Time-Dependent Rh(III)-Catalyzed Chemodivergent Reactions of 2-Pyridylthiophenes with Nitroalkenes

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1. General information

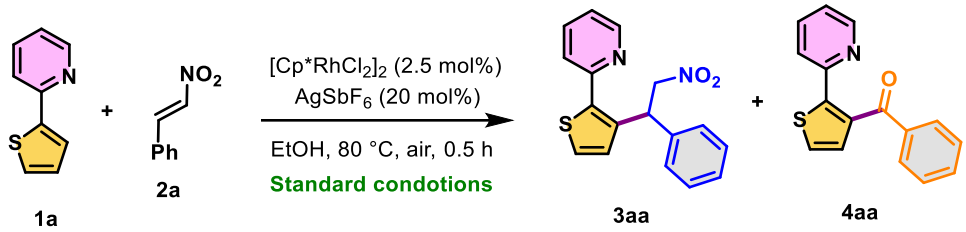
All the reagents were purchased from Bide Pharmatech Ltd. and Energy Chemical. All solvents were purchased from Greagent (Shanghai Titansci incorporated company) and used without further purification. Unless otherwise stated, all reactions were carried out in oven-dried glassware under air atmosphere. All heating reactions were heated by metal sand bath (WATTCAS, LAB-600).

^{1}H-NMR spectra were obtained on Bruker-600. NMR spectra for all the samples were recorded in deuterochloroform ($CDCl_3$). Chemical shifts (δ) were reported in parts per million relative to residual chloroform (7.28 ppm for ^{1}H; 77.23 ppm for ^{13}C), constants were reported in Hertz. ^{1}H NMR assignment abbreviations were the following: singlet (s), doublet (d), triplet (t), quartet (q), doublets of doublet (dd), doublets of triplet(dt), triplets of doublet(td), triplets of triplet (tt) and multiplet (m), integration and coupling constant(s) *J* in hertz (Hz). ^{13}C NMR spectra were recorded at 151 MHz on the same spectrometer and reported in ppm. All spectra were processed using the MestReNova program.

High-resolution mass spectra (HRMS) were recorded on a mass spectrometer (Thermo fisher Q Exactive HRMS) using electrospray ionization-time of flight (ESI-TOF) reflection experiments.

2. Optimization of the reaction conditions

Table S1. Optimization of the reaction conditions [a]

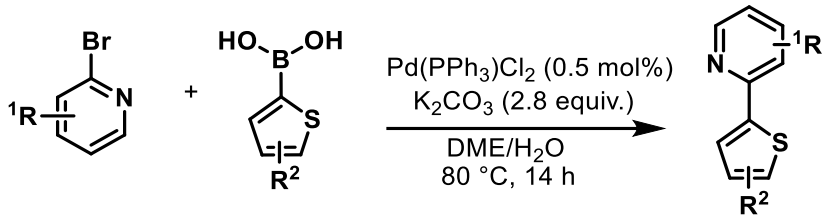


entry	variation from "standard conditions"	yield[%][b] 3aa/4aa
1	none	80/trace
2	CH_3OH instead of EtOH	68/12
3	HFIP instead of EtOH	41/trace
4	DCE instead of EtOH	66/trace
5	1,4-dixane instead of EtOH	48/trace
6	CH_3CN instead of EtOH	15/n.d
7	hexane instead of EtOH	58/trace
8	without $[Cp^*RhCl_2]_2$	n.d/n.d
9	without $AgSbF_6$	n.d/n.d
10	carried out at 100 °C	79/trace
11	carried out at 60 °C	55/trace
12	carried out for 12 hours	trace/83

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol%), $AgSbF_6$ (20 mol%) and EtOH (1.5 mL). [b]Isolated yield.

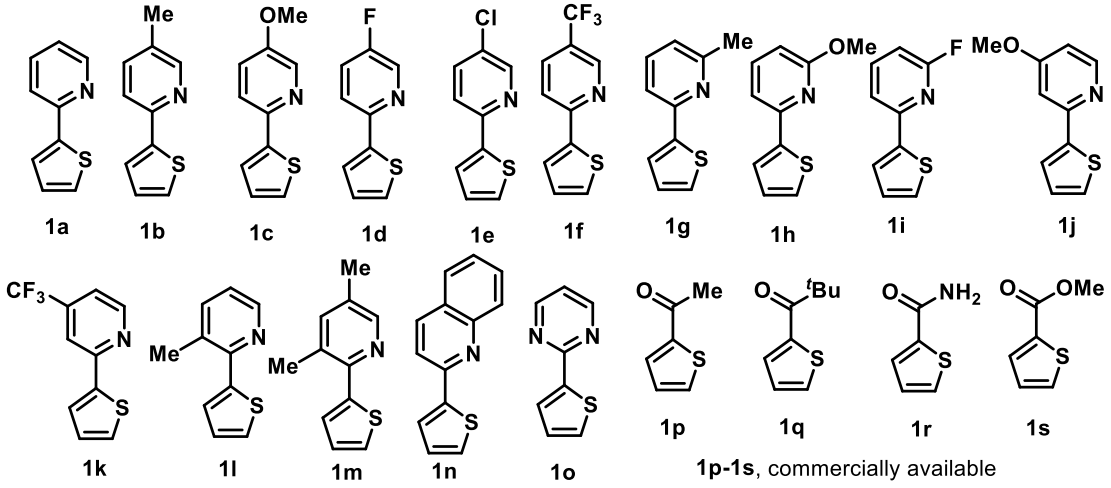
3. Experimental procedure

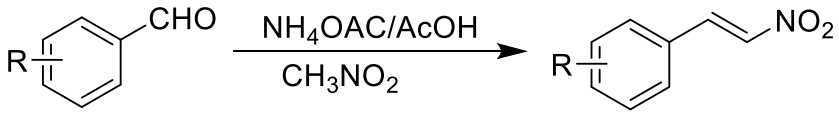
3.1 Procedure for the synthesis of starting materials



1a-1o

Synthesis of substrates 1a-1o[1]: To a solution of boronic acid derivatives (1.2 mmol, 1.2 equiv.), K_2CO_3 (2.8 mmol, 2.8 equiv.) and [$Pd(PPh_3)_2Cl_2$] (3.5 mg, 0.5 mol%) in DME (30 mL) and H_2O (14 mL) was added substituted 2-bromopyridine derivatives (1.0 mmol, 1.0 equiv.). The reaction mixture was stirred at 80 °C for 14 h. Then the reaction mixture was quenched with water (10 mL) and extracted with EtOAc (3 x 20 mL). The combined organic phases were washed with brine (25 mL), dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by flash chromatography (petroleum ether/ethyl acetate = 30:1) to get the desired products.

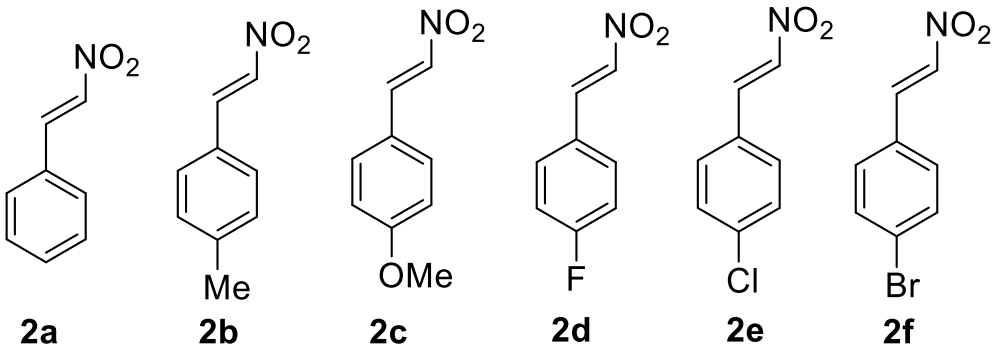




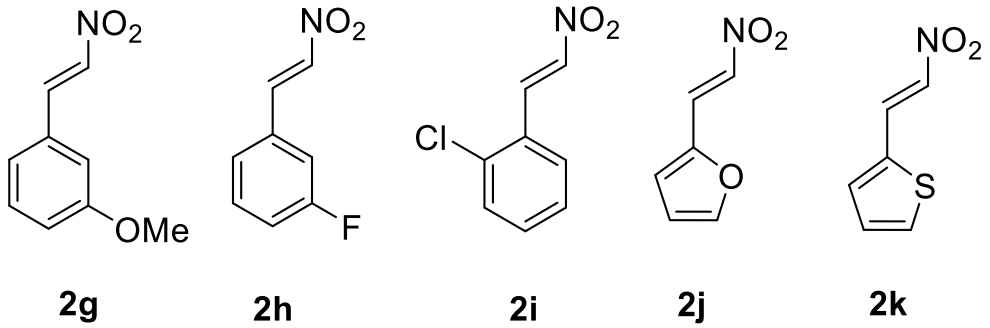
2a-2k

Synthesis of substrates 2a-2k[2]: A round bottom flask was charged with NH_4OAc (5 mmol) and acetic acid(20 mL). The solution was stirred until fully dissolved. To this was added nitromethane (8 mmol) followed by benzaldehyde derivatives (6 mmol). The flask was fitted with a reflux condenser and heated at 100 °C for six hours. The reaction was cooled to room temperature and stirred overnight. The reaction mixture was poured into distilled water (30 mL) and adjusted to pH 7 with NaOH (aq, 2M). The resulting aqueous solution was extracted

with EtOAc (5 x 20 mL). The organic extracts were combined, washed with brine (1 x 20 mL), dried over Na_2SO_4 and filtered. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel to get the desired products.



2a **2b** **2c** **2d** **2e** **2f**



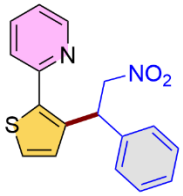
2g **2h** **2i** **2j** **2k**

3.2 Rh(III)-catalyzed C3-alkylation of 2-pyridylthiophenes

General Procedure A: To a 15 mL oven dried Schlenk tube, $AgSbF_6$ (0.04 mmol, 20 mol%), **1** (0.2 mmol, 1 equiv.), $[Cp^*RhCl_2]_2$ (0.005 mmol, 2.5 mol%), **2** (0.4 mmol, 2 equiv.) and EtOH (1.5 mL) were successively added. The reaction mixture was stirred at 80 °C (metal sand bath temperature) for 0.5 hours under air. After cooling the reaction at room temperature and concentration, the crude mixture was purified by silica column chromatography to afford the desired alkylated products **3**.

3.3 Rh(III)-catalyzed C3-acylation of 2-pyridylthiophenes

General Procedure B: To a 15 mL oven dried Schlenk tube, $AgSbF_6$ (0.04 mmol, 20 mol%), **1** (0.2 mmol, 1 equiv.), $[Cp^*RhCl_2]_2$ (0.005 mmol, 2.5 mol%), **2** (0.4 mmol, 2 equiv.) and EtOH (1.5 mL) were successively added. The reaction mixture was stirred at 80 °C (metal sand bath temperature) for 12 hours under air. After cooling the reaction at room temperature and concentration, the crude mixture was purified by silica column chromatography to afford the desired acylated products **4**.

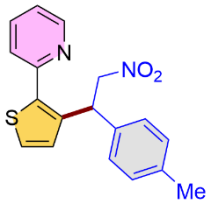


2-(3-(2-Nitro-1-phenylethyl)thiophen-2-yl)pyridine (3aa). Following the general procedure **A** using 2-(thiophen-2-yl)pyridine (32.2 mg, 0.2 mmol) and *(E)*-(2-nitrovinyl)benzene (59.6 mg, 0.4 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to afford **3aa** (49.6 mg, 80%) as a brown liquid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.71 (d, J = 4.8 Hz, 1H), 7.73 (td, J = 7.8, 1.8 Hz, 1H), 7.54 (d, J = 7.9 Hz, 1H), 7.35 (s, 2H), 7.35 (d, J = 2.3 Hz, 2H), 7.31 (d, J = 5.3 Hz, 1H), 7.28 – 7.23 (m, 2H), 6.98 (d, J = 5.3 Hz, 1H), 5.95 (dd, J = 9.2, 7.0 Hz, 1H), 5.19 (dd, J = 13.0, 6.9 Hz, 1H), 5.04 (dd, J = 13.0, 9.2 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 152.7, 149.6, 139.4, 138.9, 137.5, 136.8, 128.9, 128.5, 127.7, 127.4, 126.0, 122.7, 122.1, 78.8, 42.6.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{15}N_2O_2S$ 311.0849; Found 311.0853.

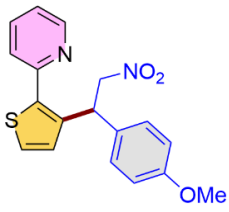


2-(3-(2-Nitro-1-(*p*-tolyl)ethyl)thiophen-2-yl)pyridine (3ab). Following the general procedure **A** using 2-(thiophen-2-yl)pyridine (32.2 mg, 0.2 mmol) and (*E*)-1-methyl-4-(2-nitrovinyl)benzene (65.3 mg, 0.4 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to afford **3ab** (40.2 mg, 62%) as a brown liquid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.68 (d, J = 4.8 Hz, 1H), 7.71 (t, J = 7.8 Hz, 1H), 7.51 (d, J = 7.9 Hz, 1H), 7.29 (d, J = 5.3 Hz, 1H), 7.23 – 7.21 (m, 2H), 7.20 (s, 1H), 7.13 (d, J = 8.0 Hz, 2H), 6.96 (d, J = 5.3 Hz, 1H), 5.87 – 5.82 (m, 1H), 5.14 (dd, J = 12.9, 6.9 Hz, 1H), 4.98 (dd, J = 12.9, 9.3 Hz, 1H), 2.31 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 152.9, 149.8, 139.0, 137.7, 137.2, 136.9, 136.4, 129.7, 128.6, 127.7, 126.1, 122.8, 122.2, 79.0, 42.4, 21.2.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{17}N_2O_2S$ 325.1005; Found 325.1010.

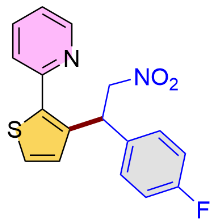


2-(3-(1-(4-Methoxyphenyl)-2-nitroethyl)thiophen-2-yl)pyridine(3ac). Following the general procedure **A** using 2-(thiophen-2-yl)pyridine (32.2 mg, 0.2 mmol) and (*E*)-1-methoxy-4-(2-nitrovinyl)benzene (71.7 mg, 0.4mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to afford **3ac** (44.9 mg, 66%) as a black liquid.

^{1}H NMR (600 MHz, $CDCl_3$)δ 8.68 (d, J = 4.8 Hz, 1H), 7.70 (td, *J* = 7.8, 1.8 Hz, 1H), 7.50 (d, *J* = 7.9 Hz, 1H), 7.29 (d, *J* = 5.3 Hz, 1H), 7.24 (d, *J* = 8.7 Hz, 2H), 7.21 (d, *J* = 2.7 Hz, 1H), 6.96 (d, *J* = 5.3 Hz, 1H), 6.85 (d, *J* = 8.7 Hz, 2H), 5.83 (dd, *J* = 9.2, 7.0 Hz, 1H), 5.13 (dd, *J* = 12.9, 6.9 Hz, 1H), 4.96 (dd, *J* = 12.9, 9.3 Hz, 1H), 3.76 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) 158.9, 152.8, 149.7, 138.9, 137.9, 136.9, 131.4, 128.9, 128.5, 126.1, 122.7, 122.1, 114.4, 79.2, 55.3, 42.0.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{17}N_2O_3S$ 341.0954; Found 341.0960.



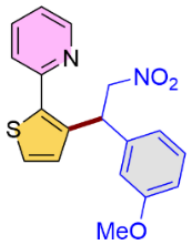
(*S*)-2-(3-(1-(4-Fluorophenyl)-2-nitroethyl)thiophen-2-yl)pyridine (3ad). Following the general procedure **A** using 2-(thiophen-2-yl)pyridine (32.2 mg, 0.2 mmol) and (*E*)-1-fluoro-4-(2-nitrovinyl)benzene (66.8 mg, 0.4 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to afford **3ad** (41.7 mg, 61%) as a brown liquid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.67 (dd, *J* = 4.8, 0.9 Hz, 1H), 7.71 (td, *J* = 7.7, 1.9 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.32 – 7.29 (m, 2H), 7.29 (s, 1H), 7.22 (dd, *J* = 6.6, 5.0 Hz, 1H), 7.00 (t, *J* = 8.7 Hz, 2H), 6.92 (d, *J* = 5.3 Hz, 1H), 5.95 (dd, *J* = 9.4, 6.7 Hz, 1H), 5.15 (dd, *J* = 13.0, 6.7 Hz, 1H), 4.97 (dd, *J* = 13.0, 9.5 Hz, 1H)

^{13}C NMR (151 MHz, $CDCl_3$) δ 162.7, 161.1, 152.7, 149.6, 138.8, 137.4, 136.9, 135.2 (d, *J* = 3.3 Hz), 129.34, 129.3, 128.3, 126.0, 122.7, 122.2, 115.8 (d, *J* = 21.5 Hz), 78.8, 41.9.

^{19}F NMR (565 MHz, $CDCl_3$) δ -114.93 (s).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{14}FN_2O_2S$ 343.0911; Found 343.0913.

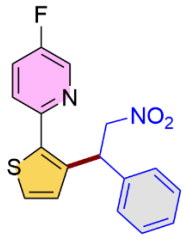


2-(3-(1-(3-Methoxyphenyl)-2-nitroethyl)thiophen-2-yl)pyridine (3ag). Following the general procedure **A** using 2-(thiophen-2-yl)pyridine (32.2 mg, 0.2 mmol) and (*E*)-1-methoxy-3-(2-nitrovinyl)benzene (71.7 mg, 0.4 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to afford **3ag** (37.4 mg, 55%) as a brown liquid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.70 (d, *J* = 5.6 Hz, 1H), 7.75 – 7.71 (m, 1H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.31 (d, *J* = 5.3 Hz, 1H), 7.29 – 7.25 (m, 1H), 7.23 (d, *J* = 6.6 Hz, 1H), 6.98 (d, *J* = 5.3 Hz, 1H), 6.94 (d, *J* = 7.7 Hz, 1H), 6.90 (s, 1H), 6.81 (d, *J* = 8.2 Hz, 1H), 5.92 (dd, *J* = 9.1, 7.0 Hz, 1H), 5.17 (dd, *J* = 13.1, 6.9 Hz, 1H), 5.02 (dd, *J* = 13.1, 9.2 Hz, 1H), 3.78 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 160.0, 152.8, 149.7, 141.0, 139.0, 137.4, 136.9, 130.0, 128.6, 126.0, 122.8, 122.2, 119.9, 114.1, 112.6, 78.8, 55.3, 42.6.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{17}N_2O_3S$ 341.0954; Found 341.0962.



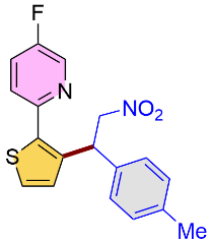
5-Fluoro-2-(3-(2-nitro-1-phenylethyl)thiophen-2-yl)pyridine (3da). Following the general procedure **A** using 5-fluoro-2-(thiophen-2-yl)pyridine (35.8 mg, 0.2 mmol) and (*E*)-(2-nitrovinyl)benzene (59.7 mg, 0.4 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to afford **3da** (49.9 mg, 73%) as a brown solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.57 (d, *J* = 2.9 Hz, 1H), 7.53 (dd, *J* = 8.7, 4.2 Hz, 1H), 7.46 (td, *J* = 8.4, 2.9 Hz, 1H), 7.35 (d, *J* = 6.6 Hz, 4H), 7.31 (d, *J* = 5.3 Hz, 1H), 7.29 – 7.26 (m, 1H), 7.00 (d, *J* = 5.3 Hz, 1H), 5.88 – 5.84 (m, 1H), 5.14 (dd, *J* = 13.0, 7.3 Hz, 1H), 5.02 (dd, *J* = 13.0, 8.9 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.3, 157.6, 149.09, 149.06, 139.3, 137.9 (d, *J* = 23.7 Hz), 137.5, 129.0, 128.5, 127.8, 127.6, 126.0, 123.9 (d, *J* = 2.8 Hz), 123.85,123.77, 78.9, 42.5.

^{19}F NMR (565 MHz, $CDCl_3$) δ -128.22 (s).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{14}FN_2O_2S$ 343.0911; Found 343.0912.



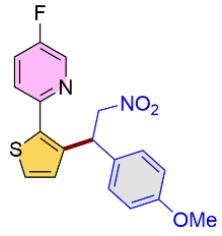
5-Fluoro-2-(3-(2-nitro-1-(*p*-tolyl)ethyl)thiophen-2-yl)pyridine (3db). Following the general procedure **A** using 5-fluoro-2-(thiophen-2-yl)pyridine (35.8 mg, 0.2 mmol) and (*E*)-1-methyl-4-(2-nitrovinyl)benzene (65.3 mg, 0.4mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to afford **3db** (45.2 mg, 66%) as a brown solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.55 (d, *J* = 2.9 Hz, 1H), 7.50 (d, *J* = 4.2 Hz, 1H), 7.45 – 7.42 (m, 1H), 7.29 (d, *J* = 5.3 Hz, 1H), 7.19 (d, *J* = 8.2 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 6.98 (d, *J* = 5.3 Hz, 1H), 5.78 – 5.74 (m, 1H), 5.09 (dd, *J* = 12.9, 7.3 Hz, 1H), 4.97 (dd, *J* = 12.9, 8.9 Hz, 1H), 2.31 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.3, 157.6, 149.14, 149.12, 137.9 (d, *J* = 23.8 Hz), 137.8 (d, *J* = 18.0 Hz), 137.3, 136.2, 129.8, 128.5, 127.6, 126.0, 123.9 (d, *J* = 3.5 Hz), 123.83, 123.76, 79.1, 42.3, 21.1.

^{19}F NMR (565 MHz, $CDCl_3$) δ -128.33 (s).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{16}FN_2O_2S$ 343.0911; Found 343.0912.



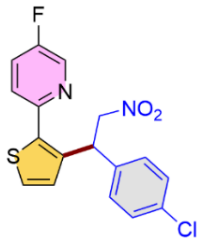
5-Fluoro-2-(3-(1-(4-methoxyphenyl)-2-nitroethyl)thiophen-2-yl)pyridine (3dc). Following the general procedure **A** using 5-fluoro-2-(thiophen-2-yl)pyridine (35.8 mg, 0.2 mmol) and (*E*)-1-methoxy-4-(2-nitrovinyl)benzene (71.7 mg, 0.4 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to afford **3dc** (51.6 mg, 72%) as a black liquid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.55 – 8.53 (m, 1H), 7.49 (d, *J* = 4.2 Hz, 1H), 7.43 (d, *J* = 2.9 Hz, 1H), 7.29 (d, *J* = 5.3 Hz, 1H), 7.22 (d, *J* = 8.7 Hz, 2H), 6.97 (d, *J* = 5.2 Hz, 1H), 6.85 (d, *J* = 8.7 Hz, 2H), 5.76 – 5.72 (m, 1H), 5.08 (dd, *J* = 12.8, 7.3 Hz, 1H), 4.94 (dd, *J* = 12.8, 9.0 Hz, 1H), 3.77 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.3, 158.9, 157.6, 149.13, 149.11, δ 137.9 (d, *J* = 23.8 Hz), 137.8 (d, *J* = 16.5 Hz), 131.3, 128.8, 128.4, 126.0, 123.9 (d, *J* = 4.9 Hz), 123.82, 123.76, 114.4, 79.2, 55.3, 41.9.

^{19}F NMR (565 MHz, $CDCl_3$) δ -128.31 (s).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{16}FN_2O_3S$ 359.0860; Found 359.0855.



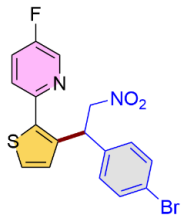
2-(3-(1-(4-Chlorophenyl)-2-nitroethyl)thiophen-2-yl)-5-fluoropyridine (3de). Following the general procedure **A** using 5-fluoro-2-(thiophen-2-yl)pyridine (35.8 mg, 0.2 mmol) and (*E*)-1-chloro-4-(2-nitrovinyl)benzene (73.4 mg, 0.4 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to afford **3de** (49.2 mg, 68%) as a brown liquid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.55 (d, *J* = 2.9 Hz, 1H), 7.52 (d, *J* = 4.2 Hz, 1H), 7.45 (d, *J* = 2.9 Hz, 1H), 7.30 (d, *J* = 1.9 Hz, 1H), 7.29 (d, *J* = 1.3 Hz, 2H), 7.26 (d, *J* = 8.5 Hz, 2H), 6.93 (d, *J* = 5.3 Hz, 1H), 5.91 – 5.87 (m, 1H), 5.12 (dd, *J* = 13.1, 7.0 Hz, 1H), 5.00 – 4.95 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.3, 157.6, 148.99, 148.96, 137.9 (d, *J* = 3.3 Hz), 137.8 (d, *J* = 4.9 Hz), 137.1, 133.4, 129.2, 128.3, 126.1, 124.0, 123.9 (d, *J* = 3.9 Hz), 78.6, 41.9.

^{19}F NMR (565 MHz, $CDCl_3$) δ -127.96 (s).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{13}ClFN_2O_2S$ 363.0365; Found 363.0361.



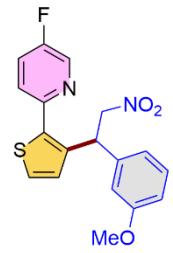
2-(3-(1-(4-Bromophenyl)-2-nitroethyl)thiophen-2-yl)-5-fluoropyridine (3df). Following the general procedure **A** using 5-fluoro-2-(thiophen-2-yl)pyridine (35.8 mg, 0.2 mmol) and (*E*)-1-bromo-4-(2-nitrovinyl)benzene (91.2 mg, 0.4 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to afford **3df** (58.5 mg, 72%) as a yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.53 (d, *J* = 2.9 Hz, 1H), 7.51 (dd, *J* = 8.7, 4.2 Hz, 1H), 7.45 (dd, *J* = 5.4, 2.5 Hz, 2H), 7.43 – 7.42 (m, 1H), 7.29 (d, *J* = 5.3 Hz, 1H), 7.20 (d, *J* = 8.5 Hz, 2H), 6.92 (d, *J* = 5.3 Hz, 1H), 5.86 (dd, *J* = 9.0, 7.1 Hz, 1H), 5.10 (dd, *J* = 13.1, 6.9 Hz, 1H), 4.96 (dd, *J* = 13.0, 9.2 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.3, 157.6, 149.0, 148.9, 138.4, 137.9, 137.8, 137.7 (d, *J* = 3.9 Hz), 132.8, 132.1, 129.5, 128.3, 126.1, 124.0 (d, *J* = 16.1 Hz), 123.9 (d, *J* = 1.8 Hz), 121.5, 78.5, 42.0.

^{19}F NMR (565 MHz, $CDCl_3$) δ -127.92 (s).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{13}BrFN_2O_2S$ 406.9860; Found 406.9856.



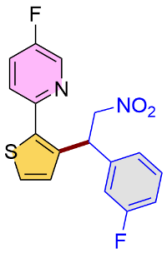
5-Fluoro-2-(3-(1-(3-methoxyphenyl)-2-nitroethyl)thiophen-2-yl)pyridine (3dg). Following the general procedure **A** using 5-fluoro-2-(thiophen-2-yl)pyridine (35.8, 0.2 mmol) and (*E*)-1-methoxy-3-(2-nitrovinyl)benzene (71.7 mg, 0.4 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to afford **3dg** (45.9 mg, 64%) as a yellow liquid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.55 (d, *J* = 2.9 Hz, 1H), 7.50 (d, *J* = 4.2 Hz, 1H), 7.44 (d, *J* = 2.9 Hz, 1H), 7.29 (d, *J* = 5.3 Hz, 1H), 7.25 (t, *J* = 8.0 Hz, 1H), 6.98 (d, *J* = 5.2 Hz, 1H), 6.90 (d, *J* = 7.7 Hz, 1H), 6.86 (s, 1H), 6.79 (d, *J* = 8.2 Hz, 1H), 5.80 (t, *J* = 8.1 Hz, 1H), 5.10 (dd, *J* = 13.0, 7.3 Hz, 1H), 4.98 (dd, *J* = 13.0, 8.9 Hz, 1H), 3.76 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 160.0, 159.3, 157.6, 149.11, 149.08, 140.9, 137.9 (d, *J* = 20.9 Hz), 137.8, 137.4 , 130.1, 128.5, 126.0, 123.9 (d, *J* = 2.7 Hz), 123.87, 123.79, 119.9, 114.2, 112.5, 78.8, 55.3, 42.5.

^{19}F NMR (565 MHz, $CDCl_3$) δ -128.26 (s).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{16}FN_2O_3S$ 359.0860; Found 359.0858.

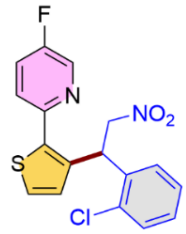


5-Fluoro-2-(3-(1-(3-fluorophenyl)-2-nitroethyl)thiophen-2-yl)pyridine (3dh). Following the general procedure **A** 5-fluoro-2-(thiophen-2-yl)pyridine (35.8, 0.2 mmol) and (*E*)-1-fluoro-3-(2-nitrovinyl)benzene (66.84 mg, 0.4 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to afford **3dh** (49.2 mg, 71%) as a brown solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.54 (d, *J* = 2.9 Hz, 1H), 7.52 (d, *J* = 4.2 Hz, 1H), 7.44 (d, *J* = 2.9 Hz, 1H), 7.30 (q, *J* = 4.4, 3.8 Hz, 2H), 7.11 (d, *J* = 7.8 Hz, 1H), 7.03 (d, *J* = 9.9 Hz, 1H), 6.94 (d, *J* = 5.3 Hz, 2H), 5.93 – 5.88 (m, 1H), 5.11 (dd, *J* = 13.1, 7.0 Hz, 1H), 4.98 (dd, *J* = 13.1, 9.0 Hz, 1H).

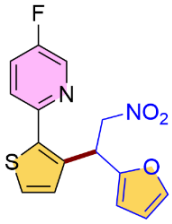
^{13}C NMR (151 MHz, $CDCl_3$) δ 163.9, 162.3, 159.3, 157.6, 149.0 (d, *J* = 4.1 Hz), 141.94, 141.89, 138.0, 137.9, 137.8, 137.0, 130.6, 130.5, 128.3, 126.1, 124.0, 123.93, 123.89, 123.3 (d, *J* = 2.9 Hz), 114.8 (dd, *J* = 76.7, 21.6 Hz), 78.6, 42.2, 42.1.

^{19}F NMR (565 MHz, $CDCl_3$) δ -111.89 (s), -128.00 (s).
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{13}F_2N_2O_2S$ 347.0660; Found 347.0658.



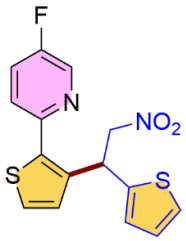
2-(3-(1-(2-Chlorophenyl)-2-nitroethyl)thiophen-2-yl)-5-fluoropyridine (3di). Following the general procedure **A** using 5-fluoro-2-(thiophen-2-yl)pyridine (35.8 mg, 0.2 mmol) and (*E*)-1-chloro-2-(2-nitrovinyl)benzene (73.4 mg, 0.4 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to afford **3di** (55.8 mg, 77%) as a brown liquid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.50 (d, *J* = 2.9 Hz, 1H), 7.49 (dd, *J* = 8.7, 4.2 Hz, 1H), 7.41 (td, *J* = 8.3, 2.9 Hz, 1H), 7.37 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.32 (d, *J* = 6.8 Hz, 1H), 7.30 (d, *J* = 5.3 Hz, 1H), 7.23 (t, *J* = 7.2 Hz, 1H), 7.21 – 7.18 (m, 1H), 6.95 (d, *J* = 5.3 Hz, 1H), 6.16 (t, *J* = 8.1 Hz, 1H), 5.16 (dd, *J* = 13.5, 7.9 Hz, 1H), 5.00 (dd, *J* = 13.5, 8.3 Hz, 1H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 159.2, 157.5, 149.0, 138.4, 137.8 (d, *J* = 23.8 Hz), 136.8, 135.9, 134.4, 130.3, 128.8, 128.5, 128.0, 127.3, 125.8, 123.8 (d, *J* = 18.8 Hz), 123.45, 123.42, 40.3.
^{19}F NMR (565 MHz, $CDCl_3$) δ -128.33 (s).
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{13}ClFN_2O_2S$ 363.0365; Found 363.0363.



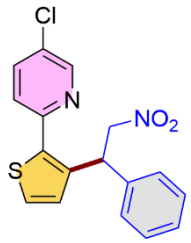
5-Fluoro-2-(3-(1-(furan-2-yl)-2-nitroethyl)thiophen-2-yl)pyridine (3dj). Following the general procedure **A** using 5-fluoro-2-(thiophen-2-yl)pyridine (35.8 mg, 0.2 mmol) and (*E*)-2-(2-nitrovinyl)furan (55.6 mg, 0.4 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **3dj** (47.7 mg, 75%) as a black solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.53 (d, *J* = 3.0 Hz, 1H), 7.57 (dd, *J* = 8.7, 4.3 Hz, 1H), 7.48 – 7.44 (m, 1H), 7.38 (d, *J* = 1.1 Hz, 1H), 7.29 (d, *J* = 5.2 Hz, 1H), 6.99 (d, *J* = 5.3 Hz, 1H), 6.32 (dd, *J* = 3.3, 1.9 Hz, 1H), 6.19 (d, *J* = 3.2 Hz, 1H), 5.90 (dd, *J* = 9.2, 6.2 Hz, 1H), 5.05 – 4.98 (m, 2H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 159.3, 157.6, 152.3, 149.0 (d, *J* = 4.1 Hz), 142.4, 138.0, 137.9, 137.8, 135.5, 129.0, 125.9, 124.0 (d, *J* = 18.8 Hz), 123.79, 123.7, 110.6, 107.5, 77.5, 37.4.
^{19}F NMR (565 MHz, $CDCl_3$) δ -128.12 (s).
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{12}FN_2O_3S$ 319.0547; Found 319.0546.



5-Fluoro-2-(3-(2-nitro-1-(thiophen-2-yl)ethyl)thiophen-2-yl)pyridine (3dk). Following the general procedure **A** using 5-fluoro-2-(thiophen-2-yl)pyridine (35.8 mg, 0.2 mmol) and (*E*)-2-(2-nitrovinyl)thiophene (62.1 mg, 0.4 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **3dk** (51.5 mg, 77%) as a brown solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.55 (d, *J* = 2.9 Hz, 1H), 7.54 (dd, *J* = 8.7, 4.2 Hz, 1H), 7.45 (td, *J* = 8.3, 2.9 Hz, 1H), 7.31 (d, *J* = 5.3 Hz, 1H), 7.21 (d, *J* = 3.9 Hz, 1H), 7.05 (d, *J* = 5.3 Hz, 1H), 6.98 – 6.94 (m, 2H), 6.15 – 6.10 (m, 1H), 5.09 (dd, *J* = 12.9, 7.0 Hz, 1H), 4.98 (dd, *J* = 12.9, 8.7 Hz, 1H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 159.3, 157.6, 149.0, 148.9, 142.5, 137.9 (d, *J* = 23.8 Hz), 137.1, 128.3, 127.1, 126.1, 125.1 (d, *J* = 5.2 Hz), 123.9 (d, *J* = 18.8 Hz), 123.81, 123.78, 79.6, 38.3.
^{19}F NMR (565 MHz, $CDCl_3$) δ -128.03 (s).
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{12}FN_2O_2S_2$ 335.0319; Found 335.0317.

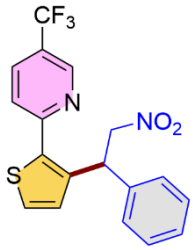


5-Chloro-2-(3-(2-nitro-1-phenylethyl)thiophen-2-yl)pyridine (3ea). Following the general procedure **A** using 5-chloro-2-(thiophen-2-yl)pyridine (39.1 mg, 0.2 mmol) and (*E*)-(2-nitrovinyl)benzene (59.7 mg, 0.4 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to afford **3ea** (50.2 mg, 73%) as a brown solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.66 (d, *J* = 2.5 Hz, 1H), 7.71 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.34 (s, 2H), 7.33 (s, 1H), 7.29 – 7.27 (m, 1H), 7.00 (d, *J* = 5.3 Hz, 1H), 5.93 – 5.90 (m, 1H), 5.14 (dd, *J* = 13.0, 7.3 Hz, 1H), 5.02 (dd, *J* = 13.0, 8.9 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 151.0, 148.5, 139.3, 138.2, 137.7, 136.7, 130.6, 129.1, 128.7, 127.8, 127.6, 126.4, 123.4, 78.9, 42.6.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{14}ClN_2O_2S$ 345.0459; Found 345.0456.



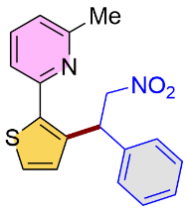
2-(3-(2-Nitro-1-phenylethyl)thiophen-2-yl)-5-(trifluoromethyl)pyridine (3fa). Following the general procedure **A** using 2-(thiophen-2-yl)-5-(trifluoromethyl)pyridine (45.8 mg, 0.2 mmol) and (*E*)-(2-nitrovinyl)benzene (59.7 mg, 0.4 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate =20:1) to afford **3fa** (31.1 mg, 41%) as a yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.96 (s, 1H), 7.94 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.64 (d, *J* = 8.3 Hz, 1H), 7.39 (d, *J* = 5.3 Hz, 1H), 7.34 (d, *J* = 1.8 Hz, 2H), 7.34 (s, 2H), 7.29 – 7.26 (m, 1H), 7.03 (d, *J* = 5.2 Hz, 1H), 6.06 – 6.01 (m, 1H), 5.14 (dd, *J* = 13.0, 7.4 Hz, 1H), 5.01 (dd, *J* = 13.0, 8.7 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 156.1, 146.59, 146.57, 146.54, 146.5 (q, *J* = 4.0 Hz), 139.4 (d, *J* = 80.2 Hz), 137.3, 134.2, 134.19, 134.17, 128.8, 128.7, 127.6 (d, *J* = 28.6 Hz), 122.0, 78.8, 42.7.

^{19}F NMR (565 MHz, $CDCl_3$) δ -62.3 (s).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{14}F_3N_2O_2S$ 379.0723; Found 379.0720.

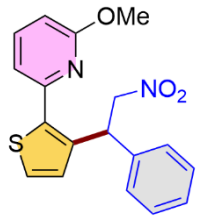


2-Methyl-6-(3-(2-nitro-1-phenylethyl)thiophen-2-yl)pyridine (3ga). Following the general procedure **A** using 2-methyl-6-(thiophen-2-yl)pyridine (35.0 mg, 0.2 mmol) and (*E*)-(2-nitrovinyl)benzene (59.6 mg, 0.4 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to afford **3ga** (45.4 mg, 70%) as a brown liquid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 (t, *J* = 7.8 Hz, 1H), 7.38 (s, 1H), 7.37 (s, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 6.7 Hz, 1H), 7.25 (d, *J* = 5.3 Hz, 1H), 7.11 (d, *J* = 7.7 Hz, 1H), 6.90 (d, *J* = 5.3 Hz, 1H), 6.01 (dd, *J* = 9.9, 6.3 Hz, 1H), 5.32 (dd, *J* = 13.1, 6.2 Hz, 1H), 5.06 (dd, *J* = 13.0, 9.9 Hz, 1H), 2.63 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.5, 152.1, 139.5, 138.7, 137.7, 137.1, 128.9, 128.9, 127.9, 127.4, 125.4, 121.7, 119.8, 78.6, 42.8, 24.5.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{17}N_2O_2S$ 325.1005; Found 325.1004.

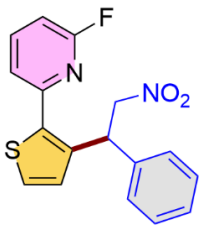


2-Methoxy-6-(3-(2-nitro-1-phenylethyl)thiophen-2-yl)pyridine (3ha). Following the general procedure **A** using 2-methoxy-6-(thiophen-2-yl)pyridine (45.8 mg, 0.2 mmol) and (*E*)-(2-nitrovinyl)benzene (59.6 mg, 0.4 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to afford **3ha** (49.7 mg, 73%) as a black solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 – 7.60 (m, 1H), 7.36 (s, 2H), 7.35 (s, 2H), 7.28 (dd, *J* = 10.3, 4.9 Hz, 2H), 7.18 (d, *J* = 7.4 Hz, 1H), 6.95 (d, *J* = 5.3 Hz, 1H), 6.75 (d, *J* = 8.1 Hz, 1H), 6.36 – 6.32 (m, 1H), 5.10 (dd, *J* = 8.3, 2.4 Hz, 2H), 4.03 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.7, 150.2, 139.4, 139.4, 138.9, 137.0, 129.0, 128.6, 127.5, 127.4, 125.9, 115.6, 110.0, 78.6, 53.7, 42.0.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{17}N_2O_3S$ 341.0954; Found 341.0953.



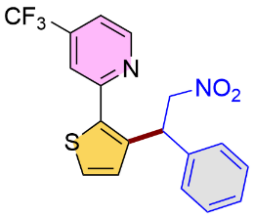
2-Fluoro-6-(3-(2-nitro-1-phenylethyl)thiophen-2-yl)pyridine (3ia). Following the general procedure **A** using 2-fluoro-6-(thiophen-2-yl)pyridine (35.8 mg, 0.2 mmol) and (*E*)-(2-nitrovinyl)benzene (59.6 mg, 0.4 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to afford **3ia** (42.0 mg, 64%) as a brown liquid.

^{1}H NMR (600 MHz, $CDCl_3$)δ 7.82 (q, *J* = 8.0 Hz, 1H), 7.42 (dd, *J* = 7.5, 2.4 Hz, 1H), 7.39 (d, *J* = 6.9 Hz, 2H), 7.37 - 7.35 (m, 2H), 7.34 (d, *J* = 6.1 Hz, 1H), 7.30 - 7.26 (m, 1H), 7.04 (d, *J* = 5.3 Hz, 1H), 6.88 (dd, *J* = 8.1, 3.0 Hz, 1H), 6.00 (t, *J* = 8.1 Hz, 1H), 5.15 (dd, *J* = 13.0, 7.7 Hz, 1H), 5.01 (dd, *J* = 13.1, 8.6 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.7, 162.1, 151.4, 151.3, 141.9 (d, *J* = 8.0 Hz), 139.2, 138.7, 137.2, 128.9, 128.7, 128.0, 127.6, 126.7, 119.7, 119.7, 108.0, 107.8, 79.0, 42.5.

^{19}F NMR (565 MHz, $CDCl_3$) δ -66.03 (s).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{14}FN_2O_2S$ 329.0755; Found 329.0752.



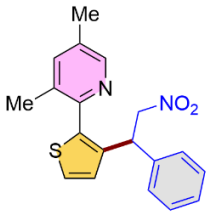
2-(3-(2-Nitro-1-phenylethyl)thiophen-2-yl)-4-(trifluoromethyl)pyridine (3ka). Following the general procedure **A** using2-(thiophen-2-yl)-4-(trifluoromethyl)pyridine (45.8 mg, 0.2 mmol) and (*E*)-(2-nitrovinyl)benzene (59.6 mg, 0.4 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to afford **3ka** (40.1 mg, 53%) as a brown liquid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.86 (d, *J* = 5.0 Hz, 1H), 7.70 (s, 1H), 7.44 (d, *J* = 5.0 Hz, 1H), 7.39 (d, *J* = 5.3 Hz, 1H), 7.34 (s, 1H), 7.33 (s, 2H), 7.32 (s, 1H), 7.29 – 7.26 (m, 1H), 7.04 (d, *J* = 5.3 Hz, 1H), 5.94 – 5.90 (m, 1H), 5.15 (dd, *J* = 13.1, 7.3 Hz, 1H), 5.01 (dd, *J* = 13.0, 8.8 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 154.1, 150.7, 139.0 (d, *J* = 11.9 Hz), 137.6, 130.6, 130.0, 129.2, 128.9, 127.9, 127.7, 127.2, 118.2 (q, *J* = 3.4 Hz), 117.5 (q, *J* = 3.2 Hz), 78.9, 42.8.

^{19}F NMR (565 MHz, $CDCl_3$) δ -64.85 (s).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{14}F_3N_2O_2S$ 379.0723; Found 379.0720.

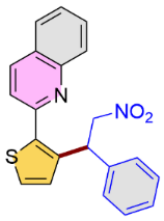


3,5-Dimethyl-2-(3-(2-nitro-1-phenylethyl)thiophen-2-yl)pyridine (3ma). Following the general procedure **A** using 3,5-dimethyl-2-(thiophen-2-yl)pyridine (37.7 mg, 0.4 mmol) and (*E*)-(2-nitrovinyl)benzene (59.6 mg, 0.4 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to afford **3ma** (32.4 mg, 48%) as a black liquid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.40 (s, 1H), 7.35 (d, *J* = 5.3 Hz, 1H), 7.28 – 7.25 (m, 2H), 7.22 (d, *J* = 7.2 Hz, 1H), 7.16 (d, *J* = 7.1 Hz, 2H), 6.99 (d, *J* = 5.2 Hz, 1H), 5.04 – 4.97 (m, 2H), 4.87 (dd, *J* = 9.1, 7.2 Hz, 1H), 2.40 (s, 3H), 2.10 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 148.7, 147.8, 139.1, 139.0, 138.2, 137.5, 133.5, 133.2, 128.9, 127.5, 127.4, 126.4, 125.8, 78.9, 43.0, 19.5, 18.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{19}N_2O_2S$ 339.1162; Found 339.1158.

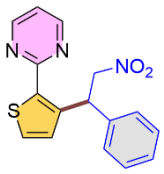


2-(3-(2-Nitro-1-phenylethyl)thiophen-2-yl)quinoline (3na). Following the general procedure **A** using 2-(thiophen-2-yl)quinoline (42.3 mg, 0.2 mmol) and (*E*)-(2-nitrovinyl)benzene (59.6 mg, 0.4 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to afford **3na** (54.1 mg, 75%) as a black liquid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.16 (t, *J* = 8.0 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.75 (t, *J* = 7.6 Hz, 1H), 7.71 (d, *J* = 8.5 Hz, 1H), 7.55 (t, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 7.4 Hz, 2H), 7.36 (t, *J* = 7.7 Hz, 2H), 7.32 – 7.27 (m, 2H), 6.92 (d, *J* = 5.2 Hz, 1H), 6.36 (dd, *J* = 10.0, 6.1 Hz, 1H), 5.48 (dd, *J* = 13.1, 6.0 Hz, 1H), 5.11 (dd, *J* = 13.1, 10.0 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 152.6, 147.9, 139.5, 139.4, 138.2, 137.0, 130.2, 129.7, 129.0, 128.0, 127.5, 127.5, 126.8, 126.7, 126.2, 120.8, 78.3, 43.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{17}N_2O_2S$ 361.1005; Found 361.1011.

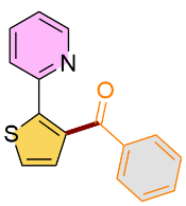


(S)-2-(3-(2-nitro-1-phenylethyl)thiophen-2-yl)pyrimidine (3oa). Following the general procedure **A** using 2-(thiophen-2-yl)pyrimidine (64.8 mg, 0.4 mmol) and (*E*)-(2-nitrovinyl)benzene (119.2 mg, 0.8 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to afford **3oa** (22.4 mg, 18%) as a yellow liquid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.74 (d, *J* = 4.9 Hz, 2H), 7.38 (s, 1H), 7.37 (d, *J* = 5.2 Hz, 2H), 7.32 (t, *J* = 7.7 Hz, 2H), 7.24 (d, *J* = 7.3 Hz, 1H), 7.12 (t, *J* = 4.9 Hz, 1H), 6.93 (d, *J* = 5.3 Hz, 1H), 6.54 (dd, *J* = 9.3, 6.9 Hz, 1H), 5.12 (dd, *J* = 13.1, 6.8 Hz, 1H), 5.02 (dd, *J* = 13.1, 9.3 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.8, 157.1, 156.0, 141.4, 139.3, 137.9, 129.3, 129.0, 128.8, 127.9, 127.4, 118.4, 78.3, 42.5.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{13}N_3O_2S$ 312.0795; Found 312.0799.

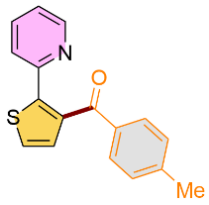


Phenyl(2-(pyridin-2-yl)thiophen-3-yl)methanone (4aa). Following the general procedure **B** using 2-(thiophen-2-yl)pyridine (32.2 mg, 0.2 mmol) and (*E*)-(2-nitrovinyl)benzene (59.6 mg, 0.4 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **4aa** (44.0 mg, 83%) as a brown liquid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.47 (d, *J* = 4.4 Hz, 1H), 7.82 (dd, *J* = 8.2, 1.1 Hz, 2H), 7.48 – 7.45 (m, 2H), 7.42 (d, *J* = 5.2 Hz, 1H), 7.35 (t, *J* = 8.0 Hz, 3H), 7.22 (d, *J* = 5.1 Hz, 1H), 7.06 (ddd, *J* = 7.5, 4.8, 1.1 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 193.9, 151.4, 149.5, 145.9, 137.9, 137.7, 136.4, 133.2, 130.0, 130.0, 128.5, 126.7, 122.6, 122.5.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{12}NOS$ 266.0634; Found 266.0631.

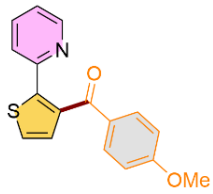


(2-(Pyridin-2-yl)thiophen-3-yl)(*p*-tolyl)methanone (4ab). Following the general procedure **B** using 2-(thiophen-2-yl)pyridine (32.2 mg, 0.2 mmol) and (*E*)-1-methyl-4-(2-nitrovinyl)benzene (65.3 mg, 0.4 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **4ab** (39.7 mg, 71%) as a yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.48 (d, *J* = 4.2 Hz, 1H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.46 (td, *J* = 7.7, 1.8 Hz, 1H), 7.41 (d, *J* = 5.2 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.18 (d, *J* = 5.2 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.07 – 7.05 (m, 1H), 2.35 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 193.7, 151.4, 149.5, 145.4, 144.3, 138.1, 136.4, 135.0, 130.2, 129.9, 129.3, 129.2, 126.7, 122.4, 21.8.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{14}NOS$ 280.0791; Found 280.0790.

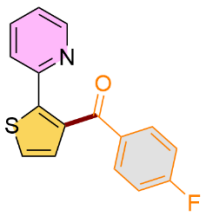


(4-Methoxyphenyl)(2-(pyridin-2-yl)thiophen-3-yl)methanone (4ac). Following the general procedure **B** using 2-(thiophen-2-yl)pyridine (32.2 mg, 0.2 mmol) and (*E*)-1-methoxy-4-(2-nitrovinyl)benzene (71.7 mg, 0.4 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **4ac** (35.4 mg,60%) as a brown solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.50 (dd, *J* = 4.8, 0.8 Hz, 1H), 7.82 (d, *J* = 8.9 Hz, 2H), 7.47 (td, *J* = 7.8, 1.8 Hz, 1H), 7.42 (d, *J* = 5.2 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.18 (d, *J* = 5.1 Hz, 1H), 7.07 (dd, *J* = 6.6, 4.9 Hz, 1H), 6.83 (d, *J* = 8.9 Hz, 2H), 3.82 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 192.9, 163.9, 151.5, 149.6, 145.0, 138.2, 136.5, 132.5, 130.5, 129.8, 126.8, 122.5, 122.4, 113.8, 55.6.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{14}NO_2S$296.0740; Found 296.0738.



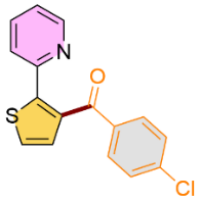
(4-Fluorophenyl)(2-(pyridin-2-yl)thiophen-3-yl)methanone (4ad). Following the general procedure **B** using 2-(thiophen-2-yl)pyridine (32.2 mg, 0.2 mmol) and (*E*)-1-fluoro-4-(2-nitrovinyl)benzene (66.8 mg, 0.4 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **4ad** (36.3 mg, 64%) as a brown liquid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.45 (dd, *J* = 4.9, 0.8 Hz, 1H), 7.83 (dd, *J* = 8.8, 5.5 Hz, 2H), 7.48 (td, *J* = 7.8, 1.8 Hz, 1H), 7.43 (d, *J* = 5.1 Hz, 1H), 7.35 – 7.33 (m, 1H), 7.21 (d, *J* = 5.2 Hz, 1H), 7.07 (ddd, *J* = 7.5, 4.8, 1.1 Hz, 1H), 7.00 (t, *J* = 8.6 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 192.4, 166.6, 164.9, 151.3, 149.6, 145.7, 137.7, 136.5, 134.1 (d, J = 2.8 Hz), 132.6, 132.5, 129.8, 126.9, 122.61, 122.58, 115.6 (d, J = 21.8 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -104.87 (s).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{11}FNOS$ 284.0540; Found 284.0537.

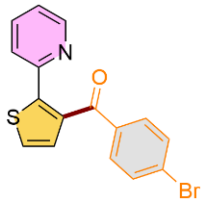


(4-Chlorophenyl)(2-(pyridin-2-yl)thiophen-3-yl)methanone (4ae). Following the general procedure **B** using 2-(thiophen-2-yl)pyridine (32.2 mg, 0.2 mmol) and (*E*)-1-chloro-4-(2-nitrovinyl)benzene (73.4 mg, 0.4 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **4ae** (39.5 mg, 66%) as a brown solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.44 (d, *J* = 4.7 Hz, 1H), 7.74 (d, *J* = 8.5 Hz, 2H), 7.50 (td, *J* = 7.7, 1.8 Hz, 1H), 7.43 (d, *J* = 5.1 Hz, 1H), 7.36 – 7.34 (m, 1H), 7.30 (d, *J* = 8.5 Hz, 2H), 7.21 (d, *J* = 5.1 Hz, 1H), 7.08 (dd, *J* = 7.1, 5.1 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 192.62, 151.20, 149.57, 145.81, 139.57, 137.60, 136.54, 136.13, 131.24, 129.83, 128.78, 126.88, 122.65, 122.56.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{11}ClNOS$ 300.0244; Found 300.0243.

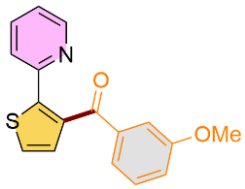


(4-Bromophenyl)(2-(pyridin-2-yl)thiophen-3-yl)methanone (4af). Following the general procedure **B** using 2-(thiophen-2-yl)pyridine (32.2 mg, 0.2 mmol) and (*E*)-1-bromo-4-(2-nitrovinyl)benzene (91.2 mg, 0.4 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **4af** (47.3 mg, 69%) as a brown solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.44 (d, *J* = 4.7 Hz, 1H), 7.66 (d, *J* = 8.5 Hz, 2H), 7.51 – 7.48 (m, 1H), 7.47 (d, *J* = 1.8 Hz, 1H), 7.46 (d, *J* = 1.7 Hz, 1H), 7.43 (d, *J* = 5.2 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.21 (d, *J* = 5.2 Hz, 1H), 7.09 – 7.06 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 192.8, 151.2, 149.6, 145.8, 137.5, 136.5, 131.8, 131.3, 129.8, 128.3, 126.9, 122.6, 122.5.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{11}BrNOS$ 343.9739; Found 343.9737.

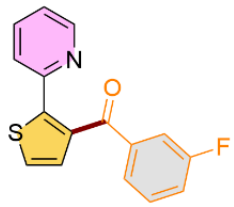


(3-Methoxyphenyl)(2-(pyridin-2-yl)thiophen-3-yl)methanone (4ag). Following the general procedure **B** using 2-(thiophen-2-yl)pyridine (32.2 mg, 0.2 mmol) and (*E*)-1-methoxy-3-(2-nitrovinyl)benzene (71.7 mg, 0.4 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **4ag** (38.9 mg,66%) as a brown liquid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.48 (dd, *J* = 4.8, 0.8 Hz, 1H), 7.48 (td, *J* = 7.8, 1.8 Hz, 1H), 7.42 (d, *J* = 5.1 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 7.7 Hz, 1H), 7.23 – 7.20 (m, 2H), 7.08 – 7.06 (m, 1H), 7.03 (dd, *J* = 8.3, 1.7 Hz, 1H), 3.79 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 193.6, 159.7, 151.4, 149.5, 145.9, 139.0, 137.9, 136.4, 130.0, 129.5, 126.6, 123.1, 122.6, 122.5, 120.1, 113.5, 55.5.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{14}NO2S$ 296.0740; Found 296.0739.



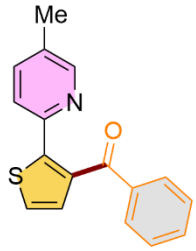
(3-Fluorophenyl)(2-(pyridin-2-yl)thiophen-3-yl)methanone (4ah). Following the general procedure **B** using 2-(thiophen-2-yl)pyridine (32.2 mg, 0.2 mmol) and (*E*)-1-fluoro-3-(2-nitrovinyl)benzene (66.8 mg, 0.4 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **4ah** (30.0 mg, 53%) as an orange liquid .

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.46 (d, *J* = 4.5 Hz, 1H), 7.56 (d, *J* = 7.1 Hz, 2H), 7.52 (d, *J* = 7.7 Hz, 1H), 7.46 (d, *J* = 5.1 Hz, 1H), 7.40 (d, *J* = 8.2 Hz, 1H), 7.31 (dd, *J* = 8.0, 5.6 Hz, 1H), 7.25 (d, *J* = 5.1 Hz, 1H), 7.18 (t, *J* = 7.7 Hz, 1H), 7.11 – 7.08 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 192.5, 163.5, 161.9, 151.2, 149.5, 146.1, 140.0, 139.9, 137.5, 136.5, 130.1, 130.0, 129.9, 126.8, δ 125.8 (d, *J* = 2.8 Hz), 122.6 (d, *J* = 18.2 Hz)., 120.2, 116.3.

^{19}F NMR (565 MHz, $CDCl_3$) δ -112.18 (s).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{11}FNOS$ 284.0540; Found 284.0538.

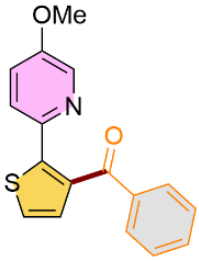


(2-(5-Methylpyridin-2-yl)thiophen-3-yl)(phenyl)methanone (4ba). Following the general procedure **B** using 5-methyl-2-(thiophen-2-yl)pyridine (35.0 mg, 0.2 mmol) and(*E*)-(2-nitrovinyl)benzene (59.6 mg, 0.4 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **4ba** (40.8 mg, 73%) as a brown liquid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.82 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.47 (d, *J* = 7.5 Hz, 1H), 7.38 (d, *J* = 5.2 Hz, 1H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.27 – 7.26 (m, 2H), 7.20 (d, *J* = 5.2 Hz, 1H), 2.24 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 193.9, 149.9, 148.7, 146.2, 137.7, 137.4, 136.9, 133.1, 132.3, 130.0, 129.9, 128.4, 126.1, 122.2, 18.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{14}NOS$ 280.0791; Found 280.0790.

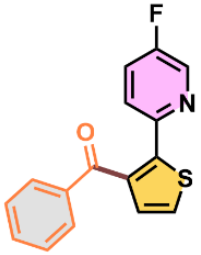


(2-(5-Methoxypyridin-2-yl)thiophen-3-yl)(phenyl)methanone (4ca). Following the general procedure **B** using 5-methoxy-2-(thiophen-2-yl)pyridine (38.2 mg, 0.2 mmol) and (*E*)-(2-nitrovinyl)benzene (59.6 mg, 0.4 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **4ca** (35.4 mg, 60%) as a brown solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 (d, *J* = 3.0 Hz, 1H), 7.81 (d, *J* = 7.9 Hz, 2H), 7.48 (t, *J* = 7.2 Hz, 1H), 7.35 (d, *J* = 5.4 Hz, 2H), 7.34 – 7.31 (m, 2H), 7.20 (d, *J* = 5.2 Hz, 1H), 6.98 (dd, *J* = 8.7, 2.9 Hz, 1H), 3.79 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 193.9, 155.0, 146.4, 144.1, 137.8, 137.2, 136.7, 133.1, 130.0, 130.0, 128.5, 125.6, 123.3, 120.6, 55.7.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{14}NO2S$ 296.0740; Found 296.0737.



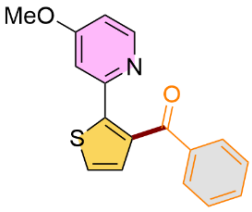
(2-(5-Fluoropyridin-2-yl)thiophen-3-yl)(phenyl)methanone (4da). Following the general procedure **B** using 5-methoxy-2-(thiophen-2-yl)pyridine (38.2 mg, 0.2 mmol) and (*E*)-(2-nitrovinyl)benzene (59.6 mg, 0.4 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **4da** (48.9 mg, 81%) as a brown solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.30 (d, *J* = 2.9 Hz, 1H), 7.80 (d, *J* = 1.2 Hz, 1H), 7.79 (d, *J* = 1.3 Hz, 1H), 7.49 (ddt, *J* = 8.7, 7.2, 1.3 Hz, 1H), 7.42 (d, *J* = 4.2 Hz, 1H), 7.40 (d, *J* = 2.5 Hz, 1H), 7.36 – 7.33 (m, 2H), 7.22 – 7.18 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 193.5, 159.4, 157.7, 147.7 (d, *J* = 4.0 Hz), 144.9, 137.8, 137.63, 137.60, 133.3, 130.1, 129.9, 128.5, 126.5, 123.6 (d, *J* = 4.5 Hz), 123.3, 123.2.

^{19}F NMR (565 MHz, $CDCl_3$) δ -127.57 (s).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{10}FNOS$ 284.0539; Found 284.0537.

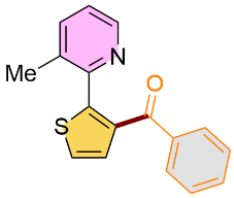


(2-(4-Methoxypyridin-2-yl)thiophen-3-yl)(phenyl)methanone (4ja). Following the general procedure **B** using 4-methoxy-2-(thiophen-2-yl)pyridine (38.2 mg, 0.2 mmol) and (*E*)-(2-nitrovinyl)benzene (59.6 mg, 0.4 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **4ja** (36.7 mg, 62%) as a brown solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.28 (d, *J* = 5.8 Hz, 1H), 7.81 (d, *J* = 6.8 Hz, 2H), 7.47 (d, *J* = 7.5 Hz, 1H), 7.42 (d, *J* = 5.2 Hz, 1H), 7.35 (d, *J* = 7.6 Hz, 2H), 7.23 (d, *J* = 5.2 Hz, 1H), 6.90 (d, *J* = 2.4 Hz, 1H), 6.60 (dd, *J* = 5.7, 2.4 Hz, 1H), 3.66 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 193.9, 165.9, 152.8, 150.6, 145.9, 137.9, 137.7, 133.3, 130.0, 130.0, 128.5, 126.7, 109.3, 108.6, 55.2.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{14}NO_2S$ 296.0740; Found 296.0736.

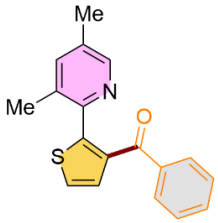


(2-(3-Methylpyridin-2-yl)thiophen-3-yl)(phenyl)methanone (4la). Following the general procedure **B** using 3-methyl-2-(thiophen-2-yl)pyridine (35.0 mg, 0.2 mmol) and (*E*)-(2-nitrovinyl)benzene (59.6 mg, 0.4 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **4la** (30.2 mg, 54%) as a brown liquid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.41 (d, *J* = 3.7 Hz, 1H), 7.73 (d, *J* = 7.9 Hz, 2H), 7.46 (d, *J* = 5.2 Hz, 1H), 7.43 – 7.39 (m, 2H), 7.35 (d, *J* = 7.9 Hz, 1H), 7.30 (d, *J* = 7.8 Hz, 2H), 7.06 (dd, *J* = 7.7, 4.7 Hz, 1H), 2.18 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 191.8, 151.6, 147.0, 146.8, 138.7, 138.0, 137.9, 133.0, 132.5, 129.8, 129.5, 128.0, 125.7, 123.1, 19.7.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{14}NOS$ 280.0791; Found 280.0789.



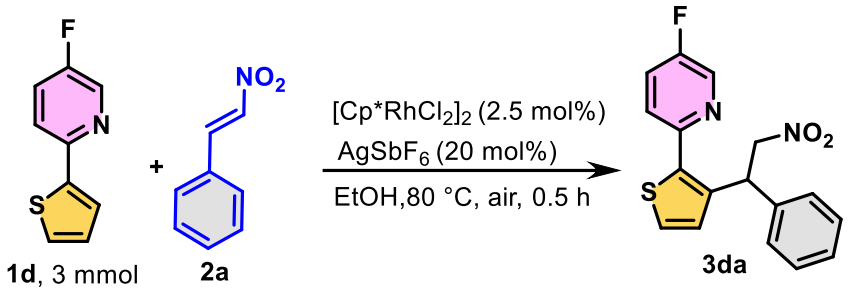
(2-(3,5-Dimethylpyridin-2-yl)thiophen-3-yl)(phenyl)methanone (4ma). Following the general procedure **B** using 3,5-dimethyl-2-(thiophen-2-yl)pyridine (37.9 mg, 0.2 mmol) and (*E*)-(2-nitrovinyl)benzene (59.6 mg, 0.4 mmol), the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **4ma** (34.0 mg, 58%) as a brown liquid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.72 (d, *J* = 1.2 Hz, 1H), 7.70 (d, *J* = 1.5 Hz, 1H), 7.41 – 7.38 (m, 2H), 7.36 (d, *J* = 5.3 Hz, 1H), 7.29 – 7.26 (m, 2H), 7.15 (s, 1H), 2.23 (s, 3H), 2.11 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 191.8, 148.7, 147.3, 147.3, 138.6, 138.4, 137.9, 132.8, 132.4, 132.4, 129.8, 129.5, 128.0, 125.4, 19.5, 18.1.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{16}NOS$ 294.0947; Found 294.0944.

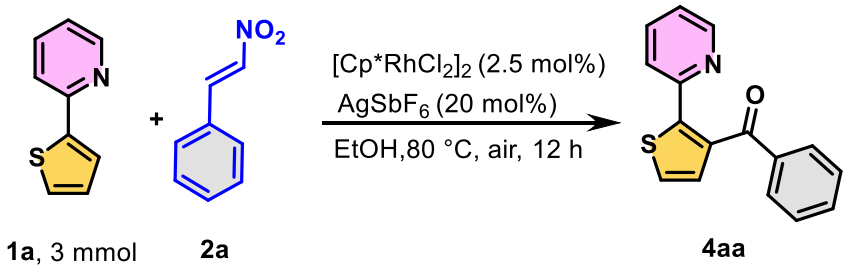
3.4 Rh(III)-catalyzed C3-alkylation: reaction on 3 mmol scale



1d, 3 mmol **2a** **3da**

To a 100 mL oven dried Schlenk tube, **1d** (3 mmol, 1 equiv.), $[Cp^*RhCl_2]_2$ (0.075 mmol, 2.5 mol%), (*E*)-(2-nitrovinyl)benzene **2a** (4.5 mmol, 1.5 equiv.), $AgSbF_6$ (0.6 mmol, 20 mol%) and EtOH (30 mL) were successively added. The reaction mixture was stirred at 80°C (metal sand bath temperature) for 0.5 hour under air. After cooling the reaction at room temperature and concentration, the crude mixture was purified by silica column chromatography (petroleum ether/ethyl acetate = 30:1) to afford the desired alkynylated product **3da** (0.67 g, 65%).

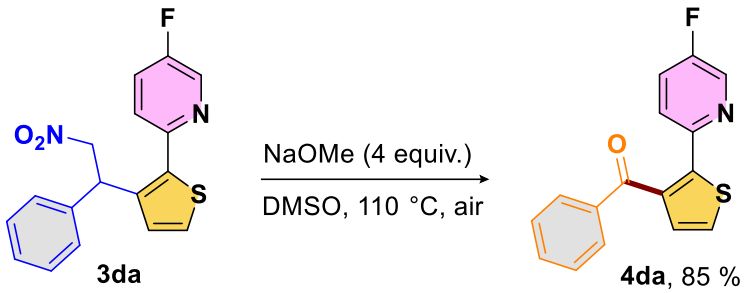
3.5 Rh(III)-catalyzed C3-acylation: reaction on 3 mmol scale



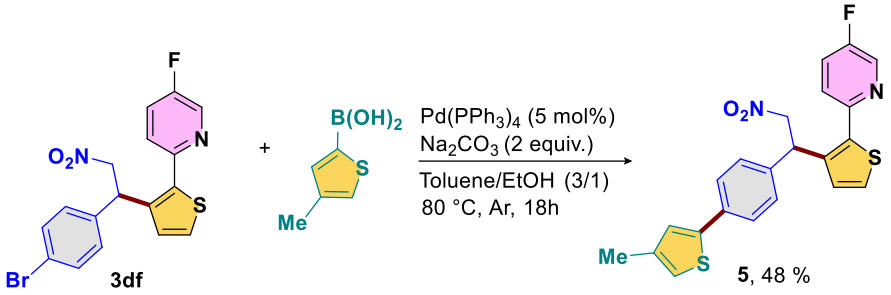
1a, 3 mmol **2a** **4aa**

To a 100 mL oven dried Schlenk tube, **1a** (3 mmol, 1 equiv.), $[Cp^*RhCl_2]_2$ (0.075 mmol, 2.5 mol%), (*E*)-(2-nitrovinyl)benzene **2a** (4.5 mmol, 1.5 equiv.), $AgSbF_6$ (0.6 mmol, 20 mol%) and EtOH (30 mL) were successively added. The reaction mixture was stirred at 80°C (metal sand bath temperature) for 12 hours under air. After cooling the reaction at room temperature and concentration, the crude mixture was purified by silica column chromatography (petroleum ether/ethyl acetate = 30:1) to afford the desired alkynylated product **4aa** (0.60 g, 76%).

3.6 Preparation and characterization of products 4da, 5, 6, 7, 8



(2-(5-Fluoropyridin-2-yl)thiophen-3-yl)(phenyl)methanone (4da). To a 15 mL oven dried Schlenk tube, **3da** (65.7 mg, 0.2 mmol, 1 equiv.), NaOMe (43.2 mg, 0.8 mmol, 4 equiv.), and DMSO (1.5 ml) were successively added. The reaction mixture was stirred at 110 °C (metal sand bath temperature) for 12 hours under air. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate (7.5 mL) and water (7.5 mL), and then filtered through a plug of celite. The organic phase was separated and washed with water (5 mL×2). The aqueous layers were further extracted with ethyl acetate. The combined organic extracts were dried, filtered and solvents removed in vacuo. The crude mixture was purified by silica column chromatography (petroleum ether/ethyl acetate = 30:1) to afford the desired product **4da** (48.1 mg, 85%) as a brown solid.



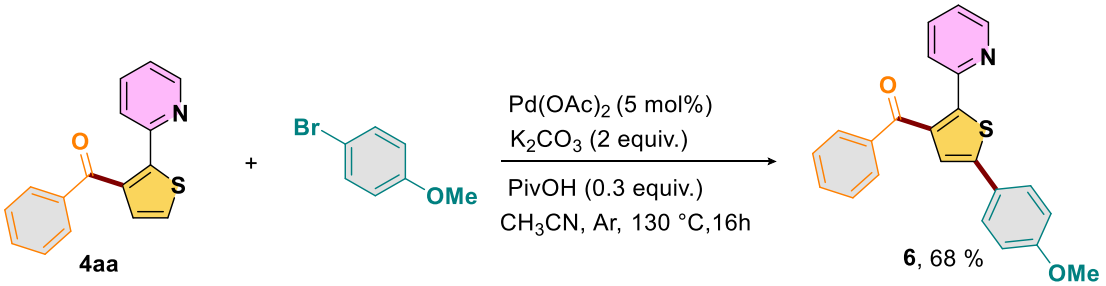
5-Fluoro-2-(3-(1-(4-(4-methylthiophen-2-yl)phenyl)-2-nitroethyl)thiophen-2-yl)pyridine (5). To oven dried Schlenk tube was added $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol, 5 mol%), (*R*)-2-(3-(1-(4-bromophenyl)-2-nitroethyl)thiophen-2-yl)-5-fluoropyridine **3df** (81.5 mg, 0.2 mmol, 1 equiv.), (4-methylthiophen-2-yl)boronic acid (42.6 mg, 0.3 mmol, 1.5 equiv.), dry toluene (3 mL), absolute ethanol (1 mL) and 2M sodium carbonate (0.35 mL). The reaction mixture was evacuated by vacuum-argon cycles (5 times) and stirred at 80 °C (metal sand bath temperature) for 12 hours, cooled down to room temperature. The solvent was removed under reduced pressure. The crude mixture was washed with water (10 mL) then extracted with ethyl acetate (10 mL x 6), then purified by column chromatography (petroleum ether/ ethyl acetate = 5:1) to afford the yellow solid **5** (40.7 mg, 48%).

^{1}H NMR (600 MHz, $CDCl_3$) ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.56 (d, *J* = 2.9 Hz, 1H), 7.54 (s, 2H), 7.52 – 7.50 (m, 1H), 7.45 – 7.42 (m, 1H), 7.30 (d, *J* = 2.1 Hz, 2H), 7.29 (s, 1H), 7.09 (s, 1H), 6.98 (d, *J* = 5.3 Hz, 1H), 6.84 (s, 1H), 5.86 – 5.83 (m, 1H), 5.12 (dd, *J* = 13.0, 7.2 Hz, 1H), 4.99 (dd, *J* = 13.0, 8.9 Hz, 1H), 2.27 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.3, 157.6, 149.1 (d, *J* = 4.1 Hz), 143.4, 138.8, 138.3, 138.0, 137.8, 137.4, 133.9, 128.5, 128.2, 126.3, 126.0, 125.7, 123.9 (dd, *J* = 11.5, 7.2 Hz), 120.5, 78.8, 42.3, 15.9.

^{19}F NMR (565 MHz, $CDCl_3$) δ-128.13 (s).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{17}FN_2O_2S_2$ 425.0788; Found 425.0796.

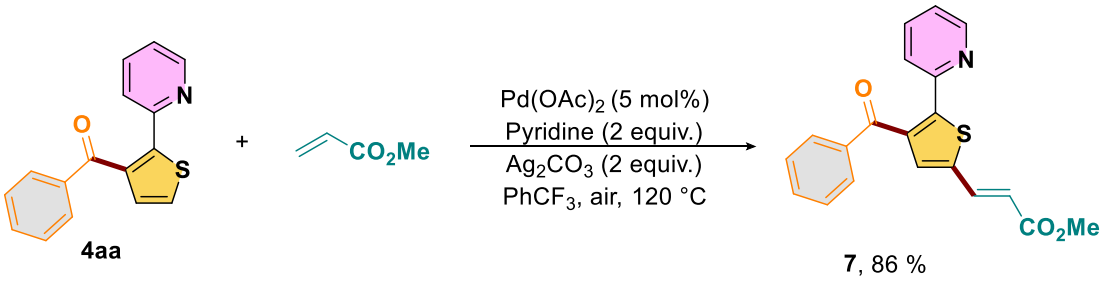


(5-(4-Methoxyphenyl)-2-(pyridin-2-yl)thiophen-3-yl)(phenyl)methanone (6). To a 15 mL oven dried Schlenk tube, **4aa** (53.1 mg, 0.2 mmol, 1 equiv.), 1-bromo-4-methoxybenzene (56.1 mg, 0.3 mmol, 1.5 equiv.), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol, 5 mol%), K_2CO_3 (55.2 mg, 0.4 mmol, 2 equiv.) PivOH (6.1 mg, 0.06 mmol, 0.3 equiv.) and CH_3CN (1.5 ml) were successively added. The reaction mixture was evacuated by vacuum-argon cycles (5 times) and stirred at 130 °C (metal sand bath temperature) for 16 hours, cooled down to room temperature. After concentration of reaction mixture, the crude mixture was purified by silica column chromatography (petroleum ether/ethyl acetate = 20:1) to afford the desired product **6** (50.5 mg, 68%) as a brown solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.47 (d, *J* = 4.8 Hz, 1H), 7.89 (d, *J* = 7.1 Hz, 2H), 7.59 (d, *J* = 8.8 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 6.9 Hz, 1H), 7.37 (d, *J* = 7.5 Hz, 2H), 7.35 (s, 1H), 7.30 (s, 1H), 7.06 – 7.03 (m, 1H), 6.93 (d, *J* = 8.8 Hz, 2H), 3.83 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 193.9, 160.0, 151.3, 149.4, 145.2, 143.3, 138.7, 137.6, 136.4, 133.3, 130.0, 128.5, 127.3, 126.2, 124.5, 122.3, 122.2, 114.6, 55.5.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{17}NO_2S$ 372.1053; Found 372.1050.



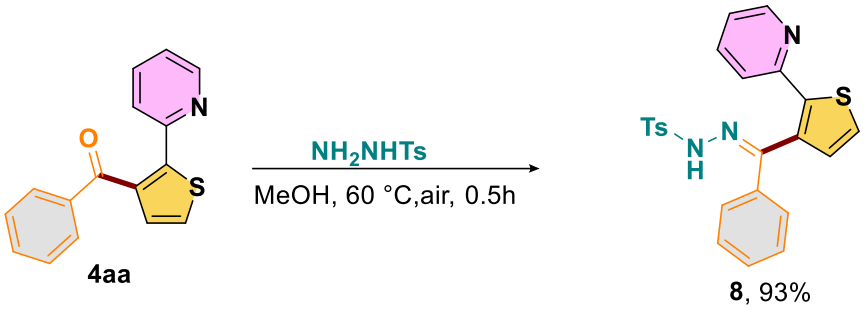
Methyl (*E*)-3-(4-Benzoyl-5-(pyridin-2-yl)thiophen-2-yl)acrylate (7). To oven dried Schlenk tube equipped with magnetic stir bar was introduced **4aa** (53.2 mg, 0.2 mmol), Ag_2CO_3 (110.3 mg, 0.4 mmol, 2 equiv.), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol, 5 mol%), pyridine (31.6 mg, 0.4 mmol, 2 equiv.), methyl acrylate (34.4 mg, 0.4 mmol, 2 equiv.) and $PhCF_3$ (1.5 mL) were successively added. The reaction mixture was stirred at 120 °C (metal sand bath temperature) for 12 hours under air. After cooling the reaction at room temperature and concentration, the crude mixture was purified by silica column chromatography to afford the desired product **7** (60.0

mg, 86%) as a yellow solid.

^{1}H NMR (600 MHz, CDCl $_3$) δ 8.46 (d, *J* = 4.5 Hz, 1H), 7.82 (d, *J* = 7.3 Hz, 2H), 7.72 (d, *J* = 15.7 Hz, 1H), 7.51 – 7.47 (m, 2H), 7.39 – 7.35 (m, 3H), 7.31 (s, 1H), 7.11 – 7.07 (m, 1H), 6.33 (d, *J* = 15.7 Hz, 1H), 3.79 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 193.0, 166.9, 150.5, 149.6, 147.4, 139.7, 138.5, 137.2, 136.6, 136.5, 133.6, 132.9, 129.9, 128.6, 123.1, 122.5, 118.5, 51.9.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{15}NO_3S$ 350.0845; Found 350.0841.



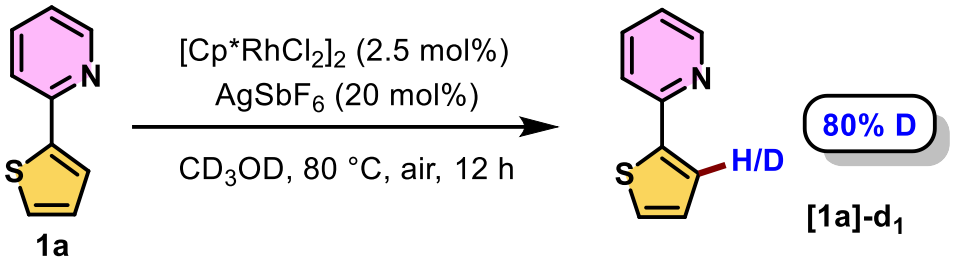
(*E*)-4-methyl-N'-(phenyl(2-(pyridin-2-yl)thiophen-3-yl)methylene)benzenesulfonohydrazide (8). A solution of $TsNHNH_2$ (2 mmol) in ethanol (2 mL) was stirred and heated to 60 °C until the $TsNHNH_2$ was completely dissolved. Then **4aa** (53.2 mg, 0.2 mmol) were added to the mixture slowly. After approximately 30 minutes the crude products was obtained as precipitates. The precipitates were washed by petroleum ether then were dried in vacuo to afford the pure products. The reaction provides the **8** (80.6 mg, 93%) as a black solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.32 (d, *J* = 4.4 Hz, 1H), 8.18 (s, 1H), 7.82 (d, *J* = 8.3 Hz, 2H), 7.56 (d, *J* = 5.1 Hz, 1H), 7.54 (d, *J* = 7.1 Hz, 2H), 7.32 (d, *J* = 7.2 Hz, 1H), 7.29 (s, 2H), 7.28 – 7.28 (m, 2H), 7.27 (s, 1H), 7.09 (d, *J* = 8.0 Hz, 1H), 7.05 (dd, *J* = 7.1, 5.2 Hz, 1H), 6.78 (d, *J* = 5.1 Hz, 1H), 2.44 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 151.2, 150.6, 149.5, 144.0, 143.2, 137.2, 135.9, 135.7, 130.2, 129.7, 129.2, 128.9, 128.6, 128.3, 128.0, 127.2, 122.7, 119.9, 21.7.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{19}N_3O_2S_2$ 434.0991; Found 434.0990.

3.7 H/D exchange experiment.



To a 15 mL oven dried Schlenk tube, 2-(thiophen-2-yl)pyridine **1a** (32.2mg, 0.2 mmol, 1 equiv.), $AgSbF_6$ (13.7 mg, 0.04 mmol, 20 mol%), $[Rh^*CpCl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol%), and CD_3CD_2OD (1.5 mL) were successively added. The mixture was then stirred at 80 °C for 12 h. Then, the reaction mixture was cooled to room temperature and filtered through a plug of celite. The organic phase was concentrated under reduced pressure, and the residue was purified by silica gel chromatography (petroleum ether/ethyl acetate = 20:1) to afford **[1a]-d_1**. Upon analyzing the ^{1}H NMR spectra as shown in **Figure S1**, the estimated deuterium incorporation at the C3-position of the thiophene ring was 80%.

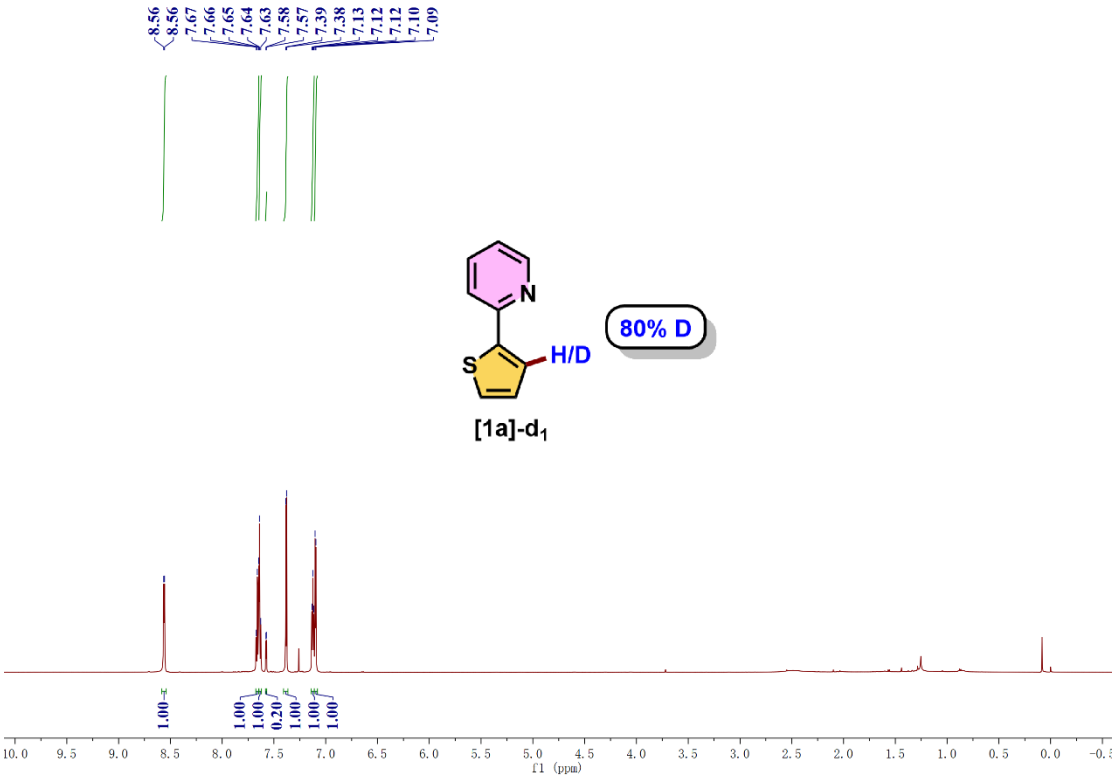
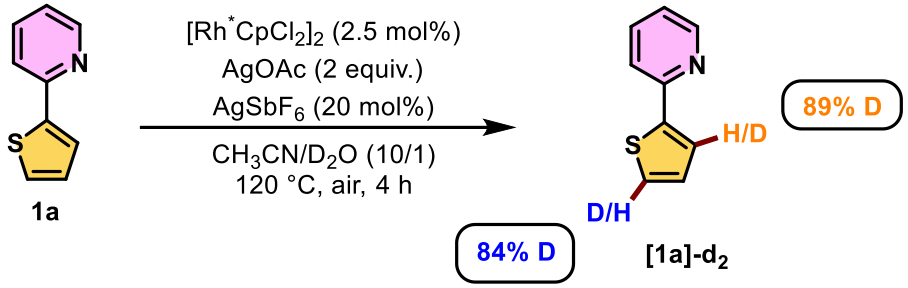


Figure S1. The ^{1}H NMR spectra of **[1a]-d_1**

3.8 KIE determination



Modified procedure for the synthesis of [1a]-d_2 of 2-pyridylthiophene[3]: To a 15 mL oven dried Schlenk tube, 2-(thiophen-2-yl)pyridine **1a** (32.2 mg, 0.2 mmol, 1 equiv.), AgOAc (68.8 mg, 0.4 mmol, 2 equiv.), $AgSbF_6$ (13.7 mg, 0.04 mmol, 20 mol%), $[Rh^*CpCl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol%), D_2O (0.15 mL) and CH_3CN (1.5 mL) were successively added. The mixture was then stirred at 120 °C for 4 h. Then, the reaction mixture was cooled to room temperature and filtered through a plug of celite. The organic phase was concentrated under reduced pressure, and the residue was purified by silica gel chromatography (petroleum ether/ethyl acetate = 20:1) to afford **[1a]-d_2**. Upon analyzing the ^{1}H NMR spectra as shown in **Figure S2**, the estimated deuterium incorporation at the C3-position of the thiophene ring was 89% and at the C5-position was 84%.

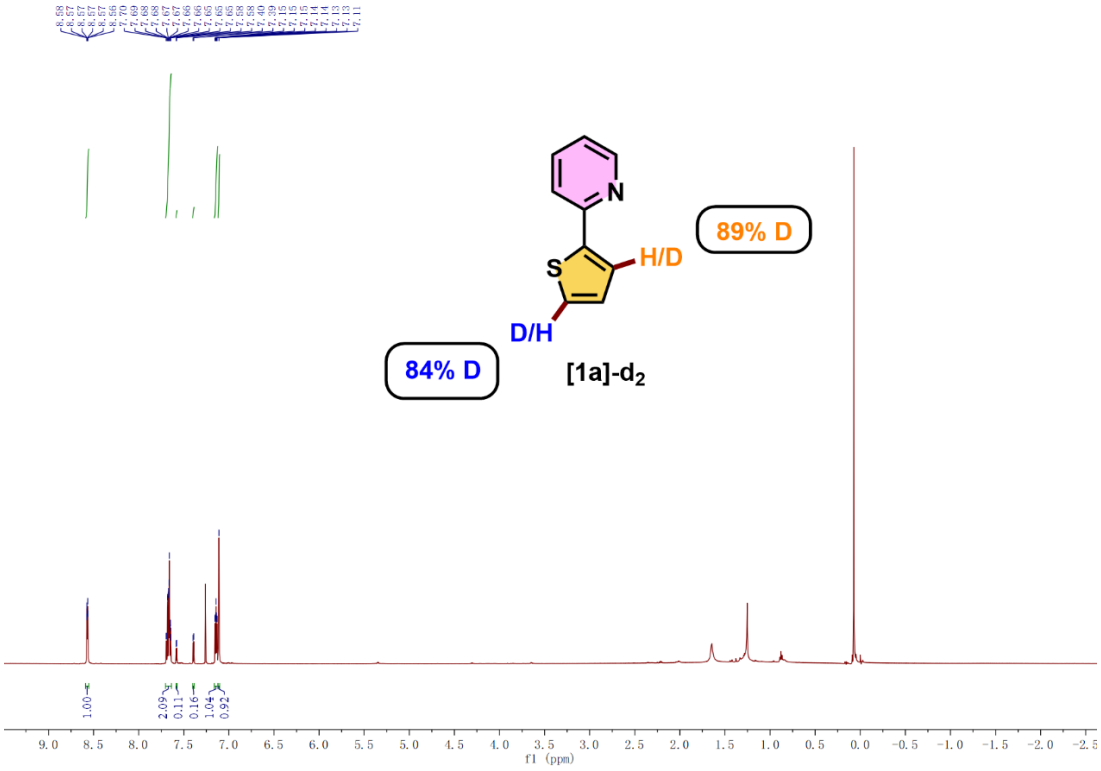
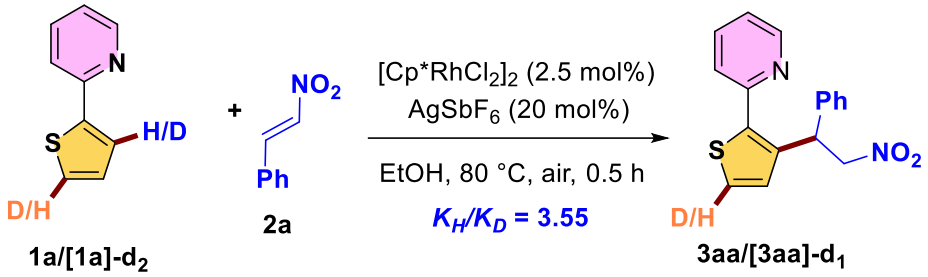


Figure S2. The ^{1}H NMR spectra of **[1a]-d_2**



To a 15 mL oven dried Schlenk tube, **1a** (16.1mg, 0.1 mmol, 1 equiv.), **[1a]-d_2** (16.1mg, 0.1 mmol, 1 equiv.). (*E*)-(2-nitrovinyl)benzene (59.6 mg, 0.4 mmol, 2 equiv.), $AgSbF_6$ (13.7 mg, 0.04 mmol, 20 mol%), $[Rh^*CpCl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol%), and EtOH (1.5 mL) were successively added. The mixture was then stirred at 80 °C for 0.5 h. The organic phase was concentrated under reduced pressure, and the residue was purified by silica gel chromatography (petroleum ether/ethyl acetate = 20:1) to afford **3aa/[3aa]-d_1**. By analyzing the ^{1}H NMR of the spectra as shown in **Figure S3**, the ratio of **3aa** and **[3aa]-d_1** was determined to be 0.78:0.22. Accordingly, the intermolecular **KIE** (k_H/k_D) = 0.78/0.22 = 3.55.

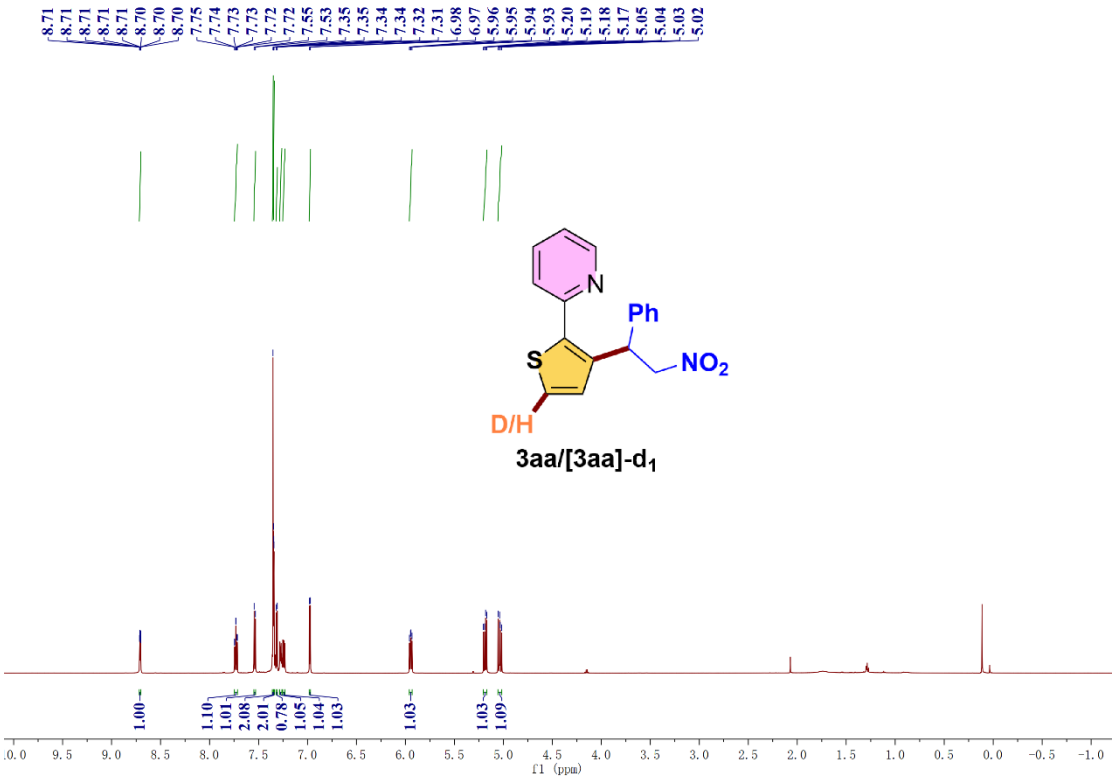
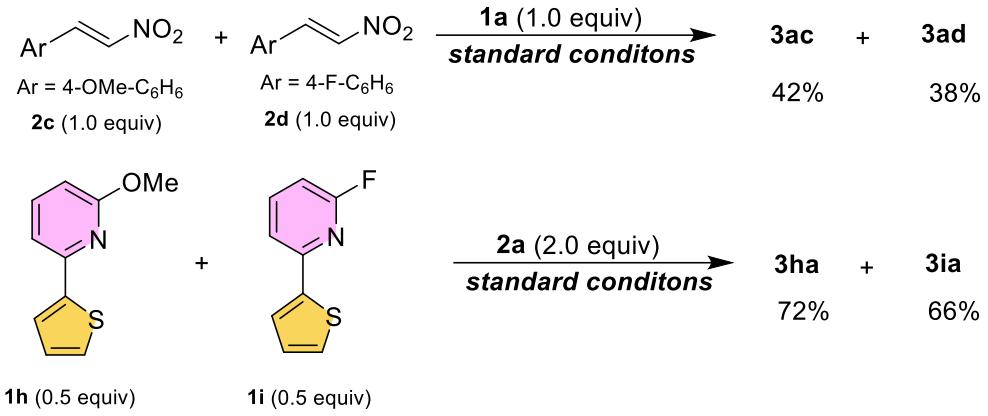


Figure S3. The ^{1}H NMR spectra of **3aa/[3aa]-d_1**

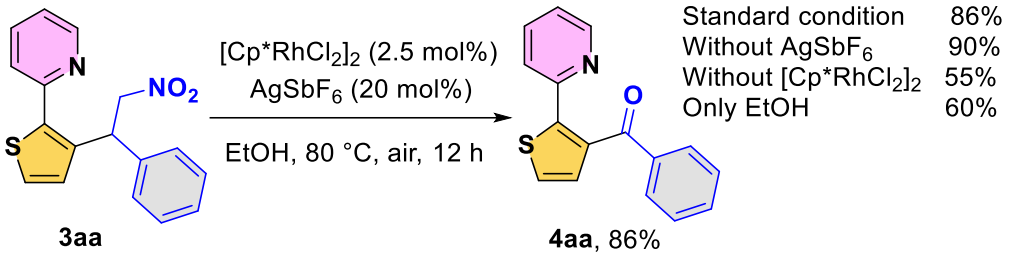
3.9 Intermolecular competition experiments



A 15 mL oven dried Schlenk tube was charged with **1a** (16.1 mg, 0.1 mmol), (*E*)-1-methoxy-4 (2-nitrovinyl)benzene (**2c**) (17.9 mg, 0.1 mmol), (*E*)-1-(2-nitrovinyl)-4 (fluoro)benzene (**2d**) (16.7 mg, 0.1 mmol), $AgSbF_6$ (0.04 mmol, 20 mol%), $[Cp^*RhCl_2]_2$ (0.005 mmol, 2.5 mol%) and EtOH (1.5 mL). The reaction was stirred in an oil bath at 80 °C for 0.5 h under air. Then the mixture was cooled to room temperature and transferred into a round-bottom flask with EA. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to give the desired product **3ac** (14.3 mg, 42%) and **3ad** (13.03 mg, 38%).

A 15 mL oven dried Schlenk tube was charged with **1h** (19.1 mg, 0.1 mmol), **1i** (17.9 mg, 0.1 mmol), (*E*)-(2-nitrovinyl)benzene (**2a**) (29.8 mg, 0.2 mmol), $AgSbF_6$ (0.04 mmol, 20 mol%), $[Cp^*RhCl_2]_2$ (0.005 mmol, 2.5 mol%) and EtOH (2.0 mL). The reaction was stirred in an oil bath at 80 °C for 0.5 h under air. Then the mixture was cooled to room temperature and transferred into a round-bottom flask with EA. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to give the desired product **3ha** (24.5 mg, 72%) and **3ad** (21.7 mg, 66%).

3.10 Control reactions



To a 15 mL oven dried Schlenk tube, $AgSbF_6$ (0.04 mmol, 20 mol%), **3aa** (0.2 mmol, 1 equiv.), $[Cp^*RhCl_2]_2$ (0.005 mmol, 2.5 mol%) and EtOH (1.5 mL) were successively added as the standard conditon. The reaction mixture was stirred at 80 °C (metal sand bath temperature)

for 12 hours under air. After cooling the reaction at room temperature and concentration, the crude mixture was purified by silica column chromatography to afford the desired product **4aa (**45.6 mg, 86%). Upon alteration of the reaction conditions, the following observations were made: First, in the absence of Additive $AgSbF_6$, the yield increased to 90%. Second, when Catalyst $[Cp^*RhCl_2]_2$ was omitted, the yield significantly decreased to 55%, underscoring the critical role of Catalyst 3. Finally, with both Additive $AgSbF_6$ and Catalyst $[Cp^*RhCl_2]_2$ excluded and only ethanol as the solvent, the yield modestly improved to 60%.

4. Crystallographic description

White block-like single crystals of **3da** were grown by layering a dichlormethane solution with hexane at ambient temperature. X-Ray diffraction data of one these crystals were collected on a R-AXIS SPIDER diffractometer. The measurements were performed with Mo-Kα radiation (λ = 0.71073 Å). Data were collected at 298(2) K, using the *ω*- and *φ*- scans to a maximum θ value of 28.327°. The data were refined by full-matrix least-squares techniques on F^2 with SHELXL-2018/3. And the structures were solved by direct methods SHELXL-2018/3. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included at geometrically idealized positions. And an ORTEP representation of the structure is shown below. CCDC: 2478277.

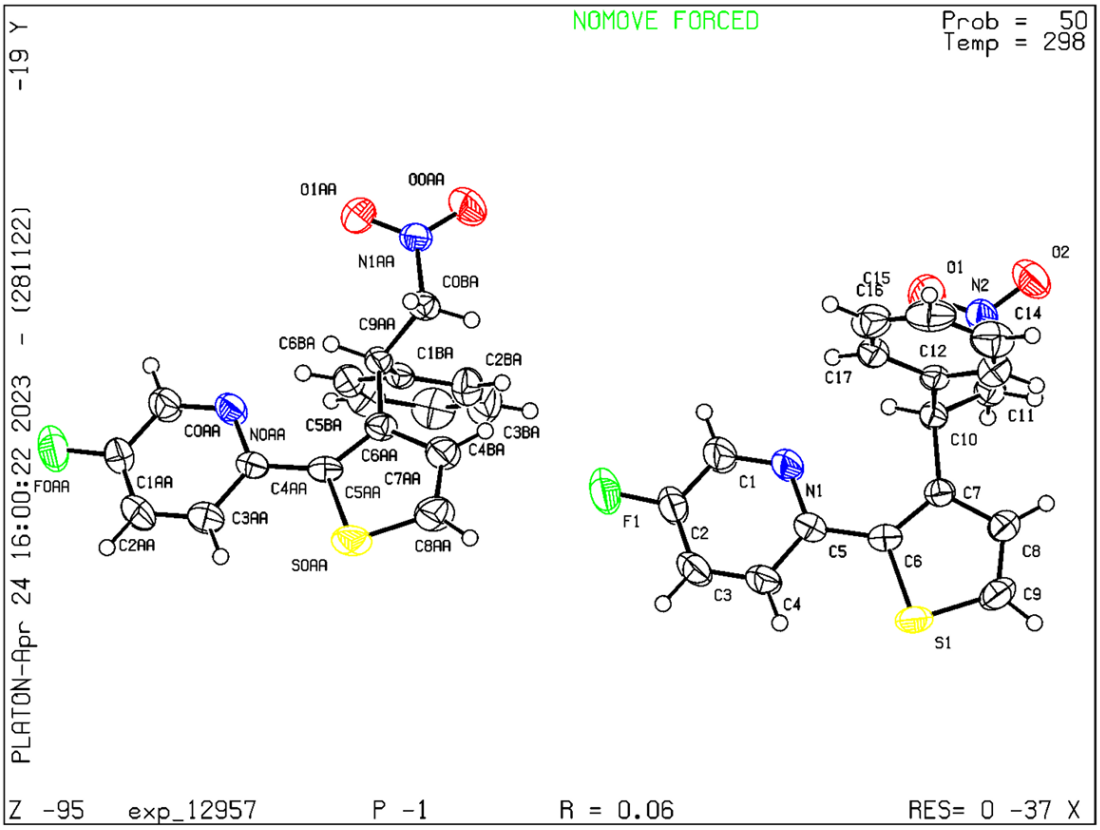


Figure S5. ORTEP diagram of **3da** with the thermal ellipsoids set at 50% probability.

Table 1 Crystal data and structure refinement for **3da.**

Identification code	exp_12957
Empirical formula	$C_{17}H_{13}FN_2O_2S$
Formula weight	328.35
Temperature/K	298
Crystal system	triclinic
Space group	P-1
a/Å	9.8276(5)
b/Å	11.1008(7)
c/Å	15.5044(8)

α/°	103.401(5)
β/°	106.506(5)
γ/°	98.916(5)
Volume/Å^3	1532.72(16)
Z	4
ρ_{calc}g/cm^3	1.423
μ/mm^{-1}	0.233
F(000)	680.0
Crystal size/mm^3	0.3 × 0.2 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	7.452 to 58.508
Index ranges	-12 ≤ h ≤ 12, -14 ≤ k ≤ 13, -14 ≤ l ≤ 20
Reflections collected	12313
Independent reflections	6999 [R_{int} = 0.0248, R_{sigma} = 0.0526]
Data/restraints/parameters	6999/0/415
Goodness-of-fit on F^2	1.020
Final R indexes [I>=2σ (I)]	R_1 = 0.0573, wR_2 = 0.1147
Final R indexes [all data]	R_1 = 0.0898, wR_2 = 0.1306
Largest diff. peak/hole / e Å^{-3}	0.27/-0.34

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

Atom	***x***	***y***	***z***	**U(eq)**
S1	-1531.6(6)	2702.9(6)	4566.5(5)	47.15(18)
S0AA	164.1(7)	11109.3(7)	1737.3(5)	51.38(19)
F0AA	2022.6(19)	13016.1(17)	-1559.7(12)	72.8(5)
N1AA	6538.4(19)	10151(2)	2464.6(13)	39.2(4)
N2	4849(2)	1702(2)	5319.1(14)	44.2(5)
O0AA	7189(2)	9466(2)	2839.1(14)	68.9(6)
F1	1145(2)	6096(2)	2230.0(15)	104.4(8)
O1AA	6996(2)	10754(2)	2011.2(15)	75.3(6)
N0AA	2886(2)	11576(2)	307.9(13)	43.6(5)
O1	5274(2)	2141(2)	4778.8(16)	83.2(7)
C1BA	3568(2)	8735(2)	991.7(14)	33.0(5)
C12	3612(2)	3884(2)	6070.1(15)	32.6(5)
N1	1704(2)	4091(2)	3740.0(16)	56.6(6)
C9AA	3922(2)	10079(2)	1654.1(14)	32.7(5)
C4AA	1723(2)	11593(2)	589.1(15)	34.5(5)
C10	2777(2)	2771(2)	5194.2(15)	33.5(5)

C17	4152(2)	5060(2)	5970.5(18)	42.0(6)
C6AA	2551(2)	10394(2)	1834.6(14)	34.8(5)
C7	1148(2)	2551(2)	5035.0(15)	34.1(5)
O2	5640(2)	1360(3)	5916.8(17)	94.9(8)
C5AA	1649(2)	11034(2)	1350.3(15)	36.1(5)
C5	403(2)	3859(2)	3854.3(14)	36.0(5)
C6	189(2)	3065(2)	4467.9(15)	35.2(5)
C6BA	3430(2)	8578(2)	52.8(15)	39.6(5)
C11	3277(2)	1542(2)	5235.1(17)	39.5(5)
C0BA	5112(2)	10278(2)	2594.8(14)	38.2(5)
C13	3799(3)	3782(2)	6970.0(17)	46.0(6)
C1AA	1889(3)	12563(2)	-839.9(17)	47.1(6)
C0AA	2964(3)	12061(3)	-392.3(17)	48.2(6)
C8	452(3)	1872(2)	5529.2(18)	46.4(6)
C2BA	3332(3)	7658(2)	1284.0(18)	48.5(6)
C7AA	2011(3)	9986(3)	2502.1(16)	48.2(6)
C5BA	3048(3)	7377(3)	-572.9(18)	53.4(7)
C4	-711(3)	4383(3)	3416.9(17)	50.1(7)
C15	5000(3)	5995(3)	7629(2)	61.7(8)
C4BA	2805(3)	6313(3)	-273(2)	60.8(8)
C16	4849(3)	6100(3)	6743(2)	55.6(7)
C9	-978(3)	1877(3)	5340.1(19)	53.2(7)
C2	846(3)	5347(3)	2759.3(19)	60.6(8)
C8AA	740(3)	10311(3)	2523.1(18)	57.2(7)
C14	4478(3)	4839(3)	7743.9(19)	59.7(8)
C3AA	610(3)	12116(3)	153(2)	61.9(8)
C3	-483(3)	5131(3)	2863.4(19)	58.6(8)
C3BA	2946(3)	6455(3)	657(2)	60.3(7)
C1	1913(3)	4825(3)	3202(2)	71.9(9)
C2AA	700(3)	12608(3)	-569(2)	69.9(9)

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

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	26.7(3)	53.8(4)	58.3(4)	15.5(3)	12.8(3)	5.7(3)
S0AA	35.8(3)	69.3(5)	58.3(4)	19.0(3)	23.5(3)	23.6(3)
F0AA	83.8(12)	84.3(13)	77.9(11)	56.7(10)	32.2(9)	38.0(10)
N1AA	31.1(10)	50.9(13)	36.6(10)	14.6(9)	10.8(8)	10.4(9)
N2	45.0(12)	51.0(13)	51.8(12)	24.3(10)	24.6(10)	24.8(10)
O0AA	57.6(12)	86.2(15)	90.1(14)	51.4(13)	30.7(11)	43.8(11)
F1	85.1(13)	166(2)	130.0(17)	122.5(17)	56.7(12)	63.6(14)
O1AA	49.6(11)	122.7(19)	85.2(14)	70.1(14)	35.7(10)	25.0(12)
N0AA	40.5(11)	58.9(14)	42.8(11)	23.6(10)	16.9(9)	24.5(10)
O1	69.1(14)	133(2)	99.7(16)	78.6(16)	57.1(13)	51.1(14)
C1BA	26.2(10)	42.6(13)	35.0(12)	14.5(10)	11.9(8)	13.9(9)

C12	24.6(10)	35.6(12)	42.3(12)	14.7(10)	13.2(9)	11.4(9)
N1	41.5(12)	85.2(18)	70.7(15)	50.6(14)	28.2(10)	33.3(12)
C9AA	30.4(11)	42.2(13)	30.6(11)	15.0(10)	11.9(8)	12.9(9)
C4AA	27.8(11)	32.5(12)	38.7(12)	6.8(10)	6.4(9)	8.5(9)
C10	31.8(11)	36.3(12)	38.6(12)	15.9(10)	14.6(9)	12.3(9)
C17	35.2(12)	42.8(14)	54.2(14)	21.2(12)	16.5(10)	13.2(10)
C6AA	30.6(11)	43.1(13)	30.9(11)	8.2(10)	11.8(8)	9.8(10)
C7	29.6(11)	32.1(12)	38.8(12)	9.1(10)	10.3(9)	6.3(9)
O2	59.7(13)	164(3)	111.0(18)	100.1(19)	39.2(12)	57.8(15)
C5AA	25.9(11)	40.1(13)	40.5(12)	6.3(10)	11.6(9)	9.6(9)
C5	33.1(12)	41.0(13)	32.2(11)	7.7(10)	8.5(9)	12.9(10)
C6	28.0(11)	35.3(12)	37.9(12)	4.1(10)	10.4(9)	6.1(9)
C6BA	41.4(13)	45.7(14)	37.8(12)	14.8(11)	17.2(10)	16.3(11)
C11	37.1(12)	38.1(13)	48.6(14)	15.1(11)	18.2(10)	12.4(10)
C0BA	33.1(12)	52.1(15)	32.9(12)	12.8(10)	13.0(9)	15.6(10)
C13	42.7(13)	48.5(15)	48.5(15)	16.2(12)	17.1(11)	8.6(11)
C1AA	48.9(15)	45.3(15)	51.9(15)	24.6(12)	13.2(11)	15.1(12)
C0AA	46.0(14)	61.2(17)	48.9(14)	24.7(13)	20.2(11)	23.4(13)
C8	38.7(13)	44.7(15)	61.4(16)	23.7(13)	18.9(11)	8.6(11)
C2BA	56.8(15)	51.1(16)	44.6(14)	20.5(12)	20.7(11)	15.0(13)
C7AA	42.6(14)	68.4(18)	43.5(14)	22.5(13)	20.0(11)	20.9(13)
C5BA	59.6(16)	60.6(18)	40.9(14)	8.1(13)	19.9(12)	21.1(14)
C4	34.5(13)	70.4(19)	55.0(15)	27.6(14)	16.1(11)	23.5(12)
C15	39.6(15)	53.1(18)	70(2)	-9.7(15)	10.1(13)	4.9(13)
C4BA	65.8(18)	46.5(17)	61.0(18)	0.9(14)	18.7(14)	14.6(14)
C16	44.5(15)	39.4(15)	79(2)	14.6(14)	18.6(13)	6.9(12)
C9	41.6(14)	50.0(16)	71.6(18)	22.7(14)	25.1(12)	1.5(12)
C2	57.5(17)	87(2)	63.8(17)	51.6(17)	27.5(14)	34.7(16)
C8AA	47.4(15)	84(2)	51.2(15)	22.7(15)	28.4(12)	20.0(14)
C14	50.8(16)	79(2)	42.5(15)	7.3(15)	14.1(12)	14.3(15)
C3AA	39.9(15)	81(2)	89(2)	48.8(18)	29.1(14)	31.4(14)
C3	46.3(15)	84(2)	60.9(17)	40.3(16)	16.2(12)	34.2(15)
C3BA	70.2(19)	43.7(17)	72(2)	23.8(15)	26.7(15)	12.6(14)
C1	51.6(17)	116(3)	91(2)	73(2)	40.1(16)	44.3(18)
C2AA	50.0(17)	90(2)	96(2)	62(2)	23.6(15)	39.0(16)

Table 4 Bond Lengths for **3da**.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
S1	C6	1.735(2)	C4AA	C3AA	1.396(3)
S1	C9	1.694(3)	C10	C7	1.519(3)
S0AA	C5AA	1.735(2)	C10	C11	1.529(3)
S0AA	C8AA	1.689(3)	C17	C16	1.373(3)
F0AA	C1AA	1.356(3)	C6AA	C5AA	1.386(3)
N1AA	O0AA	1.212(2)	C6AA	C7AA	1.419(3)
N1AA	O1AA	1.204(3)	C7	C6	1.384(3)
N1AA	C0BA	1.495(3)	C7	C8	1.425(3)

N2	O1	1.200(3)	C5	C6	1.474(3)
N2	O2	1.205(2)	C5	C4	1.397(3)
N2	C11	1.492(3)	C6BA	C5BA	1.378(3)
F1	C2	1.352(3)	C13	C14	1.383(4)
N0AA	C4AA	1.335(3)	C1AA	C0AA	1.362(3)
N0AA	C0AA	1.334(3)	C1AA	C2AA	1.353(4)
C1BA	C9AA	1.526(3)	C8	C9	1.353(3)
C1BA	C6BA	1.389(3)	C2BA	C3BA	1.380(4)
C1BA	C2BA	1.384(3)	C7AA	C8AA	1.360(3)
C12	C10	1.523(3)	C5BA	C4BA	1.377(4)
C12	C17	1.391(3)	C4	C3	1.363(4)
C12	C13	1.388(3)	C15	C16	1.373(4)
N1	C5	1.335(3)	C15	C14	1.377(4)
N1	C1	1.328(3)	C4BA	C3BA	1.377(4)
C9AA	C6AA	1.526(3)	C2	C3	1.353(4)
C9AA	C0BA	1.531(3)	C2	C1	1.368(3)
C4AA	C5AA	1.469(3)	C3AA	C2AA	1.372(4)

Table 5 Bond Angles for **3da**.

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
C9	S1	C6	92.38(12)	C6AA	C5AA	C4AA	131.96(19)
C8AA	S0AA	C5AA	92.60(11)	N1	C5	C6	118.21(18)
O0AA	N1AA	C0BA	118.1(2)	N1	C5	C4	120.5(2)
O1AA	N1AA	O0AA	123.4(2)	C4	C5	C6	121.3(2)
O1AA	N1AA	C0BA	118.43(19)	C7	C6	S1	110.42(17)
O1	N2	O2	122.4(2)	C7	C6	C5	131.6(2)
O1	N2	C11	118.96(19)	C5	C6	S1	117.92(15)
O2	N2	C11	118.6(2)	C5BA	C6BA	C1BA	120.6(2)
C0AA	N0AA	C4AA	119.12(19)	N2	C11	C10	111.35(19)
C6BA	C1BA	C9AA	119.2(2)	N1AA	C0BA	C9AA	111.40(16)
C2BA	C1BA	C9AA	122.38(19)	C14	C13	C12	120.3(3)
C2BA	C1BA	C6BA	118.4(2)	F0AA	C1AA	C0AA	119.3(2)
C17	C12	C10	119.27(19)	C2AA	C1AA	F0AA	120.4(2)
C13	C12	C10	122.1(2)	C2AA	C1AA	C0AA	120.3(2)
C13	C12	C17	118.5(2)	N0AA	C0AA	C1AA	122.3(2)
C1	N1	C5	118.5(2)	C9	C8	C7	113.4(2)
C1BA	C9AA	C6AA	110.57(17)	C3BA	C2BA	C1BA	120.9(2)
C1BA	C9AA	C0BA	112.91(17)	C8AA	C7AA	C6AA	113.3(2)
C6AA	C9AA	C0BA	109.35(16)	C4BA	C5BA	C6BA	120.3(2)
N0AA	C4AA	C5AA	118.15(17)	C3	C4	C5	120.4(2)
N0AA	C4AA	C3AA	120.0(2)	C16	C15	C14	120.0(3)
C3AA	C4AA	C5AA	121.8(2)	C3BA	C4BA	C5BA	119.7(3)
C12	C10	C11	113.01(17)	C15	C16	C17	120.1(3)
C7	C10	C12	109.98(16)	C8	C9	S1	112.1(2)
C7	C10	C11	110.15(18)	F1	C2	C3	120.6(2)
C16	C17	C12	120.9(2)	F1	C2	C1	119.1(2)

C5AA	C6AA	C9AA	125.5(2)	C3	C2	C1	120.2(3)
C5AA	C6AA	C7AA	111.92(19)	C7AA	C8AA	S0AA	111.9(2)
C7AA	C6AA	C9AA	122.53(19)	C15	C14	C13	120.2(3)
C6	C7	C10	125.1(2)	C2AA	C3AA	C4AA	120.3(2)
C6	C7	C8	111.71(19)	C2	C3	C4	117.8(2)
C8	C7	C10	122.94(19)	C4BA	C3BA	C2BA	120.1(3)
C4AA	C5AA	S0AA	117.81(15)	N1	C1	C2	122.5(3)
C6AA	C5AA	S0AA	110.21(17)	C1AA	C2AA	C3AA	118.0(2)

Table 6 Torsion Angles for **3da**.

A	**B**	**C**	**D**	**Angle/°**	**A**	**B**	**C**	**D**	**Angle/°**
F0AA	C1AA	C0AA	N0AA	-178.6(2)	C5AA	C4AA	C3AA	C2AA	-178.7(3)
F0AA	C1AA	C2AA	C3AA	178.9(3)	C5AA	C6AA	C7AA	C8AA	-0.1(3)
O0AA	N1AA	C0BA	C9AA	-130.7(2)	C5	N1	C1	C2	-0.2(5)
F1	C2	C3	C4	-179.1(3)	C5	C4	C3	C2	-0.3(4)
F1	C2	C1	N1	179.3(3)	C6	S1	C9	C8	0.4(2)
O1AA	N1AA	C0BA	C9AA	50.9(3)	C6	C7	C8	C9	-0.1(3)
N0AA	C4AA	C5AA	S0AA	177.90(17)	C6	C5	C4	C3	179.0(2)
N0AA	C4AA	C5AA	C6AA	-4.1(4)	C6BA	C1BA	C9AA	C6AA	102.2(2)
N0AA	C4AA	C3AA	C2AA	0.4(4)	C6BA	C1BA	C9AA	C0BA	-134.9(2)
O1	N2	C11	C10	-50.6(3)	C6BA	C1BA	C2BA	C3BA	-1.0(3)
C1BA	C9AA	C6AA	C5AA	-95.0(3)	C6BA	C5BA	C4BA	C3BA	-0.1(4)
C1BA	C9AA	C6AA	C7AA	81.4(2)	C11	C10	C7	C6	-141.3(2)
C1BA	C9AA	C0BA	N1AA	64.0(2)	C11	C10	C7	C8	44.6(3)
C1BA	C6BA	C5BA	C4BA	-0.3(4)	C0BA	C9AA	C6AA	C5AA	140.1(2)
C1BA	C2BA	C3BA	C4BA	0.7(4)	C0BA	C9AA	C6AA	C7AA	-43.6(3)
C12	C10	C7	C6	93.5(2)	C13	C12	C10	C7	73.7(2)
C12	C10	C7	C8	-80.6(3)	C13	C12	C10	C11	-49.9(3)
C12	C10	C11	N2	-60.8(2)	C13	C12	C17	C16	-0.3(3)
C12	C17	C16	C15	-1.1(3)	C0AA	N0AA	C4AA	C5AA	179.0(2)
C12	C13	C14	C15	-1.3(4)	C0AA	N0AA	C4AA	C3AA	-0.1(3)
N1	C5	C6	S1	-176.86(18)	C0AA	C1AA	C2AA	C3AA	-1.0(5)
N1	C5	C6	C7	5.5(4)	C8	C7	C6	S1	0.3(2)
N1	C5	C4	C3	0.4(4)	C8	C7	C6	C5	178.1(2)
C9AA	C1BA	C6BA	C5BA	-177.1(2)	C2BA	C1BA	C9AA	C6AA	-75.6(2)
C9AA	C1BA	C2BA	C3BA	176.9(2)	C2BA	C1BA	C9AA	C0BA	47.2(3)
C9AA	C6AA	C5AA	S0AA	176.67(17)	C2BA	C1BA	C6BA	C5BA	0.8(3)
C9AA	C6AA	C5AA	C4AA	-1.4(4)	C7AA	C6AA	C5AA	S0AA	0.0(2)
C9AA	C6AA	C7AA	C8AA	-176.9(2)	C7AA	C6AA	C5AA	C4AA	-178.1(2)
C4AA	N0AA	C0AA	C1AA	-0.8(4)	C5BA	C4BA	C3BA	C2BA	-0.1(4)
C4AA	C3AA	C2AA	C1AA	0.2(5)	C4	C5	C6	S1	4.5(3)
C10	C12	C17	C16	176.85(19)	C4	C5	C6	C7	-173.2(2)
C10	C12	C13	C14	-175.6(2)	C16	C15	C14	C13	-0.1(4)
C10	C7	C6	S1	-174.36(17)	C9	S1	C6	C7	-0.40(18)
C10	C7	C6	C5	3.5(4)	C9	S1	C6	C5	-178.55(18)
C10	C7	C8	C9	174.8(2)	C8AA	S0AA	C5AA	C4AA	178.49(19)

C17	C12	C10	C7	-103.3(2)	C8AA	S0AA	C5AA	C6AA	0.10(19)
C17	C12	C10	C11	133.1(2)	C14	C15	C16	C17	1.3(4)
C17	C12	C13	C14	1.5(3)	C3AA	C4AA	C5AA	S0AA	-3.0(3)
C6AA	C9AA	C0BA	N1AA	-172.40(19)	C3AA	C4AA	C5AA	C6AA	174.9(3)
C6AA	C7AA	C8AA	S0AA	0.2(3)	C3	C2	C1	N1	0.3(5)
C7	C10	C11	N2	175.75(17)	C1	N1	C5	C6	-178.8(3)
C7	C8	C9	S1	-0.3(3)	C1	N1	C5	C4	-0.1(4)
O2	N2	C11	C10	130.9(3)	C1	C2	C3	C4	-0.1(5)
C5AA	S0AA	C8AA	C7AA	-0.2(2)	C2AA	C1AA	C0AA	N0AA	1.4(4)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **3da.**

Atom	***x***	***y***	***z***	**U(eq)**
H9AA	4274.26	10679.29	1346.5	39
H10	2947.84	3001.92	4654.42	40
H17	4039.74	5143.4	5372.52	50
H6BA	3596.32	9290.82	-155.5	48
H11A	3129.73	1299.13	5770.06	47
H11B	2689.02	862.19	4670.11	47
H0BA	5230.55	11119.17	3006.78	46
H0BB	4813.68	9654.15	2892.58	46
H13	3466.24	2999.69	7052.59	55
H0AA	3781.49	12055.88	-581.17	58
H8	933.78	1464.53	5941.37	56
H2BA	3435.55	7745.63	1912.07	58
H7AA	2479.92	9540.24	2887.26	58
H5BA	2953.96	7283.47	-1200.32	64
H4	-1611.75	4219.39	3503.9	60
H15	5455.46	6704.28	8150.89	74
H4BA	2546.68	5503.38	-696.48	73
H16	5219.27	6876.94	6666.86	67
H9	-1585.27	1473.89	5603.9	64
H8AA	245.89	10116.86	2922.33	69
H14	4582.05	4769.25	8344.32	72
H3AA	-195.89	12131.73	352.75	74
H3	-1218.04	5480.79	2566.92	70
H3BA	2781.43	5739.83	861.77	72
H1	2819.78	4990.27	3122.6	86
H2AA	-33.4	12961.17	-862.71	84

White block-like single crystals of **4ac** were grown by layering a dichlormethane solution with hexane at ambient temperature. X-Ray diffraction data of one these crystals were collected on a R-AXIS SPIDER diffractometer. The measurements were performed with Mo-Kα radiation (λ = 0.71073 Å). Data were collected at 298(2) K, using the *ω*- and *φ*- scans to a maximum θ value of 28.327°. The data were refined by full-matrix least-squares techniques on F^2 with SHELXL-2018/3. And the structures were solved by direct methods SHELXL-2018/3. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included at geometrically idealized positions. And an ORTEP representation of the structure is shown below. CCDC:2478147.

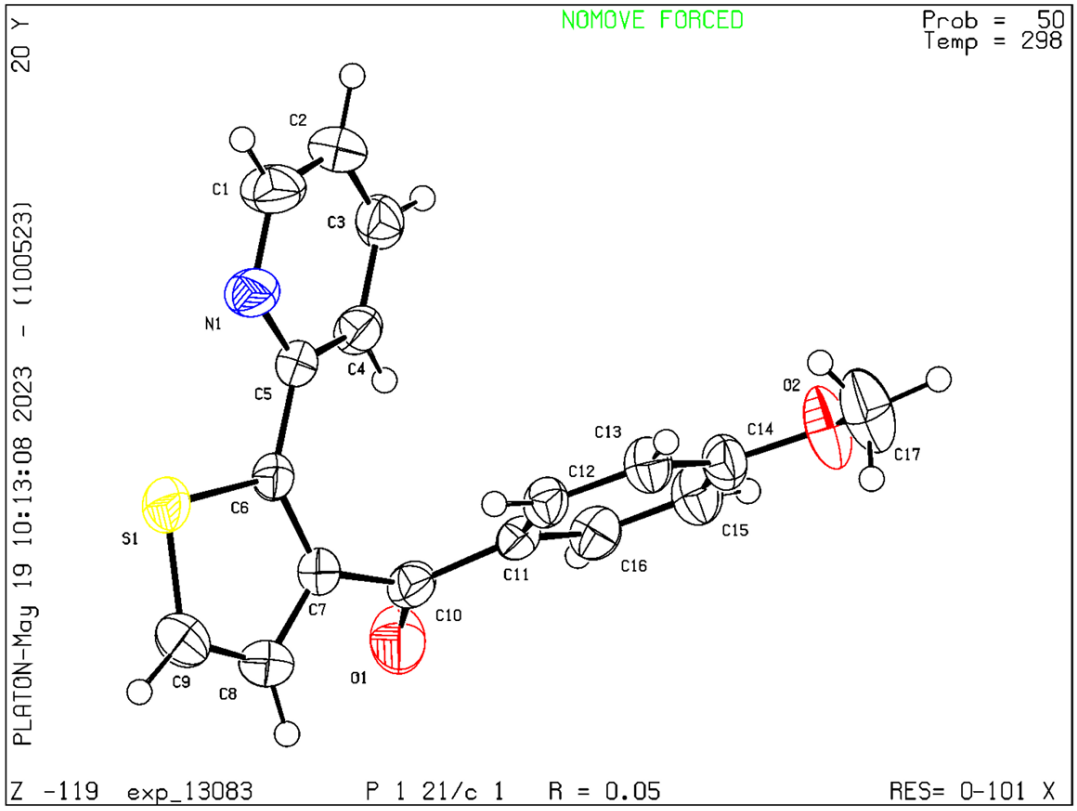


Figure S6. ORTEP diagram of **4ac** with the thermal ellipsoids set at 50% probability.

Table 1 Crystal data and structure refinement for **4ac**.

Identification code	exp_13083
Empirical formula	$C_{17}H_{13}NO_2S$
Formula weight	295.34
Temperature/K	298
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	9.5107(18)
b/Å	14.457(2)
c/Å	11.2450(18)
α/°	90
β/°	111.41(2)
γ/°	90

Volume/Å^3	1439.4(5)
Z	4
ρ_{calc}g/cm^3	1.363
μ/mm^{-1}	0.228
F(000)	616.0
Crystal size/mm^3	0.3 × 0.2 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	7.278 to 59.182
Index ranges	-12 ≤ h ≤ 12, -18 ≤ k ≤ 18, -14 ≤ l ≤ 15
Reflections collected	10266
Independent reflections	3518 [R_{int} = 0.0475, R_{sigma} = 0.0556]
Data/restraints/parameters	3518/0/192
Goodness-of-fit on F^2	1.033
Final R indexes [I>=2σ (I)]	R_1 = 0.0519, wR_2 = 0.1149
Final R indexes [all data]	R_1 = 0.0827, wR_2 = 0.1343
Largest diff. peak/hole / e Å^{-3}	0.24/-0.26

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

Atom	***x***	***y***	***z***	**U(eq)**
S1	3492.2(6)	4152.7(4)	2800.4(5)	50.3(2)
O1	287.7(18)	2860.9(12)	4780.9(15)	64.3(5)
O2	2921(2)	4997.9(11)	9955.7(14)	68.2(5)
N1	6034.0(18)	3725.9(13)	5071.3(16)	48.1(5)
C5	4762(2)	3434.7(13)	5199.0(16)	34.2(4)
C11	1806(2)	3865.0(13)	6372.5(17)	34.1(4)
C7	1898(2)	3753.1(14)	4117.8(17)	38.0(5)
C12	2593(2)	4688.2(13)	6646.6(17)	36.7(5)
C6	3373(2)	3745.2(13)	4197.0(16)	35.3(4)
C4	4792(2)	2865.7(13)	6195.4(18)	39.7(5)
C3	6152(2)	2639.9(15)	7123.4(18)	44.6(5)
C10	1286(2)	3439.7(14)	5093.7(19)	39.9(5)
C13	2988(2)	5093.1(14)	7831.1(18)	40.9(5)
C16	1443(2)	3430.7(14)	7329.7(19)	41.1(5)
C14	2597(2)	4658.2(15)	8765.0(18)	43.5(5)
C2	7451(2)	2965.3(16)	7020(2)	51.3(6)
C15	1845(2)	3824.0(15)	8511.3(19)	47.1(5)
C8	906(2)	4077.6(16)	2932(2)	52.2(6)
C1	7328(2)	3488.4(17)	5969(2)	56.9(6)
C9	1602(3)	4317.1(18)	2130(2)	59.2(7)
C17	3449(4)	5916.8(17)	10226(2)	78.5(9)

Table 3 Anisotropic Displacement Parameters (Å^2×10^3) for **4ac**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+...]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	53.4(4)	67.0(4)	36.8(3)	9.5(2)	23.8(3)	11.8(3)
O1	56.6(10)	81.9(12)	61.4(10)	-24.7(9)	29.8(8)	-29.3(9)
O2	112.5(14)	62.8(11)	35.3(8)	-5.8(8)	34.0(9)	-13.9(10)
N1	35.4(9)	66.5(13)	44.4(10)	8.4(9)	17.2(8)	1.7(8)
C5	34.3(10)	37.8(11)	32.5(9)	-2.2(8)	14.8(8)	2.9(8)
C11	29.6(9)	39.9(11)	35.8(10)	0.1(8)	15.6(8)	3.9(8)
C7	36.0(10)	45.6(12)	32.4(9)	-6.2(8)	12.6(8)	3.0(8)
C12	39.5(10)	41.5(12)	34.9(10)	4.0(8)	20.4(8)	-0.5(8)
C6	37.5(10)	40.9(11)	29.7(9)	0.1(8)	14.9(8)	4.9(8)
C4	37.8(11)	43.2(12)	41.9(11)	2.9(9)	19.1(9)	4.7(9)
C3	53.9(13)	43.8(12)	36.4(10)	4.4(9)	17.1(10)	11.1(10)
C10	31.2(10)	46.7(12)	44.0(11)	-6.8(9)	16.3(9)	-2.2(9)
C13	48.8(11)	38.4(12)	38.3(10)	0.0(9)	19.3(9)	-5.1(9)
C16	42.3(11)	38.5(12)	47.0(11)	1.3(9)	21.6(10)	-4.3(9)
C14	53.0(12)	47.7(13)	32.0(10)	1.3(9)	18.1(9)	4.1(10)
C2	37.7(11)	63.5(15)	43.6(12)	1.7(11)	4.1(9)	6.8(10)
C15	57.1(13)	51.0(13)	39.7(11)	9.2(10)	25.4(10)	-3.8(10)
C8	39.7(11)	68.9(16)	42.9(12)	1.7(11)	9.1(10)	12.5(10)
C1	34.4(11)	74.4(17)	59.7(14)	8.8(13)	14.6(11)	-1.7(11)
C9	58.9(15)	79.0(18)	34.9(11)	11.8(11)	11.6(11)	18.9(12)
C17	124(3)	63.8(18)	45.1(14)	-11.6(12)	27.6(16)	-3.5(16)

Table 4 Bond Lengths for **4ac.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	C6	1.7193(18)	C7	C6	1.372(3)
S1	C9	1.693(2)	C7	C10	1.489(3)
O1	C10	1.217(2)	C7	C8	1.403(3)
O2	C14	1.352(2)	C12	C13	1.376(3)
O2	C17	1.414(3)	C4	C3	1.372(3)
N1	C5	1.338(2)	C3	C2	1.365(3)
N1	C1	1.321(3)	C13	C14	1.386(3)
C5	C6	1.459(3)	C16	C15	1.365(3)
C5	C4	1.382(2)	C14	C15	1.378(3)
C11	C12	1.380(3)	C2	C1	1.372(3)
C11	C10	1.474(3)	C8	C9	1.344(3)
C11	C16	1.394(3)			

Table 5 Bond Angles for **4ac.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C9	S1	C6	92.38(10)	C3	C4	C5	119.55(18)
C14	O2	C17	119.28(17)	C2	C3	C4	118.95(19)
C1	N1	C5	117.61(17)	O1	C10	C11	121.17(18)
N1	C5	C6	114.81(16)	O1	C10	C7	118.04(18)
N1	C5	C4	121.49(17)	C11	C10	C7	120.66(17)
C4	C5	C6	123.69(17)	C12	C13	C14	119.13(19)

C12	C11	C10	122.65(17)	C15	C16	C11	120.24(19)
C12	C11	C16	118.89(17)	O2	C14	C13	124.0(2)
C16	C11	C10	118.42(18)	O2	C14	C15	115.85(18)
C6	C7	C10	127.98(17)	C15	C14	C13	120.17(18)
C6	C7	C8	112.39(18)	C3	C2	C1	117.9(2)
C8	C7	C10	119.59(18)	C16	C15	C14	120.38(18)
C13	C12	C11	121.16(17)	C9	C8	C7	113.5(2)
C5	C6	S1	117.90(13)	N1	C1	C2	124.3(2)
C7	C6	S1	110.15(14)	C8	C9	S1	111.57(16)
C7	C6	C5	131.92(16)				

Table 6 Torsion Angles for **4ac**.

A	**B**	**C**	**D**	**Angle/°**	**A**	**B**	**C**	**D**	**Angle/°**
O2	C14	C15	C16	178.83(19)	C4	C3	C2	C1	-1.5(3)
N1	C5	C6	S1	17.3(2)	C3	C2	C1	N1	2.5(4)
N1	C5	C6	C7	-165.2(2)	C10	C11	C12	C13	176.27(17)
N1	C5	C4	C3	4.3(3)	C10	C11	C16	C15	-177.05(18)
C5	N1	C1	C2	-0.1(3)	C10	C7	C6	S1	178.47(17)
C5	C4	C3	C2	-1.7(3)	C10	C7	C6	C5	0.8(4)
C11	C12	C13	C14	0.6(3)	C10	C7	C8	C9	-178.5(2)
C11	C16	C15	C14	0.7(3)	C13	C14	C15	C16	-1.7(3)
C7	C8	C9	S1	0.0(3)	C16	C11	C12	C13	-1.6(3)
C12	C11	C10	O1	-160.9(2)	C16	C11	C10	O1	17.0(3)
C12	C11	C10	C7	15.0(3)	C16	C11	C10	C7	-167.12(17)
C12	C11	C16	C15	0.9(3)	C8	C7	C6	S1	0.6(2)
C12	C13	C14	O2	-179.56(19)	C8	C7	C6	C5	-177.0(2)
C12	C13	C14	C15	1.0(3)	C8	C7	C10	O1	53.2(3)
C6	S1	C9	C8	0.3(2)	C8	C7	C10	C11	-122.8(2)
C6	C5	C4	C3	-177.35(18)	C1	N1	C5	C6	178.16(19)
C6	C7	C10	O1	-124.5(2)	C1	N1	C5	C4	-3.3(3)
C6	C7	C10	C11	59.4(3)	C9	S1	C6	C5	177.50(16)
C6	C7	C8	C9	-0.4(3)	C9	S1	C6	C7	-0.51(17)
C4	C5	C6	S1	-161.23(15)	C17	O2	C14	C13	11.5(3)
C4	C5	C6	C7	16.3(3)	C17	O2	C14	C15	-169.1(2)

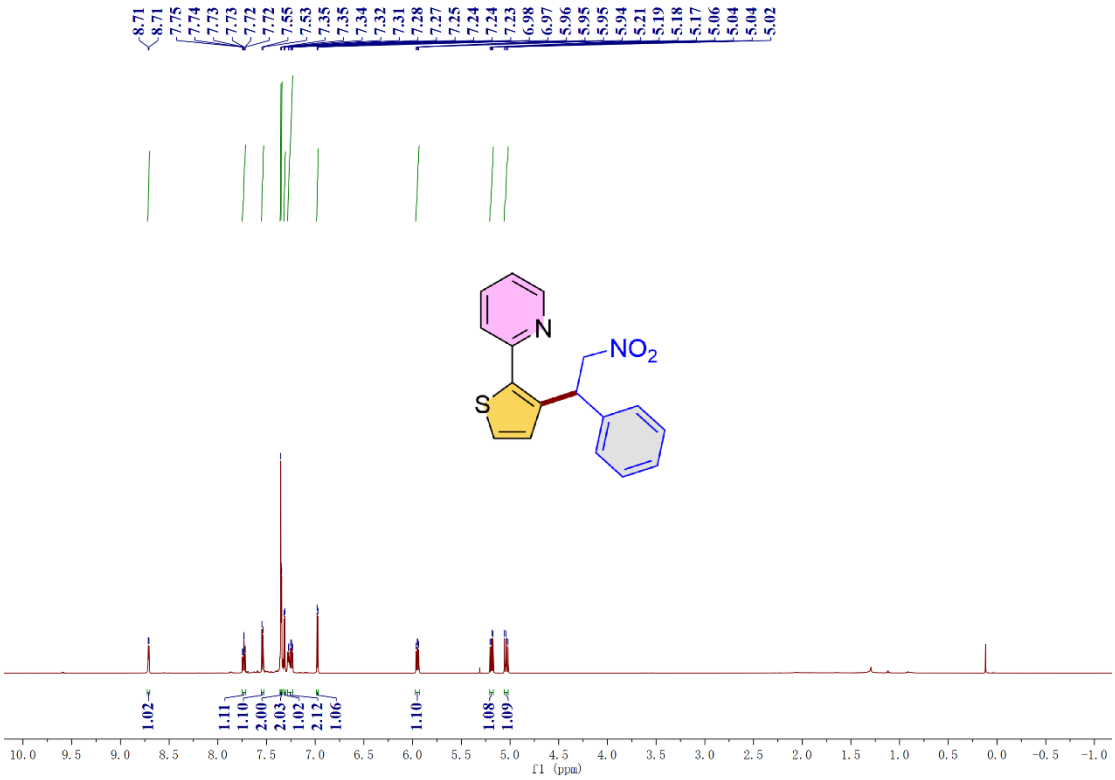
Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **4ac**.

Atom	***x***	***y***	***z***	**U(eq)**
H12	2861.35	4974.52	6019.67	44
H4	3897.23	2637.31	6236.92	48
H3	6189.3	2271.13	7811.82	53
H13	3509.52	5651.3	8002.86	49
H16	925.22	2871.06	7162.77	49
H2	8388.87	2836.46	7642.88	62
H15	1609.65	3527.25	9148.57	56

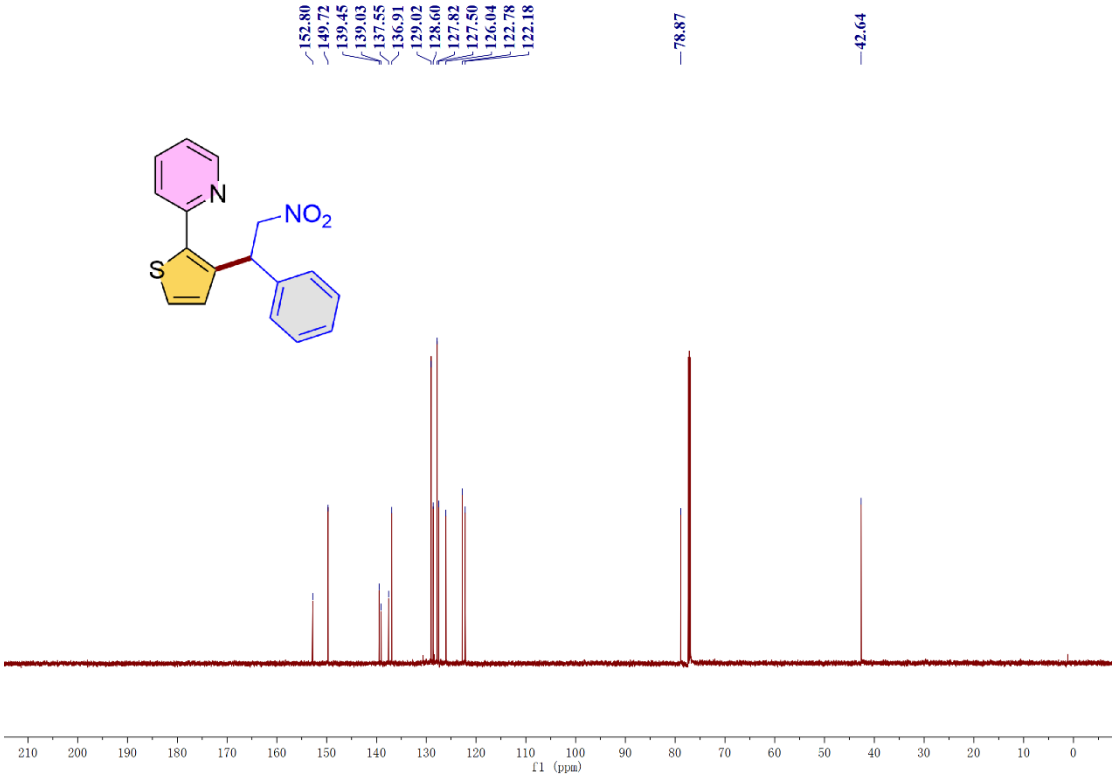
H8	-132.06	4122.49	2721.44	63
H1	8214.96	3689.04	5882.34	68
H9	1106.99	4544.79	1308.95	71
H17A	2664.39	6337.98	9751.33	118
H17B	4312.03	6002	9988.25	118
H17C	3728.52	6034.58	11123.63	118

5. NMR charts

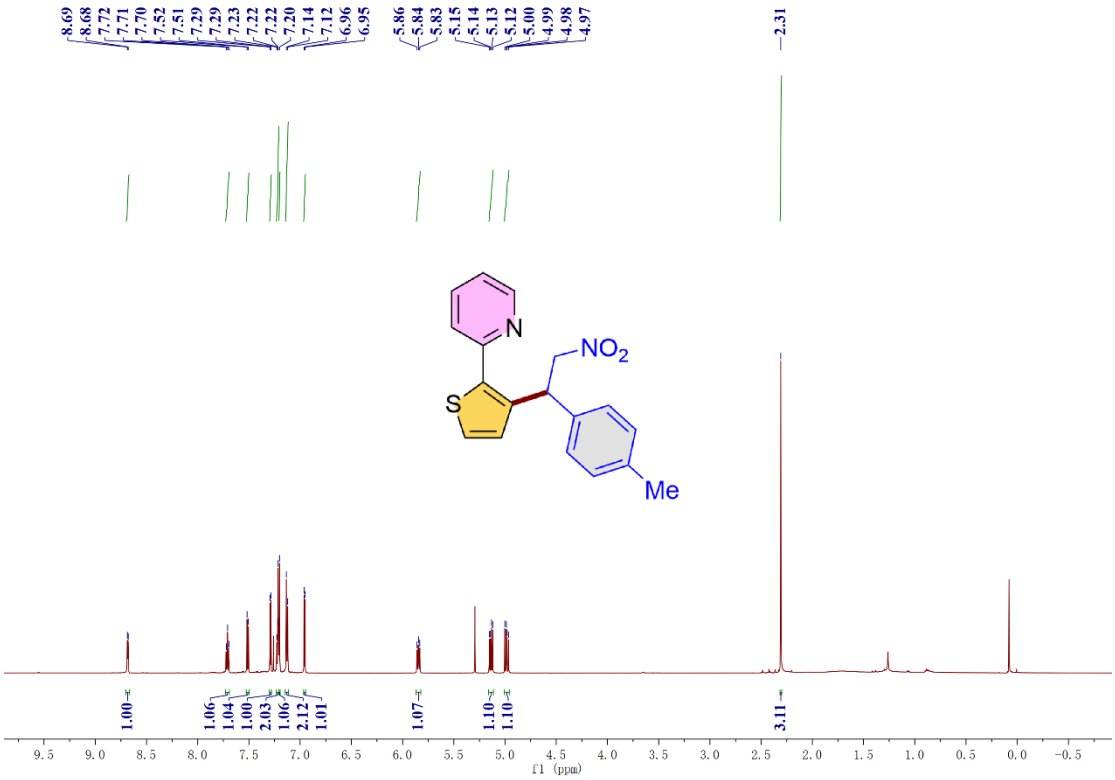
3aa | ^{1}H NMR ($CDCl_3$, 600 MHz)



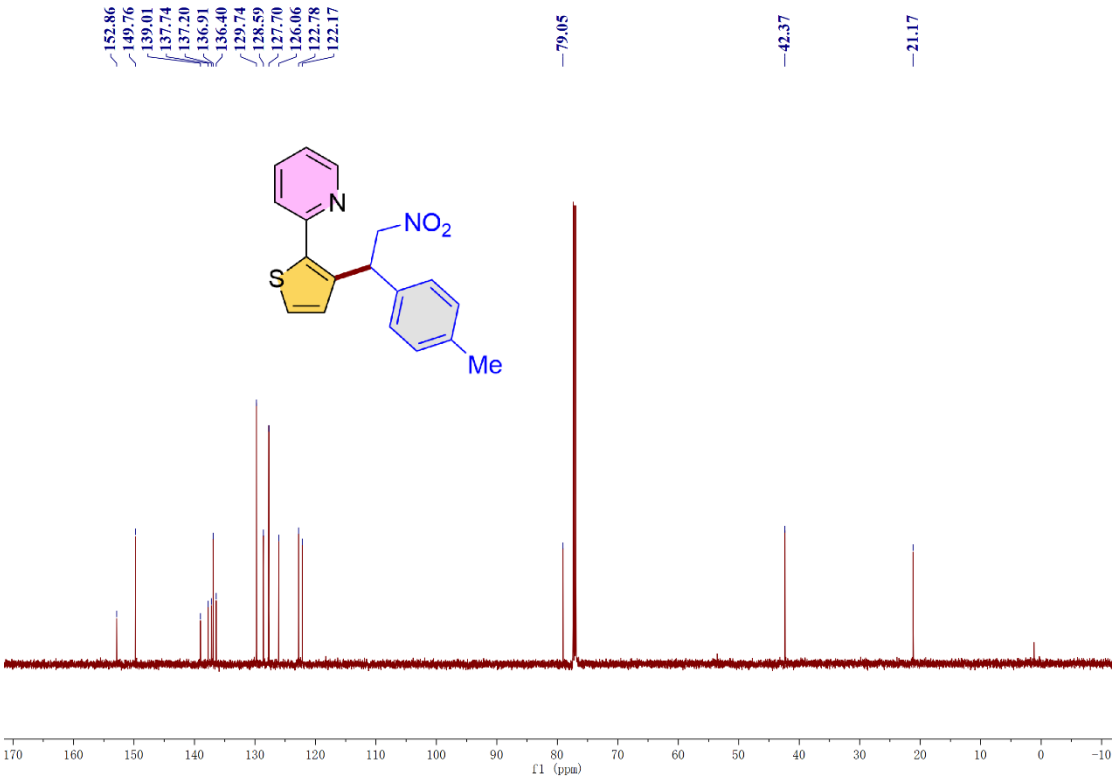
3aa | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



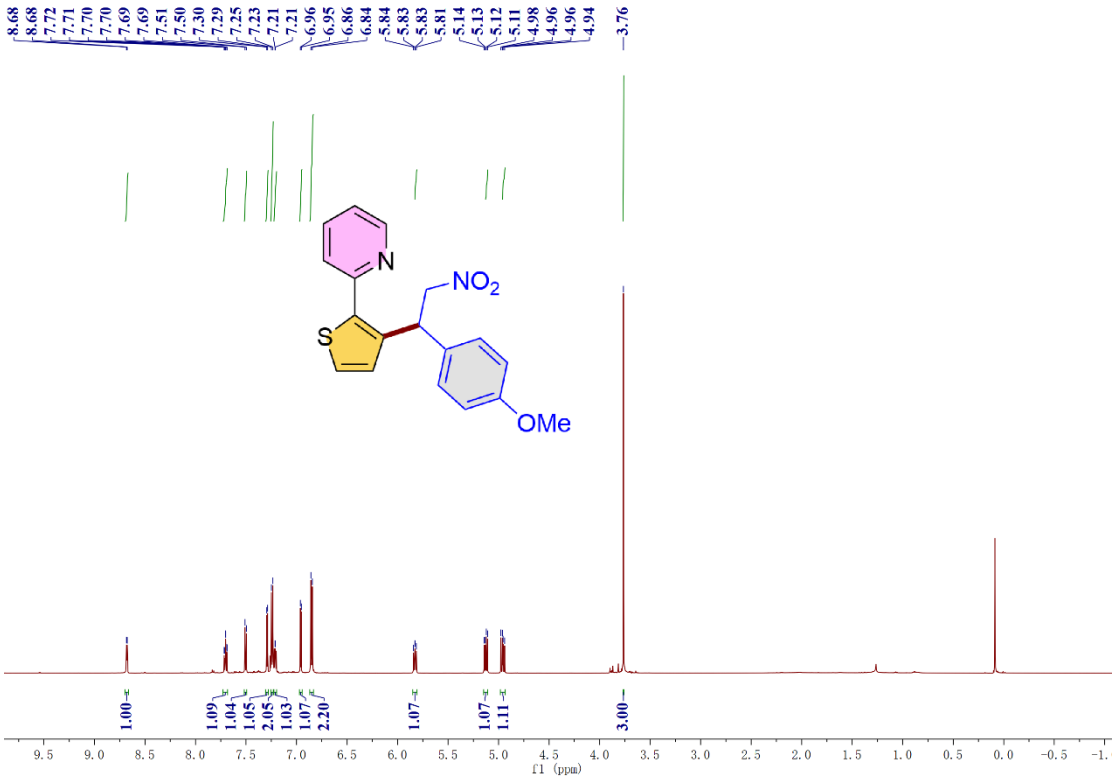
3ab | ^{1}H NMR ($CDCl_3$, 600 MHz)



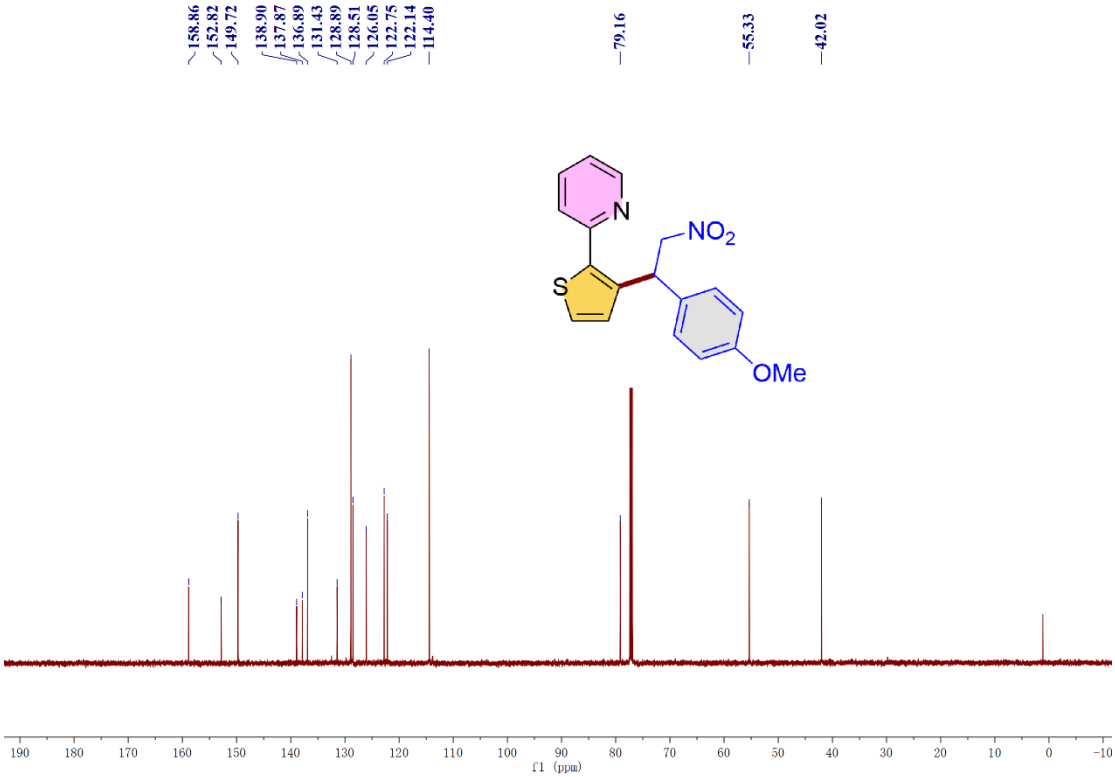
3ab | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



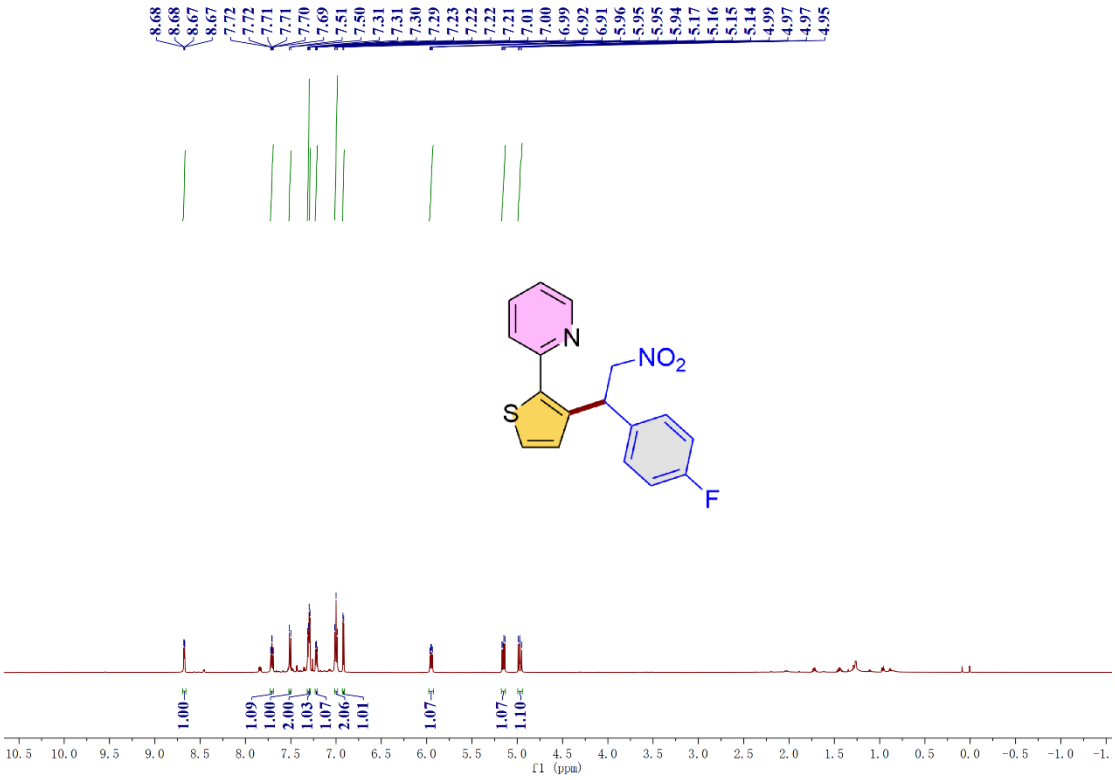
3ac | ^{1}H NMR ($CDCl_3$, 600 MHz)



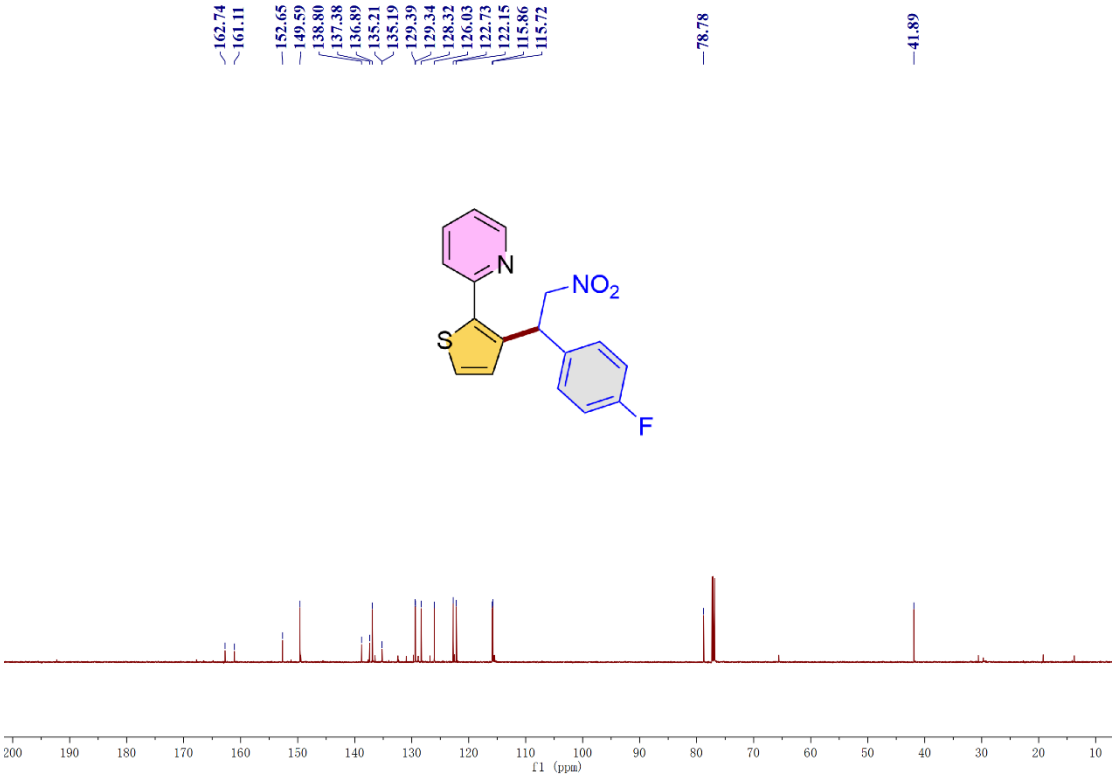
3ac | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



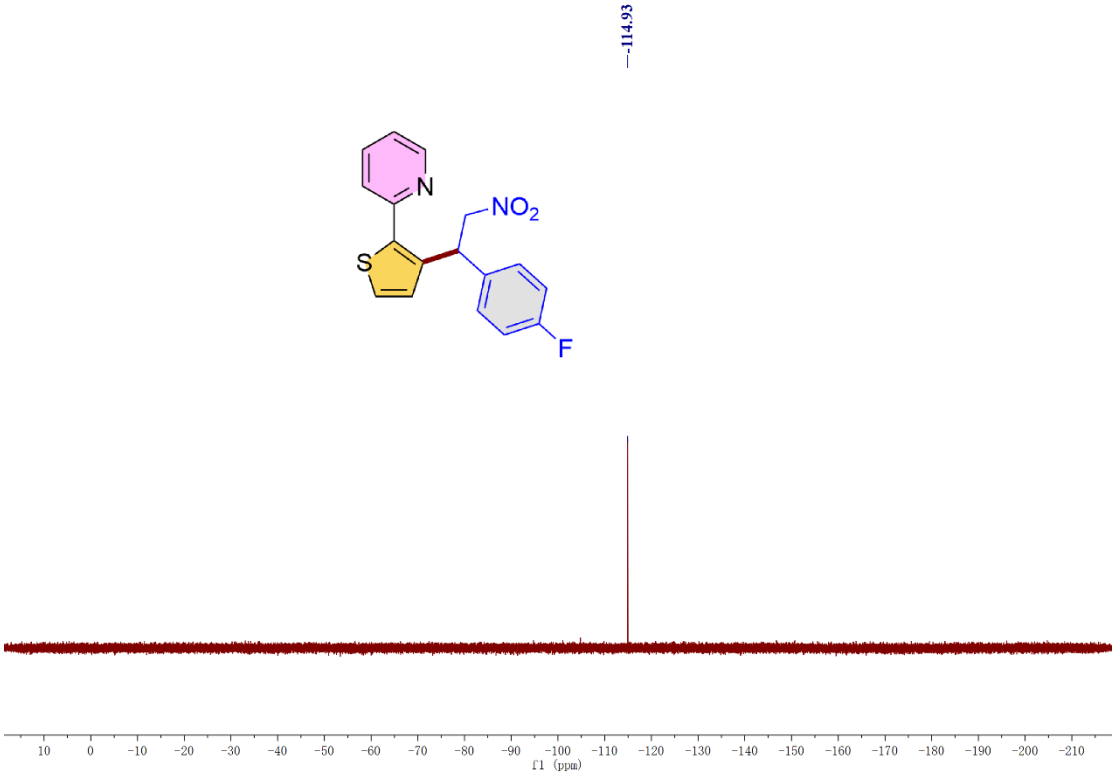
3ad | ^{1}H NMR ($CDCl_3$, 600 MHz)



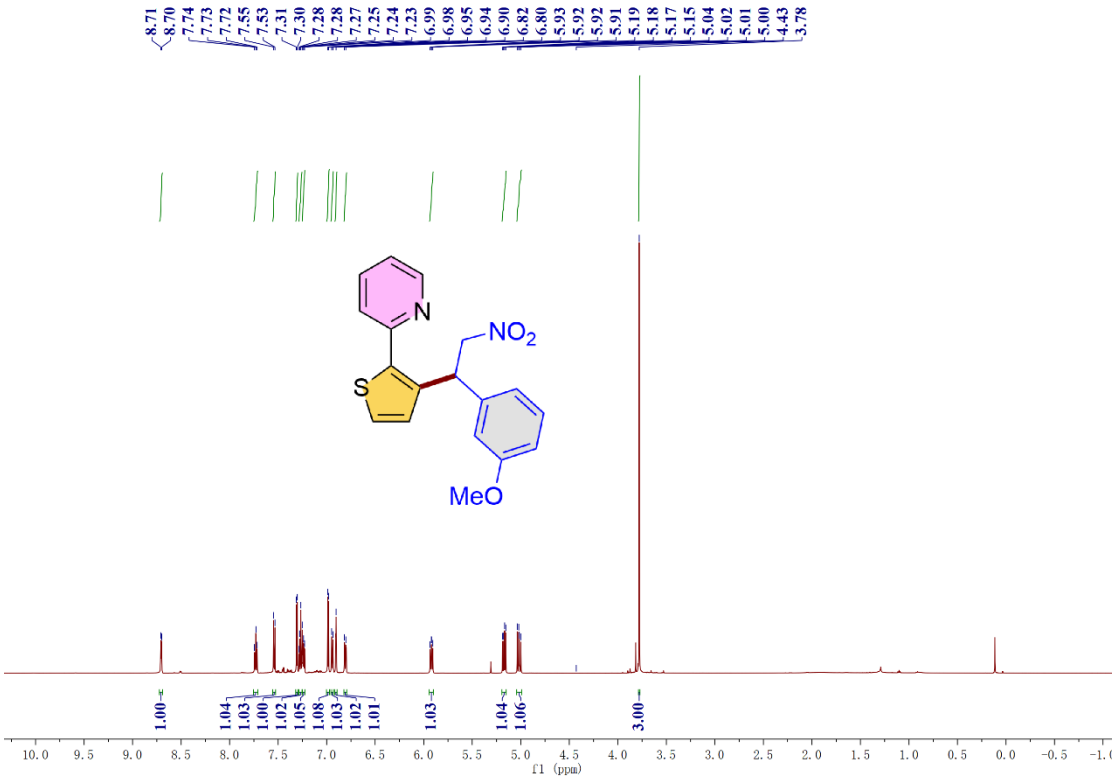
3ad | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



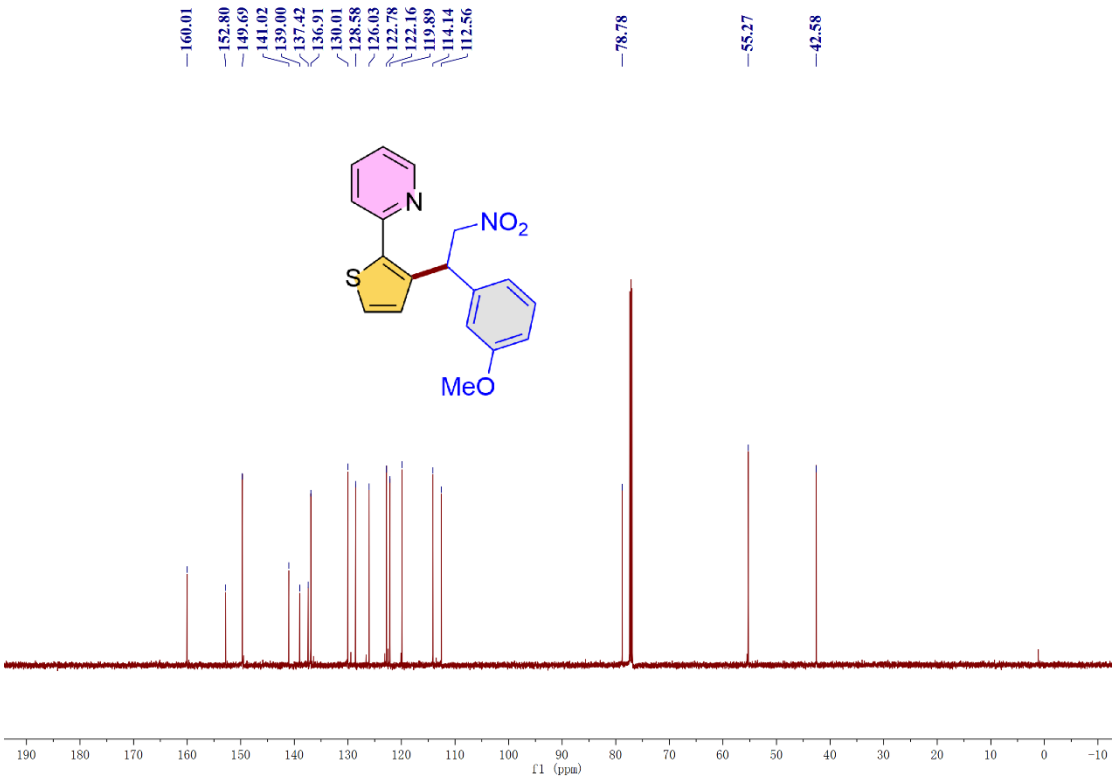
3ad | $^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 565 MHz)



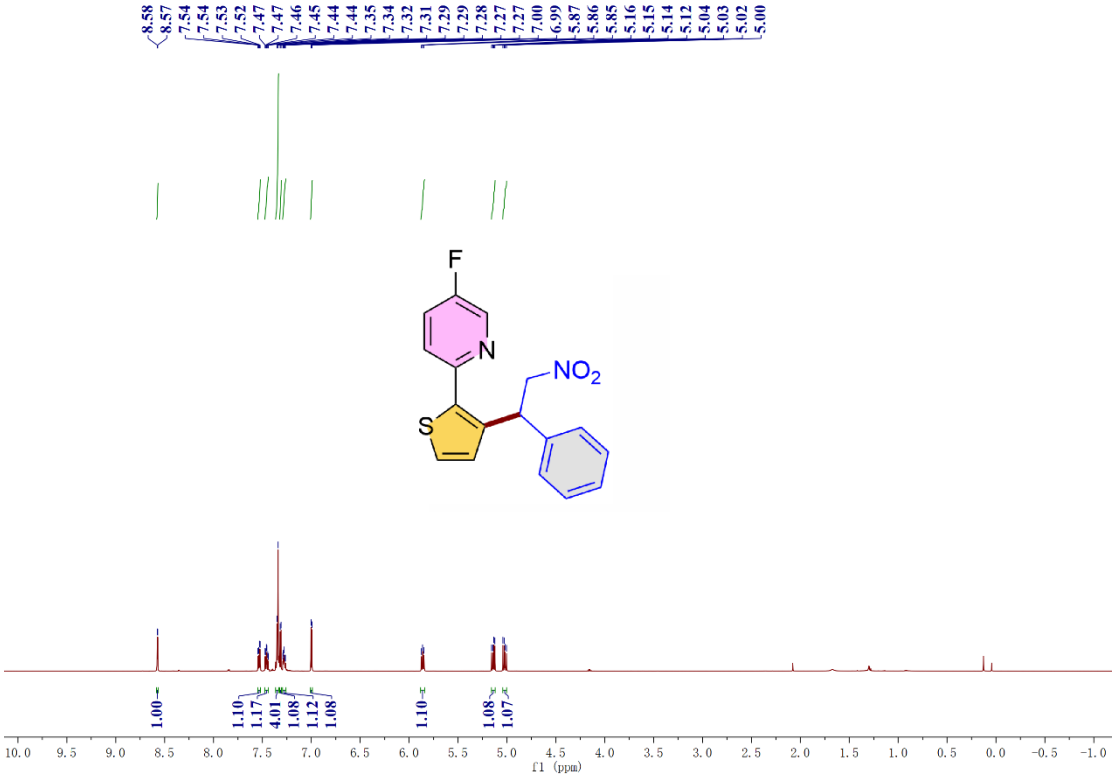
3ag | ^{1}H NMR ($CDCl_3$, 600 MHz)



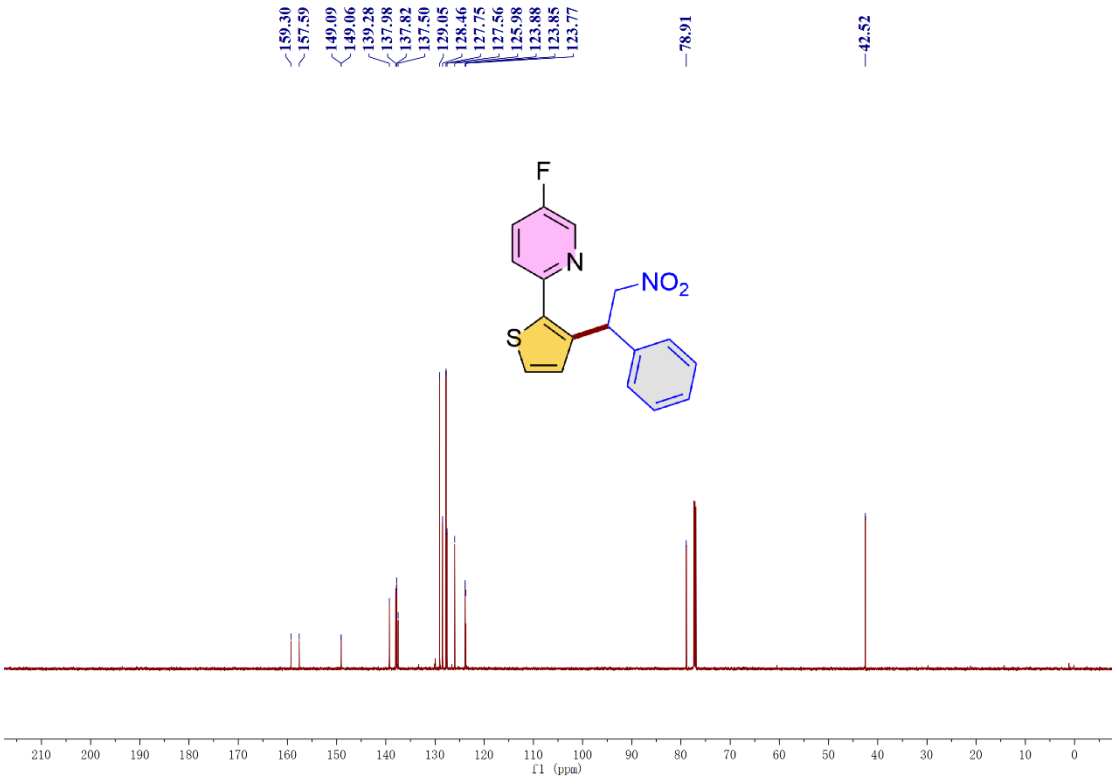
3ag | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



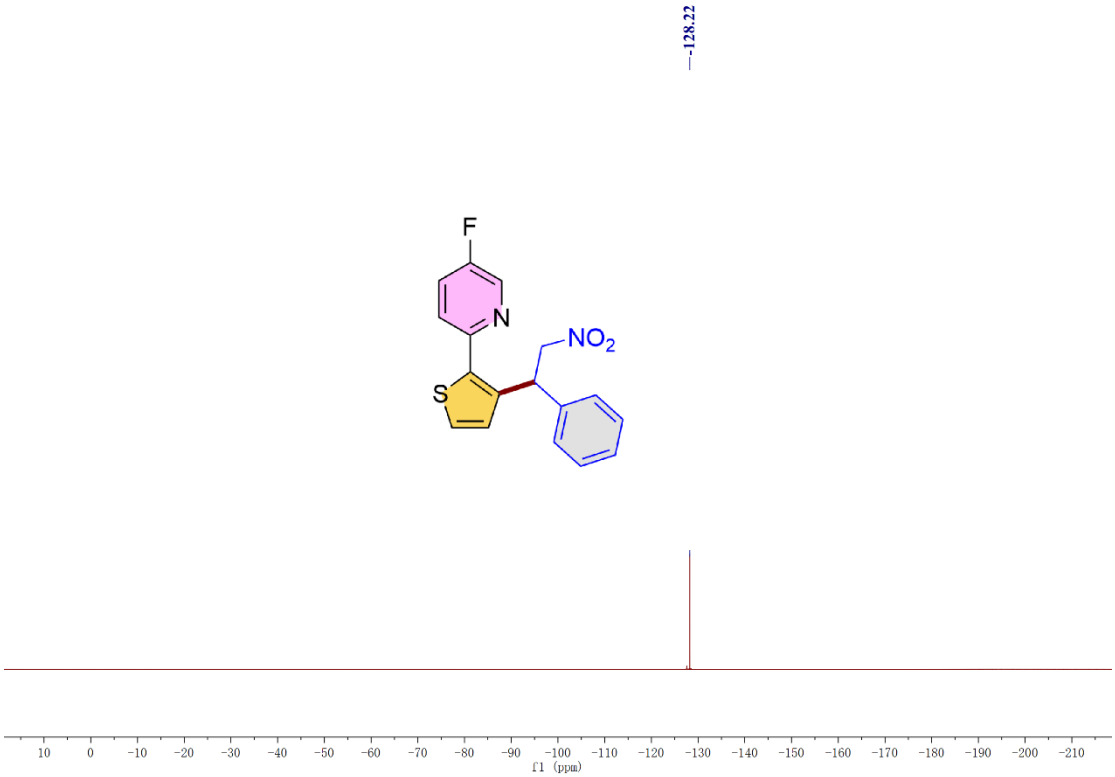
3da | ^{1}H NMR ($CDCl_3$, 600 MHz)



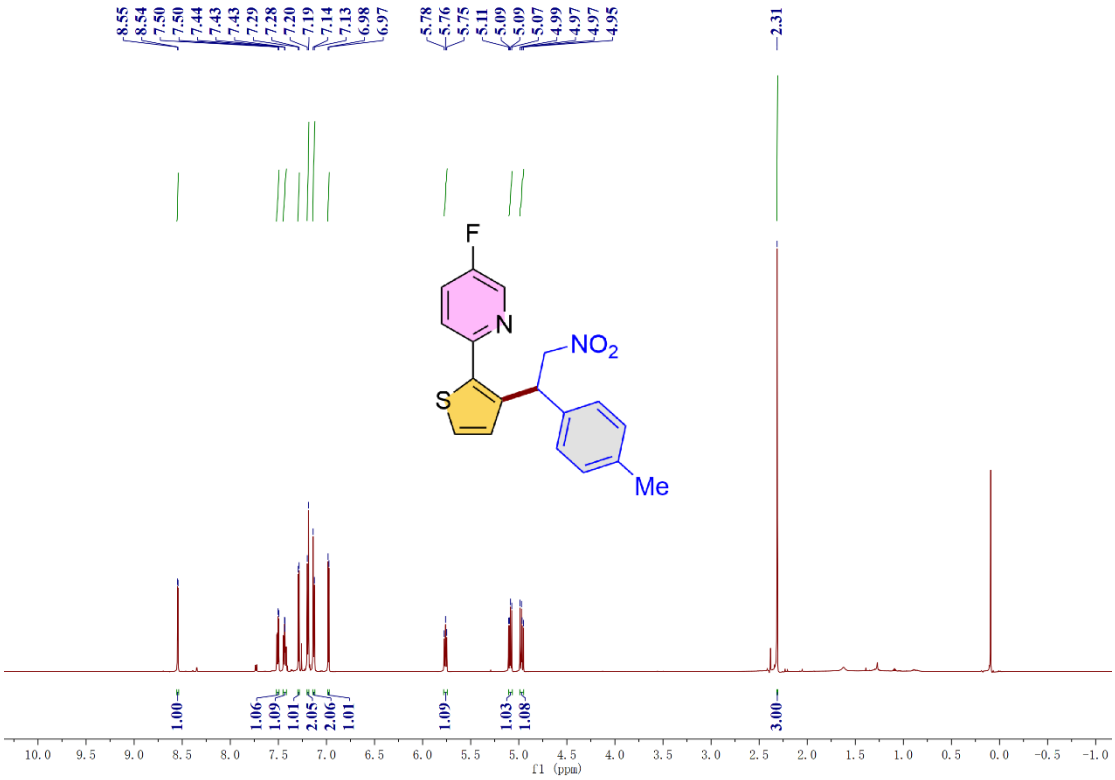
3da | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



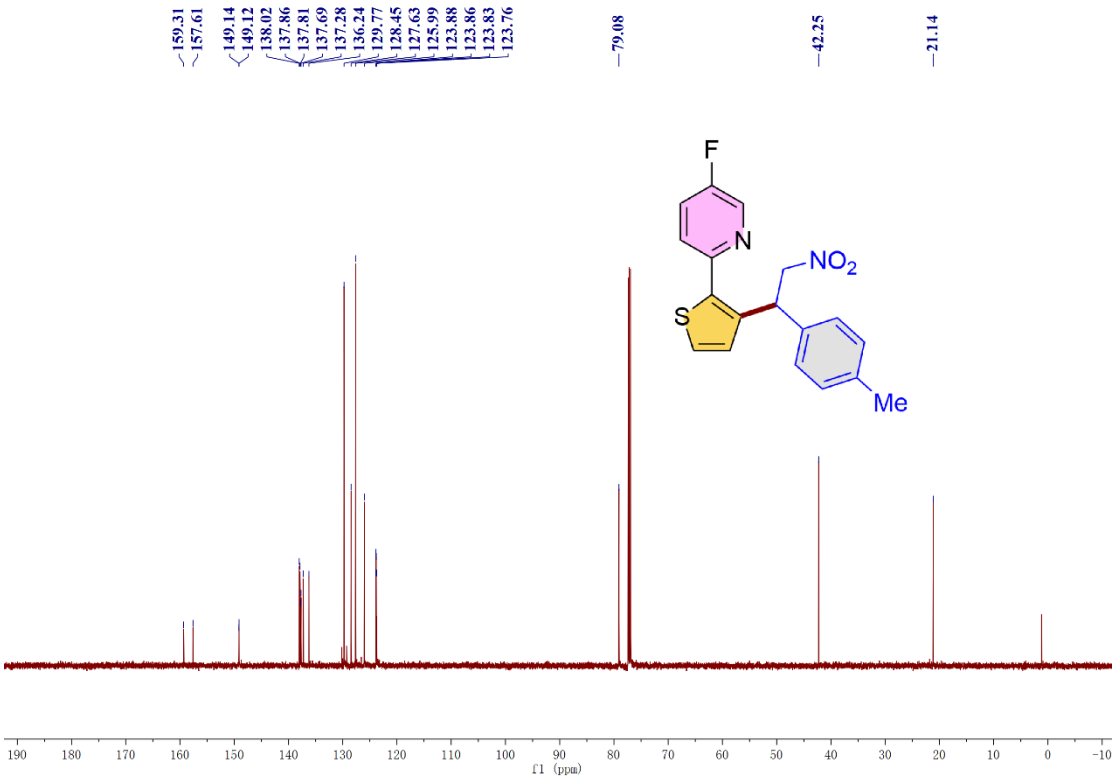
3da | $^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 565 MHz)



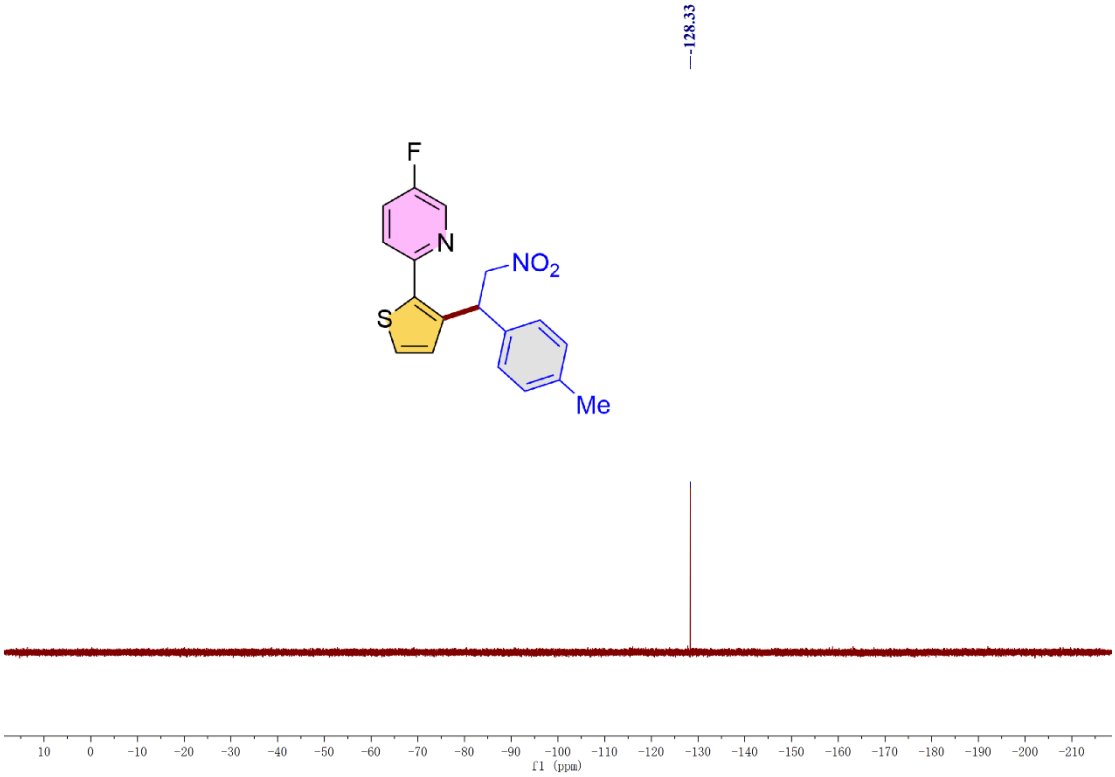
3db | ^{1}H NMR ($CDCl_3$, 600 MHz)



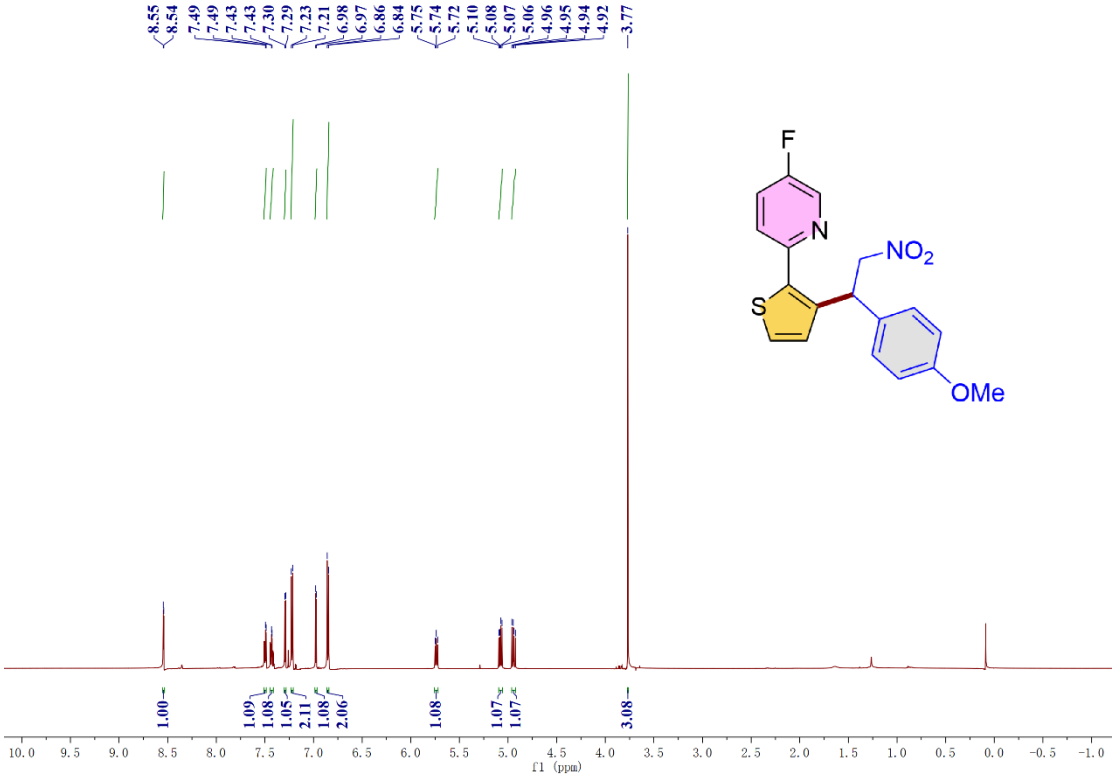
3db | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



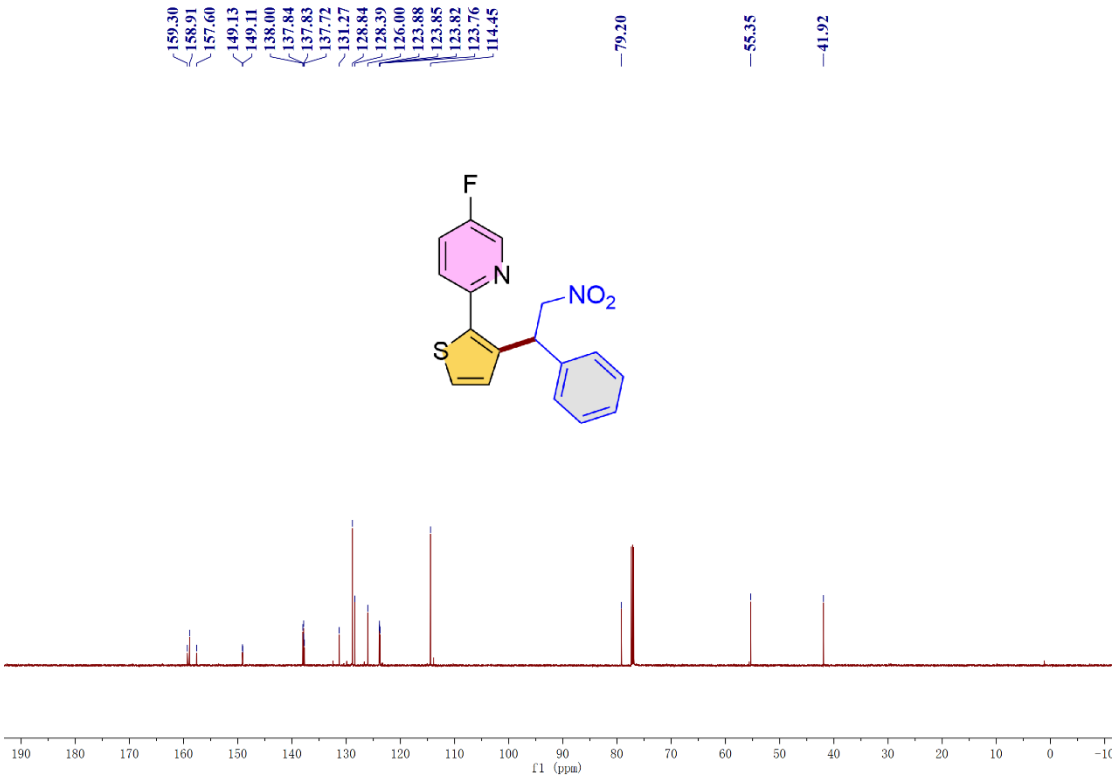
3db | $^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 565 MHz)



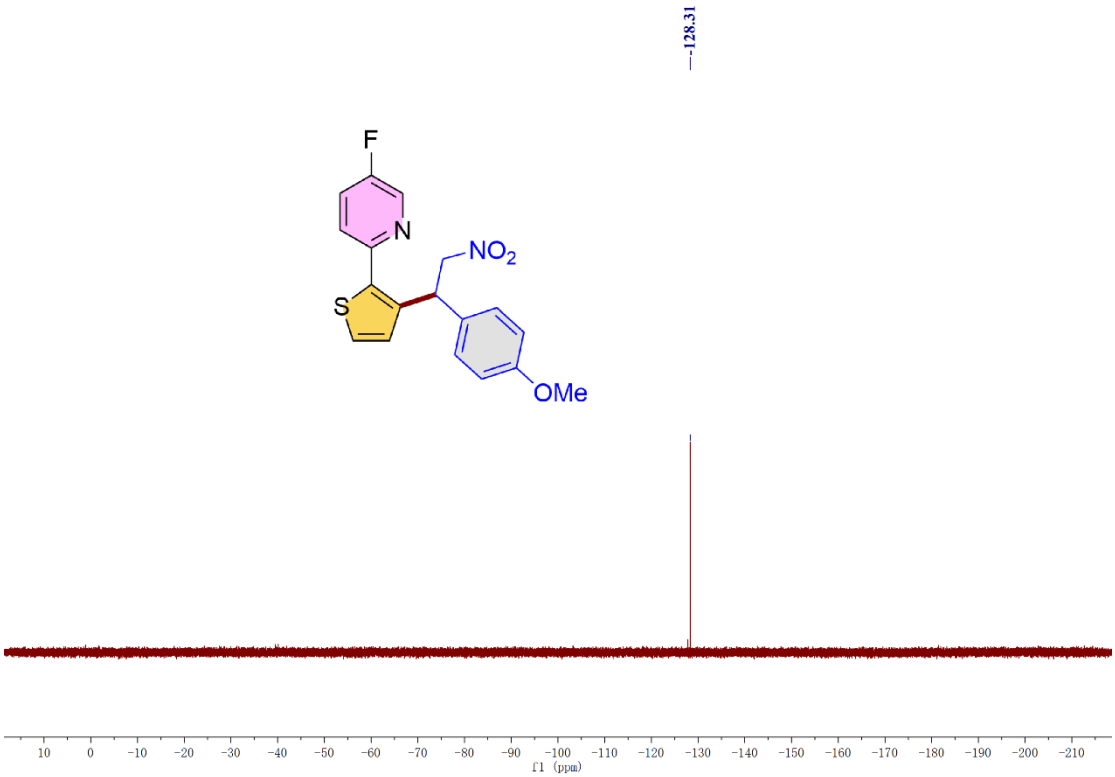
3dc | ^{1}H NMR ($CDCl_3$, 600 MHz)



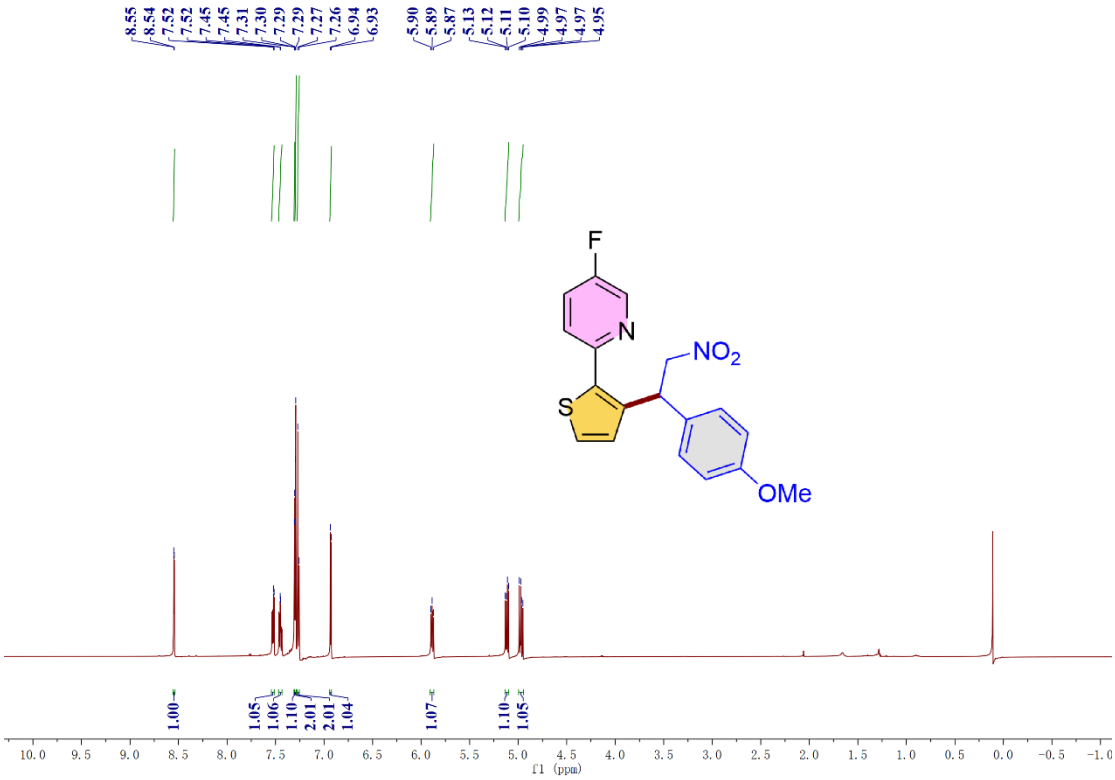
3dc | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



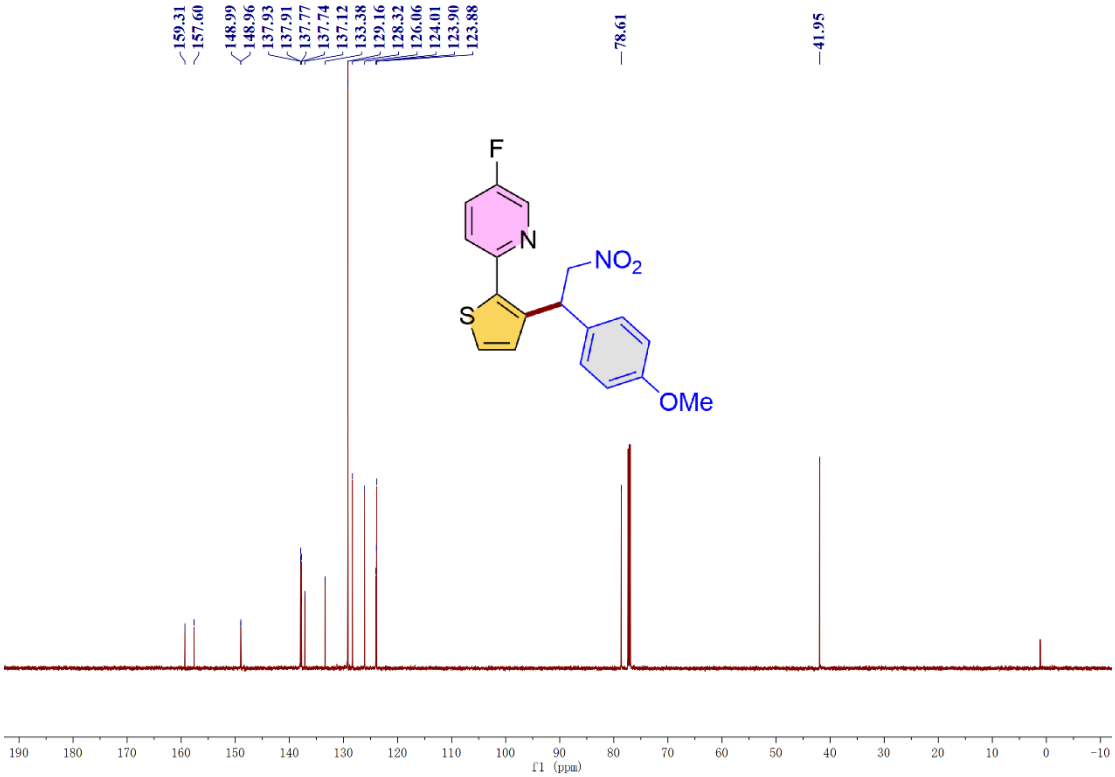
3dc | $^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 565 MHz)



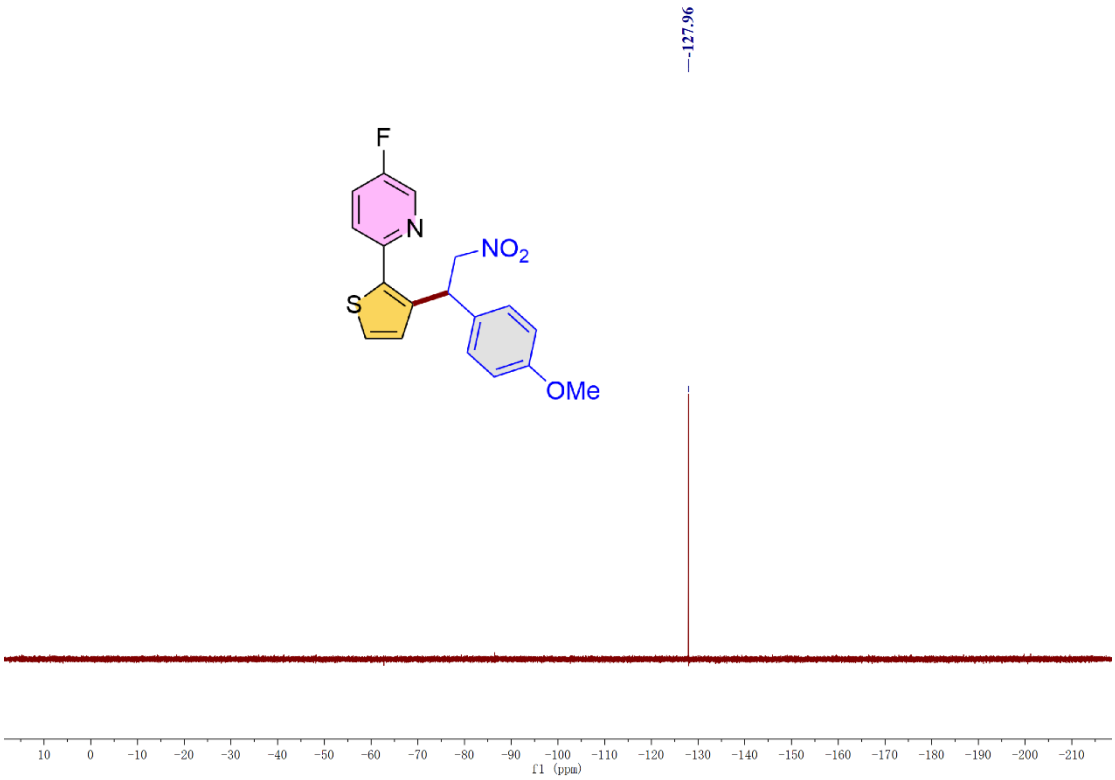
3de | ^{1}H NMR ($CDCl_3$, 600 MHz)



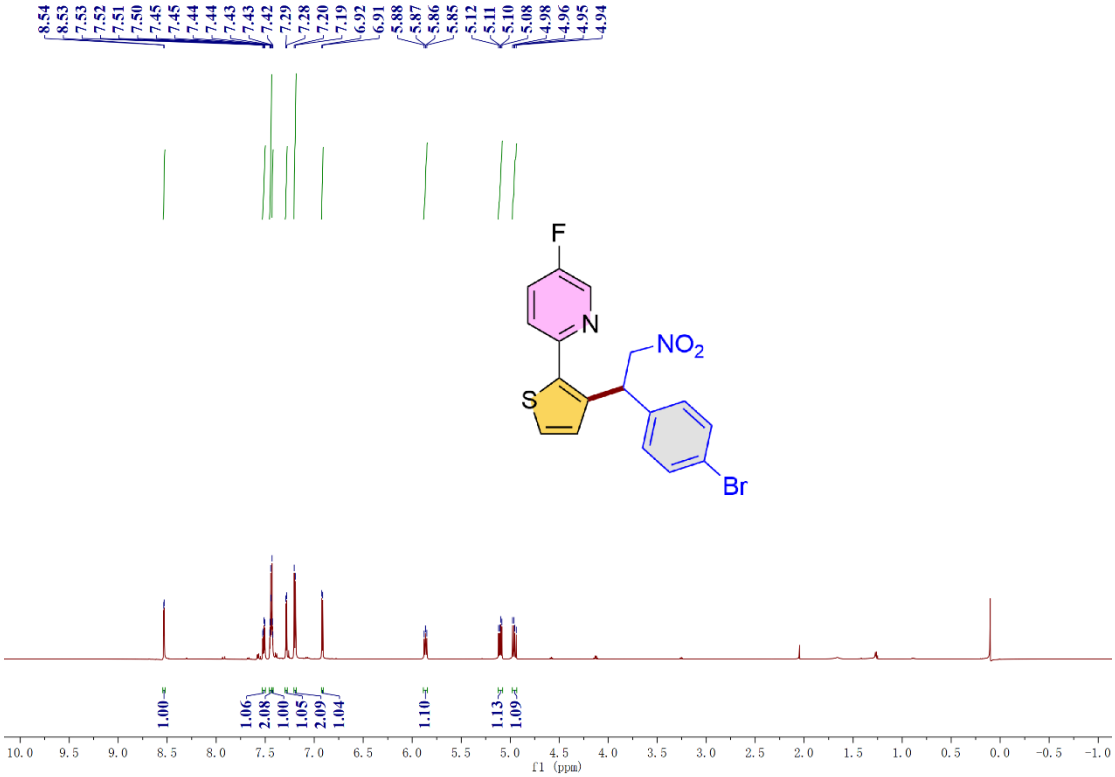
3de | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



3de | $^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 565 MHz)



3df | ^{1}H NMR ($CDCl_3$, 600 MHz)



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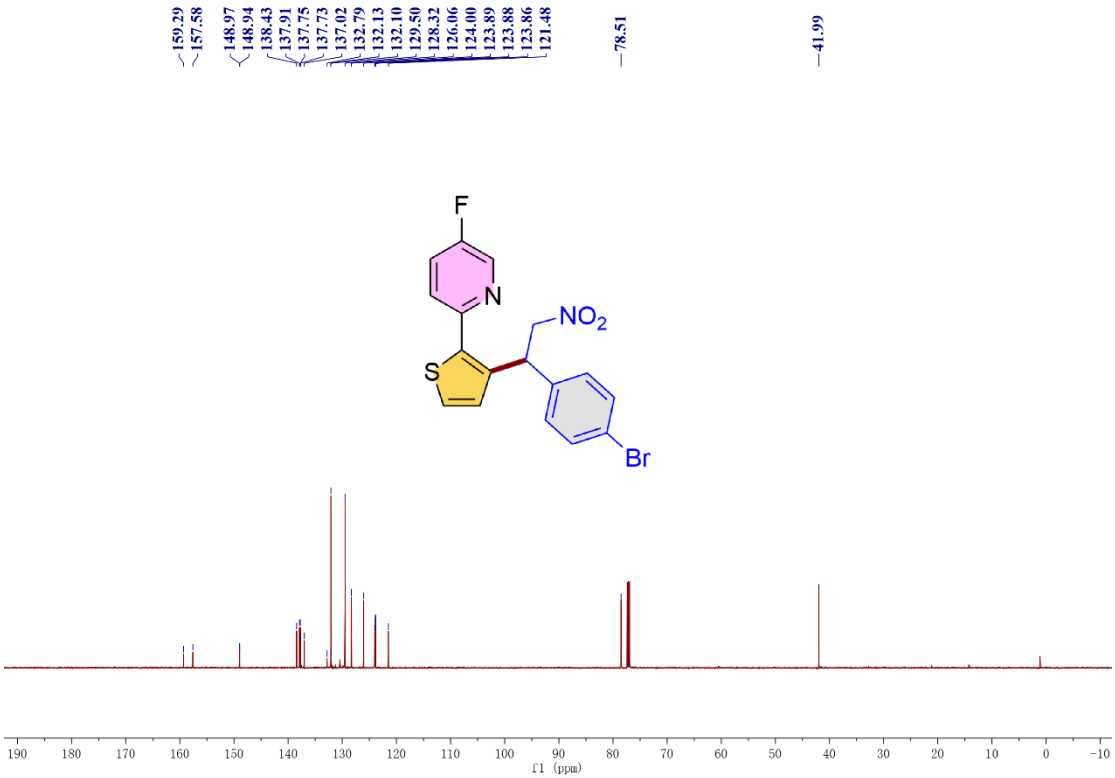
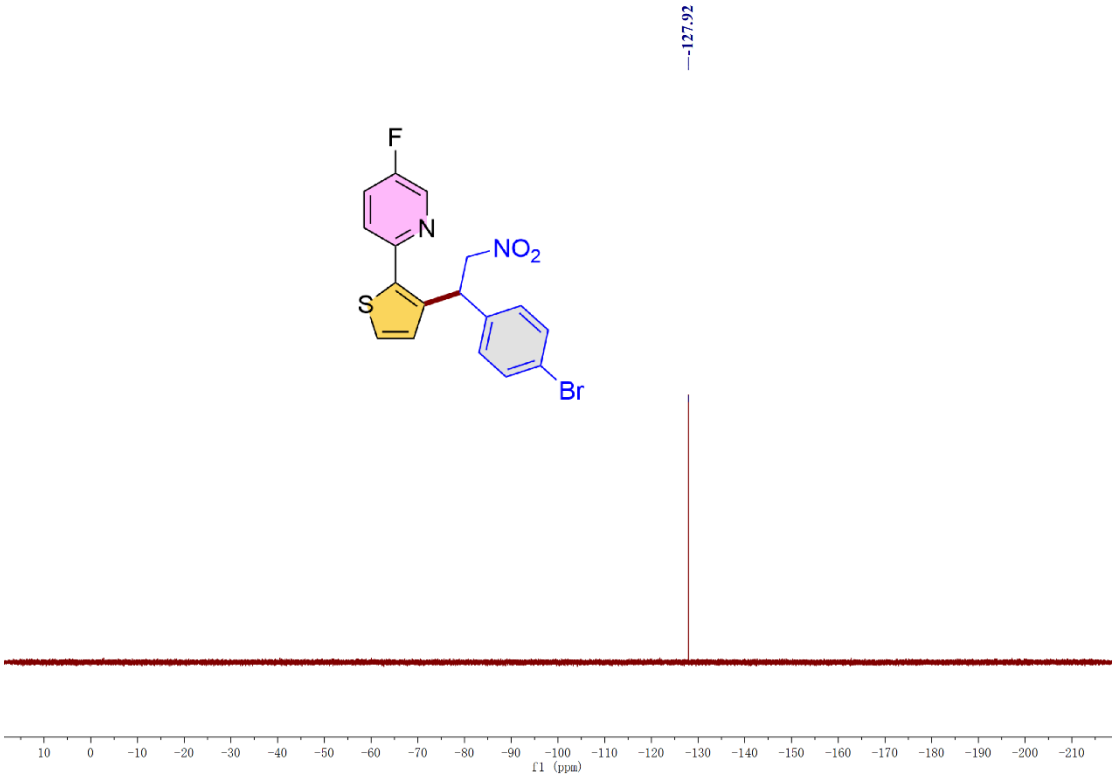
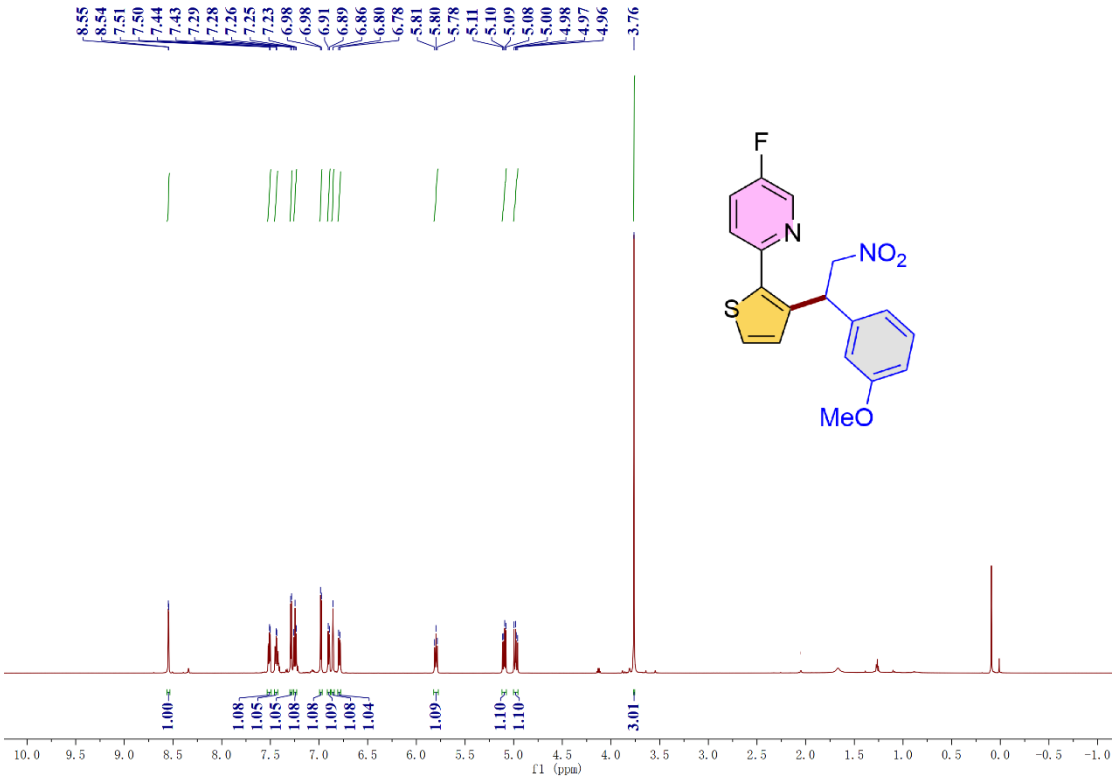


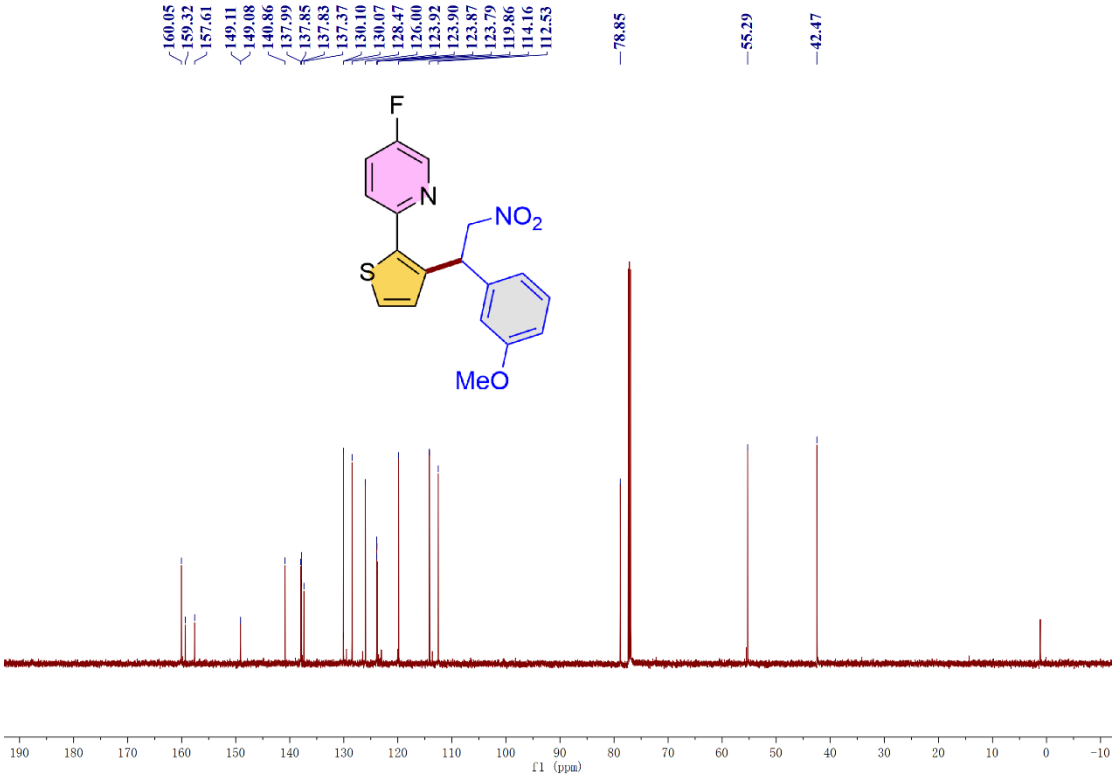
3df | $^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 565 MHz)



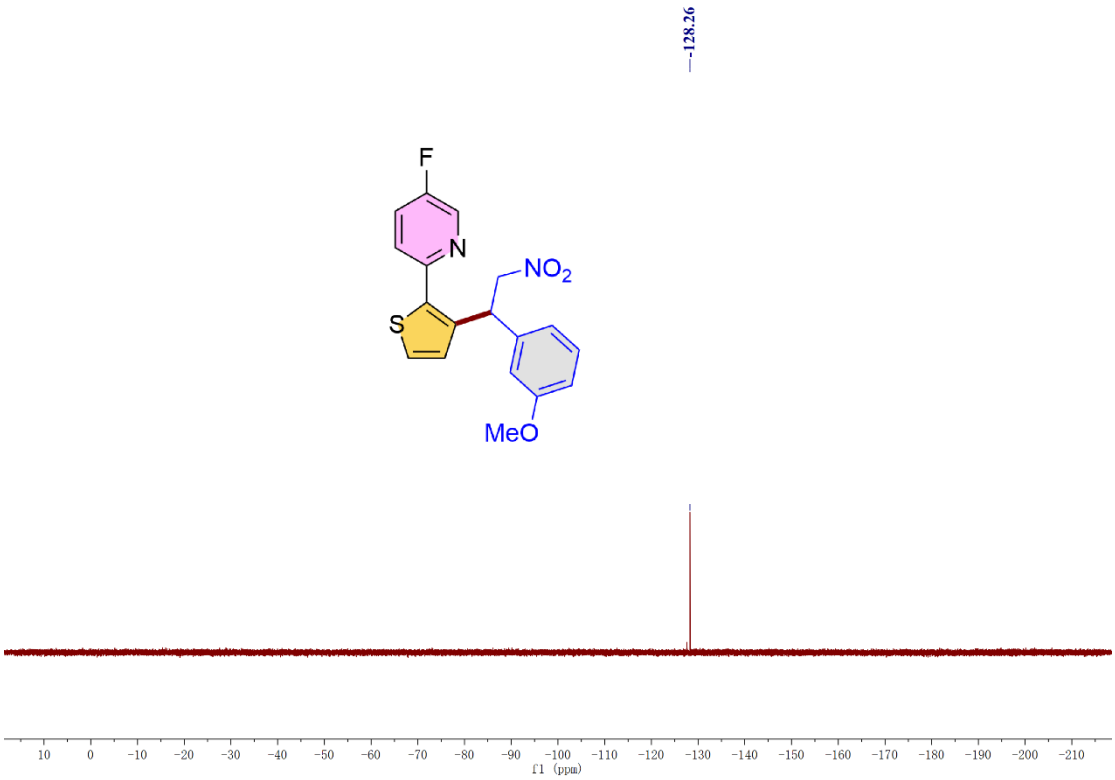
3dg | ^{1}H NMR ($CDCl_3$, 600 MHz)



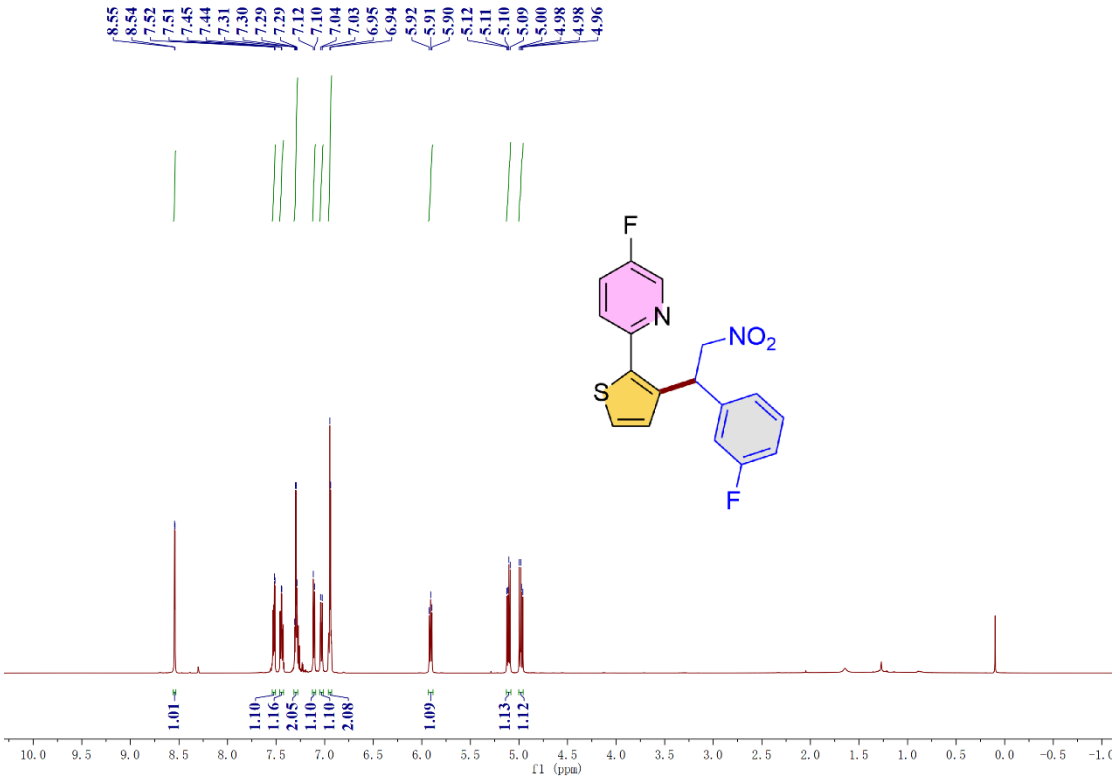
3dg | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



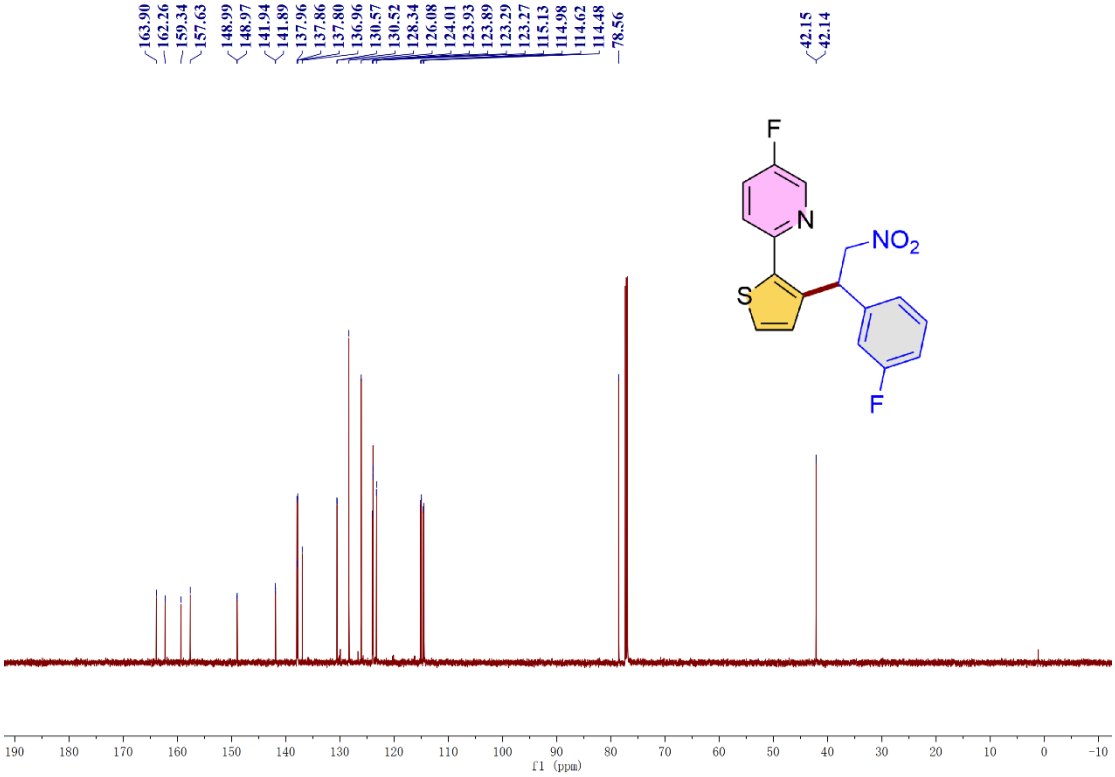
3dg | $^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 565 MHz)



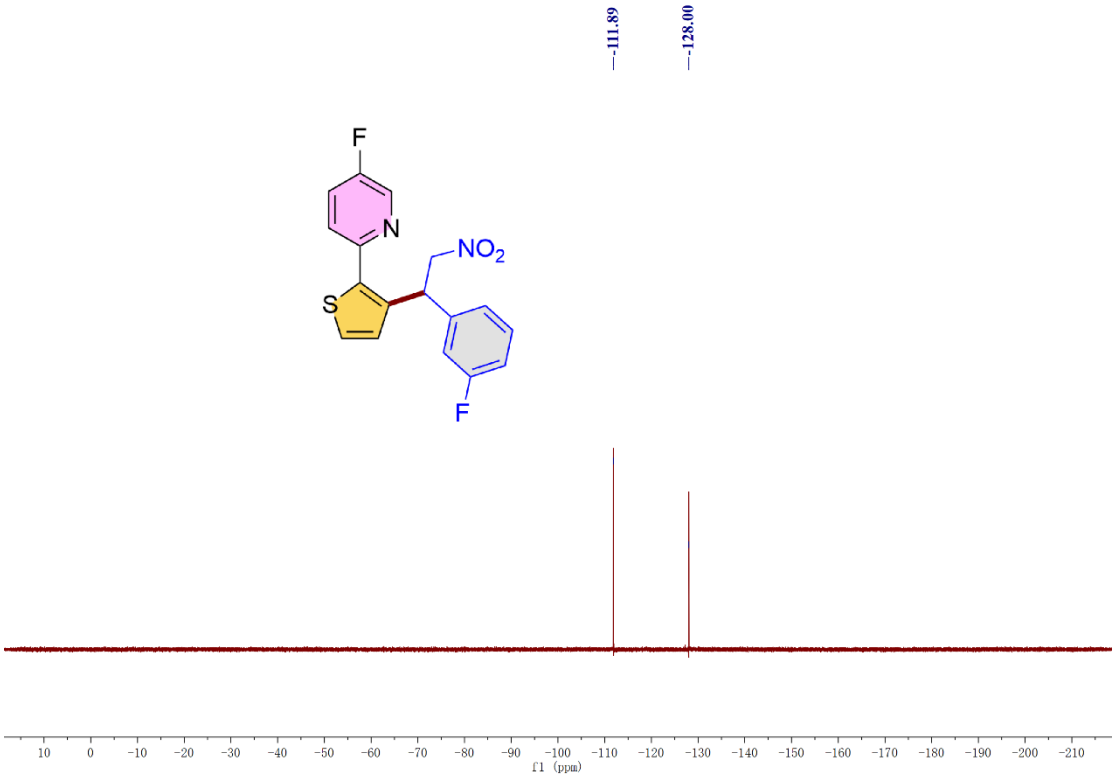
3dh | ^{1}H NMR ($CDCl_3$, 600 MHz)



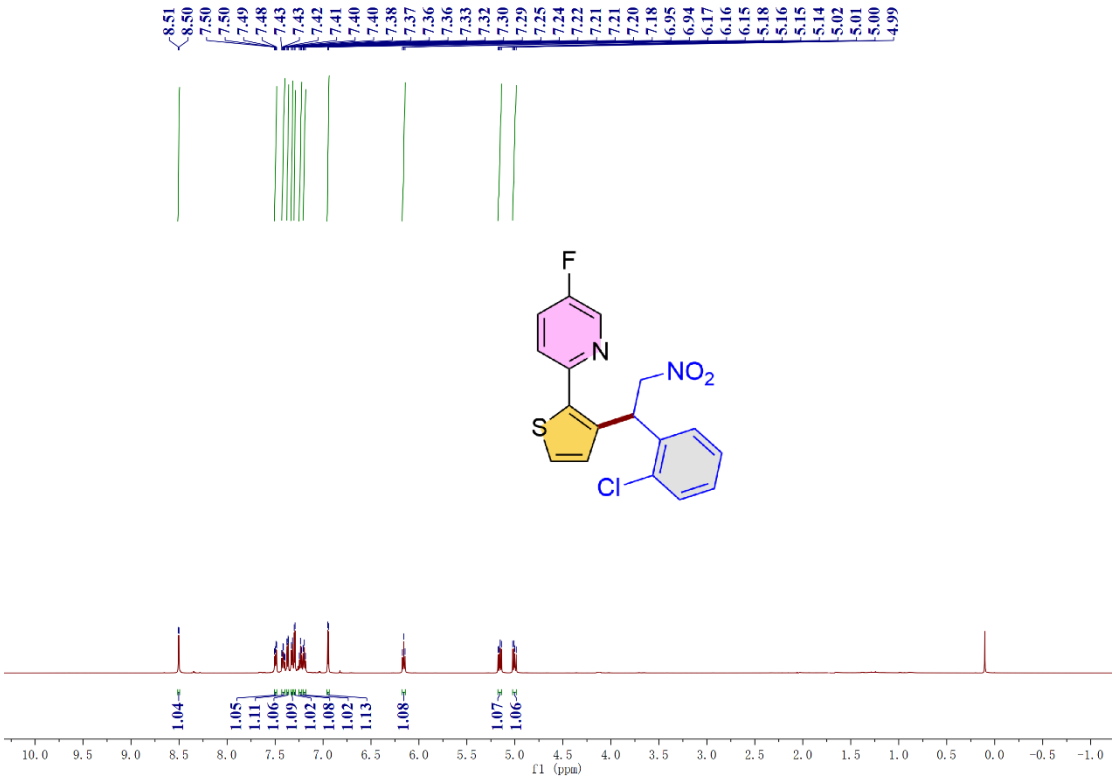
3dh | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



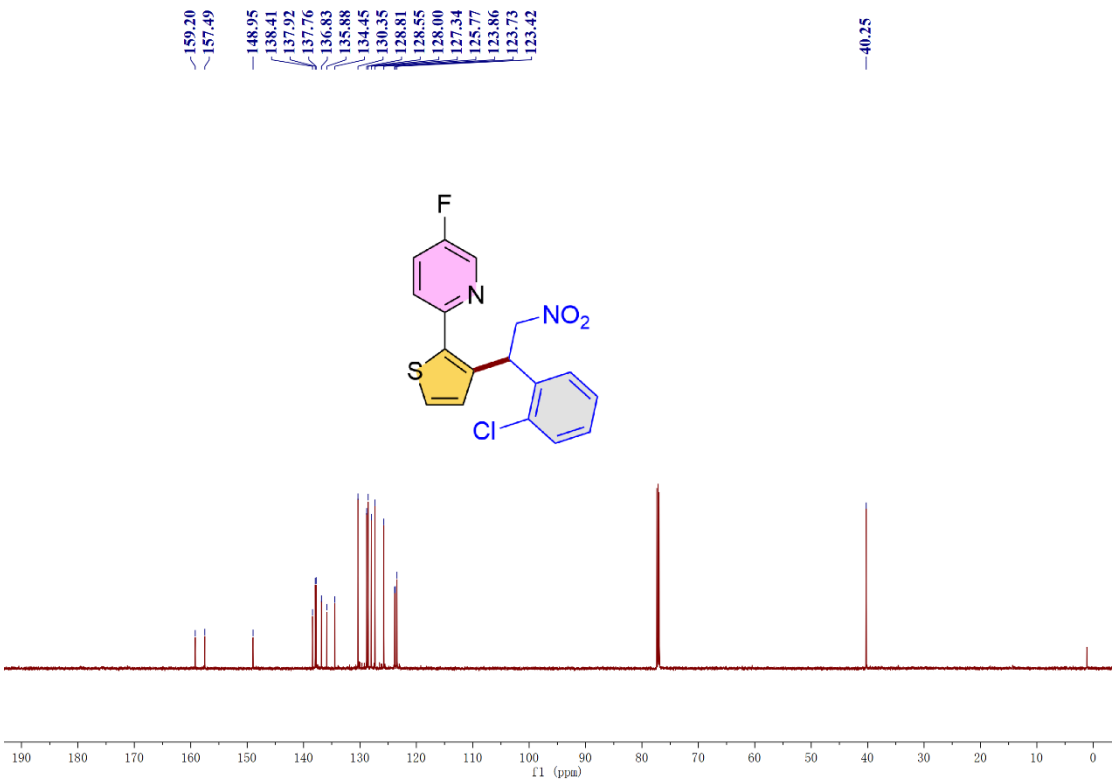
3dh | $^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 565 MHz)



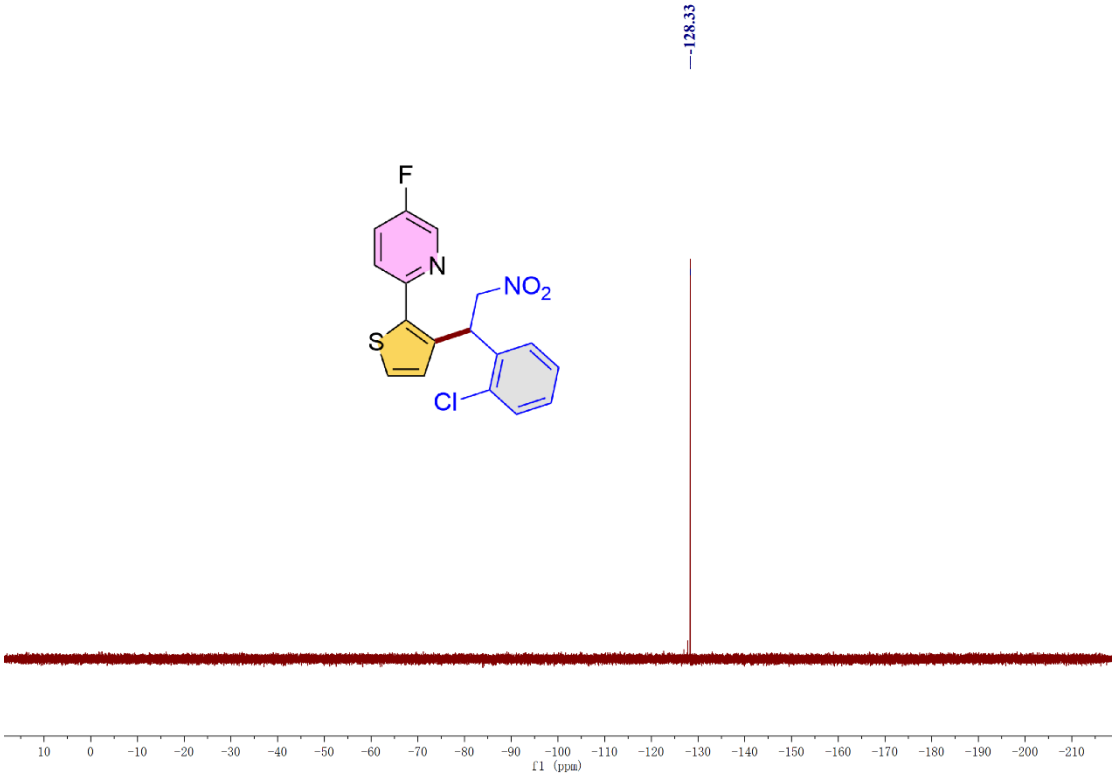
3di | ^{1}H NMR ($CDCl_3$, 600 MHz)



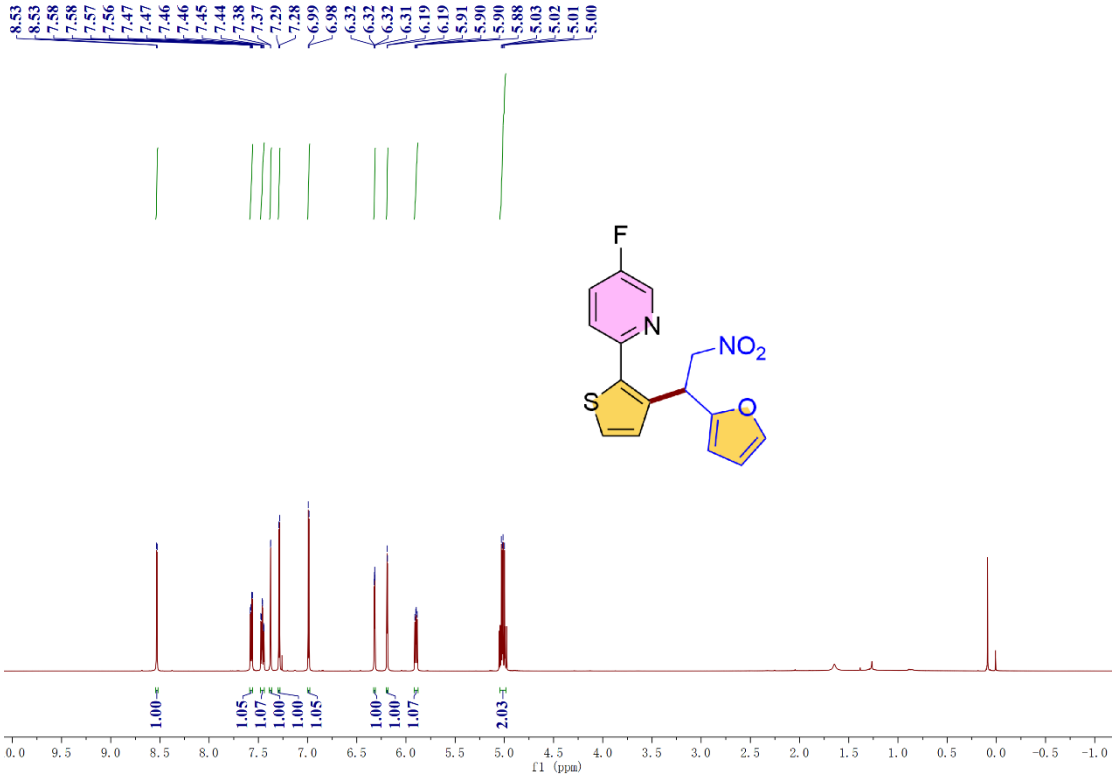
3di | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



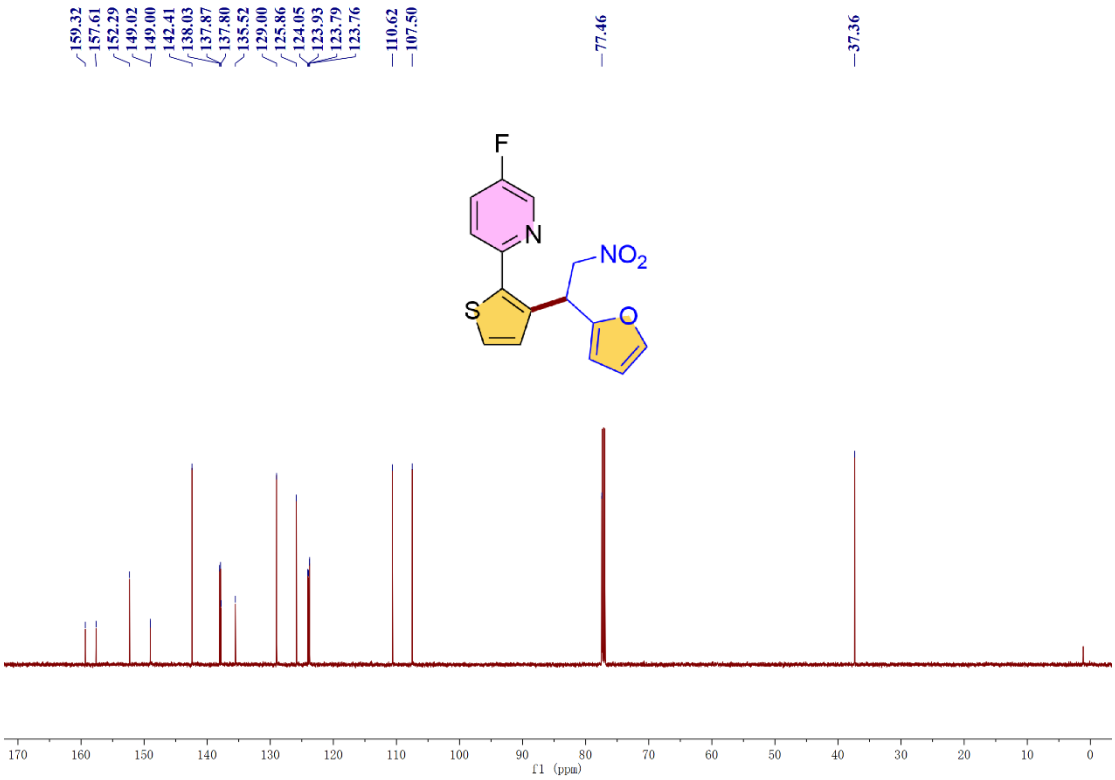
3di | $^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 565 MHz)



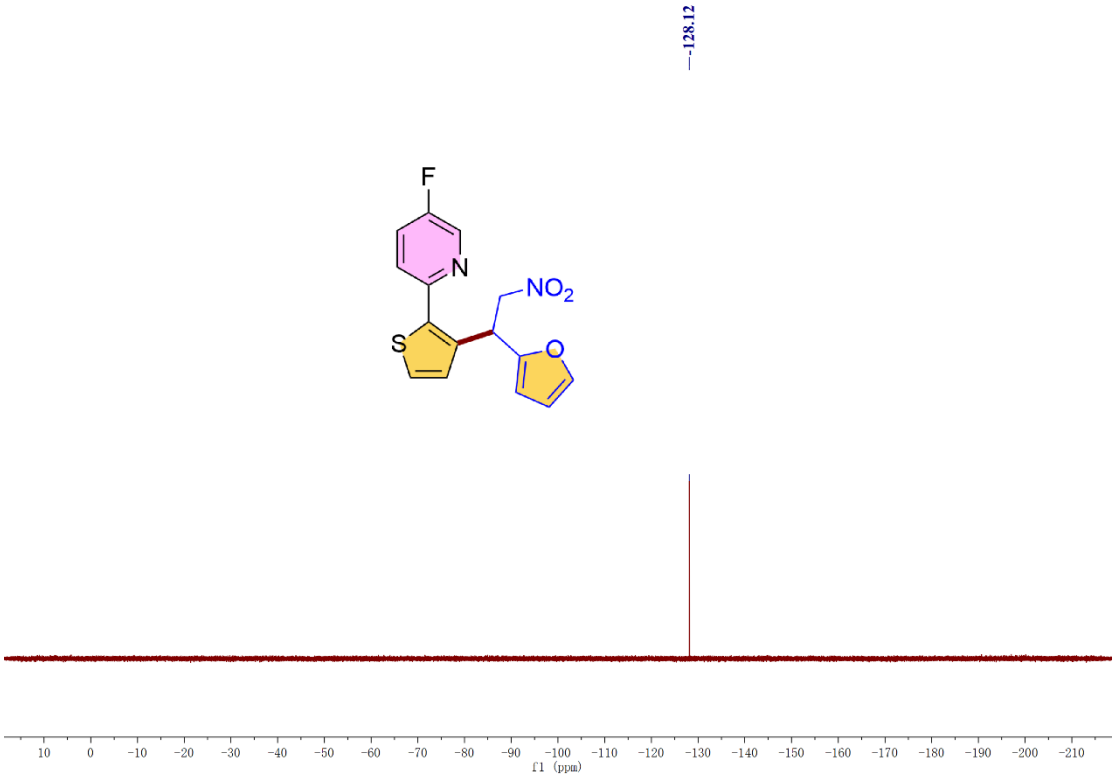
3dj | ^{1}H NMR ($CDCl_3$, 600 MHz)



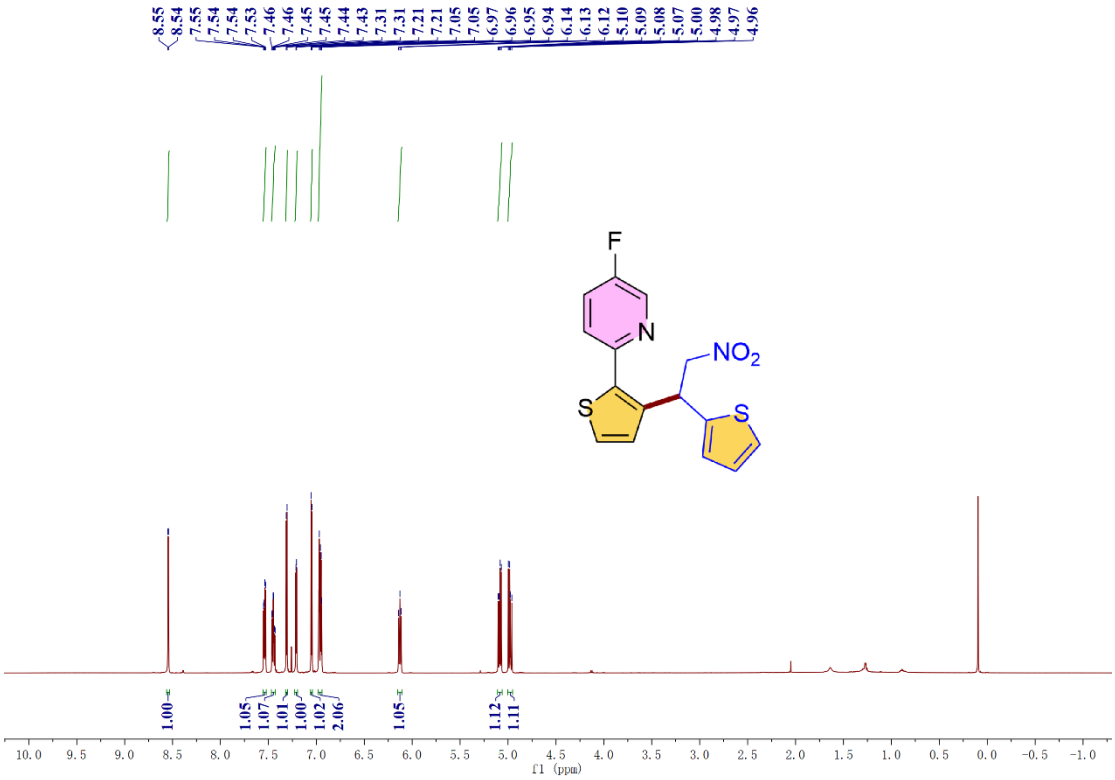
3dj | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



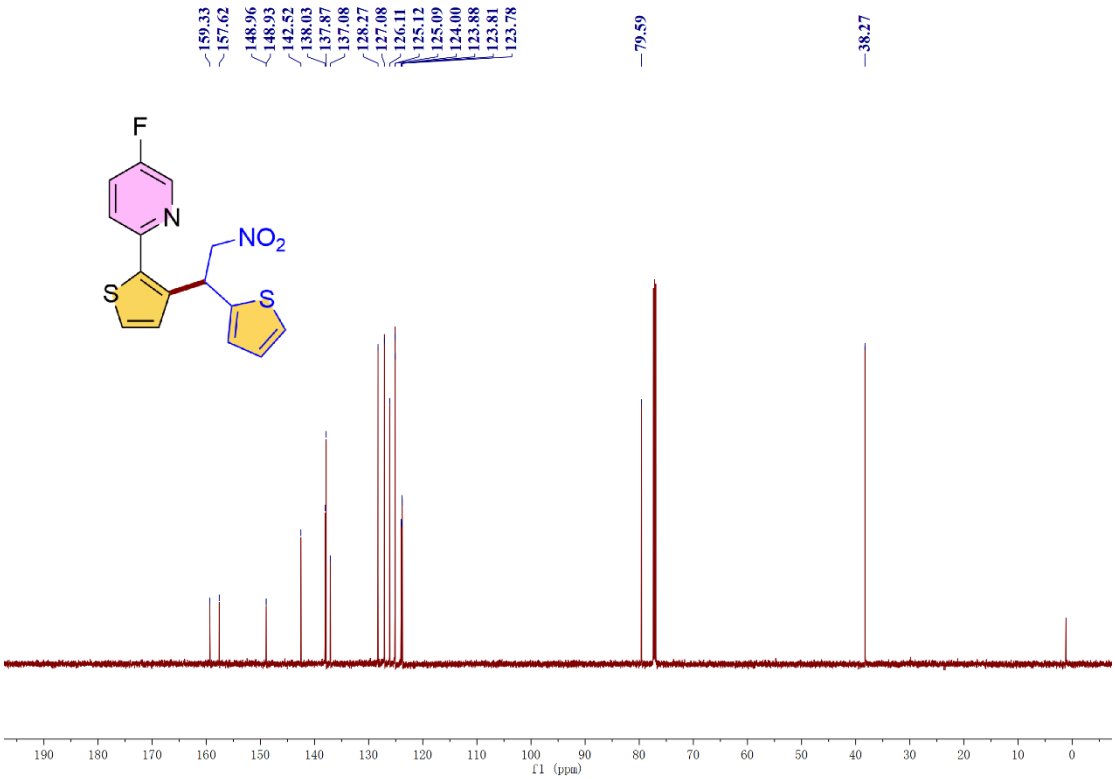
3dj | $^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 565 MHz)



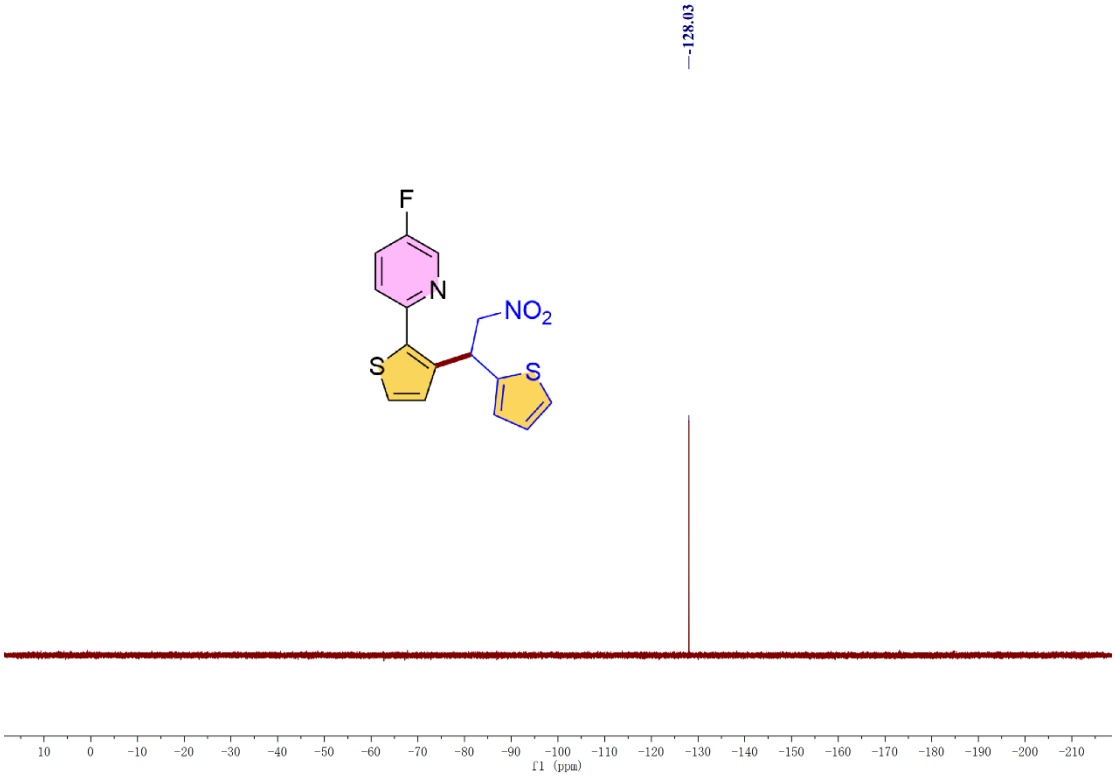
3dk | ^{1}H NMR ($CDCl_3$, 600 MHz)



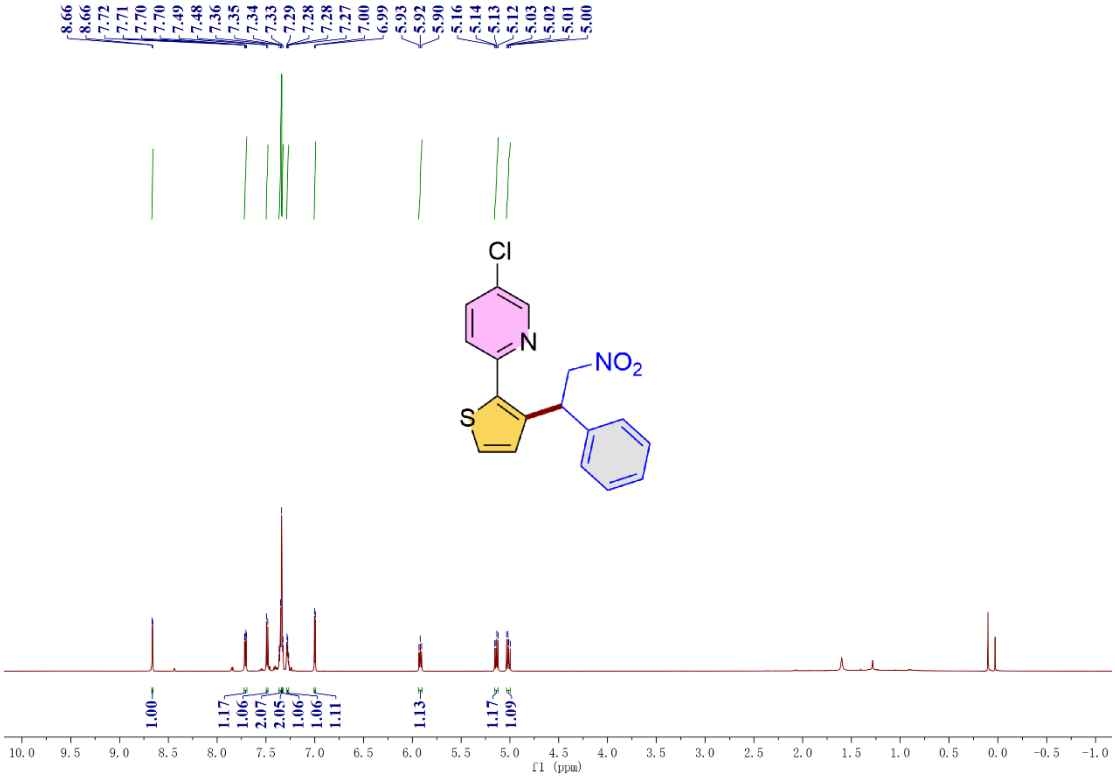
3dk | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



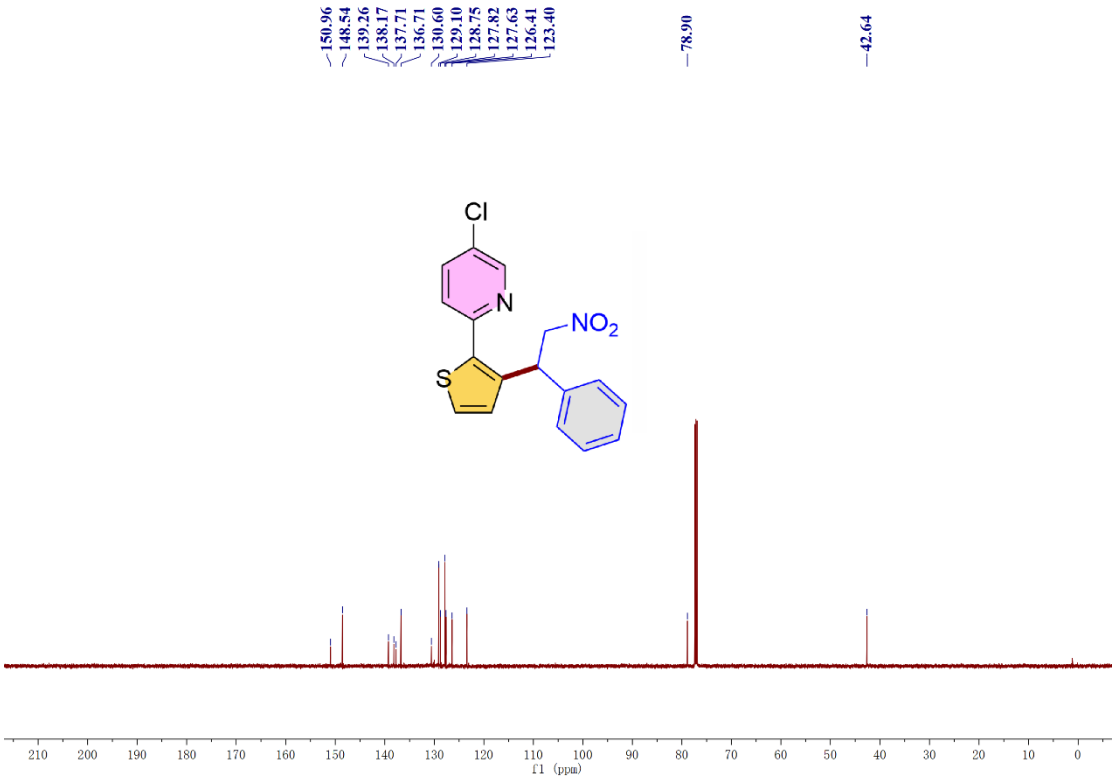
3dk | $^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 565 MHz)



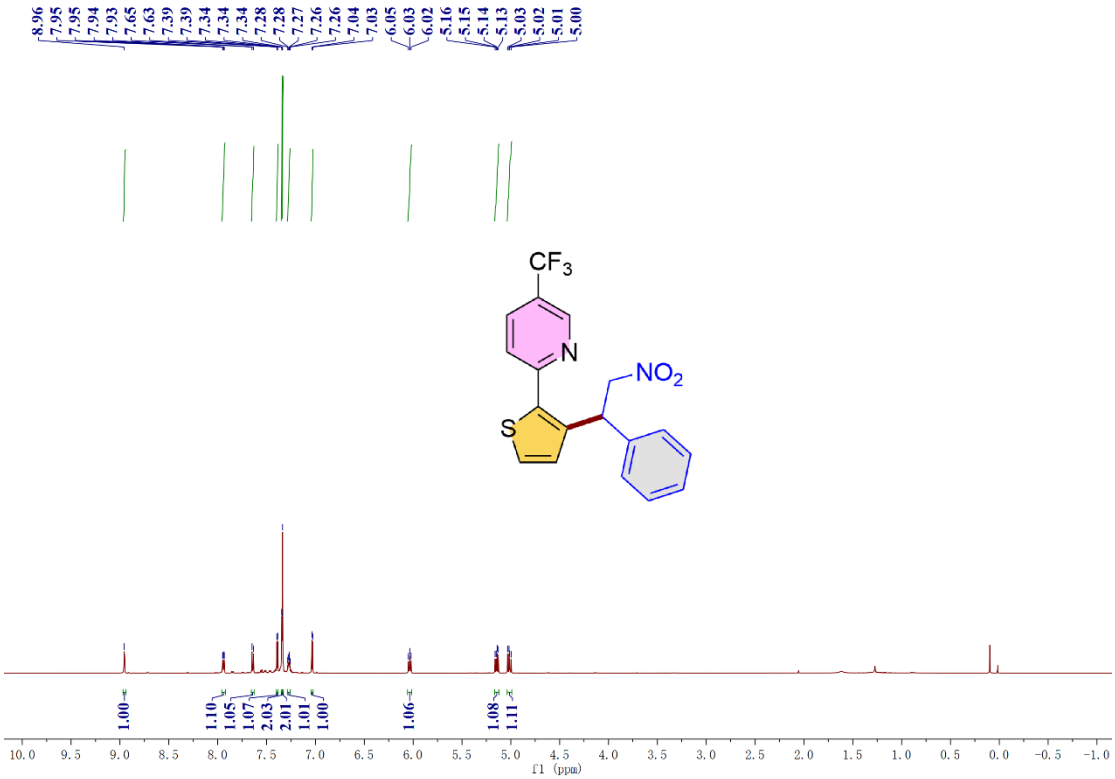
3ea | ^{1}H NMR ($CDCl_3$, 600 MHz)



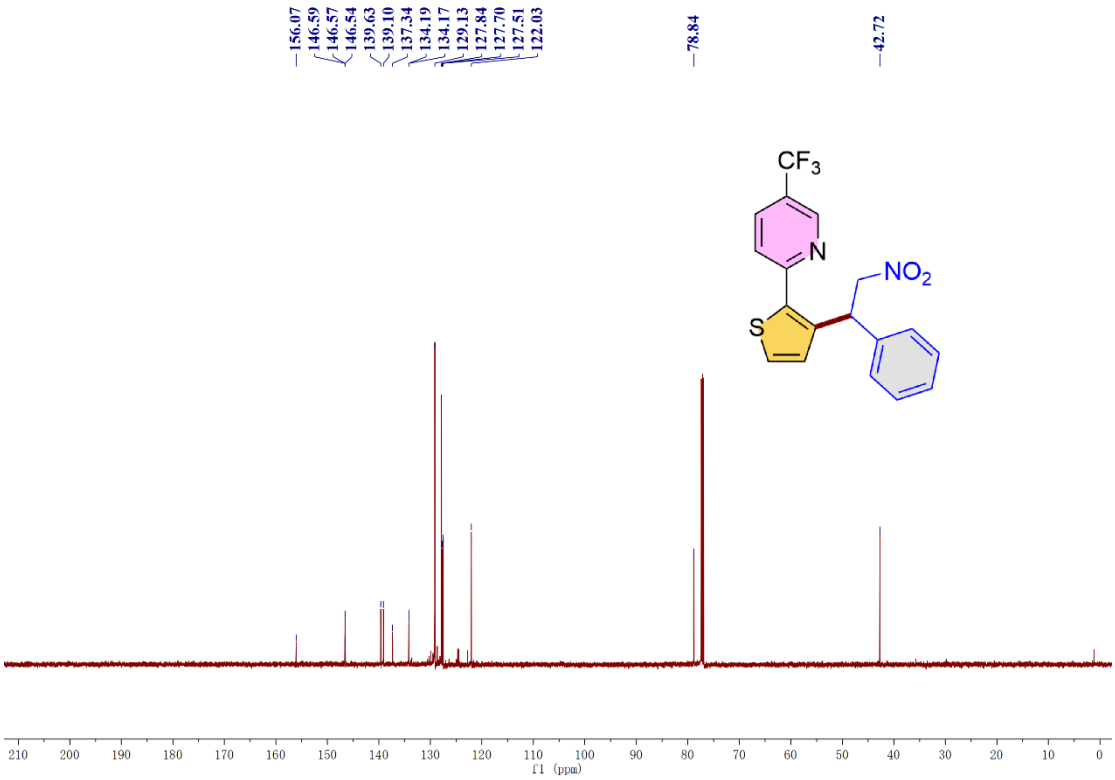
3ea | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



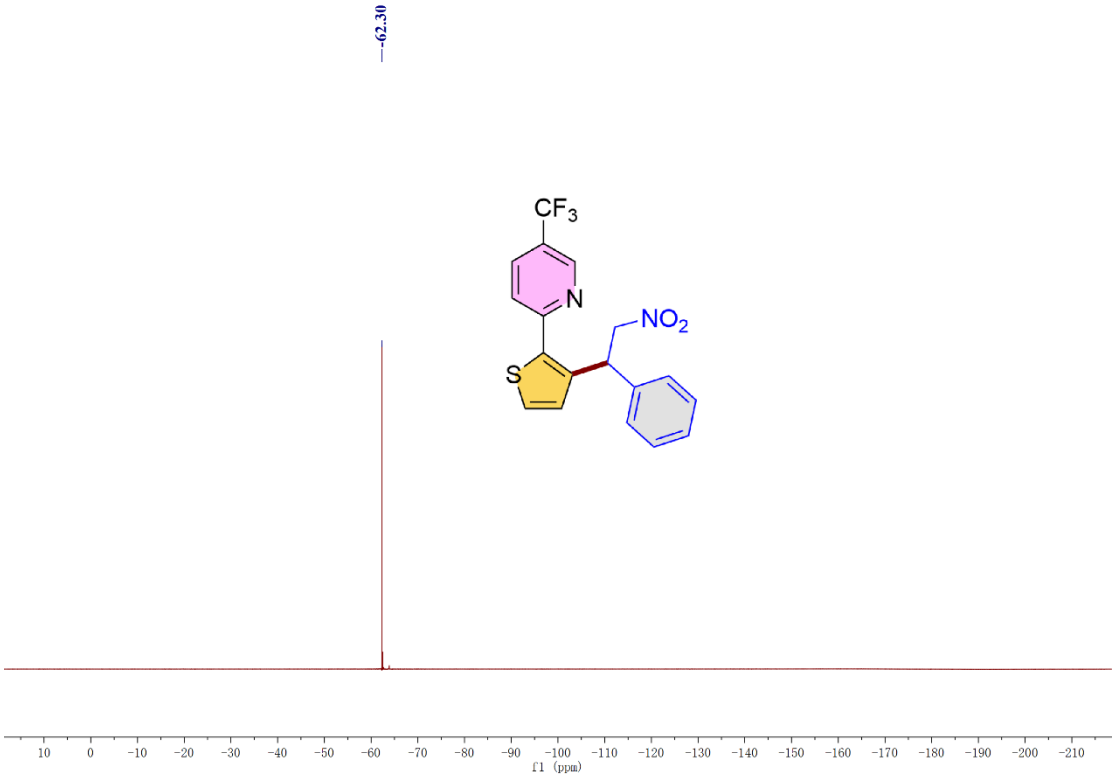
3fa | ^{1}H NMR ($CDCl_3$, 600 MHz)



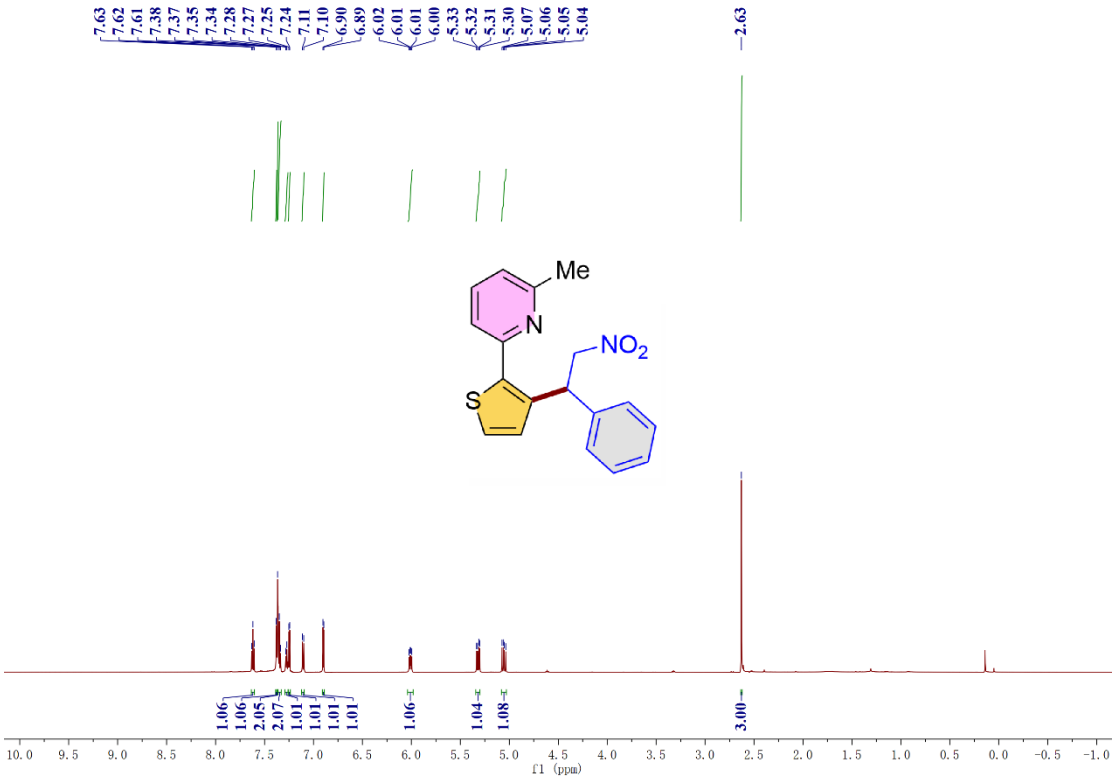
3fa | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



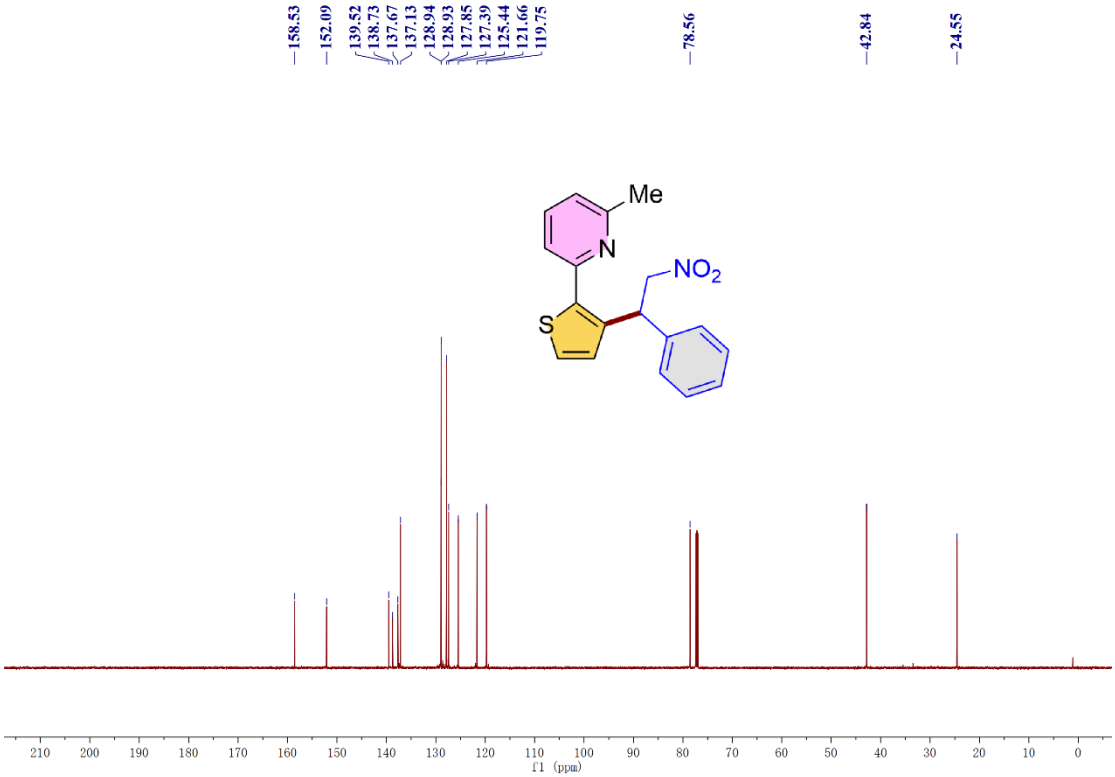
3fa | $^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 565 MHz)



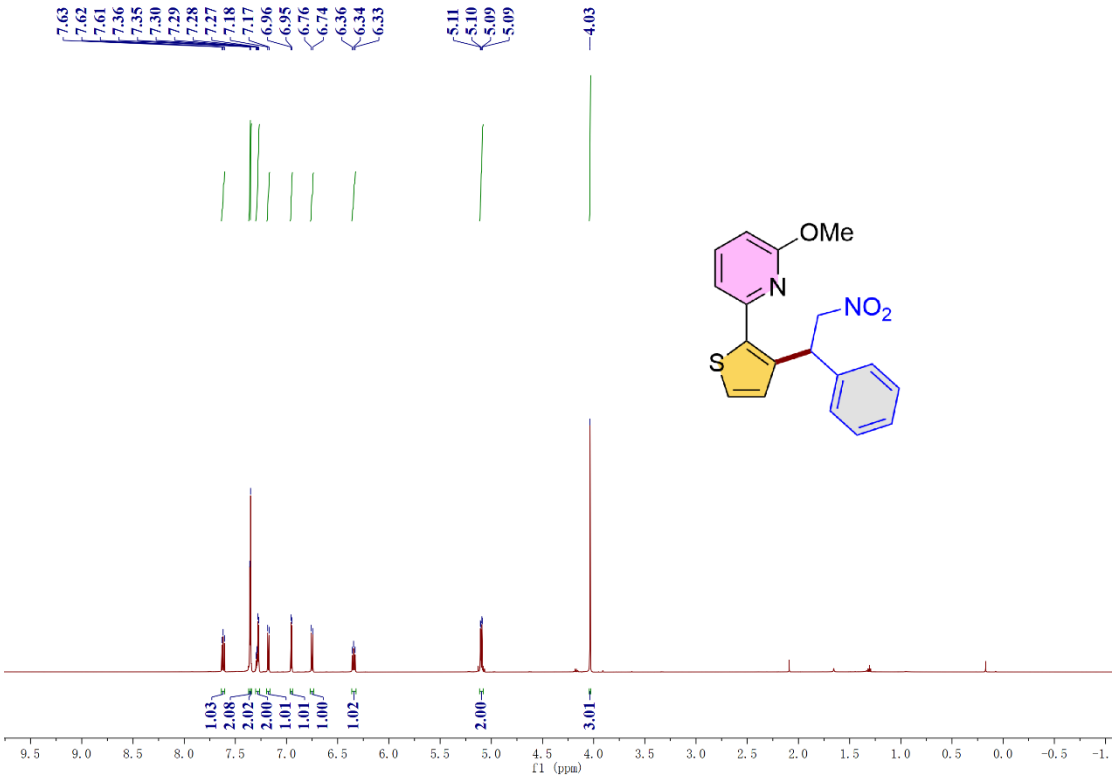
3ga | ^{1}H NMR ($CDCl_3$, 600 MHz)



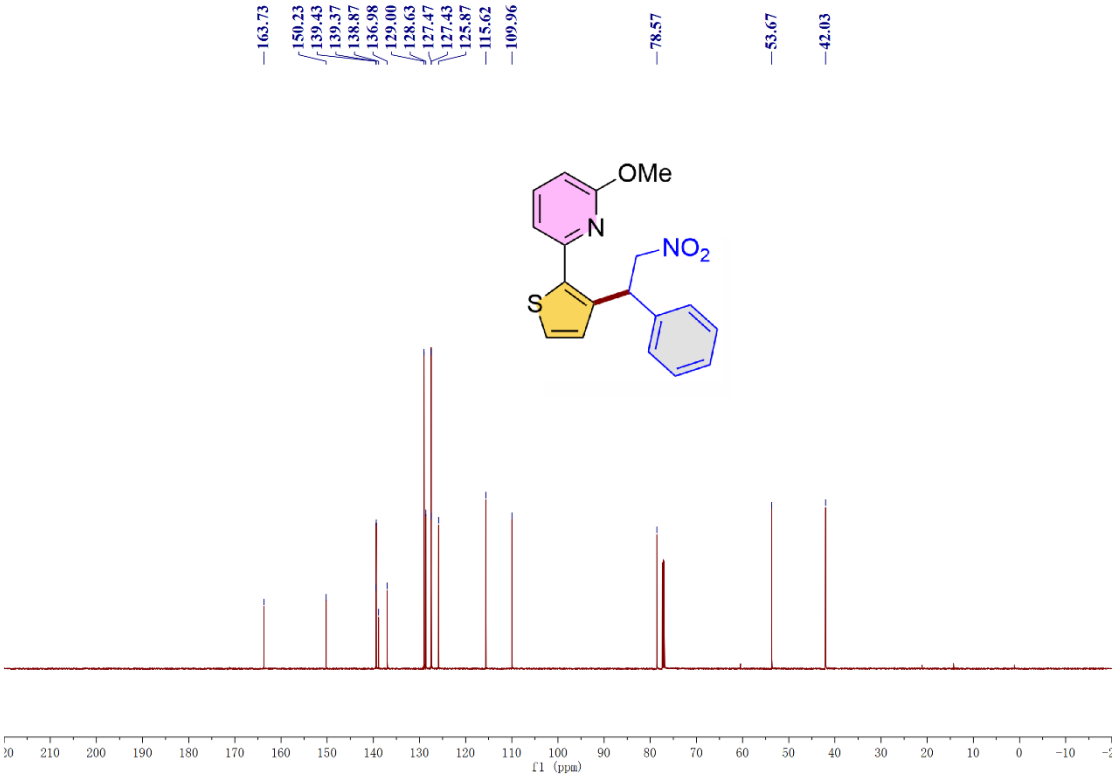
3ga | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



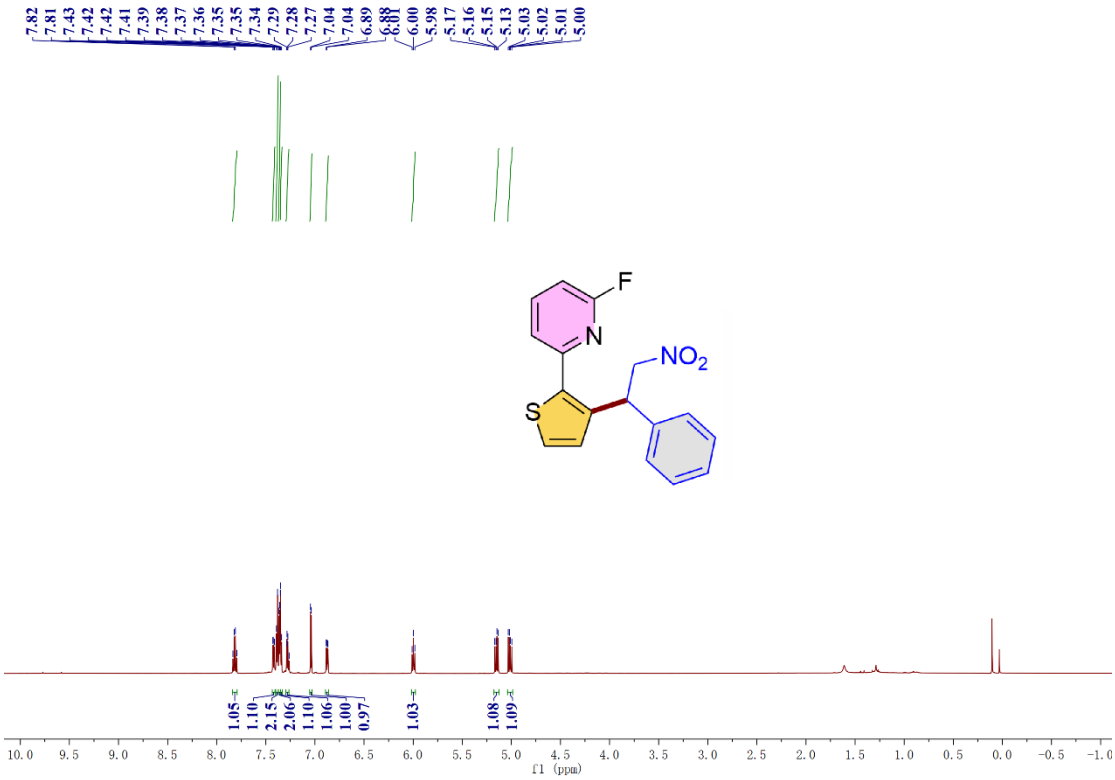
3ha | ^{1}H NMR ($CDCl_3$, 600 MHz)



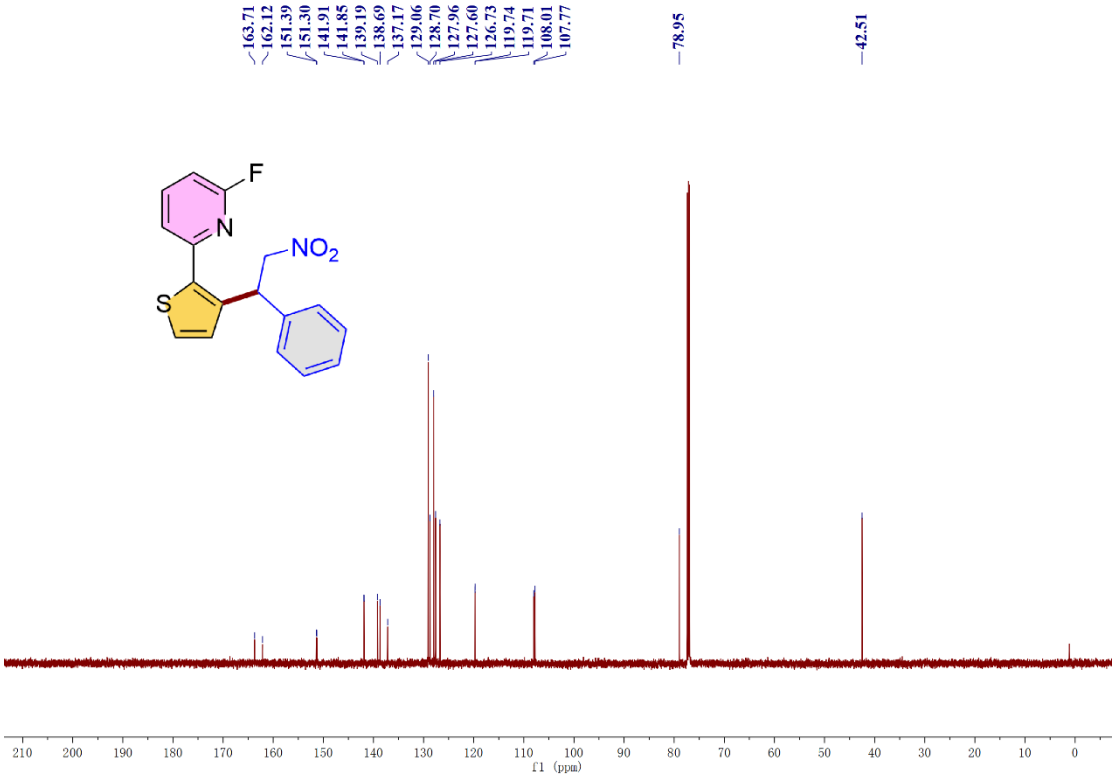
3ha | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



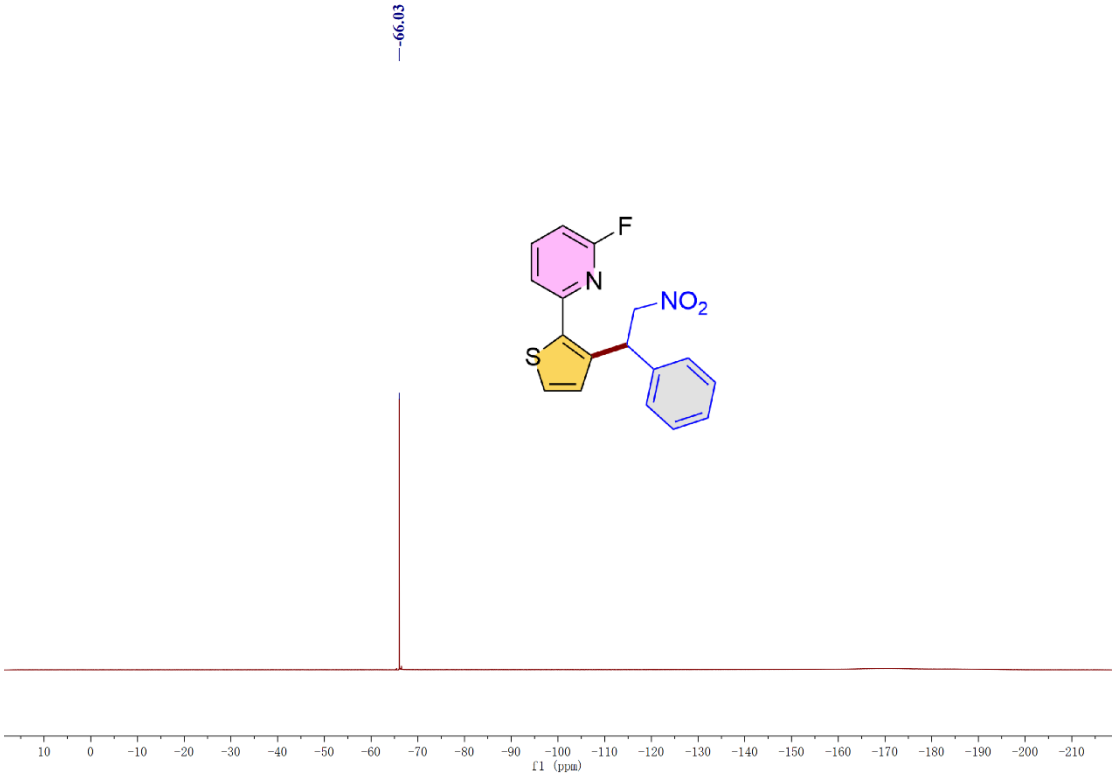
3la | ^{1}H NMR ($CDCl_3$, 600 MHz)



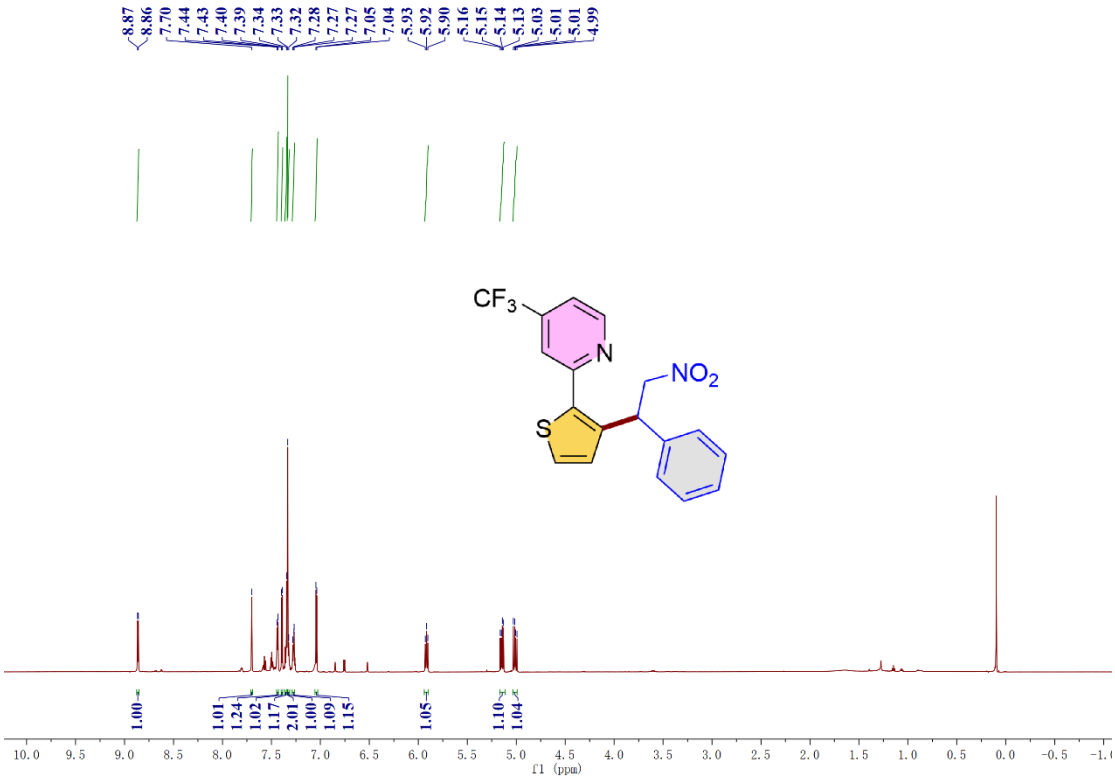
3la | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



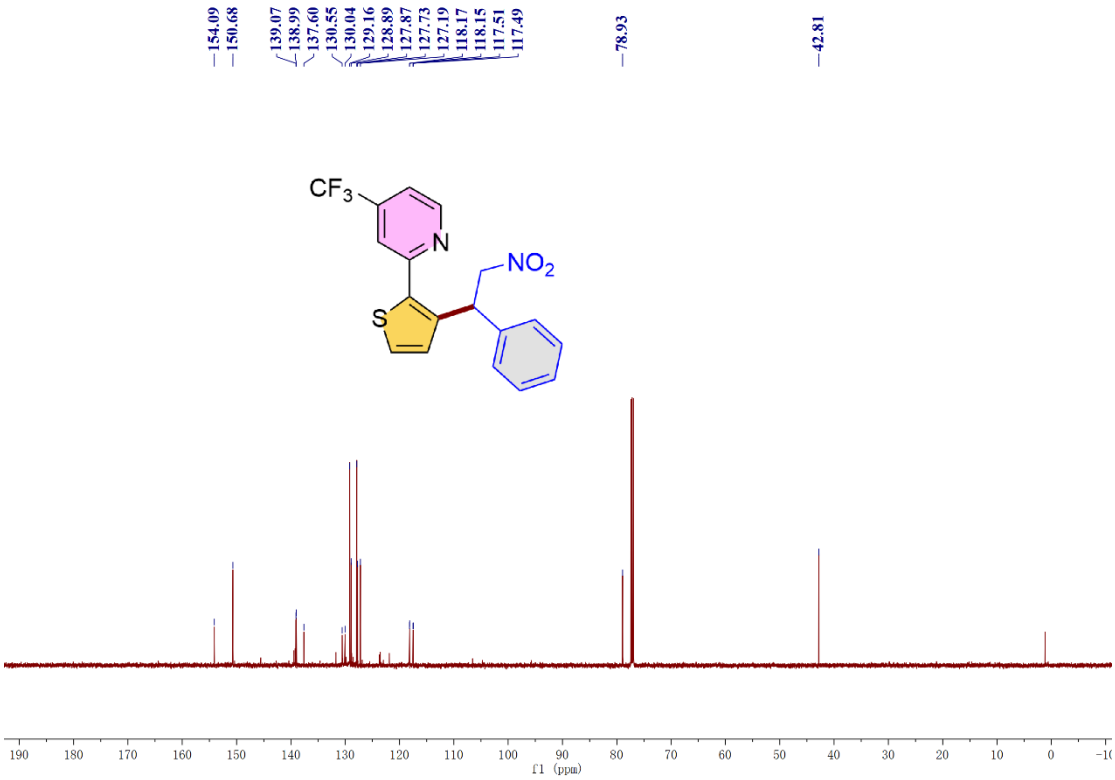
3fa | $^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 565 MHz)



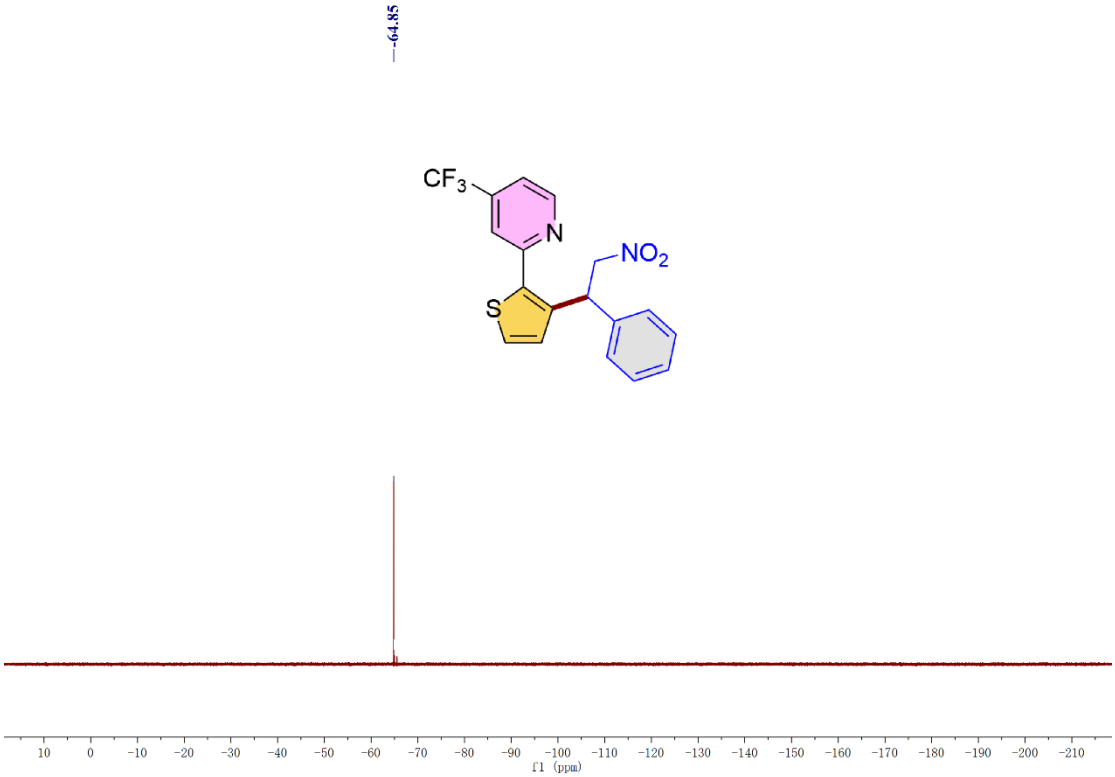
3ka | ^{1}H NMR ($CDCl_3$, 600 MHz)



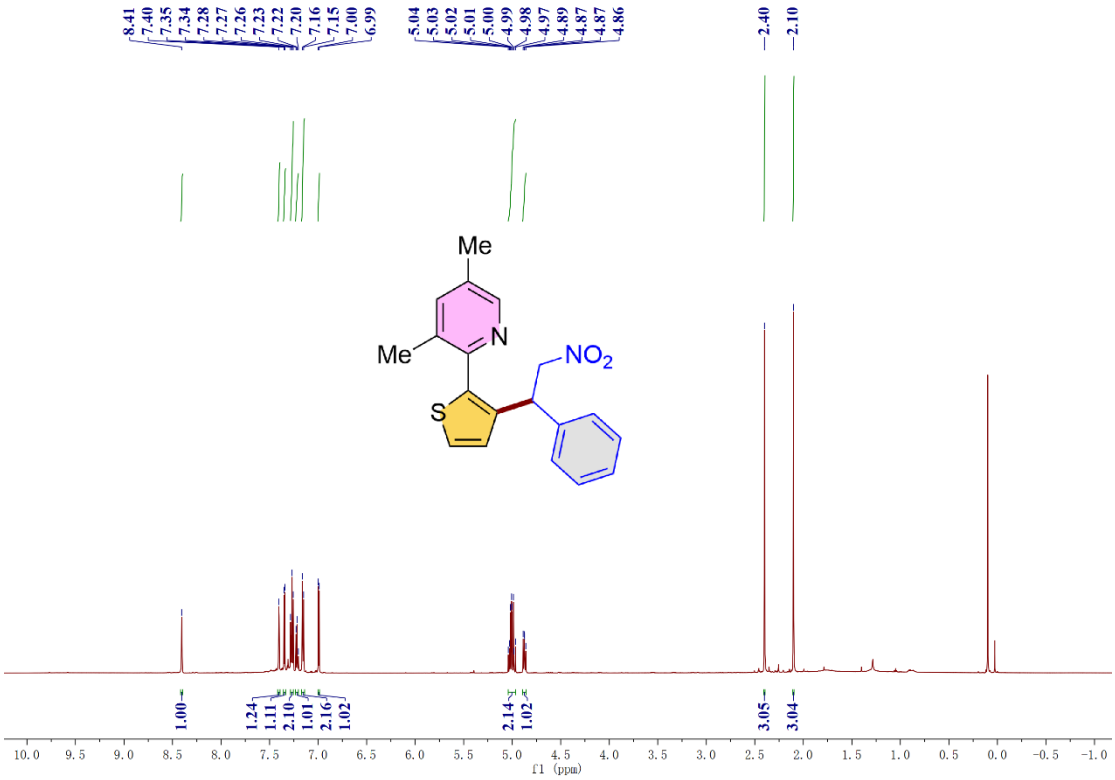
3ka | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



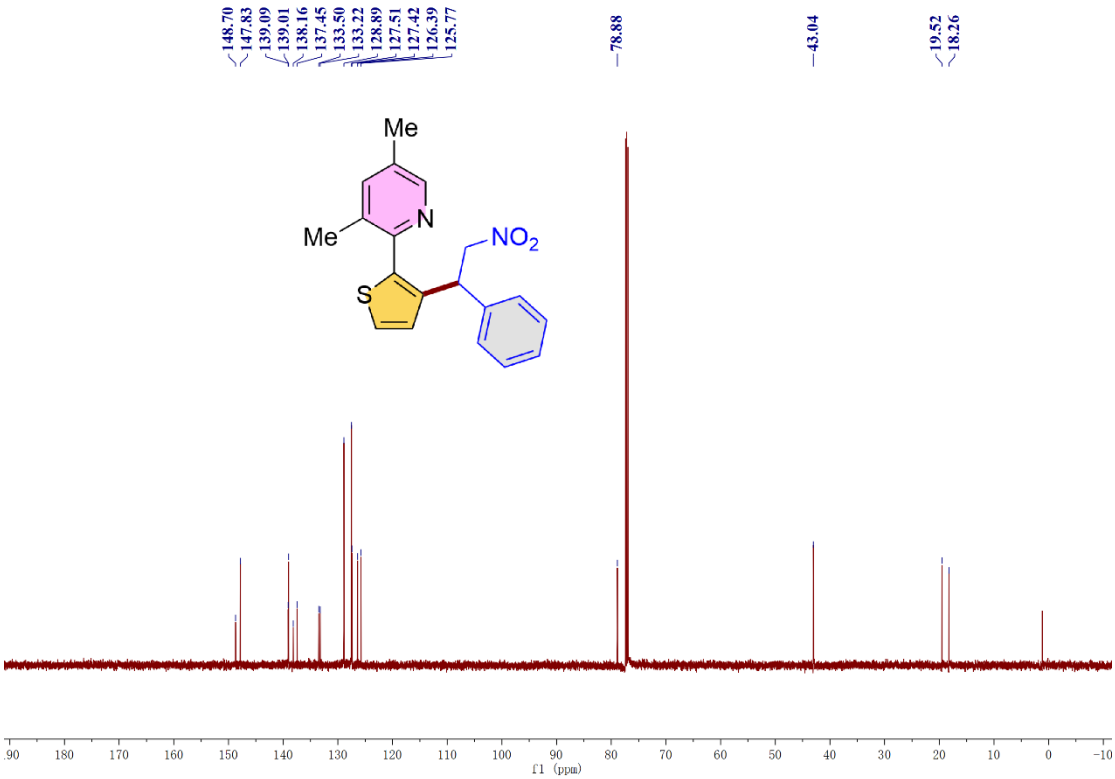
3ka | $^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 565 MHz)



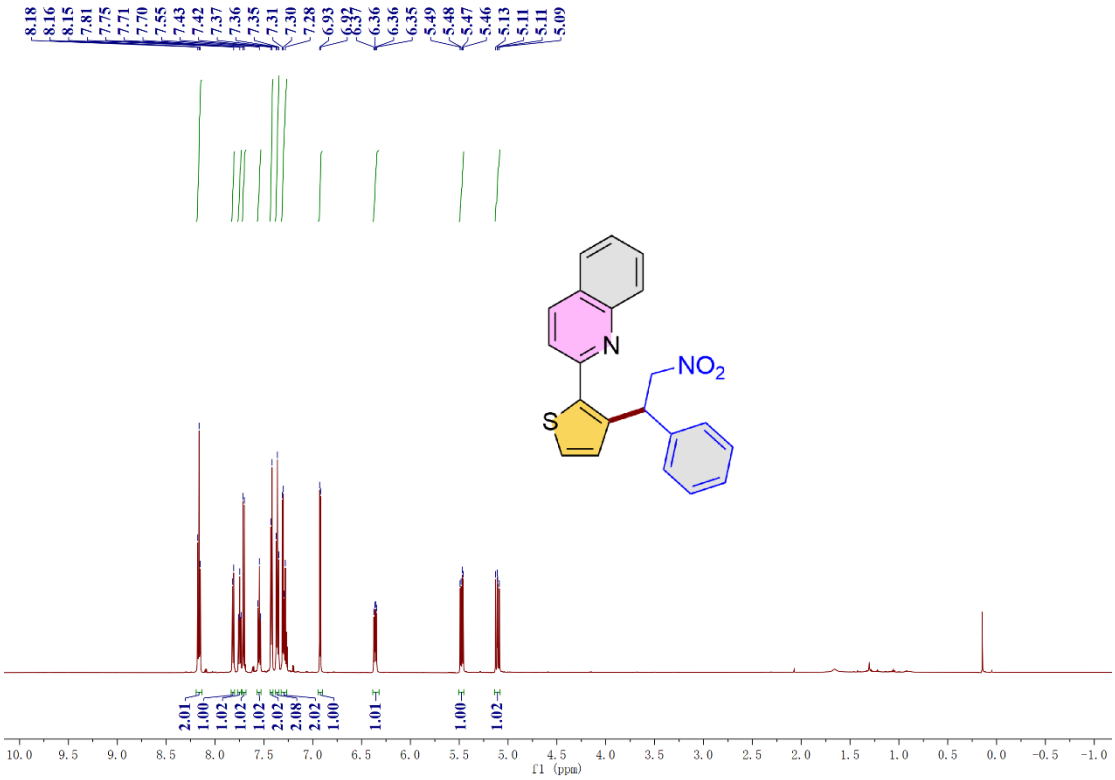
3ma | ^{1}H NMR ($CDCl_3$, 600 MHz)



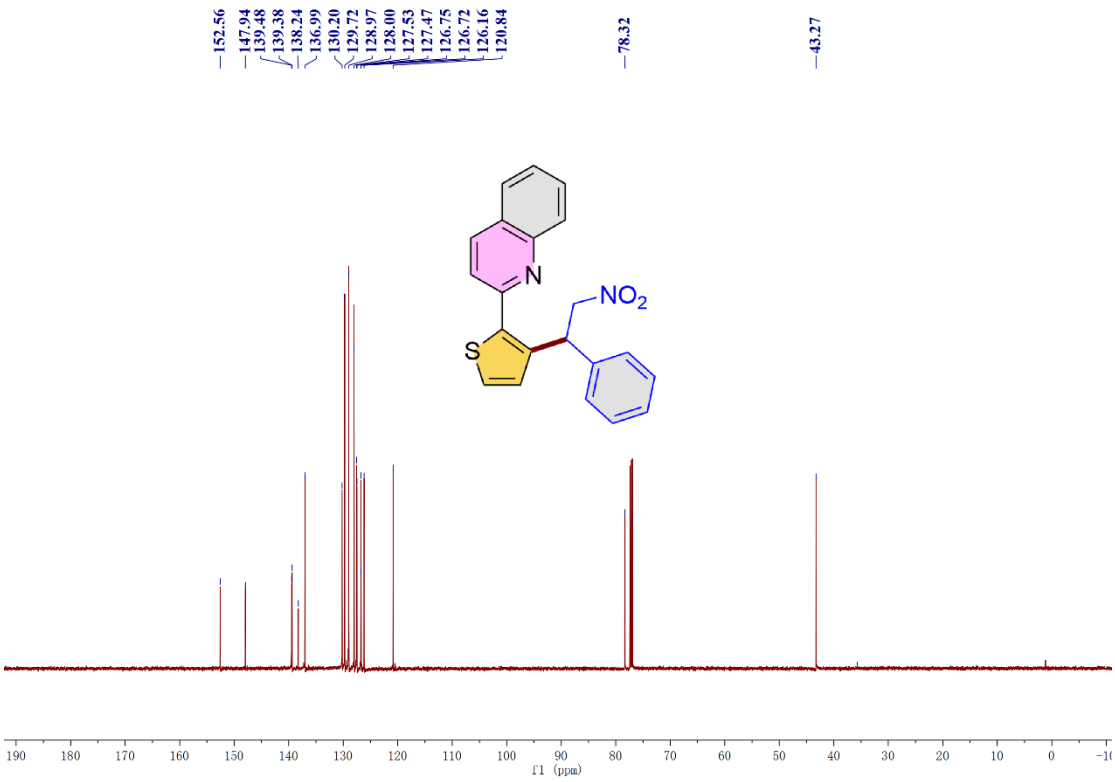
3ma | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



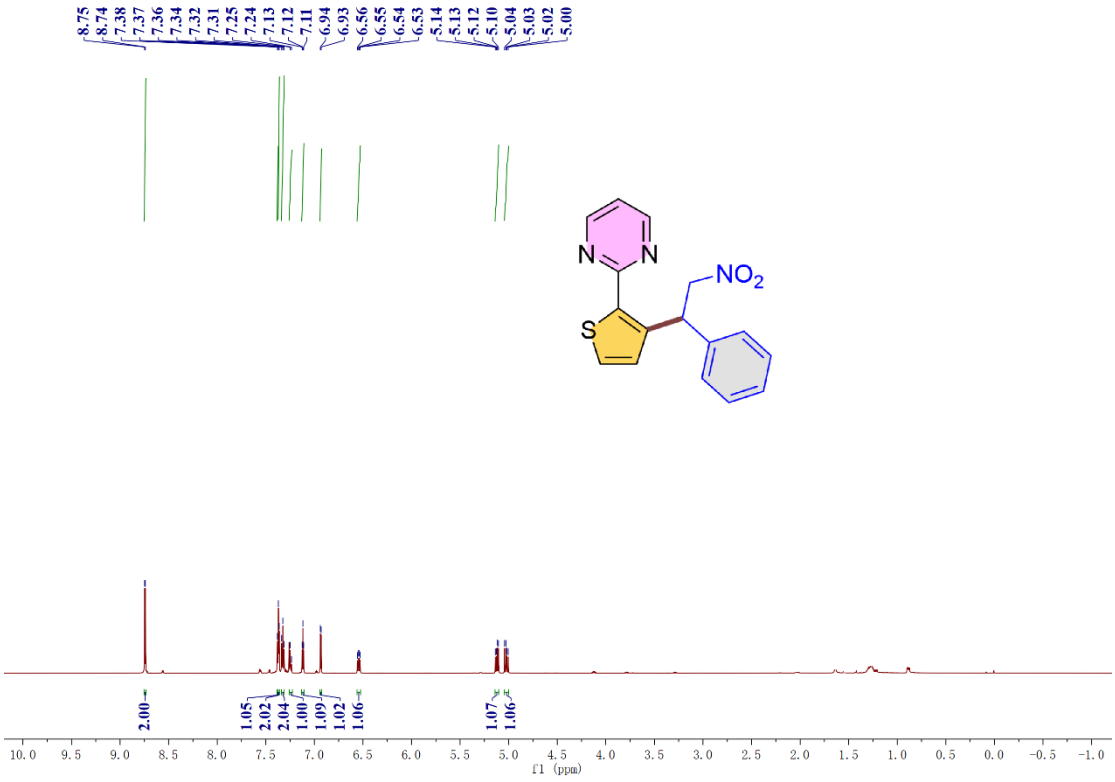
3na | ^{1}H NMR ($CDCl_3$, 600 MHz)



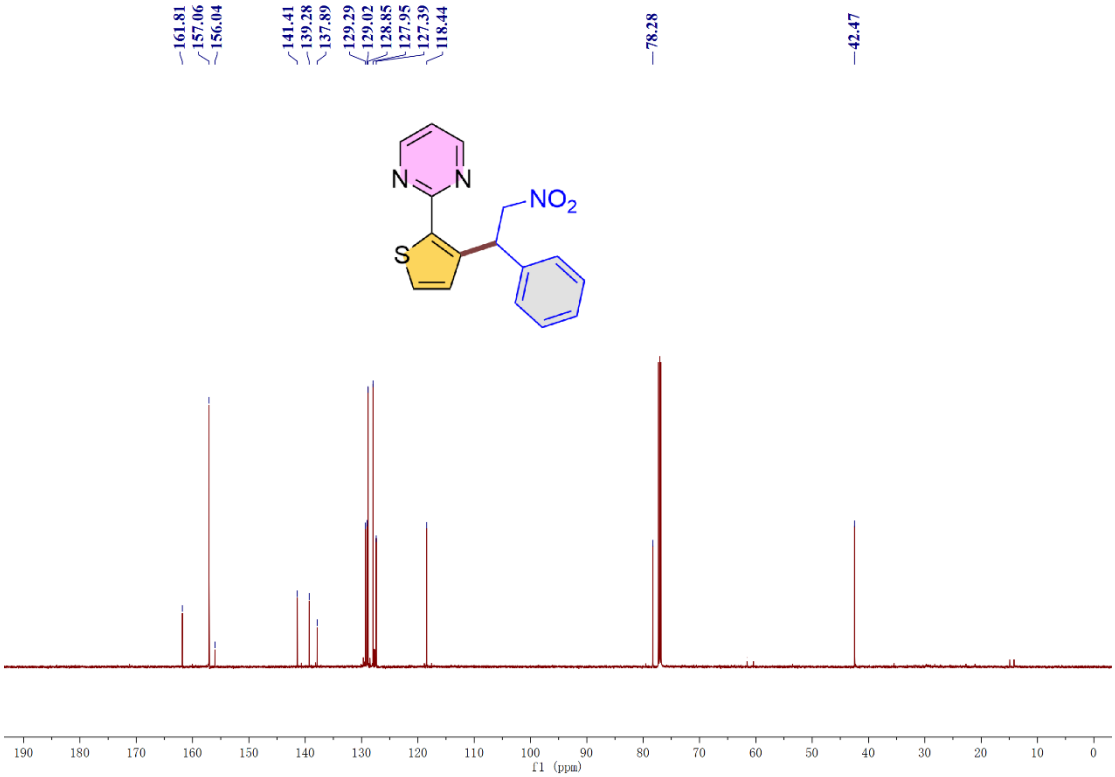
3na | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



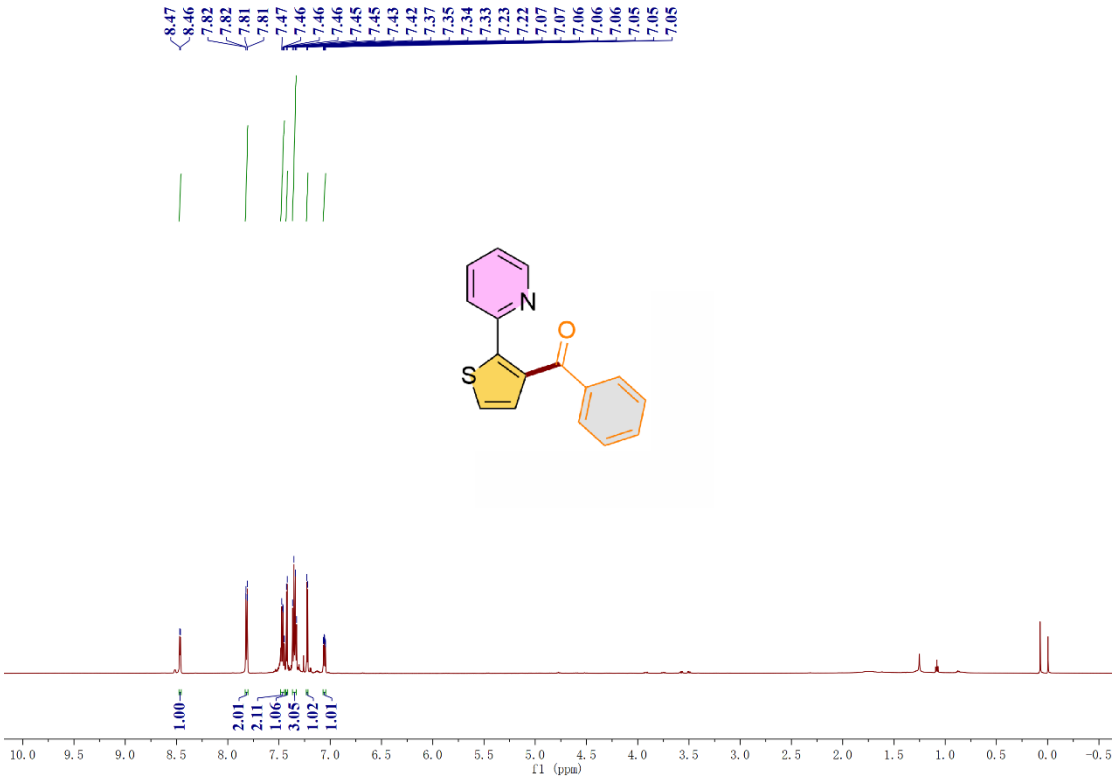
3oa | ^{1}H NMR ($CDCl_3$, 600 MHz)



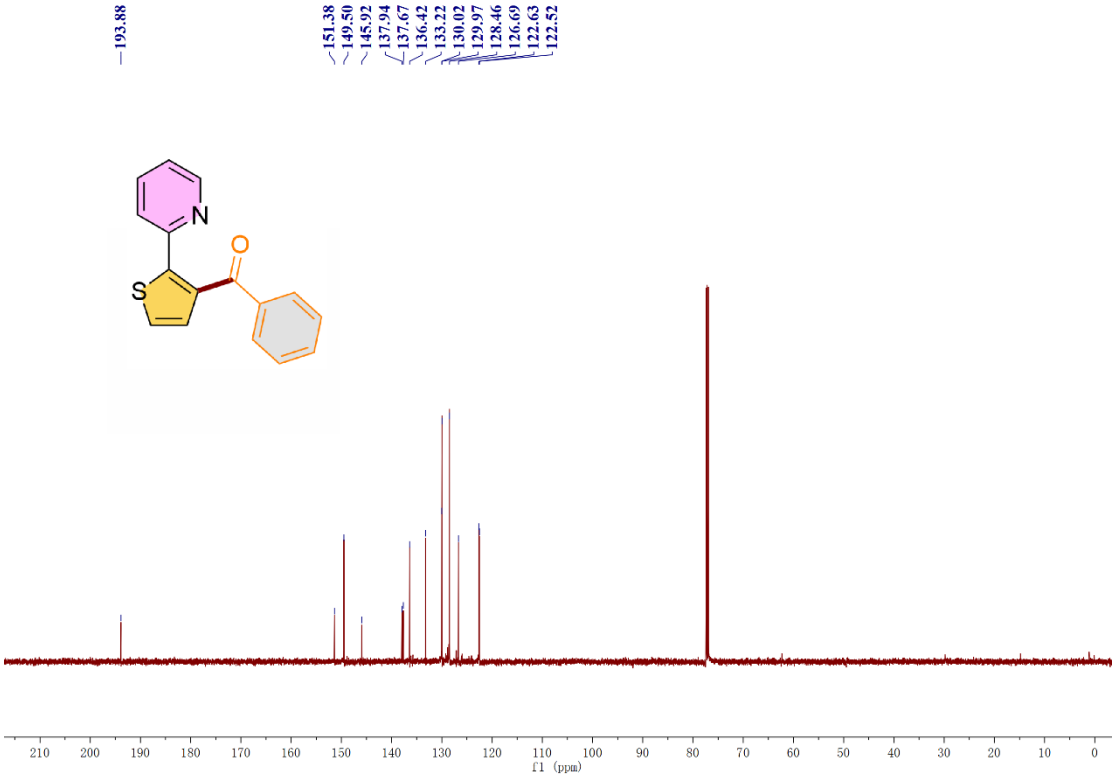
3oa | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



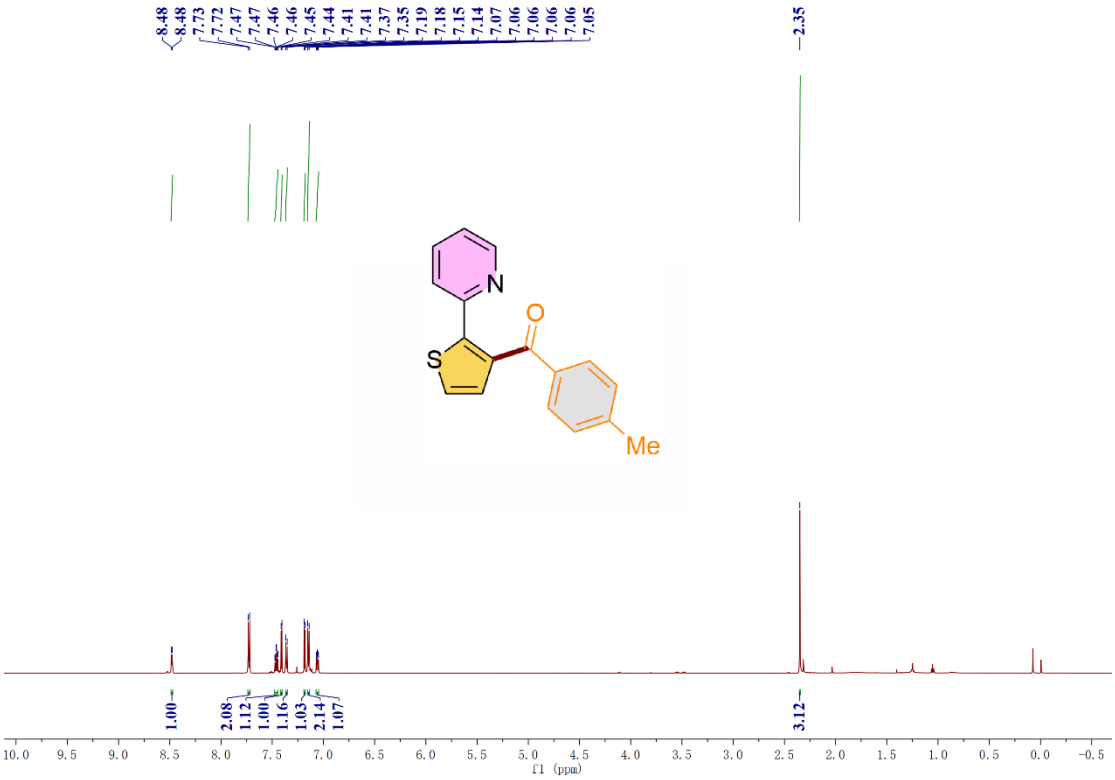
4aa | ^{1}H NMR ($CDCl_3$, 600 MHz)



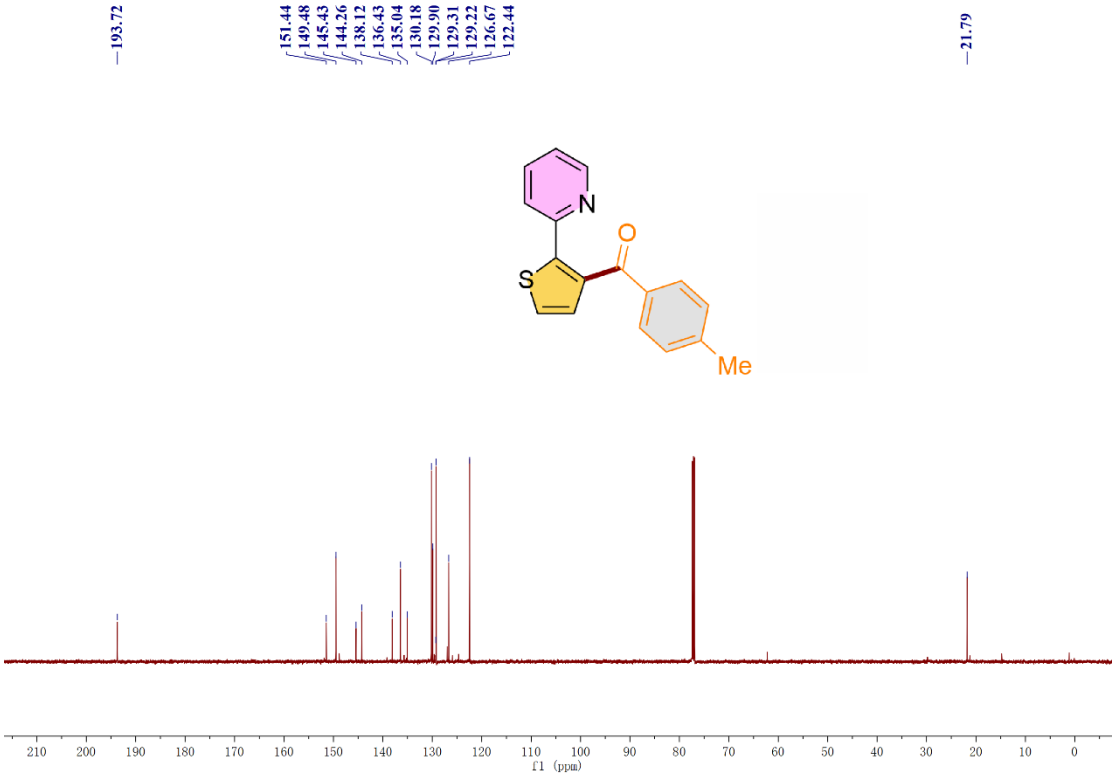
4aa | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



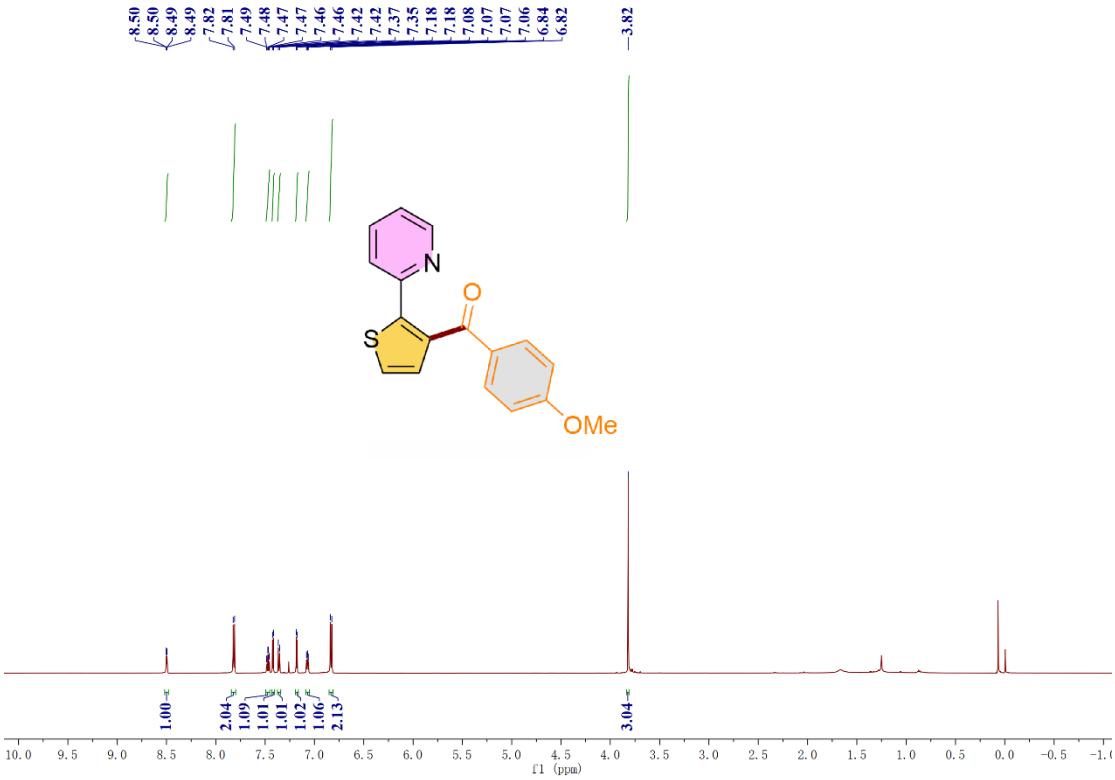
4ab | ^{1}H NMR ($CDCl_3$, 600 MHz)



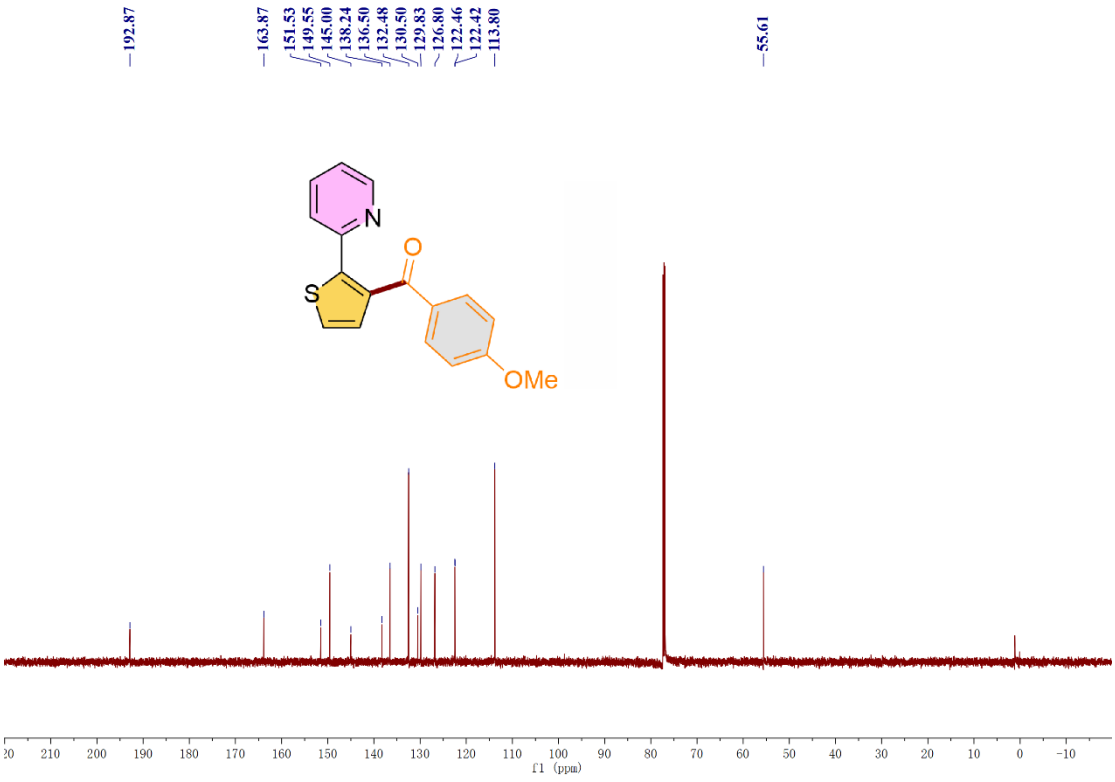
4ab | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



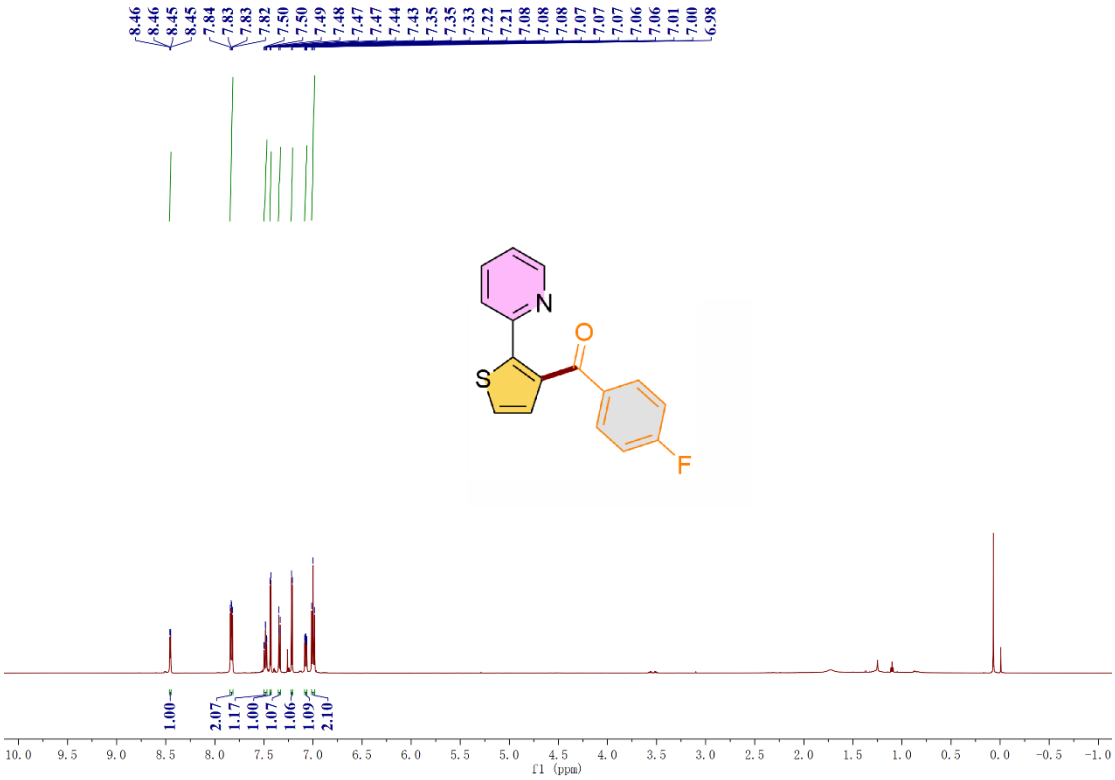
4ac | ^{1}H NMR ($CDCl_3$, 600 MHz)



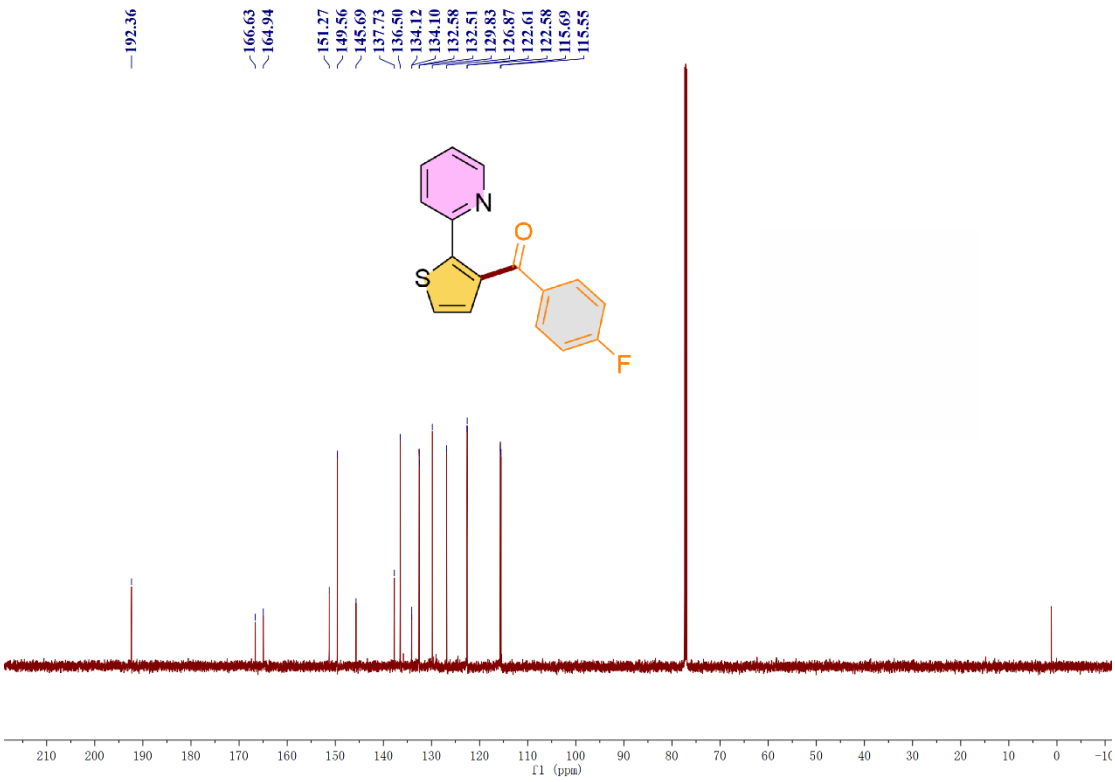
4ac | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



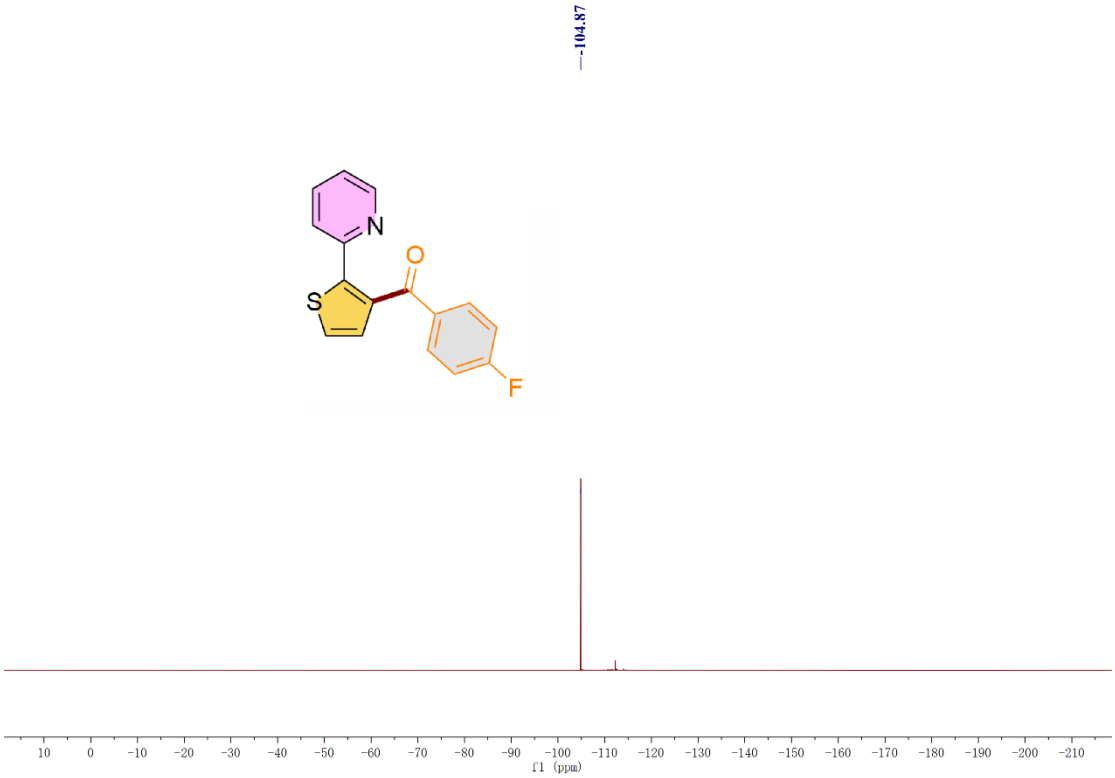
4ad | ^{1}H NMR ($CDCl_3$, 600 MHz)



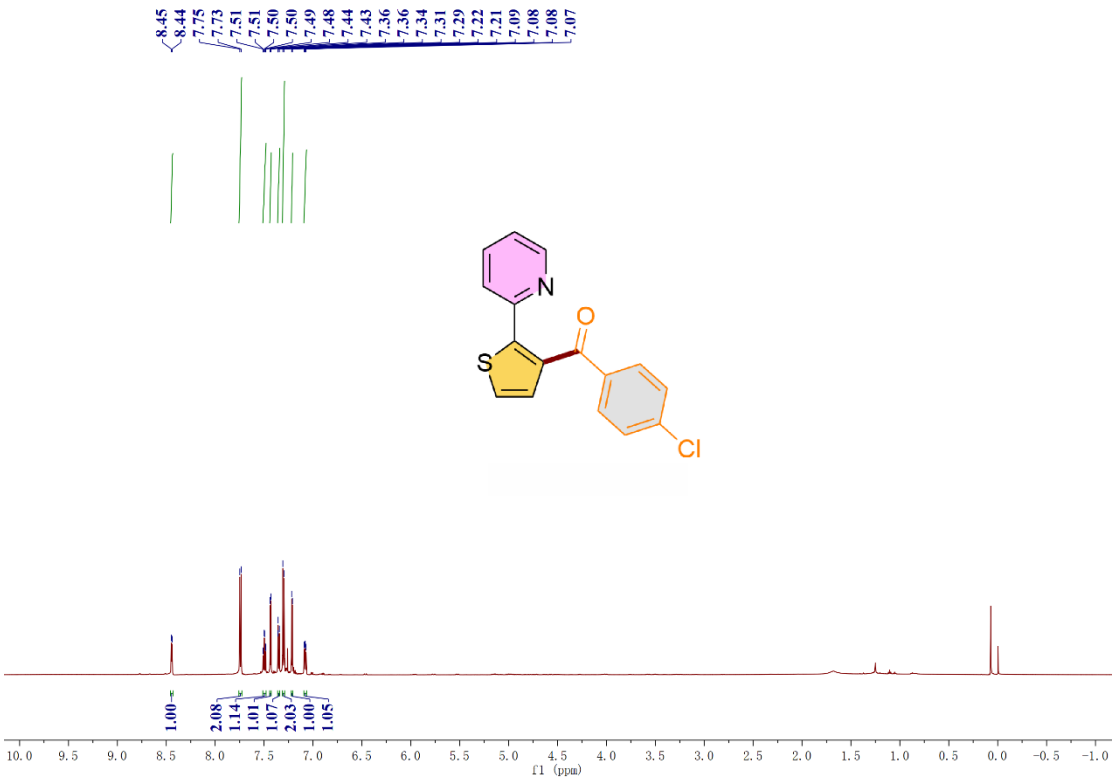
4ad | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



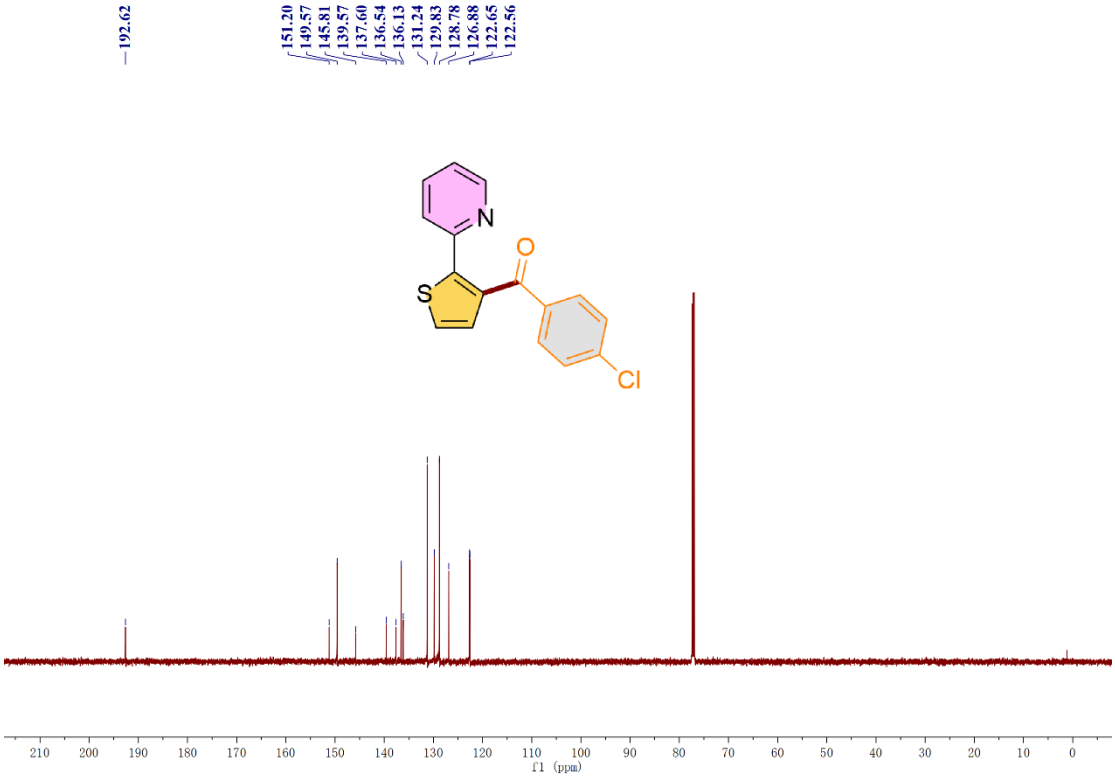
4ad | $^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 565 MHz)



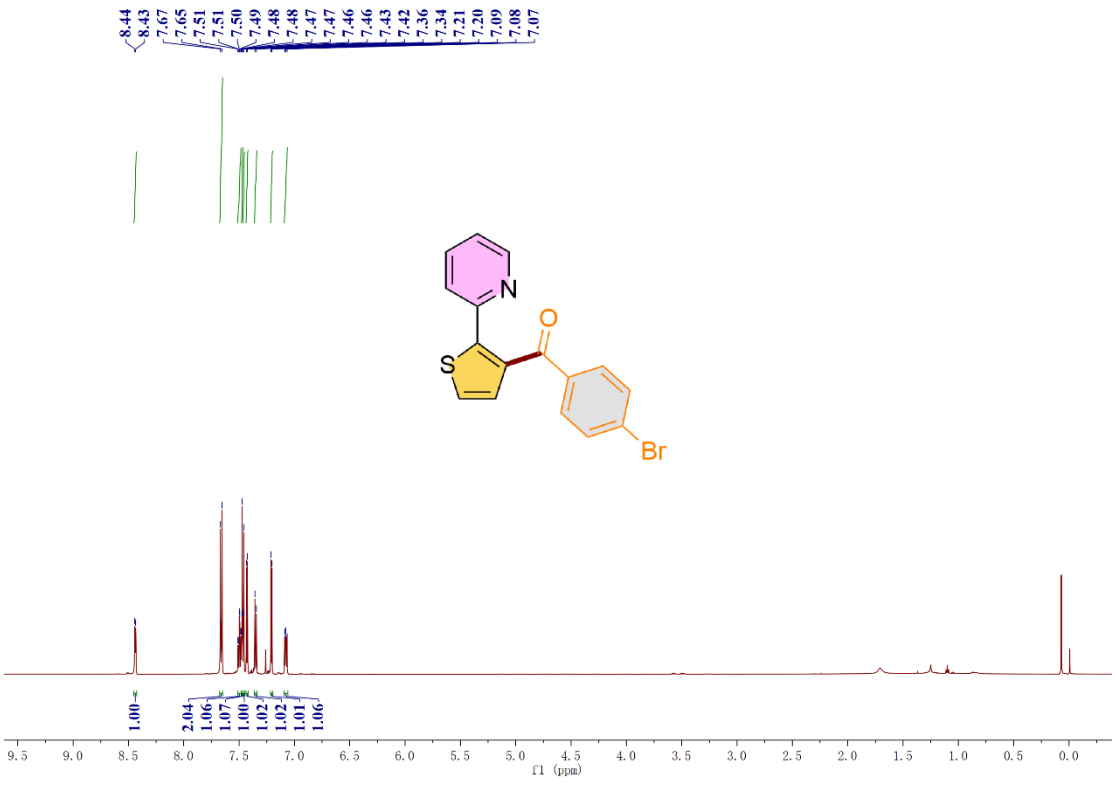
4ae | ^{1}H NMR ($CDCl_3$, 600 MHz)



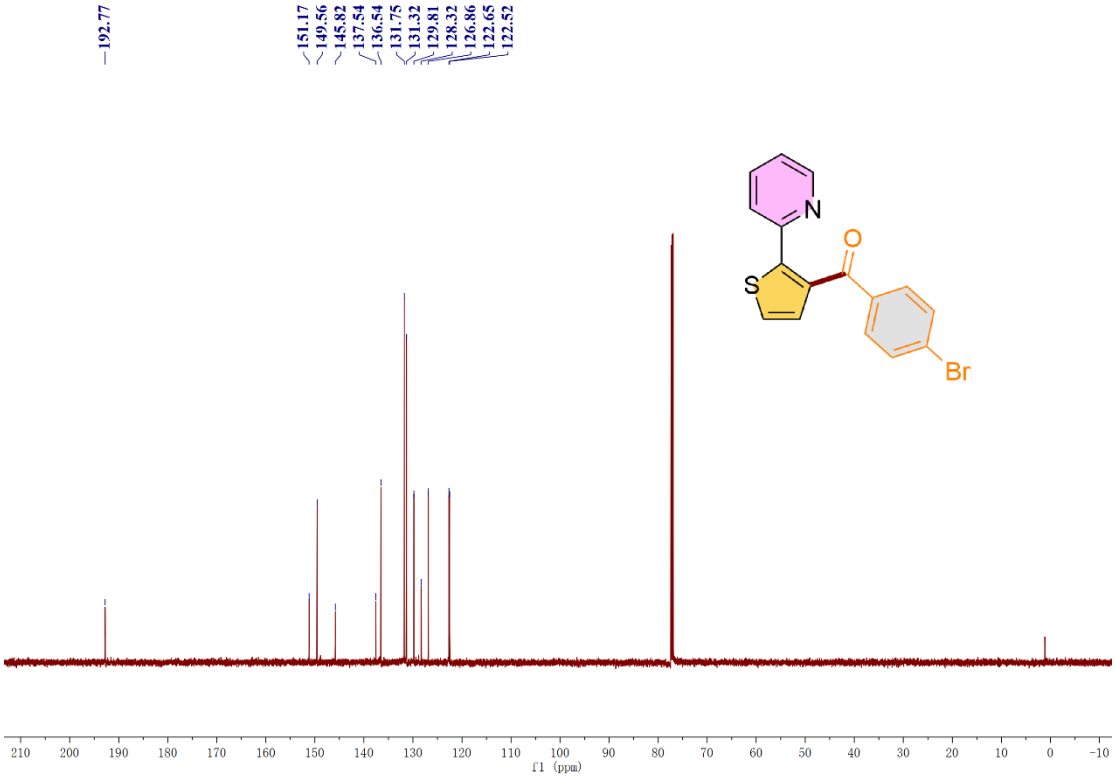
4ae | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



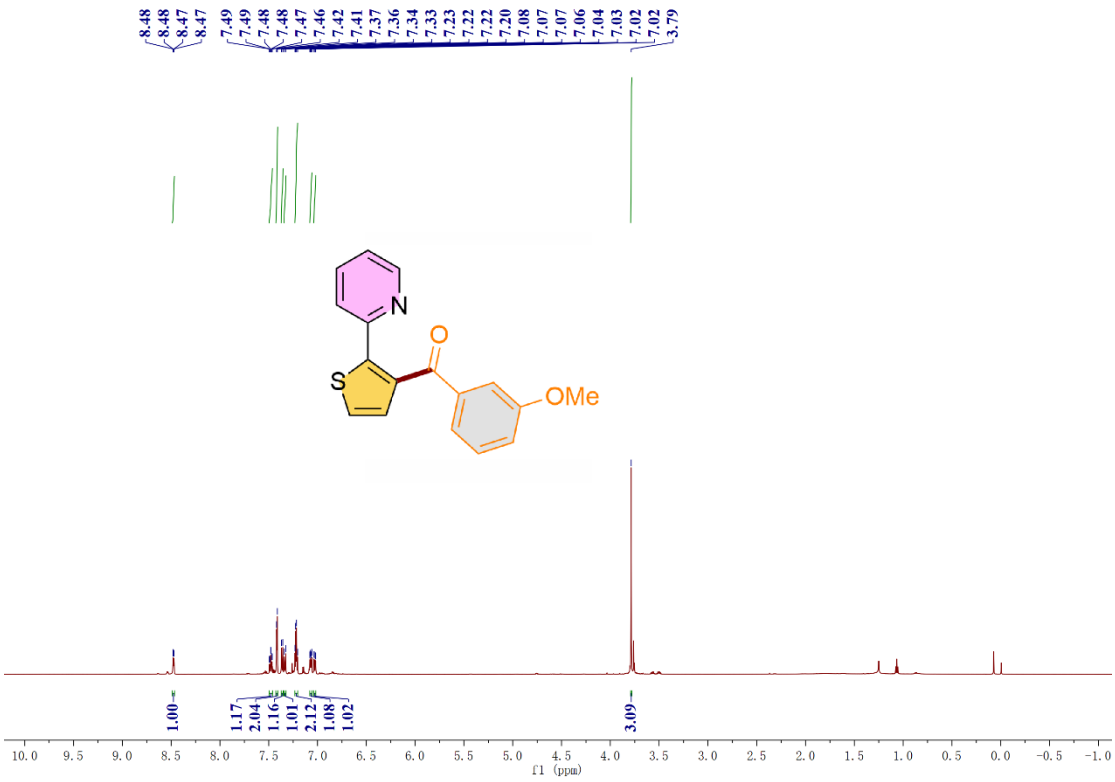
4af | ^{1}H NMR ($CDCl_3$, 600 MHz)



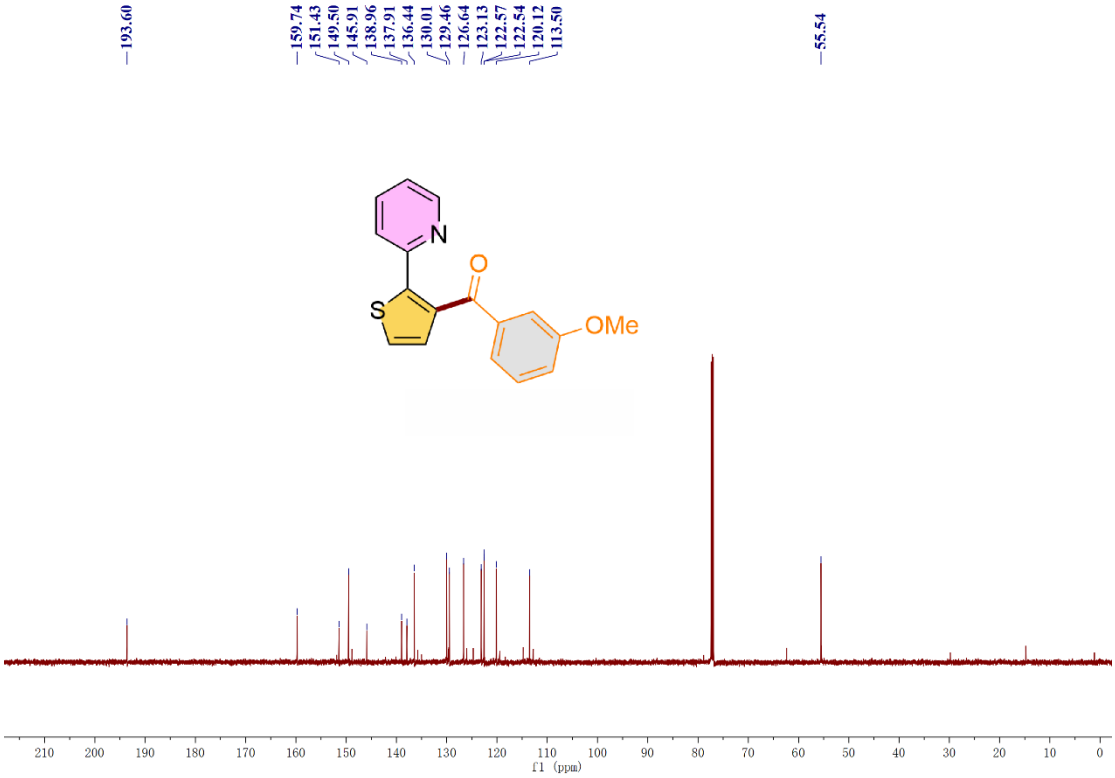
4af | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



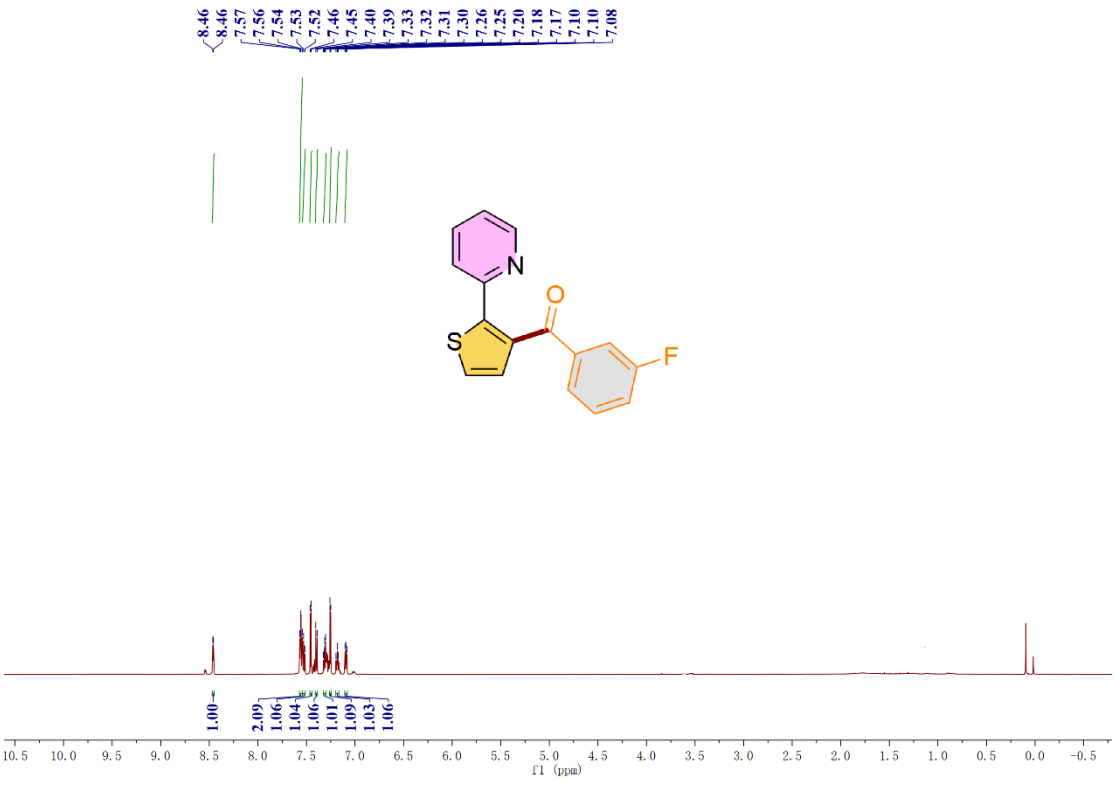
4ag | ^{1}H NMR ($CDCl_3$, 600 MHz)



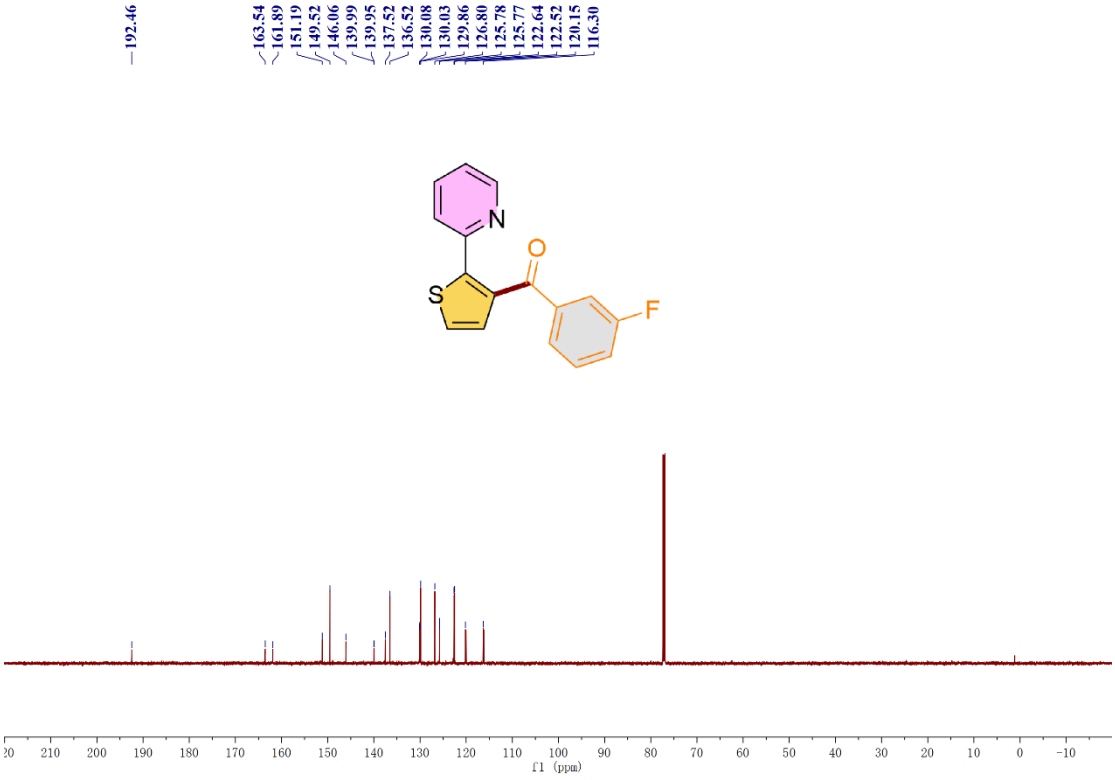
4ag | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



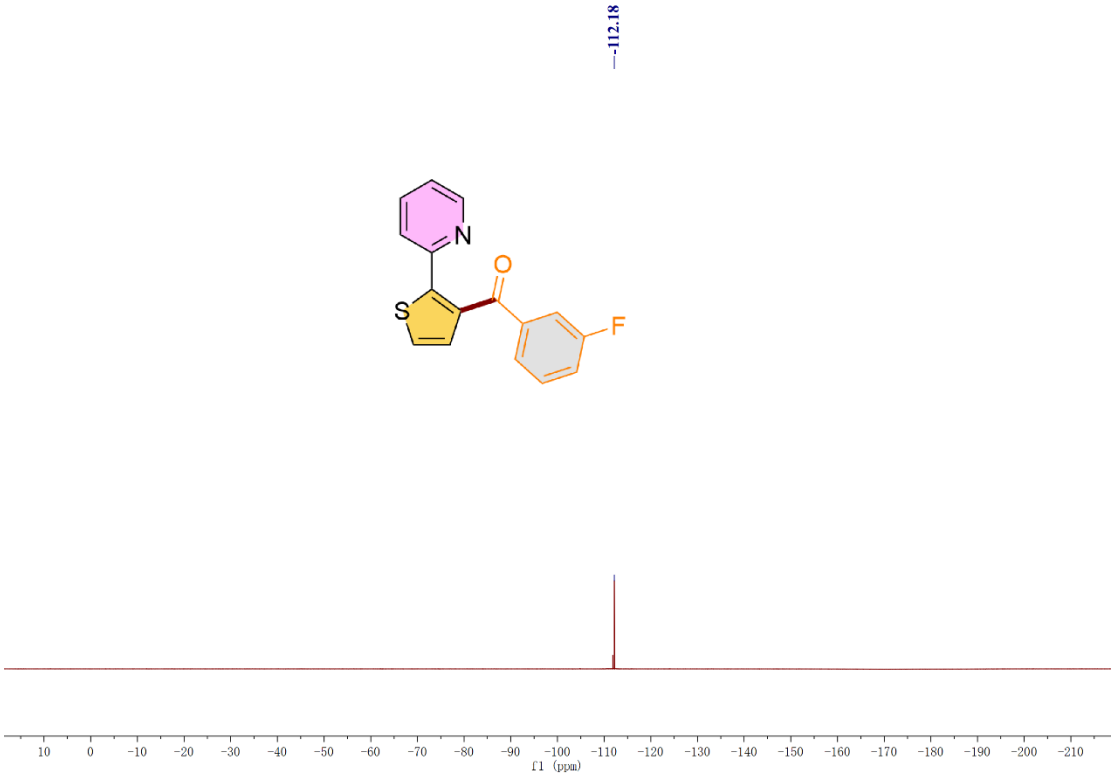
4ah | ^{1}H NMR ($CDCl_3$, 600 MHz)



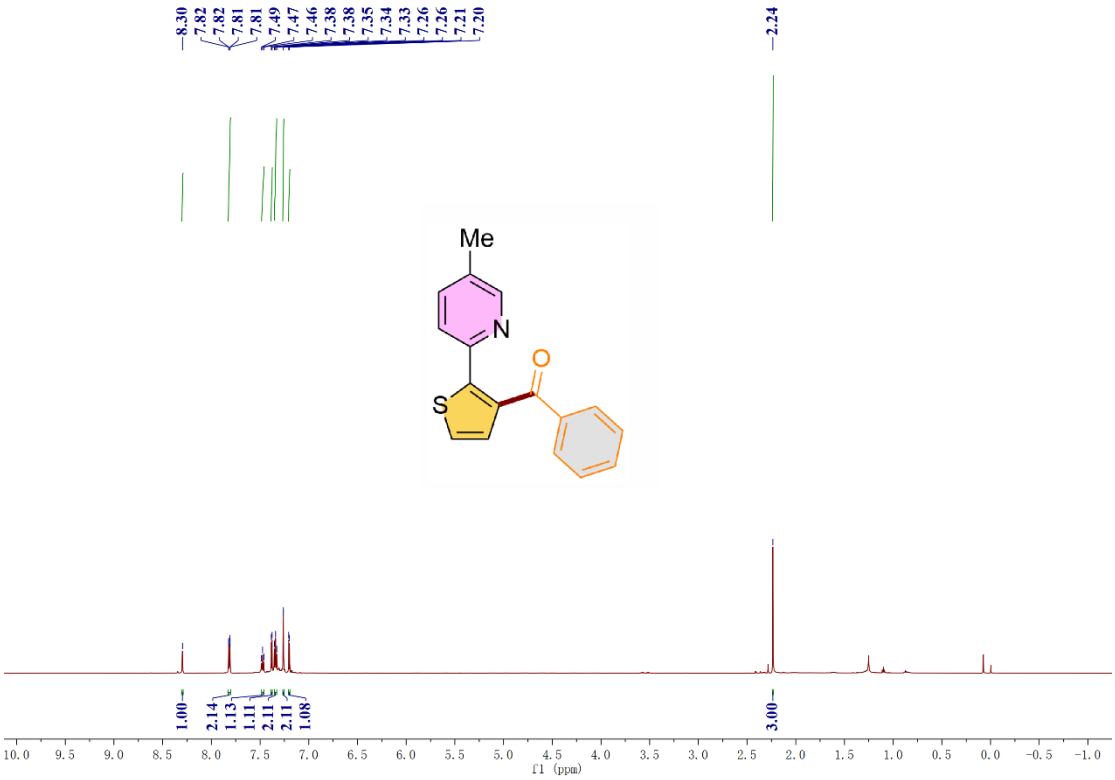
4ah | $^{13}C\{^{1}H\}$ NMR (CCl_3, 151 MHz)



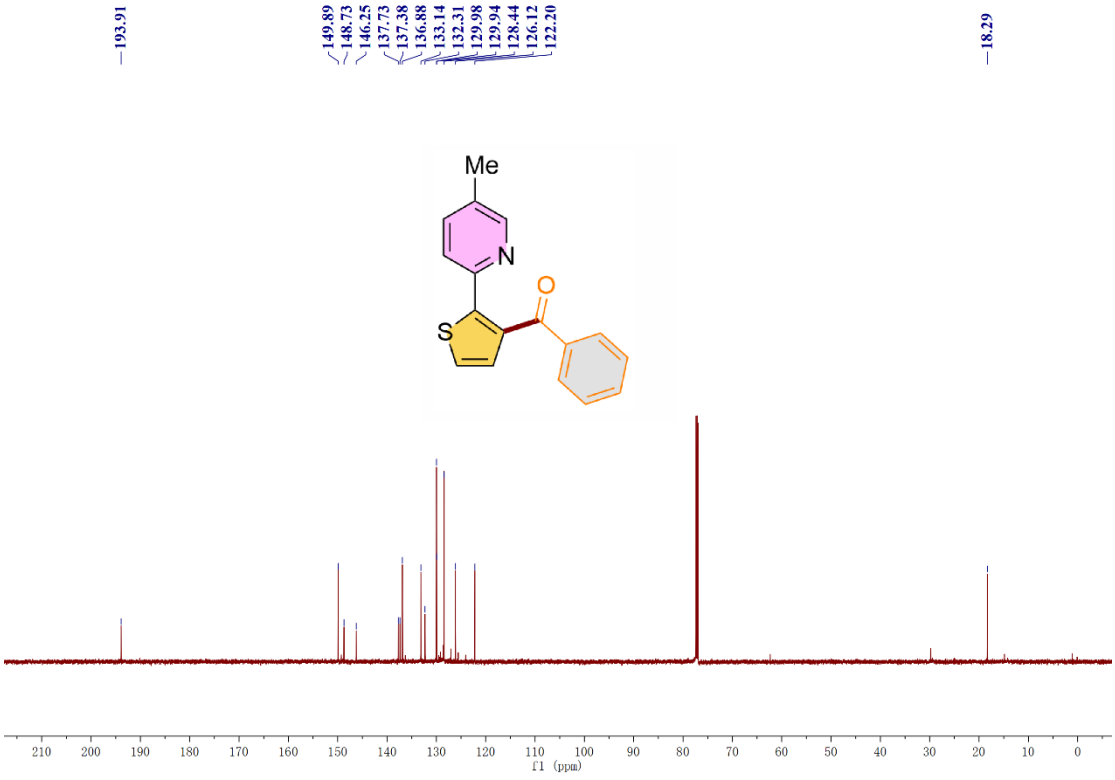
4ah | $^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 565 MHz)



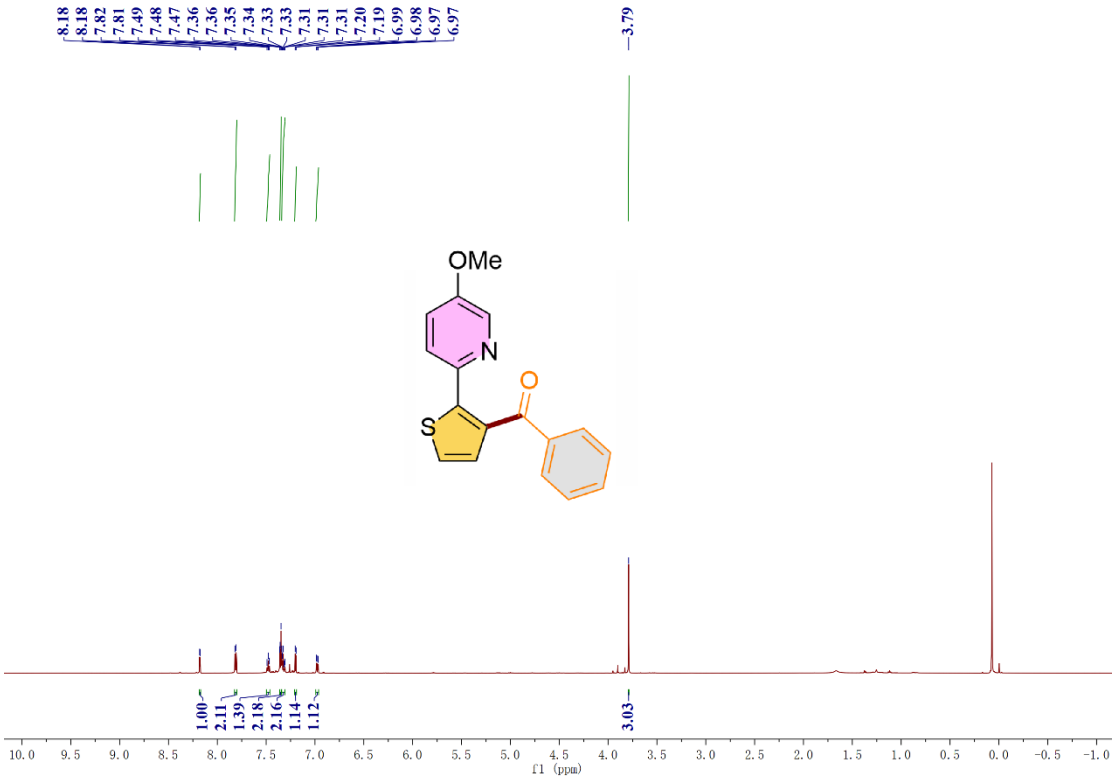
4ba | ^{1}H NMR ($CDCl_3$, 600 MHz)



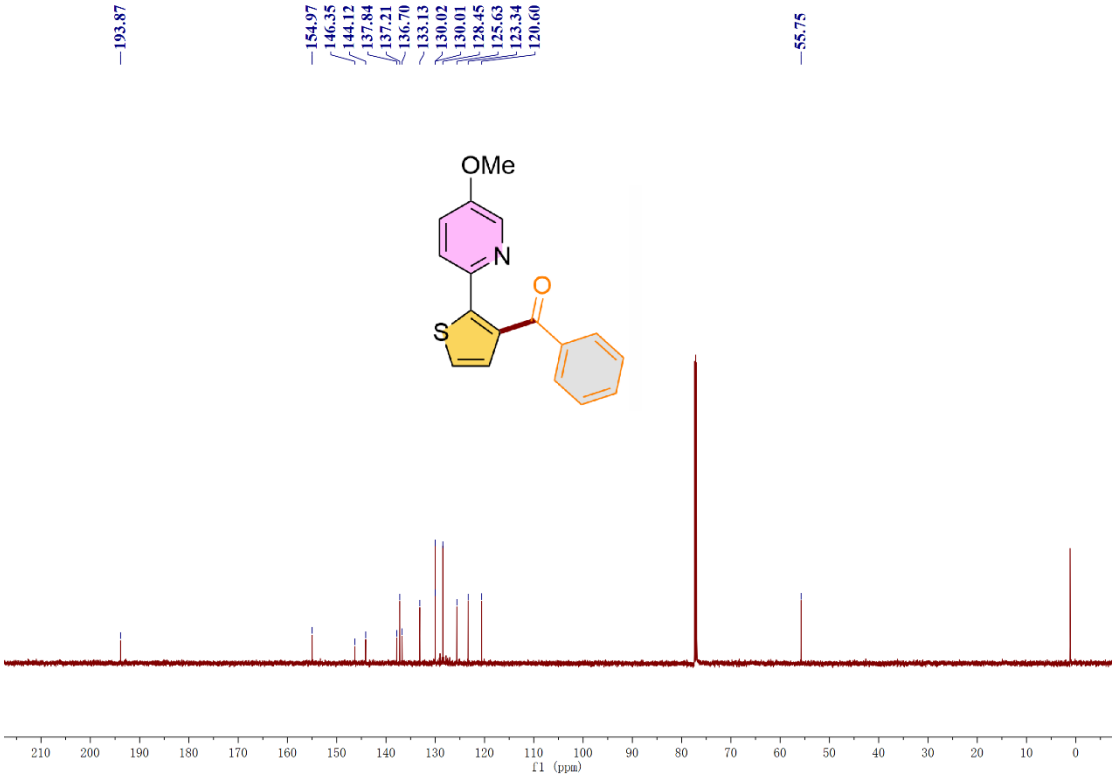
4ba | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



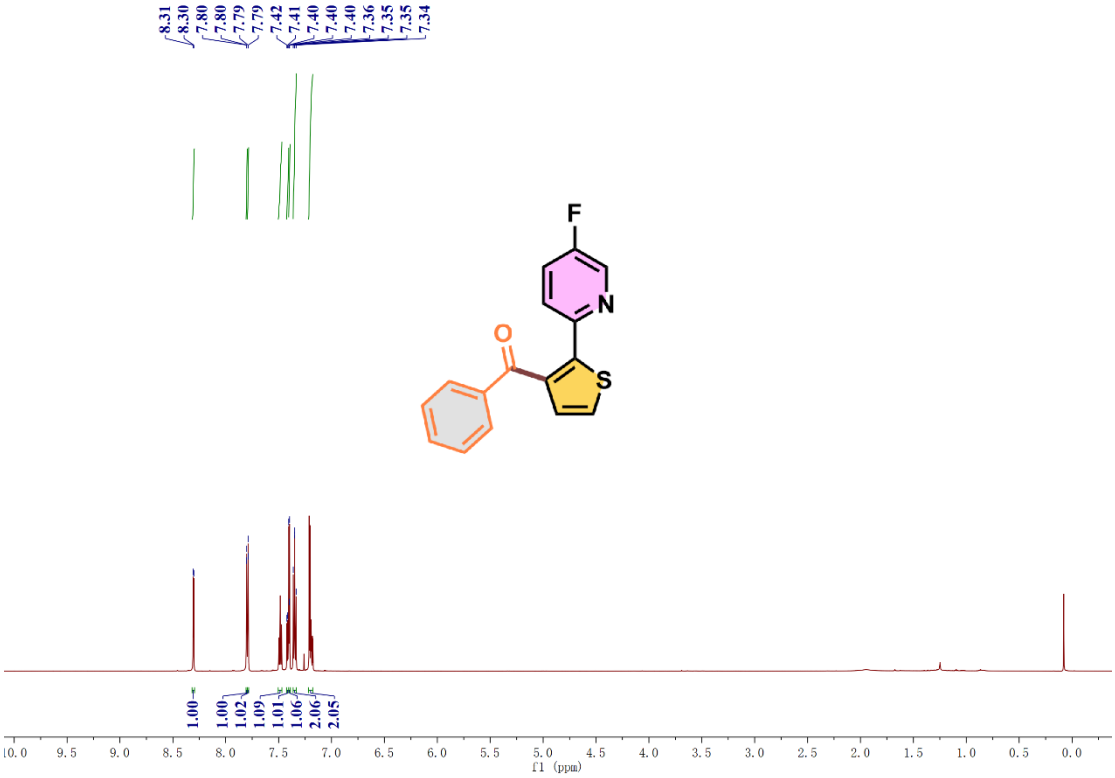
4ca | ^{1}H NMR ($CDCl_3$, 600 MHz)



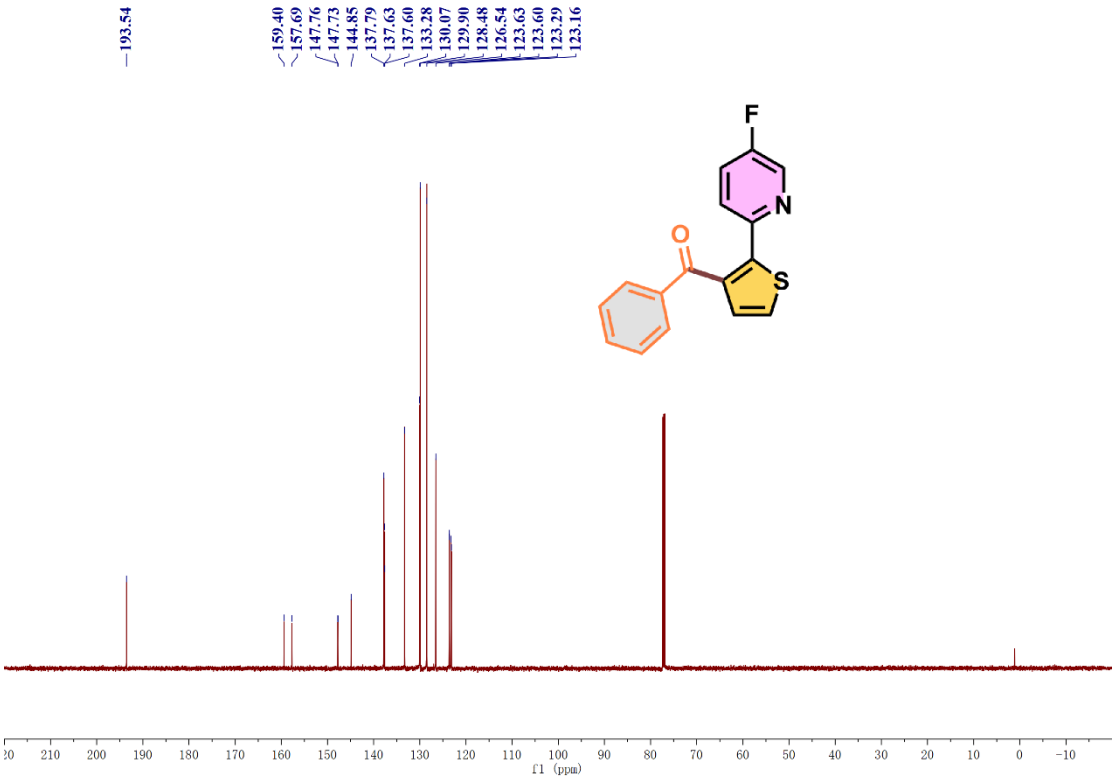
4ca | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



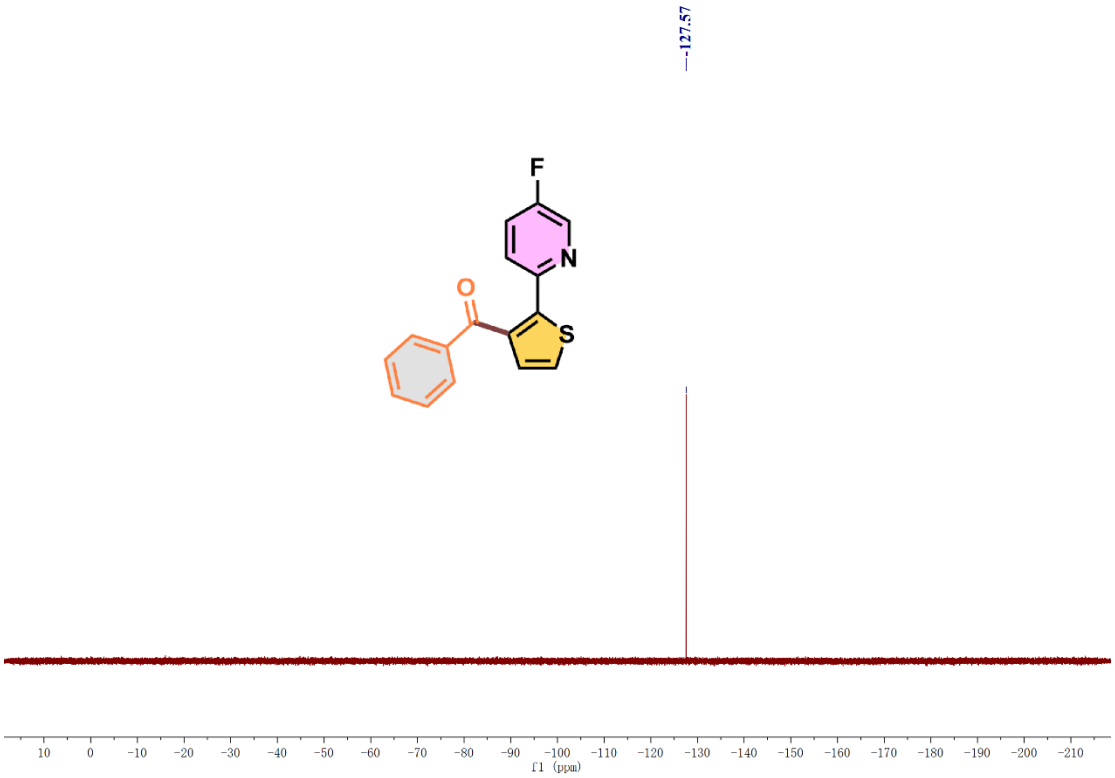
4da | ^{1}H NMR ($CDCl_3$, 600 MHz)



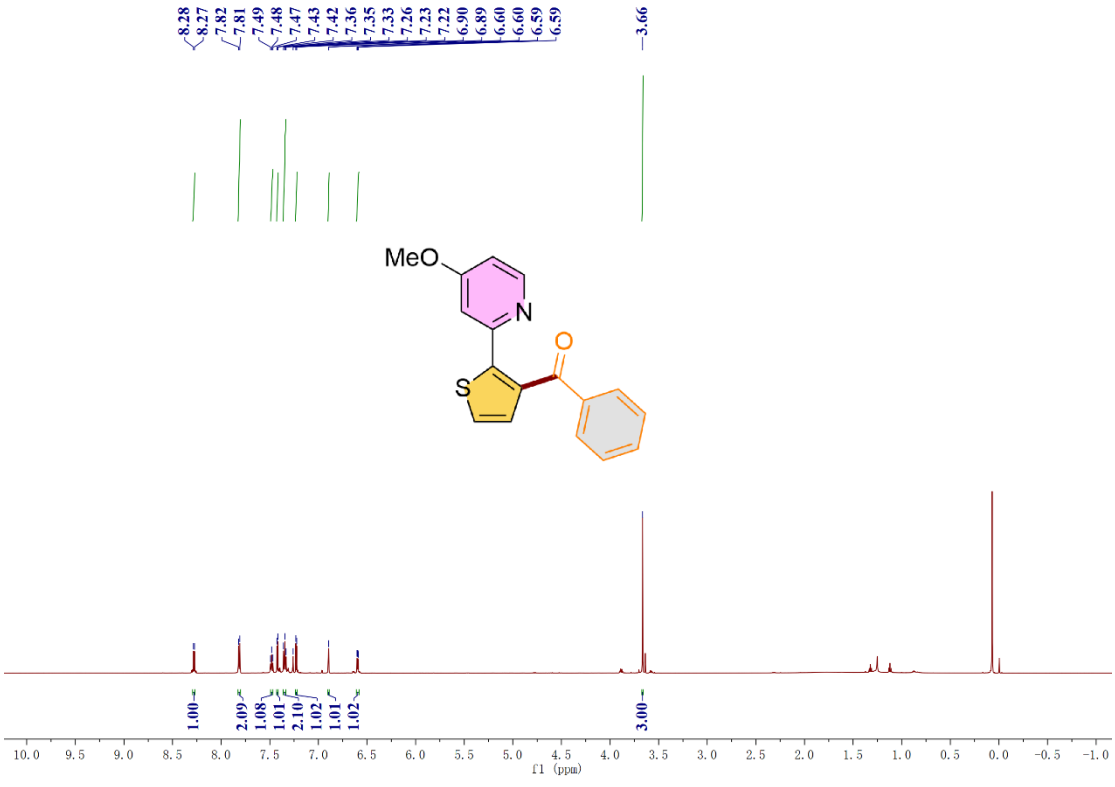
4da | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



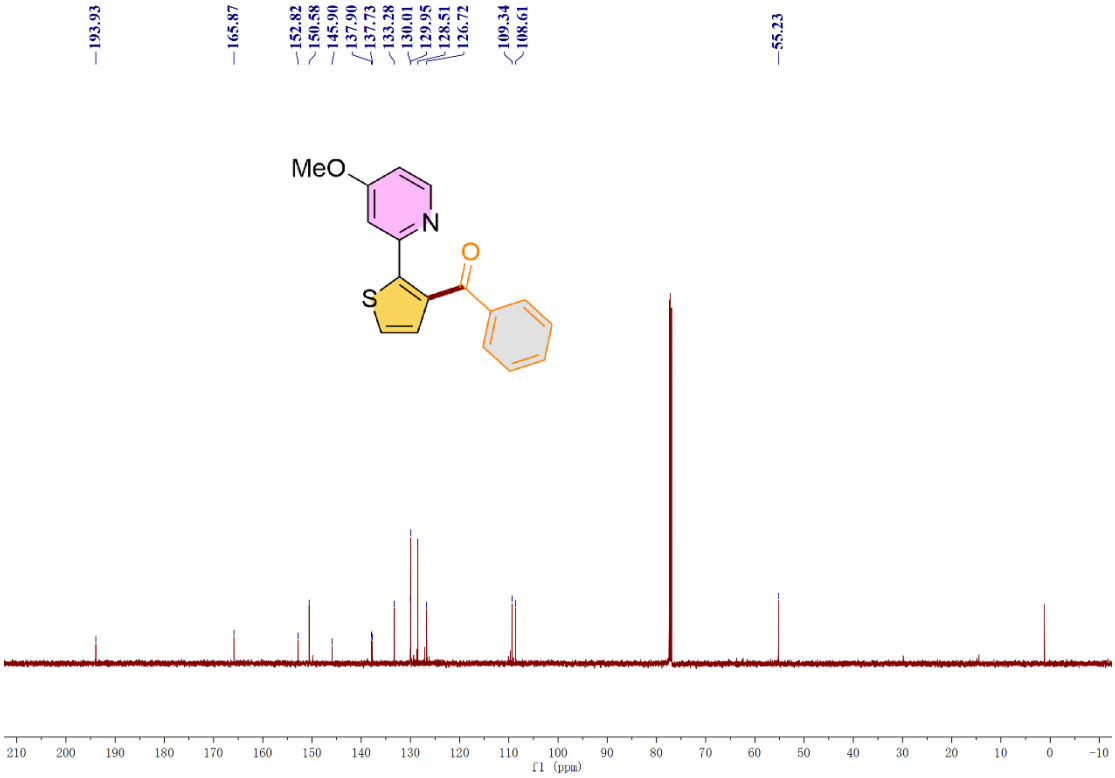
4da | $^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 565 MHz)



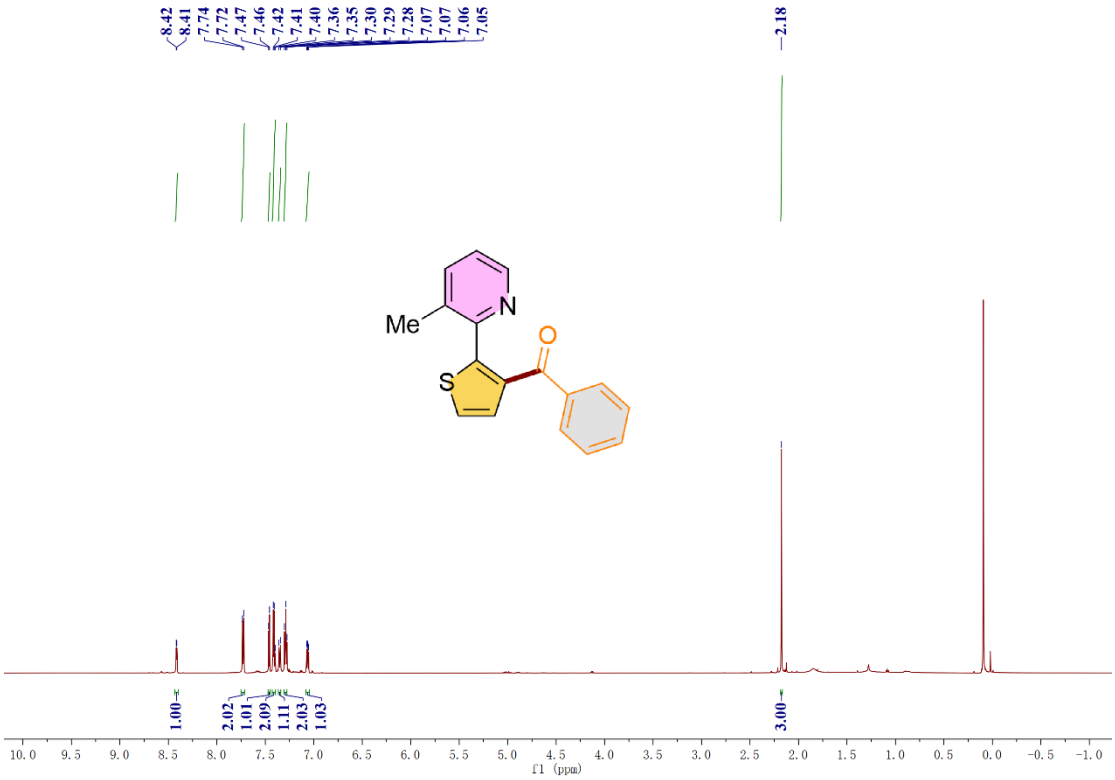
4ja | ^{1}H NMR ($CDCl_3$, 600 MHz)



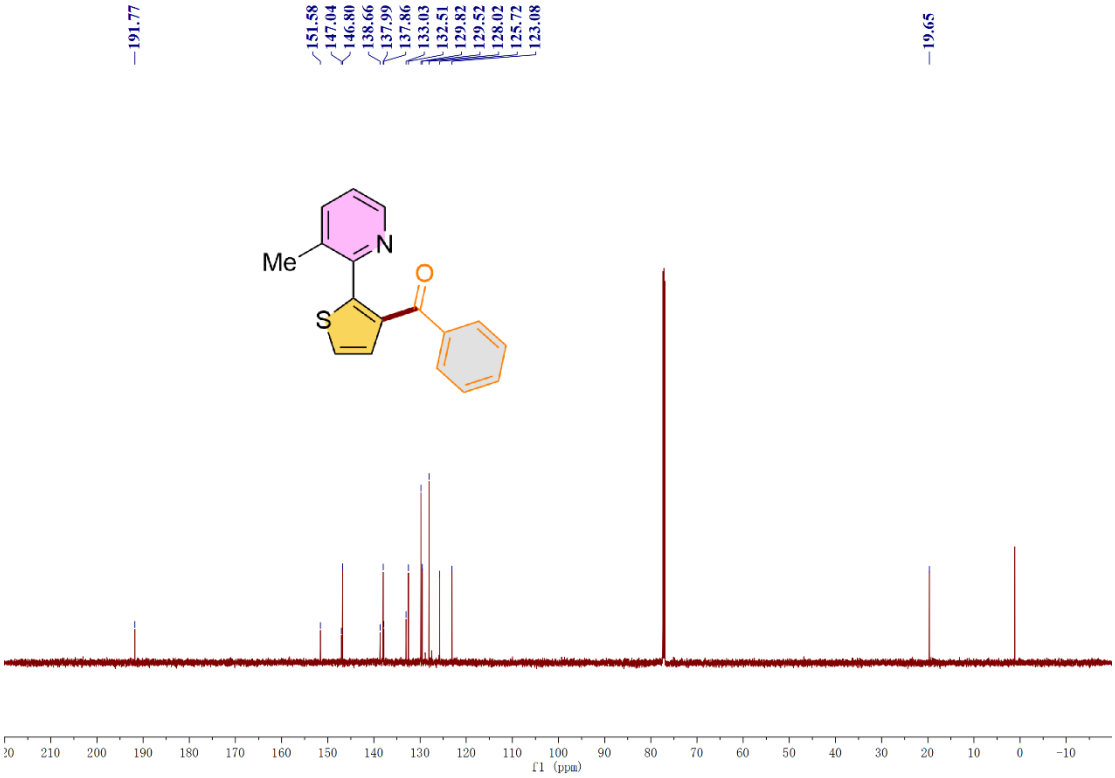
4ja | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



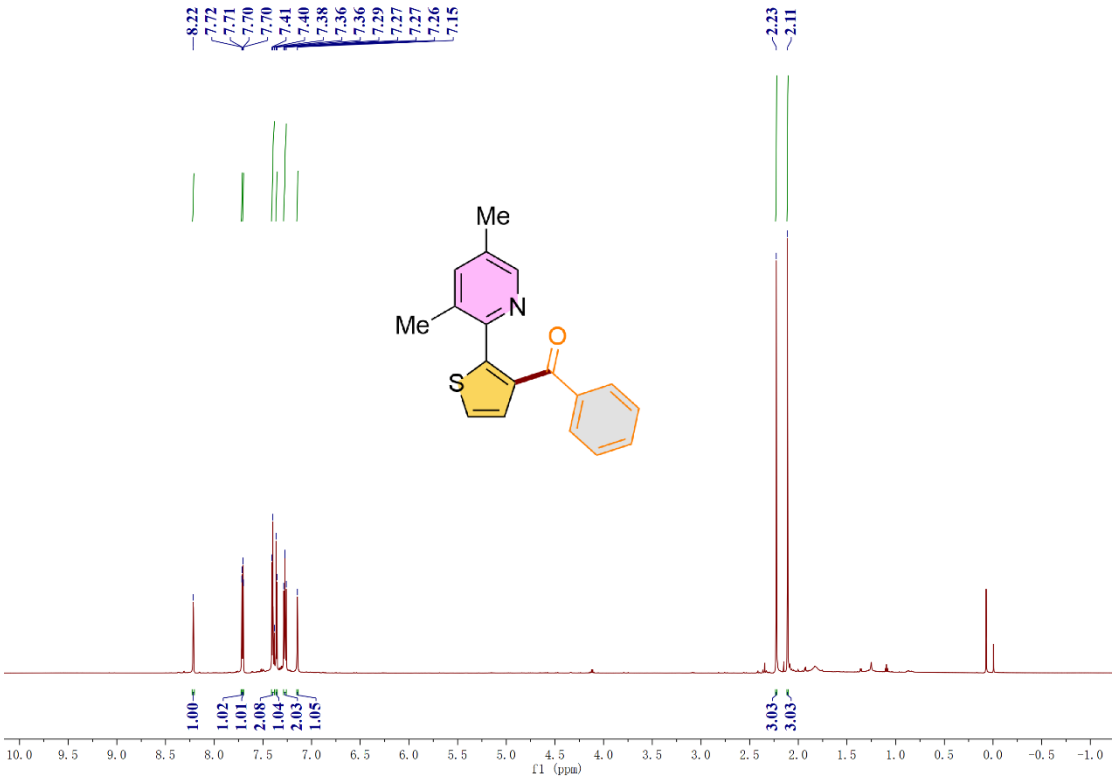
4la | ^{1}H NMR ($CDCl_3$, 600 MHz)



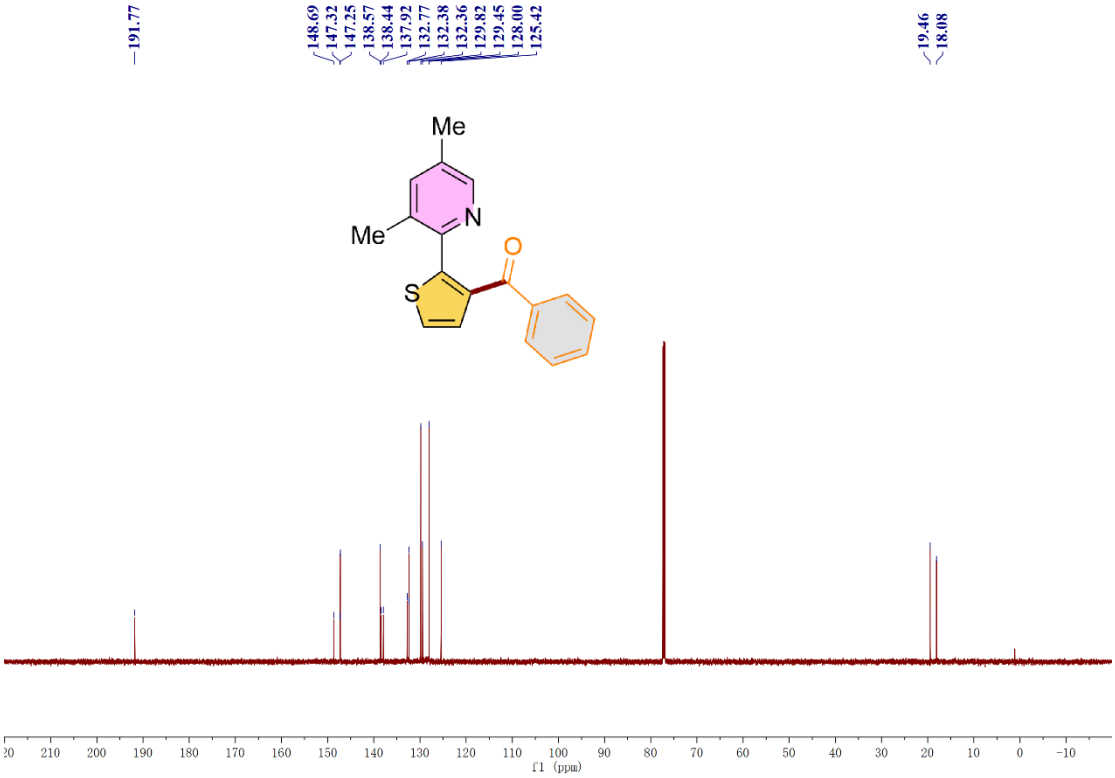
4la | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



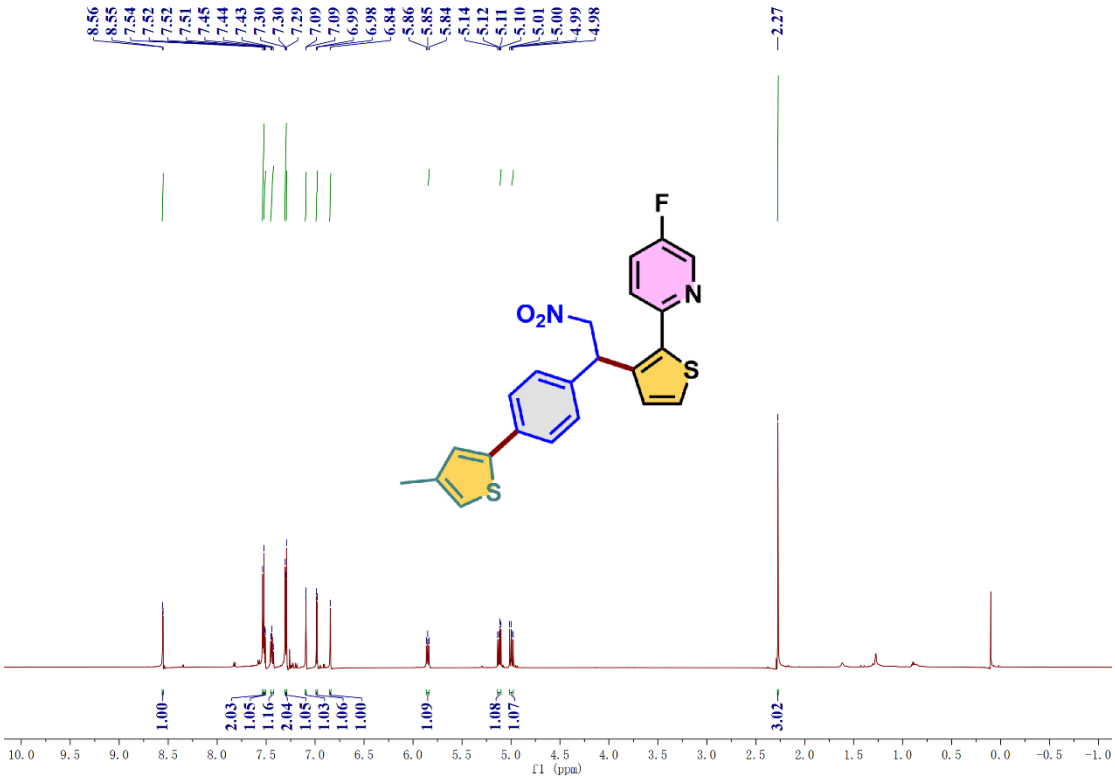
4ma | ^{1}H NMR ($CDCl_3$, 600 MHz)



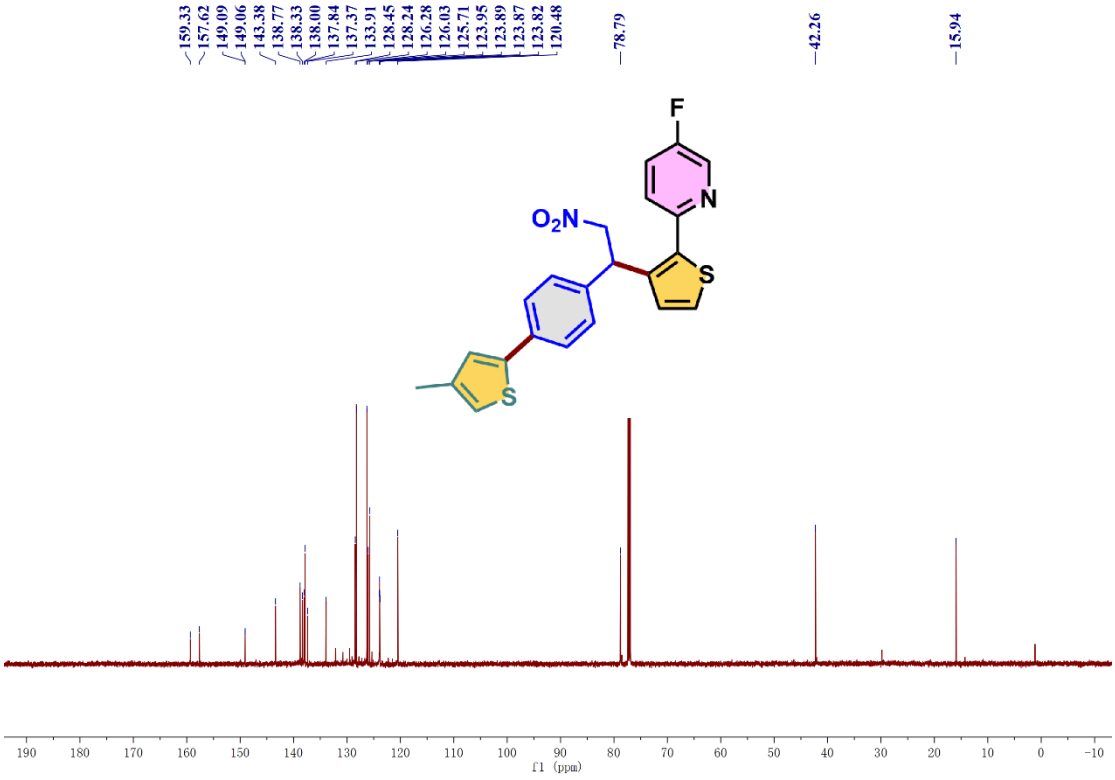
4ma | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



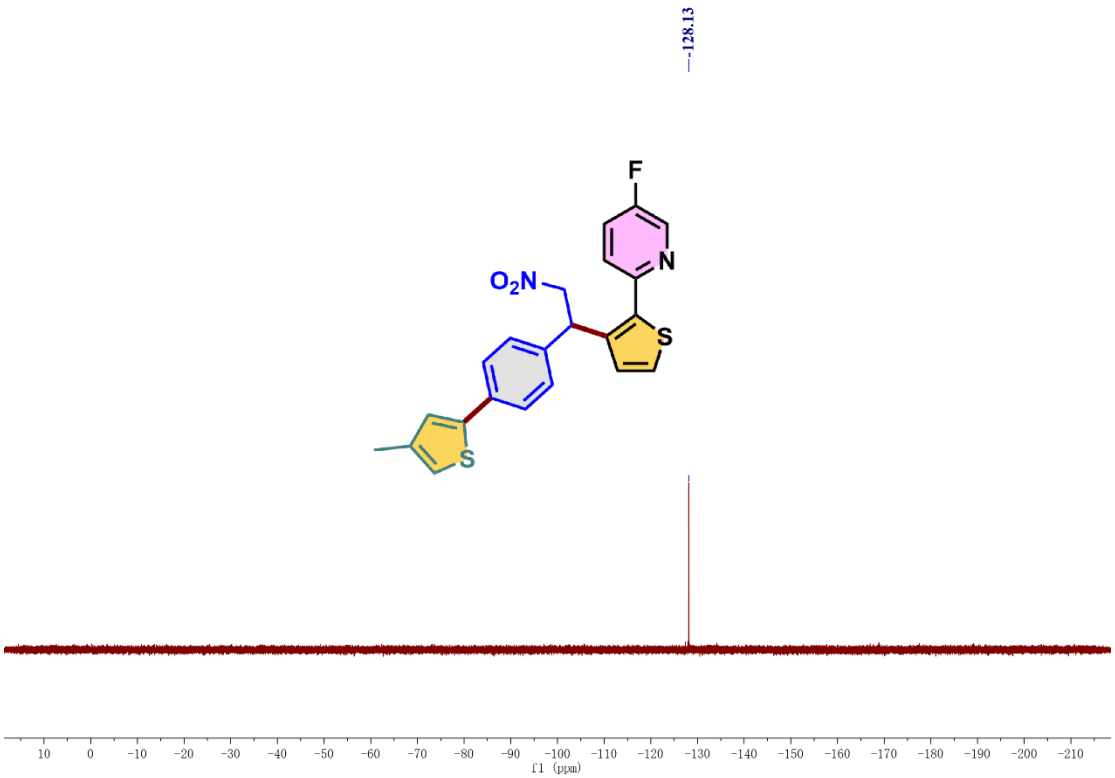
5 | ^{1}H NMR ($CDCl_3$, 600 MHz)



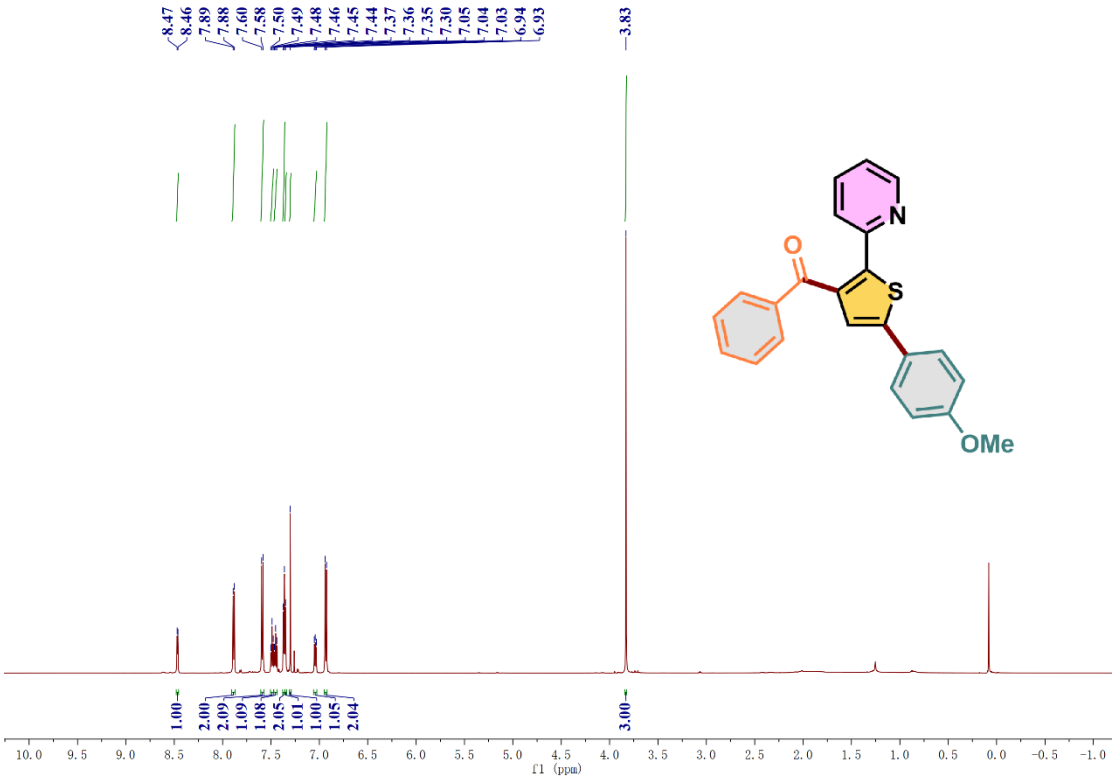
5 | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



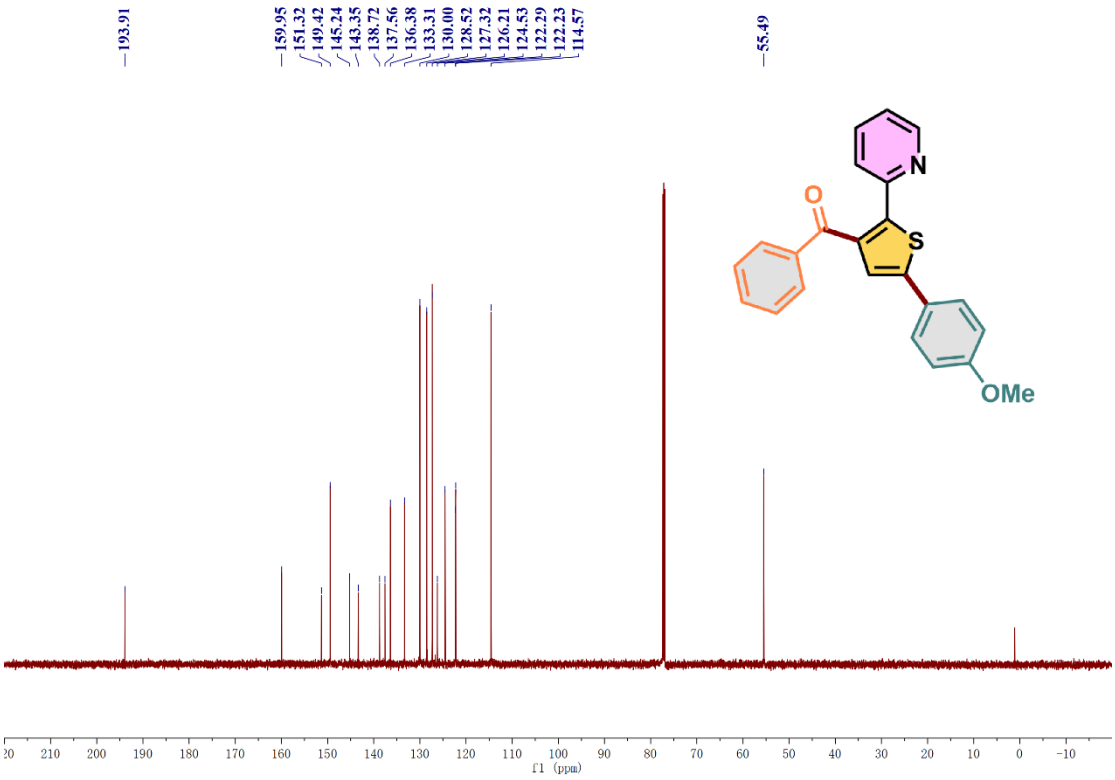
5 | $^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 565 MHz)



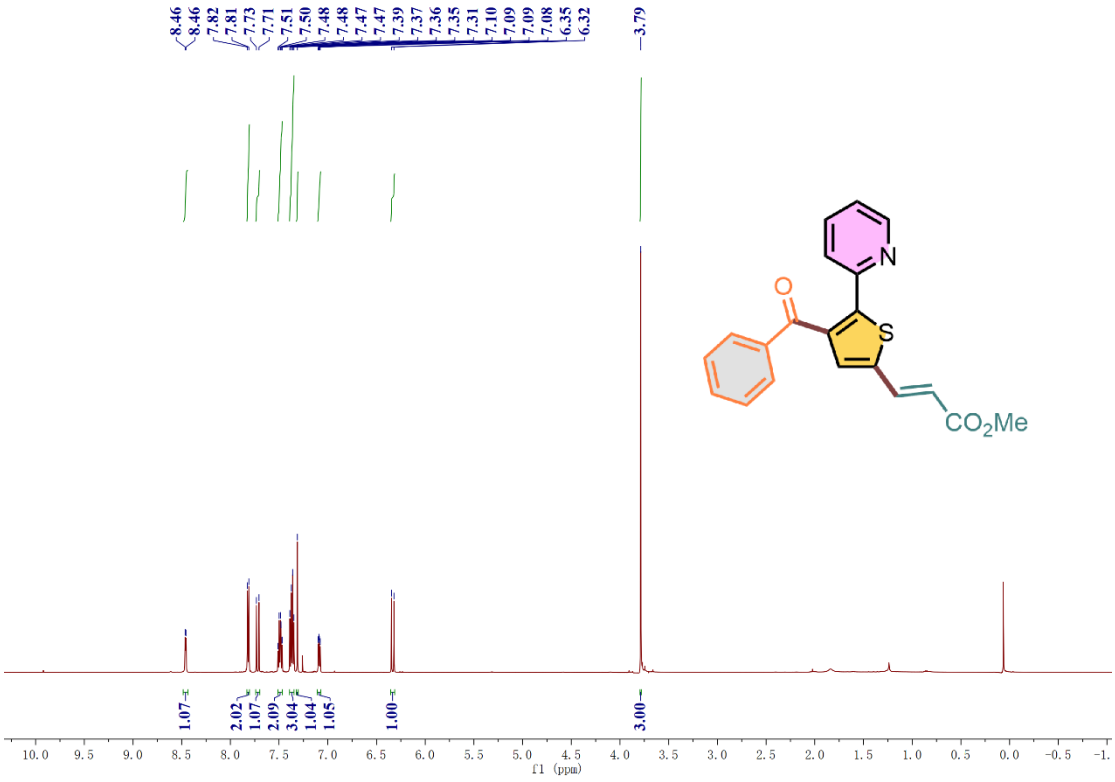
6 | ^{1}H NMR ($CDCl_3$, 600 MHz)



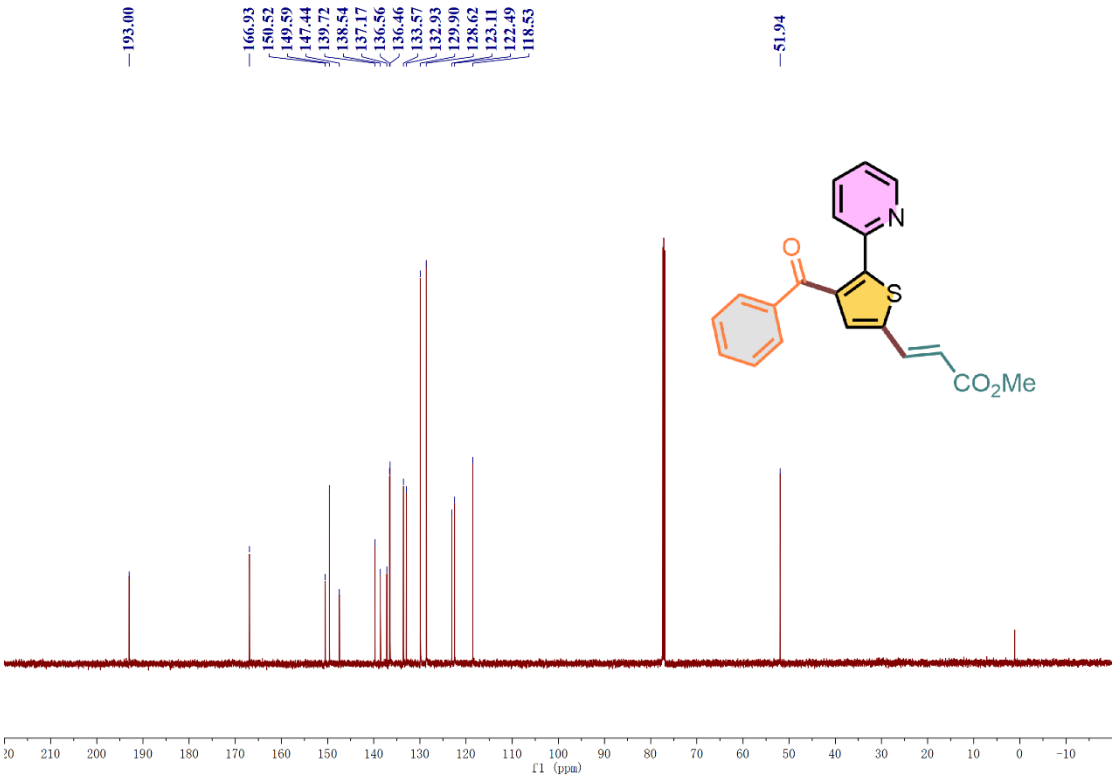
6 | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



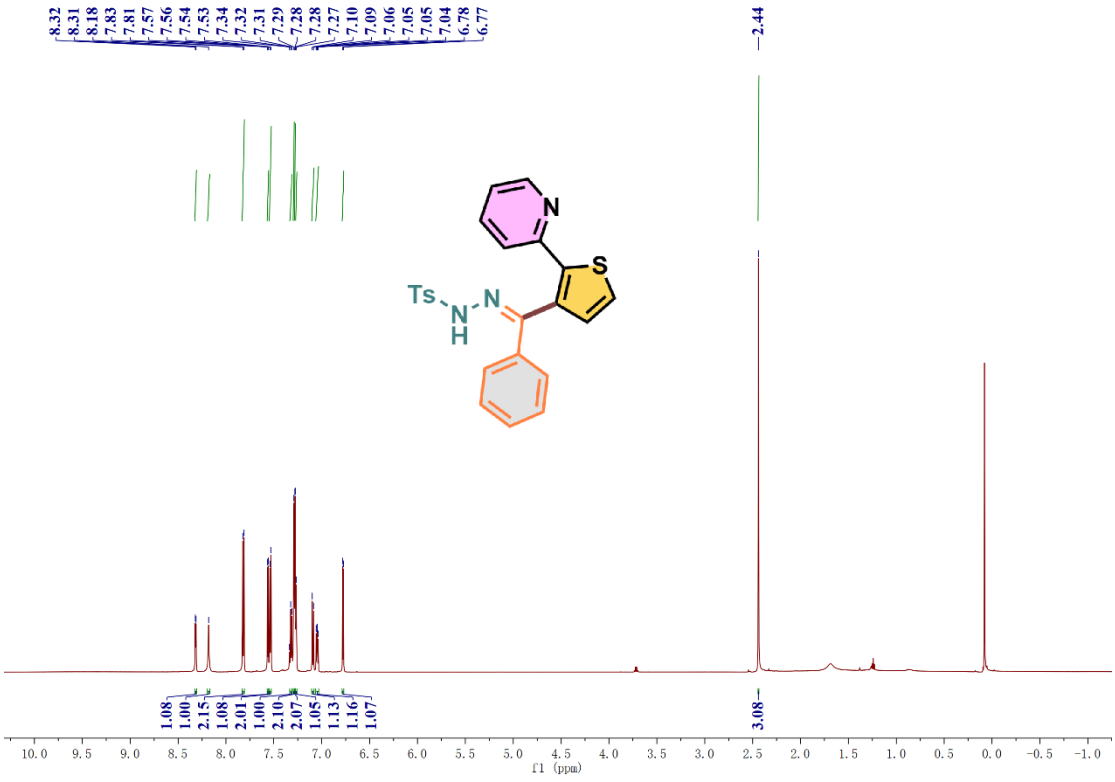
7 | ^{1}H NMR ($CDCl_3$, 600 MHz)



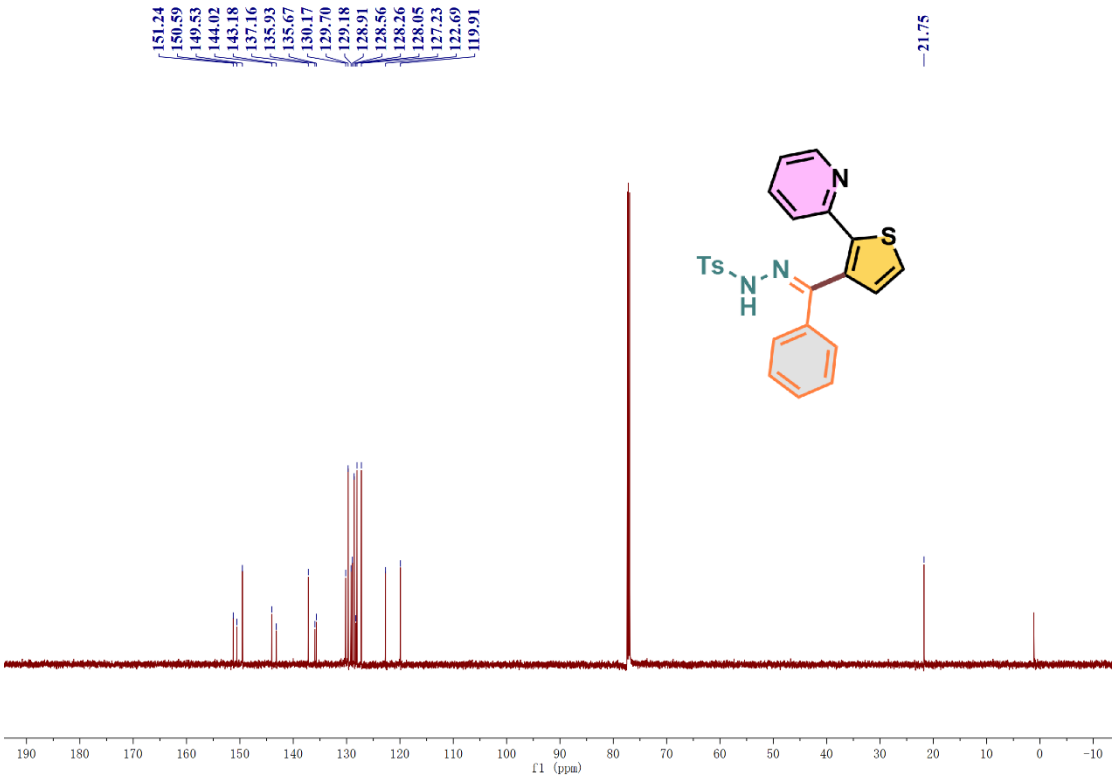
7 | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)



8 | ^{1}H NMR ($CDCl_3$, 600 MHz)



8 | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz)


151.24
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128.26
128.05
127.23
122.69
119.91
21.75
N
S
Ts
N
N
H
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180
170
160
150
140
130
120
110
100
90
80
70
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50
40
30
20
10
0
−10
f1 (ppm)

6. References

1. Gao, D.; Wang, F.; Liu, X. Y.; Feng, K. R.; Zhao, J. Y.; Wang, Y. H.; Yang, X. D.; Tian, P.; Lin, G. Q. Synthesis of Decahydrocyclobuta [cd] indene Skeletons: Rhodium(III)–Catalyzed Hydroarylation and Relay Thiophene–Promoted Intramolecular [2+ 2] Cycloaddition. *Adv. Synth. Catal.* **2020,** *362*, 4384-4390.
2. Lopchuk, J. M.; Hughes, R. P.; Gribble, G. W. What Controls the Regiochemistry in 1, 3–Dipolar Cycloaddition of Münchnones with β–Nitrostyrenes? *Org. Lett.* **2013,** *15*, 5218–5221.
3. Gui, Y.; Zhao, Y.; Li, X.; Liang, T.; Zhao, S.; Zhang, Z. Catalyst–Controlled Regiodivergent C–H Alkynylation of 2–Pyridylthiophenes. *Adv. Synth. Catal.* **2024**. *367.*