Exploration of Photophysical and Nonlinear Properties of Salicylaldehyde Based Functionalized Materials: A Facile Synthetic and DFT Approach

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Supplementary Information

Table S1. Natural bond orbital (NBO) analysis of **Compound 1** by using M06/6-311G(d,p).

Donor (*i*)	**Type**	**Acceptor (*j*)**	**Type**	**E(2) [*kcal/mol*]**	**E(j)-E(i) [a.u.]**	**F(i,j) [a.u.]**
C1-C6	π	C2-C3	π^*	21.84	0.30	0.073
C1-C6	π	C4-C5	π^*	22.24	0.30	0.073
C2-C3	π	C1-C6	π^*	22.07	0.30	0.073
C2-C3	π	C4-C5	π^*	21.37	0.30	0.072
C4-C5	π	C1-C6	π^*	21.62	0.30	0.072
C4-C5	π	C2-C3	π^*	22.86	0.30	0.075
N15-H16	σ	C17-S18	π^*	5.12	0.92	0.062
C17-S18	σ	C17-S18	σ^*	7.61	0.35	0.051
C17-S18	π	C17-S18	π^*	0.57	0.90	0.020
C17-C19	σ	N19-H20	σ^*	0.52	1.21	0.023
C22-H23	σ	N19-N21	σ^*	9.09	0.92	0.082
C24-C26	σ	C28-Cl35	σ^*	5.14	0.87	0.060
C24-C26	π	C25-C27	π^*	23.48	0.29	0.075
C24-C26	π	C28-C30	π^*	19.56	0.29	0.069
C25-C27	σ	C24-C25	σ^*	5.49	1.29	0.075
C25-C27	π	C24-C26	π^*	18.78	0.31	0.068

C25-C27	π	C28-C30	π^*	26.43	0.30	0.080
C27-C30	σ	C28-Cl35	σ^*	5.49	0.87	0.062
C28-C30	π	C24-C26	π^*	23.95	0.31	0.078
C28-C30	π	C25-C27	π^*	17.42	0.31	0.066
N15	LP(1)	C12-H14	σ^*	7.80	0.66	0.069
N15	LP(1)	C17-S18	σ^*	51.48	0.29	0.112
S18	LP(2)	N15-C17	σ^*	12.93	0.64	0.083
S18	LP(2)	C17-N19	σ^*	15.37	0.60	0.087
N19	LP(1)	C17-S18	σ^*	36.13	0.30	0.095
N19	LP(1)	N21-C22	π^*	31.04	0.33	0.093
N21	LP(1)	N19-H20	σ^*	9.46	0.74	0.076
N21	LP(1)	C22-H23	σ^*	5.52	0.78	0.059
N21	LP(1)	C22-C24	σ^*	12.34	0.84	0.092
O33	LP(1)	C25-C27	σ^*	6.38	1.20	0.078
O33	LP(2)	C25-C27	π^*	31.77	0.37	0.103
Cl35	LP(3)	C28-C30	π^*	13.0	0.34	0.065
Cl35	LP(2)	C24-C26	σ^*	0.52	0.89	0.019
C17-S18	σ^*	C17-S18	π^*	17.89	0.25	0.121
C24-C26	π^*	N21-C22	π^*	52.48	0.02	0.056

Table S2. Natural bond orbital (NBO) analysis of **Compound 2** by using M06/6-311G(d,p).

Donor (*i*)	**Type**	**Acceptor (*j*)**	**Type**	**E(2) [*kcal/mol*]**	**E(j)–E(i) [a.u.]**	**F(i,j) [a.u.]**
C1-C6	π	C2-C3	π^*	24.17	0.30	0.076
C1-C6	π	C4-C5	π^*	20.94	0.29	0.070
C2-C3	π	C1-C6	π^*	20.05	0.30	0.070
C2-C3	π	C4-C5	π^*	24.94	0.29	0.077
C3-C4	σ	C4-C5	σ^*	5.33	1.30	0.074
C3-C11	σ	C11-H13	σ^*	0.54	1.04	0.021
C4-C5	σ	C3-C4	σ^*	5.61	1.30	0.077
C4-C5	π	C1-C6	π^*	22.91	0.31	0.076
C4-C5	π	C2-C3	π^*	20.85	0.31	0.072
C4-C5	π	C4-C5	π	0.51	0.30	0.011
C16-S17	σ	C16-S17	σ^*	6.93	0.32	0.047
C21-H22	σ	N18-N20	σ^*	9.09	0.92	0.082
C23-C25	σ	C27-Cl34	σ^*	5.13	0.87	0.060
C23-C25	π	N20-C21	π^*	10.07	0.32	0.053
C23-C25	π	C24-C26	π^*	23.52	0.29	0.075
C23-C25	π	C27-C29	π^*	19.58	0.29	0.069
C24-C26	σ	C23-C24	σ^*	5.49	1.29	0.075
C24-C26	π	C23C25	π^*	18.73	0.31	0.068
C24-C26	π	C27-C29	π^*	26.37	0.30	0.080
C26-C29	σ	C27-Cl34	σ^*	5.47	0.87	0.062
C27-C29	π	C23-C25	π^*	23.93	0.31	0.078

C27-C29	π	C24-C26	π^*	17.45	0.31	0.066
N14	LP(1)	C11-H13	σ^*	7.26	0.66	0.066
N14	LP(1)	C16-S17	σ^*	57.49	0.27	0.115
N14	LP(1)	C16-S17	π^*	0.61	0.55	0.017
S17	LP(2)	N14-C16	σ^*	12.94	0.65	0.083
S17	LP(2)	C16-N18	σ^*	15.29	0.60	0.087
N18	LP(1)	C16-S17	σ^*	40.32	0.28	0.098
N18	LP(1)	N20-C21	π^*	31.14	0.33	0.093
N20	LP(1)	N18-H19	σ^*	9.49	0.74	0.076
N20	LP(1)	C21-H22	σ^*	5.52	0.78	0.059
N20	LP(1)	C21-C23	σ^*	12.35	0.84	0.092
O32	LP(1)	C24-C26	σ^*	6.37	1.20	0.078
O32	LP(2)	C24 -C26	π^*	31.69	0.37	0.103
Cl34	LP(3)	C27-C29	π^*	13.06	0.34	0.065
F35	LP(2)	C3-C4	π^*	6.32	1.01	0.071
F35	LP(2)	C4-C5	σ^*	6.23	1.01	0.071
F35	LP(3)	C4-C5	π^*	20.12	0.46	0.093
C16-S17	σ^*	C16-S17	π^*	11.72	0.28	0.104
C23-C25	π^*	N20-C21	π^*	53.91	0.02	0.056

Table S3. Natural bond orbital (NBO) analysis of **Compound 3** by using M06/6-311G(d,p).

Donor (i)	**Type**	**Acceptor (j)**	**Type**	**E(2) [*kcal/mol*]**	**E(j)-E(i) [a.u.]**	**F(i,j) [a.u.]**
C1-C6	π	C2-C3	π^*	22.84	0.32	0.076
C1-C6	π	C4-C5	π^*	20.30	0.31	0.071
C2-C3	π	C1-C6	π^*	20.56	0.29	0.070
C2-C3	π	C4-C5	π^*	23.61	0.30	0.075
C4-C5	π	C1-C6	π^*	24.58	0.29	0.077
C4-C5	π	C2-C3	π^*	20.41	0.31	0.071
N12-H13	σ	C14-S15	π^*	5.13	0.91	0.062
C14-S15	σ	C14-S15	σ^*	7.77	0.37	0.053
C14-S15	π	C14-S15	π^*	0.75	0.89	0.023
C19-H20	σ	N16-N18	σ^*	9.06	0.92	0.082
C21-C23	σ	C25-Cl32	σ^*	5.14	0.87	0.060
C21-C23	π	N18-C19	π^*	10.00	0.32	0.052
C21-C23	π	C22-C24	π^*	23.43	0.30	0.075
C21-C23	π	C25-C27	π^*	19.54	0.29	0.069
C22-C24	σ	C 21-C 22	σ^*	5.49	1.29	0.075
C22-C24	π	C 21-C23	π^*	18.80	0.31	0.068
C22-C24	π	C25-C27	π^*	26.47	0.30	0.080
C24-C27	σ	C25-Cl32	σ^*	5.47	0.87	0.062
C25-C27	π	C21-C23	π^*	23.99	0.31	0.078
C25-C27	π	C22-C24	π^*	17.44	0.31	0.066
C27-H29	σ	C24-H28	σ^*	0.80	0.93	0.024
N12	LP(1)	C3-C9	σ^*	0.65	0.73	0.021

N12	LP(1)	C9-H11	σ^*	7.85	0.66	0.069
N12	LP(1)	C14-S15	σ^*	48.81	0.30	0.111
S15	LP(2)	N 12-C14	σ^*	13.01	0.64	0.083
S15	LP(2)	C14-N16	σ^*	15.37	0.61	0.088
N16	LP(1)	C14-S15	σ^*	34.19	0.31	0.093
N16	LP(1)	N18-C19	π^*	30.86	0.33	0.093
N18	LP(1)	N16-H17	σ^*	9.45	0.74	0.076
N18	LP(1)	C19-H20	σ^*	5.50	0.78	0.059
N18	LP(1)	C19-C21	σ^*	12.32	0.85	0.092
O30	LP(1)	C 22-C24	σ^*	6.39	1.20	0.078
O30	LP(2)	C22-C24	π^*	31.80	0.37	0.103
Cl32	LP(3)	C25-C27	π^*	13.00	0.34	0.065
F35	LP(2)	C1-C6	σ^*	6.38	1.01	0.072
F35	LP(2)	C5-C6	σ^*	6.41	1.01	0.072
F35	LP(3)	C1-C6	π^*	20.25	0.46	0.093
C1-C6	π^*	C2-C3	π^*	281.67	0.01	0.084
C14-S15	σ^*	C14-S15	π^*	21.21	0.23	0.128
C21-C23	π^*	N18-C19	π^*	53.40	0.02	0.056

Table S4. Natural bond orbital (NBO) analysis of **Compound 4** by using M06/6-311G(d,p).

Donor (*i*)	**Type**	**Acceptor (*j*)**	**Type**	**E(2) [*kcal/mol*]**	**E(j)–E(i) [a.u.]**	**F(i,j) [a.u.]**
C1-C2	π	C3-C4	π^*	21.80	0.31	0.073
C1-C2	π	C5-C6	π^*	22.80	0.30	0.O74
C2-C3	σ	C3-C4	σ^*	5.27	1.30	0.074
C2-H7	σ	C3-C4	σ^*	5.08	1.11	0.067
C3-C4	π	C1-C2	π^*	23.80	0.29	0.075
C3-C4	π	C5-C6	π^*	21.54	0.29	0.072
C5-C6	π	C1-C2	π^*	22.05	0.30	0.072
C5-C6	π	C3-C4	π^*	23.44	0.30	0.076
N19-C20	π	N19-C20	π^*	1.01	0.39	0.018
C20-H21	σ	N1-N19	σ^*	8.85	0.92	0.081
C20-C22	σ	C20-H21	σ^*	0.58	1.08	0.022
C22-C24	σ	C26-Cl33	σ^*	5.19	0.87	0.060
C22-C24	π	N19-C20	π^*	9.53	0.32	0.051
C23-C25	σ	C22-C23	σ^*	5.54	1.29	0.076
C25-C28	σ	C26-Cl33	σ^*	5.46	0.87	0.062
N13	LP(1)	C10-H12	σ^*	7.59	0.66	0.068
N13	LP(1)	C15-S16	σ^*	69.80	0.23	0.118
S16	LP(2)	C3-C10	σ^*	0.53	0.63	0.017
S16	LP(2)	N 3-C15	σ^*	12.56	0.65	0.082
S16	LP(2)	C15-N17	σ^*	14.97	0.61	0.087
N17	LP(1)	C15-S16	σ^*	56.61	0.25	0.110
N17	LP(1)	N19-C20	π^*	29.39	0.33	0.091
N19	LP(1)	N17-H18	σ^*	9.12	0.74	0.074
N19	LP(1)	C20-H21	σ^*	5.30	0.78	0.058

N19	LP(1)	C 20-C22	σ^*	12.04	0.85	0.091
C23	LP(1)	C22-C24	π^*	64.69	0.15	0.109
C23	LP(1)	C25-C28	π^*	65.08	0.15	0.110
C26	LP(1)	C22-C24	π^*	70.47	0.17	0.115
C26	LP(1)	C 25-C28	π^*	69.66	0.17	0.115
O31	LP(1)	C23-C25	σ^*	6.43	1.19	0.078
C22-C24	π^*	N19-C20	π^*	47.60	0.02	0.054

Table S5. Natural bond orbital (NBO) analysis of **Compound 5** by using M06/6-311G(d,p).

Donor (*i*)	**Type**	**Acceptor (*j*)**	**Type**	**E(2) [*kcal/mol*]**	**E(j)–E(i) [a.u.]**	**F(i,j) [a.u.]**
C1-C2	π	C3-C4	π^*	24.60	0.30	0.077
C1- C2	π	C5-C6	π^*	21.07	0.30	0.071
C1-H34	σ	C1-C2	σ^*	0.69	1.11	0.025
C3-C4	π	C1-C2	π^*	21.44	0.30	0.071
C 3-C4	π	C5 -C6	π^*	24.29	0.30	0.077
C5-C6	π	C1-C2	π^*	24.70	0.29	0.076
C5-C6	π	C3-C4	π^*	21.95	0.29	0.072
N12-H13	σ	C14-S15	π^*	5.11	0.93	0.063
N18-C19	π	N18-C19	π^*	1.12	0.39	0.019
C14-S15	σ	C14-S15	σ^*	7.39	0.34	0.049
C21-C23	σ	C25-Cl32	σ^*	5.16	0.87	0.060
C21-C23	π	N18-C19	π^*	9.75	0.32	0.052
C21-C23	π	C22-C24	π^*	23.47	0.29	0.075
C21-C23	π	C25-C27	π^*	19.61	0.29	0.069
C22-C24	σ	C21-C22	σ^*	5.50	1.29	0.075
C22-C24	π	C21-C23	π^*	18.83	0.31	0.068
C22-C24	π	C25-C27	π^*	26.43	0.30	0.080
C24-C27	σ	C25-Cl32	σ^*	5.50	0.87	0.062
C25-C27	π	C21-C23	π^*	23.93	0.31	0.078
C25-C27	π	C22-C24	π^*	17.40	0.31	0.066
N12	LP(1)	C 9-H11	σ^*	7.87	0.66	0.069
N12	LP(1)	C14 -S15	σ^*	54.13	0.28	0.114
S15	LP(1)	C14-S15	σ^*	0.79	0.69	0.023
S15	LP(2)	N12-C14	σ^*	12.89	0.64	0.083
S15	LP(2)	C14-N16	σ^*	15.35	0.60	0.087
N16	LP(1)	C14-S15	σ^*	38.20	0.29	0.096
N16	LP(1)	N18-C19	π^*	31.23	0.33	0.093
N18	LP(1)	N16-H17	σ^*	9.49	0.74	0.076
N18	LP(1)	C19-H 20	σ^*	5.48	0.78	0.059
N18	LP(1)	C19-C21	σ^*	12.29	0.84	0.092
O30	LP(1)	C22-C24	σ^*	6.39	1.19	0.078
O30	LP(2)	C22-C24	π^*	31.80	0.37	0.103
Cl32	LP(2)	C21-C23	σ^*	0.52	0.89	0.019
Cl32	LP(3)	C25-C27	π^*	12.94	0.34	0.065
C14-S15	σ^*	C 14-S15	π^*	15.0	0.26	0.114

C21-C23	π^*	N18-C19	π^*	50.46	0.02	0.056

Table S6. Natural bond orbital (NBO) analysis of **Compound 6** by using M06/6-311G(d,p).

Donor (i)	**Type**	**Acceptor (j)**	**Type**	**E(2) [*kcal/mol*]**	**E(j)–E(i) [a.u.]**	**F(i,j) [a.u.]**
C1-C6	π	C2-C3	π^*	23.51	0.30	0.075
C1-C6	π	C4-C5	π^*	21.01	0.30	0.071
C1-H7	σ	C2-H8	σ^*	0.76	0.93	0.024
C2-C3	π	C1-C6	π^*	20.46	0.31	0.071
C2-C3	π	C4-C5	π^*	21.87	0.30	0.073
C4-C5	π	C1-C6	π^*	22.45	0.31	0.075
C4-C5	π	C2-C3	π^*	21.58	0.30	0.073
N14-H15	σ	C16-S17	π^*	5.10	0.93	0.062
N20-C21	π	N20-C21	π^*	1.13	0.39	0.019
C16-S17	σ	C16-S17	σ^*	7.36	0.33	0.049
C21-H22	σ	N18-N20	σ^*	9.08	0.92	0.082
C23-C25	σ	C27-Cl34	σ^*	5.14	0.87	0.060
C23-C25	π	N 20-C21	π^*	10.02	0.32	0.053
C23-C25	π	C24-C26	π^*	23.41	0.29	0.075
C23-C25	π	C27-C29	π^*	19.62	0.29	0.069
C24-C26	σ	C23-C24	σ^*	5.48	1.29	0.075
C24-C26	π	C23-C25	π^*	18.77	0.31	0.068
C24-C26	π	C27-C29	π^*	26.42	0.30	0.080
C26-C29	σ	C27-Cl34	σ^*	5.48	0.87	0.062
C27-C29	π	C23-C25	π^*	23.87	0.31	0.078
C27-C29	π	C24-C26	π^*	17.43	0.31	0.066
N14	LP(1)	C3-C11	σ^*	0.52	0.73	0.019
N14	LP(1)	C11-H13	σ^*	7.69	0.66	0.068
N14	LP(1)	C16-S17	σ^*	54.80	0.28	0.114
S17	LP(2)	N14-C16	σ^*	12.88	0.65	0.083
S17	LP(2)	C16-N18	σ^*	15.42	0.60	0.087
N18	LP(1)	C16-S17	σ^*	39.43	0.29	0.098
N18	LP(1)	N20-C21	π^*	31.36	0.33	0.094
N20	LP(1)	N18-H19	σ^*	9.50	0.74	0.076
N20	LP(1)	C21-H22	σ^*	5.55	0.78	0.059
N20	LP(1)	C21-C23	σ^*	12.40	0.84	0.092
O32	LP(1)	C24-C26	σ^*	6.38	1.20	0.078
O32	LP(2)	C24-26	π^*	31.80	0.37	0.103
Cl34	LP(3)	C27-C29	π^*	12.98	0.34	0.065
C16-S17	σ^*	C16- S17	π^*	14.41	0.27	0.112
C23-C25	π^*	N20-C21	π^*	53.22	0.02	0.057

E(2) means energy of hyper conjugative interaction (stabilization energy in kcal/mol); Energy difference between donor & acceptor *i* & *j* NBO orbitals.; F(*i*,*j*) is the Fock matrix element between *i* & *j* NBO orbitals.

Table S7. Computed transition energy (*eV*), maximum absorption wavelengths (λ_{max}/*nm*), oscillator strengths (*f*), and transition studies compounds.

Comp	EXP λ(*nm*)	DFT λ(*nm*)	*E* (*eV*)	*f*	MO transitions
1	241	390	3.1803	0.001	H→L (86%) H→L+1 (3%), H→L+4 (9%)
		322	3.8499	0.2131	H-1→L (95%) H-2→L (3%)
		309	4.0101	0.0013	H→L (13%), H→L+1 (38%), H→L+4 (33%) H→L+2 (6%), H→L+3 (3%), H→L+7 (2%), H→L+8 (2%)
		286	4.3299	0.0846	H-2→L (78%) H-7→L+1 (2%), H-3→L (6%), H-2→L+1 (2%), H-1→L (3%), H-1→L+1 (4%)
		278	4.4598	0.0145	H→L+1 (51%), H→L+2 (25%), H→L+4 (16%) H→L+7 (2%)
		272	4.5583	0.0819	H-3→L (64%), H-2→L (10%) H-6→L (4%), H-4→L (5%), H-2→L+1 (3%), H-1→L+1 (7%)
2	240	388	3.1962	0.0005	H→L (86%) H→L+1 (2%), H→L+4 (8%)
		323	3.8421	0.2103	H-1→L (94%) H-2→L (3%)
		307	4.0376	0.0009	H→L (12%), H→L+1 (27%), H→L+2 (13%), H→L+4 (31%) H→L+3 (8%), H→L+5 (2%), H→L+9 (4%)
		287	4.3177	0.029	H-2→L (20%), H→L+1 (37%), H→L+2 (34%)
		286	4.3287	0.093	H-2→L (60%), H→L+1 (10%), H→L+2 (14%) H-3→L (4%), H-1→LUMO (3%)
		277	4.4831	0.0025	H→L+1 (19%), H→L+2 (34%), H→L+3 (22%), H→L+4 (16%) H→L+7 (2%)
3	220	388	3.19230	0.001	H→L (85%), H→L+4 (10%) H→L+1 (4%)
		321	3.86280	0.2259	H-1→L (94%) H-2→L (3%)
		309	4.01490	0.002	H→L (13%), H→L+1 (44%), H→L+4 (34%) H→L+8 (2%)
		286	4.3368	0.073	H-2→L (77%) H-3→L (7%), H-1→L (3%), H-1→L+1 (4%)
		281	4.4185	0.0033	H→L+2 (96%)
		275	4.5094	0.006	H→L+1 (51%), H→L+4 (40%) H→L+7 (3%)
4	219	389	3.1864	0.0013	H→L (86%) H→L+1 (5%), H→L+3 (2%), H→L+4 (4%)
		325	3.8108	0.1717	H-1→L (92%) H-2→L (3%)
		313	3.9633	0.0096	H→L (12%), H→L+1 (52%), H→L+4 (10%) H-1→L (2%), H→L+2 (4%), H→L+3 (9%), H→L+5 (3%), H→L+8 (4%)
		289	4.2927	0.0935	H-2→L (81%) H-3→L (5%), H-1→L (4%), H-1→L+1 (3%)
		277	4.4784	0.0238	H-4→L (26%), H-3→L (29%), H-1→L+1 (11%) H-5→L (6%), H-2→L (4%), H-2→L+1 (3%), H→L+1 (6%), H→L+3 (4%)
		275	4.5018	0.0095	H→L+1 (33%), H→L+3 (24%), H→L+4 (10%) H-4→L (6%), H-3→L (7%), H→L+2 (7%), H→L+5 (3%), H→L+7 (2%)

5	296	391	3.1735	0.001	H→L (86%) H→L+1 (3%), H→L+3 (2%), H→L+4 (7%)
		324	3.8318	0.198	H-1→L (95%) H-2→L (3%)
		310	3.9998	0.0012	H→L (13%), H→L+1 (40%), H→L+3 (11%), H→L+4 (25%) H→L+2 (3%), H→L+5 (2%), H→L+7 (2%), H→L+8 (2%)
		287	4.3207	0.0898	H-2→L (79%) H-4→L (2%), H-3→L (3%), H-2→L+1 (2%), H-1→L (3%), H-1→L+1 (4%)
		278	4.4524	0.0128	H→L+1 (53%), H→L+2 (13%), H→L+4 (17%) H→L+3 (9%), H→L+7 (3%)
		273	4.5450	0.0688	H-4→L (34%), H-3→L (28%) H-6→L (3%), H-5→L (9%), H-2→L (9%), H-2→L+1 (3%), H-1→L+1 (9%)
6	245	392	3.1623	0.0012	H→L (87%) H→L+1 (3%), H→L+4 (8%)
		324	3.8246	0.2032	H-1→L (95%) H-2→L (3%)
		309	4.0120	0.0007	H→L (12%), H→L+1 (37%), H→L+4 (33%) H→L+2 (9%), H→L+5 (2%), H→L+7 (2%), H→L+8 (3%)
		288	4.3096	0.0988	H-2→L (78%) H-3→L (6%), H-1→L (3%), H-1→L+1 (4%)
		279	4.4362	0.0146	H→L+1 (57%), H→L+2 (16%), H→L+4 (19%)H→L+7 (3%)
		273	4.5435	0.0723	H-4→L (37%), H-3→L (32%), H-2→L (10%) H-6→L (4%), H-2→L+1 (3%), H-1→L+1 (8%)

H = HOMO, L = LUMO, H-1 = HOMO-1, L+1 = LUMO+1.

Table S8: Calculated vibrational frequencies of **compound 1**.

DFT Frequencies	**Scaling**	**Exp Frequencies**	**Intensities**	**Vibrational assignments**
3886	3723	3687,3388	134.931	υ(O-H)
3564	3414		22.306	υ (N-H)
3460	3315	3148	29.467	υ (N-H)+
3181	3047	3097	19.852	υ_s(C-H)
3170	3037	3153	24.217	υ_s(C-H_{Ben})+ υ(N-H)
3060	2931		8.821	υ(C-H)
3011	2885	3002	24.522	υ_s (C-H)+ υ(N-H)
1692	1663		19.022	υ_{as}(C-N)+ υ_s (N-H)
1649	1621	1548	23.154	υ_s(C=N)+ ρ(C-H)+ υ_s+υ_{as} (C-C_{Ben})
1659	1631		3.4	υ (C-C_{Ben})
1631	1603		9.5421	υ(N-H)+ υ (C-C_{Ben})
1546	1520		350.670	δ_{as}(N-H)
1520	1494		27.817	υ_s+υ_{as} (C-C_{Ben})
1518	1492		89.791	υ (C=C-C=C_{Ben})
1514	1488	1523	361.227	δ_{as} (N-H)+ ρ(C-H_{Ben})
1475	1450		11.315	υ (C=C-C=C_{Ben})
1471	1446		18.932	ρ(C-H)+ δ(C-H)
1440	1416		100.676	ρ(C-H)+ δ(C-H_{Ben})
1382	1359		117.161	ρ(C-H)+ ρ(N-H)+

1361	1338	1326	338.200	δ_{as}(N-H) + δ(C-H_{Ben})
1278	1256		55.632	ρ(N-H)+ δ_{as}(C-H_{Ben})
1247	1226	1229	402.815	υ(C=S)+ δ(N-H)
1167	1147		83.133	δ+ρ(C-H_{Ben})
1120	1101		99.986	δ + δ_{as}(C-H_{Ben})
1098	1079		7.656	ρ(O-H)+δ + δ_s (C-H_{Ben})
1071	1053		49.055	δ_{as}(N-H)+ δ(C-H_{Ben})
942	926		15.033	δ(N-H)+ δ_{as}(C-H_{Ben})
925	909		23.207	δ + δ_{as}(C-H_{Ben})+ υ(C-Cl)
866	851		39.348	δ(N-H)+ δ_{as}(C-H_{Ben})+ υ(C-Cl)
810	796		47.873	δ(C=N) +δ_s(C-H_{Ben})
721	709		22.724	δ(N-H) +ρ(C-H_{Ben})
659	648		22.791	υ(C-Cl)+ δ_{as}(C-H_{Ben})

Table S9: Calculated vibrational frequencies of **compound 2**.

DFT	Scaling	Exp	Intensities	Vibrational assignments
3887	3724	3687	133.411	υ(O-H)
3573	3423		23.121	υ(N-H)
3463	3318	3323	29.718	υ_{as}(N-H)
3192	3058		1.332	υ_s(C-H_{Ben})
3189	3055		6.926	υ_s(C-H_{Ben})+υ(N-H)
3179	3045	3187	12.472	υ_{as}(C-H_{Ben})
3144	3012	3125	13.545	υ (C-H)+υ(N-H)
3068	2939		6.536	υ(C-H)
3024	2897	3062	20.888	υ(C-H)
1691	1662		18.742	υ(C-H)+ υ(N-H)
1669	1641		13.220	υ (C=C-C=C_{Ben})
1648	1620		22.336	υ_s(C-H_{Ben})+ υ (C=C-C=C_{Ben})
1642	1614		18.024	υ (C=C-C=C_{Ben})
1548	1522	1532	379.589	υ_s(C-H)+ υ(C=N)
1526	1500	1532	84.595	υ (C=C-C=C_{Ben})
1518	1492		130.199	υ (C=C-C=C_{Ben})+ υ(N-H)
1516	1490	1532	326.421	δ_{as}(N-H)
1474	1449		36.383	δ(C-H)+ ρ(C-H_{Ben})
1439	1415		100.410	δ(C-H_{Ben})+ υ (C=C-C=C_{Ben})
1382	1359		228.540	δ(C-H)+ ρ(N-H)
1360	1337		305.704	δ(C-H_{Ben})+ δ_s (N-H)
1280	1258		60.763	υ(F-C_{Ben})+ ρ(C-H_{Ben})
1246	1225		374.193	ρ(N-H)
1231	1210	1222	59.243	δ_{as}(N-H)+ υ(C=S)
1220	1199		19.873	δ_{as}(O-H)+ δ_{as}(C-H_{Ben})
1167	1147		82.356	δ +ρ(C-H_{Ben})
1120	1101		100.367	δ+ δ_{as}(C-H_{Ben})+
1117	1098		13.660	δ + δ_{as} (C-H_{Ben})

1073	1055	51.450	δ (C-H_{Ben})+ δ_{as}(N-H)
1052	1034	7.933	δ +δ_s (C-H_{Ben})
951	935	6.012	δ+ δ_{as}(C-H_{Ben})
941	925	13.569	δ_{as}(C-H_{Ben})
924	908	18.776	υ(C-Cl)+ δ_{as}(C-H_{Ben})
866	851	33.388	δ_{as}(C-H_{Ben})+ δ_s(N-H)
810	796	43.127	δ_s(C-H_{Ben})+ δ(N-H)
805	791	21.805	υ(C-F)+ δ(N-H)
797	783	35.216	υ(C-S)+ δ_{as}(N-H)+ υ(C-F)
764	751	60.500	δ_s(C-H_{Ben})
659	648	23.056	υ(C-Cl)+ δ_{as}(C-H_{Ben})

Table S10: Calculated vibrational frequencies of **compound 3**.

DFT Frequencies	**Scaling**	**Exp Frequencies**	**Intensities**	**Vibrational assignments**
3889	3726	3656	135.643	υ(O-H)
3561	3411		20.940	υ(N-H)
3456	3311	3450	30.635	υ(N-H)
3164	3031	3187	5.821	υ_{as}(C-H_{Ben})+ υ(N-H)
3163	3030	3125	6.603	υ_{as} (C-H)+ υ(N-H)
3150	3018		13.855	υ_{as}(C-H_{Ben})
3053	2925	3094	8.431	υ_{as}(C-H)
3010	2884		23.887	υ_s(C-H)
1693	1664		16.881	υ_{as}(C-N)
1664	1636		37.374	δ(C-H)+ υ (C=C-C=C_{Ben})
1648	1620	1548	22.037	υ_{as}(C=N)+ρ(C-H)+ υ (C=C-C=C_{Ben})
1544	1518	1530	77.449	υ (C=C-C=C_{Ben}) + υ(N-H)
1534	1508		452.470	υ_{as} (N-H)+ δ(C-H_{Ben})+ υ (C=C-C=C_{Ben})
1517	1491	1530	111.130	ρ(N-H)+ δ(C-H_{Ben})+ υ (C=C-C=C_{Ben})
1508	1482		321.428	υ_{as}(N-H)+ δ_{as}(C-H_{Ben})
1474	1449		19.621	δ(C-H)+ ρ(N-H)
1441	1417		36.316	δ(C-H_{Ben})+ υ(O-H)+ υ (C=C-C=C_{Ben})
1441	1417		67.547	δ(N-H)+ δ(C-H_{Ben})+ υ (C=C-C=C_{Ben})
1377	1354		195.973	δ_{as}(N-H)+δ(C=C_{Ben})
1357	1334		362.409	υ(C=S)+ υ_{as}(N-H)
1314	1292		100.262	υ(C-O)+ δ_{as}(C-H_{Ben})
1281	1259		105-650	δ_{as}(F-C_{Ben})+ ρ(N-H)+ρ(C-H)
1240	1219	1217	366.156	υ(C=S)+ρ(N-H)
1170	1150		75.811	δ(C-H_{Ben})

1121	1102	106.911	δ(O-H)+ δ(C-H_{Ben})
1069	1051	49.021	υ_{as} (N-N)+δ_{as}(C-H_{Ben})
1021	1004	5.746	δ(C-H_{Ben})
941	925	14.956	δ_{as}(C-H_{Ben})
923	907	17.274	δ(N-H)+ δ_{as} (C-H_{Ben})+ υ(C-Cl)
874	859	17.928	υ(C-F)+ δ (C-H_{Ben})
864	849	63.787	δ_{as}(N-H)+ δ(C-H_{Ben})+ υ(C-Cl)
845	831	46.026	υ(C-F)
794	781	33.388	υ(C=S)+ δ_s(C-H_{Ben})+ υ(C-Cl)
718	706	4.521	υ_{as}(C-F)+ δ_s(C-H_{Ben})
659	648	24.516	υ_{as}(C-Cl)+ δ_{as}(C-H_{Ben})

Table S11: Calculated vibrational frequencies of **compound 4**.

DFT Frequencies	**Scaling**	**Exp Frequencies**	**Intensities**	**Vibrational assignments**
3887	3724	3386	139.268	υ(O-H)
3572	3422		21.457	υ(N-H)
3458	3313		27.984	υ(N-H)
3177	3044		24.938	υ_s(C-H_{Ben})
3163	3030	3134	21.729	υ_{as}(C-H_{Ben})+ υ(N-H)
3112	2981		13.912	υ_s(CH-CH_3)
3075	2946		28.419	υ_{as}(CH-CH_3)
3019	2892		42.658	υ(C-H)+ υ(N-H)
3015	2888	2996	39.611	υ_s(C-H)+υ_{as}(CH-CH_3)
1691	1662		14.347	υ_s(N-H)+ υ_{as}(C=N)
1652	1624		24.582	υ_{as} (C-H_{Ben})+ υ (C=C-C=C_{Ben})
1550	1524	1541	329.194	υ_{as} (N-H)+ υ_s(C=N) + υ (C=C-C=CBen)
1522	1496		132.885	υ (C=C-C=C_{Ben}) + υ_{as} (N-H)+ υ_s(C=N)
1518	1492		201.412	δ_s(C-H_{Ben})+δ_{as}(N-H)+υ(C=C-C=C_{Ben})
1499	1474		12.956	δ_{as}(C-CH_3)+ δ_s(C-H_{Ben})
1442	1417		101.916	δ_{as}(C-H_{Ben})+ υ (C=C-C=C_{Ben})
1387	1363		236.482	δ_{as}(C-H_{Ben})+ δ_{as}(N-H)
1352	1329		188.576	δ(C-H)+ υ(C=S)+δ_{as}(N H)
1254	1233		305.280	δ_s(C-H_{Ben})+ δ_{as}(N-H)
1240	1219	1228	73.868	υ_{as}(C=S)+ δ_{as}(N-H)
1170	1150		82.895	δ_{as}(C-H_{Ben})+ ρ(N-H)
1124	1105		100.990	δ_{as}(C-H_{Ben})+ υ_{as}(O-H)+ υ_{as}(C-Cl)
1075	1057		11.838	δ(C-H_{Ben})+ δ_{as}(N-H)
959	943		19.467	δ_{as}(C-H_{Ben})
926	910		19.231	δ(N-H)+ δ_{as}(C-H_{Ben})+ υ(C-Cl)

868	853	829	33.206	δ(C-H_{Ben})+ δ_{as}(N-H)+ υ(C-Cl)
807	793		43.405	ρ(C-H_{Ben})+ δ_s (C=N)
799	785		37.255	δ_{as}(C-H_{Ben})+ δ_s(N-H)
755	742		21.015	δ_{as}(C-H_{Ben})
659	648		21.957	δ(C-H_{Ben})+ υ(C-Cl)

Table S12: Calculated vibrational frequencies of **compound 5**.

DFT Frequencies	**Scaling**	**Exp Frequencies**	**Intensities**	**Vibrational assignments**
3888	3725	3687	135.094	υ(O-H)
3565	3415		22.939	υ(N-H)
3458	3313	3342	28.617	υ(N-H)
3177	3044	3218	21.844	υ_s(C-H_{Ben})+ υ(N-H)
3156	3023	3125	11.706	υ_{as}(C-H_{Ben}) + υ(N-H)
3115	2984		15.496	υ_s(CH-CH_3)
3090	2960	3094	16.317	υ(C-H)
3022	2895		26.221	υ_s(CH-CH_3)+ υ(N-H)
3009	2883		26.585	υ(C-H)
1687	1658		20.152	δ(N-H)+ υ_{as}(C=N)+ υ_{as}(C-H_{Ben})
1661	1633		11.975	δ(C-H_{Ben})+δ_{as}(C+H_{Ben})+ υ (C=C-C=C_{Ben})
1655	1627		25.203	δ_{as}(C-H_{Ben})+ υ (C=C-C=C_{Ben})
1546	1520	1543	324.181	υ(C=N)+δ_{as}(N-H)+ δ(C-H)
1521	1495		184.742	υ_{as}(O-H)+ υ(C-Cl)+υ_{as}(N-H)+
1519	1493		207.601	υ_{as}(N-H)+δ(C-H_{Ben})+υ(C=S)+ υ (C=C-C=C_{Ben})
1514	1488	1538	99.601	υ (C=C-C=C_{Ben}) + υ_{as}(CH-CH_3)
1487	1462		18.463	ρ(N-H)+δ(C-H_{Ben})
1472	1447		18.627	δ(C-H)+ δ_{as}(CH-CH_3)+ ρ(N-H)
1443	1418		97.547	υ(C-Cl)+ δ+δ_s(C-H_{Ben}) + υ (C=C-C=C_{Ben})
1314	1292		95.625	δ_{as}(C-H_{Ben})+ υ(C=O)
1278	1256		51.554	δ_{as}(C-H_{Ben})+ , ρ(N-H)
1272	1250		51.147	δ (C-H_{Ben})+ ρ(N-H)
1241	1220	1223	389.142	υ(C=S)+ δ_{as}(N-H)
1170	1150		75.091	δ+ ρ(C-H_{Ben})+ υ(C=O)
1123	1104		109.157	υ(C-Cl)+ δ_{as}(C-H_{Ben})
1070	1052		45.023	υ(C=S)+ δ+ ρ(C-H_{Ben})
1050	1032		4.935	δ_{as}(CH-CH_3)+) ρ(C-H_{Ben})
942	926		16.767	δ_{as}(C-H_{Ben})+ υ(C-Cl)
925	909		24.717	υ(C-Cl)+ δ_{as}(C-H_{Ben})+ δ(N-H)
864	849		50.460	υ(C-Cl)+ δ(C-H_{Ben})+ υ_{as} (C=S)
811	797		49.526	ρ(C-H_{Ben})+ δ_{as}(N-H)
792	779		22.361	δ(C-H_{Ben})+ υ(C=O)+δ_{as}(C=S)+
722	710		14.964	δ_{as}(C-H_{Ben})
660	649		21.927	υ(C-Cl)+ δ+ ρ(C-H_{Ben})

Table S13: Calculated vibrational frequencies of **compound 6**.

DFT Frequencies	Scaling	Exp Frequencies	Intensities	Vibrational assignments
3890	3727	3719	134.631	υ(O-H)
3565	3415		23.549	υ(N-H)
3456	3311	3282	27.648	υ(N-H)
3160	3027		25.142	υ_s(C-H_{Ben})
3149	3017	3130	14.241	υ_{as} (C-H)+ υ(N-H)
3112	2981	3094	13.257	υ_{as} (CH-CH_3)+ υ(N-H)
3085	2955		13.854	υ_s(C-H)+υ_{as}(CH-CH_3)
3019	2892	2988	35.283	υ_s(C-H)
3010	2884		21.449	υ_s(C-H)
1694	1665		19.957	υ_{as} (N-H)+ δ + δ_{as} (C-H_{Ben})
1649	1621	1539	21.932	υ(C-Cl)+ υ(C=N)+ υ (C=C-C=C_{Ben})
1534	1508	1532	433.191	δ_s(C-H_{Ben})+ υ (C=C-C=C_{Ben})
1518	1492	1514	112.702	υ(C=O)+ δ_{as}(N-H)+ δ(C-H_{Ben})+ υ (C=C-C=C_{Ben})
1509	1483		337.185	δ (N-H)+ ρ(C-H_{Ben})+ υ(C=O)
1476	1451		19.037	δ_{as}(CH-CH_3)+ ρ(N-H)+ δ(C-H_{Ben})
1471	1446		19.342	δ +δ_{as} (C-H_{Ben})+ υ (C=C-C=C_{Ben})
1456	1431		8.598	δ_{as}(C-CH_3)
1441	1417		98.729	υ_{as}(C=O)+ δ+δ_s(C-H_{Ben})+ υ (C=C-C=C_{Ben})
1378	1355		220.683	υ(C=S)+ ρ(N-H)+ δ +δ_{as} (C-H_{Ben})
1357	1334		330.549	υ(C=S)+ δ_s(N-H)+ ρ(C-H_{Ben})
1238	1217	1225	177.045	ρ(N-H)+ υ(C=S)
1237	1216		149.108	υ(C=S)+ ρ(N-H)+ δ_s(C-H_{Ben})
1170	1150		76.243	υ_{as}(O-H)+ υ(C-Cl)+ δ+ ρ(C-H_{Ben})
1121	1102		106.527	υ(C=O)+δ+δ_{as}(C-H_{Ben})
1070	1052		47.232	δ+ρ(C-H_{Ben})+ δ_{as}(C=N)+ υ(C=S)
1041	1023		8.808	υ_{as}(CH-CH_3)+ ρ+ δ_s(C-H_{Ben})
941	925		14.291	υ(C-Cl)+ δ_{as}(C-H_{Ben})
923	907		16.554	υ(C-Cl)+ δ_{as}(C-H_{Ben})+ δ(N-H)
861	846		51.237	δ_{as}(N-H)+ υ(C=S)+ υ(C=O)+ υ(C-Cl)
810	796		41.215	δ_{as}(C-H_{Ben})+ υ_{as}(C=O)
792	779		35.362	υ(C=S)+ υ_{as}(C=O)+δ(N-H)
786	773		3.850	ρ+ δ_s(C-H_{Ben})+ υ(C=S)
659	648		23.202	υ_{as} (C=O)+ δ_s(N-H)+ δ_{as}(C-H_{Ben})+ υ(C-Cl)
629	618		14.733	υ_{as} (C=S)+ υ(C-Cl)+ δ(C-H_{Ben})

Frequencies are given in cm^{-1}, υ =stretching, β=in-plane bending, γ=out-plane bending, δ =scissoring, ρ=rocking, w= wagging, s =symmetric, as=asymmetric,τ=twisting, Ben=benzene ring.

Table S14. Frontier molecular orbital energies of **Compounds 1-6**.

	1		**2**		**3**		**4**		**5**		**6**	
$MO_{(S)}$	**E(*eV*)**	**ΔE**	**E(*eV*)**	**ΔE**	**E(*eV*)**	**ΔE**	**E(*eV*)**	**ΔE**	**E(*eV*)**	**ΔE**	**E(*eV*)**	**ΔE**
HOMO-1	-6.284	5.523	-6.244	5.495	-6.354	5.533	-6.291	5.468	-6.263	5.498	-6.241	5.499
LUMO+1	-0.761		-0.749		-0.821		-0.823		-0.765		-0.742	
HOMO-2	-6.858	6.366	-6.832	6.13	-6.918	6.192	-6.850	6.454	-6.841	6.399	-6.811	6.4
LUMO+2	-0.492		-0.702		-0.726		-0.396		-0.442		-0.411	

E = energy, ΔE = E_{LUMO}-E_{HOMO}, MO(s) = molecular orbitals, HOMO = highest occupied molecular orbital, LUMO = lowest unoccupied molecular orbital.

Table S15. Polarizability in unit a.u of the studied **compounds 1-6.**

Polarizability	**1**	**2**	**3**	**4**	**5**	**6**
α_{xx}	265.957	258.305	263.797	281.227	275.51	280.456
α_{yy}	266.052	263.095	267.861	271.942	285.626	287.266
α_{zz}	161.144	169.774	161.502	171.918	169.131	169.383
α_{total}	231.051	230.391	231.053	241.695	243.422	245.701

α = polarizability

Table S16. Hyperpolarizability in unit a.u of the studied **Compounds 1-6.**

Hyperpolariazability	**1**	**2**	**3**	**4**	**5**	**6**
β_{xxx}	17.235	122.278	32.12	-89.754	55.285	-19.555
β_{xxy}	-131.492	-147.897	-34.611	-154.108	-137.458	-86.067
β_{xyy}	-20.545	-14.754	-97.256	2.307	-12.974	74.15
β_{yyy}	-211.872	-207.695	-113.713	-205.311	-206.471	-214.305
β_{xxz}	-58.489	-113.2	-37.352	-32.267	-32.909	33.973
β_{yyz}	-22.352	-34.92	2.651	11.931	-57.926	19.454
β_{xzz}	11.831	68.652	23.575	7.152	-1.024	-46.386

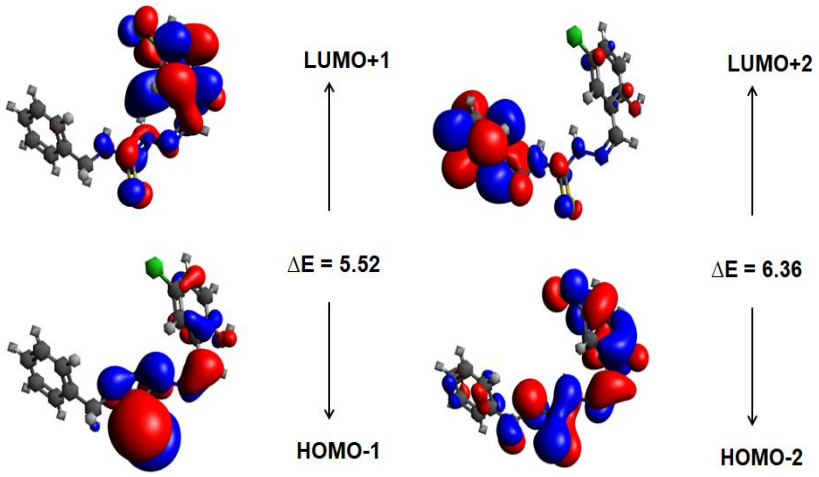
β_{yzz}	-30.593	-42.701	-26.705	-39.83	-24.414	-36.445
β_{zzz}	-39.08	-100.951	-34.588	-16.763	-30.724	39.178
β_{total}	392.807	501.709	192.778	408.93	390.074	349.412

β = hyperpolarizability

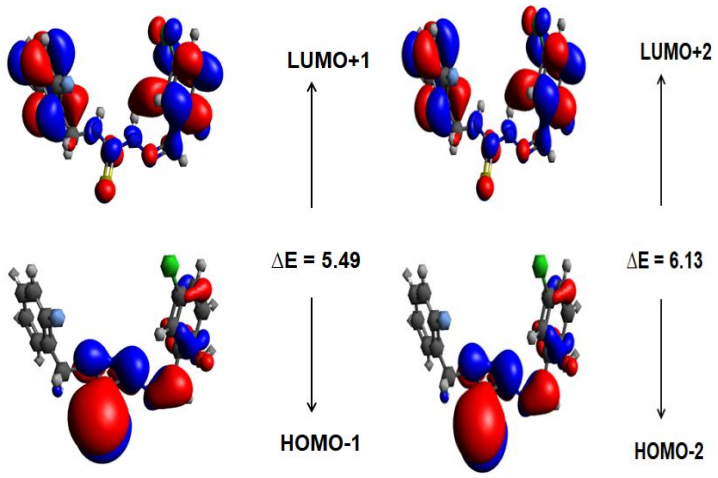
Table S17. Dipole moment in unit debye of the studied **Compounds 1-6.**

Dipole moment	**1**	**2**	**3**	**4**	**5**	**6**
μx	2.8122	1.9416	3.0797	3.3364	-2.4592	1.6493
μy	-5.2381	-5.3212	-4.5110	-5.1885	5.6831	-6.2007
μz	4.4826	5.5825	4.1008	4.3639	4.4947	4.1709
μ_{total}	7.4458	7.9529	6.8301	7.5562	7.6516	7.6528

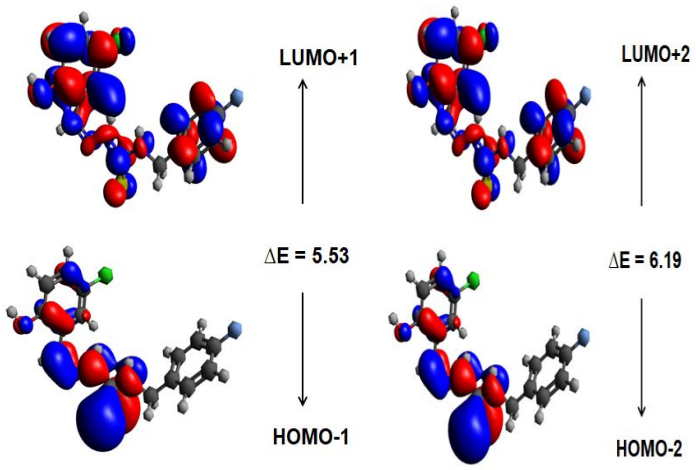
μ = dipole moment



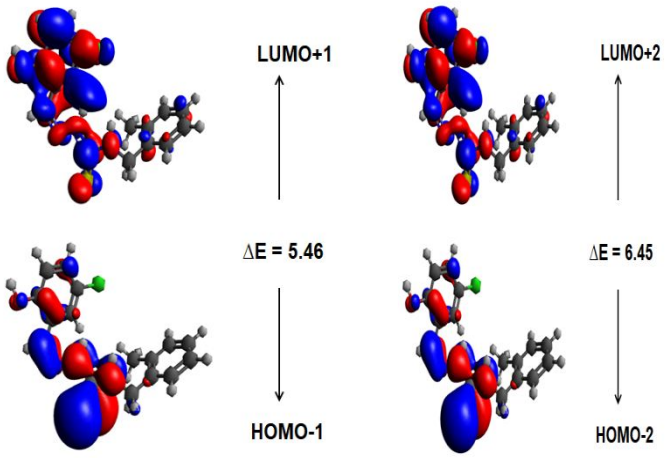
Compound 1



Compound 2



Compound 3



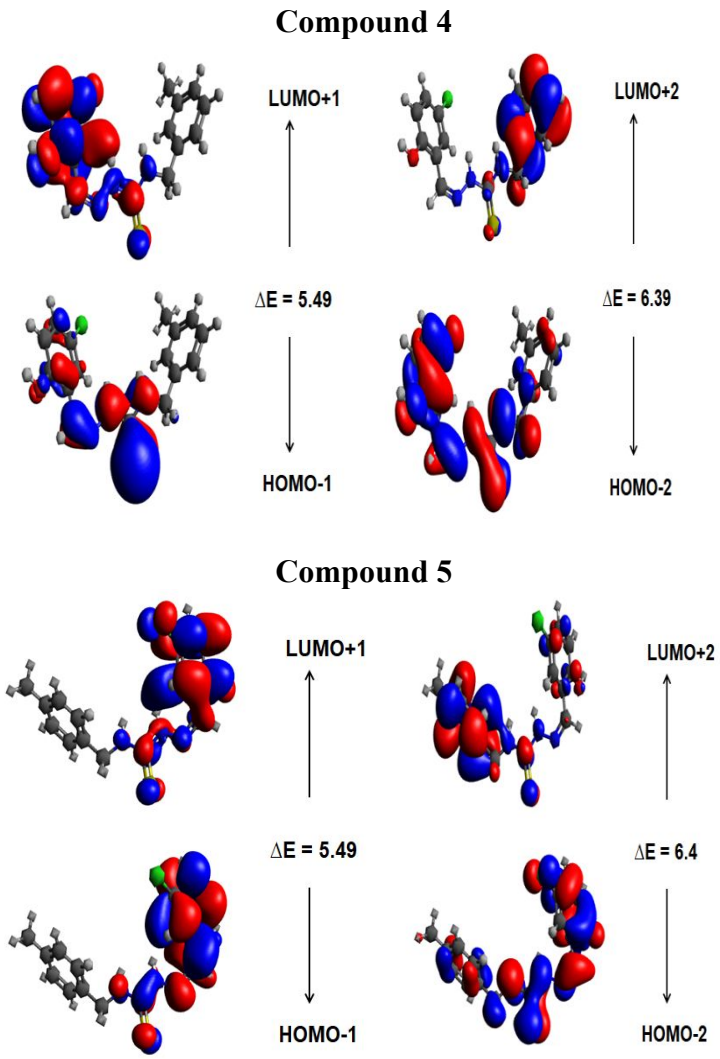


Figure S1: Frontier molecular orbitals of entitled compounds.

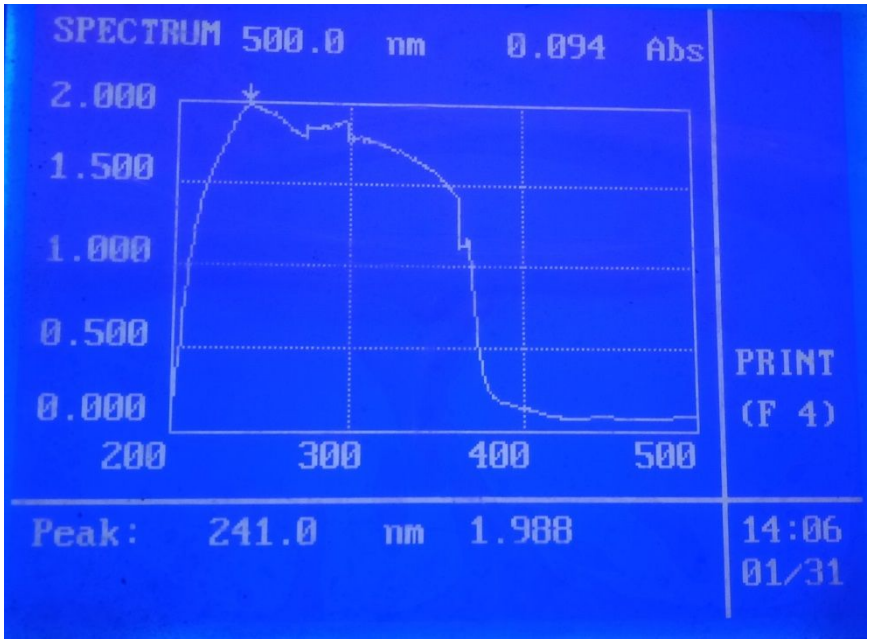


Figure S2: UV-Vis spectra of compound 1.

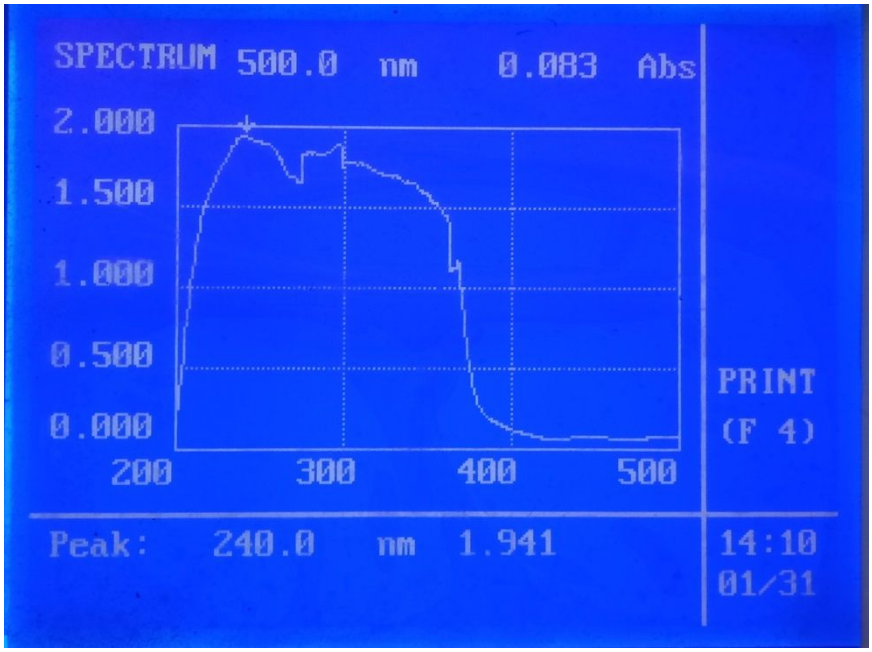


Figure S3: UV-Vis spectra of compound 2.

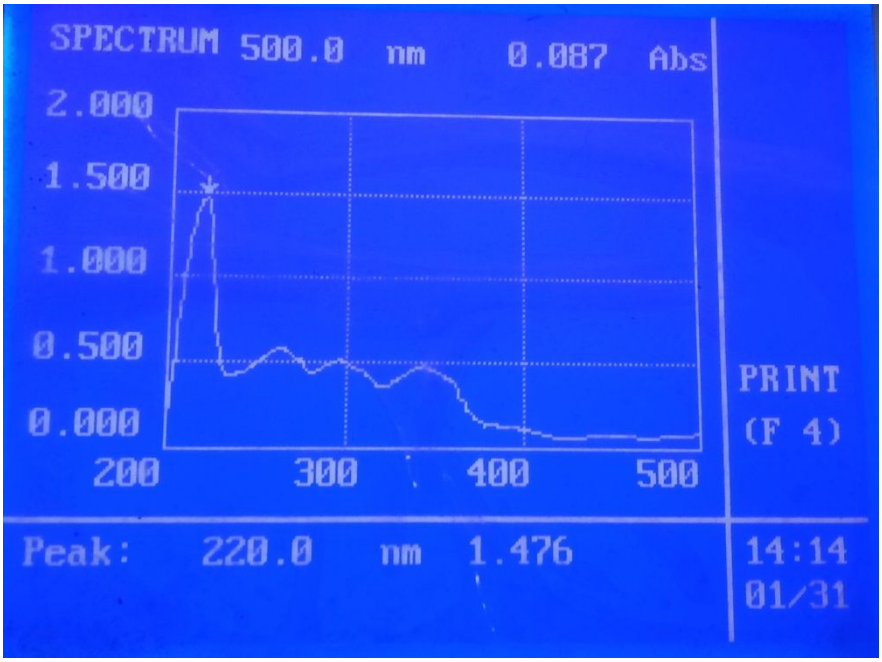


Figure S4: UV-Vis spectra of compound 3.

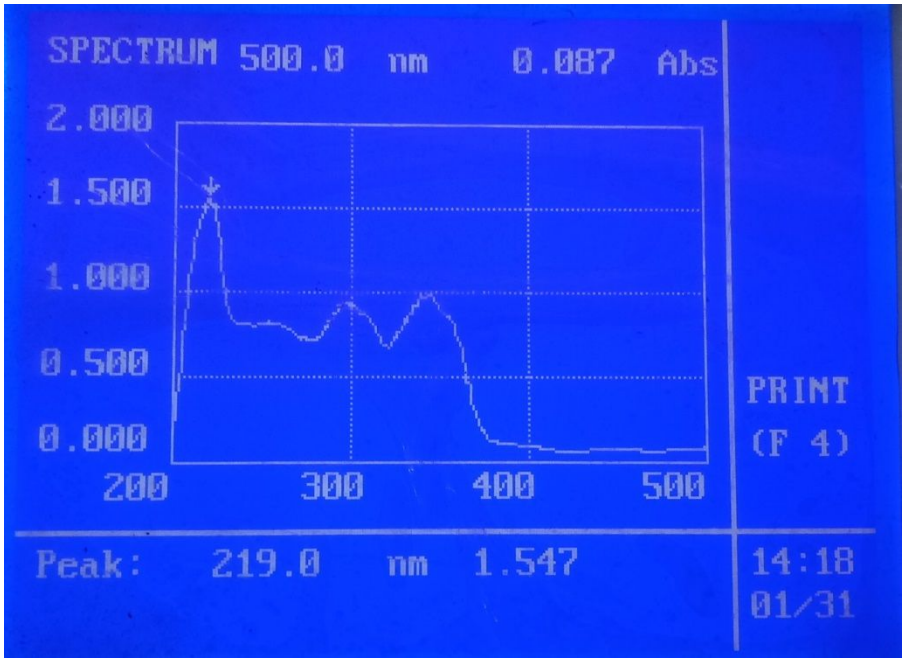


Figure S5: UV-Vis spectra of compound 4.

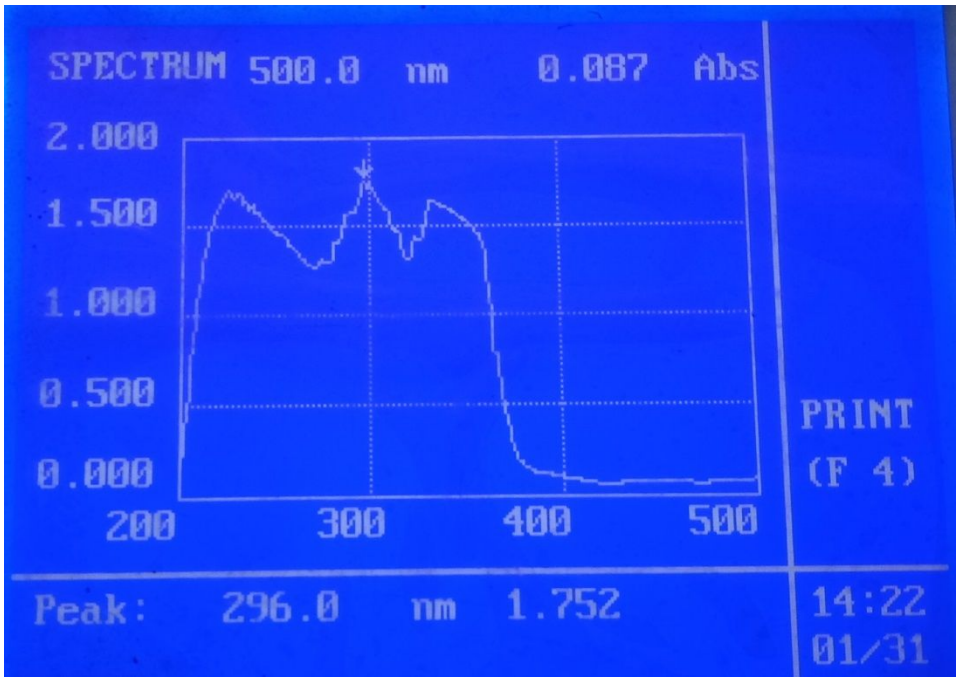


Figure S6: UV-Vis spectra of compound 5.

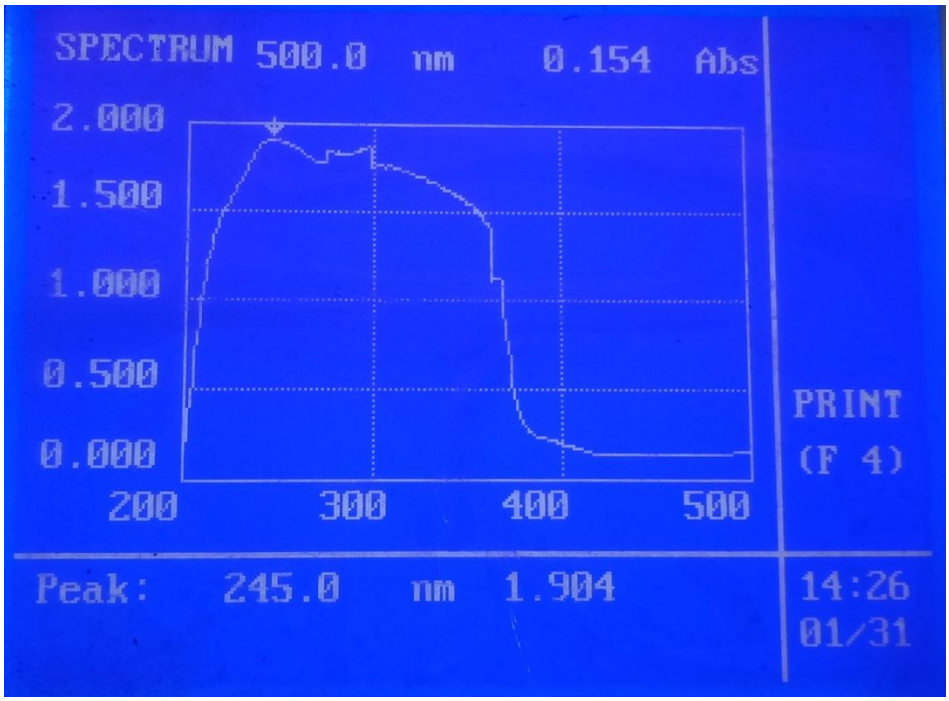


Figure S7: UV-Vis spectra of compound 6.

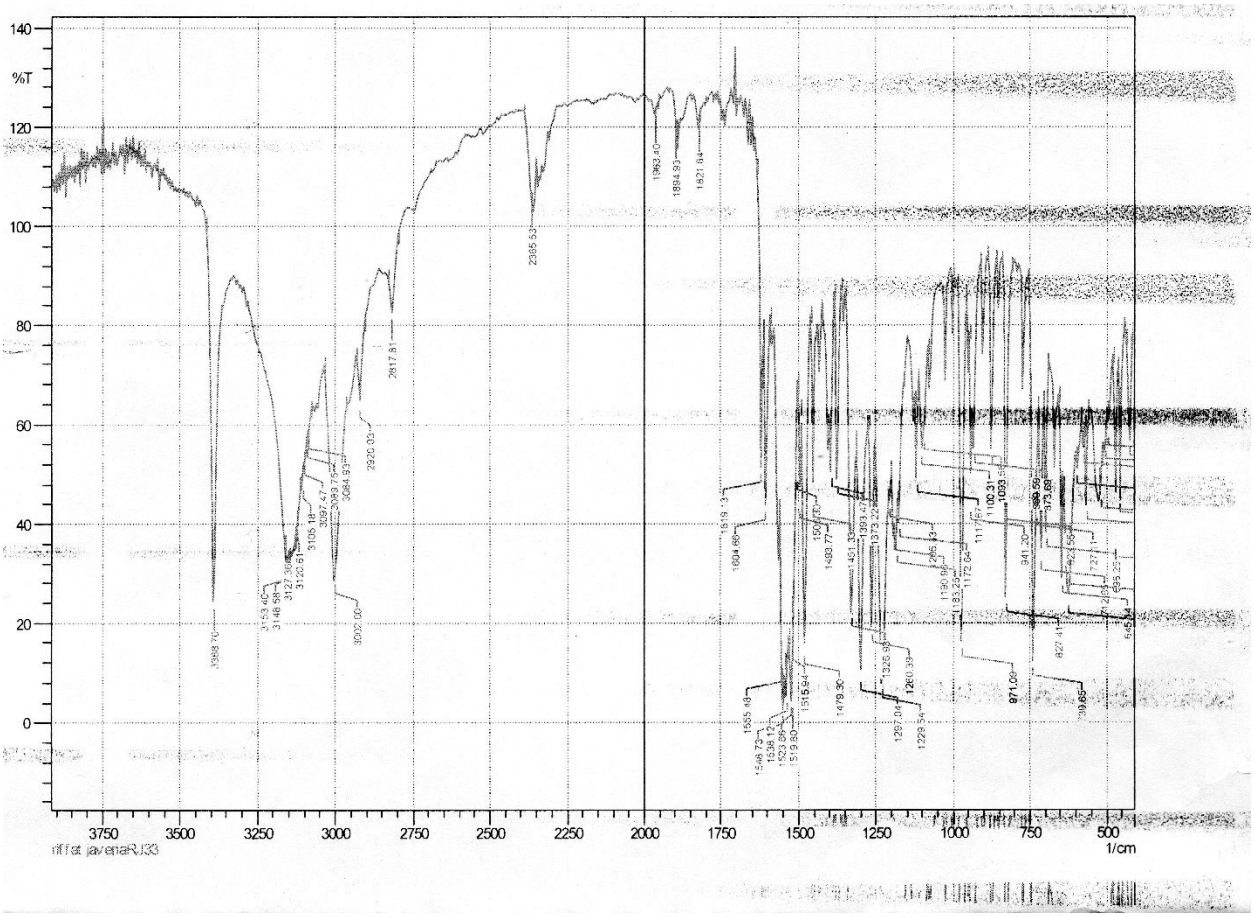


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Figure S8: IR Spectra of compound 1

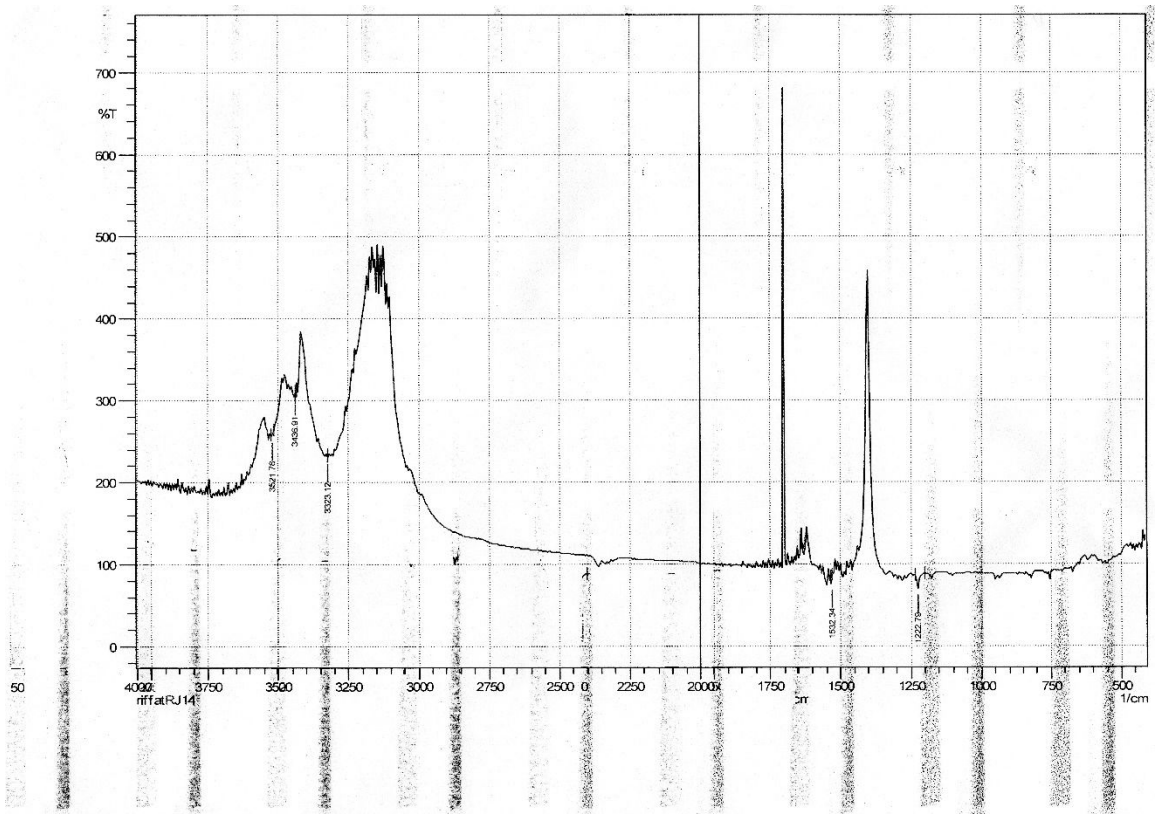

Figure S9: IR Spectra of compound 2

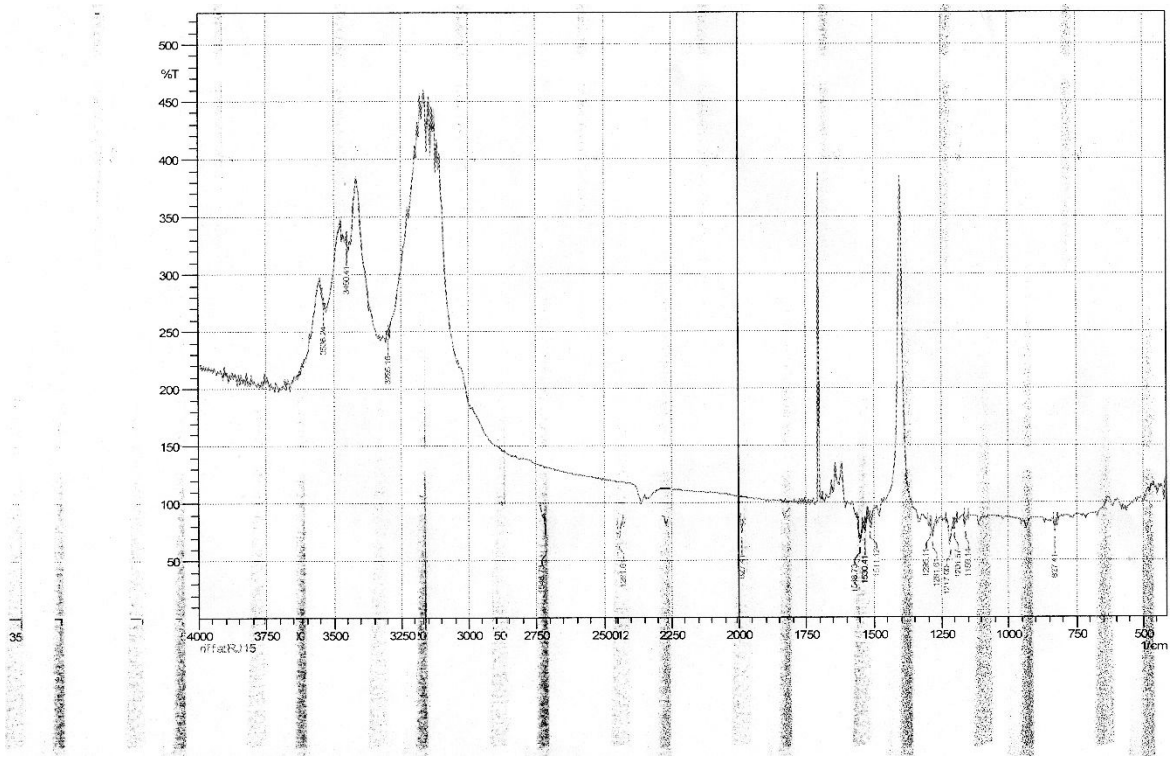

Figure S10: IR Spectra of compound 3

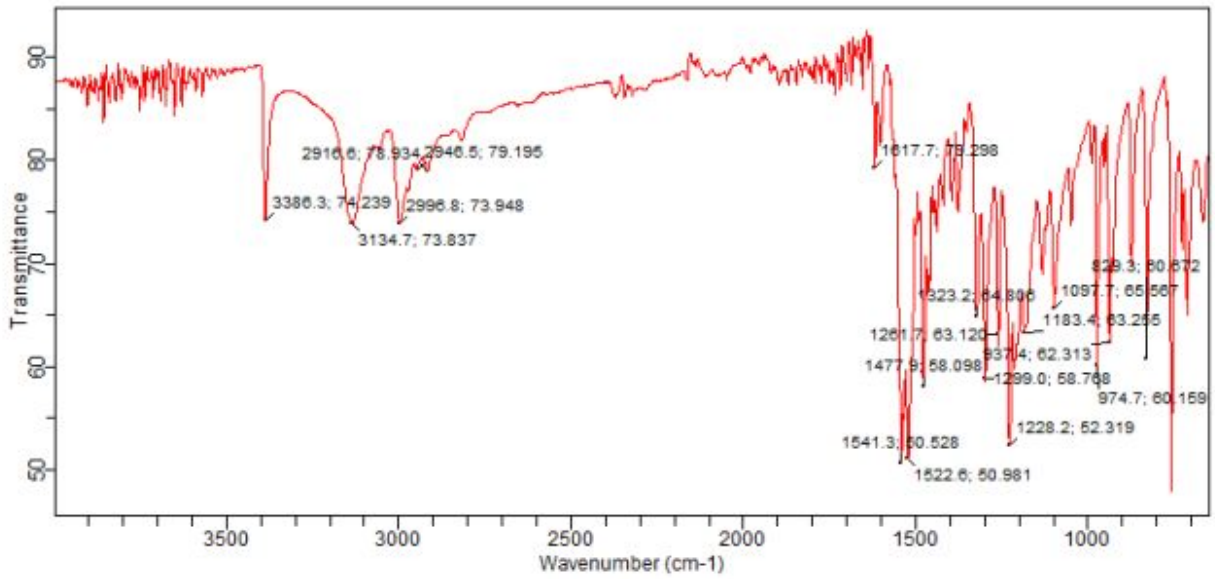

Figure S11: IR Spectra of compound 4

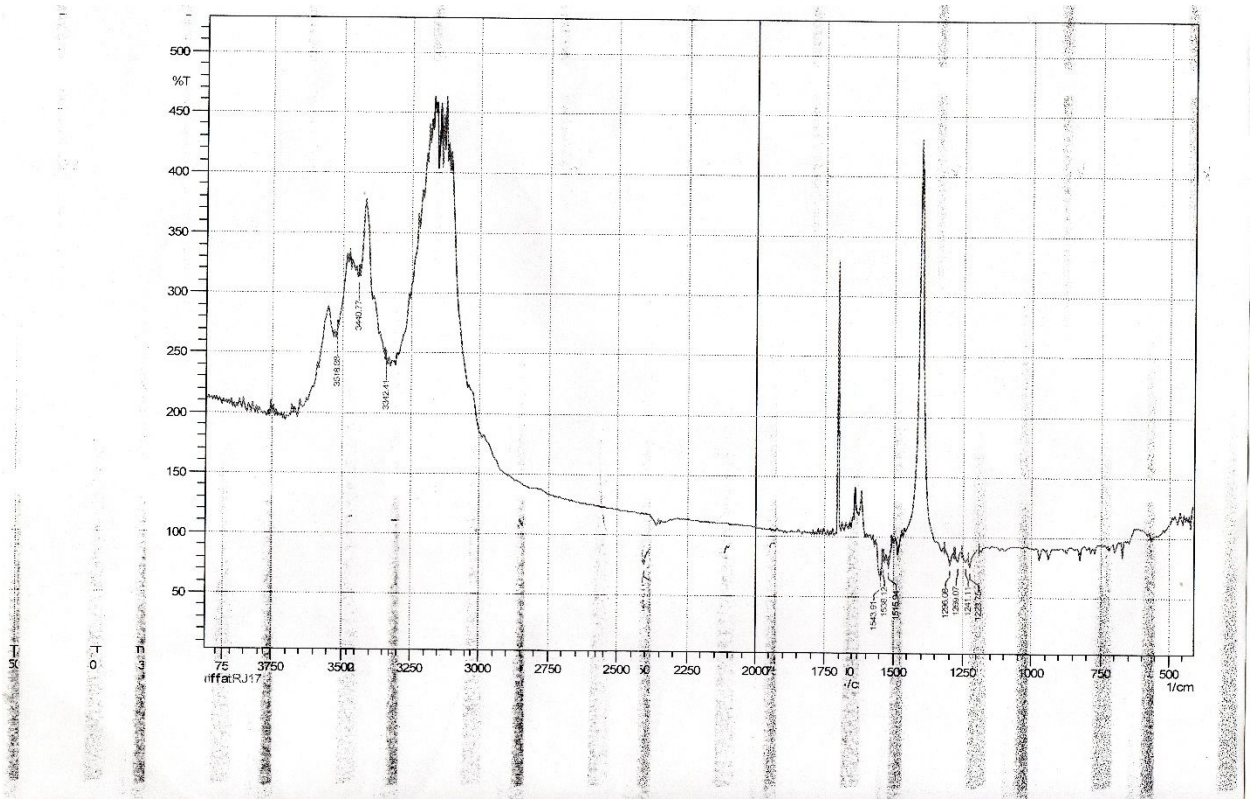

Figure S12: IR Spectra of compound 5

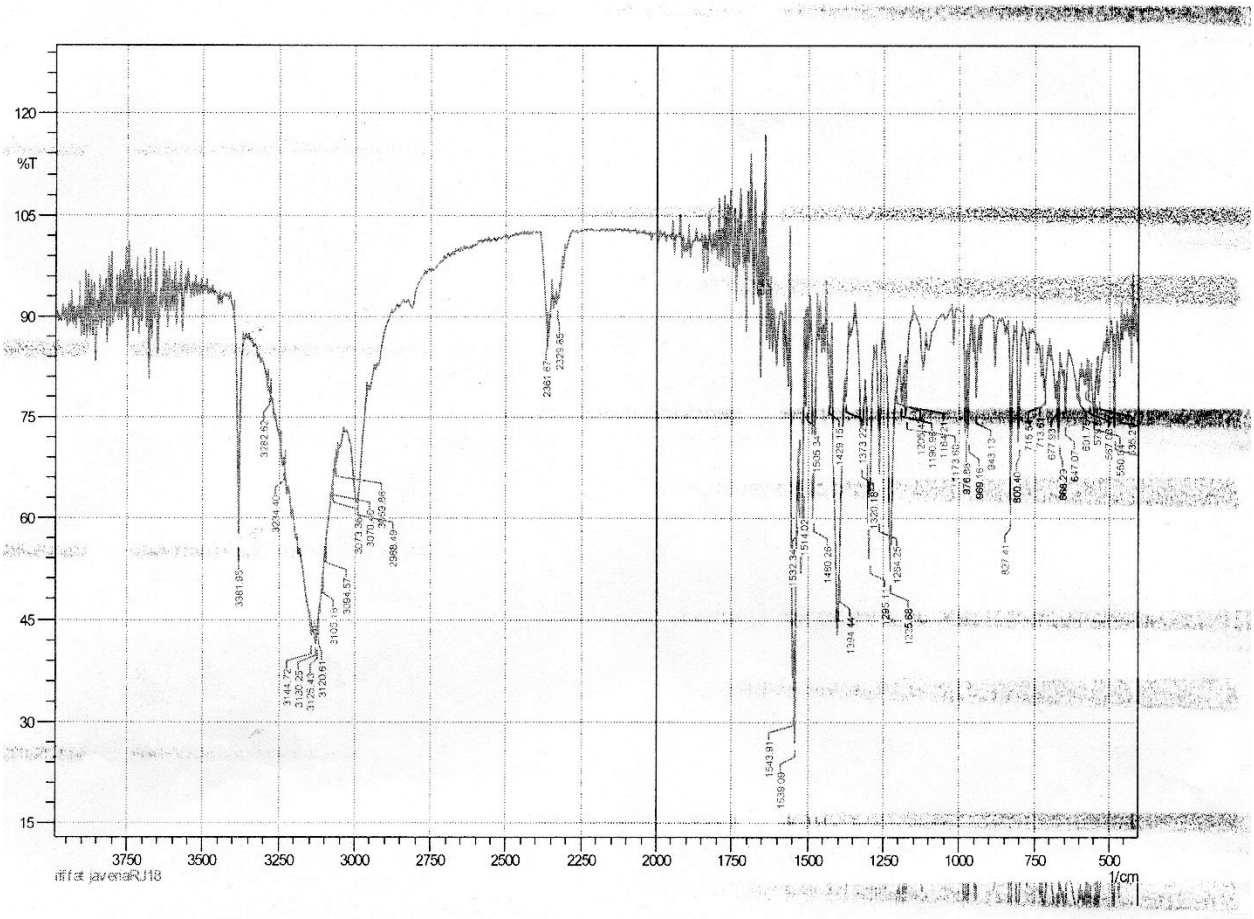

Figure S13: IR Spectra of compound 6

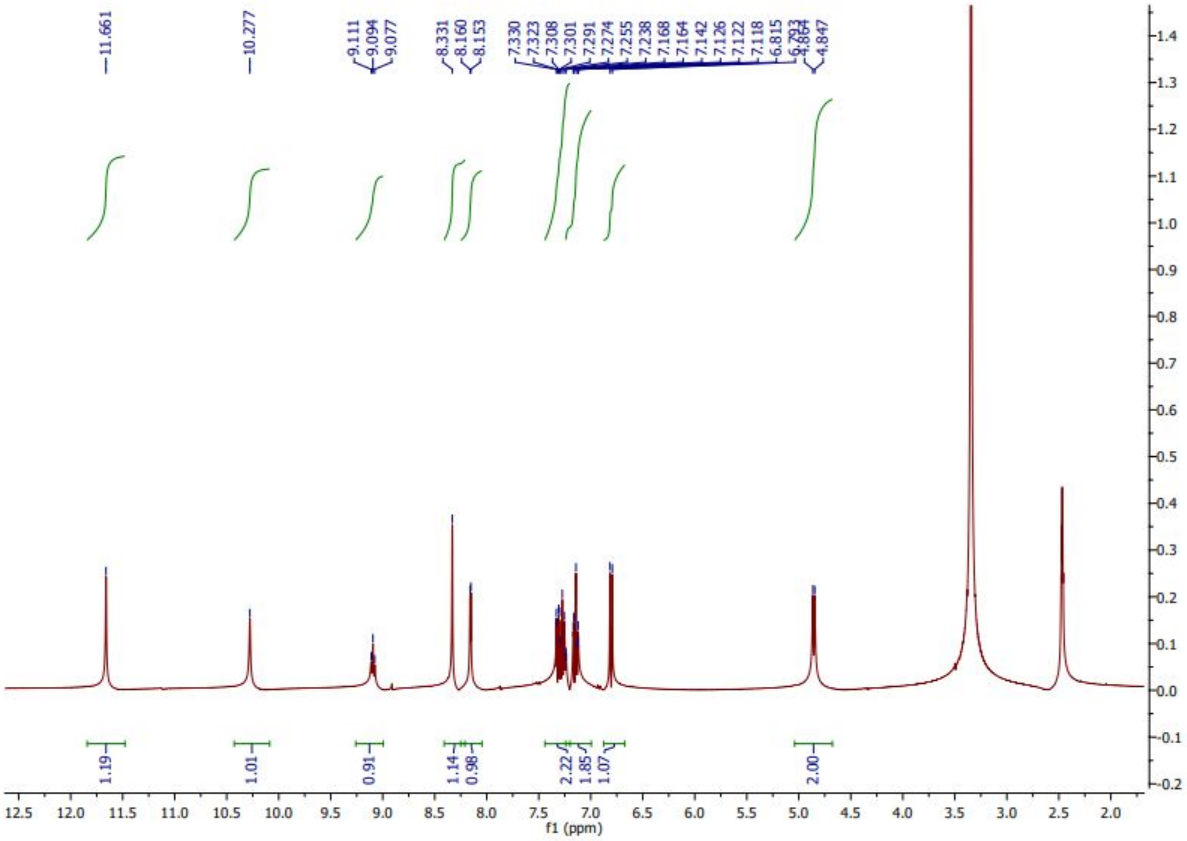

Figure S14: [1]HNMR Spectra of compound 1

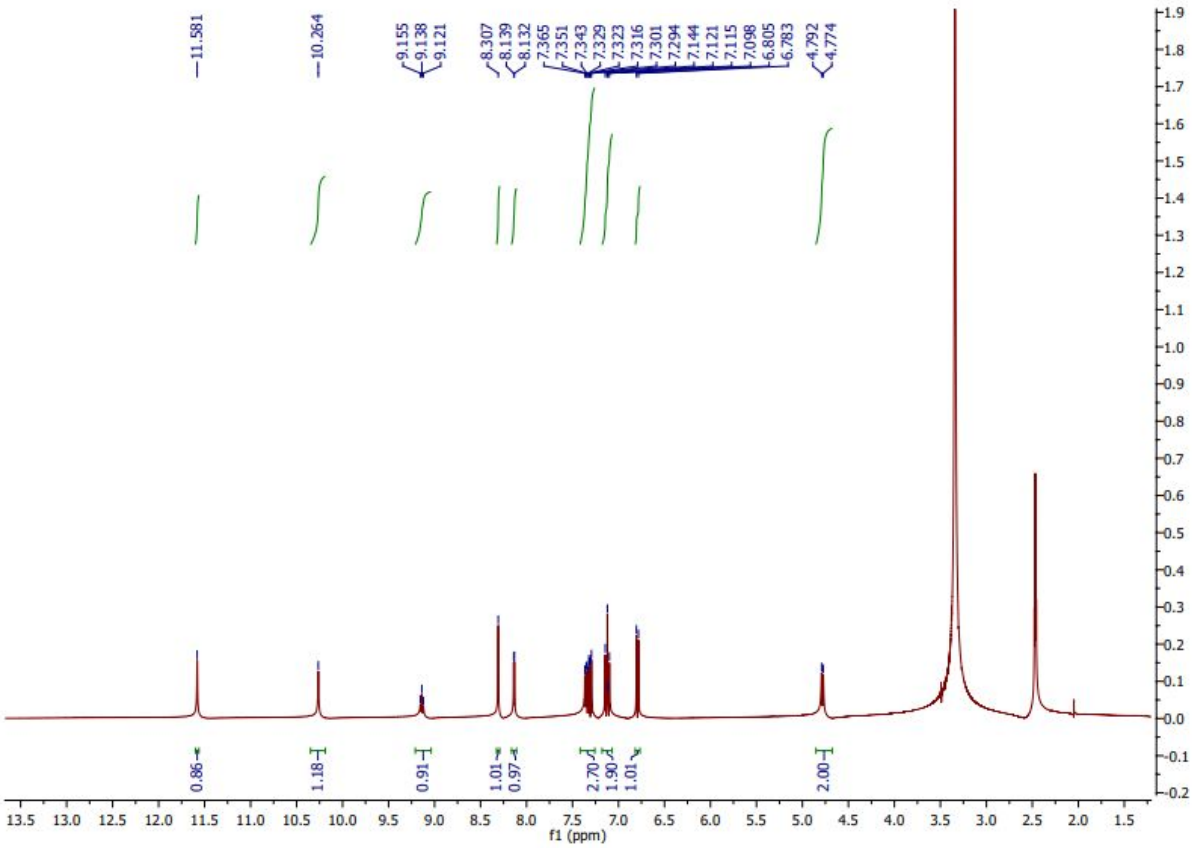

Figure S15: [1]HNMR Spectra of compound 2

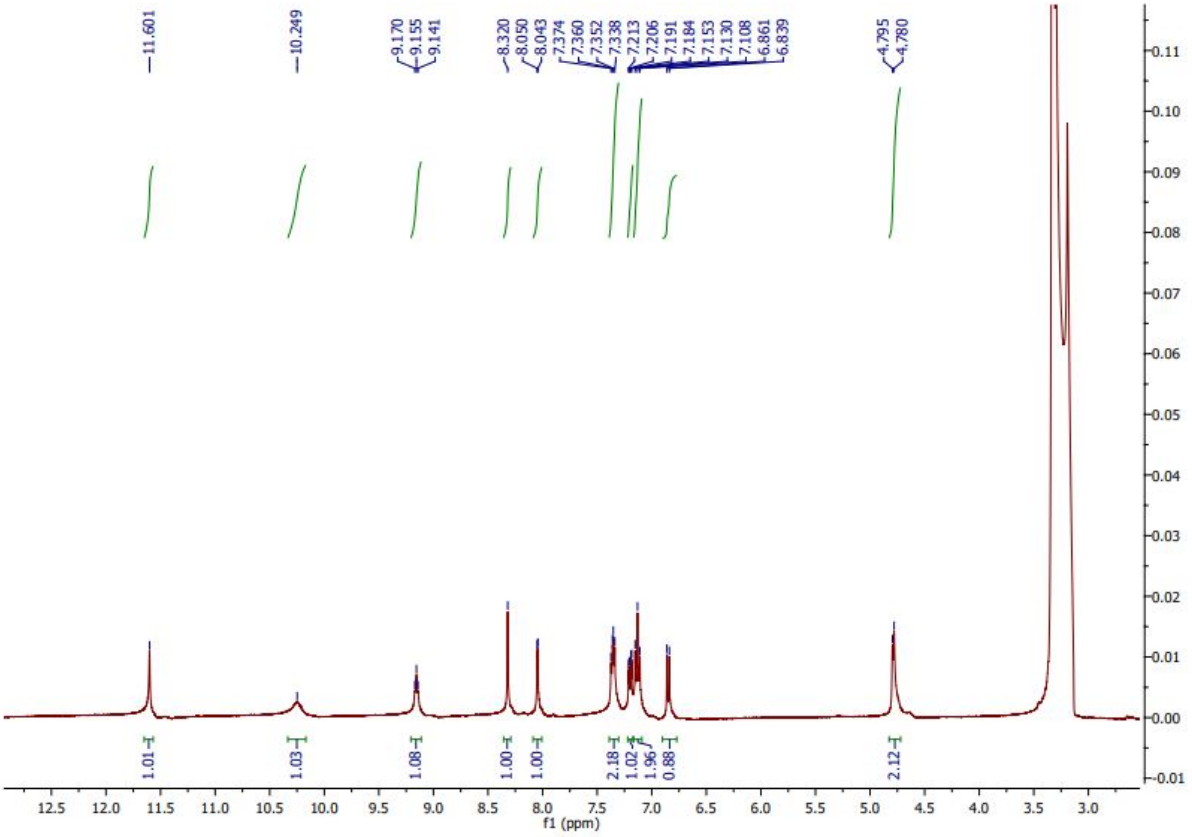

Figure S16: [1]HNMR Spectra of compound 3

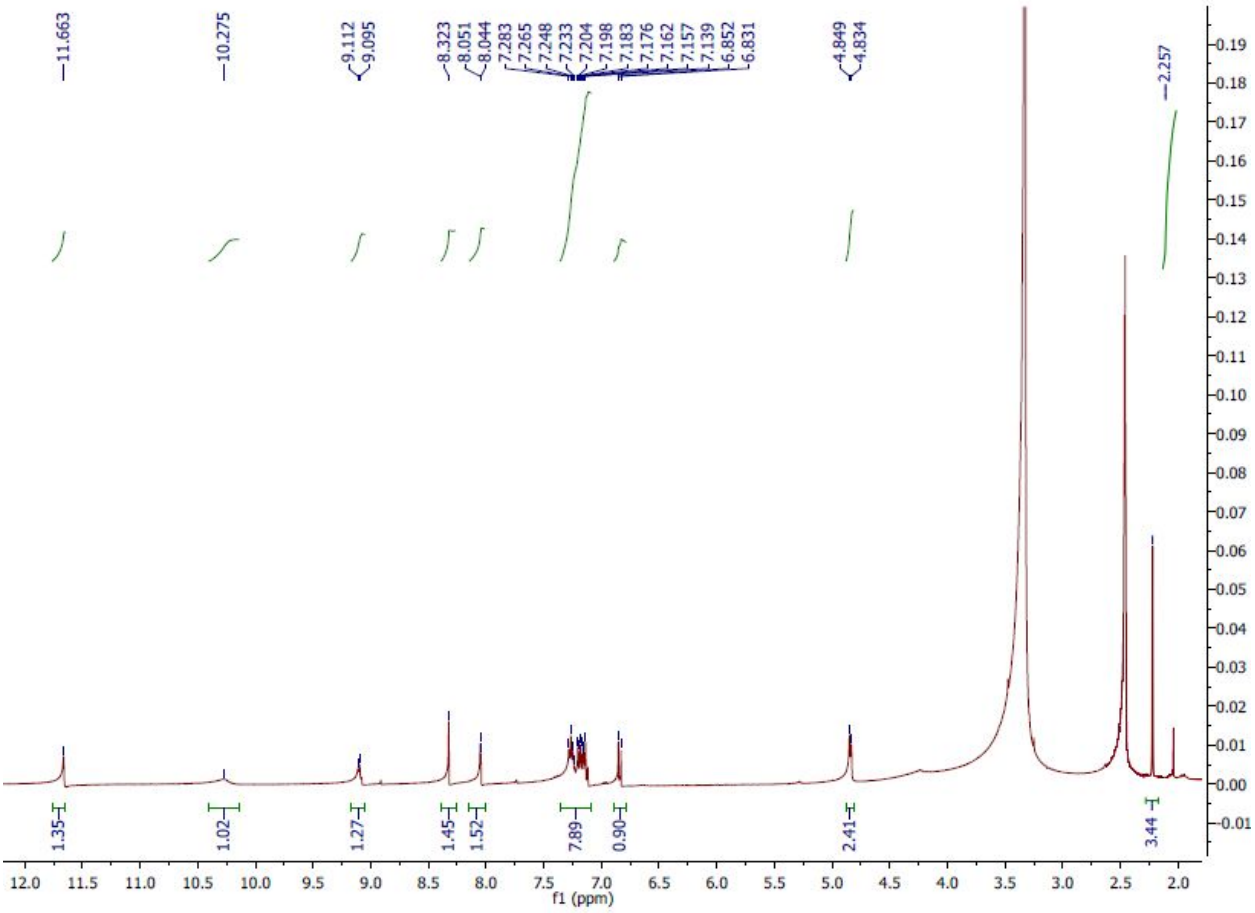

Figure S17: [1]HNMR Spectra of compound 4

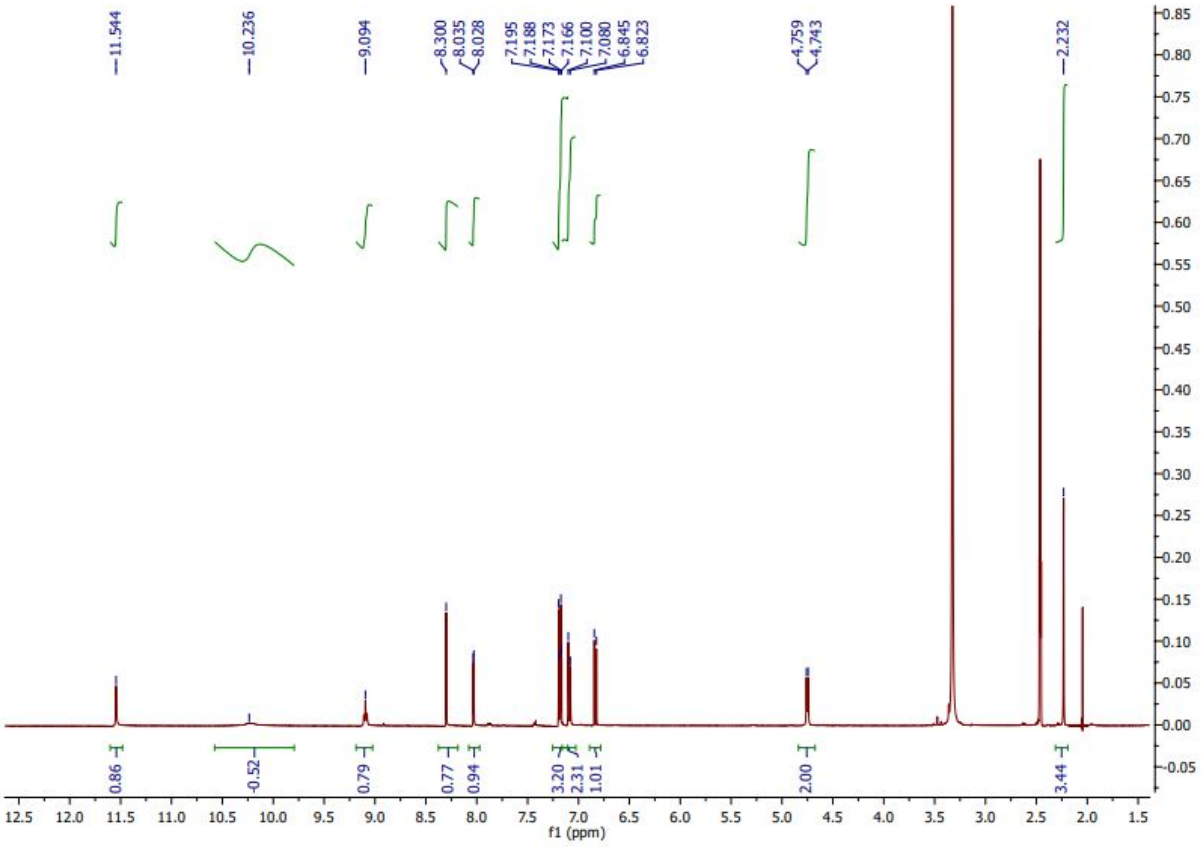

Figure S18: [1]HNMR Spectra of compound 5

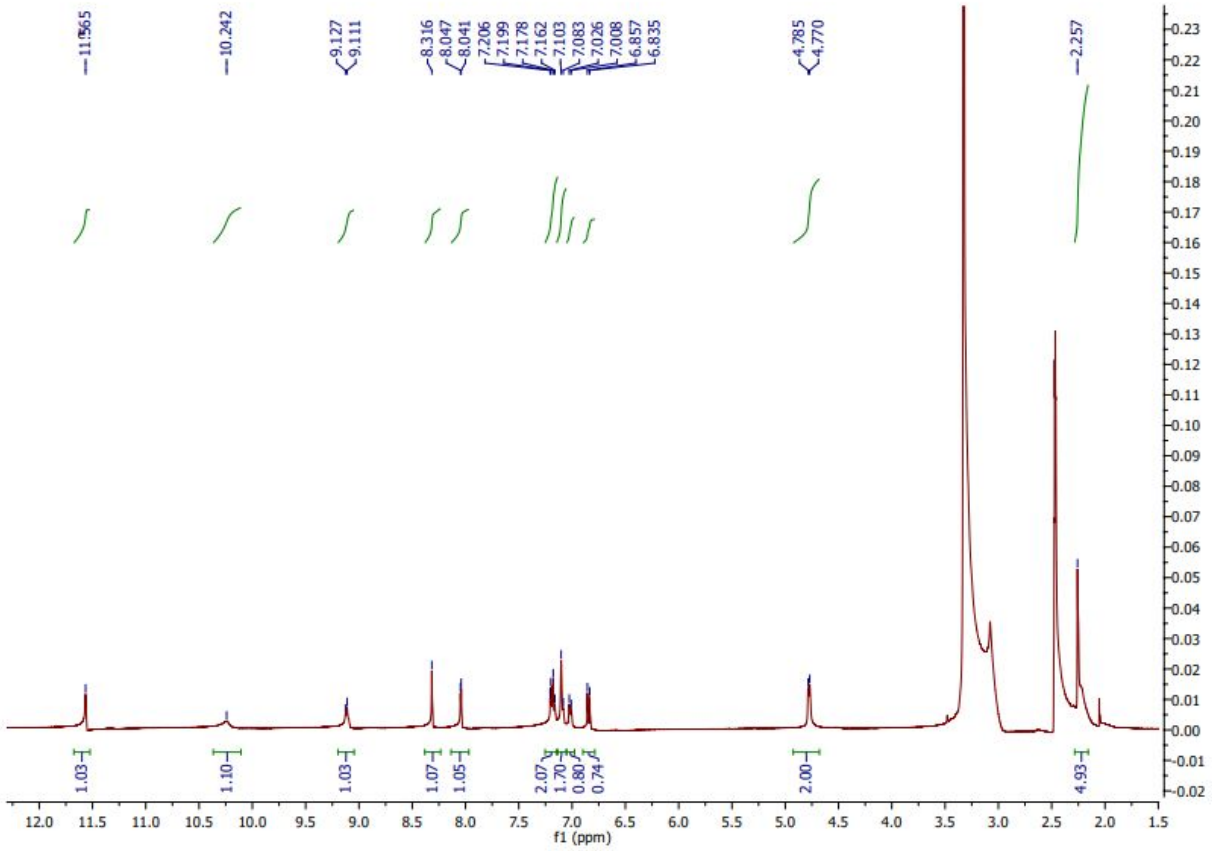

Figure S19: [1]HNMR Spectra of compound 6