Supporting Information

Exploring Intermolecular Interactions and Energetics in Crystalline Substituted Thieno[2,3-*d*]pyrimidines

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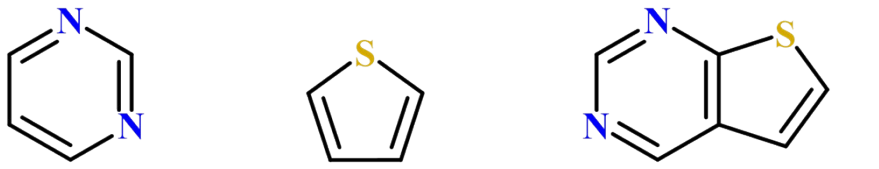


Pyrimidine **Thiophene** **Thieno[2,3-*d*]pyrimidine**

Figure S1: Chemical structures of pyrimidine, thiophene and thieno[2,3-*d*]pyrimidine.

Characterization via Nuclear Magnetic Resonance (NMR) Spectroscopy

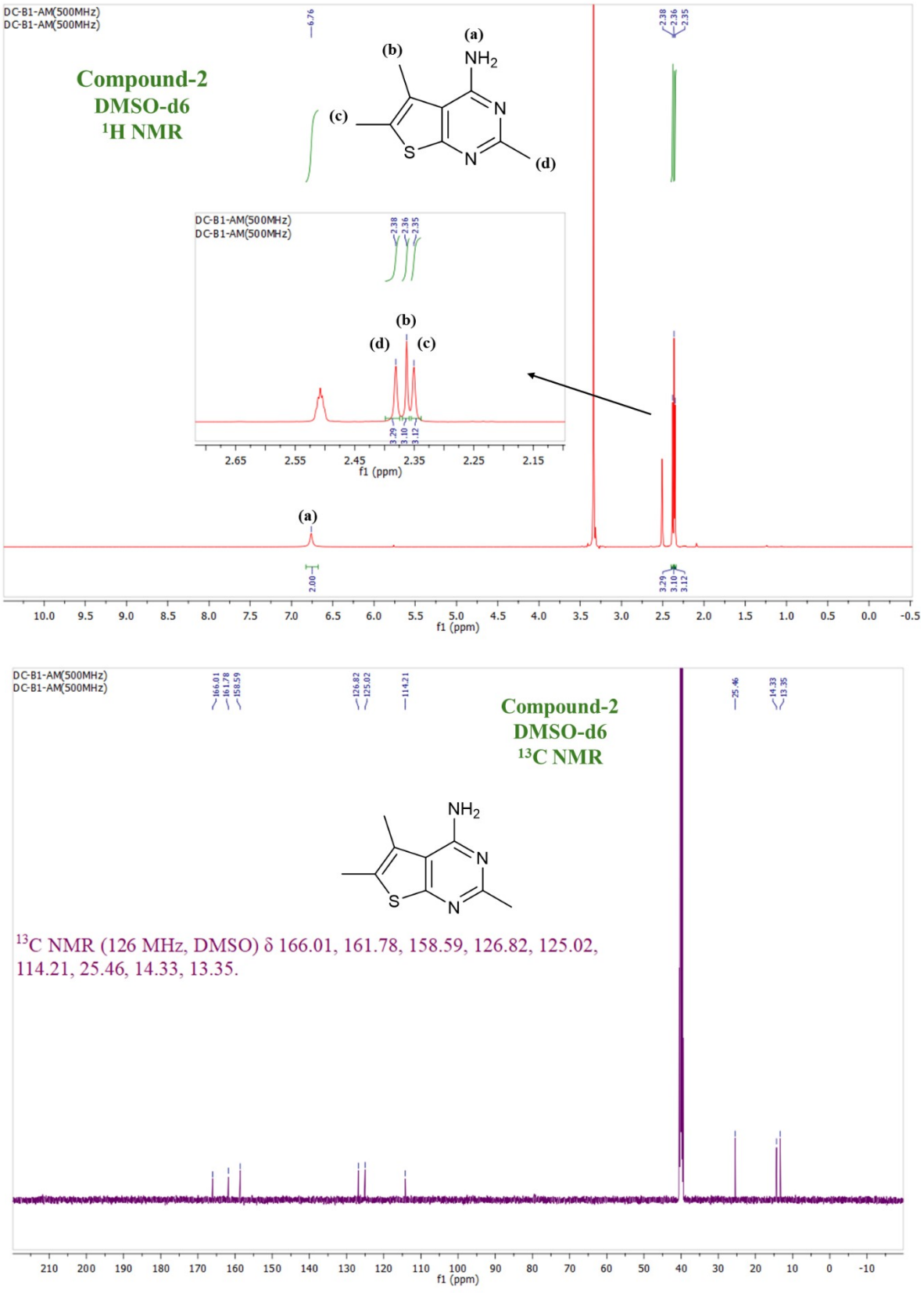


Figure S2. ^{1}H and ^{13}C NMR characterization of compound **2**.

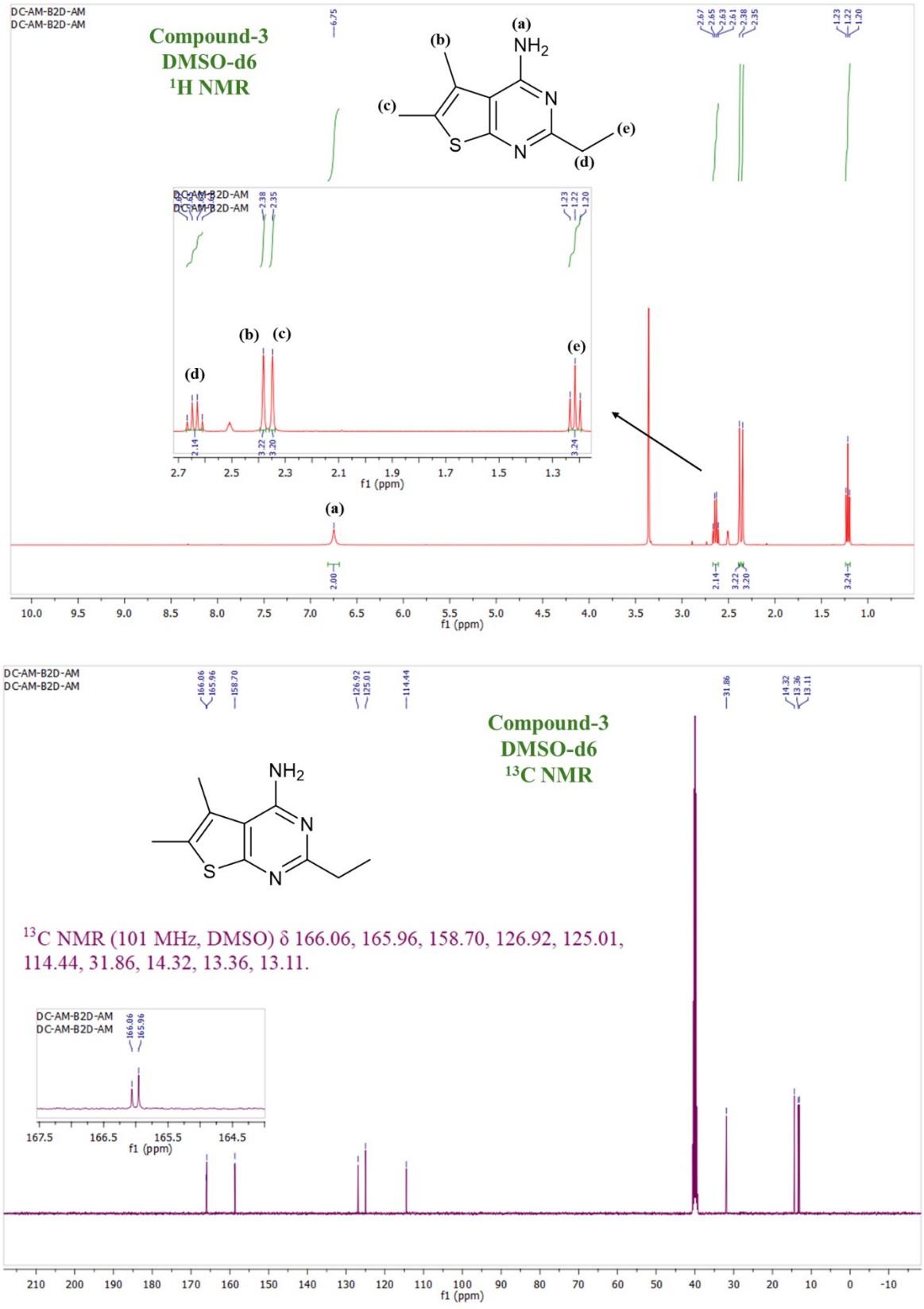


Figure S3. ^{1}H and ^{13}C NMR characterization of compound **3**.

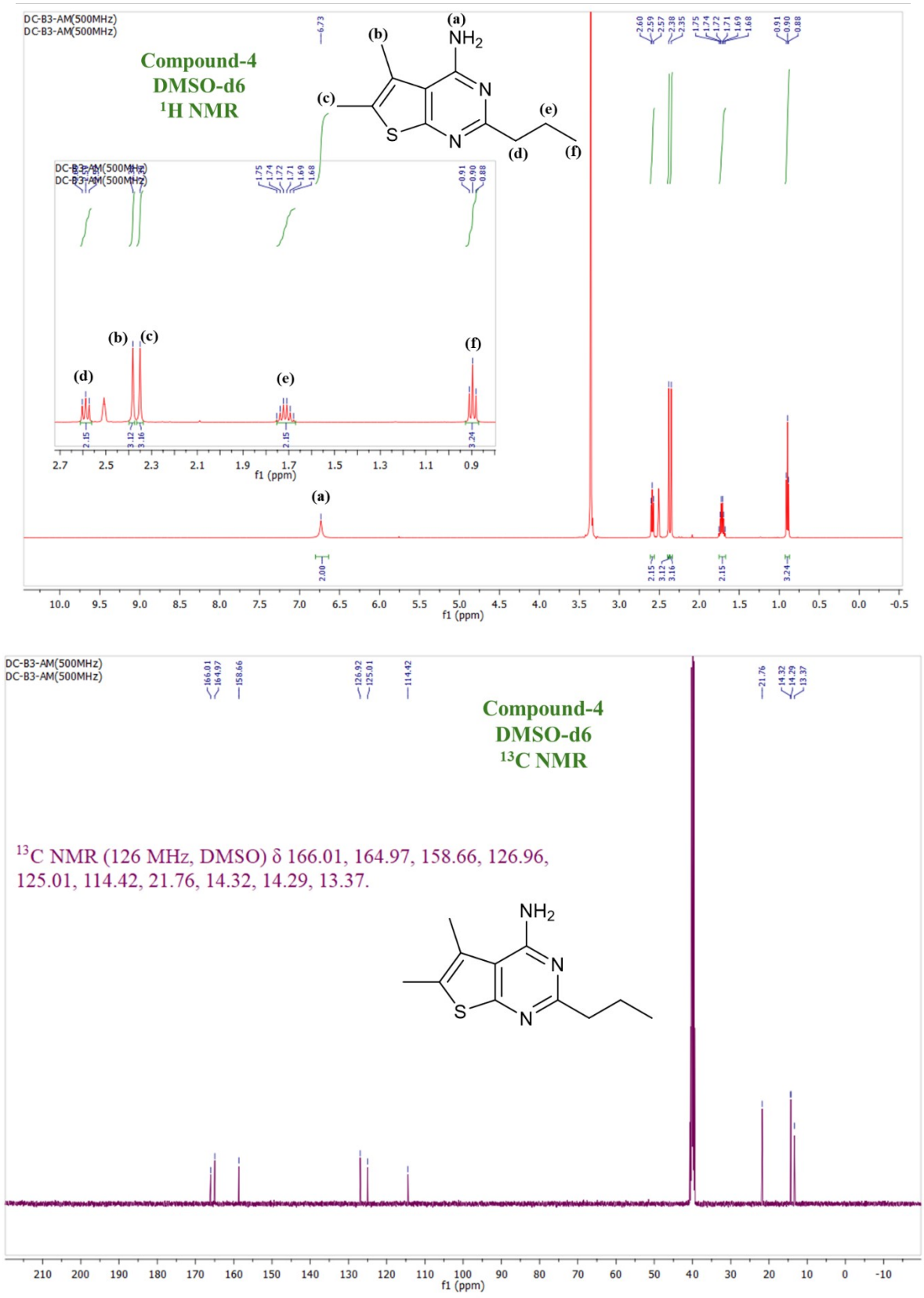


Figure S4. ^{1}H and ^{13}C NMR characterization of compound **4**.

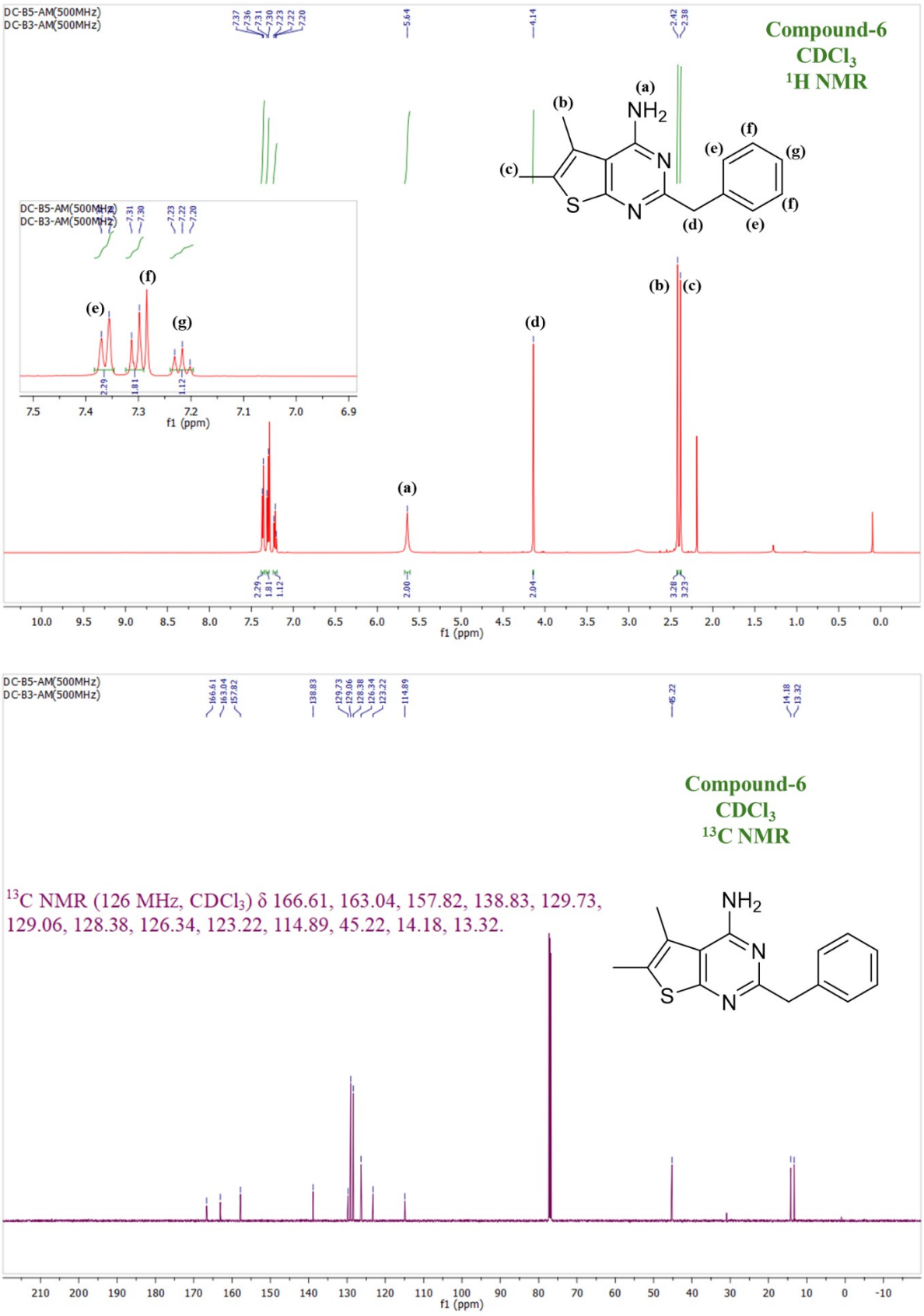


Figure S5. ^{1}H and ^{13}C NMR characterization of compound **6**.

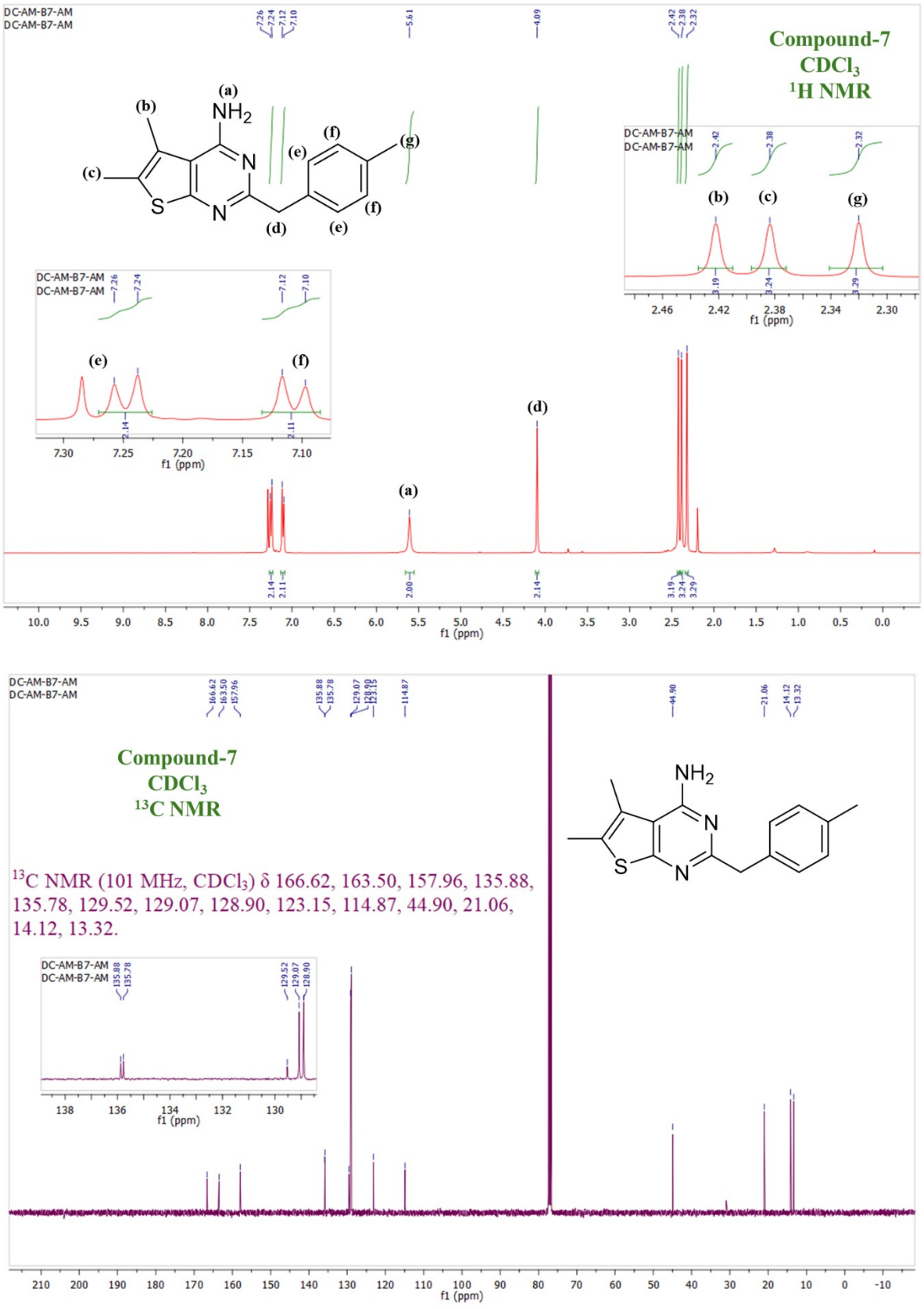


Figure S6. ^{1}H and ^{13}C NMR characterization of compound **7**.

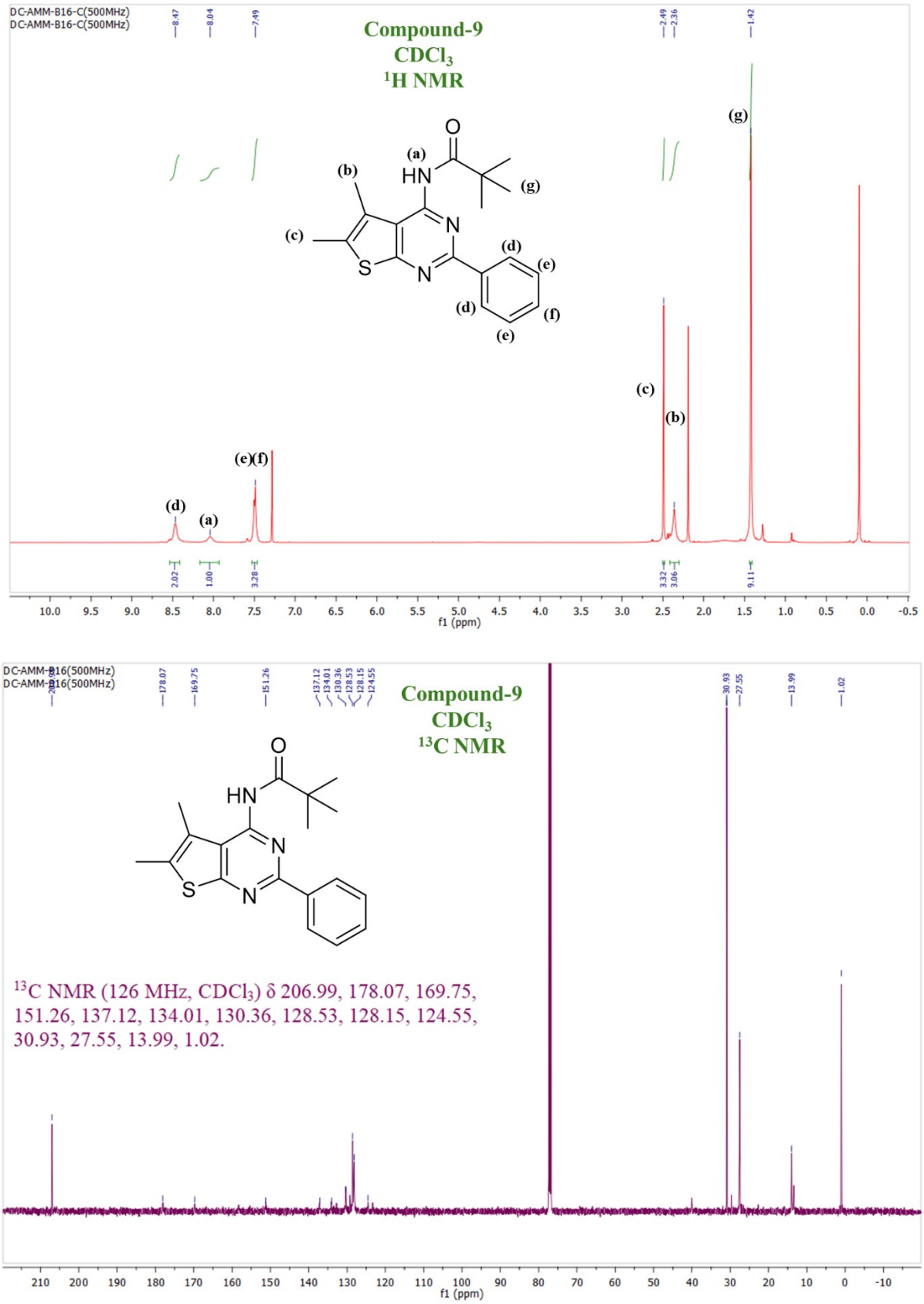


Figure S7. ^{1}H and ^{13}C NMR characterization of compound **9**.

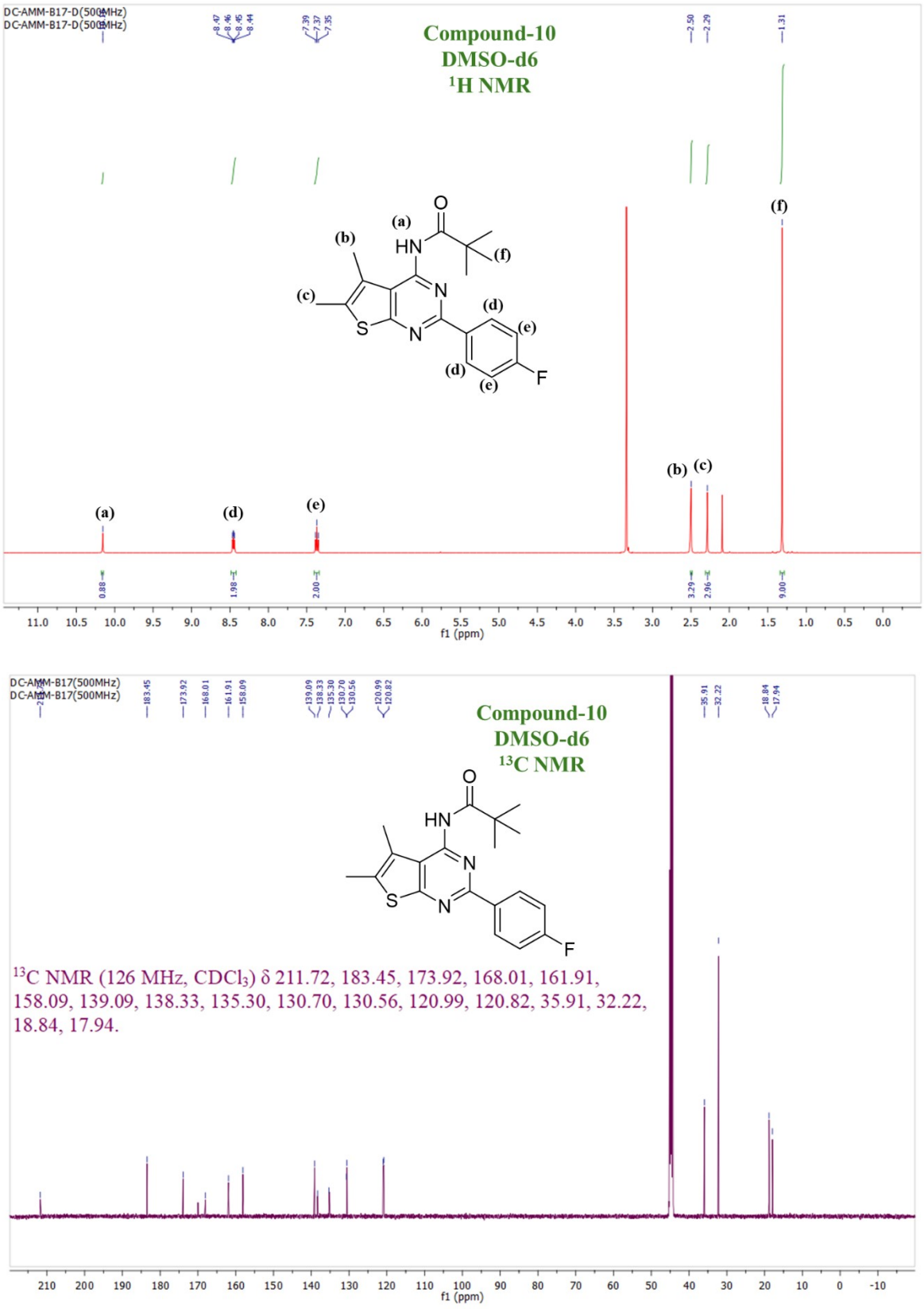


Figure S8. ^{1}H and ^{13}C NMR characterization of compound **10**.

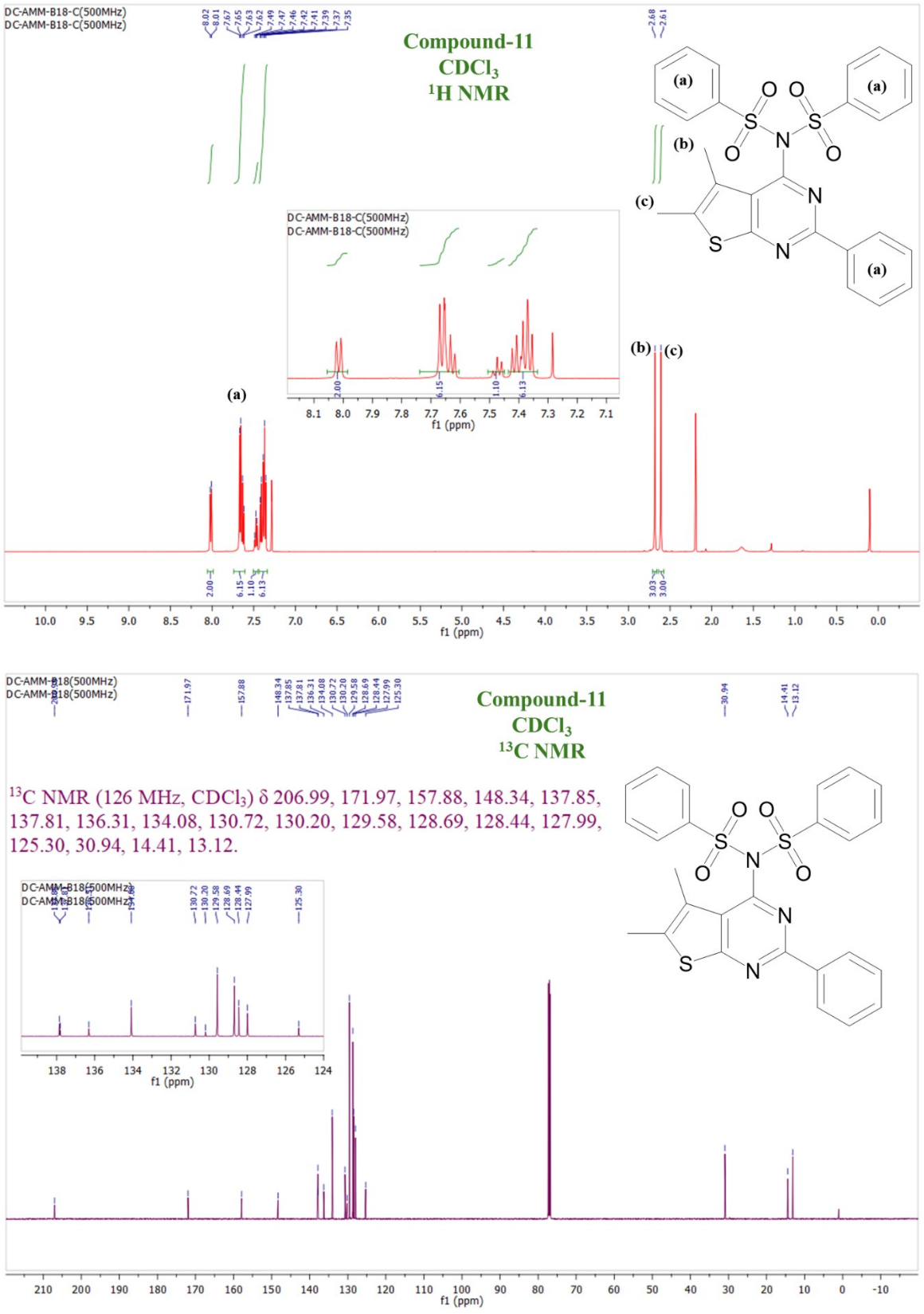
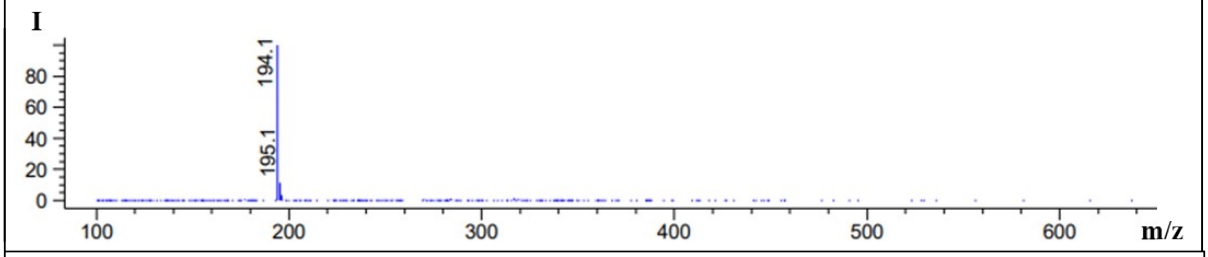


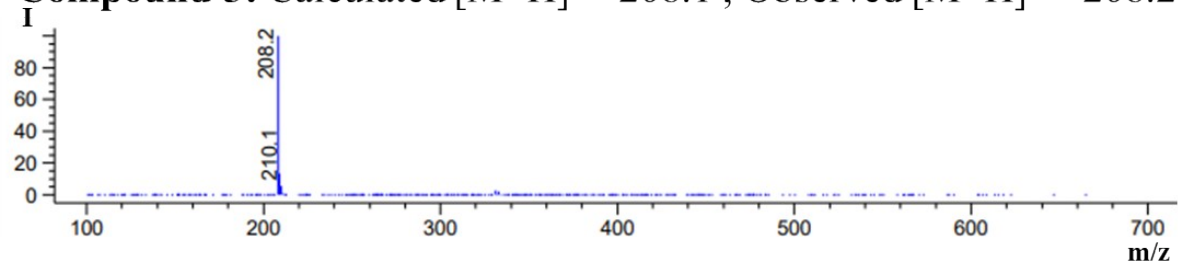
Figure S9. [1]H and [13]C NMR characterization of compound **11**.

Liquid Chromatography Mass Spectrometry (LCMS)

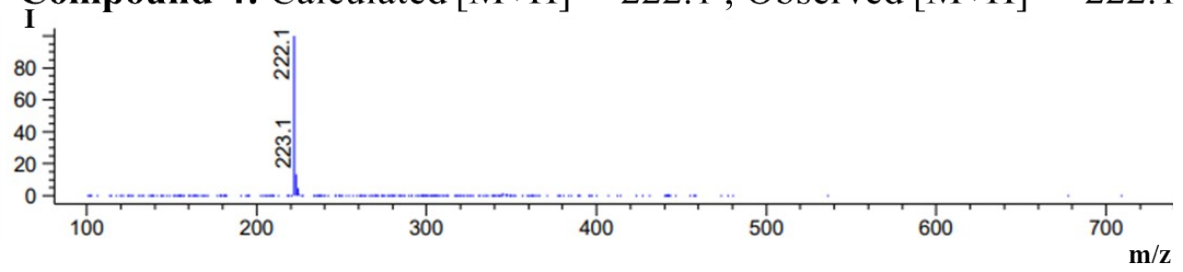
Compound 2: Calculated $[M+H]^+$ =194.1 ; Observed $[M+H]^+$ = 194.1



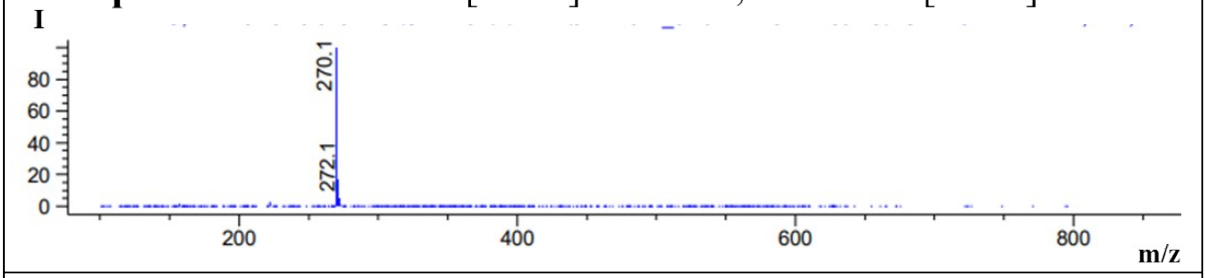
Compound 3: Calculated $[M+H]^+$ =208.1 ; Observed $[M+H]^+$ = 208.2



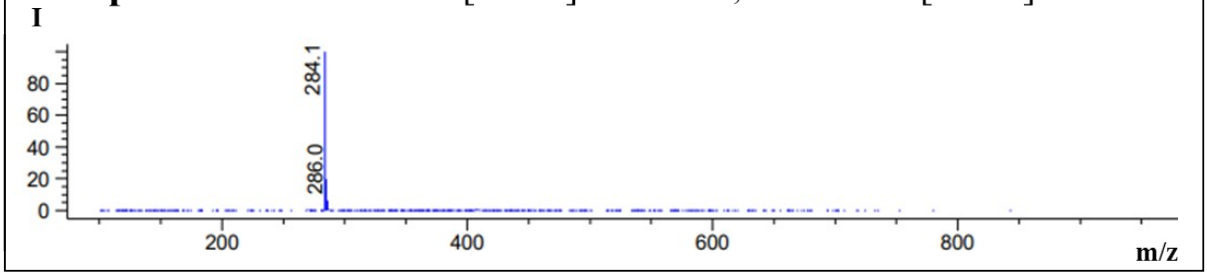
Compound 4: Calculated $[M+H]^+$ =222.1 ; Observed $[M+H]^+$ = 222.1



Compound 6: Calculated $[M+H]^+$ = 270.1; Observed $[M+H]^+$ = 270.1



Compound 7: Calculated $[M+H]^+$ = 284.1; Observed $[M+H]^+$ = 284.1



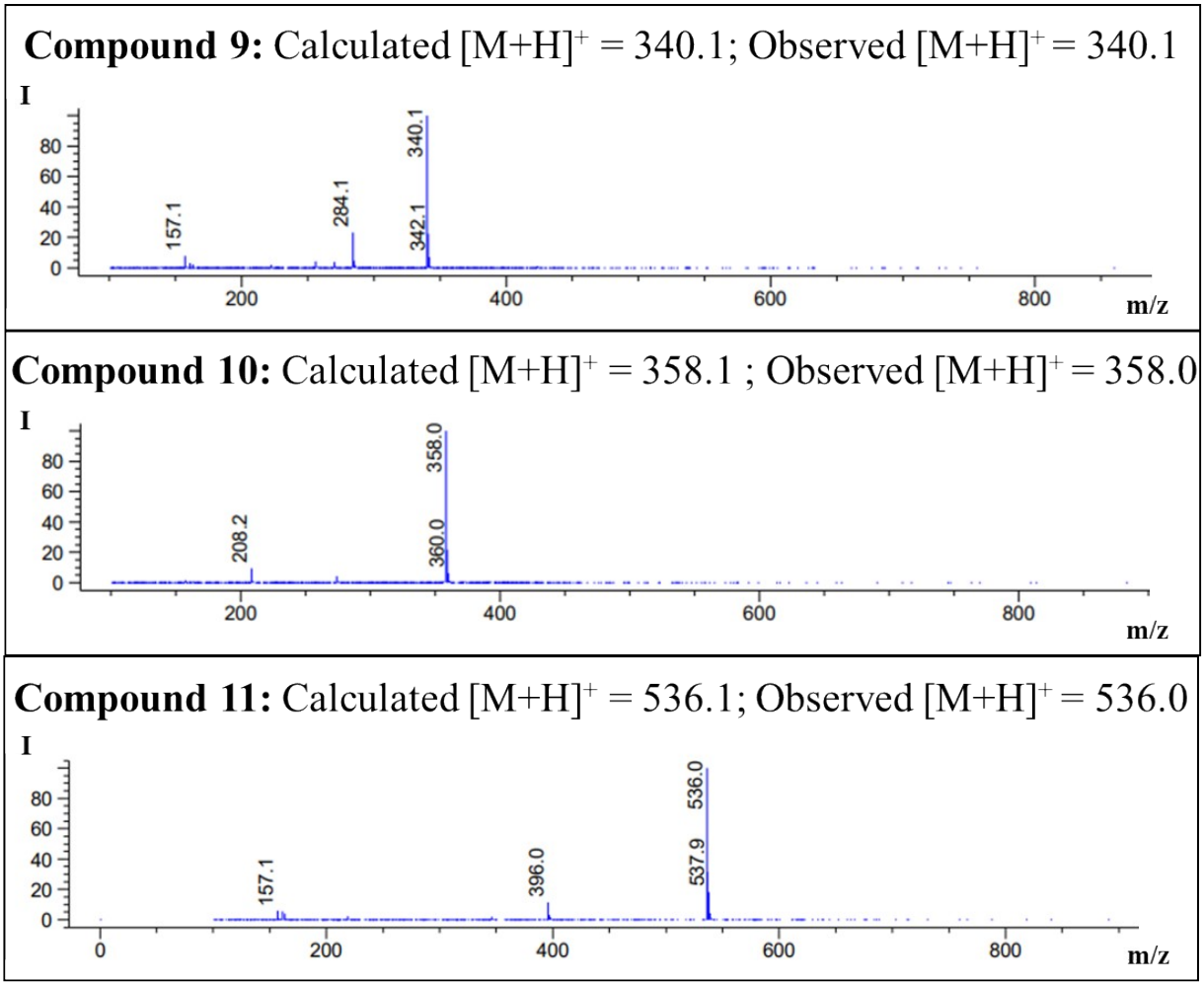
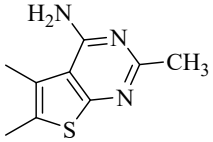
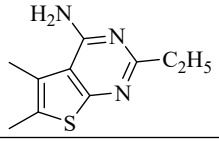
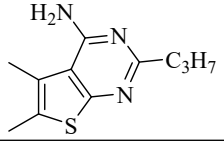
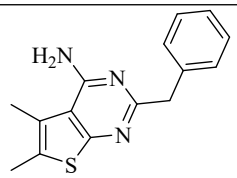
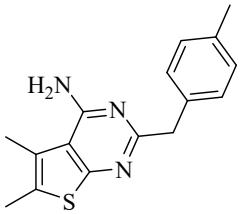
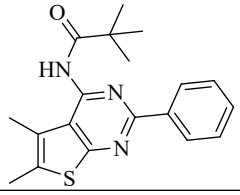
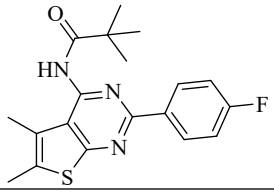
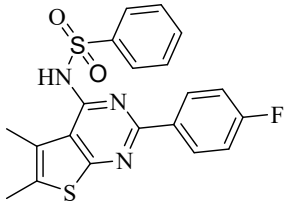


Figure S10. Low resolution LCMS spectra for all eight compounds exhibiting good correlation among the calculated and observed mass.

Table S1: Molecular formula, molecular weight, percentage yield, melting point, R_f values for all eight compounds (2-4, 6, 7, 9-11).

CODE	COMPOUND	M.F	MWT	Yield (%)	MP (◦C)	R_f value (H : E)*
2		$C_9H_{11}N_3S$	193.27	150	268-270	0.04 (7:3)
3		$C_{10}H_{13}N_3S$	207.30	135	212-213	0.15 (7:3)
4		$C_{11}H_{15}N_3S$	221.32	165	172-173	0.24 (7:3)

6		$C_{15}H_{15}N_3S$	269.37	175	226-228	0.66 (6:4)
7		$C_{16}H_{17}N_3S$	283.39	75	208-210	0.30 (7:3)
9		$C_{19}H_{21}N_3OS$	339.46	45	228-229	0.86 (6:4)
10		$C_{19}H_{20}FN_3OS$	357.45	37.5	225-226	0.89 (6:4)
11		$C_{20}H_{16}FN_3O_2S_2$	413.49	27.5	231-233	0.83 (6:4)

***Rf value (H : E) = Hexane : Ethyl acetate**

Single Crystal X-ray Diffraction (SCXRD)

Table S2: Crystallization screens of eight compounds (2-4, 6, 7, 9-11).

Sample Code	Solvent used	Crystallization conditions*	Morphology
2	Dichloromethane	Δ-Soluble/ LT	Needle
	Methanol	Δ-Soluble/ LT	Aggregate
	Ethanol	Δ-Soluble/ LT	Aggregate
	DMSO*	Soluble/ RT	Needle
	Toluene	Soluble/ LT	Needle
3	Dichloromethane	Soluble/ LT	Plate
	Methanol	Soluble/ LT	Plate
	Toluene	Soluble/ LT	Aggregate
	DMSO*	Soluble/ RT	Plate
	Nitromethane	Soluble/ LT	Plate
4	Dichloromethane	Δ-Soluble/ LT	Plate
	Isopropanol	Δ-Soluble/ LT	Aggregate
	Toluene	Soluble/ LT	Plate
	DMSO*	Soluble/ RT	Plate
	Nitromethane	Soluble/ LT	Plate
6	Dichloromethane	Δ-Soluble/ LT	Plate
	Methanol	Δ-Soluble/ LT	Plate
	Nitromethane	Soluble/ LT	Plate
	DMSO*	Soluble/ RT	Plate
	Toluene	Soluble/ LT	Plate

7	Dichloromethane	Δ-Soluble/ LT	Block
	Methanol	Δ-Soluble/ LT	Block
	Toluene	Soluble/ LT	Block
	DMSO*	Soluble/ RT	Block
	Isopropanol	Δ-Soluble/ LT	Block
9	Dichloromethane	Δ-Soluble/ LT	Needle
	Isopropanol	Δ-Soluble/ LT	Aggregate
	Toluene	Soluble/ LT	Aggregate
	DMSO*	Soluble/ RT	Needle
	Nitromethane	Soluble/ LT	Needle
10	Dichloromethane	Δ-Soluble/ LT	Needle
	Isopropanol	Δ-Soluble/ LT	Needle
	Methanol	Δ-Soluble/ LT	Needle
	DMSO*	Soluble/ RT	Needle
	Nitromethane	Soluble/ LT	Needle
11	Dichloromethane	Soluble/ LT	Plate
	Methanol	Soluble/ LT	Aggregate
	Toluene	Soluble/ LT	Aggregate
	DMSO*	Soluble/ RT	Plate
	Nitromethane	Soluble/ LT	Plate

*LT = 4 °C; RT = 22-25 °C.*SCXRD data on crystals were collected from these solvent systems.

Table S3. Crystallographic and refinement data.

Data	**2**	**3**	**4**	**6**
Crystal System	Monoclinic	Monoclinic	Triclinic	Triclinic
Formula	$C_9H_{11}N_3S$	$C_{10}H_{13}N_3S$	$C_{11}H_{15}N_3S$	$C_{15}H_{15}N_3S$
Formula weight	193.27	207.29	221.32	269.36
CCDC no.	**2402896**	**2402893**	**2402905**	**2402899**
Space Group	$P2_1/c$	$P2_1/n$	P-1	P-1
Temperature(K)	100	100	100	100
***a* (Å)**	8.2226 (5)	13.9025(10)	16.9046 (13)	7.7792(8)
***b*(Å)**	7.7209 (5)	13.7290(10)	17.1968 (14)	8.2162(9)
***c*(Å)**	14..3343 (11)	15.9725(10)	17.8048 (15)	10.8622(9)
***α* (˚)**	90	90	61.562 (3)	86.331(4)
***β* (˚)**	94.293 (3)	98.472 (3)	79.591 (3)	69.979(4)
***γ* (˚)**	90	90	88.984 (3)	88.546(4)
Volume [V(Å^3)]	907.47 (11)	3015.4(4)	4462.5 (6)	650.97(11)
Density (g/cm^3)	1.415	1.370	1.318	1.374
Z, Z'	1, 4	3, 12	8, 16	1, 2
Size of crystal (mm^3)	0.589 × 0.098 × 0.048	0.457 × 0.298 × 0.078	0.296 × 0.201 × 0.155	0.220 × 0.118 × 0.09
μ/mm^{-1}	0.309	0.284	0.261	0.237
***F* (000)**	408	1320	1888	284
θ $_{min,max}$	2.48, 30.09	2.96, 29.94	2.33, 24.47	2.48, 27.82
h $_{min,max}$	-11, 11	-19, 19	-22, 22	-10, 10

$k_{min,max}$	-10, 10	-19, 19	-22, 22	-11, 11
$l_{min,max}$	-20, 20	-22, 22	-23, 23	-15, 15
No. of reflections	32694	148353	151665	50887
No. of unique/ observed reflections	2650, 2161	8841, 6621	22151, 10792	3839, 2489
No.of parameters	129	412	1170	182
R_{all}, R_{obs}	0.0467, 0.0371	0.0563, 0.0428	0.1762, 0.0888	0.0954, 0.0595
$wR2_{all}$, $wR2_{obs}$	0.1028, 0.0997	0.1310, 0.1257	0.2799, 0.2217	0.1508, 0.1406
$\Delta\rho_{max,min}$(e·Å^{-3})	0.40, -0.24	0.42, -0.45	0.59, -0.50	0.35, -0.40
G.o.F	1.089	1.103	0.913	1.071

Data	**7**	**9**	**10**	**11**
Crystal System	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Formula	$C_{16}H_{17}N_3S$	$C_{19}H_{21}N_3SO$	$C_{19}H_{20}N_3SOF$	$C_{26}H_{21}N_3O_4S_3$
Formula weight	283.38	339.45	357.44	535.64
CCDC no.	**2402902**	**2402903**	**2402904**	**2402900**
Space Group	$P2_1/c$	$P2_1/c$	$Pca2_1$	$P2_1/c$
Temperature(K)	100	100	100	100
***a* (Å)**	11.2278(5)	14.0960(12)	8.5844(7)	16.9149(12)
***b*(Å)**	9.7330(4)	13.0340(11)	19.2443(15)	9.8296(6)
***c*(Å)**	13.8833(5)	9.5091(6)	21.3684(18)	16.9361(12)
***α* (°)**	90	90	90	90
***β* (°)**	110.469(2)	94.556(3)	90	118.803(3)
***γ* (°)**	90	90	90	90
Volume [V(Å^3)]	1421.38(10)	1741.6(2)	3530.1(5)	2467.5(3)
Density (g/cm^3)	1.324	1.295	1.345	1.442
Z, Z'	1, 4	1, 4	2, 8	1, 4
Size of crystal (mm^3)	0.362 × 0.161 × 0.114	0.331 × 0.11 × 0.076	0.242 × 0.089 × 0.069	0.355 × 0.214 × 0.109
μ/mm^{-1}	0.221	0.196	0.205	0.340
***F* (000)**	600	720	1504	1112
$\theta_{min,max}$	2.61, 29.93	2.66, 28.11	2.77, 26.14	2.41, 29.90
$h_{min,max}$	-15, 15	-19, 19	-12, 12	-22, 22
$k_{min,max}$	-13, 13	-18, 18	-27, 26	-13, 13
$l_{min,max}$	-19, 19	-13, 12	-30, 30	-22, 22
No. of reflections	57862	77370	1247003	45875
No. of unique/ observed reflections	4169, 3142	5121, 3313	10326, 6548	6379, 4347
No.of parameters	191	222	469	327

R_{all}, R_{obs}	0.0641, 0.0483	0.0943, 0.0564	0.1255, 0.0725	0.0780, 0.0506
$wR2_{all}$, $wR2_{obs}$	0.1420, 0.1367	0.1556, 0.1418	0.1596, 0.1432	0.1269, 0.1194
$\Delta\rho_{max,min}(e\cdot Å^{-3})$	0.61, -0.49	0.45, -0.44	0.34, -0.37	0.39, -0.40
G.o.F	1.146	1.068	1.037	1.055

Table S4: List of intermolecular interactions. (Neutron normalised values[1-2] referred here are obtained from the *PARST* output file)

Sample code	D-H···A	D-H/Å	D···A/Å	H···A/Å	D-H···A/°	Symmetry
2	N3-H3B···N1	1.030	3.579(2)	2.69	144	x, -y+1/2+1, z-1/2
	C8-H8A···N1	1.080	3.515(2)	2.60	142	x, -y+1/2+1, z-1/2
	C7-H7A···N3	1.080	3.779(2)	2.75	159	x, -y+1/2+1, z+1/2
	N3-H3A···N2	1.030	3.026(2)	2.00	178	-x+2, -y+1, -z+1
	C9-H9A···N2	1.080	3.609(2)	2.73	138	x-1, y, z
	C8-H8A···S1	1.080	3.600(2)	2.87	125	-x+1, -y+2, -z+1
	C8-H8C···π(C6)	0.980	3.660(2)	2.74	156	-x+1, -y+1, -z+1
	C8-H8C···π(C3)	0.980	3.571(2)	2.83	133	-x+1, -y+1, -z+1
	S1···π(C8)	-	3.600(2)	-	-	-x+1,-y+2,-z+1
3	N6-H6A···N8	1.030	2.930(2)	1.90	175	x, y, z
	N9-H9A···N5	1.030	3.098(2)	2.07	176	x, y, z
	N9-H9B···N1	1.030	3.149(2)	2.23	147	x, y, z
	C7-H27B···N6	1.080	3.477(2)	2.66	132	x, y, z
	C29-H29A···N1	1.080	3.462(2)	2.60	136	x, y, z
	N3-H3B···N7	1.030	3.354(2)	2.47	144	x+1, y, z
	C9-H9E···N7	1.080	3.492(2)	2.62	137	x+1, y, z
	C28-H28C···N3	1.080	3.609(2)	2.55	167	x-1, y, z
	N3-H3A···N2	1.030	3.080(2)	2.05	177	-x+2, -y, -z+1
	C28-H28B···N4	1.080	3.436(2)	2.67	128	-x+1, -y+1, -z+1
	C19-H19A···π(C6)	0.980	3.631(1)	2.74	151	x-1/2, -y+1/2, z-1/2
	C9-H9C···π(C16)	0.980	3.669(1)	2.76	155	x+1/2, -y+1/2, z+1/2
	C20-H20A···π(C24)	0.980	3.643(2)	2.78	148	-x+1, -y+1, -z+1
	C30-H30B···π(C5)	0.980	3.611(2)	2.80	140	-x+1/2+1, y-1/2, -z+1/2+1
	C10-H10A···π(C25)	0.980	3.669(2)	2.79	150	-x+1/2+1, y-1/2, -z+1/2+1
	S2···S3	-	3.586(4)	-	134, 134	x+1/2,-y+1/2,+z-1/2

4	N12-H12A ···N14	1.030	3.005(1)	1.98	177	x,y,z
	N15-H15A ···N11	1.030	3.054(2)	2.03	172	x,y,z
	N15-H15B ···N19	1.030	3.400(2)	2.53	142	x,y,z
	N9-H9E ···N4	1.030	3.381(2)	2.56	137	x,y,z
	C18-H18D ···N9	1.080	3.639(2)	2.63	156	x,y,z
	C73-H73B ···N15	1.080	3.612(2)	2.59	158	x,y,z
	C54-H54C ···N19	1.080	3.656(2)	2.68	139	x,y,z
	C7-H7A ···N13	1.080	3.616(2)	2.63	152	x,y,z
	C84-H84A···N7	1.080	3.499(4)	2.72	129	x,y,z
	C84A-H84D···N7	1.080	3.499(4)	2.64	136	x,y,z
	C75-H75C ···N11	1.080	3.662(2)	2.74	144	x,y,z
	C85-H85B···S3	1.080	3.786(3)	2.75	161	x,y,z
	C52-H52A ···S8	1.080	3.865(1)	2.92	146	x,y,z
	C53-H53C ···N22	1.080	3.675(2)	2.68	153	x,y,z
	C41A-H41D···N15	1.080	3.386(2)	2.44	145	x,y,z
	C84A-H84D···N7	1.080	3.492(4)	2.65	134	x,y,z
	C11-H11C ···N23	1.080	3.424(2)	2.54	139	-x+2,-y+1,-z
	C88-H88C ···N2	1.080	3.533(2)	2.57	148	-x+2,-y+1,-z
	C54-H54A ···S3	1.080	3.781(2)	2.76	158	-x+1,-y+1,-z+1
	C33-H33C ···N14	1.080	3.732(3)	2.74	152	-x+1,-y+1,-z+1
	C33-H33C ···N15	1.080	3.660(3)	2.71	147	-x+1,-y+1,-z+1
	C22-H22C ···N21	1.080	3.595(2)	2.71	139	-x,-y+1,-z+1
	C21-H21E ···N6	1.080	3.659(2)	2.67	152	-x,-y+1,-z+1
	C63-H63B ···N9	1.080	3.508(2)	2.66	135	x,+y-1,+z
	N18-H18B ···N8	1.030	3.067(1)	2.04	174	x,+y-1,+z
	C62-H62A ···N4	1.080	3.644(2)	2.62	158	x,+y-1,+z
	N6-H6A ···N23	1.030	2.932(2)	1.90	176	x,+y-1,+z
	C62-H62B ···N3	1.080	3.672(2)	2.69	151	x,+y-1,+z
	N21-H21A ···N2	1.030	2.979(2)	1.95	179	x,+y-1,+z
	C43-H43C ···N12	1.080	3.774(2)	2.73	163	-x+1,-y+1,-z
	C66-H66C ···N12	1.080	3.614(3)	2.68	144	-x+1,-y+1,-z
	C43-H43A ···S6	1.080	3.912(2)	2.86	164	-x+1,-y+1,-z
	C86-H86C···N6	1.080	3.494(2)	2.52	150	x+1,+y,+z
	N3-H3B ···N20	1.030	3.152(2)	2.12	176	x+1,+y,+z
	C87-H87A ···S4	1.080	3.754(2)	2.85	141	x+1,+y,+z
	N24-H24A ···N5	1.030	3.091(2)	2.06	176	x+1,+y,+z

	C10-H10A ···S6	1.080	3.723(2)	2.83	140	x+1,+y,+z
	N24-H24B ···N10	1.030	3.277(2)	2.42	141	x+1,+y,+z
	N3-H3A ···N16	1.030	3.251(2)	2.36	145	x+1,+y,+z
	C8-H8A ···N21	1.080	3.516(2)	2.64	138	x+1,+y,+z
	C76-H76C ···N21	1.080	3.760(3)	2.68	176	-x,-y,-z+1
	N9-H9D ···N17	1.030	2.999(1)	1.99	167	x,+y+1,+z
	C31-H31B ···N1	1.080	3.725(2)	2.69	160	x,+y+1,+z
	C11-H11A ···C5	0.980	3.584(2)	2.87	131	-x+2,-y,-z
	C65-H65A ···C39	0.980	3.588(3)	2.86	132	-x+1,-y+1,-z
	C43-H43A ···C61	0.980	3.588(2)	2.87	131	-x+1,-y+1,-z
	C64-H64C ···C67	0.980	3.577(2)	2.73	145	x,y,z
	C21-H21C ···C72	0.980	3.564(2)	2.81	134	-x,-y+1,-z+1
	C22 -H22C ···C68	0.980	3.529(2)	2.84	128	-x,-y+1,-z+1
	C76-H76A ···C17	0.980	3.675(2)	2.88	139	-x,-y+1,-z+1
	C22-H22A ···C53	0.980	3.842(2)	2.87	170	-x+1,-y+1,-z+1
	C88-H88C ···C22	0.980	3.348(2)	2.86	112	x-1,+y,+z+1
	C33-H33C ···C46	0.980	3.561(3)	2.70	147	-x+1,-y+1,-z+1
6	C13-H13···N3	1.080	3.681(3)	2.69	153	-x+1, -y+2, -z+1
	N3-H3A···N2	1.030	3.017(3)	1.99	171	-x+1, -y+2, -z+1
	C10-H10···N1	1.080	3.593(3)	2.64	146	-x, -y+1, -z+2
	C14-H14A···N1	1.080	3.725(3)	2.73	153	-x+1, -y+1, -z+1
	C11-H11···N1	1.080	3.262(4)	2.47	129	x-1, y, z
	C14-H14A···π(C6)	0.980	3.812(2)	2.80	155	-x+1, -y+1, -z+1
7	N3-H3A···N2	1.030	3.150(2)	2.12	173	-x, -y+1, -z
	C15-H15A···N1	1.080	3.466(2)	2.63	133	x, -y+1/2, z-1/2
	N3-H3B···N1	1.030	3.226(2)	2.27	154	x, -y+1/2, z-1/2
	C12-H12···S1	1.080	3.910(1)	2.87	162	x, y+1, z
	C14-H14A···N3	1.080	3.546(3)	2.53	157	x, -y+1/2+1, z+1/2
	C15-H15A···π(C9)	0.980	3.610(2)	2.92	128	x, -y+1/2, z-1/2
	C14-H14A··· π (C2)	0.866	3.787(3)	2.92	172	x, -y+1/2, z-1/2
	C9-H9···π(C9)	0.950	3.400(1)	2.67	134	-x, -y+1, -z+1
	C7-H7A···π(C13)	0.990	2.539(2)	2.89	115	-x, y+1/2, -z+1/2
	C16-H16B···π(C13)	0.980	3.890(2)	2.97	156	-x+1, y-1/2, -z+1/2
9	N3-H3···O1	1.030	3.038(2)	2.23	134	x, -y+1/2, z-1/2
	C16-H16C···O1	1.080	3.593(3)	2.60	153	x, -y+1/2, z-1/2
	C15-H15A···O1	1.080	3.587(3)	2.60	152	x, -y+1/2, z-1/2
	C18-H18C···N2	1.080	3.525(3)	2.66	137	x, -y+1/2, z+1/2

	C19-H19C···π(C8)	0.980	3.606(3)	2.74	147	-x+1, y+1/2, -z+1/2
	C19-H19C···π(C7)	0.980	3.814(2)	2.85	166	-x+1, y+1/2, -z+1/2
10	C17-H17A···F2	1.080	3.214(7)	2.58	117	x, y, z
	C36-H36A···F1	1.080	3.468(7)	2.57	141	x, y, z
	C35-H35C···F1	1.080	3.593(8)	2.69	141	x, y, z
	C36-H36B···F1	1.080	3.409(7)	2.53	138	x-1/2, -y+1, z
	C36-H36C···N5	1.080	3.699(8)	2.63	169	x-1/2, -y+1, z
	C9-H9···O2	1.080	3.478(7)	2.43	163	x-1/2, -y+1, z
	C16-H16A···N2	1.080	3.425(7)	2.67	127	x-1/2, -y+2, z
	C17-H17C···O1	1.080	3.559(7)	2.56	154	x-1/2, -y+2, z
	N3-H3···O1	1.030	2.861(6)	1.90	153	x-1/2, -y+2, z
	C31-H31···π(C12)	0.950	3.627(8)	2.86	138	-x+1/2+1, y, z-1/2
	C12-H12···π(C31)	0.950	3.627(8)	2.80	145	-x+1/2+1, y, z-1/2
	C38-H38A ···π(C10)	0.980	3.626(8)	2.74	151	-x+1, -y+1, z+1/2
	C38-H38A···π(C11)	0.980	3.699(8)	2.87	142	-x+1, -y+1, z-1/2
	S1···π(C3)	-	3.528(5)	-	-	x-1/2,-y+2,+z
	S2···π(C20)	-	3.612(5)	-	-	x+1/2,-y+1,+z
	S2···π(C22)	-	3.642(5)	-	-	x+1/2,-y+1,+z
11	C24-H24···N2	1.080	3.476(4)	2.62	136	x, y, z
	C12-H12···O2	1.080	3.196(2)	2.36	133	-x+1, -y+1, -z+1
	C14-H14···O3	1.080	3.289(4)	2.48	130	-x, y-1/2, -z+1/2
	C15-H15···O1	1.080	3.393(3)	2.52	137	-x, y-1/2, -z+1/2
	C23-H23···O2	1.080	3.340(4)	2.50	139	x, -y+1/2, z-1/2
	C10-H10···O4	1.080	3.535(3)	2.62	142	-x+1, y-1/2, -z+1/2
	C16-H16···O4	1.080	3.459(3)	2.45	154	x, y-1, z
	C9-H9···N1	1.080	3.345(4)	2.52	132	-x+1, y-1/2, -z+1/2
	C9-H9···π(C12)	1.080	3.724(2)	2.74	154	-x+1, y-1/2, -z+1/2
	C9-H9···π(C7)	1.080	2.413(3)	2.80	138	-x+1, y-1/2, -z+1/2
	C9-H9···π(C1)	1.080	3.765(4)	2.80	130	-x+1, y-1/2, -z+1/2
	S1···π(C7)	-	3.556(5)	-	-	-x+1, -y+1, -z+1

Table S5: Total interaction energies of molecules (in kJ/mol), R is the distance between molecular centroids (mean atomic position in Å). Scale factors for the energy model form *Crystal Explorer21.5* is given below.

Compound 2

	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
	1	-x, -y, -z	7.80	B3LYP/6-31G(d,p)	-73.6	-17.5	-23.5	79.5	-62.1
	1	x, y, z	8.22	B3LYP/6-31G(d,p)	-1.6	-1.2	-12.8	9.0	-8.2
	1	x, -y+1/2, z+1/2	10.50	B3LYP/6-31G(d,p)	-2.2	-0.3	-8.2	6.0	-6.0
	0	-x, -y, -z	10.82	B3LYP/6-31G(d,p)	-1.5	-0.2	-7.2	5.8	-4.3
	0	-x, -y, -z	4.36	B3LYP/6-31G(d,p)	-17.9	-3.3	-60.3	38.3	-50.2
	1	x, -y+1/2, z+1/2	7.17	B3LYP/6-31G(d,p)	-21.0	-3.8	-19.8	25.9	-26.2
	0	-x, y+1/2, -z+1/2	9.96	B3LYP/6-31G(d,p)	1.9	-0.3	-1.8	0.0	0.2
	0	-x, y+1/2, -z+1/2	6.79	B3LYP/6-31G(d,p)	2.5	-0.9	-8.1	2.1	-3.8
	2	-x, y+1/2, -z+1/2	8.89	B3LYP/6-31G(d,p)	-0.2	-0.5	-10.0	5.6	-5.9
	1	-x, -y, -z	4.87	B3LYP/6-31G(d,p)	-19.3	-3.1	-50.4	43.2	-39.9

Energy Model	k_{ele}	k_{Dis}	k_{Pol}	k_{Rep}
CE-B3LYP/6-31G(d,p)	1.057	0.871	0.740	0.618

Compound 3

PURPLE

N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
0	-	7.61	B3LYP/6-31G(d,p)	-78.4	-19.0	-26.5	91.2	-63.7
1	-	7.70	B3LYP/6-31G(d,p)	-1.4	-0.9	-22.0	13.1	-13.2
0	-	6.94	B3LYP/6-31G(d,p)	-30.5	-7.7	-29.4	40.1	-38.8
1	-	8.37	B3LYP/6-31G(d,p)	0.2	-1.0	-9.6	3.6	-6.7
0	-	10.02	B3LYP/6-31G(d,p)	-2.2	-0.3	-10.4	6.9	-7.4
0	-x+1/2, y+1/2, -z+1/2	8.82	B3LYP/6-31G(d,p)	-0.8	-0.2	-5.9	2.1	-4.8
0	-	4.59	B3LYP/6-31G(d,p)	-3.6	-4.1	-57.7	39.4	-32.8
0	-	6.06	B3LYP/6-31G(d,p)	-8.3	-2.4	-20.9	28.4	-11.2
0	-	8.30	B3LYP/6-31G(d,p)	-2.3	-0.6	-5.7	3.4	-5.7
1	-	4.35	B3LYP/6-31G(d,p)	-18.2	-3.7	-68.0	43.1	-54.5
0	-x, -y, -z	6.03	B3LYP/6-31G(d,p)	-9.2	-2.4	-26.1	9.4	-28.4
1	-	8.22	B3LYP/6-31G(d,p)	-2.8	-0.6	-5.9	3.9	-6.1
0	-	10.01	B3LYP/6-31G(d,p)	-2.4	-0.2	-8.8	6.5	-6.4
0	-	9.89	B3LYP/6-31G(d,p)	2.4	-0.6	-5.7	1.9	-1.7
0	-	12.55	B3LYP/6-31G(d,p)	0.2	-0.1	-2.7	0.0	-2.2
1	-	6.97	B3LYP/6-31G(d,p)	-25.0	-5.5	-28.7	35.4	-33.6
0	x+1/2, -y+1/2, z+1/2	10.09	B3LYP/6-31G(d,p)	-1.6	-0.3	-10.1	6.6	-6.7
0	-x+1/2, y+1/2, -z+1/2	8.91	B3LYP/6-31G(d,p)	-1.5	-0.3	-5.8	5.2	-3.6
1	-	7.64	B3LYP/6-31G(d,p)	-10.1	-1.4	-24.2	20.3	-20.2
0	-	7.66	B3LYP/6-31G(d,p)	-2.8	-1.1	-23.1	15.9	-14.1
0	-x, -y, -z	11.81	B3LYP/6-31G(d,p)	-0.1	-0.1	-1.7	0.1	-1.7
0	-	8.21	B3LYP/6-31G(d,p)	1.3	-1.0	-11.4	4.5	-6.6

GREY

N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
0	-	7.61	B3LYP/6-31G(d,p)	-78.4	-19.0	-26.5	91.2	-63.7
0	-	7.70	B3LYP/6-31G(d,p)	-1.4	-0.9	-22.0	13.1	-13.2
1	-	6.94	B3LYP/6-31G(d,p)	-30.5	-7.7	-29.4	40.1	-38.8
0	-	8.37	B3LYP/6-31G(d,p)	0.2	-1.0	-9.6	3.6	-6.7
1	-	10.02	B3LYP/6-31G(d,p)	-2.2	-0.3	-10.4	6.9	-7.4
0	-x+1/2, y+1/2, -z+1/2	8.82	B3LYP/6-31G(d,p)	-0.8	-0.2	-5.9	2.1	-4.8
0	-	4.59	B3LYP/6-31G(d,p)	-3.6	-4.1	-57.7	39.4	-32.8
1	-	6.06	B3LYP/6-31G(d,p)	-8.3	-2.4	-20.9	28.4	-11.2
0	-	8.30	B3LYP/6-31G(d,p)	-2.3	-0.6	-5.7	3.4	-5.7
0	-	4.35	B3LYP/6-31G(d,p)	-18.2	-3.7	-68.0	43.1	-54.5
0	-x, -y, -z	6.03	B3LYP/6-31G(d,p)	-9.2	-2.4	-26.1	9.4	-28.4
0	-	8.22	B3LYP/6-31G(d,p)	-2.8	-0.6	-5.9	3.9	-6.1
0	-	10.01	B3LYP/6-31G(d,p)	-2.4	-0.2	-8.8	6.5	-6.4
0	-	9.89	B3LYP/6-31G(d,p)	2.4	-0.6	-5.7	1.9	-1.7
0	-	12.55	B3LYP/6-31G(d,p)	0.2	-0.1	-2.7	0.0	-2.2
1	-	6.97	B3LYP/6-31G(d,p)	-25.0	-5.5	-28.7	35.4	-33.6
0	x+1/2, -y+1/2, z+1/2	10.09	B3LYP/6-31G(d,p)	-1.6	-0.3	-10.1	6.6	-6.7
0	-x+1/2, y+1/2, -z+1/2	8.91	B3LYP/6-31G(d,p)	-1.5	-0.3	-5.8	5.2	-3.6
1	-	7.64	B3LYP/6-31G(d,p)	-10.1	-1.4	-24.2	20.3	-20.2
1	-	7.66	B3LYP/6-31G(d,p)	-2.8	-1.1	-23.1	15.9	-14.1
0	-x, -y, -z	11.81	B3LYP/6-31G(d,p)	-0.1	-0.1	-1.7	0.1	-1.7
1	-	8.21	B3LYP/6-31G(d,p)	1.3	-1.0	-11.4	4.5	-6.6
0	-x+1/2, y+1/2, -z+1/2	8.82	B3LYP/6-31G(d,p)	-1.5	-0.3	-6.9	4.6	-4.9
0	-x, -y, -z	7.68	B3LYP/6-31G(d,p)	-67.9	-16.5	-24.8	71.1	-61.7
0	-x, -y, -z	12.63	B3LYP/6-31G(d,p)	0.9	-0.1	-2.5	0.0	-1.3
0	x+1/2, -y+1/2, z+1/2	10.03	B3LYP/6-31G(d,p)	-2.3	-0.3	-9.0	6.3	-6.5

ORANGE

N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
0	-	7.61	B3LYP/6-31G(d,p)	-78.4	-19.0	-26.5	91.2	-63.7
1	-	7.70	B3LYP/6-31G(d,p)	-1.4	-0.9	-22.0	13.1	-13.2
0	-	6.94	B3LYP/6-31G(d,p)	-30.5	-7.7	-29.4	40.1	-38.8
1	-	8.37	B3LYP/6-31G(d,p)	0.2	-1.0	-9.6	3.6	-6.7
0	-	10.02	B3LYP/6-31G(d,p)	-2.2	-0.3	-10.4	6.9	-7.4
0	-x+1/2, y+1/2, -z+1/2	8.82	B3LYP/6-31G(d,p)	-0.8	-0.2	-5.9	2.1	-4.8
0	-	4.59	B3LYP/6-31G(d,p)	-3.6	-4.1	-57.7	39.4	-32.8
0	-	6.06	B3LYP/6-31G(d,p)	-8.3	-2.4	-20.9	28.4	-11.2
0	-	8.30	B3LYP/6-31G(d,p)	-2.3	-0.6	-5.7	3.4	-5.7
0	-	4.35	B3LYP/6-31G(d,p)	-18.2	-3.7	-68.0	43.1	-54.5
0	-x, -y, -z	6.03	B3LYP/6-31G(d,p)	-9.2	-2.4	-26.1	9.4	-28.4
0	-	8.22	B3LYP/6-31G(d,p)	-2.8	-0.6	-5.9	3.9	-6.1
0	-	10.01	B3LYP/6-31G(d,p)	-2.4	-0.2	-8.8	6.5	-6.4
0	-	9.89	B3LYP/6-31G(d,p)	2.4	-0.6	-5.7	1.9	-1.7
0	-	12.55	B3LYP/6-31G(d,p)	0.2	-0.1	-2.7	0.0	-2.2

Compound 6

N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
0	-x, -y, -z	7.18	B3LYP/6-31G(d,p)	-53.0	-11.9	-32.7	73.7	-47.9
1	x, y, z	7.78	B3LYP/6-31G(d,p)	-4.6	-1.3	-21.6	18.2	-13.4
1	-x, -y, -z	7.67	B3LYP/6-31G(d,p)	-10.9	-2.6	-36.4	34.9	-23.6
0	x, y, z	10.98	B3LYP/6-31G(d,p)	-2.3	-0.6	-9.3	5.7	-7.4
0	-x, -y, -z	9.69	B3LYP/6-31G(d,p)	-3.4	-2.0	-34.6	24.6	-20.1
0	-x, -y, -z	13.78	B3LYP/6-31G(d,p)	-0.5	-0.0	-1.2	0.0	-1.6
1	x, y, z	11.17	B3LYP/6-31G(d,p)	0.9	-0.3	-8.3	4.2	-3.9
1	x, y, z	8.22	B3LYP/6-31G(d,p)	-2.7	-1.0	-11.3	5.0	-10.3
0	-x, -y, -z	4.96	B3LYP/6-31G(d,p)	-28.6	-9.7	-92.9	63.0	-79.5
1	-x, -y, -z	6.99	B3LYP/6-31G(d,p)	0.6	-0.7	-10.7	3.6	-6.9
1	-x, -y, -z	9.34	B3LYP/6-31G(d,p)	0.7	-0.1	-2.4	0.0	-1.4
0	-x, -y, -z	13.51	B3LYP/6-31G(d,p)	-0.7	-0.2	-7.1	0.0	-7.0
1	-x, -y, -z	8.82	B3LYP/6-31G(d,p)	-11.5	-1.9	-39.5	22.6	-34.0

Compound 7

N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
1	-x, -y, -z	7.60	B3LYP/6-31G(d,p)	-56.1	-12.5	-28.3	57.5	-57.6
2	-x, y+1/2, -z+1/2	7.11	B3LYP/6-31G(d,p)	-1.7	0.0	-37.5	21.4	-21.3
0	x, -y+1/2, z+1/2	7.30	B3LYP/6-31G(d,p)	-35.0	-8.6	-51.2	50.2	-56.9
1	-x, -y, -z	10.29	B3LYP/6-31G(d,p)	-6.0	-0.3	-17.9	25.1	-6.6
0	-x, -y, -z	12.89	B3LYP/6-31G(d,p)	-1.7	-0.4	-11.1	0.0	-11.8
0	-x, y+1/2, -z+1/2	7.76	B3LYP/6-31G(d,p)	-8.1	-1.6	-26.6	12.4	-25.3
1	x, y, z	9.73	B3LYP/6-31G(d,p)	-1.4	-0.5	-7.4	8.6	-3.0
2	x, -y+1/2, z+1/2	10.19	B3LYP/6-31G(d,p)	-4.8	-0.4	-16.7	12.7	-12.1
0	-x, -y, -z	7.81	B3LYP/6-31G(d,p)	-7.0	-1.4	-24.5	27.8	-12.6
0	-x, -y, -z	14.36	B3LYP/6-31G(d,p)	-0.2	-0.0	-1.1	0.0	-1.2

Compound 10

ORANGE

	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
	1	-	9.28	B3LYP/6-31G(d,p)	-3.5	-1.5	-23.3	13.2	-16.9
	0	x+1/2, -y, z	4.88	B3LYP/6-31G(d,p)	-43.2	-12.1	-91.1	85.8	-81.0
	1	-	11.06	B3LYP/6-31G(d,p)	-5.7	-2.0	-13.6	12.1	-11.8
	1	-	12.04	B3LYP/6-31G(d,p)	0.0	-0.5	-15.2	0.0	-13.6
	0	-x+1/2, y, z+1/2	11.10	B3LYP/6-31G(d,p)	-0.2	-0.3	-9.0	4.0	-5.8
	0	-	10.83	B3LYP/6-31G(d,p)	-2.8	-0.6	-19.8	12.6	-12.9
	1	-	10.18	B3LYP/6-31G(d,p)	-9.5	-1.5	-26.2	26.4	-17.7
	0	-x, -y, z+1/2	11.01	B3LYP/6-31G(d,p)	-2.2	-0.3	-6.7	4.5	-5.7
	0	-	11.21	B3LYP/6-31G(d,p)	-4.9	-0.7	-20.3	14.2	-14.6
	0	-	11.83	B3LYP/6-31G(d,p)	-1.8	-0.4	-11.6	5.4	-9.0
	0	-	12.17	B3LYP/6-31G(d,p)	-0.4	-0.5	-8.1	0.0	-7.8
	1	-	13.06	B3LYP/6-31G(d,p)	2.6	-0.4	-10.3	0.0	-6.5
	1	-	12.37	B3LYP/6-31G(d,p)	0.5	-0.2	-15.6	0.0	-13.3
	1	-	12.88	B3LYP/6-31G(d,p)	-0.3	-0.1	-2.0	0.0	-2.1
	1	-	13.73	B3LYP/6-31G(d,p)	-0.3	-0.1	-1.9	0.0	-2.0
	1	x+1/2, -y, z	4.44	B3LYP/6-31G(d,p)	-22.3	-5.1	-98.8	61.9	-75.2
	0	-x+1/2, y, z+1/2	11.00	B3LYP/6-31G(d,p)	-1.5	-0.4	-10.2	7.8	-5.9

GREY

	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
	1	-	9.28	B3LYP/6-31G(d,p)	-3.5	-1.5	-23.3	13.2	-16.9
	1	x+1/2, -y, z	4.88	B3LYP/6-31G(d,p)	-43.2	-12.1	-91.1	85.8	-81.0
	0	-	11.06	B3LYP/6-31G(d,p)	-5.7	-2.0	-13.6	12.1	-11.8
	0	-	12.04	B3LYP/6-31G(d,p)	0.0	-0.5	-15.2	0.0	-13.6
	2	-x+1/2, y, z+1/2	11.10	B3LYP/6-31G(d,p)	-0.2	-0.3	-9.0	4.0	-5.8
	0	-	10.83	B3LYP/6-31G(d,p)	-2.8	-0.6	-19.8	12.6	-12.9
	1	-	10.18	B3LYP/6-31G(d,p)	-9.5	-1.5	-26.2	26.4	-17.7
	0	-x, -y, z+1/2	11.01	B3LYP/6-31G(d,p)	-2.2	-0.3	-6.7	4.5	-5.7
	1	-	11.21	B3LYP/6-31G(d,p)	-4.9	-0.7	-20.3	14.2	-14.6
	0	-	11.83	B3LYP/6-31G(d,p)	-1.8	-0.4	-11.6	5.4	-9.0
	1	-	12.17	B3LYP/6-31G(d,p)	-0.4	-0.5	-8.1	0.0	-7.8
	1	-	13.06	B3LYP/6-31G(d,p)	2.6	-0.4	-10.3	0.0	-6.5
	1	-	12.37	B3LYP/6-31G(d,p)	0.5	-0.2	-15.6	0.0	-13.3
	1	-	12.88	B3LYP/6-31G(d,p)	-0.3	-0.1	-2.0	0.0	-2.1
	1	-	13.73	B3LYP/6-31G(d,p)	-0.3	-0.1	-1.9	0.0	-2.0

Compound 9

	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
	1	x, -y+1/2, z+1/2	5.42	B3LYP/6-31G(d,p)	-32.8	-9.6	-85.2	65.5	-75.5
	1	-x, -y, -z	13.29	B3LYP/6-31G(d,p)	1.5	-0.6	-12.5	0.0	-9.8
	0	-x, y+1/2, -z+1/2	9.15	B3LYP/6-31G(d,p)	-7.5	-1.3	-23.6	17.0	-19.0
	0	-x, -y, -z	12.10	B3LYP/6-31G(d,p)	1.8	-0.4	-11.3	0.0	-8.2
	1	x, y, z	13.03	B3LYP/6-31G(d,p)	0.9	-0.2	-9.2	0.0	-7.3
	1	-x, y+1/2, -z+1/2	10.10	B3LYP/6-31G(d,p)	-4.2	-1.0	-18.9	7.9	-16.7
	0	x, -y+1/2, z+1/2	11.46	B3LYP/6-31G(d,p)	-3.1	-0.8	-17.9	13.1	-11.4
	1	-x, -y, -z	10.43	B3LYP/6-31G(d,p)	-3.6	-0.3	-15.5	11.2	-10.6
	0	-x, -y, -z	8.87	B3LYP/6-31G(d,p)	-0.5	-1.3	-28.1	23.7	-11.2
	0	-x, -y, -z	12.41	B3LYP/6-31G(d,p)	-1.6	-0.3	-6.6	0.0	-7.6

Compound 11

	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
	0	-x, -y, -z	7.33	B3LYP/6-31G(d,p)	-26.6	-5.7	-106.8	87.6	-71.2
	1	-x, -y, -z	13.70	B3LYP/6-31G(d,p)	4.1	-1.0	-7.9	0.0	-3.3
	1	-x, y+1/2, -z+1/2	9.77	B3LYP/6-31G(d,p)	-7.8	-5.3	-27.7	17.9	-25.3
	1	-x, -y, -z	10.05	B3LYP/6-31G(d,p)	-15.3	-2.9	-32.6	20.0	-34.4
	1	x, -y+1/2, z+1/2	15.47	B3LYP/6-31G(d,p)	0.1	-0.1	-1.3	0.0	-1.1
	1	x, -y+1/2, z+1/2	9.55	B3LYP/6-31G(d,p)	-12.2	-2.6	-16.2	10.1	-22.7
	1	x, y, z	9.83	B3LYP/6-31G(d,p)	-15.0	-3.1	-34.1	20.6	-35.1
	1	-x, y+1/2, -z+1/2	10.09	B3LYP/6-31G(d,p)	-9.5	-2.1	-43.2	32.7	-29.1
	0	x, -y+1/2, z+1/2	10.06	B3LYP/6-31G(d,p)	-1.0	-1.6	-20.7	8.7	-14.8
	0	-x, -y, -z	12.67	B3LYP/6-31G(d,p)	-3.2	-0.4	-9.4	0.0	-11.9

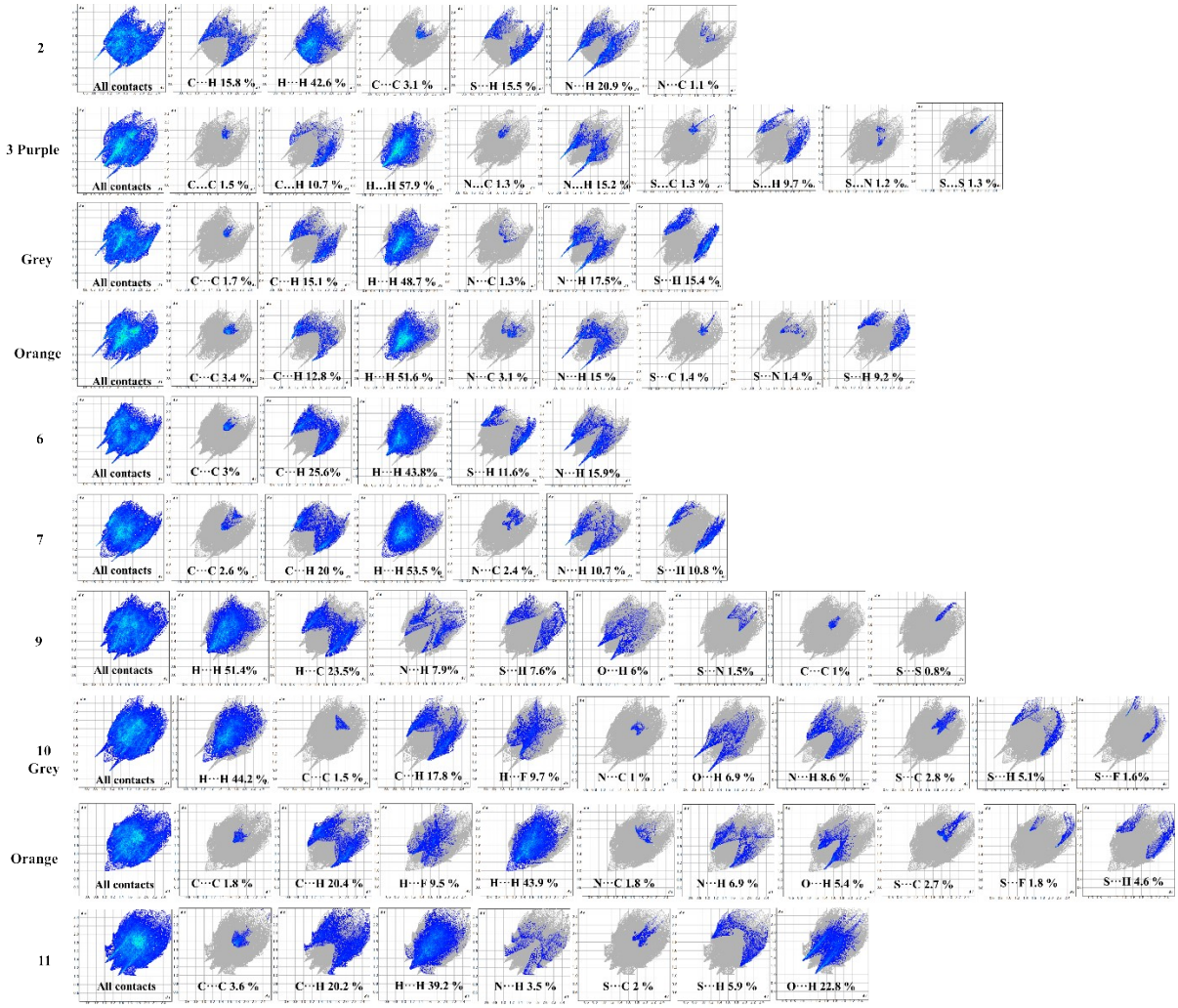


Figure S11: Fingerprint plots representing the percentage contribution of reciprocal contacts.

Table S6: Lattice energy of the compounds (in kJ/mol) calculated using *Crystal Explorer21.5*.

Compounds	***Crystal Explorer*** B3LYP/6-31G(d,p) (in kJ/mol)
2	−134.4
3	−141.4
6	−157.3
7	−175.8
9	−167.1
10	−165.6
11	−191.6

Table S7: Topological parameters for interaction obtained from QTAIM calculations in all eight compounds.

Compounds Name	Interaction	Rij (Å)	ρ (e/ Å^3)	$\nabla^2\rho$ (e/ Å^5)	V (au)	G (au)	$\lvert V\rvert / G$
2	S1···C8(π)	3.196	0.04	0.64	-0.0035	0.0051	0.69
3	H9C···S3	2.899	0.04	0.49	-0.0024	0.0038	0.65
	S2···S3	3.403	0.05	0.57	-0.0032	0.0045	0.70
6	H11···S1	3.159	0.02	0.33	-0.0015	0.0024	0.61
7	H14···S1	2.960	0.04	0.49	-0.0024	0.0037	0.64
9	H18A···S1	2.905	0.04	0.53	-0.0028	0.0041	0.67
10(GREY)	S1···C3(π)	3.337	0.04	0.46	-0.0030	0.0039	0.78
(ORANGE)	S2···C20(π)	3.420	0.04	0.43	-0.0027	0.0036	0.75
	S1···C22(π)	3.479	0.04	0.41	-0.0026	0.0034	0.77
11	S1···C7(π)	3.369	0.04	0.44	-0.0028	0.0037	0.77

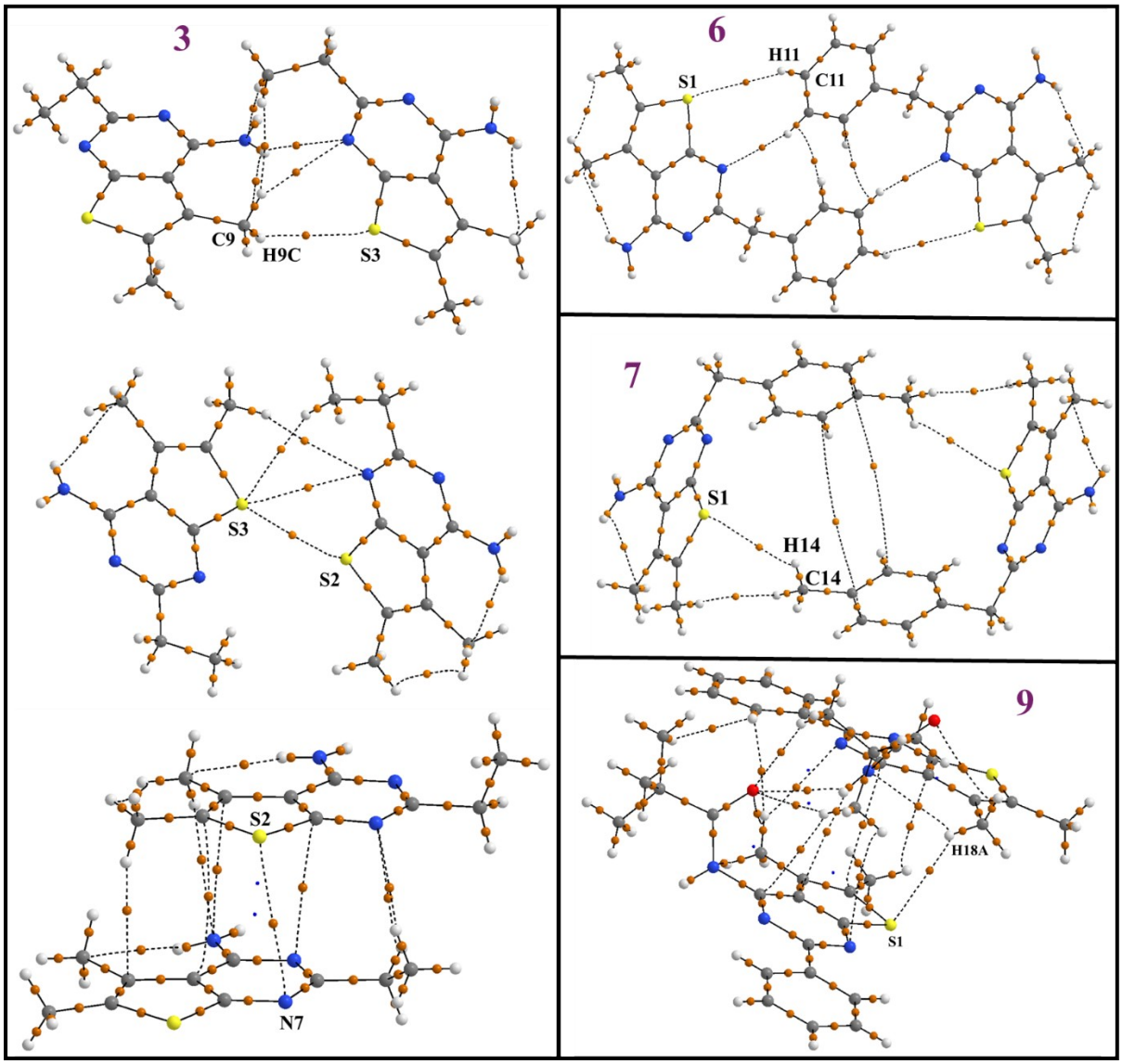


Figure S12. QTAIM analysis exhibits the bond critical points in dimeric motifs to be present along the bond path connecting the hydrogen and sulphur atom. Thus, C-H···S nature of interaction is found in compounds **3**, **6**, **7**and **9**.

Reference

1. G.A.Jeffrey & L.Lewis, *Carbohydr.Res.*1978, **60**,179.
2. R.Taylor, O.Kennard, *Acta Cryst.*1983, **B39**,133.