Supporting Information

Polymorphic Solvates, Ionic-cocrystals and C-N Bond Formation to Form Ionic Cocrystal In Sulfamethoxazole and Sulfathiazole Derived Urea

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Content list

Synthesis and characterization of the hosts, solvates, cocrystals and salts:

H**SMZU.DMF-P1**: A solution of 4-nitrophenylisocyanate (328 mg, 2 mmol) and sulfamethoxazole (507 mg, 2 mmol) in acetonitrile (30 ml) was refluxed for 2 hs after which the reaction mixture was stirred at room temperature for about 6 hs. This had resulted in the formation of a yellow precipitate. This precipitate was filtered and it was dissolved in 3 ml DMF.

The solution thus prepared was kept undisturbed, which provided the crystals of H**SMZU.DMF-P1** yield = 76 %. IR (Neat, cm^{-1}): 3272 (w), 3135 (w) 1724 (s), 1657 (s), 1615 (s), 1590 (s), 1574 (s), 1542 (s), 1495 (s), 1468 (s), 1409 (s), 1374 (s), 1384 (s), 1333 (m), 1317(s), 1251 (s), 1197 (s), 1162 (s), 1106 (s), 1091 (s), 1028 (m), 928 (s), 885 (s), 854 (s), 843 (m), 831 (s), 751 (s), 715 (s), 667 (s), 645 (s), 579 (s), 556 (s). ^{1}HNMR (600 MHz, DMSO-d_6, ppm): 11.31 (s, 1H), 9.57 (s, N-H), 9.39 (s, N-H), 8.21- 8.20 (d, J = 10 Hz, 2H), 7.95 (s, 1H), 7.79 (d, J = 8 Hz), 7.70 (d, J = 9 Hz), 7.67 (d, J = 8 Hz), 6.13 (s, 1H), 2.89 (s, 3H), 2.73 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6): 170.3, 162.3, 157.6, 151.8, 145.9, 143.6, 141.4, 132.3, 128.2, 125.2, 118.2, 117.8, 95.4, 35.8, 30.7, 12.1.

H**SMZU.DMF-P2:** A solution of the crude yellow precipitate of **SMZU** (103 mg, 0.25 mmol) was dissolved in DMF (10 ml) was stirred at 80°C for about 1 h. The solution was filtered to discard suspended material (if any) and it was kept undisturbed for crystallization. Upon standing for 8-10 days red block crystals of the H**SMZU.DMF-P2** were obtained (yield 82 %). IR (Neat, cm^{-1}): 3358 (s), 1719 (s), 1657 (s), 1618 (s), 1593 (s), 1557 (w), 1572 (s), 1538 (s), 1495 (s), 1441 (m), 1406 (s), 1376 (s), 1326 (s), 1304 (w), 1249 (s), 1198 (s), 1177 (m), 1163 (s), 1108 (s), 1092 (m), 1040 (s), 924 (m), 875 (s), 854 (s), 833 (s), 812 (s), 752 (s), 702 (s), 666 (s), 643 (s), 574 (s), 556 (s).

TBA(SMZU) Salt: The crude H**SMZU** (42 mg, 0.1 mmol) was dissolved in DMF (5 ml). To this solution TBAF trihydrate (63 mg, 0.2 mmol) was added and stirred for 30 mins. The solution was filtered and kept for crystallization, which yielded crystalline **TBA(SMZU).** The crystals were decanted and characterized (yield 85 %). IR (Neat cm^{-1}): 2959 (s), 2874 (s), 1719 (s), 1609 (s), 1592 (s), 1543 (s), 1494 (s), 1456 (s), 1404 (s), 1334 (s), 1314 (s), 1302(s), 1273 (s), 1246 (s), 1195 (s), 1175 (s), 1141(s), 1109(s), 1094(s), 1045(s), 1007(m), 931(s), 883(s), 851(s), 802(s), 750(s), 704(s), 645(s), 587(s), 566(s). ^{1}HNMR (600 MHz, DMSO-d_6, ppm): 9.58(s, N-H), 9.12(s, N-H), 8.19 (d, J = 9 Hz, 2H), 7.70 (d, J = 9 Hz, 2H), 7.58 (d, J = 8 Hz, 2H), 7.42 (d, J = 9 Hz, 2H), 5.78 (s, 1H), 3.16 (t, J = 8 Hz, 8H), 1.59- 1.54 (m, 8H), 1.34- 1.27 (m, 8H), 0.93(t, J = 7 Hz, 12H). Same reaction with excess amounts of TBABr (5 mmol) instead of TBAF yielded the same salt.

Synthesis of butyl-**SMZU.TBAI:** A solution of refluxed tetrabutylammonium iodide (185 mg, 0.5 mmol) and H**SMZU** (42 mg, 0.1 mmol) in DMF (10 ml) was stirred at 80 °C for 6 hs and the

resulting solution left undisturbed for 8 days yielded crystals of the salt. The supernatant liquid was decanted and the crystals were dried by pressing filter paper (yield 49 %). IR (Neat, cm^{-1}): 2958 (s), 2934 (w), 2873(m), 1713 (s), 1611 (m), 1590 (s), 1560 (s), 1539 (s), 1508(s), 1493 (s), 1448 (s), 1405(m), 1374(m), 1341 (s), 1314 (m), 1304 (s), 1247 (s), 1198 (s), 1162 (s), 1113 (s), 1092 (s), 1027 (s), 925 (w), 882 (s), 856 (s), 827 (m), 804 (m), 749 (s), 712 (s), 678 (s), 645 (s), 594 (s), 569 (s), 556 (s). ^{1}HNMR (600 MHz, DMSO-d_6, ppm): 9.59 (s, N-H), 9.45 (s, N-H), 8.21 (d, J = 9 Hz, 2H), 7.77 (d, J = 8 Hz, 2H), 7.70 (d, J = 10 Hz, 2H), 7.68 (d, J = 9 Hz, 2H), 6.44 (s, 1H), 3.69 (t, J = 7 Hz, 3H), 3.18-3.15 (t, J = 8 Hz, 8H), 2.37 (s, 3H), 1.59-1.54 (m, 10H), 1.34-1.28 (m, 10H), 0.94(t, J = 7Hz, 12H), 0.87 (t, J = 7 Hz, 3H). ^{13}C NMR (125 MHz, DMSO-d_6): 170.8, 159.2, 151.7, 145.8, 144.1, 141.4, 130.4, 128.4, 125.2, 118.3, 117.9, 97.8, 57.5, 48.1, 29.8, 23.1, 19.2, 13.5, 12.2.

HSTZU.DMF: A solution of 4-nitrophenylisocyanate (328 mg, 2 mmol) (20 ml), sulfathiazole (511 mg, 2 mmol) in dry acetonitrile (20 ml) was stirred for 8 h. This yielded yellow precipitate, which was filtered. It was dissolved in DMF (3 ml) and kept undisturbed condition for crystallization. Needle shaped crystals of H**STZU.DMF** were formed after 2-3 days (yield, 81 %). IR (Neat cm^{-1}) : 3093 (bs), 1725 (s), 1651 (s), 1588 (s), 1567 (s), 1526 (s), 1492 (s), 1414 (s), 1331 (s), 1301 (s), 1249 (s), 1190 (s), 1173 (s), 1145 (s), 1102 (s), 1087 (s), 927 (s), 851 (s), 828 (s), 733 (s), 711 (s), 690 (s), 669 (s), 649 (s), 631 (s), 602 (s), 575 (s), 559 (s). ^{1}HNMR (600 MHz, DMSO-d_6, ppm): 12.70 (s, 1H), 9.53 (s, N-H), 9.31 (s, N-H), 8.21 (d, J = 9 Hz, 2H), 7.94 (s, 1H), 7.74 (d, J = Hz, 2H), 7.70 (d, J = 9 Hz, 2H), 7.61 (d, J = 9 Hz, 2H), 7.24 (d, J = 5 Hz, 1H), 6.82 (d, J = 4 Hz, 1H), 2.88 (s, 3H), 2.72 (s, 3H). ^{13}CNMR (125 MHz, DMSO-d_6): 168.8, 162.5, 151.9, 146.1, 142.5, 141.4, 135.6, 127.2, 125.3, 118.1, 117.9, 108.2, 35.9, 30.9.

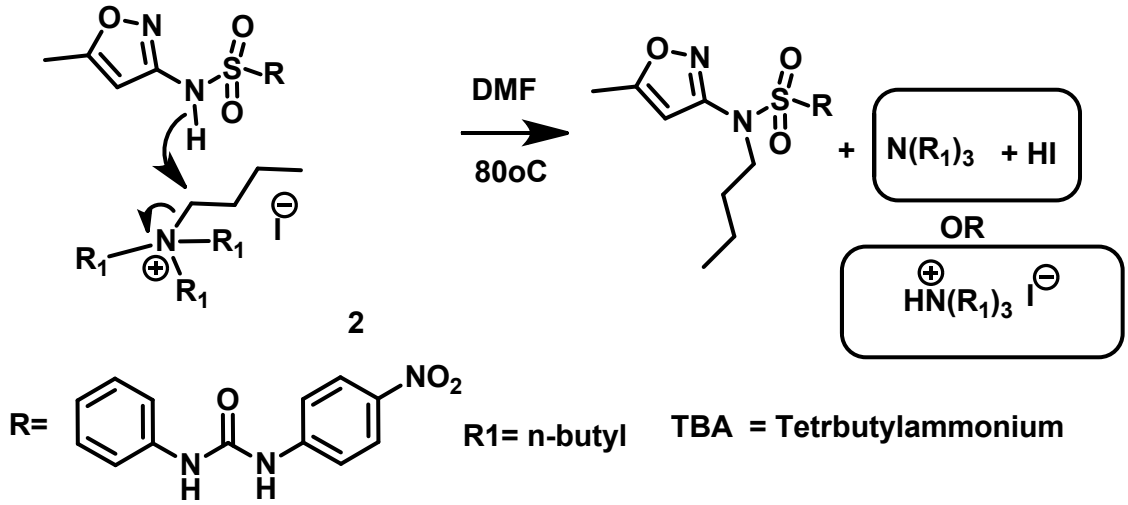
H**STZU.DMSO:** The H**STZU** (42 mg, 0.1 mmol) was dissolved in DMSO (0.5 ml) in a plastic vial (1ml capacity) and left undisturbed for crystallization. Block type of crystals of H**STZU.DMSO** were formed in a week. The crystals were collected by decanting the supernatant liquid. IR (Neat, cm^{-1}) : 3101 (bs), 1716 (s), 1595 (s), 1538 (s), 1489 (s), 1435 (s), 1332 (s), 1299 (s), 1246 (s), 1195 (s), 1174 (s), 1143 (s), 1113 (s), 1088 (s), 1011 (s), 939 (s), 849 (s), 733 (s), 709 (s), 652 (s), 631 (s), 576 (s), 552 (s). ^{1}HNMR (600 MHz, DMSO-d_6, ppm): 12.67 (s, 1H), 9.51(s, N-H), 9.29 (s, N-H), 8.21 (d, J = 9 Hz, 2H), 7.74 (d, J = 8 Hz, 2H), 7.70 (d, J = 9 Hz, 2H), 7.60 (d, J = 9 Hz), 7.24 (d, J = 4 Hz, 1H), 6.82 (d, J = 4 Hz, 1H), 2.54 (s, 6H

) . ^{13}C NMR (125 MHz, DMSO-d_6): 168.7, 151.8, 145.9, 142.4, 141.3, 135.6, 127.1, 125.2, 124.4, 118.0, 117.8, 108.1.

HSTZU.TBAI: Cocrystal of H**STZU** with tetrabutylammonium iodide was prepared by stirring a mixture of H**STZU** (42 mg, 0.1 mmol) with ten equivalents amounts of TBAI (369 mg, 1 mmol) in DMF (10ml) for 5 mins at room temperature. The mixture was filtered and filtrate was kept in open air for slow evaporation to obtain the crystals of H**STZU.TBAI** after 12 days (yield 53 %). IR (Neat, cm^{-1}): 2958 (m), 2870 (m), 1713 (s), 1590 (s), 1560 (s), 1536 (s), 1493 (s), 1411 (s), 1302 (s), 1245 (s), 1196 (s), 1146 (s), 1112 (s), 1087 (s), 934 (s), 854 (s), 740 (s), 702 (s), 650 (s), 634 (s), 574 (s), 558 (s). ^{1}HNMR (600 MHz, DMSO-d_6, ppm): 12.67 (s, 1H), 9.52 (s, N-H), 9.29 (s, N-H), 8.20 (d, J = 9 Hz, 2H), 7.73 (d, J = 8 Hz, 2H), 7.69 (d, J = 9 Hz, 2H), 7.60 (d, J = 8 Hz, 2H), 7.24 (d, J = 5 Hz, 1H), 6.81 (d, J = 4 Hz, 1H), 3.15 (t, 8H), 1.59- 1.54 (m, 8H), 1.34- 1.28 (m, 8H), 0.93 (t, 12H). ^{13}C NMR (125 MHz, DMSO-d_6): 168.7, 151.8, 145.9, 142.4, 141.3, 135.6, 127.1, 125.2, 124.4, 117.9, 117.8, 108.1, 57.5, 23.1, 19.2, 13.5.

TBA(STZU) : A solution of tetrabutylammonium fluoride trihydrate (63 mg, 0.2 mmol) H**STZU** (42 mg, 0.1 mmol) in DMF (5 ml) was stirred for 1 h to obtain **TBA(STZU)** as a white precipitate. IR (Neat cm^{-1}) : 2959 (m), 2872 (m), 1709 (s), 1657 (s), 1592 (s), 1539 (s), 1495 (s), 1433 (s), 1304 (s), 1266 (m), 1233 (s), 1201 (s), 1178 (s), 1164 (m), 1141 (s), 1091 (s), 948 (s), 856 (s), 842 (s), 752 (s), 736 (s), 697 (s), 655 (s), 644 (s), 618 (s), 576 (s), 560 (s). ^{1}HNMR (600 MHz, DMSO-d_6, ppm): 9.61 (s, N-H), 9.17 (s, N-H), 8.18 (d, J = 9 Hz, 2H), 7.69 (d, J = 9 Hz, 2H), 7.63 (d, J = 8 Hz, 2H), 7.42 (d, J = 9 Hz, 2H), 6.920 (d, J = 4 Hz, 1H), 6.43 (d, J = 4 Hz, 1H), 3.16 (t, 8H), 1.59- 1.54 (m, 8H), 1.33- 1.27 (m, 8H), 0.93 (t, 12H). ^{13}C NMR (125 MHz, DMSO-d_6): 169.6, 151.8, 146.3, 141.1, 140.4, 139.7, 136.9, 126.9, 125.1, 117.6, 117.4, 107.1, 57.5, 23.1, 19.2, 13.5.

All the solvates and cocrystals were stable at room temperature under ambient conditions at least for a week.



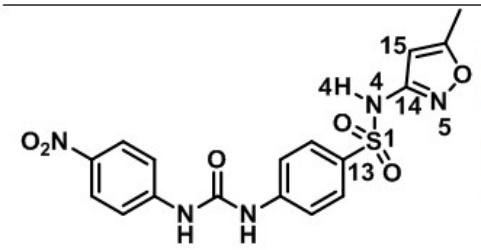
Scheme S1: A plausible mechanism of the C-N bond formation from reaction of H**STZU with TBAI**

Table S1: Hydrogen bond parameters of solvates, cocrystals and salt.

Solvate/salt/cocrystal	D-H⋯A (Symmetry)	d_{D-H} (Å)	$d_{H\cdots A}$ (Å)	$d_{D\cdots A}$ (Å)	∠D-H⋯A (°)
HSMZU.DMF-P1	N(2) -H(2N) ⋯O(7) [1/2-x, 1/2+y, 1/2 –z]	0.80(4)	2.15(4)	2.897(6)	155(4)
	N(3) -H(3N) ⋯O(7) [1/2-x, 1/2+y, 1/2 –z]	0.77(4)	2.12(4)	2.839(6)	156(4)
	N(4) -H(4N) ⋯O(5) [1+x, y, z]	0.85(4)	2.27(4)	3.091(4)	163(4)
	C(2)-H(2) ⋯O(3) [2-x, 1-y, -z]	0.93	2.56(5)	3.455(5)	161
	C(9)-H(9) ⋯O(1) [2-x, 1-y, -z]	0.93	2.53	3.234(5)	133
	C(15)-H(15) …N(5) [-1+x, y, z]	0.93	2.30	3.198(5)	161
	C(19)-H(19C) …O(2) [-x, 1- y, -z]	0.96	2.37	3.151(19)	138
HSMZU.DMF-P2	N(2) -H(2N) ⋯O(5)) [-x, 1-y, -z]	0.86	2.21	2.975(3)	148
	N(3) -H(3N) ⋯N(5) [-x, 1-y, -z]	0.86	2.19	3.050(3)	174
	N(4) -H(4N) ⋯O(7) [-1+x,1+y, z]	0.86	1.99	2.704(3)	139
	C(2) -H(2A) …O(3) [1-x, 1-y, 1-z]	0.93	2.57	3.424(3)	152
	C(15) -H(15) …O(2) [-1+x,1+y, z]	0.93	2.54	3.331(4)	142
TBA(SMZU)	N(2) -H(2N) …N(4) [1+x, y, z]	0.86	2.28	3.081(3)	162
	N(3) -H(3N) ...N(4) [1+x, y, z]	0.86	2.09	2.928(3)	159
	C(9) -H(9) …O(1) [2-x, 1-y, 1-z]	0.93	2.50	3.192(3)	172
	C(17) -H(17B) …O(5) [1-x, 1-y, -z]	0.96	2.42	3.322(4)	153
	C(22) –H(22A) …O(4) [x, y, z]	0.97	2.39	3.340(3)	166

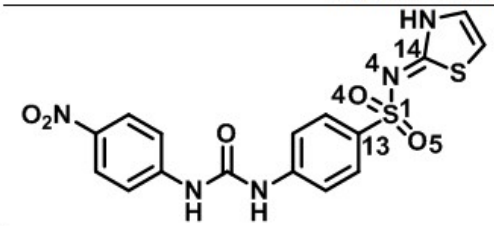
butyl-SMZU.TBAI	N(2) -H(2N) …I1 [-1+x, y, z]	0.86	2.77	3.594(4)	163
	N(3) -H(3N) ...I1 [-1+x, y, z]	0.86	2.75	3.569(5)	160
	C(33) -H(33B) …O(4) [x, 1+y, z]	0.97	2.35	3.294(6)	163
	C(34) -H(34BB) … O(1) [1-x, 2-y, 1-z]	0.97	2.42	3.326(7)	156
	C(37) –H(37B) … O(2) [-x, 2-y, 1-z]	0.97	2.49	3.40(3)	156
HSTZU.DMF	N(2) -H(2N) ··· O(6)) [1+x, y, z]	0.77	2.13	2.843(5)	154
	N(3) -H(3N) ··· O(6) [1+x, y, z]	0.77	2.17	2.881(5)	152
	N(5) -H(5N) ··· N(4) [-x, 1-y, -z]	0.85	2.04	2.896(5)	177
	C(9) -H(9) … O(1) [1-x, 1-y, 1-z]	0.93	2.55	3.187(6)	126
	C(18) -H(18C) … S(2) [1/2+x, 1/2-y 1/2+z]	0.96	2.83	3.591(6)	137
HSTZU.DMSO	N(2) -H(2N) ···O(6)) [x, 1/2-y, -1/2+z]	1.01(5)	1.94(5)	2.913(8)	160(4)
	N(3) -H(3N) ···O(6) [x, 1/2-y, -1/2+z]	0.90(5)	2.08(5)	2.907(8)	153(4)
	N(5) -H(5N) ···N(4) [-x, 1-y, -z]	0.97(5)	1.88(5)	2.838(9)	173(4)
	C(2) -H(2) …O(1) [1-x, 1/2+y, 1/2-z]	0.93	2.52	3.216(11)	132
	C(3) -H(3) …O(2) [1-x, -2-y, -z]	0.93	2.42	3.328(11)	166
	C(17) -H(17B) …O(3) [x, y, z]	0.96	2.46	3.335(10)	152
HSTZU.TBAI	N(2) -H(2N) ···I(1)) [1+x, y, z]	0.79(6)	2.93(6)	3.669(6)	159(6)
	N(3) -H(3N) ···I(1) [1+x, y, z]	0.71(5)	2.83(5)	3.511(7)	160(5)
	N(5) -H(5N) ···N(4) [1-x, 1-y, -z]	0.83(7)	2.04(7)	2.854(8)	166(5)
	C(20) -H(20B) …O(2) [1-x, -y, 1-z]	0.97	2.50	3.436(8)	162
	C(21) -H(21B) …O(5) [x, -1+y, z]	0.97	2.30	3.253(8)	168

Table S2: Torsion angles of solvates, ionic cocrystals and salts of HSMZU



Torsion angle(°)	**HSMZU.DMF-P2**	**HSMZU.DMF-P1**
C13-S1-N4-C14	57.6(2)	60.6(4)
C13-S1-N4-H4N	-122.4	-86(3)
H4N-N4-C14-C15	23.6	179(3)
H4N-N4-C14-N5	-154.8	-2(3)

Table S3: Torsion angles of solvates of HSTZU



Torsion angles(°)	HSTZU.DMF	HSTZU.DMSO
C13-S1-N4-C14	79.6(7)	84.5(5)
S1-N4-C14-N5	-178.9(6)	-173.3(4)
S1-N4-C14-S2	4(1)	8.2(8)
O4-S1-N4-C14	-168.9(6)	-32.2(5)
O5-S1-N4-C14	-37.6(7)	-163.4(4)

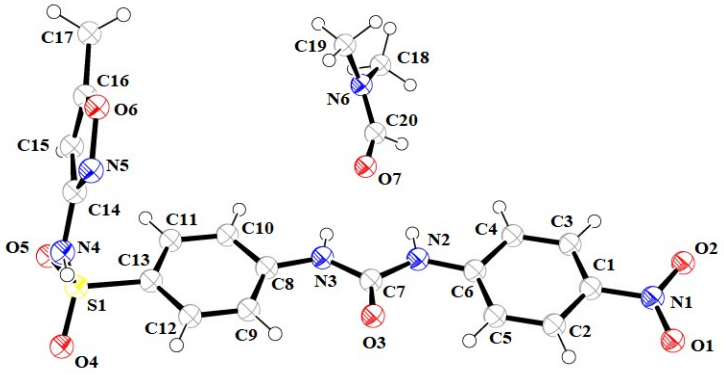


Figure **S1**: ORTEP diagram of **HSMZU.DMF-P1** drawn with 50% ellipsoid probability.

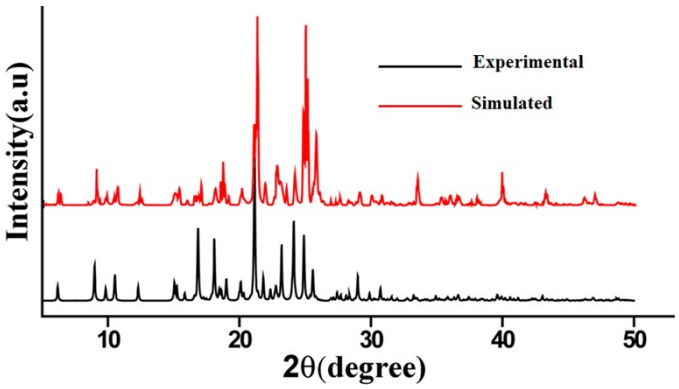


Figure **S2**: Powder X-ray diffraction patterns of the **HSMZU.DMF-P1**.

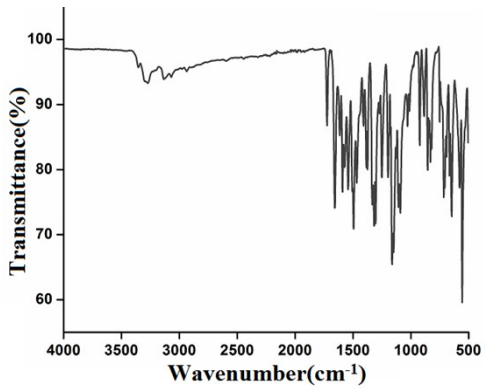


Figure **S3**: FT-IR spectrum (neat) of the **HSMZU.DMF-P1**.

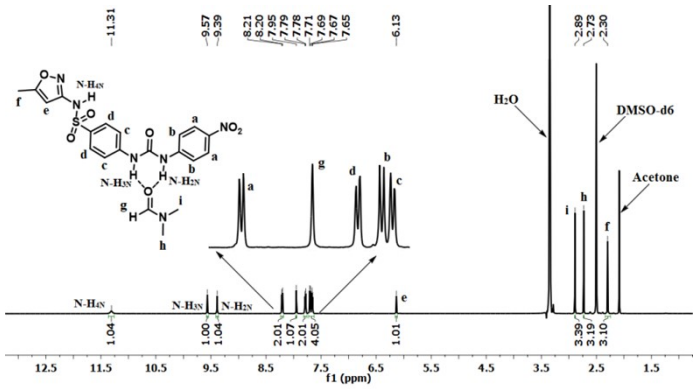


Figure **S4**: ^{1}HNMR (DMSO-d_6, 600 MHz) spectra of the **HSMZU.DMF-P1**.

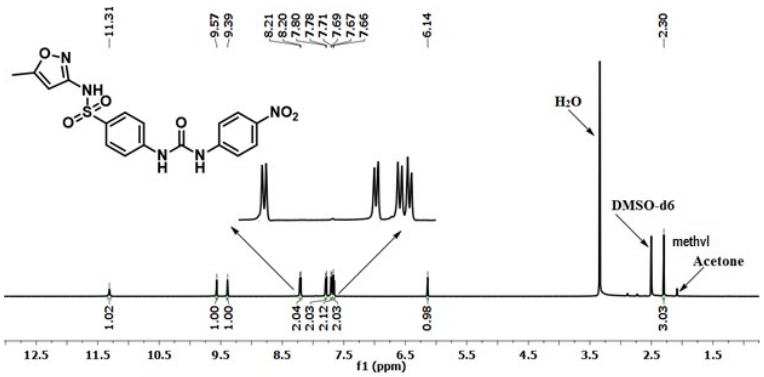


Figure **S5**: ^{1}HNMR (DMSO-d6, 600 MHz) spectra of the H**SMZU**.

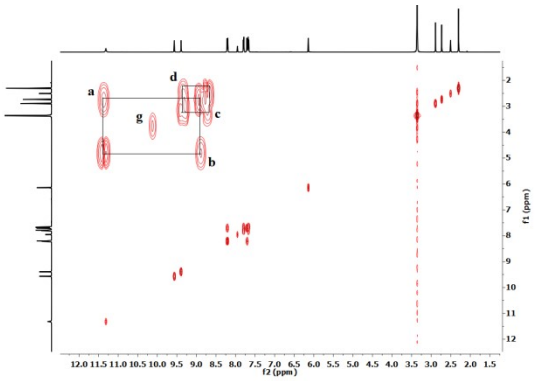


Figure **S6**: ^{1}H-2D-HOMOCOSY (600 MHz, DMSO-d_6) spectrum of the **HSMZU.DMF-P1.**

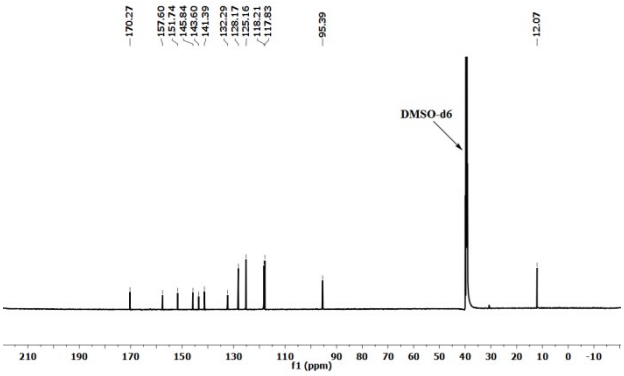


Figure **S7**: ^{13}CNMR (125 MHz, DMS Figure **S6**: ^{1}H-2D-HOMOCOSY (600 MHz, DMSO-d_6) spectrum of the **HSMZU.DMF-P1.**

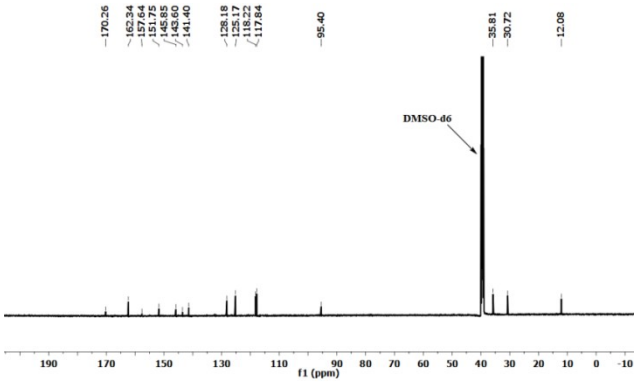


Figure **S8**: ^{13}CNMR (125 MHz, DMSO-d_6) spectra of the **HSMZU.DMF-P1.**

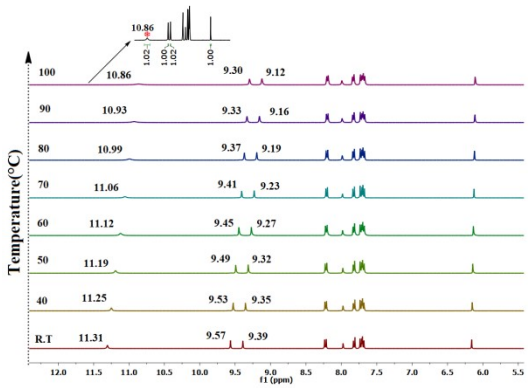


Figure **S9**: ^{1}HNMR (DMSO-d_6, 600 MHz) spectra of the **HSMZU.DMF-P1** at variable temperatures.

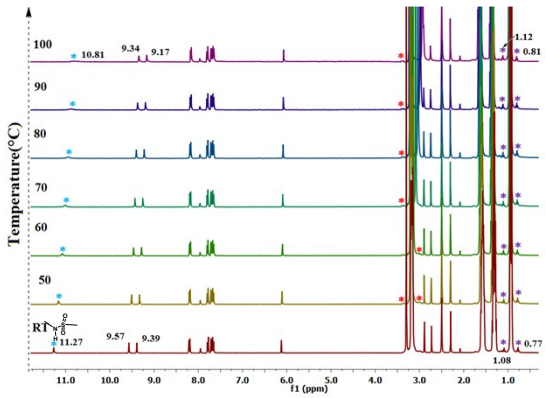
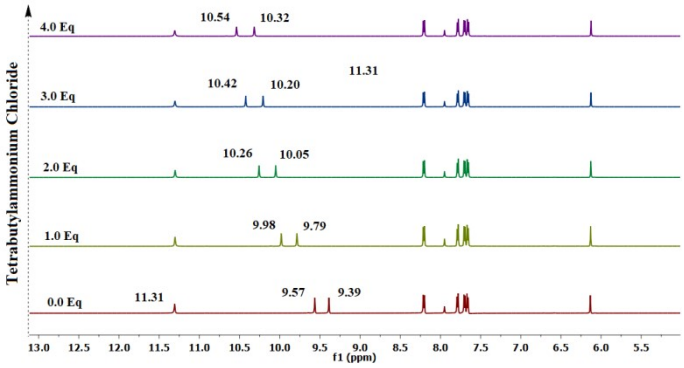
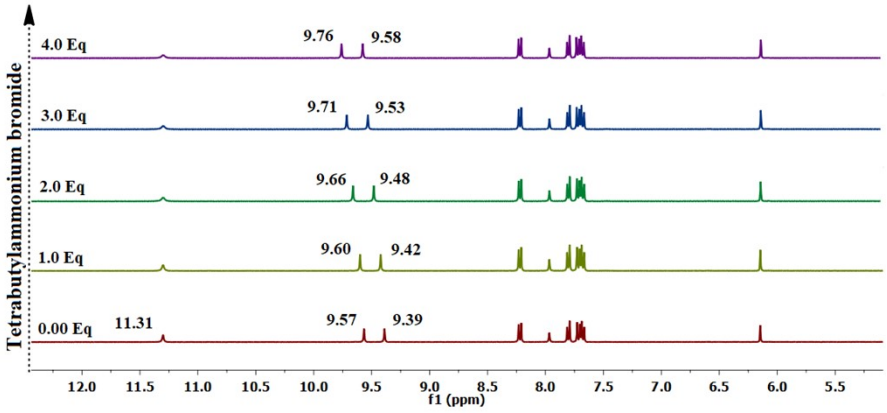


Figure **S10**: Variable temperature ^{1}HNM**R** spectra (DMSO-d_6, 600 MHz) of **HSMZU.DMF-P1** with 10 equivalent of **TBAI** showing C-N bond formation to form the butyl-**SMZU.TBAI** (In in situ in the reaction mixture. {As per the Scheme S1 there are three types of butyl environments from the three compounds in the reaction mixture which are $\mathbf{N^{+}(CH_2^aCH_2^bCH_2^cCH_3^d)_4I}$, $\mathbf{(CH_2^{a'}CH_2^{b'}CH_2^{c'}CH_3^{d'})}$**-SMZU** and $\mathbf{N(CH_2^{a''}CH_2^{b''}CH_2^{c''}CH_3^{d''})_3}$**.** The protons from the $\mathbf{CH_2^bCH_2^c}$**,** $\mathbf{CH_2^{b'}CH_2^{c'}}$**,** $\mathbf{CH_2^{b''}CH_2^{c''}}$ are indistinguishable as they overlap each other; the peaks with * (red asterisk) are from $CH_2^{a'}$ and $CH_2^{a''}$ and with * (violet asterisk) are from are from $CH_3^{d'}$ and $CH_3^{d''}$ respectively. The peak at 11.17 marked with *(blue asterisk) is from the N-H next to the heterocycle).



(a)



(b)

Figure **S11**: ^{1}H NMR (600 MHz, DMSO-d_6) titration of **HSMZU.DMF-P1** by adding different amounts of tetrabutylammonium (a) chloride and (b) bromide (showing the aromatic protons of **HSMZU.DMF-P1**).

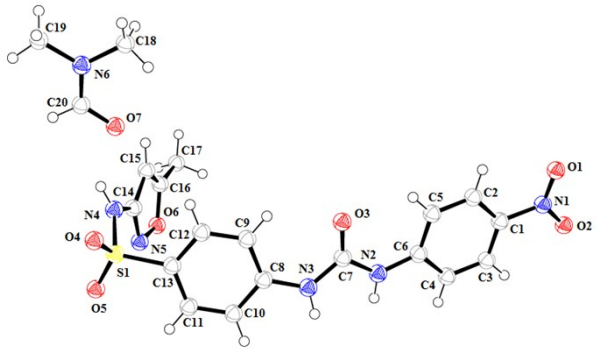


Figure **S12**: ORTEP diagram of **HSMZU.DMF-P2** drawn with 50% ellipsoid probability.

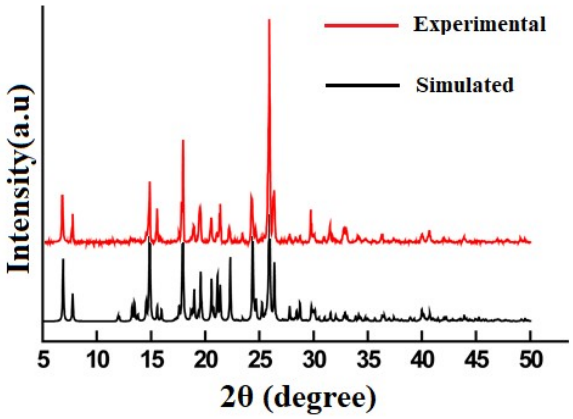


Figure **S13** : Powder X-ray diffraction patterns of the **HSMZU.DMF-P2**.

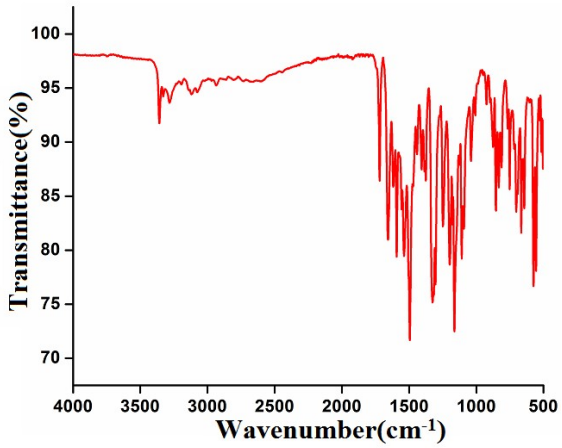


Figure **S14**: FT-IR spectrum (neat) of the **HSM** Figure **S13**: Powder X-ray diffraction patterns of the **HSMZU.DMF-P2**.

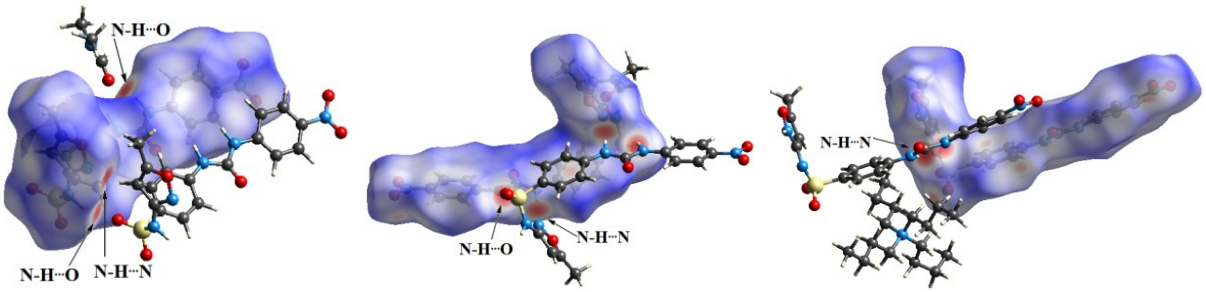


Figure **S15** : Hirshfeld surfaces of (d) H**SMZU.DMF-P1**, (e) H**SMZU.DMF-P2**, (f) TBA(**SMZU)**

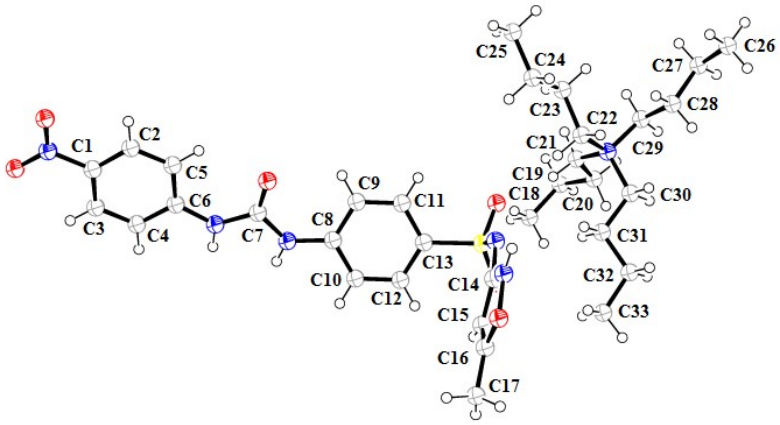


Figure **S16**: ORTEP diagram of TBA(**SMZU**) drawn with 50% ellipsoid probability.

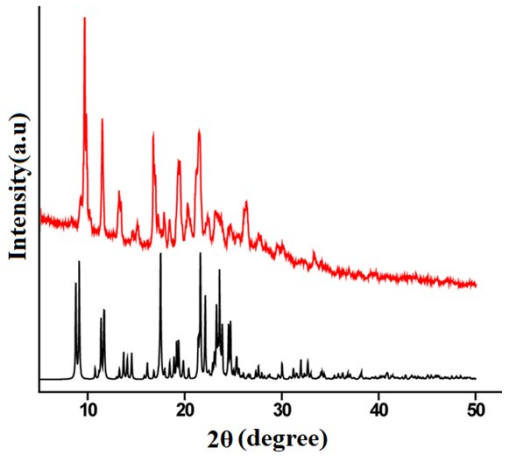


Figure **S17**: Powder X-ray diffraction patterns of the TBA(**SMZU**).

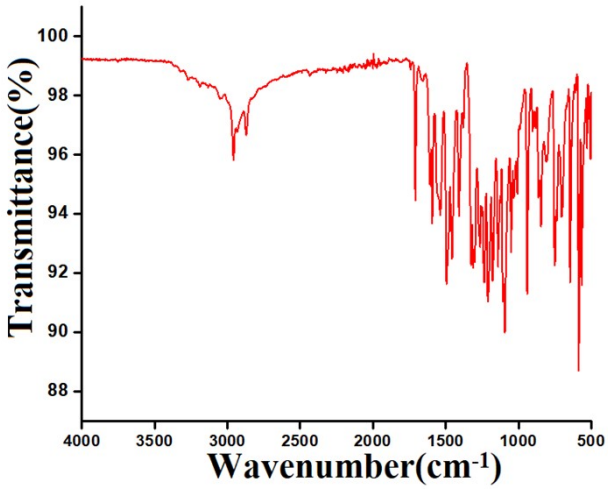


Figure **S18**: FT-IR spectrum (neat) of the TBA(**SMZU**).

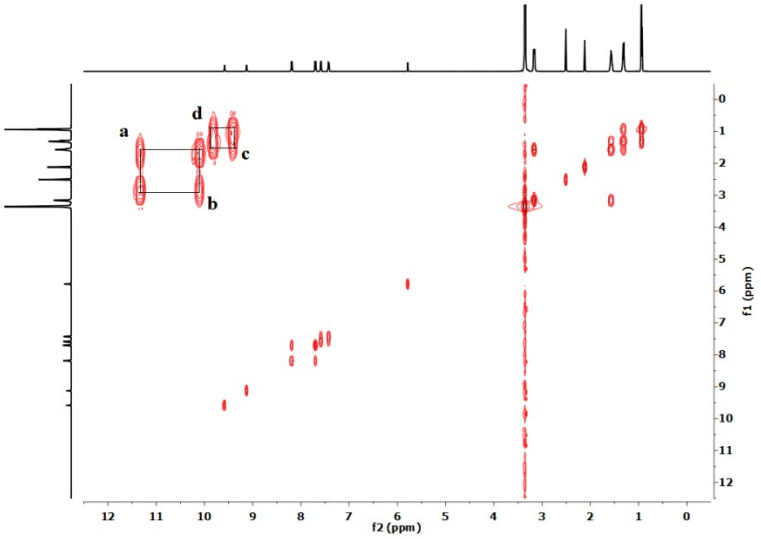


Figure **S19**: ^{1}H 2D-HOMOCOSY (600 MHz, DMSO-d_6) spectrum of the TBA(**SMZU**).

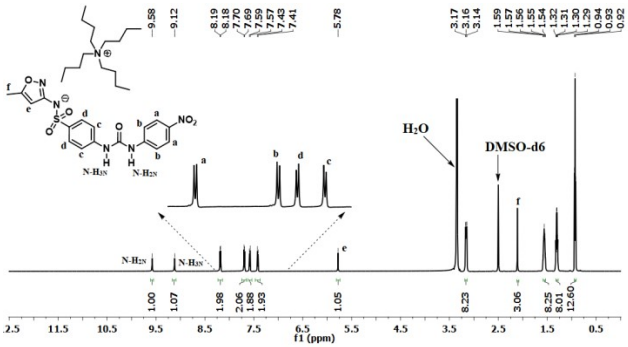


Figure **S20**: ^{1}HNMR (DMSO-d_6, 600 MHz) spectra of the TBA(**SMZU**). Figure **S18**: ^{1}H 2D-HOMOCOSY (600 MHz, DMSO-d_6) spectrum of the TBA(**SMZU**).

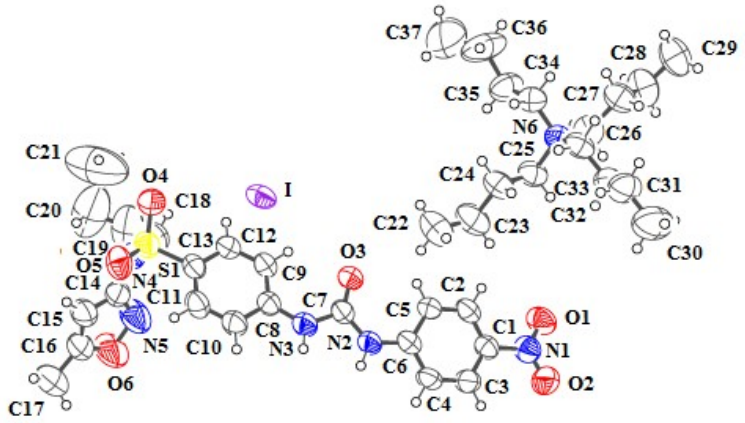


Figure **S21**: ORTEP diagram of butyl-**SMZU.TBAI** drawn with 50% ellipsoid probability.

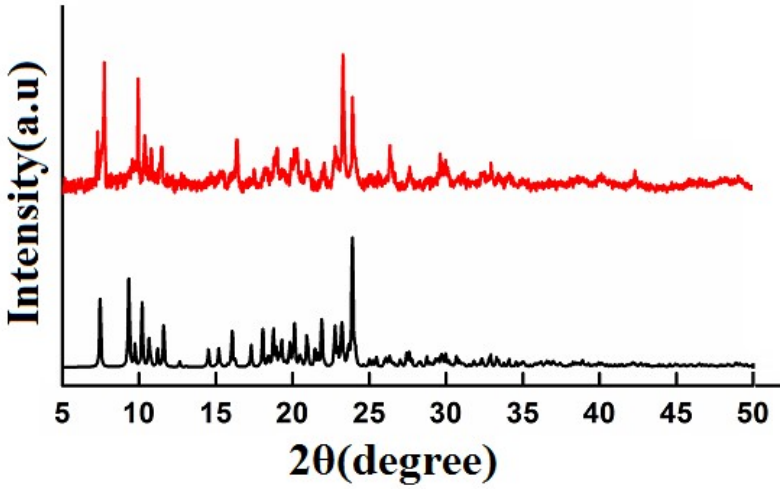


Figure **S22**: Powder X-ray diffraction patterns of the butyl-**SMZU.TBAI**

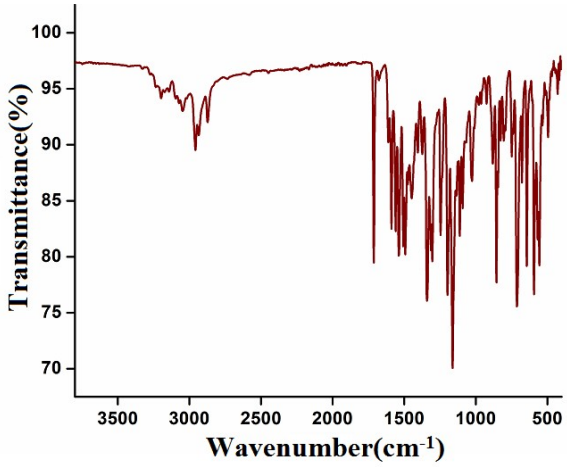


Figure **S23**: FT-IR spectrum (neat) of the butyl-**SMZU.TBAI.**

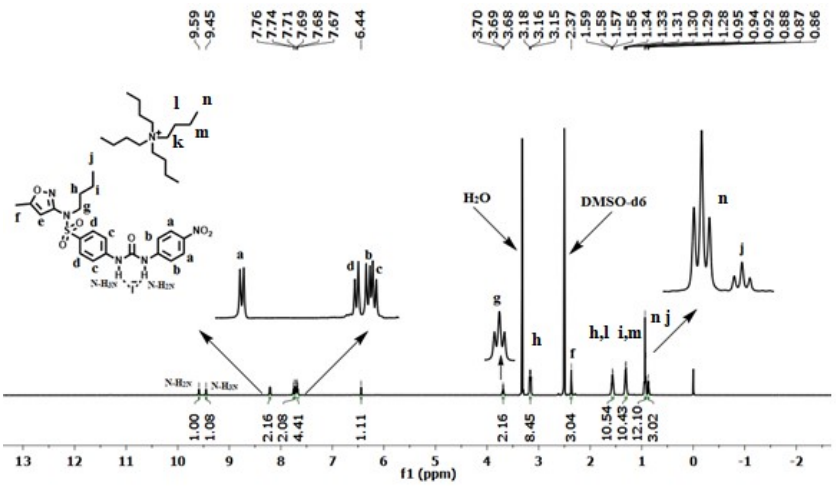


Figure **S24**: ^{1}HNMR (DMSO-d_6, 600 MHz) spectra of the butyl-**SMZU.TBAI.**

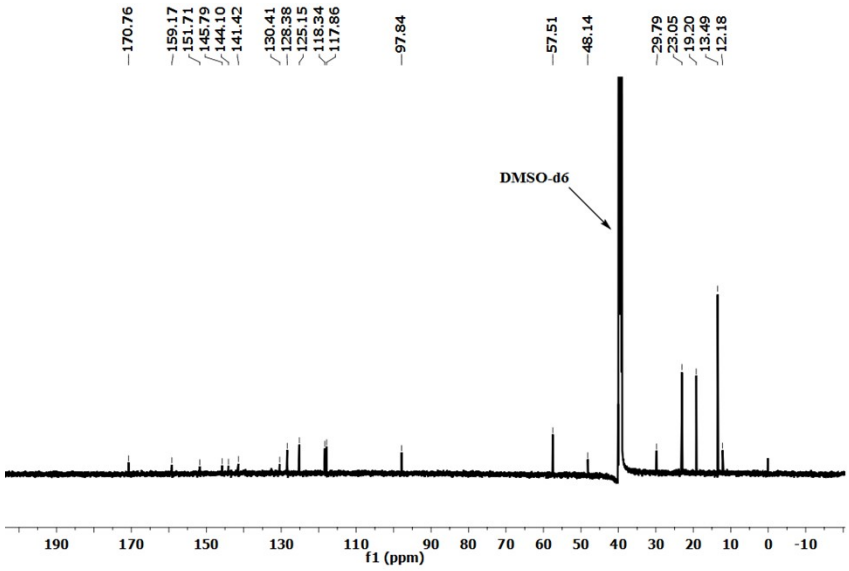


Figure **S25**: ^{13}CNMR (125 MHz, DMSO-d_6) spectra of the butyl-**SMZU.TBAI**.

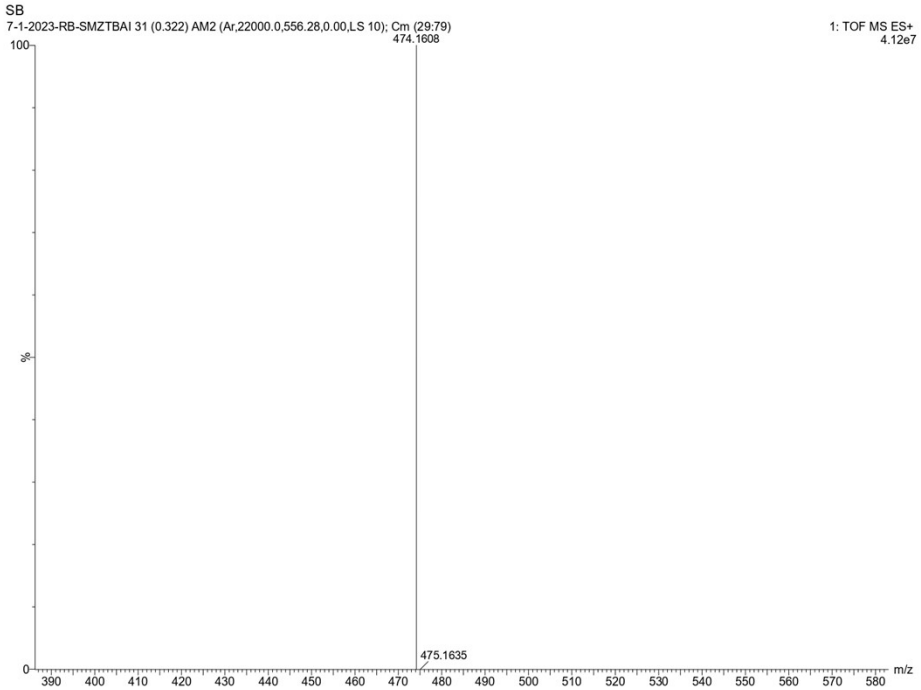


Figure S26: ESI mass spectrum of the butyl-**SMZU.**

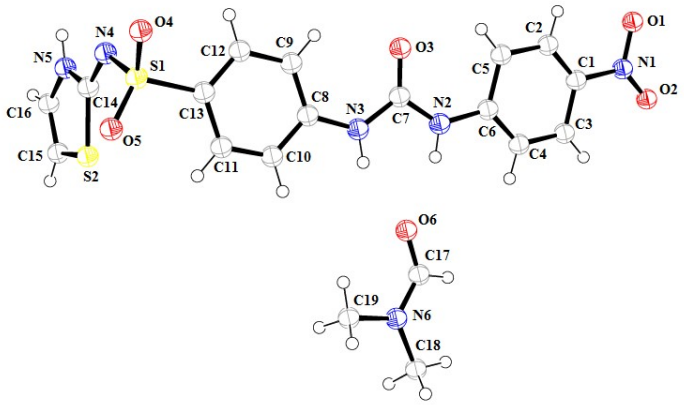


Figure **S27**: ORTEP diagram of H**STZU.DMF** drawn with 50% ellipsoid probability.

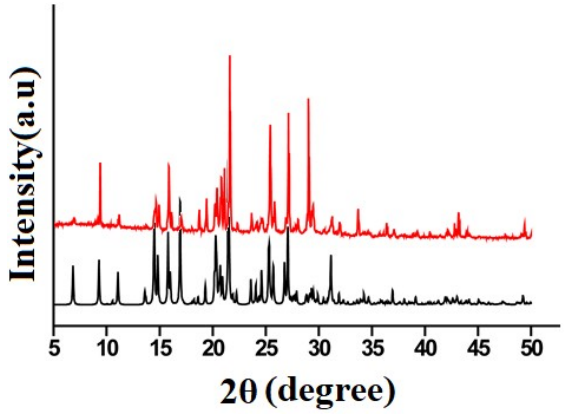


Figure **S28**: Powder X-ray diffraction patterns of the H**STZU.DMF.**

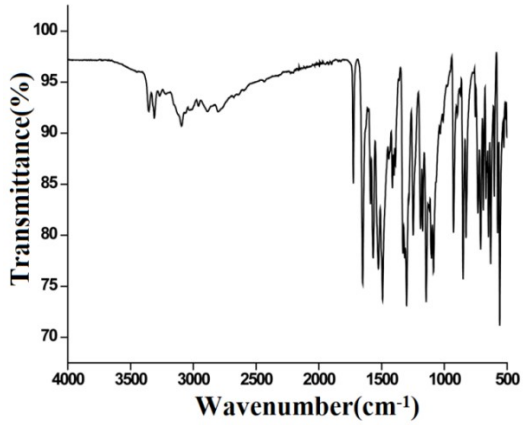


Figure **S29**: FT-IR spectrum (neat) of the H**STZU.DMF**.

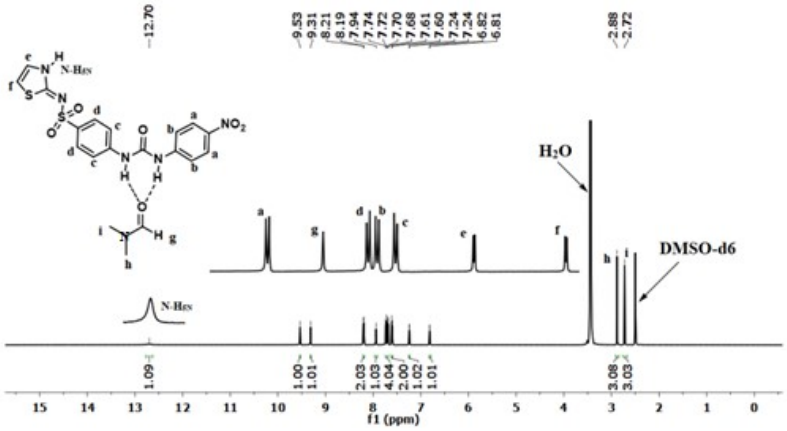


Figure **S30**: ^{1}HNMR (DMSO-d_6, 600 MHz,) spectra of the H**STZ.DMF**.

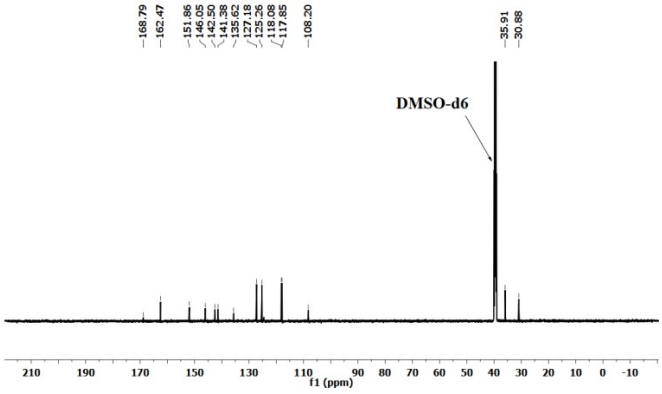
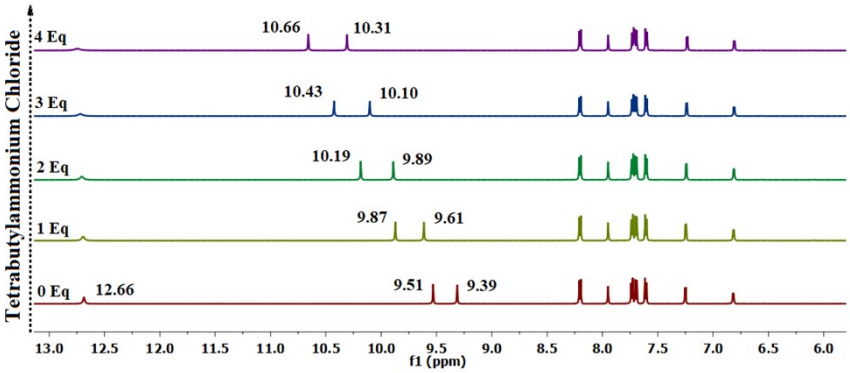
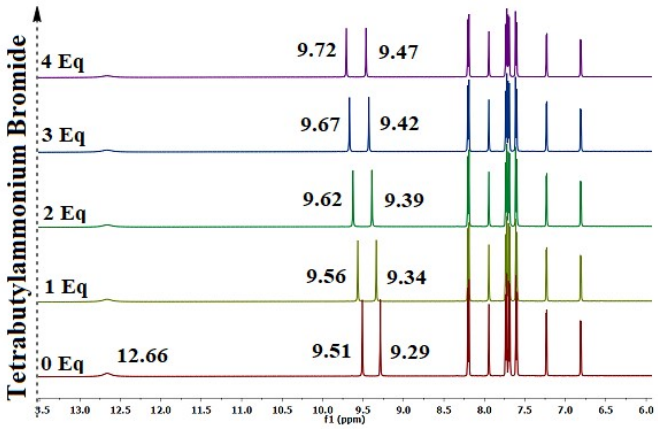


Figure **S31**: ^{13}CNMR (125 MHz, DMSO-d_6) spectra of the H**STZ.DMF.**



(a)



(b)

Figure **S32**: ^{1}H NMR (600 MHz, DMSO-d_6) titration showing the aromatic protons of H**STZU**.**DMF** recorded by adding different amounts of tetrabutylammonium (a) chloride and (b) bromide.

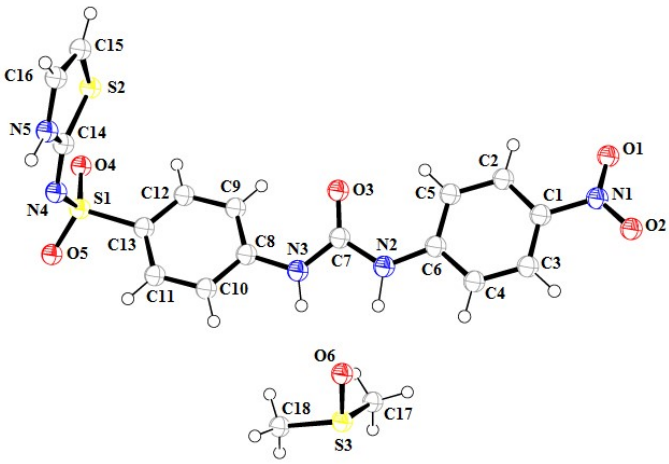


Figure **S33**: ORTEP diagram of H**STZU.DMSO** drawn with 50% ellipsoid probability.

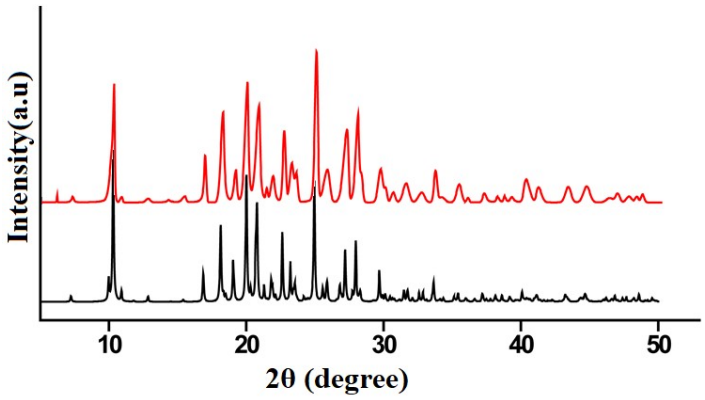


Figure **S34**: Powder X-ray diffraction patterns of the H**STZU.DMSO**.

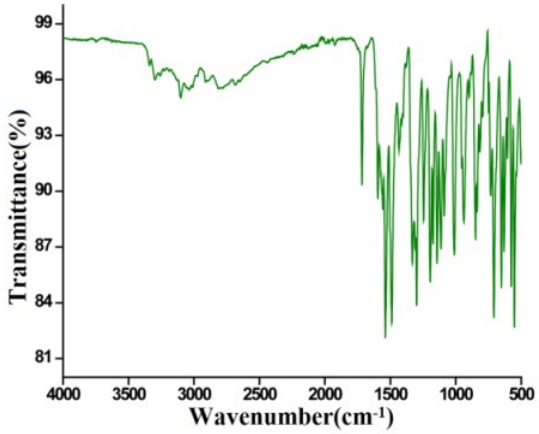


Figure **S35**: FT-IR spectrum (neat) of the H**STZU.DMSO**.

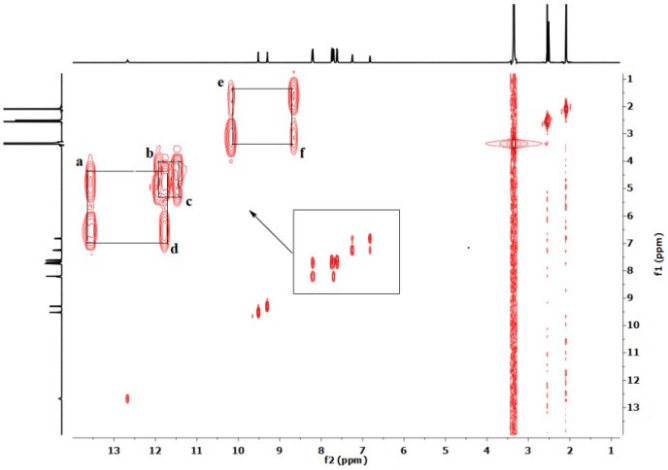


Figure **S36**: ^{1}H 2D-HOMOCOSY (600 MHz, DMSO-d_6) spectrum of the H**STZU .DMSO.**

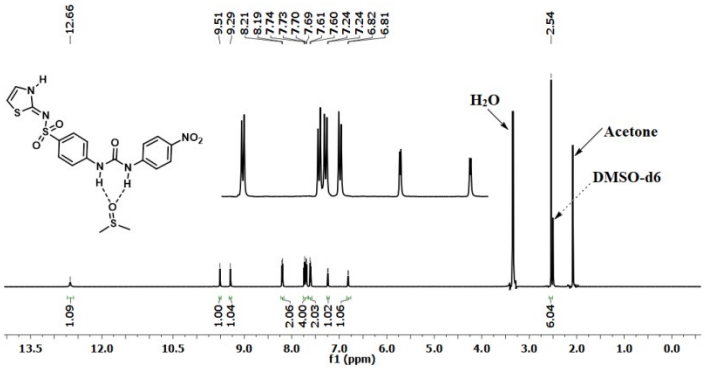


Figure **S37**: ^{1}HNMR (DMSO-d_6, 600 MHz,) spectra of the H**STZU.DMSO**.

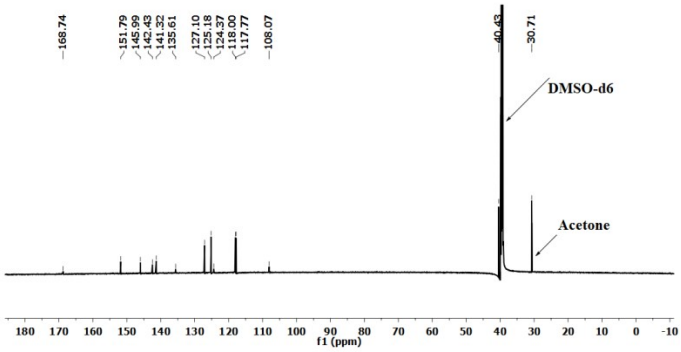


Figure **S38**: ^{13}CNMR (125 MHz, DMSO-d_6) spectra of the H**STZU.DMSO.**

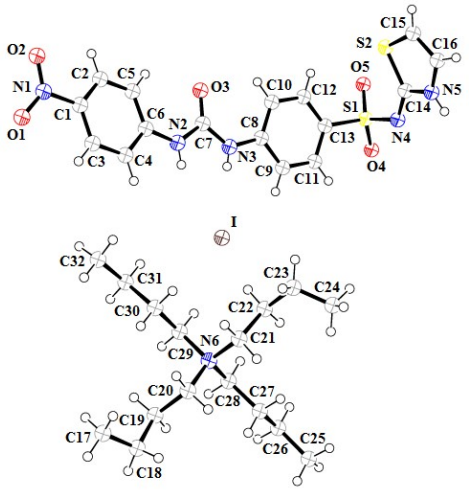


Figure **S39**: ORTEP diagram of H**STZU.TBAI** with 50 % ellipsoid probability.

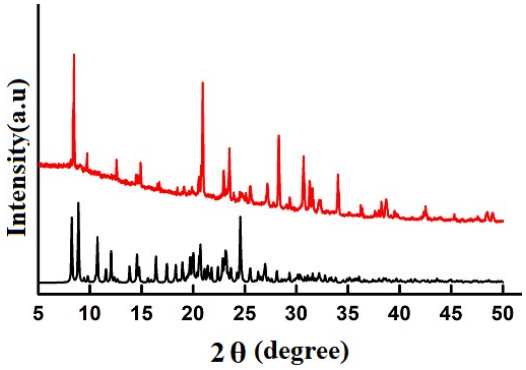


Figure **S40**: Powder X-ray diffraction patterns of the H**STZU.TBAI.**

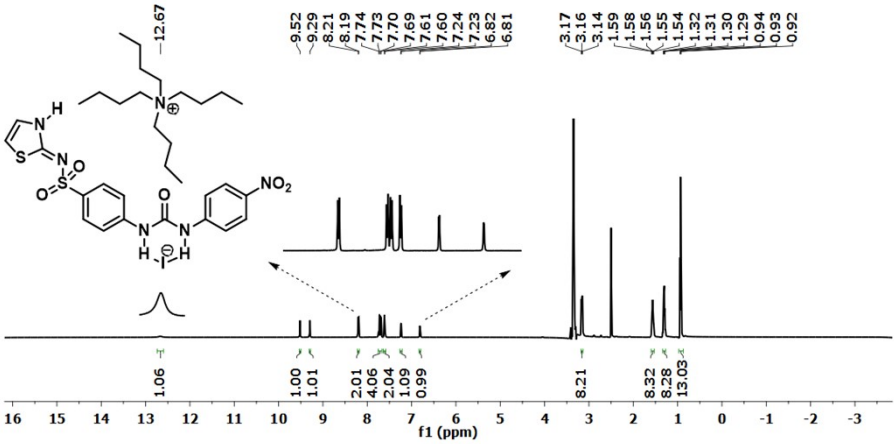


Figure **S41**: ^{1}HNMR (DMSO-d_6, 600 MHz) spectra of the H**STZU.TBAI.**

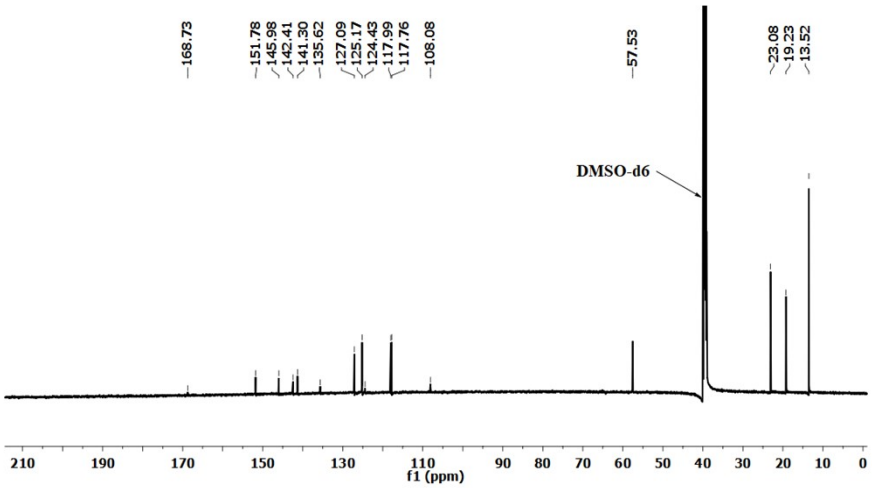


Figure **S42**: ^{13}CNMR (125 MHz, DMSO-d_6) spectra of the H**STZU.TBAI.**

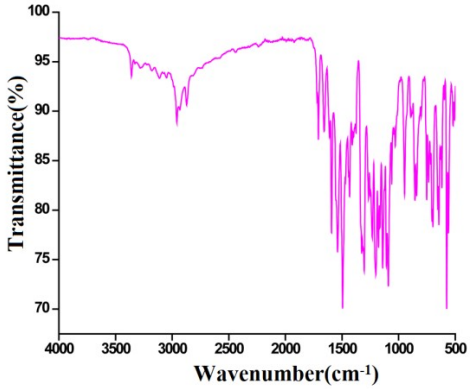


Figure **S43**: FT-IR spectrum (neat) of the TBA(**STZU**).

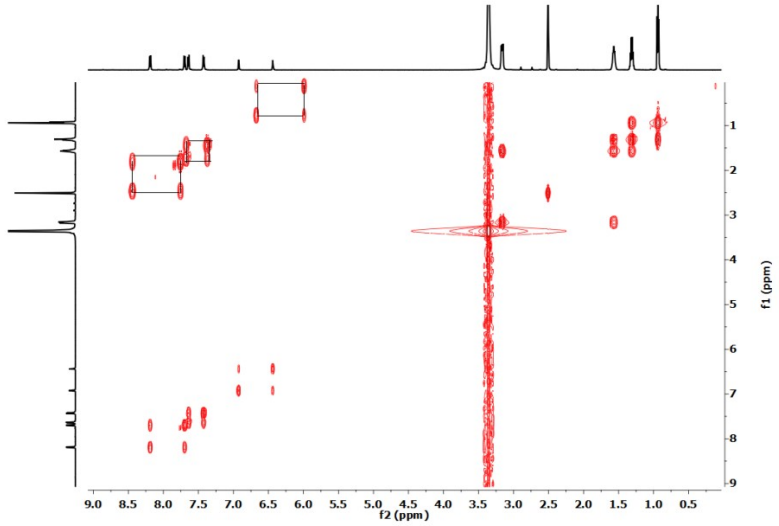


Figure **S44**: ^{1}H 2D-HOMOCOSY (600 MHz, DMSO-d_6) spectrum of the TBA(**STZU**)**.**

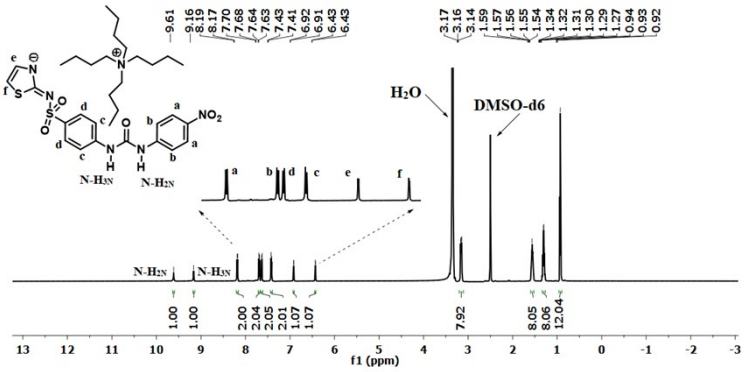


Figure **S45**: ^{1}HNMR (DMSO-d_6, 600 MHz) spectra of the TBA(**STZU**)**.**

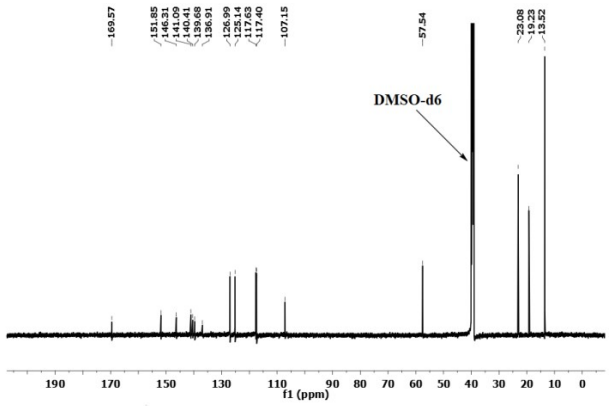
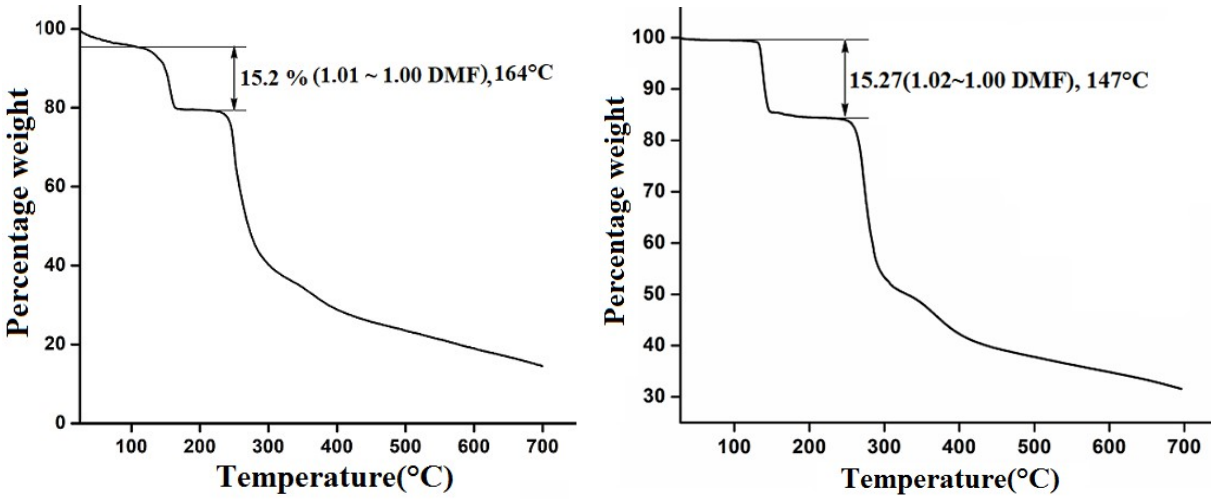
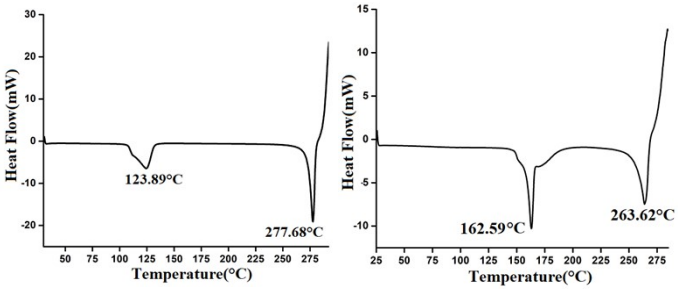


Figure S**46**: ^{13}CNMR (125 MHz, DMSO-d_6) spectra of the TBA(**STZU).**



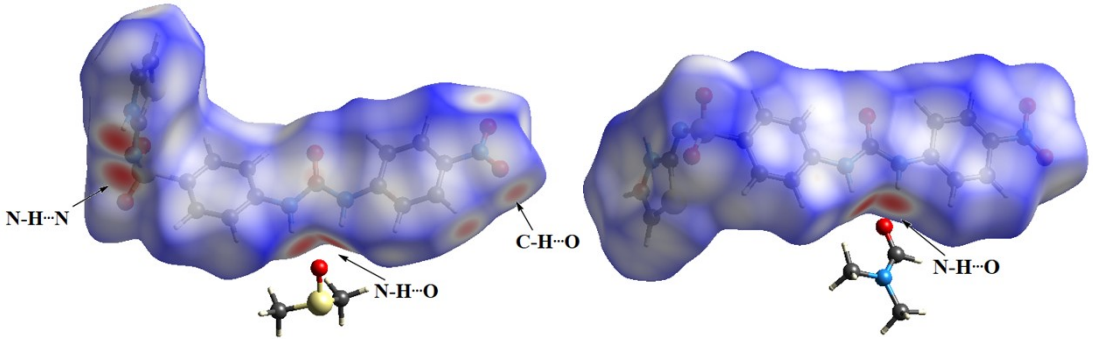
(a) (b)

Figure S**47**: Thermogram of the polymorph (a) H**SMZU.DMF-P1** (b) H**SMZU.DMF-P2.**

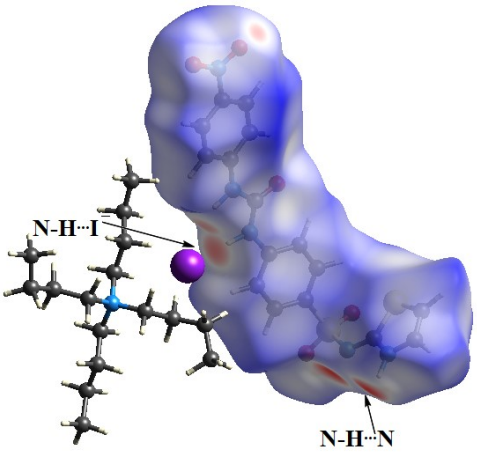


(a) (b)

Figure **S48**: Differential scanning calorimetry of **(**a) H**STZU.DMF (**b) H**STZU.DMSO** (heating rate 10ºC/min under nitrogen atmosphere).



(a) (b)



(c)

Figure **S49**: Hirshfeld surfaces of (a) H**STZU.DMF** (b) H**STZU.DMSO**, (c) H**STZU.TBAI**.

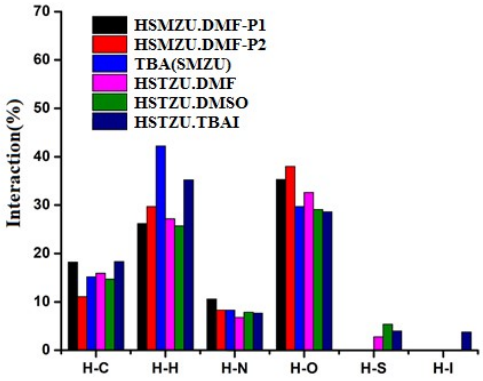


Figure S**50**: Percentages of the H···C, H···H, H···O, H···N, H···S and H···anion interaction (include reciprocal contacts) in 2D fingerprint plots

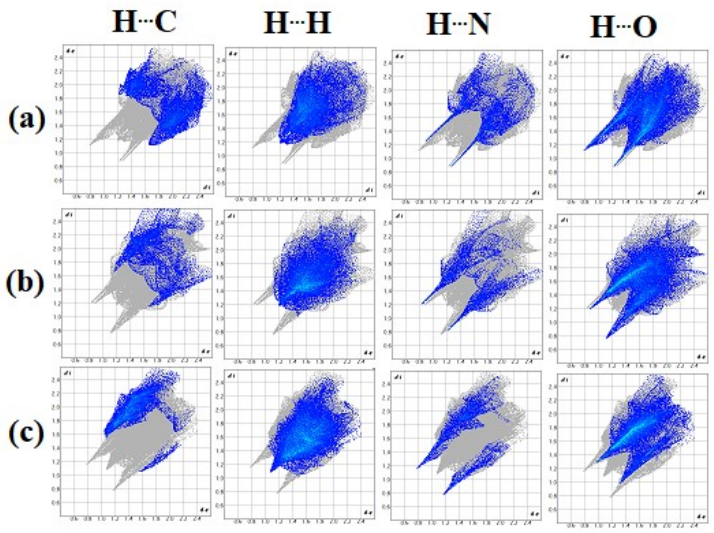


Figure **S51**: 2D fingerprint plots (including reciprocal contacts) of the H···C, H···H, H···O, H···N and H···anion interactions of a) H**SMZU.DMF-P1** b) H**SMZU.DMF-P2** c) TBA(**SMZU).**

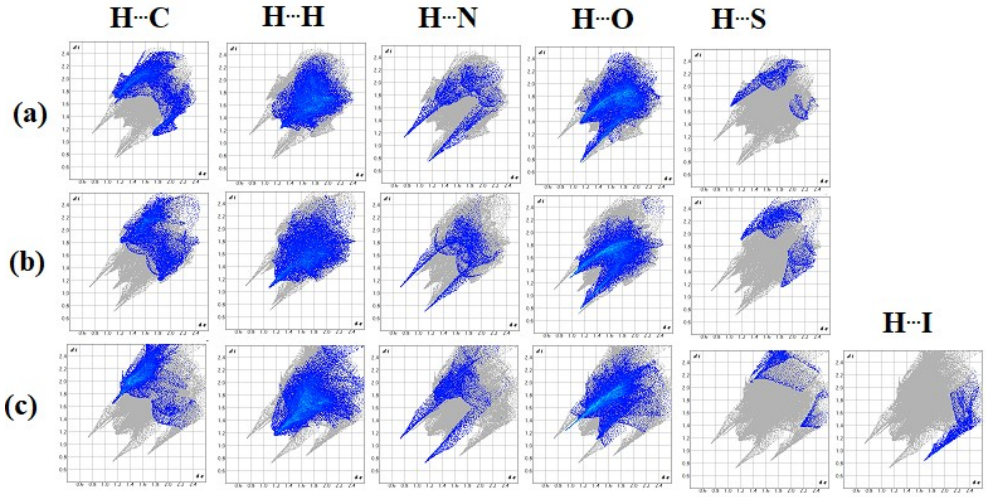
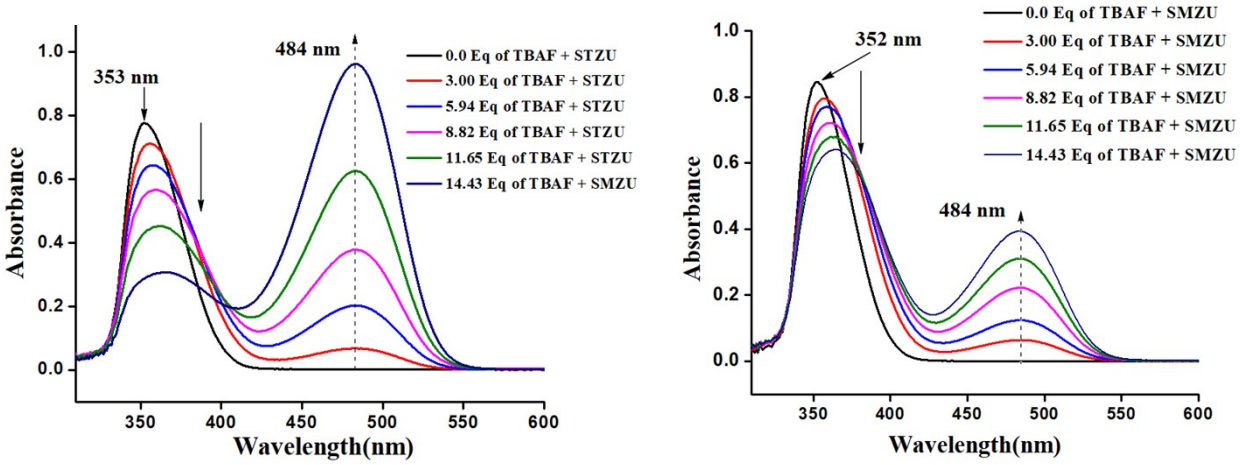
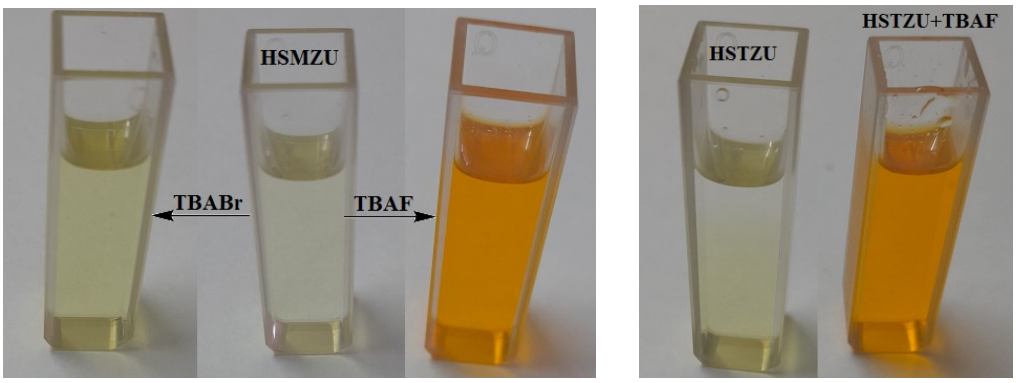


Figure **S52**: 2D fingerprint plots (including reciprocal contacts) of the H···C, H···H, H···O, H···N and H···anion interactions of (a) H**STZU.DMF (**b) H**STZU.DMSO (**c) H**STZU.TBAI.**



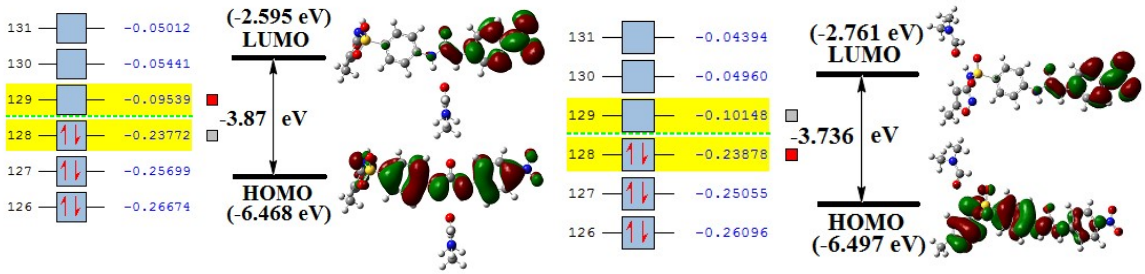
(a) (b)

Figure S**53:** Changes in the UV-visible spectra of (a) H**STZU** and (b) **HSMZU** (3.3×10^{-5} M, 2mL in each case) in dimethylsulfoxide by aliquots (30 µL) of tetrabutylammonium fluoride (10^{-2} M).

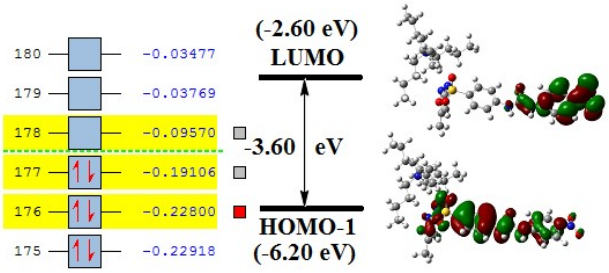


(a) (b)

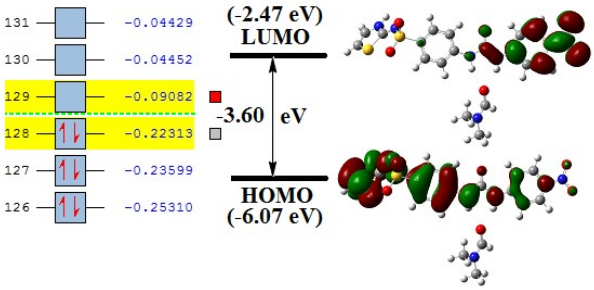
Figure S**54:** Visual color change of a) H**SMZU** b) H**STZU** after addition of TBAF and TBABr respectively.



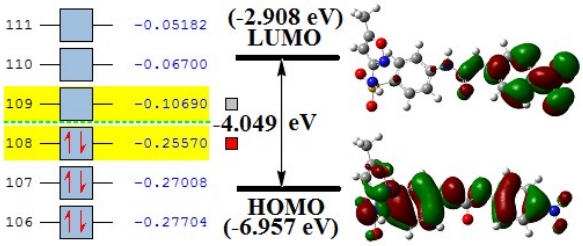
(a) (b)


180 -0.03477
179 -0.03769
178 -0.09570
177 -0.19106
176 -0.22800
175 -0.22918
(-2.60 eV)
LUMO
-3.60 eV
HOMO-1
(-6.20 eV)

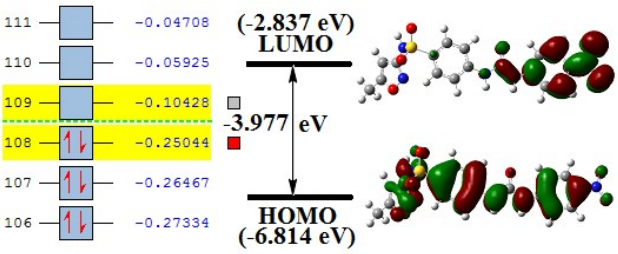
(c)


131 -0.04429
130 -0.04452
129 -0.09082
128 -0.22313
127 -0.23599
126 -0.25310
(-2.47 eV)
LUMO
-3.60 eV
HOMO
(-6.07 eV)

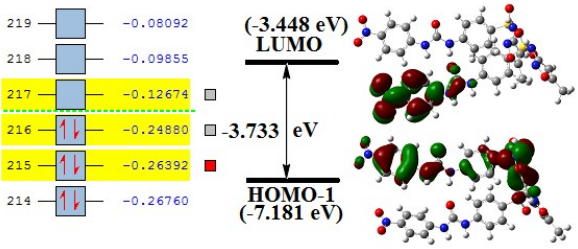
(d)


111 -0.05182
110 -0.06700
109 -0.10690
108 -0.25570
107 -0.27008
106 -0.27704
(-2.908 eV)
LUMO
-4.049 eV
HOMO
(-6.957 eV)

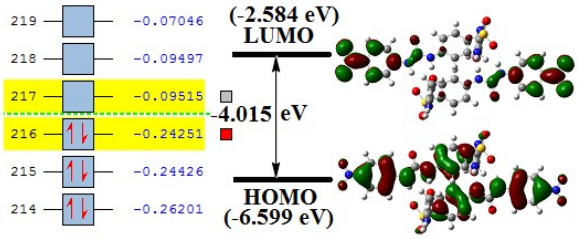
(e)


111 -0.04708
110 -0.05925
109 -0.10428
108 -0.25044
107 -0.26467
106 -0.27334
(-2.837 eV)
LUMO
-3.977 eV
HOMO
(-6.814 eV)

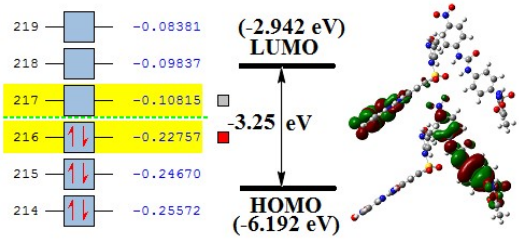
(f)


219 -0.08092
218 -0.09855
217 -0.12674
216 -0.24880
215 -0.26392
214 -0.26760
(-3.448 eV)
LUMO
-3.733 eV
HOMO-1
(-7.181 eV)

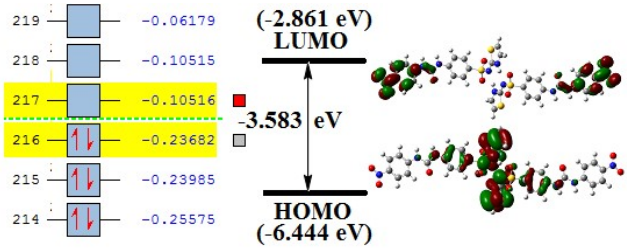
(g)


219 -0.07046
218 -0.09497
217 -0.09515
216 -0.24251
215 -0.24426
214 -0.26201
(-2.584 eV)
LUMO
-4.015 eV
HOMO
(-6.599 eV)

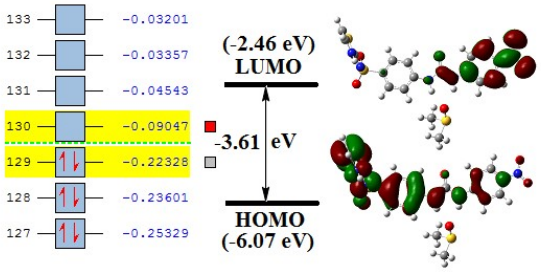
(h)


219 -0.08381
218 -0.09837
217 -0.10815
216 -0.22757
215 -0.24670
214 -0.25572
(-2.942 eV)
LUMO
-3.25 eV
HOMO
(-6.192 eV)

(i)


219 -0.06179
218 -0.10515
217 -0.10516
216 -0.23682
215 -0.23985
214 -0.25575
(-2.861 eV)
LUMO
-3.583 eV
HOMO
(-6.444 eV)

(j)



(k)

Figure **S55**: HOMO and LUMO gap in the (a) H**SMZU.DMF-P1** (b) H**SMZU.DMF-P2** (c) TBA(**SMZU**), (d) H**STZU.DMF (**e) H**SMZU-P1 (**f) H**SMZU-P2 (**g) dimer of H**SMZU-P1** (h) dimer of H**SMZU-P2** (i) dimer of TBA(**SMZU**) **(**j) dimer of H**STZU.DMF (**k) H**SMZU.DMSO** calculated by DFT using B3LYP/6-31+G (d, p) as basis set.