Supplementary information

Synthesis, Crystal Structure and Supramolecular Understanding of 1,3,5-*Tris*(1-phenyl-1*H*-pyrazol-5-yl)benzenes

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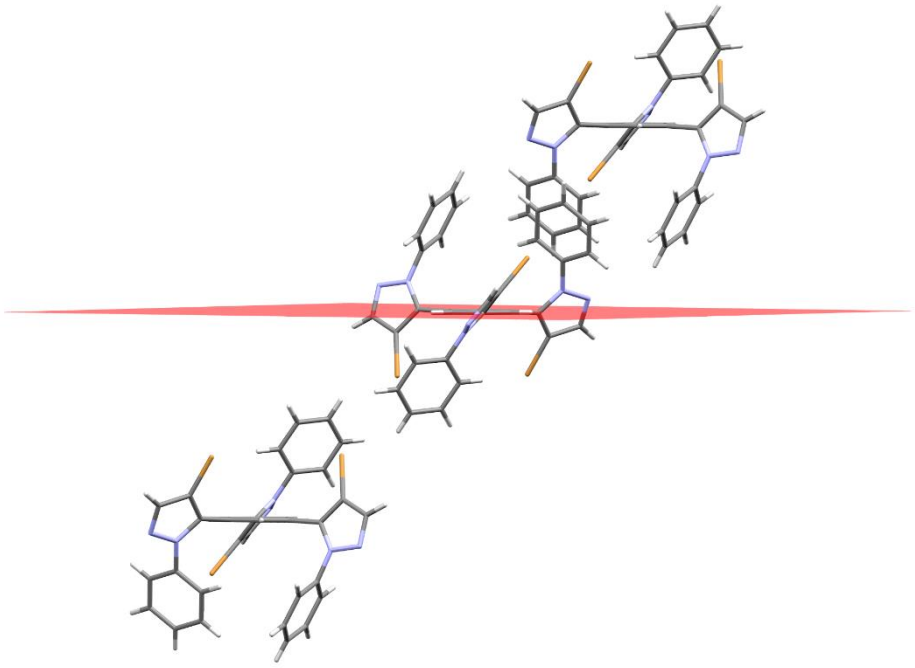
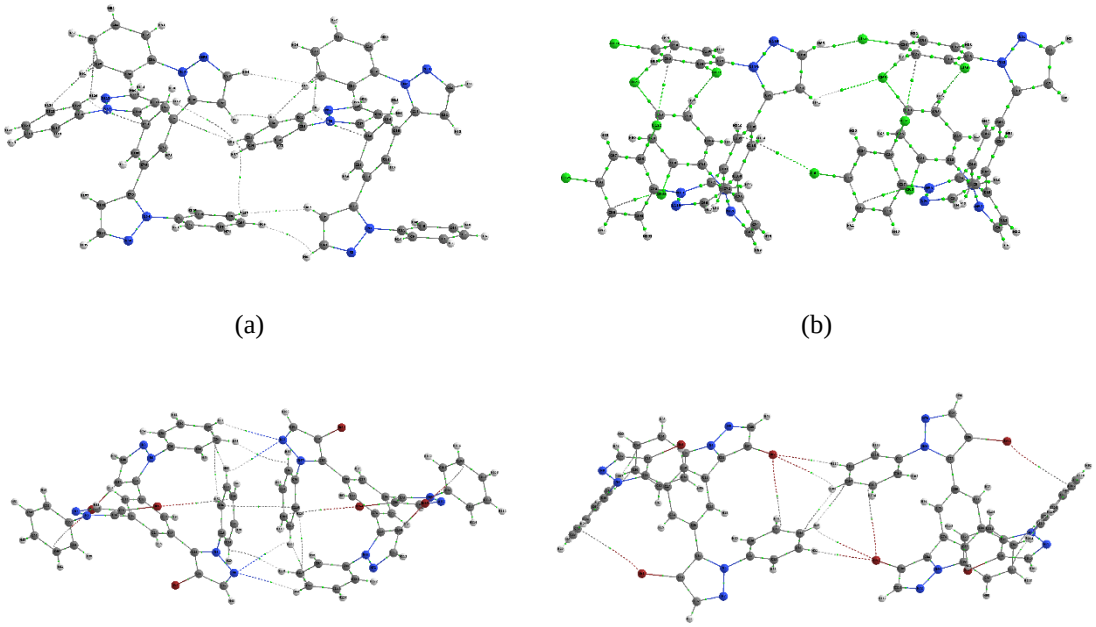


Figure S1. 1D arrangement for compound **9b**.



(a) (b)

(c) (d)

Figure S2. BCPs for the dimers involved in the 1D arrangement for compounds **5** (a), **7** (b), and **9b** (c, d).

Table S1. Data collection and structure refinement for structures **5**, **7** and **9b**.

Compound	(**5**)	(**7**)	(**9b**)
Crystal data			
Chemical formula	$C_{33}H_{24}N_6$	$C_{33}H_{18}Cl_6N_6$	$C_{33}H_{21}Br_3N_6$
CCDC number	1501480	1484377	1484578
M_r	504.58	711.23	741.26
Crystal system, space group	Monoclinic, $P\,2_1/n$	Monoclinic, $P\,2_1/n$	Triclinic, $P\bar{1}$
Temperature (K)	293	293	293
a, *b*, *c* (Å)	8.811(7), 31.67(2), 9.691(9)	10.3914(2), 31.6622(2), 10.5723(2)	8.7732(3), 10.8040(3), 16.7315(5)
α, β, γ (°)	90, 97.85, 90	90, 110.8580(10), 90	76.0570(10), 87.256(2), 79.5720(10)
V (Å^3)	2679(4)	3250.48(12)	1513.74(8)
Z	4	4	2
F(000)	1056	1440	732
D_x (Mg m^{-3})	1.251	1.453	1.626
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.076	0.56	4.03
Crystal size (mm)	0.434 x 0.233 x 0.084	0.520 x 0.490 x 0.220	0.506 x 0.210 x 0.164
Data collection			
Diffractometer	X8 APEX II	X8 APEX II	X8 APEX II
Absorption correction (Coppens *et al.*, 1965)	Gaussian	Gaussian	Gaussian
T_{min}, T_{max}	0.980, 0.994	0.873, 0.908	0.435, 0.639
Reflections collected, unique	44903, 5466	50606, 7215	39956, 6708
R_{int}	0.123	0.035	0.052
θ_{max} (°)	26.52	27.16	27.18
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.061, 0.110, 1.00	0.082, 0.249, 1.06	0.039, 0.087, 1.02
N°. of reflections	5466	7215	6708
N°. of parameters	353	406	379
$\Delta\varrho_{max}$, $\Delta\varrho_{min}$ (e Å^{-3})	0.173, −0.190	2.563[a], −0.408	0.440,-0.749

[a] Highest peak: 2,536 (e Å^{-3}) at 0.6044, -0.0557, 0.8186 [0.761 Å from H16C].

Table S2. QTAIM data of intramolecular interactions of compounds **5**, **7**, and **9b**.

Comp.	Interaction	ρ (a.u.)	$\nabla^2\rho$ (a.u.)	G (a.u.)	V (a.u)	BPL (Å)	ε
5	$CH_B\cdots\pi_{ph}$	+0.001709	+0.005703	+0.001064	-0.000703	+7.029502	+1.348943
	$CH_B\cdots\pi_{ph}$	+0.002334	+0.007711	+0.001482	-0.001036	+6.764544	+0.735388
	$CH_B\cdots\pi_{bz}$	+0.008895	+0.036788	+0.006966	-0.004735	+5.741479	+0.940599
7	$CH_A\cdots Cl_C$	+0.002861	+0.009384	+0.001869	-0.001392	+6.295619	+0.069233
	$Cl_B\cdots\pi_{phA}$	+0.006076	+0.017295	+0.003573	-0.002822	+6.775708	+1.182899
	$Cl_A\cdots\pi_{phC}$	+0.006672	+0.019205	+0.003951	-0.003100	+6.850917	+1.548697
	$Cl_C\cdots\pi_{phB}$	+0.007134	+0.021533	+0.004408	-0.003432	+6.503711	+1.295082
9b	$CH_B\cdots\ \pi_{PhC}$	+0.002607	+0.008188	+0.001588	-0.001129	+6.239854	+0.810114
	$Br_C\cdots\ \pi_{PhA}$	+0.003151	+0.007538	+0.001608	-0.001331	+7.876611	+1.152721
	$CH_B\cdots\pi_{PhC}$	+0.003635	+0.012417	+0.002331	-0.001559	+5.851308	+0.247889
	$Br_A\cdots\ \pi_{PhB}$	+0.004203	+0.010958	+0.002338	-0.001936	+7.214326	+2.528119

Table S3. Geometric data of intramolecular interactions of compounds **5**, **7**, and **9b**.

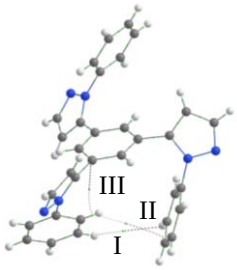
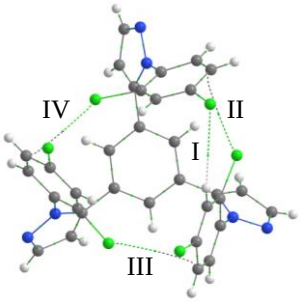
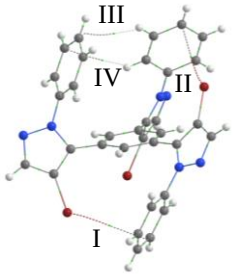
Comp.	Molecular Structure	Intramolecular Interaction	Atom-atom distance (Å)	Interaction angle (°)	Atom-centroid distance (Å)
5		I $CH_B\cdots\pi_{ph}$	3.448	130.56	4.213
		II $CH_B\cdots\pi_{ph}$	3.362	129.51	3.411
		III $CH_B\cdots\pi_{bz}$	2.684	108.43	3.218
7		I $CH_A\cdots Cl_C$	3.294	156.89	-
		II $Cl_B\cdots\pi_{phA}$	3.445	131.58	3.609
		III $Cl_A\cdots\pi_{phC}$	3.469	141.54	3.688
		IV $Cl_C\cdots\pi_{phB}$	3.377	142.53	3.456
9b		I $Br_C\cdots\pi_{PhA}$	4.006	123.71	4.326
		II $Br_A\cdots\pi_{PhB}$	3.778	151.45	3.789
		III $CH_B\cdots\pi_{PhC}$	2.993	142.63	3.788
		IV $CH_B\cdots\pi_{PhC}$	3.252	135.12	3.560

Table S4. QTAIM data of intermolecular interactions for the dimers involved in the 1D arrangement for compounds **5** (a), **7** (b), and **9b** (c, d).

Comp.	Interaction	ρ (au)	∇2ρ (a.u.)	ε	K (a.u.)	V (a.u.)	G (a.u.)	BPL (Å)
5	C13C-H13C···H4C-C4C	0.000625	+0.002109	0.385237	-0.000166	-0.000196	+0.000361	7.917284
	C14C-H14C···H13A-C13A	0.001150	+0.003850	10.87582	-0.000286	-0.000391	+0.000677	7.159302
	C4A-H4A···H13A-C13A	0.001691	+0.007862	0.228573	-0.000606	-0.000753	+0.001359	5.405544
	C15B-H15B···C3B-H3B	0.001810	+0.008470	0.069926	-0.000649	-0.000820	+0.001469	5.340153
	C3A-H3A···H14A-C14A	0.002610	+0.010479	1.451658	-0.000755	-0.001110	+0.001865	5.903538
	C14C-H14C···C51B(π)	0.003203	+0.009717	0.835703	-0.000487	-0.001455	+0.001942	6.392775
	C15C-H15C···H4B-C4B	0.003941	+0.016360	0.367039	-0.001078	-0.001934	+0.003012	5.003101
	Total	0.015030						
7	C4A-H4A···Cl2C	0.002102	+0.007701	0.396783	-0.000507	-0.000912	+0.001418	6.755820
	C3A-H3A···Cl2A	0.002453	+0.008534	0.872875	-0.000557	-0.001020	+0.001577	7.028604
	Cl2B···C51A(πBz)	0.005733	+0.016697	2.503532	-0.000721	-0.002732	+0.003453	7.029595
	Total	0.010288						
9b (dimer 1)	C14C-H14C···N2B	0.001974	+0.008350	0.064986	-0.000589	-0.000909	+0.001498	6.305415
	C14C-H14C···N2B	0.001974	+0.008349	0.065009	-0.000589	-0.000909	+0.001498	6.305415
	C15B-H15B···N2B	0.003039	+0.012084	0.473979	-0.000777	-0.001467	+0.002244	6.126470
	C15B-H15B···N2B	0.003039	+0.012084	0.473798	-0.000777	-0.001467	+0.002244	6.126470
	C15C-H15C···C12B	0.003828	+0.013741	0.602985	-0.000879	-0.001678	+0.002557	6.014947
	C16B···C16B	0.003576	+0.008290	3.038742	-0.000278	-0.001517	+0.001795	7.049161
	C15C-H15C···C12B	0.003827	+0.013740	0.603086	-0.000879	-0.001678	+0.002556	6.015115
	Total	0.021257						
9b (dimer 2)	C13A-H13A···Br3C	0.004336	+0.015844	0.238205	-0.000914	-0.002133	+0.003047	6.078877
	C13A-H13A···Br3C	0.004336	+0.015844	0.238206	-0.000914	-0.002133	+0.003047	6.078877
	C14A-H14A···Br3C	0.003426	+0.011924	1.270349	-0.000714	-0.001553	+0.002267	6.625252
	C14A-H14A···Br3C	0.003426	+0.011924	1.270401	-0.000714	-0.001553	+0.002267	6.625252
	Total	0.015524						

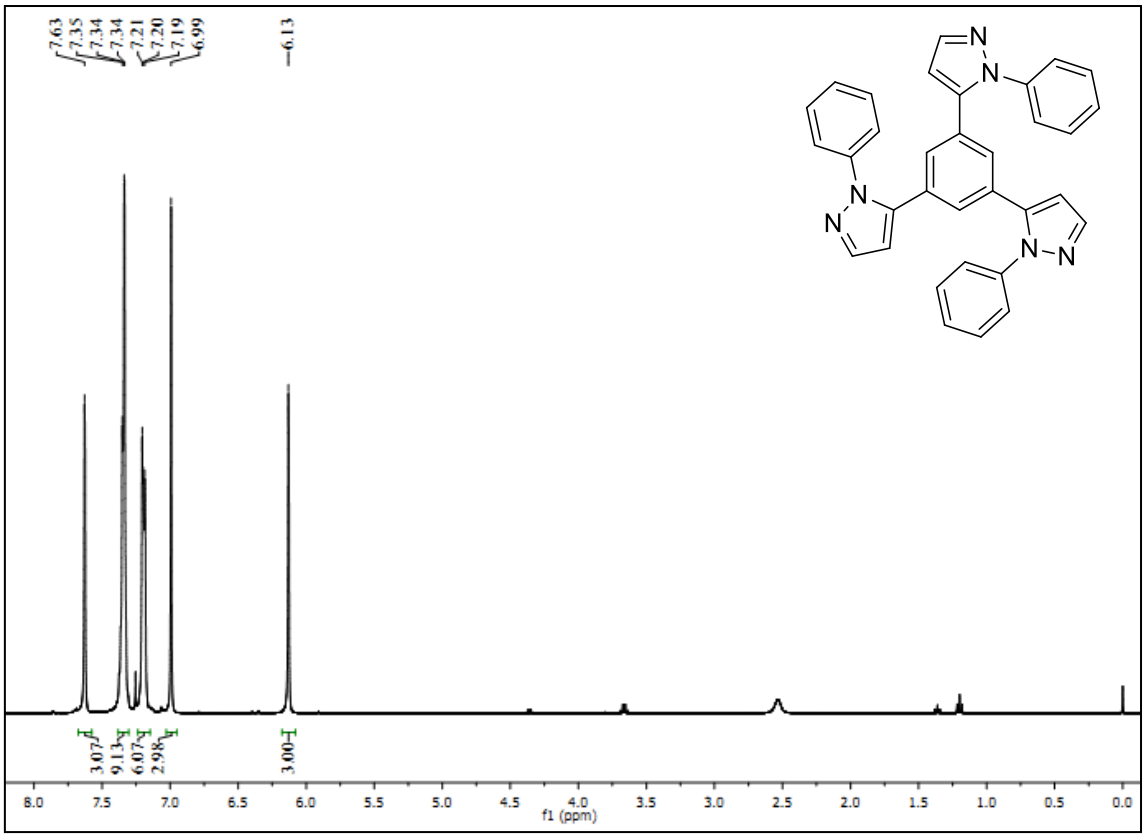


Figure S3. [1]H NMR spectrum of 1,3,5-tris(1-phenyl-1H-pyrazol-5-yl)benzene **5**.

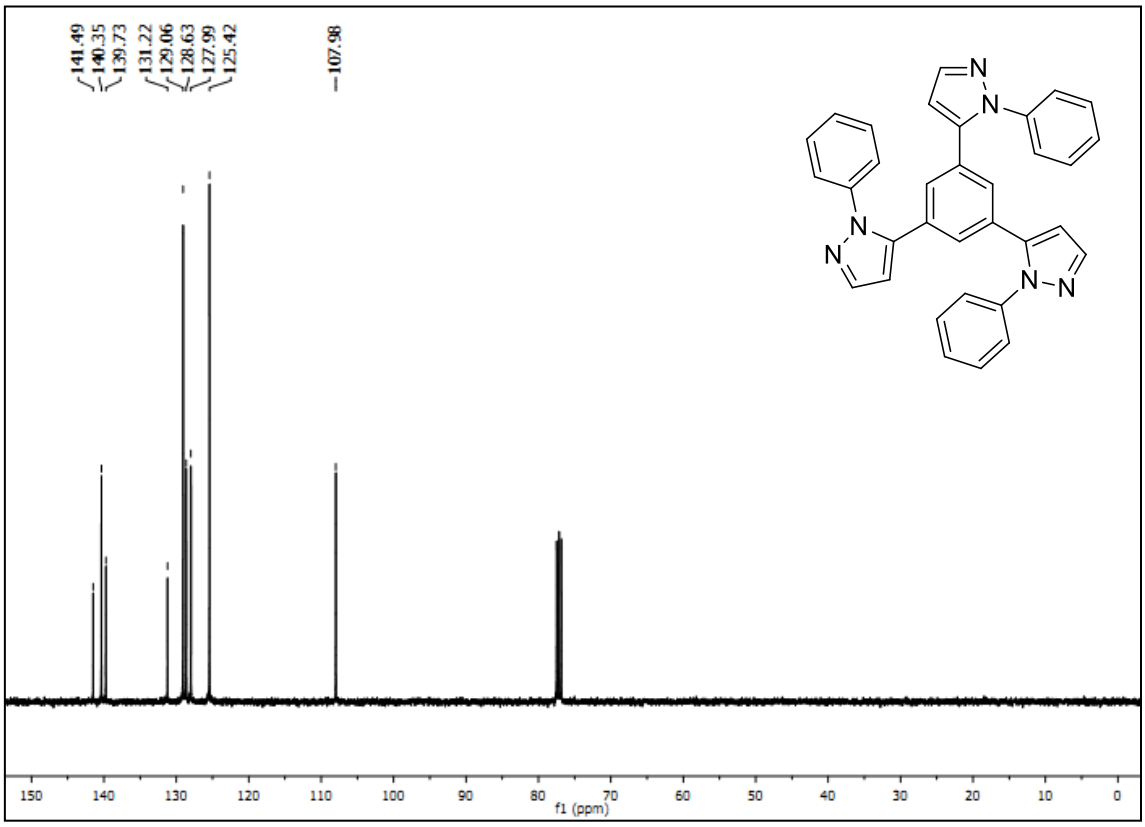


Figure S4. [13]C NMR spectrum of 1,3,5-tris(1-phenyl-1H-pyrazol-5-yl)benzene **5**.

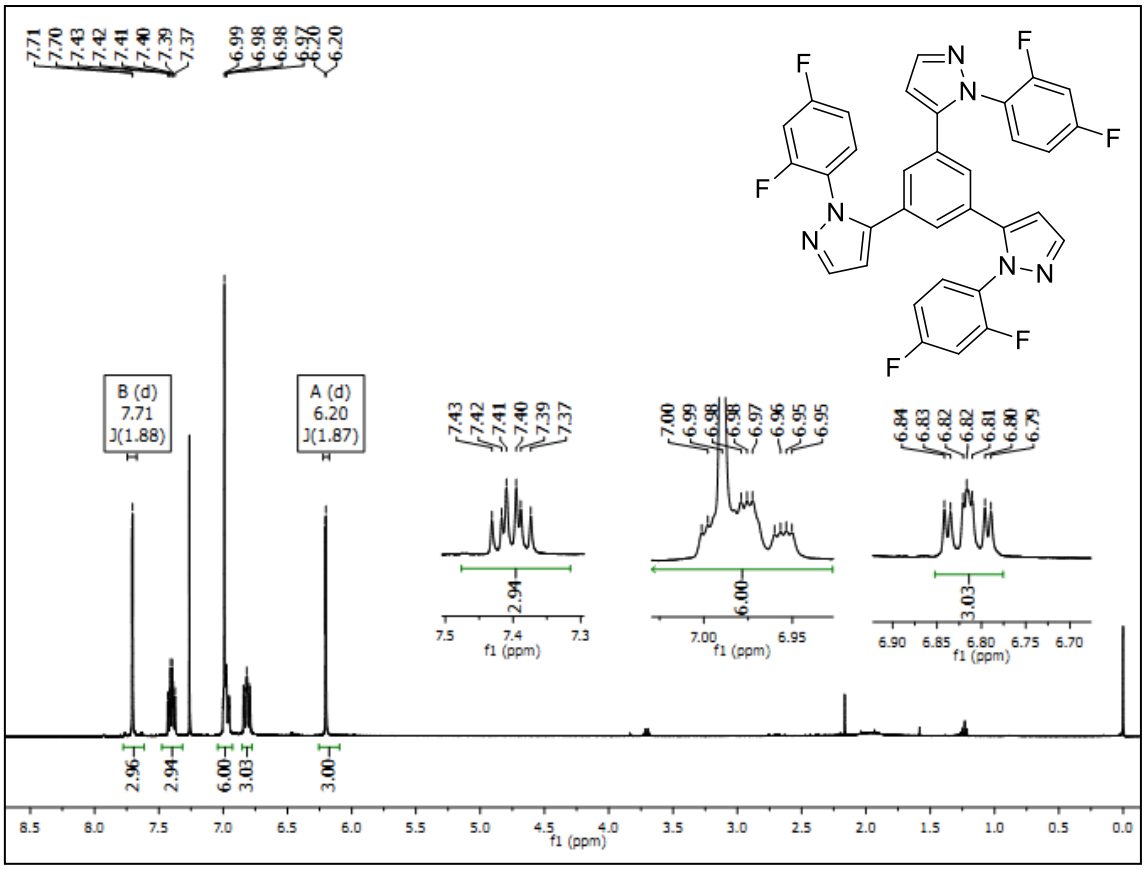


Figure S5. [1]H NMR spectrum of 1,3,5-tris(1-(2,4-difluorophenyl)-1H-pyrazol-5-yl)benzene **6**.

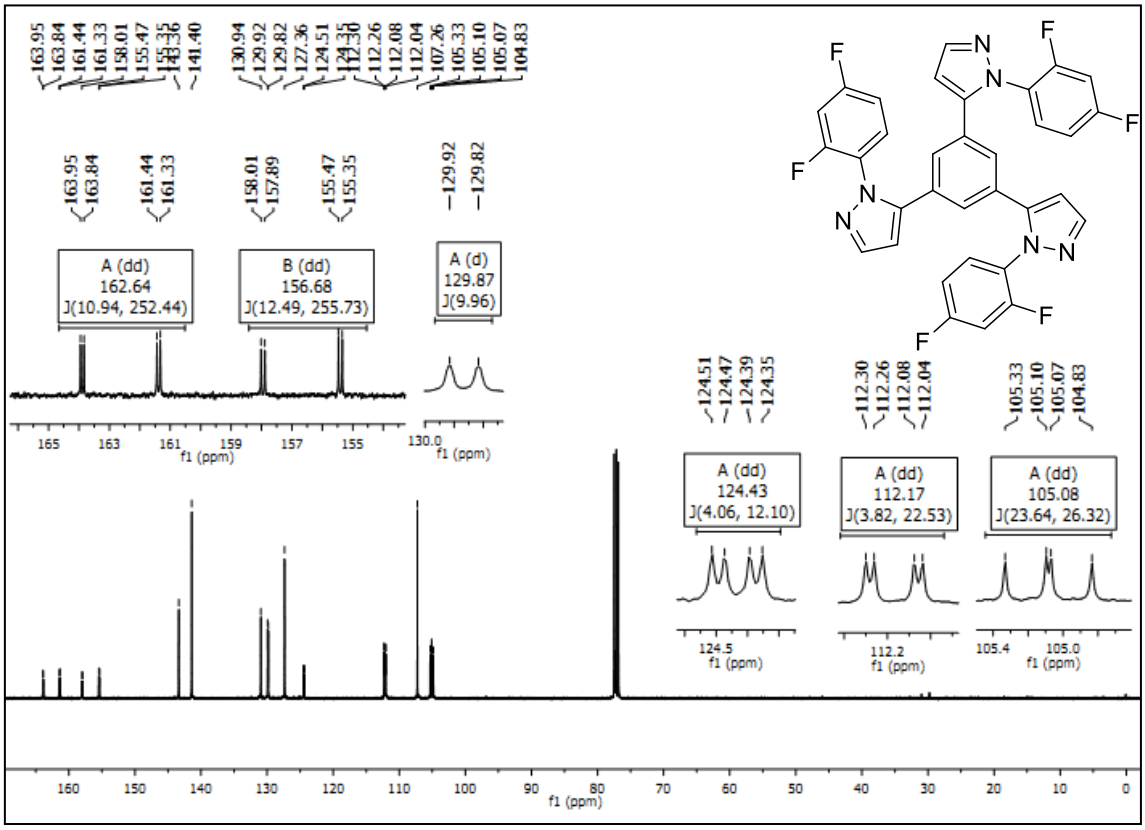


Figure S6. [13]C NMR spectrum of 1,3,5-tris(1-(2,4-difluorophenyl)-1H-pyrazol-5-yl)benzene **6**.

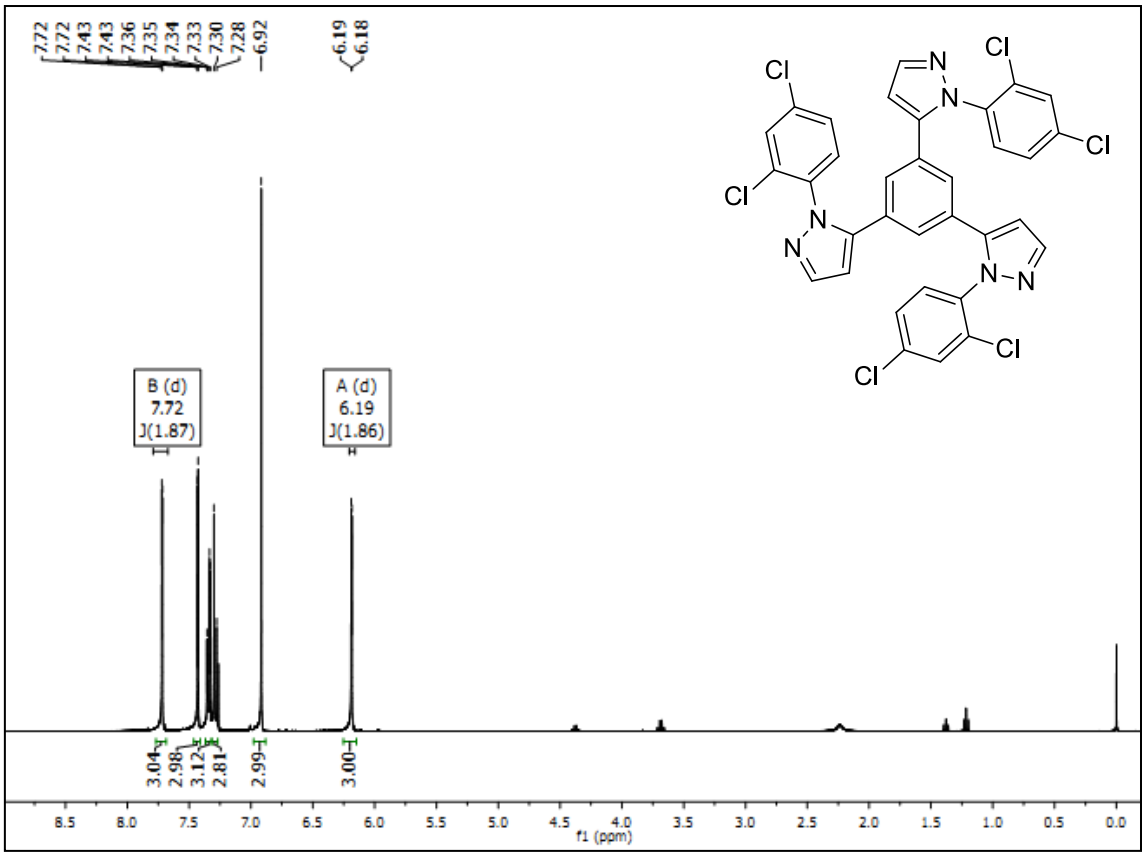


Figure S7. [1]H NMR spectrum of 1,3,5-tris(1-(2,4-dichlorophenyl)-1H-pyrazol-5-yl)benzene **7**.

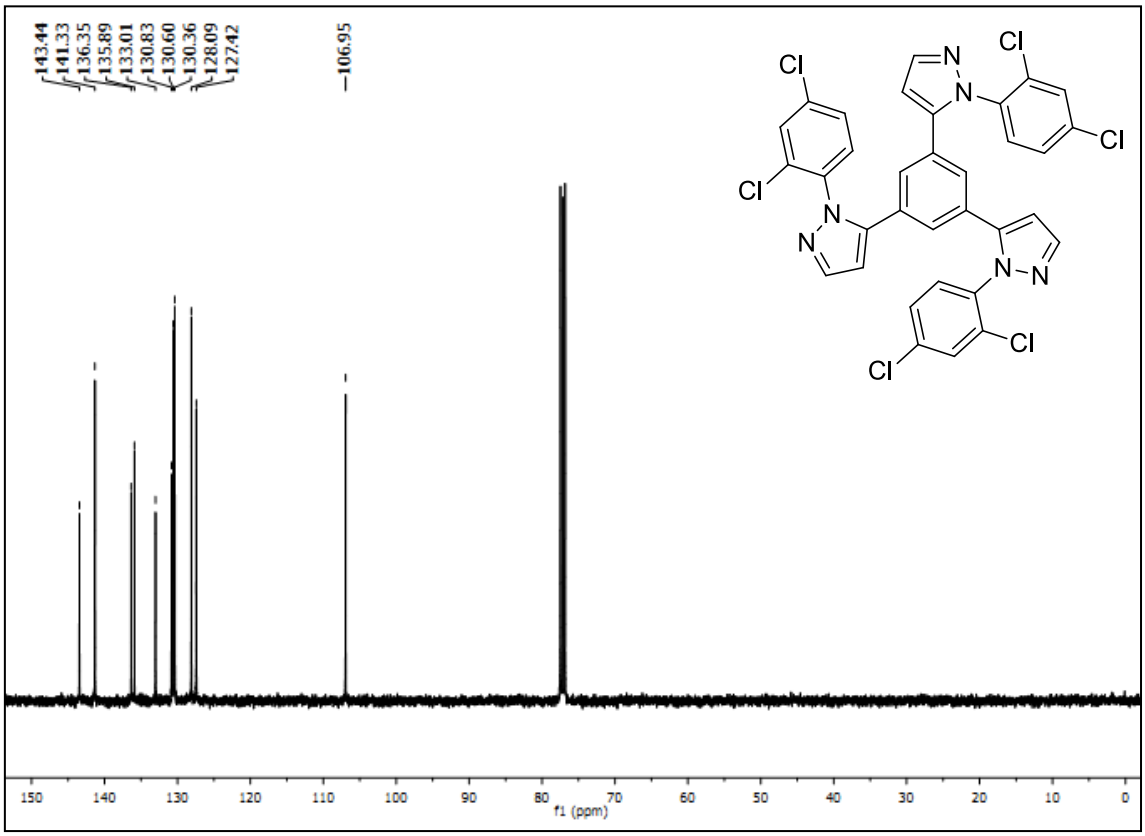


Figure S8. [13]C NMR spectrum of 1,3,5-tris(1-(2,4-dichlorophenyl)-1H-pyrazol-5-yl)benzene **7**.

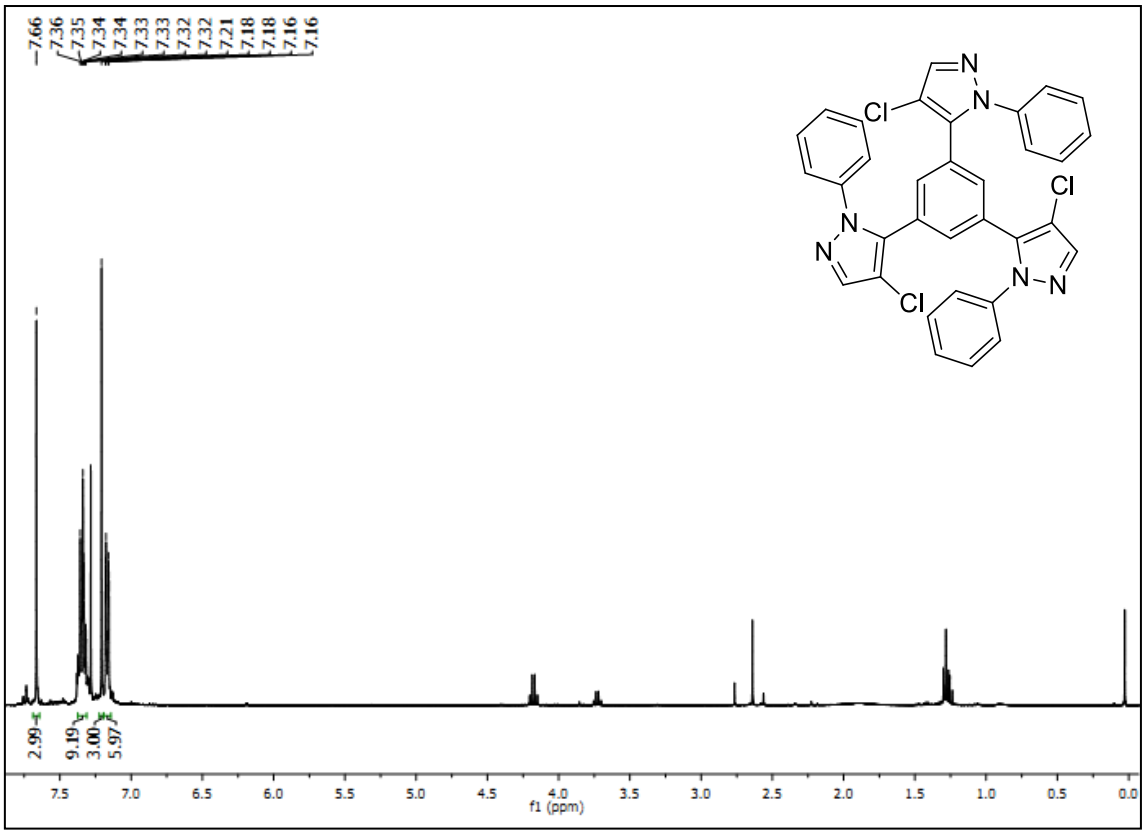


Figure S9. [1]H NMR spectrum of 1,3,5-tris(4-chloro-1-phenyl-1H-pyrazol-5-yl)benzene **9a**.

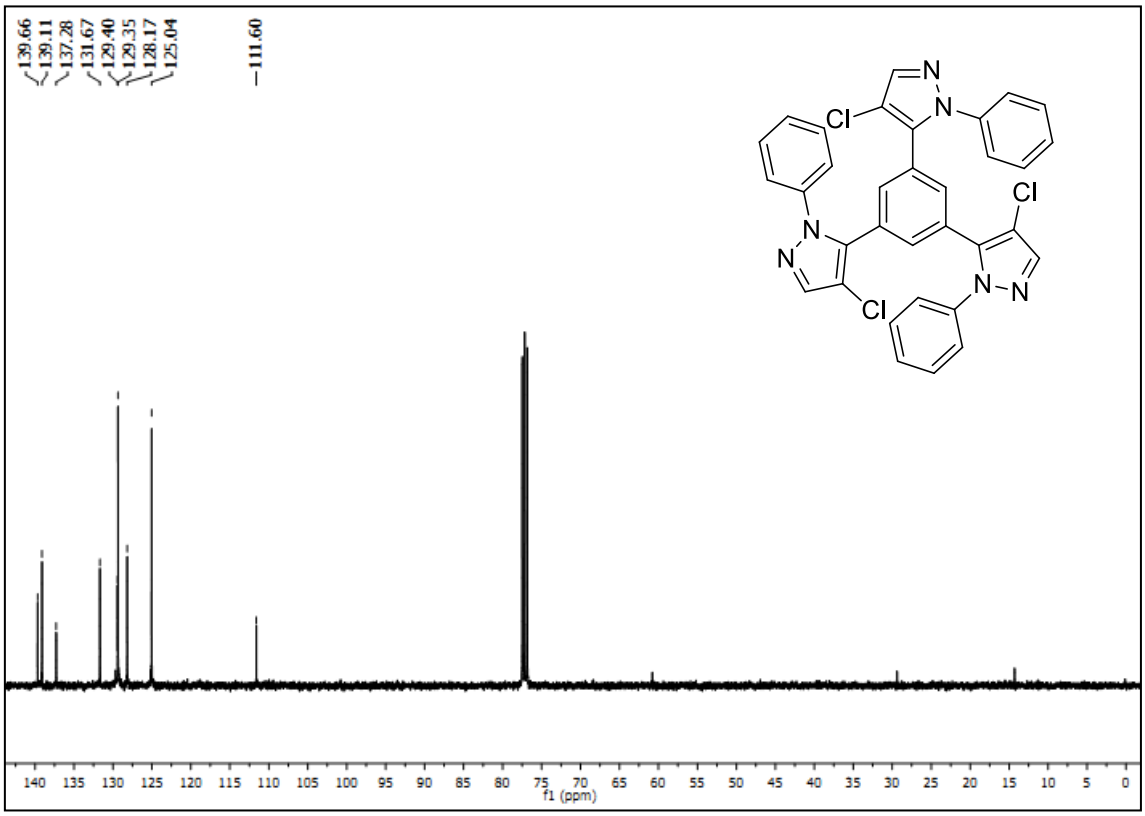


Figure S10. [13]C NMR spectrum of 1,3,5-tris(4-chloro-1-phenyl-1H-pyrazol-5-yl)benzene **9a**.

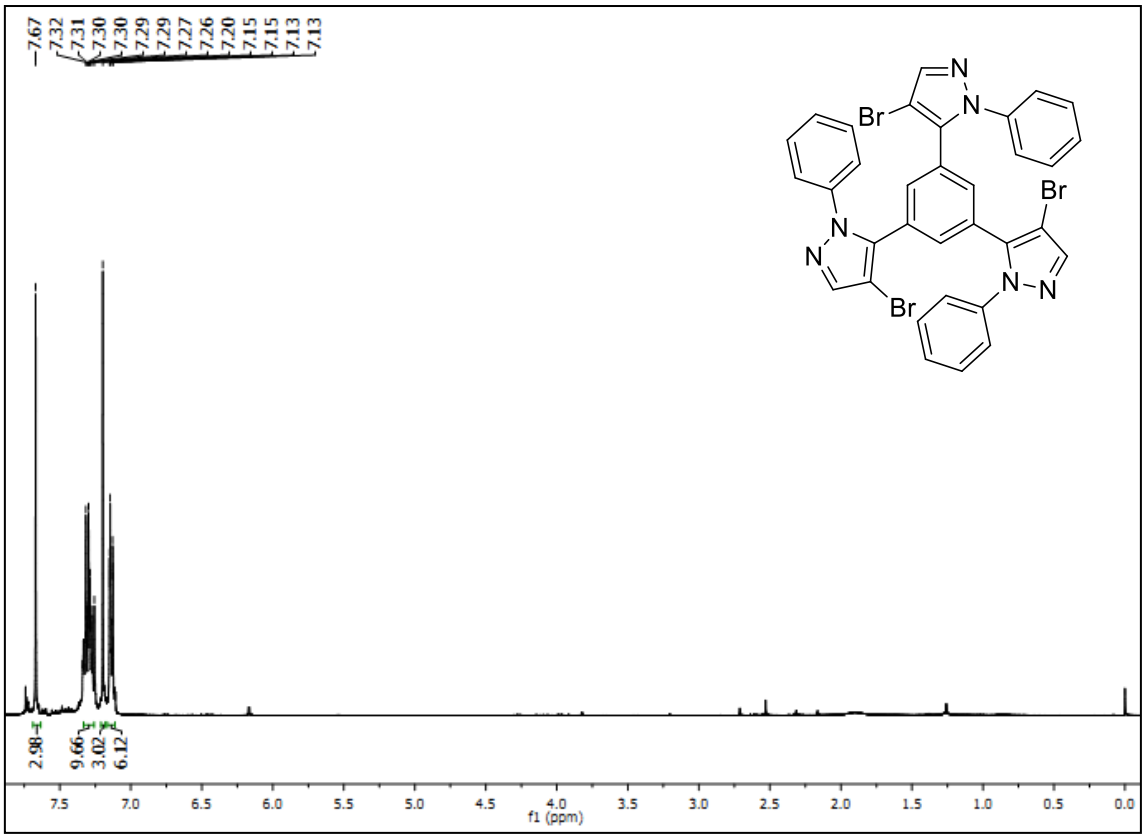


Figure S11. ^{1}H NMR spectrum of 1,3,5-tris(4-bromo-1-phenyl-1H-pyrazol-5-yl)benzene **9b**.

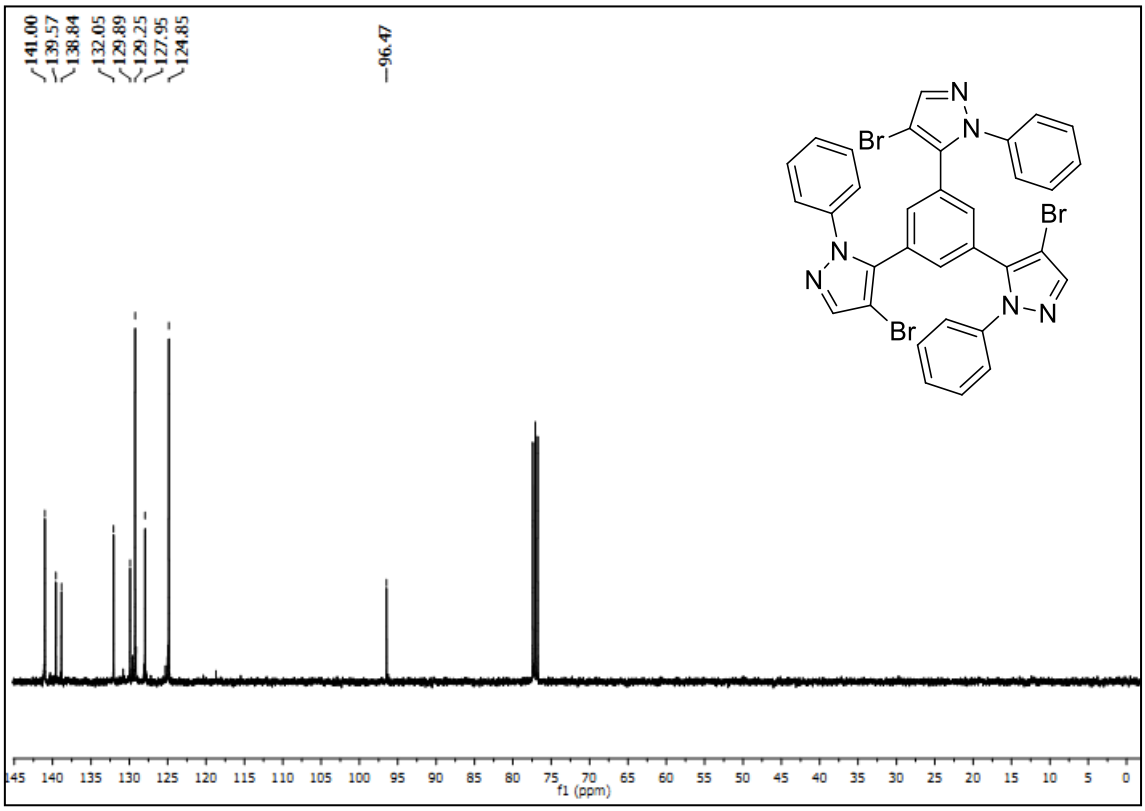


Figure S12. ^{13}C NMR spectrum of 1,3,5-tris(4-bromo-1-phenyl-1H-pyrazol-5-yl)benzene **9b**.

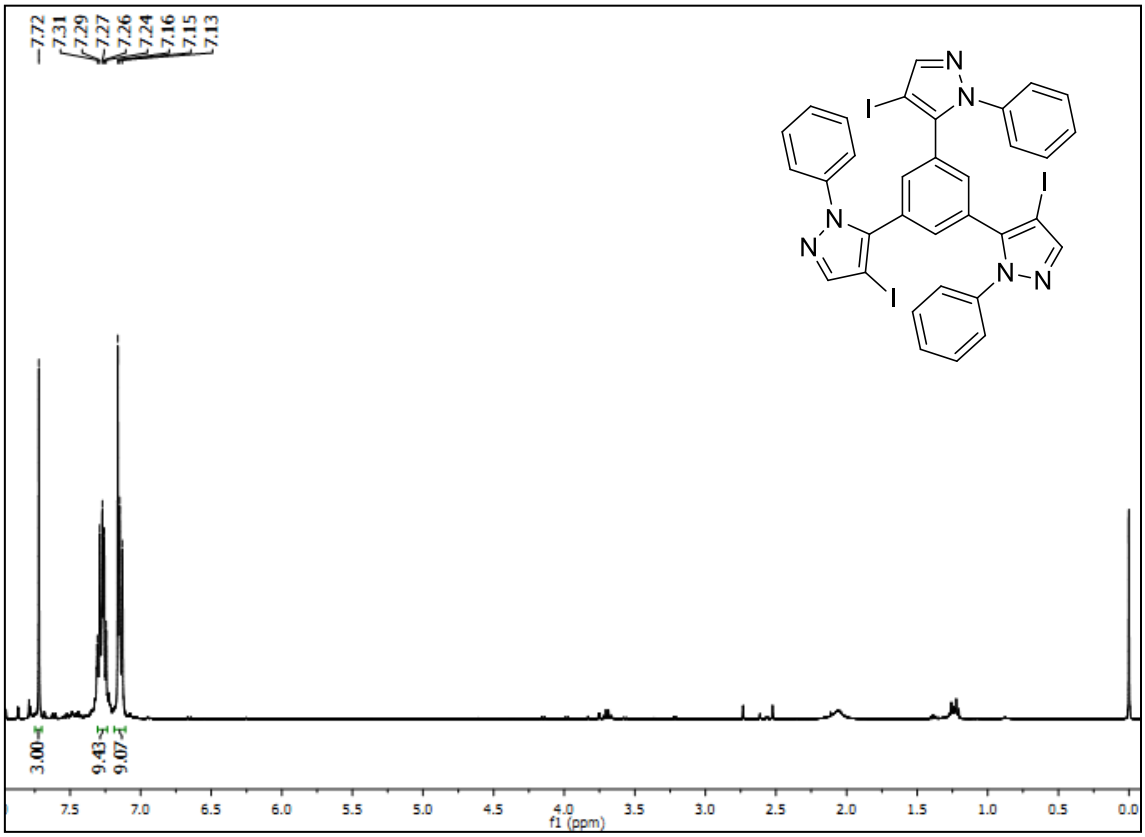


Figure S13. [1]H NMR spectrum of 1,3,5-tris(4-iodo-1-phenyl-1H-pyrazol-5-yl)benzene **9c**.

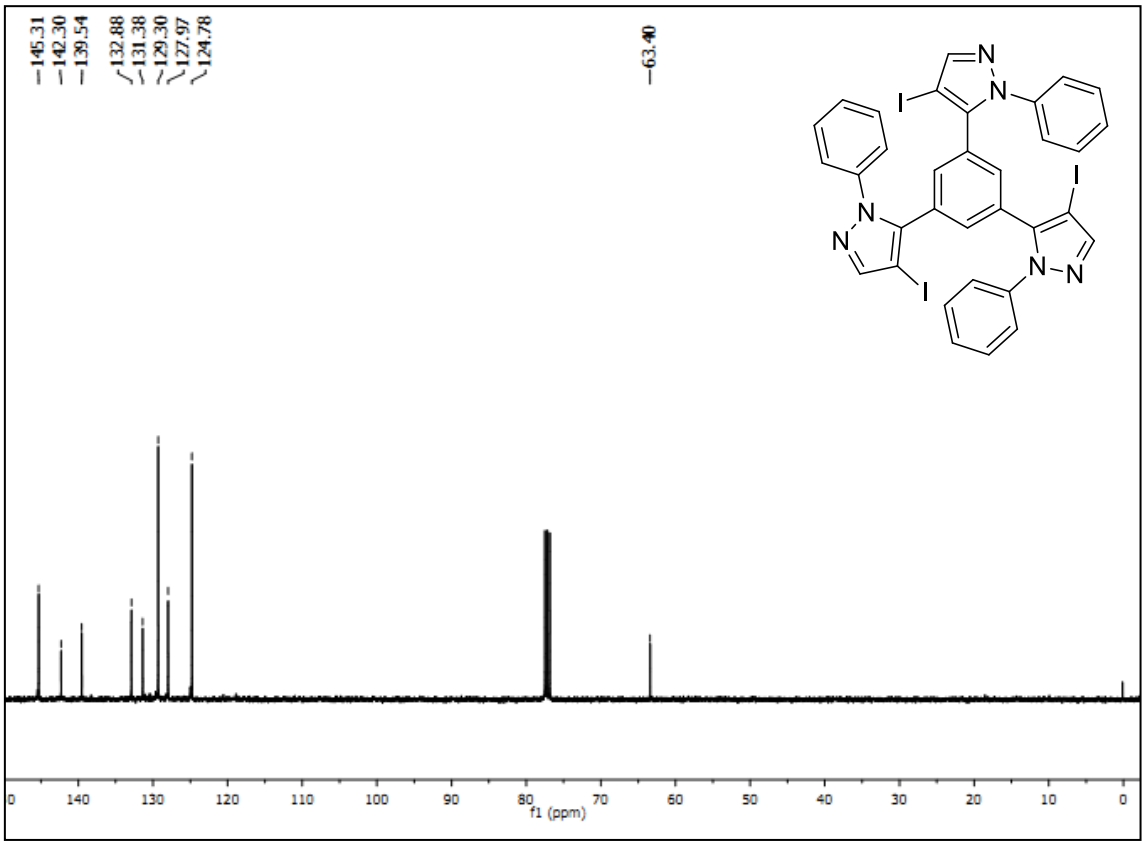


Figure S14. [13]C NMR spectrum of 1,3,5-tris(4-iodo-1-phenyl-1H-pyrazol-5-yl)benzene **9c**.

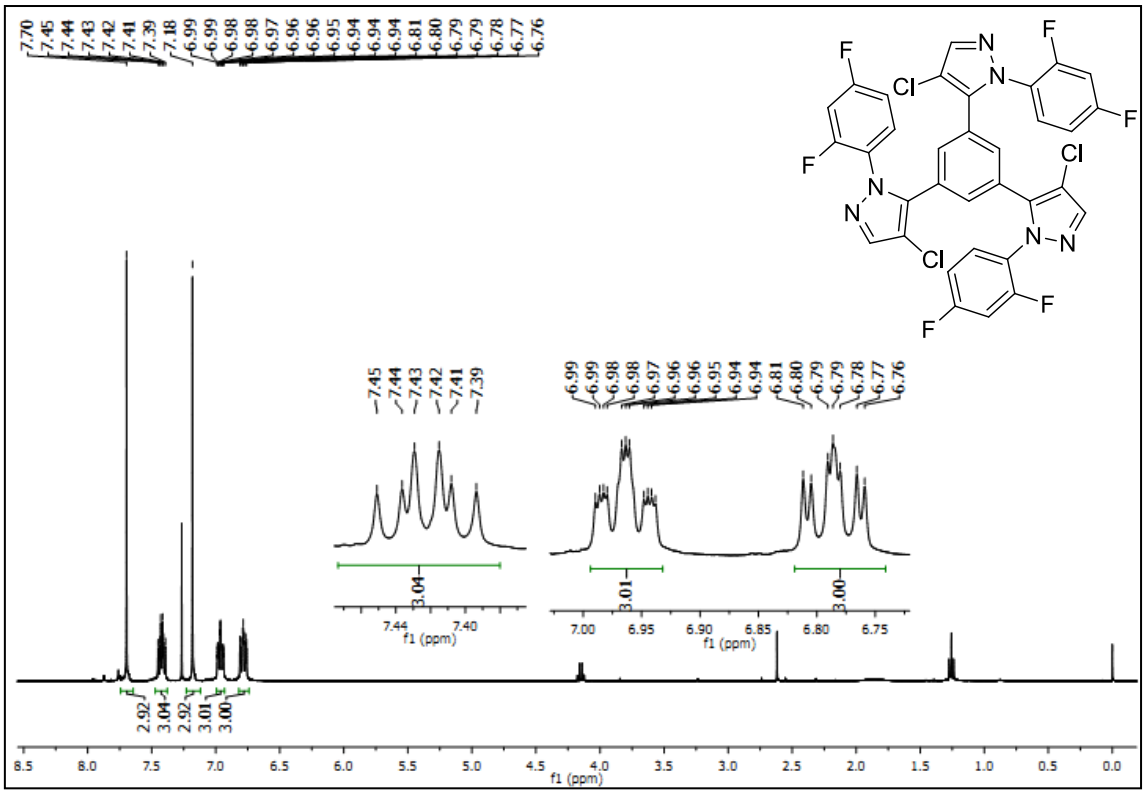


Figure S15. ^{1}H NMR spectrum of 1,3,5-tris(4-chloro-1-(2,4-difluorophenyl)-1H-pyrazol-5-yl)benzene **10a**.

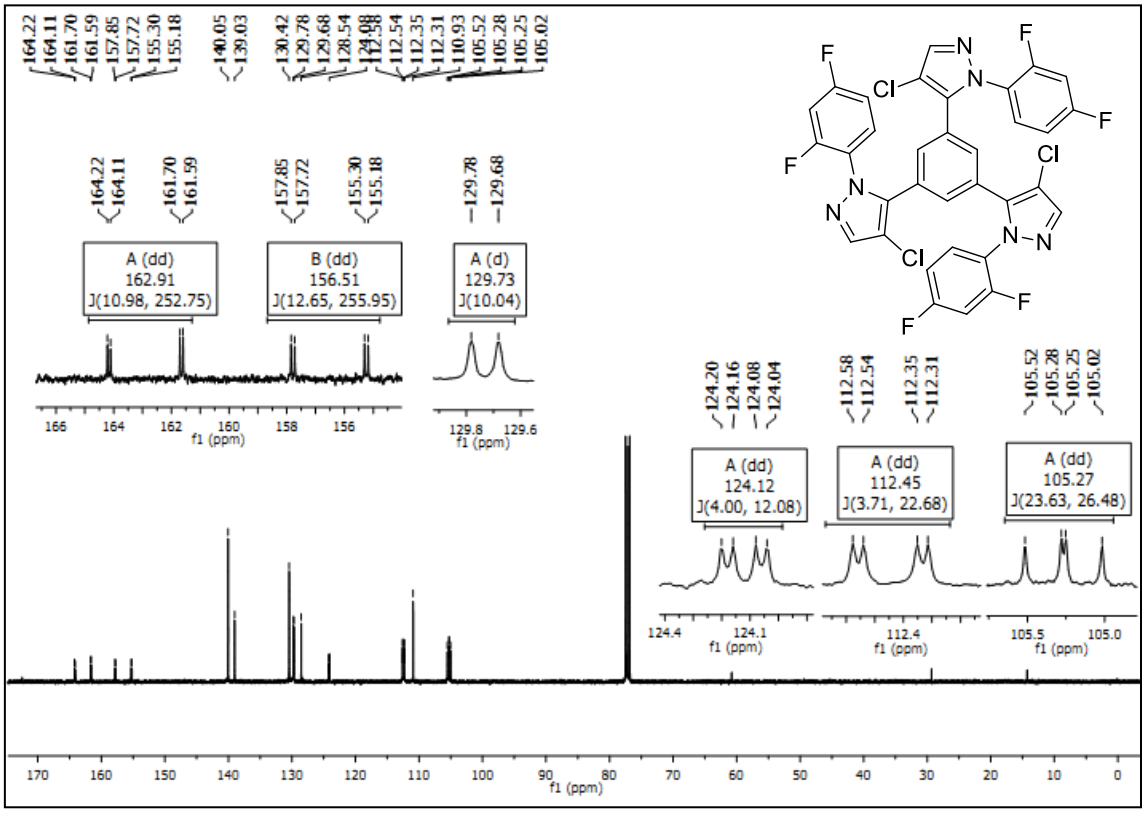


Figure S16. ^{13}C NMR spectrum of 1,3,5-tris(4-chloro-1-(2,4-difluorophenyl)-1H-pyrazol-5-yl)benzene **10a**.

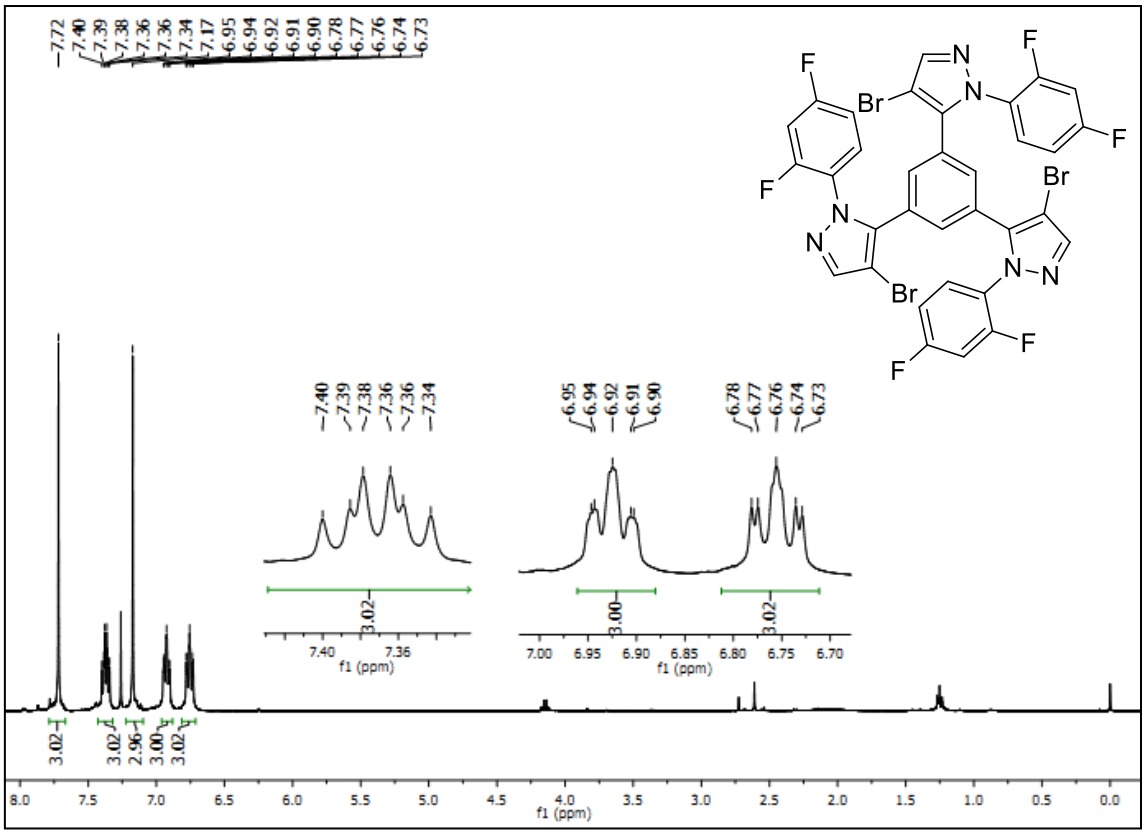


Figure S17. ^{1}H NMR spectrum of 1,3,5-tris(4-bromo-1-(2,4-difluorophenyl)-1H-pyrazol-5-yl)benzene **10b**.

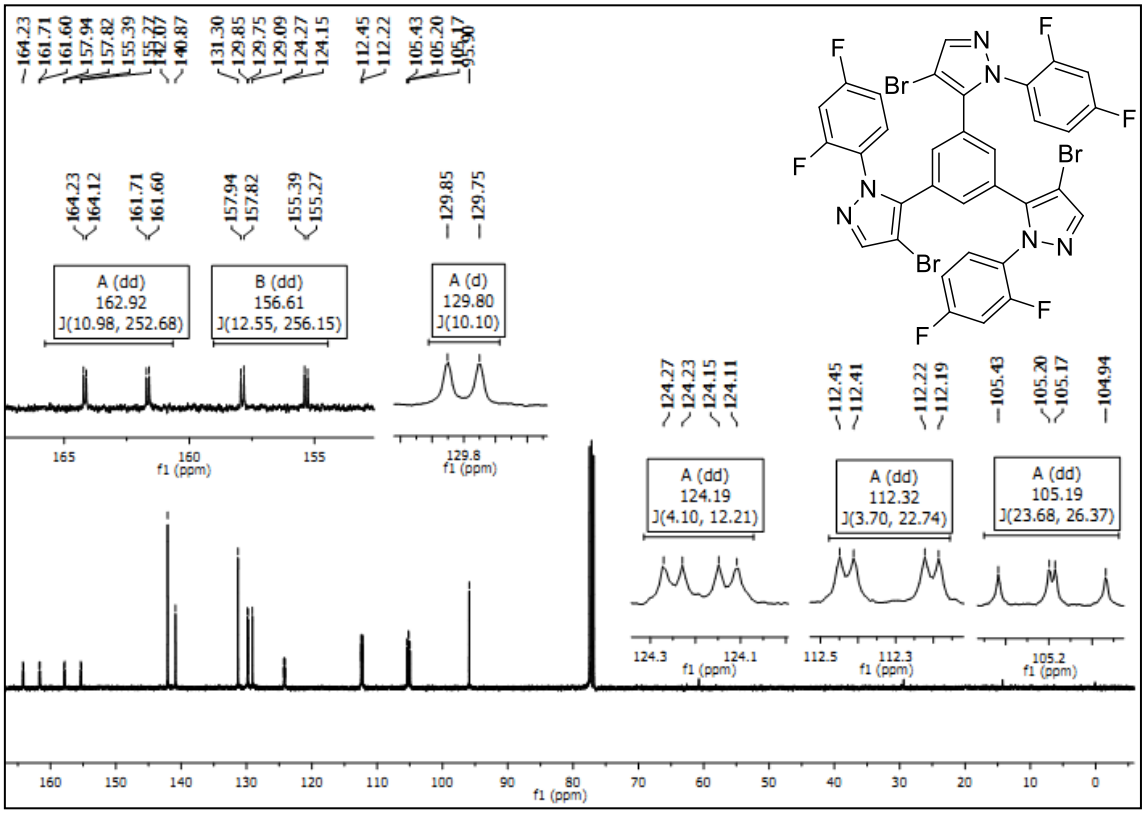


Figure S18. ^{13}C NMR spectrum of 1,3,5-tris(4-bromo-1-(2,4-difluorophenyl)-1H-pyrazol-5-yl)benzene **10b**.

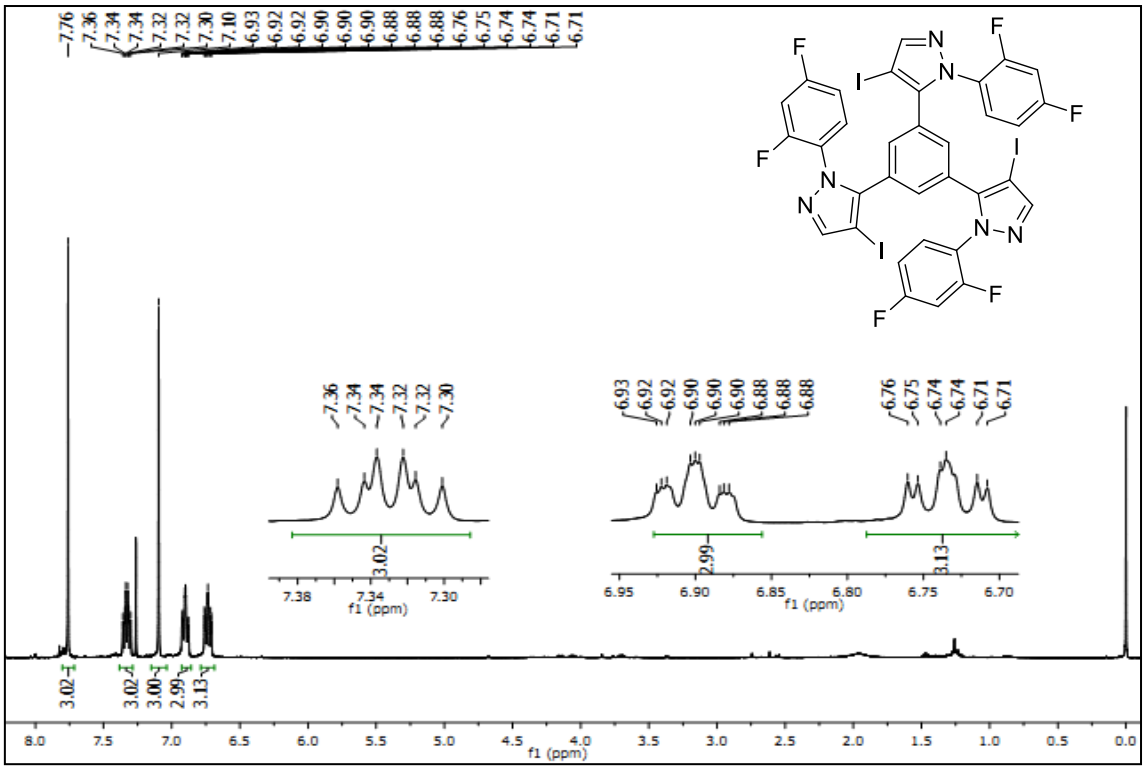


Figure S19. ^{1}H NMR spectrum of 1,3,5-tris(4-iodo-1-(2,4-difluorophenyl)-1H-pyrazol-5-yl)benzene **10c**.

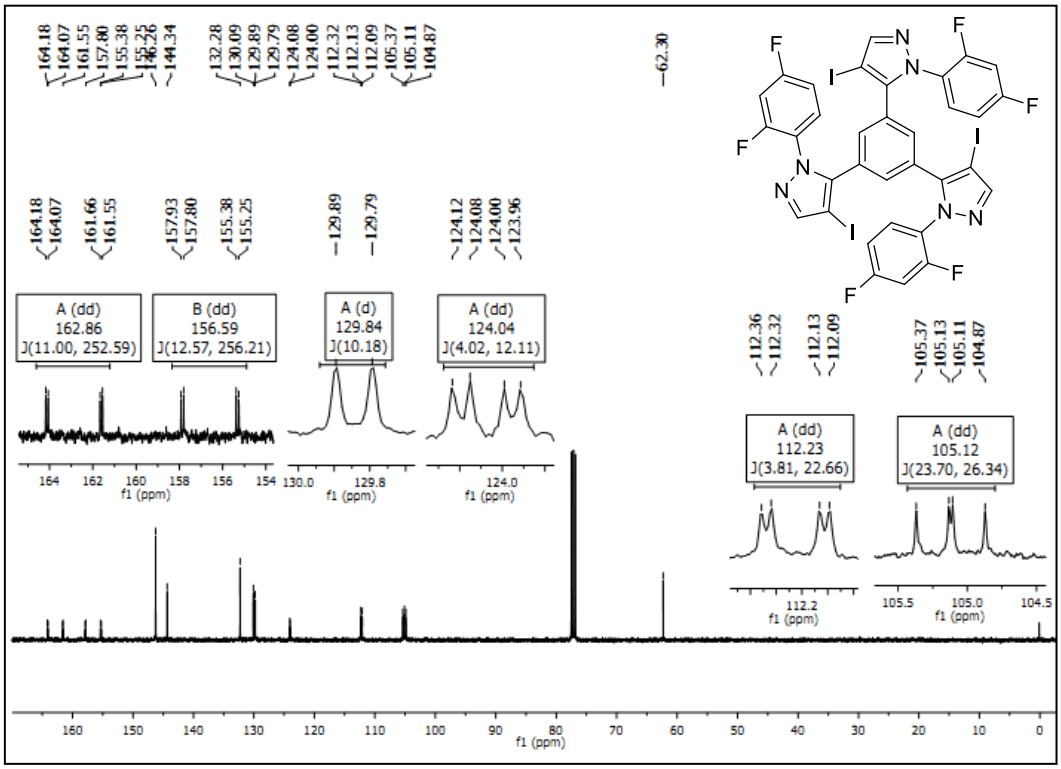


Figure S20. ^{13}C NMR spectrum of 1,3,5-tris(4-iodo-1-(2,4-difluorophenyl)-1H-pyrazol-5-yl)benzene **10c**.

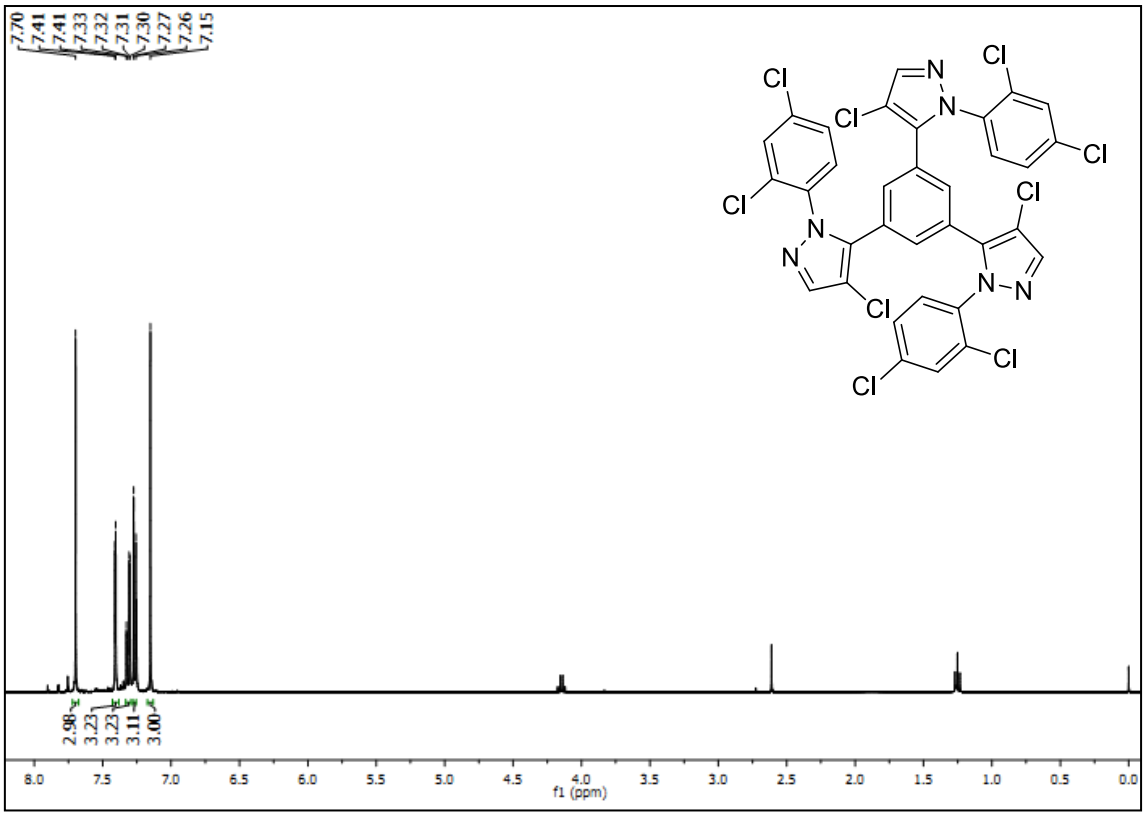


Figure S21. [1]H NMR spectrum of 1,3,5-tris(4-chloro-1-(2,4-dichlorophenyl)-1H-pyrazol-5-yl)benzene **11a**.

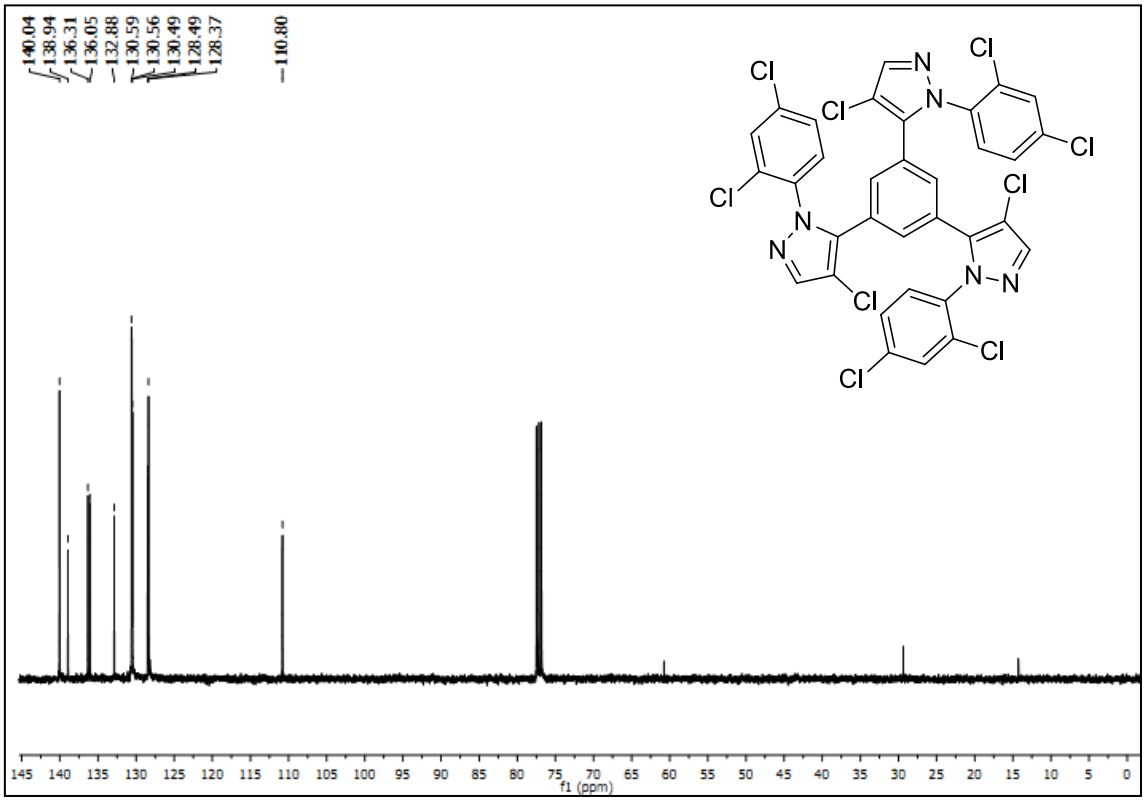


Figure S22. [13]C NMR spectrum of 1,3,5-tris(4-chloro-1-(2,4-dichlorophenyl)-1H-pyrazol-5-yl)benzene **11a**.

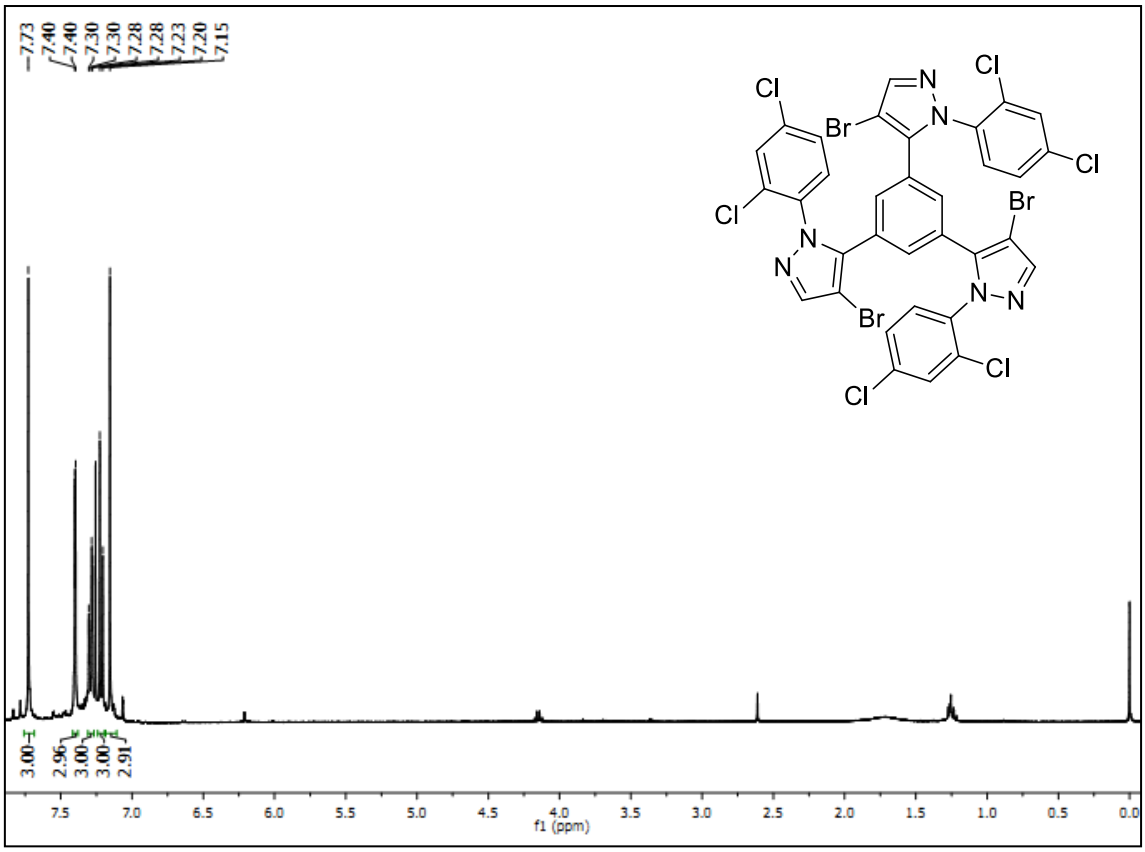


Figure S23. ^{1}H NMR spectrum of 1,3,5-tris(4-Bromo-1-(2,4-dichlorophenyl)-1H-pyrazol-5-yl)benzene **11b**.

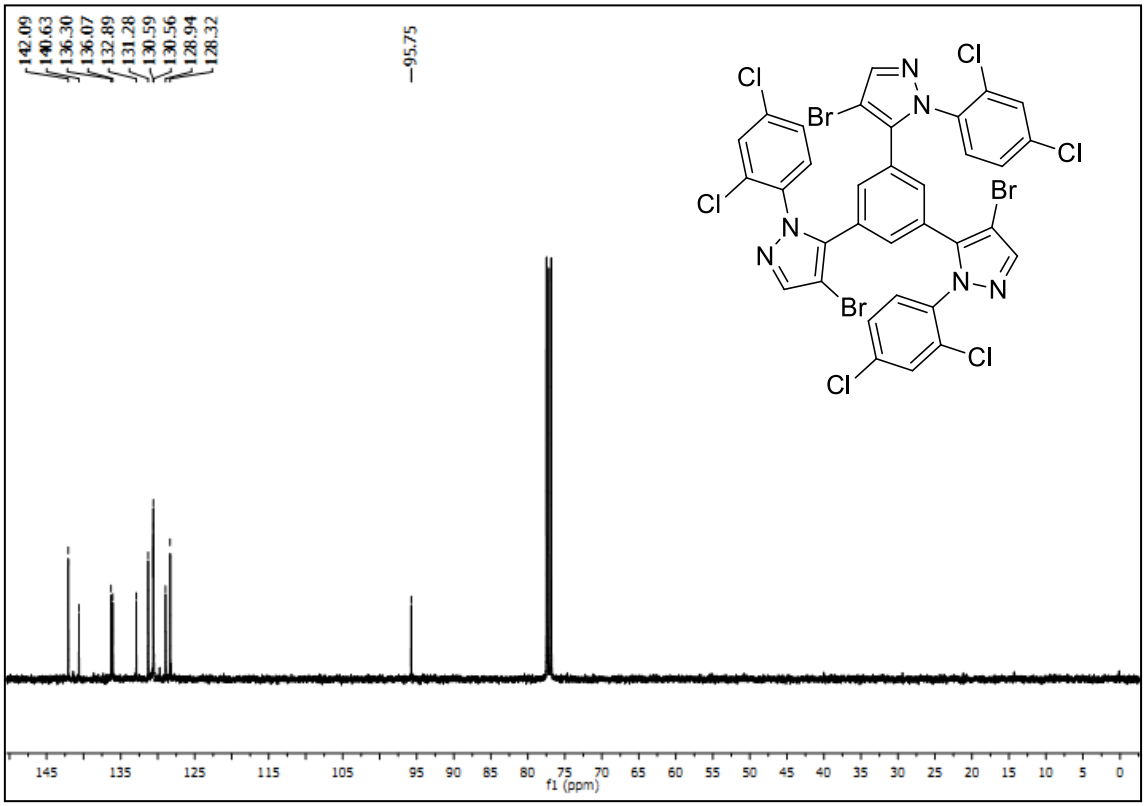


Figure S24. ^{13}C NMR spectrum of 1,3,5-tris(4-Bromo-1-(2,4-dichlorophenyl)-1H-pyrazol-5-yl)benzene **11b**.

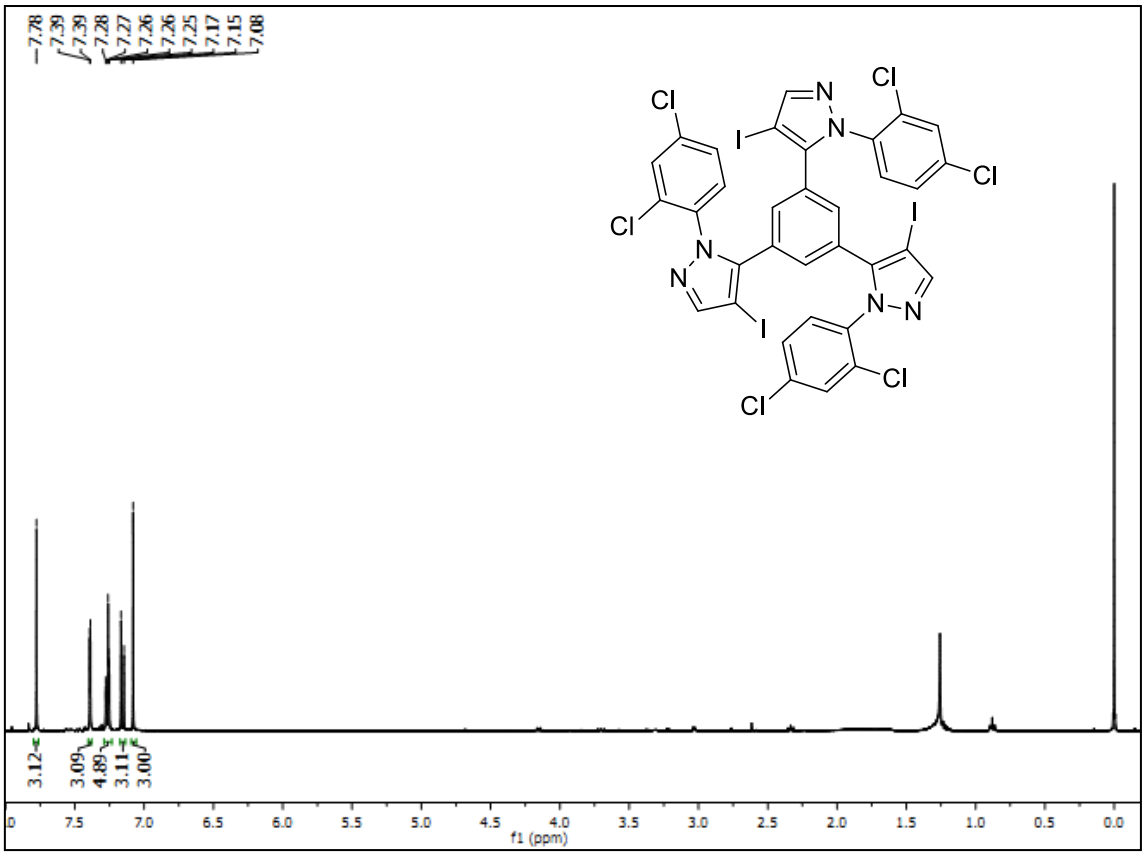


Figure S25. [1]H NMR spectrum of 1,3,5-tris(4-iodo-1-(2,4-dichlorophenyl)-1H-pyrazol-5-yl)benzene **11c**.

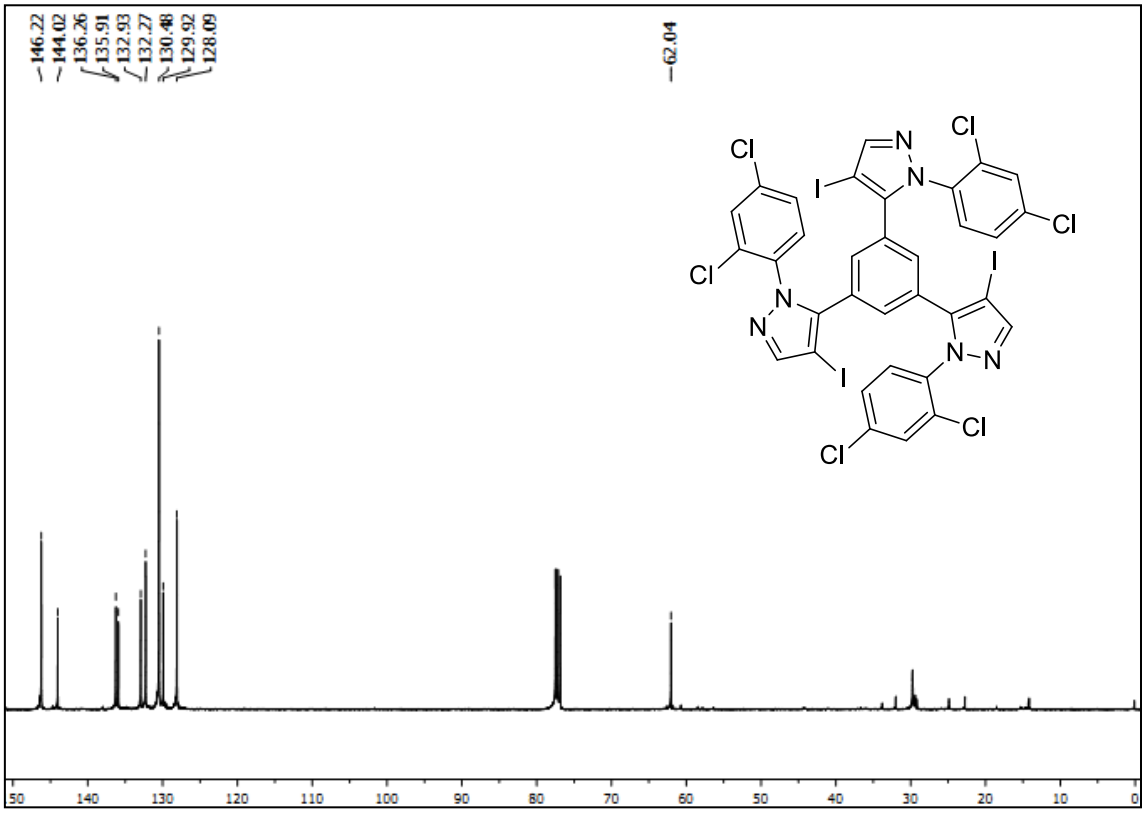


Figure S26. [13]C NMR spectrum of 1,3,5-tris(4-iodo-1-(2,4-dichlorophenyl)-1H-pyrazol-5-yl)benzene **11c**.

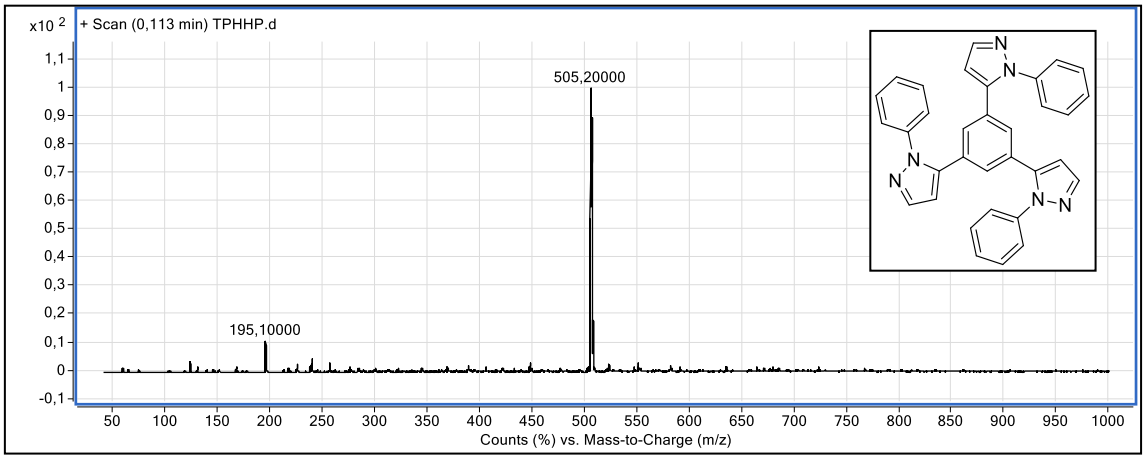


Figure S27. LCMS spectra NMR spectrum of 1,3,5-tris(1-phenyl-1H-pyrazol-5-yl)benzene **5**.

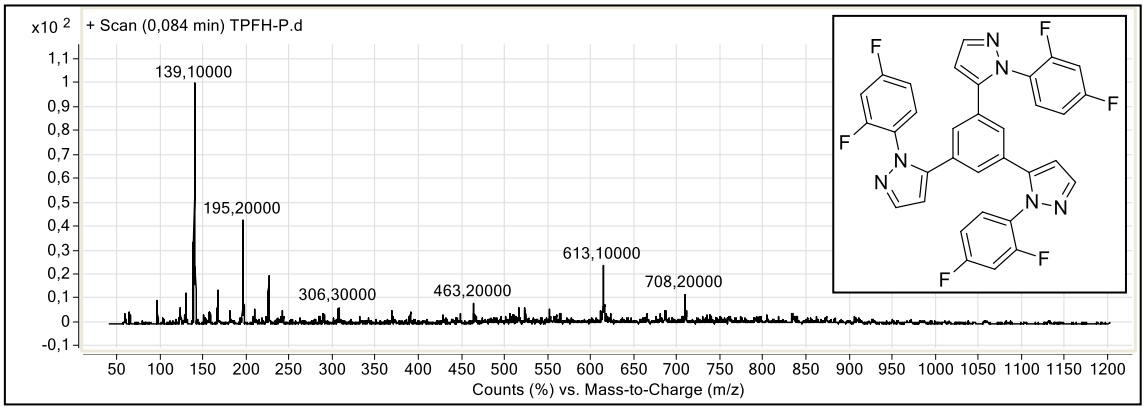


Figure S28. LCMS spectra of 1,3,5-tris(1-(2,4-difluorophenyl)-1H-pyrazol-5-yl)benzene **6**.

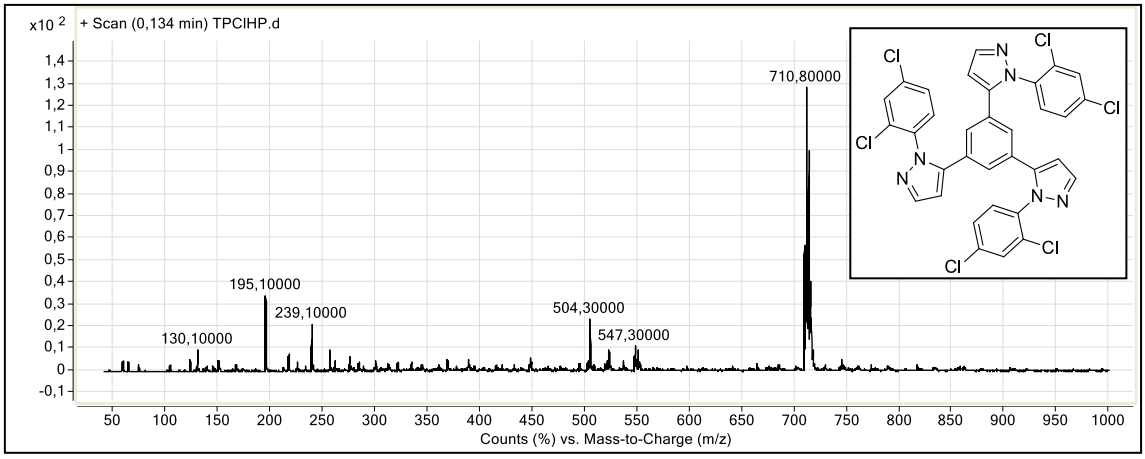


Figure S29. LCMS spectra of 1,3,5-tris(1-(2,4-dichlorophenyl)-1H-pyrazol-5-yl)benzene **7**.

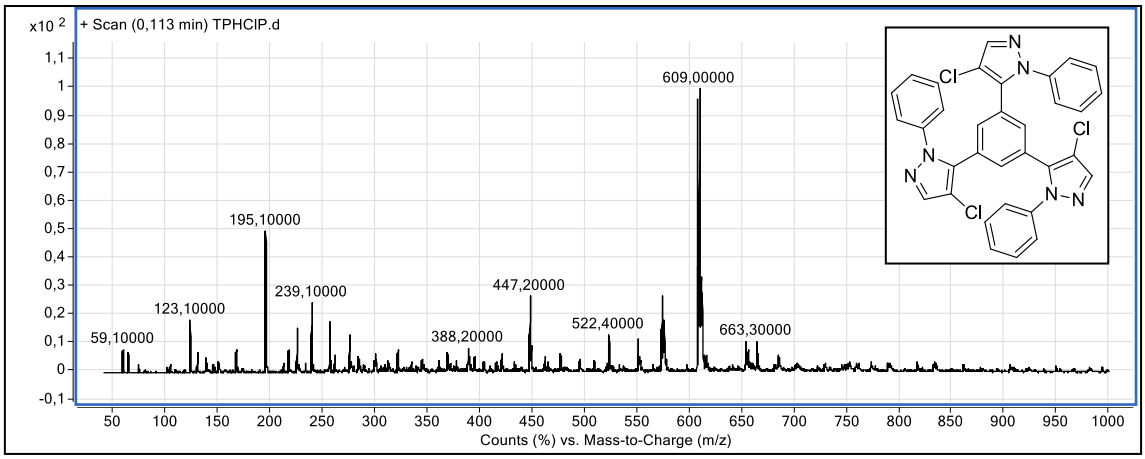


Figure S30. LCMS spectra of 1,3,5-tris(4-chloro-1-phenyl-1H-pyrazol-5-yl)benzene **9a**.

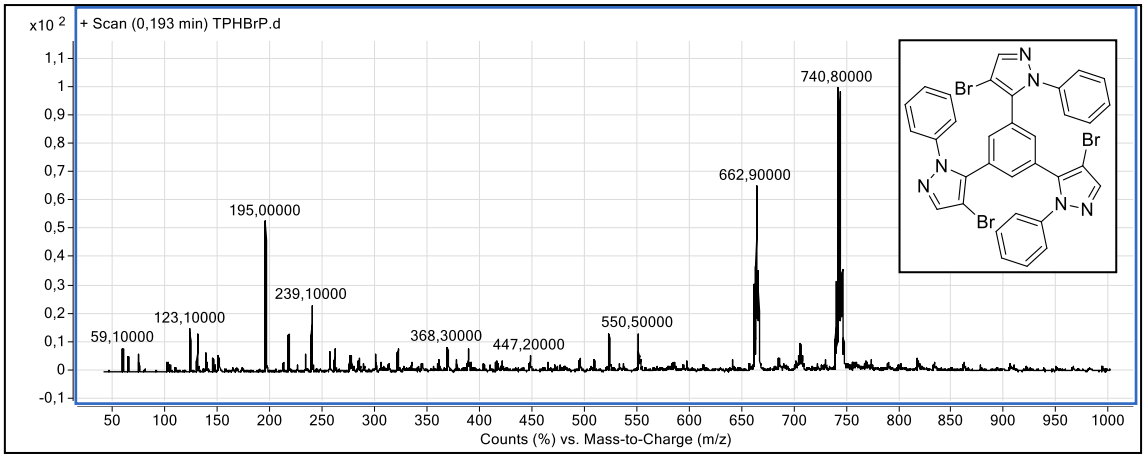


Figure S31. LCMS spectra of 1,3,5-tris(4-bromo-1-phenyl-1H-pyrazol-5-yl)benzene **9b**.

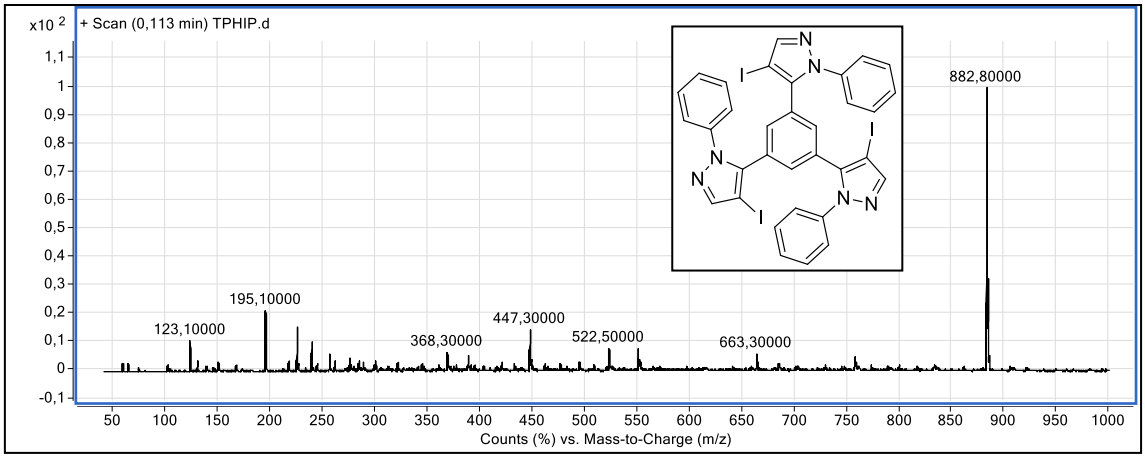


Figure S32. LCMS spectra of 1,3,5-tris(4-iodo-1-phenyl-1H-pyrazol-5-yl)benzene **9c**.

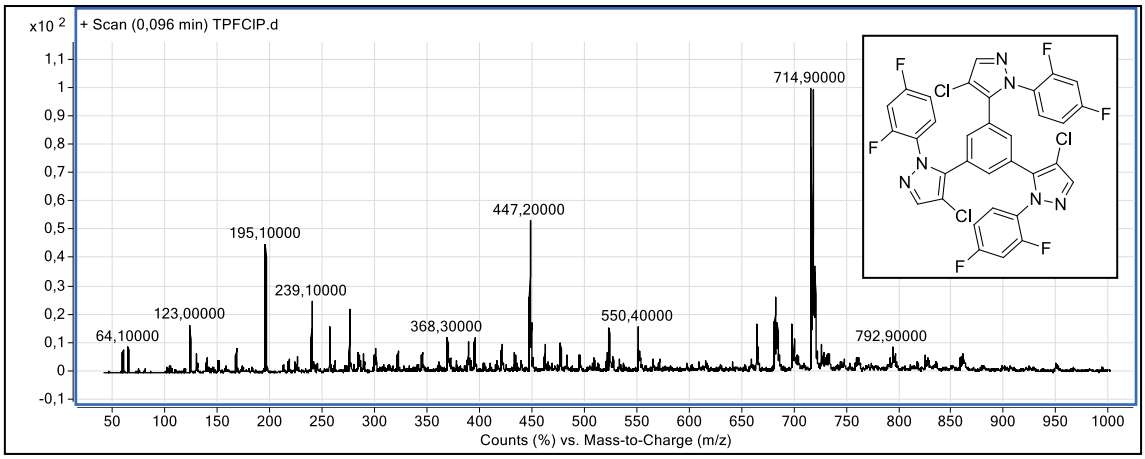


Figure S33. LCMS spectra of 1,3,5-tris(4-chloro-1-(2,4-difluorophenyl)-1H-pyrazol-5-yl)benzene **10a**.

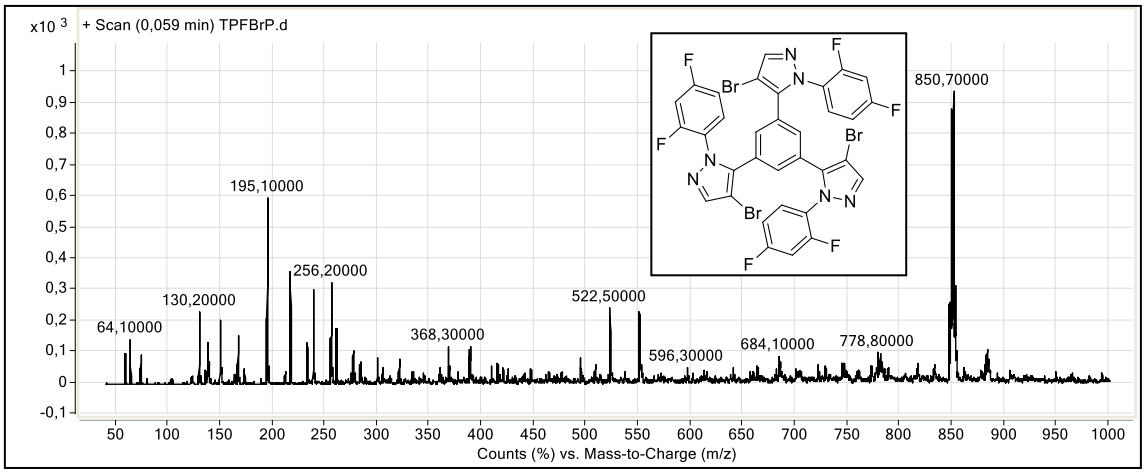


Figure S34. LCMS spectra of 1,3,5-tris(4-bromo-1-(2,4-difluorophenyl)-1H-pyrazol-5-yl)benzene **10b**.

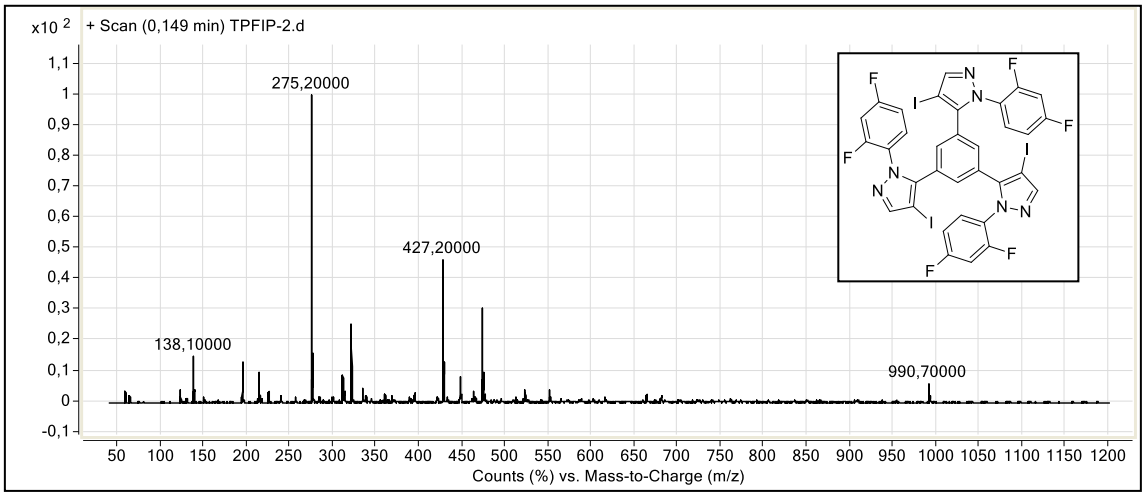


Figure S35. LCMS spectra of 1,3,5-tris(4-iodo-1-(2,4-difluorophenyl)-1H-pyrazol-5-yl)benzene **10c**.

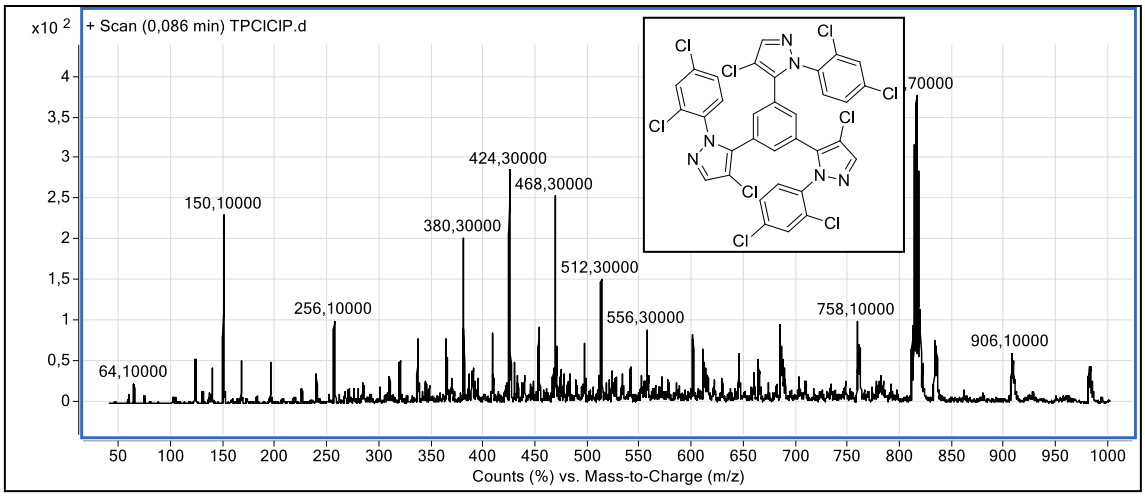


Figure S36. LCMS spectra of 1,3,5-tris(4-chloro-1-(2,4-dichlorophenyl)-1H-pyrazol-5-yl)benzene **11a**.

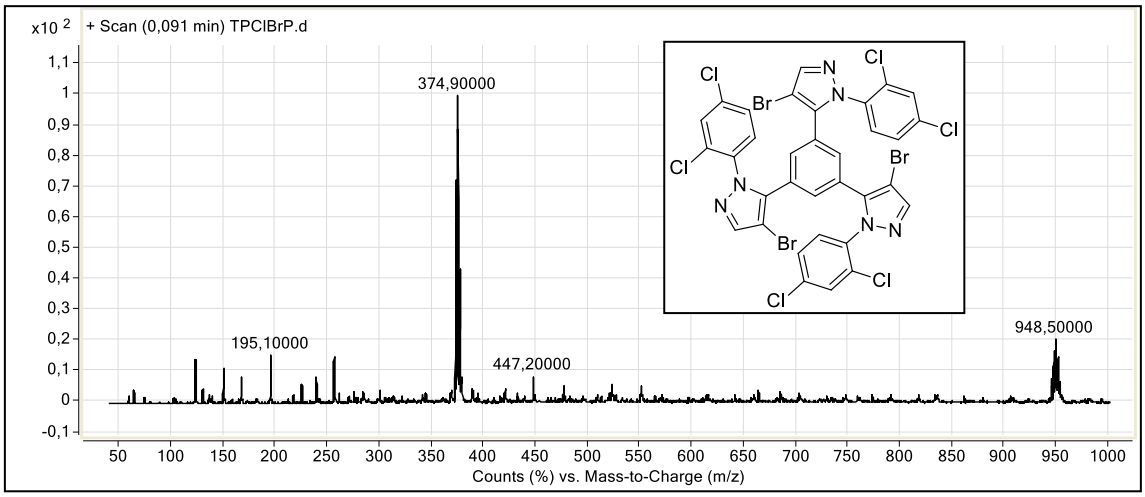


Figure S37. LCMS spectra of 1,3,5-tris(4-Bromo-1-(2,4-dichlorophenyl)-1H-pyrazol-5-yl)benzene **11b**.

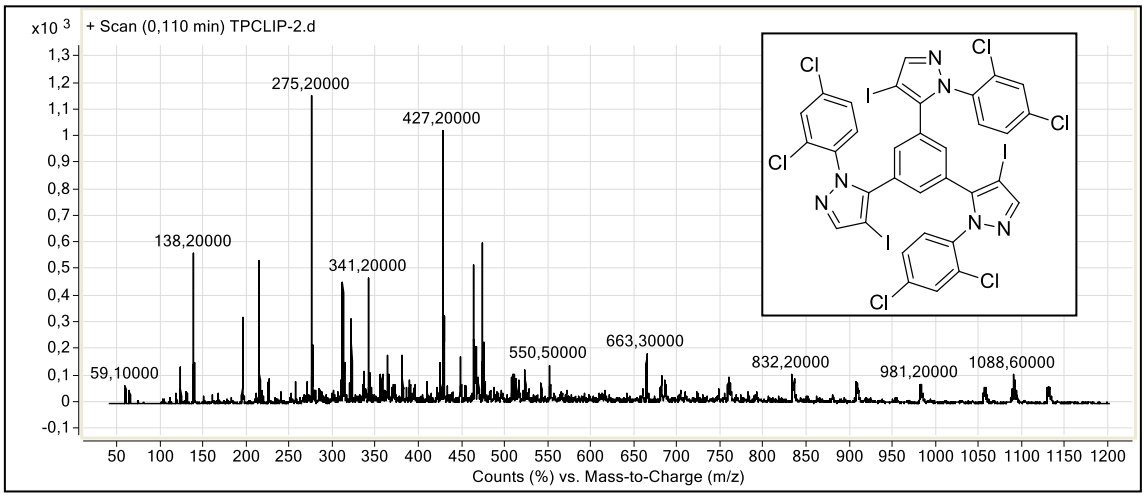


Figure S38. LCMS spectra of 1,3,5-tris(4-iodo-1-(2,4-dichlorophenyl)-1H-pyrazol-5-yl)benzene **11c**.