Supplementary Information

Exploration of chromone-based thiosemicarbazone derivatives: SCXRD/DFT, spectral (IR, UV–Vis) characterization and quantum chemical analysis

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Table S1: Comparison of selected bond lengths (Å) and angles (°) of **3a** by using B3LYP/6-311+G(d,p)

Bond length			**Bond angel**		
	EXP	**DFT**		**EXP**	**DFT**
N6-N7	1.371	1.359	N7-N6-C14	120.1	122.5
N5-C8	1.447	1.464	N6-N7-C15	116.5	116.4
C8-C9	1.501	1.536	N5-C8-C9	106.4	109.6
C9-C10	1.506	1.537	N5-C8-C13	114.3	111.5
C10-C11	1.528	1.536	C8-N5-C14	124.4	125.7
C11-C12	1.475	1.536	C8-C9-C10	111.7	111.1
C12-C13	1.525	1.536	C9-C8-C13	110	111.5
C8-C13	1.537	1.54	C9-C10-C11	112.6	111.9
S1-C14	1.681	1.687	C10-C11-C12	110.5	111.3

N5-C14	1.331	1.343	C11-C12-C13	112.8	111.5
N6-C14	1.348	1.38	C12-C13-C8	108.1	111.2
N7-C15	1.276	1.29	S1-C14-N5	124.3	126.9
C15-C16	1.459	1.459	S1-C14-N6	119	118.2
C16-C17	1.386	1.404	N5-C14-N6	116.7	115
C17-C18	1.367	1.391	N7-C15-C16	120.2	122.7
C18-C19	1.361	1.397	C15-C16-C17	120.9	122.6
C19-C20	1.373	1.395	C15-C16-C21	121.4	119
C20-C21	1.382	1.398	C16-C17-C18	121.1	121.2
C16-C21	1.39	1.416	C17-C16-C21	117.7	118.3
O2-C21	1.381	1.37	C17-C18-C19	120.2	119.6
O2-C22	1.414	1.426	C18-C19-C20	120.9	120.5
C22-C23	1.492	1.506	C19-C20-C21	118.8	119.8
C23-C24	1.322	1.356	C20-C21-C16	121.3	120.5
C24-C25	1.425	1.438	C20-C21-O2	122.7	123.6
C25-C26	1.377	1.408	C16-C21-O2	116	115.9
C26-C27	1.366	1.387	C21-O2-C22	116.8	118.9
C27-C28	1.362	1.404	O2-C22-C23	110	108.2
C28-C29	1.363	1.391	C22-C23-C24	126.5	124.1
O3-C30	1.38	1.369	C22-C23-C31	113.2	115.7
C25-C30	1.374	1.406	C23-C24-C25	121.7	121.2
C29-C30	1.382	1.395	C24-C23-C31	120.3	120.2
C23-C31	1.463	1.218	C24-C25-C26	124.4	124.1
O3-C31	1.359	1.378	C24-C25-C30	118	117.6
O4-C31	1.201	1.461	C25-C26-C27	120.5	120.5
N37-N38	1.372	1.354	C26-C25-C30	117.6	118.3
36-C39	1.453	1.464	C26-C27-C28	120.9	120
C39-C40	1.506	1.54	C27-C28-C29	120.3	120.8
C40-C41	1.516	1.537	C28-C29-C30	118.3	118.7
C41-C42	1.499	1.536	O3-C30-C25	120.6	120.8
C42-C43	1.506	1.536	O3-C30-C29	117	117.4
C39-C44	1.508	1.538	C30-O3-C31	122.4	122.8
C43-C44	1.509	1.537	C25-C30-C29	122.3	121.8
S32-C45	1.67	1.382	C23-C31-O3	117	117.6
N36-C45	1.325	1.69	C23-C31-O4	124.1	125.1
N37-C45	1.349	1.34	O3-C31-O4	118.9	117.3
N38-C46	1.273	1.291	N38-N37-C45	120.4	123.3
C46-C47	1.456	1.461	N37-N38-C46	115.4	117.1
C47-C48	1.385	1.404	N36-C39-C40	112	111.3
C48-C49	1.365	1.392	N36-C39-C44	108.6	110
C49-C50	1.37	1.396	C39-N36-C45	125.7	124.9
C50-C51	1.371	1.397	C39-C40-C41	110.3	111.2
O33-C52	1.365	1.368	C40-C39-C44	111.4	111.3
C47-C52	1.389	1.417	C40-C41-C42	110.5	111.6
C51-C52	1.378	1.399	C41-C42-C43	111	111.2
O33-C53	1.409	1.422	C42-C43-C44	112.1	111.7
C53-C54	1.479	1.505	C39-C44-C43	112.1	111.1
C54-C55	1.334	1.354	S32-C45-N36	124.7	117.2
C55-C56	1.422	1.44	S32-C45-N37	119.7	115.8
C56-C57	1.391	1.408	N36-C45-N37	115.6	127
C57-C58	1.374	1.387	N38-C46-C47	121.6	122.2

C58-C59	1.37	1.403	C46-C47-C48	122.3	122
C59-C60	1.365	1.391	C46-C47-C52	119.6	119.6
C60-C61	1.385	1.368	C47-C48-C49	121.5	121.2
C56-C61	1.38	1.395	C48-C47-C52	118.1	118.4
O35-C61	1.377	1.407	C48-C49-C50	119.9	119.6
O35-C62	1.366	1.385	C49-C50-C51	119.8	120.6
C54-C62	1.45	1.213	C50-C51-C52	120.6	119.7
O34-C62	1.211	1.464	O33-C52-C47	115.7	115.7

EXP=experiment, DFT=density functional theory

Table S1: Continued…Comparison of selected bond lengths (Å) and angles (°) of **3a** by using B3LYP/6-311+G(d,p)

BOND ANGLE		
	EXP	**DFT**
O33-C52-C51	124.2	123.9
C52-O33-C53	117.9	119.3
C47-C52-C51	120.1	120.4
O33-C53-C54	108.9	108.5
C53-C54-C55	126.5	124.7
C53-C54-C62	113.9	114.7
C54-C55-C56	122.2	121
C55-C54-C62	119.5	120.6
C55-C56-C57	124.7	123.9
C55-C56-C61	117.6	117.8
C56-C57-C58	120.8	120.5
C57-C56-C61	117.7	118.4
C57-C58-C59	119.6	119.9
C58-C59-C60	121.6	120.7
C59-C60-C61	118	118.9
C60-C61-C56	122.2	117.5
C60-C61-O35	116.9	121
C56-C61-O35	120.9	122.7
C61-O35-C62	121.8	121.6
O35-C62-C54	118	118.2
O35-C62-O34	116.9	117.1
C54-C62-O34	125.1	124.8

EXP=experiment, DFT=density functional theory

Table S2: Comparison of selected bond lengths (Å) and angles (°) of **3b** by using B3LYP/6-311+G(d,p)

BOND LENGTH			**BOND ANGLE**		
	EXP	**DFT**		**EXP**	**DFT**
S1-25	1.682	1.675	S1-C25-N6	120.2	119.2
O2-8	1.375	1.364	S1-C25-N7	124.2	126.6
O2-16	1.375	1.391	C8-O2-C16	122.3	123.2
O3-16	1.207	1.202	O2-C8-C9	117.3	117.6
O4-17	1.435	1.435	O2-C8-C13	120.5	121
O4-18	1.364	1.366	O2-C16-O3	116.8	117.9
N5-N6	1.377	1.355	O2-C16-C15	117.4	116.4

N5-24	1.277	1.286	O3-C16-C15	125.8	125.8
N6-25	1.35	1.378	C17-O4-C18	120.6	119.1
N7-25	1.338	1.351	O4-C17-C15	106.3	107.5
N7-26	1.438	1.433	O4-C18-C19	125.5	123.7
C8-C9	1.376	1.393	O4-C18-C23	114.9	116
C8-C13	1.386	1.404	N6-N5-C24	115.5	117.4
C9-C10	1.382	1.389	N5-N6-C25	120	122.4
C10-C11	1.372	1.402	N5-C24-C23	120.2	122.1
C11-C12	1.369	1.385	N6-C25-N7	115.6	114.2
C12-C13	1.402	1.407	C25-N7-C26	123.2	125.8
C13-C14	1.439	1.437	N7-C26-C27	120.3	120.8
C14-C15	1.332	1.353	N7-C26-C31	118.8	118.6
C15-C16	1.45	1.468	C9-C8-C13	122.1	121.4
C15-C17	1.501	1.5	C8-C9-C10	118.9	118.9
C18-C19	1.392	1.397	C8-C13-C12	117.2	118.6
C18-C23	1.4	1.415	C8-C13-C14	117.8	117.4
C19-C20	1.376	1.394	C9-C10-C11	120.5	120.8
C20-C21	1.376	1.393	C10-C11-C12	120.1	119.8
C21-C22	1.378	1.389	C11-C12-C13	121.1	120.5
C22-C23	1.395	1.401	C12-C13-C14	125	124
C23-C24	1.465	1.46	C13-C14-C15	121.5	121.6
C26-C27	1.382	1.404	C14-C15-C16	120.3	120.4
C26-C31	1.375	1.393	C14-C15-C17	124.2	122.8
C27-C28	1.393	1.397	C16-C15-C17	115.6	116.8
C27-C32	1.507	1.506	C19-C18-C23	119.6	120.3
C28-C29	1.388	1.398	C18-C19-C20	119.9	120
C29-C30	1.371	1.396	C18-C23-C22	119.1	118.3
C29-C33	1.528	1.51	C18-C23-C24	120	119.5
C30-C31	1.387	1.392	C19-C20-C21	120.7	120.5

EXP=experiment, DFT=density functional theory

Table S2: Continued…Comparison of selected bond lengths (Å) and angles (°) of **3b** by using B3LYP/6-311+G(d,p

BOND ANGLE		
	EXP	**DFT**
C20-C21-C22	120.1	119.5
C21-C22-C23	120.4	121.5
C22-C23-C24	120.9	122.2
C27-C26-C31	120.9	120.5
C26-C27-C28	117.5	117.7
C26-C27-C32	120.3	121.6
C26-C31-C30	120.3	120.6
C28-C27-C32	122.2	120.7
C27-C28-C29	122.7	122.7
C28-C29-C30	118	118.1
C28-C29-C33	120.8	120.7
C30-C29-C33	121.2	121.2
C29-C30-C31	120.7	120.4

EXP=experiment, DFT=density functional theory

Table S3: Natural bond orbital (NBO) analysis of compound**3a** by using B3LYP/6-311+G (d, p).

Donor(i)	Type	Acceptor(j)	Type	E(2)[a] [kJ/mol]	E(J)E(i)[b](a.u)	F(I,j)[c](a.u)
C43-C44	π	O4-C56	π*	25.15	0.28	0.077
C37-C39	π	C33-C35	π*	21.85	0.29	0.072
C47-C49	π	C51-C53	π*	20.86	0.28	0.069
C30-C31	π	N9-C28	π*	18.52	0.26	0.064
C47-C49	π	C46-C55	π*	18.04	0.27	0.065
C51-C53	π	C47-C49	π*	17.41	0.29	0.064
C46-C55	π	C51-C53	π*	16.47	0.29	0.064
C46-C55	π	C43-C44	π*	15.52	0.3	0.065
C43-C44	π	C46-C55	π*	11.66	0.3	0.056
N9-C28	π	C30-C31	π*	7.52	0.37	0.051
O4-C56	π	C43-C44	π*	5.24	0.41	0.043
C43-C44	π	C40-H41	∂*	1.32	0.75	0.029
O4-C56	π	O4-C56	π*	1.01	0.38	0.019
N9-C28	π	N9-C28	π*	0.87	0.34	0.016
C43-C44	π	O2-C40	∂*	0.77	0.57	0.02
C37-C39	π	C37-C39	π*	0.6	0.28	0.012
N5-H6	∂	S1-C27	∂*	5.51	0.94	0.064
C35-C37	∂	O2-C39	∂*	4.85	1.06	0.064
C40-H42	∂	C43-C44	π*	4.42	0.55	0.046
C37-C39	∂	C30-C39	∂*	3.99	1.26	0.063
C47-H48	∂	C49-C51	∂*	3.61	1.09	0.056
C46-C55	∂	C46-C47	∂*	3.29	1.27	0.058
C21-H22	∂	C15-C18	∂*	3.08	0.87	0.046
C44-C46	∂	C43-C44	∂*	2.99	1.31	0.056
C10-H11	∂	C12-H13	∂*	2.64	0.93	0.044
C31-C33	∂	C33-C35	∂*	2.49	1.27	0.05
C31-C33	∂	C35-H36	∂*	2.32	1.18	0.047
C30-C39	∂	C37-H38	∂*	2.04	1.17	0.044
C37-C39	∂	C35-H36	∂*	1.99	1.19	0.044
C40-H41	∂	C43-C44	π*	1.71	0.55	0.028
C53-H54	∂	C51-C53	∂*	1.14	1.11	0.032
N5-H6	∂	C10-H11	∂*	1.09	1.13	0.031
C37-H38	∂	C35-C37	∂*	1.02	1.11	0.03
C31-H32	∂	C30-C31	∂*	0.99	1.09	0.029
C53-H54	∂	C53-C55	∂*	0.81	1.09	0.027
C10-C24	∂	C21-C24	∂*	0.66	0.98	0.023
N7-N9	∂	N9-C28	∂*	0.59	1.47	0.026
C12-C15	∂	C12-H13	∂*	0.51	1.01	0.02

C40-H42	∂	C40-C43	∂*	0.5	0.94	0.019
O3	LP(2)	O4-C56	π*	41.09	0.34	0.106
O4	LP(2)	O3-C56	∂*	35.24	0.6	0.131
O3	LP(2)	C46-C55	π*	28.86	0.35	0.094
O2	LP(2)	C37-C39	π*	25.21	0.35	0.09
O4	LP(2)	C43-C56	∂*	15.96	0.71	0.097
S1	LP(2)	N5-C27	∂*	10.33	0.68	0.076
N9	LP(1)	N7-H8	∂*	8.57	0.83	0.076
O3	LP(1)	C46-C55	∂*	6.92	1.08	0.077
O2	LP(2)	C40-H41	∂*	5.02	0.79	0.058
S1	LP(1)	N5-C27	∂*	3.46	1.18	0.058
S1	LP(2)	C10-H11	∂*	1.05	0.66	0.024
O4	LP(2)	O2-C40	∂*	0.55	0.55	0.016
S1	LP(1)	N7-H8	∂*	2.5	1.11	0.021

[a] E(2) means energy of hyper conjugative interaction (stabilization energy).
[b] Energy difference between donor and acceptor i and j NBO orbitals.
[c] F(i,j) is the Fock matrix element between i and j NBO orbitals.

Table S4: Natural bond orbital (NBO) analysis of investigated compound **3b**by usingB3LYP/6-311+G (d, p).

Donor(i)	Type	Acceptor(j)	Type	E(2)[a] [kJ/mol]	E(J)E(i)[b](a.u)	F(I,j)[c](a.u)
C44-C45	π	C40-C47	π*	23.27	0.28	0.072
C34-C36	π	N5-C37	π*	18.02	0.25	0.063
C27-C28	π	C30-C32	π*	14.96	0.44	0.072
C34-C36	π	C30-C32	π*	12.22	0.42	0.064
C20-C22	π	C10-C19	π*	11.31	0.3	0.055
C27-C28	π	C34-C36	π*	7.87	0.6	0.062
C20-C22	π	O4-C24	∂*	6.37	0.56	0.056
O3-C23	π	C20-C22	π*	4.96	0.41	0.042
C41-C42	π	C49-H50	∂*	2.91	0.65	0.043
C41-C42	π	C49-H52	∂*	2.15	0.66	0.037
C20-C22	π	C24-H26	∂*	1.26	0.67	0.027
C10-C19	π	C10-C19	π*	1.12	0.28	0.016
N5-C37	π	N5-C37	π*	0.89	0.34	0.016
C27-C28	π	C27-C28	π*	0.62	0.29	0.012
C53-H56	∂	C53-H55	∂*	42.91	4.22	0.382
C53-H56	∂	C34-C36	π*	18.31	0.81	0.12
C53-H56	∂	C30-C32	π*	11.96	0.65	0.086
C44-C53	∂	C53-H56	∂*	10.15	3.13	0.159
C44-C53	∂	C34-C36	π*	6.35	0.95	0.077
N8-H9	∂	S1-C39	∂*	5.85	0.95	0.067
C53-H54	∂	C37-H38	∂*	4.96	1.17	0.068
C53-H54	∂	C36-C37	∂*	3.92	1.11	0.059

C15-C17	∂	C17-C19	∂*	2.99	1.26	0.055
C53-H54	∂	C44-C45	π*	2.02	0.54	0.032
C42-C44	∂	C42-H43	∂*	1.01	1.15	0.031
C40-C47	∂	C47-H48	∂*	0.99	1.16	0.03
N8-C39	∂	C40-C47	π*	0.58	0.89	0.022
C44-C53	∂	C40-C47	∂*	0.5	1.24	0.022
O3	LP(2)	O2-C23	∂*	37.01	0.57	0.131
O3	LP(2)	C22-C23	∂*	15.67	0.7	0.096
N5	LP(1)	N6-H7	∂*	8.35	0.77	0.072
O2	LP(1)	C22-C23	∂*	4.32	0.99	0.059
S1	LP(1)	N8-C39	∂*	3.87	1.16	0.06
S1	LP(2)	C10-H11	∂*	1.55	0.66	0.029
O2	LP(1)	C40-H41	∂*	1.12	0.99	0.030
O2	LP(1)	C40-H42	∂*	1.20	0.99	0.031
O2	LP(1)	O3-C23	∂*	2.07	1.17	0.044
N5	LP(1)	C36-C37	∂*	1.74	1.02	0.038
O4	LP(1)	C22-C24	∂*	1.32	0.97	0.032
O2	LP(1)	C10-C11	∂*	0.92	1.1	0.028
S1	LP(2)	C40-C47	π*	0.77	0.22	0.013
N5	LP(1)	S1-C39	∂*	0.57	0.7	0.018

[a] E(2) means energy of hyper conjugative interaction (stabilization energy).
[b] Energy difference between donor and acceptor i and j NBO orbitals.
[c] F(i,j) is the Fock matrix element between i and j NBO orbitals.

Table S5: Calculated vibrational frequencies of **3a.**

[a]***Freq (unscaled)***	***Freq (scaled)***	[a]I_{IR}	**Vibrational assignments**
3575	3460.243	32	υN-H
3546	3432.173	184	υN-H
3532	3418.623	31	υN-H
3228	3124.381	7	υ (s)C-H_{Ben}
3218	3114.702	16	υ(as)+(s)C-H_{Ben}
3216	3112.766	12	υ(as)+(s)C-H_{Ben}
3205	3102.12	10	υ(as)+(s)C-H_{Ben}
3199	3096.312	8	υ(s)+(as)C-H_{Ben}
3124	3023.72	17	υ C-H
3107	3007.265	25	υ C-H
3100	3000.49	17	υ(as)C-H_{Cyh}
3099	2999.522	43	υ(as)C-H_{Cyh}
3095	2995.651	2	υ(as)C-H_{CH2}
3083	2984.036	27	υ(s)+(as)C-H_{Cyh}
3079	2980.164	28	υ(as)C-H_{Cyh}
3076	2977.26	42	υ(as)C-H_{Cyh}
3072	2973.389	80	υ(as)C-H_{Cyh}
3069	2970.485	78	υ(s)+(as)C-H_{Cyh}

3032	2934.673	34	υ(s) C-H_{Cyh}
3027	2929.833	27	υ(s) C-H_{Cyh}
3027	2929.833	19	υ(s)C-H_{CH2}
3020	2923.058	24	υ(s) C-H_{Cyh}
2996	2899.828	15	υ(s) C-H_{Cyh}
1806	1748.027	508	υC=$O_{H\text{-}Pyran}$ + υ (C=C-C=C_{Ben})
1783	1725.766	750	υC=$O_{H\text{-}Pyran}$ + υ (C=C-C=C_{Ben}) + ρN-H
1694	1639.623	29	υ (C=C-C=C_{Ben}) + υ C=$C_{H\text{-}Pyran}$ + w C-H_{CH2}
1668	1614.457	34	υ (C=C-C=C_{Ben}) + δ C-H_{Ben} + υC=N + ρC-H
1663.	1609.618	88	υ (C=C-C=C_{Ben}) + (δ + ρ)C-H_{Ben}
1663.	1609.618	58	υ (C=C-C=C_{Ben}) + δ C-H_{Ben} + υC=N + ρC-H
1626	1573.805	24	υ (C=C-C=C_{Ben}) + δ C-H_{Ben} + υC=N
1620	1567.998	37	υ (C=C-C=C_{Ben}) + (δ + ρ)C-H_{Ben} + υ C=$C_{H\text{-}Pyran}$
1578	1527.346	539	υ C-N + ρN-H
1571	1520.571	772	υ C-N + ρN-H
1540	1490.566	336	υC=S + υ C-N + ρN-H + υ N-N
1532	1482.823	48	υC=S + ρN-H + δC-H_{CH2}
1531	1481.855	60	υC=S + υ C-N + ρN-H + δC-H_{CH2}
1528	1478.951	179	υC=S + υ C-N + ρN-H + δC-H_{CH2}
1499	1450.882	96	δC-H_{Cyh} +ρC-H_{Ben} + υC-O
1497	1448.946	21	υ (C=C-C=C_{Ben}) + ρC-H_{Ben} + υC-$O_{H\text{-}Pyran}$
1494	1446.043	39	ρC-H_{Ben} + υC-O +δC-H_{CH2}
1450	1403.455	51	υ C=S + υ C-N + ρ N-H + w C-H_{CH2}
1442	1395.712	43	υC-$C_{H\text{-}Pyran}$ + w C-H_{CH2} + υ C-O
1394	1349.253	28	(w + τ)C-H_{Cyh}
1377	1332.798	136	w C-H_{Cyh} + ρN-H
1374	1329.895	151	w C-H_{Cyh} + ρN-H + υ C-N
1327	1284.403	74	ρC-H_{Ben} + υ C-O
1301	1259.238	148	(w + τ)C-H_{Cyh}
1291	1249.559	301	(ρ + δ)C-H_{Ben} + υC-O
1284	1242.784	93	w C-H_{Cyh} + ρN-H
1243	1203.1	214	214 υC=S + υ C-N + υ N-N
1222	1182.774	153	υC=S + υ C-N + ρN-H + τ C-H_{Cyh}
1211	1172.127	147	(w + τ)C-H_{Cyh} + υC=S + υ C-N + ρN-H
1198	1159.544	667	υC=$O_{H\text{-}Pyran}$+δC-H_{Ben}
1136	1099.534	199	υC=S + υ C-N + ρN-H
1135	1098.567	90	(ρ + δ)C-H_{Ben}
1076	1041.46	30	(ρ + δ)C-H_{Ben} + υC=$O_{H\text{-}Pyran}$
1039	1005.648	50	w C-H_{Cyh}
1036	1002.744	112	υC=$O_{H\text{-}Pyran}$
969	937.8951	19	(w + τ)C-H_{Ben} + γC-$H_{H\text{-}Pyran}$
940	909.826	13	(w + τ)C-H_{Ben} + γC-$H_{H\text{-}Pyran}$
902	873.0458	24	υC=S + ρN-H + τ C-H_{Cyh}
843	815.9397	27	υC-O
800	774.32	9	ρC-H_{Cyh} + υC=S
776	751.0904	42	w 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,5,6-dihydro-2H-Pyran-2-one = H-Pyran, Cyclohexane = Cyh, Ben=benzene ring. [a]scaling factor= 0.9679 [1]

Table S6: Calculated vibrational frequencies for **3b** by B3LYP/6-311+G(d,p)

[a]*Freq (unscaled)*	[a]*Freq (scaled)*	[a]I_{IR}	**Vibrational assignments**
3540	3426.366	86	υ N-H
3520	3407.008	21	υ N-H
3201	3098.248	12	υ(s)+ υ(as) C-H_{Ben}
3187	3084.697	13	υ(s)+ υ(as) C-H_{Ben}
3106	3006.297	22	υ(s)+ υ(as) C-H_{CH3}
3099	2999.522	25	υ C-H
3082	2983.068	6	υ(as) C-H_{CH2}
3075	2976.293	18	υ(s)+ υ(as) C-H_{CH3}
3029	2931.769	22	υ(s) C-H_{CH3}
3023	2925.962	35	υ(s) C-H_{CH2}
3021	2924.026	40	υ(s) C-H_{CH3}
1797	1739.316	585	υ C=O
1676	1622.2	79	υ C=C + υ (C=C-C=C_{Ben}) + υ C-H
1656	1602.842	49	υ C=N + υ(ρ) C-H
1647	1594.131	81	υ(δ)+ υ(ρ) C-H_{Ben} + υ (C=C-C=C_{Ben})
1612	1560.255	35	υ C=N + υ(ρ) + (δ) C-H_{Ben}
1604	1552.512	47	υ (C=C-C=C_{Ben}) + υ(ρ) + (δ) C-H_{Ben}
1546	1496.373	809	υ(ρ) N-H + υ C-N
1535	1485.727	38	υ(δ)+ υ(τ) C-H_{CH3} + υ(ρ)N-H + υ(ρ)C-H_{Ben}
1527	1477.983	51	υ C=S + υ C-N + υ(ρ) N-H
1513	1464.433	128	υ C=S + υ(ρ) N-H + υ(δ)C-H_{CH2}
1501	1452.818	64	υ(δ)+ υ(τ) C-H_{CH3} + υ(δ)C-H_{CH2}
1485	1437.332	40	υ(ρ) C-H_{Ben} + υ (C=C-C=C_{Ben})
1483	1435.396	84	υ(δ) + υ(τ) C-H_{CH3} + υ(ρ) C-H_{Ben}
1424	1378.29	41	υ(w) C-H_{CH2} + υ(ρ) C-H + υ(ρ) N-H
1416	1370.546	14	υ(w) C-H_{CH3}
1348	1304.729	238	υ(ρ) N-H + υ (C=C-C=C_{Ben}) + υ C-H
1315	1272.789	65	υ(ρ) N-H + υ(ρ) C-H_{Ben}
1312	1269.885	87	υ(ρ) N-H + υ(ρ) C-H_{Ben}
1279	1237.944	58	υ C-N + υ (C=C-C=C_{Ben}) + υ(ρ) N-H
1270	1229.233	62	υ(τ)C-H_{CH2}
1258	1217.618	332	υ(τ)C-H_{CH2} + υ (C=C-C=C_{Ben}) + υ C-C + υ C-O
1229	1189.549	73	υ C=S + υ(δ)+ υ(ρ) C-H_{Ben} + υ(ρ) N-H
1206	1167.287	400	υ C-N + υ(ρ) N-H + υ C=S

1200	1161.48	116	υ(ρ) C-H_{Pyran} + υ(δ) C-H_{Ben} + υ C-C
1106	1070.497	167	υ N-N + υ(ρ) C-H + υ C-O
1055	1021.135	41	υ(δ)+ υ(ρ) C-H_{Ben} + υ (C=C-C=C_{Ben}) + υ C-O_{Pyran}
1028	995.0012	138	υ C-O + υ(γ)C-H_{Pyran}
1022	989.1938	40	υ C-O_{Pyran} + υ(ρ)C-H_{CH2}
973	941.7667	32	υ(τ) + υ(*w*) C-H_{Ben}
952	921.4408	21	υ(τ) + υ(*w*) C-H_{Ben} + υ(γ)C-H
952	921.4408	14	υ(τ) + υ(*w*) C-H_{Ben} + υ(γ)C-H
877	848.8483	21	υ(τ) + υ(*w*) C-H_{Ben}
769	744.3151	63	υ(*w*) C-H_{Ben}
765	740.4435	56	υ(*w*) C-H_{Ben} + υ(τ)C-H_{CH3}
763	738.5077	63	υ(*w*) C-H_{Ben}
657	635.9103	14	β(C=C-C=C_{Ben})
622	602.0338	18	β(C=C-C=C_{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,3,6-dihydro-2H-Pyran = Pyran [a]scaling factor= 0.9679 [1]

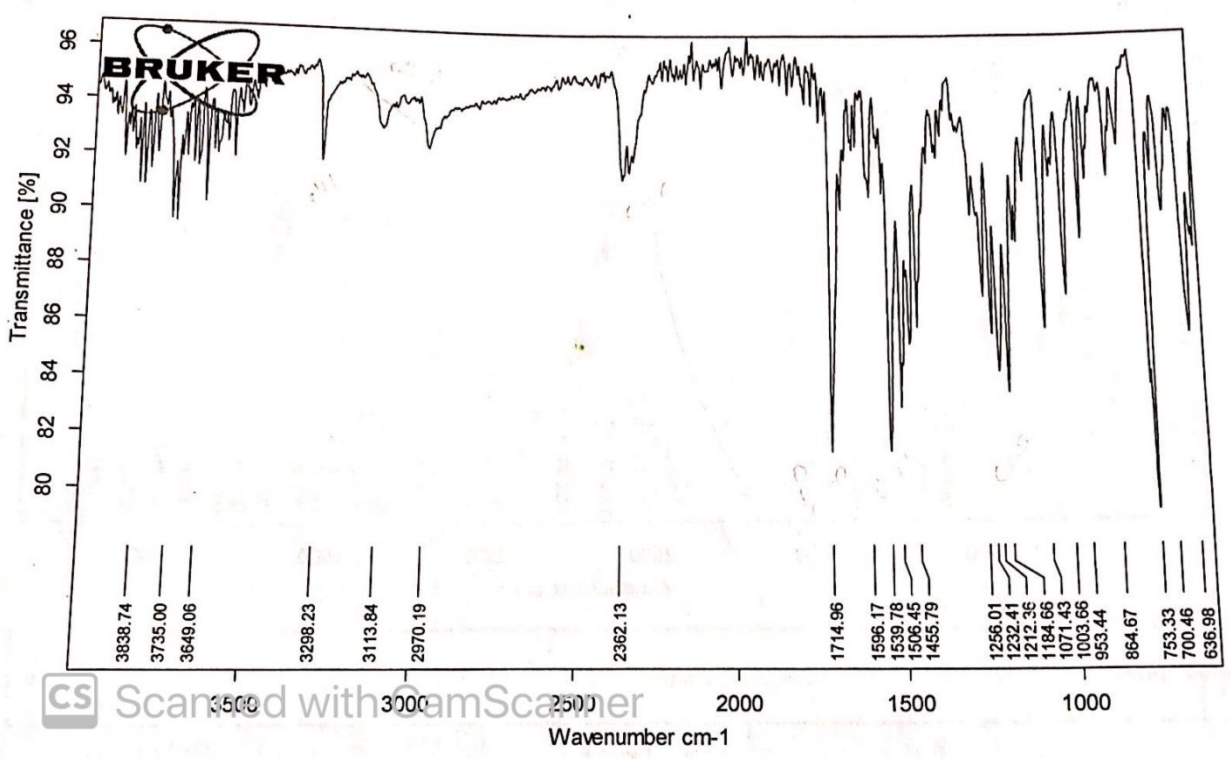


Figure S1: Experimental vibrational frequencies for **3a**

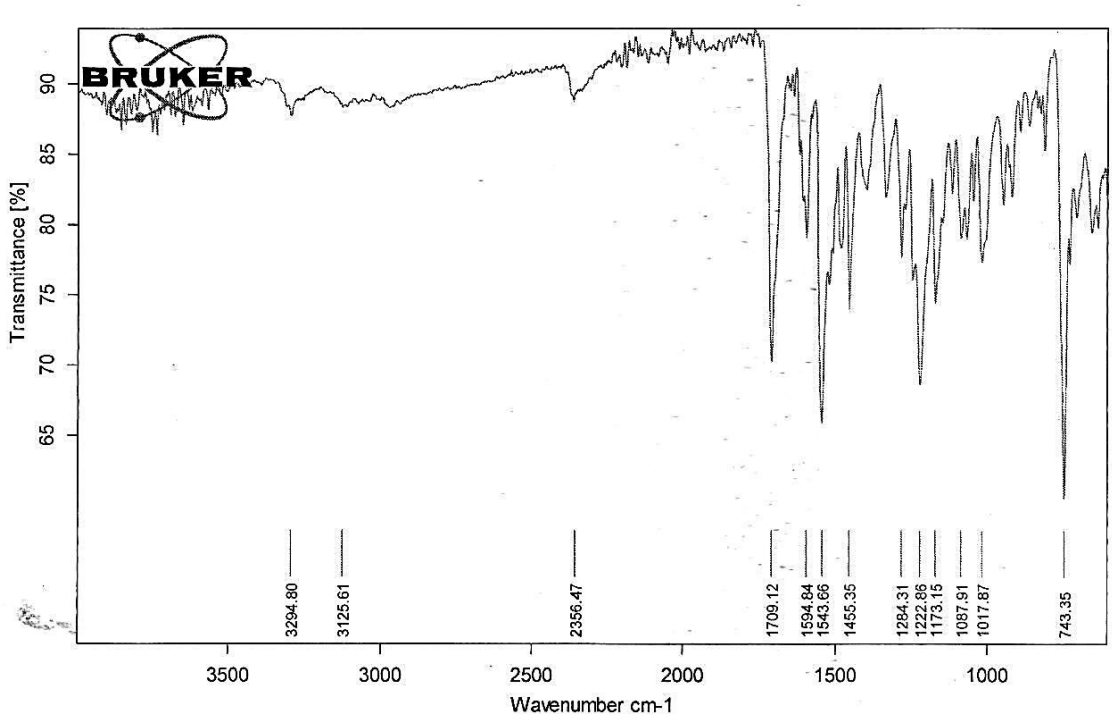


Figure S2: Experimental vibrational frequencies for**3b.**

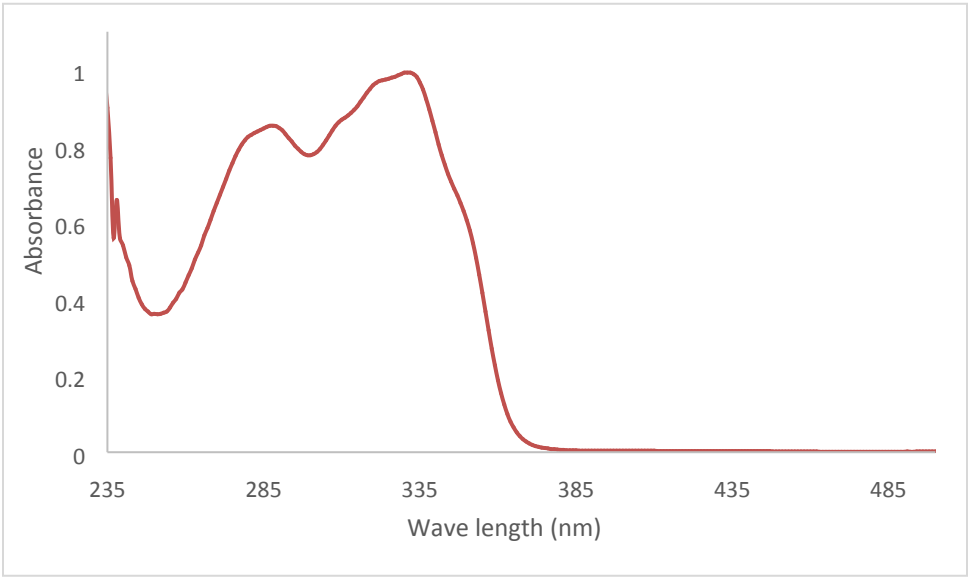


Figure S3:UV-Vis spectra of **3a** molecule.

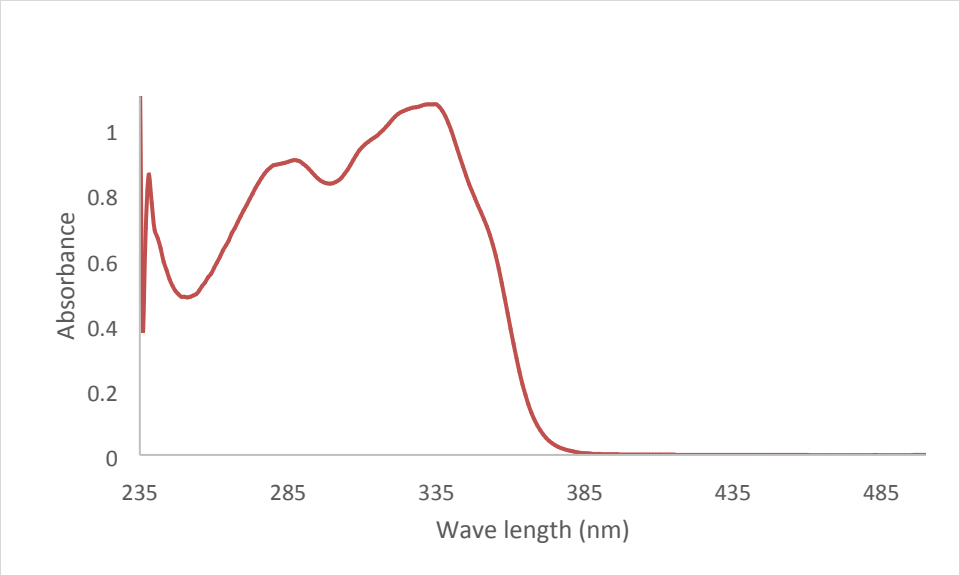


Figure S4: UV-Vis spectra of **3b** molecule.

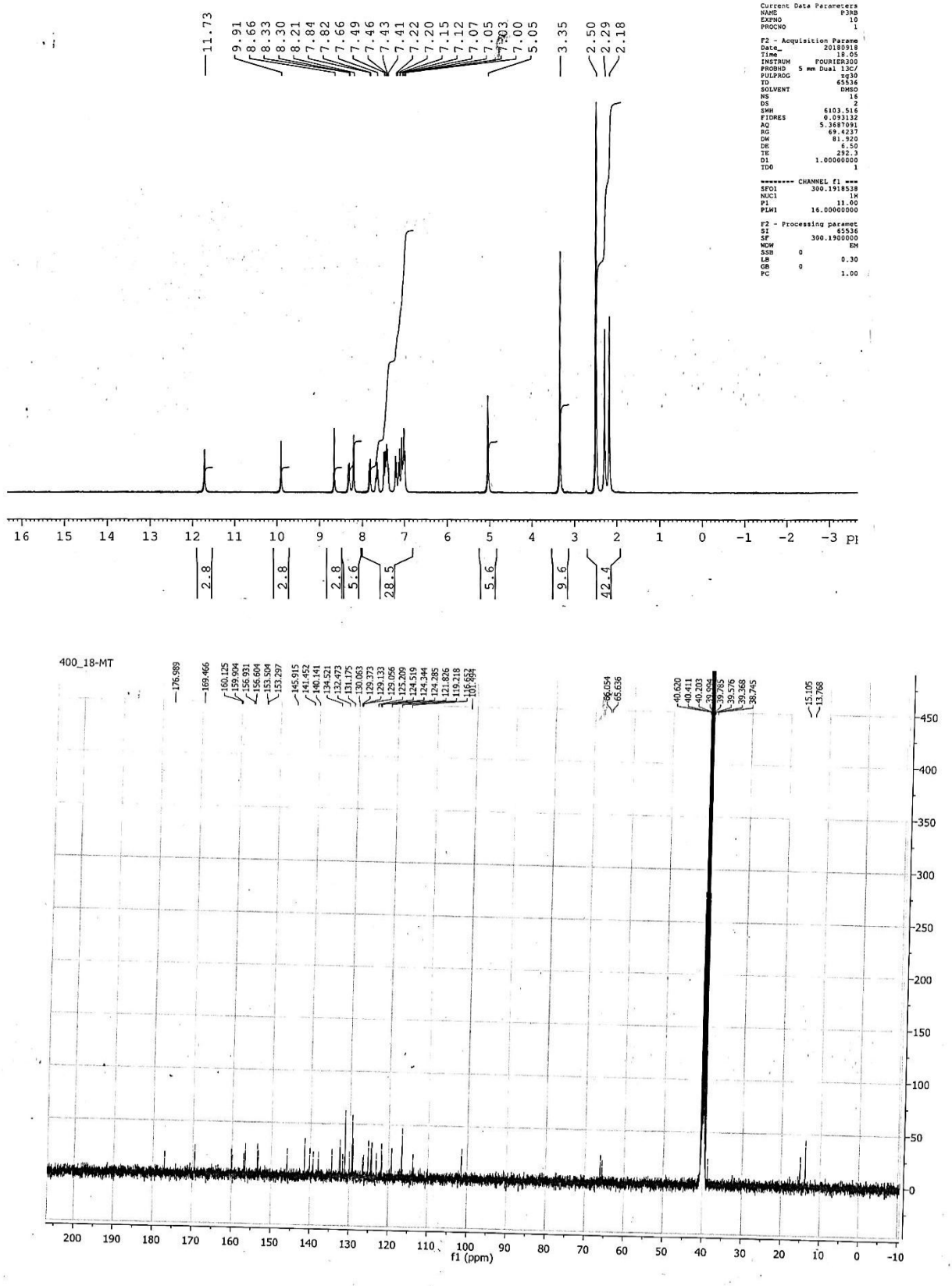
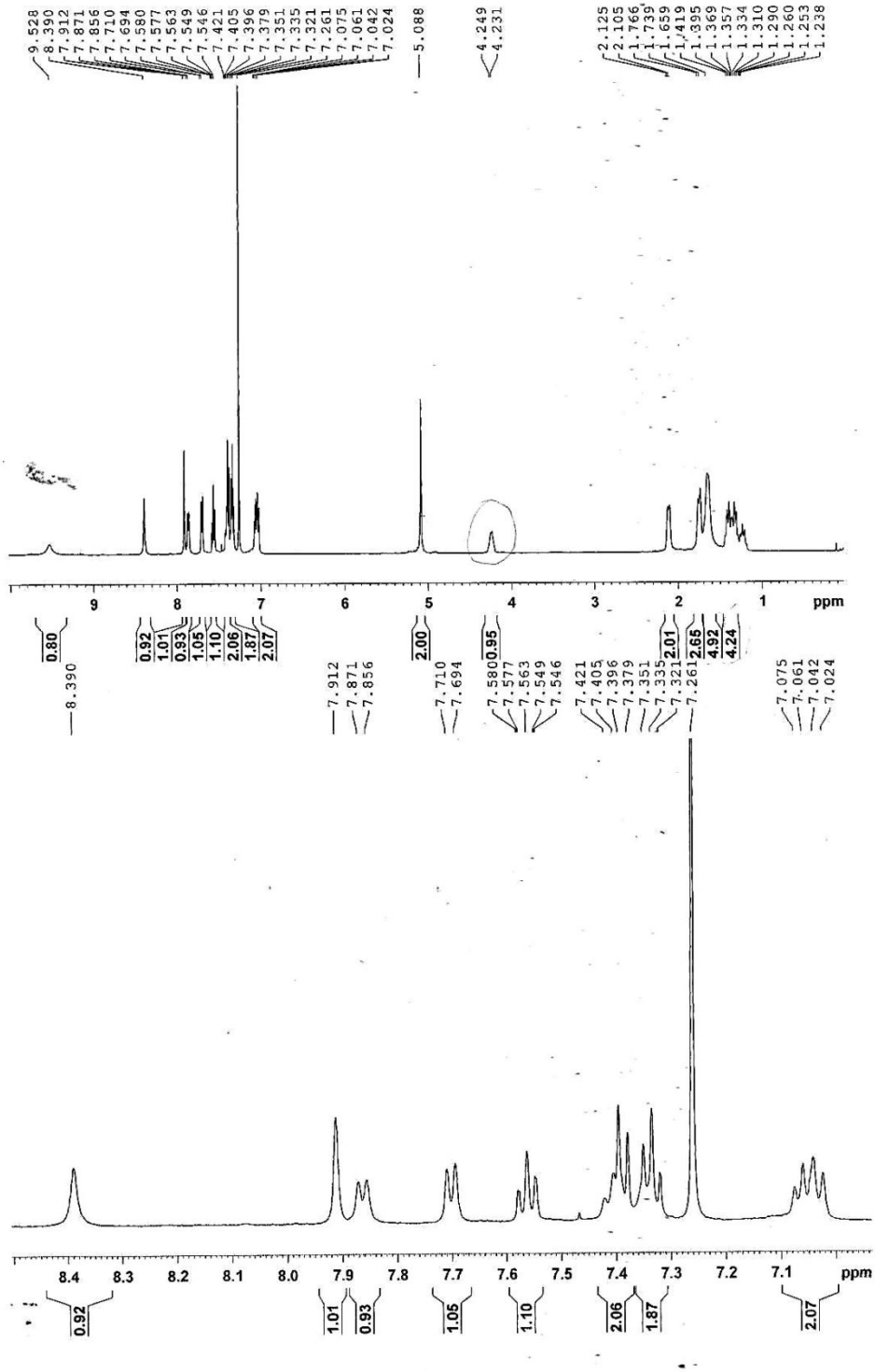


Figure S5: NMR spectra of **3a** molecule.

HF-RAFIQ-20180704-03H-RB-3



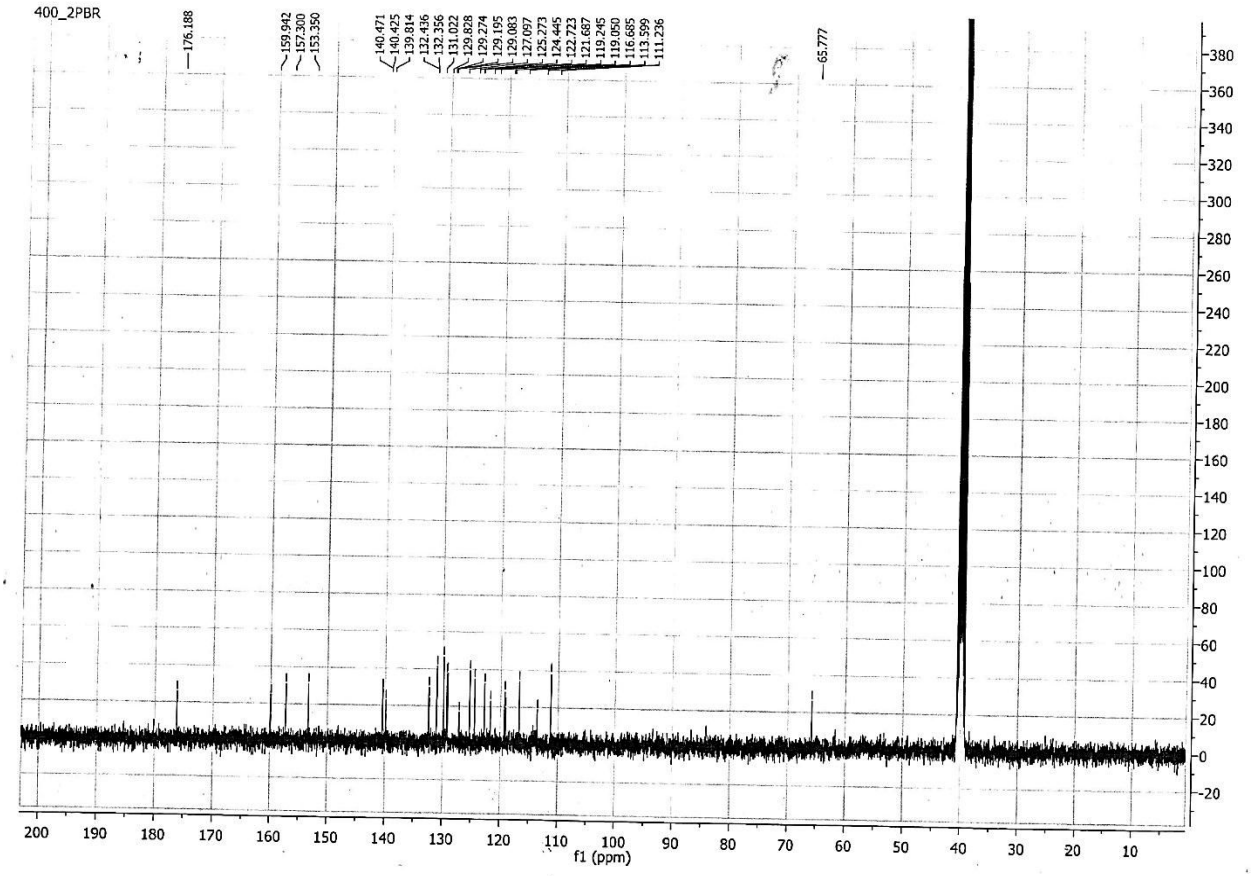


Figure S6: NMR spectra of **3b** molecule