Electronic Supporting Information

Polar Stacking of Dipole Parallel-Aligned Monolayers of Unsymmetrical 1,4-Diphenyl-1,3-Butadienes Creates Nonlinear Optical Materials. Insights from Experiments Guide Structure Assignments

Harmeet Bhoday,[a] Justin Nulsen,[a] Steven P. Kelley,[b] and Rainer Glaser[a,]*

[a] Department of Chemistry, Missouri University of Science and Technology, Rolla, Missouri 65409, USA. Email: glaserr@mst.edu

[b] Department of Chemistry, University of Missouri, Columbia, Missouri 65211, USA

Table of Contents

Table S1. Longitudinal Offset and Characteristic Parameters of Arene-Arene Interactions[a]

T-Cont.[b]	Parameter	Butadienes						T-Cont.[b]	Parameter	Azines
		BD-**1**	BD-**2**	BD-**3**	BD-**4**	Avg.[c]	SD[c]			AZ-**4**
fe	$d(\Sigma_{PhY}\cdots H_o)$	2.95	2.91	2.85	2.81	2.86	0.04	ef	$d(H_m\cdots\Sigma_{PhY})$	2.99
fe	$\angle(C_i\cdots\Sigma_{PhY}\cdots H_o)$	93.7	90.4	89.3	90.5	90.1	0.54	ef	$\angle(H_m\cdots\Sigma_{PhY}\cdots C_i)$	87.6
fe	$\angle(\Pi_{PhY}\cdots\Pi_{PhY})$	58.6	56.9	53.8	53.3			ef	$\angle(\Pi_{PhY}\cdots\Pi_{PhY})$	57.0
fe	$d(\Sigma_{PhOMe}\cdots H_m)$	2.72	2.83	2.85	2.82	2.83	0.01	fe	$d(\Sigma_{PhOMe}\cdots H_m)$	2.83
fe	$\angle(C_i\cdots\Sigma_{PhOMe}\cdots H_m)$	86.5	89.6	91.2	88.3	89.7	1.19	fe	$\angle(C_i\cdots\Sigma_{PhOMe}\cdots H_m)$	85.8
fe	$\angle(\Pi_{PhOMe}\cdots\Pi_{PhOMe})$	61.4	61.7	59.7	59.5			fe	$\angle(\Pi_{PhOMe}\cdots\Pi_{PhOMe})$	63.9
ef’	$d(\Sigma_{PhY}\cdots H_m)$	2.86	2.91	2.90	2.94	2.92	0.02	fe’	$d(\Sigma_{PhY}\cdots H_o)$	2.70
ef’	$\angle(C_i\cdots\Sigma_{PhY}\cdots H_m)$	84.4	89.0	89.9	89.1	89.3	0.40	fe’	$\angle(C_i\cdots\Sigma_{PhY}\cdots H_o)$	92.8
ef’	$\angle(\Pi_{PhY}\cdots\Pi_{PhY})$	58.6	56.9	53.8	53.3			fe’	$\angle(\Pi_{PhY}\cdots\Pi_{PhY})$	57.0
ef’	$d(\Sigma_{PhOMe}\cdots H_o)$	2.87	2.91	2.89	2.90	2.90	0.01	ef’	$d(H_o\cdots\Sigma_{PhY})$	2.81
ef’	$\angle(C_i\cdots\Sigma_{PhOMe}\cdots H_o)$	94.1	90.1	89.3	91.6	90.3	0.95	ef’	$\angle(H_o\cdots\Sigma_{PhY}\cdots C_i)$	94.0
ef’	$\angle(\Pi_{PhOMe}\cdots\Pi_{PhOMe})$	61.4	61.7	59.7	59.5			ef’	$\angle(\Pi_{PhOMe}\cdots\Pi_{PhOMe})$	63.9

[a]Distances in Å and angles in degree.
[b]T-contacts defined in Figure 1.
[c]Averages and standard deviations for the non-fluorine halogen species.

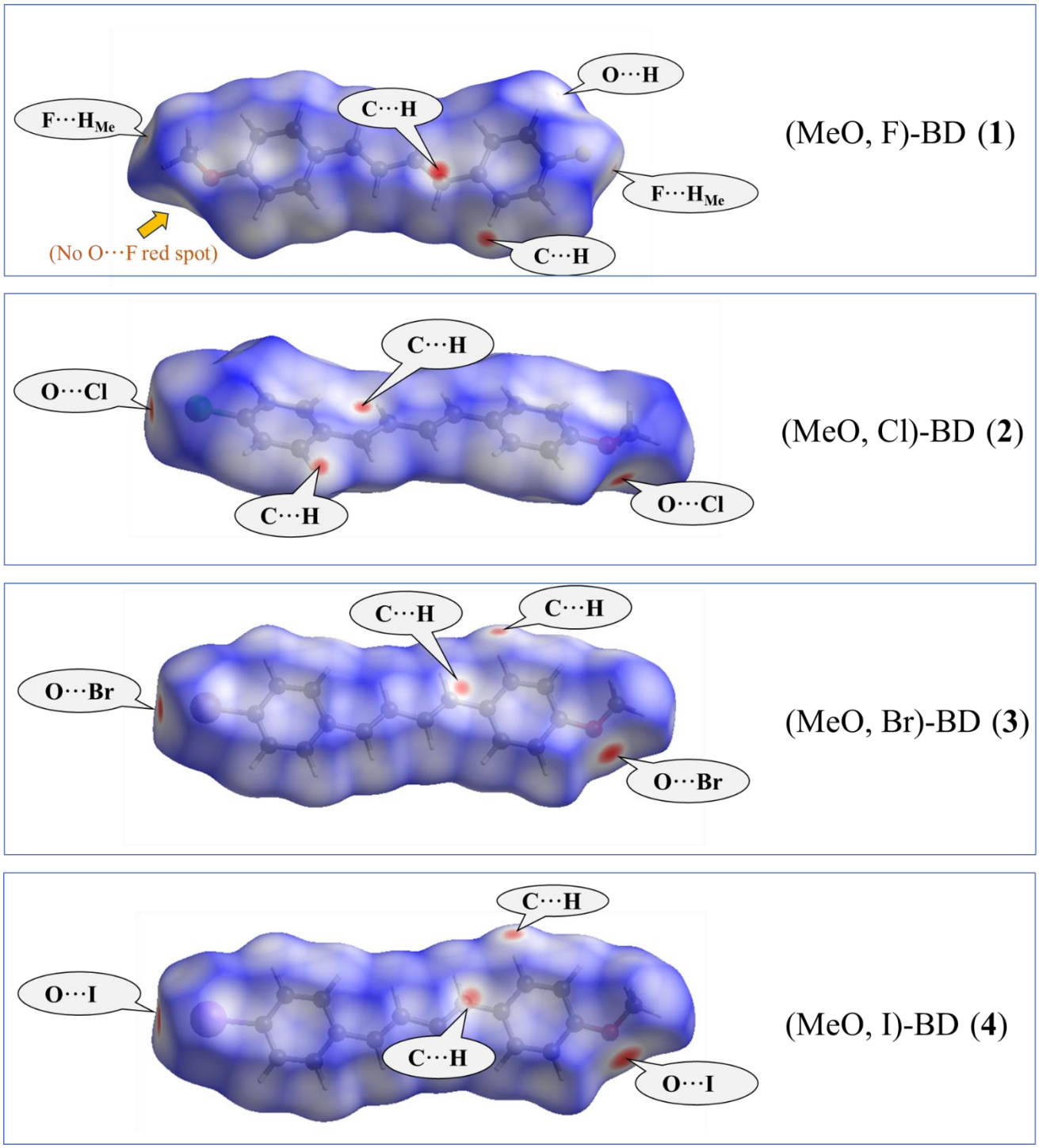
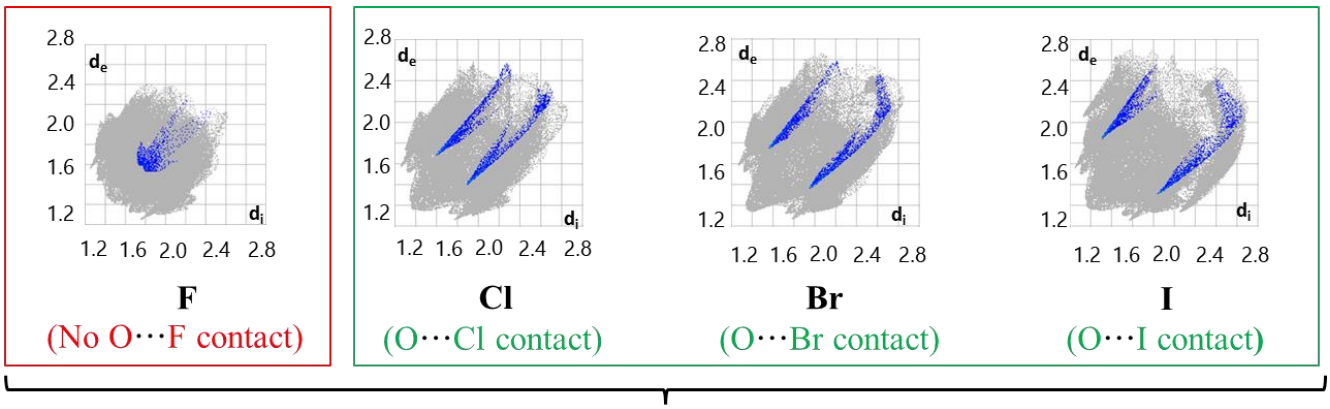
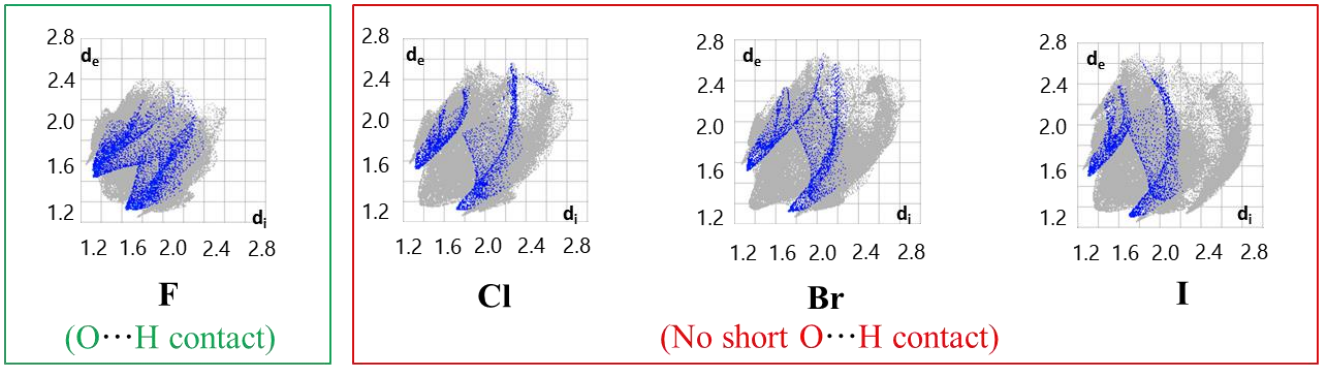


Figure S1. Hirshfeld surfaces for (MeO, Y)-BDs **1**-**4**.



(a) O···Y Halogen Bonding



(b) O···H Contact

Figure S2. Hirshfeld 2-D fingerprint plots for (MeO, Y)-BDs **1-4** resolved into (a) O···Y and (b) O···H contacts.

Table S2. Solvent Parameters ε, n, and Δf

Solvent	Dielectric constant, ε	Refractive index, n	Δf
Benzene	2.27	1.5011	0.00
Chloroform	4.81	1.4458	0.15
Dichloromethane	8.93	1.4241	0.22
Methanol	32.7	1.3284	0.31

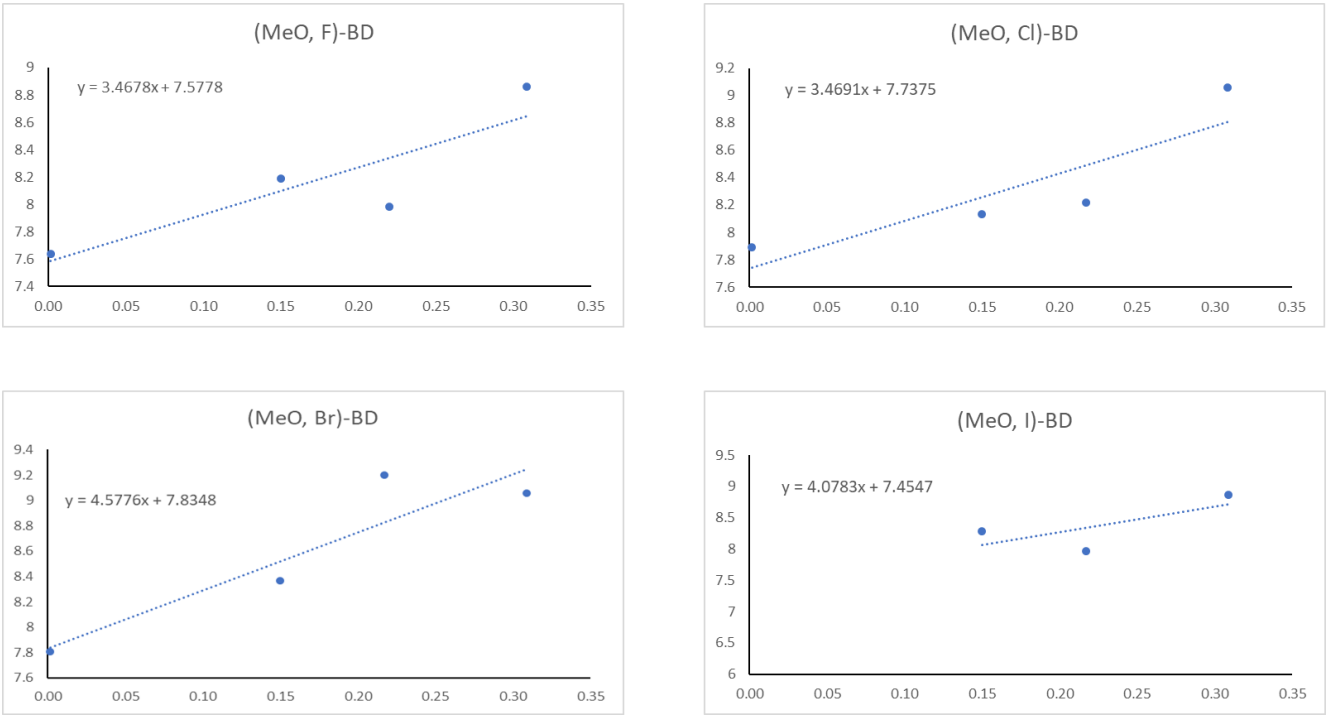


Figure S3. Plots of $\Delta \nu_{ex}$ as a function of Δf for **1**-**4**.

Table S3. Solvent Dependency of Absorption and Emission Maxima

Solvent	λ_{abs} (nm)	ν_{abs} (cm^{-1})	λ_{em} (nm)	ν_{em} (cm^{-1})	$\Delta\lambda_{ex}$ (nm)	$\Delta\nu_{ex}$ (cm^{-1})
MeOF, **1**						
Benzene	342	29,239.77	394	25,380.71	52	3,859.06
Chloroform	341	29,325.51	397	25,188.92	56	4,136.60
Dichloromethane	340	29,411.76	394	25,380.71	54	4,031.05
Methanol	335	29,850.75	394	25,380.71	59	4,470.04
MeOCl, **2**						
Benzene	348	28,735.63	404	24,752.48	56	3,983.15
Chloroform	348	28,735.63	406	24,630.54	58	4,105.09
Dichloromethane	346	28,901.73	404	24,752.48	58	4,149.25
Methanol	341	29,325.51	400	24,752.48	59	4,573.03
MeOBr, **3**						
Benzene	349	28,653.30	406	24,630.54	57	4,022.76
Chloroform	348	28,735.63	408	24,509.80	60	4,225.83
Dichloromethane	347	28,818.44	408	24,509.80	61	4,644.72
Methanol	341	29,325.51	404	24,752.48	63	4,573.03
MeOI, **4**						
Benzene	352	28,571.43	422	23,696.68	70	4,874.75
Chloroform	350	28,571.43	410	24,390.24	60	4,181.18
Dichloromethane	349	28,653.30	406	24,630.54	57	4,022.76
Methanol	345	28,985.51	408	24,509.80	63	4,475.71

NMR Spectra

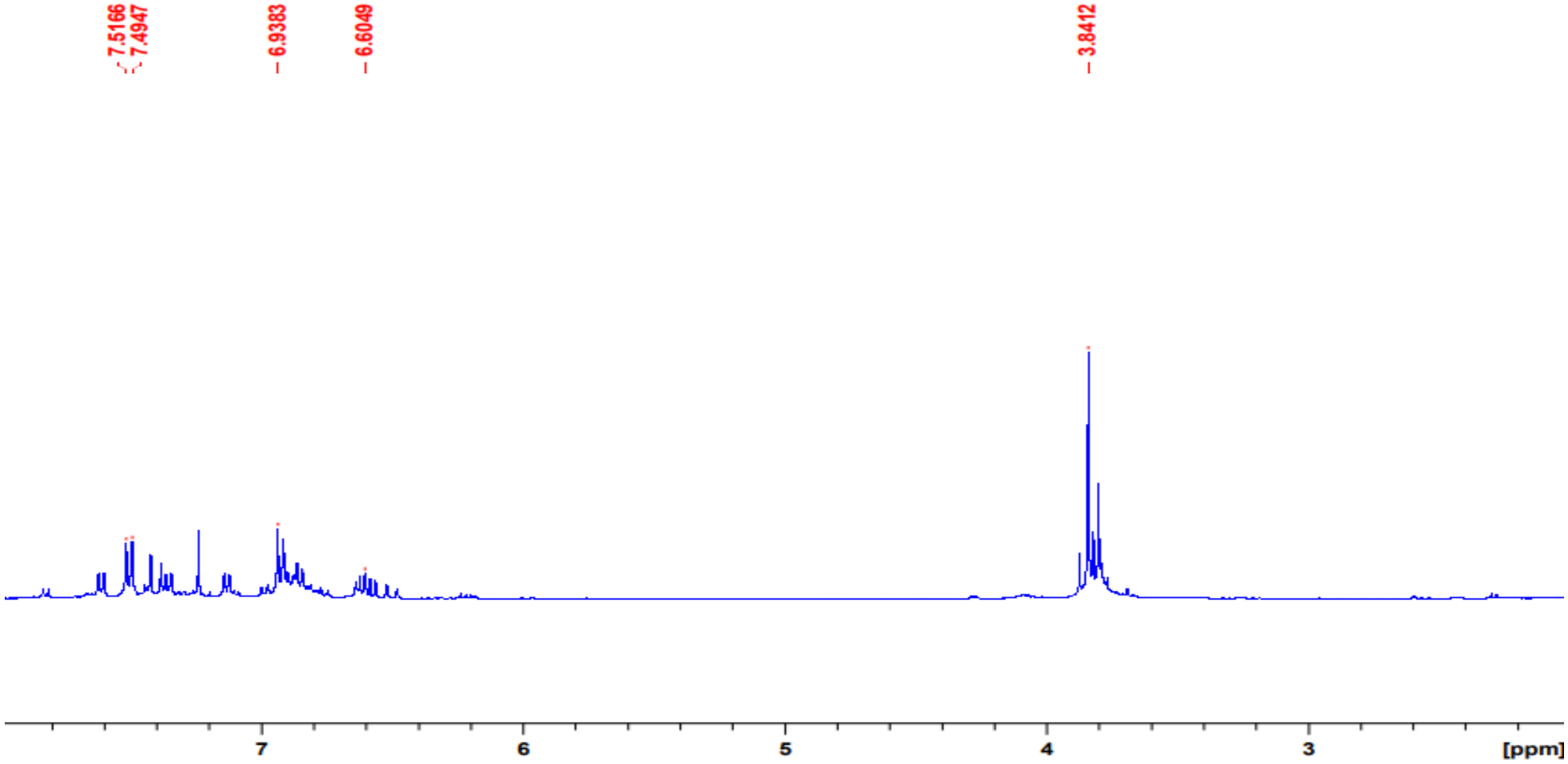


Figure S4. ^{1}H NMR spectrum of (MeO, F)-BD.

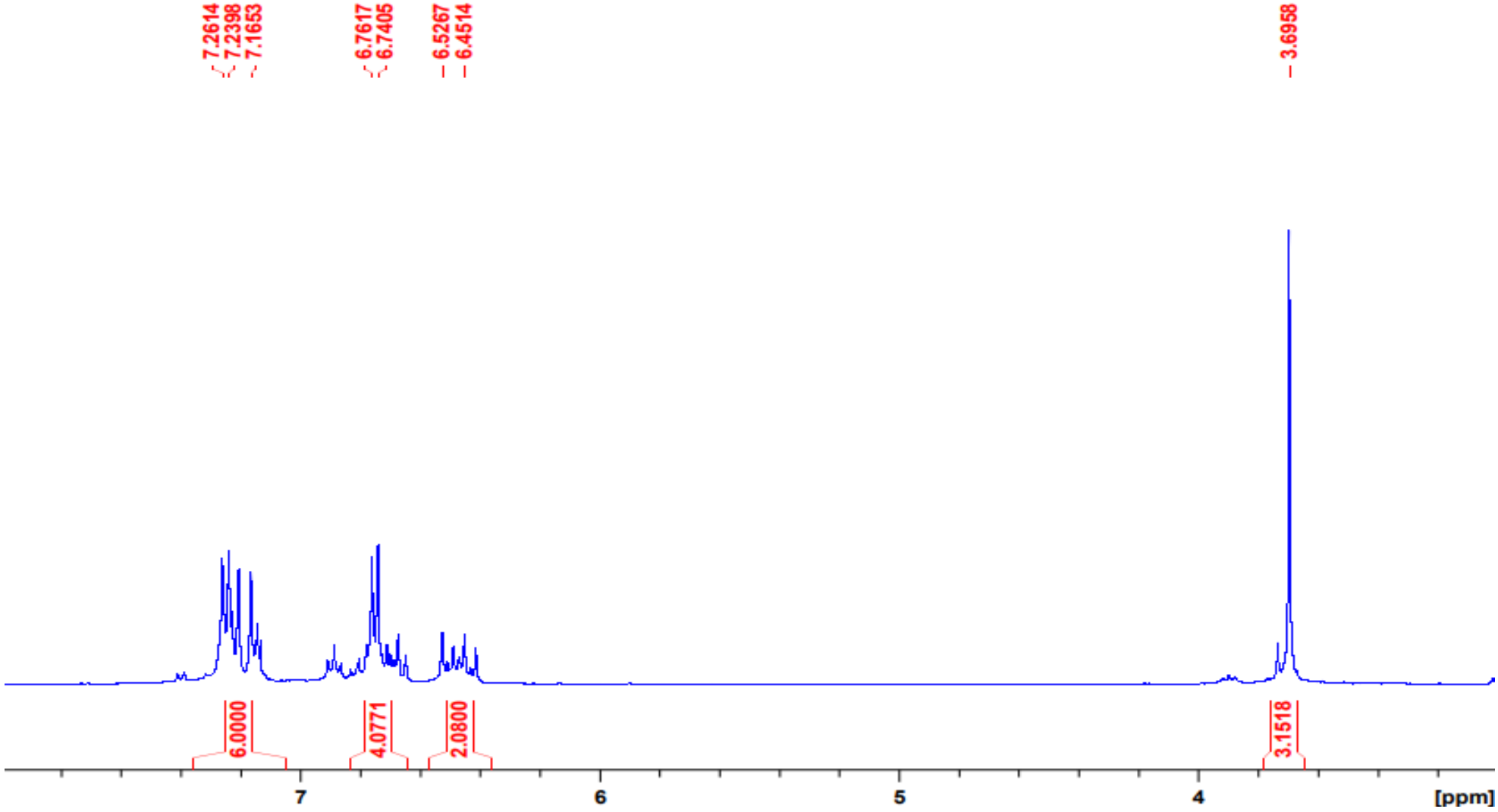


Figure S5. ^{1}H NMR spectrum of (MeO, Cl)-BD.

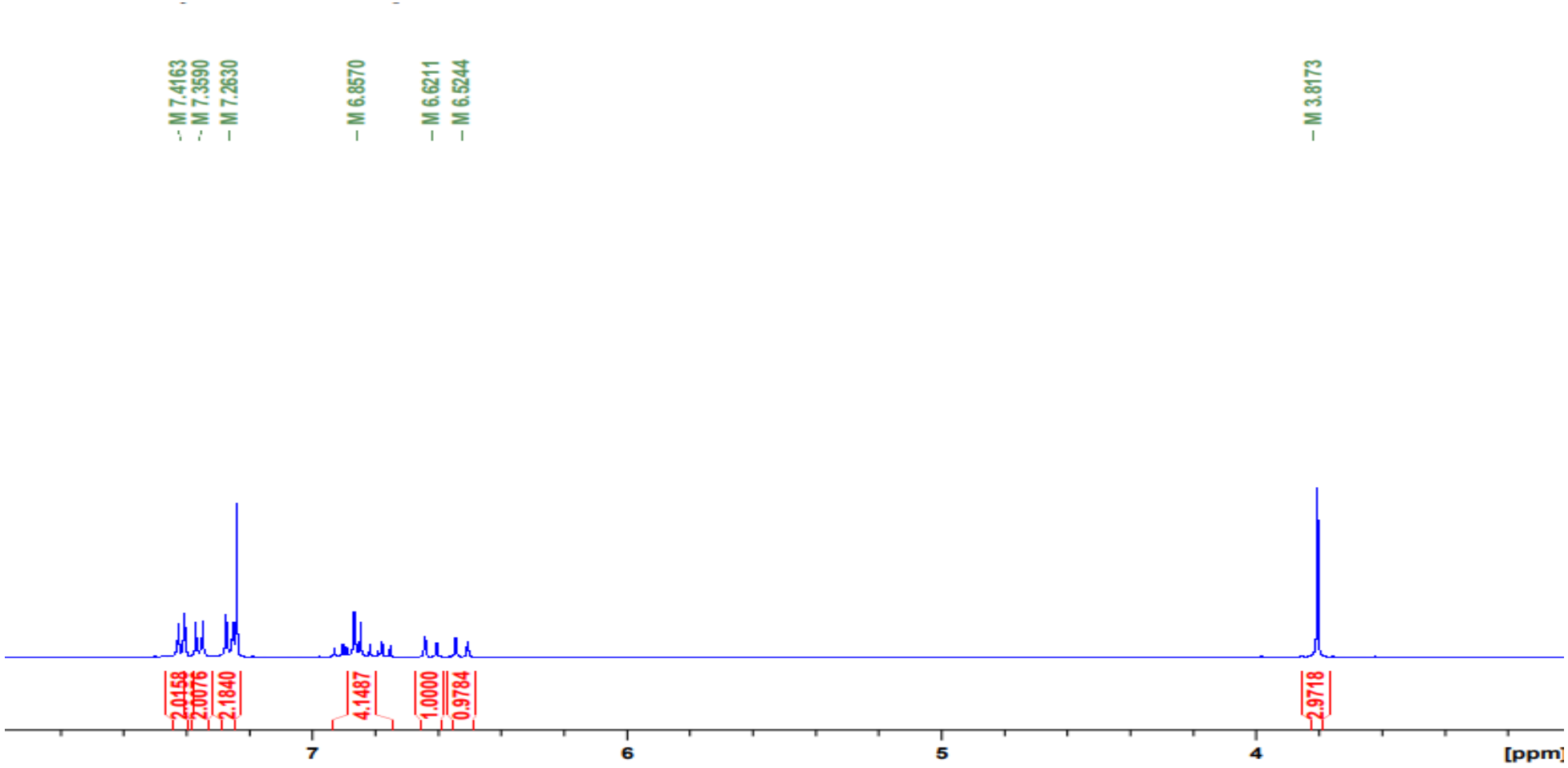


Figure S6. ^{1}H NMR spectrum of (MeO, Br)-BD.

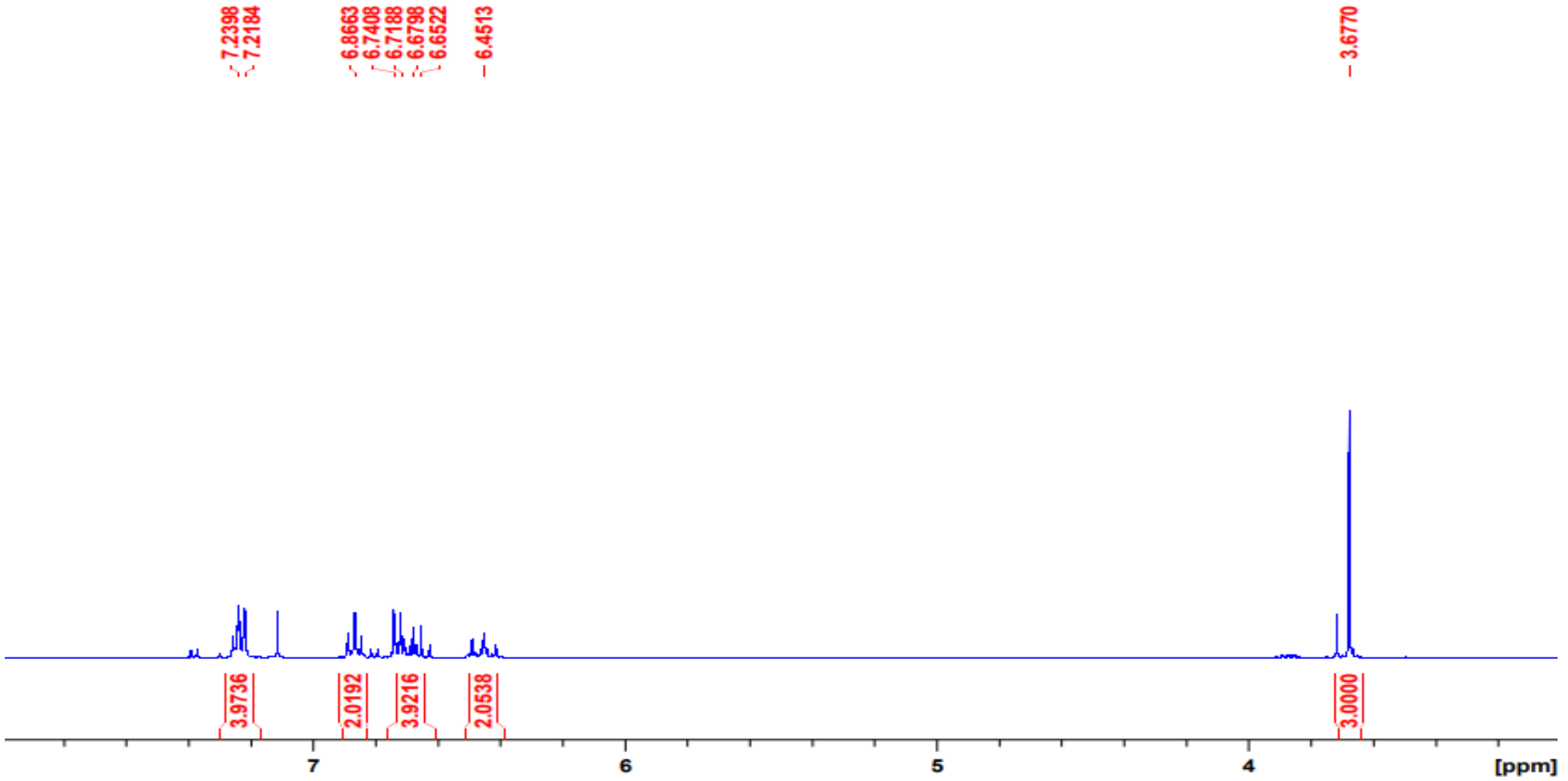


Figure S7. ^{1}H NMR spectrum of (MeO, I)-BD.

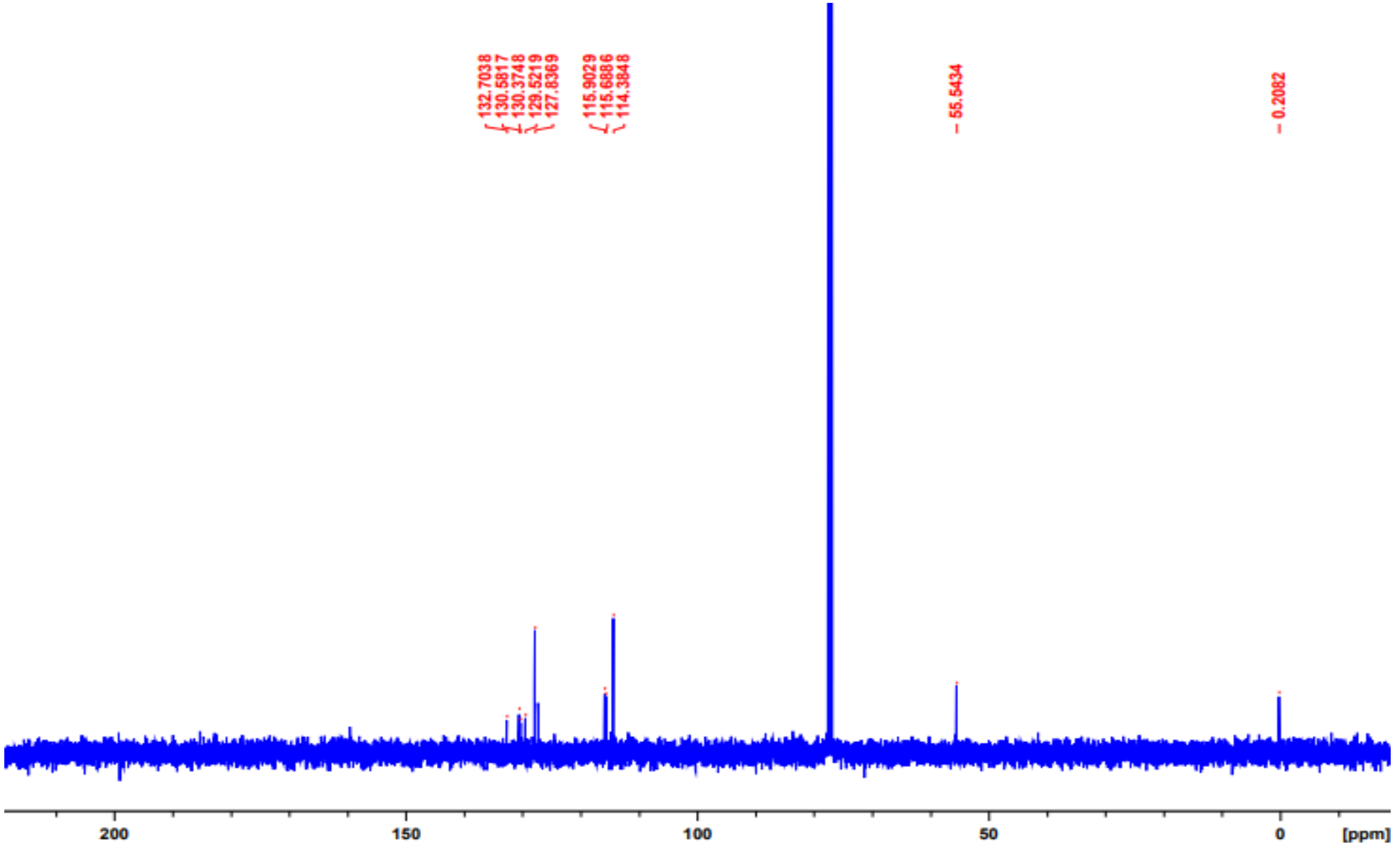


Figure S8. ^{13}C NMR spectrum of (MeO, F)-BD.

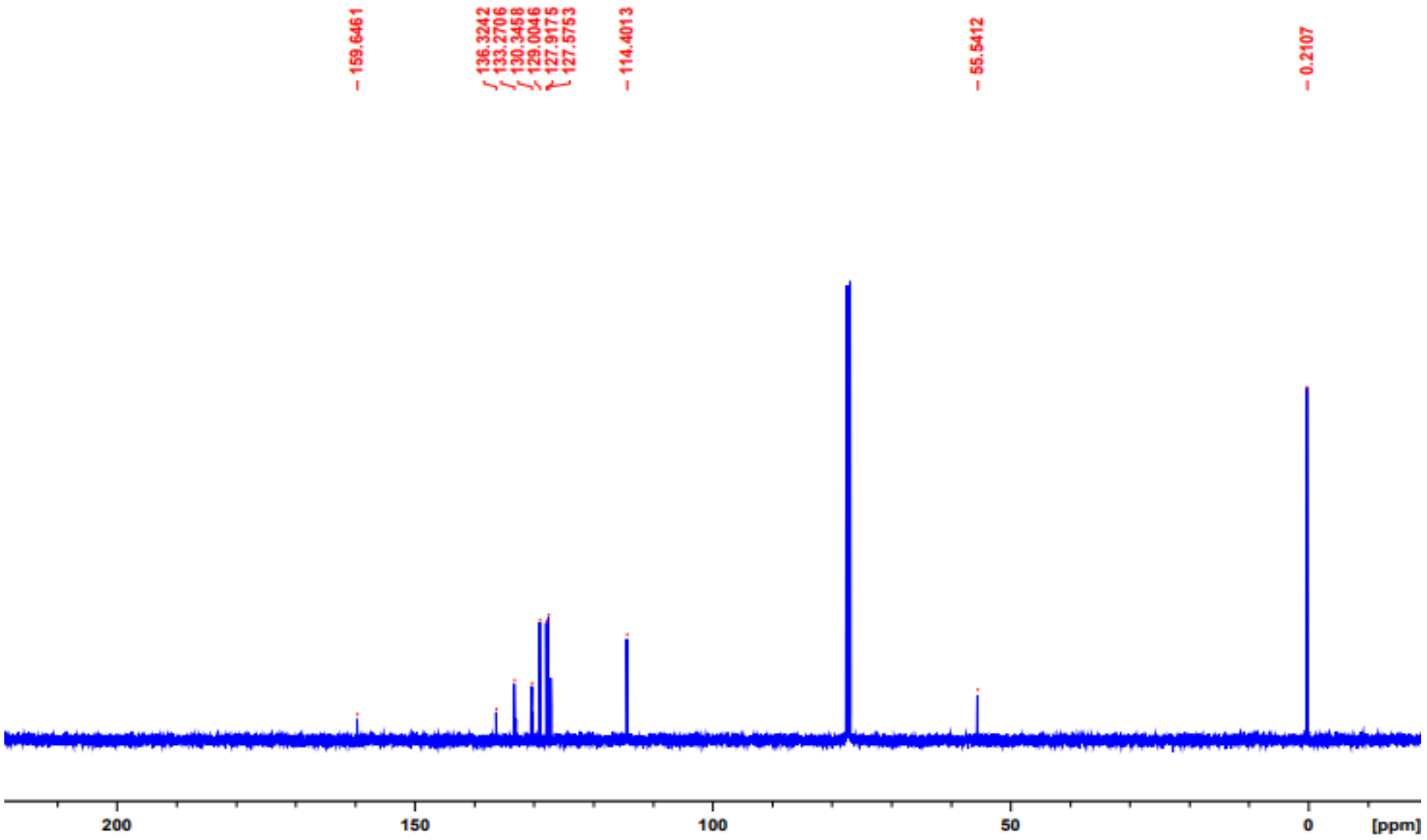


Figure S9. ^{13}C NMR spectrum of (MeO, Cl)-BD.

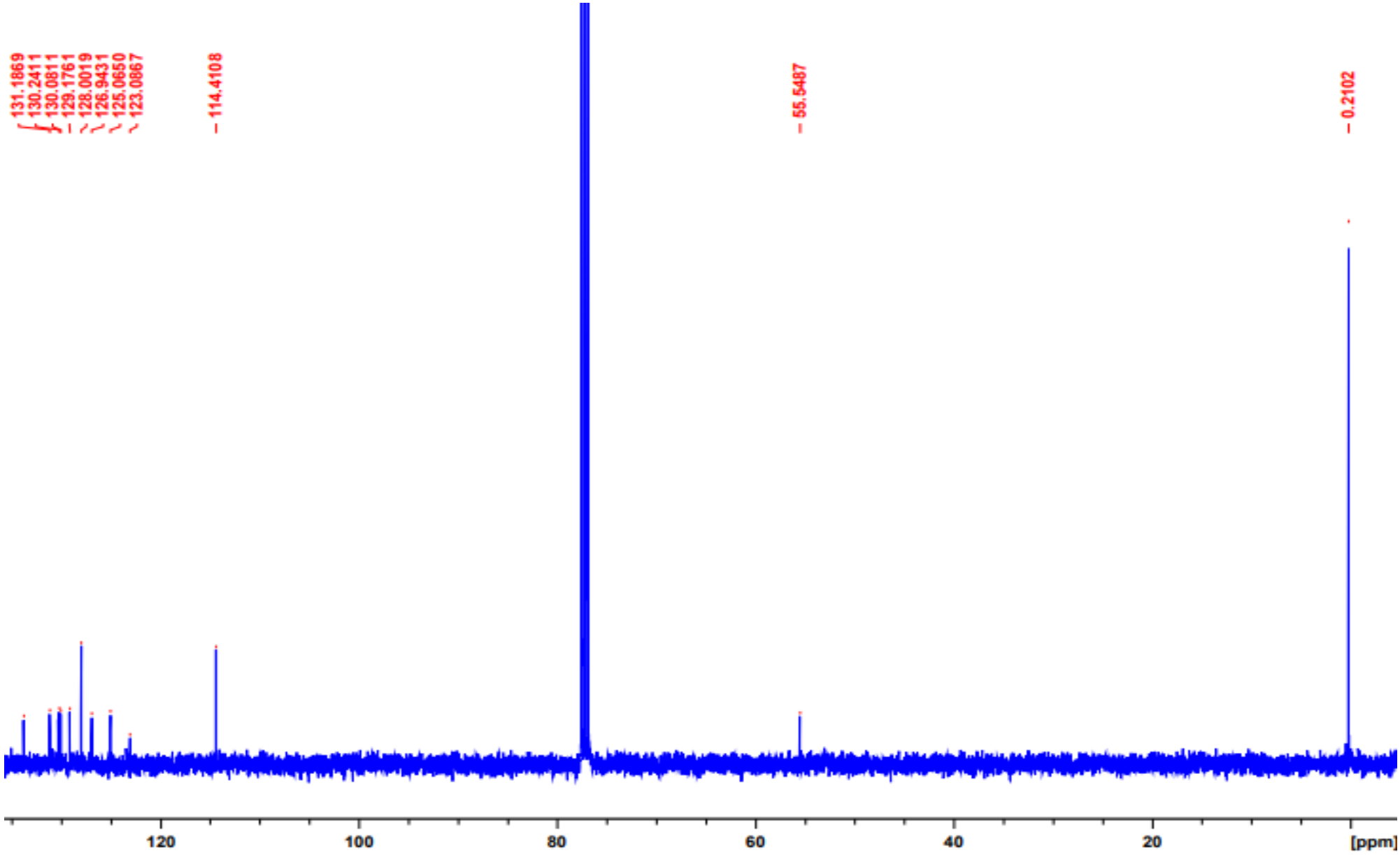


Figure S10. ^{13}C NMR spectrum of (MeO, Br)-BD.

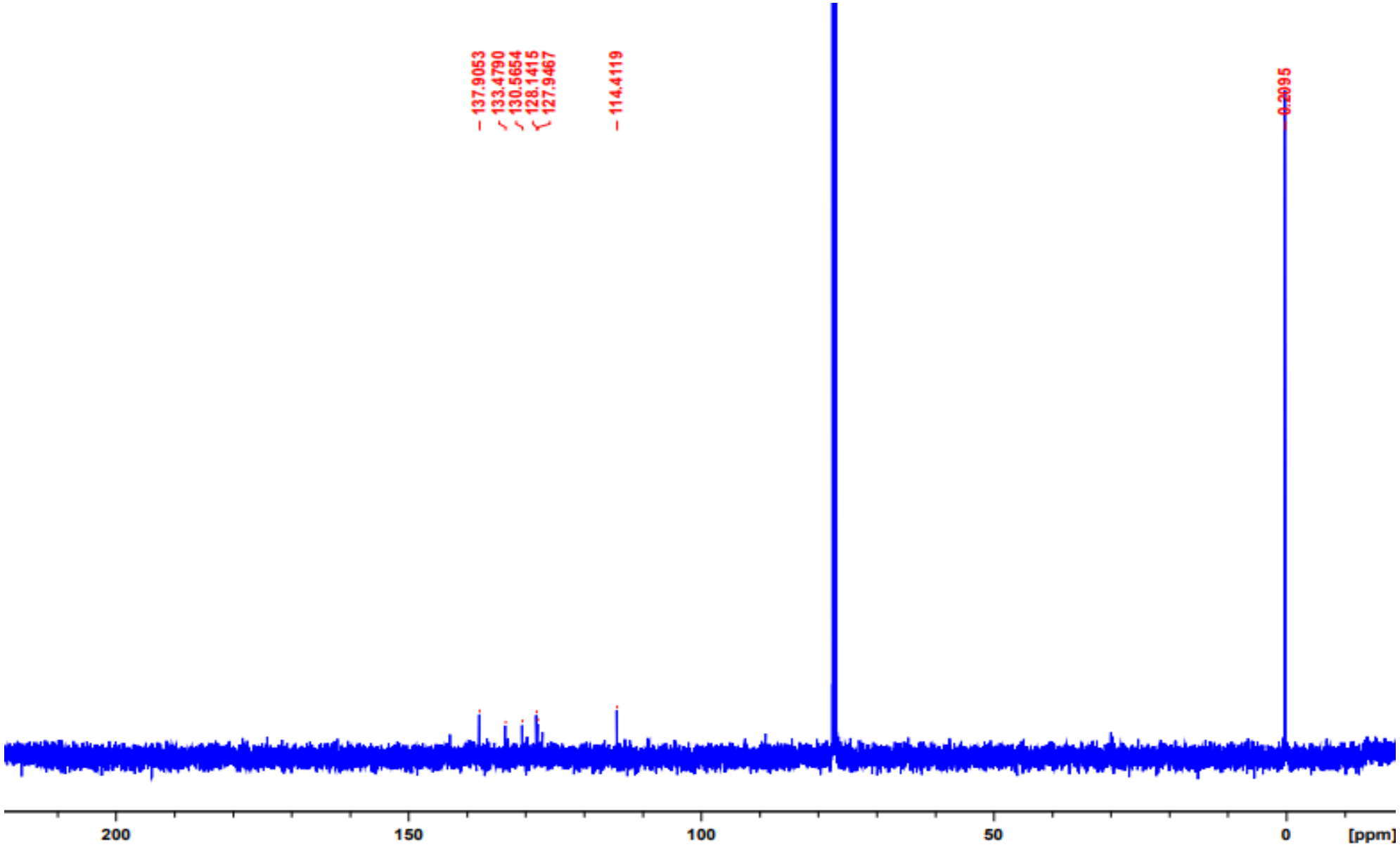


Figure S11. ^{13}C NMR spectrum of (MeO, I)-BD.

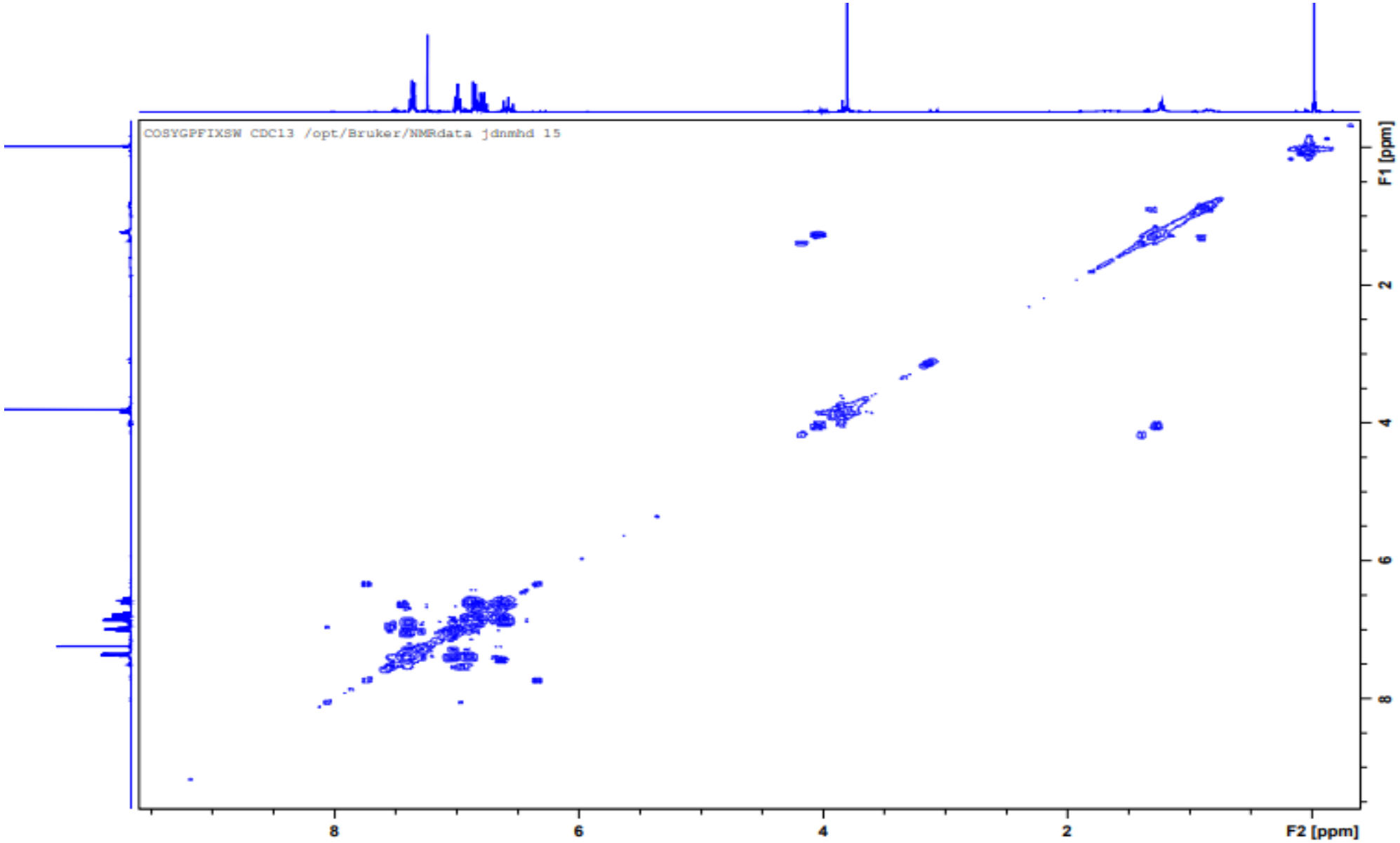


Figure S12. COSY NMR spectrum of (MeO, F)-BD.

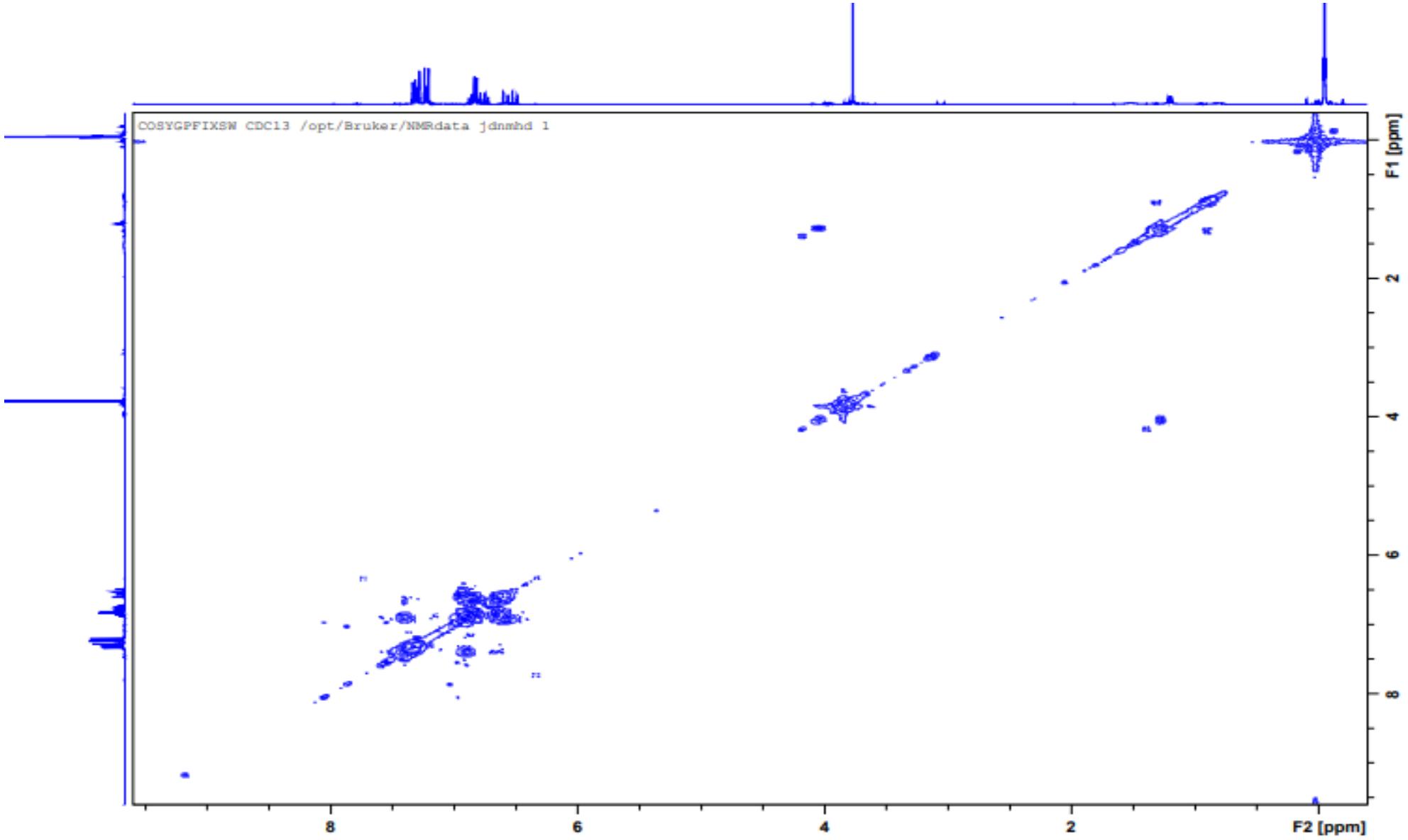


Figure S13. COSY NMR spectrum of (MeO, Cl)-BD.

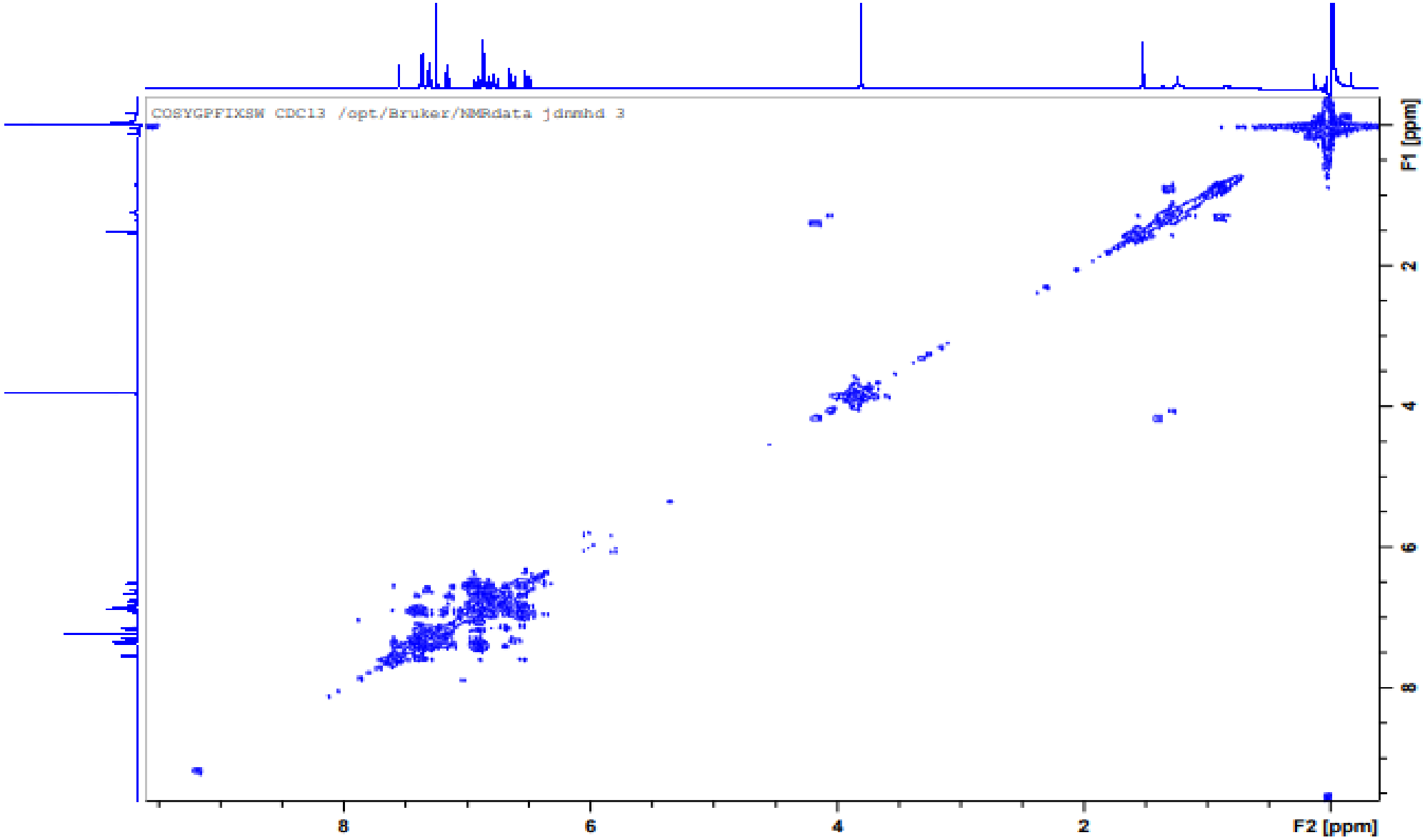


Figure S14. COSY NMR spectrum of (MeO, Br)-BD.

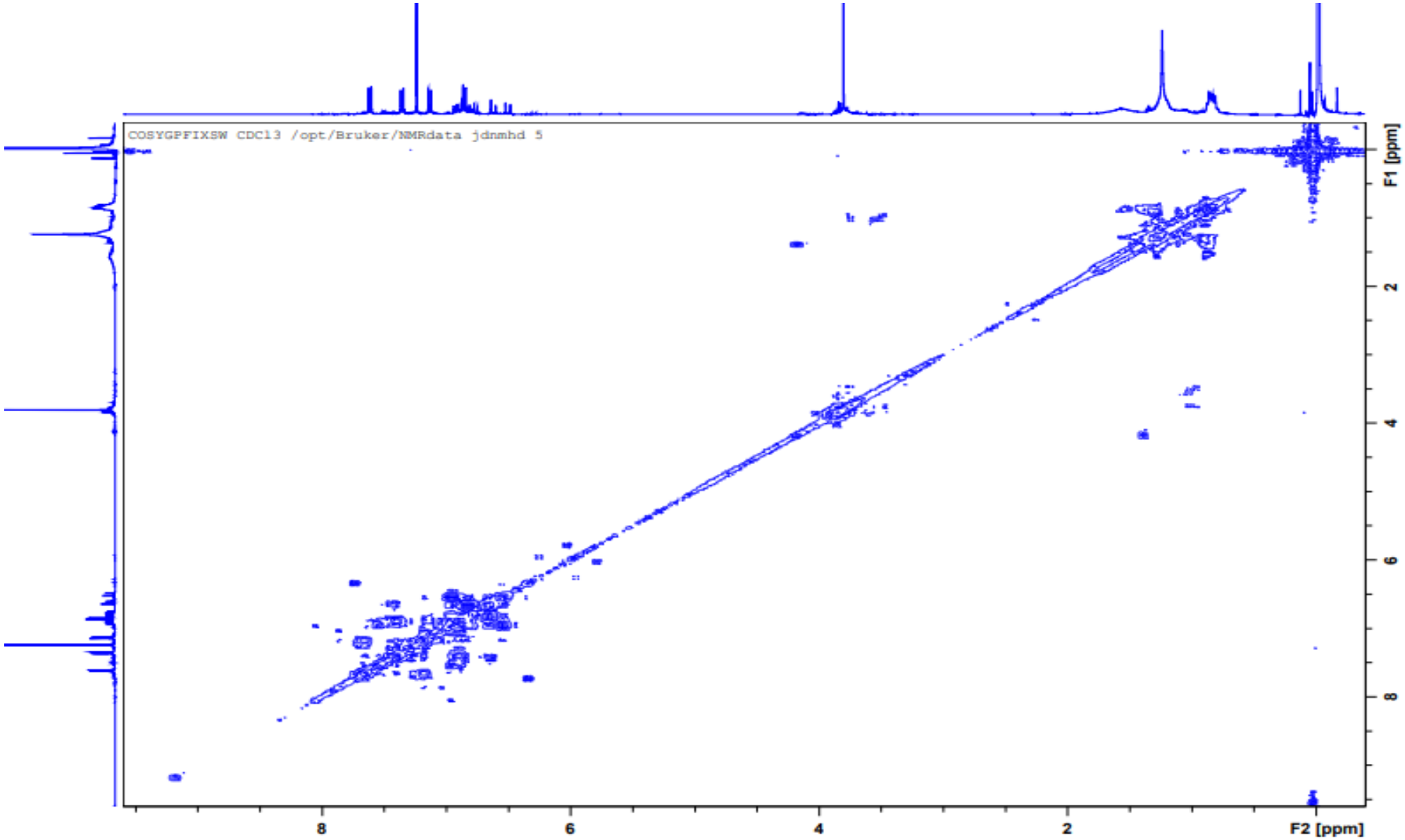


Figure S15. COSY NMR spectrum of (MeO, I)-BD.

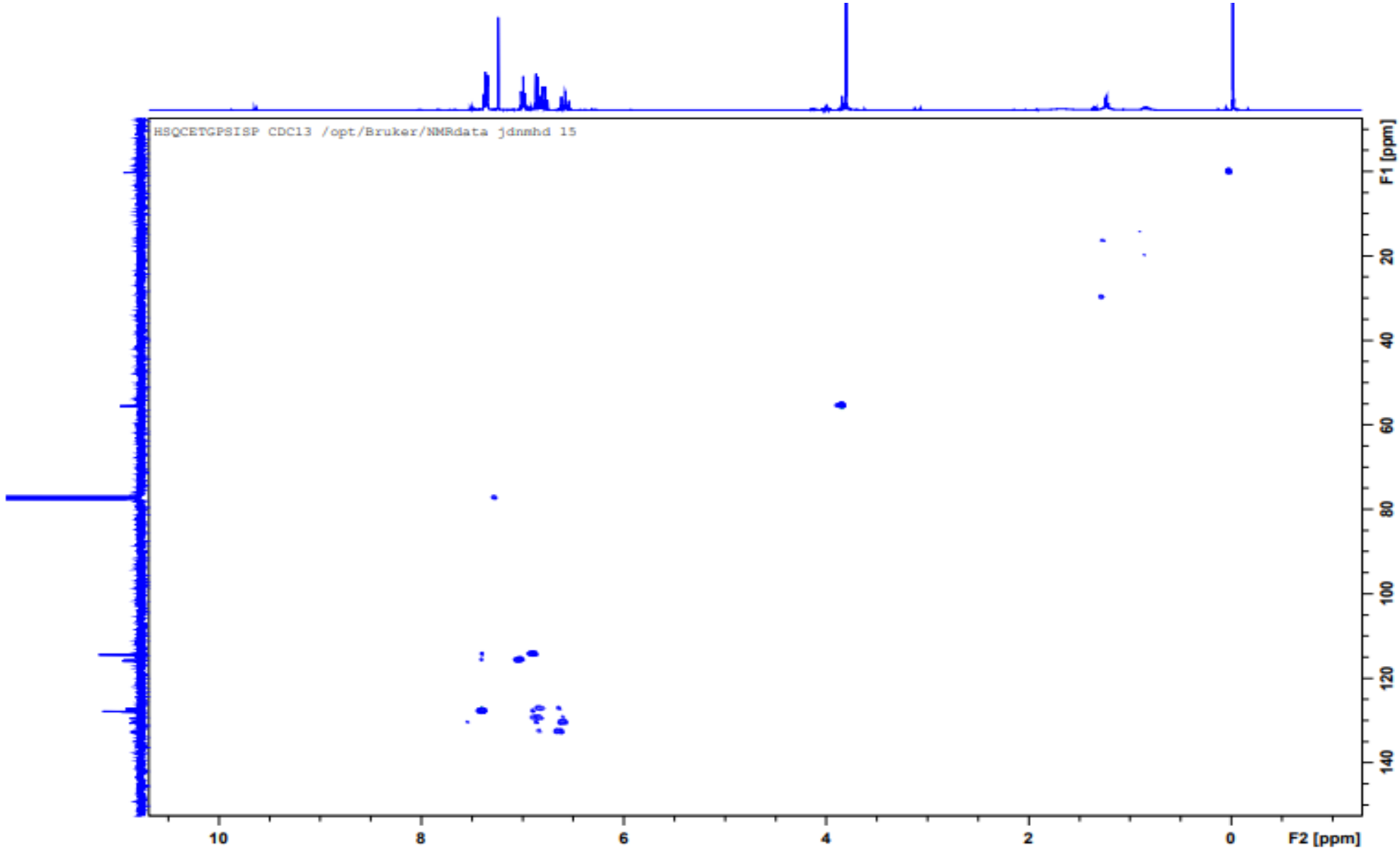


Figure S16. HSQC NMR spectrum of (MeO, F)-BD.

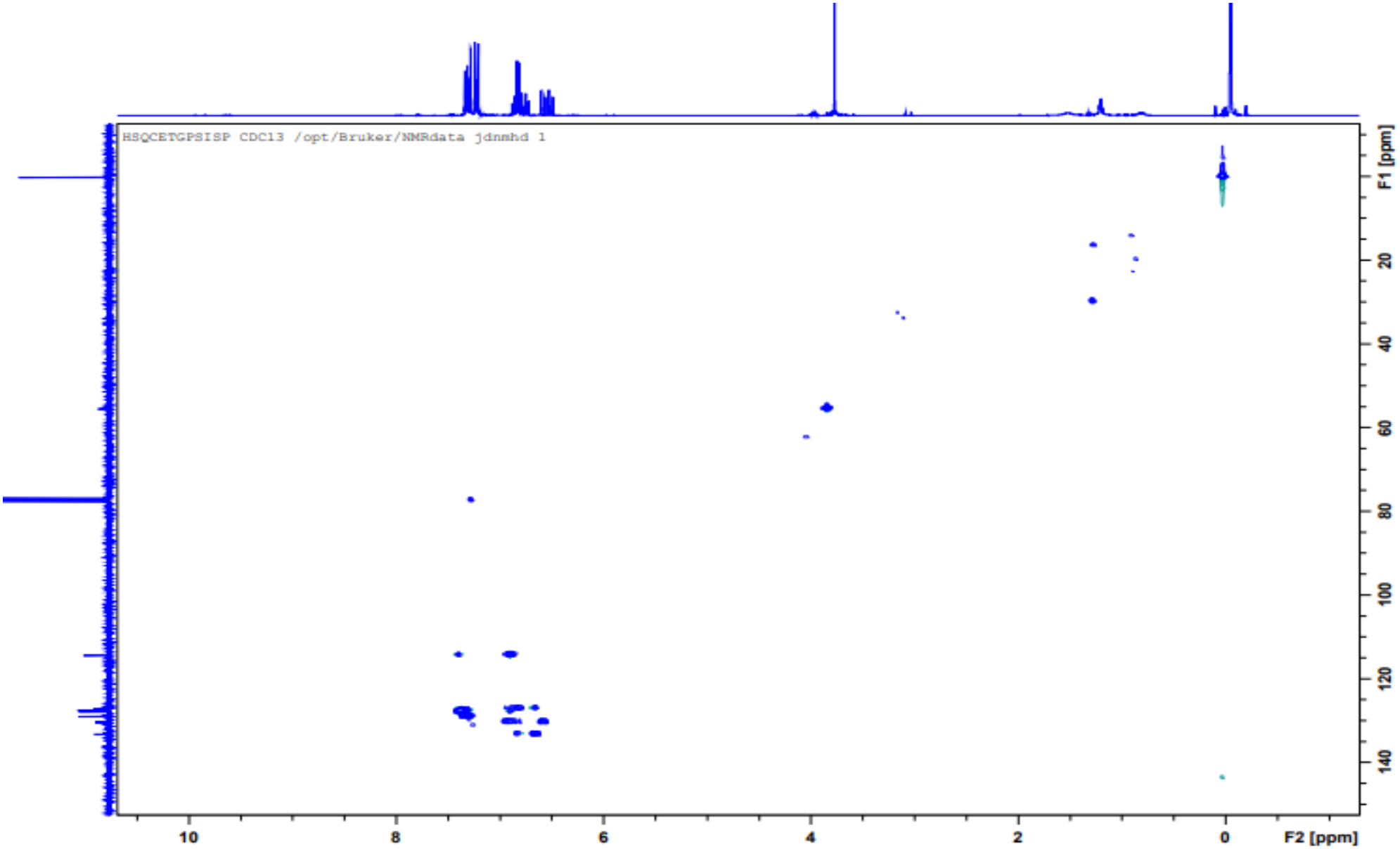


Figure S17. HSQC NMR spectrum of (MeO, Cl)-BD.

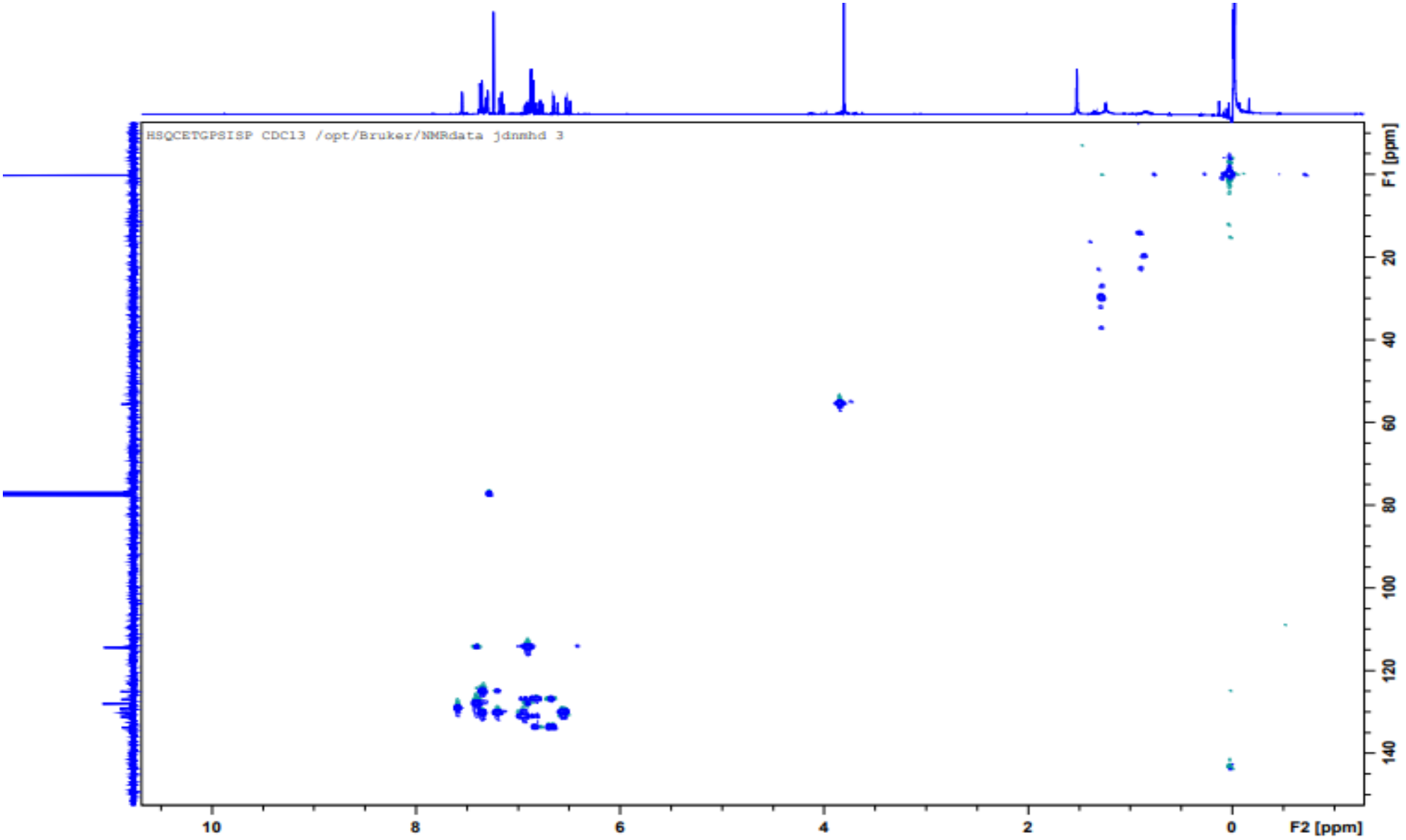


Figure S18. HSQC NMR spectrum of (MeO, Br)-BD.

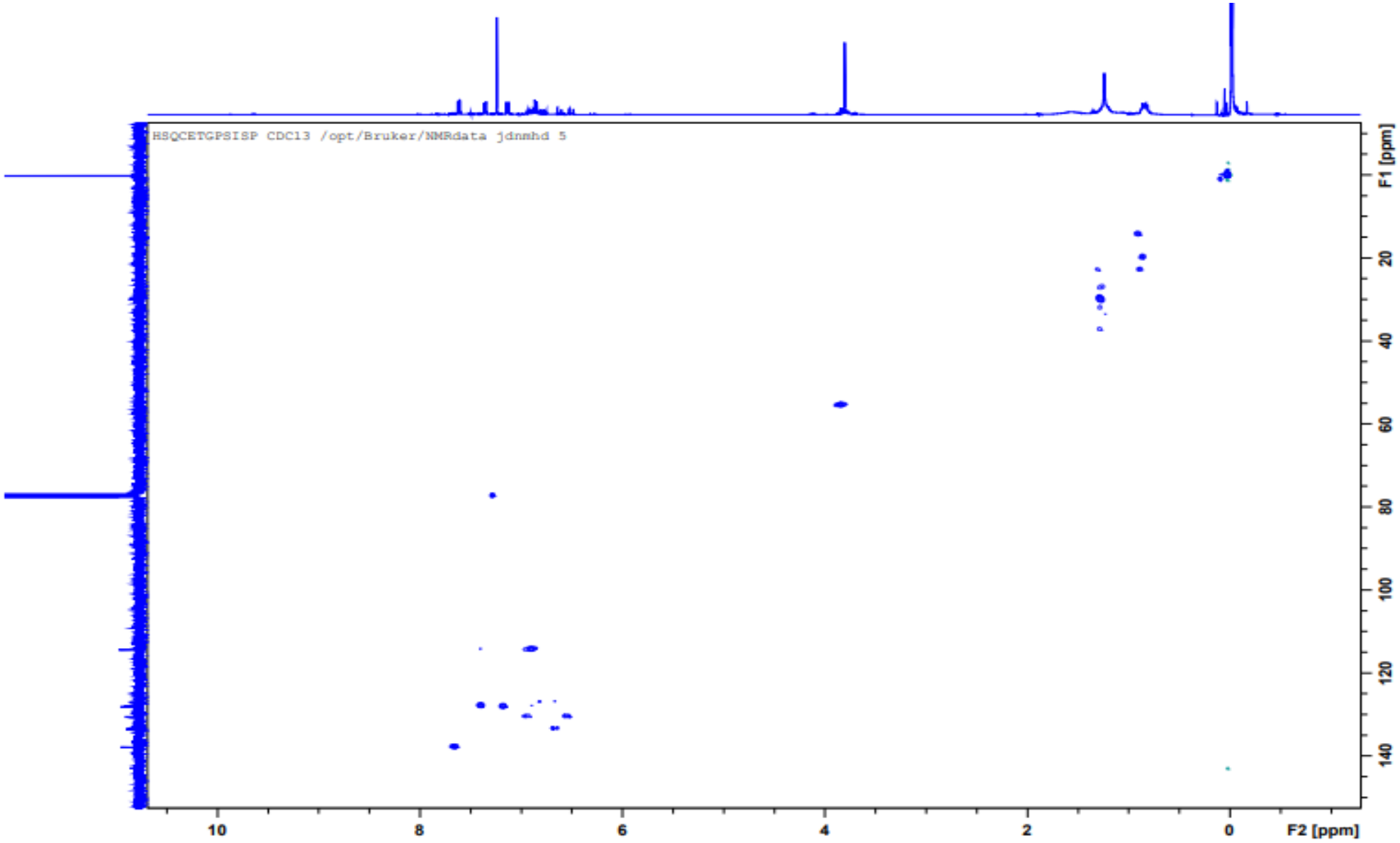


Figure S19. HSQC NMR spectrum of (MeO, I)-BD**.**

FTIR Spectra

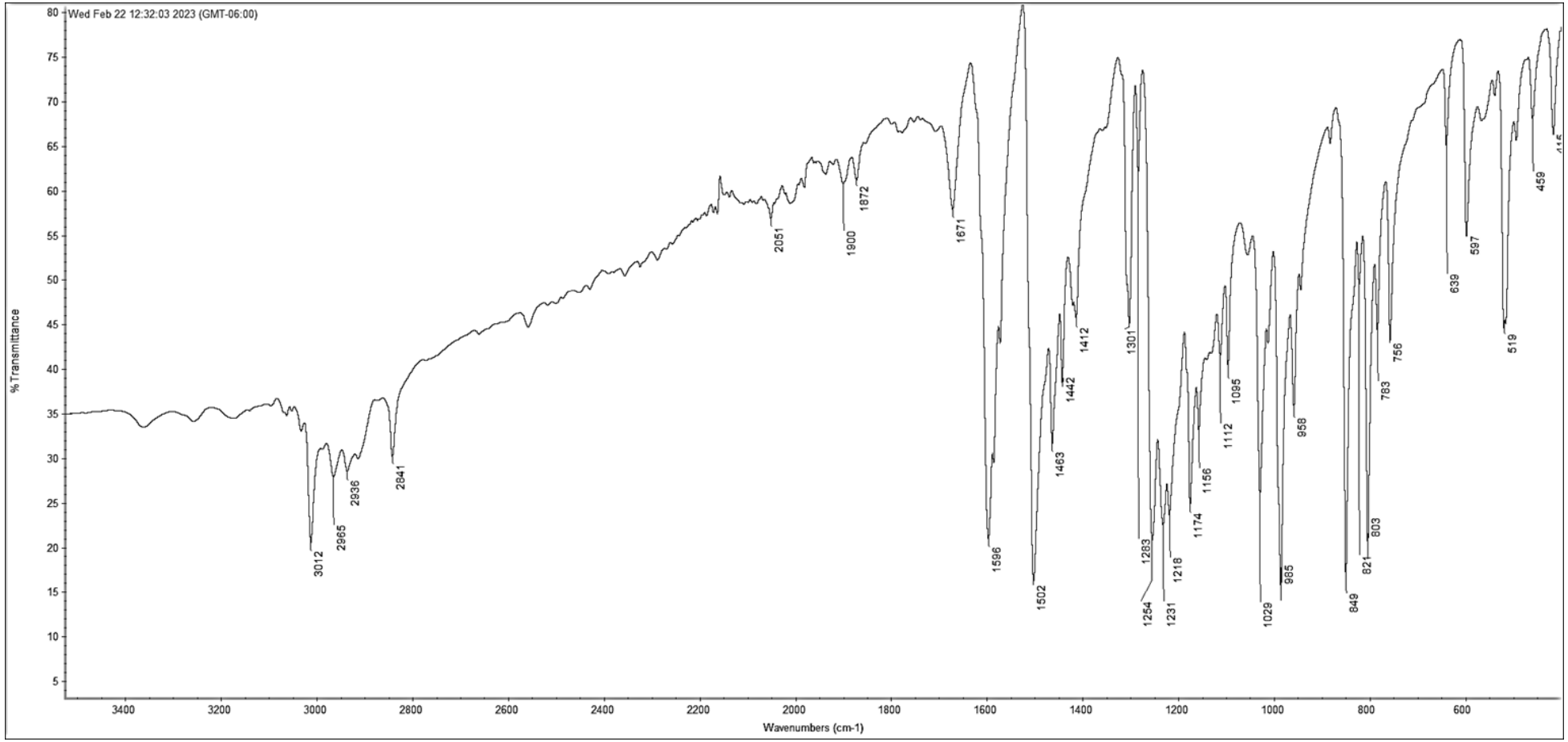


Figure S20. SS-FTIR spectrum of (MeO, F)-BD.

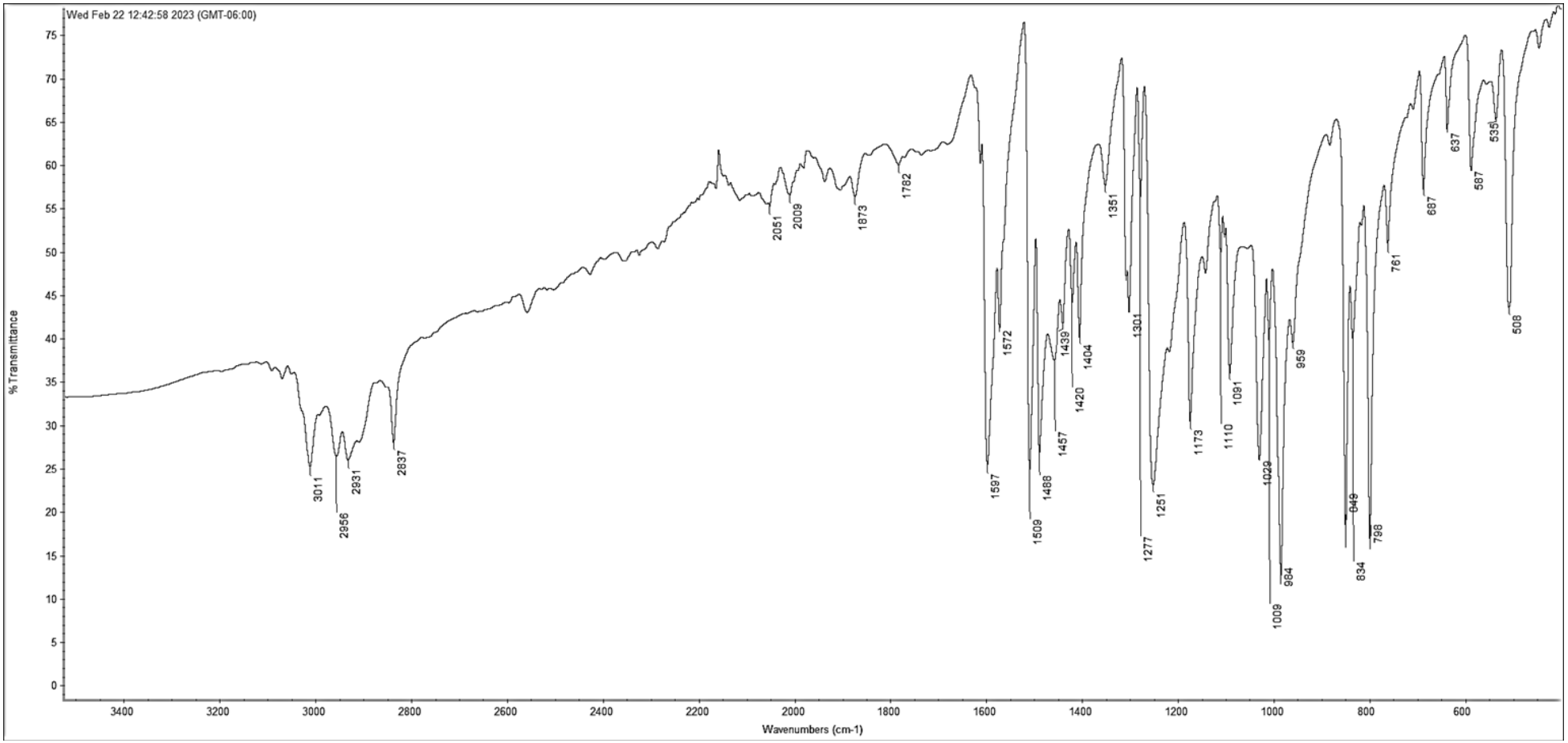


Figure S21. SS-FTIR spectrum of (MeO, Cl)-BD **.**

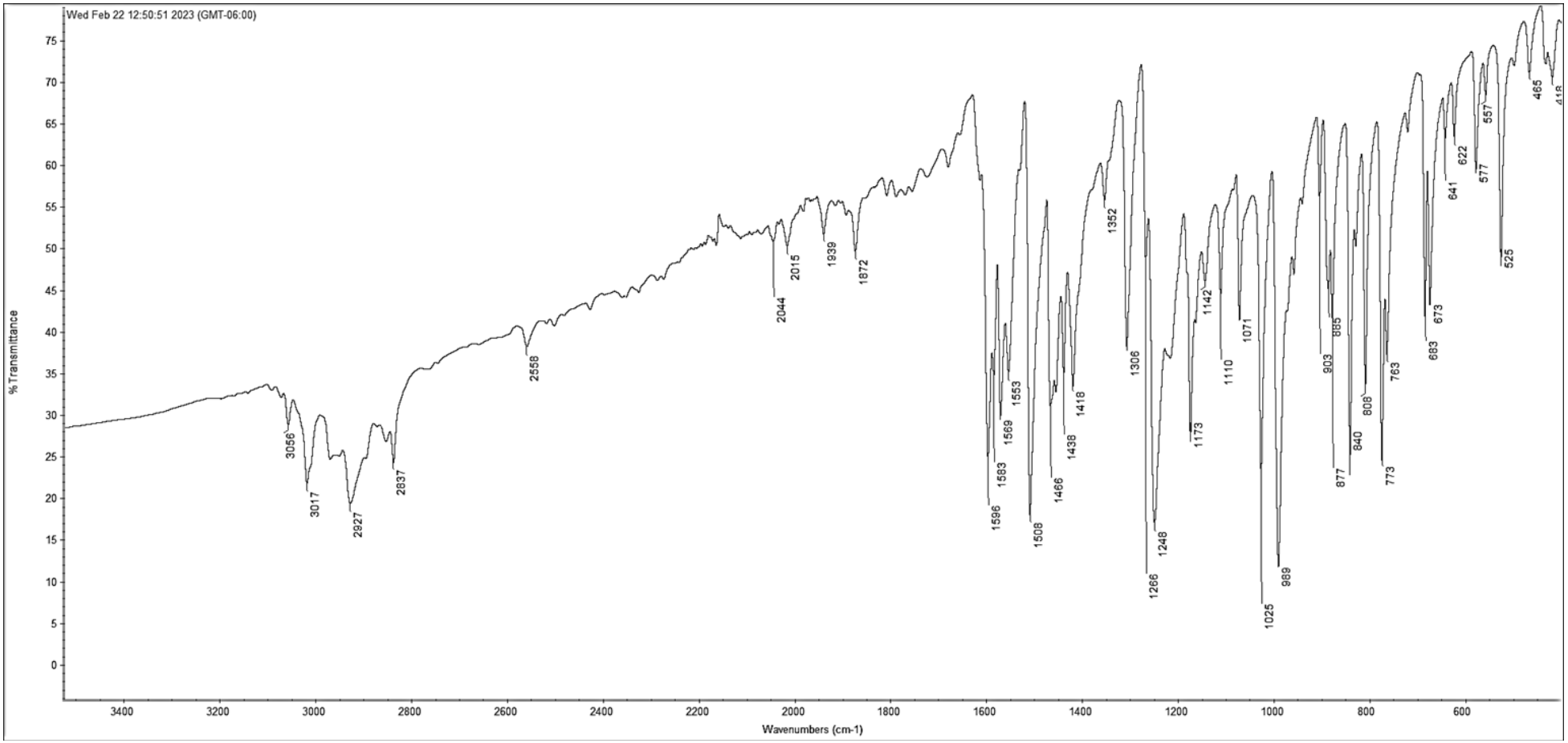


Figure S22. SS-FTIR spectrum of (MeO, Br)-BD**.**

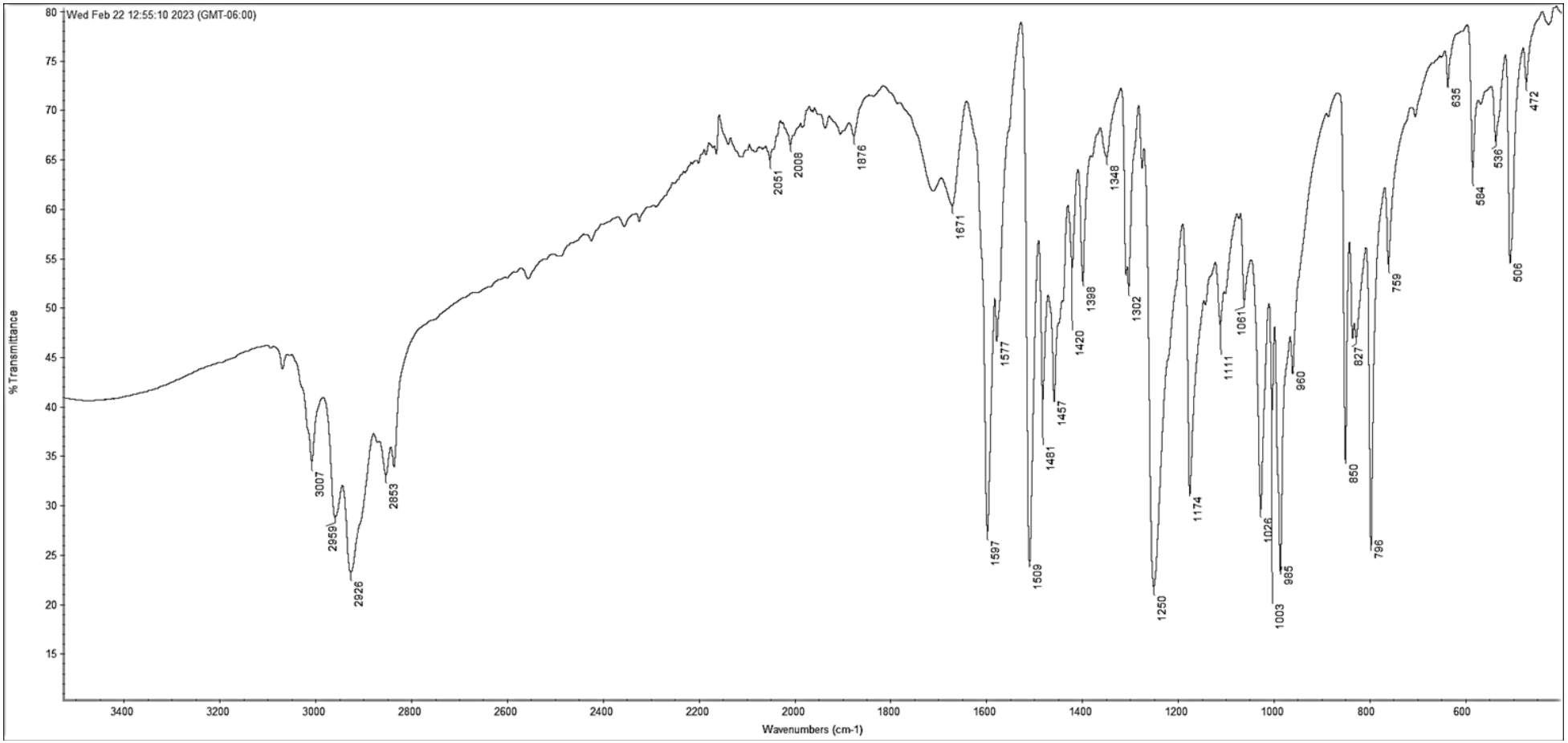


Figure S23. SS-FTIR spectrum of (MeO, I)-BD.

Table S4. (MeO, F)-BD, **1b** at APFD/6-311G*

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.435703
3	6	0	1.000860	-0.512641	-0.745756
4	6	0	-0.997185	0.510708	2.186555
5	1	0	1.849575	-0.946940	-0.215647
6	1	0	-1.848866	0.946639	1.663452
7	6	0	1.090375	-0.558928	-2.195049
8	6	0	-1.076753	0.551557	3.639121
9	6	0	2.216141	-1.132775	-2.794339
10	6	0	2.363410	-1.208592	-4.174955
11	6	0	1.361745	-0.698928	-5.002337
12	6	0	0.225242	-0.119651	-4.422771
13	6	0	0.095169	-0.052546	-3.052238
14	1	0	3.004778	-1.534128	-2.162255
15	1	0	3.256346	-1.663660	-4.588612
16	8	0	1.385247	-0.711912	-6.355717
17	1	0	-0.543708	0.271478	-5.081657
18	1	0	-0.798386	0.402600	-2.635905
19	6	0	-2.204840	1.126474	4.243123
20	6	0	-2.339819	1.195477	5.622930
21	6	0	-1.328589	0.680448	6.416314
22	6	0	-0.194610	0.102652	5.861564
23	6	0	-0.076033	0.041975	4.483013
24	1	0	-2.995117	1.528986	3.614772
25	1	0	-3.213289	1.640586	6.088109
26	9	0	-1.444994	0.740063	7.754411
27	1	0	0.577447	-0.290428	6.515141
28	1	0	0.813752	-0.411164	4.057577
29	6	0	2.504417	-1.282906	-6.994445
30	1	0	3.427650	-0.749568	-6.740494
31	1	0	2.615474	-2.342979	-6.739071
32	1	0	2.319094	-1.189390	-8.063031
33	1	0	-0.868123	0.444681	-0.485515
34	1	0	0.869669	-0.445556	1.918266

Table S5. (MeO, F)-BD, **1c** at APFD/6-311G*

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.435639
3	6	0	0.877562	0.703168	-0.745633
4	6	0	-0.874502	-0.700456	2.186435
5	1	0	1.620938	1.299322	-0.214732
6	1	0	-1.621276	-1.298500	1.663212
7	6	0	0.958622	0.767596	-2.195254
8	6	0	-0.944636	-0.756540	3.638946
9	6	0	1.949726	1.565527	-2.792482
10	6	0	2.074817	1.665383	-4.164510
11	6	0	1.204176	0.963369	-5.002128
12	6	0	0.208550	0.161629	-4.432961
13	6	0	0.096935	0.072701	-3.052938
14	1	0	2.636891	2.119541	-2.157446
15	1	0	2.842584	2.283541	-4.618988
16	8	0	1.406324	1.125141	-6.331029
17	1	0	-0.482788	-0.396036	-5.054879
18	1	0	-0.685165	-0.557508	-2.640102
19	6	0	-1.933758	-1.547219	4.242604
20	6	0	-2.052585	-1.642024	5.622356
21	6	0	-1.166409	-0.933491	6.416081
22	6	0	-0.172125	-0.138791	5.861681
23	6	0	-0.067667	-0.055471	4.483173
24	1	0	-2.626336	-2.100938	3.614010
25	1	0	-2.818458	-2.254202	6.087270
26	9	0	-1.268992	-1.015306	7.754105
27	1	0	0.504453	0.402077	6.515472
28	1	0	0.712484	0.567989	4.058080
29	6	0	0.556586	0.439516	-7.222352
30	1	0	0.633855	-0.646606	-7.097112
31	1	0	-0.488402	0.746117	-7.098583
32	1	0	0.892350	0.709030	-8.222169
33	1	0	-0.761346	-0.609997	-0.485400
34	1	0	0.762626	0.610951	1.918139

Table S6. (MeO, Cl)-BD, **2b** at APFD/6-311G*

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.435217
3	6	0	0.515281	-1.001177	-0.743959
4	6	0	-0.512663	0.995986	2.186965
5	1	0	0.950705	-1.848094	-0.211930
6	1	0	-0.950863	1.847489	1.665756
7	6	0	0.563059	-1.093136	-2.192627
8	6	0	-0.551518	1.071566	3.638956
9	6	0	1.139316	-2.219295	-2.789024
10	6	0	1.216664	-2.368976	-4.169122
11	6	0	0.706161	-1.369419	-4.998777
12	6	0	0.124502	-0.232544	-4.421942
13	6	0	0.055869	-0.100040	-3.051874
14	1	0	1.541231	-3.006079	-2.155026
15	1	0	1.673451	-3.261893	-4.580839
16	8	0	0.720446	-1.395318	-6.351590
17	1	0	-0.267085	0.534488	-5.082740
18	1	0	-0.400978	0.793557	-2.637548
19	6	0	-0.038183	0.071525	4.480758
20	6	0	-0.097514	0.187128	5.859168
21	6	0	-0.677687	1.317334	6.427632
22	6	0	-1.195690	2.326348	5.627326
23	6	0	-1.128612	2.195626	4.247575
24	1	0	0.417690	-0.816727	4.054775
25	1	0	0.303468	-0.594039	6.496310
26	17	0	-0.753370	1.464926	8.160309
27	1	0	-1.645953	3.203434	6.079791
28	1	0	-1.535029	2.987281	3.623294
29	6	0	1.293726	-2.514691	-6.988458
30	1	0	2.353728	-2.623549	-6.732092
31	1	0	0.761465	-3.438217	-6.733562
32	1	0	1.200632	-2.330842	-8.057292
33	1	0	-0.446157	0.866753	-0.486369
34	1	0	0.447317	-0.868774	1.917650

Table S7. (MeO, Cl)-BD, **2c** at APFD/6-311G*

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.435157
3	6	0	-0.156784	-1.115087	-0.743770
4	6	0	0.155913	1.109411	2.186779
5	1	0	-0.289184	-2.057584	-0.210845
6	1	0	0.288964	2.057682	1.665364
7	6	0	-0.171731	-1.220675	-2.192742
8	6	0	0.167887	1.194088	3.638705
9	6	0	-0.347813	-2.482352	-2.786874
10	6	0	-0.370475	-2.643806	-4.158395
11	6	0	-0.216326	-1.537714	-4.998419
12	6	0	-0.039542	-0.270214	-4.432149
13	6	0	-0.019236	-0.125890	-3.052614
14	1	0	-0.469456	-3.355123	-2.149827
15	1	0	-0.506785	-3.620935	-4.610843
16	8	0	-0.252621	-1.796951	-6.326231
17	1	0	0.082782	0.608055	-5.056119
18	1	0	0.119520	0.869748	-2.641884
19	6	0	0.341415	2.445942	4.246748
20	6	0	0.361774	2.592132	5.626411
21	6	0	0.206273	1.469005	6.427256
22	6	0	0.031971	0.210334	5.859373
23	6	0	0.013918	0.080960	4.481022
24	1	0	0.463410	3.327146	3.622054
25	1	0	0.497098	3.568916	6.078433
26	17	0	0.229285	1.634124	8.159819
27	1	0	-0.088265	-0.659174	6.496905
28	1	0	-0.122864	-0.908237	4.055523
29	6	0	-0.101673	-0.717840	-7.220669
30	1	0	-0.901481	0.021388	-7.098005
31	1	0	0.870030	-0.226089	-7.097528
32	1	0	-0.161390	-1.147127	-8.219197
33	1	0	0.135822	0.965512	-0.486257
34	1	0	-0.136122	-0.967627	1.917556

Table S8. (MeO, Br)-BD, **3b** at APFD/6-311G*

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.435167
3	6	0	1.116273	0.151298	-0.743301
4	6	0	-1.110105	-0.150603	2.186871
5	1	0	2.059535	0.278927	-0.210489
6	1	0	-2.059110	-0.279188	1.665758
7	6	0	1.220326	0.165561	-2.191792
8	6	0	-1.193963	-0.162172	3.638789
9	6	0	2.474900	0.333431	-2.786672
10	6	0	2.643498	0.356238	-4.166529
11	6	0	1.531941	0.207869	-4.997512
12	6	0	0.265469	0.038549	-4.422195
13	6	0	0.115964	0.018252	-3.052311
14	1	0	3.349866	0.450251	-2.151614
15	1	0	3.638099	0.489275	-4.577023
16	8	0	1.562797	0.212294	-6.350234
17	1	0	-0.587390	-0.075163	-5.084032
18	1	0	-0.879296	-0.114626	-2.639150
19	6	0	-0.080007	-0.012519	4.480512
20	6	0	-0.207921	-0.030085	5.859311
21	6	0	-1.467868	-0.199762	6.429610
22	6	0	-2.592514	-0.350880	5.627357
23	6	0	-2.446035	-0.330832	4.247406
24	1	0	0.909689	0.120633	4.054795
25	1	0	0.664958	0.087152	6.492611
26	35	0	-1.647386	-0.224527	8.323059
27	1	0	-3.571459	-0.482736	6.075471
28	1	0	-3.328211	-0.449407	3.623284
29	6	0	2.810107	0.378756	-6.985700
30	1	0	3.266183	1.341805	-6.729376
31	1	0	3.502682	-0.431084	-6.729463
32	1	0	2.607002	0.351722	-8.054757
33	1	0	-0.965834	-0.130999	-0.486651
34	1	0	0.968237	0.131373	1.917681

Table S9. (MeO, Br)-BD, **3c** at APFD/6-311G*

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.435085
3	6	0	0.704772	-0.878440	-0.743598
4	6	0	-0.700863	0.873961	2.186859
5	1	0	1.300625	-1.620465	-0.210506
6	1	0	-1.299920	1.621208	1.665795
7	6	0	0.771298	-0.962019	-2.192501
8	6	0	-0.753774	0.940059	3.638750
9	6	0	1.570905	-1.953781	-2.786546
10	6	0	1.672757	-2.081150	-4.158045
11	6	0	0.971166	-1.212274	-4.998115
12	6	0	0.167759	-0.216045	-4.431913
13	6	0	0.076814	-0.102095	-3.052415
14	1	0	2.124450	-2.639383	-2.149456
15	1	0	2.292034	-2.849187	-4.610459
16	8	0	1.134906	-1.416545	-6.325870
17	1	0	-0.389438	0.473694	-5.055965
18	1	0	-0.554500	0.680224	-2.641743
19	6	0	-0.051939	0.062117	4.480442
20	6	0	-0.132431	0.163009	5.859241
21	6	0	-0.926177	1.156061	6.429620
22	6	0	-1.634838	2.042355	5.627386
23	6	0	-1.542660	1.926835	4.247437
24	1	0	0.571456	-0.718020	4.054750
25	1	0	0.417518	-0.524963	6.492463
26	35	0	-1.039180	1.297721	8.323023
27	1	0	-2.251600	2.813895	6.075557
28	1	0	-2.098542	2.622088	3.623367
29	6	0	0.450177	-0.569001	-7.220398
30	1	0	-0.636022	-0.646945	-7.096827
31	1	0	0.756052	0.476315	-7.098200
32	1	0	0.721805	-0.906847	-8.218887
33	1	0	-0.610091	0.760493	-0.486347
34	1	0	0.611407	-0.762220	1.917506

Table S10. (MeO, I)-BD, **4b** at APFD/6-311G*

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.435038
3	6	0	1.117569	0.144659	-0.742797
4	6	0	-1.110923	-0.143894	2.186992
5	1	0	2.061271	0.266628	-0.209448
6	1	0	-2.060983	-0.266615	1.666458
7	6	0	1.222509	0.158364	-2.191113
8	6	0	-1.193528	-0.154991	3.638811
9	6	0	2.478441	0.318971	-2.785177
10	6	0	2.647974	0.340855	-4.164888
11	6	0	1.536003	0.198969	-4.996515
12	6	0	0.268174	0.036969	-4.421971
13	6	0	0.117744	0.017484	-3.052219
14	1	0	3.353675	0.430682	-2.149579
15	1	0	3.643548	0.468131	-4.574828
16	8	0	1.567657	0.203267	-6.349083
17	1	0	-0.584905	-0.071772	-5.084347
18	1	0	-0.878495	-0.109650	-2.639627
19	6	0	-2.446014	-0.314985	4.248604
20	6	0	-2.591213	-0.334210	5.628912
21	6	0	-1.465797	-0.191244	6.434238
22	6	0	-0.205333	-0.030246	5.858869
23	6	0	-0.078138	-0.013283	4.479762
24	1	0	-3.329829	-0.427331	3.625466
25	1	0	-3.573784	-0.459674	6.070910
26	53	0	-1.664120	-0.218090	8.539555
27	1	0	0.673218	0.081309	6.485320
28	1	0	0.912426	0.112977	4.053716
29	6	0	2.816259	0.362503	-6.984010
30	1	0	3.277741	1.322892	-6.727442
31	1	0	3.503950	-0.451368	-6.727460
32	1	0	2.613441	0.336663	-8.053139
33	1	0	-0.966453	-0.125188	-0.486888
34	1	0	0.969007	0.125513	1.917536

Table S11. (MeO, I)-BD, **4c** at APFD/6-311G*

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.434955
3	6	0	0.694667	0.886936	-0.743141
4	6	0	-0.690276	-0.882268	2.186964
5	1	0	1.281849	1.635491	-0.209567
6	1	0	-1.280469	-1.636875	1.666460
7	6	0	0.760579	0.971888	-2.191878
8	6	0	-0.741552	-0.948037	3.638752
9	6	0	1.551333	1.971140	-2.785259
10	6	0	1.652292	2.099999	-4.156644
11	6	0	0.958614	1.225209	-4.997213
12	6	0	0.163961	0.221580	-4.431624
13	6	0	0.073817	0.106198	-3.052241
14	1	0	2.098604	2.661361	-2.147746
15	1	0	2.264721	2.873739	-4.608643
16	8	0	1.120726	1.431533	-6.324713
17	1	0	-0.387053	-0.472702	-5.056116
18	1	0	-0.550791	-0.681708	-2.642008
19	6	0	-1.517664	-1.944007	4.248575
20	6	0	-1.607472	-2.059691	5.628873
21	6	0	-0.910031	-1.164953	6.434230
22	6	0	-0.129140	-0.162518	5.858815
23	6	0	-0.050450	-0.061161	4.479710
24	1	0	-2.065381	-2.646720	3.625459
25	1	0	-2.216247	-2.841080	6.070890
26	53	0	-1.032711	-1.323204	8.539452
27	1	0	0.415188	0.536103	6.485209
28	1	0	0.563087	0.726729	4.053726
29	6	0	0.443772	0.578379	-7.219927
30	1	0	0.758925	-0.464211	-7.098157
31	1	0	-0.643091	0.646664	-7.096607
32	1	0	0.712705	0.919178	-8.218130
33	1	0	-0.600906	-0.767597	-0.486558
34	1	0	0.602243	0.769468	1.917367

Table S12. (F, F)-BD, **5** at APFD/6-311G*

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.436128
3	6	0	0.884245	0.692373	-0.746299
4	6	0	-0.884247	-0.692370	2.182427
5	1	0	1.635620	1.281064	-0.219118
6	1	0	-1.635625	-1.281057	1.655246
7	6	0	0.960116	0.751601	-2.198333
8	6	0	-0.960117	-0.751599	3.634461
9	6	0	1.957611	1.536490	-2.795319
10	6	0	2.082095	1.634101	-4.174228
11	6	0	1.193166	0.934194	-4.972719
12	6	0	0.190724	0.145217	-4.424412
13	6	0	0.080705	0.058998	-3.046713
14	1	0	2.651948	2.083219	-2.162638
15	1	0	2.854087	2.241614	-4.634967
16	9	0	1.301024	1.018730	-6.309269
17	1	0	-0.487190	-0.388773	-5.082359
18	1	0	-0.705309	-0.559988	-2.625953
19	6	0	-1.957640	-1.536453	4.231447
20	6	0	-2.082125	-1.634060	5.610356
21	6	0	-1.193171	-0.934187	6.408847
22	6	0	-0.190699	-0.145247	5.860540
23	6	0	-0.080678	-0.059031	4.482840
24	1	0	-2.651998	-2.083155	3.598767
25	1	0	-2.854140	-2.241546	6.071095
26	9	0	-1.301030	-1.018720	7.745397
27	1	0	0.487236	0.388716	6.518486
28	1	0	0.705360	0.559923	4.062080
29	1	0	-0.768605	-0.601650	-0.484170
30	1	0	0.768606	0.601650	1.920297

Table S13. (Cl, Cl)-BD, **6** at APFD/6-311G*

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.435592
3	6	0	0.894286	-0.681100	-0.745284
4	6	0	-0.894283	0.681104	2.180875
5	1	0	1.653327	-1.259721	-0.218231
6	1	0	-1.653317	1.259734	1.653822
7	6	0	0.969675	-0.738272	-2.196654
8	6	0	-0.969668	0.738285	3.632245
9	6	0	1.975726	-1.509947	-2.795398
10	6	0	2.099825	-1.604635	-4.174018
11	6	0	1.204132	-0.916983	-4.981637
12	6	0	0.192896	-0.141078	-4.422005
13	6	0	0.082176	-0.056653	-3.044697
14	1	0	2.678096	-2.049220	-2.165024
15	1	0	2.884296	-2.206431	-4.620127
16	17	0	1.345081	-1.024465	-6.711774
17	1	0	-0.499827	0.391021	-5.065269
18	1	0	-0.711850	0.553078	-2.625229
19	6	0	-1.975638	1.510066	4.230987
20	6	0	-2.099724	1.604775	5.609606
21	6	0	-1.204101	0.917035	6.417227
22	6	0	-0.192947	0.141021	5.857597
23	6	0	-0.082240	0.056576	4.480290
24	1	0	-2.677953	2.049409	3.600612
25	1	0	-2.884132	2.206655	6.055714
26	17	0	-1.345037	1.024540	8.147364
27	1	0	0.499719	-0.391150	6.500864
28	1	0	0.711715	-0.553248	4.060824
29	1	0	-0.776267	0.590963	-0.484779
30	1	0	0.776269	-0.590960	1.920370

Table S14. (Br, Br)-BD, **7** at APFD/6-311G*

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.435523
3	6	0	0.884447	0.694091	-0.745118
4	6	0	-0.884446	-0.694092	2.180642
5	1	0	1.635136	1.283513	-0.218109
6	1	0	-1.635134	-1.283515	1.653632
7	6	0	0.958691	0.752210	-2.196450
8	6	0	-0.958688	-0.752215	3.631973
9	6	0	1.954394	1.536846	-2.795253
10	6	0	2.077728	1.633740	-4.174109
11	6	0	1.190530	0.934230	-4.983603
12	6	0	0.188813	0.144699	-4.421984
13	6	0	0.080045	0.059290	-3.044264
14	1	0	2.649970	2.085301	-2.165110
15	1	0	2.855690	2.246857	-4.615942
16	35	0	1.342729	1.053758	-6.874505
17	1	0	-0.499192	-0.397931	-5.061330
18	1	0	-0.706191	-0.560708	-2.624960
19	6	0	-1.954385	-1.536860	4.230775
20	6	0	-2.077717	-1.633759	5.609631
21	6	0	-1.190526	-0.934241	6.419126
22	6	0	-0.188815	-0.144701	5.857509
23	6	0	-0.080047	-0.059289	4.479788
24	1	0	-2.649956	-2.085321	3.600631
25	1	0	-2.855673	-2.246884	6.051463
26	35	0	-1.342724	-1.053773	8.310028
27	1	0	0.499186	0.397934	6.496855
28	1	0	0.706184	0.560715	4.060486
29	1	0	-0.767490	-0.602152	-0.484928
30	1	0	0.767490	0.602152	1.920451

Table S15. (I, I)-BD, **8** at APFD/6-311G*

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.435409
3	6	0	0.521171	-0.996391	-0.744933
4	6	0	-0.521166	0.996393	2.180341
5	1	0	0.963282	-1.842349	-0.218139
6	1	0	-0.963268	1.842357	1.653547
7	6	0	0.564675	-1.079202	-2.196203
8	6	0	-0.564671	1.079205	3.631611
9	6	0	1.149053	-2.203638	-2.795599
10	6	0	1.221267	-2.341804	-4.174805
11	6	0	0.700960	-1.339658	-4.987778
12	6	0	0.113071	-0.208207	-4.421515
13	6	0	0.049088	-0.085897	-3.043508
14	1	0	1.557487	-2.990303	-2.166095
15	1	0	1.679304	-3.223304	-4.610164
16	53	0	0.800444	-1.529879	-7.090579
17	1	0	-0.292755	0.573695	-5.054371
18	1	0	-0.412338	0.802819	-2.624159
19	6	0	-1.148983	2.203675	4.231007
20	6	0	-1.221189	2.341846	5.610213
21	6	0	-0.700944	1.339668	6.423187
22	6	0	-0.113124	0.208180	5.856924
23	6	0	-0.049147	0.085867	4.478917
24	1	0	-1.557369	2.990365	3.601502
25	1	0	-1.679174	3.223372	6.045572
26	53	0	-0.800419	1.529893	8.525987
27	1	0	0.292652	-0.573748	6.489780
28	1	0	0.412221	-0.802879	4.059567
29	1	0	-0.452222	0.864228	-0.485081
30	1	0	0.452221	-0.864229	1.920489

Table S16. (MeO, MeO)-BD, **9b** at APFD/6-311G*

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.435667
3	6	0	0.143949	-1.112733	-0.749593
4	6	0	-0.143945	1.112733	2.185260
5	1	0	0.266343	-2.060166	-0.222964
6	1	0	-0.266335	2.060167	1.658632
7	6	0	0.156289	-1.207238	-2.199713
8	6	0	-0.156280	1.207238	3.635381
9	6	0	0.316314	-2.458015	-2.804521
10	6	0	0.336837	-2.617131	-4.186042
11	6	0	0.194113	-1.499666	-5.009322
12	6	0	0.032690	-0.236963	-4.424778
13	6	0	0.014574	-0.096905	-3.053389
14	1	0	0.428760	-3.338264	-2.175911
15	1	0	0.463815	-3.609891	-4.603139
16	8	0	0.197071	-1.521395	-6.363959
17	1	0	-0.076850	0.621527	-5.080176
18	1	0	-0.112259	0.896327	-2.633374
19	6	0	-0.316258	2.458020	4.240189
20	6	0	-0.336777	2.617135	5.621711
21	6	0	-0.194095	1.499665	6.444990
22	6	0	-0.032717	0.236956	5.860445
23	6	0	-0.014607	0.096899	4.489055
24	1	0	-0.428669	3.338274	3.611580
25	1	0	-0.463721	3.609900	6.038809
26	8	0	-0.197055	1.521392	7.799627
27	1	0	0.076791	-0.621539	6.515841
28	1	0	0.112183	-0.896338	4.069040
29	6	0	0.356126	-2.765498	-7.005719
30	1	0	1.316690	-3.229002	-6.752584
31	1	0	-0.457095	-3.455649	-6.752822
32	1	0	0.329644	-2.557179	-8.073940
33	1	0	-0.125345	0.968314	-0.484040
34	1	0	0.125346	-0.968314	1.919707
35	6	0	-0.356065	2.765500	8.441387
36	1	0	0.457181	3.455624	8.188493
37	1	0	-1.316611	3.229038	8.188251
38	1	0	-0.329606	2.557178	9.509608

Table S17. (MeO, MeO)-BD, **9c** at APFD/6-311G*

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.435497
3	6	0	-0.159208	-1.110407	-0.749916
4	6	0	0.159209	1.110407	2.185412
5	1	0	-0.294559	-2.055927	-0.223061
6	1	0	0.294563	2.055926	1.658556
7	6	0	-0.173094	-1.206426	-2.200435
8	6	0	0.173096	1.206428	3.635931
9	6	0	-0.351067	-2.463253	-2.804128
10	6	0	-0.372814	-2.615701	-4.177118
11	6	0	-0.215822	-1.505021	-5.009847
12	6	0	-0.037146	-0.242285	-4.434790
13	6	0	-0.017795	-0.107025	-3.053822
14	1	0	-0.475038	-3.340175	-2.173140
15	1	0	-0.510691	-3.589829	-4.635765
16	8	0	-0.251450	-1.755653	-6.341003
17	1	0	0.087493	0.640233	-5.052445
18	1	0	0.122489	0.885747	-2.636623
19	6	0	0.351088	2.463254	4.239621
20	6	0	0.372836	2.615706	5.612610
21	6	0	0.215826	1.505030	6.445342
22	6	0	0.037132	0.242296	5.870289
23	6	0	0.017780	0.107033	4.489321
24	1	0	0.475073	3.340173	3.608630
25	1	0	0.510727	3.589833	6.071255
26	8	0	0.251459	1.755665	7.776498
27	1	0	-0.087522	-0.640218	6.487946
28	1	0	-0.122521	-0.885738	4.072125
29	6	0	-0.098039	-0.670085	-7.225936
30	1	0	-0.896406	0.070084	-7.098077
31	1	0	0.874313	-0.180353	-7.098329
32	1	0	-0.157651	-1.090562	-8.228368
33	1	0	0.138719	0.966757	-0.483724
34	1	0	-0.138719	-0.966757	1.919221
35	6	0	0.098012	0.670105	8.661434
36	1	0	-0.874350	0.180396	8.533815
37	1	0	0.896363	-0.070085	8.533590
38	1	0	0.157619	1.090585	9.663865

Table S18. Thermochemical Energies Obtained at APFD/6-311G*

	Total Energy (Hartree)	**ZPVE (kcal mol^{-1})**	**Thermal Energy, TE (kcal mol^{-1})**	**Entropy, *S* (cal K^{-1} mol^{-1})**
1, (MeO, F)	-831.368980	171.54	182.14	137.82
2, (MeO, Cl)	-1191.678500	170.69	181.54	140.49
3, (MeO, Br)	-3305.520900	170.27	181.28	143.42
4, (MeO, I)	-7650.890700	170.03	181.16	145.46
5, (F, F)	-816.105830	145.90	155.43	130.24
6, (Cl, Cl)	-1536.724600	144.20	154.23	135.65
7, (Br, Br)	-5764.409300	143.36	153.73	141.26
8, (I, I)	-14455.149000	142.90	153.48	145.38
9, (MeO, MeO)	-846.631760	197.17	208.84	145.54
10, (H, H)	-617.707060	156.17	164.67	121.63