Supporting information

Access to 4-Substituted Isothiazoles through Three-Component Cascade Annulation and Its Application in C-H Activation

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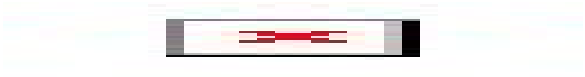
(A). General Information

Chemicals and solvents were purchased from commercial suppliers and used as received unless noted. All products were purified by flash chromatography on silica gel. The chemical yields referred are isolated products.^{1}H NMR and ^{13}C NMR spectra were recorded on 400 MHz, 500MHz and 600 MHz Bruker spectrometers. Chemical shifts of ^{1}H were reported in part per million relative to the $CDCl_3$ residual peak (δ 7.260). Chemical shifts of ^{13}C NMR were reported relative to $CDCl_3$ (δ 77.00). The used abbreviations are as follows: s (singlet), d (doublet), t (triplet), quart. (quartet), quint. (quintet), m (multiplet), br (broad). Multiplets which arise from accidental equality of coupling constants of magnetically non-equivalent protons are marked as virtual (*virt.*). High resolution mass spectra (HRMS) data were measured on a ESI-microTOF Ⅱ. Melting points were measured on a SGW® X-4B and are not corrected. Reactions were monitored by TLC analysis using silica gel 60 Å F-254 thin layer plates and compounds were visualized with a UV light at 254 nm or 365 nm. Most of the isopropene derivatives in this study were sourced from reagent service companies.

Initially, when treated with elemental sulfur and NH_4I at 130 °C, **1a** afforded 4-phenylisothiazole (**2a**) in 53% yield (Table 1, entry 1). Attempts to improve the yield by employing other sulfur sources, and using $EtOCS_2K$, gave a satisfactory yield, while thiourea and Na_2S gave similar results to that of elemental sulfur (entries 2–4). The reaction efficiency showed no obvious change, even when the amount of H_2O was increased or decreased (entries 5–7). Notably, NH_4I played an important role in the annulation reaction. No desired product was detected when similar ammonium salts Et_4NI or NH_4Br were used (entries 8 and 9). Furthermore, the screening of alternative solvents, such as DMF, NMP, DMAc, and 1,4-dioxane, did not give improved results (entries 10–13). The dosage of NH_4I was found to have a significant effect on the desired product yield (entry 14). Notably, shortening the reaction time decreased the yield (entry 15). The reaction did not occur in the absence of $EtOCS_2K$ (entry 16). When butylated hydroxytoluene or 2,2,6,6-tetramethyl-1-piperidinyloxy were added as radical scavengers, the intermolecular annulation process was

completely inhibited (entries 17 and 18), indicating that this transition-metal-free cascade annulation reaction proceeded *via* a radical pathway.

Table 1. Optimization of reaction conditions [a,b]



entry	"N" source	"sulphur" source	solvent(v/v)	yield[%][b]
1	NH_4I	S_8	DMSO/H_2O(2:1)	53
2	NH_4I	thiourea	DMSO/H_2O(2:1)	49
3	NH_4I	$EtOCS_2K$	DMSO/H_2O(2:1)	87 (84)
4	NH_4I	Na_2S	DMSO/H_2O(2:1)	34
5	NH_4I	$EtOCS_2K$	DMSO/H_2O(1:1)	62
6	NH_4I	$EtOCS_2K$	DMSO/H_2O(3:1)	59
7	NH_4I	$EtOCS_2K$	DMSO/H_2O(3:0)	54
8	Et_4NI	$EtOCS_2K$	DMSO/H_2O(2:1)	< 5
9	NH_4Br	$EtOCS_2K$	DMSO/H_2O(2:1)	< 5
10	NH_4I	$EtOCS_2K$	DMF/H_2O(2:1)	28
11	NH_4I	$EtOCS_2K$	NMP/H_2O(2:1)	18
12	NH_4I	$EtOCS_2K$	DMAc/H_2O(2:1)	13
13	NH_4I	$EtOCS_2K$	dioxane/H_2O(2:1)	9
14[c]	NH_4I	$EtOCS_2K$	DMSO/H_2O(2:1)	64
15[d]	NH_4I	$EtOCS_2K$	DMSO/H_2O(2:1)	75
16	NH_4I	-	DMSO/H_2O(2:1)	-
17[e]	NH_4I	$EtOCS_2K$	DMSO/H_2O(2:1)	< 5
18[f]	NH_4I	$EtOCS_2K$	DMSO/H_2O(2:1)	< 5

[a] Reaction conditions: α-Methylstyrene (**1a**, 1.0 mmol), nitrogen source (2.0 mmol), sulfur source (1.2 mmol) in solvent (3.0 mL) at 130 °C for 24 h; [b] Yield determined by GC-MS analysis; [c] NH_4I (1.5 mmol) was used; [d] Reaction conducted at 130 °C for 18 h; [e] TEMPO (1.0 mmol) was used; [f] BHT (1.0 mmol) was used.

(B). General procedures

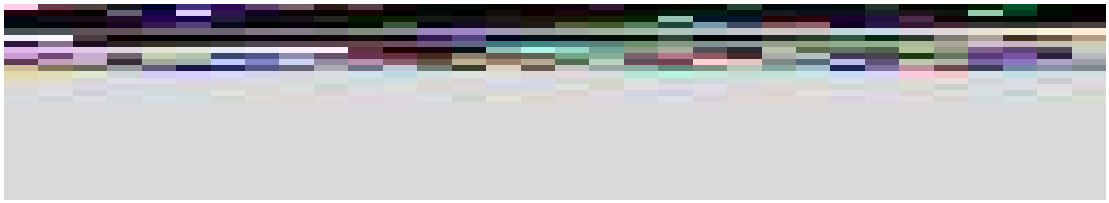
General procedures for synthesis of 4-substituted isothiazoles: A mixture of prop-1-en-2-ylbenzene (1.0 mmol), NH_4I (2.0 mmol, 290 mg), $EtOCS_2K$ (1.2 mmol, 192 mg), DMSO (2.0 ml) and H_2O (1.0 ml) was added successively in a 20 mL Schlenk tube. The Schlenk tube was then immersed in an oil bath at 130 ^oC stirring for 24 h. After cooling down to room temperature, the solution was filtered through a small amount of silica gel. Then the residue was concentrated in vacuo and the crude was purified by flash chromatography with n-hexane/ethyl acetate (20/1, v/v) to afford the 4-phenylisothiazole (**2a**) as a yellow viscous liquid in 84% yield.

General procedures for synthesis of 5,5'-diisothiazole: A mixture of 4-(p-tolyl)isothiazole (87.5 mg, 0.5 mmol), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol, 10 mol%), 1,10-phenanthroline (9.0 mg, 0.05 mmol, 10 mol%), Ag_2CO_3 (27.6 mg, 0.1 mmol), K_2CO_3 (13.8 mg, 0.1 mmol) and toluene (1.0 ml) was added successively in a 20 mL Schlenk tube. The Schlenk tube was then immersed in an oil bath at 130 ^oC stirring for 24 h. After cooling down to room temperature, the solution was filtered through a small amount of silica gel. Then the residue was concentrated in vacuo and the crude was purified by flash chromatography with n-hexane/ethyl acetate (20/1, v/v) to afford the 4,4'-di-p-tolyl-5,5'-biisothiazole (**3a**) as a yellow solid in 89% yield.

General procedures for synthesis of 4,5-diphenylisothiazoles: A mixture of 4-phenylisothiazole (**2a**) (80 mg, 0.5 mmol), Iodobenzene (153 mg, 0.75 mmol), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol, 10 mol%), 1,10-phenanthroline (9.0 mg, 0.05 mmol, 10 mol%), Ag_2CO_3 (27.6 mg, 0.1 mmol), K_2CO_3 (13.8 mg, 0.1 mmol) and toluene (1.0 ml) was added successively in a 20 mL Schlenk tube. The Schlenk tube was then immersed in an oil bath at 130 ^oC stirring for 24 h. After cooling down to room temperature, the solution was filtered through a small amount of silica gel. Then the residue was concentrated in vacuo and the crude was purified by flash chromatography with n-hexane/ethyl acetate (20/1, v/v) to afford the 4,5-diphenylisothiazole (**4a**) as a yellow solid in 65% yield.

Gram-scale synthesis of 4-phenylisothiazole: A mixture of prop-1-en-2-ylbenzene (1g, 8.5 mmol), NH_4I (2.47g, 17 mmol), $EtOCS_2K$ (1.63g, 10.2 mmol), DMSO (15

ml) and H_2O (7.0 ml) was added successively in a 50 mL Schlenk tube. The Schlenk tube was then immersed in an oil bath at 130 ^oC stirring for 36 h. After cooling down to room temperature, the solution was filtered through a small amount of silica gel. Then the residue was concentrated in vacuo and the crude was purified by flash chromatography with n-hexane/ethyl acetate (20/1, v/v) to afford the 4-phenylisothiazole **2a** as a yellow viscous liquid in 76% yield.



(C) Plausible mechanism for synthesis 5,5'-bisisothiazoles from 4-substituted isothiazole derivatives

The 4-substituted isothiazoles **2** undergo ligand-assisted dissociation with $Pd(OAc)_2$, adjusting to coordinate to the palladium complex through its л-system, to facilitate C5–H activation of 4-substituted isothiazoles **D**. A similar C–H activation process then occurs to give bi(hetero)arene-palladium(II) complex **E**, followed by reductive elimination to give the desired product **3**. Finally, Pd(II) is oxidized by Ag_2CO_3 to regenerate $Pd(OAc)_2$ and 1,10- phenanthroline with the assistance of KOAc.

Scheme 1. Plausible mechanism for synthesis 5,5'-bisisothiazoles

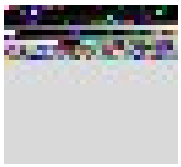
(D) Single-Crystal X-ray diffraction analysis

Scheme 2. Molecular structures of 2g, 2x, and 3k from Single-Crystal X-ray diffraction analysis

(E) Analytical data of all products

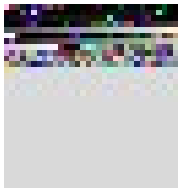
4-phenylisothiazole (2a) [1]

Yellow viscous liquid (135 mg, 84% yield); R_f = 0.48 (Hexane/EtOAc = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (s, 1H), 8.71 (s, 1H), 7.59 (d, J = 7.9 Hz, 2H), 7.52 – 7.40 (m, 2H), 7.36 (dd, J = 10.5, 4.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 142.6, 140.0, 132.6, 129.1 (2C), 128.0, 126.9 (2C); GC-MS (EI, 70 eV) m/z (%) 161 (l00), 134 (57), 77.



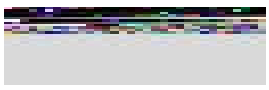
4-(*o*-Tolyl)isothiazole (2b)[2]

Yellow viscous liquid (98 mg, 56% yield); R_f = 0.47 (Hexane/EtOAc = 20:1); ^{1}H NMR (600 MHz, Acetone-d_6) δ 8.93 (s, 1H), 8.62 (s, 1H), 7.37 – 7.26 (m, 4H), 2.33 (s, 3H); ^{13}C NMR (150 MHz, Acetone-d_6) δ 158.9, 146.6, 140.1, 136.6, 133.7, 131.5, 130.6, 128.9, 127.0, 20.8; HRMS (ESI-TOF): *m/z* [M+H]$^+$: calcd for $C_{10}H_{10}NS$ 176.0529; found 176.0527.



4-(3-methylphenyl)-isothiazole (2c)

Yellow viscous liquid, (126 mg, 72% yield); R_f = 0.47 (Hexane/EtOAc = 20:1); ^{1}H NMR (600 MHz, Acetone-d_6) δ 9.12 (s, 1H), 8.92 (s, 1H), 7.61 – 7.59(m, 1H), 7.56 – 7.53 (m, 1H), 7.35 – 7.31 (m, 1H), 7.19 – 7.16(m, 1H), 2.38 (s, 3H); ^{13}C NMR (150 MHz, Acetone-d_6) δ 156.1, 143.1, 139.9, 138.7 132.6, 129.0, 128.6, 127.5, 123.9 20.6. HRMS (ESI-TOF) *m/z* [M+H]$^+$: calcd for $C_{10}H_{10}NS$ 176.0529; found 176.0529.



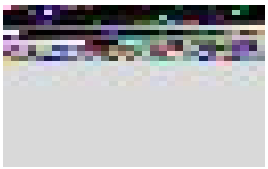
4-(*p*-Tolyl)isothiazole (2d)

Yellow viscous liquid, (141.8 mg, 81% yield); R_f = 0.47 (Hexane/EtOAc = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 8.62 (s, 1H), 7.46 (d, J = 8.1 Hz, 2H), 7.27 – 7.16 (m, 2H), 2.37 (s, 3H); ^{13}C NMR (100 MHz,

$CDCl_3$) δ 155.9, 141.9, 139.8, 137.8, 129.7 (2C), 129.7 (2C), 126.7, 21.1. HRMS (ESI-TOF) *m/z* $[M+H]^+$: calcd for $C_{10}H_{10}NS$ 176.0529; found 176.0528.

4-(4-isobutylphenyl)isothiazole (2e)

Yellow viscous liquid, (141.1 mg, 65% yield); R_f = 0.36 (Hexane/EtOAc = 20:1); ^1H NMR (600 MHz, Acetone-d_6) δ 9.12 (s, 1H), 8.93 (s, 1H), 7.70 – 7.69 (m, 2H), 7.28 – 7.127 (m, 2H), 2.51 (d, J = 7.2 Hz, 2H), 1.95 – 1.82 (m, 1H), 0.92(s, 1H), 0.91(s, 1H); ^{13}C NMR (150 MHz, Acetone-d_6) δ 160.0, 143.6, 142.4, 140.7, 131.2, 130.7 (2C), 127.5 (2C), 45.6, 31.0, 22.6 (2C). HRMS (ESI-TOF) *m/z* $[M+H]^+$: calcd for $C_{13}H_{16}NS$ 218.0998; found 218.0996.



4-(4-methoxyphenyl)isothiazole (2f)

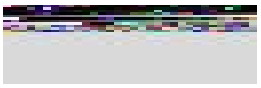
Yellow solid, (149 mg, 78% yield); m.p.: 73–75 ^oC; R_f = 0.35 (Hexane/EtOAc = 20:1); ^1H NMR (600 MHz, $CDCl_3$) δ 8.72 (s, 1H), 8.57 (s, 1H), 7.52 – 7.49 (m, 2H), 6.97 – 6.93 (m, 2H), 3.83 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.3, 155.8, 141.2, 139.5, 127.9 (2C), 125.1, 114.4 (2C), 55.2. HRMS (ESI-TOF) *m/z* $[M+H]^+$: calcd for $C_{10}H_{10}NOS$ 192.0478; found 192.0477.

4-(benzo[d][1,3]dioxol-5-yl)isothiazole (2g)

Brown solid, (143.5 mg, 70% yield); m.p.: 69–72 ^oC; R_f = 0.55 (Hexane/EtOAc = 20:1); ^1H NMR (600 MHz, Acetone-d_6) δ 9.04 (s, 1H), 8.86 (s, 1H), 7.28 – 7.26 (m, 2H), 6.91 – 6.92 (m, 1H), 6.04 (s, 2H); ^{13}C NMR (150 MHz, Acetone-d_6) δ 156.9, 149.4, 148.4, 143.2, 140.4, 127.8, 121.4, 109.6, 108.1, 102.4. HRMS (ESI-TOF) *m/z* $[M+H]^+$: calcd for $C_{10}H_8NO_2S$ 206.0270; found 206.0270.

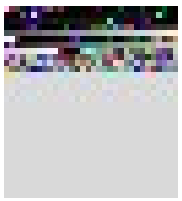
4-(naphthalen-2-yl)isothiazole (2h)[2]

Brown solid, (151.9 mg, 72% yield); R_f = 0.55 (Hexane/EtOAc = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (s, 1H), 8.81 (s, 1H), 8.06 (s, 1H), 7.89 (dd, J = 18.9, 8.1 Hz, 3H), 7.70 (d, J = 8.4 Hz, 1H), 7.56 – 7.46 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 142.8, 139.9, 133.6, 132.8, 129.9, 128.9, 128.0, 127.7, 126.7, 126.3, 125.5, 125.0. HRMS (ESI-TOF) *m/z* $[M+H]^+$: calcd for $C_{13}H_{10}NS$ 212.0529; found 212.0527.



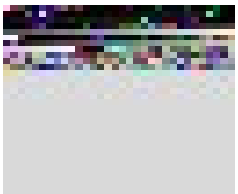
4-(4-chlorophenyl)isothiazole (2i)

Yellow viscous liquid, (156 mg, 80% yield); R_f = 0.30 (Hexane /EtOAc = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 8.69 (s, 1H), 7.52 (d, J = 8.5 Hz, 2H), 7.41 (d, J = 8.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 142.9, 138.8, 133.9, 131.0, 129.3 (2C), 128.0 (2C). HRMS (ESI-TOF) *m/z* $[M+H)^+$: calcd for C_9H_7ClNS 195.9982; found 195.9982.



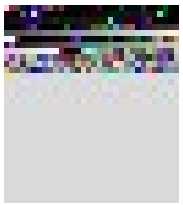
4-(3-chlorophenyl)isothiazole (2j)

Yellow viscous liquid, (144.3 mg, 74% yield); R_f = 0.30 (Hexane/EtOAc = 20:1); ^{1}H NMR (600 MHz, Acetone-d_6) δ 9.27 (s, 1H), 8.98 (s, 1H), 7.83 – 7.81 (m, 1H), 7.74 – 7.71 (m, 1H), 7.48 – 7.40 (m, 1H), 7.38 – 7.36 (m, 1H); ^{13}C NMR (150 MHz, Acetone-d_6) δ 156.9, 145.3, 139.0, 135.47, 135.3, 131.5, 128.5, 127.4, 126.1. HRMS (ESI-TOF) *m/z* $[M+H]^+$: calcd for C_9H_7ClNS 195.9982; found 195.9981.



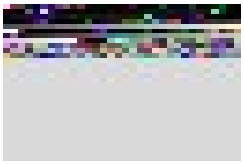
4-(3,4-dichlorophenyl)isothiazole (2k)

Yellow viscous liquid, (139.7, 61% yield); R_f = 0.30 (Hexane/EtOAc = 20:1); ^{1}H NMR (600 MHz, Acetone-d_6) δ 9.32 (s, 1H), 8.99 (s, 1H), 7.99 (d, J = 2.2 Hz, 1H), 7.76 (dd, J = 8.4, 2.1 Hz, 1H), 7.62 (d, J = 8.4 Hz, 1H). ^{13}C NMR (150 MHz, Acetone-d_6) δ 156.0, 144.8, 137.2, 133.2, 132.6, 131.1, 131.06, 128.6, 126.7; HRMS (ESI-TOF) *m/z* $[M+H)^+$: calcd for $C_9H_6Cl_2NS$ 229.9593; found 229.9591.



4-(3-bromophenyl)isothiazole (2l)

Yellow viscous liquid, (149.4 mg, 62% yield); R_f = 0.35 (Hexane/EtOAc = 20:1); ^{1}H NMR (600 MHz, Acetone-d_6) δ 9.29 (s, 1H), 8.99 (s, 1H), 7.99-7.97 (m, 1H), 7.81-7.78 (m, 1H), 7.55 – 7.53 (m, 1H), 7.44-7.40 (m, 1H). ^{13}C NMR (150 MHz, Acetone-d_6) δ 156.7, 145.1, 138.7, 135.6, 131.6, 131.3, 131.2, 126.3, 123.3; HRMS (ESI-TOF) *m/z* [M+H]$^+$: calcd for C_9H_7BrNS 241.9456; found 241.9455.



4-(4-bromophenyl)isothiazole (2m)

Yellow viscous liquid, (159.1 mg, 66% yield); R_f = 0.35 (Hexane/EtOAc = 20:1); ^{1}H NMR (600 MHz, Acetone-d_6) δ 9.24 (s, 1H), 8.96 (s, 1H), 7.77 – 7.73 (m, 2H), 7.66 – 7.63 (m, 2H); ^{13}C NMR (150 MHz, Acetone-d_6) δ 156.2, 144.2, 138.7, 132.4 (2C), 132.2, 129.0 (2C), 121.5; HRMS (ESI-TOF) *m/z* [M+H]$^+$: calcd for C_9H_7BrNS 241.9456; found 241.9455.

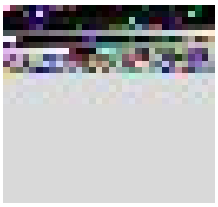
4-(4-fluorophenyl)isothiazole (2n)

Yellow viscous liquid, (139.6 mg, 78% yield); R_f = 0.35 (Hexane/EtOAc = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (s, 1H), 8.65 (s, 1H), 7.60 – 7.50 (m, 2H), 7.17 – 7.08 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5 (d, J = 246.3 Hz, 1C), 155.8, 142.5, 138.9, 128.7(d, J = 3.4 Hz, 1C), 128.5 (d, J = 8.1 Hz, 2C), 116.0 (d, J = 21.6 Hz, 2C); HRMS (ESI-TOF) *m/z* [M+H]$^+$: calcd for C_9H_7FNS 180.0278; found 180.0277

4-(2-fluorophenyl)isothiazole (2o)

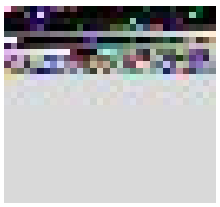
Yellow viscous liquid, (75.2 mg, 42% yield); R_f = 0.34 (Hexane/EtOAc = 20:1); ^{1}H NMR (600 MHz, Acetone-d_6) δ 9.23

(d, J = 1.3 Hz, 1H), 8.91 (d, J = 1.7 Hz, 1H), 7.81 (td, J = 7.7, 1.8 Hz, 1H), 7.46 – 7.41 (m, 1H), 7.32 – 7.27 (m, 2H); ^{13}C NMR (150 MHz, Acetone-d_6) δ 160.5 (d, J = 245.6 Hz, 1C), 157.9 (d, J = 4.5 Hz, 1C), 147.1 (d, J = 5.5 Hz, 1C), 134.0 (d, J = 2.2 Hz, 1C), 130.8 (d, J = 6.1 Hz, 1C), 130.7, 125.9 (d, J = 3.7 Hz, 1C), 121.4 (d, J = 13.6 Hz, 1C), 117.17 (d, J = 22.6 Hz, 1C); HRMS (ESI-TOF) *m/z* [M+H]$^+$: calcd for C_9H_7FNS 180.0278; found 180.0277.



4-(3,4-difluorophenyl)isothiazole (2p)

Yellow viscous liquid, (124.1 mg, 63% yield); R_f =0.30 (Hexane/EtOAc =0.43); ^{1}H NMR (600 MHz, Acetone-d_6) δ 9.25 (s, 1H), 8.96 (s, 1H), 7.81 – 7.77 (m, 1H), 7.66 – 7.62 (m, 1H), 7.44 – 7.39 (m, 1H); ^{13}C NMR (150 MHz, Acetone-d_6) δ 156.9, 151.8 (dd, J =12.75 Hz, 100.05 Hz, 1C), 150.2 (dd, J =12.75 Hz, 101.3 Hz, 1C), 145.2, 138.5 (d, J = 1.95 Hz, 1C), 131.1 (dd, J = 6.8, 4.0 Hz, 1C), 124.4 (dd, J = 6.4, 3.5 Hz, 1C), 118.9 (d, J = 17.4 Hz, 1C), 116.8(d, J = 18.3 Hz, 1C); HRMS (ESI-TOF) *m/z* [M+H]$^+$: calcd for: $C_9H_6F_2NS$ 198.0184; found 198.0183.

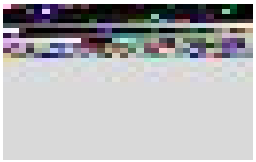


4-(3-bromo-4-fluorophenyl)isothiazole (2q）

Yellow solid, (138.8 mg, 54% yield); m.p.: 79–82 ^{o}C; R_f = 0.50 (Hexane/EtOAc = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, J = 7.2 Hz, 2H), 7.76 (dd, J = 6.4, 2.3 Hz, 1H), 7.51 – 7.46 (m, 1H), 7.18 (t, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8 (d, J = 247.5 Hz, 1C), 155.6, 143.2, 137.6, 131.8, 130.2 (d, J = 3.9 Hz, 1C), 127.4 (d, J = 7.3 Hz, 1C), 117.3 (d, J = 22.5 Hz, 1C), 110.0 (d, J = 21.3 Hz, 1C); HRMS (ESI-TOF) *m/z* [M+H]$^+$: calcd for C_9H_6BrFNS 257.9383; found 257.9380.

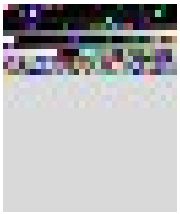
4-(4-iodophenyl)isothiazole (2r)

Yellow solid, (238.2 mg, 83% yield); m.p.: 102–104 °C; R_f = 0.32 (Hexane/EtOAc = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (s, 1H), 8.70 (s, 1H), 7.75 (d, J = 8.3 Hz, 2H), 7.31 (d, J = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 142.9, 138.2 (2C), 132.0 128.5 (2C), 93.4; HRMS (ESI-TOF) *m/z* $[M+H]^+$: calcd for C_9H_7INS 287.9338; found 287.9339.



4-(4-(trifluoromethyl)phenyl)-isothiazole (2s)

Yellow liquid, (155.7 mg, 68% yield); R_f = 0.45 (Hexane/EtOAc = 20:1); ^{1}H NMR (600 MHz, Acetone-d_6) δ 9.37 (s, 1H), 9.04 (s, 1H), 8.04 – 8.01 (m, 2H), 7.82 – 7.78 (m, 2H); ^{13}C NMR (150 MHz, Acetone-d_6) δ 157.1, 146.2, 139.1, 137.5, 130.0 (q, J = 29.1 Hz), 128.3 (2C), 126.8 (q, J = 3.9 Hz, 2C), 125.3 (d, J = 269.6 Hz, 1C); HRMS (ESI-TOF) *m/z* $[M+H]^+$: calcd for $C_{10}H_7F_3NS$ 230.0246; found 230.0243.



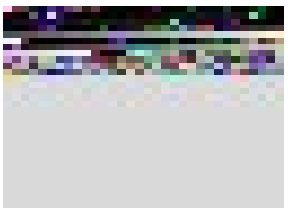
4-(3-(trifluoromethyl)phenyl)-isothiazole (2t)

Yellow viscous liquid, (148.9 m, 65% yield); R_f = 0.45 (Hexane/EtOAc = 20:1); ^{1}H NMR (600 MHz, Acetone-d_6) δ 9.41 (s, 1H), 9.07 (s, 1H), 8.13 (s, 1H), 8.11 – 8.09 (m, 1H), 7.72-7.71 (m, 2H); ^{13}C NMR (150 MHz, Acetone-d_6) δ 157.1, 145.8, 139.1, 134.7, 131.8 (d, J = 32.1 Hz, 1C), 131.5 (d, J = 0.9 Hz, 1C), 130.9, 125.3 (q, J = 266.9 Hz, 1C), 125.2 (q, J = 4.3 Hz, 1C), 124.3 (q, J = 3.9 Hz, 1C); HRMS (ESI-TOF) *m/z* $[M+H]^+$: calcd for $C_{10}H_7F_3NS$ 230.0246; found 230.0244.

4-(4-cyclohexylphenyl)isothiazole (2u)

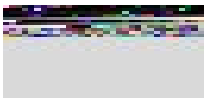
Yellow solid, (136.1 mg, 56% yield); m.p.: 67–70 °C; R_f = 0.40 (Hexane/EtOAc = 20:1); ^{1}H NMR (600 MHz, Acetone-d_6) δ 9.10

(s, 1H), 8.91 (s, 1H), 7.79 – 7.58 (m, 2H), 7.47 – 7.17 (m, 2H), 2.58 – 2.52 (m, 1H), 1.89 – 1.80 (m, 5H), 1.75 – 1.71 (m, 1H), 1.47 – 1.38(m, 4H); ^{13}C NMR (150 MHz, Acetone-d_6) δ 157.0, 148.7, 143.4, 140.7, 131.2, 128.4 (2C), 127.7 (2C), 45.1, 35.1 (2C), 27.5 (2C), 26.7; HRMS (ESI-TOF) *m/z* [M+H)$^+$]: calcd for $C_{15}H_{18}NS$ 244.1155; found 244.1153.



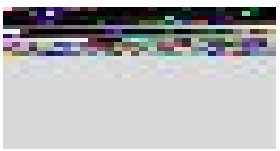
4-(4-phenylphenyl)-isothiazole (2v)

Yellow solid, (144.6 mg, 61% yield); m.p.: 157–159 °C; TLC: R_f = 0.43 (Hexane/EtOAc = 20:1); ^{1}H NMR (600 MHz, Acetone-d_6) δ 9.23 (s, 1H), 9.00 (s, 1H), 7.90 – 7.83 (m, 2H), 7.78 – 7.75 (m, 2H), 7.72 – 7.70 (m, 2H), 7.49-7.47 (m, 2H), 7.39 (d, J = 7.4 Hz, 1H); ^{13}C NMR (150 MHz, Acetone-d_6) δ 156.6, 143.8, 140.9, 140.7, 139.8, 132.2, 129.4 (2C), 129.4, 128.0 (2C), 128.0 (2C), 127.8 (2C); HRMS (ESI-TOF) *m/z* [M+H]$^+$: calcd for $C_{15}H_{12}NS$ 238.0685; found 238.0682.



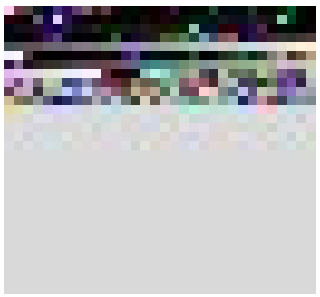
4-(thiophen-2-yl)isothiazole (2w)

Yellow viscous liquid, (71.8 mg, 43% yield); R_f = 0.41 (Hexane/EtOAc = 20:1); ^{1}H NMR (600 MHz, Acetone-d_6) δ 9.04 (s, 1H), 8.84 (s, 1H), 7.51 – 7.48 (m, 2H), 7.14 – 7.12 (m, 1H); ^{13}C NMR (150 MHz, Acetone-d_6) δ 156.4, 143.1, 135.8, 134.2, 129.0, 126.2, 125.8; HRMS (ESI-TOF) *m/z* [M+H]$^+$: calcd for $C_7H_6NS_2$ 167.9936; found: 167.9933.



1,3-di(isothiazol-4-yl)benzene (2x)

Yellow solid, (100.1 mg, 41% yield) m.p.: 107–109 °C; R_f = 0.32 (Hexane/EtOAc = 5:1); ^{1}H NMR (600 MHz, Acetone-d_6) δ 9.31 (s, 2H), 9.06 (s, 2H), 8.25-8.23 (m, 1H), 7.79 (d, J = 1.8 Hz, 1H), 7.78 (d, J = 1.8 Hz, 1H), 7.58–7.54 (m, 1H); ^{13}C NMR (150 MHz, Acetone-d_6) δ 157.3 (2C), 144.8 (2C), 140.3, 134.5, 130.8 (2C), 127.2 (2C), 126.3 (2C); HRMS (ESI-TOF) *m/z* [M+H]$^+$: calcd for $C_{12}H_9N_2S_2$ 245.0202; found 245.0201.



4,4'-di-p-tolyl-5,5'-biisothiazole (3a)

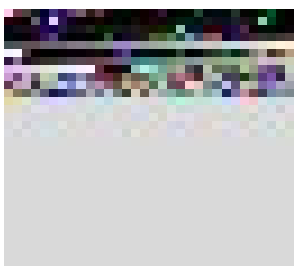
Yellow solid, (154.9 mg, 89% yield); m.p.: 134–137 °C; R_f = 0.34 (Hexane/EtOAc = 20:1); ^{1}H NMR (600 MHz, Acetone-d6) δ 8.60 (s, 2H), 7.22 – 7.10 (m, 8H), 2.33 (s, 6H); ^{13}C NMR (150 MHz, Acetone-d6) δ 159.6 (2C), 149.6 (2C), 140.1 (2C), 139.2 (2C), 130.4 (4C), 129.8 (2C), 129.5 (4C), 21.3 (2C); HRMS (ESI-TOF) *m/z* $[M+H]^+$: calcd for $C_{20}H_{17}N_2S_2$ 349.0828; found 349.0828.

4,4'-di-m-tolyl-5,5'-biisothiazole (3b)

Yellow solid, (161.8 mg, 93% yield); R_f = 0.53 (Hexane/EtOAc = 20:1); ^{1}H NMR (600 MHz, Acetone-d_6) δ 7.18 (t, J = 7.5 Hz, 2H), 7.14 (d, J = 7.5 Hz, 2H), 7.00 (dd, J = 5.7, 5.0 Hz, 4H), 2.25 (s, 6H); ^{13}C NMR (150 MHz, Acetone-d_6) δ 158.9 (2C), 149.2 (2C), 139.3 (2C), 138.6 (2C), 132.0 (2C), 129.4 (2C), 129.1 (2C), 128.8 (2C), 126.0 (2C), 20.7 (2C); HRMS (ESI-TOF) *m/z* $[M+H]^+$: calcd for $C_{20}H_{17}N_2S_2$ 349.0828; found 349.0826.

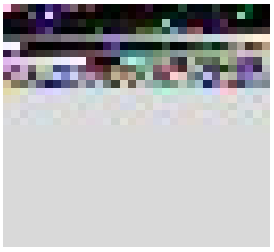
4,4'-bis(4-methoxyphenyl)-5,5'-biisothiazole (3c)

Yellow solid, (163.4 mg, 86% yield); m.p.: 79–83 °C; R_f = 0.22 (Hexane /EtOAc = 20:1); ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.74 (s, 2H), 7.26 (d, J = 8.7 Hz, 4H), 6.94 (d, J = 8.8 Hz, 4H), 3.76 (s, 6H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 159.4 (2C), 159.0 (2C), 147.7 (2C), 138.5 (2C), 129.9 (4C), 123.4 (2C), 114.4 (4C), 55.2 (2C); HRMS (ESI-TOF) *m/z* $[M+H]^+$: calcd for $C_{20}H_{17}N_2O_2S_2$ 381.0726; found 381.0725.



4,4'-bis(benzo[d][1,3]dioxol-5-yl)-5,5'-biisothiazole (3d)

Brown solid, (114.2 mg, 56% yield); R_f = 0.20 (Hexane /EtOAc = 10:1); ^{1}H NMR (600 MHz, Acetone-d_6) δ 8.57 (s, 2H), 6.81 (d, J = 8.0 Hz, 2H), 6.75 – 6.68 (m, 4H), 6.03 (s, 4H); ^{13}C NMR (150 MHz, Acetone-d_6) δ 159.8 (2C), 149.5 (2C), 149.1 (2C), 149.0 (2C), 139.5 (2C), 126.4 (2C), 123.7 (2C), 109.7 (2C), 109.4 (2C), 102.5 (2C); HRMS (ESI-TOF) *m/z* [M+H]$^+$: calcd for $C_{20}H_{13}N_2O_4S_2$ 409.0311; found 409.0309.

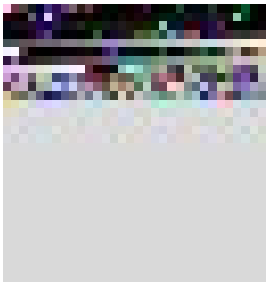


4,4'-bis(3-chlorophenyl)-5,5'-biisothiazole (3e)

Yellow solid, (163.0 mg, 84% yield); m.p.: 142–145 ^{o}C; R_f = 0.20 (Hexane /EtOAc = 20:1) ^{1}H NMR (400 MHz, Acetone) δ 8.66 (s, 2H), 7.32 – 7.25 (m, 4H), 7.09 (s, 2H), 7.06 (d, J = 7.5 Hz, 2H); ^{13}C NMR (100 MHz, Acetone-d6) δ 159.9 (2C), 150.3 (2C), 138.0 (2C), 135.0 (2C), 134.6 (2C), 131.2 (2C), 129.2 (2C), 129.0 (2C); 128.0 (2C). HRMS (ESI-TOF) *m/z* [M+H]$^+$: calcd for $C_{18}H_{11}Cl_2N_2S_2$ 388.9735; found 388.9732.

4,4'-bis(4-chlorophenyl)-5,5'-biisothiazole (3f)

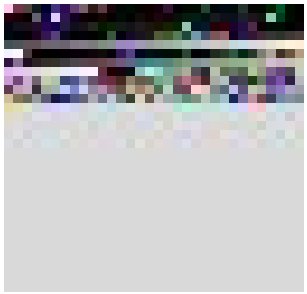
Yellow solid, (164.9 mg, 85% yield); m.p.: 129-132 ^{o}C; R_f = 0.40 (Hexane /EtOAc = 20:1); ^{1}H NMR (600 MHz, Acetone-d_6) δ 8.65 (s, 2H), 7.33 – 7.29 (m, 4H), 7.21 – 7.17 (m, 4H); ^{13}C NMR (150 MHz, Acetone-d_6) δ 159.1 (2C), 149.3 (2C), 137.6 (2C), 134.1 (2C), 130.8 (2C), 130.4 (4C), 129.0 (4C); HRMS (ESI-TOF) *m/z* [M+H)]$^+$: calcd for $C_{18}H_{11}Cl_2N_2S_2$ 388.9735; found 388.9732.



4,4'-bis(4-fluorophenyl)-5,5'-biisothiazole (3g)

Yellow solid, (160.2 mg, 90% yield); m.p.: 105–108 ^{o}C; R_f = 0.38 (Hexane /EtOAc = 20:1); ^{1}H NMR (600 MHz, Acetone-d_6) δ 8.66 (s, 2H), 7.29 – 7.17 (m, 4H), 7.12 – 7.00 (m, 4H); ^{13}C

NMR (150 MHz, Acetone-d_6) δ 1632.9 (d, J = 245.1 Hz, 2C), 159.1 (2C), 149.1 (2C), 137.9 (2C), 130.9 (d, J = 8.7 Hz, 2C), 128.3 (d, J = 3.0 Hz, 4C), 115.8 (d, J = 21.9 Hz, 4C); HRMS (ESI-TOF) *m/z* $[M+H]^+$: calcd for $C_{18}H_{10}F_2N_2S_2$ 357.0326; found 357.0325.

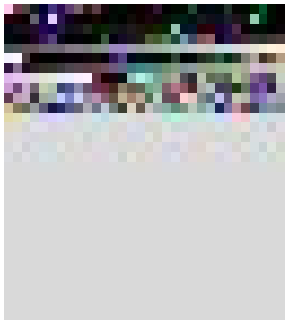


4,4'-bis(4-bromophenyl)-5,5'-biisothiazole (3h)

Yellow solid, (183.3 mg, 77% yield); m.p.: 151–154 °C; R_f = 0.36 (Hexane /EtOAc = 20:1). ^{1}H NMR (600 MHz, Acetone-d_6) δ 8.66 (s, 2H), 7.48 – 7.43 (m, 4H), 7.14 – 7.07 (m, 4H); ^{13}C NMR (150 MHz, Acetone-d_6) δ 159.8 (2C), 150.0 (2C), 138.4 (2C), 132.7 (4C), 131.9 (2C), 131.4 (4C), 123.0 (2C); HRMS (ESI-TOF) *m/z* $[M+H]^+$: calcd for $C_{18}H_{11}Br_2N_2S_2$ 476.8725; found 476.8720.

4,4'-di(thiophen-2-yl)-5,5'-biisothiazole (3i)

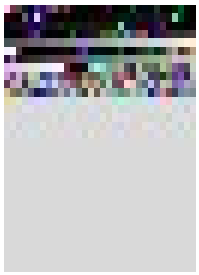
Yellow solid, (146.1 mg, 88% yield); m.p.: 143–146 °C; R_f = 0.36 (Hexane/EtOAc = 20:1); ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.16 (s, 2H), 7.49 (dd, J = 17.0, 4.3 Hz, 4H), 7.15 – 6.91 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 158.0 (2C), 144.9 (2C), 133.5 (2C), 132.4 (2C), 128.0 (2C), 127.6 (2C), 127.2 (2C); HRMS (ESI-TOF) *m/z* $[M+H]^+$: calcd for $C_{14}H_9N_2S_4$ 332.9643; found 332.9640.



4-(4-cyclohexylphenyl)-4'-phenyl-5,5'-biisothiazole (3j)

Yellow viscous liquid, (86.4 mg, 43% yield); R_f = 0.48 (Hexane/EtOAc = 20:1); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.8 (s, 1H), 8.75 (s, 1H), 7.31 (dd, J = 5.0, 1.8 Hz, 2H), 7.22 (dd, J = 6.4, 3.0 Hz, 2H), 7.18 – 7.07 (m, 5H), 2.47 (d, J = 2.9

Hz, 1H), 1.77 (s, 5H), 1.42 – 1.31 (m, 5H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 159.2, 159.2, 148.6, 147.9, 147.8, 138.7, 138.6, 131.2, 128.8 (2C), 128.6, 128.4(2C), 128.3 (2C), 128.2, 127.1 (2C), 43.5, 33.8 (2C), 26.3 (2C), 25.5; HRMS (ESI-TOF) *m/z* $[M+H]^+$: calcd for $C_{24}H_{23}N_2S_2$ 403.1297; found 403.1294.



4,4'-diphenyl-5,5'-biisothiazole (3k)

White solid, (146 mg, 91% yield); m.p.: 153–156 ^{o}C; R_f = 0.36 (Hexane/EtOAc = 20:1); ^{1}H NMR (500 MHz, Acetone-d_6) δ 8.63 (s, 2H), 7.35 – 7.29 (m, 6H), 7.26 (ddd, J = 7.9, 5.0, 2.6 Hz, 4H); ^{13}C NMR (125 MHz, Acetone-d_6) δ 158.8 (2C), 149.0 (2C), 139.1 (2C), 131.8 (2C), 128.8 (4C), 128.7 (4C), 128.3 (2C); HRMS (ESI-TOF) *m/z* $[M+H]^+$: calcd for $C_{18}H_{13}N_2S_2$ 321.0515; found 321.0512.

4-(4-(phenylethynyl)phenyl)isothiazole (2y)

Yellow solid, (120.1 mg, 92% yield); R_f = 0.40 (Hexane /EtOAc = 15:1). ^{1}H NMR (600 MHz, DMSO-d_6+Acetone-d_6) δ 9.47 (s, 1H), 9.13 (s, 1H), 7.90 (d, J = 8.4 Hz, 2H), 7.64 (d, J = 8.4 Hz, 2H), 7.62 – 7.54 (m, 2H), 7.44 (dd, J = 5.1, 1.8 Hz, 3H); ^{13}C NMR (150 MHz, DMSO-d_6+Acetone-d_6) δ 156.3, 144.8, 138.1, 132.2, 132.0 (2C), 131.3 (2C), 128.7, 128.7 (2C), 126.8 (2C), 122.1, 121.5, 90.0, 89.0; HRMS (ESI-TOF) *m/z* $[M+H]^+$: calcd for $C_{17}H_{12}NS$ 262.0685; found 262.0683.

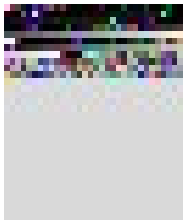
4-(4-bromophenyl)isothiazole (2m)

Yellow viscous liquid, (104.0 mg, 87% yield); R_f = 0.32 (Hexane/EtOAc = 20:1); ^{1}H NMR (500 MHz, Acetone-d_6) δ 9.23 (s, 1H), 8.95 (s, 1H), 7.77 – 7.72 (m, 2H), 7.66 – 7.60 (m, 2H). ^{13}C NMR (125 MHz, Acetone-d_6) δ

156.0, 144.0, 138.5, 132.1 (2C), 128.7 (2C), 121.3. HRMS (ESI-TOF) *m/z* $[M+H]^+$: calcd for C_9H_7BrNS 241.9456; found 241.9455.

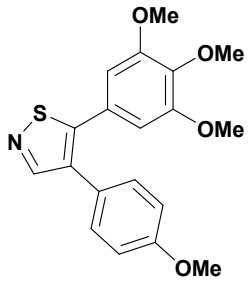
4-phenylisothiazole-5-d

Yellow viscous liquid (135 mg, 84% yield); R_f = 0.48 (Hexane/EtOAc = 20:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.78 (s, 1H), 7.59 (dd, *J* = 5.2, 3.2 Hz, 2H), 7.48 – 7.41 (m, 2H), 7.36 (ddd, *J* = 7.5, 3.9, 1.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ* 155.9, 142.5, 139.7, 132.4, 129.0 (2C), 127.9, 126.8 (2C).



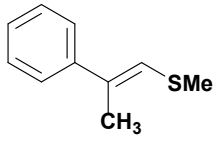
4,5-diphenylisothiazole (4a)[3]

Yellow solid, (77.0 mg, 65% yield); R_f = 0.38 (Hexane/EtOAc = 20:1); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.72 (s, 1H), 7.44 – 7.31 (m, 10H); ^{13}C NMR (100 MHz, DMSO-d_6) *δ* 160.8, 159.7, 135.5, 132.2, 129.9, 129.3, 129.2 (2C), 128.8 (2C), 128.7 (2C), 128.4 (2C), 127.8.



4-(4-methoxyphenyl)-5-(3,4,5-trimethoxyphenyl)isothiazole

Yellow solid, (mg, 58% yield); m.p.: °C; R_f = 0.20 (Hexane /EtOAc = 10:1); ^{1}H NMR (500 MHz, DMSO-d_6) *δ* 8.65 (s, 1H), 7.45 – 7.24 (m, 2H), 6.97 (d, *J* = 8.7 Hz, 2H), 6.60 (s, 2H), 3.76 (s, 3H), 3.68 (s, 3H), 3.63 (s, 6H); ^{13}C NMR (125 MHz, DMSO-d_6) *δ* 159.9, 159.6, 159.0, 153.1 (2C), 138.1, 135.2, 130.1 (2C), 125.4, 124.5, 114.2 (2C), 105.9 (2C), 60.1, 55.8 (2C), 55.2.



methyl(2-phenylprop-1-en-1-yl)sulfane ()[4]

Yellow liquid, (104.0 mg, 87% yield); R_f = 0.32 (Hexane/EtOAc = 20:1);^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.41 (m, 2H), 7.38 (t, J = 7.7 Hz, 2H), 7.31 – 7.26 (m, 1H), 6.35 (s, 1H), 2.45 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.8, 132.8, 128.2 (2C), 126.5, 125.3, 125.0 (2C), 17.4, 17.2.

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(F) X-ray Crystallographic Data of 2g

The X-ray crystallographic structures for **2g**. ORTEP representation with 50% probability thermal ellipsoids. Solvent and hydrogen are omitted for clarity. Solvent and hydrogen are omitted for clarity. Crystal data have been deposited to CCDC, number 1902238.

Crystal structure determination of 2g

Crystal Data for $C_{10}H_7NO_2S$ (M = 205.23 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 6.9853(19)Å, b= 8.3741(16)Å, c = 14.638(3)Å, β = 99.28(2), V= 845.1(3) Å^3, Z = 4, T = 100.01(10) K, μ(MoKα) = 0.348 mm^{-1}, $Dcalc$ = 1.613 g/cm^3, 3223 reflections measured ($5.622 \leq 2\Theta \leq 50$), 1438 unique ($R_{int}$ = 0.0434, R_{sigma} = 0.0530) which were used in all calculations. The final R_1 was 0.0532 ($I > 2\sigma(I)$) and wR_2 was 0.1685 (all data).

Table 1. Crystal data and structure refinement for 2g.

Identification code	**2g**
Empirical formula	$C_{10}H_7NO_2S$
Formula weight	205.23
Temperature/K	100.01(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	6.9853(19)
b/Å	8.3741(16)
c/Å	14.638(3)
α/°	90
β/°	99.28(2)
γ/°	90

Volume/Å^3	845.1(3)
Z	4
ρ_{calc}g/cm^3	1.613
μ/mm^{-1}	0.348
F(000)	424.0
Crystal size/mm^3	0.13 × 0.12 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.622 to 50
Index ranges	$-6 \leq h \leq 8$, $-9 \leq k \leq 9$, $-15 \leq l \leq 17$
Reflections collected	3223
Independent reflections	1438 [R_{int} = 0.0434, R_{sigma} = 0.0530]
Data/restraints/parameters	1438/0/127
Goodness-of-fit on F^2	1.069
Final R indexes [I>=2σ (I)]	R_1 = 0.0532, wR_2 = 0.1579
Final R indexes [all data]	R_1 = 0.0646, wR_2 = 0.1685
Largest diff. peak/hole / e Å^{-3}	0.44/-0.44

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

Atom	*x*	*y*	*z*	U(eq)
S(1)	1622.3(12)	9144.0(11)	4455.3(6)	27.1(4)

O(2)	10464(3)	4518(3)	6344.1(16)	26.2(6)
O(1)	9387(3)	3591(3)	7664.7(15)	27.7(6)
N(1)	3460(4)	9015(3)	3914.6(19)	24.4(7)
C(5)	7516(5)	6038(4)	5741(2)	19.2(8)
C(4)	5663(4)	6474(4)	5921(2)	17.6(7)
C(1)	7993(5)	4539(4)	7158(2)	20.1(8)
C(6)	8616(5)	5088(4)	6370(2)	20.7(8)
C(3)	5070(5)	5924(4)	6732(2)	21.0(8)
C(2)	6211(5)	4943(4)	7363(2)	23.0(8)
C(9)	2560(5)	7989(4)	5360(2)	23.3(8)
C(8)	4381(5)	7478(4)	5268(2)	18.7(7)
C(10)	4818(5)	8104(4)	4424(2)	22.3(8)
C(7)	10989(5)	3628(4)	7179(2)	26.8(8)

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

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S(1)	22.8(6)	32.9(6)	25.1(6)	1.5(4)	2.9(4)	2.8(4)
O(2)	17.9(13)	39.0(15)	22.6(12)	7.3(10)	6.1(10)	6.4(10)
O(1)	22.1(13)	37.4(15)	24.2(13)	10.5(11)	5.2(11)	6.7(11)
N(1)	34.6(18)	23.1(16)	16.3(14)	1.2(11)	6.6(13)	-4.2(13)
C(5)	19.2(18)	24.4(18)	14.6(16)	-0.4(13)	4.5(14)	-3.2(13)
C(4)	17.3(17)	18.3(16)	17.3(16)	-4.7(13)	2.9(13)	-4.0(13)

C(1)	20.5(18)	21.3(17)	17.8(16)	0.6(13)	0.5(14)	-3.4(13)
C(6)	18.7(18)	24.5(18)	19.4(17)	-6.0(14)	5.0(14)	-4.5(14)
C(3)	20.5(18)	23.1(18)	20.4(17)	-1.1(13)	6.1(14)	-0.3(13)
C(2)	27(2)	25.7(18)	18.0(17)	-1.2(14)	8.6(15)	-4.6(15)
C(9)	23.4(19)	28.6(19)	18.5(17)	-0.7(14)	5.2(15)	-1.6(14)
C(8)	16.4(17)	20.2(17)	19.2(16)	-5.8(13)	2.0(13)	-5.4(13)
C(10)	21.5(18)	23.9(18)	22.1(17)	-0.3(14)	5.5(14)	2.4(14)
C(7)	22.3(19)	34(2)	24.0(18)	6.5(16)	2.6(15)	2.0(16)

Table 4. Bond Lengths for 2g.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S(1)	N(1)	1.617(3)	C(5)	C(6)	1.358(5)
S(1)	C(9)	1.685(3)	C(4)	C(3)	1.397(4)
O(2)	C(6)	1.382(4)	C(4)	C(8)	1.465(4)
O(2)	C(7)	1.428(4)	C(1)	C(6)	1.375(4)
O(1)	C(1)	1.377(4)	C(1)	C(2)	1.370(5)
O(1)	C(7)	1.420(4)	C(3)	C(2)	1.388(5)
N(1)	C(10)	1.345(4)	C(9)	C(8)	1.369(4)
C(5)	C(4)	1.410(4)	C(8)	C(10)	1.420(4)

Table 5. Bond Angles for 2g.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N(1)	S(1)	C(9)	96.18(15)	C(5)	C(6)	O(2)	127.8(3)

C(6)	O(2)	C(7)	105.6(2)	C(5)	C(6)	C(1)	122.9(3)
C(1)	O(1)	C(7)	105.3(2)	C(1)	C(6)	O(2)	109.3(3)
C(10)	N(1)	S(1)	108.1(2)	C(2)	C(3)	C(4)	123.0(3)
C(6)	C(5)	C(4)	117.5(3)	C(1)	C(2)	C(3)	116.4(3)
C(5)	C(4)	C(8)	120.7(3)	C(8)	C(9)	S(1)	110.6(2)
C(3)	C(4)	C(5)	118.7(3)	C(9)	C(8)	C(4)	126.5(3)
C(3)	C(4)	C(8)	120.7(3)	C(9)	C(8)	C(10)	107.7(3)
C(6)	C(1)	O(1)	110.6(3)	C(10)	C(8)	C(4)	125.8(3)
C(2)	C(1)	O(1)	127.8(3)	N(1)	C(10)	C(8)	117.4(3)
C(2)	C(1)	C(6)	121.5(3)	O(1)	C(7)	O(2)	109.0(3)

Table 6. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 2g.

Atom	***x***	***y***	***z***	**U(eq)**
H(5)	7967.84	6388.32	5211.85	23
H(3)	3856.81	6229.47	6854.16	25
H(2)	5787.35	4579.69	7896.64	28
H(9)	1928.76	7733.88	5853.63	28
H(10)	5996.59	7891.99	4230.17	27
H(7A)	11345.87	2547.99	7034.62	32
H(7B)	12095.48	4121.66	7560.13	32

(G) X-ray Crystallographic Data of 2x

The X-ray crystallographic structures for **2x**. ORTEP representation with 50% probability thermal ellipsoids. Solvent and hydrogen are omitted for clarity. Solvent and hydrogen are omitted for clarity. Crystal data have been deposited to CCDC, number 1978413.

Crystal structure determination of 2x

Crystal Data for $C_{12}H_8N_2S_2$ (M = 244.32 g/mol): orthorhombic, space group Pbca (no. 61), a = 6.0865(10) Å, b = 17.576(4) Å, c = 20.351(3) Å, V = 2177.1(7)Å^3, Z = 8, T = 100.00(10) K, μ(MoKα) = 0.458 mm^{-1}, $Dcalc$ = 1.491 g/cm^3, 8203 reflections measured (4.634 ≤ 2Θ ≤ 49.998), 1914 unique (R_{int} = 0.0825, R_{sigma} = 0.0694) which were used in all calculations. The final R_1 was 0.0701 (I > 2σ(I)) and wR_2 was 0.1832 (all data).

Table 7. Crystal data and structure refinement for 2x.

Identification code	**2x**
Empirical formula	$C_{12}H_8N_2S_2$
Formula weight	244.32
Temperature/K	100.00(10)
Crystal system	orthorhombic
Space group	Pbca
a/Å	6.0865(10)
b/Å	17.576(4)
c/Å	20.351(3)
α/°	90
β/°	90

γ/°	90
Volume/Å^3	2177.1(7)
Z	8
ρ_{calc}g/cm^3	1.491
μ/mm^{-1}	0.458
F(000)	1008.0
Crystal size/mm^3	0.13 × 0.12 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.634 to 49.998
Index ranges	-5 ≤ h ≤ 7, -19 ≤ k ≤ 20, -23 ≤ l ≤ 23
Reflections collected	8203
Independent reflections	1914 [R_{int} = 0.0825, R_{sigma} = 0.0694]
Data/restraints/parameters	1914/0/145
Goodness-of-fit on F^2	1.022
Final R indexes [I>=2σ (I)]	R_1 = 0.0701, wR_2 = 0.1640
Final R indexes [all data]	R_1 = 0.0960, wR_2 = 0.1832
Largest diff. peak/hole / e Å^{-3}	0.61/-0.46

Table 8. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 2x. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
S(1)	-3708.1(19)	4214.0(7)	4993.7(5)	24.3(4)

S(2)	9042(2)	1515.6(7)	6830.5(6)	30.1(4)
N(1)	-2868(6)	3330(2)	4921.6(17)	25.7(9)
N(2)	6773(7)	1172(2)	6487.3(18)	30.0(10)
C(1)	-361(7)	3871(2)	5655.3(19)	20.0(10)
C(10)	6073(7)	2483(2)	6611(2)	21.3(10)
C(4)	1594(7)	3859(2)	6095.8(19)	18.7(10)
C(9)	2874(7)	3211(2)	6153.0(19)	20.7(10)
C(8)	4729(7)	3183(2)	6556.1(19)	19.5(10)
C(6)	4024(7)	4494(3)	6858(2)	22.9(10)
C(5)	2176(7)	4511(2)	6458(2)	22.5(10)
C(11)	8151(8)	2421(3)	6870(2)	25.0(11)
C(12)	5383(8)	1739(3)	6405(2)	26.5(11)
C(3)	-1099(7)	3226(3)	5287(2)	24.9(11)
C(7)	5299(8)	3843(2)	6907(2)	23.0(11)
C(2)	-1714(7)	4479(2)	5535(2)	22.9(10)

Table 9. Anisotropic Displacement Parameters ($Å^2×10^3$) for 2x. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S(1)	28.4(7)	26.2(7)	18.2(6)	-0.2(5)	-1.9(5)	2.5(5)
S(2)	32.3(7)	32.0(8)	25.9(7)	0.1(5)	-5.3(5)	3.7(5)
N(1)	29(2)	30(2)	19(2)	-2.0(16)	-1.0(17)	2.6(18)
N(2)	37(2)	32(2)	21(2)	-3.7(17)	-3.5(19)	6.9(19)

C(1)	29(2)	21(2)	10(2)	-1.0(17)	7.1(18)	-3.5(19)
C(10)	30(3)	28(3)	6(2)	1.9(17)	5(2)	-5(2)
C(4)	24(2)	23(2)	9(2)	2.4(17)	4.4(18)	-2.4(19)
C(9)	30(2)	22(3)	10(2)	-0.9(17)	5.4(19)	-3(2)
C(8)	25(2)	24(3)	9(2)	0.7(18)	1.5(18)	-0.6(19)
C(6)	32(3)	24(3)	13(2)	-1.7(18)	3(2)	-8(2)
C(5)	33(3)	23(2)	11(2)	-0.7(18)	1(2)	-1(2)
C(11)	34(3)	28(3)	13(2)	-0.7(18)	0(2)	-3(2)
C(12)	28(3)	34(3)	17(2)	-2(2)	-2(2)	0(2)
C(3)	30(3)	27(3)	18(2)	0(2)	0(2)	6(2)
C(7)	30(3)	28(3)	11(2)	1.0(18)	-0.5(19)	-4(2)
C(2)	29(3)	25(3)	15(2)	-5.0(18)	1(2)	2(2)

Table 10. Bond Lengths for 2x.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S(1)	N(1)	1.642(4)	C(10)	C(8)	1.481(6)
S(1)	C(2)	1.703(4)	C(10)	C(11)	1.375(6)
S(2)	N(2)	1.661(4)	C(10)	C(12)	1.436(6)
S(2)	C(11)	1.683(5)	C(4)	C(9)	1.385(6)
N(1)	C(3)	1.322(5)	C(4)	C(5)	1.406(6)
N(2)	C(12)	1.318(6)	C(9)	C(8)	1.396(6)
C(1)	C(4)	1.490(6)	C(8)	C(7)	1.407(6)
C(1)	C(3)	1.431(6)	C(6)	C(5)	1.389(6)

C(1)	C(2)	1.370(6)	C(6)	C(7)	1.385(6)		

Table 11. Bond Angles for 2x.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N(1)	S(1)	C(2)	95.4(2)	C(5)	C(4)	C(1)	120.3(4)
N(2)	S(2)	C(11)	95.5(2)	C(4)	C(9)	C(8)	122.2(4)
C(3)	N(1)	S(1)	109.6(3)	C(9)	C(8)	C(10)	121.3(4)
C(12)	N(2)	S(2)	108.2(3)	C(9)	C(8)	C(7)	117.9(4)
C(3)	C(1)	C(4)	123.6(4)	C(7)	C(8)	C(10)	120.7(4)
C(2)	C(1)	C(4)	126.8(4)	C(5)	C(6)	C(7)	120.9(4)
C(2)	C(1)	C(3)	109.6(4)	C(6)	C(5)	C(4)	119.6(4)
C(11)	C(10)	C(8)	127.1(4)	C(10)	C(11)	S(2)	110.7(3)
C(11)	C(10)	C(12)	108.0(4)	N(2)	C(12)	C(10)	117.6(4)
C(12)	C(10)	C(8)	124.9(4)	N(1)	C(3)	C(1)	116.1(4)
C(9)	C(4)	C(1)	120.8(4)	C(6)	C(7)	C(8)	120.4(4)
C(9)	C(4)	C(5)	118.9(4)	C(1)	C(2)	S(1)	109.3(3)

Table 12. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 2x.

Atom	*x*	*y*	*z*	U(eq)
H(9)	2485.09	2780.04	5914.83	25
H(6)	4411.37	4925.23	7095.49	27
H(5)	1328.47	4949.63	6429.28	27

H(11)	8953.88	2823.84	7043.41	30
H(12)	4004.96	1660.21	6219.69	32
H(3)	-375.62	2760.05	5304.95	30
H(7)	6538.28	3843.33	7174.5	28
H(2)	-1566.72	4959.87	5719.37	28

(H) X-ray Crystallographic Data of 3k

The X-ray crystallographic structures for **3k**. ORTEP representation with 50% probability thermal ellipsoids. Solvent and hydrogen are omitted for clarity. Solvent and hydrogen are omitted for clarity. Crystal data have been deposited to CCDC, number 1978414.

Crystal structure determination of 3k

Crystal Data for $C_{18}H_{12}N_2S_2$ (M =320.42 g/mol): monoclinic, space group I2 (no. 5), a = 7.8212(6) Å, b = 5.9264(4)Å, c = 16.1736(11)Å, β = 91.155(7), V = 749.52(9)Å^3, Z = 2, T = 100.00(10)K, μ(MoKα) = 0.352 mm^{-1}, *Dcalc* = 1.420 g/cm^3, 3560 reflections measured ($5.038 \leq 2\Theta \leq 58.226$), 1748 unique ($R_{int}$ = 0.0275, R_{sigma} = 0.0449) which were used in all calculations. The final R_1 was 0.0352 ($I > 2\sigma(I)$) and wR_2 was 0.0822 (all data).

Table 13. Crystal data and structure refinement for 3k.

Identification code	**3k**
Empirical formula	$C_{18}H_{12}N_2S_2$
Formula weight	320.42
Temperature/K	100.00(10)

Crystal system	monoclinic
Space group	I2
a/Å	7.8212(6)
b/Å	5.9264(4)
c/Å	16.1736(11)
α/°	90
β/°	91.155(7)
γ/°	90
Volume/Å^3	749.52(9)
Z	2
ρ_{calc}g/cm^3	1.420
μ/mm^{-1}	0.352
F(000)	332.0
Crystal size/mm^3	0.13 × 0.12 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.038 to 58.226
Index ranges	$-9 \leq h \leq 9$, $-7 \leq k \leq 7$, $-21 \leq l \leq 21$
Reflections collected	3560
Independent reflections	1748 [R_{int} = 0.0275, R_{sigma} = 0.0449]
Data/restraints/parameters	1748/1/100
Goodness-of-fit on F^2	1.047
Final R indexes [I>=2σ (I)]	R_1 = 0.0352, wR_2 = 0.0798
Final R indexes [all data]	R_1 = 0.0374, wR_2 = 0.0822

Largest diff. peak/hole / e Å^{-3}	0.27/-0.27
Flack parameter	0.03(6)

Table 14. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 3k. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
S1	7138.6(8)	776.3(12)	5577.5(4)	20.94(19)
N1	7570(3)	1689(4)	6526.7(14)	23.4(5)
C1	3920(3)	5662(5)	6221.5(13)	14.7(5)
C7	5236(3)	3913(5)	6088.1(16)	15.5(5)
C6	2252(3)	5448(5)	5910.7(16)	20.6(6)
C9	5469(3)	2599(4)	5400.0(15)	15.2(5)
C2	4326(4)	7563(4)	6700.3(15)	17.0(5)
C4	1467(4)	8992(5)	6524.8(17)	22.6(6)
C5	1040(4)	7089(5)	6062.4(17)	23.6(6)
C8	6489(4)	3310(5)	6705.6(16)	19.1(6)
C3	3111(4)	9203(5)	6849.9(17)	21.3(6)

Table 15. Anisotropic Displacement Parameters (Å^2×10^3) for 3k. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	23.6(4)	23.1(3)	16.2(3)	1.9(3)	0.7(2)	8.1(3)

N1	20.9(13)	32.2(13)	16.9(11)	3.6(10)	-3.4(9)	5.3(10)
C1	15.4(12)	16.9(12)	11.8(10)	2.3(13)	-0.5(8)	1.3(12)
C7	13.3(13)	18.3(12)	14.8(12)	2.1(10)	-2.2(10)	-2.0(10)
C6	20.2(14)	25.8(17)	15.5(11)	-3.8(12)	-4.8(10)	2.3(12)
C9	16.5(13)	15.6(12)	13.5(12)	2.0(10)	1.1(10)	-0.6(10)
C2	17.6(13)	19.5(13)	13.7(12)	1.7(10)	1.1(10)	-2.4(11)
C4	24.6(15)	24.9(15)	18.4(13)	3.4(12)	4.3(11)	8.9(12)
C5	16.8(14)	35.3(17)	18.7(14)	-0.7(13)	-2.6(11)	6.1(12)
C8	19.0(14)	25.5(15)	12.7(12)	0.8(11)	-3.1(11)	1.1(11)
C3	28.4(16)	17.5(13)	18.1(13)	-0.9(11)	5.6(11)	-1.8(12)

Table 16. Bond Lengths for 3k.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	N1	1.656(2)	C7	C8	1.431(4)
S1	C9	1.714(3)	C6	C5	1.384(4)
N1	C8	1.316(4)	C9	C9[1]	1.475(5)
C1	C7	1.479(4)	C2	C3	1.384(4)
C1	C6	1.395(4)	C4	C5	1.390(4)
C1	C2	1.400(4)	C4	C3	1.385(4)
C7	C9	1.374(4)			

Table 17. Bond Angles for 3k.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°

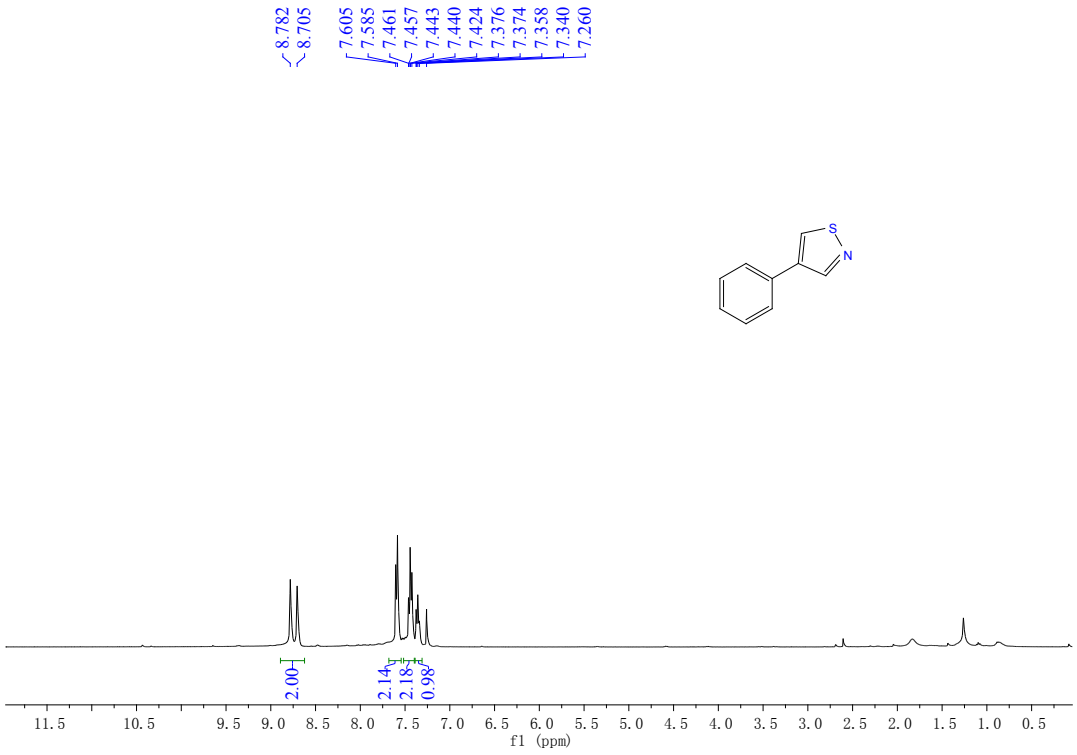
N1	S1	C9	95.15(12)	C7	C9	S1	109.6(2)
C8	N1	S1	108.8(2)	C7	C9	C9[1]	129.7(2)
C6	C1	C7	122.1(3)	C9[1]	C9	S1	120.73(18)
C6	C1	C2	118.2(3)	C3	C2	C1	120.9(3)
C2	C1	C7	119.6(2)	C3	C4	C5	119.3(3)
C9	C7	C1	128.3(2)	C6	C5	C4	120.5(3)
C9	C7	C8	108.9(2)	N1	C8	C7	117.6(2)
C8	C7	C1	122.8(2)	C4	C3	C2	120.4(3)
C5	C6	C1	120.8(3)				

Table 18. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3k.

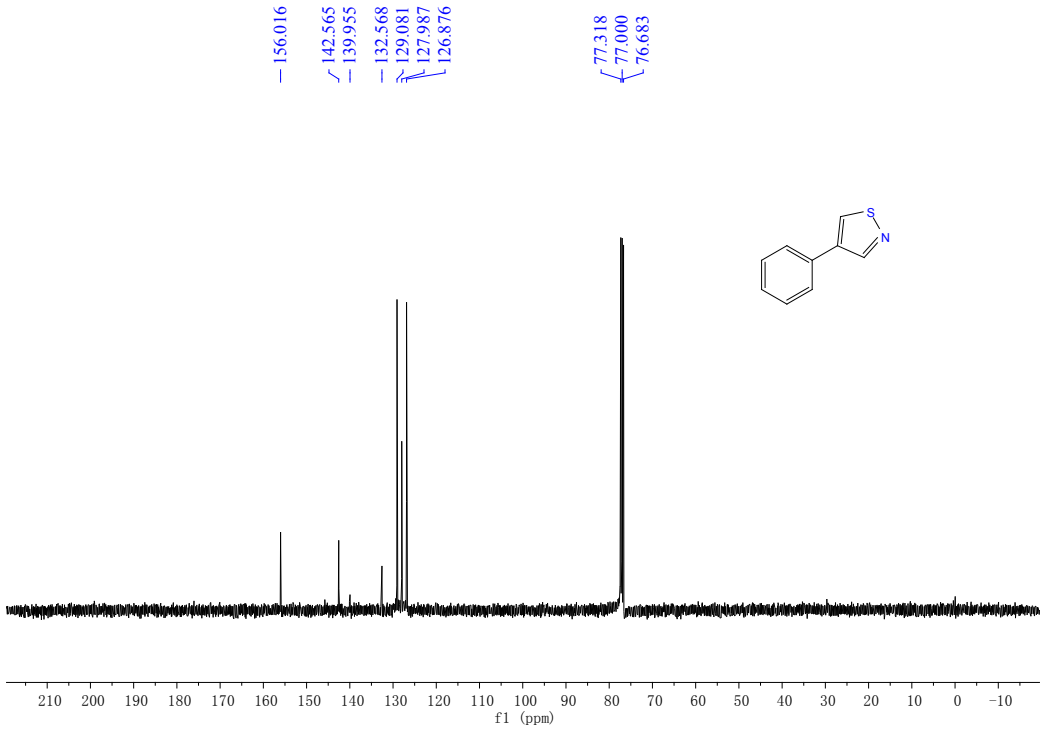
Atom	*x*	*y*	*z*	U(eq)
H6	1950.96	4187.56	5597.87	25
H2	5426.93	7725.82	6920.72	20
H4	658.28	10110.43	6614.87	27
H5	-69.13	6918.56	5853.4	28
H8	6538.06	4037.07	7215.05	23
H3	3400.01	10453.96	7170.49	26

(I) ^{1}H and ^{13}C NMR spectra data of all products

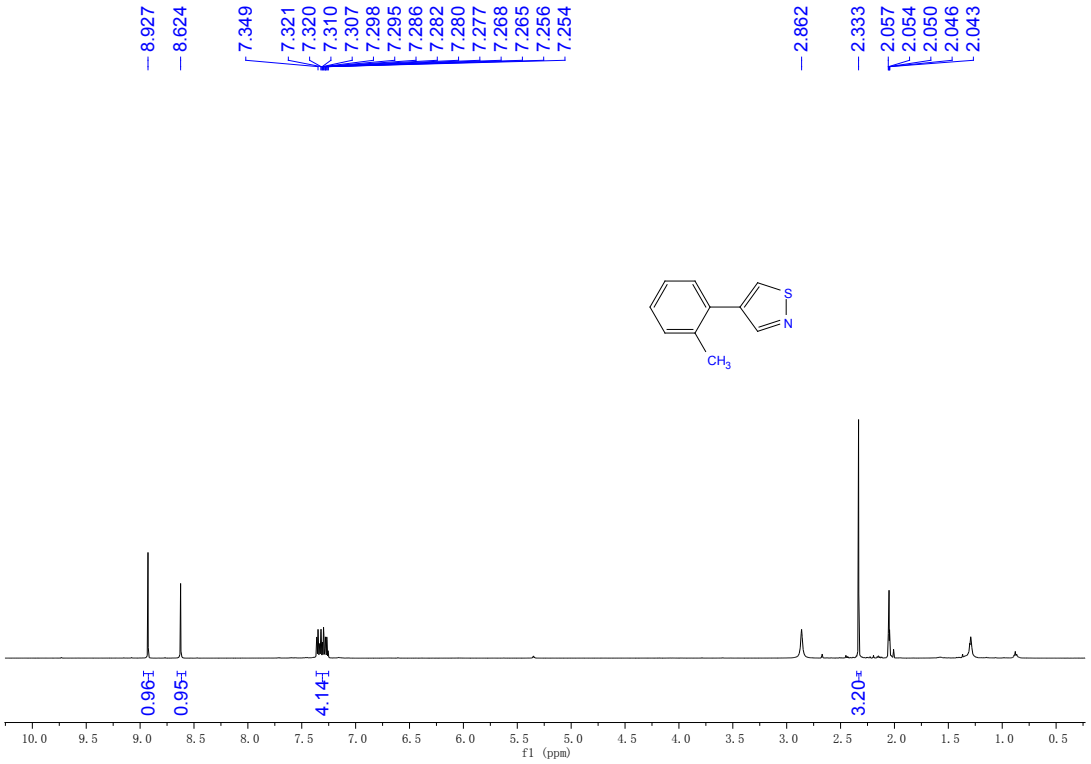
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 2a



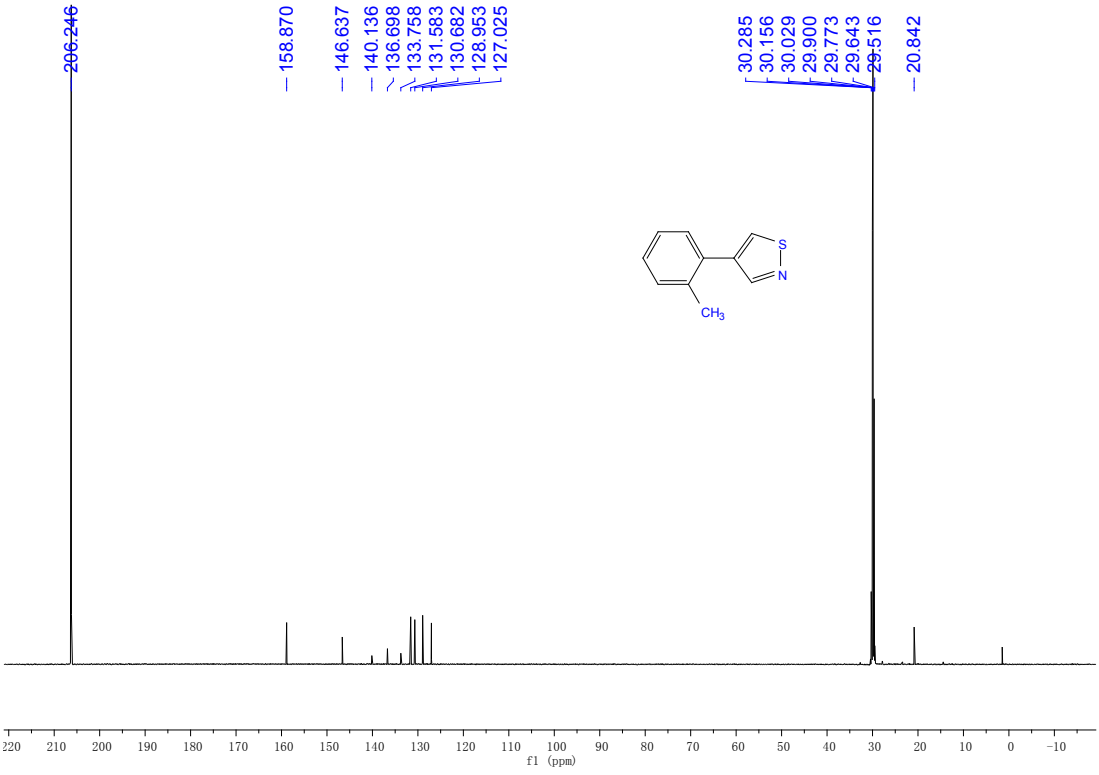
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 2a



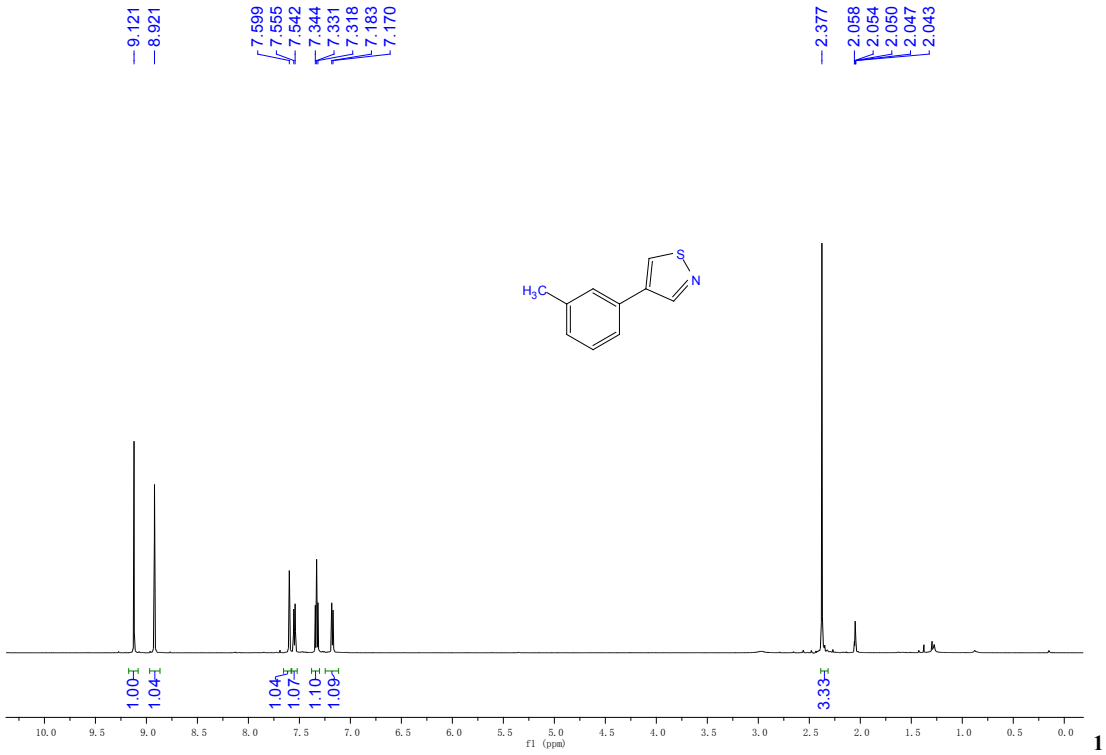
^{1}H NMR (600 MHz, Acetone-d_6) spectrum of compound 2b



^{13}C NMR (150 MHz, Acetone-d_6) spectrum of compound 2b



^{1}H NMR (600 MHz, Acetone-d_6) spectrum of compound 2c



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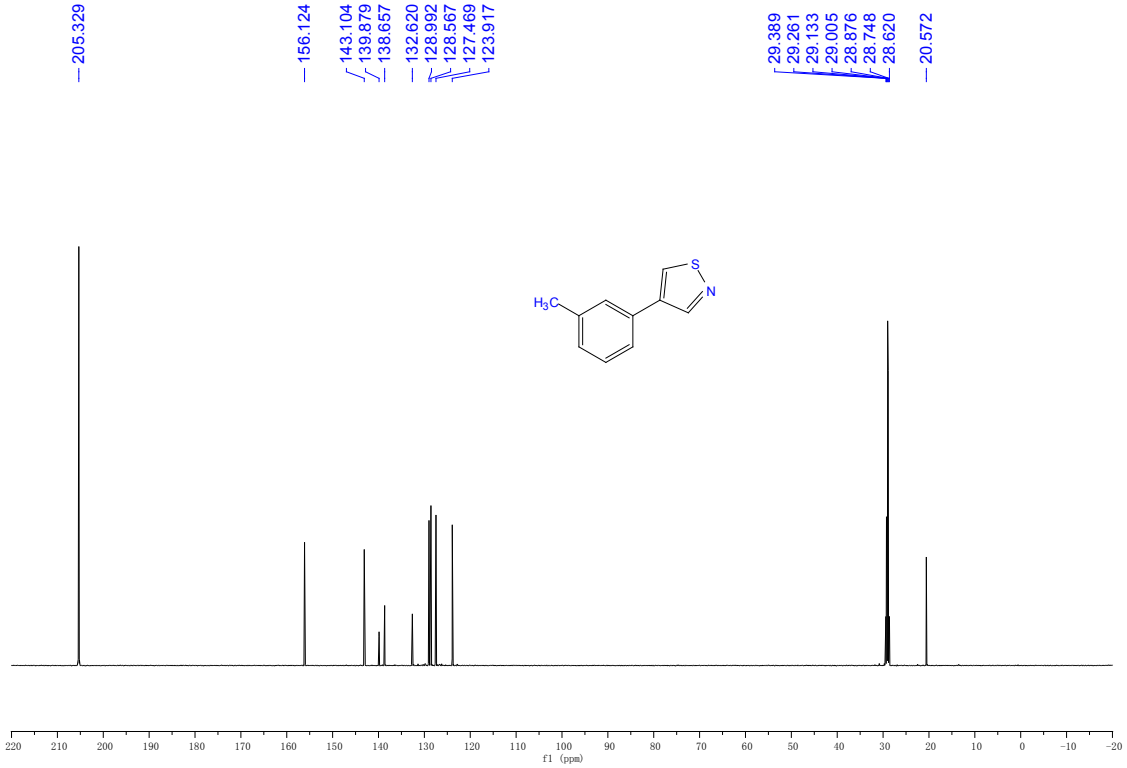
^{3}C NMR (150 MHz, Acetone-d_6) spectrum of compound 2c



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 2d

^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 2d

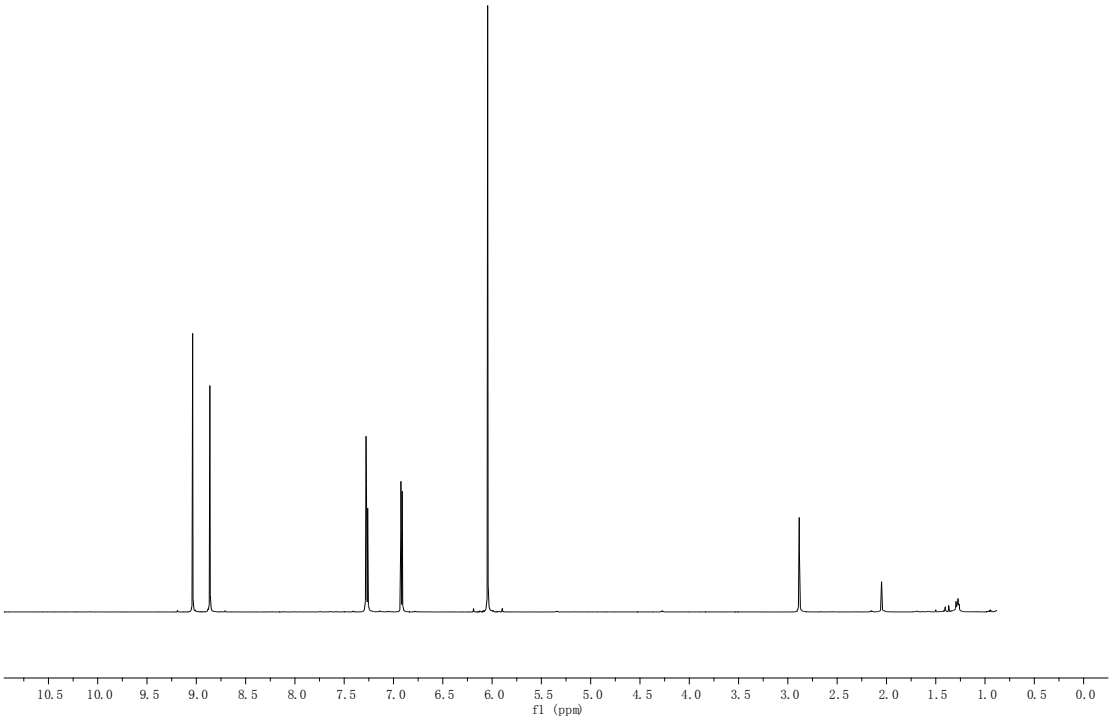
^{1}H NMR (600 MHz, Acetone-d_6) spectrum of compound 2e

^{13}C NMR (150 MHz, Acetone-d_6) spectrum of compound 2e

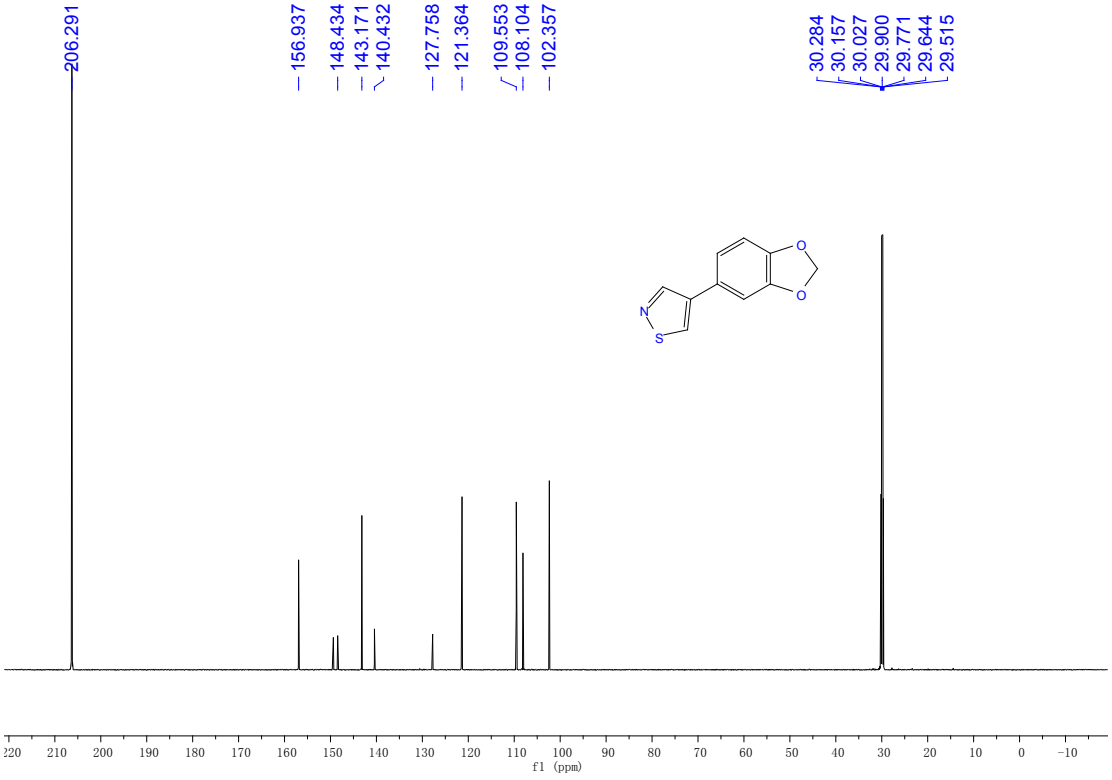
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 2f

^{13}C NMR (150 MHz, $CDCl_3$) spectrum of compound 2f

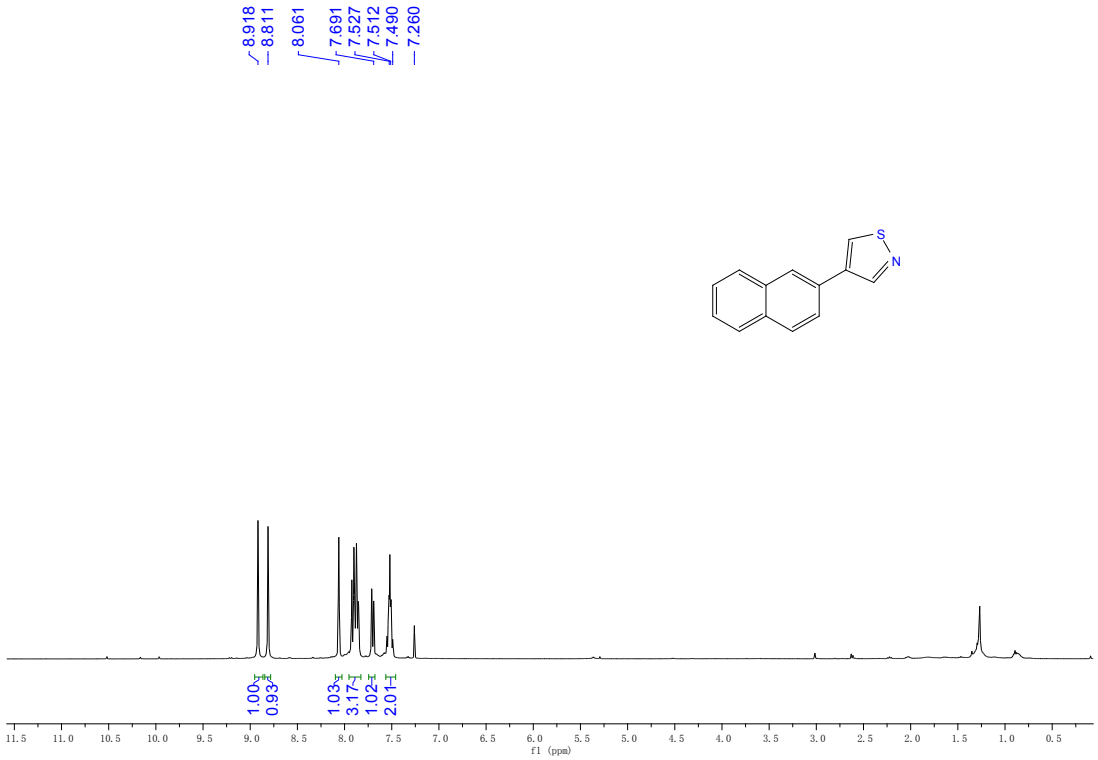
^{1}H NMR (600 MHz, Acetone-d_6) spectrum of compound 2g



^{13}C NMR (150 MHz, Acetone-d_6) spectrum of compound 2g

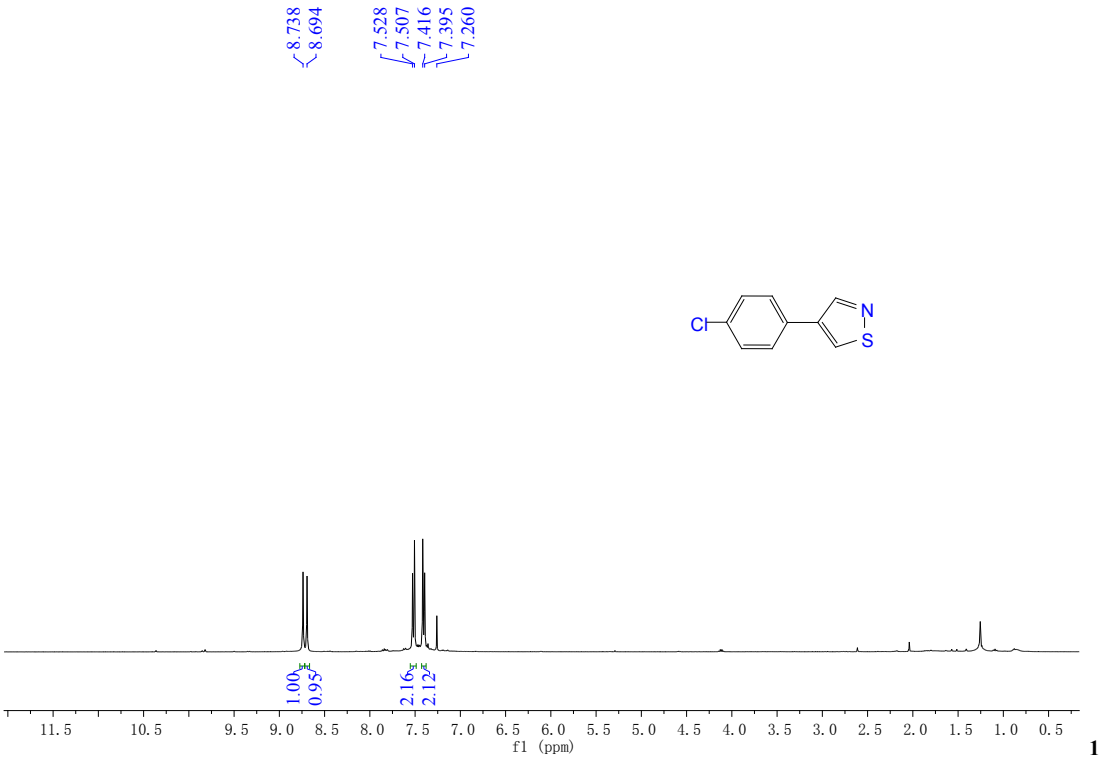


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 2h



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 2h

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 2i



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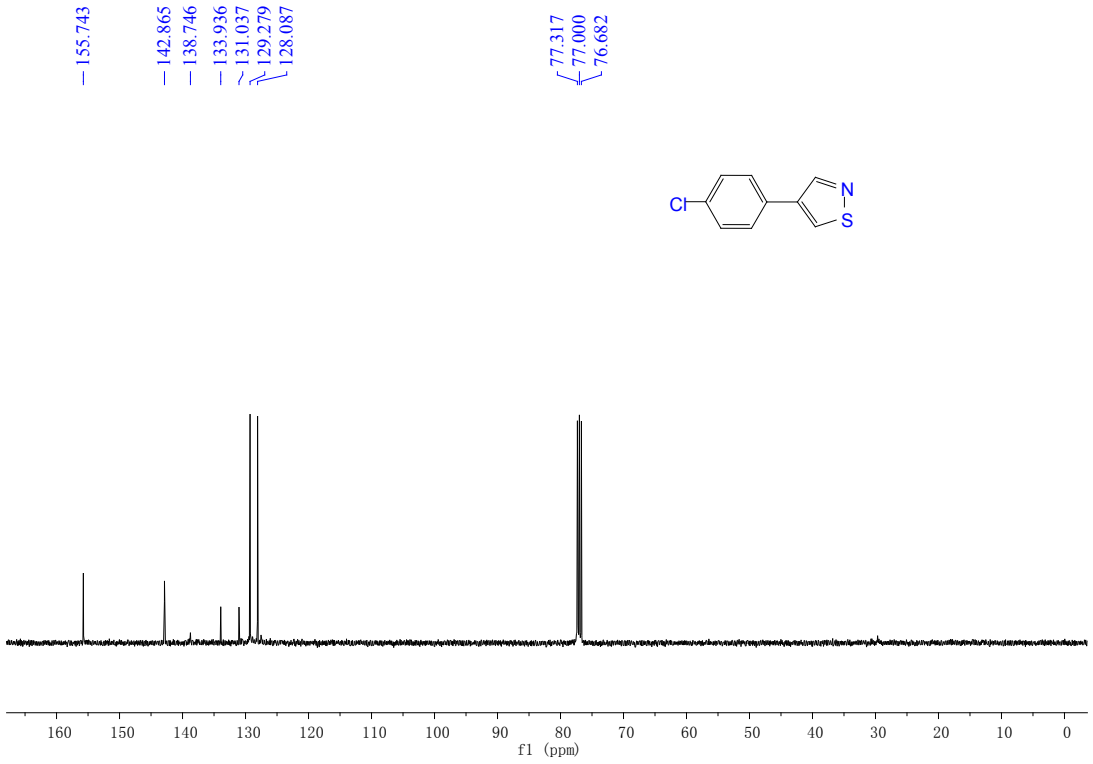
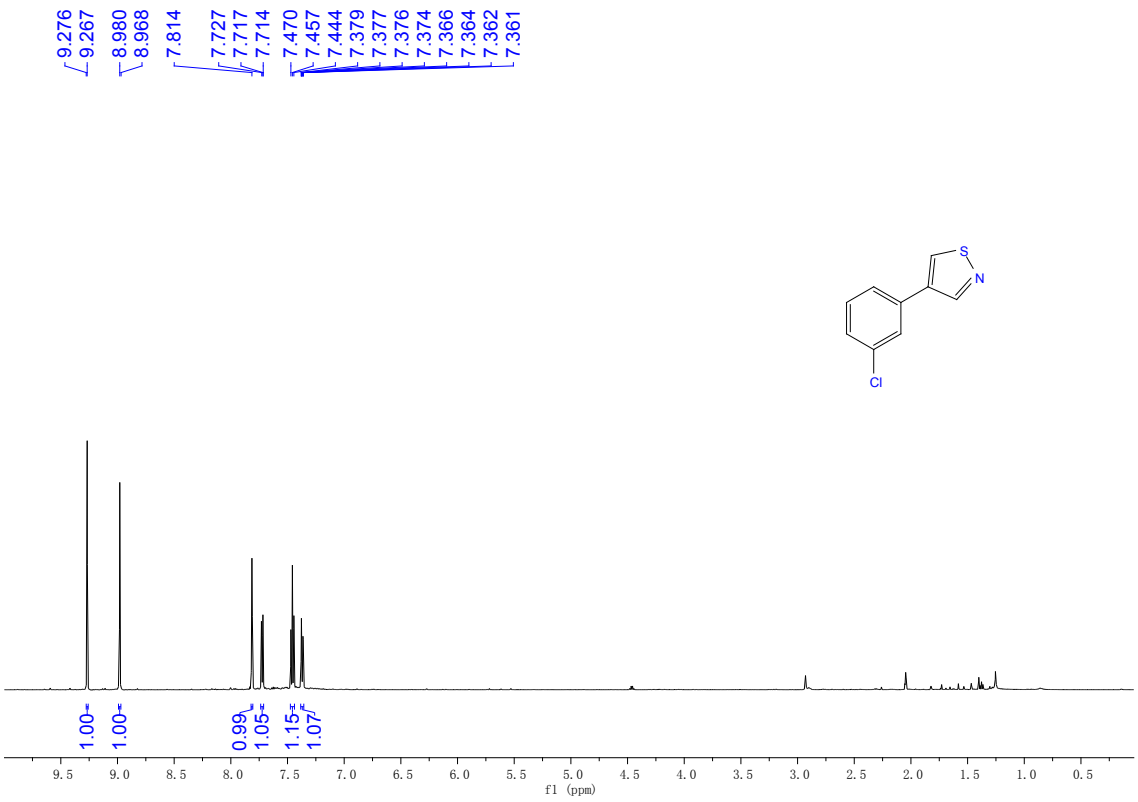
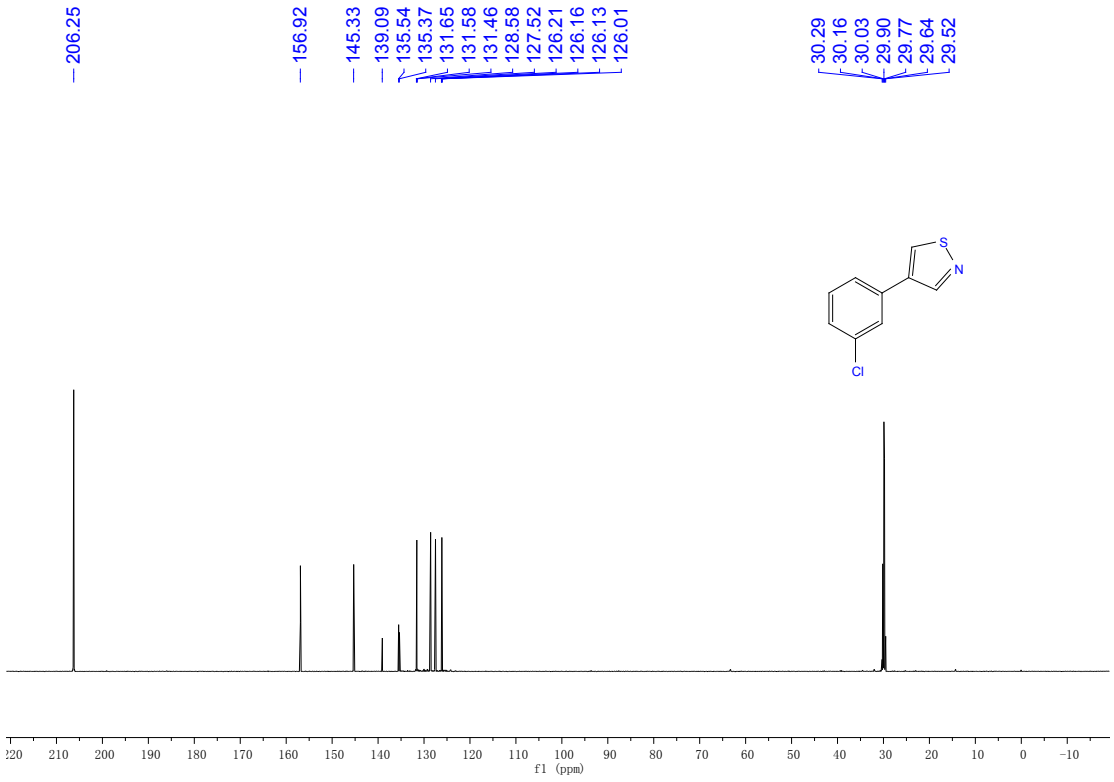
^{3}C NMR (100 MHz, $CDCl_3$) spectrum of compound 2i



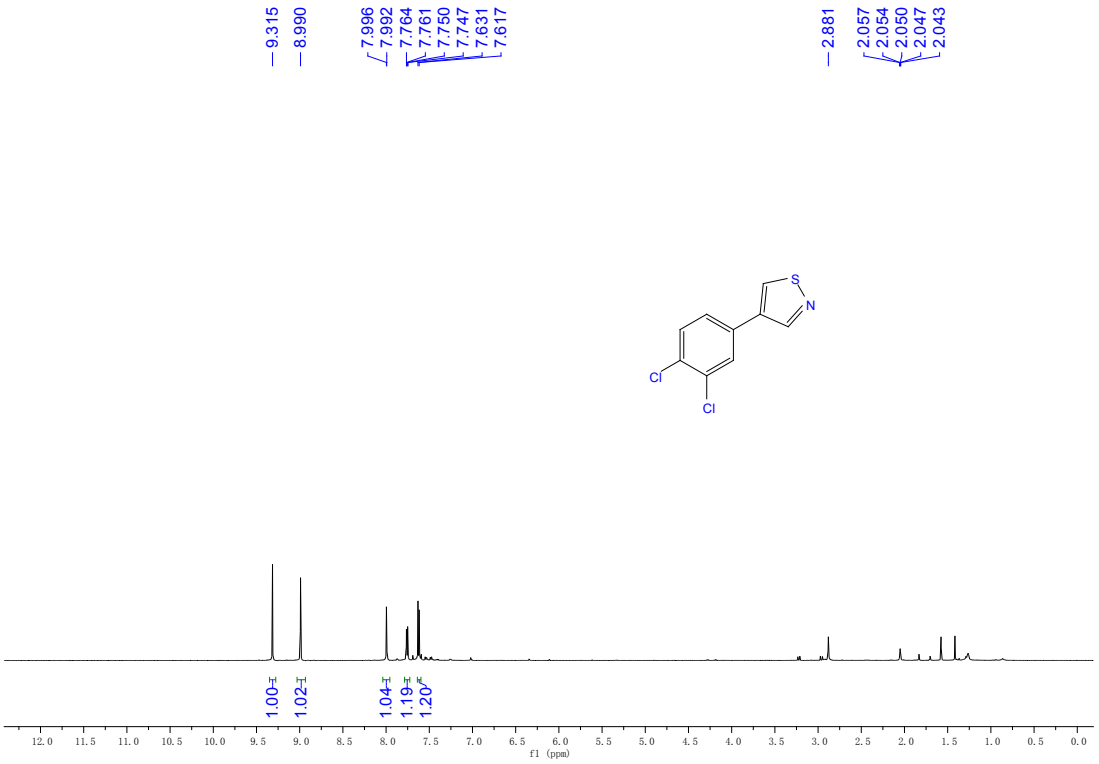
^{1}H NMR (600 MHz, Acetone-d_6) spectrum of compound 2j



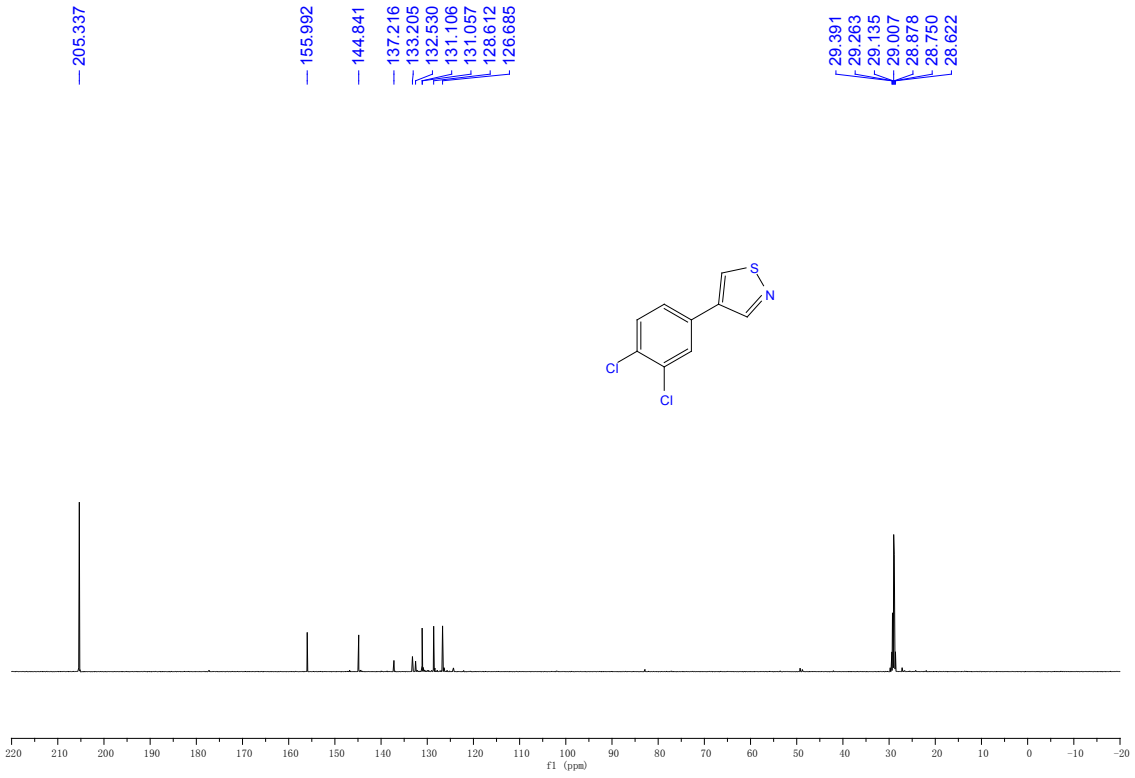
^{13}C NMR (150 MHz, Acetone-d_6) spectrum of compound 2j



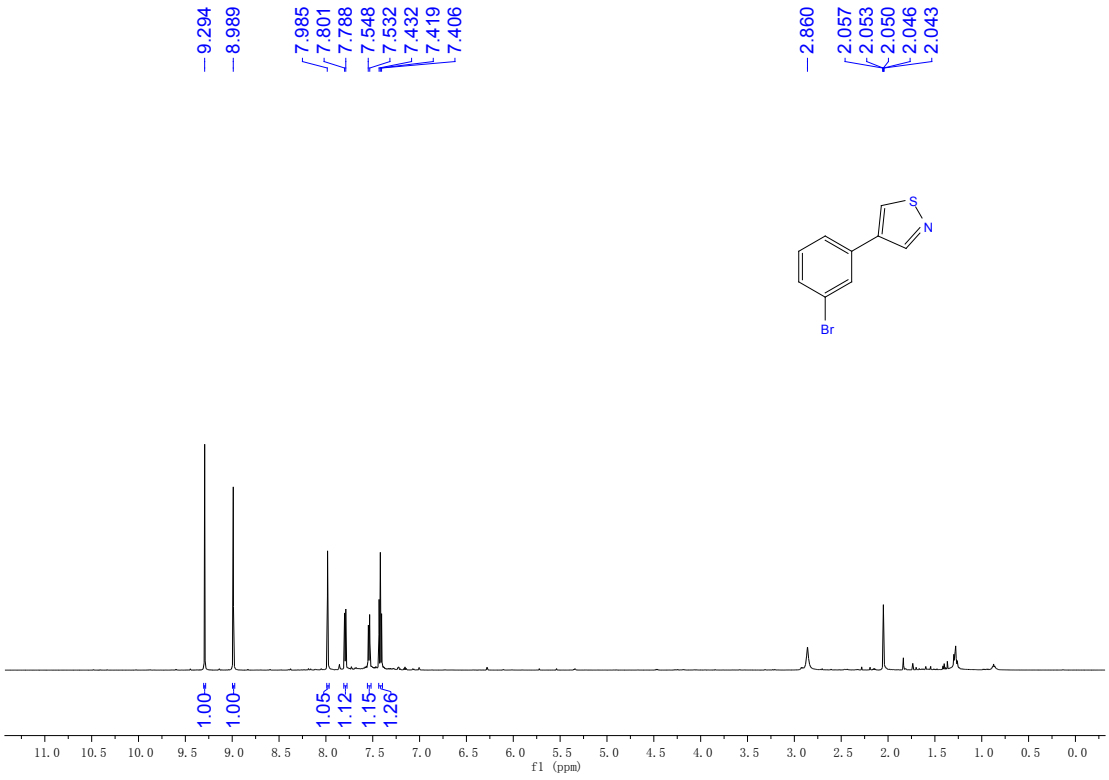
^{1}H NMR (600 MHz, Acetone-d_6) spectrum of compound 2k



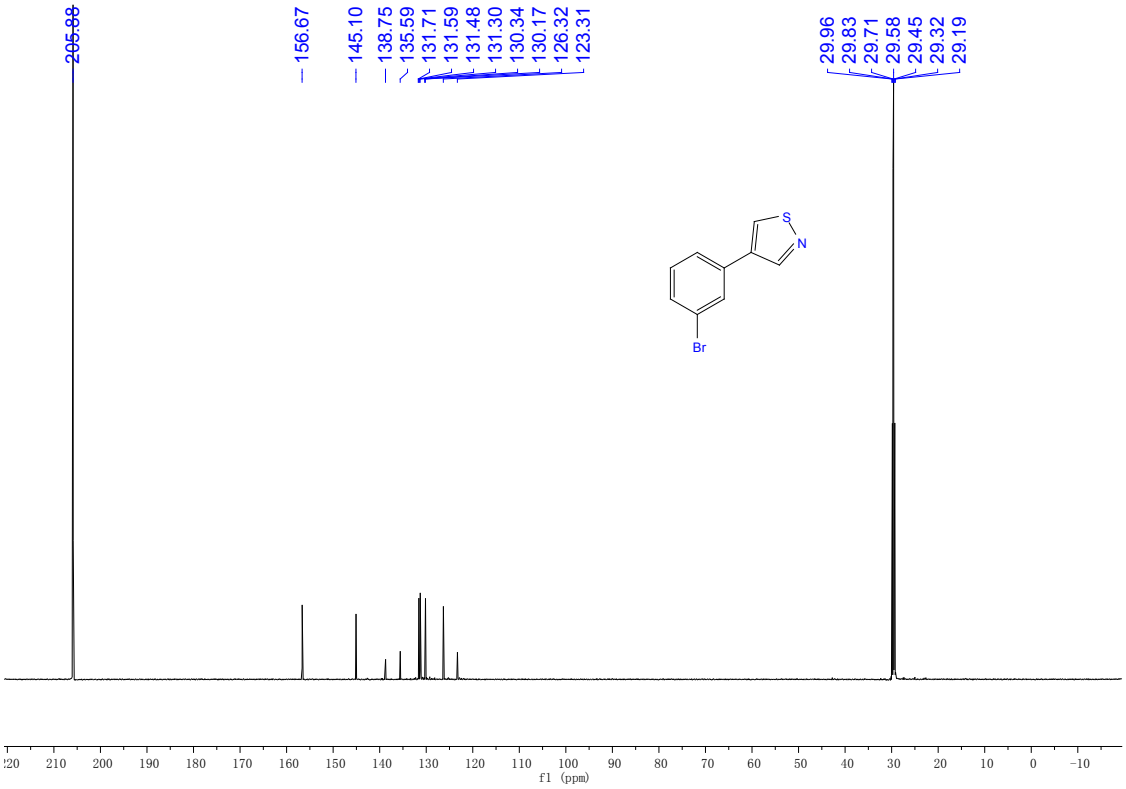
^{13}C NMR (150 MHz, Acetone-d_6) spectrum of compound 2k



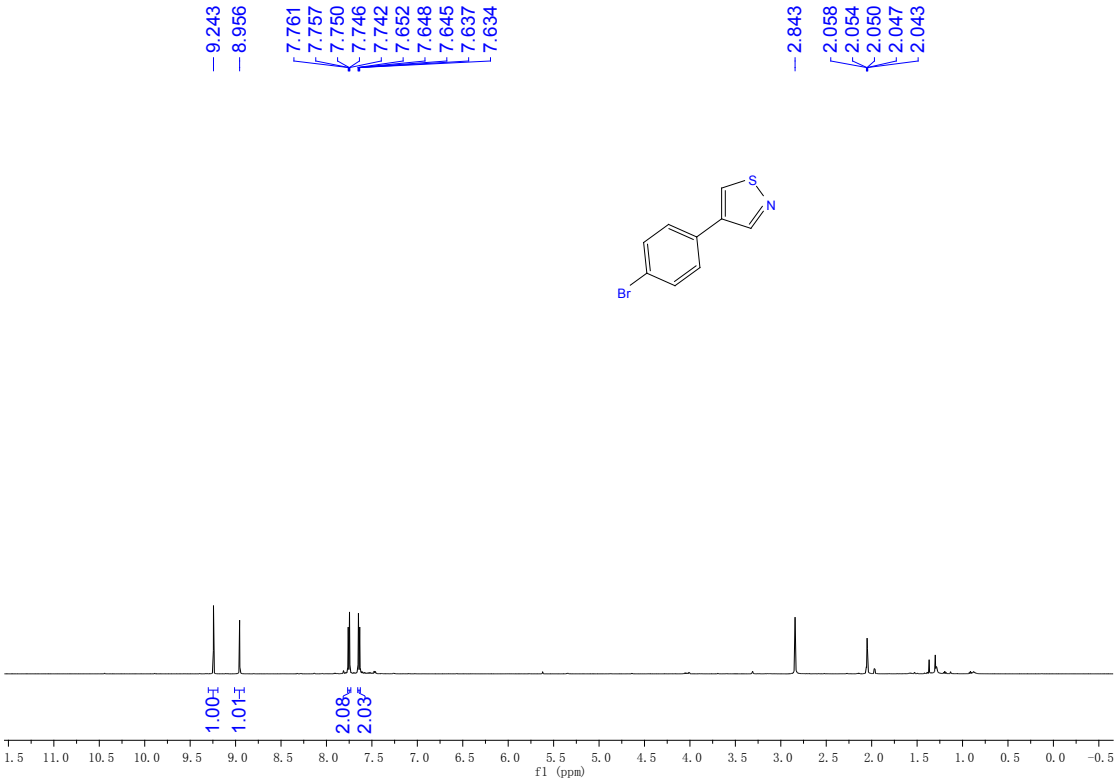
^{1}H NMR (600 MHz, Acetone-d_6) spectrum of compound 2l



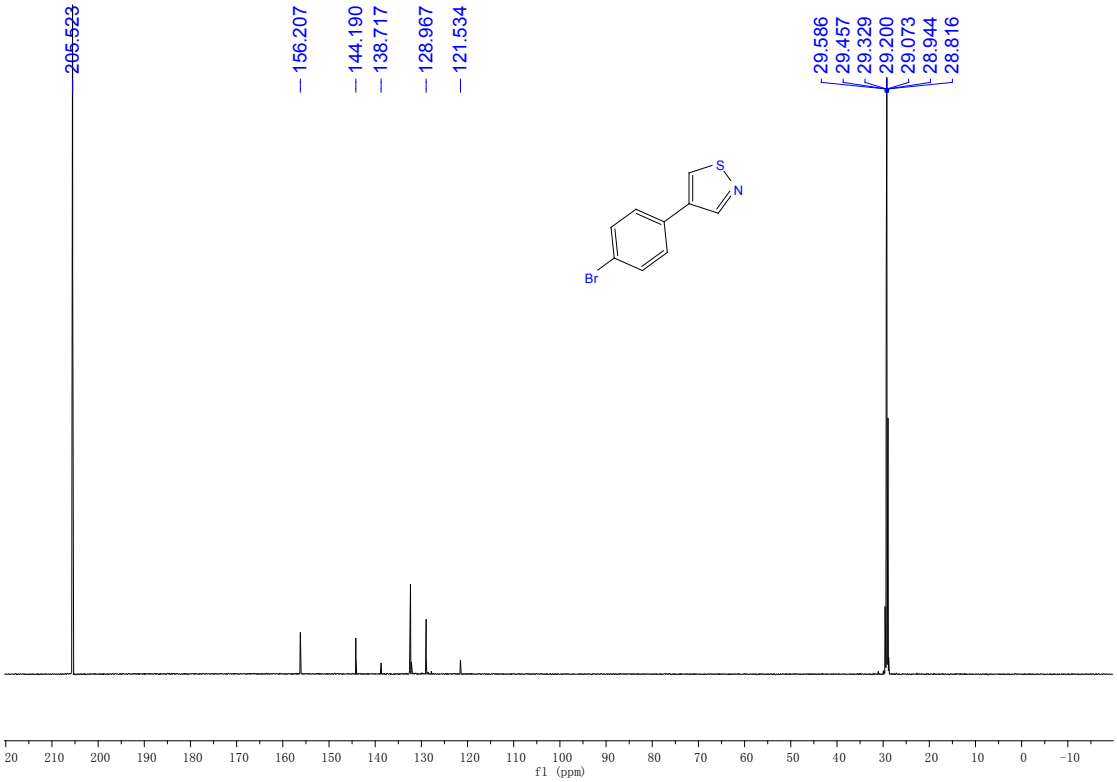
^{13}C NMR (150 MHz, Acetone-d_6) spectrum of compound 2l



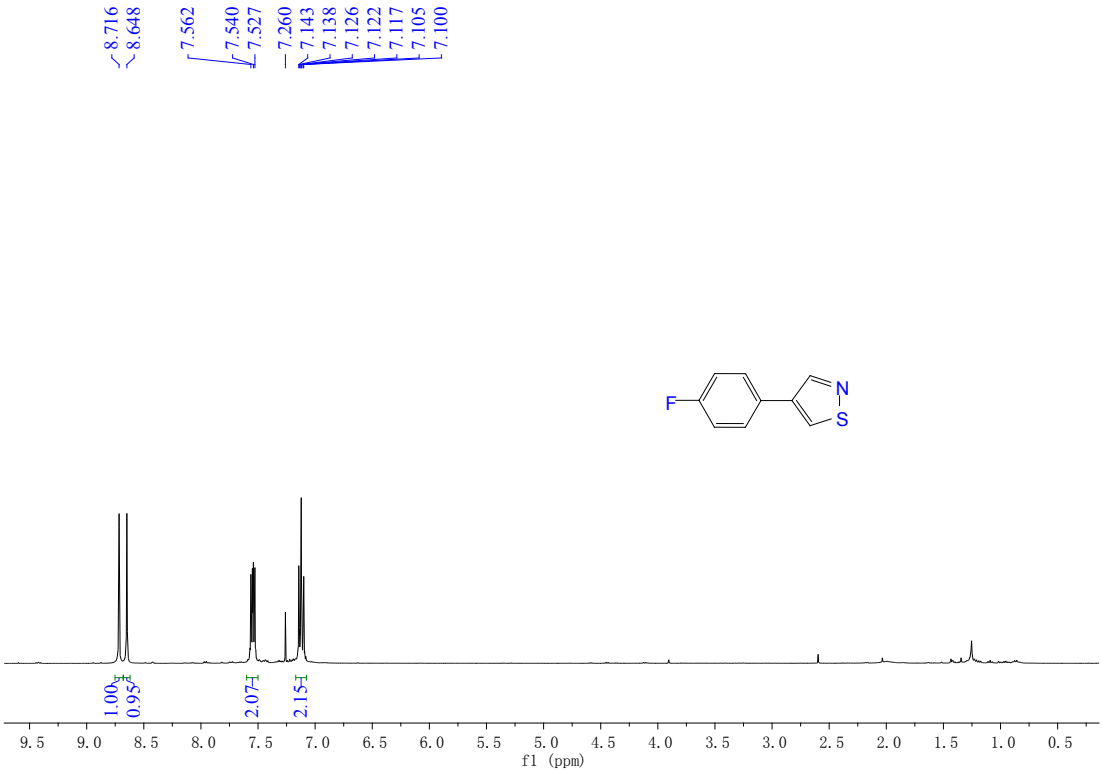
^{1}H NMR (600 MHz, Acetone-d_6) spectrum of compound 2m



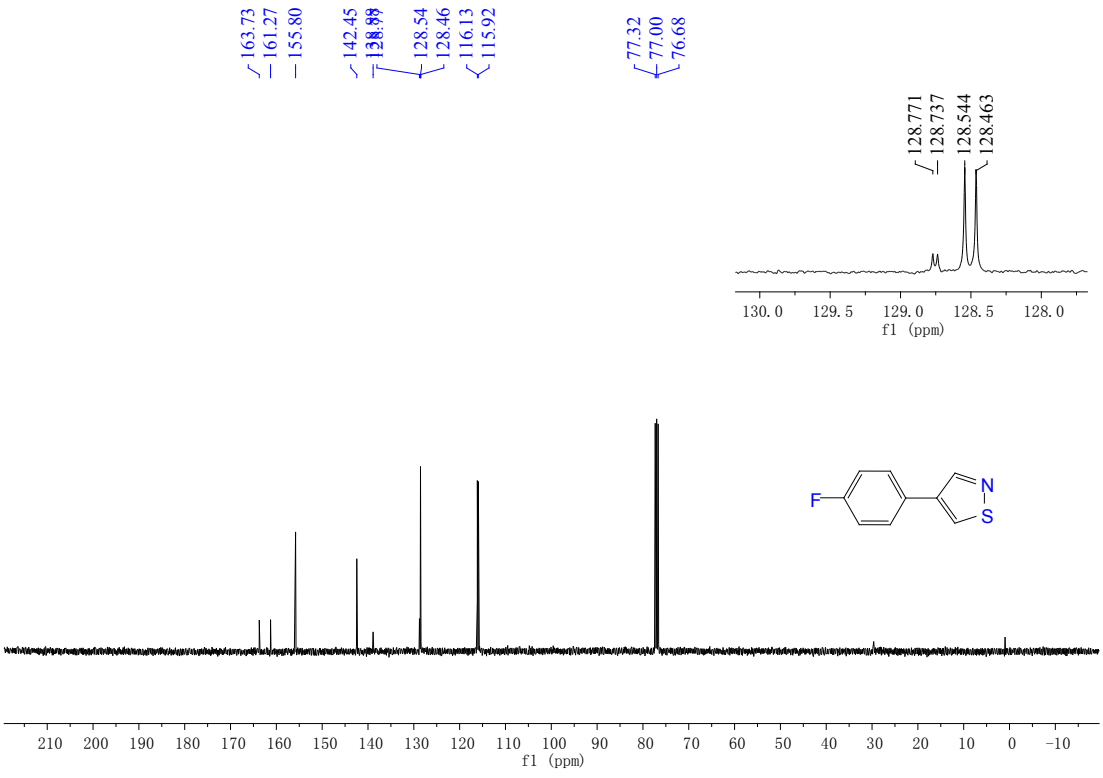
^{13}C NMR (150 MHz, Acetone-d_6) spectrum of compound 2m



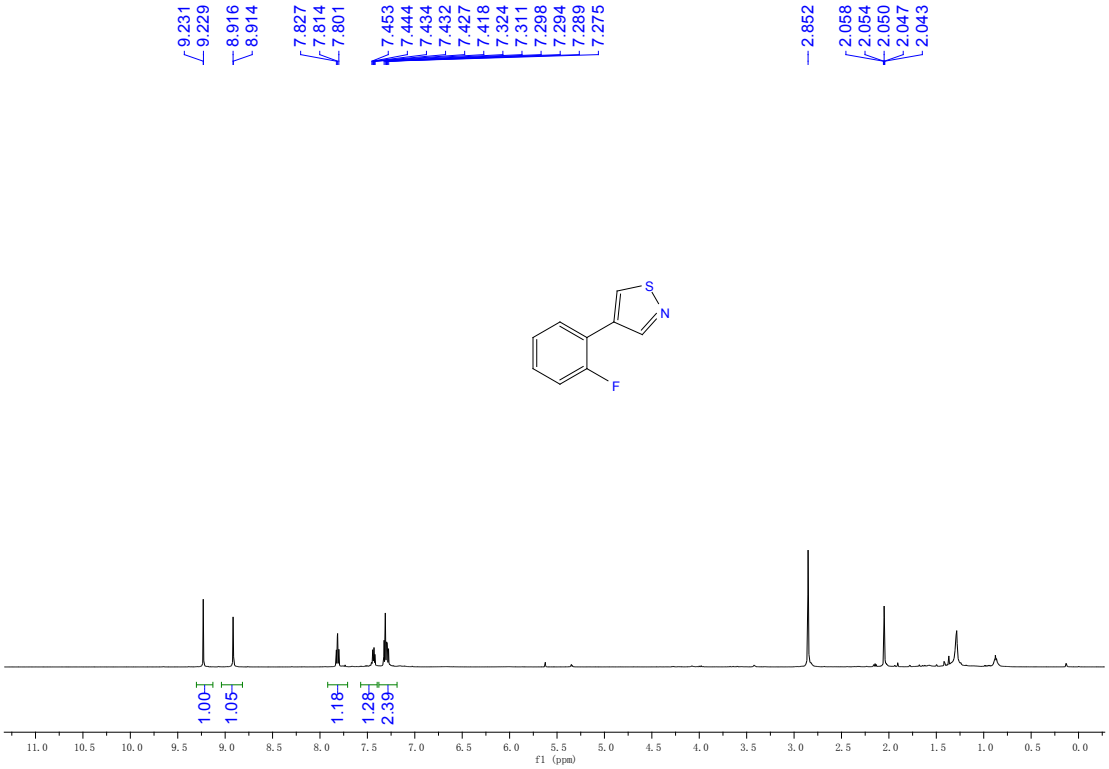
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 2n



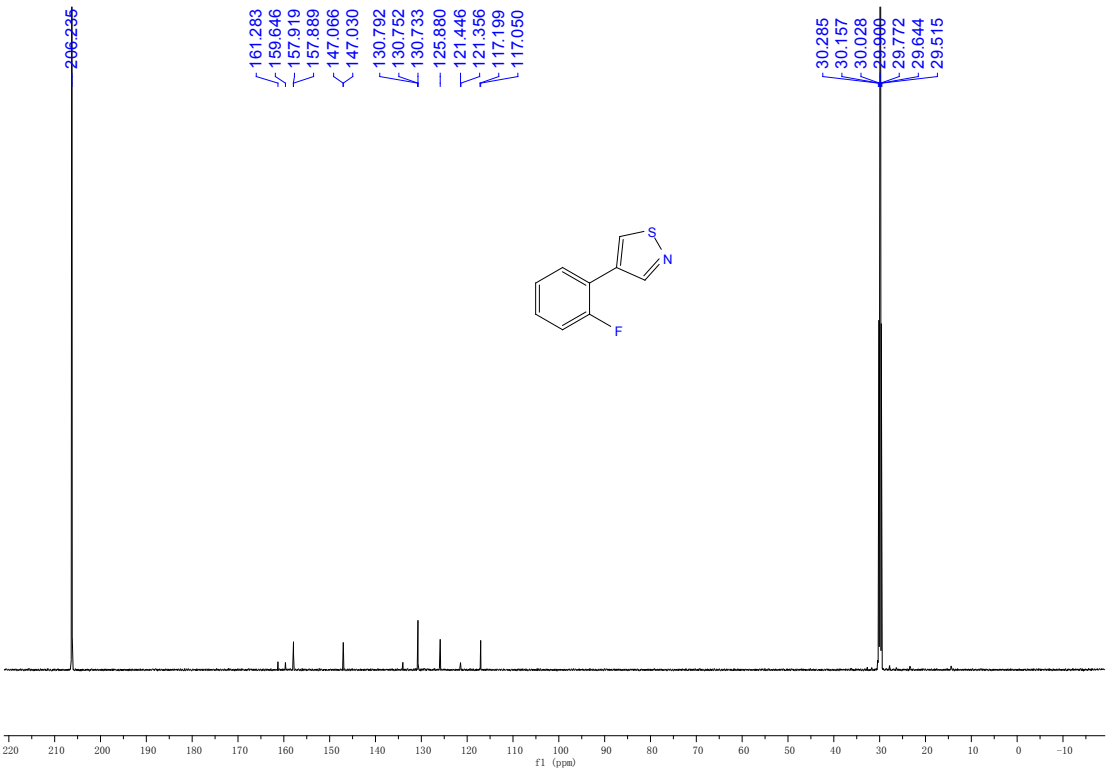
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 2n



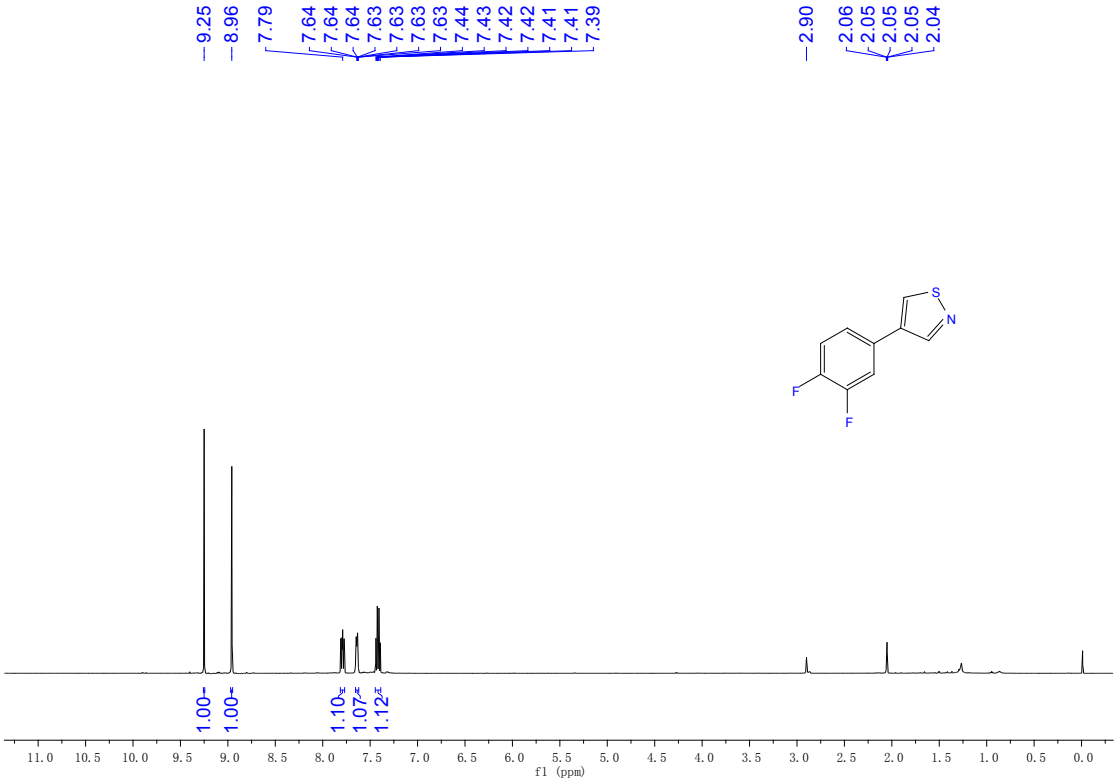
^{1}H NMR (600 MHz, Acetone-d_6) spectrum of compound 2o



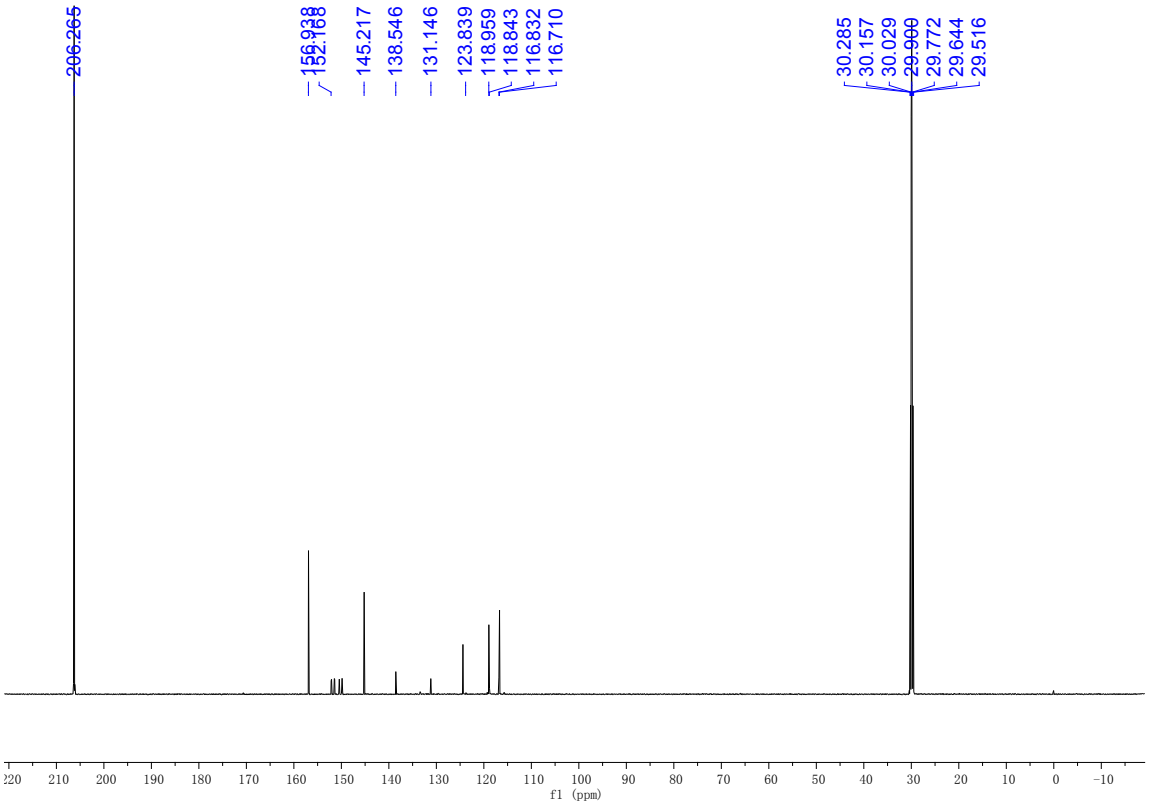
^{13}C NMR (150 MHz, Acetone-d_6) spectrum of compound 2o



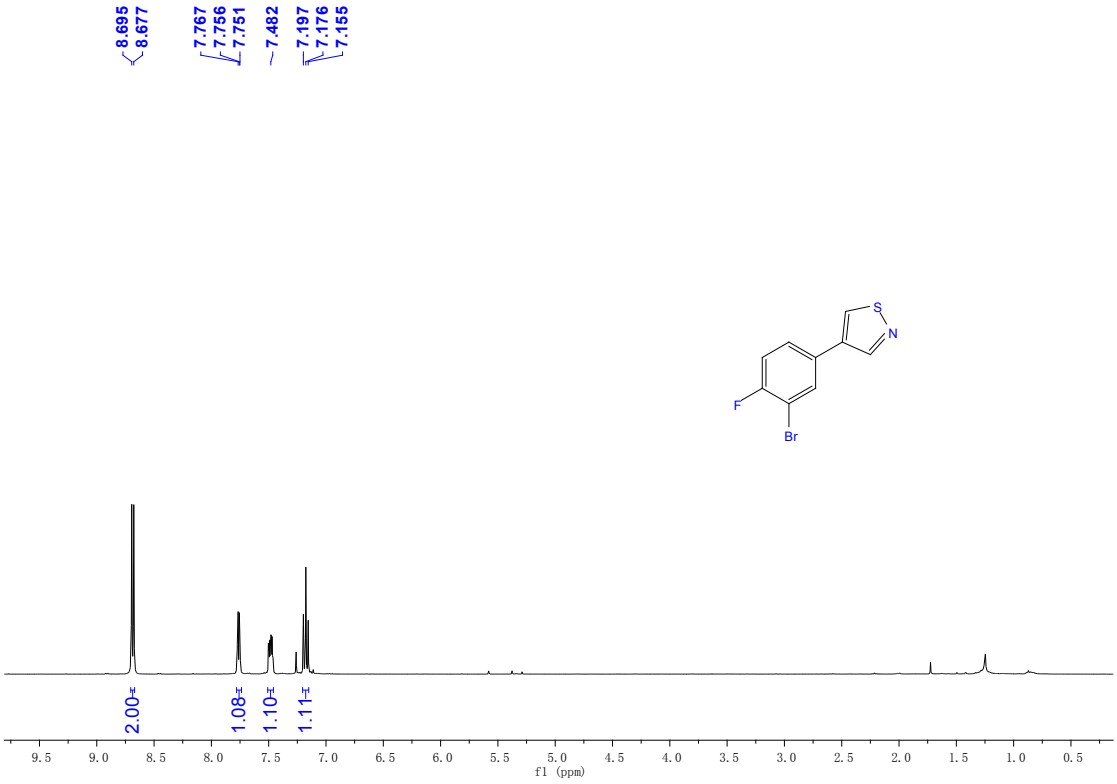
^{1}H NMR (600 MHz, Acetone-d_6) spectrum of compound 2p



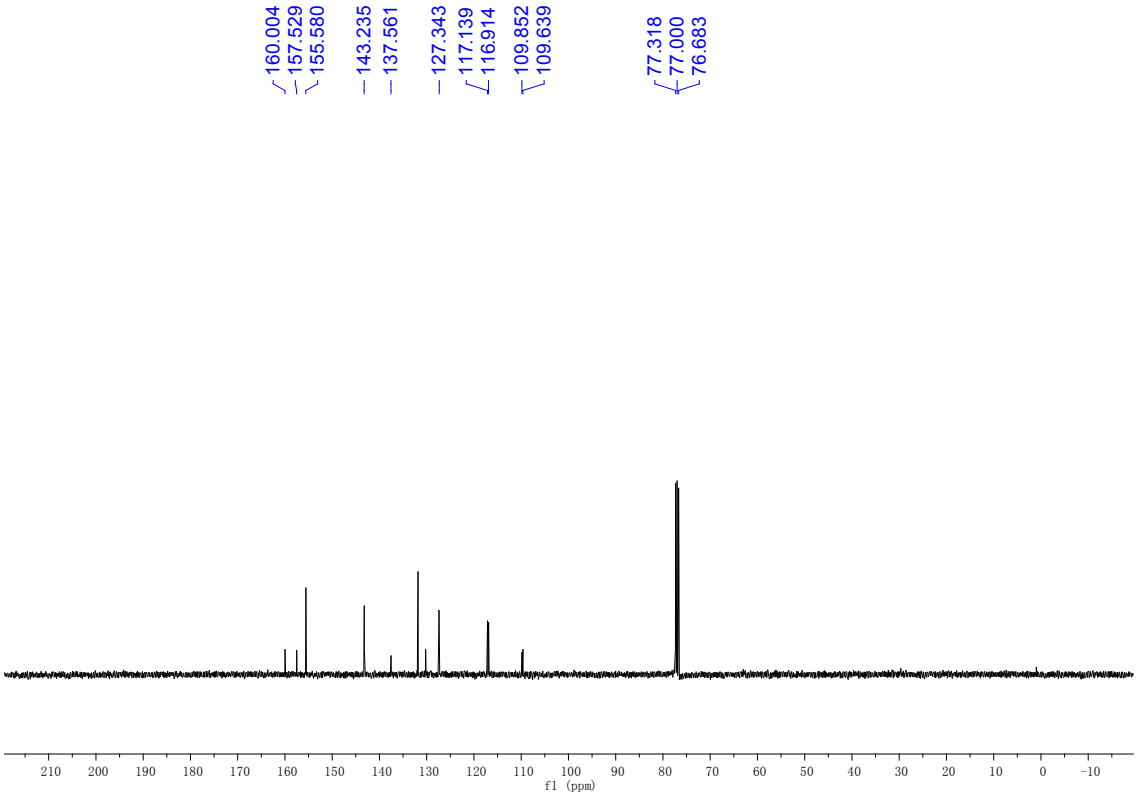
^{13}C NMR (150 MHz, Acetone-d_6) spectrum of compound 2p



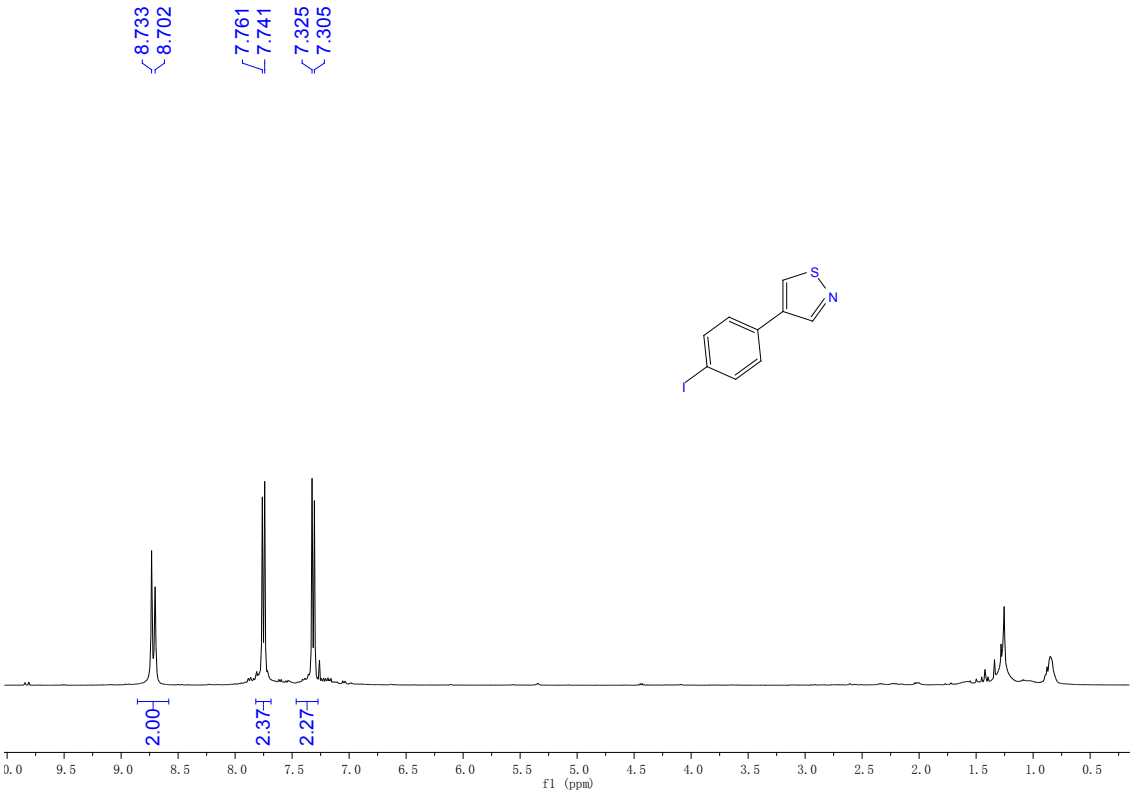
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 2q



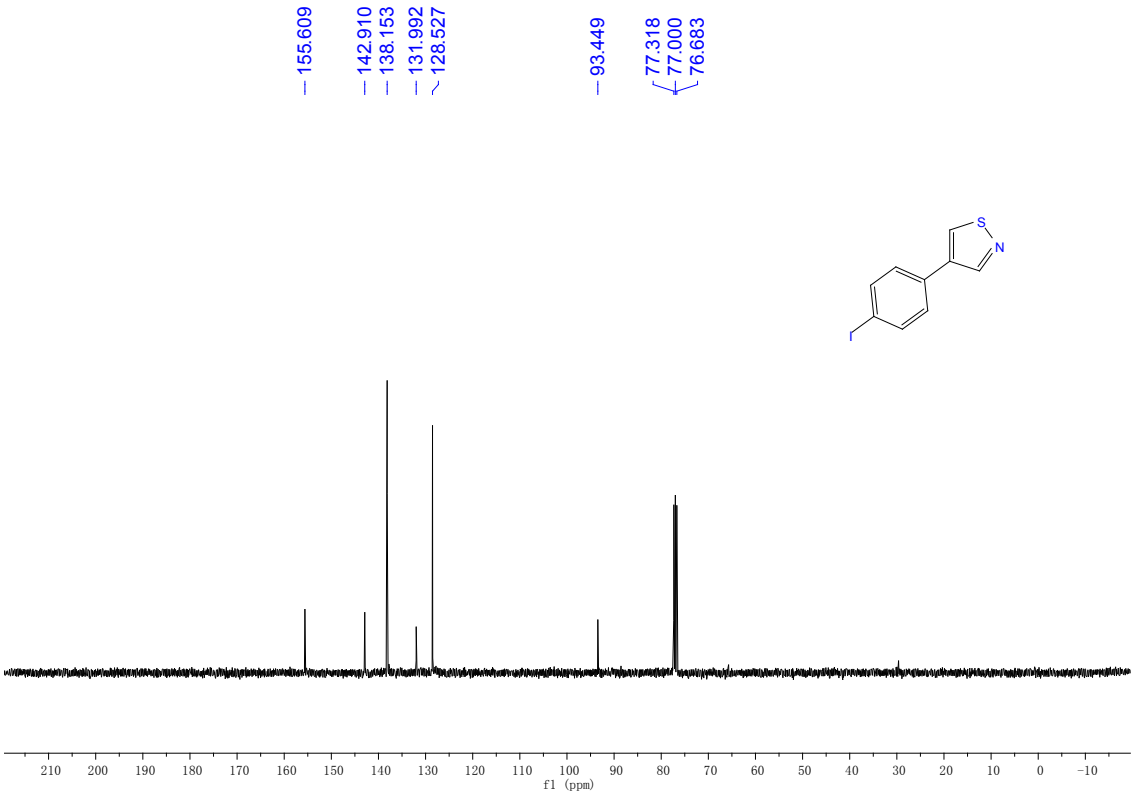
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 2q



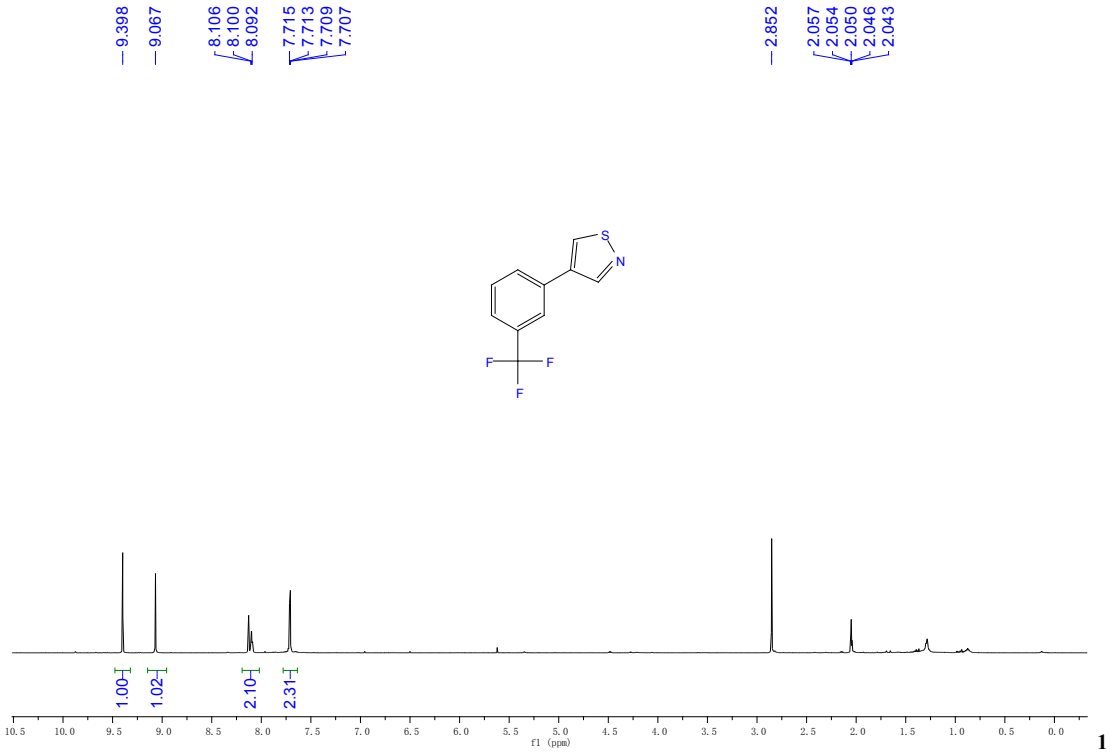
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 2r



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 2r



^{1}H NMR (600 MHz, Acetone-d_6) spectrum of compound 2s



^{3}C NMR (150 MHz, Acetone-d_6) spectrum of compound 2s

^{1}H NMR (600 MHz, Acetone-d_6) spectrum of compound 2t

^{13}C NMR (150 MHz, Acetone-d_6) spectrum of compound 2t

^{1}H NMR (600 MHz, Acetone-d_6) spectrum of compound 2u

^{13}C NMR (150 MHz, Acetone-d_6) spectrum of compound 2u

^{1}H NMR (600 MHz, Acetone-d_6) spectrum of compound 2v

^{13}C NMR (150 MHz, Acetone-d_6) spectrum of compound 2v

^{1}H NMR (600 MHz, Acetone-d_6) spectrum of compound 2w

^{13}C NMR (150 MHz, Acetone-d_6) spectrum of compound 2w

^{1}H NMR (600 MHz, Acetone-d_6) spectrum of compound 2x

^{13}C NMR (150 MHz, Acetone-d_6) spectrum of compound 2x

^{1}H NMR (600 MHz, Acetone-d_6) spectrum of compound 3a

^{13}C NMR (150 MHz, Acetone-d_6) spectrum of compound 3a

^{1}H NMR (600 MHz, Acetone-d_6) spectrum of compound 3b

^{13}C NMR (150 MHz, Acetone-d_6) spectrum of compound 3b

^{1}H NMR (400 MHz, Acetone-d_6) spectrum of compound 3c

^{13}C NMR (100 MHz, Acetone-d_6) spectrum of compound 3c

^{1}H NMR (600 MHz, Acetone-d_6) spectrum of compound 3d

^{13}C NMR (150 MHz, Acetone-d_6) spectrum of compound 3d

^{1}H NMR (600 MHz, Acetone-d_6) spectrum of compound 3e

^{13}C NMR (150 MHz, Acetone-d_6) spectrum of compound 3e

^{1}H NMR (600 MHz, Acetone-d_6) spectrum of compound 3f

^{13}C NMR (150 MHz, Acetone-d_6) spectrum of compound 3f

^{1}H NMR (600 MHz, Acetone-d_6) spectrum of compound 3g

^{13}C NMR (150 MHz, Acetone-d_6) spectrum of compound 3g

^{1}H NMR (600 MHz, Acetone-d_6) spectrum of compound 3h

^{13}C NMR (150 MHz, Acetone-d_6) spectrum of compound 3h

^{1}H NMR (400 MHz, DMSO-d_6) spectrum of compound 3i

^{13}C NMR (100 MHz, DMSO-d_6) spectrum of compound 3i

^{1}H NMR (400 MHz, DMSO-d_6) spectrum of compound 3j

^{3}C NMR (100 MHz, DMSO-d_6) spectrum of compound 3j

^{1}H NMR (500 MHz, Acetone-d_6) spectrum of compound 3k

^{13}C NMR (125 MHz, Acetone-d_6) spectrum of compound 3k

^{1}H NMR (600 MHz, Acetone-d_6 +DMSO-d_6) spectrum of compound 2y

^{3}C NMR (150 MHz, Acetone-d_6 +DMSO-d_6) spectrum of compound 2y

^{1}H NMR (500 MHz, Acetone-d_6) spectrum of compound 3m

^{3}C NMR (125 MHz, Acetone-d_6) spectrum of compound 3m

^{1}H NMR (400 MHz, DMSO-d_6) spectrum of compound 4a

^{13}C NMR (100 MHz, C DMSO-d_6) spectrum of compound 4a

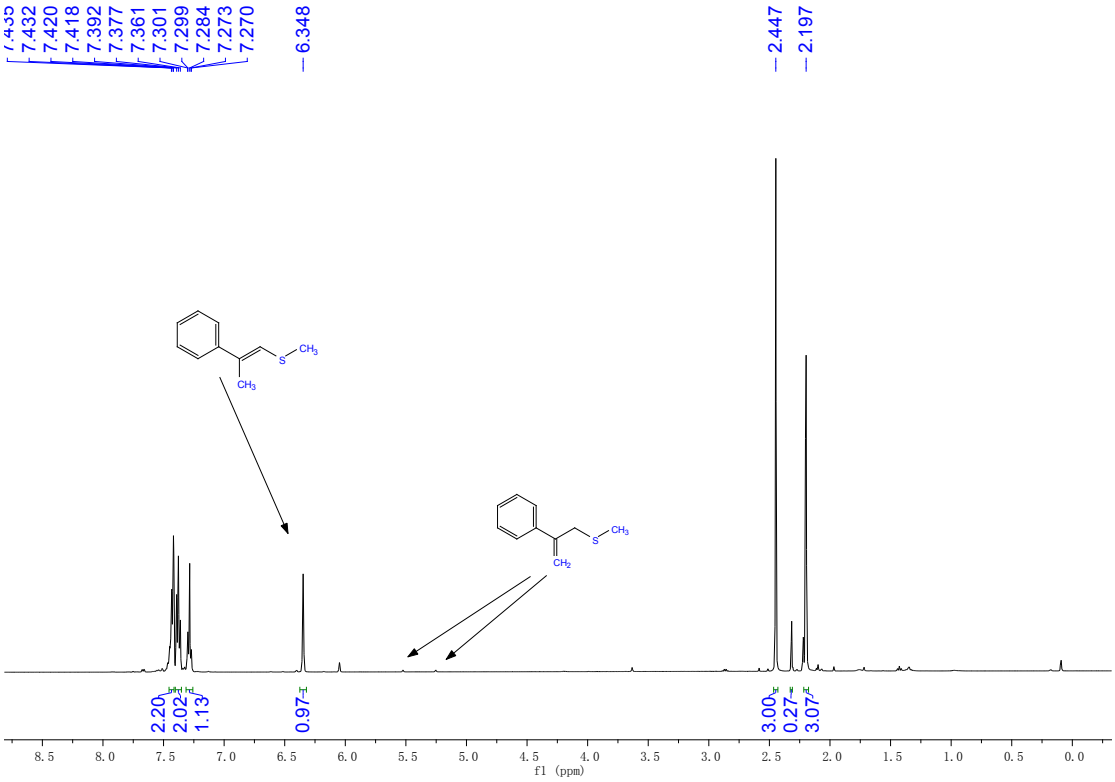
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of compound 4a

^{13}C NMR (100 MHz, C DMSO-d_6) spectrum of compound 4a

^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 2a-D

^{13}C NMR (125 MHz, C $CDCl_3$) spectrum of compound 2a-D

^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound



^{13}C NMR (125 MHz, C $CDCl_3$) spectrum of compound