Supporting Information

Visible-Light-Induced meta-Selective Sulfonylation of Pyridine via an EDA Complex

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Table of Contents

1. General Information

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. Light source used for illuminating the reaction vessel (commercial supplier: Synthware) consisted of white light LEDs were purchased from Taobao (https://gpiled.taobao.com). The emission spectra of the lamps and photoreaction setup were shown in figure S1. In the reaction system, the photoreaction tube (8 mm ID/10 mm OD) was placed 2 cm from the front of the lamp source. The bottom of the light source was aligned flush with the magnetic stirring platform. A clip fan was placed over the reaction vial to cool down the reaction system during the whole process of the reaction. ^{1}H NMR spectra were recorded at Bruker AVANCE III 400 MHz or 500 MHz. The chemical shifts were recorded in *ppm* relative to tetramethylsilane and with the solvent resonance as the internal standard. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br s = broad singlet, p = quintet, h = sextet, hept = septet, m = multiplet), coupling constants (Hz), integration. ^{13}C NMR data were collected at 101 MHz or 126 MHz with complete proton decoupling. ^{19}F NMR data were collected at 376 MHz with complete proton decoupling. Infrared spectra (IR) were measured by FT-IR apparatus (Thermofisher IS10). High resolution mass spectroscopy (HRMS) was recorded at a Bruker quadrupole time of flight MS system equipped with an electrospray ionization source (Bruker compact, Bremen, Germany), and acetonitrile or methanol was used to dissolve the sample. Emission intensities were recorded using Perkin-Elemer LS 55 fluorescence spectrometer. Column chromatography was carried out on silica gel (200 - 300 mesh). Melting points (m.p.) were measured by Büchi 510 melting point apparatus and uncorrected. Some sulfonylation products (eg. **4e**, **4f** et. al.), containing aliphatic impurities or residual solvent, were quantified by ^{1}H-NMR analysis with an internal reference, 0.05 mmol 1,3,5-trimethoxybenzene added into the sulfonylation products.

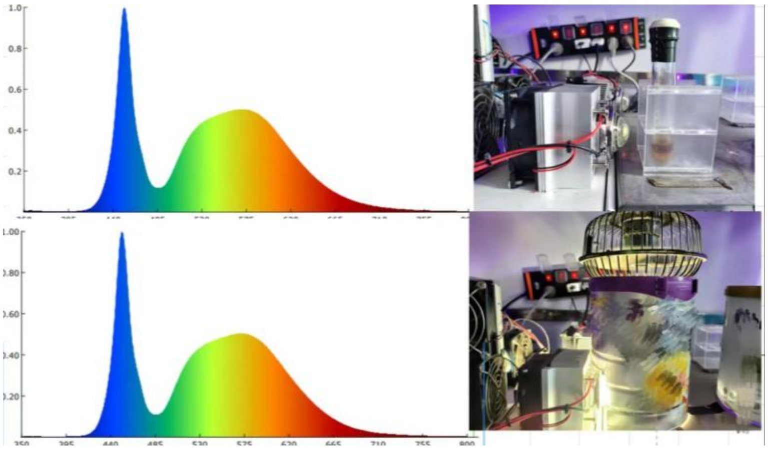


Figure S1. Emission spectra of the lamps used and the photoreaction setup

2. Procedures for the Synthesis of Starting Materials and Products.

2.1 Preparation of the oxazino pyridine intermediates 1a-1n[1]

A solution of substituted pyridine (10 mmol, 1.0 equiv.), methyl pyruvate (2.0 equiv.) in acetonitrile (0.5 M, 20 mL) was added in a 100 mL round-bottom flask equipped with a magnetic stirring bar. Then, dimethyl acetylenedicarboxylate (2.0 equiv.) was added dropwise to the stirred reaction mixture. The reaction mixture was stirred at room temperature for 2 to 7 day. After the reaction was completed, as monitored by TLC, the solvent was removed with a rotary evaporator under reduced pressure and the residue was subjected to flash column chromatography over silica gel to give the corresponding dearomatized heteroarene product.

2.2 Preparation of the sulfonylated oxazino pyridine intermediates 3a

1a (0.15 mmol, 1.0 equiv.), TsCl (0.6 mmol, 4.0 equiv.), KI (0.3 mmol, 2.0 equiv.), K_2HPO_4 (0.45 mmol, 3.0 equiv.), in acetonitrile (3.0 mL) was stirred at room temperature for 8 h under irradiation of 30 W white light (distance app. 2 cm) for synthesis of **3a**. The reaction tube was evacuated and backfilled with argon three times before light irradiation. After the reaction was completed, the solvent was removed with a rotary evaporator under reduced pressure and the product was then purified by flash chromatography using silica gel (petroleum ether/EtOAc =3:1 - 1:1).

2.3 Preparation of the product 4a – 4n, 4p – 4x, 4ab – 4ac

1 (0.15 mmol, 1.0 equiv.), **2** (0.6 mmol, 4.0 equiv.), KI (0.3 mmol, 2.0 equiv.), K_2HPO_4 (0.45 mmol, 3.0 equiv.), in acetonitrile (3 mL) was stirred at room temperature for 8 h under irradiation of 30 W white light (distance app. 2 cm) for the synthesis of **4a – 4n, 4p – 4x, 4ab – 4ac**. Then, the reaction mixture was added to ethyl acetate (30 mL) and washed by water (3 × 3 mL), and concentrated under reduced pressure. After that, the residual was transferred to a 25 mL round-bottom flask, with acetonitrile (3 mL) and 6 N HCl (5 mL) added. The flask was heated at 80 °C for 24 h. The reaction mixture was neutralized with saturated Na_2CO_3 and extracted by dichloromethane or ethyl acetate (3 × 10 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The product was purified by flash chromatography using silica gel (petroleum ether/EtOAc =9:1 - 4:1).

2.4 Preparation of the product 4o

4-Quinolone (0.15 mmol, 1.0 equiv.), **2a** (0.6 mmol, 4.0 equiv.), KI (0.3 mmol, 2.0 equiv.), K_2HPO_4 (0.45 mmol, 3.0 equiv.), in acetonitrile (3 mL) was stirred at room temperature for 8 h under irradiation of 30 W white light (distance app. 2 cm) for the synthesis of **4o**. Then, the reaction mixture was concentrated under reduced pressure. The product was purified by flash chromatography using silica gel (petroleum ether/EtOAc =9:1 - 4:1).

2.5 Preparation of the product 4y-4aa

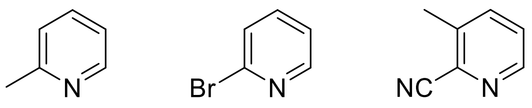
1 (0.15 mmol, 1.0 equiv.), **2** (0.6 mmol, 4.0 equiv.), KI (0.3 mmol, 2.0 equiv.), K_2HPO_4 (0.45 mmol, 3.0 equiv.) in tetrahydrofuran (3 mL) was stirred at room temperature for 24 h under irradiation of 30 W white light (distance app. 2 cm) for the synthesis of **4y – 4aa**. Then, the reaction mixture was added to ethyl acetate (30 mL) and washed by water (3 × 3 mL), and concentrated under reduced pressure. Then, acetonitrile (3 mL) and 6 N HCl (5 mL) was added to the 25 mL round-bottom flask and the flask was heated at 80 °C for 24 h. The reaction mixture was neutralized with saturated Na_2CO_3 and extracted by dichloromethane or ethyl acetate (3 × 10 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The product was purified by flash chromatography using silica gel (petroleum ether/EtOAc =9:1 - 4:1).

2.6 Scale-up reaction

1a (1.5 mmol, 1.0 equiv.), **2a** (6.0 mmol, 4.0 equiv.), KI (3.0 mmol, 2.0 equiv.), K_2HPO_4 (4.5 mmol, 3.0 equiv.) in acetonitrile (30 mL) was stirred at room temperature for 24 h under irradiation of 2 × 30 W white light (distance app. 2 cm). Then, the reaction mixture was added to ethyl acetate

(100 mL) and washed by water (3 × 10 mL), and concentrated under reduced pressure. Then, acetonitrile (3 mL) and 6 N HCl (50 mL) was added to the 250 mL round-bottom flask and the flask was heated at 80 °C for 24 h. The reaction mixture was neutralized with saturated Na_2CO_3 and extracted by dichloromethane (3 × 80 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The product was purified by flash chromatography using silica gel (petroleum ether/EtOAc =9:1 - 4:1).

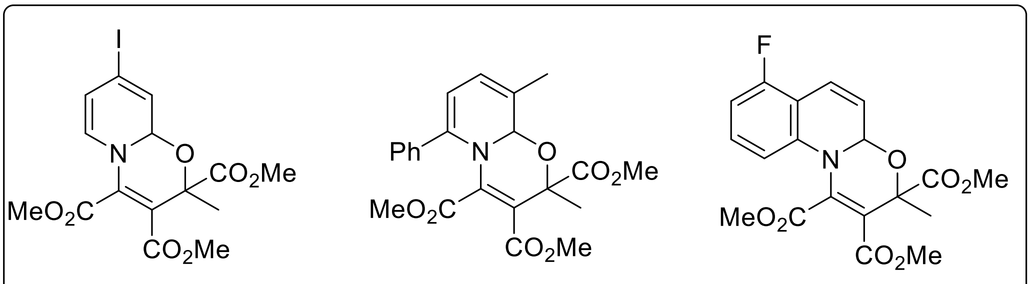
2.7 Unsuccessful substrates for the preparation of oxazino pyridine intermediates



1aa **1ab** **1ac**

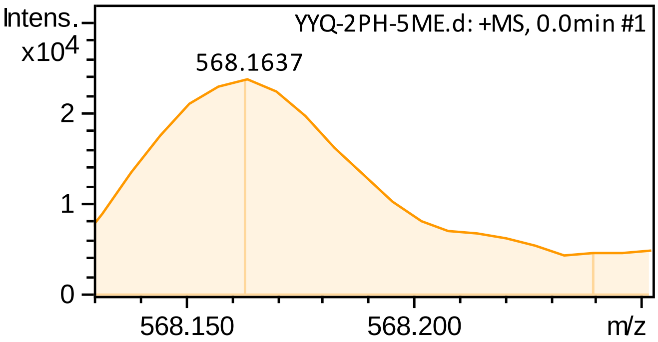
unsuccessful cases

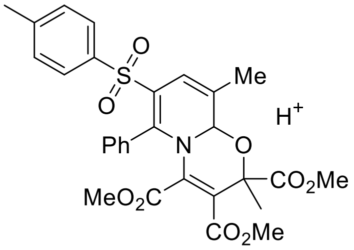
2.8 Unsuccessful substrates for the sulfonylation transformation



unsuccessful cases

For 2-Ph-5-Me pyridine substrate was evaluated under the standard reaction conditions. However, most of the starting material remained unreacted, and the sulfonylation products were not observed, as monitored by TLC analysis. High-resolution mass spectrometry (HRMS) analysis of the reaction mixture suggested the formation of a potential C3-sulfonylation product, albeit in trace quantities.





Exact Mass: 568.1636

3. Mechanistic studies

3.1 UV-Vis spectrum experiments

A variety of solutions of TsCl, KI, TsCl+KI (1:1) in acetonitrile were prepared. Then, the UV/Vis absorption spectra of a series of solutions were recorded on Shimadzu UV-2600 spectrometer.

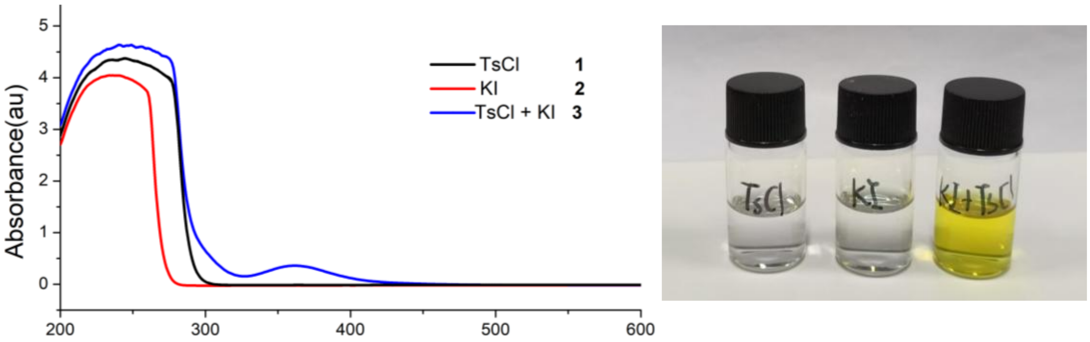


Figure S2. Absorbance of 5×10^{-4} M solution of TsCl, KI, TsCl+KI (1:1) in acetonitrile

The solutions of cyclopropanesulfonyl chloride **2y**, KI, and **2y**+KI (1:1) in tetrahydrofuran were prepared. Then, the UV/Vis absorption spectra were recorded on Shimadzu UV-2600 spectrometer.

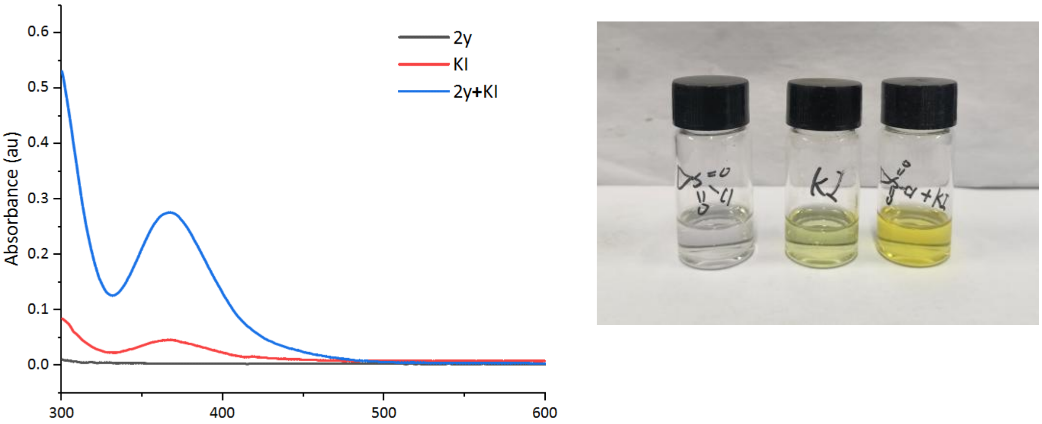
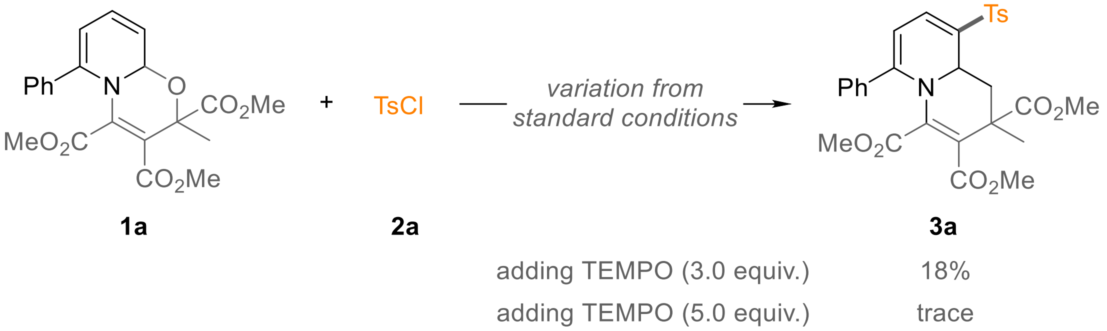


Figure S3. Absorbance of 5×10^{-3} M solution of **2y**, KI, **2y**+KI (1:1) in tetrahydrofuran

3.2 Trapping experiment



Oxazino pyridine intermediate **1a** (0.15 mmol, 1.0 equiv.), sulfonyl chlorides **2a** (0.6 mmol, 4.0 equiv.), KI (0.3 mmol, 2.0 equiv.), K_2HPO_4 (0.45 mmol, 3.0 equiv.), TEMPO (3.0 or 5.0 equiv.) in acetonitrile (3 mL) was stirred at room temperature for 8 h under irradiation of 30 W white light (distance app. 3 cm). In the presence of 3.0 equivalents of TEMPO, only 18% yield of product **3a** was obtained. The reaction seemed to be fully suppressed with 5.0 equivalents of TEMPO, as the desired product was not detected by TCL.

3.3 Time profile of the transformation with light ON/OFF over time

The reaction of **1a** and 2-fluorobenzenesulfonyl chloride **2q** was set up on a 0.15 mmol scale according to the standard procedure, and extra 1.0 equiv. of benzotrifluoride was added as the internal standard. The reaction tube was placed under light-on/light-off environment with 10 min interval. At every 10th minutes, an aliquot (200 μL) from the reaction mixture was transferred into a nuclear magnetic tube charged with 0.4 mL of $CDCl_3$. The yield of product was determined by ^{19}F NMR analysis (Figure S2).

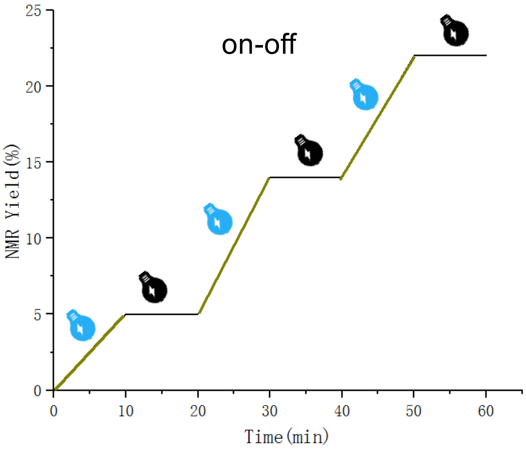
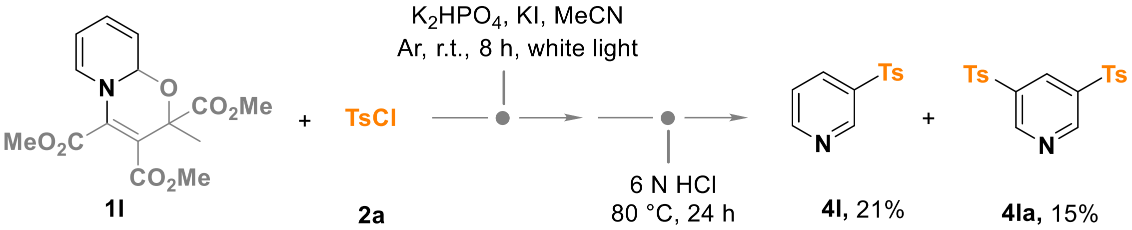
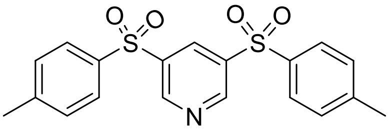


Figure S4: Time profile of the transformation with the light ON/OFF over time.

3.4 Determination of difunctionalized product



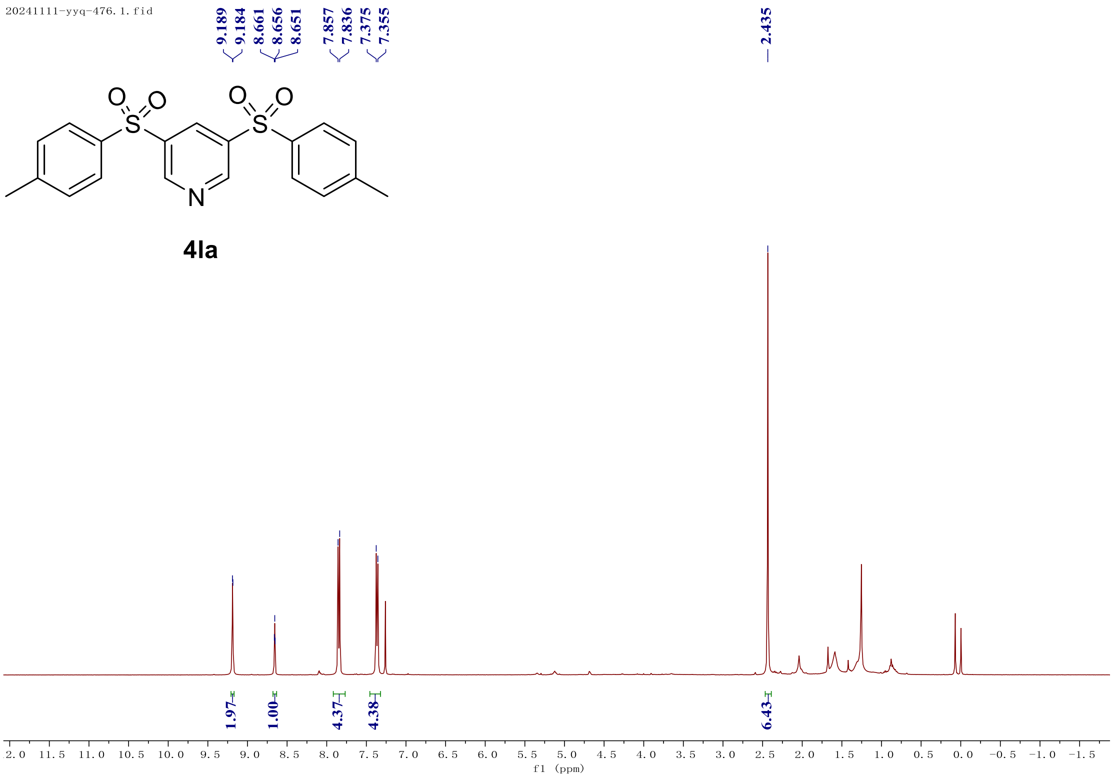
Oxazino pyridine intermediate **1l** (0.15 mmol, 1.0 equiv.), sulfonyl chloride **2a** (0.6 mmol, 4.0 equiv.), K_2HPO_4 (0.45 mmol, 3.0 equiv.), KI (0.3 mmol, 2.0 equiv.) in acetonitrile (3 mL) was stirred at room temperature for 8 h under irradiation of 30 W white light (distance app. 2 cm). Then, the reaction mixture was added to ethyl acetate (30 mL) and washed by water (3 × 3 mL), and concentrated under reduced pressure. After that, the residual was transferred to a 25 mL round-bottom flask, with acetonitrile (3 mL) and 6 N HCl (5 mL) added. The flask was heated at 80 °C for 24 h. The reaction mixture was neutralized with saturated Na_2CO_3 and extracted by dichloromethane or ethyl acetate (3 × 10 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The product was purified by flash chromatography using silica gel (petroleum ether/EtOAc =9:1 - 4:1).



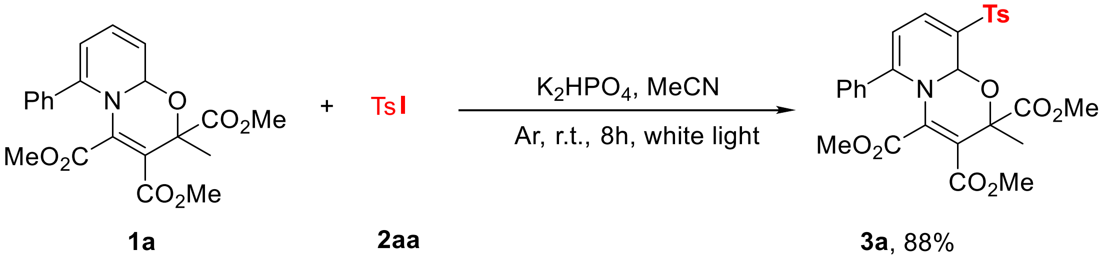
4la

4la, ^1H NMR (400 MHz, Chloroform-*d*) δ 9.19 (d, *J* = 2.2 Hz, 2H), 8.67 – 8.64 (m, 1H), 7.85 (d, *J* = 8.2 Hz, 4H), 7.37 (d, *J* = 8.1 Hz, 4H), 2.43 (s, 6H).

4la: ^{1}H NMR (400 MHz, $CDCl_3$).

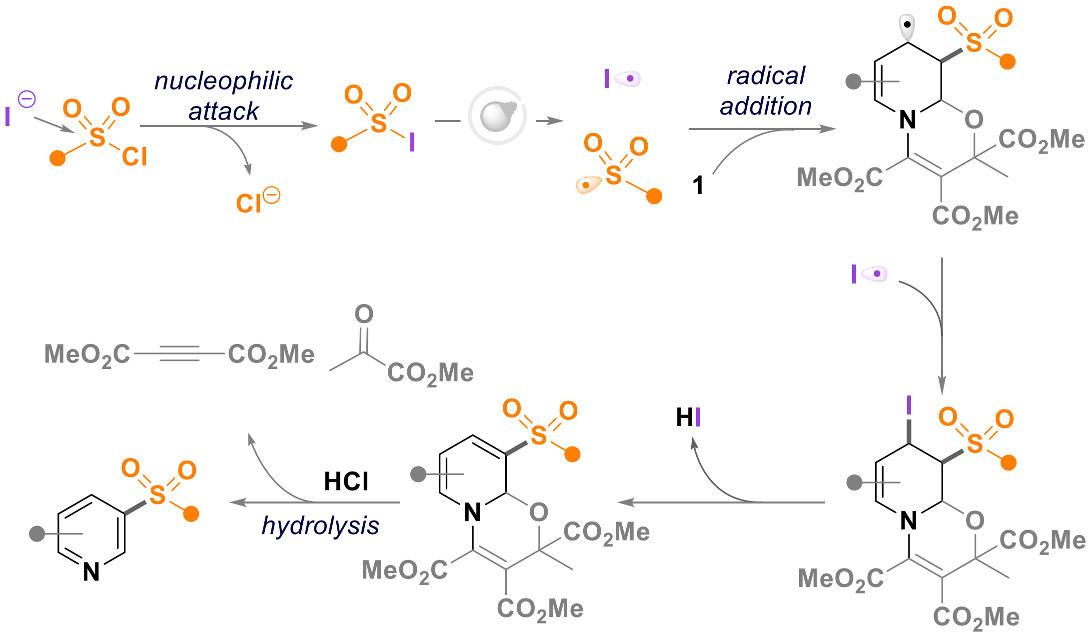


3.5 Determination of RSO_2I intermediate



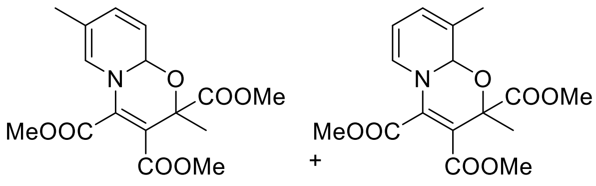
Scheme S1. TsI-promoted sulfonylation

Oxazino pyridine intermediate **1a** (0.15 mmol, 1.0 equiv.), sulfonyl idoine **2aa** (0.6 mmol, 4.0 equiv.), K_2HPO_4 (0.45 mmol, 3.0 equiv.) in acetonitrile (3 mL) was stirred at room temperature for 8 h under irradiation of 30 W white light (distance app. 2 cm). The reaction mixture concentrated under reduced pressure. The product was purified by flash chromatography using silica gel (petroleum ether/EtOAc =4:1 - 1:1).



Scheme S2. Plausible reaction mechanism through RSO_2I intermediate.

4. Characterization Data of Compounds

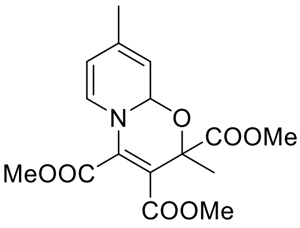


1d

1d, yellow solid, the product was purified by flash column chromatography (PE/EtOAc = 3:1 to 1:1) to afford the desired product; mp 104 - 106 °C; IR (neat) ν 3001, 2949, 1734, 1693, 1580, 1434, 1242, 1124, 1065, 732, 665 cm^{-1}; ^{1}H NMR (500 MHz, Chloroform-*d*), a mixture of regioisomers and diastereoisomers, δ 6.15 – 6.14 (m, 1 H), 5.97 – 5.95 (m, 1 H), 5.60 – 5.41 (m, 1 H), 5.22 – 5.18 (m, 1H), 3.904 – 3.898 (m, 3H), 3.75 – 3.74 (m, 3H), 3.71 – 3.70 (m, 3H), 1.86 – 1.85 (m, 3H), 1.74 – 1.73 (m, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*), a mixture of regioisomers and diastereoisomers, δ 171.5, 170.9, 165.04, 164.95, 163.8, 143.2, 142.6, 125.1, 124.7, 123.2, 123.0, 121.5, 121.1, 113.2, 112.0, 101.5, 101.4, 82.4, 81.5, 78.1, 77.3, 53.3, 53.2, 52.8, 52.7, 52.04, 51.98, 24.0, 23.8, 18.9, 18.8.

HRMS (ESI), $C_{16}H_{20}NO_7^+$ [M+H]$^+$ Calcd 338.1234, Found 338.1243.

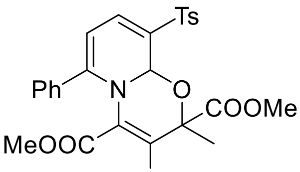


1j

1j, yellow solid, the product was purified by flash column chromatography (PE/EtOAc = 3:1 to 1:1) to afford the desired product; mp 143 - 145 °C; IR (neat) ν 2952, 1727, 1697, 1575, 1434, 1243, 1123, 1005, 914, 779, 663 cm-1; ^{1}H NMR (400 MHz, Chloroform-*d*), a mixture of diastereoisomers, δ 6.19 – 6.17 (m, 1H), 5.68 – 5.51 (m, 1H), 5.31 – 5.27 (m, 1H), 5.11 – 5.09 (m, 1H), 3.87 (s, 3H), 3.71 (s, 3H), 3.67 (s, 3H), 1.82 (s, 3H), 1.71 – 1.68 (m, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.2, 170.6, 164.8, 164.7, 163.6, 163.5, 142.7, 142.3, 134.7, 134.4, 125.0, 124.8, 113.2, 112.3, 111.5, 111.3, 104.6, 104.5, 79.5, 78.7, 77.6, 76.5, 53.3, 53.1, 52.9, 52.7, 52.0, 51.6, 23.9, 23.6, 21.3.

HRMS (ESI), $C_{16}H_{20}NO_7^+$ [M+H]$^+$ Calcd 338.1234, Found 338.1241.

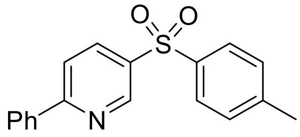


3a

3a, yellow solid, the product was purified by flash column chromatography (PE/EtOAc = 3:1 to 1:1) to afford the desired product; mp 160 - 161 °C; IR (neat) ν 3006, 2955, 1749, 1538, 1423, 1272, 1146, 1077, 924, 819, 670 cm^{-1}; ^{1}H NMR (500 MHz, Chloroform-*d*), a complex of two diastereoisomers, δ 7.82 – 7.76 (m, 2H), 7.53 – 7.40 (m, 2H), 7.41 – 7.27 (m, 5H), 7.24 – 7.22 (m, 1H), 6.10 – 5.77 (m, 1H), 5.51 – 5.41 (m, 1H), 3.95 – 3.89 (m, 3H), 3.69 – 3.67 (m, 3H), 3.15 – 3.14 (m, 3H), 2.42 (s, 3H), 1.79 – 1.64 (m, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*), a complex of two diastereoisomers, δ 169.3, 169.2, 165.2, 164.6, 162.3, 161.7, 145.8, 144.7, 144.2, 144.0, 141.0, 139.4, 139.0, 138.8, 135.8, 135.3, 134.7, 134.2, 130.2, 130.0, 129.9, 129.8, 129.7, 129.6, 128.6, 128.5, 128.18, 128.14 , 126.4 , 124.5 , 123.2 , 101.6, 101.5, 80.1, 79.8, 79.5, 79.1, 53.4, 53.1, 52.8, 52.5, 52.5, 52.4, 24.1. 21.72, 21.70.

HRMS (ESI), $C_{28}H_{28}NO_9S^+$ [M+H]$^+$ Calcd 554.1479, Found 554.1487.

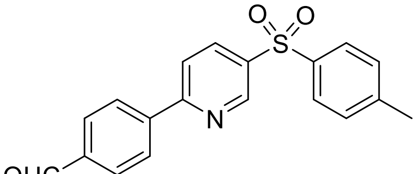


4a

4a, white solid (38.9 mg, 84%), the product was purified by flash column chromatography (PE/EtOAc = 9:1 to 4:1) to afford the desired product; mp 223 - 224 °C; IR (neat) v 2923, 2852, 1727, 1578, 1293, 1147, 1079, 733, 681, 584, 532 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.18 (d, *J* = 3.2 Hz, 1H), 8.38 (dd, *J* = 8.5, 2.5 Hz, 1H), 8.18 (dd, *J* = 8.5, 0.8 Hz, 1H), 8.16 – 8.06 (m, 2H), 7.99 – 7.89 (m, 2H), 7.55 – 7.51 (m, 3H), 7.50 – 7.42 (m, 2H), 2.37 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 160.1, 148.0, 144.9, 137.8, 136.9, 136.5, 136.2, 130.6, 130.4, 129.1, 127.6, 127.4, 120.9, 21.1.

HRMS (ESI), $C_{18}H_{15}NNaO_2S^+$ [M+Na]$^+$ Calcd 332.0716, Found 332.0733.

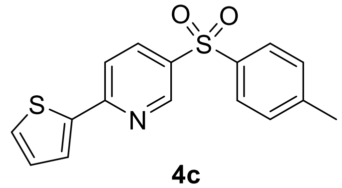


4b

4b, white solid (23.2 mg, 46%) (purity: 87%, determined by ^{1}H-NMR analysis),, the product was purified by flash column chromatography (PE/EtOAc = 9:1 to 4:1) to afford the desired product; mp 189 - 190°C; IR (neat) v 3053, 2918, 2848, 2740, 1702, 1581, 1305, 1159, 1014, 824, 759 cm^{-1}; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.08 (s, 1H), 9.19 (d, *J* = 2.3 Hz, 1H), 8.28 (dd, *J* = 8.4, 2.2 Hz, 1H), 8.18 (d, *J* = 8.2 Hz, 2H), 7.99 (d, *J* = 8.2 Hz, 2H), 7.92 - 7.87 (m, 3H), 7.34 (d, *J* = 8.1 Hz, 2H), 2.41 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.8, 159.6, 148.9, 145.2, 142.9, 138.0, 137.7, 137.4, 136.3, 130.4, 130.3, 128.3, 128.0, 121.1, 21.8.

HRMS (ESI), $C_{19}H_{15}NNaO_3S^+$ [M+Na]+ Calcd 360.0665, Found 360.0662.

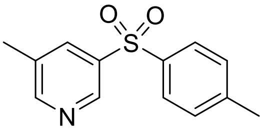


4c

4c, white solid (22.7 mg, 48%), the product was purified by flash column chromatography (PE/EtOAc = 9:1 to 4:1) to afford the desired product; mp 263 - 264 °C; IR (neat) v 3046, 2505, 1580, 1313, 1114, 827, 727, 668, 554, 526, 488 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.03 (s, 1H), 8.31 (dd, J = 8.5, 2.4 Hz, 1H), 8.12 (d, J = 8.5 Hz, 1H), 7.99 (dd, J = 3.8, 1.0 Hz, 1H), 7.92 (d, J = 8.3 Hz, 2H), 7.80 (dd, J = 5.0, 1.0 Hz, 1H), 7.45 (d, J = 8.1 Hz, 2H), 7.22 (dd, J = 5.0, 3.8 Hz, 1H), 2.37 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 155.7, 148.2, 144.8, 142.5, 137.9, 136.4, 135.5, 131.4, 130.4, 129.1, 128.4, 127.5, 119.1, 21.1.

HRMS (ESI), $C_{16}H_{13}KNO_2S_2^+$ [M+K]$^+$ Calcd 354.0019, Found 354.0022.

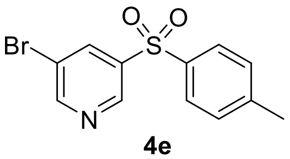


4d

4d, white solid (21.5mg, 58%), the product was purified by flash column chromatography (PE/EtOAc = 9:1 to 4:1) to afford the desired product; mp 149- 150 °C; IR (neat) v 2922, 1594, 1437, 1310, 1147, 1024, 815, 690, 656, 557, 499 cm^{-1}; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.91 (d, *J* = 2.2 Hz, 1H), 8.57 (s, 1H), 7.97 (s, 1H), 7.83 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 2.40 (s, 3H), 2.39 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.5, 146.2, 145.3, 138.7, 138.4, 135.5, 134.5, 130.6, 130.2, 129.2, 128.2, 22.0, 18.8.

HRMS (ESI), $C_{13}H_{13}KNO_2S^+$ [M+K]$^+$ Calcd 286.0299, Found 286.0321.

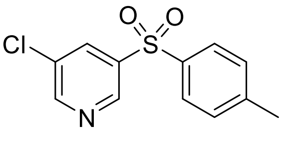


4e

4e, white solid (12.5 mg, 27%) (purity: 82%, determined by ^{1}H-NMR analysis), the product was purified by flash column chromatography (PE/EtOAc = 9:1 to 4:1) to afford the desired product; mp 179 - 180 °C; IR (neat) v 2920, 2850, 1594, 1410, 1325, 1151, 824, 688, 578, 557, 460 cm^{-1}; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.00 (d, J = 2.0 Hz, 1H), 8.81 (d, J = 2.2 Hz, 1H), 8.31 (t, J = 2.1 Hz, 1H), 7.84 (d, J = 8.3 Hz, 2H), 7.36 (d, J = 8.2 Hz, 2H), 2.43 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.8, 146.6, 145.6, 140.0, 137.5, 137.3, 130.5, 128.1, 121.1, 21.8.

HRMS (ESI), $C_{12}H_{11}BrNO_2S^+$ [M+H]$^+$ Calcd 311.9688, Found 311.9716.

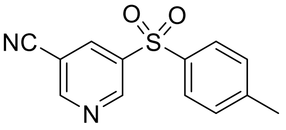


4f

4f, white solid (18.8 mg, 45%) (purity: 85%, determined by ^{1}H-NMR analysis), the product was purified by flash column chromatography (PE/EtOAc = 9:1 to 4:1) to afford the desired product; mp 148 - 149 °C; IR (neat) v 3061, 2920, 2850, 1595, 1411, 1325, 1294, 1152, 1097, 1015, 689 cm^{-1}; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.97 (d, J = 2.0 Hz, 1H), 8.70 (d, J = 2.3 Hz, 1H), 8.16 (t, J = 2.2 Hz, 1H), 7.85 (d, J = 8.3 Hz, 2H), 7.36 (d, J = 8.1 Hz, 2H), 2.43 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.7, 146.3, 145.6, 139.7, 137.3, 134.7, 132.8, 130.5, 128.1, 21.8.

HRMS (ESI), $C_{12}H_{11}ClNO_2S^+$ [M+H]$^+$ Calcd 268.0194, Found 268.0224.

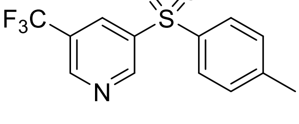


4g

4g, faint yellow solid (12.2 mg, 32%), the product was purified by flash column chromatography (PE/EtOAc = 9:1 to 4:1) to afford the desired product; mp 183 - 184 °C; IR (neat) v 3070, 2920, 2850, 2239, 1432, 1310, 1153, 1018, 818, 681, 580cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.36 (d, J = 2.2 Hz, 1H), 9.28 (d, J = 1.9 Hz, 1H), 8.99 (t, J = 2.1 Hz, 1H), 7.97 (d, J = 8.4 Hz, 2H), 7.47 (d, J = 8.0 Hz, 2H), 2.38 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 156.6, 150.9, 145.5, 139.4, 138.0, 136.6, 130.4, 128.0, 115.6, 110.3, 21.1.

HRMS (ESI), $C_{13}H_{11}N_2O_2S^+$ [M+H]$^+$ Calcd 259.0536, Found 259.0549.



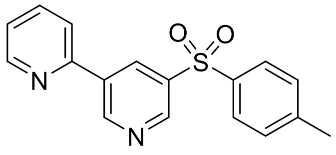
4h

4h, white solid (28.5 mg, 63%), the product was purified by flash column chromatography (PE/EtOAc = 9:1 to 4:1) to afford the desired product; mp 120 - 121 °C; IR (neat) v 2919, 2849, 1594, 1336, 1301, 1130, 1072, 912, 820, 671, 547 cm^{-1}; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.27 (d, J = 2.1 Hz, 1H), 9.02 – 9.01 (m, 1H), 8.42 (s, 1H), 7.87 (d, J = 8.3 Hz, 2H), 7.37 (d, J = 8.1 Hz, 2H), 2.43 (s, 3H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.5.

^{13}C NMR (101 MHz, Chloroform-*d*) 151.70, 150.3 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 145.9, 139.3, 137.0, 132.7 (q, $^3J_{C\text{-}F}$ = 3.7 Hz), 130.7, 128.2, 127.3 (q, $^2J_{C\text{-}F}$ = 34.2 Hz), 122.6 (q, $^1J_{C\text{-}F}$ = 273.4 Hz), 21.8.

HRMS (ESI), $C_{13}H_{11}F_3NO_2S^+$ [M+H]$^+$ Calcd 302.0457, Found 302.0478.

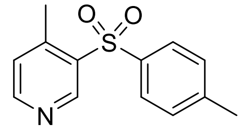


4i

4i, white solid (18.8 mg, 39%) (purity: 82%, determined by ^{1}H-NMR analysis), the product was purified by flash column chromatography (PE/EtOAc = 9:1 to 4:1) to afford the desired product; mp 134 - 135 °C; IR (neat) v 2920, 2851, 1727, 1589, 1428, 1148, 1100, 809, 698, 660, 574 cm^{-1}; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.36 (d, J = 2.1 Hz, 1H), 9.13 (d, *J* = 2.2 Hz, 1H), 8.81 (t, *J* = 2.2 Hz, 1H), 8.74 - 8.72(m, 1H), 7.89 (d, *J* = 8.3 Hz, 2H), 7.86 – 7.73 (m, 2H), 7.37 – 7.31 (m, 3H), 2.40 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.8, 151.8, 150.4, 148.3, 145.1, 138.9, 137.9, 137.4, 135.4, 133.3, 130.3, 128.0, 123.8, 121.0, 21.7.

HRMS (ESI), $C_{17}H_{15}N_2O_2S^+$ $[M+H]^+$ Calcd 311.0849, Found 311.0850.

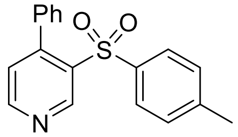


4j

4j, white solid (27.0 mg, 64%), the product was purified by flash column chromatography (PE/EtOAc = 9:1 to 4:1) to afford the desired product; mp 99 - 101 °C; IR (neat) v 2917, 1589, 1441, 1314, 1154, 1042, 821, 720, 659, 587, 560 cm^{-1}; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.24 (s, 1H), 8.63 (s, 1H), 7.78 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 4.8 Hz, 1H), 2.48 (s, 3H), 2.41 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.5, 149.4, 147.1, 144.6, 137.2, 130.4, 129.7, 127.8, 126.8, 21.4, 19.6.

HRMS (ESI), $C_{13}H_{14}NO_2S^+$ $[M+H]^+$ Calcd 248.0740, Found 248.0754.

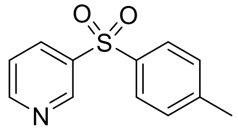


4k

4k, white solid (29.4 mg, 63%), the product was purified by flash column chromatography (PE/EtOAc = 9:1 to 4:1) to afford the desired product; mp 125 - 126 °C; IR (neat) v 2919, 2849, 1579, 1304, 1149, 1110, 810, 770, 658, 580, 537 cm^{-1}; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.50 (s, 1H), 8.78 (d, *J* = 4.9 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.27 (t, *J* = 7.6 Hz, 2H), 7.19 – 7.12 (m, 3H), 7.03 – 7.01 (m, 4H), 2.34 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.5, 150.3, 149.4, 144.2, 137.3, 136.3, 135.8, 129.7, 128.8, 128.0, 127.7, 126.6, 21.6.

HRMS (ESI), $C_{18}H_{15}NNaO_2S^+$ $[M+Na]^+$ Calcd 332.0716, Found 332.0708

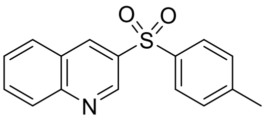


4l

4l, this is a known compound,[2] white solid (7.5 mg, 21%) (purity: 80%, determined by ^{1}H-NMR analysis), product was purified by flash column chromatography (PE/EtOAc = 9:1 to 4:1) to afford the desired product; mp 122 - 123 °C; IR (neat) v 2919, 2850, 1724, 1568, 1313, 1156, 1112, 1017, 739, 660, 550 cm^{-1}; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.12 (s, 1H), 8.77 (d, *J* = 4.7 Hz, 1H), 8.20 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 8.2 Hz, 2H), 7.43 (dd, *J* = 8.1, 4.8 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 2H), 2.41 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.6, 148.7, 145.1, 138.8, 137.9, 135.2, 130.4, 128.0, 123.9, 21.8.

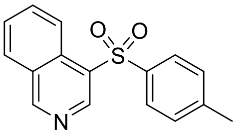
HRMS (ESI), $C_{12}H_{12}NO_2S^+$ $[M+H]^+$ Calcd 234.0583, Found 234.0609.


4m

4m, this is a known compound,[3] white solid (10.1 mg, 21%), product was purified by flash column chromatography (PE/EtOAc = 9:1 to 4:1) to afford the desired product; mp 83 - 84 °C; IR (neat) v 2918, 1589, 1441, 1314, 1154, 1079, 821, 720, 659, 587, 560 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.29 (d, *J* = 2.4 Hz, 1H), 9.15 (d, *J* = 2.1 Hz, 1H), 8.26 (d, *J* = 9.2 Hz, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 8.01 – 7.94 (m, 3H), 7.80 – 7.76 (m, 1H), 7.45 (d, *J* = 8.0 Hz, 2H), 2.35 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 148.7, 146.7, 144.9, 137.8, 137.2, 134.5, 133.2, 130.4, 129.8, 128.9, 128.5, 127.6, 126.1, 21.1.

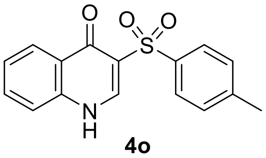
HRMS (ESI), $C_{16}H_{13}NNaO_2S^+$ [M+Na]$^+$ Calcd 306.0559, Found 306.0563.


4n

4n, white solid (9.0 mg, 19%), product was purified by flash column chromatography (PE/EtOAc = 9:1 to 4:1) to afford the desired product; mp 84 - 85 °C; IR (neat) v 2918, 1589, 1441, 1314, 1154, 1043, 804, 720, 859, 587, 560 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.65 (s, 1H), 9.25 (s, 1H), 8.54 – 8.47 (m, 1H), 8.33 (d, *J* = 8.0 Hz, 1H), 8.02 – 7.94 (m, 3H), 7.86 – 7.92 (m, 1H), 7.42 (d, *J* = 8.0 Hz, 2H), 2.34 (s, 3H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 159.2, 144.8, 144.7, 137.7, 133.4, 130.2, 129.7, 129.5, 128.8, 128.3, 127.5, 122.8, 21.0.

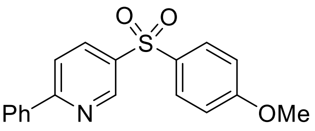
HRMS (ESI), $C_{16}H_{13}NNaO_2S^+$ [M+Na]$^+$ Calcd 306.0559, Found 306.0557.


4o

4o, white oil (26.5 mg, 51%), product was purified by flash column chromatography (PE/EtOAc = 9:1 to 4:1) to afford the desired product; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.84 (d, *J* = 5.0 Hz, 1H), 8.07 (d, *J* = 8.5 Hz, 1H), 7.99 – 7.84 (m, 1H), 7.80 (d, *J* = 8.2 Hz, 2H), 7.70 (t, *J* = 7.7 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.25 (s, 1H), 2.41 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.9, 150.5, 149.9, 145.9, 132.0, 130.2, 129.9, 129.1, 128.2, 127.1, 122.1, 121.4, 112.0, 21.6.

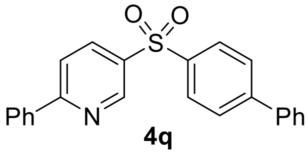
HRMS (ESI), $C_{16}H_{14}NO_3S^+$ [M+H]$^+$ Calcd 300.0689, Found 300.0701.


4p

4p, this is a known compound,[3] white solid (39.2 mg, 80%), the product was purified by flash column chromatography (PE/EtOAc = 9:1 to 4:1) to afford the desired product; mp 205 - 206 °C; IR (neat) v 2919, 2849, 1589, 1497, 1442, 1299, 1260, 1113, 1014, 732, 683 cm^{-1}; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.15 (d, *J* = 2.1 Hz, 1H), 8.20 (dd, *J* = 8.4, 2.4 Hz, 1H), 8.06 – 7.98 (m, 2H), 7.92 (d, *J* = 8.9 Hz, 2H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.50 – 7.46 (m, 3H), 6.99 (d, *J* = 8.9 Hz, 2H), 3.84 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.8, 161.0, 148.5, 137.6, 136.9, 135.8, 132.6, 130.5, 130.0, 129.1, 127.5, 120.3, 114.9, 55.8.

HRMS (ESI), $C_{18}H_{15}NNaO_3S^+$ [M+Na]$^+$ Calcd 350.1197, Found 350.1199.

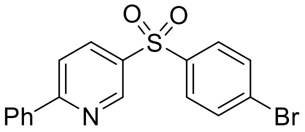


4q

4q, white solid (47.4 mg, 85%), the product was purified by flash column chromatography (PE/EtOAc = 9:1 to 4:1) to afford the desired product; mp 168 - 169 °C; IR (neat) v 3064, 2919, 2850, 1575, 1309, 1156, 1114, 1006, 845, 764, 682 cm^{-1}; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.23 (d, *J* = 2.3 Hz, 1H), 8.28 (dd, *J* = 8.4, 2.4 Hz, 1H), 8.07 (s, 1H), 8.06 – 7.99 (m, 3H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.74 (d, *J* = 8.5 Hz, 2H), 7.59 – 7.54 (m, 2H), 7.53 – 7.39 (m, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.4, 148.8, 146.8, 139.7, 139.1, 137.5, 136.4, 136.2, 130.6, 129.2, 129.1, 128.8, 128.0, 128.3, 127.6, 127.5, 120.4.

HRMS (ESI), $C_{23}H_{18}NO_2S^+$ [M+H]$^+$ Calcd 372.1053, Found 371.1062.

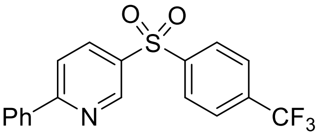


4r

4r, this is a known compound,[5] white solid (36.8 mg, 66%), the product was purified by flash column chromatography (PE/EtOAc = 9:1 to 4:1) to afford the desired product; mp 102 - 103 °C; IR (neat) v 3113, 2919, 2850, 1581, 1396, 1310, 1144, 1007, 730, 682, 575 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.21 (dd, *J* = 2.5, 0.8 Hz, 1H), 8.42 (dd, *J* = 8.5, 2.5 Hz, 1H), 8.21 (dd, *J* = 8.5, 0.8 Hz, 1H), 8.18 – 8.11 (m, 2H), 8.05 – 7.96 (m, 2H), 7.92 – 7.84 (m, 2H), 7.57 – 7.49 (m, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 160.4, 148.2, 139.9, 136.8, 136.8, 135.4, 133.1, 130.7, 129.6, 129.1, 128.5, 127.4, 121.0.

HRMS (ESI), $C_{17}H_{12}BrKNO_2S^+$ [M+K]$^+$ Calcd 411.9404, Found 411.9391.



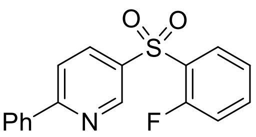
4s

4s, this is a known compound,[5] white solid (45.8 mg, 84%), the product was purified by flash column chromatography (PE/EtOAc = 9:1 to 4:1) to afford the desired product; mp 198 - 199 °C; IR (neat) v 3060, 1581, 1404, 1320, 1139, 1060, 1013, 844, 714, 594, 547 cm^{-1}; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.20 (s, 1H), 8.26 – 8.24 (m, 1H), 8.13 (d, *J* = 8.1 Hz, 2H), 8.04 – 8.02 (m, 2H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 2H), 7.50 – 7.48 (m, 3H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -63.3.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.7, 148.7, 144.6, 137.0, 136.1, 135.1 (q, $^2J_{C-F}$ = 33.0 Hz), 134.9, 130.5, 128.9, 128.1, 127.3, 126.5 (q, $^3J_{C-F}$ = 3.7 Hz), 122.8 (q, $^1J_{C-F}$ = 274.1 Hz), 120.2.

HRMS (ESI), $C_{18}H_{13}F_3NO_2S^+$ [M+H]$^+$ Calcd 364.0614, Found 364.0624.



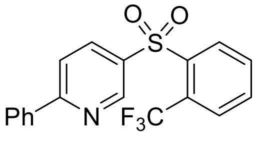
4t

4t, white solid (33.7 mg, 72 %), the product was purified by flash column chromatography (PE/EtOAc = 9:1 to 4:1) to afford the desired product; mp 164 - 165 °C; IR (neat) v 3097, 2919, 2849, 1578, 1325, 1167, 1106, 826, 764, 686, 577 cm^{-1}; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.22 (s, 1H), 8.34 (dt, *J* = 8.4, 1.9 Hz, 1H), 8.14 (td, *J* = 7.5, 1.8 Hz, 1H), 8.08 – 8.02 (m, 2H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.64 – 7.59 (m, 1H), 7.52 – 7.48 (m, 3H), 7.35 (td, *J* = 7.7, 1.1 Hz, 1H), 7.14 (ddd, *J* = 9.7, 8.3, 1.1 Hz, 1H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -107.66.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.5, 159.0 (d, J = 257.2 Hz), 149.1, 137.2, 136.6 (d, J = 2.5 Hz), 136.2 (d, J = 8.5 Hz), 135.1, 130.4, 129.5, 128.8, 127.3, 124.7 (d, J = 3.9 Hz), 119.9, 117.2 (d, J = 21.1 Hz).

HRMS (ESI), $C_{17}H_{13}FNO_2S^+$ [M+H]$^+$ Calcd314.0646, Found 314.0676.



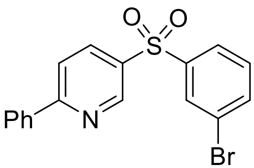
4u

4u, white solid (52.3 mg, 96%), the product was purified by flash column chromatography (PE/EtOAc = 9:1 to 4:1) to afford the desired product; mp 128 - 129 °C; IR (neat) v 3081, 1963, 1576, 1332, 1308, 1161, 1114, 731, 672, 596, 574 cm^{-1}; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.07 (d, J = 2.2 Hz, 1H), 8.54 (d, J = 7.8 Hz, 1H), 8.22 (dd, J = 8.5, 2.2 Hz, 1H), 8.09 – 7.99 (m, 2H), 7.93 – 7.70 (m, 4H), 7.48 (dd, J = 5.2, 2.0 Hz, 3H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -56.58.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.4, 149.1, 139.6, 137.4, 136.5 (q, J = 1.5 Hz), 135.9, 134.1, 133.0, 132.6, 130.7, 129.1, 129.0 (q, J = 18.9 Hz), 128.8 (q, J = 6.3 Hz), 127.6, 122.6 (q, J = 274.4 Hz), 120.1.

HRMS (ESI), $C_{18}H_{13}F_3NO_2S^+$ [M+H]$^+$ Calcd 364.0614, Found 364.0640.

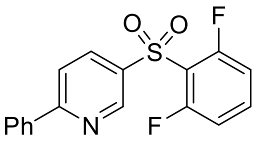


4v

4v, white solid (48.1 mg, 86%), the product was purified by flash column chromatography (PE/EtOAc = 9:1 to 4:1) to afford the desired product; mp 149 - 150 °C; IR (neat) v 3059, 2920, 1577, 1320, 1157, 1067, 734, 680, 606, 572, 540 cm^{-1}; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.18 (d, J = 2.3 Hz, 1H), 8.23 (dd, J = 8.4, 2.4 Hz, 1H), 8.13 (s, 1H), 8.03 (dd, J = 6.7, 3.0 Hz, 2H), 7.92 (d, J = 7.9 Hz, 1H), 7.86 (d, J = 8.5 Hz, 1H), 7.72 (d, J = 8.1 Hz, 1H), 7.80 – 7.48 (m, 3H), 7.42 (t, J = 8.0 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.8, 148.9, 143.2, 137.4, 136.8, 136.3, 135.5, 131.2, 130.8, 130.6, 129.1, 127.6, 126.3, 123.7, 120.5.

HRMS (ESI), $C_{17}H_{13}BrNO_2S^+$ [M+H]$^+$ Calcd 373.9845, Found373.9874.



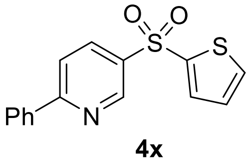
4w

4w, white solid (38.7 mg, 78%), the product was purified by flash column chromatography (PE/EtOAc = 9:1 to 4:1) to afford the desired product; mp 165 - 167 °C; IR (neat) v 3082, 2918, 2850, 1576, 1463, 1342, 1166, 1002, 678, 629, 527 cm^{-1}; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.30 (d, J = 1.9 Hz, 1H), 8.38 (dd, J = 8.5, 2.4 Hz, 1H), 8.10 – 8.02 (m, 2H), 7.90 (d, J = 8.4 Hz, 1H), 7.62 – 7.45 (m, 4H), 7.01 (t, J = 8.7 Hz, 2H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -105.81.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.4, 160.2 (dd, J = 261.3, 3.5 Hz), 149.4, 137.7, 136.8, 136.6, 136.5 (t, J = 11.2 Hz), 131.1, 129.5, 128.0, 120.5, 119.5 (t, J = 15.1 Hz), 113.9 (dd, J = 23.0, 3.8 Hz).

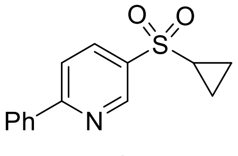
HRMS (ESI), $C_{17}H_{12}F_2NO_2S^+$ [M+H]$^+$ Calcd 332.0551, Found 332.0563.



4x

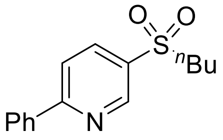
4x, this is a known compound,[5] white solid(36.4 mg, 81%)(purity: 79%, determined by ^{1}H-NMR analysis) , the product was purified by flash column chromatography (PE/EtOAc = 9:1 to 4:1) to afford the desired product; mp 213 - 214 °C; IR (neat) v 3063, 2918, 2848, 1513, 1578, 1310,

1133, 1062, 840, 677, 561 cm^{-1}; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.22 (d, *J* = 2.4 Hz, 1H), 8.28 (dd, *J* = 8.4, 2.4 Hz, 1H), 8.10 – 8.00 (m, 2H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.77 (dd, *J* = 3.8, 1.3 Hz, 1H), 7.70 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.50 - 7.48 (m, 3H), 7.13 (dd, *J* = 5.0, 3.8 Hz, 1H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.5, 148.6, 142.7, 137.5, 136.7, 135.9, 134.7, 134.0, 130.7, 129.2, 128.3, 127.6, 120.4.
HRMS (ESI), $C_{15}H_{12}NO_2S_2^+$ [M+H]$^+$ Calcd 302.0304, Found 302.0303.



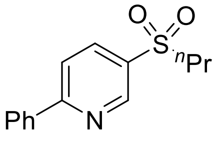
4y

4y, this is a known compound,[5] white solid (29.1mg, 75%), the product was purified by flash column chromatography (PE/EtOAc = 9:1 to 4:1) to afford the desired product; mp 178 -179 °C; IR (neat) v 3033, 2919, 2850, 1556, 1465, 1291, 1141, 1103, 880, 783, 686 cm^{-1}; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.14 (d, *J* = 2.3 Hz, 1H), 8.21 (dd, *J* = 8.4, 2.4 Hz, 1H), 8.06 (dd, *J* = 7.6, 2.1 Hz, 2H), 7.90 (d, *J* = 8.3 Hz, 1H), 7.61 – 7.38 (m, 3H), 2.53 (tt, *J* = 7.9, 4.8 Hz, 1H), 1.43 - 1.39 (m, 2H), 1.24 – 0.97 (m, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.3, 148.4, 137.3, 135.9, 134.9, 130.3, 128.8, 127.3, 120.0, 33.1, 6.0.
HRMS (ESI), $C_{14}H_{13}NNaO_2S^+$ [M+Na]$^+$ Calcd 282.0559, Found 282.0579.



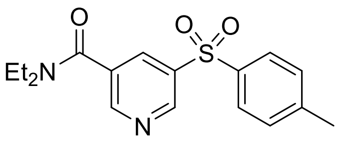
4z

4z, this is a known compound,[5] white solid (15.3 mg, 37%), the product was purified by flash column chromatography (PE/EtOAc = 9:1 to 4:1) to afford the desired product; mp 104 - 105 °C; IR (neat) v 2956, 2928, 2872, 1578, 1467, 1311, 1152, 1099, 1016, 709, 681 cm^{-1}; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.15 (dd, *J* = 2.4, 0.8 Hz, 1H), 8.22 (dd, *J* = 8.4, 2.4 Hz, 1H), 8.08 (dd, *J* = 7.6, 2.1 Hz, 2H), 7.92 (dd, *J* = 8.4, 0.9 Hz, 1H), 7.59 – 7.43 (m, 3H), 3.27 – 3.00 (m, 2H), 1.94 – 1.63 (m, 2H), 1.53 – 1.34 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.0, 149.3, 137.6, 136.9, 133.7, 130.7, 129.2, 127.7, 120.3, 56.8, 24.8, 21.7, 13.6.
HRMS (ESI), $C_{15}H_{18}NO_2S^+$ [M+H]$^+$ Calcd 276.1053, Found 276.1080.



4aa

4aa, white solid (8.0 mg, 20 %) (purity: 85%, determined by ^{1}H-NMR analysis), the product was purified by flash column chromatography (PE/EtOAc = 9:1 to 4:1) to afford the desired product; mp 138 - 139 °C; IR (neat) v 2917, 2850, 1579, 1371, 1286, 1134, 1098, 1012, 783, 733, 685 cm^{-1}; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.14 (d, *J* = 2.3 Hz, 1H), 8.22 (dd, *J* = 8.3, 2.4 Hz, 1H), 8.13 – 8.01 (m, 2H), 7.91 (d, *J* = 8.3 Hz, 1H), 7.57 – 7.45 (m, 3H), 3.19 – 3.08 (m, 2H), 1.90 – 1.73 (m, 2H), 1.04 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.0, 149.3, 137.6, 136.9, 133.6, 130.7, 129.2, 127.7, 120.3, 58.6, 16.7, 13.0.
HRMS (ESI), $C_{14}H_{16}NO_2S^+$ [M+H]$^+$ Calcd 262.0896, Found 262.0921.



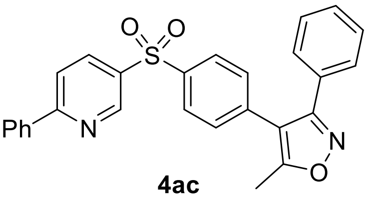
4ab

4ab, yellow oil (24.8 mg, 50%), the product was purified by flash column chromatography (PE/EtOAc = 9:1 to 4:1) to afford the desired product; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.13 (s, 1H), 8.77 (s, 1H), 8.20 (s, 1H), 7.84 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.1

Hz, 2H), 3.59 - 3.54 (m, 2H), 3.24 - 3.17 (m, 2H), 2.42 (s, 3H), 1.28 - 1.25 (m, 3H), 1.17 - 1.13(m, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.1, 151.2, 149.2, 145.8, 139.0, 137.6, 133.6, 130.8, 128.4, 44.0, 40.3, 22.1, 14.7, 13.2.

HRMS (ESI), $C_{17}H_{20}N_2NaO_3S^+$ [M+Na]$^+$ Calcd 355.1087, Found 355.1107.



4ac

4ac, this is a known compound,[5] white solid (57.0 mg, 84%), the product was purified by flash column chromatography (PE/EtOAc = 9:1 to 4:1) to afford the desired product; mp 85 - 57 °C; IR (neat) v 3649, 3057, 2252, 1577, 1464, 1323, 1158, 1114, 1012, 907, 775 cm^{-1}; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.19 (d, *J* = 2.0 Hz, 1H), 8.28 (dd, *J* = 8.4, 2.4 Hz, 1H), 8.05 – 8.02 (m, 2H), 7.97 (d, *J* = 8.5 Hz, 2H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.51 – 7.47 (m, 3H), 7.43 – 7.28 (m, 7H), 2.46 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.5, 161.5, 161.1, 148.9, 140.2, 137.3, 136.4, 136.3, 135.9, 130.7, 129.9, 129.1, 128.9, 128.5, 128.4, 128.2, 127.5, 120.4, 114.3, 11.9.

HRMS (ESI), $C_{27}H_{22}N_2NaO_3S^+$ [M+Na]$^+$ Calcd 475.1087, Found 475.1095.

5. References

(1) Cao, H.; Cheng, Q.; Studer, A.; Radical and ionic meta-C–H functionalization of pyridines, quinolines, and isoquinolines. *Science,* **2022**, 378, 779-785.

(2). Qin, S.; Yang, M.-K.; Xu, M.-Y.; Peng, Z.-H.; Cai, J.-T.; Wang, S.-D.; Gao, H.; Zhou, Z.; Hashmi, A.; Yi, W.; Zheng, Z.-Y.; Electrochemical meta-C–H sulfonylation of pyridines with nucleophilic sulfonates. Nat Commun, **2024**, 10.1038/s41467-024-50644-y

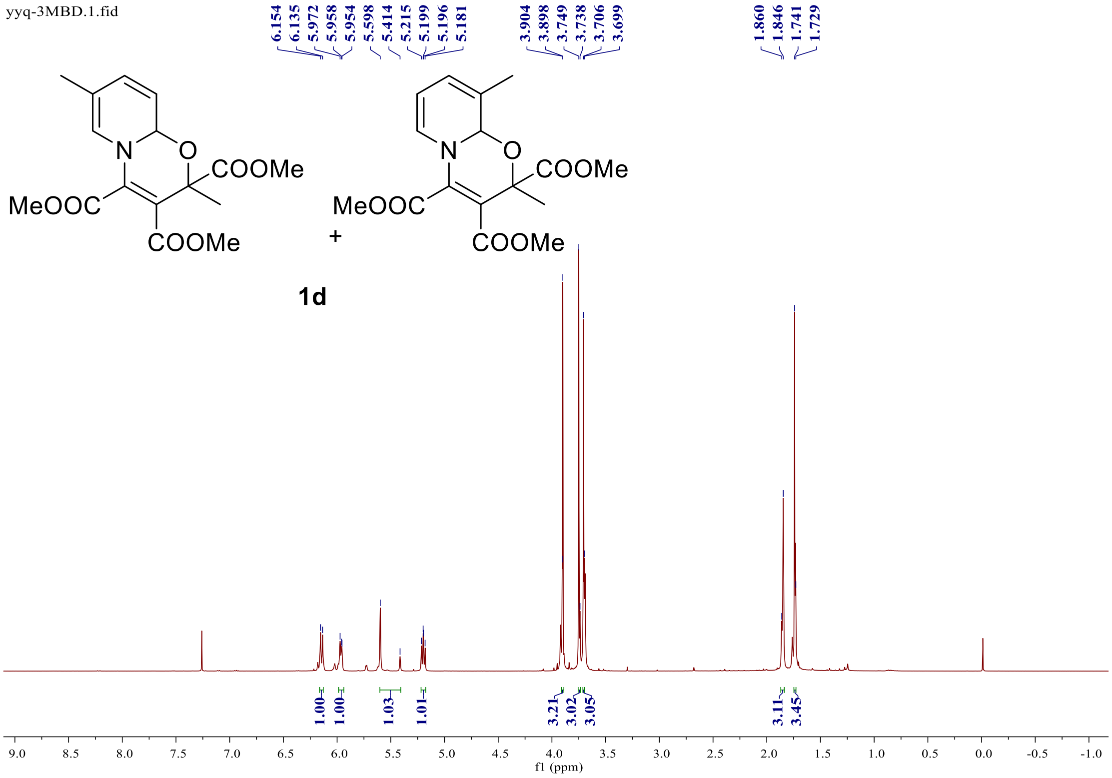
(3) Yue, H.-F.; Zhou, C.; Rueping, M.; Cross-Coupling of Sodium Sulfinates with Aryl, Heteroaryl, and Vinyl Halides by Nickel/Photoredox Dual Catalysis. *Angew. Chem. Int. Ed.* **2018**, 57, 1371-1375.

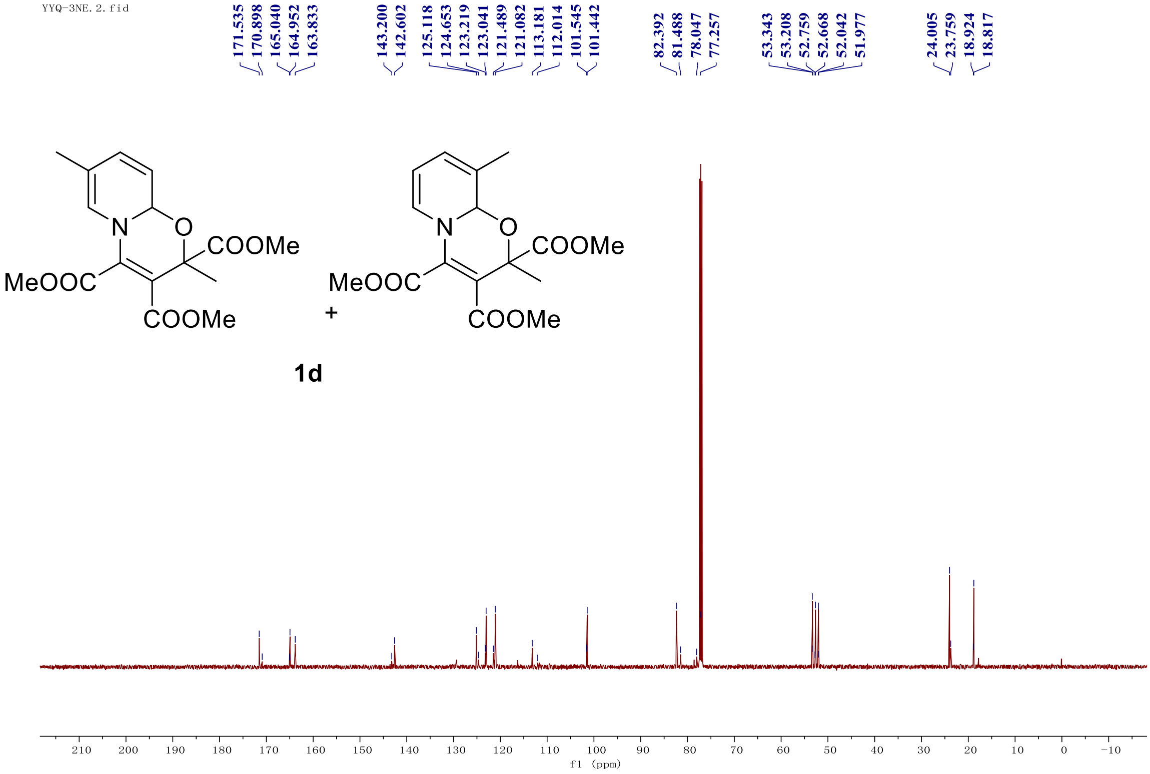
(4) Bondarev, V.-L.; Festa, A.-A.; Storozhenko, O.-A.; Kokorekin, V.- A.; Novikov, A.- P.; Varlamov, A.- V.; Voskressensky, L.- G.; Electrochemical Synthesis of 3-(Sulfonyl)quinol-4-ones from o-Alkynyl-N-(formyl)anilides and Sulfinates. *Org. Let*t. **2025**, 27, 212–216.

(5) Kim, J.; Kim, Y.-E.; Hong, S.; Traceless Nucleophile Strategy for C5-Selective C–H Sulfonylation of Pyridines. *Angew. Chem. Int. Ed*. **2024**, *10.1002/anie.202409561.*

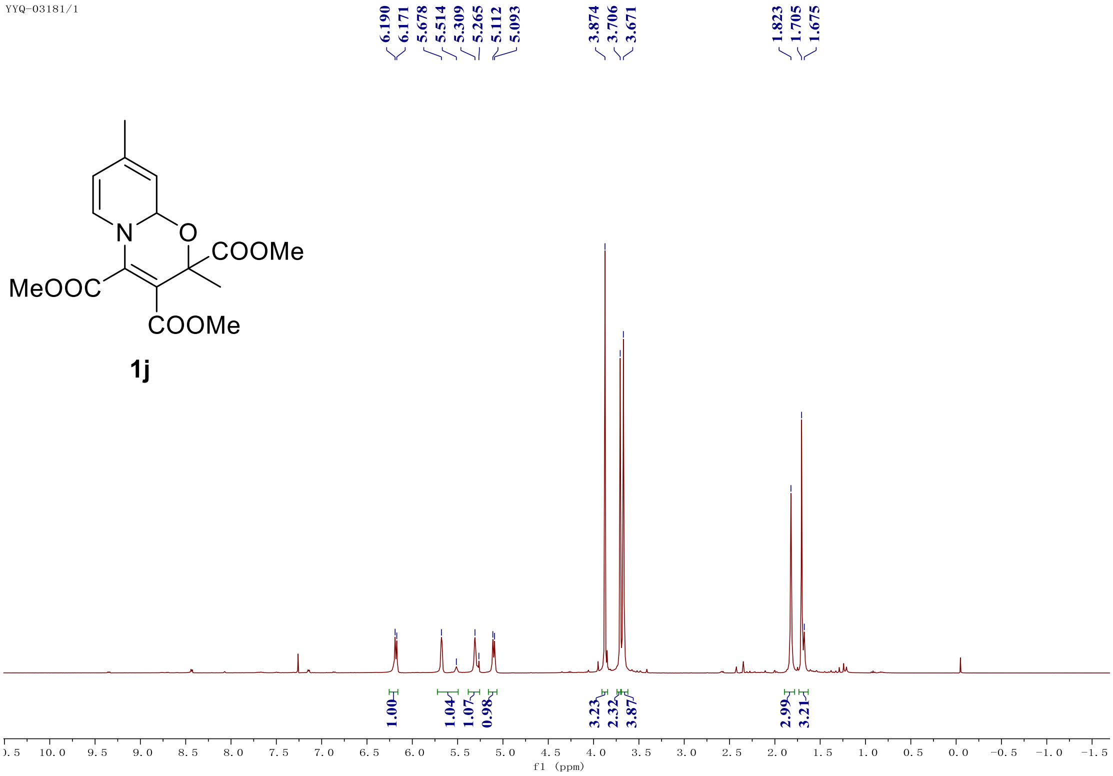
6. Copies of NMR Spectra

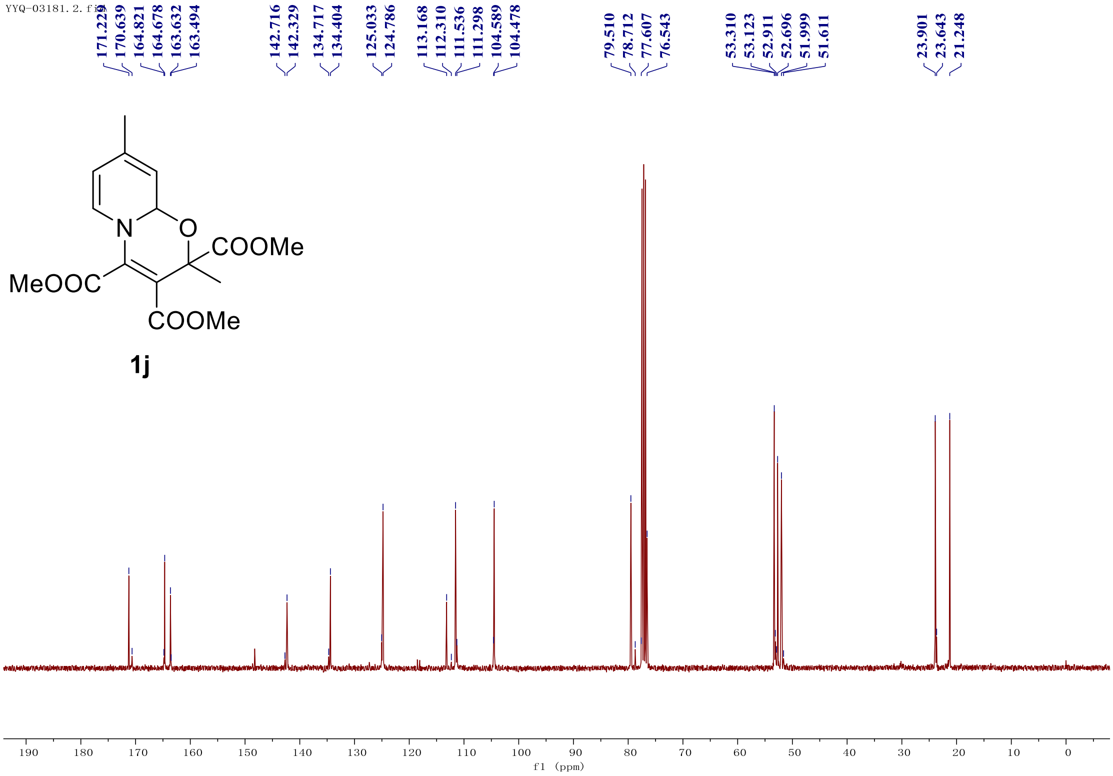
Materials 1d: ^{1}H NMR (500 MHz, CDCl$_3$) and ^{13}C NMR (126MHz, CDCl$_3$).



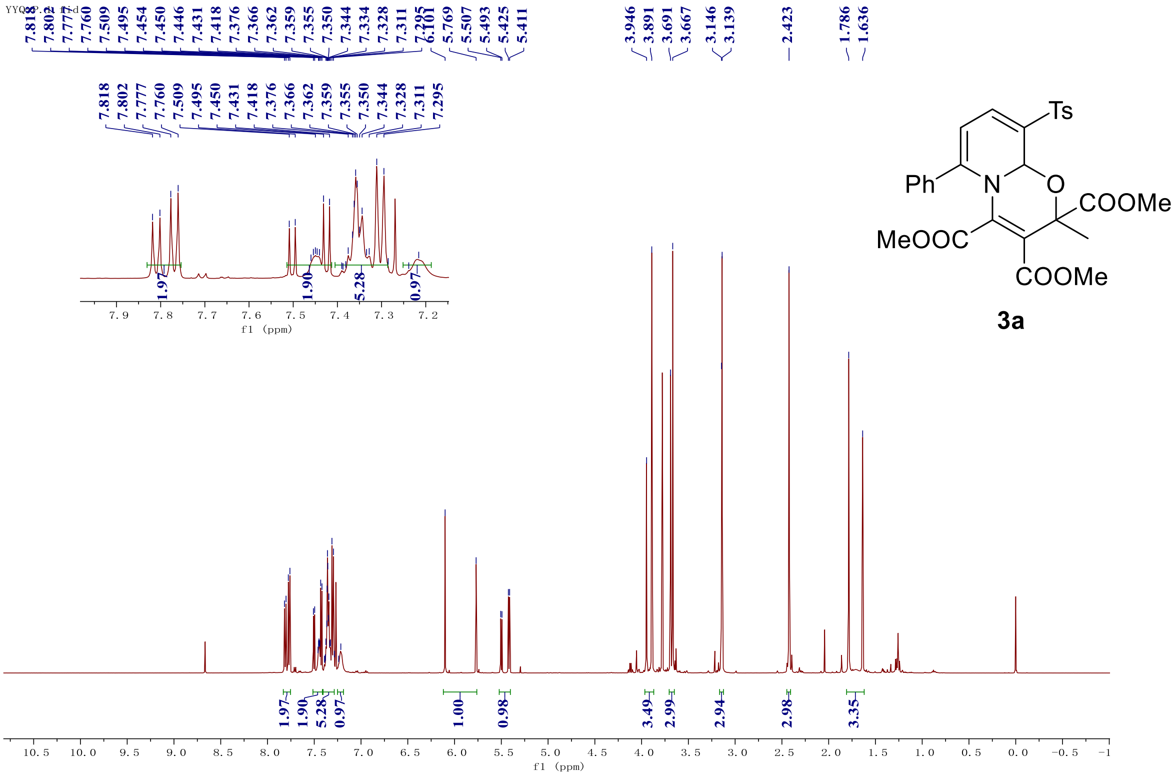


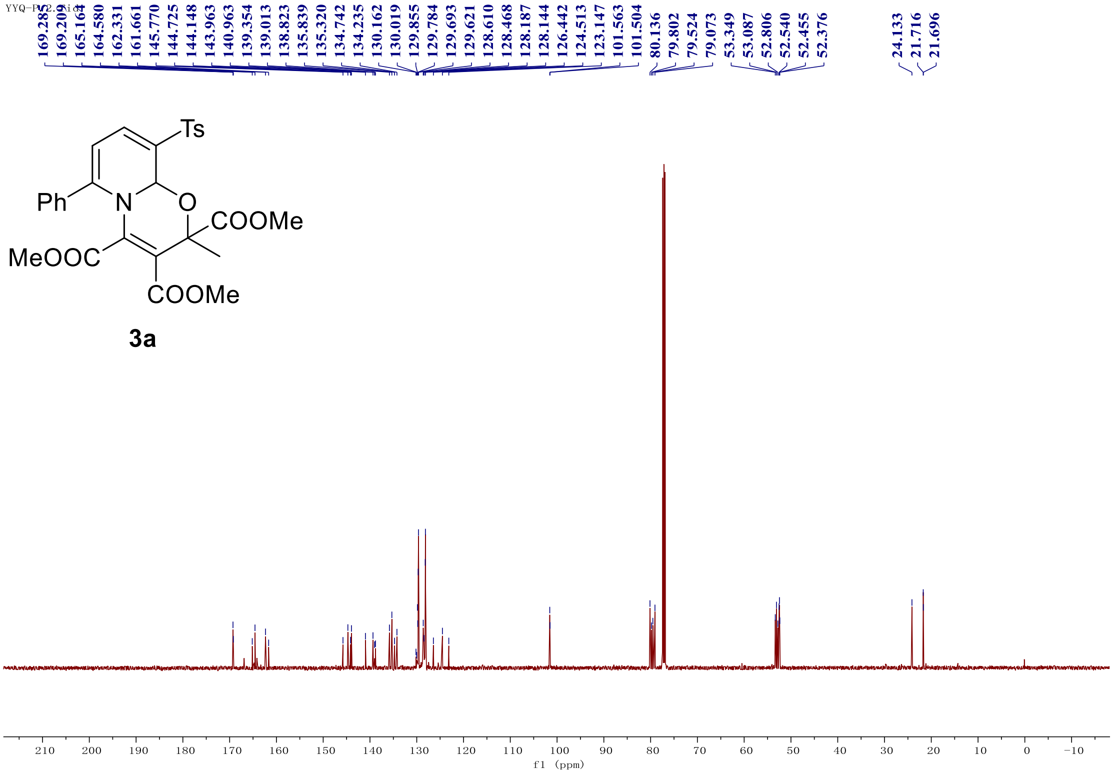
Materials 1j: ^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C NMR (101 MHz, CDCl$_3$).



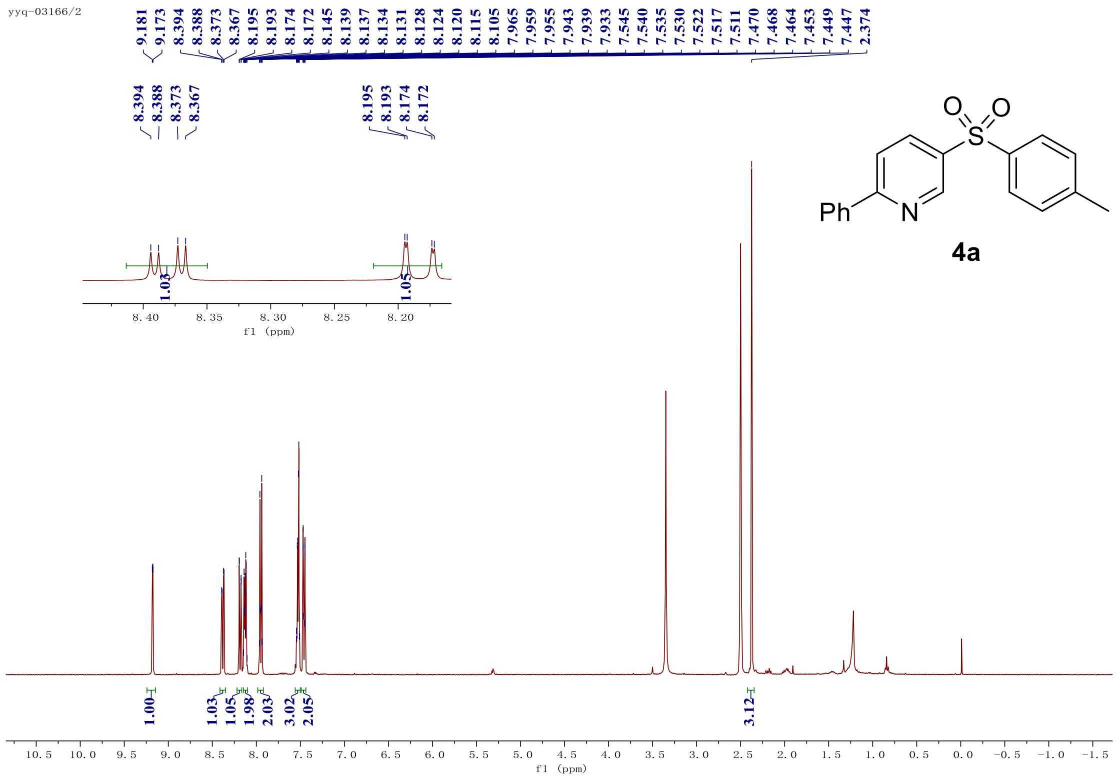


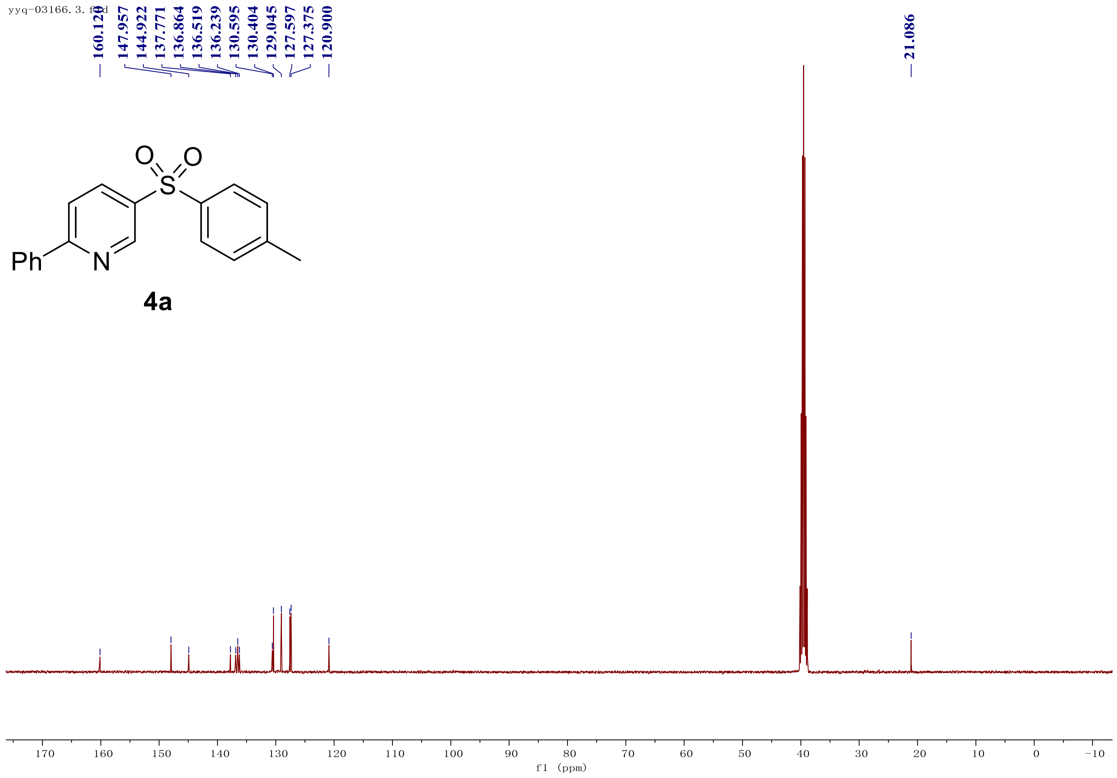
Materials 3a: ^{1}H NMR (500 MHz, CDCl$_3$) and ^{13}C NMR (126 MHz, CDCl$_3$).



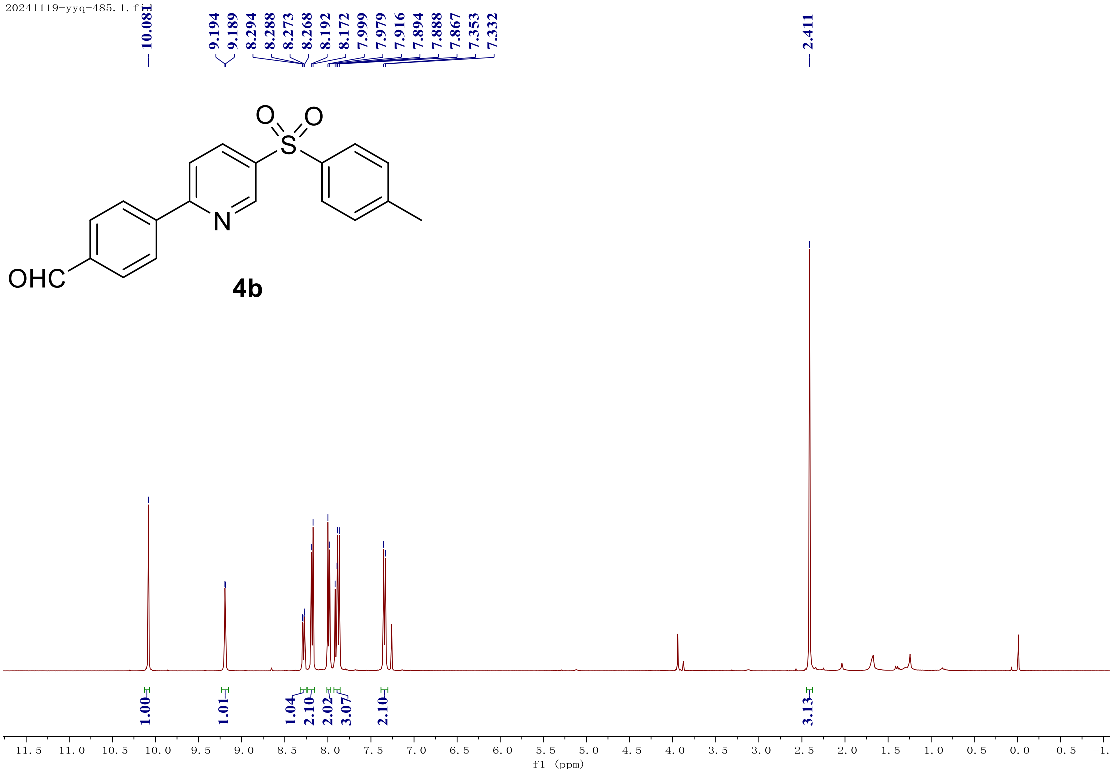


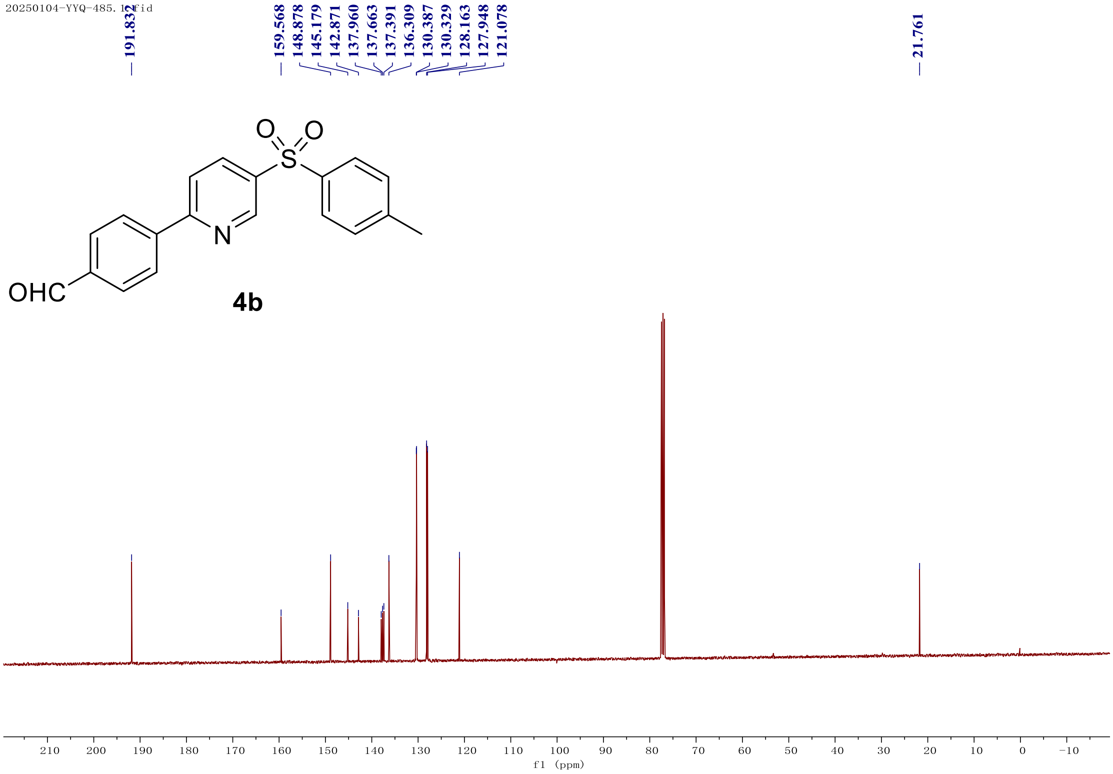
Materials 4a: ^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (101MHz, DMSO-d_6)..



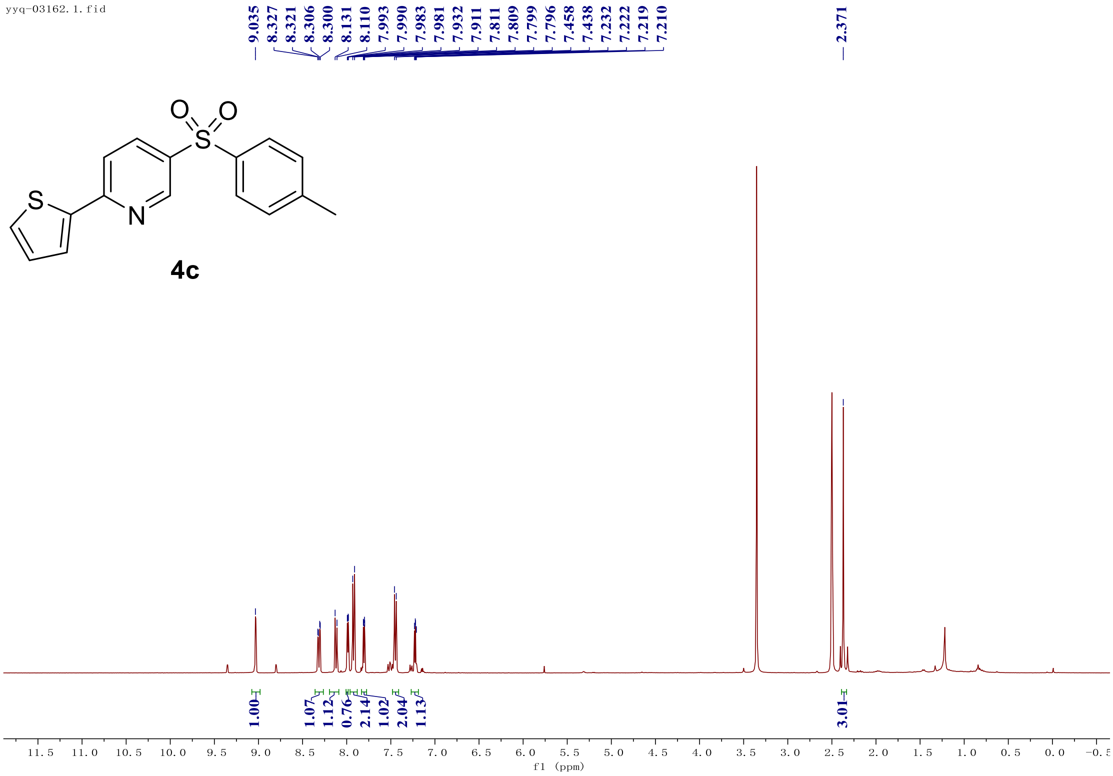


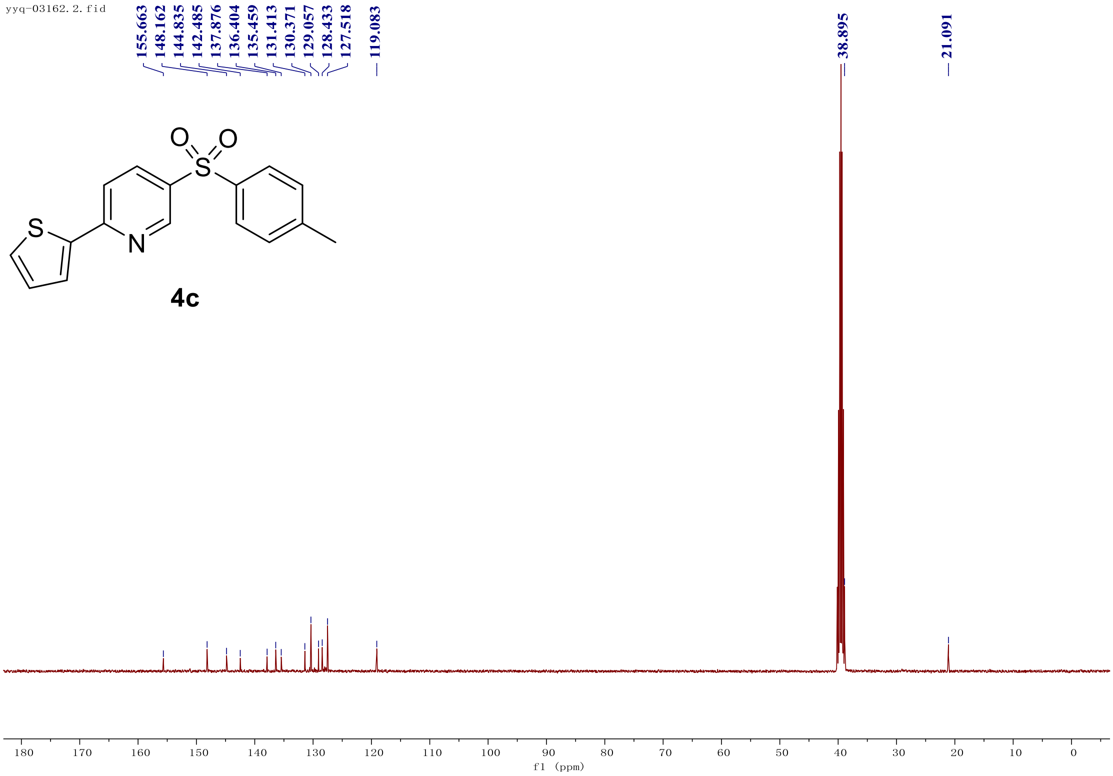
Materials 4b: ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$).



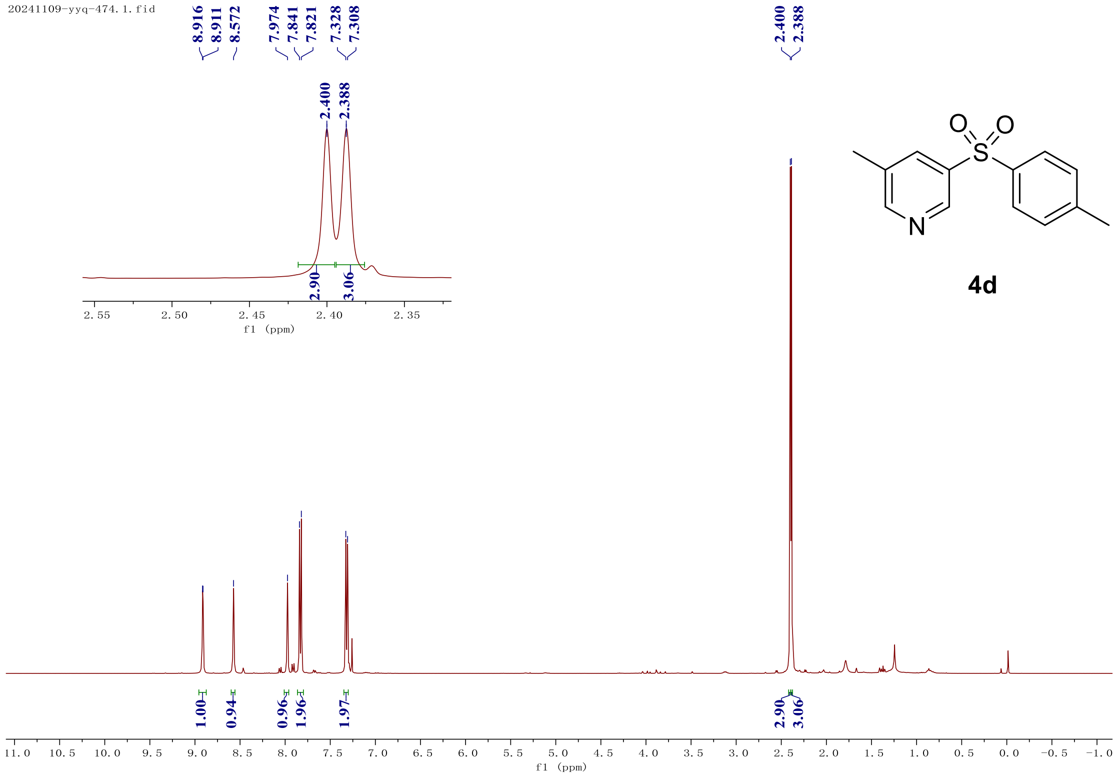


Materials 4c: ^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (101 MHz, DMSO-d_6).

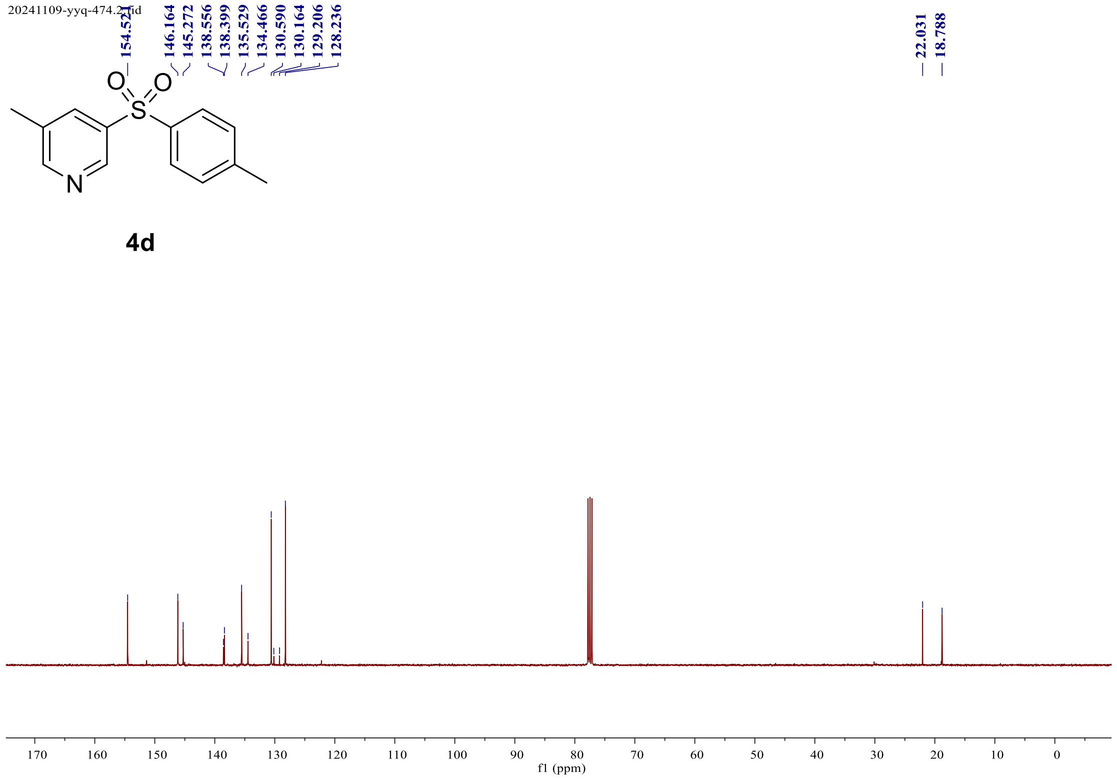




Materials 4d: ^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C NMR (101 MHz, CDCl$_3$).

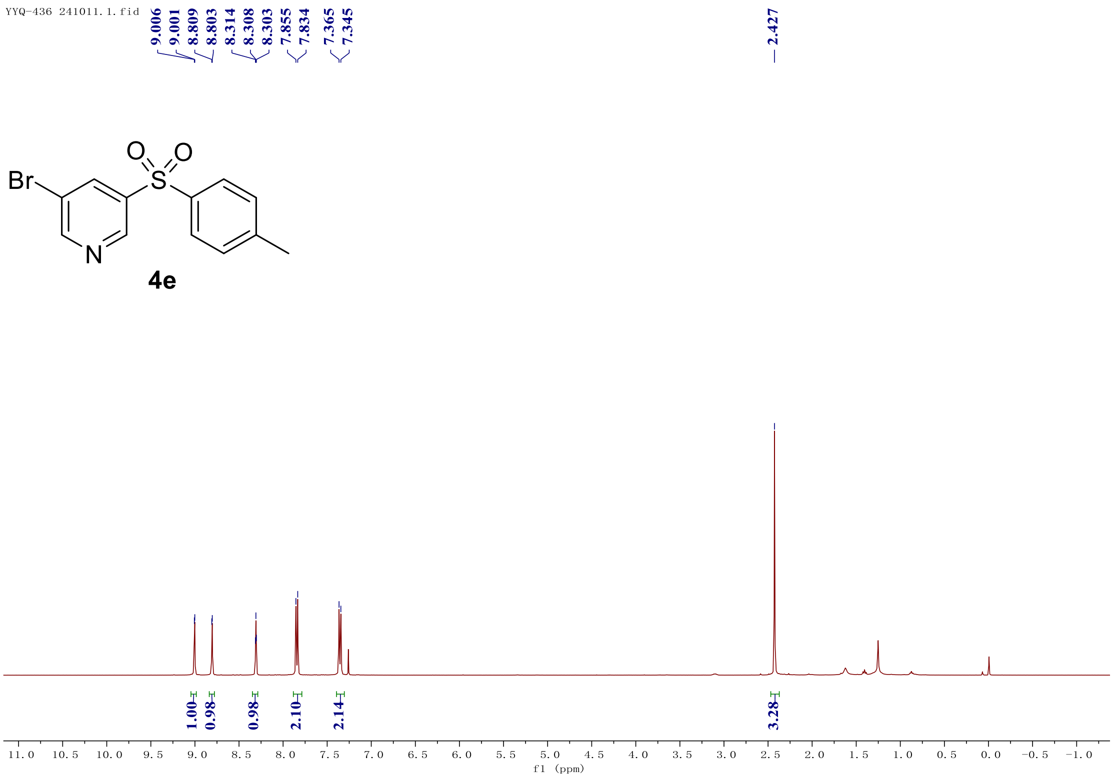


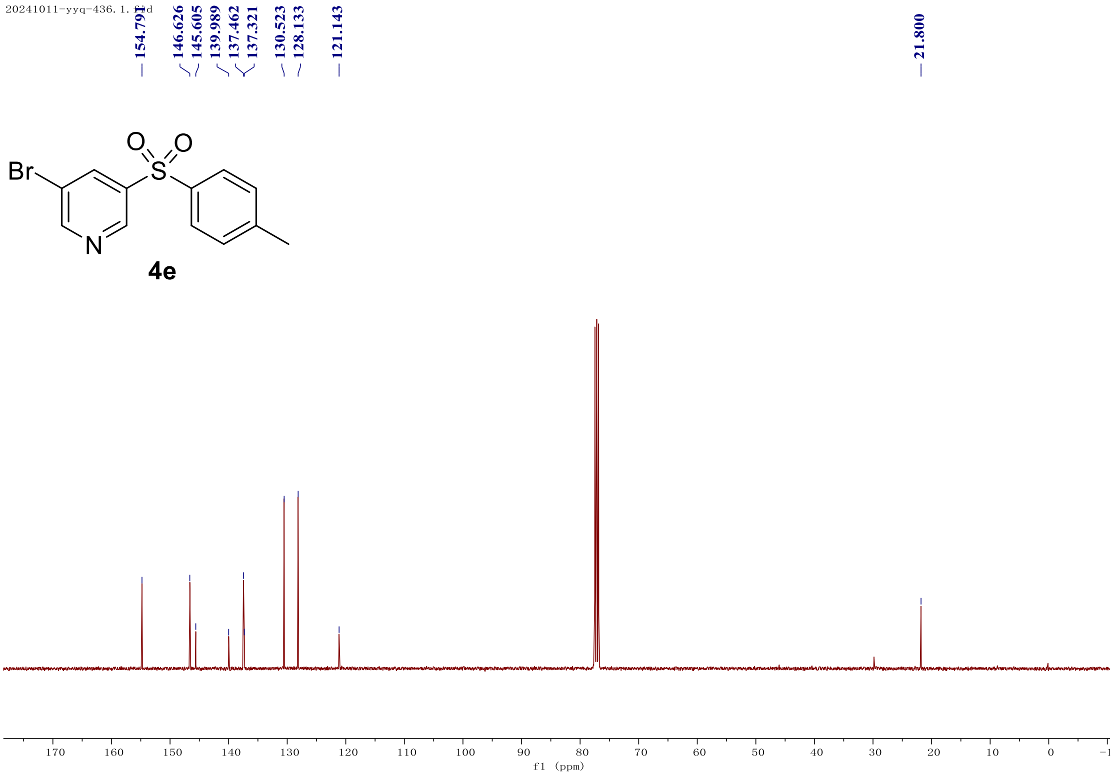
4d



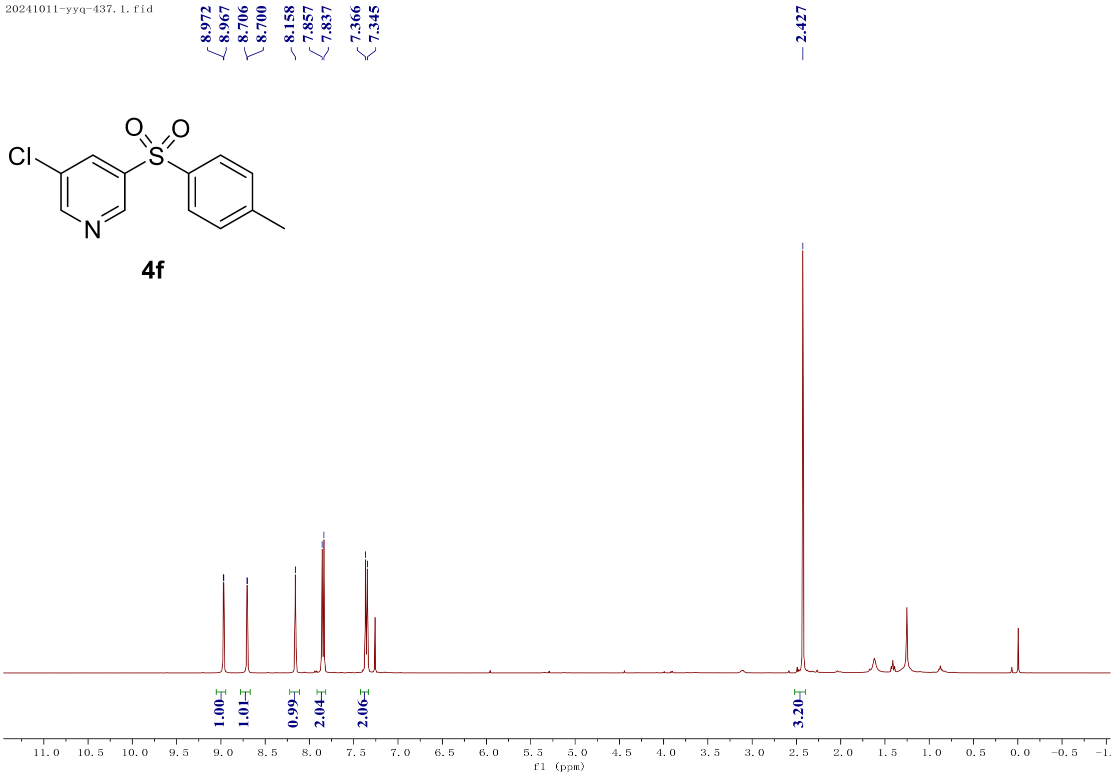
4d

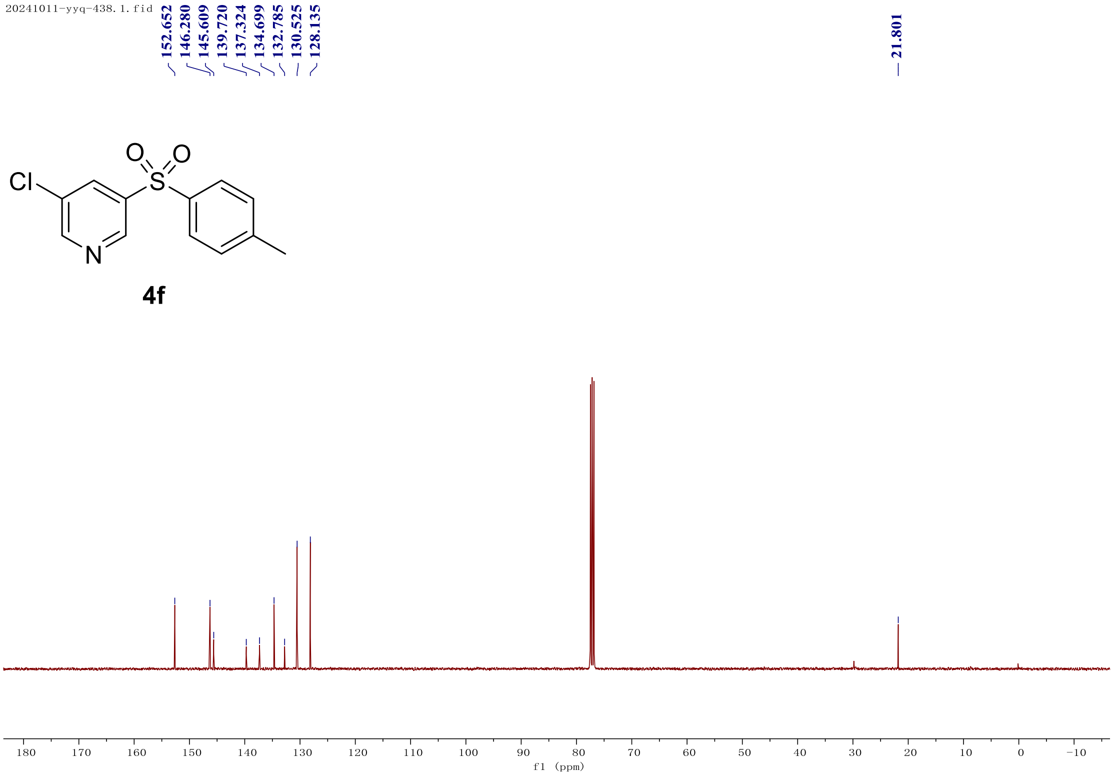
Materials 4e: ^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C NMR (101 MHz, CDCl$_3$).



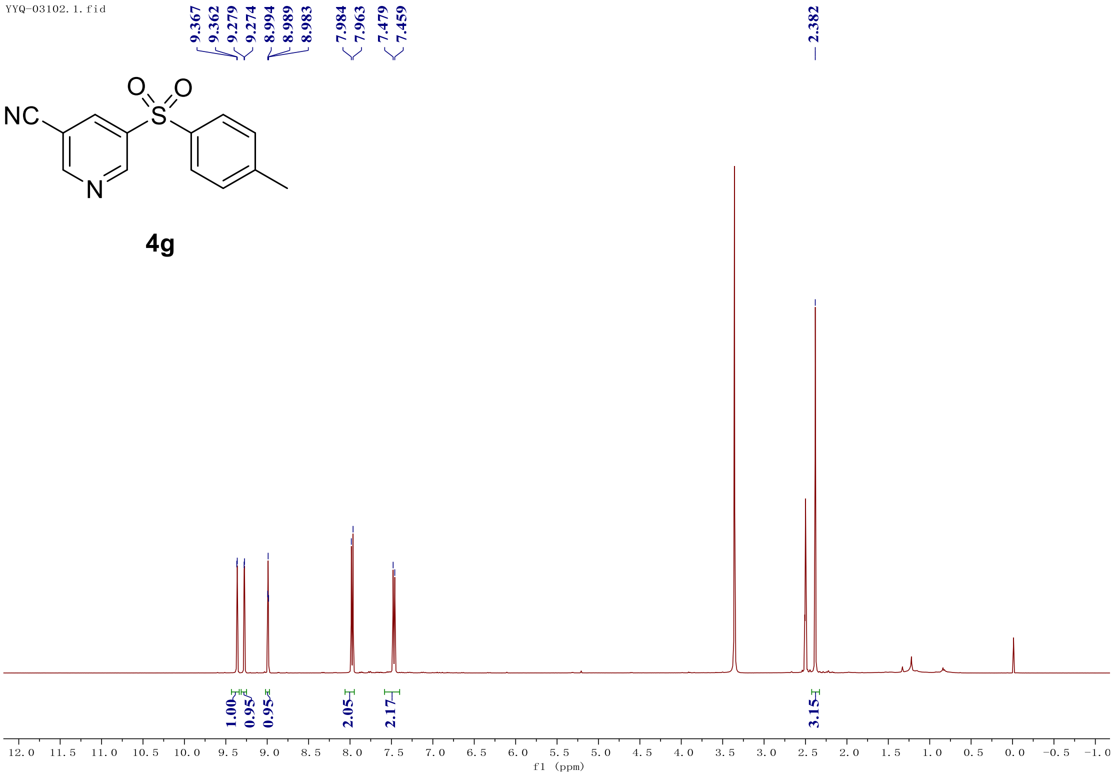


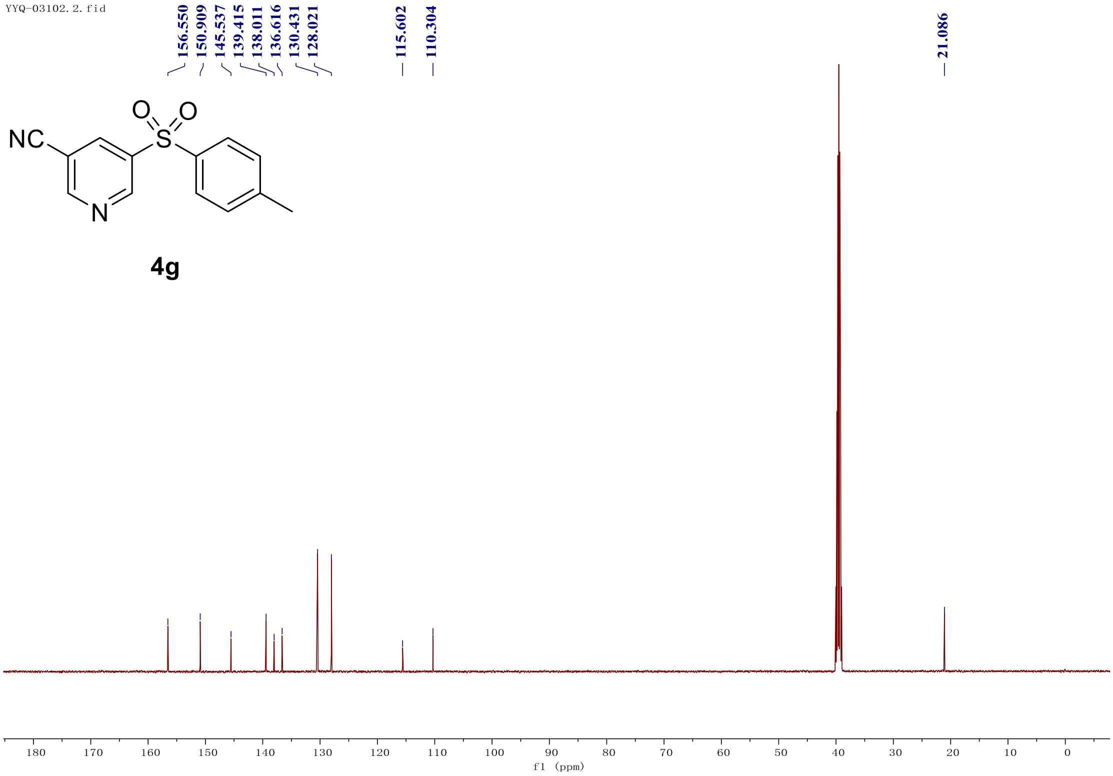
Materials 4f: ^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C NMR (101 MHz, CDCl$_3$).



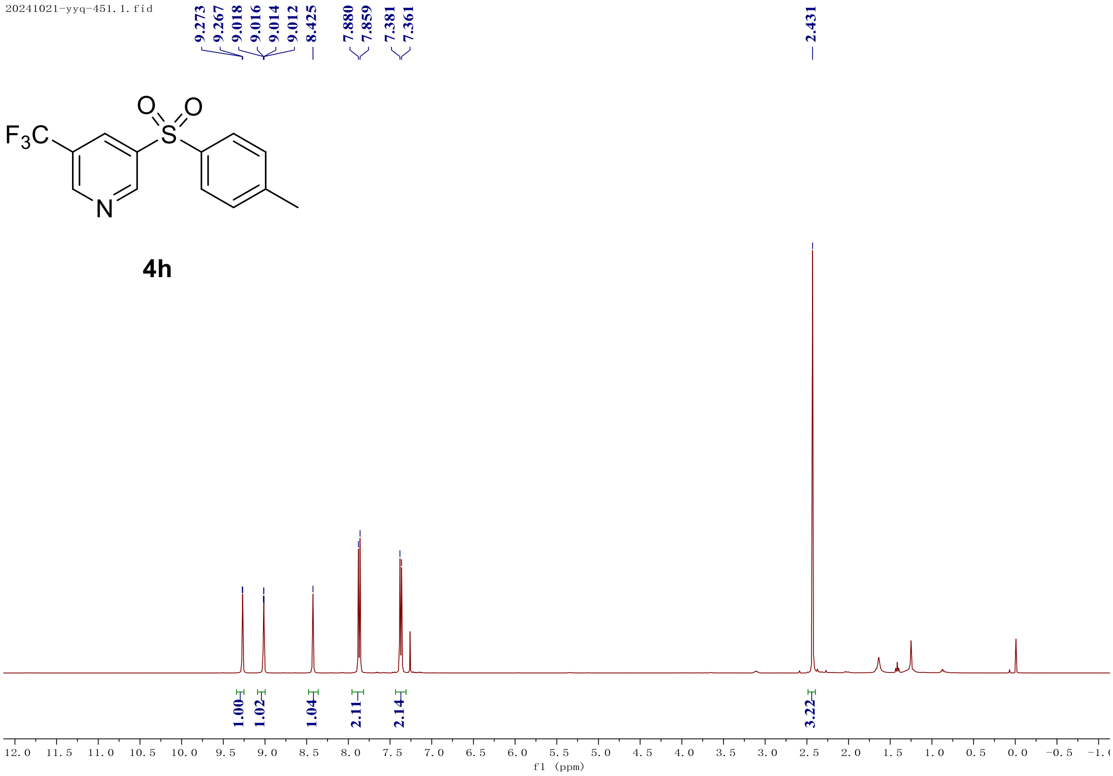


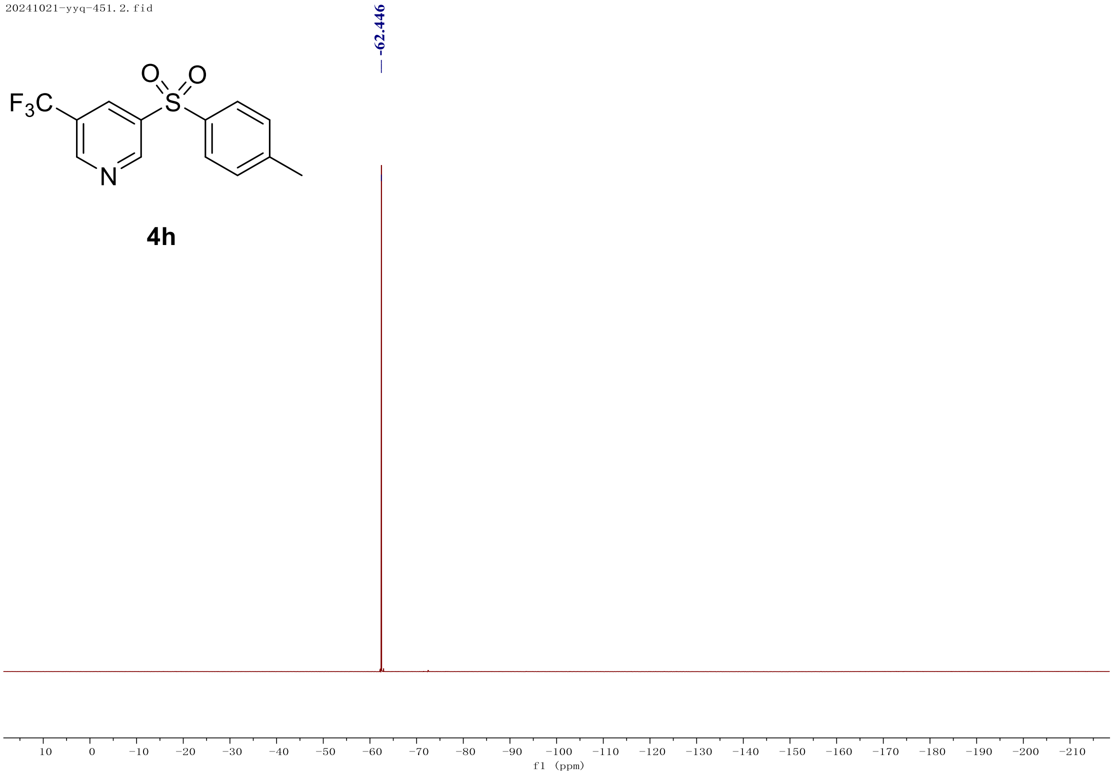
Materials 4g: ^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (101 MHz, DMSO-d_6).

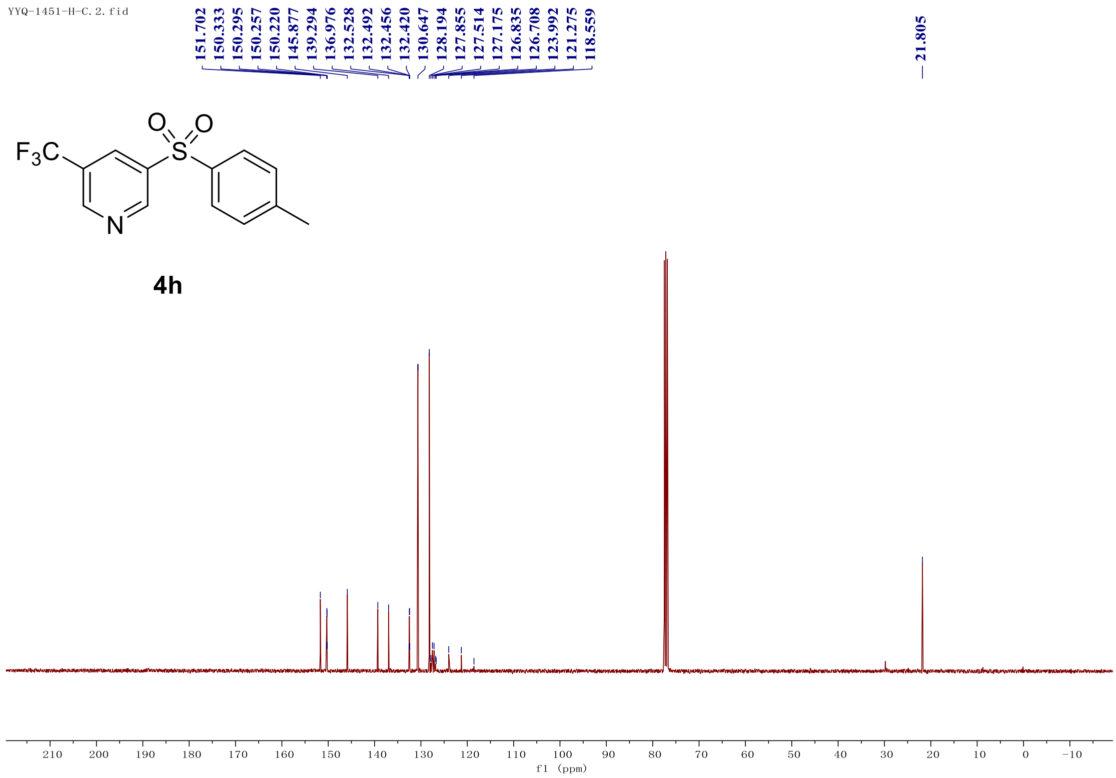




Materials 4h: ^{1}H NMR (400 MHz, CDCl$_3$), ^{19}F NMR (376 MHz, CDCl$_3$) and ^{13}C NMR (101 MHz, CDCl$_3$).



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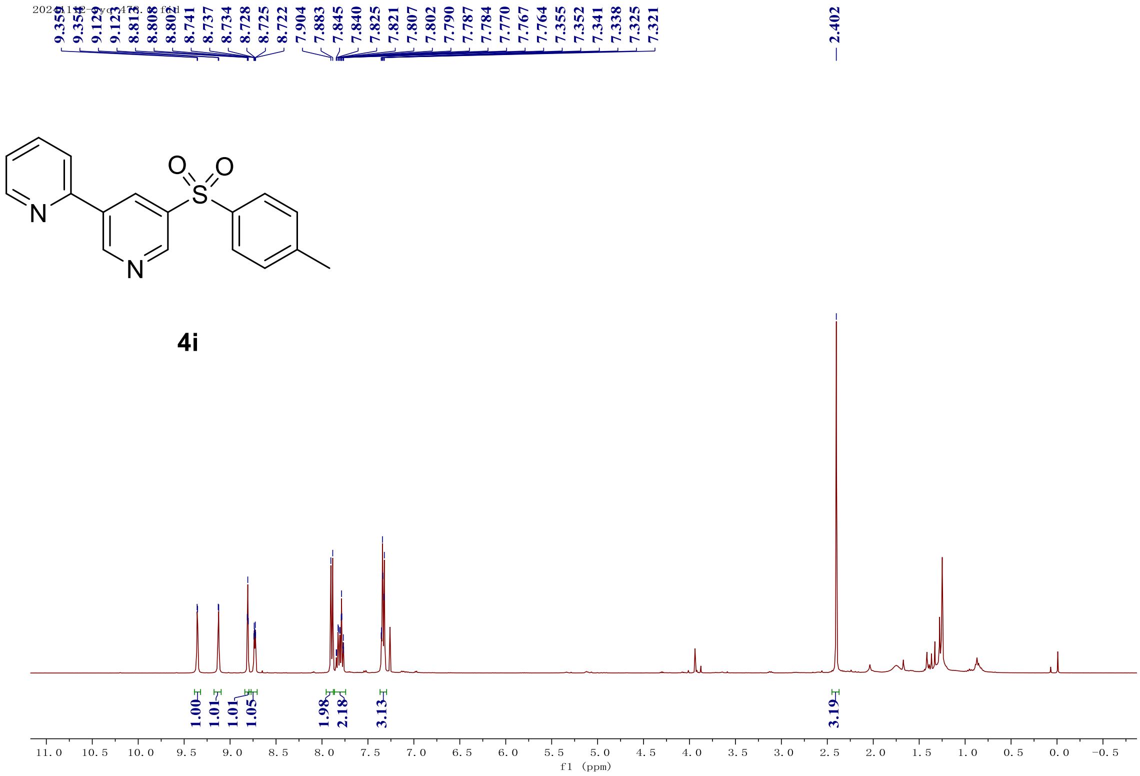
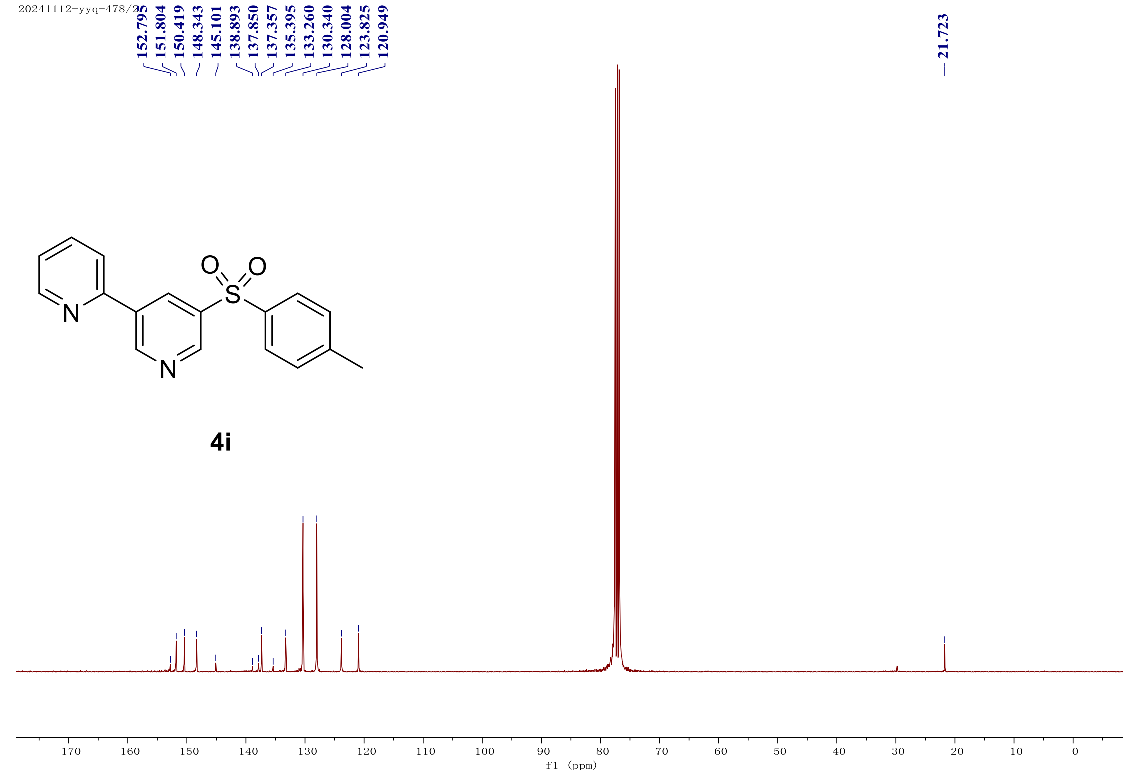
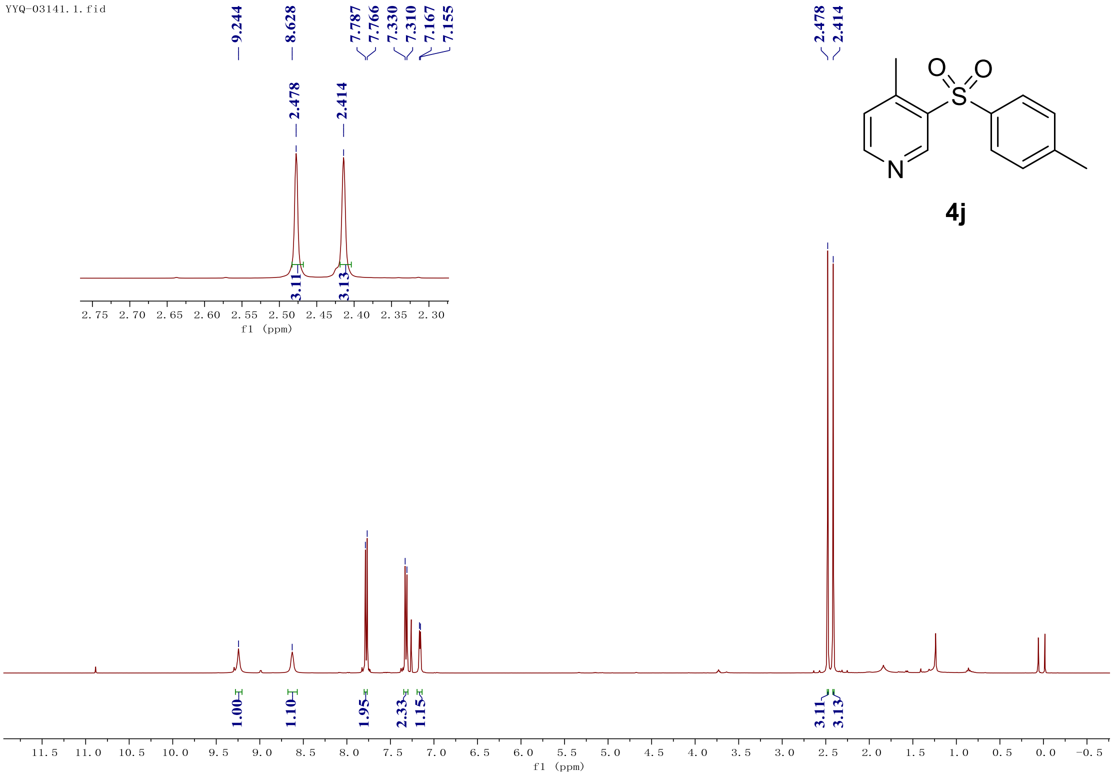
4h

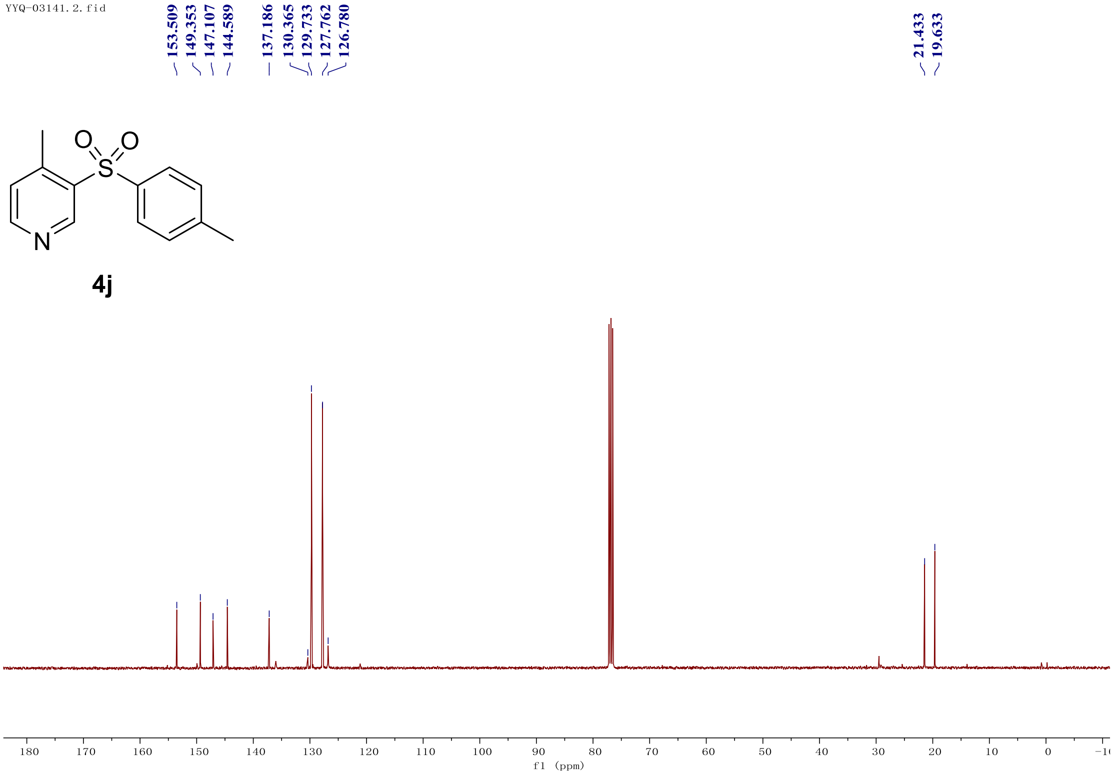
Materials 4i: ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$).



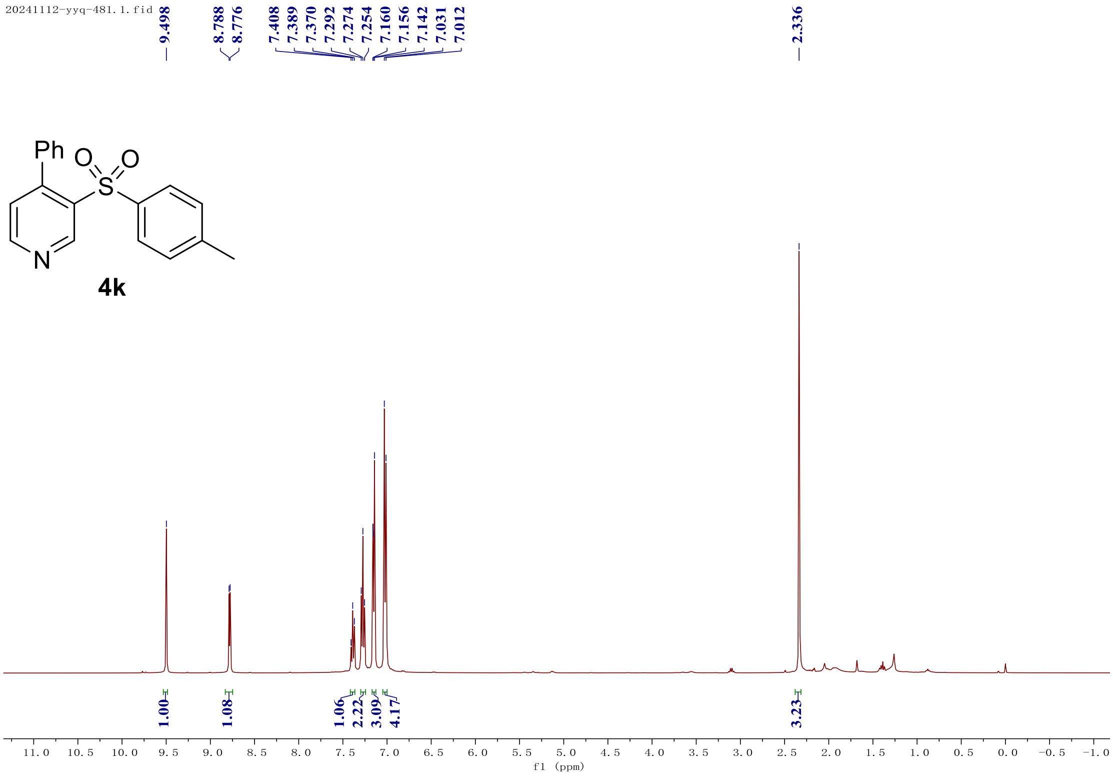


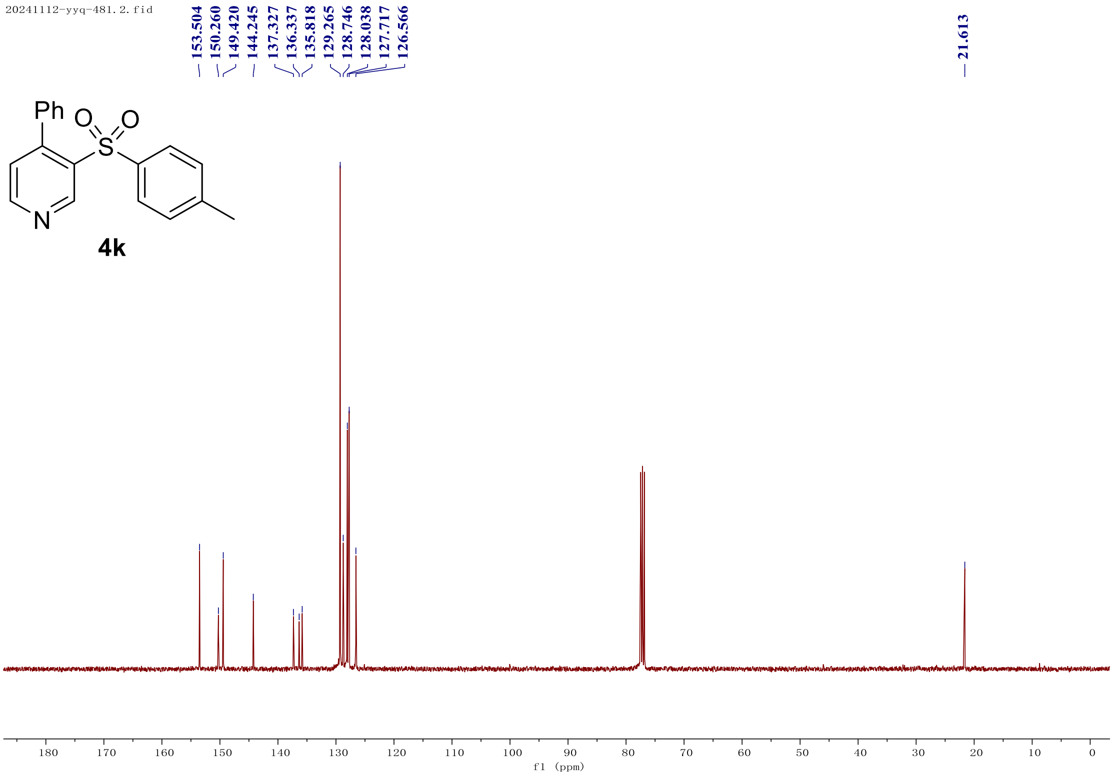
Materials 4j: ^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C NMR (101 MHz, CDCl$_3$).



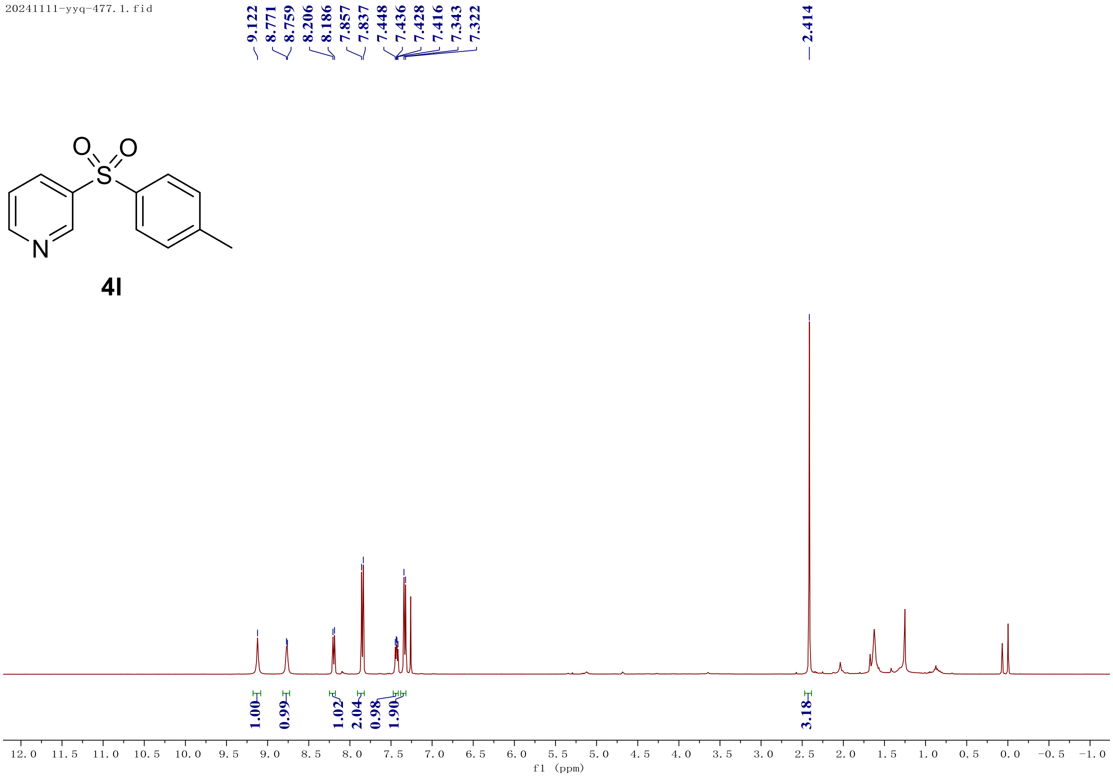


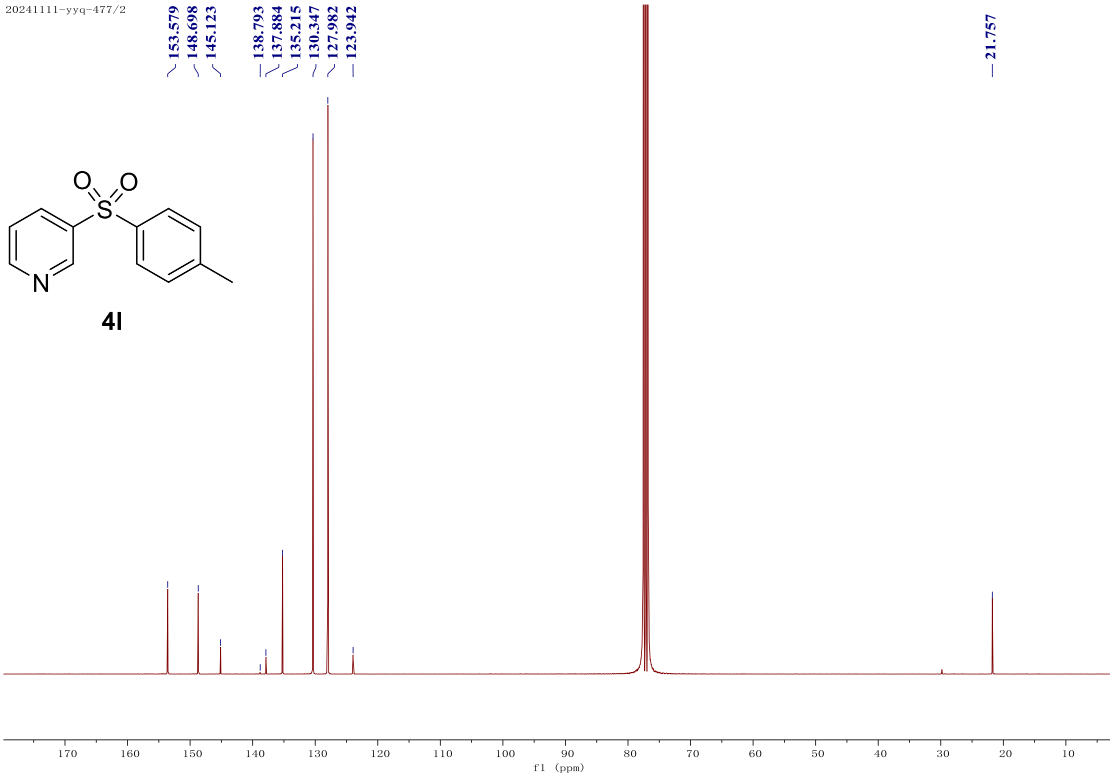
Materials 4k: ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$).



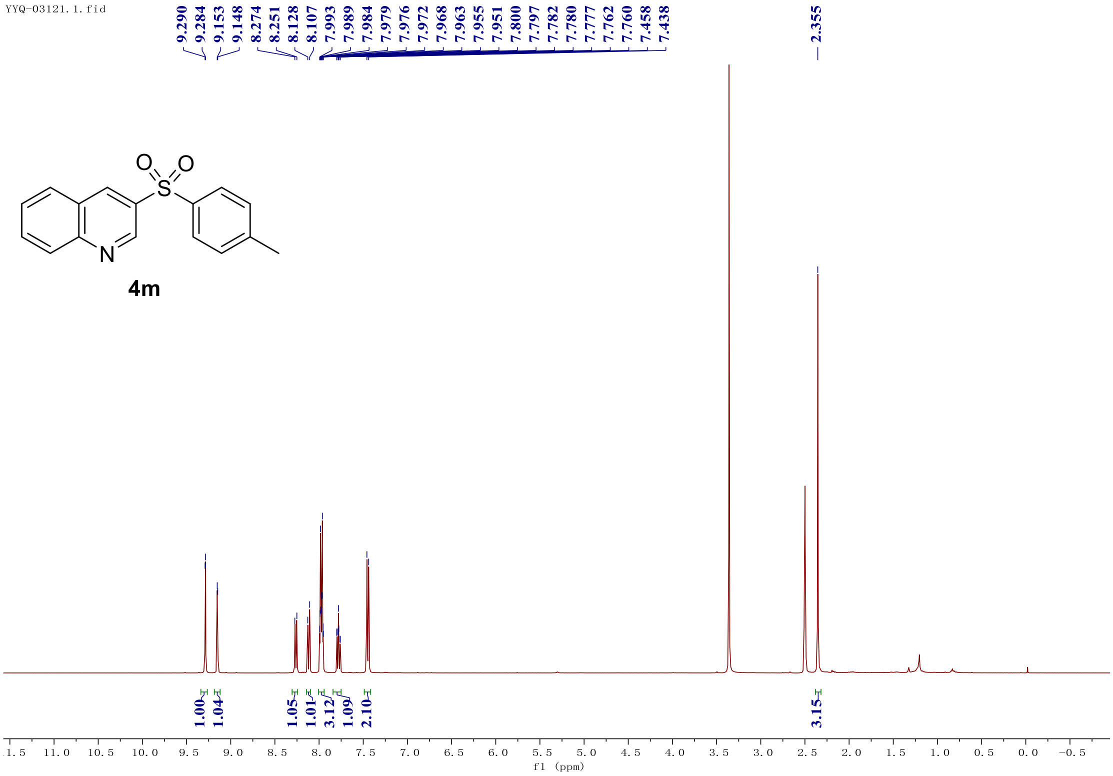


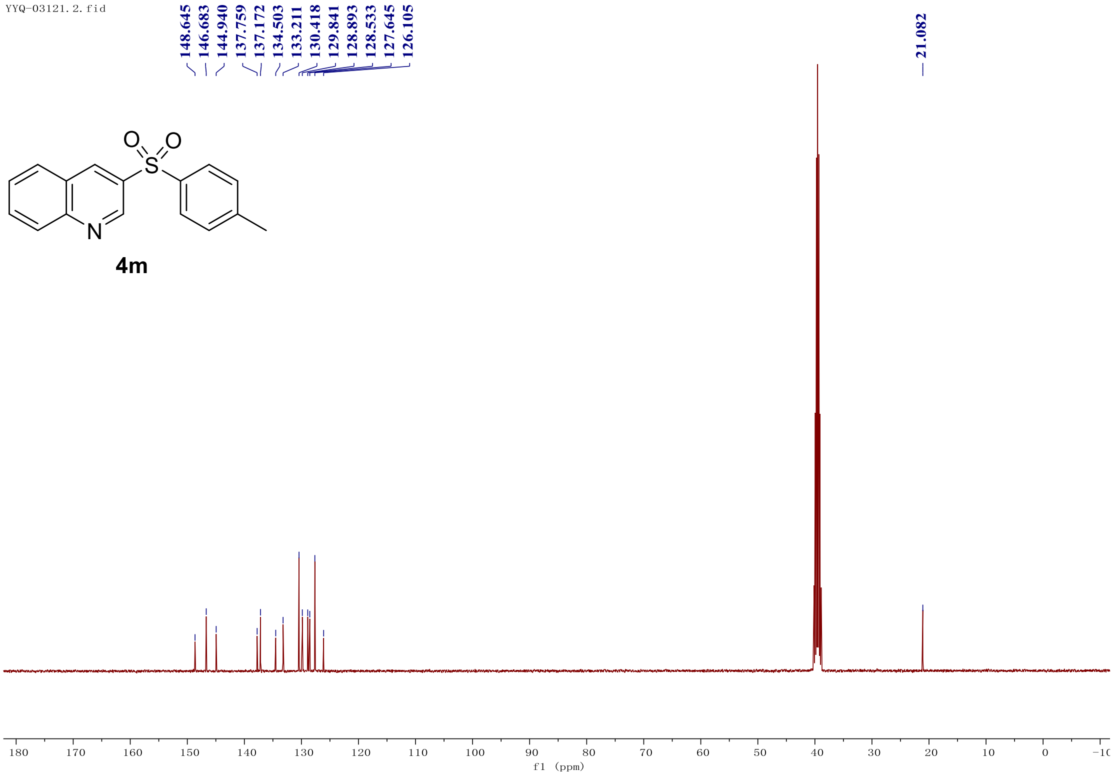
Materials 4l: ^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C NMR (101 MHz, CDCl$_3$).



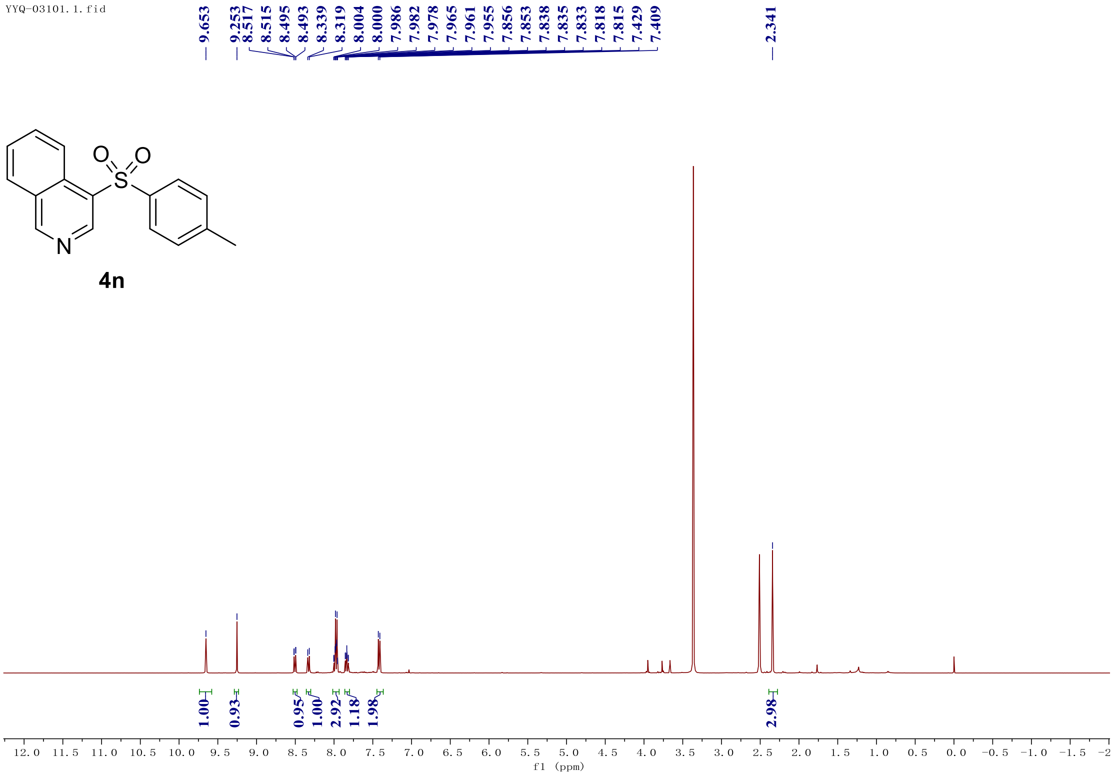


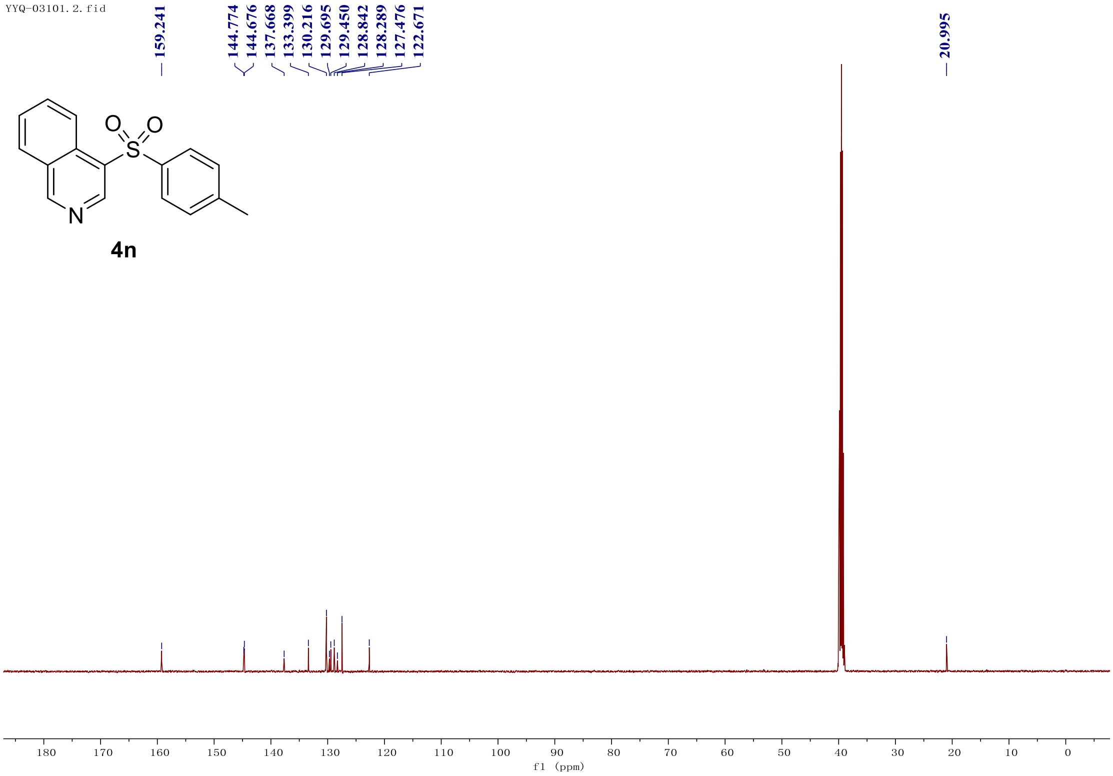
Materials 4m: ^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (101 MHz, DMSO-d_6).



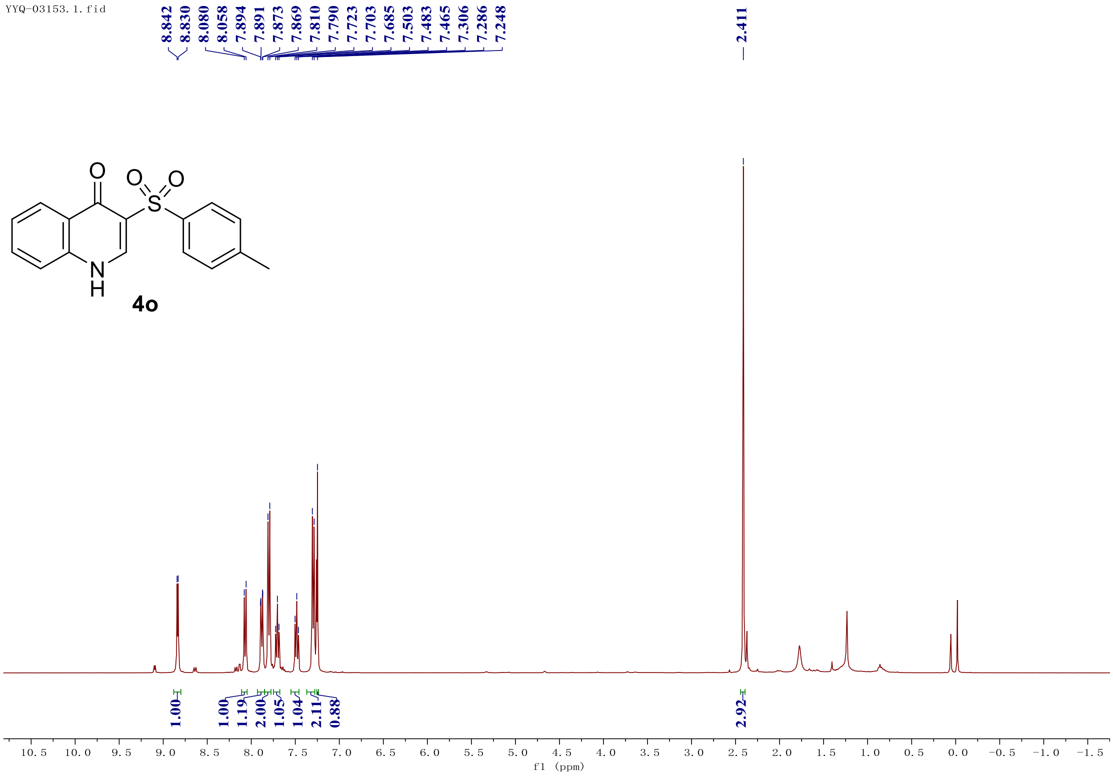


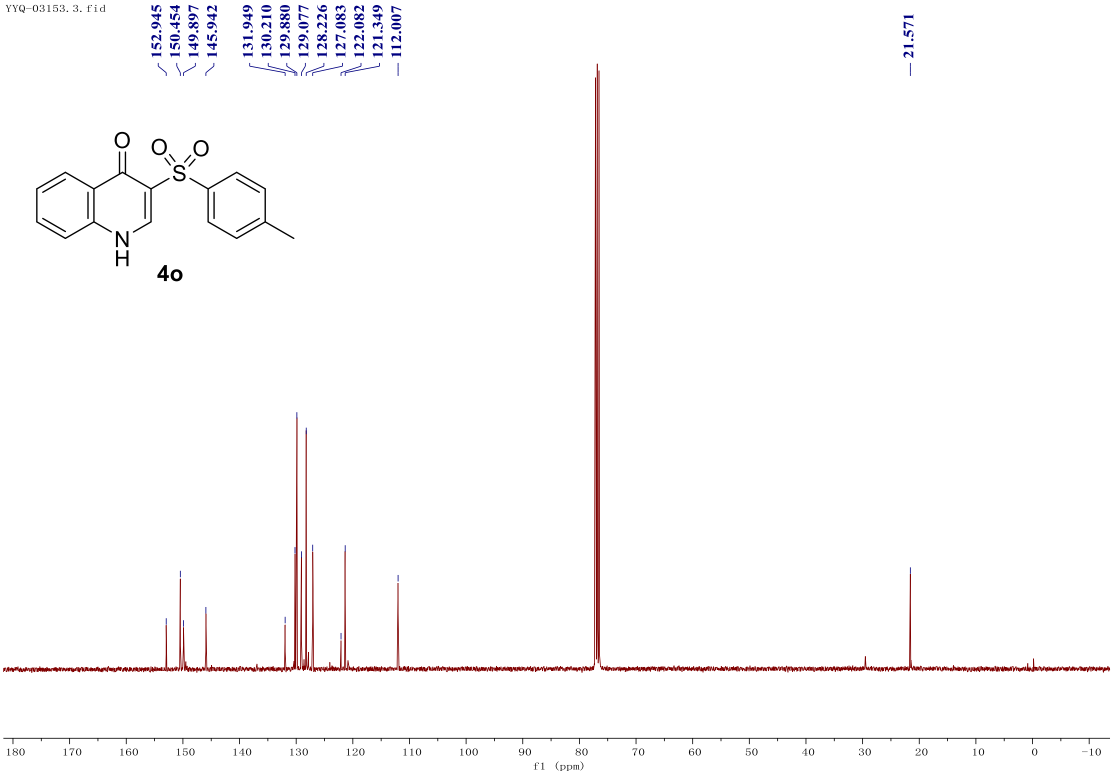
Materials 4n: ^{1}H NMR (500 MHz, DMSO-d_6) and ^{13}C NMR (126 MHz, DMSO-d_6).



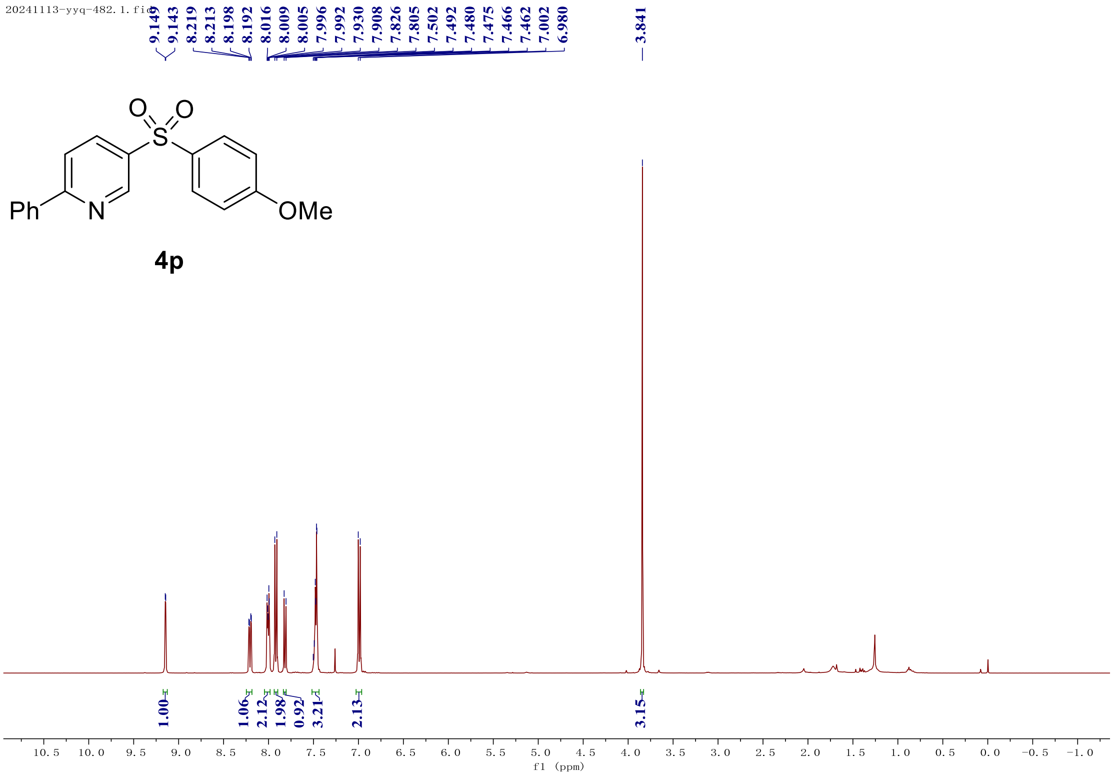


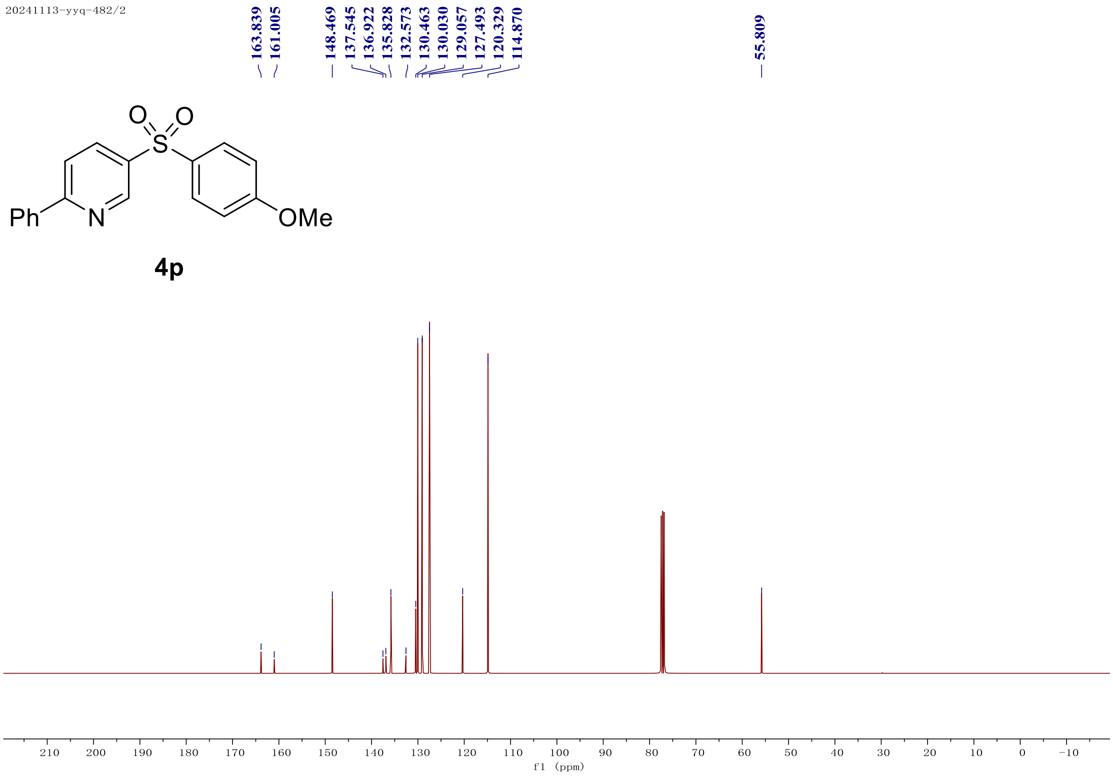
Materials 4o: ^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C NMR (101 MHz, CDCl$_3$).



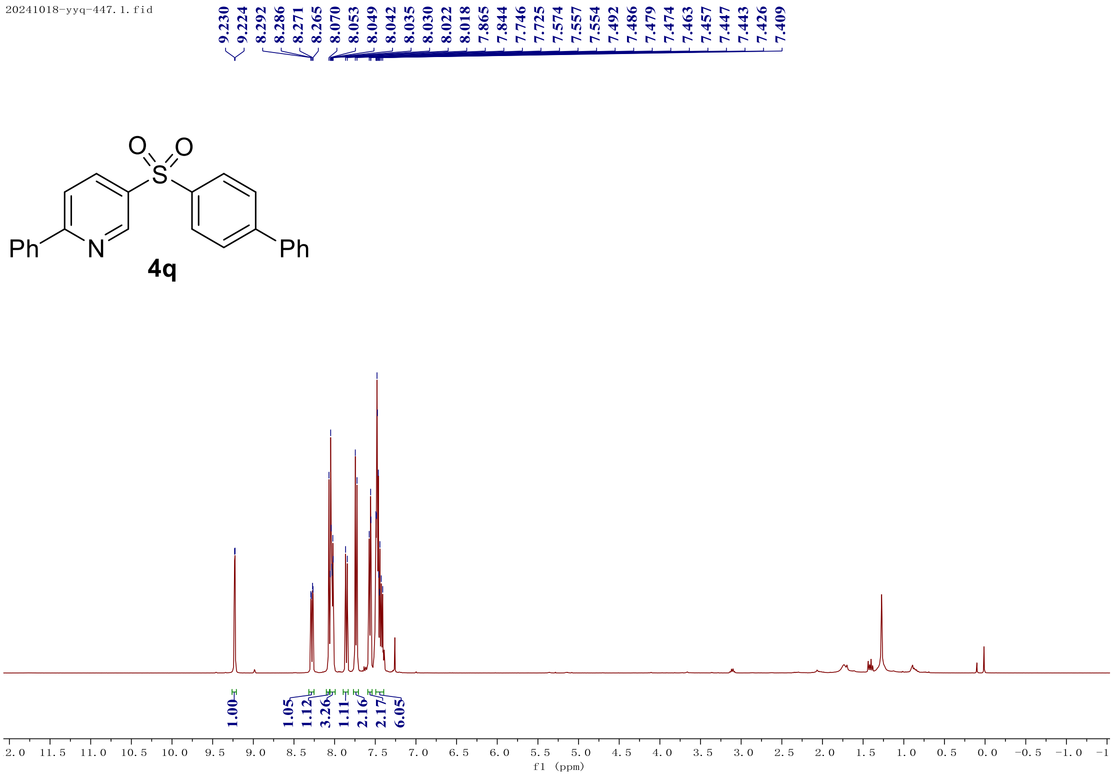


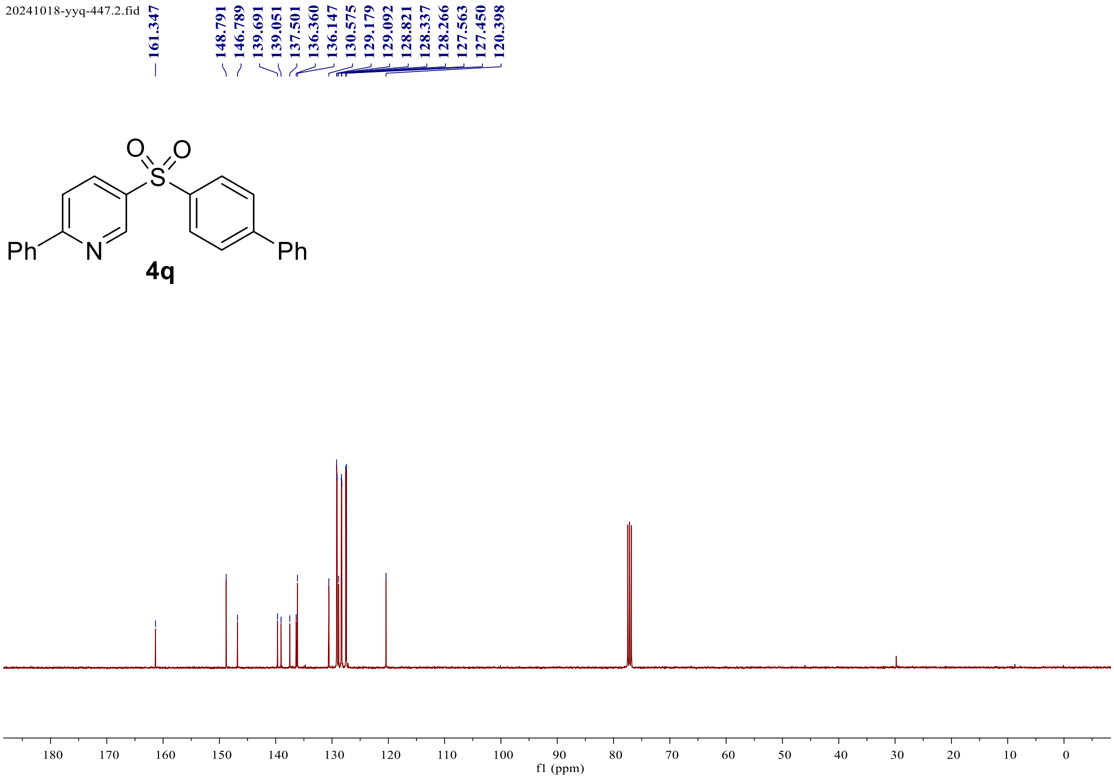
Materials 4p: ^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C NMR (101 MHz, CDCl$_3$).



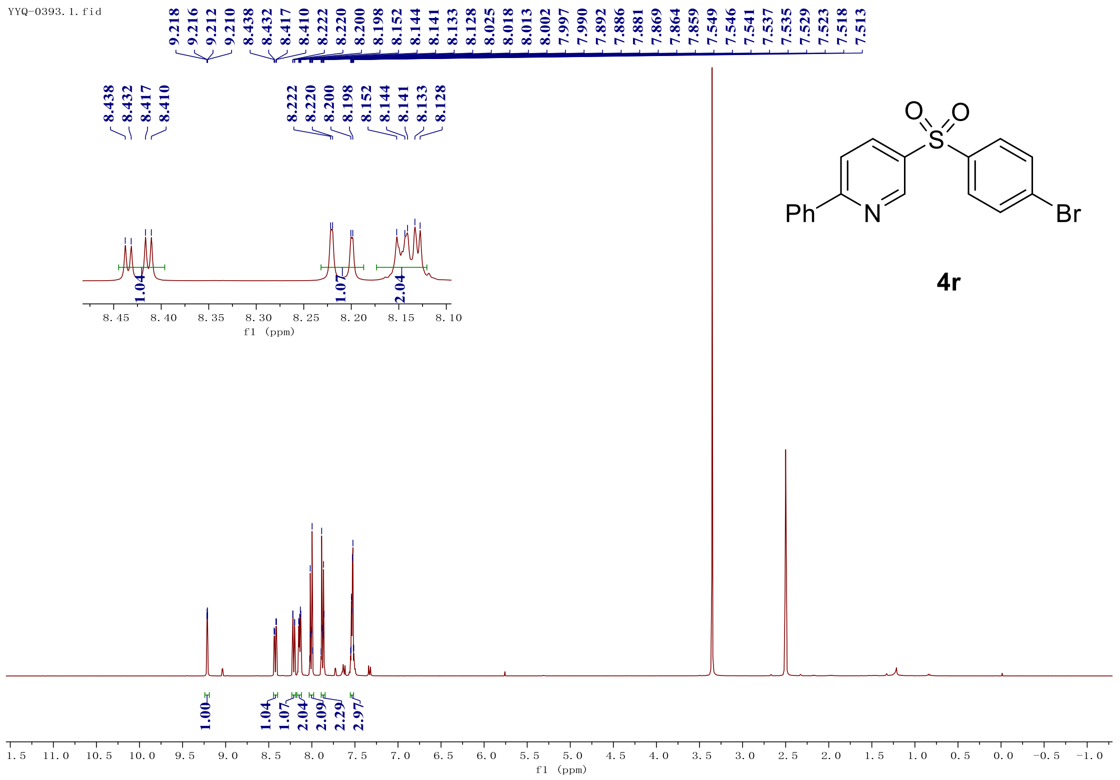


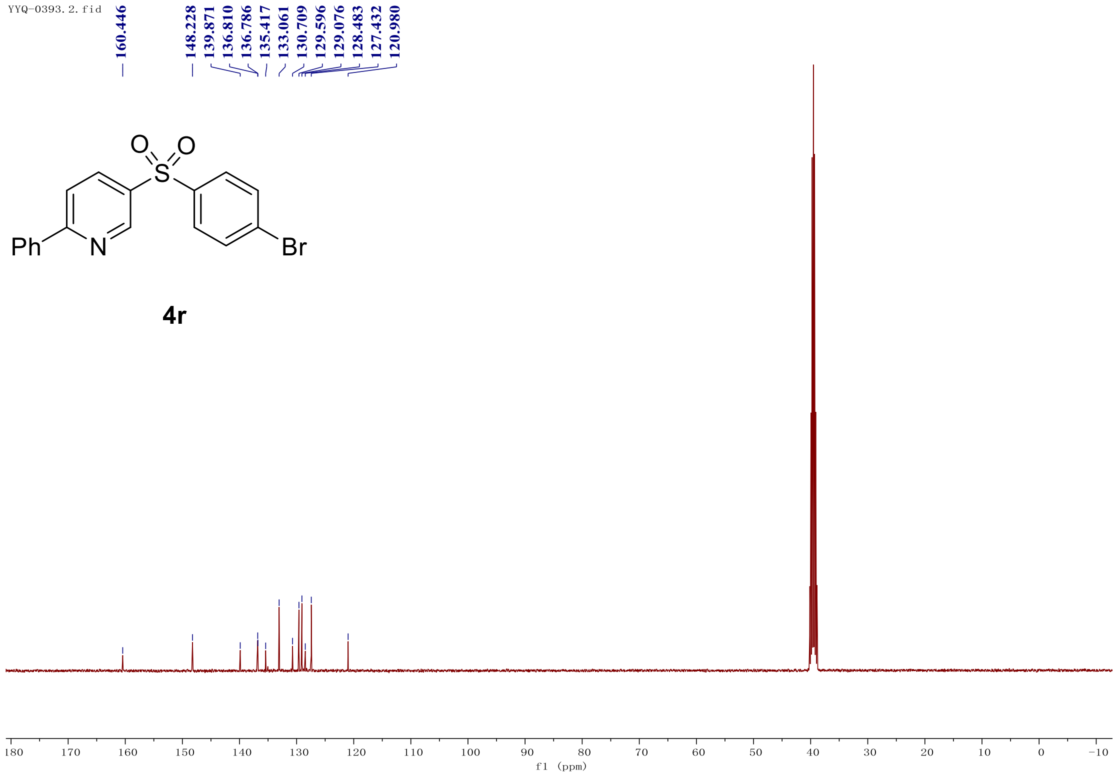
Materials 4q: ^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C NMR (101 MHz, CDCl$_3$).



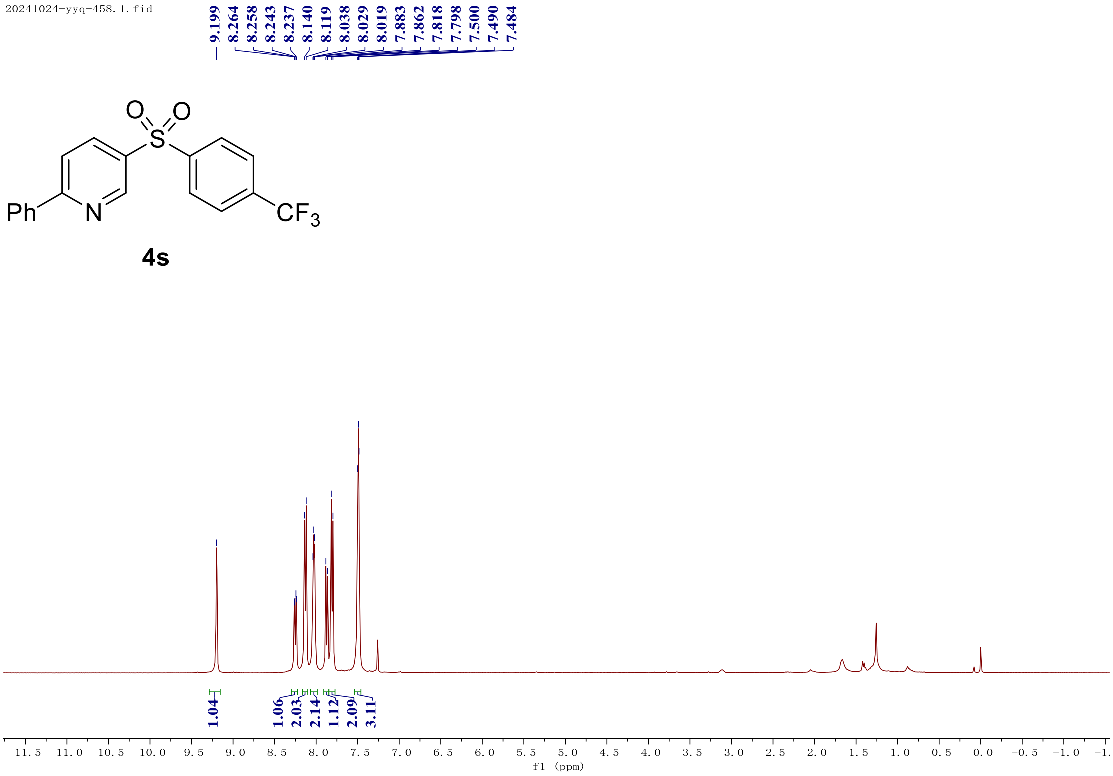


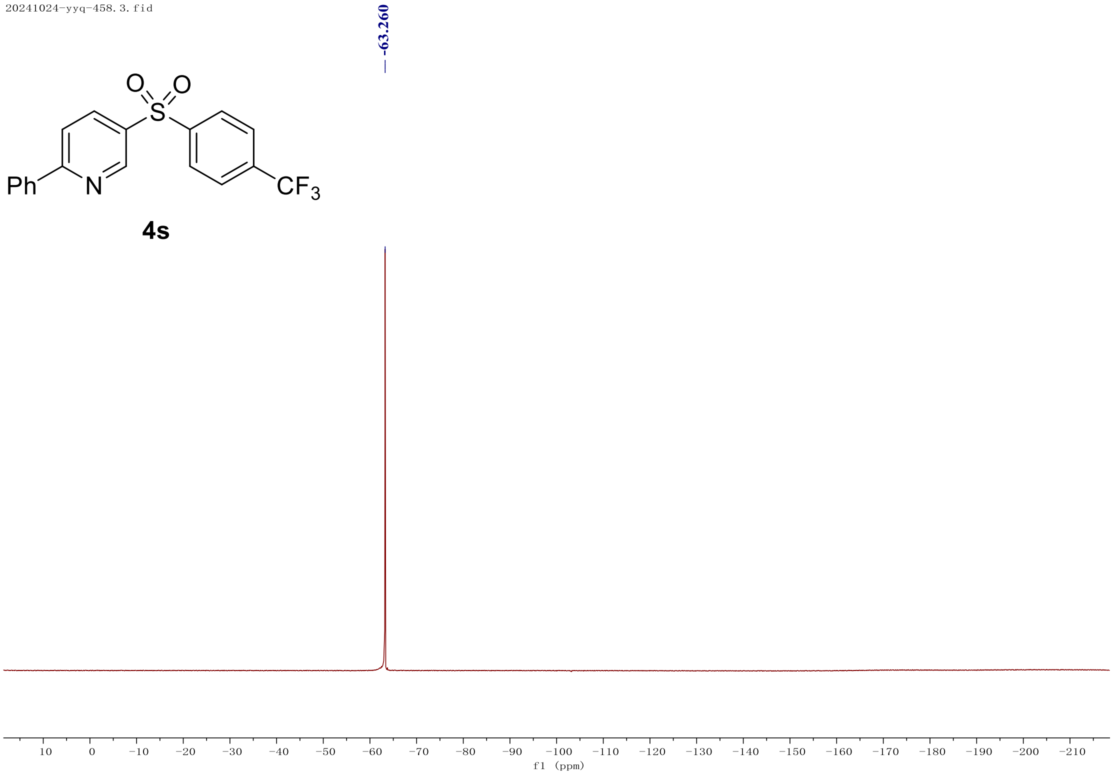
Materials 4r: ^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (101 MHz, DMSO-d_6).

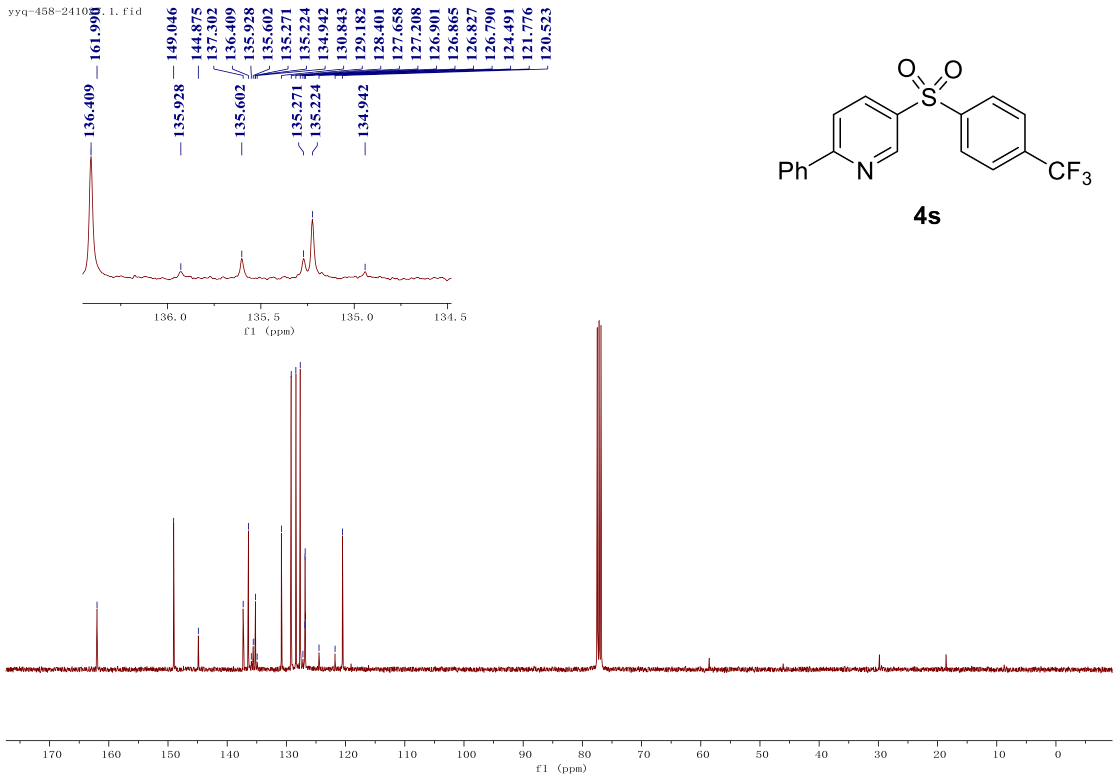




Materials 4s: ^{1}H NMR (400 MHz, CDCl$_3$), ^{19}F NMR (376 MHz, CDCl$_3$) and ^{13}C NMR (101 MHz, CDCl$_3$).

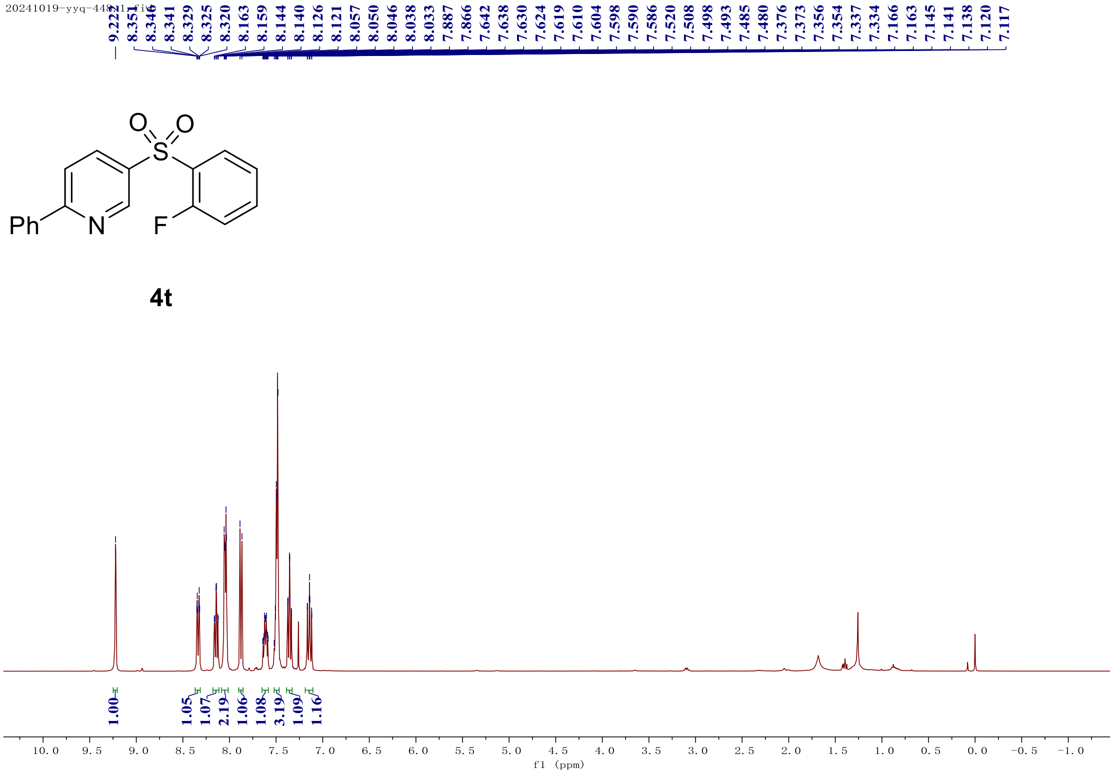


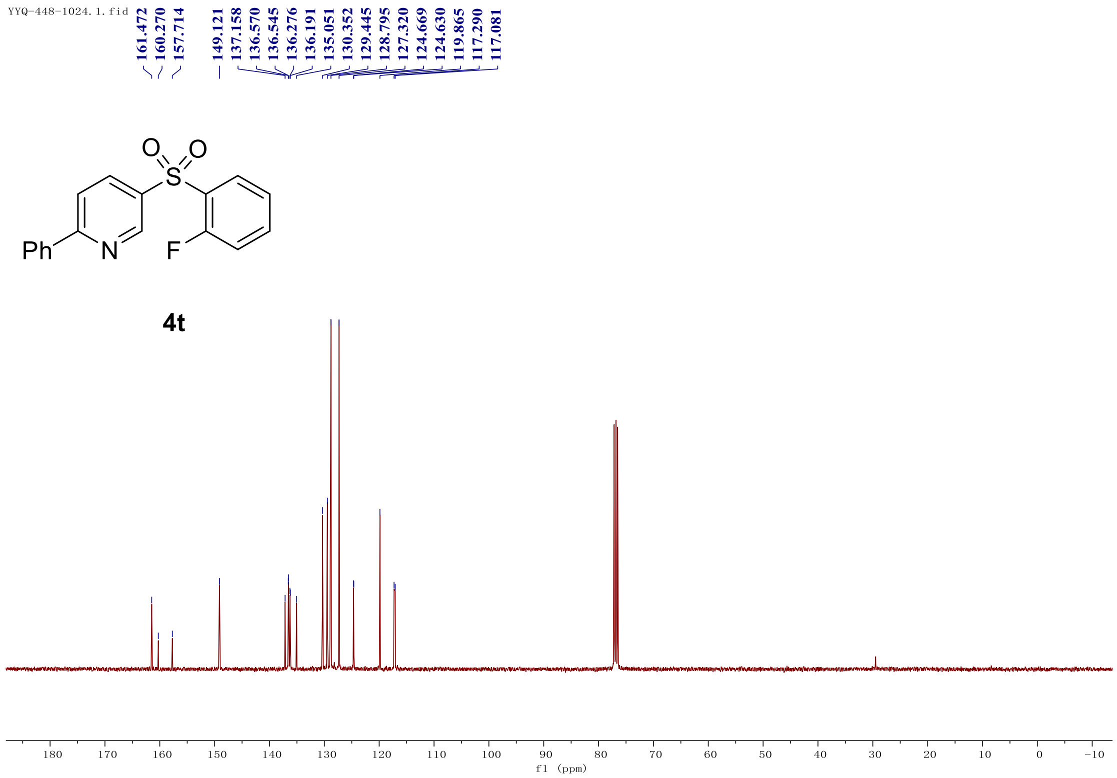



yyq-458-241027.1.fid
161.990
149.046
144.875
137.302
136.409
135.928
135.602
135.271
135.224
134.942
130.843
129.182
128.401
127.658
127.208
126.901
126.865
126.827
126.790
124.491
121.776
120.523
136.409
135.928
135.602
135.271
135.224
134.942
136.0
135.5
135.0
134.5
f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
O
O
S
Ph
N
CF3

4s

Materials 4t: ^{1}H NMR (400 MHz, CDCl$_3$), ^{19}F NMR (376 MHz, CDCl$_3$) and ^{13}C NMR (101 MHz, CDCl$_3$).

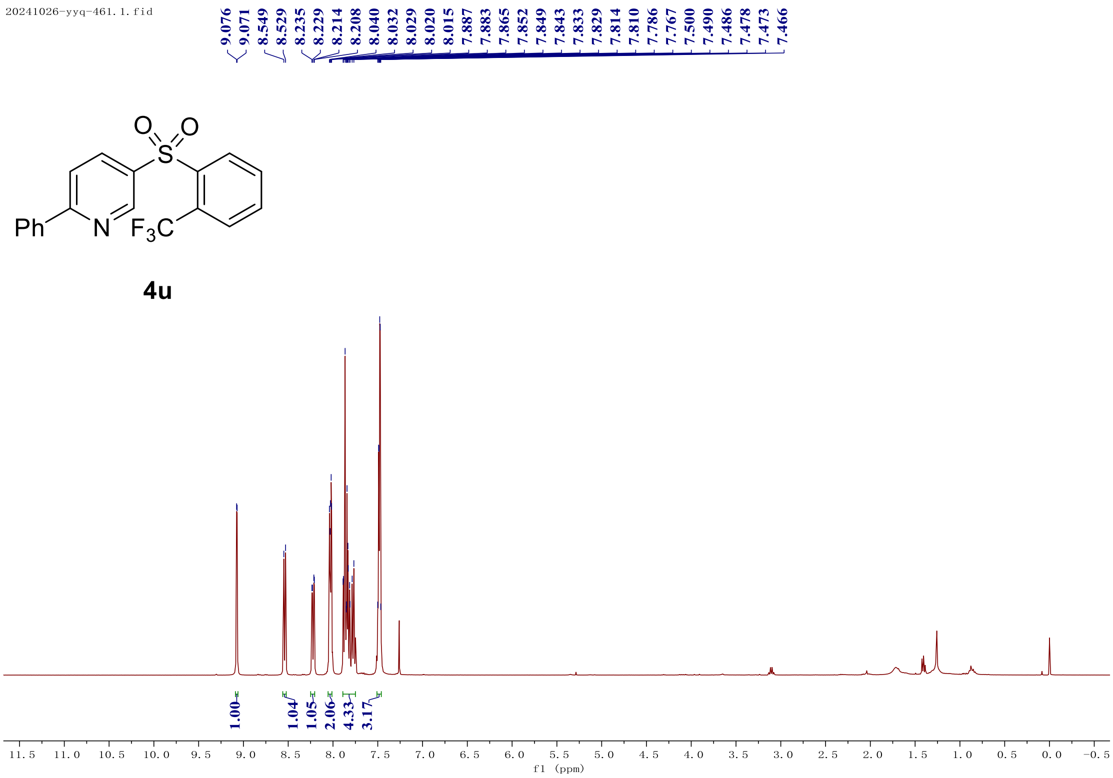


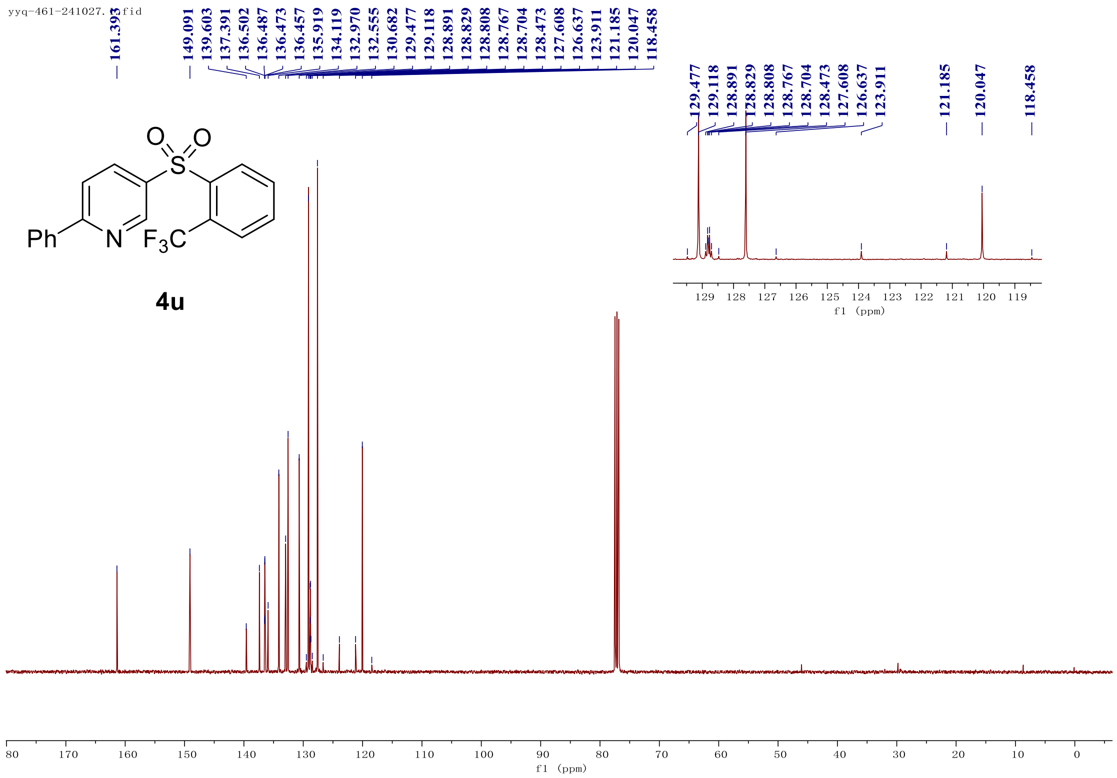


4t

YYQ-448-1024.1.fid
161.472
160.270
157.714
149.121
137.158
136.570
136.545
136.276
136.191
135.051
130.352
129.445
128.795
127.320
124.669
124.630
119.865
117.290
117.081
O
O
S
Ph
N
F
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

Materials 4u: ^{1}H NMR (400 MHz, CDCl$_3$), ^{19}F NMR (376 MHz, CDCl$_3$) and ^{13}C NMR (101 MHz, CDCl$_3$).




yyq-461-241027.1.fid
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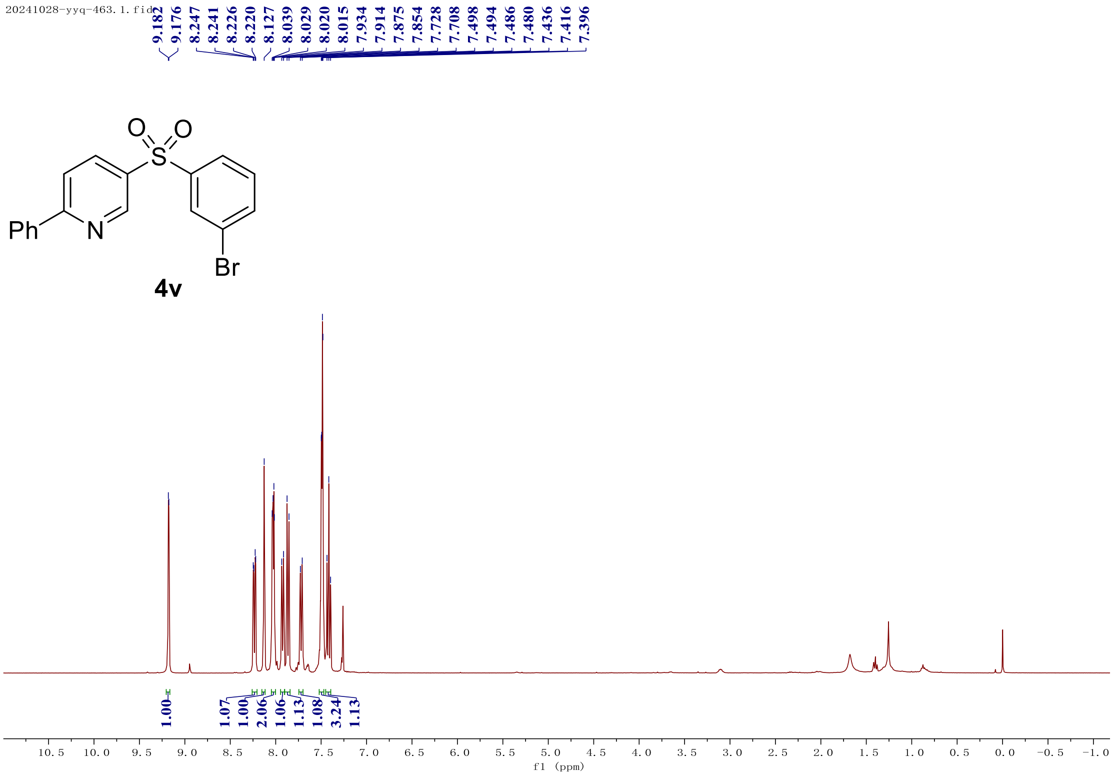
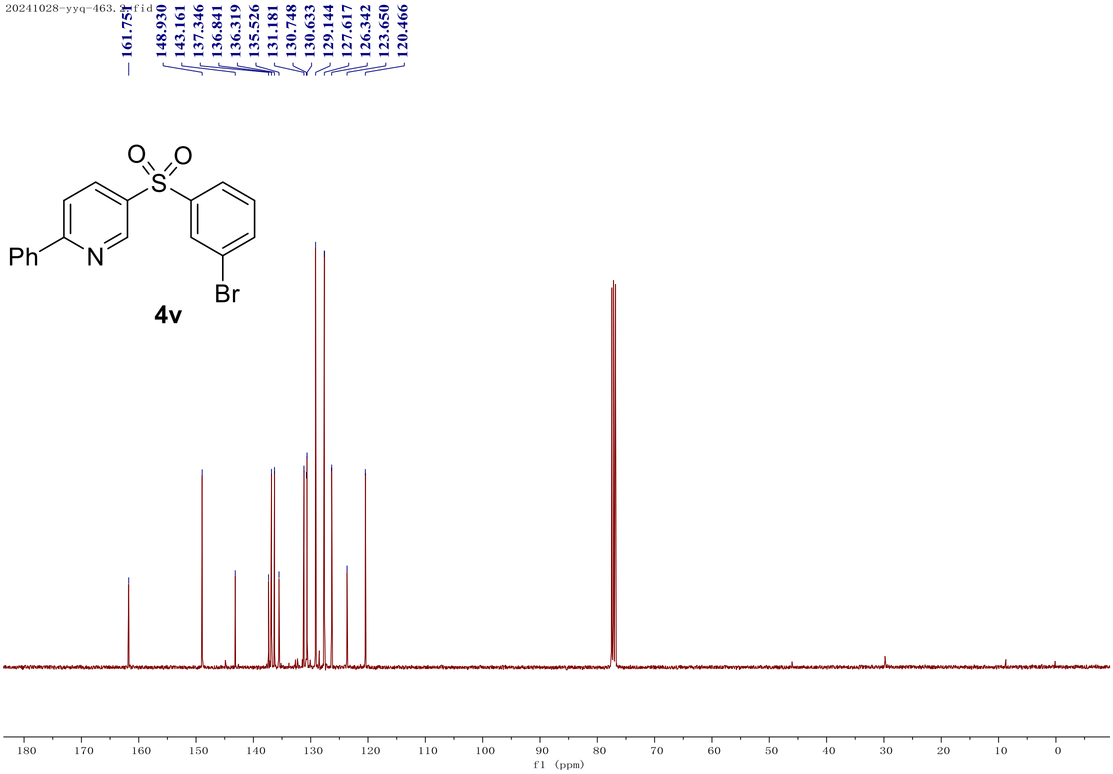
149.091
139.603
137.391
136.502
136.487
136.473
136.457
135.919
134.119
132.970
132.555
130.682
129.477
129.118
128.891
128.829
128.808
128.767
128.704
128.473
127.608
126.637
123.911
121.185
120.047
118.458
O
O
S
Ph
N
F3C
129 128 127 126 125 124 123 122 121 120 119
f1 (ppm)
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

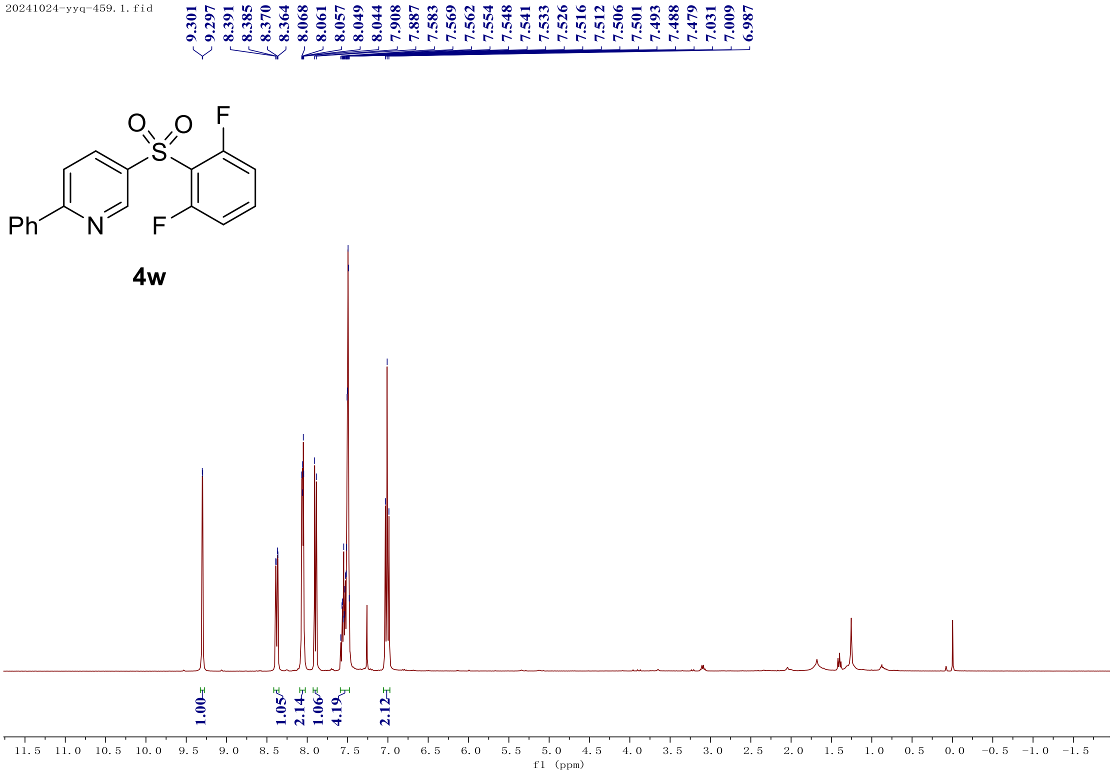
4u

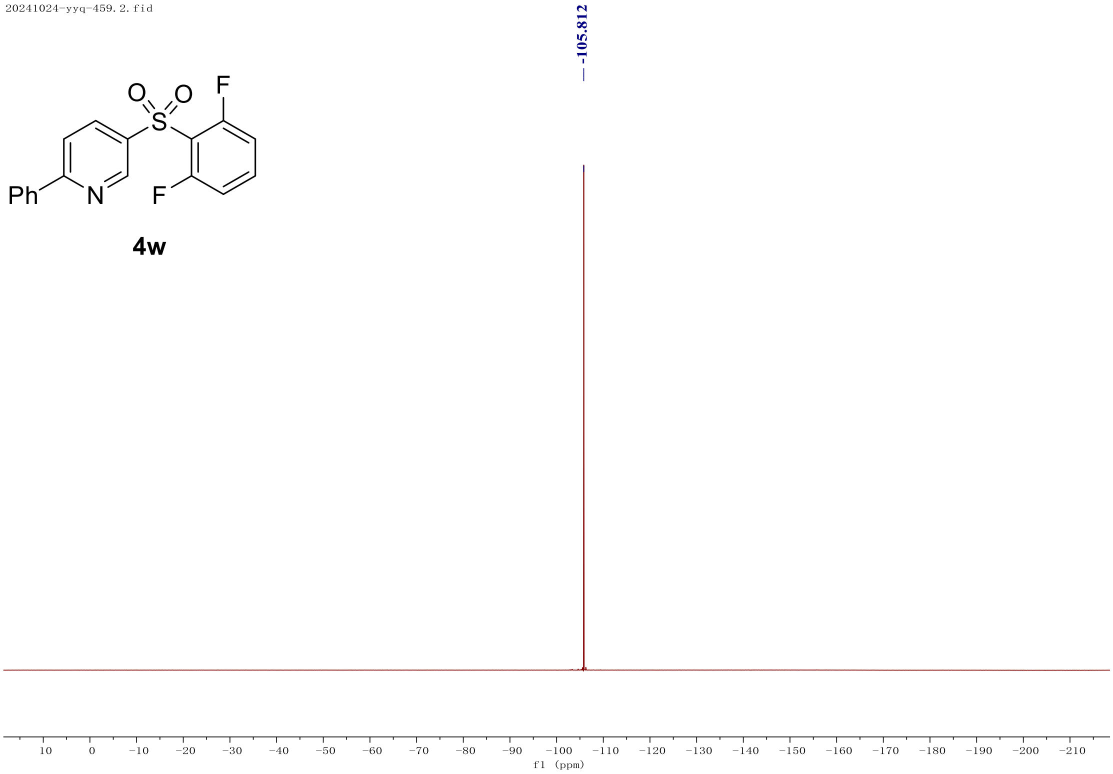
Materials 4v: ^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C NMR (101 MHz, CDCl$_3$).

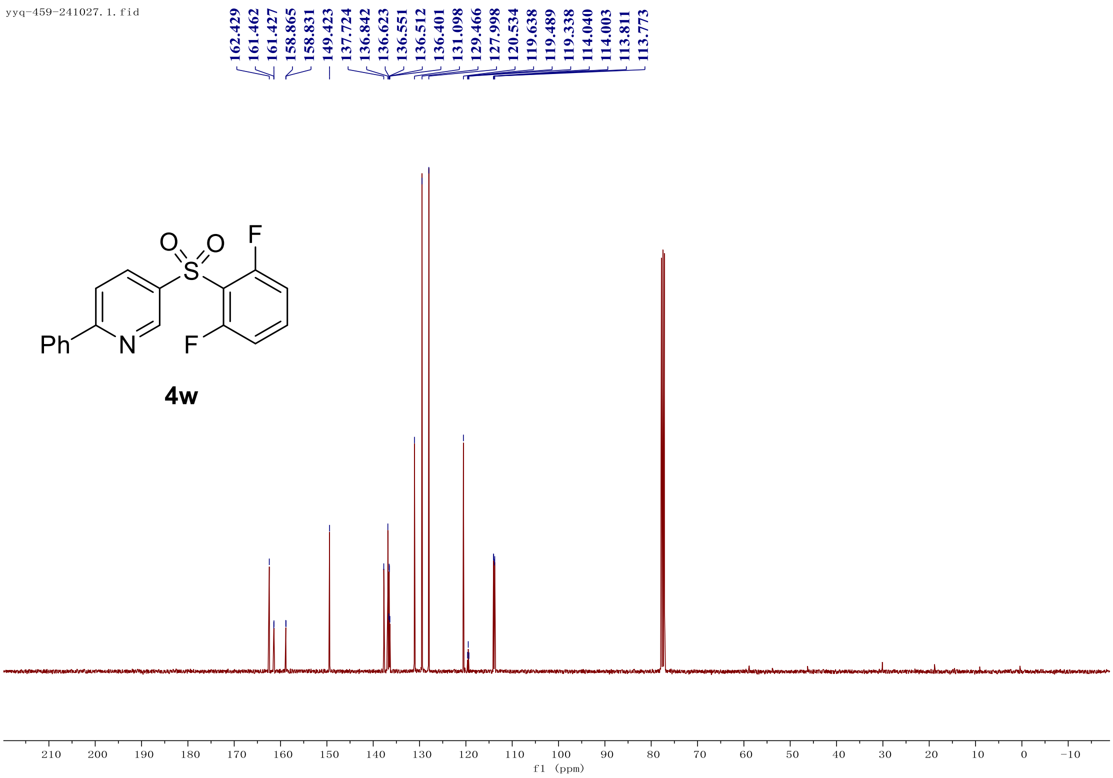




Materials 4w: ^{1}H NMR (400 MHz, CDCl$_3$), ^{19}F NMR (376 MHz, CDCl$_3$) and ^{13}C NMR (101 MHz, CDCl$_3$).

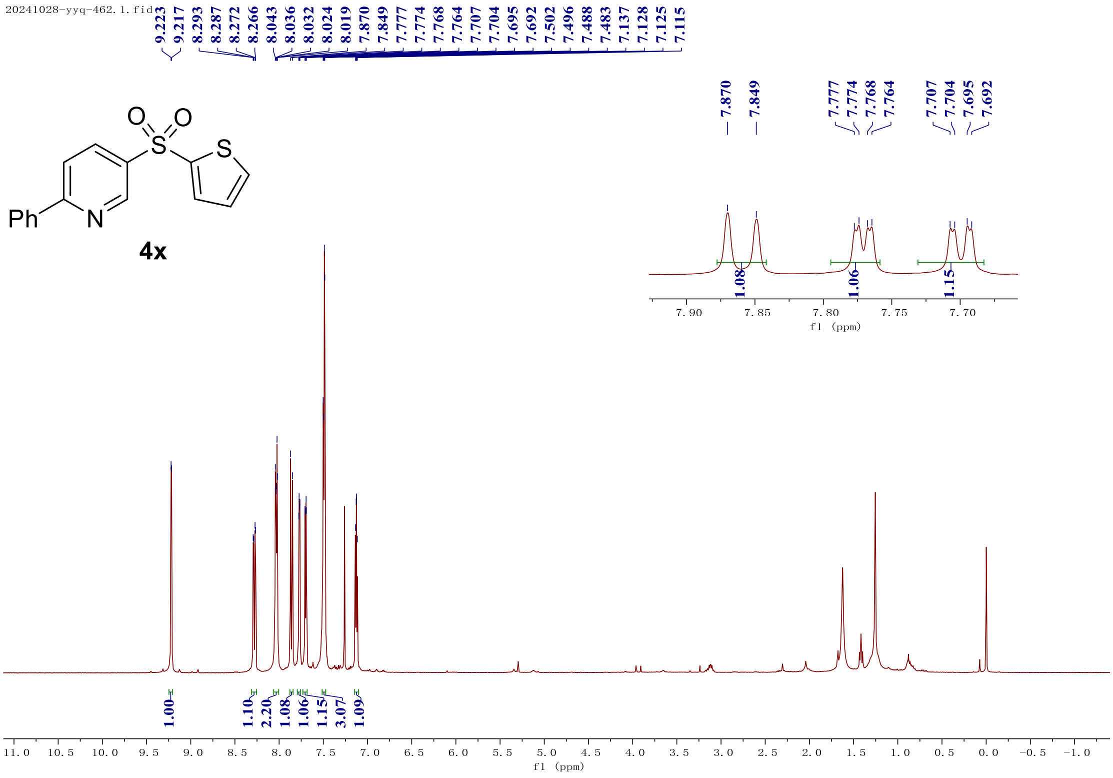


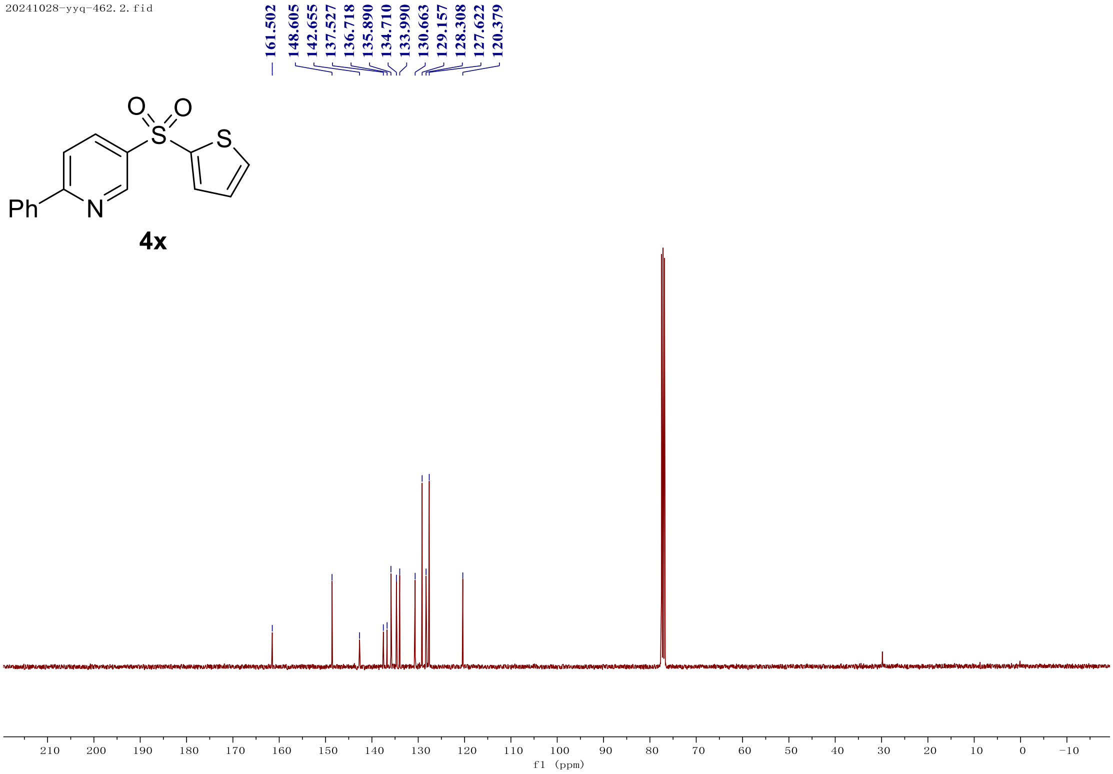



yyq-459-241027.1.fid
162.429
161.462
161.427
158.865
158.831
149.423
137.724
136.842
136.623
136.551
136.512
136.401
131.098
129.466
127.998
120.534
119.638
119.489
119.338
114.040
114.003
113.811
113.773
O
O
S
F
F
Ph
N
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

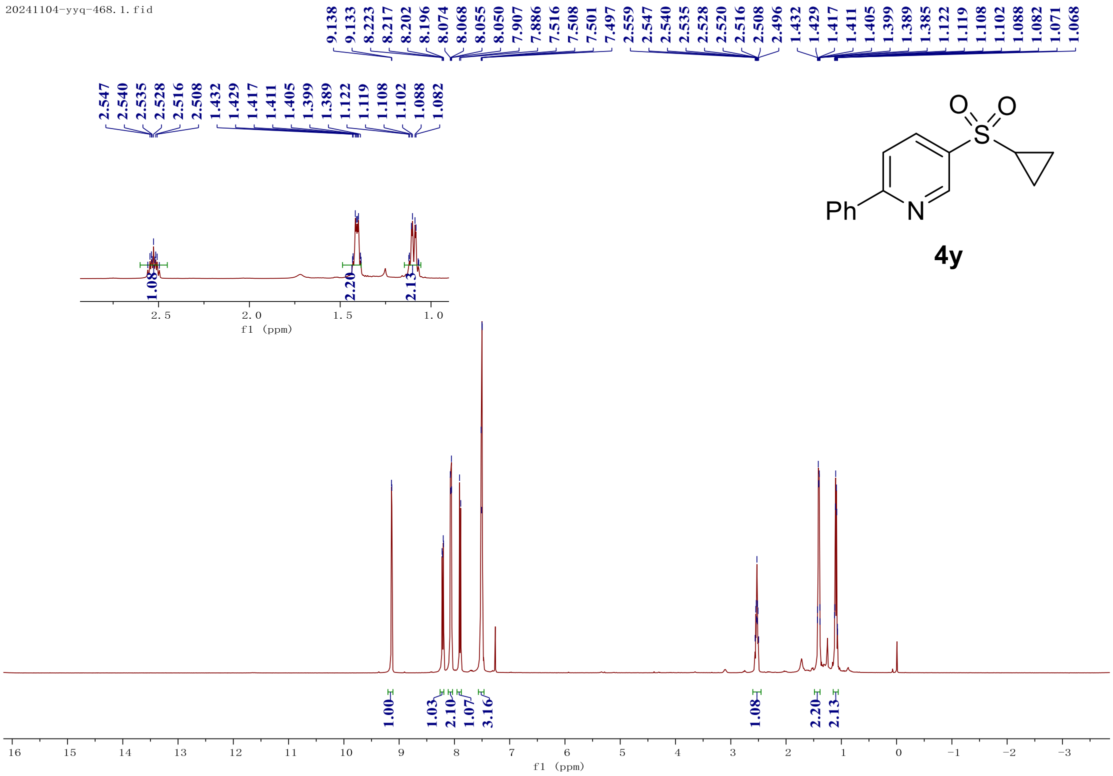
4w

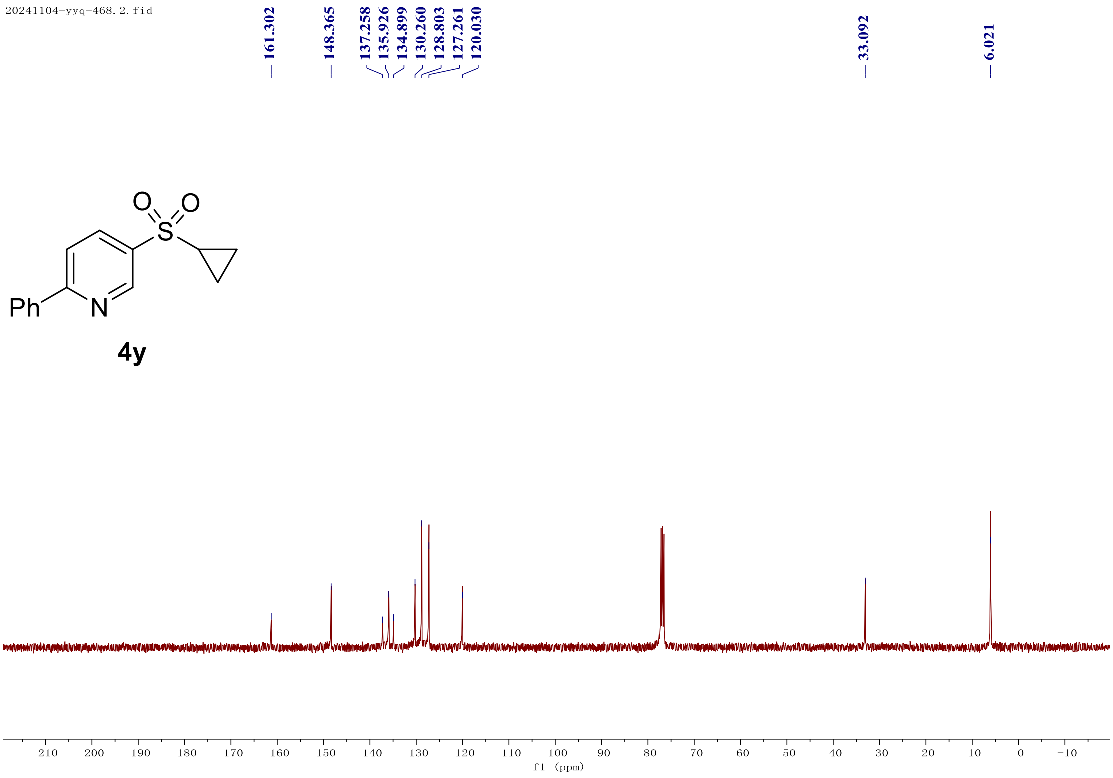
Materials 4x: ^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C NMR (101 MHz, CDCl$_3$).



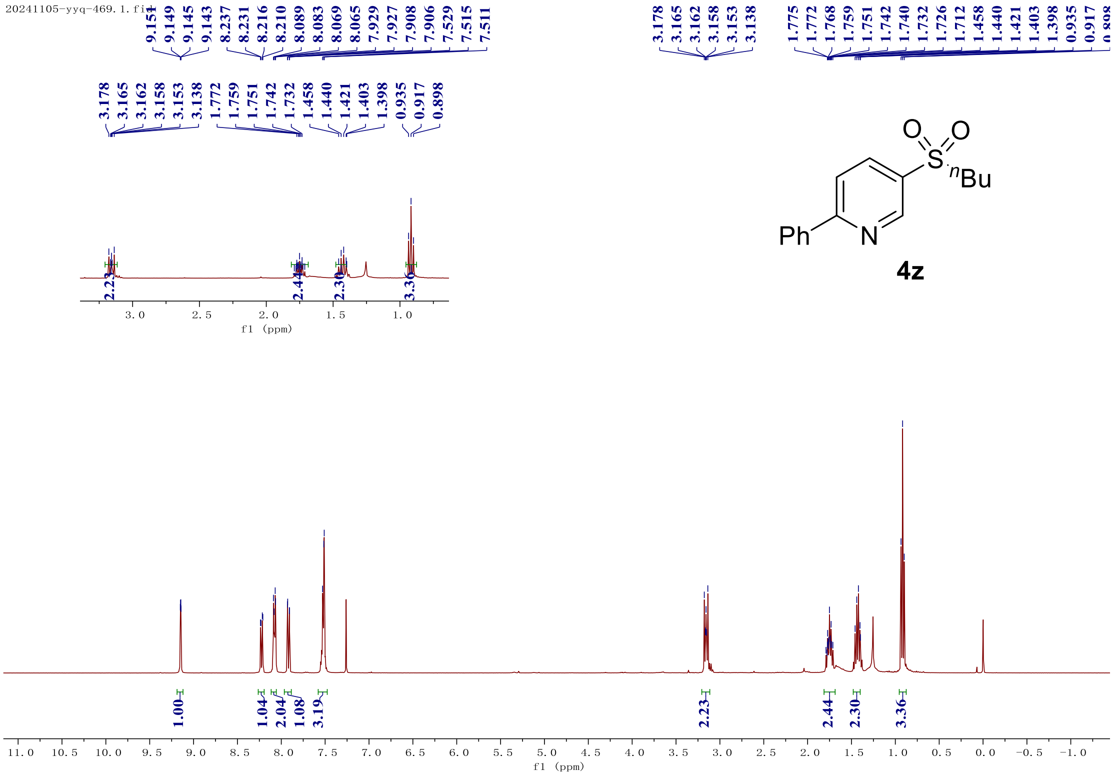


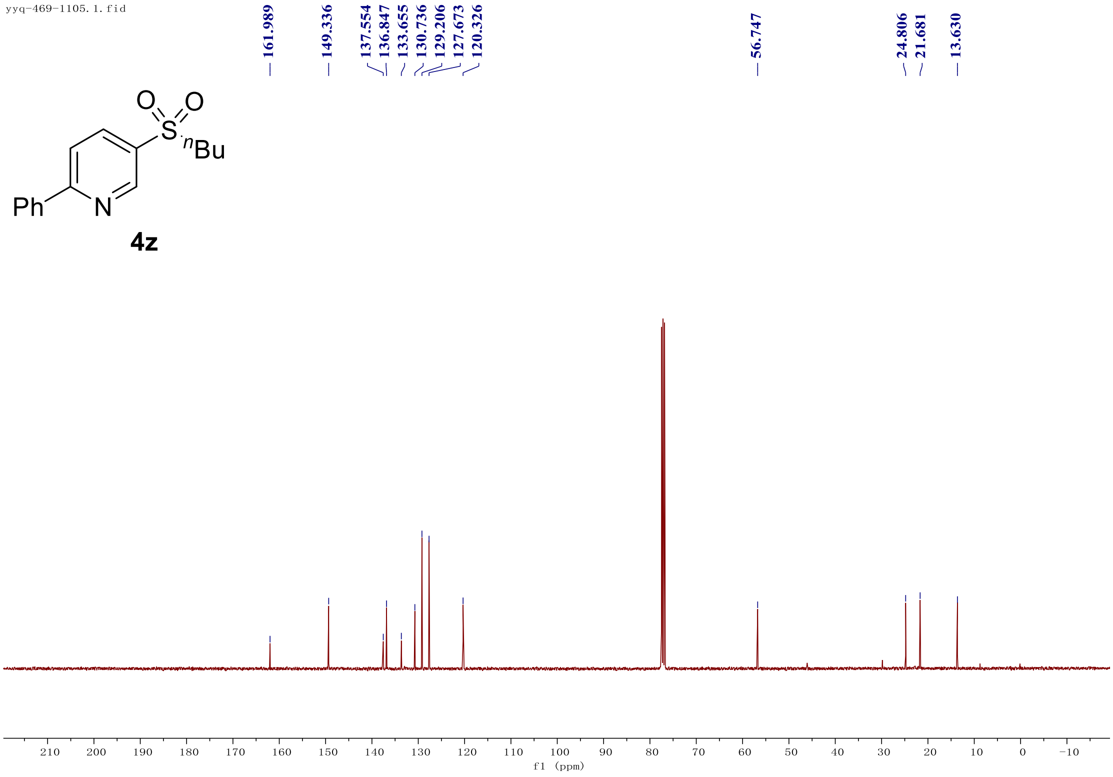
Materials 4y: ^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C NMR (101 MHz, CDCl$_3$).



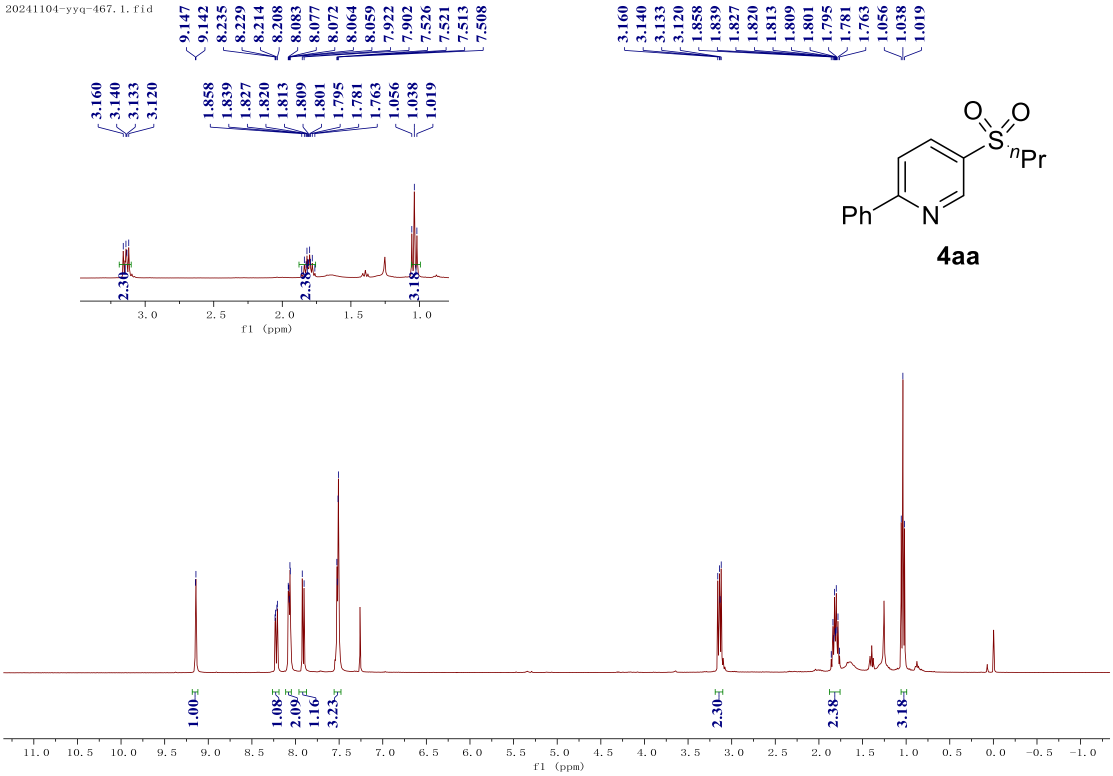


Materials 4z: ^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C NMR (101 MHz, CDCl$_3$).

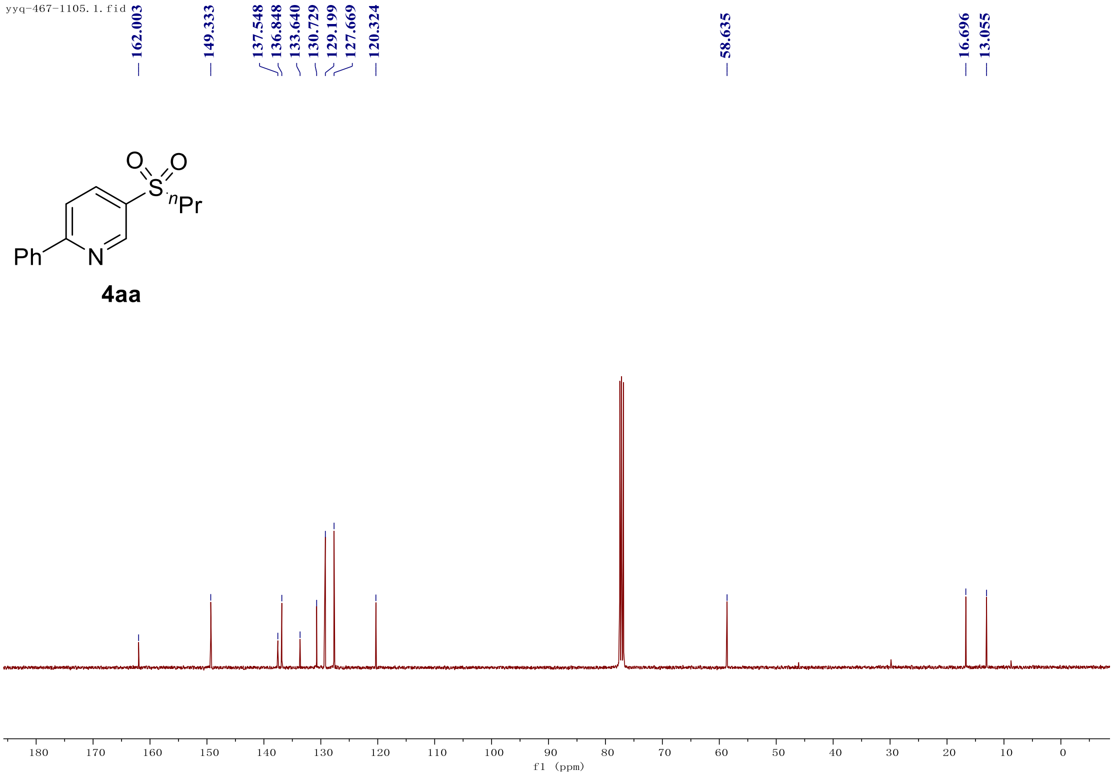




Materials 4aa: ^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C NMR (101 MHz, CDCl$_3$).

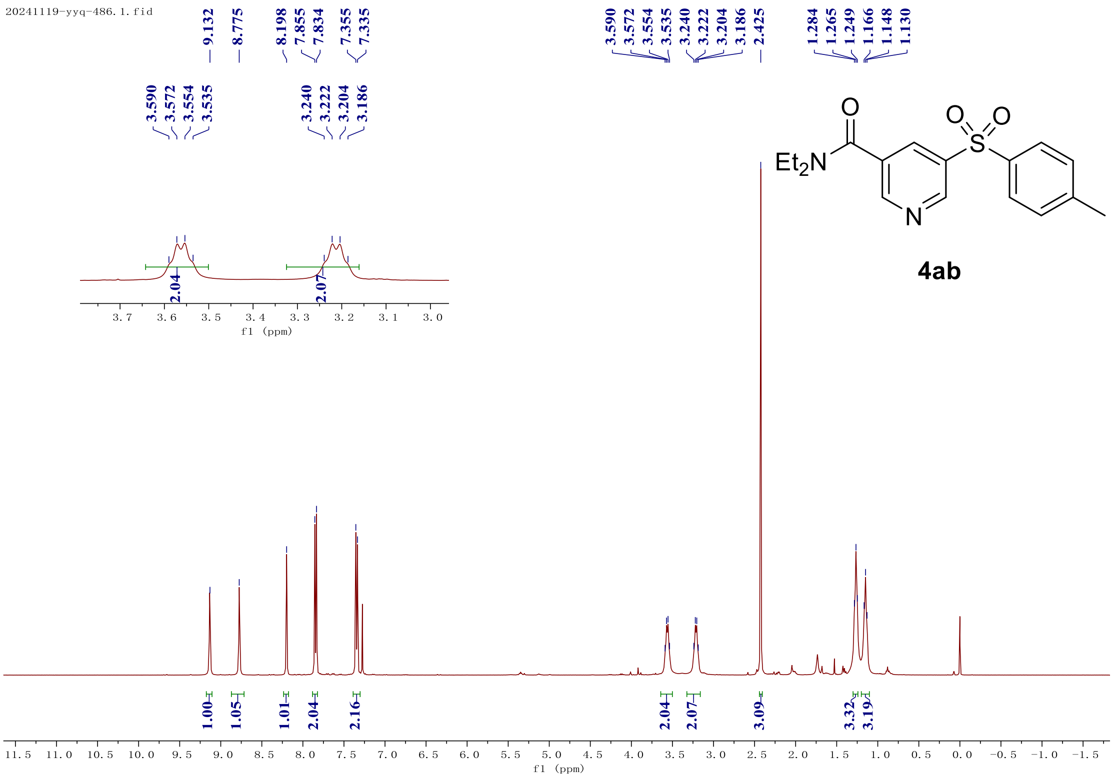


4aa

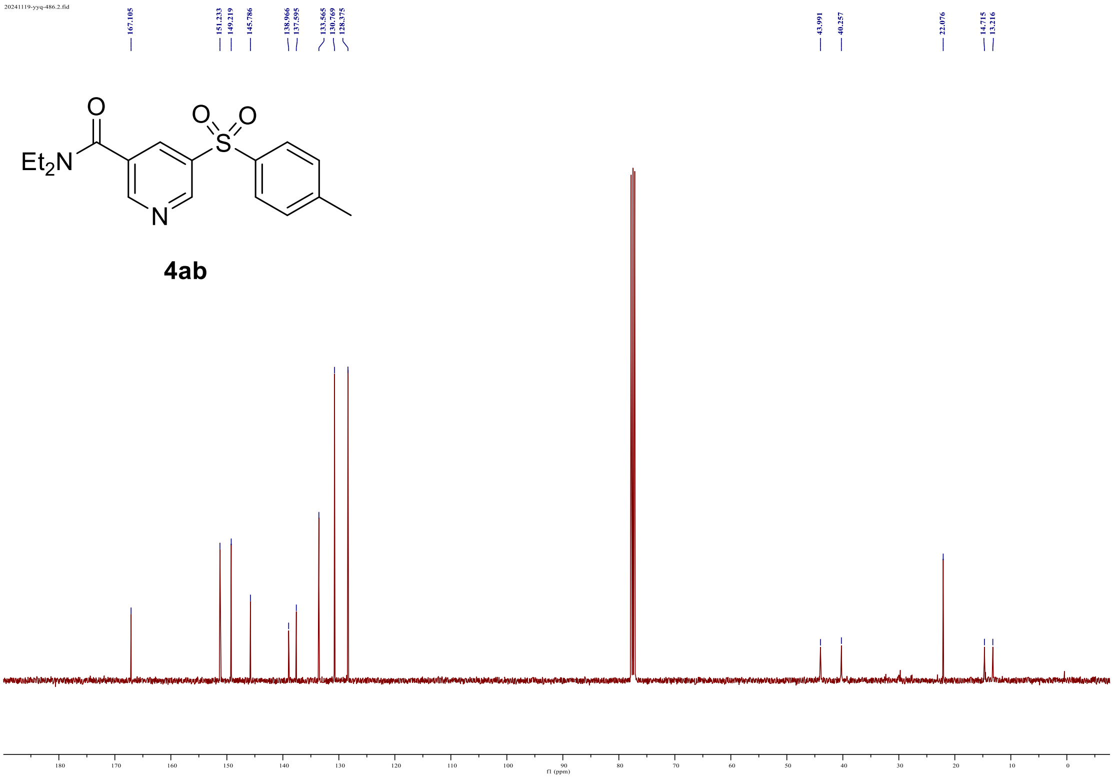


4aa

Materials 4ab: ^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C NMR (101 MHz, CDCl$_3$).



4ab



4ab

Materials 4ac: ^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C NMR (101 MHz, CDCl$_3$).