Supporting information for

Self-assembled triazole AIE-active nanofibers: synthesis, morphology and photophysical properties

Luminita Marin[1]*, Sergiu Shova[1], Carmen Dumea[2], Elena Bicu[2], Dalila Belei[2]
[1] *"Petru Poni" Institute of Macromolecular Chemistry of Romanian Academy, Iasi, Romania*
[2] *"Alexandru Ioan Cuza" University, Department of Organic Chemistry, Iasi, Romania*

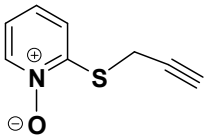
*email: lmarin@icmpp.ro

The research leading to these results has received funding from the Romanian National Authority for Scientific Research, MEN – UEFISCDI, project number PN-II-PT-PCCA-2013-4-1861 (contract number 272/2014). We also thank the POSCCE-O 2.2.1, SMIS-CSNR 13984-901, Project no.257/28.09.2010, CERNESIM, for the NMR analysis.

Experimental

Synthesis

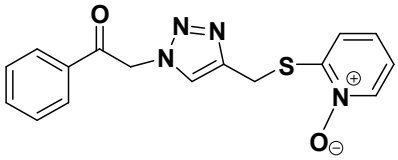
2-(prop-2-yn-1-ylthio)pyridine-N-oxide (2)



In a round bottom flask, propargyl bromide (12 mmol) was added to a suspension of sodium 2-sulfidopyridine-*N*-oxide (10 mmoli) in 15 mL CH_3CN. The reaction mixture was stirred at reflux for 48 hours. The resulting solid was collected by filtration, dried and recrystallized from ethanol to give pure 2-(prop-2-yn-1-ylthio)pyridine-*N*-oxide, as an ochre solid with a 68% yield; m.p. 134-136 °C. IR ν cm^{-1}: 3168 (νH-C≡), 2107 (νC≡C), 1588, 1553, 1472 (νC=C in aromatic rings), 1235 (νN→O), 1149 (ν pyridine), 836 (ν aromatic ring). ^{1}H NMR (DMSO-d_6, 400 MHz), δ(ppm): 8.33 (d, J = 6.4 Hz, 1H, Ar<u>H</u>); 7.41-7.49 (m, 2H, Ar<u>H</u>);

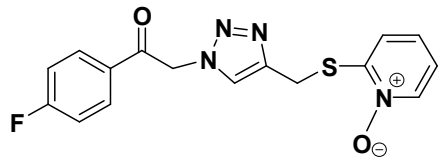
7.26 (dt, J = 8.6, 2.0 Hz, 1H, Ar<u>H</u>); 3.93 (d, J = 2.4 Hz, 2H, C<u>H</u>$_2$); 3.25 (t, J = 2.4 Hz, 1H, <u>H</u>-C≡). ^{13}C NMR (DMSO-d_6, 100 MHz), δ(ppm): 149.7 (<u>C</u>), 138.0 (<u>C</u>H), 125.4 (<u>C</u>H), 122.2 (<u>C</u>H), 121.4 (<u>C</u>H), 79.2 (<u>C</u>), 74.1 (<u>C</u>H), 17.7 (<u>C</u>H$_2$). Elemental analysis calcd (%) for C_8H_7NOS: C 58.16, H 4.27 ; found: C 58.12, H 4.24.

2-[4-(1-Oxy-pyridin-2-ylsulfanylmethyl)-[1,2,3]triazol-1-yl]-1-phenyl-ethanone (5a)



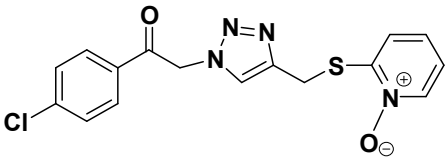
General procedure was followed by using 2-(prop-2-yl-1-ylthio)pyridine-*N*-oxide **2** (1.65 g, 10 mmol), 2-azido-1-phenylethanone **4a** (1.61 g, 10 mmol), $CuSO_4 \cdot 5H_2O$ (0.25 g, 1 mmol), sodium ascorbate (0.39 g, 2 mmol), *t*-BuOH (20 mL), MeCN (12 mL) and H_2O (8 mL) to provide triazole **5a** as a white solid in 71 % yield (2.31 g). By recrystallization from chloroform, proper crystals for single crystal X-ray diffraction analysis were obtained. IR ν cm^{-1}: 1696 (ν C=O), 1468 (ν C=C), 1224 (ν N→O), 1137 (ν pyridine), 842, 752 (ν aromatic ring). ^{1}H NMR (DMSO-d_6, 400 MHz) δ(ppm): 8.32 (d, J = 6.0, 1H, Ar<u>H</u>) 8.11 (s, 1H, Ar<u>H</u>), 8.06 (d, J = 7.2 Hz, 2H, Ar<u>H</u>), 7.74 (t, J = 7.2 Hz, 2H, Ar<u>H</u>), 7.59-7.66 (m, 2H, Ar<u>H</u>), 7.39 (t, J = 7.6 Hz, 1H, Ar<u>H</u>), 7.24 (t, J = 6.4 Hz, 1H, Ar<u>H</u>), 6.20 (s, 2H, C<u>H</u>$_2$CO), 4.40 (s, 2H, C<u>H</u>$_2$S). ^{13}C NMR (DMSO-d_6, 100 MHz) δ(ppm): 192.1 (<u>C</u>), 150.4 (<u>C</u>), 142.4 (<u>C</u>), 138.1 (<u>C</u>H), 134.2 (<u>C</u>H), 134.1 (<u>C</u>), 129.0 (2<u>C</u>H), 128.1 (2<u>C</u>H), 125.4 (<u>C</u>H), 125.3 (<u>C</u>H), 122.2 (<u>C</u>H), 121.2 (<u>C</u>H), 55.9 (<u>C</u>H$_2$), 24.4 (<u>C</u>H$_2$). Elemental analysis calcd (%) for $C_{16}H_{14}N_4O_2S$: C 58.88, H 4.32 ; found: C 58.64, H 4.27.

1-(4-Fluoro-phenyl)-2-[4-(1-oxy-pyridin-2-ylsulfanylmethyl)-[1,2,3]triazol-1-yl]-ethanone (5b)



General procedure was followed by using 2-(prop-2-yl-1-ylthio)pyridine-*N*-oxide **2** (1.65 g, 10 mmol), 2-azido-1-(4-fluoro-phenyl)-ethanone **4b** (1.79 g, 10 mmol), $CuSO_4 \cdot 5H_2O$ (0.25 g, 1 mmol), sodium ascorbate (0.39 g, 2 mmol), *t*-BuOH (20 mL), MeCN (12 mL) and H_2O (8 mL) to provide triazole **5b** as a cream solid in 72 % yield (2.47 g). By recrystallization from chloroform, white thin needle crystals were obtained. IR ν cm^{-1}: 1703 (ν C=O), 1597, 1470 (ν C=C), 1222 (ν N→O), 1160 (ν pyridine), 815, 751 (ν aromatic ring). ^{1}H NMR (DMSO-d_6, 400 MHz) δ(ppm): 8.31 (s, 1H, ArH), 8.15 (s, 2H, Ar<u>H</u>), 8.10 (s, 1H, Ar<u>H</u>), 7.64 (d, J = 7.6 Hz, 1H, Ar<u>H</u>), 7.45 (t, J = 8.4 Hz, 2H, Ar<u>H</u>), 7.38 (t, J = 7.2 Hz, 1H, Ar<u>H</u>), 7.23 (s, 1H, Ar<u>H</u>), 6.17 (s, 2H, C<u>H</u>$_2$), 4.39 (s, 2H, C<u>H</u>$_2$).^{13}C NMR (DMSO-d_6, 100 MHz) δ(ppm): 190.8 (<u>C</u>), 166.8 (<u>C</u>), 164.3 (<u>C</u>), 150.4 (<u>C</u>), 138.1 (<u>C</u>H), 131.3 (<u>C</u>H), 131.2 (<u>C</u>H), 130.9 (<u>C</u>), 125.4 (<u>C</u>H), 125.3 (<u>C</u>H), 122.2 (<u>C</u>H), 121.2 (<u>C</u>H), 116.2 (<u>C</u>H), 116.0 (<u>C</u>H), 55.8 (<u>C</u>H$_2$),24.4 (<u>C</u>H$_2$). Elemental analysis calcd (%) for $C_{16}H_{13}FN_4O_2S$: C 55.81, H 3.81 ; found: C 55.77, H 3.78.

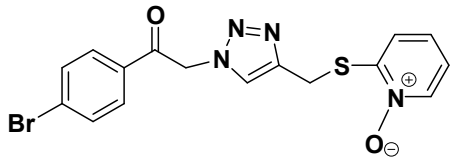
1-(4-Chloro-phenyl)-2-[4-(1-oxy-pyridin-2-ylsulfanylmethyl)-[1,2,3]triazol-1-yl] ethanone (5c)



General procedure was followed by using 2-(prop-2-yl-1-ylthio)pyridine-*N*-oxide **2** (1.65 g, 10 mmol), 2-azido-1-(4-chloro-phenyl)-ethanone **4c** (1.96 g, 10 mmol), $CuSO_4 \cdot 5H_2O$ (0.25 g, 1 mmol), sodium ascorbate (0.39 g, 2 mmol), *t*-BuOH (20 mL), MeCN (12 mL) and H_2O (8 mL) to provide triazole **5c** as a white solid in 80 % yield (2.88 g). By recrystallization

from chloroform, white thin needle crystals were obtained. IR ν cm^{-1}: 1708 (ν C=O), 1591, 1470 (ν C=C), 1220 (ν N→O), 1136 (ν pyridine), 818, 781 (ν aromatic ring). ^{1}H NMR (DMSO-d_6, 400 MHz) δ(ppm): 8.31 (d, J = 6.4 Hz, 1H, Ar<u>H</u>) 8.10 (s, 1H, Ar<u>H</u>), 8.07 (d, J = 8.4 Hz, 2H, Ar<u>H</u>), 7.69 (d, J = 8.4 Hz, 2H, Ar<u>H</u>), 7.64 (d, J = 8.4 Hz, 1H, Ar<u>H</u>), 7.39 (t, J = 8.4 Hz, 1H, Ar<u>H</u>), 7.23 (dt, J = 8.0, 6.4 Hz, 1H, Ar<u>H</u>), 6.18 (s, 2H, C<u>H</u>$_2$CO), 4.39 (s, 2H, C<u>H</u>$_2$S). ^{13}C NMR (DMSO-d_6, 100 MHz) δ(ppm): 191.3 (<u>C</u>), 150.4 (<u>C</u>), 142.5 (<u>C</u>), 139.1 (<u>C</u>), 138.1 (<u>C</u>H), 132.8 (<u>C</u>), 130.1 (2<u>C</u>H), 129.1 (2<u>C</u>H), 125.4 (<u>C</u>H), 125.2 (<u>C</u>H), 122.2 (<u>C</u>H), 121.2 (<u>C</u>H), 55.9 (<u>C</u>H$_2$), 24.4 (<u>C</u>H$_2$). Elemental analysis calcd (%) for $C_{16}H_{13}ClN_4O_2S$: C 53.26, H 3.63 ; found: C 53.21, H 3.59.

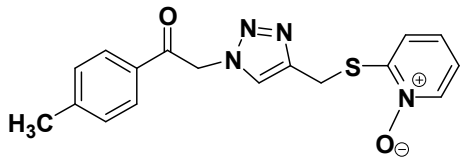
1-(4-Bromo-phenyl)-2-[4-(1-oxy-pyridin-2-ylsulfanylmethyl)-[1,2,3]triazol-1-yl]-ethanone (5d)



General procedure was followed by using 2-(prop-2-yl-1-ylthio)pyridine-*N*-oxide **2** (1.65 g, 10 mmol), 2-azido-1-(4-bromo-phenyl)-ethanone **4d** (2.4 g, 10 mmol), $CuSO_4{\cdot}5H_2O$ (0.25 g, 1 mmol), sodium ascorbate (0.39 g, 2 mmol), *t*-BuOH (20 mL), MeCN (12 mL) and H_2O (8 mL) to provide triazole **5d** as a white solid in 81 % yield (3.28 g). By recrystallization from chloroform, white thin needle crystals were obtained. By recrystallization from dimethyl formamide, proper crystals for single crystal X-ray diffraction analysis were obtained. IR ν cm^{-1}: 1698 (ν C=O), 1587, 1469 (ν C=C), 1220 (ν N→O), 1139 (ν pyridine), 817, 778 (ν aromatic ring). ^{1}H NMR (DMSO-d_6, 400 MHz) δ(ppm): 8.31 (d, J = 6.4 Hz, 1H, Ar<u>H</u>), 8.09 (s, 1H, Ar<u>H</u>), 7.99 (d, J = 8.4 Hz, 2H, Ar<u>H</u>), 7.83 (d, J = 8.4 Hz, 2H, Ar<u>H</u>), 7.64 (d, J = 8.4 Hz, 1H, Ar<u>H</u>), 7.39 (t, J = 8.0 Hz, 1H, Ar<u>H</u>), 7.23 (t, J = 6.4 Hz, 1H, Ar<u>H</u>), 6.17 (s, 2H, C<u>H</u>$_2$CO), 4.39 (s, 2H, C<u>H</u>$_2$S). ^{13}C NMR (DMSO-d_6, 100 MHz) δ(ppm): 191.3 (<u>C</u>), 150.4 (<u>C</u>),

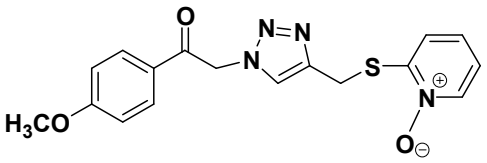
142.4 (C), 139.0 (C), 138.1 (CH), 132.6 (C), 130.1 (2CH), 128.0 (2CH), 125.3 (CH), 125.1 (CH), 122.2 (CH), 121.1 (CH), 55.9 (CH_2), 24.4 (CH_2). Elemental analysis calcd (%) for $C_{16}H_{13}BrN_4O_2S$: C 47.42, H 3.23 ; found: C 47.39, H 3.19.

2-[4-(1-Oxy-pyridin-2-ylsulfanylmethyl)-[1,2,3]triazol-1-yl]-1-*p*-tolyl-ethanone (5e)



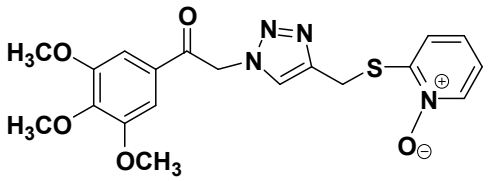
General procedure was followed by using 2-(prop-2-yl-1-ylthio)pyridine-*N*-oxide **2** (1.65 g, 10 mmol), 2-azido-1-*p*-tolyl-ethanone **4e** (1.75 g, 10 mmol), $CuSO_4 \cdot 5H_2O$ (0.25 g, 1 mmol), sodium ascorbate (0.39 g, 2 mmol), *t*-BuOH (20 mL), MeCN (12 mL) and H_2O (8 mL) to provide triazole **5e** as a white solid in 88 % yield (2.99 g). By recrystallization from ethyl acetate/acetone mixture (1/1) white crystals proper for single crystal X-ray diffraction measurements were obtained. IR ν cm^{-1}: 1697 (ν C=O), 1606, 1474 (ν C=C), 1232 (ν N→O), 1122 (ν pyridine), 841, 759 (ν aromatic ring). ^{1}H NMR (DMSO-d_6, 400 MHz) δ(ppm): 8.32 (d, J = 6.4 Hz, 1H, ArH), 8.11 (s, 1H, ArH), 7.96 (d, J = 8.0 Hz, 2H, ArH), 7.64 (d, J = 8.0 Hz, 1H, ArH), 7.36-7.42 (m, 3H, ArH), 7.23 (t, J = 6.4 Hz, 1H, ArH), 6.14 (s, 2CH, CH_2CO), 4.40 (s, 2H, CH_2S), 2.41 (s, 3H, CH_3). ^{13}C NMR (DMSO-d_6, 100 MHz) δ(ppm): 191.5 (C), 150.4 (C), 144.8 (C), 142.4 (C), 138.1 (CH), 131.6 (C), 129.5 (2CH), 128.2 (2CH), 125.4 (CH), 125.3 (CH), 122.2 (CH), 121.2 (CH), 55.8 (CH_2), 24.4 (CH_2),21.3 (CH_3). Elemental analysis calcd (%) for $C_{17}H_{16}N_4O_2S$: C 59.98, H 4.74 ; found: C 59.93, H 4.70.

1-(4-Methoxy-phenyl)-2-[4-(1-oxy-pyridin-2-ylsulfanylmethyl)-[1,2,3]triazol-1-yl]-ethanone (5f)



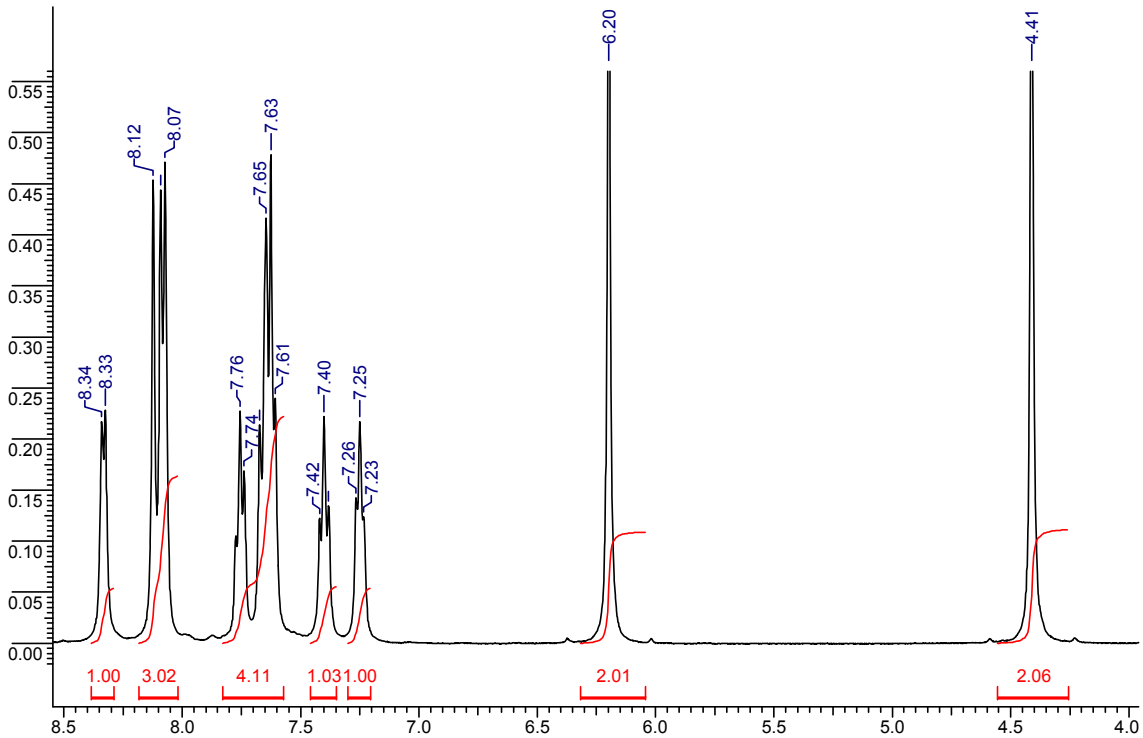
General procedure was followed by using 2-(prop-2-yl-1-ylthio)pyridine-*N*-oxide **2** (1.65 g, 10 mmol), 2-azido-1-(4-methoxy-phenyl)-ethanone **4f** (1.91 g, 10 mmol), $CuSO_4 \cdot 5H_2O$ (0.25 g, 1 mmol), sodium ascorbate (0.39 g, 2 mmol), *t*-BuOH (20 mL), MeCN (12 mL) and H_2O (8 mL) to provide triazole **5f** as a yellowish solid in 75 % yield (2.67 g). Recrystallization from 1:1 ethyl acetate/acetone mixture gave white crystals suitable for single crystal X-ray analysis. IR ν cm^{-1}: 1685 (ν C=O), 1603, 1575, 1509 (ν C=C), 1237 (ν N→O), 1022 (ν pyridine), 820, 762(ν aromatic ring). ^{1}H NMR (DMSO-d_6, 400 MHz) δ(ppm): 8.31 (d, J = 6.4 Hz, 1H, Ar<u>H</u>), 8.09 (s, 1H, Ar<u>H</u>), 8.04 (d, J = 8.0 Hz, 2H, Ar<u>H</u>), 7.64 (d, J = 8.0 Hz, 1H, Ar<u>H</u>), 7.38 (t, J = 8.0 Hz, 1H, Ar<u>H</u>), 7.23 (t, J = 6.4 Hz, 1H, Ar<u>H</u>), 7.12 (d, J = 8.8 Hz, 2H, Ar<u>H</u>), 6.11 (s, 2H, C<u>H</u>$_2$), 4.39 (s, 2H, C<u>H</u>$_2$), 3.88 (s, 3H, C<u>H</u>$_3$). ^{13}C NMR (DMSO-d_6, 100 MHz) δ(ppm): 190.3 (<u>C</u>), 163.9 (<u>C</u>), 150.4 (<u>C</u>), 142.3 (<u>C</u>), 138.1 (<u>C</u>H), 130.5 (2<u>C</u>H), 126.9 (<u>C</u>), 125.3 (2<u>C</u>H), 122.2 (<u>C</u>H), 121.2 (<u>C</u>H), 114.2 (2<u>C</u>H), 55.7 (<u>C</u>H$_3$), 55.5 (<u>C</u>H$_2$), 24.4 (<u>C</u>H$_2$). Elemental analysis calcd (%) for $C_{17}H_{16}N_4O_3S$: C 57.29, H 4.52 ; found: C 57.25, H 4.48.

2-[4-(1-Oxy-pyridin-2-ylsulfanylmethyl)-[1,2,3]triazol-1-yl]-1-(3,4,5-trimethoxy-phenyl)-ethanone (5g)

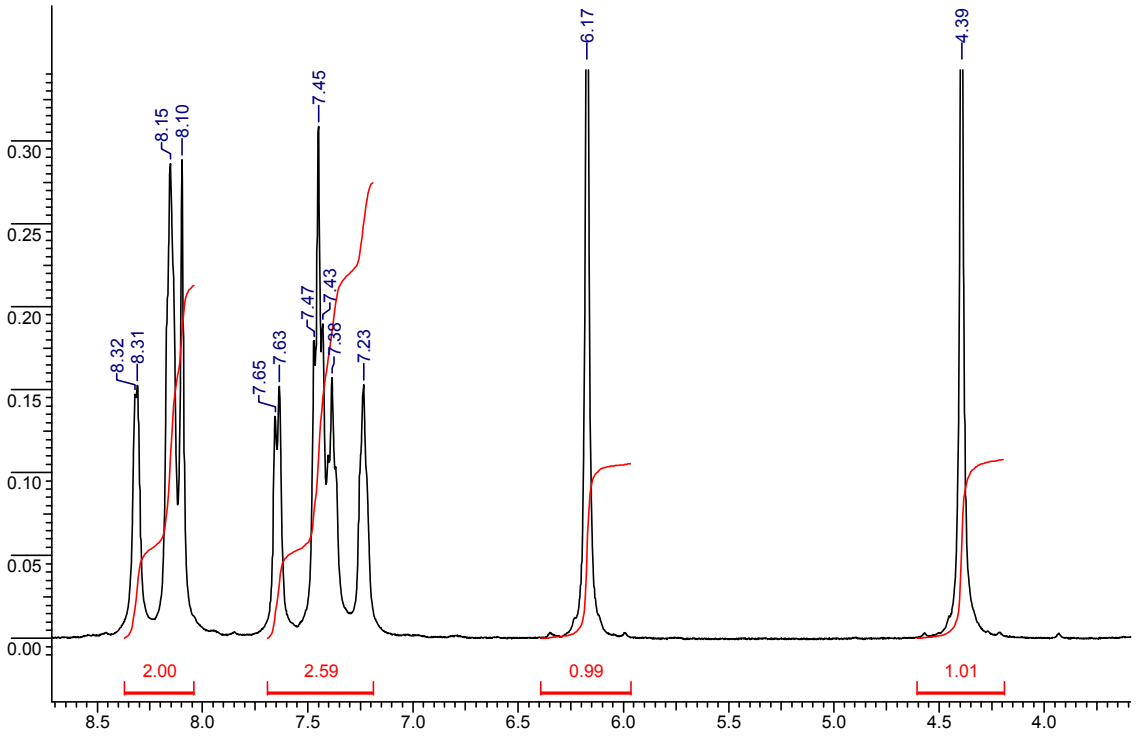


General procedure was followed by using 2-(prop-2-yl-1-ylthio)pyridine-*N*-oxide **2** (1.65 g, 10 mmol), 2-azido-1-(3,4,5-trimethoxy-phenyl)-ethanone **4g** (2.51 g, 10 mmol), $CuSO_4 \cdot 5H_2O$ (0.25 g, 1 mmol), sodium ascorbate (0.39 g, 2 mmol), *t*-BuOH (20 mL), MeCN (12 mL) and H_2O (8 mL) to provide triazole **5g** as a white solid in 75 % yield (3.12 g). By recrystallization from ethyl acetate, white thin needle crystals were obtained. IR ν cm^{-1}: 2910, 2837 (ν C-H), 1700 (ν C=O), 1584, 1504 (ν C=C), 1232 (ν N→O), 1122 (ν pyridine), 822,

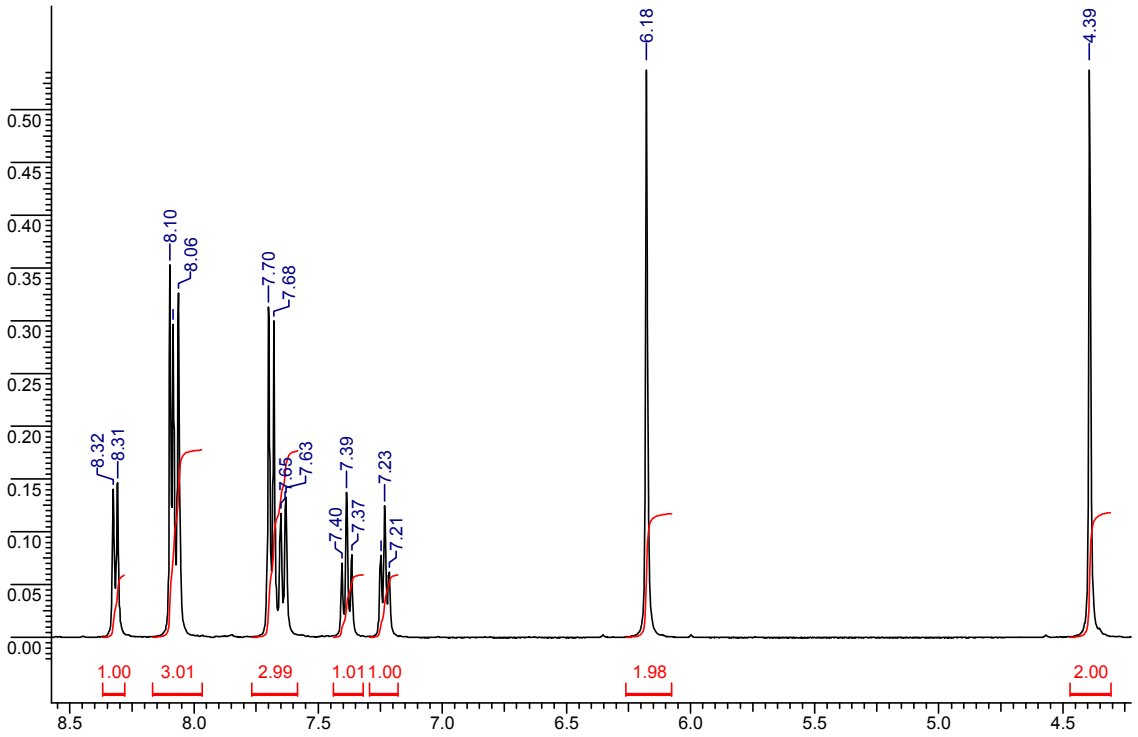
753 (ν aromatic ring). ^{1}H NMR (DMSO-d_6, 400 MHz), δ(ppm): 8.32 (d, J = 6.4 Hz, 1H, Ar<u>H</u>), 8.11 (s, 1H, Ar<u>H</u>), 7.63 (d, J = 8.4 Hz, 1H, Ar<u>H</u>), 7.36-7.41 (m, 3H, Ar<u>H</u>), 7.22 (t, J = 6.4 Hz, 1H, ArH), 6.19 (s, 2CH, C<u>H</u>$_2$CO), 4.40 (s, 2H, C<u>H</u>$_2$S). 3.88 (s, 6H, 2 x OC<u>H</u>$_3$), 3.79 (s, 3H, OC<u>H</u>$_3$). ^{13}C NMR (DMSO-d_6, 100 MHz) δ(ppm): 191.1 (<u>C</u>), 174.5 (<u>C</u>), 153.0 (<u>C</u>), 150.4 (<u>C</u>), 142.6 (<u>C</u>), 142.5 (<u>C</u>), 138.1 (<u>C</u>H), 129.3 (<u>C</u>), 125.4 (<u>C</u>H), 125.3 (<u>C</u>H), 122.2 (<u>C</u>H), 121.3 (<u>C</u>H), 105.8 (2<u>C</u>H), 60.3 (<u>C</u>H$_3$), 56.2 (2<u>C</u>H$_3$), 55.9 (<u>C</u>H$_2$), 24.4 (<u>C</u>H$_2$). Elemental analysis calcd (%) for $C_{19}H_{20}N_4O_5S$: C 54.81, H 4.84 ; found: C 54.77, H 4.80.



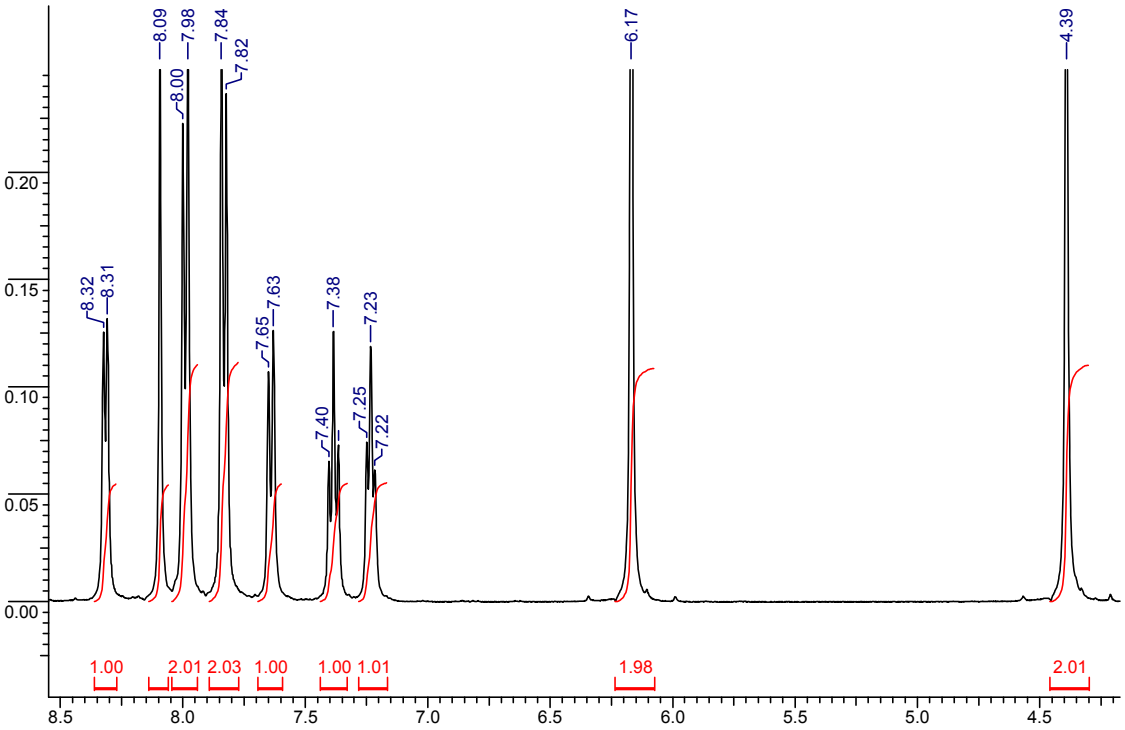
a) **5a**


8.32
8.31
8.15
8.10
7.65
7.63
7.47
7.45
7.43
7.38
7.23
6.17
4.39
2.00
2.59
0.99
1.01

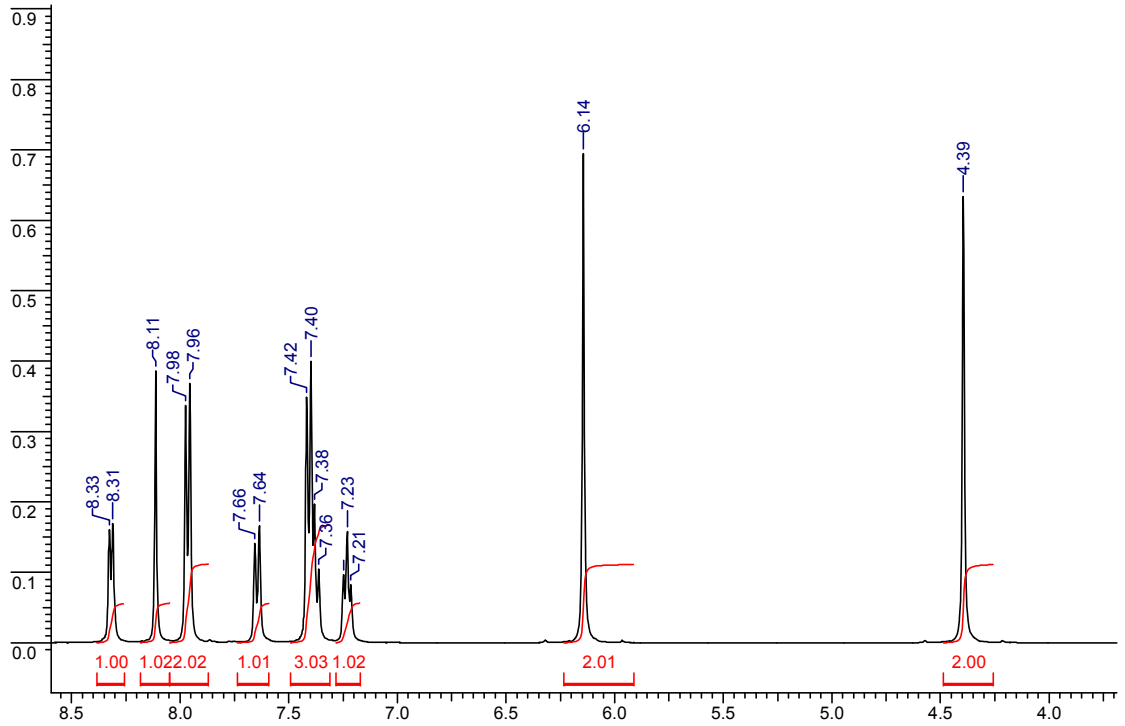
b) **5b**


8.32
8.31
8.10
8.06
7.70
7.68
7.65
7.63
7.40
7.39
7.37
7.23
7.21
6.18
4.39
1.00
3.01
2.99
1.01
1.00
1.98
2.00

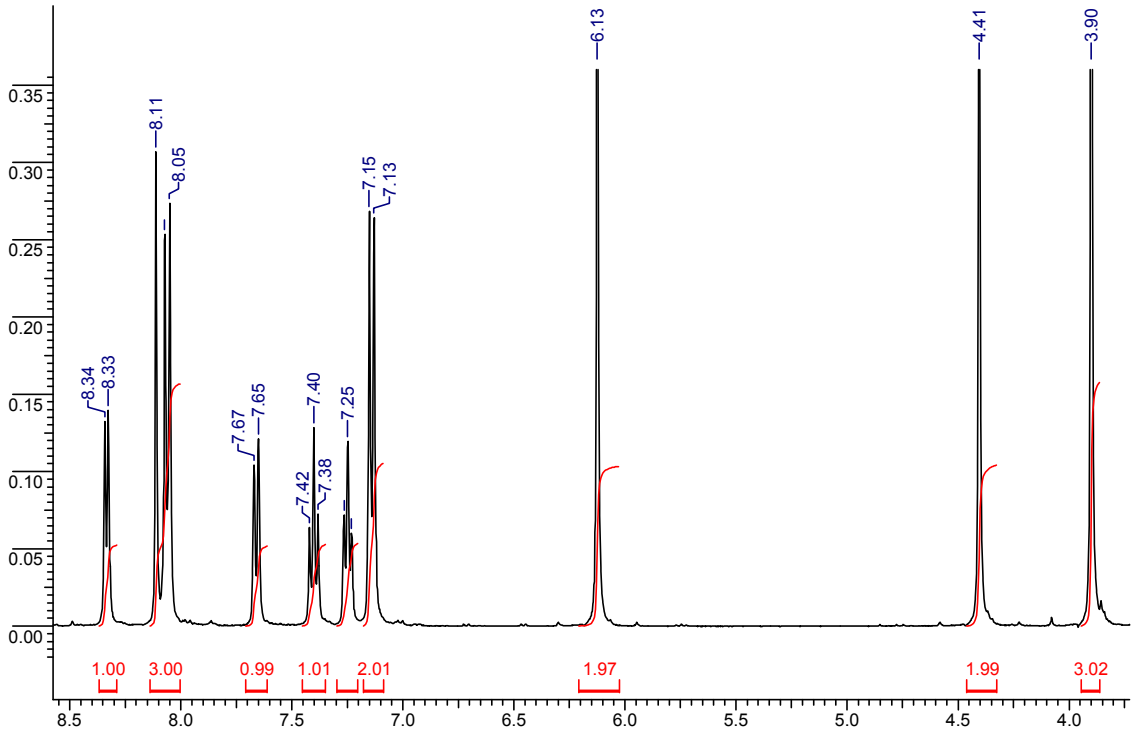
c) **5c**


8.09
7.98
7.84
7.82
8.00
6.17
4.39
8.32
8.31
7.65
7.63
7.38
7.23
7.40
7.25
7.22
0.20
0.15
0.10
0.05
0.00
1.00
2.01
2.03
1.00
1.00
1.01
1.98
2.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5

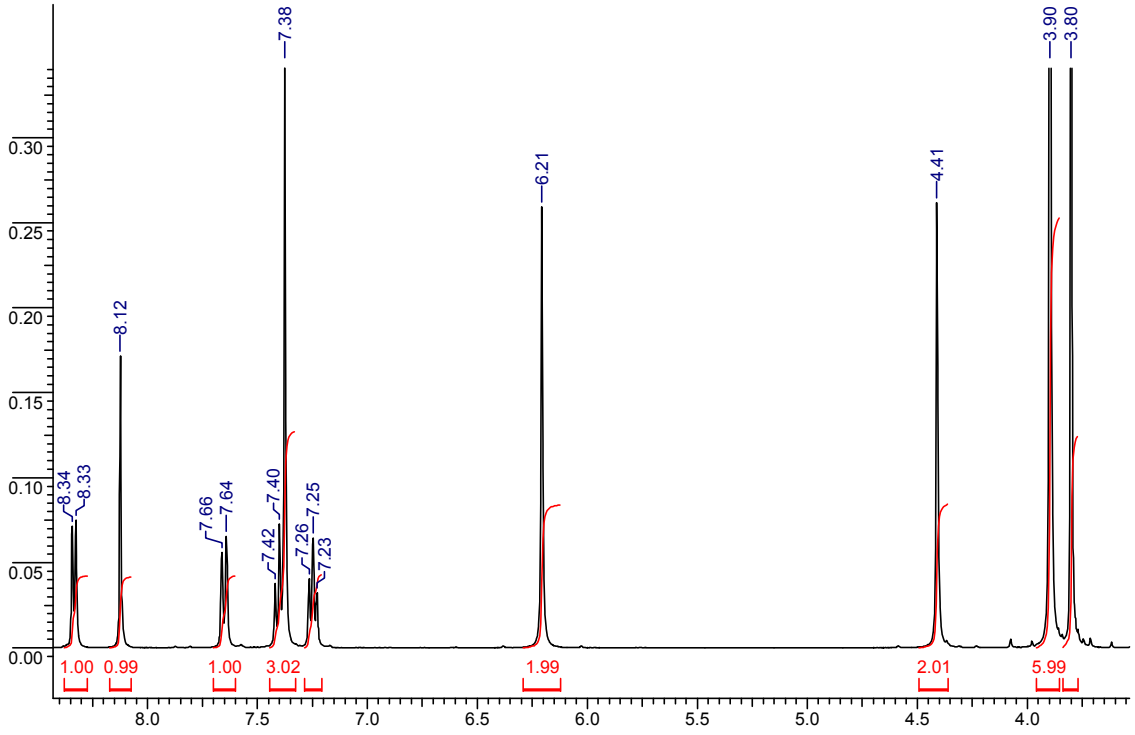
d) **5d**


6.14
4.39
8.11
7.98
7.96
7.42
7.40
8.33
8.31
7.66
7.64
7.38
7.36
7.23
7.21
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
1.00
1.02
2.02
1.01
3.03
1.02
2.01
2.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0

e) **5e**

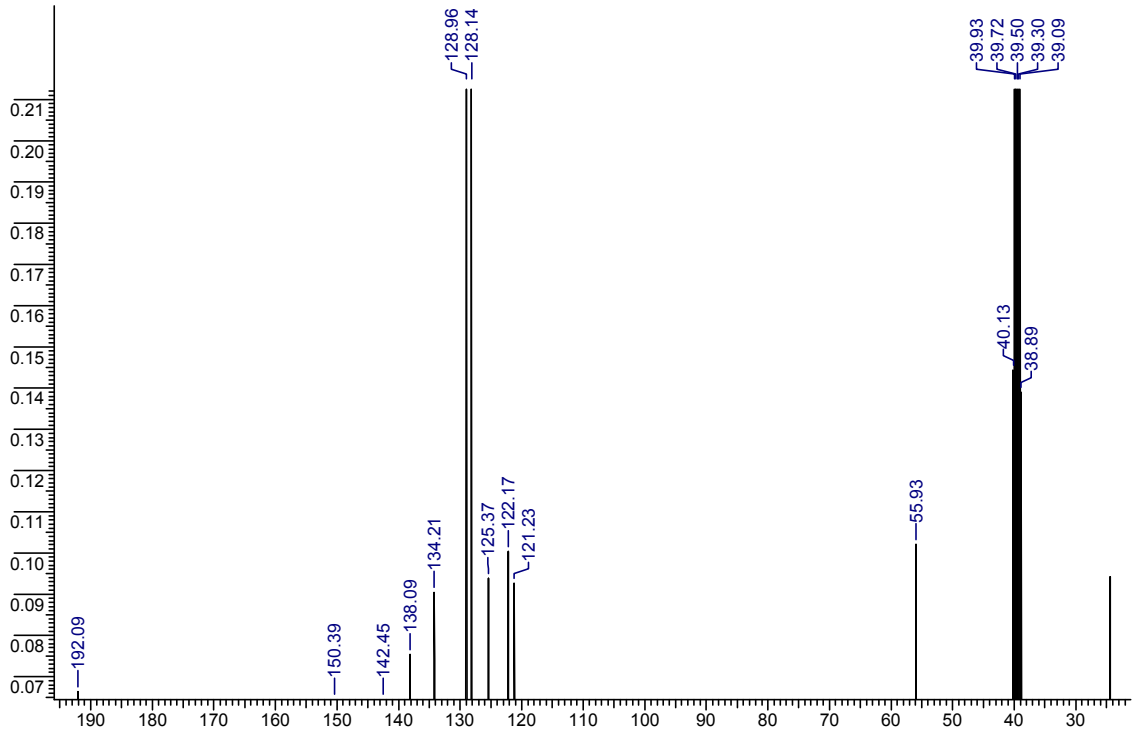


f) **5f**

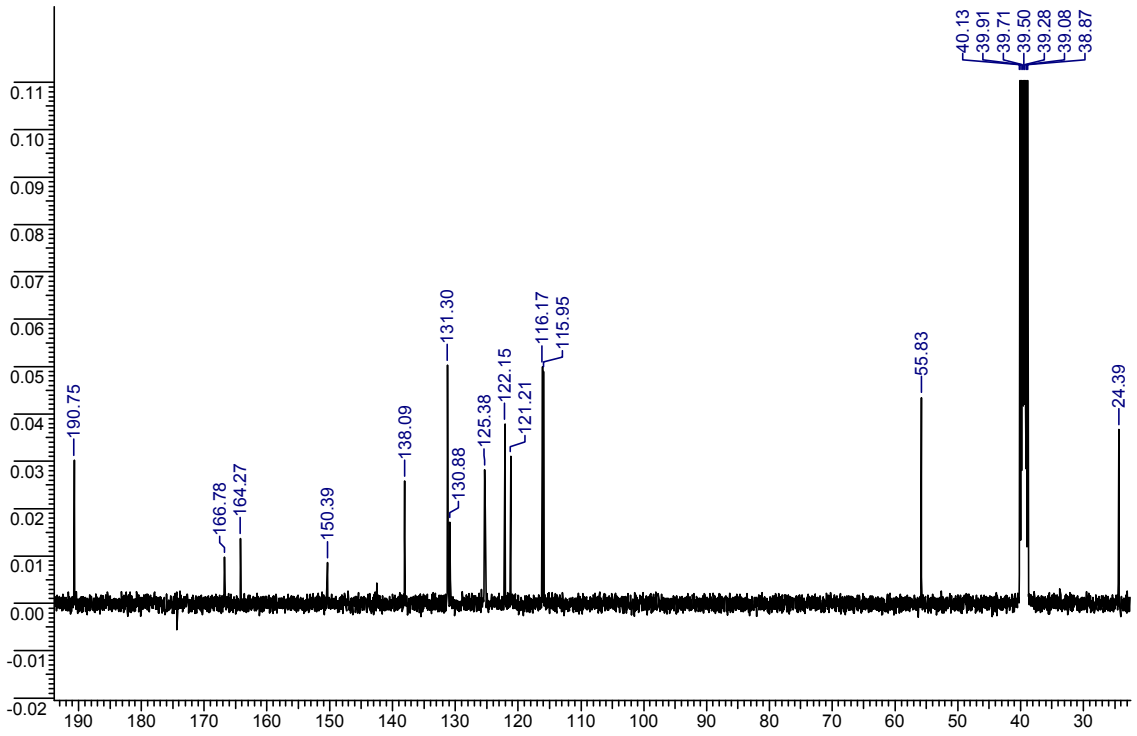


g) **5g**

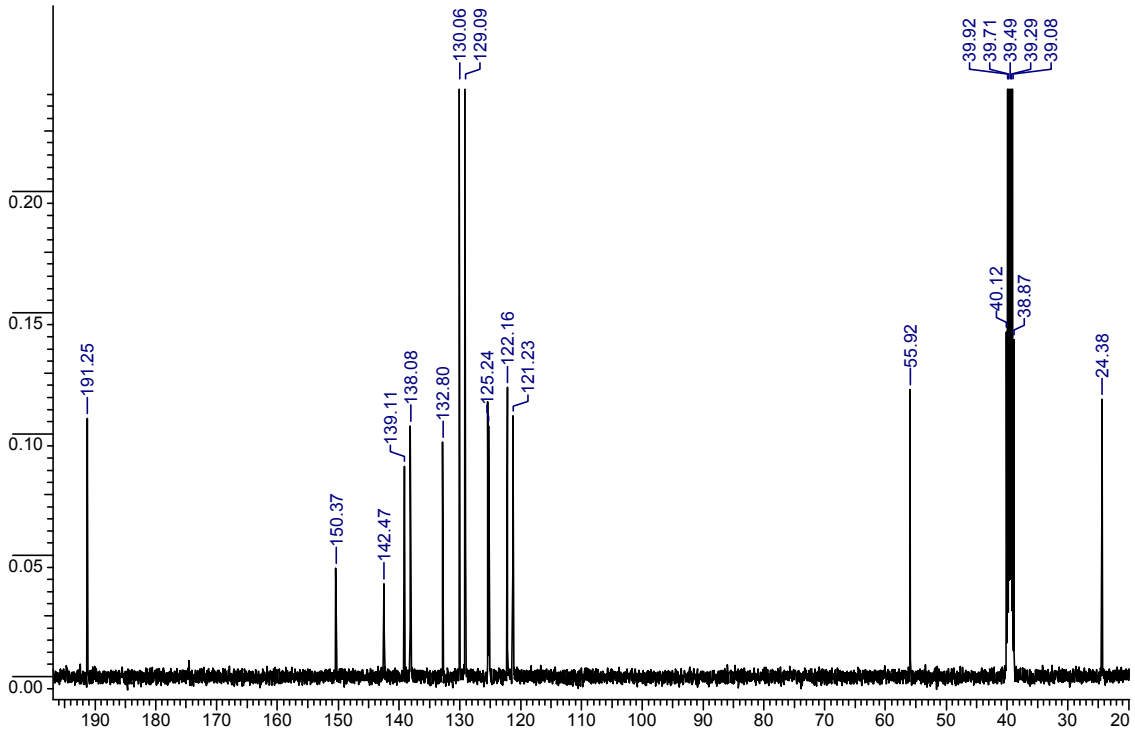
Figure 1s. ^{1}H-NMR spectra of the understudy triazoles


128.96
128.14
39.93
39.72
39.50
39.30
39.09
40.13
38.89
192.09
150.39
142.45
138.09
134.21
125.37
122.17
121.23
55.93

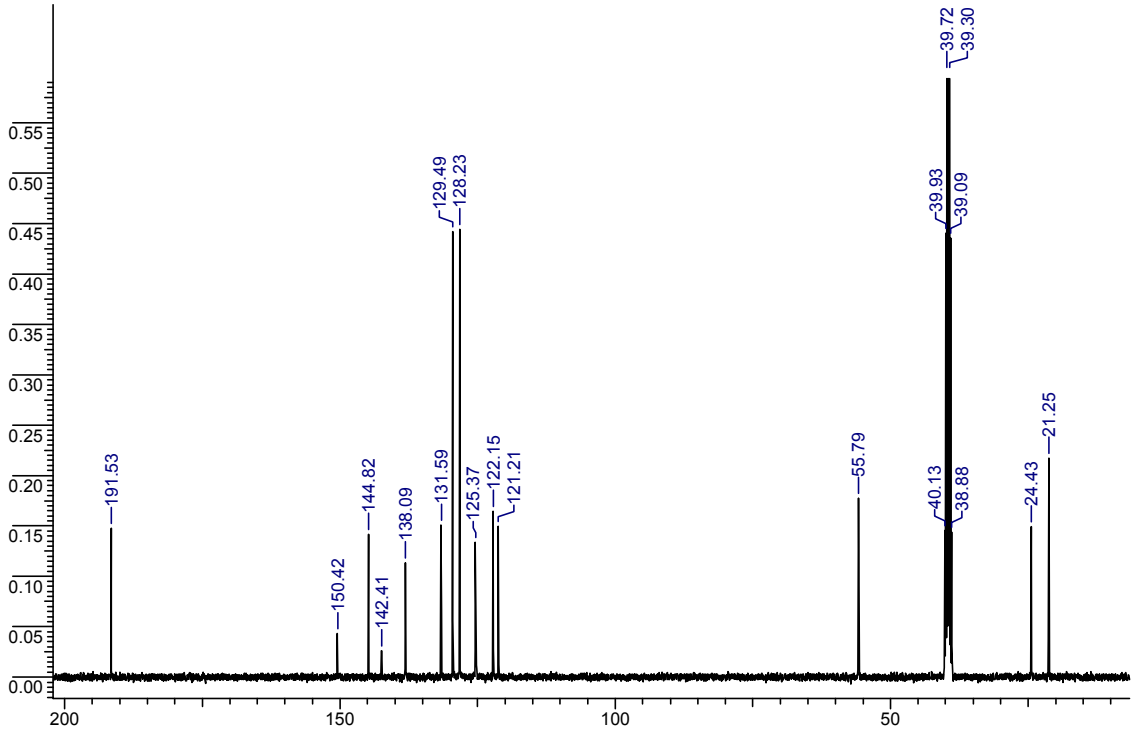
a) **5a**


40.13
39.91
39.71
39.50
39.28
39.08
38.87
190.75
166.78
164.27
150.39
138.09
131.30
130.88
125.38
122.15
121.21
116.17
115.95
55.83
24.39

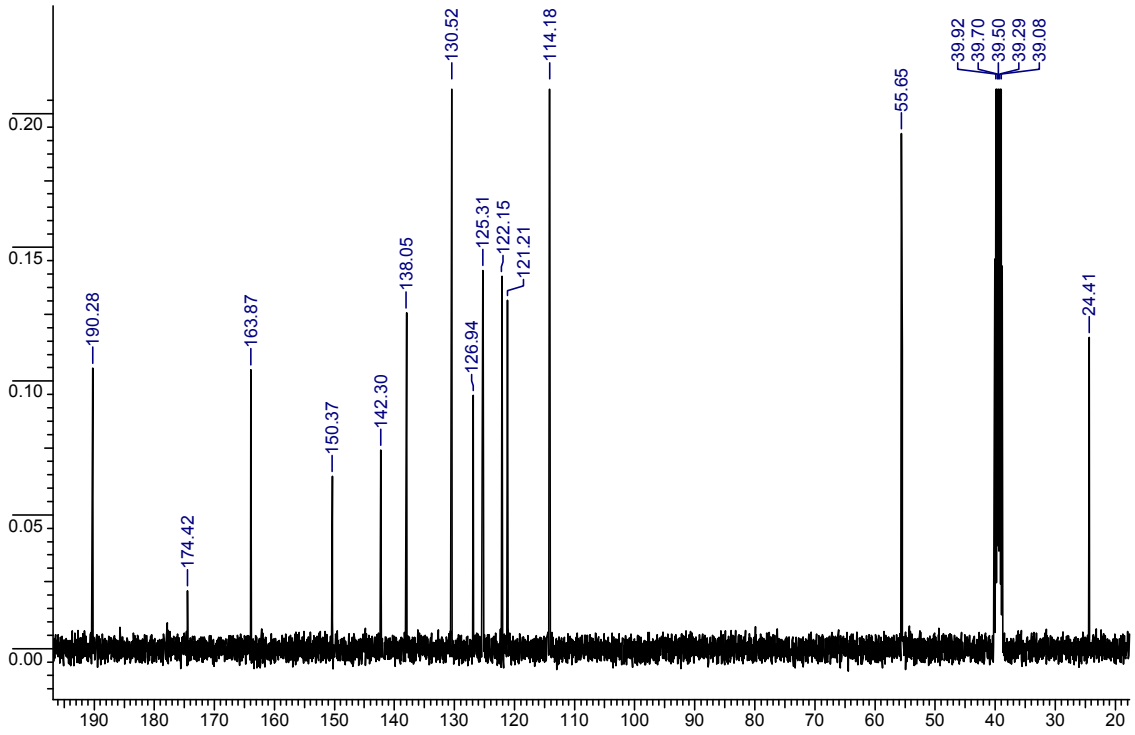
b) **5b**


191.25
150.37
142.47
139.11
138.08
132.80
130.06
129.09
125.24
122.16
121.23
55.92
40.12
39.92
39.71
39.49
39.29
39.08
38.87
24.38

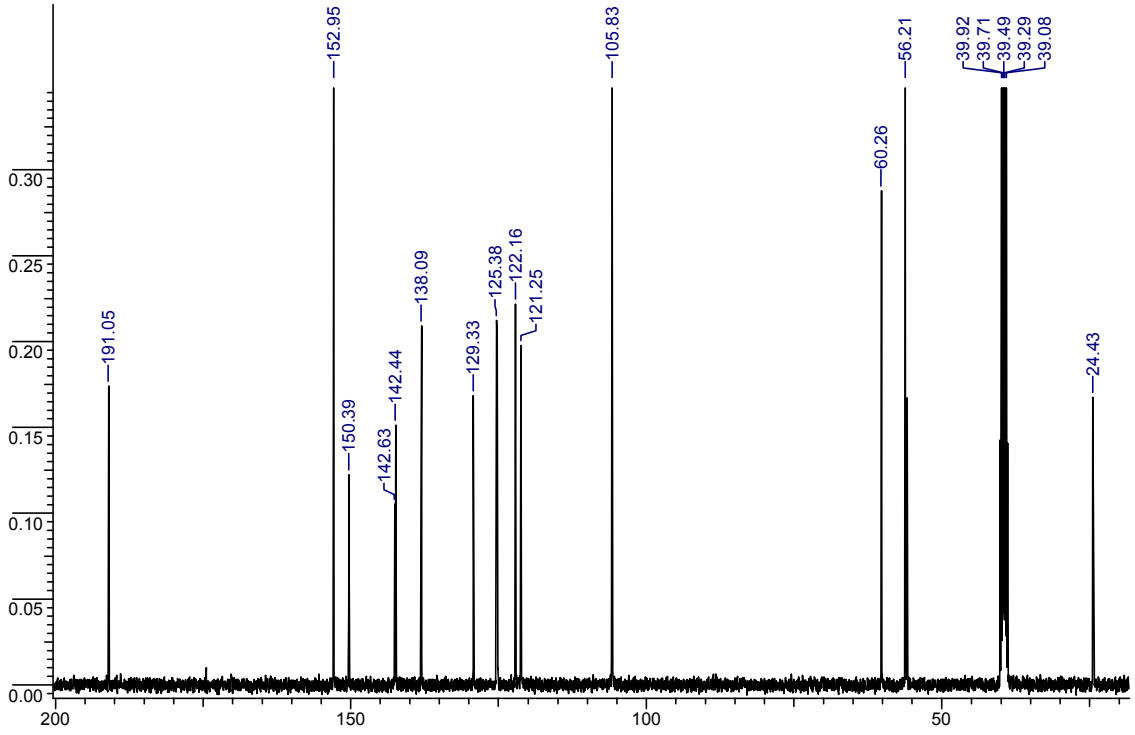
c) **5c**


191.53
150.42
144.82
142.41
138.09
131.59
129.49
128.23
125.37
122.15
121.21
55.79
40.13
39.93
39.72
39.30
39.09
38.88
24.43
21.25

d) **5e**



e) **5f**

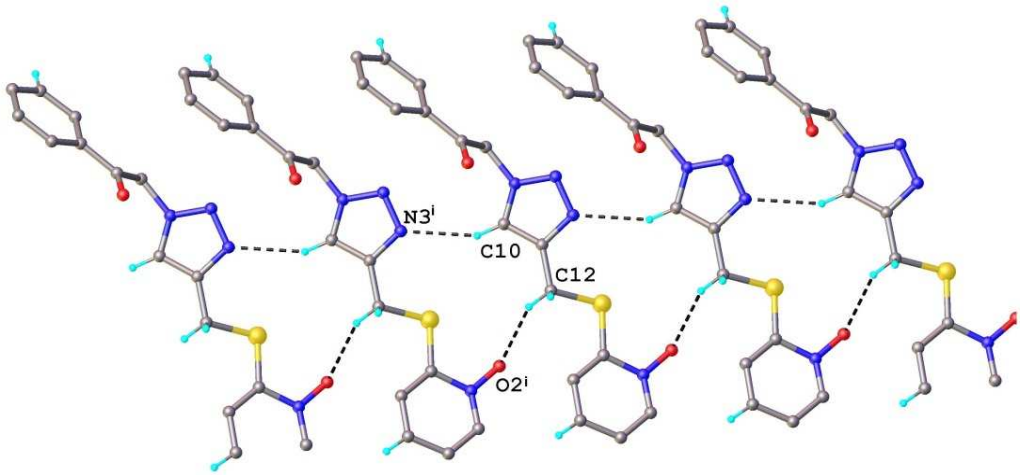


f) **5g**

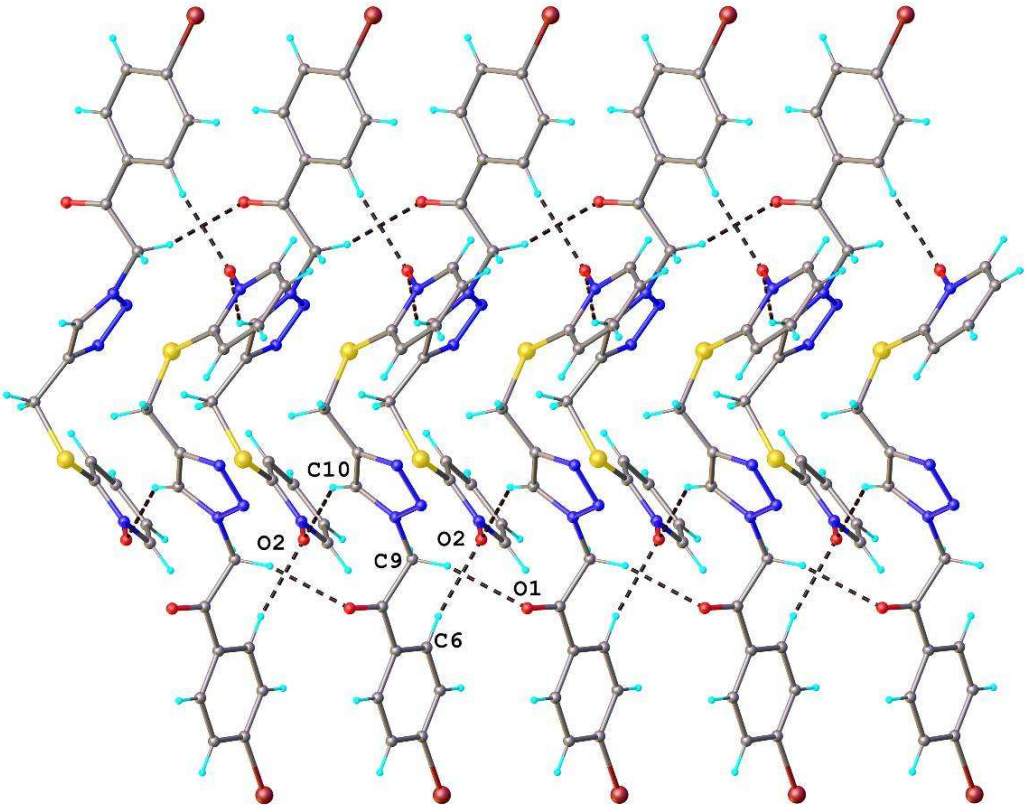
Figure 2s. ^{13}C-NMR spectra of the understudy triazoles

a) **5b**, 200x, RT b) **5f**, 200x, RT

Figure 3s. Representative images of the amorphous films under polarized light



a)



b)

Figure 4s. A view of the supramolecular ribbons in the crystal structure of a) **5a**; and b) **5d**. The hydrogen atoms not involved in hydrogen bonds were omitted for clarity. The π-π stacked aromatic rings were shown in orange.

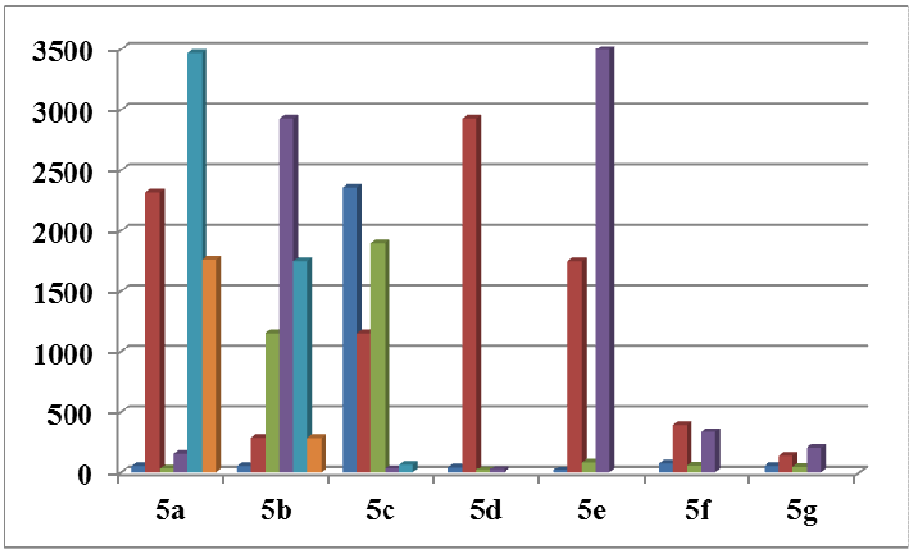
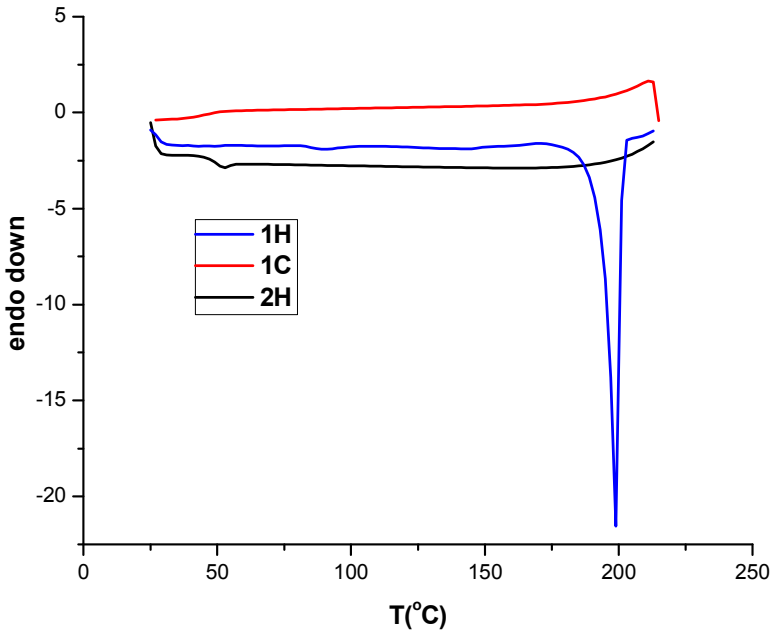
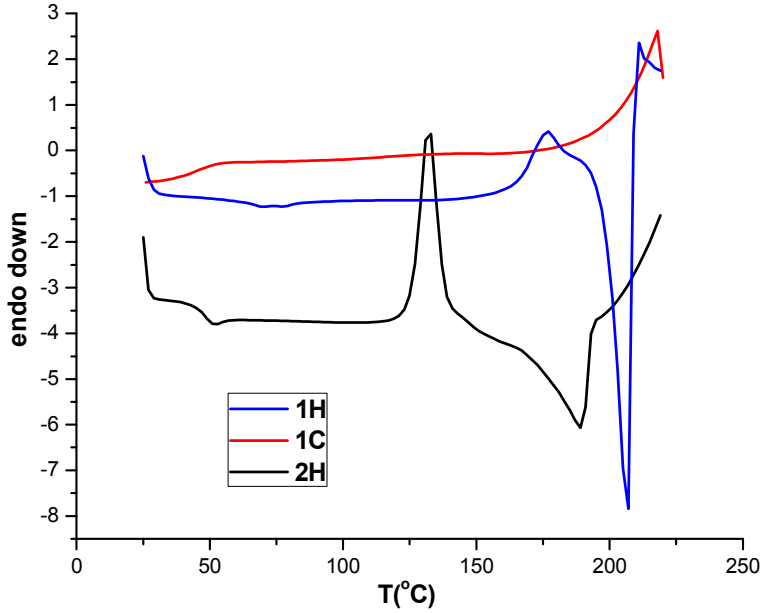


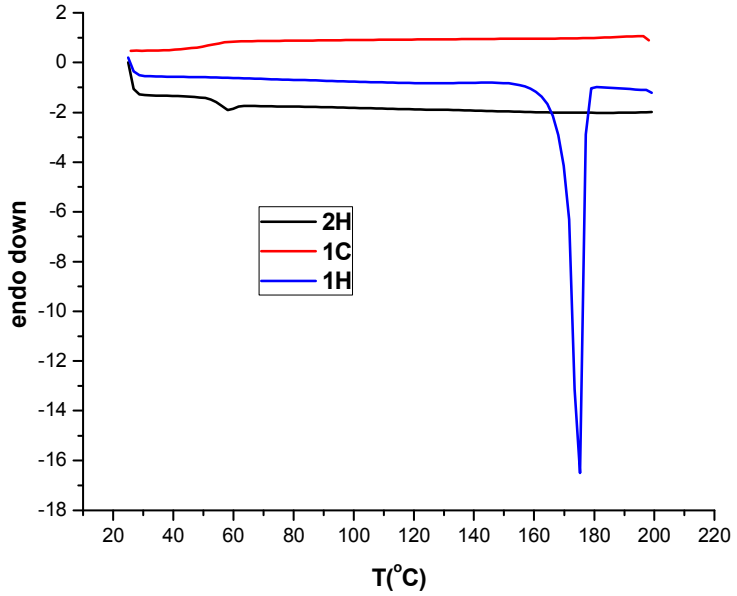
Figure 5 Graphical representation of the fiber diameter in nm, as determined by DLS on water suspensions ($11x10^{-5}$ M, water fraction 99.6)



a) 5a

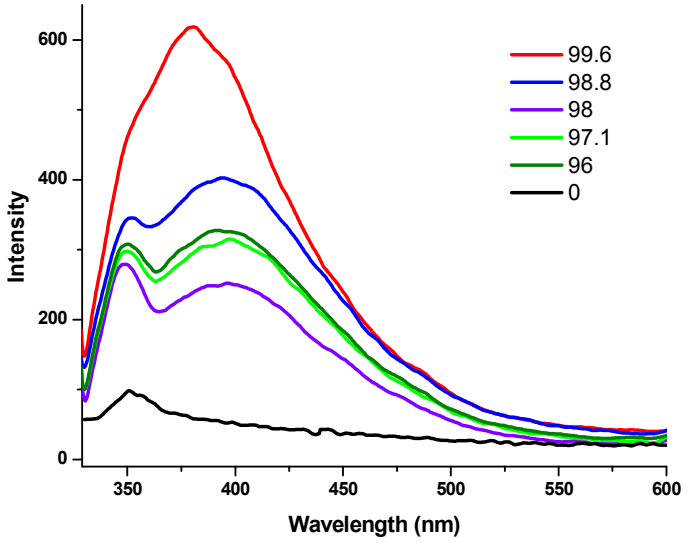


b) **5b**

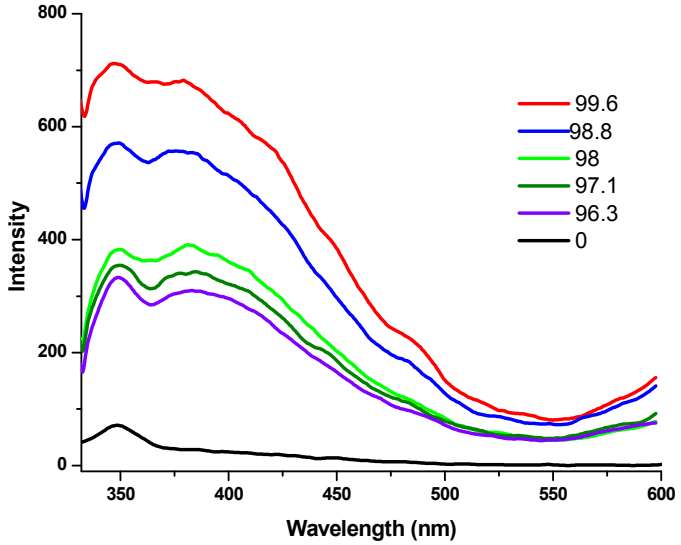


c) 5f

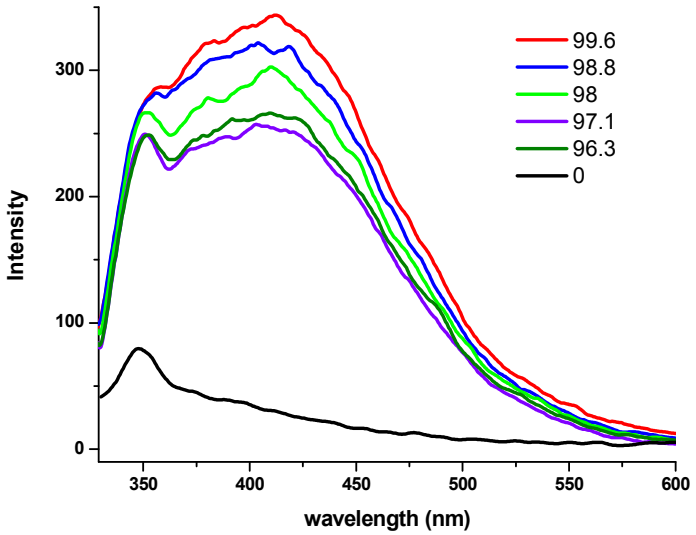
Figure 6s. Representative DSC curves


Intensity
Wavelength (nm)
0
200
400
600
350
400
450
500
550
600
99.6
98.8
98
97.1
96
0

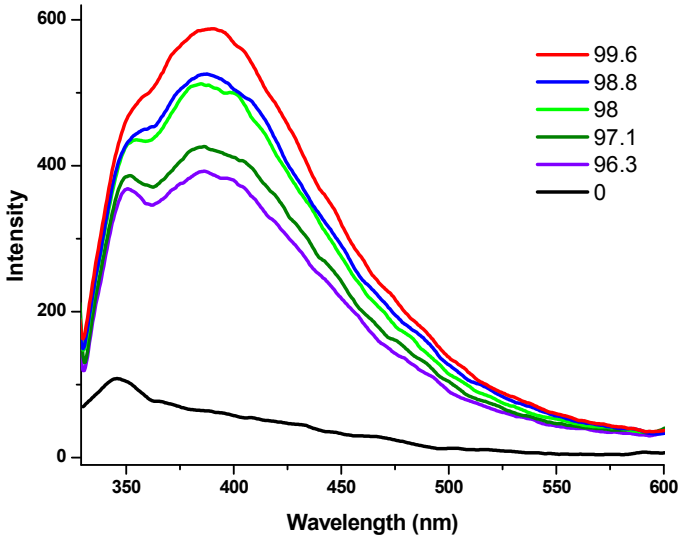
a) 5a


Intensity
Wavelength (nm)
0
200
400
600
800
350
400
450
500
550
600
99.6
98.8
98
97.1
96.3
0

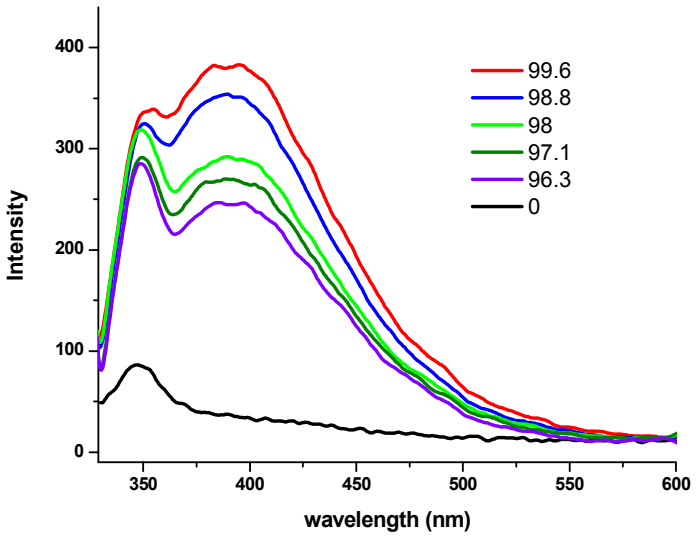
b) 5b


99.6
98.8
98
97.1
96.3
0
Intensity
300
200
100
0
350
400
450
500
550
600
wavelength (nm)

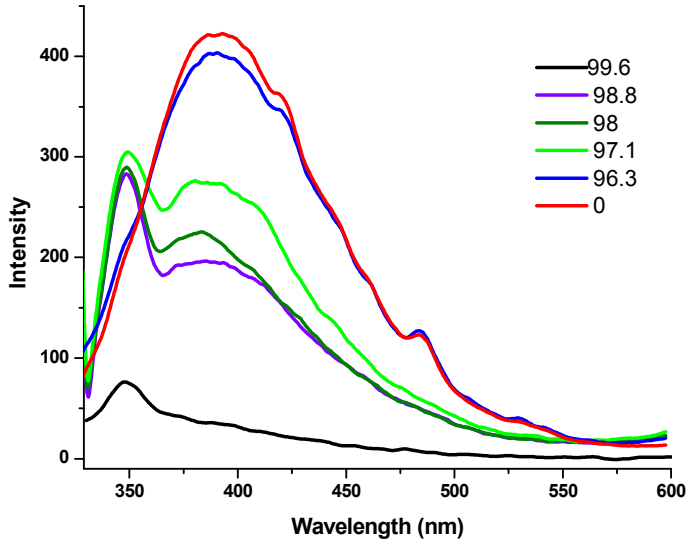
c) 5c


99.6
98.8
98
97.1
96.3
0
Intensity
600
400
200
0
350
400
450
500
550
600
Wavelength (nm)

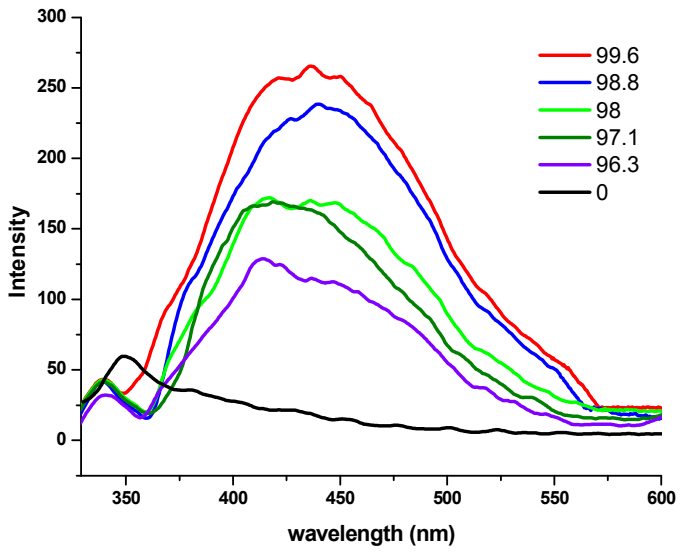
d) 5d


Intensity
wavelength (nm)
99.6
98.8
98
97.1
96.3
0
0
100
200
300
400
350
400
450
500
550
600

e) 5e


Intensity
Wavelength (nm)
99.6
98.8
98
97.1
96.3
0
0
100
200
300
400
350
400
450
500
550
600

f) 5f



g) 5g

Figure 7s. Photoluminescence spectra of water suspensions with different water factions (the inset indicates the water fraction). The slit width was set at 3 nm for excitation monochromator and 18 nm for the emision monochromator for the samples **5a**, **5b**, **5c**, **5d**, **5f**; 3 and 15 for the sample **5e** and 3 and 14 for the sample **5g**

a) **5b** b) **5c** c) **5d**

Figure 8s. Fluorescence microscopy images of the studied compounds excited with UV light

Table 1s. H-bonds parameters in the crystal structure of **5a, 5d, 5e** and **5f**

D-H···*A*	*D*-H	H···*A*	*D*···*A*	*D*-H···*A*	Symmetry code
5a					
C15-H···O1	0.93	2.47	3.33(2)	153.6	0.5 - *x*, -*y*, 0.5+ *z*
C12-H···O2	0.97	2.54	3.45(2)	155.8	0.5 + *x*, 0.5 - *y*, -*z*
C10···N3	0.93	2.47	3.32(2)	152.3	0.5 + *x*, 0.5 - *y*, -*z*
C7···O2	0.93	2.46	3.38(2)	169.5	-*x*, 0.5 + *y*, 0.5 -*z*
5d					
C6-H···O2	0.93	2.41	3.329(9)	171.0	1 – *x*, -0.5 + *y*, 2 – *z*
C9-H···O1	0.97	2.41	3.35(1)	161.9	*x*, -*1* +*y*, *z*
C10···O2	0.93	2.38	3.170(7)	142.4	*1* – *x*, *0.5* + *y*, *2* - *z*
5e					
C4-H···O1	0.93	2.64	3.318(3)	130.1	1 - *x*, 2 - *y*, -*z*
C10-H···O2	0.93	2.32	3.083(3)	138.7	-*x*, 2 - *y*, 1 -*z*
C6···O2	0.93	2.42	3.317(3)	160.7	1 - *x*, 2 - *y*, 1 -*z*
C14···N3	0.93	2.42	3.268(6)	151.6	1 - *x*, 1 - *y*, 1 -*z*
5f					
C9-H···O2	0.97	2.42	3.343(2)	158.2	*x*, -1 + *y*, *z*
C10-H···O3	0.93	2.49	3.185(2)	132.0	-1 -*x*, -2 - *y*, -1 - *z*
C17···O2	0.93	2.47	3.387(2)	170.4	-1 - *x*, -*y*, -*z*

Table 2s. Crystallographic data, details of data collection and structure refinement parameters

Code	**5a**	**5d**	**5e**	**5f**
Empirical formula	$C_{17}H_{15}Cl_3N_4O_2S$	$C_{16}H_{13}BrN_4O_2S$	$C_{17}H_{16}N_4O_2S$	$C_{17}H_{16}N_4O_3S$
Formula weight	445.74	405.27	340.40	356.40
Temperature/K	293	293	120	120
Crystal system	orthorhombic	orthorhombic	triclinic	triclinic
Space group	$P2_12_12_1$	$Pn2_1a$	*P*-1	*P*-1
***a*/Å**	5.5247(7)	10.0346(10)	5.2792(7)	7.1718(4)
***b*/Å**	25.568(4)	4.7652(5)	11.1752(12)	10.1236(7)
***c*/Å**	13.849(3)	34.985(2)	13.635(2)	12.1981(9)
***α*/°**	90.00	90.00	83.268(10)	68.022(6)
***β*/°**	90.00	90.00	83.569(12)	80.927(5)
***γ*/°**	90.00	90.00	83.924(10)	82.205(5)
***V*/Å^3**	1956.2(6)	1672.9(3)	790.36(18)	808.16(9)
Z	4	4	2	2
***D*$_{calc}$/mg/mm^3**	1.514	1.609	1.430	1.465
***μ*/mm^{-1}**	5.425	4.667	0.223	0.226
Crystal size/mm^3	0.15 × 0.01 × 0.01	0.3 × 0.02 × 0.01	0.6 × 0.1 × 0.1	0.6 × 0.3 × 0.3
***θ*$_{min}$, *θ*$_{max}$(°)**	6.92 to 100.88	9.16 to 133.12	3.02 to 50.06	4.36 to 50.04
Reflections collected	4272	15074	7404	8875
Independent reflections	2012 [R_{int} =	2936 [R_{int}	2796 [R_{int} =	2840 [R_{int} =

	0.0835]	0.1118]	0.0683]	0.0362]
Data/restraints/parameters	2012/36/244	2936/1/217	2796/0/218	2840/0/227
$R_1^a(I > 2\sigma(I))$	0.0970	0.0590	0.0468	0.0369
wR_2^b**(all data)**	0.2517	0.1478	0.01040	0.0919
GOF^c	1.091	1.010	1.016	1.033
Largest diff. peak/hole/e Å^{-3}	0.53/-0.40	0.99/-0.57	0.25/–0.38	0.51/-0.31
Flack parameter	0.07(8)	0.03(4)	-	-

^{a} $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, ^{b} $wR_2 = \{\Sigma[w\,(F_o^2 - F_c^2)^2]\,/\Sigma[w(F_o^2)^2\,]\}^{1/2}$. ^{c} GOF = $\{\Sigma[w(F_o^2 - F_c^2)^2]\,/(n - p)\}^{1/2}$, where n is the number of reflections and p is the total number of parameters refined.

Table 3s. Bond distances (Å) and angles (°)

Code	**5a**	**5d**	**5e**	**5f**
Br1-C2	-	1.892(7)	-	-
C1-O3	-	-	-	1.435(2)
C1-C2	-	-	1.504(3)	
C2-C3	1.36(2)	1.350(12)	1.388(3)	1.386(3)
C2-C7	1.37(2)	1.379(10)	1.388(3)	1.389(3)
C2-O3	-	-	-	1.365(2)
C3-C4	1.33(2)	1.408(10)	1.374(3)	1.389(2)
C4-C5	1.40(2)	1.395(9)	1.384(3)	1.387(3)
C5-C6	1.38(2)	1.375(9)	1.396(3)	1.397(3)
C5-C8	1.48(2)	1.489(8)	1.485(3)	1.476(2)
C6-C7	1.37(2)	1.395(9)	1.387(3)	1.376(3)
C8-C9	1.50(2)	1.513(8)	1.518(3)	1.530(3)
C8-O1	1.204(16)	1.188(7)	1.216(3)	1.214(2)
C9-N1	1.488(17)	1.455(7)	1.453(3)	1.452(2)
C10-C11	1.375(19)	1.386(8)	1.367(3)	1.367(3)
C10-N1	1.324(17)	1.350(7)	1.344(3)	1.339(2)
C11-C12	1.498(19)	1.484(8)	1.491(3)	1.499(3)
C11-N3	1.357(18)	1.347(8)	1.353(3)	1.360(2)
C12-S1	1.795(15)	1.821(7)	1.801(2)	1.814(2)
C13-C14	1.341(19)	1.372(8)	1.386(3)	1.385(3)
C13-N4	1.420(17)	1.363(7)	1.360(3)	1.370(2)
C13-S1	1.718(14)	1.734(6)	1.740(2)	1.736(2)
C14-C15	1.377(19)	1.379(10)	1.378(3)	1.380(3)
C15-C16	1.40(2)	1.358(11)	1.382(3)	1.384(3)
C16-C17	1.35(2)	1.370(10)	1.364(3)	1.364(3)
C17-N4	1.307(18)	1.350(8)	1.357(3)	1.358(2)
N1-N2	1.317(17)	1.343(7)	1.334(3)	1.345(2)

N2-N3	1.343(17)	1.341(7)	1.319(2)	1.323(2)
N4-O2	1.318(14)	1.306(6)	1.311(2)	1.317(2)
C1-Cl1	1.748(15)	-	-	-
C1-Cl2	1.723(14)	-	-	-
C1-Cl3	1.696(14)	-	-	-
C3-C2-Br1	-	119.1(5)	-	-
C7-C2-Br1	-	118.8(6)	-	-
C3-C2-C1	-	-	121.0(2)	-
C7-C2-C1	-	-	120.6(2)	-
O3-C2-C3	-	-	-	124.69(17)
O3-C2-C7	-	-	-	114.92(16)
C7-C2-C3	118.7(15)	122.1(7)	118.4(2)	120.39(16)
C4-C3-C2	120.5(15)	119.2(7)	120.8(2)	118.97(17)
C3-C4-C5	122.0(14)	120.2(5)	121.0(2)	121.33(18)
C4-C5-C6	118.0(14)	118.8(6)	118.7(2)	118.68(16)
C4-C5-C8	120.5(13)	117.(5)	119.5(2)	123.17(17)
C6-C5-C8	121.5(13)	123.4(6)	121.8(2)	118.14(16)
C7-C6-C5	118.8(15)	121.2(7)	119.9(2)	120.53(18)
C6-C7-C2	121.9(16)	118.6(7)	121.1(2)	120.05(18)
C5-C8-C9	115.8(12)	115.9(5)	116.9(2)	116.89(16)
O1-C8-C5	121.7(13)	122.2(5)	122.4(2)	123.05(17)
O1-C8-C9	121.8(12)	121.9(5)	120.7(2)	119.97(16)
N1-C9-C8	111.8(11)	112.7(4)	111.29(19)	111.24(15)
N1-C10-C11	103.7(13)	103.8(5)	104.3(2)	105.06(16)
C10-C11-C12	130.0(13)	127.1(5)	131.9(2)	128.65(17)
N3-C11-C10	107.9(12)	108.3(5)	108.6(2)	108.14(16)
N3-C11-C12	121.7(13)	124.5(5)	119.58(19)	123.21(16)
C11-C12-S1	110.3(9)	112.7(4)	110.12(15)	107.67(13)
C14-C13-S1	131.3(11)	129.2(5)	128.43(19)	129.00(15)
N4-C13-C14	116.0(12	119.0(6)	119.4(2)	119.17(17)
N4-C13-S1	112.7(10)	111.8(4)	112.15(16)	111.83(13)
C15-C14-C13	124.4(15)	120.5(7)	120.4(2)	119.94(18)
C14-C15-C16	116.8(15)	119.4(6)	118.9(2)	119.56(18)
C17-C16-C15	118.5(14)	119.7(6)	119.9(2)	119.93(18)
N4-C17-C16	123.6(16)	120.8(6)	121.0(2)	120.40(18)
C10-N1-C9	126.5(14)	127.9(5)	128.5(2)	127.61(16)
N2-N1-C9	118.5(14)	119.4(5)	119.97(19)	121.04(15)
N2-N1-C10	114.4(13)	112.7(4)	111.52(18)	111.26(15)
N3-N2-N1	104.8(13)	105.2(5)	106.80(18)	106.61(15)
N2-N3-C11	109.1(12)	110.0(5)	108.81(18)	108.93(15)

C17-N4-C13	120.0(13)	120.5(5)	120.39(19)	121.00(16)
O2-N4-C13	114.8(11)	118.8(5)	118.94(17)	118.23(15)
O2-N4-C17	124.8(14)	120.8(5)	120.7(2)	120.77(15)
C13-S1-C12	97.7(7)	103.2(3)	98.90(11)	100.73(9)
C2-O3-C1	-	-	-	117.26(15)

Table 4s. Transition temperatures of the **5a-5g** samples as measured by DSC (POM)

Code	**5a**	**5b**	**5c**	**5d**	**5e**	**5f**	**5g**
1H (T_m/^oC)	199(205)	204(207)	220(224)	205(214)	191(196)	177(183)	192(195)
1C (Tg/^oC)	45	43	59	57	48	52	47
2H (T_{cr}/^oC)	-(57*)	133(149)	-(-)	-(-)	112(118)	136(157)	-(129*)

1H: first heating; 1C: first cooling; 2H: second heating; T_m: crystalline melting; Tg: glass transition; T_{Cr}: crystallization temperature; *: observed under shear.