A comprehensive understanding of the synthons involving C–H···F–C hydrogen bond(s) from structural and computational analyses

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Keywords: *N*-benzylideneaniline, C–H···F synthons, stabilization energy, AIM.

Electronic Supplementary Information

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Table S1a: Crystallographic Data for all the compounds reported in the manuscript

Identification code	**52**	**53**	**54**	**55**	**57**
Empirical formula	$C_{13}H_7F_4N$	$C_{13}H_7F_4N$	$C_{13}H_7F_4N$	$C_{13}H_7F_4N$	$C_{13}H_7F_4N$
Formula weight	253.2	253.2	253.2	253.2	253.2
Temperature (K)	100.0	100.0	100.0	100.0	100.0
CCDC No.	1008431	1008432	1008433	1008434	1008435
Crystal System	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic
Space Group	*Pn*	$Pna2_1$	*C*2/c	$P2_1/c$	$P2_1/c$
a (Å)	4.5622(6)	13.5270(9)	12.7990(19)	5.9148(3)	25.7588(17)
b (Å)	9.9940(12)	3.7794(3)	6.5794(8)	7.4926(4)	3.7207(3)
c (Å)	11.5383(12)	21.0491(13)	25.265(4)	23.9195(13)	22.6104(16)
α (^{0})	90.00	90.00	90.00	90.00	90.00
β (^{0})	90.826(6)	90.00	95.749(8)	93.722(2)	90.424(4)
γ (^{0})	90.00	90.00	90.00	90.00	90.00
Volume (Å^3)	526.03(11)	1076.11(13)	2116.9(5)	1057.81(10)	2166.9(3)
Z	2	4	8	4	8
Z’	1	1	1	1	2
ρ (g/cm^3)	1.599	1.563	1.589	1.590	1.56
μ (mm^{-1})	0.144	0.141	0.143	0.143	0.141
F (000)	256.0	512.0	1024.0	512.0	1024.8
$\theta_{min,\ max}$	2.7, 25.0°	1.9, 25.0	1.9, 25.0	2.8, 25.03	2.4, 25.03
h_{min}, h_{max}; k_{min}, k_{max}; l_{min}, l_{max}	-5, 5; -11, 11; -13, 13	-16, 12; -3, 4; -25, 23	-15, 15; -7, 7; -30, 28	-3, 7; -8, 8; -28, 28	-30, 28; -3, 4; -26, 21
No. of measured reflections.	2281	3901	5170	7170	14247
No. of unique reflections.	1365	1750	1868	1863	3831
No. of observed reflections.	1335	1630	1598	1687	3345
R(int)	0.010	0.031	0.017	0.017	0.0424
Data/restraints/parameters	1365/0/163	1750/0/163	1868/0/163	1868/0/163	326
wR_2_obs, R_obs	0.072, 0.0268	0.097, 0.038	0.085, 0.032	0.073, 0.026	0.204, 0.037
$\Delta\rho_{min,max}$(eÅ^{-3})	0.16/-0.17	0.33/-0.25	0.20/-0.20	0.18/-0.22	0.44/ -0.51
GooF	1.078	1.080	1.053	1.052	1.135

Identification code	**58**	**59**	**60**	**61**	**63**
Empirical Formula	$C_{13}H_7F_4N$	$C_{13}H_7F_4N$	$C_{13}H_7F_4N$	$C_{13}H_7F_4N$	$C_{13}H_7F_4N$
Formula weight	253.2	253.2	253.2	253.2	253.2
Temperature (K)	100.0K	100.0K	100.0K	100.0K	100.0K
CCDC No.	1008436	1008437	1008438	1008439	1008440
Crystal System	monoclinic	monoclinic	monoclinic	orthorhombic	orthorhombic
Space Group	*Pc*	*C*2/*c*	$P2_1/c$	$P2_12_12_1$	$Pca2_1$
a (Å)	12.496(5)	25.983(2)	7.2368(5)	5.4757(11)	27.6959(14)
b (Å)	3.7100(14)	7.3160(6)	6.6503(5)	7.7423(15)	3.68490(10)
c (Å)	22.745(9)	24.834(2)	22.2218(14)	24.406(5)	21.5993(10)
α (^{0})	90.00	90.00	90.00	90.00	90.00
β (^{0})	93.123(5)	113.707(5)	97.167(3)	90.00	90.00
γ (^{0})	90.00	90.00	90.00	90.00	90.00
Volume (Å^3)	1052.9(7)	4322.3(6)	1061.11(13)	1034.7(3)	2204.35(16)
Z	4	16	4	4	8
Z’	2	8	1	1	1
ρ (g/cm^3)	1.597	1.556	1.585	1.625	1.53
μ (mm^{-1})	0.144	0.140	0.143	0.147	0.138
F (000)	512.0	2048.0	512.0	512.0	1024.0
$\theta_{min,\ max}$	2.36, 27.1	2.91, 27.32	2.85, 25.02	2.67, 25.02	1.5, 25.07
h_{min}, h_{max}; k_{min}, k_{max}; l_{min}, l_{max}	-16, 14; -2, 4; -26, 29	-30, 33; -9, 9; -32, 32	-8, 8; -6, 7; -26, 26	-5, 6; -9, 6; -29, 29	-27, 33; -4, 4; -25, 26
No. of reflections.	5417	24110	7190	5704	13533
R(int)	0.0446	0.0402	0.0150	0.0188	0.0347
No. of unique reflections.	3878	4848	1870	1812	4145
No of observed reflections	2852	3235	1755	1688	3432
No. of parameters	325	325	163	163	325
wR_2_obs, R_obs	0.123, 0.054	0.097, 0.044	0.073, 0.027	0.078, 0.027	0.095, 0.042
$\Delta\rho_{min,max}$(eÅ^{-3})	0.45/-0.34	0.56/-0.28	0.18/-0.20	0.22/-0.24	0.25, -0.32
GooF	1.036	1.033	1.057	1.184	1.034

Identification code	**64**	**65**	**66**	**68**	**69**
Empirical formula	$C_{13}H_7F_4N$	$C_{13}H_7F_4N$	$C_{13}H_7F_4N$	$C_{13}H_7F_4N$	$C_{13}H_7F_4N$
Formula weight	253.2	253.2	253.2	253.2	253.2
Temperature (K)	100.0K	100.0K	100.0K	100.0K	100.0K
CCDC No.	1008441	1008442	1008443	1008444	1008445
Crystal System	triclinic	monoclinic	triclinic	monoclinic	monoclinic
Space Group	$P\ \bar{1}$	$P2_1$	$P\ \bar{1}$	$P2_1$	$P2_1/c$
a (Å)	6.8244(6)	11.0553(15)	6.8223(8)	9.756(3)	16.497(2)
b (Å)	7.6412(7)	3.6976(4)	7.5505(8)	4.674(2)	3.7422(4)
c (Å)	10.8203(10)	13.0135(14)	11.2975(14)	11.257(4)	17.009(2)
α (^{0})	79.604(6)	90.00	80.541(7)	90.00	90.00
β (^{0})	83.948(6)	98.716(4)	86.409(7)	99.132(17)	94.425(8)
γ (^{0})	69.737(6)	90.00	66.173(7)	90.00	90.00
Volume (Å^3)	520.07(8)	525.82(3)	525.11(19)	506.81(14)	1046.96(7)
Z	2	2	2	2	4
Z’	1	1	1	1	1
ρ (g/cm^3)	1.62	1.60	1.60	1.66	1.61
μ (mm^{-1})	0.146	0.144	0.145	0.150	0.145
F (000)	256.0	256.0	256.0	256.0	512.0
$\theta_{min,\ max}$	2.9, 25.0	1.9, 25.0	3.0, 25.0	2.6, 25.0	1.8, 25.0
h_{min}, h_{max}; k_{min}, k_{max}; l_{min}, l_{max}	-7, 8; -9, 9; -12, 12	-13, 9; -4, 3; -15, 14	-8, 7; -8, 8; -13, 12	-11, 10; -4, 5; -13, 13	-19, 19; -4, 4; -20, 19
No. of reflections.	3815	2304	4918	3341	5300
R(int)	0.0160	0.022	0.020	0.029	0.026
No. of unique reflections.	1821	1766	1840	1386	1854
No of observed reflections	1597	1394	1467	1276	1501
No. of parameters	163	163	163	163	163
wR_2_obs, R_obs	0.115, 0.039	0.184,	0.083, 0.034	0.091, 0.041	0.085, 0.033
$\Delta\rho_{min,max}$(eÅ^{-3})	0.37, -0.30	0.96, -0.32	0.23, -0.24	0.47, -0.17	0.17/-0.21
GooF	1.118	1.058	1.048	1.076	1.021

Identification code	**70**	**71**	**73**	**74**	**75**
Empirical formula	$C_{13}H_7F_4N$	$C_{13}H_7F_4N$	$C_{13}H_7F_4N$	$C_{13}H_7F_4N$	$C_{13}H_7F_4N$
Formula weight	253.2	253.2	253.2	253.2	253.2
Temperature (K)	100.0K	100.0K	100.0K	100.0K	100.0K
CCDC No.	1008446	1008447	1008448	1008449	1008450
Crystal System	triclinic	monoclinic	orthorhombic	triclinic	orthorhombic
Space Group	$P\ \bar{1}$	$P2_1$	$P2_12_12_1$	$P\ \bar{1}$	$P2_12_12_1$
a (Å)	6.7242(6)	3.8029(4)	3.7270(7)	3.7169(6)	3.6872(3)
b (Å)	8.3077(7)	11.4621(14)	11.656(2)	11.5058(19)	12.9017(8)
c (Å)	10.3309(9)	12.2186(15)	25.035(5)	12.530(2)	22.262(2)
α (^{0})	74.956(4)	90.00	90.00	97.022(11)	90.00
β (^{0})	73.491(4)	94.778(6)	90.00	93.644(11)	90.00
γ (^{0})	74.437(4)	90.00	90.00	91.313(12)	90.00
Volume (Å^3)	522.43(8)	530.75(11)	1087.6(4)	530.52(15)	1059.02(1)
Z	2	2	4	2	4
Z'	1	1	1	1	1
ρ (g/cm^3)	1.61	1.59	1.55	1.58	1.59
μ (mm^{-1})	0.145	0.143	0.140	0.143	0.143
F (000)	256.0	256.0	512.0	256.0	512.0
$\theta_{min,\ max}$	2.1, 25.0	2.4, 27.1	1.6, 25.0	1.6, 25.0	2.4, 25.0
h_{min}, h_{max}; k_{min}, k_{max}; l_{min}, l_{max}	-7, 7; -9, 9; -11, 12	-4, 4; -12, 14; -15, 15	-3, 4; -13, 11; -19, 29	-4, 4; -12, 13; -14, 14	-4, 3; -15, 13; -6, 26
No. of reflections.	5125	4729	4534	2973	3637
R(int)	0.016	0.013	0.044	0.013	0.041
No. of unique reflections.	1835	1976	1771	1861	1796
No of observed reflections	1556	1936	1340	1371	1539
No. of parameters	163	191	163	171	163
wR_2_obs, R_obs	0.089, 0.032	0.066, 0.024	0.125, 0.051	0.110, 0.046	0.075, 0.037
$\Delta\rho_{min,max}$(eÅ^{-3})	0.22/-0.23	0.21, -0.18	0.40/-0.22	0.25/-0.29	0.17, -0.18
GooF	1.047	1.068	0.999	1.043	1.023

Identification code	**76**	**77**	**78**	**80**	**81**
Empirical formula	$C_{13}H_7F_4N$	$C_{13}H_7F_4N$	$C_{13}H_7F_4N$	$C_{13}H_7F_4N$	$C_{13}H_7F_4N$
Formula weight	253.2	253.2	253.2	253.2	253.2
Temperature (K)	100.0K	100.0K	100.0K	100.0K	100.0K
CCDC No.	1008462	1008463	1008464	1008465	1008466
Crystal System	monoclinic	triclinic	monoclinic	monoclinic	orthorhombic
Space Group	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_12_12_1$
a (Å)	6.8363(4)	7.3598(10)	6.6472(4)	13.7505(4)	3.7226(6)
b (Å)	13.8701(8)	12.5972(14)	15.8920(9)	3.7574(1)	13.105(2)
c (Å)	11.6974(6)	12.6690(16)	10.0448(5)	26.3533(7)	21.768(4)
α (^{0})	90.00	70.079(7)	90.00	90.00	90.00
β (^{0})	105.915(3)	75.851(8)	92.712(3)	130.149(2)	90.00
γ (^{0})	90.00	78.418(7)	90.00	90.00	90.00
Volume (Å^3)	1066.6(1)	1061.9(2)	1059.92(2)	1040.7(2)	1062.0(3)
Z	4	4	4	4	4
Z’	1	2	1	1	1
ρ (g/cm^3)	1.58	1.58	1.59	1.62	1.58
μ (mm^{-1})	0.142	0.143	0.143	0.146	0.143
F (000)	512.0	512.0	512.0	512.0	512.0
$\theta_{min,\ max}$	2.9, 28.7	1.7, 25.0	2.4, 25.0	1.7, 25.0	1.8, 25.0
h_{min}, h_{max}; k_{min}, k_{max}; l_{min}, l_{max}	-9, 4; -13, 18; -15, 15	-8, 5; -14, 13; -15, 11	-5, 7; -18, 16; -11, 11	-16, 16; -4, 4; -31, 30	-2, 4; -15, 15; -25, 25
No. of reflections.	8250	9688	5694	7150	5829
R(int)	0.024	0.040	0.017	0.026	0.046
No. of unique reflections.	2757	3727	1864	1827	1852
No of observed reflections	2196	2465	1610	1533	1542
No. of parameters	163	325	163	163	163
wR_2_obs, R_obs	0.091, 0.037	0.094, 0.042	0.080, 0.032	0.087, 0.033	0.066, 0.037
$\Delta\rho_{min,max}$(eÅ^{-3})	0.31/-0.29	0.42, -0.23	0.20, -0.19	0.31, -0.22	0.16, -0.18
GooF	1.064	1.010	1.051	1.045	1.062

Identification code	82	83	84	86	87
Empirical formula	$C_{13}H_7F_4N$	$C_{13}H_7F_4N$	$C_{13}H_7F_4N$	$C_{13}H_7F_4N$	$C_{13}H_7F_4N$
Formula weight	253.2	253.2	253.2	253.2	253.2
Temperature (K)	100.0K	100.0K	100.0K	100.0K	100.0K
CCDC No.	1008467	1008468	1008471	1008469	1008470
Crystal System	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space Group	*Cc*	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a (Å)	7.004(3)	10.0995(3)	7.092(2)	6.790(1)	7.345(2)
b (Å)	30.750(13)	9.0827(3)	30.276(10)	6.803(1)	21.755(6)
c (Å)	10.041(4)	18.1054(4)	10.124(3)	12.062(2)	14.366(4)
α (^{0})	90.00	90.00	90.00	84.04(1)	90.00
β (^{0})	99.000(5)	141.529(1)	99.046(4)	85.23(1)	109.888(3)
γ (^{0})	90.00	90.00	90.00	72.40(1)	90.00
Volume (Å^3)	2135.9(15)	1033.23(5)	2146.6(12)	527.4(2)	2158.6(3)
Z	8	4	8	2	8
Z’	1	1	2	1	2
ρ (g/cm^3)	1.57	1.63	1.57	1.59	1.56
μ (mm^{-1})	0.142	0.147	0.141	0.144	0.141
F (000)	1024.0	512.0	1024.0	256.0	1024.0
$\theta_{min,\ max}$	2.4, 25.0	2.3, 25.0	2.2, 27.1	1.7, 25.0	2.4, 25.0
h_{min}, h_{max}; k_{min}, k_{max}; l_{min}, l_{max}	-3, 8; -36, 36; -11, 11	-8, 12; -8, 10; -21, 15	-9, 3; -37, 38; -12, 12	-8, 7; -8, 4; -14, 14	-8, 8; -11, 25; -16, 16
No. of reflections.	5980	5467	13669	5009	12186
R(int)	0.032	0.021	0.049	0.031	0.0353
No. of unique reflections.	2697	1822	4719	1848	3800
No of observed reflections	2393	1532	3430	1361	2846
No. of parameters	325	163	325	163	325
wR_2_obs, R_obs	0.067, 0.032	0.086, 0.033	0.010, 0.044	0.223, 0.081	0.078, 0.037
$\Delta\rho_{min,max}$(eÅ^{-3})	0.15, -0.21	0.23, -0.31	0.24, -0.27	0.86, -0.38	0.19, -0.23
GooF	1.023	1.057	1.019	1.106	1.041

Structural description of the compounds:

While studying π···π interactions

Cg1: Center of gravity of the phenyl ring belonging to benzaldehyde group (A).

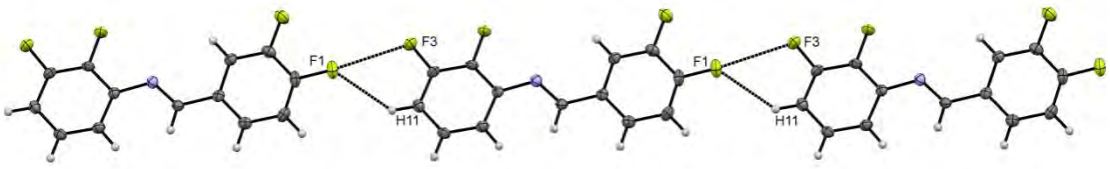
Cg2: Center of gravity of the phenyl ring belonging to aniline group (A).

Cg3: Center of gravity of the phenyl ring belonging to benzaldehyde group (A) of the 2nd molecule of the asymmetric unit wherever the case will be.

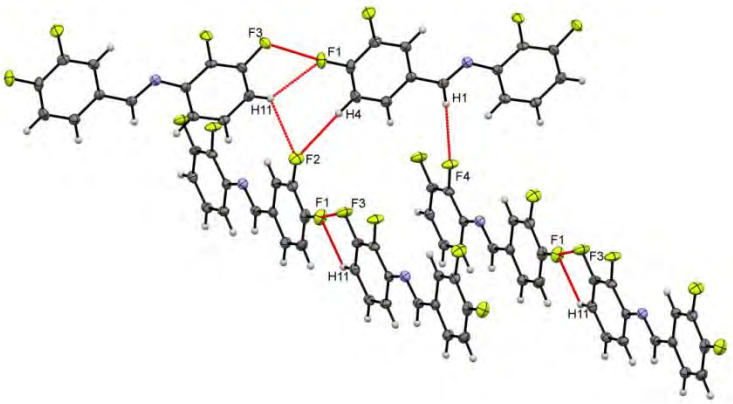
Cg4: Center of gravity of the phenyl ring belonging to aniline group (A) of the 2nd molecule of the asymmetric unit wherever the case will be.

52:

This compound has been found to crystallize in the *Pn* space group with one molecule in the asymmetric unit. Both the phenyl rings are inclined at an angle of 4.2^0, which implies that molecule is nearly planar. Linear chains have been found to form through the utilization of C–H···F and C–F···F–C interactions (table S1, figure S1a). Further, the chains interconnect among themselves through a trimeric motif as shown in figure S1b. In this motif, F2 is bifurcated and it involves in C–H···F hydrogen bond formation with the hydrogen of two different molecules both of which are related to it by *n* glide. Furthermore, C–H···F hydrogen bond involving imine hydrogen (H1) with *ortho*-fluorine on the aniline ring has also been found between the *n*-glide related molecules (table S1, figure S1b).



S1a



S1b

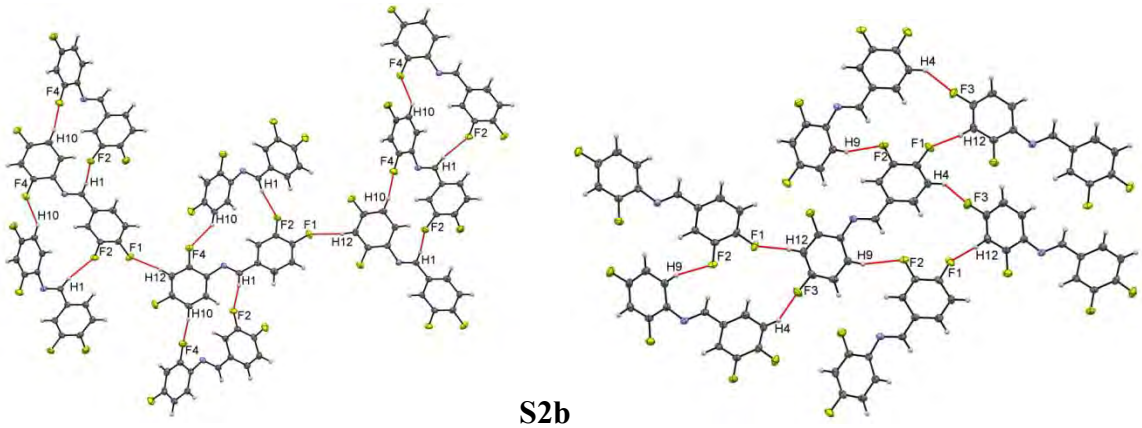
Figure S1: (a) Formation of chains through C–H···F and C–F···F–C interactions, **(b)** trimer formation through C–H···F hydrogen bonds between the chains formed.

Table S1: Details of the geometrical parameters for all the C–H···F hydrogen bonds, the values of electron densities and Laplacians at their BCPs

Code	C–D···F (D = H, F)	*d* (D···F/Å)	θ (∠C–D···F/°)	Symmetry Code	SE_{G09} kcal/mol	ρ (e Å^{-3})	$\nabla^2\rho$ (e Å^{-5})
52	C1–H1···F4	2.47	136	$x+^1/_2,-y-2,z+^1/_2$	-3.4	0.05	0.89
	C11–H11···F2	2.65	123	$x-^3/_2,-y-2,z+^1/_2$	-1.3	0.05	0.92
	C11–H11···F1	2.57	135	x-2,y-1,z	0.2	0.04	0.70
	C12–F3···F1–C5	2.934(2)	170.6(1) 106.3(1)	x-2,y-1,z		0.03	0.73

53:

This structure crystallizes in the *Pna*2_1 space group with one molecule in the asymmetric unit. On changing the substituent position on B ring from 2,3 to 2,4; the inter planar angle between the two phenyl rings got increased from 4.2° to 36.9° and thus made the molecule completely non-planar. Dimers are formed through C–H···F hydrogen bond involving H1 with F2 and H10 with F4 by the utilization of *a* glide (table S2, figure S2a). Then, these dimers further extend in the lattice again through C–H···F hydrogen bonds by the application of *n* glide involving H12 with F1 (table S2, figure S2a). Trimeric network of molecules has also been found in the crystal structure of this compound through C–H···F hydrogen bonds (table S2, figure S2b).



S2a **S2b**

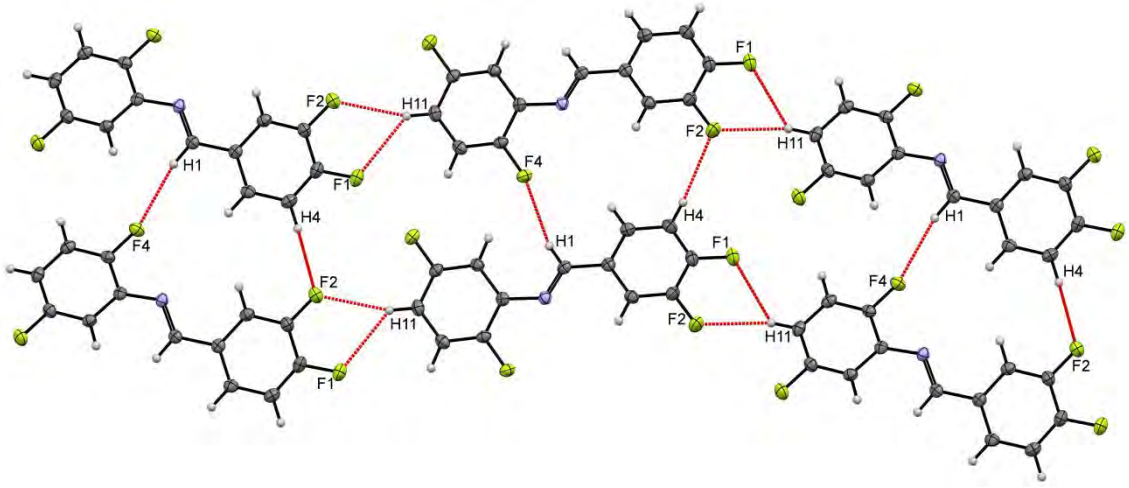
Figure S2: (a) Dimer formation and its propagation in the latice through C–H···F hydrogen bonds, **(b)** trimeric network of molecules formed through C–H···F hydrogen.

Table S2: Details of the geometrical parameters for all the C–H···F hydrogen bonds, the values of electron densities and Laplacians at their BCPs

Code	C–H···F	*d* (H···F/Å)	θ (∠C–H···F/°)	Symmetry Code	SE_{G09} kcal/mol	ρ (e Å^{-3})	$\nabla^2\rho$ (e Å^{-5})
53	C1–H1···F2	2.68	157	$x+^{1}/_{2},-y+^{3}/_{2},+z$	-3.9	0.04	0.67
	C10–H10···F4	2.52	142	$x+^{1}/_{2},-y+^{3}/_{2},+z$		0.03	0.66
	C12–H12··· F1	2.45	163	$-x+^{3}/_{2},y+^{3}/_{2},z+^{1}/_{2}$	-1.2	0.04	0.76
	C4–H4···F3	2.50	129	$1-x,1-y,^{1}/_{2}+z$	-1.3	0.04	0.81
	C9–H9···F2	2.63	164	$x+^{1}/_{2},-y+^{5}/_{2},+z$	-2.7	0.03	0.60

54:

This structure is solved in *C*2/*c* space group. This molecule has also been found to be non-planar in its crystal structure with the interplanar angle of 22.1° between the two phenyl rings, which is quite less than the angle which was found in the compound **40**. Molecules related by *c* glide lead to the formation of chains through C–H···F hydrogen bond (table S3, figure S3). The hydrogen involved in this interaction is bifurcated and it interacts with two fluorine atoms of the aldehyde ring, which are adjacent to each other. The chains formed propagate in the lattice through highly directional C–H···F hydrogen bonds involving H4 with F2 and H1 with F4, having very high stabilization energies (-4.71 kcal/mol) (table S3, figure S3). Thus a molecular sheet type structure has been formed.



S3

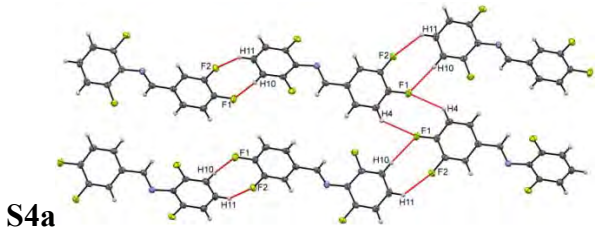
Figure S3: Formation of sheet like sructure in the latice through C–H···F hydrogen bonds.

Table S3: Details of the geometrical parameters for all the C–H···F hydrogen bonds, the values of electron densities and Laplacians at their BCPs

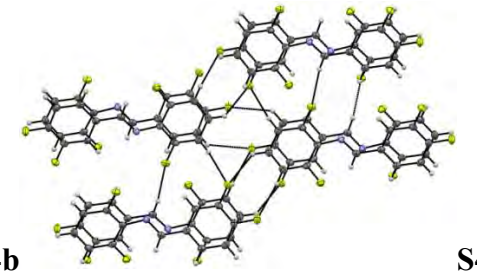
Code	C–H···F	*d* (H···F/Å)	θ (∠C–H···F/°)	Symmetry Code	SE_{G09} kcal/mol	ρ (e Å^{-3})	$\nabla^2\rho$ (e Å^{-5})
54	C4–H4···F2	2.60	155	x,+y-1,+z	-4.7	0.03	0.65
	C1–H1···F4	2.52	162	x,+y-1,z		0.04	0.72
	C11–H11···F1	2.63	133	x,-y+1,z-$^1/_2$	-1.7	0.03	0.65
	C11–H11···F2	2.48	163	x,-y+1,z-$^1/_2$		0.04	0.81

55:

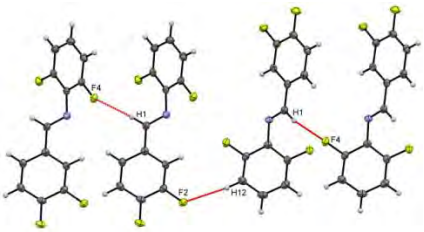
This compound crystallizes in the monoclinic $P2_1/c$ space group with Z = 4. Due to the presence of both the fluorine atoms at the *ortho* position of the aniline ring, the phenyl rings become highly non-planar and are inclined at an angle of 51.6° with respect to each other. The fluorine atoms present at the adjacent position of the aldehyde ring are involved in the formation of hetero dimers resulting in the formation of chains. Molecules related to each other by the center of inversion are interacting through the formation of homo dimers involving C–H···F hydrogen bond (H12 with F1) and thus resulting into the interconnections of the chains formed (table S4, figure S4a). The sheet kind of structure thus formed interacts with other sheets along *b*-axis through π···π interactions (table S4b, figure S4b). Another very short and highly directional C–H···F hydrogen bond involving H1 with F4 (present at the *ortho* position of aldehyde ring) has also been found in the crystal structure of this compound (table S3, figure S4c).



S4a



S4b



S4c

Figure S4: (a) Molecular layer formation and their interconnection through C–H···F hydrogen bonds, **(b)** stacking interaction which interlink the layers along *b*-axis, **(c)** very short and highly directional C–H···F hydrogen bond in the crystal structure of compound **55**.

Table S4a: Details of the geometrical parameters for all the C–H···F hydrogen bonds, the values of electron densities and Laplacians at their BCPs

Code	C–H···F	*d* (H···F/Å)	θ (∠C–H···F/^{o})	Symmetry Code	SE_{G09} kcal/mol	ρ (e Å^{-3})	$\nabla^2\rho$ (e Å^{-5})
55	C1–H1···F4	2.34	166	x+1,y,z	-3.9	0.06	1.04
	C12–H12···F2	2.69	164	-x+1,y-$^{1}/_{2}$,-z+$^{1}/_{2}$	-1.9	0.02	0.51
	C11–H11···F2	2.60	127	x,-y+$^{1}/_{2}$,z-$^{1}/_{2}$	-1.9	0.03	0.66
	C10–H10···F1	2.59	168	x,-y+$^{1}/_{2}$,z-$^{1}/_{2}$		0.03	0.64
	C4–H4···F1	2.66	138	3-x, -y,1-z	-2.0	0.03	0.54

Table S4b: Details of the geometrical parameters for π···π interactions

	π···π	*d*/Å	D_1/Å	D_2/Å	symmetry
55	Cg1···Cg2	3.7628(7)	3.3114(5)	-3.4164(5)	-x,-$^{1}/_{2}$+y,$^{1}/_{2}$-z
	Cg1···Cg2	3.7463(7)	-3.3429(5)	3.4027(5)	-x,$^{1}/_{2}$+y,$^{1}/_{2}$-z

Where, D_1 = Perpendicular distance of Cg1 on ring containing Cg2, D2 = Perpendicular distance of Cg2 on ring containing Cg1.

57

This compound crystallizes in the monoclinic $P2_1/c$ space group. There are two molecules in the asymmetric unit. One of the molecules of the asymmetric unit has been found to be disordered due to rotation of the phenyl ring along C–C bond. But, for the structural description only one part of the molecule has been considered. In One of the molecule of the asymmetric unit, weak C–H···F hydrogen bonds (involving H22 with F7 in figure S5a and involving H16 with F7 in figure S5b) leads to the formation of dimers with the molecules, which is related with center of inversion symmetry. Further, these dimers propagates in the lattice through highly short (2.46 Å) C–H···F hydrogen bonds (involving H20 with F8) by the utilization of 2_1 screw axis (table S5, figure S5a and S5b).A dimer involving highly stabilizing C–H···F hydrogen bond (-3.67 kcal/mol) has also been found between one of the molecule of asymmetric unit involving imine H with the one of the *m*-F on the aniline ring (table S5, figure S5c). Molecular layers have been found to form by both the molecules of the asymmetric unit in which *para*-H of one of molecule interacts with *para*-F of the other molecule and vice-versa as shown in figure S5d. These layers consist of the highly short and directional C–H···F hydrogen bonds (2.44 Å and 151^{0}) involving H11 with F5 and bifurcated C–H···F hydrogen bonds involving H24 with F1B, which also interconnects these molecular layers (table S5, figure S5d).

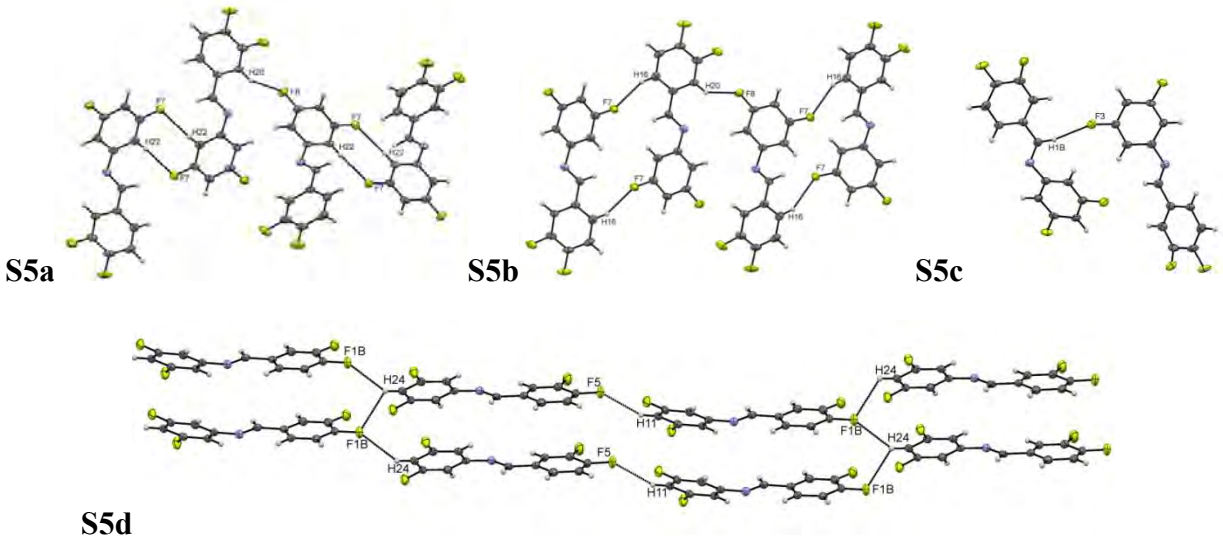


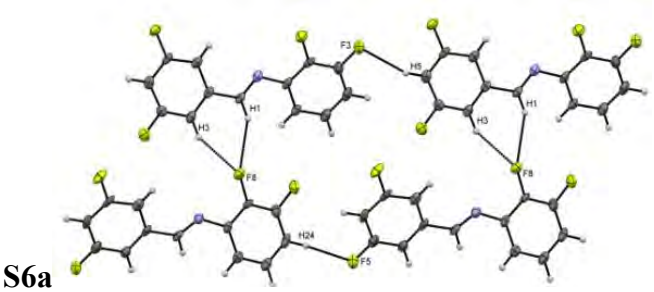
Figure S5: (a) Molecular dimer formation and their propagation through C–H···F hydrogen bonds, **(b)** C–H···F hydrogen bondsbetween the inversion center symmetry related molecules, **(c)** very short and highly directional C–H···F hydrogen bond in the crystal structure of compound **57**. **(d)** Molecular layer formation and their interconnection through C–H···F hydrogen bonds.

Table S5: Details of the geometrical parameters for all the C–H···F hydrogen bonds, the values of electron densities and Laplacians at their BCPs

Code	C–H···F	*d* (H···F/Å)	θ (∠C–H···F/°)	Symmetry Code	SE_{G09} kcal/mol	ρ (e Å^{-3})	$\nabla^2\rho$ (e Å^{-5})
57	C22–H22···F7	2.52	169	-x+1,-y+2,-z	-4.2	0.04	0.70
	C16–H16···F7	2.70	153	-x+1,-y+1,-z	-3.3	0.03	0.58
	C20–H20···F8	2.46	139	$-x+1,y+^{1}/_{2},-z+^{1}/_{2}$	-3.4	0.06	1.01
	C1–H1···F3	2.45	164	$-x,y+^{1}/_{2},-z+^{1}/_{2}$	-3.7	0.05	0.92
	C11–H11···F5	2.45	151	$-x+1,y+^{1}/_{2},-z+^{1}/_{2}$	-1.3	0.06	1.04
	C24–H24···F1B	2.66	125	$-x,y+^{1}/_{2},-z+^{1}/_{2}$	-1.4	0.03	0.62

58:

This compound crystallizes in the monoclinic *Pc* space group with $Z' = 2$. The two molecules of the asymmetric unit have been found to interact through highly stabilizing C–H···F hydrogen bond involving H1 (imine proton) and H3 with F8 (present at *ortho*-position of the aniline ring). These dimers further propagate in the crystal lattice again through the involvement of C–H···F hydrogen bond (table S6, figure S6a). Moreover, a complex network of molecules have also been found to form in this structure by the involvement of different kind of C–H···F hydrogen bonds (table S6, figure S6b).



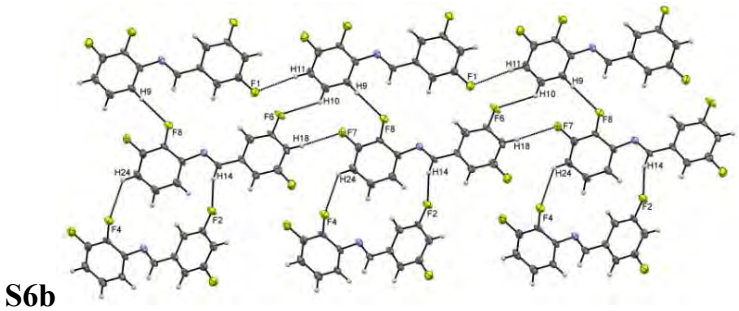


Figure S6: (a) Formation of dimers between two molecules of the asymmetric units and their interconnection throughC–H···F hydrogen bonds, **(b)** a complex network formation by molecules of compound 58 in their crystal lattice *via* C–H···F hydrogen bonds.

Table S6: Details of the geometrical parameters for all the C–H···F hydrogen bonds, the values of electron densities and Laplacians at their BCPs

Code	C–H···F	*d* (H···F/Å)	θ (∠C–H···F/°)	Symmetry Code	SE_{G09} kcal/mol	ρ (e Å^{-3})	$\nabla^2\rho$ (e Å^{-5})
58	C1–H1···F8	2.63	145	x,-y+2,z+$^1/_2$	-4.0	0.03	0.59
	C3–H3···F8	2.44	153	x-1,-y+2,z-$^1/_2$		0.04	0.86
	C5–H5···F3	2.70	136	x-1,y,z	-0.9	0.03	0.54
	C24–H24···F5	2.51	135	x+1,+y,+z	-1.2	0.04	0.83
	C24–H24···F4	2.67	125	x+1,+y,+z	-4.4	0.03	0.60
	C14–H14···F2	2.49	157	x+1,+y,+z		0.04	0.79
	C11–H11···F1	2.65	172	x+1,+y-1,+z	-1.0	0.03	0.57
	C10–H10···F6	2.67	130	x,-y,+z-$^1/_2$	-1.0	0.03	0.59
	C18–H18···F7	2.59	165	x-1,+y-1,+z	-1.1	0.03	0.64
	C9–H9···F8	2.63	171	x,1-y, $^1/_2$+z	-3.8	0.03	0.60

59:

This structure is solved in the monoclinic *C2/c* space group with *Z′* = 2. If one of the molecule of asymmetric unit is denoted A and other by B, then ….ABABAB…. linear chains have been found along *a* and *c* axis through C–H···F hydrogen bond (involving H18 with F1 and H25 with F3 along *a*-axis and by involving H14 with F4 and H1 with F8 along *b*-axis) (table S7a, figure S7a). Molecule related by either center of inversion (H10 with F3) or by 2 fold symmetry (H5 with F2) and are part of two different chains are involved in the formation

of homo dimers *via* C–H···F hydrogen bonds (table S7a, figure S7a). Due to these interactions, a sheet has been found to form in the *ac* plane. Then these sheets are found to be stacked by π···π interactions on viewing down the *b*-axis, this stacking is further assisted by C–H···F hydrogen bonds (involving H23 with F5 and H12 with F2) (table S7a, figure S7b).

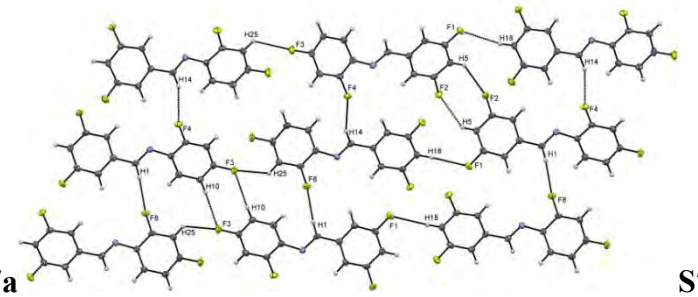
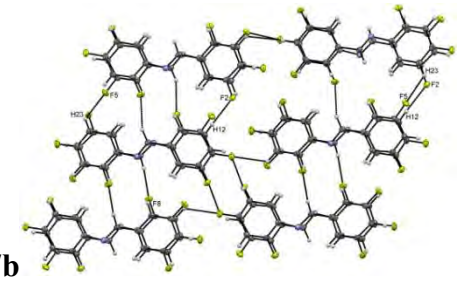
S7a  **S7b** 

Figure S7: (a) Formation of sheet kind of structure in the *ac* plane by the utilization of weak C–H···F hydrogen bonds, **(b)** stacking of sheets *via* π···π interactions.

Table S7a: Details of the geometrical parameters for all C–H···F hydrogen bonds, the values of electron densities and Laplacians at their BCPs.

Code	C–H···F	*d* (H···F/Å)	θ (∠C–H···F/°)	Symmetry Code	SE_{G09} kcal/mol	ρ (e Å^{-3})	$\nabla^2\rho$ (e Å^{-5})
59	C1–H1···F8	2.40	173	$-x+^1/_2,-y+^1/_2,-z$	-3.5	0.05	0.90
	C14–H14···F4	2.42	159	$-x+^1/_2,y+^1/_2,-z+^1/_2$	-4.4	0.05	0.91
	C10–H10···F3	2.53	147	-x,-y+1,-z	-2.0	0.04	0.77
	C5–H5···F2	2.56	138	$-x+1,y,-z+^1/_2$	-1.6	0.03	0.69
	C18–H18···F1	2.68	156	$x-^1/_2,y-^1/_2,+z$	-1.0	0.03	0.53
	C25–H25···F3	2.63	125	$x+^1/_2,y-^1/_2,z$	-1.2	0.03	0.64
	C23–H23···F5	2.49	128	$-x+^1/_2,y-^1/_2,-z+^1/_2$	-1.3	0.04	0.82
	C12–H12···F2	2.42	177	$-x+^1/_2,y+^1/_2,-z+^1/_2$	-1.5	0.05	0.90

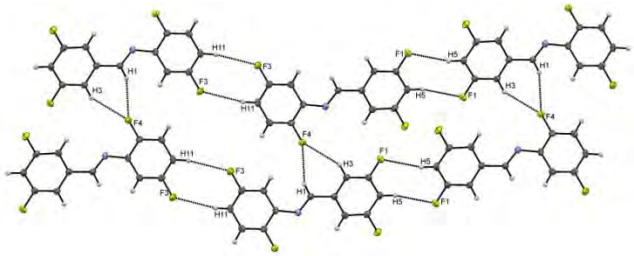
Table S7b: Details of the geometrical parameters for π···π interactions

Code	π···π	*d*/Å	D_1/Å	D_2/Å	symmetry
59	Cg1···Cg4	3.6732(9)	3.5030(6)	-3.4635(6)	x,-1+y,z
	Cg2···Cg3	3.6797(9)	3.4822(6)	-3.3913(6)	x,-1+y,z

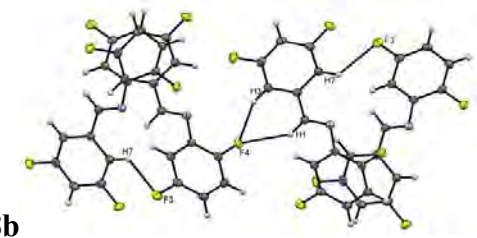
Where, D_1 = Perpendicular distance of Cg1 on ring containing Cg4, D2 = Perpendicular distance of Cg2 on ring containing Cg3.

60:

This compound has been crystallized in the monoclinic $P2_1/c$ space group. Molecules related by center of symmetry are forming head to head and tail to tail dimers by C–H···F hydrogen bonds (involving H5 with F1 and H11 with F3) (table S8a, figure S8a), which is extending in the lattice in form of layers. Further, these layers are interconnected through short and highly stabilizing bifurcated C–H···F hydrogen bonds (involving H3 and H1 with F4) (table S8a, figure S8a). Due to these interactions, on viewing down the *a*-axis, a sheet kind of structure has been found to be formed. Then stacking of these sheets occurs by the utilization of weak π···π interactions (table S8b, figure S8b), which are further assisted by C–H···F hydrogen bonds (involving H7 with F3) (table S8a, figure S8b).



S8a



S8b

Figure S8: (a) Formation of sheet like structure through C–H···F hydrogen bonds, **(b)** stacking of sheets by π···π interactions.

Table S8a: Details of the geometrical parameters for all the C–H···F hydrogen bonds, the values of electron densities and Laplacians at their BCPs

Code	C–H···F	*d* (H···F/Å)	θ (∠C–H···F/°)	Symmetry Code	SE_{G09} kcal/mol	ρ (e Å^{-3})	$\nabla^2\rho$ (e Å^{-5})
60	C1–H1···F4	2.40	173	$-x+1/2,-y+1/2,-z$	-4.4	0.04	0.71
	C3–H3···F4	2.53	147	-x,-y+1,-z		0.03	0.58
	C5–H5···F1	2.56	138	$-x+1,y,-z+1/2$	-1.3	0.04	0.75
	C11–H11···F3	2.42	159	$-x+1/2,y+1/2,-z+1/2$	-2.0	0.03	0.54
	C7–H7···F3	2.72	146	$-x+1/2,y+1/2,-z+1/2$	-7.7	0.03	0.60

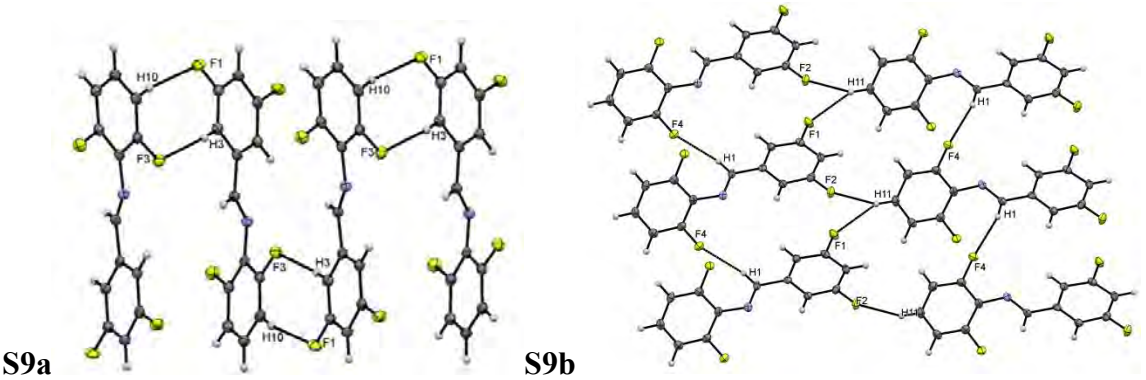
Table S8b: Details of the geometrical parameters for π···π interactions

Code	π···π	*d*/Å	D_1/Å	D_2/Å	symmetry
60	Cg1···Cg2	3.8841(7)	-3.3694(5)	-3.3630(5)	$-x, 1/2+y, 1/2-z$
	Cg1···Cg2	3.7339(7)	3.2952(5)	3.4274(5)	$1-x, 1/2+y, 1/2-z$

Where, D_1 = Perpendicular distance of Cg1 on ring containing Cg2, D2 = Perpendicular distance of Cg2 on ring containing Cg1.

61:

The structure of the compound **61** with $P2_12_12_1$space group has been found to have head to tail dimers through C–H···F hydrogen bonds (table S9, figure S9a). The molecules which are involved in such kind of dimers are related to each other 2_1 screw along *b*-axis. Furthermore, *ortho*-F of the aniline has also been involved in the formation of C–H···F hydrogen bonds with imine H along *a*-axis and thus resulting into the formation of chains (table S9, figure S9b). These chains have been found to interact through bifurcated C–H···F hydrogen bonds by involving H11 with F1 and F2 (table S9, figure S9b).



S9a **S9b**

Figure S9: (a) Formation of head to tail dimers through C–H···F hydrogen bonds, **(b)** chain formation through highly directional C–H···F hydrogen bond and their interconnection through bifurcated C–H···F hydrogen bonds.

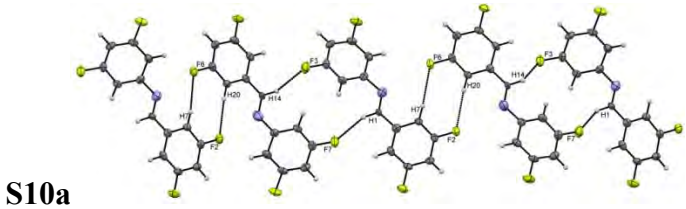
Table S9: Details of the geometrical parameters for all the C–H···F hydrogen bonds, the values of electron densities and Laplacians at their BCPs

Code	C–H···F	*d* (H···F/Å)	θ (∠C–H···F/°)	Symmetry Code	SE_{G09} kcal/mol	ρ (e Å^{-3})	$\nabla^2\rho$ (e Å^{-5})
61	C1–H1···F4	2.53	166	x-1,+y,+z	-5.0	0.04	0.70
	C3–H3···F3	2.47	169	-x,+y+$^1/_2$,-z+$^1/_2$	-2.5	0.04	0.83
	C10–H10···F1	2.65	168	-x,+y-$^1/_2$,-z+$^1/_2$		0.03	0.57
	C11–H11···F1	2.56	141	-x+$^1/_2$,-y+1,z-$^1/_2$	-0.8	0.04	0.74
	C11–H11···F2	2.59	150	-x+$^3/_2$,-y+1,z-$^1/_2$	-1.0	0.04	0.68
	C12–H12···F2	2.56	173	-x+2,y+$^1/_2$,-z+$^1/_2$	-1.8	0.05	0.90

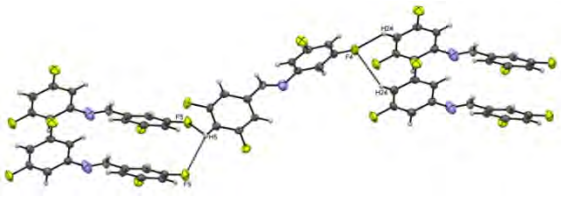
63:

The structure of the compound **63** has been solved in the orthorhombic $Pca2_1$ space group. The structure involves the formation of a dimer between the two molecules of the asymmetric unit with the stabilization energy of ~2kcal/mol (table S10, figure S10a). Then, the

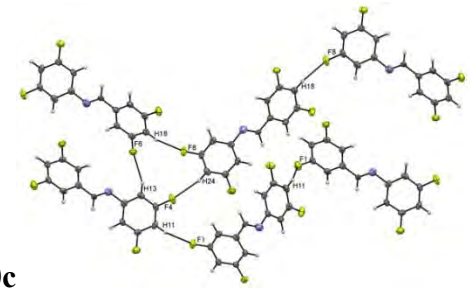
imine hydrogen interacts with the *meta*-F of the B ring along *b*-axis and thus results in propagation of these dimers (table S10, figure S10a). Furthermore, in the crystal packing of this compound, bifurcated C–H···F hydrogen bonds have been found between the molecules related by 2_1 screw axis as shown in figure S10b. Zigzag chains *via* C–H···F hydrogen bonds have also been found to form by involving H18 with F8 in one of molecule of asymmetric unit and H11 with F1 in the other (table S10, figure S10c). The molecules interacting through these interactions have stabilization energy of about 1 kcal/mol. C–H···F hydrogen bonds involving H13 with F6 and H24 with F4 have also been found to interconnect those zigzag chains (table S10, figure S10c).



S10a



S10b



S10c

Figure S10: (a) Dimer formation through C–H···F hydrogen bonds, **(b)** bifurcated C–H···F hydrogen bonds in the crystal lattice of 63, **(c)** C–H···F hydrogen, which leads to the formation of zigzag chain and their interconnection through a trimer formation.

Table S10: Details of the geometrical parameters for all the C–H···F hydrogen bonds, the values of electron densities and Laplacians at their BCPs

Code	C–H···F	*d* (H···F/Å)	θ (∠C–H···F/°)	Symmetry Code	SE_{G09} kcal/mol	ρ (e Å^{-3})	$\nabla^2\rho$ (e Å^{-5})
63	C20–H20···F2	2.50	175	x-$^1/_2$,-y,+z	-2.0	0.03	0.68
	C7–H7···F6	2.57	168	x+$^1/_2$,-y,+z		0.04	0.78
	C1–H1···F7	2.61	139	x,+y+1,+z	-4.5	0.03	0.65
	C14–H14···F3	2.66	125	x,+y-1,+z		0.03	0.64
	C18–H18···F8	2.43	148	-x+$^1/_2$,y-1,z+$^1/_2$	-1.0	0.05	0.88
	C13–H13···F6	2.57	149	x+$^1/_2$,-y+1,+z	-3.0	0.03	0.68
	C11–H11···F1	2.51	150	1-x,2-y, $^1/_2$+z	-1.5	0.04	0.76
	C5–H5···F5	2.51	121	-x+1,-y+1,z-$^1/_2$	-2.3	0.04	0.87
	C5–H5··F5	2.64	148	-x+1,-y,+z-$^1/_2$	-1.9	0.03	0.59
	C24–H24···F4	2.70	126	-x+1,-y+1,+z-$^1/_2$	-1.8	0.03	0.58
	C24–H24···F4	2.55	143	-x+1,-y+2,z-$^1/_2$	-2.0	0.03	0.67

64:

This compound has been found to crystallize in the triclinic $P\bar{1}$ space group with Z' =1. The molecules of the asymmetric unit are involved in the formation of homo dimers as well as head to tail dimers *via* C–H···F hydrogen (table S11, figure S11a and S11b). Moreover, molecular chains involving head to tail dimers further interconnects among themselves by the involvement of imine H with the *ortho*-F of the benzaldehyde ring (table S11, figure S11b).

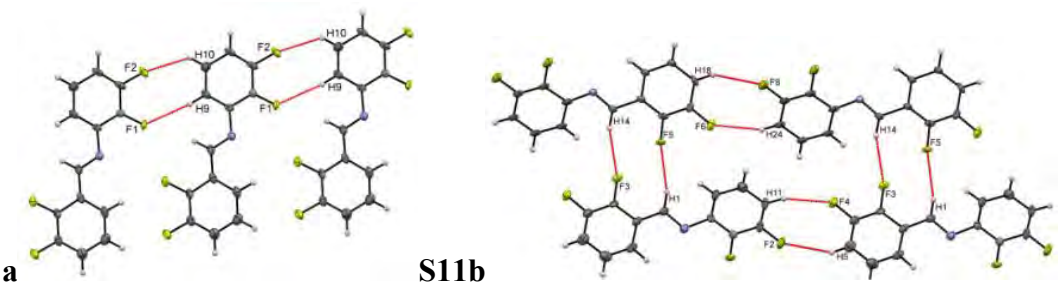


Figure S11: (a) Formation of homo dimers through C–H···F hydrogen bond in 1st and 2nd molecule of the asymmetric unit respectively; **(b)** sheet formation through C–H···F hydrogen bonds in the structure of 64.

Table S11: Details of the geometrical parameters for all the C–H···F hydrogen bonds, the values of electron densities and Laplacians at their BCPs

Code	C–H···F	*d* (H···F/Å)	θ (∠C–H···F/°)	Symmetry Code	SE_{G09} kcal/mol	ρ (e Å^{-3})	$\nabla^2\rho$ (e Å^{-5})
64	C10–H10···F4	2.48	134	x-1,y,z	-4.2	0.04	0.82
	C9–H9···F3	2.58	172	x-1,y,z		0.03	0.65
	C5–H5···F4	2.68	150	x-1,+y+1,z-1	-2.1	0.03	0.53
	C11–H11···F2	2.47	160	x+1,+y-1,z+1		0.04	0.79
	C1–H1···F1	2.53	150	x-1,y,z	-1.6	0.04	0.70
	C1–H1···F1	2.53	150	x+1,y,z		0.04	0.74

65:

This compound got crystallized in the monoclinic $P2_1$ space group with Z = 2. Molecules have been found to form chains through C–H···F hydrogen bonds (table S12, figure S12). Molecules related by 2_1 screw along *b*-axis are interacting through another C–H···F hydrogen bonds involving H9 with F2 and thus results in propagation of these chains in the lattice (table S12, figure S12).

S12:

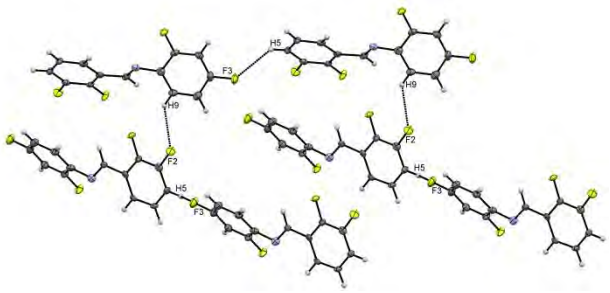


Figure S12: Formation of chains and their propagation in the crystal lattice of 54 through C–H···F hydrogen bonds.

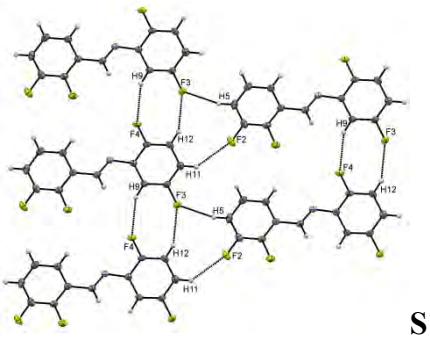
Table S12: Details of the geometrical parameters for all the C–H···F hydrogen bonds, the values of electron densities and Laplacians at their BCPs

Code	C–H···F	*d* (H···F/Å)	θ (∠C–H···F/°)	Symmetry Code	SE_{G09} kcal/mol	ρ (e Å^{-3})	$\nabla^2\rho$ (e Å^{-5})
65	C5–H5···F3	2.59	138	x,y+1,z-1	-0.7	0.03	0.67
	C9–H9···F2	2.52	131	-1+x, $^1/_2$+y,-3-z	-4.1	0.04	0.82

66:

This compound crystallizes in $P\bar{1}$ space group. Molecules have been found to form head to tails dimers *via* C–H···F hydrogen bonds along *a*-axis (table S13, figure S13a). These dimeric layers are again interacting through C–H···F hydrogen bonds, thus resulting in the formation of ladder type structure (table S13a, figure S13a). These ladders are further found to be stacked through weak π···π interactions, which is also assisted by highly short and directional C–H···F hydrogen bonds involving imine hydrogen with the *ortho*-fluorine of the A ring (table S13b, figure S13b).

S13a



S13b

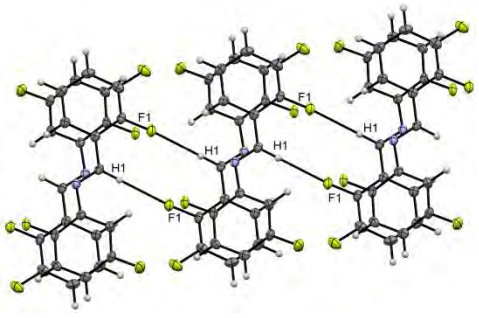


Figure S13: (a) Formation of ladder type structure through C–H···F hydrogen bonds, **(b)** stacking of ladders through π···π interactions, which are further aided by C–H···F hydrogen bonds.

Table S13: Details of the geometrical parameters for all the C–H···F hydrogen bonds, the values of electron densities and Laplacians at their BCPs

Code	C–H···F	*d* (H···F/Å)	θ (∠C–H···F/°)	Symmetry Code	SE_{G09} kcal/mol	ρ (e Å^{-3})	$\nabla^2\rho$ (e Å^{-5})
66	C1–H1···F1	2.54	162	-x+2,-y+2,-z+1	-3.6	0.04	0.68
	C5–H5···F3	2.44	151	x,+y-1,z+1	-0.8	0.03	0.67
	C12–H12···F3	2.45	153	x-1,y,+z	-3.8	0.04	0.84
	C9–H9···F4	2.44	154	x+1,y,+z		0.04	0.86
	C11–H11···F2	2.61	140	x-1,y+1,+z-1	-1.1	0.03	0.60

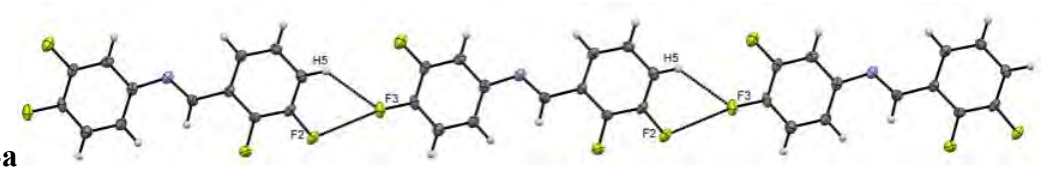
Table S13b: Details of the geometrical parameters for π···π interactions

Code	π···π	*d*/Å	D_1/Å	D_2/Å	slippage	symmetry
66	Cg1···Cg1	3.8784(11)	3.4125(6)	3.4124(6)	1.843	-x,1-y,1-z
	Cg1···Cg2	3.7906(11)	-3.3778(6)	-3.6584(6)	--	1-x,-y,1-z
	Cg2···Cg2	3.8025(11)	3.3491(6)	3.3492(6)	1.801	1-x,-y,2-z

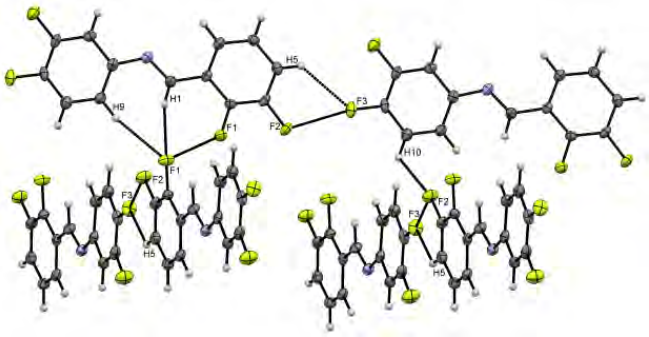
Where, D_1 = Perpendicular distance of Cg1/Cg2 on ring containing Cg1/Cg2, D2 = Perpendicular distance of Cg2/Cg1 on ring containing Cg2/Cg1.

68:

This compound crystallizes in the monoclinic $P2_1$ space group. Molecules in the crystal lattice have been found to form linear chains through type I C–F···F–C interactions and C–H···F hydrogen bonds involving H5 with F3 (table S14, figure S14a). Additionally, in the crystal lattice of this compound, it has been seen that in an interaction which occurs between the molecules related by 2_1 screw axis fluorine is trifurcated. This fluorine forms two hydrogen bonds with H1 and H9 and along with that it is also involved in type I C–F···F–C interactions (table S14, figure S14b). These interactions result in the interconnection of molecular chains. Furthermore, another C–H···F hydrogen bond has also been found between the screw axis related molecules, which involves an interaction of H10 with F2 (table S14, figure S14b)



S14a



S14b

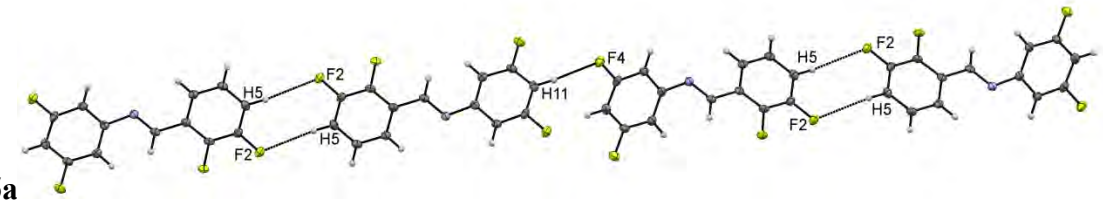
Figure S14: (a) Formation of linear chains through C–H···F hydrogen bonds C–F···F–C interactions, **(b)** propagation of the chains formed in the crystal lattice through C–H···F hydrogen bonds by the screw axis related molecules.

Table S14: Details of the geometrical parameters for all the C–H···F hydrogen bonds, the values of electron densities and Laplacians at their BCPs

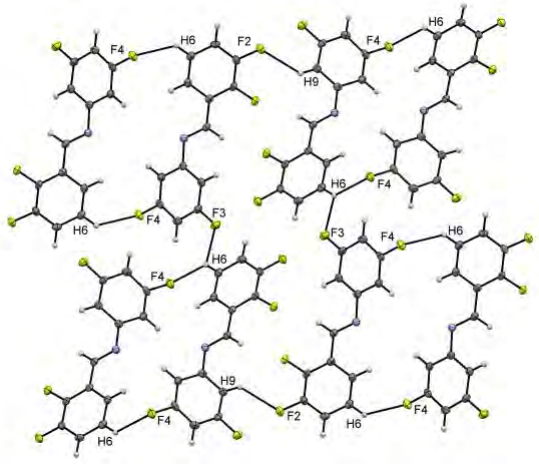
Code	C–H···F	*d* (H···F/Å)	θ (∠C–H···F/°)	Symmetry Code	SE_{G09} kcal/mol	ρ (e Å^{-3})	$\nabla^2\rho$ (e Å^{-5})
68	C5–H5···F3	2.55	134	x-1,y+2,+z	-1.3	0.04	0.71
	C1–H1···F1	2.55	160	-x+1,y-1/2,-z+2	-3.0	0.03	0.68
	C9–H9···F1	2.65	153	-x+1,y-1/2,-z+2		0.03	0.57
	C10–H10···F2	2.68	123	-x+1,y-3/2,-z+2	-1.1	0.04	0.54

69:

This compound crystallizes in the monoclinic $P2_1/c$ space group. Across, the center of inversion, molecular dimers have been found to form involving H5 with F2 and H6 with F4 (table S15, figure S15a and S15b). Further, these dimers propagates in the lattice by the utilization of 2_1 screw axis involving H11 with F4 in figure S15a and involving H9 with F2 and H6 with F3 in figure S15b.



S15a



S15b

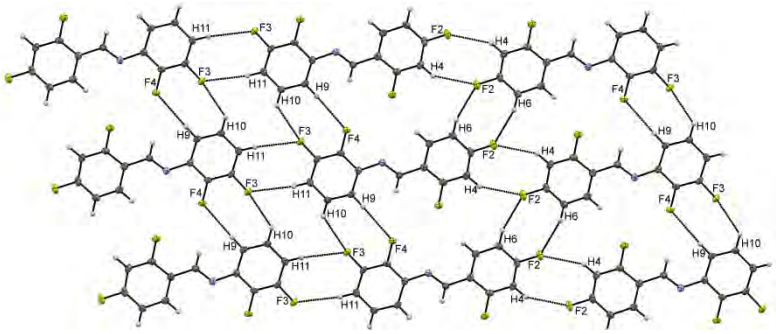
Figure S15: (a) Molecular layer formation and their propagation through C–H···F hydrogen bonds, **(b)** C–H···F hydrogen bonds, leading to the formation of molecular network.

Table S15: Details of the geometrical parameters for all the C–H···F hydrogen bonds, the values of electron densities and Laplacians at their BCPs

Code	C–H···F	*d* (H···F/Å)	θ (∠C–H···F/°)	Symmetry Code	SE_{G09} kcal/mol	ρ (e Å^{-3})	$\nabla^2\rho$ (e Å^{-5})
69	C11–H11···F4	2.68	144	$-x+\frac{5}{2},y+\frac{1}{2},-z+\frac{1}{2}$	-1.1	0.03	0.55
	C6–H6···F3	2.64	125	$x-\frac{1}{2},-y+\frac{3}{2},z-\frac{1}{2}$	-1.3	0.05	0.51
	C6–H6···F4	2.56	133	-x+2,-y+1,-z	-3.6	0.04	0.76
	C5–H5···F2	2.69	161	-x+1,-y+1,-z	-1.9	0.04	0.66
	C9–H9···F2	2.63	136	$-x+\frac{3}{2},y+\frac{1}{2},-z+\frac{1}{2}$	-3.7	0.03	0.62

70:

This structure has been found to crystallize in the triclinic $P\bar{1}$ space group. Both the phenyl rings are inclined at angle of 8.6°. Molecular sheet has been found to form in the crystal structure of **70** through the various kinds of molecular dimers through C–H···F hydrogen bonds (table S16, figure S16).



S16

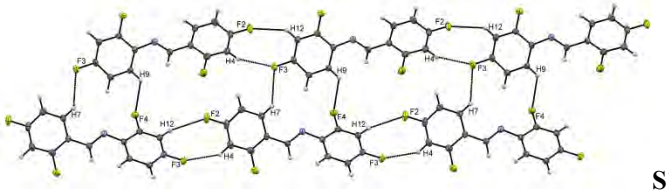
Figure S16: (a) Molecular sheet formation through C–H···F hydrogen bonds.

Table S16: Details of the geometrical parameters for all the C–H···F hydrogen bonds, the values of electron densities and Laplacians at their BCPs

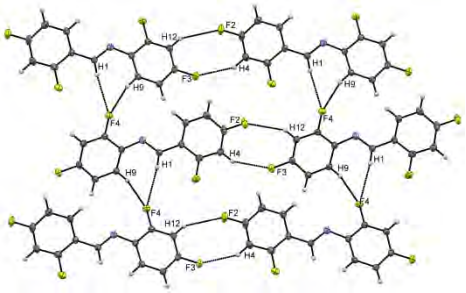
Code	C–H···F	*d* (H···F/Å)	θ (∠C–H···F/°)	Symmetry Code	SE_{G09} kcal/mol	ρ (e Å^{-3})	$\nabla^2\rho$ (e Å^{-5})
70	C11–H11···F3	2.63	160	-x,-y,-z+2	-2.3	0.03	0.59
	C10–H10···F3	2.49	127	x+1,y,z	-3.2	0.04	0.84
	C9–H9···F4	2.61	166	x+1,y,z		0.03	0.62
	C4–H4···F2	2.52	151	1-x,-1-y,1-z	-1.9	0.04	0.73
	C6–H6···F2	2.64	132	2-x,-1-y,1-z	-1.6	0.03	0.62

71:

The structure was solved in the monoclinic $P2_1$ space group. Head to tail dimers have been found to form through C–H···F hydrogen bonds involving H12 with F2 and H4 with F3 along *a*-axis (table S17, figure S17a). The layers formed further got interconnected by the molecules related by 2_1 screw axis *via* C–H···F hydrogen bonds (table S17, figure S17b).



S17a



S17b

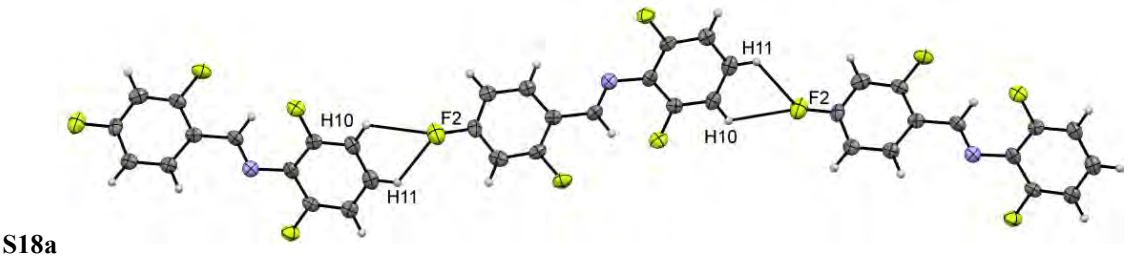
Figure S17: (a) Molecular dimer formation through and their propagation along *a*-axis through C–H···F hydrogen bonds, **(b)** Molecules related by the center of inversion symmetry were found to interact *via* C–H···F hydrogen bonds and thus the layers get propagated in the lattice.

Table S17: Details of the geometrical parameters for all the C–H···F hydrogen bonds, the values of electron densities and Laplacians at their BCPs

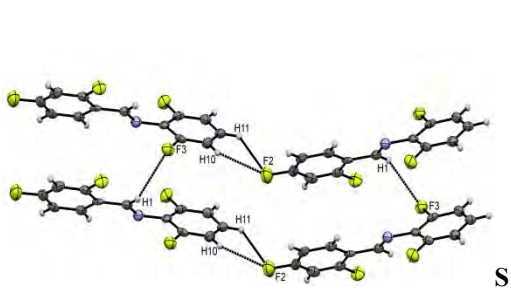
Code	C–H···F	*d* (H···F/Å)	θ (∠C–H···F/°)	Symmetry Code	SE_{G09} kcal/mol	ρ (e Å^{-3})	$\nabla^2\rho$ (e Å^{-5})
71	C1–H1···F4	2.66	173	-x+1,y-$^1/_2$,-z	-4.1	0.03	0.53
	C9–H9···F4	2.54	122	-x+1,y-$^1/_2$,-z		0.04	0.80
	C4–H4···F3	2.47	146	x-1,y,z+1	-1.7	0.04	0.82
	C12–H12···F2	2.67	131	x+1,y,z-1		0.03	0.56
	C7–H7···F3	2.68	134	-x+2,y+1/2,-z	-4.1	0.03	0.59
	C9–H9···F4	2.69	122	-x+2,y-1/2,-z		0.03	0.61

73:

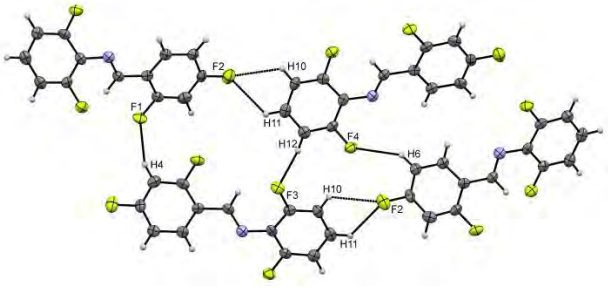
This compound crystallizes in the orthorhombic non-centrosymmetric $P2_12_12_1$ space group. By the utilization of 2_1 screw along *c*-axis, zigzag molecular chains have been found to form *via* C–H···F hydrogen bonds (table S18, figure S18a) involving H10 and H11 with F2. Then these chains were found to propagate in the lattice through C–H···F hydrogen bonds across the center of inversion or by the utilization of 2_1 screw axis (table S18, figure S18b and S18c).



S18a



S18b



S18c

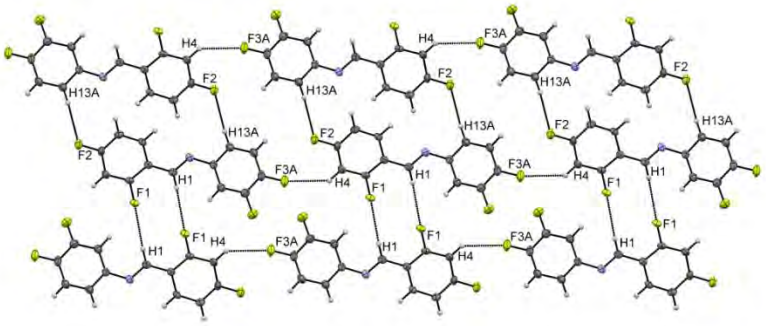
Figure S18: (a) Molecular chains, which are formed through bifurcated C–H···F hydrogen bonds, and their propagation through C–H···F hydrogen bonds, **(b)** C–H···F hydrogen bonds, interconnects the chains formed, **(c)** C–H···F hydrogen bonds, propagates the chains formed in the lattice.

Table S18: Details of the geometrical parameters for all the C–H···F hydrogen bonds, the values of electron densities and Laplacians at their BCPs

Code	C–H···F	*d* (H···F/Å)	θ (∠C–H···F/°)	Symmetry Code	SE_{G09} kcal/mol	ρ (e Å^{-3})	$\nabla^2\rho$ (e Å^{-5})
73	C4–H4···F1	2.62	149	x-$^1/_2$,-y+$^1/_2$,-z+1	-1.9	0.03	0.63
	C1–H1···F3	2.53	133	x-1,y,+z	-9.6	0.04	0.82
	C11–H11···F2	2.69	121	-x+$^3/_2$,-y+1,z+$^1/_2$	-1.2	0.03	0.62
	C10–H10···F2	2.64	123	-x+$^3/_2$,-y+1,z+$^1/_2$		0.03	0.64
	C12–H12···F3	2.61	149	-x+1,y+$^1/_2$,-z+$^3/_2$	-2.0	0.03	0.66
	C6–H6···F4	2.62	140	x+$^1/_2$,-y+$^3/_2$,-z+1	-3.6	0.03	0.61

74:

This compound crystallizes in the triclinic $P\bar{1}$ space group. Positional disorder in the A ring has been observed about the C–N bond. The molecules were found to form linear chains through C–H···F hydrogen bonds involving H4 with F3A. These chains have been further found to interconnect by C–H···F hydrogen bonds with the molecules, which are related by center of inversion involving H13A with F2 and H1 with F1 (table S19, figure S19). The disordered F atoms did not participate in any intermolecular interactions.



S19

Figure S19: (a) Formation of molecular sheets through C–H···F hydrogen bonds.

Table S19: Details of the geometrical parameters for all the C–H···F hydrogen bonds, the values of electron densities and Laplacians at their BCPs

Code	C–D···F (D = H, F)	*d* (D···F/Å)	θ (∠C–D···F/°)	Symmetry Code	SE_{G09} kcal/mol	ρ (e Å^{-3})	$\nabla^2\rho$ (e Å^{-5})
74	C1–H1···F1	2.66	172	-x+1,-y,-z+1	-3.9	0.02	0.48
	C9–H9···F1	2.76	134	-x+1,-y,-z+1		0.02	0.46
	C4–H4···F3A	2.53	139	x+1,y,z-1	-1.5	0.03	0.67
	C13A–H13A···F2	2.63	166	-x+1,-y+1,-z+1	-4.1	0.03	0.56

75:

The compound crystallizes in the non-centrosymmetric orthorhombic $P2_12_12_1$ space group, involves the formation of highly stabilizing dimer *via* C–H···F hydrogen bonds (H1 with F1 and H9 with F1) (table S20, figure S20). This dimer has also been seen in the system of dihalo (F, F; F, Br; F, Cl) substituted *N*-benzylideneanilines. Then, a complex molecular network formation have been seen in the crystal lattice of this compound by the propagation of these dimers through C–H···F hydrogen bonds by the utilization of 2_1 screw along *b*- and *c*-axis, which involves the interaction of H6 with F2 and F4 as well as H13 with F3 (table S20, figure S20).

S20

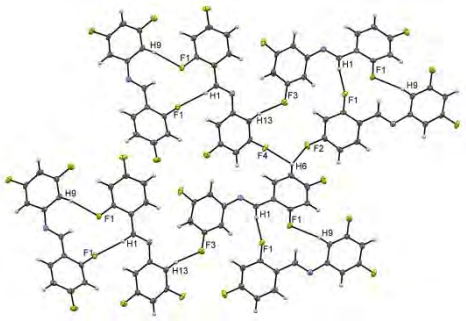


Figure S20: (a) Molecular dimers through the formation of robust synthon involving H1 and H9 with F1 and their interconnection through C–H···F hydrogen bonds.

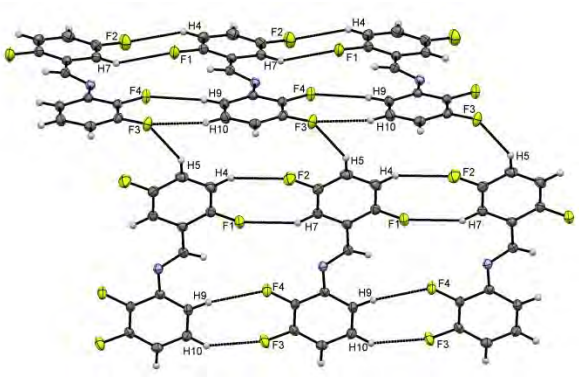
Table S20: Details of the geometrical parameters for all the C–H···F hydrogen bonds, the values of electron densities and Laplacians at their BCPs

Code	C–D···F (D = H, F)	*d* (D···F/Å)	θ (∠C–D···F/^{o})	Symmetry Code	SE_{G09} kcal/mol	ρ (e Å^{-3})	$\nabla^2\rho$ (e Å^{-5})
75	C9–H9···F1	2.51	169	x-$^1/_2$,-y+$^3/_2$,-z	-3.9	0.04	0.78
	C1–H1···F1	2.71	162	x+$^1/_2$,-y+$^3/_2$,-z		0.02	0.48
	C6–H6···F2	2.59	147	x-$^1/_2$,-y+$^5/_2$,-z	-1.6	0.03	0.67
	C6–H6···F4	2.69	128	-x,y+$^1/_2$,-z+$^1/_2$	-2.5	0.03	0.58
	C13–H13···F3	2.60	155	-x+1,y+$^1/_2$,-z+$^1/_2$	-2.6	0.03	0.66

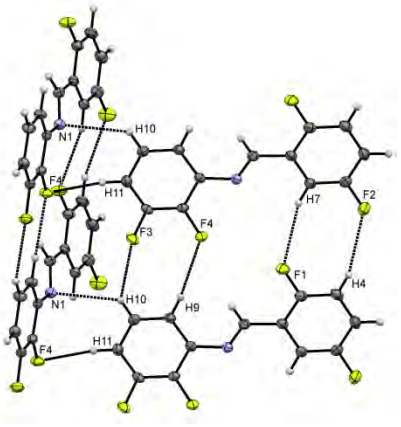
76:

The structure which was solved in the monoclinic $P2_1/c$ space group, has been found to form head to tail dimers by the involvement of four C–H···F hydrogen bonds and thus leads to the formation of molecular layers along *a*-axis (table S21, figure S21a). Then, these layers further found to extend in the lattice by the utilization of 2_1 screw along *b*-axis by the involvement of C–H···F hydrogen bonds between H5 and F3 (table S21, figure S21a).

Moreover, dimers formed through C–H···N and C–H···F hydrogen bonds involving H11 with F4 and H10 with N1 interconnect the molecular layers along *ac* plane (table S21, figure S21b).



S21a



S21b

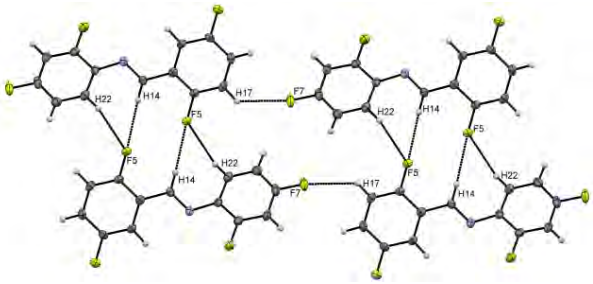
Figure S21: (a) Molecular layers formed through C–H···F hydrogen bonds, got interconnected through another C–H···F hydrogen bonds involving H5 with F3, **(b)** C–H···F and C–H···N hydrogen bonds, interconnect the layers formed along *ac* plane.

Table S21: Details of the geometrical parameters for all C–H···F hydrogen bonds, the values of electron densities and Laplacians at their BCPs.

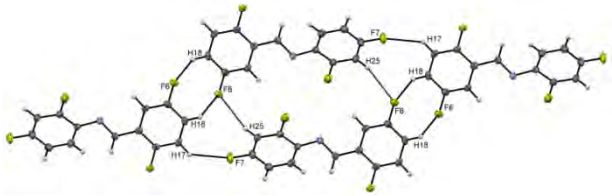
Code	C–H···F	*d* (H···F/Å)	θ (∠C–H···F/^{o})	Symmetry Code	SE_{G09} kcal/mol	ρ (e Å^{-3})	$\nabla^2\rho$ (e Å^{-5})
76	C4–H4···F2	2.63	155	x+1,+y,+z	-4.3	0.03	0.59
	C10–H10···F3	2.48	136	x+1,+y,+z		0.04	0.81
	C7–H7···F1	2.62	155	x-1,+y,+z		0.03	0.59
	C9–H9···F4	2.57	172	x+1,+y,+z		0.03	0.67
	C5–H5···F3	2.67	150	$-x+^{1}/_{2},y-^{1}/_{2},-z+^{1}/_{2}$	-2.6	0.03	0.56
	C11–H11···F1	2.75	133	$x-^{1}/_{2},-y+^{3}/_{2},z+^{1}/_{2}$	-1.8	0.02	0.50
	C11–H11···F4	2.50	145	$x+^{1}/_{2},-y+^{3}/_{2},z+^{1}/_{2}$	-3.6	0.04	0.84
	C10–H10···N1	2.70	130	$x+^{1}/_{2},-y+^{3}/_{2},z+^{1}/_{2}$		0.05	0.64

77:

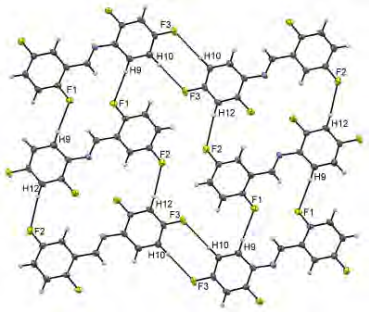
The compound got crystallized in the triclinic $P\bar{1}$ space group with $Z' = 2$. The structure was found to form highly stabilizing dimers across the center of inversion involving four C–H···F hydrogen bonds in its crystal lattice (table S22, figure S22a). These dimers have been found to be interconnected along *a*-axis through another C–H···F hydrogen bonds involving H17 with F7 (table S22, figure S22a). Moreover, a molecular network, which involves the formation of dimer and trimers through C–H···F hydrogen bonds has also been found in the crystal lattice of compound 77 (table S22, figure S22b and S22c).



S22a



S22b



S22c

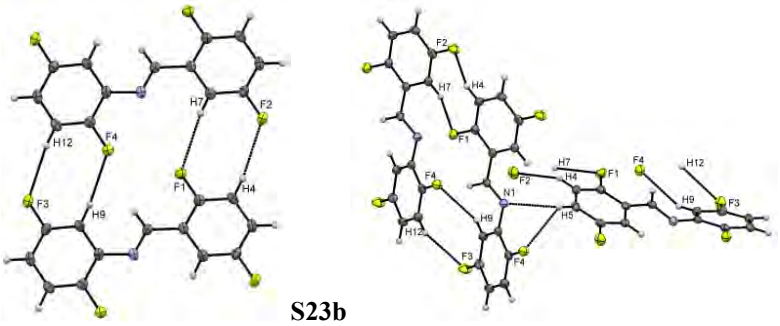
Figure **S22**: **(a)** Four C–H···F hydrogen bonds involving H1 and H9 with F1 leading to the formation of molecular dimer, which got interconnected linearly by C–H···F hydrogen bonds, **(b)** formation of dimers, trimers and tetramers *via* C–H···F hydrogen bonds, **(c)** dimers formed through C–H···F hydrogen bonds leads to the formation of ladder type structure in the crystal lattice of compound **77**.

Table S22: Details of the geometrical parameters for all the C–H···F hydrogen bonds, the values of electron densities and Laplacians at their BCPs

Code	C–H···F	*d* (H···F/Å)	θ (∠C–H···F/º)	Symmetry Code	SE_{G09} kcal/mol	ρ (e Å^{-3})	$\nabla^2\rho$ (e Å^{-5})
77	C17–H17···F7	2.61	131	x-1,y+1,+z	-1.4	0.03	0.63
	C18–H18···F6	2.53	133	-x,-y+2,-z+1	-2.1	0.04	0.77
	C25–H25···F6	2.58	146	-x+1,-y+1,-z+1	-2.3	0.03	0.68
	C22–H22···F5	2.58	134	-x,-y+1,-z+2	-2.8	0.04	0.72
	C14–H14···F5	2.45	167	-x,-y+1,-z+2		0.04	0.75
	C12–H12···F2	2.70	162	-x+1,-y+1,-z+2	-2.3	0.02	0.51
	C10–H10···F3	2.59	162	-x+1,-y+2,-z+1	-2.1	0.03	0.67
	C9–H9···F1	2.59	164	-x+2,-y+1,-z+1	-2.4	0.04	0.67

78:

This compound has been found to crystallize in the monoclinic $P2_1/c$ space group. Four C–H···F hydrogen bonds along *a*-axis lead to the formation of a highly stabilizing dimers (-4.21 kcal\mol) (table S23, figure S23a). Then by the utilization of 2_1 screw along *c*-axis, these dimers extend in the lattice *via* C–H···F and C–H···N hydrogen bonds (table S23, figure S23b).



S23a **S23b**

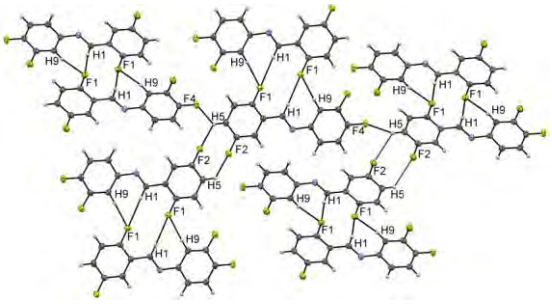
Figure S23: (a) Molecular dimer formation through C–H···F hydrogen bonds, **(b)** propagation of molecular dimers formed in figure 23a *via* C–H···F and C–H···N hydrogen bonds, where H is a bifurcated donor.

Table S23: Details of the geometrical parameters for all the C–H···F hydrogen bonds, the values of electron densities and Laplacians at their BCPs

Code	C–D···F (D = H, F)	*d* (D···F/Å)	θ (∠C–D···F/°)	Symmetry Code	SE_{G09} kcal/mol	ρ (e Å^{-3})	$\nabla^2\rho$ (e Å^{-5})
78	C12–H12···F3	2.59	155	x+1,y,z	-4.2	0.03	0.66
	C9–H9···F4	2.57	154	x-1,y,z		0.04	0.70
	C7–H7···F1	2.63	147	x+1,y,z		0.03	0.60
	C4–H4···F2	2.64	147	x-1,y,z		0.03	0.60
	C5–H5···F4	2.68	131	$x-^1/_2,-y+^1/_2,z+^1/_2$	-3.6	0.03	0.61

80:

This compound crystallizes in the monoclinic $P2_1/c$ space group. Highly stabilizing dimmers with the involvement of imine hydrogen with *ortho*-F of the aldehyde ring has been found to form across the center of inversion in the crystal lattice of the compound 80 (table S24, figure S24). These dimers interconnect among themselves through another dimer *via* C–H···F hydrogen bond involving H5 with F2 and also by the involvement of H5 with F4 by the utilization of *c*-glide (table S24, figure S24).



S24

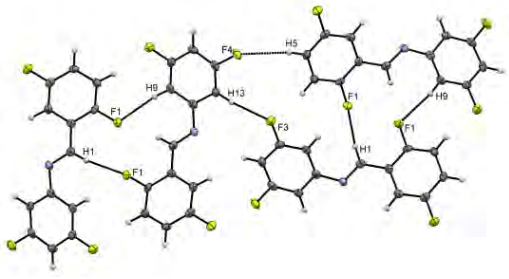
Figure S24: (a) Four C–H···F hydrogen bonds lead the formation of molecular dimer, which get further interconnected again *via* C–H···F hydrogen bonds, by the involvement of H5 with F2.

Table S24: Details of the geometrical parameters for all the C–H···F hydrogen bonds, the values of electron densities and Laplacians at their BCPs

Code	C–H···F	*d* (H···F/Å)	θ (∠C–H···F/°)	Symmetry Code	SE_{G09} kcal/mol	ρ (e Å^{-3})	$\nabla^2\rho$ (e Å^{-5})
80	C5–H5···F2	2.63	125	-x+1,-y+2,-z	-1.9	0.03	0.65
	C5–H5···F4	2.65	121	$x,-y+^{3}/_{2},z-^{1}/_{2}$	-1.6	0.03	0.64
	C9–H9···F1	2.59	161	-x,-y+1,-z	-5.0	0.03	0.63
	C1–H1···F1	2.66	164	-x,-y+1,-z		0.02	0.51

81:

The structure was solved in the non-centrosymmetric orthorhombic $P2_12_12_1$ space group. The crystal structure of **81** involves the formation of a robust synthon, which was also seen in the dihalo-substituted *N*-benzylideneanilines. C–H···F hydrogen bonds (involving H5 with F4 and H13 with F3) between the molecules related by 2_1 screw propagate those dimers in its crystal lattice (table S25, figure S25).



S25

Figure S25: (a) formation of dimers through the formation of robust synthon involving H1 and H9 with F1 and their interconnection through H5 with F4 and H13 with F3.

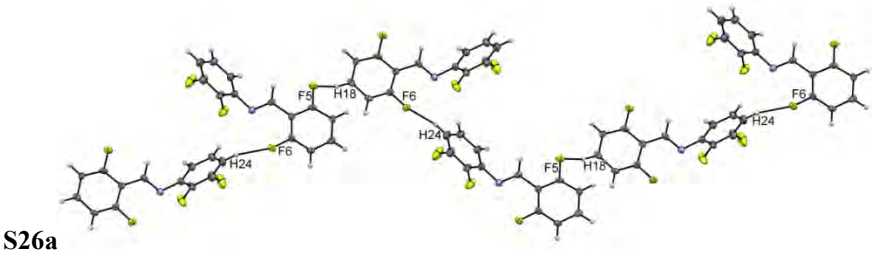
Table S25: Details of the geometrical parameters for all the C–H···F hydrogen bonds, the values of electron densities and Laplacians at their BCPs

Code	C–H···F	*d* (H···F/Å)	θ (∠C–H···F/°)	Symmetry Code	SE_{G09} kcal/mol	ρ (e Å^{-3})	$\nabla^2\rho$ (e Å^{-5})
81	C1–H1···F1	2.63	159	$x-^{1}/_{2},-y-^{1}/_{2},-z-2$	-4.7	0.03	0.60
	C9–H9···F1	2.48	172	$x+^{1}/_{2},-y-^{1}/_{2},-z-2$		0.04	0.82
	C5–H5···F4	2.66	163	$-x-^{3}/_{2},-y-1,z-^{1}/_{2}$	-1.1	0.03	0.53
	C13–H13···F3	2.50	158	$-x-2,y-^{1}/_{2},-z-^{3}/_{2}$	-2.2	0.04	0.79

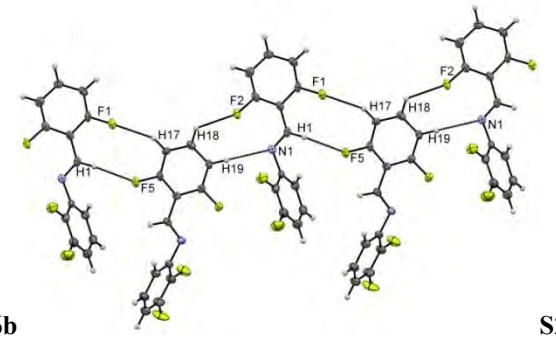
82:

This compound crystallizes in the centrosymmetric monoclinic *Cc* space group. Molecular zigzag chains have been fashioned through C–H···F hydrogen bonds in the crystal lattice of this compound by the utilization of *c* glide (table S26, figure S26a). Moreover, a layer

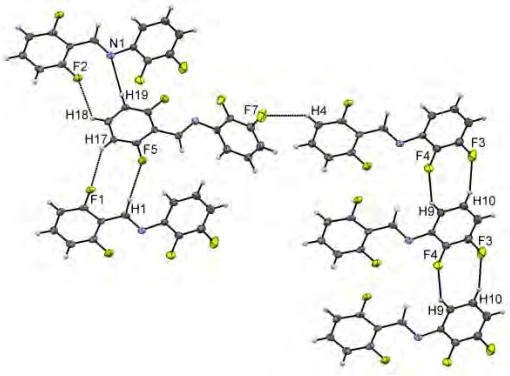
of molecular dimers has also been formed *via* C–H···F hydrogen bonds (table S26, figure S26b). Then this molecular layer of dimers interacts with other layer of dimers, which has also been formed by C–H···F hydrogen bonds (involving H10 with F3 and H9 with F4) through the interaction of H4 with F7 (table S26, figure S26c).



S26a



S26b



S26c

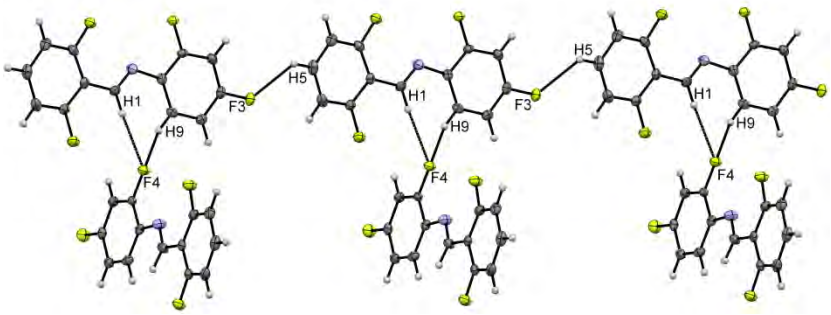
Figure S26: (a) Molecular chain formation through C–H···F hydrogen bonds and their propagation through C–H···F hydrogen bonds, **(b)** C–H···F and C–H···N hydrogen bonds leading to the formation of molecular layers, **(c)** C–H···F hydrogen bond involve H4 with F7, interconnect the layers formed in figure (b).

Table S26: Details of the geometrical parameters for all the C–H···F hydrogen bonds, the values of electron densities and Laplacians at their BCPs

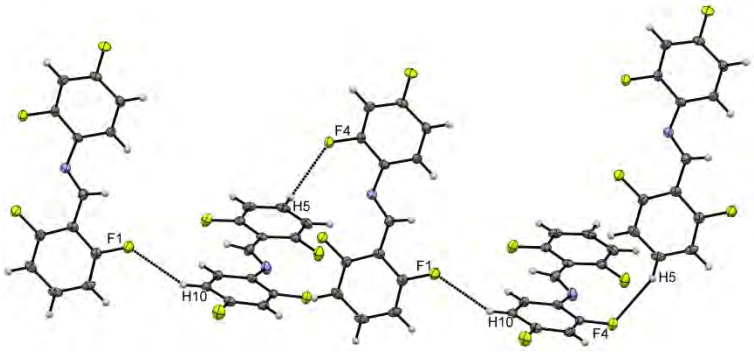
Code	C–H···F	*d* (H···F/Å)	θ (∠C–H···F/°)	Symmetry Code	SE_{G09} kcal/mol	ρ (e Å^{-3})	$\nabla^2\rho$ (e Å^{-5})
82	C4–H4···F7	2.68	125	x-$^1/_2$,-y+$^1/_2$,z+$^1/_2$	-1.4	0.03	0.62
	C18–H18···F5	2.67	132	x,-y+1,z+$^1/_2$	-1.0	0.03	0.61
	C17–H17···F1	2.49	143	x,-y+1,z-$^1/_2$	-3.9	0.04	0.79
	C1–H1···F5	2.44	175	x,-y+1,z+$^1/_2$		0.05	0.86
	C24–H24···F6	2.58	131	x-$^1/_2$,-y+$^1/_2$,z-$^1/_2$	-3.7	0.04	0.71
	C18–H18···F2	2.48	122	x+1,-y+1,z+$^1/_2$	-4.6	0.05	0.92
	C10–H10···F3	2.67	159	x+1,y,z	-2.6	0.03	0.57
	C9–H9···F4	2.63	149	x+1,y,z		0.02	0.52

83:

This compound crystallizes in the monoclinic $P2_1/c$ space group. By the utilization of *c* glide molecular dimer has been found to form through the involvement of imine hydrogen with the *ortho*-F of the aniline ring (table S27, figure S27a). These dimers interact further through C–H···F hydrogen bonds by the involvement of H5 with F3 along *a*-axis (table S27, figure S27a). Moreover, molecules related by 2_1 screw axis also interact through C–H···F hydrogen bonds and thus lead to the formation of a molecular chains (table S27, figure S27b).



S27a



S27b

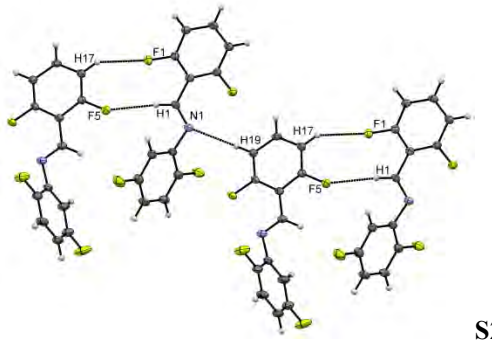
Figure S27: (a) Molecular chains, which get formed through C–H···F hydrogen bonds, and to which other chains are hanging by bifurcated C–H···F hydrogen bonds, **(b)** C–H···F hydrogen bonds leading to the formation of zigzag chains in the crystal lattice of compound **83**.

Table S27: Details of the geometrical parameters for all the C–H···F hydrogen bonds, the values of electron densities and Laplacians at their BCPs

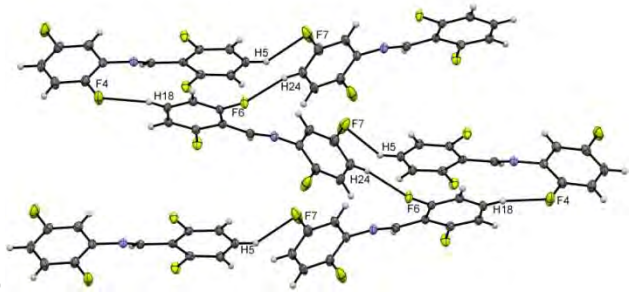
Code	C–H···F	*d* (H···F/Å)	θ (∠C–H···F/°)	Symmetry Code	SE_{G09} kcal/mol	ρ (e Å^{-3})	$\nabla^2\rho$ (e Å^{-5})
83	C10–H10···F1	2.66	142	$-x+1,y-1/2,-z+1/2$	-1.2	0.03	0.56
	C5–H5···F4	2.68	128	$-x+2,y+1/2,-z+3/2$	-4.4	0.03	0.59
	C9–H9···F4	2.51	148	$x-1,-y+1/2,z-1/2$	-2.1	0.04	0.83
	C1–H1···F4	2.47	162	$x-1,-y+1/2,z-1/2$		0.05	0.86
	C5–H5···F3	2.52	138	x-1,y+1,z	-1.2	0.04	0.78

84:

The structure was solved in the centrosymmetric monoclinic $P2_1/c$ space group with $Z' = 2$. Molecular dimers formed through C–H···F hydrogen bonds by the involvement of H1 with F5 and H17 with F1 interacts through C–H···N hydrogen bonds (table S28, figure S28a). Moreover, a complex network of molecules has also been found to form in the crystal lattice of this compound through C–H···F hydrogen bonds (table S28, figure S28b).



S28a



S28b

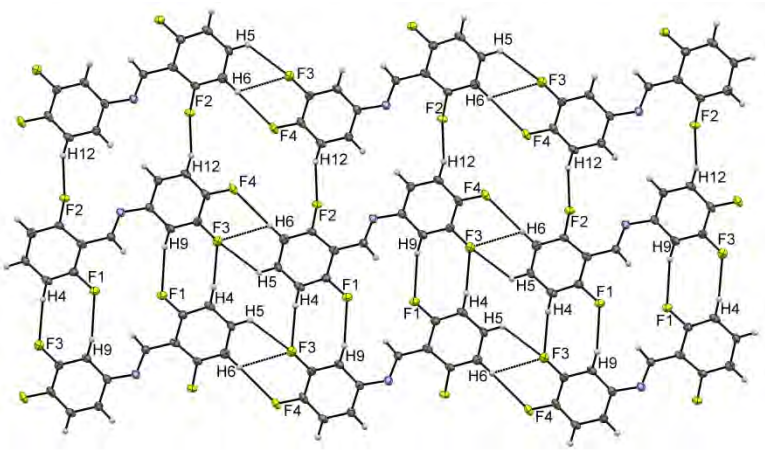
Figure S28: (a) Molecular dimer formation and their propagation through C–H···F and C–H···N hydrogen bonds respectively, **(b)** zigzag chain formation *via* C–H···F hydrogen bonds.

Table S28: Details of the geometrical parameters for all the C–H···F hydrogen bonds, the values of electron densities and Laplacians at their BCPs

Code	C–H···F	*d* (D···F/Å)	θ (∠C–D···F/°)	Symmetry Code	SE_{G09} kcal/mol	ρ (e Å^{-3})	$\nabla^2\rho$ (e Å^{-5})
84	C5–H5···F7	2.68	135	$-x+1,y+1/2,-z+3/2$	-1.3	0.03	0.58
	C17–H17···F5	2.69	124	-x,-y+1,-z+1	-1.6	0.03	0.62
	C24–H24···F6	2.51	122	$x,-y+1/2,z+1/2$	-4.2	0.05	0.91
	C1–H1···F5	2.49	174	x,y,z	-4.7	0.04	0.78
	C17–H17···F1	2.56	143	x,y,z		0.03	0.68
	C18–H18···F4	2.56	129	-x+1,-y+1,-z+1	-7.9	0.04	0.74
	C18–H18···F2	2.47	120	x-1,y,z-1	-4.2	0.05	0.94

86:

This compound crystallizes in the triclinic $P\bar{1}$ space group. Along the *c*-axis molecules have been found to form chains *via* C–H···F hydrogen bonds, which involve the interaction between H5 and H6 with F3 and F4 (table S29, figure S29). Then these layers interacts with the similar layers through C–H···F hydrogen bonds across the centre of inversion by the involvement of H4 with F3; H9 with F1 and H12 with F2 (table S29, figure S29).



S29

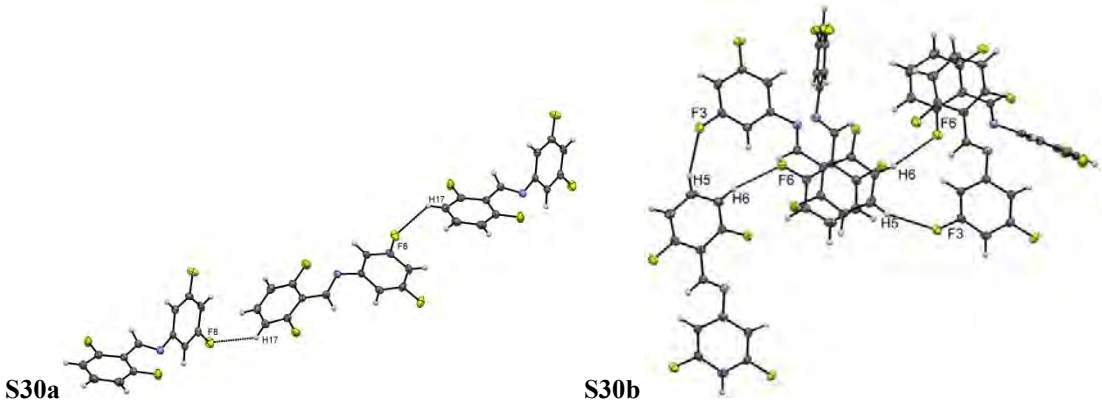
Figure S29: (a) Molecular sheet formation through C–H···F hydrogen bonds.

Table S29: Details of the geometrical parameters for all the C–H···F hydrogen bonds, the values of electron densities and Laplacians at their BCPs

Code	C–D···F (D = H, F)	*d* (D···F/Å)	θ (∠C–D···F/º)	Symmetry Code	SE_{G09} kcal/mol	ρ (e Å^{-3})	$\nabla^2\rho$ (e Å^{-5})
86	C5–H5···F3	2.63	120	x,+y,z-1	-1.9	0.03	0.66
	C6–H6···F3	2.63	120	x,+y,z-1		0.03	0.71
	C6–H6···F4	2.69	159	x,+y,z-1		0.02	0.52
	C4–H4···F3	2.66	134	-x+1,-y,-z+1	-4.7	0.03	0.61
	C9–H9···F1	2.70	134	-x+1,-y,-z+1		0.03	0.56
	C5–H5···F4	2.67	127	x+1,y,z-1	-1.2	0.03	0.60
	C12–H12···F2	2.54	126	-x-1,-y+1,-z+1	-4.3	0.04	0.79

87:

The structure was solved in the centrosymmetric monoclinic $P2_1/c$ space group with $Z' = 2$. The crystal structure of this molecule involves the formation of chains through C–H···F hydrogen bonds involving H17 with F8 (table S30, figure S30a). Additionally, a complex network of molecules has also been found to form in the crystal lattice of this compound by the involvement of C–H···F hydrogen bonds between the molecules related by *c* glide and π···π interactions (table S30, figure S30b).



S30a **S30b**

Figure S30: (a) Molecular chain formation through C–H···F hydrogen bonds, **(b)** C–H···F hydrogen bonds and π···π interactions, leading to the formation of a complex network in the crystal lattice of compound **87**.

Table S30: Details of the geometrical parameters for all the C–H···F hydrogen bonds, the values of electron densities and Laplacians at their BCPs

Code	C–H···F	*d* (H···F/Å)	θ (∠C–H···F/°)	Symmetry Code	SE_{G09} kcal/mol	ρ (e Å^{-3})	$\nabla^2\rho$ (e Å^{-5})
87	C5–H5···F3	2.58	160	$x-{}^{1}/_{2},-y+{}^{1}/_{2},z+1/2$	-1.5	0.03	0.64
	C6–H6···F6	2.56	161	$x+{}^{1}/_{2},-y+{}^{1}/_{2},z+{}^{1}/_{2}$	-2.1	0.03	0.68
	C17–H17···F8	2.56	127	$-x+{}^{1}/_{2},y+{}^{1}/_{2},-z+{}^{3}/_{2}$	-1.9	0.04	0.80

Table S30b: Details of the geometrical parameters for π···π interactions

Code	π···π	*d*/Å	D_1/Å	D_2/Å	slippage	symmetry
87	Cg1···Cg3	3.8879(17)	3.5428(9)	-3.4558(9)	--	-1+x,y,z
	Cg1···Cg3	3.6324(17)	-3.4296(9)	3.5073(9)	--	x,y,z
	Cg2···Cg2	3.6155(17)	-3.4548(9)	-3.4548(9)	1.07	-x,1-y,-z

Where, D_1 = Perpendicular distance of Cg1/Cg2 on ring containing Cg3/Cg2, D2 = Perpendicular distance of Cg2/Cg3 on ring containing Cg2/Cg1.

Table S31: Details of the geometrical parameters for all the C–H···F hydrogen bonds, the values of electron densities, Laplacians at their BCPs, local energy density E($\mathbf{r}_{CP}$) of the electrons,local potential energy density (V_{rcp}), local kinetic energy density (G_{rcp}) and the bond paths (R_{ij}) as calculated by AIM2000, which are found in the structures reported herein

Code	C–H···F	D (C···F/Å)	*d* (H···F/Å)	∠C–H···F (°)	R_{cp} (Å)	ρ (e Å^{-3})	$\nabla^2\rho$ (e Å^{-5})	$G(r_{CP})$ (kcal\ mol)	$V(r_{CP})$ (kcal\ mol)	$E(r_{CP})$ (kcal\ mol)	symmetry
52	C1–H1···F4	3.222(2)	2.47	136	2.50	0.05	0.89	4.33	-2.87	1.46	x+1/2,-y-2,z+1/2
	C11–H11···F2	3.266(2)	2.65	123	2.72	0.05	0.92	4.39	-2.83	1.56	x-3/2,-y-2,z+1/2
	C11–H11···F1	3.315(2)	2.57	135	2.60	0.04	0.70	3.34	-2.10	1.24	x-2,+y-1,+z
	C4–H4···F2	3.612(2)	2.74	153	2.76	0.02	0.48	2.20	-1.31	0.89	x+1/2,-y-1,z+1/2
53	C9–H9···F2	3.557(4)	2.63	164	2.66	0.03	0.60	2.83	-1.75	1.08	x+1/2,-y-1/2,+z
	C1–H1···F2	3.574(4)	2.68	157	2.61	0.04	0.67	3.18	-2.04	1.15	x+1/2,-y+3/2,+z
	C10–H10···F4	3.328(4)	2.52	142	2.64	0.03	0.66	3.07	-1.87	1.20	x+1/2,-y+3/2,+z
	C12–H12···F1	3.375(4)	2.45	163	2.51	0.04	0.76	3.63	-2.30	1.33	-x+3/2,y+3/2,z+1/2
	C4–H4···F3	3.180(4)	2.50	129	2.54	0.04	0.81	3.86	-2.48	1.38	1-x,1-y,1/2+z
54	C4–H4···F2	3.483(2)	2.60	155	2.62	0.03	0.65	3.07	-1.91	1.16	x,+y-1,+z
	C1–H1···F4	3.432(2)	2.52	162	2.54	0.04	0.72	3.43	-2.19	1.24	x,+y-1,+z
	C12–H12···F3	3.570(2)	2.71	150	2.74	0.02	0.51	2.38	-1.43	0.95	x,y+1,+z
	C9–H9···F4	3.553(3)	2.72	147	2.75	0.03	0.52	2.43	-1.47	0.96	x,+y-1,+z
	C11–H11···F1	3.347(2)	2.63	133	2.66	0.03	0.65	3.05	-1.88	1.17	x,-y+1,+z-1/2
	C11–H11···F2	3.398(2)	2.48	163	2.51	0.04	0.81	3.91	-2.52	1.38	x,-y+1,+z-1/2
55	C1–H1···F4	3.274(1)	2.34	166	2.37	0.06	1.04	5.19	-3.61	1.59	x+1,+y,+z
	C12–H12···F2	3.613(1)	2.69	164	2.72	0.02	0.51	2.36	-1.42	0.95	-x+1,+y-1/2,-z+1/2
	C11–H11···F2	3.262(2)	2.60	127	2.64	0.03	0.66	3.10	-1.92	1.19	x,-y+1/2,+z-1/2
	C10–H10···F1	3.522(1)	2.59	168	2.61	0.03	0.64	3.02	-1.87	1.15	x,-y+1/2,+z-1/2
	C4–H4···F1	3.420(3)	2.66	138	2.69	0.03	0.54	2.53	-1.52	1.01	3-x, -y, 1-z
57	C22–H22···F7	3.453(5)	2.52	169	2.60	0.04	0.70	3.30	-2.08	1.22	-x+1,-y+2,-z
	C16–H16···F7	3.568(6)	2.70	153	2.68	0.03	0.58	2.73	-1.69	1.04	-x+1,-y+1,-z
	C17–H17···F2	3.425(6)	2.52	160	2.52	0.04	0.74	3.54	-2.26	1.28	x+1,-y-1/2,+z-1/2
	C20–H20···F8	3.237(6)	2.46	139	2.40	0.06	1.01	5.00	-3.42	1.58	-x+1,+y+1/2,-z+1/2
	C11–H11···F5	3.308(5)	2.45	151	2.34	0.06	1.04	5.18	-3.61	1.57	-x+1,+y+1/2,-z+1/2
	C1–H1···F3	3.371(5)	2.45	164	2.42	0.05	0.92	4.56	-3.11	1.45	-x,y+1/2,-z+1/2
	C24–H24···F1B	3.298(5)	2.66	125	2.75	0.03	0.62	2.96	-1.85	1.11	-x,y+1/2,-z+1/2
	C24–H24···F1A	3.382(6)	2.57	144	2.59	0.04	0.68	3.24	-2.03	1.21	-x,+y+3/2,-z+1/2
	C7–H7···F4	3.352(6)	2.71	126	2.74	0.03	0.59	2.75	-1.68	1.07	-x,-y+2,-z+1
	C4–H4···F6	3.428(6)	2.70	134	2.73	0.03	0.54	2.51	-1.52	0.99	x-1,+y,+z
58	C24–H24···F4	3.305(5)	2.67	125	2.72	0.03	0.60	2.79	-1.71	1.08	x+1,+y,+z
	C14–H14···F2	3.386(5)	2.49	157	2.52	0.04	0.79	3.81	-2.49	1.32	x+1,+y,+z
	C11–H11···F1	3.595(5)	2.65	172	2.68	0.03	0.57	2.66	-1.62	1.04	x+1,+y-1,+z
	C24–H24···F5	3.255(5)	2.51	135	2.54	0.04	0.83	4.02	-2.62	1.40	x+1,+y,+z
	C1–H1···F8	3.450(6)	2.63	145	2.66	0.03	0.59	2.79	-1.73	1.07	x,-y+2,+z+1/2
	C3–H3···F8	3.315(5)	2.44	153	2.47	0.04	0.86	4.14	-2.71	1.43	x-1,-y+2,+z-1/2
	C5–H5···F3	3.452(5)	2.70	136	2.73	0.03	0.54	2.51	-1.52	1.00	x-1,+y,+z
	C10–H10···F6	3.355(5)	2.67	130	2.70	0.03	0.59	2.77	-1.70	1.07	x,-y,+z-1/2
	C18–H18···F7	3.518(5)	2.59	165	2.62	0.03	0.64	2.99	-1.85	1.14	x-1,+y-1,+z
	C9–H9···F8	3.572(4)	2.63	171	2.66	0.03	0.60	2.84	-1.75	1.09	X,1-y,1/2+z
	C10–H10···F7	3.389(4)	2.74	126	2.78	0.03	0.51	2.38	-1.42	0.95	X,1-y,1/2+z
59	C1–H1···F8	3.343(2)	2.40	173	2.42	0.05	0.89	4.37	-2.91	1.45	-x+1/2,-y+1/2,-z
	C10–H10···F3	3.365(2)	2.53	147	2.56	0.04	0.77	3.67	-2.35	1.32	-x,-y+1,-z
	C5–H5···F2	3.330(2)	2.56	138	2.59	0.03	0.69	3.28	-2.05	1.23	-x+1,+y,-z+1/2
	C14–H14···F4	3.321(2)	2.42	159	2.44	0.05	0.91	4.45	-3.00	1.45	-x+1/2,y+1/2,-z+1/2
	C16–H16···F4	3.550(2)	2.72	146	2.75	0.02	0.48	2.20	-1.31	0.90	-x+1/2,y+1/2,-z+1/2
	C23–H23···F5	3.162(2)	2.49	128	2.53	0.04	0.82	3.94	-2.52	1.42	-x+1/2,y-1/2,-z+1/2
	C25–H25···F3	3.266(3)	2.63	125	2.68	0.03	0.64	3.04	-1.89	1.15	x+1/2,y-1/2,+z
	C12–H12···F2	3.369(3)	2.42	177	2.44	0.05	0.90	4.40	-2.92	1.48	-x+1/2,y+1/2,-z+1/2
	C18–H18···F1	3.572(2)	2.68	156	2.71	0.03	0.53	2.45	-1.47	0.98	x-1/2,+y-1/2,+z

60	C1–H1···F4	3.353(1)	2.54	143	2.57	0.04	0.71	3.40	-2.17	1.23	x,1+y,z
	C3–H3···F4	3.446(1)	2.63	144	2.66	0.03	0.58	2.74	-1.67	1.07	x,+y+1,+z
	C5–H5···F1	3.430(1)	2.53	157	2.56	0.04	0.75	3.55	-2.26	1.29	-x,1-y,1-z
	C11–H11···F3	3.573(1)	2.66	162	2.69	0.03	0.54	2.53	-1.53	1.00	-x+1,-y,-z
	C7–H7···F3	3.383(1)	2.61	133	2.69	0.03	0.60	2.84	-1.74	1.09	-x+1,+y-1/2,-z+1/2
61	C1–H1···F4	3.464(2)	2.53	166	2.57	0.04	0.70	3.36	-2.13	1.22	x-1,+y,+z
	C3–H3···F3	3.408(3)	2.47	169	2.50	0.04	0.83	3.99	-2.61	1.38	-x,+y+1/2,-z+1/2
	C10–H10···F1	3.582(2)	2.65	168	2.67	0.03	0.57	2.66	-1.62	1.04	-x,+y-1/2,-z+1/2
	C11–H11···F1	3.352(3)	2.56	141	2.59	0.04	0.74	3.54	-2.25	1.28	-x+1/2,-y+1,+z-1/2
	C11–H11···F2	3.442(3)	2.59	150	2.61	0.04	0.68	3.22	-2.02	1.20	-x+1/2+1,-y+1,+z-1/2
	C12–H12···F2	3.504(3)	2.56	173	2.44	0.05	0.90	4.40	-2.92	1.48	-x+2,+y+1/2,-z+1/2
	C7–H7···F4	3.648(3)	2.72	166	2.89	0.02	0.35	1.57	-0.90	0.67	-x+2,+y-1/2,-z+1/2
63	C1–H1···F7	3.370(5)	2.76	123	2.80	0.03	0.53	2.47	-1.51	0.96	x,y,z
	C14–H14···F3	3.393(5)	2.64	136	2.67	0.03	0.61	2.91	-1.82	1.09	x,y,z
	C1–H1···F7	3.390(5)	2.61	139	2.69	0.03	0.65	3.09	-1.95	1.14	x,+y+1,+z
	C14–H14···F3	3.290(5)	2.66	125	2.64	0.03	0.64	3.04	-1.91	1.12	x,+y-1,+z
	C20–H20···F2	3.446(5)	2.50	175	2.59	0.03	0.68	3.22	-2.01	1.21	x-1/2,-y,+z
	C7–H7···F6	3.501(5)	2.57	168	2.52	0.04	0.78	3.74	-2.40	1.34	x+1/2,-y,+z
	C13–H13···F6	3.423(5)	2.57	149	2.60	0.03	0.68	3.20	-2.00	1.20	x+1/2,-y+1,+z
	C11–H11···F1	3.368(4)	2.51	150	2.54	0.04	0.76	3.60	-2.29	1.31	1-x,2-y,1/2+z
	C5–H5···F5	3.110(5)	2.51	121	2.58	0.04	0.87	4.20	-2.75	1.45	-x+1,-y+1,+z-1/2
	C5–H5··F5	3.482(5)	2.64	148	2.67	0.03	0.59	2.78	-1.70	1.08	-x+1,-y,+z-1/2
	C24–H24···F4	3.351(5)	2.70	126	2.76	0.03	0.58	2.72	-1.68	1.04	-x+1,-y+1,+z-1/2
	C24–H24···F4	3.363(5)	2.55	143	2.58	0.03	0.67	3.17	-1.97	1.20	-x+1,-y+2,+z-1/2
	C18–H18···F8	3.272(5)	2.43	148	2.45	0.05	0.88	4.25	-2.78	1.47	-x+1/2,+y-1,+z+1/2
64	C5–H5···F2	3.537(8)	2.68	150	2.70	0.03	0.53	2.48	-1.50	0.99	x-1,+y+1,+z-1
	C11–H11···F4	3.382(7)	2.47	160	2.51	0.04	0.79	3.80	-2.44	1.35	x+1,+y-1,+z+1
	C1–H1···F5	3.385(9)	2.53	150	2.57	0.04	0.70	3.33	-2.11	1.22	x-1,+y,+z
	C14–H14···F3	3.389(9)	2.53	150	2.54	0.04	0.74	3.56	-2.29	1.27	x+1,+y,+z
	C10–H10···F2	3.217(10)	2.48	134	2.51	0.04	0.82	3.90	-2.50	1.40	x-1,+y,+z-1
	C9–H9···F1	3.519(8)	2.58	172	2.61	0.03	0.65	3.07	-1.91	1.16	x-1,+y,+z
	C6–H6···F4	3.430(6)	2.77	127	2.82	0.02	0.46	2.12	-1.26	0.86	x-1,+y,+z
	C23–H23···F8	3.229(8)	2.48	135	2.51	0.04	0.81	3.90	-2.50	1.40	x+1,+y,+z
	C22–H22···F7	3.525(8)	2.58	172	2.60	0.03	0.66	3.13	-1.96	1.17	x+1,+y,+z
	C19–H19···F6	3.408(5)	2.76	126	2.80	0.02	0.48	2.25	-1.35	0.90	x+1,+y,+z
	C18–H18···F8	3.540(7)	2.69	149	2.72	0.02	0.51	2.35	-1.41	0.95	x+1,+y-1,+z+1
	C24–H24···F6	3.392(7)	2.49	158	2.51	0.04	0.79	3.78	-2.43	1.35	x-1,+y+1,+z-1
65	C12–H12···F4	3.681(6)	2.76	162	2.79	0.02	0.45	2.07	-1.22	0.85	-x,+y-$^1/_2$,-z-2
	C5–H5···F3	3.356(6)	2.59	138	2.62	0.03	0.67	3.15	-1.97	1.18	x,+y+1,+z-1
	C9–H9···F2	3.231(5)	2.52	131	2.55	0.04	0.82	3.91	-2.52	1.39	-1+x,$^1/_2$+y,-3-z
	C9–H9···F1	3.669(4)	2.74	168	2.76	0.02	0.48	2.22	-1.32	0.90	-1+x,$^1/_2$+y,-3-z
66	C1–H1···F1	3.458(2)	2.54	162	2.57	0.03	0.68	3.21	-2.02	1.19	-x+2,-y+2,-z+1
	C5–H5···F3	3.296(2)	2.44	151	2.62	0.03	0.67	3.15	-1.97	1.18	x,+y-1,+z+1
	C12–H12···F3	3.324(2)	2.45	153	2.48	0.04	0.84	4.06	-2.64	1.42	x-1,+y,+z
	C9–H9···F4	3.315(2)	2.44	154	2.47	0.04	0.86	4.18	-2.74	1.44	x+1,+y,+z
	C11–H11···F2	3.387(2)	2.61	140	2.64	0.03	0.60	2.83	-1.73	1.10	x-1,+y+1,+z-1
68	C5–H5···F3	3.283(4)	2.55	134	2.60	0.04	0.71	3.37	-2.11	1.26	x-1,+y+2,+z
	C1–H1···F1	3.459(3)	2.55	160	2.60	0.03	0.68	3.23	-2.02	1.21	-x+1,+y-$^1/_2$,-z+2
	C9–H9···F1	3.524(3)	2.65	153	2.69	0.03	0.57	2.67	-1.62	1.05	-x+1,+y-$^1/_2$,-z+2
	C10–H10···F2	3.299(4)	2.68	123	2.76	0.04	0.54	2.48	-1.53	0.95	-x+1,+y-$^3/_2$,-z+2
69	C11–H11···F4	3.496(2)	2.68	144	2.71	0.03	0.55	2.57	-1.55	1.01	-x+$^5/_2$,y+$^1/_2$,-z+$^1/_2$
	C6–H6···F3	3.272(2)	2.64	125	2.68	0.05	0.51	3.06	-1.93	1.13	x-$^1/_2$,-y+$^3/_2$,+z-$^1/_2$
	C5–H5···F3	3.315(2)	2.74	120	2.82	0.04	0.76	2.23	-1.41	0.82	x-$^1/_2$,-y+$^3/_2$,+z-$^1/_2$
	C6–H6···F4	3.278(2)	2.56	133	2.59	0.04	0.76	3.63	-2.32	1.31	-x+2,-y+1,-z
	C5–H5···F2	3.604(2)	2.69	161	2.71	0.04	0.66	2.35	-1.45	0.90	-x+1,-y+1,-z
	C9–H9···F2	3.386(2)	2.63	136	2.66	0.03	0.62	2.91	-1.79	1.12	-x+$^3/_2$,+y+$^1/_2$,-z+$^1/_2$
70	C11–H11···F3	3.540(2)	2.63	160	2.66	0.03	0.59	2.75	-1.69	1.07	-x,-y,-z+2
	C10–H10···F3	3.154(2)	2.49	127	2.53	0.04	0.84	4.02	-2.58	1.43	x+1,+y,+z
	C9–H9···F4	3.542(2)	2.61	166	2.63	0.03	0.62	2.94	-1.82	1.12	x+1,+y,+z
	C4–H4···F2	3.380(3)	2.52	151	2.55	0.04	0.73	3.44	-2.17	1.28	1-x,-1-y,1-z
	C6–H6···F2	3.355(2)	2.64	132	2.68	0.03	0.62	2.93	-1.82	1.11	2-x,-1-y,1-z
71	C1–H1···F4	3.605(2)	2.66	173	2.69	0.03	0.53	2.47	-1.49	0.97	-x+1,+y-1/2,-z
	C9–H9···F4	3.152(2)	2.54	122	2.60	0.04	0.80	3.83	-2.48	1.35	-x+1,+y-1/2,-z

	C4–H4···F3	3.299(2)	2.47	146	2.50	0.04	0.82	3.91	-2.52	1.39	x-1,+y,+z+1
	C12–H12···F2	3.374(2)	2.67	131	2.71	0.03	0.56	2.63	-1.60	1.03	x+1,+y,+z-1
	C7–H7···F3	3.404(2)	2.68	134	2.70	0.03	0.59	2.76	-1.68	1.07	-x+2,+y+1/2,-z
	C9–H9···F4	3.293(2)	2.69	122	2.75	0.03	0.61	2.89	-1.79	1.10	-x+2,+y-1/2,-z
	C12–H12···F2	3.452(2)	2.76	131	2.80	0.02	0.49	2.30	-1.39	0.91	x,+y,+z-1
73	C4–H4···F1	3.466(6)	2.62	149	2.64	0.03	0.63	2.95	-1.82	1.13	x-1/2,-y+1/2,-z+1
	C1–H1···F3	3.257(5)	2.53	133	2.57	0.04	0.82	3.93	-2.55	1.38	x-1,+y,+z
	C11–H11···F2	3.282(6)	2.69	121	2.73	0.03	0.62	2.90	-1.78	1.12	-x+3/2,-y+1,z+1/2
	C10–H10···F2	3.256(6)	2.64	123	2.69	0.03	0.64	2.98	-1.83	1.15	-x+1/2,-y+1,z+1/2
	C12–H12···F3	3.459(6)	2.61	149	2.64	0.03	0.66	3.13	-1.95	1.18	-x+1,y+1/2,-z+3/2
	C10–H10···F4	3.557(6)	2.88	130	2.94	0.02	0.38	1.73	-1.02	0.72	-x+1,y+1/2,-z+3/2
	C6–H6···F4	3.398(6)	2.62	140	2.65	0.03	0.61	2.87	-1.76	1.11	x+1/2,-y+3/2,-z+1
74	C1–H1···F1	3.607(1)	2.66	172	2.71	0.02	0.48	2.23	-1.33	0.90	-x+1,-y,-z+1
	C9A–H9A···F1	3.488(1)	2.76	134	2.82	0.02	0.46	2.13	-1.27	0.86	-x+1,-y,-z+1
	C4–H4···F4	3.321(3)	2.56	139	2.59	0.03	0.67	3.15	-1.94	1.20	-x+1,-y+1,-z+1
	C13A–H13A···F2	3.560(1)	2.63	166	2.68	0.03	0.56	2.63	-1.60	1.03	-x+1,-y+1,-z+1
75	C4–H4···F3	3.487(4)	2.74	136	2.78	0.02	0.51	2.37	-1.42	0.95	x-1/2,-y+3/2,-z
	C9–H9···F1	3.444(3)	2.51	169	2.53	0.04	0.78	3.77	-2.44	1.33	x-1/2,-y+3/2,-z
	C1–H1···F1	3.622(3)	2.71	162	2.94	0.02	0.48	2.21	-1.33	0.88	x+1/2,-y+3/2,-z
	C6–H6···F2	3.425(4)	2.59	147	2.62	0.03	0.67	3.15	-1.97	1.18	x-1/2,-y+5/2,-z
	C6–H6···F4	3.363(4)	2.69	128	2.73	0.03	0.58	2.71	-1.65	1.05	-x,y+1/2,-z+1/2
	C13–H13···F3	3.481(4)	2.60	155	2.62	0.03	0.65	3.09	-1.93	1.17	-x+1,y+1/2,-z+1/2
76	C4–H4···F2	3.513(2)	2.63	155	2.66	0.03	0.59	2.78	-1.70	1.08	x+1,y,+z
	C10–H10···F3	3.233(2)	2.48	136	2.51	0.04	0.81	3.85	-2.47	1.39	x+1,y,+z
	C7–H7···F1	3.504(2)	2.62	155	2.65	0.03	0.59	2.77	-1.68	1.08	x-1,y,+z
	C9–H9···F4	3.511(2)	2.57	172	2.60	0.03	0.67	3.17	-1.98	1.18	x+1,y,+z
	C5–H5···F3	3.526(1)	2.67	150	2.70	0.03	0.56	2.60	-1.57	1.03	-x+1/2,y-1/2,-z+1/2
	C11–H11···F1	3.467(2)	2.75	133	2.79	0.02	0.50	2.32	-1.40	0.92	x-1/2,-y+3/2,z+1/2
	C11–H11···F4	3.321(2)	2.50	145	2.75	0.04	0.84	4.01	-2.59	1.42	x+1/2,-y+3/2,z+1/2
77	C17–H17···F7	3.306(2)	2.61	131	2.65	0.03	0.63	2.97	-1.83	1.14	x-1,+y+1,+z
	C18–H18···F6	3.254(2)	2.53	133	2.57	0.04	0.77	3.67	-2.34	1.33	-x,-y+2,-z+1
	C20–H20···F8	3.668(2)	2.75	164	2.77	0.02	0.46	2.09	-1.23	0.86	-x+1,-y+1,-z+1
	C25–H25···F6	3.413(3)	2.58	146	2.61	0.03	0.68	3.21	-2.01	1.20	-x+1,-y+1,-z+1
	C22–H22···F5	3.313(2)	2.58	134	2.62	0.04	0.72	3.46	-2.20	1.25	-x,-y+1,-z+2
	C14–H14···F5	3.421(2)	2.45	167	2.51	0.04	0.75	3.56	-2.27	1.29	-x,-y+1,-z+2
	C22–H22···F4	3.465(3)	2.71	137	2.74	0.03	0.54	2.53	-1.54	0.99	-x+1,-y+1,-z+2
78	C12–H12···F3	3.475(2)	2.59	155	2.62	0.03	0.66	3.11	-1.94	1.17	x+1,+y,+z
	C9–H9···F4	3.447(2)	2.57	154	2.59	0.04	0.70	3.33	-2.11	1.23	x-1,+y,+z
	C1–H1···F4	3.612(2)	2.73	155	2.76	0.02	0.45	2.08	-1.23	0.85	x-1,+y,+z
	C7–H7···F1	3.468(2)	2.63	147	2.66	0.03	0.60	2.81	-1.71	1.10	x+1,+y,+z
	C4–H4···F2	3.476(2)	2.64	147	2.67	0.03	0.60	2.82	-1.73	1.08	x-1,+y,+z
	C5–H5···F4	3.382(2)	2.68	131	2.72	0.03	0.61	2.84	-1.73	1.11	x-1/2,-y+1/2,z+1/2
80	C5–H5···F2	3.261(3)	2.63	125	2.69	0.03	0.57	3.08	-1.92	1.16	-x+1,-y+2,-z
	C5–H5···F4	3.239(2)	2.65	121	2.72	0.02	0.52	3.04	-1.88	1.16	x,-y+3/2,+z-1/2
	C9–H9···F1	3.502(2)	2.59	161	2.63	0.02	0.42	2.99	-1.85	1.14	-x,-y+1,-z
	C1–H1···F1	3.582(2)	2.66	164	2.70	0.02	0.49	2.34	-1.40	0.94	-x,-y+1,-z
	C4–H4···F3	3.684(2)	2.78	160	2.82	0.02	0.41	1.87	-1.09	0.78	-x,-y+1,-z
81	C1–H1···F1	3.533(3)	2.63	159	2.66	0.03	0.62	2.83	-1.75	1.08	x-1/2,-y-1/2,-z-2
	C9–H9···F1	3.425(3)	2.48	172	2.51	0.03	0.61	3.98	-2.61	1.37	x+1/2,-y-1/2,-z-2
	C4–H4···F3	3.508(3)	2.76	136	2.79	0.04	0.79	2.31	-1.38	0.93	x+1/2,-y-1/2,-z-2
	C5–H5···F4	3.580(3)	2.66	163	2.69	0.05	0.86	2.46	-1.48	0.98	-x-3/2,-y-1,+z-1/2
	C13–H13···F3	3.405(3)	2.50	158	2.53	0.04	0.71	3.78	-2.44	1.34	-x-2,+y-1/2,-z-3/2
82	C4–H4···F7	3.312(4)	2.68	125	2.72	0.03	0.62	2.93	-1.79	1.13	x-1/2,-y+1/2,z+1/2
	C18–H18···F5	3.378(4)	2.67	132	2.70	0.03	0.61	2.89	-1.79	1.10	x,-y+1,z+1/2
	C17–H17···F1	3.298(4)	2.49	143	2.51	0.04	0.79	3.78	-2.43	1.35	x,-y+1,+z-1/2
	C1–H1···F5	3.387(4)	2.44	175	2.47	0.05	0.86	4.18	-2.78	1.41	x,-y+1,z+1/2
	C24–H24···F6	3.281(4)	2.58	131	2.61	0.04	0.71	3.34	-2.09	1.25	x-1/2,-y+1/2,z-1/2
	C18–H18···F2	3.079(4)	2.48	122	2.52	0.05	0.92	4.46	-2.94	1.53	x+1,-y+1,z+1/2
	C10–H10···F3	3.573(5)	2.67	159	2.66	0.03	0.57	2.66	-1.61	1.04	x+1,+y,+z

	C9–H9···F4	3.478(4)	2.63	149	2.70	0.02	0.52	2.43	-1.46	0.97	x+1,+y,+z
	C22–H22···F8	3.403(5)	2.72	130	2.75	0.02	0.49	2.27	-1.34	0.92	x-1,+y,+z
83	C10–H10···F1	3.456(1)	2.66	142	2.69	0.03	0.56	2.63	-1.59	1.03	$-x+1,+y-\frac{1}{2},-z+\frac{1}{2}$
	C5–H5···F4	3.346(4)	2.68	128	2.73	0.03	0.59	2.74	-1.68	1.06	$-x+2,+y+\frac{1}{2},-z+\frac{3}{2}$
	C9–H9···F4	3.353(2)	2.51	148	2.53	0.04	0.83	3.99	-2.59	1.39	$x-1,-y+\frac{1}{2},z-\frac{1}{2}$
	C1–H1···F4	3.385(1)	2.47	162	2.49	0.05	0.86	4.15	-2.75	1.40	$x-1,-y+\frac{1}{2},z-\frac{1}{2}$
	C5–H5···F3	3.284(3)	2.52	138	2.54	0.04	0.78	3.74	-2.40	1.34	x-1,y+1,+z
84	C5–H5···F7	3.422(2)	2.68	135	2.71	0.03	0.58	2.71	-1.65	1.06	$-x+1,+y+\frac{1}{2},-z+\frac{3}{2}$
	C17–H17···F5	3.316(2)	2.69	124	2.76	0.03	0.62	2.91	-1.81	1.09	-x,-y+1,-z+1
	C24–H24···F6	3.120(2)	2.51	122	2.55	0.05	0.91	4.40	-2.88	1.52	$x,-y+\frac{1}{2},z+\frac{1}{2}$
	C1–H1···F5	3.433(2)	2.49	174	2.52	0.04	0.78	3.75	-2.43	1.31	x,y,z
	C17–H17···F1	3.371(2)	2.56	143	2.59	0.03	0.68	3.20	-2.00	1.20	x,y,z
	C18–H18···F4	3.250(2)	2.56	129	2.60	0.04	0.74	3.52	-2.21	1.31	-x+1,-y+1,-z+1
	C22–H22···F8	3.495(3)	2.73	138	2.76	0.05	0.94	4.57	-3.01	1.56	x+1,+y,+z
	C25–H25···F7	3.507(3)	2.74	138	2.78	0.06	0.84	4.34	-3.23	1.11	x-1,+y,+z
	C9–H9···F4	3.523(2)	2.71	144	2.74	0.04	0.46	2.34	-1.72	0.62	x-1,+y,+z
	C12–H12···F3	3.523(3)	2.71	144	2.74	0.02	0.37	1.73	-1.08	0.65	x+1,+y,+z
	C18–H18···F2	3.058(2)	2.47	120	2.38	0.05	0.94	4.57	-3.01	1.56	x-1,+y,+z-1
86	C5–H5···F3	3.216(5)	2.63	120	2.69	0.03	0.66	3.07	-1.88	1.19	x,+y,+z-1
	C6–H6···F3	3.214(4)	2.63	120	2.69	0.03	0.71	3.33	-2.07	1.26	x,+y,+z-1
	C6–H6···F4	3.594(5)	2.69	159	2.71	0.02	0.52	2.43	-1.46	0.97	x,+y,+z-1
	C4–H4···F3	3.386(4)	2.66	134	2.69	0.03	0.61	2.88	-1.79	1.10	-x+1,-y,-z+1
	C9–H9···F1	3.423(4)	2.70	134	2.73	0.03	0.56	2.63	-1.61	1.02	-x+1,-y,-z+1
	C1–H1···F1	3.854(4)	2.90	178	2.95	0.01	0.30	1.35	-0.77	0.58	-x+1,-y,-z+1
	C5–H5···F4	3.336(4)	2.67	127	2.70	0.03	0.60	2.83	-1.74	1.10	x+1,+y,+z-1
	C12–H12···F2	3.194(4)	2.54	126	2.58	0.04	0.79	3.81	-2.46	1.35	-x-1,-y+1,-z+1
87	C5–H5···F3	3.488(2)	2.58	160	2.61	0.03	0.64	3.02	-1.87	1.15	$x-\frac{1}{2},-y+\frac{1}{2},+z+\frac{1}{2}$
	C6–H6···F6	3.474(3)	2.56	161	2.59	0.04	0.68	3.24	-2.03	1.21	$x+\frac{1}{2},-y+\frac{1}{2},+z+\frac{1}{2}$
	C19–H19···F2	3.554(2)	2.78	139	2.81	0.02	0.45	2.10	-1.24	0.85	$x-\frac{1}{2},-y+\frac{1}{2},+z-\frac{1}{2}$
	C14–H14···F1	3.653(2)	2.73	164	2.84	0.02	0.37	1.67	-0.96	0.71	$x-\frac{1}{2},-y+\frac{1}{2},+z+\frac{1}{2}$
	C1–H1···F5	3.700(2)	2.82	155	2.76	0.02	0.46	2.10	-1.25	0.85	$x+\frac{1}{2},-y+\frac{1}{2},+z-\frac{1}{2}$
	C9–H9···F5	3.547(2)	2.81	135	2.84	0.02	0.42	1.95	-1.16	0.79	$x+\frac{1}{2},-y+\frac{1}{2},+z-\frac{1}{2}$
	C17–H17···F8	3.222(3)	2.56	127	2.60	0.04	0.80	3.83	-2.46	1.37	$-x+\frac{1}{2},+y+\frac{1}{2},-z+\frac{3}{2}$

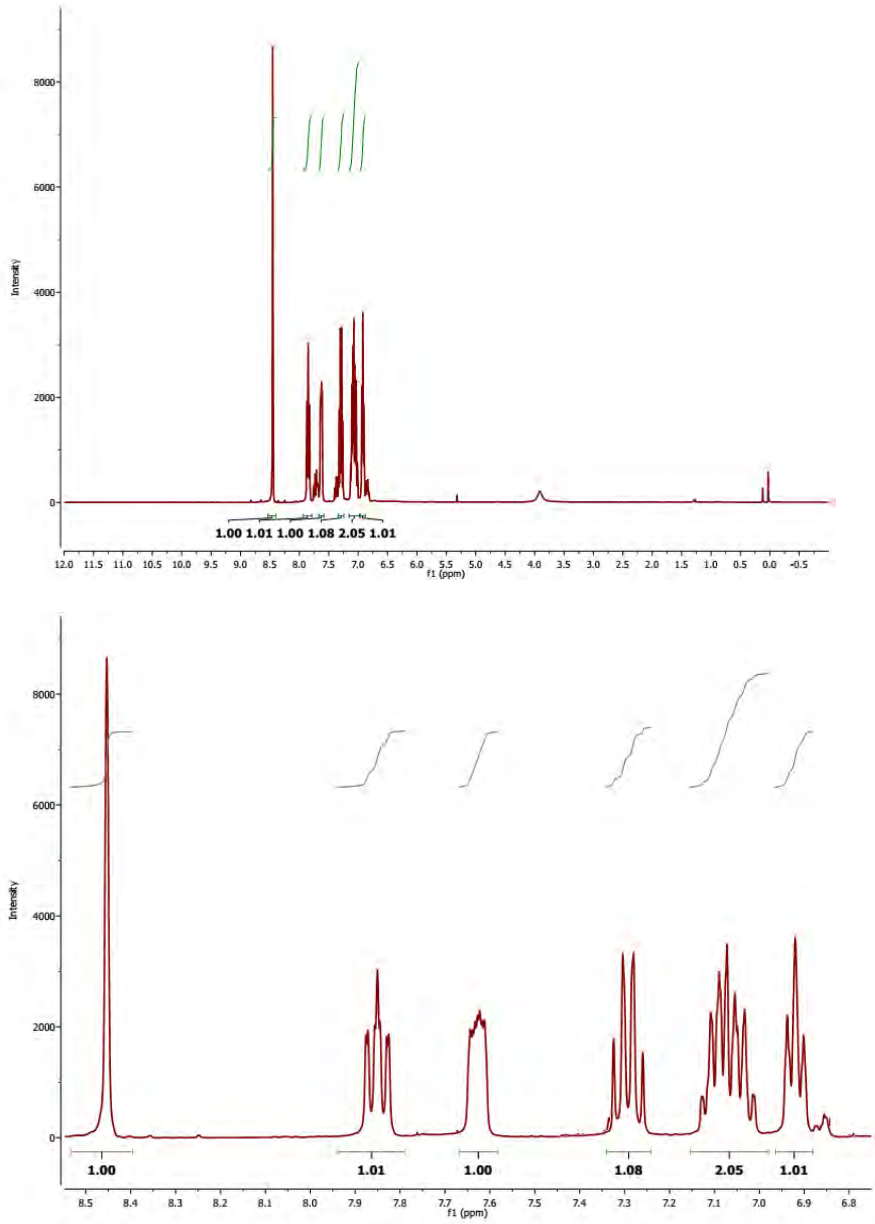
Table S32: Details of the geometrical parameters for the selected C–H···F hydrogen bonds (for dimers of those molecules which are interacting through only one C–H···F hydrogen bond) along with their interaction energies, which have been used to plot 3D graph between interaction energies, distances and angles.

Code	C–H···F	*d* (H···F/Å)	θ (∠C–H···F/^{o})	Symmetry Code	SE_{G09} kcal/mol
52	C11–H11···F2	2.65	123	$x-\frac{3}{2},-y-2,z+\frac{1}{2}$	-1.4
	C4–H4···F2	2.74	153	$x+\frac{1}{2},-y-1,z+\frac{1}{2}$	-0.8
53	C12–H12··· F1	2.45	163	$-x+\frac{3}{2},y+\frac{3}{2},z+\frac{1}{2}$	-1.2
	C4–H4···F3	2.50	129	$1-x,1-y,\frac{1}{2}+z$	-0.1
55	C4–H4···F1	2.66	138	3-x, -y,1-z	-2.0
57	C24–H24···F1B	2.66	125	$-x,y+\frac{1}{2},-z+\frac{1}{2}$	-1.4
	C24 H24···F1A	2.57	144	$-x,+y+\frac{3}{2},-z+\frac{1}{2}$	-0.9
	C11–H11···F5	2.45	151	$-x+1,y+\frac{1}{2},-z+\frac{1}{2}$	-1.3
	C17–H17···F2	2.52	160	$x+1,-y-\frac{1}{2},+z-\frac{1}{2}$	-1.5

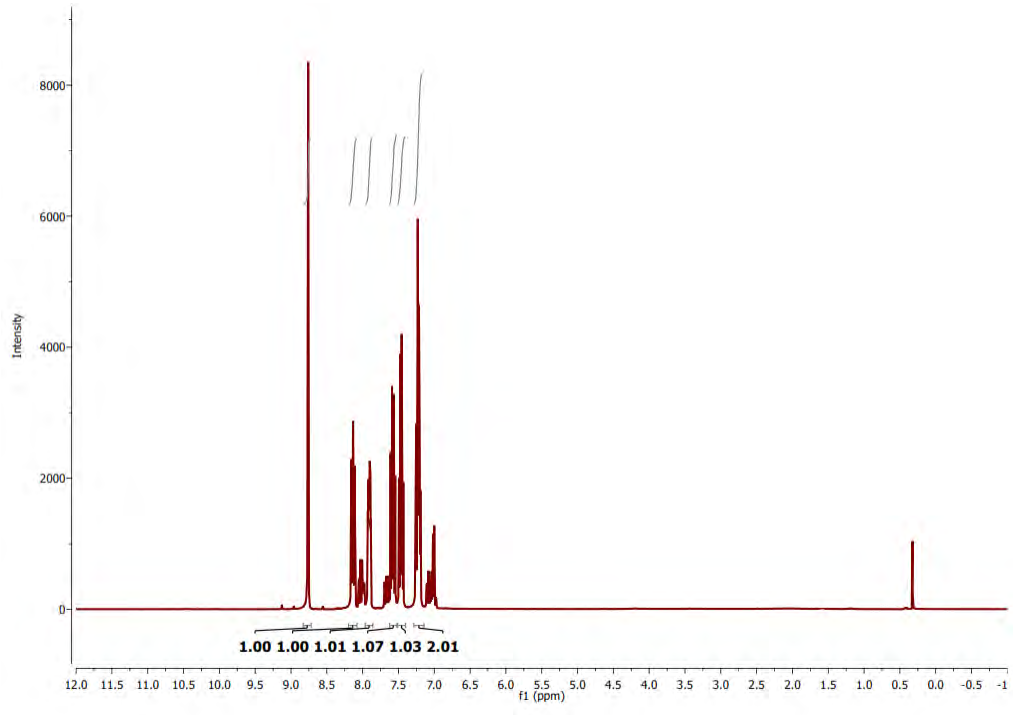
58	C5–H5···F3	2.70	136	x-1,y,z	-0.9
	C10–H10···F6	2.67	130	x,-y,+z-$^1/_2$	-1.0
	C18–H18···F7	2.59	165	x-1,+y-1,+z	-1.1
	C11–H11···F1	2.65	172	x+1,+y-1,+z	-1.0
	C24–H24···F5	2.51	135	x+1,+y,+z	-1.2
59	C10–H10···F3	2.53	147	-x,-y+1,-z	-2.0
	C5–H5···F2	2.56	138	-x+1,y,-z+$^1/_2$	-1.6
	C25–H25···F3	2.63	125	x+$^1/_2$,y-$^1/_2$,z	-1.2
	C18–H18···F1	2.68	156	x-$^1/_2$,y-$^1/_2$,+z	-1.0
60	C5–H5···F1	2.56	138	-x+1,y,-z+$^1/_2$	-1.3
	C11–H11···F3	2.66	162	-x+1,-y,-z	-2.0
61	C11–H11···F1	2.56	141	-x+1/2,-y+1,+z-1/2	-0.8
	C11–H11···F2	2.59	150	-x+1/2+1,-y+1,+z-1/2	-1.0
63	C11–H11···F1	2.51	150	1-x,2-y,1/2+z	-1.5
	C5–H5···F5	2.51	121	-x+1,-y+1,+z-1/2	-2.3
	C5–H5···F5	2.64	148	-x+1,-y,+z-1/2	-1.9
	C24–H24···F4	2.70	126	-x+1,-y+1,+z-1/2	-1.8
	C24–H24···F4	2.55	143	-x+1,-y+2,+z-1/2	-2.0
64	C18–H18···F8	2.69	149	x+1,+y-1,+z+1	-2.1
	C5–H5···F2	2.68	150	x-1,+y+1,+z-1	-2.1
65	C5–H5···F3	2.59	138	x,y+1,z-1	-0.7
66	C1–H1···F1	2.54	162	-x+2,-y+2,-z+1	-3.6
	C5–H5···F3	2.44	151	x,+y-1,z+1	-0.8
	C11–H11···F2	2.61	140	x-1,y+1,+z-1	-1.1
68	C10–H10···F2	2.68	123.	-x+1,+y-$^3/_2$,-z+2	-1.1
69	C11–H11···F4	2.68	144	-x+$^5/_2$,y+$^1/_2$,-z+$^1/_2$	-1.1
	C6–H6···F3	2.64	125	x-$^1/_2$,-y+$^3/_2$,+z-$^1/_2$	-1.3
	C5–H5···F2	2.69	161	-x+1,-y+1,-z	-1.9
70	C11–H11···F3	2.63	160	-x,-y,-z+2	-2.3
	C4–H4···F2	2.52	151	1-x,-1-y,1-z	-1.9
	C6–H6···F2	2.64	132	2-x,-1-y,1-z	-1.6
71	C4–H4···F3	2.4	146	x-1,+y,+z+1	-1.7
	C12–H12···F2	2.76	131	x,+y,+z-1	-1.1
73	C11–H11···F2	2.69	121	-x+$^3/_2$,-y+1,z+$^1/_2$	-1.2
74	C4–H4···F4	2.56	139	-x+1,-y+1,-z+1	-1.5
75	C6–H6···F2	2.59	147	x-$^1/_2$,-y+$^5/_2$,-z	-1.6
77	C17–H17···F7	2.61	131	x-1,+y+1,+z	-1.4
	C18–H18···F6	2.53	133	-x,-y+2,-z+1	-2.1
80	C5–H5···F2	2.63	125	-x+1,-y+2,-z	-1.9
	C5–H5···F4	2.65	121	x,-y+$^3/_2$,+z-$^1/_2$	-1.6
81	C5–H5···F4	2.66	163	-x-$^3/_2$,-y-1,+z-$^1/_2$	-1.1
82	C4–H4···F7	2.68	125	x-$^1/_2$,-y+$^1/_2$,z+$^1/_2$	-1.4
	C18–H18···F5	2.67	132	x,-y+1,z+$^1/_2$	-1.0
87	C5–H5···F3	2.58	160	x-$^1/_2$,-y+$^1/_2$,+z+$^1/_2$	-1.5

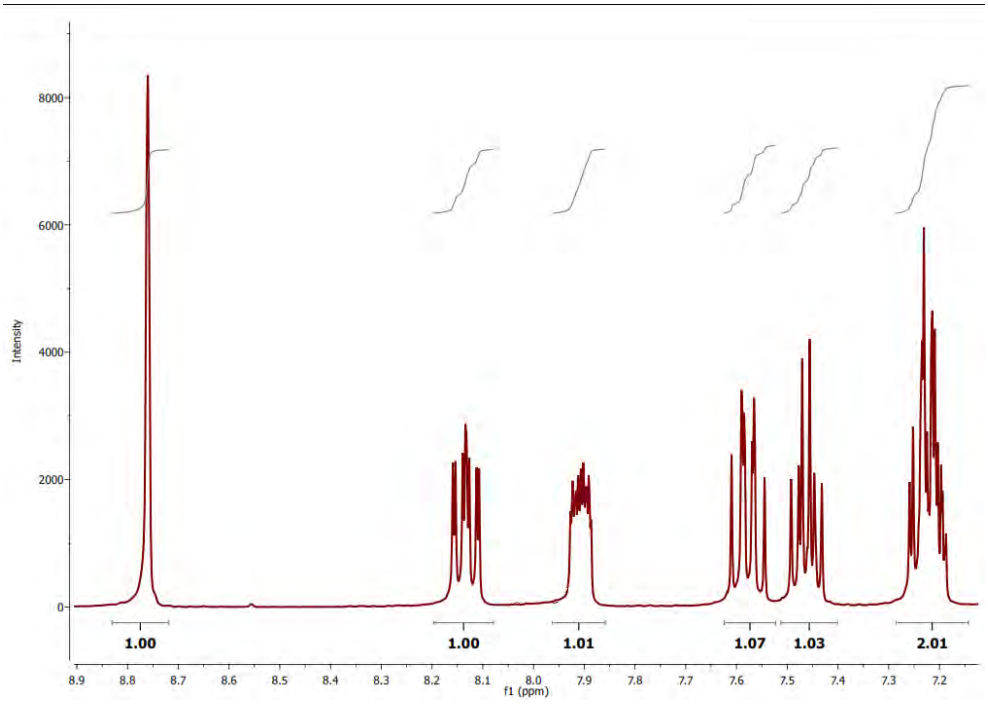
Figure S1: ^{1}H NMR of all compounds: All NMR experiments were recorded on 400 MHz spectrometer (from Bruker) in $CDCl_3$ as solvent.

FigureS1:1 Compound **52**: ^{1}H NMR ($CDCl_3$) δ 8.45 (s, 1H), 7.82-7.88 (t, 1H), 7.60-7.65 (m, 1H), 7.26-7.33 (q, 1H), 7.01-7.13 (m, 2H), 6.89-\6.94 (t, 1H).

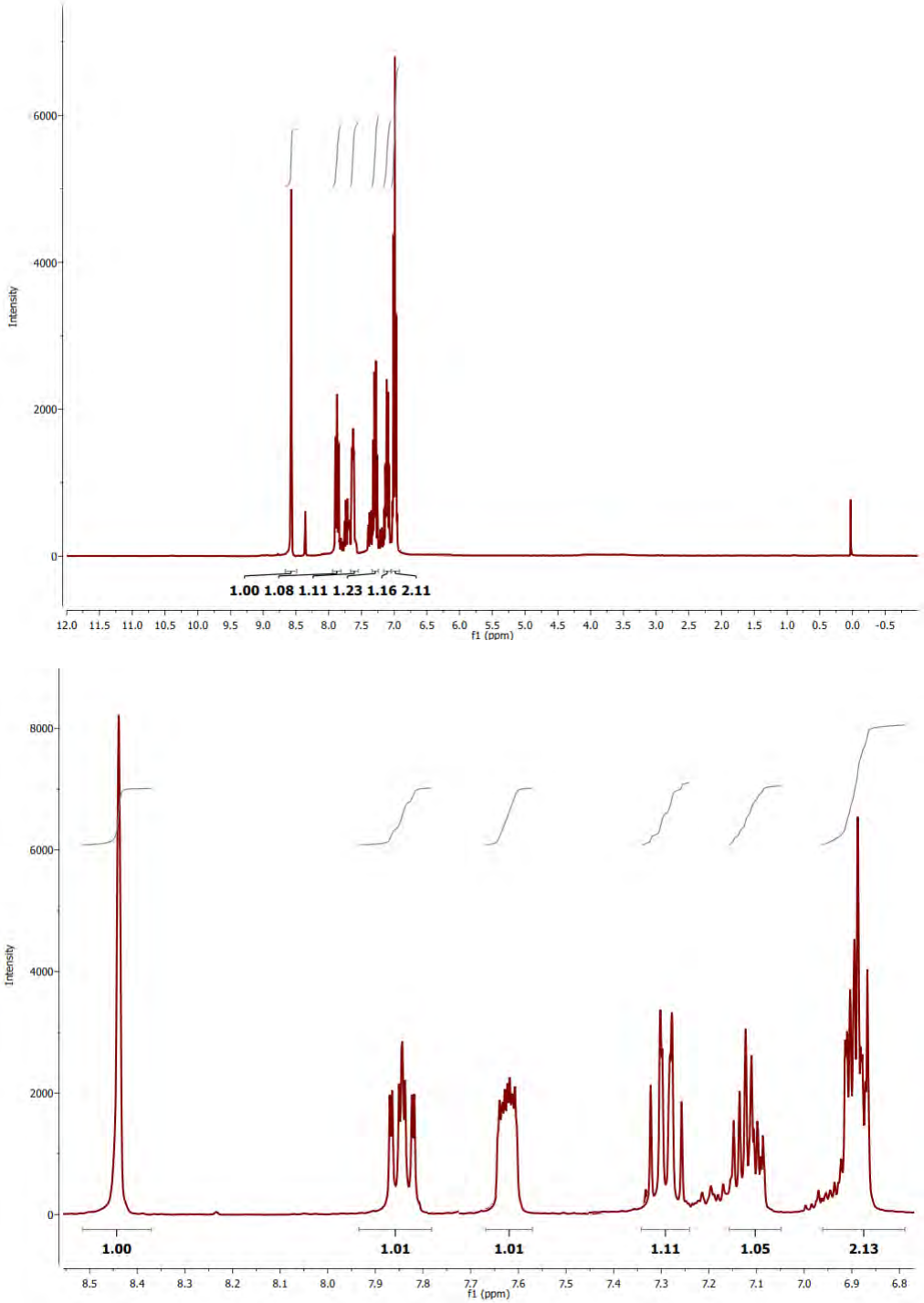


FigureS1:2 Compound **53**: ^{1}H NMR ($CDCl_3$)δ 8.46 (s, 1H), 7.81-7.86 (m, 1H), 7.59-7.63 (m, 1H), 7.25-7.31 (m, 1H), 7.13-7.19 (m, 1H), 6.88-6.96 (m, 2H).

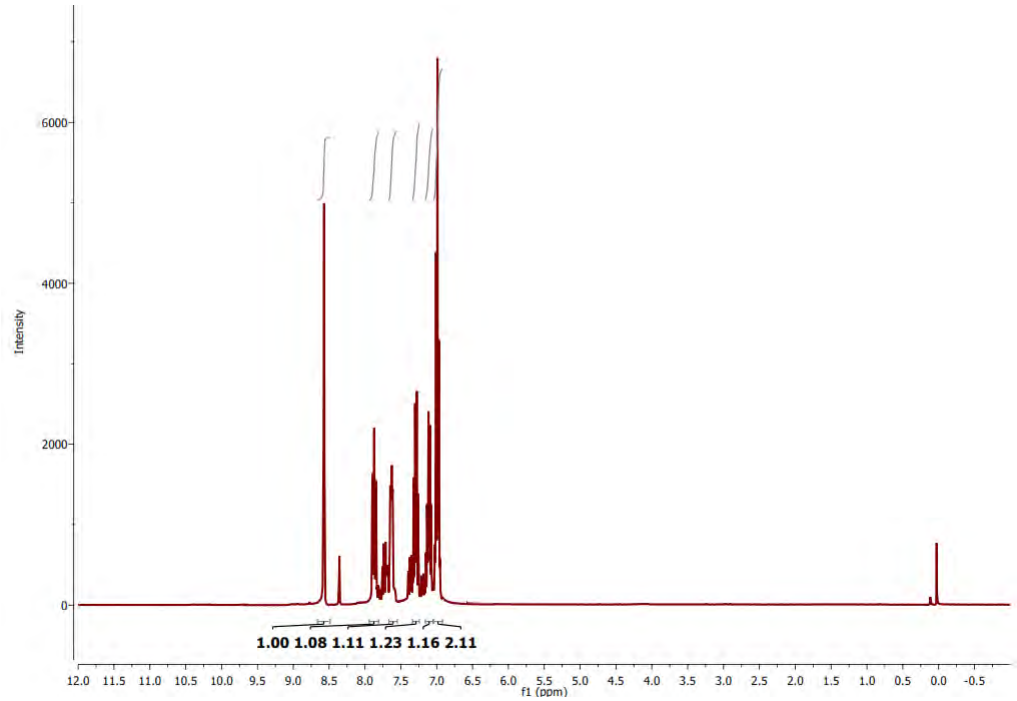


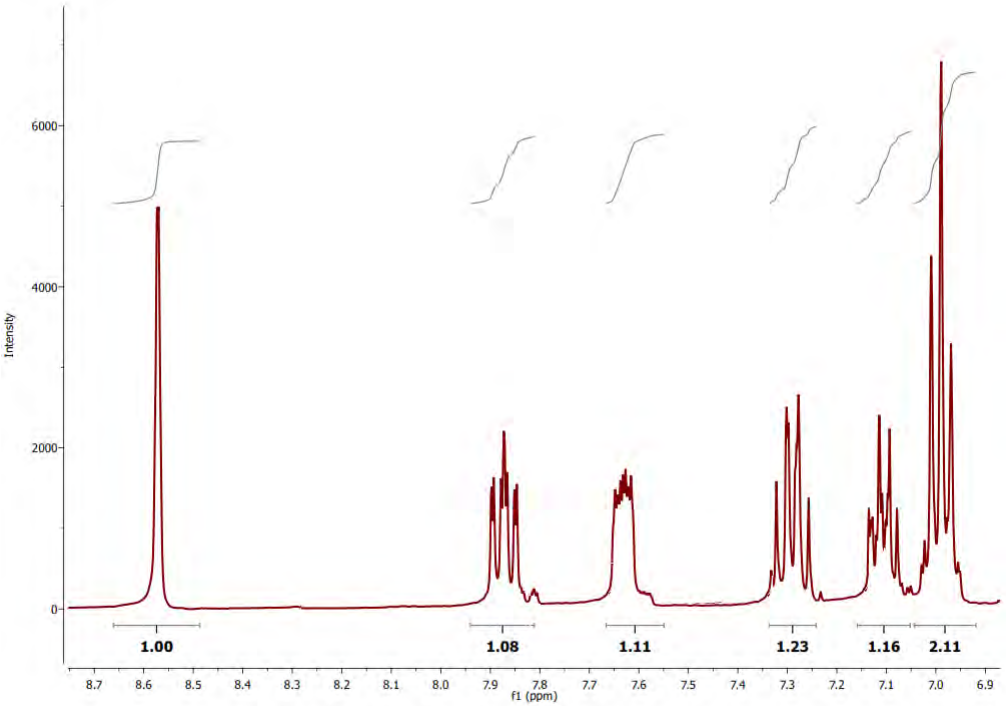


FigureS1:3 Compound **54**: ^{1}H NMR ($CDCl_3$) δ 8.44 (s, 1H), 7.82-7.87 (t, 1H), 7.60-7.64 (m, 1H), 7.25-7.32 (q, 1H), 7.08-7.15 (m, 1H), 6.86-6.91 (m, 2H).

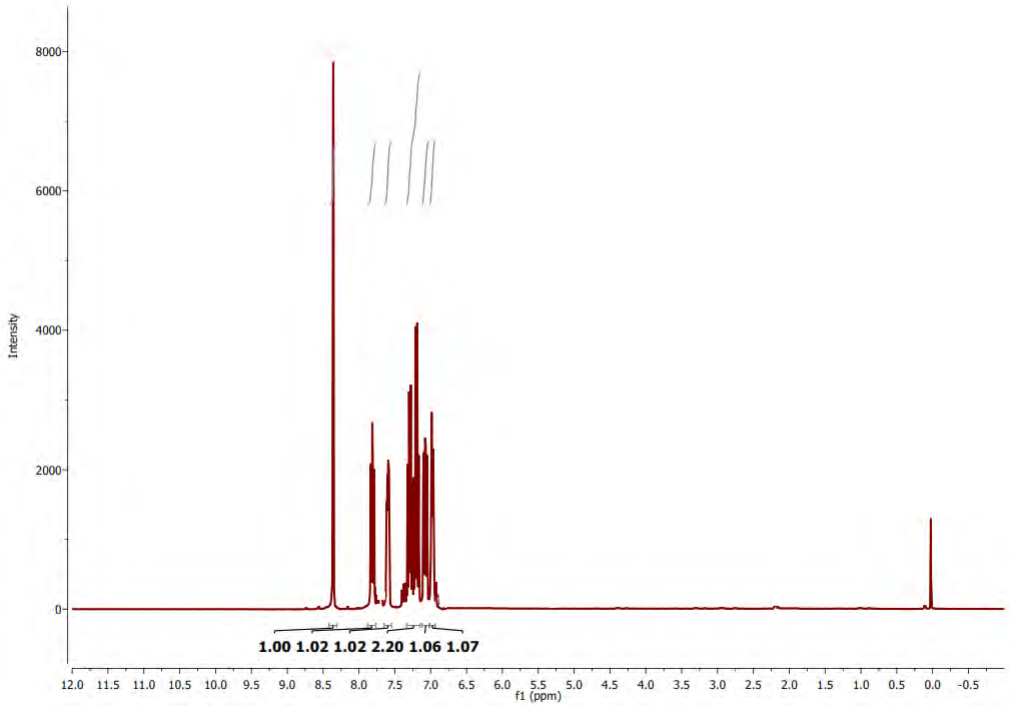


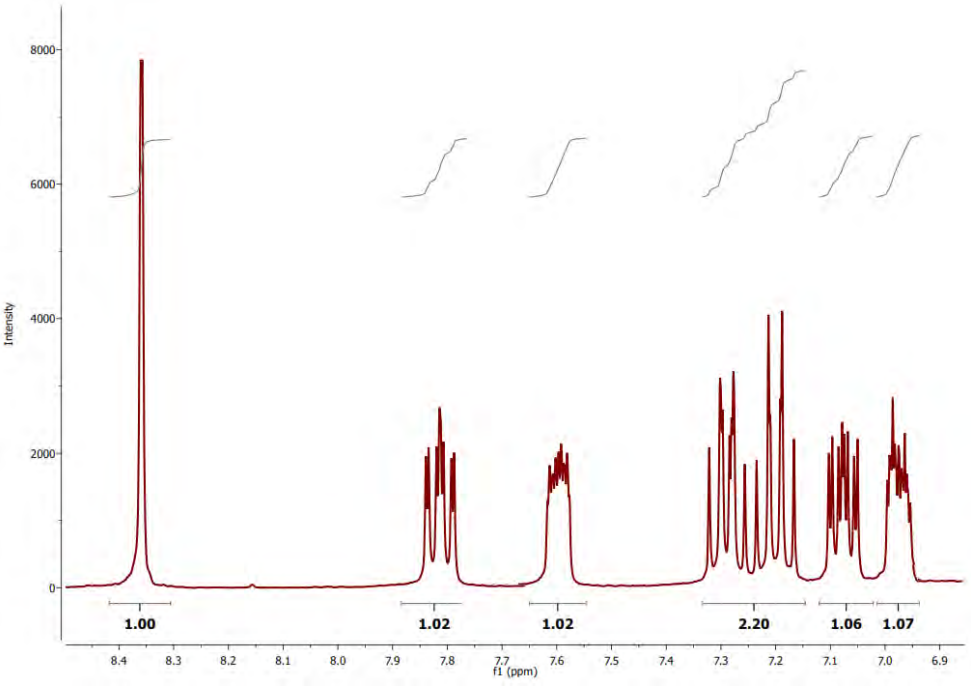
FigureS1:4 Compound **55**: ^{1}H NMR ($CDCl_3$) δ 8.57 (s, 1H), 7.84-7.90 (t, 1H), 7.61-7.65 (m, 1H), 7.25-7.32 (q, 1H), 7.07-7.12 (m, 1H), 6.96-7.01 (t, 2H).



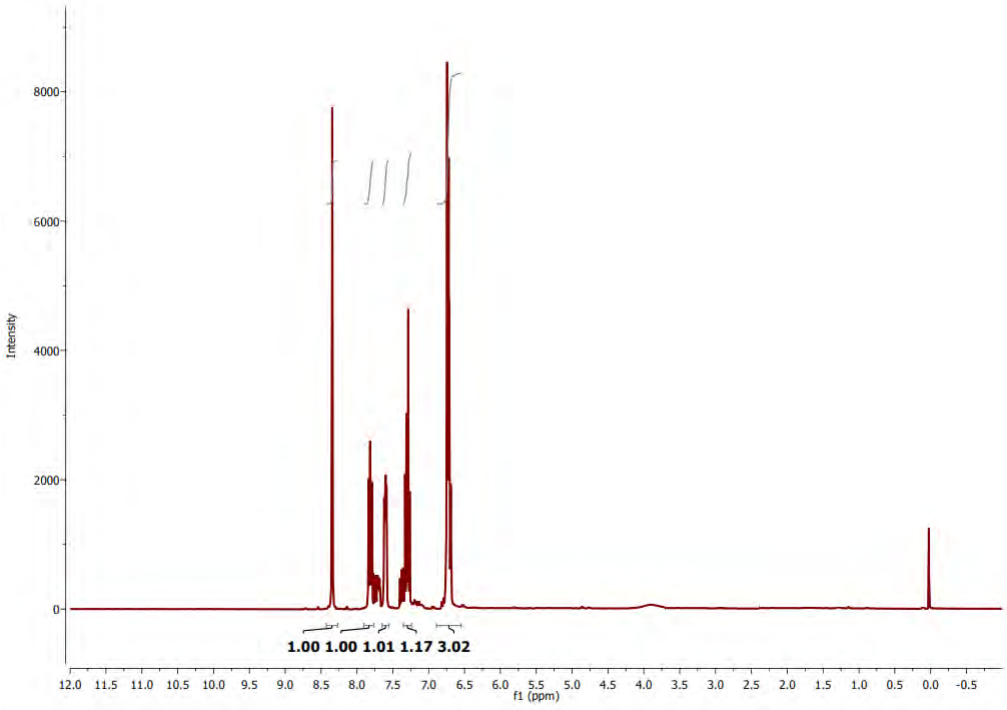


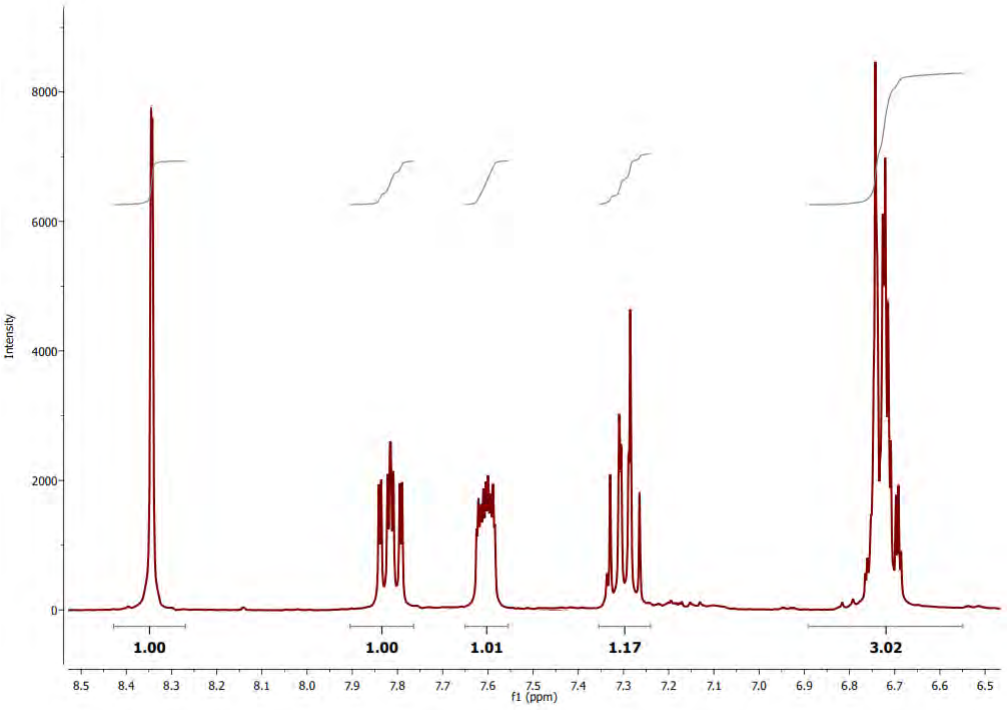
FigureS1:5 Compound **56**: ^{1}H NMR ($CDCl_3$) δ 8.36 (s, 1H), 7.79-7.84 (m, 1H), 7.58-7.62 (m, 1H), 7.16-7.32 (m, 2H), 7.05-7.10 (m, 1H), 6.95-6.99 (m, 1H).



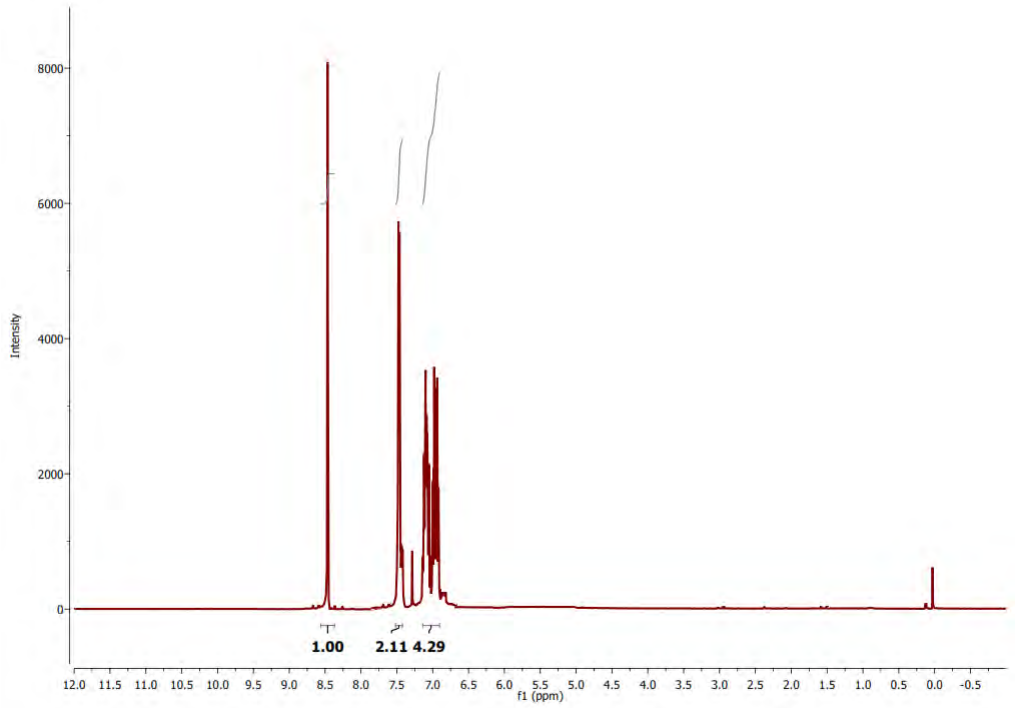


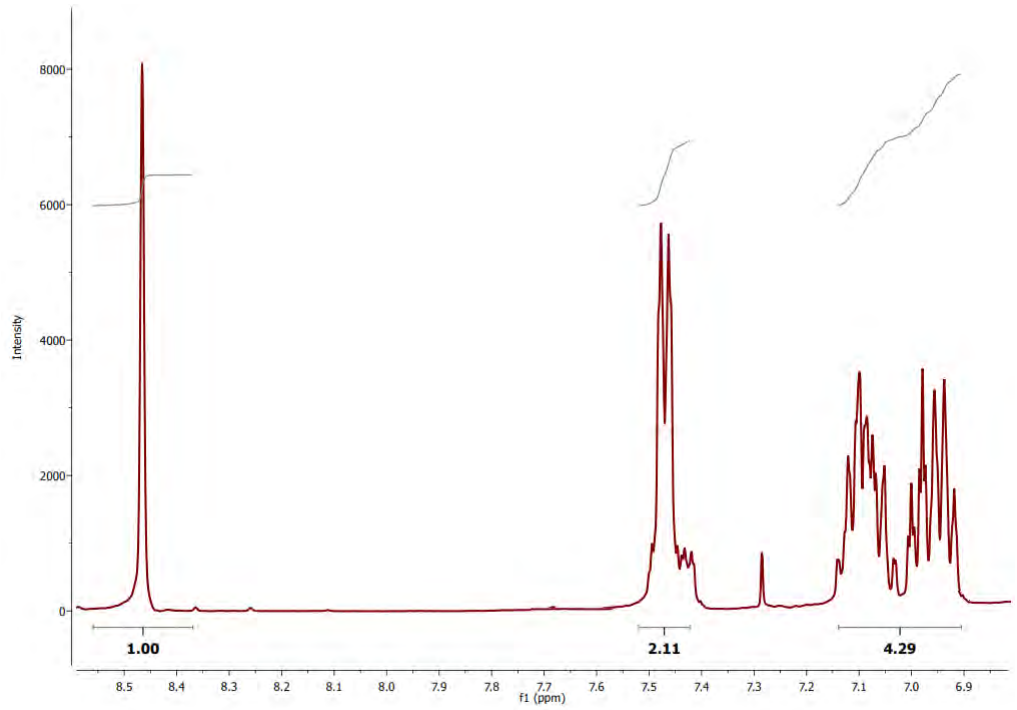
FigureS1:6 Compound **57**: ^{1}H NMR ($CDCl_3$) δ 8.34 (s, 1H), 7.78-7.83 (t, 1H), 7.58-7.63 (m, 1H), 7.26-7.33 (q, 1H), 6.69-6.75 (m, 3H).



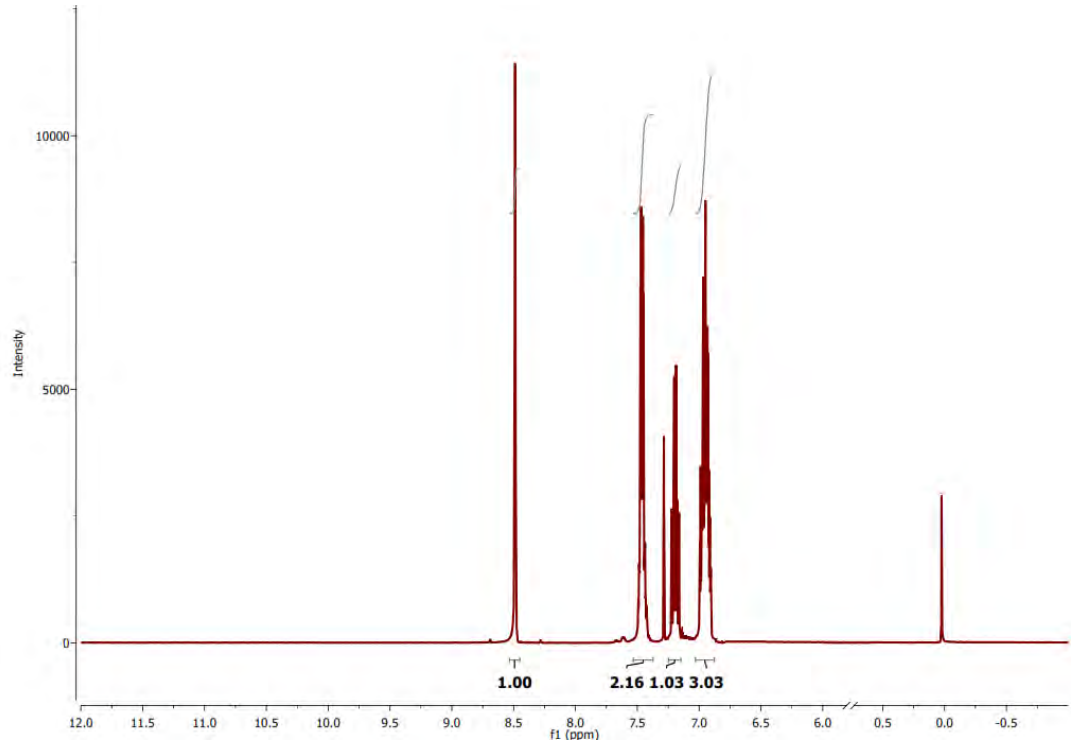


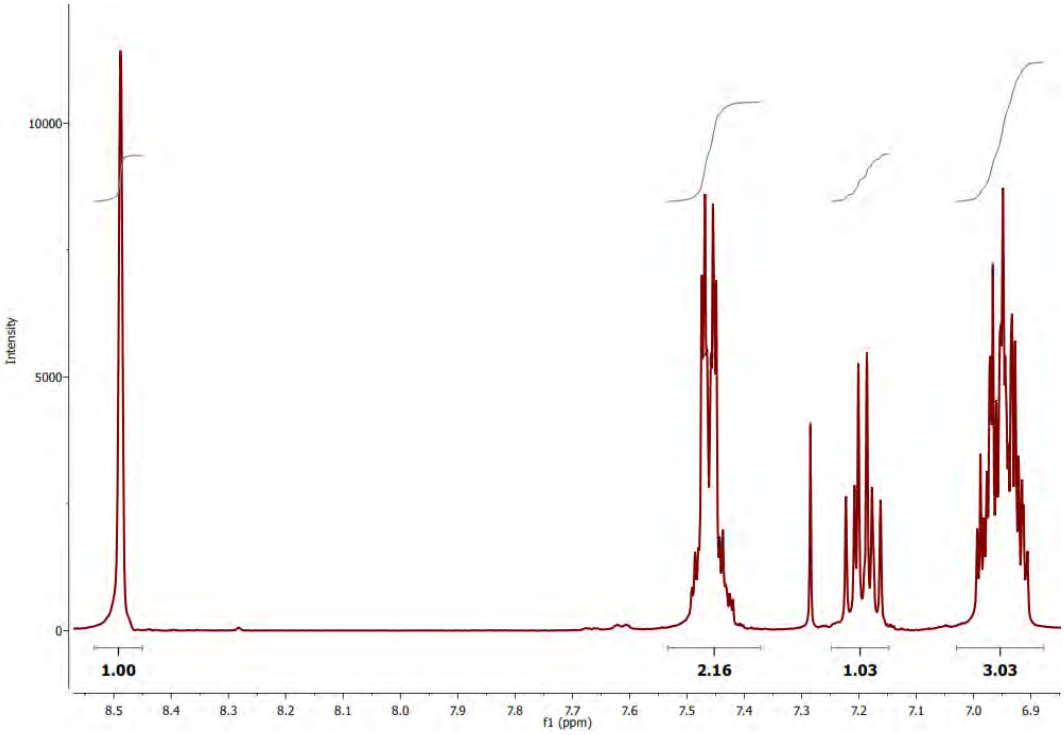
FigureS1:7 Compound **58**: ^{1}H NMR ($CDCl_3$) δ 8.47 (s, 1H), 7.45-7.49 (m, 2H), 7.05-7.13 (m, 2H), 6.92-7.01 (m, 2H).



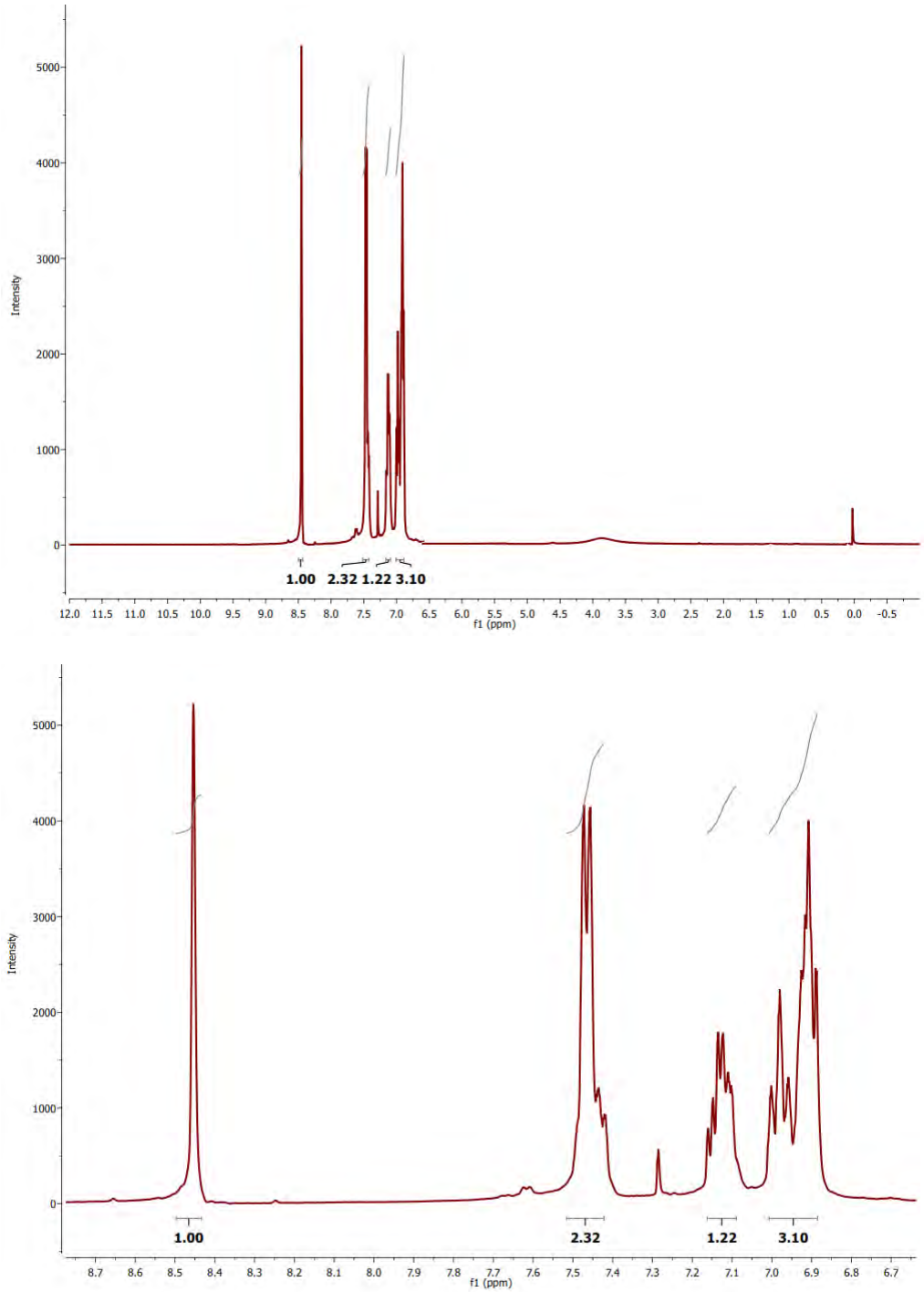


FigureS1:8 Compound **59**: ^{1}H NMR ($CDCl_3$) δ 8.49 (s, 1H), 7.44-7.48 (m, 2H), 7.16-7.22 (m, 1H), 6.91-7.00 (m, 3H).

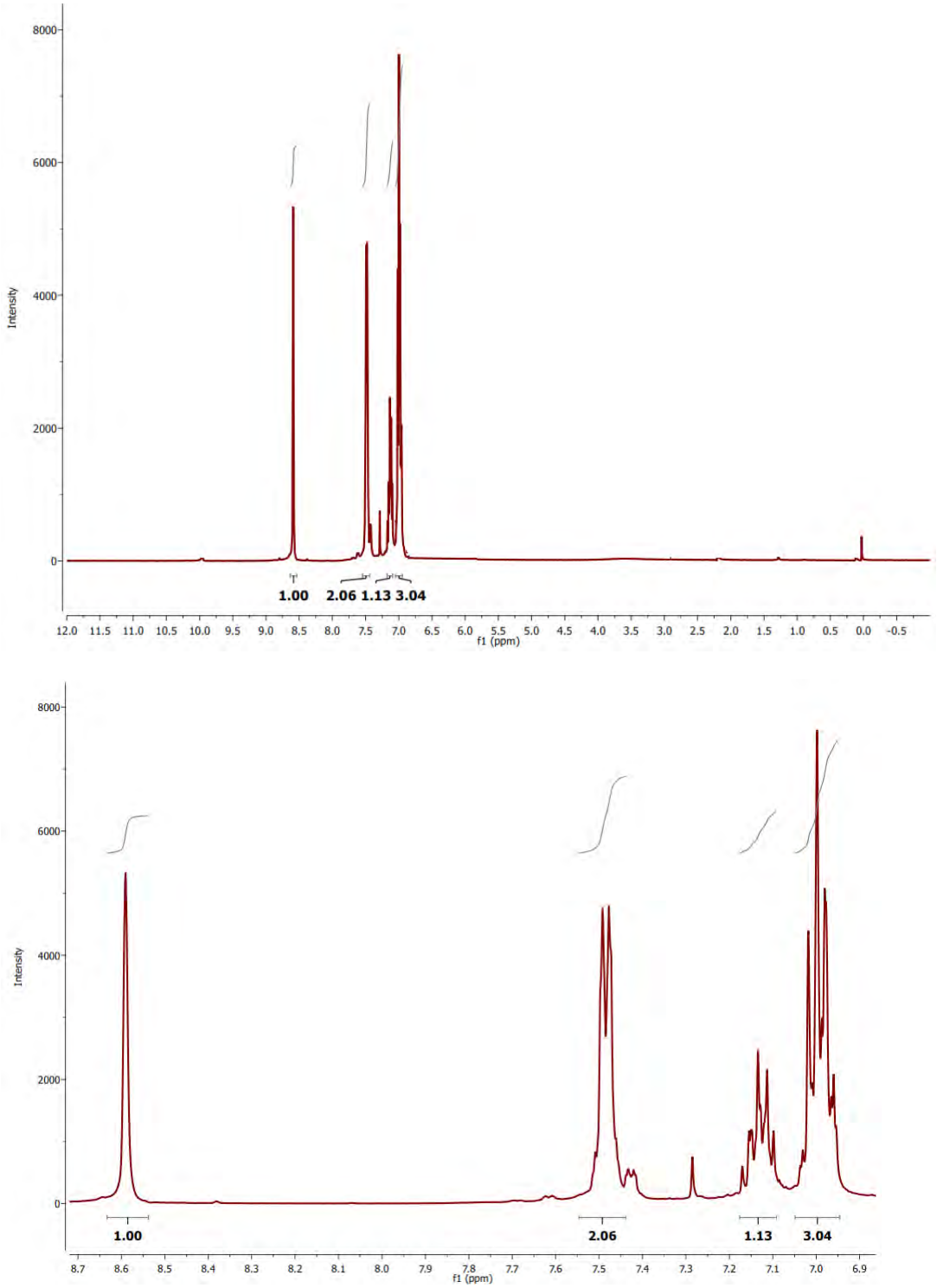




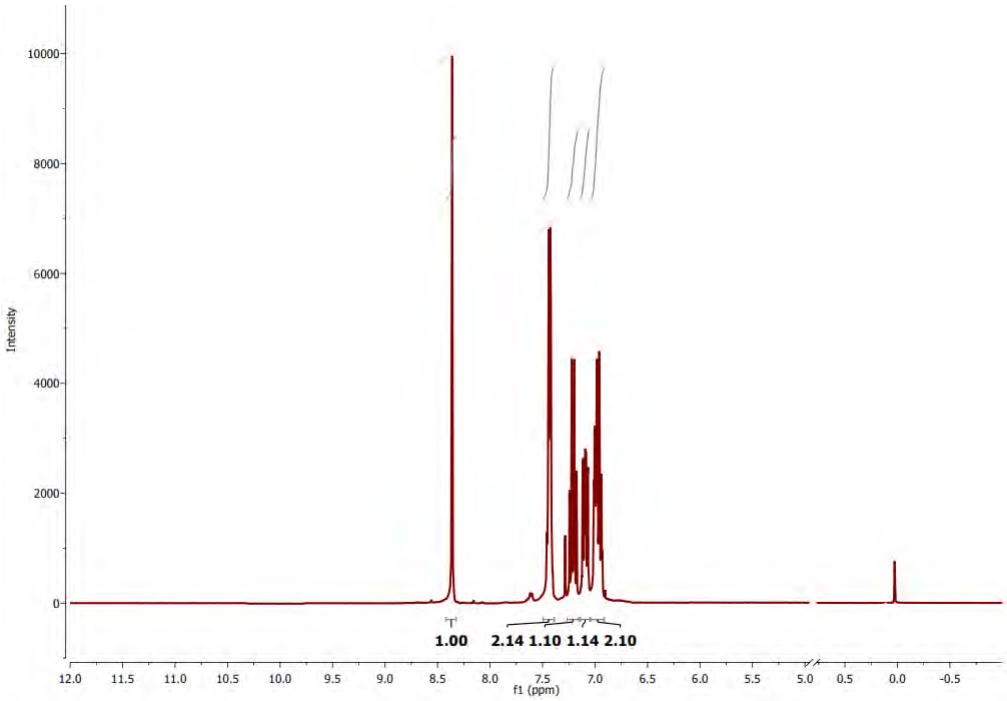
FigureS1:9 Compound **60**: ^{1}H NMR ($CDCl_3$) δ 8.45 (s, 1H), 7.42-7.49 (m, 2H), 7.10-7.16 (m, 1H), 6.88-7.00 (m, 3H).

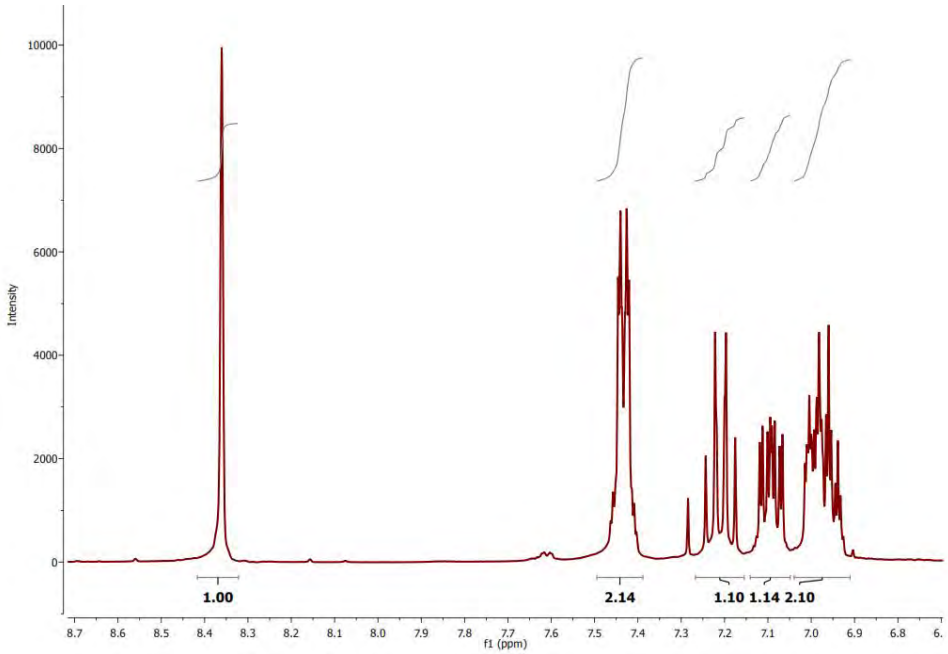


FigureS1:10 Compound **61**: ^{1}H NMR ($CDCl_3$) δ 8.59 (s, 1H), 7.46-7.49 (m, 2H), 7.09-7.15 (m, 1H), 6.95-7.03 (m, 3H).

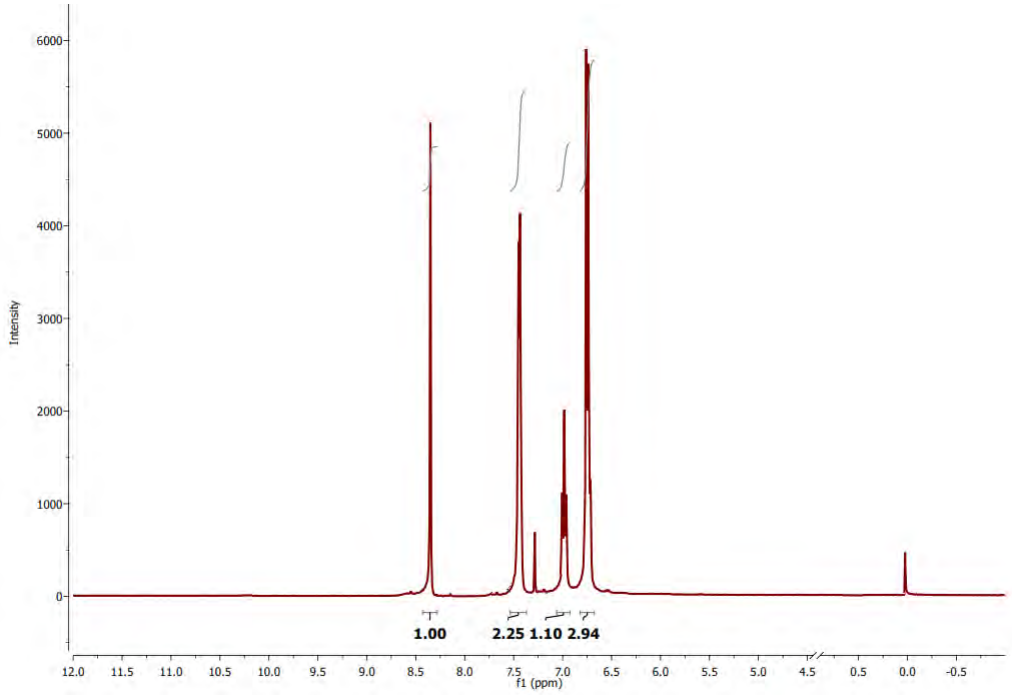


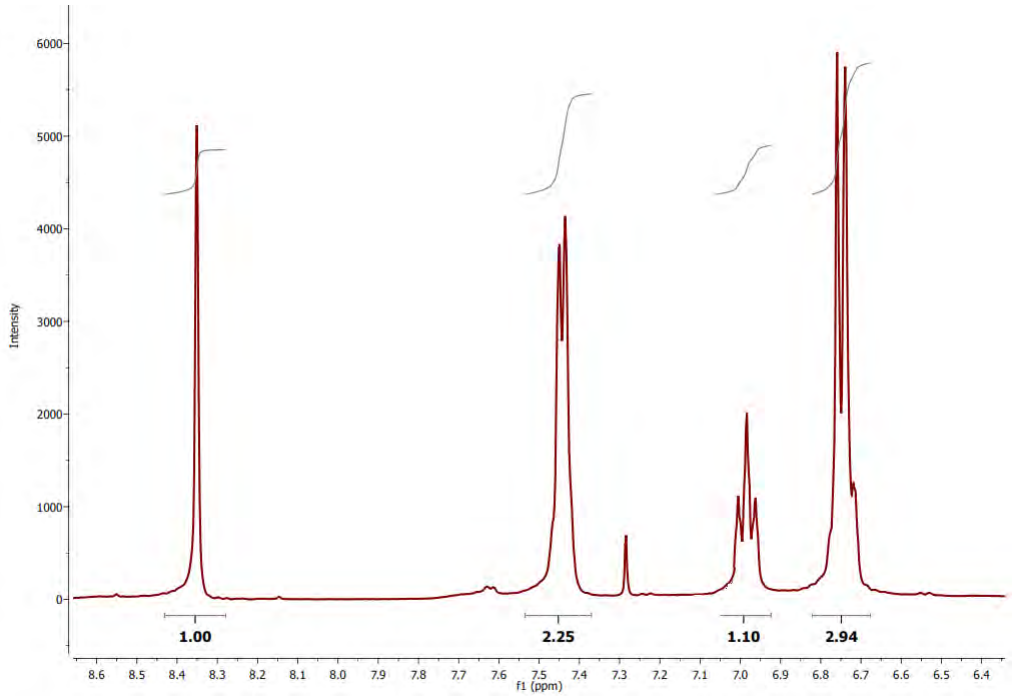
FigureS1:11 Compound **62**: ^{1}H NMR ($CDCl_3$) δ 8.36 (s, 1H), 7.42-7.45 (m, 2H), 7.17-7.25 (q, 1H), 7.06-7.12 (m, 1H), 6.93-7.01 (m, 2H).



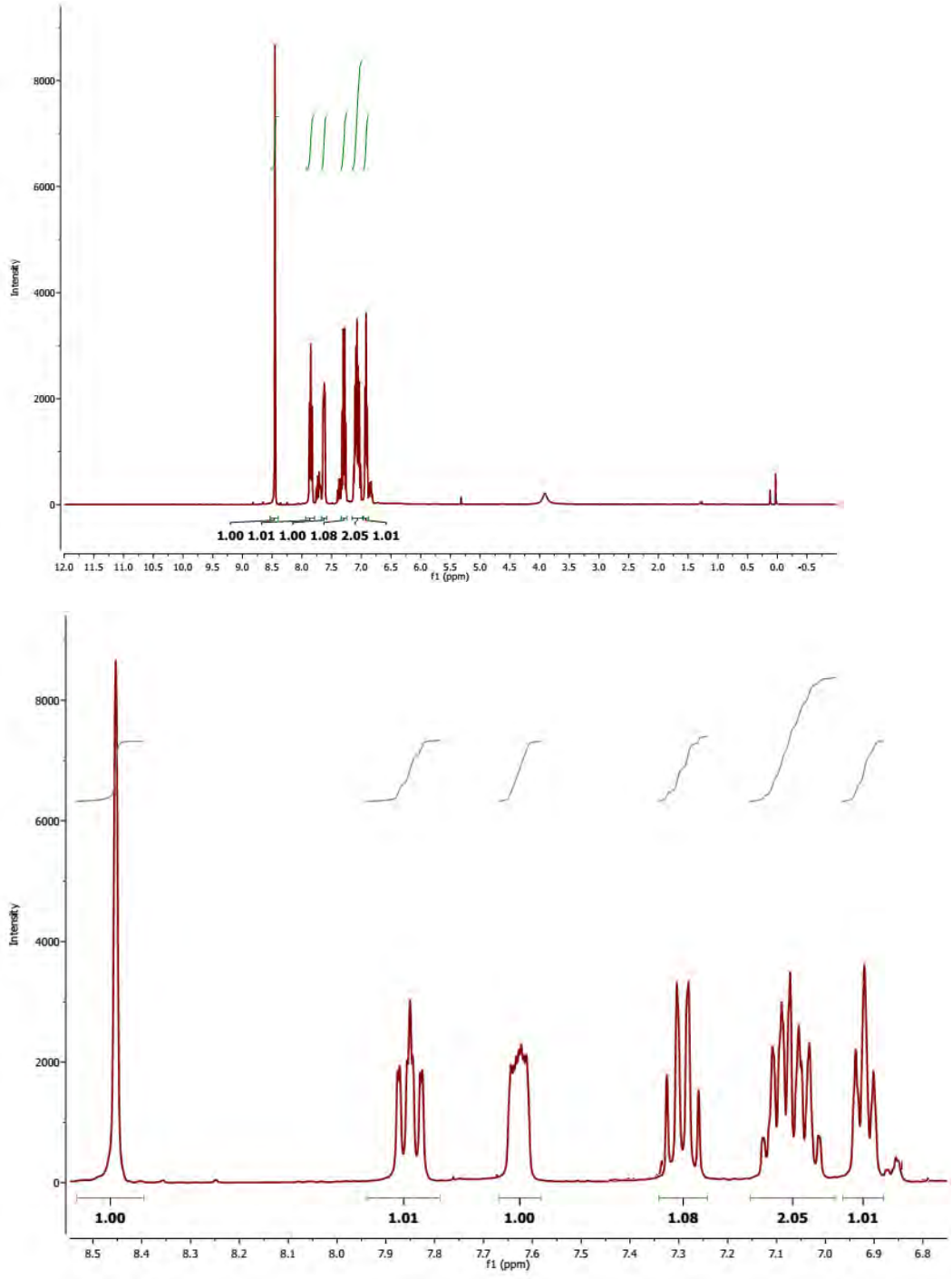


FigureS1:12 Compound **63**: ^{1}H NMR ($CDCl_3$) δ 8.35 (s, 1H), 7.42-7.45 (d, 2H), 6.96-7.01 (t, 1H), 6.71-6.77 (m, 3H).

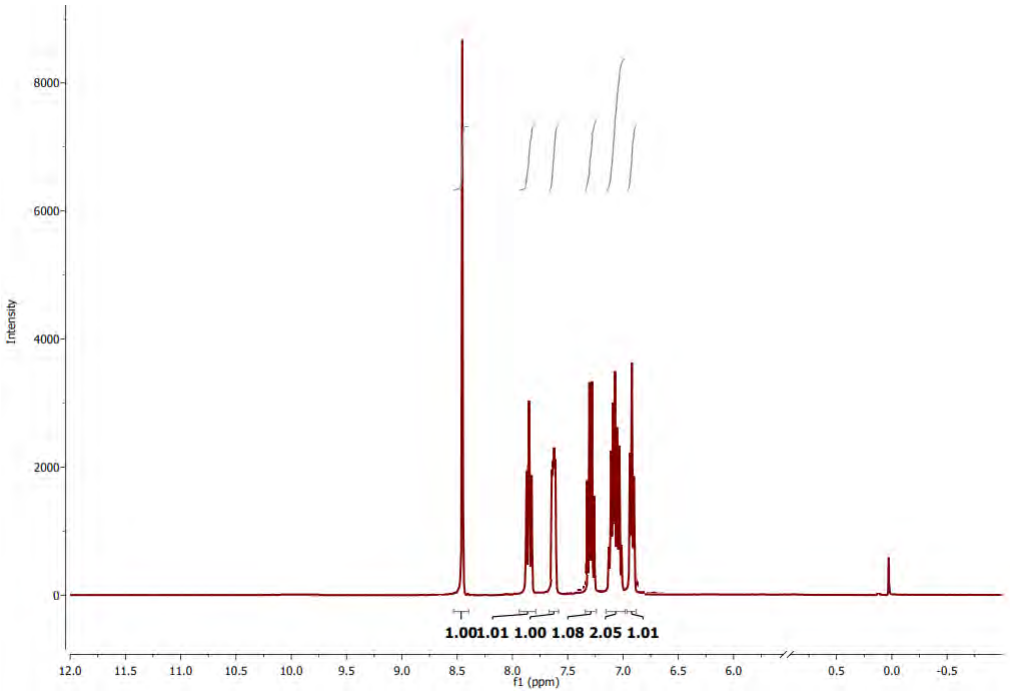


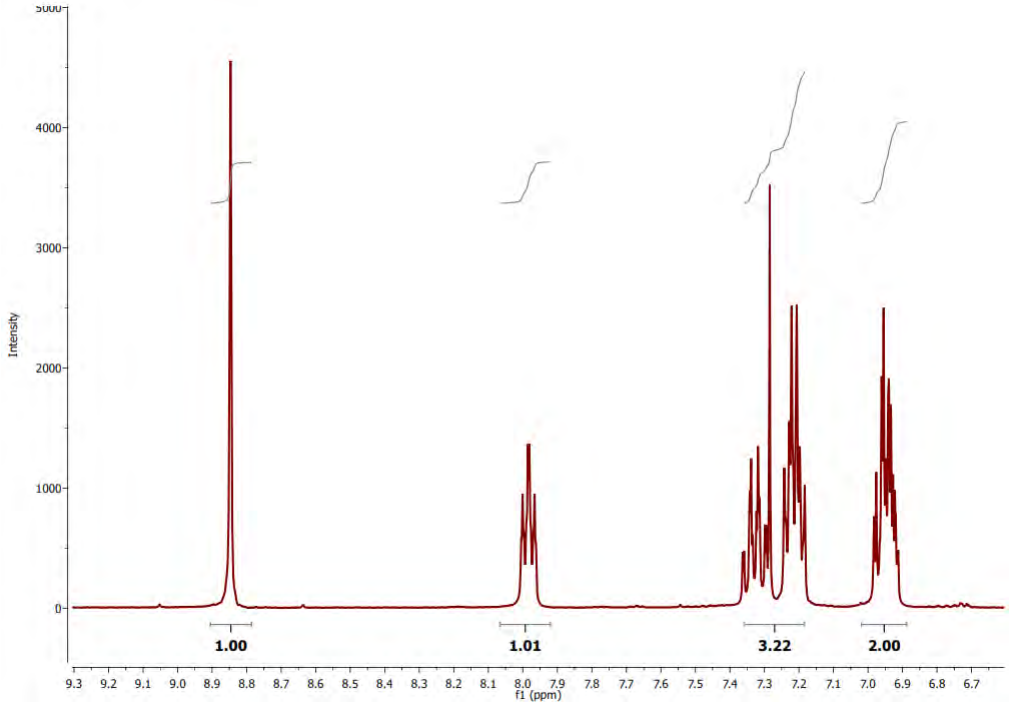


FigureS1:13 Compound **64**: ^{1}H NMR ($CDCl_3$) δ 8.45 (s, 1H), 7.82-7.88 (t,1H), 7.60-7.65 (m, 1H), 7.26-7.33 (q, 1H), 7.01-7.13 (m, 2H), 6.89-6.94 (t, 1H).

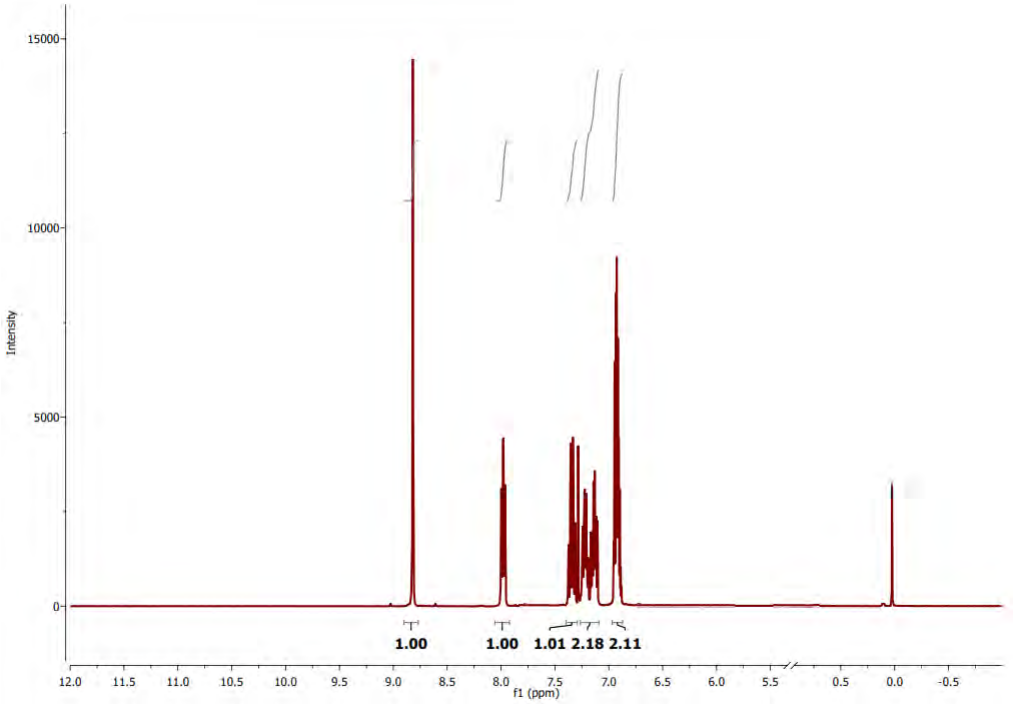


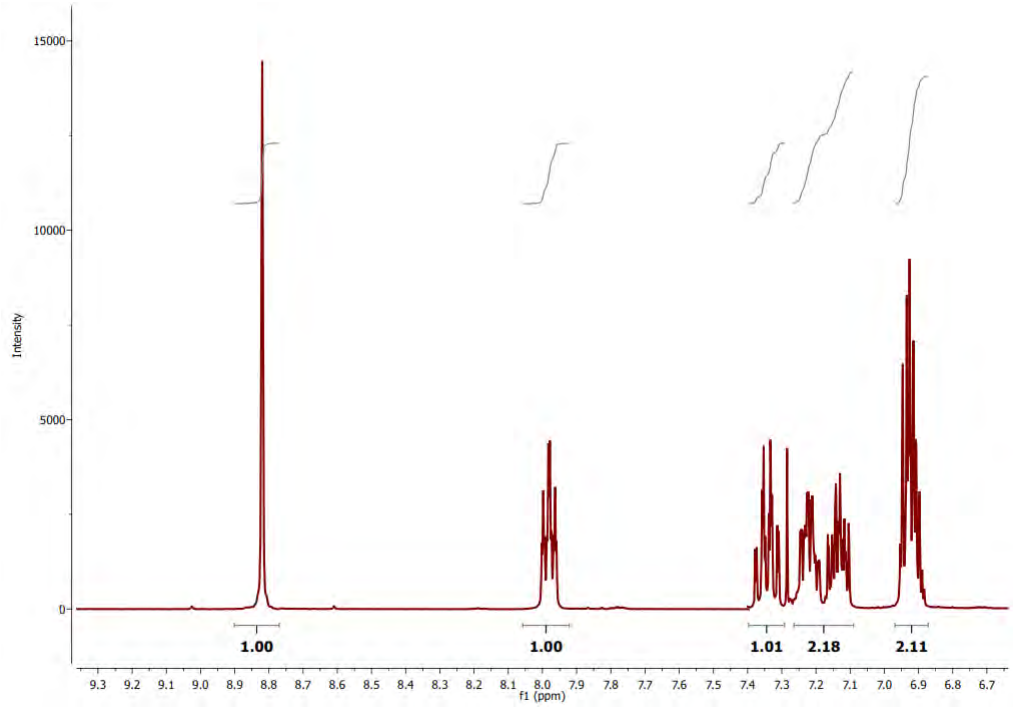
FigureS1:14 Compound **65**: ^{1}H NMR ($CDCl_3$) δ 8.8 (s, 1H), 7.96-8.01 (t,1H), 7.18-7.36 (m, 3H), 6.91-6.98 (m, 2H).



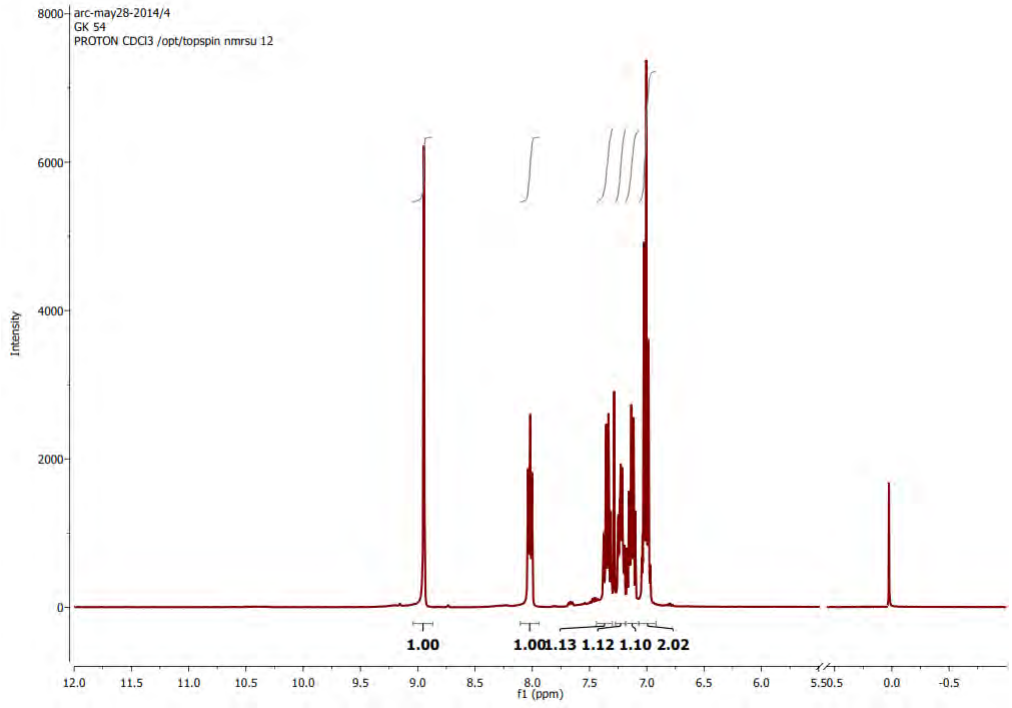


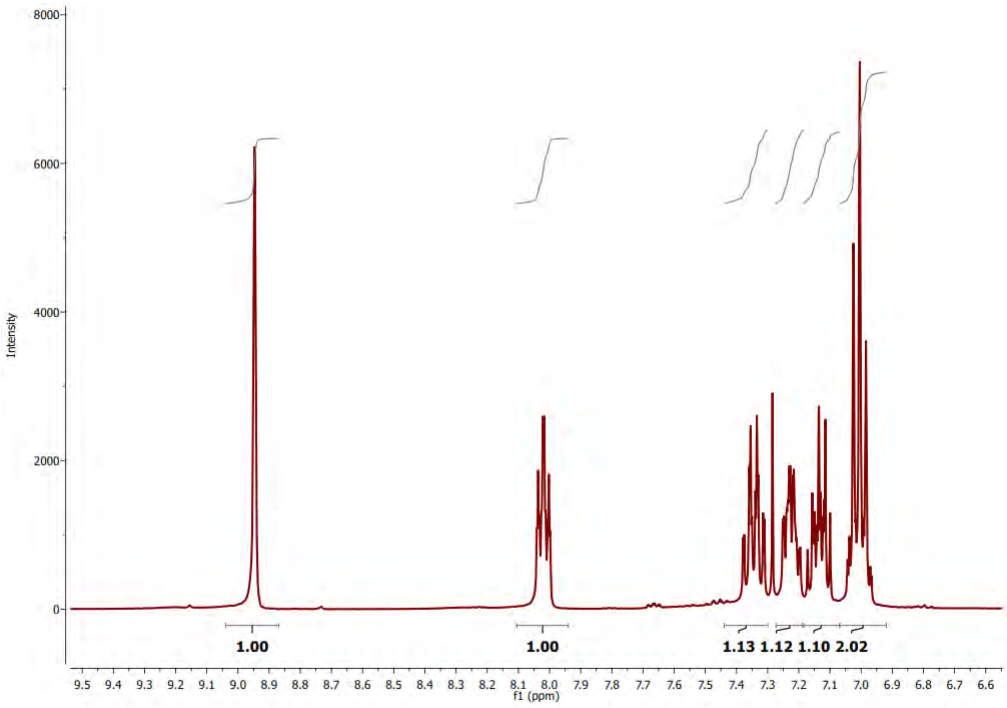
FigureS1:15 Compound **66**: ^{1}H NMR ($CDCl_3$) δ 8.81 (s, 1H), 7.95-8.01 (t,1H), 7.31-7.38 (m, 1H), 7.10-7.25 (m, 2H), 6.89-6.95 (m, 2H).



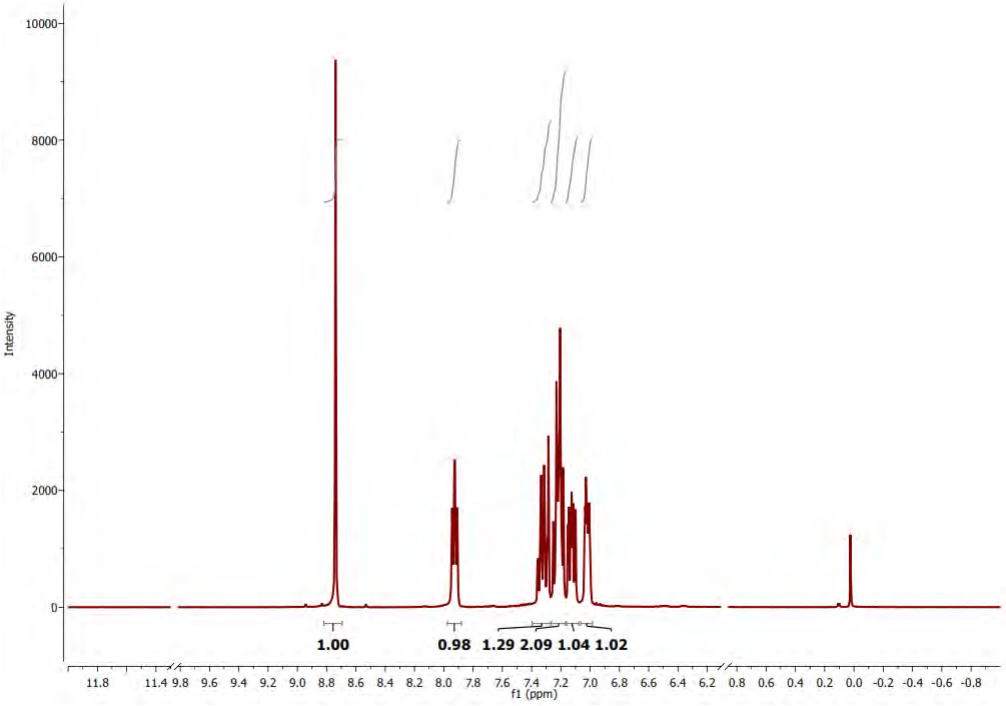


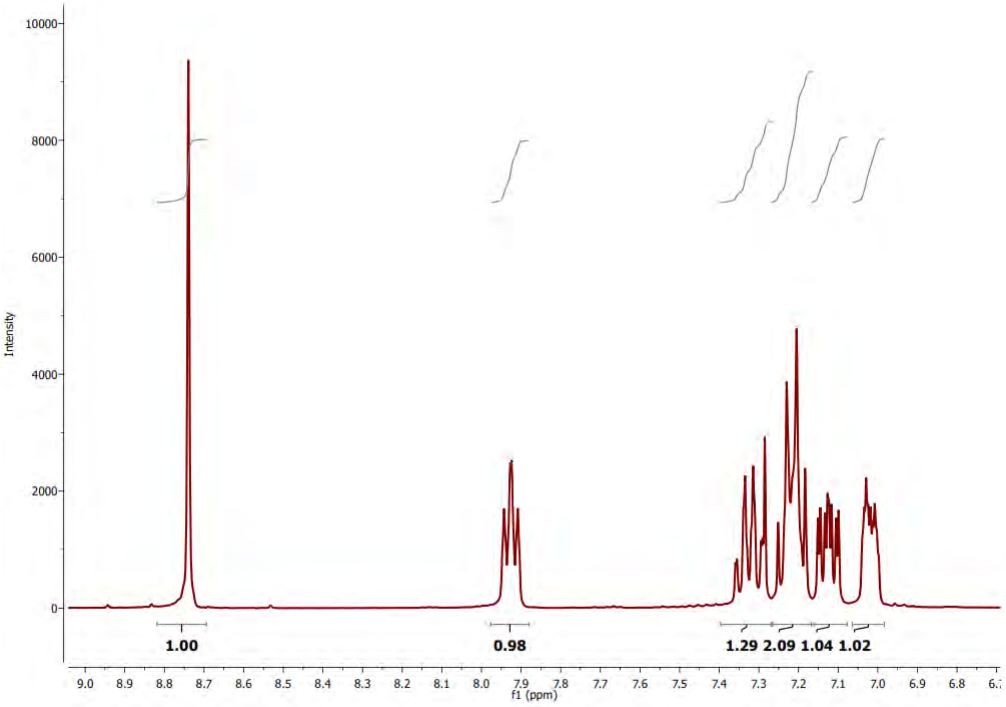
FigureS1:16 Compound **67**: ^{1}H NMR ($CDCl_3$) δ 8.95 (s, 1H), 8.00-8.04 (t,1H), 7.30-7.38 (m, 1H), 7.10-7.25 (m, 2H), 6.97-7.04 (m, 2H).



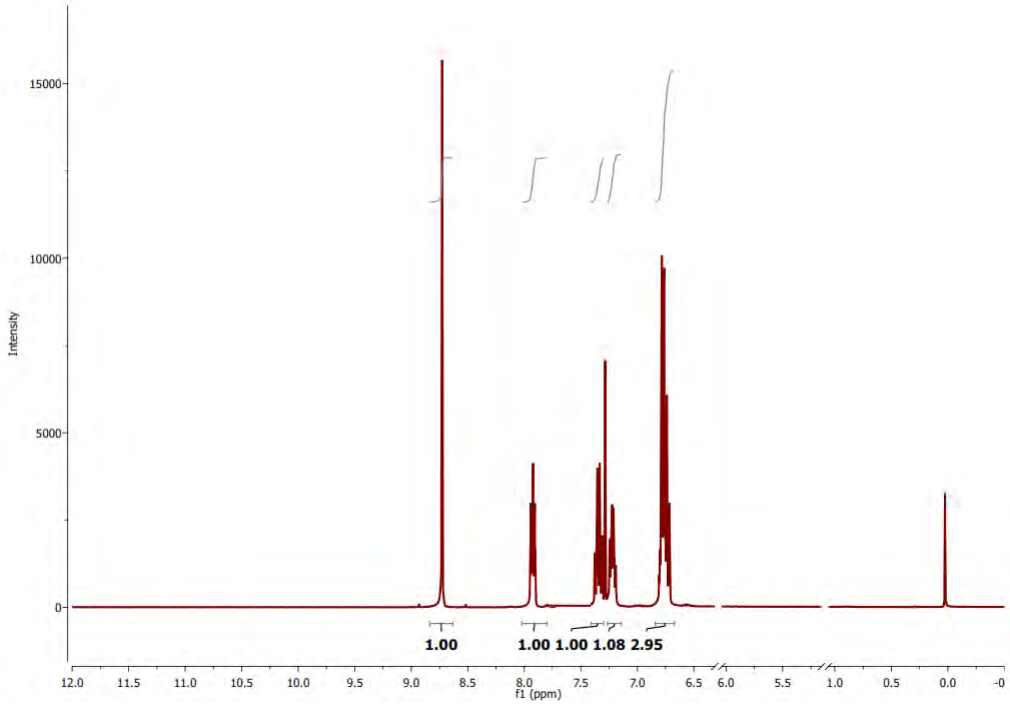


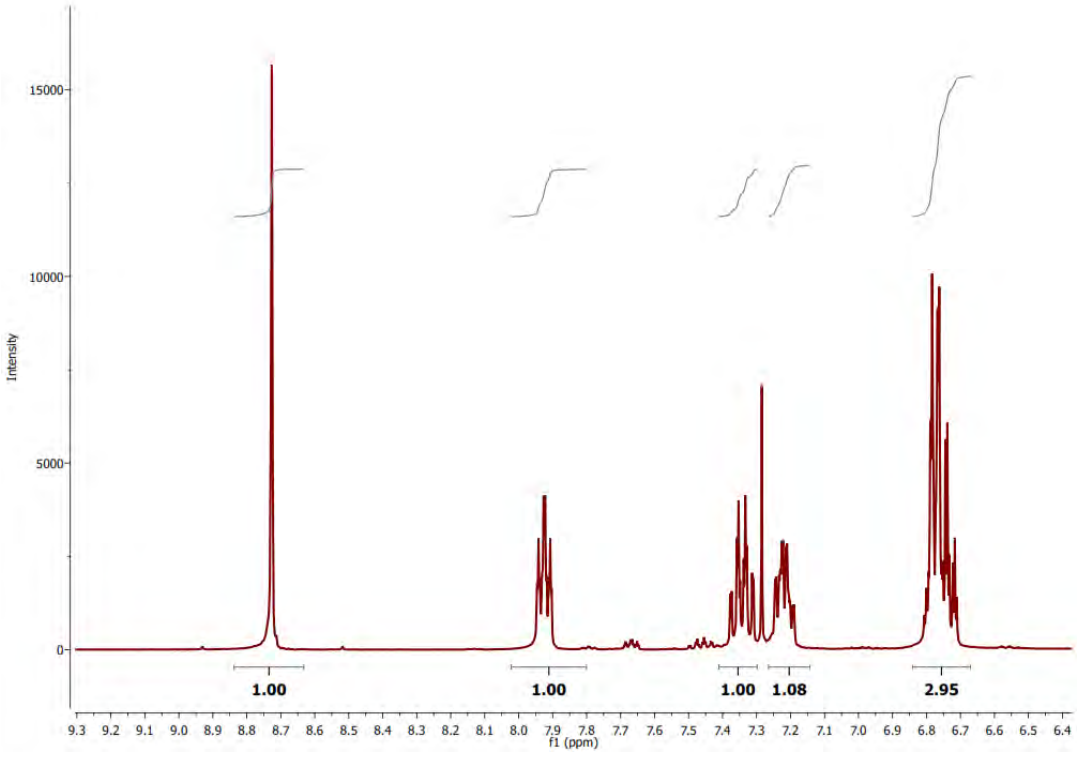
FigureS1:17 Compound **68**: ^{1}H NMR ($CDCl_3$) δ 8.74 (s, 1H), 7.90-7.95 (t,1H), 7.29-7.35 (m, 1H), 7.18-7.24 (m, 2H), 7.09-7.15 (m, 1H), 6.99-7.04 (m, 1H).



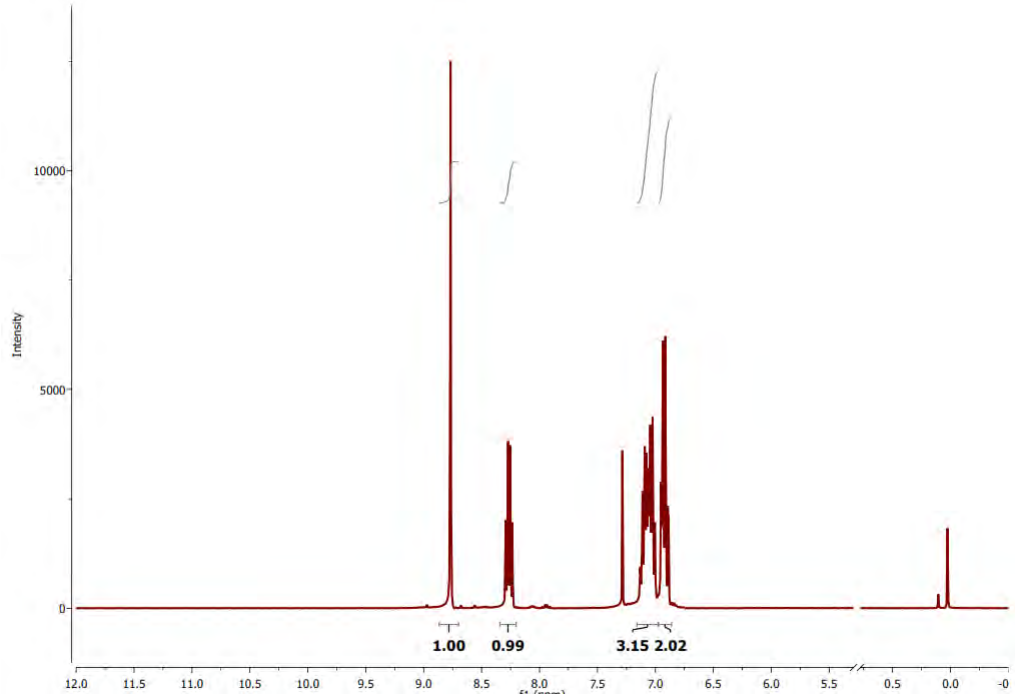


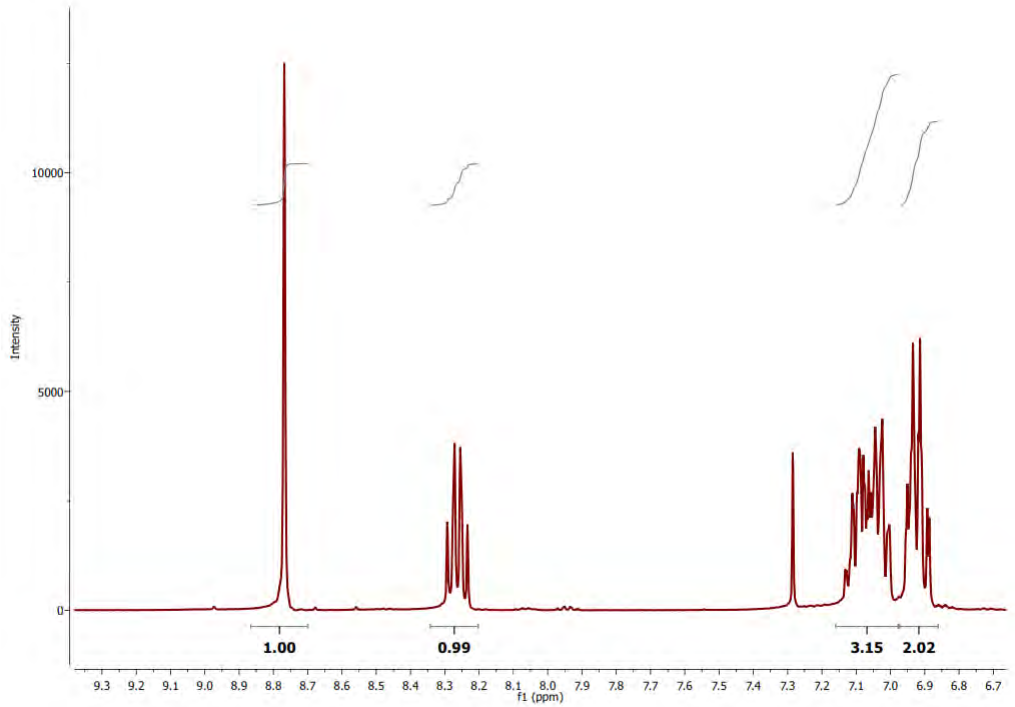
FigureS1:18 Compound **69**: ^{1}H NMR ($CDCl_3$) δ 8.73 (s, 1H), 7.90-7.94 (t,1H), 7.30-7.37 (m, 1H), 7.19-7.25 (m, 1H), 6.71-6.81 (m, 3H).



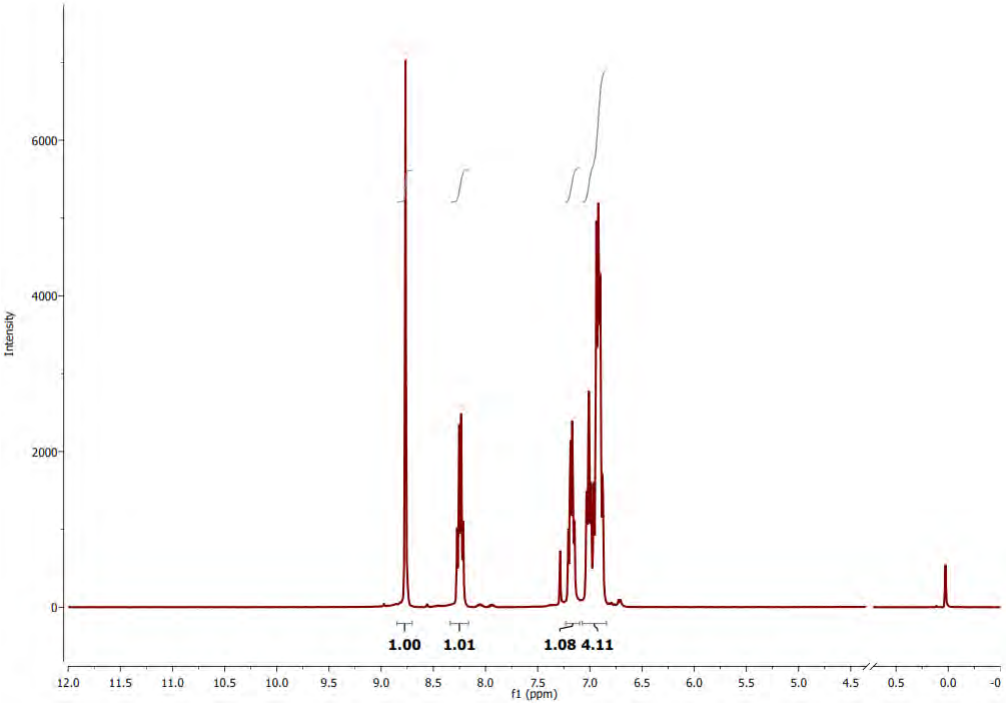


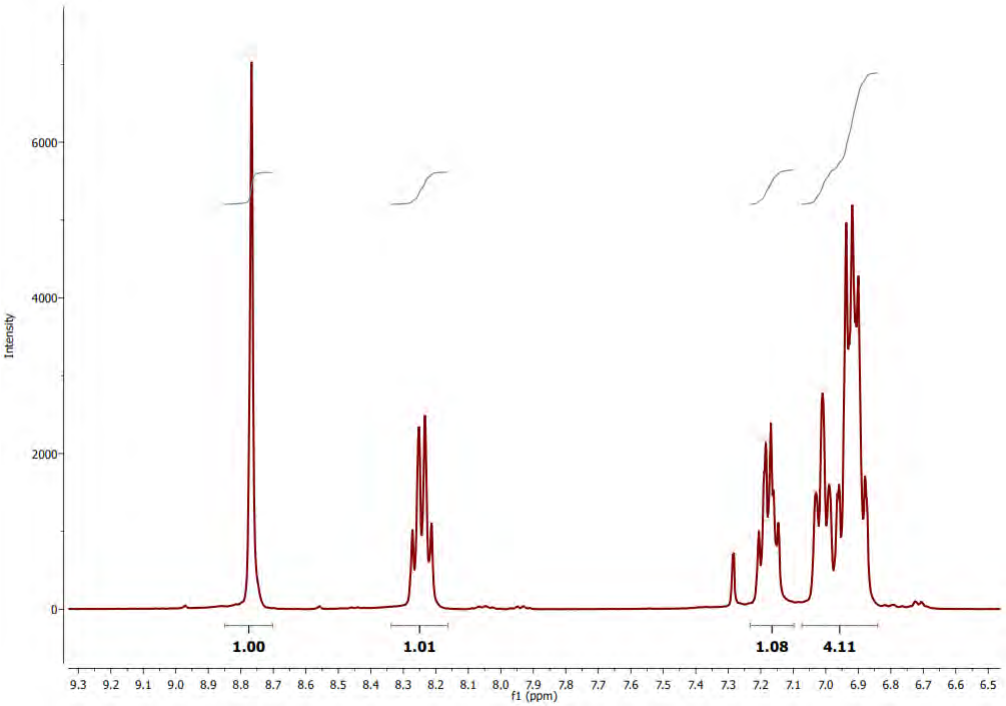
FigureS1:19 Compound **70**: ^{1}H NMR ($CDCl_3$)δ 8.77 (s, 1H), 8.23-8.29 (q,1H), 6.99-7.13 (m, 3H), 6.88-6.96 (m, 2H).



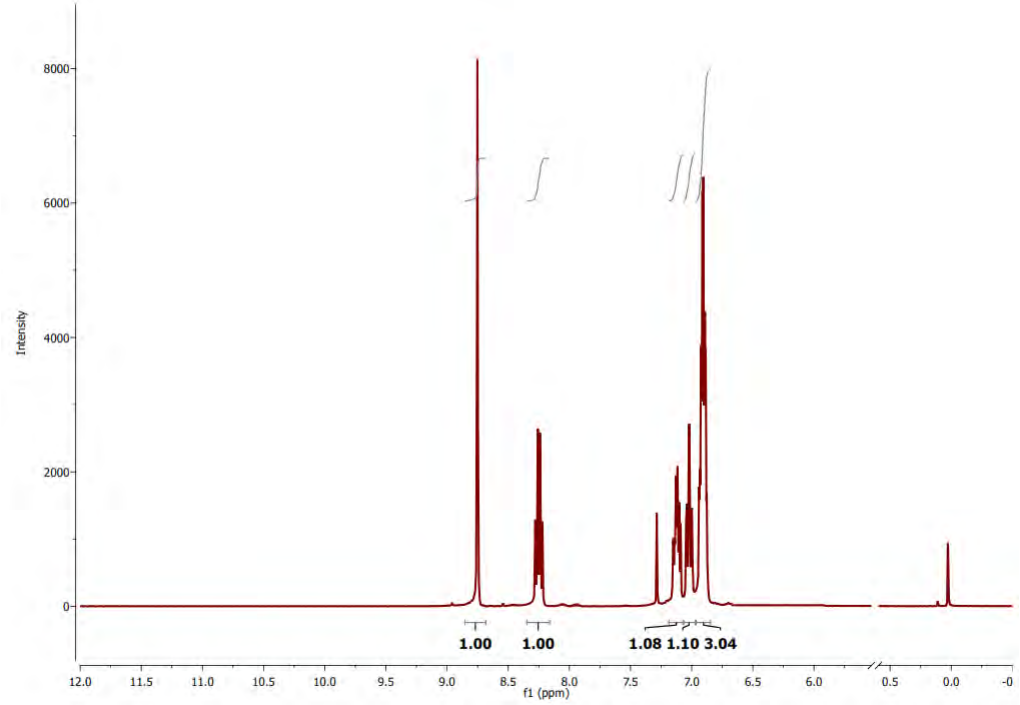


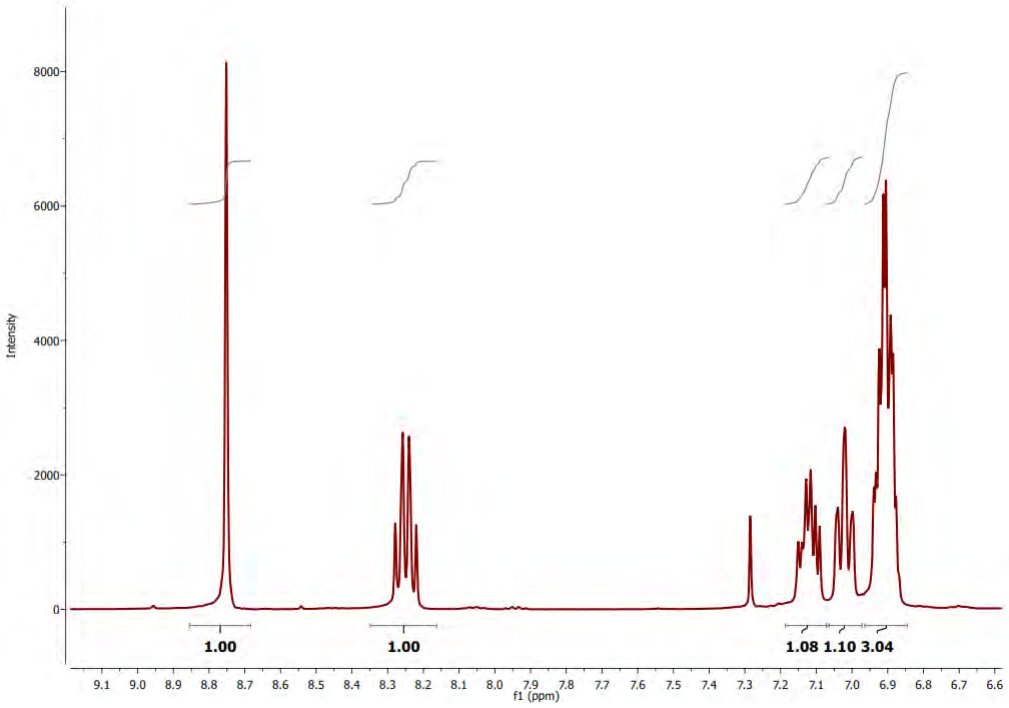
FigureS1:20 Compound **71**: ^{1}H NMR ($CDCl_3$)δ 8.76 (s, 1H), 8.21-8.28 (q,1H), 7.14-7.21 (m, 1H), 6.87-7.03 (m, 4H).



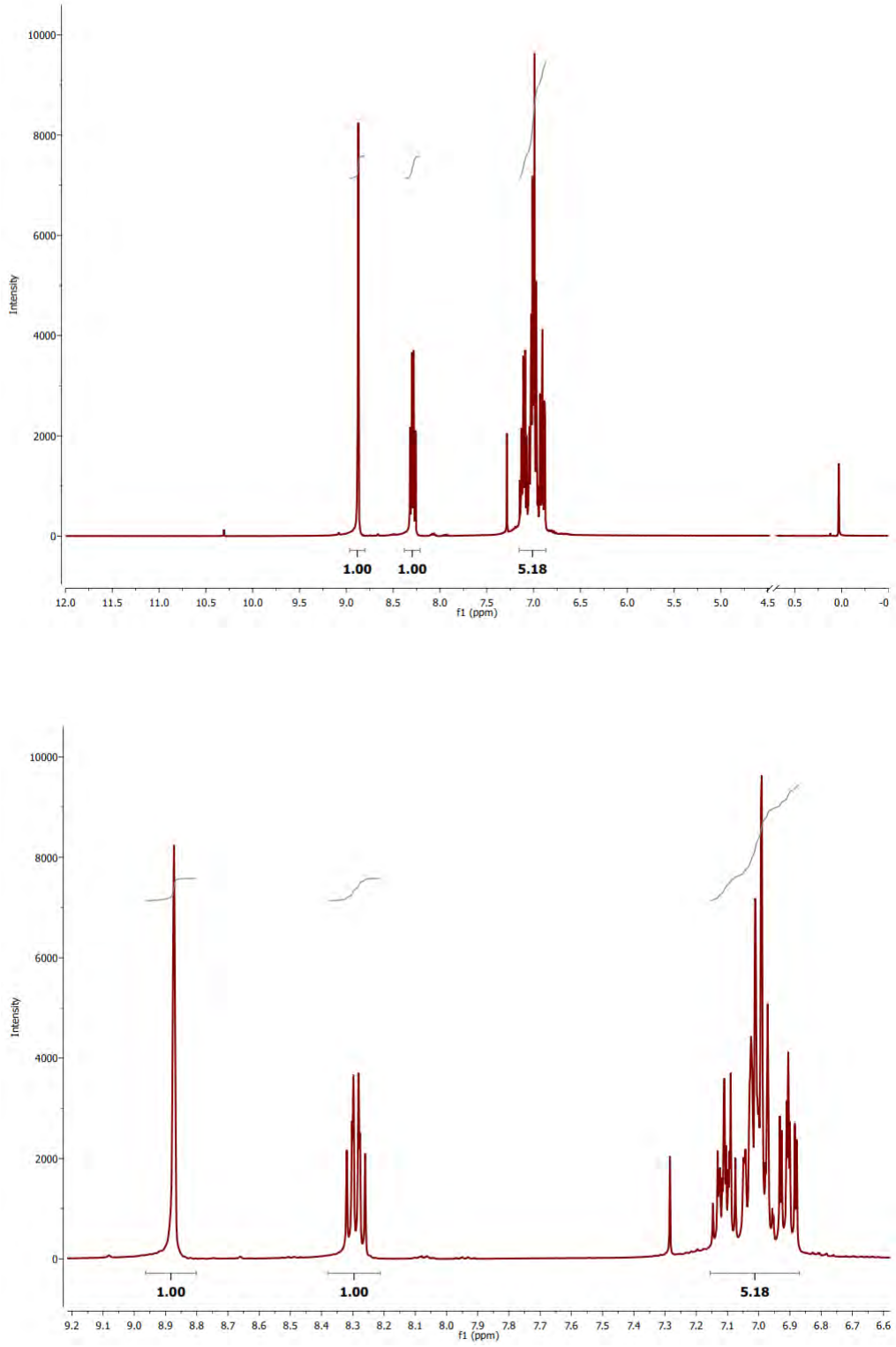


FigureS1:21 Compound **72**: ^{1}H NMR ($CDCl_3$) δ 8.75 (s, 1H), 8.21-8.28 (q,1H), 7.09-7.15 (m, 1H), 6.99-7.04 (m, 1H), 6.87-6.94 (m, 3H).

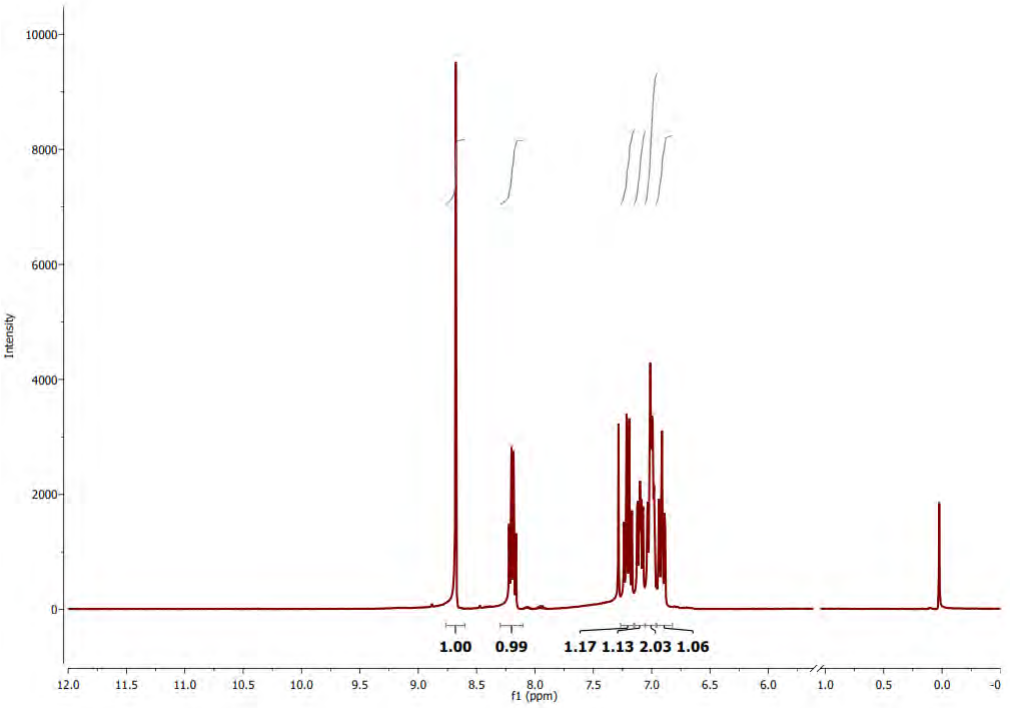


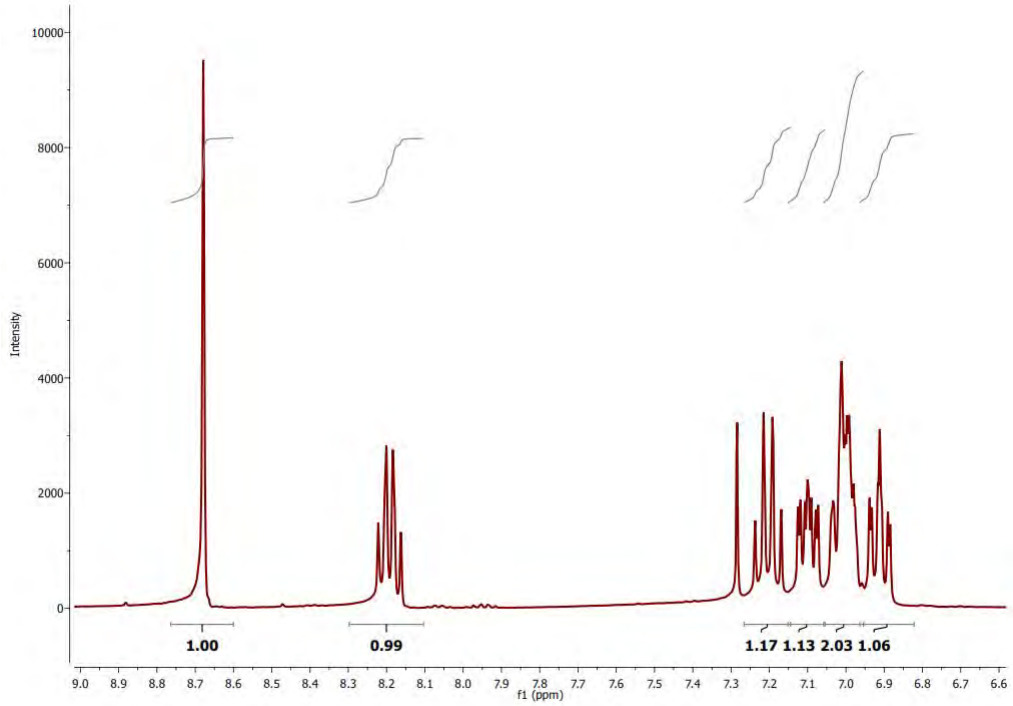


FigureS1:22 Compound **73**: ^{1}H NMR ($CDCl_3$) δ 8.87 (s, 1H), 8.26-8.32 (q,1H), 6.88-7.14 (m, 5H).

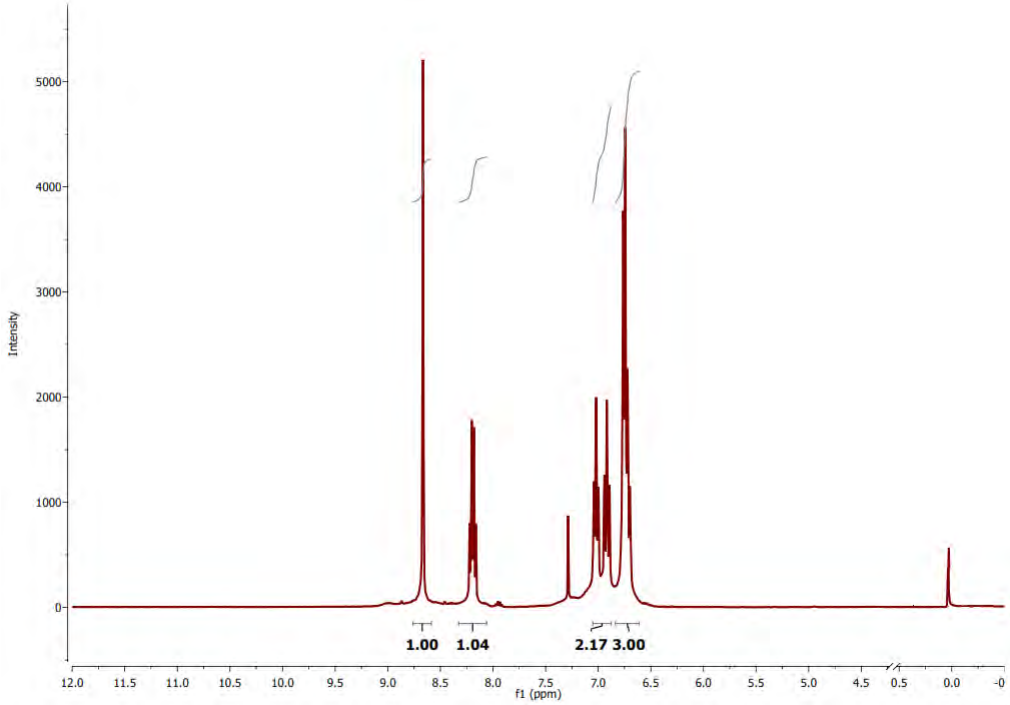


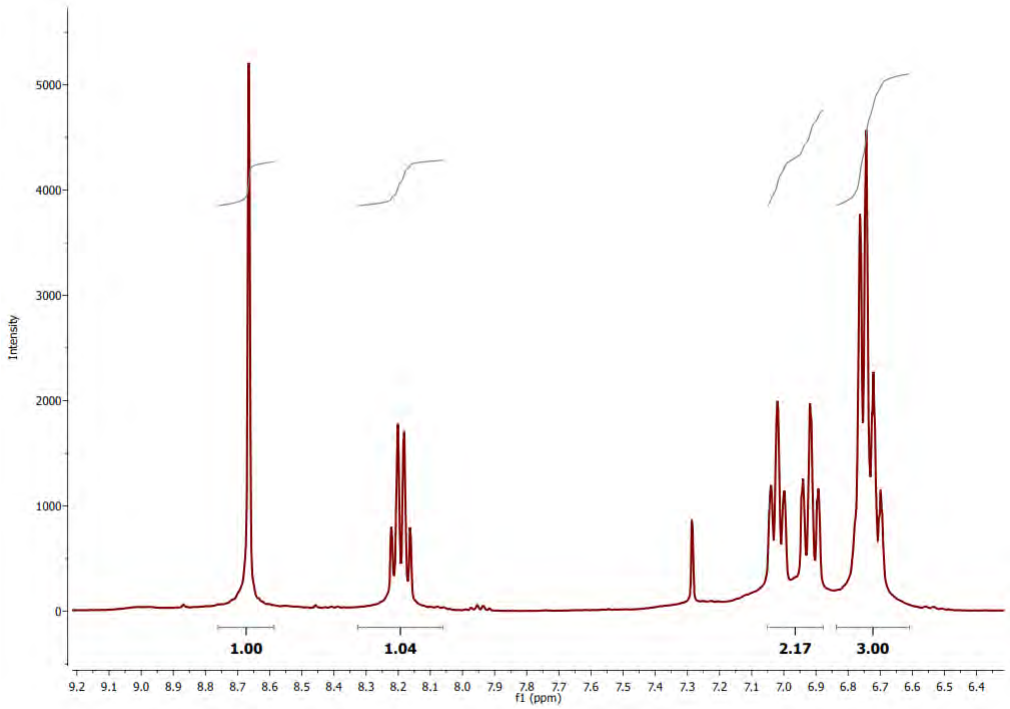
FigureS1:23 Compound **74**: ^{1}H NMR ($CDCl_3$)δ 8.68 (s, 1H), 8.16-8.22 (q,1H), 7.17-7.24 (q, 1H), 7.07-7.12 (m, 1H), 6.97-7.04 (m, 2H), 6.88-6.94 (m, 1H).



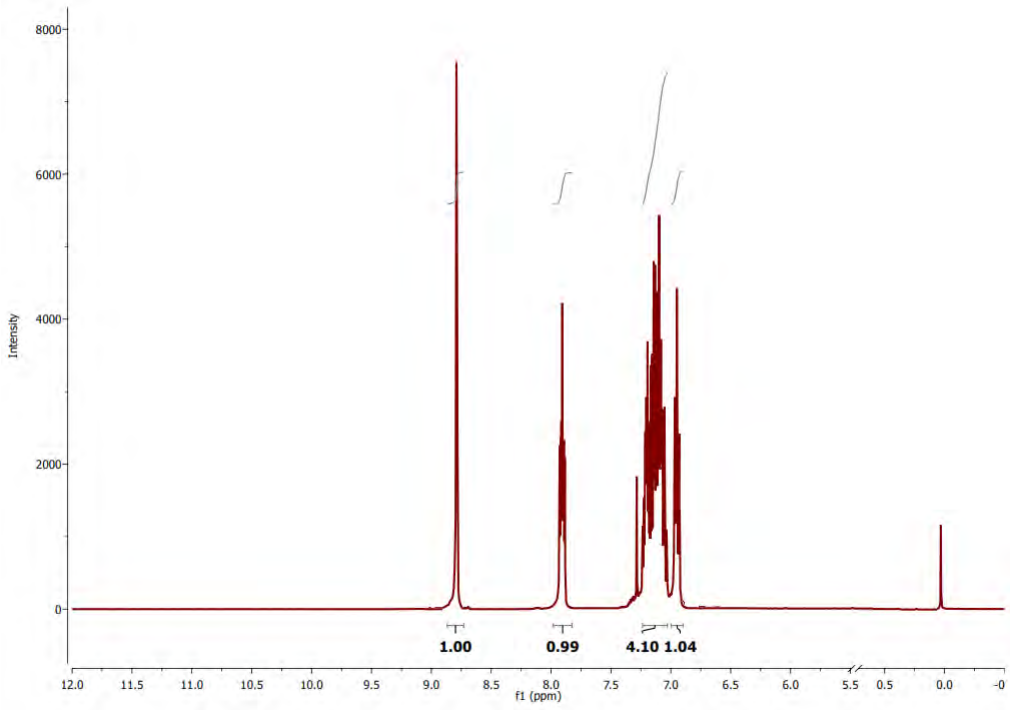


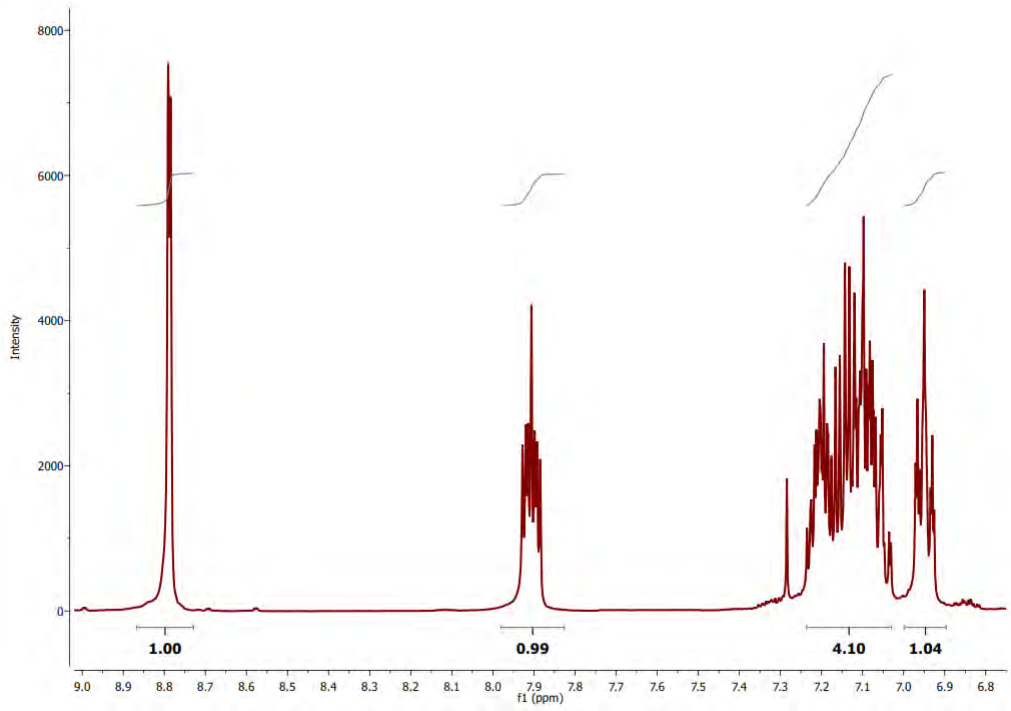
FigureS1:24 Compound **75**: ^{1}H NMR ($CDCl_3$)δ 8.66 (s, 1H), 8.16-8.22 (q,1H), 6.88-7.05 (dt, 2H), 6.69-6.77 (t, 3H).



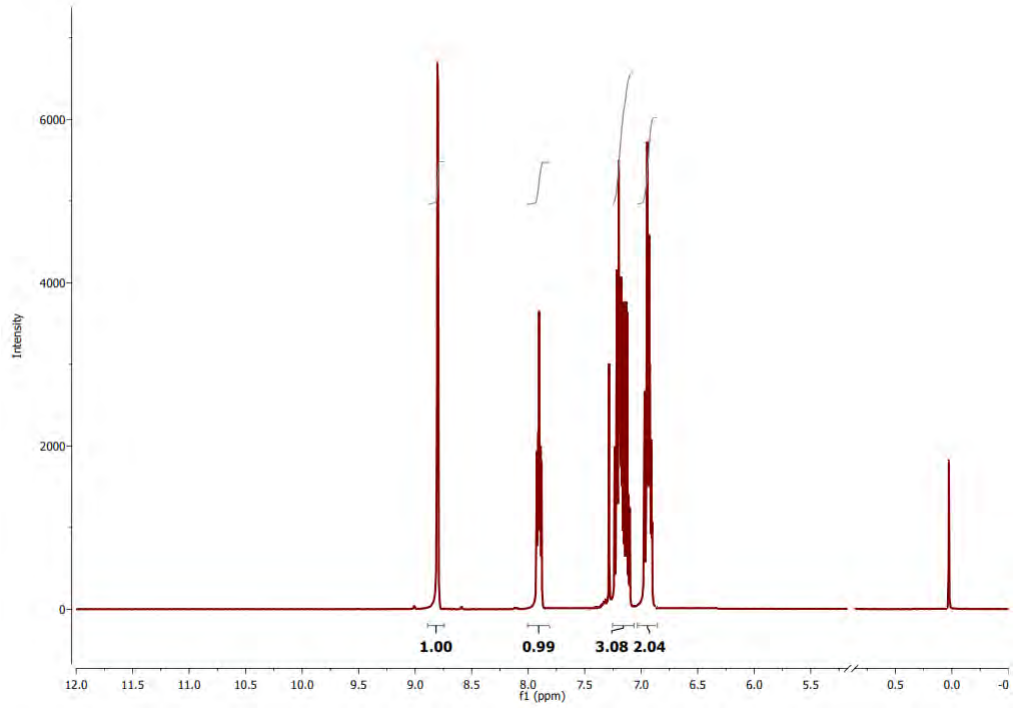


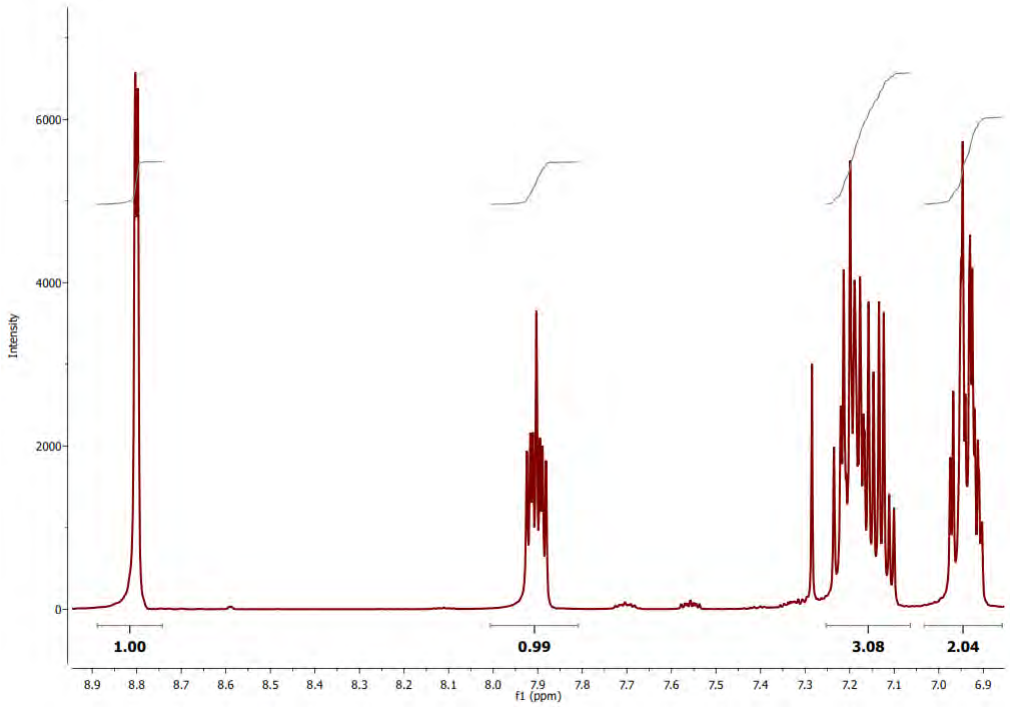
FigureS1:25 Compound **76**: ^{1}H NMR ($CDCl_3$) δ 8.79 (s, 1H), 7.88-7.93 (m,1H), 7.02-7.24 (m, 4H), 6.92-6.97 (m, 1H).



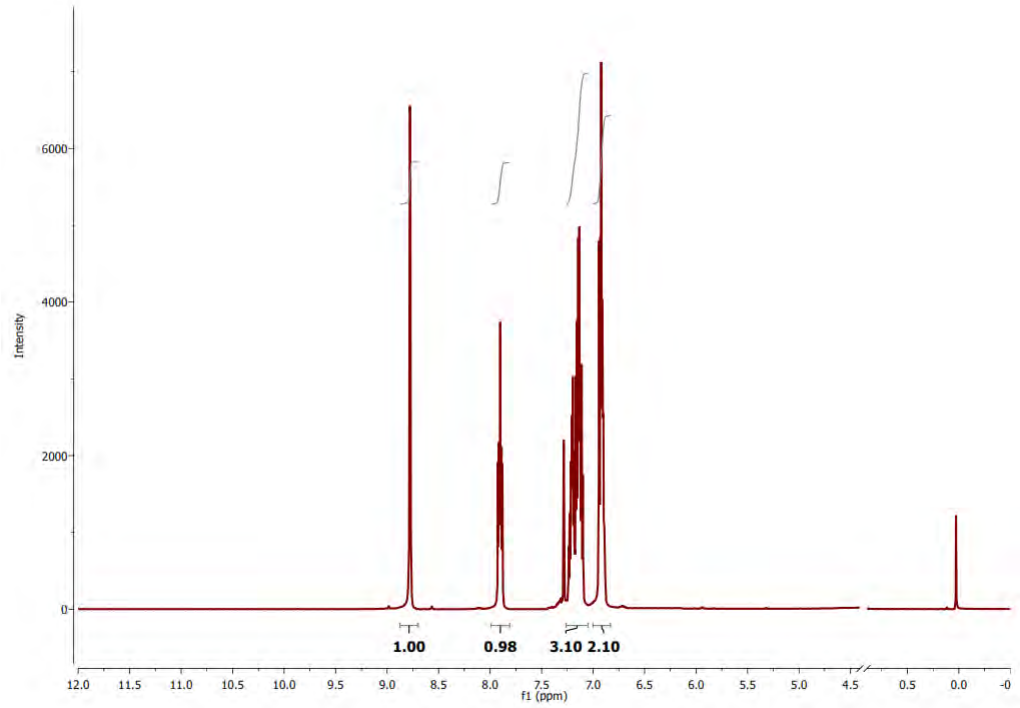


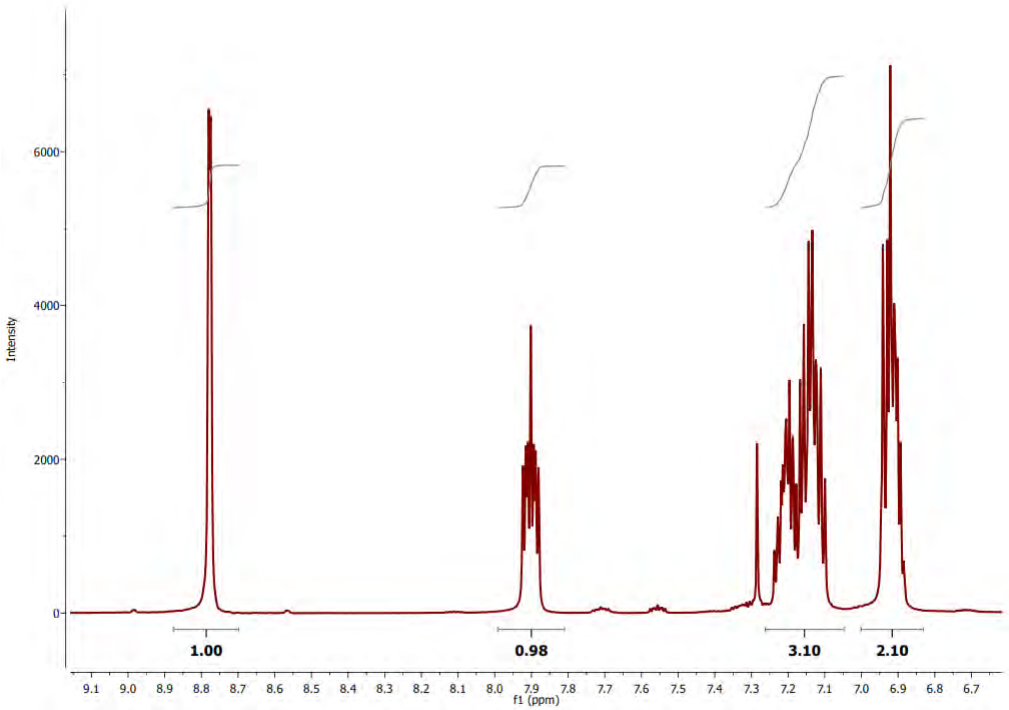
FigureS1: 26 Compound **77**: ^{1}H NMR ($CDCl_3$) δ 8.80 (s, 1H), 7.88-7.93 (m,1H), 7.10-7.24 (m, 3H), 6.91-6.97 (m, 2H).



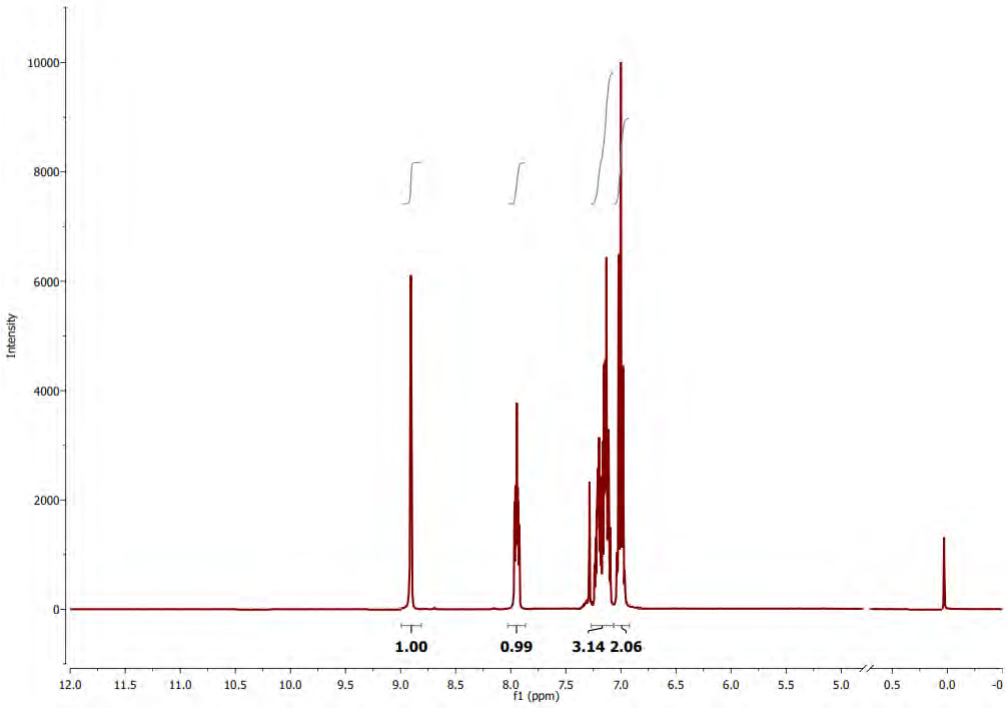


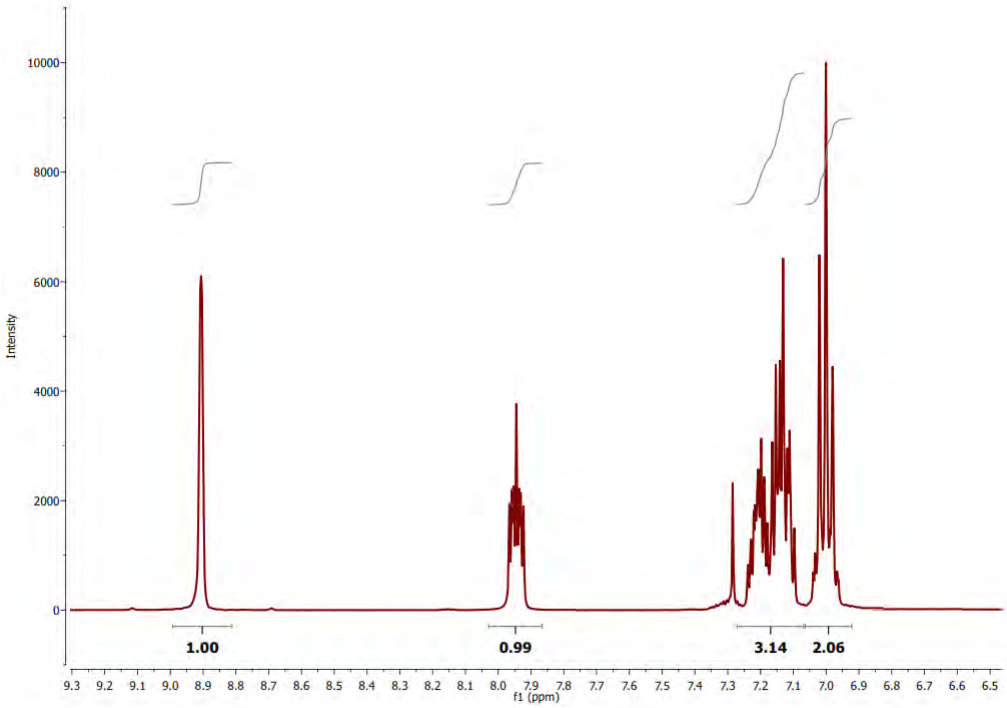
FigureS1: 27 Compound **78**: ^{1}H NMR ($CDCl_3$) δ 8.78 (s, 1H), 7.88-7.93 (m,1H), 7.09-7.24 (m, 3H), 6.88-6.95 (m, 2H).



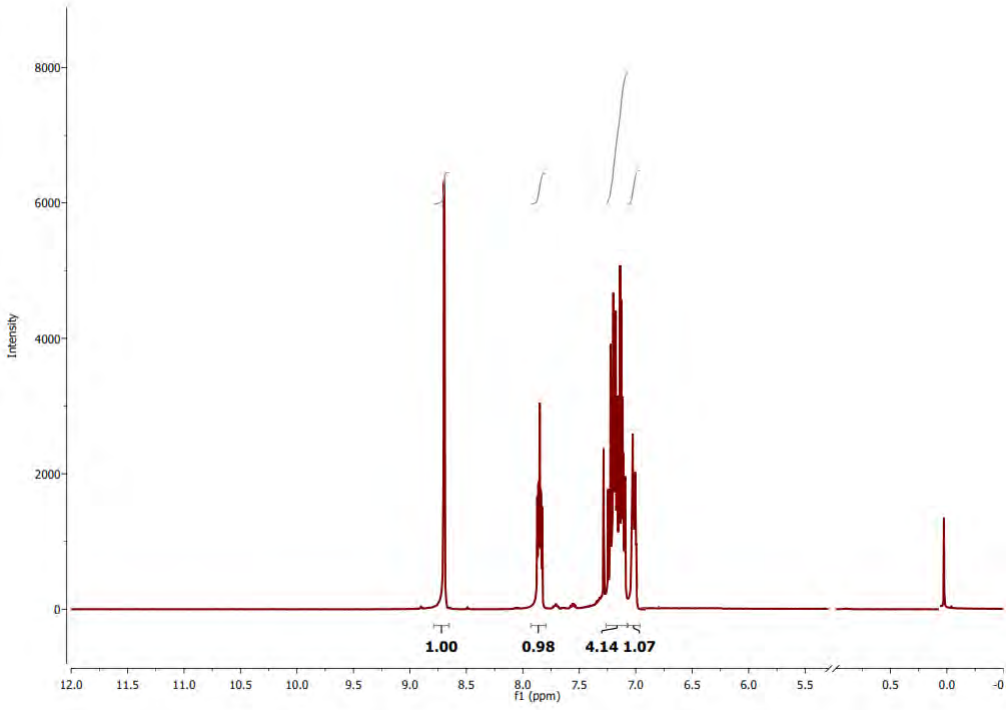


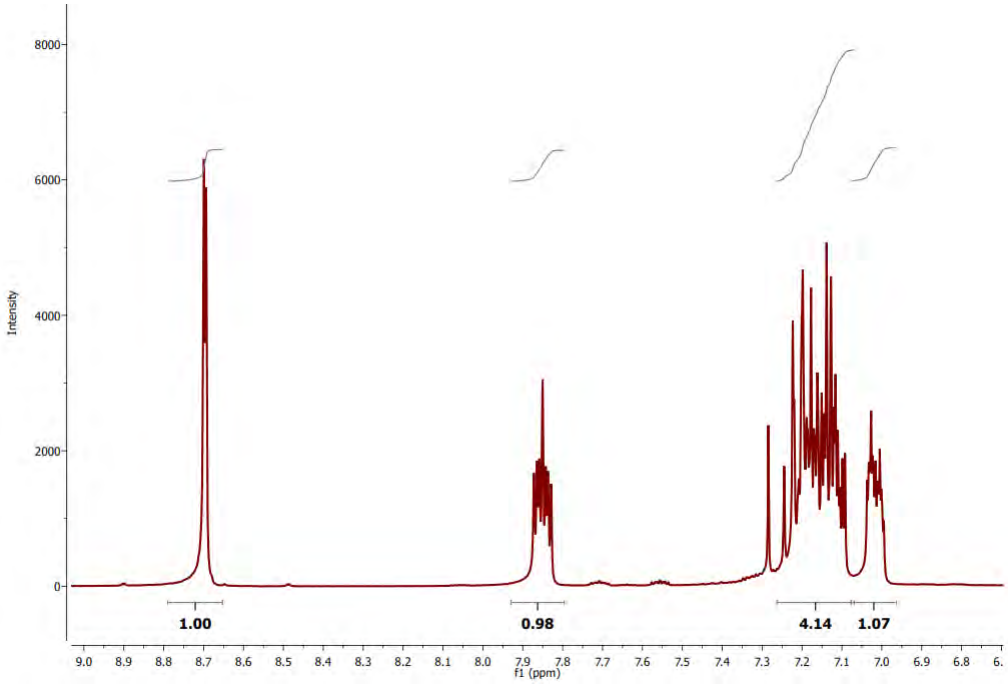
FigureS1:28 Compound **79**: ^{1}H NMR ($CDCl_3$) δ 8.90 (s, 1H), 7.92-7.97 (m,1H), 7.09-7.23 (m, 3H), 6.97-7.02 (m, 2H).



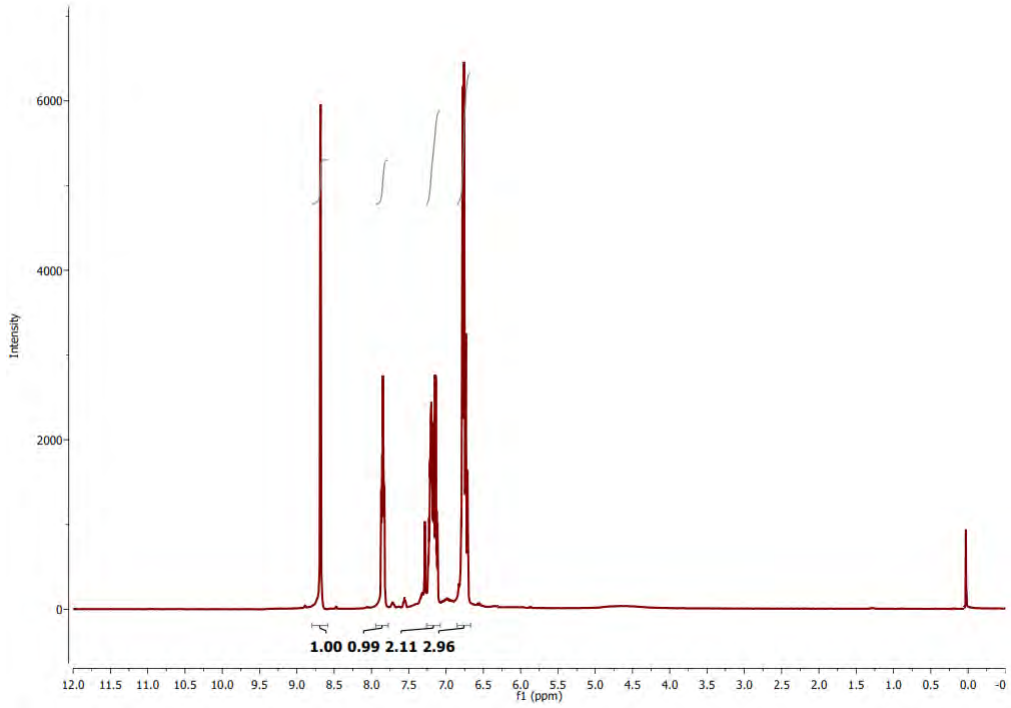


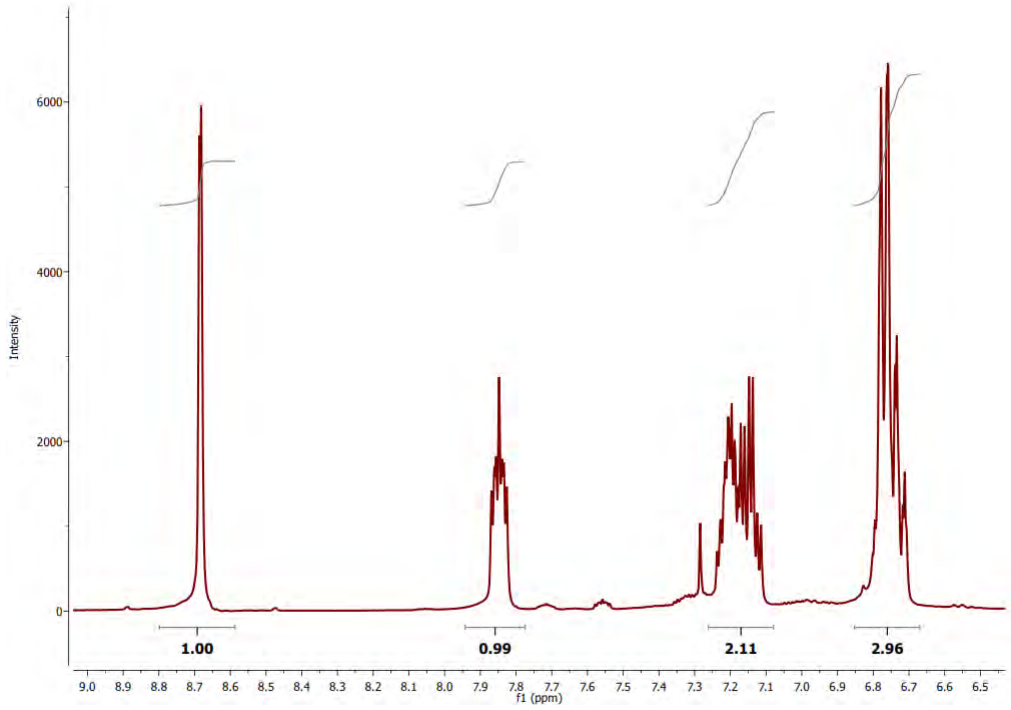
FigureS1:29 Compound **80**: ^{1}H NMR ($CDCl_3$) δ 8.70 (s, 1H), 7.82-7.88 (m,1H), 7.09-7.23 (m, 4H), 6.99-7.04 (m, 1H).



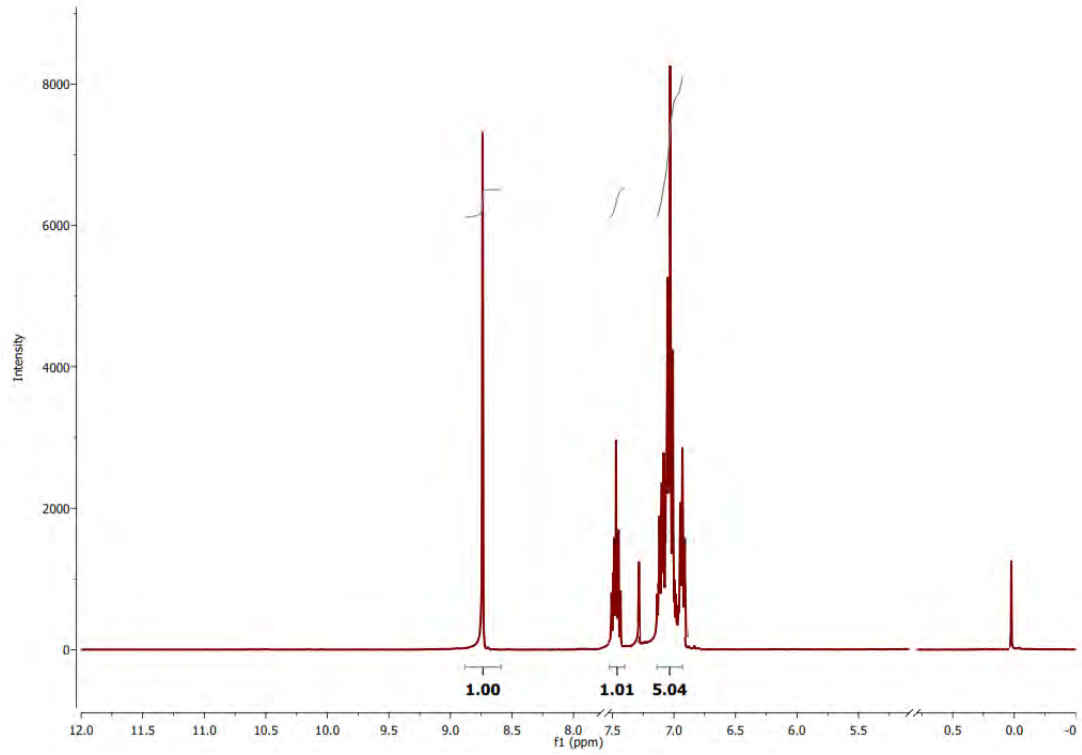


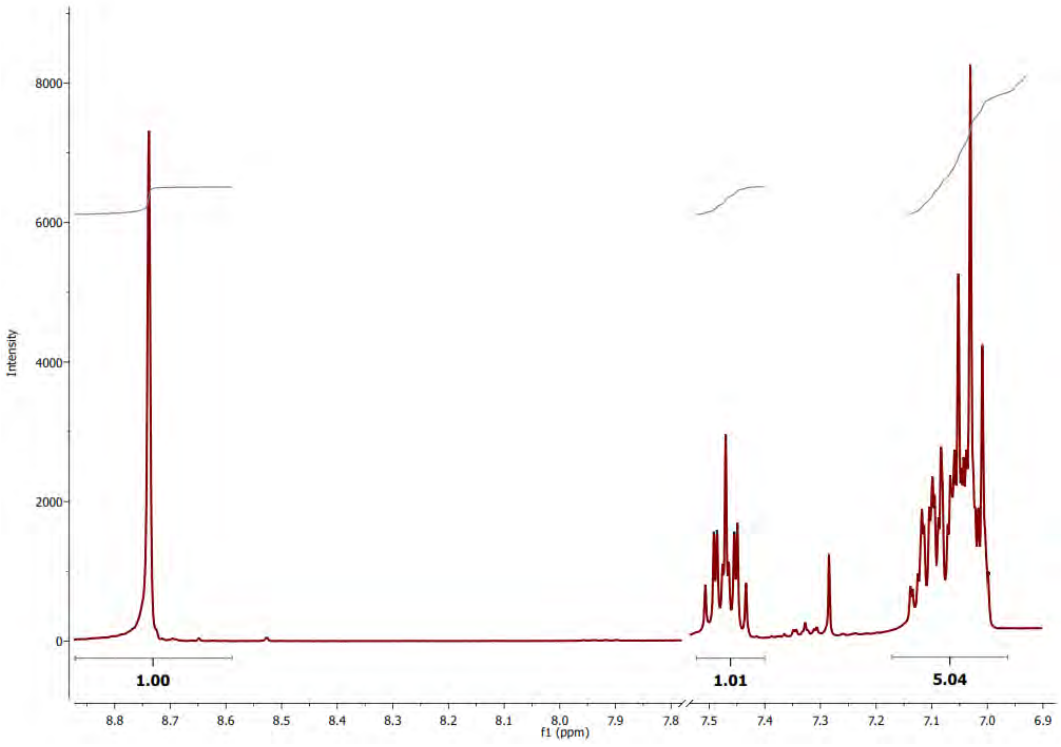
FigureS1:30 Compound **81**: ^{1}H NMR ($CDCl_3$) δ 8.68 (s, 1H), 7.82-7.87 (m,1H), 7.11-7.24 (m, 2H), 6.71-6.80 (m, 3H).



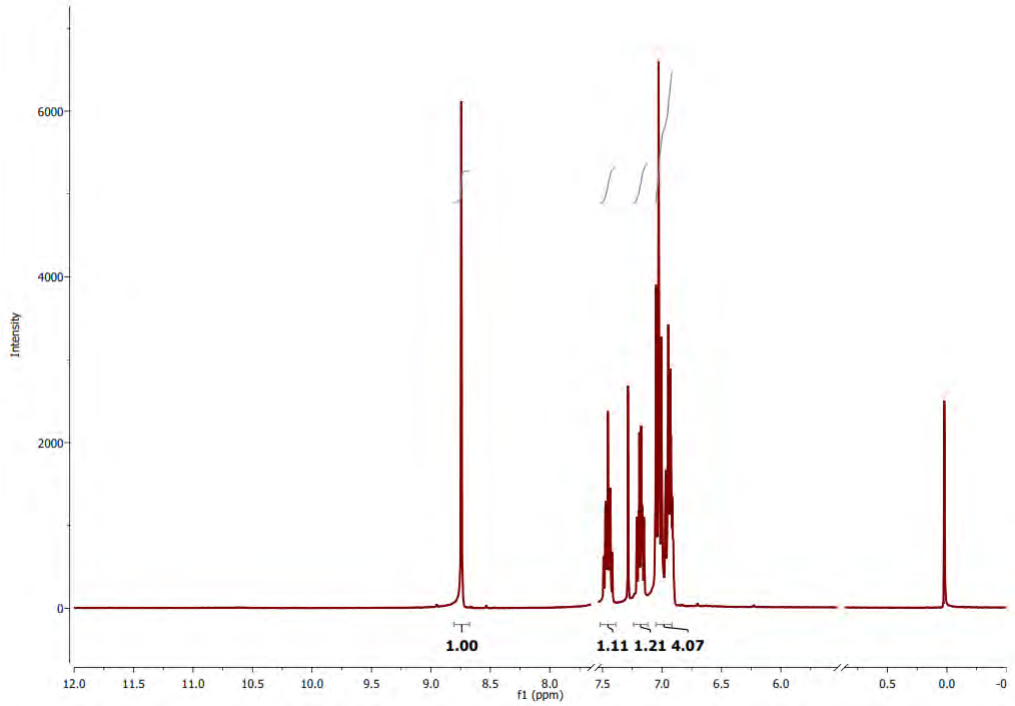


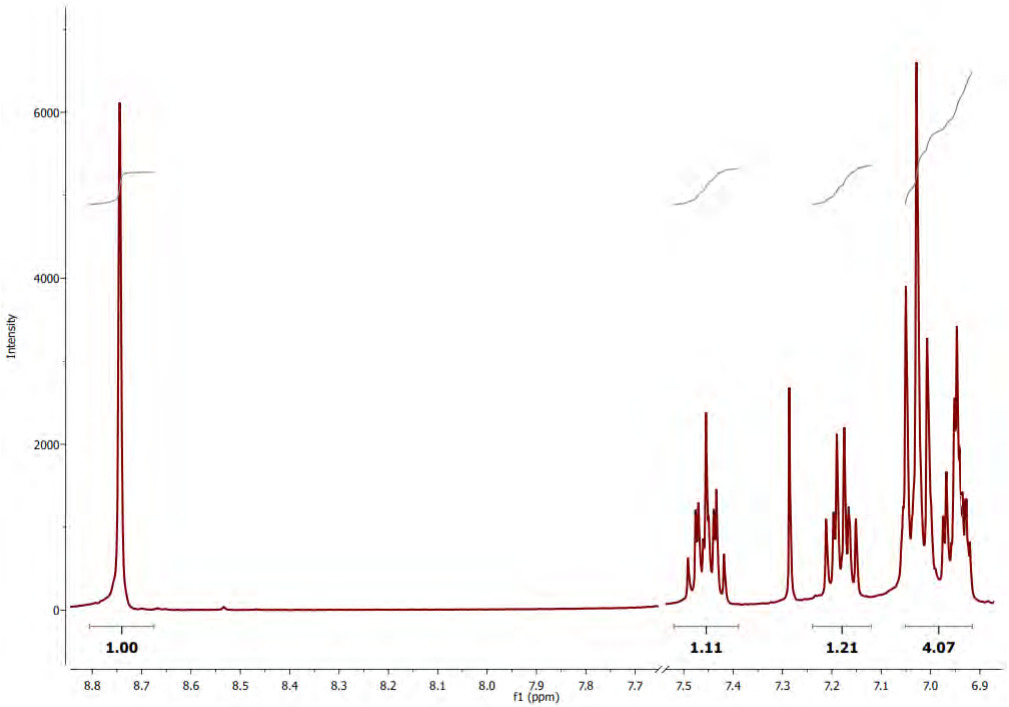
FigureS1:31 Compound **82**: ^{1}H NMR ($CDCl_3$) δ 8.74 (s, 1H), 7.43-7.51 (m,1H), 6.99-7.14 (m, 5H).



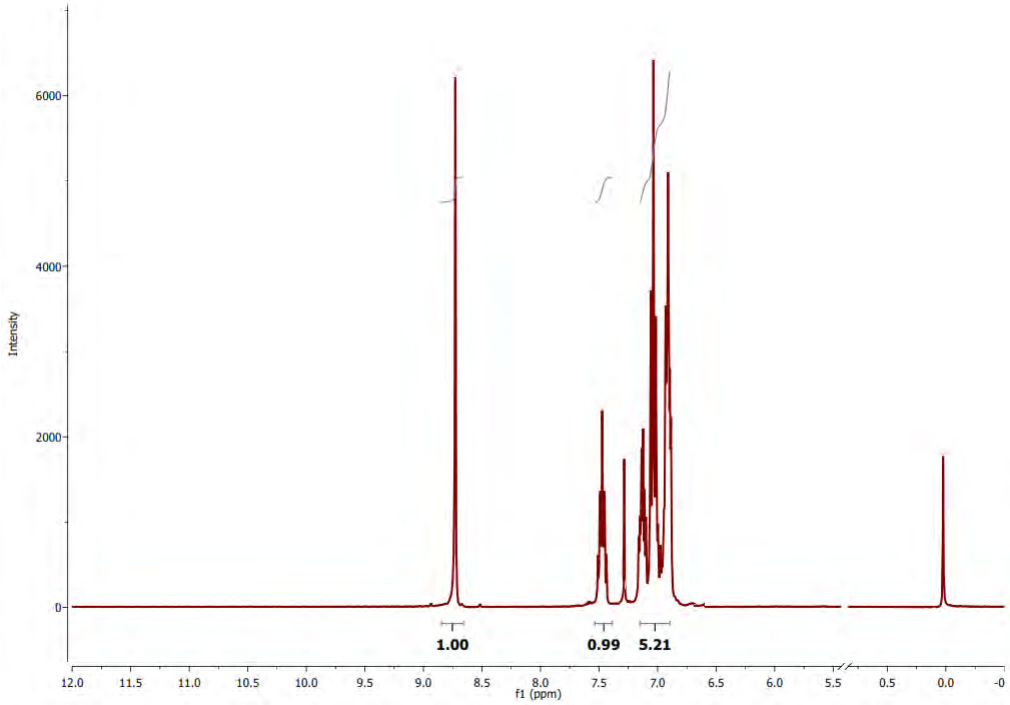


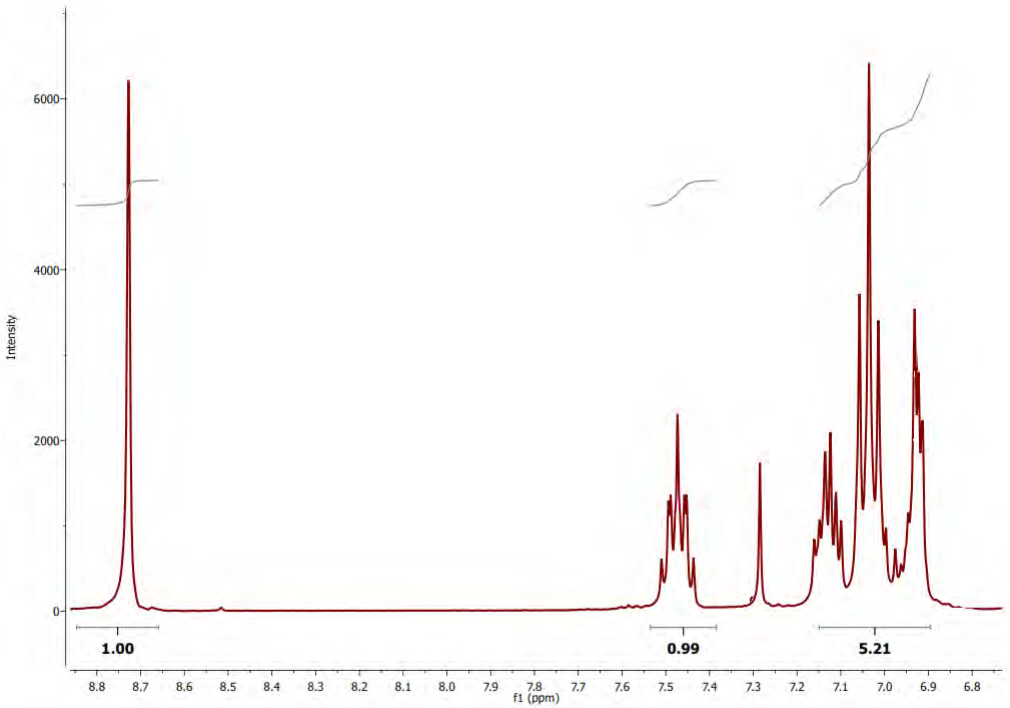
FigureS1:32 Compound **83**: ^{1}H NMR ($CDCl_3$) δ 8.75 (s, 1H), 7.41-7.50 (m,1H), 7.15-7.21 (m, 1H), 6.91-7.05 (m, 4H).



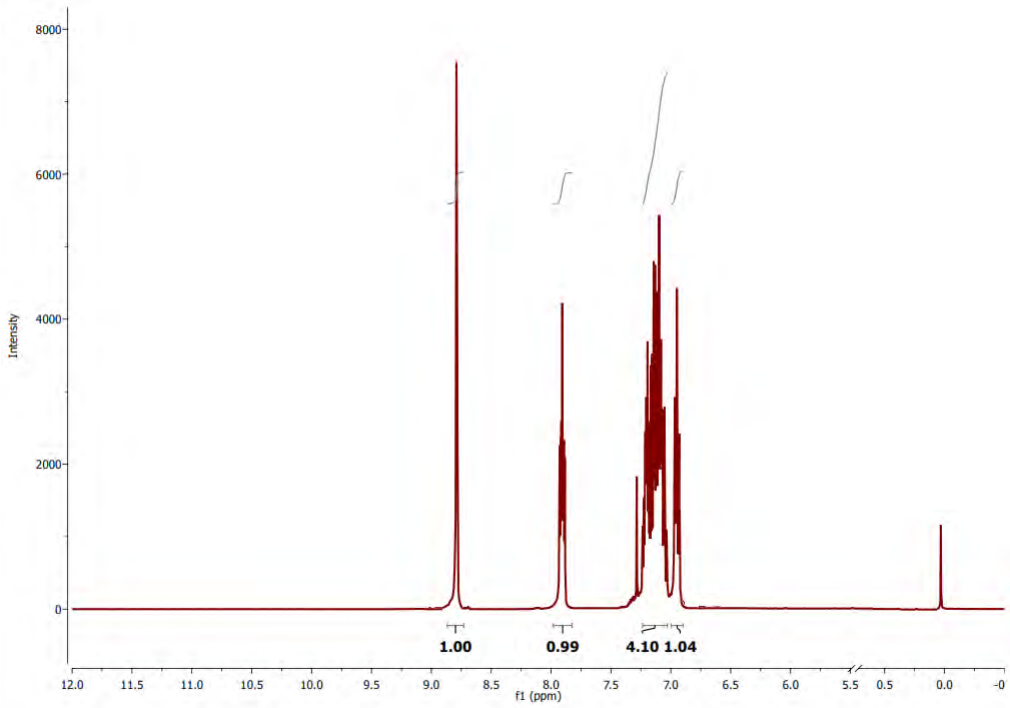


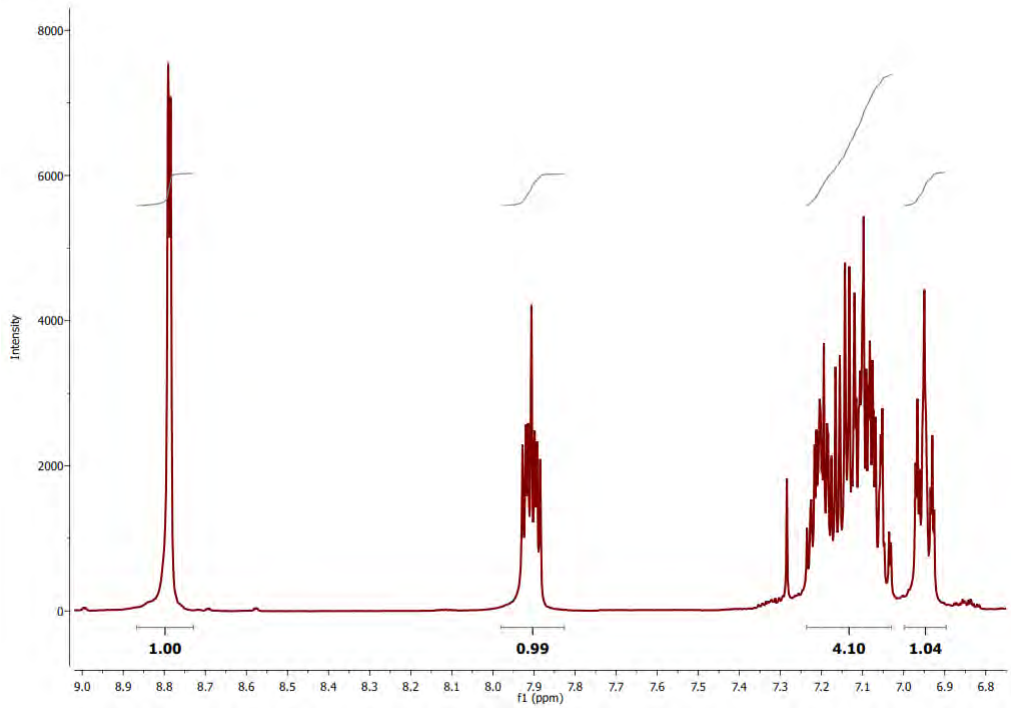
FigureS1:33 Compound **84**: ^{1}H NMR ($CDCl_3$) δ 8.73 (s, 1H), 7.44-7.51 (m,1H), 6.89-7.16 (m, 5H).



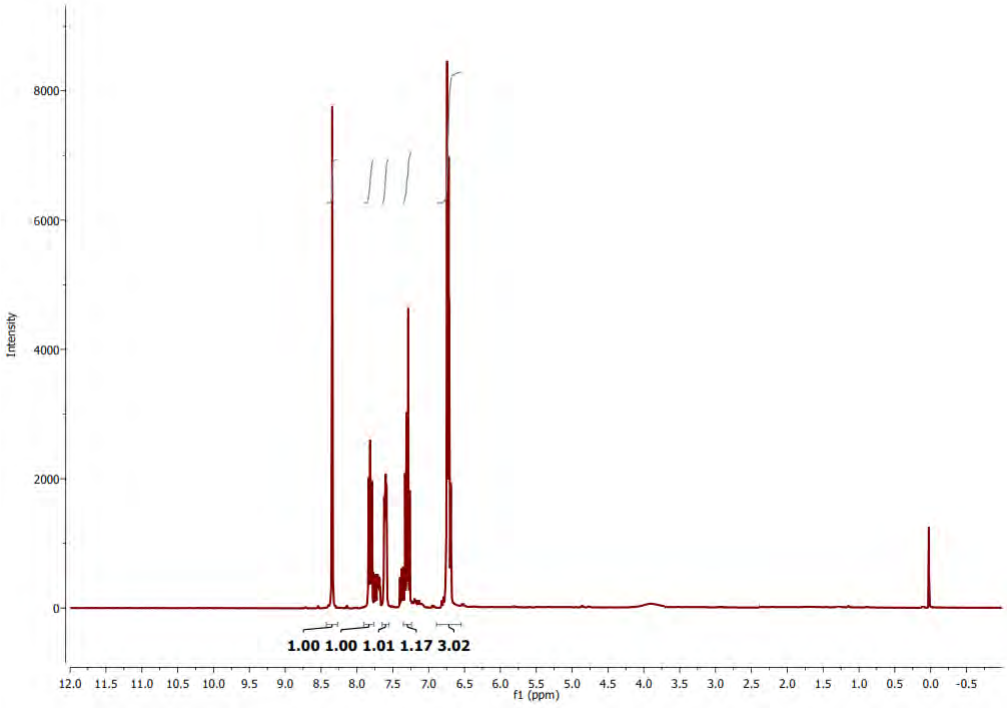


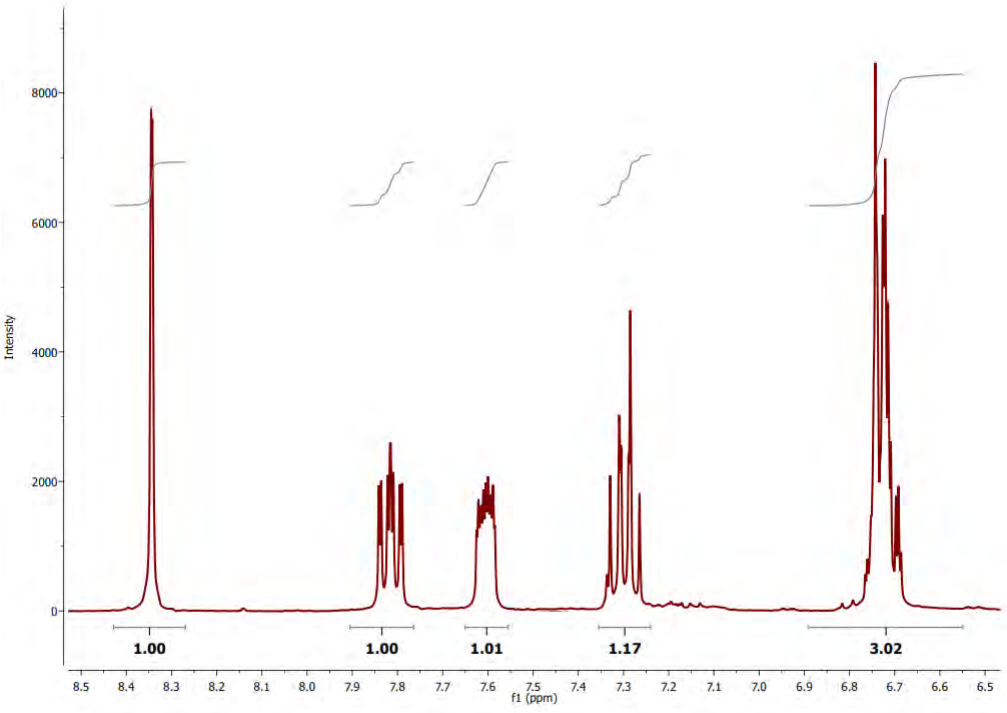
FigureS1:34 Compound **85:** ^{1}H NMR ($CDCl_3$) δ 8.79 (s, 1H), 7.88-7.93 (m,1H), 7.02-7.24 (m, 4H), 6.92-6.97 (m, 1H).



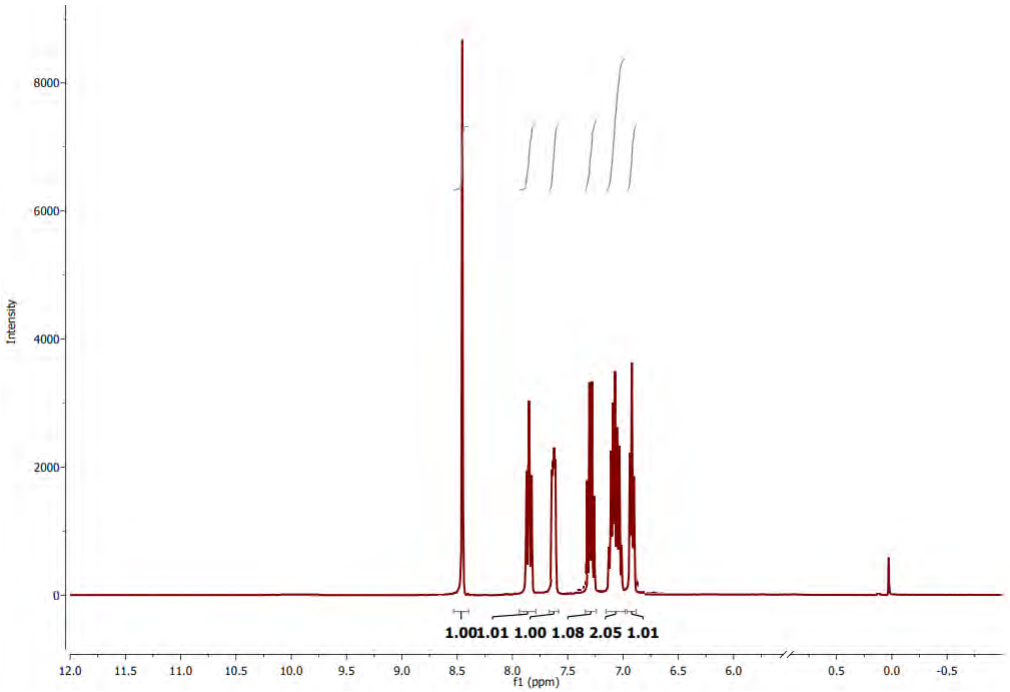


FigureS1:35 Compound **86:** ^{1}H NMR ($CDCl_3$), δ 8.34 (s, 1H), 7.78-7.83 (t, 1H), 7.58-7.63 (m, 1H), 7.26-7.33 (q, 1H), 6.69-6.75 (m, 3H).





FigureS1:36 Compound **87:** ^{1}H NMR ($CDCl_3$) δ 8.8 (s, 1H), 7.96-8.01 (t,1H), 7.18-7.36 (m, 3H), 6.91-6.98 (m, 2H).



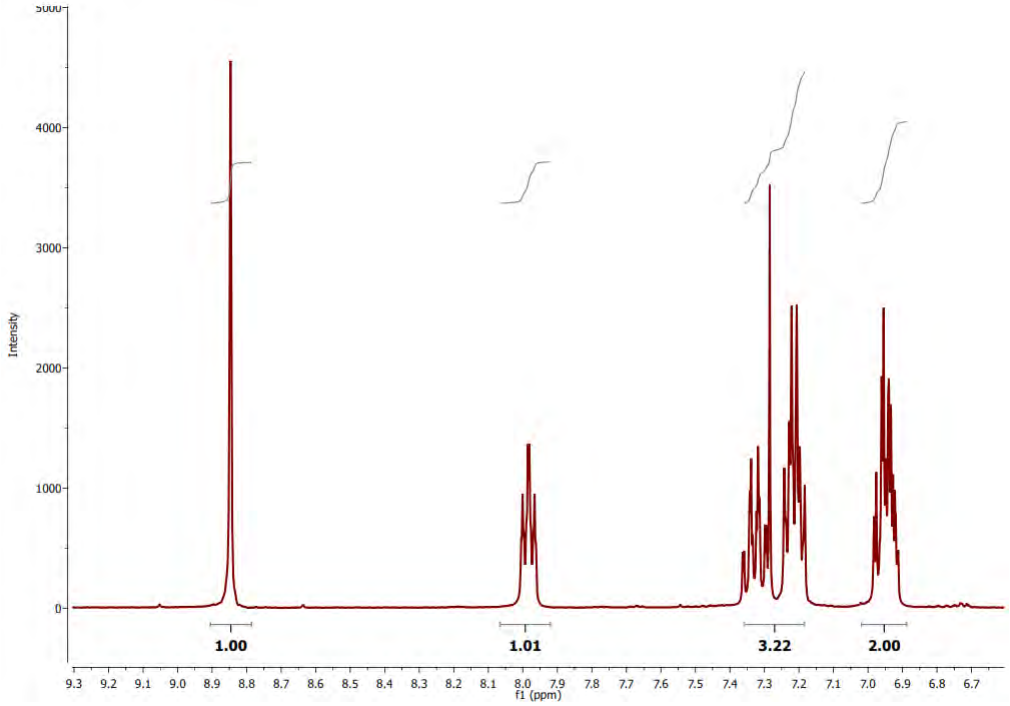


Figure S2: IR-S1pectra of the compounds

Figure S2: 1 C.N. 52

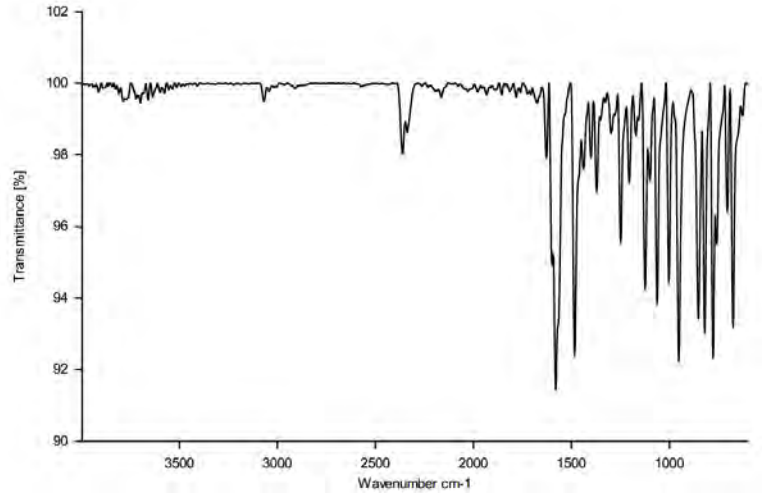


Figure S2: 2 C.N. 53

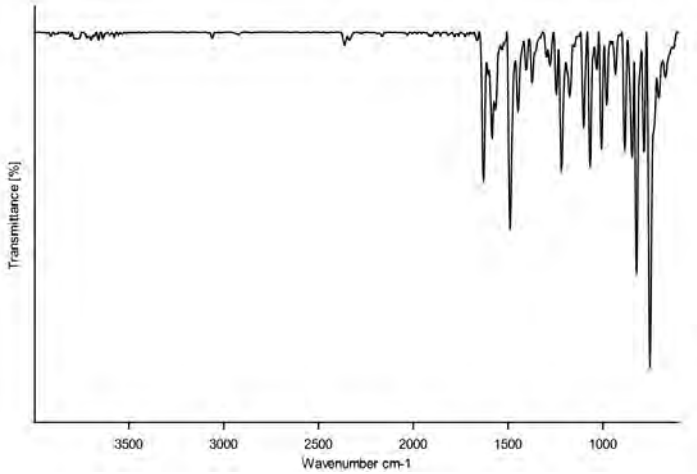


Figure S2: 3 C.N. 54

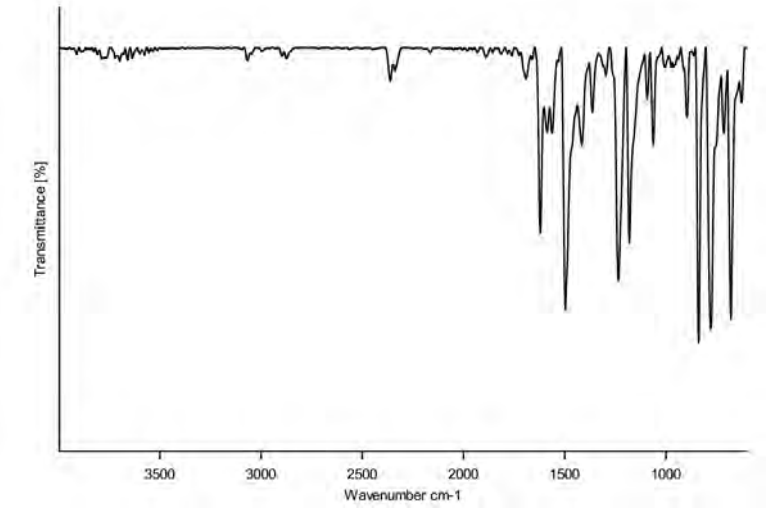


Figure S2: 4 C.N. 55

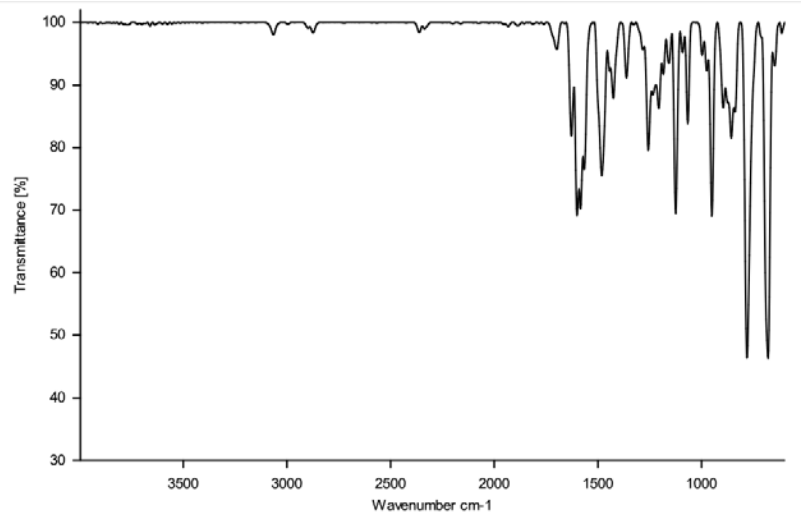


Figure S2: 5 C.N. 56

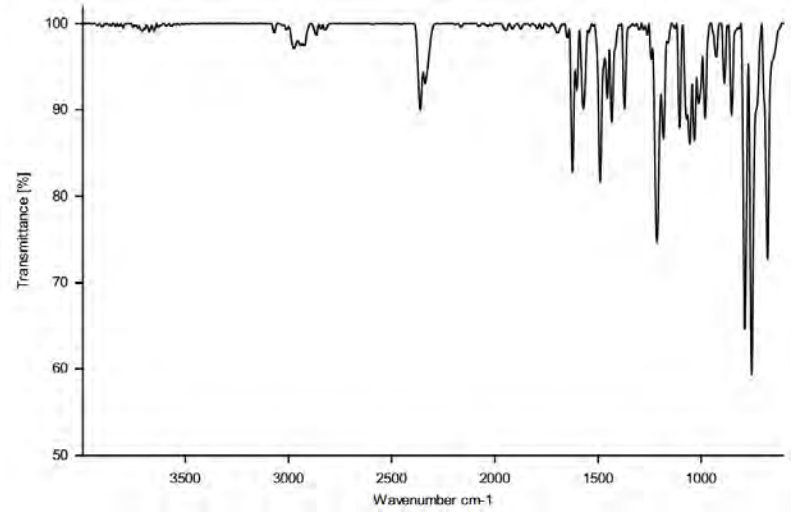


Figure S2: 6 C.N. 57

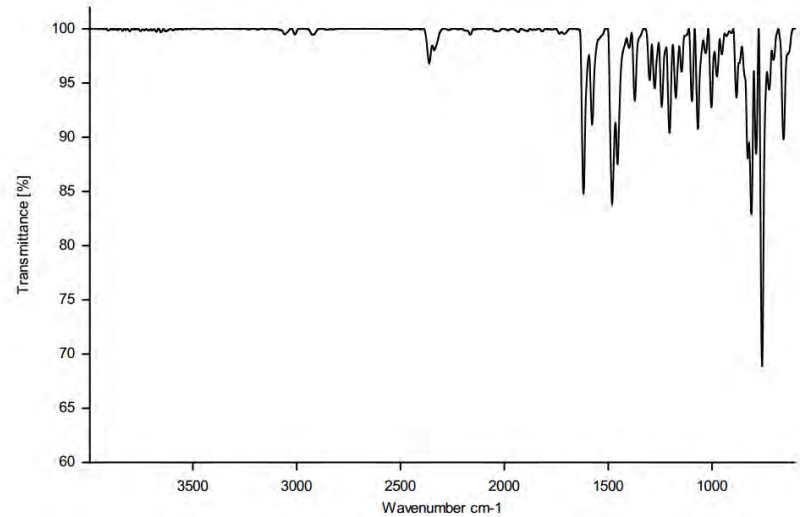


Figure S2: 7 C.N. 58

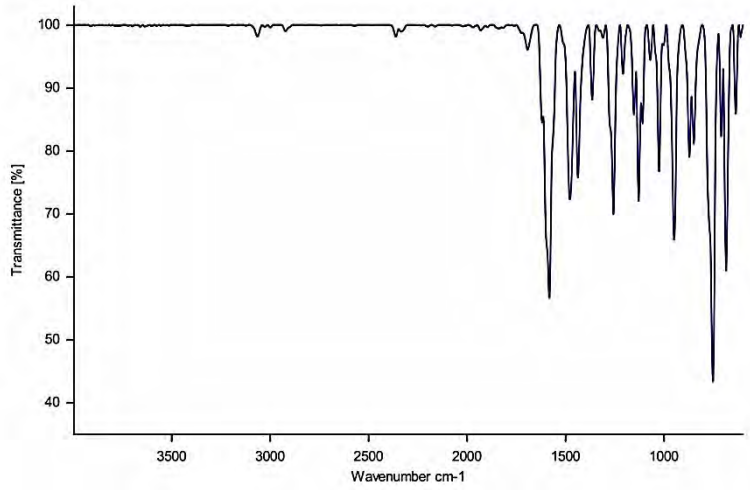


Figure S2: 8 C.N. 59

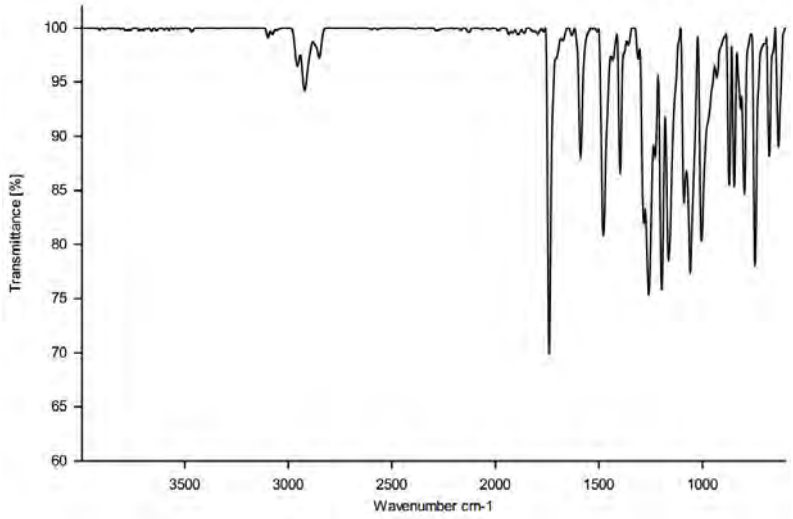


Figure S2: 9 C.N. 60

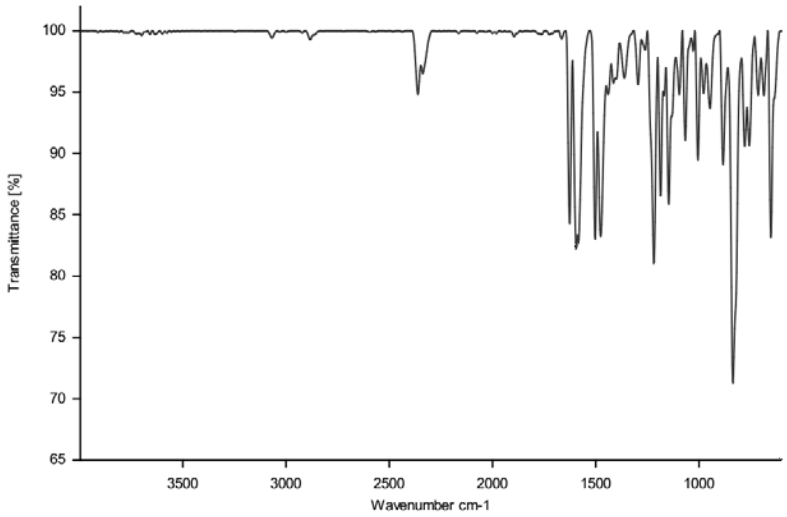


Figure S2: 10 C.N. 61

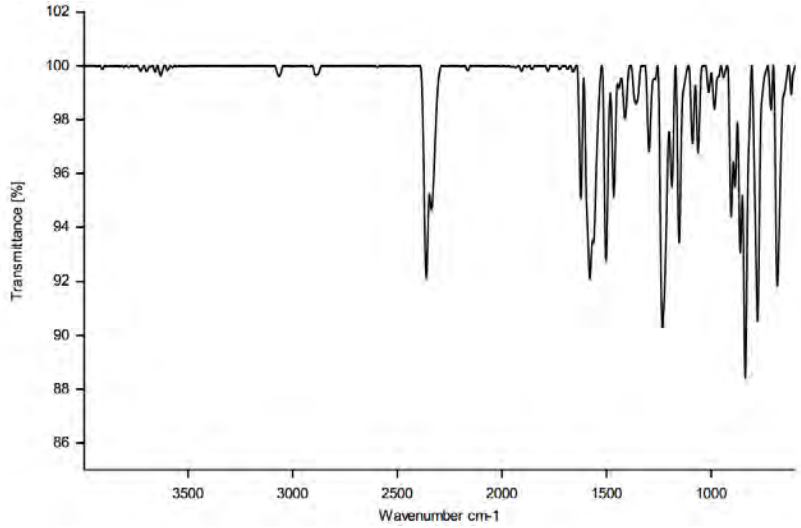


Figure S2: 11 C.N. 62

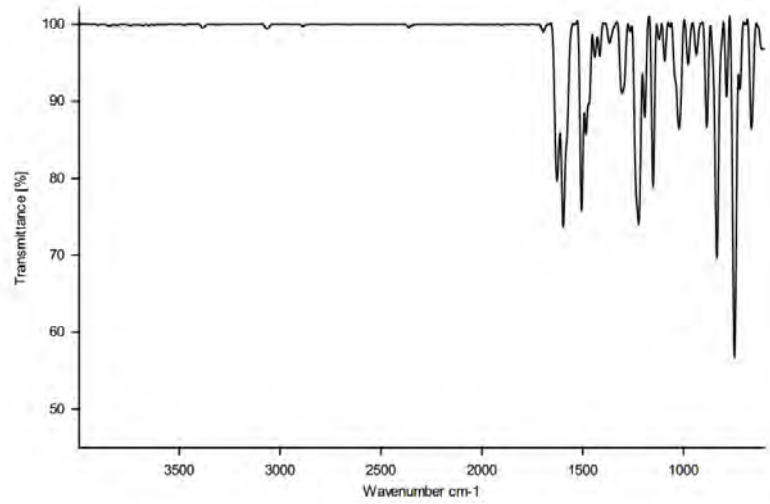


Figure S2: 12 C.N. 63

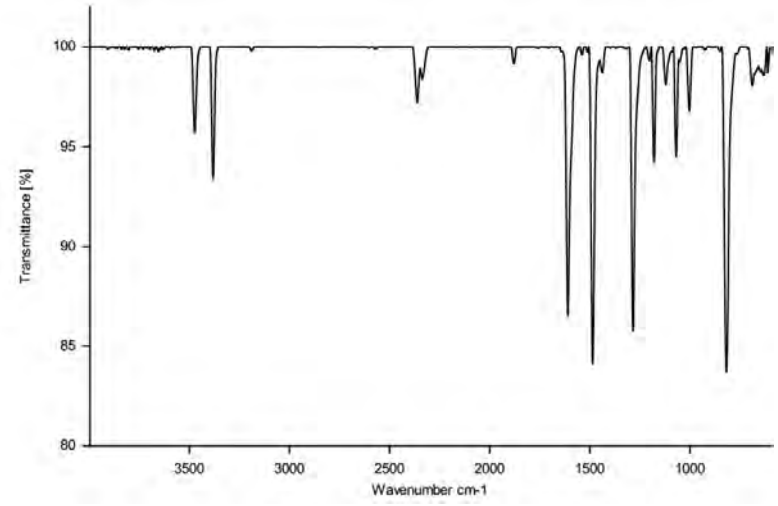


Figure S2: 13 **C.N. 64**

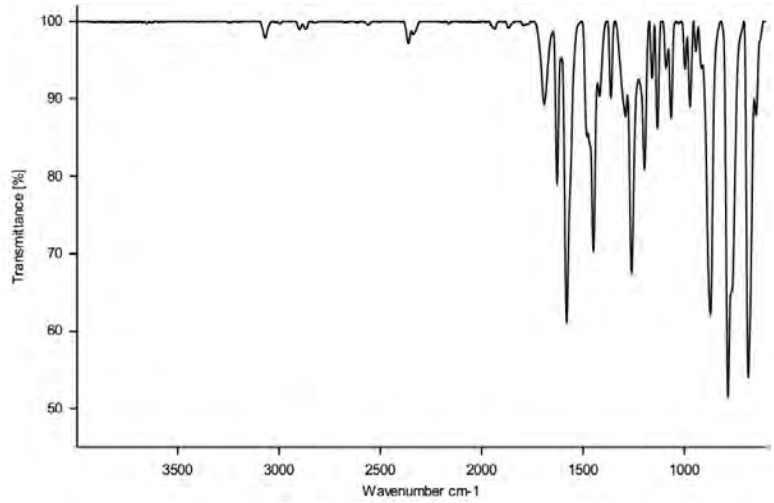


Figure S2: 14 **C.N. 65**

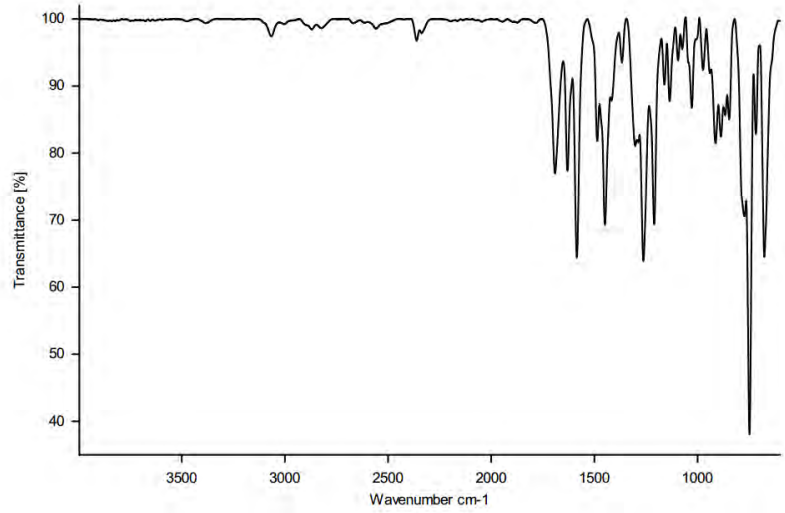


Figure S2: 15 **C.N. 66**

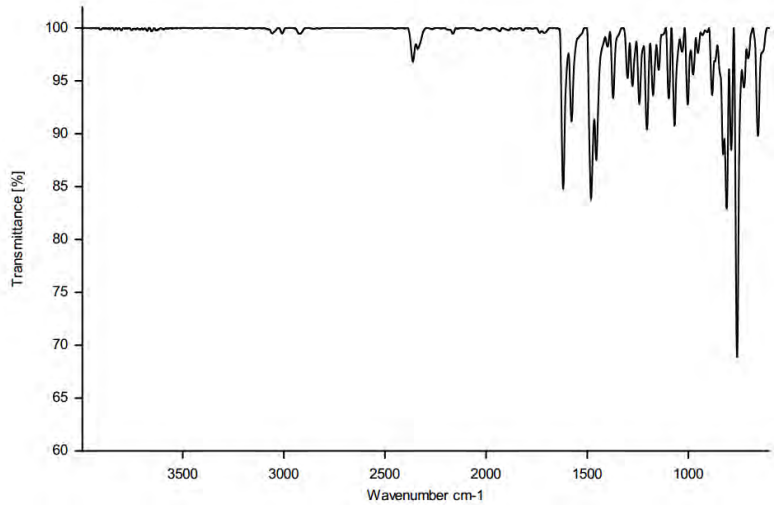


Figure S2: 16 C.N. 67

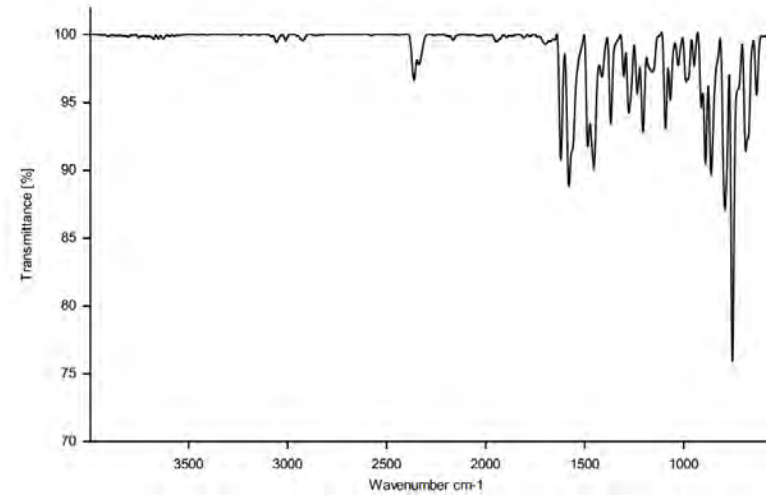


Figure S2: 17 C.N. 68

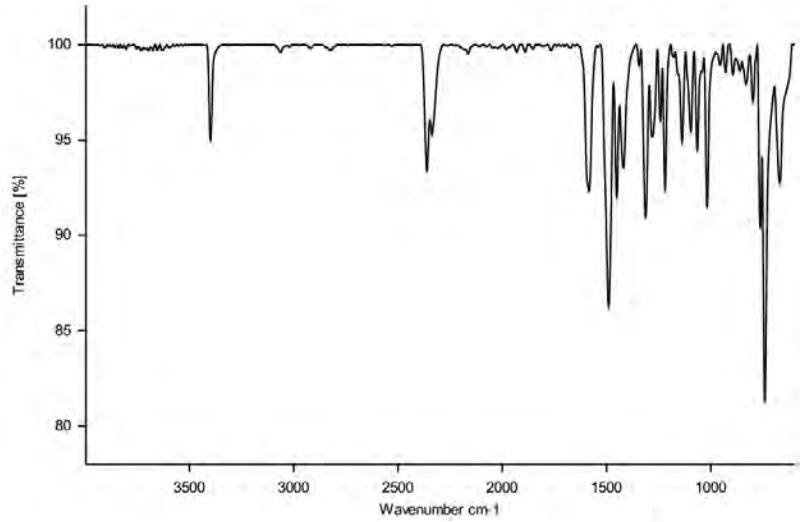


Figure S2: 18 C.N. 69

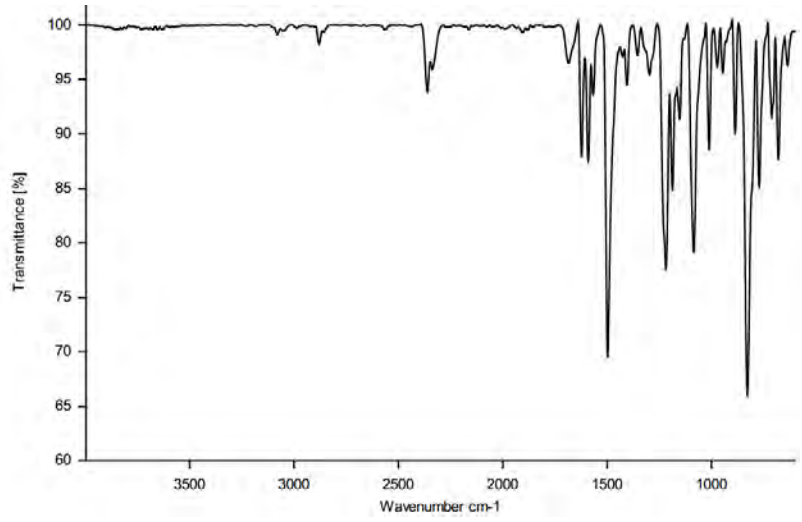


Figure S2: 19 **C.N. 70**

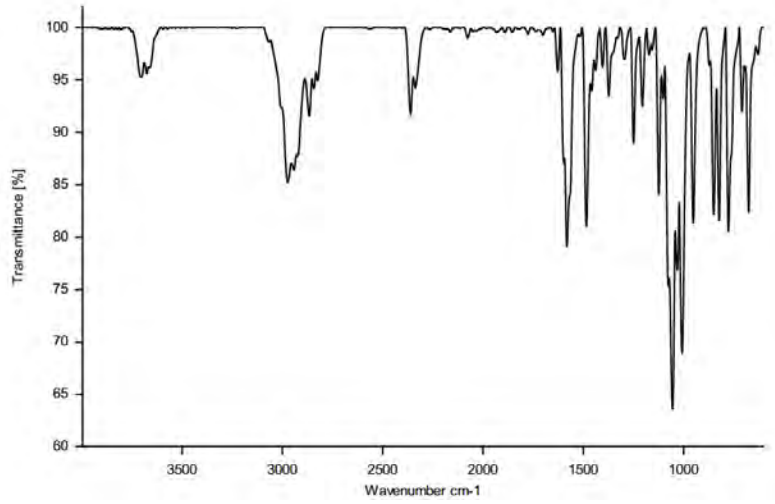


Figure S2: 20 **C.N. 71**

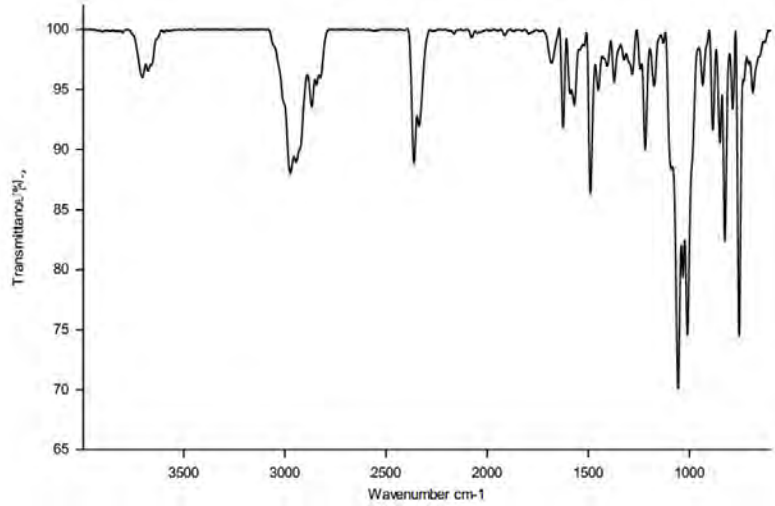


Figure S2: 21 **C.N. 72**

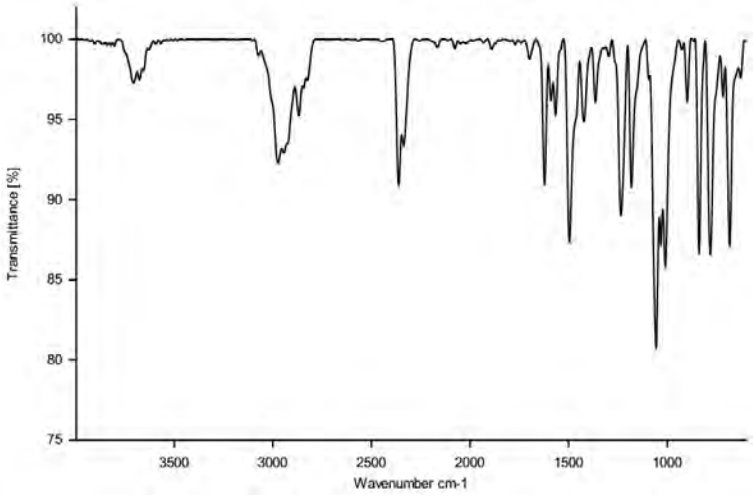


Figure S2: 22 **C.N. 73**

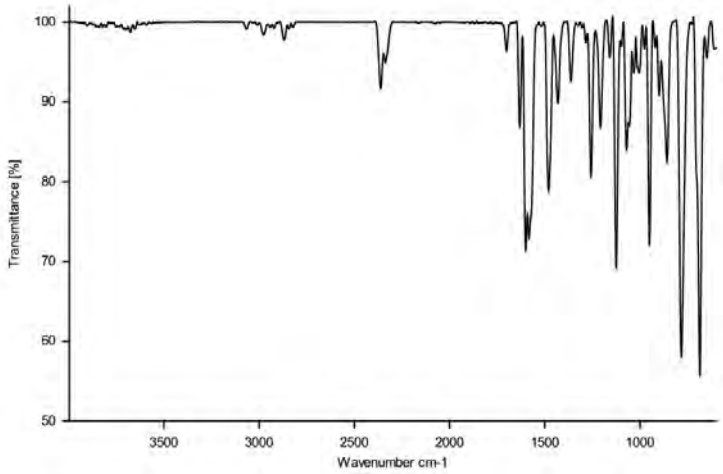


Figure S2: 23 **C.N. 74**

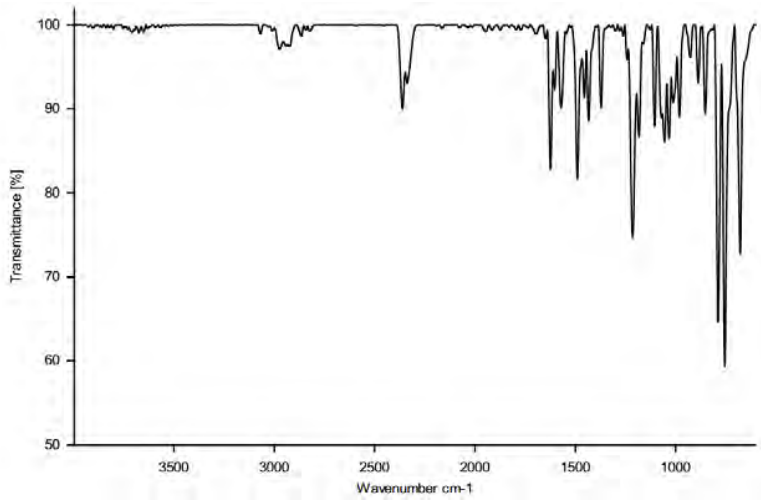


Figure S2: 24 **C.N. 75**

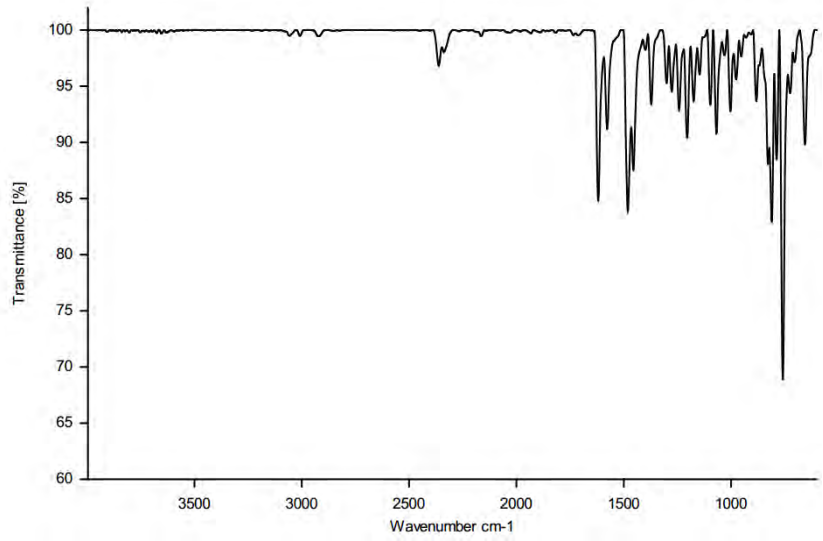


Figure S2: 25 **C.N. 76**

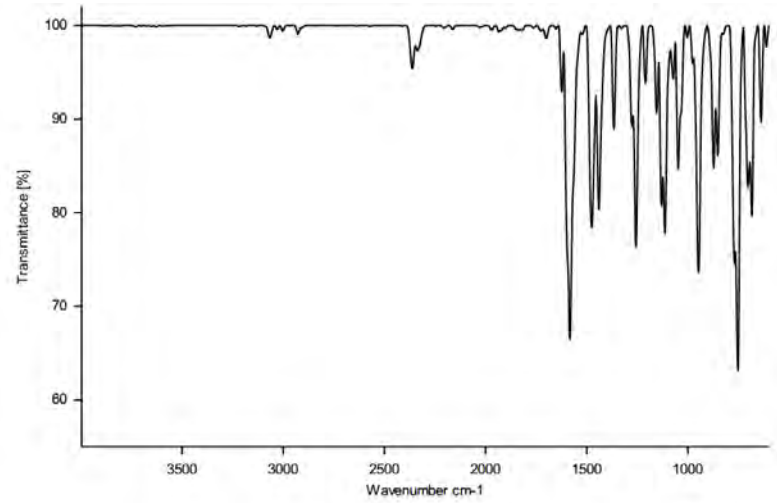


Figure S2: 26 **C.N. 77**

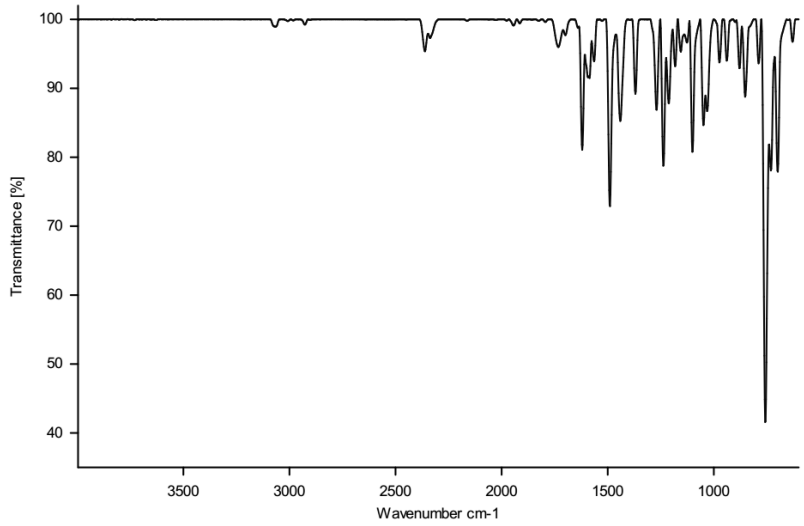


Figure S2: 27 **C.N. 78**

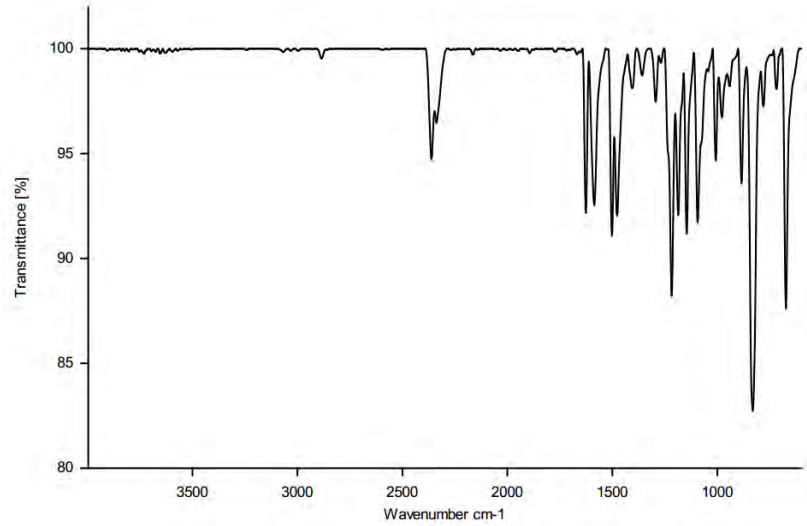


Figure S2: 28 **C.N. 79**

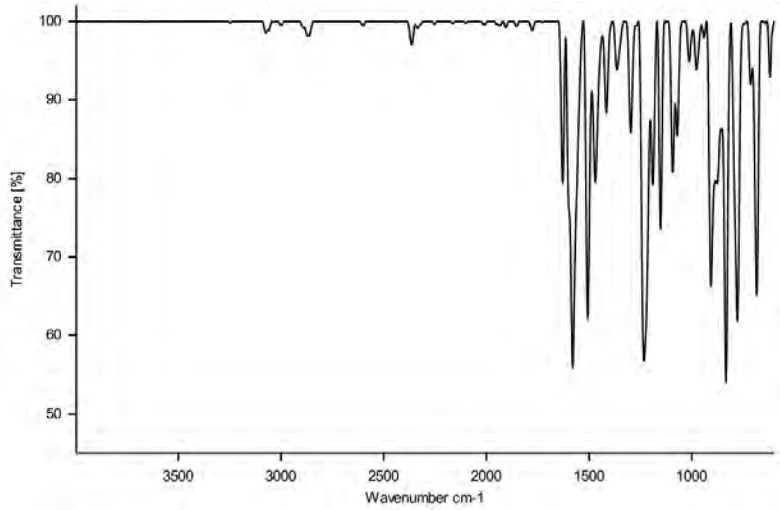


Figure S2: 29 **C.N. 80**

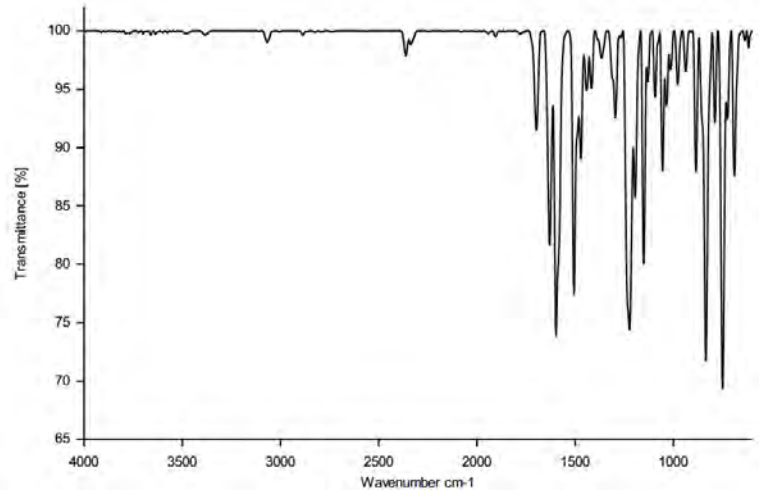


Figure S2: 30 **C.N. 81**

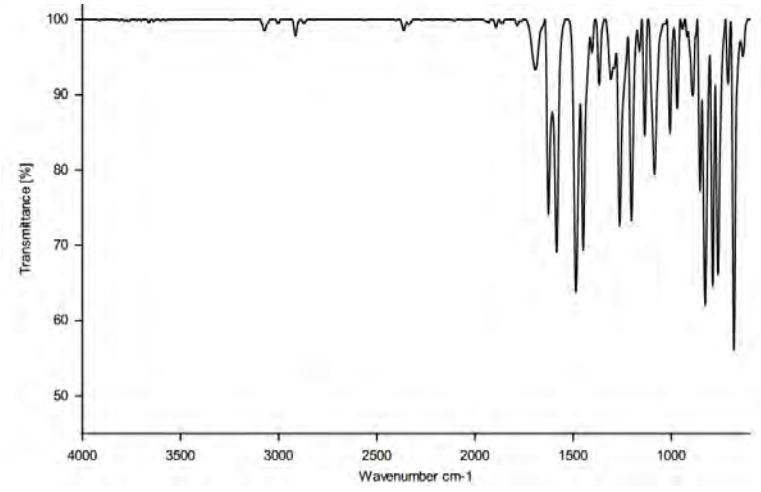


Figure S2: 31 **C.N. 82**

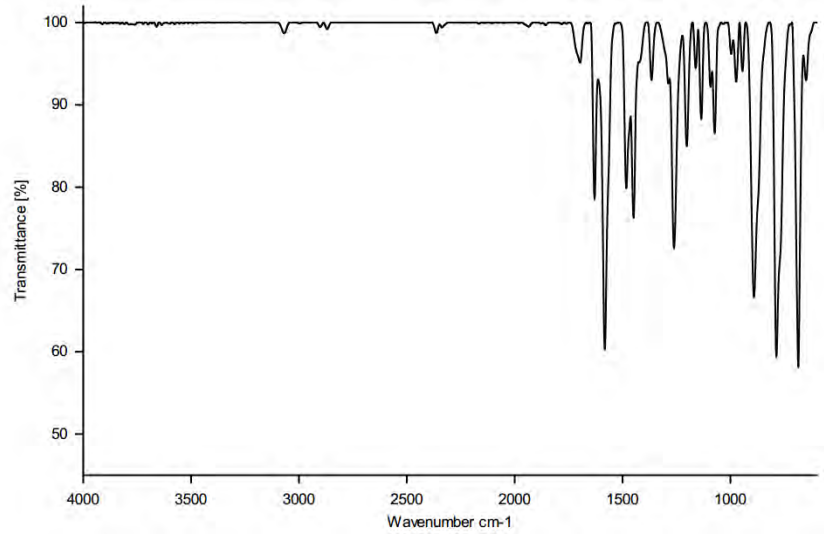


Figure S2: 32 **C.N. 83**

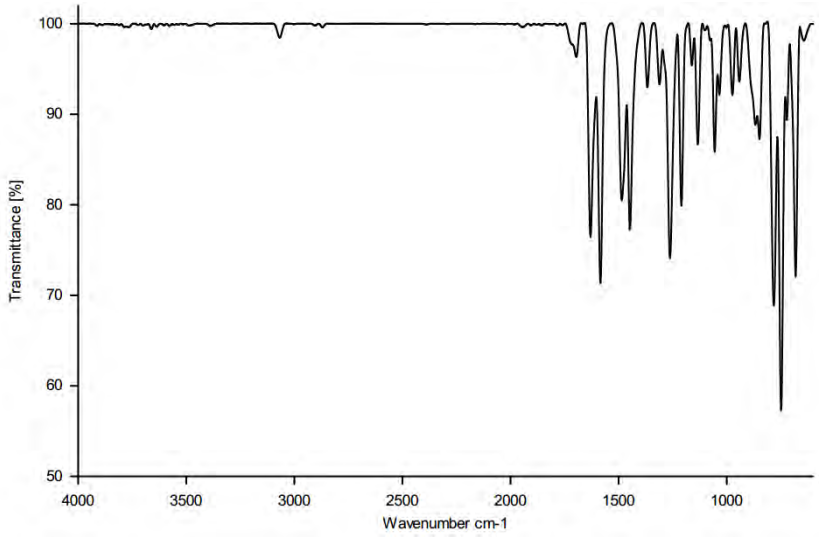


Figure S2: 33 **C.N. 84**

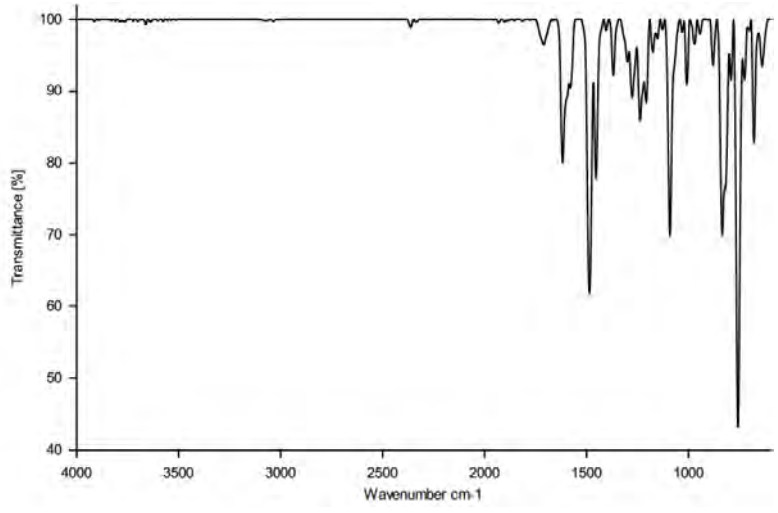


Figure S2: 34 **C.N. 85**

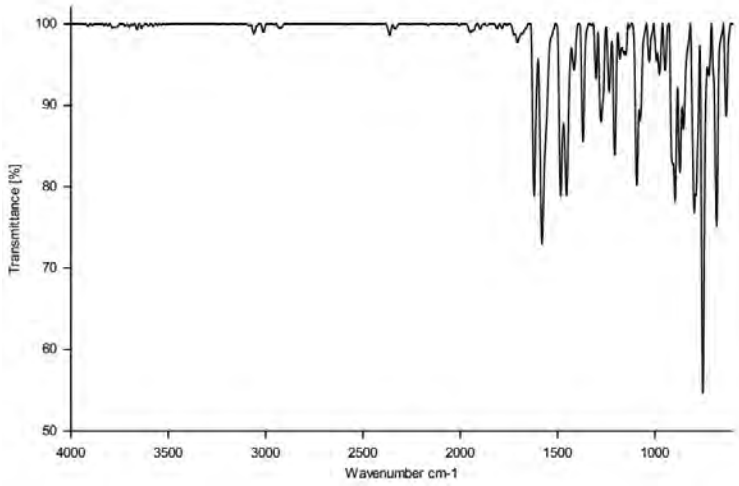


Figure S2: 35 **C.N. 86**

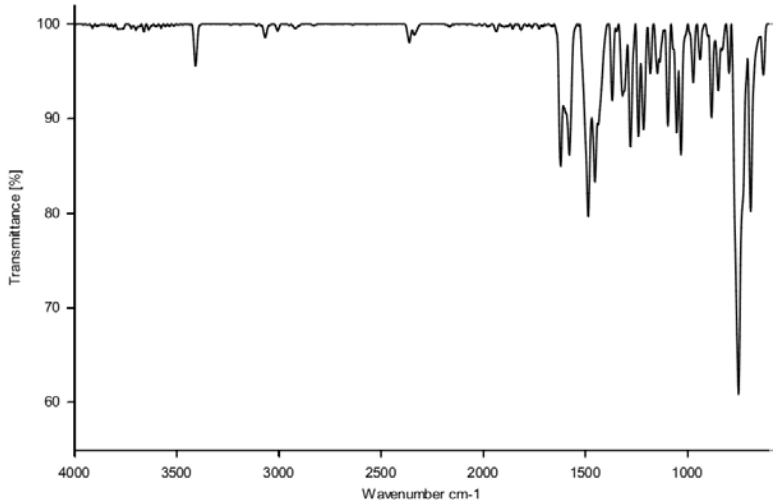


Figure S2: 36 **C.N. 87**

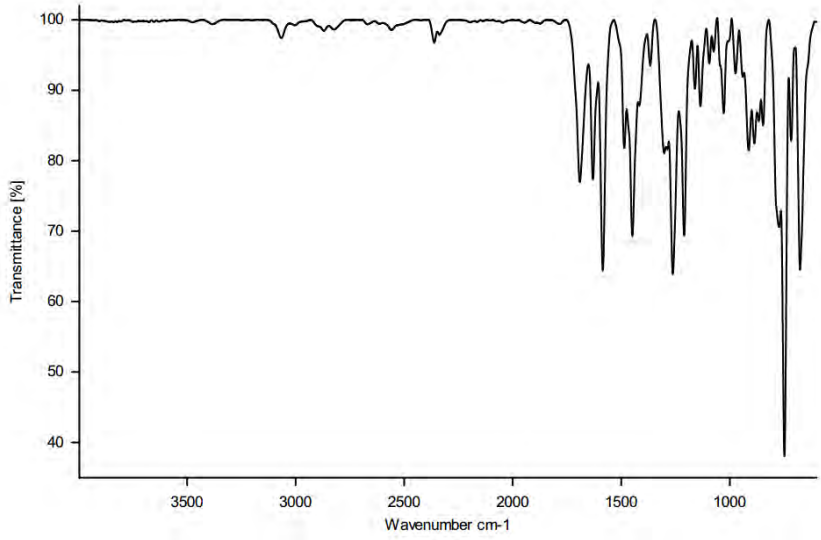


Figure S3: Powder X-ray Data for all solid compounds recorded on and their comparison with stimulated PXRD pattern. Patterns displayed in blue colour were recorded on the purified product, while the patterns simulated from the single crystal data are shown in red colour.

Figure S3: 1 **C.N. 52**

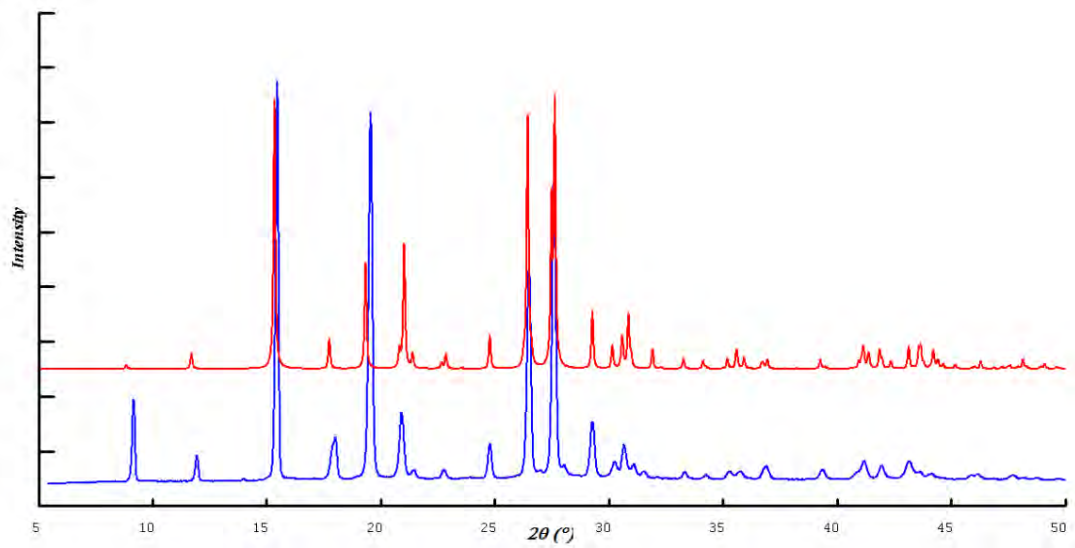


Figure S3: 2 **C.N. 53**

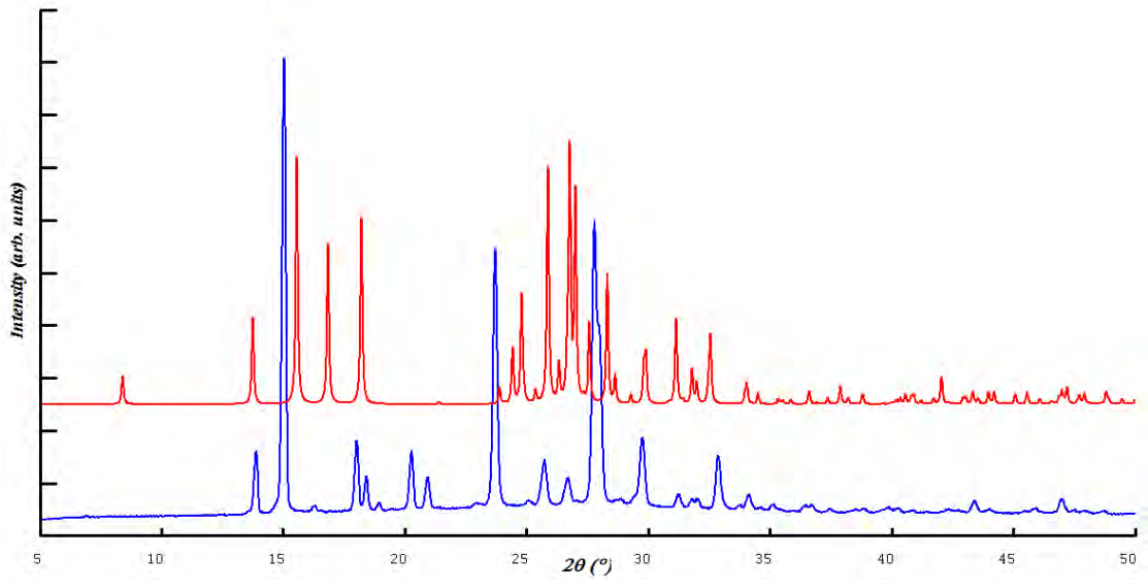


Figure S3: 3 **C.N. 54**

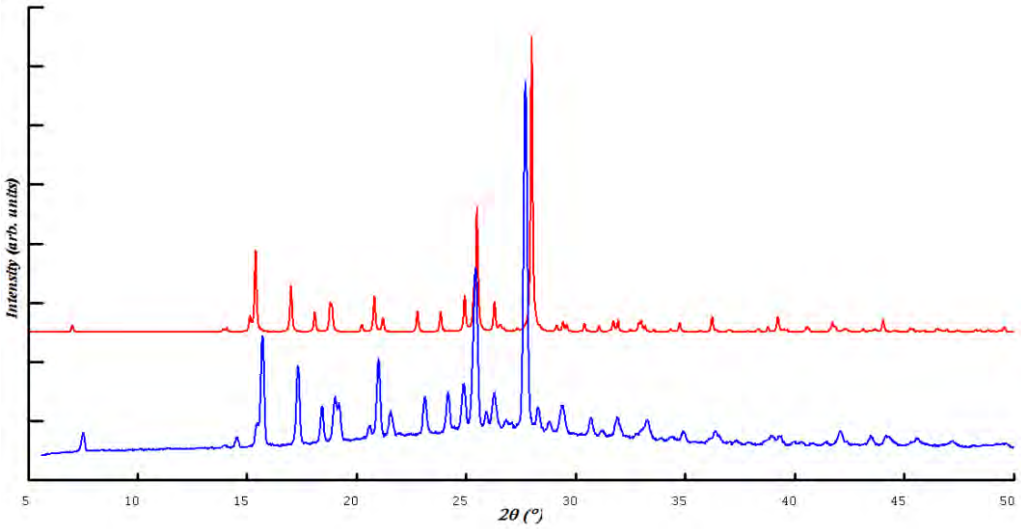


Figure S3: 4 **C.N. 55**

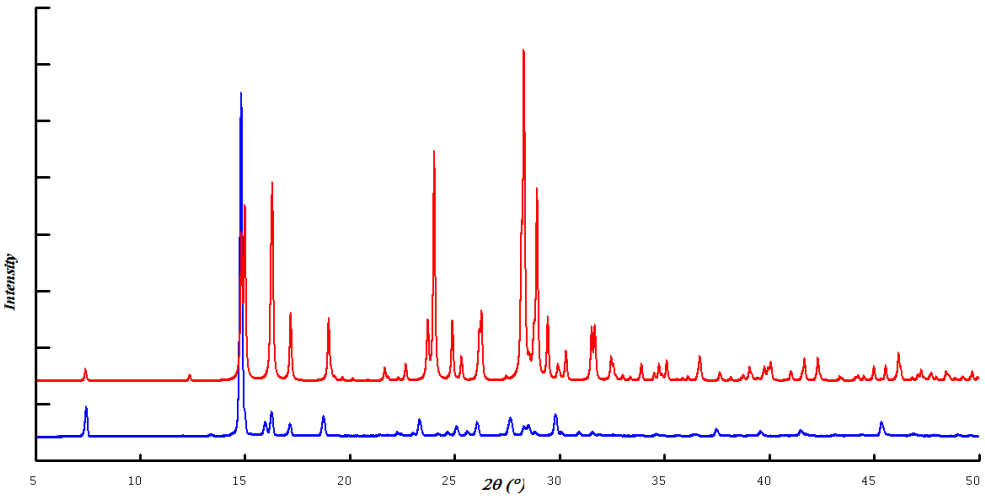


Figure S3: 5 **C.N. 56**

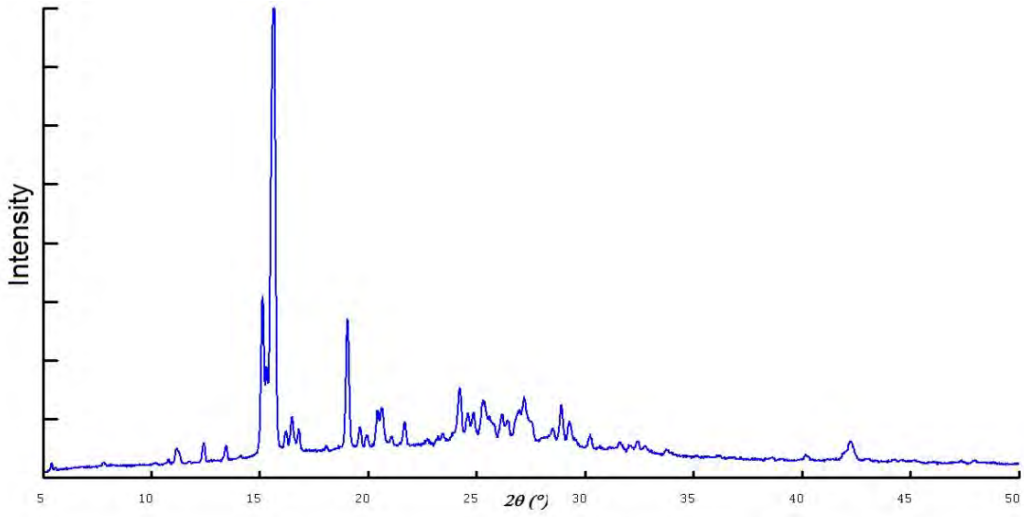


Figure S3: 6 **C.N. 57**

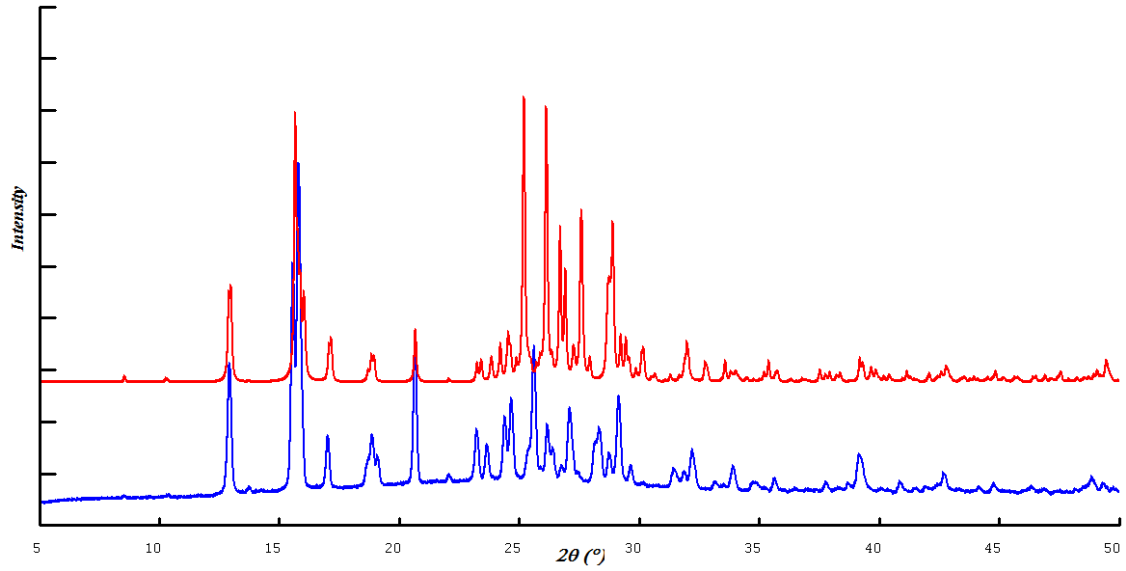


Figure S3: 7 **C.N. 58**

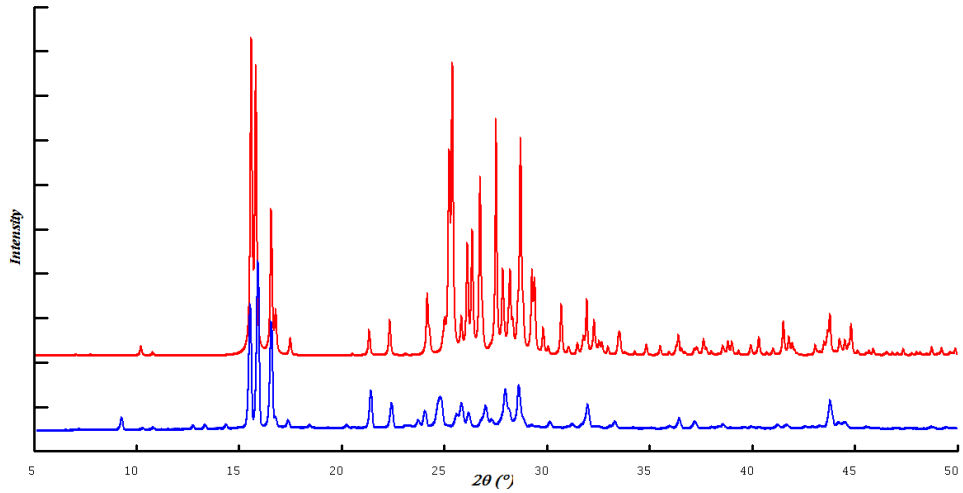


Figure S3: 8 **C.N. 59**

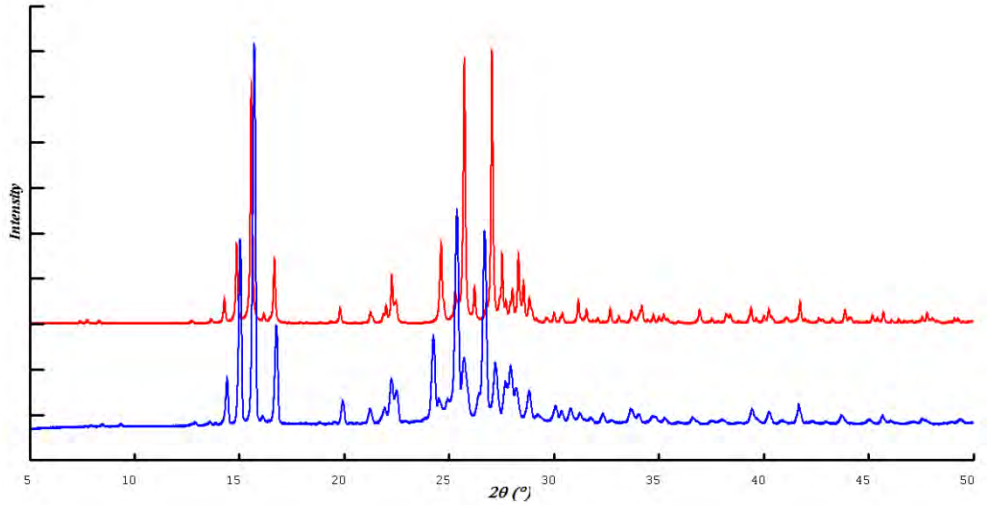


Figure S3: 9 **C.N. 60**

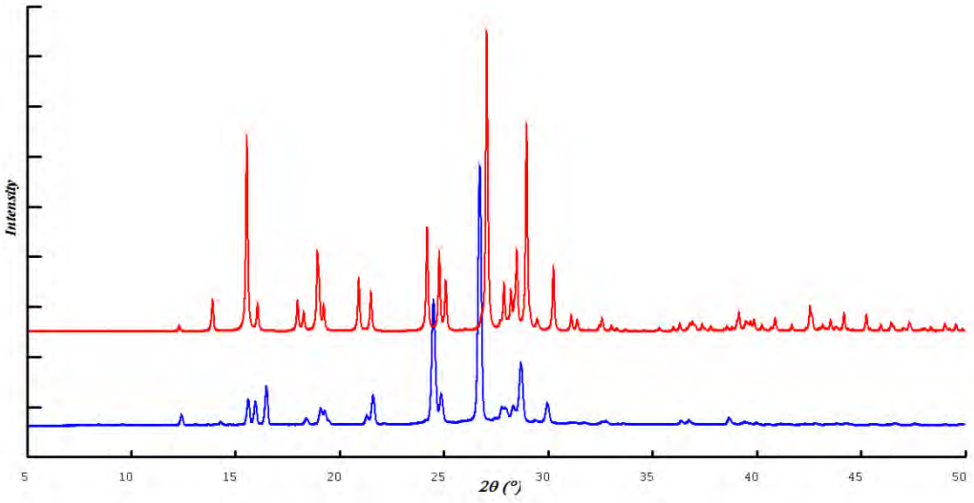


Figure S3: 10 **C.N. 61**

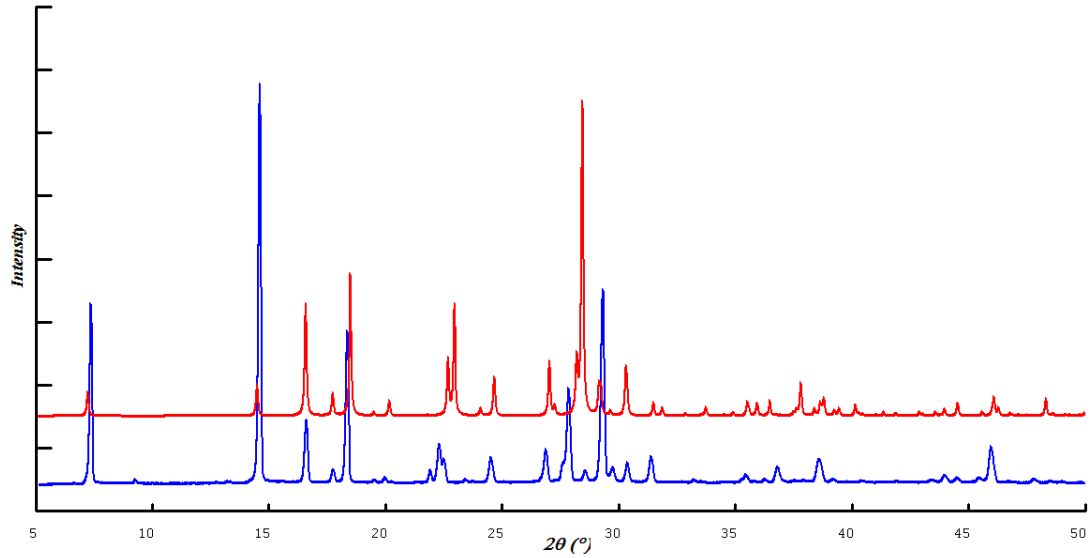


Figure S3: 11 **C.N. 62**

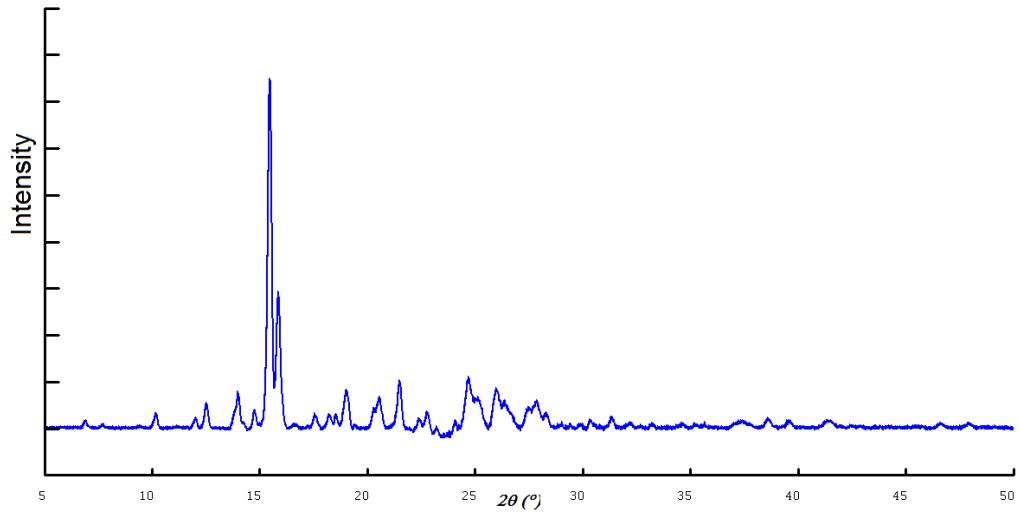


Figure S3: 12 **C.N. 63**

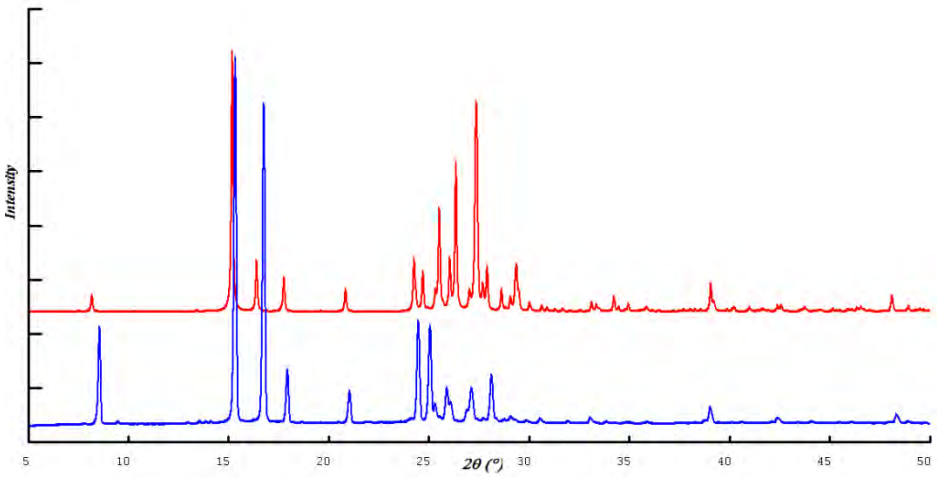


Figure S3: 13 **C.N. 64**

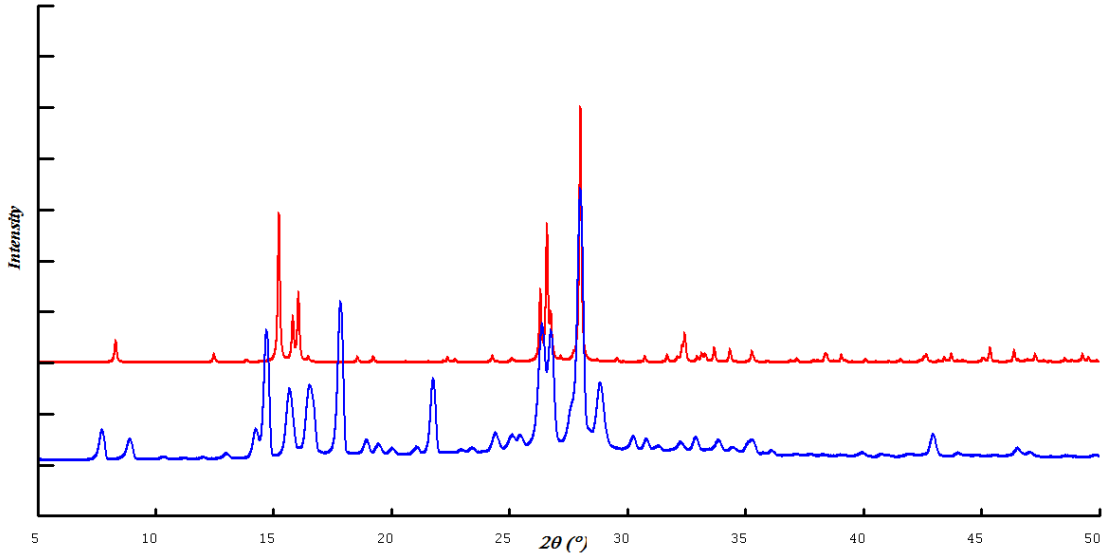


Figure S3: 14 **C.N. 65**

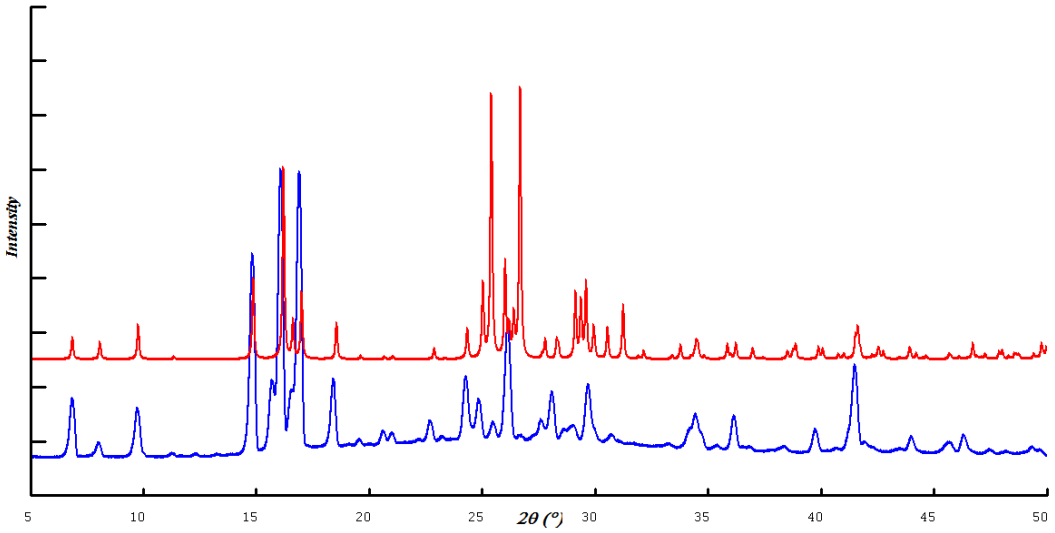


Figure S3: 15 **C.N. 66**

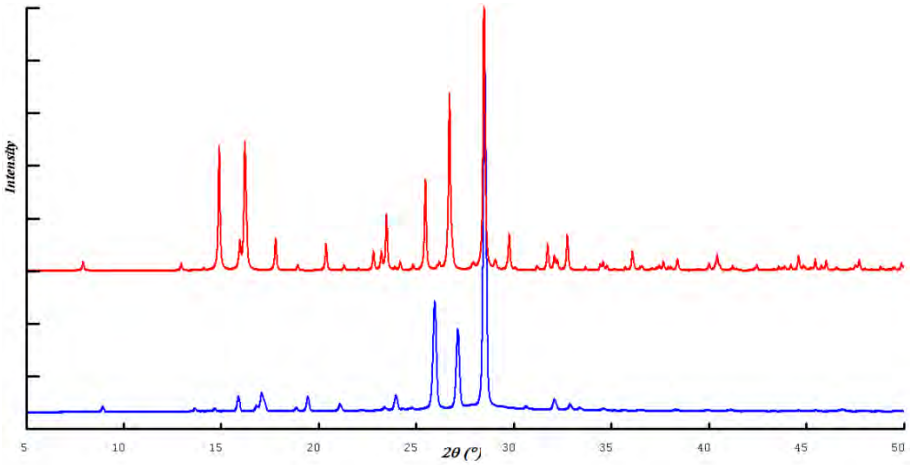


Figure S3: 16 **C.N. 67**

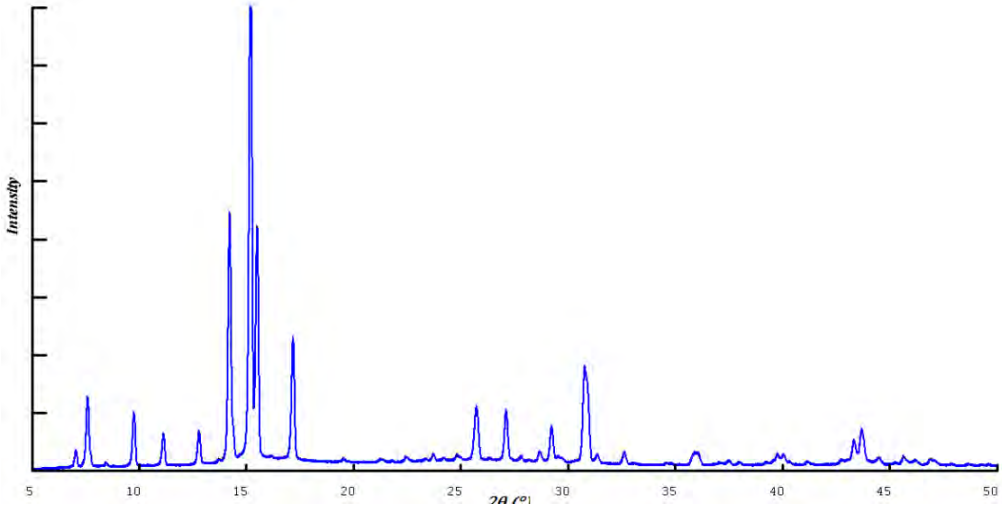


Figure S3: 17 **C.N. 68**

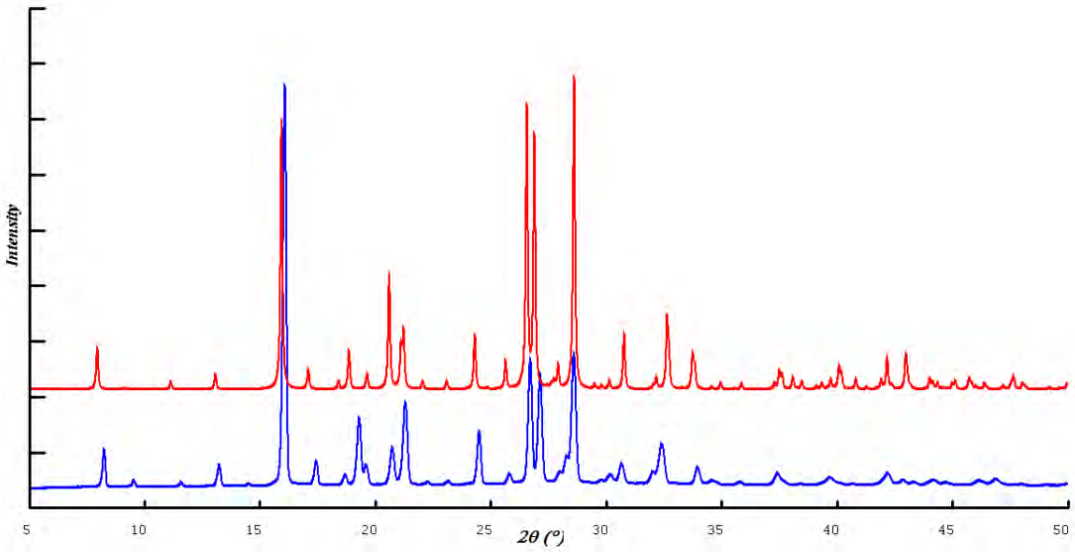


Figure S3: 18 **C.N. 69**

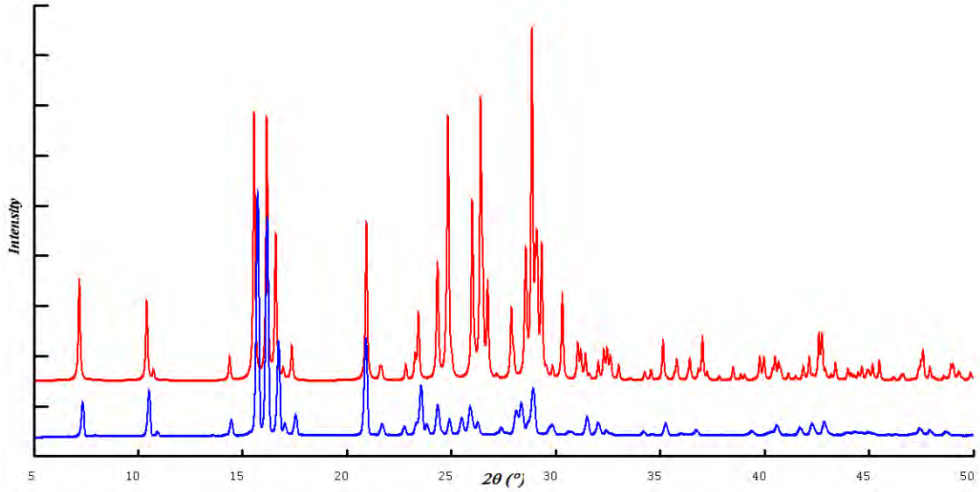


Figure S3: 19 **C.N. 70**

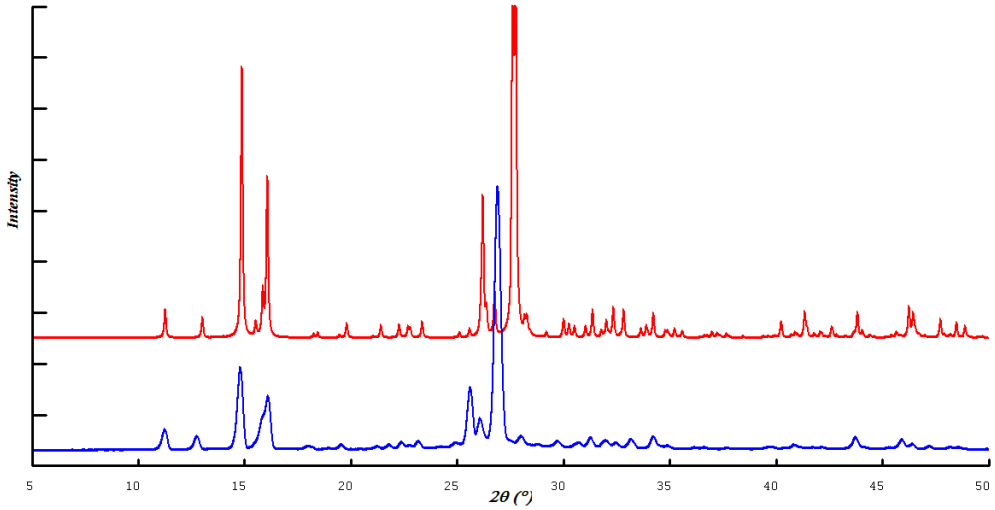


Figure S3: 20 **C.N. 71**

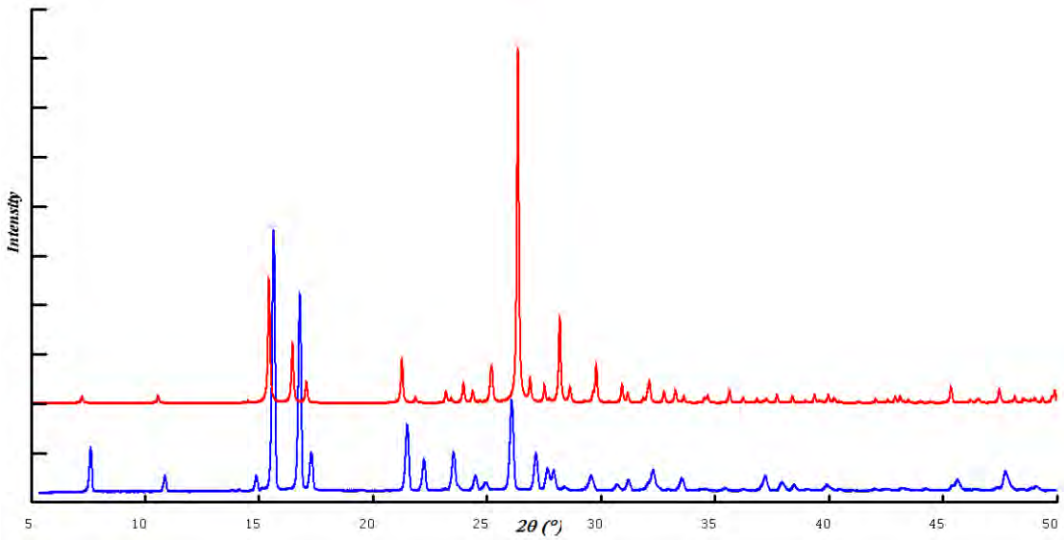


Figure S3: 21 **C.N. 72**

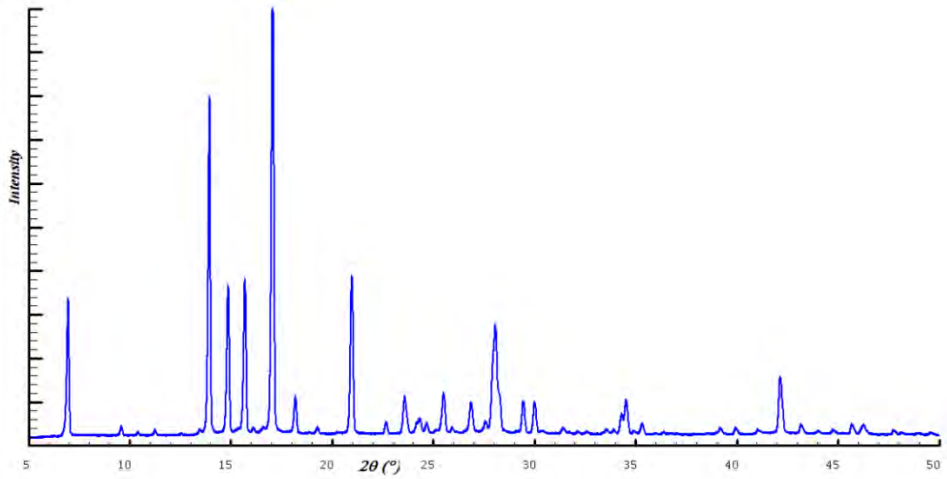


Figure S3: 22 **C.N. 73**

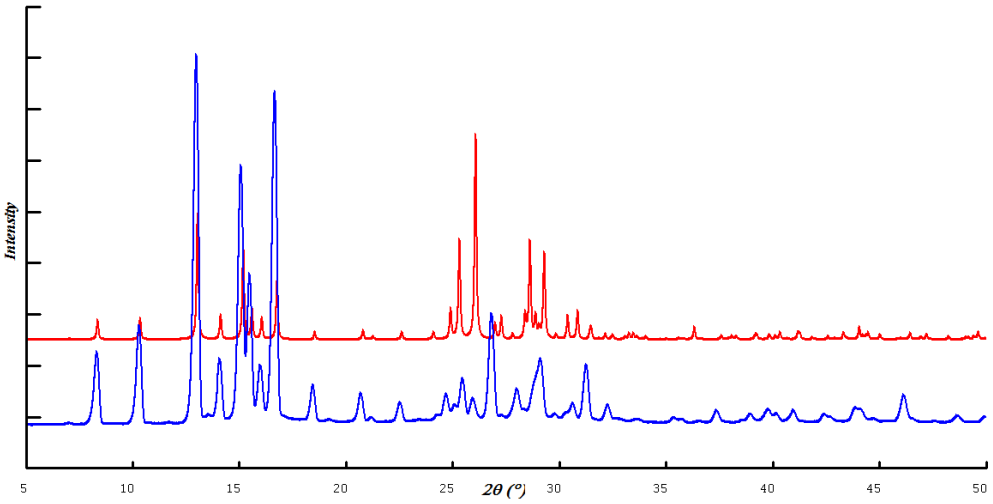


Figure S3: 23 **C.N. 74**

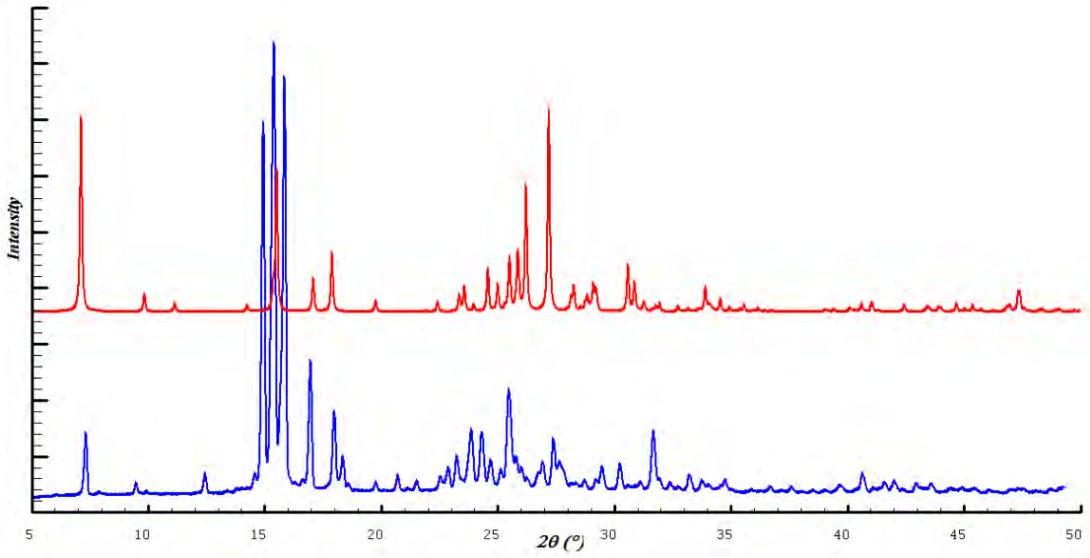


Figure S3: 24 **C.N. 75**

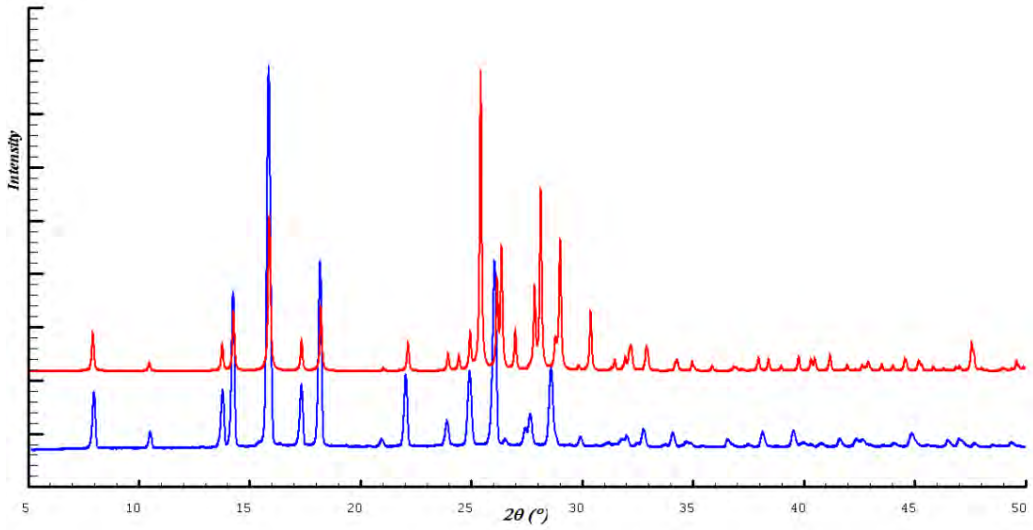


Figure S3: 25 **C.N. 76**

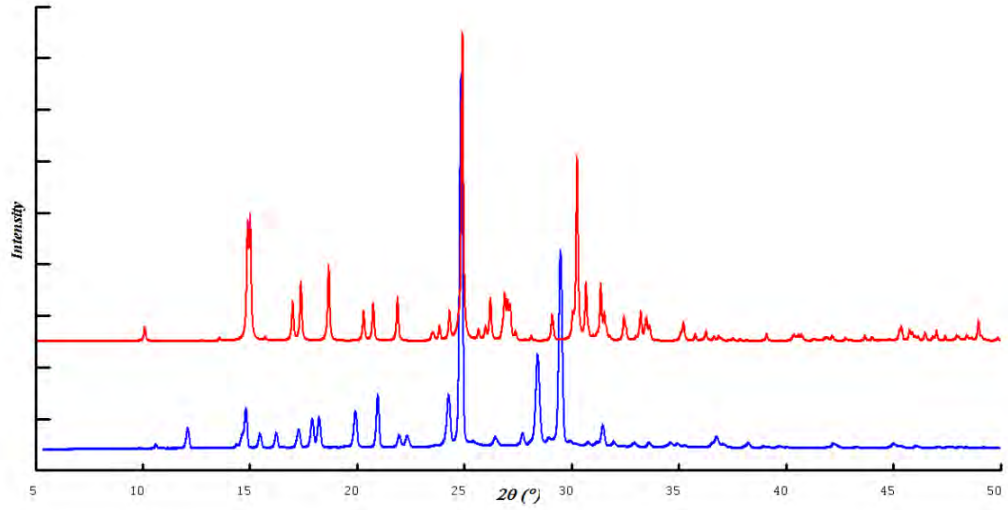


Figure S3: 26 **C.N. 77**

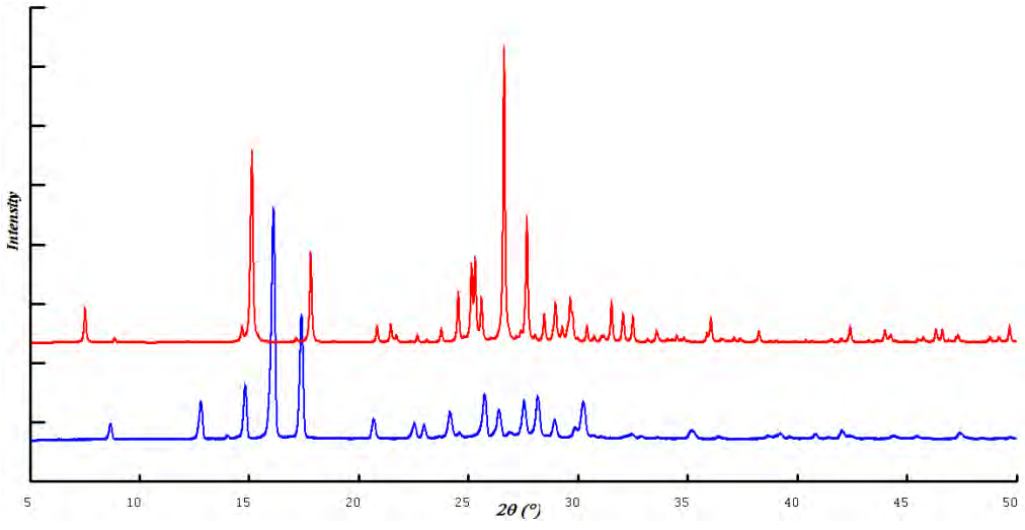


Figure S3: 27 **C.N. 78**

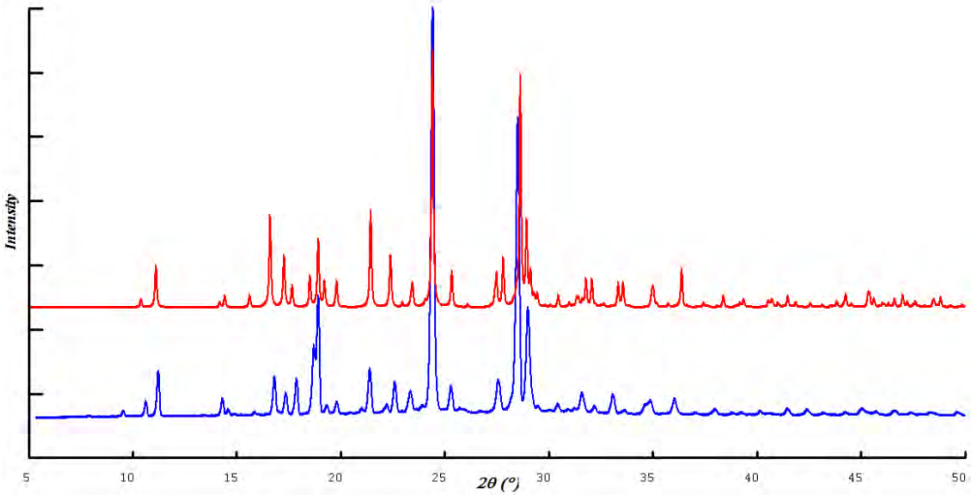


Figure S3: 28 **C.N. 79**

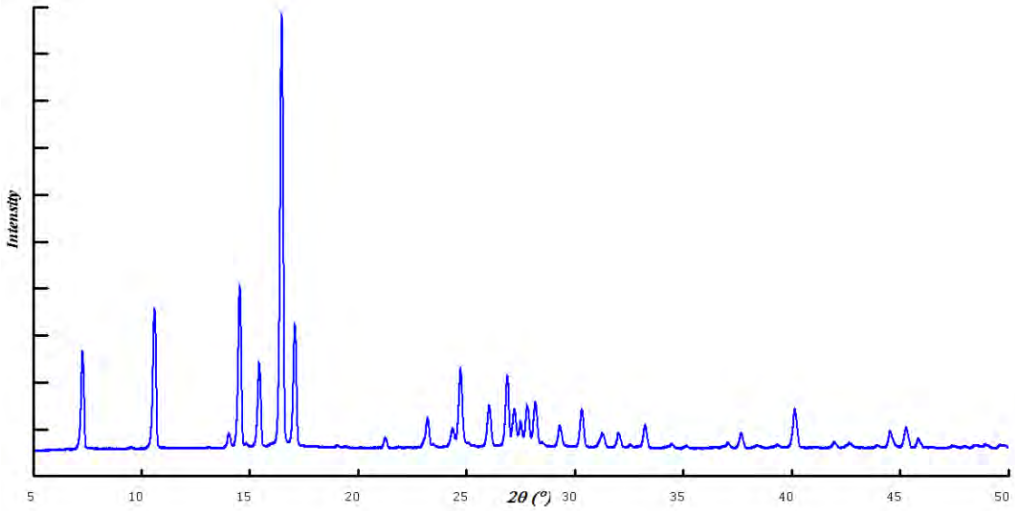


Figure S3: 29 **C.N. 80**

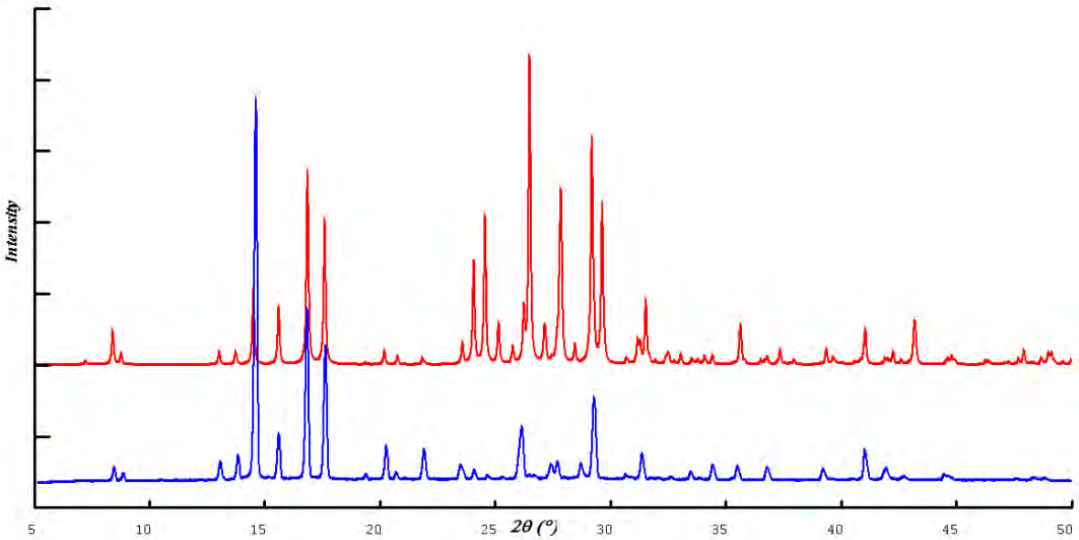


Figure S3: 30 **C.N. 81**

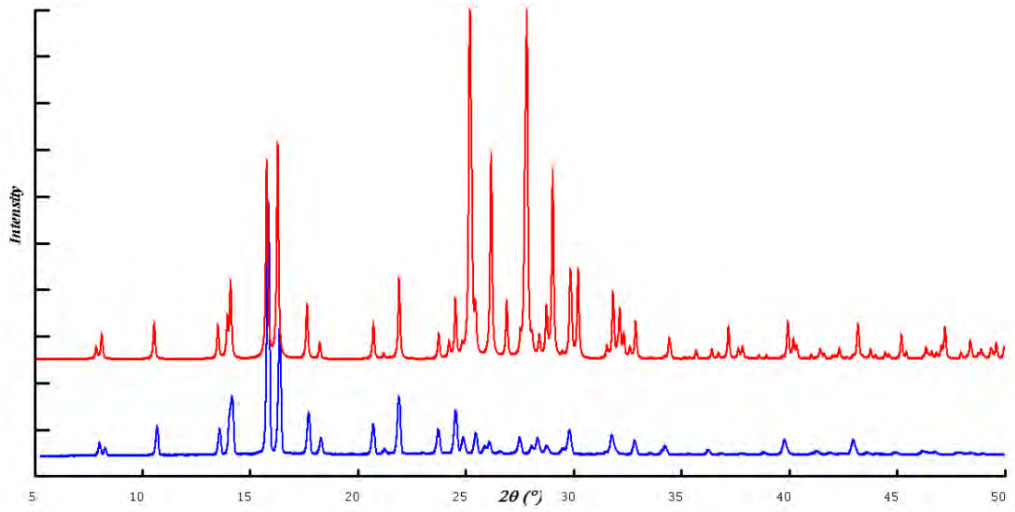


Figure S3: 31 **C.N. 82**

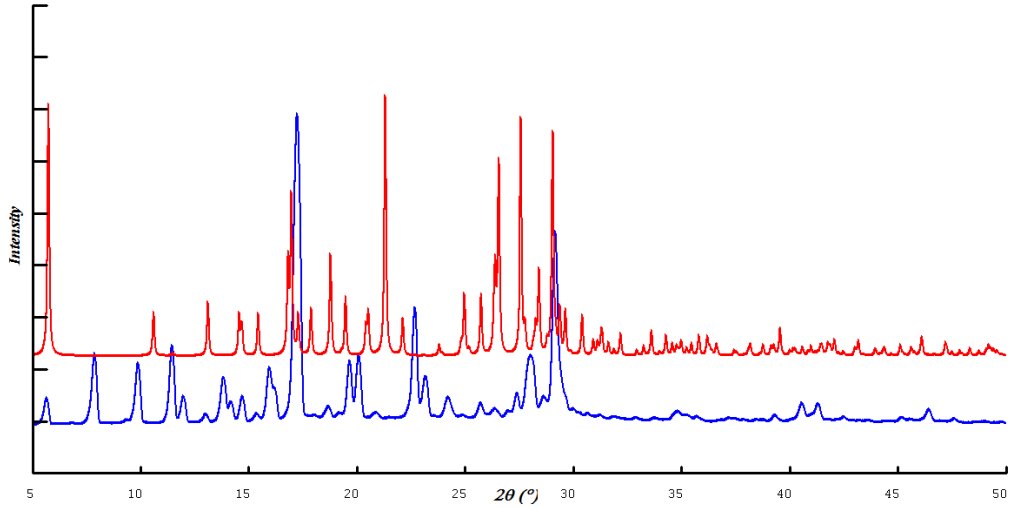


Figure S3: 32 **C.N. 83**

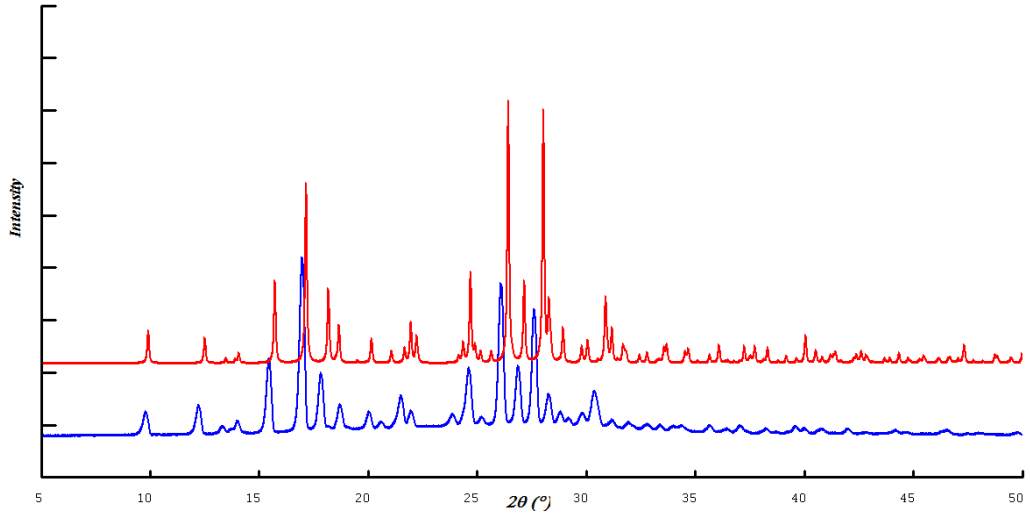


Figure S3: 33 **C.N. 84**

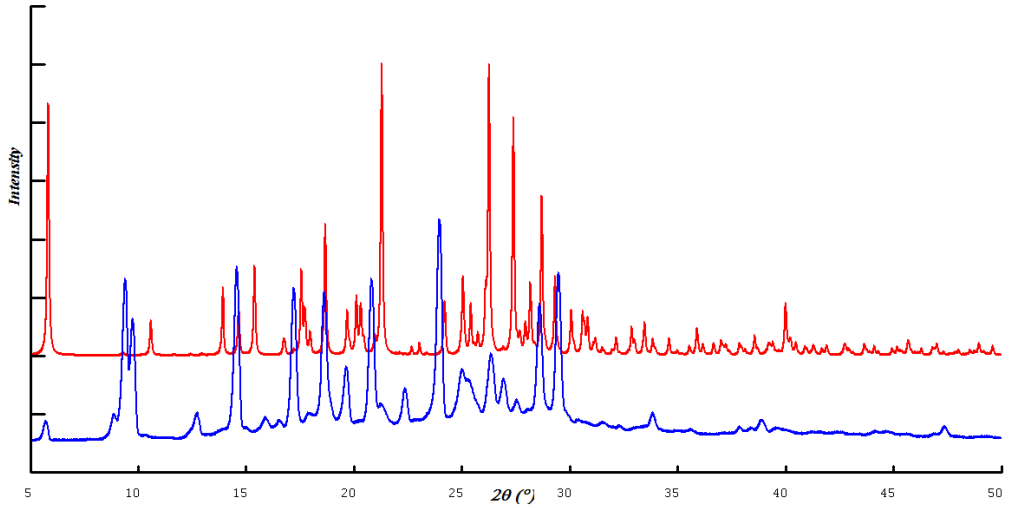


Figure S3: 34 **C.N. 86**

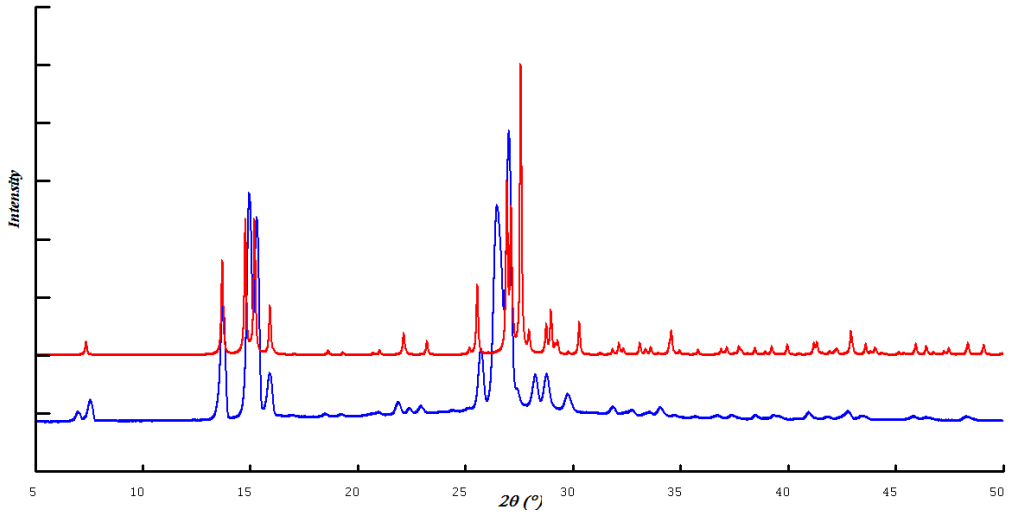


Figure S3: 35 **C.N. 87**

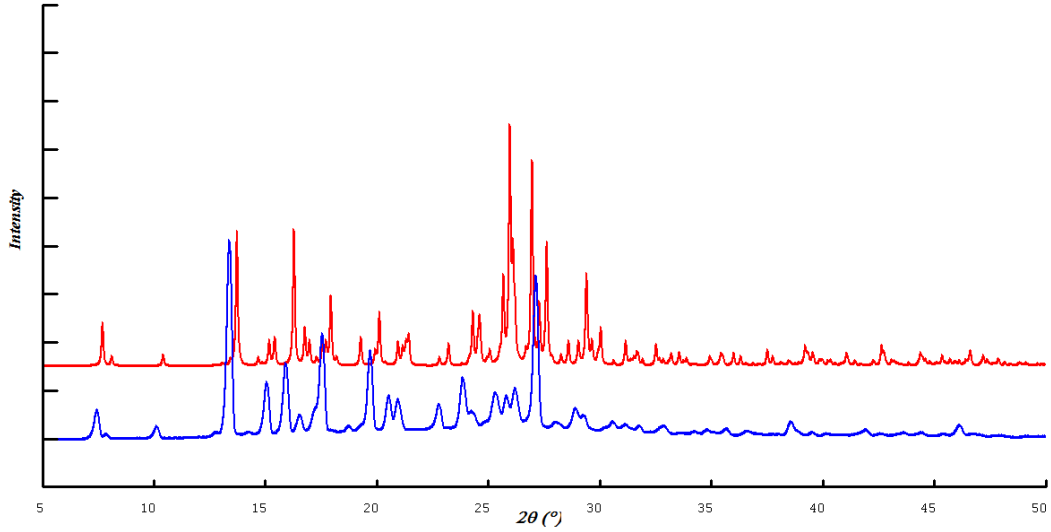


Table S32: Melting Point (in ^{0}C) of solid compounds determined from DSC data:

Compound Code	Melting point (M.P.) /^{o}C (Onset value from DSC)	ΔH (J/g)
52	81.4	96.8
53	55.6	105.2
54	50.9	71.3
55	67.9	85.2
56	46.4	67.3
57	44.3	106.0
58	54.5	26.3
59	65.0	87.7
60	65.3	93.4
61	68.3	93.1
62	45.7	82.9
63	73.4	67.1
64	56.0	98.0
65	71.2	95.9
66	52.0	95.0
67	61.1	82.6
68	79.8	128.0
69	70.8	95.3
70	58.0	90.5
71	82.2	95.7
72	68.0	79.7
73	44.9	69.8
74	47.8	81.6
75	67.0	83.0
76	84.4	97.4
77	64.2	97.0
78	81.6	91.3
79	63.0	73.9
80	52.5	82.2
81	56.2	64.5
82	52.0	84.4
83	71.2	94.1
84	53.3	56.0
85	--	--
86	72.7	95.4
87	52.0	95.0

The symbol "--" signifies that the compound has not shown any characteristic in its DSC traces.

Figure S4: DSC traces of all compounds

Figure S4: 1 **C.N. 52**

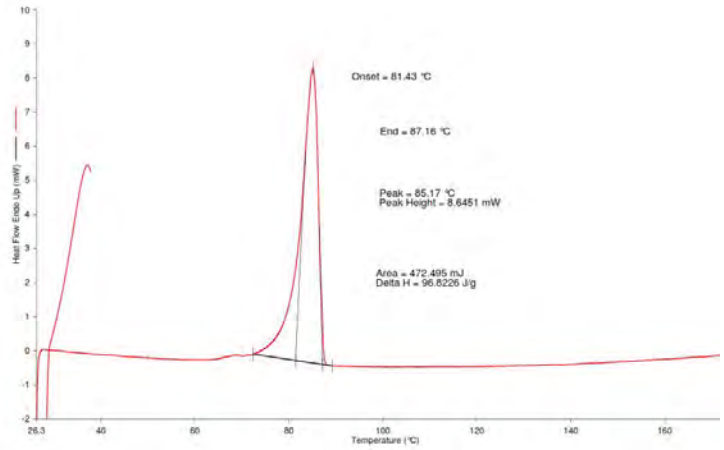


Figure S4: 2 **C.N. 53**

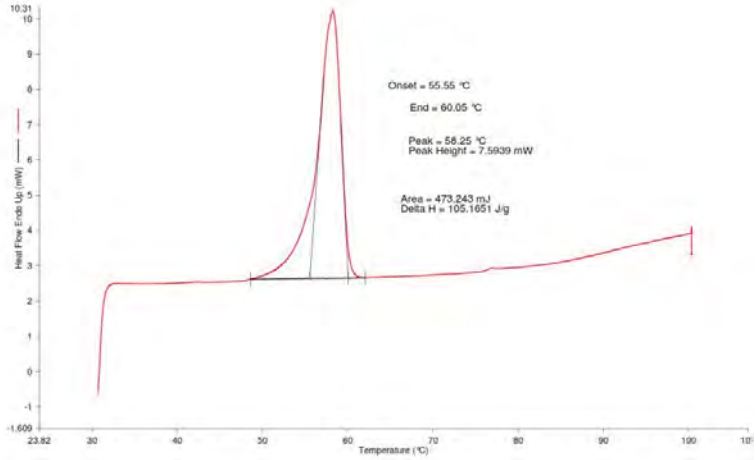


Figure S4: 3 **C.N. 54**

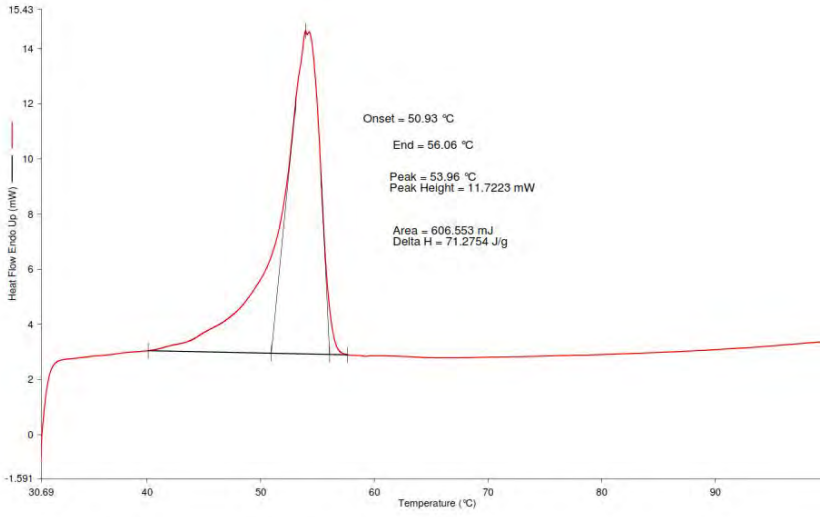


Figure S4: 4 **C.N. 55**

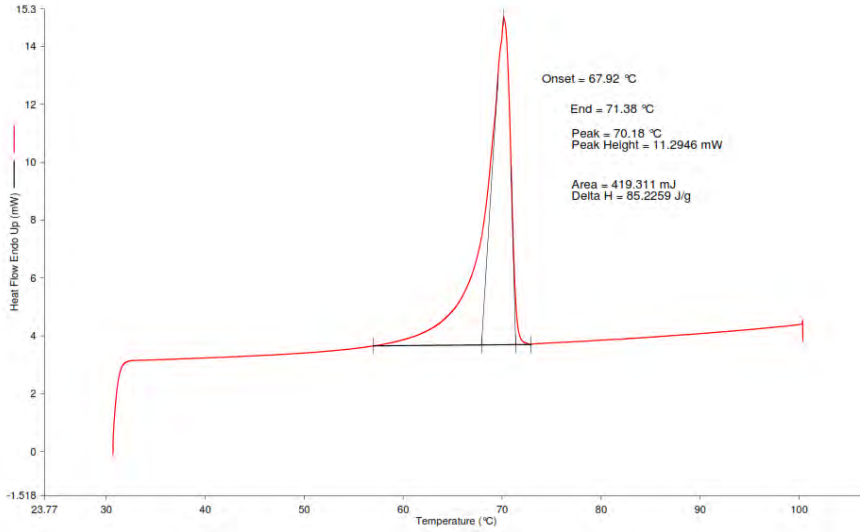


Figure S4: 5 **C.N. 56**

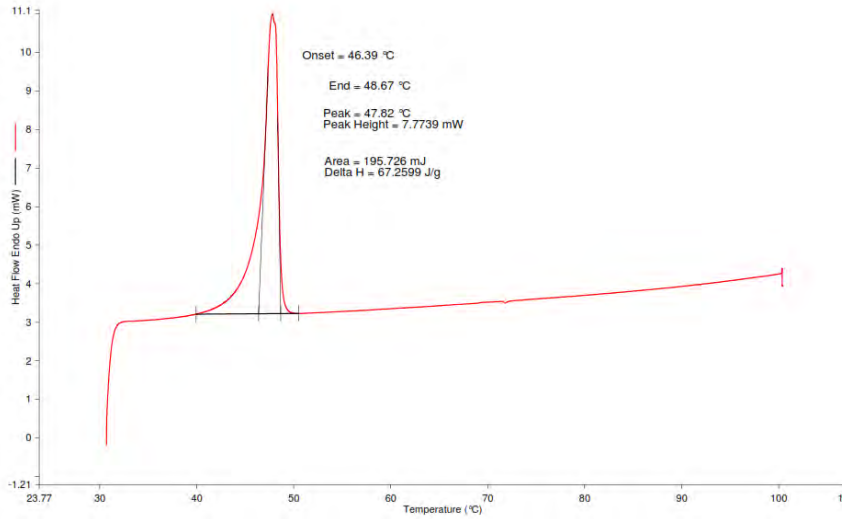


Figure S4:6 **C.N. 57**

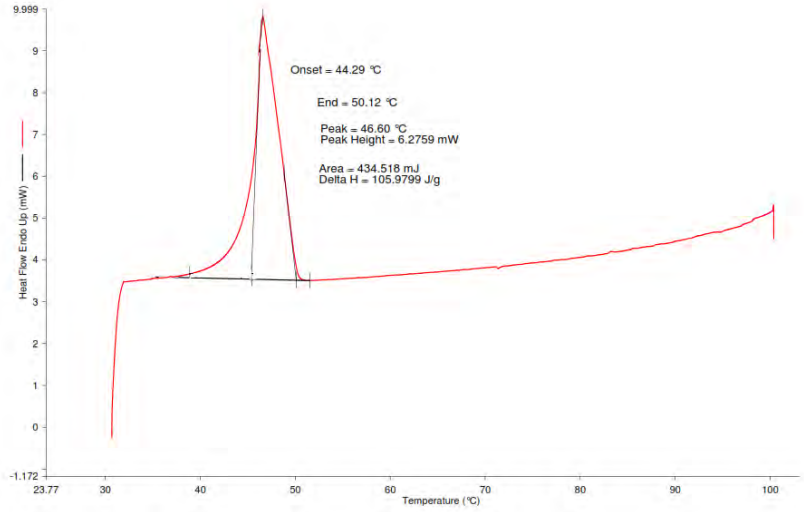


Figure S4: 7 **C.N. 58**

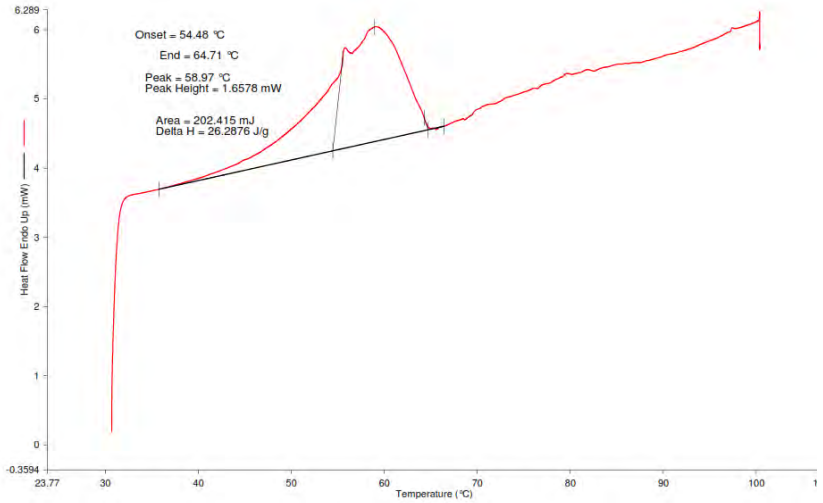


Figure S4: 8 **C.N. 59**

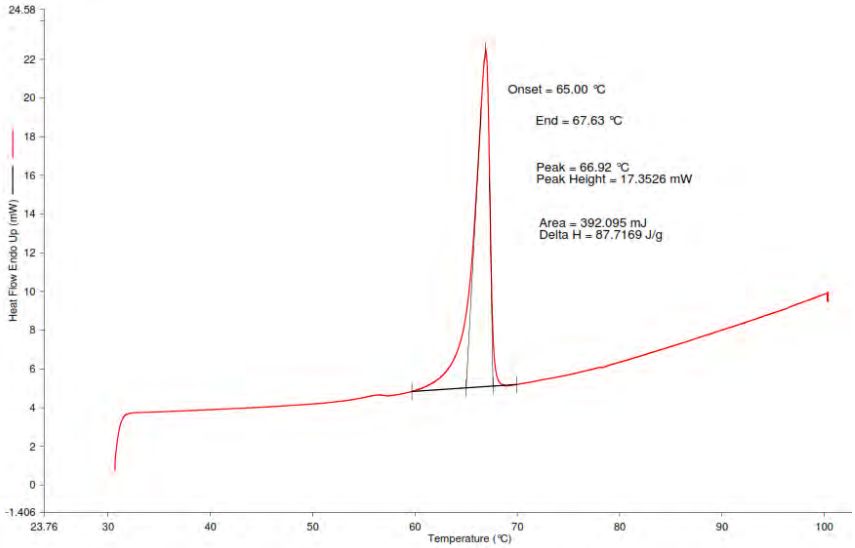


Figure S4: 9 **C.N. 60**

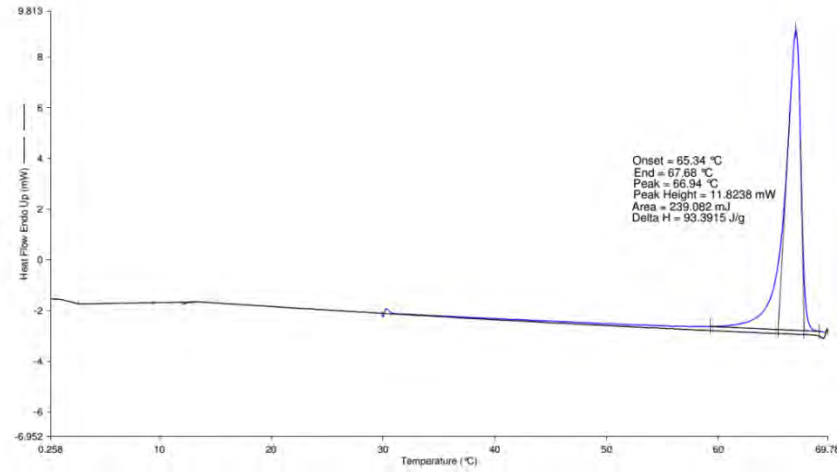


Figure S4: 10 **C.N. 61**

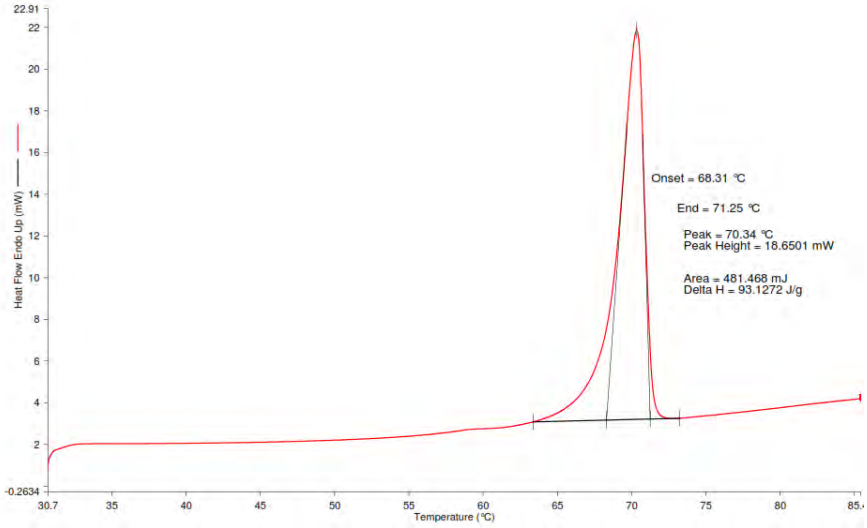


Figure S4: 11 **C.N. 62**

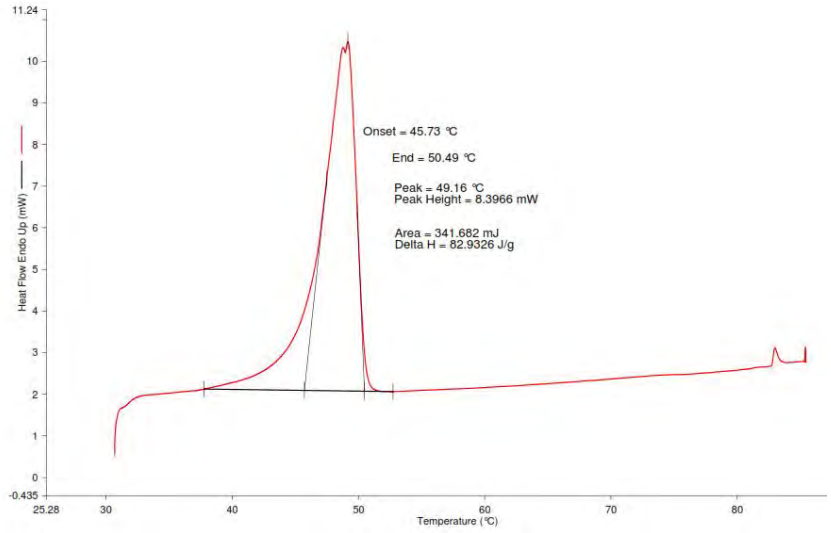


Figure S4: 12 **C.N. 63**

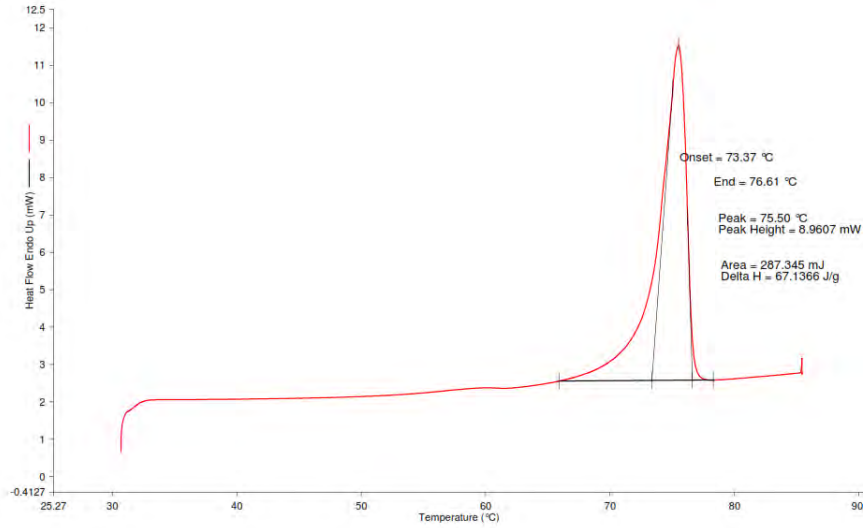


Figure S4: 13 **C.N. 64**

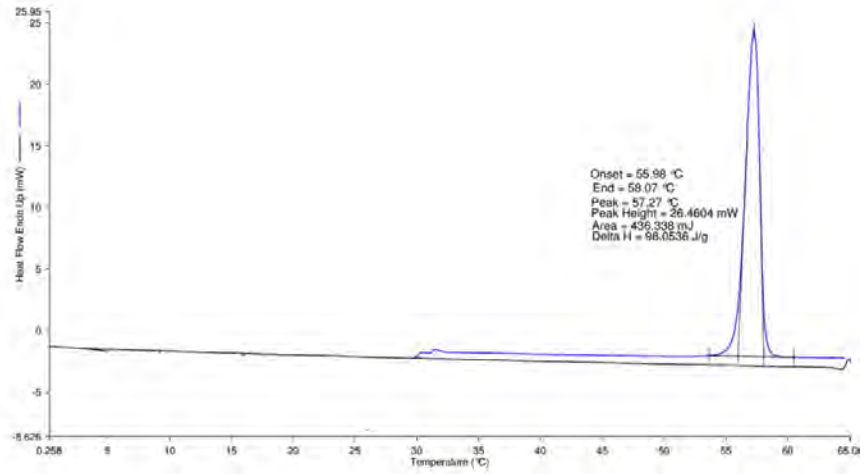


Figure S4: 14 **C.N. 65**

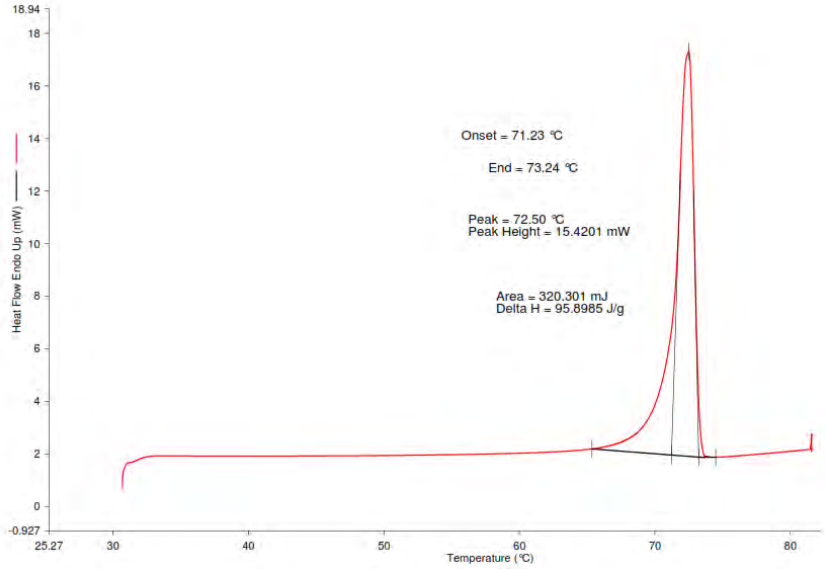


Figure S4:15 **C.N. 66**

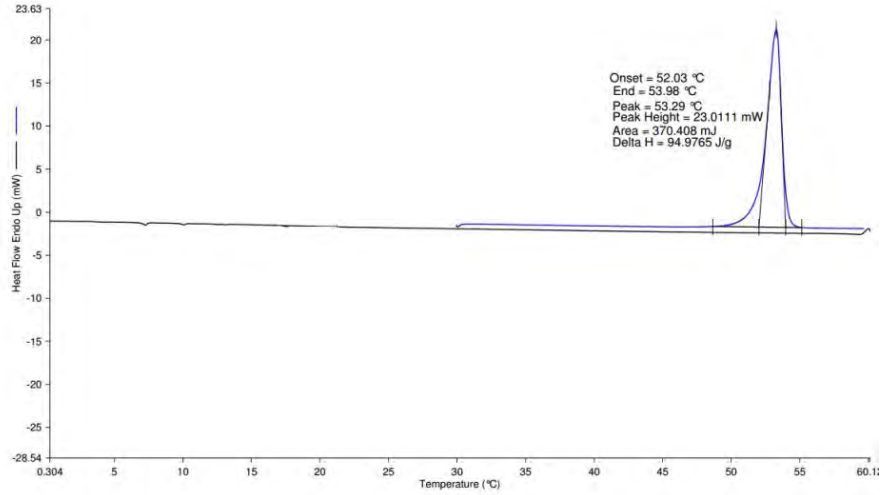


Figure S4:16 **C.N. 67**

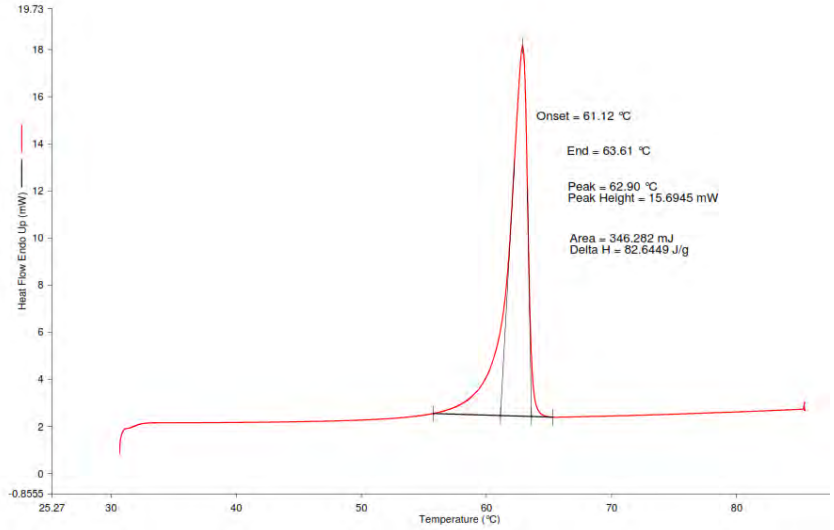


Figure S4:17 **C.N. 68**

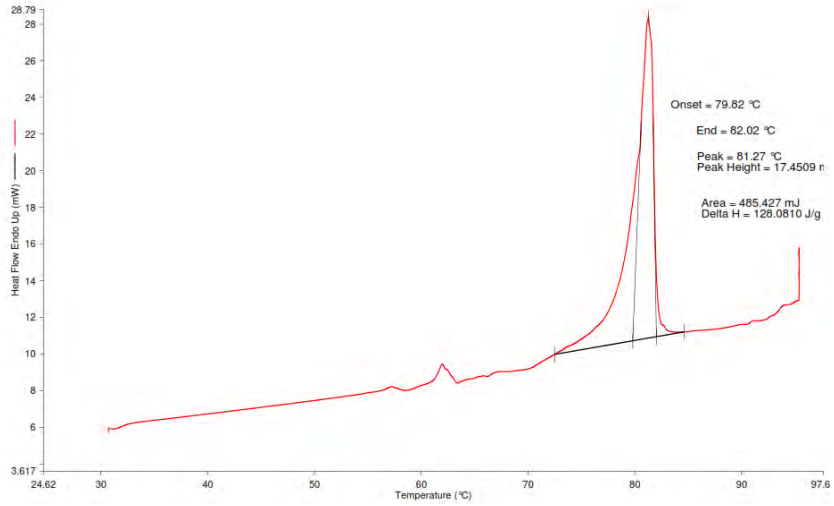


Figure S4:18 **C.N. 69**

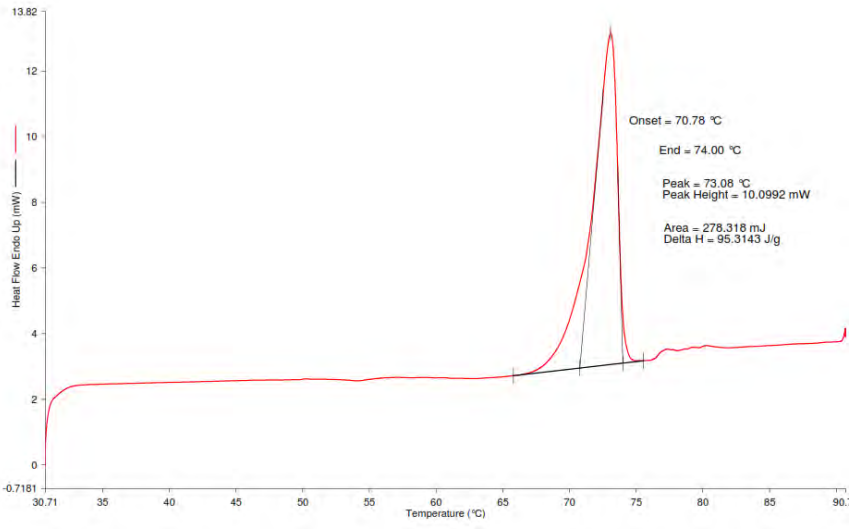


Figure S4:19 **C.N. 70**

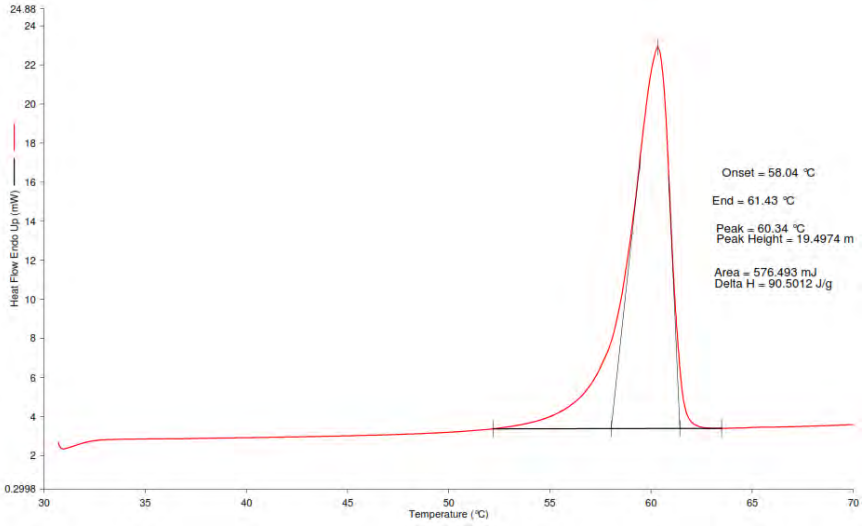


Figure S4:20 **C.N. 71**

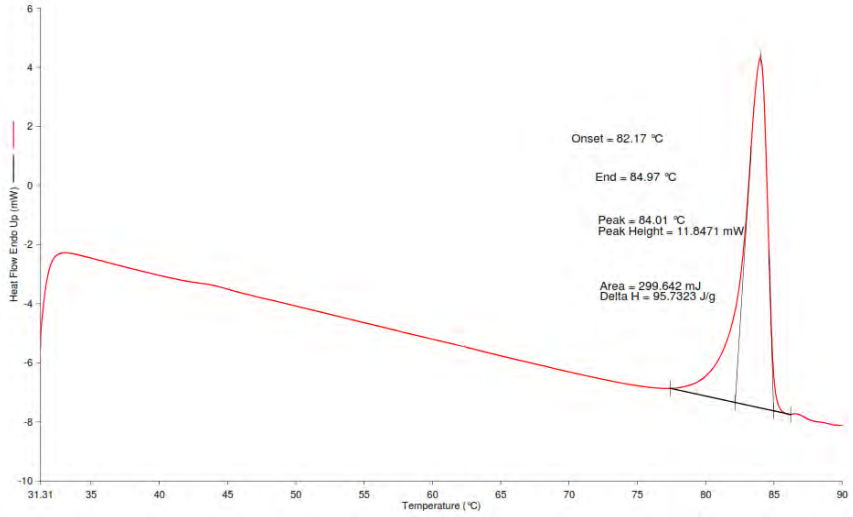


Figure S4:21 **C.N. 72**

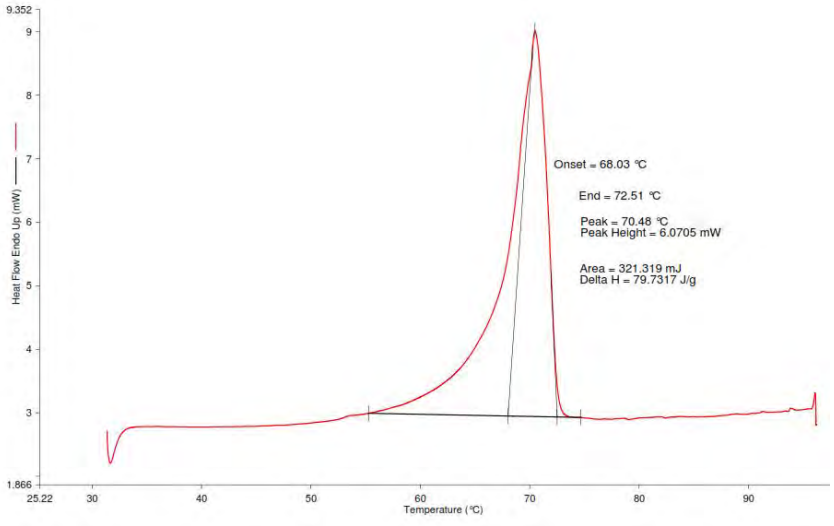


Figure S4:22 **C.N. 73**

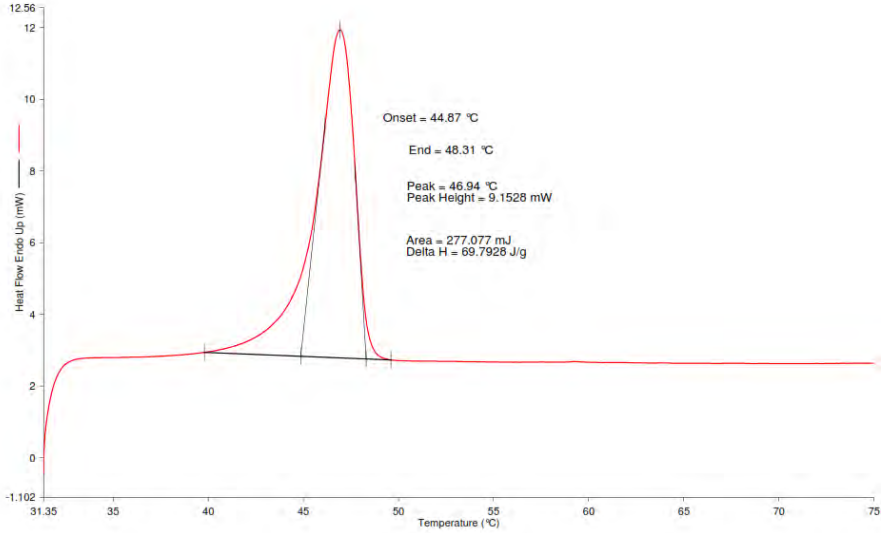


Figure S4:23 **C.N. 74**

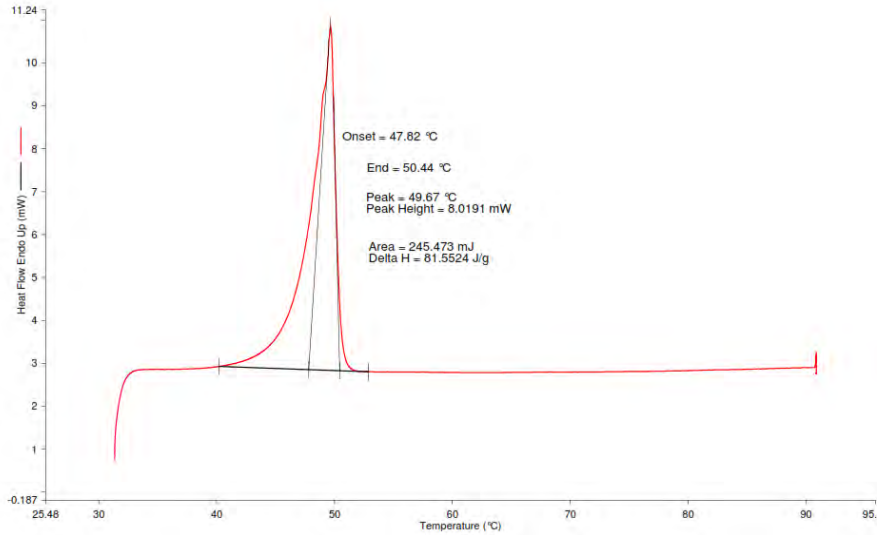


Figure S4:24 **C.N. 75**

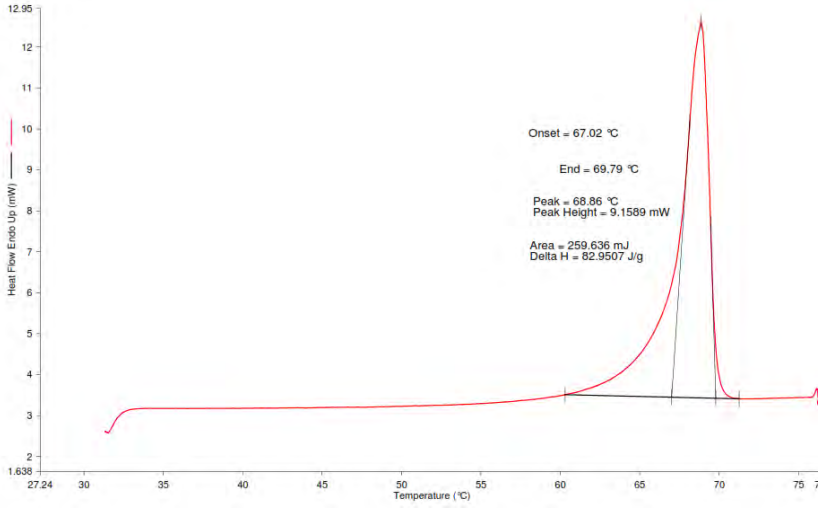


Figure S4:25 **C.N. 76**

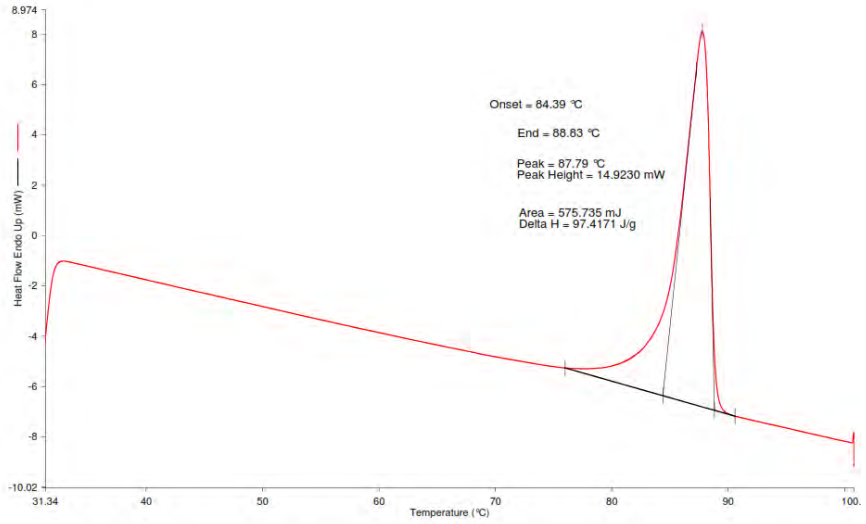


Figure S4:26 **C.N. 77**

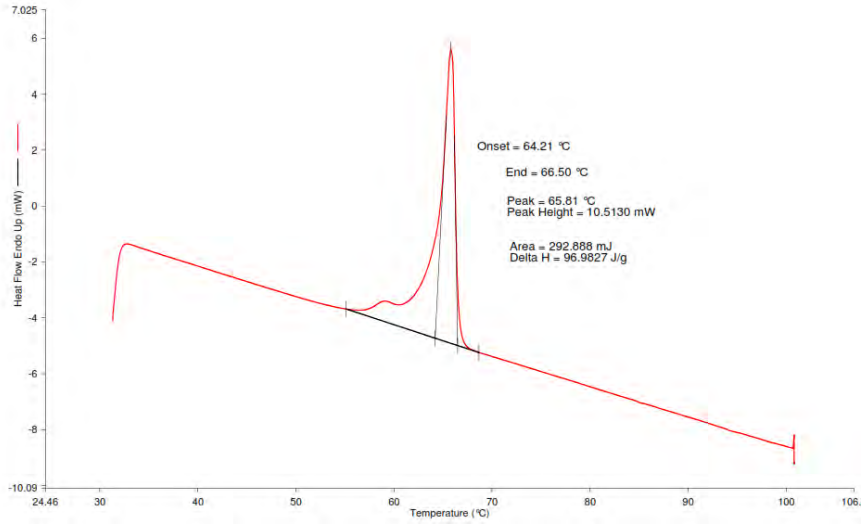


Figure S4:27 **C.N. 78**

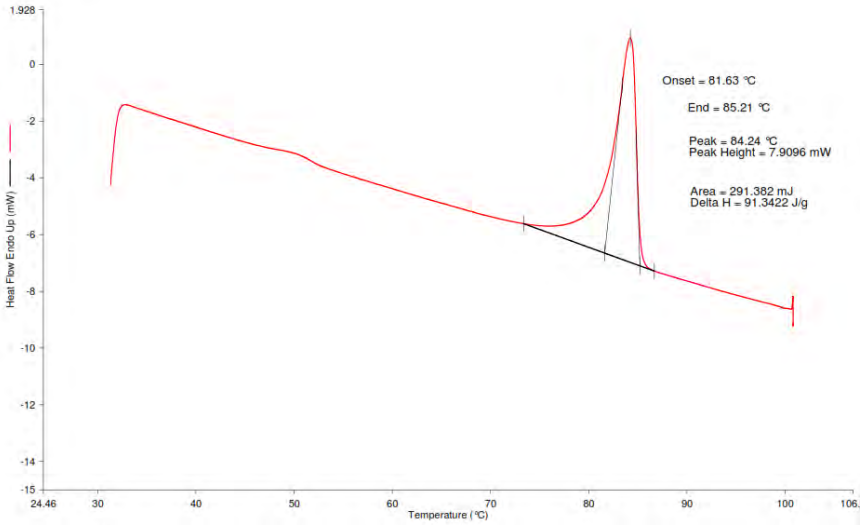


Figure S4:28 **C.N. 79**

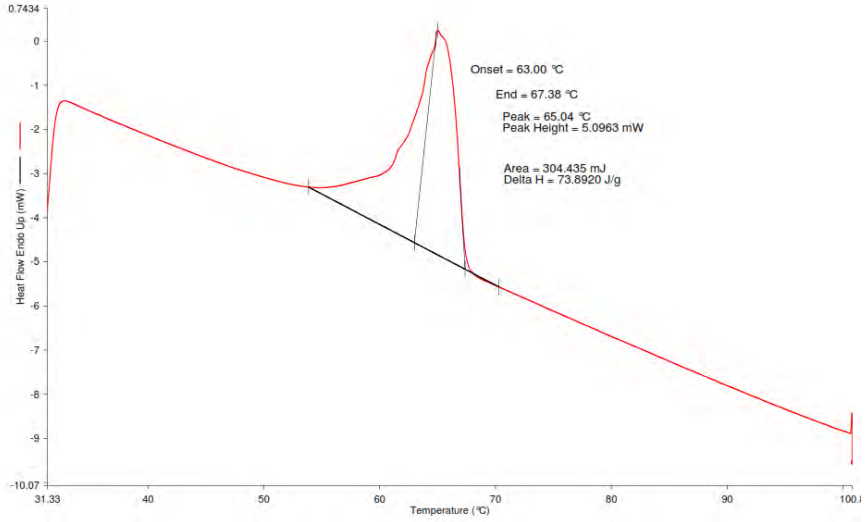


Figure S4:29 **C.N. 80**

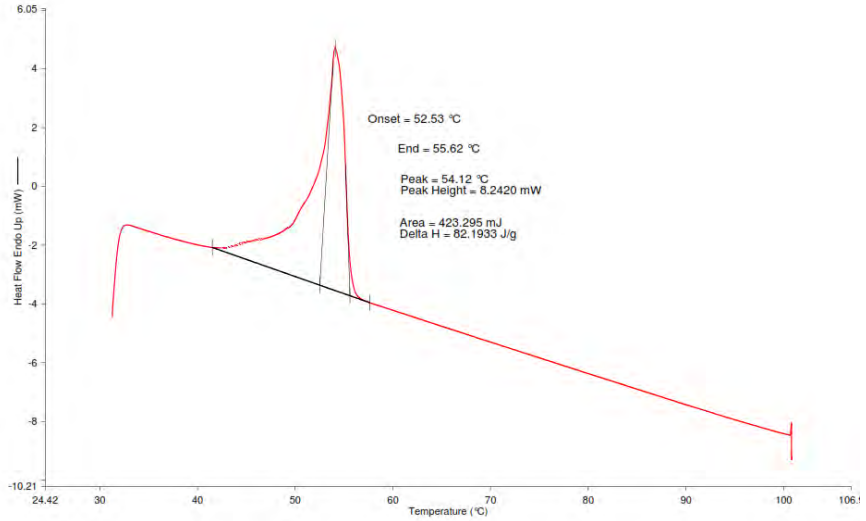


Figure S4:30 **C.N. 81**

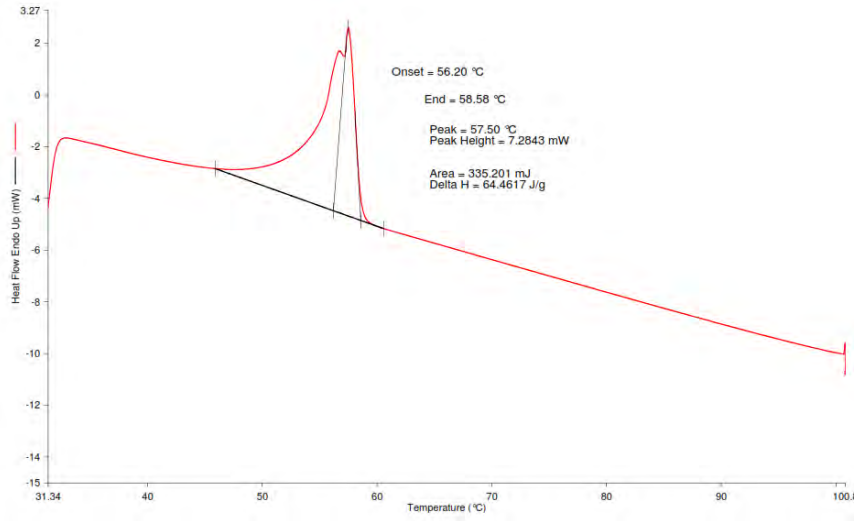


Figure S4:31 **C.N. 82**

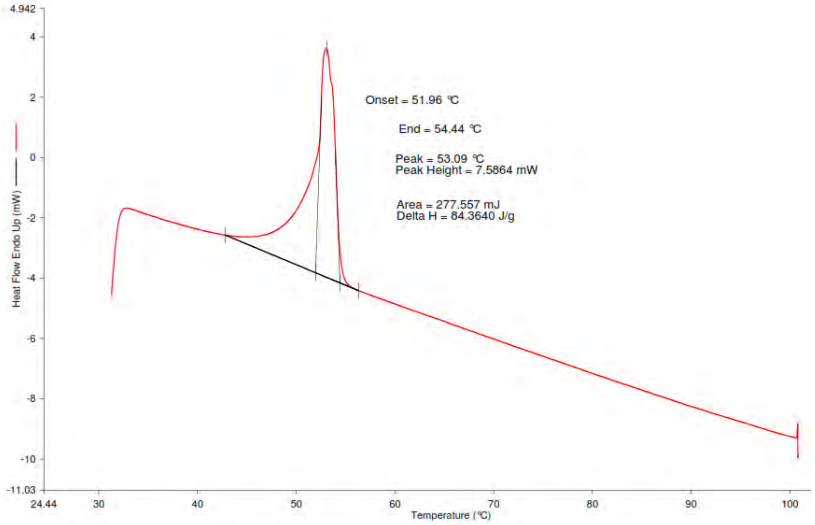


Figure S4:32 **C.N. 83**

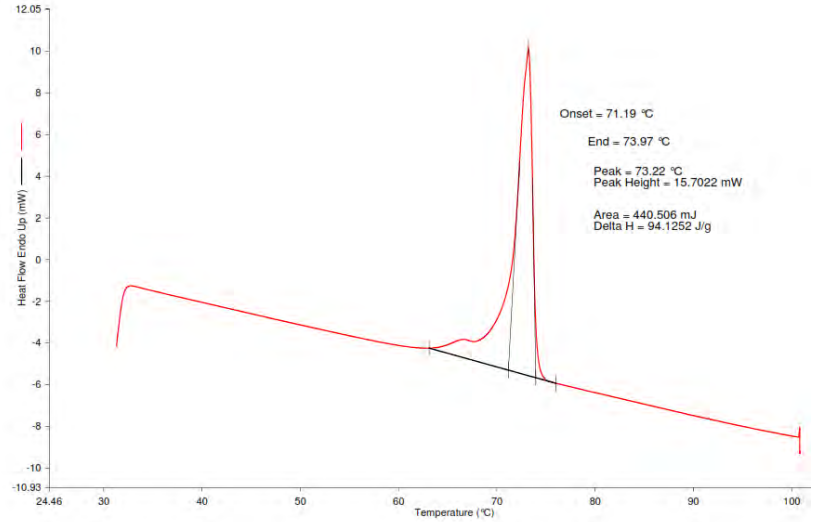


Figure S4:33 **C.N. 84**

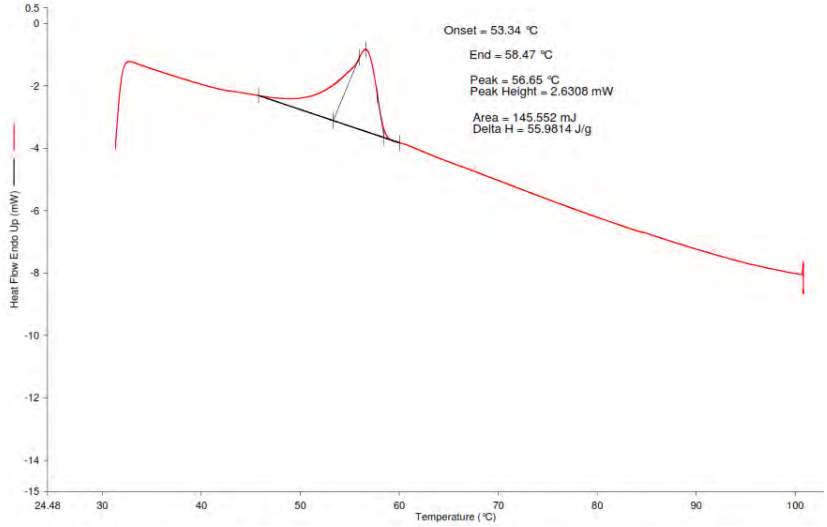


Figure S4:34 **C.N. 85**

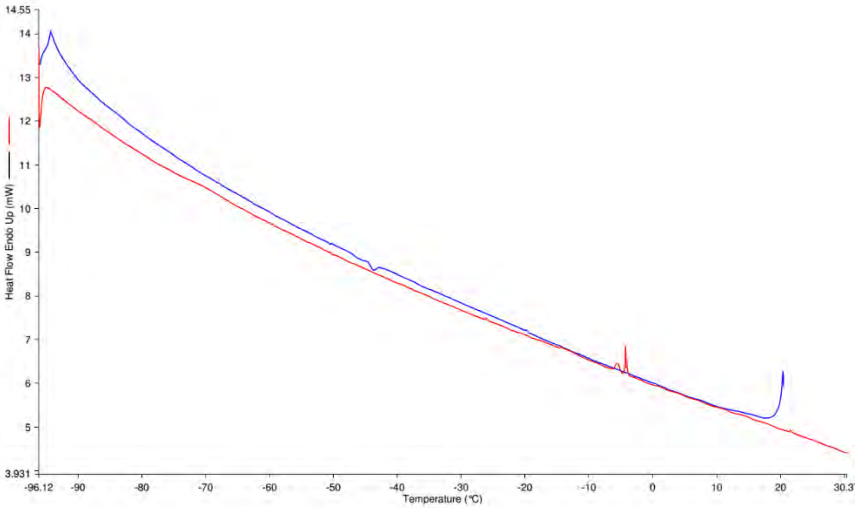


Figure S4:35 **C.N. 86**

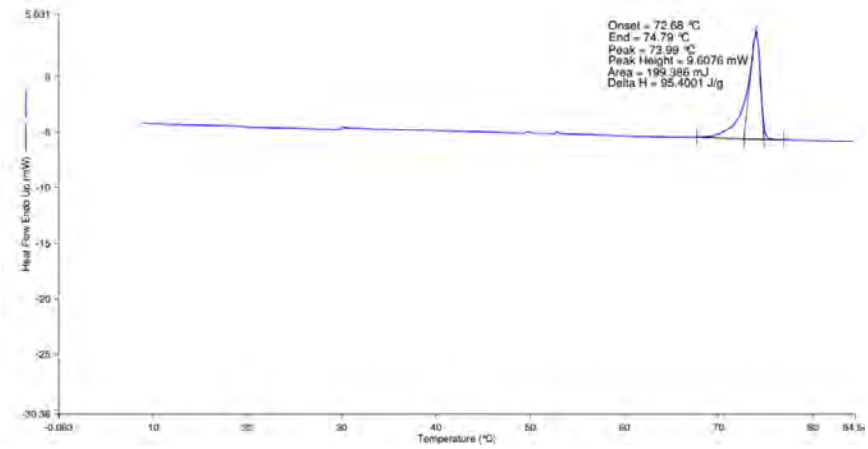


Figure S4:36 **C.N. 87**

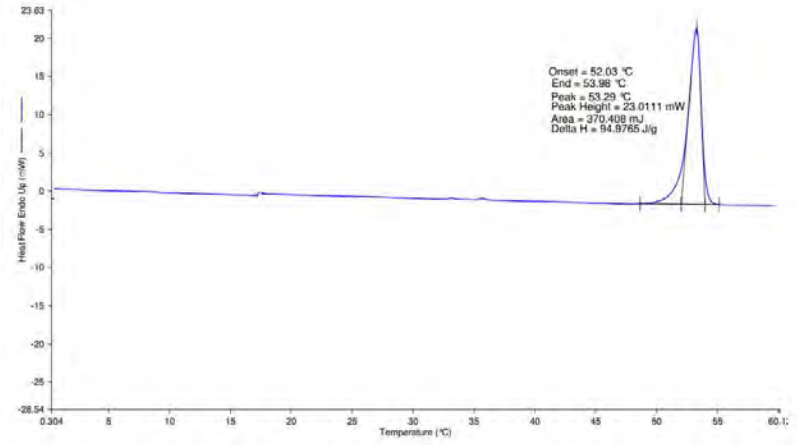


Figure S5: *ORTEP* of all compounds drawn with 50% ellipsoidal probability with atom-numbering scheme.

Figure S5:1 **C.N. 52**

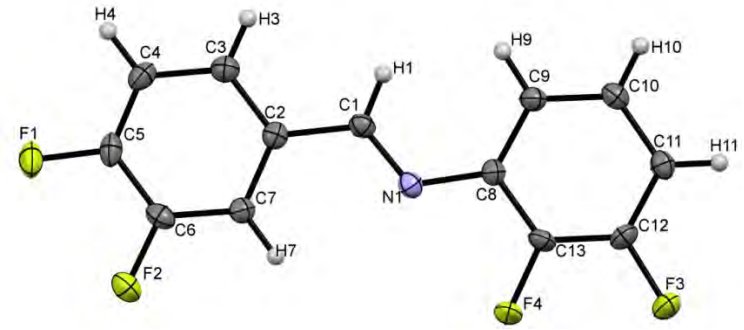


Figure S5:2 **C.N. 53**

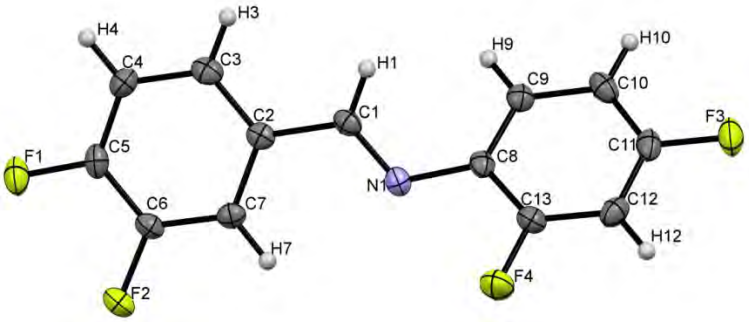


Figure S5:3 **C.N. 54**

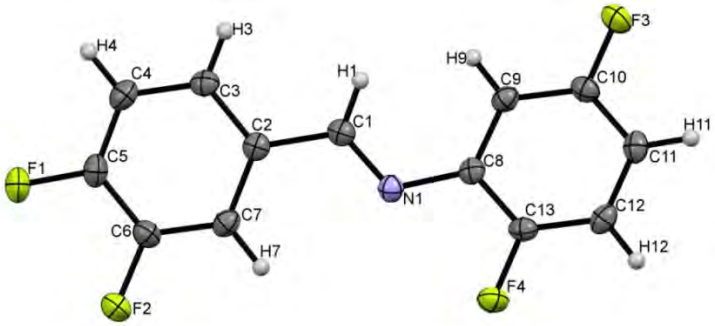


Figure S5:4 **C.N. 55**

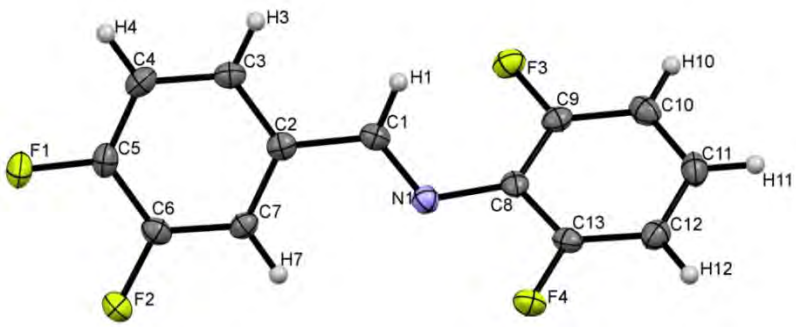


Figure S5:5 **C.N. 57**

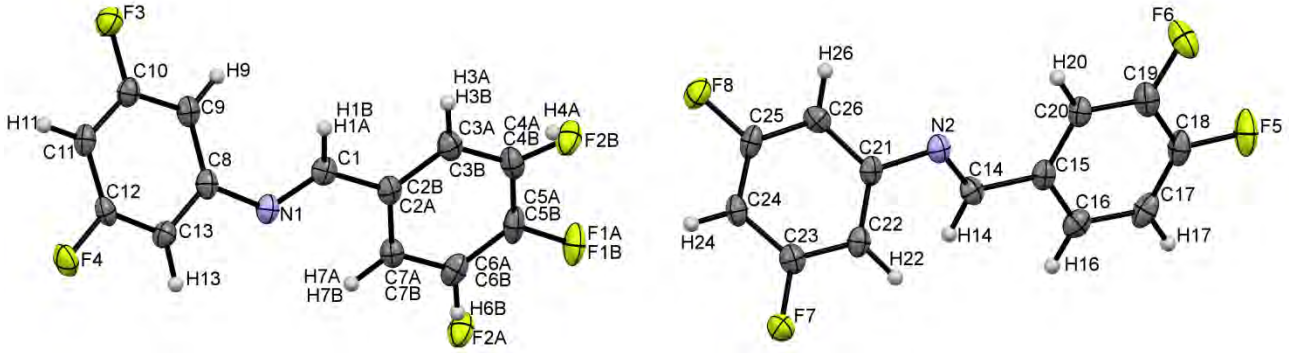


Figure S5:6 **C.N. 58**

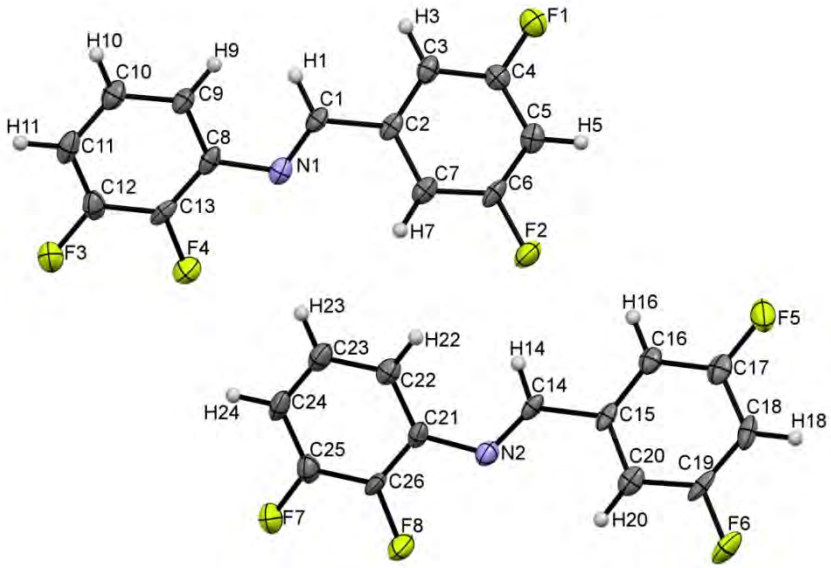


Figure S5:7 **C.N. 59**

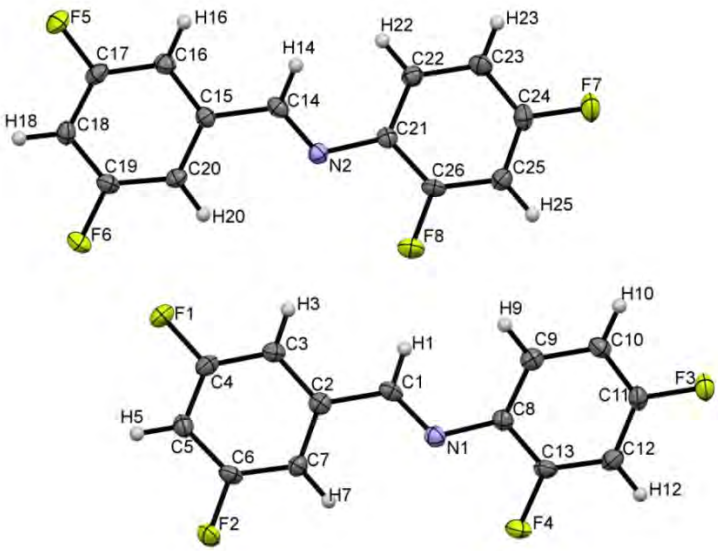


Figure S5:8 **C.N. 60**

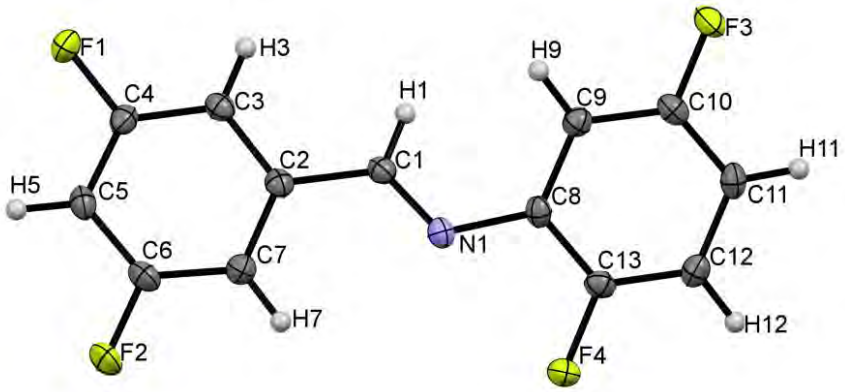


Figure S5:9 **C.N. 61**

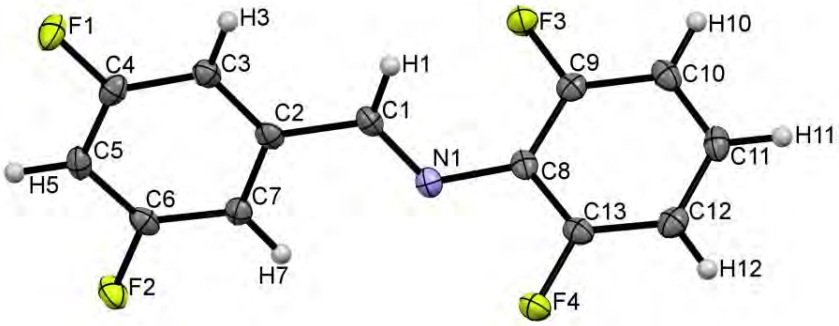


Figure S5:10 **C.N. 63**

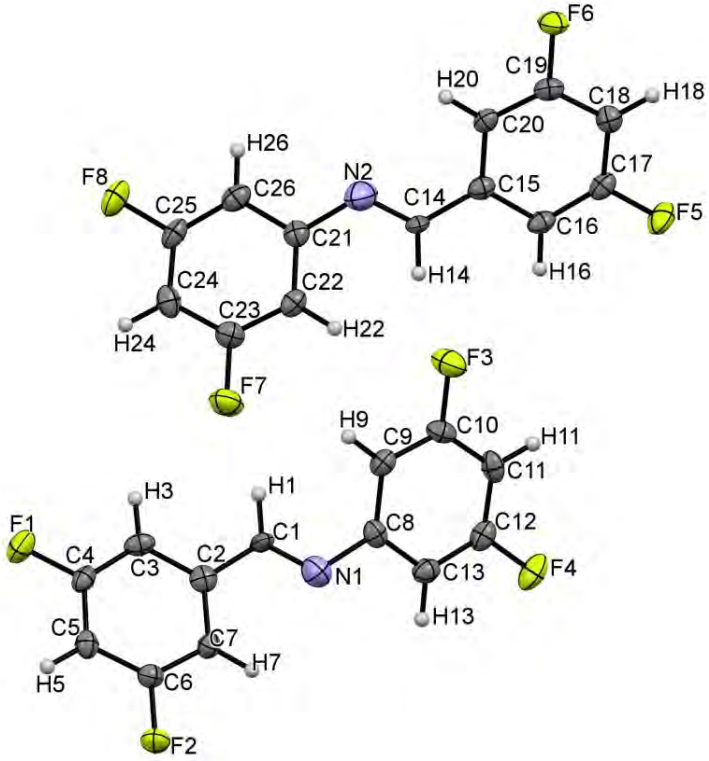


Figure S5:11 **C.N. 64**

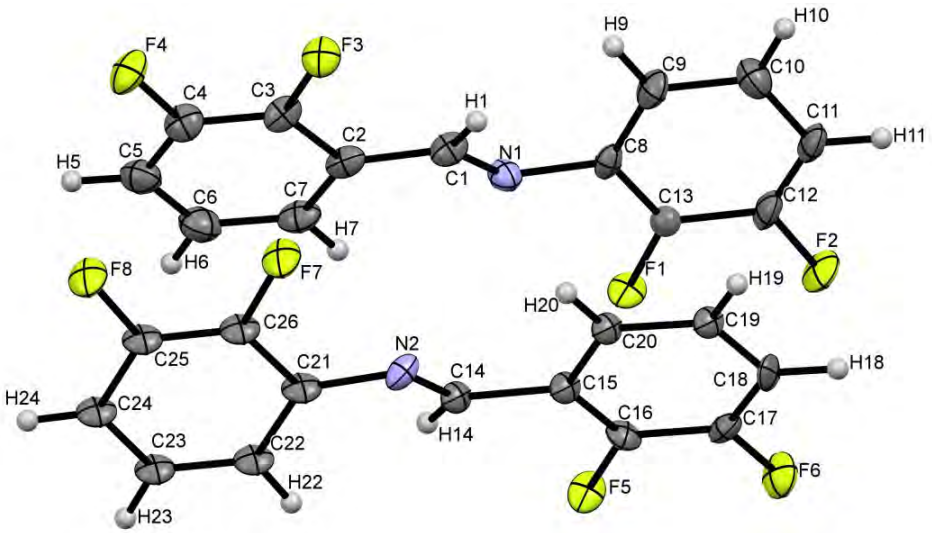


Figure S5:12 **C.N. 65**

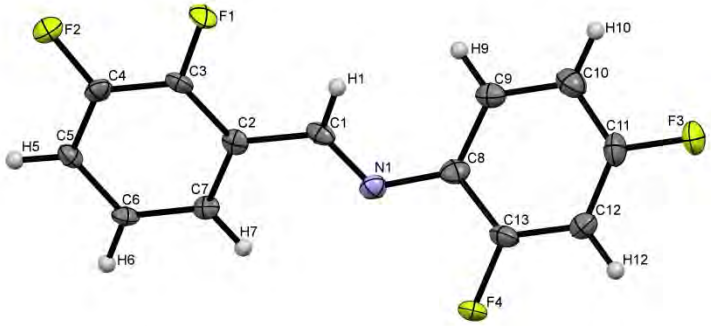


Figure S5:13 **C.N. 66**

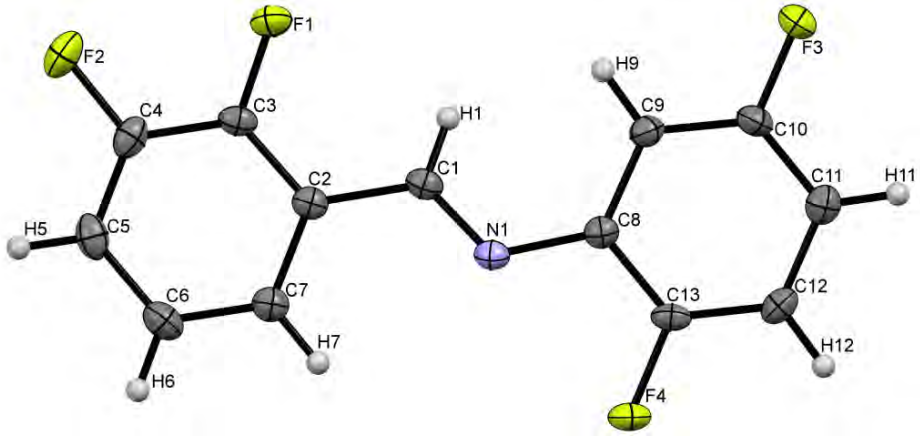


Figure S5:14 **C.N. 68**

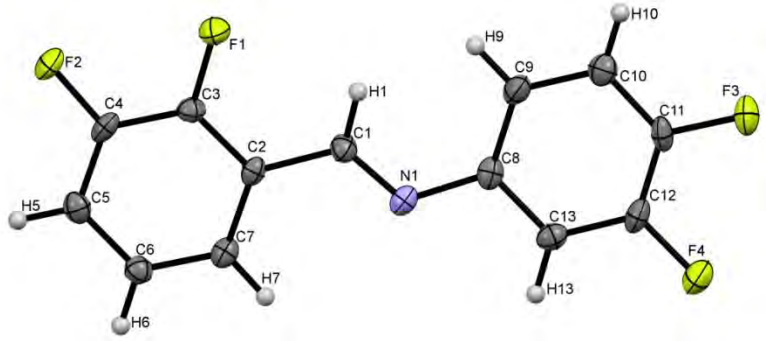


Figure S5:15 **C.N. 69**

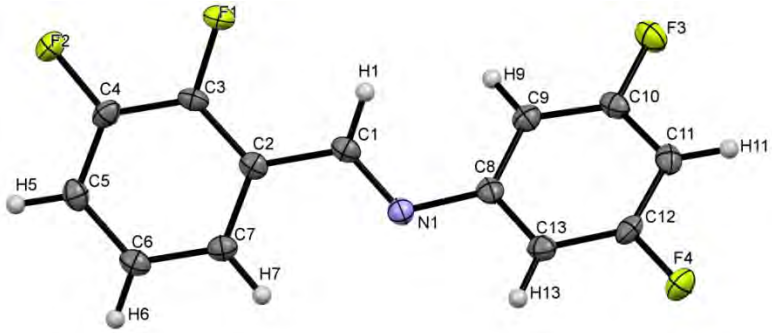


Figure S5:16 **C.N. 70**

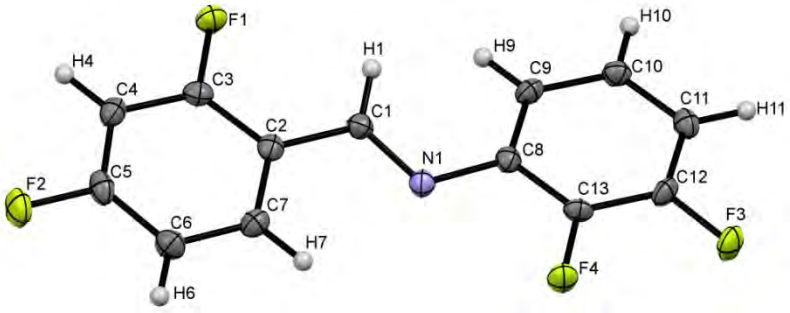


Figure S5:17 **C.N. 71**

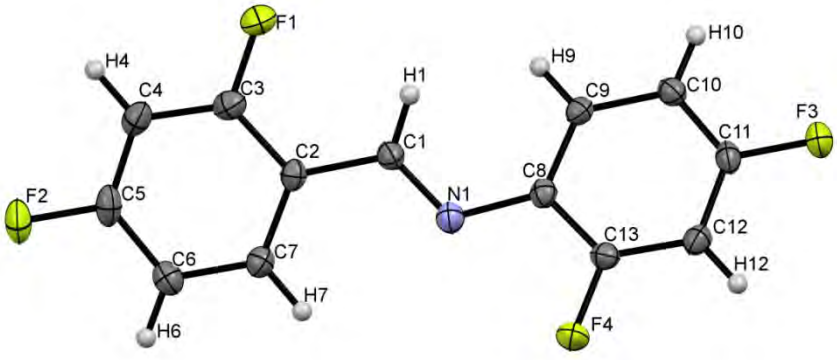


Figure S5:18 **C.N. 73**

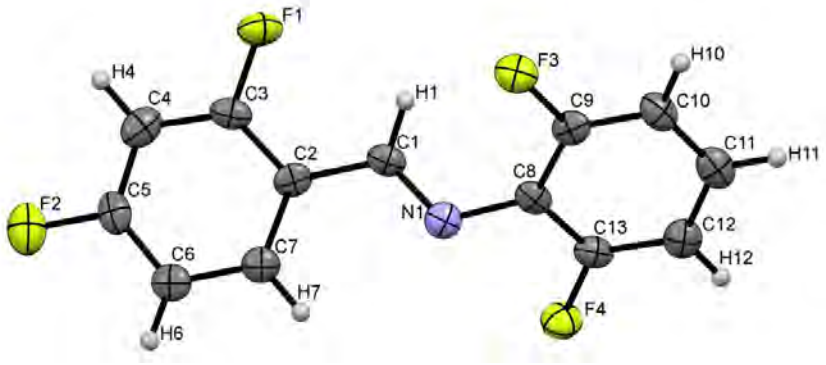


Figure S5:19 **C.N. 74**

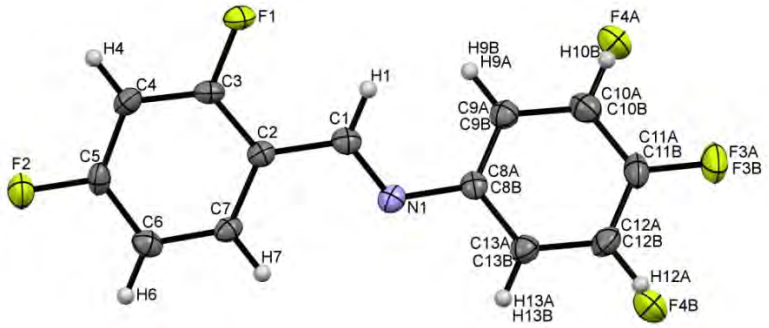


Figure S5:20 **C.N. 75**

Figure S5:21 **C.N. 76**

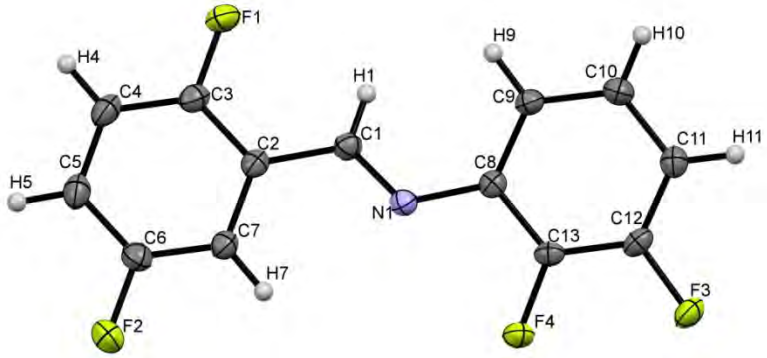


Figure S5:22 **C.N. 77**

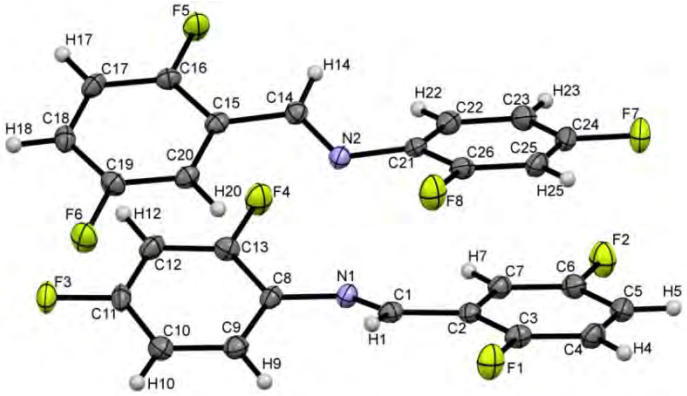


Figure S5:23 **C.N. 78**

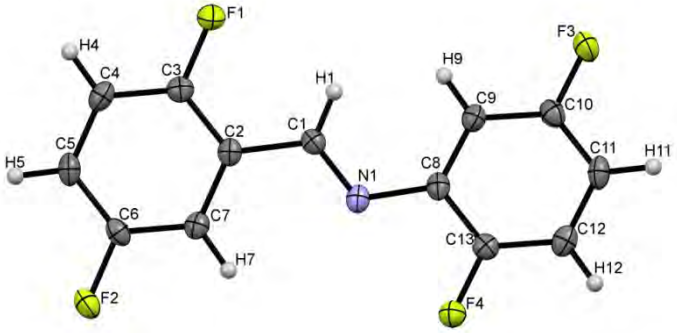


Figure S5:24 **C.N. 80**

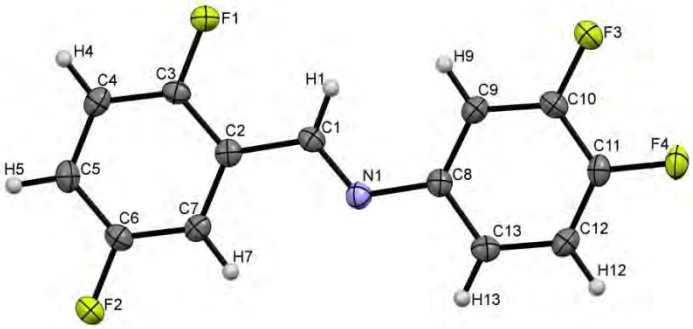


Figure S5:25 **C.N. 81**

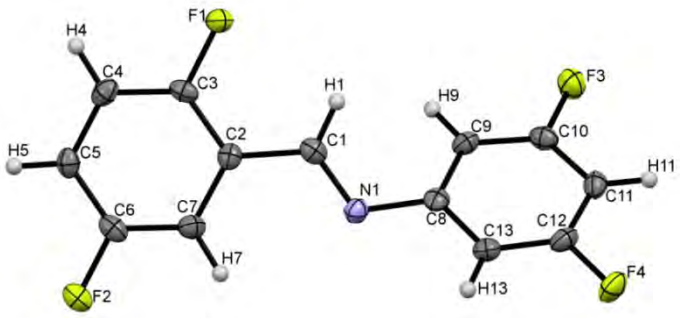


Figure S5:26 **C.N. 82**

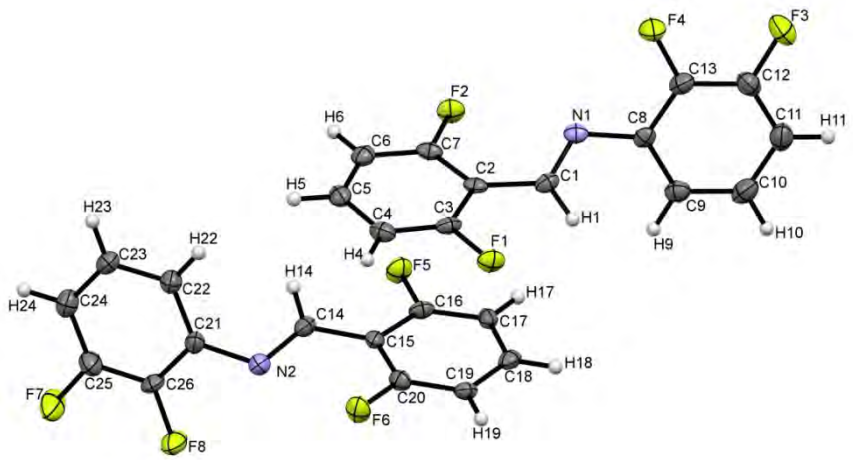


Figure S5:27 **C.N. 83**

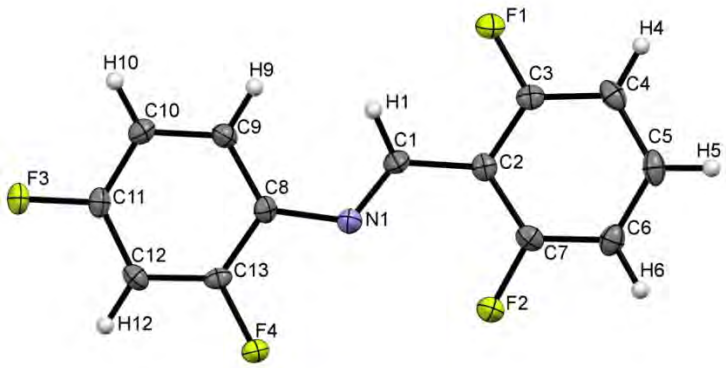


Figure S5:28 **C.N. 84**

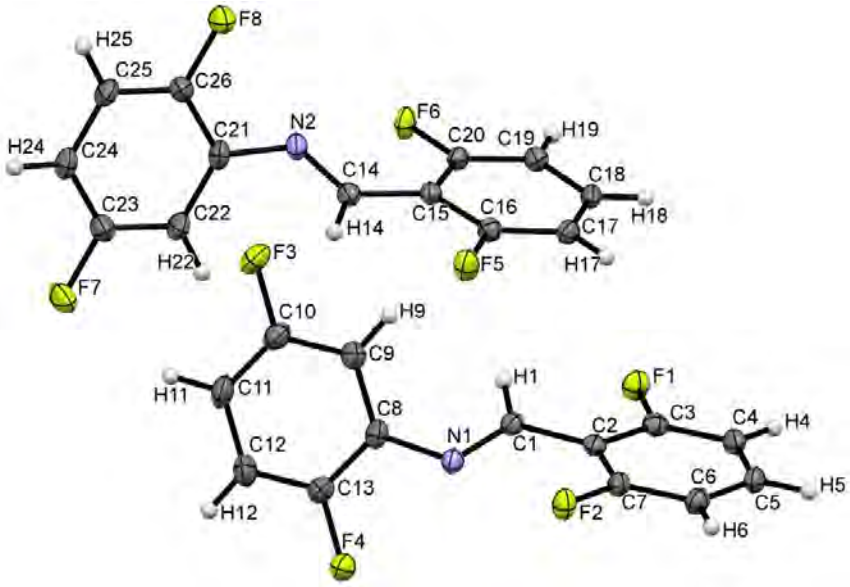


Figure S5:29 **C.N. 86**

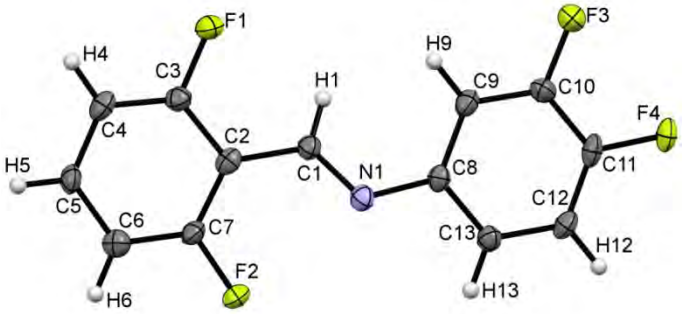


Figure S5:30 **C.N. 87**