SUPPORTING INFORMATION

Palladium-Catalyzed Direct C–H Arylation of 3-(Methylsulfinyl)thiophenes

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1. General Information

All reactions were carried out under an atmosphere of dry nitrogen. Anhydrous cyclopentyl methyl ether (CPME), dioxane, and DME were purchased from Sigma-Aldrich and used as solvent without further purification. THF was dried through activated alumina columns. Unless otherwise stated, reagents were commercially available and used as purchased. Chemicals were obtained from Sigma-Aldrich, Acros, or Matrix Scientific and solvents were purchased from Fisher Scientific. The progress of the reactions was monitored by thin-layer chromatography using Whatman Partisil K6F 250 μmprecoated 60 Å silica gel plates and visualized by short-wave ultraviolet light as well as by treatment with iodine. Flash chromatography was performed with silica gel (230–400 mesh). NMR spectra were obtained using a Brüker 500 MHz Fourier-transform NMR spectrometer. Infrared spectra were obtained with KBr plates using a Perkin-Elmer Spectrum 1600 Series spectrometer. High-resolution mass spectrometry (HRMS) data were obtained on a Waters LC-TOF mass spectrometer (model LCT-XE Premier) using electrospray ionization (ESI) in positive mode. Melting points were determined on a Unimelt Thomas-Hoover melting point apparatus and are uncorrected.

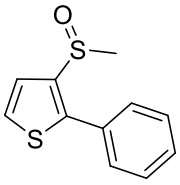
2. Preparation of 3-(Methylsulfinyl)thiophene: 3-(methylsulfinyl)thiophene was prepared according to literature Procedures.[1]

3. Procedures and Characterization of Palladium Catalyzed Arylation of 3-(Methylsulfinyl)thiophene

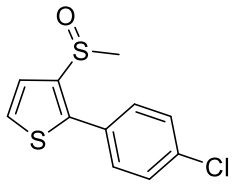
General Procedure A: An oven-dried 10 mL reaction vial equipped with a stir bar was charged with *t*-BuOLi (24.0 mg, 0.3 mmol, 3 equiv) under a nitrogen atmosphere. A solution (from a stock solution) of $Pd(dba)_2$ (5.75 mg, 0.01 mmol) and PhDavePhos (7.63 mg, 0.02 mmol) in 1 mL of dry CPME was added to the reaction vial by syringe. 3-(Methylsulfinyl)thiophene (**1a**) (14.6 mg, 0.1 mmol, 1 equiv) was added to the reaction mixture followed by aryl bromides (0.2 mmol, 2 equiv). Note that aryl bromide in a solid form was added to the reaction vial prior to *t*-BuOLi. The reaction mixture was stirred for 12 h at 100 °C, quenched with two drops of H_2O, diluted with 3 mL of acetone, and filtered over a pad of $MgSO_4$ and silica. The pad was rinsed with additional 7 mL of acetone, and the solution was concentrated *in vacuo*. The crude material was loaded onto a silica gel column and purified by flash chromatography eluting in the conditions described below.

General Procedure B: An oven-dried 10 mL reaction vial equipped with a stir bar was charged with CsOAc (57.6 mg, 0.3 mmol, 3 equiv) under a nitrogen atmosphere. A solution (from a stock solution) of $Pd(dba)_2$ (0.29 mg, 0.0005 mmol) and cataCXium A (0.36 mg, 0.001 mmol) in 1 mL dry CPME was added to the reaction vial by syringe. 3-(Methylsulfinyl)thiophene (**1a**) (14.6 mg, 0.1 mmol, 1 equiv) was added to the reaction mixture followed by aryl bromides (0.3 mmol, 3 equiv). Note that aryl bromide in a solid form was added to the reaction vial prior to CsOAc. The reaction mixture was stirred for 12 h at 100 °C, quenched with two drops of H_2O, diluted with 3 mL of acetone, and filtered over a pad of $MgSO_4$ and silica. The pad was rinsed with additional 7 mL of acetone, and the solution was concentrated *in vacuo*. The crude material was loaded onto a silica gel column and purified by flash chromatography eluting in the conditions described below.

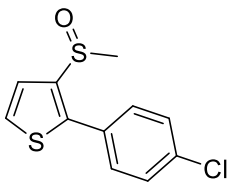
General Procedure C: An oven-dried 10 mL reaction vial equipped with a stir bar was charged with CsOAc (57.6 mg, 0.3 mmol, 3 equiv) under a nitrogen atmosphere. A solution (from a stock solution) of $Pd(dba)_2$ (0.58 mg, 0.001 mmol) and cataCXium A (0.72 mg, 0.002 mmol) in 1 mL of dry CPME was added to the reaction vial by syringe. 3-(Methylsulfinyl)-2-phenylthiophene (22.2 mg, 0.1 mmol, 1 equiv) was added to the reaction mixture followed by aryl bromides (0.2 mmol, 2 equiv). Note that aryl bromide in a solid form was added to the reaction vial prior to CsOAc. The reaction mixture was stirred for 12 h at 100 °C, quenched with two drops of H_2O, diluted with 3 mL of acetone, and filtered over a pad of $MgSO_4$ and silica. The pad was rinsed with additional 7 mL of acetone, and the solution was concentrated *in vacuo*. The crude material was loaded onto a silica gel column and purified by flash chromatography eluting in the conditions described below.



3-(Methylsulfinyl)-2-phenylthiophene (3a): The reaction was performed following the General Procedure A with **1a** (14.6 mg, 0.1 mmol), *t*-BuOLi (24.0 mg, 0.3 mmol) and bromobenzene (**2a**) (31.4 mg, 0.2 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:1 to EtOAc) to give the product **3a** (20.1 mg, 90% yield) as a white solid. M.P. = 72–74 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 22.2, 6.9 Hz, 1H), 7.45 – 7.26 (m, 6H), 2.69 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 144. 6, 140.0, 131.5, 129.4, 129.0, 128.9, 126.5, 124.6, 41.9 ppm; IR (thin film):3932, 3399, 2094, 1642, 1484, 1445, 1414, 1299, 1156, 1030, 760 cm^{-1}; HRMS calculated for $C_{11}H_{10}OS_2Na^+$ 245.0071, found 245.0061$[M+Na]^+$.

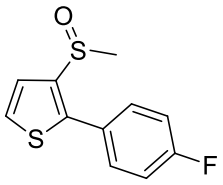


2-(4-Chlorophenyl)-3-(methylsulfinyl)thiophene (3b): The reaction was performed following the General Procedure A with **1a** (14.6 mg, 0.1 mmol), *t*-BuOLi (24.0 mg, 0.3 mmol) and 1-bromo-4-chlorobenzene (**2b**) (38.0 mg, 0.2 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:1 to EtOAc) to give the product **3b** (23.6 mg, 92% yield) as a pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 5.4, 3.2 Hz, 1H), 7.50 – 7.45 (m, 1H), 7.45 – 7.31 (m, 4H), 2.77 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 143.4, 140.5, 135.3, 130.7, 130.0, 129.2, 126.9, 124.8, 41.9 ppm; IR (thin film): 3432, 2102, 1645, 1482, 1400, 1155, 1091, 1014, 951, 828 cm^{-1}; HRMS calculated for $C_{11}H_{10}OS_2Cl^+$ 256.9862, found 256.9856 $[M+H]^+$.

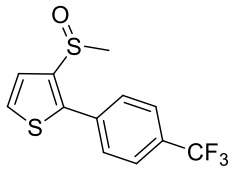


2-(4-Chlorophenyl)-3-(methylsulfinyl)thiophene (3b) (2 mmol scale): To a 50 mL oven-dried round-bottom Schlenk flask equipped with a stir bar was added $Pd(dba)_2$ (115 mg, 0.2 mmol) and PhDavePhos (152.6 mg, 0.4 mmol) under a nitrogen atmosphere inside a glove box. Next, 20.0 mL of dry CPME was added via syringe and the solution was stirred for 2 h at 24 ℃. 3-(Methylsulfinyl)thiophene (**1a**) (292.0 mg, 2 mmol) was added to the reaction mixture followed by 1-bromo-4-chlorobenzene (**2b**) (760.0 mg, 4 mmol) and *t*-BuOLi (480.0 mg, 6 mmol). The reaction mixture was removed from the glove box and stirred for 16 h at 100 °C, then quenched with two drops of H_2O,

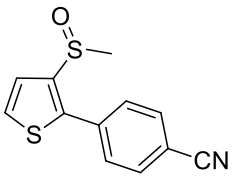
diluted with 60 mL of acetone, and filtered over a pad of $MgSO_4$ and silica. The pad was rinsed with additional 100 mL of acetone, and the solution was concentrated *in vacuo*. The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:1 to EtOAc) to give the product **3b** (430.5 mg, 84% yield) as a pale yellow oil.



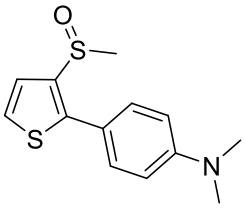
2-(4-Fluorophenyl)-3-(methylsulfinyl)thiophene (3c): The reaction was performed following the General Procedure A with **1a** (14.6 mg, 0.1 mmol), *t*-BuOLi (24.0 mg, 0.3 mmol) and 1-bromo-4-fluorobenzene (**2c**) (35.0 mg, 0.2 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:1 to EtOAc) to give the product **3c** (21.9 mg, 91% yield) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, J = 5.4 Hz, 1H), 7.49 – 7.41 (m, 3H), 7.14 (t, J = 8.4, 2H), 2.77 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 163.2 (d, $J_{C\text{-}F}$ = 252 Hz), 143.7, 140.2, 131.3 (d, $J_{C\text{-}F}$ = 13 Hz), 127.6, 126.7, 124.6, 116.1 (d, $J_{C\text{-}F}$ = 21 Hz), 41.9 ppm; IR (thin film):3073, 2915, 1603, 1525, 1492, 1231, 1159, 953, 837, 761 cm^{-1}; HRMS calculated for $C_{11}H_9ONaS_2F^+$ 262.9977, found 262.9978 $[M+Na]^+$.



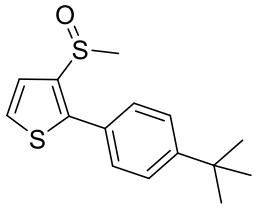
3-(Methylsulfinyl)-2-(4-(trifluoromethyl)phenyl)thiophene (3d): The reaction was performed following the General Procedure A with **1a** (14.6 mg, 0.1 mmol), *t*-BuOLi (24.0 mg, 0.3 mmol) and 4-bromobenzotrifluoride (**2d**) (45.0 mg, 0.2 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:1 to EtOAc) to give the product **3d** (17.5 mg, 60% yield) as a yellow solid. M.P. = 48–50 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (t, J = 13.0 Hz, 2H), 7.64 (t, J = 4.9 Hz, 1H), 7.63 – 7.57 (m, 2H), 7.52 (d, J = 5.4 Hz, 1H), 2.79 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 142.7, 141.3, 135.1, 131.1, 130.9, 129.8, 129.4, 129.0, 127.6, 126.0 (q, $J_{C\text{-}F}$ = 4 Hz), 125.0, 122.7, 42.1 ppm; IR (thin film):3670, 1615, 1408, 1324, 1166, 1068, 1017, 840 cm^{-1}; HRMS calculated for $C_{12}H_{10}OF_3S_2^+$ 291.0125, found 291.0126 $[M+H]^+$.



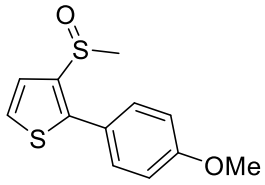
4-(3-(Methylsulfinyl)thiophen-2-yl)benzonitrile (3e): The reaction was performed following the General Procedure A with **1a** (14.6 mg, 0.1 mmol), *t*-BuOLi (24.0 mg, 0.3 mmol) and 4-bromobenzonitrile (**2e**) (36.4 mg, 0.2 mmol) at 100 ℃ for 36 h . The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:1 to EtOAc) to give the product **3e** (18.6 mg, 75% yield) as a white solid. M.P. = 113–115 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 – 7.70 (m, 2H), 7.65 (d, J = 5.4 Hz, 1H), 7.63 – 7.59 (m, 2H), 7.56 (d, J = 5.4 Hz, 1H), 2.80 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 142.2, 141.8, 136.1, 132.7, 130.0, 128.2, 125.3, 118.2, 112.7, 42.0 ppm; IR (thin film):3893, 3790, 2228, 1604, 1488, 1407, 1043, 954, 839 cm^{-1}; HRMS calculated for $C_{12}H_{10}NOS_2^+$ 248.0204, found 248.0209 $[M+H]^+$.



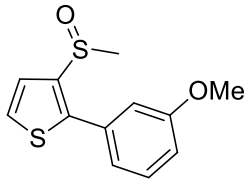
***N,N*-dimethyl-4-(3-(methylsulfinyl)thiophen-2-yl)aniline (3f):** The reaction was performed following the General Procedure A with **1a** (14.6 mg, 0.1 mmol), *t*-BuOLi (24.0 mg, 0.3 mmol) and 4-bromo-*N,N*-dimethylaniline (**2f**) (40.0 mg, 0.2 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:1 to EtOAc) to give the product **3f** (17.8 mg, 67% yield) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 5.5 Hz, 1H), 7.37 – 7.29 (m, 3H), 6.75-6.72 (m, 2H), 3.01 (s, 6H), 2.77 (s, 3H) ppm; ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 150.7, 146.1, 138.1, 130.3, 125.0, 124.4, 119.1, 112.1, 41.9, 40.2 ppm; IR (thin film): 3752, 3583, 3077, 2805, 1607, 1535, 1497, 1360, 1196, 1050, 945, 873 cm^{-1}; HRMS calculated for $C_{13}H_{16}NOS_2^+$ 266.0673, found 266.0672 $[M+H]^+$.



2-(4-(*tert*-Butyl)phenyl)-3-(methylsulfinyl)thiophene (3g): The reaction was performed following the General Procedure A with **1a** (14.6 mg, 0.1 mmol), *t*-BuOLi (24.0 mg, 0.3 mmol) and 1-bromo-4-*tert*-butylbenzene (**2g**) (42.4 mg, 0.2 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:1 to EtOAc) to give the product **3g** (24.8 mg, 89% yield) as a yellow solid. M.P. = 74–76 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (t, *J* = 5.0 Hz, 1H), 7.49 – 7.43 (m, 2H), 7.43 – 7.36 (m, 3H), 2.77 (s, 3H), 1.35 (s, 9H) ppm; ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 152.3, 144.8, 139.6, 129.0, 128.6, 126.2, 125.8, 124.5, 42.0, 34.7, 31.1 ppm; IR (thin film):3431, 2968, 2091, 1644, 1492, 1269, 1154, 1111, 1027 cm^{-1}; HRMS calculated for $C_{15}H_{19}OS_2^+$ 279.0877, found 279.0881 $[M+H]^+$.

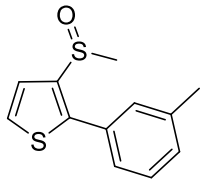


2-(4-Methoxyphenyl)-3-(methylsulfinyl)thiophene (3h): The reaction was performed following the General Procedure A with **1a** (14.6 mg, 0.1 mmol), *t*-BuOLi (24.0 mg, 0.3 mmol) and 1-bromo-4-methoxybenzene (**2h**) (37.2 mg, 0.2 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:1 to EtOAc) to give the product **3h** (19.7 mg, 78% yield) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 5.4 Hz, 1H), 7.39 (m, 3H), 7.00 – 6.91 (m, 2H), 3.85 (s, 3H), 2.76 (s,3H) ppm; ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 160.3, 144.9, 139.3, 130.7, 125.9, 124.5, 124.0, 114.4, 55.4, 41.9 ppm; IR (thin film):3450, 2800, 1560, 1484, 1290, 1267, 1204, 1042, 955, 784 cm^{-1}; HRMS calculated for $C_{12}H_{13}O_2S_2^+$ 253.0357, found 253.0360 [$M+H]^+$.

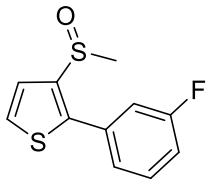


2-(3-Methoxyphenyl)-3-(methylsulfinyl)thiophene (3i): The reaction was performed following the General Procedure A with **1a** (14.6 mg, 0.1 mmol), *t*-BuOLi (24.0 mg, 0.3 mmol) and 1-bromo-3-methoxybenzene (**2i**) (37.2 mg, 0.2 mmol) at 100 ℃ for 16 h. The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:1 to EtOAc) to give the product **3i** (20.7 mg, 82% yield) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 5.4, 1.5 Hz, 1H), 7.46-7.42 (m, 1H), 7.35 (m, 1H), 7.12 – 7.00 (m, 2H), 6.96 (d, *J* = 8.4 Hz, 1H), 3.85 (s, 3H), 2.76 (s, 3H) ppm; ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 159.8, 144.1, 140.2, 132.7, 130.0, 126.4, 124.6, 121.7, 114.8,

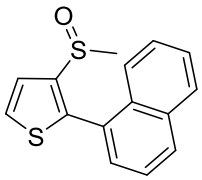
114.6, 55.3, 42.0 ppm; IR (thin film):3448, 2836, 1598, 1482, 1290, 1267, 1204, 1042, 955, 784 cm^{-1} ; HRMS calculated for $C_{12}H_{12}O_2S_2Na^+$ 275.0176, found 275.0165 $[M+Na]^+$.



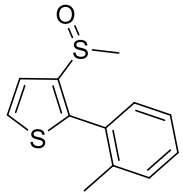
3-(Methylsulfinyl)-2-(m-tolyl)thiophene (3j): The reaction was performed following the General Procedure A with **1a** (14.6 mg, 0.1 mmol), *t*-BuOLi (24.0 mg, 0.3 mmol) and 3-bromotoluene (**2j**) (34.0 mg, 0.2 mmol) at 100 ℃ for 16 h. The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:1 to EtOAc) to give the product **3j** (20.1 mg, 85% yield) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 5.5 Hz, 1H), 7.49 – 7.41 (m, 1H), 7.37 – 7.19 (m, 4H), 2.78 (s, 3H), 2.42 (s, 3H) ppm; ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 144.9, 139.9, 138.8, 131.5, 130.0, 129.9, 128.8, 126.6, 126.5, 124. 6, 42.1, 21.5 ppm; IR (thin film):3450, 2832, 1600, 1480, 1280, 1267, 1209, 1056, 955, 776 cm^{-1}; HRMS calculated for $C_{12}H_{13}OS_2^+$ 237.0402, found 237.0399 $[M+H]^+$.



2-(3-Fluorophenyl)-3-(methylsulfinyl)thiophene (3k): The reaction was performed following the General Procedure A with **1a** (14.6 mg, 0.1 mmol), *t*-BuOLi (24.0 mg, 0.3 mmol) and 1-bromo-3-fluorobenzene (**2k**) (35.0 mg, 0.2 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:1 to EtOAc) to give the product **3k** (19.2 mg, 80% yield) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 5.4 Hz, 1H), 7.58 – 7.38 (m, 2H), 7.38 – 7.04 (m, 3H), 2.78 (s, 3H) ppm; ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 162.7 (d, $J_{C\text{-}F}$ = 250 Hz), 142.9 (d, $J_{C\text{-}F}$ = 3 Hz), 140.8, 133.5 (d, $J_{C\text{-}F}$ = 9 Hz), 130.6 (d, $J_{C\text{-}F}$ = 9 Hz), 127.2, 125.2, 124.8, 116.4 (d, $J_{C\text{-}F}$ = 23 Hz), 116.0 (d, $J_{C\text{-}F}$ = 21 Hz), 42.0 ppm; IR (thin film): 3029, 2920, 1603, 1552, 1490, 1229, 1160, 953, 837, 756 cm^{-1}; HRMS calculated for $C_{11}H_{10}OFS_2^+$ 241.0152, found 241.0148 $[M+H]^+$.

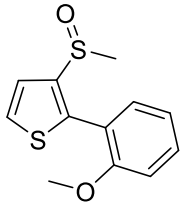


3-(Methylsulfinyl)-2-(naphthalen-1-yl)thiophene (3l): The reaction was performed following the General Procedure A with **1a** (14.6 mg, 0.1 mmol), *t*-BuOLi (24.0 mg, 0.3 mmol) and 1-bromonaphthalene (**2l**) (41.2 mg, 0.2 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:1 to EtOAc) to give the product **3l** (23.2 mg, 85% yield) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 – 7.89 (m, 2H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.69 (d, *J* = 5.4 Hz, 1H), 7.61 (d, *J* = 5.3 Hz, 1H), 7.56 – 7.47 (m, 4H), 2.62 (s, 3H) ppm; ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 142.9, 141.3, 133.6, 132.4, 130.1, 129.4, 128.5, 128.4, 127.7, 127.2, 126.5, 125.2, 125.0, 123.7, 42.4 ppm; IR (thin film):3582, 3069, 1591, 1502, 1387, 1296, 1156, 1042, 953, 800, 776 cm^{-1} ; HRMS calculated for $C_{15}H_{13}OS_2^+$ 273.0402, found 273.0406 $[M+H]^+$.

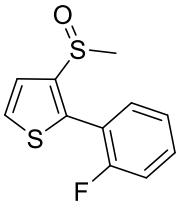


3-(Methylsulfinyl)-2-(*o*-tolyl)thiophene (3m): The reaction was performed following the General Procedure A with **1a** (14.6 mg, 0.1 mmol), *t*-BuOLi (24.0 mg, 0.3 mmol) and 1-bromo-2-methylbenzene (**2m**) (34.0 mg, 0.2 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:1 to EtOAc) to give the product **3m** (18.9 mg, 80% yield) as a yellow oil. ^{1}H NMR (500

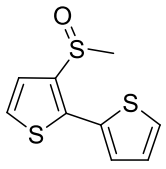
MHz, $CDCl_3$) δ 7.58 (d, *J* = 5.4 Hz, 1H), 7.50 (d, *J* = 5.4 Hz, 1H), 7.37 – 7.32 (m, 1H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 3.9 Hz, 2H), 2.66 (s, 3H), 2.27 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 142.9, 141.5, 137.5, 131.2, 130.6, 130.5, 129.6, 127.2, 125.8, 123.5, 42.1, 20.4 ppm; IR (thin film):3447, 2921, 2126, 1644, 1481, 1231, 1158, 1117, 952, 759 cm^{-1}; HRMS calculated for $C_{12}H_{12}ONaS_2^+$ 259.0227, found 259.0234 $[M+Na]^+$.



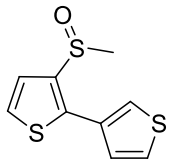
2-(2-Methoxyphenyl)-3-(methylsulfinyl)thiophene (3n): The reaction was performed following the General Procedure A with **1a** (14.6 mg, 0.1 mmol), *t*-BuOLi (24.0 mg, 0.3 mmol) and 2-bromoanisole (**2n**) (37.2 mg, 0.2 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:1 to EtOAc) to give the product **3n** (19.7 mg, 78% yield) as a yellow oil. ^1H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 5.5 Hz, 1H), 7.51 (d, *J* = 5.5 Hz, 1H), 7.46 – 7.41 (m, 1H), 7.39 – 7.30 (m, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 7.00 (d, *J* = 8.3 Hz, 1H), 3.85 (s, 3H), 2.80 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 156.3, 141.3, 140.1, 132.1, 130.9, 127.2, 123.8, 120.9, 120.2, 111.2, 55.4, 41.7 ppm; IR (thin film):3452, 2810, 1598, 1480, 1295, 1267, 1240, 1049, 955, 786 cm^{-1} ; HRMS calculated for $C_{12}H_{13}O_2S_2^+$ 253.0352, found 253.0349 $[M+H]^+$.



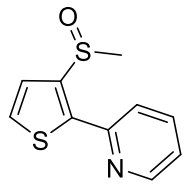
2-(2-Fluorophenyl)-3-(methylsulfinyl)thiophene (3o): The reaction was performed following the General Procedure A with **1a** (14.6 mg, 0.1 mmol), *t*-BuOLi (24.0 mg, 0.3 mmol) and 1-bromo-2-fluorobenzene (**2o**) (35.0 mg, 0.2 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:1 to EtOAc) to give the product **3o** (20.6 mg, 86% yield) as a yellow oil. ^1H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 5.4 Hz, 1H), 7.56 (d, *J* = 5.4 Hz, 1H), 7.50 – 7.37 (m, 2H), 7.26 – 7.21 (m, 1H), 7.18 (t, *J* = 9.0 Hz, 1H), 2.83 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 159.2 (d, $J_{C\text{-}F}$ = 248 Hz), 142.2, 137.1, 132.2 (d, $J_{C\text{-}F}$ = 3 Hz), 131.4 (d, $J_{C\text{-}F}$ = 8 Hz), 128.3, 124.6 (d, $J_{C\text{-}F}$ = 4 Hz), 124.07, 119.3 (d, $J_{C\text{-}F}$ = 14 Hz), 116.1 (d, $J_{C\text{-}F}$ = 21 Hz), 41.89 ppm; IR (thin film): 3030, 2922, 1623, 1548, 1337, 1249, 1157, 953, 856, 759 cm^{-1}; HRMS calculated for $C_{11}H_{10}OFS_2^+$ 241.0152, found 241.0146 $[M+H]^+$.



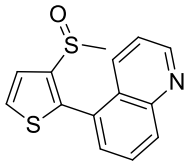
3-(Methylsulfinyl)-2,2'-bithiophene (3p): The reaction was performed following the General Procedure A with **1a** (14.6 mg, 0.1 mmol), *t*-BuOLi (24.0 mg, 0.3 mmol) and 2-bromothiophene (**2p**) (32.4 mg, 0.2 mmol) at 100 °C for 36 h. The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:1 to EtOAc) to give the product **3p** (14.4 mg, 63% yield) as a yellow oil. ^1H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 5.5 Hz, 1H), 7.40 (dd, *J* = 5.1, 1.0 Hz, 1H), 7.37 (d, *J* = 5.5 Hz, 1H), 7.23 (dd, *J* = 3.6, 1.0 Hz, 1H), 7.08 (dd, *J* = 5.1, 3.7 Hz, 1H), 2.81 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 140.6, 136.4, 132.7, 128.0(4), 128.0(1), 127.8, 126.2, 124.9, 42.3 ppm; IR (thin film): 3400, 2091, 1622, 1480, 1411, 1338, 1289, 1243, 1150,1085, 1024, 898 cm^{-1}; HRMS calculated for $C_9H_8OS_3Na^+$ 250.9635, found 250.9639 $[M+Na]^+$.



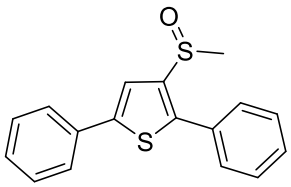
3-(Methylsulfinyl)-2,3'-bithiophene (3q): The reaction was performed following the General Procedure A with **1a** (14.6 mg, 0.1 mmol), *t*-BuOLi (24.0 mg, 0.3 mmol) and 3-bromothiophene (**2q**) (32.4 mg, 0.2 mmol) at 100 °C for 36 h. The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:1 to EtOAc) to give the product **3q** (18.2 mg, 80% yield) as a yellow solid. M.P. = 58–60 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 5.4 Hz, 1H), 7.48-7.46 (m, 1H), 7.42 (m, 1H), 7.38 (d, *J* = 5.4 Hz, 1H), 7.30 – 7.20 (m, 1H), 2.78 (s, 3H) ppm; ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 139.9, 138.8, 131.8, 128.0, 126.9, 125.7, 124.6, 124.5(7), 41.8 ppm; IR (thin film): 3435, 2091, 1643, 1486, 1413, 1336, 1297, 1246, 1153,1085, 1024 cm^{-1}; HRMS calculated for $C_9H_9OS_3^+$ 228.9816, found 228.9804 $[M+H]^+$.



2-(3-(Methylsulfinyl)thiophen-2-yl)pyridine (3r): The reaction was performed following the General Procedure A with **1a** (14.6 mg, 0.1 mmol), *t*-BuOLi (24.0 mg, 0.3 mmol) and 2-bromopyridine (**2r**) (31.4 mg, 0.2 mmol) at 100 ℃ for 36 h. The crude product was purified by flash chromatography on silica gel (eluted with EtOAc) to give the product **3r** (17.6 mg, 79% yield) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.69 – 8.55 (m, 1H), 7.84 – 7.68 (m, 2H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 5.3 Hz, 1H), 7.22-7.18 (m, 1H), 3.00 (s, 3H) ppm; ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 150.9, 148.9, 145.6, 138.9, 137.0, 126.3, 126.1, 122.1, 121.3, 43.0 ppm; IR (thin film): 3582, 1585, 1470, 1438, 1293, 1261, 1157, 1029, 958, 783 cm^{-1} ; HRMS calculated for $C_{10}H_{10}NOS_2^+$ 224.0204 , found 224.0202 $[M+H]^+$.

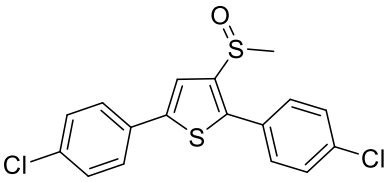


5-(3-(Methylsulfinyl)thiophen-2-yl)quinolone (3s): The reaction was performed following the General Procedure A with **1a** (14.6 mg, 0.1 mmol), *t*-BuOLi (24.0 mg, 0.3 mmol) and 5-bromoquinoline (**2s**) (41.4 mg, 0.2 mmol) at 100 °C for 24 h. The crude product was purified by flash chromatography on silica gel (eluted with EtOAc) to give the product **3s** (18.1 mg, 66% yield) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.97 (dd, *J* = 4.1, 1.6 Hz, 1H), 8.29 – 8.20 (m, 1H), 8.12 (d, *J* = 8.5 Hz, 1H), 7.75 (m, 1H), 7.69 (d, *J* = 5.5 Hz, 1H), 7.63 (d, *J* = 5.5 Hz, 1H), 7.58 (d, *J* = 7.1 Hz, 1H), 7.44 (m, 1H), 2.62 (s, 3H) ppm; ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 150.9, 148.1, 143.2, 139.7, 133.5, 131.4, 129.8, 128.6, 128.5, 128.2, 127.4, 123.9, 122.0, 42.2 ppm; IR (thin film): 3447, 3067, 2995, 2917, 1594, 1494, 1311, 1205, 1042, 954, 878 cm^{-1}; HRMS calculated for $C_{14}H_{12}NOS_2^+$ 274.0360, found 274.0348 $[M+H]^+$.

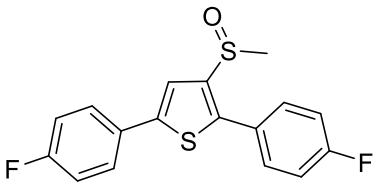


3-(Methylsulfinyl)-2,5-diphenylthiophene (4a): The reaction was performed following the General Procedure B with **1a** (14.6 mg, 0.1 mmol), CsOAc (57.6 mg, 0.3 mmol) and bromobenzene (**2a**) (46.8mg, 0.3 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc) to give the product **4a** (28.4 mg, 95% yield) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.70 – 7.61 (m, 2H), 7.57 – 7.39 (m, 7H), 7.34 (m, 1H), 2.81 (s, 3H) ppm; ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 145.3, 143.0, 141.0, 133.1, 131.6, 129.2, 129.1(5), 129.1(0), 129.0(5), 128.5, 125.8, 120.0, 42.1 ppm; IR (thin film): 3583, 3057, 2917, 1597, 1484, 1455, 1444, 1295,

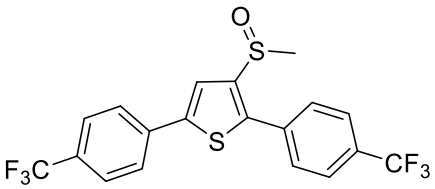
1141, 1047, 1000, 952, 845, 759, 691, 666 cm^{-1}; HRMS calculated for $C_{17}H_{15}OS_2^+$ 299.0564, found 299.0568 $[M+H]^+$.



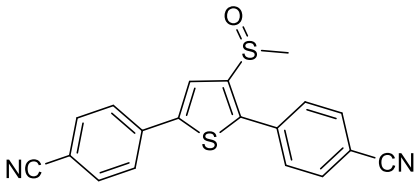
2,5-Bis(4-chlorophenyl)-3-(methylsulfinyl)thiophene (4b): The reaction was performed following the General Procedure B with **1a** (14.6 mg, 0.1 mmol), CsOAc (57.6 mg, 0.3 mmol) and 1-bromo-4-chlorobenzene (**2b**) (57.0mg, 0.3 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc) to give the product **4b** (36.2 mg, 99% yield) as a white solid. M.P. = 105–107 ^oC; ^1H NMR (500 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.54 (dd, J = 6.6, 1.9 Hz, 2H), 7.49 – 7.33 (m, 6H), 2.79 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 144.3, 141.8, 141.7, 135.5, 134.6, 131.4, 130.4, 129.8, 129.3(8), 129.3(7), 127.0, 120.6, 42.1 ppm; IR (thin film): 3583, 1530, 1482, 1401, 1145, 1094, 1052, 1013, 977, 952, 821, 732, 666 cm^{-1}; HRMS calculated for $C_{17}H_{13}OS_2Cl_2^+$ 366.9785, found 366.9777 $[M+H]^+$.



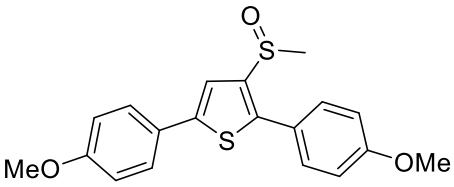
2,5-Bis(4-fluorophenyl)-3-(methylsulfinyl)thiophene (4c): The reaction was performed following the General Procedure B with **1a** (14.6 mg, 0.1 mmol), CsOAc (57.6 mg, 0.3 mmol) and 1-bromo-4-fluorobenzene (**2c**) (52.2mg, 0.3 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc) to give the product **4c** (30.8 mg, 92% yield) as a white solid. M.P. = 110–112 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.67 – 7.54 (m, 2H), 7.53 – 7.39 (m, 2H), 7.23 – 6.78 (m, 4H), 2.79 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 163.2 (d, $J_{C\text{-}F}$ = 251 Hz), 162.9 (d, $J_{C\text{-}F}$ = 250 Hz), 161.9, 144.3, 142.0, 141.2, 131.1 (d, $J_{C\text{-}F}$ = 16 Hz), 129.2 (d, $J_{C\text{-}F}$ = 3 Hz), 127.6 (d, $J_{C\text{-}F}$ = 9 Hz), 127.5 (d, $J_{C\text{-}F}$ = 3 Hz), 112.0, 116.2 (d, $J_{C\text{-}F}$ = 23 Hz), 42.0 ppm; IR (thin film): 3583, 1601, 1495, 1234, 1160, 1100, 1045, 953, 830, 666 cm^{-1} ; HRMS calculated for $C_{17}H_{13}OF_2S_2^+$ 335.0376, found 335.0378 $[M+H]^+$.



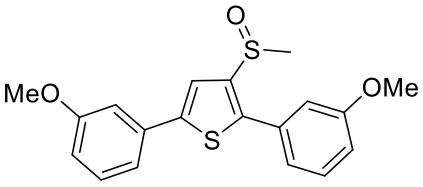
3-(Methylsulfinyl)-2,5-bis(4-(trifluoromethyl)phenyl)thiophene (4d): The reaction was performed following the General Procedure B with **1a** (14.6 mg, 0.1 mmol), CsOAc (57.6 mg, 0.3 mmol) and 4-bromobenzotrifluoride (**2d**) (67.5 mg, 0.3 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc) to give the product **4d** (38.6 mg, 89% yield) as a white solid. M.P. = 158–160 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.82 – 7.53 (m, 8H), 2.82 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 144.4, 142.8, 141.8, 136.0, 134.8, 131.4, 131.1, 130.7, 130.4, 129.5, 126.2(7), 126.2(4), 126.2(1), 126.1(7), 126.1(4), 126.1(1), 126.0(2) 125.0, 124.8, 122.8, 122.7, 121.9, 42.2 ppm; IR (thin film): 3434, 2919, 1614, 1411, 1323, 1249, 1168, 1114, 1069, 1016, 954, 834, 701, 600, 559 cm^{-1}; HRMS calculated for $C_{19}H_{13}F_6OS_2^+$ 435.0312, found 435.0316 $[M+H]^+$.



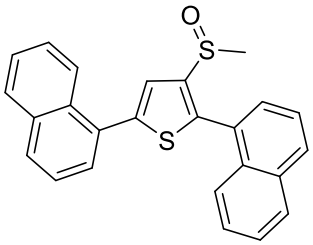
4,4'-(3-(Methylsulfinyl)thiophene-2,5-diyl)dibenzonitrile (4e): The reaction was performed following the General Procedure B with **1a** (14.6 mg, 0.1 mmol), CsOAc (57.6 mg, 0.3 mmol) and 4-bromobenzonitrile (**2e**) (54.6 mg, 0.3 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc) to give the product **4e** (34.1 mg, 98% yield) as a yellow solid. M.P. = 238–240 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.78 – 7.72 (m, 2H), 7.72 – 7.69 (m, 4H), 7.67 – 7.53 (m, 2H), 2.81 (s, 3H) ppm; $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 144.3, 143.7, 141.7, 136.7, 135.5, 133.1, 132.9, 129.7, 126.2, 122.8, 118.3, 118.0, 113.1, 112.3, 42.3 ppm; IR (thin film): 2227, 1602, 1490, 1407, 1180, 1046, 955, 832, 730, 536 cm^{-1}; HRMS calculated for $C_{19}H_{13}N_2OS_2^+$ 349.0469, found 349.0476 $[M+H]^+$.



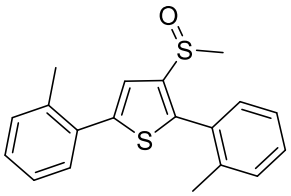
2,5-Bis(4-Methoxyphenyl)-3-(methylsulfinyl)thiophene (4h): The reaction was performed following the General Procedure B with **1a** (14.6 mg, 0.1 mmol), CsOAc (57.6 mg, 0.3 mmol) and 1-bromo-4-methoxybenzene (**2h**) (55.8 mg, 0.3 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc) to give the product **4h** (28.7 mg, 80% yield) as a yellow solid. M.P. = 110–112 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.58 – 7.50 (m, 2H), 7.45 – 7.39 (m, 2H), 7.06 – 6.83 (m, 4H), 3.87 – 3.82 (m, 6H), 2.79 (s, 3H) ppm; $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 160.2, 159.9, 144.6, 142.4, 139.9, 130.5, 127.1, 126.0, 124.1, 118.7, 114.5, 114.4, 55.4(3), 55.4(1), 42.0 ppm; IR (thin film): 3440, 1607, 1496, 1294, 1252, 1179, 1032, 952, 827, 638, 510 cm^{-1}; HRMS calculated for $C_{19}H_{19}O_3S_2^+$ 359.0776, found 359.0768 $[M+H]^+$.



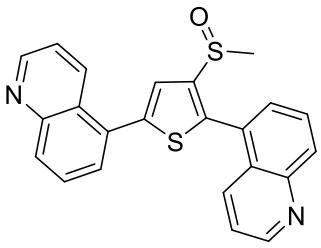
2,5-Bis(3-Methoxyphenyl)-3-(methylsulfinyl)thiophene (4i): The reaction was performed following the General Procedure B with **1a** (14.6 mg, 0.1 mmol), CsOAc (57.6 mg, 0.3 mmol) and 1-bromo-3-methoxybenzene (**2i**) (55.8 mg, 0.3 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc) to give the product **4i** (29.4 mg, 82% yield) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.42 – 7.29 (m, 2H), 7.21 (dd, *J* = 7.6, 0.9 Hz, 1H), 7.15 (dd, *J* = 8.5, 6.3 Hz, 1H), 7.12 – 7.01 (m, 2H), 6.96 – 6.88 (m, 2H), 3.85 (d, *J* = 1.8 Hz, 6H), 2.78 (s, 3H) ppm; $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 160.1, 159.9, 145.1, 142.5, 141.2, 134.3, 132.8, 130.1(9), 130.1(3), 121.5, 120.2, 118.3, 114.7(3), 114.6(7), 114.3, 111.1, 55.4(3), 55.4(1), 42.2 ppm; IR (thin film): 3077, 2999, 2935, 2835, 1598, 1578, 1479, 1290, 1208, 1169, 1048 cm^{-1}; HRMS calculated for $C_{19}H_{19}O_3S_2^+$ 359.0776, found 359.0751 $[M+H]^+$.



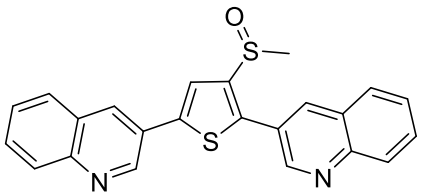
3-(Methylsulfinyl)-2,5-di(naphthalen-1-yl)thiophene (4l): The reaction was performed following the General Procedure B with **1a** (14.6 mg, 0.1 mmol), CsOAc (57.6 mg, 0.3 mmol) and 1-bromonaphthalene (**2l**) (61.8 mg, 0.3 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc) to give the product **4l** (32.7 mg, 82% yield) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (dd, *J* = 13.5, 12.7 Hz, 1H), 8.03 – 7.91 (m, 5H), 7.85 (s, 1H), 7.70 (dd, *J* = 7.1, 1.1 Hz, 1H), 7.67 – 7.63 (m, 1H), 7.63 – 7.49 (m, 6H), 2.72 (s, 3H) ppm; ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 144.4, 143.0, 141.4, 134.0, 133.7, 132.4, 131.4, 130.9, 130.2, 129.5, 129.4, 128.5(9), 128.5(7), 128.4(2), 128.3(5), 127.3, 127.1, 126.6, 126.4, 125.4(2), 125.3(9), 125.3, 125.1, 123.2, 42.3(4) ppm; IR (thin film): 3056, 2995, 1591, 1506, 1391, 1339, 1293, 1046, 952, 866, 800, 774 cm^{-1}; HRMS calculated for $C_{25}H_{19}OS_2^+$ 399.0877, found 399.0880 $[M+H]^+$.



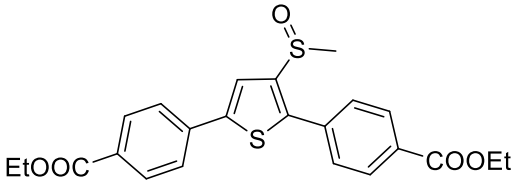
3-(Methylsulfinyl)-2,5-di-*o*-tolylthiophene (4m): The reaction was performed following the General Procedure B with **1a** (14.6 mg, 0.1 mmol), CsOAc (57.6 mg, 0.3 mmol) and 1-bromo-2-methylbenzene (**2m**) (51.0 mg, 0.3 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc) to give the product **4m** (31.3 mg, 96% yield) as a white solid. M.P. = 118–120 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.46 (d, *J* = 7.1 Hz, 1H), 7.39 – 7.33 (m, 1H), 7.33 – 7.28 (m, 4H), 7.28 – 7.19 (m, 2H), 2.71 (s, 3H), 2.51 (s, 3H), 2.35 (s, 3H) ppm; ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 145.1, 142. 5, 141.3, 137.5, 136.1, 132.8, 131.3, 131.1, 130.6, 130.4, 130.2, 129.6, 128.6, 126.2, 125.9, 122.0, 42.1, 21.2, 20.5 ppm; IR (thin film): 3440, 3059, 2918, 1591, 1479, 1457,1384, 1292, 1117, 1048, 975, 951, 801, 759, 725 cm^{-1}; HRMS calculated for $C_{19}H_{19}OS_2^+$ 327.0877, found 327.0871[$M+H]^+$.



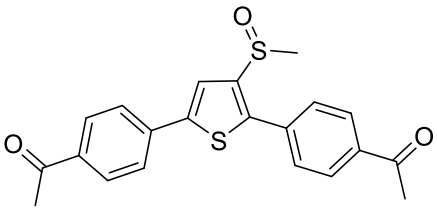
5,5'-(3-(Methylsulfinyl)thiophene-2,5-diyl)diquinoline (4s): The reaction was performed following the General Procedure B with $Pd(dba)_2$ (0.58 mg, 0.001 mmol) and cataCXium A (0.72 mg, 0.002 mmol) in 1 mL of dry CPME, **1a** (14.6 mg, 0.1 mmol), CsOAc (57.6 mg, 0.3 mmol) and 5-bromoquinoline (**2s**) (62.1 mg, 0.3 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:Acetone = 1:1) to give the product **4s** (37.6 mg, 94% yield) as a yellow solid. M.P. = 250–252 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.97 (dd, *J* = 5.8, 3.0 Hz, 2H), 8.66 (dd, *J* = 8.6, 0.7 Hz, 1H), 8.44 – 8.07 (m, 3H), 7.95 – 7.63 (m, 5H), 7.49 – 7.46 (m, 2H), 2.70 (s, 3H) ppm; ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 147.2, 146.9, 144.7, 144.3, 139.8, 139.5, 136.1, 129.7, 129.6, 127.8, 126.9(2), 126.8(7), 126.0, 124.9, 124.8, 124.7, 124.4, 123.5, 122.6, 119.8, 118.3, 118.0, 38.4 ppm; IR (thin film): 3455, 3067, 3000, 2920, 1594, 1499, 1322, 1210, 1042, 955, 882 cm^{-1}; HRMS calculated for $C_{23}H_{17}N_2OS_2^+$ 401.0782, found 401.0787 $[M+H]^+$.



3,3'-(3-(Methylsulfinyl)thiophene-2,5-diyl)diquinoline (4t): The reaction was performed following the General Procedure B with $Pd(dba)_2$ (0.58 mg, 0.001 mmol) and cataCXium A (0.72 mg, 0.002 mmol) in 1 mL of dry CPME, **1a** (14.6 mg, 0.1 mmol), CsOAc (57.6 mg, 0.3 mmol) and 3-bromoquinoline (**2t**) (62.1 mg, 0.3 mmol). The crude product was purified by flash chromatography on silica gel (EtOAc:Acetone = 1:1) to give the product **4t** (36.4 mg, 91% yield) as a yellow solid. M.P. = 230–232 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.24 (d, *J* = 2.3 Hz, 1H), 9.06 (d, *J* = 2.3 Hz, 1H), 8.38 (d, *J* = 2.2 Hz, 1H), 8.34 (d, *J* = 2.2 Hz, 1H), 8.17 – 8.12 (m, 2H), 8.06 (s, 1H), 7.96 – 7.85 (m, 2H), 7.83 – 7.79 (m, 1H), 7.77 – 7.73 (m, 1H), 7.67 – 7.59 (m, 2H), 2.90 (s, 3H) ppm; ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 149.7, 147.9(3), 147.9(0), 147.8, 143.3, 143.1, 140.1, 136.1, 132.0, 130.9, 130.2, 129.5(3), 129.4(9), 128.3, 128.1, 127.9, 127.7(4), 127.6(6), 127.3, 126.0, 124.7, 121.7, 42.4 ppm; IR (thin film): 3432, 2093, 1643, 1617, 1568, 1491, 1419, 1375, 1126, 1044, 957, 907, 858, 785, 751 cm^{-1}; HRMS calculated for $C_{23}H_{17}N_2OS_2^+$ 401.0782, found 401.0782 $[M+H]^+$.

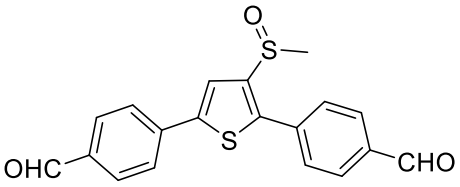


Diethyl4,4'-(3-(Methylsulfinyl)thiophene -2,5-diyl) dibenzoate (4u): The reaction was performed following the General Procedure B with **1a** (14.6 mg, 0.1 mmol), CsOAc (57.6 mg, 0.3 mmol) and ethyl 4-bromobenzoate (**2u**) (68.7 mg, 0.3 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc) to give the product **4u** (41.6 mg, 94% yield) as a yellow solid. M.P. = 130–132 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 – 8.01 (m, 4H), 7.91 (s, 1H), 7.79 – 7.64 (m, 2H), 7.63 – 7.51 (m, 2H), 4.39 (q, *J* = 7.1 Hz, 4H), 2.80 (s, 3H), 1.42 – 1.38 (m, 6H) ppm; ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 165.9, 165.8, 144.7, 142.7, 142.2, 136.7, 135.5, 131.0, 130.5, 130.4, 130.3, 129.0, 125.5, 121.9, 61.3, 61.2, 42.2, 14.3(4),14.3(3) ppm; IR (thin film): 2981, 1715, 1605, 1409, 1367, 1274, 1185, 1107, 1021, 852, 770 cm^{-1}; HRMS calculated for $C_{23}H_{23}O_5S_2^+$ 443.0981, found 443.0994 $[M+H]^+$.

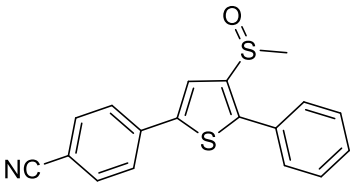


1,1'-((3-(Methylsulfinyl)thiophene-2,5-diyl)bis(4,1-phenylene))bis(ethan-1-one) (4v): The reaction was performed following the General Procedure B with $Pd(dba)_2$ (0.58 mg, 0.001 mmol) and cataCXium A (0.72 mg, 0.002 mmol) in 1 mL of dry CPME, **1a** (14.6 mg, 0.1 mmol), CsOAc (57.6 mg, 0.3 mmol) and 4-bromoacetophenone (**2v**) (59.7 mg, 0.3 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc) to give the product **4v** (36.3 mg, 95% yield) as a yellow solid. M.P. = 133–135 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 – 7.96 (m, 4H), 7.93 (s, 1H), 7.72 (d, *J* = 8.2 Hz, 2H), 7.61 (d, *J* = 8.1 Hz,2H), 2.81 (s, 3H), 2.64 (s,3H), 2.62 (s, 3H) ppm; ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 197.0, 196.9(7), 144.6, 142.8, 142.1, 137.1, 136.9, 136.7, 135.7, 129.2, 129.0, 125.7, 122.0, 42.2,

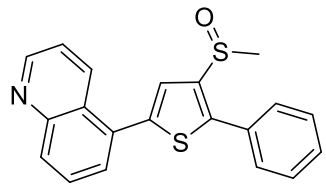
26.6, 26.5(6) ppm; IR (thin film): 2923, 2853, 1681, 1601, 1359, 1268, 1190, 1049, 959, 830 cm^{-1}; HRMS calculated for $C_{21}H_{19}O_3S_2^+$ 383.0776, found 383.0773$[M+H]^+$.



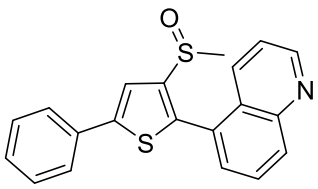
4,4'-(3-(Methylsulfinyl)thiophene-2,5-diyl)dibenzaldehyde (4w): The reaction was performed following the General Procedure B with $Pd(dba)_2$ (0.58 mg, 0.001 mmol) and cataCXium A (0.72 mg, 0.002 mmol) in 1 mL of dry CPME, **1a** (14.6 mg, 0.1 mmol), CsOAc (57.6 mg, 0.3 mmol) and 4-bromobenzaldehyde (**2w**) (55.5 mg, 0.3 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc) to give the product **4w** (33.3 mg, 94% yield) as a yellow solid. M.P. = 158–160 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.07 (s, 1H), 10.03 (s, 1H), 8.17 – 7.89 (m, 5H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.69 (d, *J* = 8.2 Hz, 2H), 2.83 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 191.1(0), 191.0(5), 144.6, 143.3, 142.1, 138.0, 136.9, 136.3, 136.0, 130.6, 130.3, 129.6, 126.1, 122.5, 42.2 ppm; IR (thin film): 2844, 2700, 1696, 1600, 1565, 1390, 1213, 1171, 1049, 823 cm^{-1}; HRMS calculated for $C_{19}H_{15}O_3S_2^+$ 355.0463, found 355.0468 [$M+H]^+$.



4-(4-(Methylsulfinyl)-5-phenylthiophen-2-yl)benzonitrile (5a): The reaction was performed following the General Procedure C with **3a** (22.2 mg, 0.1 mmol), CsOAc (57.6 mg, 0.3 mmol) and 4-bromobenzonitrile (**2e**) (36.4 mg, 0.2 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc) to give the product **5a** (25.2 mg, 78% yield) as a white solid. M.P. = 158–160 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.76 – 7.65 (m, 4H), 7.53 – 7.40 (m, 5H), 2.79 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 144.5, 142.5, 142.0, 137.2, 133.0, 131.1, 129.6, 129.2, 129.1, 126.0, 122.4, 118.5, 111.7, 42.2 ppm; IR (thin film): 2235, 1645, 1490, 1407, 1199, 1055, 955, 830, 730 cm^{-1}; HRMS calculated for $C_{18}H_{13}NNaOS_2^+$ 346.0336, found 346.0343 $[M+Na]^+$.



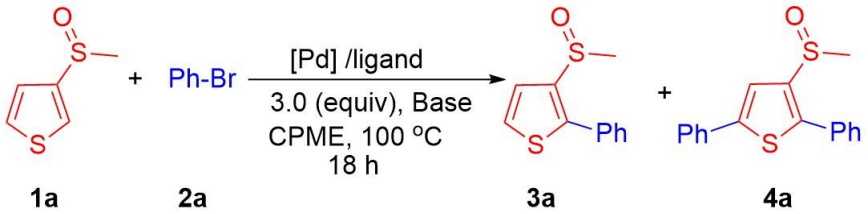
5-(4-(Methylsulfinyl)-5-phenylthiophen-2-yl)quinolone (5b): The reaction was performed following the General Procedure C with **3a** (22.2 mg, 0.1 mmol), CsOAc (57.6 mg, 0.3 mmol) and 5-bromoquinoline (**2s**) (41.4 mg, 0.2 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc to EtOAc:Acetone = 1:1) to give the product **5b** (29.7 mg, 85% yield) as a white solid. M.P. = 138–140 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.97 (dd, *J* = 4.0, 1.4 Hz, 1H), 8.63 (d, *J* = 8.5 Hz, 1H), 8.18 (d, *J* = 8.4 Hz, 1H), 7.83 – 7.66 (m, 3H), 7.60 – 7.36 (m, 6H), 2.85 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 150.8, 148.6, 144.9, 141.6, 140. 7, 133.8, 131.3, 131.2, 130.7, 129.4, 129.3, 129.1, 128.8, 128.5, 126.6, 124.6, 121.8, 42.1 ppm; IR (thin film): 3850, 3435, 2089, 1642, 1502, 1445, 1311, 1035, 830, 730 cm^{-1}; HRMS calculated for $C_{20}H_{16}NOS_2^+$ 350.0673, found 350.0672$[M+H]^+$.



5-(3-(Methylsulfinyl)-5-phenylthiophen-2-yl)quinolone (5c): The reaction was performed following the General Procedure C with **3s** (27.3 mg, 0.1 mmol), CsOAc (57.6 mg, 0.3 mmol) and bromobenzene (**2a**) (31.4 mg, 0.2 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc to EtOAc:Acetone = 1:1) to give the product **5c** (27.9 mg, 80% yield) as a white solid. M.P. = 178–180 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.96 (dd, *J* = 4.1, 1.6 Hz, 1H), 8.32 – 8.10 (m, 2H), 7.85 (s, 1H), 7.75 (dd, *J* = 8.5, 7.1 Hz, 1H), 7.70 – 7.54 (m, 3H), 7.48 – 7.39 (m, 3H), 7.38 – 7.31 (m, 1H), 2.64 (s, 3H) ppm; ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 151.1, 148.3, 147.2, 144.1, 138.1, 133.6, 132.8, 131.6, 129.8, 129.3, 128.8, 128.5(6), 128.5(4), 127.5, 125.9, 122.1, 119.2, 42.4 ppm; IR (thin film): 3903, 3508, 2089, 1645, 1520, 1459, 1310, 1035, 835, 758 cm^{-1}; HRMS calculated for $C_{20}H_{16}NOS_2^+$ 350.0673, found 350.0675 $[M+H]^+$.

High-throughput Experimentation Screenings

Bases and Pd catalysts screening:



Set up:

Experiments were set up inside a glovebox under a nitrogen atmosphere. A 2x24 well plate containing 1 mL glass vials was predosed with the Pd source (1 μmol) and the phosphine ligands (2 μmol for monodentate ligands and 1 μmol for bidentate ligands) in THF. The solvent was removed to dryness using a GeneVac and bases (30 μmol) in THF were added to the ligand/catalyst mixture. The solvent was removed on the GeneVac and a parylene stir bar was then added to each reaction vial. 3-(methylsulfinyl)thiophene (**1a**) (10 μmol/reaction) and bromobenzene (**2a**) (20 μmol) and 4,4′-di-*tert*-butylbiphenyl (1 μmol/reaction) (used as an internal standard to measure HPLC yields) were then dosed together into each reaction vial as a solution in CPME (100 μL, 0.1 M). The 48-well plate was then sealed and stirred for 18 h at 100 °C.

Work up:

Upon opening the plate to air, 500 μL of acetonitrile was added into each vial. The plate was covered again and the vials stirred for 10 min to ensure good homogenization. Into a separate LC block was added 700 μL of acetonitrile, followed by 25 μL of the diluted reaction mixtures. The LC block was then sealed with a silicon-rubber storage mat and mounted on an automated HPLC instrument for analysis.

Base: *t*-BuOLi, *t*-BuONa, *t*-BuOK, $LiN(SiMe_3)_2$, $NaN(SiMe_3)_2$ and $KN(SiMe_3)_2$.

Pd source: $Pd(dba)_2$, and $Pd(OAc)_2$.

Ligand: NiXantphos, CyJohnPhos, PhDavePhos and dppf.

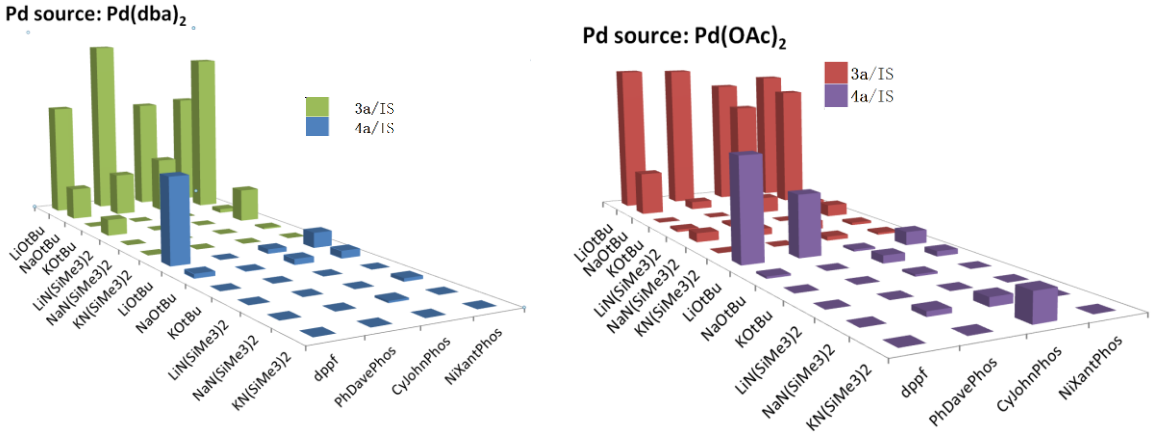
Table S1. Initial screening

Well	Base	Pd	Ligand	3a/IS[a]	4a/IS[a]
A01	*t*-BuOLi	$Pd(dba)_2$	NiXantPhos	2.64	0.34
B01			CyJohnPhos	2.56	0.10
C01			PhDavePhos	4.10	0.00
D01			dppf	2.60	1.89
A02	*t*-BuONa		NiXantPhos	3.75	0.16
B02			CyJohnPhos	1.27	0.12
C02			PhDavePhos	0.98	0.00
D02			dppf	0.73	0.09
A03	*t*-BuOK		NiXantPhos	0.09	0.00
B03			CyJohnPhos	0.00	0.00
C03			PhDavePhos	0.00	0.00
D03			dppf	0.00	0.00
A04	$LiN(SiMe_3)_2$	$Pd(dba)_2$	NiXantPhos	0.75	0.07
B04			CyJohnPhos	0.00	0.00
C04			PhDavePhos	0.00	0.00
D04			dppf	0.37	0.00
A05	$NaN(SiMe_3)_2$		NiXantPhos	0.03	0.00
B05			CyJohnPhos	0.00	0.04
C05			PhDavePhos	0.00	0.00
D05			dppf	0.00	0.00
A06	$KN(SiMe_3)_2$		NiXantPhos	0.00	0.00
B06			CyJohnPhos	0.00	0.00
C06			PhDavePhos	0.00	0.00
D06			dppf	0.00	0.00
A07	*t*-BuOLi	$Pd(OAc)_2$	NiXantPhos	2.81	0.26
B07			CyJohnPhos	2.65	0.04
C07			PhDavePhos	3.04	1.20
D07			dppf	3.07	2.01
A08	*t*-BuONa		NiXantPhos	2.54	0.10
B08			CyJohnPhos	2.24	0.15
C08			PhDavePhos	0.16	0.00
D08			dppf	0.89	0.04
A09	*t*-BuOK		NiXantPhos	0.15	0.00
B09			CyJohnPhos	0.32	0.04
C09			PhDavePhos	0.00	0.00

D09			dppf	0.00	0.00
A10	$LiN(SiMe_3)_2$		NiXantPhos	0.24	0.00
B10			CyJohnPhos	0.00	0.00
C10			PhDavePhos	0.05	0.00
D10			dppf	0.05	0.00
A11	$NaN(SiMe_3)_2$		NiXantPhos	0.05	0.00
B11			CyJohnPhos	0.17	0.16
C11			PhDavePhos	0.13	0.09
D11			dppf	0.18	0.00
A12	$KN(SiMe_3)_2$		NiXantPhos	0.04	0.00
B12			CyJohnPhos	0.08	0.52
C12			PhDavePhos	0.00	0.00
D12			dppf	0.00	0.00

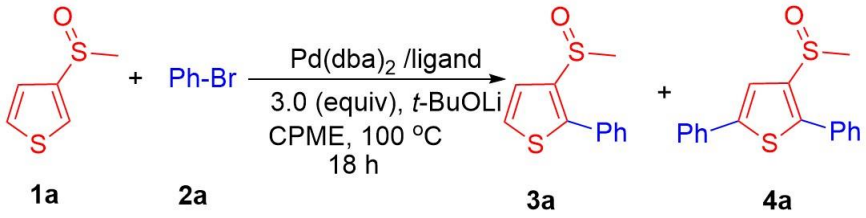
[a]Product-internal standard radio.

Figure S1. Initial screening illustrated in graph



From this screen, $Pd(dba)_2$, *t*-BuOLi in CPME was the leading hit.

Ligand screening:



Set up:

Experiments were set up inside a glovebox under a nitrogen atmosphere. A 24 well plate containing 1 mL glass vials was predosed with the $Pd(dba)_2$ (1 μmol) and the phosphine ligands (2 μmol for monodentate ligands and 1 μmol for bidentate ligands) in THF. The solvent was removed to dryness using a GeneVac and *t*-BuOLi (30 μmol) in THF was added to the ligand/catalyst mixture. The solvent was removed on the

GeneVac and a parylene stir bar was then added to each reaction vial. 3-(methylsulfinyl)thiophene (**1a**) (10 μmol/reaction) and bromobenzene (**2a**) (20 μmol) and 4,4′-di-*tert*-butylbiphenyl (1 μmol/reaction) (used as an internal standard to measure HPLC yields) were then dosed together into each reaction vial as a solution in CPME (100 μL, 0.1 M). The 24-well plate was then sealed and stirred for 18 h at 100 °C.

Work up:

Upon opening the plate to air, 500 μL of acetonitrile was added into each vial. The plate was covered again and the vials stirred for 10 min to ensure good homogenization. Into a separate LC block was added 700 μL of acetonitrile, followed by 25 μL of the diluted reaction mixtures. The LC block was then sealed with a silicon-rubber storage mat and mounted on an automated HPLC instrument for analysis.

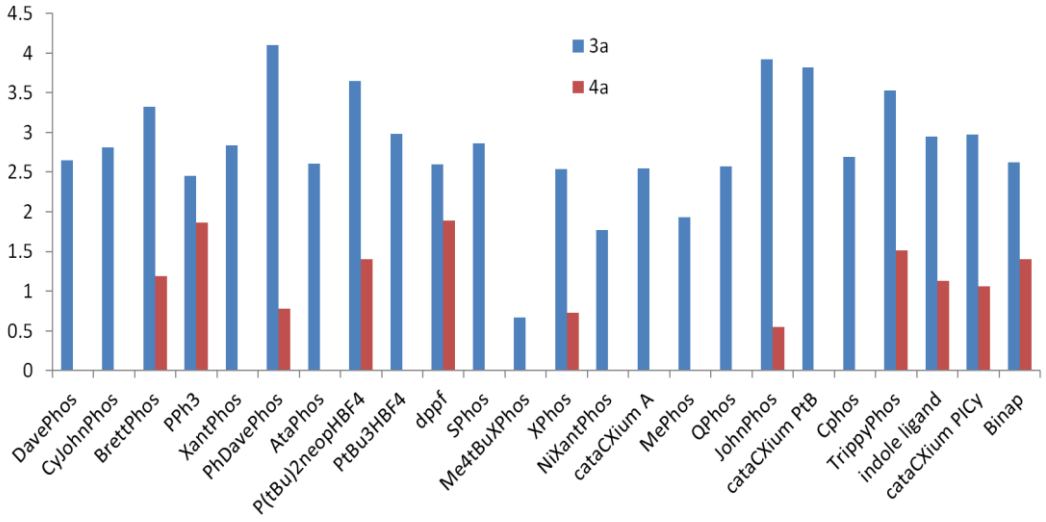
Table S2. Ligand screen.

	Ligand	**3a**/IS[a]	**4a**/IS[a]
1	2-Dicyclohexylphosphino-2′-(*N*,*N*-dimethylamino)biphenyl (DavePhos)	2.65	0.00
2	(2-Biphenyl)dicyclohexylphosphine (CyJohnPhos)	2.81	0.00
3	2-(Dicyclohexylphosphino)3,6-dimethoxy-2′,4′,6′-triisopropyl-1,1′-biphenyl (BrettPhos)	3.32	1.19
4	PPh_3	2.45	1.86
5	4,5-Bis(diphenylphosphino)-9,9-dimethylxanthene (XantPhos)	2.84	0.00
6	2-Diphenylphosphino-2′-(*N*,*N*-dimethylamino)biphenyl (PhDavePhos)	**4.10**	0.78
7	*N*,*N*-Dimethyl 4-(Di(*tert*-butyl)phosphino)aniline (A^{ta}Phos)	2.61	0.00
8	$P(^tBu)_2$neopHBF_4	3.65	1.40
9	Tri-*tert*-butylphosphoniumtetrafluoroborate ($P^tBu_3HBF_4$)	2.98	0.00
10	1,1'-Bis(diphenylphosphino)ferrocene (dppf)	2.60	1.89
11	2-Dicyclohexylphosphino-2,6-dimethoxybiphenyl (SPhos)	2.86	0.00
12	2-Di-*tert*-butylphosphino-3,4,5,6-tetramethyl-2′,4′,6′-triisopropyl-1,1′-biphenyl ($Me_4{}^tBu$XPhos)	0.67	0.00
13	2-Dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl (XPhos)	2.54	0.73
14	4,6-Bis(diphenylphosphino)phenoxazine (NiXantPhos)	1.77	0.00
15	Di(1-adamantyl)-n-butylphosphine (cataCXium A)	2.55	0.00
16	2-Dicyclohexylphosphino-2'-methyl-)-1,1'-biphenyl (MePhos)	1.93	0.00
17	1,2,3,4,5-Pentaphenyl-1′-(di-*tert*-butylphosphino)ferrocene (QPhos)	2.57	0.00
18	(2-Biphenyl)di-*tert*-butylphosphine (JohnPhos)	**3.92**	0.55
19	2-(Di-*tert*-butyl-phosphino)-1-phenyl-1H-pyrrole (cataCXium P^tB)	3.82	0.00
20	2-Dicyclohexylphosphino-2,6-bis(*N*,*N*-dimethylamino)biphenyl (CPhos)	2.69	0.00
21	1-[2-Bis(*tert*-butyl)phosphinophenyl]-3,5-diphenyl-1*H*-pyrazole (TrippyPhos)	3.53	1.51
22	N-(dicyclohexylphosphino)-2-(2′-tolyl)indole (Kwong's indole ligand)	2.95	1.13
23	2-(Dicyclohexylphosphino)-1-(2,4,6-trimethyl-phenyl)-1H-imidazole (cataCXium PICy)	2.97	1.06

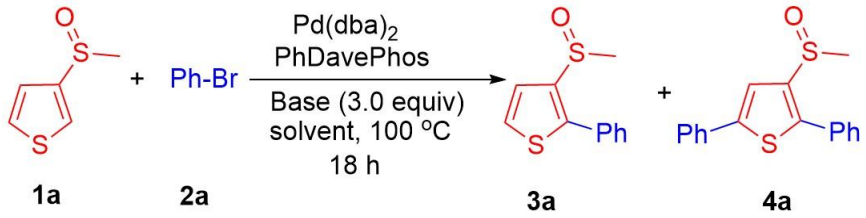
24	(2,2'-bis(diphenylphosphino)-1,1'-binaphthyl) (Binap)	2.62	1.40

[a]Product-internal standard radio.

Figure S2. Ligand screen illustrated in graph



Bases and solvents screening (for bisarylated products):



Set up:

Experiments were set up inside a glovebox under a nitrogen atmosphere. A 4x24 well plate containing 1 mL glass vials was predosed with the $Pd(dba)_2$ (1 μmol) and PhDavePhos (2 μmol) in THF. The solvent was removed to dryness using a GeneVac and Bases (30 μmol) in THF was added to the mixture. The solvent was removed on the GeneVac and a parylene stir bar was then added to each reaction vial. 3-(methylsulfinyl)thiophene (**1a**) (10 μmol/reaction) and bromobenzene (**2a**) (40 μmol) and 4,4′-di-*tert*-butylbiphenyl (1 μmol/reaction) (used as an internal standard to measure HPLC yields) were then dosed together into each solvent (100 μL, 0.1 M). The 96-well plate was then sealed and stirred for 18 h at 100 °C.

Work up:

Upon opening the plate to air, 500 μL of acetonitrile was added into each vial. The plate was covered again and the vials stirred for 10 min to ensure good homogenization. Into a separate LC block was added 700 μL of acetonitrile, followed by 25 μL of the diluted reaction mixtures. The LC block was then sealed with a silicon-rubber storage mat and mounted on an automated HPLC instrument for analysis.

Bases: *t*-BuOLi, *t*-BuONa, *t*-BuOK, $LiN(SiMe_3)_2$, $NaN(SiMe_3)_2$, $KN(SiMe_3)_2$, LiOAc, LiH, NaH, K_3PO_4, CsOAc and CS_2CO_3.

Solvents: toluene, 2-Me-THF, DME (dimethoxyethane), DMF (Dimethylformamide), CPME (cyclopentyl methyl ether), 1,4-dioxane, DMAc (Dimethylacetamid) and MeCN.

Table S3. Bases and solvents screening**.**

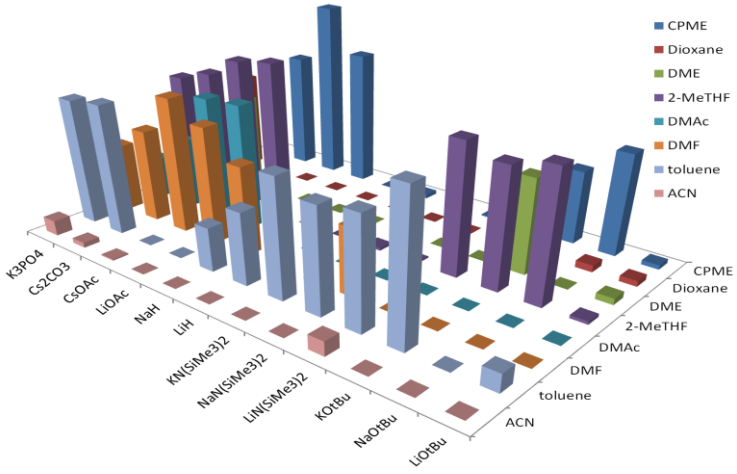
Well	Base	Solvent	Prod 4a/IS[a]
A01	*t*-BuOLi	CPME	0.07
B01		Dioxane	0.09
C01		DME	0.10
D01		2-MeTHF	0.05
E01		DMAc	0.00
F01		DMF	0.00
G01		toluene	0.29
H01		ACN	0.00
A02	*t*-BuONa	CPME	1.60
B02		Dioxane	0.11
C02		DME	0.00
D02		2-MeTHF	2.04
E02		DMAc	0.00
F02		DMF	0.00
G02		toluene	0.00
H02		ACN	0.00
A03	*t*-BuOK	CPME	1.16
B03		Dioxane	0.00
C03		DME	1.49
D03		2-MeTHF	1.88
E03		DMAc	0.00
F03		DMF	0.00
G03		toluene	2.27
H03		ACN	0.00
A04	$LiN(SiMe_3)_2$	CPME	0.07
B04		Dioxane	0.00
C04		DME	0.00
D04		2-MeTHF	2.05
E04		DMAc	0.00
F04		DMF	0.00
G04		toluene	1.72
H04		ACN	0.23
A05		CPME	0.02

B05	$NaN(SiMe_3)_2$	Dioxane	0.00
C05		DME	0.00
D05		2-MeTHF	0.02
E05		DMAc	0.00
F05		DMF	1.06
G05		toluene	1.63
H05		ACN	0.00
A06	$KN(SiMe_3)_2$	CPME	0.00
B06		Dioxane	0.00
C06		DME	0.00
D06		2-MeTHF	0.04
E06		DMAc	0.00
F06		DMF	0.00
G06		toluene	1.83
H06		ACN	0.00
A07	LiH	CPME	0.06
B07		Dioxane	0.00
C07		DME	0.00
D07		2-MeTHF	0.00
E07		DMAc	0.00
F07		DMF	0.00
G07		toluene	1.13
H07		ACN	0.00
A08	NaH	CPME	0.00
B08		Dioxane	0.00
C08		DME	0.00
D08		2-MeTHF	0.00
E08		DMAc	0.00
F08		DMF	1.40
G08		toluene	0.69
H08		ACN	0.00
A09	LiOAc	CPME	2.13
B09		Dioxane	0.00
C09		DME	0.00
D09		2-MeTHF	2.43
E09		DMAc	1.97
F09		DMF	1.82

G09		toluene	0.00
H09		ACN	0.00
A10	CsOAc	CPME	**2.78**
B10		Dioxane	0.00
C10		DME	0.00
D10		2-MeTHF	2.34
E10		DMAc	1.93
F10		DMF	2.10
G10		toluene	0.00
H10		ACN	0.02
A11	Cs_2CO_3	CPME	1.85
B11		Dioxane	1.65
C11		DME	1.45
D11		2-MeTHF	2.03
E11		DMAc	1.11
F11		DMF	1.45
G11		toluene	2.03
H11		ACN	0.08
A12	K_3PO_4	CPME	1.67
B12		Dioxane	1.54
C12		DME	0.45
D12		2-MeTHF	1.85
E12		DMAc	0.65
F12		DMF	1.06
G12		toluene	1.96
H12		ACN	0.24

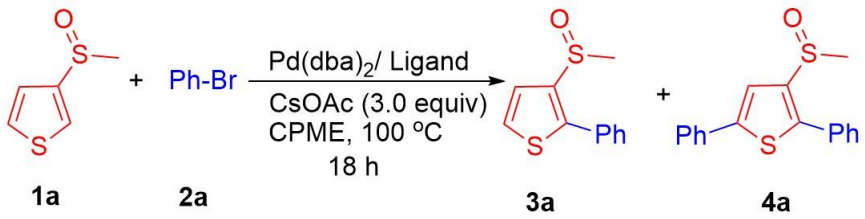
[a]Product-internal standard radio.

Figure S3. Bases and solvents screening illustrated in graph



From this screen, CsOAc in CPME was the leading hit.

Ligands screening (for bisarylated products):



Set up:

Experiments were set up inside a glovebox under a nitrogen atmosphere. A 24 well plate containing 1 mL glass vials was predosed with the $Pd(dba)_2$ (1 μmol) and the phosphine ligands (2 μmol for monodentate ligands and 1 μmol for bidentate ligands) in THF. The solvent was removed to dryness using a GeneVac and CsOAc (30 μmol) in THF was added to the mixture. The solvent was removed on the GeneVac and a parylene stir bar was then added to each reaction vial. 3-(methylsulfinyl)thiophene (**1a**) (10 μmol/reaction) and bromobenzene (**2a**) (40 μmol) and 4,4′-di-*tert*-butylbiphenyl (1 μmol/reaction) (used as an internal standard to measure HPLC yields) were then dosed together into CPME (100 μL, 0.1 M). The 24 well-plate was then sealed and stirred for 18 h at 100 °C.

Work up:

Upon opening the plate to air, 500 μL of acetonitrile was added into each vial. The plate was covered again and the vials stirred for 10 min to ensure good homogenization. Into a separate LC block was added 700 μL of acetonitrile, followed by 25 μL of the diluted reaction mixtures. The LC block was then sealed with a silicon-rubber storage mat and mounted on an automated HPLC instrument for analysis.

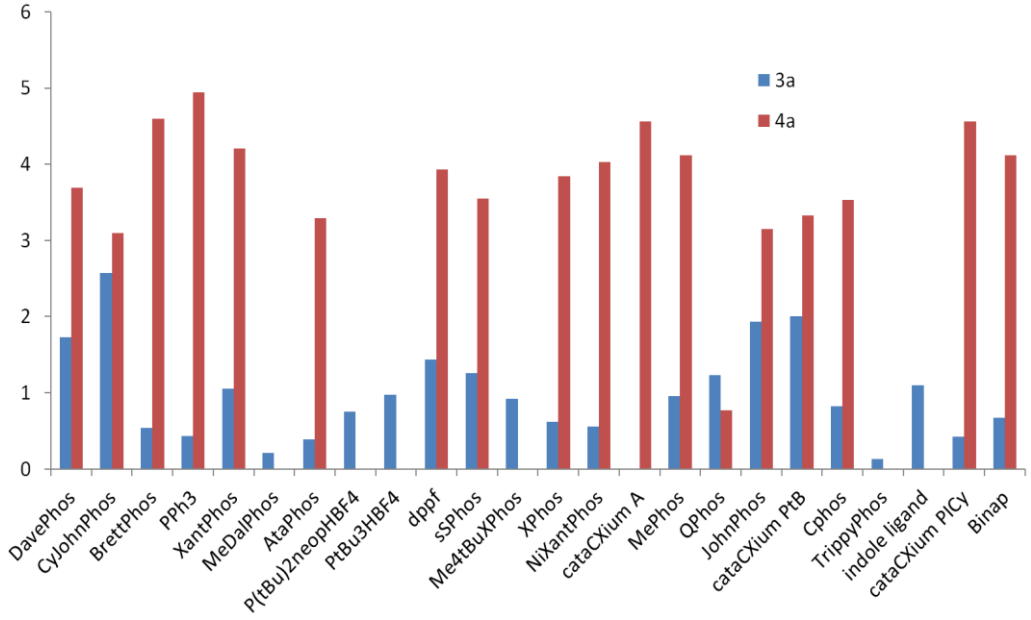
Table S4. Ligand screen.

	Ligand	**3a/IS**[a]	**4a/IS**[a]
1	2-Dicyclohexylphosphino-2′-(*N*,*N*-dimethylamino)biphenyl (DavePhos)	1.73	3.69
2	(2-Biphenyl)dicyclohexylphosphine (CyJohnPhos)	2.57	3.10
3	2-(Dicyclohexylphosphino)3,6-dimethoxy-2′,4′,6′-triisopropyl-1,1′-bi phenyl (BrettPhos)	0.54	4.60
4	PPh_3	0.43	4.94
5	4,5-Bis(diphenylphosphino)-9,9-dimethylxanthene (XantPhos)	1.05	4.21
6	2-(Di-1-adamantylphosphino)-*N*,*N*-dimethylaniline (MeDalPhos)	0.21	0.00
7	*N*,*N*-Dimethyl 4-(Di(*tert*-butyl)phosphino)aniline (A^{ta}Phos)	0.39	3.29
8	$P(^tBu)_2$neopHBF_4	0.75	0.00
9	Tri-*tert*-butylphosphoniumtetrafluoroborate ($P^tBu_3HBF_4$)	0.97	< 0.01
10	1,1'-Bis(diphenylphosphino)ferrocene (dppf)	1.44	3.93
11	Sodium2′-dicyclohexylphosphino-2,6-dimethoxy-1,1′-biphenyl-3-sulf onate hydrate (^{s}SPhos)	1.26	3.55

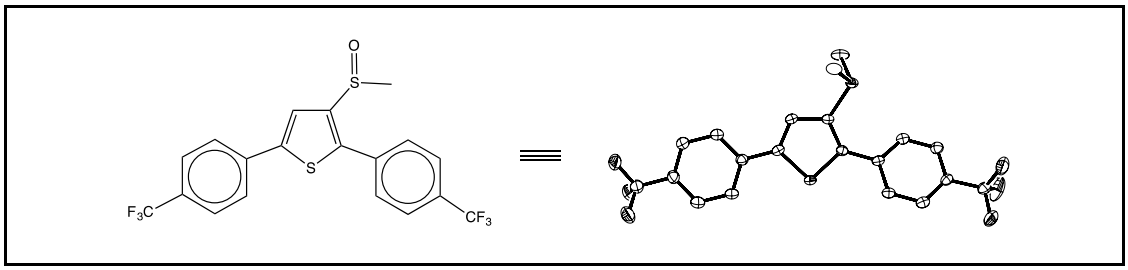
12	2-Di-*tert*-butylphosphino-3,4,5,6-tetramethyl-2′,4′,6′-triisopropyl-1,1′-biphenyl (Me_4^{t}BuXPhos)	0.92	< 0.01
13	2-Dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl (XPhos)	0.62	3.84
14	4,6-Bis(diphenylphosphino)phenoxazine (NiXantPhos)	0.56	4.03
15	Di(1-adamantyl)-n-butylphosphine (cataCXium A)	**0.00**	**4.56**
16	2-Dicyclohexylphosphino-2'-methyl-)-1,1'-biphenyl (MePhos)	0.96	4.12
17	1,2,3,4,5-Pentaphenyl-1′-(di-*tert*-butylphosphino)ferrocene (QPhos)	1.23	0.77
18	(2-Biphenyl)di-*tert*-butylphosphine (JohnPhos)	1.93	3.15
19	2-(Di-*tert*-butyl-phosphino)-1-phenyl-1H-pyrrole (cataCXium P^{t}B)	2.00	3.33
20	2-Dicyclohexylphosphino-2,6-bis(*N*,*N*-dimethylamino)biphenyl (CPhos)	0.82	3.53
21	1-[2-Bis(*tert*-butyl)phosphinophenyl]-3,5-diphenyl-1*H*-pyrazole (TrippyPhos)	0.13	0.00
22	N-(dicyclohexylphosphino)-2-(2′-tolyl)indole (Kwong's indole ligand)	1.10	< 0.01
23	2-(Dicyclohexylphosphino)-1-(2,4,6-trimethyl-phenyl)-1H-imidazole (cataCXium PICy)	0.42	4.56
24	(2,2'-bis(diphenylphosphino)-1,1'-binaphthyl) (Binap)	0.67	4.12

[a]Product-internal standard radio.

Figure S4. Ligand screen illustrated in graph



X-ray Structure of compound 4d



Compound **4d**, $C_{38}H_{24}F_{12}O_2S_4$, crystallizes in the triclinic space group $P\bar{1}$ with a=8.3690(4) Å, b=13.3028(6) Å, c=16.2860(8) Å, α=95.133(2)°, β=90.067(2)°, γ=91.338(2)°, V=1805.37(15)Å^3, Z=2, and d_{calc}=1.598 g/cm$_3$. X-ray intensity data were collected on a Bruker APEXII CCD area detector employing graphite-monochromated Mo-Kα radiation (λ=0.71073 Å) at a temperature of 100K. Preliminary indexing was performed from a series of thirty-six 0.5 ° rotation frames with exposures of 10 seconds. A total of 3591 frames were collected with a crystal to detector distance of 59.9 mm, rotation widths of 0.5 ° and exposures of 20 seconds:

scan type	2θ	ω	φ	χ	Frames
ϕ	-23.00	334.99	345.26	-33.72	739
ϕ	32.00	33.96	332.91	-56.95	739
ω	24.50	310.81	18.22	62.65	97
ϕ	-25.50	14.38	15.69	25.13	723
ϕ	32.00	44.52	349.55	-24.38	739
ω	17.00	321.76	294.44	82.07	144
ω	-30.50	311.87	203.97	-93.68	124
ω	34.50	312.19	168.84	96.92	166
ω	-30.50	311.92	311.49	-90.90	120

Rotation frames were integrated using SAINT[2], producing a listing of unaveraged F^2 and σ (F^2) values. A total of 54660 reflections were measured over the ranges $3.074 \leq 2\theta \leq 55.192°$, $-10 \leq h \leq 10$, $-17 \leq k \leq 17$, $0 \leq l \leq 21$ yielding 8297 unique reflections (R_{int} = 0.0593). The intensity data were corrected for Lorentz and polarization effects and for absorption using SADABS[3] (minimum and maximum transmission 0.610821, 0.745551). The structure was solved by direct methods - SHELXS-97.[4] Refinement was by full-matrix least squares based on F^2 using SHELXL-2014.[5] All reflections were used during refinement. The weighting scheme used was $w=1/[\sigma^2(F_o^2)+ (0.0940P)^2 + 0.2277P]$ where $P = (F_o^2 + 2F_c^2)/3$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model. Refinement converged to R1=0.0486 and wR2=0.1252 for 7105 observed reflections for which $F > 4\sigma$ (F) and R1=0.0589 and wR2=0.1319 and GOF =1.020 for all 8297 unique, non-zero reflections and 536 variables. The maximum

Δ/σ in the final cycle of least squares was 0.000 and the two most prominent peaks in the final difference Fourier were +1.45 and -0.42 e/Å^3.

Table S5. lists cell information, data collection parameters, and refinement data. Final positional and equivalent isotropic thermal parameters are given in Tables S6. and S7. Anisotropic thermal parameters are in Table S8. Tables S9. and S10. list bond distances and bond angles. Figures S5. and S6. are ORTEP representations of the molecule with 50% probability thermal ellipsoids displayed.

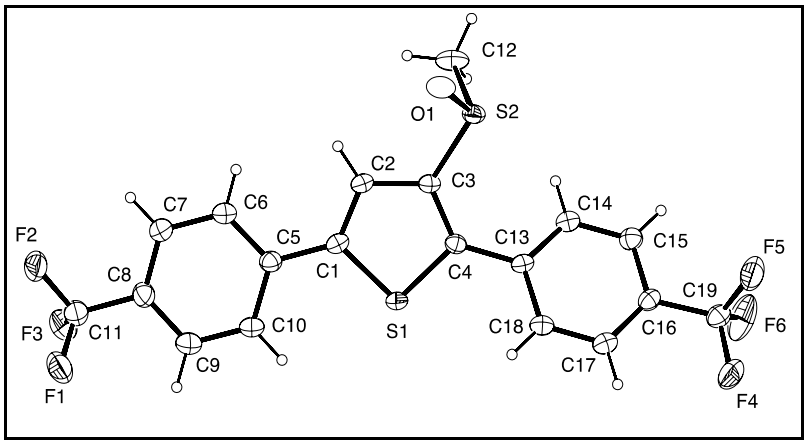


Figure S5. ORTEP drawing of molecule no. 1 of the asymmetric unit with 50% thermal ellipsoids.

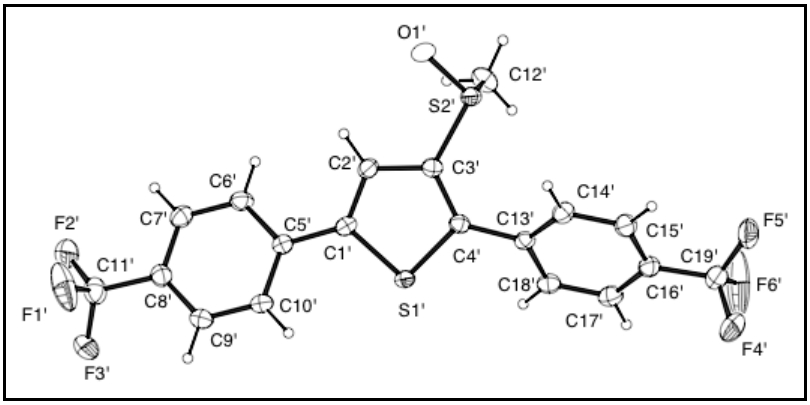


Figure S6. ORTEP drawing of molecule no. 2 of the asymmetric unit with 50% thermal ellipsoids.

Table S5. Summary of Structure Determination of Compound 4d

Empirical formula	$C_{38}H_{24}F_{12}O_2S_4$

Formula weight	868.81
Temperature/K	100
Crystal system	triclinic
Space group	$P\bar{1}$
a	8.3690(4) Å
b	13.3028(6) Å
c	16.2860(8) Å
α	95.133(2) °
β	90.067(2) °
γ	91.338(2) °
Volume	1805.37(15) $Å^3$
Z	2
d_{calc}	1.598 g/cm^3
μ	0.361 mm^{-1}
F(000)	880.0
Crystal size, mm	0.3 × 0.15 × 0.08
2θ range for data collection	3.074 - 55.192 °
Index ranges	$-10 \leq h \leq 10$, $-17 \leq k \leq 17$, $0 \leq l \leq 21$
Reflections collected	54660
Independent reflections	8297 [R(int) = 0.0593]
Data/restraints/parameters	8297/42/536
Goodness-of-fit on F^2	1.020
Final R indexes [I>=2σ (I)]	R_1 = 0.0486, wR_2 = 0.1252
Final R indexes [all data]	R_1 = 0.0589, wR_2 = 0.1319
Largest diff. peak/hole	1.45/-0.42 $eÅ^{-3}$

Table S6. Refined Positional Parameters for Compound 4d

Atom	***x***	***y***	***z***	**U(eq)**
S1	0.76824(8)	0.80696(4)	0.49376(4)	0.02175(14)
S2	0.72732(7)	1.05521(4)	0.67811(4)	0.02152(14)
F1	0.8511(2)	0.29068(12)	0.59791(12)	0.0420(4)
F2	0.7347(3)	0.32103(13)	0.71506(10)	0.0503(5)
F3	0.5957(2)	0.29703(12)	0.60404(12)	0.0394(4)
F4	0.8994(3)	1.23706(15)	0.25549(13)	0.0524(5)
F5	0.8335(3)	1.33693(14)	0.35756(11)	0.0582(7)

F6	0.6553(2)	1.26644(18)	0.27697(14)	0.0565(6)
O1	0.8405(2)	1.04397(14)	0.74783(11)	0.0278(4)
C1	0.7469(3)	0.76530(18)	0.59120(14)	0.0216(5)
C2	0.7262(3)	0.84419(18)	0.64934(14)	0.0214(5)
C3	0.7272(3)	0.93880(17)	0.61477(14)	0.0190(5)
C4	0.7499(3)	0.93180(17)	0.53088(14)	0.0184(4)
C5	0.7460(3)	0.65704(18)	0.60286(15)	0.0223(5)
C6	0.6973(3)	0.6232(2)	0.67742(16)	0.0278(6)
C7	0.6960(4)	0.5209(2)	0.68892(17)	0.0301(6)
C8	0.7395(4)	0.45154(19)	0.62544(16)	0.0280(6)
C9	0.7906(4)	0.4835(2)	0.55129(17)	0.0392(7)
C10	0.7942(4)	0.5856(2)	0.54000(16)	0.0359(7)
C11	0.7308(4)	0.3410(2)	0.63578(17)	0.0322(6)
C12	0.5312(3)	1.0420(2)	0.72105(18)	0.0315(6)
C13	0.7578(3)	1.01174(18)	0.47396(14)	0.0192(5)
C14	0.6618(3)	1.09636(18)	0.48597(15)	0.0222(5)
C15	0.6724(3)	1.17296(19)	0.43393(15)	0.0235(5)
C16	0.7792(3)	1.16483(18)	0.36800(14)	0.0207(5)
C17	0.8719(3)	1.08024(19)	0.35298(15)	0.0232(5)
C18	0.8610(3)	1.00383(19)	0.40567(15)	0.0217(5)
C19	0.7911(3)	1.2512(2)	0.31472(16)	0.0259(5)
S1'	0.25969(7)	-0.02944(4)	0.89408(4)	0.02011(14)
S2'	0.31609(7)	0.21722(4)	1.08220(4)	0.02015(14)
F1'	0.3602(3)	-0.52311(14)	1.07147(18)	0.0668(8)
F2'	0.1204(3)	-0.50754(13)	1.11267(12)	0.0516(5)
F3'	0.1673(2)	-0.55175(12)	0.98619(11)	0.0387(4)
F4'	0.3119(9)	0.4098(4)	0.6538(2)	0.0667(17)
F5'	0.2963(8)	0.5076(2)	0.7607(2)	0.0533(15)
F6'	0.0841(5)	0.4396(5)	0.7064(7)	0.096(3)
F4"	0.3506(12)	0.4500(12)	0.6889(12)	0.081(5)
F5"	0.174(2)	0.5004(7)	0.7700(5)	0.073(5)
F6"	0.125(2)	0.4037(9)	0.6665(7)	0.071(4)
O1'	0.3793(2)	0.18790(14)	1.16230(11)	0.0267(4)
C1'	0.2700(3)	-0.07111(18)	0.99180(14)	0.0198(5)
C2'	0.2883(3)	0.00843(18)	1.05034(15)	0.0218(5)
C3'	0.2966(3)	0.10254(17)	1.01613(15)	0.0197(5)
C4'	0.2813(3)	0.09577(17)	0.93175(14)	0.0190(5)

C5'	0.2549(3)	-0.17867(17)	1.00432(14)	0.0183(4)
C6'	0.2003(3)	-0.20664(19)	1.08059(15)	0.0238(5)
C7'	0.1855(3)	-0.3073(2)	1.09465(16)	0.0248(5)
C8'	0.2255(3)	-0.38161(18)	1.03290(16)	0.0232(5)
C9'	0.2779(3)	-0.35503(18)	0.95707(15)	0.0232(5)
C10'	0.2924(3)	-0.25451(18)	0.94249(15)	0.0208(5)
C11'	0.2184(4)	-0.4902(2)	1.05039(18)	0.0311(6)
C12'	0.1067(3)	0.2371(2)	1.09674(19)	0.0297(6)
C13'	0.2741(3)	0.17652(17)	0.87545(14)	0.0185(4)
C14'	0.3766(3)	0.26132(18)	0.88754(16)	0.0232(5)
C15'	0.3630(3)	0.34057(19)	0.83770(16)	0.0249(5)
C16'	0.2500(3)	0.33429(18)	0.77493(15)	0.0236(5)
C17'	0.1533(3)	0.24845(19)	0.76065(16)	0.0250(5)
C18'	0.1659(3)	0.16986(19)	0.81003(15)	0.0228(5)
C19'	0.2312(4)	0.4221(2)	0.72464(17)	0.0300(6)

Table S7. Positional Parameters for Hydrogens in Compound 4d

Atom	*x*	*y*	*z*	U(eq)
H2	0.7129	0.837	0.7052	0.028
H6	0.6653	0.6695	0.72	0.037
H7	0.6658	0.4992	0.7395	0.04
H9	0.8225	0.4367	0.509	0.052
H10	0.829	0.6069	0.49	0.048
H12a	0.5249	0.9816	0.7491	0.047
H12b	0.4531	1.0381	0.6776	0.047
H12c	0.5109	1.0993	0.7594	0.047
H14	0.5899	1.1013	0.5295	0.03
H15	0.609	1.2294	0.4428	0.031
H17	0.9408	1.0747	0.3081	0.031
H18	0.9227	0.9468	0.3957	0.029
H2'	0.2946	0.0015	1.1066	0.029
H6'	0.1739	-0.1571	1.122	0.032
H7'	0.1489	-0.3254	1.1453	0.033
H9'	0.3034	-0.4049	0.9158	0.031
H10'	0.3272	-0.2371	0.8913	0.028
H12a'	0.0575	0.1784	1.1172	0.045

H12b'	0.0585	0.249	1.0451	0.045
H12c'	0.0918	0.2945	1.1358	0.045
H14'	0.4538	0.2647	0.9289	0.031
H15'	0.4295	0.3975	0.8465	0.033
H17'	0.0797	0.2438	0.7176	0.033
H18'	0.1017	0.1121	0.7995	0.03

Table S8. Refined Thermal Parameters (U's) for Compound 4d

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	0.0288(3)	0.0212(3)	0.0147(3)	-0.0014(2)	0.0026(2)	0.0012(2)
S2	0.0245(3)	0.0214(3)	0.0177(3)	-0.0030(2)	0.0020(2)	-0.0004(2)
F1	0.0478(11)	0.0266(8)	0.0519(11)	0.0032(8)	0.0022(9)	0.0083(7)
F2	0.0987(16)	0.0264(8)	0.0262(9)	0.0049(7)	-0.0068(10)	0.0014(10)
F3	0.0428(10)	0.0277(8)	0.0466(11)	-0.0020(7)	-0.0023(9)	-0.0033(7)
F4	0.0679(14)	0.0485(11)	0.0448(11)	0.0231(9)	0.0289(10)	0.0146(10)
F5	0.117(2)	0.0302(9)	0.0272(9)	0.0066(7)	-0.0087(11)	-0.0185(11)
F6	0.0376(10)	0.0758(15)	0.0626(14)	0.0447(12)	-0.0122(10)	-0.0036(10)
O1	0.0255(9)	0.0334(10)	0.0225(9)	-0.0075(7)	-0.0033(8)	-0.0003(7)
C1	0.0231(12)	0.0260(12)	0.0158(11)	0.0018(9)	0.001(1)	-0.0001(9)
C2	0.0235(12)	0.0249(12)	0.0154(11)	0.0006(9)	0.0021(9)	0.0004(9)
C3	0.0189(11)	0.0207(11)	0.0166(11)	-0.0019(8)	0.0010(9)	-0.0004(9)
C4	0.0165(11)	0.0193(11)	0.0191(11)	-0.0005(8)	0.0007(9)	0.0004(8)
C5	0.0247(13)	0.0235(12)	0.0185(11)	0.0001(9)	-0.001(1)	0.0015(9)
C6	0.0360(15)	0.0266(13)	0.0205(12)	-0.0006(10)	0.0032(11)	0.0037(11)
C7	0.0421(16)	0.0261(13)	0.0220(12)	0.0024(10)	0.0034(12)	0.0009(11)
C8	0.0376(15)	0.0222(12)	0.0242(12)	0.0018(9)	-0.0044(11)	0.0005(10)
C9	0.066(2)	0.0294(14)	0.0218(13)	-0.0028(11)	0.0043(14)	0.0072(14)
C10	0.062(2)	0.0268(13)	0.0180(12)	-0.0027(10)	0.0062(13)	0.0043(13)
C11	0.0445(17)	0.0267(13)	0.0254(13)	0.0017(10)	-0.0025(12)	0.0024(12)
C12	0.0217(13)	0.0462(16)	0.0247(13)	-0.0086(12)	0.0026(11)	0.0036(11)
C13	0.0185(11)	0.0233(11)	0.0151(10)	-0.0010(8)	0.0010(9)	-0.0013(9)
C14	0.0207(12)	0.0266(12)	0.0191(12)	0.0004(9)	0.0014(9)	0.0003(9)
C15	0.0225(13)	0.0268(12)	0.0212(12)	0.0020(9)	-0.0007(10)	0.0027(9)
C16	0.0204(12)	0.0246(12)	0.0170(11)	0.0019(9)	-0.0012(9)	-0.0043(9)
C17	0.0209(12)	0.0290(13)	0.0194(12)	0.0005(10)	0.0011(9)	-0.0023(9)
C18	0.0192(12)	0.0251(12)	0.0201(12)	-0.0017(9)	0.0018(9)	0.0011(9)

C19	0.0284(14)	0.0301(13)	0.0191(12)	0.002(1)	-0.0024(10)	-0.0003(10)
S1'	0.0255(3)	0.0201(3)	0.0143(3)	-0.0002(2)	0.0006(2)	-0.0008(2)
S2'	0.0220(3)	0.0209(3)	0.0172(3)	-0.0001(2)	0.0010(2)	-0.0016(2)
F1'	0.0480(12)	0.0293(10)	0.125(2)	0.0190(11)	-0.0363(13)	0.0000(8)
F2'	0.0887(16)	0.0282(9)	0.0387(10)	0.0092(8)	0.0123(11)	-0.0062(10)
F3'	0.0576(11)	0.0220(8)	0.0352(9)	-0.0028(7)	0.0006(9)	-0.0063(7)
F4'	0.128(5)	0.046(2)	0.0293(19)	0.0166(15)	0.020(2)	0.018(2)
F5'	0.097(4)	0.0240(14)	0.0400(19)	0.0119(12)	-0.020(2)	-0.0130(18)
F6'	0.030(2)	0.070(4)	0.202(9)	0.090(5)	-0.028(3)	-0.001(2)
F4"	0.039(5)	0.087(9)	0.128(12)	0.077(9)	0.020(6)	0.006(5)
F5"	0.156(14)	0.036(4)	0.028(4)	0.001(3)	-0.003(6)	0.047(7)
F6"	0.107(11)	0.050(6)	0.062(6)	0.040(5)	-0.055(6)	-0.016(6)
O1'	0.0332(10)	0.0306(9)	0.0161(8)	-0.0003(7)	-0.0025(8)	0.0008(8)
C1'	0.0191(12)	0.0245(12)	0.0158(11)	0.0024(9)	-0.0001(9)	-0.0009(9)
C2'	0.0253(13)	0.0231(11)	0.0173(11)	0.0036(9)	-0.0013(10)	-0.0018(9)
C3'	0.0199(12)	0.0201(11)	0.0188(11)	-0.0001(8)	-0.0005(9)	-0.0006(9)
C4'	0.0186(11)	0.0195(11)	0.0186(11)	-0.0002(8)	0.0016(9)	-0.0005(8)
C5'	0.0157(11)	0.0214(11)	0.0178(11)	0.0016(8)	-0.0003(9)	0.0009(8)
C6'	0.0253(13)	0.0257(12)	0.0199(12)	-0.0017(9)	0.0045(10)	-0.0006(10)
C7'	0.0248(13)	0.0282(13)	0.0217(12)	0.0047(9)	0.0021(10)	-0.002(1)
C8'	0.0230(12)	0.0214(11)	0.0251(12)	0.0021(9)	-0.0028(10)	0.0001(9)
C9'	0.0235(12)	0.0234(12)	0.0219(12)	-0.0028(9)	0.0004(10)	0.0018(9)
C10'	0.0192(12)	0.0257(12)	0.0169(11)	-0.0008(9)	0.0000(9)	0.0016(9)
C11'	0.0321(15)	0.0252(13)	0.0364(15)	0.0056(11)	-0.0056(12)	-0.0045(11)
C12'	0.0258(14)	0.0248(13)	0.0374(16)	-0.0029(11)	0.0020(12)	-0.0011(10)
C13'	0.0176(11)	0.0215(11)	0.0162(11)	0.0007(8)	0.0036(9)	0.0023(8)
C14'	0.0225(13)	0.0262(12)	0.0210(12)	0.0031(9)	-0.0018(10)	-0.0008(9)
C15'	0.0261(13)	0.0236(12)	0.0248(12)	0.0025(10)	0.0004(10)	-0.0043(10)
C16'	0.0267(13)	0.0243(12)	0.0202(12)	0.0023(9)	0.0023(10)	0.0041(10)
C17'	0.0232(13)	0.0312(13)	0.0201(12)	-0.0003(10)	-0.0017(10)	0.003(1)
C18'	0.0214(12)	0.0261(12)	0.0204(12)	-0.0007(9)	0.0025(10)	0.0017(9)
C19'	0.0364(16)	0.0287(13)	0.0253(13)	0.0054(10)	-0.0022(12)	-0.0011(11)

Table S9. Bond Distances in Compound 4d (Å)

S1-C1	1.735(2)	S1-C4	1.726(2)	S2-O1	1.4978(19)

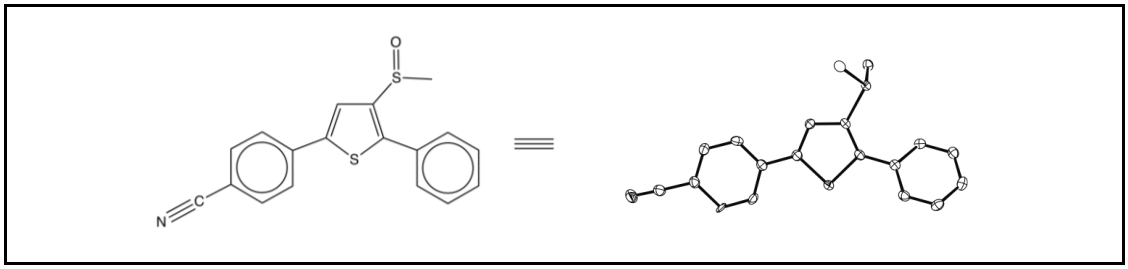
S2-C3	1.782(2)	S2-C12	1.796(3)	F1-C11	1.342(4)
F2-C11	1.342(3)	F3-C11	1.342(4)	F4-C19	1.329(3)
F5-C19	1.323(3)	F6-C19	1.320(3)	C1-C2	1.364(3)
C1-C5	1.469(3)	C2-C3	1.424(3)	C3-C4	1.375(3)
C4-C13	1.472(3)	C5-C6	1.391(3)	C5-C10	1.400(3)
C6-C7	1.390(4)	C7-C8	1.378(4)	C8-C9	1.381(4)
C8-C11	1.495(4)	C9-C10	1.387(4)	C13-C14	1.398(3)
C13-C18	1.407(3)	C14-C15	1.384(3)	C15-C16	1.396(4)
C16-C17	1.386(4)	C16-C19	1.502(3)	C17-C18	1.389(3)
S1'-C1'	1.734(2)	S1'-C4'	1.728(2)	S2'-O1'	1.4942(18)
S2'-C3'	1.791(2)	S2'-C12'	1.791(3)	F1'-C11'	1.330(4)
F2'-C11'	1.338(4)	F3'-C11'	1.333(3)	F4'-C19'	1.337(5)
F5'-C19'	1.336(4)	F6'-C19'	1.296(5)	F4''-C19'	1.224(10)
F5''-C19'	1.319(8)	F6''-C19'	1.300(11)	C1'-C2'	1.365(3)
C1'-C5'	1.466(3)	C2'-C3'	1.415(3)	C3'-C4'	1.375(3)
C4'-C13'	1.476(3)	C5'-C6'	1.402(3)	C5'-C10'	1.401(3)
C6'-C7'	1.382(4)	C7'-C8'	1.392(4)	C8'-C9'	1.384(4)
C8'-C11'	1.497(3)	C9'-C10'	1.381(3)	C13'-C14'	1.401(3)
C13'-C18'	1.393(3)	C14'-C15'	1.394(3)	C15'-C16'	1.388(4)
C16'-C17'	1.386(4)	C16'-C19'	1.497(3)	C17'-C18'	1.381(4)

Table S10. Bond Angles in Compound 4d (ᵒ)

C4-S1-C1	92.57(11)	O1-S2-C3	106.58(11)	O1-S2-C12	105.24(12)
C3-S2-C12	97.70(12)	C2-C1-S1	111.12(18)	C2-C1-C5	127.9(2)
C5-C1-S1	120.89(18)	C1-C2-C3	112.3(2)	C2-C3-S2	121.60(17)
C4-C3-S2	123.78(18)	C4-C3-C2	114.0(2)	C3-C4-S1	109.95(17)
C3-C4-C13	129.9(2)	C13-C4-S1	120.16(17)	C6-C5-C1	120.4(2)
C6-C5-C10	118.3(2)	C10-C5-C1	121.3(2)	C7-C6-C5	120.7(2)
C8-C7-C6	120.0(3)	C7-C8-C9	120.3(2)	C7-C8-C11	120.5(3)
C9-C8-C11	119.3(2)	C8-C9-C10	119.8(3)	C9-C10-C5	120.8(3)
F1-C11-C8	112.5(3)	F2-C11-F1	106.7(2)	F2-C11-C8	112.9(2)
F3-C11-F1	105.9(2)	F3-C11-F2	106.1(2)	F3-C11-C8	112.2(2)
C14-C13-C4	120.8(2)	C14-C13-C18	118.6(2)	C18-C13-C4	120.5(2)

C15-C14-C13	120.9(2)	C14-C15-C16	119.4(2)	C15-C16-C19	117.7(2)
C17-C16-C15	120.9(2)	C17-C16-C19	121.3(2)	C16-C17-C18	119.3(2)
C17-C18-C13	120.8(2)	F4-C19-C16	112.8(2)	F5-C19-F4	105.8(2)
F5-C19-C16	112.0(2)	F6-C19-F4	105.8(2)	F6-C19-F5	107.4(3)
F6-C19-C16	112.5(2)	C4'-S1'-C1'	92.67(11)	O1'-S2'-C3'	105.98(11)
O1'-S2'-C12'	106.50(13)	C3'-S2'-C12'	96.76(12)	C2'-C1'-S1'	110.78(18)
C2'-C1'-C5'	127.8(2)	C5'-C1'-S1'	121.35(17)	C1'-C2'-C3'	112.6(2)
C2'-C3'-S2'	120.07(18)	C4'-C3'-S2'	125.68(18)	C4'-C3'-C2'	114.2(2)
C3'-C4'-S1'	109.71(17)	C3'-C4'-C13'	129.8(2)	C13'-C4'-S1'	120.42(17)
C6'-C5'-C1'	118.9(2)	C10'-C5'-C1'	122.2(2)	C10'-C5'-C6'	118.9(2)
C7'-C6'-C5'	120.4(2)	C6'-C7'-C8'	119.9(2)	C7'-C8'-C11'	119.5(2)
C9'-C8'-C7'	120.2(2)	C9'-C8'-C11'	120.2(2)	C10'-C9'-C8'	120.1(2)
C9'-C10'-C5'	120.4(2)	F1'-C11'-F2'	105.7(2)	F1'-C11'-F3'	106.5(3)
F1'-C11'-C8'	112.3(2)	F2'-C11'-C8'	112.9(2)	F3'-C11'-F2'	105.8(2)
F3'-C11'-C8'	113.0(2)	C14'-C13'-C4'	120.0(2)	C18'-C13'-C4'	120.8(2)
C18'-C13'-C14'	119.1(2)	C15'-C14'-C13'	120.1(2)	C16'-C15'-C14'	119.8(2)
C15'-C16'-C19'	119.2(2)	C17'-C16'-C15'	120.1(2)	C17'-C16'-C19'	120.7(2)
C18'-C17'-C16'	120.3(2)	C17'-C18'-C13'	120.4(2)	F4'-C19'-C16'	111.6(3)
F5'-C19'-F4'	102.4(3)	F5'-C19'-C16'	112.8(3)	F6'-C19'-F4'	107.4(5)
F6'-C19'-F5'	107.9(4)	F6'-C19'-C16'	114.0(3)	F4"-C19'-F5"	108.4(9)
F4"-C19'-F6"	104.4(9)	F4"-C19'-C16'	116.4(5)	F5"-C19'-C16'	110.8(4)
F6"-C19'-F5"	103.8(7)	F6"-C19'-C16'	112.1(5)		

X-ray Structure of Compound 5a



Compound **5a**, $C_{18}H_{13}NOS_2$, crystallizes in the monoclinic space group $P2_1/c$ (systematic absences 0k0: k=odd and h0l: l=odd) with a=9.1299(4) Å, b=30.1997(10) Å, c=5.4771(2) Å, β=96.868(2)°, V=1499.31(10) $Å^3$, Z=4, and d_{calc}=1.433 g/cm_3. X-ray intensity data were collected on a Bruker APEXII CCD area detector employing graphite-monochromated Mo-Kα radiation (λ=0.71073 Å) at a temperature of 100K. Preliminary indexing was performed from a series of thirty-six 0.5 °rotation frames with exposures of 10 seconds. A total of 1878 frames were collected with a crystal to detector distance of 37.4 mm, rotation widths of 0.5 ° and exposures of 30 seconds:

scan type	2θ	ω	φ	χ	Frames
ϕ	-23.00	315.83	15.20	28.88	730
ϕ	-23.00	334.21	269.64	73.66	254
ω	-15.50	342.15	341.11	-63.64	94
ϕ	19.50	59.55	349.20	-26.26	737
ω	17.00	346.62	318.36	83.36	63

Rotation frames were integrated using SAINT[2], producing a listing of unaveraged F^2 and σ (F^2) values. A total of 24346 reflections were measured over the ranges $4.494 \leq 2\theta \leq 50.844°$, $-11 \leq h \leq 11$, $-36 \leq k \leq 36$, $-6 \leq l \leq 6$ yielding 2759 unique reflections (R_{int} = 0.0302). The intensity data were corrected for Lorentz and polarization effects and for absorption using SADABS[3] (minimum and maximum transmission 0.7157, 0.7452). The structure was solved by direct methods - SHELXS-97.[4] Refinement was by full-matrix least squares based on F^2 using SHELXL-2014.[5] All reflections were used during refinement. The weighting scheme used was $w=1/[\sigma^2(F_o^2)+ (0.0251P)^2 + 1.5788P]$ where $P = (F_o^2 + 2F_c^2)/3$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model. Refinement converged to R1=0.0350 and wR2=0.0751 for 2459 observed reflections for which $F > 4\sigma(F)$ and R1=0.0413 and wR2=0.0779 and GOF =1.091 for all 2759 unique, non-zero reflections and 237 variables. The maximum Δ/σ in the final cycle of least squares was 0.001 and the two most prominent peaks in the final difference Fourier were +0.34 and -0.33 e/Å^3.

Table S11. lists cell information, data collection parameters, and refinement data. Final positional and equivalent isotropic thermal parameters are given in Tables S12. and S13. Anisotropic thermal parameters are in Table S14. Tables S15. and S16. list bond distances and bond angles. Figure S7. is an ORTEP representation of the molecule with 50% probability thermal ellipsoids displayed.

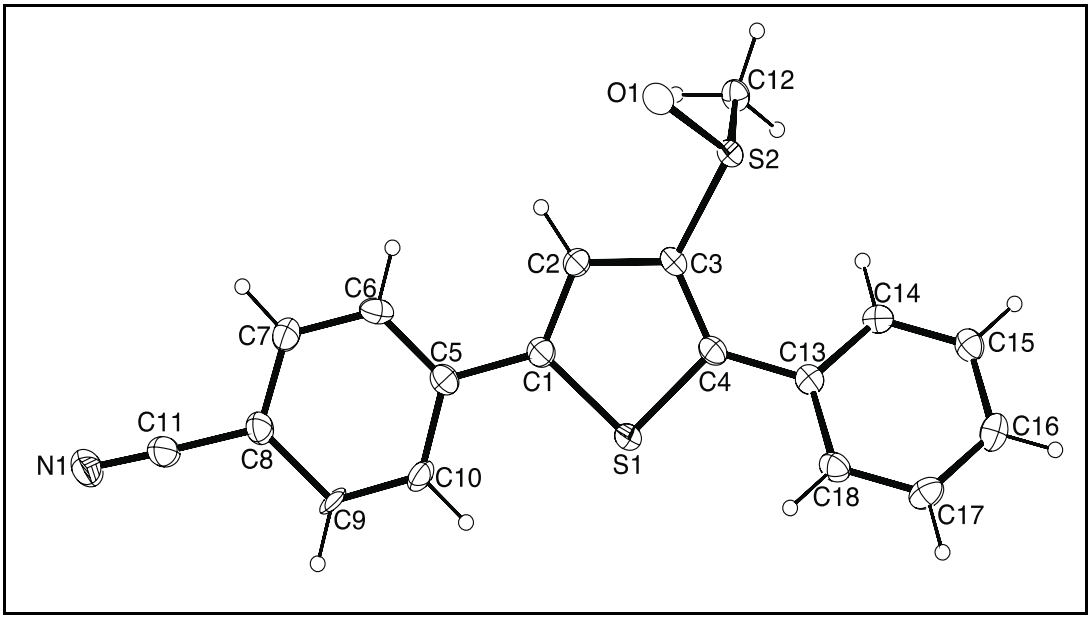


Figure S7. ORTEP drawing of the title compound with 50% thermal ellipsoids.

Table S11. Summary of Structure Determination of Compound 5a

Empirical formula	$C_{18}H_{13}NOS_2$
Formula weight	323.41
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/c$
a	9.1299(4) Å
b	30.1997(10) Å
c	5.4771(2) Å
β	96.868(2) °
Volume	1499.31(10) $Å^3$
Z	4
d_{calc}	1.433 g/cm^3
μ	0.355 mm^{-1}
F(000)	672.0
Crystal size, mm	0.4 × 0.1 × 0.01
2θ range for data collection	4.494 - 50.844 °
Index ranges	$-11 \leq h \leq 11$, $-36 \leq k \leq 36$, $-6 \leq l \leq 6$
Reflections collected	24346
Independent reflections	2759[R(int) = 0.0302]
Data/restraints/parameters	2759/84/237
Goodness-of-fit on F^2	1.091
Final R indexes [I>=2σ (I)]	R_1 = 0.0350, wR_2 = 0.0751
Final R indexes [all data]	R_1 = 0.0413, wR_2 = 0.0779
Largest diff. peak/hole	0.34/-0.33 $eÅ^{-3}$

Table S12. Refined Positional Parameters for Compound 5a

Atom	***x***	***y***	***z***	**U(eq)**
S1	0.43645(6)	0.41255(2)	1.03027(10)	0.02178(14)
S2	0.16191(5)	0.29747(2)	1.04078(9)	0.01499(12)
O1	0.08854(16)	0.28987(4)	0.7841(2)	0.0208(3)
N1	0.1559(2)	0.58655(6)	-0.0044(4)	0.0318(5)
C1	0.2793(2)	0.41656(6)	0.8196(3)	0.0181(4)
C2	0.1893(2)	0.38119(6)	0.8421(3)	0.0159(4)
C3	0.2461(2)	0.35088(6)	1.0270(3)	0.0152(4)
C4	0.3807(2)	0.36274(6)	1.1479(4)	0.0170(4)

C5	0.2566(2)	0.45339(6)	0.6456(4)	0.0180(4)
C6	0.1359(16)	0.4537(5)	0.467(3)	0.019(2)
C7	0.1094(14)	0.4888(4)	0.310(2)	0.023(2)
C6'	0.1689(12)	0.4466(4)	0.421(2)	0.0205(16)
C7'	0.1466(10)	0.4806(3)	0.2513(18)	0.0226(14)
C8	0.2079(2)	0.52309(7)	0.3119(4)	0.0209(4)
C9	0.3332(18)	0.5238(6)	0.511(3)	0.021(3)
C10	0.3572(16)	0.4886(5)	0.660(3)	0.021(2)
C9'	0.2931(14)	0.5295(4)	0.515(3)	0.028(2)
C10'	0.3162(13)	0.4956(4)	0.691(2)	0.0241(18)
C11	0.1803(2)	0.55885(7)	0.1376(4)	0.0248(5)
C12	0.0144(2)	0.31204(7)	1.2129(4)	0.0180(4)
C13	0.4751(2)	0.34037(6)	1.3467(3)	0.0169(4)
C14	0.4119(2)	0.31461(6)	1.5186(3)	0.0177(4)
C15	0.5000(2)	0.29304(7)	1.7045(4)	0.0197(4)
C16	0.6518(2)	0.29730(7)	1.7261(4)	0.0220(4)
C17	0.7155(2)	0.32316(7)	1.5586(4)	0.0231(5)
C18	0.6285(2)	0.34422(7)	1.3686(4)	0.0202(4)

Table S13. Positional Parameters for Hydrogens in Compound 5a

Atom	*x*	*y*	*z*	U(eq)
H2	0.0992	0.3773	0.7456	0.021
H6	0.0717	0.4297	0.4533	0.026
H7	0.0233	0.4894	0.2009	0.031
H6'	0.1254	0.4191	0.3864	0.027
H7'	0.0922	0.4757	0.0991	0.03
H9	0.3948	0.5484	0.5317	0.029
H10	0.4414	0.4876	0.7734	0.027
H9'	0.3396	0.5567	0.5441	0.037
H10'	0.3722	0.5014	0.8409	0.032
H12a	-0.0385	0.3368	1.1364	0.027
H12b	0.0539	0.3198	1.3777	0.027
H12c	-0.0514	0.2873	1.217	0.027

H14	0.3099	0.312	1.5079	0.023
H15	0.4568	0.2755	1.8158	0.026
H16	0.7106	0.2829	1.8521	0.029
H17	0.8175	0.3264	1.5736	0.031
H18	0.6726	0.361	1.2552	0.027

Table S14. Refined Thermal Parameters (U's) for Compound 5a

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	0.0223(3)	0.0196(3)	0.0220(3)	0.0057(2)	-0.0031(2)	-0.0073(2)
S2	0.0165(2)	0.0131(2)	0.0157(2)	0.00041(18)	0.00323(18)	-0.00036(18)
O1	0.0270(8)	0.0180(7)	0.0176(7)	-0.0015(6)	0.0029(6)	-0.0044(6)
N1	0.0274(10)	0.0265(10)	0.0413(12)	0.0131(9)	0.0042(9)	0.0009(8)
C1	0.021(1)	0.0178(10)	0.0154(10)	-0.0009(8)	0.0020(8)	-0.0016(8)
C2	0.0158(10)	0.0167(9)	0.0152(9)	-0.0011(8)	0.0013(7)	0.0005(7)
C3	0.0177(10)	0.0124(9)	0.0162(9)	0.0008(7)	0.0055(8)	-0.0003(7)
C4	0.0197(10)	0.0159(9)	0.0161(10)	0.0001(7)	0.0055(8)	-0.0015(8)
C5	0.0201(10)	0.0165(10)	0.0181(10)	0.0001(8)	0.0053(8)	0.0001(8)
C6	0.016(5)	0.015(5)	0.028(5)	-0.003(3)	0.005(3)	-0.002(3)
C7	0.020(4)	0.026(4)	0.022(4)	0.005(3)	-0.001(3)	0.002(3)
C6'	0.022(4)	0.014(3)	0.026(4)	-0.002(2)	0.003(3)	0.005(3)
C7'	0.024(3)	0.019(3)	0.024(3)	-0.003(2)	-0.001(2)	0.002(2)
C8	0.0195(11)	0.0187(10)	0.0246(11)	0.0050(8)	0.0031(9)	0.0025(8)
C9	0.018(6)	0.020(5)	0.023(4)	0.000(3)	-0.015(4)	-0.003(4)
C10	0.016(5)	0.020(4)	0.024(4)	0.002(3)	-0.007(3)	0.004(3)
C9'	0.026(5)	0.013(3)	0.042(3)	0.013(2)	-0.008(4)	-0.002(3)
C10'	0.027(5)	0.018(3)	0.025(3)	0.001(2)	-0.007(3)	-0.004(3)
C11	0.0189(11)	0.0219(11)	0.0336(12)	0.0045(10)	0.0026(9)	-0.0013(8)
C12	0.0184(10)	0.0195(10)	0.017(1)	0.0015(8)	0.0054(8)	0.0018(8)
C13	0.0195(10)	0.0156(9)	0.0158(9)	-0.0019(8)	0.0036(8)	0.0001(8)
C14	0.017(1)	0.0191(10)	0.0172(10)	-0.0029(8)	0.0035(8)	-0.0015(8)
C15	0.0246(11)	0.019(1)	0.0158(10)	-0.0006(8)	0.0040(8)	-0.0008(8)
C16	0.0251(11)	0.0235(10)	0.0169(10)	-0.0008(8)	-0.0002(8)	0.0060(9)
C17	0.0162(10)	0.0305(11)	0.0223(11)	-0.0032(9)	0.0019(8)	0.0006(9)
C18	0.0212(11)	0.022(1)	0.0183(10)	0.0008(8)	0.0063(8)	-0.0038(8)

Table S15. Bond Distances in Compound 5a (Å)

S1-C1	1.734(2)	S1-C4	1.7363(19)	S2-O1	1.5010(14)
S2-C3	1.7924(19)	S2-C12	1.7888(19)	N1-C11	1.146(3)
C1-C2	1.363(3)	C1-C5	1.463(3)	C2-C3	1.416(3)
C3-C4	1.372(3)	C4-C13	1.470(3)	C5-C6	1.384(15)
C5-C6'	1.398(11)	C5-C10	1.401(15)	C5-C10'	1.397(11)
C6-C7	1.365(16)	C7-C8	1.372(10)	C6'-C7'	1.384(12)
C7'-C8	1.424(8)	C8-C9	1.482(16)	C8-C9'	1.292(15)
C8-C11	1.444(3)	C9-C10	1.34(2)	C9'-C10'	1.406(17)
C13-C14	1.398(3)	C13-C18	1.397(3)	C14-C15	1.383(3)
C15-C16	1.382(3)	C16-C17	1.385(3)	C17-C18	1.385(3)

Table S16. Bond Angles in Compound 5a (°)

C1-S1-C4	92.96(9)	O1-S2-C3	104.11(8)	O1-S2-C12	104.57(9)
C12-S2-C3	98.90(9)	C2-C1-S1	110.17(15)	C2-C1-C5	127.94(18)
C5-C1-S1	121.88(15)	C1-C2-C3	113.45(18)	C2-C3-S2	119.29(14)
C4-C3-S2	125.36(15)	C4-C3-C2	114.00(17)	C3-C4-S1	109.41(14)
C3-C4-C13	130.50(17)	C13-C4-S1	120.09(14)	C6-C5-C1	120.3(6)
C6-C5-C10	119.6(8)	C6'-C5-C1	118.8(5)	C10-C5-C1	120.0(6)
C10'-C5-C1	123.8(5)	C10'-C5-C6'	117.4(6)	C7-C6-C5	121.1(11)
C6-C7-C8	121.0(9)	C7'-C6'-C5	120.4(8)	C6'-C7'-C8	119.3(7)
C7-C8-C9	117.6(9)	C7-C8-C11	119.9(5)	C7'-C8-C11	119.2(4)
C9'-C8-C7'	121.0(7)	C9'-C8-C11	119.8(6)	C11-C8-C9	122.3(8)
C10-C9-C8	119.4(13)	C9-C10-C5	120.6(11)	C8-C9'-C10'	120.5(10)
C5-C10'-C9'	121.2(9)	N1-C11-C8	178.3(2)	C14-C13-C4	120.18(17)
C18-C13-C4	121.24(18)	C18-C13-C14	118.59(18)	C15-C14-C13	120.52(18)
C16-C15-C14	120.53(19)	C15-C16-C17	119.48(19)	C16-C17-C18	120.52(19)
C17-C18-C13	120.36(19)				

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(1) (a) Holland, H. L.; Turner, C. D.; Andreana, P. R.; Nguyen, D. *Can. J. Chem.* **1999,** *77*, 463; (b) Eberhart, A. J.; Shrives, H. J.; Alvarez, E.; Carrer, A.; Zhang, Y.; Procter, D. J. *Chem. - Eur. J.* **2015,** *21*, 7428.

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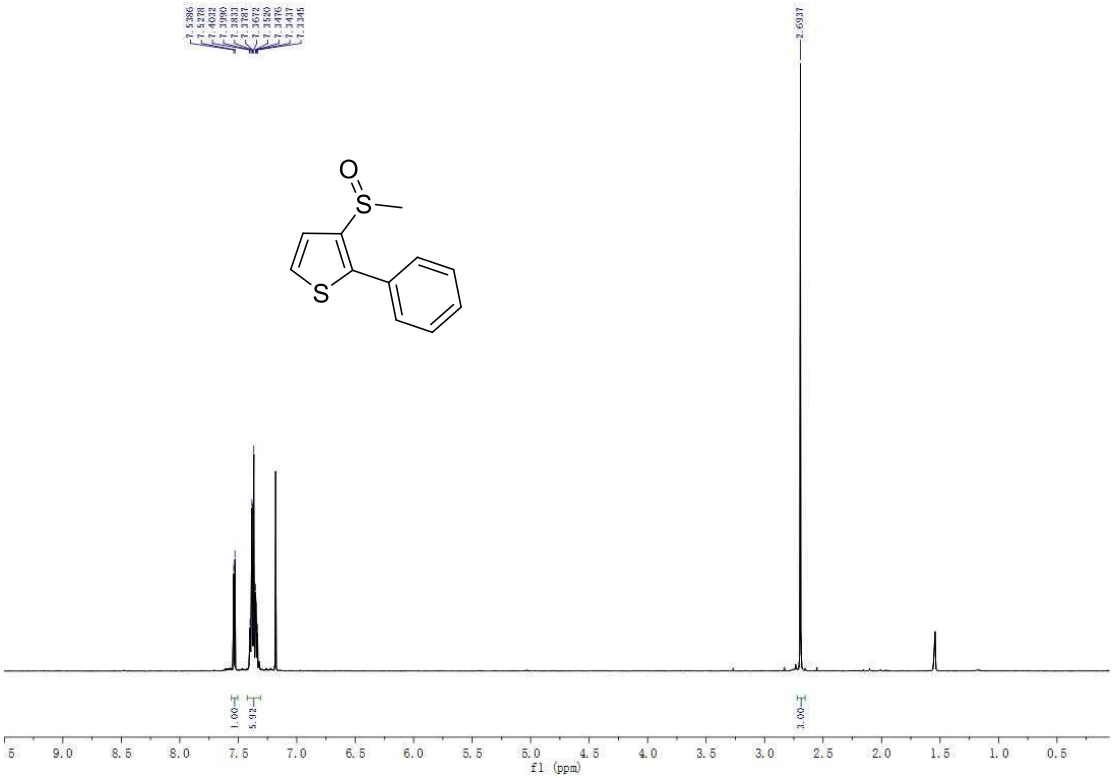
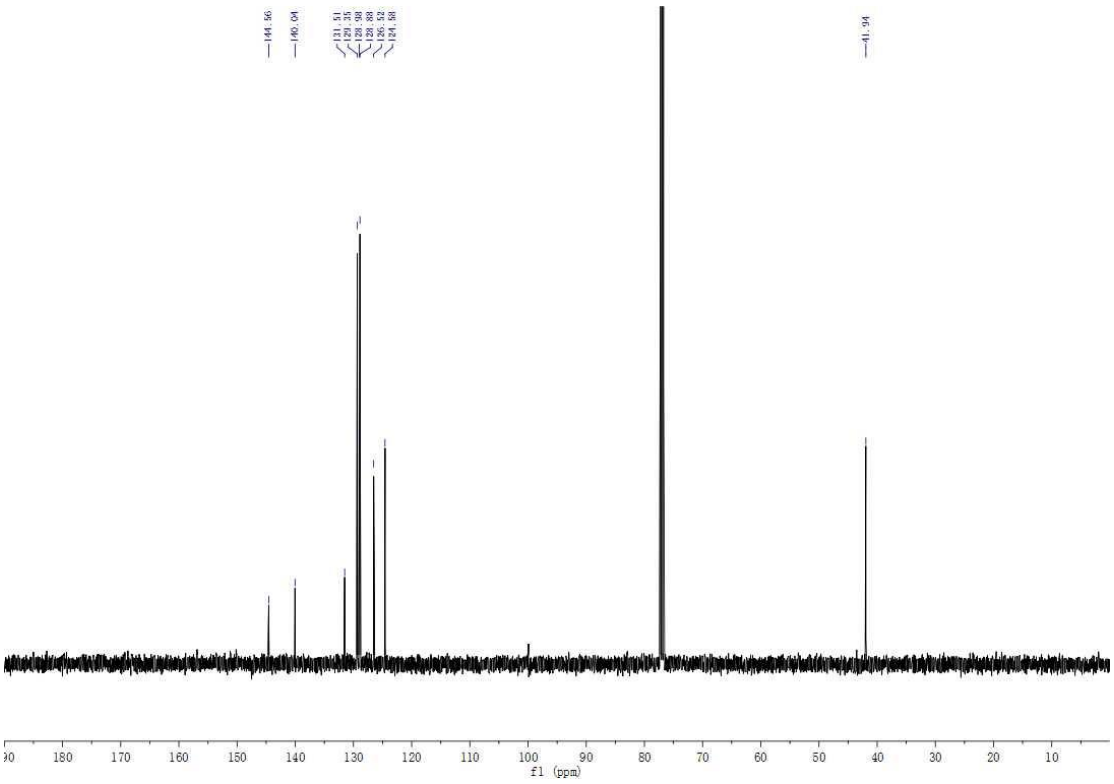
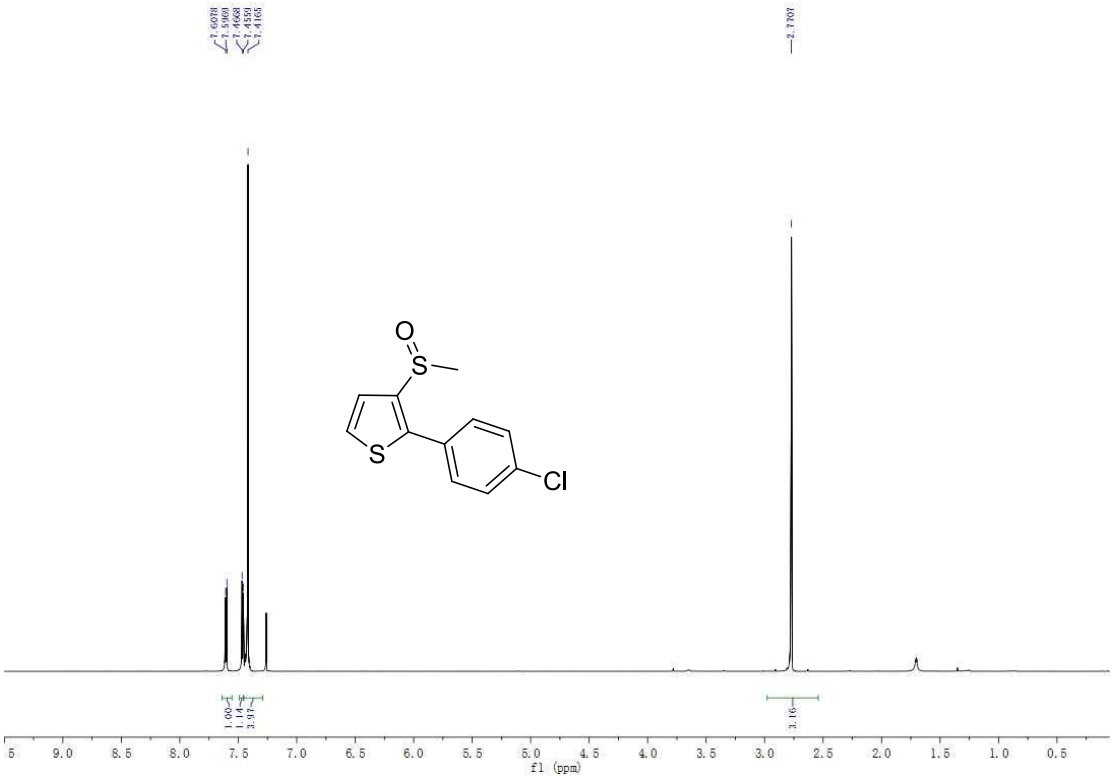
^{1}H NMR spectra ($CDCl_3$, 500 MHz) of 3-(Methylsulfinyl)-2-phenylthiophene (3a)



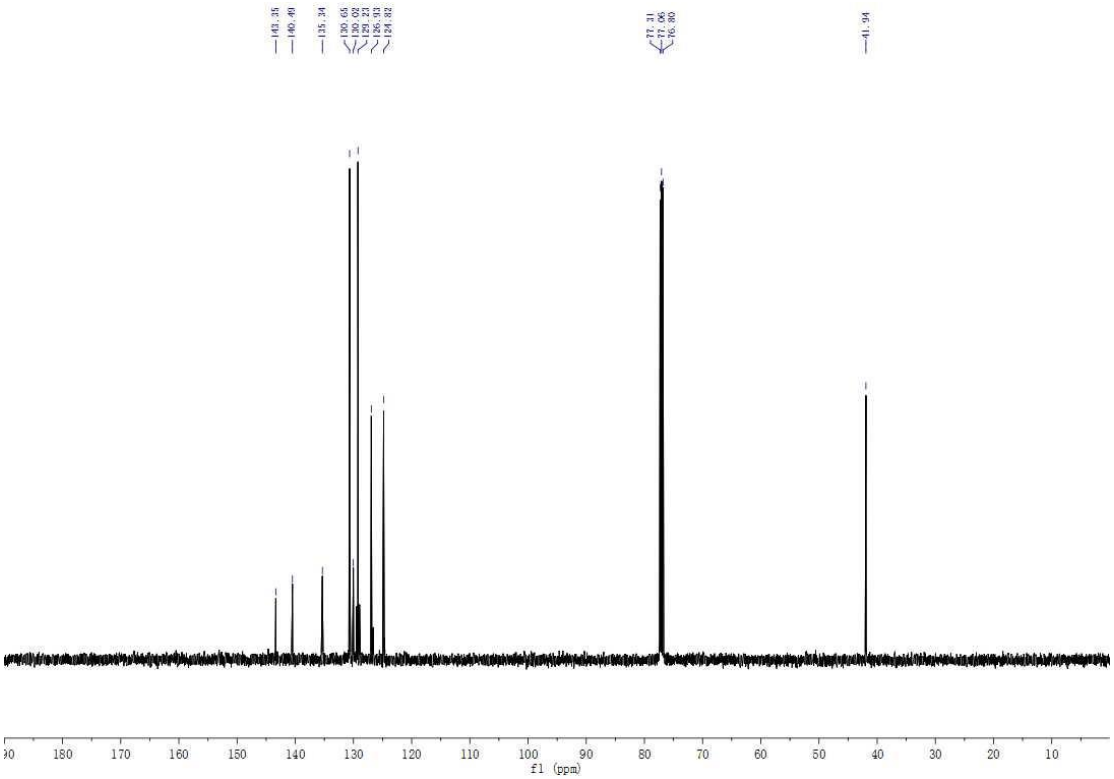
^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of 3-(Methylsulfinyl)-2-phenylthiophene (3a)



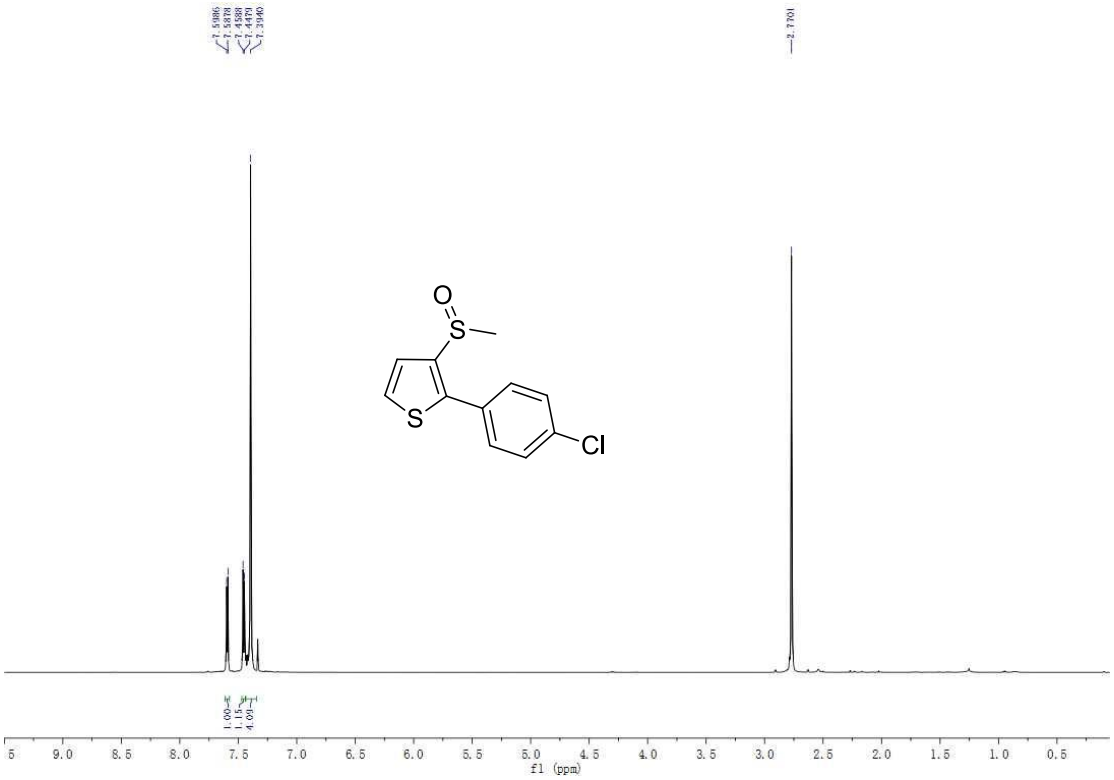
^{1}H NMR spectra ($CDCl_3$, 500 MHz) of 2-(4-Chlorophenyl)-3-(methylsulfinyl)thiophene (3b)



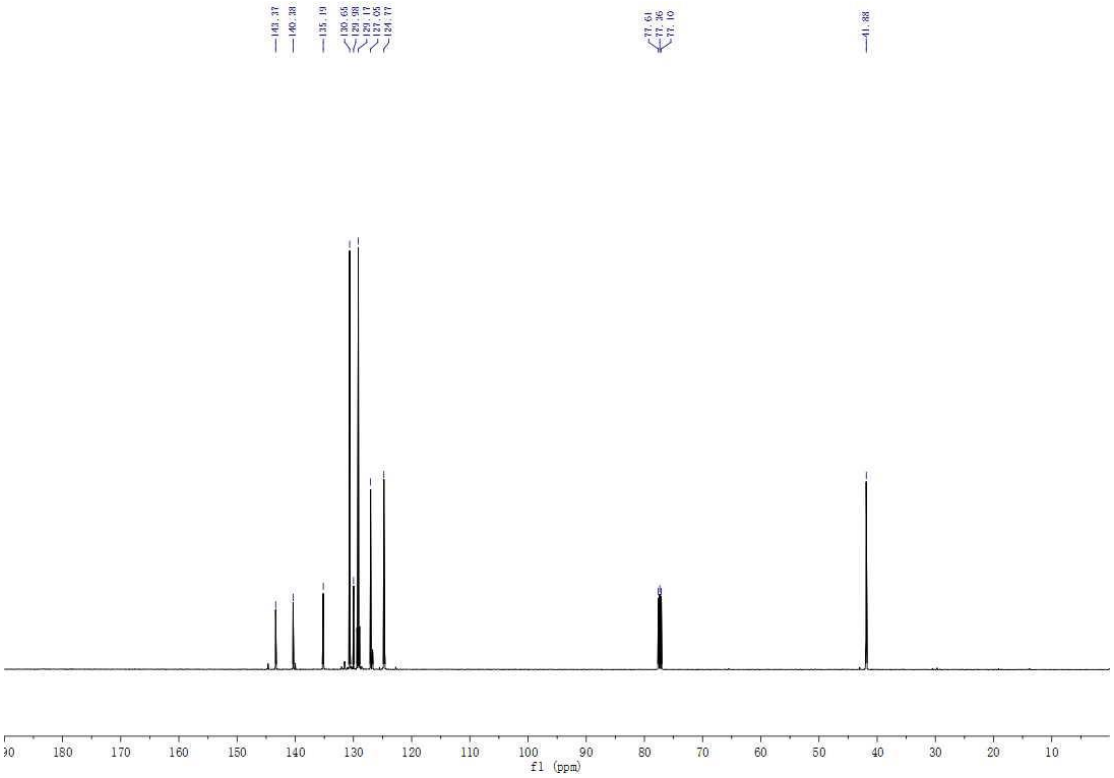
^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of 2-(4-Chlorophenyl)-3-(methylsulfinyl)thiophene (3b)



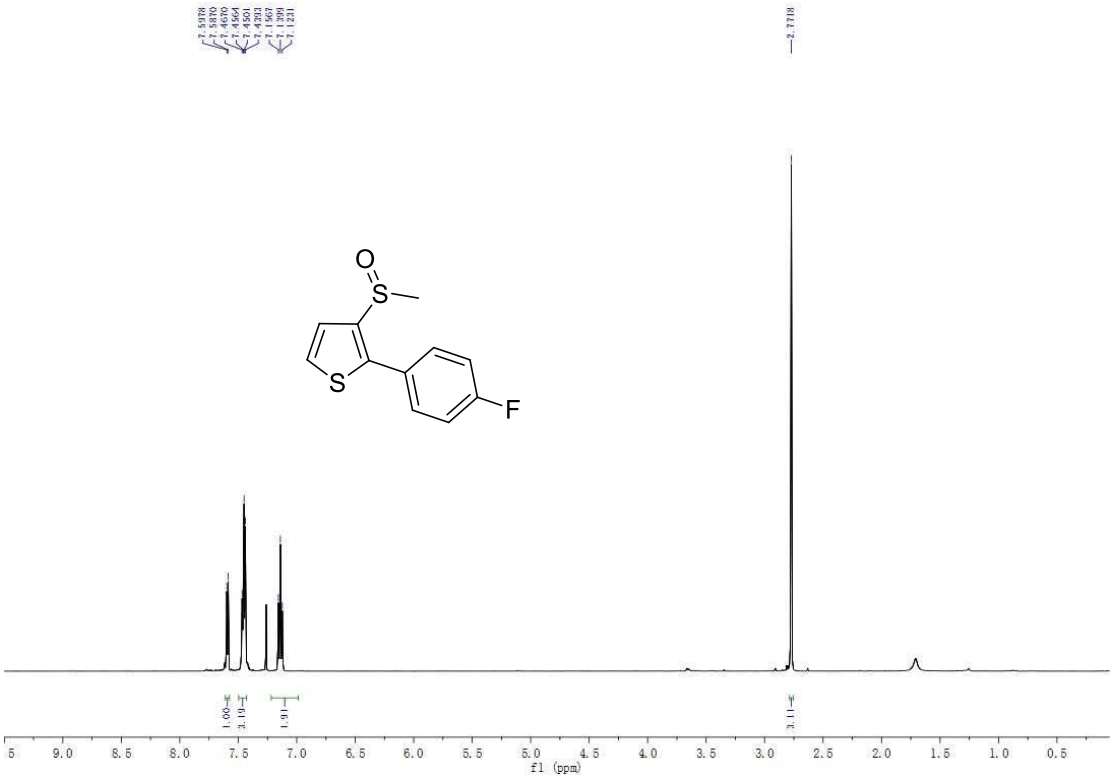
^{1}H NMR spectra ($CDCl_3$, 500 MHz) of 2-(4-Chlorophenyl)-3-(methylsulfinyl)thiophene (3b) from 2 mmol scale



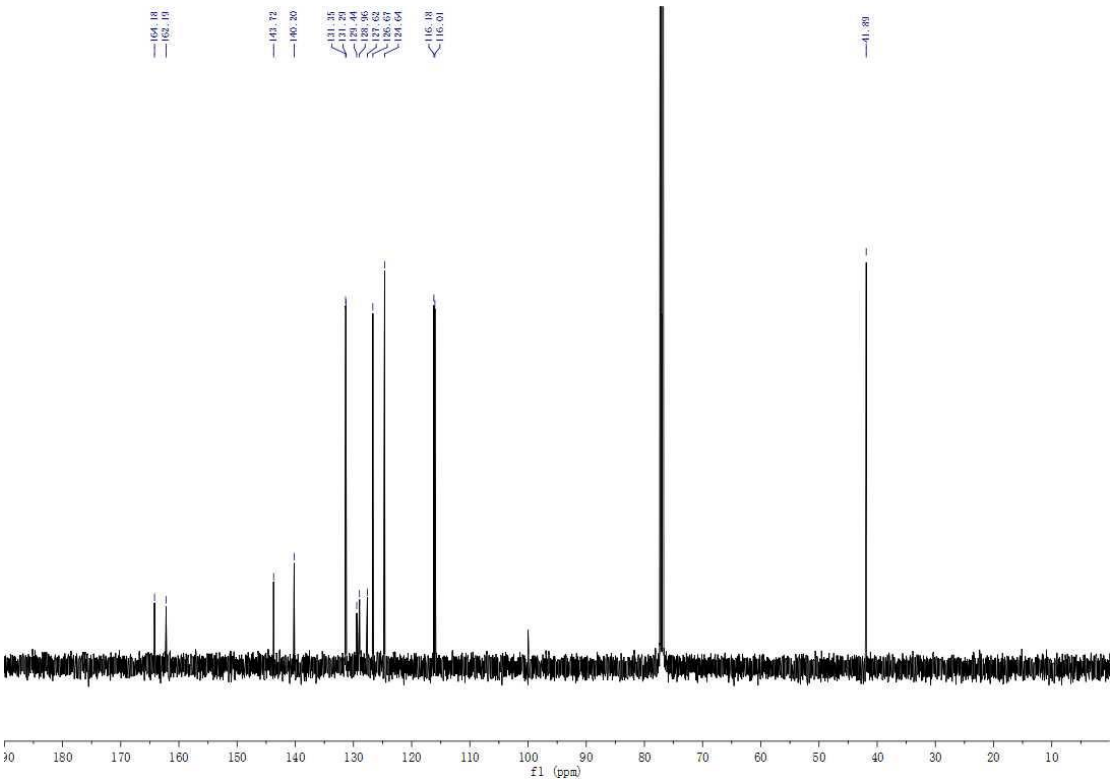
^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of 2-(4-Chlorophenyl)-3-(methylsulfinyl)thiophene (3b) from 2 mmol scale



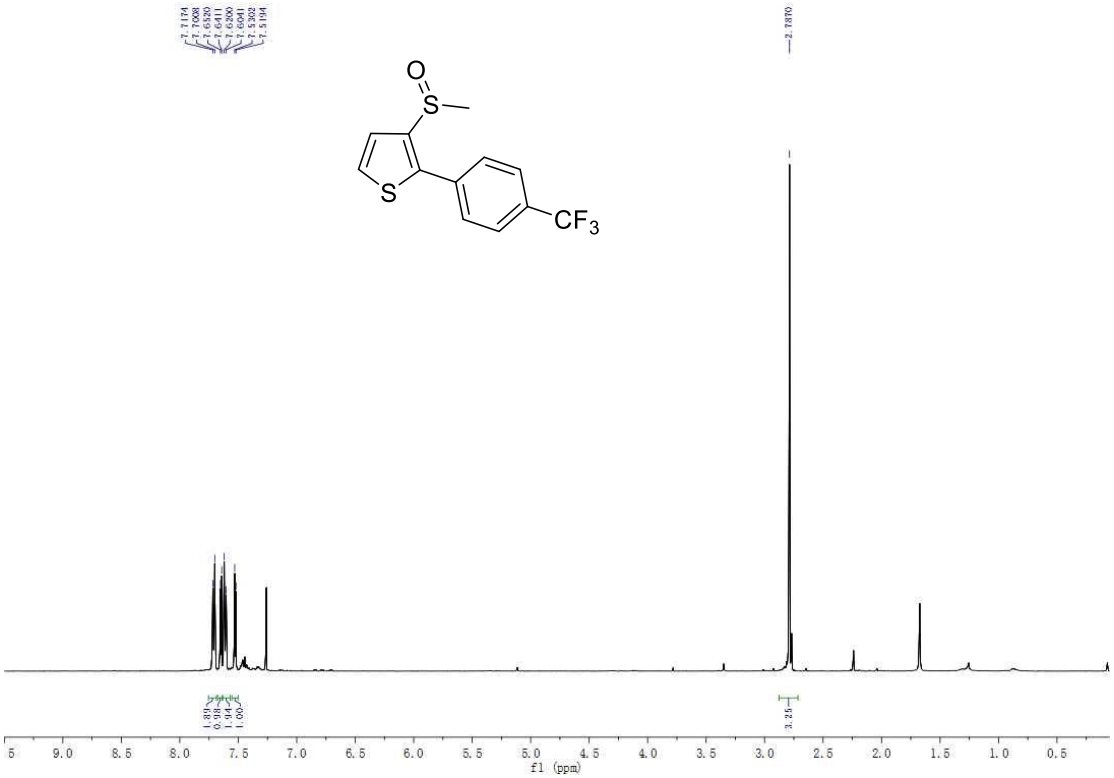
^{1}H NMR spectra ($CDCl_3$, 500 MHz) of 2-(4-Fluorophenyl)-3-(methylsulfinyl)thiophene (3c)



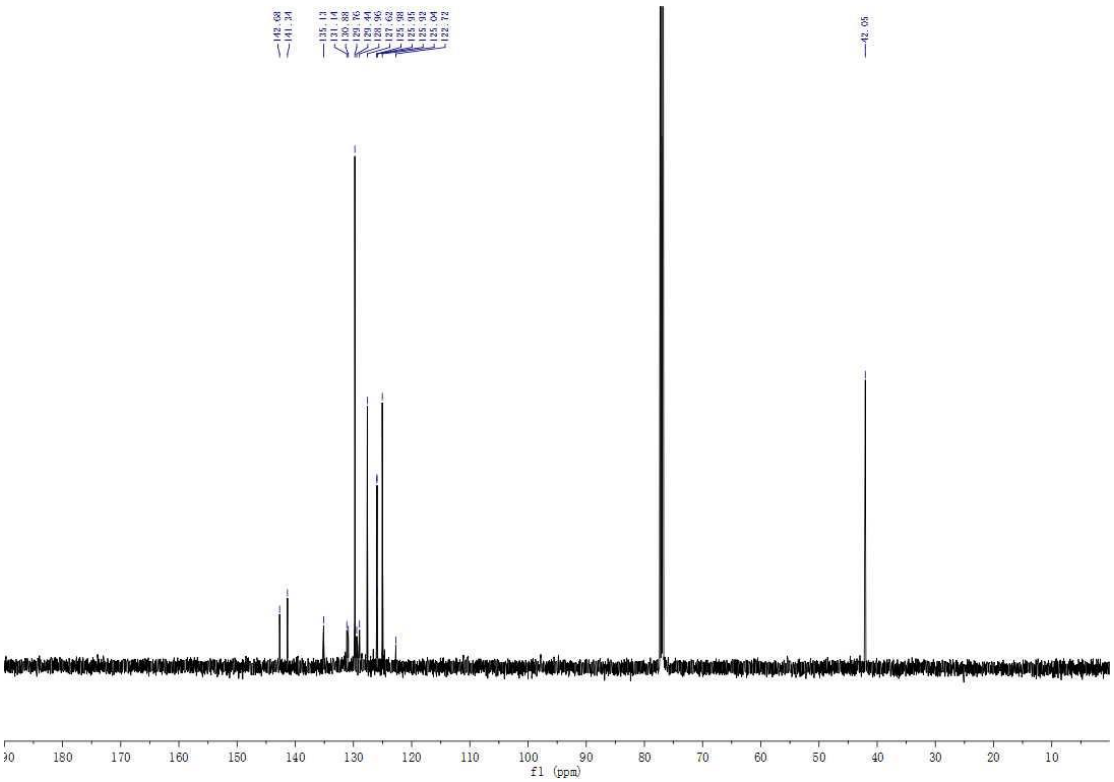
^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of 2-(4-Fluorophenyl)-3-(methylsulfinyl)thiophene (3c)



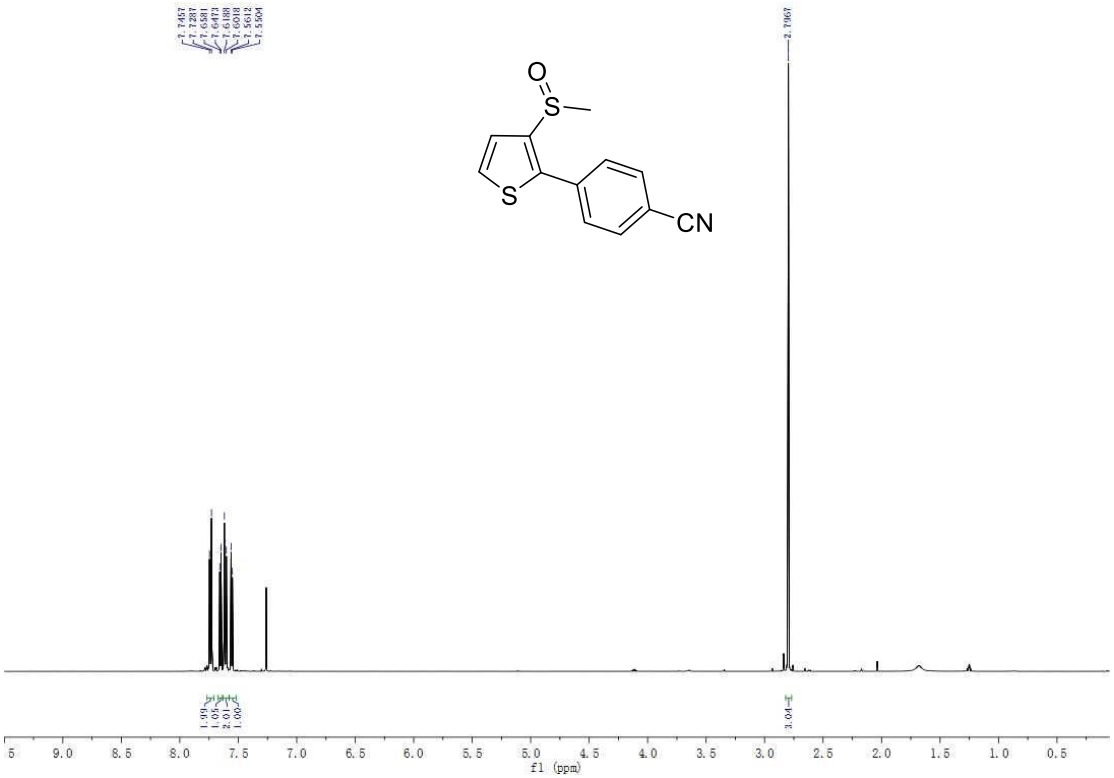
^{1}H NMR spectra ($CDCl_3$, 500 MHz) of 3-(Methylsulfinyl)-2-(4-(trifluoromethyl)phenyl)thiophene (3d)



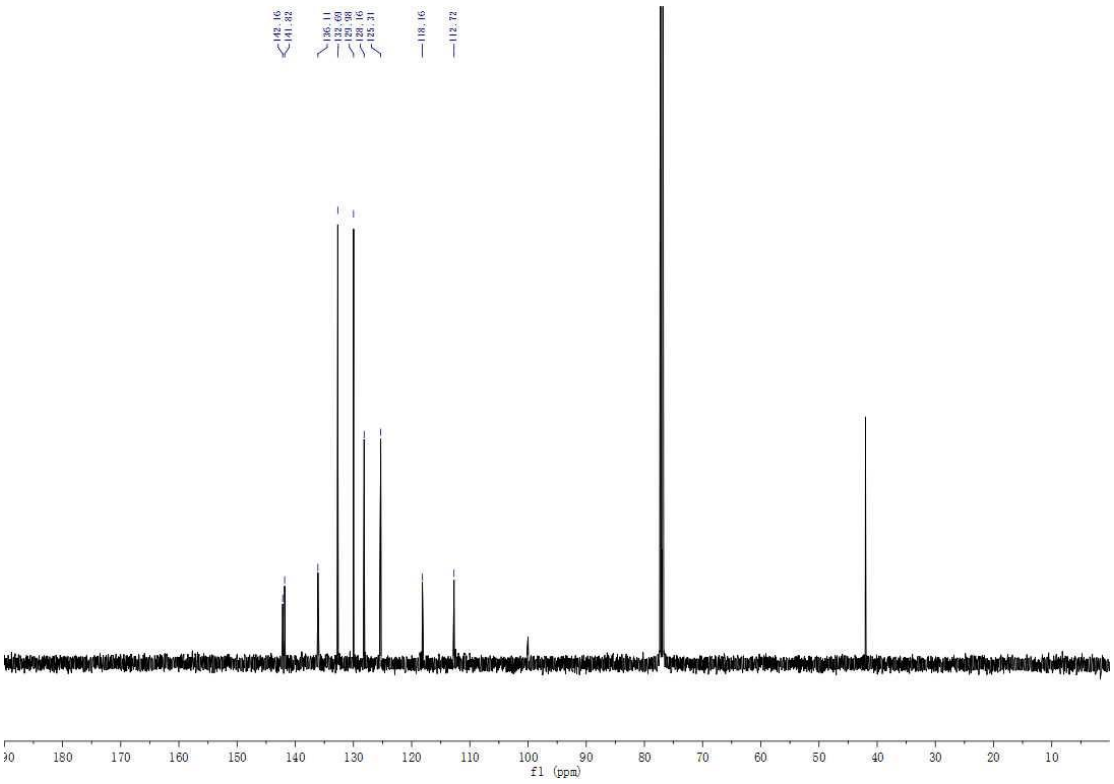
^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of 3-(Methylsulfinyl)-2-(4-(trifluoromethyl)phenyl)thiophene (3d)



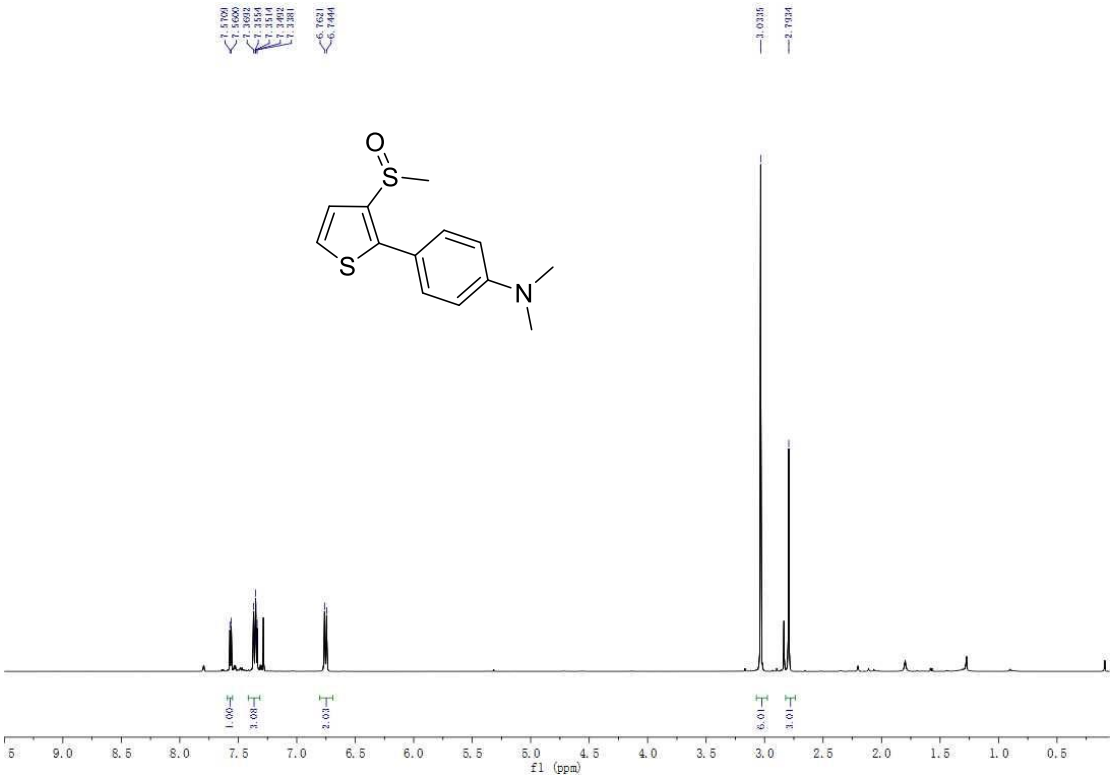
^{1}H NMR spectra ($CDCl_3$, 500 MHz) of 4-(3-(Methylsulfinyl)thiophen-2-yl)benzonitrile (3e)



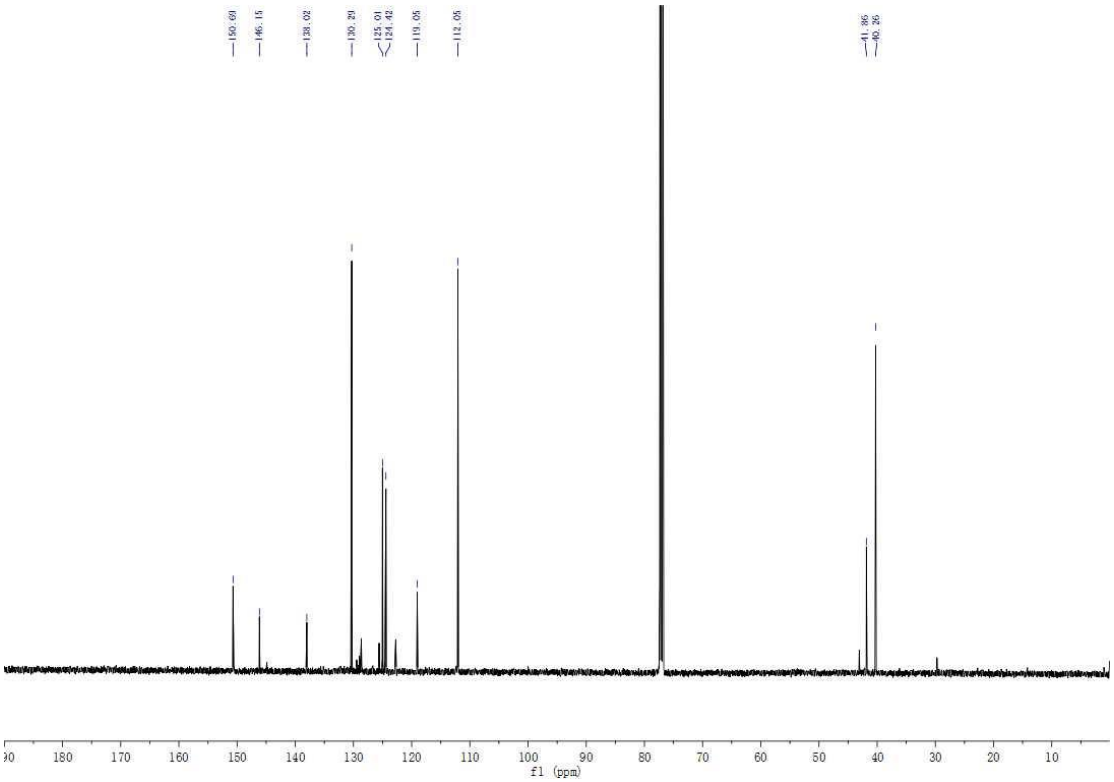
^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of 4-(3-(Methylsulfinyl)thiophen-2-yl)benzonitrile (3e)



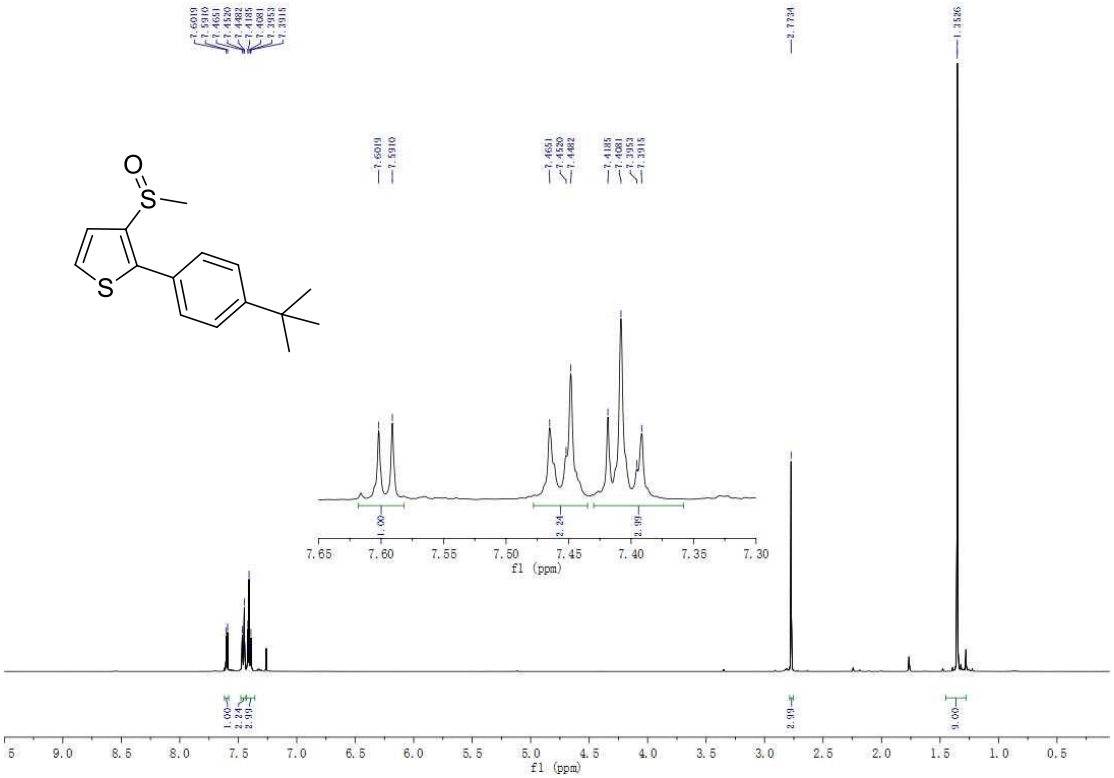
^{1}H NMR spectra ($CDCl_3$, 500 MHz) of *N*,*N*-dimethyl-4-(3-(methylsulfinyl)thiophen-2-yl)aniline (3f)



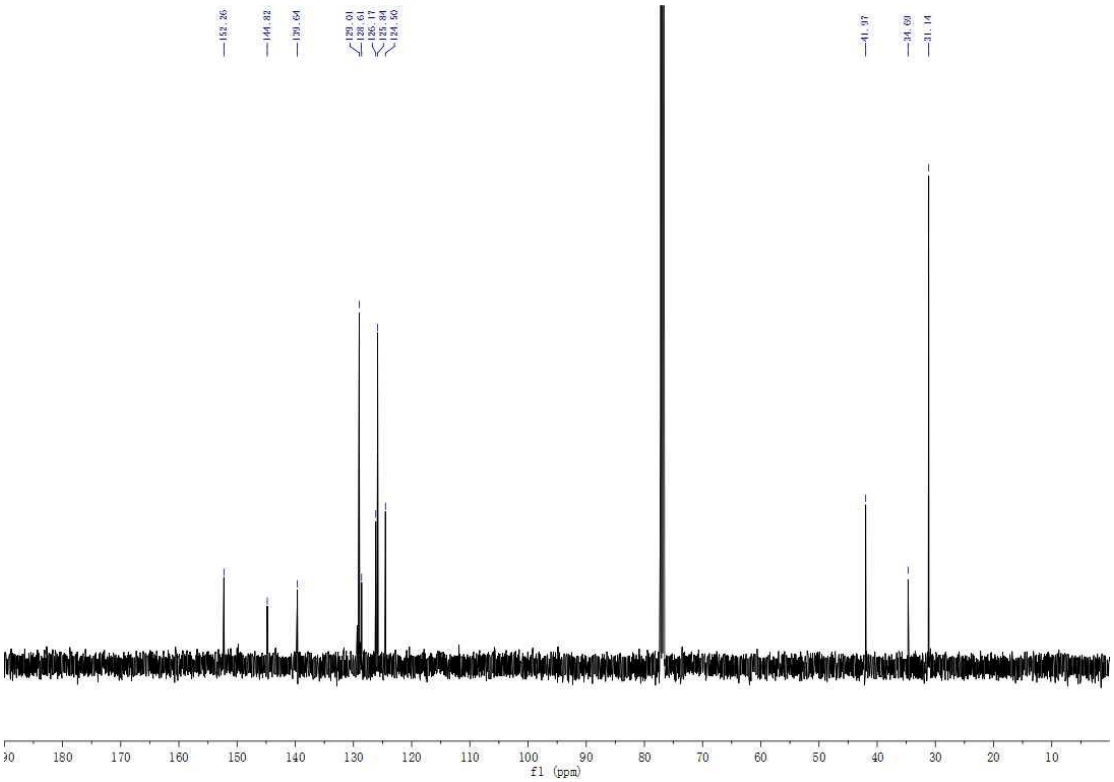
^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of *N*,*N*-dimethyl-4-(3-(methylsulfinyl)thiophen-2-yl)aniline (3f)



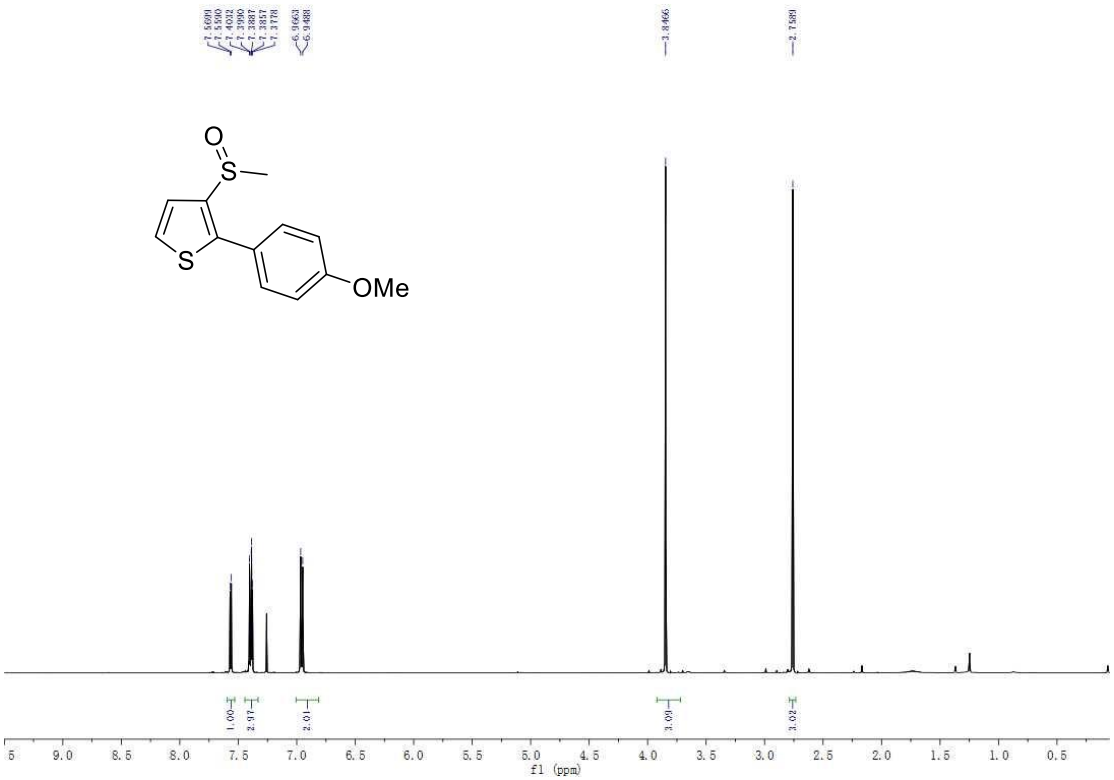
^{1}H NMR spectra ($CDCl_3$, 500 MHz) of 2-(4-(*tert*-Butyl)phenyl)-3-(methylsulfinyl)thiophene (3g)



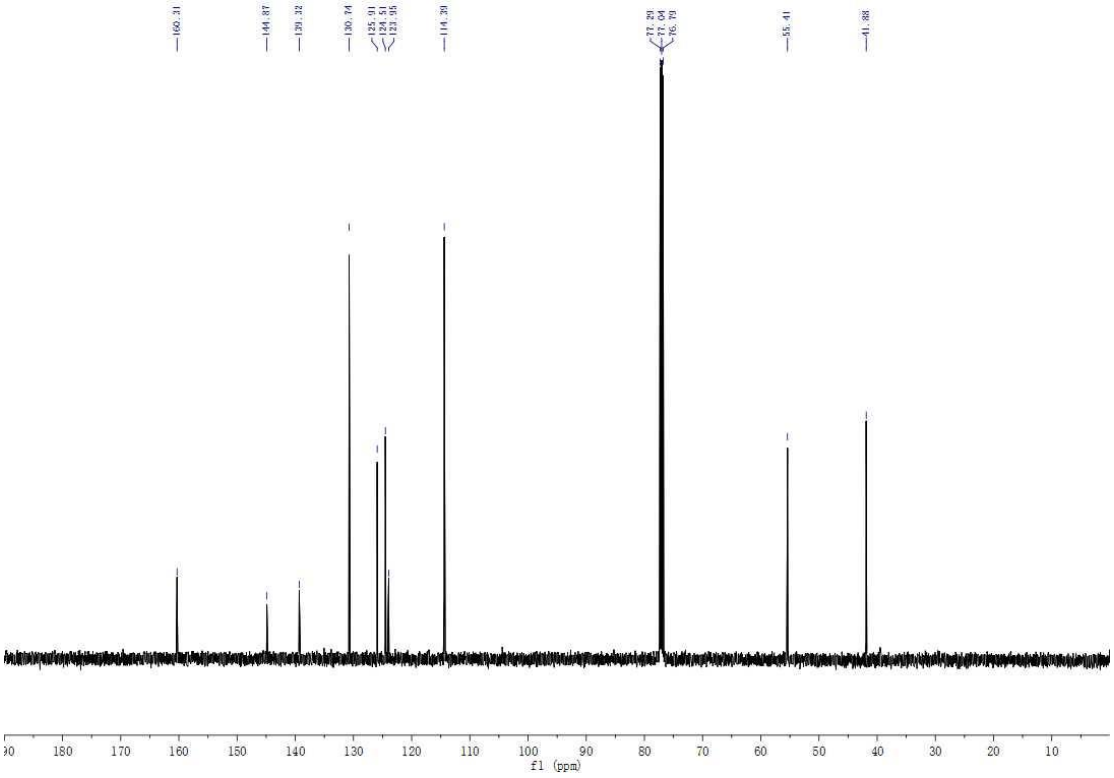
^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of 2-(4-(*tert*-Butyl)phenyl)-3-(methylsulfinyl)thiophene (3g)



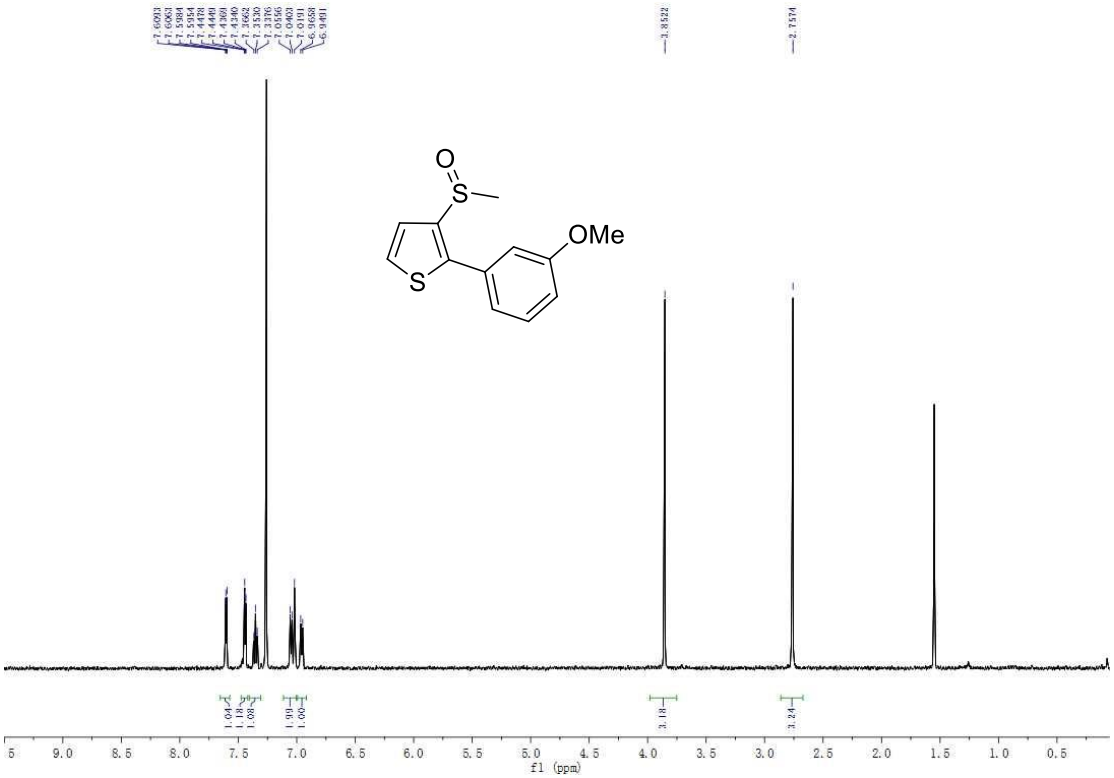
^{1}H NMR spectra ($CDCl_3$, 500 MHz) of 2-(4-Methoxyphenyl)-3-(methylsulfinyl)thiophene (3h)



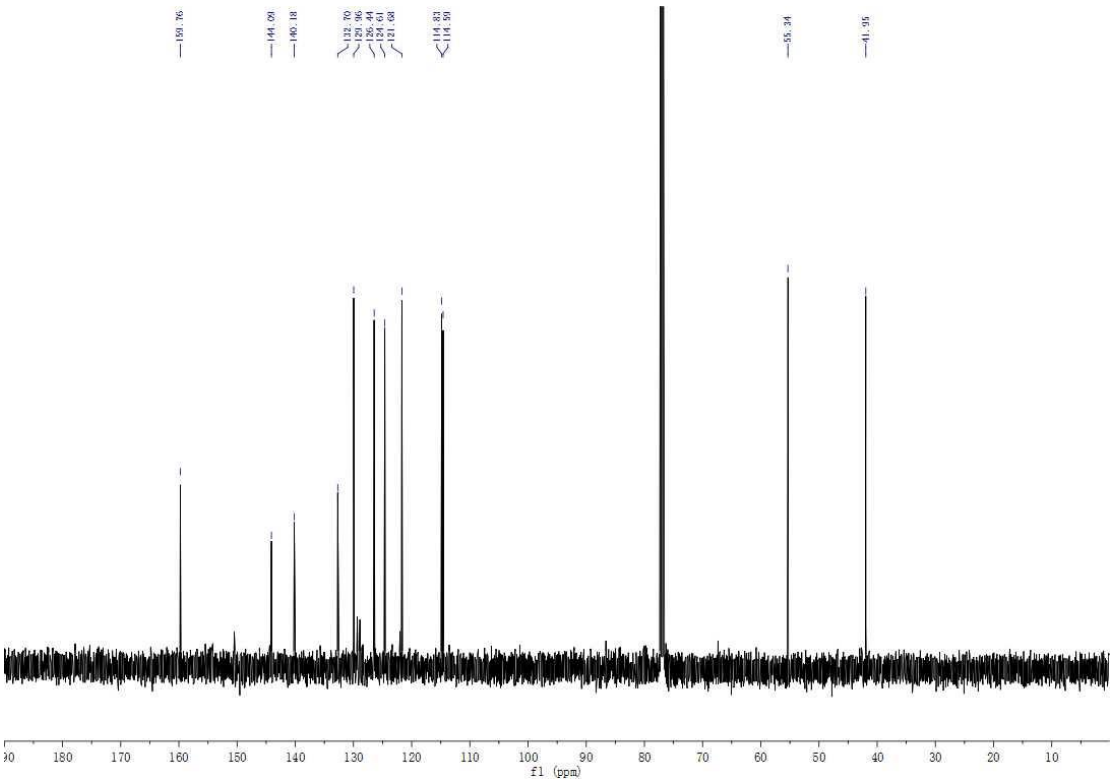
^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of 2-(4-Methoxyphenyl)-3-(methylsulfinyl)thiophene (3h)



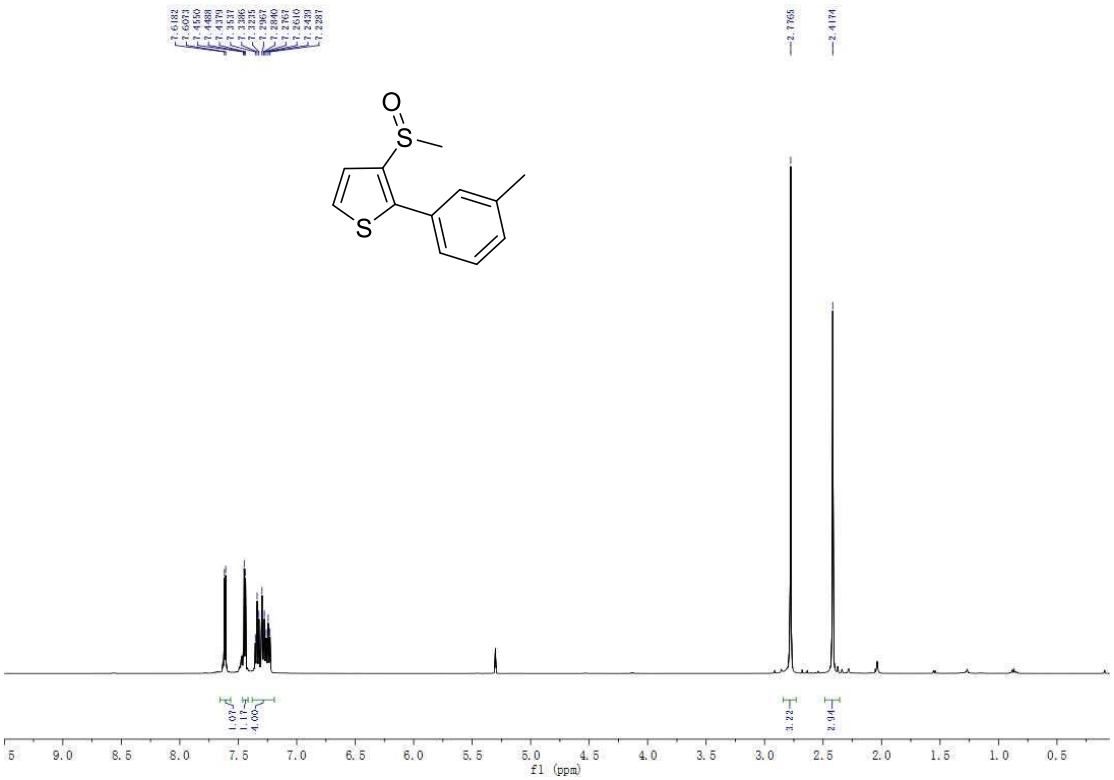
^{1}H NMR spectra ($CDCl_3$, 500 MHz) of 2-(3-Methoxyphenyl)-3-(methylsulfinyl)thiophene (3i)



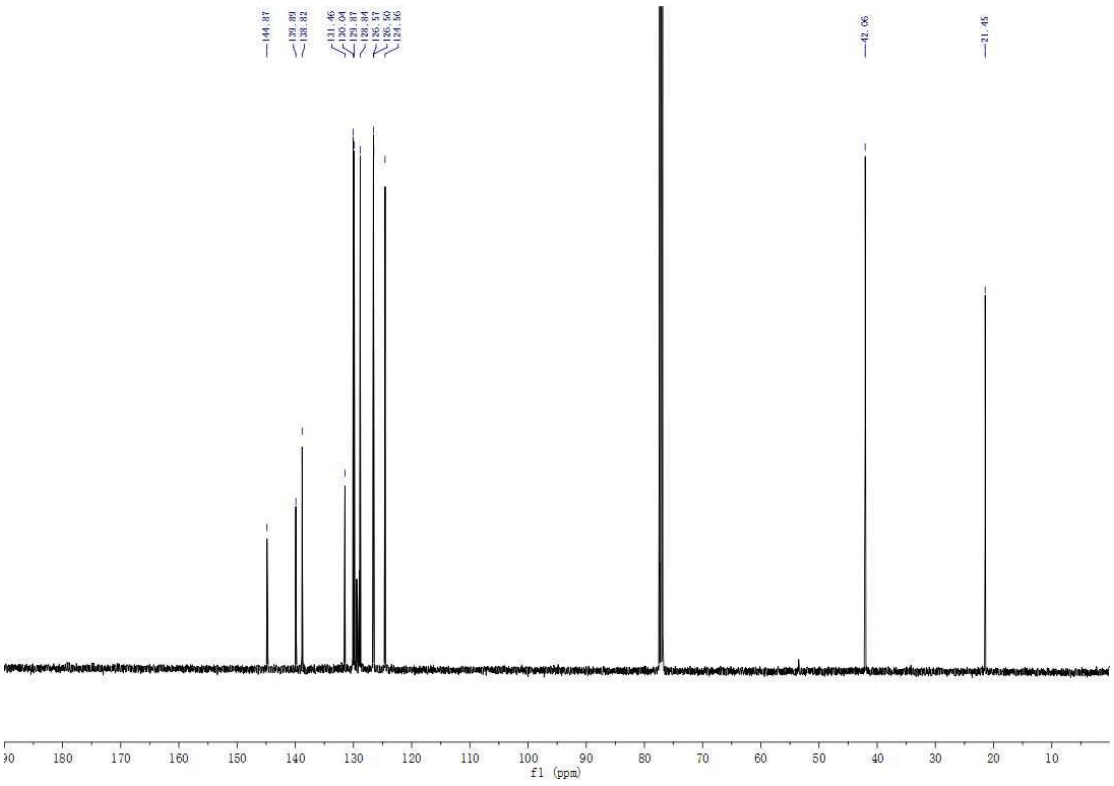
^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of 2-(3-Methoxyphenyl)-3-(methylsulfinyl)thiophene (3i)



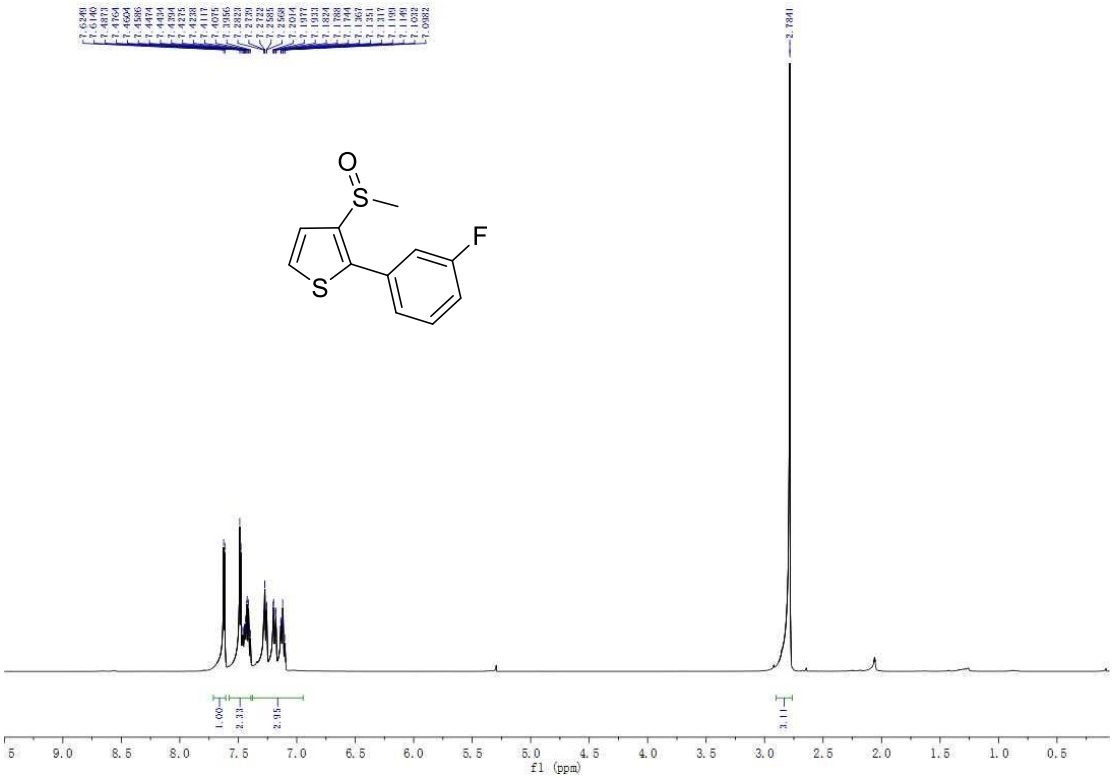
^{1}H NMR spectra ($CDCl_3$, 500 MHz) of 3-(methylsulfinyl)-2-(*m*-tolyl)thiophene (3j)



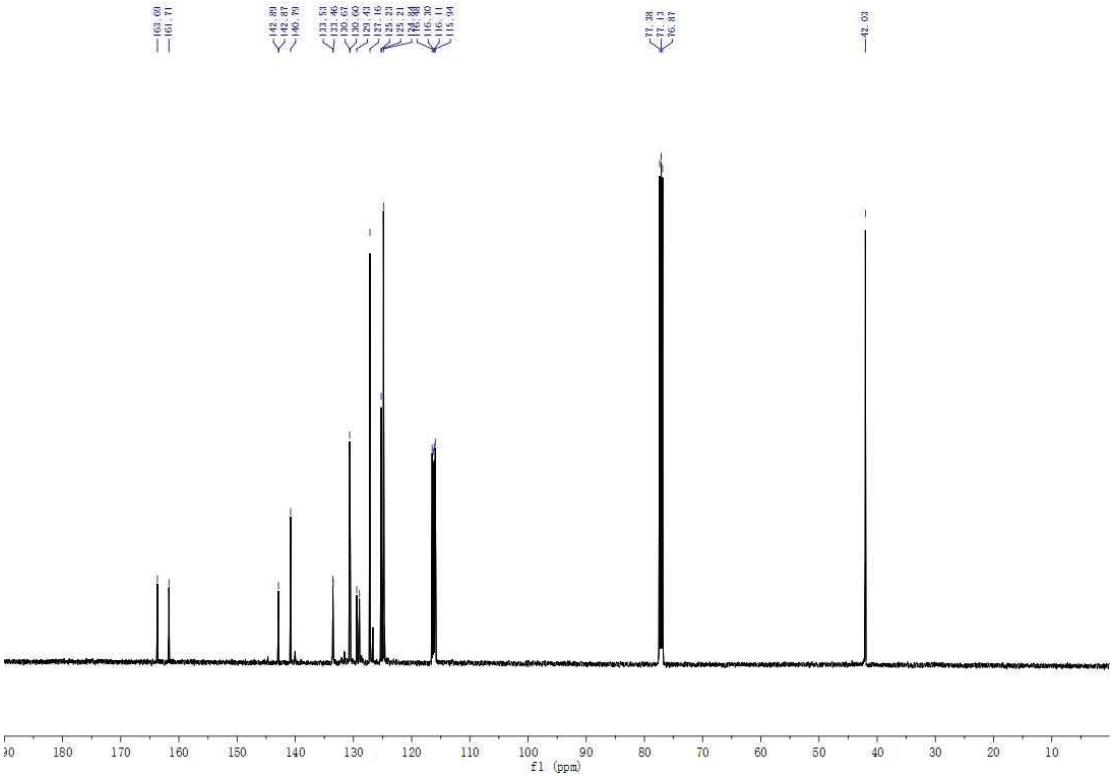
^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of 3-(methylsulfinyl)-2-(*m*-tolyl)thiophene (3j)



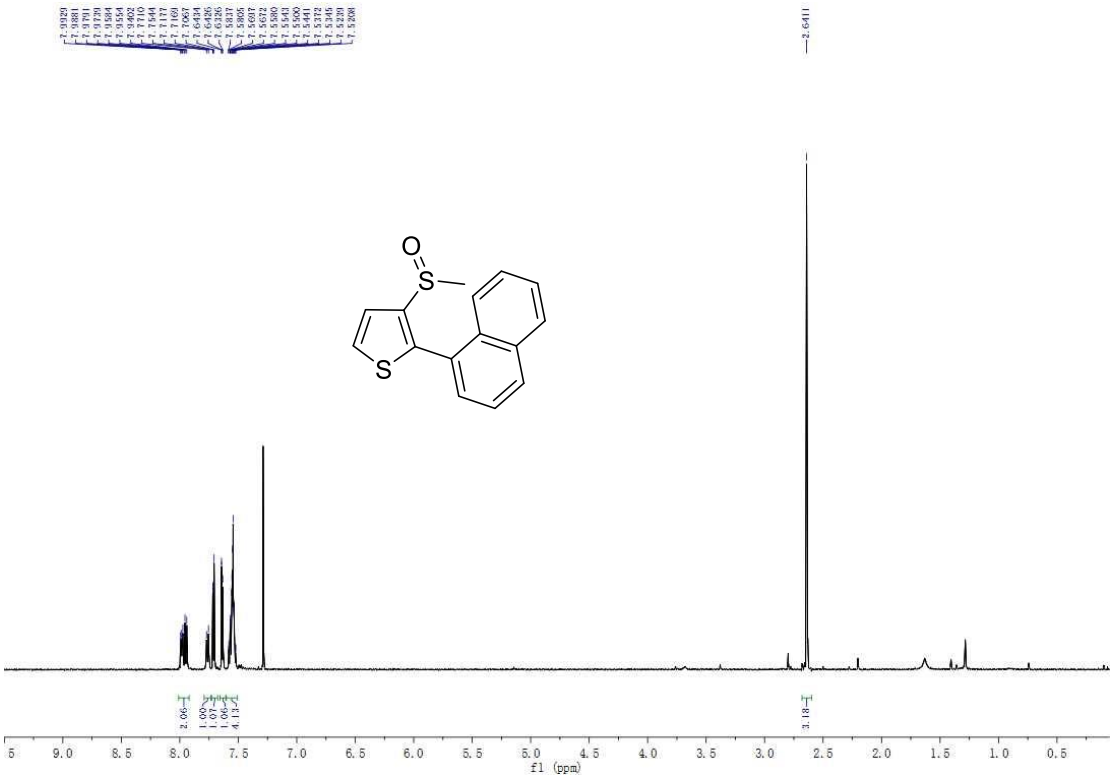
^{1}H NMR spectra ($CDCl_3$, 500 MHz) of 2-(3-fluorophenyl)-3-(methylsulfinyl)thiophene (3k)



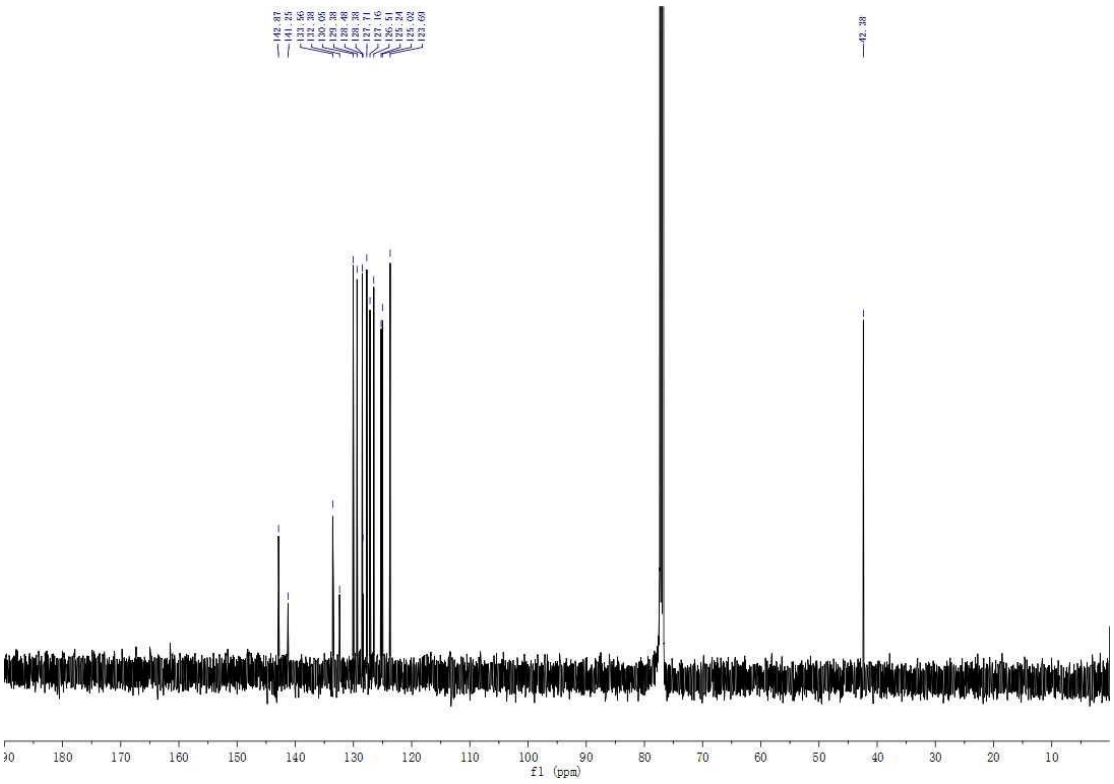
^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of 2-(3-fluorophenyl)-3-(methylsulfinyl)thiophene (3k)



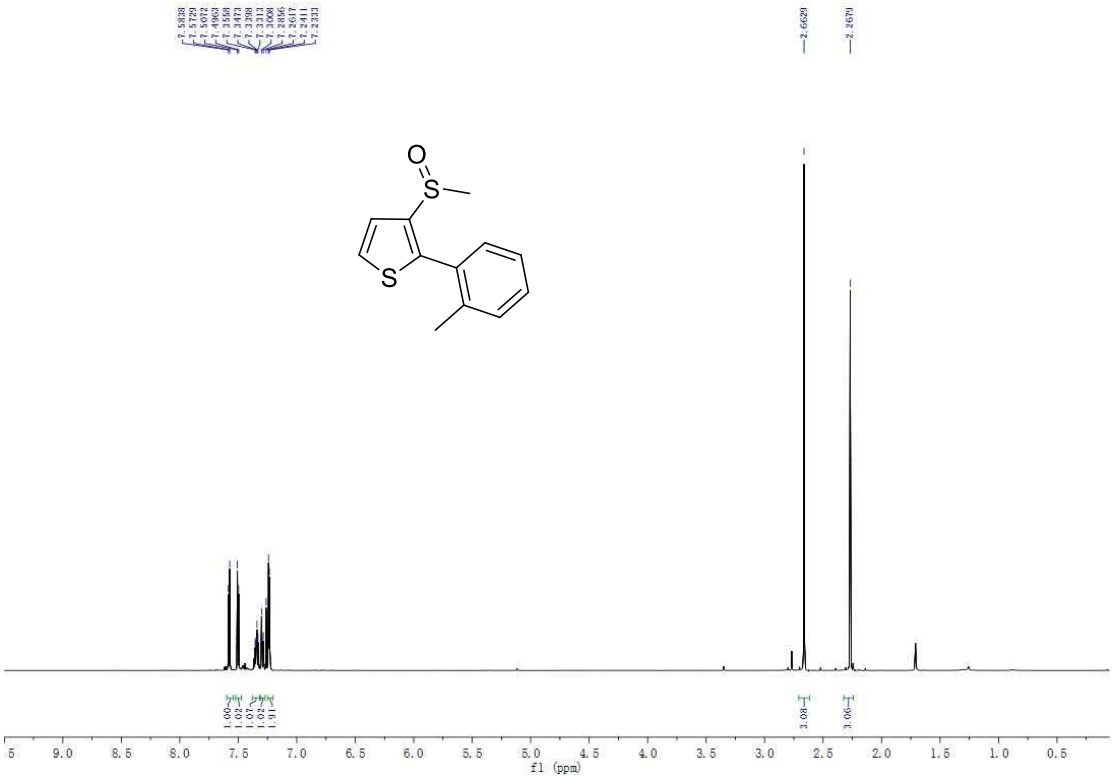
^{1}H NMR spectra ($CDCl_3$, 500 MHz) of 3-(Methylsulfinyl)-2-(naphthalen-1-yl)thiophene (3l)



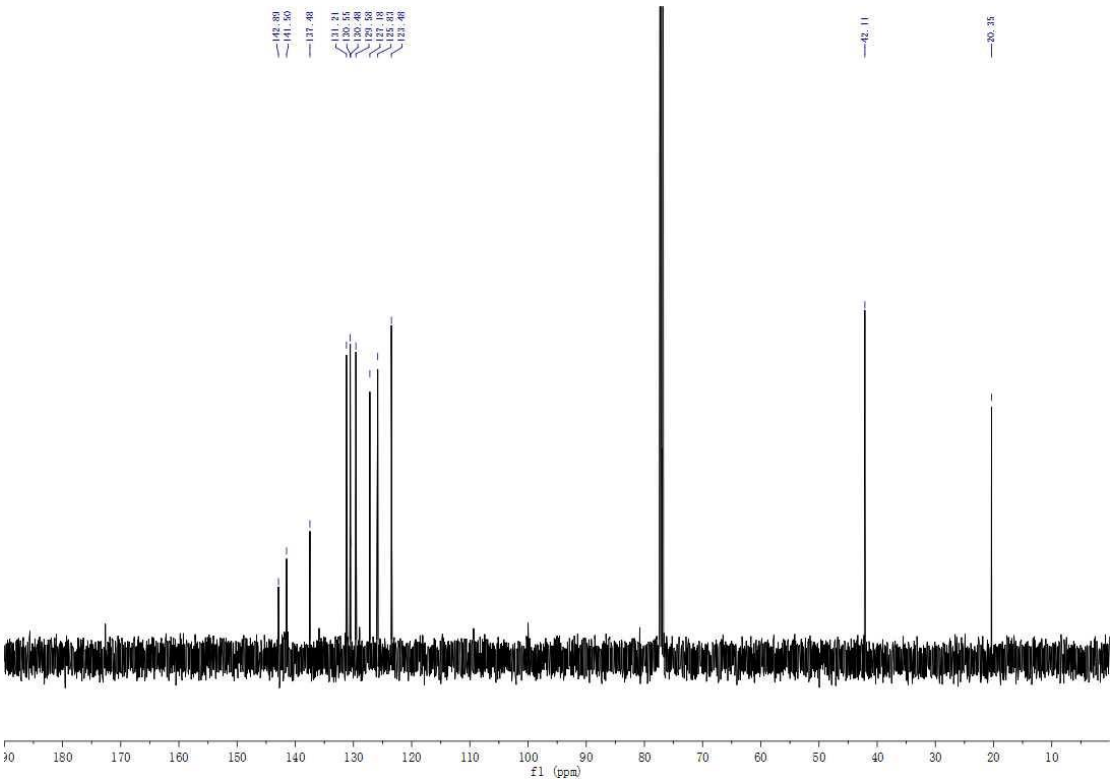
^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of 3-(Methylsulfinyl)-2-(naphthalen-1-yl)thiophene (3l)



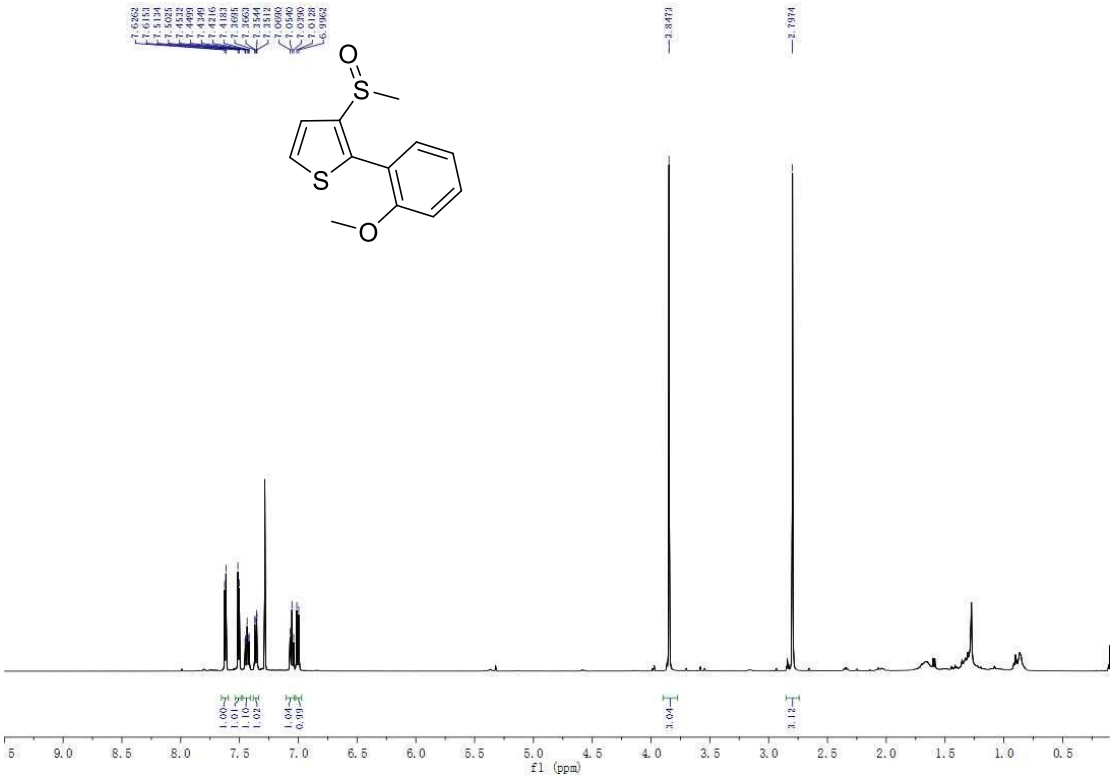
^{1}H NMR spectra ($CDCl_3$, 500 MHz) of 3-(Methylsulfinyl)-2-(*o*-tolyl)thiophene (3m)



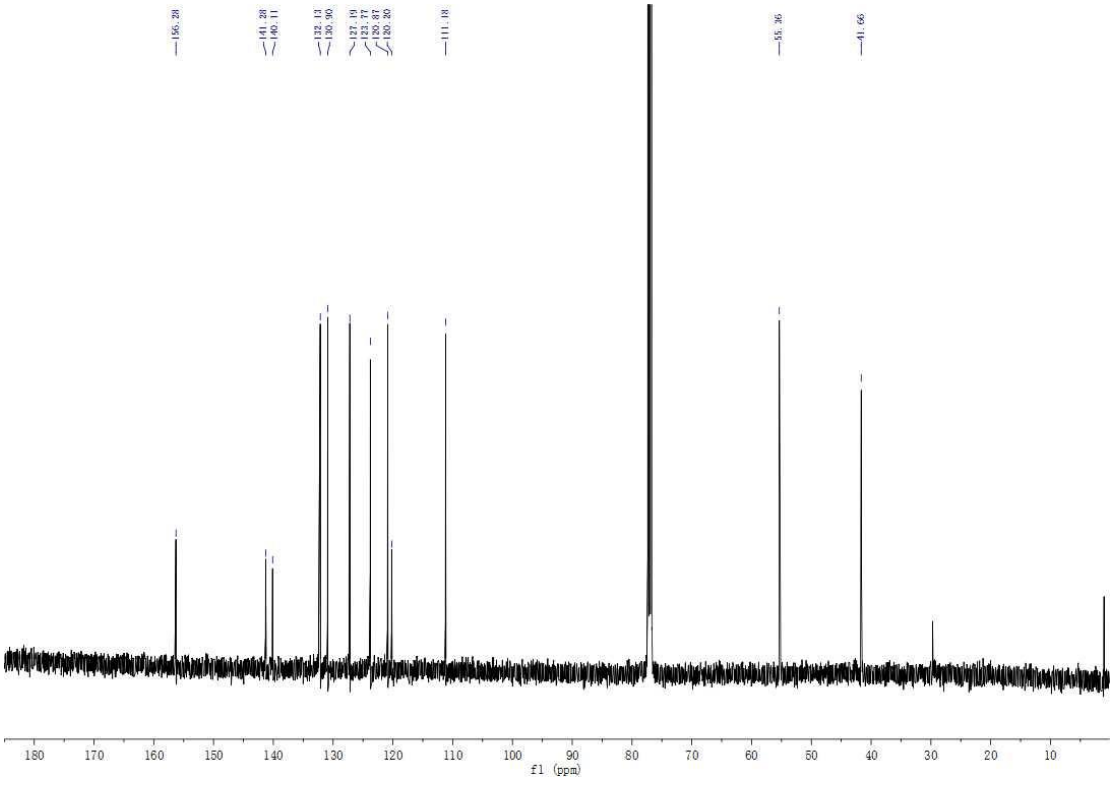
^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of 3-(Methylsulfinyl)-2-(*o*-tolyl)thiophene (3m)



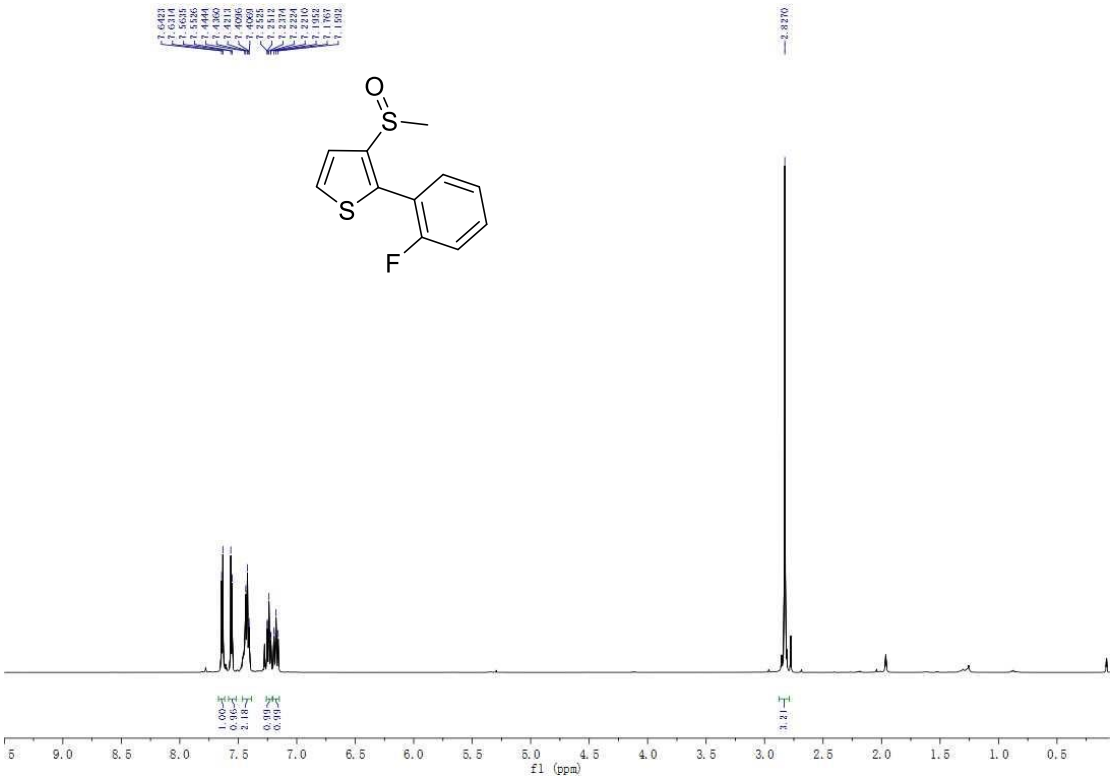
^{1}H NMR spectra ($CDCl_3$, 500 MHz) of 2-(2-methoxyphenyl)-3-(methylsulfinyl)thiophene (3n)



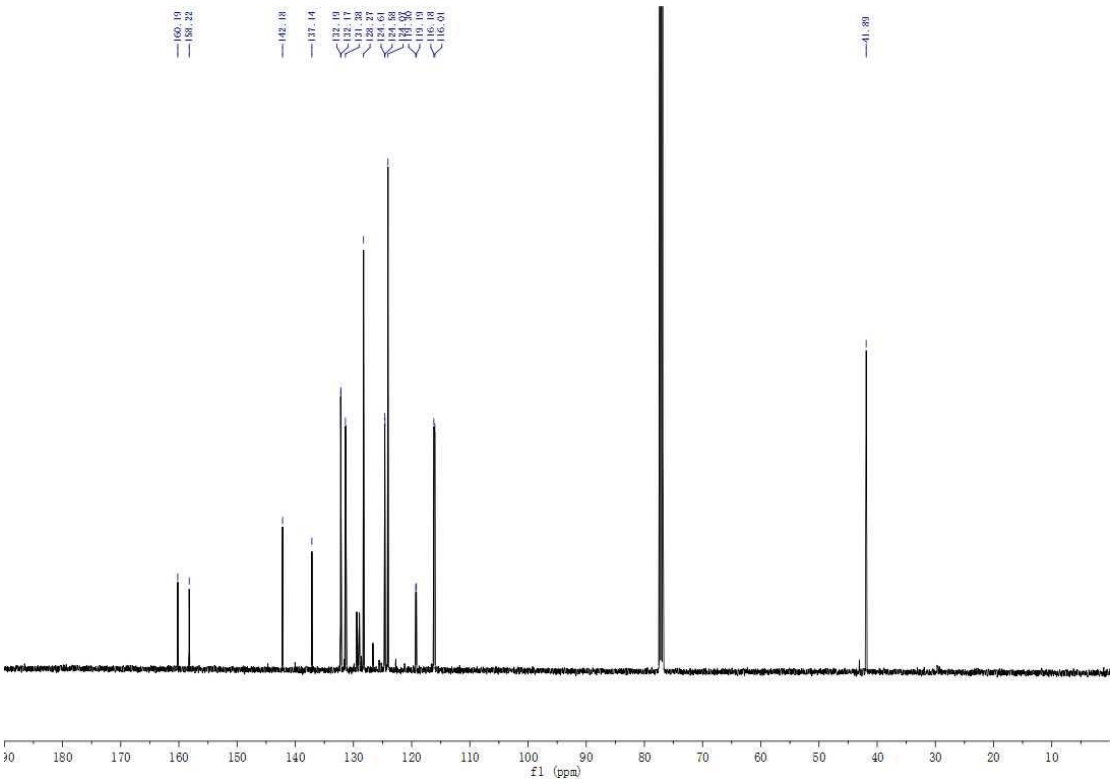
^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of 2-(2-methoxyphenyl)-3-(methylsulfinyl)thiophene (3n)



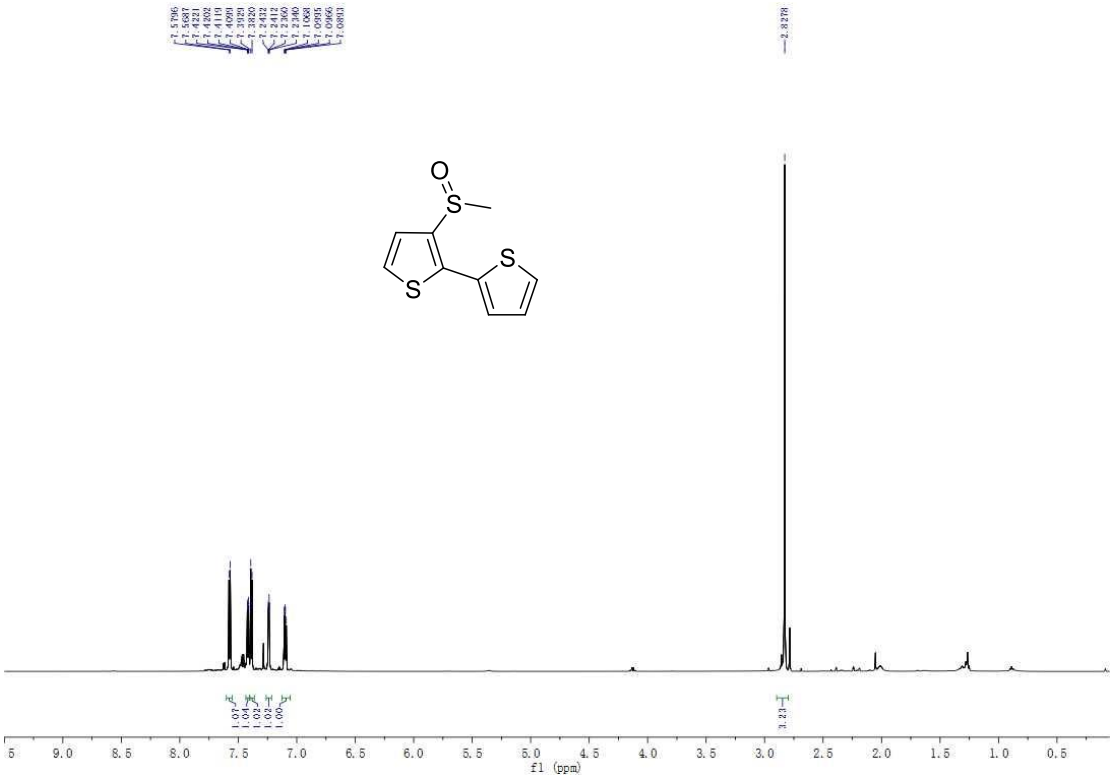
^{1}H NMR spectra ($CDCl_3$, 500 MHz) of 2-(2-fluorophenyl)-3-(methylsulfinyl)thiophene (3o)



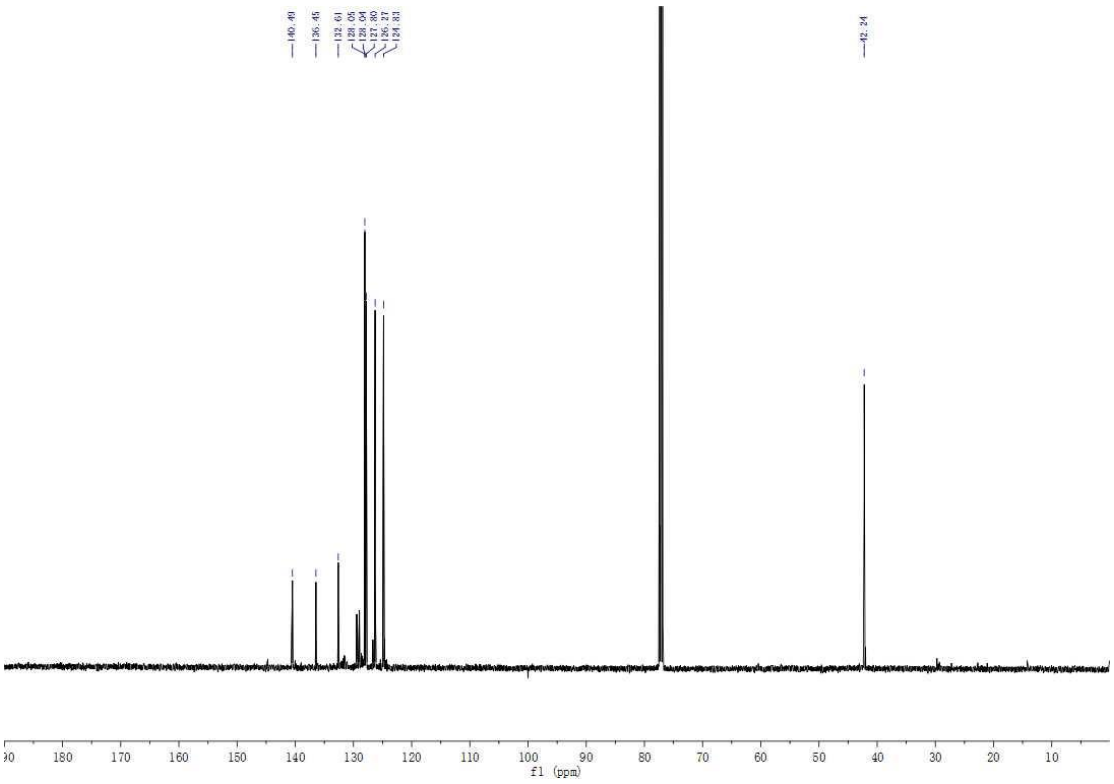
^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of 2-(2-fluorophenyl)-3-(methylsulfinyl)thiophene (3o)



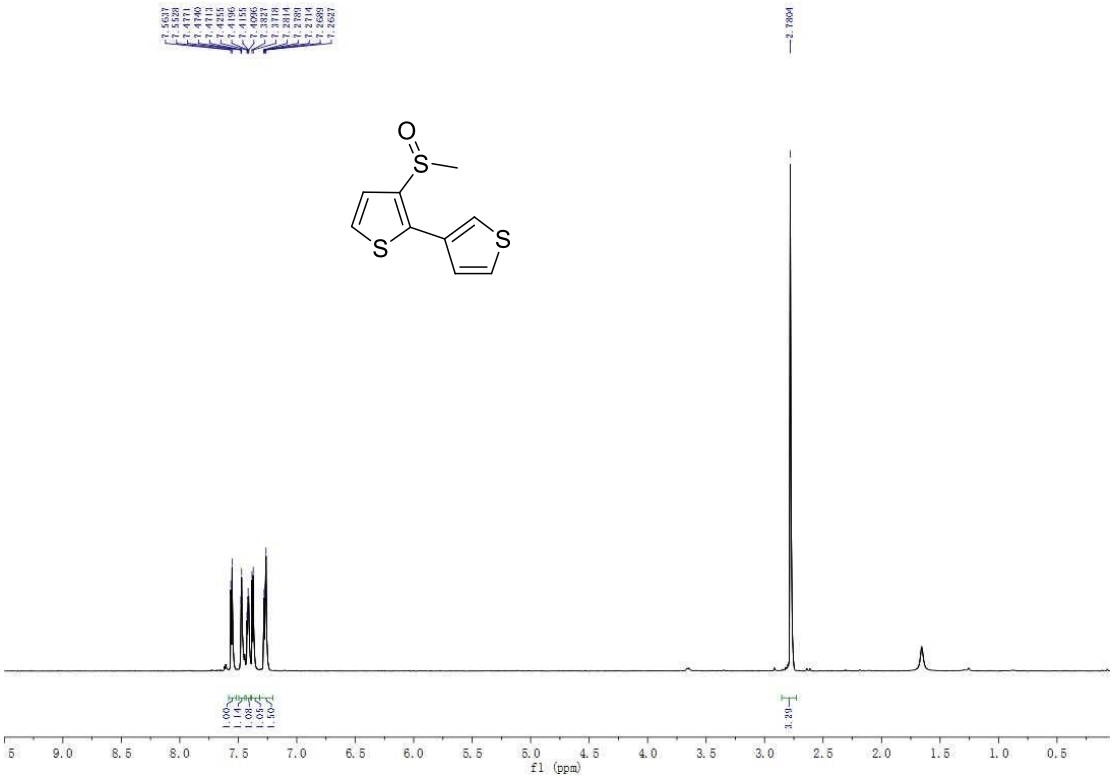
^{1}H NMR spectra ($CDCl_3$, 500 MHz) of 3-(Methylsulfinyl)-2,2'-bithiophene (3p)



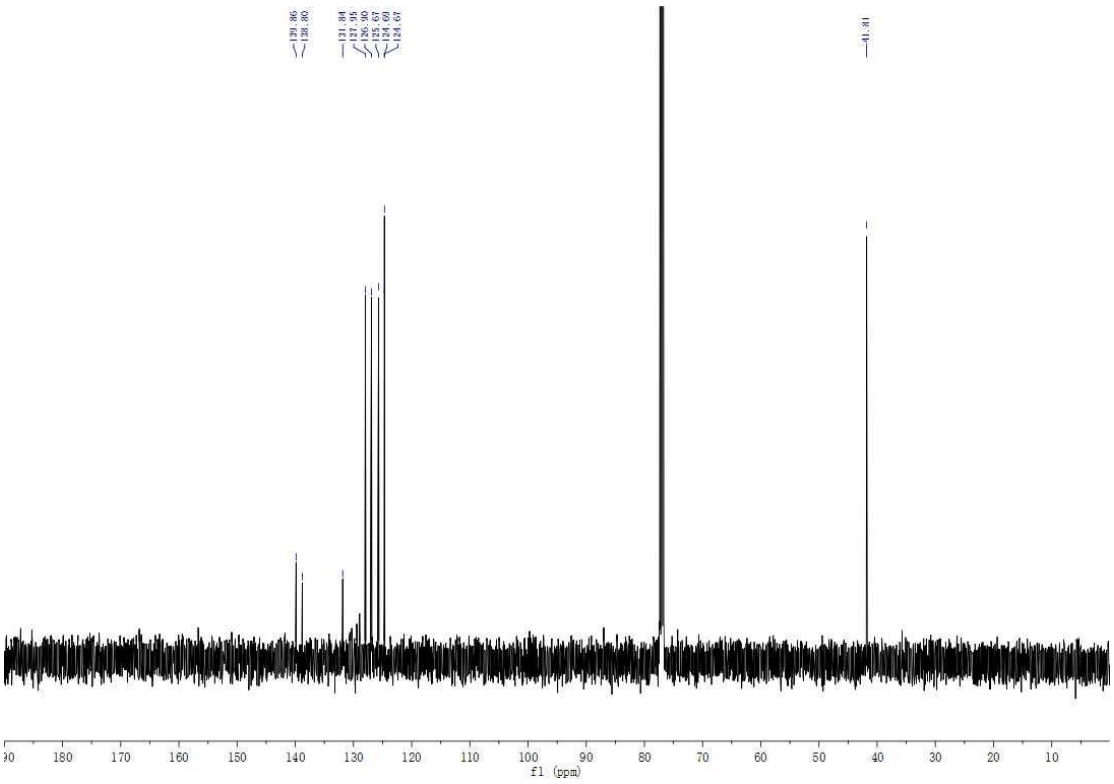
^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of 3-(Methylsulfinyl)-2,2'-bithiophene (3p)



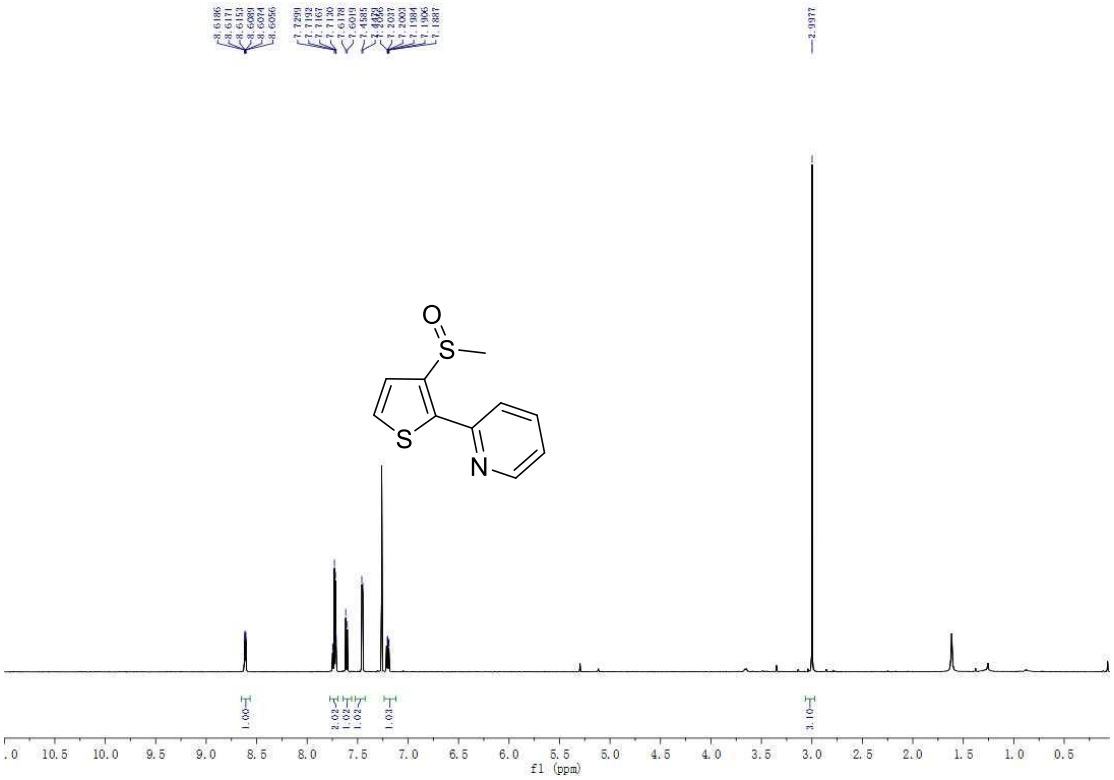
^{1}H NMR spectra ($CDCl_3$, 500 MHz) of 3-(Methylsulfinyl)-2,3'-bithiophene (3q)



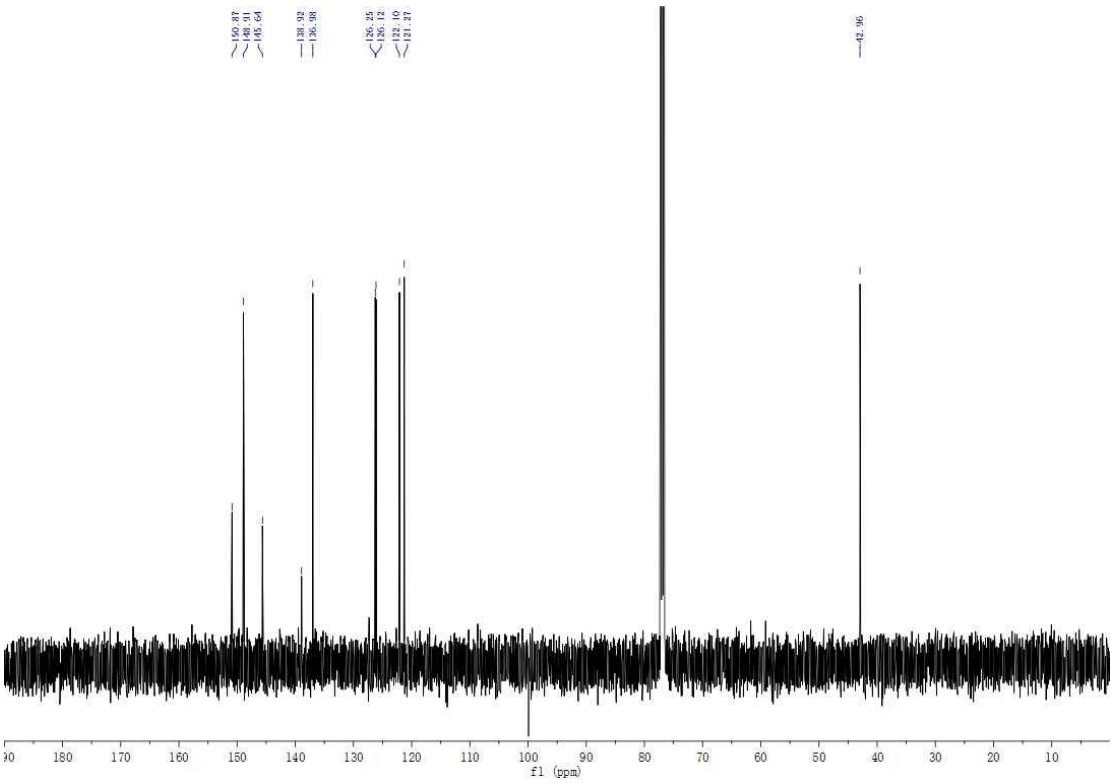
^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of 3-(Methylsulfinyl)-2,3'-bithiophene (3q)



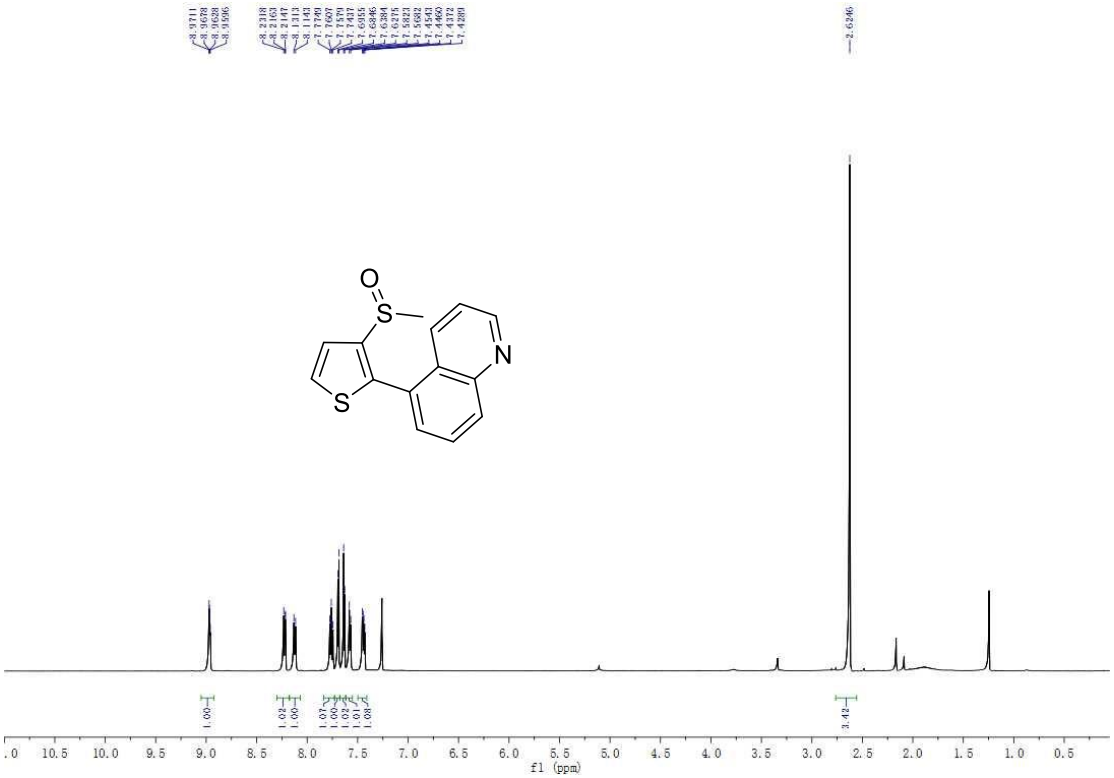
^{1}H NMR spectra ($CDCl_3$, 500 MHz) of 2-(3-(Methylsulfinyl)thiophen-2-yl)pyridine (3r)



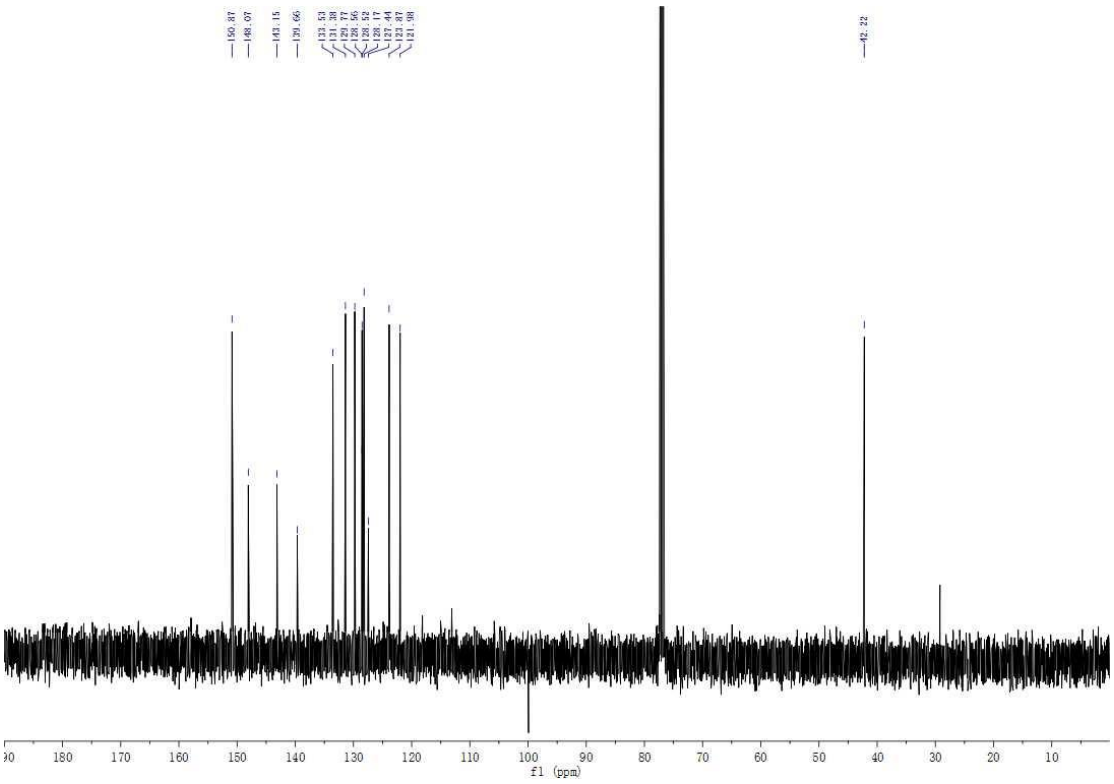
^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of 2-(3-(Methylsulfinyl)thiophen-2-yl)pyridine (3r)



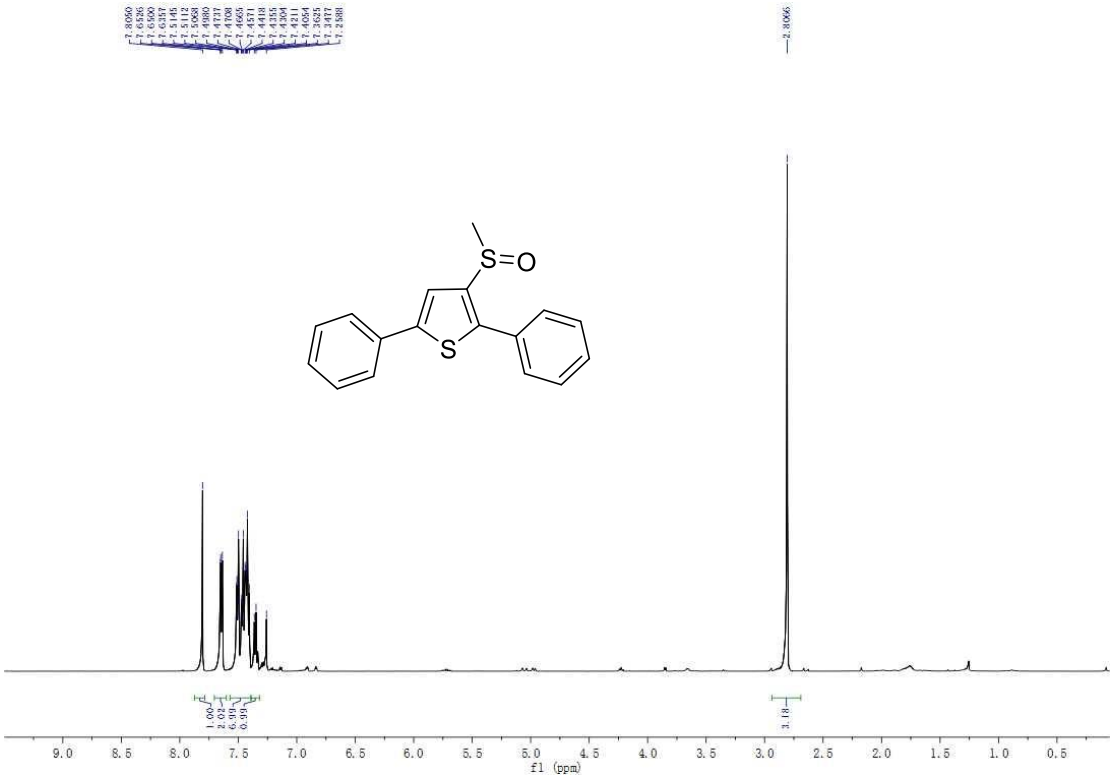
^{1}H NMR spectra ($CDCl_3$, 500 MHz) of 5-(3-(Methylsulfinyl)thiophen-2-yl)quinolone (3s)



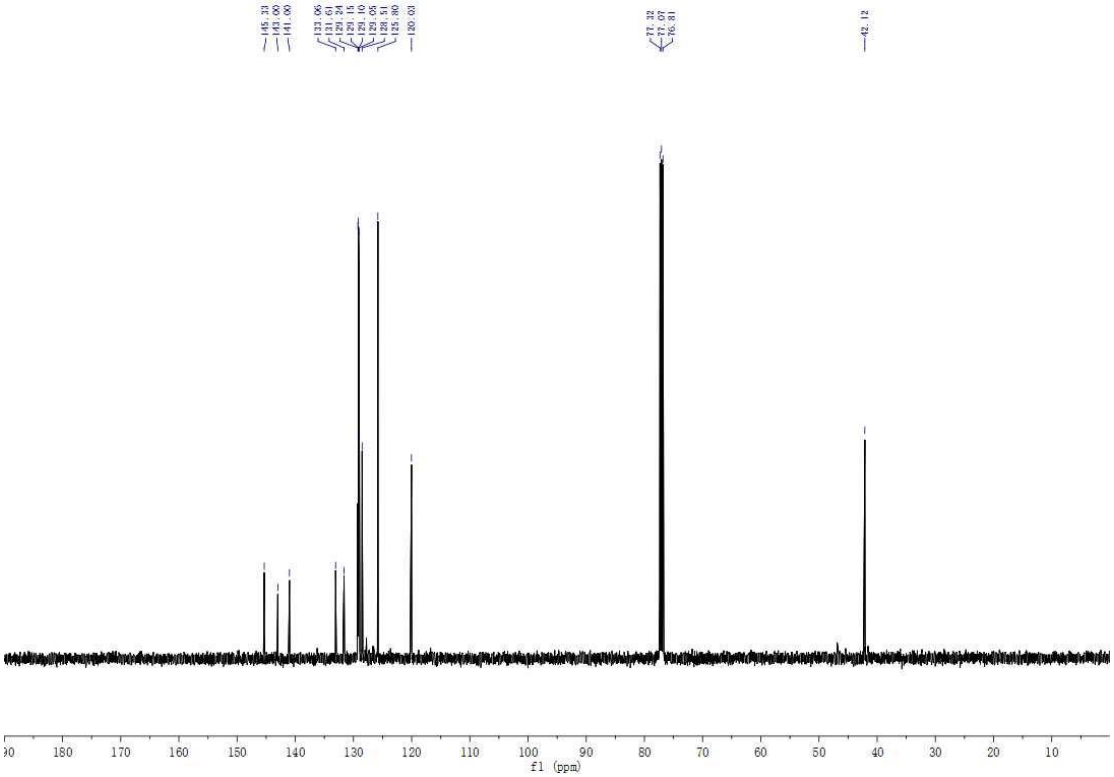
^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of 5-(3-(Methylsulfinyl)thiophen-2-yl)quinolone (3s)



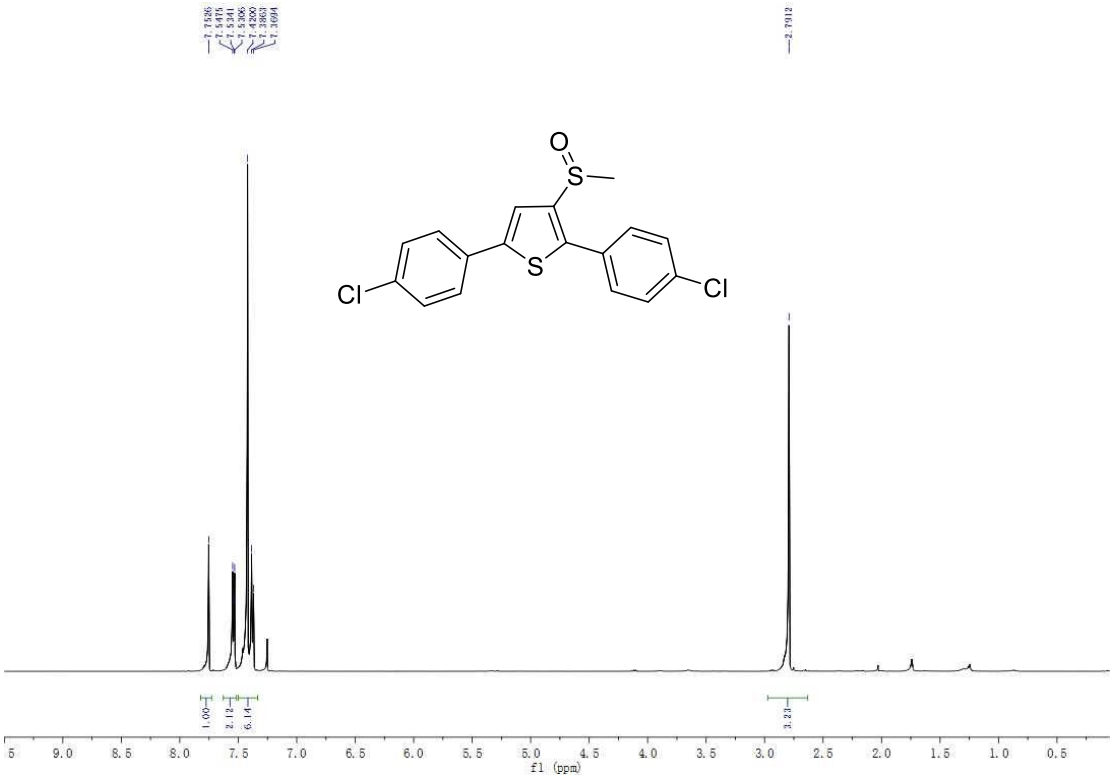
^{1}H NMR spectra ($CDCl_3$, 500 MHz) of 3-(Methylsulfinyl)-2,5-diphenylthiophene (4a)



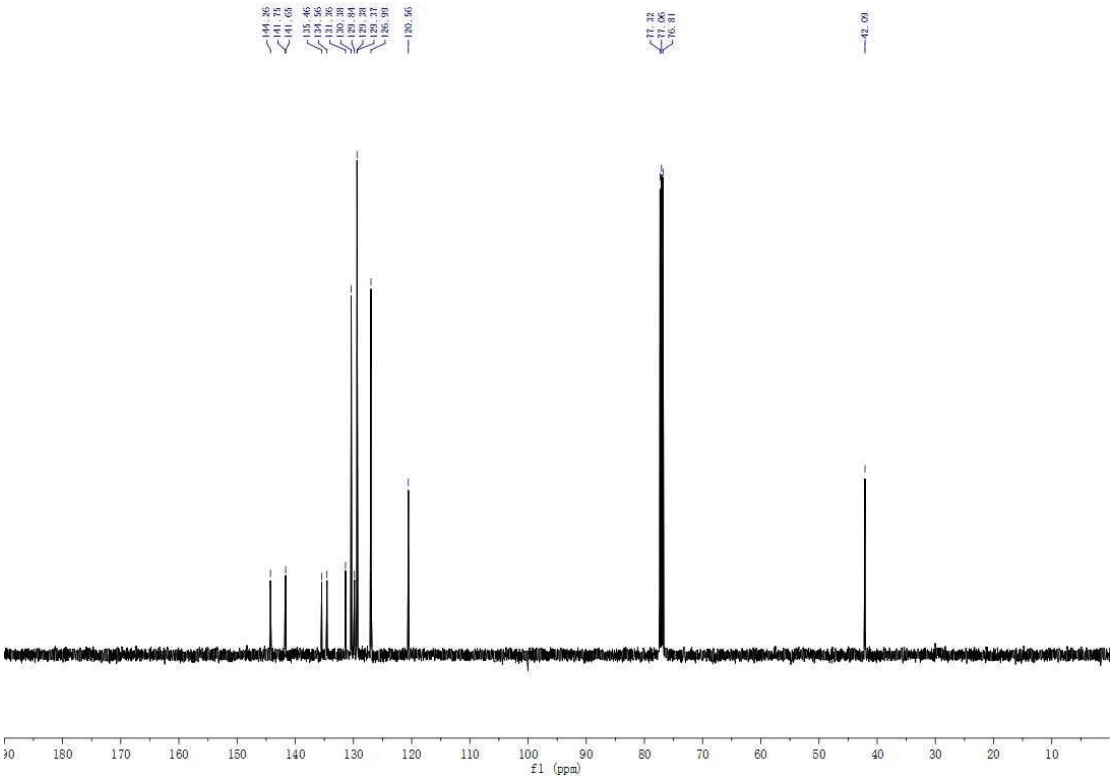
^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of 3-(Methylsulfinyl)-2,5-diphenylthiophene (4a)



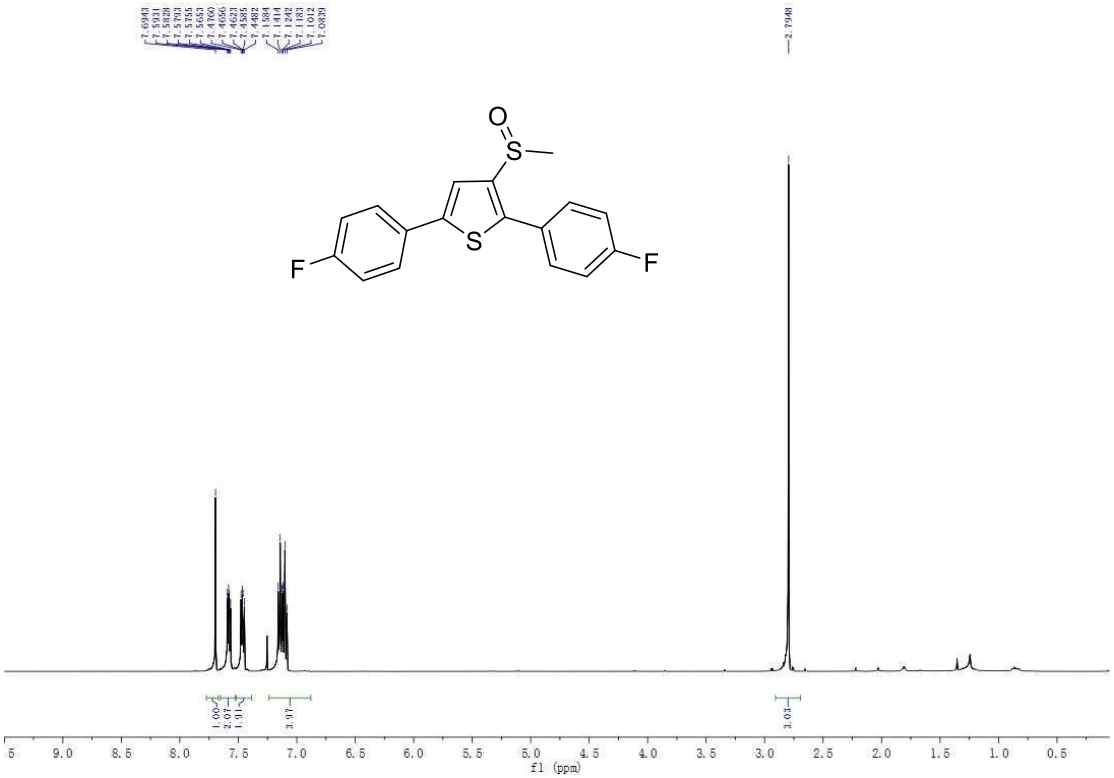
^{1}H NMR spectra ($CDCl_3$, 500 MHz) of 2,5-Bis(4-chlorophenyl)-3-(methylsulfinyl)thiophene (4b)



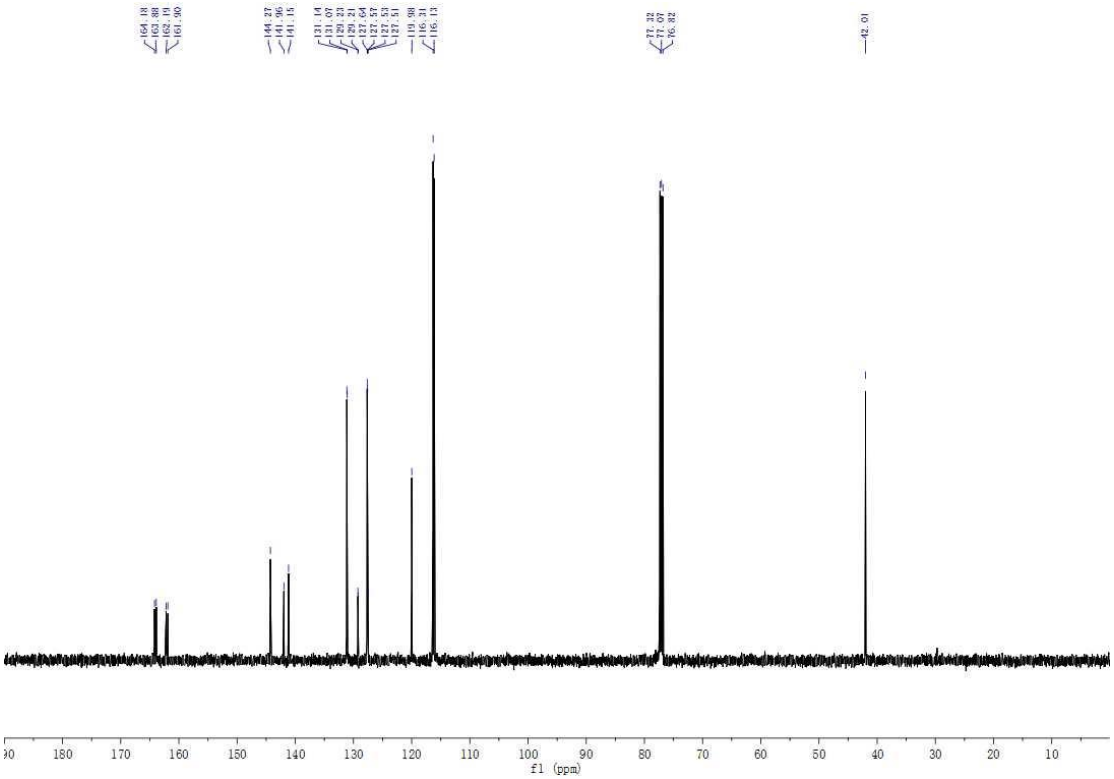
^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of 2,5-Bis(4-chlorophenyl)-3-(methylsulfinyl)thiophene (4b)



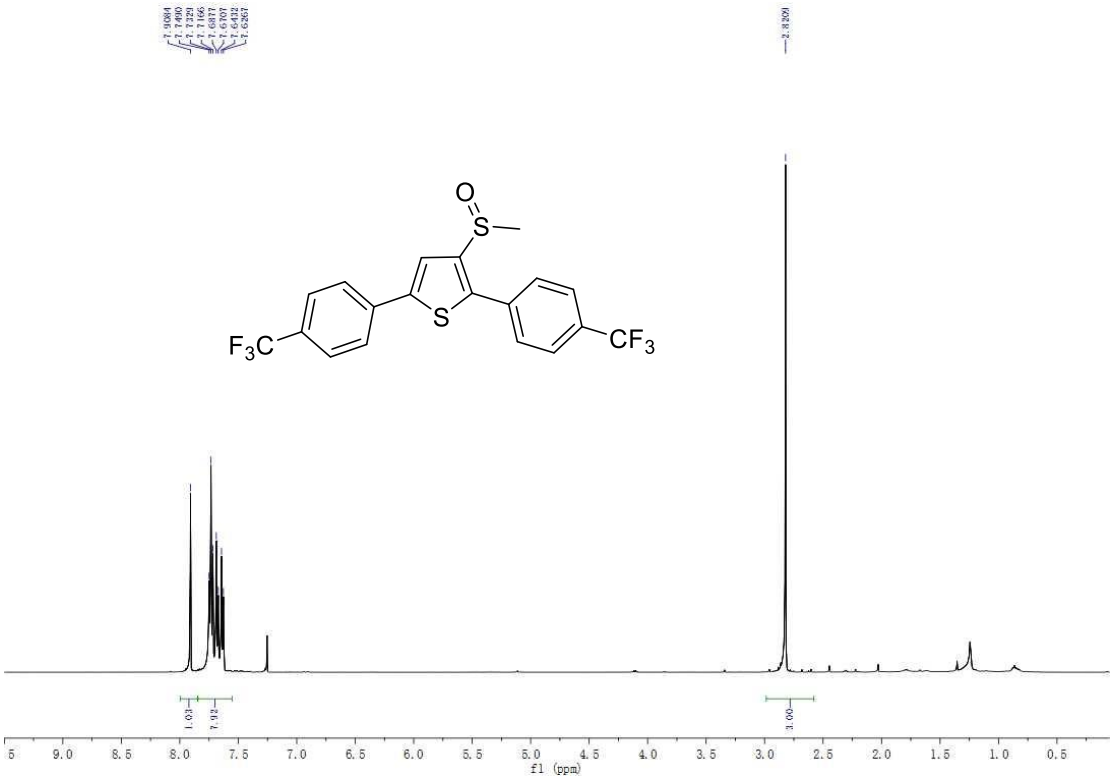
^{1}H NMR spectra ($CDCl_3$, 500 MHz) of 2,5-Bis(4-fluorophenyl)-3-(methylsulfinyl)thiophene (4c)



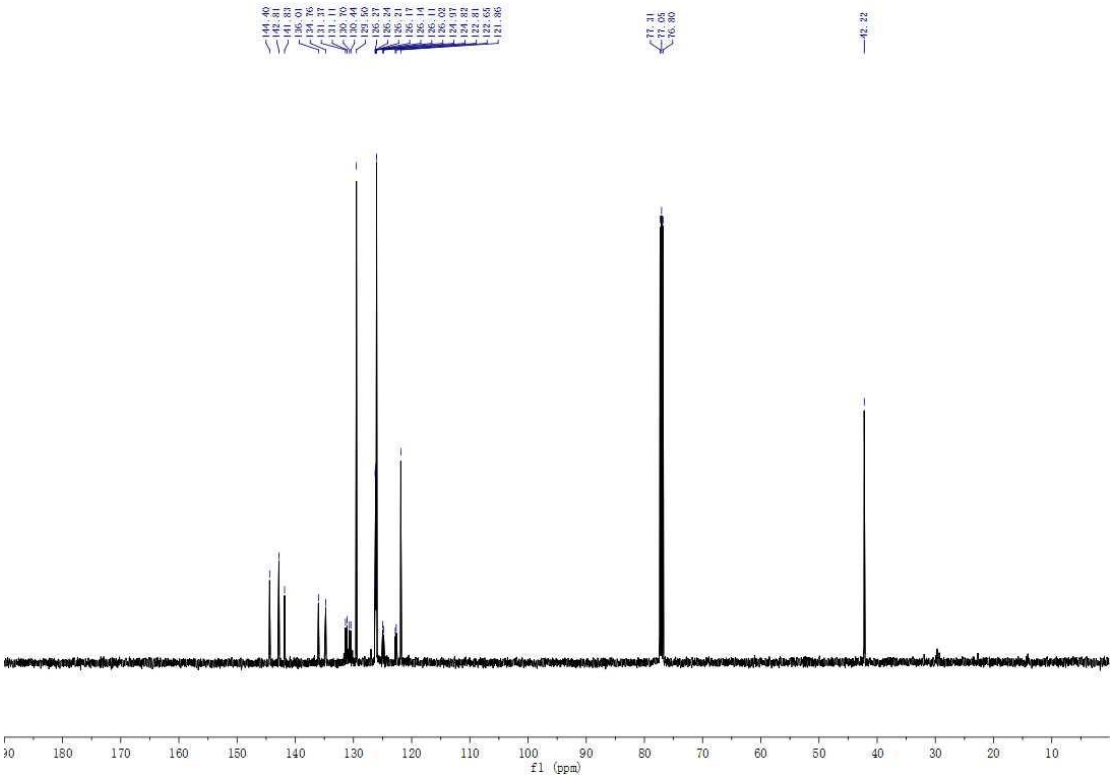
^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of 2,5-Bis(4-fluorophenyl)-3-(methylsulfinyl)thiophene (4c)



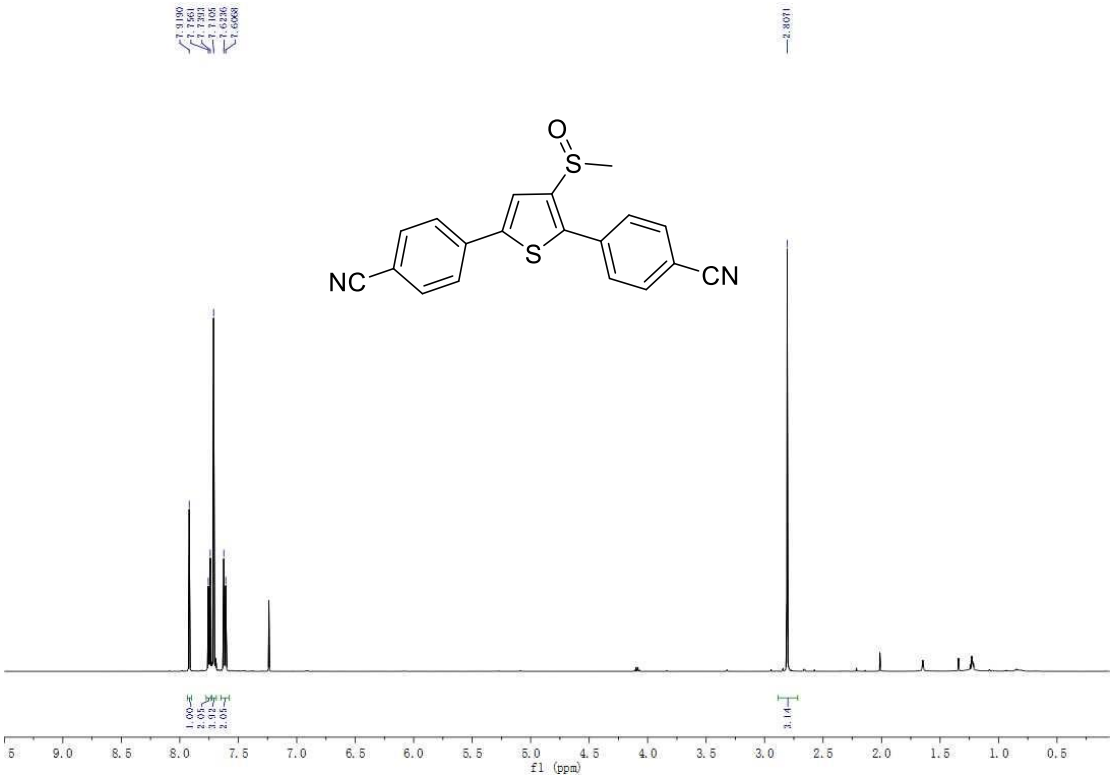
^{1}H NMR spectra ($CDCl_3$, 500 MHz) of 3-(Methylsulfinyl)-2,5-bis(4-(trifluoromethyl)phenyl)thiophene (4d)



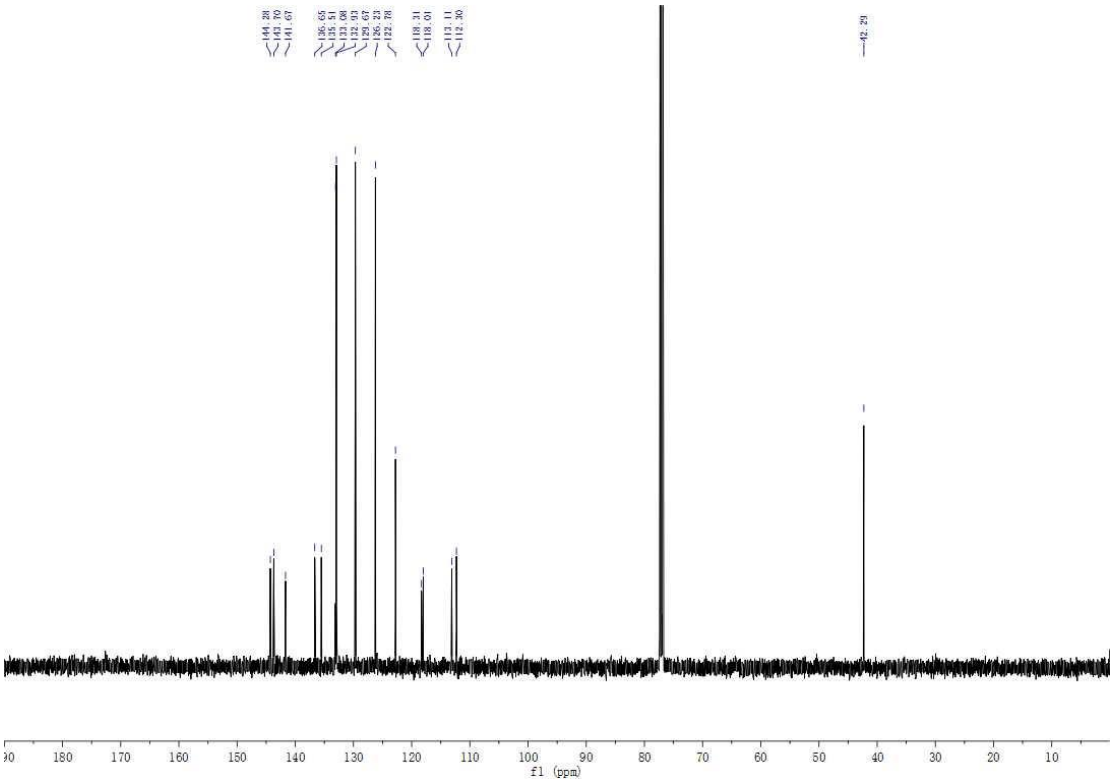
^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of 3-(Methylsulfinyl)-2,5-bis(4-(trifluoromethyl)phenyl) thiophene (4d)



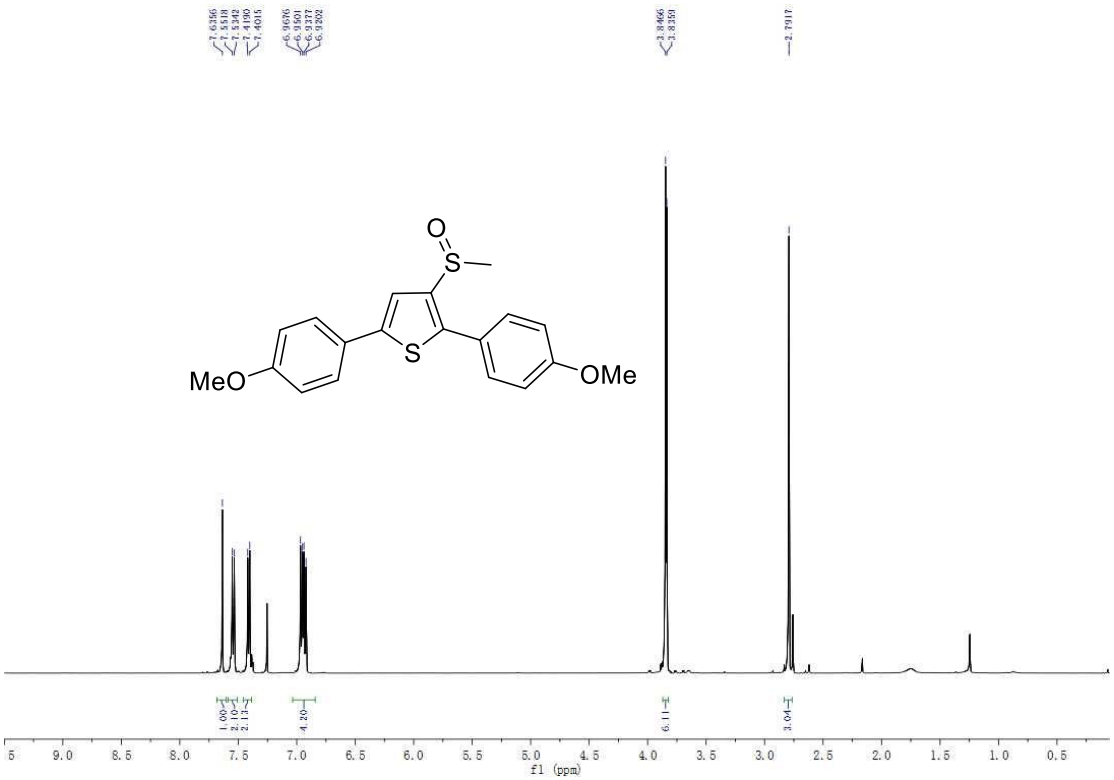
^{1}H NMR spectra ($CDCl_3$, 500 MHz) of 4,4'-(3-(Methylsulfinyl)thiophene-2,5-diyl)dibenzonitrile (4e)



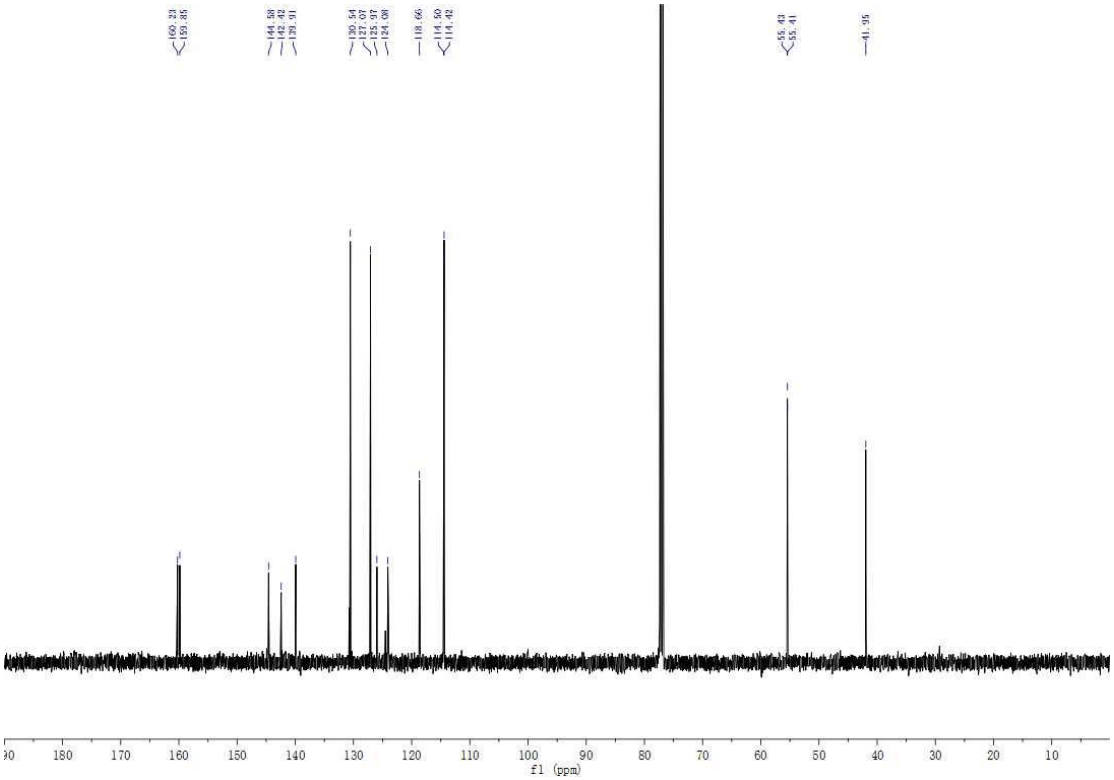
^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of 4,4'-(3-(Methylsulfinyl)thiophene-2,5-diyl)dibenzonitrile (4e)



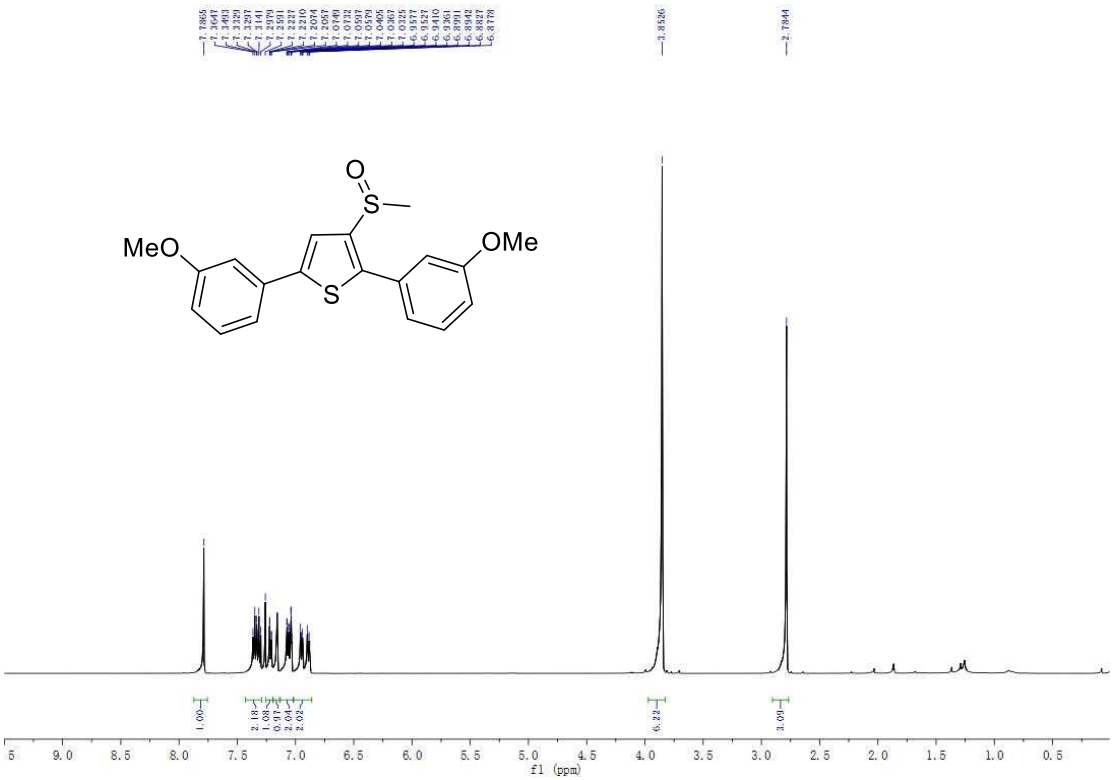
^{1}H NMR spectra ($CDCl_3$, 500 MHz) of 2,5-Bis(4-methoxyphenyl)-3-(methylsulfinyl)thiophene (4h)



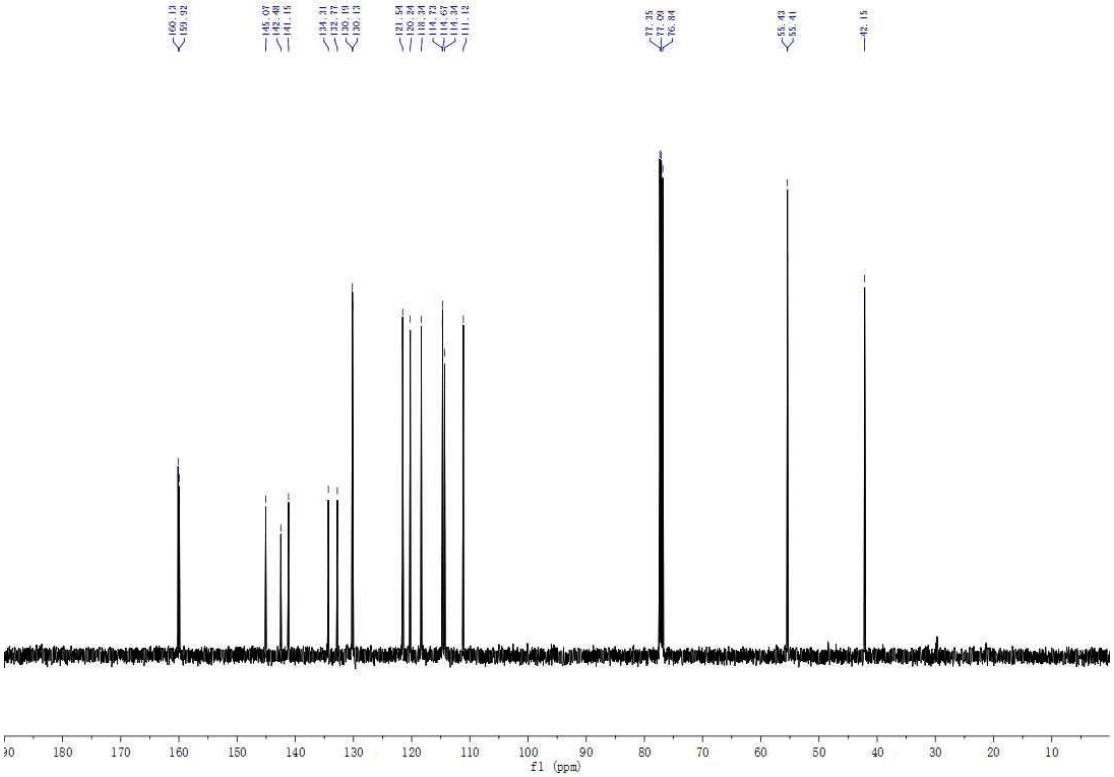
^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of 2,5-Bis(4-methoxyphenyl)-3-(methylsulfinyl)thiophene (4h)



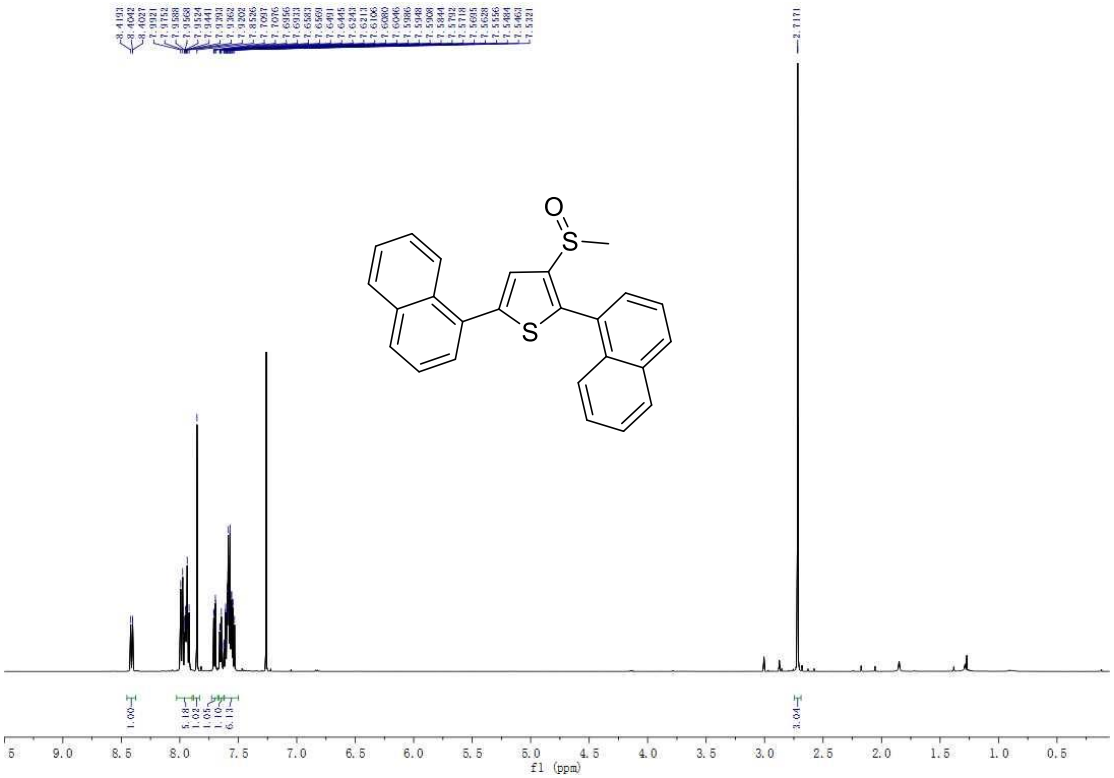
^{1}H NMR spectra ($CDCl_3$, 500 MHz) of 2,5-Bis(3-methoxyphenyl)-3-(methylsulfinyl)thiophene (4i)



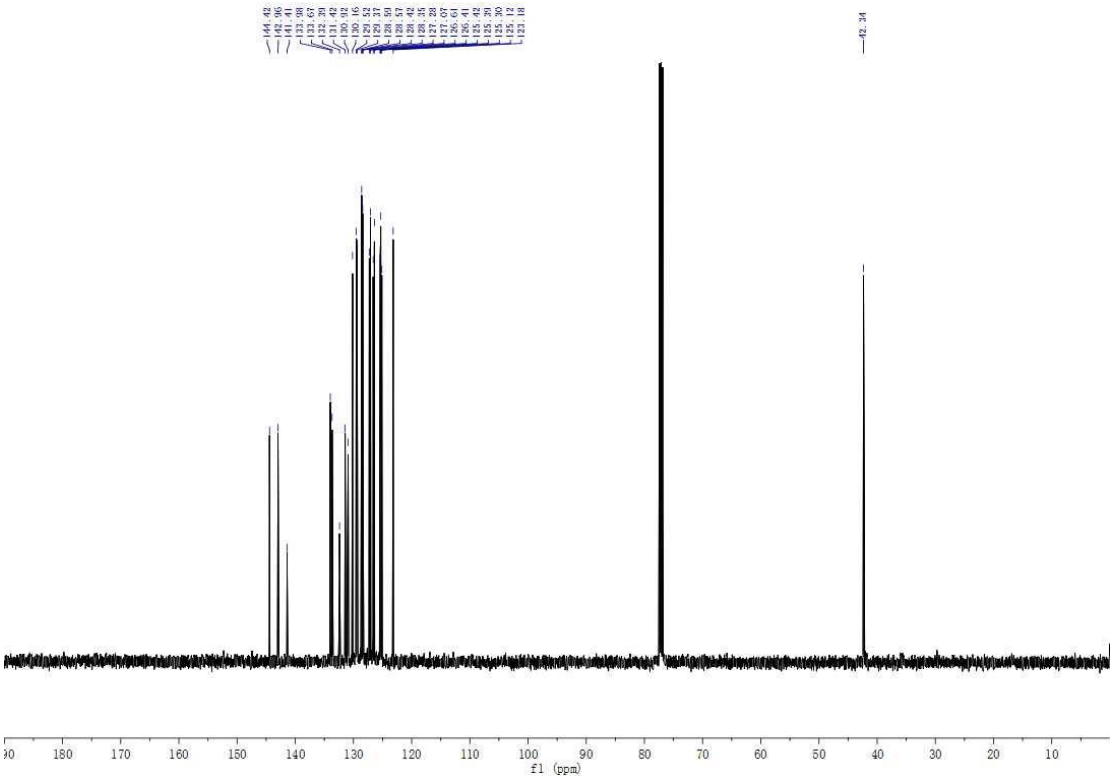
^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of 2,5-Bis(3-methoxyphenyl)-3-(methylsulfinyl)thiophene (4i)



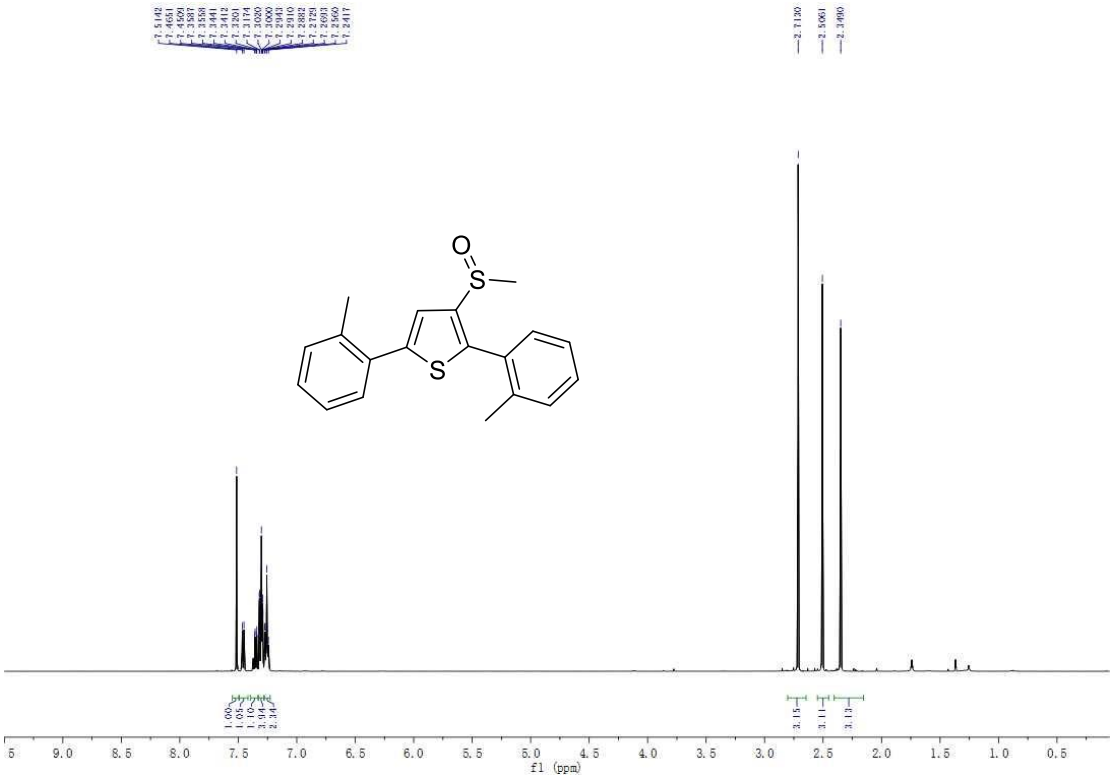
^{1}H NMR spectra ($CDCl_3$, 500 MHz) of 3-(Methylsulfinyl)-2,5-di(naphthalen-1-yl)thiophene (4l)



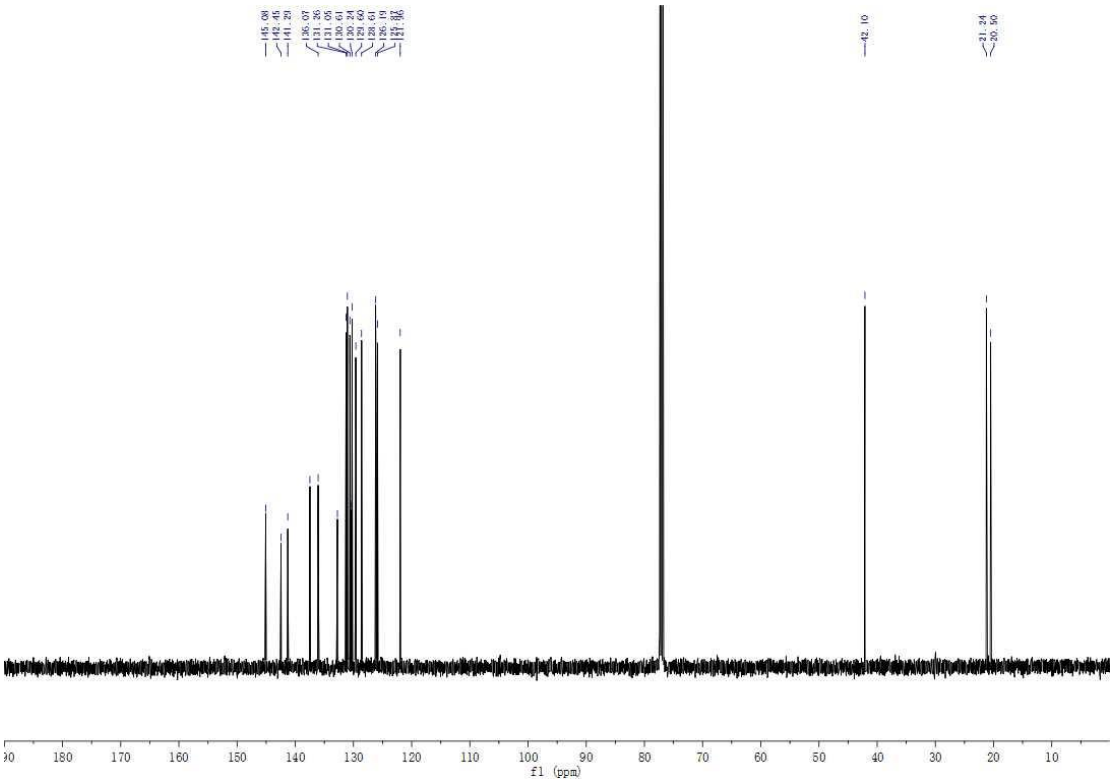
^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of 3-(Methylsulfinyl)-2,5-di(naphthalen-1-yl)thiophene (4l)



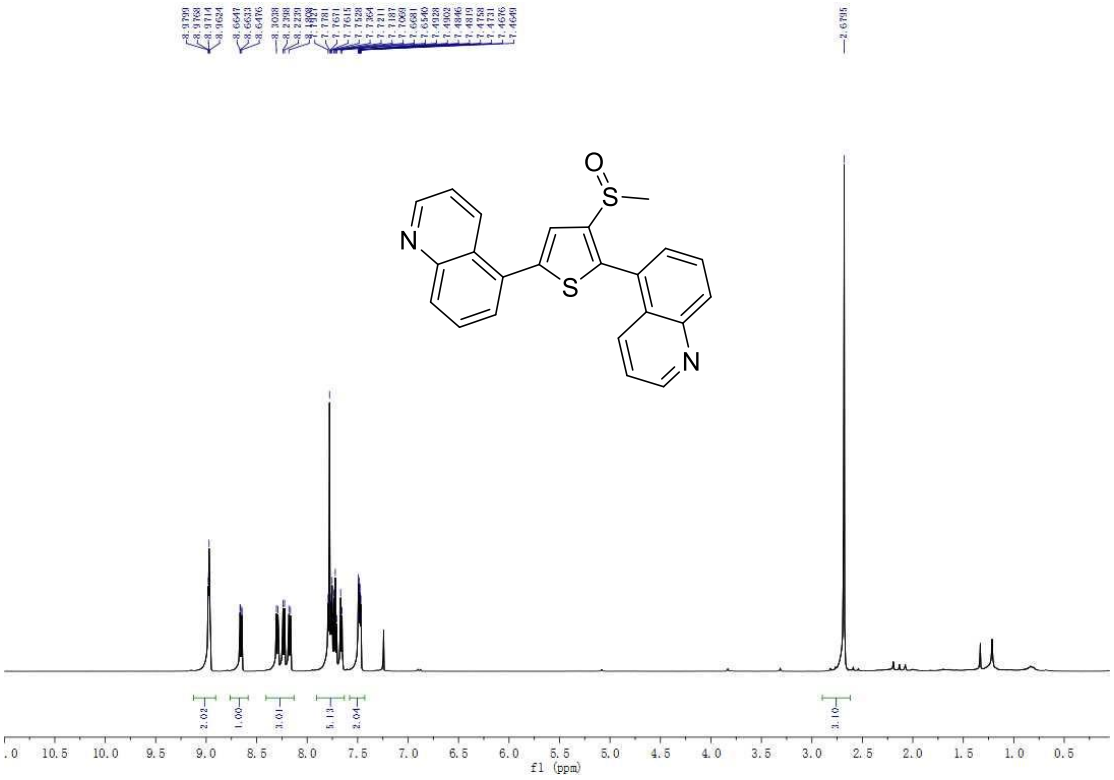
^{1}H NMR spectra ($CDCl_3$, 500 MHz) of 3-(Methylsulfinyl)-2,5-di-*o*-tolylthiophene (4m)



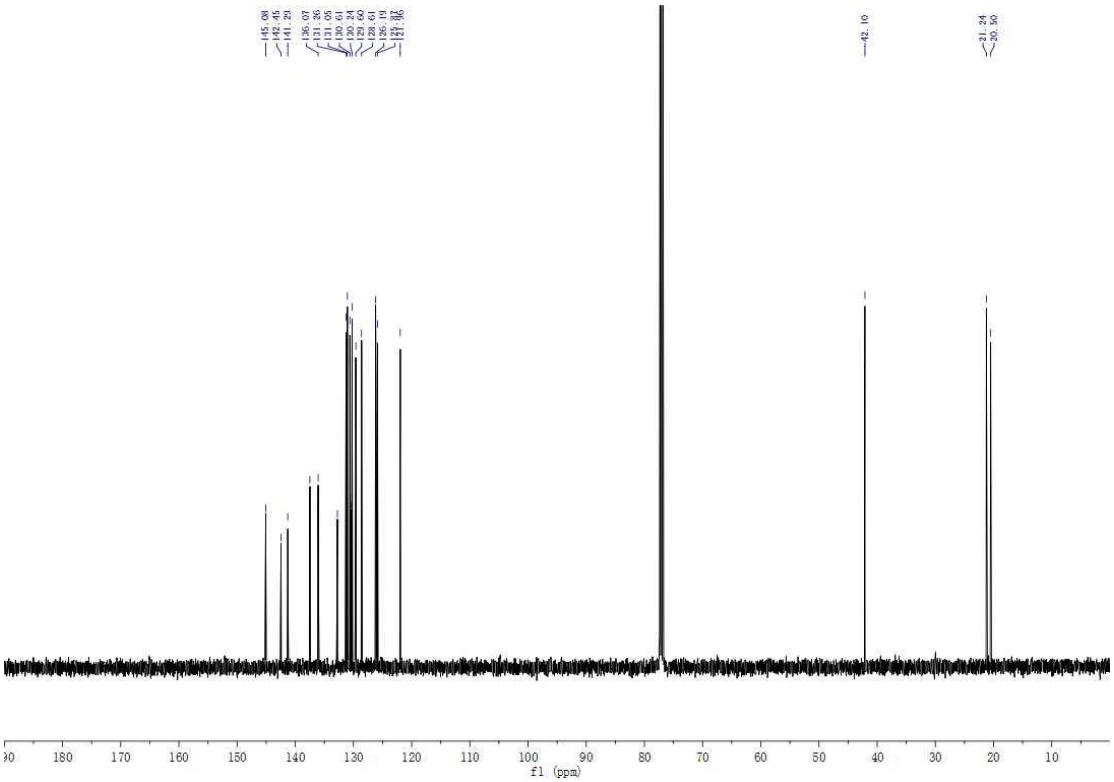
^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of 3-(Methylsulfinyl)-2,5-di-*o*-tolylthiophene (4m)



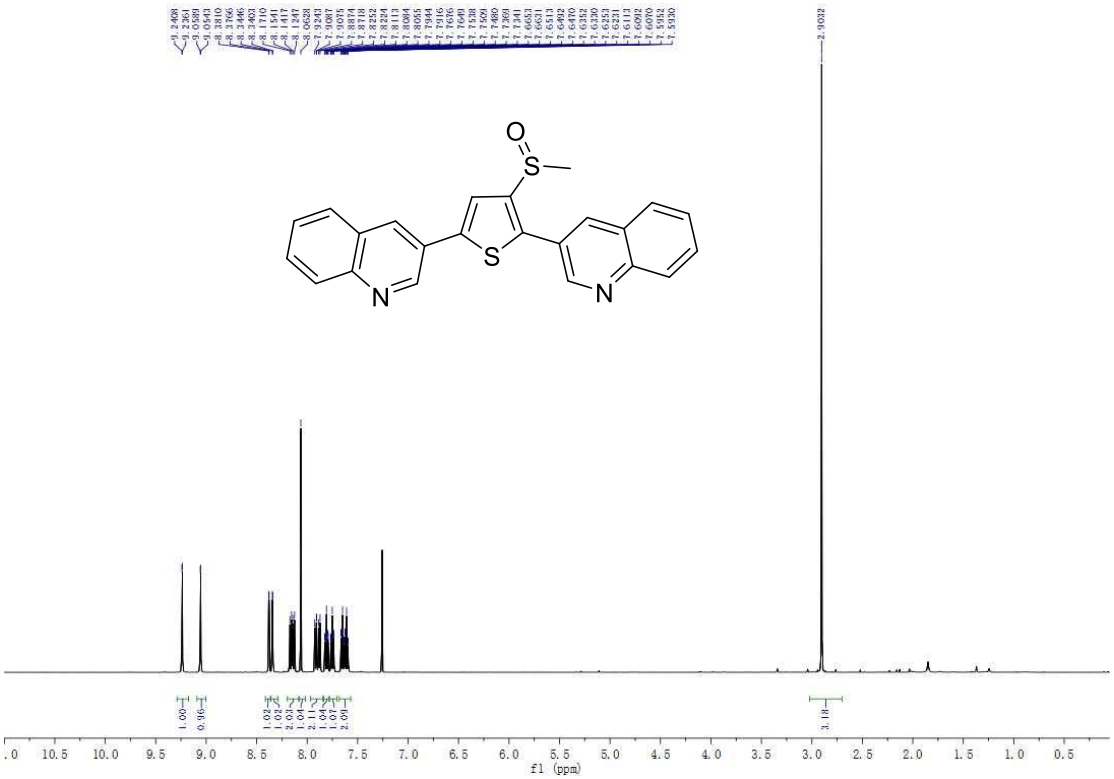
^{1}H NMR spectra ($CDCl_3$, 500 MHz) of 5,5'-(3-(Methylsulfinyl)thiophene-2,5-diyl)diquinoline (4s)



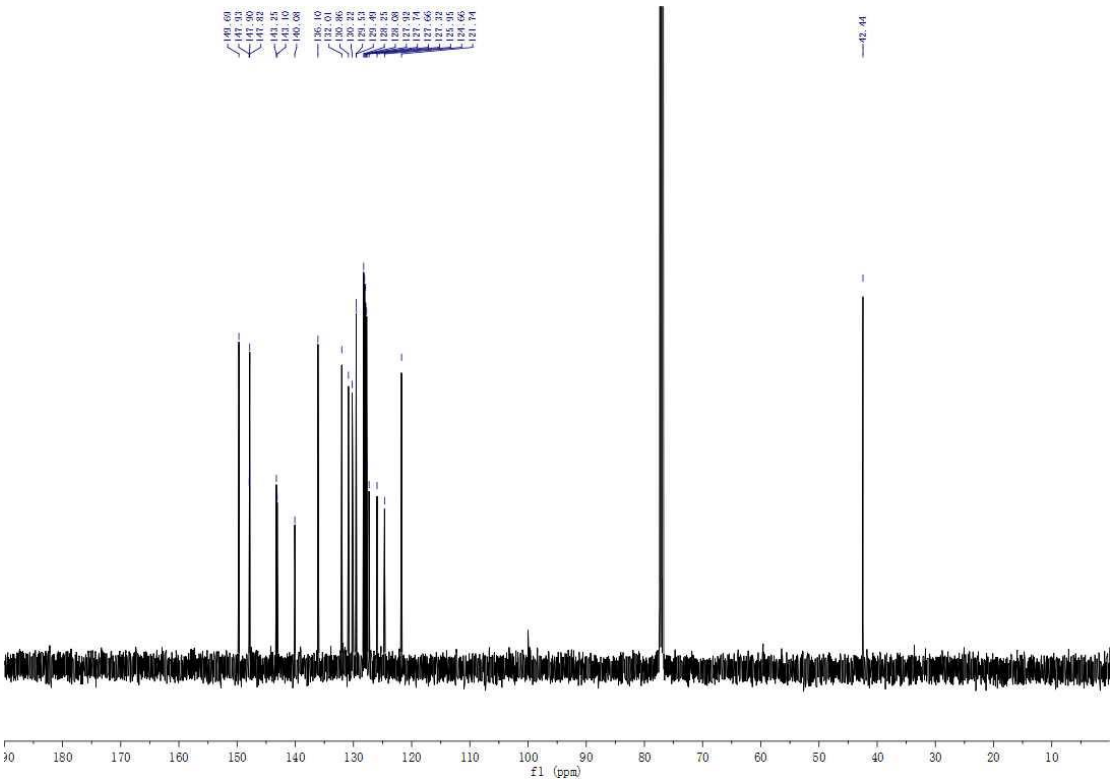
^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of 5,5'-(3-(Methylsulfinyl)thiophene-2,5-diyl)diquinoline (4s)



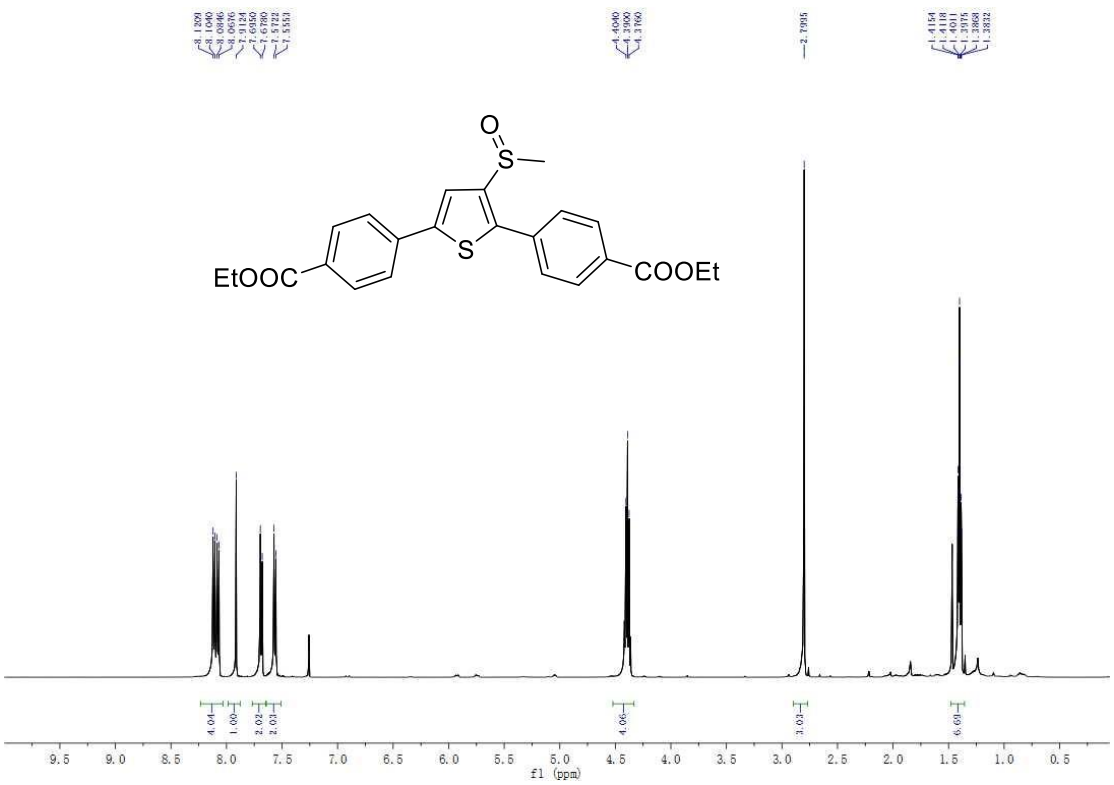
^{1}H NMR spectra ($CDCl_3$, 500 MHz) of 3,3'-(3-(Methylsulfinyl)thiophene-2,5-diyl)diquinoline (4t)



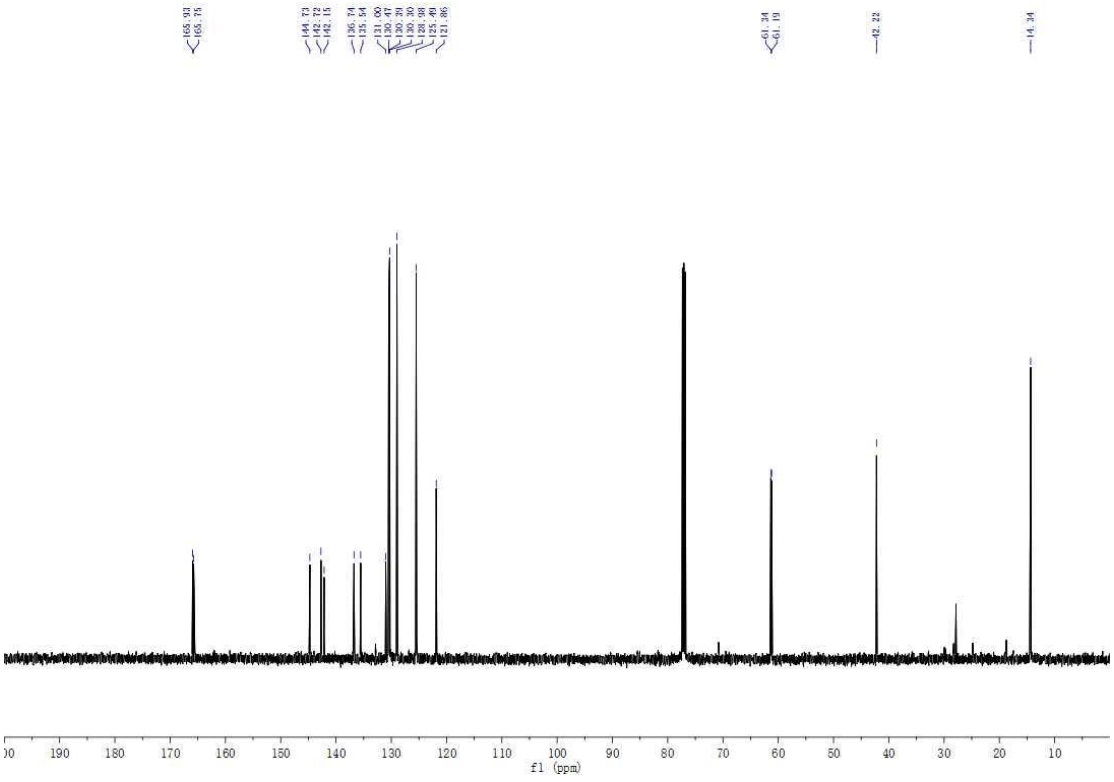
^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of 3,3'-(3-(Methylsulfinyl)thiophene-2,5-diyl)diquinoline (4t)



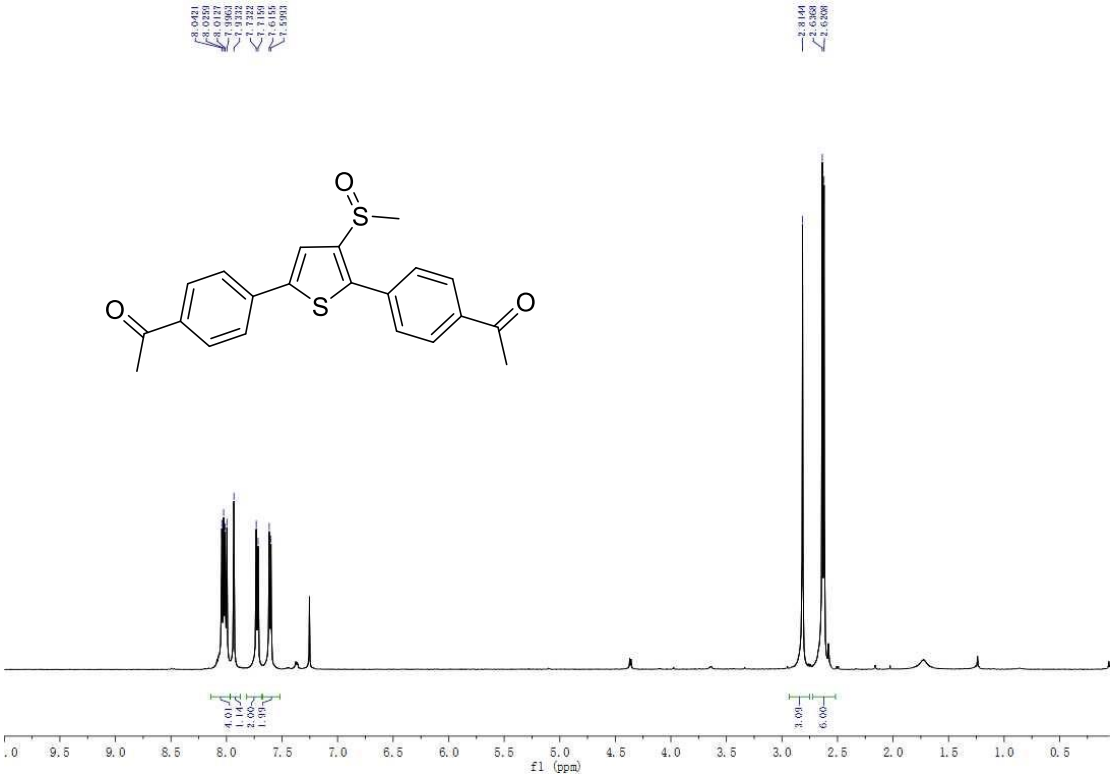
^{1}H NMR spectra ($CDCl_3$, 500 MHz) of Diethyl 4,4'-(3-(methylsulfinyl)thiophene-2,5-diyl)dibenzoate (4u)



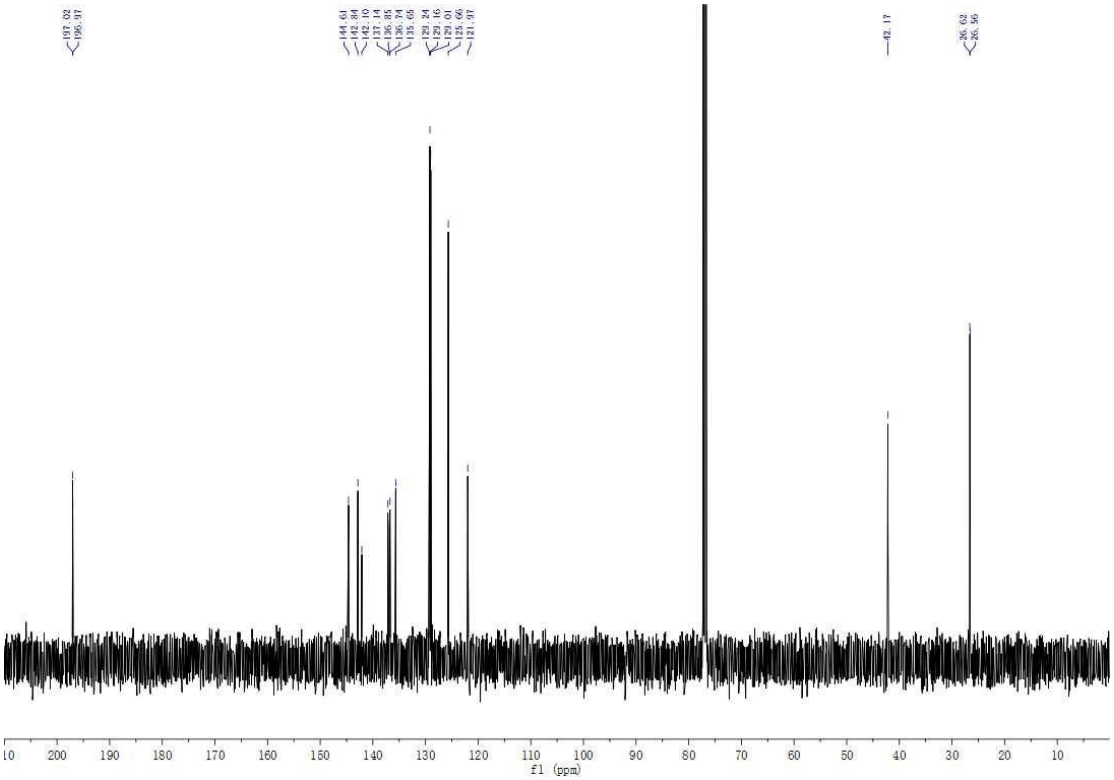
^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of Diethyl 4,4'-(3-(methylsulfinyl)thiophene-2,5-diyl) dibenzoate (4u)



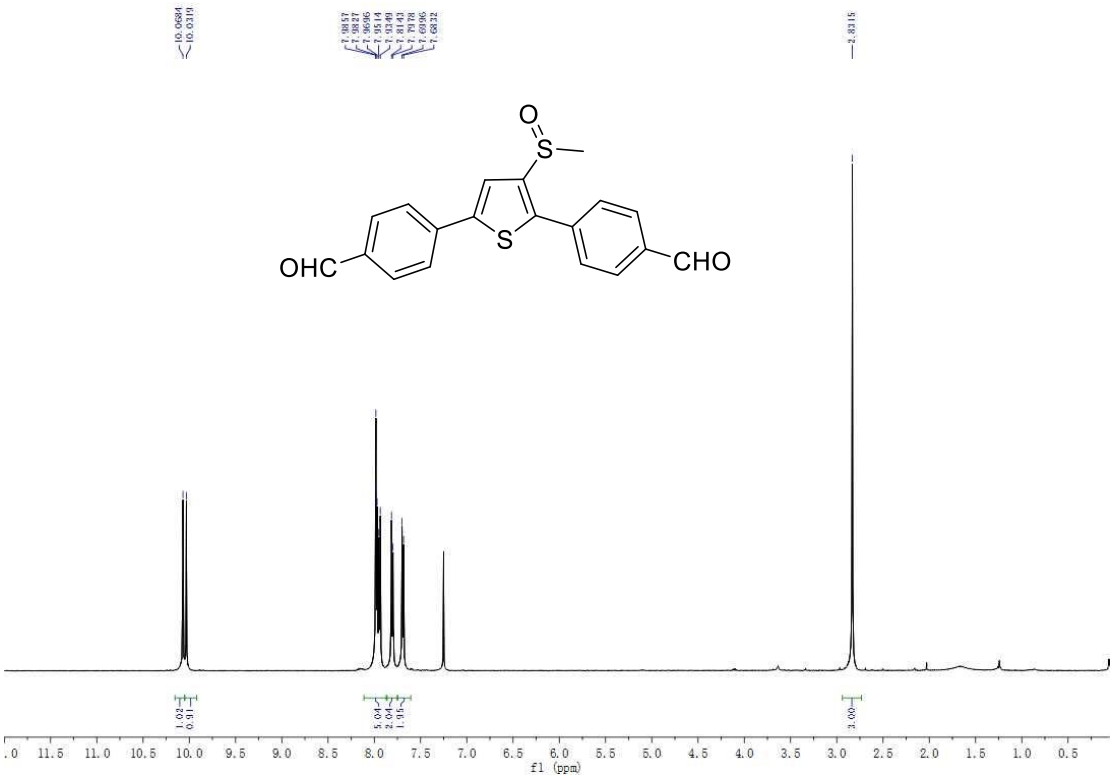
^{1}H NMR spectra ($CDCl_3$, 500 MHz) of 1,1'-((3-(Methylsulfinyl)thiophene-2,5-diyl)bis(4,1-phenylene)) bis(ethan-1-one) (4v)



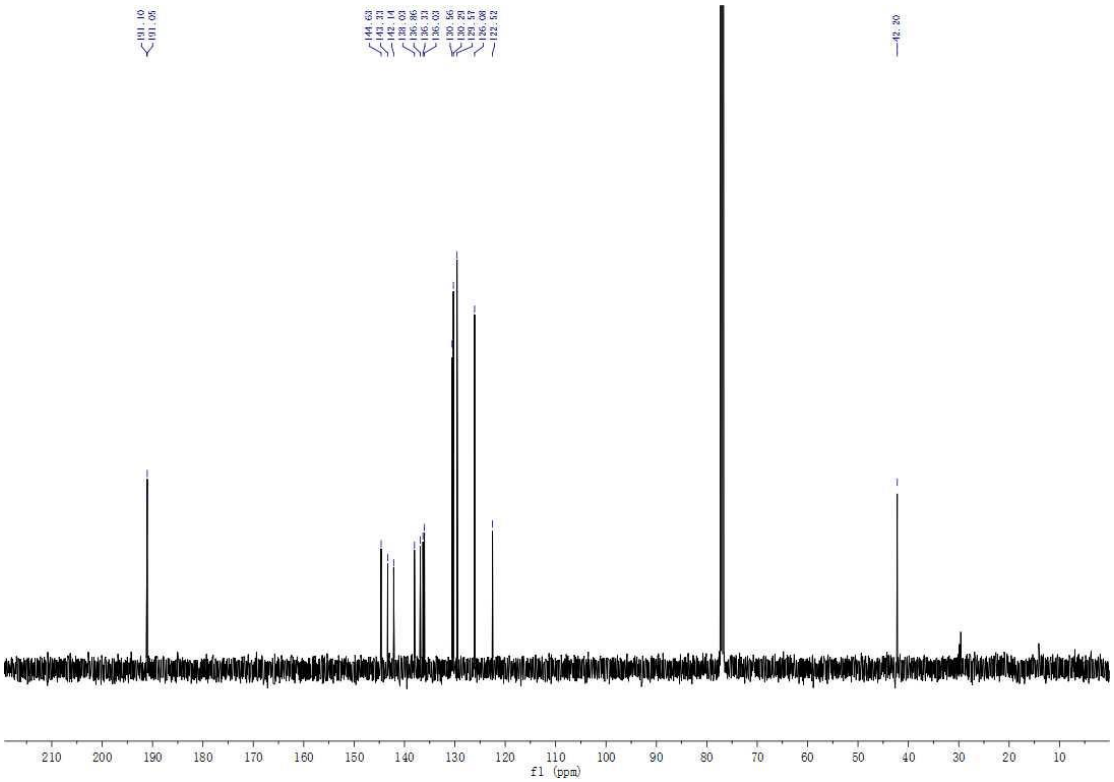
^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of 1,1'-((3-(Methylsulfinyl)thiophene-2,5-diyl) bis (4,1-phenylene))bis(ethan-1-one) (4v)



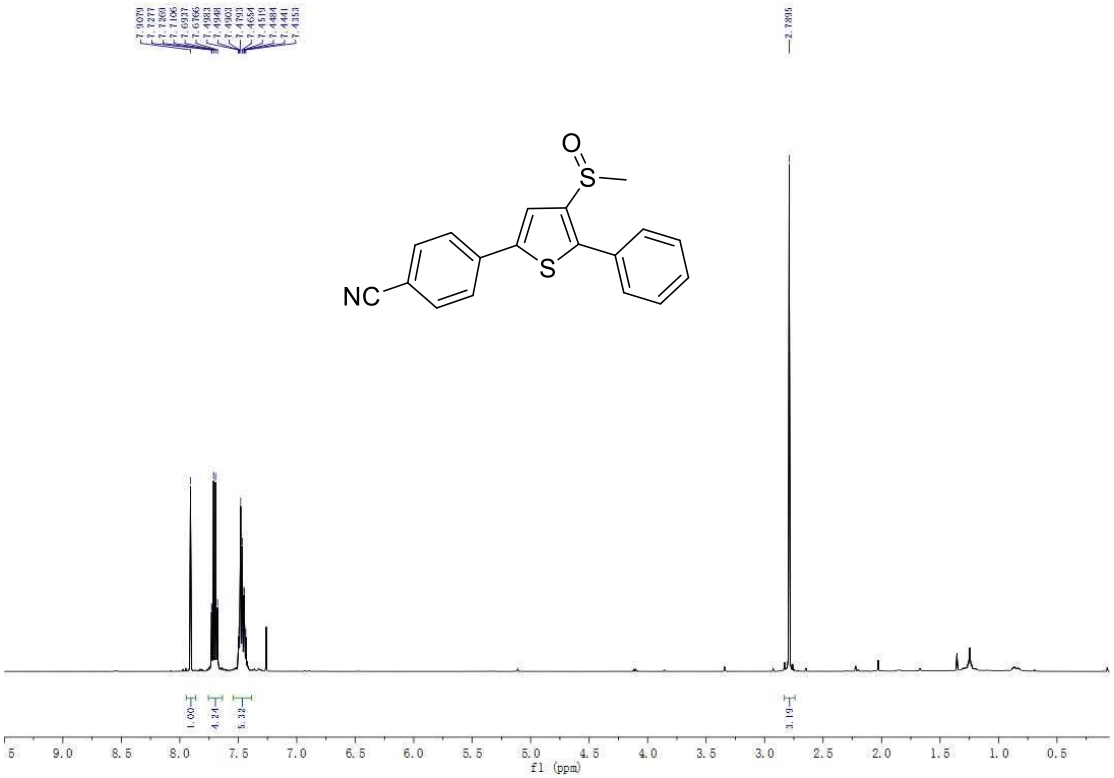
^{1}H NMR spectra ($CDCl_3$, 500 MHz) of 4,4'-(3-(Methylsulfinyl)thiophene-2,5-diyl)dibenzaldehyde (4w)



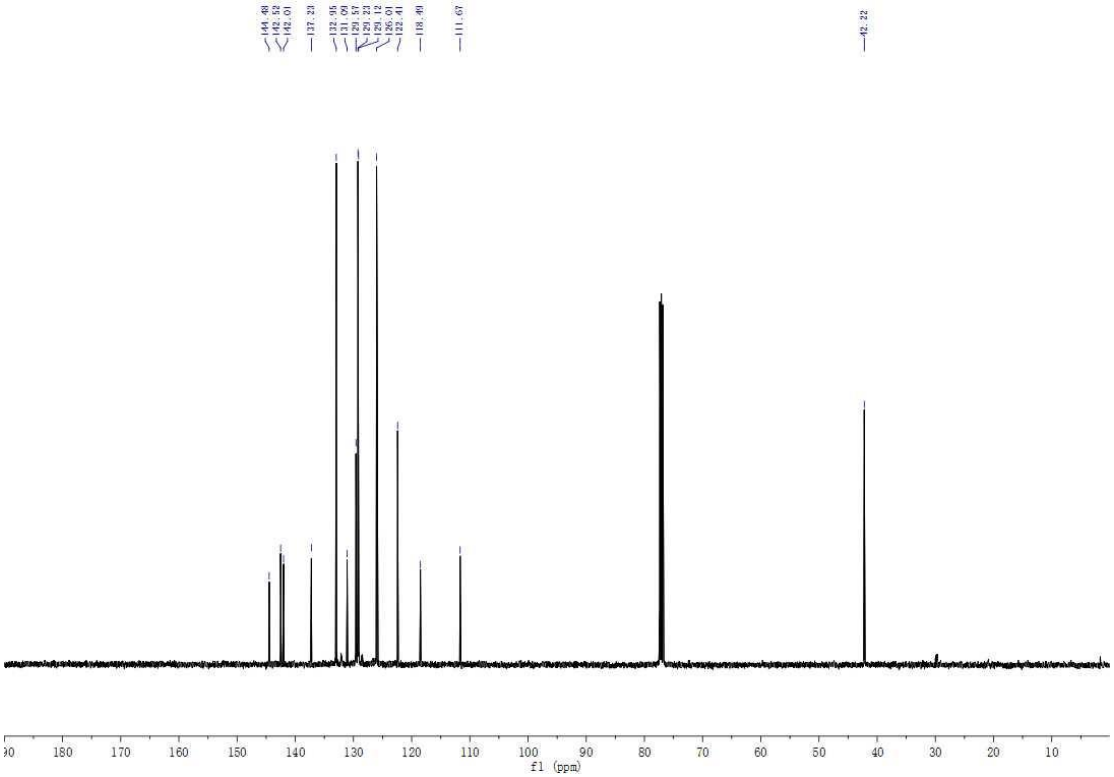
^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of 4,4'-(3-(Methylsulfinyl)thiophene-2,5-diyl)dibenzaldehyde (4w)



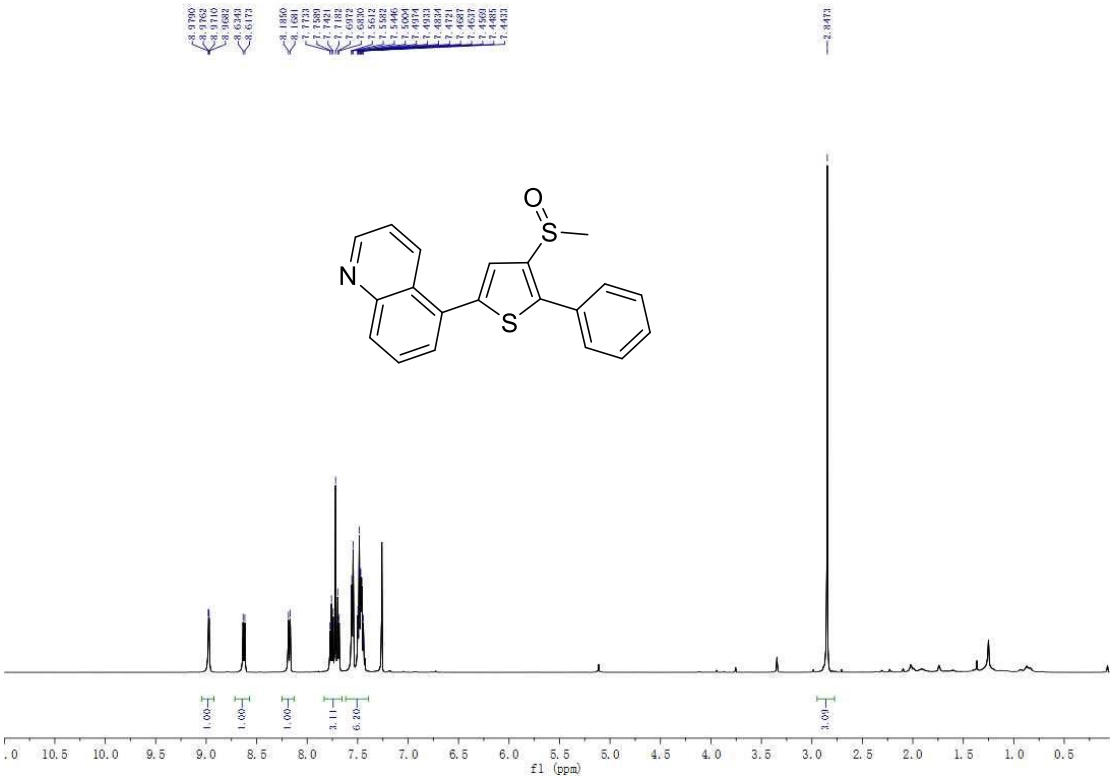
^{1}H NMR spectra ($CDCl_3$, 500 MHz) of 4-(4-(Methylsulfinyl)-5-phenylthiophen-2-yl)benzonitrile (5a)



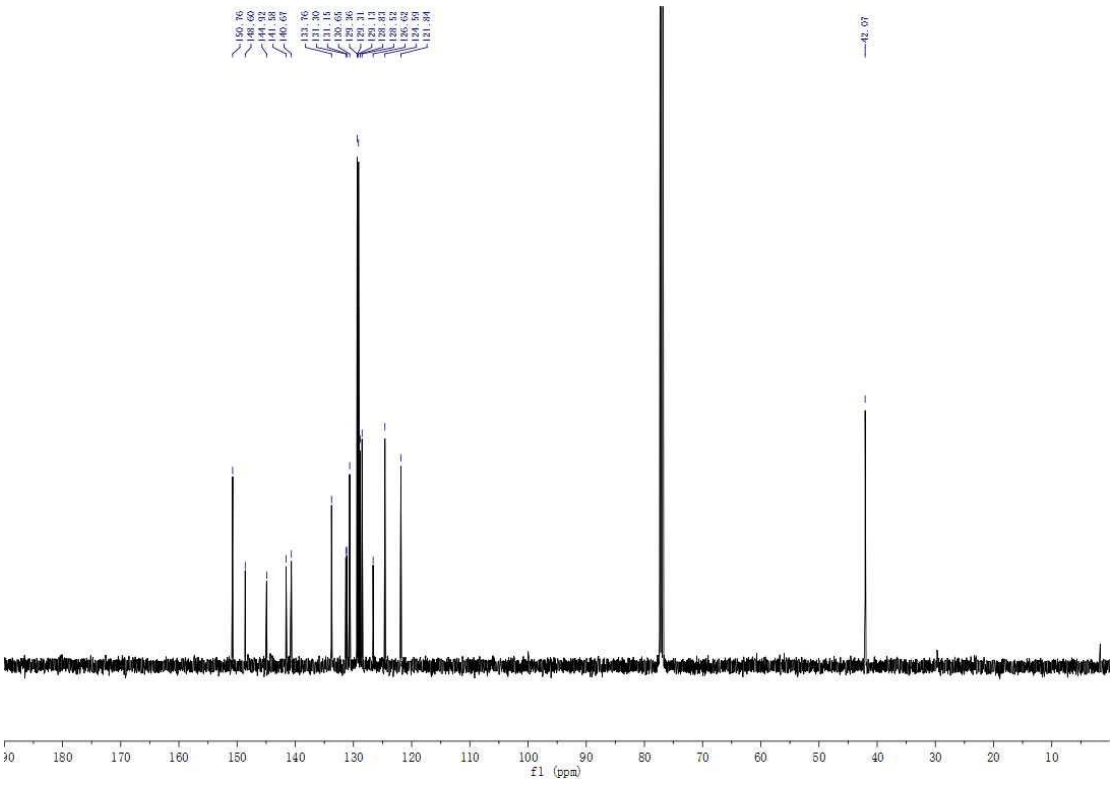
^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of 4-(4-(Methylsulfinyl)-5-phenylthiophen-2-yl)benzonitrile (5a)



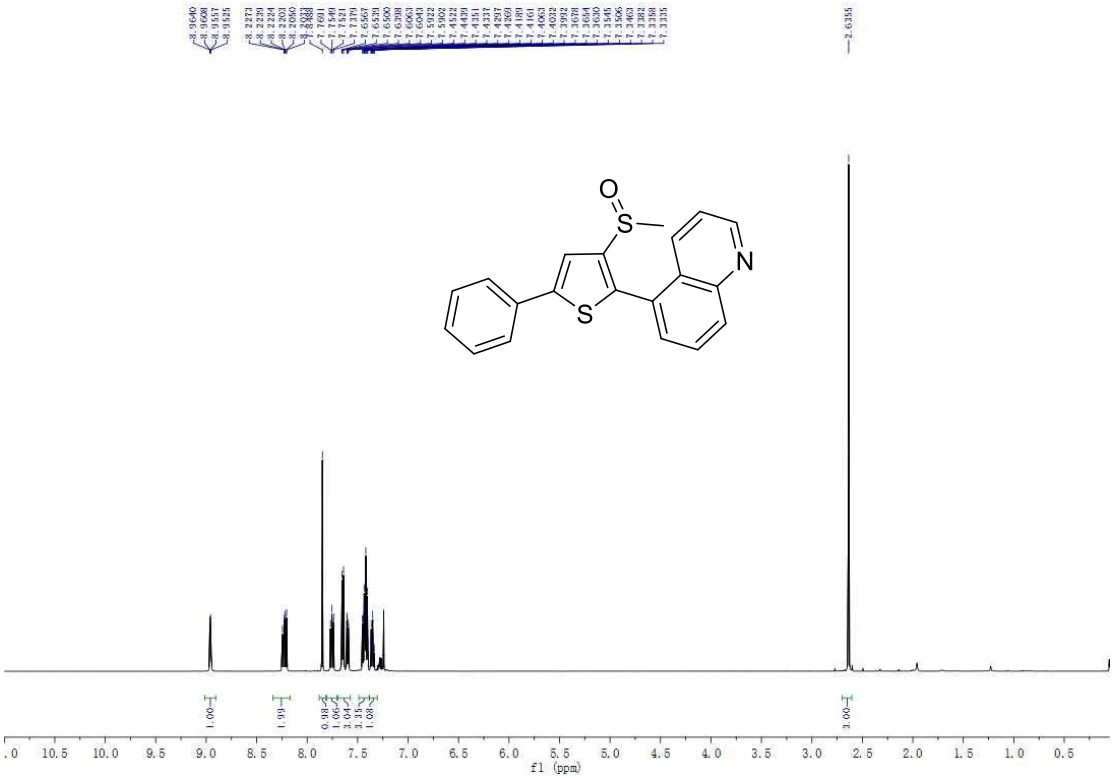
^{1}H NMR spectra ($CDCl_3$, 500 MHz) of 5-(4-(Methylsulfinyl)-5-phenylthiophen-2-yl)quinolone (5b)



^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of 5-(4-(Methylsulfinyl)-5-phenylthiophen-2-yl)quinolone (5b)



^{1}H NMR spectra ($CDCl_3$, 500 MHz) of 5-(3-(Methylsulfinyl)-5-phenylthiophen-2-yl)quinolone (5c)



^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of 5-(3-(Methylsulfinyl)-5-phenylthiophen-2-yl)quinolone (5c)