Electronic supplementary materials *Mendeleev Commun.*, 2020, **30**, 103–105

Crystal structure and conformational diversity of fluorinated alkyl tosylates

Dmitry E. Arkhipov, Alexander V. Lyubeshkin, Alexander D. Volodin and Alexander A. Korlyukov

Table of contents

General procedure for the synthesis of fluorinated alkyl tosylates.

Tosyl chloride (2.10 g, 11 mmol) in dichloromethane (20 ml) was added to a stirred suspension of an alcohol (10 mmol), KOH (0.84 g, 15 mmol), triethylamine (0.14 ml, 1 mmol) and trimethylamine hydrochloride (0.10 g, 1 mmol) in dichloromethane (20 ml) at 5–10°C, and the mixture was stirred for 1 h and at room temperature for 3–5 h. Aqueous 1 M hydrochloric acid solution (20 ml) was added to the mixture, the organic layer was separated, washed once with 20 ml of water and dried with anhydrous sodium sulfate. The precipitate was filtered off; the solvent was removed by a rotary evaporator, obtaining the desired tosylates.

2,2,3,4,4,4-hexafluorobutyl 4-methylbenzenesulfonate (1) yield 85 %, M.p., °C 28–30

^{1}H NMR (500 MHz, $CDCl_3$) δ 2.48 (s, 3H, CH_3), 4.25-4.42 (m, 2H, CH_2), 4.95 (dm, 1H, $^{2}J_{HF}$ 43 Hz, CHF). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.28 (s, C^{Ar}), 131.61(s, C^{Ar}), 130.38 (s, CH^{Ar}), 128.24 (s, CH^{Ar}), 120.4 (qd, $^{1}J_{CF}$ 282.3 Hz, $^{2}J_{CF}$ 25.5 Hz, CF_3), 115.2 (td, $^{1}J_{CF}$ 252.7 Hz, $^{2}J_{CF}$ 24.9 Hz, CF_2), 83.4 (dtq, $^{1}J_{CF}$ 196.4 Hz, $^{2}J_{CF}$ 35.2, 25.6 Hz, CHF), 65.1 ((dd, $^{2}J_{CF}$ 38.6, 27.4 Hz, CH_2), 21.7 (s, CH_3). ^{19}F NMR (471.29 MHz, $CDCl_3$) δ –74.0 (m, 3F, CF_3), –115.6 (AB, 1F, d, $^{2}J_{FF}$ 280 Hz, CF_2), –121.1 (AB, 1F, d, $^{2}J_{FF}$ 280 Hz, CF_2), –212.8 (m, 1F, $^{2}J_{FH}$ 43 Hz, CHF).

Found, %: C, 39.33; H, 3.08; F, 33.29. Calcd, %: C, 39.29; H, 3.00; F, 33.90.

2,2,3,3,4,4,5,5-octafluoropentyl 4-methylbenzenesulfonate (2) yield 94 %, M.p., °C 14–15

^{1}H NMR (500 MHz, $CDCl_3$) δ 2.48 (s, 3H, CH_3), 4.46 (t, 2H, $^{3}J_{HF}$ 13 Hz, CH_2), 6.02 (tt, 1H, $^{2}J_{HF}$ 53 Hz, $^{3}J_{HF}$ 5.3 Hz, CHF_2), 7.40 (d, 2H, $^{3}J_{HH}$ 8.2 Hz, CH^{Ar}), 7.82 (d, 2H, $^{3}J_{HH}$ 8.2 Hz, CH^{Ar}). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.16 (s, C^{Ar}), 131.87 (s, C^{Ar}), 130.29 (s, CH^{Ar}), 128.22 (s, CH^{Ar}), 113.81 (tt, $^{1}J_{CF}$ 259.0 Hz, $^{2}J_{CF}$ 31.7 Hz, CF_2), 110.68 (tt, 2C, $^{1}J_{CF}$ 263.8 Hz, $^{2}J_{CF}$ 32.7 Hz, CF_2), 107.63 (tt, $^{1}J_{CF}$ 254.8 Hz, $^{2}J_{CF}$ 31.3 Hz, CHF_2), 63.94 (t, $^{2}J_{CF}$ 27.4 Hz, CH_2), 21.7 (s, CH_3). ^{19}F NMR (471 MHz, $CDCl_3$) δ –119.7 (m, 2F, CF_2), –125.0 (m, 2F, CF_2), –129.8 (m, 2F, CF_2), –137.2 (dm, 2F, $^{2}J_{HF}$ 53 Hz, CHF_2).

Found, %: C, 37.28; H, 2.70; F, 38.72. Calcd, %: C, 37.32; H, 2.61; F, 39.35.

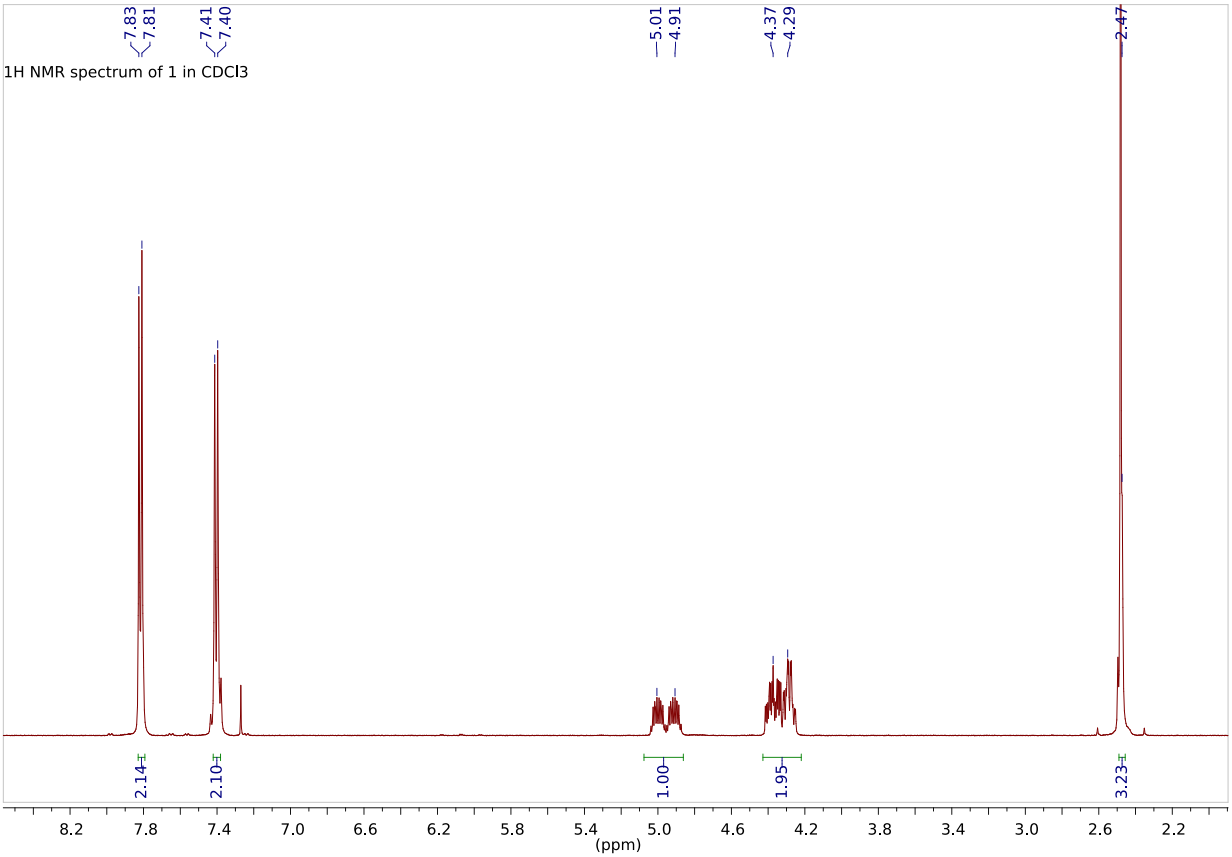


Figure S1 ^{1}H spectrum of compound **1**.

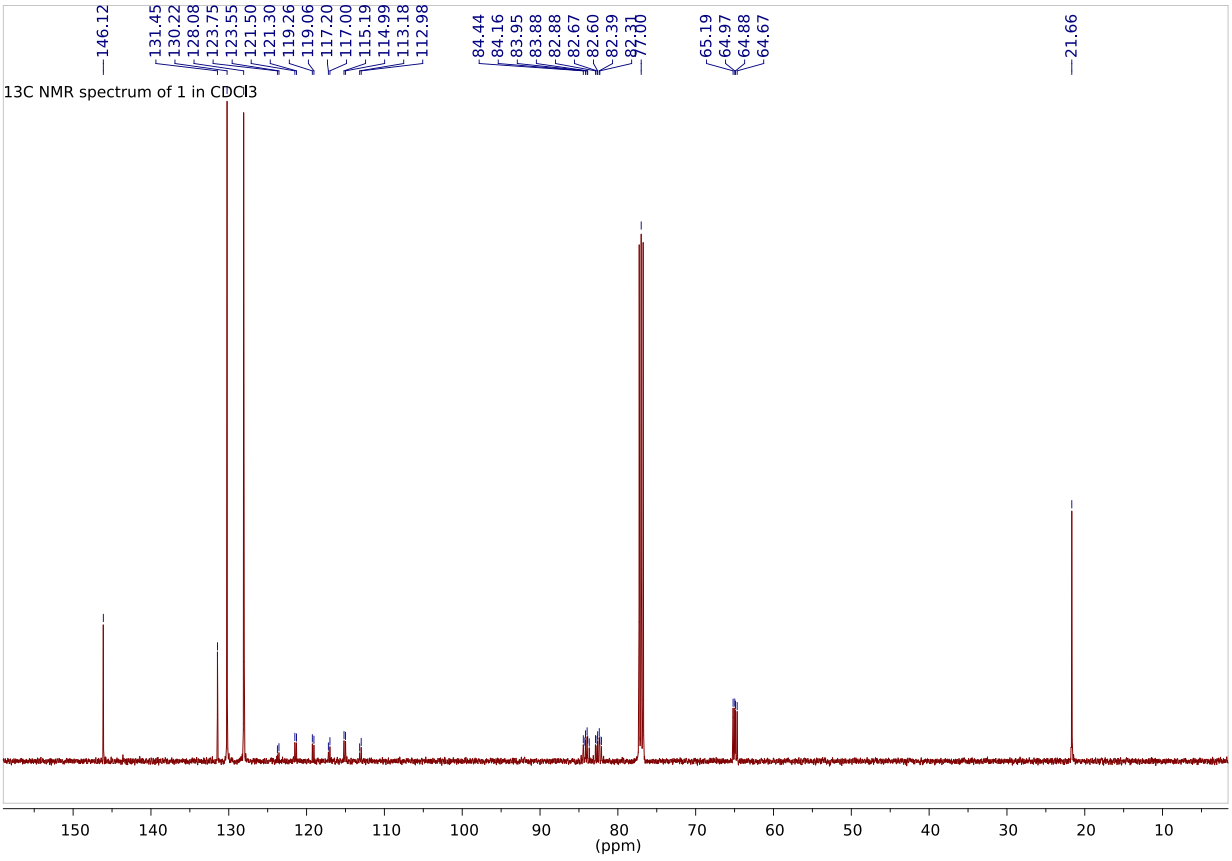


Figure S2 ^{13}C spectrum of compound **1**.

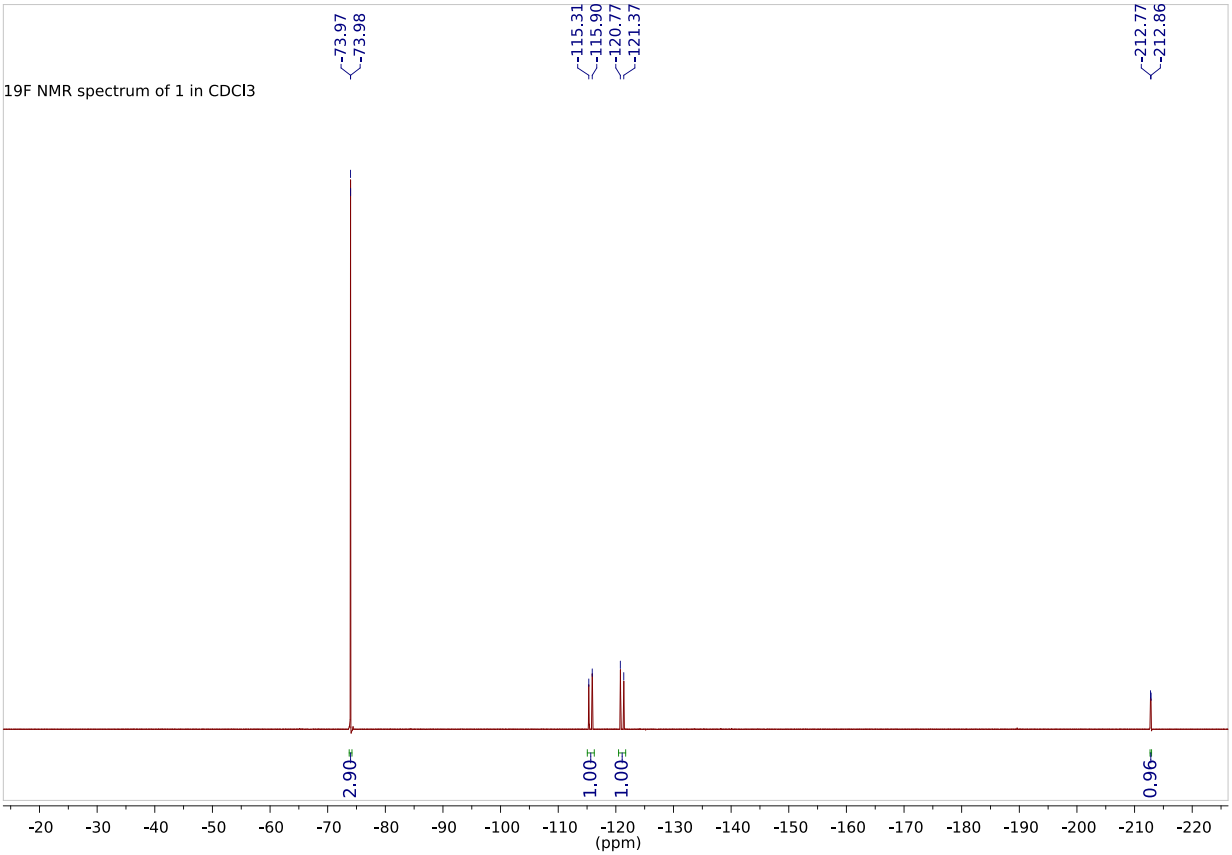


Figure S3 ^{19}F spectrum of compound **1**.

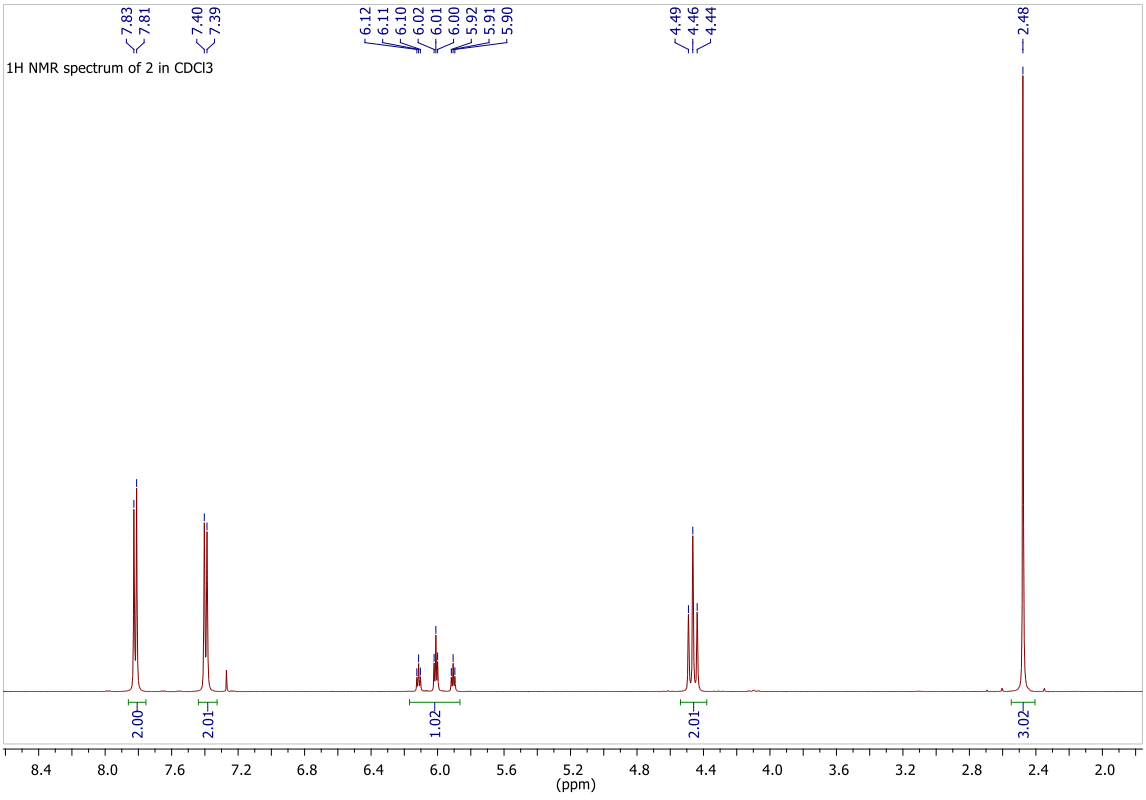


Figure S4 ^{1}H spectrum of compound **2**.

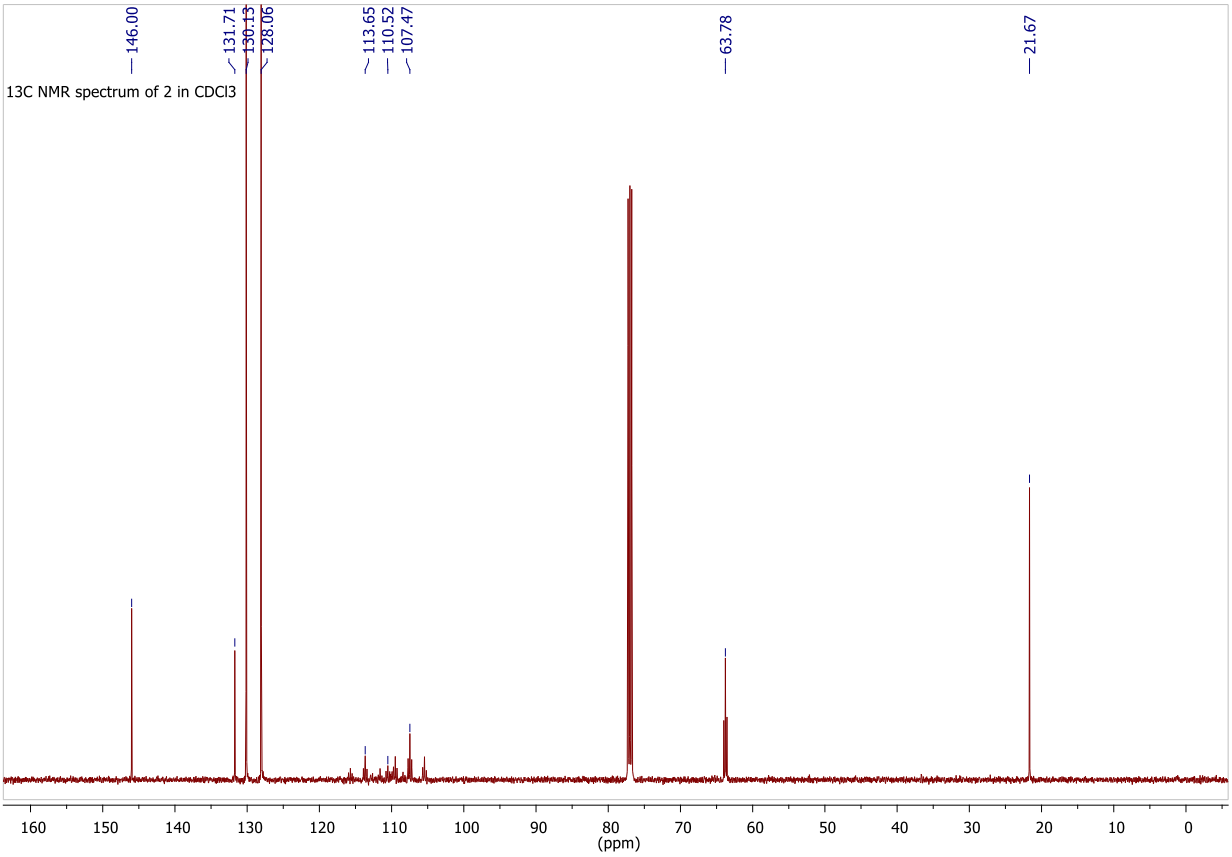
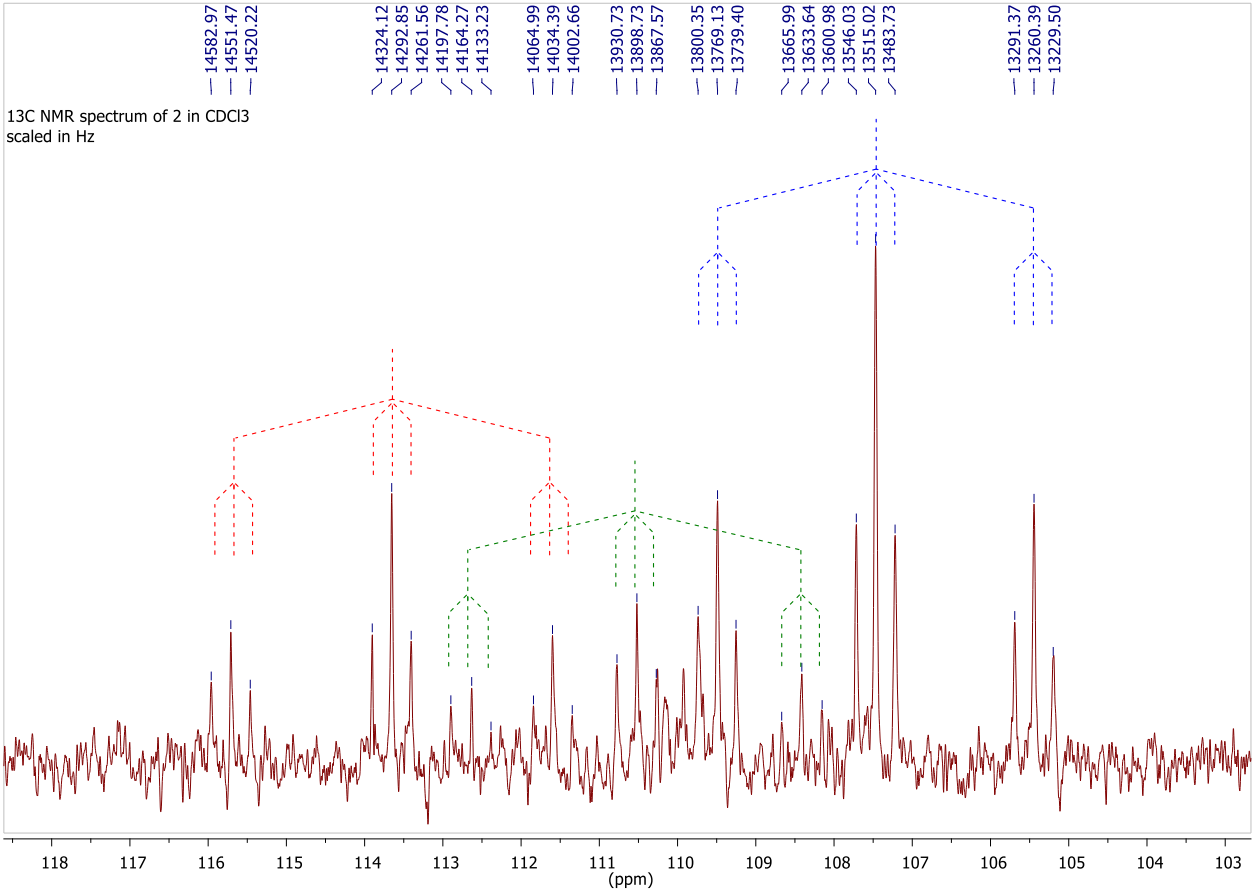


Figure S5 ^{13}C spectrum of compound **2**.



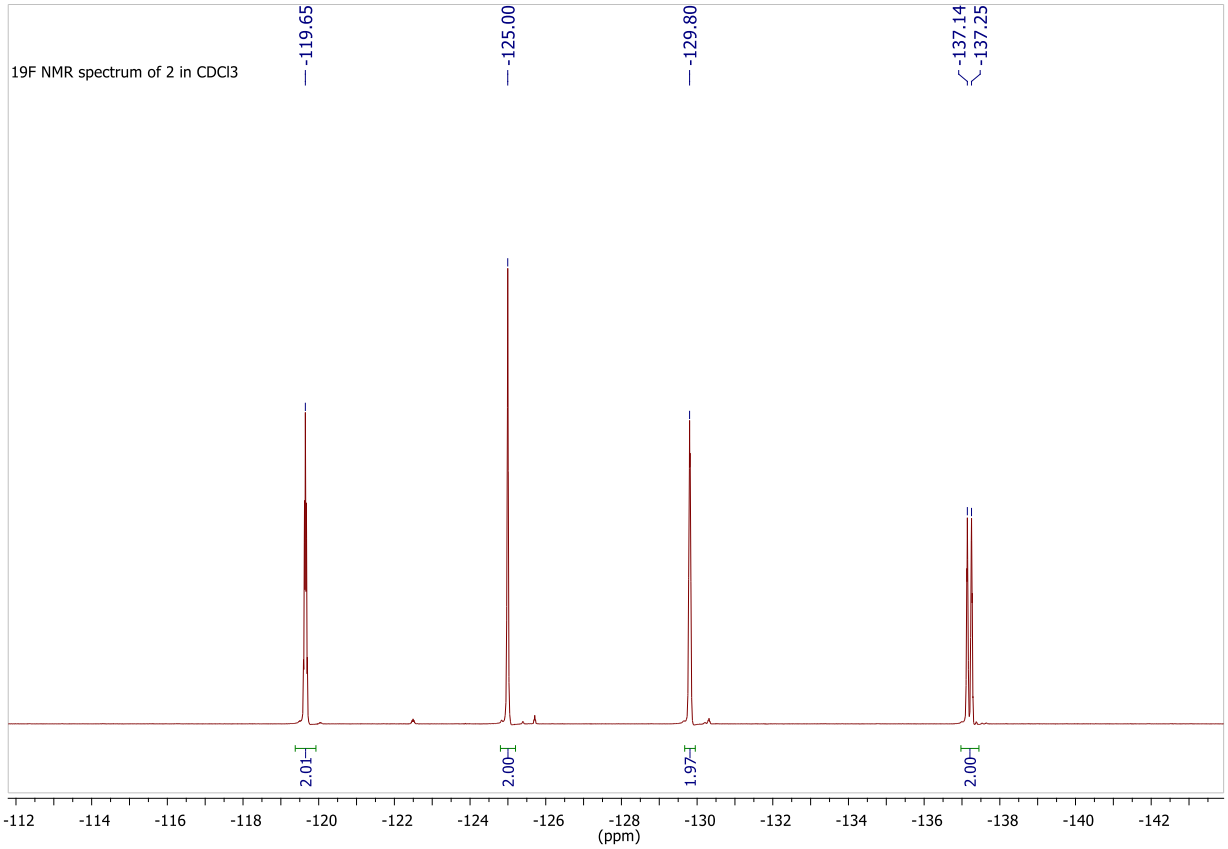


Figure S6 Interval of 102-119 ppm in ^{13}C spectrum of compound **2**.

Figure S7 ^{19}F spectrum of compound **2**.

Quantum chemical calculations

All calculations were carried out using NWCHEM 6.6 software[1]. PBE0 hybrid functional and 6-311G(d,p) basis set were used for geometry optimization, Hessian matrix calculations and electron density calculation. Dispersion correction D3[2] was applied to account van-der-Waals interactions. Topological analysis of electron density NCI study were carried out using AIMALL[3] and Multiwfn software[4].

Optimized structures of molecules 1 and 2

Optimized structure of isolated molecule **1** in head-to-tail conformation

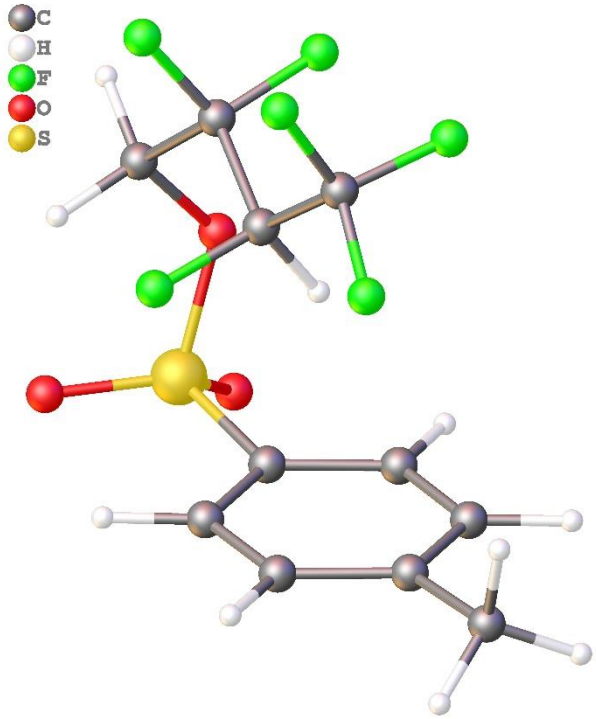


Figure S8 General view of optimized head-to-tail conformation of compound **1**.

Total DFT Energy = -1646.996215672838

Zero-Point correction to Energy = 131.489 kcal/mol

Optimized structure of isolated molecule **1** in linear conformation

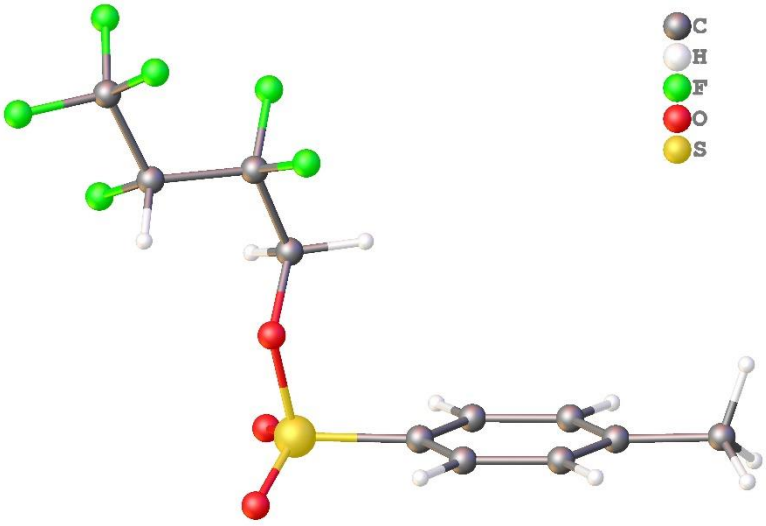


Figure S9 General view of optimized linear conformation of compound **1**.

Total DFT Energy = -1646.993132970825

Zero-Point correction to Energy = 131.461 kcal/mol

Optimized structure of dimer taken from crystal packing of compound **1**

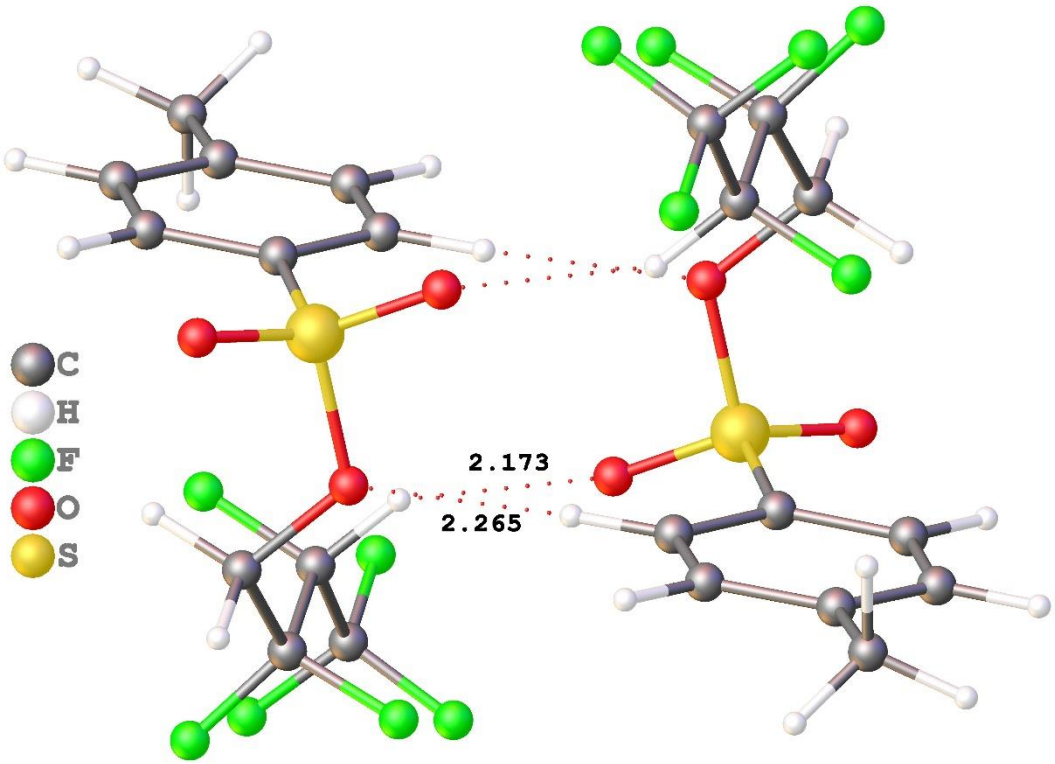


Figure S10 General view of dimer of compound **1** formed by C–H…O interactions. The shortest H…O (Å) distances are shown on picture.

Total DFT energy = -3294.019451538339 a.u.

The geometry of this dimer is close to that in crystal, even interatomic distances corresponding weak C-H…O hydrogen bonds are similar.

Optimized structure of isolated molecule **2** in linear conformation

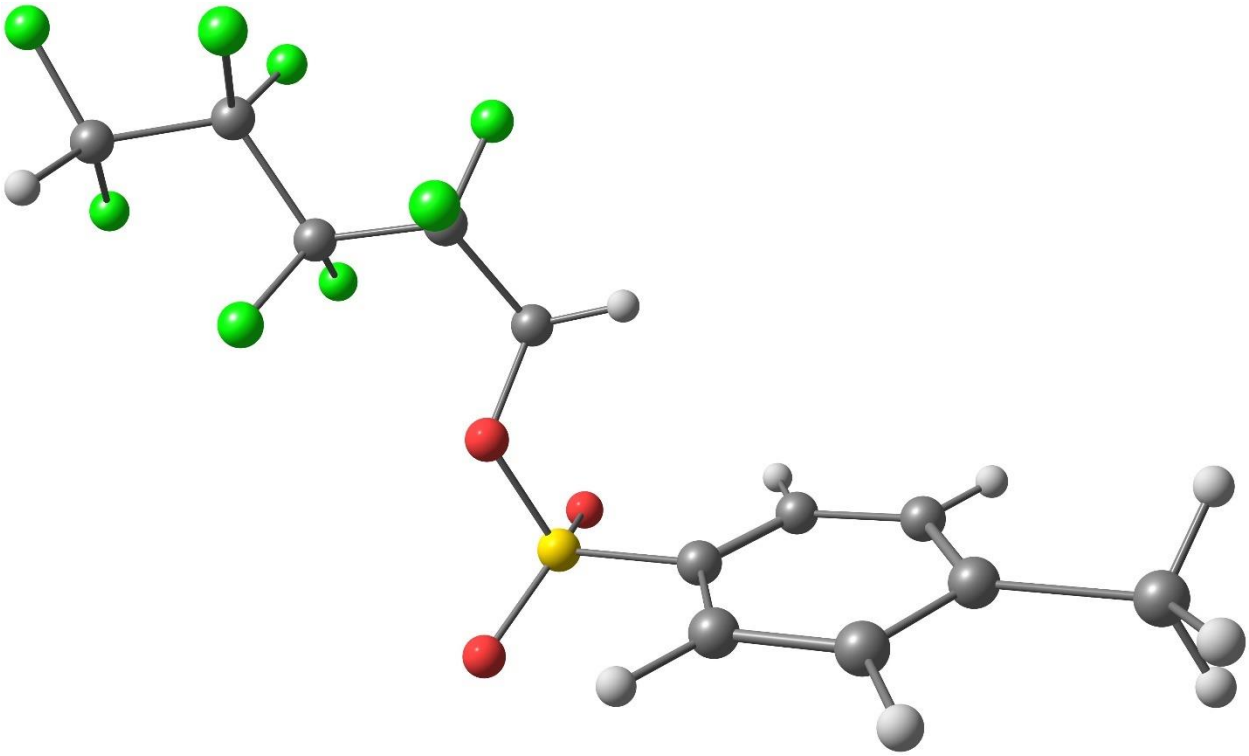


Figure S11 General view of linear conformation of compound **2**

Total DFT Energy = -1884.60611608 a.u.

Zero-Point correction to Energy = 140.861 kcal/mol

Optimized structure of isolated molecule **2** in L-shaped conformation

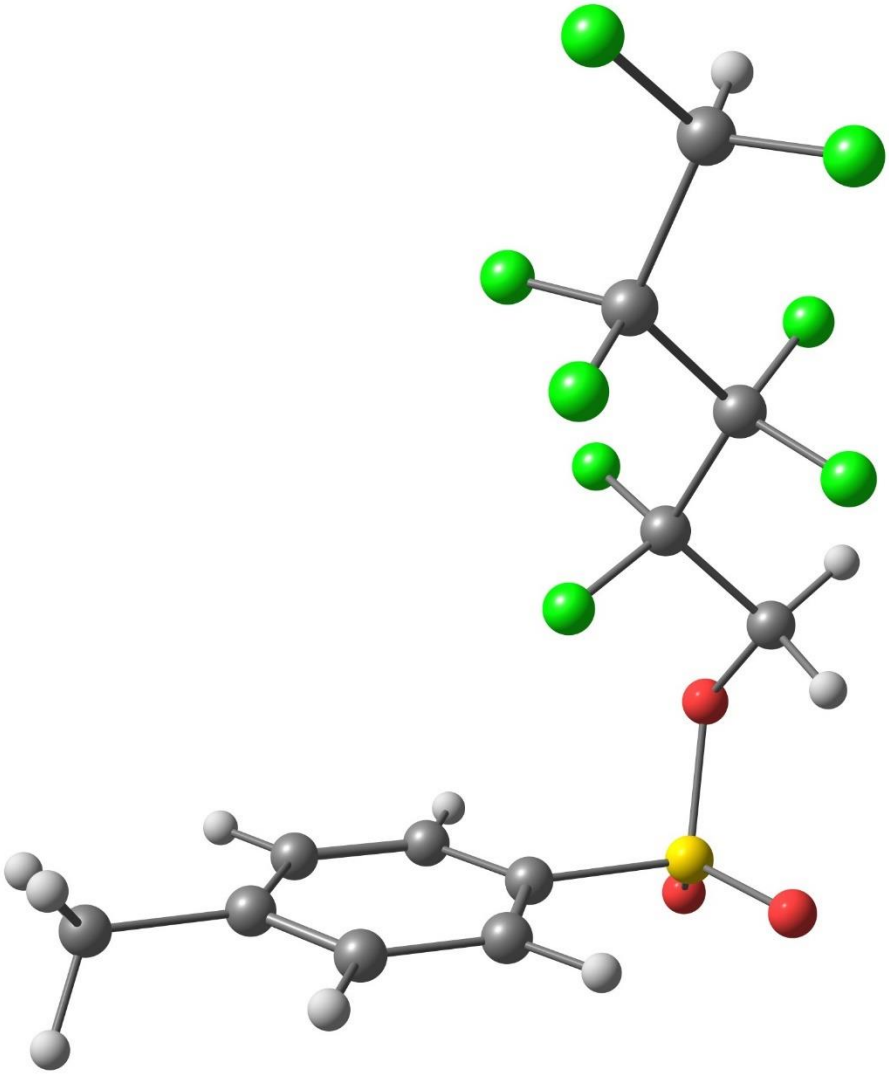


Figure S12 General view of L-shaped conformation of compound **2**.

Total DFT energy = -1884.606374212985 a.u.

Zero-Point correction to Energy = 140.882 kcal/mol

Optimized structure of dimer taken from crystal packing of compound **2**

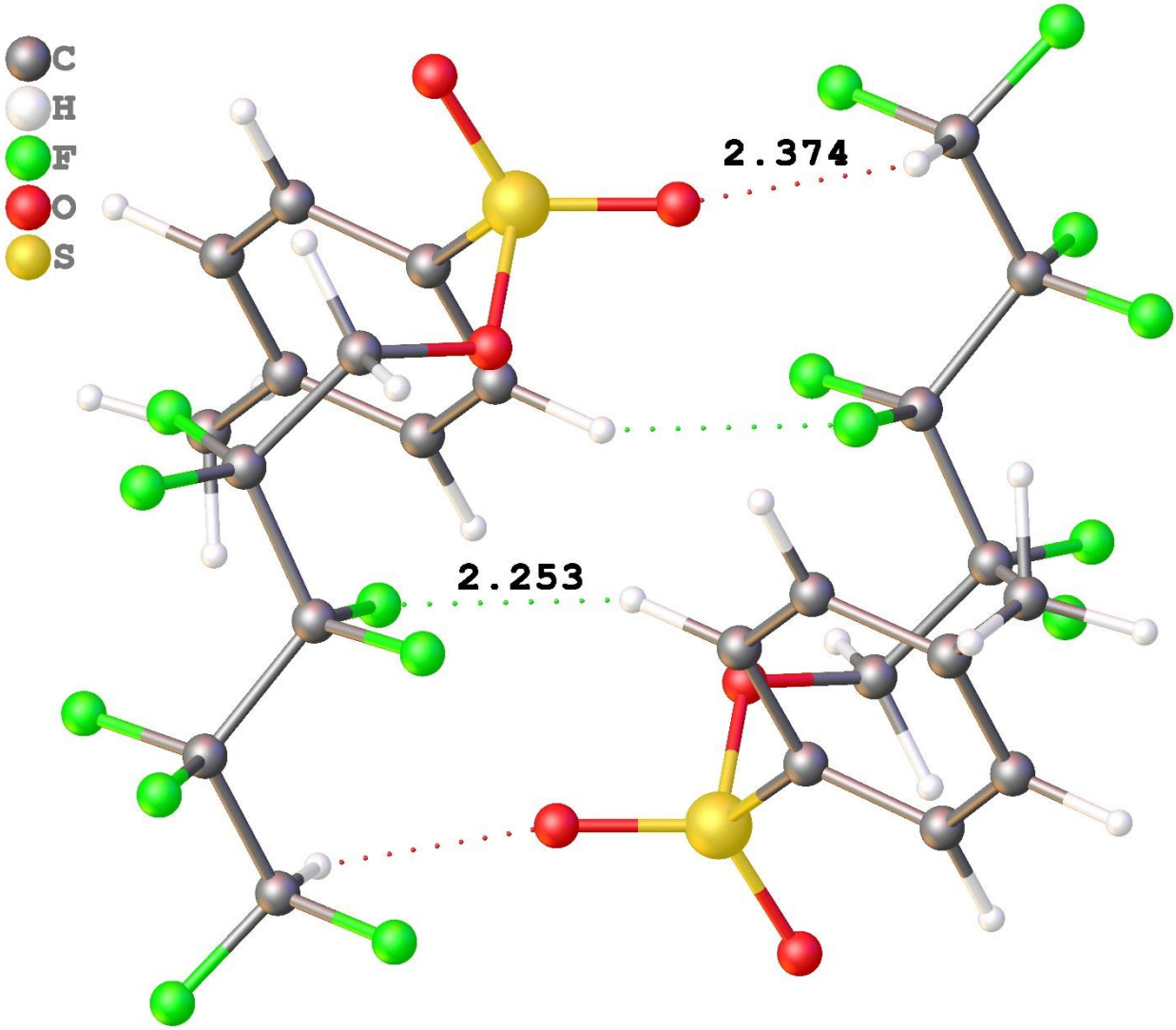


Figure S13 General view of dimer of compound **2**. Shortest H…O and H…F distances are shown under dotted lines.

Total DFT energy = -3769.24680253 a.u.

Initial geometry for calculation was obtained using -x, -y, 1-z symmetry operation. The optimization of geometry resulted to structure that is significantly different as compared to crystal. To C-H…F hydrogen bonds are formed.

Bond critical points for 1 (dimer)

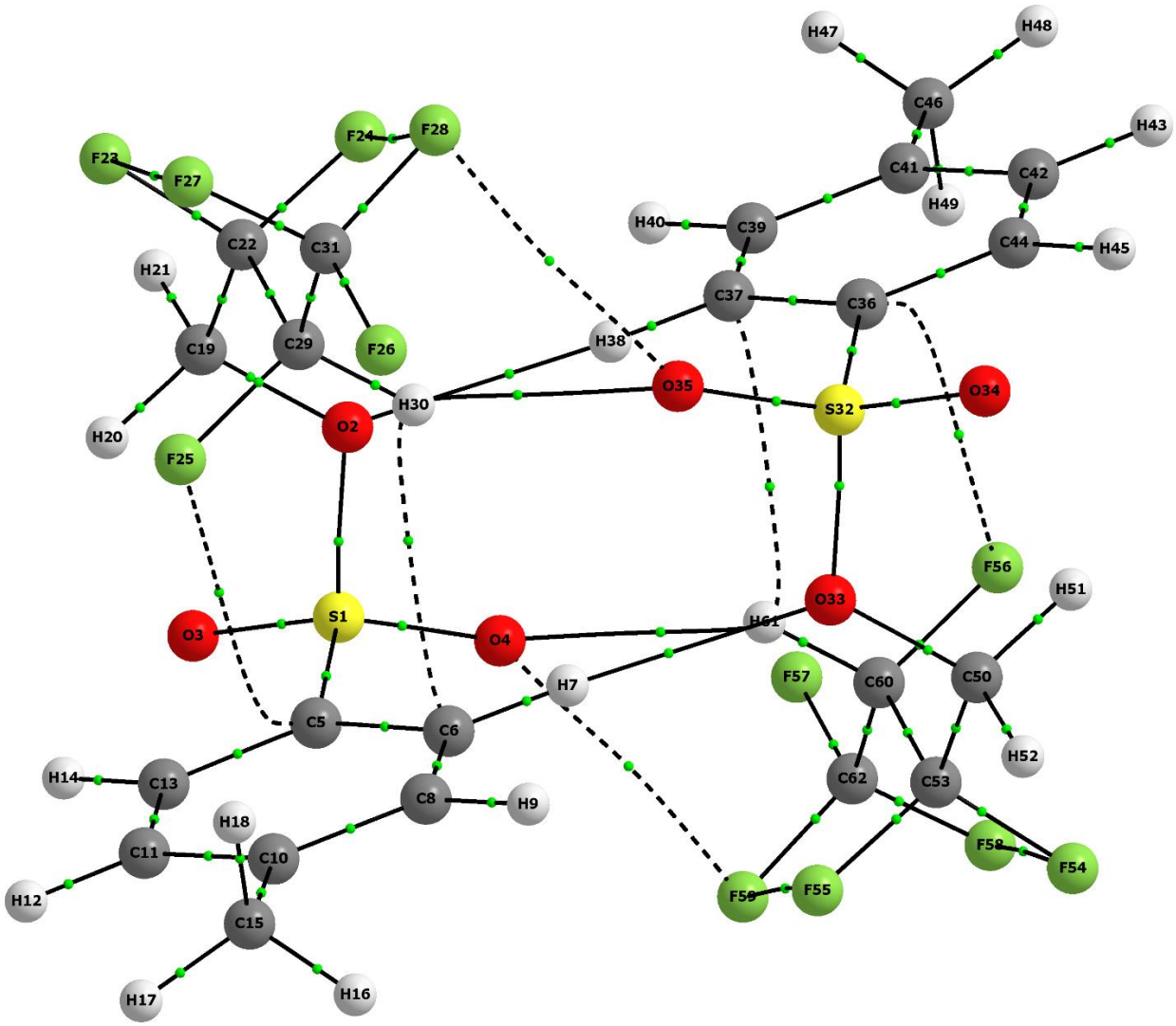


Figure S14 Molecular graph illustrating intermolecular bonding in dimer of compound **2**.

BCP #	Name	Atoms	Rho	DelSqRho	Ellipticity	K	V
1	BCP1	S1 - O2	0.210065	-0.15649	0.058307	0.248002	-0.45688
2	BCP2	S1 - O3	0.299253	1.146787	0.028569	0.357417	-1.00153
3	BCP3	S1 - O4	0.299427	1.149568	0.014573	0.356957	-1.00131
4	BCP4	S1 - C5	0.216351	-0.44975	0.101842	0.166536	-0.22063
5	BCP5	C5 - C6	0.306446	-0.84966	0.191145	0.31615	-0.41989
6	BCP6	C6 - H7	0.285861	-1.01252	0.012096	0.286762	-0.32039
7	BCP7	C6 - C8	0.313357	-0.89006	0.205608	0.32888	-0.43525
8	BCP8	C8 - H9	0.281599	-0.97732	0.016945	0.281425	-0.31852
9	BCP9	C8 - C10	0.307388	-0.86161	0.189614	0.31437	-0.41334
10	BCP10	C10 - C15	0.255684	-0.62752	0.035487	0.21844	-0.28
11	BCP11	C5 - C13	0.308032	-0.85491	0.207064	0.318983	-0.42424
12	BCP12	C11 - C13	0.311158	-0.88051	0.203568	0.324306	-0.42849
13	BCP13	C10 - C11	0.309119	-0.86808	0.201371	0.318004	-0.41899
14	BCP14	C11 - H12	0.281229	-0.9738	0.019019	0.281242	-0.31903
15	BCP15	C13 - H14	0.283539	-0.99412	0.014171	0.283616	-0.3187
16	BCP16	C6 - H30	0.006151	0.018904	0.301445	-0.00085	-0.00303

BCP #	Name	Atoms	Rho	DelSqRho	Ellipticity	K	V
17	BCP17	C15 - H17	0.274576	-0.91984	0.01248	0.272187	-0.31441
18	BCP18	C15 - H16	0.273488	-0.91288	0.013222	0.270495	-0.31277
19	BCP19	C15 - H18	0.270823	-0.89612	0.01069	0.26623	-0.30843
20	BCP20	O2 - C19	0.243392	-0.27057	0.031875	0.322468	-0.57729
21	BCP21	C19 - H20	0.284093	-0.98885	0.032718	0.281829	-0.31644
22	BCP22	C5 - F25	0.006454	0.025372	2.716652	-0.001	-0.00435
23	BCP23	O2 - H38	0.013036	0.046424	0.080539	-0.00168	-0.00826
24	BCP24	C19 - H21	0.284725	-0.99473	0.040472	0.282827	-0.31697
25	BCP25	C19 - C22	0.265947	-0.68532	0.076352	0.228436	-0.28554
26	BCP26	C22 - F23	0.260633	-0.08652	0.209718	0.35403	-0.68643
27	BCP27	C22 - F24	0.262087	-0.08863	0.209408	0.356903	-0.69165
28	BCP28	F23 - F27	0.010374	0.048583	1.047302	-0.00103	-0.01009
29	BCP29	C22 - C29	0.263091	-0.67084	0.07137	0.222071	-0.27643
30	BCP30	C29 - C31	0.266796	-0.69549	0.064259	0.228776	-0.28368
31	BCP31	F25 - C29	0.241592	0.048776	0.058432	0.317334	-0.64686
32	BCP32	H30 - O35	0.014791	0.059298	0.024321	-0.00251	-0.00981
33	BCP33	F24 - F28	0.010863	0.049705	0.542155	-0.00095	-0.01052
34	BCP34	F27 - C31	0.281678	-0.18819	0.116186	0.39684	-0.74663
35	BCP35	F26 - C31	0.279389	-0.19552	0.119863	0.391881	-0.73488
36	BCP36	F28 - C31	0.284148	-0.17525	0.116166	0.40183	-0.75985
37	BCP37	C29 - H30	0.290927	-1.05056	0.035708	0.292704	-0.32277
38	BCP38	H7 - O33	0.013036	0.046424	0.080539	-0.00168	-0.00826
39	BCP39	S32 - O33	0.210065	-0.15649	0.058307	0.248002	-0.45688
40	BCP40	S32 - O34	0.299253	1.146787	0.028569	0.357417	-1.00153
41	BCP41	F28 - O35	0.004025	0.019864	0.745207	-0.00089	-0.00319
42	BCP42	S32 - O35	0.299427	1.149568	0.014573	0.356957	-1.00131
43	BCP43	S32 - C36	0.216351	-0.44975	0.101842	0.166536	-0.22063
44	BCP44	C36 - C37	0.306446	-0.84966	0.191145	0.31615	-0.41989
45	BCP45	C37 - H38	0.285861	-1.01252	0.012096	0.286762	-0.32039
46	BCP46	C37 - C39	0.313357	-0.89006	0.205608	0.32888	-0.43525
47	BCP47	C39 - H40	0.281599	-0.97732	0.016945	0.281425	-0.31852
48	BCP48	C39 - C41	0.307388	-0.86161	0.189614	0.31437	-0.41334
49	BCP49	C41 - C46	0.255684	-0.62752	0.035487	0.21844	-0.28
50	BCP50	C36 - C44	0.308032	-0.85491	0.207064	0.318983	-0.42424
51	BCP51	C42 - C44	0.311158	-0.88051	0.203568	0.324306	-0.42849
52	BCP52	C41 - C42	0.309119	-0.86808	0.201371	0.318004	-0.41899
53	BCP53	C42 - H43	0.281229	-0.9738	0.019019	0.281242	-0.31903
54	BCP54	C44 - H45	0.283539	-0.99412	0.014171	0.283616	-0.3187
55	BCP55	C37 - H61	0.006151	0.018904	0.301445	-0.00085	-0.00303
56	BCP56	C46 - H48	0.274576	-0.91984	0.01248	0.272187	-0.31441
57	BCP57	C46 - H47	0.273488	-0.91288	0.013222	0.270495	-0.31277
58	BCP58	C46 - H49	0.270823	-0.89612	0.01069	0.26623	-0.30843
59	BCP59	O33 - C50	0.243392	-0.27057	0.031875	0.322468	-0.57729
60	BCP60	C50 - H51	0.284093	-0.98885	0.032718	0.281829	-0.31644
61	BCP61	C36 - F56	0.006454	0.025372	2.716652	-0.001	-0.00435
62	BCP62	C50 - H52	0.284725	-0.99473	0.040472	0.282827	-0.31697
63	BCP63	C50 - C53	0.265947	-0.68532	0.076352	0.228436	-0.28554

BCP #	Name	Atoms	Rho	DelSqRho	Ellipticity	K	V
64	BCP64	C53 - F54	0.260633	-0.08652	0.209718	0.35403	-0.68643
65	BCP65	F55 - F59	0.010863	0.049705	0.542155	-0.00095	-0.01052
66	BCP66	C53 - F55	0.262087	-0.08863	0.209408	0.356903	-0.69165
67	BCP67	O4 - H61	0.014791	0.059298	0.024321	-0.00251	-0.00981
68	BCP68	F54 - F58	0.010374	0.048583	1.047302	-0.00103	-0.01009
69	BCP69	C53 - C60	0.263091	-0.67084	0.07137	0.222071	-0.27643
70	BCP70	C60 - C62	0.266796	-0.69549	0.064259	0.228776	-0.28368
71	BCP71	F56 - C60	0.241592	0.048776	0.058432	0.317334	-0.64686
72	BCP72	O4 - F59	0.004025	0.019864	0.745208	-0.00089	-0.00319
73	BCP73	F58 - C62	0.281678	-0.18819	0.116186	0.39684	-0.74663
74	BCP74	F57 - C62	0.279389	-0.19552	0.119863	0.391881	-0.73488
75	BCP75	F59 - C62	0.284148	-0.17525	0.116166	0.40183	-0.75985
76	BCP76	C60 - H61	0.290927	-1.05056	0.035708	0.292704	-0.32277

Bond critical points for 1 (optimized head-to-tail conformation)

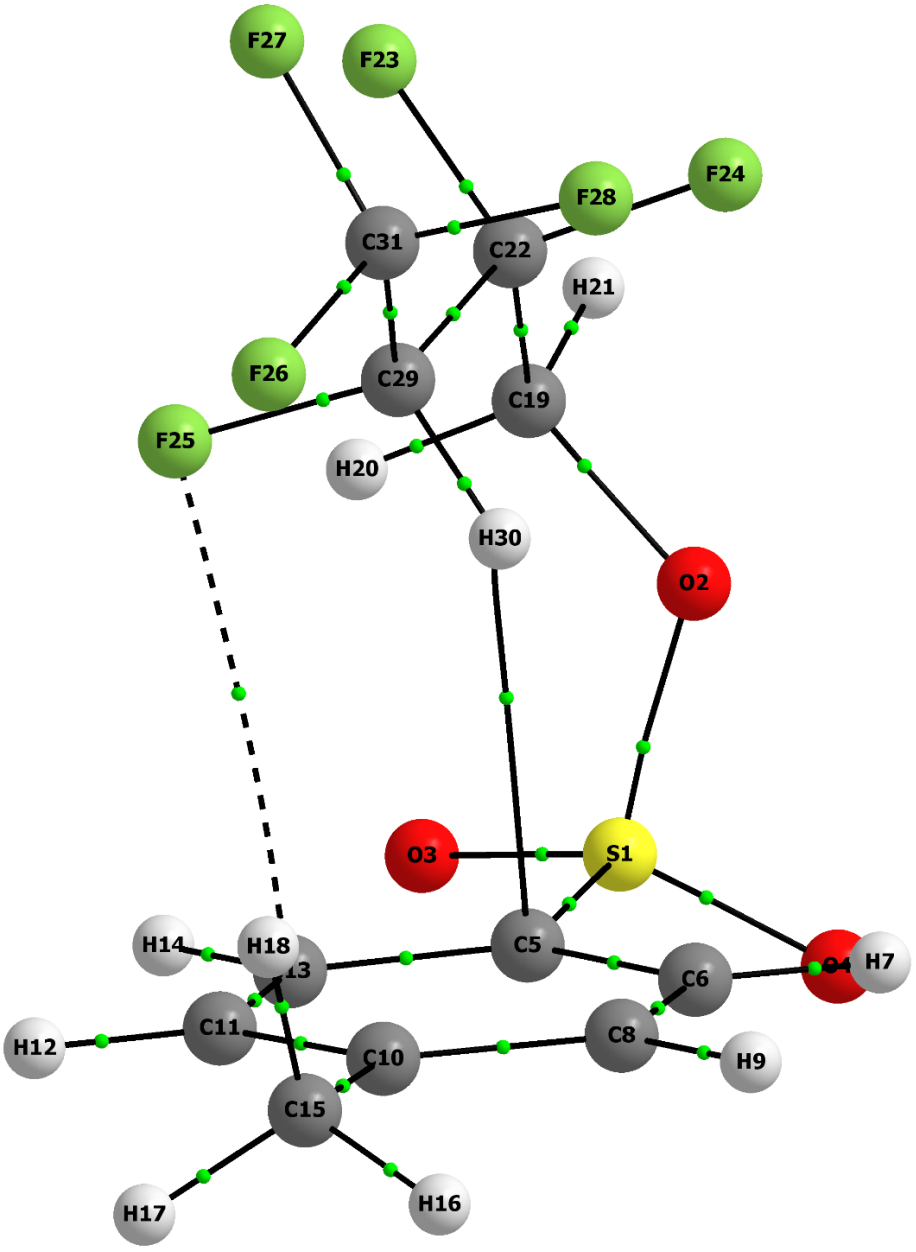


Figure S15 Molecular graph of head-to-tail conformation of compound **1**

BCP #	Name	Atoms	Rho	DelSqRho	Ellipticity	K	V
1	BCP1	S1 - O2	0.221052	-0.08356	0.106269	0.274298	-0.52771
2	BCP2	S1 - O3	0.307434	1.073395	0.030954	0.386627	-1.0416
3	BCP3	S1 - O4	0.312445	1.14008	0.014142	0.393528	-1.07208
4	BCP4	S1 - C5	0.220088	-0.48721	0.09583	0.174025	-0.22625
5	BCP5	C5 - H30	0.010083	0.031124	0.660768	-0.00118	-0.00541
6	BCP6	C5 - C6	0.316849	-0.9264	0.189045	0.340305	-0.44901
7	BCP7	C6 - H7	0.292218	-1.1086	0.010835	0.315376	-0.3536
8	BCP8	C6 - C8	0.322467	-0.95816	0.198217	0.350225	-0.46091
9	BCP9	C8 - H9	0.289795	-1.08291	0.015517	0.311636	-0.35255
10	BCP10	C8 - C10	0.316638	-0.93306	0.183214	0.337163	-0.44106

11	BCP11	C5 - C13	0.318943	-0.9359	0.196084	0.344839	-0.4557
12	BCP12	C10 - C11	0.3188	-0.94226	0.189582	0.341441	-0.44732
13	BCP13	C11 - C13	0.321029	-0.95303	0.190035	0.347268	-0.45628
14	BCP14	C11 - H12	0.289957	-1.08433	0.015127	0.31192	-0.35276
15	BCP15	C13 - F25	0.005995	0.024561	0.159601	-0.0014	-0.00333
16	BCP16	C13 - H14	0.293304	-1.11762	0.010959	0.31727	-0.35513
17	BCP17	C10 - C15	0.261882	-0.69603	0.030747	0.238842	-0.30368
18	BCP18	C15 - H16	0.282053	-1.01398	0.011979	0.299087	-0.34468
19	BCP19	C15 - H17	0.281724	-1.01199	0.012041	0.298571	-0.34414
20	BCP20	C15 - H18	0.278168	-0.98895	0.009874	0.292932	-0.33863
21	BCP21	O2 - C19	0.251392	-0.46699	0.042175	0.355152	-0.59356
22	BCP22	C19 - H20	0.293364	-1.11497	0.036568	0.314602	-0.35046
23	BCP23	C19 - C22	0.268514	-0.74508	0.088595	0.242958	-0.29965
24	BCP24	C19 - H21	0.292089	-1.10207	0.047886	0.312277	-0.34904
25	BCP25	C22 - F23	0.271038	-0.31424	0.201455	0.41913	-0.7597
26	BCP26	C22 - F24	0.272358	-0.31144	0.199805	0.42216	-0.76646
27	BCP27	C22 - C29	0.264955	-0.73088	0.079745	0.234937	-0.28716
28	BCP28	C29 - H30	0.295443	-1.13135	0.046826	0.316666	-0.35049
29	BCP29	C29 - C31	0.268387	-0.75207	0.068622	0.240614	-0.29321
30	BCP30	F27 - C31	0.294936	-0.42933	0.112755	0.472607	-0.83788
31	BCP31	F25 - C29	0.254654	-0.15668	0.044458	0.383679	-0.72819
32	BCP32	F26 - C31	0.287464	-0.45158	0.123688	0.455068	-0.79724
33	BCP33	F28 - C31	0.291887	-0.43306	0.116303	0.465683	-0.8231

Bond critical points for compound 2 (optimized L-shaped configuration)

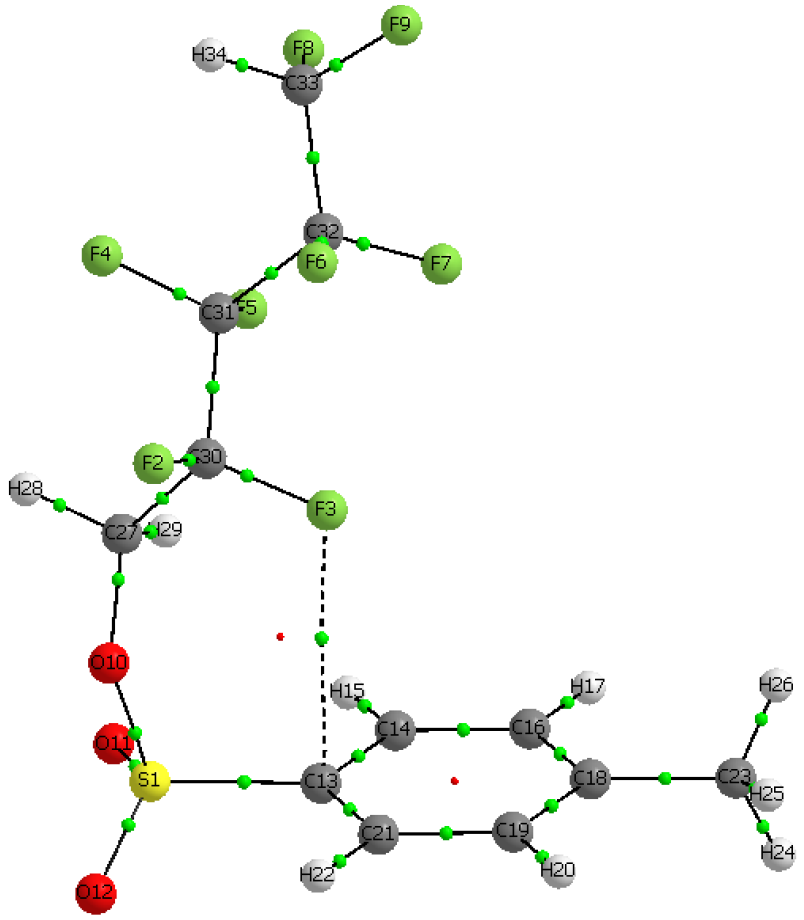


Figure S16 Molecular graph of L-shaped conformation of compound **2**.

BCP #	Name	Atoms	Rho	DelSqRho	Ellipticity	K	V
1	BCP1	F3 - C30	0.274144	-0.312140	0.185066	+0.426068	-0.774101
2	BCP2	C30 - C31	0.261432	-0.720167	0.063776	+0.227136	-0.274231
3	BCP3	F4 - C31	0.271526	-0.294927	0.196866	+0.420221	-0.766711
4	BCP4	C31 - C32	0.260439	-0.714672	0.064384	+0.225267	-0.271865
5	BCP5	F6 - C32	0.276679	-0.304442	0.187469	+0.431218	-0.786326
6	BCP6	F9 - C33	0.276432	-0.270217	0.211619	+0.431424	-0.795294
7	BCP7	C32 - C33	0.266488	-0.747770	0.028289	+0.235259	-0.283576
8	BCP8	C33 - H34	0.304218	-1.211628	0.026188	+0.330821	-0.358734
9	BCP9	F8 - C33	0.275205	-0.270072	0.207231	+0.428903	-0.790288
10	BCP10	F7 - C32	0.281481	-0.287177	0.184860	+0.441741	-0.811689
11	BCP11	S1 - O10	0.220241	-0.095747	0.104834	+0.273219	-0.522501
12	BCP12	C27 - C30	0.267606	-0.738967	0.037384	+0.242558	-0.300374
13	BCP13	S1 - O11	0.307261	+1.066893	0.029000	+0.386624	-1.039971

14	BCP14	S1 - O12	0.312481	+1.138884	0.017497	+0.393621	-1.071962
15	BCP15	S1 - C13	0.220403	-0.486492	0.102763	+0.174662	-0.227701
16	BCP16	F3 - C13	0.005733	+0.023861	0.265487	-0.001414	-0.003136
17	BCP17	C13 - C14	0.318580	-0.935517	0.193093	+0.343907	-0.453935
18	BCP18	C14 - H15	0.292457	-1.109373	0.012865	+0.315942	-0.354541
19	BCP19	C14 - C16	0.321708	-0.955755	0.193649	+0.348671	-0.458404
20	BCP20	C16 - H17	0.289302	-1.078468	0.015658	+0.310941	-0.352265
21	BCP21	C16 - C18	0.318255	-0.939862	0.187529	+0.340324	-0.445683
22	BCP22	C13 - C21	0.318741	-0.937406	0.188548	+0.344038	-0.453724
23	BCP23	C18 - C19	0.317760	-0.938324	0.187517	+0.339435	-0.444288
24	BCP24	C19 - C21	0.322457	-0.959582	0.194532	+0.350090	-0.460284
25	BCP25	C19 - H20	0.289669	-1.081656	0.015722	+0.311568	-0.352722
26	BCP26	C21 - H22	0.292390	-1.110094	0.009722	+0.315788	-0.354051
27	BCP27	C23 - H24	0.278312	-0.989113	0.010406	+0.293304	-0.339329
28	BCP28	C18 - C23	0.261581	-0.694663	0.030097	+0.238171	-0.302677
29	BCP29	C23 - H25	0.282522	-1.016979	0.011549	+0.299837	-0.345428
30	BCP30	C23 - H26	0.280814	-1.005729	0.011716	+0.297163	-0.342893
31	BCP31	O10 - C27	0.256848	-0.514353	0.031107	+0.361969	-0.595349
32	BCP32	C27 - H28	0.292144	-1.101314	0.042680	+0.312145	-0.348962
33	BCP33	C27 - H29	0.293647	-1.113555	0.034745	+0.315036	-0.351684
34	BCP34	F2 - C30	0.276776	-0.317062	0.187033	+0.431623	-0.783981
35	BCP35	F5 - C31	0.276849	-0.289763	0.196263	+0.431979	-0.791518

Pictures of crystal packing

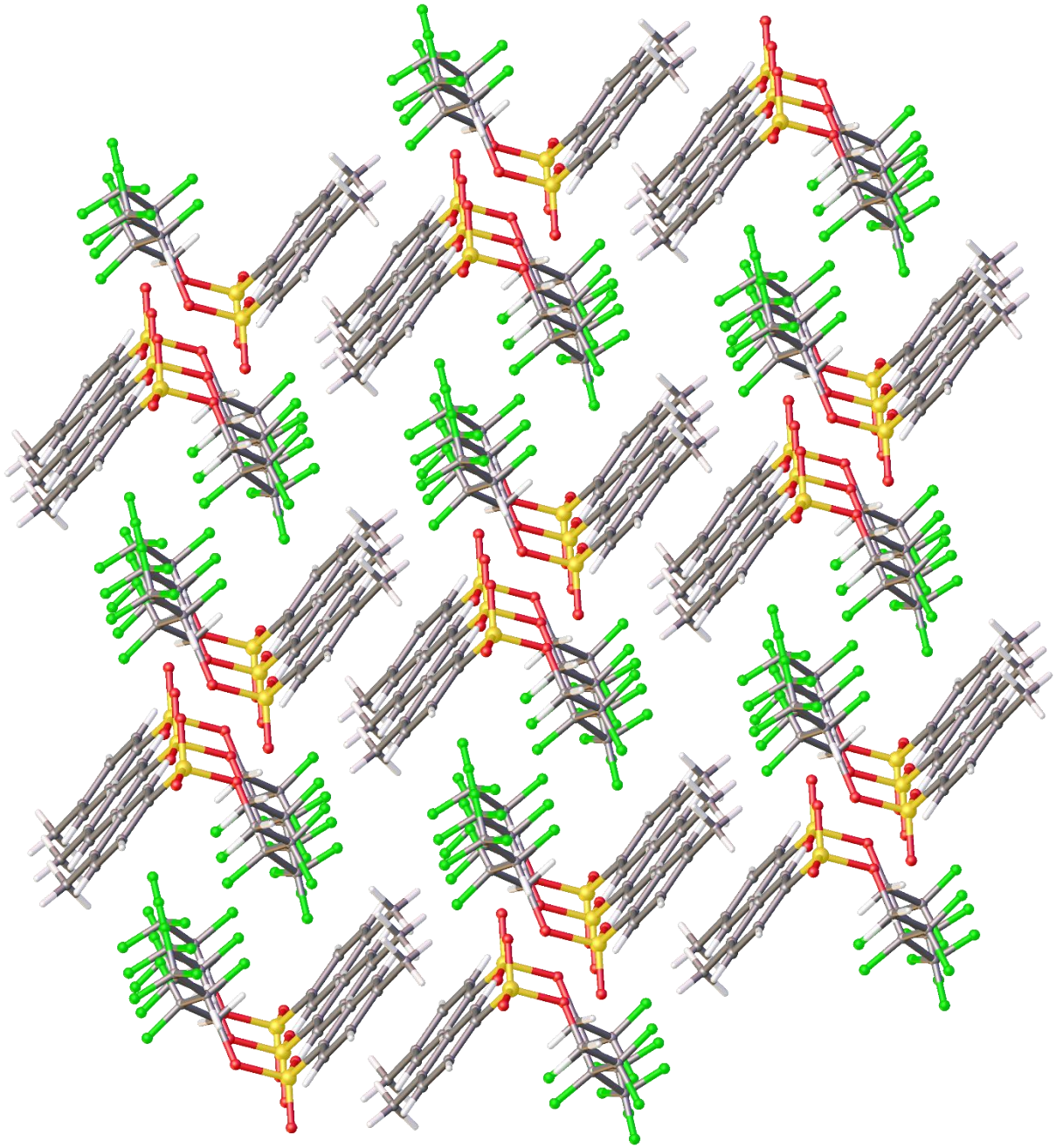


Figure S17 Crystal packing of compound **1**.

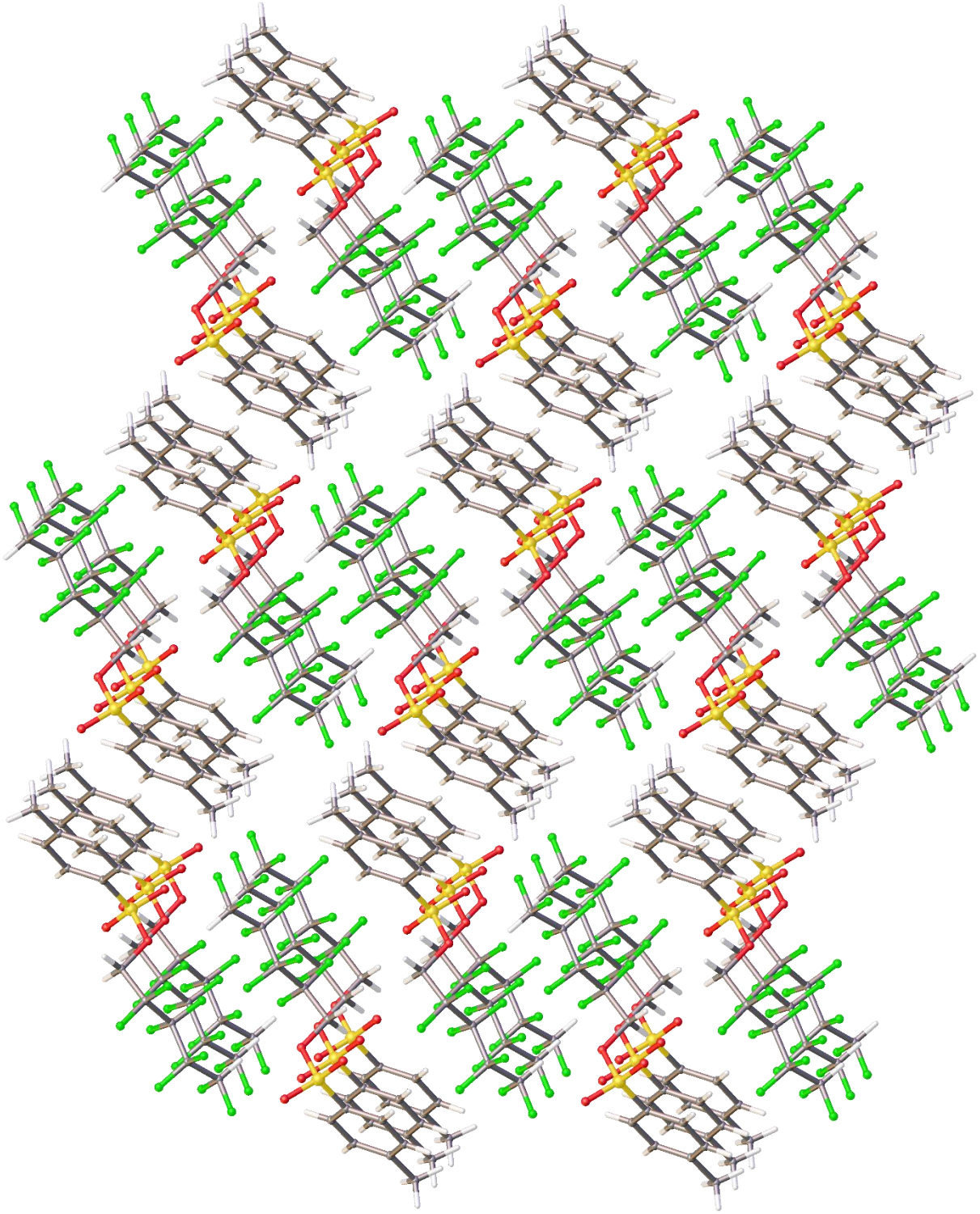
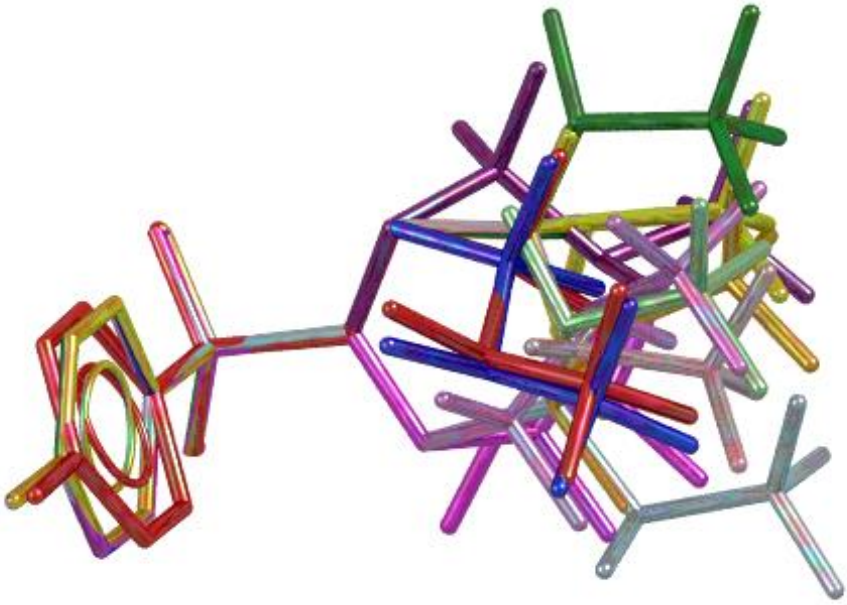
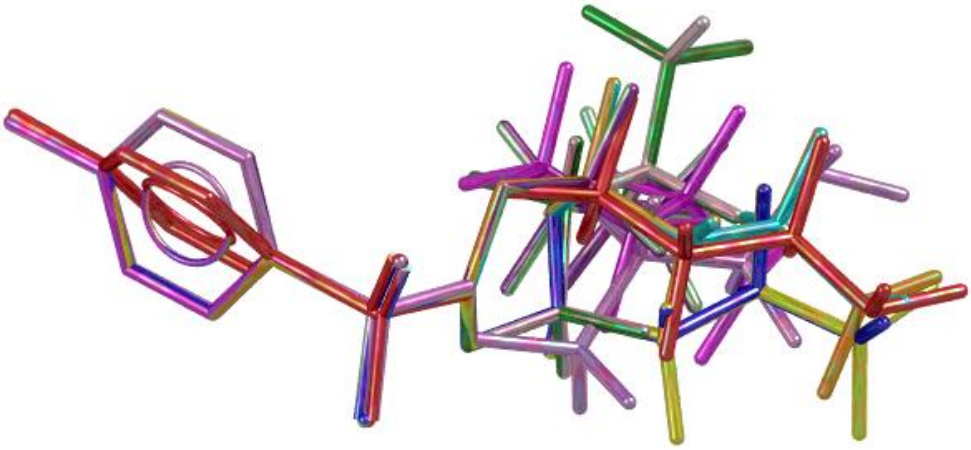


Figure S18 Crystal packing of compound **2**.

Conformations generated by Mercury 2.0 software



(**1**)



(**2**)

Figure S19 Generated conformations of compounds **1** and **2** with ofitted SO_2C_2 fragments. Experimental geometry is shown in red.

References

1 M. Valiev, E. J. Bylaska, N. Govind, K. Kowalski, T. P. Straatsma, H. J. J. Van Dam, D. Wang, J. Nieplocha, E. Apra, T. L. Windus and W. A. de Jong, *Comput. Phys. Commun.*, 2010, **181**, 1477–1489.

2 J. Moellmann and S. Grimme, *Phys. Chem. Chem. Phys.*, 2010, **12**, 8500.

3 T. A. Keith, *AIMALL, version 09.04.23, http://aim.tkgristmill.com/*, .

4 T. Lu and F. Chen, *J. Comput. Chem.*, 2012, **33**, 580–592.