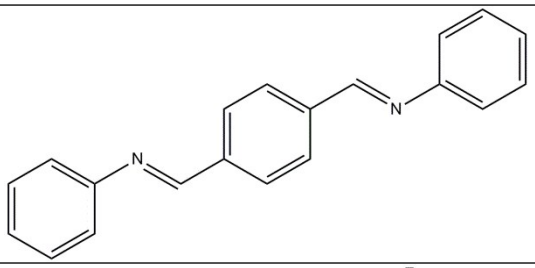
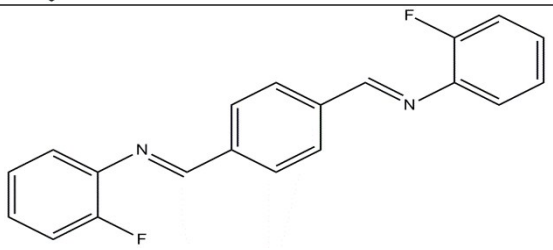
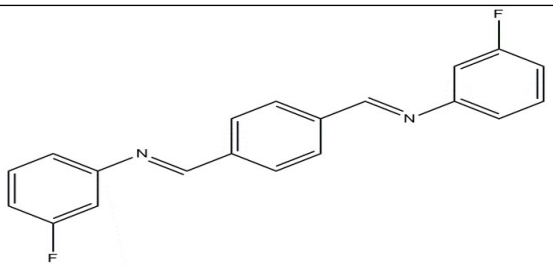
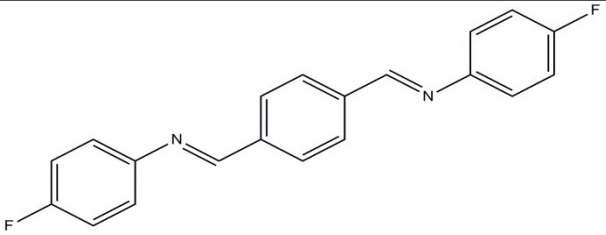
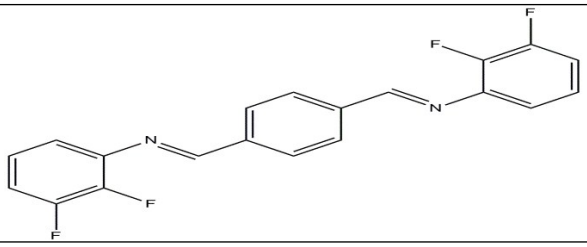
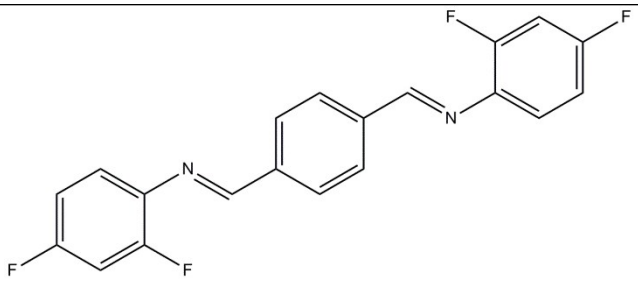
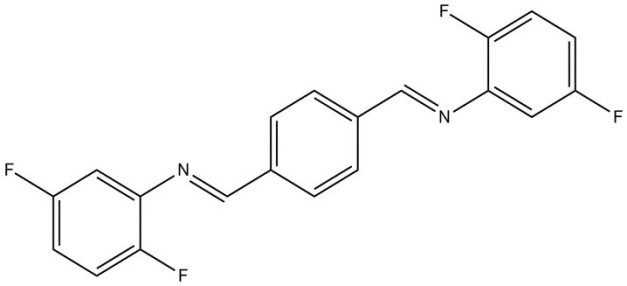
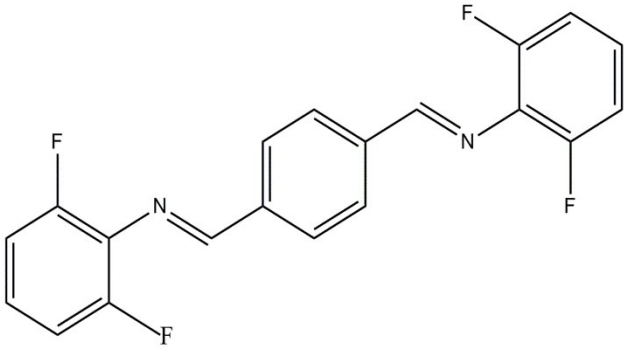
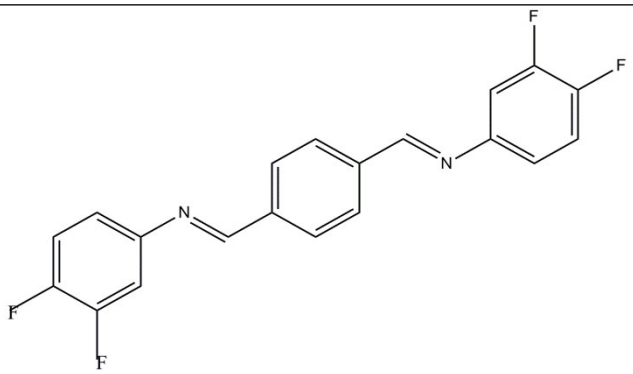
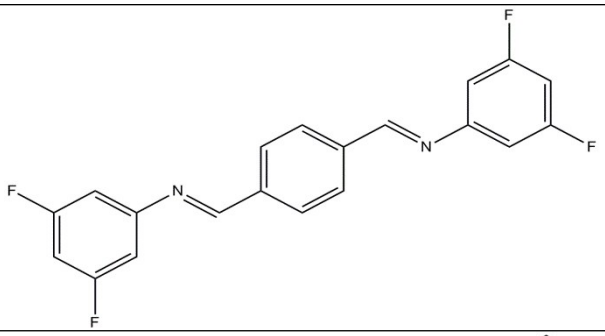
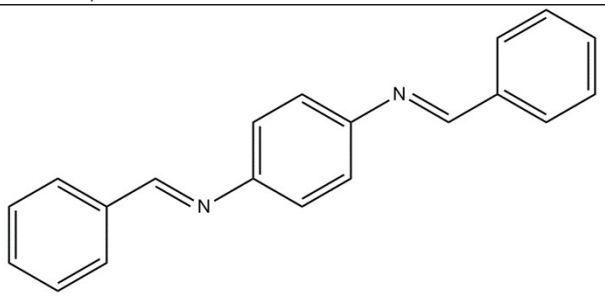
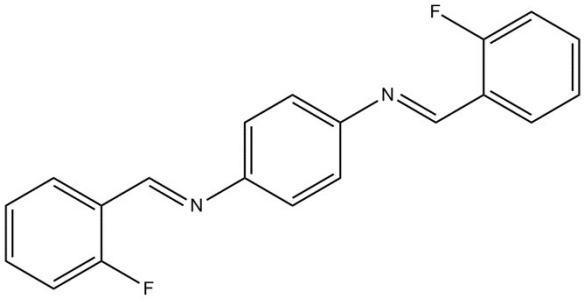
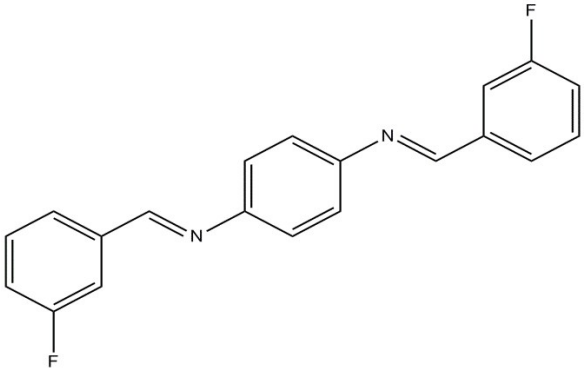
Electronic Supplementary Material (ESI) for CrystEngComm.

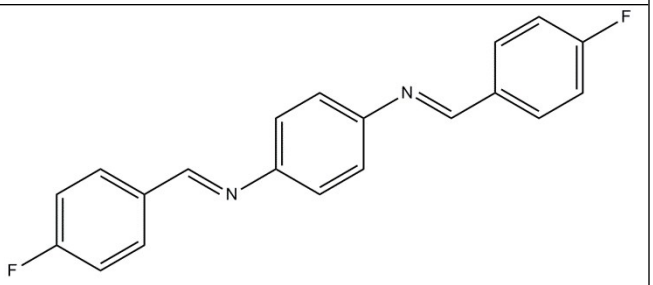
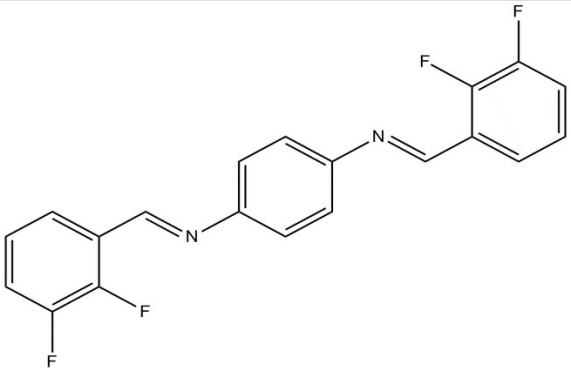
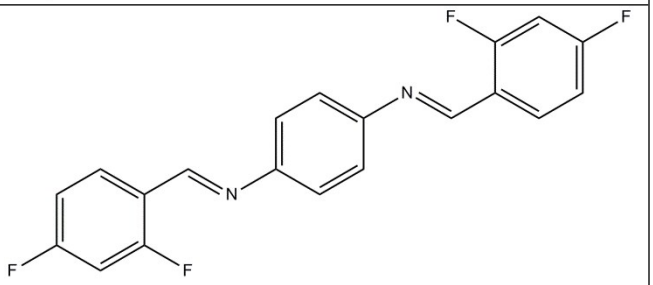
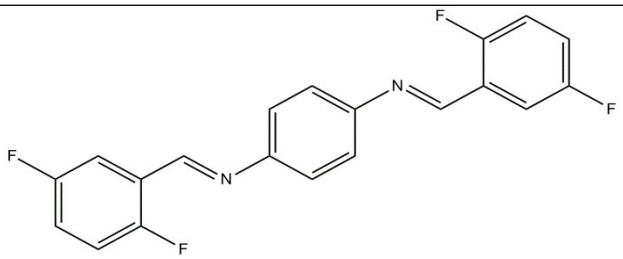
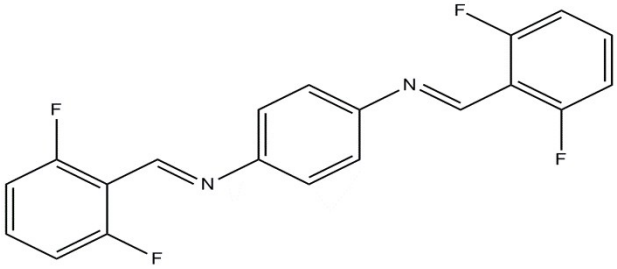
SUPPORTING INFORMATION (ESI)

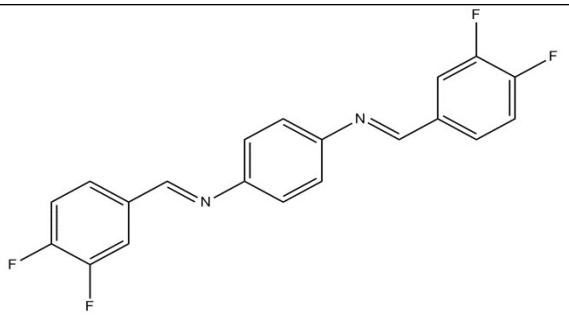
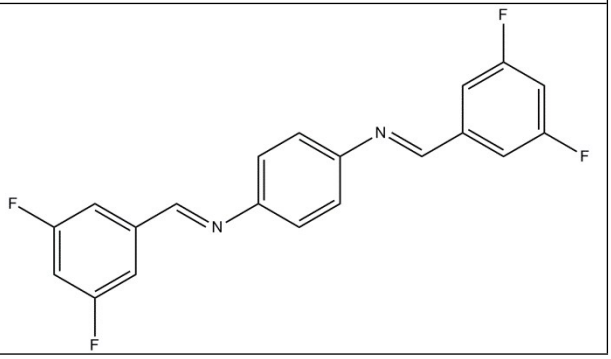
TABLE–1:

Serial No.	IUPAC NAME	MOLECULAR SKETCH
1.	(N,N'Z,N,N'Z)–N,N'–(1,4–phenylenebis(methanylylidene))dianiline	
2.	(N,N'Z,N,N'Z)–N,N'–(1,4–phenylenebis(methanylylidene))bis(2–fluoroaniline)	
3.	(N,N'Z,N,N'Z)–N,N'–(1,4–phenylenebis(methanylylidene))bis(3–fluoroaniline)	
4.	(N,N'Z,N,N'Z)–N,N'–(1,4–phenylenebis(methanylylidene))bis(4–fluoroaniline)	
5.	(N,N'Z,N,N'Z)–N,N'–(1,4–phenylenebis(methanylylidene))bis(2,3–difluoroaniline)	

Serial No.	IUPAC NAME	MOLECULAR SKETCH
6.	(N,N'Z,N,N'Z)–N,N'–(1,4–phenylenebis(methanylylidene))bis(2,4–difluoroaniline)	
7.	(N,N'Z,N,N'Z)–N,N'–(1,4–phenylenebis(methanylylidene))bis(2,5–difluoroaniline)	
8.	(N,N'Z,N,N'Z)–N,N'–(1,4–phenylenebis(methanylylidene))bis(2,6–difluoroaniline)	
9.	(N,N'Z,N,N'Z)–N,N'–(1,4–phenylenebis(methanylylidene))bis(3,4–difluoroaniline)	

Serial No.	IUPAC NAME	MOLECULAR SKETCH
10.	(N,N'Z,N,N'Z)–N,N'–(1,4–phenylenebis(methanylylidene))bis(3,5–difluoroaniline)	
11.	(N1E,N4E)–N1,N4–dibenzylidenebenzene–1,4–diamine	
12.	(N1E,N4E)–N1,N4–bis(2–fluorobenzylidene)benzene–1,4–diamine	
13.	(N1E,N4E)–N1,N4–bis(3–fluorobenzylidene)benzene–1,4–diamine	

Serial No	IUPAC NAME	MOLECULAR SKETCH
14.	(N1E,N4E)–N1,N4–bis(4–fluorobenzylidene)benzene–1,4–diamine	
15.	(N1E,N4E)–N1,N4–bis(2,3–difluorobenzylidene)benzene–1,4–diamine	
16.	(N1E,N4E)–N1,N4–bis(2,4–difluorobenzylidene)benzene–1,4–diamine	
17.	(N1E,N4E)–N1,N4–bis(2,5–difluorobenzylidene)benzene–1,4–diamine	
18.	(N1E,N4E)–N1,N4–bis(2,6–difluorobenzylidene)benzene–1,4–diamine	

Serial No	IUPAC NAME	MOLECULAR SKETCH
19.	(N1E,N4E)–N1,N4–bis(3,4–difluorobenzylidene)benzene–1,4–diamine	
20.	(N1E,N4E)–N1,N4–bis(3,5–difluorobenzylidene)benzene–1,4–diamine	

Coulomb−London−Pauli (CLP) Energy Calculations

The initial NAME.cif files were generated using the Olex2 package and edited manually to convert into the CSD CIF format. NAME.oih files were generated using the retcif module available within the CLP package. NAME.oeh and NAME.dat files were generated subsequently using rector interface module of CLP package. The required input files for PIXELC were generated using the pixmt2 server module which reads NAME.oeh and generates NAME.gjf and NAME.inp files. NAME.den files (files that contain the molecular electron density generated at the MP2 level and the 6-31G** basis set) were then generated by running Gaussian09 using the NAME.gjf file as the input. NAME.inp and NAME.den files along with the parameter controller file, PIXPAR.par, were used to calculate lattice energy of a cluster of molecules with a maximum distance from the central molecule of 40 Å and a top radius for search of 50 Å. After successful completion of the calculation, the output file contains partitioned total energies in the form of E_{COUL}, E_{POL}, E_{DISP}, and E_{REP}. The package generates two output files, namely, NAME.pri (a printout file with the results of the calculation) and NAME.mlc (a file with molecule−molecule energies).

Characterizations of above compounds:

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6. **Powder X–ray Diffraction (PXRD)- Fig. S6.a – t**
7. **Anisotropic ellipsoid (50% probability) plots with atom numbering -Fig. S7.a – r**
8. **Pair wise comparison of bridge flipped isomers.**
9. **CCDC search on C–N···π interaction**

- ^{1}H NMR (400 HZ, $CDCl_3$):δ 7.24–7.44[m(10H),H3,H4,H5,H6,H7] , δ 8.01–8.01[m(4H), H9,H10] ,δ 8.52 [s(2H),H1]

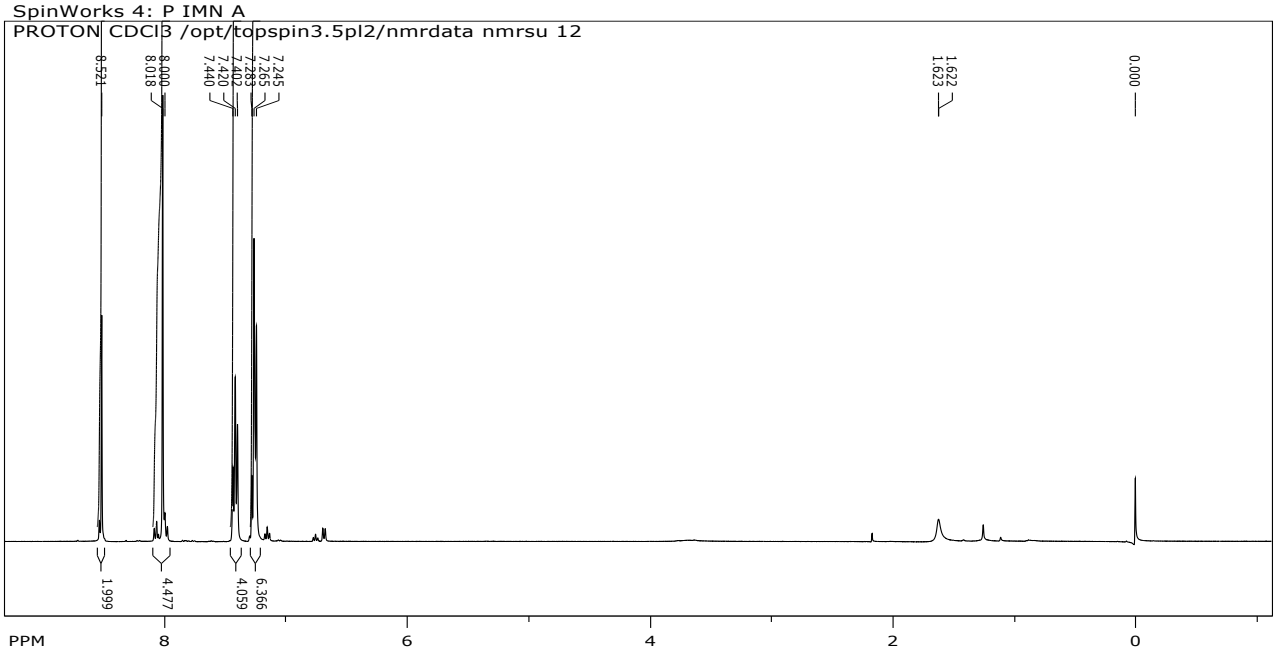


Figure: S1.a) ^{1}H NMR Spectra of compound 1.

^{1}H NMR (400 HZ, $CDCl_3$): δ 7.19–7.28[m(8H), H4,H5,H6,H7] , δ 8.05[m(4H),H9,H10] ,δ 8.60 [s(2H),H1]

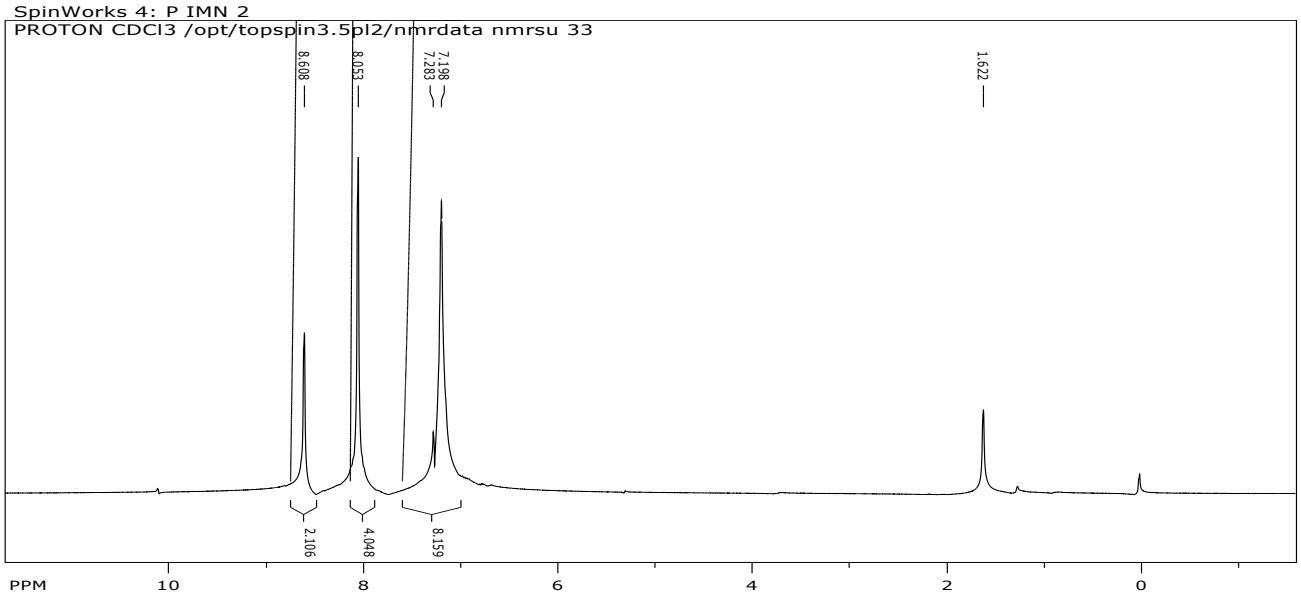


Figure: S1.b) ^{1}H NMR Spectra of compound 2.

- ^{1}H NMR (400 HZ, $CDCl_3$): δ 6.94–7.39[m(8H), H3,H5,H6,H7] , δ 8.01[m(4H) ,H9,H10]δ 8.49 [s(2H),H1]

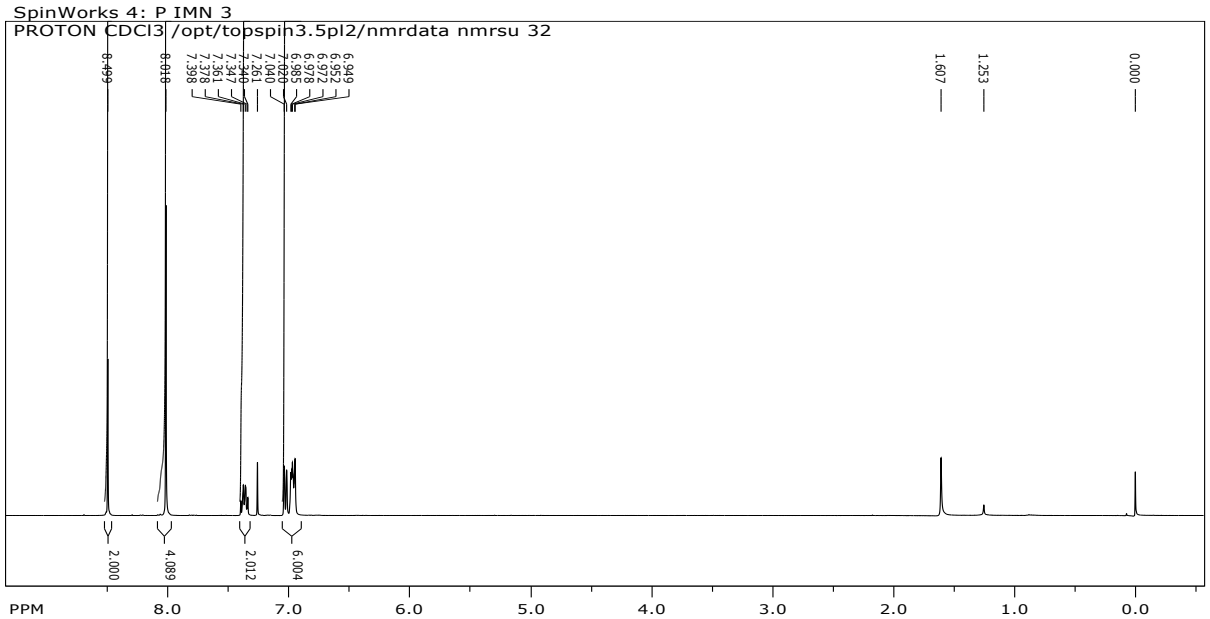


Figure: S1.c) ^{1}H NMR Spectra of compound 3.

- ^{1}H NMR (400 HZ, $CDCl_3$): δ 7.09–7.27[m(8H),H3,H4,H6,H7] , δ 8.01[m(4H) ,H9,H10]δ 8.51 [s(2H),H1]

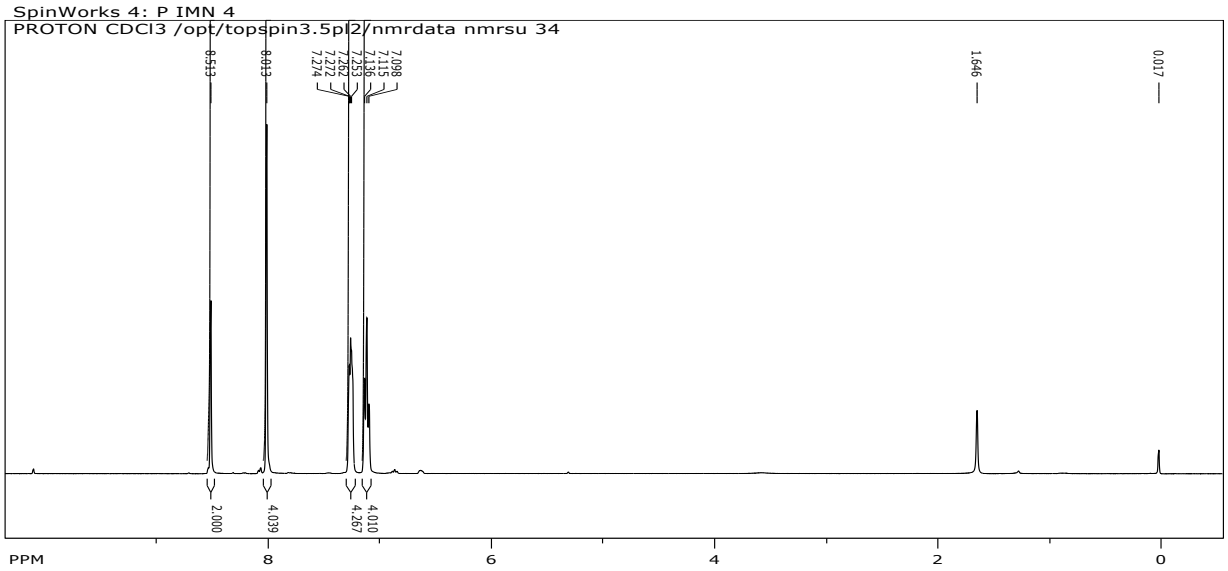


Figure: S1.d) ^{1}H NMR Spectra of compound 4.

- ^{1}H NMR (400 HZ, $CDCl_3$): δ 6.93–7.26[m(6H),H5,H6,H7] , δ7.99–8.11[m(4H)H9,H10]δ 8.58–8.60[s(2H),H1]

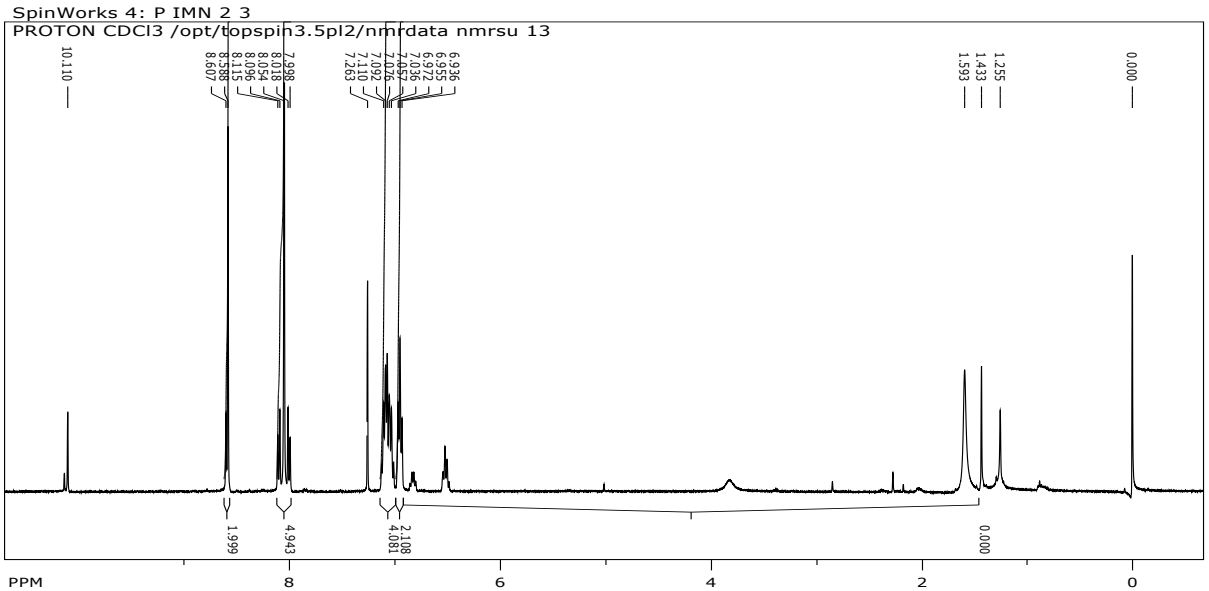


Figure: S1.e) ^{1}H NMR Spectra of compound 5.

- ^{1}H NMR (400 HZ, $CDCl_3$):δ 6.89,7.05–7.26[m(6H),H4,H6,H7] , δ 7.98–8.09[m(4H)H9,H10] ,δ 8.58–8.61[s(2H),H1]

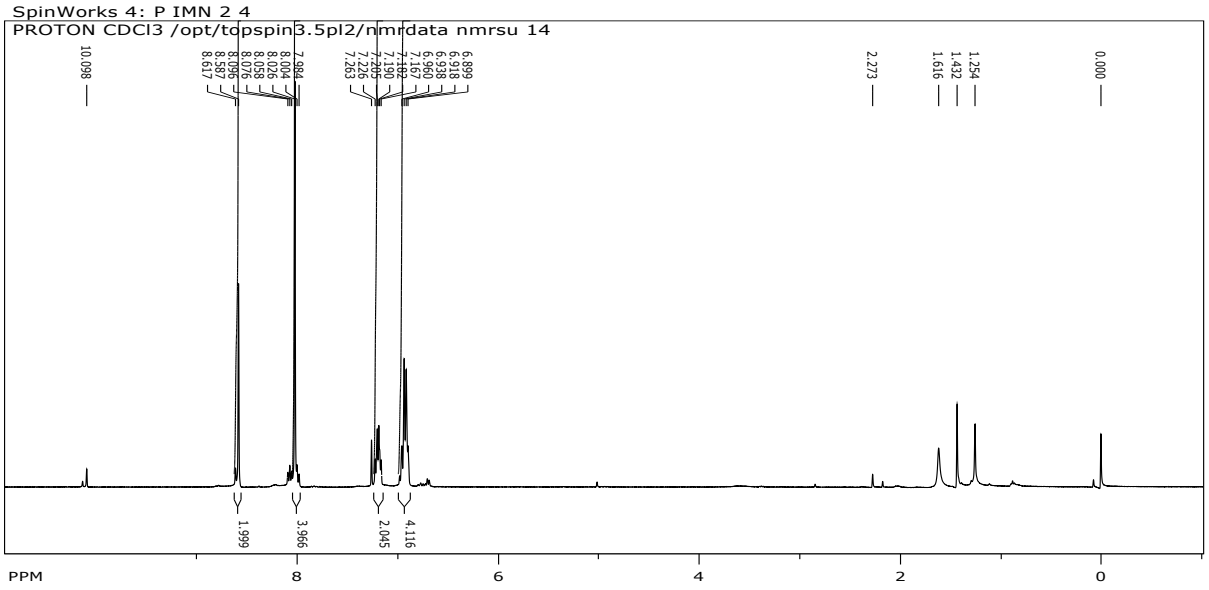


Figure: S1.f) ^{1}H NMR Spectra of compound 6.

- ^{1}H NMR (400 HZ, $CDCl_3$):δ 7.99–8.10 [m(6H),H4,H5,H7] , δ 6.89–7.26 [m(4H)H9,H10] ,δ 8.57–8.59[s(2H),H1]

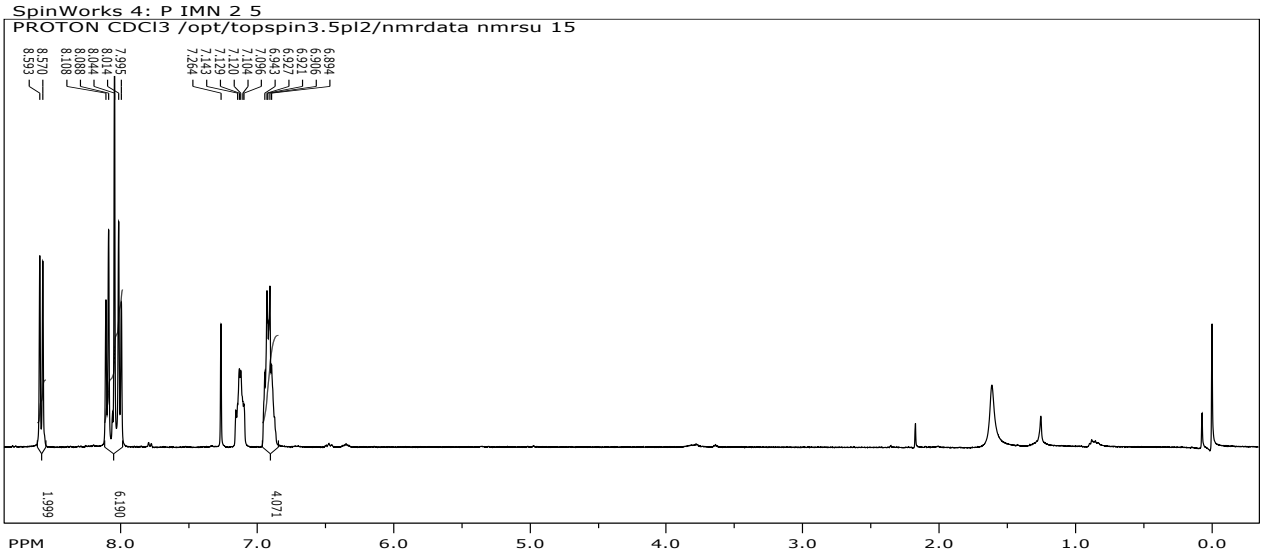


Figure: S1.g) ^{1}H NMR Spectra of compound 7.

- ^{1}H NMR (400 HZ, $CDCl_3$):δ6.33–6.46[m(6H),H4,H5,H6] , δ5.13–5.61 [m(4H)H9,H10] ,δ 8.45–8.48[s(2H),H1]

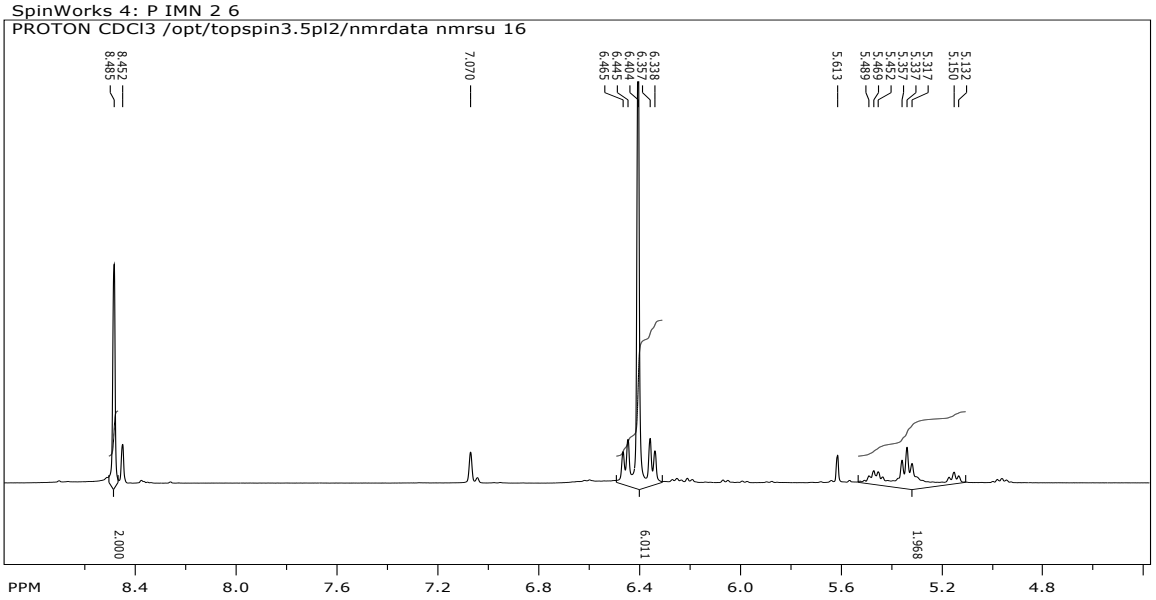


Figure: S1.h) ^{1}H NMR Spectra of compound 8.

- ^{1}H NMR (400 HZ, $CDCl_3$):δ6.99–7.26[m(6H),H3,H6,H7] , δ 8.00 [m(4H)H9,H10] , δ8.48[s(2H),H1]

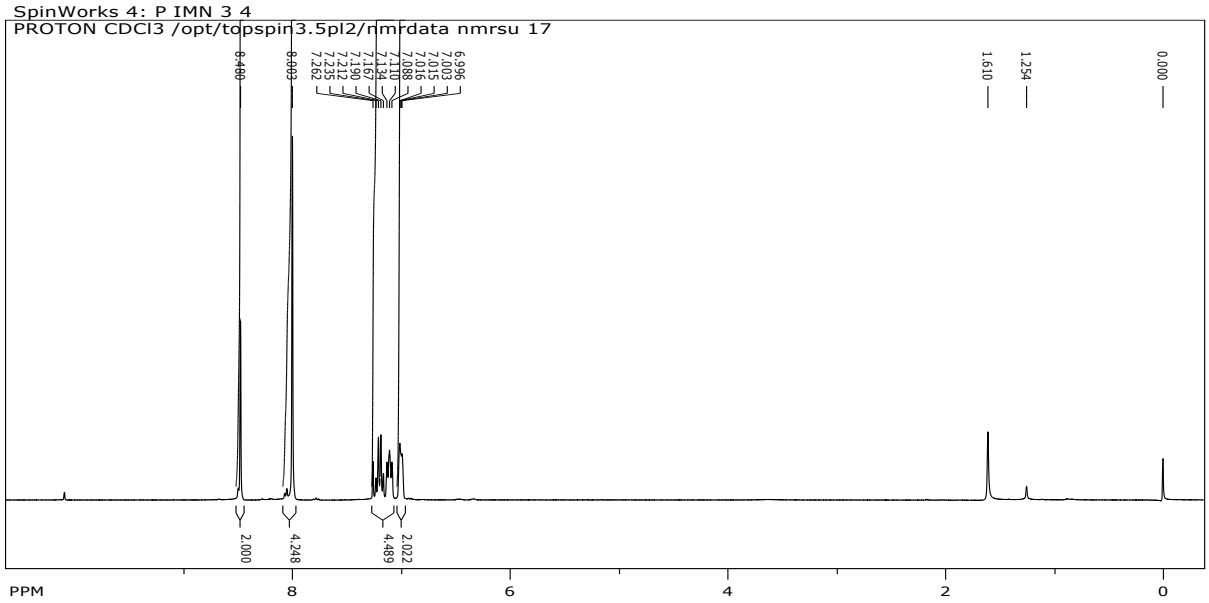


Figure: S1.i) ^{1}H NMR Spectra of compound 9.

- ^{1}H NMR (400 HZ, $CDCl_3$):δ6.69–7.26[m(6H),H3,H6,H7] , δ 8.01–8.05 [m(4H)H9,H10] ,δ 8.46–8.48[s(2H),H1]

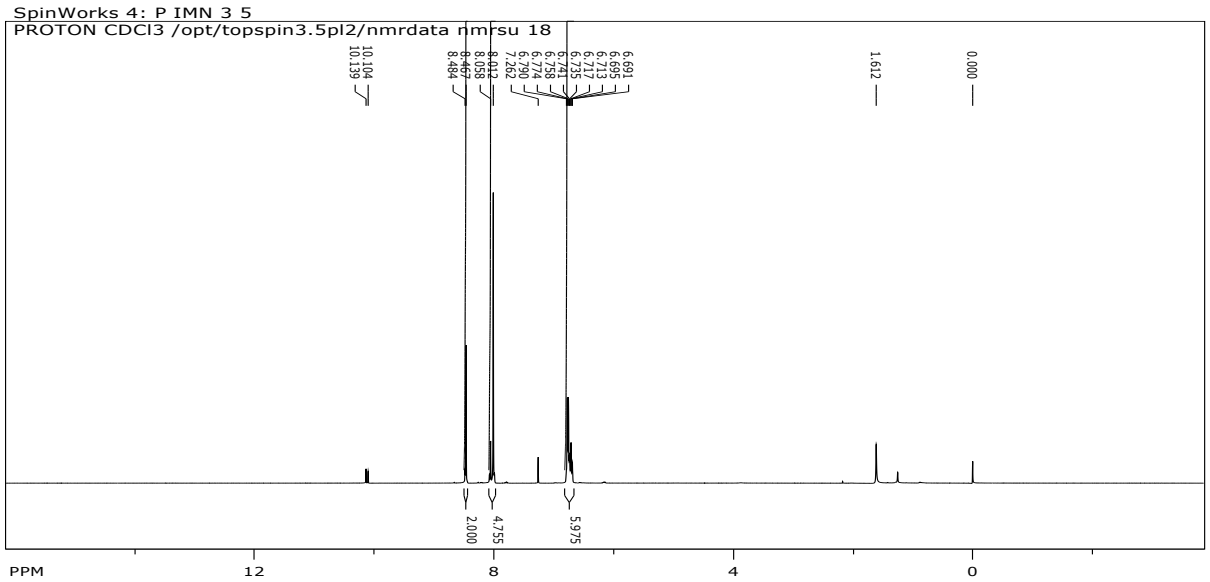


Figure: S1.j) ^{1}H NMR Spectra of compound 10.

- ^{1}H NMR (400 HZ, $CDCl_3$):δ6.70–7.54[m(10H),H3,H4,H5,H6,H7] , δ7.86–7.92 [m(4H)H9,H10] ,δ 8.49–8.52[s(2H),H1]

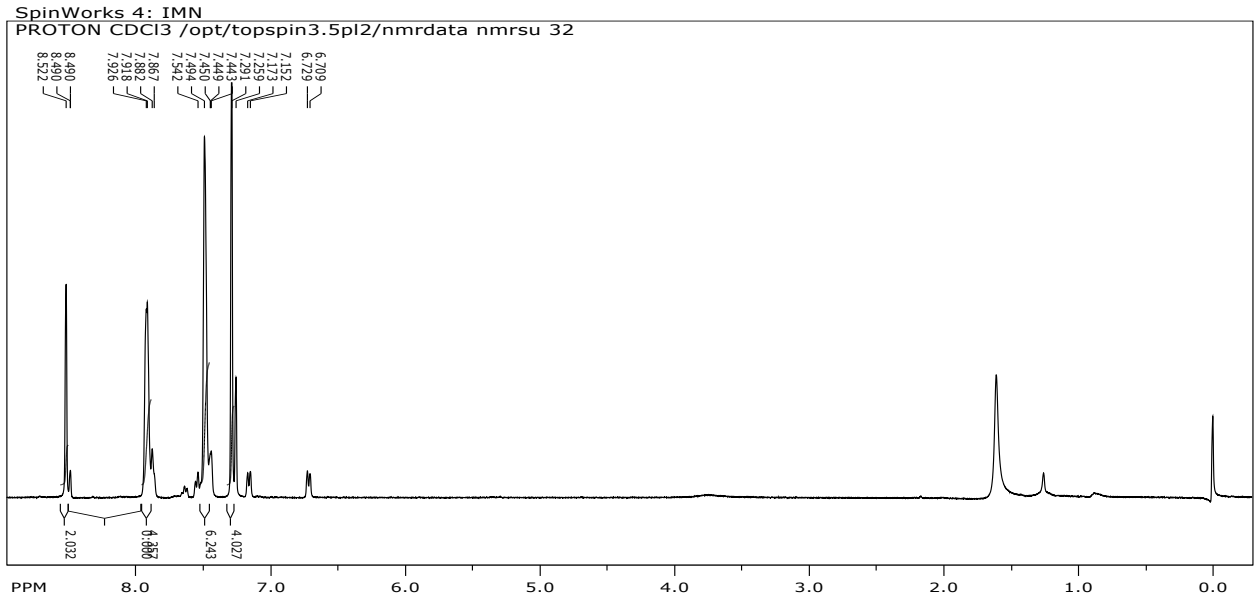


Figure: S1.k) ^{1}H NMR Spectra of compound 11.

- ^{1}H NMR (400 HZ, $CDCl_3$):δ 7.19–7.28[m(8H),H4,H5,H6,H7] , δ 8.05[m(4H),H9,H10] ,δ 8.60 [s(2H),H1]

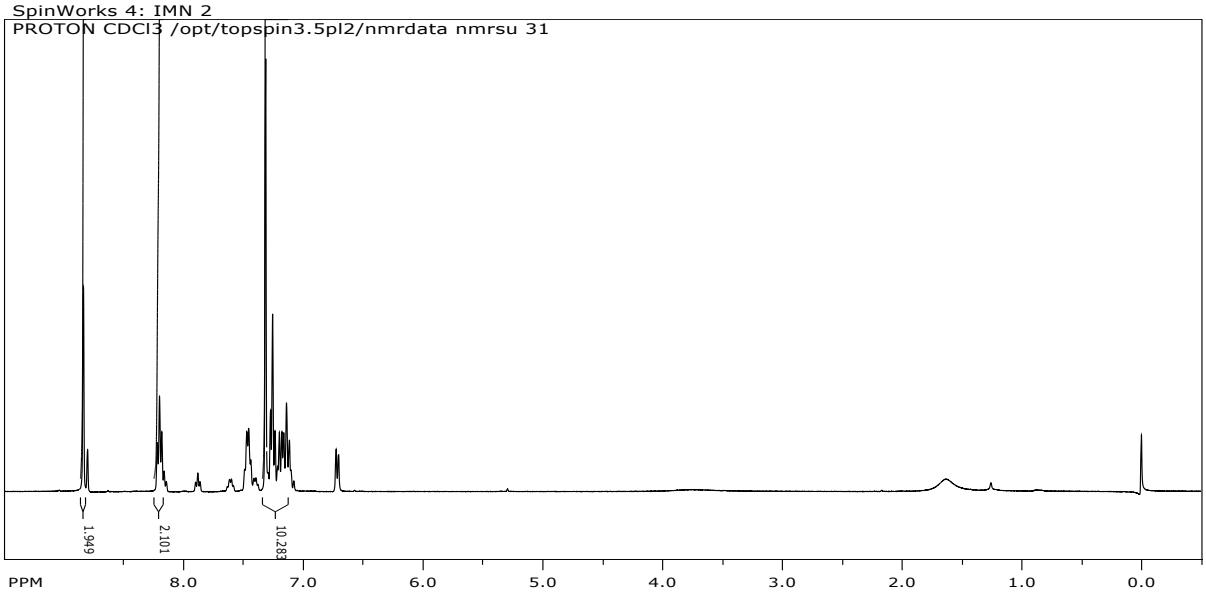


Figure: S1.l) ^{1}H NMR Spectra of compound 12.

- ^{1}H NMR (400 HZ, $CDCl_3$):δ7.16–7.48[m(8H),H3,H5,H6,H7] , δ 7.63–7.69 [m(4H)H9,H10] ,δ 8.49[s(2H),H1]

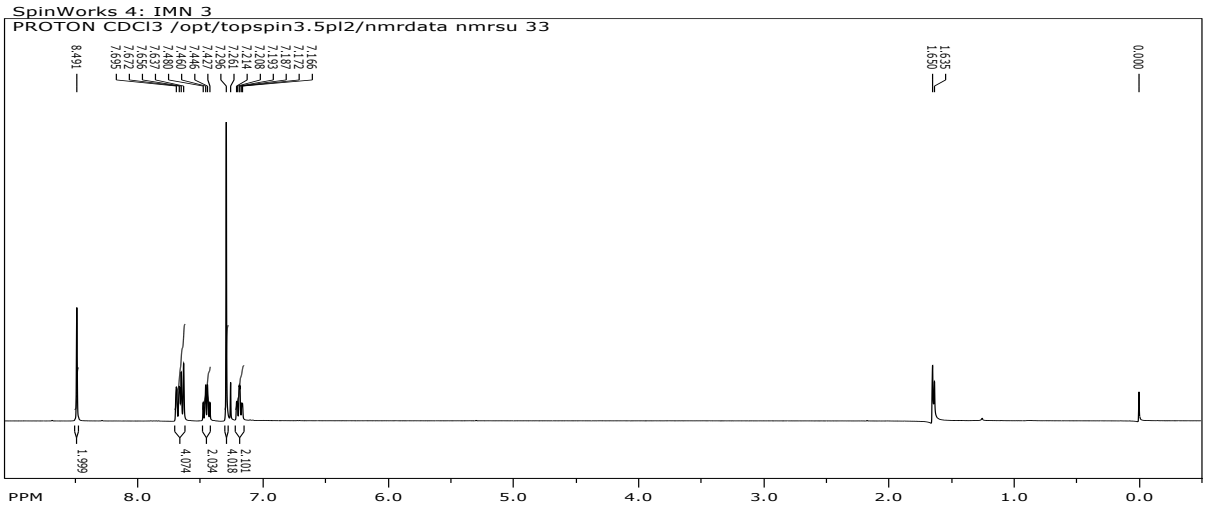


Figure: S1.m) ^{1}H NMR Spectra of compound 13.

- ^{1}H NMR (400 HZ, $CDCl_3$):δ7.14–7.27[m(8H),H3,H4,H6,H7] , δ 7.89–7.91[m(4H)H9,H10] ,δ 8.47[s(2H),H1]

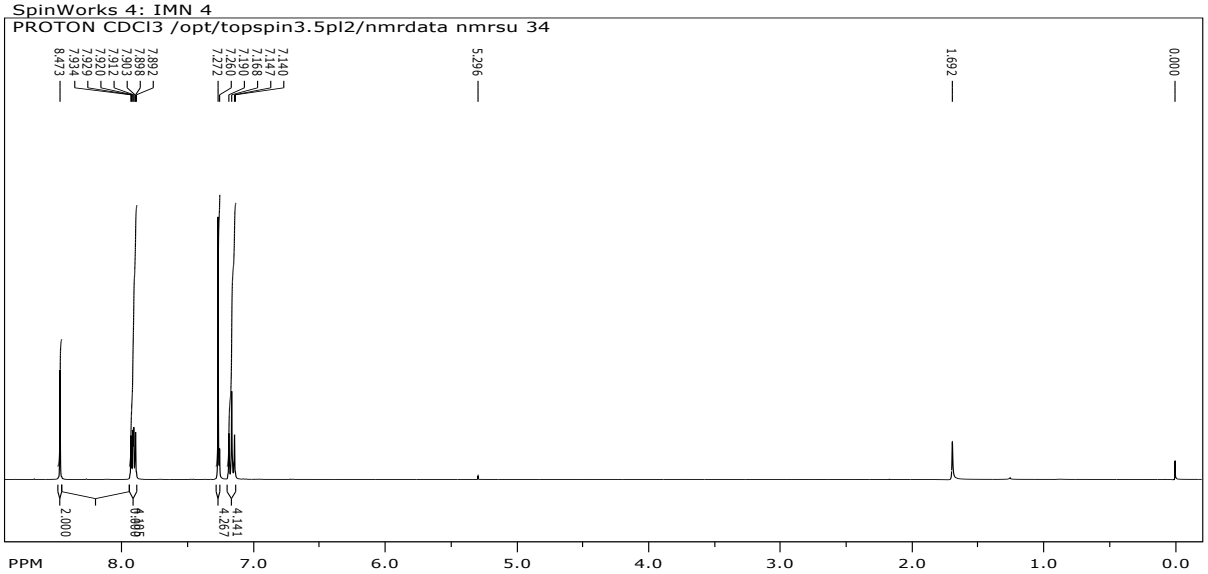


Figure: S1.n) ^{1}H NMR Spectra of compound 14.

- ^{1}H NMR (400 HZ, $CDCl_3$):δ7.19–7.33[m(6H),H4,H6,H7] , δ7.94–7.97 [m(4H)H9,H10] ,δ 8.82[s(2H),H1]

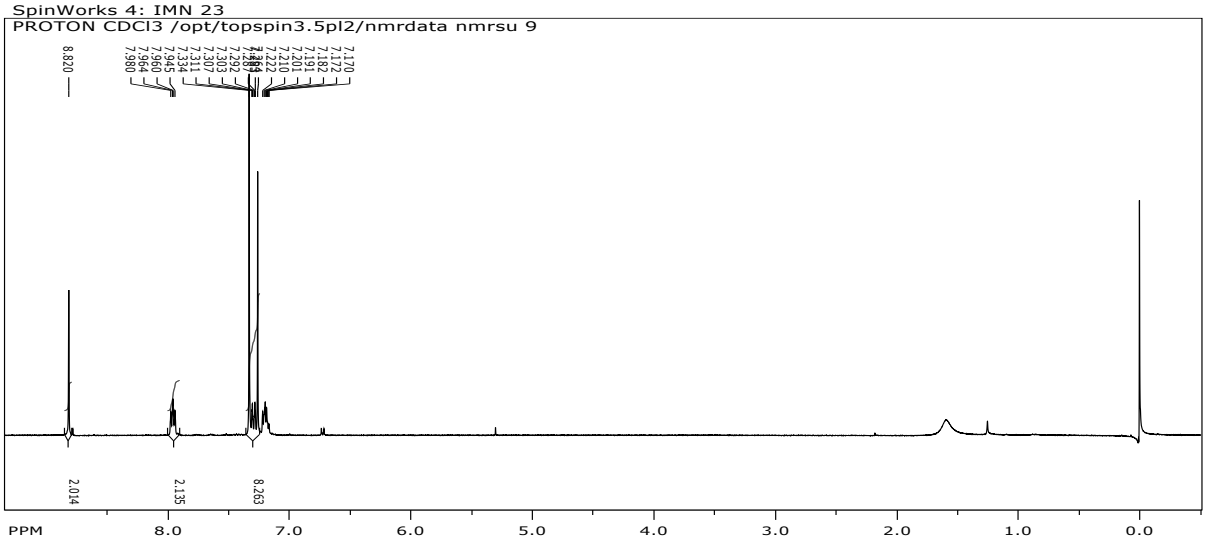


Figure: S1.o) ^{1}H NMR Spectra of compound 15.

- ^{1}H NMR (400 HZ, $CDCl_3$):δ7.86–7.29[m(6H),H4,H6,H7] , δ8.19–8.25 [m(4H)H9,H10] ,δ 8.75[s(2H),H1]

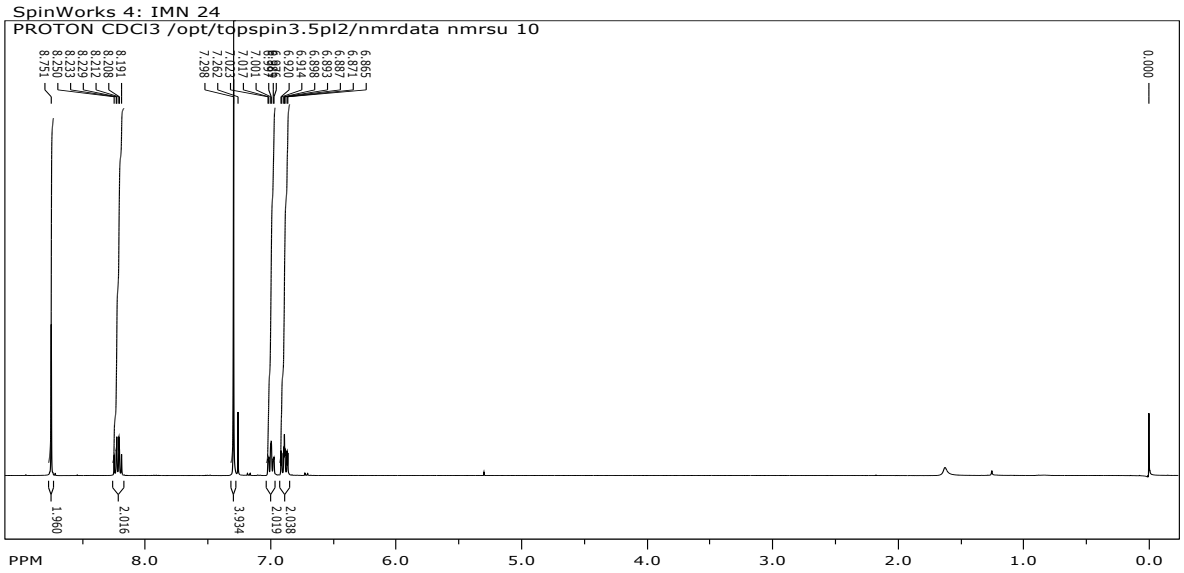


Figure: S1.p) ^{1}H NMR Spectra of compound 16.

- ^{1}H NMR (400 HZ, $CDCl_3$):δ7.21–7.91[m(6H),H4,H6,H7] , δ 6.71–7.16 [m(4H)H9,H10] ,δ 8.77[s(2H),H1]

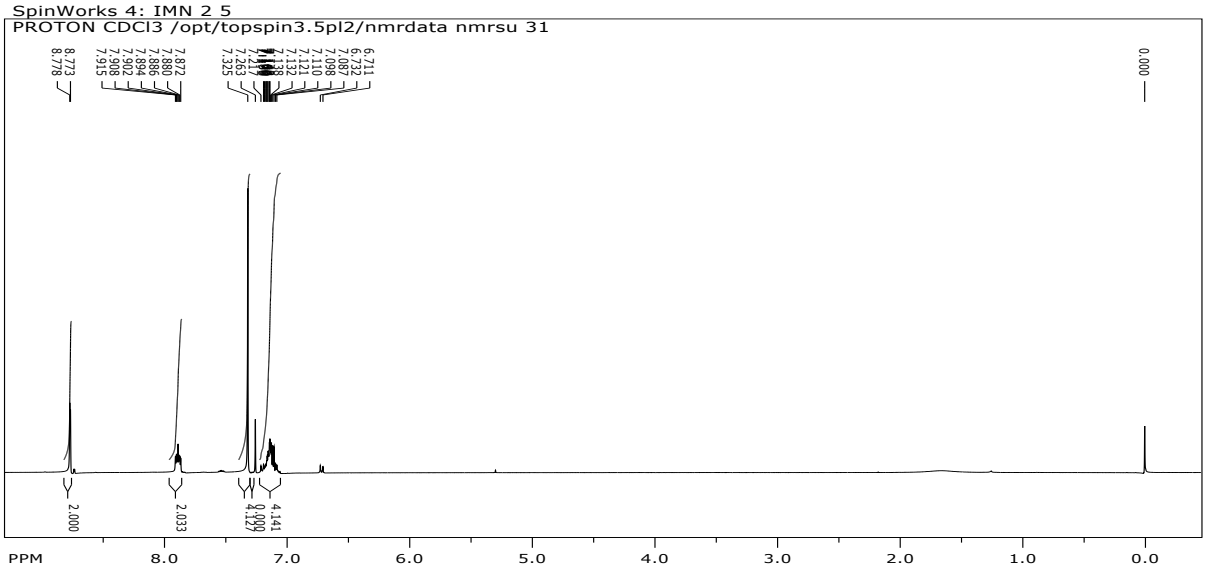


Figure: S1.q) ^{1}H NMR Spectra of compound 17.

- ^{1}H NMR (400 HZ, $CDCl_3$):δ7.17–7.45[m(6H),H4,H5,H6] , δ6.71–7.03[m(4H)H9,H10] ,δ 8.77[s(2H),H1]

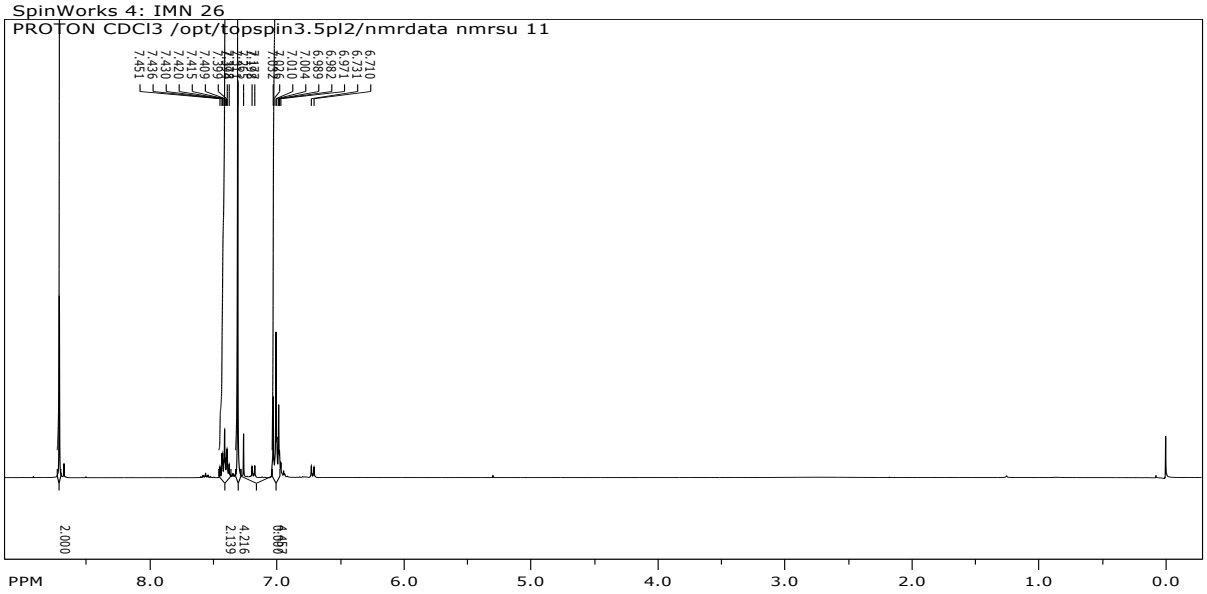


Figure: S1.r) ^{1}H NMR Spectra of compound 18.

- ^{1}H NMR (400 HZ, $CDCl_3$):δ7.23–7.61[m(6H),H3,H6,H7] , δ7.80–7.85[m(4H)H9,H10]δ 8.43[s(2H),H1]

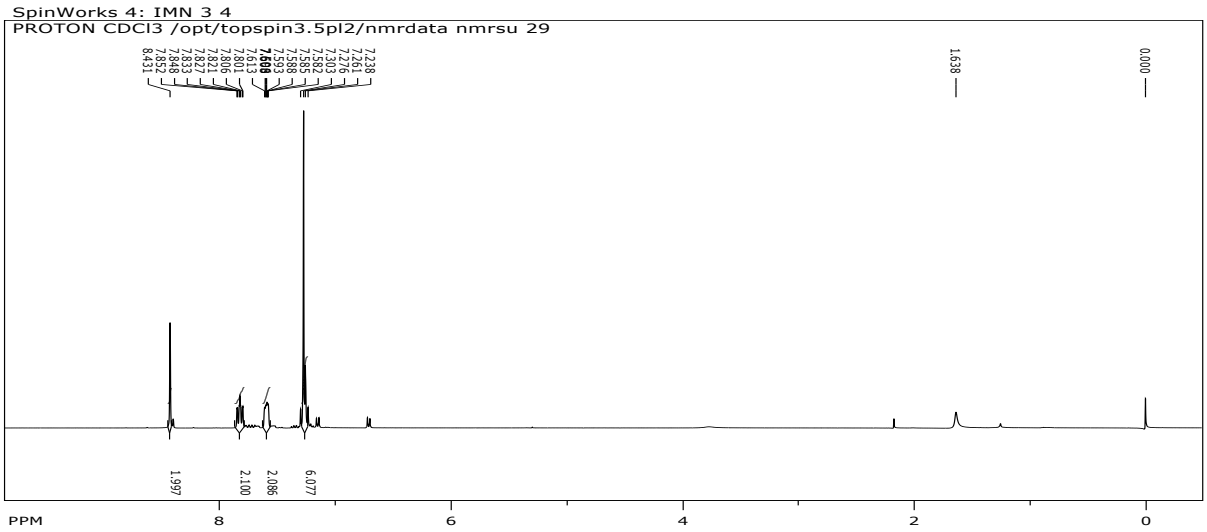


Figure: S1.s) ^{1}H NMR Spectra of compound 19.

- ^{1}H NMR (400 HZ, $CDCl_3$):δ6.67–7.29[m(6H),H3,H6,H7] , δ7.40–7.45[m(4H)H9,H10]δ 8.41–8.43[s(2H),H1]

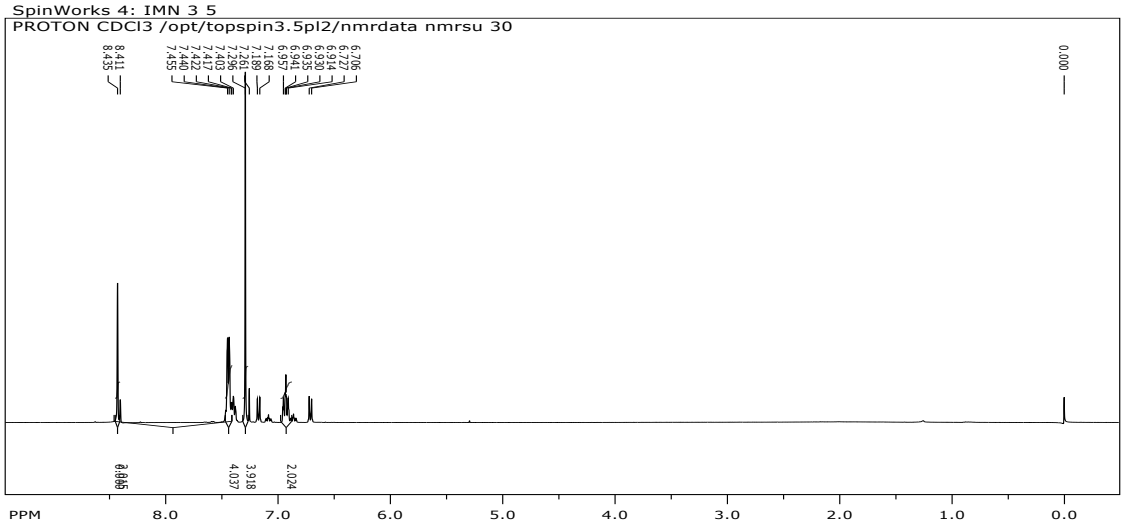


Figure: S1.t) ^{1}H NMR Spectra of compound 20.

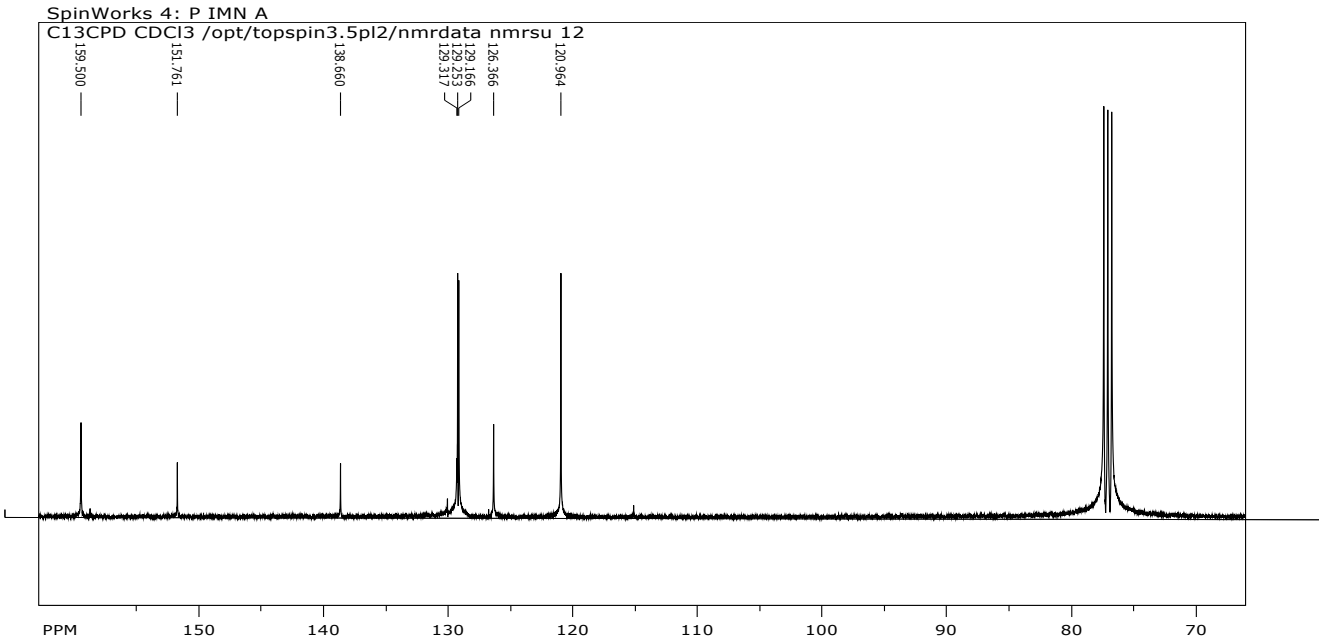


Figure: S2.a) ^{13}C NMR Spectra of compound 1

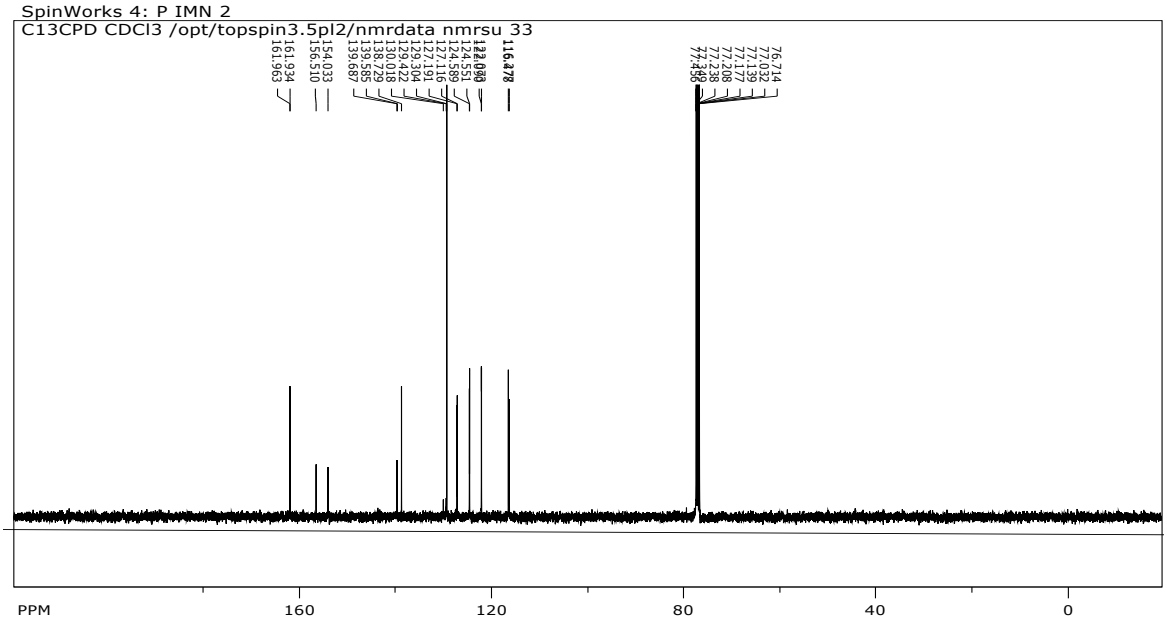


Figure: S2.b) ^{13}C NMR Spectra of compound 2.

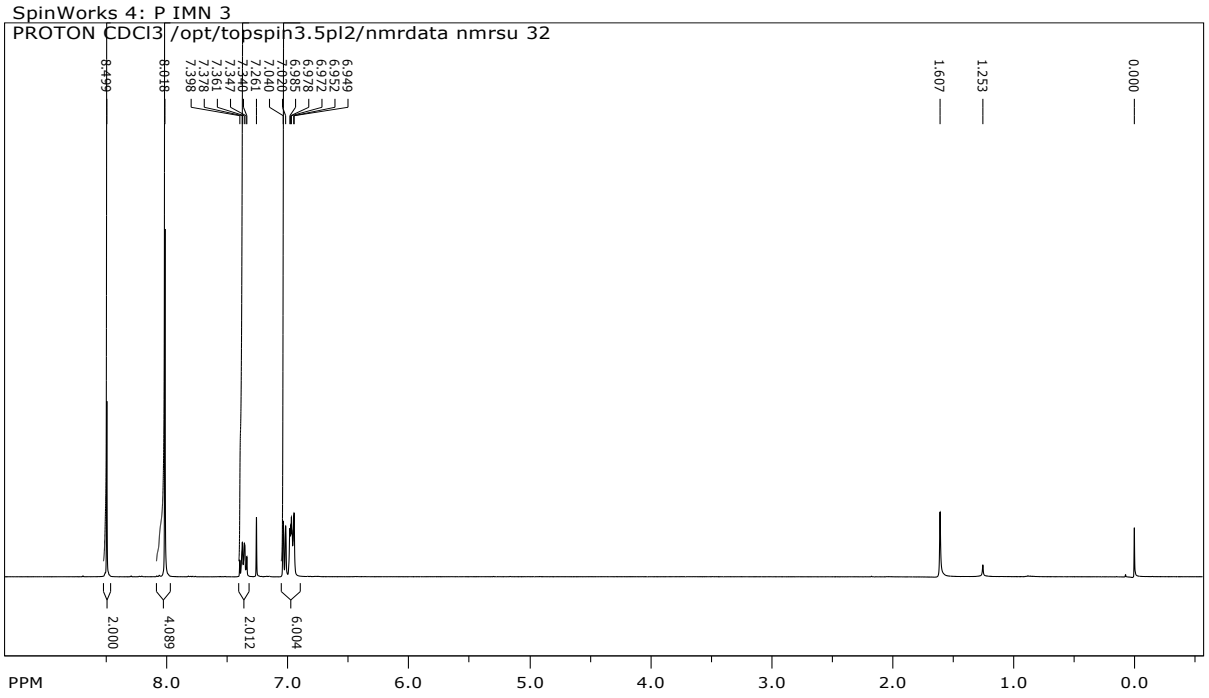


Figure: S2.c) ^{13}C NMR Spectra of compound 3.

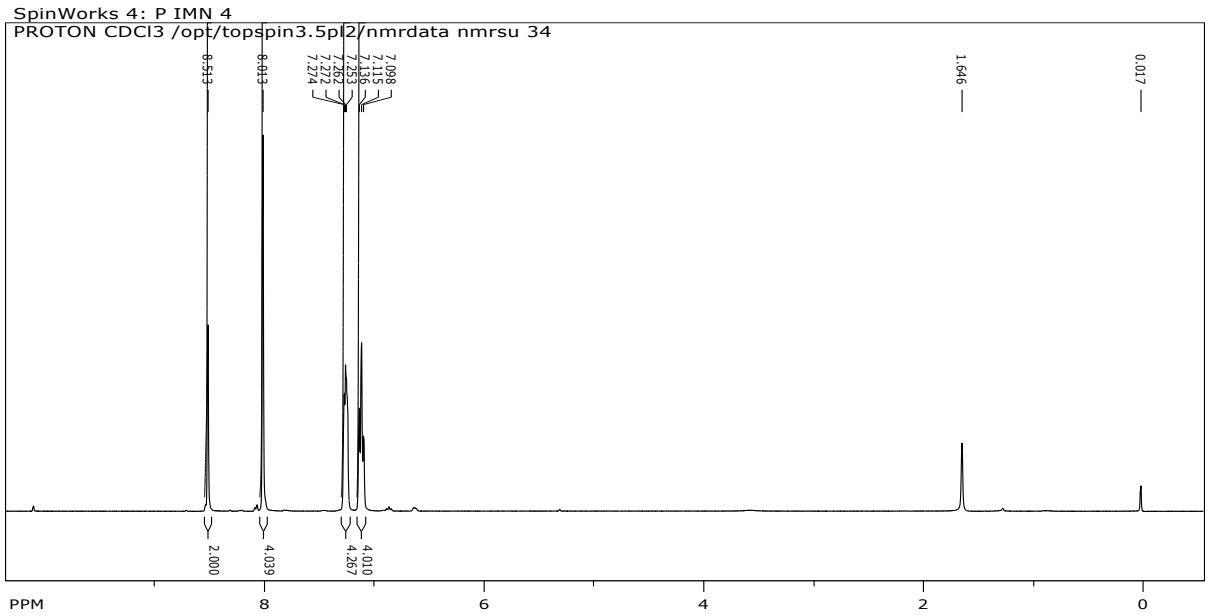


Figure: S2.d) ^{13}C NMR Spectra of compound 4.

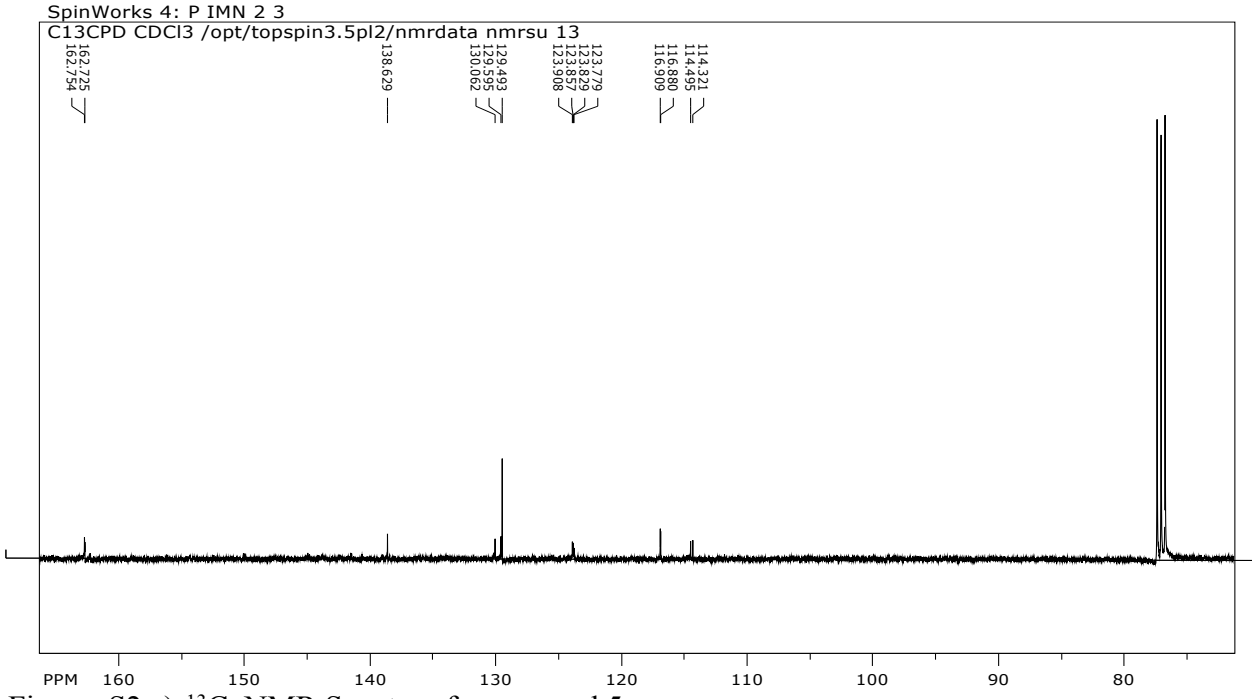


Figure: S2.e) ^{13}C NMR Spectra of compound 5.

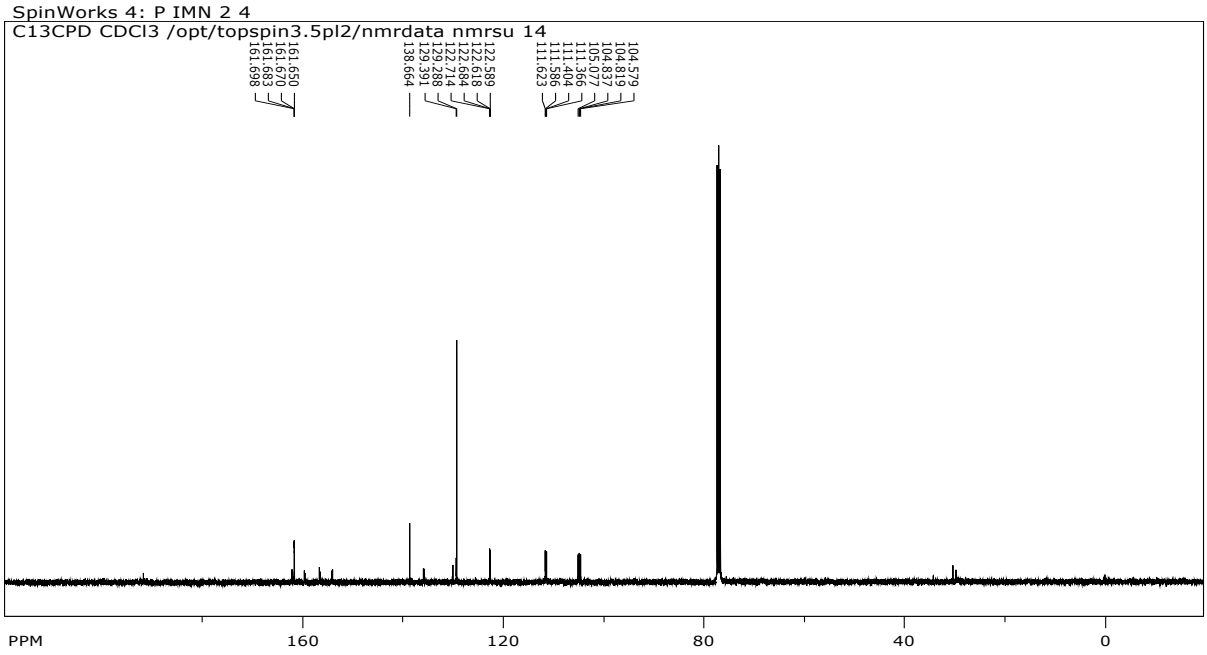


Figure: S2.f) ^{13}C NMR Spectra of compound 6.

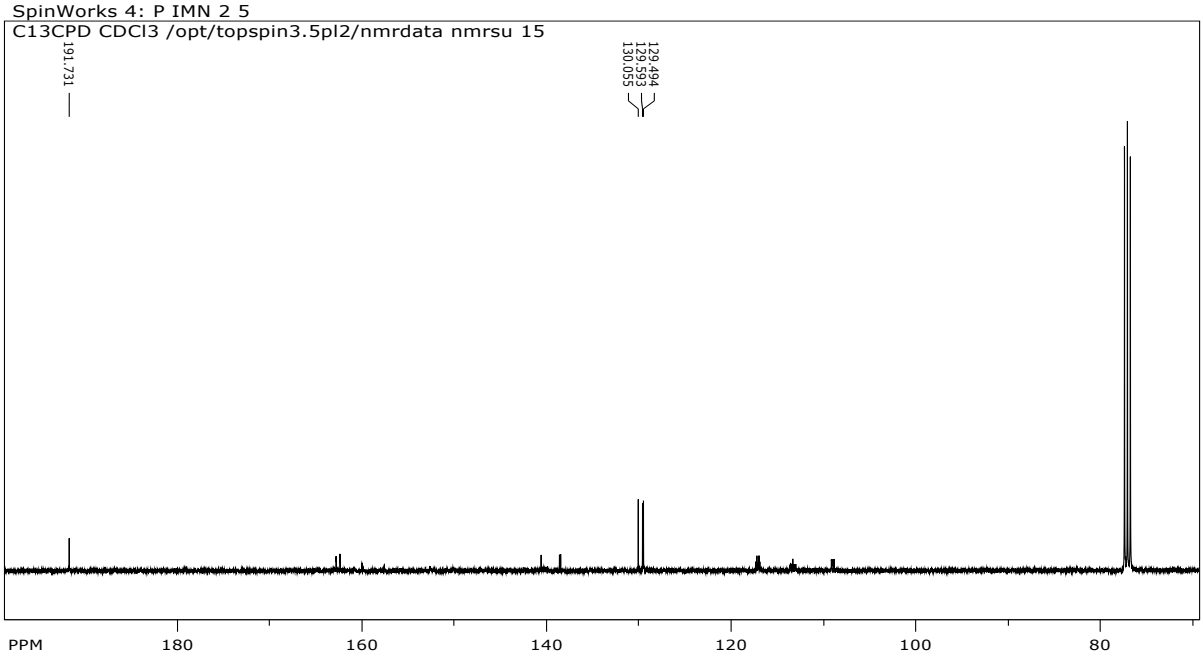


Figure: S2.g) ^{13}C NMR Spectra of compound 7.

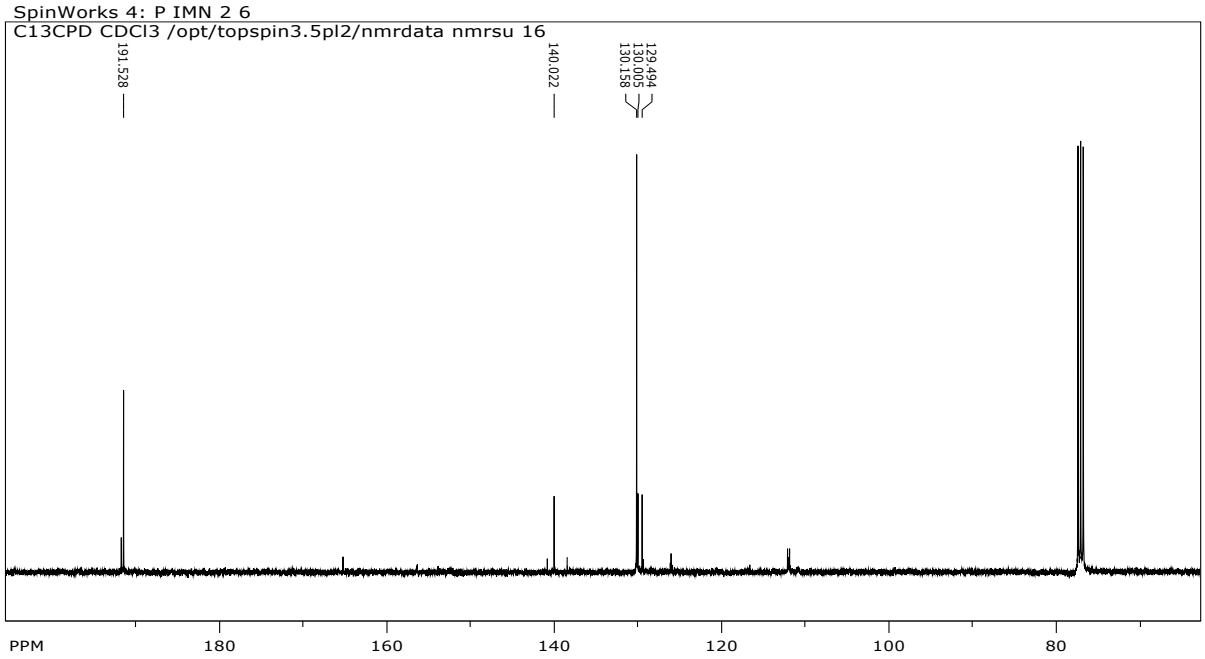


Figure: S2.h) ^{13}C NMR Spectra of compound 8

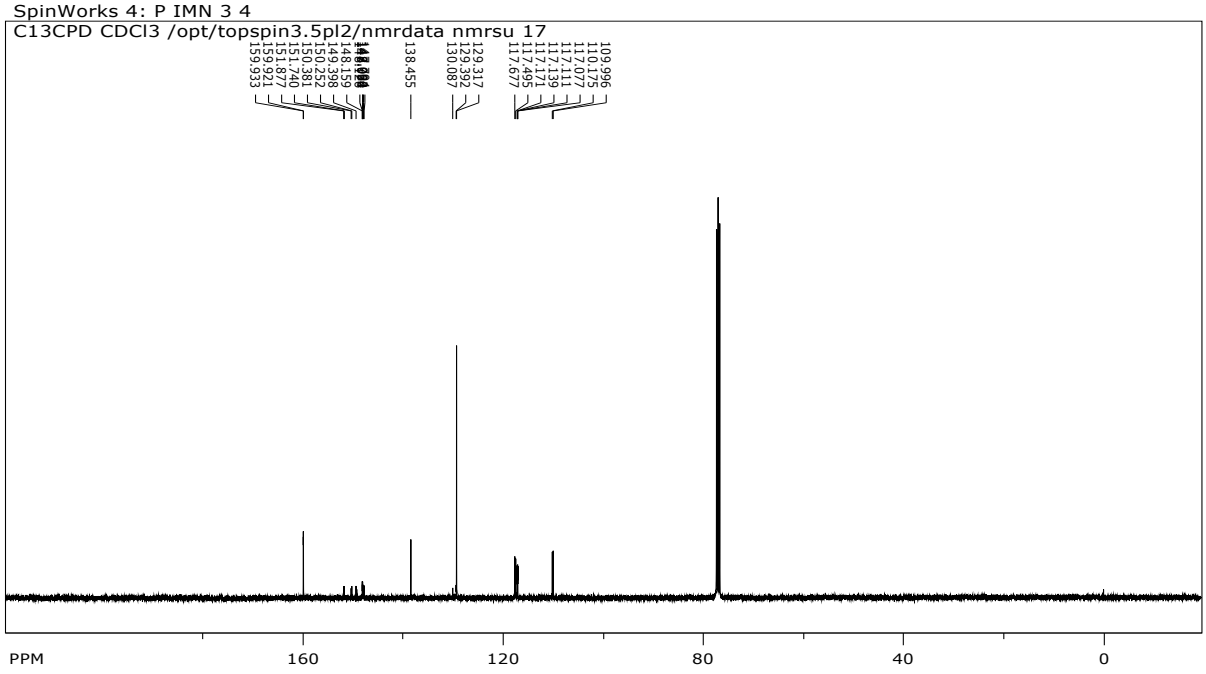


Figure: S2.i) ^{13}C NMR Spectra of compound 9.

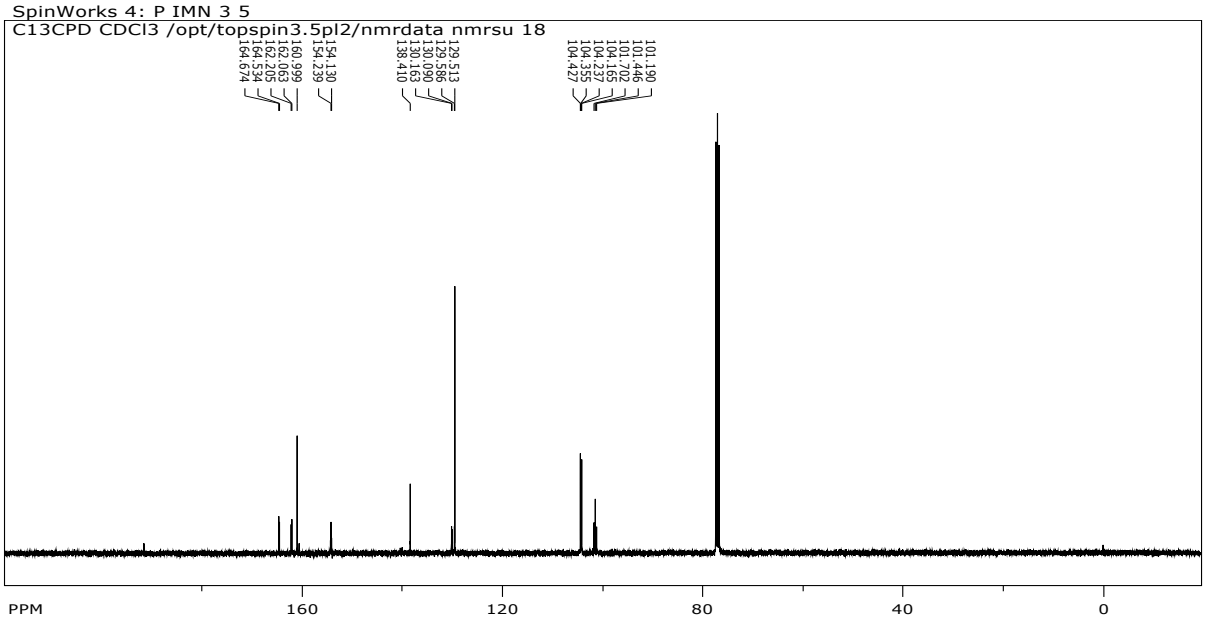


Figure: S2.j) ^{13}C NMR Spectra of compound 10.

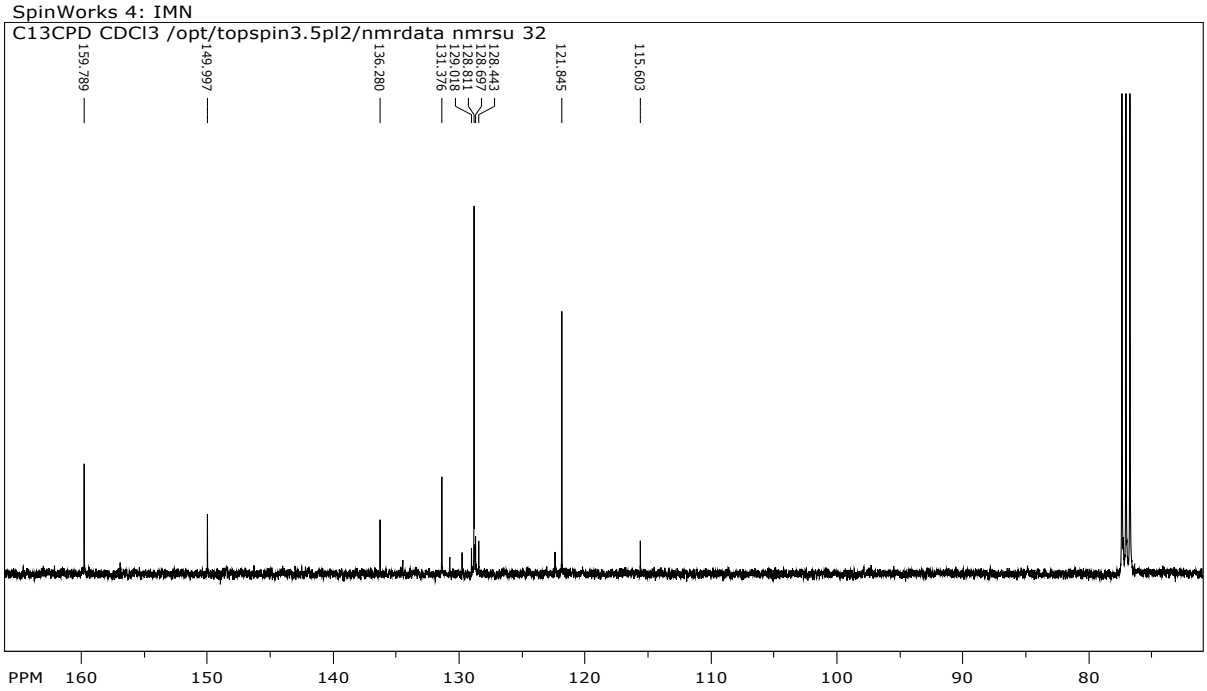


Figure: S2.k) ^{13}C NMR Spectra of compound 11.

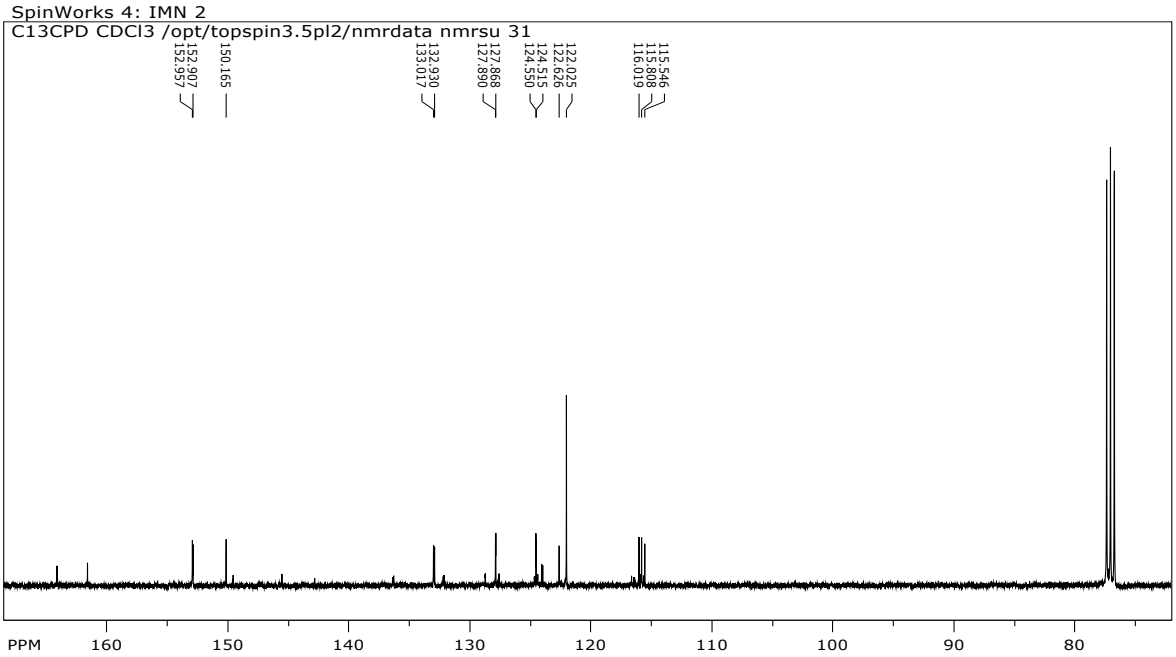


Figure: S2.l) ^{13}C NMR Spectra of compound 12.

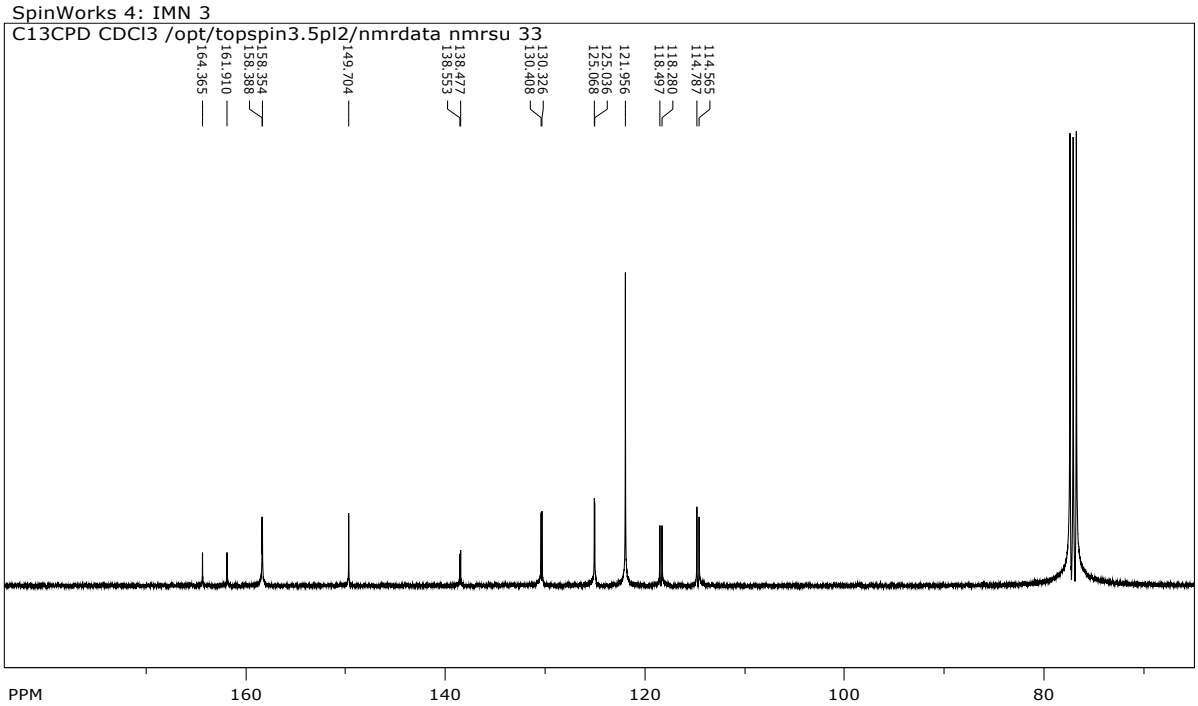


Figure: S2.m) ^{13}C NMR Spectra of compound 13.

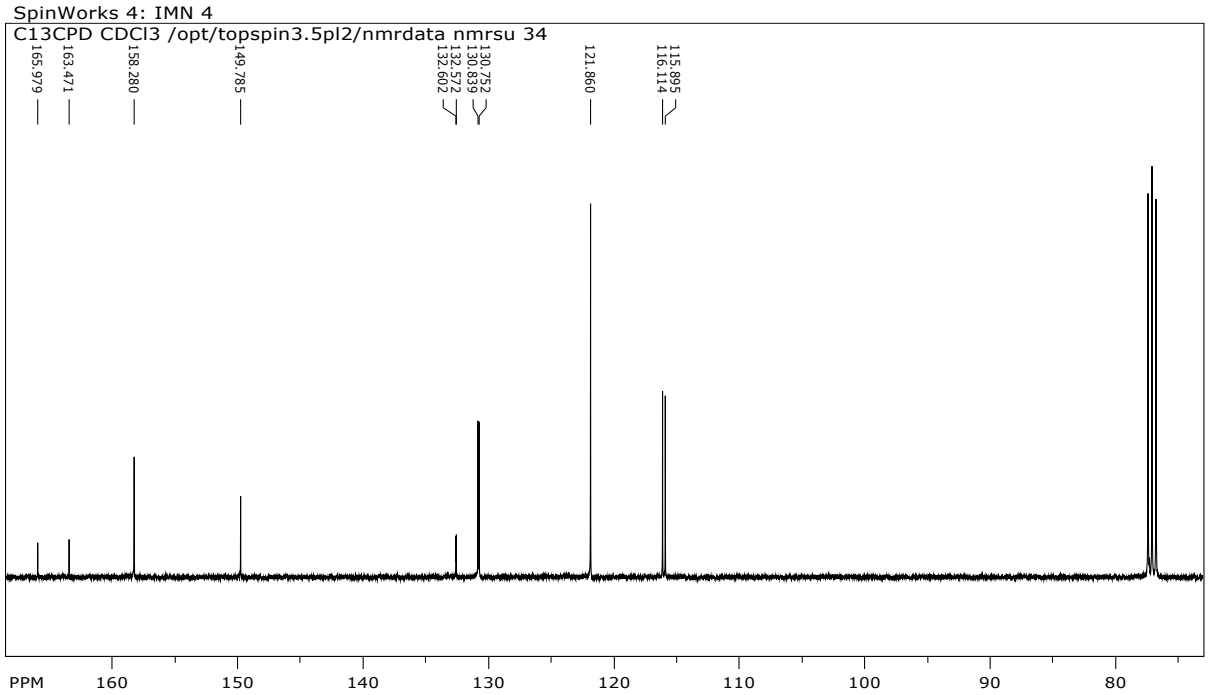


Figure: S2.n) ^{13}C NMR Spectra of compound 14.

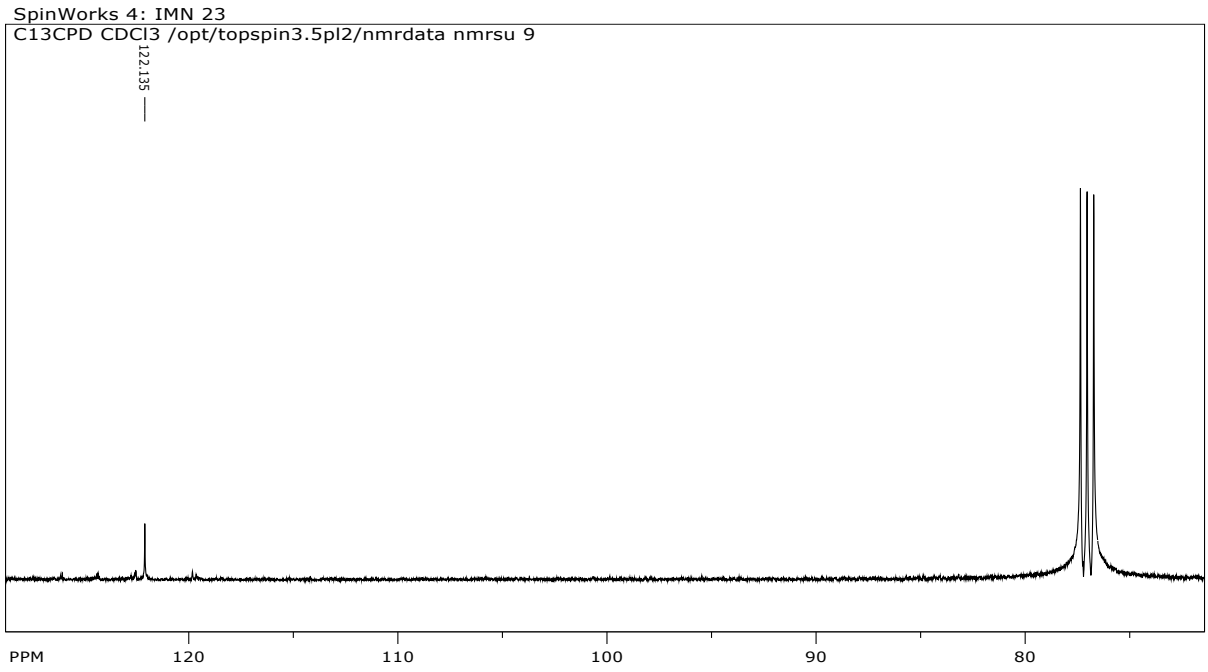


Figure: S2.o) ^{13}C NMR Spectra of compound 15.

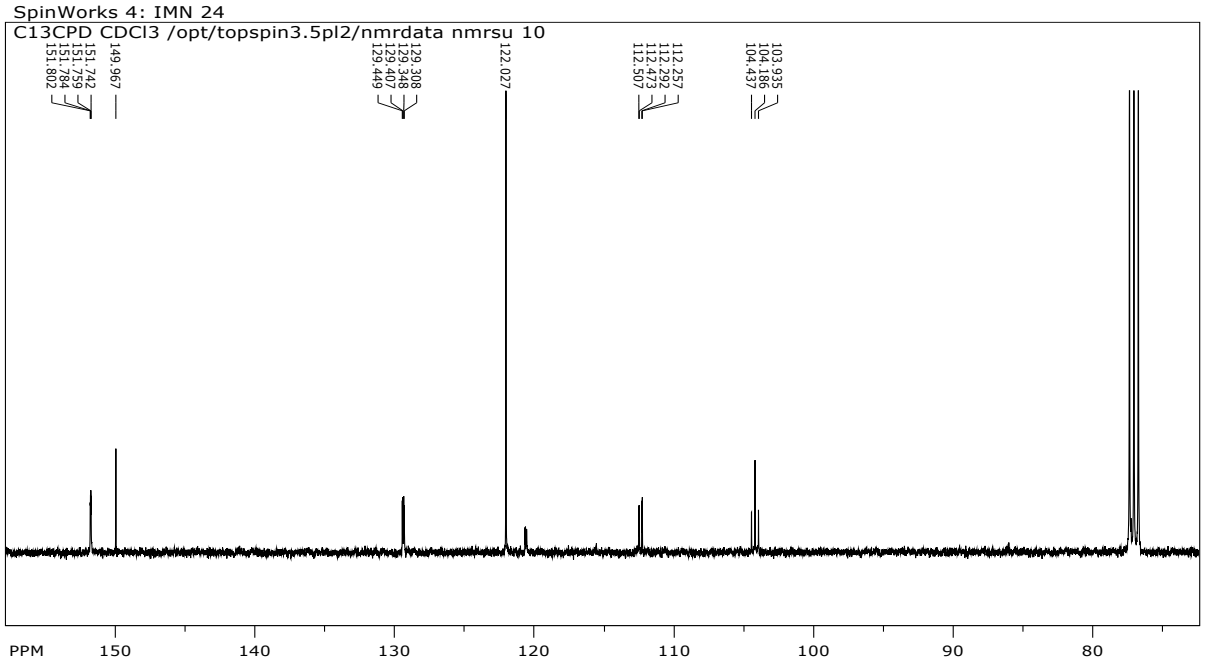


Figure: S2.p) ^{13}C NMR Spectra of compound 16.

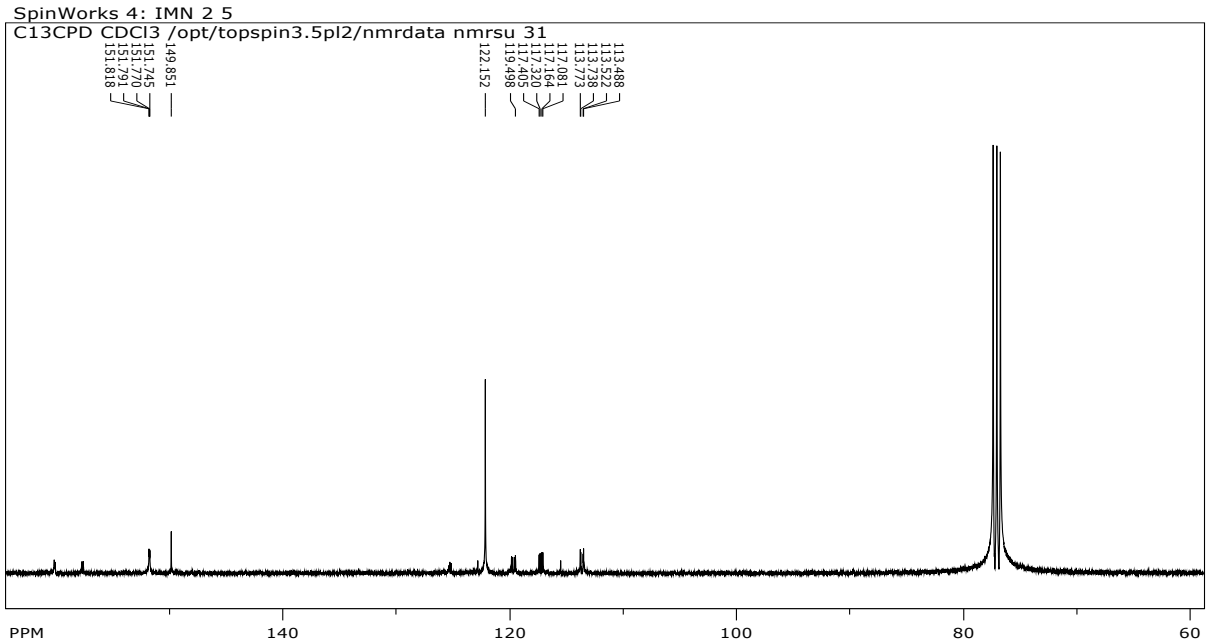


Figure: S2.q) ^{13}C NMR Spectra of compound 17.

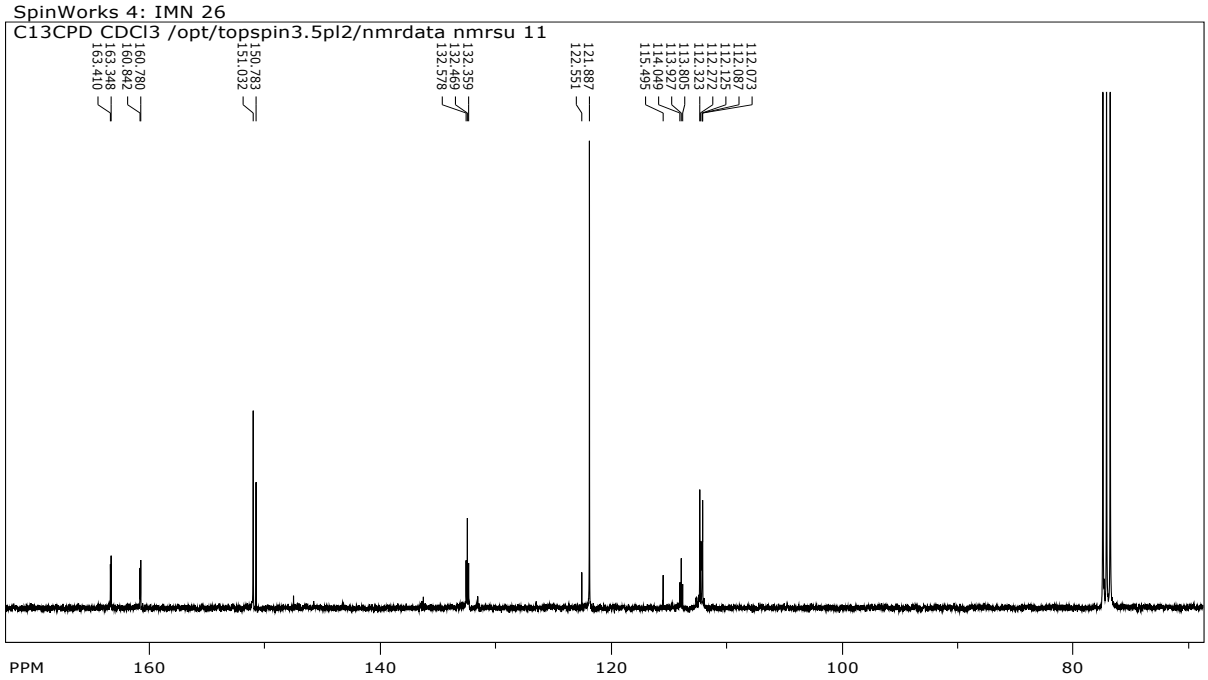


Figure: S2.r) ^{13}C NMR Spectra of compound 18.

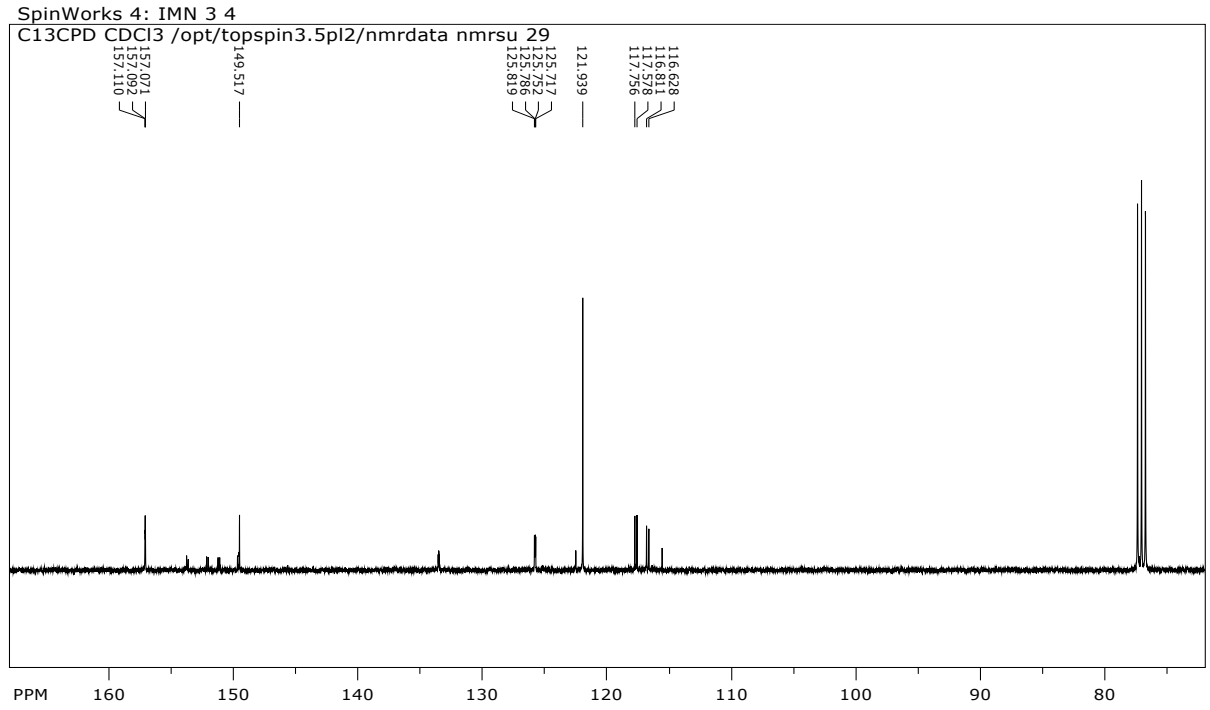


Figure: S2.s) ^{13}C NMR Spectra of compound 19.

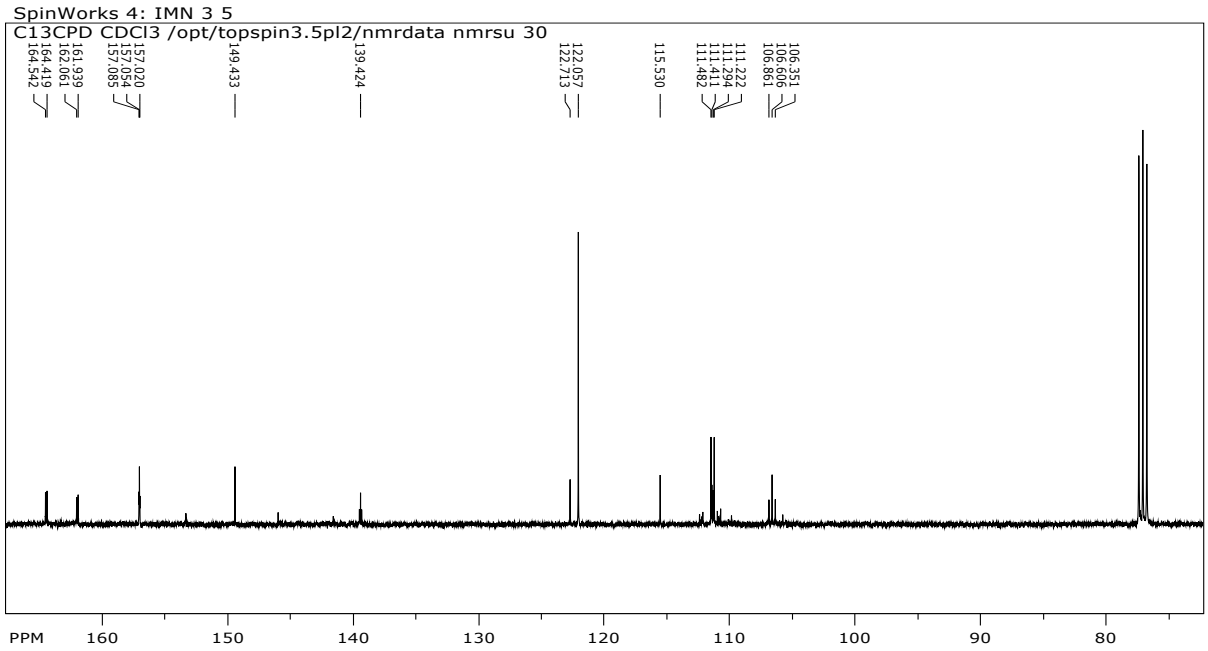


Figure: S2.t) ^{13}C NMR Spectra of compound 20.

NOTE: As compound 1 does not contain any fluorine in it. So, it doesn't show any peak in the ^{19}F NMR Spectra.

Figure: S3.a) ^{19}F NMR Spectra of compound 1.

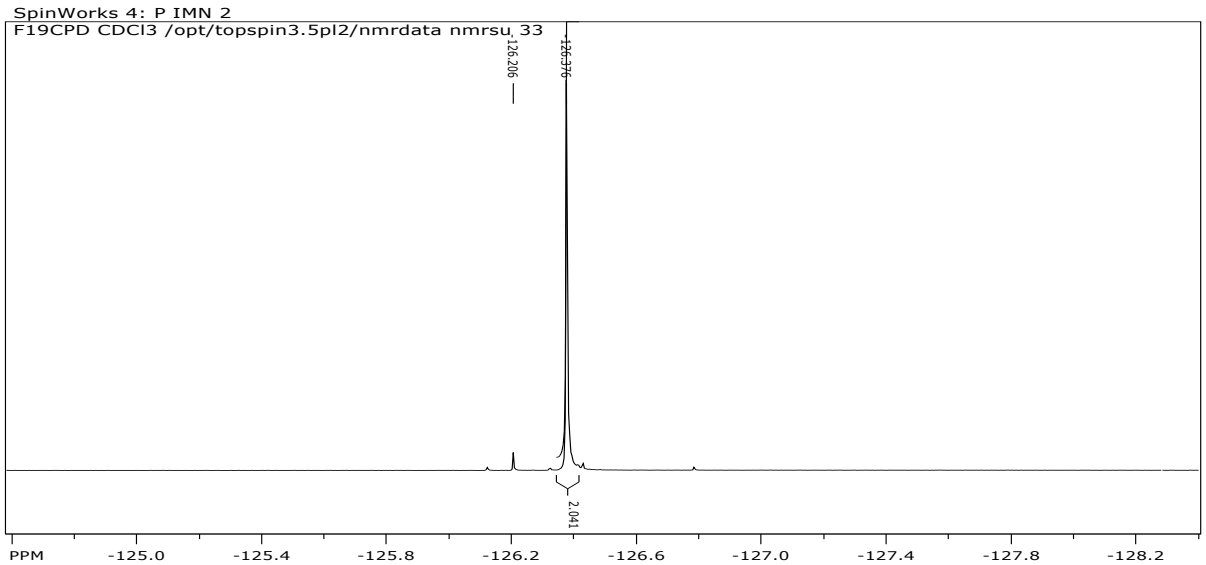


Figure: S3.b) ^{19}F NMR Spectra of compound 2.

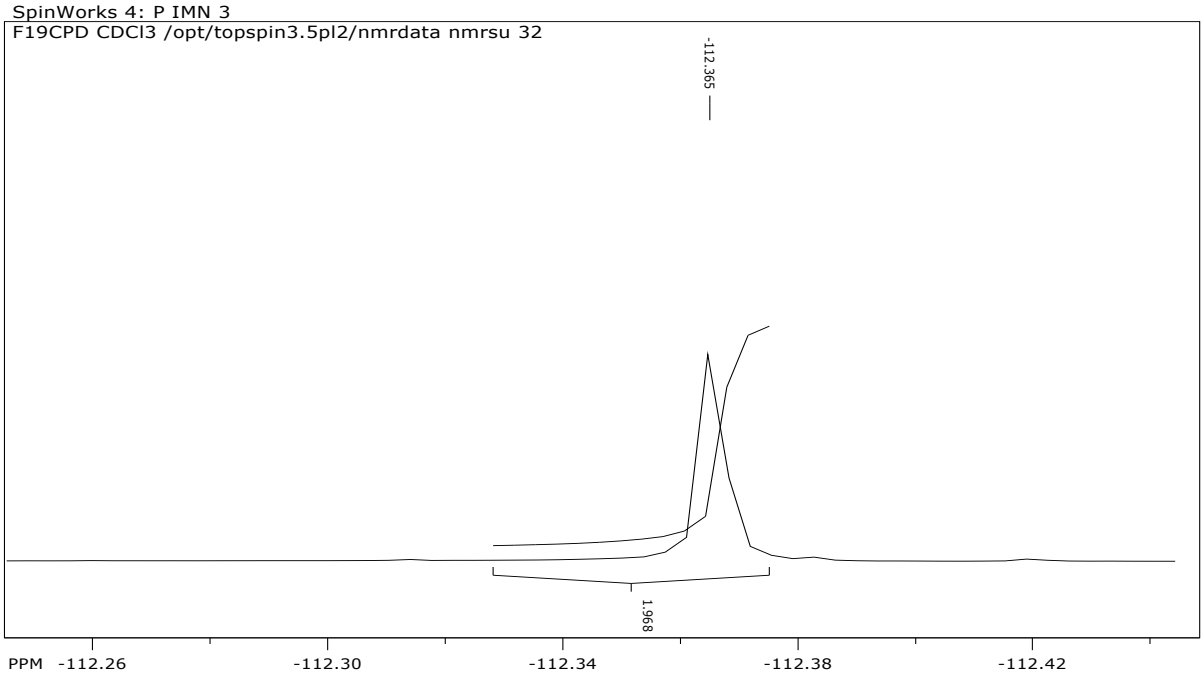


Figure: S3.c) ^{19}F NMR Spectra of compound 3.

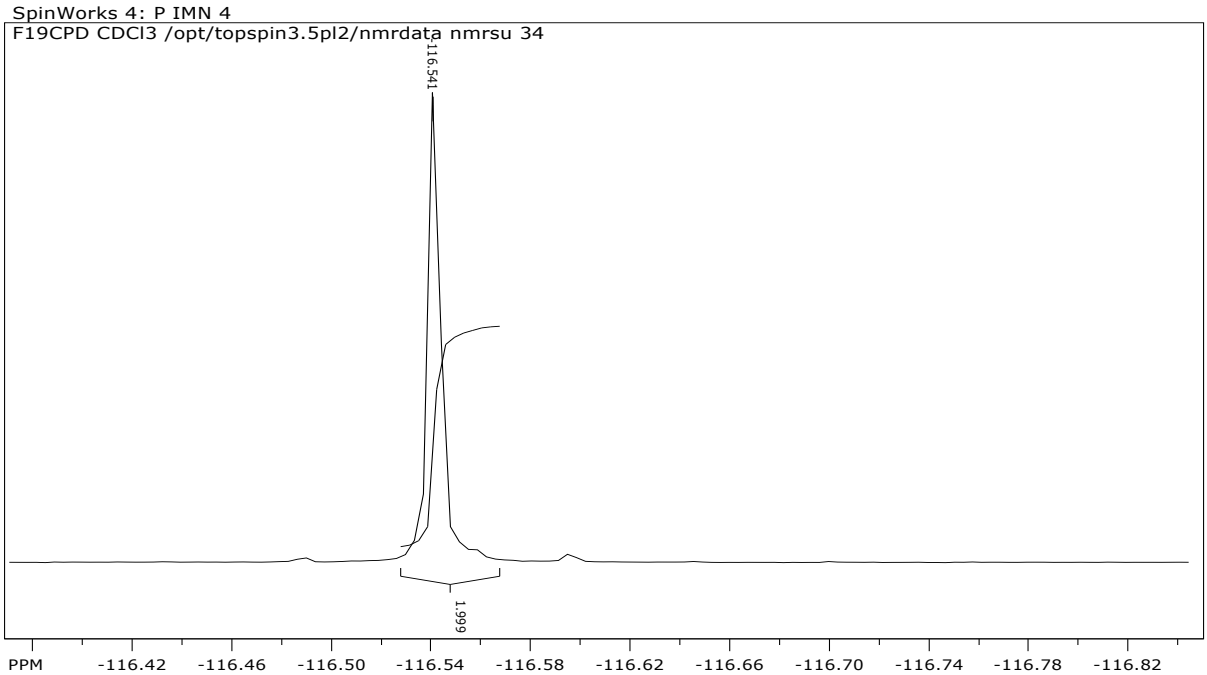


Figure: S3.d) ^{19}F NMR Spectra of compound 4.

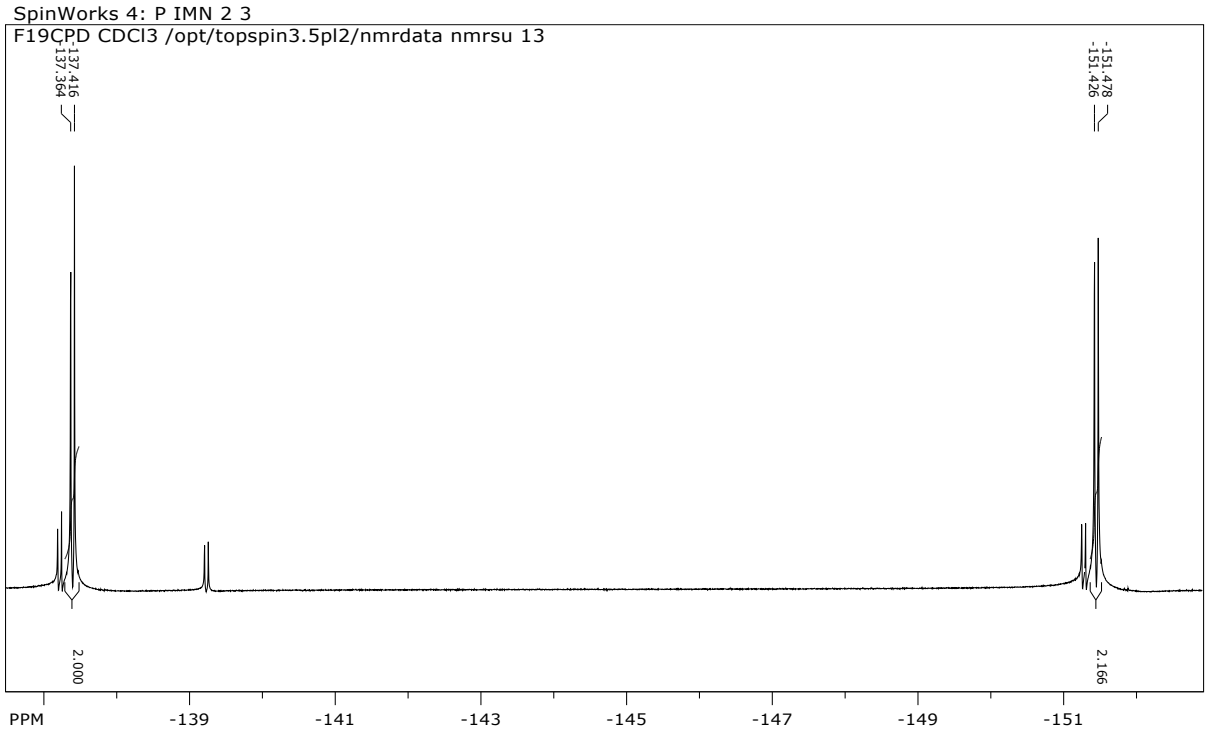


Figure: S3.e) ^{19}F NMR Spectra of compound 5.

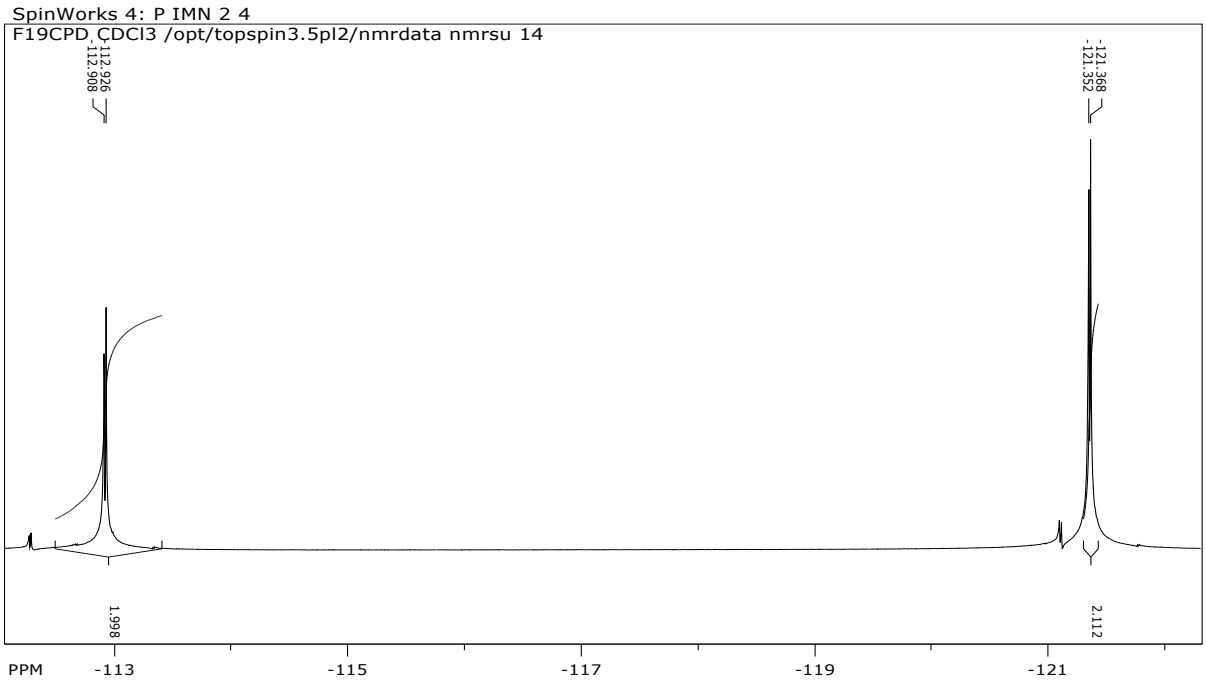


Figure: S3.f) ^{19}F NMR Spectra of compound 6.

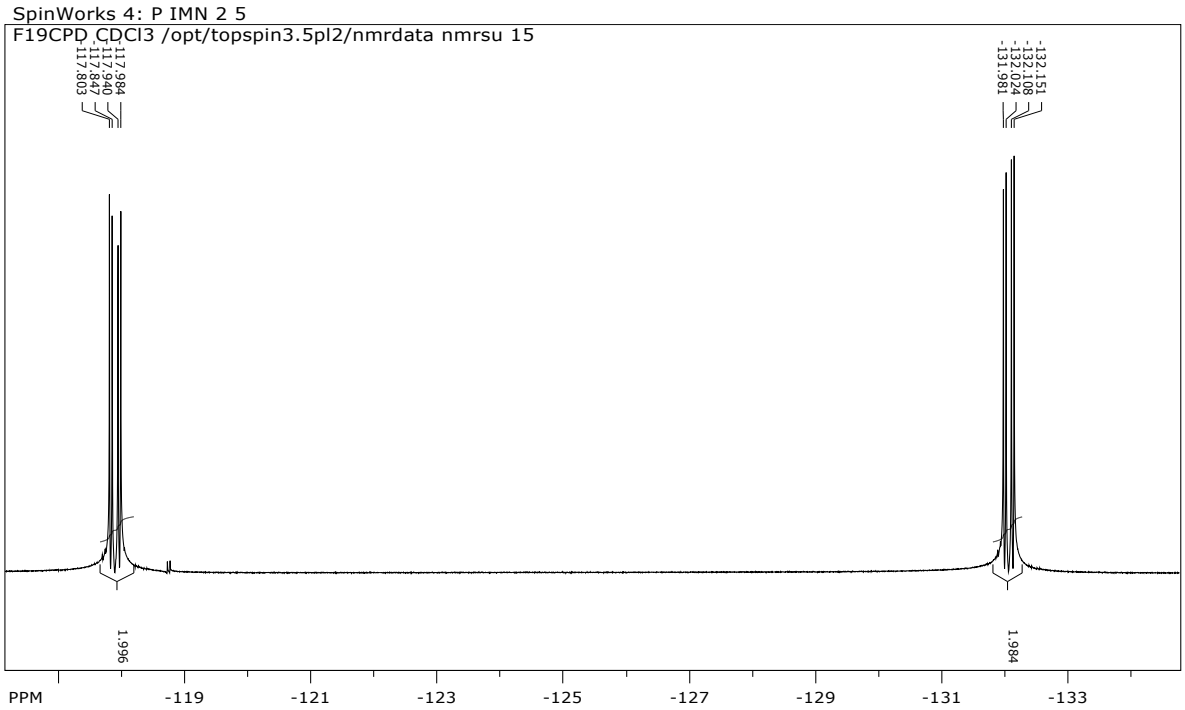


Figure: S3.g) ^{19}F NMR Spectra of compound 7.

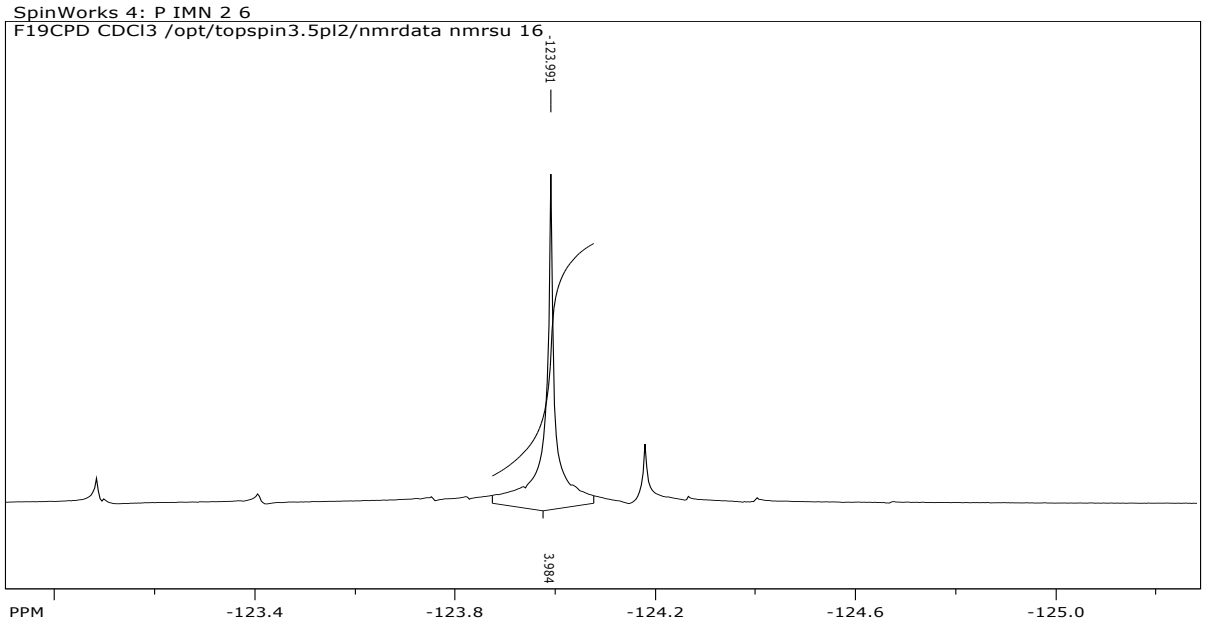


Figure: S3.h) ^{19}F NMR Spectra of compound 8.

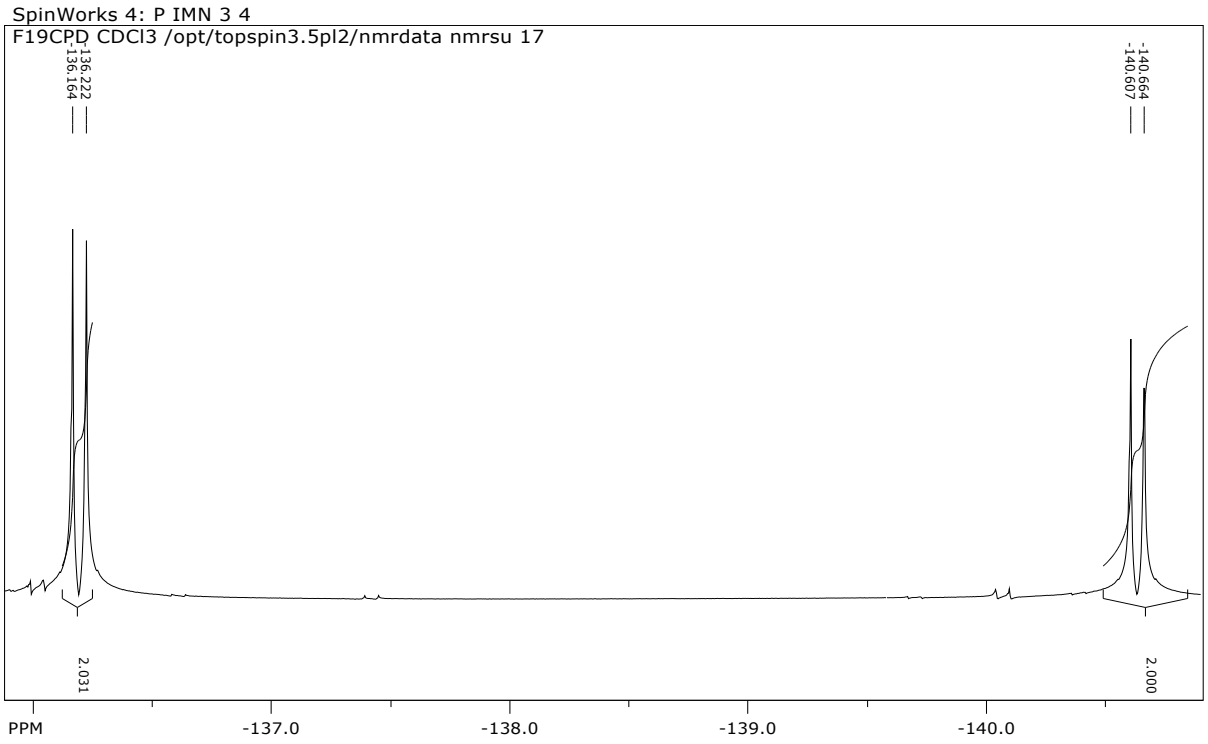


Figure: S3.i) ^{19}F NMR Spectra of compound 9.

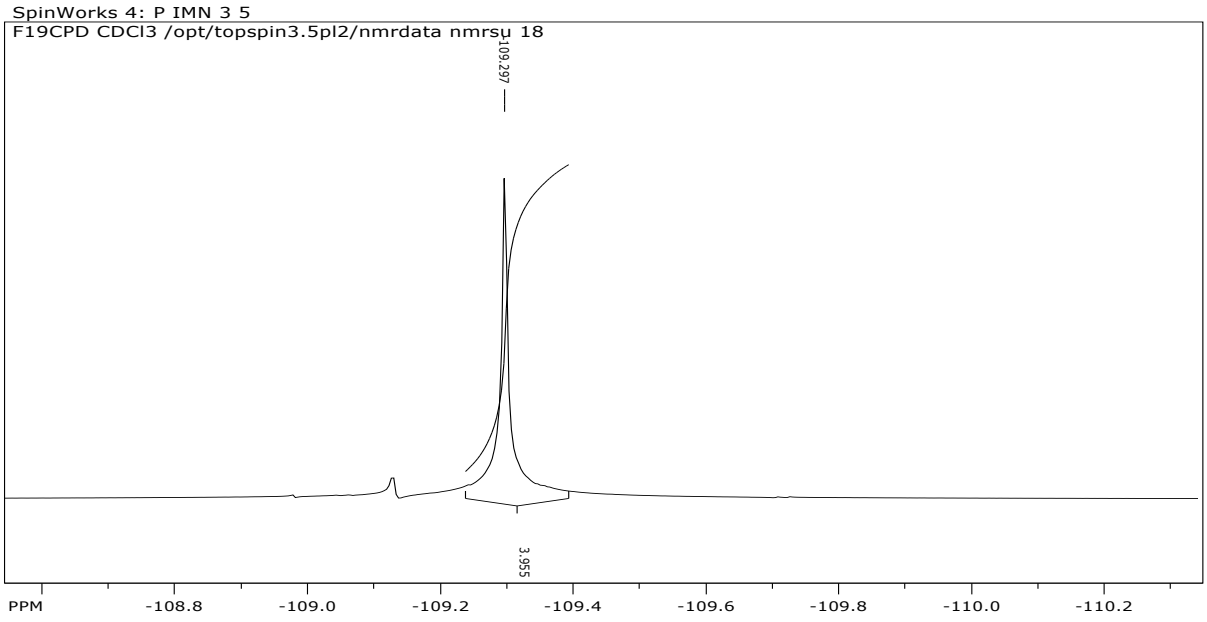


Figure: S3.j) ^{19}F NMR Spectra of compound 10.

NOTE: As compound 11 does not contain any fluorine in it. So, it doesn't show any peak in the ^{19}F NMR Spectra.

Figure: S3.k) ^{19}F NMR Spectra of compound 11.

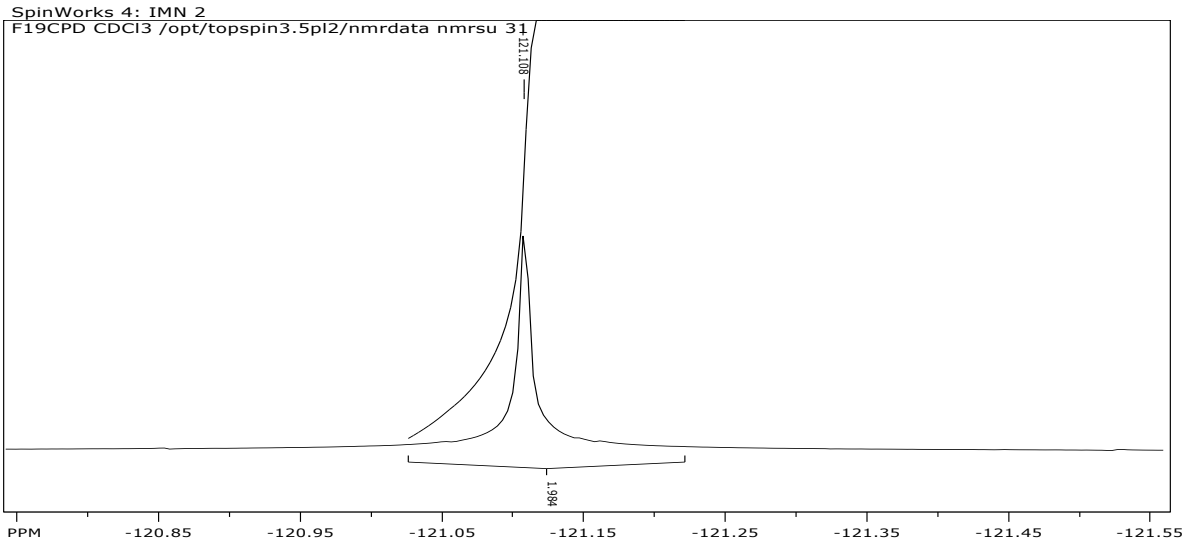


Figure: S3.l) ^{19}F NMR Spectra of compound 12.

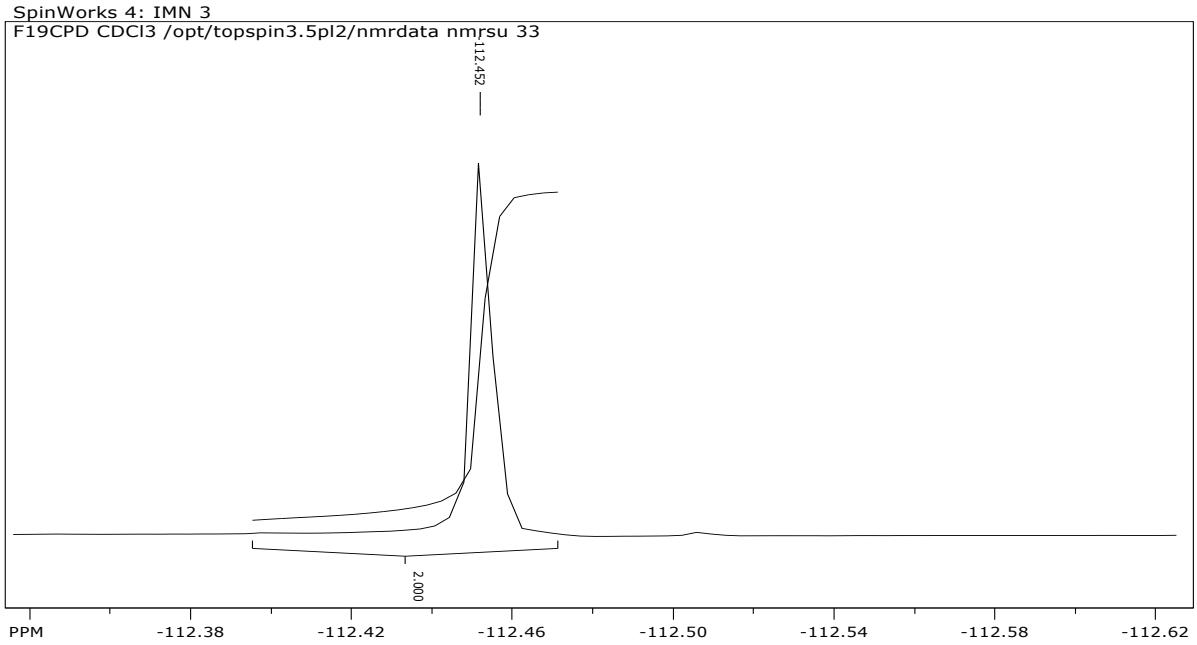


Figure: S3.m) ^{19}F NMR Spectra of compound 13.

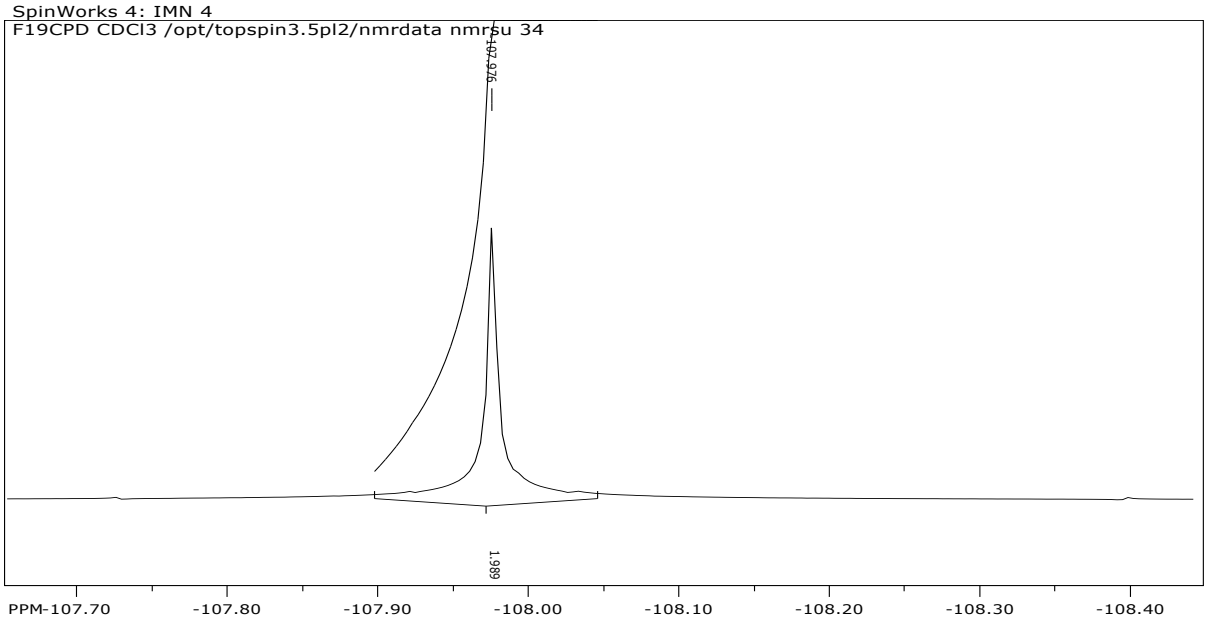


Figure: S3.n) ^{19}F NMR Spectra of compound 14.

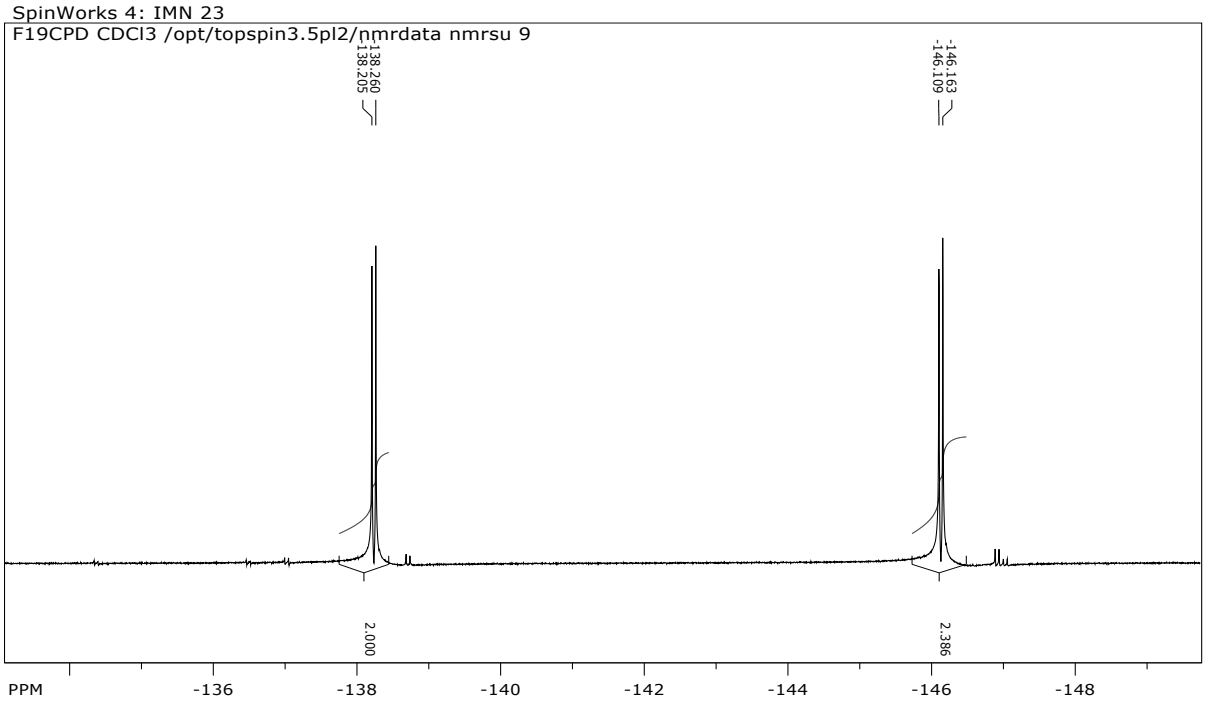


Figure: S3.o) ^{19}F NMR Spectra of compound 15.

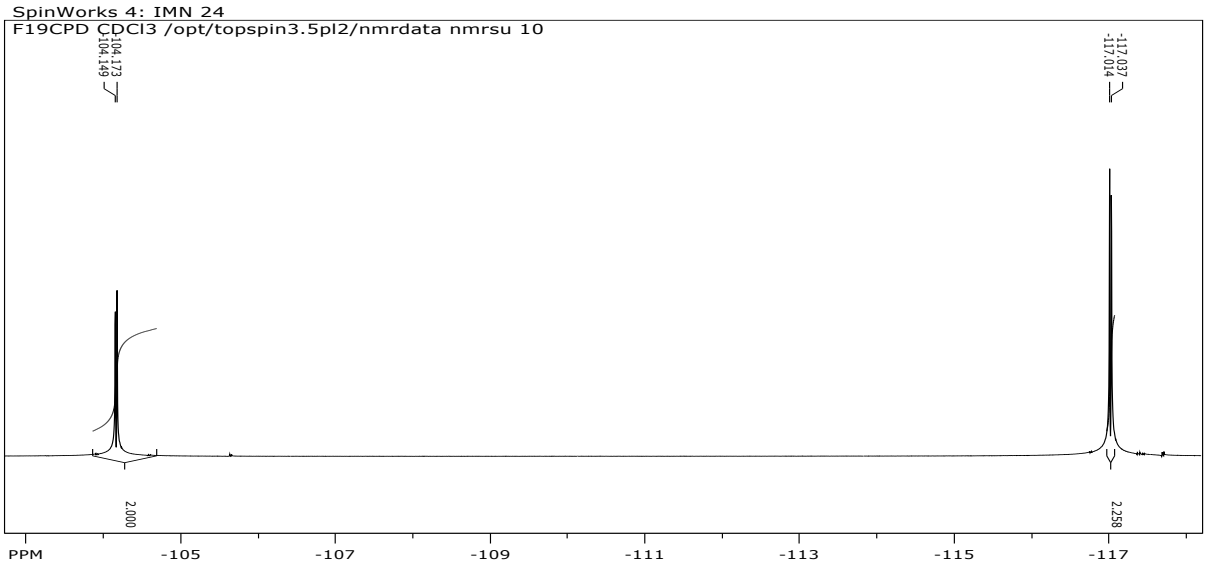


Figure: S3.p) ^{19}F NMR Spectra of compound 16.

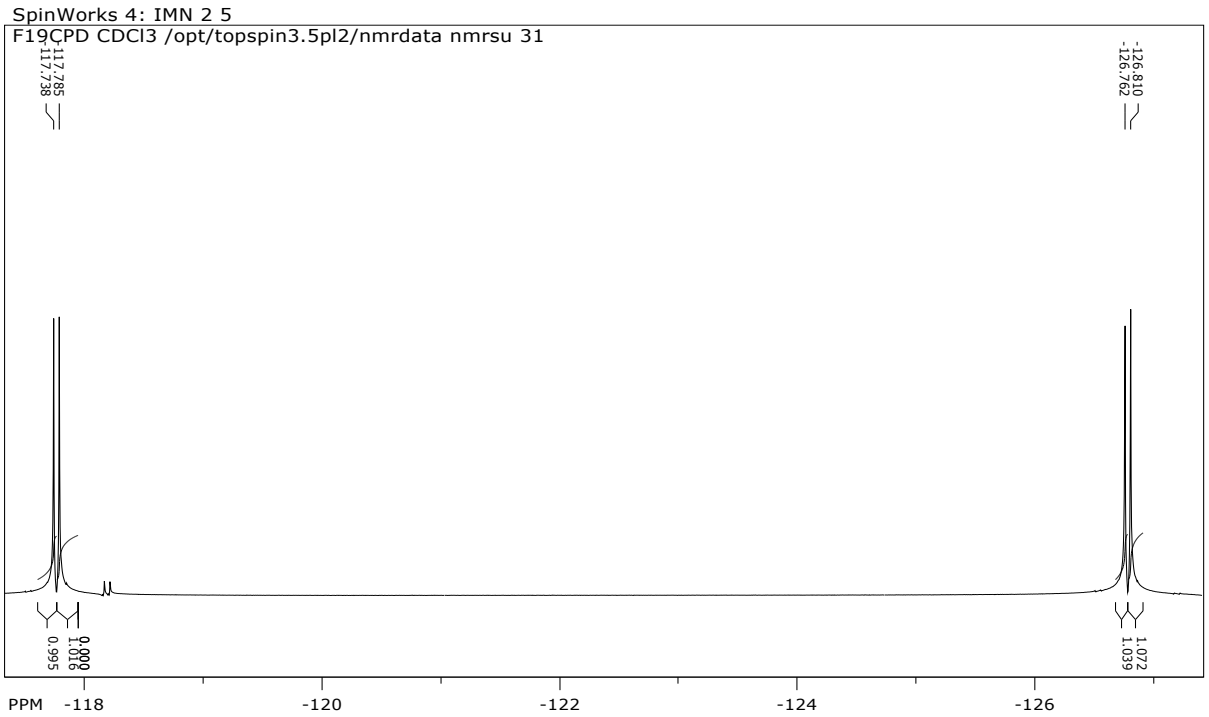


Figure: S3.q) ^{19}F NMR Spectra of compound 17.

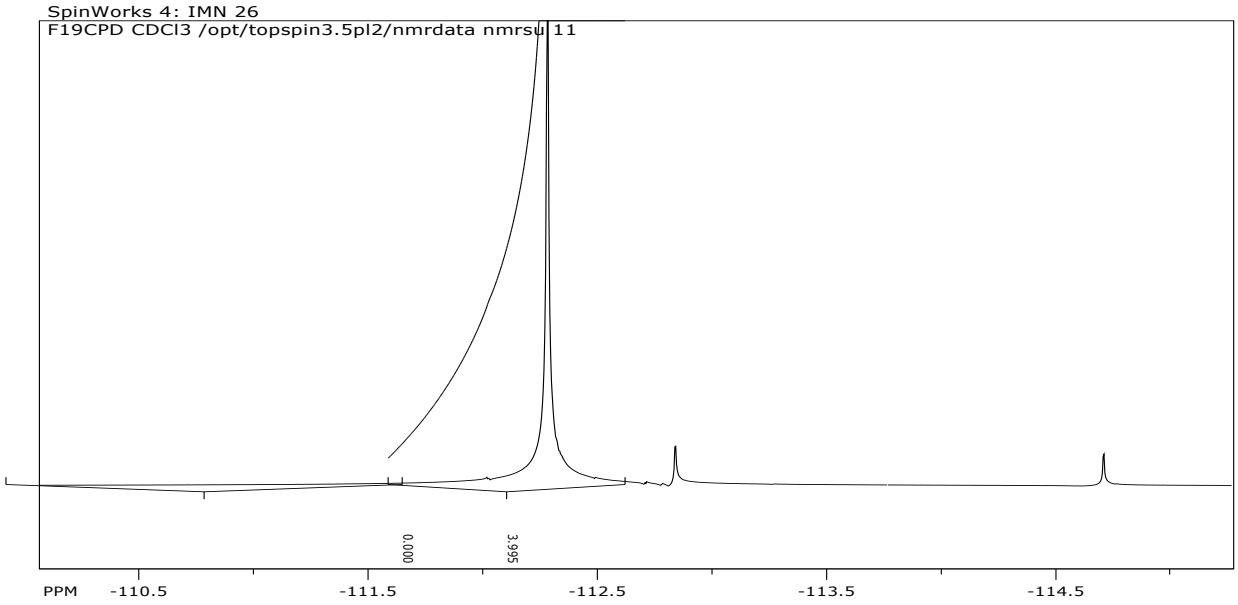


Figure: S3.r) ^{19}F NMR Spectra of compound 18.

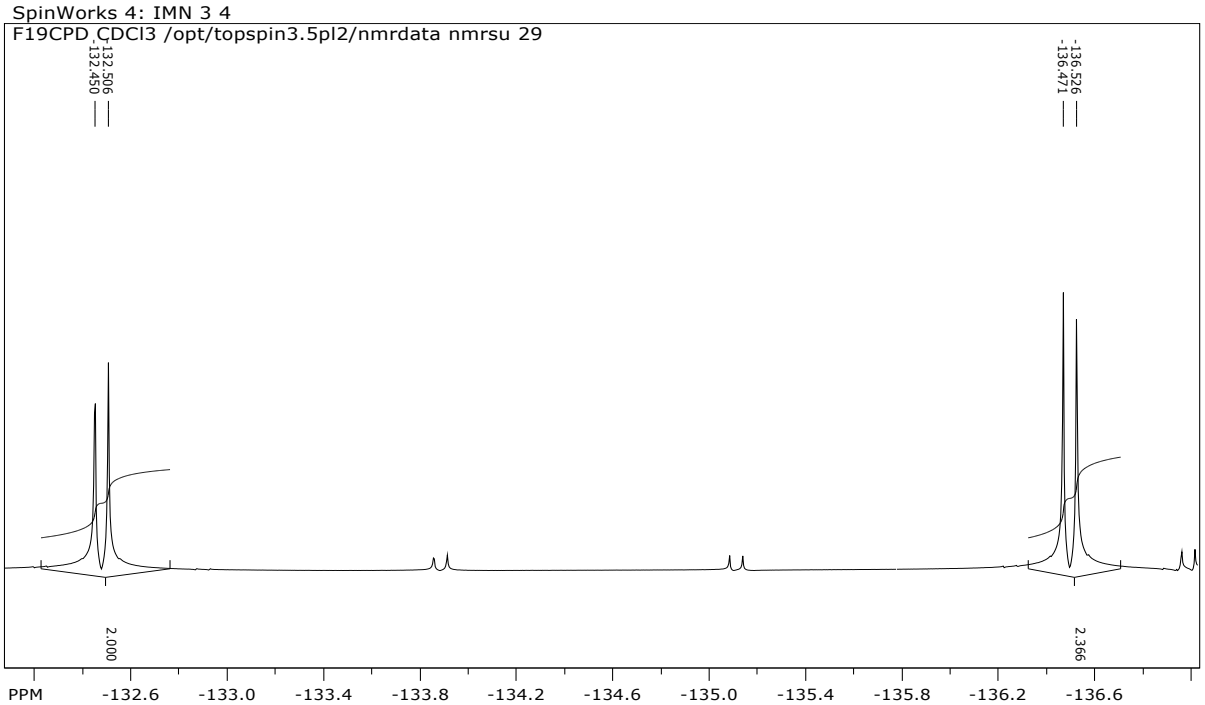


Figure: S3.s) ^{19}F NMR Spectra of compound 19.

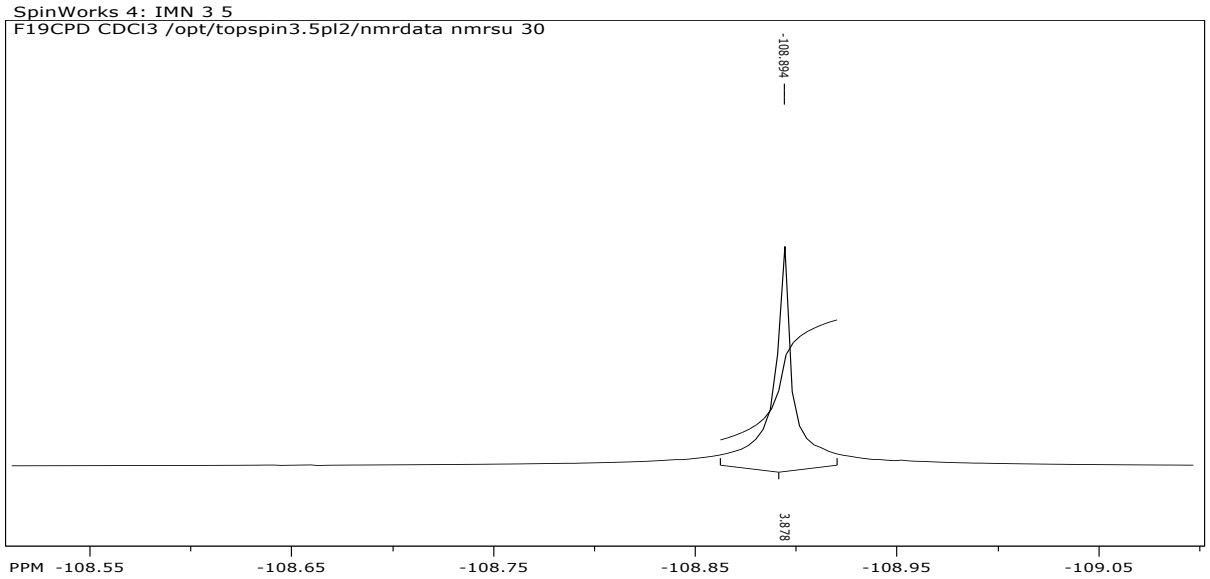


Figure: S3.t) ^{19}F NMR Spectra of compound 20.

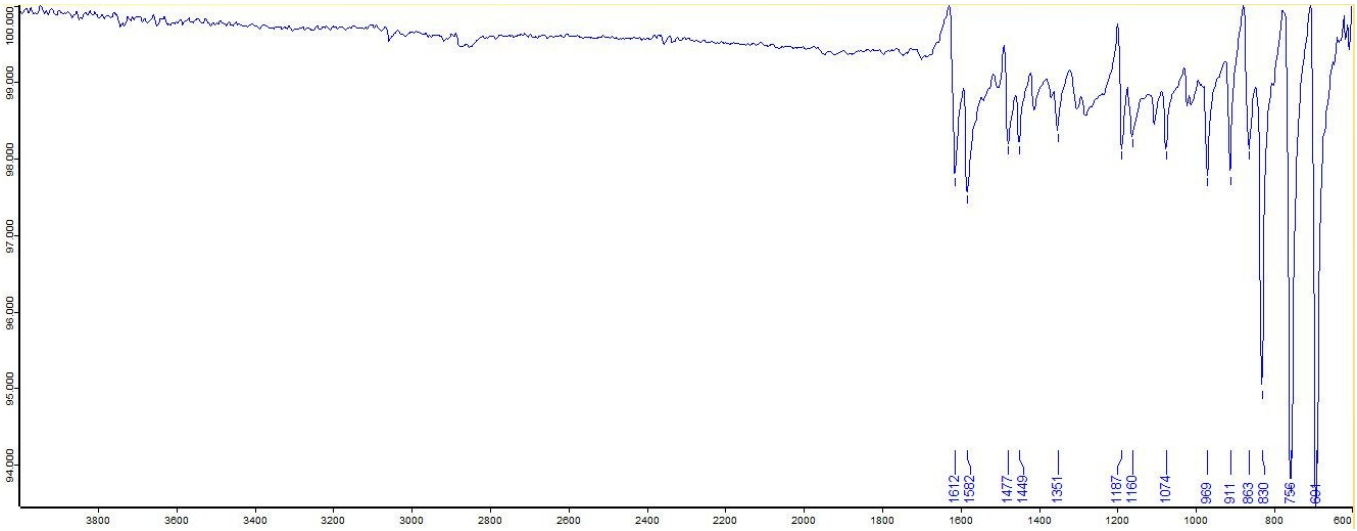


Figure: S4.a) FTIR of compound 1(stretching frequency of imine $\nu_{C=N}$ = 1612, 1582 cm^{-1}).

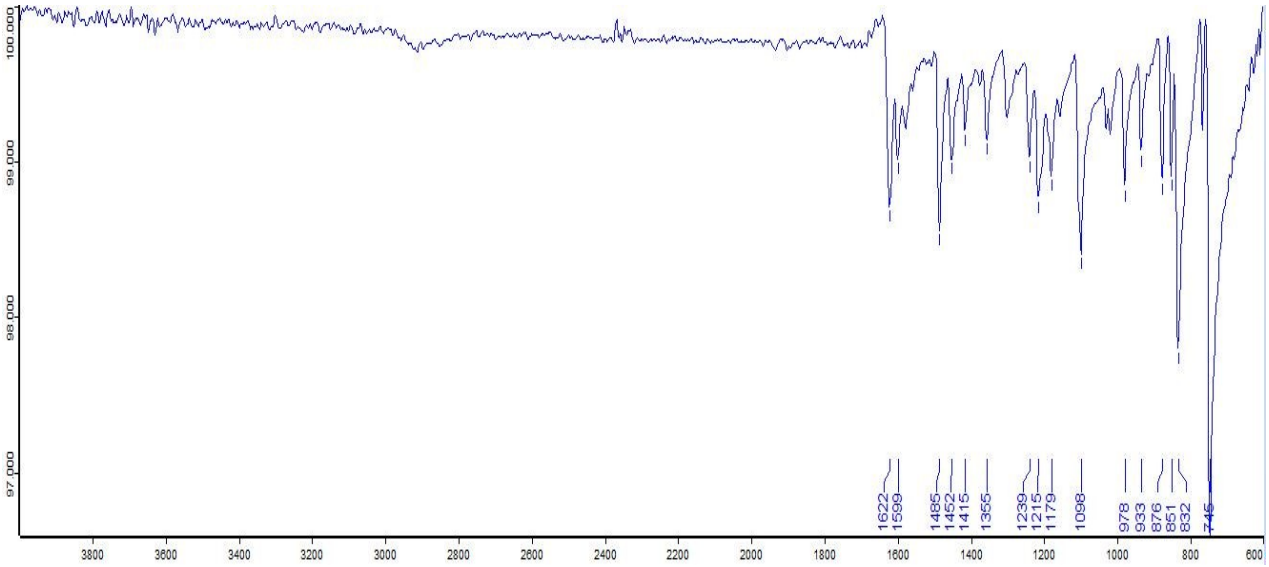


Figure: S4.b) FTIR of compound 2 (stretching frequency of imine $\nu_{C=N}$ = 1622, 1599 cm^{-1}).

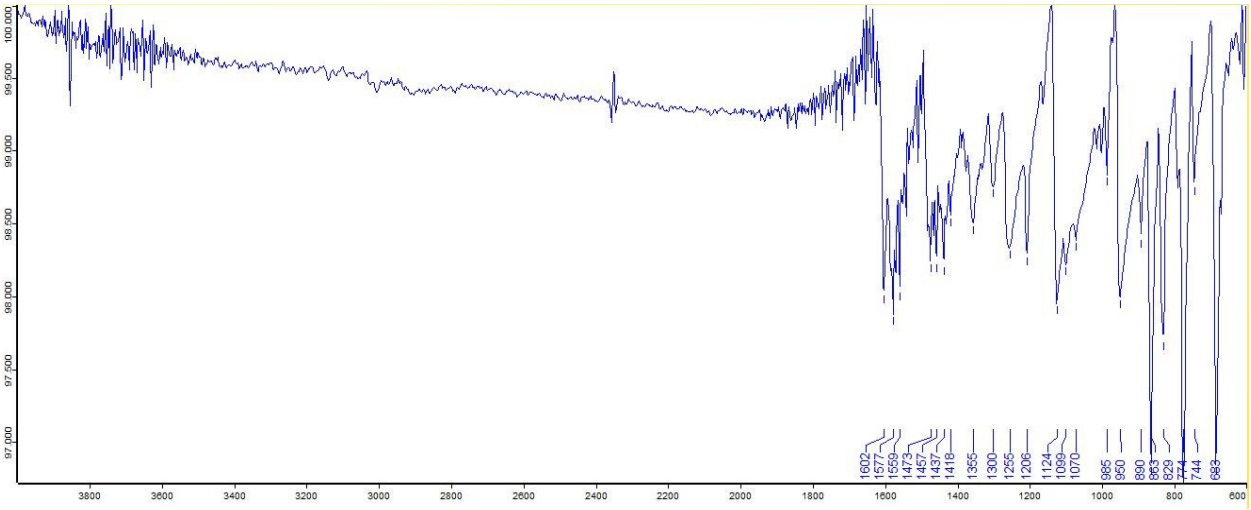


Figure: S4.c) FTIR of compound 3(stretching frequency of imine $\nu_{C=N}$ = 1602, 1577 cm^{-1}).

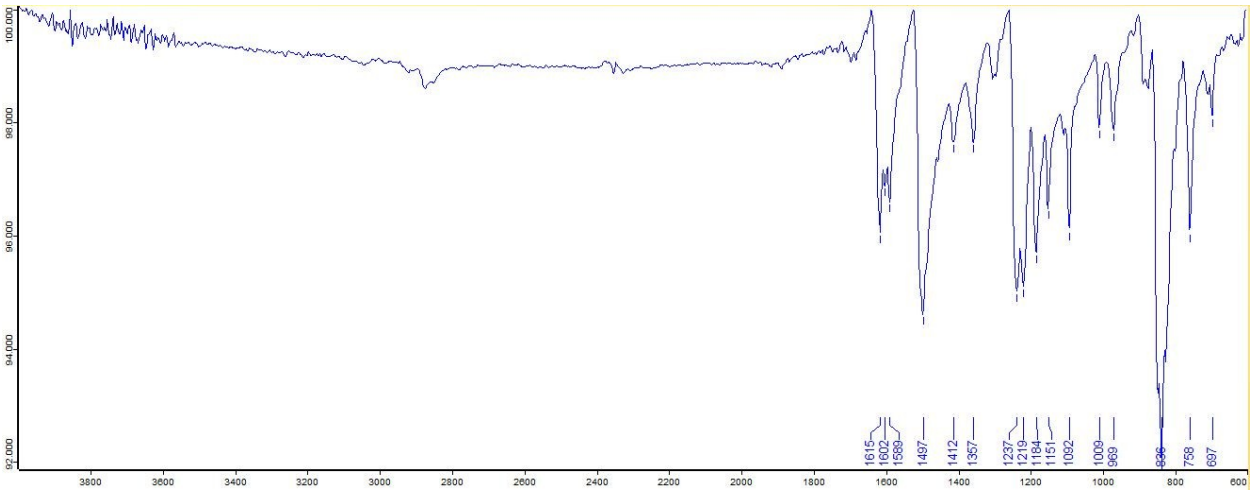


Figure: S4.d) FTIR of compound 4(stretching frequency of imine $\nu_{C=N}$ = 1615, 1589 cm^{-1}).

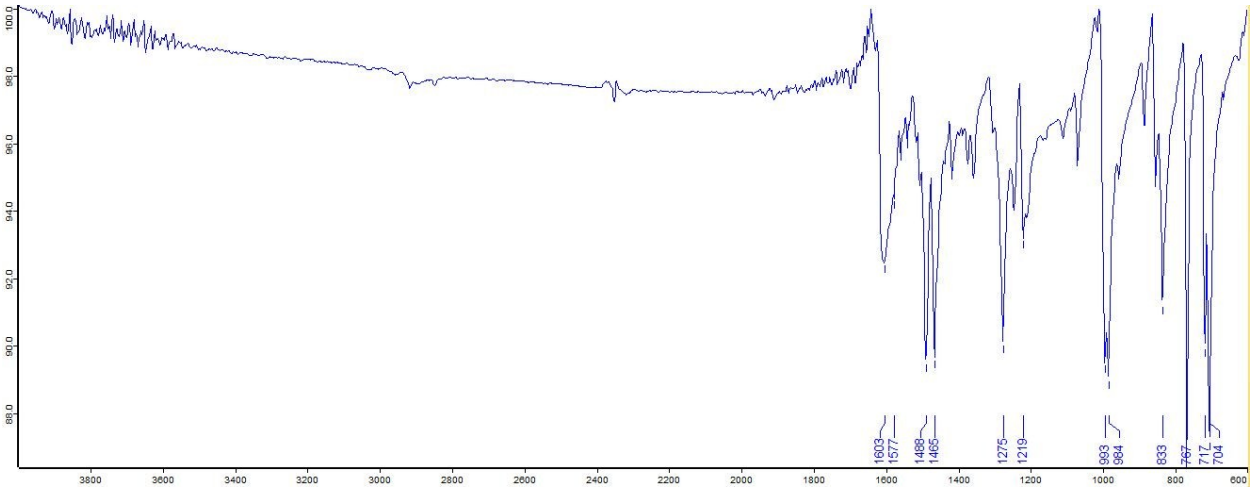


Figure: S4.e) FTIR of compound 5(stretching frequency of imine $\nu_{C=N}$ = 1603, 1577 cm^{-1}).

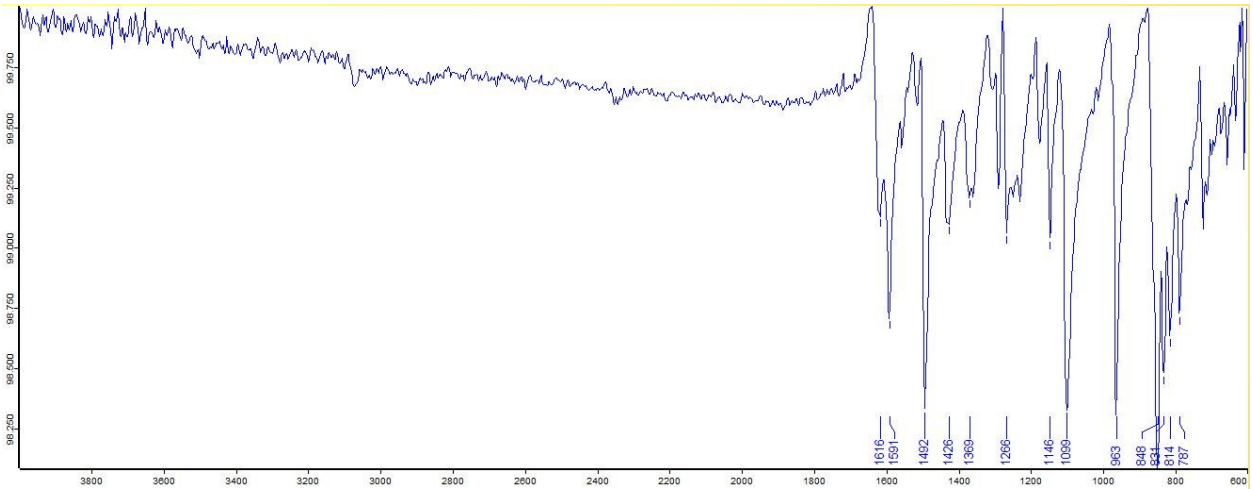


Figure: S4.f) FTIR of compound 6 (stretching frequency of imine $\nu_{C=N}$ = 1616, 1591 cm^{-1}).

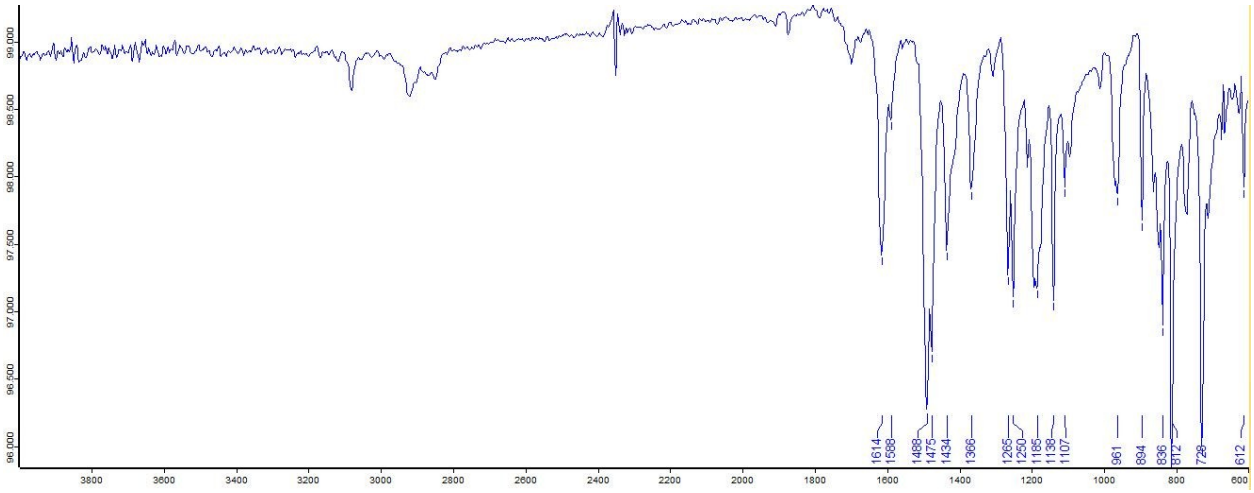


Figure: S4.g) FTIR of compound 7(stretching frequency of imine $\nu_{C=N}$ = 1614, 1588 cm^{-1}).

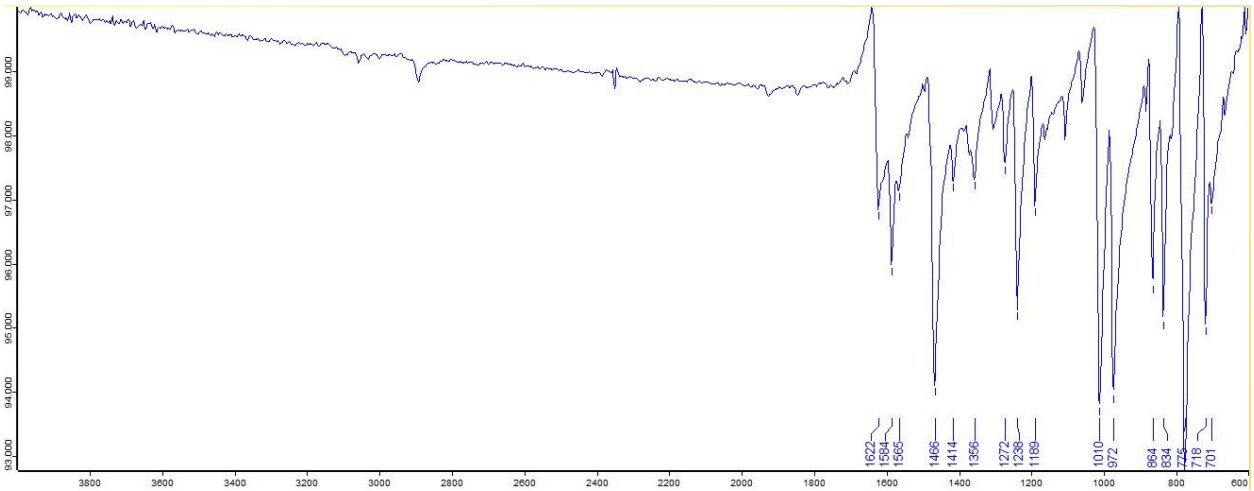


Figure: S4.h)FTIR of compound 8(stretching frequency of imine $\nu_{C=N}$ = 1622, 1584 cm^{-1}).

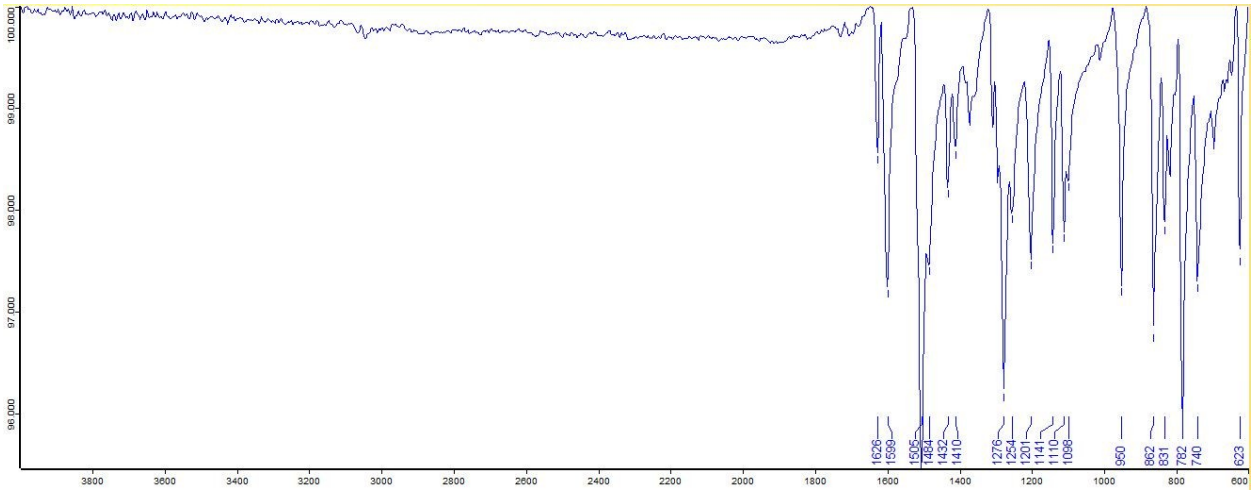


Figure: S4.i) FTIR of compound 9(stretching frequency of imine $\nu_{C=N}$ = 1626, 1599 cm^{-1}).

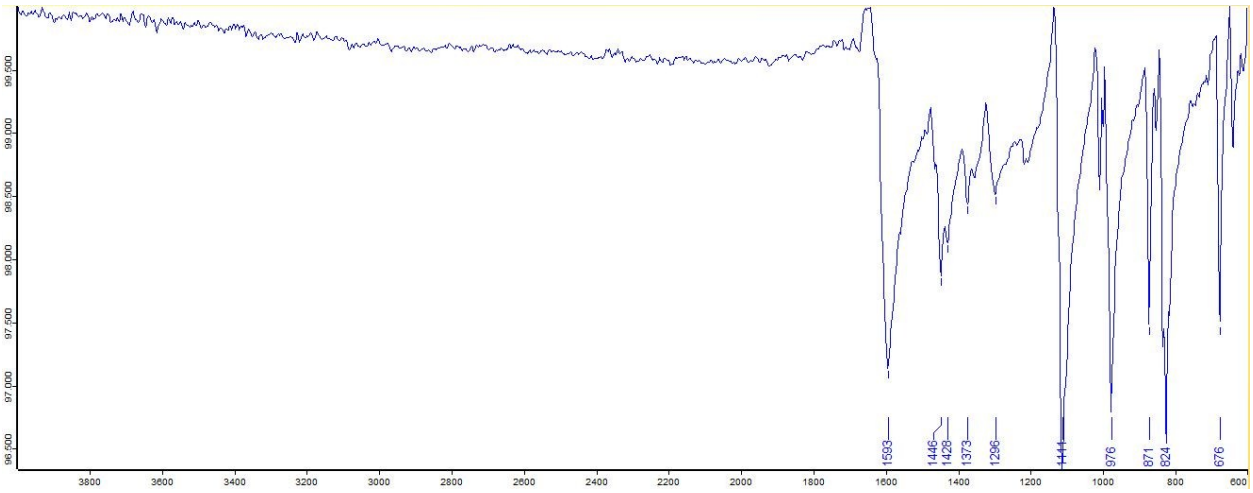


Figure: S4.j) FTIR of compound 10 (stretching frequency of imine $\nu_{C=N}$ =1593 cm^{-1}).

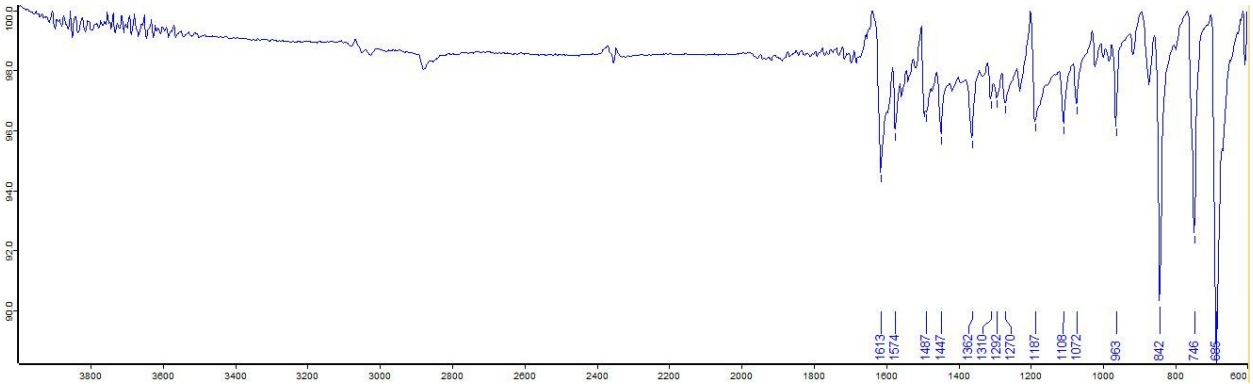


Figure: S4.k) FTIR of compound 11(stretching frequency of imine $\nu_{C=N}$ = 1613, 1574 cm^{-1}).

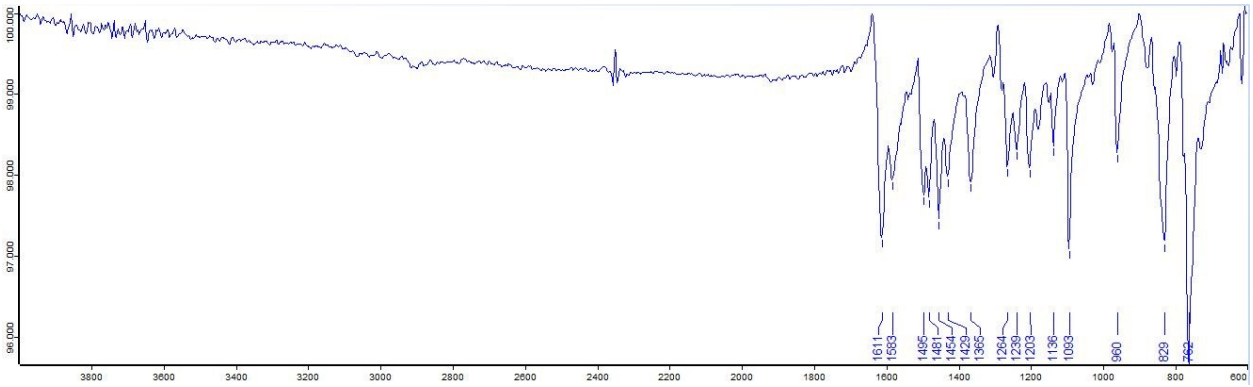


Figure: S4.l) FTIR of compound 12 (stretching frequency of imine $\nu_{C=N}$ = 1611, 1583 cm^{-1}).

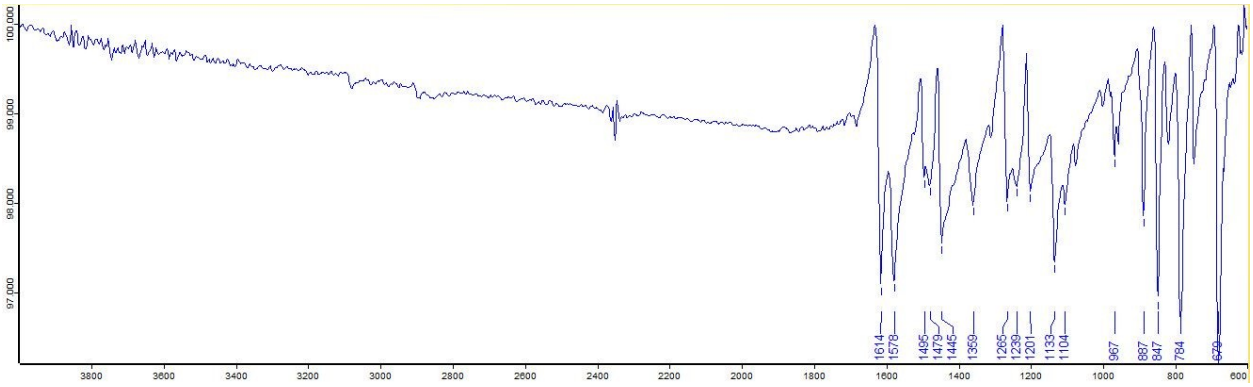


Figure: S4.m) FTIR of compound 13 (stretching frequency of imine $\nu_{C=N}$ = 1614, 1578 cm^{-1}).

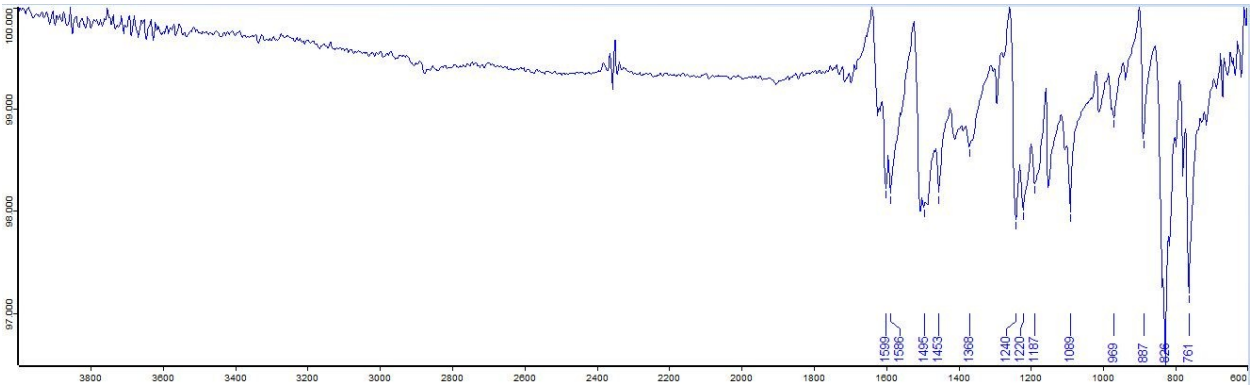


Figure: S4.n) FTIR of compound 14 (stretching frequency of imine $\nu_{C=N}$ = 1599, 1596 cm^{-1}).

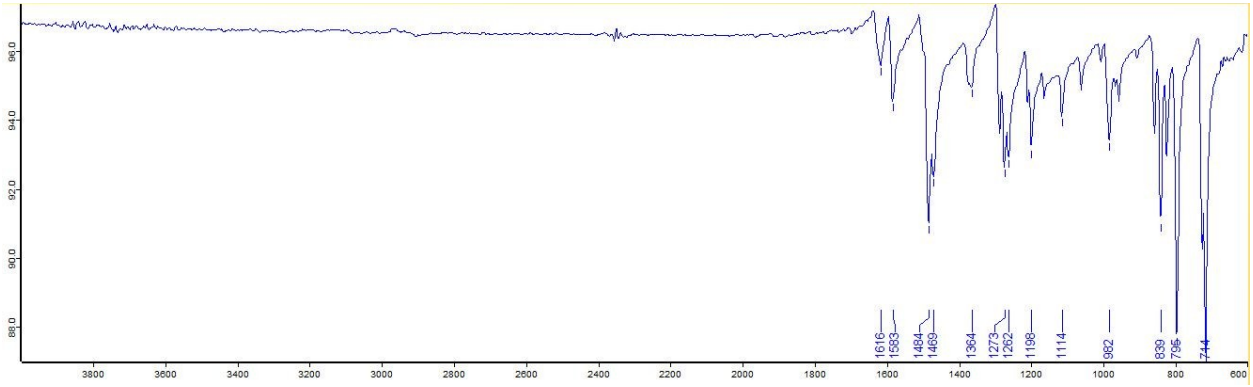


Figure: S4.o) FTIR of compound 15(stretching frequency of imine $\nu_{C=N}$ = 1616, 1583 cm^{-1}).

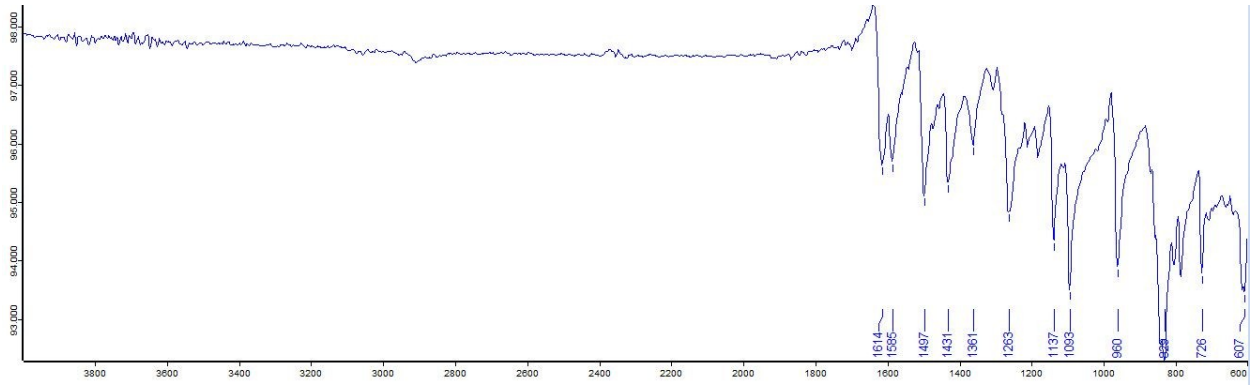


Figure: S4.p) FTIR of compound 16 (stretching frequency of imine $\nu_{C=N}$ = 1614, 1585 cm^{-1}).

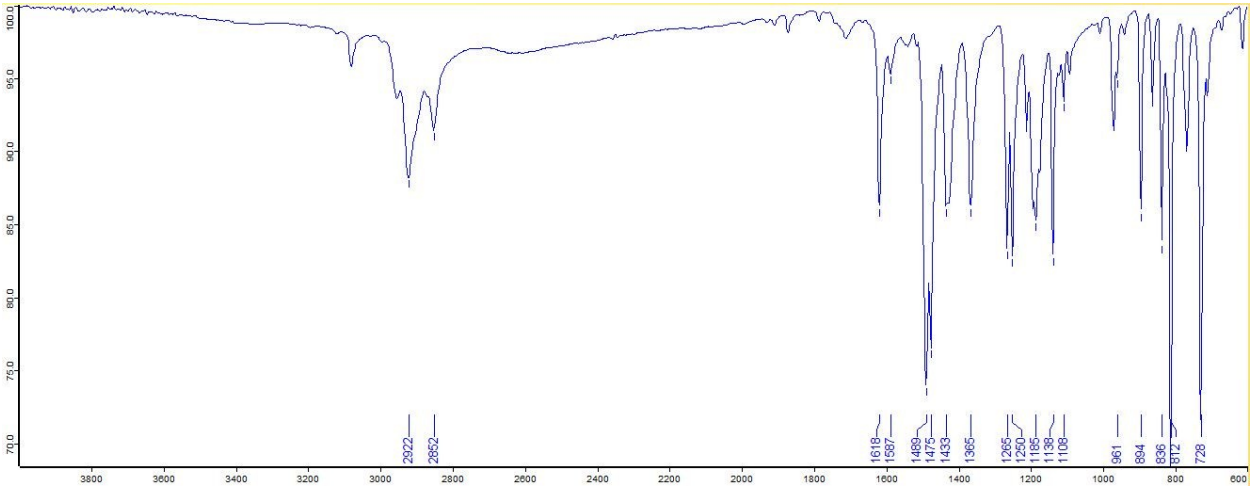


Figure: S4.q) FTIR of compound 17 (stretching frequency of imine $\nu_{C=N}$ = 1618, 1587 cm^{-1}).

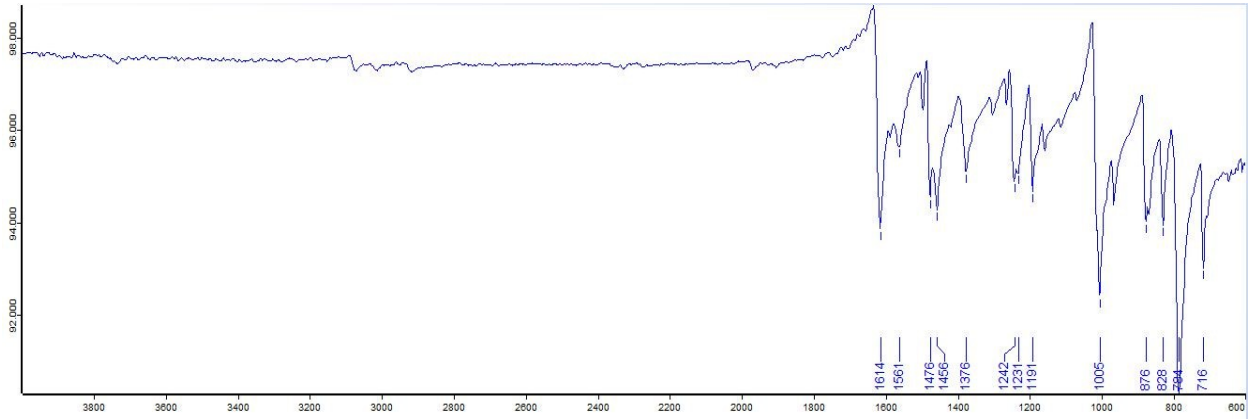


Figure: S4.r) FTIR of compound 18 (stretching frequency of imine $\nu_{C=N}$ = 1614, 1561 cm^{-1}).

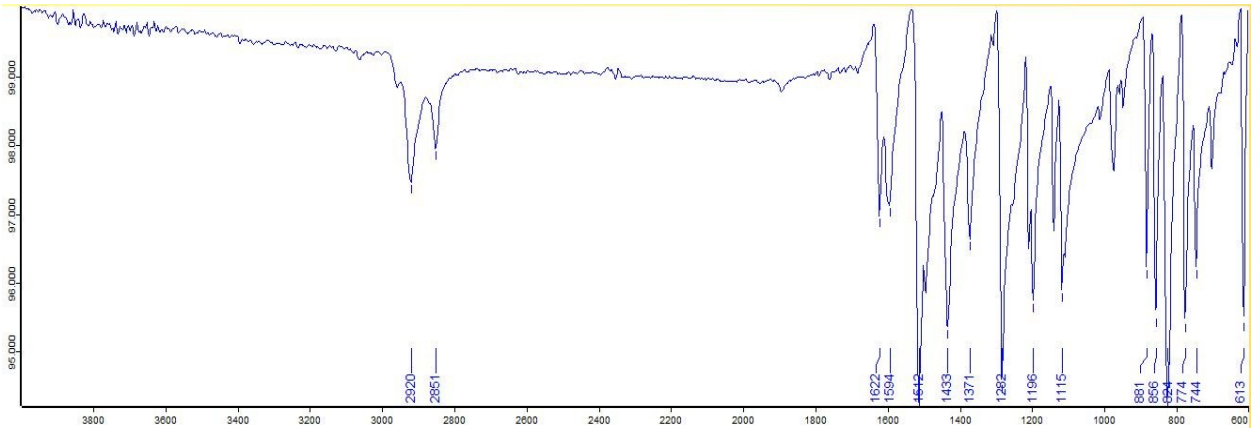


Figure: S4.s) FTIR of compound 19 (stretching frequency of imine $\nu_{C=N}$ = 1622, 1594 cm^{-1}).

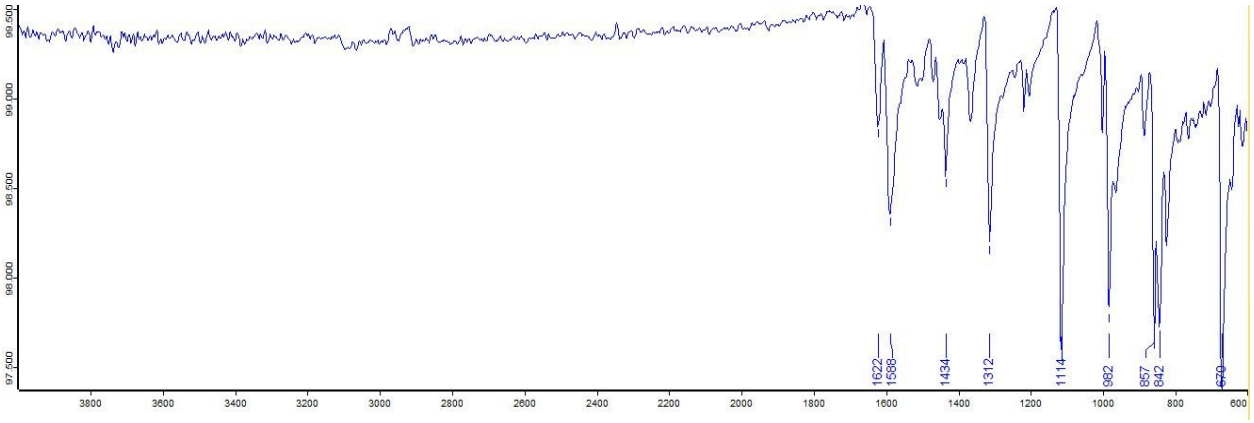


Figure: S4.t) FTIR of compound 20 (stretching frequency of imine $\nu_{C=N}$ = 1622, 1588 cm^{-1}).

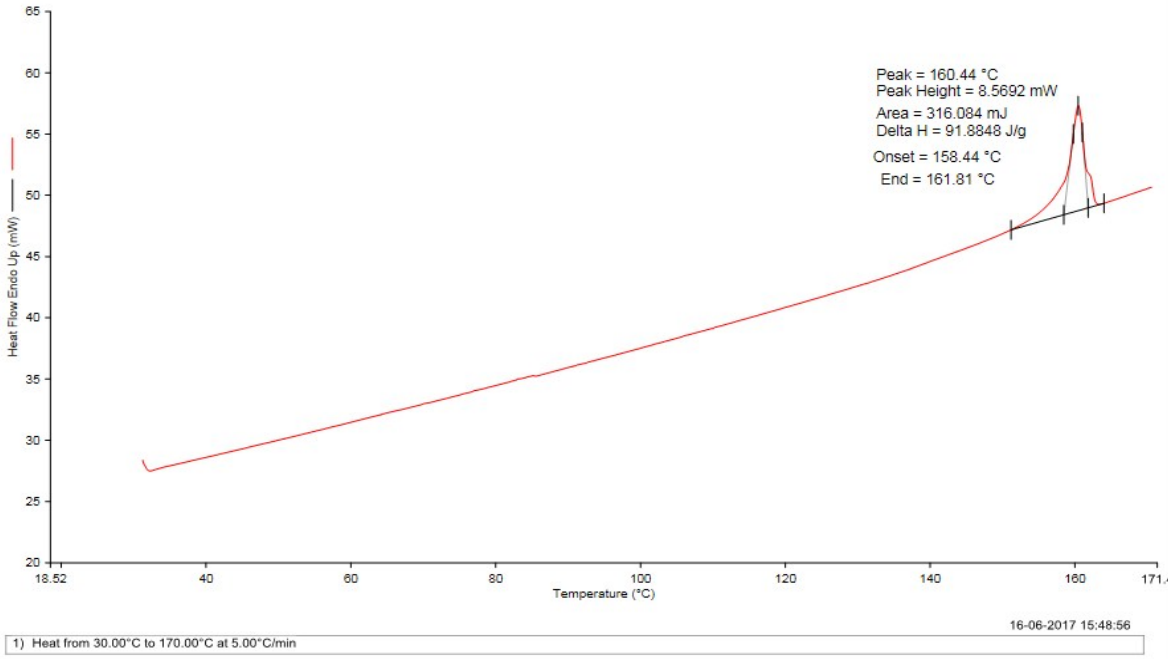


Figure: S5.a) DSC of compound 1.

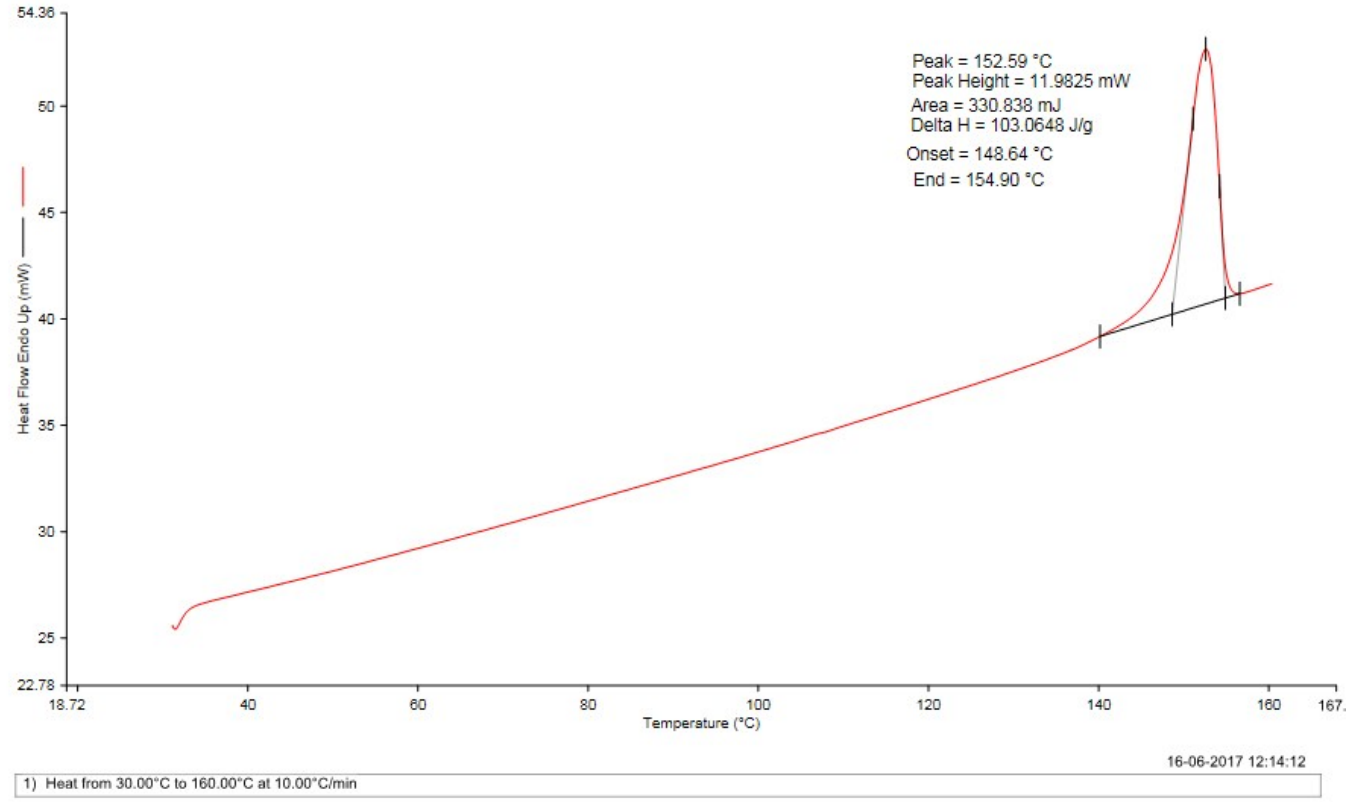


Figure: S5.b) DSC of compound 2.

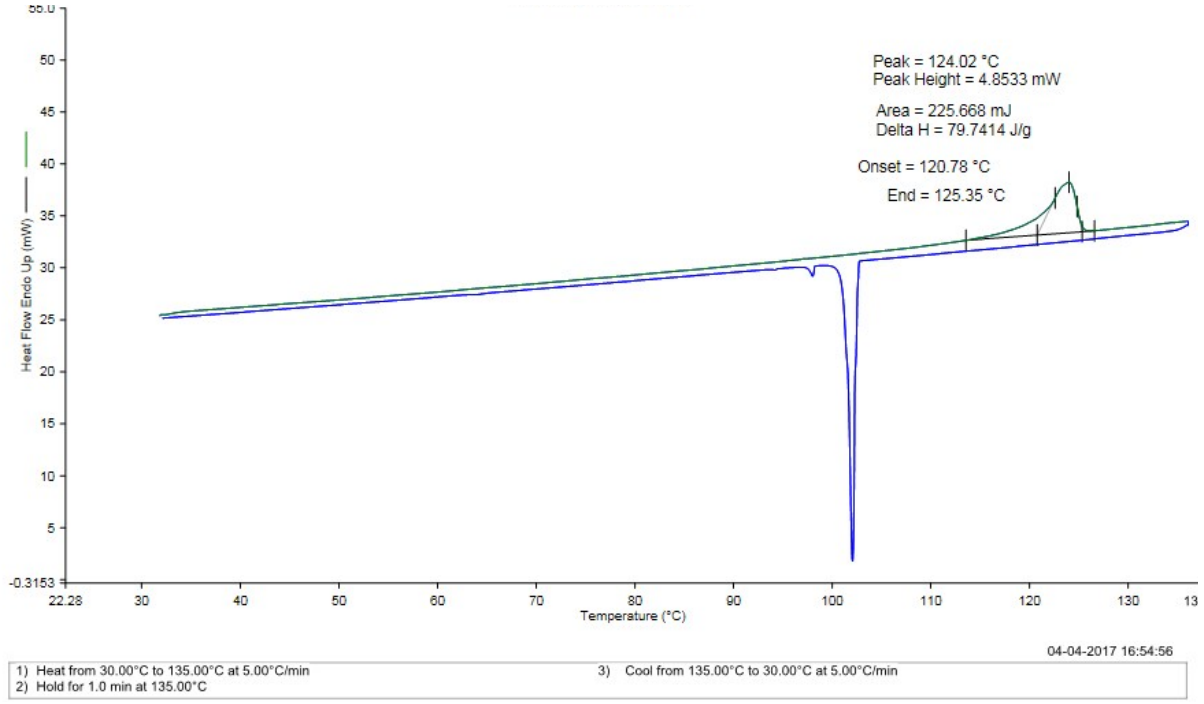


Figure: S5.c) DSC of compound 3.

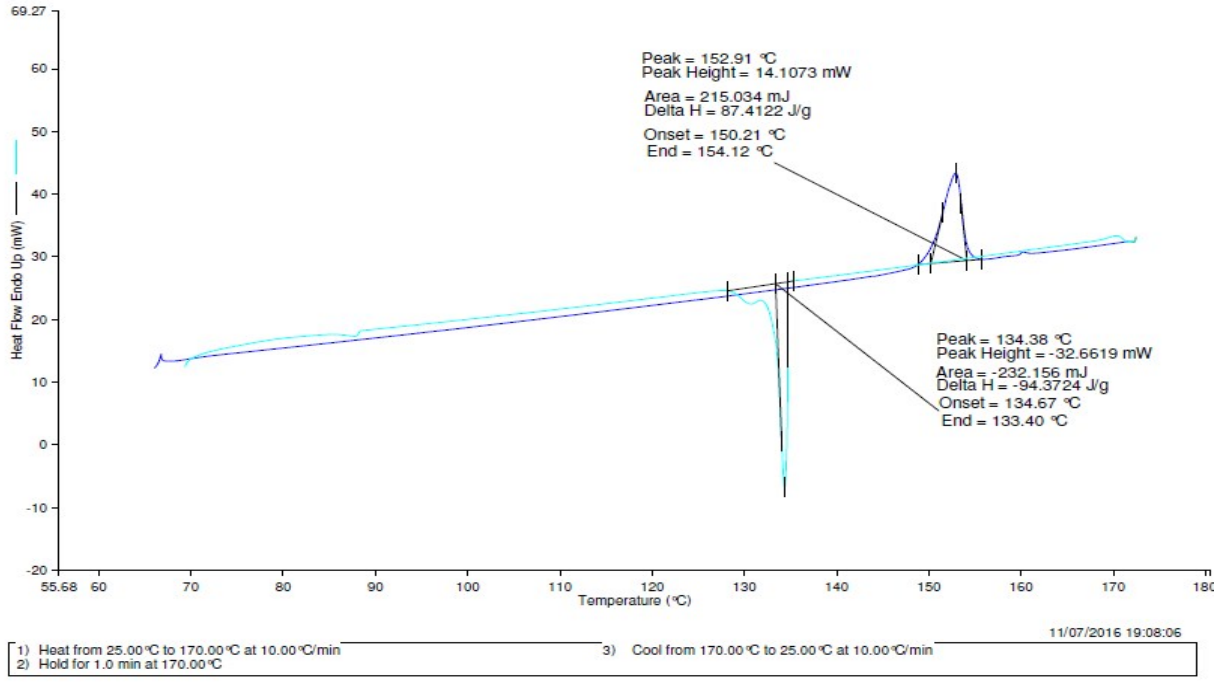


Figure: S5.d) DSC of compound 4

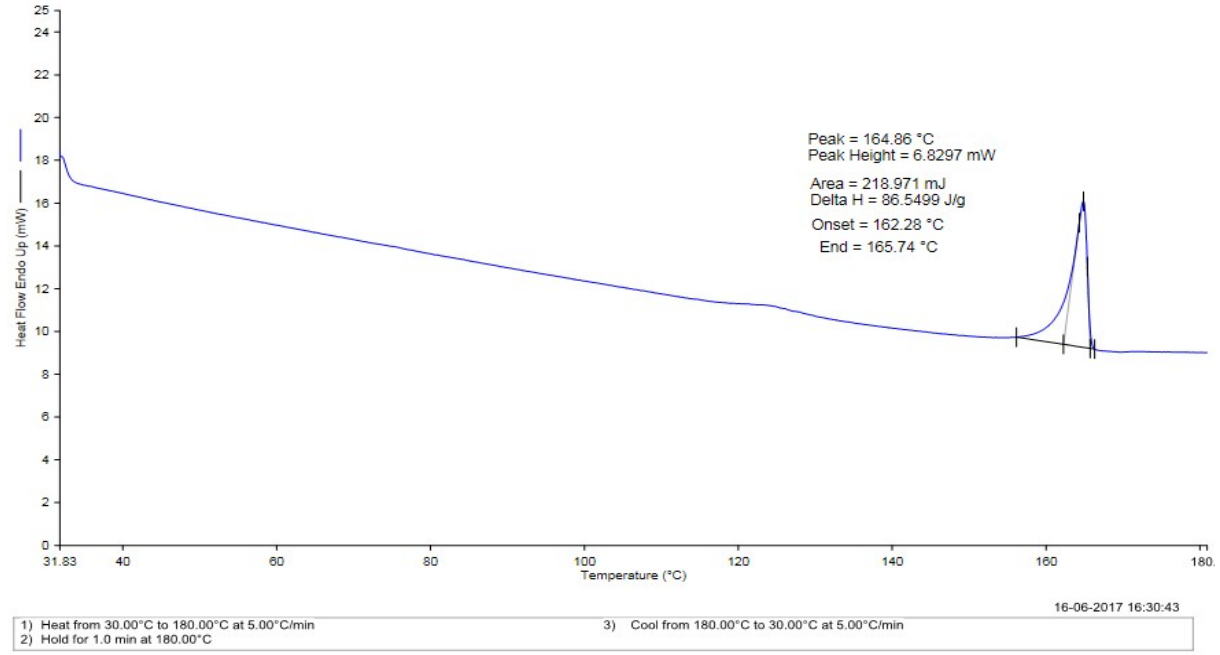


Figure: S5.e) DSC of compound 5.

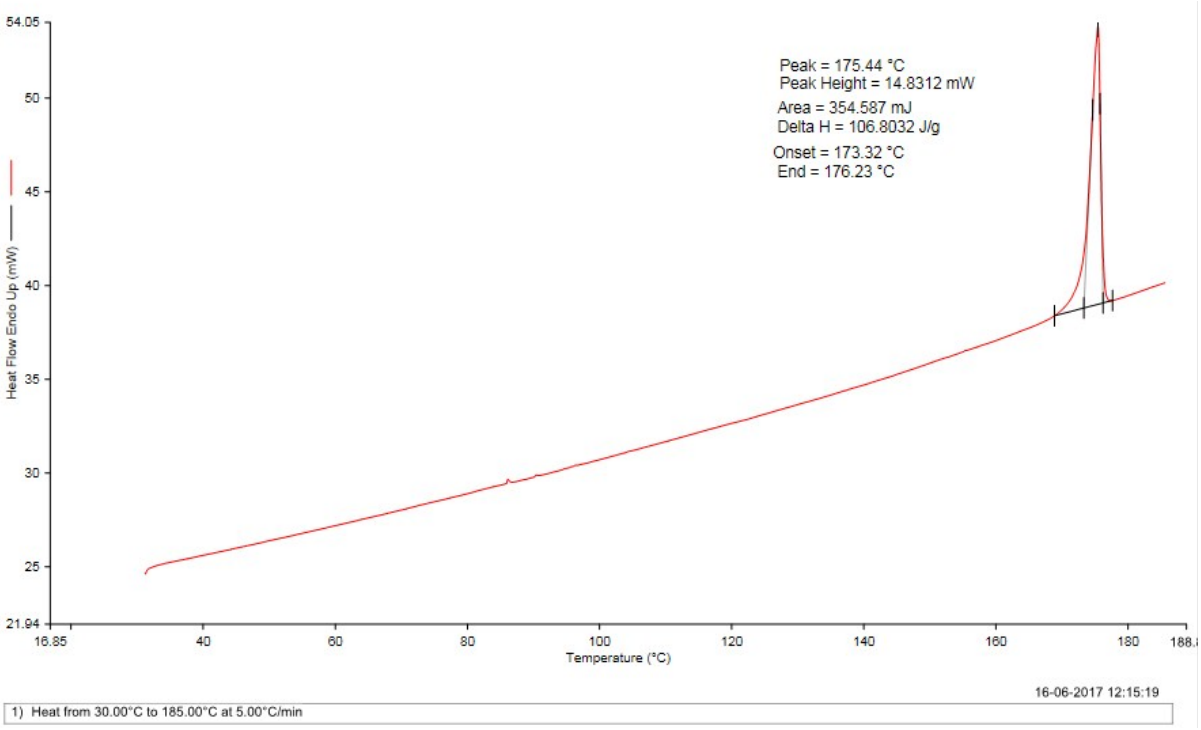


Figure: S5.f) DSC of compound 6

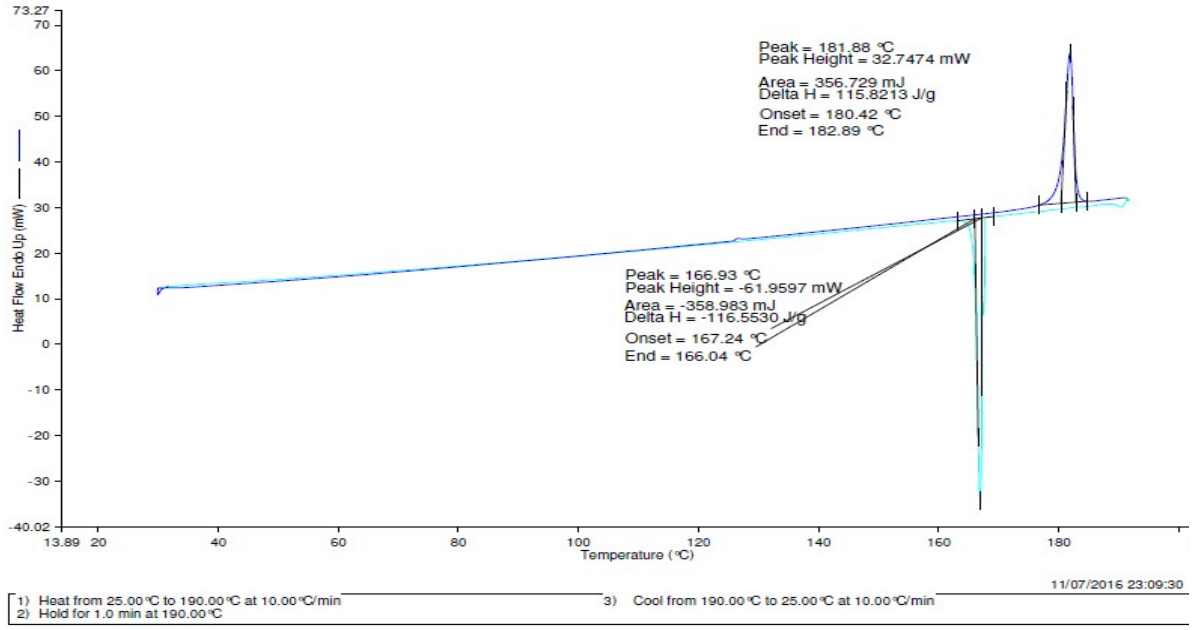


Figure: S5.g) DSC of compound 7.

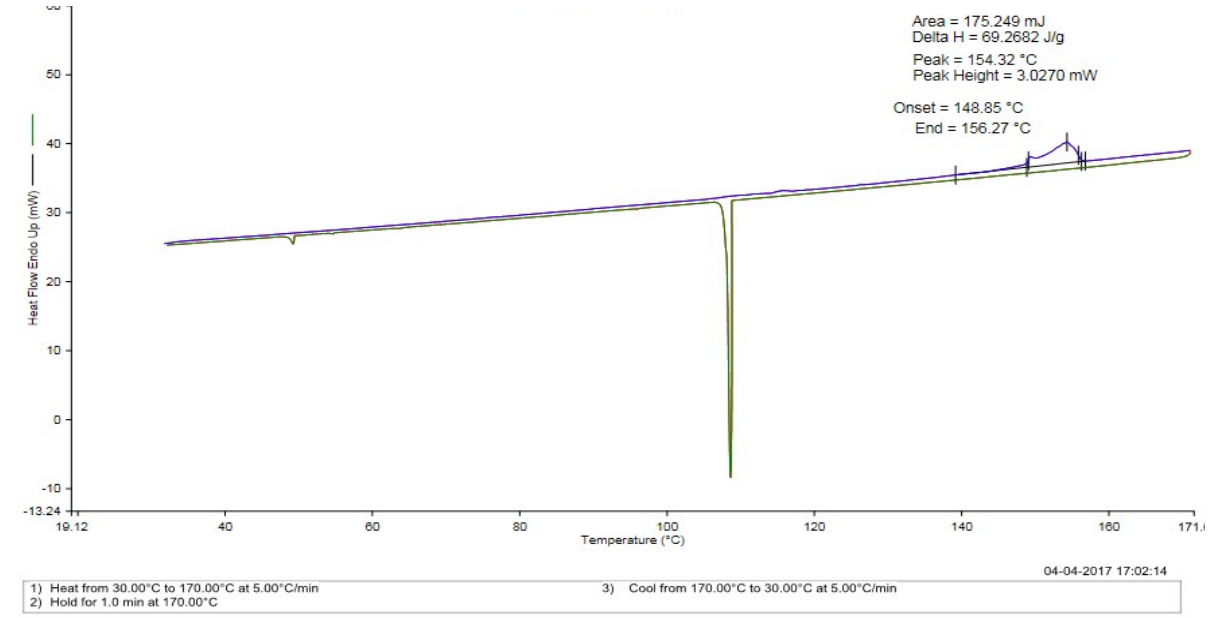


Figure: S5.h) DSC of compound 8.

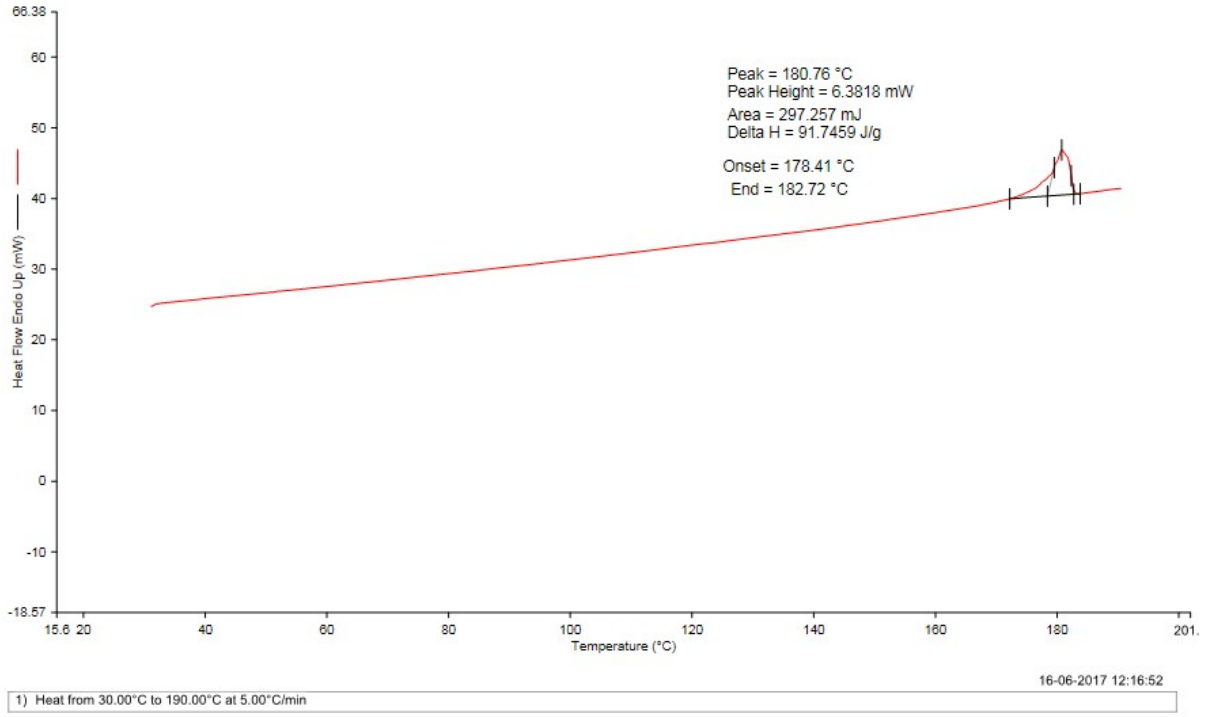


Figure: S5.i) DSC of compound 9.

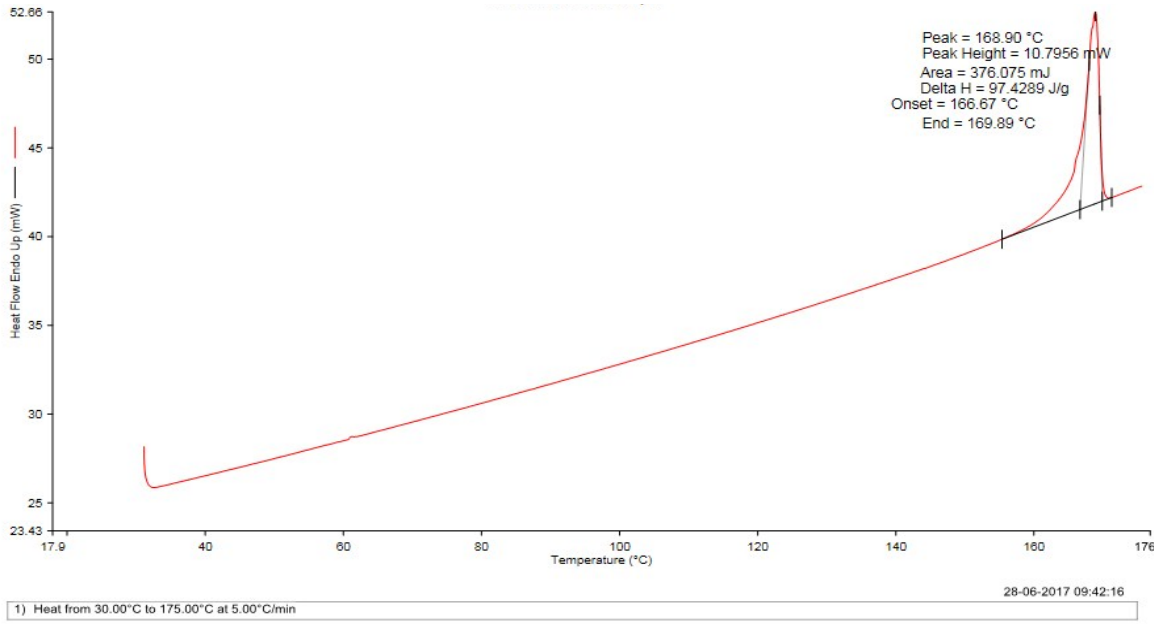


Figure: S5.j) DSC of compound 10.

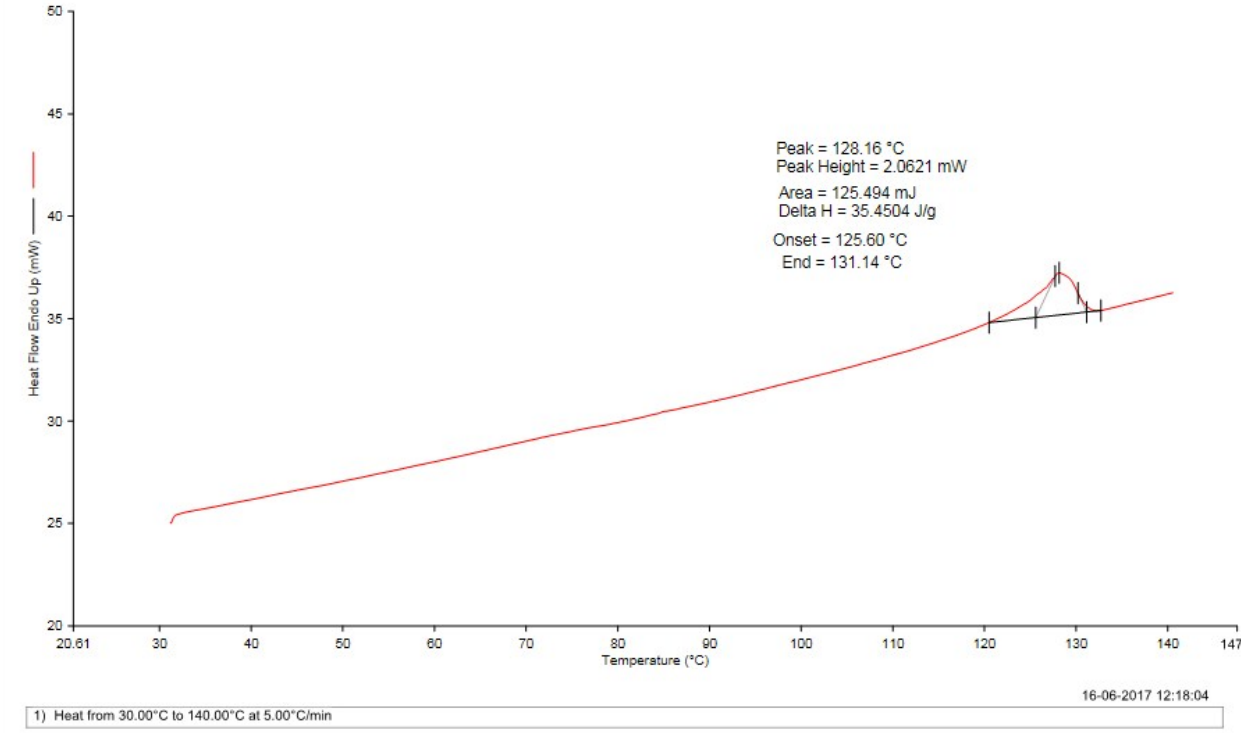


Figure: S5.k) DSC of compound 11.

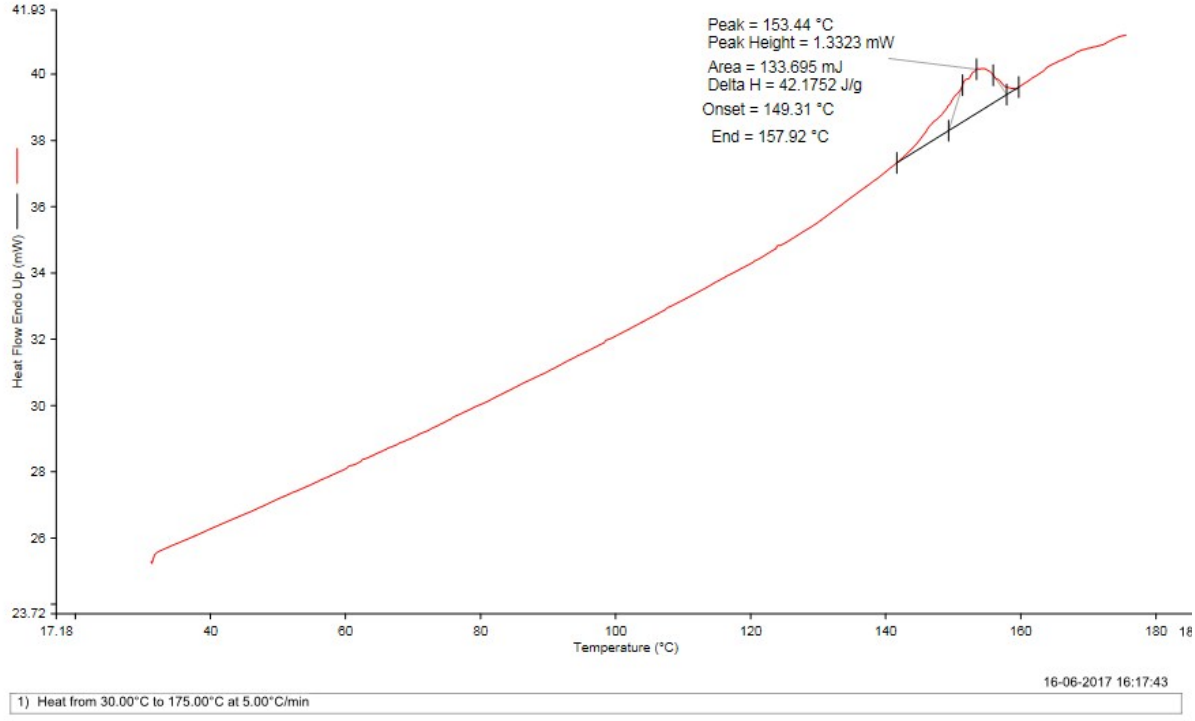


Figure: S5.l) DSC of compound 12.

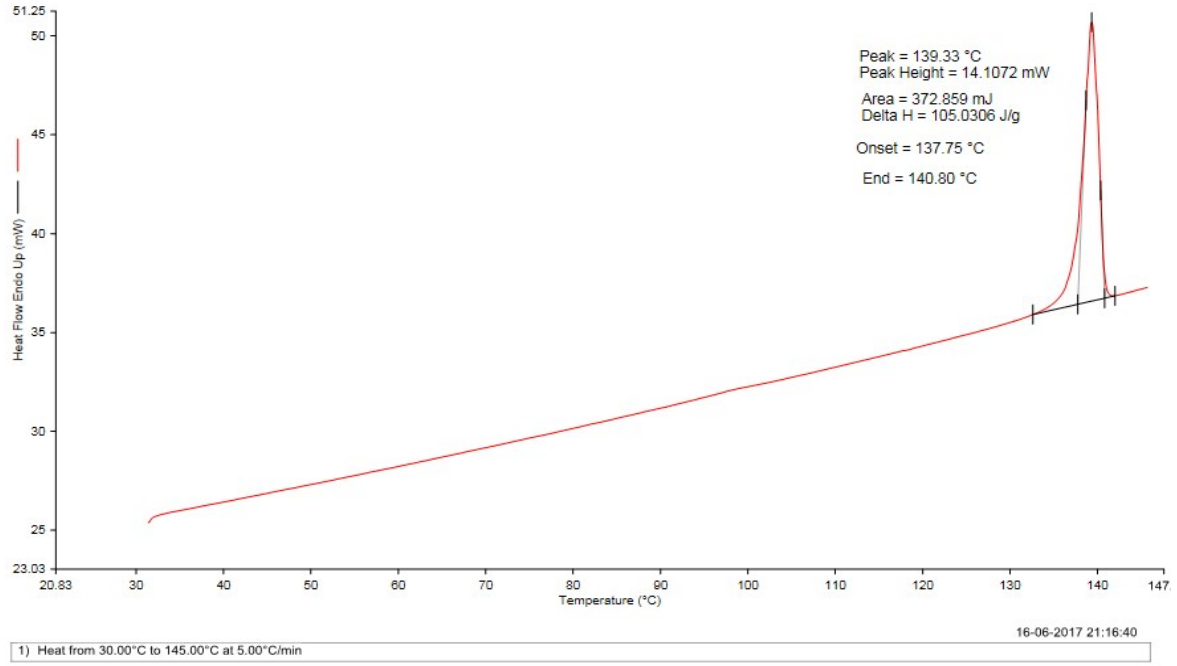


Figure: S5.m) DSC of compound 13.

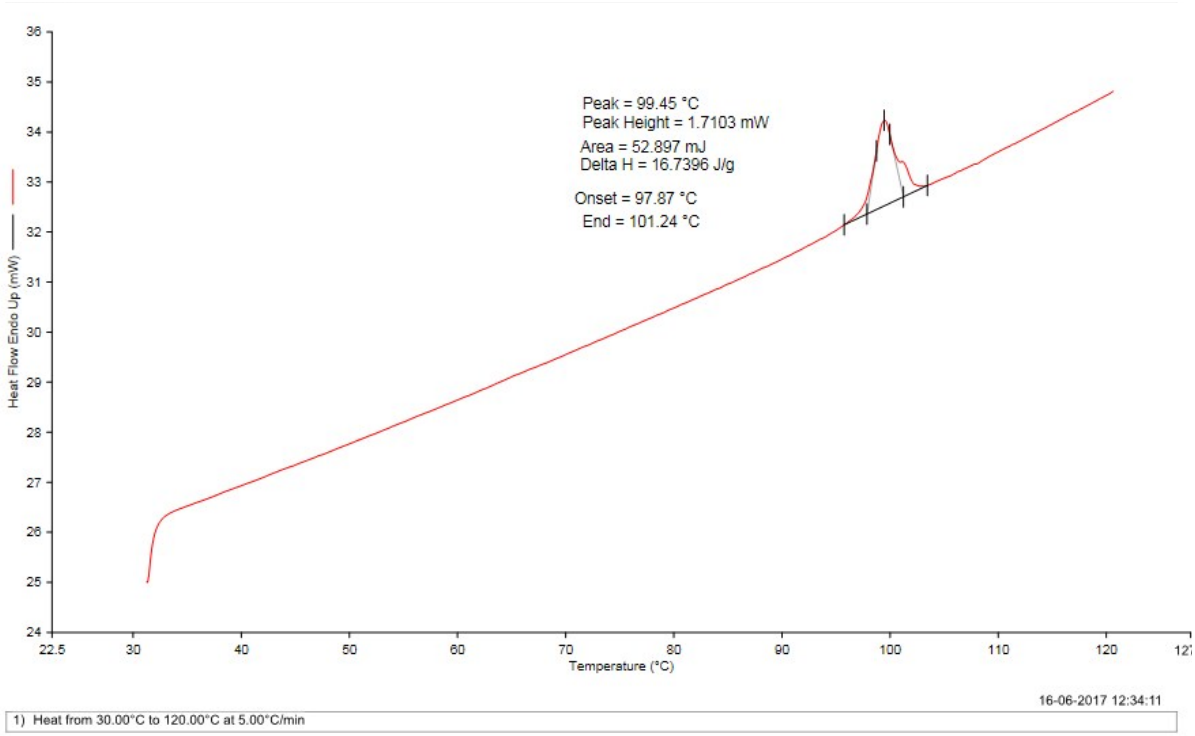


Figure: S5.n) DSC of compound 14.

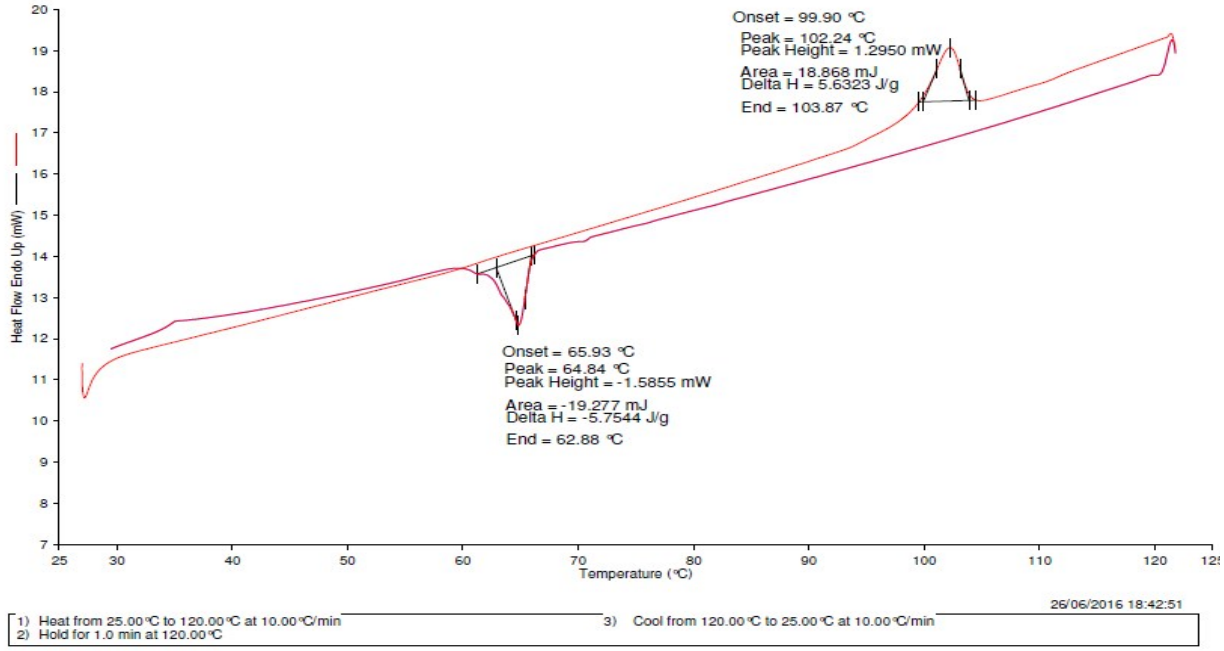


Figure: S5.o) DSC of compound 15.

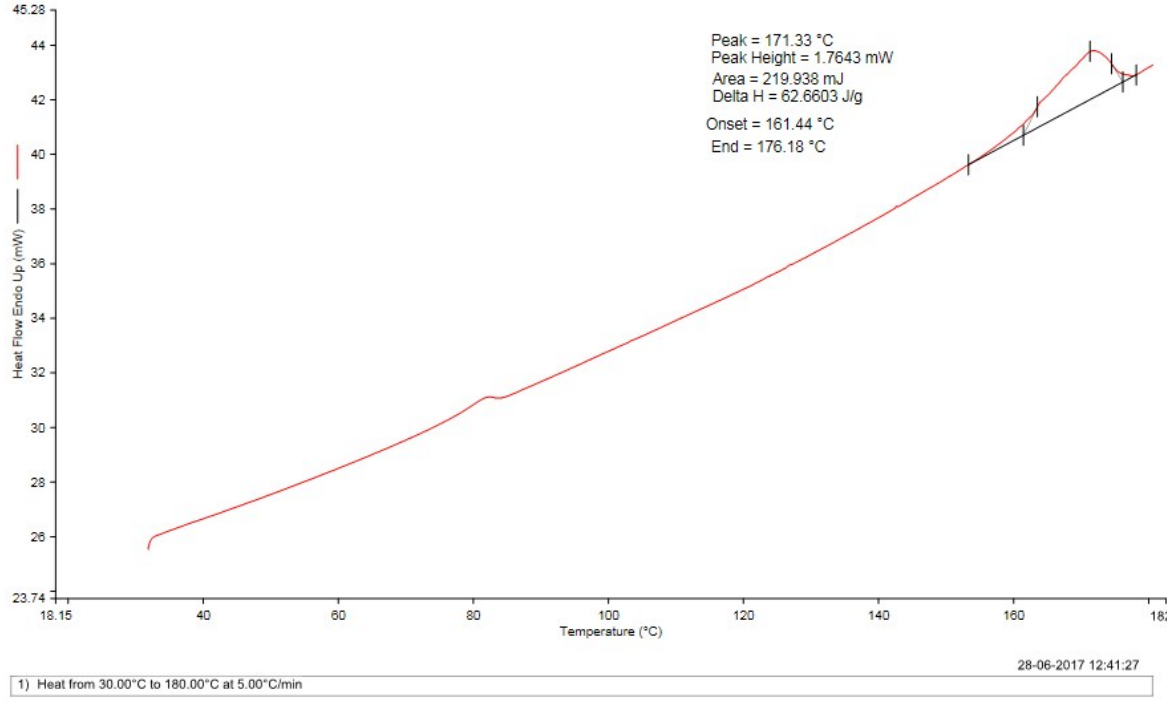


Figure: S5.p) DSC of compound 16.

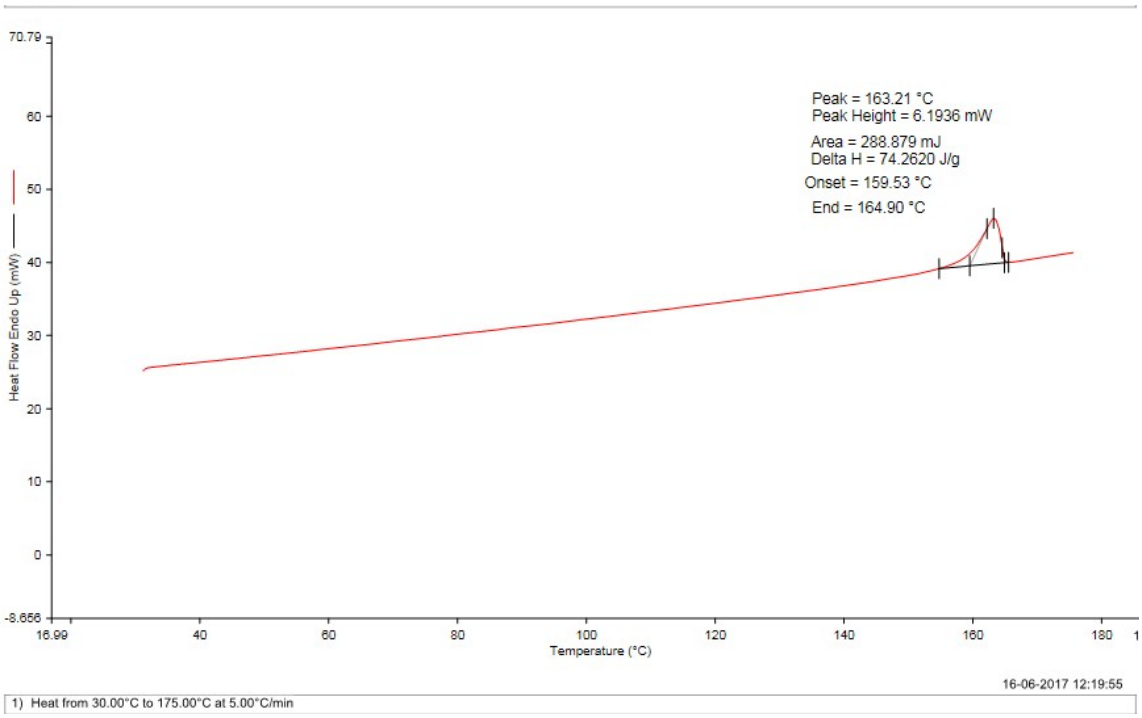


Figure: S5.q) DSC of compound 17.

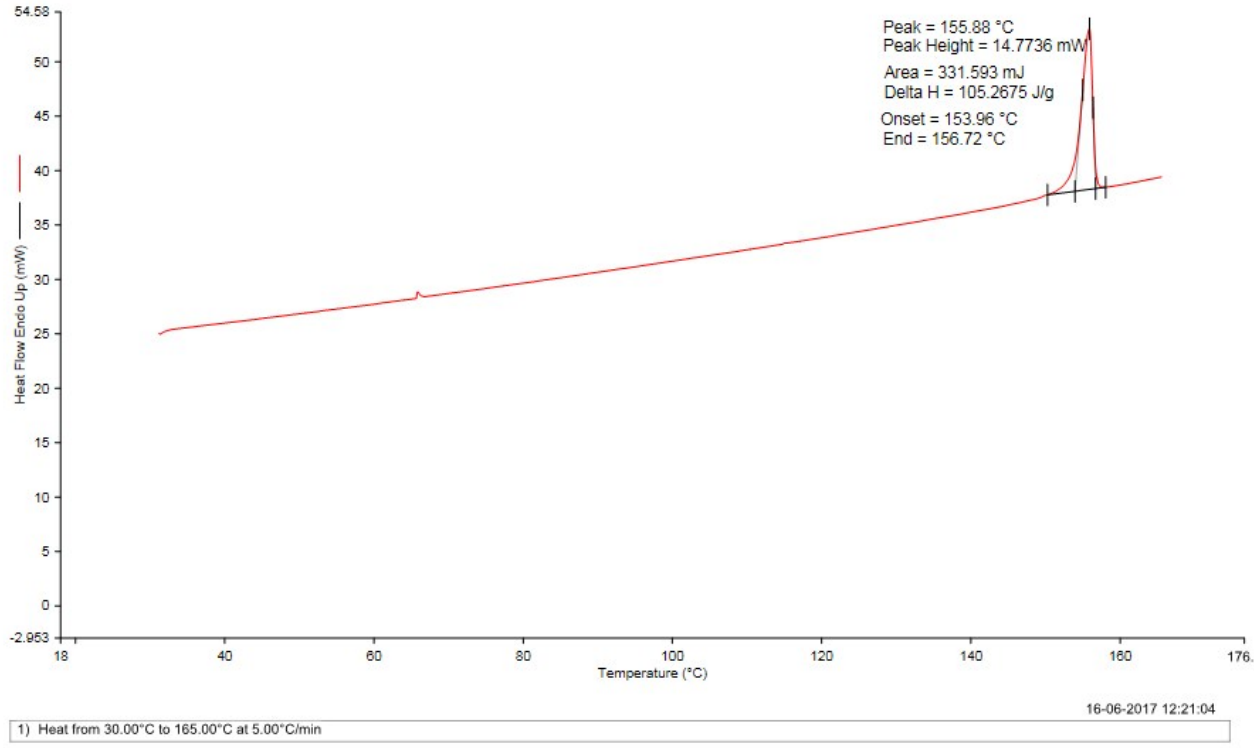


Figure: S5.r) DSC of compound 18.

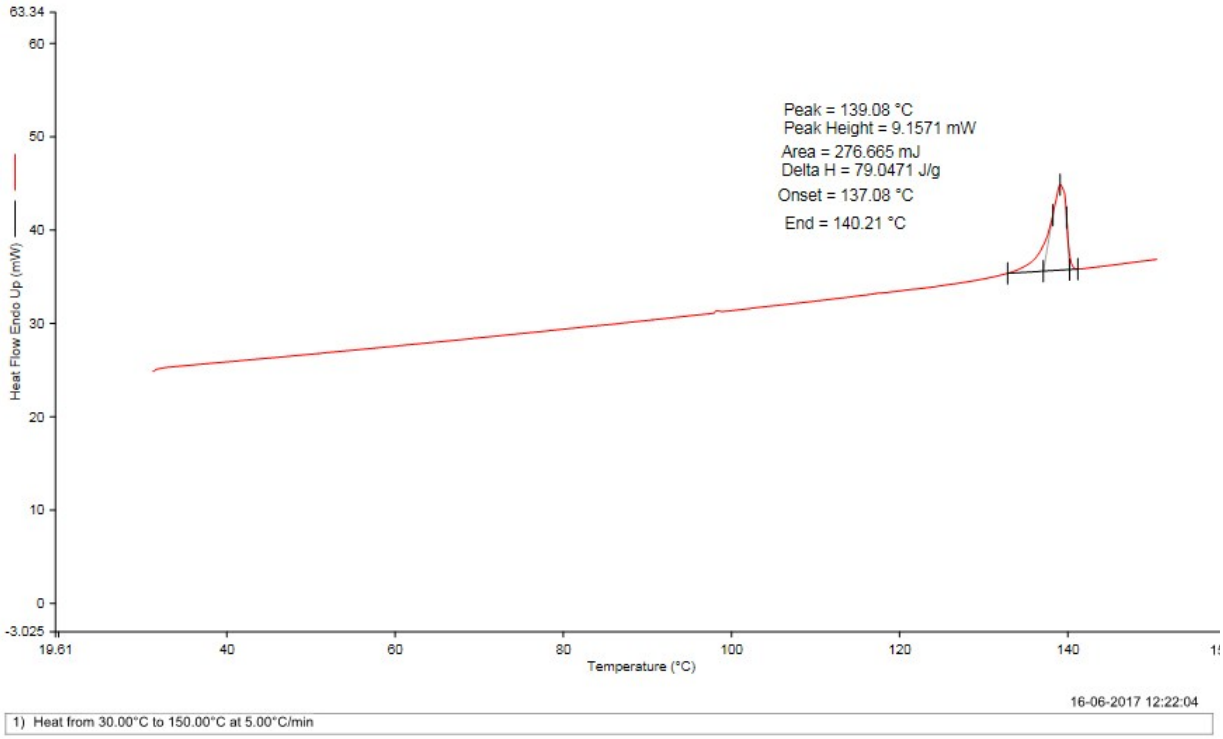


Figure: S5.s) DSC of compound 19.

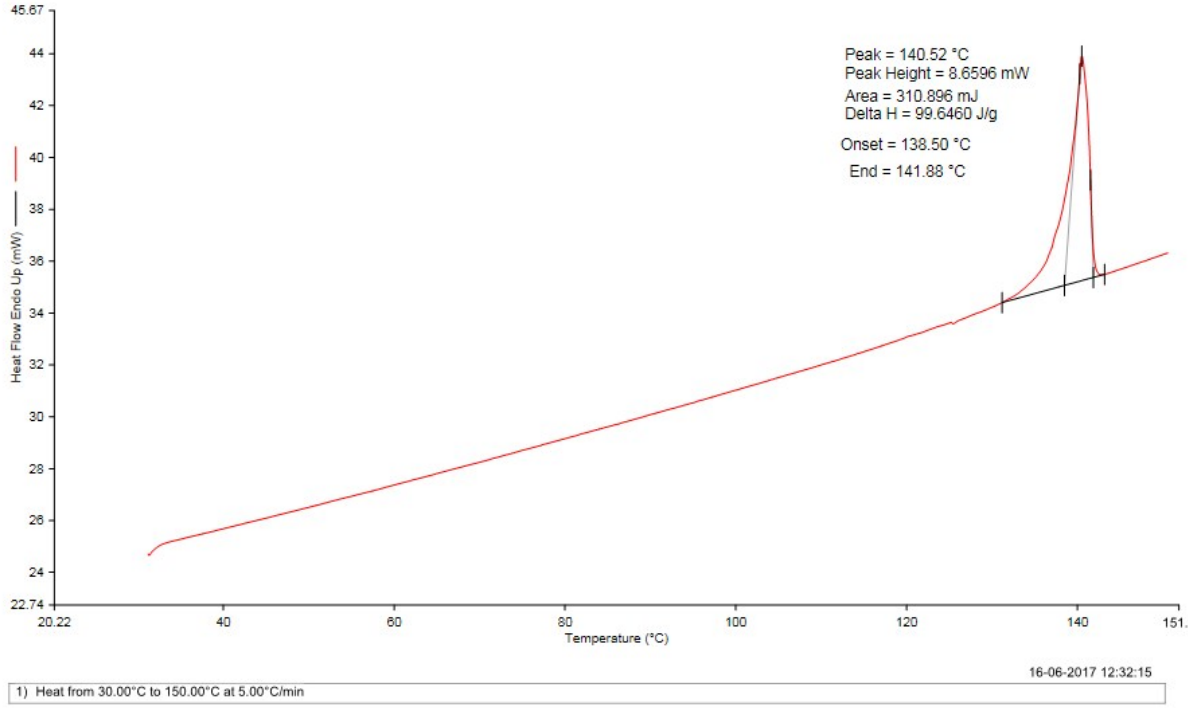


Figure: S5.t) DSC of compound 20.

Table 2: Melting Points of all the Compounds Synthesized

:

Compound No.	Melting range(^{o}C)	Enthalpy of melting(J/g)
1.	158-161	91.88
2.	148-154	103.06
3.	120-125	79.7
4.	150-154	87.4
5.	162-165	93.4
6.	173-176	106.60
7.	180-182	115.8
8.	148-156	69.3
9.	178-182	91.74
10.	166-169	97.43
11.	125-131	35.45
12.	149-157	42.17
13.	137-140	105.03
14.	97-101	16.74
15.	99-103	5.63
16.	161-176	62.7
17.	159-164	74.26
18.	153-156	105.26
19.	137-140	79.05
20.	138-141	99.65

NOTE: Following are the PXRD plots the bulk material (blue) and the simulated pattern (red) from the single crystal X–ray data

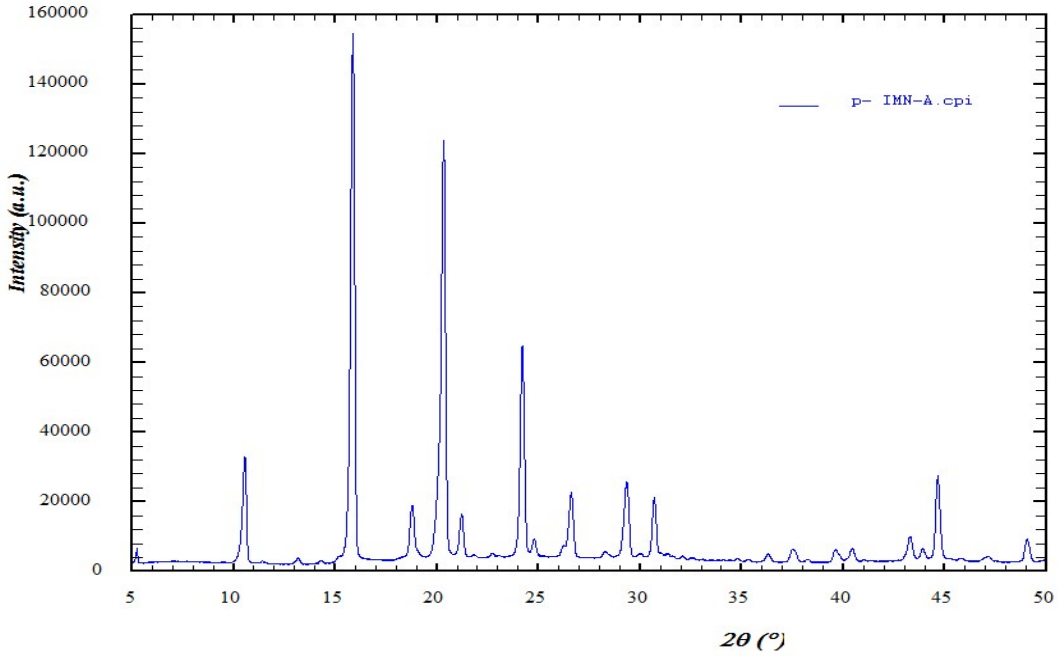


Figure: S6.a) PXRD of compound 1.

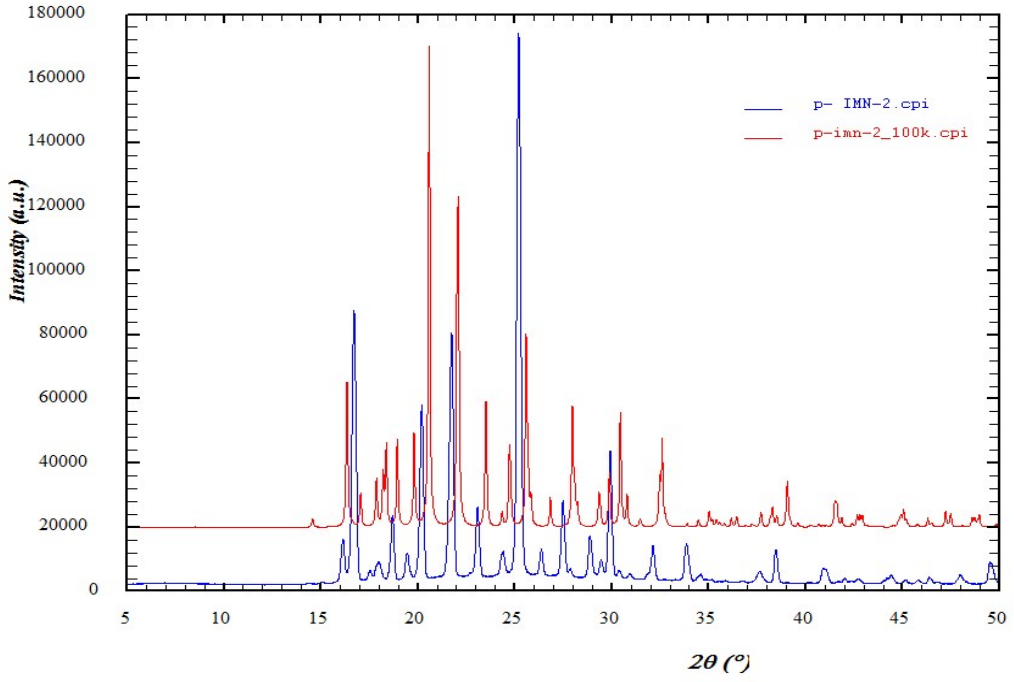


Figure: S6.b) PXRD of compound 2.

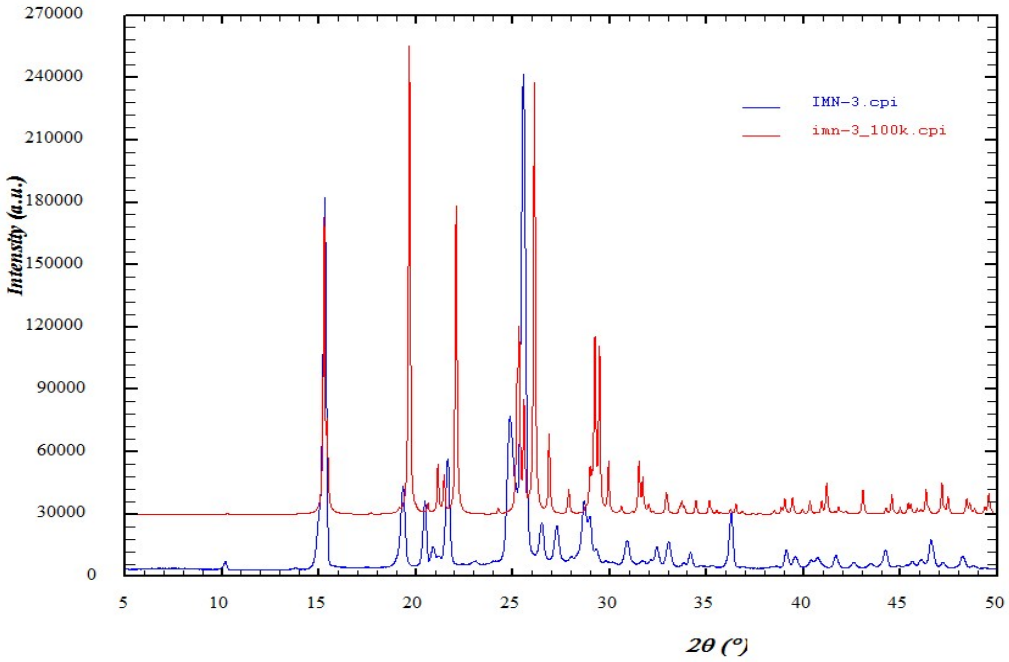


Figure: S6.c) PXRD of compound 3.

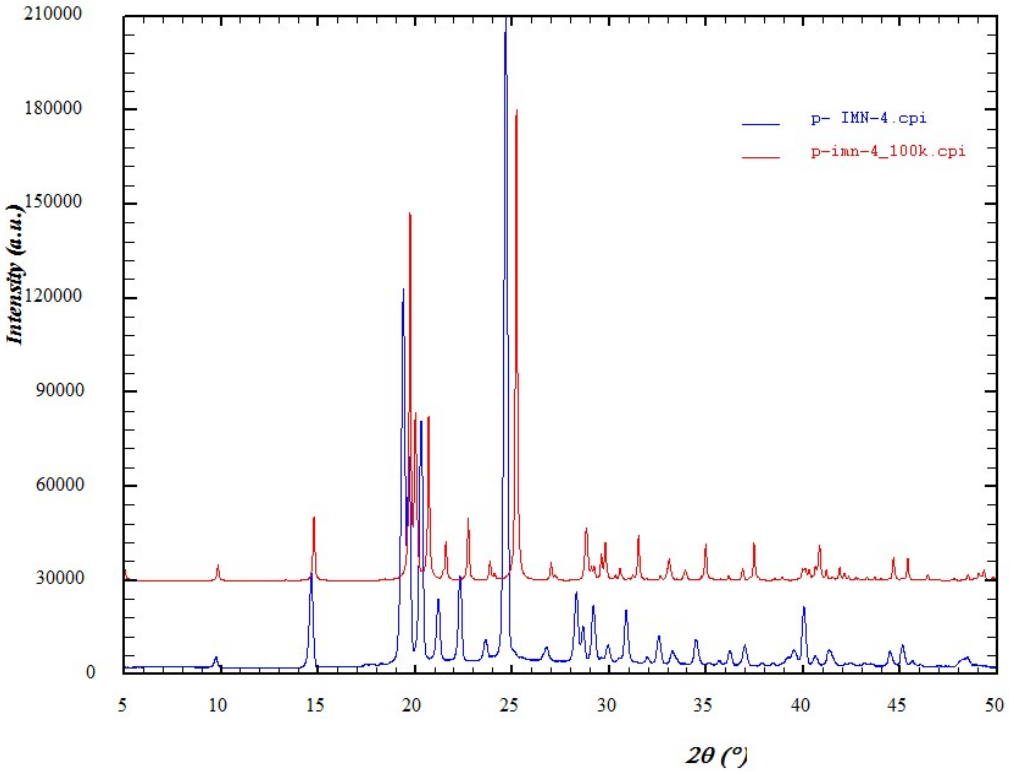


Figure: S6.d) PXRD of compound 4.

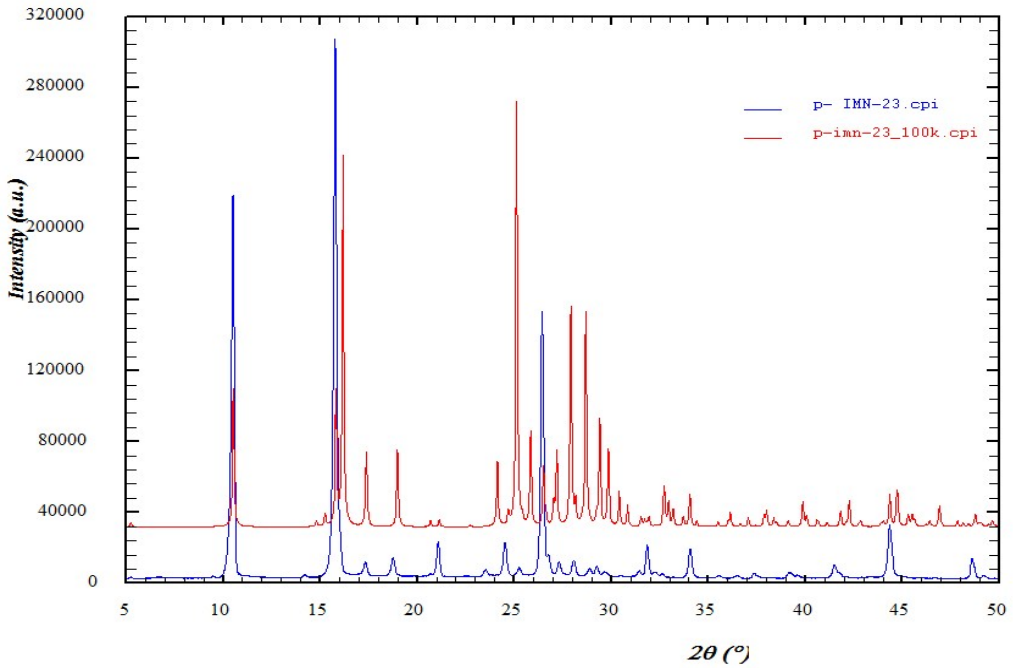


Figure: S6.e) PXRD of compound 5.

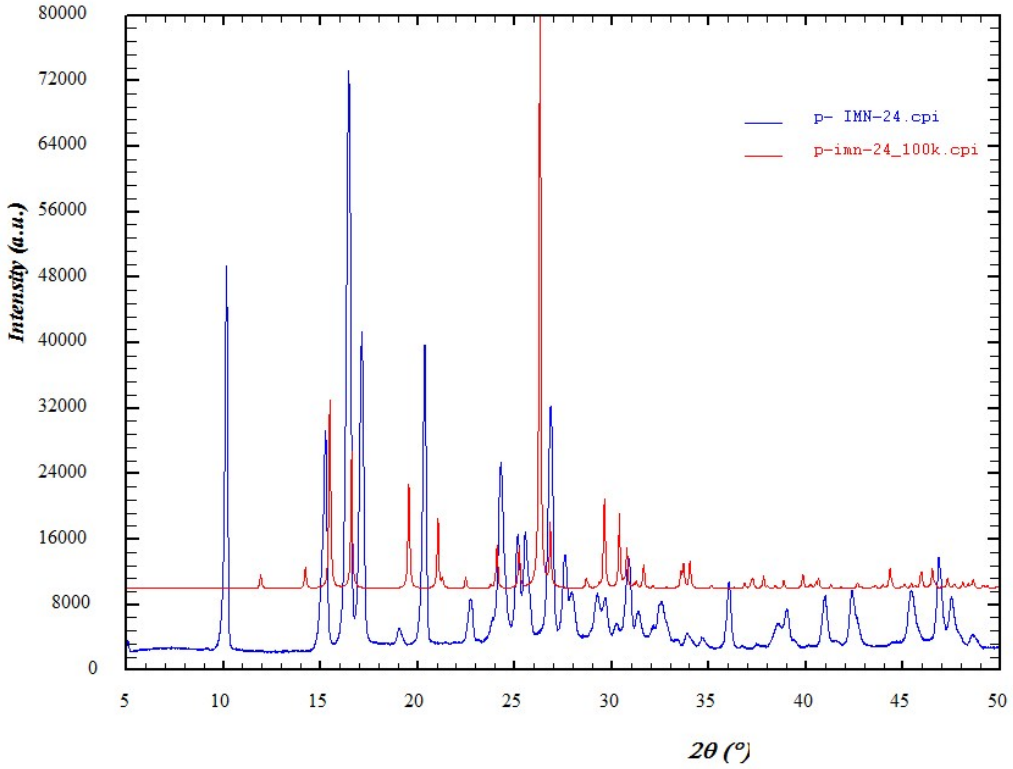


Figure: S6.f) PXRD of compound 6.

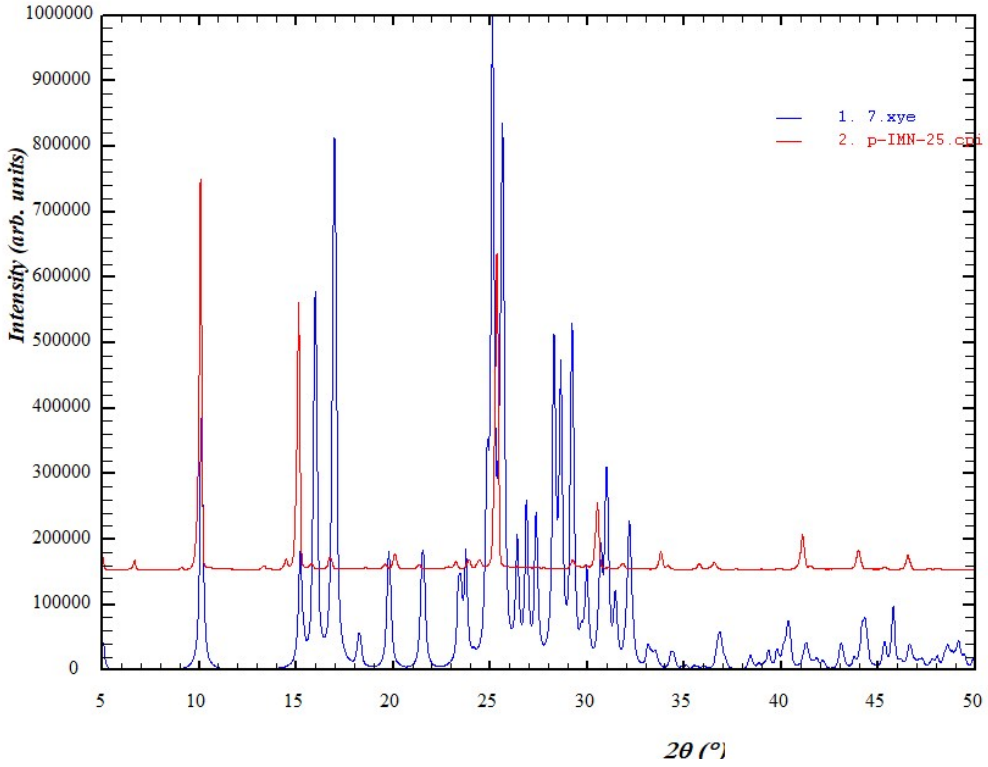


Figure: S6.g) PXRD of compound 7.

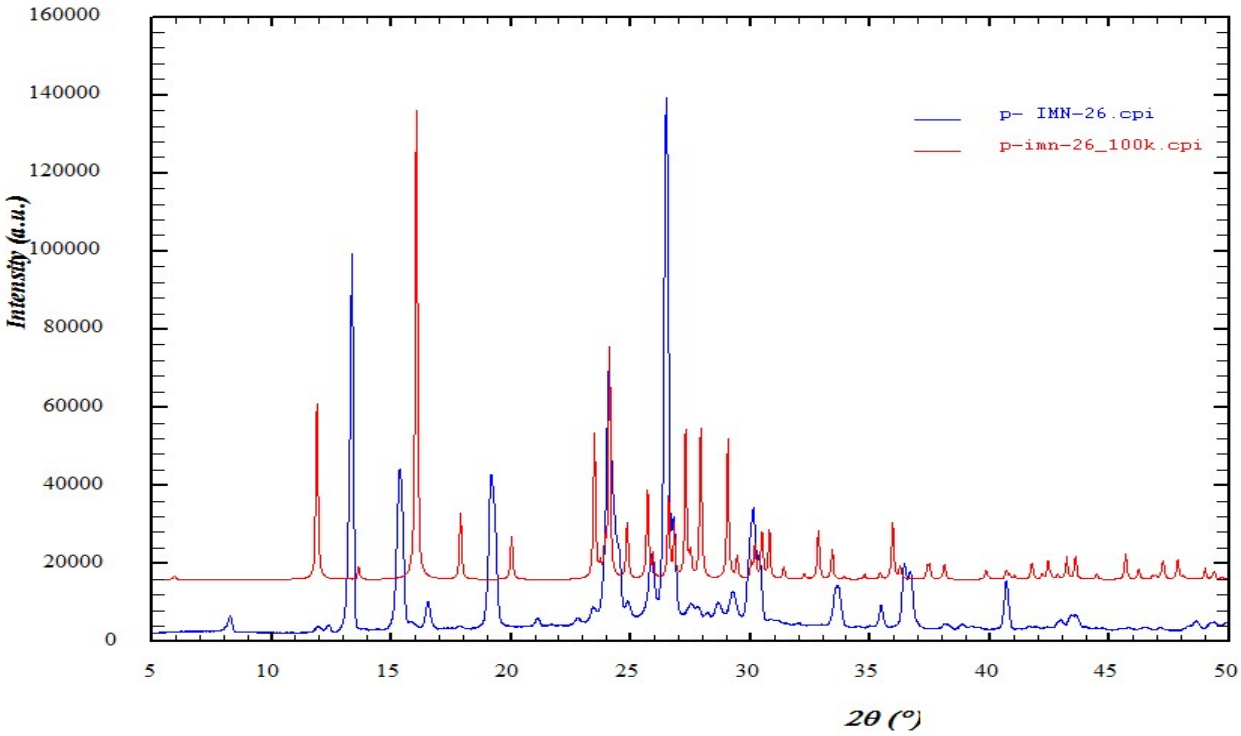


Figure: S6.h) PXRD of compound 8.

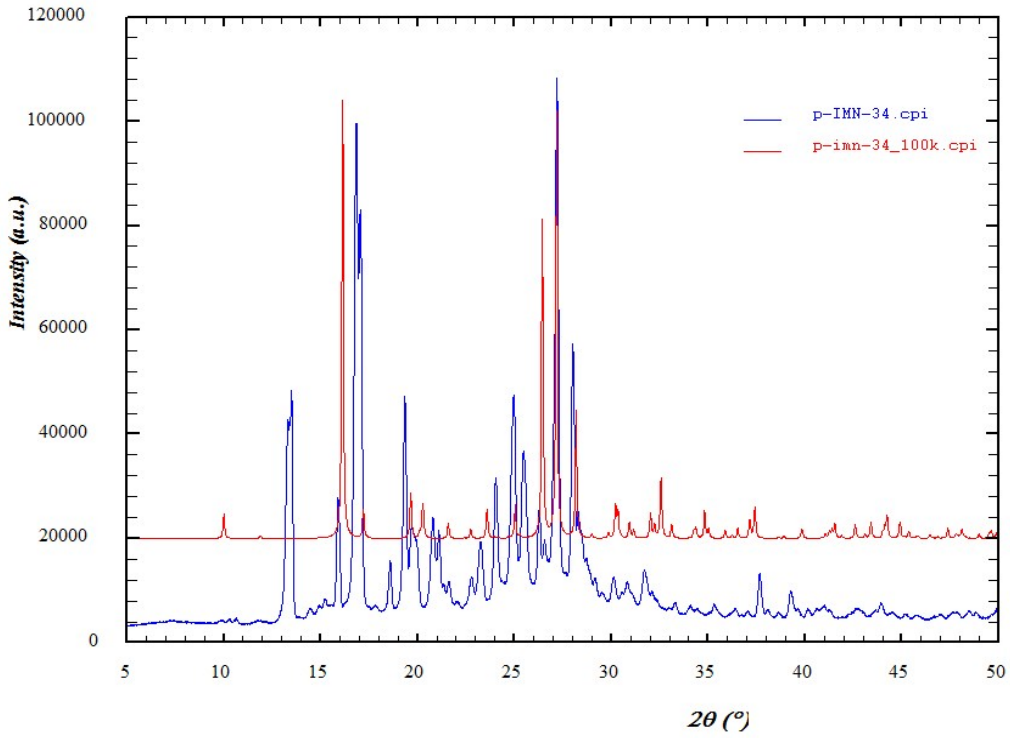


Figure: S6.i) PXRD of compound 9.

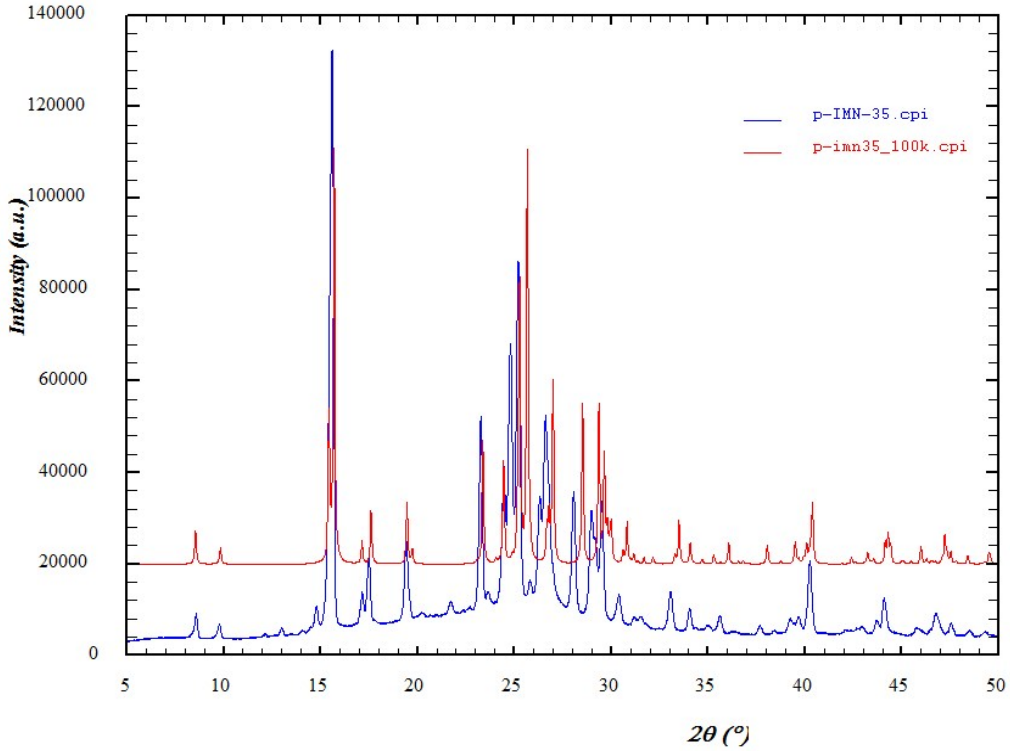


Figure: S6.j) PXRD of compound 10.

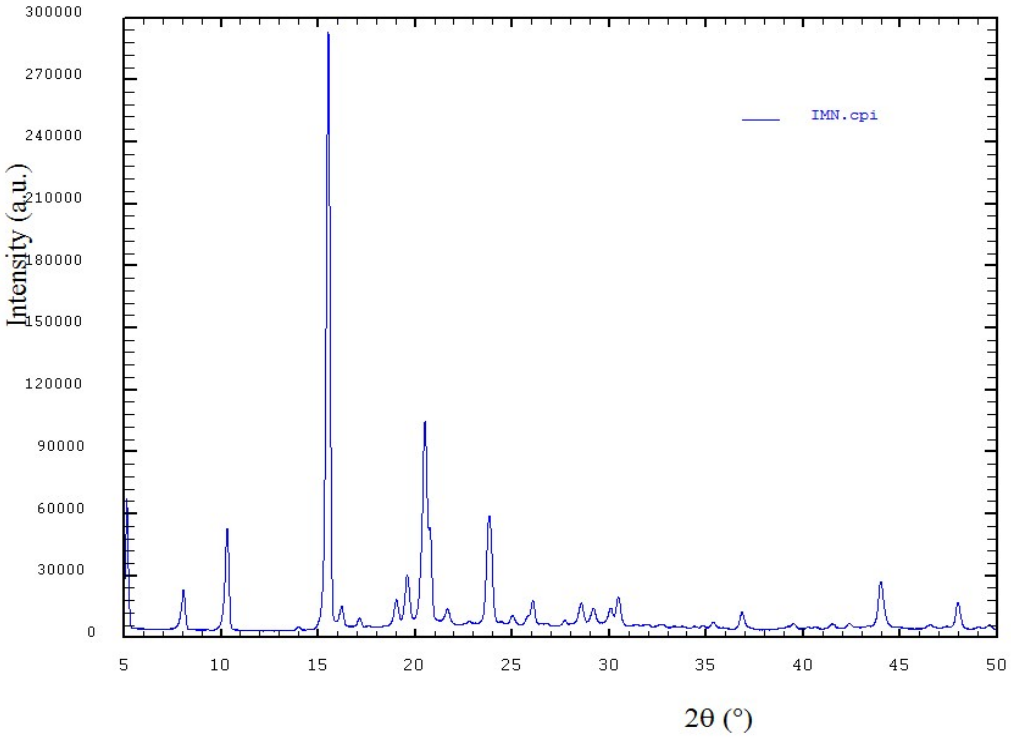


Figure: S6.k) PXRD of compound 11

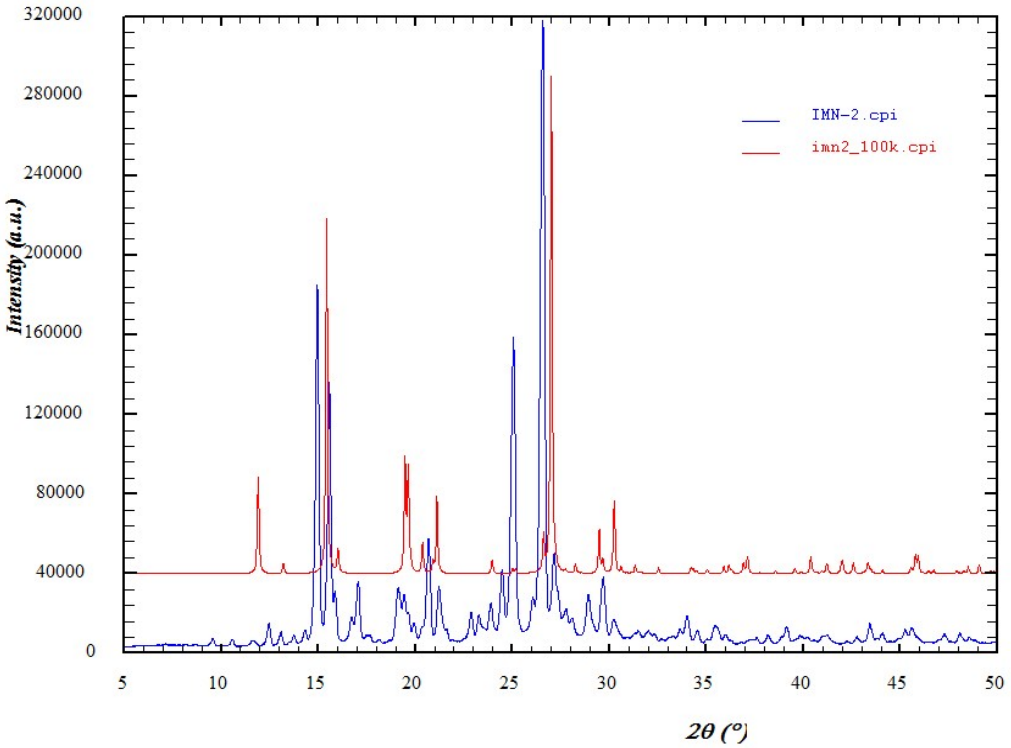


Figure: S6.l) PXRD of compound 12.

Figure: S6.m) PXRD of compound 13.

.

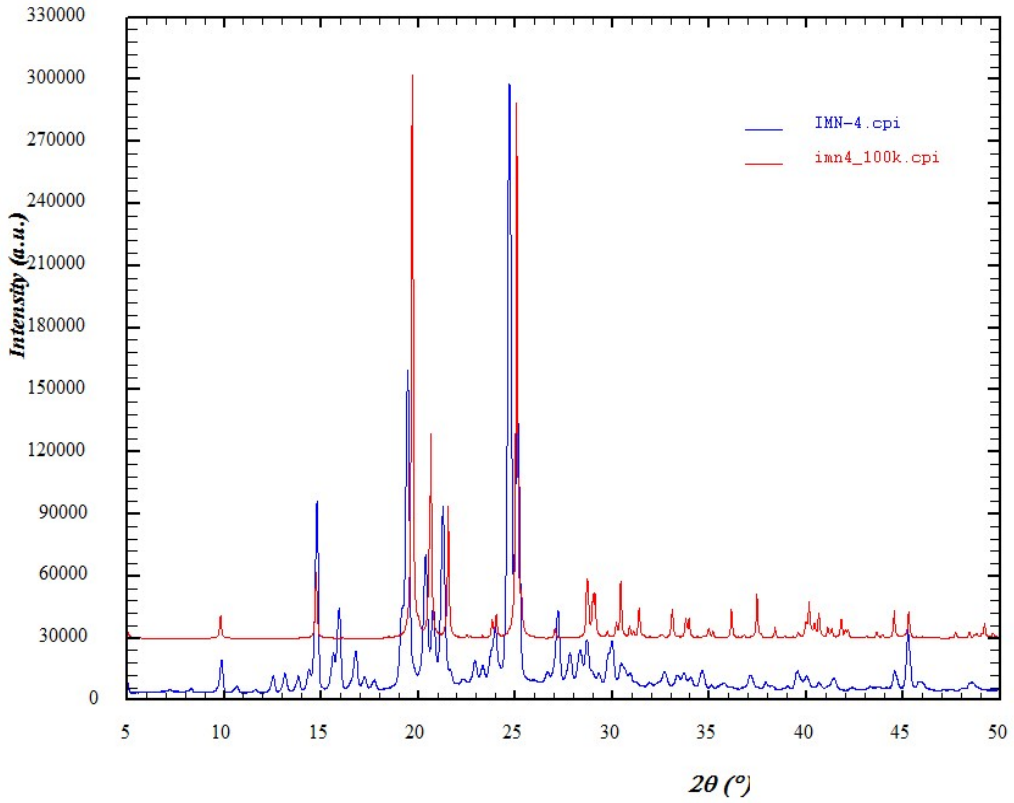


Figure: S6.n) PXRD of compound 14

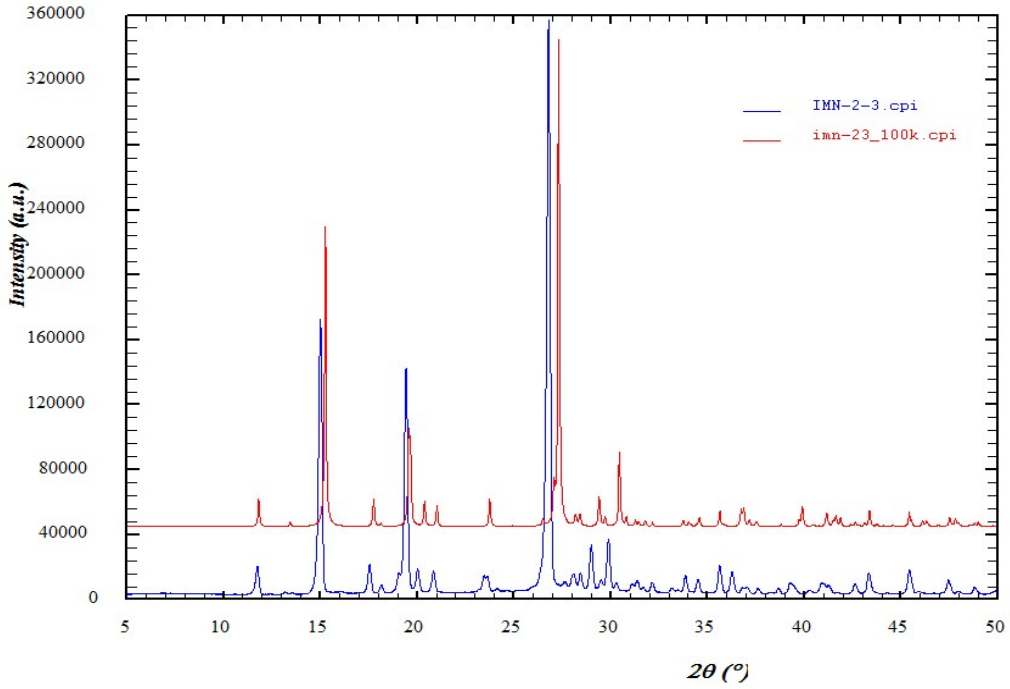


Figure: S6.o) PXRD of compound 15.

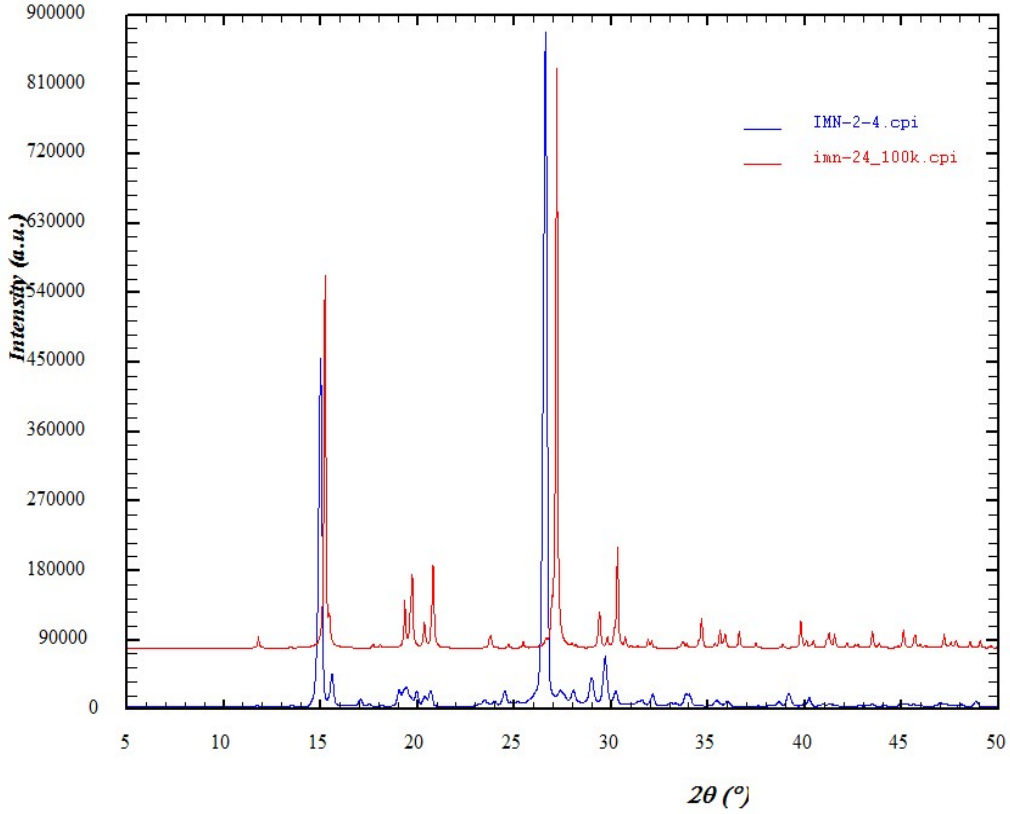


Figure: S6.p) PXRD of compound 16.

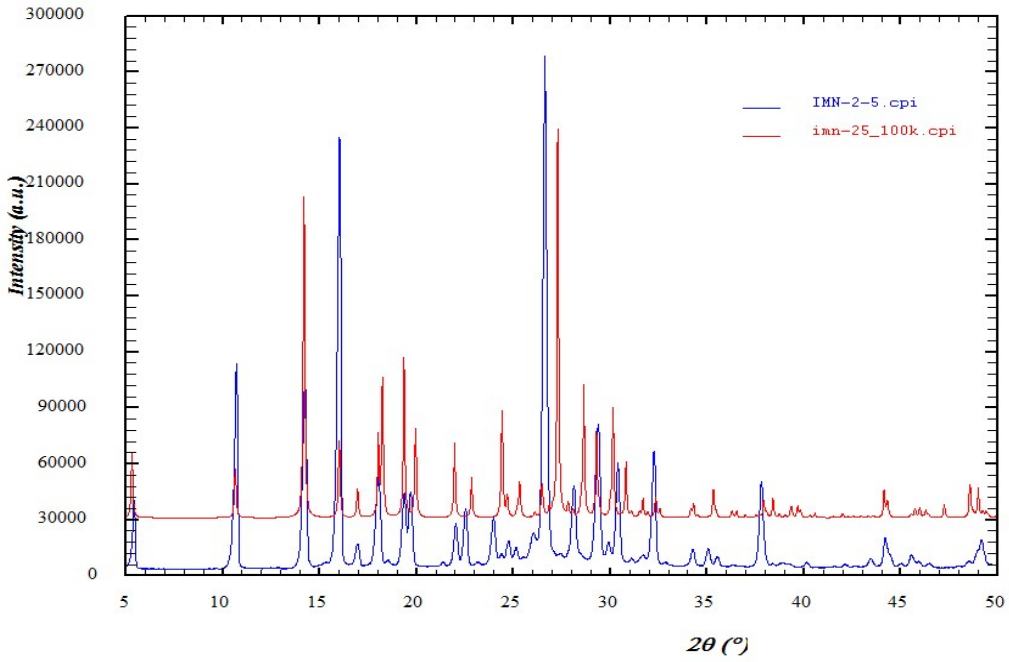


Figure: S6.q) PXRD of compound 17.

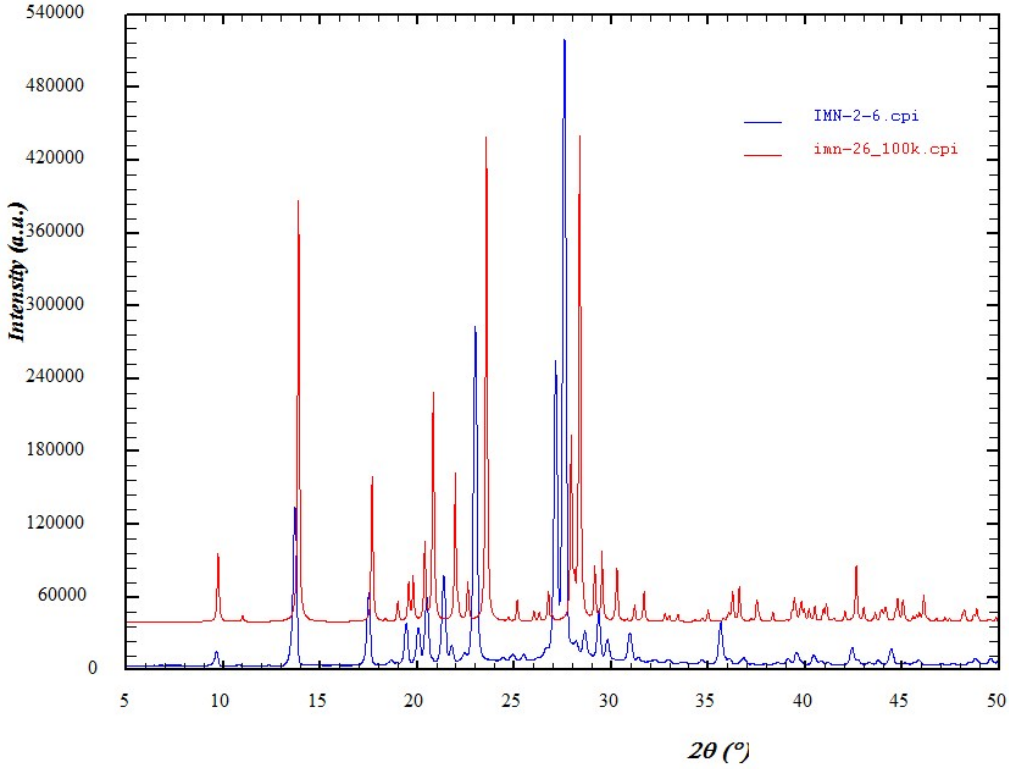


Figure: S6.r) PXRD of compound 18.

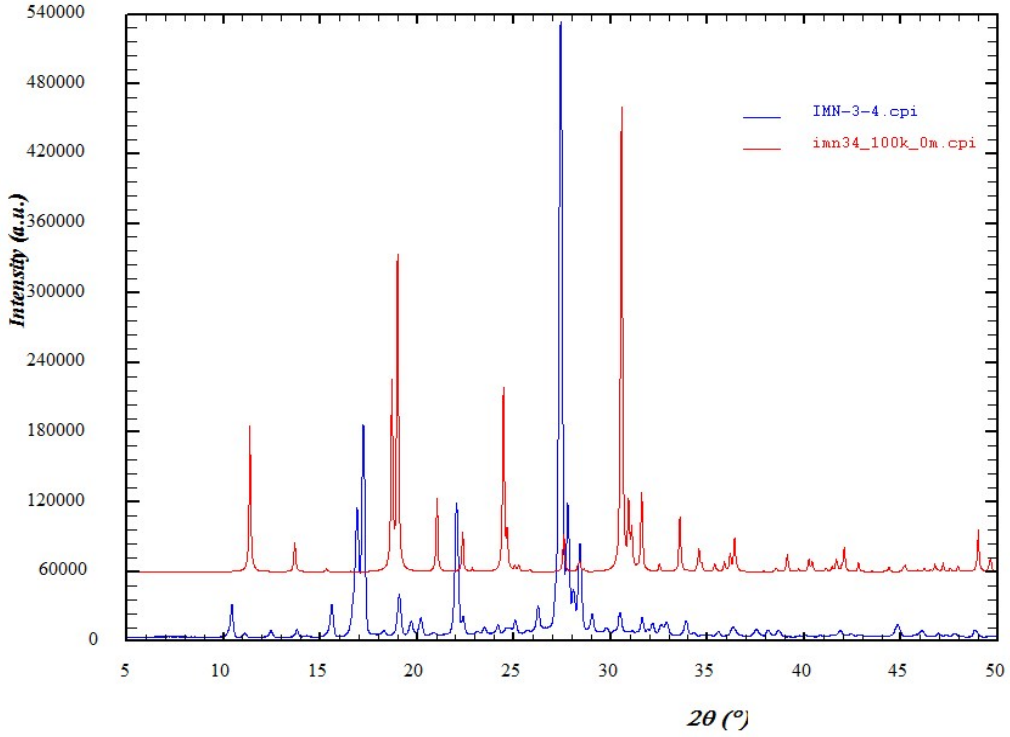


Figure: S6.s) PXRD of compound 19.

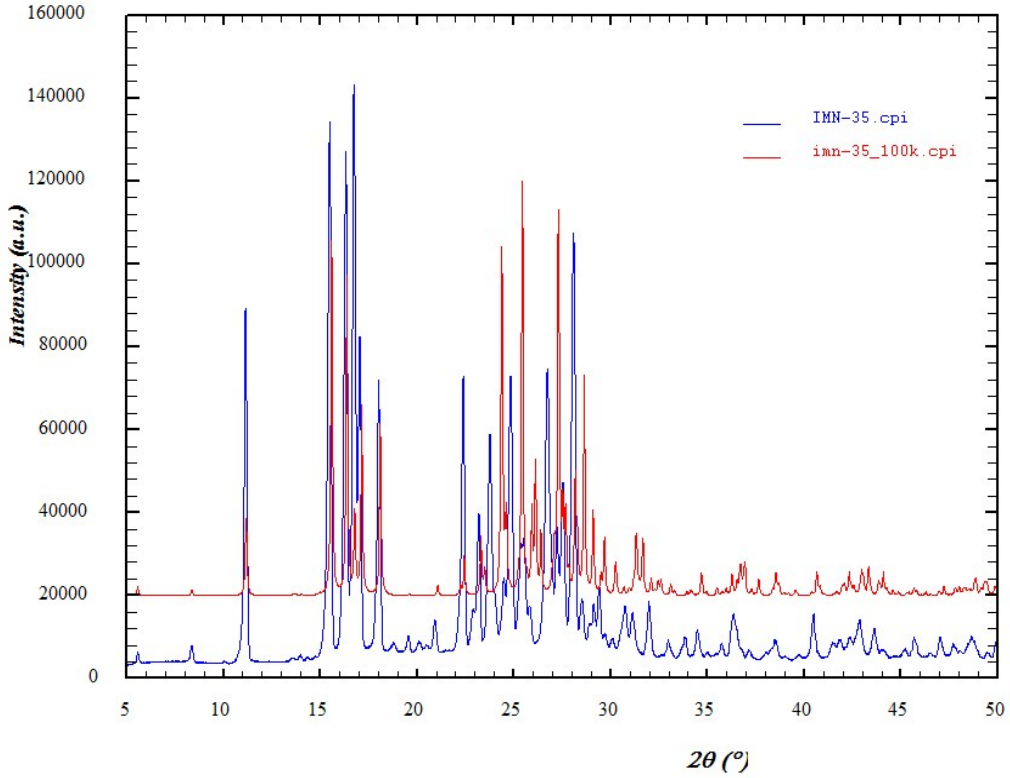


Figure: S6.t) PXRD of compound 20.

Compound No.	**14**
Empirical formula	$C_{20}H_{14}F_2N_2$
Formula weight	320.3
Temperature (K)	100.0
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	7.4632(5)
b (Å)	5.6697(4)
c (Å)	37.578(3)
α (°)	90
β (°)	106.491(7)
γ (°)	90
V (Å^3)	1524.68(19)
Z	4
ρ_{calc} (g cm^{-3})	1.396
μ/ mm^{-1}	0.125
F(000)	664.0
$2\theta_{min,max}$(°)	5.48,65.54
$h_{min,max}$; $k_{min,max}$; $l_{min,max}$	-10,10; -6,8; -56,56
Total no. of reflections	17673
R_{int}	0.0711
No. of unique reflections	5418
R_1 [I > 2σ(I)]	0.1215
wR_2 (all data)	0.3661
GooF	1.112
$\Delta\rho_{max,min}$(eÅ^{-3})	2.45, -0.52

Anisotropic ellipsoid (50% probability) plots with atom numbering

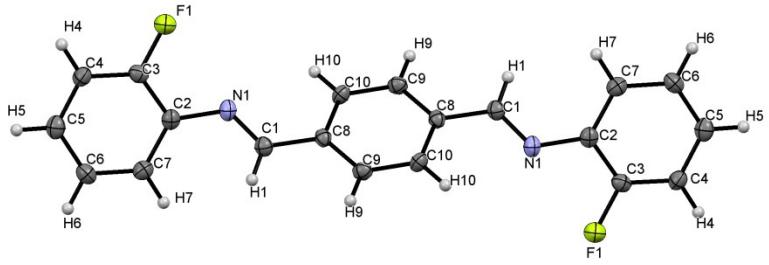


Fig.S7.a. Anisotropic ellipsoid (50% probability) plot of 2 with atom numbering

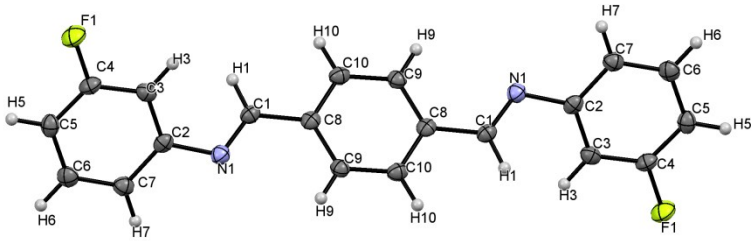


Fig.S7.b. Anisotropic ellipsoid (50% probability) plot of 3 with atom numbering

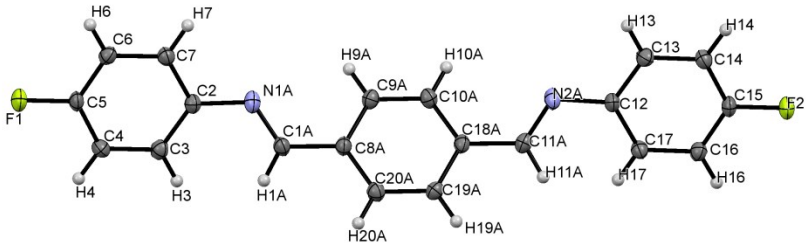


Fig.S7.c. Anisotropic ellipsoid (50% probability) plot of 4 with atom numbering

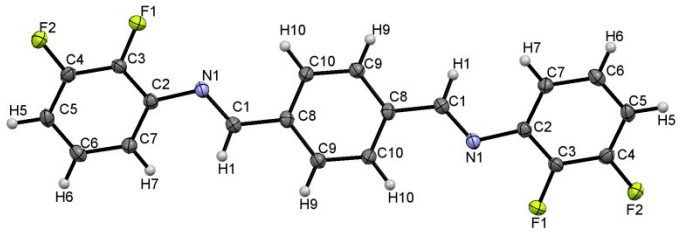


Fig.S7.d. Anisotropic ellipsoid (50% probability) plot of 5 with atom numbering

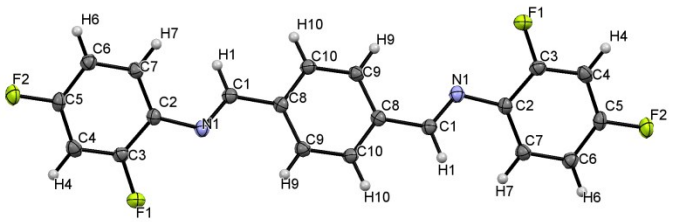


Fig.S7.e. Anisotropic ellipsoid (50% probability) plot of 6 with atom numbering

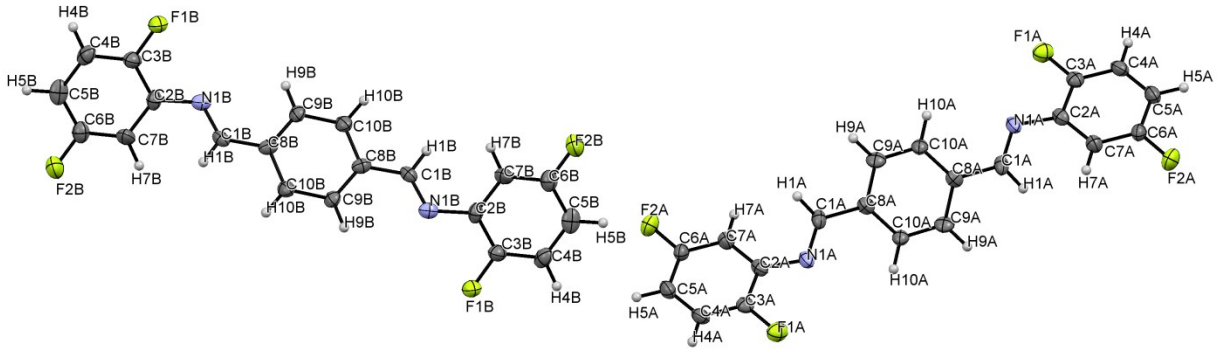


Fig.S7.f. Anisotropic ellipsoid (50% probability) plot of 7 with atom numbering

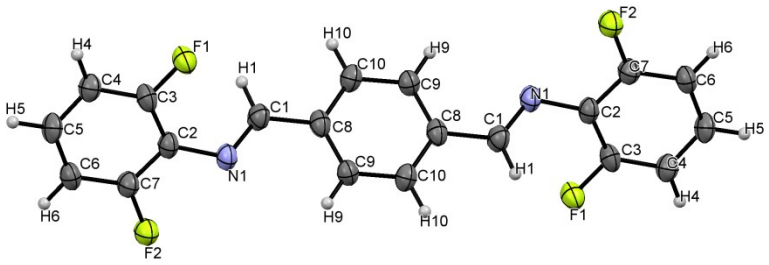


Fig.S7.g. Anisotropic ellipsoid (50% probability) plot of 8 with atom numbering

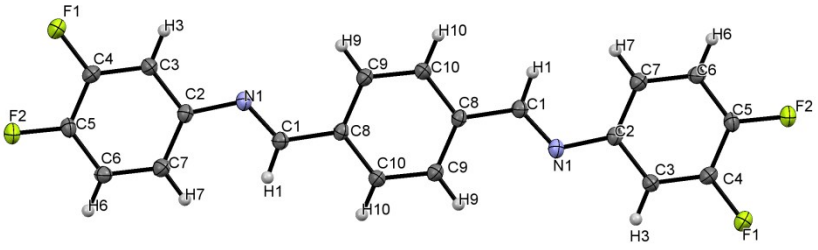


Fig.S7.h. Anisotropic ellipsoid (50% probability) plot of 9 with atom numbering

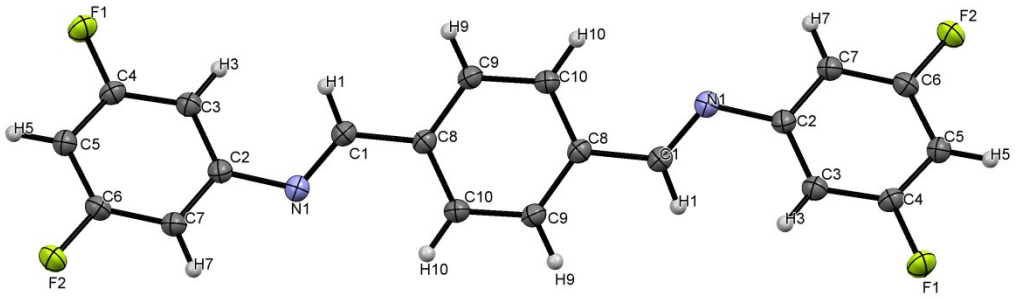


Fig.S7.i. Anisotropic ellipsoid (50% probability) plot of 10 with atom numbering

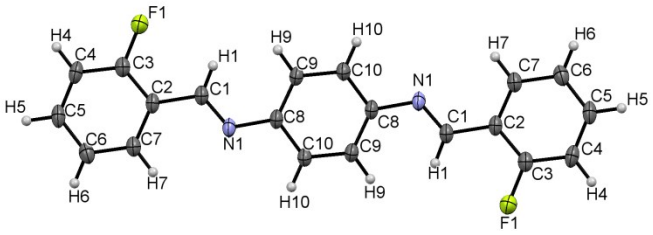


Fig.S7.j. Anisotropic ellipsoid (50% probability) plot of 12 with atom numbering

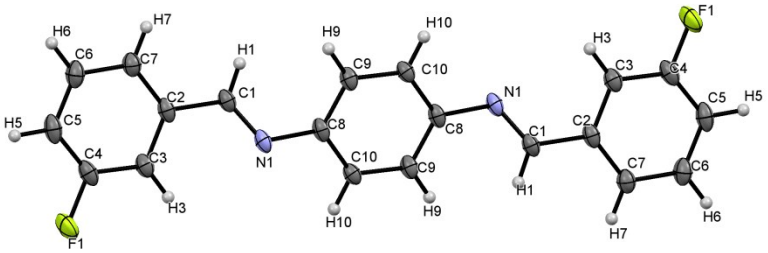


Fig.S7.k. Anisotropic ellipsoid (50% probability) plot of13 with atom numbering

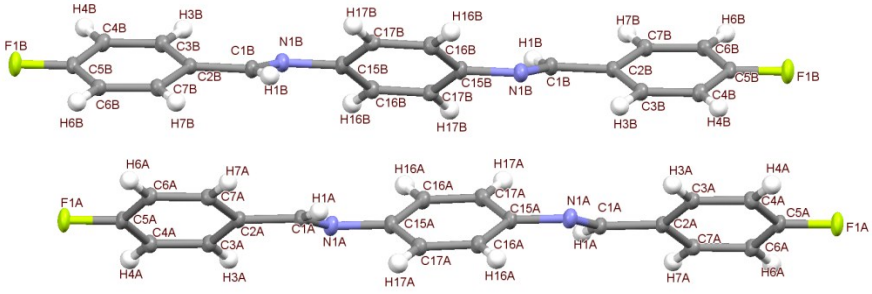


Fig.S7.l. Anisotropic ellipsoid (50% probability) plot of 14 with atom numbering

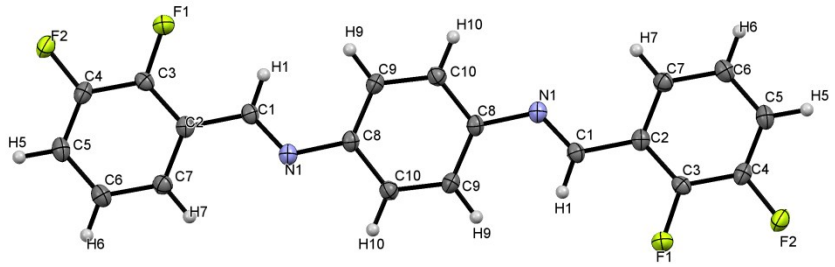


Fig.S7.m. Anisotropic ellipsoid (50% probability) plot of 15 with atom numbering

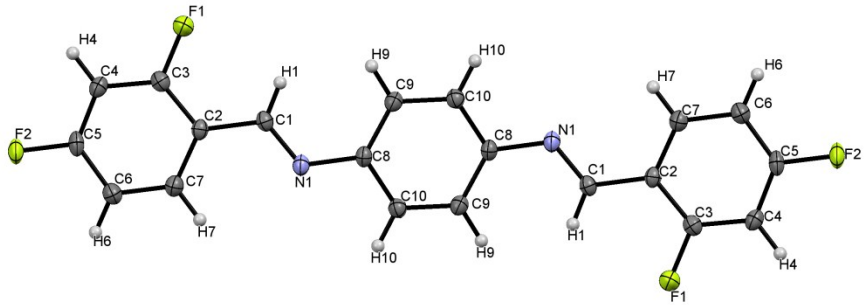


Fig.S7.n. Anisotropic ellipsoid (50% probability) plot of 16 with atom numbering

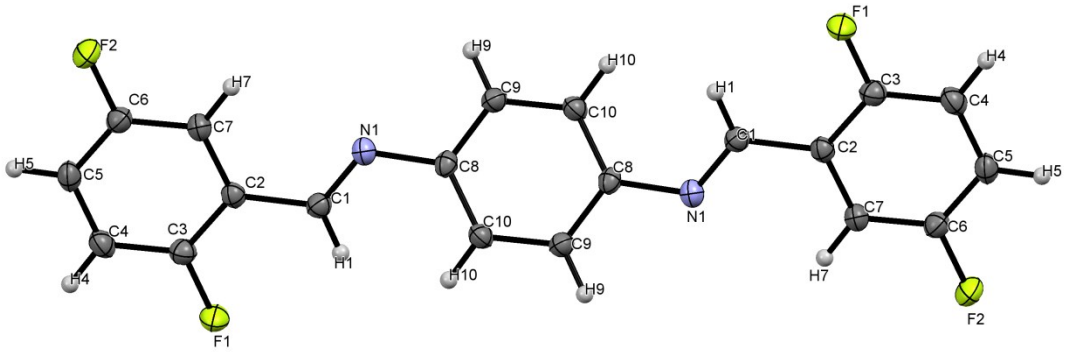


Fig.S7.o. Anisotropic ellipsoid (50% probability) plot of 17 with atom numbering

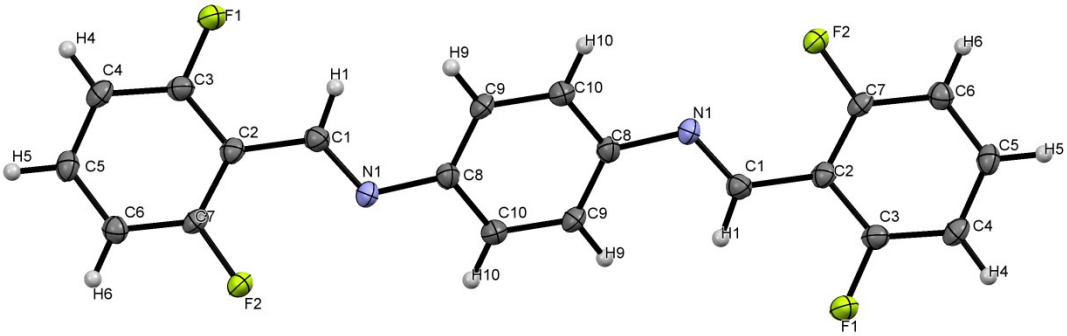


Fig.S7.p. Anisotropic ellipsoid (50% probability) plot of 18 with atom numbering

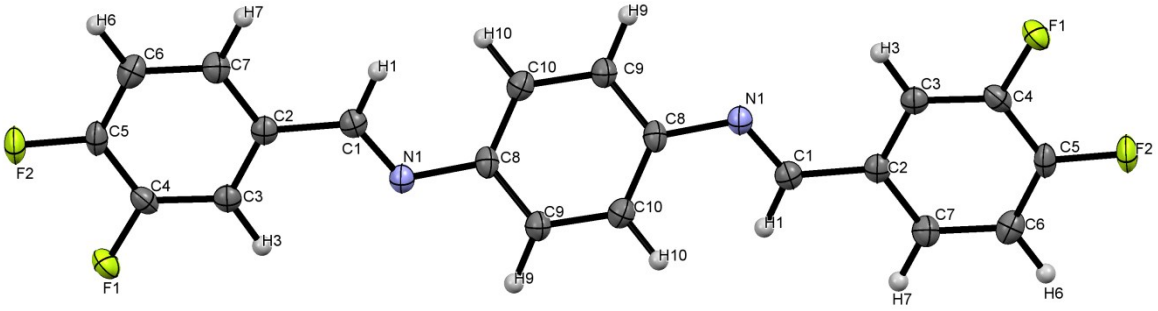


Fig.S7.q. Anisotropic ellipsoid (50% probability) plot of 19with atom numbering

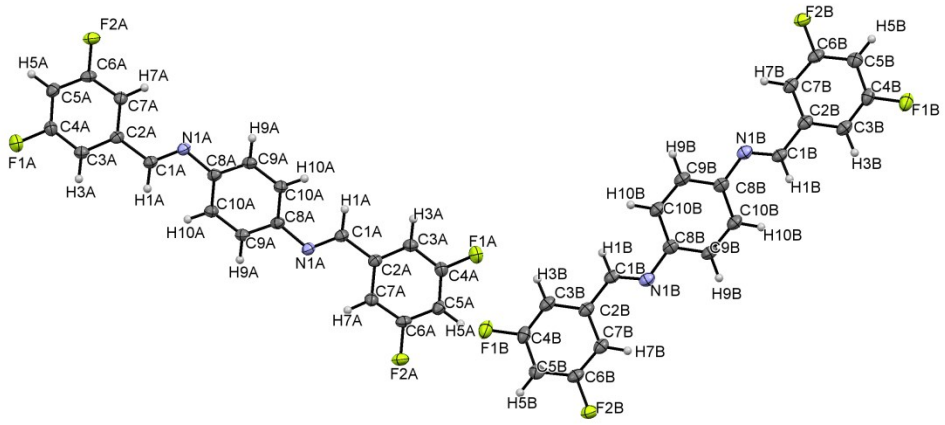


Fig.S7.r. Anisotropic ellipsoid (50% probability) plot of 20 with atom numbering

Pair wise comparison of bridge flipped isomers.

8.1. *Structural comparison of the compounds**2-12***

The structures of **2** and **12**have been solved and refined in the monoclinic centrosymmetric $P2_1/n$ and $P2_1/c$ space group respectively (Table 2 in main paper). The compounds **2** and **12** adopt different unit cell parameters and have different overall molecular conformation. Compound **2** with fluorine at the *ortho*-position, forms a dimer adopting the robust synthon I(A)involving C–H···F hydrogen bond (Table 3a, Figure S8a) involving the imine has reported recently[3k]. Molecular sheets have been formed involving this hydrogen bond. These sheets are further interconnected via weak C−H···π intermolecular interactions in the solid state (Table 3b, Figure S8b)

Compound **12**forms herring bone structure involving intermolecular C–H···F and C–H···N hydrogen bonds (Figure S8c) simultaneously in the lattice along with C−H···π interactions (Figure S8d). The compounds **2** and **12** are not isostructural (isomorphous).

Table 3: (a) Intermolecular C−H···F and C−H···N Interactions and (b) Intermolecular C−H···π and C=N···π Interactions in the Crystallized Compounds**2** and**12**.

(a) Intermolecular C−H···F and C−H···N Interactions

Compd.	D–H···A	D–H/Å	*D*(D···A)/Å	*d*(H···A)/Å	∠D–H···A/º	SYMMETRY	SYNTHON
2	**C1–H1···F1**	1.080	3.484(5)	2.42	168.0	x - 1, y, z+1	IVa
12	**C6–H6···N1**	1.080	3.578(2)	2.54	161.6	x, $^1/_2$- y, z -$^1/_2$	IVc
	C9–H9···F1	1.080	3.220(2)	2.49	124.4	x, $^3/_2$–y, ½ +z	IVb
	C10–H10···F1	1.080	3.292(2)	2.65	117.9		IVb

(b) Intermolecular C−H···π and C=N···π Interactions

Compd.	C−H/ C=N···π	C···π (Å)	H/N···π/Å	C−H/C=N···π/º	SYMMETRY	SYNTHON
2	**C9–H9··· Cg1(Ar_F)**	3.444	2.80	125.87	x +1, y, z	IIb
	C5–H5··· Cg1(Ar_F)	3.708	2.92	141.69	x -1, y, z+1	IIb
12	**C5–H5··· Cg2(Ar_H)**	3.706	3.37	103.10	x, y,z+1	IIIb

	C1=N1⋯ Cg1(Ar_F)	3.420	3.50	75.93	1-x, 1 - y, 1 - z	V

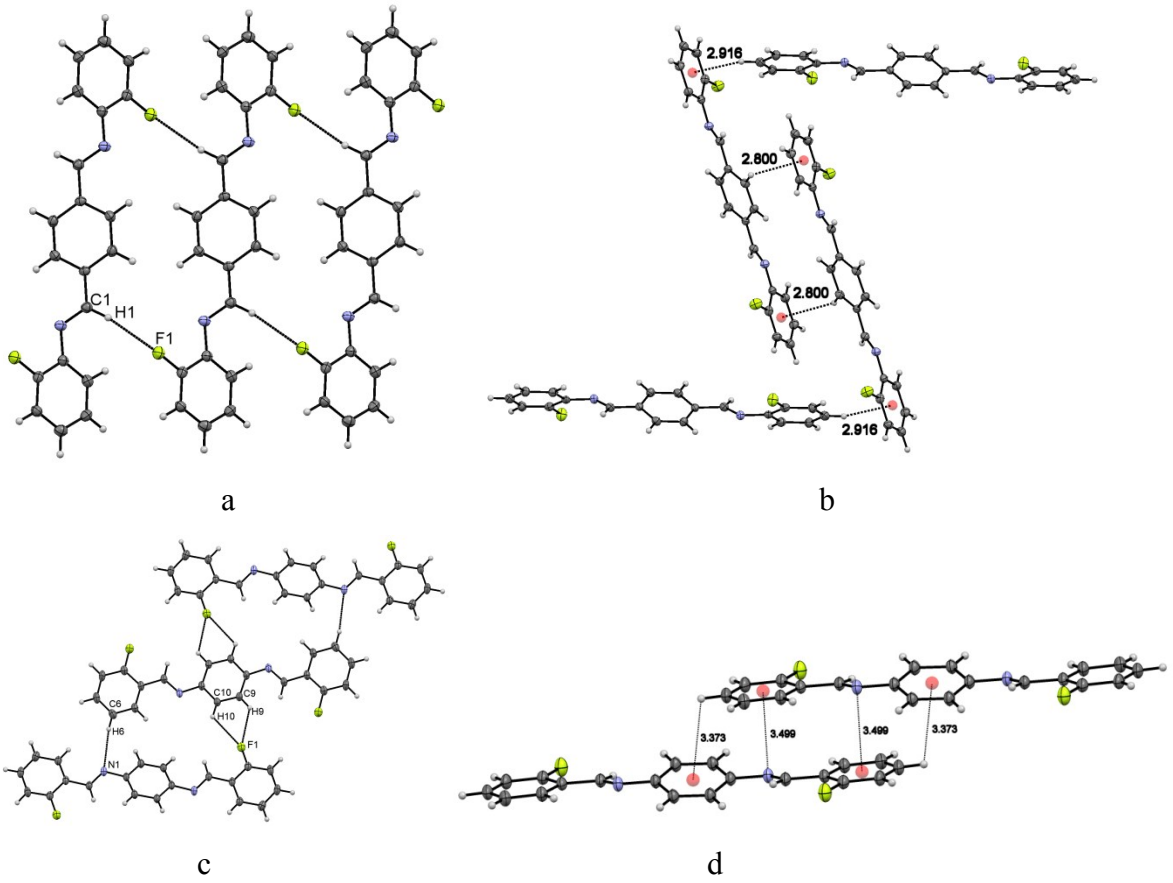


Figure S8. (a)Molecular sheet formation *via* C–H···F intermolecular hydrogen bonds involving imine hydrogen in **2**;(b) weak C−H···π intermolecular interactions in **2**;(c) C–H···F and C–H···N intermolecular hydrogen bonds in **12**;(d) C−H···π and N···π interactions forming dimers in **12**.

8.2. *Structural comparison of the compounds **3-13***

Structures of **3** and **13** were solved and refined in the monocyclic centrosymmetric $P2_1/n$ *and* $P2_1/c$ space groups respectively (Table 2 in the main paper). The compounds were found to have different C–H···F hydrogen bonds in their crystal lattice. Compound 3 was forming herring bone structure (Figure S9a) involving the imine H atom while the compound 13 was found to form molecular steps (Figure S9c) utilizing a different set of C–H···F hydrogen bond involving the aromatic H atoms.

In spite of non-planarity of phenyl rings in **3**, they are stacked in the offset (parallel displaced) orientation (Figure S9b) with a distance of 3.929 Å between the centroid of aromatic rings, while in **13**, steps are connected through weak C−H···π interactions (Figure S9d).

Table 4: a) Intermolecular C−H···F Interactions and (b) Intermolecular C−H···π Interactions in the Crystallized Compounds**3** and**13**.

(a) Intermolecular C−H···F Interactions

Compd.	**D–H···F**	**D–H/Å**	***D*(D···F)/Å**	***d*(H···F)/Å**	**∠D–H···F/º**	**SYMMETRY**	**SYNTHON**
3	**C1–H1···F1**	1.080	3.410(4)	2.40	155.0	½ -x, ½ + y, ½ -z	IVa
13	**C5–H5···F1**	1.080	3.421(1)	2.47	147.0	2 - x, ½ + y, ½ - z	IVb

(b) Intermolecular C−H···π Interactions

Compd.	**C−H···π**	**C···π/Å**	**H···π/Å**	**C−H···π/º**	**SYMMETRY**	**SYNTHON**
13	**C9–H9···Cg2(Ar$_H$)**	3.416	2.628	140.58	x, ½ -y, ½ + z	IIIb

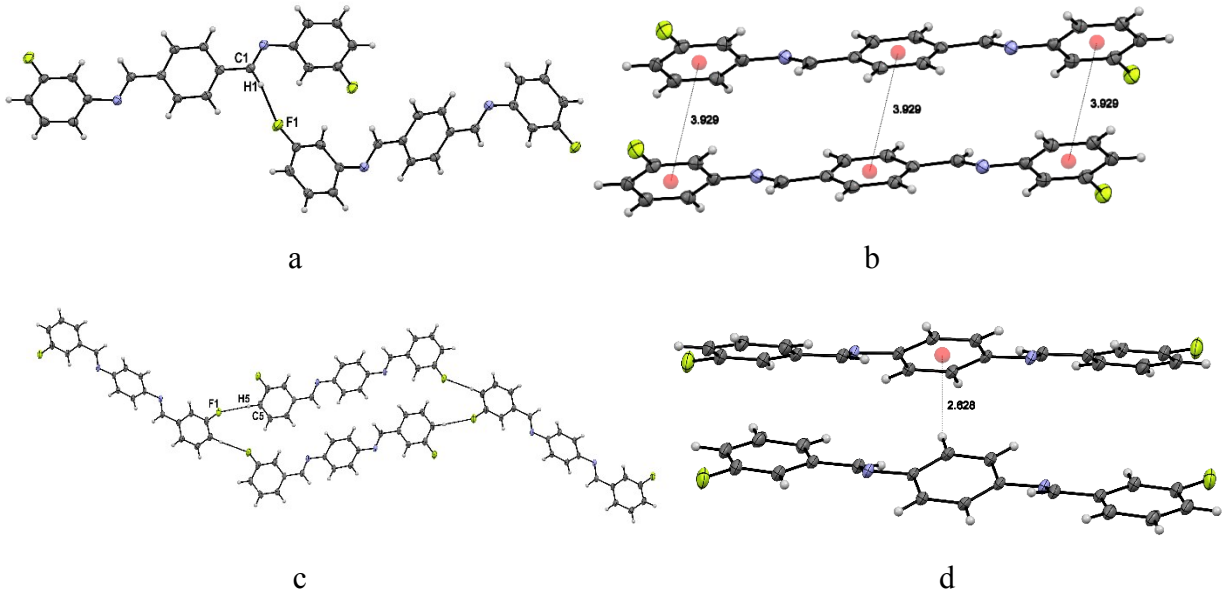


Figure S9. (a) C–H···F intermolecular hydrogen bonds in **3**; (b) offset stacking π···π interaction in **3**; (c) C–H···F intermolecular hydrogen bonds in **13**; (d) C-H···πinteraction in **13**.

*8.3. Structural comparison of the compound **4** and **14***

Structures of **4** and **14** have been solved and refined in the monoclinic centrosymmetric $P2_1/c$ space group (Table 2 in the main paper). Interestingly, the compound **4** has a full molecule in the asymmetric unit and the molecule is disordered in the lattice about a 2-fold molecular axis of symmetry (Fig 7.c). The molecules pack in the unit cell involving C–H···F and C–H···N hydrogen bonds. Molecular sheet is formed by weak C–H···F hydrogen bonds (Figure S10a) and these sheets are interlinked by C−H···π interactions and C–H···N hydrogen bonds (Figure S10 b, c). Compound **14** has two independent half molecules in the asymmetric unit. Both the molecules are found to form molecular sheets involving C–H···F hydrogen bonds (Figure S10d) as seen in 4. These sheets are interlinked through C–H···N hydrogen bonds (Figure S10e) and C−H···π interactions (Figure S10f) same as in **4.**

Table 5: a) Intermolecular C−H···F and C−H···N Interactions and (b) Intermolecular C−H···π Interactions in the Crystallized Compounds**4** and**14**.

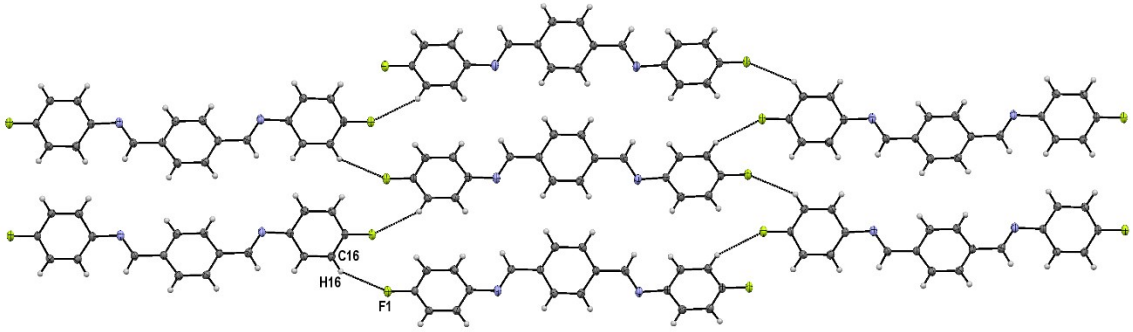
(a) Intermolecular C−H···F and C−H···N Interactions

Compd.	D–H···A	D–H/Å	*D*(D···A)/Å	*d*(H···A)/Å	∠D–H···A/º	SYMMETRY	SYNTHON
4.	**C9B–H9···N2A**	1.080	3.550(3)	2.68	137.6	2 – x, ½ + y, $^{3}/_{2}$ – z	IVc
	C9B–H9···N2B	1.080	3.550(3)	2.68	137.6		IVc
	C6–H6···F2	1.080	3.335(3)	2.56	128.2	x – 1, $^{3}/_{2}$ – y, z – ½	IVb
	C16–H16···F1	1.080	3.340(3)	2.55	128.6	1 + x, ½ – y, ½ + z	IVb
	C17–H17···N1A	1.080	3.492(3)	2.62	137.9	2 – x, y – ½, $^{3}/_{2}$ – z	IVc
14.	**C6A–H6A···F1A**	1.080	3.368(2)	2.56	130.9	– ½ – x, y – ½, ½ – z	IVb
	C4B–H4B···F1B	1.080	3.338(2)	2.54	130.1		IVb
	C17A–H17A···N1B	1.080	3.539(3)	2.65	139.8	1 – x, 1 – y, 1 – z	IVc

(b) Intermolecular C−H···π Interactions

Serial No	C−H ···π	C···π/Å	H···π/Å	C−H···π/º	SYMMETRY	SYNTHON
4	**C6–H6···Cg1(Ar_F)**	3.515	2.837	130.70	1 - x, -½ + y, ½ - z	IIb

	C13–H13···Cg1'(Ar_F)	3.510	2.870	127.05	1 - x, -½ + y, ½ - z	IIb
	C20A–H20A···Cg2(Ar_H)	3.526	2.915	124.48	1 - x, -½ + y, ½ - z	IIIb
14	**C6A–H6A···Cg1(Ar_F)**	2.875	3.539	129.41	x, y, z	IIb
	C3A–H3A···Cg1'(Ar_F)	2.843	3.496	128.23	2 - x, 1 - y, 1 - z	IIb
	C17B–H17B···Cg2(Ar_H)	2.805	3.499	132.29	x, y, z	IIIb



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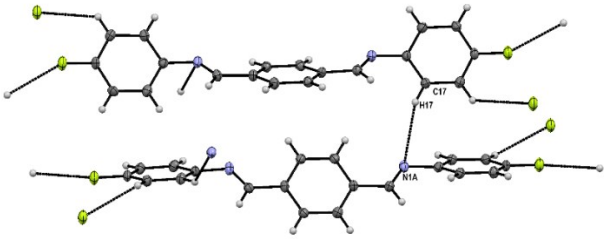

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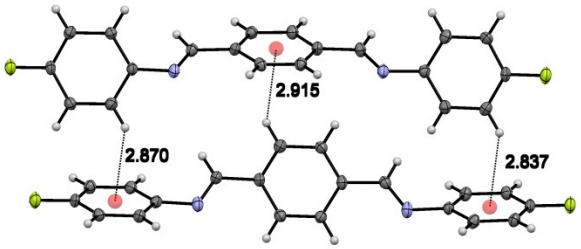

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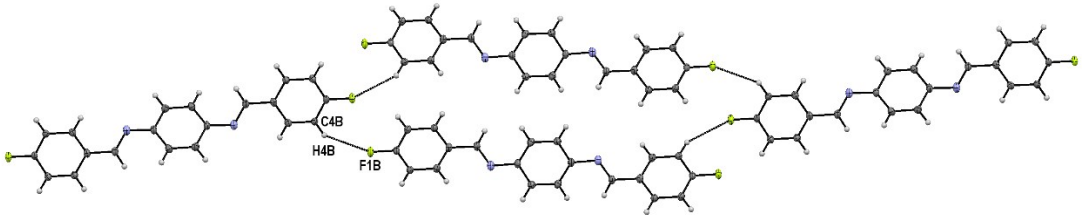

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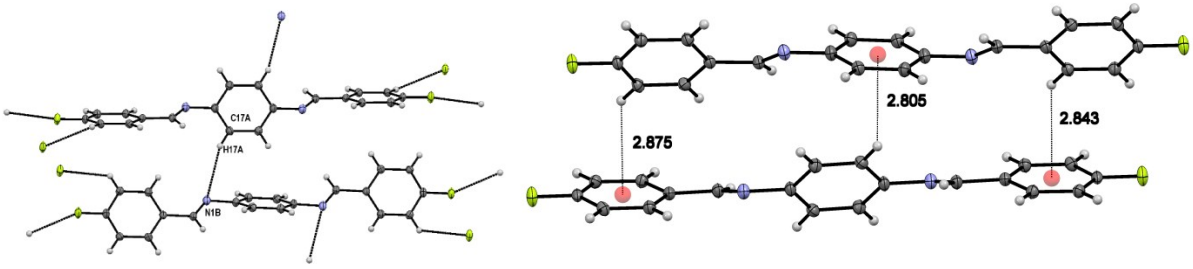


e f

Figure S10: (a)C–H···F, (b)C–H···N, (c)C–H···π interactions in **4**; (e)C–H···F, (f)C–H···N, (g)C–H···πinteractions in **14**

*8.4. Structural comparison of the compounds **5-15***

The structures of **5** and **15** were solved and refined in the monoclinic centrosymmetric $P2_1/c$ space group (Table 2 in the main paper). The compounds **5** and **15** differ in their unit cell parameters and in crystal packing as well. In compound **5**, the *o*-fluorine forms bifurcated C–H···F hydrogen bonds simultaneously with the imine H and with an aromatic H forming a 3D network of molecules (Figure S11a). The *meta*-F also forms bifurcated C–H···F hydrogen bonds (Figure S11a). Molecules of **5** are separated by a distance of 3.777Å between the centroids of aromatic rings (Figure S11b). Compound **15**forms herring bone structure involving C–H···F (*ortho*-F) and C–H···N hydrogen bonds together (Figure S11c), as was seen in the case of compound **12**. Further C–H···F hydrogen bonds have been identified through the *meta*-F forming head to head and tail to tail dimers (Figure S11c) utilizing synthon II reported recently along with C−H···π Interaction.[3k]

Table6a) Intermolecular C−H···F and C−H···N Interactions and (b) Intermolecular C−H···π and C=N···π Interaction in the Crystallized Compounds**5** and**15**.

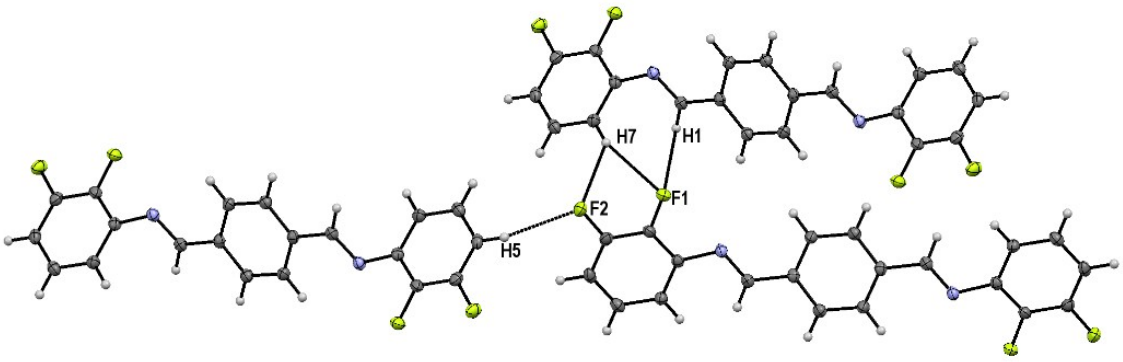
(a) Intermolecular C−H···F and C−H···N Interactions

Compd.	D–H···A	D–H/Å	*D*(D···A)/Å	*d*(H···A)/Å	∠D–H···A/º	SYMMETRY	SYNTHON
5.	**C7–H7···F1**	1.080	3.683(2)	2.64	162.4	x, ½ – y, ½ + z	IVb
	C1–H1···F1	1.080	3.705(2)	2.69	155.7		IVa
	C7–H7···F2	1.080	3.319(2)	2.47	134.7	x, $^{3}/_{2}$– y, ½+z	IVb

	C5–H5···F2	1.080	3.413(2)	2.52	139.2	2 – x, ½ + y, ½ – z	IVb
15.	**C5–H5···F2**	1.080	3.532(2)	2.46	169.6	2 – x, 1 – y,2 – z	IVb
	C6–H6···N1	1.080	3.625(2)	2.57	164.3	x, $^{3}/_{2}$ – y, ½ + z	IVc
	C9–H9···F1	1.080	3.238(2)	2.50	125.0	x, ½ – y, – ½ +z	IVb
	C10–H10···F1	1.080	3.322(2)	2.68	118		IVb

(b) Intermolecular C−H···π and C=N···π Interactions

Compd.	**C−H/ C=N···π**	**C···π/Å**	**H/N···π/Å**	**C−H/ C=N···π/º**	**SYMMETRY**	**SYNTHON TYPE**
15	**C5–H5···Cg2(Ar_H)**	3.678	3.329	104.12	-1+x, y, -1+z	IIIb
	C1=N1···Cg1(Ar_F)	3.363	3.450	75.38	-1+x, y, -1+z	V



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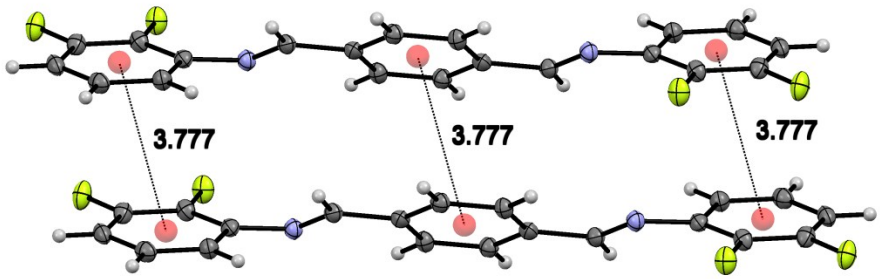

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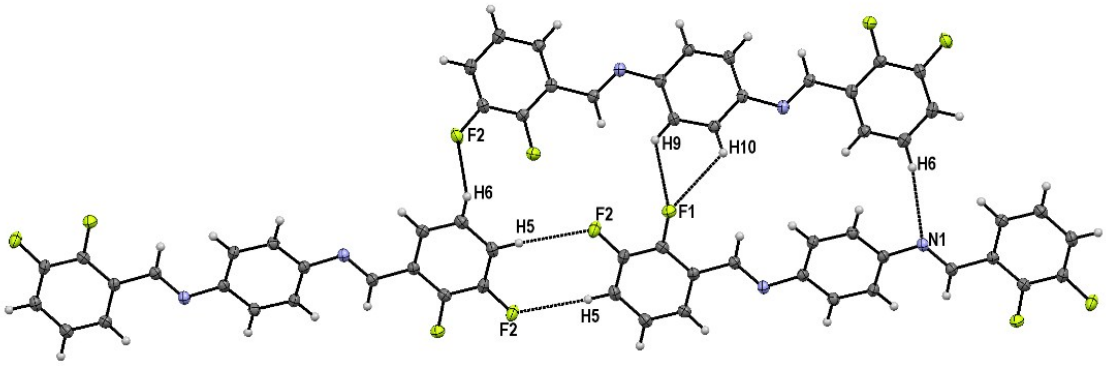

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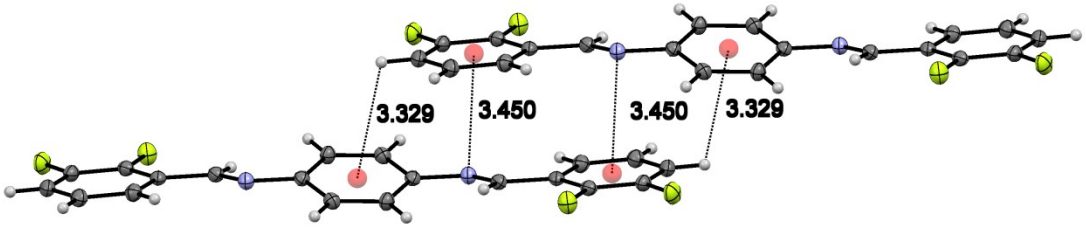

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Figure S11. (a) 3D network of molecules involving bifurcated C–H···F hydrogen bonds through *o*-F and *m*-F in **5**, (b)offset stacking π···π interaction in **5**; (c)3D network of molecules involving C–H···F and C–H···N hydrogen bonds through both *o*-F and *m*-F simultaneouslyin**15**; (d) C–H···π and N···π interaction in **15**.

8.5. Structural comparison of the compounds ***6-16***

The structures of **6** and **16** were solved and refined in the monoclinic centrosymmetric $P2_1/c$ space Group (Table 2). The compounds **6** and **16** adopt different unit cell parameters. In compound **6**, *o*-F is involved in bifurcated hydrogen bonding (Figure S12a) and *p*-F prefers to form dimer (Figure S12a). Thus, the head to tail dimers involving a pair of C–H···F hydrogen bonds (through *p*-F) are interlinked through a bifurcated C–H···F hydrogen bond involving the *o*-F atom (Figure S12a). Compound **16** forms herring bone structure involving C–H···F (*o*-F) and C–H···N hydrogen bonds simultaneously, same as was seen in compound **12**, in addition to H10 with F1 and C–H···F (*para*-F) involves in the formation of head to head and tail to tail dimers (Figure S12c) utilizing synthon II reported recently[3k]. Compound **16**wasfound to have

different C–H···F/C–H···N hydrogen bonds in their crystal lattice when compared to compound **6**.

Table 7: a) Intermolecular C−H···F and C−H···N Interactions and (b) Intermolecular C−F···π and C=N ···π Interactions in the Crystallized Compounds**6** and**16**.

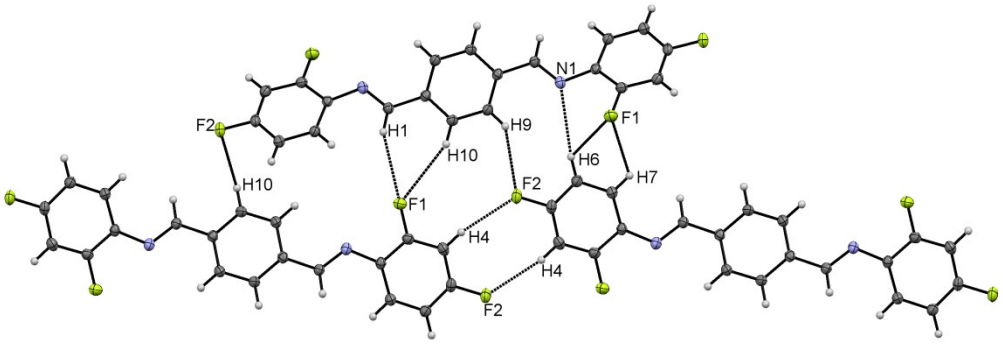
(a) Intermolecular C−H···F and C−H···N Interactions

Compd.	D–H···A	D–H/Å	*D*(D···A)/Å	*d*(H···A)/Å	∠D–H···A/º	SYMMETRY	SYNTHON TYPE
6.	**C6–H6···N1**	1.080	3.717(1)	2.64	173.6	2 – x, –½ + y, $^{3}/_{2}$–z	IVc
	C10–H10···F2	1.080	3.422(1)	2.69	124.5	1 – x, ½ + y, $^{3}/_{2}$–z	IVb
	C9–H9···F2	1.080	3.409(1)	2.61	130.5		IVb
	C4–H4···F2	1.080	3.363(2)	2.29	161.9	3-x, -y,1-z	IVb
	C1–H1···F1	1.080	3.571(1)	2.62	146.7	1 – x, y – ½, $^{3}/_{2}$–z	IVa
	C6–H6···F1	1.080	3.154(2)	2.56	113.8		
	C7–H7···F1	1.080	3.156(2)	2.53	116.1		
	C10–H10···F1	1.080	3.686(2)	2.76	144.4	x – 1, -y+$^{3}/_{2}$,z-½	
16.	**C4–H4···F2**	1.080	3.307(2)	2.39	142.2	–x, 1 – y, –z	IVb
	C7–H7···F2	1.080	3.500(2)	2.73	128.0	x, -y+½, z+½	
	C6–H6···N1	1.080	3.499(1)	2.46	160.3	x, ½ – y, z –½	IVc
	C9–H9···F1	1.080	3.307(1)	2.57	124.8	x, $^{3}/_{2}$– y, ½ +z	IVb
	C10–H10···F1	1.080	3.362(1)	2.69	120.3	1 – x, y – ½, $^{3}/_{2}$–z	IVb

(a) Intermolecular C−F···π and C=N···π Interactions

Compd.	C−F/C=N ···π	C···π/Å	H/N···π/Å	C−H/C=N···π/º	SYMMETRY	SYNTHON TYPE
6	**C5–F2···Cg1(Ar_F)**	3.801	3.408	96.11	1 +x, y, z	IIa
	C1=N1···Cg1(Ar_F)	3.484	3.516	78.08	1 +x, y, z	V
	C1=N1···Cg2(Ar_H)	3.638	3.639	79.87	1 +x, y, z	VI

16	**C5–F2···Cg2(Ar_H)**	3.788	3.343	98.35	1 +x, y, z	IIIa
	C1=N1···Cg1(Ar_F)	3.362	3.518	72.50	1 +x, y, z	V



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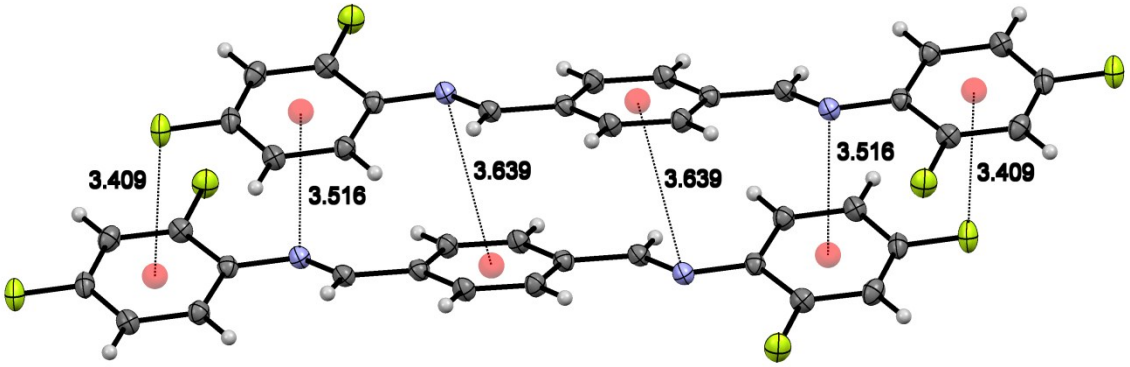

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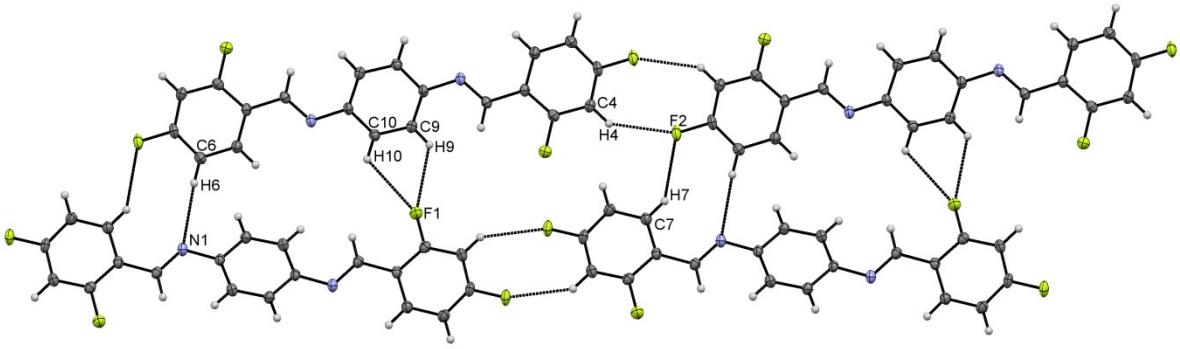

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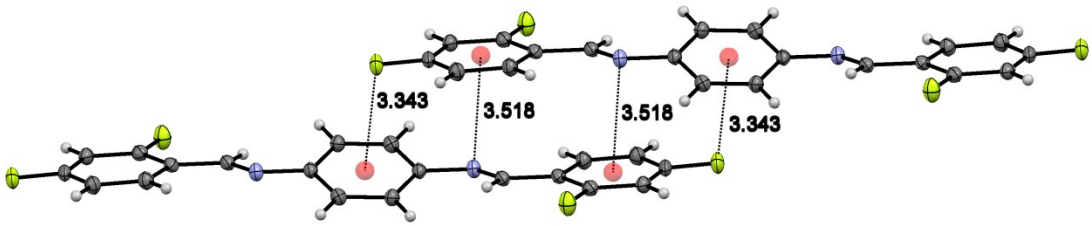

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Figure S12. (a) 3D network of molecules involving bifurcated C–H···F hydrogen bonds through *o*-F and C–H···N in **16**; (b)Molecular packing showing C–F··· π / N···π interactions as dashed lines in **6**; (c)formation of head to head and tail to tail dimers involving *p*-F which are interlinked through bifurcated C–H···F hydrogen bonds involving *o*-F in **16**; (d)Molecular packing showing C–F···π / N···π interactions as dashed lines in **16**.

*8.6. Structural comparison of the compounds **7-17***

Structures of **7** and **17** were solved and refined in the monocyclic centrosymmetric $P2_1/c$ space groups (Table 2 in the main paper) having same unit cell parameters. The asymmetric unit of the compound **7** has two half molecules connected by weak C–H···F hydrogen bond involving the *m*-F of one half molecule and the H5 of the other half molecule (Figure S13a). All the F atoms of the molecules are involved in C–H···F hydrogen bond generating a molecular tetramer (Figure S13a). Compound **17** forms head to head/tail to tail dimers utilizing C–H···F hydrogen bond involving H4 with F2 and H7 with F1 (Figure S13c). These dimers are in turn interconnected by C–H···F hydrogen bonds involving H5 and F2 forming a nine–membered ring (Figure S13c).**7** has larger number of C–H···F hydrogen bonds compared to that in **17** along with π···π stack with a distance of 3.766Å between the centroids (Figure S13b).

Table 8: (a) Intermolecular C−H···F Interactions and (b) Intermolecular C−H···π Interactions in the Crystallized Compounds**7** and**17**

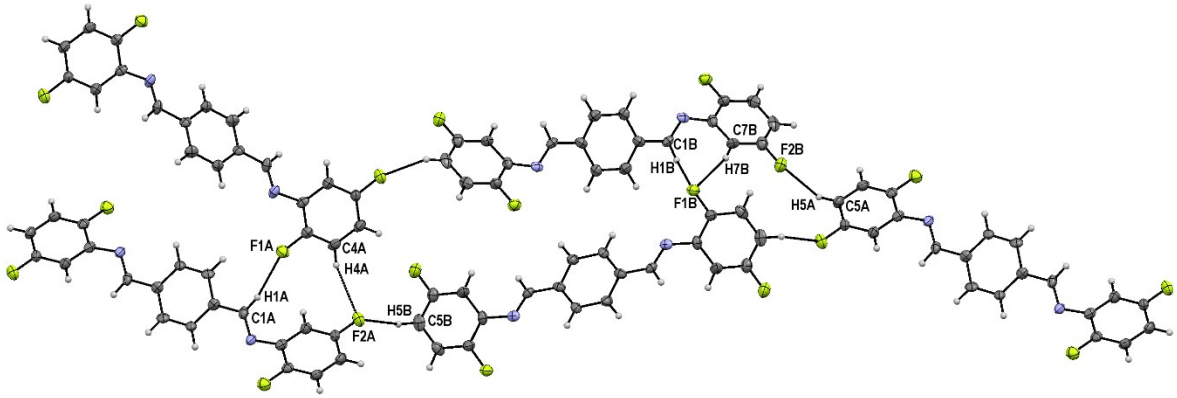
(a) Intermolecular C−H···F Interactions

Compd.	**D–H···F**	**D–H/Å**	***D*(D···F)/Å**	***d* (H···F)/Å**	**∠D–H···F/º**	**SYMMETRY**	**SYNTHON**
	C7A–H7A···F1A	1.080	3.620(9)	2.58	161.1	x, ½ -y, z- ½	IVb
	C1A–H1A···F1A	1.080	3.521(1)	2.50	158.0		IVa
	C4A–H4A···F2A	1.080	3.556(2)	2.52	161.6	x, –½–y, ½+z	IVb

	C7B–H7B···F1B	1.080	3.588(11)	2.54	164.0	x, ½ -y, z- ½	IVb
	C1B–H1B···F1B	1.080	3.572(9)	2.55	157.3		IVa
	C5B–H5B···F2A	1.080	3.504(9)	2.54	148.3	x, y+1, z	IVb
	C5A–H5A···F2B	1.080	3.174(2)	2.42	125.7	x, ½–y, ½+z	IVb
17	**C4–H4···F2**	1.080	3.432(1)	2.36	170.5	x, 1+y, z	IVb
	C5–H5···F2	1.080	3.389(1)	2.40	151.5	–x, ½ +y, –½ –z	IVb
	C7–H7···F1	1.080	3.419(1)	2.35	170.4	x, y –1, z	IVb

(b) Intermolecular C−H···π Interactions

Compd.	**C−H ···π**	**C···π/Å**	**H···π/Å**	**C−H···π/º**	**SYMMETRY**	**SYNTHON**
17	**C10–H10···Cg2(Ar_H)**	3.602	2.686	162.22	x, ½ -y, - ½ +z	IIIb



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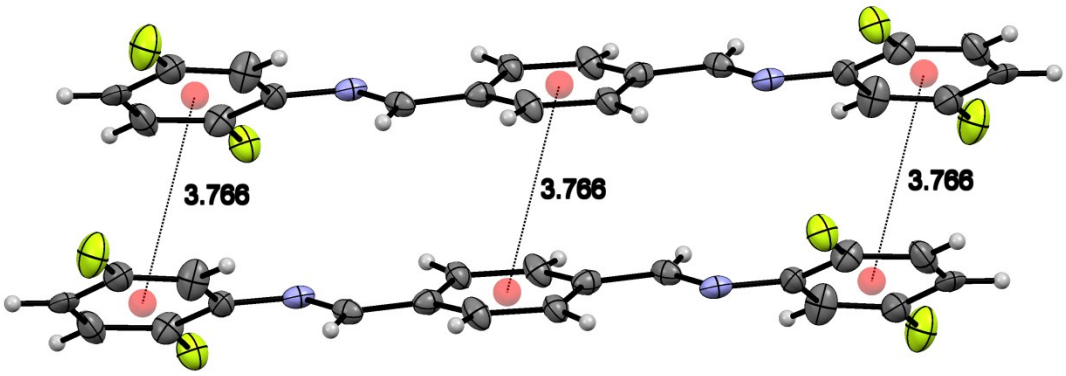

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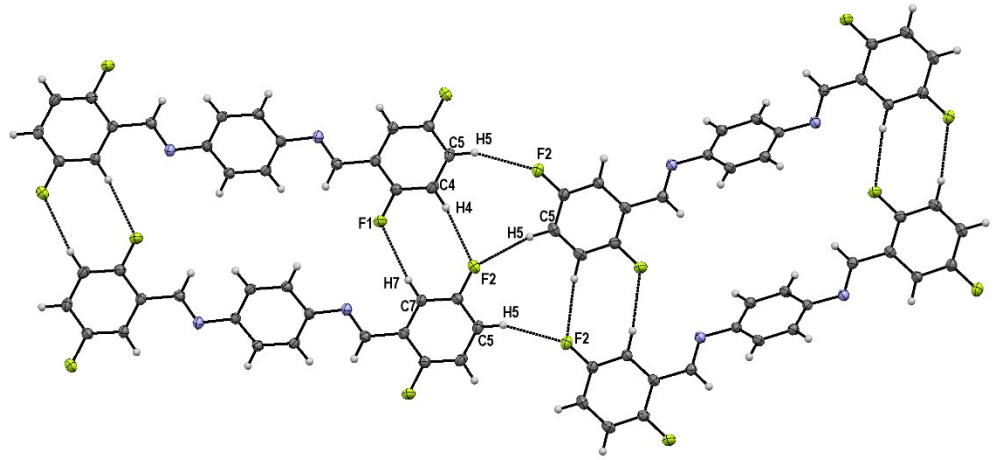

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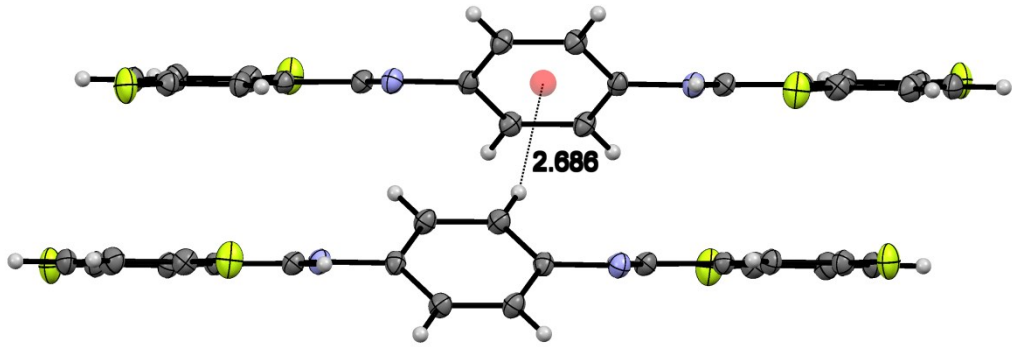

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Figure S13. (a) Intermolecular C–H···F hydrogen bonds involving all the F atoms of **7**forming a tetrameric unit;(b) π···π stacking in **7**(c) dimers interconnected by C–H···F hydrogen bonds involving H5 and F2 forming a nine–membered ring in **17**(d) Intermolecular C–H···π interaction in **17**.

8.7. Structural comparison of the compounds ***8-18***

The structures of **8** and **18** were solved and refined in the monoclinic centrosymmetric $P2_1/c$ space group (Table 2 in the main paper) though they adopted different unit cell parameters. Both the molecules adopt different interactions in the crystal lattice. The molecules of **8**and **18** form chains of head to tail dimers involving C–H···F and C–H···N hydrogen bonds (Figure S14a, c). These chains of dimers are further interlinked through C–H···F hydrogen bonds. **8** has

π···π stacking with distance of 3.914Å (Figure S14b). Interestingly, type I C–F···F–C contact has also been observed in structure of **18** (Figure S14d).

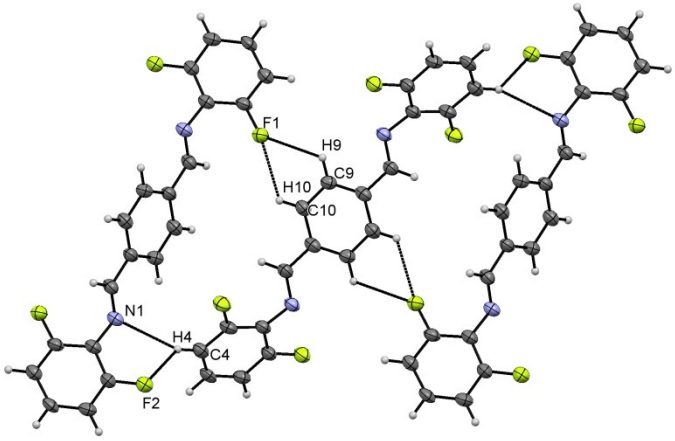
Table 9: a) Intermolecular C−H···F, F···F Interactions and (b) Intermolecular C−F···π Interactions in the Crystallized Compounds**8** and**18.**

(a) Intermolecular C−H···F Interactions

Compd.	**D–H···A**	**D–H/Å**	***D*(D···A)/Å**	***d*(H···A)/Å**	**∠D–H···A/º**	**SYMMETRY**	**SYNTHON**
8	**C4–H4···F2**	1.080	3.333(2)	2.50	133.3	x, $^{3}/_{2}$ –y, –½+z	IVb
	C4–H4···N1	1.080	3.705(3)	2.68	157.8	x, $^{3}/_{2}$–y, –½ +z	IVc
	C10–H10···F1	1.080	3.189(3)	2.47	123.1	x, ½ –y, ½ +z	IVb
	C9–H9···F1	1.080	3.265(3)	2.64	116.4		IVb
18	**C5–H5···N1**	1.080	3.475(3)	2.43	163.4	1+x, ½–y, –½ +z	IVc
	C5–H5···F2	1.080	3.197(4)	2.47	124.0	1+x, ½ –y, –½ +z	IVb
	C4–H4···F2	1.080	3.257(3)	2.62	116.8		IVb
	C9–H9···F1	1.080	3.612(5)	2.55	169.2	1–x, 1–y, 1–z	IVb
	C3–F1···F1–C3	1.359(2)	4.009(4)	2.875(3)	139.7(1)	2-x, -y, -z	IVd

(b) Intermolecular C−F···π Interaction

Compd.	**C−H ···π**	**C···π/Å**	**H···π/Å**	**C−H···π/º**	**SYMMETRY**	**SYNTHON**
9	**C7–F2···Cg1(Ar_F)**	3.957	3.384	105.21	x, ½ -y, ½ +z	IIa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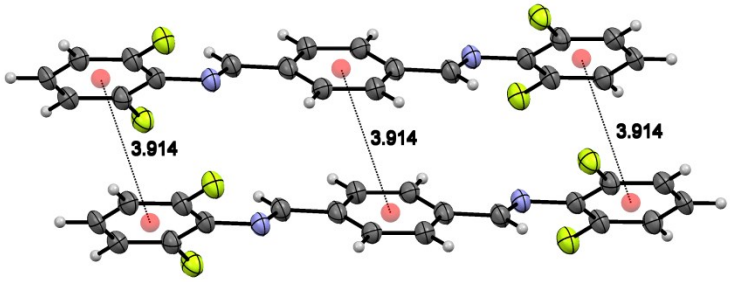
H9
C9
H10
C10
N1
H4
C4
F2

a


3.914
3.914
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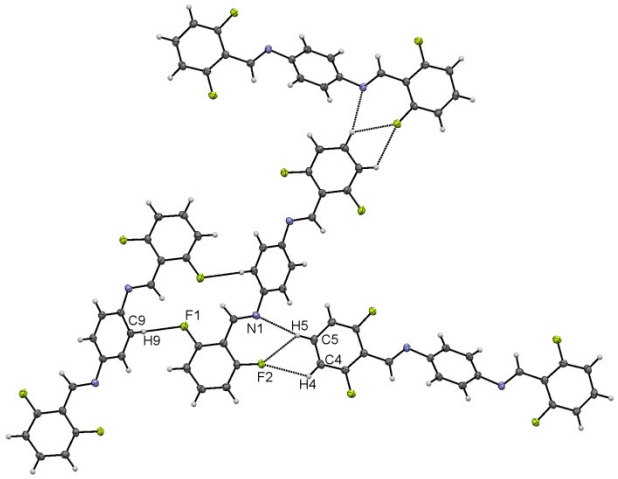
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F1
N1
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C5
C4
F2
H4

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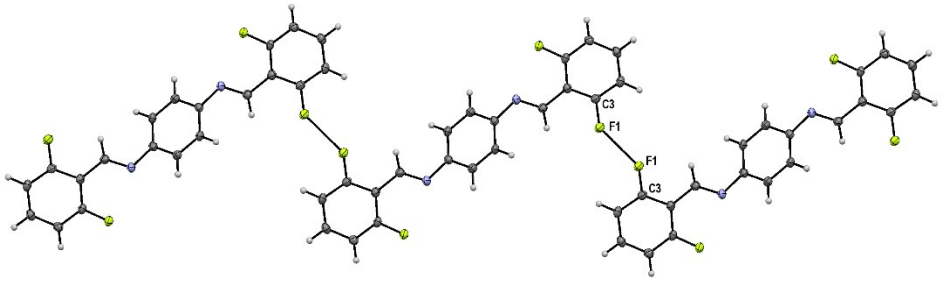

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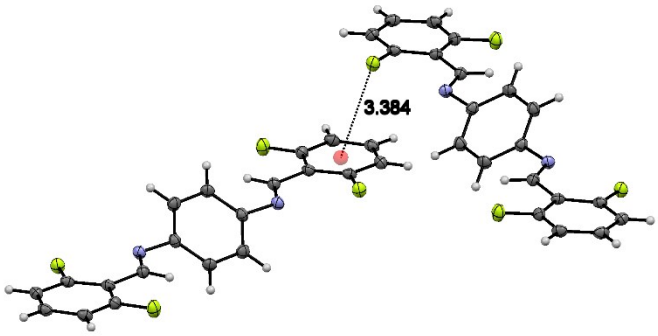

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Figure S14. (a) C–H···F and C–H···N intermolecular hydrogen bonds in **8**; (b) offset stacking in **8**; (c) C–H···F (F2) intermolecular hydrogen bonds in **18**; (d) F···F (F2) interaction in **18**; (e) F···π intermolecular interactions in **18**.

8.8. Structural comparison of the compounds ***9-19***

Structures of compounds **9** and **19** were solved and refined in the monocyclic centrosymmetric $P2_1/n$ and $P\bar{1}$space groups respectively (Table 2). Molecular chains have been identified in **9**formedby the utilization of type I (C5–F2···F2) and type II (C5–F2···F1) F···F contacts, which in turn are connected through C–H···F hydrogen bond involving H20 with F2 and C–H···N hydrogen bond involving H6 with N1(Figure S15a). Two molecules are stacked involving F···π and C=N···π (Figure S15b). Compound **19** forms head to head/tail to tail dimers utilizing trifurcated C–H···F hydrogen bonds, which in turn are connected to each other utilizing another set of C–H···F hydrogen bonds (Figure S15c) forming molecular sheet. These sheets are connected to each other through C–H···F hydrogen bond involving H9 with F2.

Table 10: (a) Intermolecular C−H···F and F···F Interactions and (b) Intermolecular C−F···π and C=N···π Interactions in the Crystallized Compounds **9** and**19.**

(a) Intermolecular C−H···F and F···F Interactions

Compd.	D–H···A	D–H/Å	*D*(D···A)/Å	*d*(H···A)/Å	∠D–H···A/º	SYMMETRY	SYNTHON
9	**C1–H1···F1**	1.080	3.531(2)	2.53	153.2	½– x, $^{3}/_{2}$– y, ½+z	IVa
	C10–H10···F2	1.080	3.328(2)	2.49	133.9	½–x, –½+y, $^{3}/_{2}$–z	IVb
	C6–H6···N1	1.080	3.532(2)	2.63	140.6	½+x, $^{3}/_{2}$–y, ½+z	IVc
	C4–F1···F2–C5	1.353(2)	4.285(2)	2.940(2)	121.4(1)	-1-x, -y,1-z	IVd
	C5–F2···F2–C5	1.346(2)	3.793(2)	2.870(1)	124.1(1)	-1-x, -y,1-z	IVd
19	**C1–H1···F1**	1.080	2.983(2)	2.06	142.1	x, y–1, z	IVa
	C7–H7···F1	1.080	3.178(3)	2.33	134.5		IVb
	C10–H10···F1	1.080	3.653(2)	2.74	142.04		IVb
	C9–H9···F2	1.080	3.118(3)	2.33	128.2	1–x, 1–y, 2–z	IVb
	C6–H6···F2	1.080	3.056(2)	2.18	136.4		IVb

(b) Intermolecular C−F···π and C=N···π Interactions

Compd.	C−H ···π	C···π/Å	H/N···π/Å	C−H/ C=N···π/º	SYMMETRY	SYNTHON
9	**C5–F2···Cg1(Ar_F)**	3.808	3.397	97.23	2+x, y, z	IIa
	C1=N1···Cg1(Ar_F)	3.517	3.426	83.40	2+x, y, z	V
	C1=N1···Cg1(Ar_H)	3.448	3.576	73.90	2+x, y, z	VI

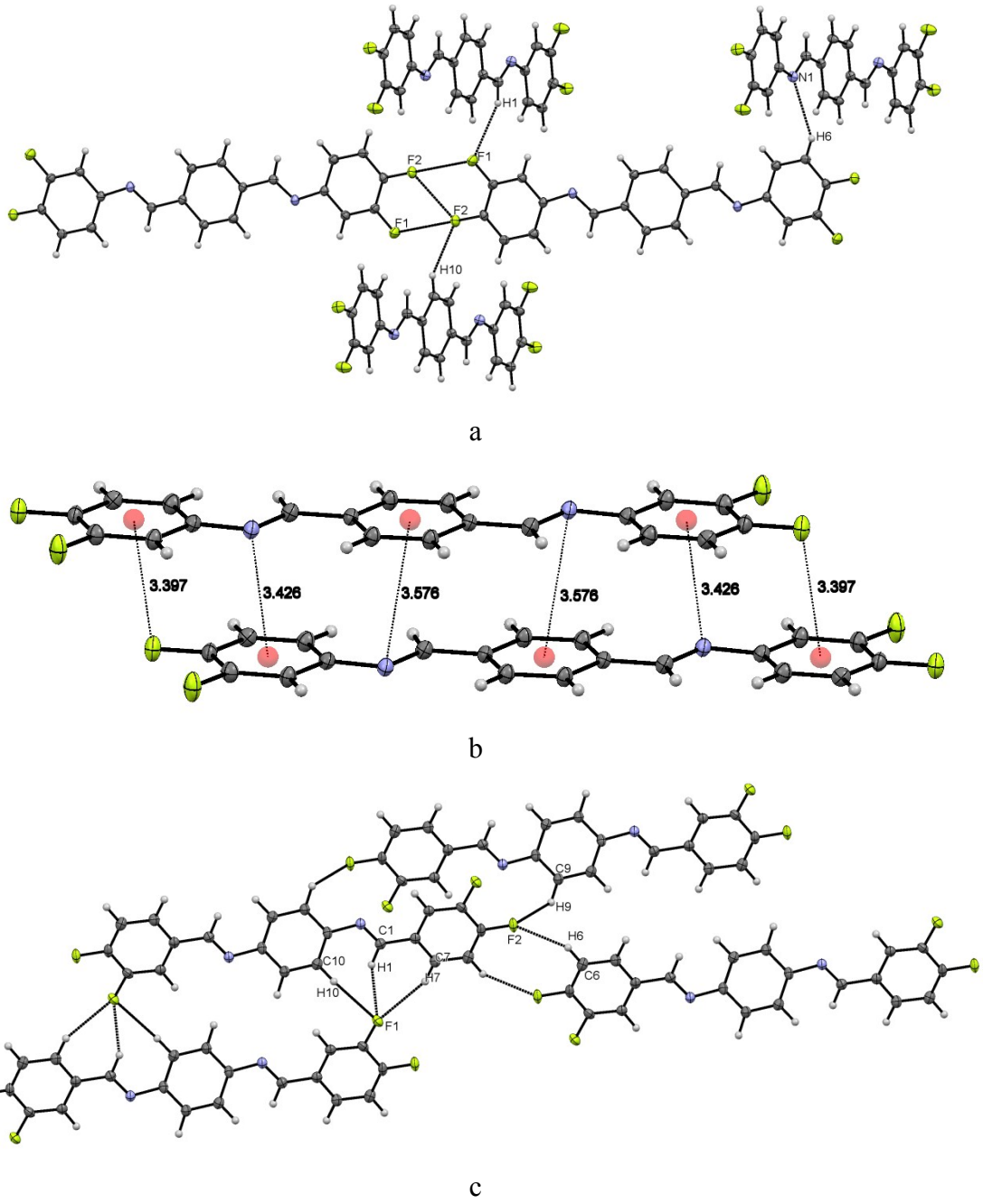


Figure S15. (a) C–H···F intermolecular hydrogen bonds in **9**;(b) molecules are stacked involving F···π and C=N···π intermolecular interactions in **9**; (c)Molecular packing showing interactions as dashed lines in **19**.

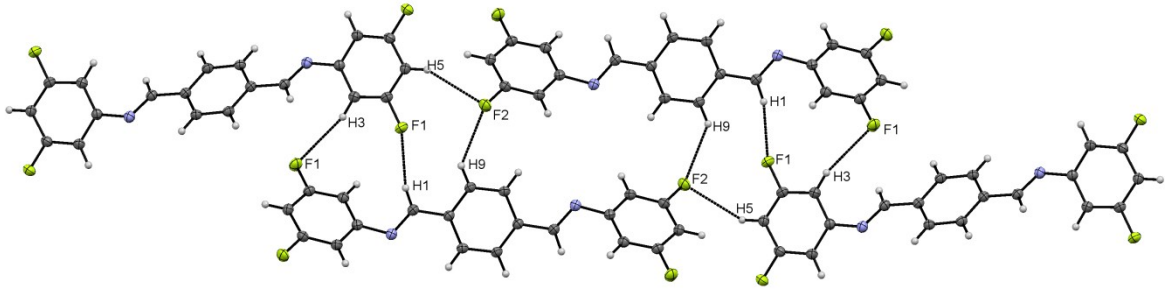
*8.9. Structural comparison of the compounds **10-20***

Structures of compounds **10** and **20** were solved and refined in the monocyclic centrosymmetric *$P2_1/n$ and $P2_1/c$* space groups respectively (Table 2) with different unit cell parameters. While **10** has a half molecule in the asymmetric unit, **20** has two half molecules in the asymmetric unit connected by weak C–H···F hydrogen bonds (between H5 and F3). The molecules in **10** forms tetrameric units involving three different C–H···F hydrogen bonds (Figure S16a). These hydrogen bonds propagate in the packing forming a complex 3D network of molecules. These tetrameric units are further connected to another set of parallel tetrameric units involving C3–H3···F1 hydrogen bonds. The distance between the two-parallel molecules in **10** is 3.75Å (Figure S16b). Among the two half molecules present in the asymmetric unit of **20**, one is centered around the origin of the unit cell (inversion center) and the other is centered around the inversion point located at the center of the *ab* face there by aligned in two different directions in the lattice. The molecules form trimetric units through three different C–H···F hydrogen bonds forming a 14-membered ring and these trimetric units propagate in the *ac* plane in the lattice (Figure S16c). These set of trimetric units are once again connected to another set of similar trimetric units involving other C–H···F hydrogen bonds (C1A–H1A···F2A and C5B–H5B···F1A) in a different direction. The distance between the two-parallel molecules in **20** is 3.81Å (Figure S16d) In both the compounds, fluorine at meta-position interacts with the imine hydrogen.

Table 11: intermolecular interaction metrics of hydrogen bonds of compounds **10** and **20**

Compd.	D–H···F	D–H/Å	*D*(D···F)/Å	*d*(H···F)/Å	∠D–H···F/º	SYMMETRY	SYNTHON
10	**C9–H9···F2**	1.080	3.438(0)	2.61	133.0	–1+ x, y, z	IVb
	C1–H1···F1	1.080	3.406(1)	2.37	160.2	½–x, –½+y, ½–z	IVa
	C3–H3···F1	1.080	3.718(1)	2.66	162.2		IVb
	C5–H5···F2	1.080	3.492(0)	2.68	131.6	$^3/_2$ – x, ½ + y, ½–z	IVb
20.	**C1B–H1B···F2B**	1.080	3.559(3)	2.56	153.3	x, $^3/_2$–y, –½ +z	IVa
	C1A–H1A···F2A	1.080	3.524(2)	2.53	152.4		IVa

	C5A–H5A···F1B	1.080	3.369(3)	2.36	154.4	x, –1+y, z	IVb
	C5B–H5B···F1A	1.080	3.404(3)	2.54	136.8	x, ½ –y, ½ +z	IVb



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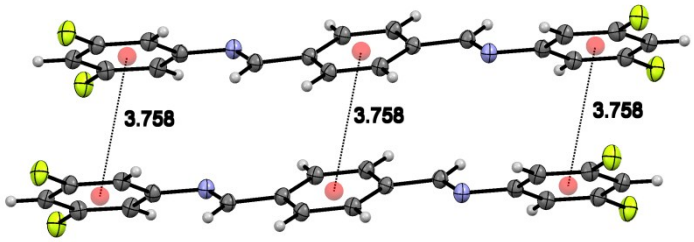

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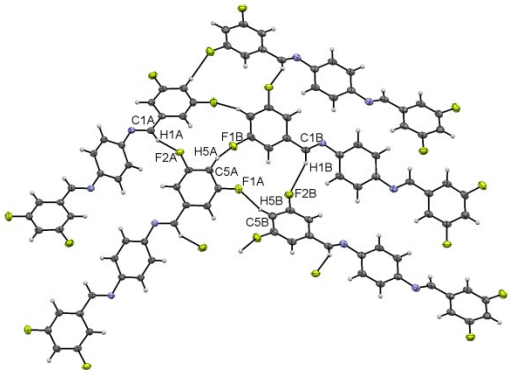

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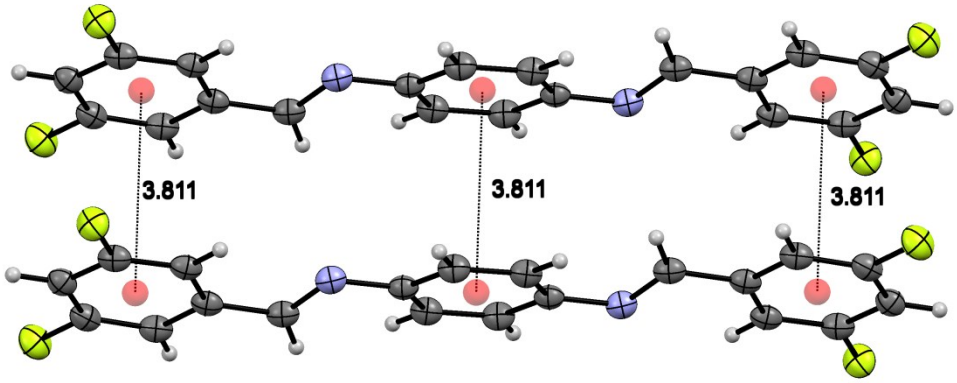
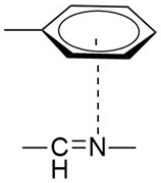


d

Figure S16: (a) tetrameric units involving three different C–H···F hydrogen bonds in **10**;(b) stacking in **10**;(c) trimetric units through three different C–H···F hydrogen bonds forming a 14-membered ring in **20**; (d) stacking in **20**.

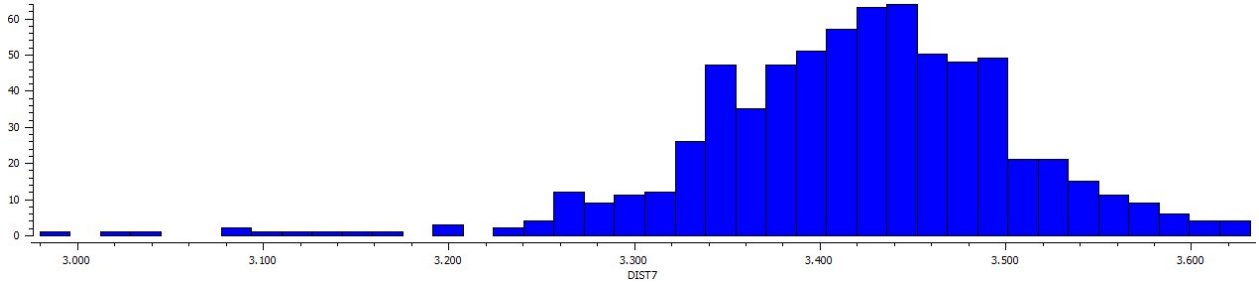
CCDC Search on C=N···π interaction

CCDC search was done on synthon VI showing C=N···π interaction, by defining contact between imine N and centroid of aromatic ring in the range of 2-4Å with the restriction that the distance between each C atom of the ring to the N falling in the range 2-4 Å. The search was restricted to organic structures only, without powder structures, without disorder and without any error. This search resulted in to 599 hits.



VI

The histogram of the distance from the centroid to the imine N is shown below from this search.



This indicates that there is a preference for this interaction near 3.4-3.5 Å distance between the centroid and the imine N with the mean at 3.420 Å and variance of 0.007.