Supporting Information

Crystal structure landscape in conformationally flexible organo-fluorine compounds

P. K. Mondal[a] *and D. Chopra**[a]

[a] *Department of Chemistry, Indian Institute of Science Education and Research Bhopal, Fax: +91-755-6692392*
E-Mail: dchopra@iiserb.ac.in

Sections:

S-1: Synthesis and Characterization

S-2: X-ray crystallography and computational

List of Tables:

T-1: Crystallographic and refinement data

T-2: Top 100 polymorph predictions for unsubstituted benzanilide.

T-3: The lattice energy (in kJ/mol) of all the experimental crystal structures.

T-4: Experimental structures of fluorinated benzanilides in decafluoro-substituted benzanilide (all the hydrogen atoms are replaced by fluorine atoms) landscape.

T-5: Top 100 polymorph predictions for decafluoro-substituted benzanilide (all the hydrogen atoms are replaced by fluorine atoms).

List of Figures:

F-1: Molecular diagram of the experimental structures depicting the atomic connectivity.

F-2: Overlay diagrams for the experimentally (green) obtained fluoro-substituted benzanilides and predicted (purple) structure of unsubstituted benzanilide.

F-3: Plot of relative lattice energies versus densities of the experimental crystal structures in different space groups.

F-4: Plot of relative lattice energies versus densities of the top 100 predicted structure of decafluoro-substituted benzanilide (all the hydrogen atoms are replaced by fluorine atoms) in different space groups.

F-5: ^{1}H-NMR Spectra of the synthesised compounds

F-6: DSC traces of synthesised compounds @5˚C/min.

S-1: Synthesis and Characterization

All the starting materials [difluoro-substituted benzoyl chlorides, difluoro- substituted anilines and dimethylaminopyridine (DMAP)] were purchased from Sigma-Aldrich and were used without further purification. Dichloromethane (CH_2Cl_2) was used as the reaction solvent that was dried using calcium hydride (CaH_2) and molecular sieves were used for storing. The fluorinated amines (1.0 equiv.) and DMAP (1.2 equiv.) were dissolved in 10 ml dry CH_2Cl_2 in a round bottomed flask. The reaction mixture was allowed to cool to 0 ˚C in an ice bath in a dry nitrogen atmosphere and then the corresponding difluoro-benzoyl chlorides (1.1 equiv.) was added dropwise. The reaction mixture was allowed to come to room temperature and kept for a period of 4-6 hours. At the end of the reaction, the reaction product was confirmed by TLC monitoring, and the reaction mixture was quenched with 5% HCl. The compound was isolated by CH_2Cl_2 extraction and dried using sodium sulfate (Na_2SO_4). The compound was purified by column chromatography using silica and CH_2Cl_2/hexane solvent system. ^{1}H NMR and melting point measurements were performed for characterization of the synthesized compounds.

S-2: X-ray crystallography and computational

Single crystal X-ray data of these compounds were collected on a Bruker D8 venture PHOTON 100 CMOS diffractometer using Mo Kα radiation (λ = 0.7107 Å) at 100(2) K and absorption was done using SADABS [1]. All crystal data [T-1] were solved by directed method using SIR92 [2], and refinement were performed using SHELXL97 [3] present in the program suite WinGX [4]. Mercury version 3.3 (CCDC) [5] program was used for molecular representations and overlay. For the PIXEL energy calculation, the molecular electron densities were generated by Gaussian09 [6] at the MP2/6-31G** level. The predicted crystal structures were compared with each experimentally determined crystal structure using the feature entitled 'crystal structure similarity' in Mercury 3.3 (CCDC) software. The experimental crystal structure, in this case, the reference crystal structure, is examined and represented by a reference molecule of its 14 closest neighbors. This set of molecules is then searched for predicted crystal structures within the default geometrical tolerances in a distance, being 20% and angles being 20˚ respectively. This search was configured by ignoring hydrogen atom positions, each atom's hydrogen count and bond type and by allowing molecular differences and structure inversion. 15 molecules of the reference and the predicted crystal structure were matched by the calculation of the overlay and a root-mean-squared deviation (RMSD15) of the atomic positions. Such overlay diagrams for the experimental crystal structure for halogenated benzanilides and the predicted structures for benzanilide are includes in the ESI. It is observed from some of the overlay diagrams that the obtained crystal structures are only found in an extremely distorted way, and some overlay are not found.

1. G. M. Sheldrick, SADABS; Bruker AXS, Inc.: Madison, WI, 2007.
2. A. Altomare, M. C. Burla, G. Camalli, , G. Cascarano, C. Giacovazzo, A. Gualiardi, G. J. Polidori, *J Appl. Crystallogr.*, 1994, **27**, 435-436.
3. G. M. Sheldrick, *ActaCrystallogr.*, 2008, **A64**, 112-122.
4. L. J. Farrugia, *J Appl. Crystallogr.*, 1999, **32**, 837-838.
5. C. F. Marcrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. Streek, P. A. Wood, *J Appl. Crystallogr.*, 2008, **41**, 466.
6. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J.Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, Revision A.02, Gaussian, Inc., Wallingford CT, 2009.

T-1: Crystallographic and refinement data

DATA	P0024	P0026	P0034	P0035	P2400
Formula	$C_{13}H_9F_2N_1O_1$	$C_{13}H_9F_2N_1O_1$	$C_{13}H_9F_2N_1O_1$	$C_{13}H_9F_2N_1O_1$	$C_{13}H_9F_2N_1O_1$
CCDC	1407974	1407975	1407976	1407977	1407982
Solvent	Dichloromethane and hexane (1 : 2)	Acetone	Dichloromethane and hexane (1 : 2)	Dichloromethane and hexane (1 : 2)	Ethyl acetate and hexane (1 : 2)
Formula weight	233.21	233.21	233.21	233.21	233.21
Temperature (K)	100(5)	100(5)	100(5)	100(5)	100(5)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic	Triclinic	Triclinic	Monoclinic
Space group, Z	$P2_1/n$, 4	$Pna2_1$, 4	P-1, 2	P-1, 2	Pn, 2
a(Å)	5.4223(3)	9.914(4)	5.43850(10)	5.1300(3)	5.535(7)
b(Å)	7.6977(4)	21.812(9)	7.5939(2)	8.8893(5)	5.035(6)
c(Å)	25.4353(14)	4.923(2)	12.8178(3)	11.6782(7)	19.29(2)
α(˚), β(˚), γ(˚)	90.00, 92.750(2), 90.00	90.00, 90.00, 90.00	106.2510(10), 90.2030(10), 100.3370(10)	101.426(3), 97.174(3), 90.881(3)	90.00, 92.048(16), 90.00
Volume($Å^3$), Density(g/cm^3)	1060.43(10), 1.461	1064.4(8), 1.455	499.16(2), 1.552	517.47(5), 1.497	537.3(11)
F(000), μ(mm^{-1})	480, 0.117	480, 0.117	240, 0.124	240, 0.120	240, 0.115
Θ(min, max)	2.76, 30.06	2.26, 27.10	1.68, 27.88	1.79, 25.34	2.11, 25.00
$h_{min,\ max}$, $k_{min,\ max}$, $l_{min,\ max}$	(-7, 7), (-10, 10), (-35, 35)	(-7, 12), (-27, 27), (-6, 6)	(-7, 7), (-9, 9), (-16, 16)	(-5, 6), (-10, 10), (-14, 14)	(-5, 6) (-5, 5), (-22, 22)
Treatment of Hydrogen	Fixed	Fixed	Fixed	Fixed	Fixed
No. unique ref./ obs. Ref.	3104/ 2447	2270/1910	2372/2226	1877/1741	1740/1402
No of parameter	154	154	154	154	158
R_all, R_obs	0.0607, 0.0474	0.0496, 0.0366	0.0383, 0.0365	0.0368, 0.0346	0.0954, 0.0808
wR_2_all, wR_2_obs	0.1370, 0.1273	0.0814, 0.0749	0.0986, 0.0969	0.0976, 0.0950	0.2561, 0.231
$\Delta\rho_{min,\ max}$ ($eÅ^{-3}$)	-0.191, 0.297	-0.187, 0.157	-0.286, 0.313	0.189, 0.217	-0.408, 0.645
G.o.F	1.047	1.036	1.032	1.042	1.097

DATA	P2500	P3400	P3500	P2323	P2324
Formula	$C_{13}H_9F_2N_1O_1$	$C_{13}H_9F_2N_1O_1$	$C_{13}H_9F_2N_1O_1$	$C_{13}H_7F_4N_1O_1$	$C_{13}H_7F_4N_1O_1$
CCDC	1407984	1407985	1407988	1407978	1407979
Solvent	Dichloromethane and hexane (1 : 2)	Dichloromethane and hexane (1 : 2)	Chloroform and hexane (1 : 2)	Ethanol	Toluene
Formula weight	233.21	233.21	233.21	269.20	269.20
Temperature(K)	100(5)	100(5)	100(5)	100(5)	100(5)
Wavelength(Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Triclinic	Monoclinic	Orthorhombic	Monoclinic

Space group, Z	$Pca2_1$, 4	P-1, 2	$P2_1/n$, 4	$P2_12_12_1$, 4	$P2_1/n$, 4
a(Å)	24.3084(10)	5.4838(2)	10.179(10)	5.0295(2)	9.456(3)
b(Å)	5.0243(2)	7.7928(4)	5.150(5)	8.8380(4)	4.7786(16)
c(Å)	8.4598(4)	12.6887(6)	20.053(20)	24.4547(9)	24.253(8)
α(˚), β(˚), γ(˚)	90.00, 90.00, 90.00	106.682(2), 98.8700(10), 90.157(2)	90.00, 103.924(12), 90.00	90.00, 90.00, 90.00	90.00, 95.145(4), 90.00
Volume(Å^3), Density(g/cm^3)	1033.22(8), 1.499	512.57(4), 1.511	1020.4(17), 1.518	1087.03(8), 1.645	1091.5(6), 1.638
F(000), μ(mm^{-1})	480, 0.120	240, 0.121	480, 0.122	544, 0.152	544, 0.151
Θ(min, max)	1.68, 25.00	2.73, 28.28	4.13, 27.10	2.45, 28.28	3.37, 27.10
$h_{min, max}$, $k_{min, max}$, $l_{min, max}$	(-27, 21), (-5, 5), (-9, 9)	(-7, 7), (-10, 10), (-16, 16)	(-11, 13), (-6, 6), (-25, 22)	(-6, 6), (-11, 11), (-32, 32)	(-12, 12), (-6, 6), (-31, 29)
Treatment of Hydrogen	Fixed	Fixed	Fixed	Fixed	Fixed
No. unique ref./ obs. Ref.	1563/ 1531	2535/2187	2240/2012	2700/2498	2391/2189
No of parameter	154	154	154	172	172
R_all, R_obs	0.0263, 0.0257	0.0491, 0.0436	0.0386, 0.0352	0.0489, 0.0455	0.0345, 0.0318
wR_2_all, wR_2_obs	0.0620, 0.0617	0.1255, 0.1207	0.0940, 0.0917	0.1311, 0.1285	0.0838, 0.0816
$\Delta\rho_{min, max}$ (eÅ^{-3})	-0.176, 0.119	-0.209, 0.316	-0.236, 0.315	-0.238, 0.378	-0.227, 0.304
G.o.F	1.111	1.057	1.076	1.089	1.056

DATA	P2334	P2335	P2423	P3423	P3435
Formula	$C_{13}H_7F_4N_1O_1$	$C_{13}H_7F_4N_1O_1$	$C_{13}H_7F_4N_1O_1$	$C_{13}H_7F_4N_1O_1$	$C_{13}H_7F_4N_1O_1$
CCDC	1407980	1407981	1407983	1407986	1407987
Solvent	Dichloromethane and hexane (1 : 2)	Ethanol	Chloroform and hexane (1 : 2)	Dichloromethane and hexane (1 : 2)	Toluene
Formula weight	269.20	269.20	269.20	269.20	269.20
Temperature(K)	100(5)	100(5)	100(5)	100(5)	100(5)
Wavelength(Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group, Z	P-1, 2	P1, 1	$P2_1/n$, 4	$P2_1/n$, 4	$P2_1/n$, 4
a(Å)	4.9918(2)	4.6457(5)	8.8818(7)	5.1818(16)	4.9514(4)
b(Å)	9.3610(5)	5.0544(5)	4.9233(3)	8.312(3)	8.6873(8)
c(Å)	12.0172(6)	11.8597(13)	24.9499(18)	25.739(10)	25.517(2)
α(˚), β(˚), γ(˚)	102.372(2), 97.440(2), 90.222(2)	100.967(4), 92.076(4), 92.987(4)	90.00, 94.162(2), 90.00	90.00, 93.172(11), 90.00	90.00, 91.829(3), 90.00
Volume (Å^3), Density (g/cm^3)	543.59(5), 1.645	272.72(5), 1.639	1088.13(13), 1.643	1106.9(7), 1.615	1097.04(17), 1.630
F(000), μ(mm^{-1})	272, 0.152	136, 0.151	544, 0.151	544, 0.149	544, 0.150

Θ (min, max)	2.52, 28.28	3.50, 26.36	2.38, 27.09	2.58, 26.37	2.48, 26.37
$h_{min, max}$, $k_{min, max}$, $l_{min, max}$	(-6, 6), (-12, 12), (-16, 16)	(-5, 5,), (-6, 6), (-14, 14)	(-11, 11), (-6, 6), (-31, 31)	(-6, 6), (-10, 10), (-32, 32)	(-6, 5), (-10, 10), (-31, 31)
Treatment of Hydrogen	Fixed	Fixed	Fixed	Fixed	Fixed
No. unique ref./ obs. Ref.	2677/2174	2091/2026	2388/1856	2250/1861	2234/1430
No of parameter	172	172	172	172	182
R_all, R_obs	0.0516, 0.0410	0.0288, 0.0277	0.0630, 0.0476	0.0511, 0.0411	0.1032, 0.0583
wR_2_all, wR_2_obs	0.1133, 0.1049	0.0756, 0.0746	0.1375, 0.1275	0.1120, 0.1055	0.1530, 0.1332
$\Delta\rho_{min, max}$($eÅ^{-3}$)	-0.305, 0.240	-0.220, 0.289	-0.240, 0.263	-0.214, 0.201	-0.234, 0.428
G.o.F	1.032	1.059	1.087	1.086	1.057

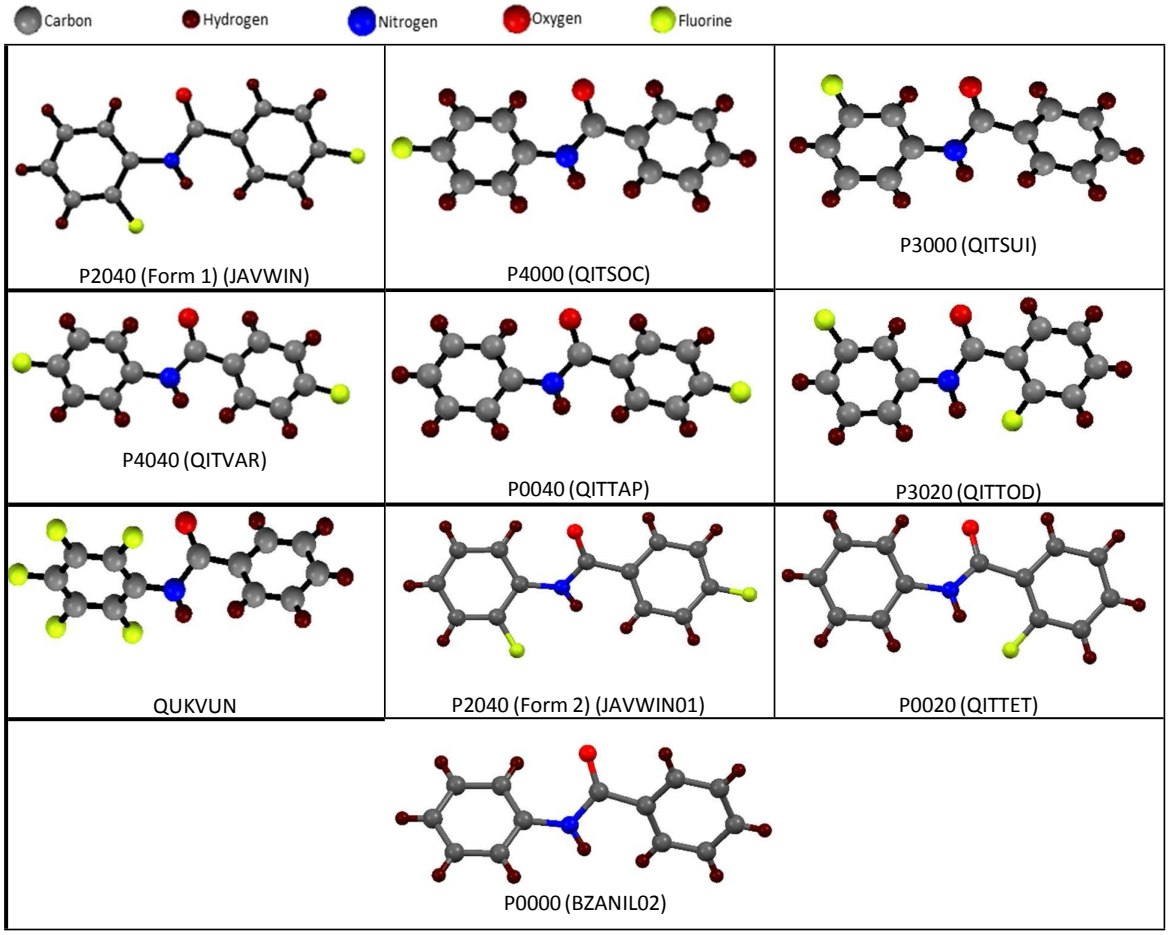
T-2: Top 100 polymorph predictions for the unsubstituted benzanilide.

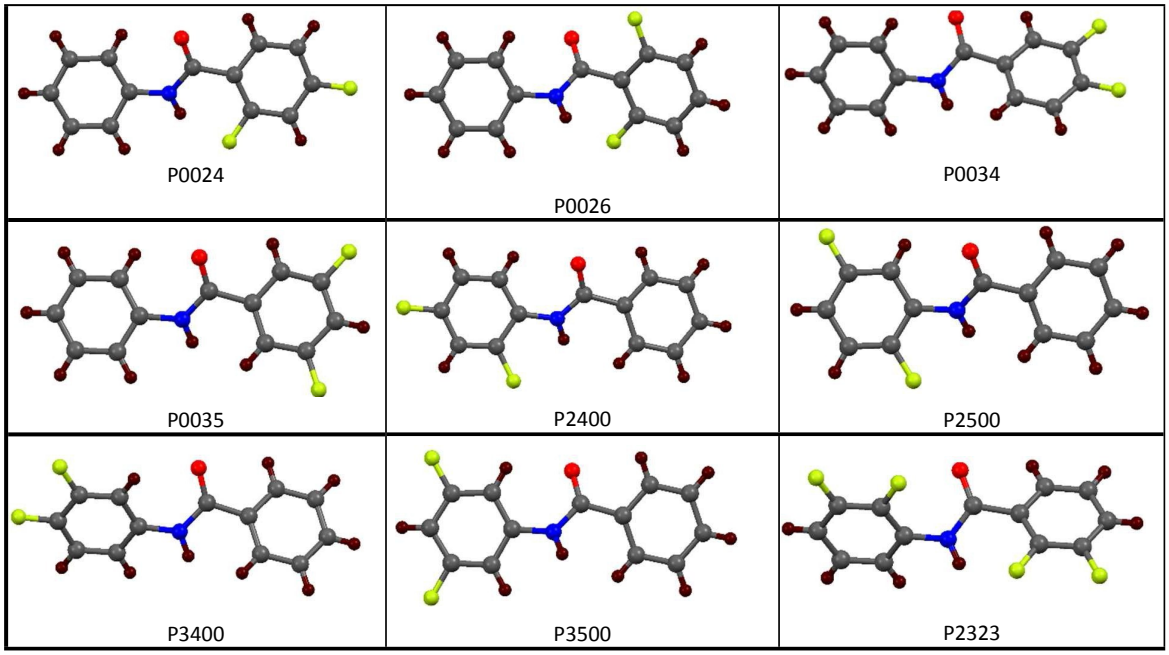
Rank	Space group	Cell volume($Å^3$)	Density(g/ml)	Total energy (kJ/mol)	Length a(Å)	Length b(Å)	Length c(Å)	Angle alpha (˚)	Angle beta (˚)	Angle gamma (˚)
1	$P2_1/c$	954.494	1.373	-171.14	16.1999	5.2016	15.8925	90	45.458	90
2	$Pca2_1$	961.607	1.362	-170.42	24.1870	5.1207	7.7640	90	90	90
3	$P2_1/c$	954.009	1.373	-170.21	24.4670	7.7394	24.6865	90	168.224	90
4	P-1	474.704	1.380	-170.02	5.2174	12.4430	7.9500	71.097	88.633	76.812
5	Pc	477.488	1.371	-169.72	14.1172	5.1911	8.0936	90	126.386	90
6	$Pca2_1$	958.811	1.366	-169.62	24.4616	5.0704	7.7305	90	90	90
7	$P2_1/c$	953.267	1.374	-169.44	33.1726	5.2241	27.9410	90	168.646	90
8	$P2_1/c$	954.454	1.373	-169.43	7.9613	5.2161	32.8773	90	135.646	90
9	$Pna2_1$	965.714	1.357	-169.39	7.7525	24.2944	5.1275	90	90	90
10	$P2_1/c$	969.940	1.351	-169.29	10.1840	5.0594	24.0695	90	128.547	90
11	P-1	482.492	1.358	-169.27	12.7786	5.1159	8.4419	87.687	116.94	100.887
12	Pc	484.576	1.352	-169.26	20.6780	5.0748	19.1652	90	166.058	90
13	$P2_12_12_1$	959.833	1.365	-169.21	5.0770	36.4098	5.1925	90	90	90
14	$P2_1$	479.888	1.365	-169.10	18.1469	5.2137	5.0922	90	95.087	90
15	$P2_1/c$	966.337	1.356	-169.05	10.2555	5.0893	19.0771	90	103.950	90
16	$P2_1$	479.990	1.365	-168.99	11.5293	5.2074	7.9971	90	91.352	90
17	$P2_1$	485.595	1.349	-168.98	5.1446	5.0502	19.5477	90	107.033	90
18	$P2_12_12_1$	971.967	1.348	-168.97	38.4426	5.0556	5.0011	90	90	90
19	$P2_1/c$	964.616	1.358	-168.96	22.7830	5.1386	24.4269	90	160.287	90
20	$C2/c$	1929.06	1.358	-168.92	60.5128	5.1375	55.5217	90	173.583	90
21	P-1	484.736	1.351	-168.89	11.4615	8.2735	9.6178	147.83	91.170	87.345
22	$P2_12_12_1$	971.679	1.348	-168.88	5.0554	37.0229	5.1915	90	90	90
23	$Pna2_1$	966.803	1.355	-168.83	9.5515	20.1345	5.0272	90	90	90
24	Pc	485.235	1.350	-168.83	5.1364	5.0638	19.4999	90	106.918	90
25	$P2_1/c$	968.413	1.353	-168.80	5.1834	24.0376	9.3948	90	124.176	90
26	$P2_1$	486.837	1.346	-168.74	5.0589	5.0582	20.1825	90	70.501	90

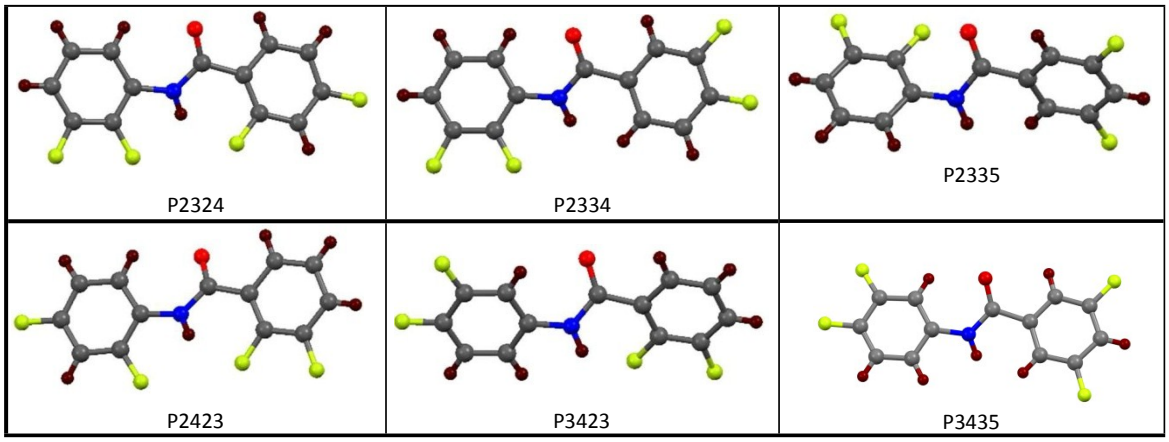
27	*P*-1	482.295	1.358	-168.69	5.1929	19.3374	9.2578	44.421	56.422	82.602
28	*C*2/*c*	1929.921	1.358	-168.56	46.6220	5.1594	46.0668	90	169.97	90
29	$P2_1/c$	966.069	1.356	-168.56	26.2238	7.7800	24.7127	90	168.953	90
30	$P2_1/c$	966.165	1.356	-168.50	24.1041	7.7651	24.6051	90	167.89	90
31	$P2_1/c$	957.975	1.368	-168.37	18.5983	5.1814	17.9417	90	146.352	90
32	*Pc*	482.096	1.359	-168.28	21.3662	5.0779	19.2742	90	166.671	90
33	*C*2/*c*	1935.125	1.354	-168.26	43.5323	5.1658	15.9098	90	147.257	90
34	*Pc*	482.129	1.359	-168.19	18.4531	5.2236	20.0364	90	165.544	90
35	$P2_1/c$	967.239	1.354	-168.10	5.0569	9.3604	20.8657	90	101.673	90
36	$P2_1/c$	971.640	1.348	-168.08	33.3383	5.0958	28.5819	90	168.457	90
37	$P2_1/c$	966.478	1.356	-168.03	12.6508	14.9558	12.7187	90	156.32	90
38	*C*2/*c*	1953.159	1.341	-167.85	25.6613	5.0537	17.8008	90	122.211	90
39	$Pca2_1$	969.636	1.351	-167.83	24.5342	5.1706	7.6436	90	90	90
40	$P2_1/c$	948.579	1.381	-167.72	22.0814	8.4100	22.3774	90	166.837	90
41	$P2_1$	479.647	1.366	-167.71	12.7151	7.7409	5.0678	90	105.929	90
42	$Pna2_1$	971.664	1.348	-167.68	7.6413	24.5927	5.1706	90	90	90
43	$P2_1/c$	973.597	1.346	-167.66	10.8480	5.0281	24.7637	90	133.879	90
44	$Pna2_1$	978.479	1.339	-167.59	16.3176	11.5668	5.1842	90	90	90
45	$P2_1/c$	968.598	1.353	-167.57	31.1888	5.1134	23.5697	90	165.068	90
46	$P2_1$	485.22	1.350	-167.54	32.4342	5.0586	5.2255	90	145.532	90
47	$Pna2_1$	968.531	1.353	-167.54	23.8276	7.7926	5.2162	90	90	90
48	$P2_1/c$	962.219	1.362	-167.47	8.2080	5.0964	24.8584	90	67.719	90
49	$P2_1/c$	963.572	1.360	-167.47	7.6630	5.0925	28.3740	90	60.485	90
50	$Pca2_1$	967.239	1.354	-167.46	7.8896	5.1992	23.5801	90	90	90
51	$P2_12_12_1$	970.572	1.350	-167.43	36.4440	5.0724	5.2503	90	90	90
52	$Pca2_1$	971.270	1.349	-167.41	24.2114	5.0935	7.8759	90	90	90
53	$Pna2_1$	961.951	1.362	-167.41	7.6432	24.6853	5.0985	90	90	90
54	$P2_1/c$	977.156	1.340	-167.33	22.5810	5.0972	8.5309	90	95.63	90
55	*P*-1	484.523	1.352	-167.21	7.8754	15.9263	5.1752	112.76	90.818	122.395
56	$P2_1/c$	966.108	1.356	-167.20	26.8729	5.0981	15.2752	90	152.506	90
57	$P2_1/c$	969.296	1.352	-167.18	8.4499	5.1102	34.0594	90	138.77	90
58	$Pna2_1$	971.598	1.348	-167.13	7.9285	24.0912	5.0867	90	90	90
59	*P*-1	484.487	1.352	-167.00	5.1543	9.3964	15.0173	55.276	79.196	55.743
60	$P2_1$	489.072	1.339	-166.99	8.5499	5.0887	11.3400	90	82.425	90
61	*C*2/*c*	1919.581	1.365	-166.87	31.1754	5.2309	22.0437	90	147.724	90
62	$P2_1/c$	967.197	1.355	-166.85	24.6617	5.2586	27.7539	90	164.412	90
63	$P2_1/c$	973.206	1.346	-166.80	7.8105	23.9631	9.3541	90	146.229	90
64	$P2_1/c$	968.779	1.352	-166.75	5.0772	5.1093	37.4772	90	94.806	90
65	$P2_1/c$	971.331	1.349	-166.74	9.4122	5.0756	21.0410	90	75.09	90
66	$P2_1/c$	972.410	1.347	-166.67	5.1682	24.2892	12.9274	90	143.186	90
67	$P2_1$	488.953	1.340	-166.60	4.8849	19.8286	5.0731	90	95.698	90
68	$P2_12_12_1$	982.801	1.333	-166.54	22.4904	5.1591	8.4702	90	90	90

69	$P2_12_12_1$	980.316	1.336	-166.53	16.6725	11.4901	5.1173	90	90	90
70	$C2/c$	1951.697	1.343	-166.42	25.1674	5.1064	36.3787	90	155.326	90
71	$P2_1/c$	979.925	1.337	-166.39	22.9563	8.2886	23.4574	90	167.318	90
72	$Pna2_1$	983.333	1.332	-166.39	14.0085	13.8821	5.0565	90	90	90
73	$P1$	241.129	1.358	-166.37	11.2906	6.5612	4.5137	129.66	103.489	69.533
74	$P2_1/c$	975.673	1.343	-166.32	23.0181	5.0928	31.4500	90	164.654	90
75	$P2_1/c$	968.459	1.353	-166.31	12.4225	15.2275	5.2350	90	77.952	90
76	Pc	486.787	1.346	-166.31	11.8101	5.1918	7.9391	90	90.114	90
77	$P2_12_12_1$	969.425	1.351	-166.23	23.8894	5.2137	7.7833	90	90	90
78	$P2_1/c$	978.664	1.339	-166.23	39.1501	7.7547	43.3093	90	175.731	90
79	$C2/c$	1957.707	1.338	-166.23	46.3304	5.1434	47.4392	90	170.027	90
80	$P2_1/c$	975.151	1.343	-166.22	5.1427	5.0666	38.9831	90	73.748	90
81	$Pna2_1$	981.815	1.334	-166.20	16.1764	11.8071	5.1405	90	90	90
82	$P2_12_12_1$	993.803	1.318	-166.15	11.6521	5.1798	16.4658	90	90	90
83	$P2_1/c$	976.827	1.341	-166.13	12.7311	15.0266	14.5171	90	159.407	90
84	$P2_1/c$	985.789	1.329	-166.13	28.5462	5.0553	38.9868	90	169.909	90
85	P-1	487.899	1.343	-166.13	12.7014	12.3689	5.0493	117.51	107.902	115.843
86	$Pna2_1$	977.183	1.341	-166.02	7.7789	24.3000	5.1695	90	90	90
87	$P2_1$	490.01	1.337	-166.01	12.5719	7.7769	5.1463	90	76.87	90
88	$P2_1/c$	974.797	1.344	-166.00	5.0360	7.8746	25.3111	90	103.795	90
89	$C2/c$	1966.379	1.332	-166.00	34.9889	5.2005	15.8439	90	136.994	90
90	$P2_1/c$	986.919	1.327	-166.00	8.3407	23.1247	5.1195	90	88.13	90
91	Pc	487.661	1.343	-166.00	10.9554	5.0646	8.9738	90	101.641	90
92	$P2_1/c$	979.632	1.337	-165.98	5.1582	16.4974	11.9000	90	104.671	90
93	$P2_1/c$	970.494	1.350	-165.94	8.08530	5.0688	26.2110	90	115.382	90
94	$C2/c$	1955.338	1.340	-165.90	39.9300	5.1290	24.7728	90	157.331	90
95	$P2_1/c$	972.779	1.347	-165.90	28.0126	5.1194	8.5908	90	127.85	90
96	$C2/c$	1964.331	1.334	-165.98	54.1981	5.1626	50.6085	90	172.026	90
97	$Pna2_1$	980.669	1.336	-165.88	5.0753	37.3935	5.1673	90	90	90
98	$Pna2_1$	983.093	1.333	-165.84	8.1693	23.4888	5.1233	90	90	90
99	$Pna2_1$	984.443	1.331	-165.80	24.4904	5.1639	7.7843	90	90	90
100	$P2_12_12_1$	981.967	1.334	-165.80	24.3438	5.1733	7.7973	90	90	90

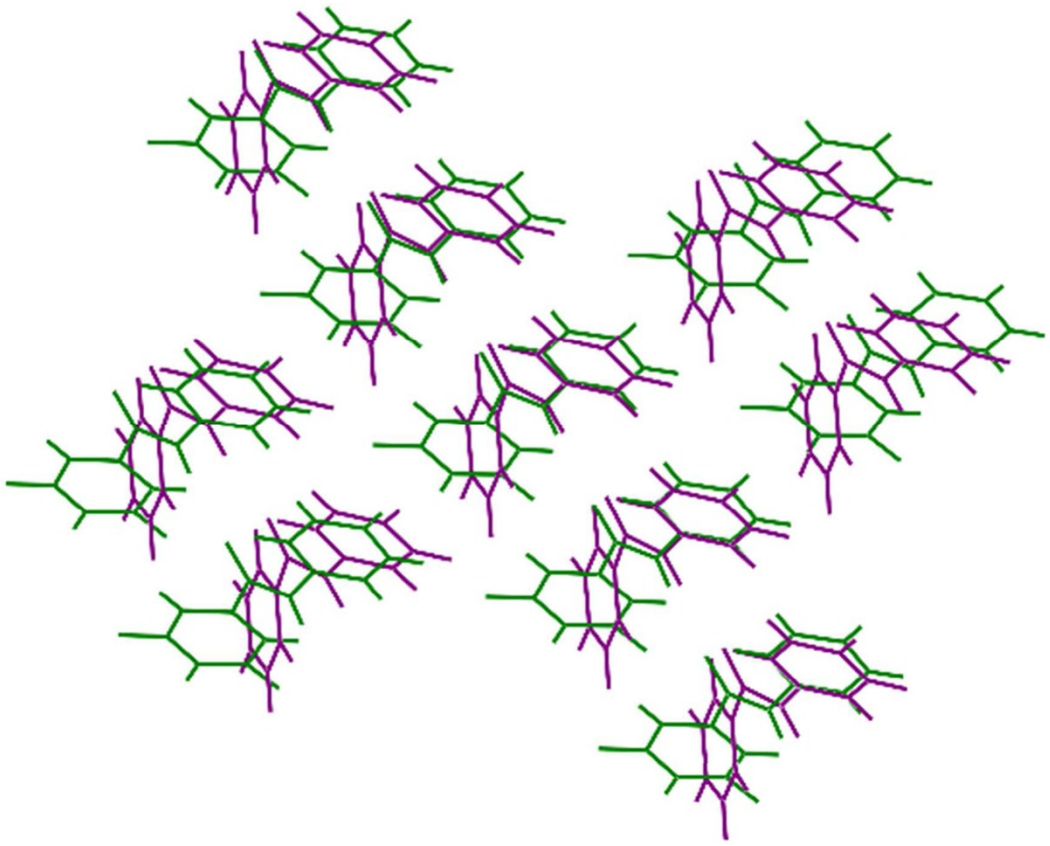
F-1: Molecular diagram of the experimental structures depicting the atomic connectivity.



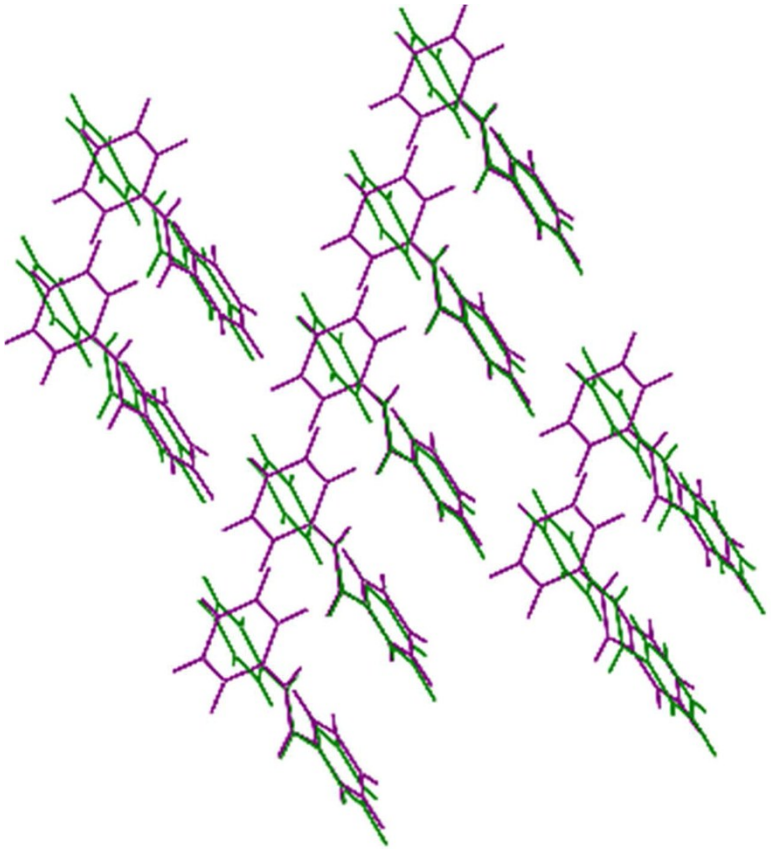




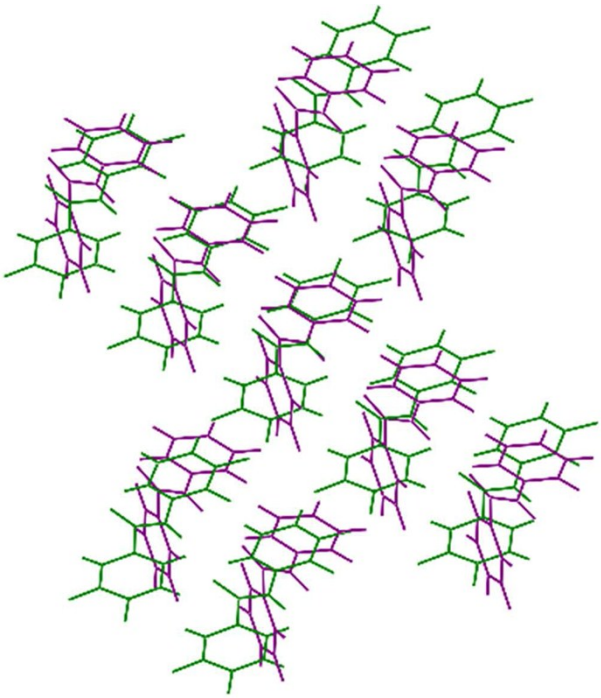
F-2: Overlay diagrams for the experimentally (green) obtained fluoro-substituted benzanilides and predicted (purple) structure of unsubstituted benzanilide.



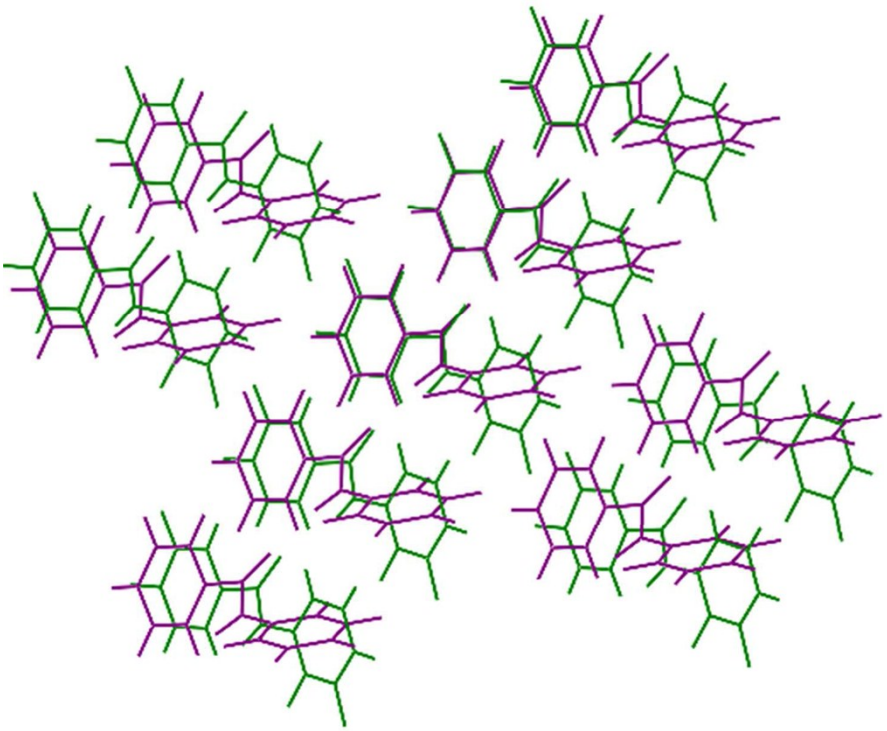
F-2(a): Overlay diagram of **P0035** and 4th rank structure depicting 9 out of 15 molecules with an RMS deviation of 0.929Å.



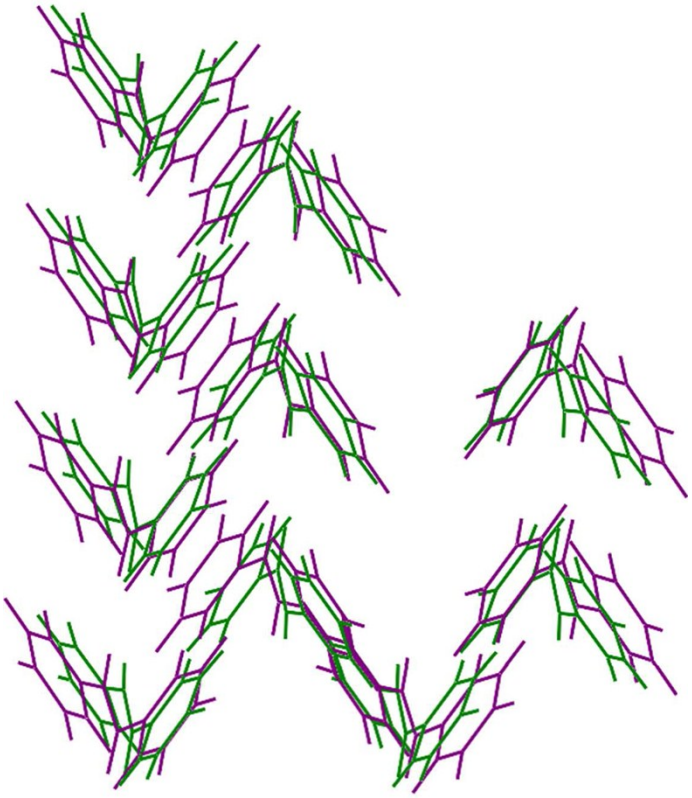
F-2(b): Overlay diagram of **P0035** and 11th rank structure depicting 9 out of 15 molecules with an RMS deviation of 0.845Å.



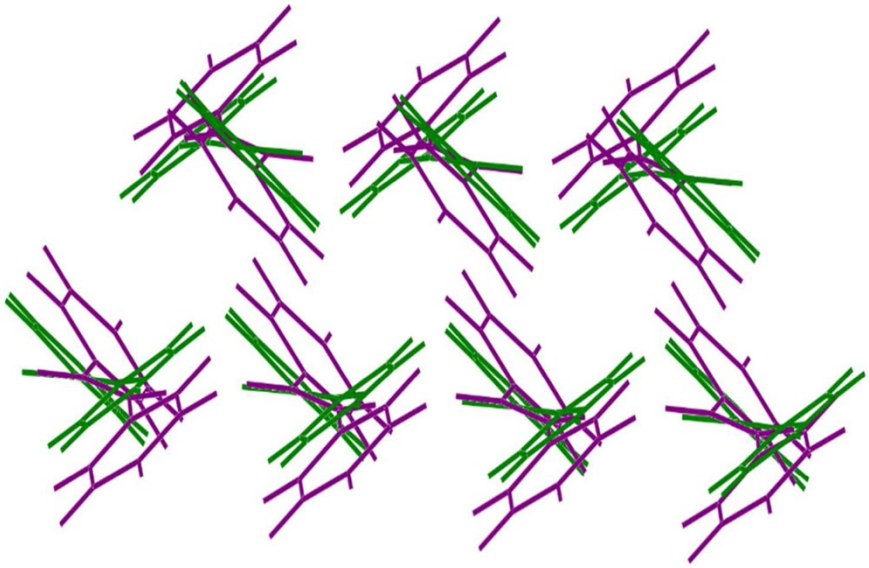
F-2(c): Overlay diagram of **P2334** and 4th rank structure depicting 9 out of 15 molecules with an RMS deviation of 1.226Å.



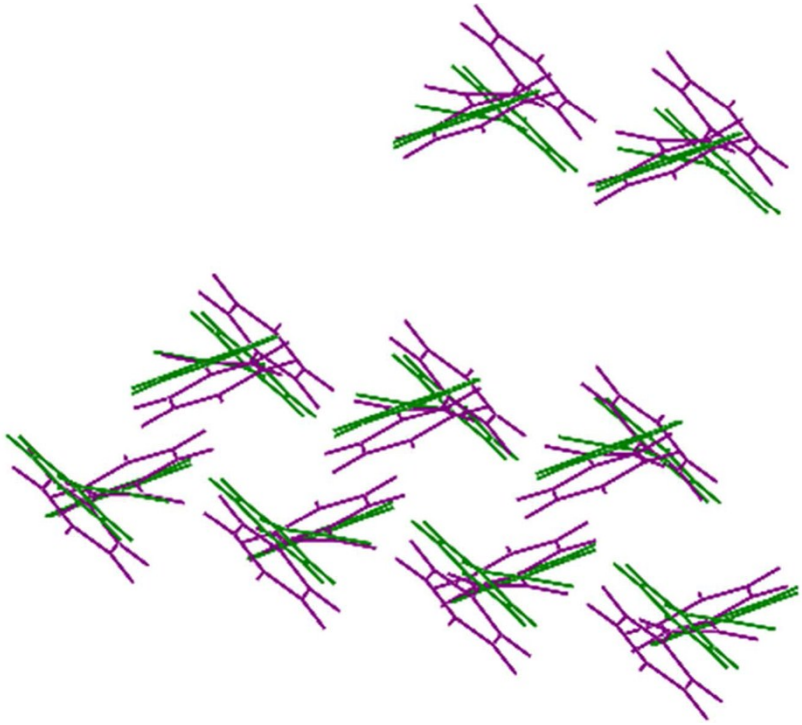
F-2(d): Overlay diagram of **P2334** and 11th rank structure depicting 9 out of 15 molecules with an RMS deviation of 0.804Å.



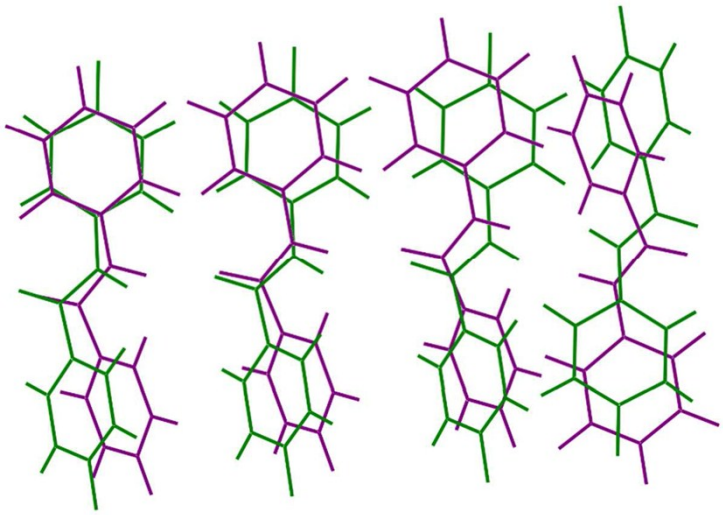
F-2(e): Overlay diagram of **P0040** and 4th rank structure depicting 10 out of 15 molecules with an RMS deviation of 0.698Å.



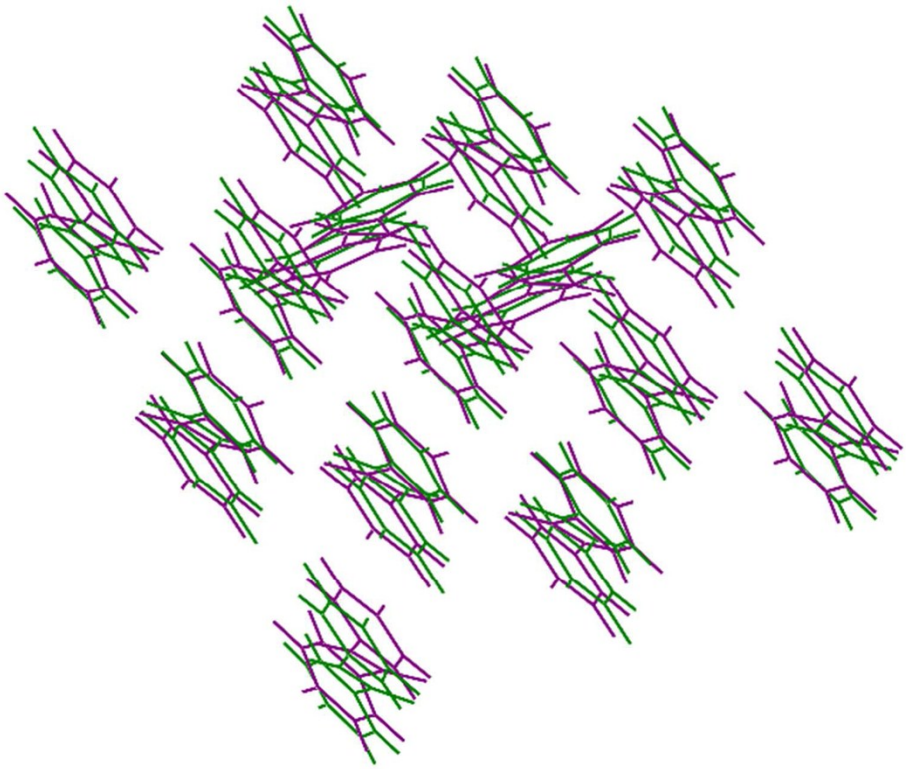
F-2(f): Overlay diagram of **P4000** and 11th rank structure depicting 7 out of 15 molecules with an RMS deviation of 1.003Å.



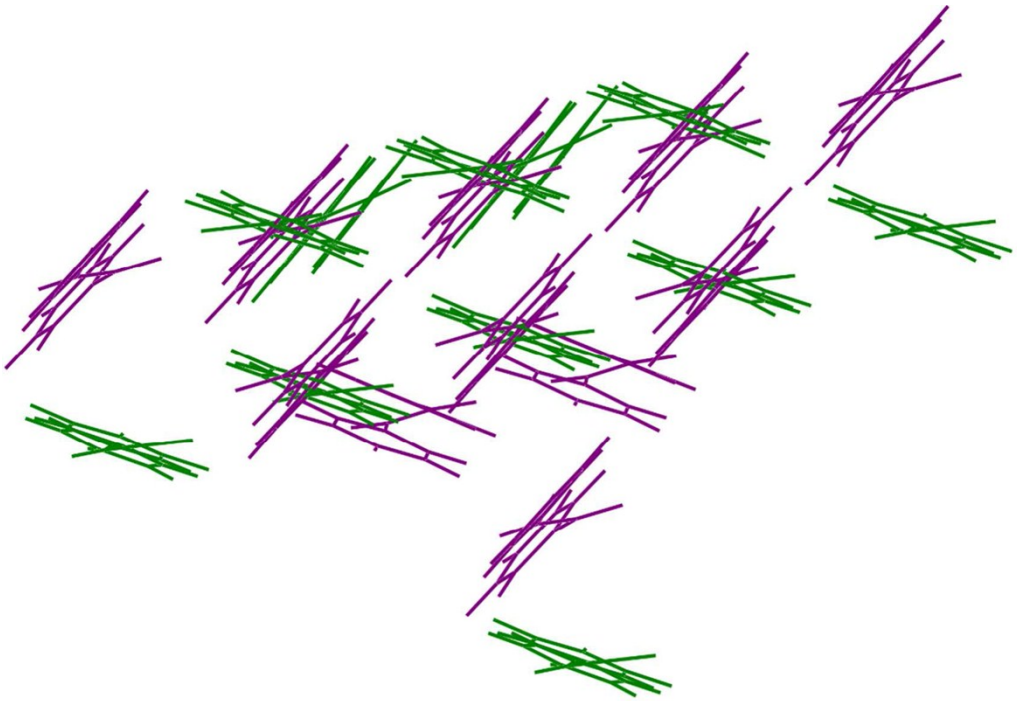
F-2(g): Overlay diagram of **P0040** and 11th rank structure depicting 9 out of 15 molecules with an RMS deviation of 0.925Å.



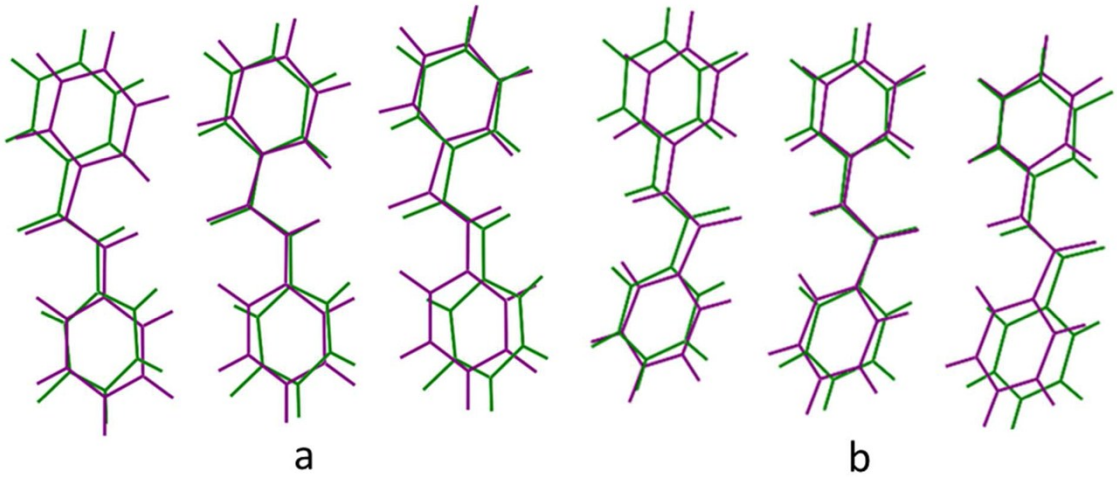
F-2(h): Overlay diagram of **P4040** and 11th rank structure depicting 4 out of 15 molecules with an RMS deviation of 0.832Å.



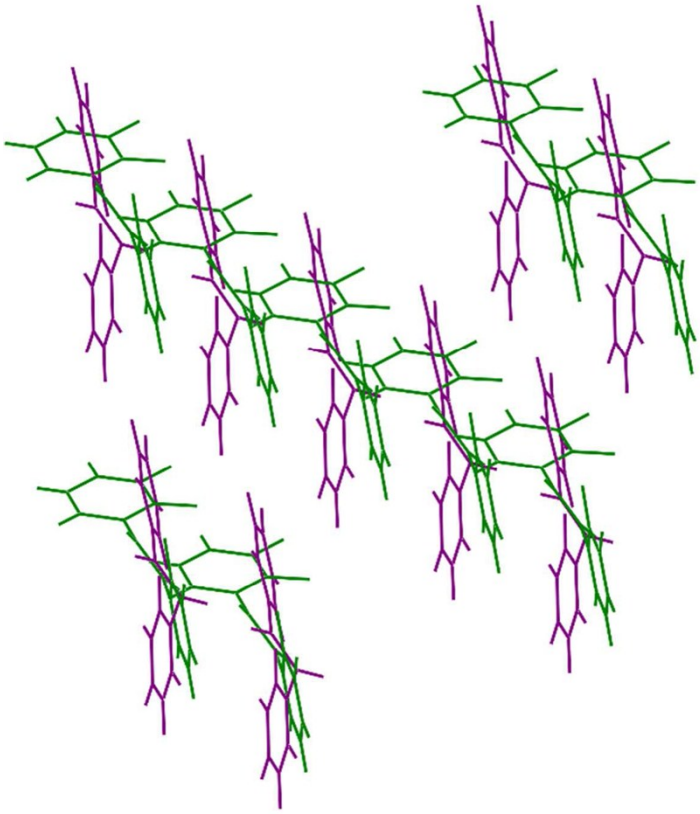
F-2(i): Overlay diagram of **P3500** and 15th rank structure depicting 14 out of 15 molecules with an RMS deviation of 0.927Å.



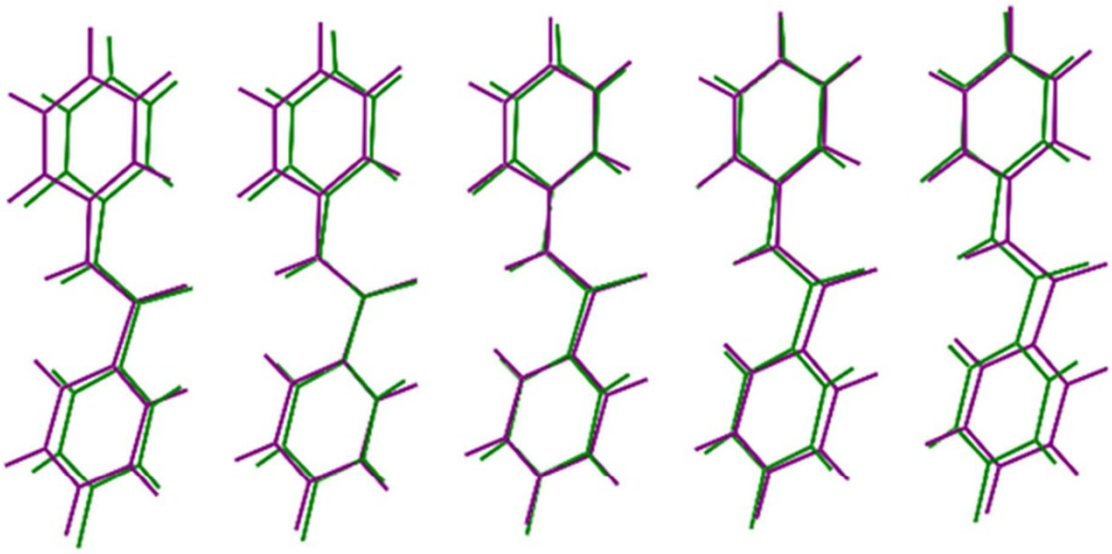
F-2(j): Overlay diagram of **P3500** and 65th rank structure depicting 11 out of 15 molecules with an RMS deviation of 4.277Å.



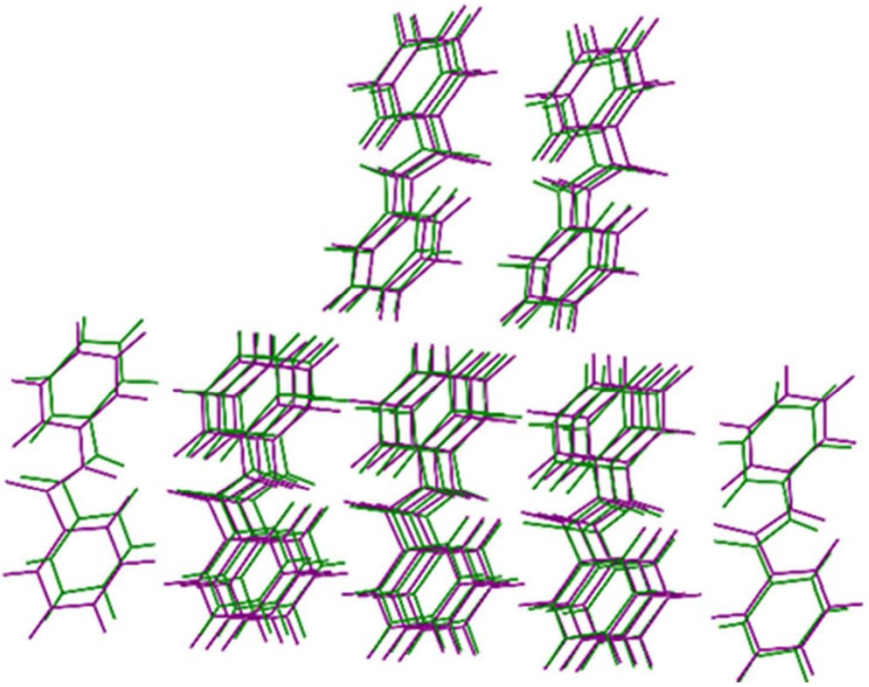
F-2(k): Overlay diagram of **P3000** with a) 48th rank structure depicting 3 out of 15 with an RMS deviation of 0.683Å. b) 93rd rank structure depicting 3 out of 15 with an RMS deviation of 0.731Å.



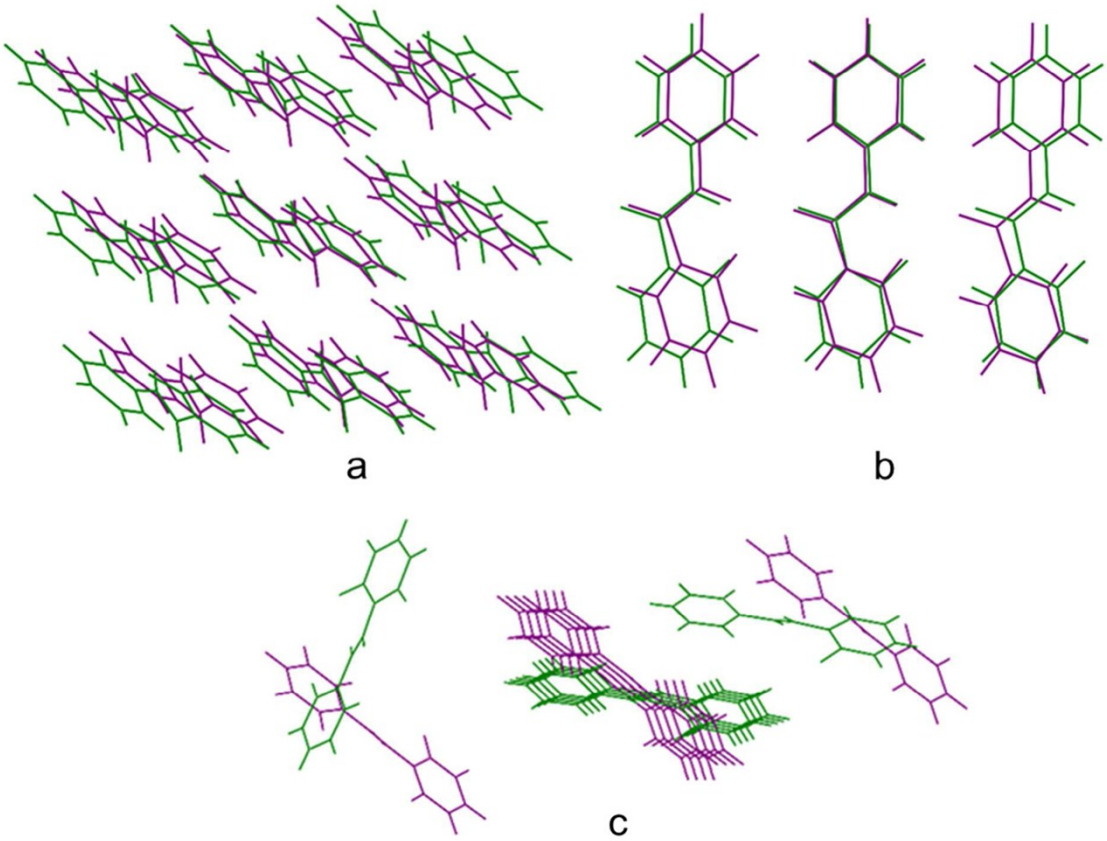
F-2(l): Overlay diagram of **P2323** and 68th rank structure depicting 9 out of 15 with an RMS deviation of 1.505Å.



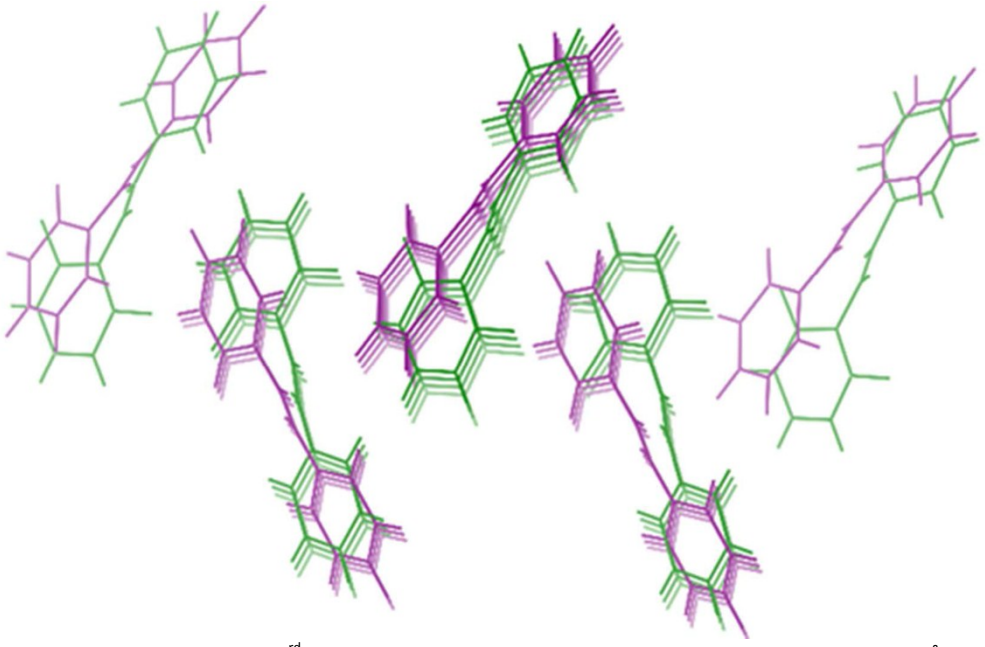
F-2(m): Overlay diagram of **P2040 (Form 2)** and 48th rank structure depicting 5 out of 15 with an RMS deviation of 0.25Å.



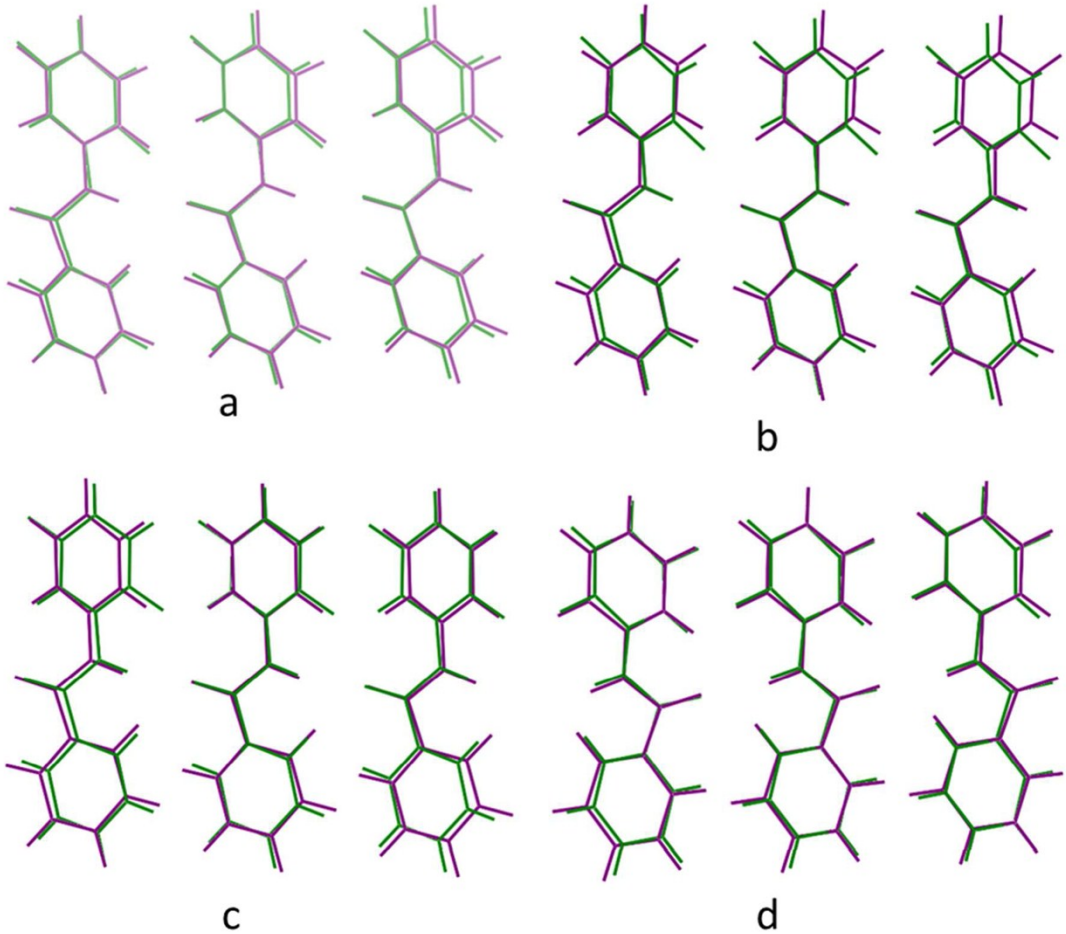
F-2(n): Overlay diagram of **P2040 (Form 2)** and 26th rank structure depicting15 out of 15 with an RMS deviation of 0.418Å.



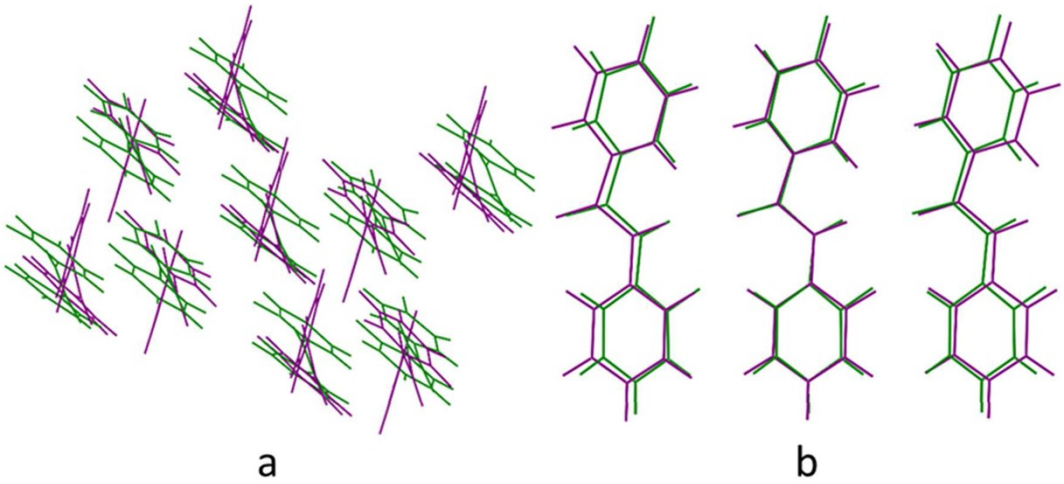
F-2(o): Overlay diagram of **P0020** with a) 14th rank structure depicting 9 out of 15 with an RMS deviation of 1.026Å. b) 17th rank structure 3 out of 15 with an RMS deviation of 0.379Å. c) 26th rank structure depicting 6 out of 15 with an RMS deviation 3.497Å.



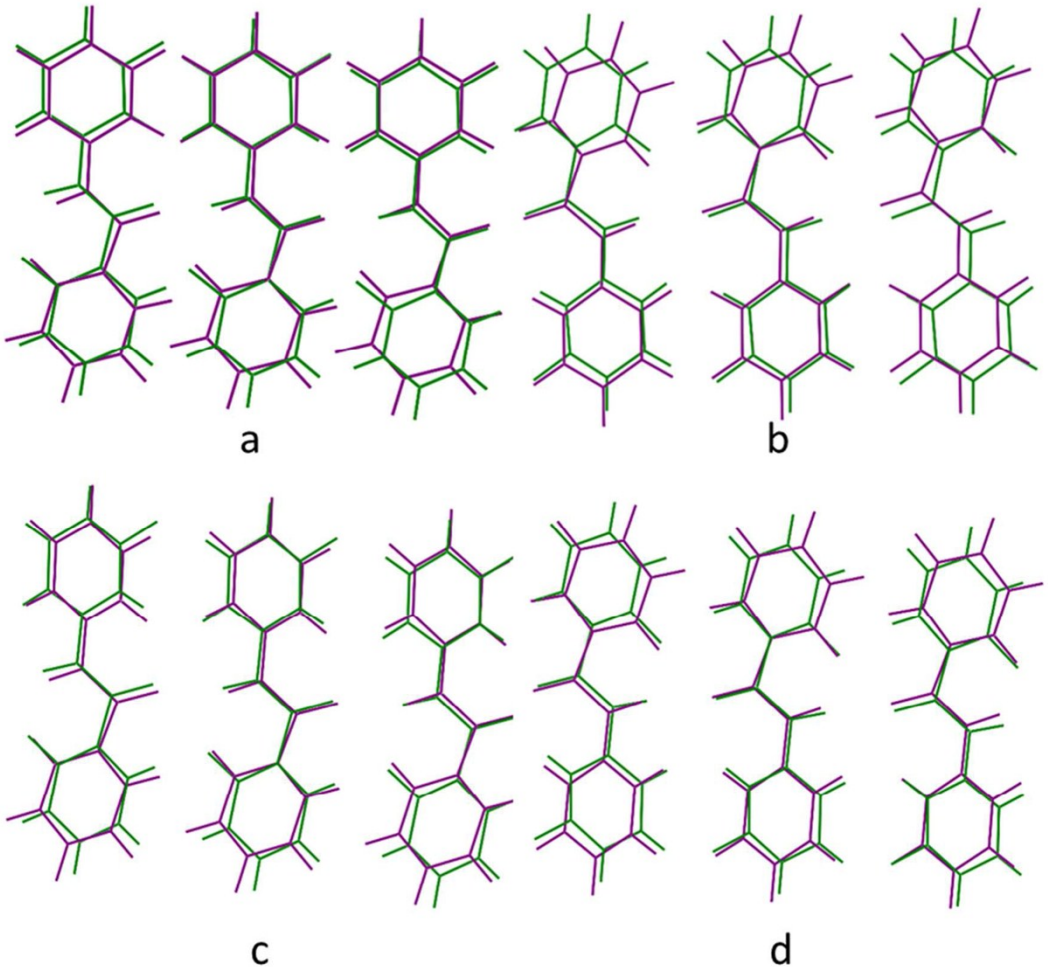
F-2(p): Overlay diagram of **P0026** and 23rd rank structure depicting 12 out of 15 with an RMS deviation of 0.862Å.



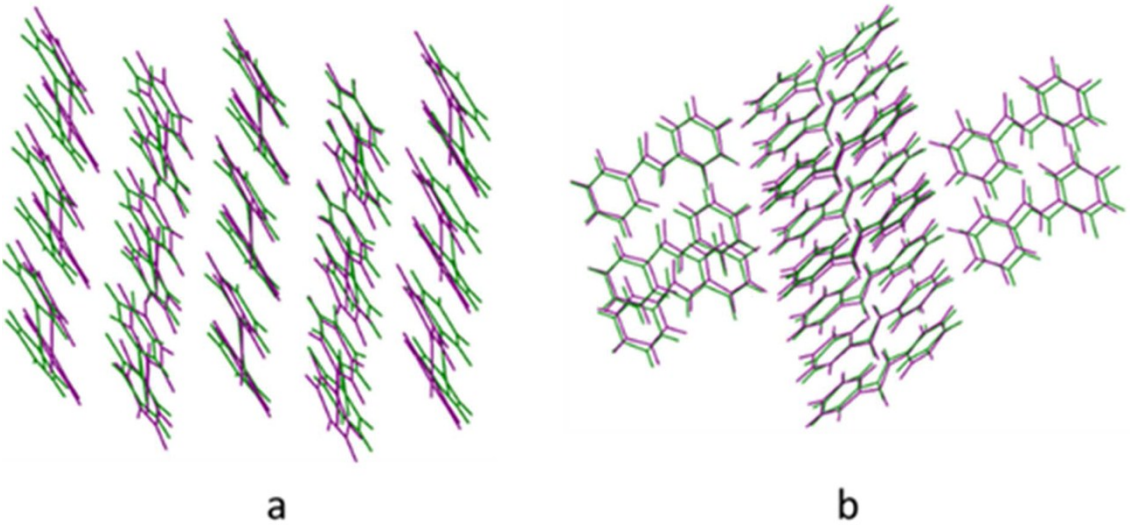
F-2(q): Overlay diagram of **P2500** with a) 2nd rank structure depicting 3 out of 15 with an RMS deviation of 0.152Å. b) 39th rank structure depicting 3 out of 15 with an RMS deviation of 0.384Å. c) 50th rank structure depicting 3 out of 15 with an RMS deviation of 0.399Å. d) 52nd rank structure depicting 3 out of 15 with an RMS deviation of 0.165Å.



F-2(r): Overlay diagram of **P2040 (Form 1)** with a) 39th rank structure depicting 9 out of 15 with an RMS deviation of 1.06Å. b) 50th rank structure depicting 3 out of 15 with an RMS deviation of 0.692Å.



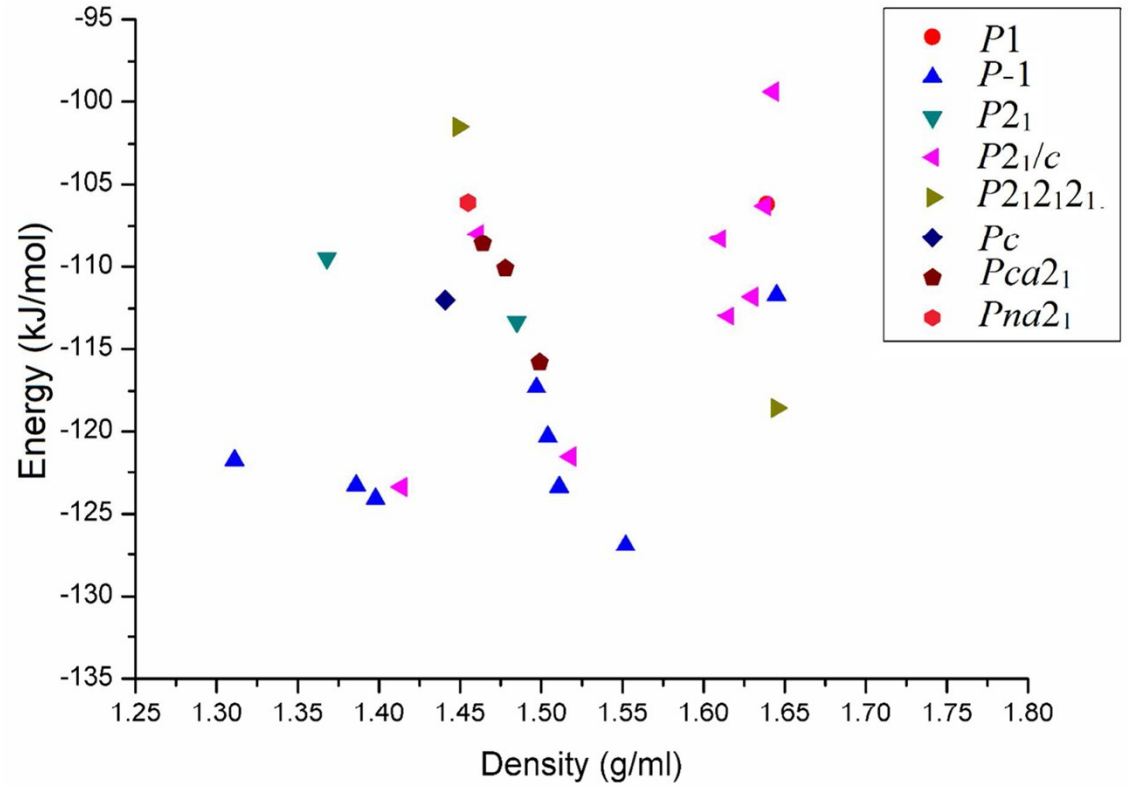
F-2(s): Overlay diagram of **P3020** with a) 2nd rank structure depicting 3 out of 15 with an RMS deviation of 0.272Å. b) 6th rank structure depicting 3 out of 15 with an RMS deviation of 0.378Å. c) 39th rank structure depicting 3 out of 15 with an RMS deviation of 0.652Å. d) 50nd rank structure depicting 3 out of 15 with an RMS deviation of 0.674Å.



F-2(t): The overlay diagram of the 15 molecules of the experimental (green) and predicted (purple) structure of a) **P2040 (Form 1)** and the 2nd rank structure with an RMS deviation of 0.488 Å. b) **P2400** and the 24th rank structure with an RMS deviation of 0.415 Å.

T-3: The lattice energy (in kJ/mol) of all the experimental crystal structures

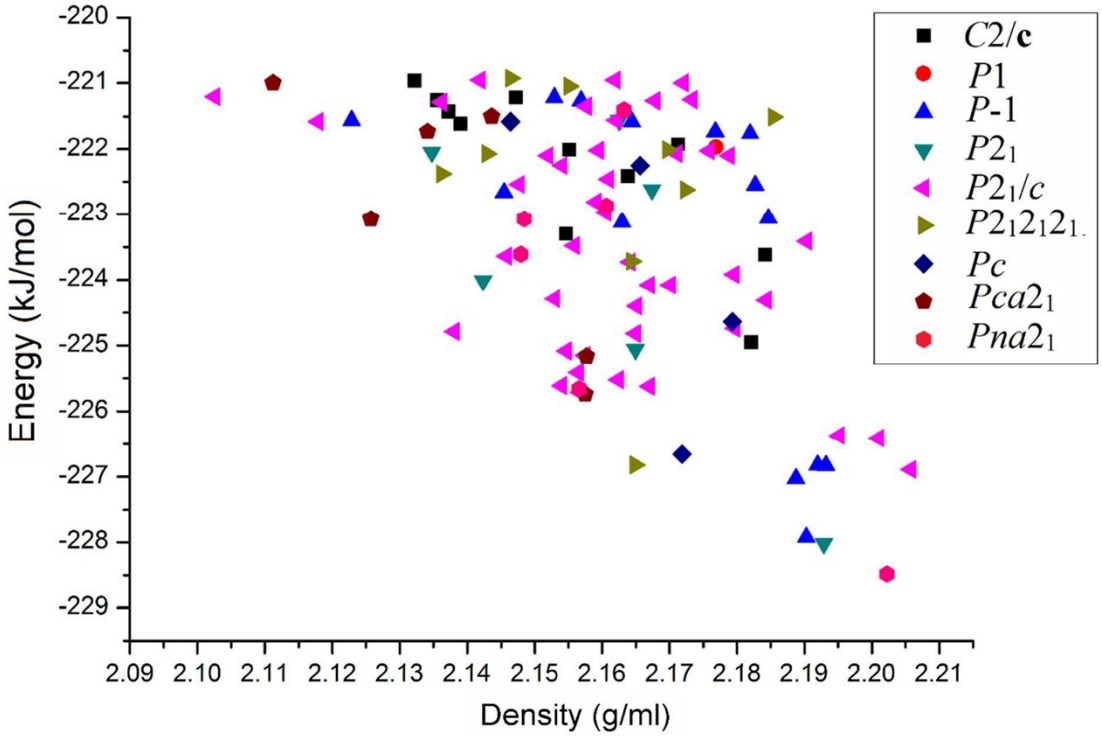
Compound code	Total energy	Compound code	Total energy
P0024	-108.0	P3435	-111.8
P0026	-106.1	P3500	-121.5
P0034	-126.9	P0000	-121.7
P0035	-117.3	P2040 (Form 1)	-110.1
P2323	-118.6	P4000	-124.1
P2324	-106.3	P3000	-123.4
P2334	-111.7	P0040	-123.3
P2335	-106.2	P0020	-109.5
P2400	-112.0	P3020	-108.6
P2423	-99.4	P4040	-120.3
P2500	-115.8	QUKVUN	-108.3
P3400	-123.4	P2040 (Form 2)	-113.4
P3423	-113.0		



F-3: Plot of relative lattice energies versus densities of experimental crystal structures in different space groups.

T-4: Experimental structures of fluorinated benzanilides in decafluoro-substituted benzanilide (all the hydrogen atoms are replaced by fluorine atoms) landscape.

Group	Compound Code	Unit Cell Type	Rank	Space Groups
Group 1	P0000, P0034, P0035, P2334, P3400, P4000, P0040, P4040	5-8-12	3rd, 4th, 6th	*P*-1
Group 2	P3500	10-5-20	10th	$P2_1/c$
Group 3	P0024, P3423, P3435, QUKVUN, P2324, P2423, P3000	5-8-25	87th	$P2_1/c$
Group 4	P2323	5-9-23	8th, 63rd, 68th, 81st, 94th, 100th	$P2_12_12_1$
Group 5	P2040 (Form 2), P002C	5-5-19	51st	$P2_1$
Group 6	P2335	5-5-12	69th	*P*1
Group 7	P0026	10-21-5	1st, 14th, 39th, 44th	$Pna2_1$
Group 8	P2500, P2040 (Form 1), P302C	24-5-8	82nd	$Pca2_1$
Group 9	P2400	5-5-19	58th	*Pc*



F-4: Plot of relative lattice energies versus densities of the top 100 predicted structure of decafluoro-substituted benzanilide (all the hydrogen atoms are replaced by fluorine atoms) in different space groups.

T-5: Top 100 polymorph predictions for decafluoro-substituted benzanilide (all the hydrogen atoms are replaced by fluorine atoms).

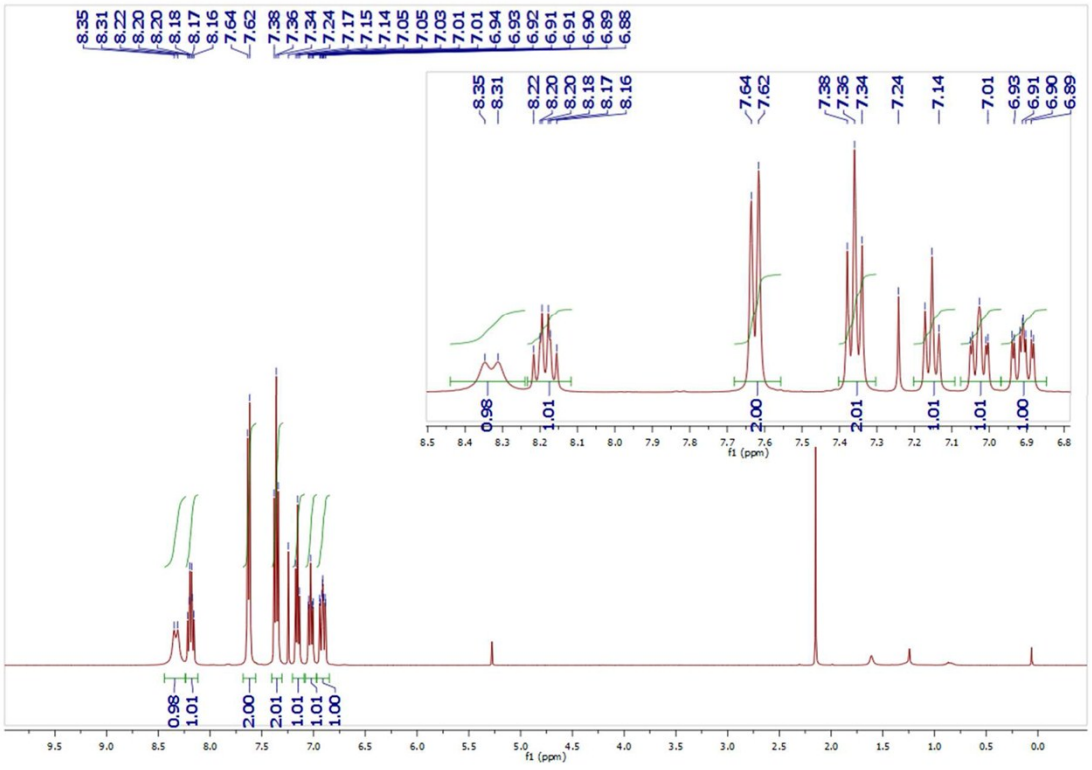
Rank	Space group	Cell volume (Å^3)	Density (g/ml)	Total energy (kJ/mol)	Length a (Å)	Length b (Å)	Length c (Å)	Angle alpha (˚)	Angle beta (˚)	Angle gamma (˚)
1	$Pna2_1$	1137.482	2.202	-228.48	21.8453	10.4265	4.9940	90	90	90
2	$P2_1$	571.168	2.193	-228.02	11.0476	5.0252	10.4528	90	100.178	90
3	*P*-1	571.846	2.190	-227.92	9.9619	12.0843	4.9040	77.015	94.921	87
4	*P*-1	572.245	2.189	-227.03	4.9026	12.0855	9.7482	88.584	92.444	82.806
5	$P2_1/c$	1135.685	2.206	-226.89	16.3784	15.3649	18.7612	90	166.081	90
6	*P*-1	571.089	2.193	-226.83	9.7489	4.8927	12.1173	82.139	93.482	92.601
7	*P*-1	571.406	2.192	-226.82	9.7540	4.8981	15.9794	100.31	128.977	92.568
8	$P2_12_12_1$	1157.095	2.165	-226.82	22.1517	10.7008	4.8814	90	90	90
9	*Pc*	576.691	2.172	-226.66	11.3683	5.0274	10.4074	90	104.18	90
10	$P2_1/c$	1138.135	2.201	-226.41	11.4286	5.0133	20.4508	90	76.249	90
11	$P2_1/c$	1141.159	2.195	-226.37	20.6450	11.6366	20.1338	90	166.354	90
12	$Pca2_1$	1161.059	2.158	-225.74	9.8225	5.1700	22.8634	90	90	90
13	$P2_1/c$	1161.486	2.157	-225.71	30.7698	5.1754	9.8149	90	132.002	90

14	$Pna2_1$	1161.541	2.157	-225.66	10.7277	22.3948	4.8349	90	90	90
15	$P2_1/c$	1155.963	2.167	-225.62	33.9408	5.0390	10.2388	90	41.31	90
16	$P2_1/c$	1162.953	2.154	-225.61	28.2205	5.1520	9.8167	90	125.432	90
17	$P2_1/c$	1158.429	2.162	-225.52	27.4028	4.9918	25.6325	90	160.707	90
18	$P2_1/c$	1161.629	2.156	-225.41	21.0203	4.9952	11.1298	90	83.722	90
19	$Pca2_1$	1160.957	2.158	-225.16	9.8007	5.2315	22.6429	90	90	90
20	$P2_1/c$	1161.059	2.158	-225.15	25.3836	5.2313	9.8023	90	116.876	90
21	$P2_1/c$	1162.593	2.155	-225.08	33.8015	5.2443	9.8548	90	138.278	90
22	$P2_1$	578.533	2.165	-225.06	10.2381	5.0075	11.5262	90	101.752	90
23	$C2/c$	2295.940	2.182	-224.95	32.6298	4.9293	48.8381	90	163.005	90
24	$P2_1/c$	1157.064	2.165	-224.82	32.1570	5.0164	10.3800	90	136.289	90
25	$P2_1/c$	1171.621	2.138	-224.79	5.2892	22.9339	9.7743	90	81.184	90
26	$P2_1/c$	1149.269	2.180	-224.74	18.5046	4.8424	23.4549	90	146.851	90
27	Pc	574.715	2.179	-224.64	10.8565	5.0335	10.6009	90	97.213	90
28	$P2_1/c$	1156.985	2.165	-224.4	22.2543	4.8304	18.7362	90	144.939	90
29	$P2_1/c$	1146.799	2.184	-224.31	4.9027	24.6070	9.5835	90	82.702	90
30	$P2_1/c$	1163.520	2.153	-224.29	12.4815	19.8456	12.1082	90	157.173	90
31	$P2_1/c$	1155.957	2.167	-224.08	20.8746	4.8409	18.6414	90	142.146	90
32	$P2_1/c$	1154.324	2.170	-224.08	13.7356	20.8928	11.8056	90	160.079	90
33	$P2_1$	584.640	2.142	-224.01	9.1333	4.9246	13.0119	90	87.388	90
34	$P2_1/c$	1149.318	2.180	-223.92	16.3998	4.8217	22.0662	90	138.8	90
35	$P2_1/c$	1157.495	2.164	-223.73	10.2595	24.6178	9.8980	90	152.418	90
36	$P2_12_12_1$	1157.347	2.164	-223.72	11.3463	5.0076	20.3692	90	90	90
37	$P2_1/c$	1167.413	2.146	-223.64	39.7538	5.0412	10.2122	90	34.779	90
38	$C2/c$	2293.814	2.184	-223.62	30.7067	4.9020	23.9053	90	39.603	90
39	$Pna2_1$	1166.245	2.148	-223.61	22.2073	4.8659	10.7926	90	90	90
40	$P2_1/c$	1161.931	2.156	-223.48	18.8219	4.8261	24.5276	90	148.566	90
41	$P2_1/c$	1143.670	2.190	-223.41	32.6384	4.9571	10.0485	90	135.294	90
42	$C2/c$	2325.182	2.155	-223.3	46.0636	5.0440	47.5293	90	167.845	90
43	P-1	579.065	2.163	-223.12	11.2084	12.5200	9.7887	76.023	26.461	83.108
44	$Pna2_1$	1165.964	2.148	-223.07	20.5092	11.3355	5.0153	90	90	90
45	$Pca2_1$	1178.432	2.126	-223.07	5.0234	21.6830	10.8190	90	90	90
46	P-1	573.315	2.185	-223.06	18.2477	4.9604	10.6174	89.113	138.297	73.577
47	$P2_1/c$	1159.433	2.161	-222.97	12.5120	19.9024	12.0547	90	157.279	90
48	$Pna2_1$	1159.369	2.161	-222.87	24.2807	9.7041	4.9205	90	90	90
49	$P2_1/c$	1160.203	2.159	-222.81	38.9091	5.0292	11.3626	90	31.453	90
50	P-1	583.803	2.145	-222.66	13.4987	10.5898	4.9507	60.858	73.278	73.823
51	$P2_1$	577.882	2.167	-222.62	4.9958	5.3145	21.7691	90	88.983	90
52	$P2_12_12_1$	1153.125	2.172	-222.62	5.3309	43.1281	5.0155	90	90	90
53	P-1	573.825	2.183	-222.55	14.7921	10.6368	4.9592	90.671	111.398	124.518
54	$P2_1/c$	1166.399	2.148	-222.54	25.7764	4.9373	30.9847	90	162.795	90
55	$P2_1/c$	1159.194	2.161	-222.46	11.5708	21.0533	11.3223	90	155.148	90

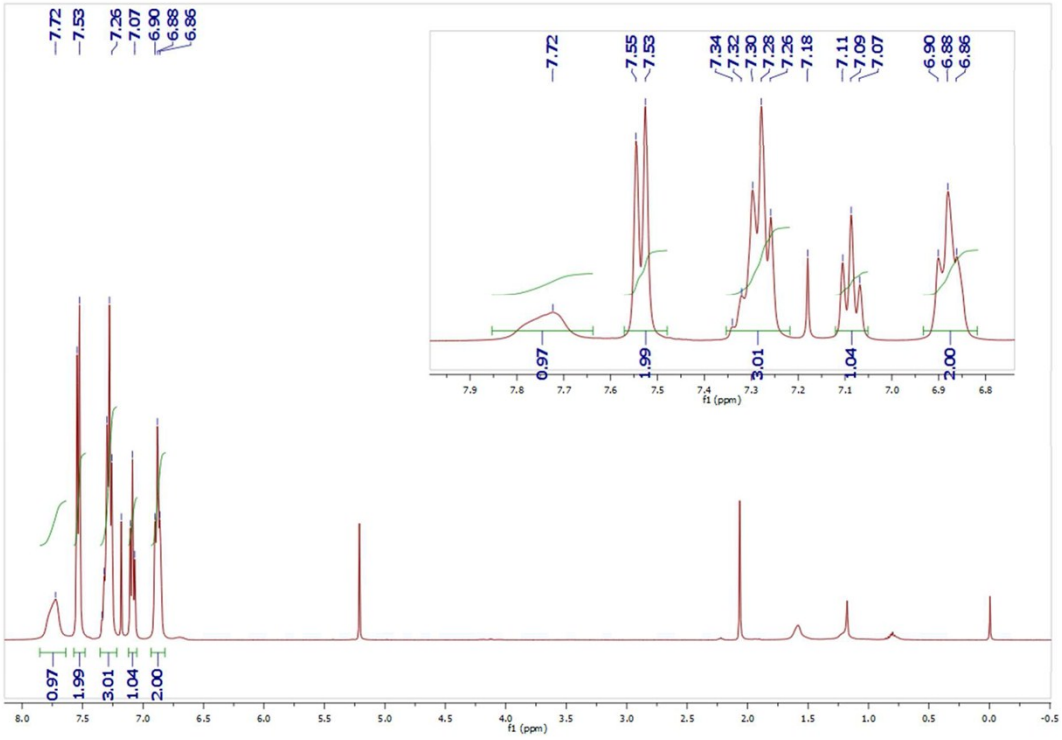
56	$C2/c$	2315.365	2.164	-222.41	58.5899	4.9940	10.0271	90	52.107	90
57	$P2_12_12_1$	1172.644	2.136	-222.38	13.6110	17.4119	4.9480	90	90	90
58	Pc	578.352	2.166	-222.25	4.9952	5.2834	24.1994	90	115.1	90
59	$P2_1/c$	1162.930	2.154	-222.25	26.7447	9.0363	28.7265	90	170.357	90
60	$P2_1/c$	1149.694	2.179	-222.1	36.9572	4.9141	10.2688	90	141.940	90
61	$P2_1/c$	1164.066	2.152	-222.1	16.6481	16.3415	15.0501	90	163.483	90
62	$P2_1/c$	1153.787	2.171	-222.07	4.9955	5.2912	43.6550	90	90.823	90
63	$P2_12_12_1$	1168.970	2.143	-222.07	10.5214	21.9574	5.0600	90	90	90
64	$P2_1$	586.721	2.135	-222.05	11.3909	4.9404	11.1585	90	69.121	90
65	$P2_1/c$	1151.246	2.176	-222.03	43.4283	5.0164	43.4296	90	173.011	90
66	$P2_1/c$	1160.023	2.159	-222.02	9.1652	25.2762	10.2930	90	150.89	90
67	$C2/c$	2324.641	2.155	-222.01	57.1753	5.0048	10.0820	90	53.685	90
68	$P2_12_12_1$	1154.536	2.170	-222.01	22.6641	4.9678	10.2542	90	90	90
69	$P1$	287.681	2.177	-221.97	5.1812	12.4866	7.3281	64.662	42.948	77.97
70	$C2/c$	2307.404	2.171	-221.92	47.4543	4.9863	49.7611	90	168.699	90
71	P-1	574.029	2.182	-221.76	5.0116	7.2693	31.0155	49.72	55.712	42.496
72	$Pca2_1$	1173.790	2.134	-221.73	10.8764	5.0410	21.4087	90	90	90
73	P-1	575.392	2.177	-221.73	4.9946	5.1996	24.3697	89.564	114.543	88.515
74	$C2/c$	2342.211	2.139	-221.61	46.3309	5.0472	47.7880	90	167.901	90
75	Pc	583.535	2.146	-221.58	18.4614	12.9520	14.3794	90	170.229	90
76	$P2_1/c$	1182.795	2.118	-221.58	12.9189	18.5492	4.9453	90	86.454	90
77	P-1	578.677	2.164	-221.58	4.8328	10.7753	12.8631	97.077	89.971	119.237
78	$P2_1$	579.178	2.163	-221.56	9.8522	4.9038	12.3330	90	76.416	90
79	$P2_1/c$	1158.611	2.162	-221.56	4.8213	20.9418	12.1013	90	108.513	90
80	P-1	590.005	2.123	-221.56	11.1632	4.9015	12.8592	87.386	117.878	107.341
81	$P2_12_12_1$	1146.256	2.185	-221.51	22.9485	5.0355	9.9194	90	90	90
82	$Pca2_1$	1168.585	2.144	-221.5	25.1368	5.0546	9.1974	90	90	90
83	$C2/c$	2344.144	2.137	-221.43	47.2613	5.0542	49.9006	90	168.658	90
84	$Pna2_1$	1157.962	2.163	-221.41	5.0122	43.7873	5.2762	90	90	90
85	$P2_1/c$	1160.992	2.158	-221.35	15.8928	10.1250	9.6428	90	131.563	90
86	$P2_1/c$	1172.627	2.136	-221.29	12.3641	4.9057	22.5217	90	120.861	90
87	$P2_1/c$	1155.545	2.168	-221.27	4.8015	10.6637	23.9115	90	70.704	90
88	P-1	580.698	2.157	-221.27	13.7469	15.0510	4.8539	107.53	109.511	125.986
89	$C2/c$	2345.967	2.136	-221.26	51.1762	5.0318	47.8853	90	169.033	90
90	$P2_1/c$	1152.616	2.173	-221.25	10.3967	22.3122	11.7080	90	154.888	90
91	P-1	581.770	2.153	-221.22	10.9997	13.8847	4.7839	111.29	102.676	111.03
92	$C2/c$	2333.318	2.147	-221.22	51.9047	4.9784	57.2266	90	170.921	90
93	$P2_1/c$	1191.381	2.103	-221.21	15.9461	19.0868	4.8895	90	126.816	90
94	$P2_12_12_1$	1162.340	2.155	-221.05	22.8664	10.5368	4.8242	90	90	90
95	$P2_1/c$	1153.277	2.172	-221.0	7.3008	44.2685	5.0162	90	134.654	90
96	$Pca2_1$	1186.515	2.111	-221.0	10.2785	5.0455	22.8793	90	90	90
97	$C2/c$	2349.670	2.132	-220.97	63.9818	5.04181	57.4259	90	172.713	90

98	$P2_1/c$	1169.530	2.142	-220.96	5.0128	11.9996	20.0274	90	103.875	90
99	$P2_1/c$	1158.677	2.162	-220.96	30.8433	5.0008	9.8618	90	130.383	90
100	$P2_12_12_1$	1167.069	2.146	-220.93	23.0425	10.1729	4.9788	90	90	90

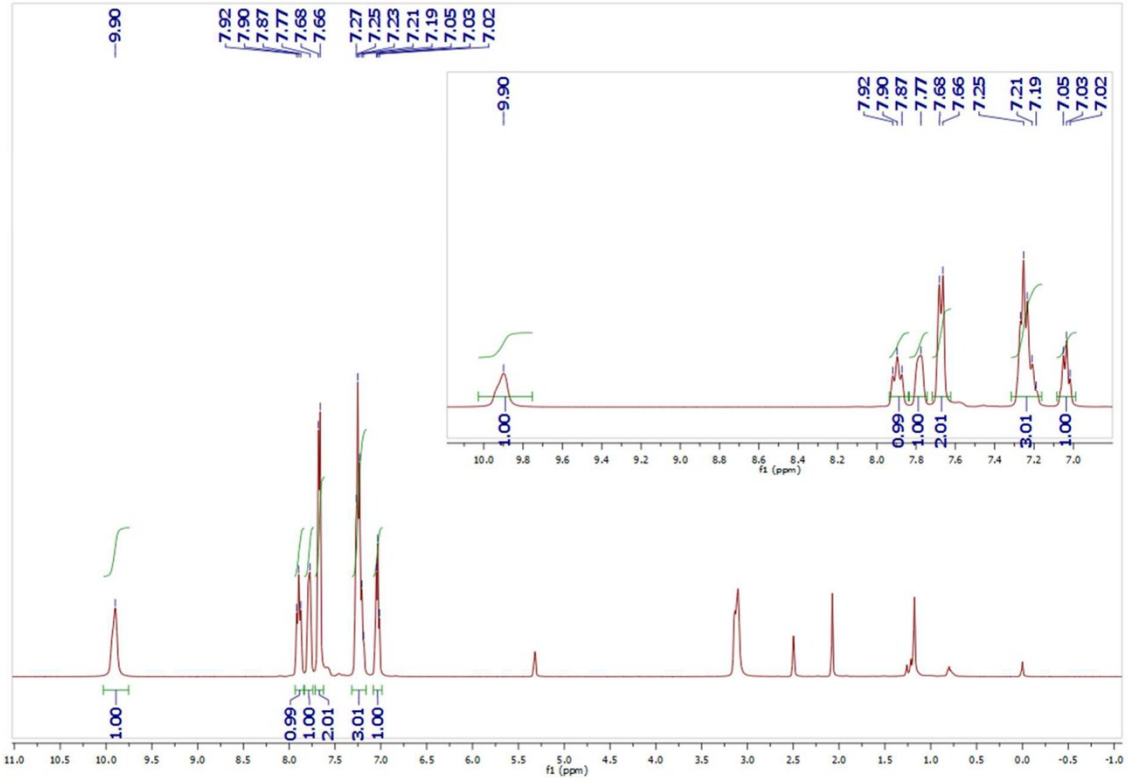
F-5(a): ^{1}H-NMR Spectra of P0024.



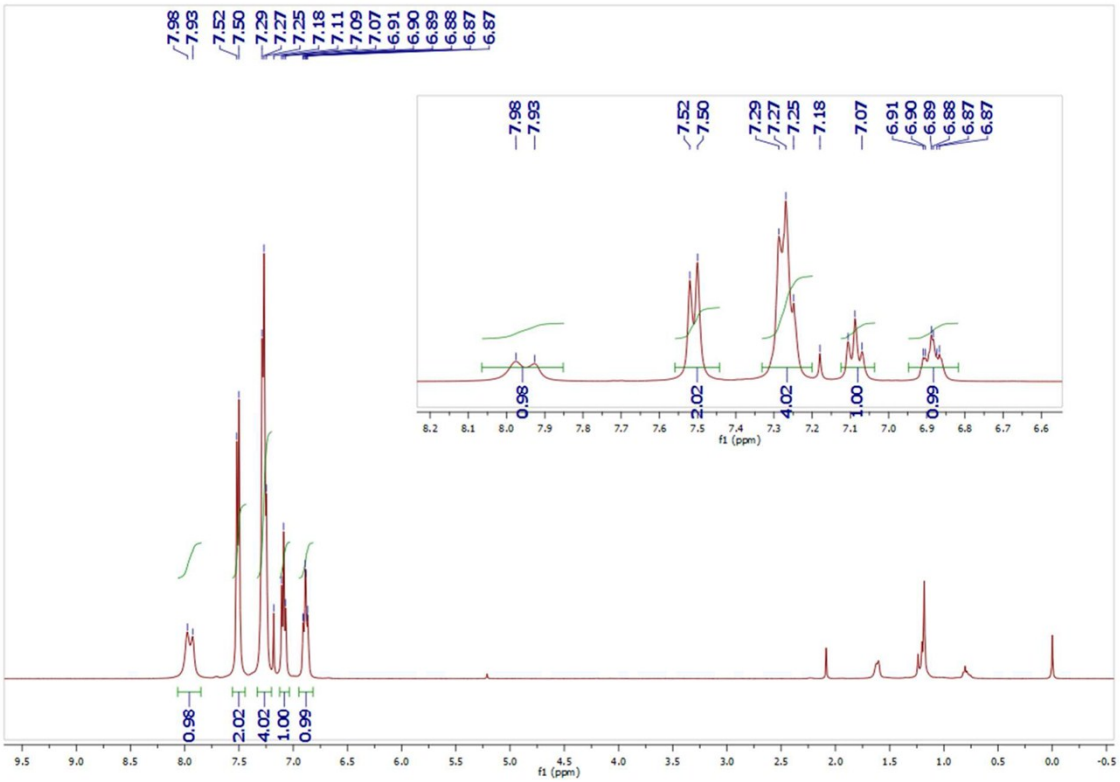
F-5(b): ^{1}H-NMR Spectra of P0026.



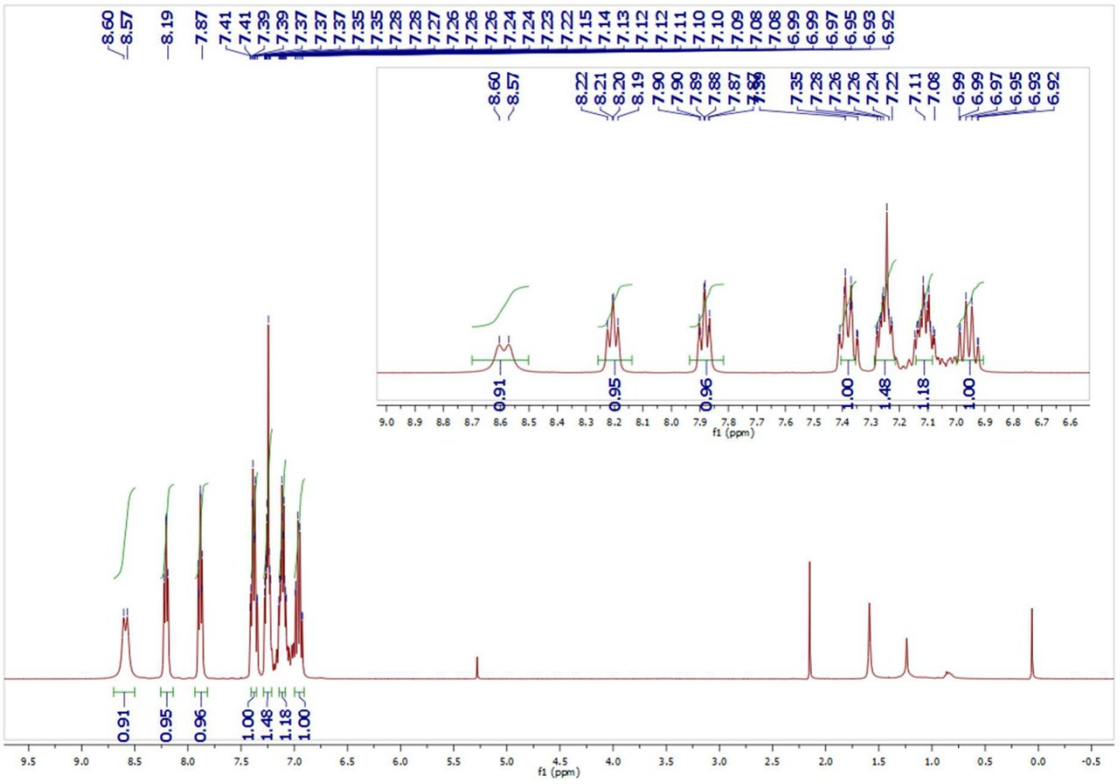
F-5(c): ^{1}H-NMR Spectra of P0034.



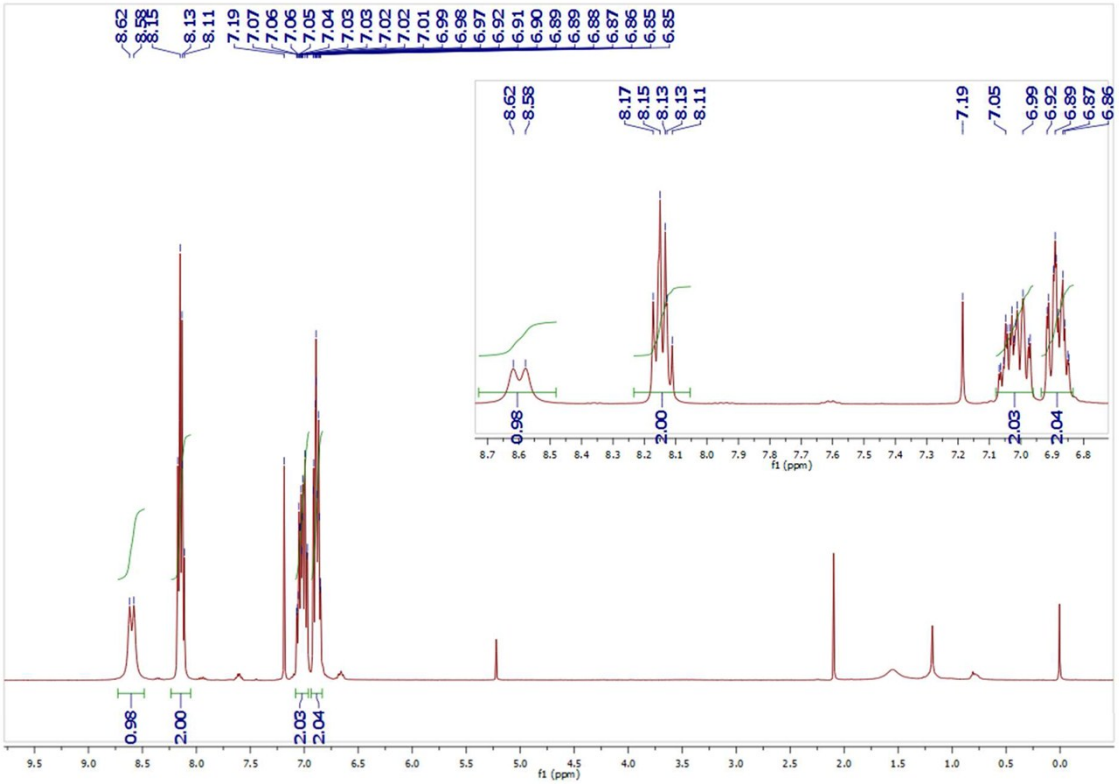
F-5(d): ^{1}H-NMR Spectra of P0035.



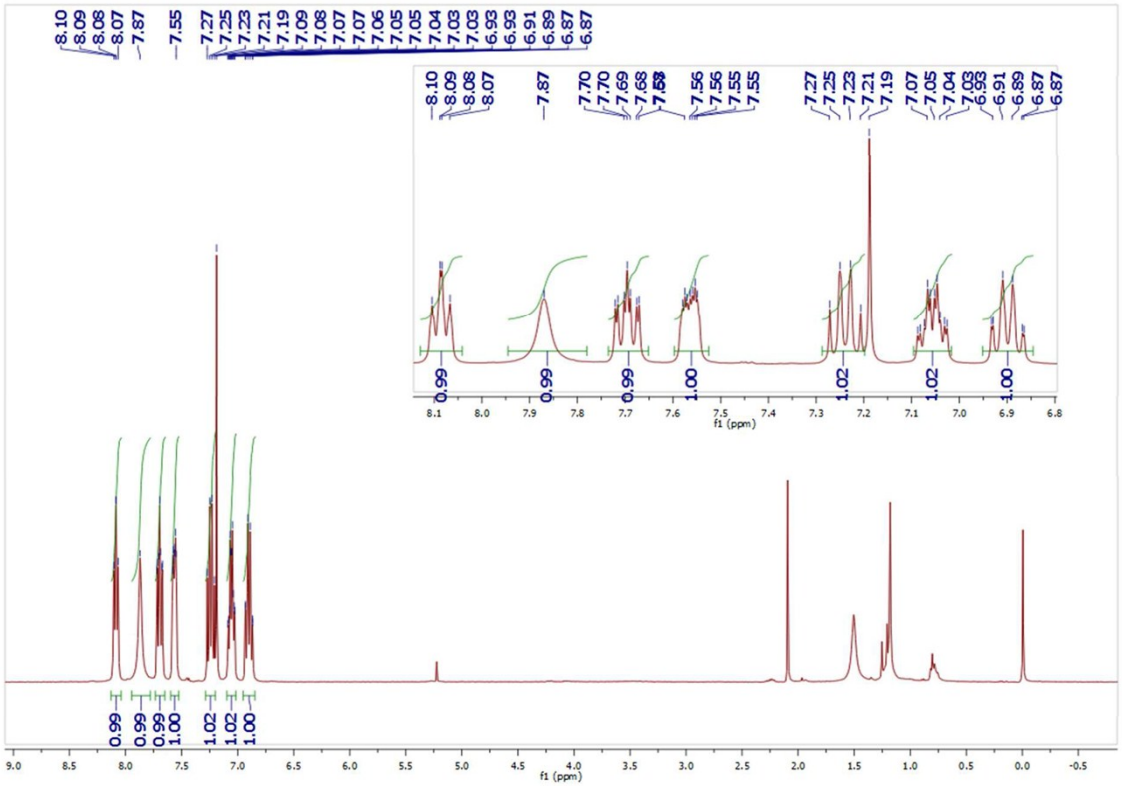
F-5(e): ^{1}H-NMR Spectra of P2323.



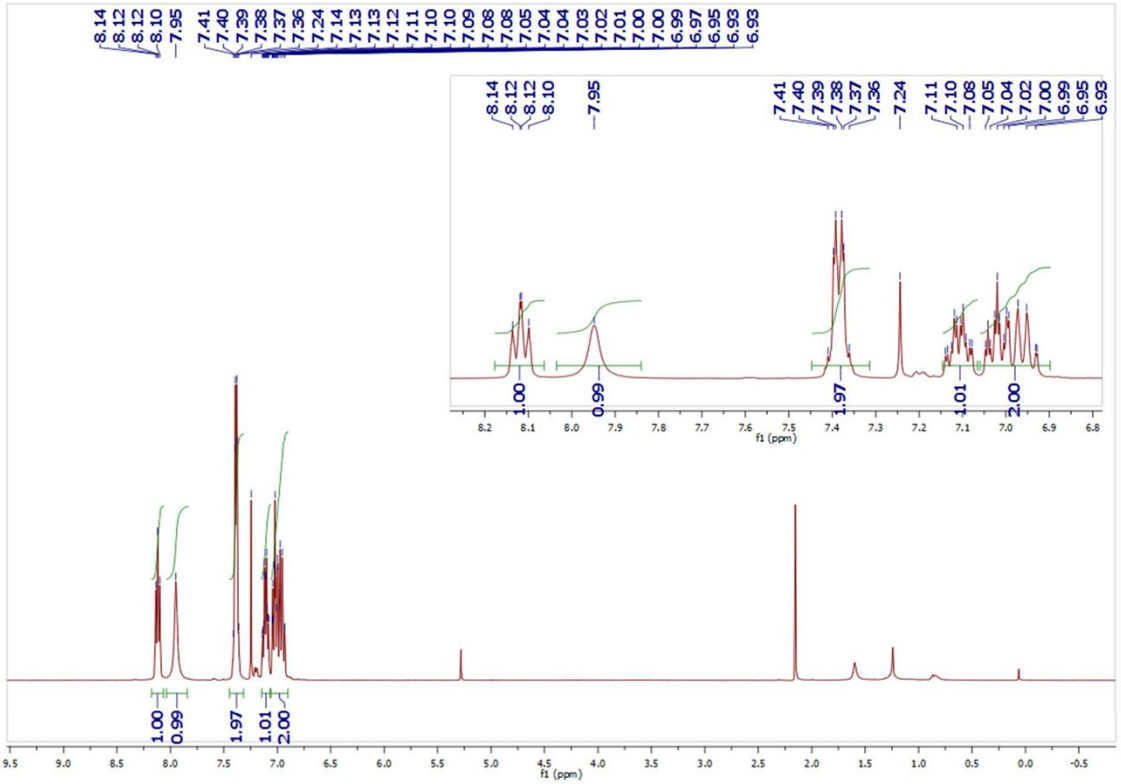
F-5(f): ^{1}H-NMR Spectra of P2324.



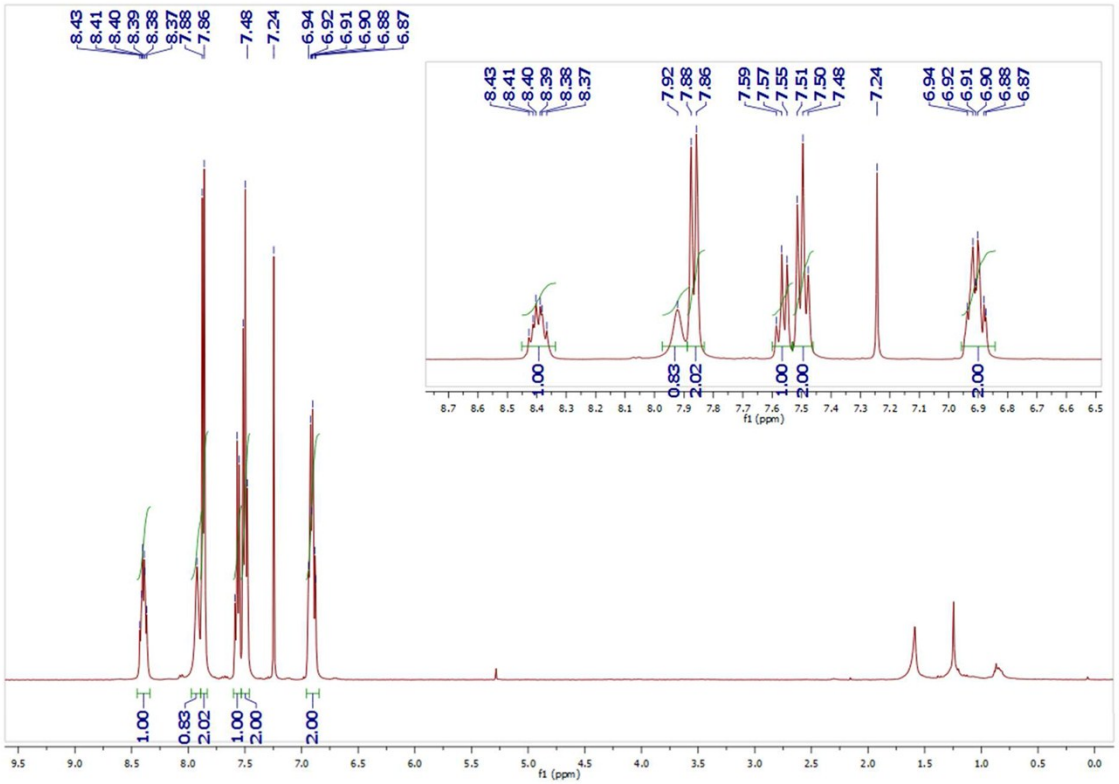
F-5(g): ^{1}H-NMR Spectra of P2334.



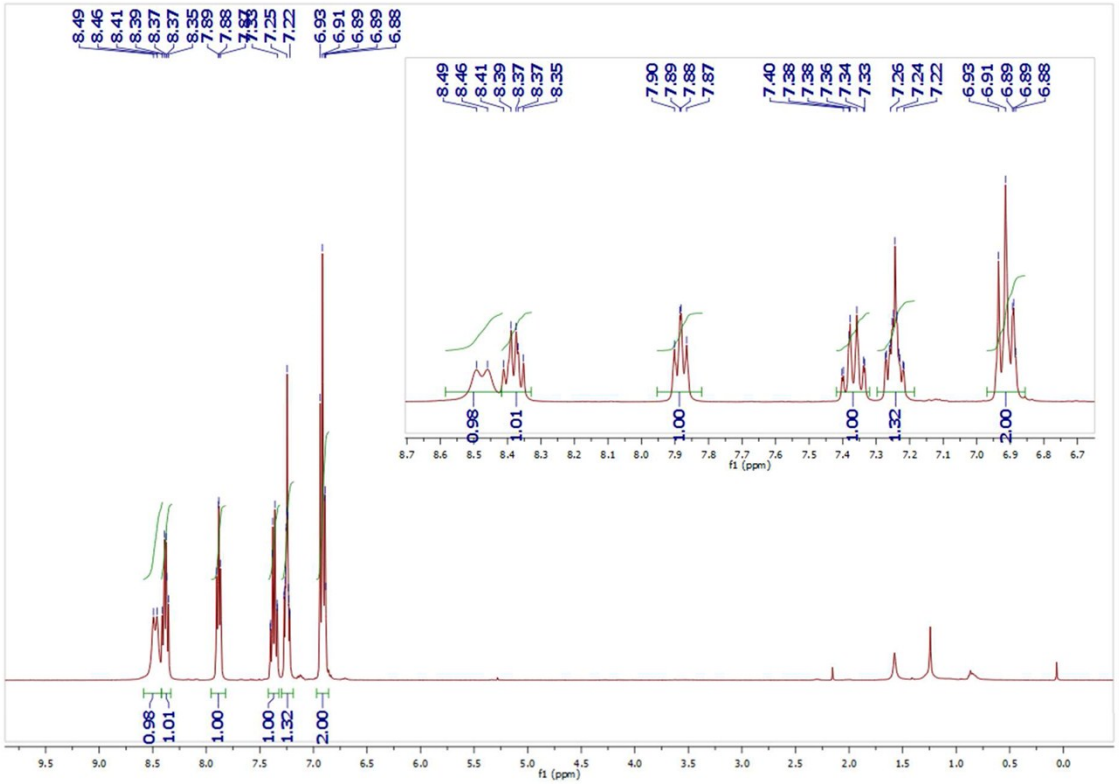
F-5(h): ^{1}H-NMR Spectra of P2335.



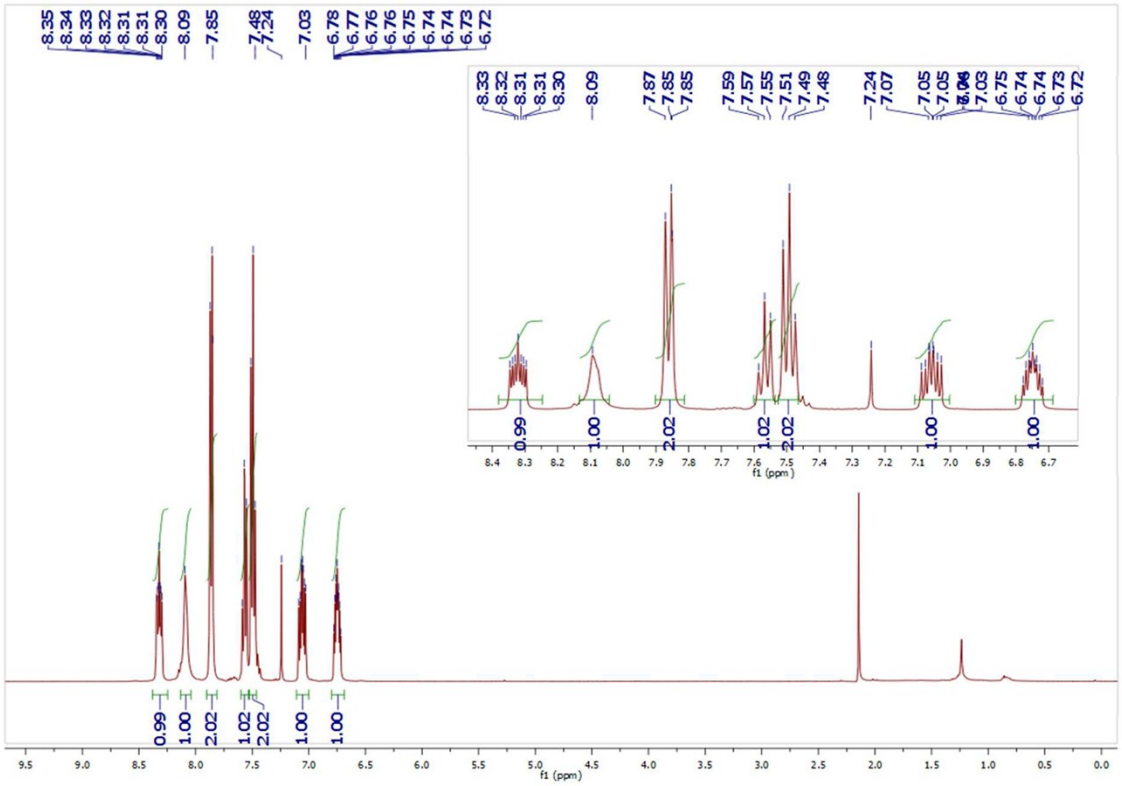
F-5(i): ^{1}H-NMR Spectra of P2400.



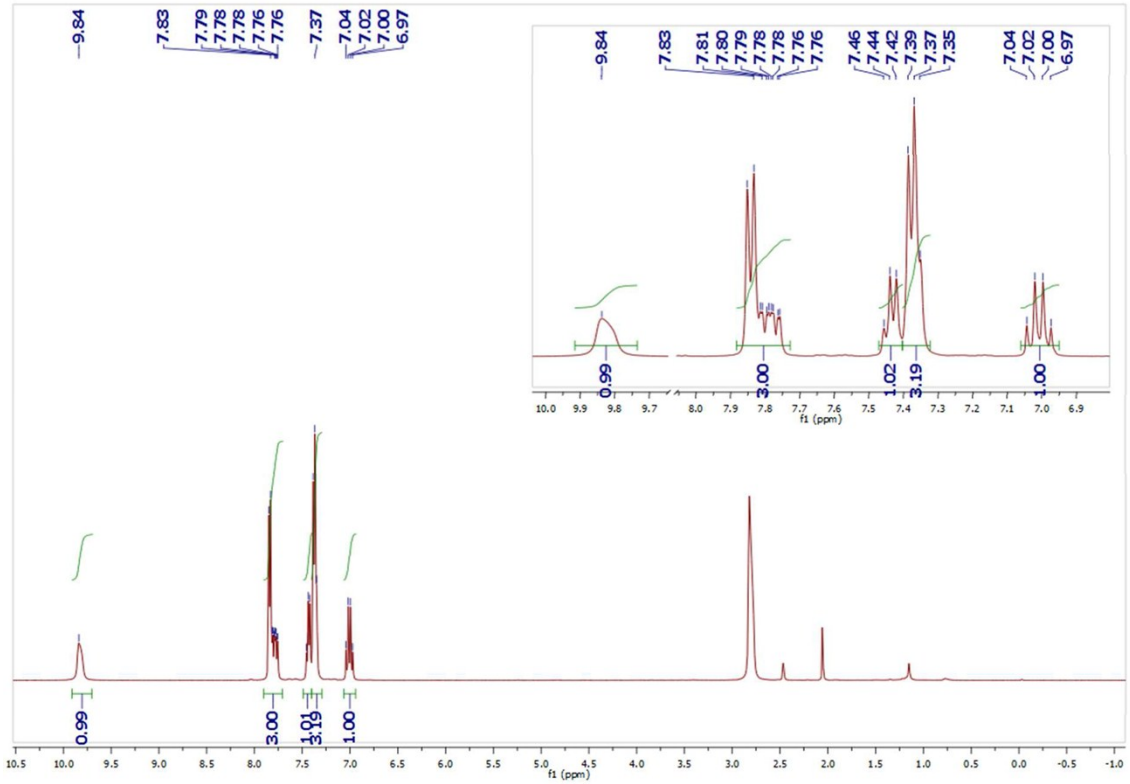
F-5(j): ^{1}H-NMR Spectra of P2423.



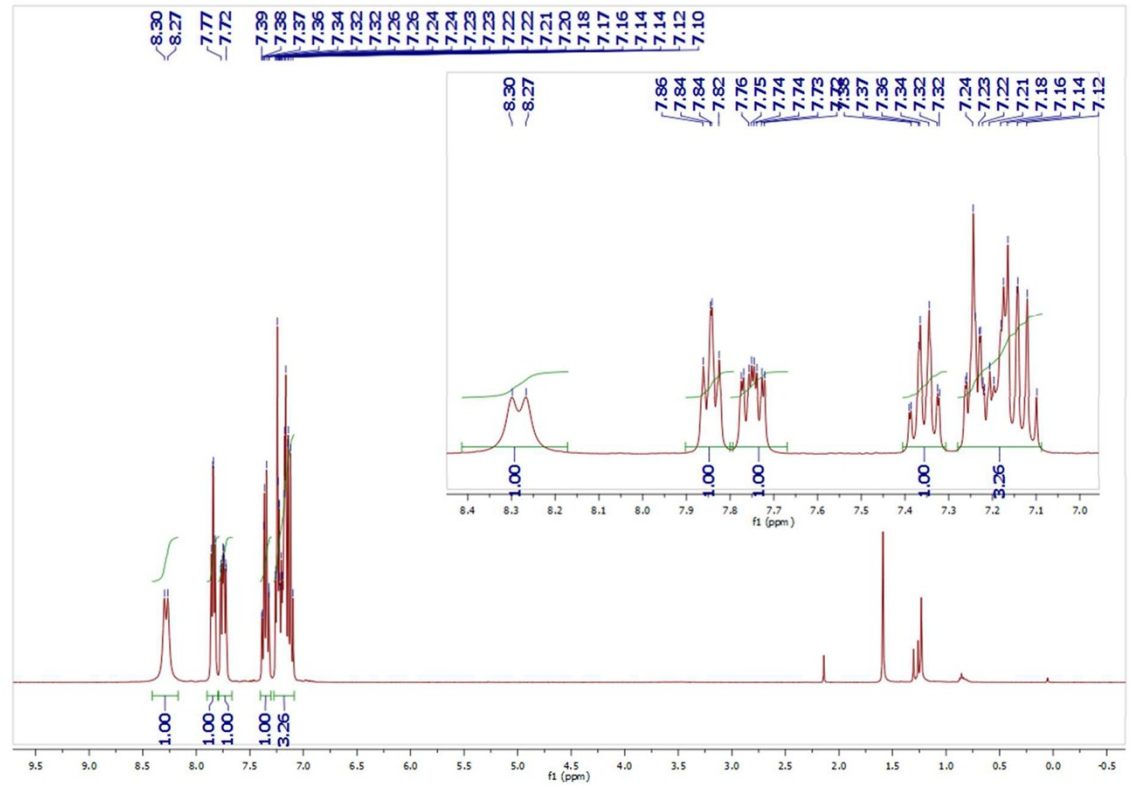
F-5(k): ^{1}H-NMR Spectra of P2500.



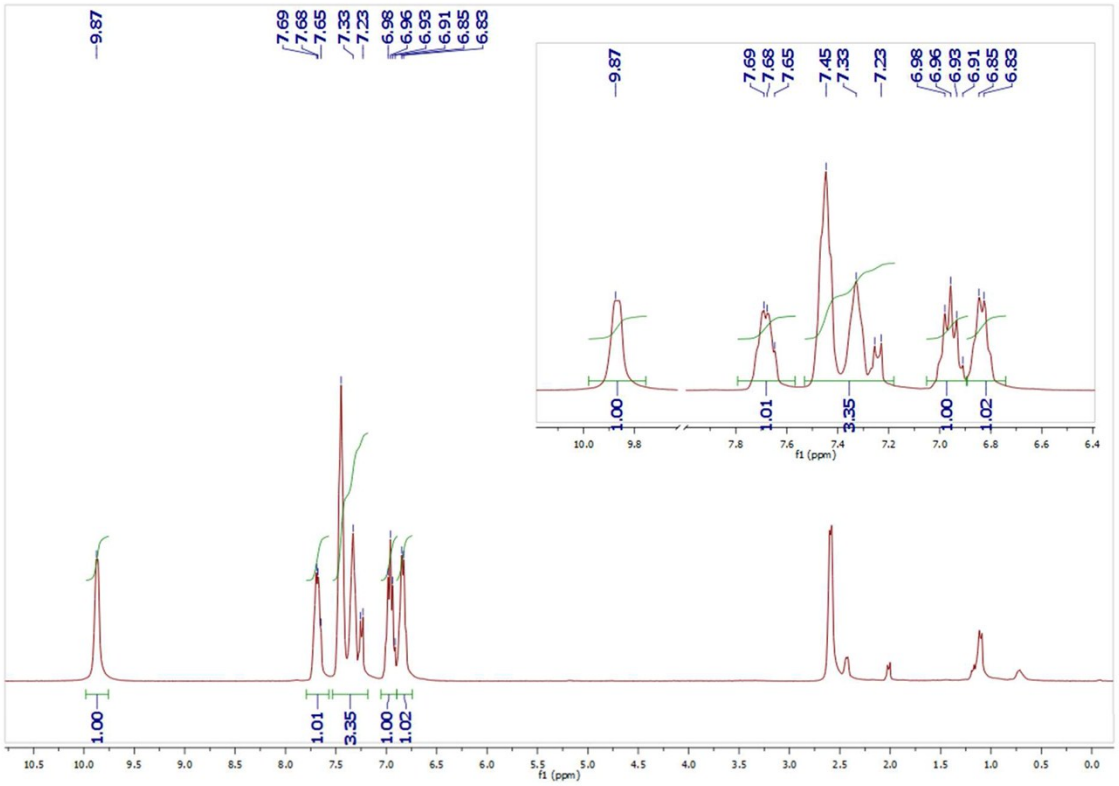
F-5(l): ^{1}H-NMR Spectra of P3400.



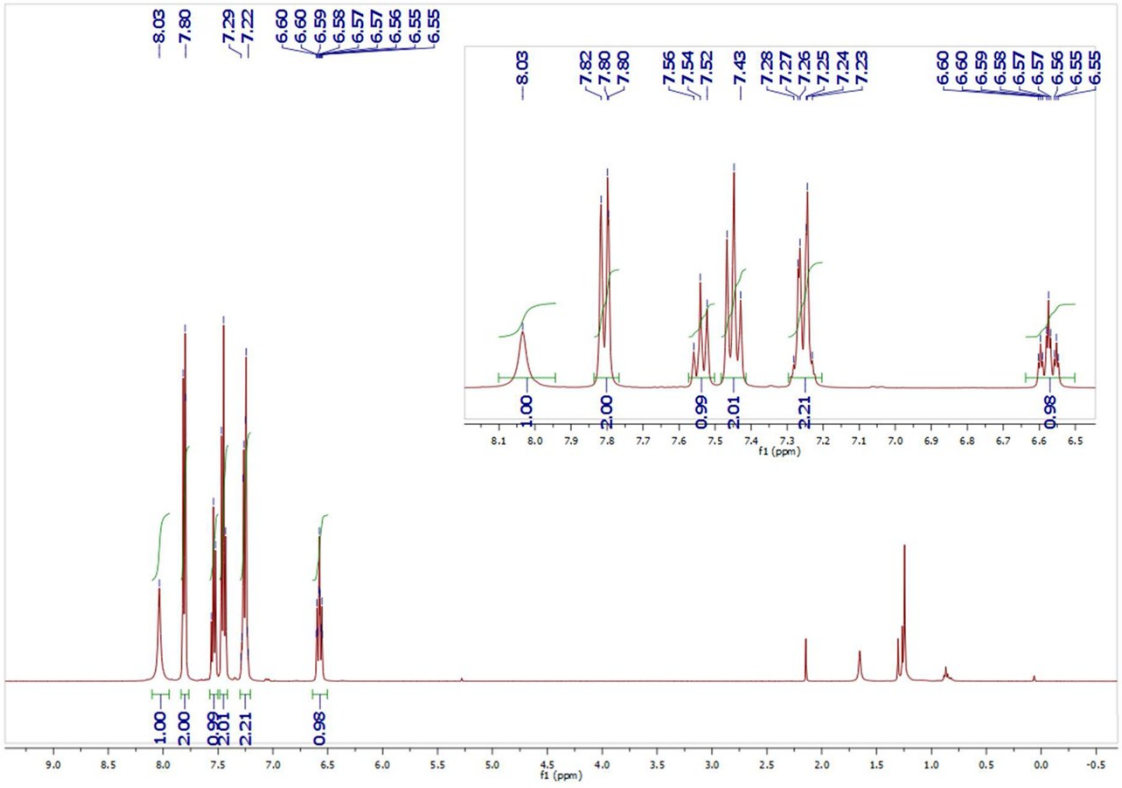
F-5(m): ^{1}H-NMR Spectra of P3423.



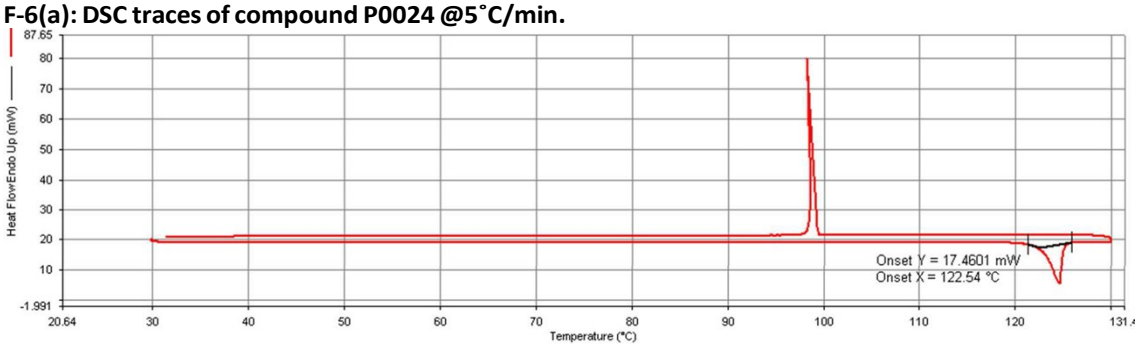
F-5(n): ^{1}H-NMR Spectra of P3435.



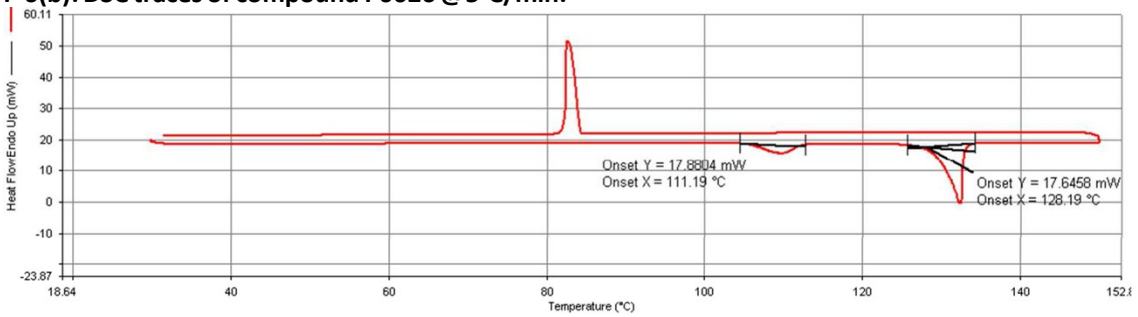
F-5(o): ^{1}H-NMR Spectra of P3500.



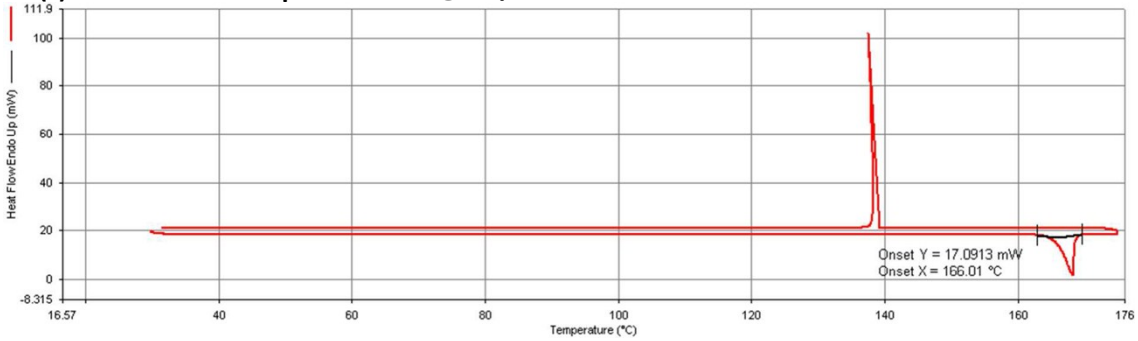
F-6(a): DSC traces of compound P0024 @5˚C/min.



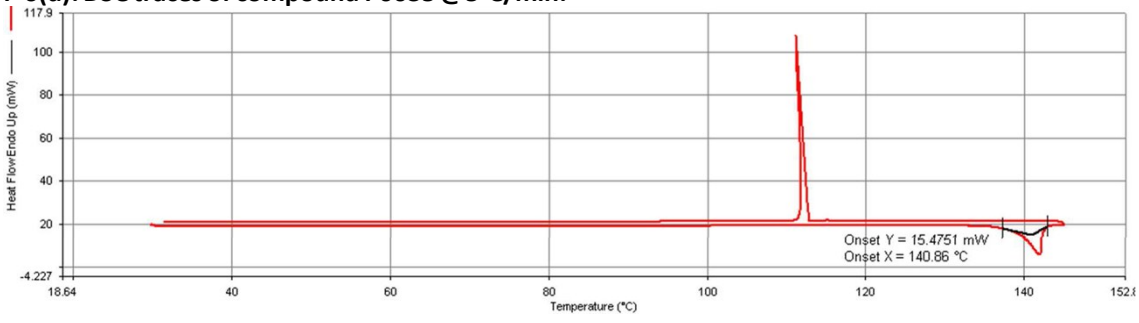
F-6(b): DSC traces of compound P0026 @5˚C/min.



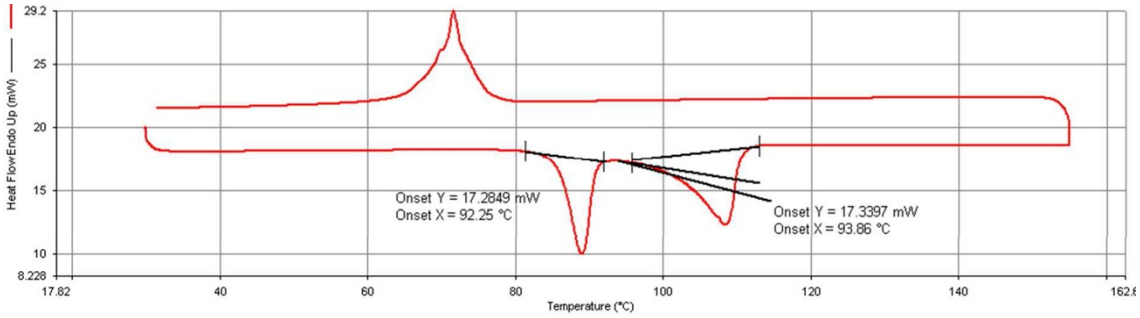
F-6(c): DSC traces of compound P0034 @5˚C/min.



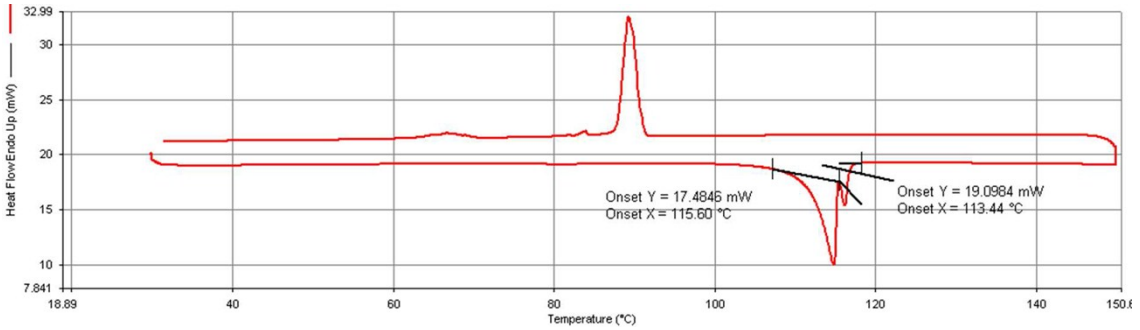
F-6(d): DSC traces of compound P0035 @5˚C/min.



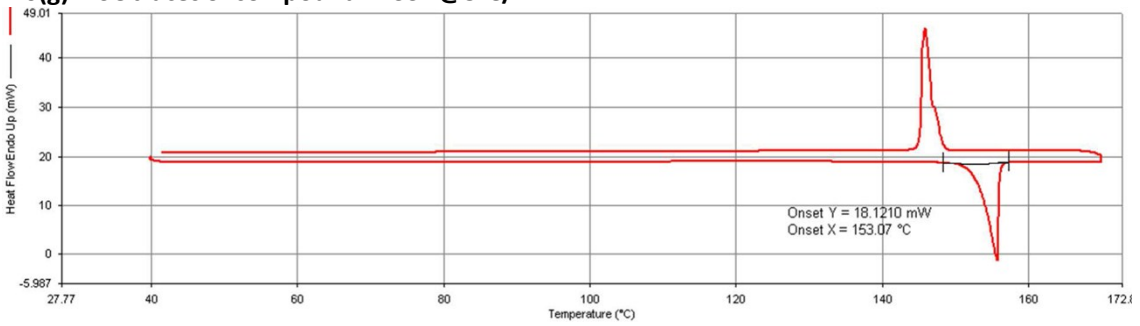
F-6(e): DSC traces of compound P2323 @5˚C/min.



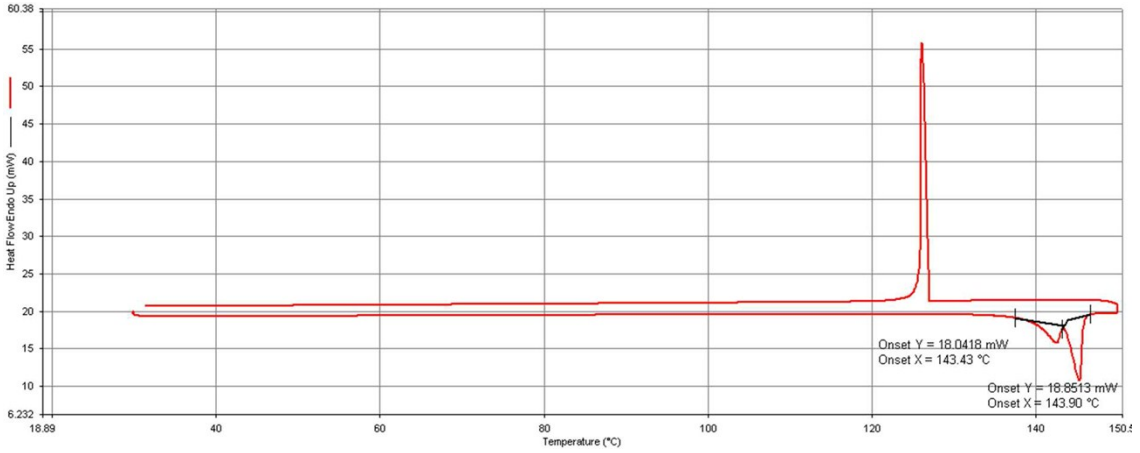
F-6(f): DSC traces of compound P2324 @5˚C/min.



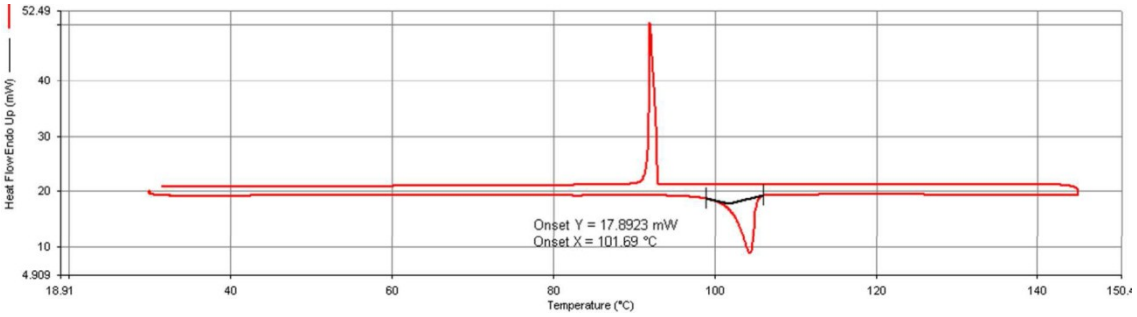
F-6(g): DSC traces of compound P2334 @5˚C/min.



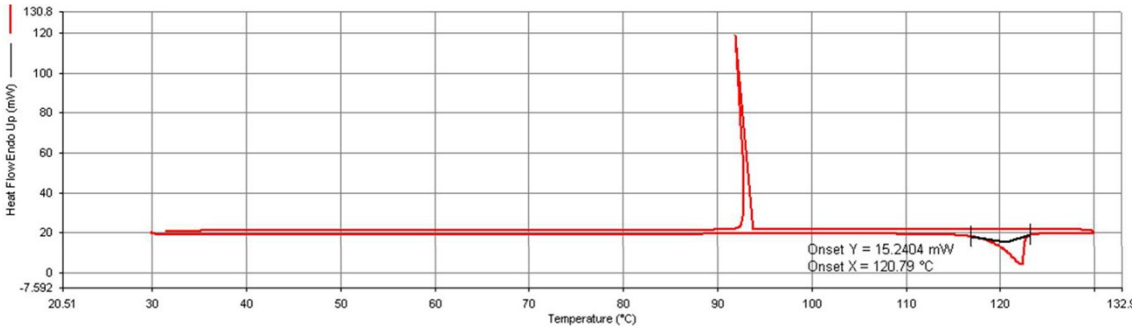
F-6(h): DSC traces of compound P2335 @5˚C/min.



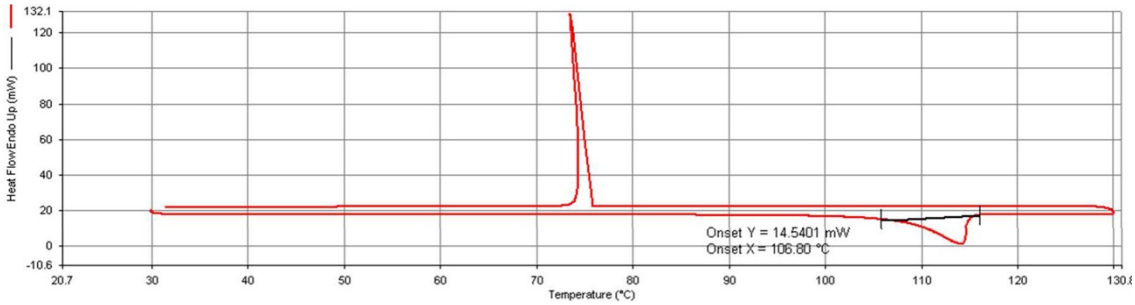
F-6(i): DSC traces of compound P2400 @5˚C/min.



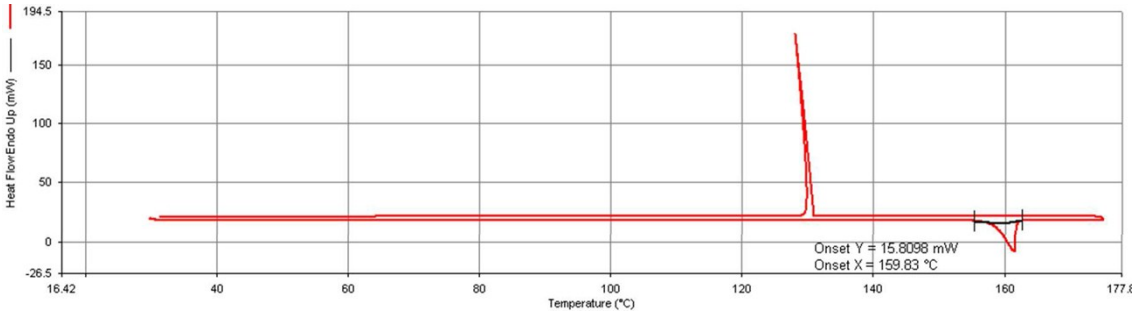
F-6(j): DSC traces of compound P2423 @5˚C/min.



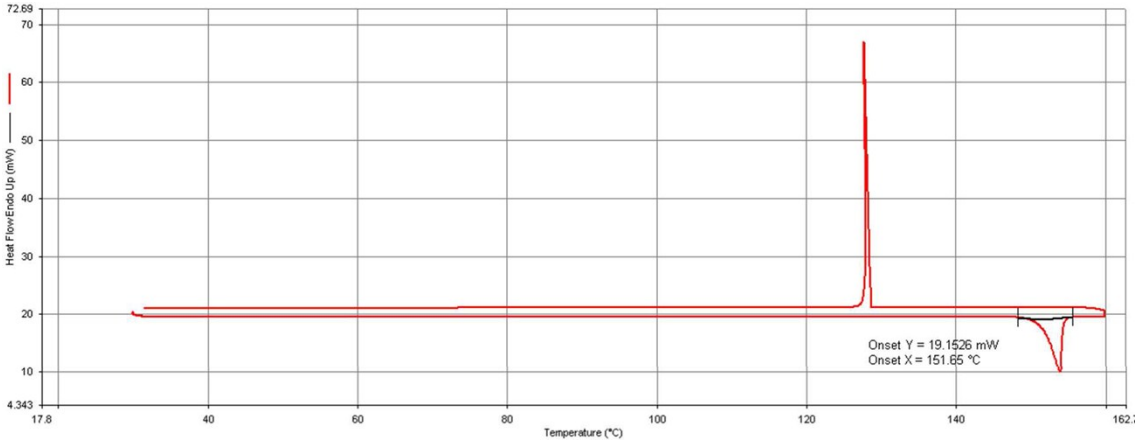
F-6(k): DSC traces of compound P2500 @5˚C/min.



F-6(l): DSC traces of compound P3400 @5˚C/min.



F-6(n): DSC traces of compound P3435 @5˚C/min.



F-6(o): DSC traces of compound P3500 @5˚C/min.