Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

Predicting molecular isomerism of symmetrical and unsymmetrical *N,N'*-diphenyl formamidines in the solid-state: crystal structure, Hirshfeld surface analysis, pairwise interaction energy, ΔH_{fusion} and ΔS_{fusion} correlations

Sizwe J. Zamisa[†], Unathi Bongoza[†], Bernard Omondi[*,‡]

[†]*School of Chemistry and Physics, University of KwaZulu-Natal, Westville Campus, Private Bag X54001, Durban 4000, South Africa*

[‡]*School of Chemistry and Physics, Pietermaritzburg Campus, University of KwaZulu-Natal, Private Bag X01, Pietermaritzburg, 3209, South Africa*

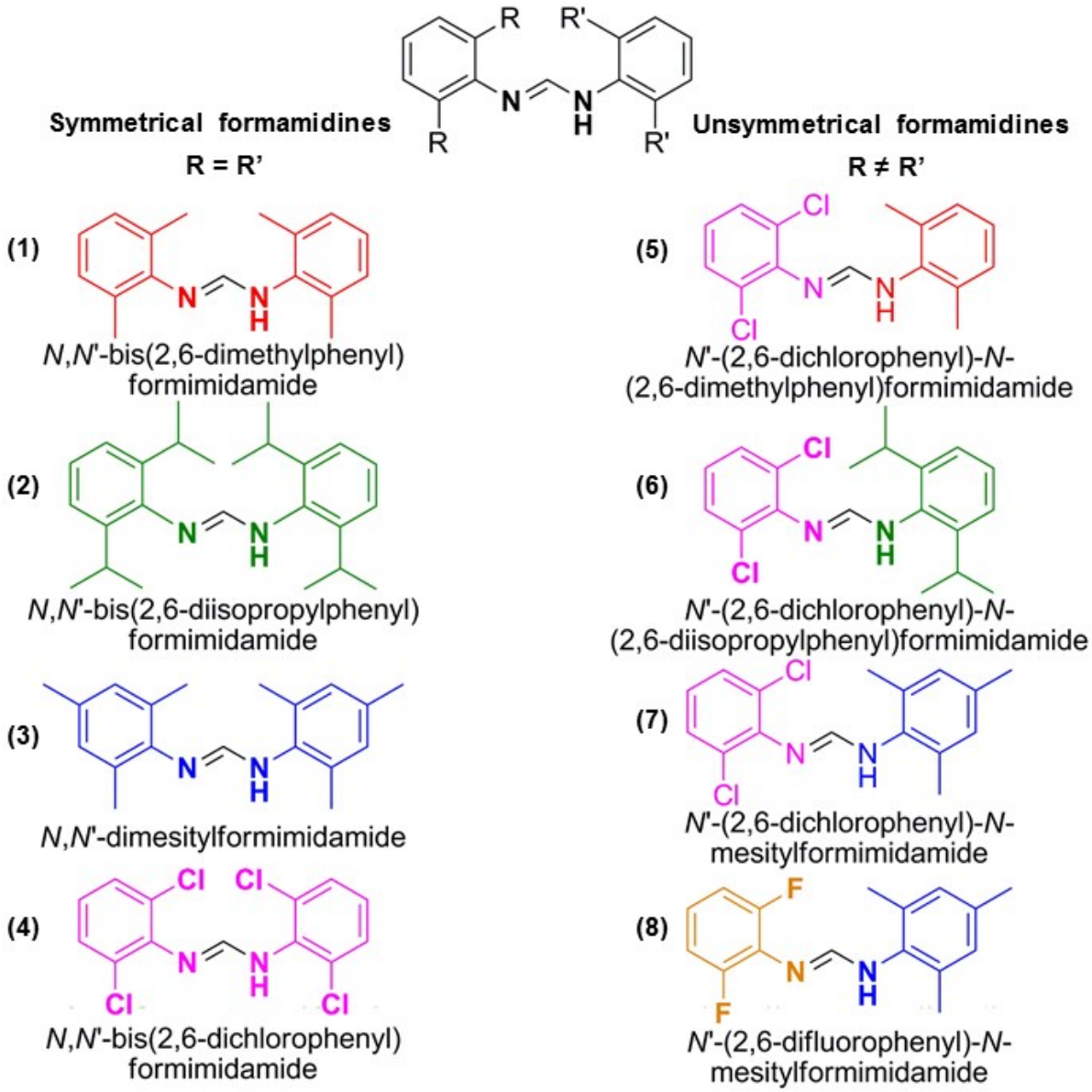

Figure S 1: Molecular structures of symmetrical and unsymmetrical formamidines investigated in this work

1. Experimental section

1.1. Materials and instrumentation

All solvents (ACS reagent grades, ≥ 99.5%) were obtained from Sigma-Aldrich and used as obtained without further purification. From the same source we obtained 2,6-diisopropylaniline (97%), 2,6-dimethylaniline (99%), 2,4,6-trimethylaniline (98%), 2,6-dichloroaniline (98%), 2,6-difluoroaniline (98%) and triethylorthoformate (99%). The NMR spectra for ^{1}H and ^{13}C were measured at room temperature using a Bruker 400MHz spectrometer in DMSO–d_6 and $CDCl_3$. Chemical shift values, reported in parts per million (ppm) relative to the solvent residual peaks in DMSO-d_6 and $CDCl_3$, are 2.5 and 7.26 ppm, respectively, for ^{1}H NMR and

39.5 and 77.00 ppm, respectively, for ^{13}C NMR. Infra-red spectra were obtained on a PerkinElmer Universal ATR spectrum 100 FTIR spectrometer. Mass spectra of compounds were obtained from a Water synaptic GR electrospray positive spectrometer, and the DSC curves were obtained using TGA/DCS Q600 TA Instruments. UV−visible absorption spectra were recorded with a Shimadzu UV−Vis−NIR spectrophotometer.

1.2. Synthetic analytical details of symmetrical N,N'-diphenylformamidine derivatives

N,N'-bis(2,6-dimethylphenyl)formamidine, 1

White solid, Yield = 89%, m.p. = 183-184 ºC, ^{1}H NMR (DMSO-d_6): δ (ppm) = *E* + *Z* isomers: 2.07-2.31 (m, 12H, 4 x —C**H**$_3$), 6.76-7.24 [m, 6H, aromatic H], 7.45 (s, 1H, —N=C(**H**)—), 8.22 [s, 1H, —N(**H**)—]. ^{13}C NMR (DMSO-d_6): δ (ppm) = 18.30, 18.89, 122.21, 126.46, 128.11, 128.65, 135.30, 146.63, 149.96; IR ν (cm^{-1}) = 3160, 3018, 2919, 2852, 2159, 1643, 1632, 1588, 1465, 1368, 1200, 1147, 1091, 759, 714, 620, 482, 449, 390; ESI-TOF MS: m/z (%); $[M + H]^+$ 253.17 (100%), $[M + K^+ + \text{acetonitrile}]^+$ 331.18 (15%)

N,N'-bis(2,6-diisopropylphenyl)formamidine, 2

White solid, Yield = 75%, m.p. = 192-195 ºC, ^{1}H NMR (DMSO-d_6): δ (ppm) = *E* + *Z* isomers: 0.94-1.29 (m, 24H, 8 x —C**H**$_3$), 3.07-3.17 (s, 2H, methine H's) 6.90-7.36 [m, 6H, aromatic H's], 7.49 (s, 1H, —N=C(**H**)—) 8.16 [s, 1H, —N(**H**)—]. ^{13}C NMR (DMSO-d_6): δ (ppm) = 24.23, 25.41, 27.32, 27.94, 28.42, 122.74, 123.29, 127.77, 134.13, 140.00, 146.82, 149.80; IR ν (cm^{-1}): 2960, 2927, 2866, 2164, 1662, 1441, 1286, 1180, 1098, 1059, 821, 799, 753, 672, 598, 536, 504, 434; ESI-TOF MS: m/z (%); $[M + H^+]^+$ 365.30 (100%).

N,N'-Bis(2,4,6-trimethylphenyl)formamidine, 3

White solid, Yield = 64%, m.p. = 207-210 ºC, ^{1}H NMR (DMSO-d_6) δ (ppm) = *E* + *Z* isomers: 2.01-2.20 (m, 18H, 6 x —C**H**$_3$), 6.75-7.09 [m, 4H, aromatic H], 7.37 (s, 1H, —N=C(**H**)—) 8.05 (s, 1H, —N(**H**)—). ^{13}C NMR (DMSO-d_6) δ (ppm) = 18.24, 18.79, 20.88, 127.72, 128.72, 128.91, 129.18, 135.11, 135.40; IR ν (cm^{-1}): 3231, 2913, 2853, 2161, 2033, 1635, 1606, 1477, 1375, 1264, 1211, 1175, 1148, 1120, 1011, 849, 775, 676, 585, 483, 409; ESI-TOF MS: m/z (%): $[M + H]^+$ 281.21 (100%)

N,N'-bis(2,6-dichlorophenyl)formamidine, 4

White solid, Yield = 82%, m.p. = 211-212 ºC, ^{1}H NMR (DMSO-d_6) δ (ppm) = 6.99-7.61 (m, 6H, aromatic H's, *E* + *Z* isomers], 7.73 (s, 0.5H, —N=C(**H**)— (E_{syn} isomer)), 8.31 (s, 0.5H, —N=C(**H**)— (E_{anti} isomer)), 9.32 (s, 0.5H, —N(**H**)—, (E_{syn} isomer)), 10.08 (s, 0.5H, —N(**H**)—,

(E_{anti} isomer)). ^{13}C NMR (DMSO-d_6) δ (ppm) = 128.89, 129.02, 129.51, 129.67, 129.81, 132.31, 133.68, 160.101, 164.87; IR ν (cm^{-1}): 2844, 1654, 1566, 1553, 1441, 1432, 1302, 1220, 1190, 771, 737, 721, 618, 532, 396; ESI-TOF MS: m/z (%); $[M + Na]^+$ 356.93 (100%), [2,6-dichloroaniline + $H_2O]^+$ 179.01 (35%).

1.3. Synthetic analytical details of unsymmetrical N,N'-diphenylformamidine derivatives

N-(2,6-dichlorophenyl)-*N'*-(2,6-dimethylphenyl)formamidine, 5
White solid, Yield = 65%, m.p. = 205-208 ºC, ^{1}H NMR (DMSO-d_6) δ (ppm) = E_{syn}: 2.351 (s, 6H, 2 x —C**H**$_3$), 6.93 (t, 1H, J = 7.99 Hz, aromatic H), 7.11 (s, 3H, aromatic H's), 7.36 (d, 2H, J = 8.00 Hz, aromatic H's), 7.68 (d, 1H, J = 3.40 Hz, —N=C(**H**)—), 8.75 (s, 1H, —N(**H**)—), Selected peaks for E_{anti}: 7.93 (d, J = 12.77 Hz, —N=C(**H**)—), 9.25 (s, —N(**H**)—). ^{13}C NMR (DMSO-d_6) δ (ppm) = 18.69, 123.56, 127.08, 127.96, 128.11, 128.68, 136.20, 136.32, 147.49, 152.29; IR ν (cm^{-1}): 3162, 2922, 2837, 2164, 2034, 1633, 1553, 1444, 1431, 1368, 1218, 1198, 1149, 999, 766, 737, 697, 590, 548, 500, 483, 393; ESI-TOF MS: m/z (%); $[M]^+$ 292.05 (100%).

N'-(2,6-chlorophenyl)-*N*-(2,6-diisopropylphenyl)formamidine, 6
White solid, Yield = 78%, m.p. = 212-216 ºC, ^{1}H NMR (DMSO-d_6) δ (ppm) = E_{syn}: 1.18 (d, 12H, 4 x —C**H**$_3$), 3.36-3.45 (m, 2H, methine H's), 6.92 (t, 1H, J = 7.99 Hz, aromatic H), 7.19 (d, 2H, J = 7.60 Hz, aromatic H's), 7.27, (d, 1H, J = 7.46 Hz, aromatic H), 7.34 (d, 2H, J = 8.01 Hz, aromatic H's), 7.74 (d, 1H, J = 3.16 Hz, —N=C(**H**)—), 8.75 (s, 1H, —N(**H**)—), Selected peaks for E_{anti}: 7.98 (d, J = 14.6 Hz, —N=C(**H**)—), 9.24 (s, —N(**H**)—). ^{13}C NMR (DMSO-d_6) δ (ppm) = 23.61, 23.98, 24.86, 27.96, 28.27, 123.36, 123.42, 123.62, 127.92, 127.97, 128.78, 133.40, 146.66, 147.65, 153.17; IR ν (cm^{-1}):2964, 2868, 1588, 1576, 1491, 1448, 1432, 1307, 1215, 1195, 1151, 1055, 823, 801, 784, 770, 736, 598, 545, 459, 406; ESI-TOF MS: m/z (%); $[M + Na]^+$ 371.13 (100%), [2,6-dichloroaniline + $H_2O]^+$ 179.03 (15%).

N-(2,6 dichlorophenyl)-*N'*-(2,4,6- trimethylphenyl) formamidine, 7
White solid, Yield = 70%, m.p. = 219-221 ºC, ^{1}H NMR (DMSO-d_6) δ (ppm) = E_{syn}: 2.24-2.29 (9H, 3 x —C**H**$_3$), 6.91 (3H, aromatic H), 7.35 (d, 2H, J = 7.99 Hz, aromatic H's), 7.65 (d, 1H, J = 3.35 Hz, —N=C(**H**)—) 8.63 (s, 1H, —N(**H**)—), Selected peaks for E_{anti}: 7.82 (d, J = 5.12 Hz, —N=C(**H**)—), 9.09 (s, —N(**H**)—); ^{13}C NMR (DMSO-d_6) δ (ppm) = 18.59, 20.99, 123.47, 127.93, 128.66, 128.72, 129.20, 133.64, 135.83, 136.02, 147.57, 152.37; IR ν (cm^{-1}): 3199, 2971, 2920, 2855, 2731, 2159, 2038, 1637, 1606, 1553, 1445, 1368, 1218, 1176, 1068, 921,

849, 769, 745, 693, 594, 501, 409, 401, 385; ESI-TOF MS: m/z (%); $[M + Na]^+$ 329.50 (100%), [2,6-dichloroaniline + $H_2O]^+$ 179.01 (10%)

N-(2,6 difluorophenyl)-*N'*-(2,4,6- trimethylphenyl) formamidine, **8**
White solid, Yield = 65%, m.p. = 233-235 ºC, ^{1}H NMR (DMSO-d_6) δ (ppm) = E_{syn}: 2.22 (s, 6H, 2 x —C**H**$_3$), 2.23 (3H, —C**H**$_3$), 6.90-6.96 (m, 5H, aromatic H's), 7.83 (s, 1H, —N=C(**H**)—), 8.69 (s, 1H, —N(**H**)—), Selected peaks for E_{anti}: 7.72 (s, —N=C(**H**)—), 9.13 (s, —N(**H**)—); ^{13}C NMR (DMSO-d_6) δ(ppm) = 18.36, 18.63, 20.94, 111.81, 111.89, 111.98, 112.05, 121.85, 121.95, 128.79, 129.28, 130.07, 130.21, 133.55, 135.19, 135.74, 152.77, 154.96, 157.31; IR v (cm^{-1}):3176, 2980, 2920, 2857, 2161, 2008, 1635, 1605, 1484, 1467, 1367, 1271, 1214, 1007, 986, 855, 775, 745, 710, 638, 580, 504, 439, 406; ESI-TOF MS: m/z (%); $[M + Na]^+$ 297.12 (100%), [1,3-difluoro-2-isocyanatobenzene + $Na^+]^+$ 179.01 (20%)

2.1. Description of the photophysical properties of compounds 1-8

The UV-vis electronic absorption studies for compounds **1 – 8** were done in acetonitrile. The absorption spectra of all compounds were recorded between 200 – 450 nm in ethanol solutions with concentrations of ~10^{-5} M and are shown in **Error! Reference source not found.**. While the primary π-π transitions seem to be similar in all compounds, the n-π electronic transitions differ. For example, in the spectrum of compound **2** with the isopropyl substituents, the secondary band appears at about 236 nm, while in the spectrum of **3** with Cl substituents, it appears at about 256 nm. In comparing the secondary bands in the spectra, those for **1** and **3,** with methyl groups, lie between those of **2** (relatively hypsochromic shifted) and **4** (relatively bathochromic shifted), which is probably as a result of the differing electronic effects of the substituents (Table 2). The bathochromic shift is more enhanced in compound **8** with Cl and F substituents. However, when both electron withdrawing and electron donating groups are present, as in **5**, **6** and **7**, the shifts seem to be minimal; all three compounds have their secondary bands at around 243 nm. The presence of electronegative substituents in both rings, as in **4** and **8,** results in a decrease in band intensity, which could be due to the inductive effect of the halogen atoms.

Table S1: Selected geometric parameters of related formamidines from the CSD.

Compound Name	CSD Refcode	Substituent(s)	Dihedral angle/°		
			$P_{(Ring1)}$-$P_{(N-C=N)}$	$P_{(N-C=N)}$-$P_{(Ring2)}$	$P_{(Ring1)}$-$P_{(Ring2)}$
ethyl 4-[(anilinomethylidene)amino]-3-bromobenzoate	BUDBUA	4-[(anilinomethylidene)amino]-3-bromobenzoate	50.768	24.796	42.924
N,N′-bis(3,5-bis(trifluoromethyl)phenyl)imidoformamide	GOVRAM	3,5-CF_3	63.17	10.682	67.65
methyl4-[({[4-(methoxycarbonyl)phenyl] imino}methyl)amino]benzoate	KEYNEK	*	39.76	9.484	34.505
N,N′-bis(m-bromophenyl)formamidine	NEDBED	3-Br	48.77	11.904	58.858
N,N′-bis(p-fluorophenyl)formamidine	NEDBIH	4-F	60.97	13.416	74.362
N,N′-bis(p-fluorophenyl)formamidine	NEDBIH	4-F	46.54	13.35	57.05
N,N′-bis(p-methoxyphenyl)formamidine	NEDBON	4-OMe	42.46	36.39	62.30
N,N'-bis(p-methoxyphenyl)formamidine	NEDBON	4-OMe	27.35	28.43	52.76
(E*)-N,N′*-bis(4-methoxyphenyl)formimidamide	NEDBON01	4-OMe	27.40	28.25	52.67
(E)-*N,N′*-bis(4-methoxyphenyl)formimidamide	NEDBON01	4-OMe	42.24	36.23	62.21
N,N′-bis(p-nitrophenyl)formamidine	NEDCAA	4-NO_2	47.99	13.69	60.35
2,3-dimethyl-2,3-bis(3-isopropyl-2-(*N′*- (2,6-diisopropylphenyl)formamidinato)phenyl)butane	NIVSER	2,3-dimethyl-2,3-bis(3-isopropyl-2-(N'- (2,6-diisopropyl	53.77	85.68	63.15
N,N′-bis(pentafluorophenyl)methanimidamide benzene solvate	NUBZAO	2,3,4,5,6-F	45.362	44.670	31.515
N,N′-bis(2,3,5-trifluorophenyl)formamidine	OWAPUY	2,3,5-F	33.86	28.63	15.46
N,N′-bis(2,3,5-trifluorophenyl)formamidine	OWAPUY	2,3,5-F	47.57	31.72	35.89
N,N′-bis(3,4,5-trifluorophenyl)formamidine	OWAQAF	3,4,5-F	55.65	8.383	64.02

N,N′-bis(pentafluorophenyl)formamidine toluene solvate	OWAQEJ	2,3,4,5,6-F	43.36	39.17	32.21
N,N′-bis(2,6-difluorophenyl)formamidine	OWAQIN	2,6-F	46.36	36.56	18.67
N,N′-di(p-tolyl)formamidine	ROLGEE	4-Me	47.71	27.06	67.14
N,N′-bis(p-tolyl)formamidine	ROLGEE01	4-Me	47.88	26.93	67.15
N,N′-di(p-tolyl)formamidine	ROLGEE02	4-Me	47.30	29.67	36.79
N,N′-di(p-tolyl)formamidine	ROLGEE02	4-Me	37.34	11.13	30.72
N,N′-bis(2,6-diisopropylphenyl)formamidine	TEVJOU	2,6-diisopropyl	85.16	71.91	44.89
N,N′-bis(2,6-diisopropylphenyl)formamidine	TEVJOU01	2,6-diisopropyl	72.91	71.86	67.22
N,N′-bis(2,6-diisopropylphenyl)imidoformamide	TEVJOU02	2,6-diisopropyl	69.53	71.80	67.64
N,N′-bis(2,6-diisopropylphenyl)formamidine	TEVJOU03	2,6-diisopropyl	87.51	69.273	43.732
N,N′-bis(2,6-diisopropylphenyl)formamidine	TEVJOU03	2,6-diisopropyl	80.24	71.815	44.863
N,N′-bis(2-methoxyphenyl)formamidine	XUGZUU	2-OMe	47.30	37.08	38.09
N,N′-bis(2-methoxyphenyl)imidoformamide	XUGZUU01	2-OMe	46.50	35.86	37.27
N,N′-bis(2-ethoxyphenyl)formamidine	XUHBAD	2-OEt	41.97	38.68	30.62
N,N′-bis(2-ethoxyphenyl)formamidine	XUHBAD	2-OEt	34.66	42.06	28.82
N,N′-bis(3-methoxyphenyl)formamidine	XUHBEH	3-OEt	46.40	11.92	40.27
N,N′-bis(3-n-butoxyphenyl)formamidine	XUHBIL	3-Obu	47.49	3.324	50.63
N,N′-bis(3,5-dichlorophenyl)imidoformamide	ZIPKUG	3,5-Cl	45.98	26.49	69.94

*[4-(methoxycarbonyl)

Table S2: Selected intermolecular interaction parameters in compounds **4 – 8**.

D—H/X···*A*	*D*—H/X	H/X···*A*	*D*···*A*	*D*—H/X···*A*
Compound 4				
N1*A*—H1*A*···N2*A*^{i}	0.88	2.04	2.917(1)	174
N1*B*—H1*B*···N2*B*^{ii}	0.88	2.01	2.878(1)	169
C7B—H7B…$\pi_{2,6\text{-dichloro}}$^{ii}	0.95	2.49	3.389(1)	158
C2B—Cl1B…$\pi_{2,6\text{-dichloro}}$^{ii}	1.728(1)	3.7038(8)	3.788(1)	82
Compound 5				
N2*A*—H2*A*···N1*A*^{i}	0.88	1.98	2.850(4)	168
N2*B*—H2*B*···N1*B*^{ii}	0.88	1.97	2.840(4)	171
C7A—H7A…$\pi_{2,6\text{-dimethyl}}$	0.95	2.49	3.306(4)	143
C7B—H7B…$\pi_{2,6\text{-dimethyl}}$	0.95	2.43	3.219(4)	141
C6B—Cl2B…$\pi_{2,6\text{-dimethyl}}$	1.709(2)	3.774(2)	3.958(2)	83
Compound 6				
N2—H2···N1^{i}	0.88	2.06	2.914(1)	163
Compound 6				
N2—H2···N1^{i}	0.88	2.17	2.953(3)	149
C7—H7…π_{mesityl}^{i}	0.95	2.58	3.451(3)	152
C16—H16A…$\pi_{2,6\text{-dichloro}}$^{ii}	0.95	2.80	3.498(4)	128
Compound 8				
N2*A*—H2*A*···N1*A*^{i}	0.88	2.22	2.971(1)	143
N2*B*—H2*B*···N1*B*	0.88	2.20	2.950(2)	143
C7A—H7A…π_{mesityl}^{i}	0.95	2.75	3.519(1)	138
C7B—H7B…π_{mesityl}	0.95	2.74	3.519(1)	140
π_{mesityl}…$\pi_{2,6\text{-difluoro}}$	-	-	3.7494(8)	-
π_{mesityl}…$\pi_{2,6\text{-difluoro}}$^{ii}	-	-	3.8303(7)	-

Symmetry codes for Compound **1**: (i) −*x*, −*y*, −*z*+1, (ii) −*x*+1, *y*−1/2, −*z*+3/2; Compound **2**: (i) *x*−1/2, −*y*+1/2, *z*−1/2, (ii) *x*, −*y*, *z*−1/2; Compound **3**: (i) 1−*x*, *y*−1/2, 3/2−*z*, 1−*x*, *y*+1/2, 3/2−*z*; Compound **4**: (i) −*x*+1, −*y*+1, −*z*+1. Compound **8**: (i) 1/2+*x*,1/2-*y*,1/2+*z*, (ii) -1/2+*x*,1/2-*y*, -1/2+z

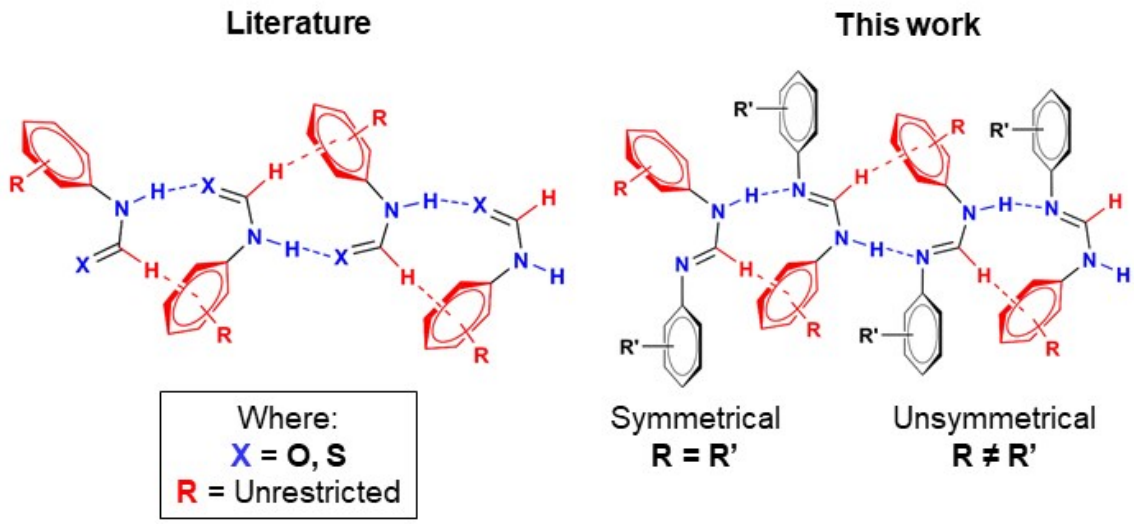

Figure S2: Comparison of C—H…π and classical hydrogen bonding patterns found in closely related crystal structures in the CSD and this work.

Table S3: CSD search hits and their respective C—H…π and classical hydrogen bonding geometric parameters

Compound Name	**Refcode**	**H…π/Å**	**H…X/Å**	**C-H…PI/°**	**N-H…X/°**
N-(2,6-Diisopropylphenyl)thioformamide	QECGOW	2.749	2.494	160	167
N-(11-(Methylamino)tricyclo[8.2.2.2$4,7!]hexadeca-1(12),4,6,10,13,15-hexaen-5-yl)formamide	QULWEB	2.683	2.019	174	168
(*Z*)-3-(4-formamidophenyl)-2,4-pentanedione	DUZYED	2.837	2.029	160	170
N-(2,6-Di-isopropylphenyl)formamide	TEVJIO01	2.803	2.038	159	171
N-(2,4,6-Trimethylphenyl)formamide	QAKDAJ	2.726	2.054	129	171
N-(2,6-Di-isopropylphenyl)formamide	TEVJIO	2.891	2.115	157	174
1,2-bis(Formylamino)benzene	ALOSAV	2.798	1.886	168	174

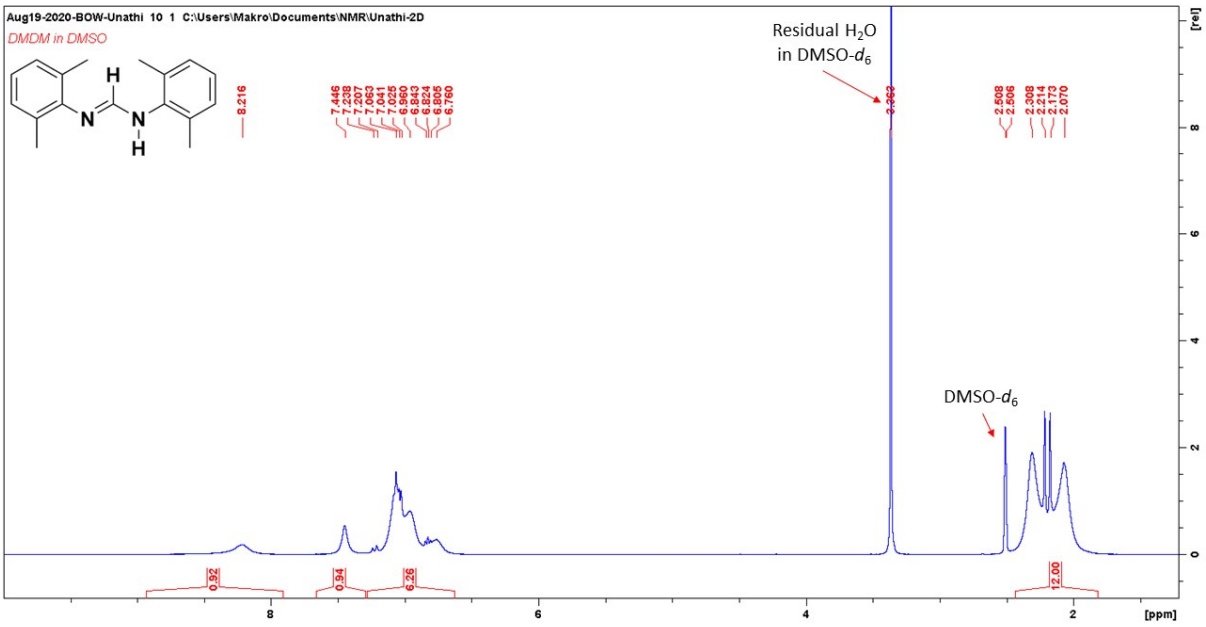

Figure S3: ^{1}H NMR spectrum of **1** in DMSO-d_6

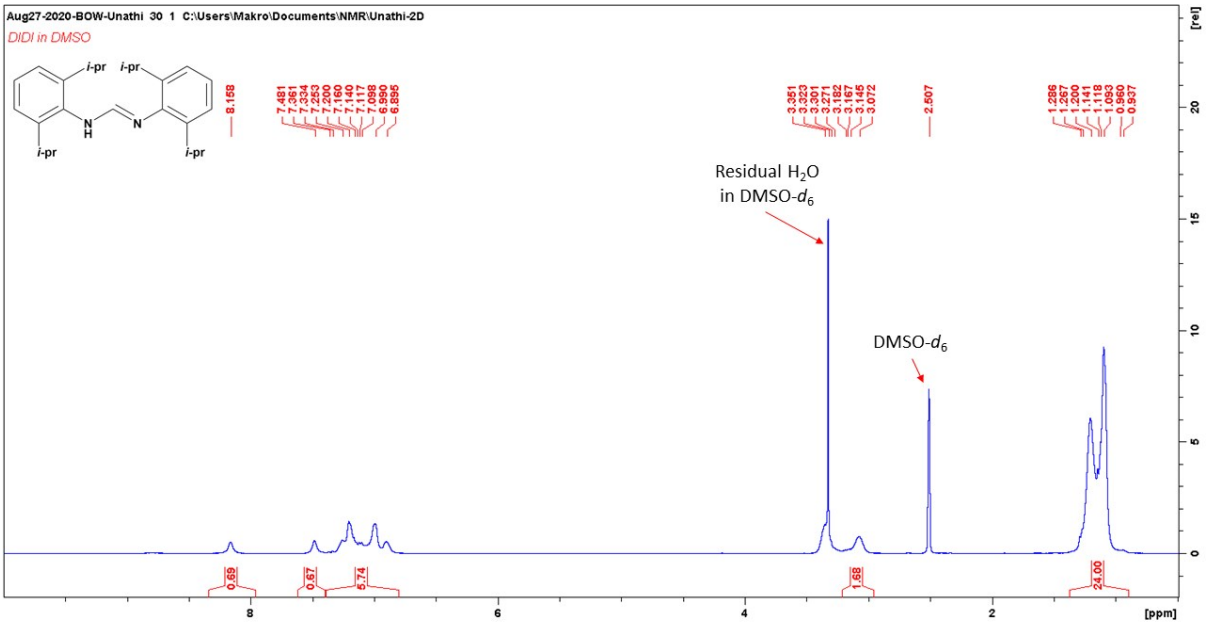

Figure S4: ^{1}H NMR spectrum of **2** in DMSO-d_6

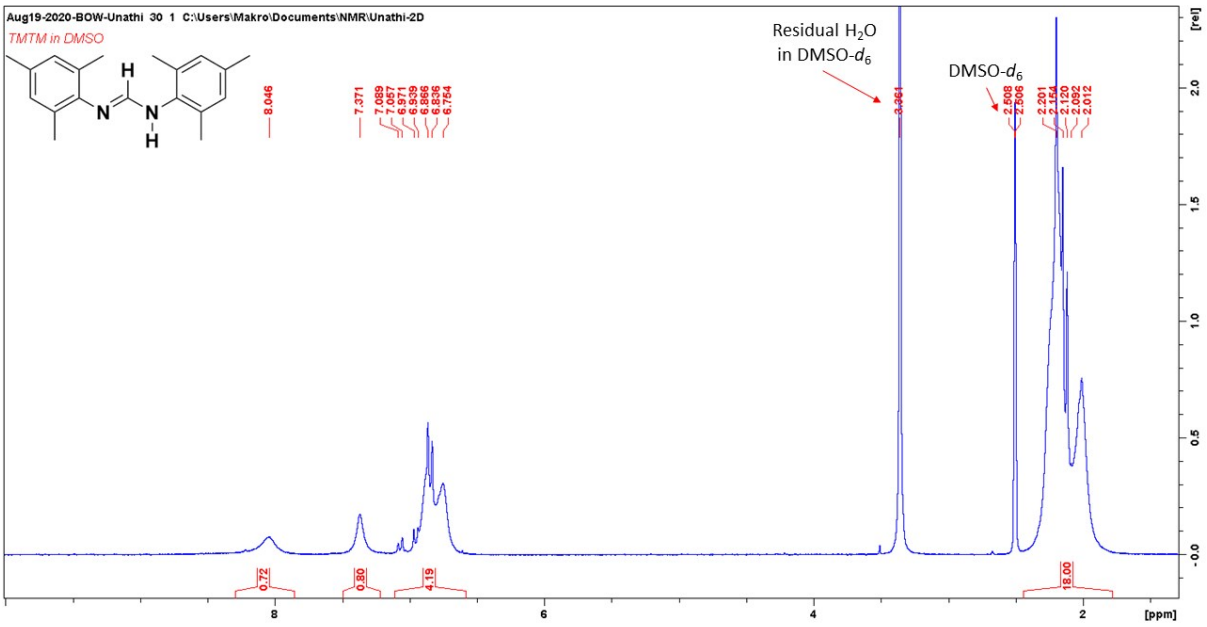

Figure S5: ^{1}H NMR spectrum of **3** in DMSO-d_6

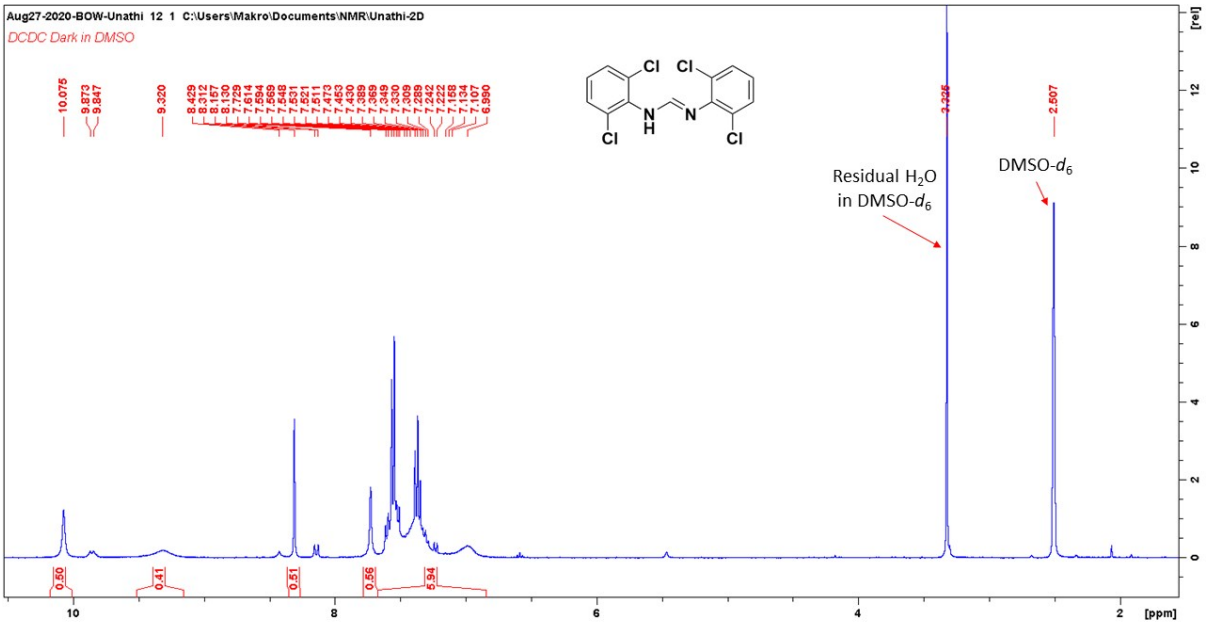

Figure S6: ^{1}H NMR spectrum of **4** in DMSO-d_6

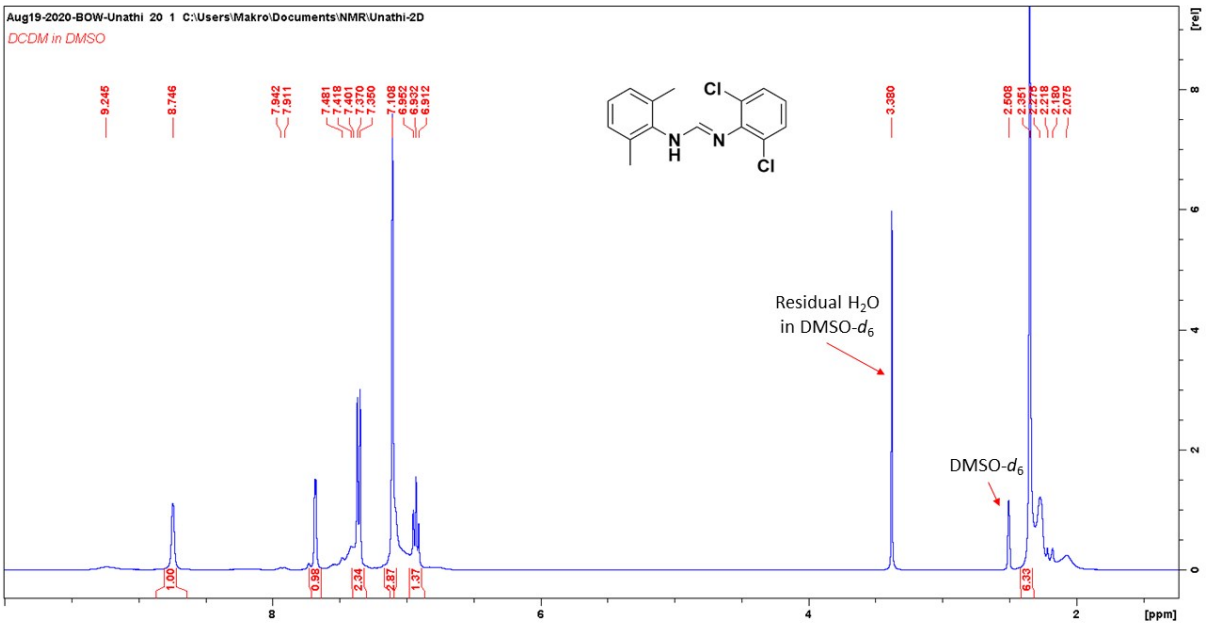

Figure S7: ^{1}H NMR spectrum of **5** in DMSO-d_6

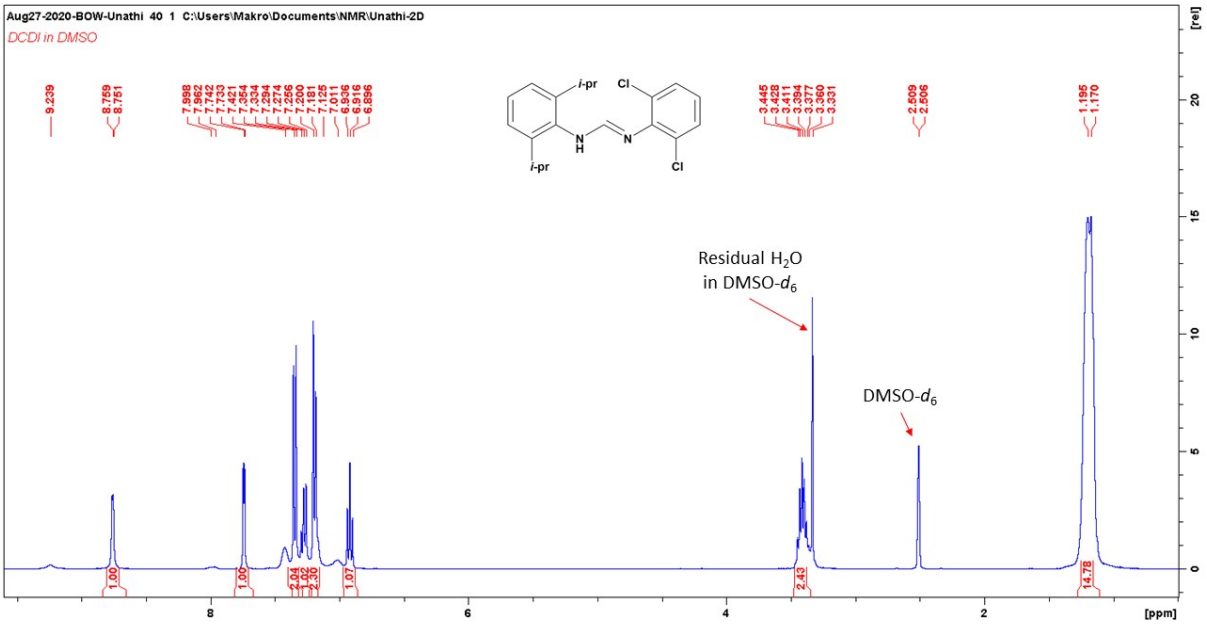

Figure S8: ^{1}H NMR spectrum of **6** in DMSO-d_6

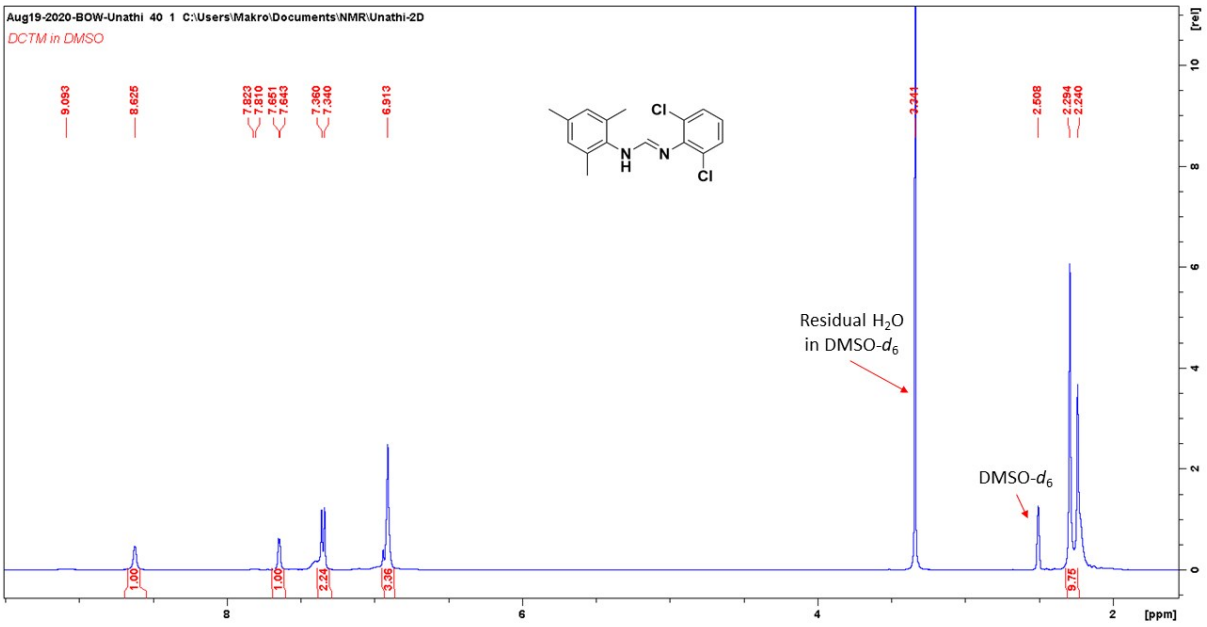

Figure S9: ^{1}H NMR spectrum of **7** in DMSO-d$_6$

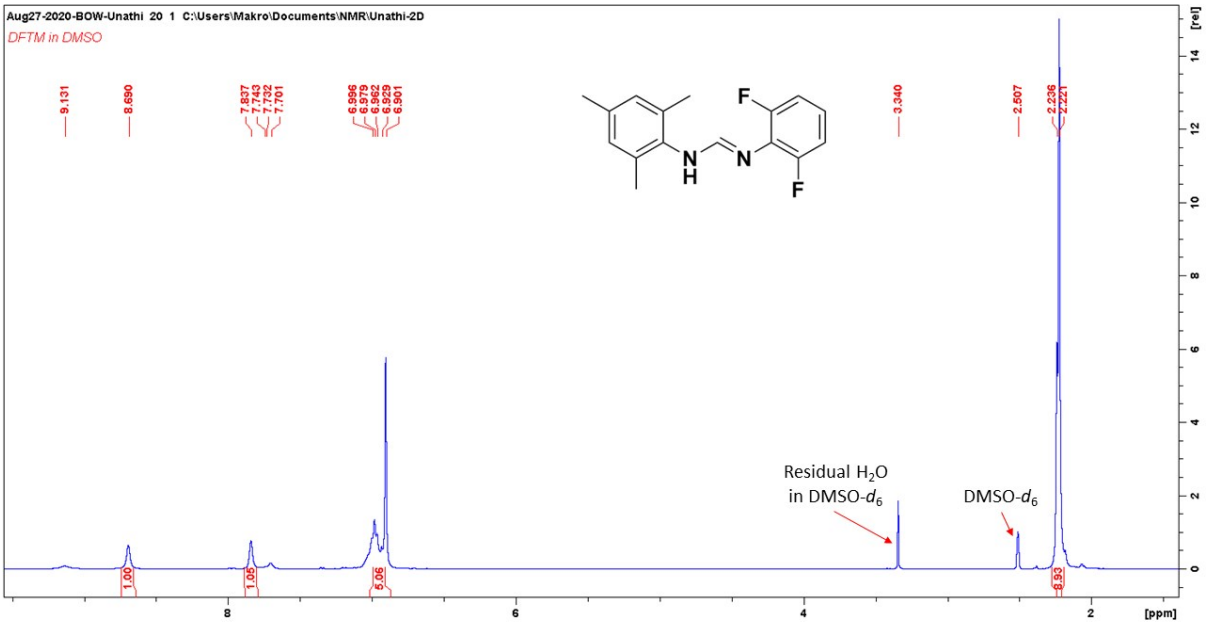

Figure S10^{1}H NMR spectrum of **8** in DMSO-d$_6$

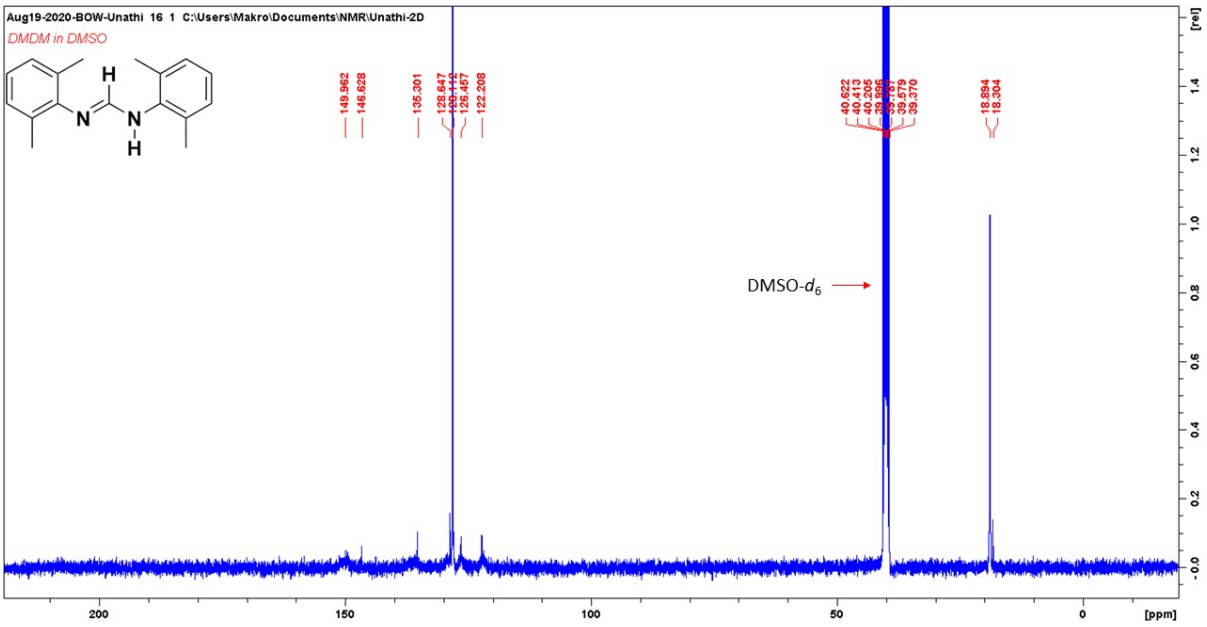

Figure S11: ^{12}C NMR spectrum of **1** in DMSO-d_6

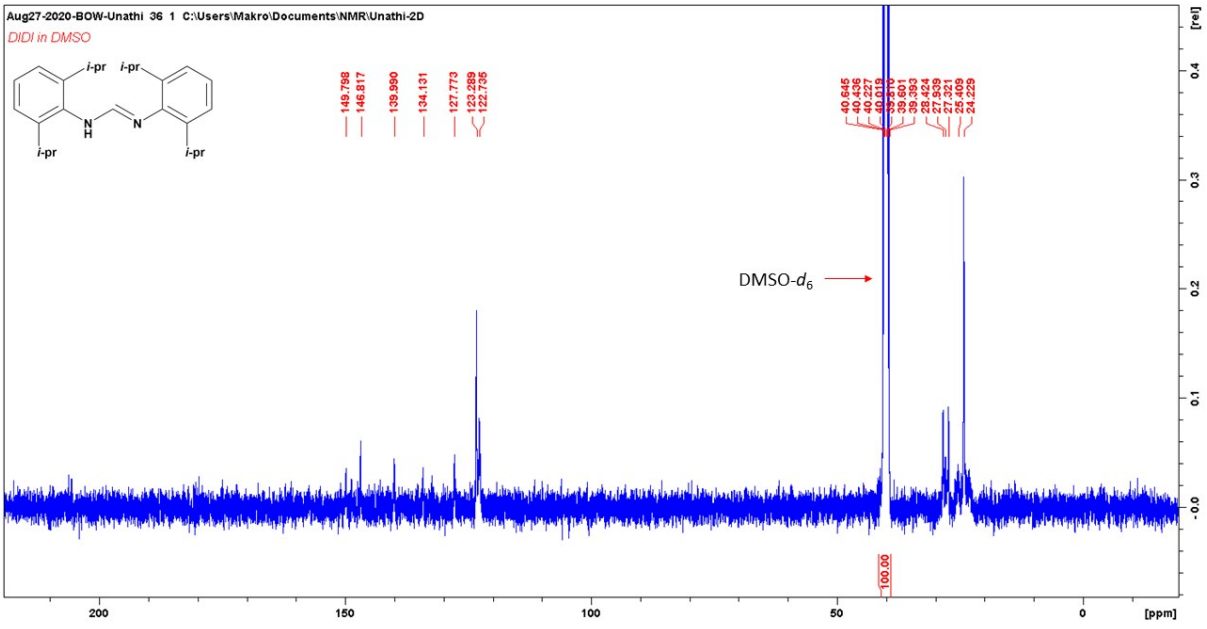

Figure S1: ^{13}C NMR spectrum of **2** in DMSO-d_6

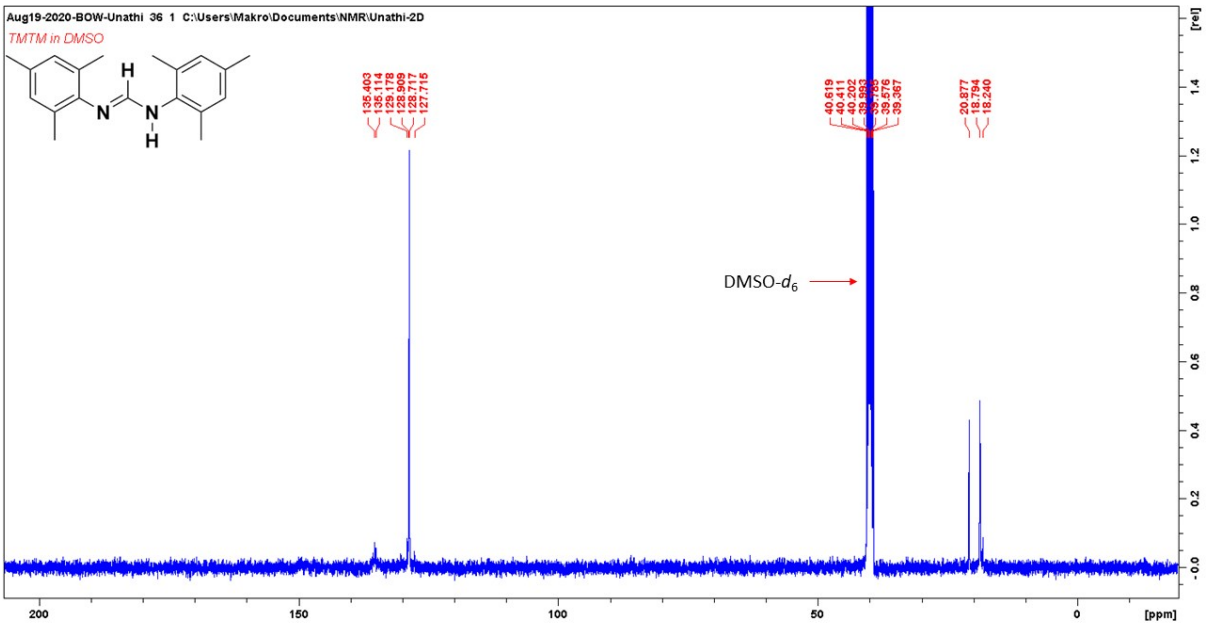

Figure S13: ^{13}C NMR spectrum of **3** in DMSO-d_6

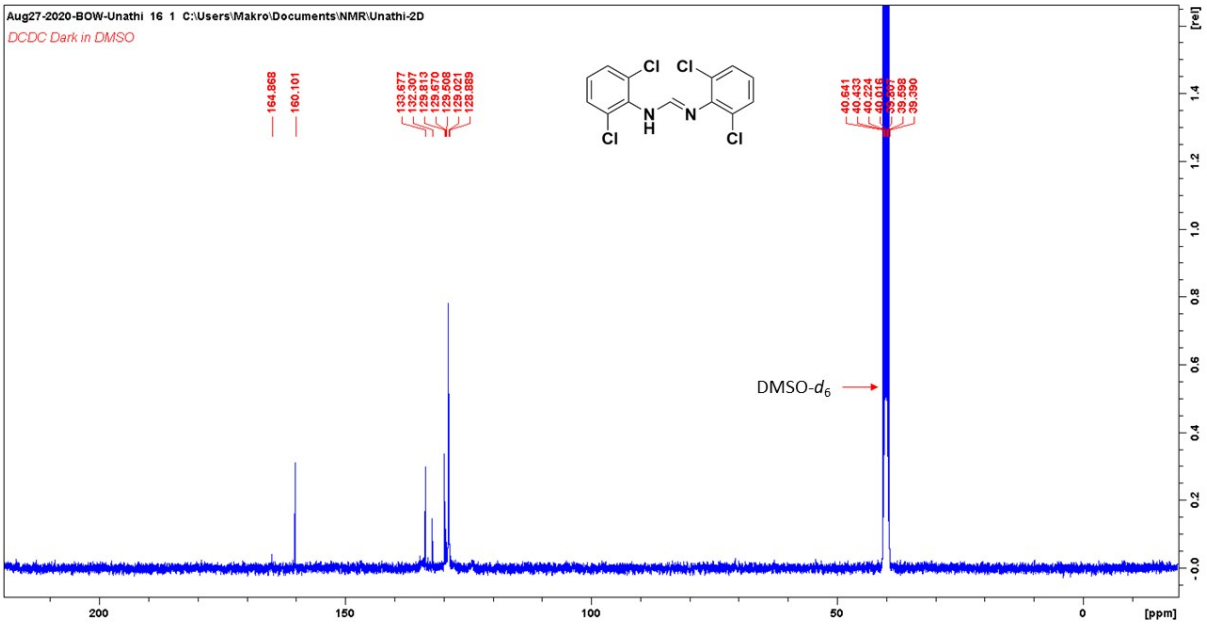

Figure S2:^{13}C NMR spectrum of **4** in DMSO-d_6

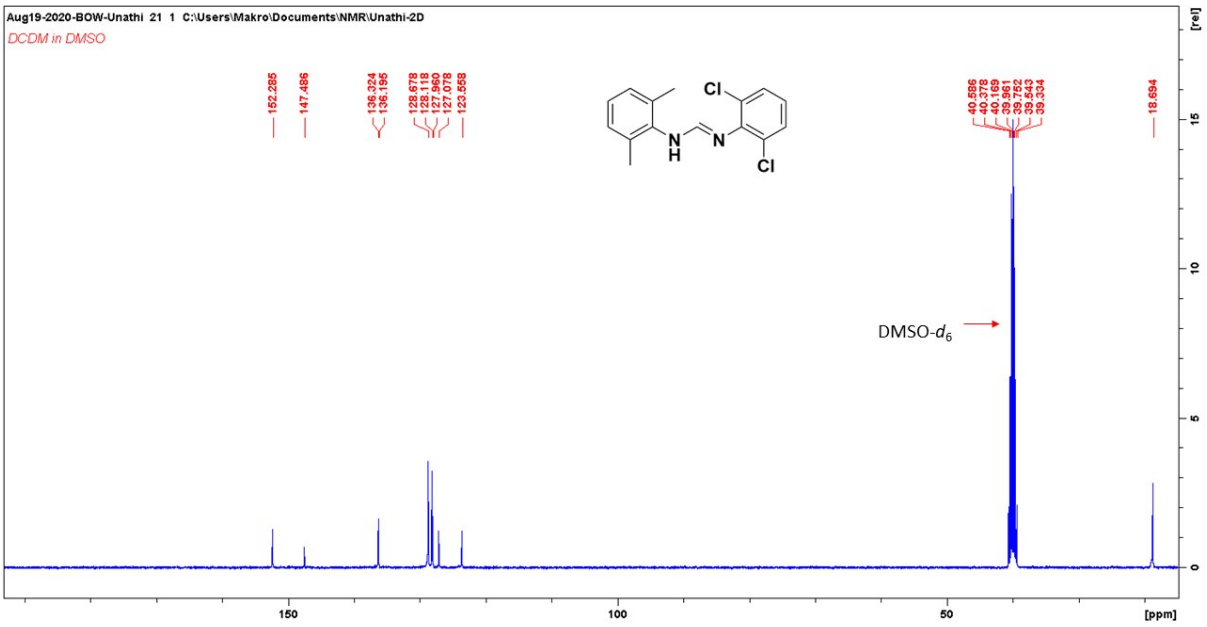

Figure S3: ^{13}C NMR spectrum of **5** in DMSO-d_6

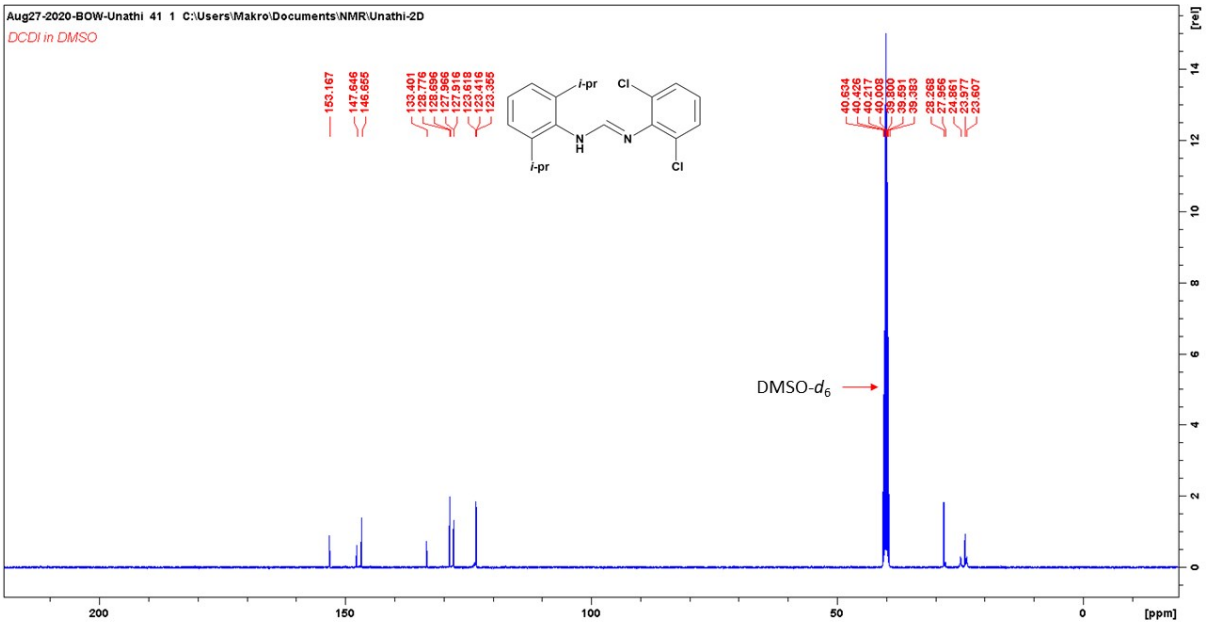

Figure S4: ^{13}C NMR spectrum of **6** in DMSO-d_6

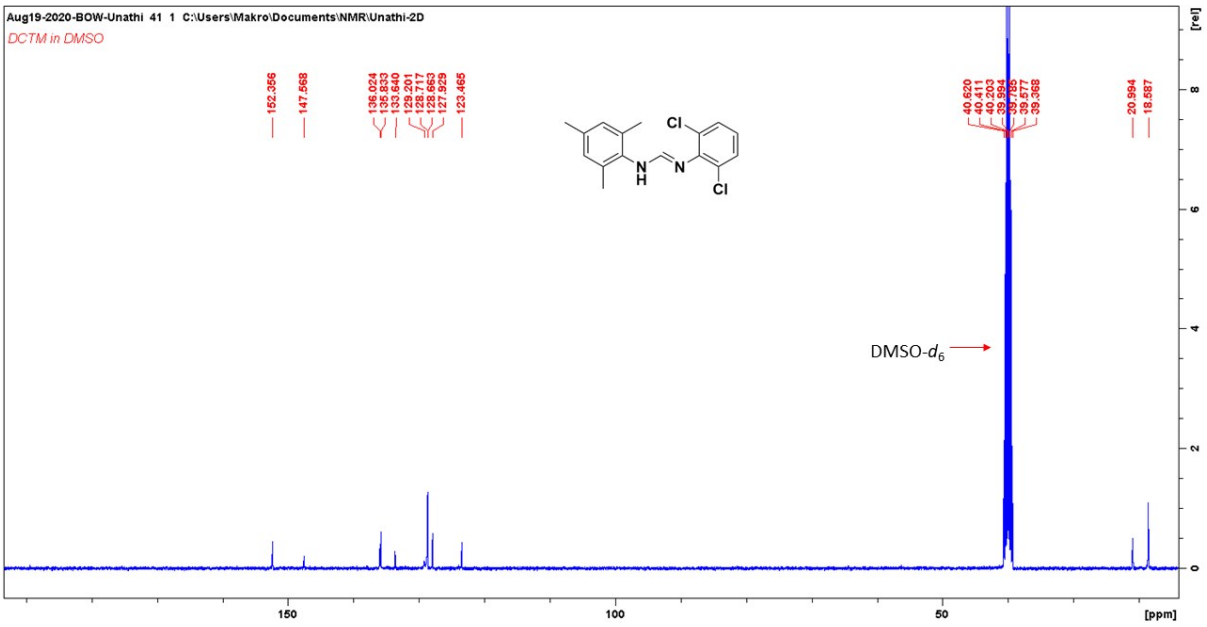

Figure S5: ^{13}C NMR spectrum of **7** in DMSO-d_6

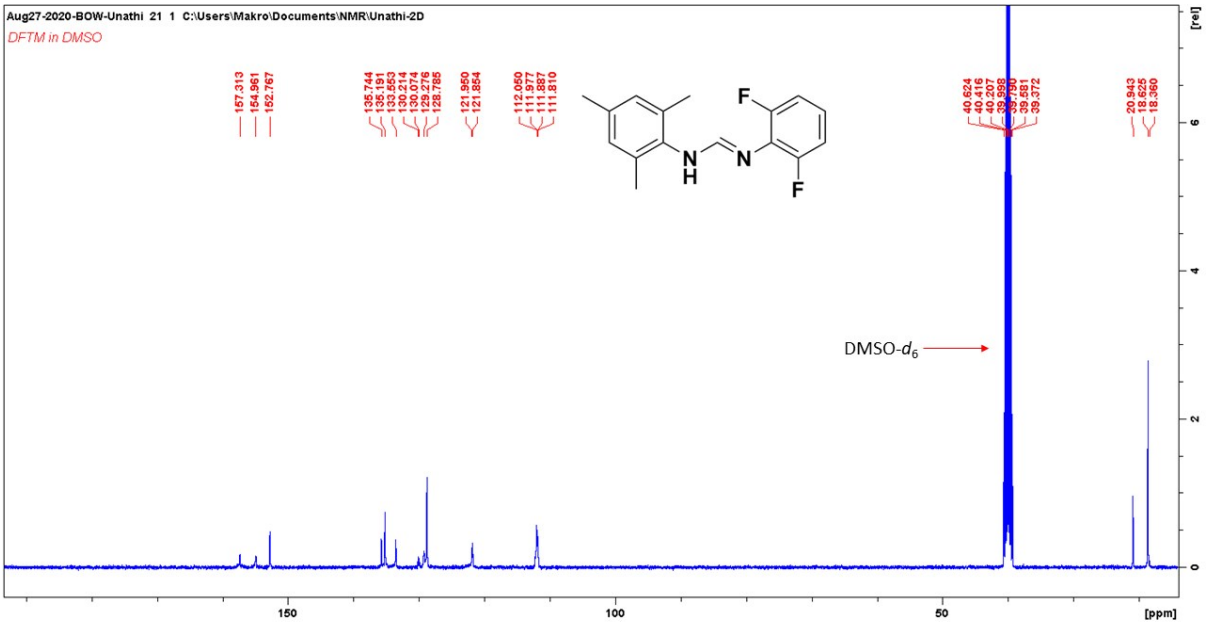

Figure S68: ^{13}C NMR spectrum of **8** in DMSO-d_6

IR spectra of compounds 1-8

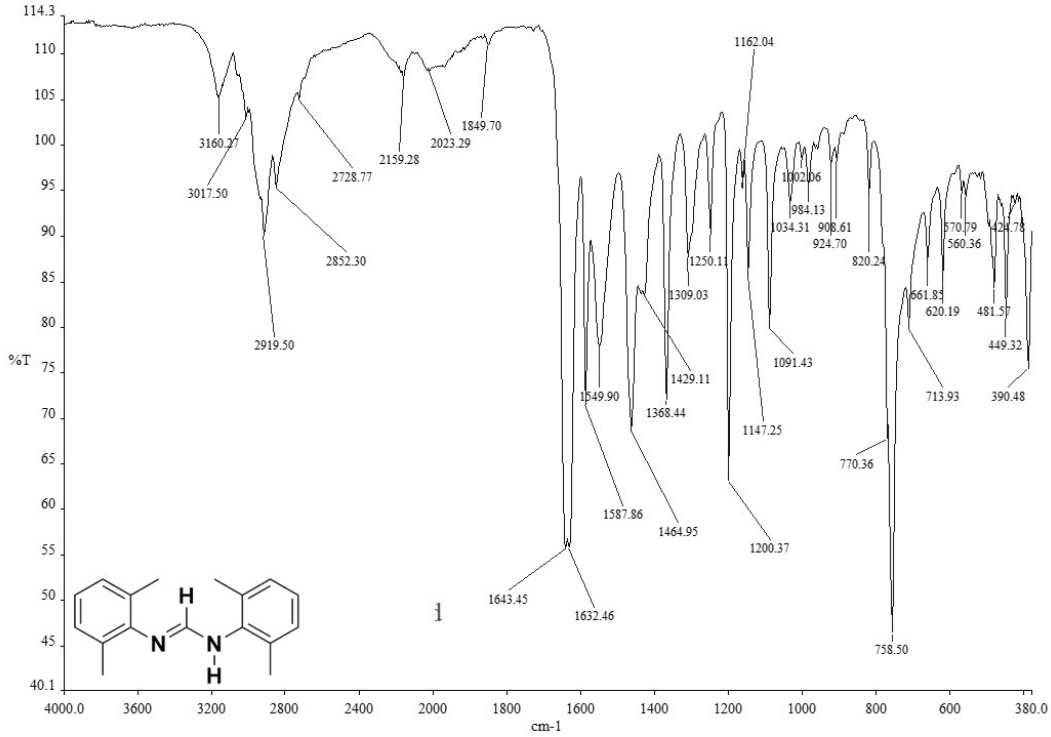

Figure S79: IR spectrum of **1**

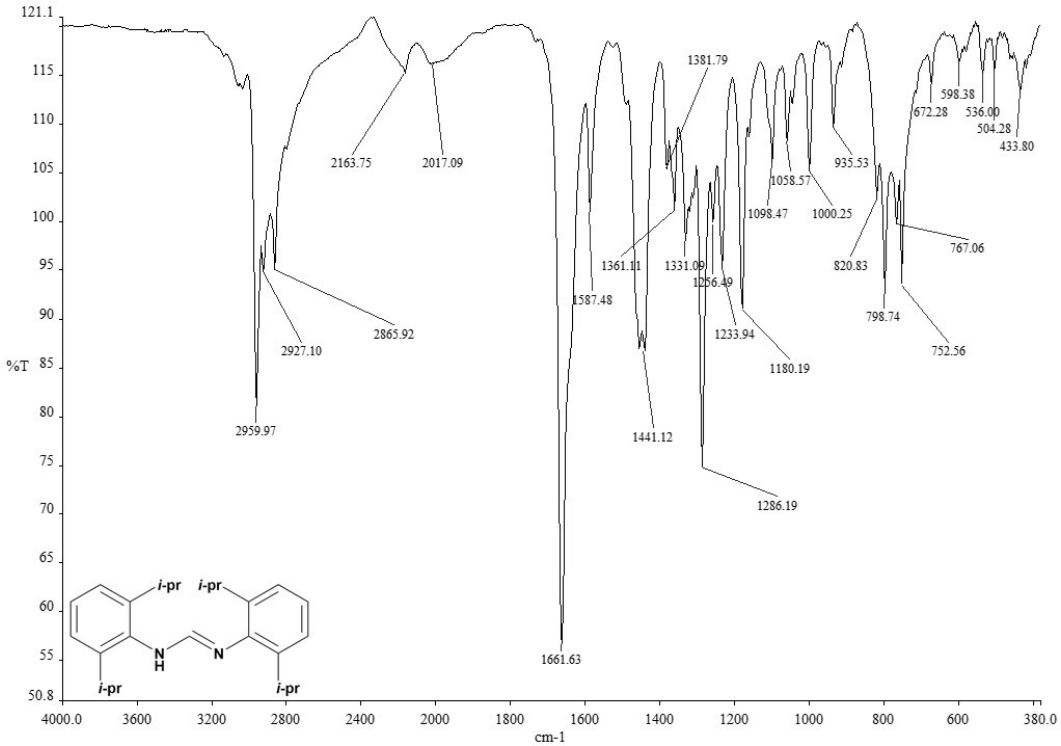

Figure S20: IR spectrum of **2**

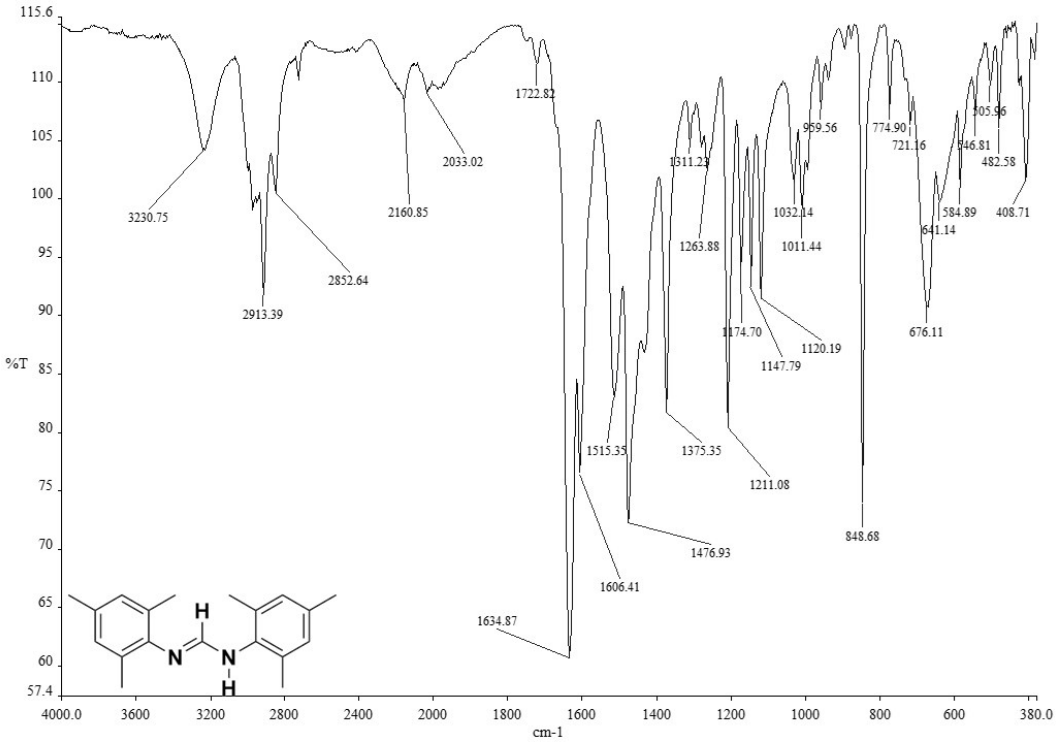

Figure S21: IR spectrum of **3**

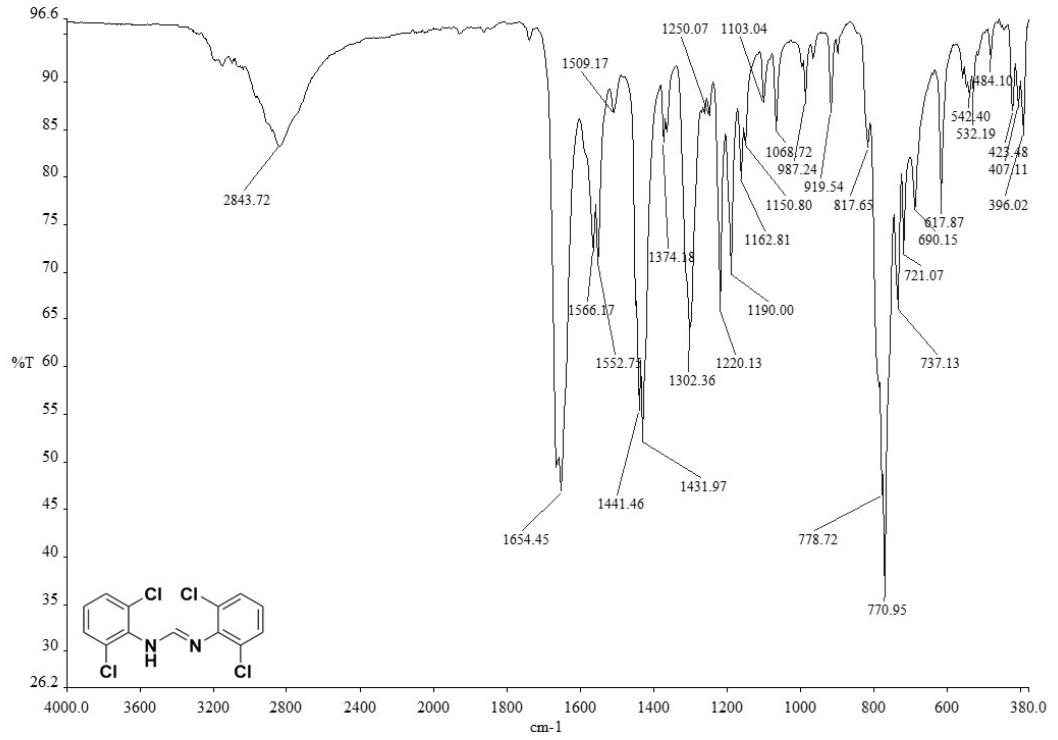

Figure S22: IR spectrum of **4**

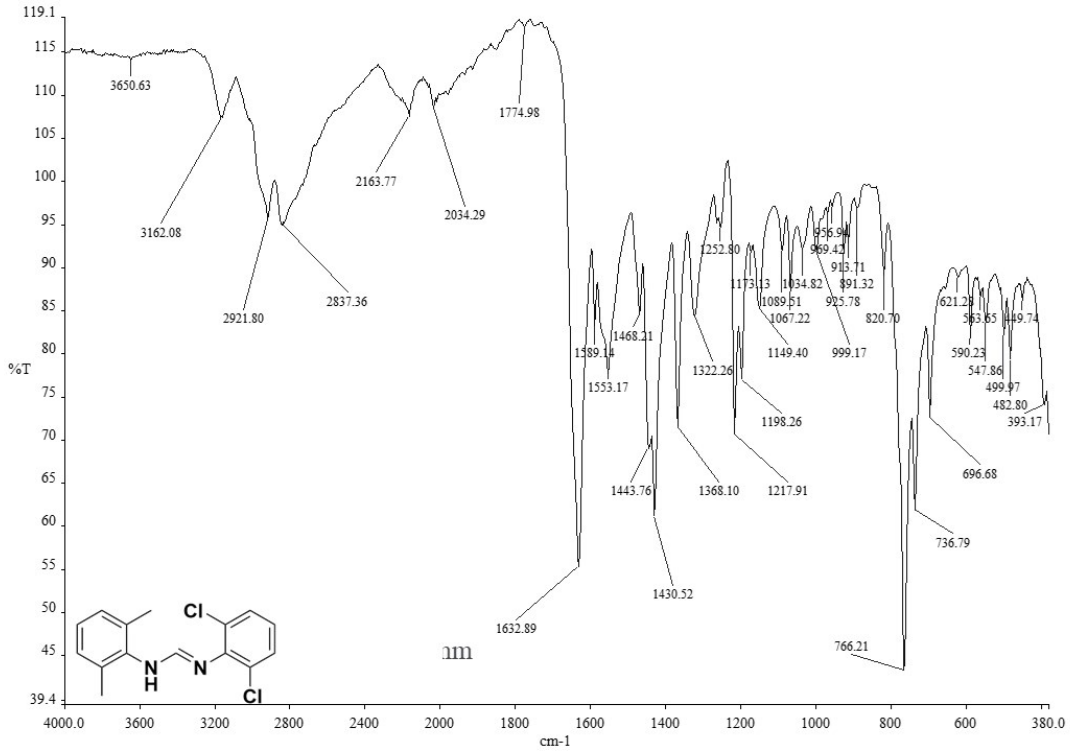

Figure S23: IR spectrum of 5

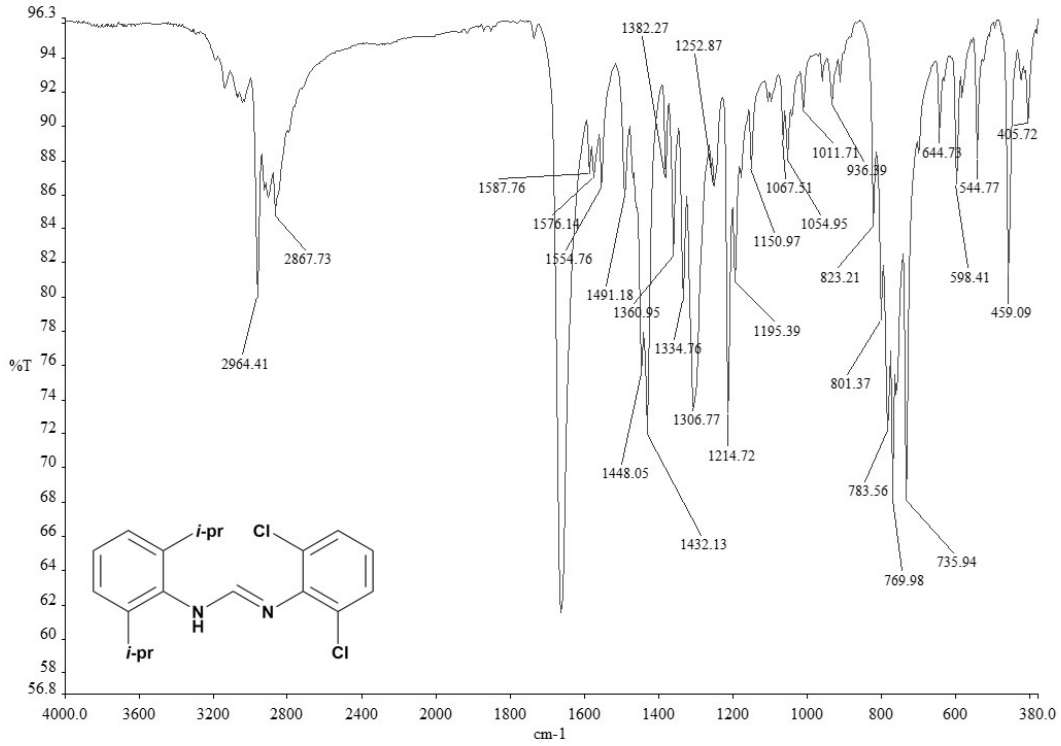

Figure S24: IR spectrum of **6**

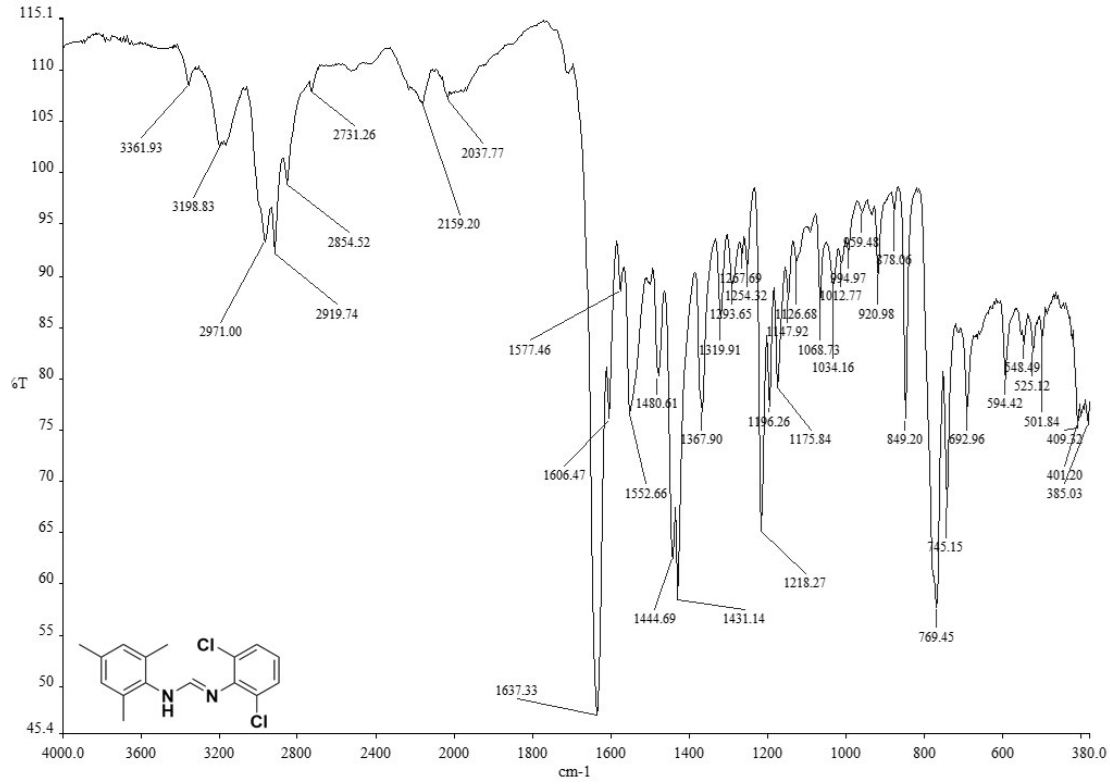

Figure S25: IR spectrum of **7**

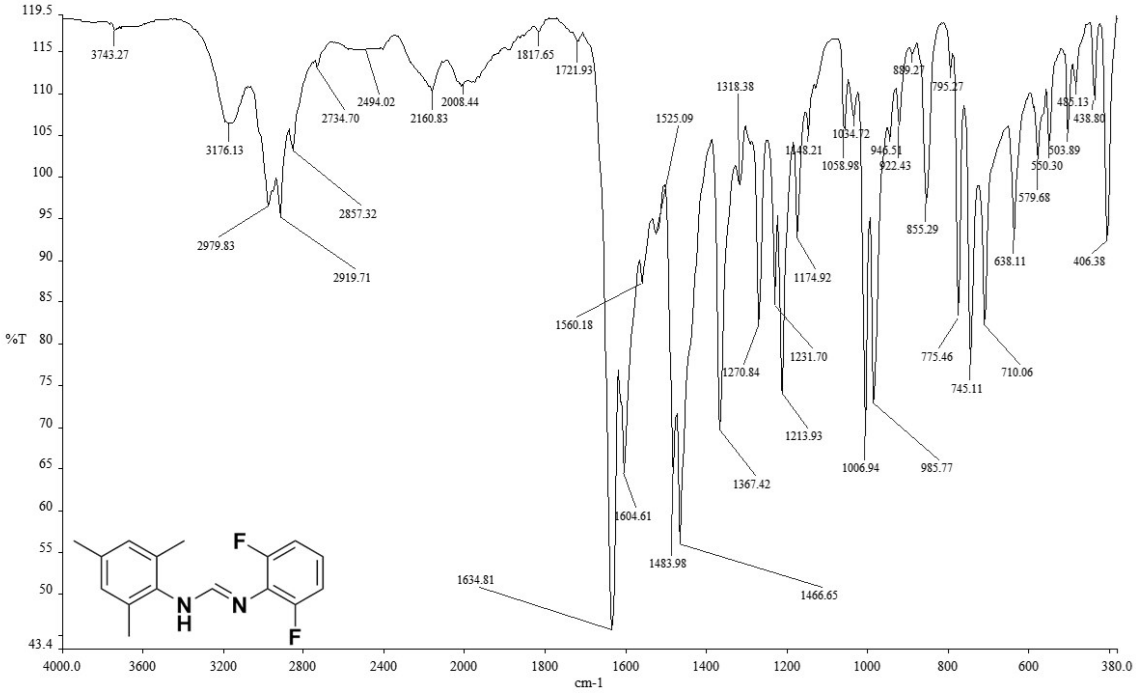

Figure S26: IR spectrum of **8**

Mass spectra of compounds 1-8

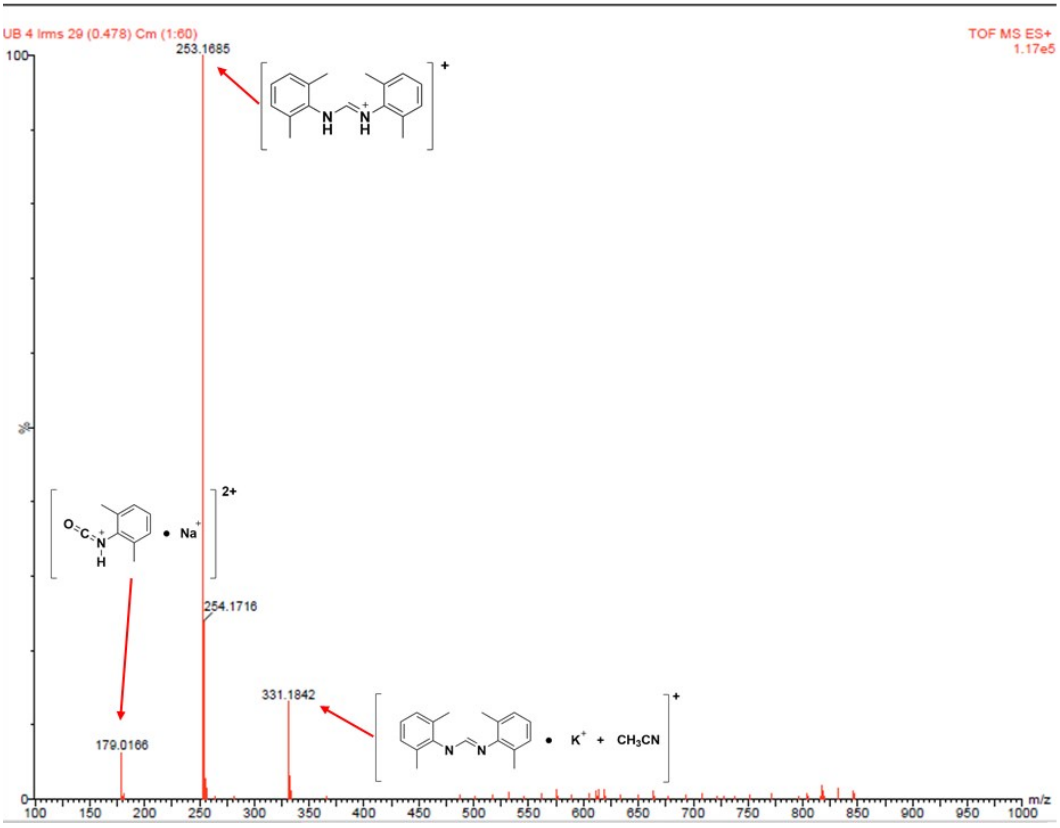

Figure S27: ESI-MS(+) spectrum of **1**

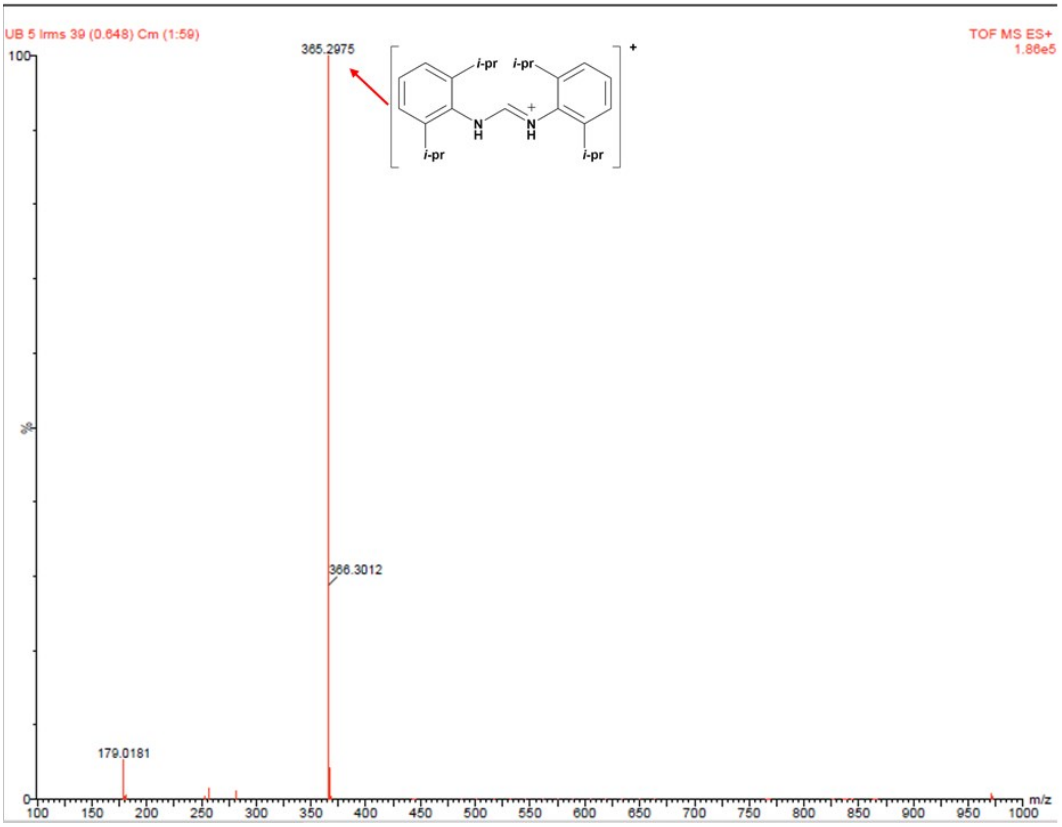

Figure S28: ESI-MS(+) spectrum of **2**

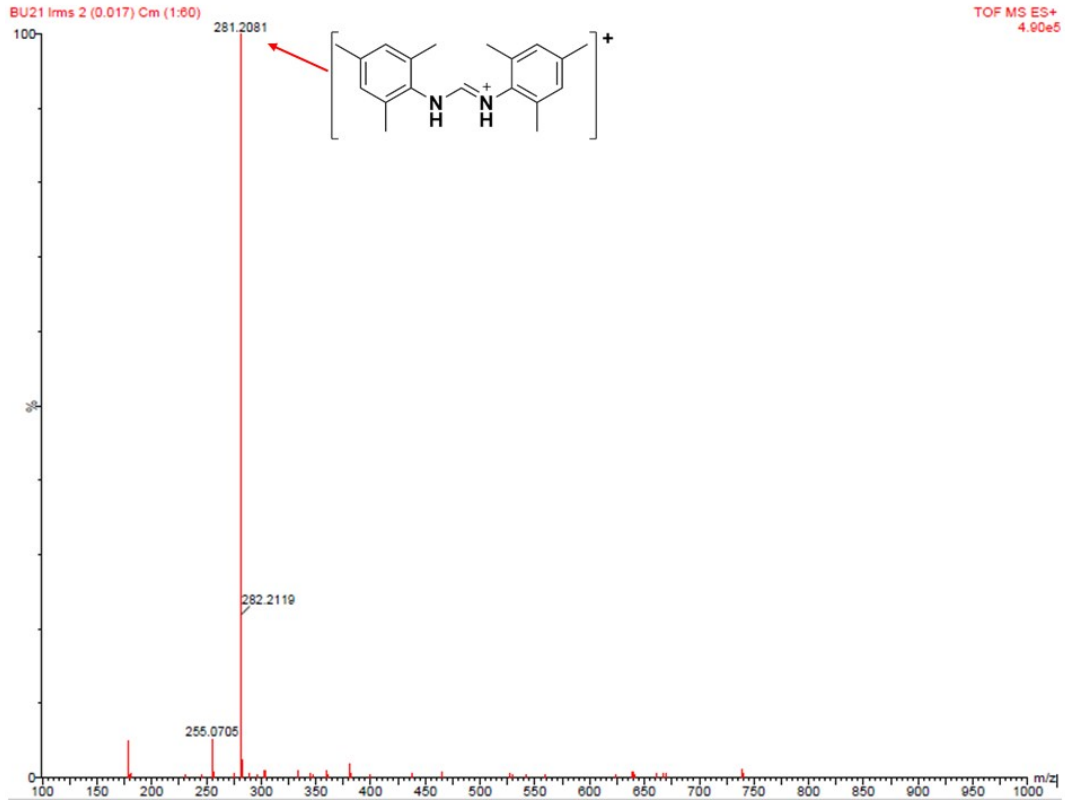

Figure S29: ESI-MS(+) spectrum of **3**

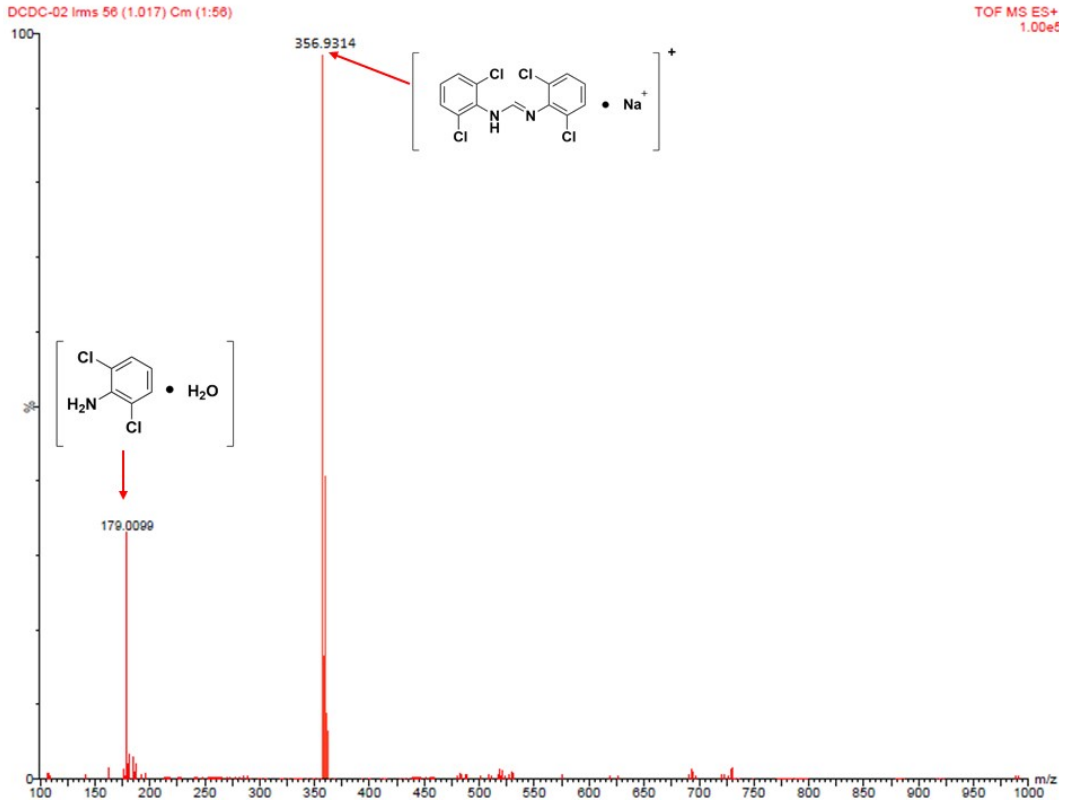

Figure S30: ESI-MS(+) spectrum of **4**

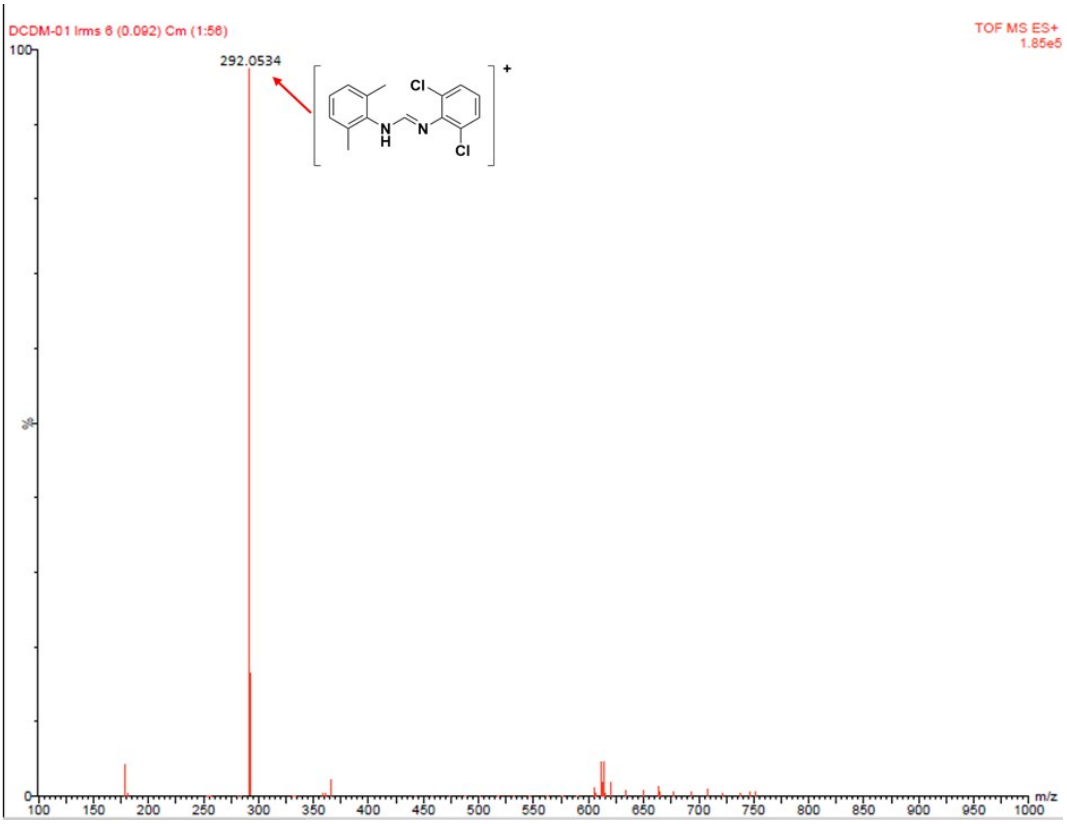

Figure S31: ESI-MS(+) spectrum of **5**

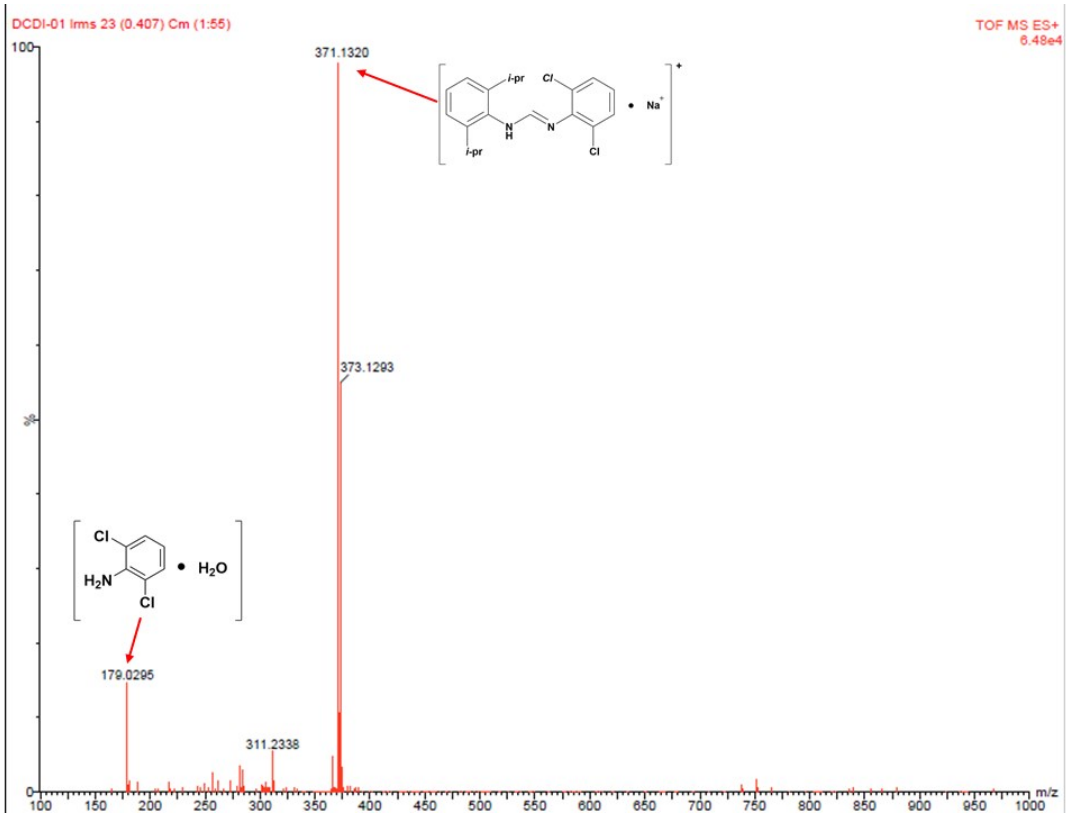

Figure S32: ESI-MS(+) spectrum of **6**

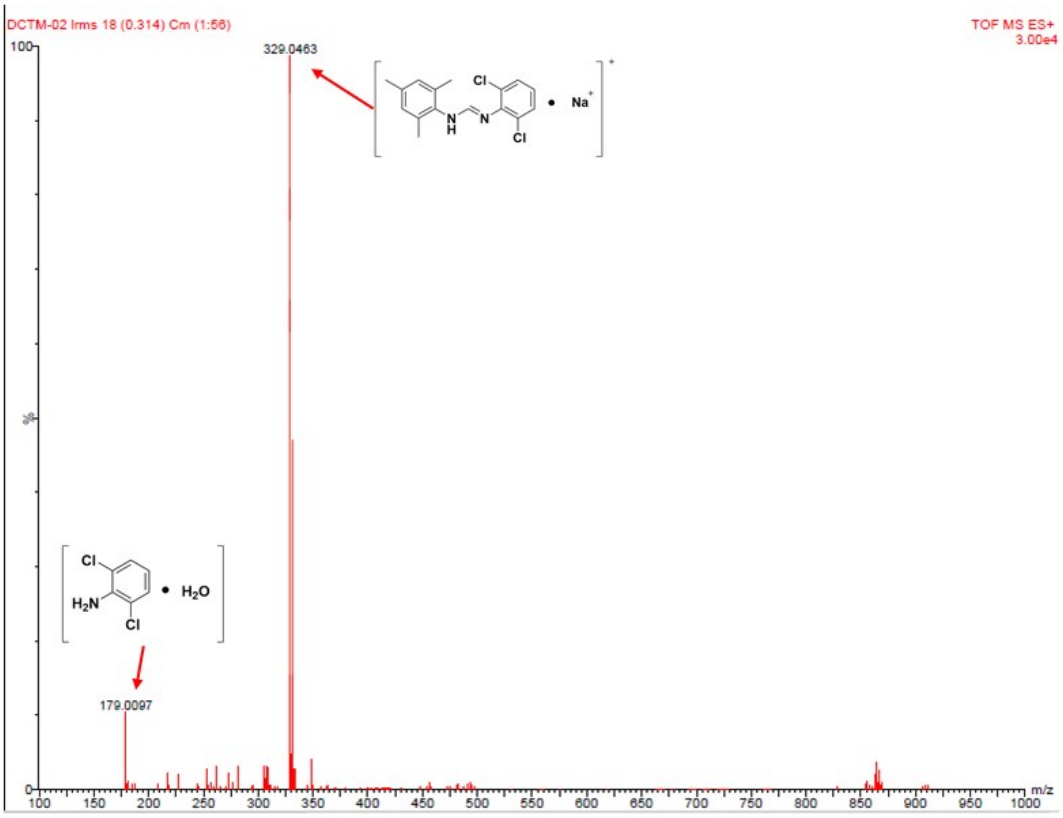

Figure S33: ESI-MS(+) spectrum of **7**

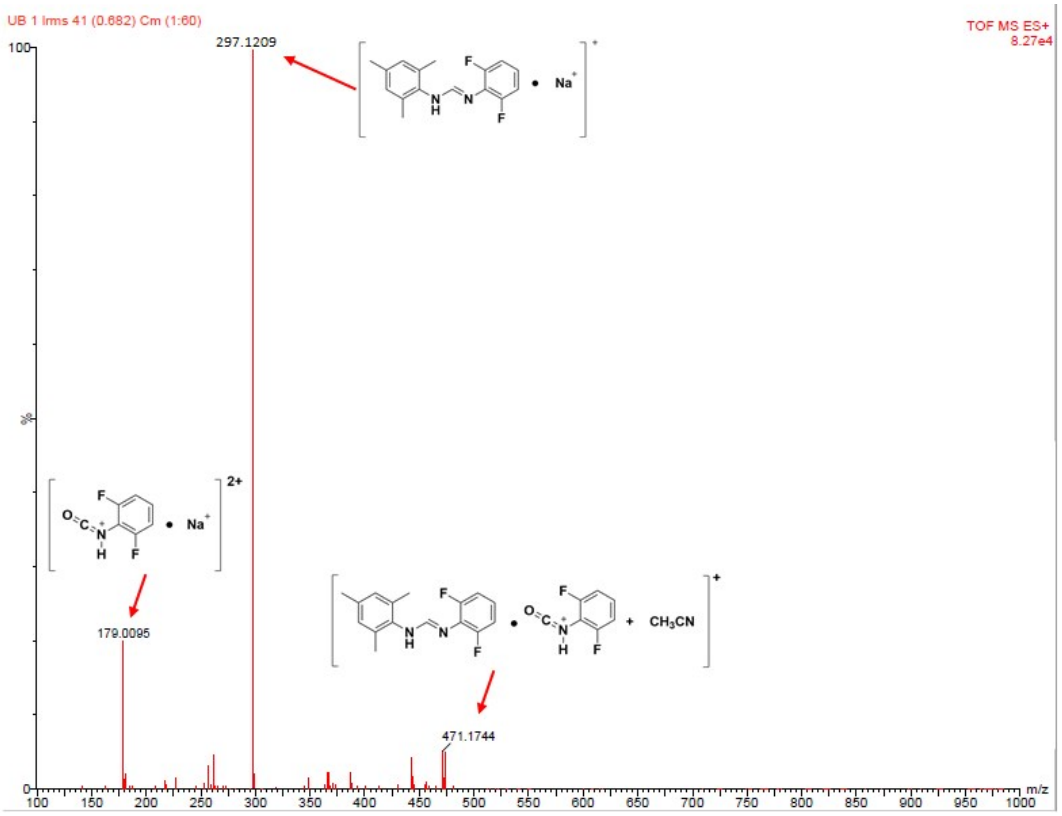

Figure S34: ESI-MS(+) spectrum of **8**

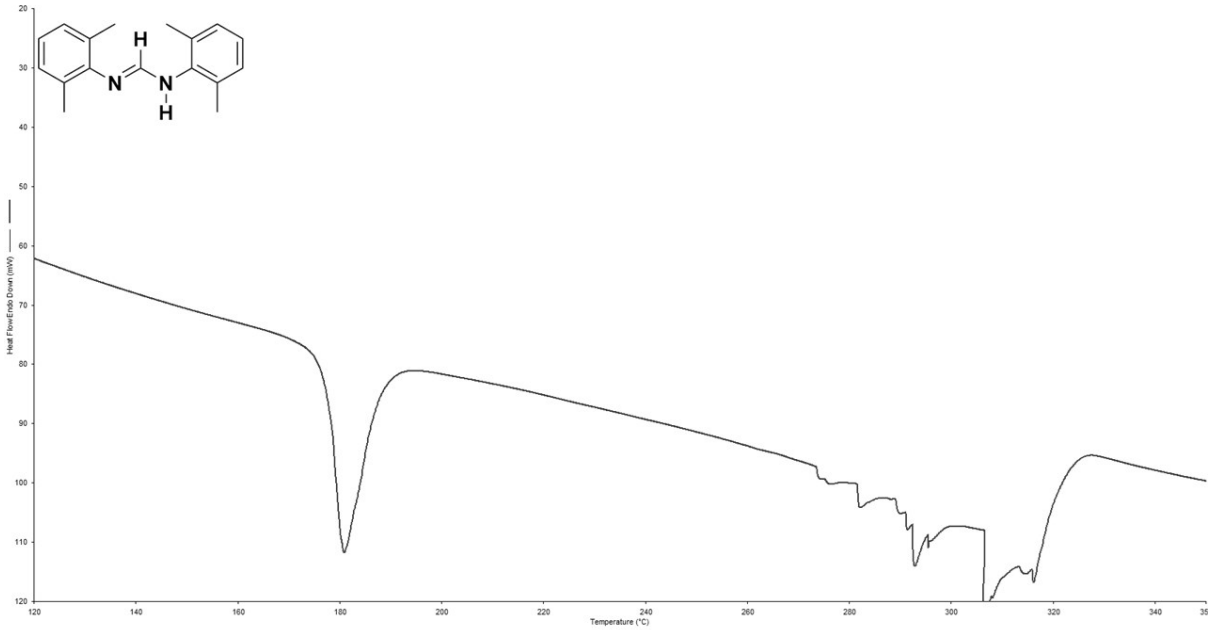

Figure S35: DSC curve of **1**

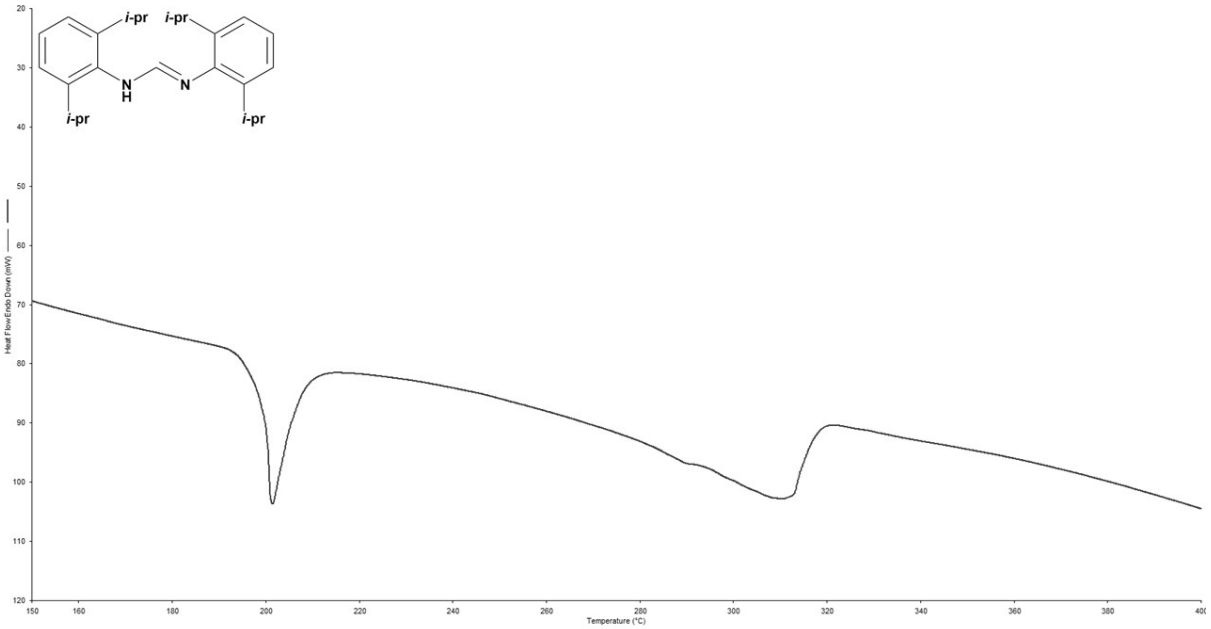

Figure S36: DSC curve of **2**

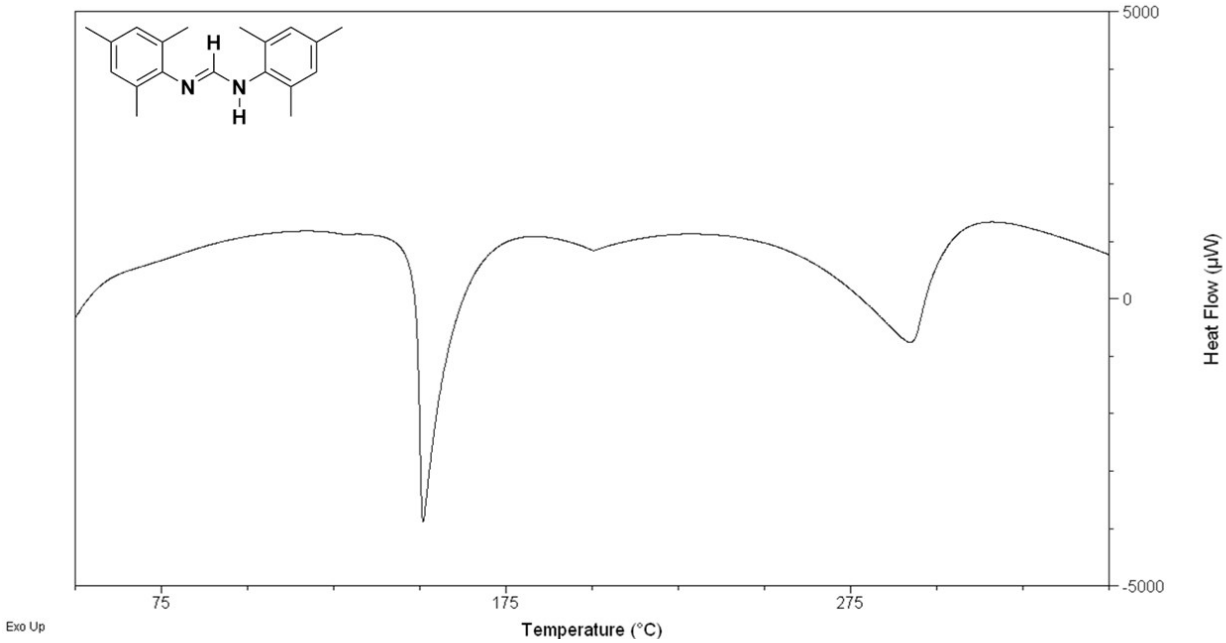

Figure S37: DSC curve of **3**

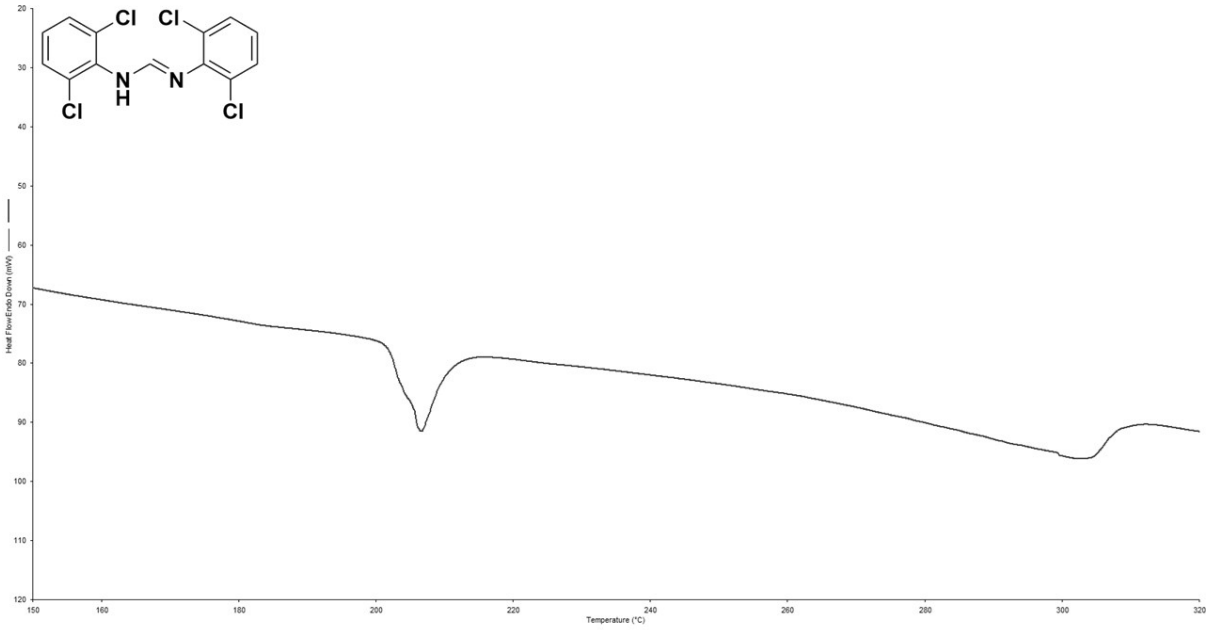

Figure S38: DSC curve of **4**

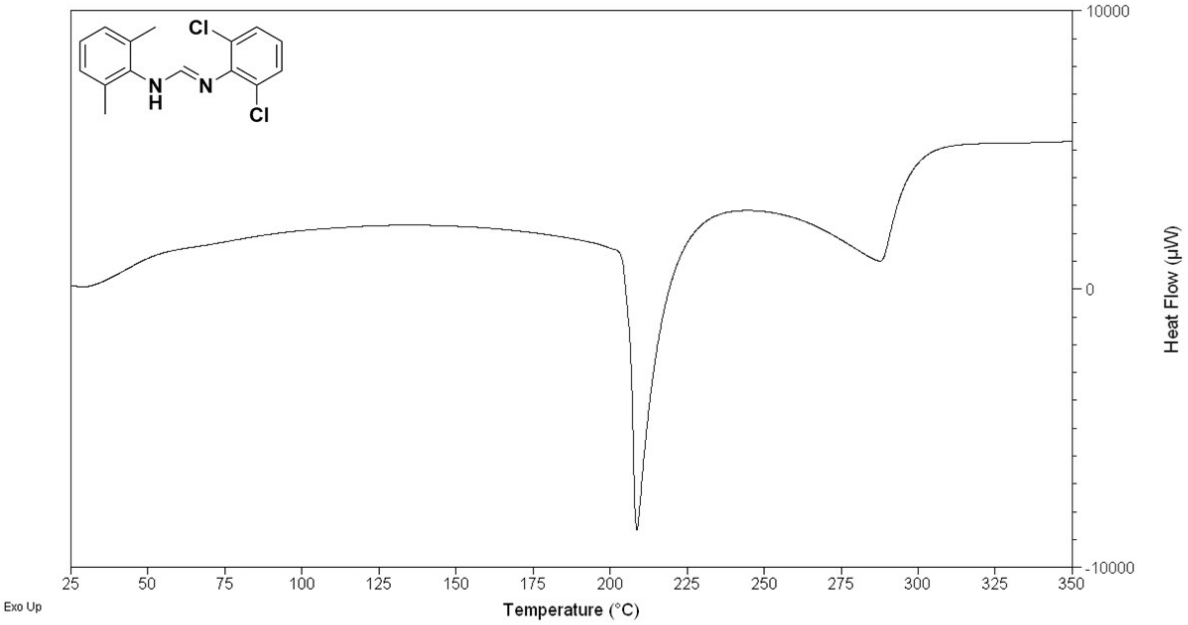

Figure S39: DSC curve of **5**

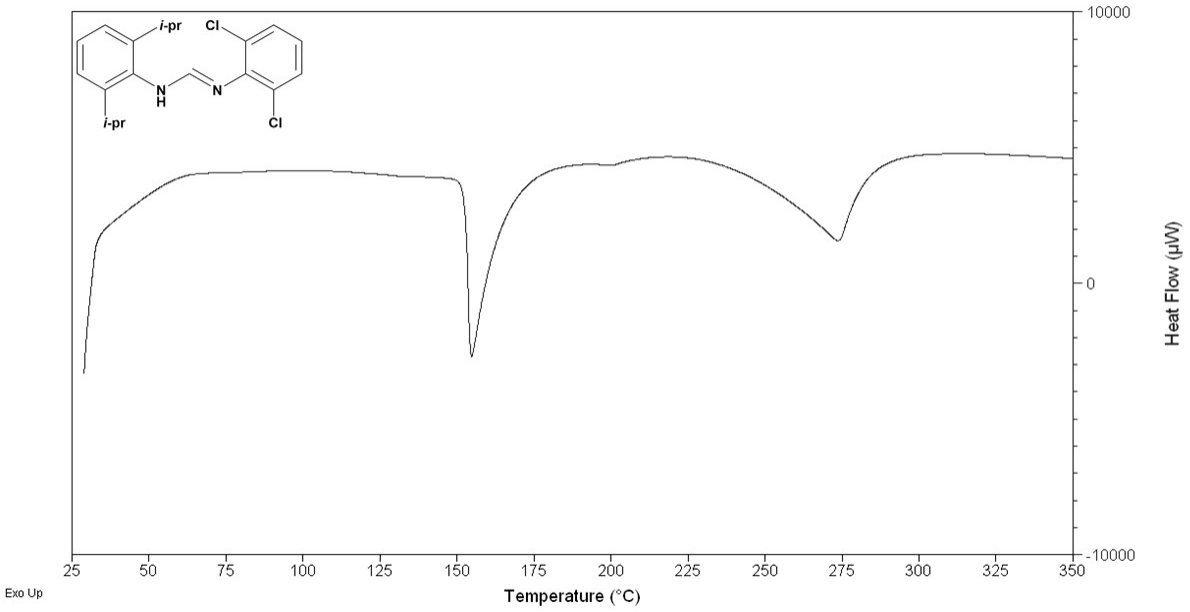

Figure S40: DSC curve of **6**

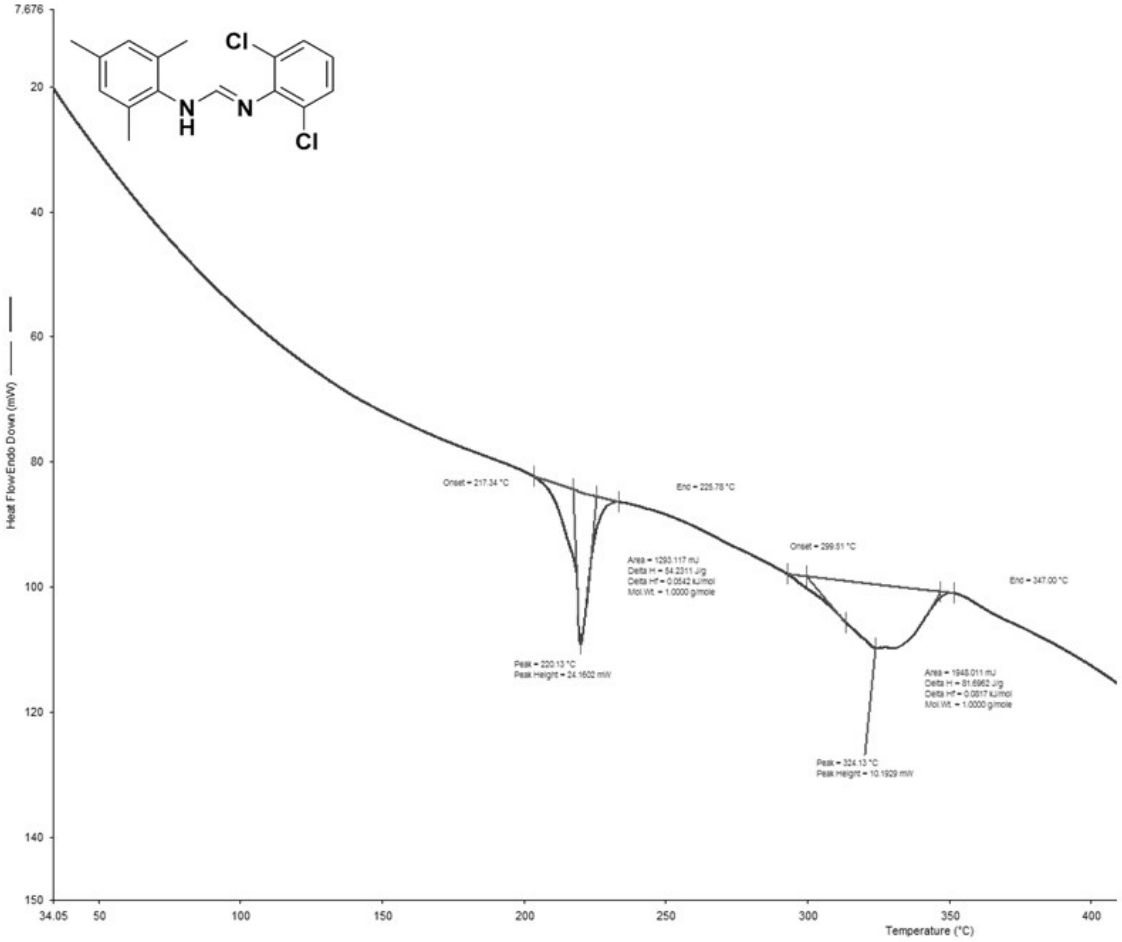

Figure S41: DSC curve of **7**

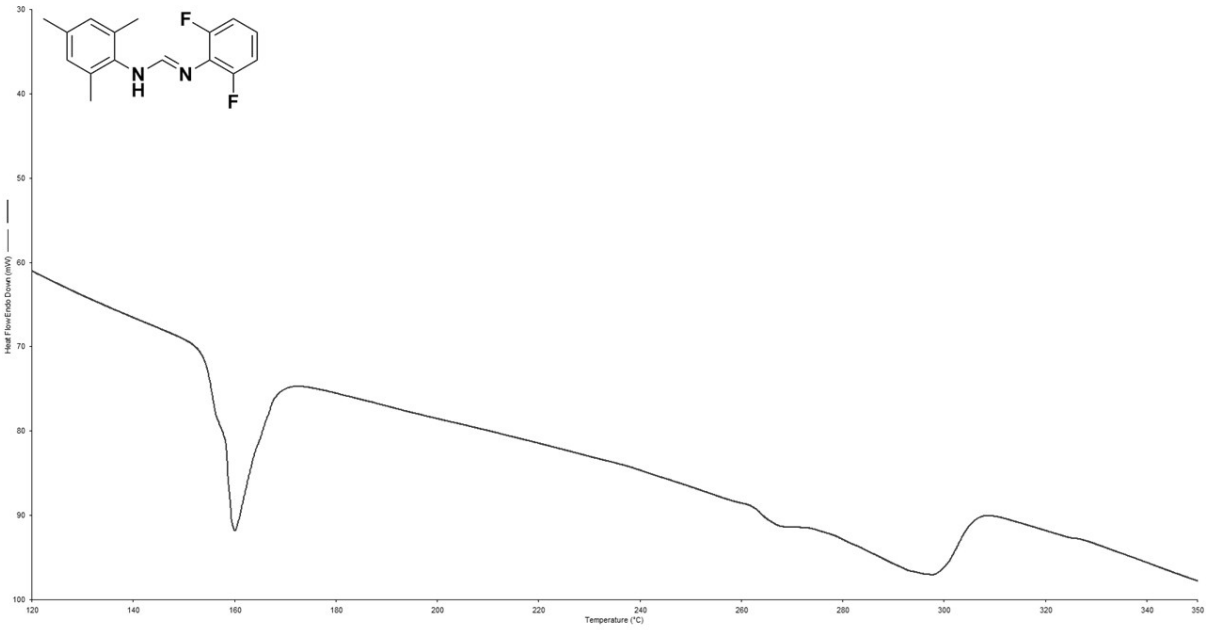

Figure S42: DSC curve of **8**