Electronic Supplementary Information

Photocatalytic oxidative cyclization of aromatic thioamides catalyzed by Cu_2O rhombic dodecahedra

Guan-Ru Wang and Michael H. Huang*
Department of Chemistry, National Tsing Hua University, Hsinchu 300044, Taiwan
E-mail: hyhuang@mx.nthu.edu.tw

Synthesis of polyhedral Cu_2O crystals

For the synthesis of Cu_2O cubes, 38.2 mL of deionized water was added to dissolve 0.348 g of SDS. The mixture was stirred at 31 ºC for 5 min. After adding 0.4 mL of 0.1 M $CuCl_2$ solution, the mixture was kept stirring for 25 min. Next, 0.8 mL of 1.0 M NaOH solution was added and stirred for 5 sec, then quickly added 0.6 mL of 0.2 M $NH_2OH{\cdot}HCl$ solution and stirred for 20 sec. After stop stirring, the solution was aged for 50 min.

To make Cu_2O rhombic dodecahedra, 27.68 mL of deionized water was added to dissolve 0.348 g of SDS. The mixture was stirred at 31 ºC for 5 min. After adding 2.0 mL of 0.1 M $CuCl_2$ solution, the mixture was kept stirring for 25 min. Next, 0.72 mL of 1.0 M NaOH solution was added and stirred for 4 sec, followed by the introduction of 9.6 mL of 0.1 M $NH_2OH{\cdot}HCl$ solution and stirred for 20 sec. After stop stirring, the solution was aged for 50 min.

For the formation of Cu_2O cotahedra, 26.20 mL of deionized water was added to dissolve 0.348 g of SDS. The mixture was stirred at 31 ºC for 5 min. After adding 0.8 mL of 0.1 M $CuCl_2$ solution, the mixture was kept stirring for 10 min. Next, 0.8 mL of 1.0 M NaOH solution was added and stirred for 3 sec. Subsequently, 2.6 mL of 0.2 M $NH_2OH{\cdot}HCl$ solution was quickly introduced and stirred for 10 sec. After stop stirring, the solution was aged for 25 min.

After aging, the solution was centrifuged at 10,000 rpm for 3 min. A 1:1 volume ratio of water and ethanol was used to wash the particles. Finally, the particles were stored in absolute ethanol.

Radical scavenging experiment

Rhombic dodecahedral Cu_2O nanocrystals (2.9 mg), thioamide (0.4 mmol, 1.0 equiv.) and 0.4 mmol DABCO (or 1.0 equiv. of 1,4-benzoquinone, $K_2S_2O_8$, potassium iodine, sodium oxalate, or isopropyl alcohol) were added to a 15 mL quartz test tube with a stir bar and sealed with a rubber septum. The tube was evacuated using a vacuum pump and refilled with O_2 for three times. After the evacuation and refill cycles, THF was injected into the tube. The mixture was sonicated for 3 min and placed approximately 2 cm from a blue LED lamp (40 W, λ = 390 nm). After the indicated

irradiation period, Cu_2O crystals were separated by centrifugation at 10,000 rpm for 3 min. The solvent was removed by a rotavapor to obtain the crude product. The residue was purified by short column chromatography.

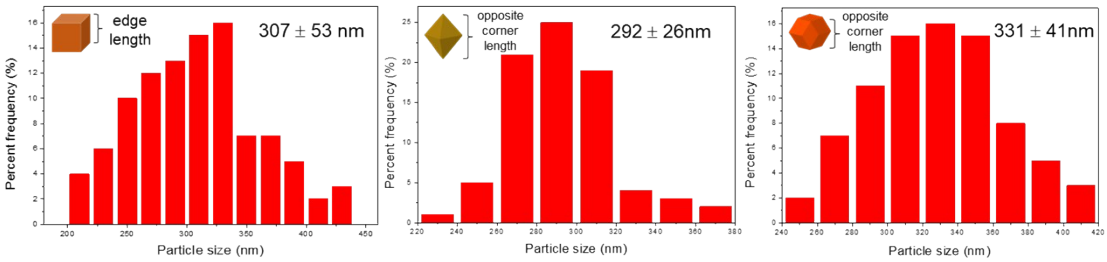


Fig. S1 Size distribution histograms of the prepared Cu_2O cubes, octahedra, and rhombic dodecahedra.

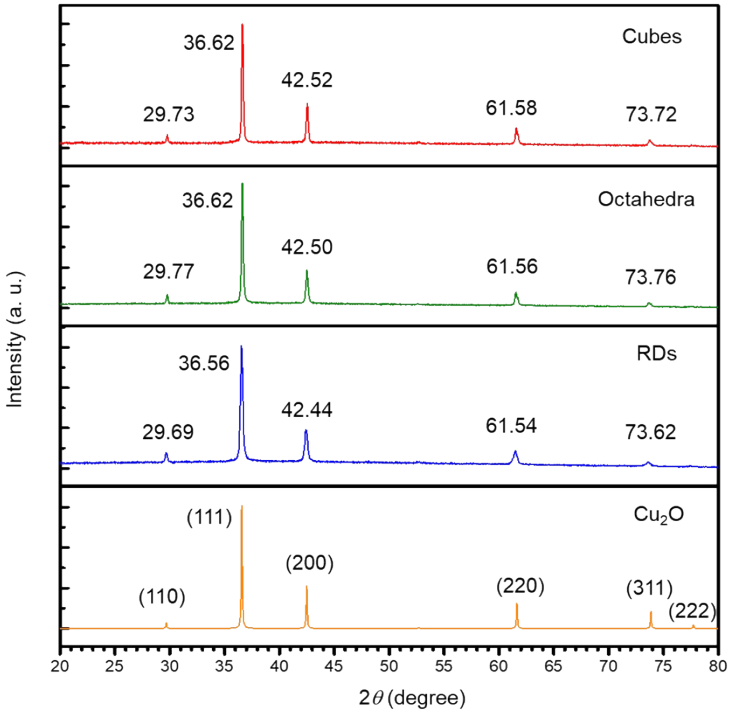
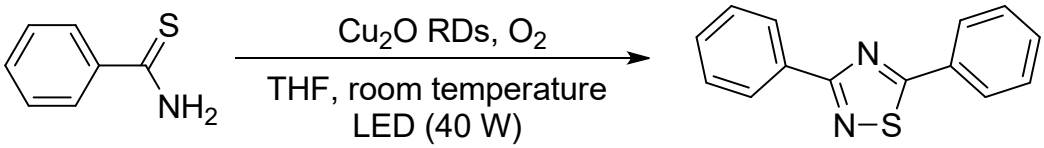


Fig. S2 XRD patterns of the synthesized Cu_2O crystals. A standard pattern of Cu_2O is also shown.

Table S1 Calculations for the particle weights needed for the photocatalysis experiment

	Cubes	Octahedra	Rhombic dodecahedra
Size (nm)	307	292	331
Surface area for single particle (nm^2)	5.65×10^5	1.48×10^5	4.65×10^5
Volume for single particle (nm^3)	2.89×10^7	4.15×10^6	2.56×10^7
Weight for single particle (mg)	1.74×10^{-13}	2.49×10^{-14}	1.54×10^{-13}
Fixed surface area (nm^2)	8.8×10^{15}		
Number of particles	1.56×10^{10}	5.96×10^{10}	1.89×10^{10}
Weight (mg)	2.7	1.5	2.9

Table S2 Effect of light wavelength on product yield[a,b]



entry[a]	time (h)	wavelength (nm)	yield (%)[b]
1	6	390	51
2	8	390	94
3	8	370	82
4	8	440	37

[a] Reagents: thiobenzamide (0.4 mmol) and Cu_2O RDs (2.9 mg) in THF (3 mL).

[b] Isolated yield.

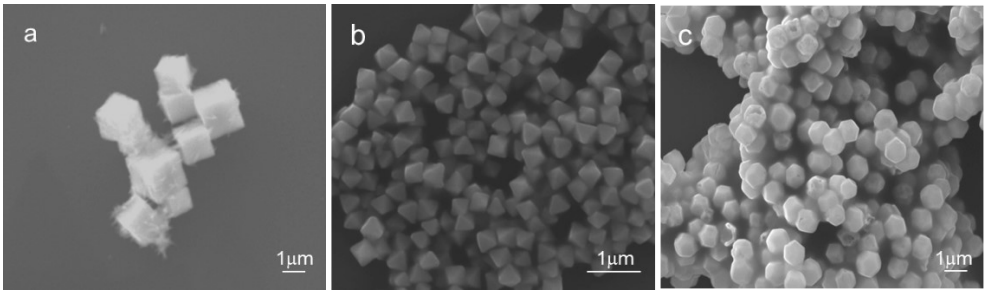


Fig. S3 SEM images of the Cu_2O (a) cubes, (b) octahedra and (c) rhombic

dodecahedra after the thiobenzamide cyclization reaction.

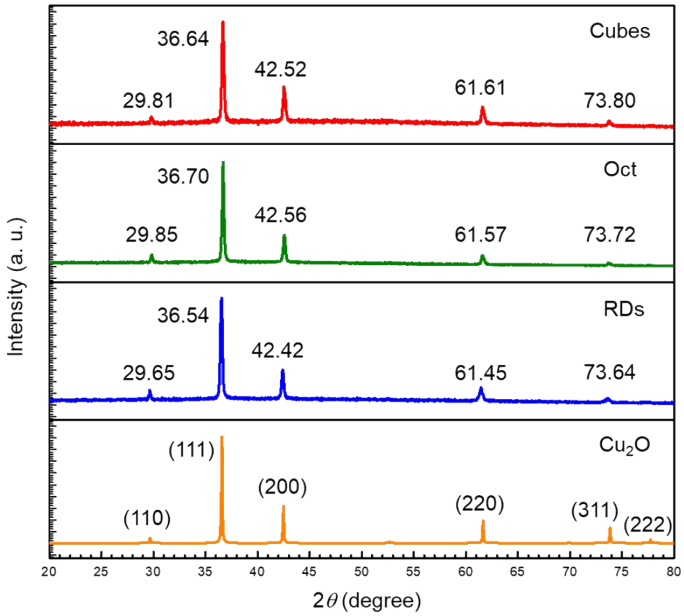


Fig. S4 XRD patterns of Cu_2O cubes, octahedra and rhombic dodecahedra after the oxidative thiobenzamide cyclization reaction.

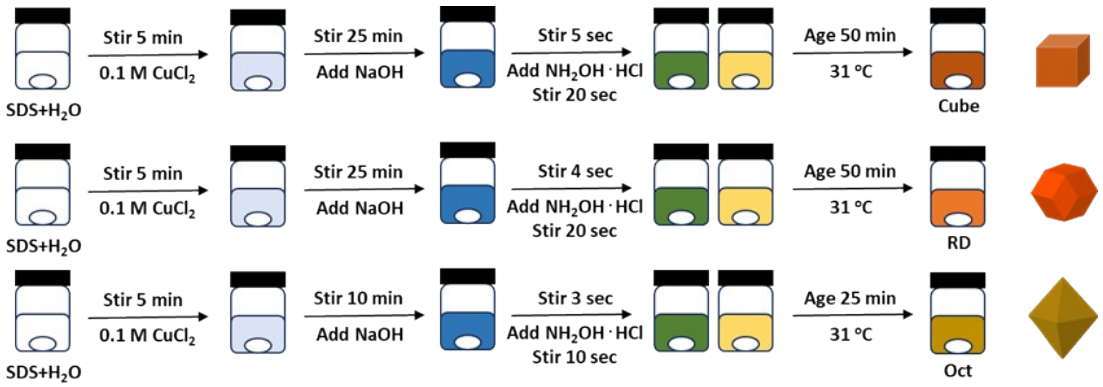


Fig. S5 Illustration of the Cu_2O crystal synthesis conditions.

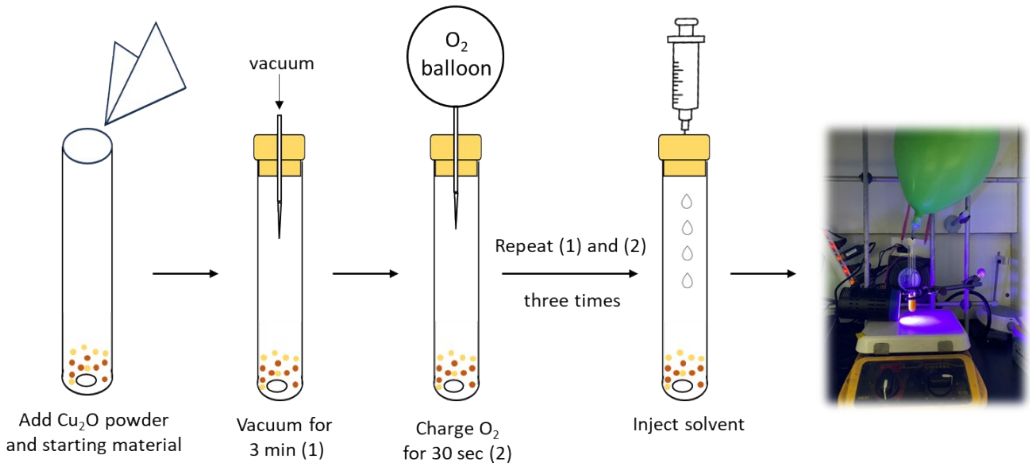
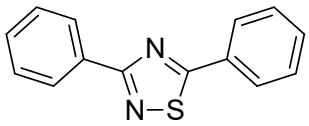


Fig. S6 Illustration of the steps before photocatalytic oxidative cyclization of

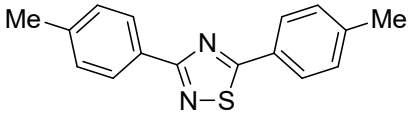
thioamides. The black square-shaped device is a fan.

Spectroscopic data of isolated products



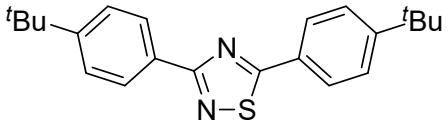
3,5-Diphenyl-1,2,4-thiadiazole (2a)

white solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42–8.40 (dd, *J* = 7.2, 1.6 Hz, 2H), 8.07–8.05 (dd, *J* = 7.2, 1.6 Hz, 2H), 7.54–7.50 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.1, 173.8, 132.9, 131.9, 130.7, 130.3, 129.2, 128.7, 128.3, 127.5.



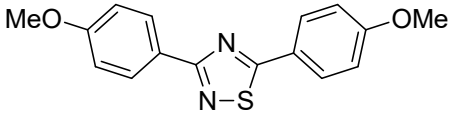
3,5-Bis(4-methylphenyl)-1,2,4-thiadiazole (2b)

white solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.0 Hz, 2H), δ 7.94 (d, *J* = 8.4 Hz, 2H), 7.33–7.30 (m, 4H), δ 2.43 (d, *J* = 3.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.0, 173.8, 142.4, 140.4, 130.4, 129.9, 129.4, 128.3, 128.2, 127.4, 21.6, 21.5.



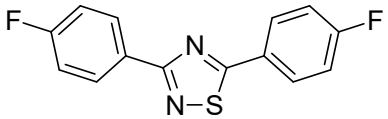
3,5-Bis(4-trimethylphenyl)-1,2,4-thiadiazole (2c)

white solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35–8.32 (m, 2H), δ 8.00–7.94 (m, 2H), δ 7.55–7.53 (dd, *J* = 8.8, 0.8 Hz, 4H), δ 1.39 (d, *J* = 3.2 Hz, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.8, 173.8, 155.5, 153.5, 130.3, 128.1, 127.3, 126.2, 125.6, 35.1, 34.9, 31.2, 31.1.



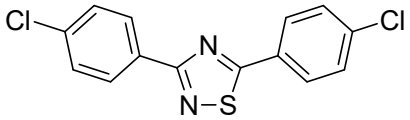
3,5-Bis(4-methoxyphenyl)-1,2,4-thiadiazole (2d)

white solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.8 Hz, 2H), δ 7.99 (d, *J* = 8.8 Hz, 2H), δ 7.02–6.99 (dd, *J* = 9.2, 2.4 Hz, 4H), δ 3.88 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.4, 173.4, 162.5, 161.3, 129.9, 129.1, 126.1, 123.7, 114.5, 114.0, 55.5, 55.4.



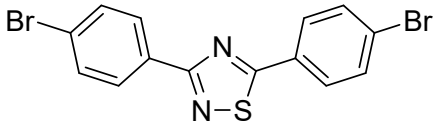
3,5-Bis(4-fluorophenyl)-1,2,4-thiadiazole (2e)

white solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38–8.36 (m, 2H), δ 8.07–8.02 (m, 2H), 7.25–7.15 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.0, 172.8, 166.2, 165.5, 163.7, 163.8, 130.5, 130.4, 129.7, 129.6, 116.6, 116.4, 115.8, 115.6.



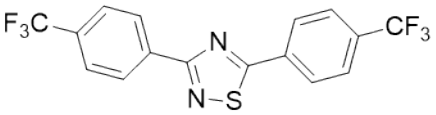
3,5-Bis(4-chlorophenyl)-1,2,4-thiadiazole (2f)

white solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33–8.30 (dd, J = 6.8, 2.0 Hz, 2H), δ 7.99–7.97 (dd, J = 6.4, 1.6 Hz, 2H), 7.52–7.46 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.0, 172.8, 138.2, 136.6, 131.2, 129.7, 129.6, 129.0, 128.7.



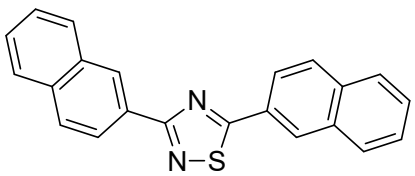
3,5-Bis(4-bromophenyl)-1,2,4-thiadiazole (2g)

white solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, J = 8.4 Hz, 2H), δ 7.90 (d, J = 6.4 Hz, 2H), δ 7.68–7.62 (dd, J = 13.2, 8.4 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.2, 172.9, 132.6, 131.9, 131.6, 129.9, 129.4, 128.8, 126.6, 125.1.



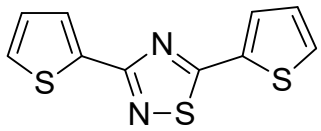
3,5-Bis(4-trifluoromethylphenyl)-1,2,4-thiadiazole (2h)

white solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, J = 6.5 Hz, 2H), δ 8.17 (d, J = 6.5 Hz, 2H), 7.76–7.81 (dd, J =13.6, 6.6 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.0, 172.7, 135.6, 134.1, 133.8, 133.6, 133.5, 133.3, 132.6, 132.4, 132.1, 131.8, 128.7, 127.8, 126.4, 125.7, 125.8, 125.1, 124.6.



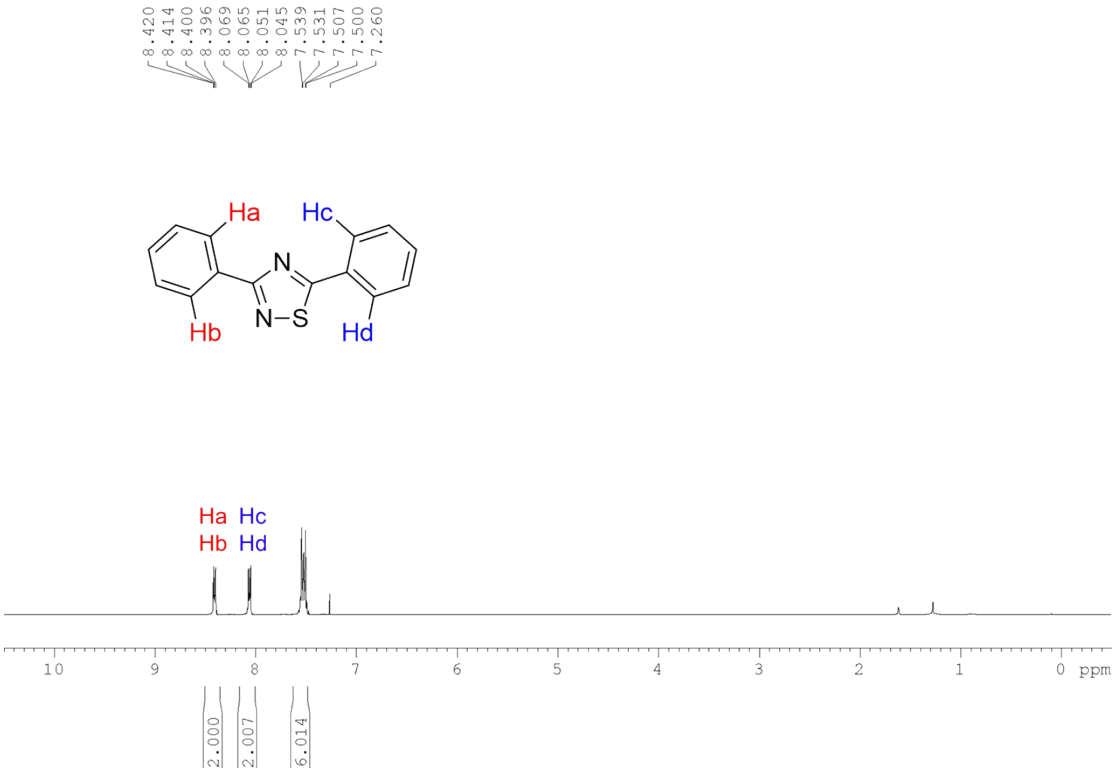
3,5-Di(naphthalen-2-yl)-1,2,4-thiadiazole (2i)

white solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (d, *J* = 0.8 Hz, 1H), δ 8.62 (s, 1H), δ 8.52–8.50 (dd, *J* = 8.6, 1.8 Hz, 1H), δ 8.15–8.13 (dd, *J* = 8.7, 1.6 Hz, 1H), δ 8.05–7.97 (m, 4H), δ 7.92–7.89 (m, 2H), δ 7.63–7.54 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.2, 174.0, 135.0, 134.4, 133.3, 133.1, 130.3, 129.2, 129.0, 128.6, 128.4, 128.0, 127.9, 127.8, 127.7, 127.2, 127.1, 126.5, 125.2, 124.2.

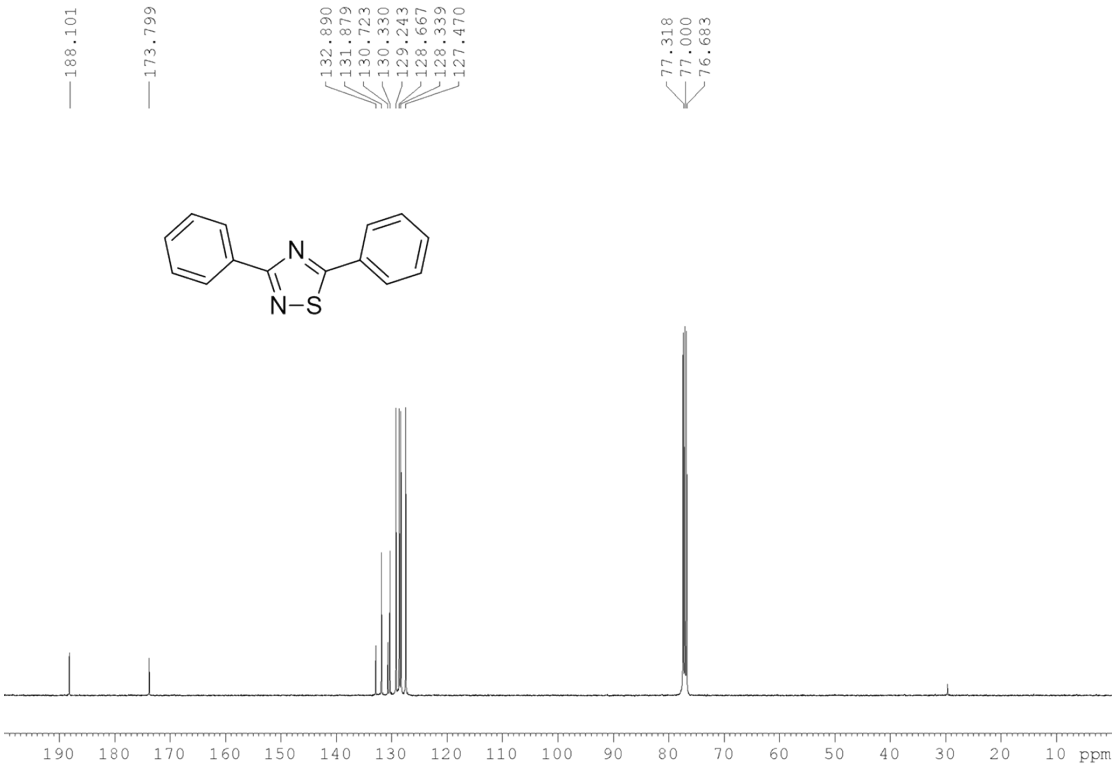


3,5-Bis(thiophen-2-yl)-1,2,4-thiadiazole (2j)

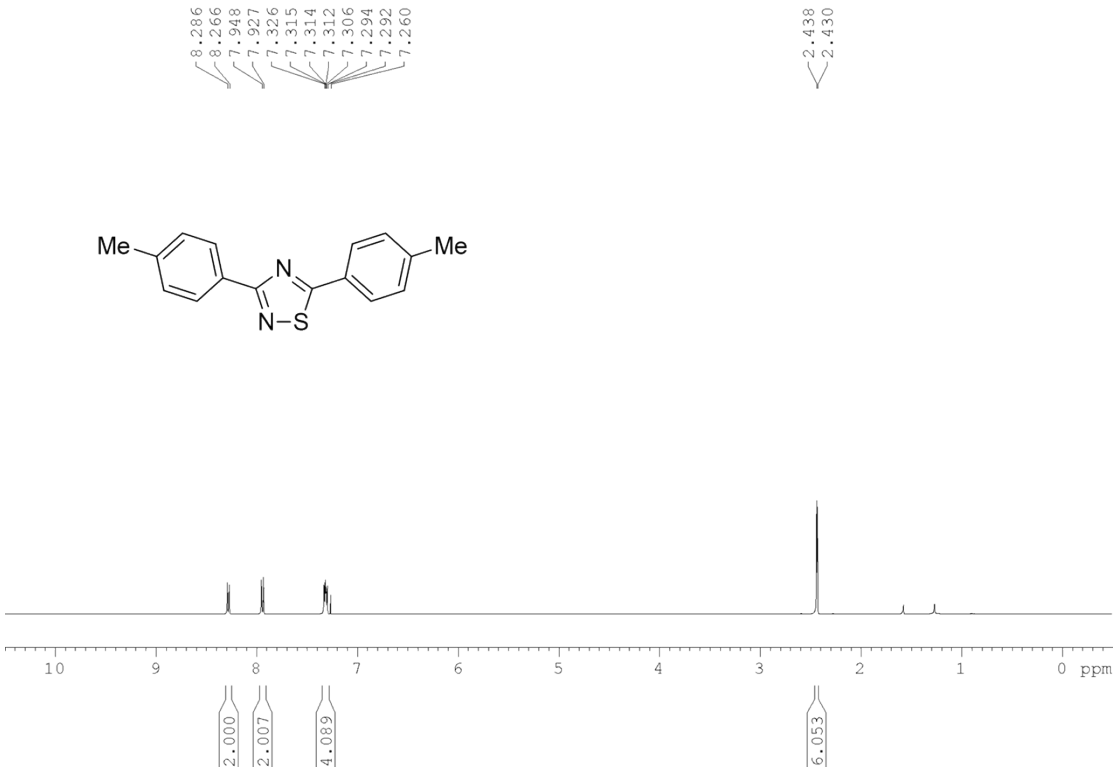
white solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94–7.92 (dd, *J* =3.6, 1.2 Hz, 1H), δ 7.70–7.68 (ddd, *J* = 3.8, 2,2, 1.1 Hz, 1H), δ 7.59–7.57 (ddd, *J* = 5.0 , 2,1, 1.1 Hz, 1H), δ 7.46–7.45 (dd, *J* = 4.8, 1.1 Hz, 1H), δ 7.17–7.13 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.7, 168.4, 136.2, 133.1, 130.5, 129.9, 129.2, 128.8, 128.4, 127.9.



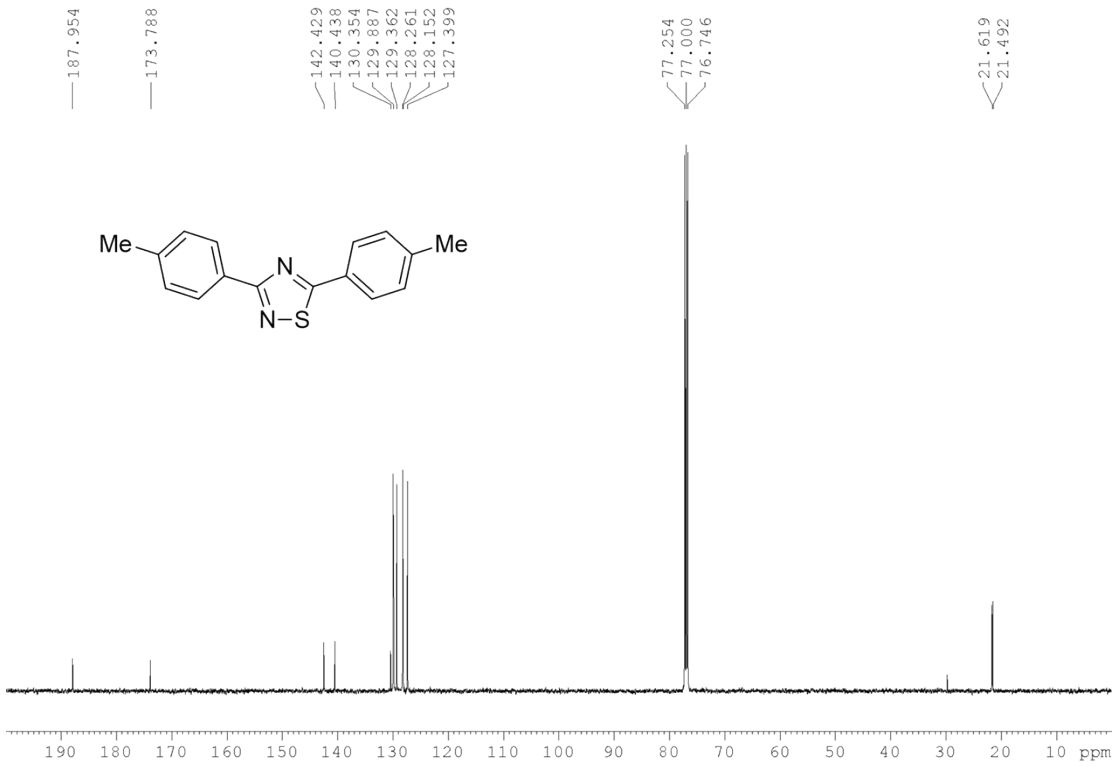
Spectrum S1 ^{1}H NMR spectrum of compound **2a**.



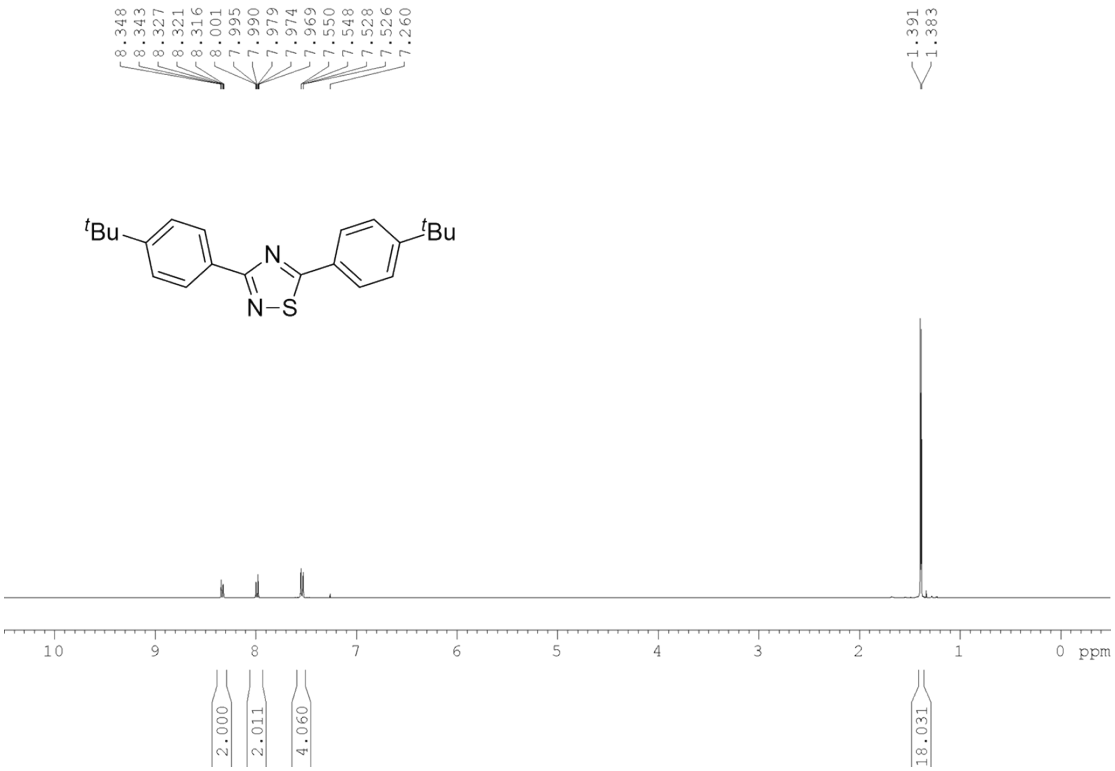
Spectrum S2 ^{13}C NMR spectrum of compound **2a**.



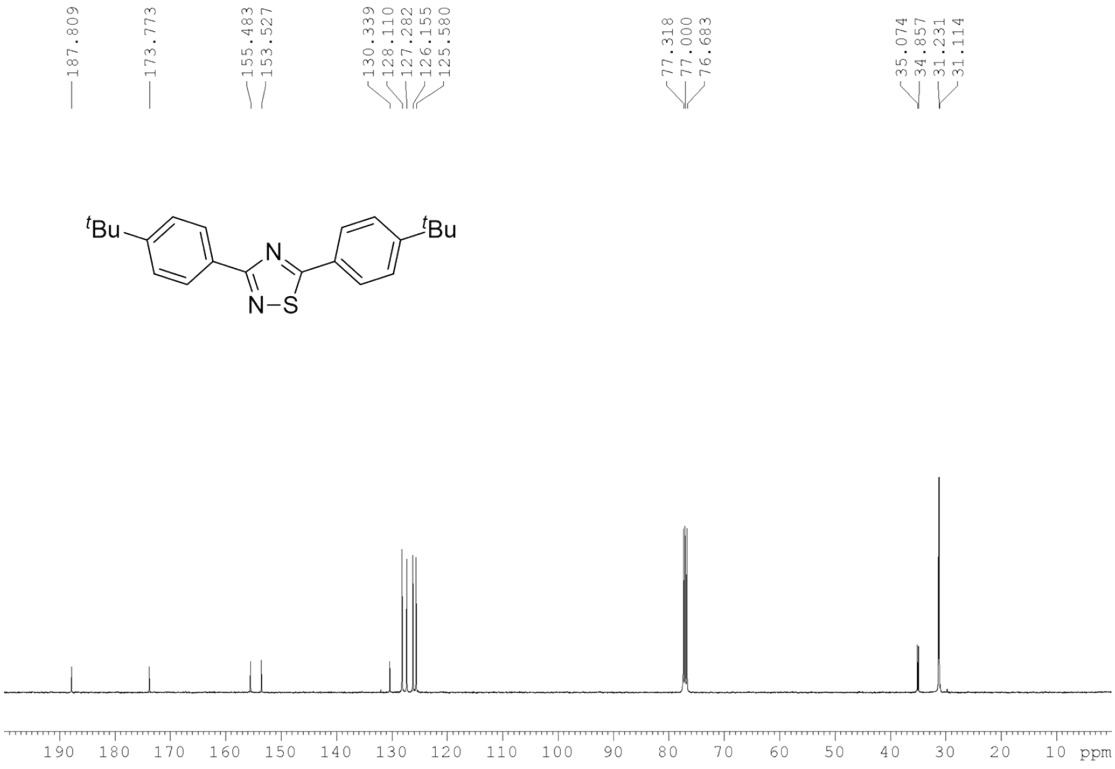
Spectrum S3 ^{1}H NMR spectrum of compound **2b**.



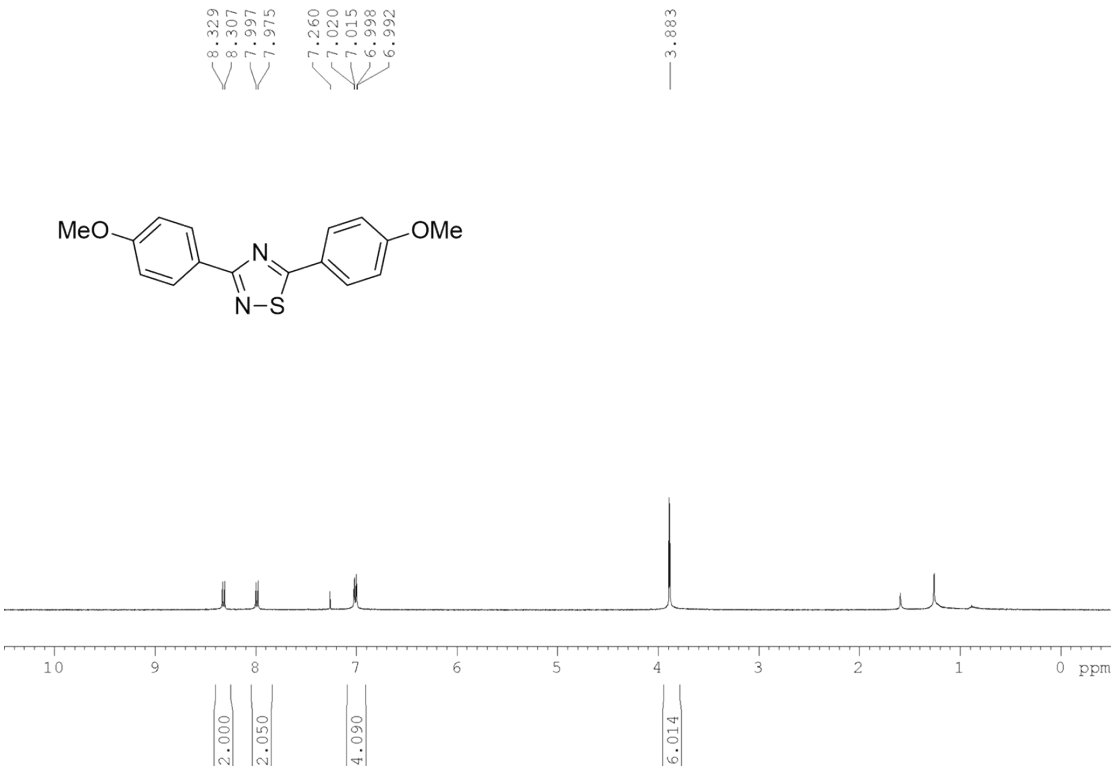
Spectrum S4 ^{13}C NMR spectrum of compound **2b**.



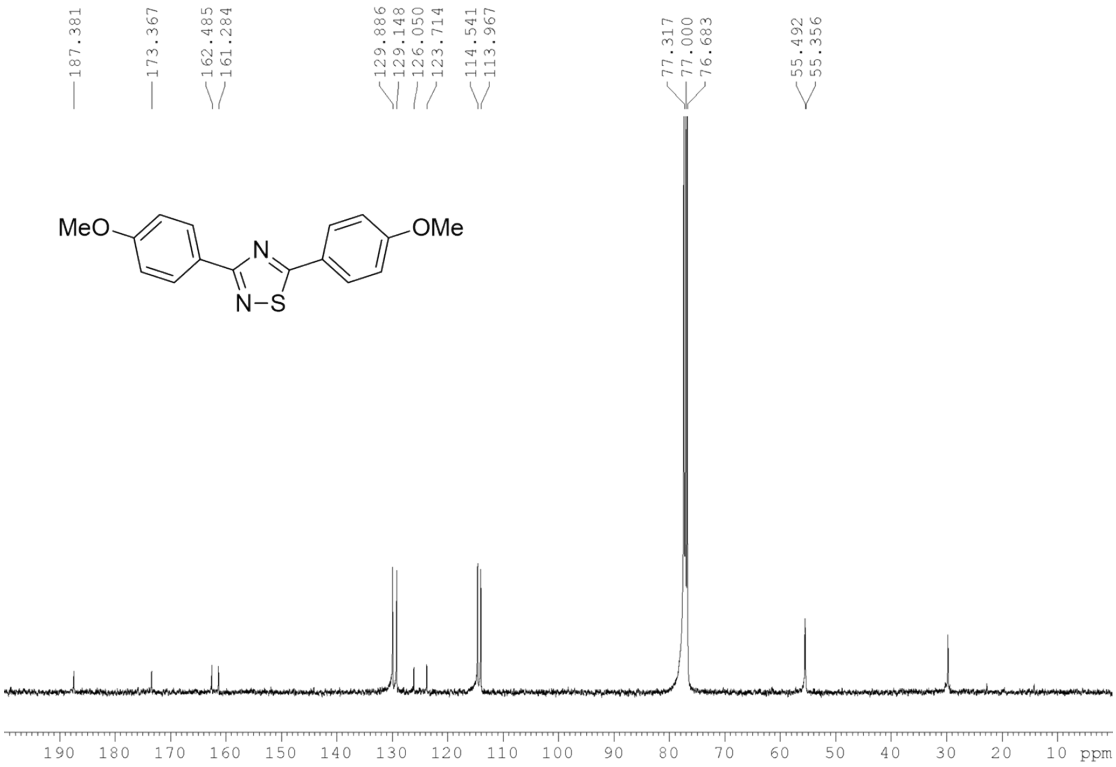
Spectrum S5 [1]H NMR spectrum of compound **2c**.



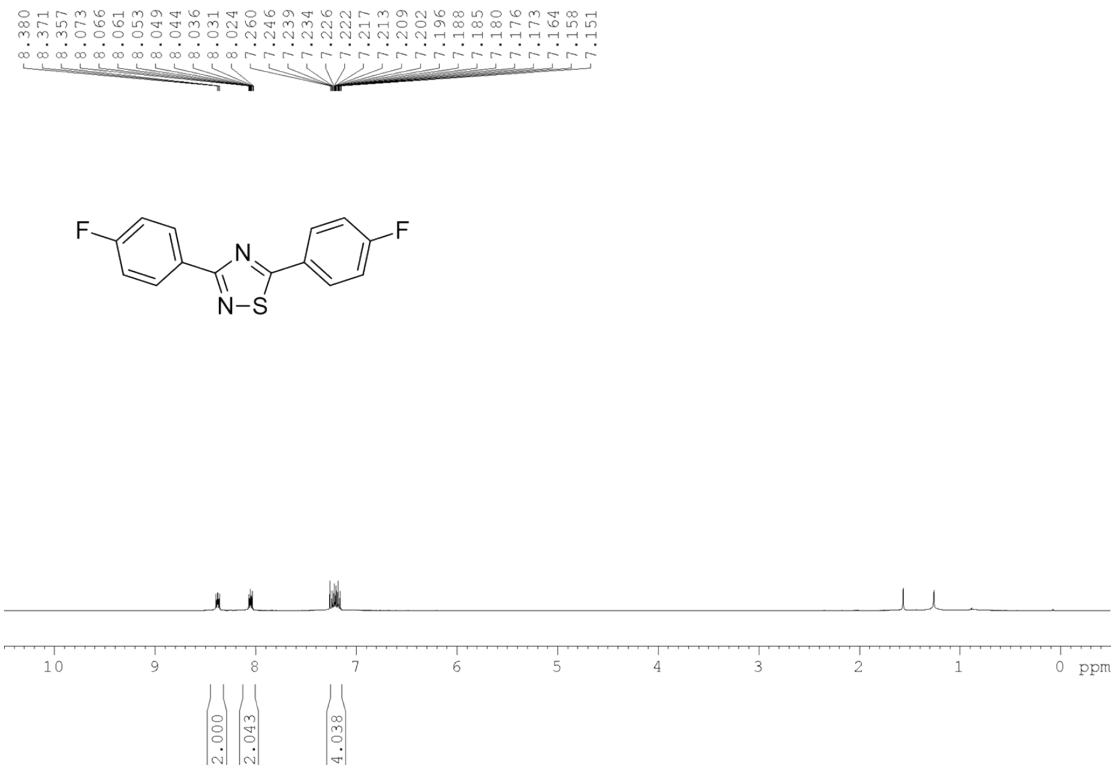
Spectrum S6 [13]C NMR spectrum of compound **2c**.



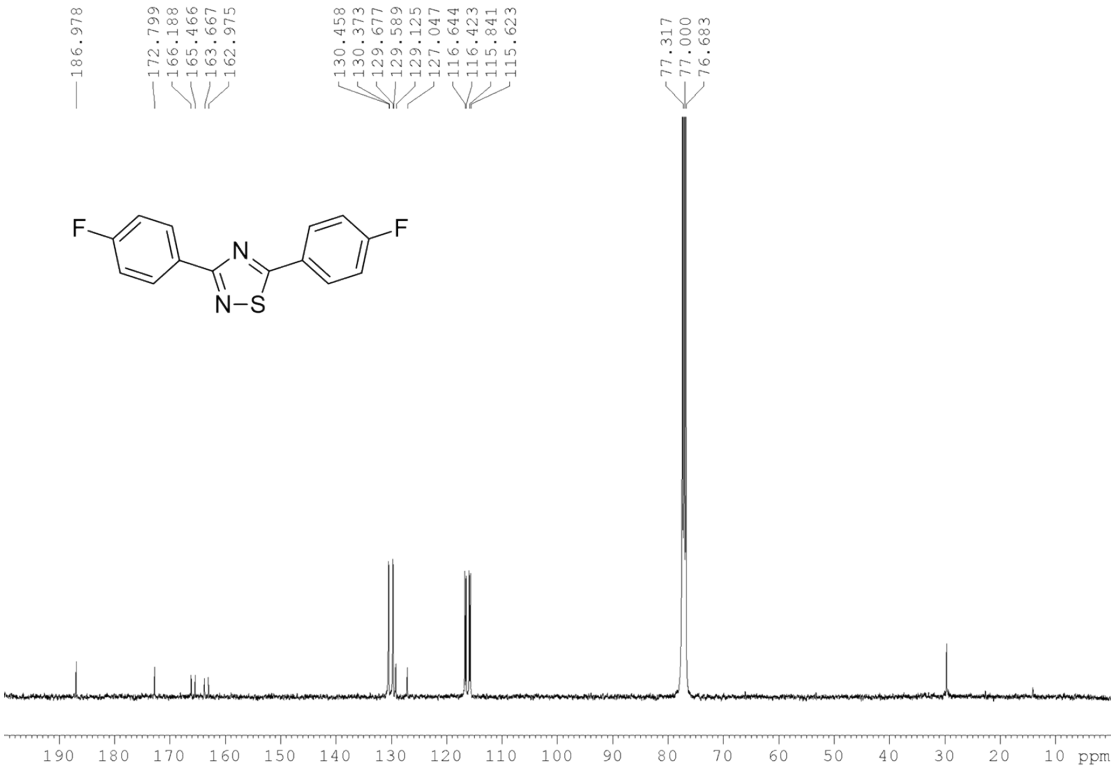
Spectrum S7 ^{1}H NMR spectrum of compound **2d**.



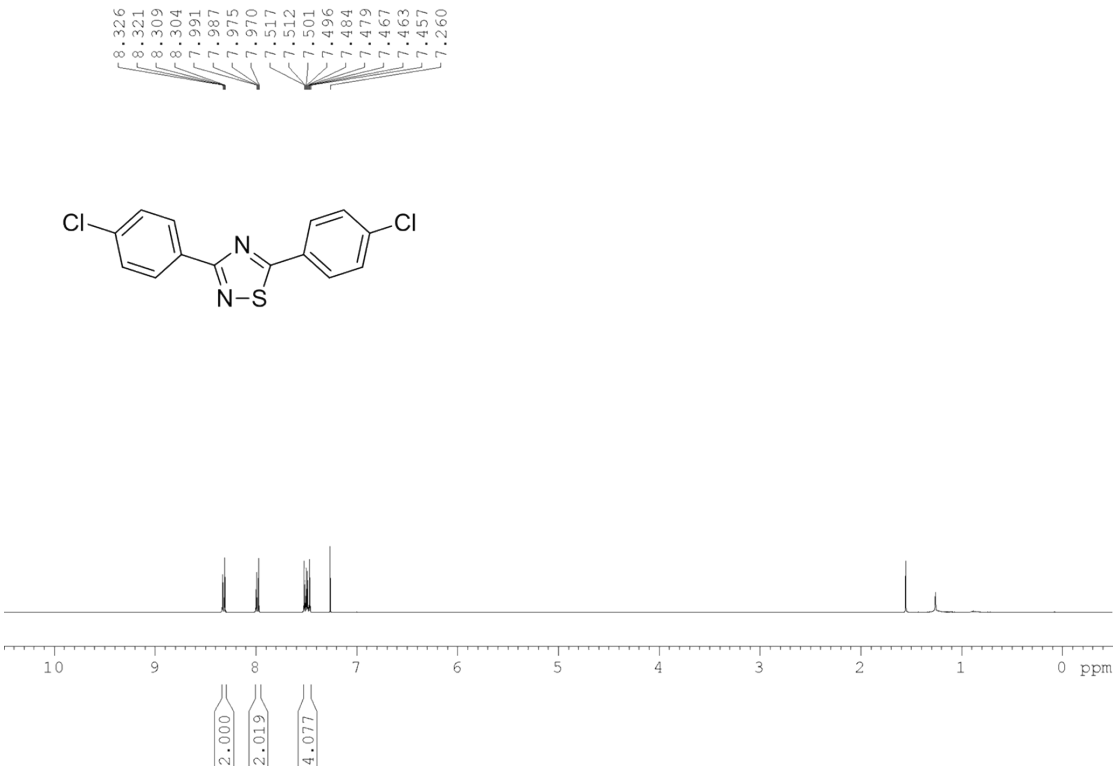
Spectrum S8 ^{13}C NMR spectrum of compound **2d**.



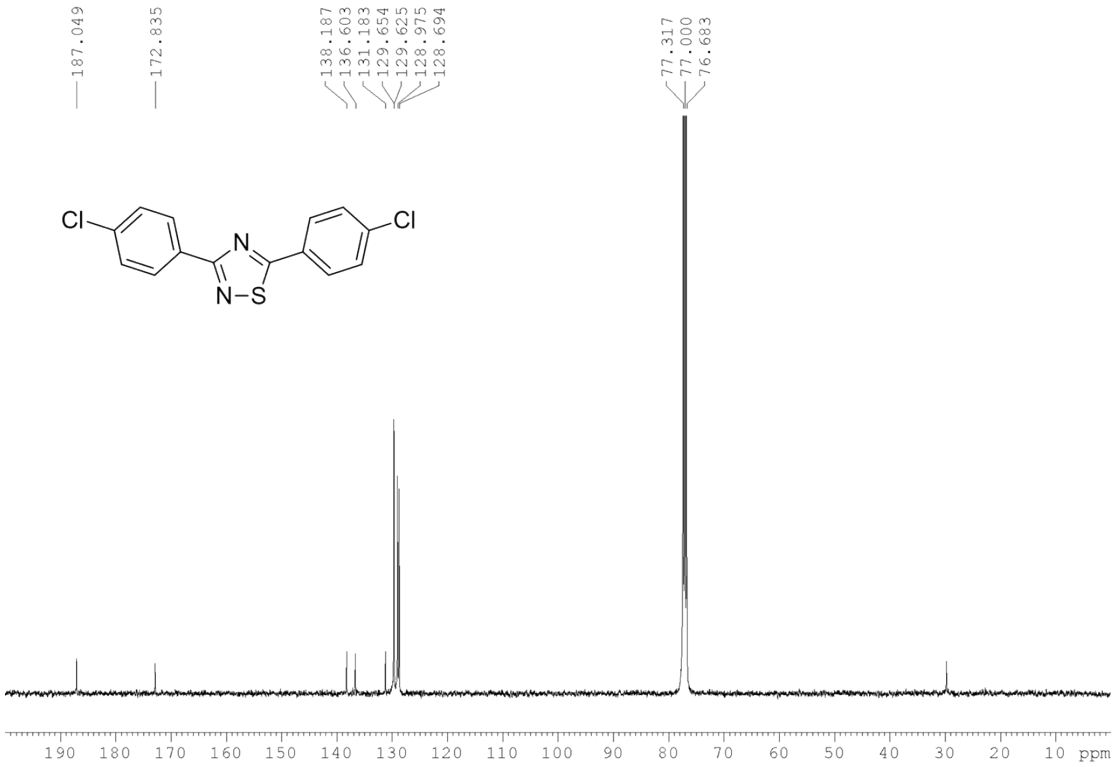
Spectrum S9 ^{1}H NMR spectrum of compound **2e**.



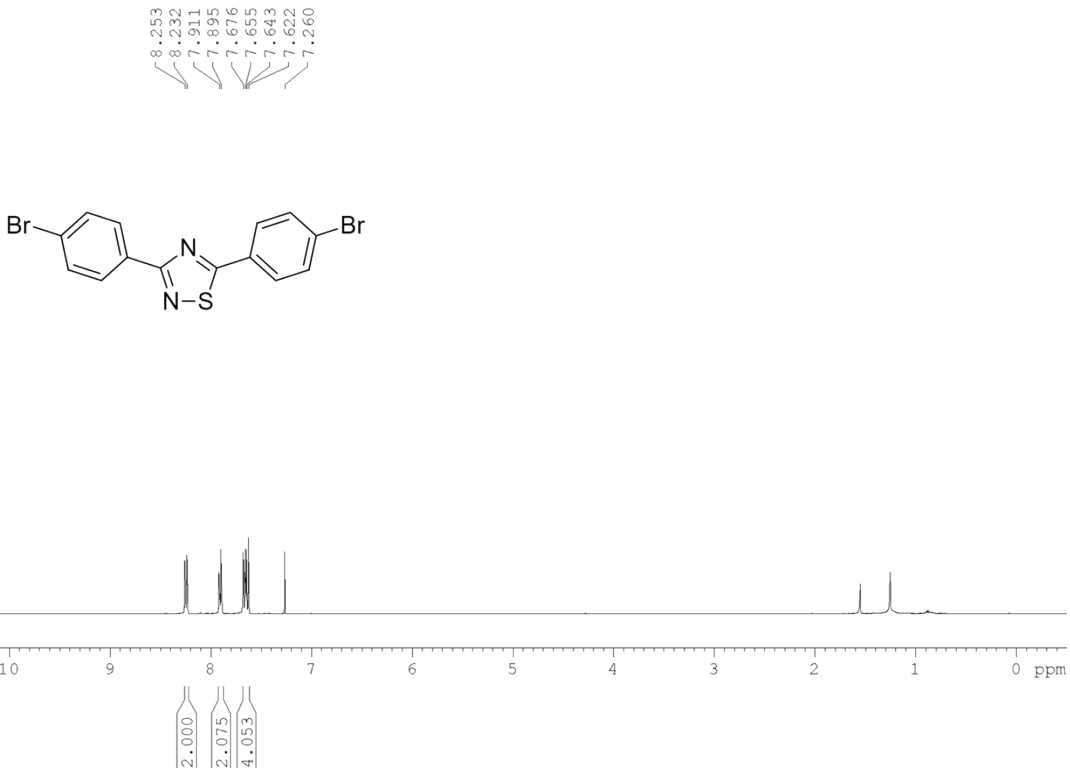
Spectrum S10 ^{13}C NMR spectrum of compound **2e**.



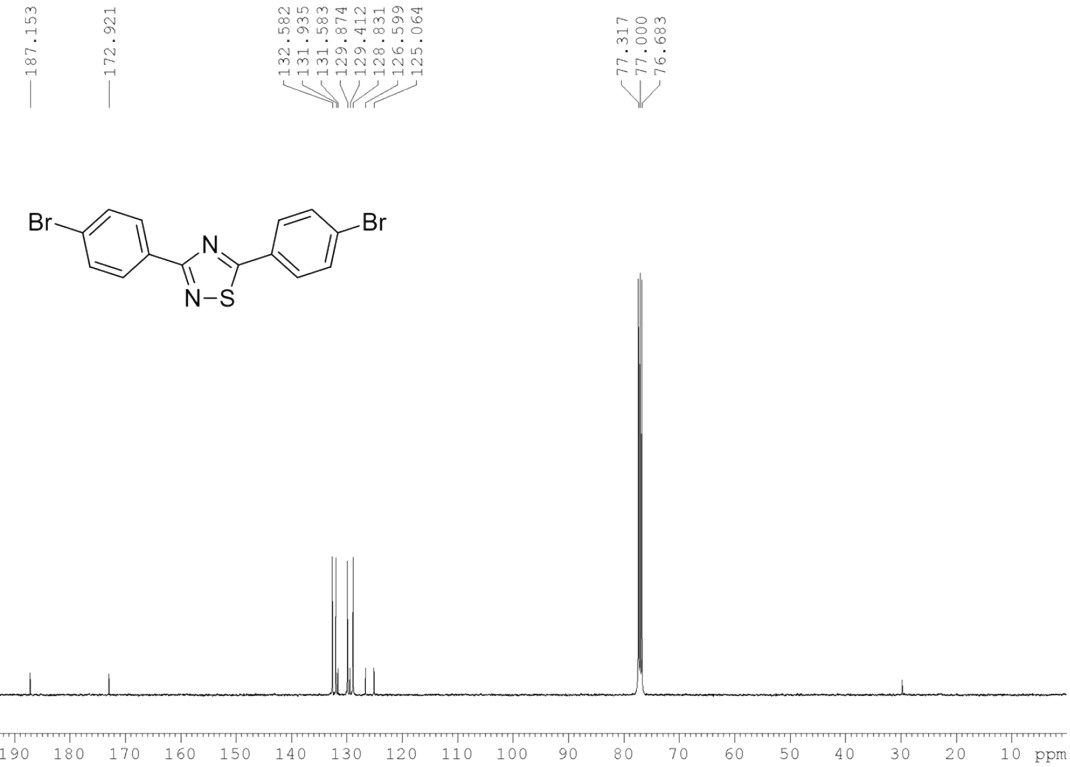
Spectrum S11 [1]H NMR spectrum of compound **2f**.



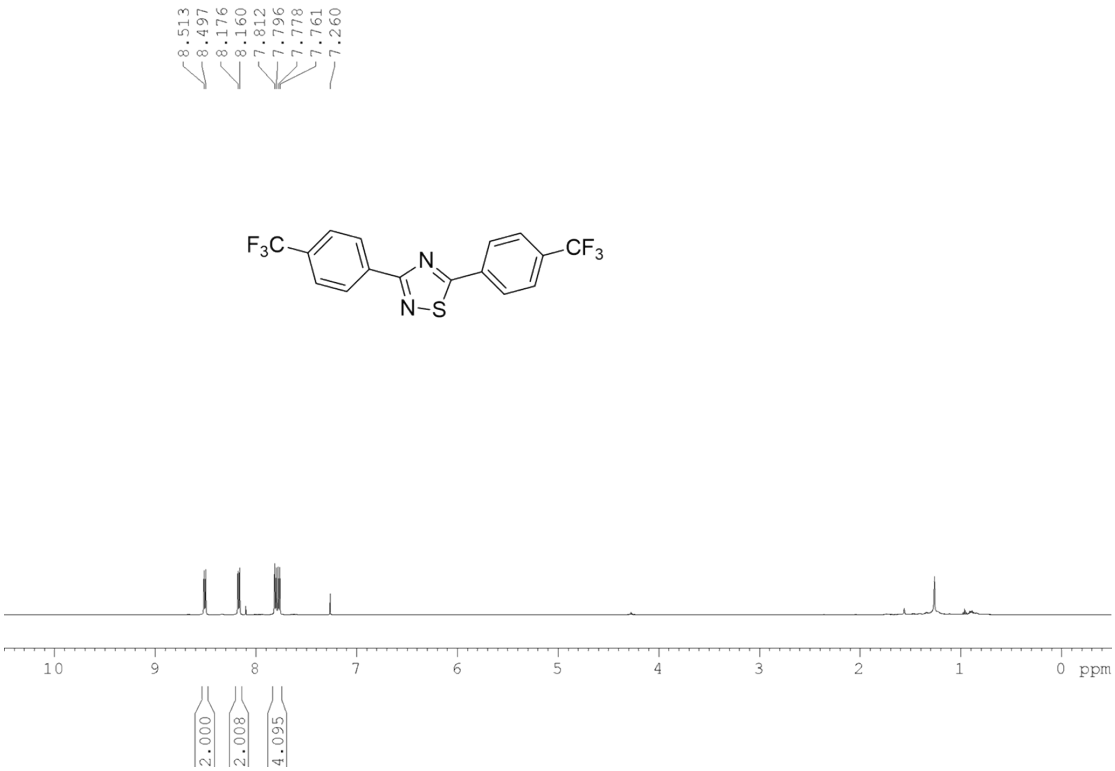
Spectrum S12 [13]C NMR spectrum of compound **2f**.



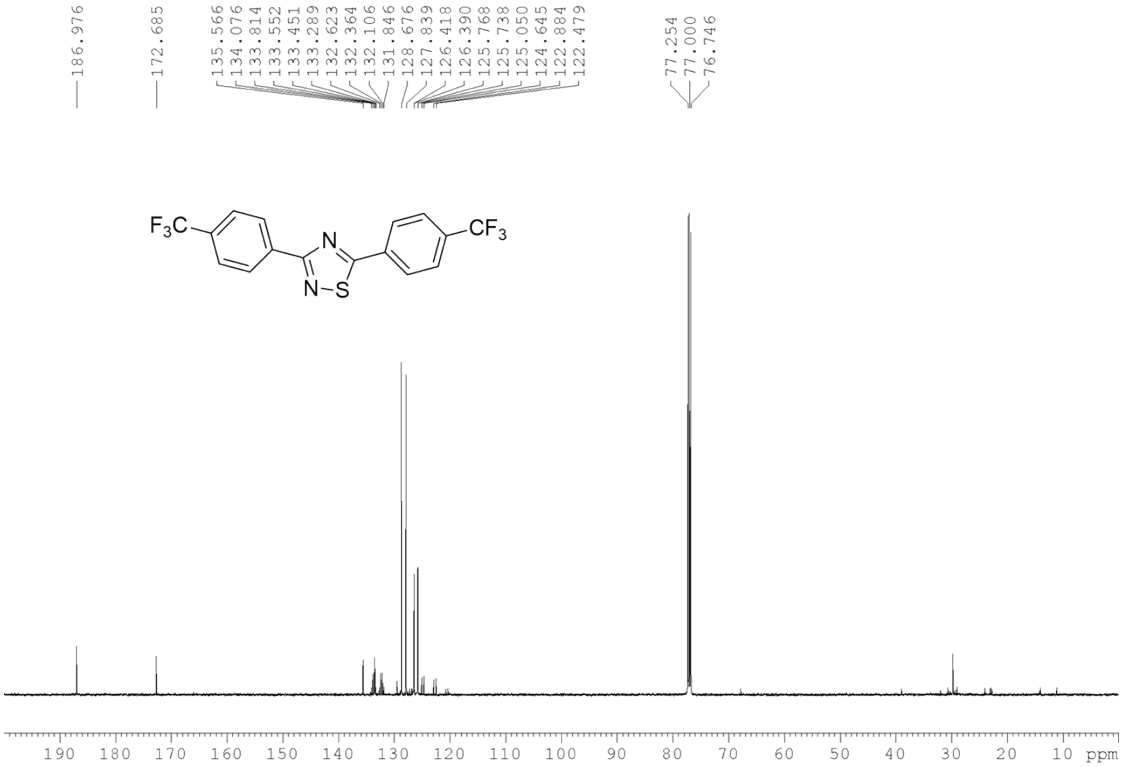
Spectrum S13 ^{1}H NMR spectrum of compound **2g**.



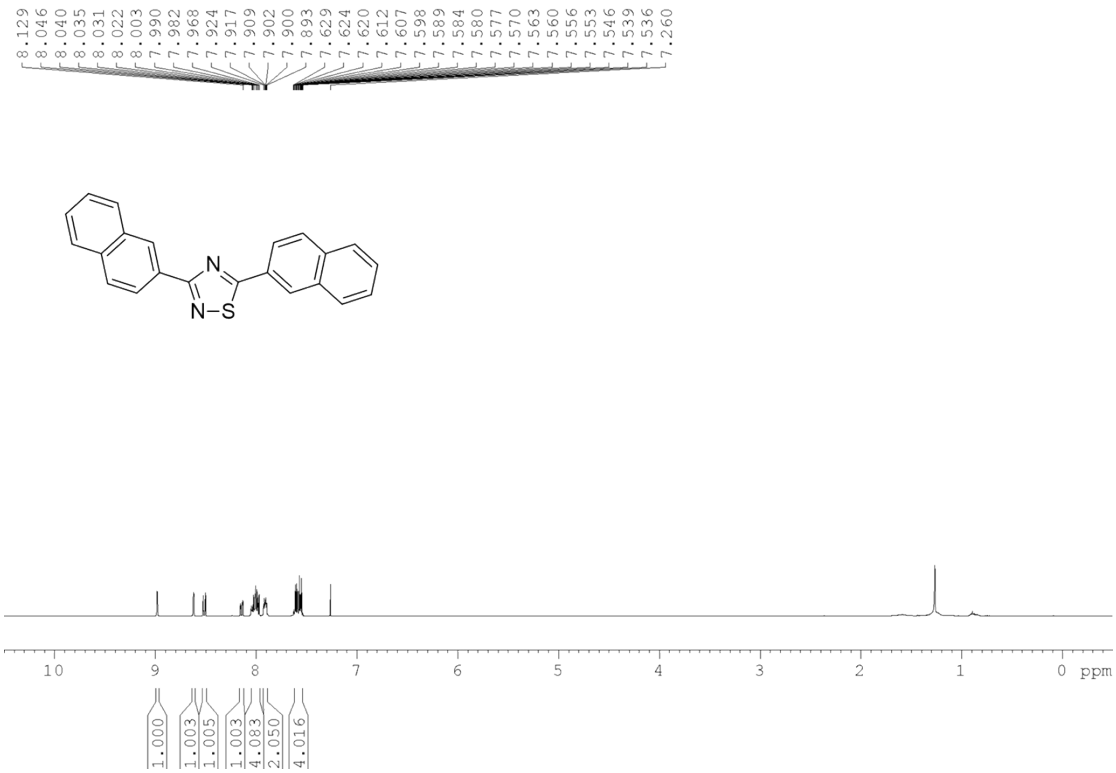
Spectrum S14 ^{13}C NMR spectrum of compound **2g**.



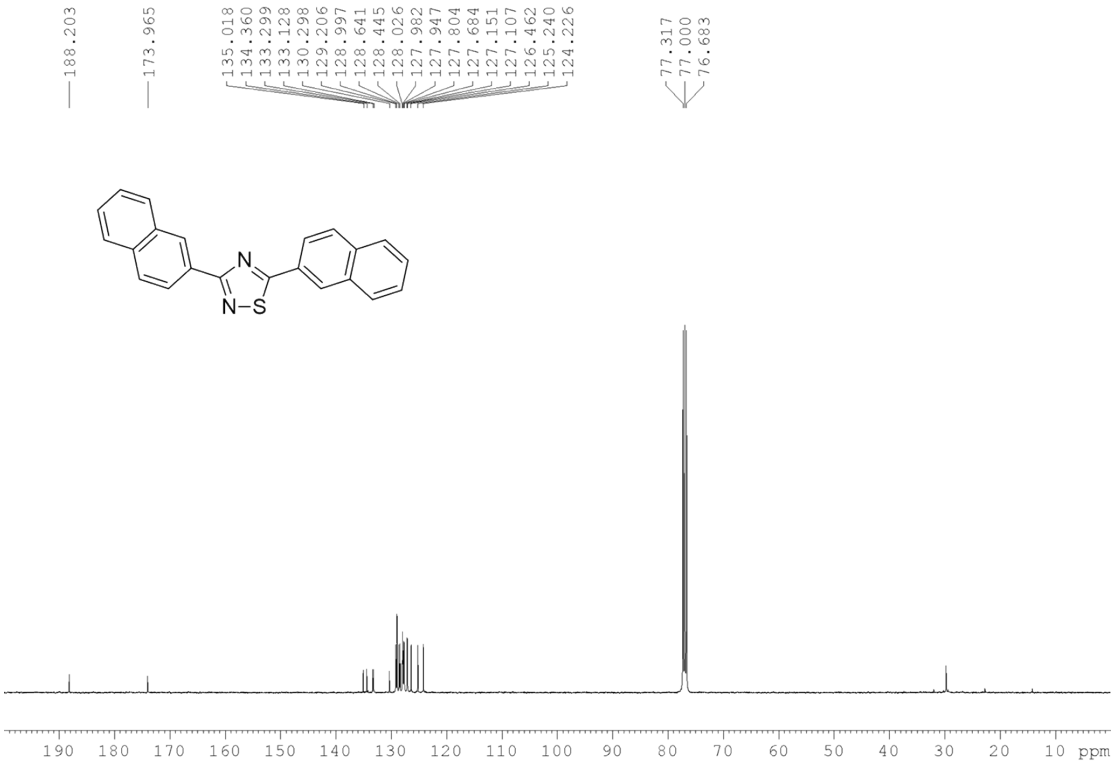
Spectrum S15 [1]H NMR spectrum of compound **2h**.



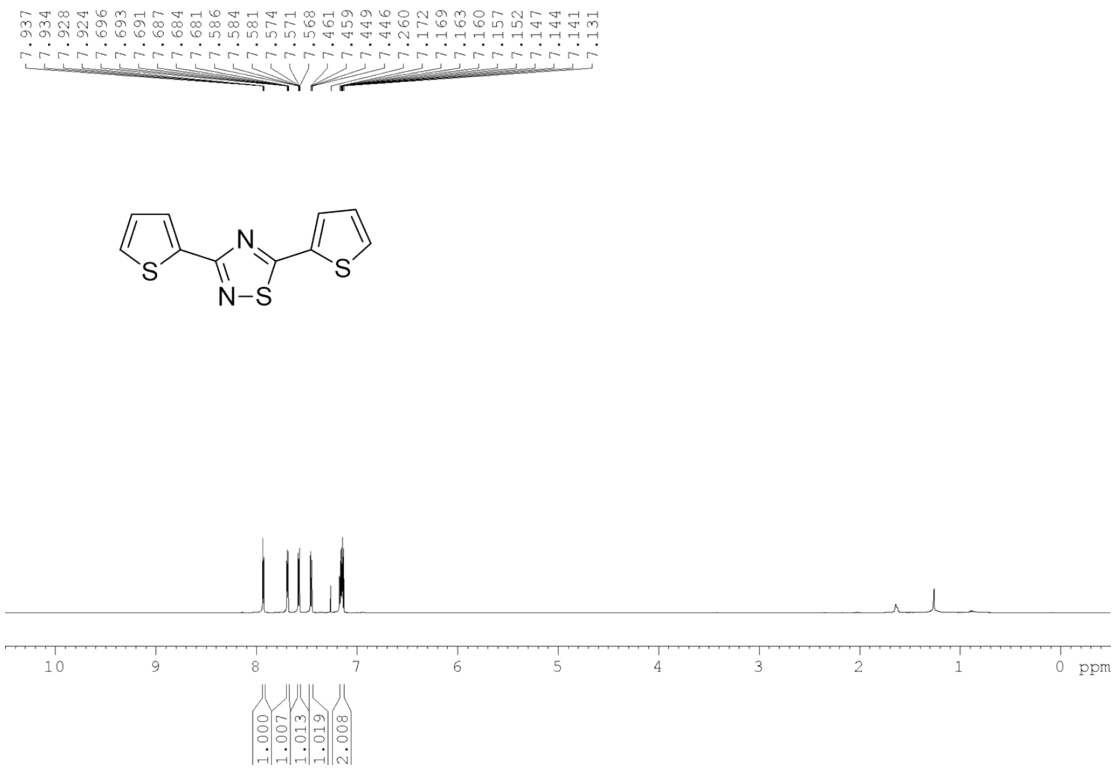
Spectrum S16 [13]C NMR spectrum of compound **2h**.



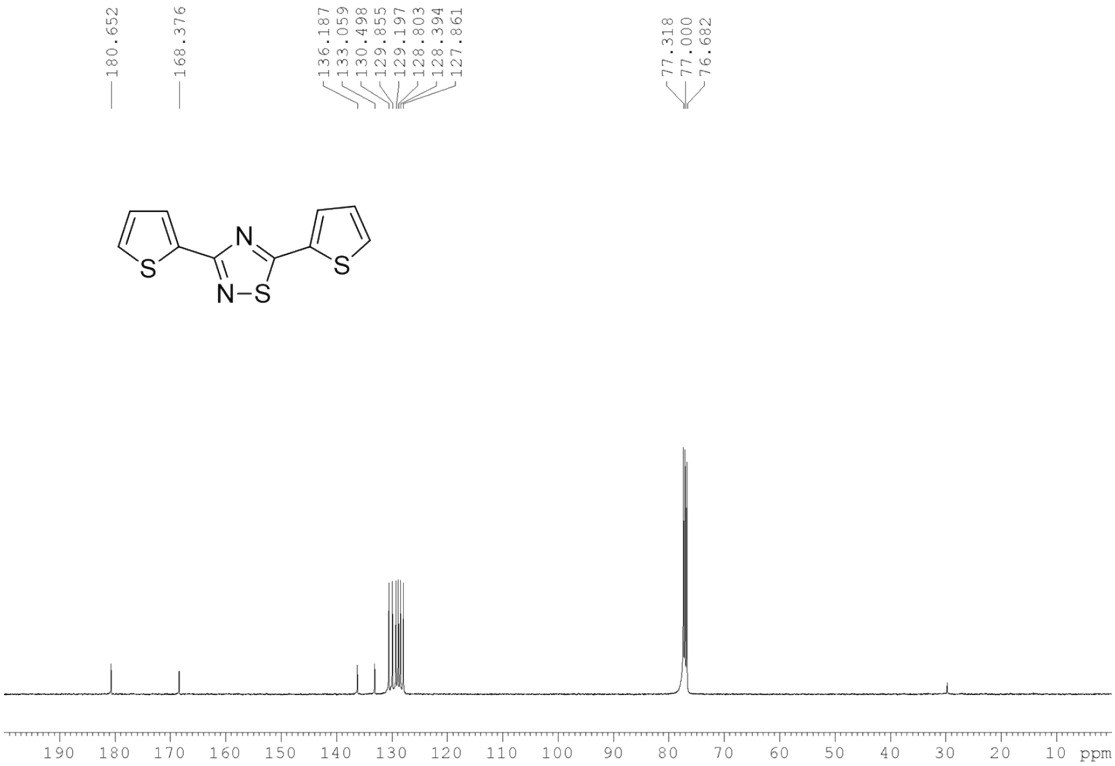
Spectrum S17 [1]H NMR spectrum of compound **2i**.



Spectrum S18 [13]C NMR spectrum of compound **2i**.



Spectrum S19 [1]H NMR spectrum of compound **2j**.



Spectrum S20 [13]C NMR spectrum of compound **2j**.