Supplementary data for the article:

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Synthesis, physicochemical characterization and TD-DFT calculations of monothiocarbohydrazone derivatives

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Benzaldehyde thiocarbohydrazone (**1**)[13,14]

White substance, recrystallized from ethanol. Yield: 84%. M.p. 203 ºC. Elemental analysis: Calculated for $C_8H_{10}N_4S$ (*Mw* = 194.26 g mol^{-1}): C, 49.39; H, 5.19; N, 28.94; S: 16.48%. Found: C, 49.11; H, 5.27; N, 28.12; S, 17.50%. IR (KBr, cm^{-1}): ν(NH_2): 3259s, ν(NH): 3160m, ν(C=N): 1628s, ν(C=S): 1267s. ^{1}H NMR (400 MHz, DMSO–*d6*, *δ* (ppm)): 4.88 (s, 2H, H2–N4), 7.39 (m, 3H, Ar–H), 7.83 (m, 2H, Ar–H), 8.01 (s, 1H, H–C7), 9.82 (s, 1H, H–N2), 11.42 (s, 1H, H–N3).^{13}C NMR (100 MHz, DMSO–*d6*, *δ* (ppm): 127.8 (2xC(Ar)), 129.1 (2xC(Ar)), 130.1 (C4),134.7 (C1), 142.5 (C7), 176.3 (C8).

Literature data: ^{1}H NMR (400 MHz, DMSO–*d6*, *δ* (ppm)): 4.91 (bs, 2H, NH_2), 7.34–8.01 (m, 5H, Ar–H), 8.03 (s, 1H, CH), 9.82 (bs, 1H, NH), 11.42 (s, 1H, NH).

2-hydroxybenzaldehyde thiocarbohydrazone (**2**)[14]

Yellow substance, recrystallized from methanol. Yield: 76%. M.p. 201 ºC. Elemental analysis: Calculated for $C_8H_{10}ON_4S$ (*Mw* = 210.54 g mol^{-1}): C, 45.34; H, 4.80; N, 26.73; O, 7.60; S, 15.23%. Found: C, 45.39; H, 4.77; N, 26.67; O, 7.60; S, 15.54%. IR (KBr, cm^{-1}): ν(OH): 3436s, ν(NH_2): 3237s, ν(NH): 3188s, ν(C=N): 1623s, ν(C=S): 1280s, ν(Ar-OH): 1241s. ^{1}H NMR (400 MHz, DMSO–*d6*,*δ* (ppm)): 4.83 (s, 2H, H2–N4), 6.76–7.27 (m, 3H, H–C3, H–C4, H–C5), 7.95 (d, 1H, H–C2), 8.31 (s, 1H, H–C7), 9.72 (s, 1H, H–OH), 9.82 (s, 1H, H–N2),

11.33 (s, 1H, H–N3). ^{13}C NMR (100 MHz, DMSO–*d6*, δ (ppm)): 116.5 (C4), 119.7 (C3), 120.8 (C5), 127.6 (C6), 131.4 (C1), 140.1 (C7), 156.7 (C2), 176.2 (C8).

3-hydroxybenzaldehyde thiocarbohydrazone (**3**)[14]

Brown substance, recrystallized from ethanol. Yield: 52%. M.p. 195 ºC. Elemental analysis: Calculated for $C_8H_{10}ON_4S$ (*Mw* = 210.54 g mol^{-1}): C, 45.34; H, 4.80; N, 26.73; O, 7.60; S, 15.23%. Found: C, 45.12; H, 4.73; N, 26.87; O, 7.22; S, 16.06%. IR (KBr, cm^{-1}): ν(OH): 3389m, ν(NH_2): 3249s, ν(NH): 3180m, ν(C=N): 1581s, ν(C=S): 1284s, ν(Ar-OH): 1246s. ^{1}H NMR (400 MHz, DMSO–*d6*, δ (ppm)): 4.81 (s, 2H, H2–N4), 6.78 (m, 1H, H–C2), 7.12–7.26 (m, 3H, H–C3, H–C4, H–C6), 7.91 (s, 1H, H–C7), 9.51 (s, 1H, H–OH), 9.71 (s, 1H, H–N2), 11.33 (s, 1H,H–N3). ^{13}C NMR (100 MHz, DMSO–*d6*, δ (ppm)): 114.1 (C4), 117.4 (C2), 119.0 (C3), 130.1 (C6), 136.0 (C1), 142.9 (C7), 158.0 (C5), 176.2 (C8).
Litearture data: ^{1}H NMR (400 MHz, DMSO–*d6*, δ (ppm)): 4.85 (s, 2H, NH_2), 6.79 (d, 1H, *J* = 7,6 Hz, ArH), 7.16–7.24 (m, 3H, Ar–H), 7.92 (s, 1H, =CH), 9.48 (s, 1H, OH), 9.72 (s, 1H, NH), 11.34 (s, 1H, NH).

4-nitrobenzaldehyde thiocarbohydrazone (**10**)[14,15]

Yellow substance, recrystallized from methanol. Yield: 77%. M.p. 230 ºC. Elemental analysis: Calculated for $C_8H_9N_5O_2S$ (*Mw* = 239.60 g mol^{-1}): C, 40.11; H, 3.79; N, 29.36; O, 13.36; S, 13.38%. Found: C, 40.24; H, 3.85; N, 29.11; O, 13.17; S, 13.63%. IR (KBr, cm^{-1}): ν(NH_2): 3296s, ν(NH): 3167m, ν(C=N): 1634s, ν(NO): 1505s i 1338s, ν(C=S): 1247s. ^{1}H NMR (400 MHz, DMSO–*d6*, δ (ppm)): 4.90 (s, 2H, H2–N4), 8.06 (s, 1H, H–C7), 8.10 (d, 2H, H–C5, H–C3), 8.20 (d, 2H, H–C2,H–C6), 10.12 (s, 1H, H–N2), 11.70 (s, 1H, H–N3). ^{13}C NMR (100 MHz, DMSO–*d6*, δ (ppm)): 124.5 (C2=C6), 128.9 (C5=C3), 139.9 (C7), 141.5 (C1), 147.8 (C4), 176.3 (C8).
Literature data: ^{1}H NMR (400 MHz, DMSO–*d6*, δ (ppm)): 4.96 (s, 2H; NH_2), 8.09 (s, 1H; CH=N), 8.13 (d, *J* = 8.0 Hz, 2H; Ar-H), 8.22 (d, *J* = 8.0 Hz, 2H; Ar-H), 10.17 (s, 1H; NH), 11.76 (s, 1H; NH).

4-metoxybenzaldehyde thiocarbohydrazone (**13**)[13,14]

Yellow substance, recrystallized from ethanol. Yield: 81%. M.p. 197 ºC. Elemental analysis: Calculated for $C_9H_{12}N_4OS$ (*Mw* = 224.57 g mol^{-1}): C, 48.14; H, 5.40; N, 25.06; O, 7.03; S, 14.32%. Found: C, 48.08; H, 5.37; N, 25.13; O, 7.19; S, 14.23%. IR (KBr, cm^{-1}): ν(NH_2): 3299s, ν(NH): 3165s, ν(O-CH3): 3002m, 2830m i 1421m, ν(C=N): 1607s, ν(C=S): 1250s. ^{1}H NMR (400 MHz, DMSO–*d6*, *δ* (ppm)): 3.78 (s, 3H, H–OCH_3), 4.82 (s, 2H, H2–N4), 6.94 (d, 2H, H–C2, H–C6), 7.76 (d, 2H, H–C3, H–C5), 7.94 (s, 1H, H–C7), 9.70 (s, 1H, H–N2), 11.29 (s, 1H, H–N3). ^{13}C NMR (100 MHz, DMSO–*d6*, *δ* (ppm)): 56.0 (C–OCH_3), 114.7 (C2=C6), 127.5 (C1), 129.6 (C5=C3), 142.7 (C7), 161.1 (C4), 176.6 (C8).
Literature data: ^{1}H NMR (400 MHz, DMSO–*d6*, *δ* (ppm)): 3.81 (s, 3H, CH_3), 4.90 (bs, 2H, NH_2), 7.54–7.95 (m, 4H, Ar-H), 8.02 (s, 1H, CH), 9.81 (bs, 1H, NH), 11.39 (s, 1H, NH).

4-clhorobenzaldehyde thiocarbohydrazone (**15**)[14]

Yellow substance, recrystallized from ethanol. Yield: 79%. M.p. 214 ºC. Elemental analysis: Calculated for $C_8H_9N_4SCl$ (*Mw* = 228.98 g mol^{-1}): C, 41.96; H, 3.97; N, 24.58; S, 14.01; Cl, 15.48%. Found: C, 41.81; H, 3.92; N, 24.66; S, 14.01; Cl, 15.60%. IR (KBr, cm^{-1}): ν(NH_2): 3275m, ν(NH): 3177m, ν(C=N): 1596s, ν(C=S): 1244s. ^{1}H NMR (400 MHz, DMSO–*d6*, *δ* (ppm)): 4.86 (*s*, 2H, H2–N4), 7.41 (*d*, 2H, H–C2, H–C6), 7.85 (*d*, 2H, H–C5, H–C3), 7.98 (*s*, 1H, H–C7), 9.88 (*s*, 1H, H–N2), 11.48 (*s*, 1H, H–N3). ^{13}C NMR (100 MHz, DMSO–*d6*, *δ* (ppm)): 129.1 (C2=C6), 129.4 (C5=C3), 133.7 (C1), 134.6 (C4), 141.2 (C7), 176.6 (C8).
Literature data: 4.88 (s, 2H, NH_2), 7.45 (d, 2H, *J* = 8.4 Hz, Ar-H), 7.89 (d, 2H, *J* = 8.4 Hz, Ar-H), 7.98 (s, 1H, =CH), 9.93 (s, 1H, NH), 11.50 (s, 1H, NH).

4-fluorobenzaldehyde thiocarbohydrazone (**18**)[14]

White substance, recrystallized from ethanol. Yield: 84%. M.p. 212 ºC. Elemental analysis: Calculated for $C_8H_9N_4SF$ (*Mw* = 212.53 g mol^{-1}): C, 45.10; H, 4.28; N, 26.48; S, 15.09; F, 8.94%. Found: C, 45.10; H, 4.17; N, 26.51; S, 15.17; F, 9.05%. IR (KBr, cm^{-1}): ν(NH_2): 3300s, ν(NH): 3158m, ν(C=N): 1600s, ν(C=S): 1272s. ^{1}H NMR (400 MHz, DMSO–*d6*, *δ* (ppm)):4.86 (*s*, 2H, H2–N4), 7.23 (*t*, 2H, H–C2, H–C6), 7.90–7.93 (*m*, 2H, H–C5, H–C3), 8.00 (*s*, 1H, H–C7), 9.87 (*s*, 1H, H–N2), 11.43 (*s*, 1H, H–N3). ^{13}C NMR (100 MHz, DMSO–*d6*,

δ (ppm)): 116.1 (C2=C6, *d*, J_{C-F} = 21.6 Hz), 130.1 (C5=C3, *d*, J_{C-F} = 8.5 Hz), 131.4 (C1, *d*, J_{C-F} = 3 Hz), 141.5 (C7), 163.4 (C4, *d*, J_{C-F} = 246 Hz), 176.6 (C8).

Literature data: ^{1}H NMR (400 MHz, DMSO–*d6*, δ (ppm)): 4.88 (s, 2H, NH_2), 7.24 (t, 2H, *J* = 8.8 Hz, Ar-H), 7.91–7.94 (m, 2H, Ar-H), 7.99 (s, 1H, =CH), 9.90 (s, 1H, NH), 11.46 (s, 1H, NH).

*Table S1 Crystal data and refinement parameters for compound **17***

Parameter	17	Parameter	17	Parameter	17
Chemical	$C_8H_9BrN_4S$	α / °	90	Color / habitus	colorless/prism
Formula	273.16	β / °	95.680(3)	Reflections	2059
Temperature /	295(2)	γ / °	90	Independent	1989
Wavelength /	1.54184	V / Å^3	1055.65(5)	R_{int}	0.0275
Crystal	Monoclinic	Z	4	Reflections I >	1989
Space group	$P\ 2_1/c$	D_c / g cm^{-3}	1.719	Restraints /	4/139
a / Å	4.63455(14)	μ / mm^{-1}	6.891 (Cu $K\alpha$)	R_1	0.0272
b / Å	9.9358(3)	F (000)	544	wR_2	0.0729
c / Å	23.0380(7)	Crystal size	0.58×0.21×0.11	S	1.096

Table S2 Calculated values of dihedral angles (in °) between phenyl group and thiocarbohydrazone residues of the E and Z isomers of monothiocarbohydrazone derivatives

Compound	*E* isomer	*Z* isomer	Compound	*E* isomer	*Z* isomer
1	8.07	55.46	**10**	5.77	54.24
2	20.50	65.65	**11**	18.14	26.38
3	8.65	52.28	**12**	8.81	51.13
4	8.85	53.45	**13**	9.12	53.08
5	8.29	68.06	**14**	7.13	56.04
6	8.24	54.69	**15**	7.65	54.28
7	8.67	54.50	**16**	7.31	56.33
8	27.90	70.70	**17**	7.57	54.26
9	6.60	56.77	**18**	8.28	55.08

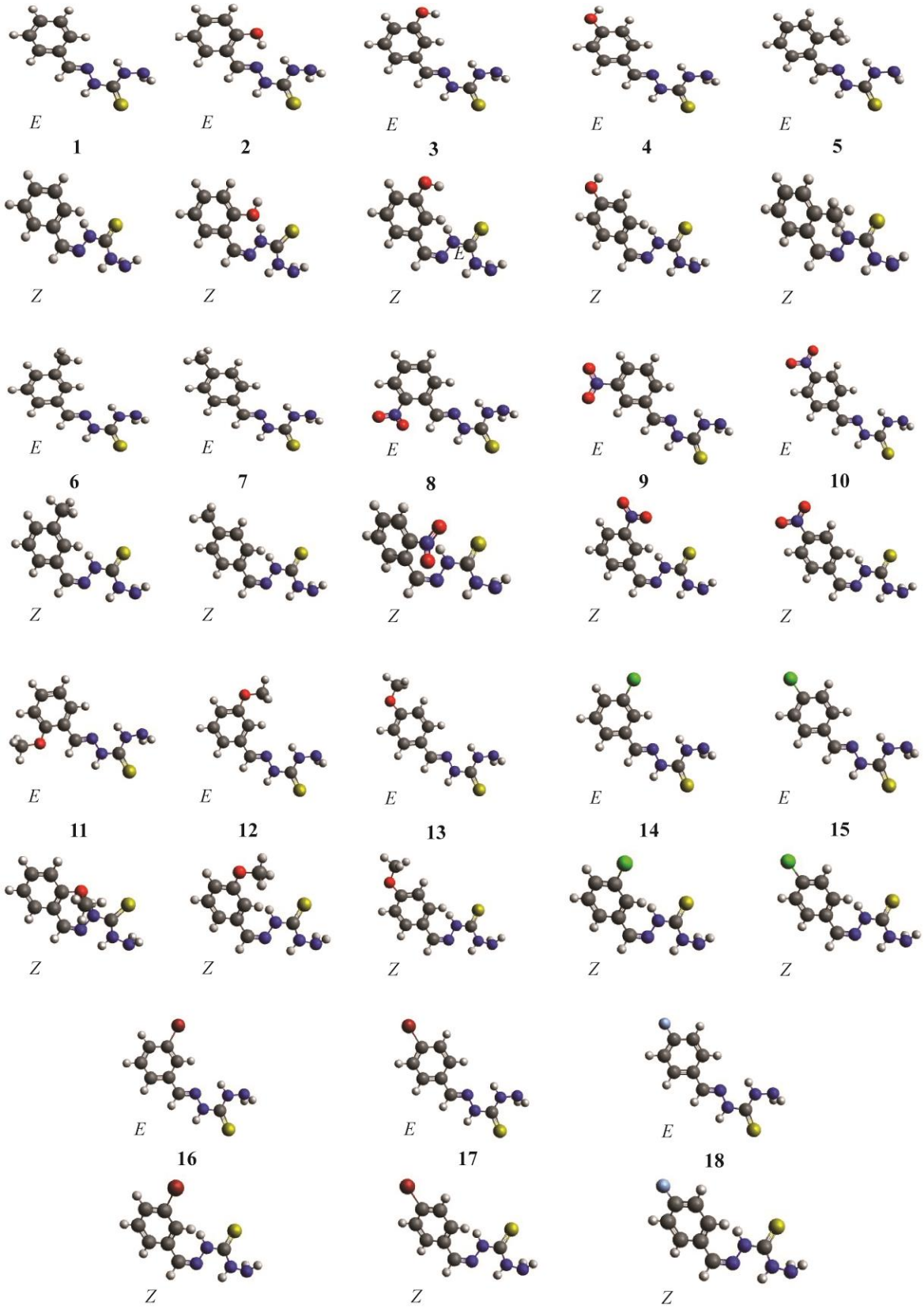

Fig. S1 Optimized structures of E and Z isomers of monothiocarbohydrazone derivatives

Table S3 Absorption frequencies, $v_{max}\cdot10^{-3}$, cm^{-1} and values of molar absorptivity of monothiocarbohydrazones in all solvents used

Compound/ solvent	Water	2–ClEtOH	Methanol	Ethanol	*n*-propanol	*n*-butanol	*n*-pentanol	*i*-butanol	*i*-propanol	*t*-butanol	Acetic acid	AcN	DMSO	DMF	DMA	DCM	Chloroform	EtAc	THF	1,4-dioxane	Diethyl-ether
1	32.41	32.16	32.04	31.93	31.88	31.83	31.76	31.80	31.79	31.64	31.98	31.75	31.66	31.60	31.57	31.59	31.55	31.53	31.49	31.47	31.43
	29500	44650	31000	39575	37150	37200	32900	38150	38950	31800	26975	38250	38975	35125	28575	37450	40725	34175	34825	43800	30800
2	30.22	29.97	30.08	29.98	29.88	29.85	29.82	29.98	29.93	29.70	30.08	29.80	29.75	29.75	29.65	29.72	29.60	29.57	29.53	29.48	29.44
	22500	27750	32000	24800	25600	24850	23625	24700	25325	24500	31600	23775	21825	22650	21225	27450	29600	40075	25475	25350	28575
3	32.29	32.00	31.96	31.60	31.54	31.49	31.40	31.60	31.71	31.32	31.81	31.51	31.25	31.21	31.20	31.24	31.19	31.10	31.04	31.03	30.94
	18000	19800	26250	26100	25675	24050	23275	27300	34450	23800	25450	26275	22800	24275	24175	24125	25025	23625	25950	25025	22425
4	31.19	30.82	30.87	30.76	30.71	30.67	30.60	30.64	30.64	30.47	30.83	30.61	30.52	30.56	30.49	30.48	30.41	30.39	30.37	30.34	30.29
	16500	19025	21550	21725	21500	20550	15350	20200	20575	16925	20775	20725	19400	19025	19375	19825	18675	20325	21050	19025	20450
5	31.96	31.51	31.49	31.31	31.26	31.24	31.23	31.33	31.28	31.14	31.39	31.22	31.08	31.04	30.93	31.02	30.99	31.00	30.93	30.85	30.81
	23275	26525	31250	30450	30475	29825	28350	29650	25475	27825	28675	31075	27400	27500	29025	27350	29575	27050	30075	27325	29925
6	32.23	31.98	31.87	31.77	31.77	31.69	31.66	31.68	31.67	31.50	31.87	31.63	31.51	31.47	31.44	31.43	31.40	31.42	31.38	31.38	31.25
	16150	16125	21500	20325	21175	20425	19225	18875	19625	19075	21225	21075	17700	20200	19675	20400	21400	19325	20575	19025	18000
7	31.80	31.64	31.60	31.42	31.54	31.49	31.41	31.38	31.33	31.37	31.60	31.38	31.27	31.26	31.20	31.14	31.11	31.09	31.13	31.12	30.97
	25350	29675	35750	34525	33875	33950	32900	47925	19775	31725	35250	35200	30025	29125	31100	31875	35000	30900	32925	30125	31675
8	35.70	32.95	32.90	32.81	32.64	32.49	32.42	32.69	3261	32.32	32.85	32.50	32.39	32.37	32.22	32.18	32.14	32.09	32.00	31.97	31.95
	17075	13200	23500	17650	15950	15000	16175	15250	16075	12500	10725	16400	16150	13775	18675	16200	15350	15500	14400	13725	18475
9	32.20	31.82	31.87	31.71	31.65	31.49	31.48	31.66	31.60	31.42	31.77	31.49	31.42	31.36	31.32	31.37	31.32	31.28	31.20	31.29	31.18
	28575	5875	28150	4700	8540	30400	26475	27050	27550	25500	32525	29475	26675	28475	28400	26600	30450	28475	27550	24025	25525
10	28.66	28.27	28.20	27.93	28.05	27.84	27.80	27.82	27.73	27.61	28.12	27.73	27.52	27.50	27.48	27.46	27.40	27.44	27.23	27.27	27.17
	22100	23225	24250	25900	17500	22600	22675	23425	23100	19900	21175	23275	21850	20575	21250	25175	24625	22900	23025	27675	18625
11	30.31	30.13	30.19	30.14	30.08	30.03	30.02	30.07	30.12	29.97	30.05	30.04	29.96	29.95	29.93	29.97	29.93	29.96	29.93	29.84	29.78
	15775	22425	17250	2715	18300	27950	26900	25125	27500	22350	17550	23950	26925	22475	21100	23950	24675	23075	24700	21500	22525
12	31.85	31.49	31.53	31.37	31.26	31.18	31.16	31.29	31.30	30.99	31.35	31.11	31.02	30.99	30.93	30.89	30.84	30.78	30.77	30.74	30.65
	15975	23325	19575	21500	15650	19175	25475	23875	21675	11025	9200	21850	12250	22475	18750	19725	25200	23125	20100	25675	20900
13	31.51	31.14	31.04	30.98	31.11	31.02	30.90	30.91	30.92	30.82	31.10	30.86	30.77	30.75	30.73	30.76	30.68	30.66	30.71	30.69	30.59
	26800	36775	20325	31350	22425	31550	31650	30125	31550	30350	23300	32600	28625	30875	35925	31125	33450	30925	27850	32600	27350
14	32.11	31.70	31.66	31.49	31.43	31.34	31.31	31.56	31.48	31.14	31.57	31.30	31.09	31.03	30.99	31.03	31.00	30.94	30.93	30.91	30.85
	13750	25275	33250	32825	33250	32600	29175	31275	29875	27375	31525	32525	28925	29950	31025	16225	31125	28575	32225	29400	30925
15	31.87	31.59	31.48	31.37	31.26	31.18	31.14	31.29	31.30	30.98	31.43	31.12	30.93	30.92	30.81	30.85	30.80	30.78	30.76	30.71	30.62
	39775	40000	26400	31225	26975	31200	31025	31350	34525	29675	22300	31775	29200	28175	28125	32050	33125	26800	27850	32150	23850
16	31.97	31.71	31.60	31.37	31.31	31.29	31.23	31.43	31.35	31.15	31.45	31.22	31.03	30.99	30.95	31.05	31.03	31.04	30.88	30.91	30.76
	11425	15725	21925	19375	21000	19375	18050	18725	17875	16000	20025	21425	18450	19250	20325	18575	21250	17825	19450	17875	17950
17	31.77	31.26	31.35	31.14	31.08	31.09	31.04	31.16	31.15	30.95	31.24	31.03	30.88	30.85	30.75	30.87	30.83	30.79	30.75	30.71	30.63
	24550	23450	31000	35250	35975	28450	30050	28075	35200	32840	28525	29950	27325	27050	27600	36400	25750	28125	34525	27600	17725
18	32.35	32.07	31.99	31.87	31.83	31.80	31.68	31.85	31.83	31.61	31.91	31.71	31.56	31.53	31.42	31.53	31.42	31.35	31.29	31.25	31.18
	24250	27025	26975	30800	20875	28225	32225	24950	30525	23775	14575	29950	27400	21375	28025	28650	28575	22150	25800	26625	19275

Table S4 Empirical parameters of solvents used

Solvent	E_T^{N}[27]	*Catalan's* solvent parameters[26]				*Hansen's* parameters[28]		
		SA	*SB*	*SP*	*SdP*	*δd*	*δp*	*δh*
Water	1.000	1.062	0.025	0.681	0.997	15.6	16.0	42.3
Methanol	0.762	0.605	0.545	0.608	0.904	15.1	12.3	22.3
2-ClEtOH	0.753	0.360	0.560	0.699	0.895	/	/	/
Ethanol	0.654	0.400	0.658	0.633	0.783	15.8	8.8	19.4
n-propanol	0.617	0.367	0.782	0.658	0.748	16.0	6.8	17.4
n-butanol	0.586	0.341	0.809	0.674	0.655	16.0	5.7	15.8
n-pentanol	0.568	0.319	0.860	0.687	0.587	/	/	/
i-butanol	0.552	0.311	0.828	0.657	0.684	15.1	5.7	15.9
i-propanol	0.546	0.283	0.830	0.633	0.808	15.8	6.1	16.4
t-butanol	0.389	0.145	0.928	0.632	0.732	/	/	/
Acetic acid	0.648	0.689	0.390	0.651	0.676	14.5	8.0	13.5
ACN	0.460	0.044	0.286	0.645	0.974	15.3	18.0	6.1
DMSO	0.444	0.072	0.647	0.830	1.000	18.4	16.4	10.2
DMF	0.386	0.031	0.613	0.759	0.977	17.4	13.7	11.3
DMA	0.377	0.028	0.650	0.763	0.987	/	/	/
DCM	0.319	0.040	0.178	0.761	0.769	18.2	6.3	6.1
Chloroform	0.259	0.047	0.071	0.783	0.614	17.8	3.1	5.7
EtAc	0.228	0.000	0.542	0.656	0.603	15.8	5.3	7.2
THF	0.207	0.000	0.591	0.714	0.634	16.8	5.7	8.0
1,4-dioxane	0.164	0.000	0.444	0.737	0.312	19.0	1.8	7.4
Diethyl-ether	0.117	0.000	0.562	0.617	0.385	14.5	2.9	5.1

Table S5 Hammett's constants of the substituents[29]

Substituent	$\sigma_{m,p}$	Substituent	$\sigma_{m,p}$	Substituent	$\sigma_{m,p}$
4-H	0.00	3-Br	0.39	3-CH_3	-0.07
4-F	0.06	3-NO_2	0.71	4-CH_3	-0.17
4-Cl	0.23	4-NO_2	0.78	4-OCH_3	-0.27
4-Br	0.23	3-OCH_3	0.12	4-OH	-0.37
3-Cl	0.37	3-OH	0.12		

Table S6 Results of TD – DFT calculations in DMSO for E isomer of all synthesized compounds

Comp.	*e.s.*	*Energy (eV)*	*Oscillator strength*	*Excitation*	*CI expansion coefficient*	*% of single particle excitation contribution*
1	1	4.2049	1.0835	HOMO → LUMO	0.67896	92.2
2	1	4.0016	0.7637	HOMO → LUMO	0.67931	92.3
				HOMO-2 → LUMO	0.60260	72.6
	3	4.6300	0.3144	HOMO → LUMO+1	0.22083	9.8
				HOMO-3 → LUMO	-0.18142	6.6
3	1	4.1501	1.0597	HOMO → LUMO	0.68028	92.6
4	1	4.1153	1.1232	HOMO → LUMO	0.68702	94.4
5	1	4.2512	1.0797	HOMO → LUMO	0.67779	91.9
6	1	4.1878	1.0922	HOMO → LUMO	0.68026	92.6
7	1	4.1611	1.1828	HOMO → LUMO	0.68406	93.6
8	1	3.8519	0.3306	HOMO → LUMO	0.50898	51.8
				HOMO-7 → LUMO	-0.24383	11.9
				HOMO-2 → LUMO	0.21438	9.2
	2	3.9637	0.1984	HOMO → LUMO	0.36909	27.2
				HOMO-7 → LUMO	0.36528	26.7
				HOMO-3 → LUMO	0.32840	21.6
				HOMO-6 → LUMO	0.17419	6.1
	5	4.5110	0.5110	HOMO → LUMO+1	0.61190	74.9
				HOMO-2 → LUMO+1	0.19210	7.4
9	1	3.9797	0.3564	HOMO → LUMO	0.57491	66.1
				HOMO → LUMO+1	0.22471	10.1
				HOMO-2 → LUMO	-0.21999	9.7
	3	4.3281	0.5208	HOMO → LUMO+1	0.52795	55.7
				HOMO-1 → LUMO+1	-0.24406	11.9
				HOMO-1 → LUMO+3	0.17963	6.5
	4	4.3722	0.2179	HOMO-1 → LUMO+1	0.46425	43.1
				HOMO-1 → LUMO+3	-0.31082	19.3
				HOMO → LUMO+1	0.28984	16.8
				HOMO-1 → LUMO	0.19664	7.7
				HOMO-1 → LUMO+2	-0.16278	5.3
				HOMO → LUMO	0.62254	77.5
10	1	3.7596	1.0824	HOMO-2 → LUMO	-0.21336	9.1
				HOMO → LUMO+1	0.17633	6.2
11	1	4.0142	0.9439	HOMO → LUMO	0.68226	93.1
	3	4.6878	0.1359	HOMO-3 → LUMO	0.55937	62.6
				HOMO-2 → LUMO	0.25107	12.6
				HOMO-2 → LUMO+1	-0.18143	6.6
				HOMO → LUMO+2	-0.17891	6.4
12	1	4.1353	1.0386	HOMO → LUMO	0.68089	92.7
13	1	4.0722	1.1523	HOMO → LUMO	0.68745	94.5
14	1	4.1701	1.0799	HOMO → LUMO	0.67340	90.7
15	1	4.1134	1.2083	HOMO → LUMO	0.67994	92.5
16	1	4.1669	1.0828	HOMO → LUMO	0.67326	90.7
17	1	4.0944	1.2522	HOMO → LUMO	0.68037	92.6
18	1	4.2026	1.0749	HOMO → LUMO	0.68046	92.6

Table S7 Results of TD – DFT calculations in DMSO for Z isomer of all synthesized compounds

Compound	*e.s.*	*Energy (eV)*	*Oscillator strength*	*Excitation*	*CI expansion* coefficient*	*% of single particle excitation contribution*
1	1	4.4448	0.1869	HOMO → LUMO	0.41497	34.44
				HOMO-1 → LUMO	0.38037	28.94
				HOMO-1 → LUMO+2	-0.37296	27.82
	2	4.5359	0.4476	HOMO → LUMO	0.50941	51.90
				HOMO-1 → LUMO	-0.34050	23.19
				HOMO-1 → LUMO+2	0.26289	13.82
2	1	4.3638	0.0111	HOMO-1 → LUMO+1	0.43161	37.26
				HOMO-1 → LUMO	-0.35261	24.87
				HOMO-2 → LUMO+1	0.27510	15.14
				HOMO-1 → LUMO	-0.22481	10.11
	2	4.5971	0.2208	HOMO → LUMO	0.61240	75.01
				HOMO-1 → LUMO	0.23763	11.29
3	1	4.3942	0.5175	HOMO → LUMO	0.61655	76.03
				HOMO-1 → LUMO+1	-0.17816	6.35
				HOMO-1 → LUMO	0.16634	5.53
	2	4.4657	0.1033	HOMO-1 → LUMO	0.46787	43.78
				HOMO-1 → LUMO+1	-0.29658	17.59
				HOMO → LUMO	-0.25193	12.69
				HOMO-1 → LUMO+2	-0.22379	10.02
				HOMO-2 → LUMO+1	0.16502	5.45
4	1	4.4082	0.5853	HOMO → LUMO	0.64098	82.17
				HOMO-1 → LUMO+2	-0.16936	5.74
5	2	4.7216	0.5919	HOMO → LUMO	0.64472	83.13
6	1	4.4403	0.2745	HOMO → LUMO	0.48123	46.32
				HOMO-1 → LUMO	0.33572	22.54
				HOMO → LUMO+2	-0.33248	22.11
	2	4.5200	0.3543	HOMO → LUMO	0.45354	41.14
				HOMO-1 → LUMO	-0.38761	30.05
				HOMO-1 → LUMO+2	0.30820	19.00
7	1	4.4357	0.4216	HOMO → LUMO	0.55401	61.39
				HOMO-1 → LUMO+2	-0.27786	15.44
				HOMO-1 → LUMO	0.26994	14.57
	2	4.5166	0.2708	HOMO-1 → LUMO	0.43674	38.15
				HOMO → LUMO	-0.37459	28.06
				HOMO-1 → LUMO +2	-0.36374	26.46
8	1	3.8677	0.0179	HOMO → LUMO	0.52620	55.38
				HOMO-2 → LUMO	0.28963	16.78
				HOMO-7 → LUMO	0.21929	9.62
	2	3.9373	0.0158	HOMO-7 → LUMO	0.42296	35.78
				HOMO-3 → LUMO	0.39128	30.62
				HOMO → LUMO	-0.22911	10.50
				HOMO-4 → LUMO	-0.17466	6.10
	3	4.4195	0.0303	HOMO-9 → LUMO	0.43276	37.46
				HOMO-4 → LUMO	-0.22234	9.89
				HOMO-1 → LUMO+1	-0.21406	9.16
				HOMO → LUMO+1	0.20496	8.40
9	2	4.2217	0.0622	HOMO → LUMO	0.55812	62.30
				HOMO-2 → LUMO	0.26575	14.12
				HOMO-3 → LUMO	0.16225	5.27
	3	4.3796	0.1030	HOMO → LUMO+1	0.38521	29.68
				HOMO-1 → LUMO+1	-0.35864	25.72
				HOMO-1 → LUMO+2	0.32055	20.55
				HOMO-1 → LUMO+3	0.21742	9.45

	4	4.4823	0.1449	HOMO-9 → LUMO	0.51086	52.20
				HOMO → LUMO+1	0.25081	12.58
				HOMO-1 → LUMO+1	0.18764	7.04
				HOMO-6 → LUMO	0.16120	5.20
	5	4.5001	0.2728	HOMO → LUMO+1	0.43244	37.40
				HOMO-9 → LUMO	-0.33288	22.16
				HOMO-1 → LUMO+1	0.26317	13.85
				HOMO-2 → LUMO+1	0.20936	8.77
10	1	3.9337	0.3447	HOMO → LUMO	0.47530	45.18
				HOMO-6 → LUMO	0.35989	25.90
				HOMO-2 → LUMO	0.23560	11.10
				HOMO-6 → LUMO+1	0.15931	5.08
	2	4.0546	0.1950	HOMO-6 → LUMO	0.50898	51.81
				HOMO → LUMO	-0.35883	25.75
				HOMO-6 → LUMO+1	0.21518	9.26
				HOMO → LUMO+1	0.16122	5.20
11	1	4.3335	0.3250	HOMO → LUMO	0.52416	54.95
				HOMO-1 → LUMO	-0.31252	19.53
				HOMO-1 → LUMO+2	-0.25245	12.75
	2	4.4662	0.3917	HOMO-1 → LUMO	0.43869	38.49
				HOMO → LUMO	0.40618	33.00
				HOMO-1 → LUMO+2	0.28012	15.69
				HOMO-2 → LUMO	-0.16889	5.70
12	1	4.3764	0.5732	HOMO → LUMO	0.65252	85.16
13	1	4.3692	0.6343	HOMO → LUMO	0.66121	87.44
14	1	4.4016	0.1782	HOMO → LUMO	0.42048	35.36
				HOMO-1 → LUMO+2	-0.37244	27.74
				HOMO-1 → LUMO	0.35929	25.82
				HOMO → LUMO+2	-0.15885	5.05
	2	4.4993	0.4314	HOMO → LUMO	0.48922	47.87
				HOMO-1 → LUMO	-0.34895	24.35
				HOMO-1 → LUMO+2	0.26653	14.21
				HOMO-2 → LUMO	-0.17072	5.83
15	1	4.3784	0.4793	HOMO → LUMO	0.58191	67.72
				HOMO-1 → LUMO+2	0.24505	12.01
				HOMO-1 → LUMO	-0.20902	8.74
	2	4.4645	0.2126	HOMO-1 → LUMO	0.45082	40.65
				HOMO-1 → LUMO+2	-0.39847	31.76
				HOMO → LUMO	0.30713	18.87
16	1	4.4032	0.1779	HOMO → LUMO	0.41941	35.18
				HOMO-1 → LUMO+2	0.36732	26.98
				HOMO-1 → LUMO	-0.36023	25.95
	2	4.5005	0.4278	HOMO → LUMO	0.49020	48.06
				HOMO-1 → LUMO	0.34771	24.18
				HOMO-1 → LUMO+2	-0.26296	13.83
				HOMO-3 → LUMO	0.15887	5.05
17	1	4.3645	0.5484	HOMO → LUMO	0.60555	73.34
				HOMO-1 → LUMO+2	0.21275	9.05
				HOMO-1 → LUMO	-0.17380	6.04
	2	4.4566	0.1674	HOMO-1 → LUMO	0.46476	43.20
				HOMO-1 → LUMO+2	-0.41648	34.69
				HOMO → LUMO	0.26211	13.74
18	1	4.4404	0.1755	HOMO → LUMO	0.40345	32.55
				HOMO-1 → LUMO	0.39116	30.60
				HOMO-1 → LUMO+2	-0.37974	28.84
	2	4.5346	0.4618	HOMO → LUMO	0.52364	54.84
				HOMO-1 → LUMO	-0.33186	22.03
				HOMO-1 → LUMO+2	0.25259	12.76
				HOMO-2 → LUMO	-0.15886	5.05

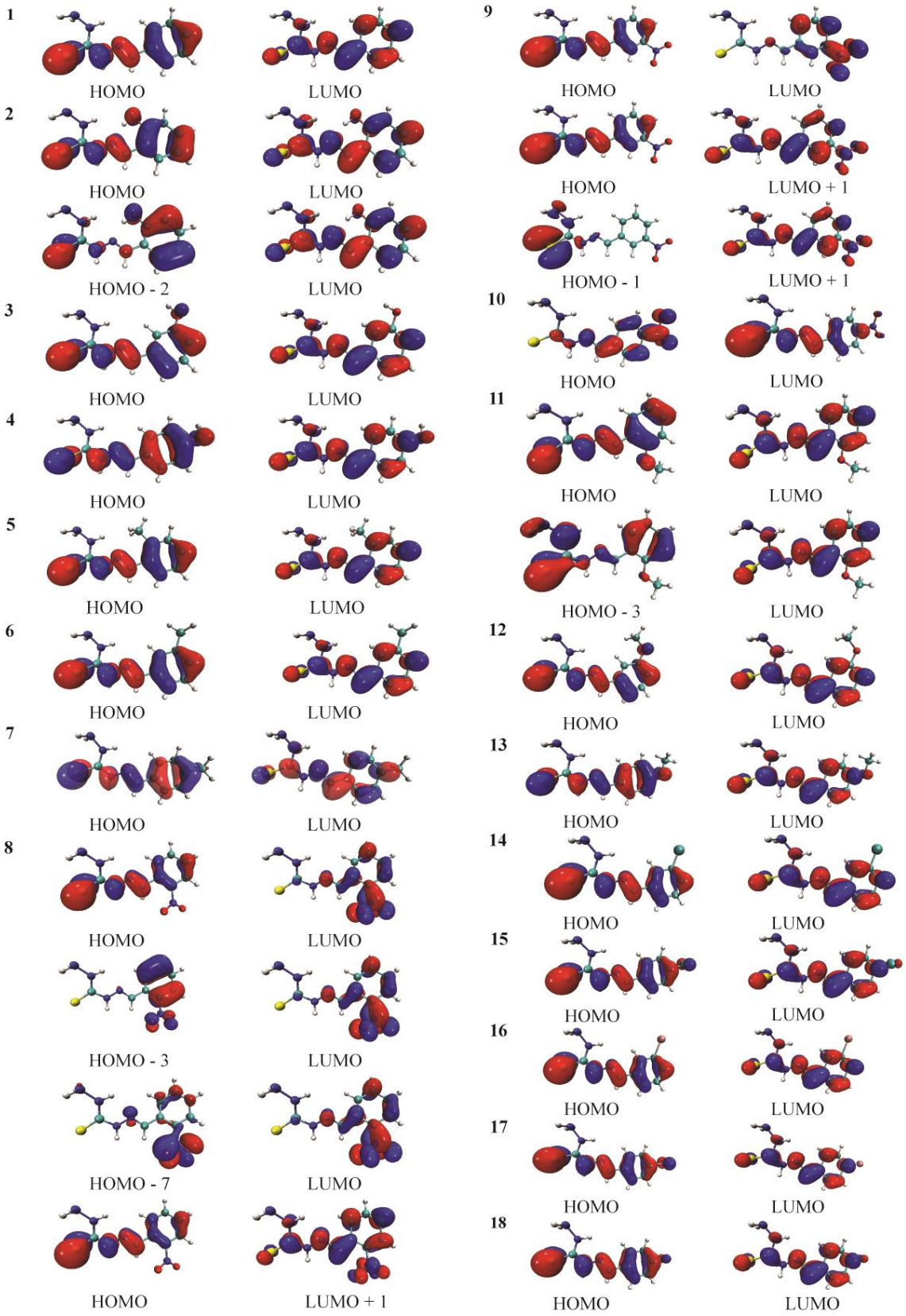

Fig. S2 HOMO/LUMO orbitals of monothiocarbohydrazone derivatives