H), 7.35-7.30 (m, 4H), 7.17-6.97 (m, 4H), 6.91 (dd, *J* = 8.5, 1.5 Hz, 1H), 6.84 (d,

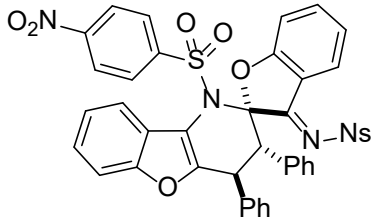
J = 8.5 Hz, 1H), 6.65 (t, *J* = 8.0 Hz, 1H);

^{13}C NMR(125 MHz, $CDCl_3$): δ 180.8, 163.1, 158.4, 150.4, 148.2, 148.0, 146.0, 142.9, 137.4, 134.6, 133.9, 133.6, 133.1, 131.7, 130.9, 130.6, 130.1, 129.3, 128.7, 128.2, 128.0, 124.2, 122.7, 121.2, 119.3, 118.5, 112.8;

IR (KBr): 3057, 1654, 1617, 1560, 1535, 1483, 1438, 1366, 1348, 1226, 1201, 1168, 1087, 978, 793, 758 cm^{-1};

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{36}H_{23}N_3NaO_6S$ 648.1200, found 648.1200.

(±)-4-Nitro-*N*-((2S,3'S,4'S,E)-1'-((4-nitrophenyl)sulfonyl)-3',4'-diphenyl-3',4'-dihydro-1'H,3H-spiro[benzofuran-2,2'-benzofuro[3,2-b]pyridin]-3-ylidene)benzenesulfonamide (**3h**)



White solid (6 mg, 15% yield); mp = 158-159 ℃;

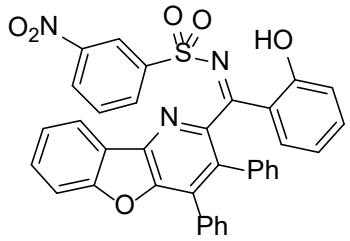
^{1}H NMR(500 MHz, $CDCl_3$): δ 8.53-8.49 (m, 3H), 8.46 (d, *J* = 8.5 Hz, 2H), 8.10 (d, *J* = 9.0 Hz, 2H), 7.82 (d, *J* = 9.0 Hz, 2H), 7.43 (td, *J* = 8.0, 1.0 Hz, 1H), 7.39 (d, *J* = 7.5 Hz, 1H), 7.18 (td, *J* = 8.0, 1.0 Hz, 1H), 7.13-7.08 (m, 3H), 7.05-7.00 (m, 3H), 6.99-6.93 (m, 3H), 6.86-6.83 (m, 3H), 6.56 (t, *J* = 7.5 Hz, 1H), 6.38 (d, *J* = 8.5 Hz, 1H), 4.72 (d, *J* = 14.0 Hz, 1H), 4.65 (d, *J* = 14.0 Hz, 1H);

^{13}C NMR(125 MHz, $CDCl_3$): δ 176.9, 174.4, 167.7, 152.4, 150.5, 150.4, 146.5, 144.4, 140.6, 131.2, 130.7, 130.2, 129.7, 129.2, 128.9, 128.7, 128.5, 128.5, 128.4, 128.2, 125.5, 124.5, 124.3, 123.8, 123.5, 123.4, 117.4, 111.4, 102.4, 59.2, 56.1;

IR (KBr): 3110, 2927, 1813, 1617, 1604, 1560, 1534, 1497, 1465, 1365, 1350, 1164, 1089, 1006, 857, 738 cm^{-1}

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{42}H_{28}N_4NaO_{10}S_2$ 835.1139, found 835.1143.

N-((3,4-Diphenylbenzofuro[3,2-b]pyridin-2-yl)(2-hydroxyphenyl)methylene)-3-nitrobenzenesulfonamide (**2i**)



White solid (14 mg, 45% yield); mp = 243-244 ℃;

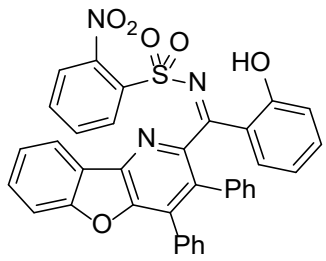
^{1}H NMR(500 MHz, $CDCl_3$): δ 11.76 (s, 1H), 8.88 (s, 1H), 8.49 (d, *J* = 8.0 Hz, 1H), 8.35 (d, *J* = 8.0 Hz, 1H), 8.17 (d, *J* = 7.5 Hz, 1H), 7.76 (t, *J* = 8.0 Hz, 1H), 7.68-7.64 (m, 2H), 7.52 (td, *J* = 7.5, 1.5 Hz, 1H), 7.43-7.39 (m, 2H), 7.37-7.30 (m, 5H), 7.25-6.95 (m, 4H), 6.92 (dd, *J* = 8.0, 1.0 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.66 (td, *J* = 8.0, 1.0 Hz, 1H);

^{13}C NMR(125 MHz, $CDCl_3$): δ 180.6, 163.0, 158.4, 148.3, 148.2, 148.0, 143.0, 142.5, 137.3, 134.6, 133.9, 133.5, 133.4, 133.1, 131.7, 130.9, 130.6, 130.5, 130.4, 130.1, 128.6, 128.2, 128.0, 127.9, 124.1, 123.4, 122.7, 121.5, 119.3, 118.6, 118.5, 112.6;

IR (KBr): 3061, 1597, 1581, 1537, 1477, 1459, 1366, 1351, 1314, 1158, 1129, 1064, 870, 831, 754 cm^{-1};

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{36}H_{23}N_3NaO_6S$ 648.1200, found 648.1198.

N-((3,4-Diphenylbenzofuro[3,2-b]pyridin-2-yl)(2-hydroxyphenyl)methylene)-2-nitrobenzenesulfonamide (**2j**)



White solid (13 mg, 42% yield); mp = 135-136 ℃;

^{1}H NMR(500 MHz, $CDCl_3$): δ 12.07 (s, 1H), 8.14 (d, *J* = 7.5 Hz, 1H), 7.99 (dd, *J* =

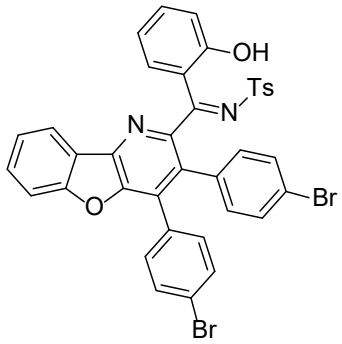
7.5, 1.0 Hz, 1H), 7.80-7.73 (m, 2H), 7.69-7.61 (m, 3H), 7.60-7.43 (m, 2H), 7.43-7.38 (m, 2H), 7.36-7.30 (m, 4H), 7.22-7.00 (m, 4H), 6.94 (dd, *J* = 8.5, 1.5 Hz, 1H), 6.89 (d, *J* = 8.5 Hz, 1H), 6.63 (td, *J* = 7.5, 1.0 Hz, 1H);

^{13}C NMR(125 MHz, $CDCl_3$): 180.3, 163.4, 158.4, 148.6, 148.4, 148.2, 142.8, 137.3, 134.6, 134.4, 134.1, 133.6, 133.5, 133.1, 132.0, 131.8, 131.4, 131.0, 130.6, 129.9, 128.6, 128.3, 128.2, 128.0, 124.6, 124.0, 122.9, 121.3, 119.0, 118.8, 118.4, 112.7;

IR (KBr): 3058, 1618, 1578, 1541, 1529, 1483, 1438, 1365, 1333, 1298, 1220, 1158, 1124, 1055, 978, 749 cm^{-1};

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{36}H_{23}N_3NaO_6S$ 648.1200, found 648.1199.

N-((3,4-Bis(4-bromophenyl)benzofuro[3,2-b]pyridin-2-yl)(2-hydroxyphenyl)-methylene)-4-methylbenzenesulfonamide (**2k**)



White solid (19 mg, 55% yield); mp = 239-240 ℃;

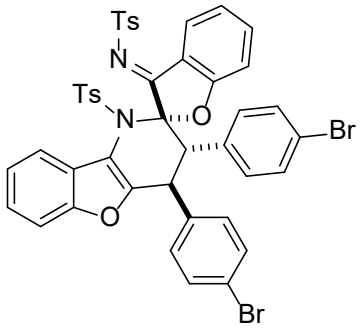
^{1}H NMR(500 MHz, $CDCl_3$): δ 12.0 (s, 1H), 8.65 (d, *J* = 8.0 Hz, 1H), 8.18 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 2H), 7.84 (d, *J* = 8.5 Hz, 1H), 7.67-7.62 (m, 3H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.25-7.24 (m, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.88-6.82 (m, 4H), 6.63 (t, *J* = 8.0 Hz, 1H), 2.48 (s, 3H).

^{13}C NMR(125 MHz, $CDCl_3$): δ 162.9, 158.4, 148.3, 147.7, 144.7, 143.9, 143.3, 137.1, 136.7, 133.5, 133.3, 132.1, 131.6, 131.5, 130.9, 130.1, 129.8, 129.7, 128.0, 127.1, 124.2, 123.3, 122.8, 122.7, 122.4, 121.6, 119.1, 118.5, 118.4, 112.6, 21.7;

IR (KBr): 3071, 2924, 1654, 1617, 1597, 1478, 1459, 1370, 1334, 1202, 1159, 1012, 872, 822, 750 cm^{-1};

HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{37}H_{25}Br_2N_2O_4S$ 750.9896, found 750.9895.

(±)-*N*-((2S,3'S,4'S,E)-3',4'-Bis(4-bromophenyl)-1'-tosyl-3',4'-dihydro-1'H,3H-spiro[benzofuran-2,2'-benzofuro[3,2-b]pyridin]-3-ylidene)-4-methylbenzenesulfonamide (**3k**)



White solid (11 mg, 24% yield); mp = 87-88 ℃;

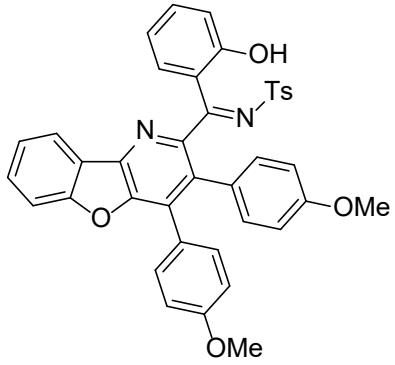
^{1}H NMR(500 MHz, $CDCl_3$): δ 8.31 (s, 1H), 8.16 (s, 1H), 7.94-7.90 (m, 2H), 7.57-7.51 (m, 3H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.30-7.27 (m, 2H), 7.25-7.20 (m, 3H), 7.19-7.14 (m, 1H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.03-6.97 (m, 3H), 6.92 (d, *J* = 8.5 Hz, 1H), 6.86 (d, *J* = 8.5 Hz, 1H), 6.67 (d, *J* = 8.0 Hz, 2H), 4.67 (d, *J* = 12.0 Hz, 1H), 3.48 (d, *J* = 12.0 Hz, 1H), 2.47 (s, 3H), 2.38 (s, 3H);

^{13}C NMR(125 MHz, $CDCl_3$): δ 177.4, 170.2, 168.0, 153.9, 144.2, 143.8, 138.1, 138.0, 135.8, 135.2, 131.6, 131.3, 131.2, 130.6, 130.5, 129.6, 129.5, 129.3, 128.1, 127.4, 125.9, 124.7, 123.3, 123.1, 122.9, 122.8, 122.5, 122.1, 121.5, 118.1, 111.5, 111.1, 99.6, 42.5, 31.6, 21.7, 21.6;

IR (KBr): 3061, 2922, 1654, 1617, 1598, 1560, 1494, 1452, 1325, 1186, 1163, 1091, 880, 814, 750, 704 cm^{-1};

HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{44}H_{32}Br_2N_2NaO_6S_2$ 928.9961, found 928.9962.

N-((3,4-Bis(4-methoxyphenyl)benzofuro[3,2-b]pyridin-2-yl)(2-hydroxyphenyl)methylene)-4-methylbenzenesulfonamide (**2l**)



White solid (10 mg, 30% yield); mp = 87-88 ℃.

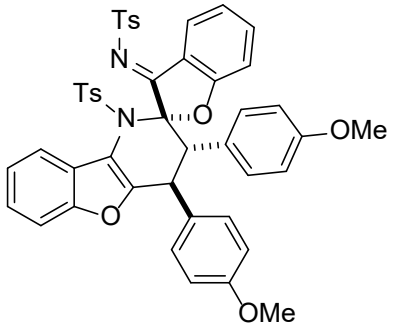
^{1}H NMR(500 MHz, $CDCl_3$): δ 12.08 (s, 1H), 8.15 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.5 Hz, 2H), 7.67-7.60 (m, 2H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.35 (d, *J* = 8.5 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.29-7.27 (m, 1H), 7.25-7.21 (m, 1H), 7.21-7.02 (m, 2H), 7.01-6.95 (m, 1H), 6.89-6.84 (m, 2H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.71-7.64 (m, 1H), 6.60 (t, *J* = 8.0 Hz, 1H), 3.82 (s, 3H), 3.70 (s, 3H), 2.43 (s, 3H);

^{13}C NMR(125 MHz, $CDCl_3$): δ 162.9, 159.6, 159.0, 158.2, 151.4, 148.6, 147.0, 144.5, 142.5, 139.4, 137.3, 136.3, 135.1, 133.6, 132.1, 129.7, 129.6, 129.5, 128.1, 127.9, 127.2, 124.1, 123.8, 123.2, 121.4, 118.9, 118.5, 118.3, 114.7, 113.7, 112.5, 110.0, 55.2, 55.1, 21.7;

IR (KBr): 3071, 2931, 1654, 1611, 1513, 1459, 1366, 1332, 1294, 1251, 1201, 1162, 1088, 1031, 978, 754 cm^{-1};

HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{39}H_{31}N_2O_6S$ 655.1897, found, 655.1985.

(±)-*N*-((2S,3'S,4'S,E)-3',4'-Bis(4-methoxyphenyl)-1'-tosyl-3',4'-dihydro-1'*H*,3*H*-spiro[benzofuran-2,2'-benzofuro[3,2-b]pyridin]-3-ylidene)-4-methylbenzenesulfonamide (**3l**)



White solid (6 mg, 15% yield); mp = 140-141 ℃.

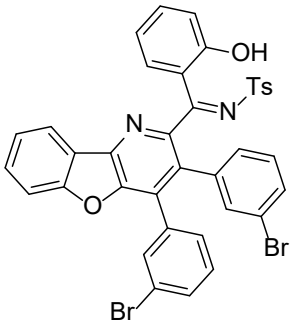
^{1}H NMR(500 MHz, $CDCl_3$): δ 8.28 (s, 1H), 8.16 (s, 1H), 7.98-7.92 (m, 2H), 7.55 (d, *J* = 7.5 Hz, 2H), 7.49 (t, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.30-7.28 (m, 1H), 7.25-7.16 (m, 3H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.96 (t, *J* = 8.0 Hz, 1H), 6.92 (d, *J* = 8.0 Hz, 2H), 6.75 (d, *J* = 8.0 Hz, 2H), 6.61 (d, *J* = 8.0 Hz, 2H), 6.41 (d, *J* = 8.0 Hz, 2H), 4.69 (d, *J* = 11.5 Hz, 1H), 3.68 (s, 3H), 3.58 (s, 3H), 2.46 (s, 3H), 2.37 (s, 3H);

^{13}C NMR(125 MHz, $CDCl_3$): δ 178.4, 158.7, 158.5, 153.8, 143.9, 143.5, 143.3, 139.2, 138.6, 138.3, 137.7, 136.1, 130.3, 130.0, 129.5, 129.4, 129.3, 128.4, 128.0, 127.4, 125.8, 124.3, 124.0, 122.9, 122.8, 122.7, 122.4, 117.6, 113.8, 113.6, 111.4, 100.2, 55.0, 54.9, 42.1, 31.6, 22.6, 21.6;

IR (KBr): 3035, 2923, 1654, 1605, 1546, 1513, 1461, 1324, 1253, 1181, 1159, 1089, 1032, 874, 828, 749 cm^{-1};

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{46}H_{38}N_2NaO_8S_2$ 833.1962, found 833.1962.

N-((3,4-Bis(3-bromophenyl)benzofuro[3,2-b]pyridin-2-yl)(2-hydroxyphenyl)-methylene)-4-methylbenzenesulfonamide (**2m**)



White solid (20 mg, 53% yield); mp = 145-146 ℃.

^{1}H NMR(500 MHz, $CDCl_3$): δ 11.82 (s, 1H), 8.23 (d, *J* = 6.5 Hz, 1H), 7.89 (d, *J* = 6.5 Hz, 2H), 7.70-7.65 (m, 2H), 7.63 (s, 1H), 7.53 (td, *J* = 8.0, 1.5 Hz, 1H), 7.51-7.44 (m, 2H), 7.41 (td, *J* = 8.0, 1.5 Hz, 1H), 7.36-7.28 (m, 4H), 7.25-7.19 (m, 3H),7.03-7.00 (m, 1H), 6.87-6.82 (m, 2H), 6.67 (t, *J* = 7.5 Hz, 1H), 2.45 (s, 3H).

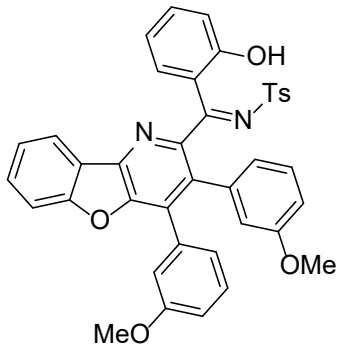
^{13}C NMR(125 MHz, $CDCl_3$): δ 162.6, 158.4, 148.5, 147.6, 144.7, 138.5, 137.2, 136.5, 133.8, 133.5, 133.3, 133.2, 132.5, 132.3, 131.8, 131.7, 131.2, 131.1, 131.0, 130.2,

129.8, 129.2, 127.9, 124.2, 122.8, 122.3, 121.7, 119.1, 118.4, 112.8, 112.7, 110.0, 21.7;

IR (KBr): 3067, 2923, 1654, 1596, 1477, 1460, 1366, 1326, 1303, 1201, 1160, 1088, 1032, 820, 753 cm^{-1};

HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{37}H_{25}Br_2N_2O_4S$ 750.9896, found 750.9897.

N-((3,4-Bis(3-methoxyphenyl)benzofuro[3,2-b]pyridin-2-yl)(2-hydroxyphenyl)-methylene)-4-methylbenzenesulfonamide (**2n**)



White solid (12 mg, 37% yield); mp = 208-209 ℃;

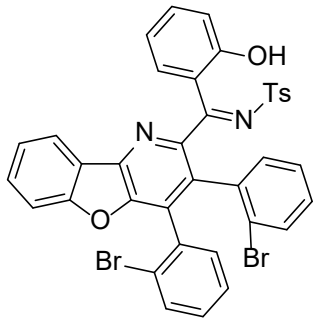
^{1}H NMR(500 MHz, $CDCl_3$): δ 12.0 (s, 1H), 8.18 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.64 (td, *J* = 8.0, 1.0 Hz, 1H), 7.51 (td, *J* = 8.0, 1.0 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.30-7.27 (m, 3H), 7.18-6.98 (m, 3H), 6.92-6.87 (m, 3H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.66-6.60 (m, 2H), 3.66 (s, 6H), 2.44 (s, 3H).

^{13}C NMR(125 MHz, $CDCl_3$): δ 162.7, 159.1, 158.3, 148.3, 148.0, 144.6, 142.9, 137.2, 136.4, 136.1, 134.5, 133.7, 133.2, 133.1, 132.6, 132.2, 129.8, 129.7, 129.2, 128.1, 123.9, 123.0, 123.0, 121.4, 118.9, 118.2, 115.7, 115.5, 114.9, 114.8, 112.6, 55.2, 21.7;

IR (KBr): 3071, 2927, 1654, 1617, 1584, 1492, 1420, 1366, 1330, 1294, 1222, 1163, 1087, 1087, 1040, 753 cm^{-1};

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{39}H_{30}N_2NaO_6S$ 677.1717, found 677.1716.

N-((3,4-Bis(2-bromophenyl)benzofuro[3,2-b]pyridin-2-yl)(2-hydroxyphenyl)-methylene)-4-methylbenzenesulfonamide (**2o**)



White solid (10 mg, 26% yield); mp = 138-139 ℃.

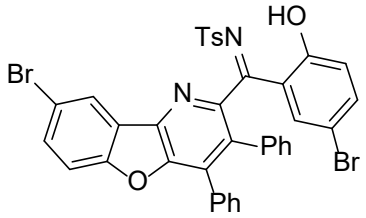
^{1}H NMR(500 MHz, $CDCl_3$): δ 11.87 (s, 1H), 8.20 (d, *J* = 7.5 Hz, 1H), 8.08 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.91 (d, *J* = 8.5 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 8.5 Hz, 1H), 7.67 (t, *J* = 8.0 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.37-7.33 (m, 3H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.30-7.27 (m, 2H), 7.20 (t, *J* = 8.0 Hz, 1H), 7.11 (d, *J* = 7.5 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.99-6.94 (m, 2H), 6.77 (d, *J* = 8.5 Hz, 1H), 6.70 (t, *J* = 8.0 Hz, 1H), 2.48 (s, 3H);

^{13}C NMR(125 MHz, $CDCl_3$): δ 178.0, 162.2, 158.4, 148.4, 147.5, 144.7, 143.4, 137.2, 136.7, 134.9, 134.6, 133.8, 133.5, 133.1, 132.9, 132.8, 132.2, 131.5, 130.2, 130.0, 129.8, 129.7, 128.2, 127.0, 125.4, 125.0, 124.5, 124.0, 122.8, 121.4, 119.2, 118.2, 117.6, 112.8, 110.0, 21.7;

IR (KBr): 3067, 2924, 1654, 1585, 1560, 1492, 1438, 1333, 1293, 1200, 1159, 1088, 1029, 978, 876, 751 cm^{-1};

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{37}H_{24}Br_2N_2NaO_4S$ 772.9716, found 772.9716.

N-((5-Bromo-2-hydroxyphenyl)(8-bromo-3,4-diphenylbenzofuro[3,2-b]pyridin-2-yl)methylene)-4-methylbenzenesulfonamide (**2q**)



White solid (21 mg, 56% yield); mp = 99-100 ℃;

^{1}H NMR(500 MHz, $CDCl_3$): δ 12.01 (s, 1H), 8.24 (d, *J* = 2.0 Hz, 1H), 7.83 (d, *J* = 8.5

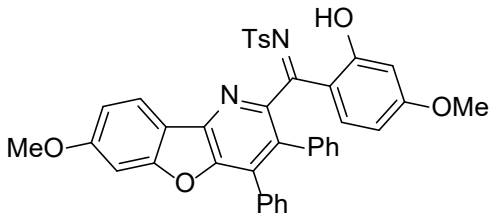
Hz, 1H), 7.74 (dd, *J* = 9.0, 2.0 Hz, 1H), 7.56 (d, *J* = 8.5 Hz, 1H), 7.42-7.39 (m, 2H), 7.37-7.32 (m, 6H), 7.30 (dd, *J* = 9.0, 2.0 Hz, 1H), 7.24-7.18 (m, 1H), 7.16-7.05 (m, 3H), 6.91 (d, *J* = 2.0 Hz, 1H), 6.70 (d, *J* = 9.0 Hz, 1H), 2.50 (s, 3H);

^{13}C NMR(125 MHz, $CDCl_3$): δ 177.3, 161.5, 157.0, 148.8, 148.1, 144.9, 141.8, 138.7, 137.1, 135.0, 134.6, 134.1, 133.3, 132.7, 131.4, 130.8, 130.6, 129.8, 128.8, 128.2, 128.1, 128.0, 124.8, 124.5, 120.2, 119.4, 117.0, 114.2, 110.5, 21.8;

IR (KBr): 3059, 2924, 1654, 1577, 1560, 1541, 1458, 1336, 1278, 1199, 1163, 1085, 984, 922, 854, 726 cm^{-1};

HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{37}H_{24}Br_2N_2NaO_4S$ 772.9716, found 772.9721.

N-((2-Hydroxy-4-methoxyphenyl)(7-methoxy-3,4-diphenylbenzofuro[3,2-b]pyridin-2-yl)methylene)-4-methylbenzenesulfonamide (**2r)**



White solid (10 mg, 31% yield); mp = 109-110 ℃;

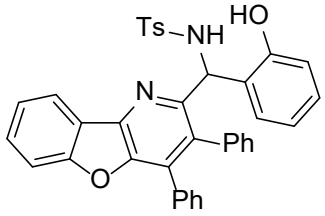
^{1}H NMR(500 MHz, $CDCl_3$): δ 12.61 (s, 1H), 8.00 (d, *J* = 9.0 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.38-7.36 (m, 2H), 7.32-7.29 (m, 4H), 7.28 (s, 1H), 7.15-7.11 (m, 2H), 7.10-7.03 (m, 3H), 6.79 (d, *J* = 9.0 Hz, 1H), 6.75-6.71 (m, 1H), 6.25 (d, *J* = 2.5 Hz, 1H), 6.18 (dd, *J* = 9.0, 2.5 Hz, 1H), 3.93 (s, 3H), 3.74 (s, 3H), 2.43 (s, 3H);

^{13}C NMR(125 MHz, $CDCl_3$): δ 166.5, 166.0, 161.9, 160.0, 148.2, 144.0, 143.0, 138.0, 135.4, 135.1, 130.6, 129.5, 128.3, 128.0, 127.9, 127.7, 121.9, 115.9, 112.8, 112.3, 108.5, 100.6, 96.8, 55.9, 55.6, 21.7;

IR (KBr): 3057, 2923, 1630, 1597, 1508, 1497, 1370, 1332, 1277, 1247, 1161, 1120, 1088, 1023, 980, 825 cm^{-1};

HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{39}H_{31}N_2O_6S$ 655.1897, found 655.1897.

N-((3,4-Diphenylbenzofuro[3,2-b]pyridin-2-yl)(2-hydroxyphenyl)methyl)-4-methylbenzenesulfonamide (**4**)



White solid (42 mg, 71% yield); mp = 127-128 ℃.

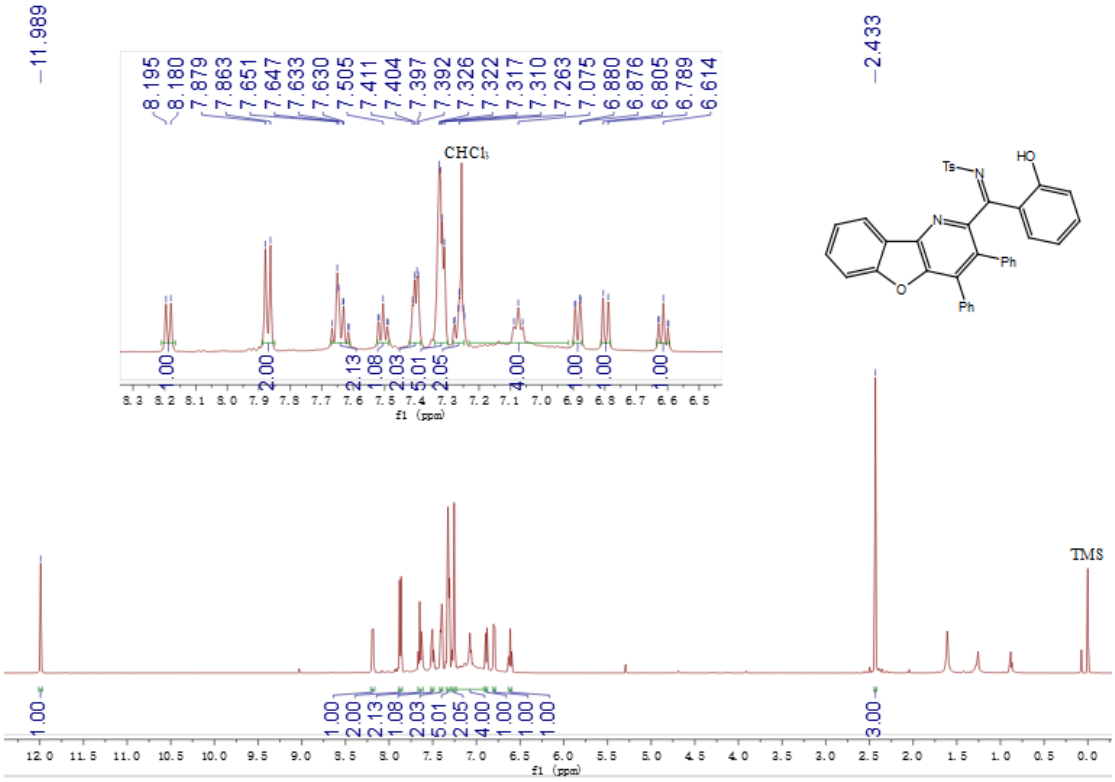
^{1}H NMR(500 MHz, $CDCl_3$) δ 11.61 (s, 1H), 8.15 (d, *J* = 7.5 Hz, 1H), 7.61 (td, *J* = 7.5, 1.0 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.50 (td, *J* = 7.5, 1.0 Hz, 1H), 7.46-7.42 (m, 2H), 7.40-7.36 (m, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.32-7.27 (m, 4H), 7.21-7.17 (m, 2H), 7.07 (td, *J* = 8.0, 1.5 Hz, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 2H), 6.82 (dd, *J* = 8.0, 1.0 Hz, 1H), 6.61 (td, *J* = 7.5, 1.0 Hz, 1H), 6.41 (dd, *J* = 7.5, 1.5 Hz, 1H), 6.31 (d, *J* = 8.0 Hz, 1H), 5.61 (*J* = 8.0 Hz, 1H), 2.01 (s, 3H).

^{13}C NMR(125 MHz, $CDCl_3$) δ 158.1, 155.6, 152.6, 147.3, 142.6, 141.6, 137.3, 135.2, 134.6, 133.5, 132.2, 131.3, 131.0, 130.1, 130.0, 129.9, 129.9, 128.8, 128.6, 128.5, 128.2, 128.1, 127.9, 125.6, 124.9, 124.0, 121.8, 121.5, 120.1, 119.5, 112.5, 60.1, 21.0.

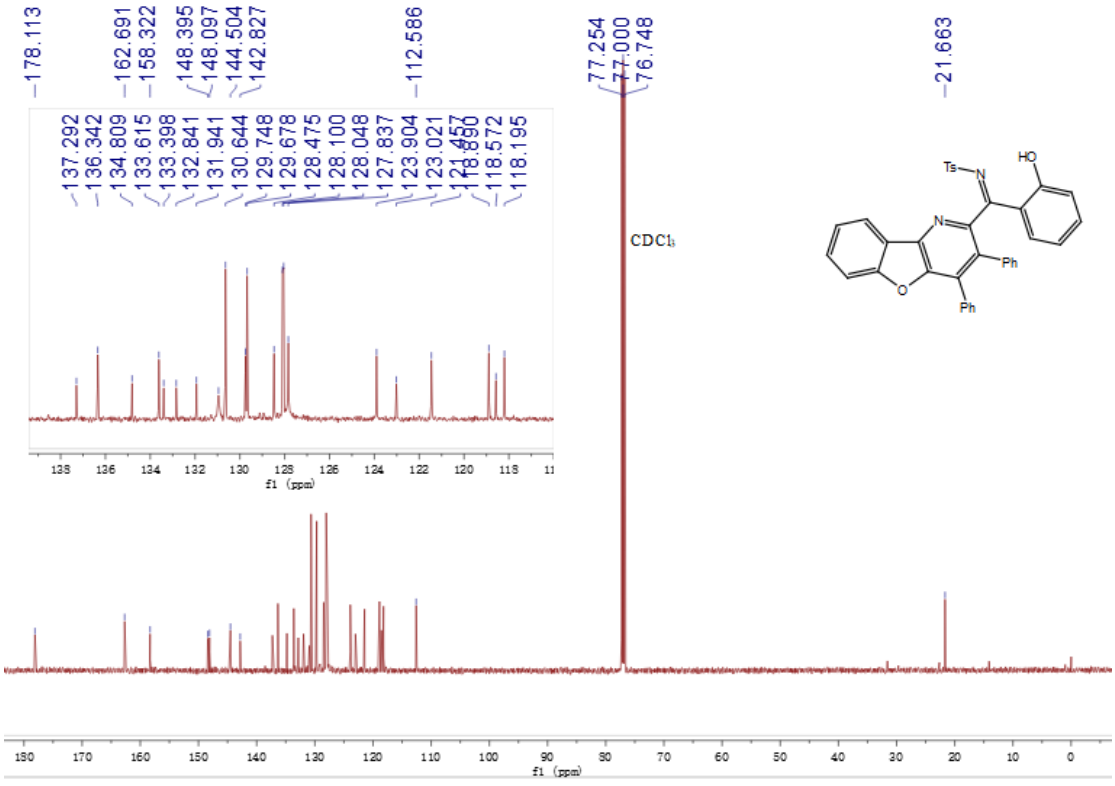
HRMS (ESI-TOF) calcd for $C_{37}H_{29}N_2O_4S^+$ ($[M+H]^+$): 597.1843; found: 597.1843.

IR (film): 3415, 3060, 2925, 2855, 1630, 1593, 1485, 1370, 1342, 1252, 1201, 1162, 1093, 1054, 812, 753 cm^{-1}.

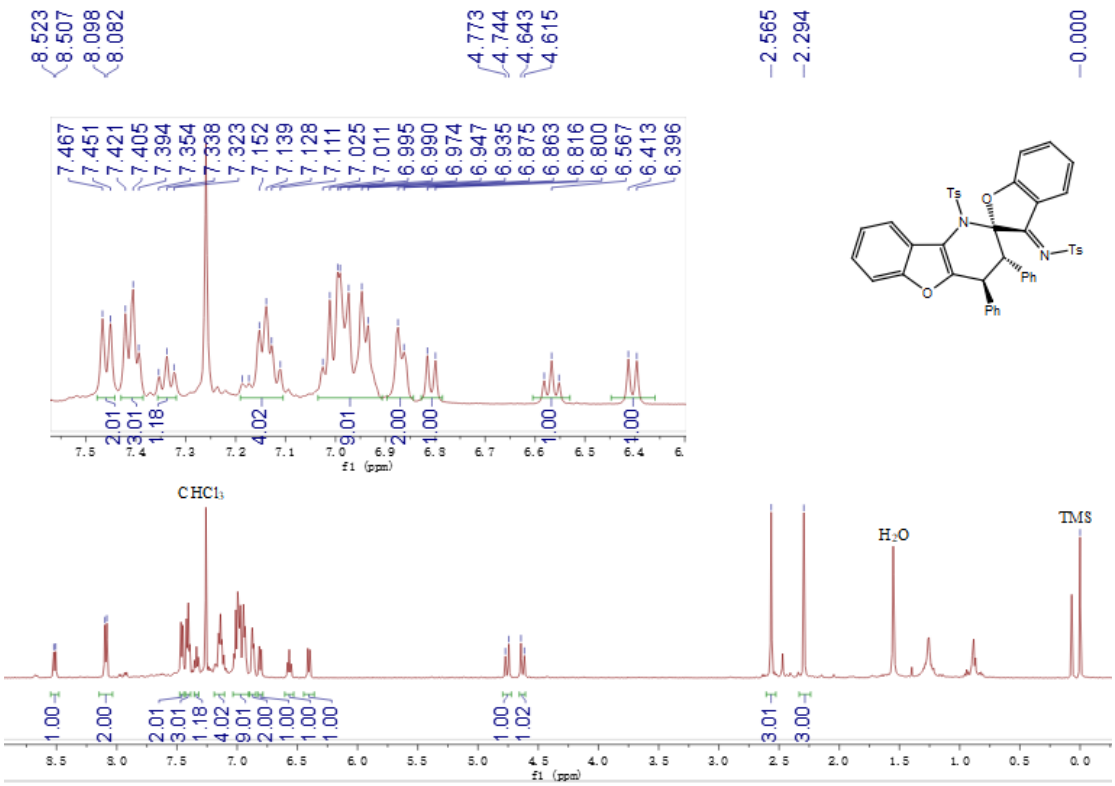
5. Copies of NMR spectra of products 2, 3 and 4



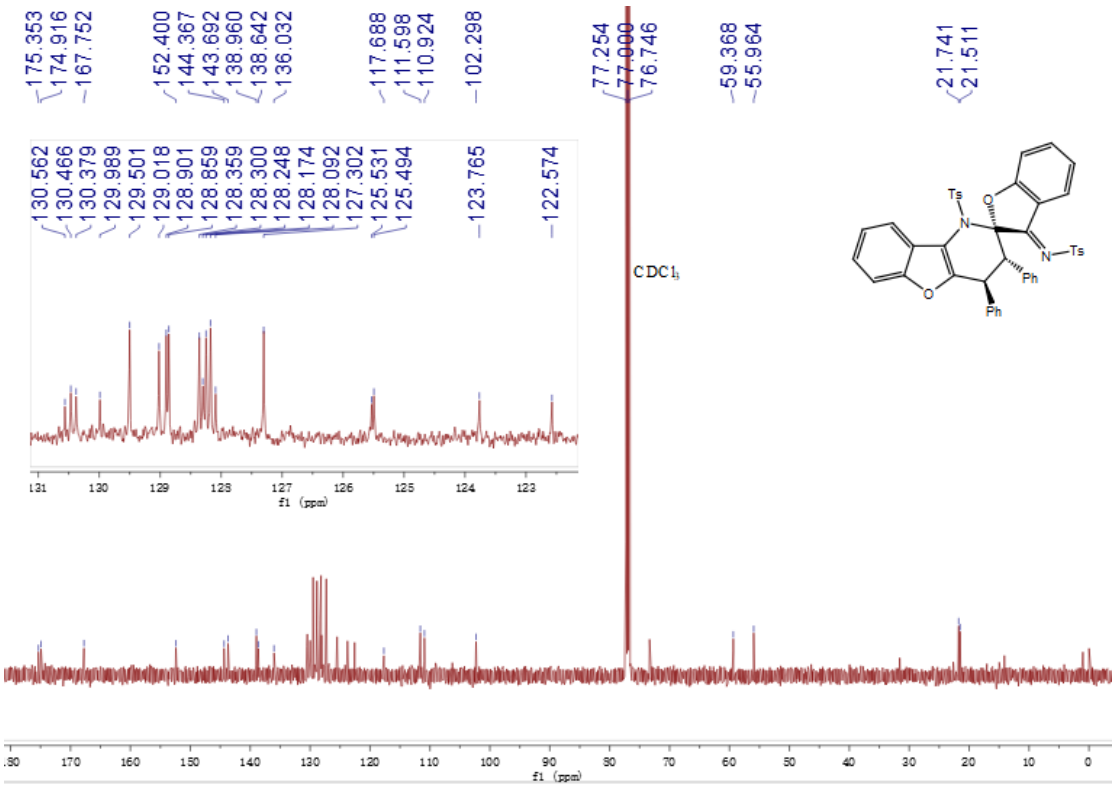
^{1}H NMR of **2a** (500 MHz, $CDCl_3$)



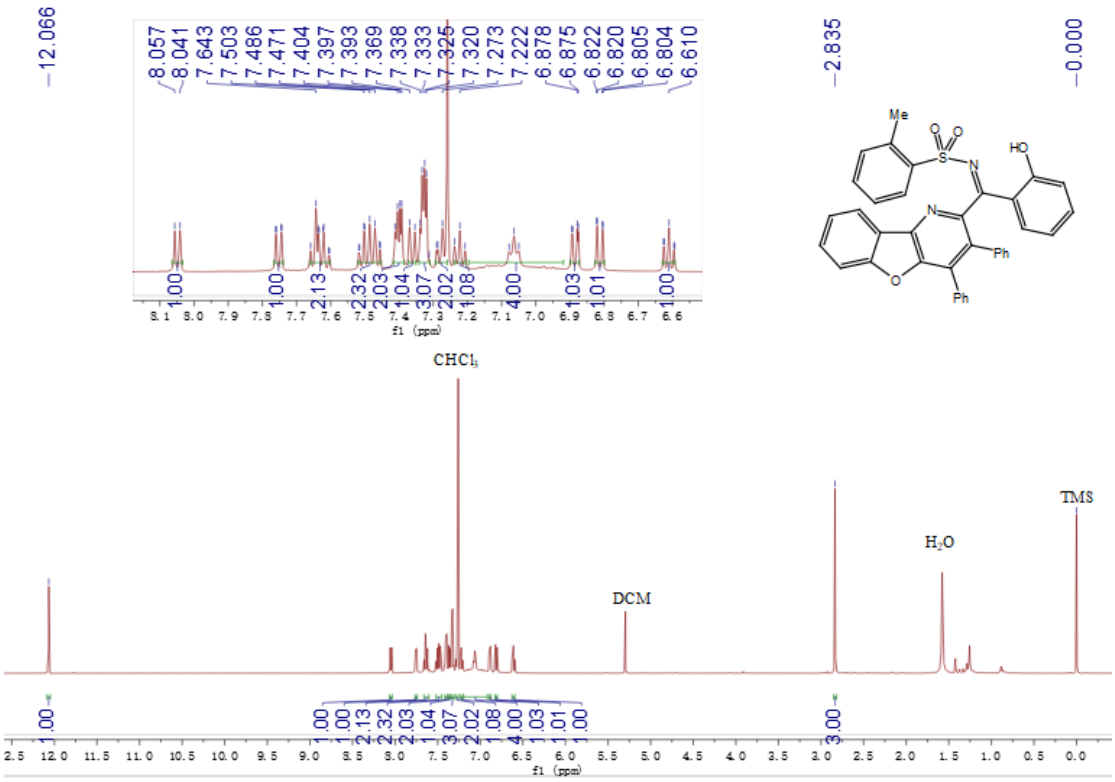
^{13}C{^{1}H} NMR of **2a** (125 MHz, $CDCl_3$)



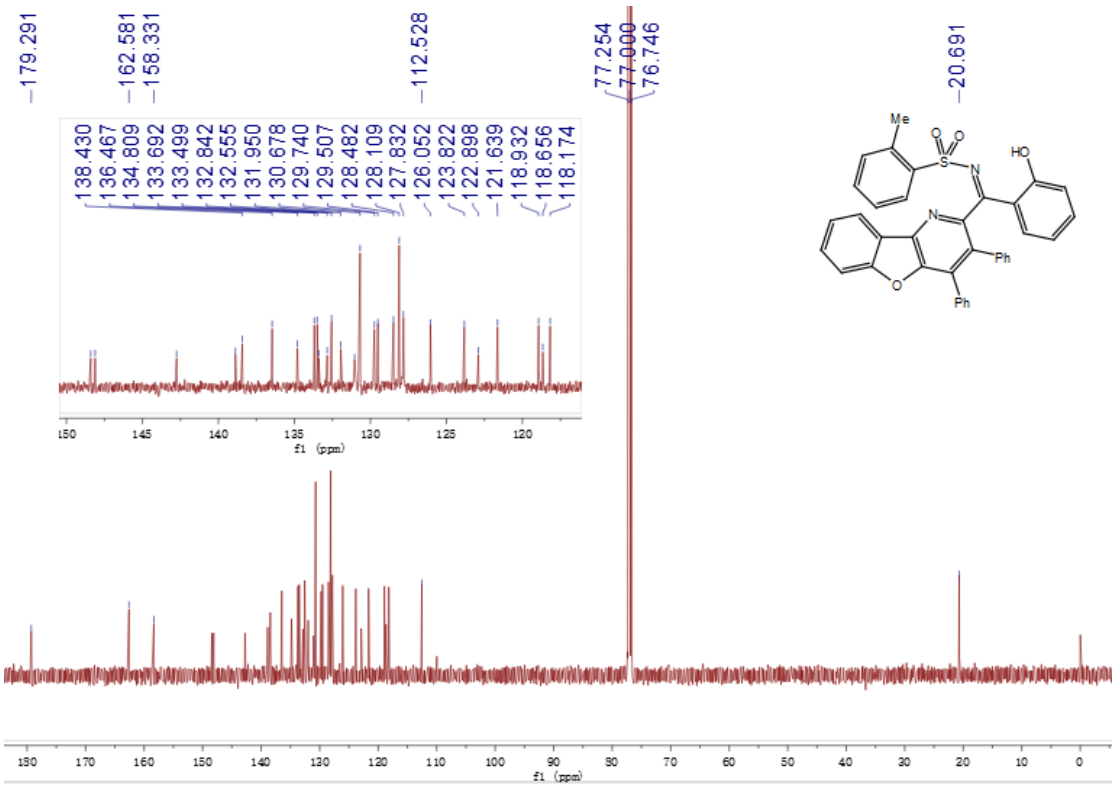
^{1}H NMR of **3a** (500 MHz, $CDCl_3$)



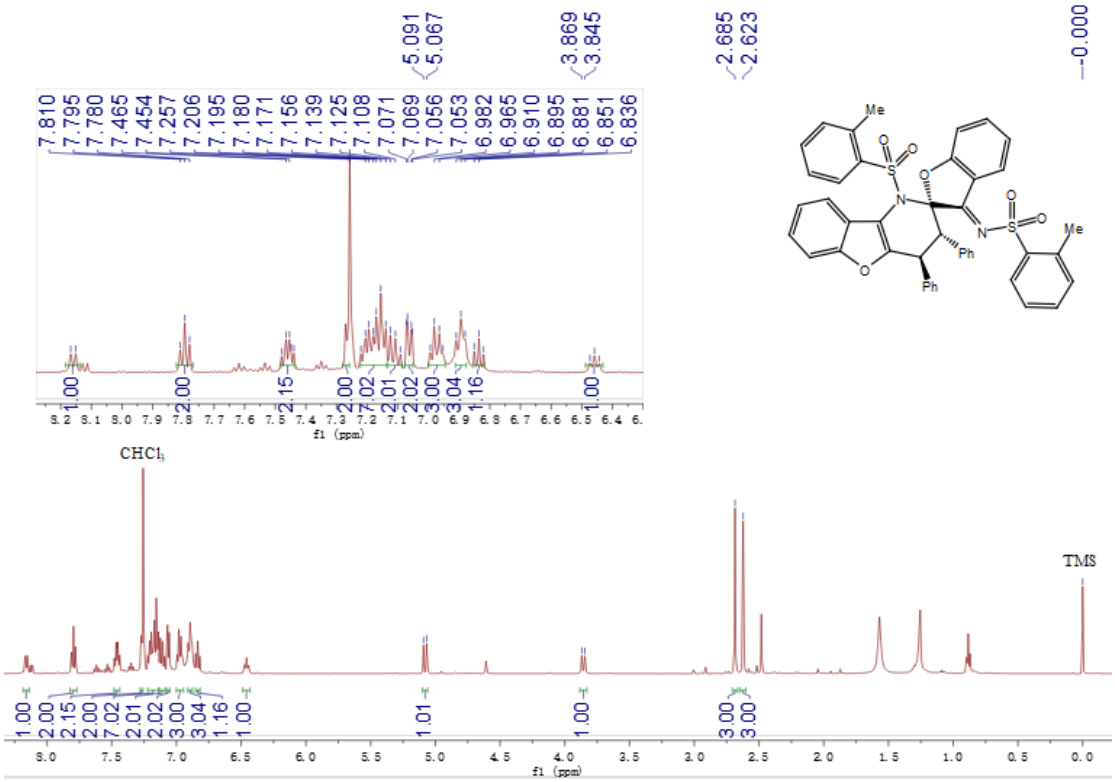
^{13}C{^{1}H} NMR of **3a** (125 MHz, $CDCl_3$)



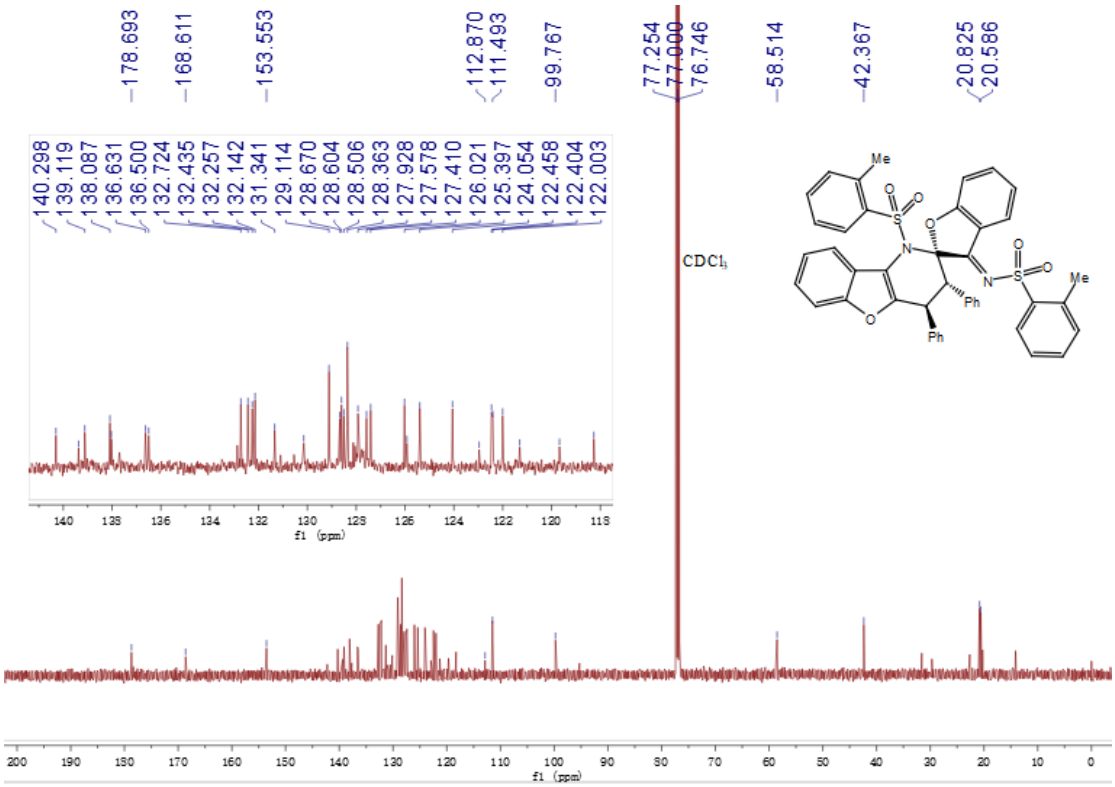
^{1}H NMR of **2b** (500 MHz, $CDCl_3$)



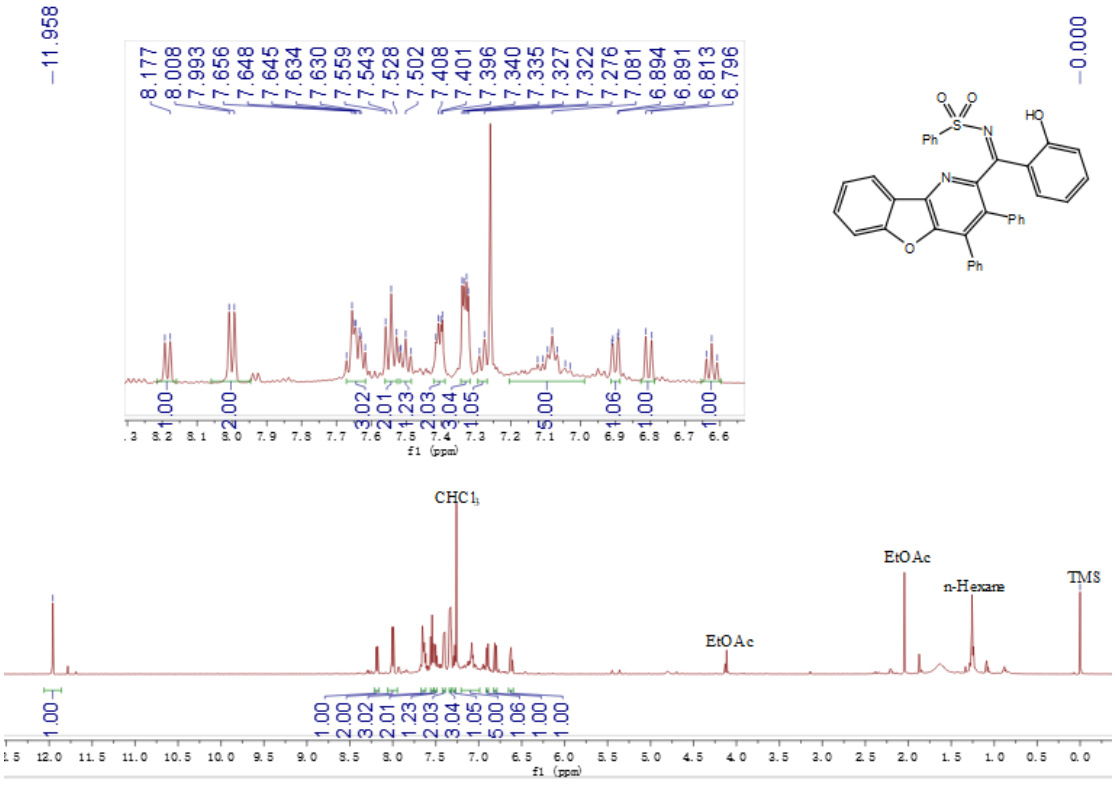
^{13}C{^{1}H} NMR of **2b** (125 MHz, $CDCl_3$)



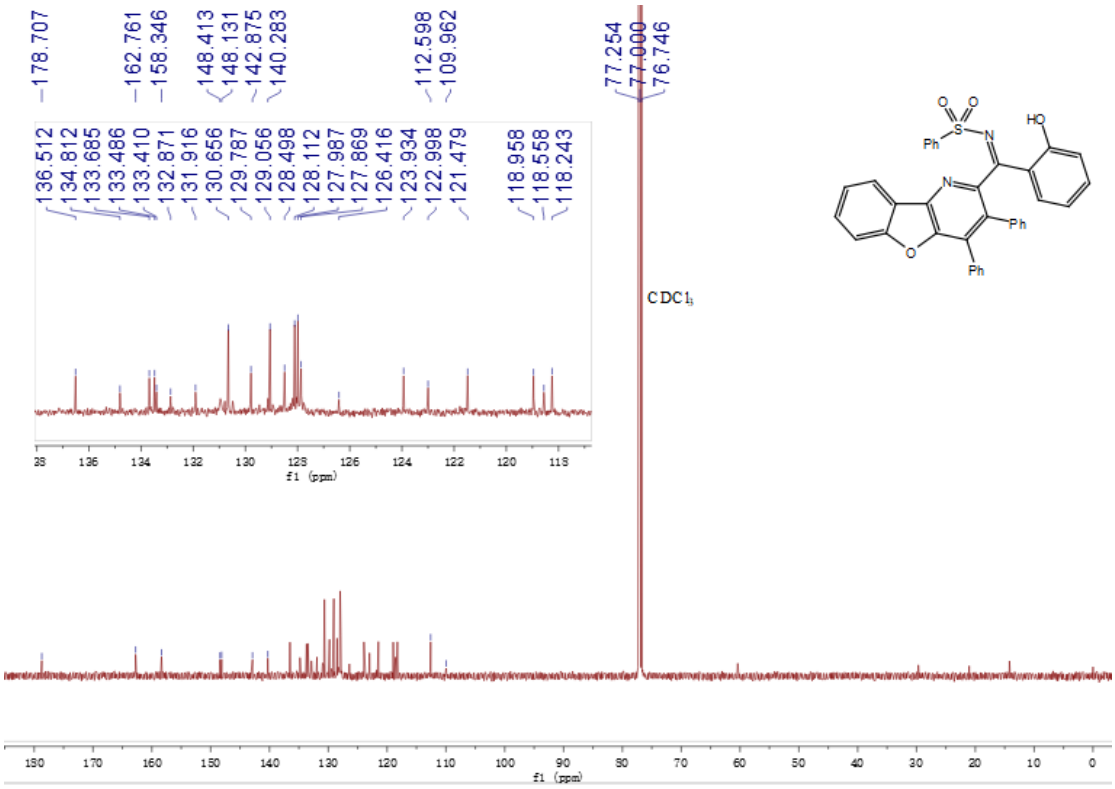
^{1}H NMR of **3b** (500 MHz, $CDCl_3$)



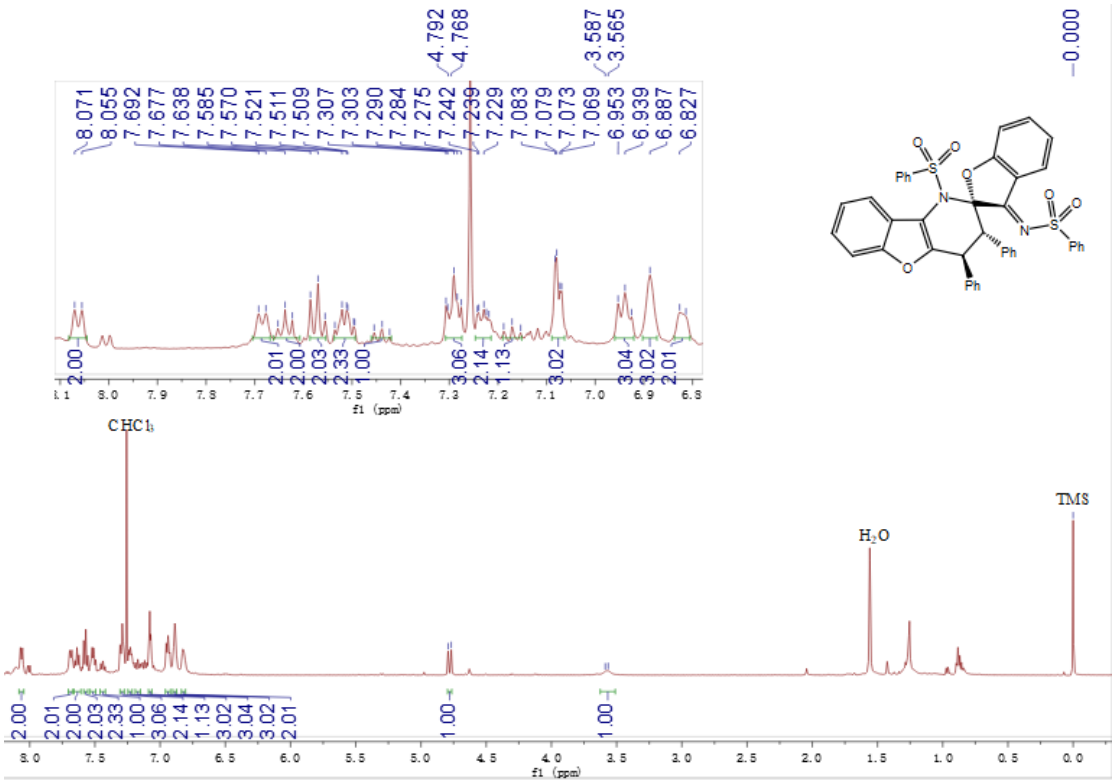
^{13}C{^{1}H} NMR of **3b** (125 MHz, $CDCl_3$)



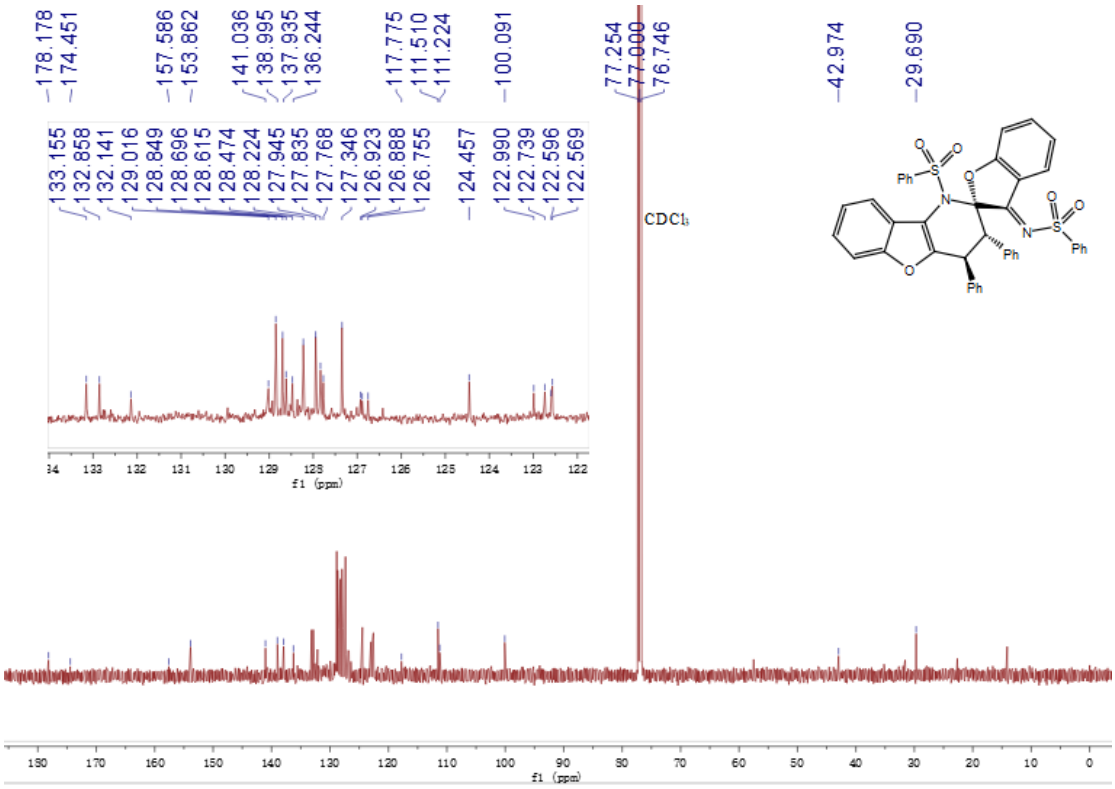
^{1}H NMR of **2c** (500 MHz, $CDCl_3$)



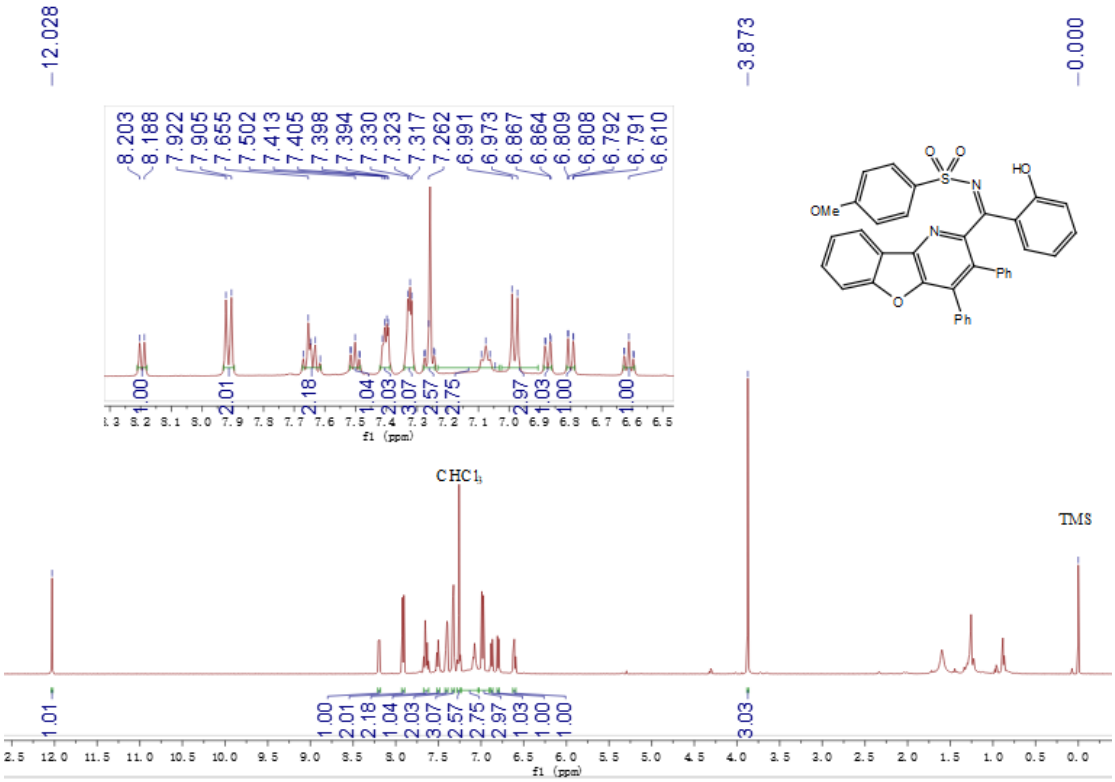
$^{13}C\{^{1}H\}$ NMR of **2c** (125 MHz, $CDCl_3$)



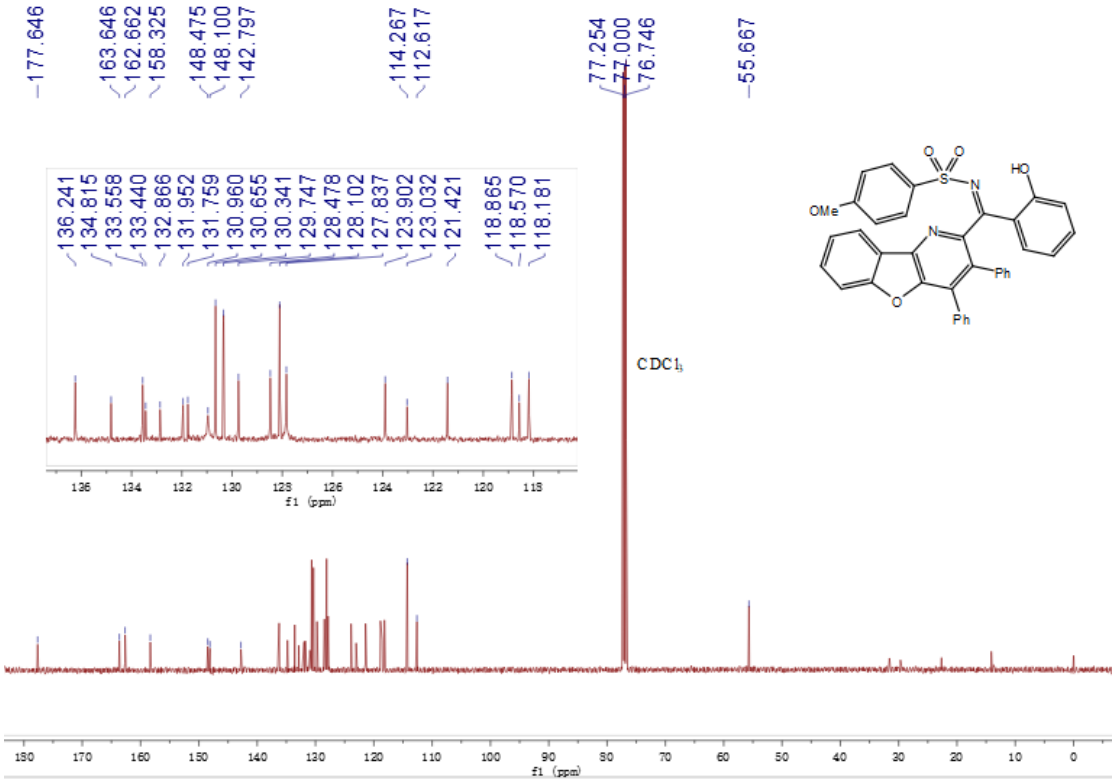
^{1}H NMR of **3c** (500 MHz, $CDCl_3$)



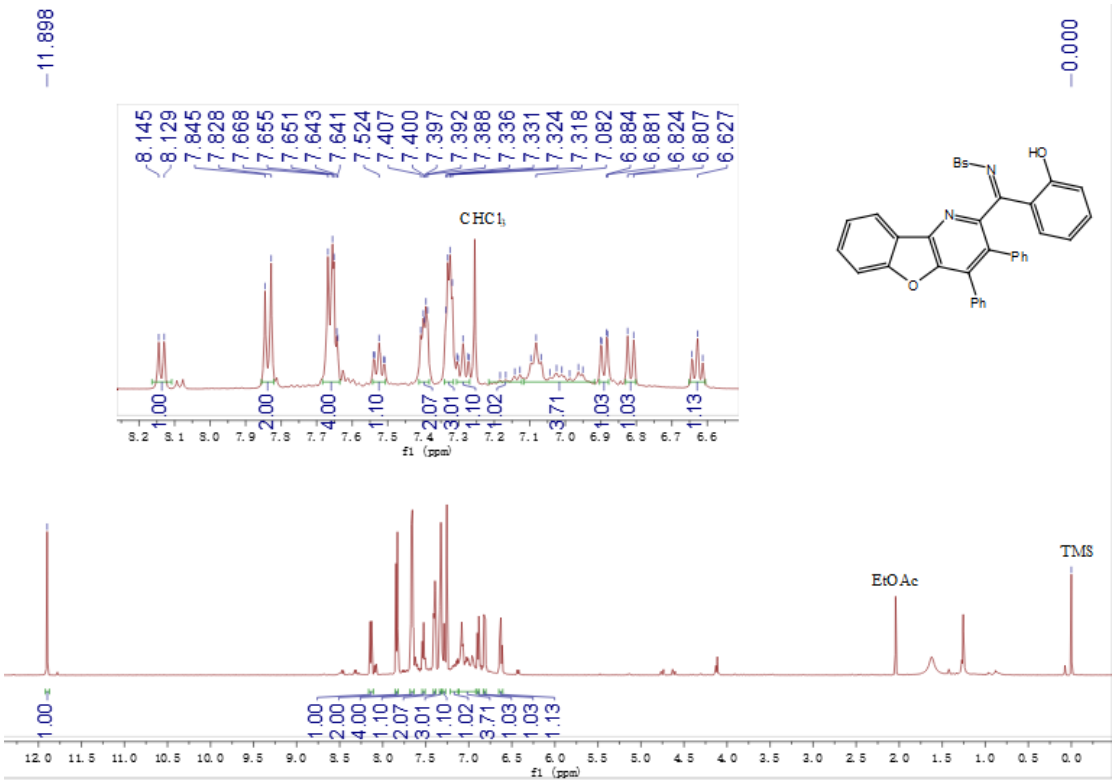
^{13}C{^{1}H} NMR of **3c** (125 MHz, $CDCl_3$)



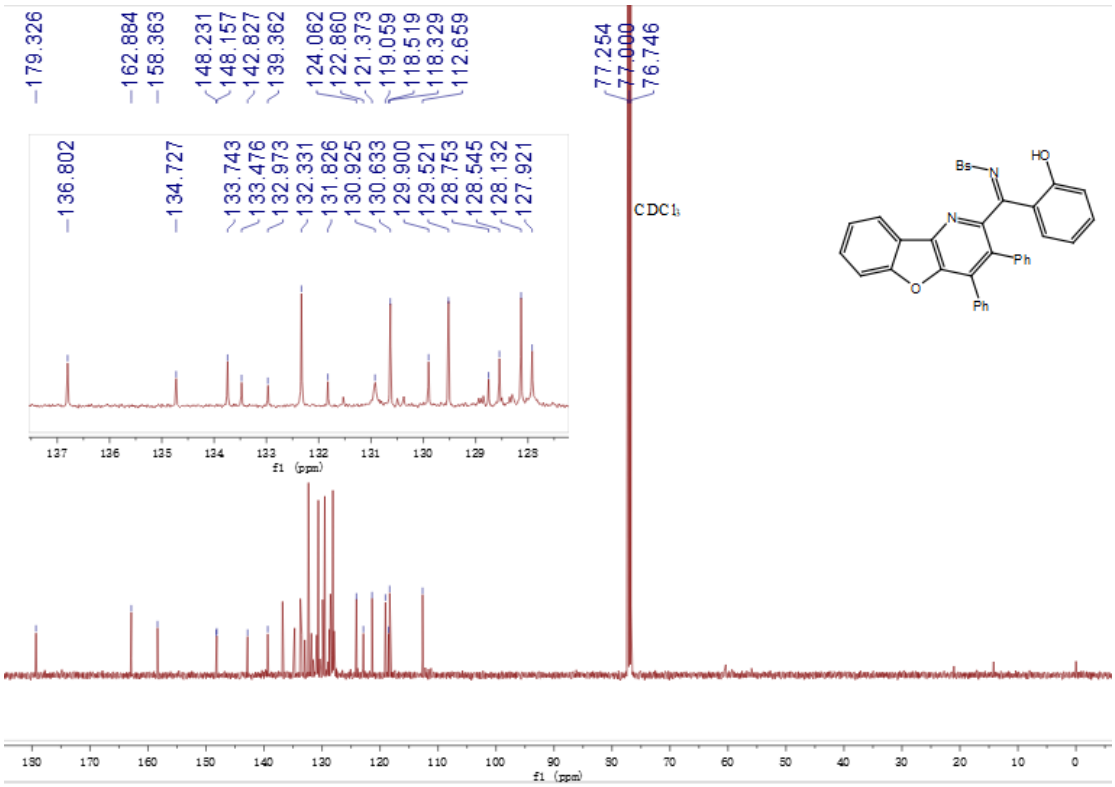
^{1}H NMR of **2d** (500 MHz, $CDCl_3$)



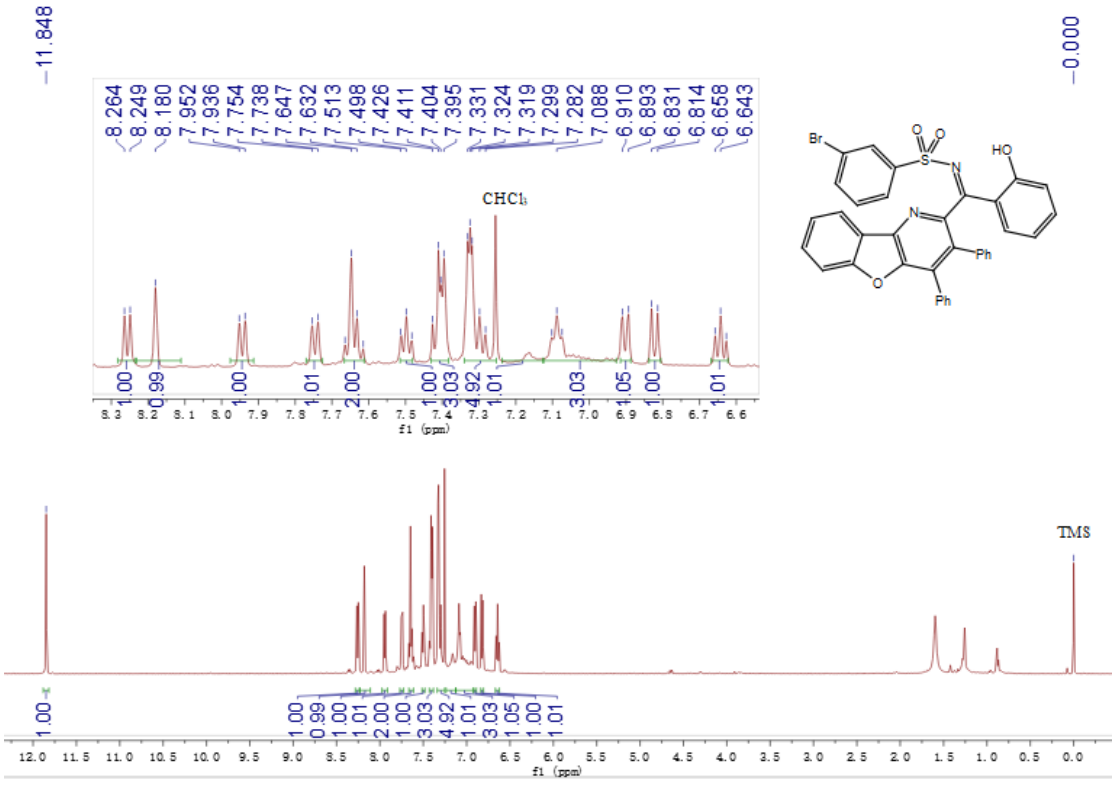
^{13}C{^{1}H} NMR of **2d** (125 MHz, $CDCl_3$)



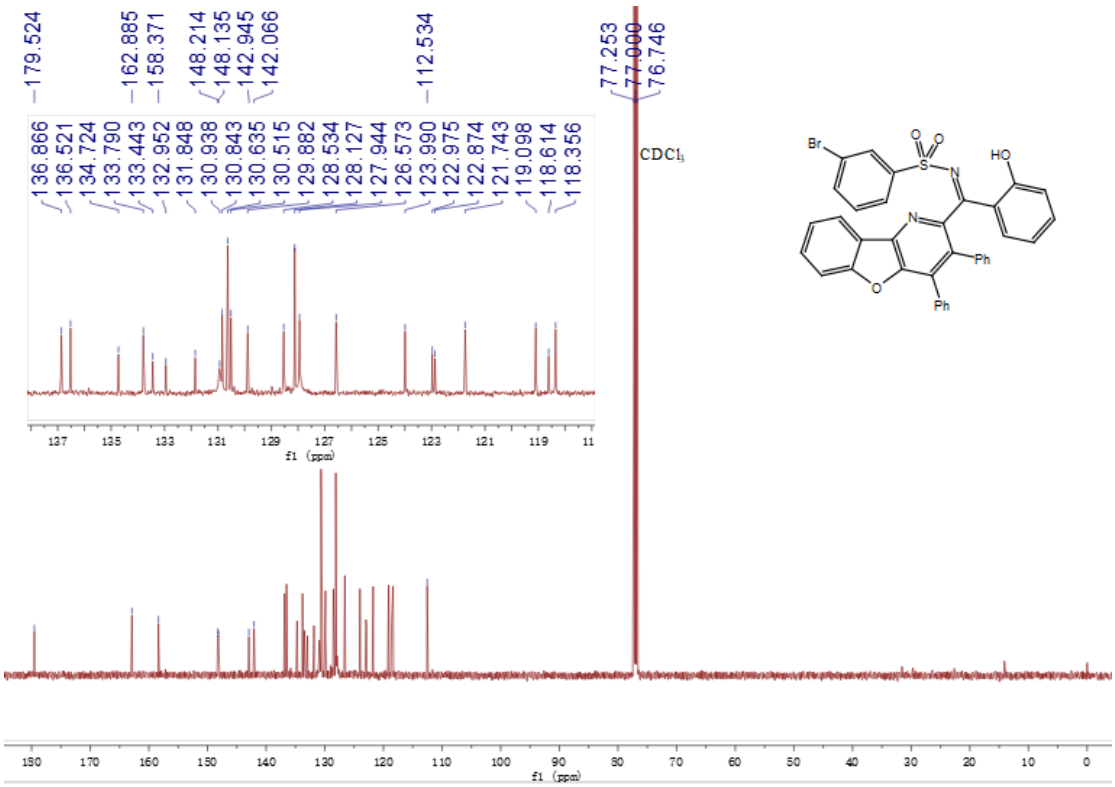
^{1}H NMR of **2e** (500 MHz, $CDCl_3$)



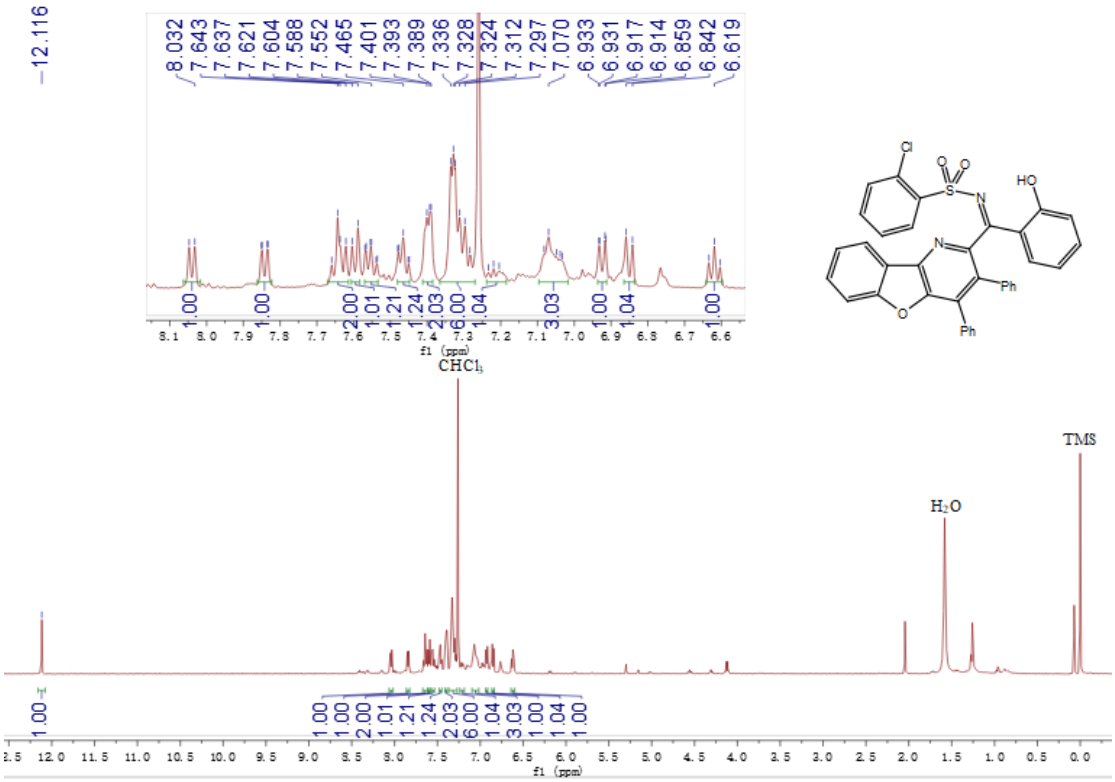
^{13}C{^{1}H} NMR of **2e** (125 MHz, $CDCl_3$)



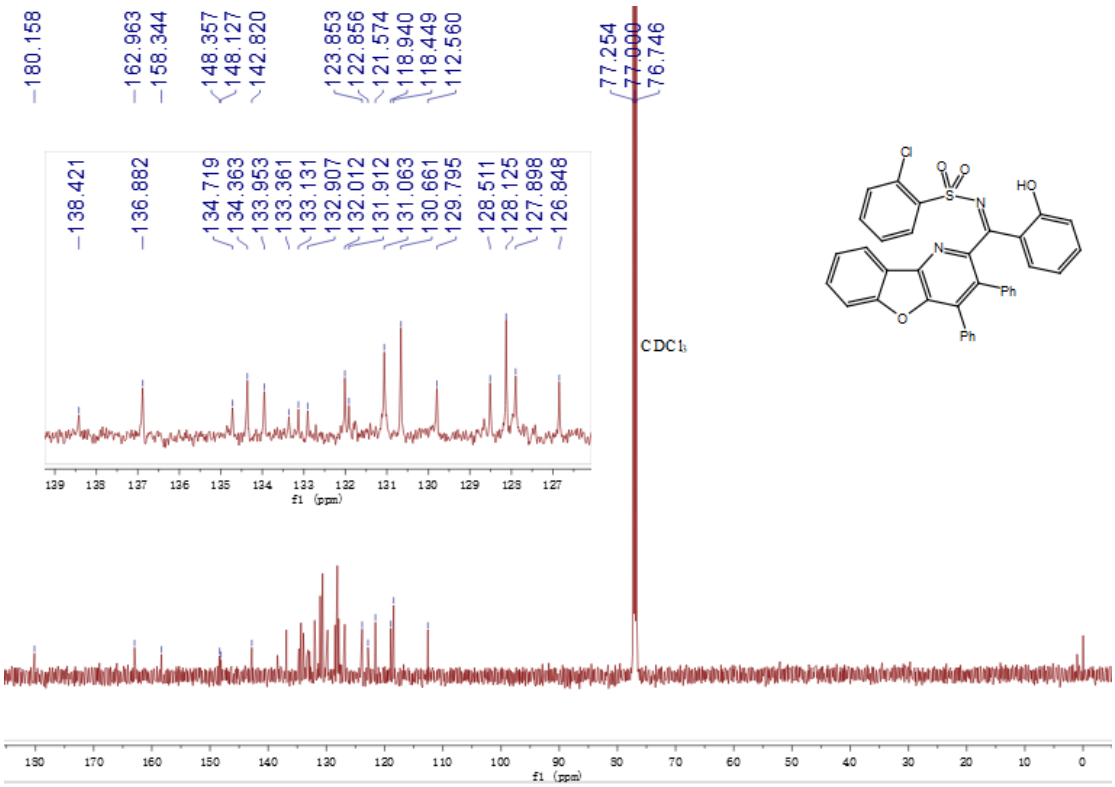
^{1}H NMR of **2f** (500 MHz, $CDCl_3$)



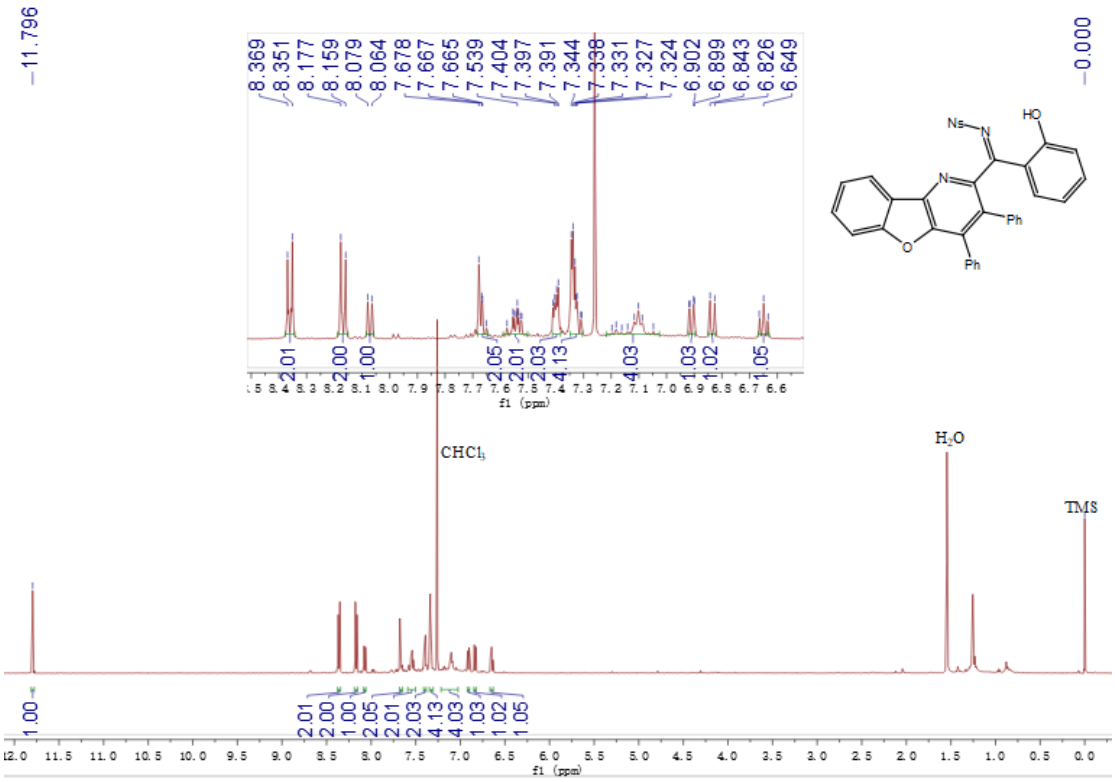
^{13}C{^{1}H} NMR of **2f** (125 MHz, $CDCl_3$)



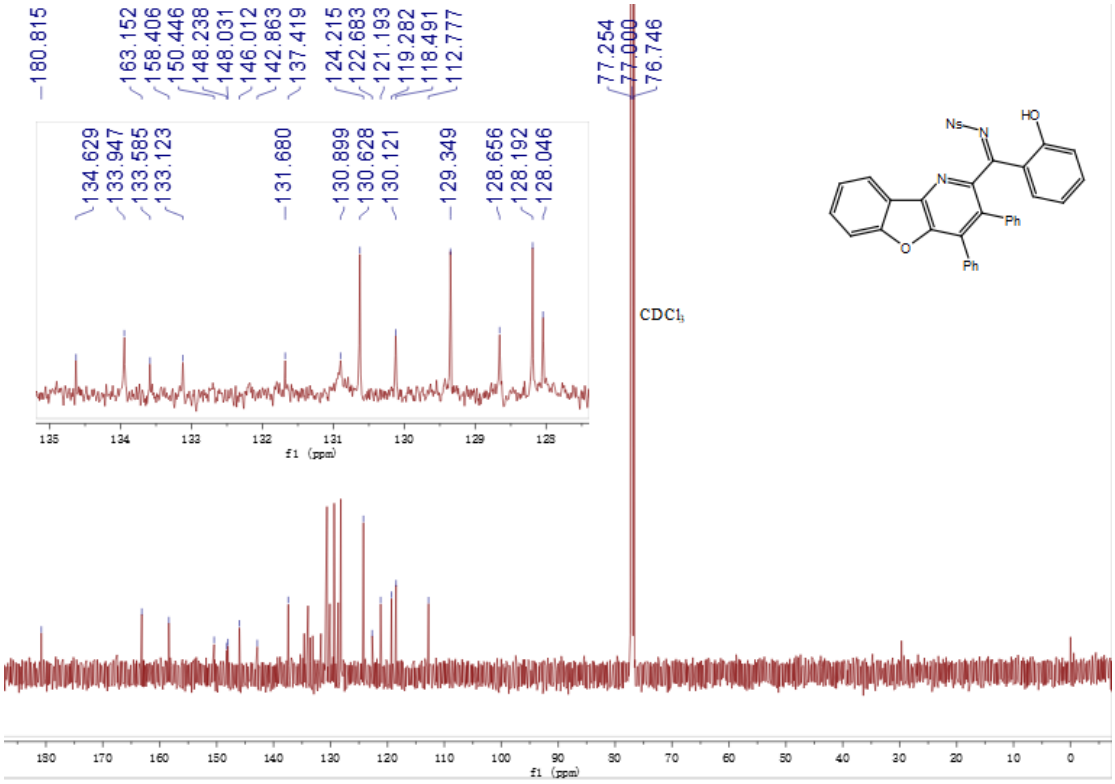
^{1}H NMR of **2g** (500 MHz, $CDCl_3$)



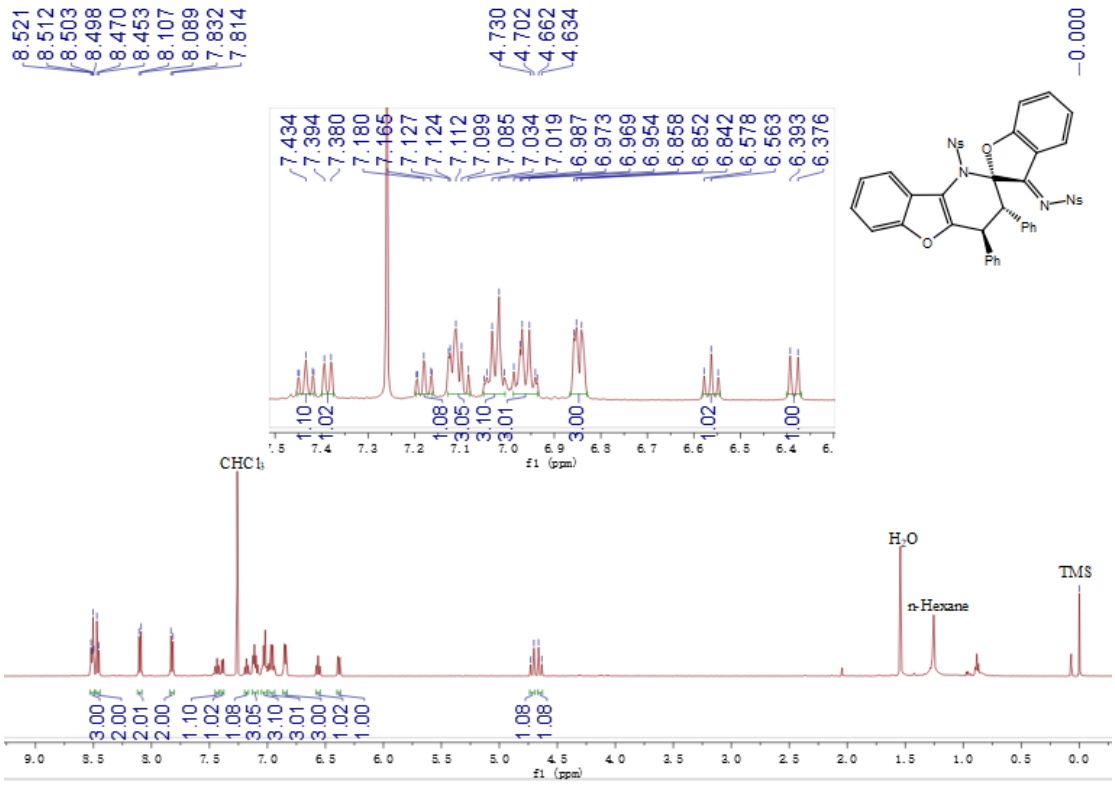
^{13}C{^{1}H} NMR of **2g** (125 MHz, $CDCl_3$)



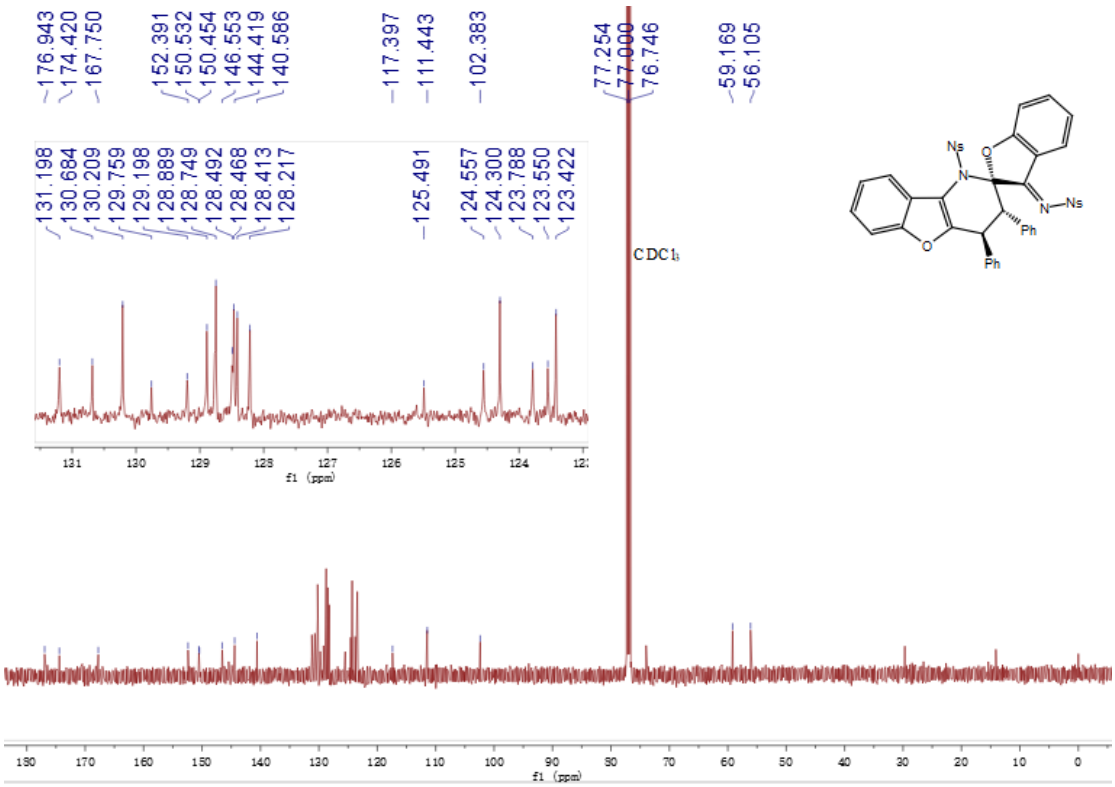
^{1}H NMR of **2h** (500 MHz, $CDCl_3$)



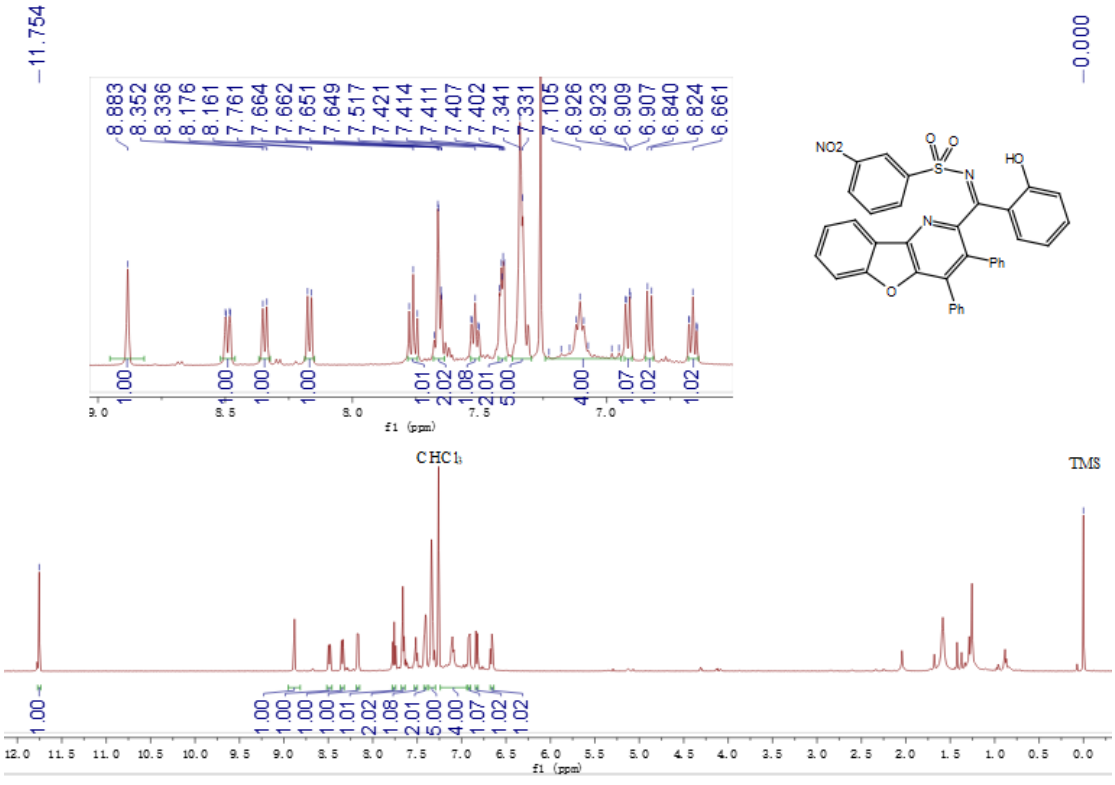
^{13}C{^{1}H} NMR of **2h** (125 MHz, $CDCl_3$)



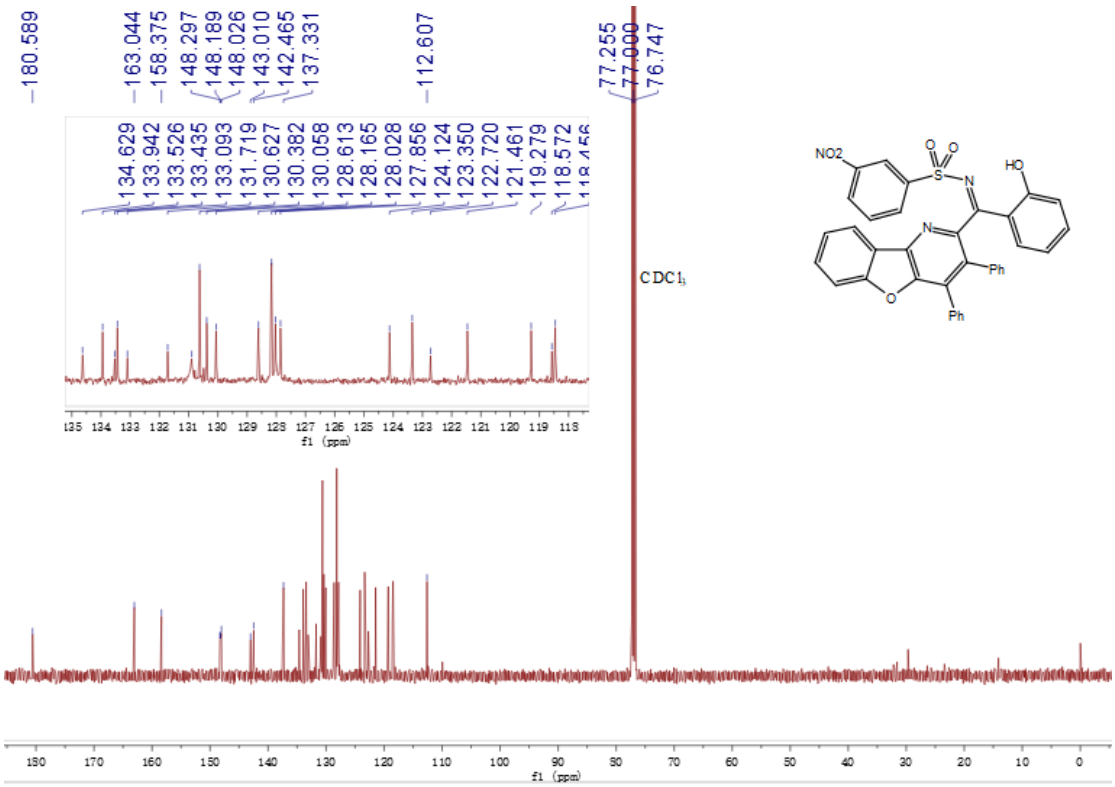
^{1}H NMR of **3h** (500 MHz, $CDCl_3$)



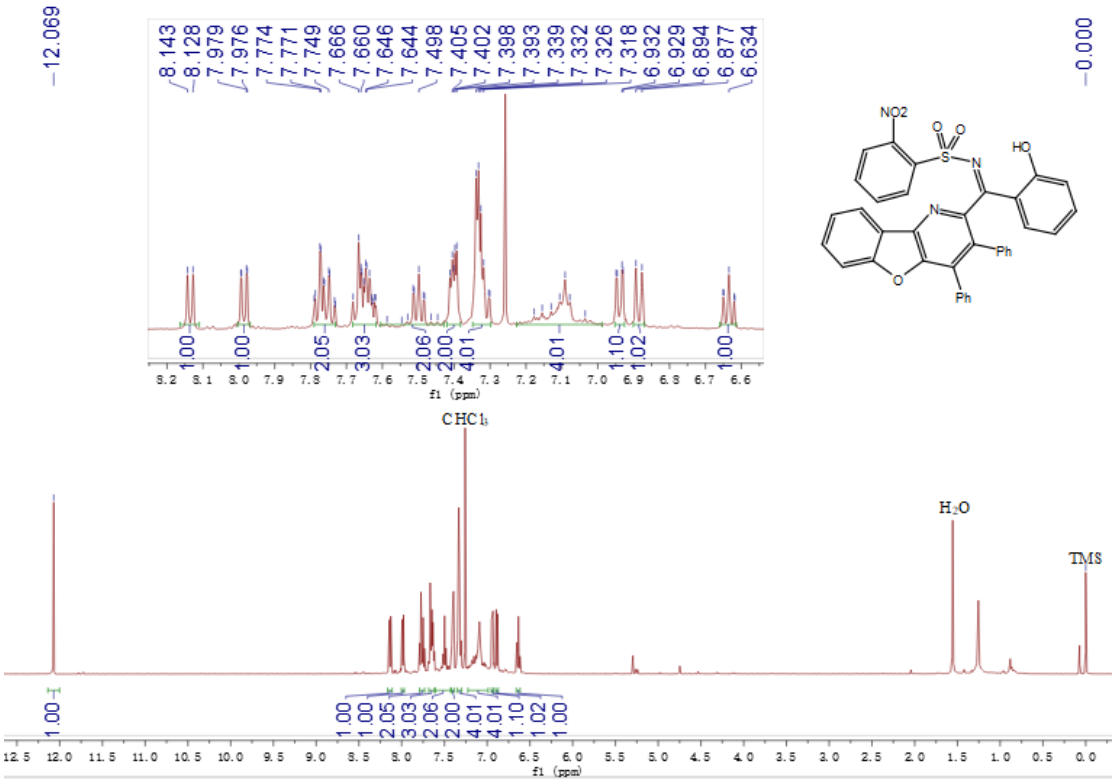
$^{13}C\{^{1}H\}$ NMR of **3h** (125 MHz, $CDCl_3$)



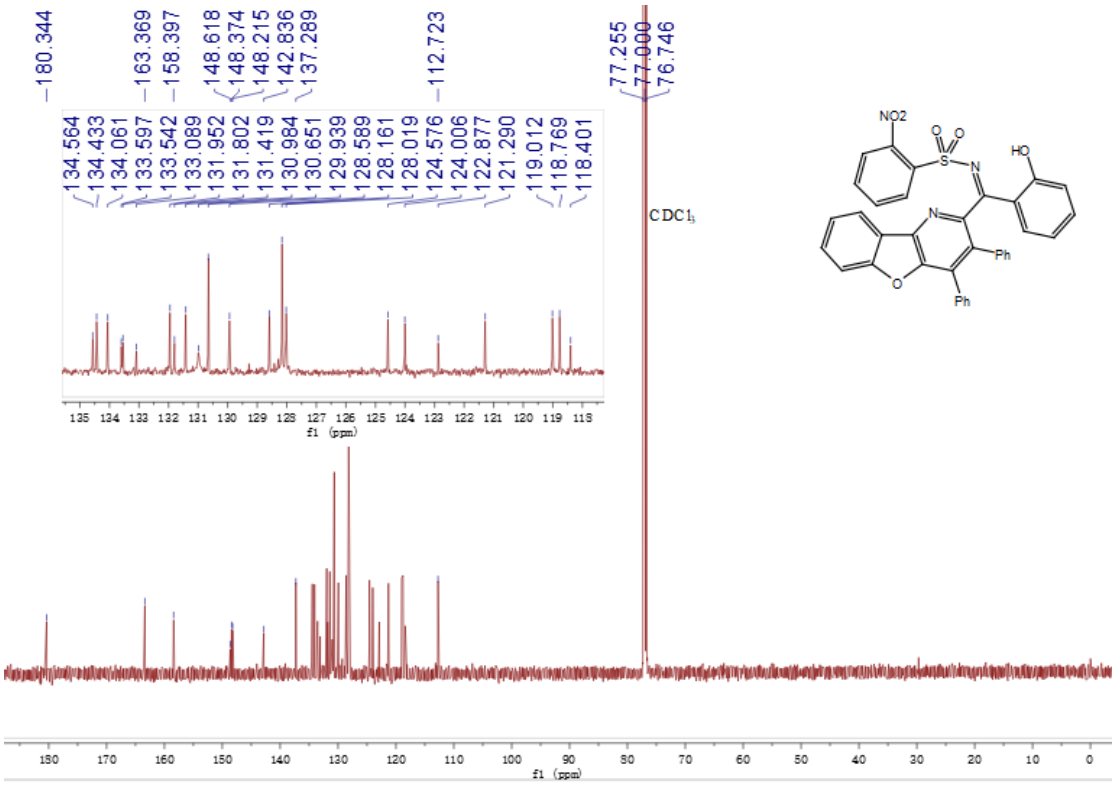
^{1}H NMR of **2i** (500 MHz, $CDCl_3$)



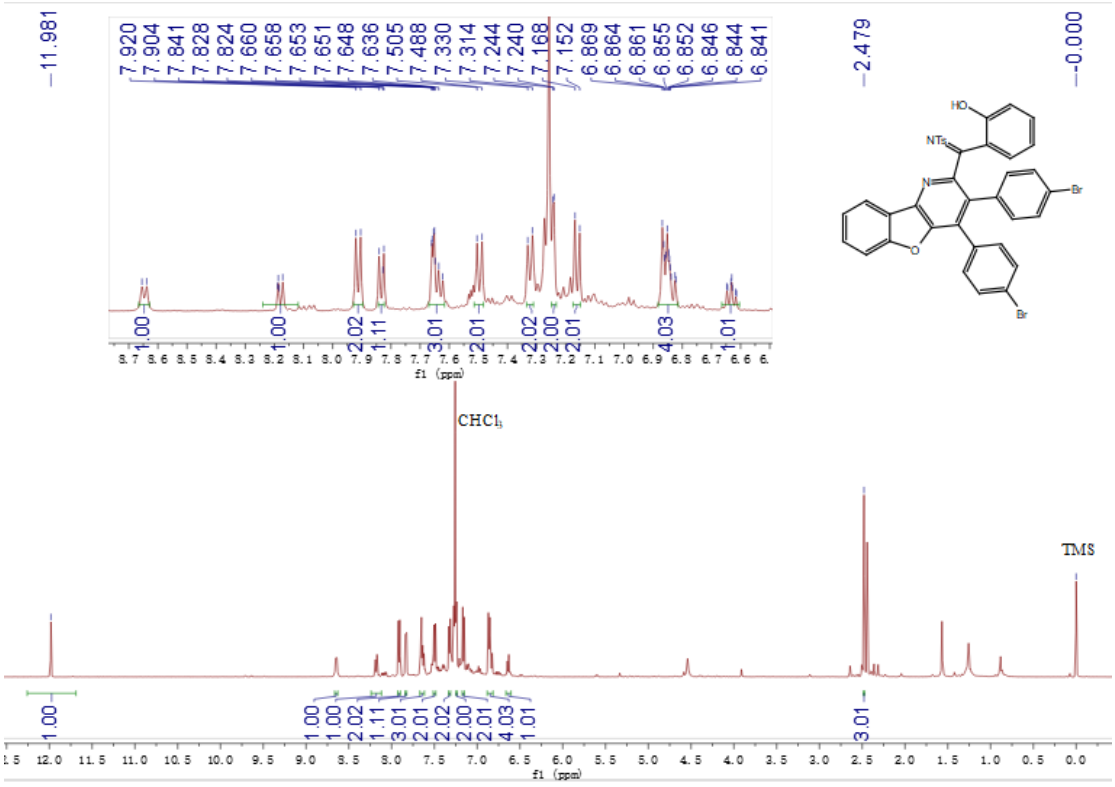
^{13}C{^{1}H} NMR of **2i** (125 MHz, $CDCl_3$)



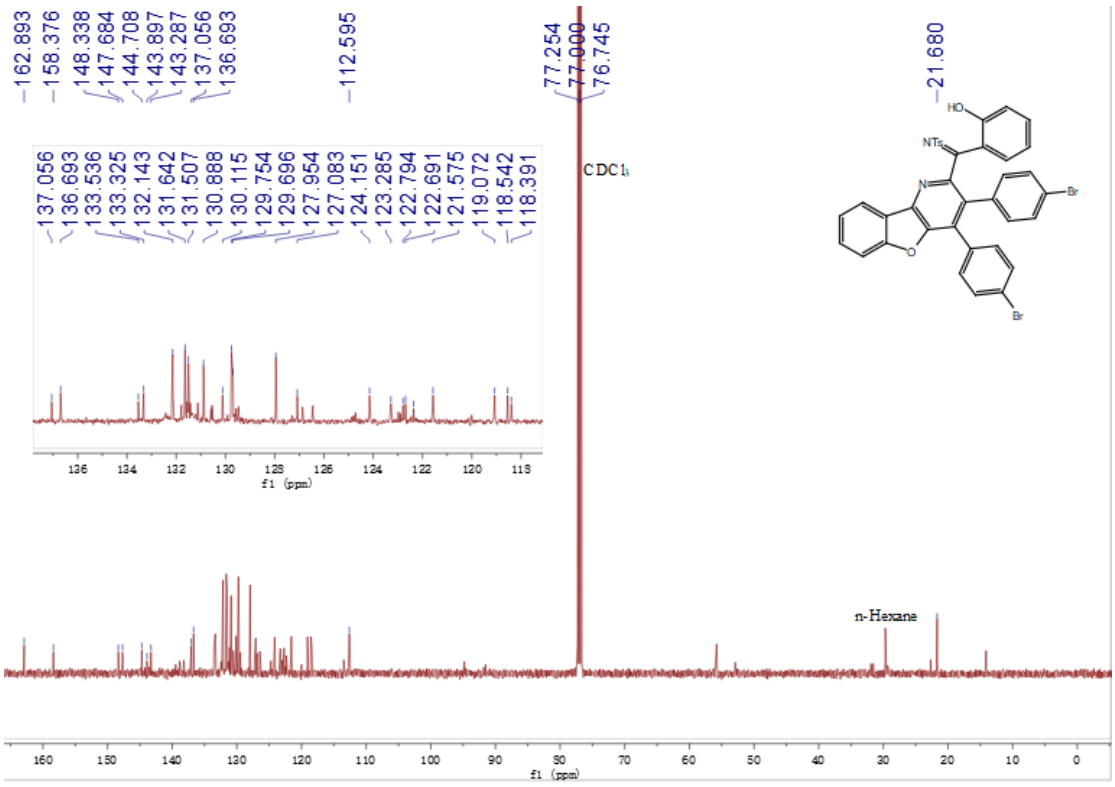
^{1}H NMR of **2j** (500 MHz, $CDCl_3$)



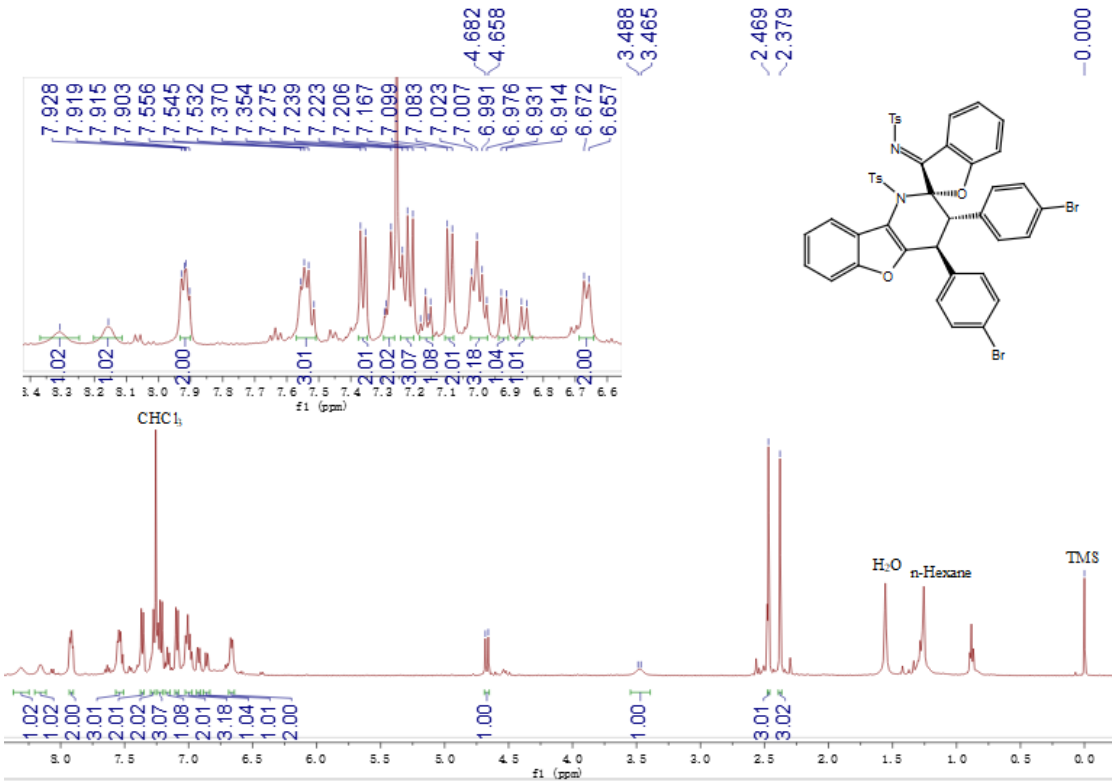
^{13}C{^{1}H} NMR of **2j** (125 MHz, $CDCl_3$)



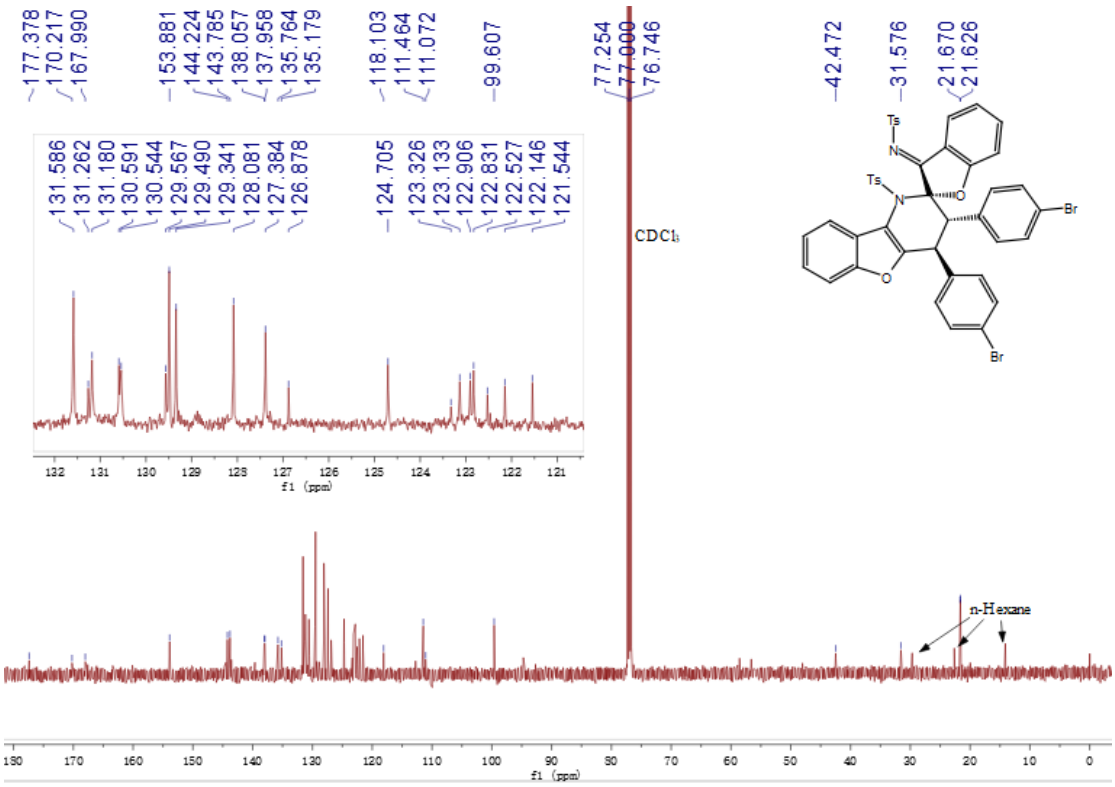
^{1}H NMR of **2k** (500 MHz, $CDCl_3$)



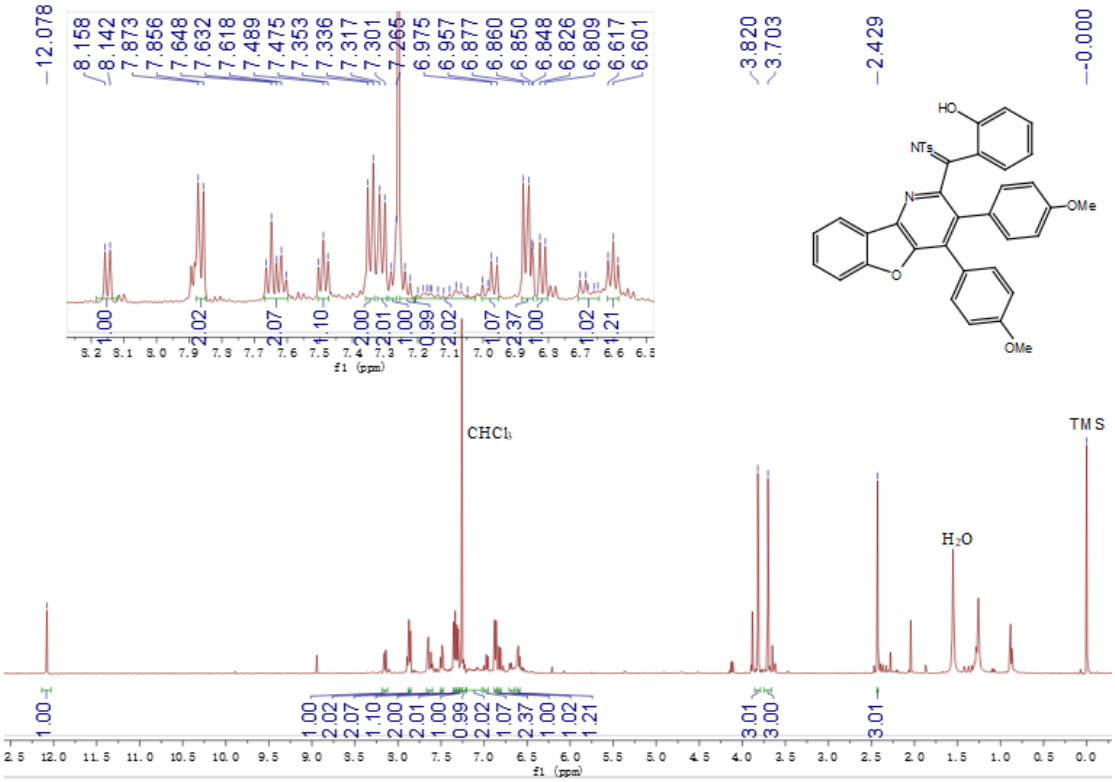
^{13}C{^{1}H} NMR of **2k** (125 MHz, $CDCl_3$)



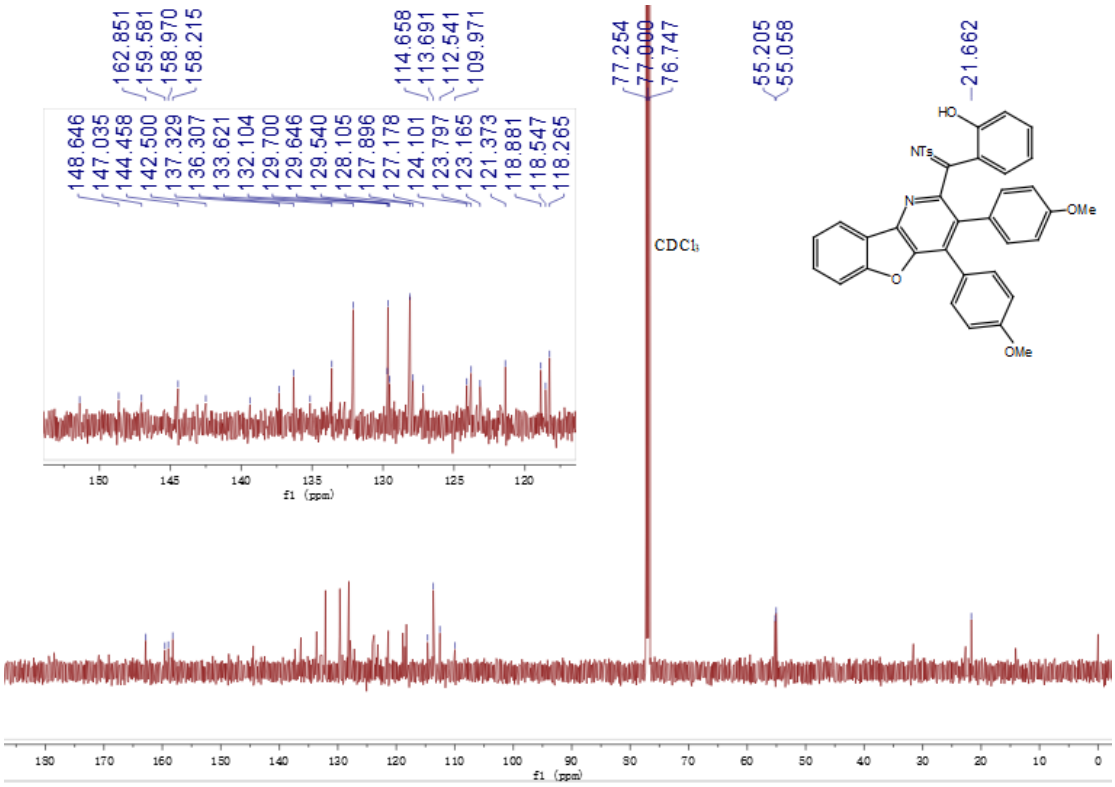
^{1}H NMR of **3k** (500 MHz, $CDCl_3$)



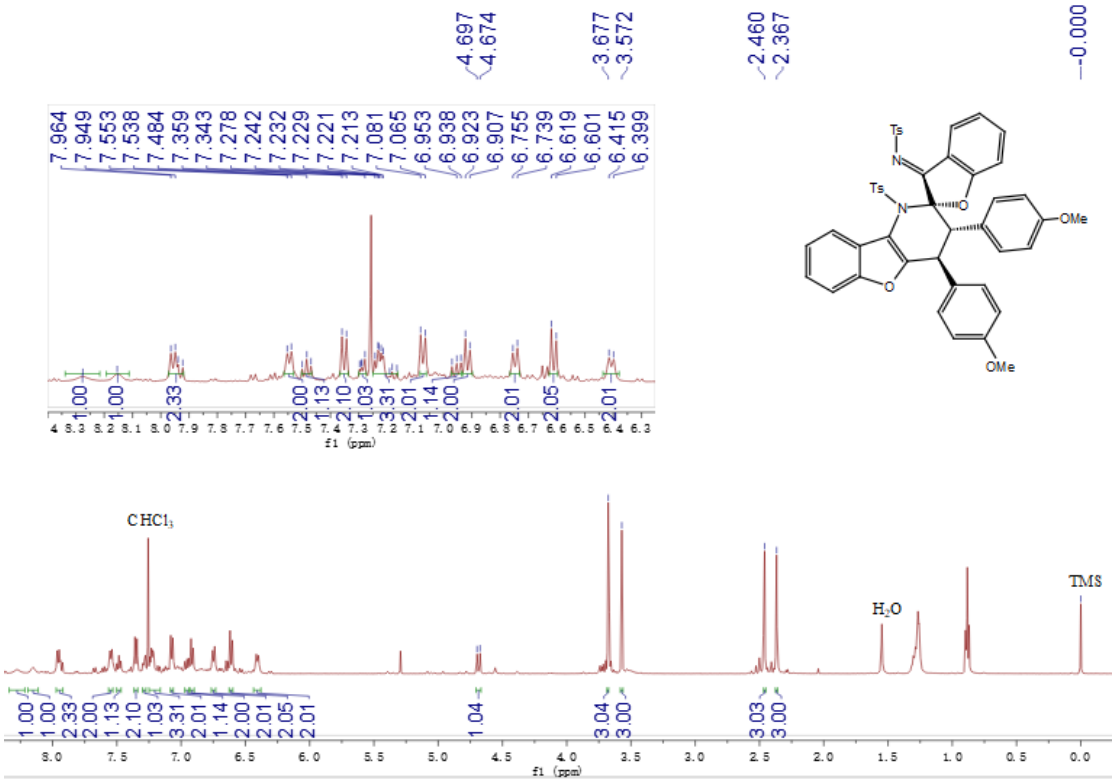
^{13}C{^{1}H} NMR of **3k** (125 MHz, $CDCl_3$)



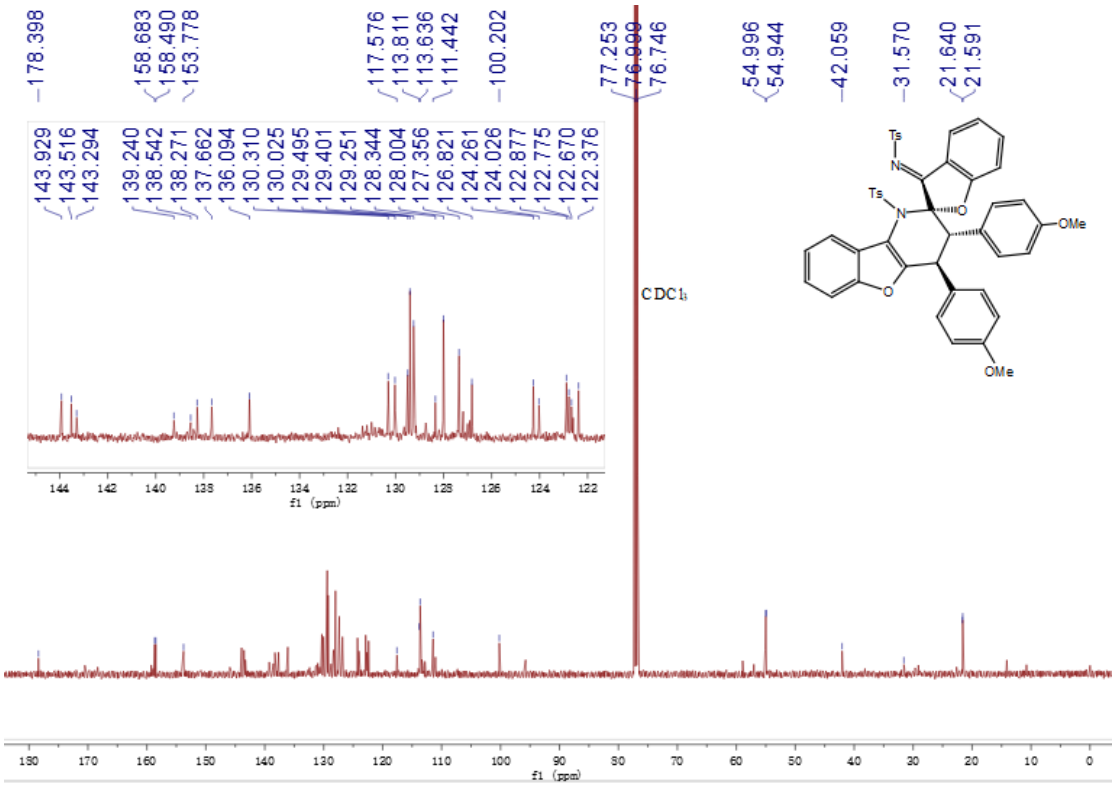
^{1}H NMR of **2l** (500 MHz, $CDCl_3$)



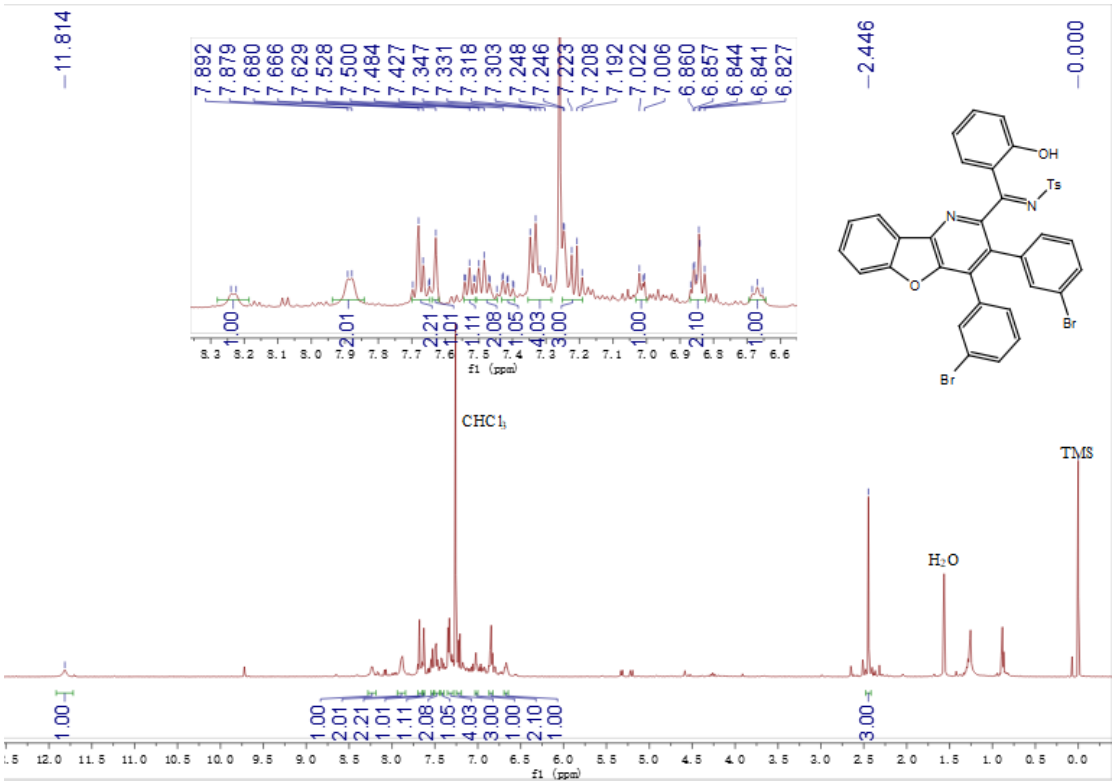
^{13}C{^{1}H} NMR of **2l** (125 MHz, $CDCl_3$)



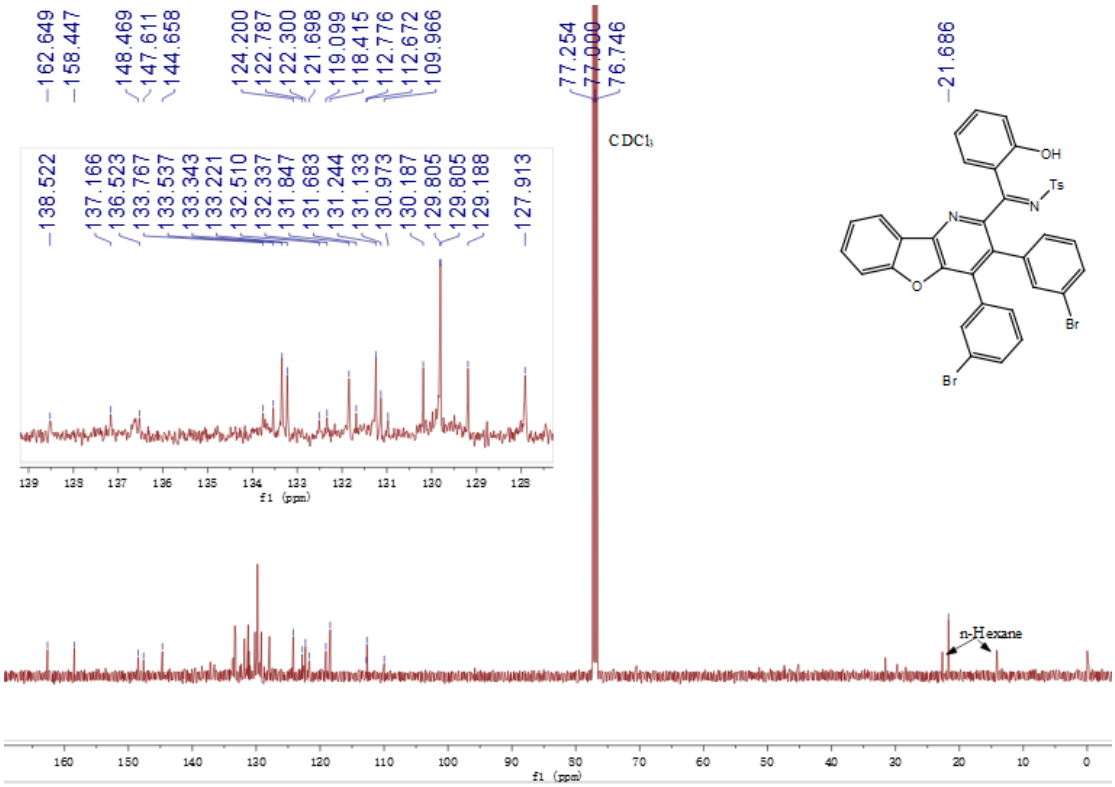
^{1}H NMR of **3l** (500 MHz, $CDCl_3$)



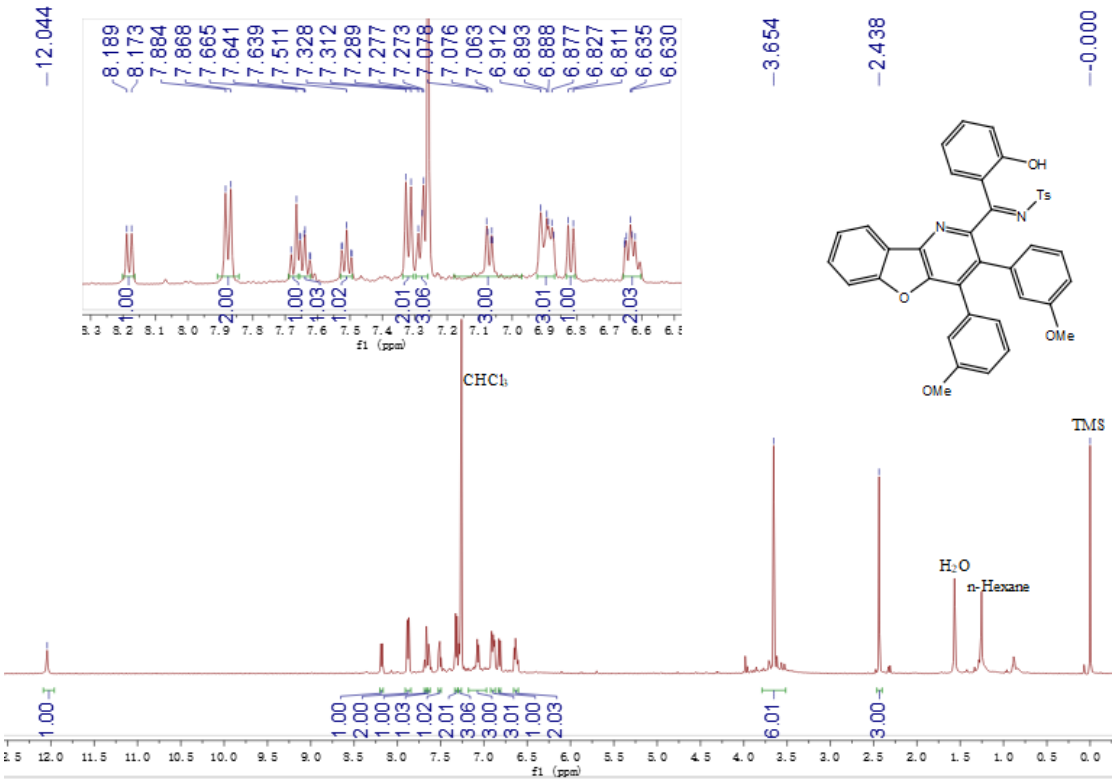
^{13}C{^{1}H} NMR of **3l** (125 MHz, $CDCl_3$)



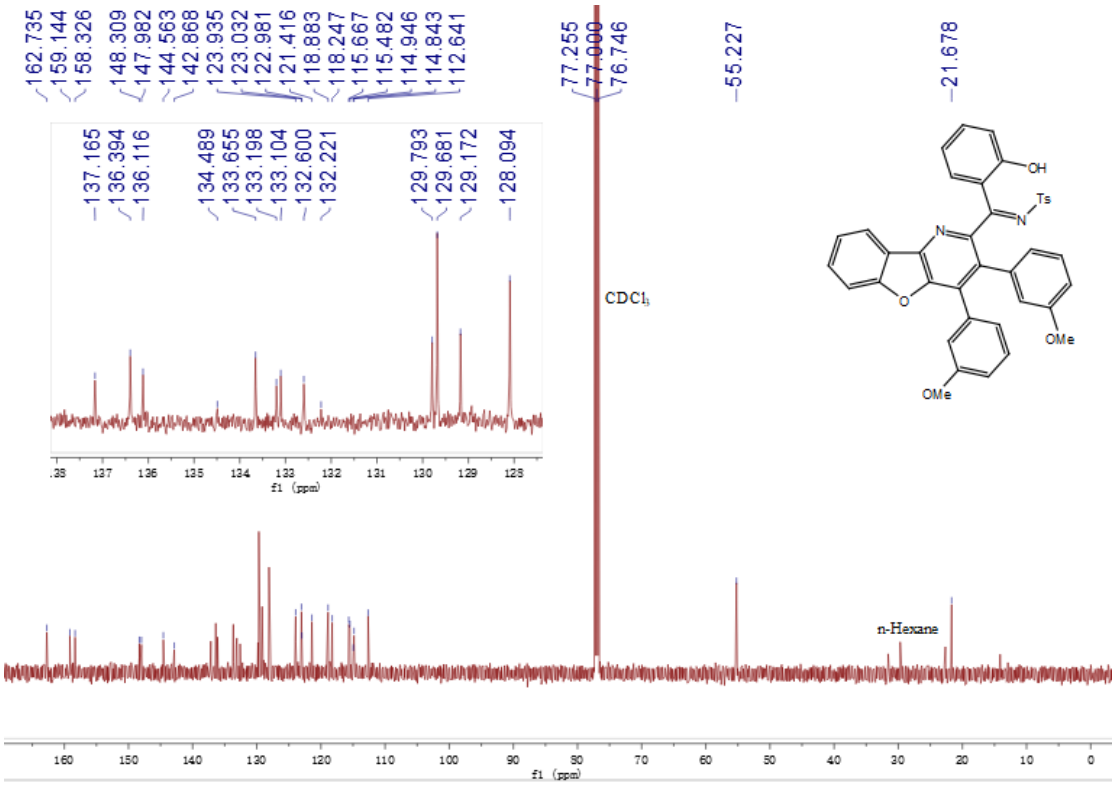
^{1}H NMR of **2m** (500 MHz, $CDCl_3$)



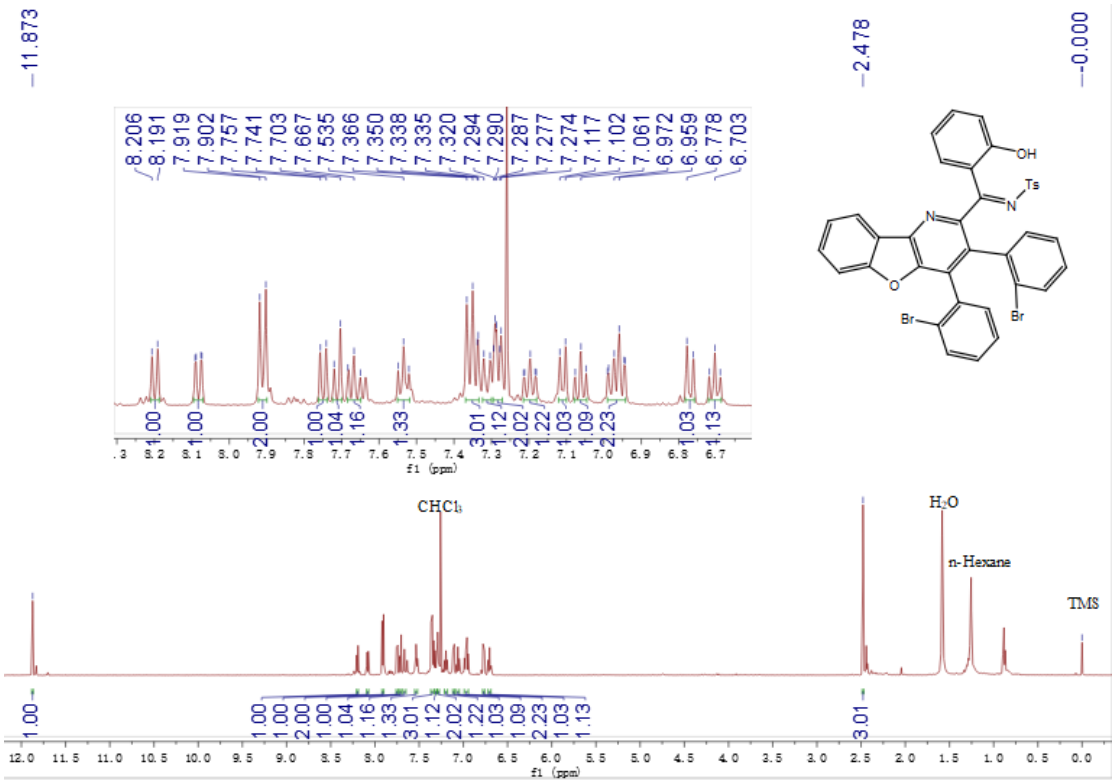
^{13}C{^{1}H} NMR of **2m** (125 MHz, $CDCl_3$)



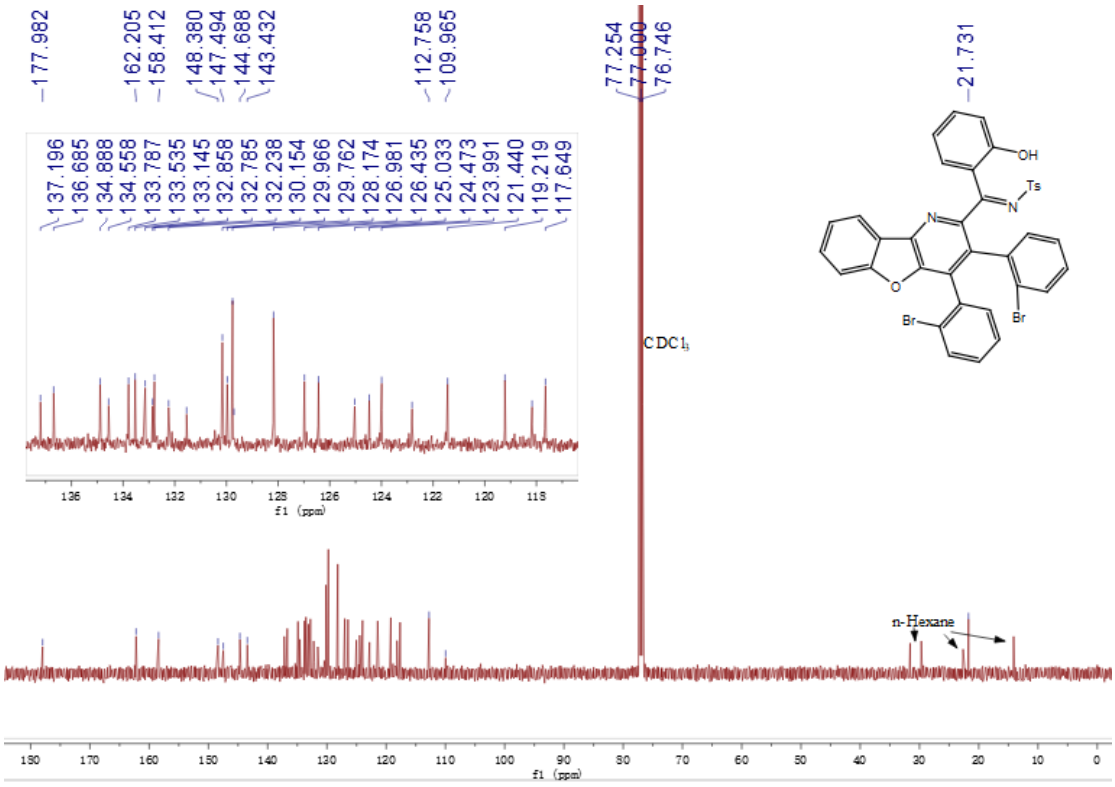
^{1}H NMR of **2n** (500 MHz, $CDCl_3$)



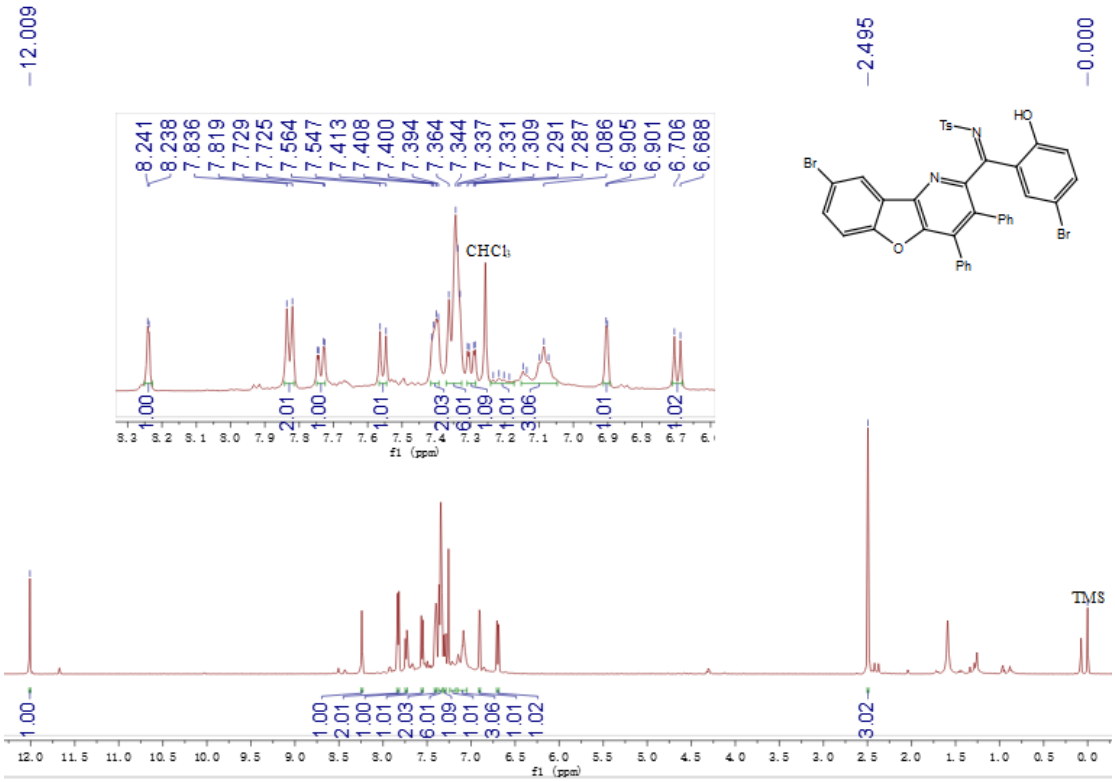
^{13}C{^{1}H} NMR of **2n** (125 MHz, $CDCl_3$)



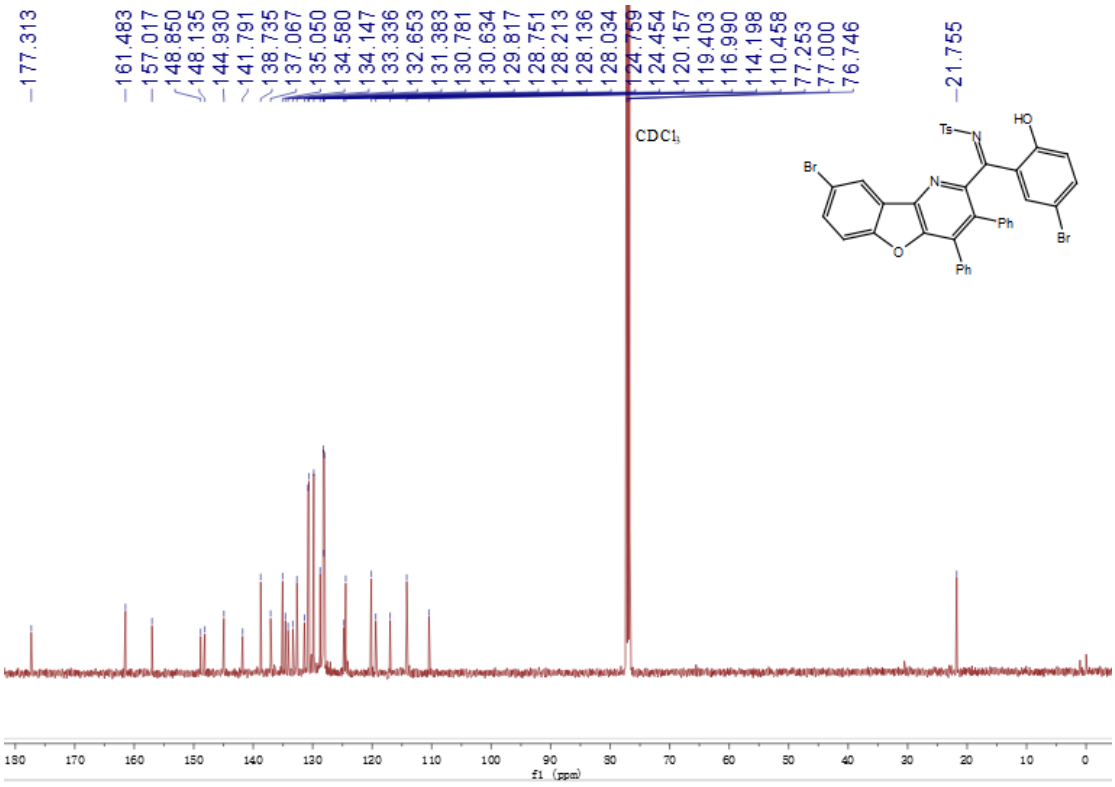
^{1}H NMR of **2o** (500 MHz, $CDCl_3$)



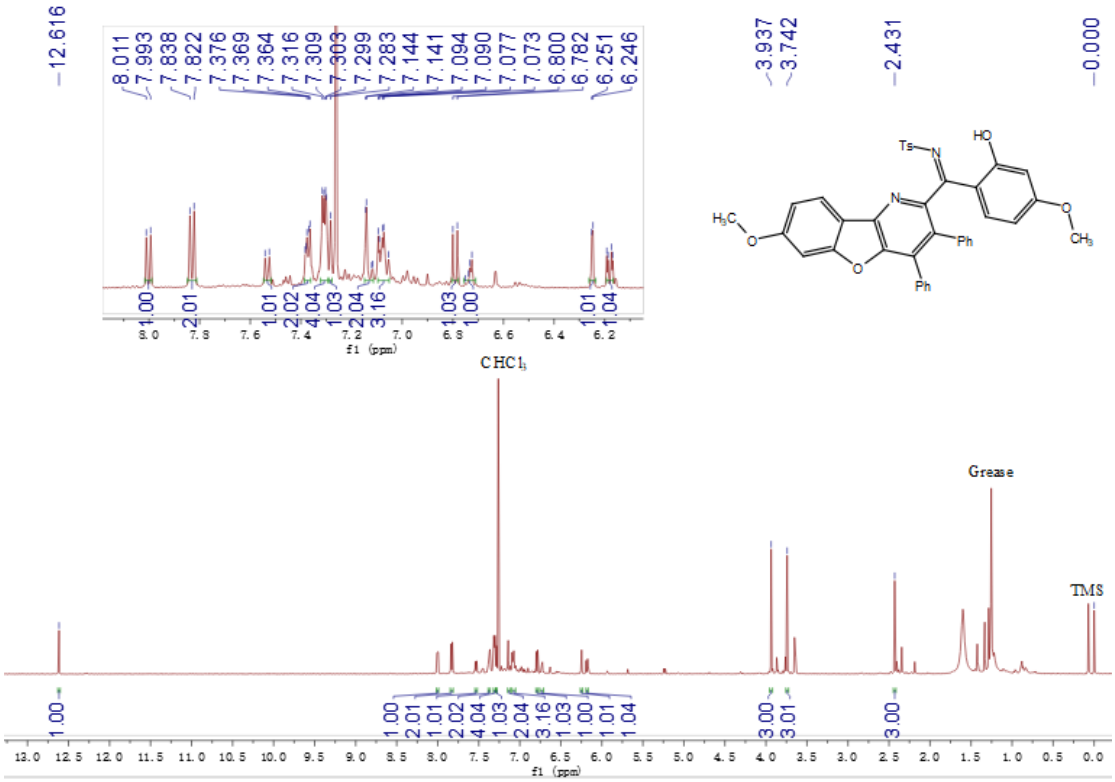
^{13}C{^{1}H} NMR of **2o** (125 MHz, $CDCl_3$)



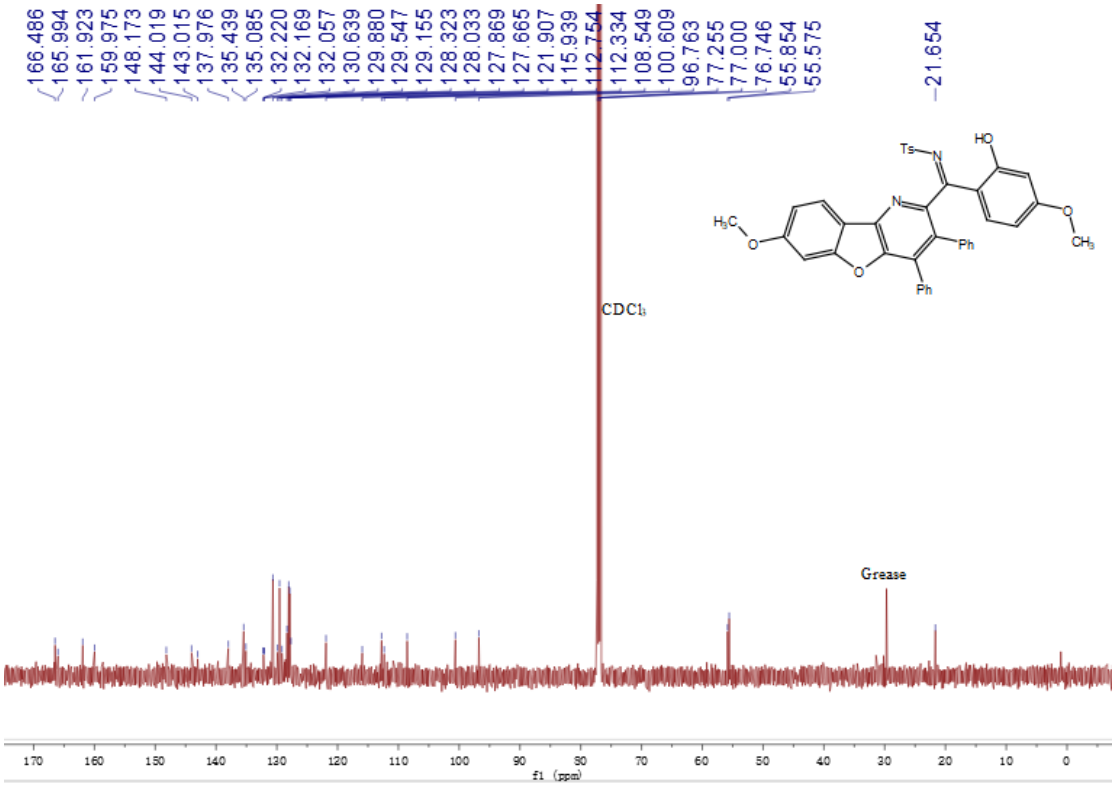
^{1}H NMR of **2q** (500 MHz, $CDCl_3$)



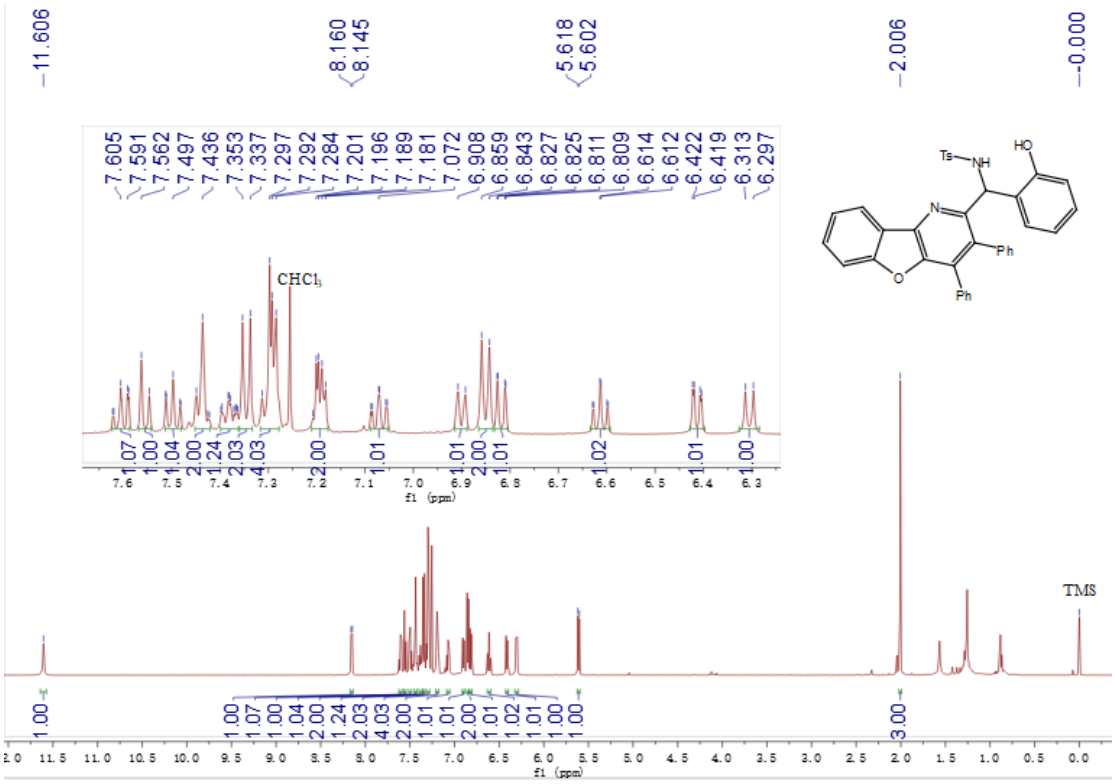
^{13}C{^{1}H} NMR of **2q** (125 MHz, $CDCl_3$)



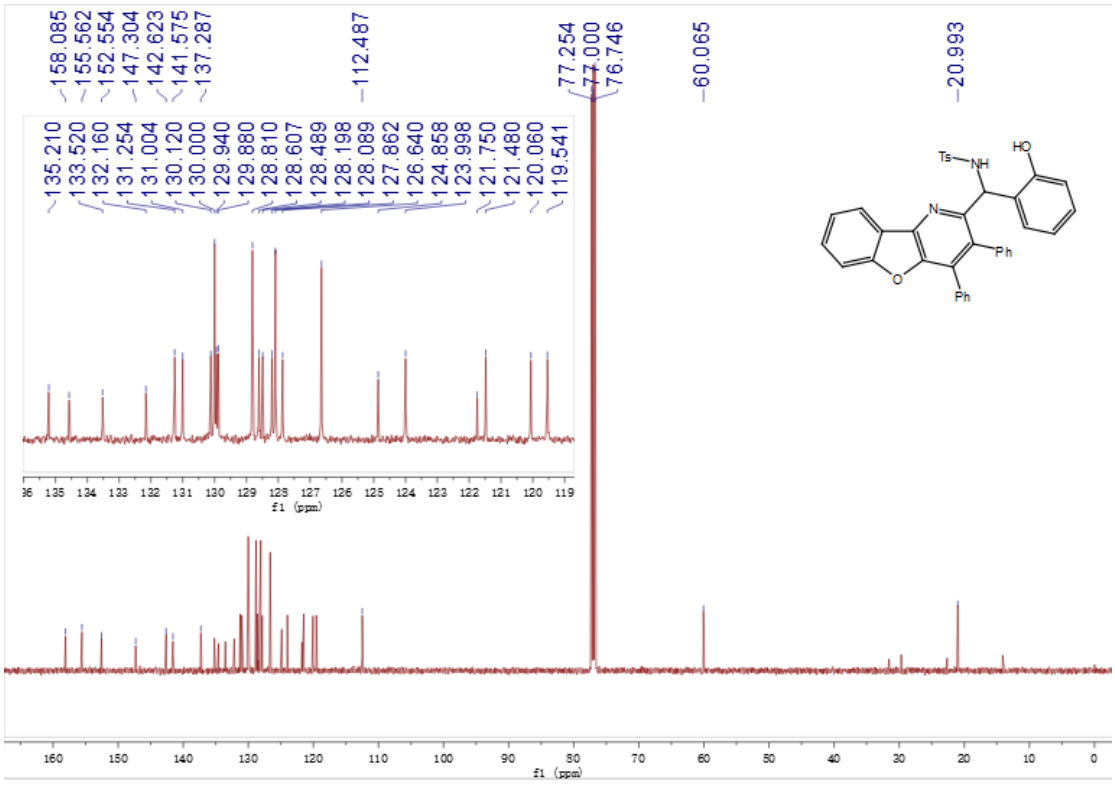
^{1}H NMR of **2r** (500 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR of **2r** (125 MHz, $CDCl_3$)



^{1}HNMR of **4** (500 MHz, $CDCl_3$)

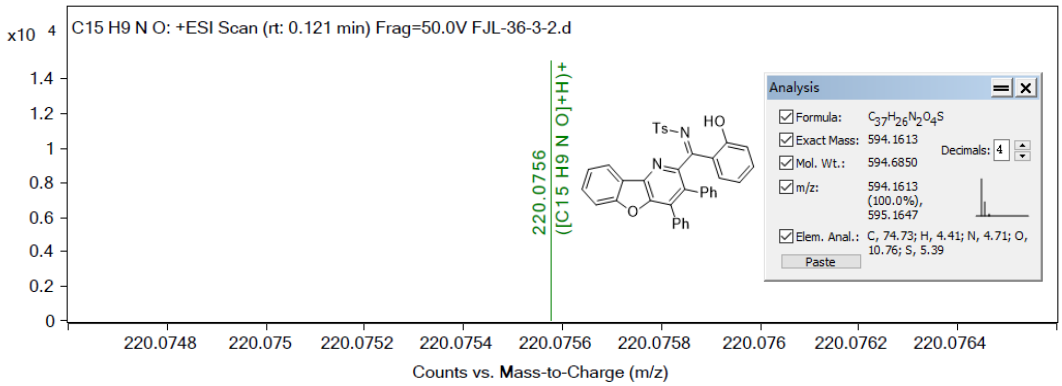


^{13}C{^{1}H} NMR of **4** (125 MHz, $CDCl_3$)

6. Copies of HRMS spectra of 2a and 3a

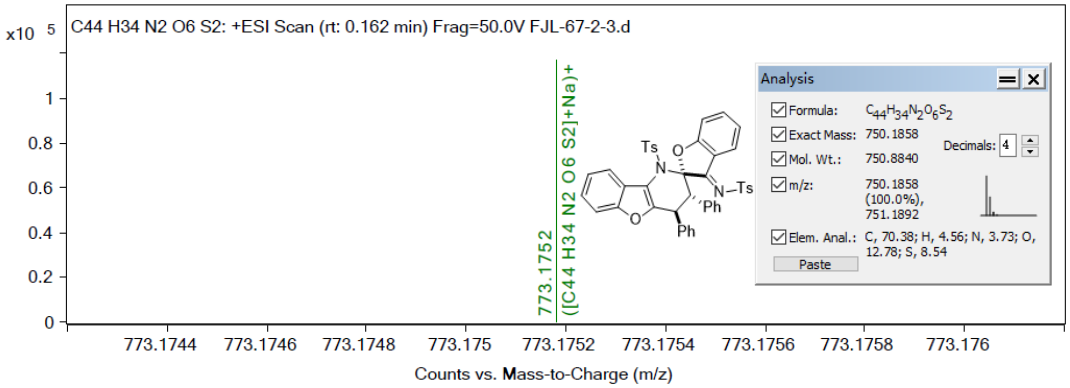
(1) HRMS (ESI-TOF) spectra of **2a**

Fragmentor Voltage	Collision Energy	Ionization Mode
50	0	ESI

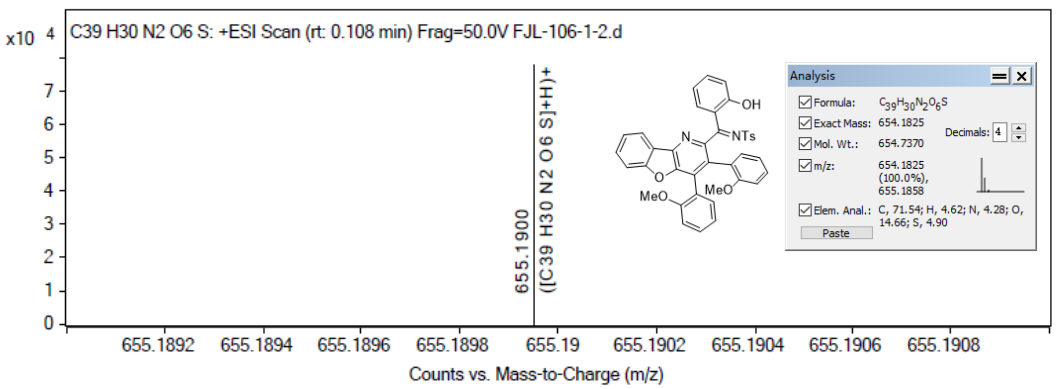


(2) HRMS (ESI-TOF) spectra of **3a**

Fragmentor Voltage	Collision Energy	Ionization Mode
50	0	ESI



(3) HRMS (ESI-TOF) spectra of **2p**



7. X-Ray crystallography of 2a and 3a

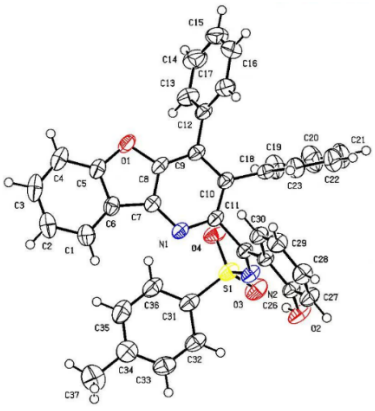
(1) Method for crystal growth of **2a** and **3a**

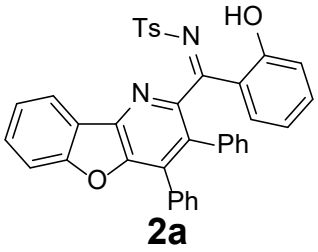
The solid product 15 mg was added to a 25 mL round bottom flask fixed with a reflux condenser. 1 mL of *n*-hexane was added to the flask and heated to the boiling point of solvent. After the nhexane started to boil and cool down by reflux condenser, 1 mL of dichloromethane (DCM) was added to the flask. The solvent system *n*-hexane/DCM was added in 1:1 ratio with continues stirring and heating, until all the solid was dissolved. Flask was kept with reflux condenser on for several days at room temperature, until tiny crystals started to grow in the bottom of flask, which subsequently grew with time.

(2) Procedure for crystal measurement of **2a** and **3a**

A suitable crystal (0.01mm*0.02mm*0.03mm) was selected and mounted on a Bruker D8 venture diffractometer with Mo Ka radiation (λ = 0.71073 Å) for cell determination and subsequent data collection at 170 K. Using Olex2,[2] the structure was solved with the ShelXT2 structure solution program using Intrinsic Phasing and refined with the ShelXL3 refinement package using Least Squares minimization.[3,4]

(3) The ORTEP and crystal parameters of **2a** wherein thermal ellipsoids are drawn at 50% probability level





2a

```
Bond precision:   C-C = 0.0037 A          Wavelength=1.34139

Cell:          a=7.8835(12)       b=14.574(2)      c=16.220(2)
               alpha=108.513(4)   beta=90.182(4)   gamma=98.579(5)
Temperature:   250 K
```

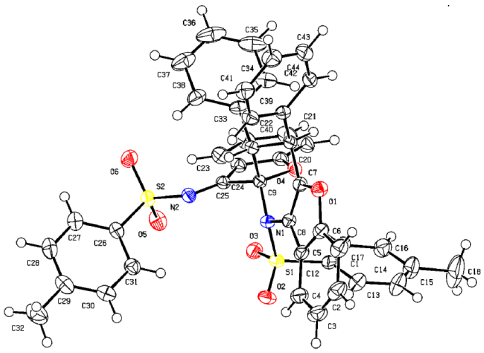
	Calculated	Reported
Volume	1744.8(4)	1744.8(4)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C37 H26 N2 O4 S, C4 H8 O2	C37 H26 N2 O4 S, C4 H8 O2
Sum formula	C41 H34 N2 O6 S	C41 H34 N2 O6 S
Mr	682.76	682.76
Dx,g cm-3	1.300	1.300
Z	2	2
Mu (mm-1)	0.807	0.807
F000	716.0	716.0
F000'	718.18	
h,k,lmax	9,18,20	9,18,20
Nref	7211	7126
Tmin,Tmax	0.962,0.984	0.649,0.751
Tmin'	0.831	

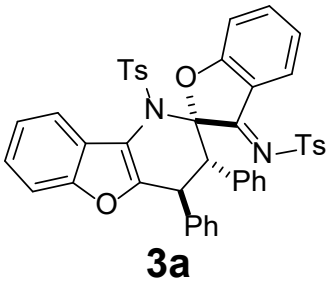
```
Correction method= # Reported T Limits: Tmin=0.649 Tmax=0.751
AbsCorr = MULTI-SCAN

Data completeness= 0.988          Theta(max)= 57.286

R(reflections)= 0.0573( 5180)                wR2(reflections)=
                                             0.1551( 7126)
S = 1.080                  Npar= 455
```

(4) The ORTEP and crystal parameters of **3a** wherein thermal ellipsoids are drawn at 50% probability level





3a

Bond precision: C-C = 0.0024 A Wavelength=1.34139

Cell: a=10.1396(5) b=16.5438(8) c=23.8646(12)
alpha=90 beta=101.338(2) gamma=90
Temperature: 170 K

	Calculated	Reported
Volume	3925.1(3)	3925.1(3)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	C44 H34 N2 O6 S2 [+ solvent]	C44 H34 N2 O6 S2
Sum formula	C44 H34 N2 O6 S2 [+ solvent]	C44 H34 N2 O6 S2
Mr	750.85	750.85
Dx,g cm-3	1.271	1.271
Z	4	4
Mu (mm-1)	1.070	1.070
F000	1568.0	1568.0
F000'	1573.68	
h,k,lmax	13,21,30	13,21,30
Nref	9005	8990
Tmin,Tmax	0.938,0.958	0.673,0.752
Tmin'	0.908	

Correction method= # Reported T Limits: Tmin=0.673 Tmax=0.752
AbsCorr = MULTI-SCAN

Data completeness= 0.998 Theta(max)= 60.636

R(reflections)= 0.0393(7532) wR2(reflections)= 0.1121(8990)

S = 1.058 Npar= 489

8. References

1. S. Wang, X. Niu, H. Zhou, J. Cao, C. Guo, J. Chang, B. Zhu. Acid-Regulated Selective Synthesis of Benzofuran Derivatives via Single-Component BDA Retro-Aldol/Michael Addition Cascade and [4 + 2] Cycloaddition Reactions. *J. Org. Chem.* 2025, **90**, 7104−7119.

2. Dolomanov, O.V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H., OLEX2: a complete structure solution, refinement and analysis program, *J. Appl. Cryst.* 2009, **42**, 339-341.

3. Sheldrick, G. M., SHELXT – Integrated space-group and crystal structure determination, *Acta Cryst.* 2015, **A71**, 3-8.

4. Sheldrick, G. M. Crystal structure refinement with SHELXL, *Acta Cryst.* 2015, **C71**, 3-8.