Electronic Support Information

Synthesis, Characterization and Crystal Structures of Novel Fluorinated Di(thiazolyl)benzene Derivatives

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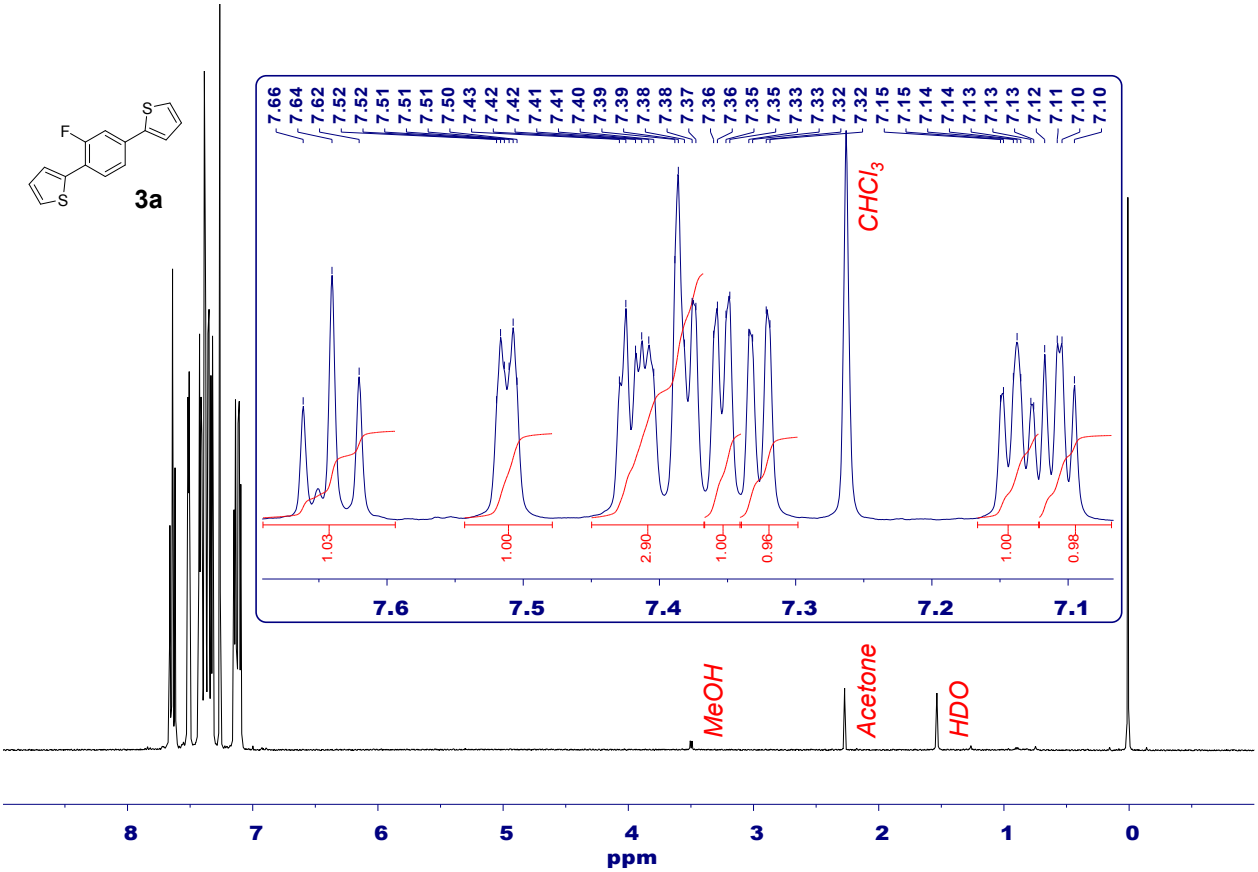

Figure S1. ^{1}H NMR spectrum of 1,4-di(thien-2-yl)-2-fluorobenzene **3a** ($CDCl_3$, 400 MHz, 298 K).

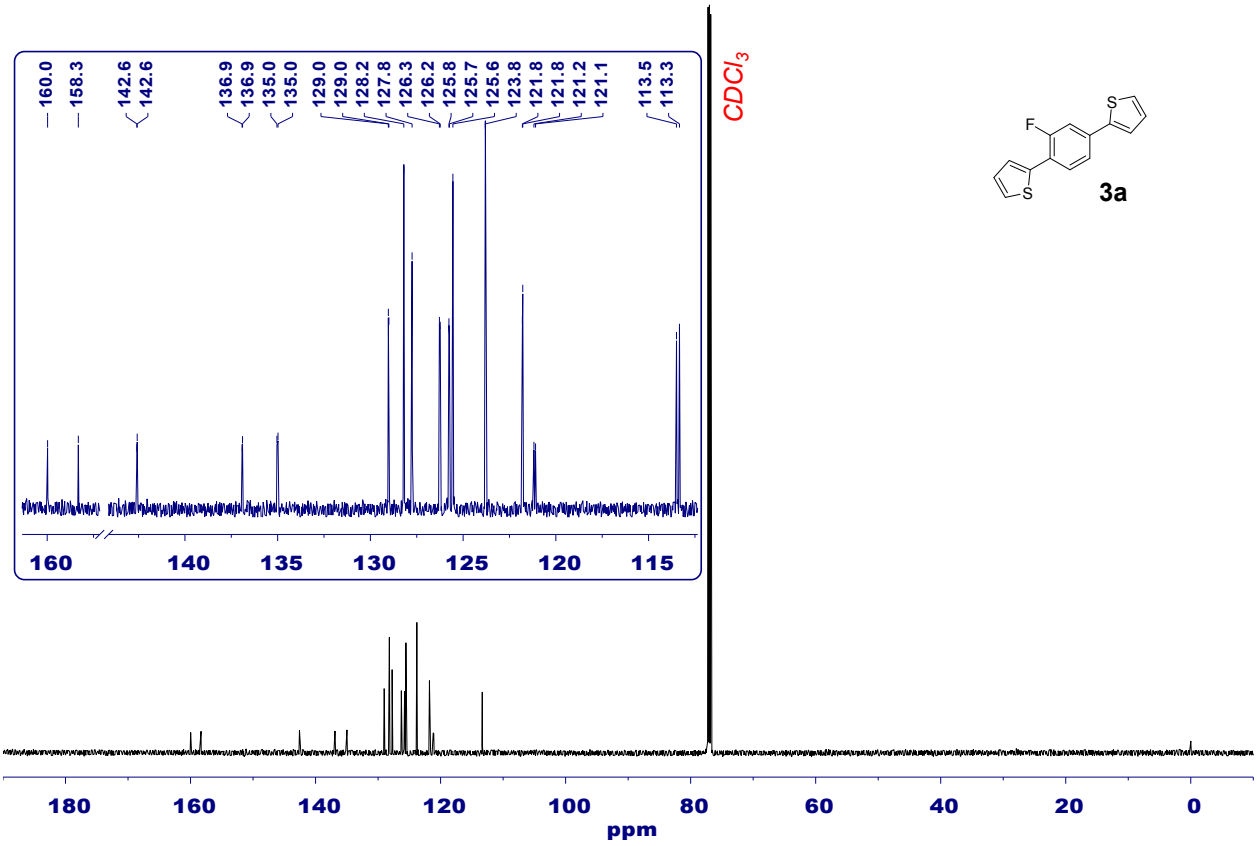

Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of 1,4-di(thien-2-yl)-2-fluorobenzene **3a** ($CDCl_3$, 150 MHz, 298 K).

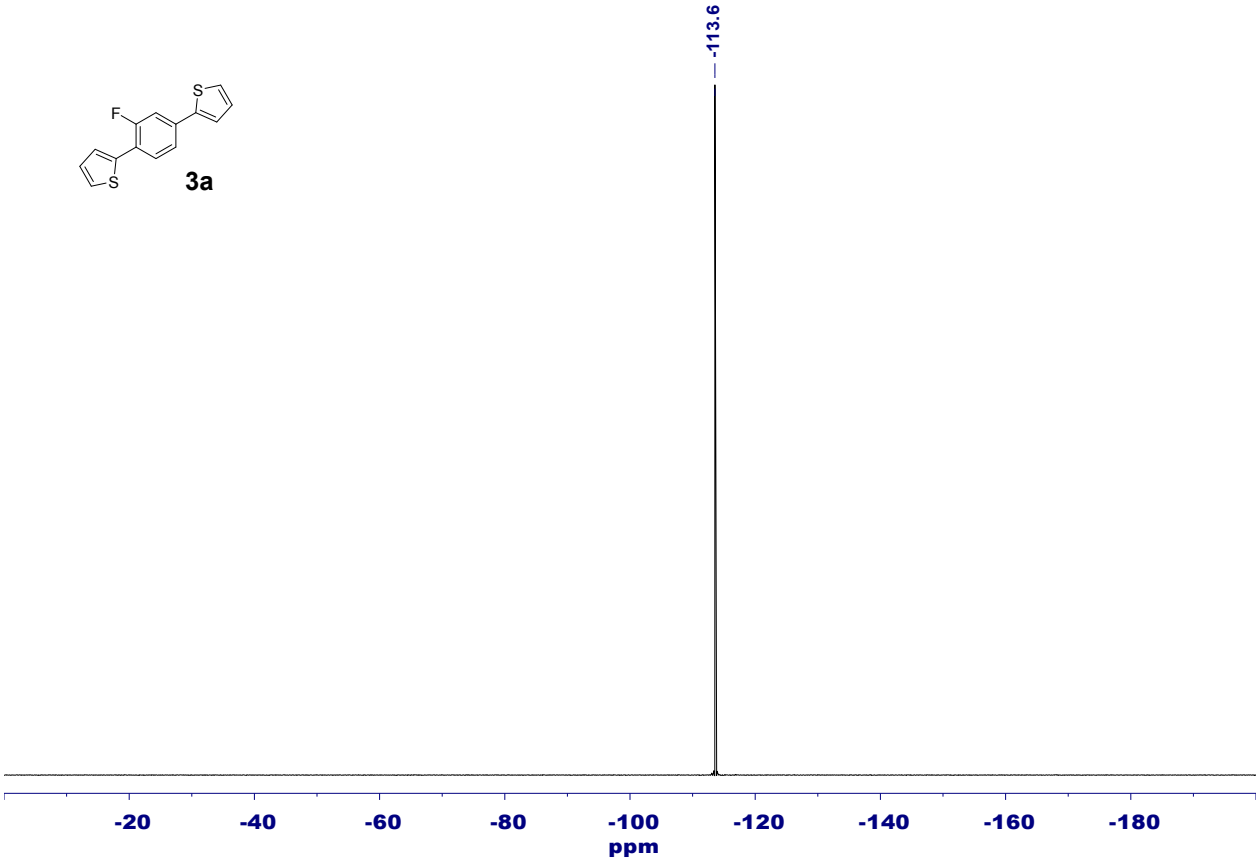

Figure S3. $^{19}F\{^{1}H\}$ NMR spectrum of 1,4-di(thien-2-yl)-2-fluorobenzene **3a** ($CDCl_3$, 564 MHz, 298 K).

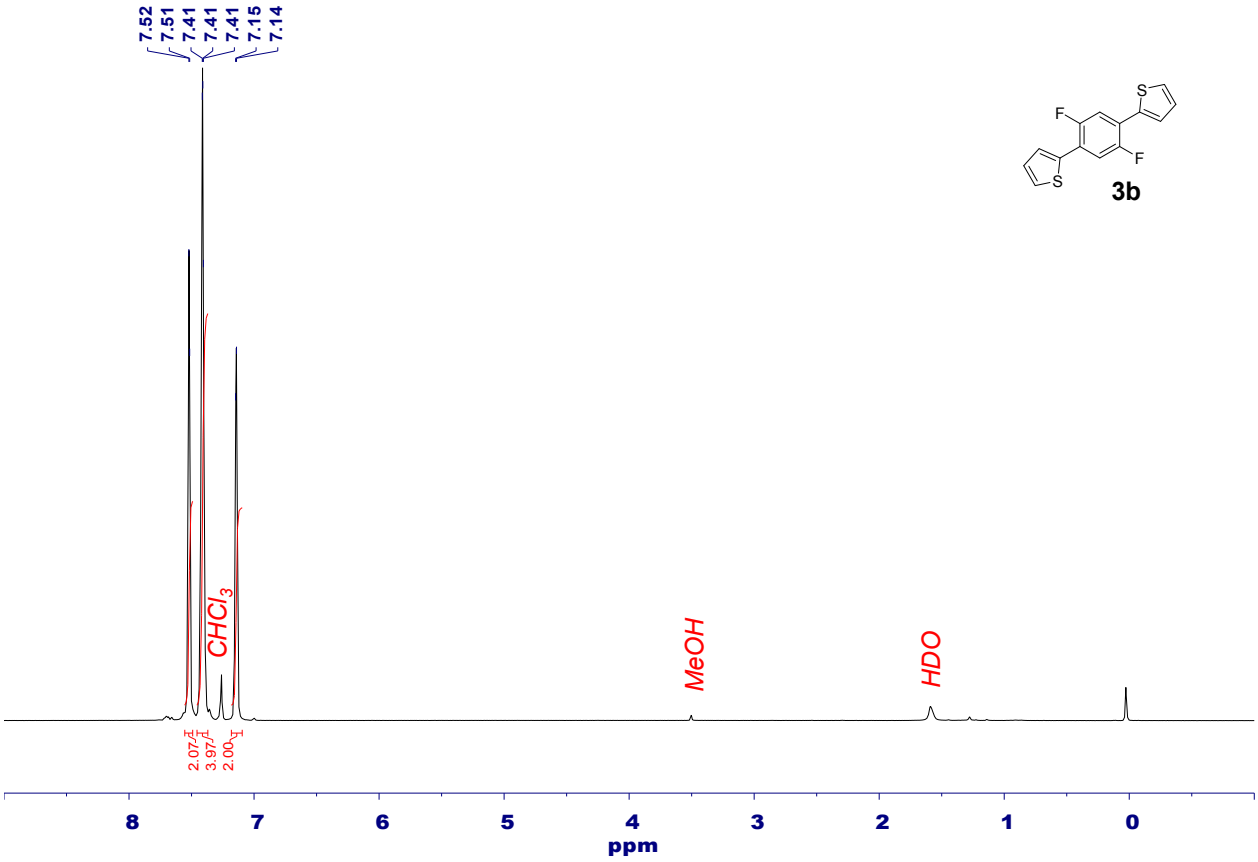

Figure S4. ^{1}H NMR spectrum of 1,4-di(thien-2-yl)-2,5-difluorobenzene **3b** ($CDCl_3$, 400 MHz, 298 K).

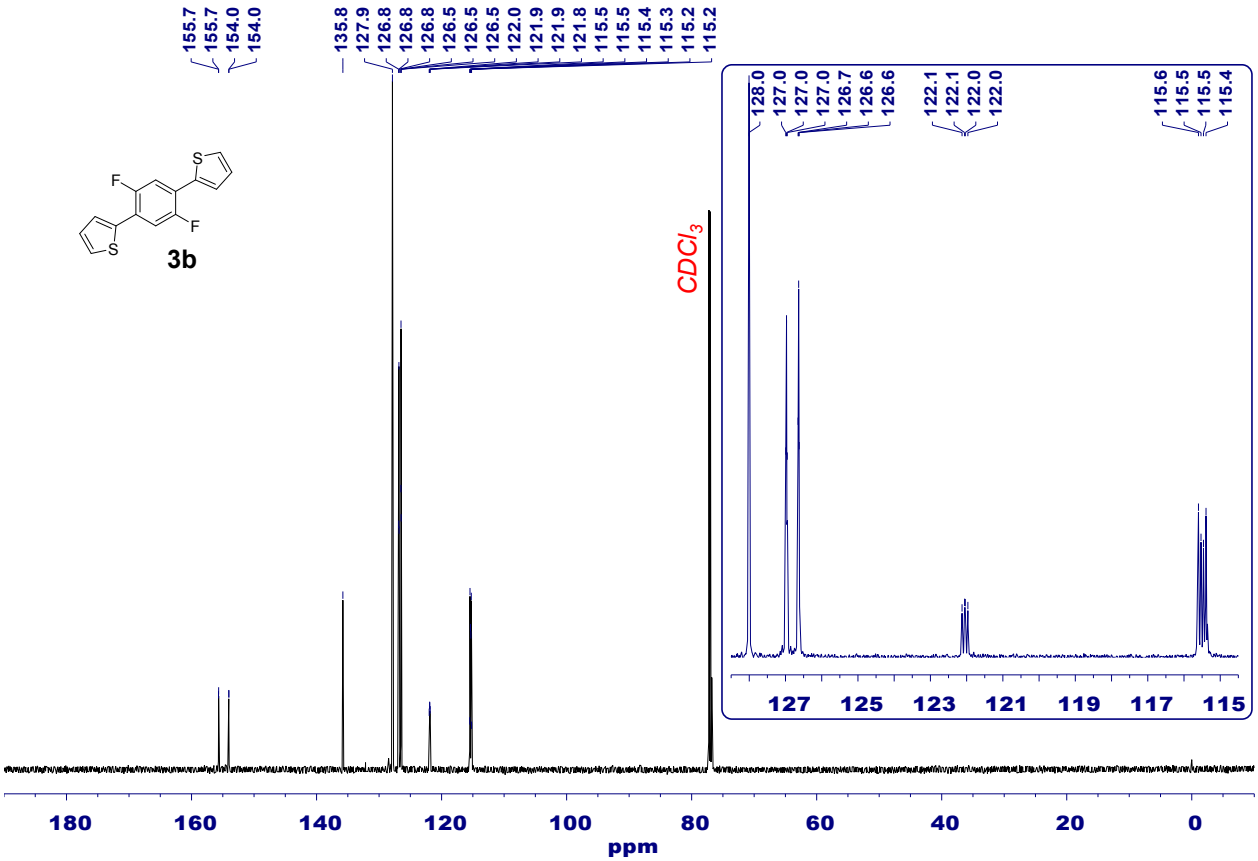

Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum of 1,4-di(thien-2-yl)-2,5-difluorobenzene **3b** ($CDCl_3$, 150 MHz, 298 K).

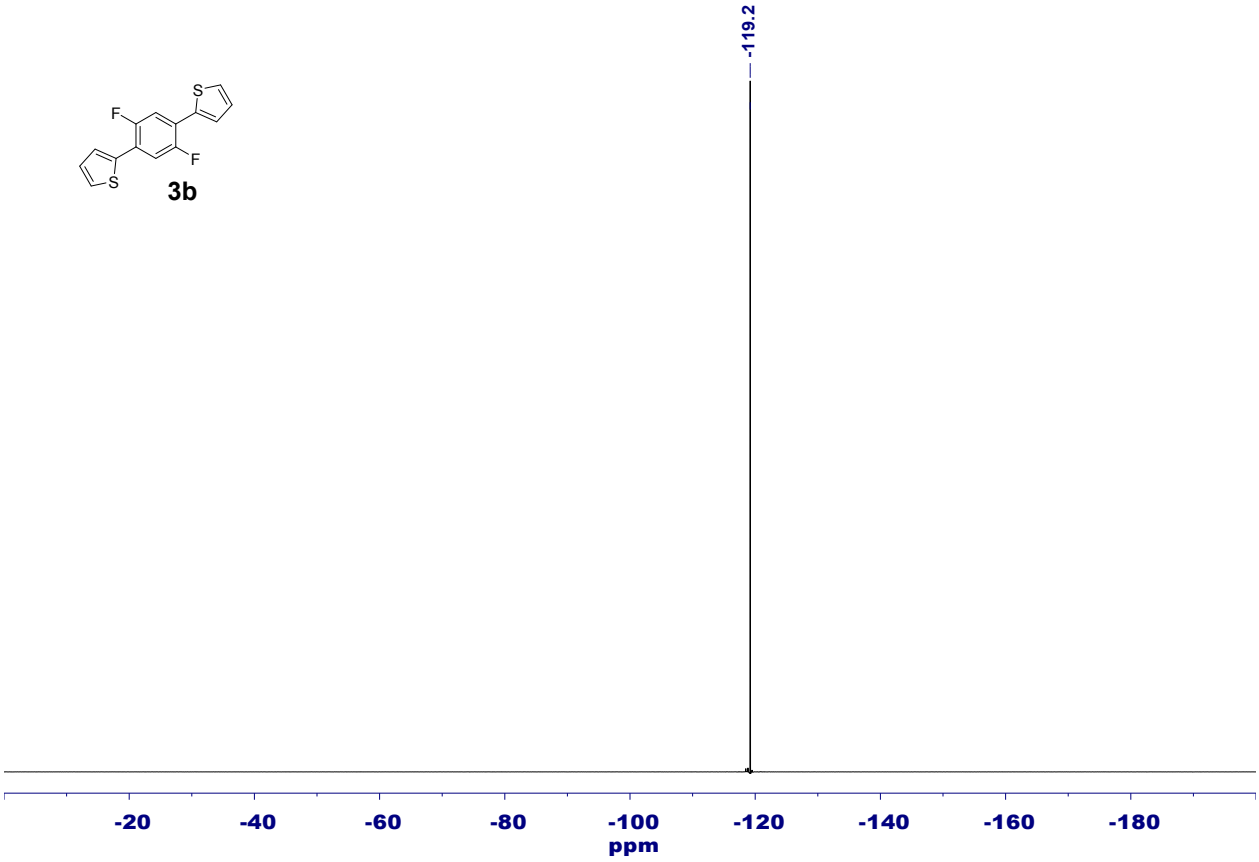

Figure S6. $^{19}F\{^{1}H\}$ NMR spectrum of 1,4-di(thien-2-yl)-2,5-difluorobenzene **3b** ($CDCl_3$, 376 MHz, 298 K).

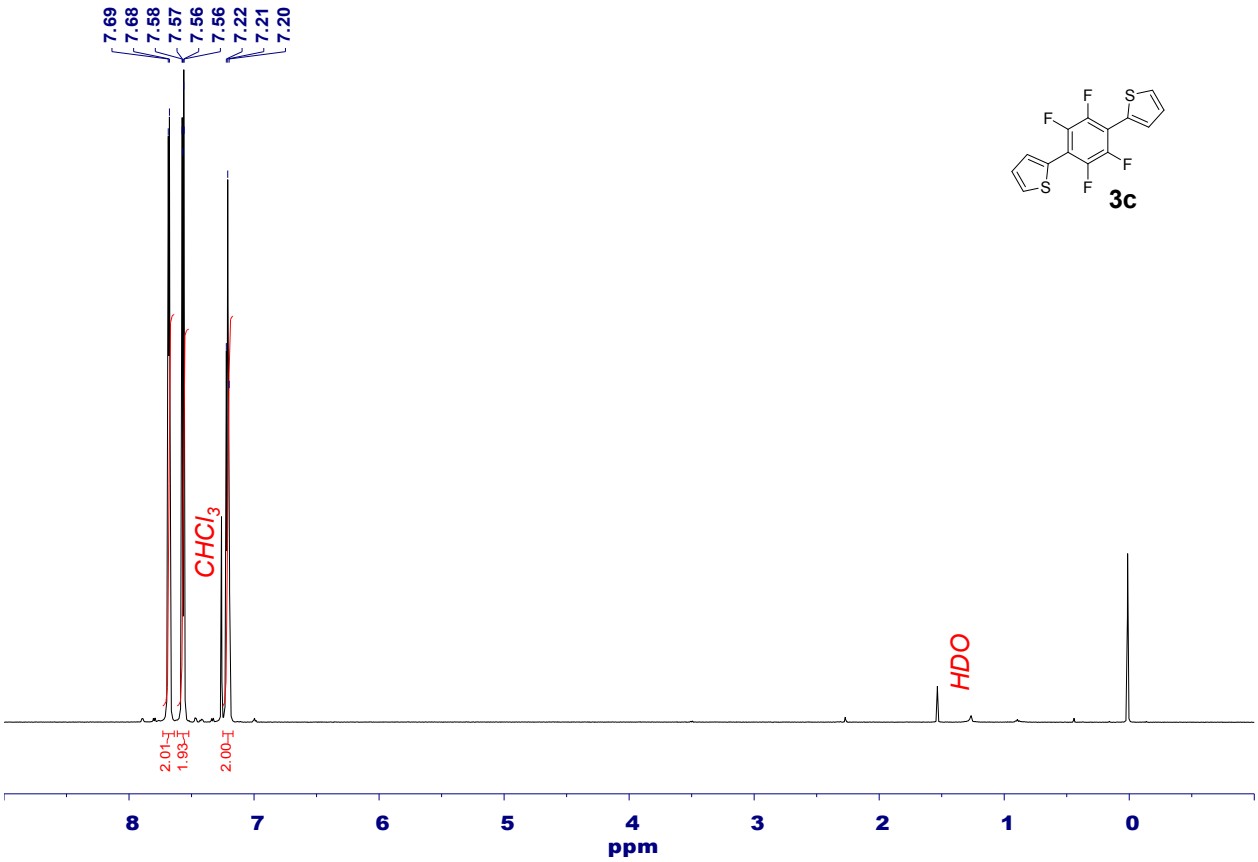

Figure S7. ^{1}H NMR spectrum of 1,4-di(thien-2-yl)-tetrafluorobenzene **3c** ($CDCl_3$, 400 MHz, 298 K).

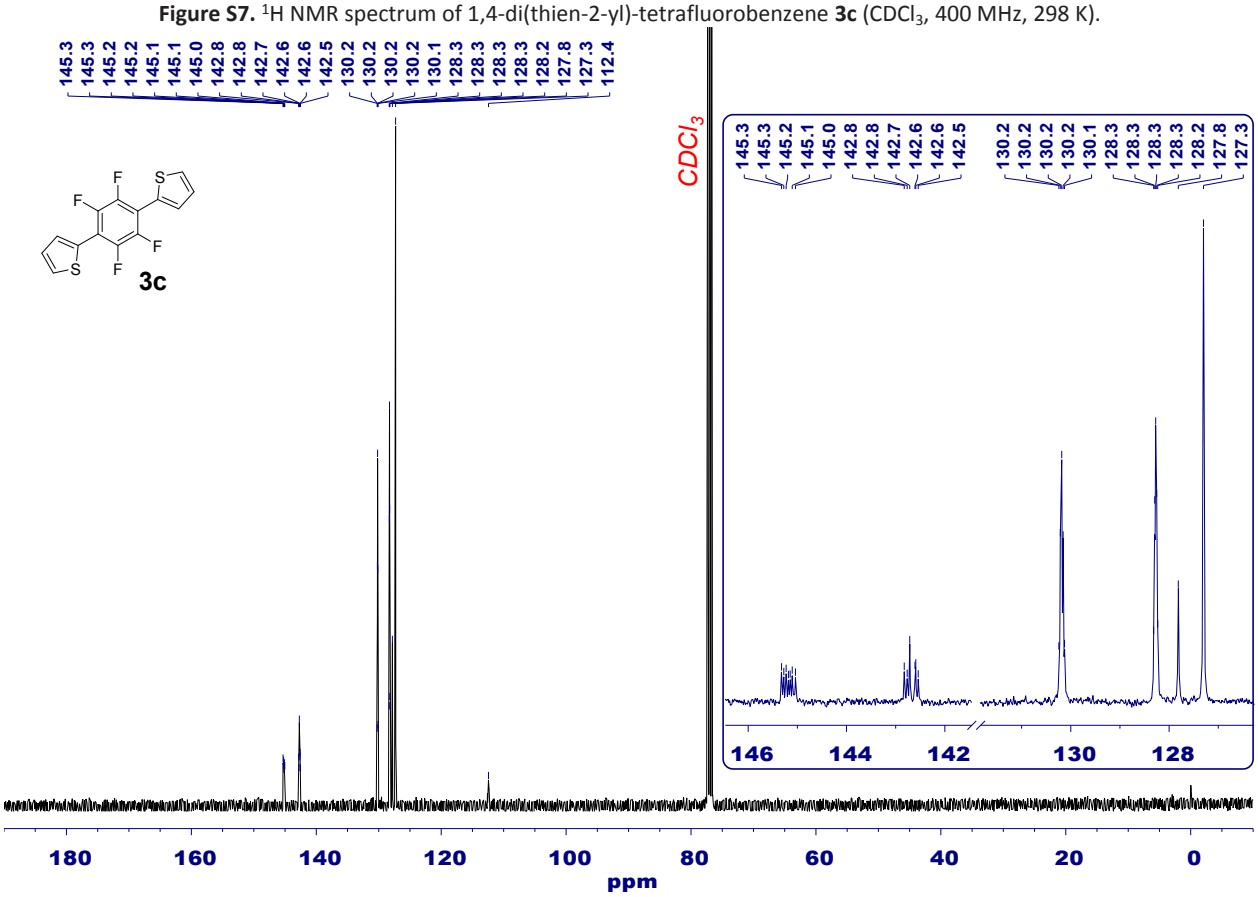

Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of 1,4-di(thien-2-yl)-tetrafluorobenzene **3c** ($CDCl_3$, 100 MHz, 298 K).

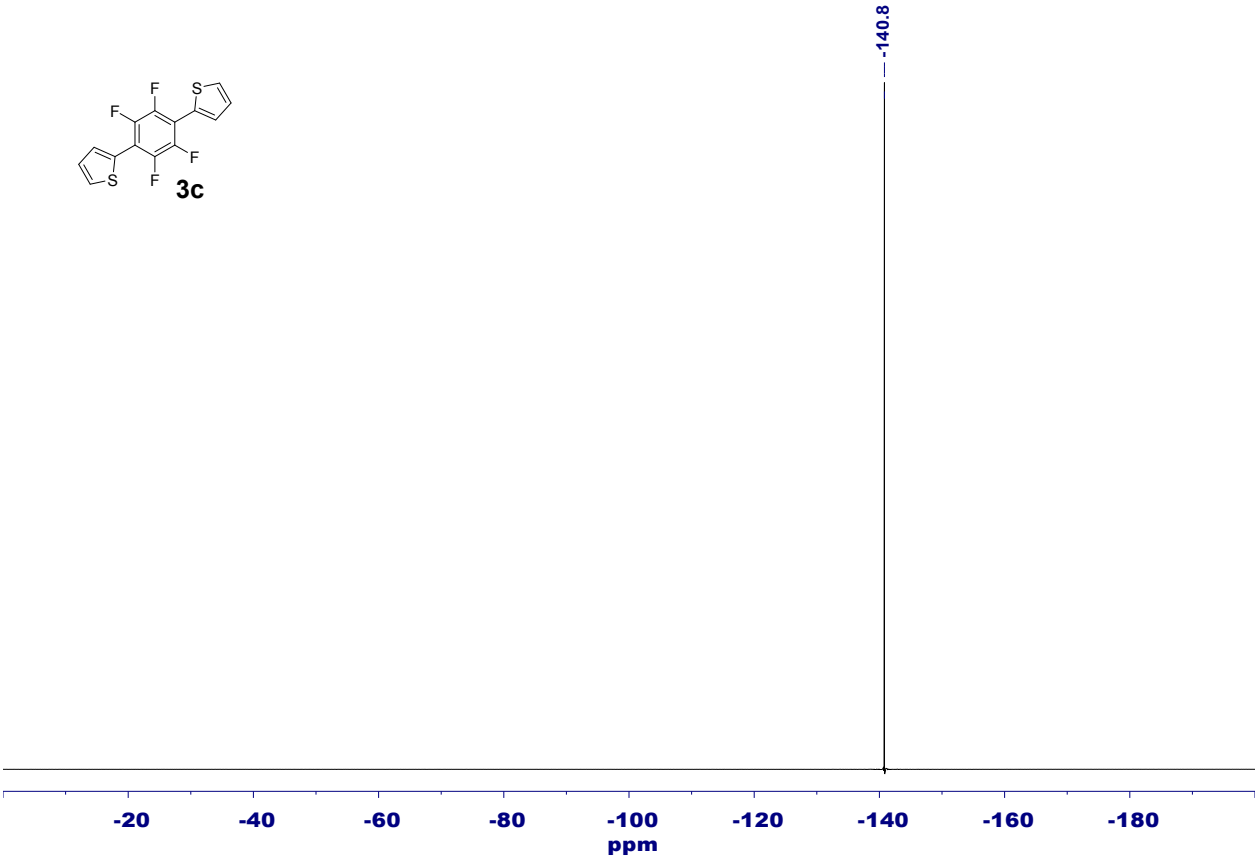

Figure S9. $^{19}F\{^{1}H\}$ NMR spectrum of 1,4-di(thien-2-yl)-tetrafluorobenzene **3c** ($CDCl_3$, 376 MHz, 298 K).

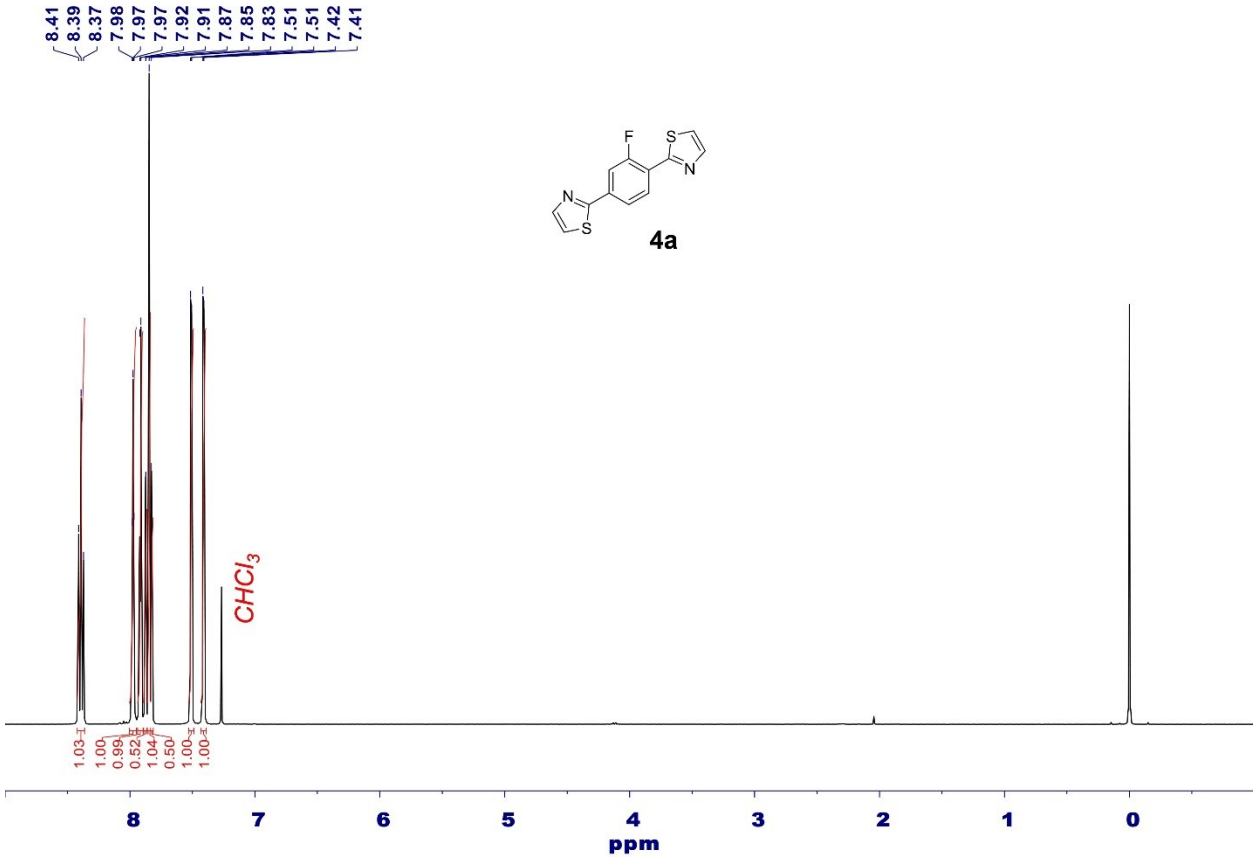

Figure S10. ^{1}H NMR spectrum of 1,4-di(thiazol-2-yl)-2-fluorobenzene **4a** ($CDCl_3$, 600 MHz, 298 K).

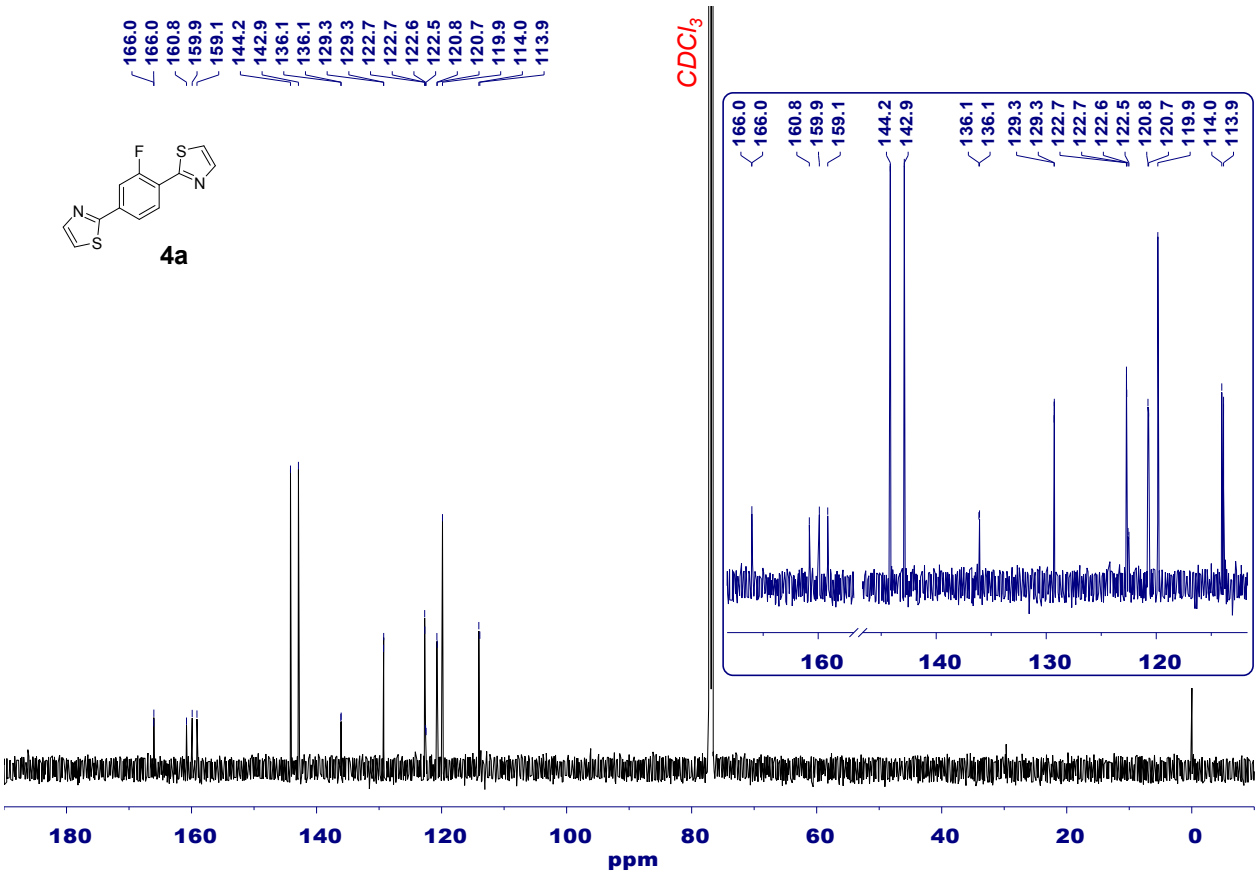

Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum of 1,4-di(thiazol-2-yl)-2-fluorobenzene **4a** ($CDCl_3$, 150 MHz, 298 K).

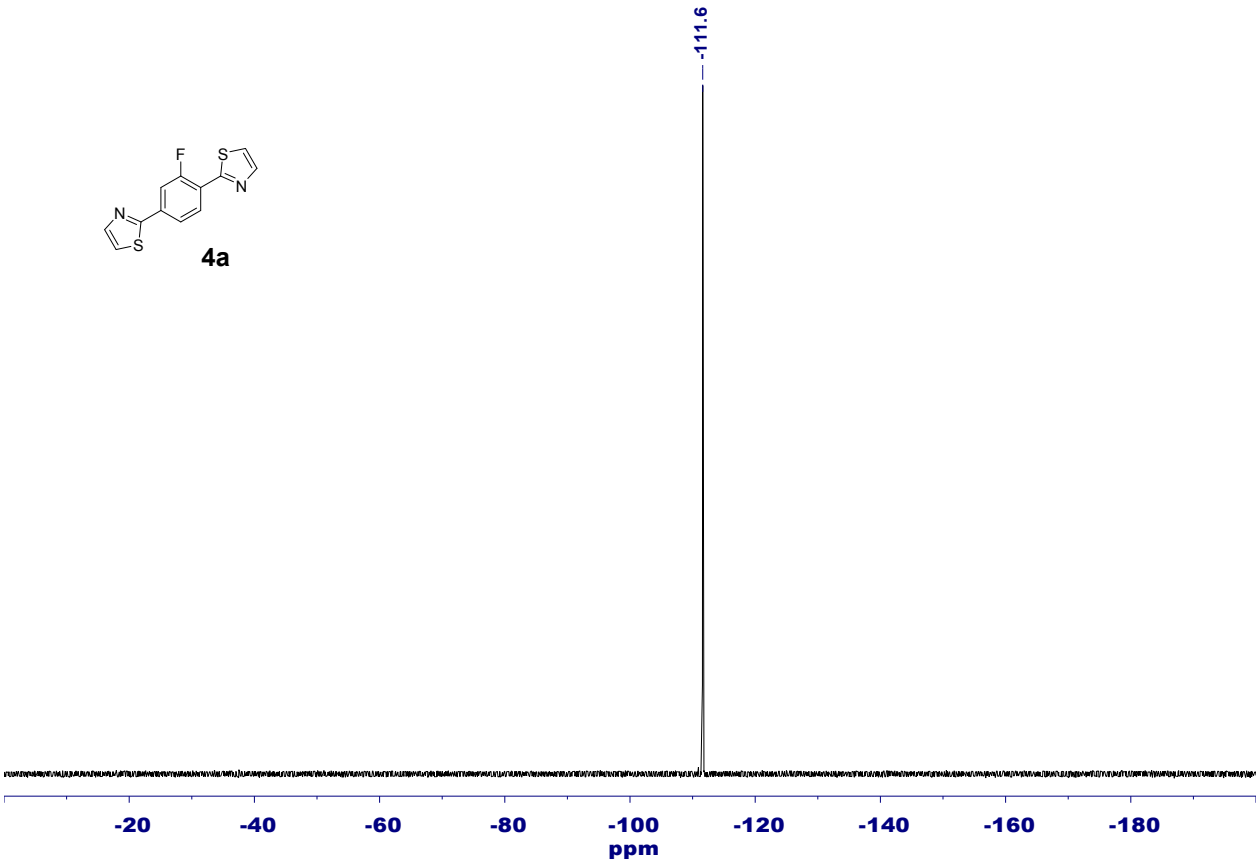

Figure S12. $^{19}F\{^{1}H\}$ NMR spectrum of 1,4-di(thiazol-2-yl)-2-fluorobenzene **4a** ($CDCl_3$, 564 MHz, 298 K).

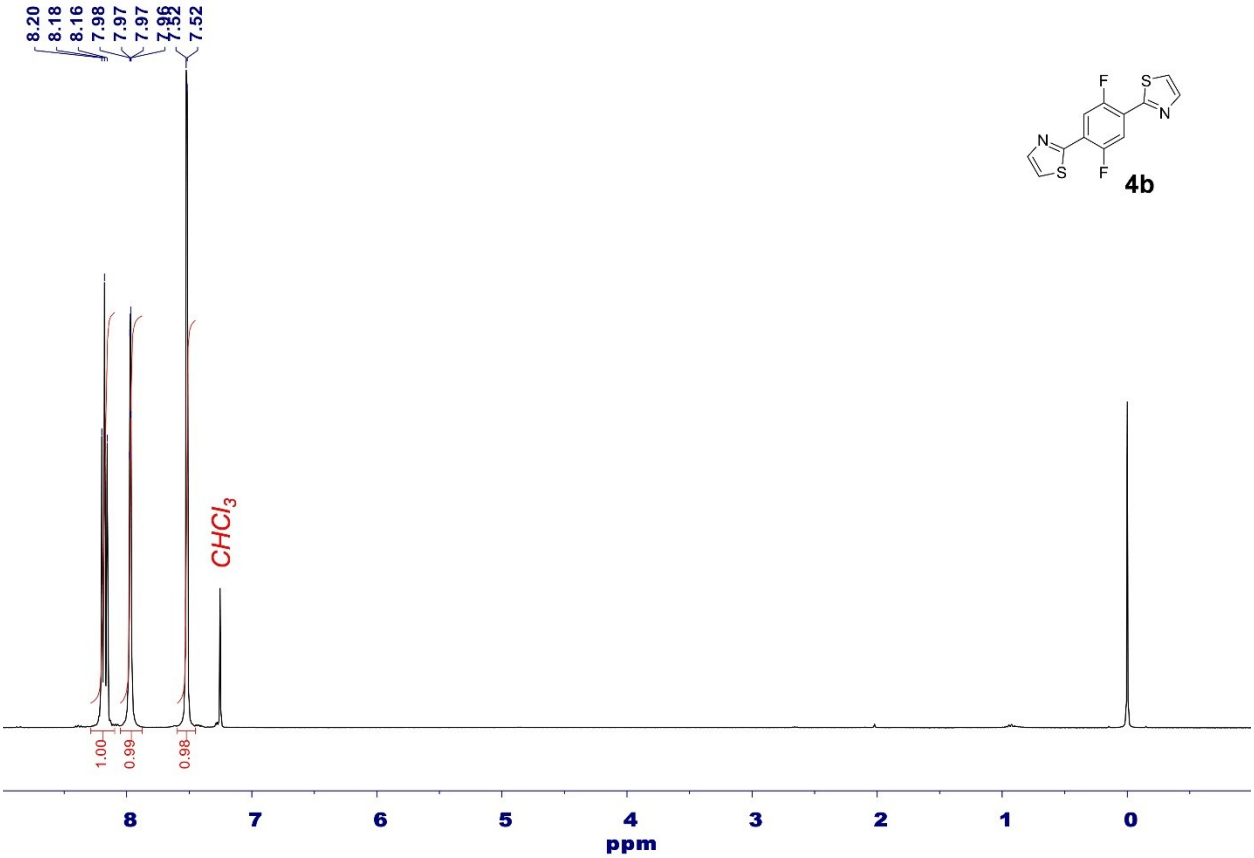

Figure S13. ^{1}H NMR spectrum of 1,4-di(thiazol-2-yl)-2,5-difluorobenzene **4b** ($CDCl_3$, 400 MHz, 323 K).

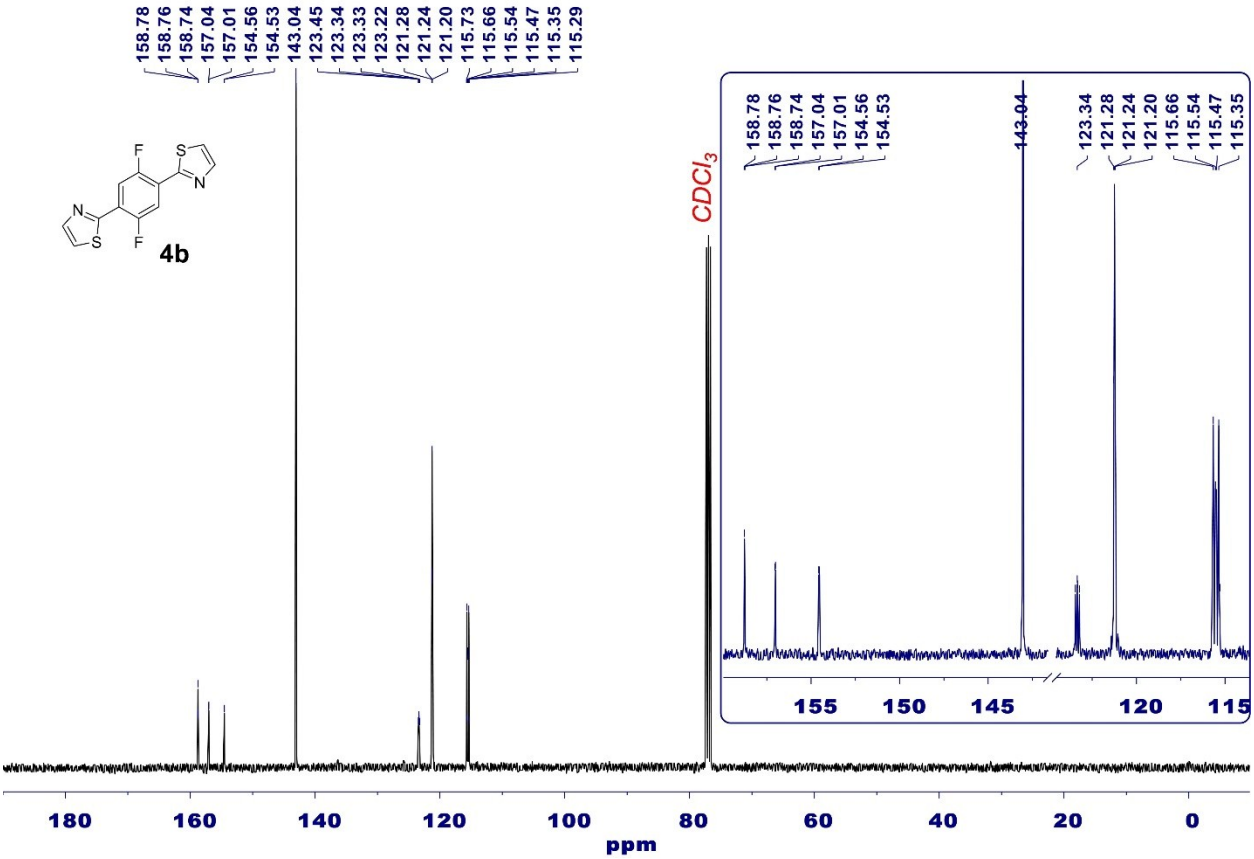

Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum of 1,4-di(thiazol-2-yl)-2,5-difluorobenzene **4b** ($CDCl_3$, 100 MHz, 323 K).

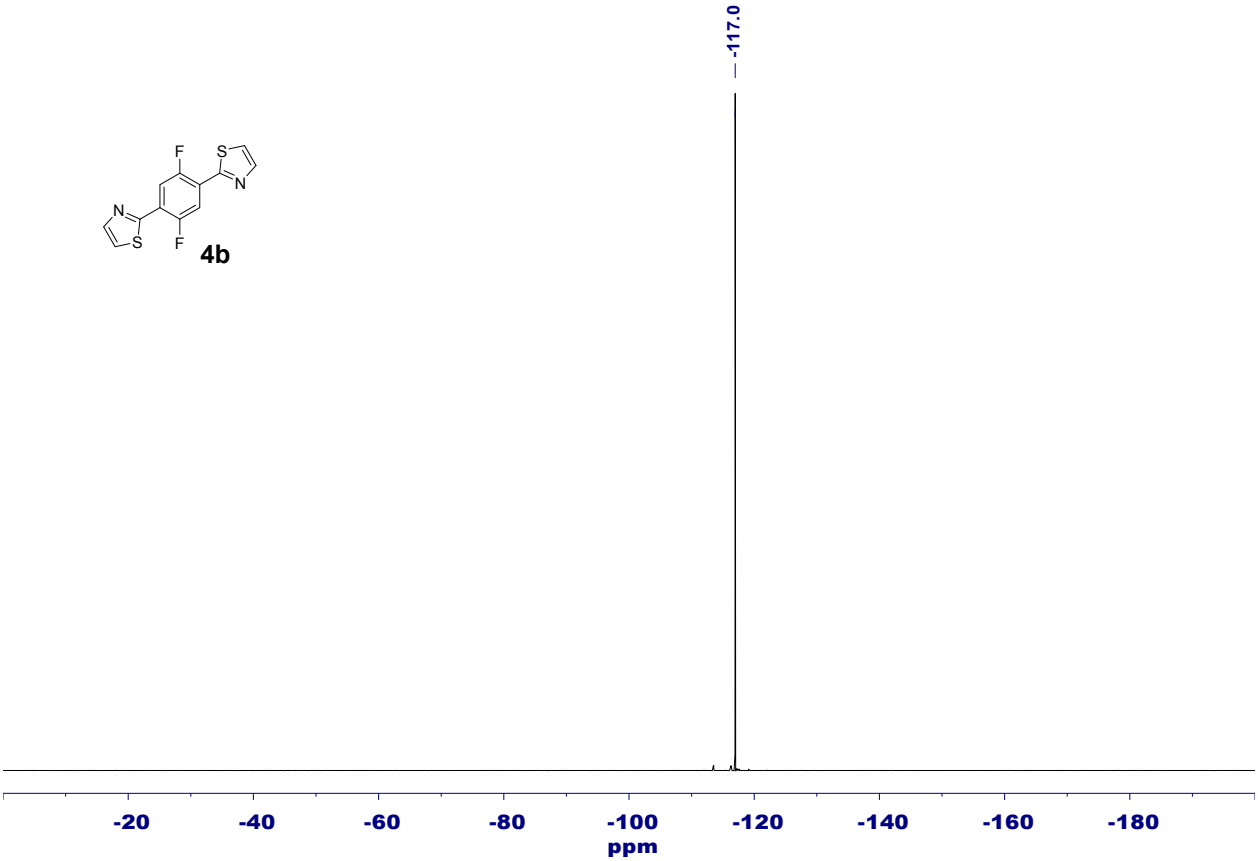

Figure S15. $^{19}F\{^{1}H\}$ NMR spectrum of 1,4-di(thiazol-2-yl)-2,5-difluorobenzene **4b** ($CDCl_3$, 564 MHz, 298 K).

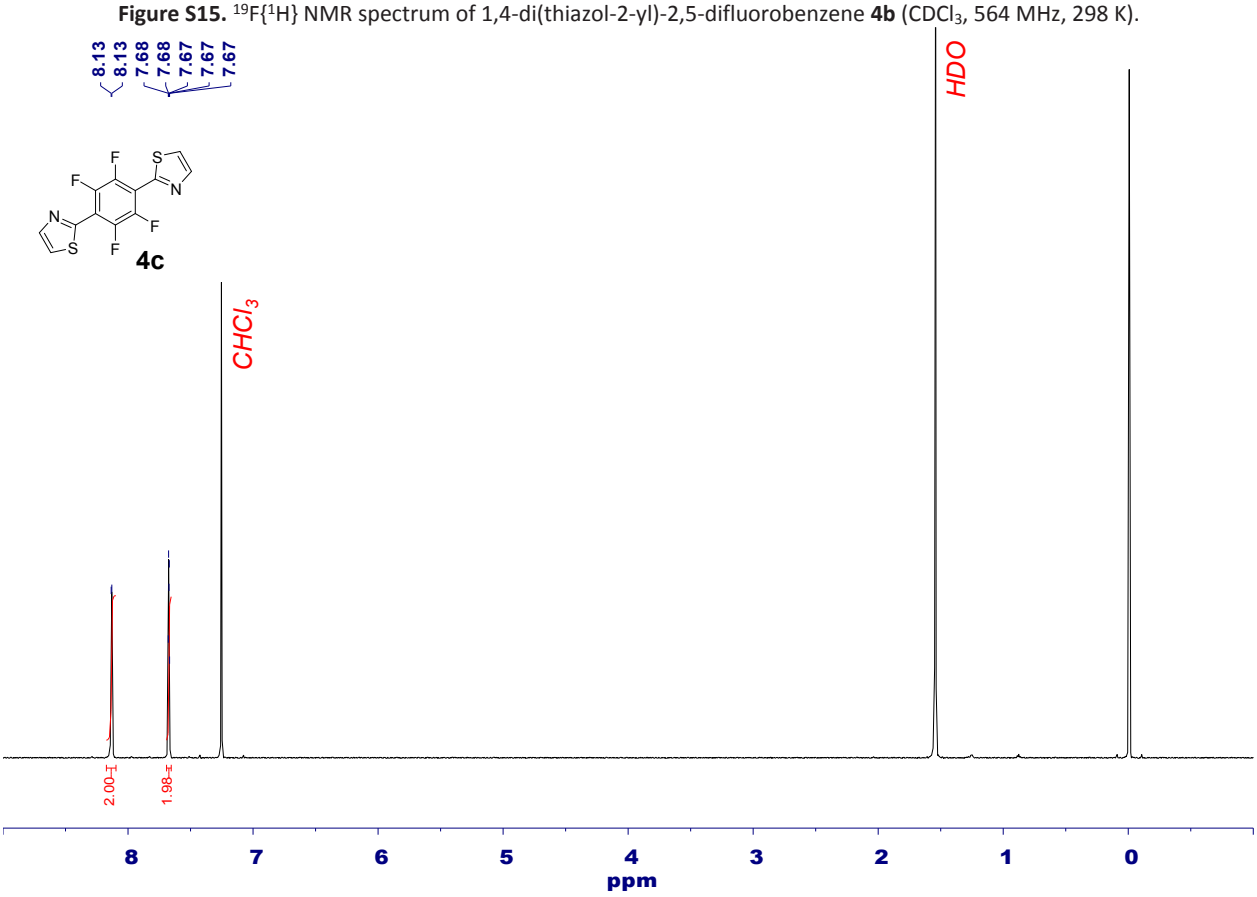

Figure S16. ^{1}H NMR spectrum of 1,4-di(thiazol-2-yl)-tetrafluorobenzene **4c** ($CDCl_3$, 600 MHz, 298 K).

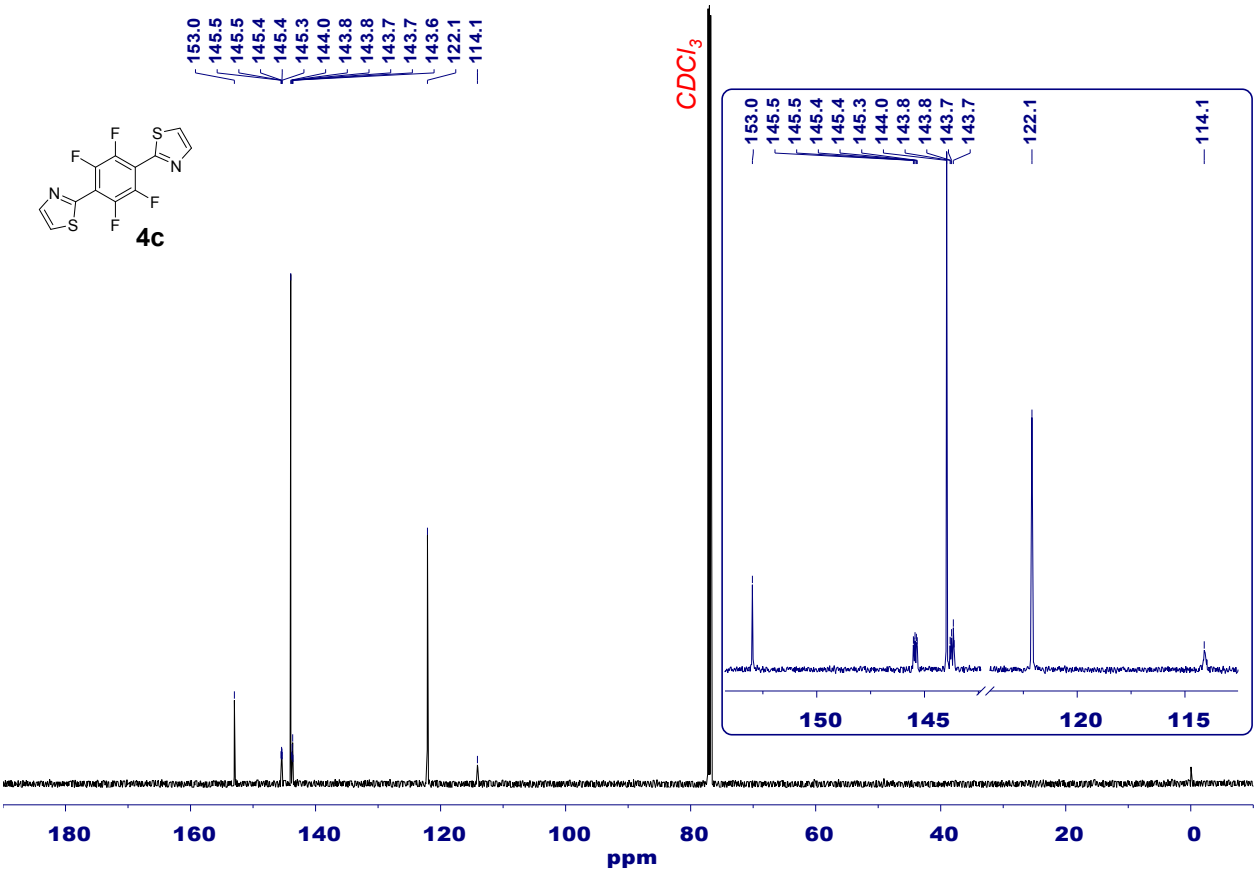

Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum of 1,4-di(thiazol-2-yl)-tetrafluorobenzene **4c** ($CDCl_3$, 150 MHz, 298 K).

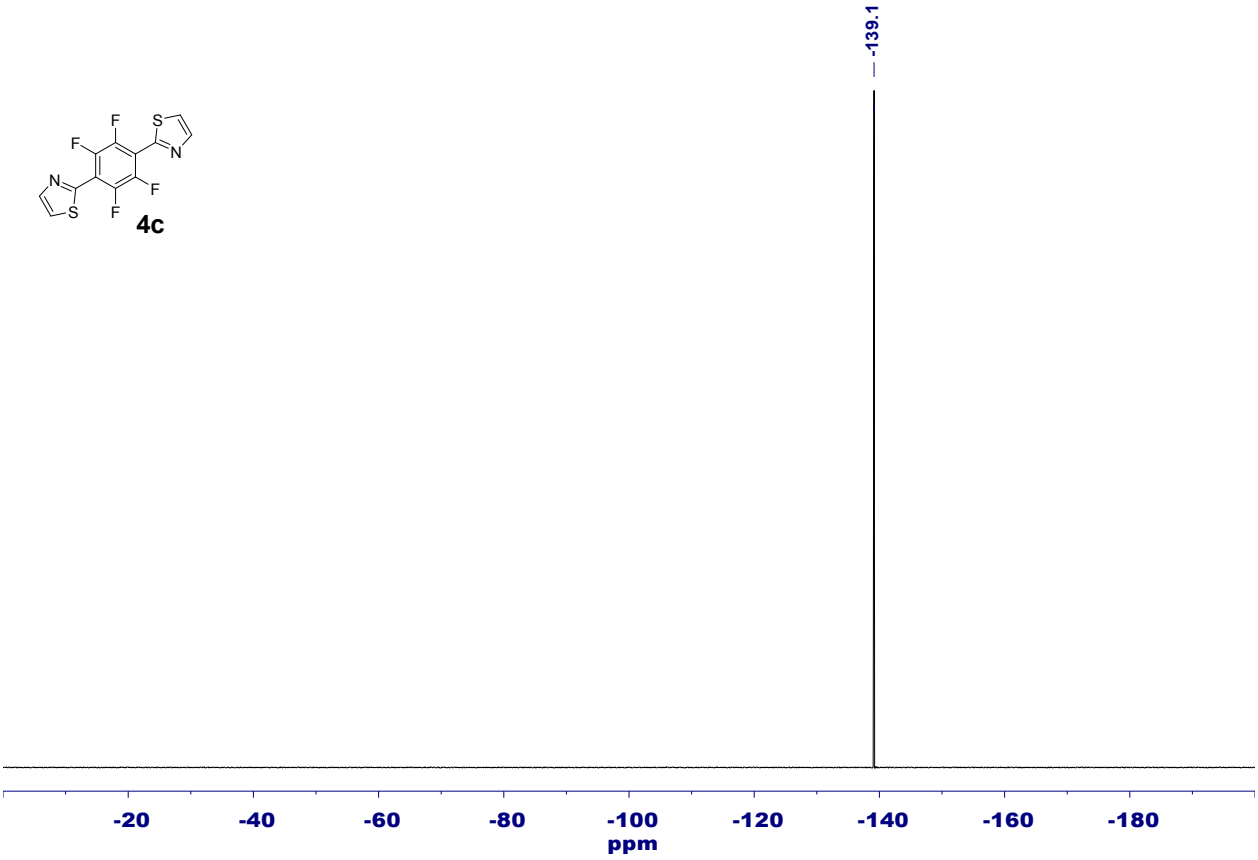

Figure S18. $^{19}F\{^{1}H\}$ NMR spectrum of 1,4-di(thiazol-2-yl)-tetrafluorobenzene **4c** ($CDCl_3$, 564 MHz, 298 K).

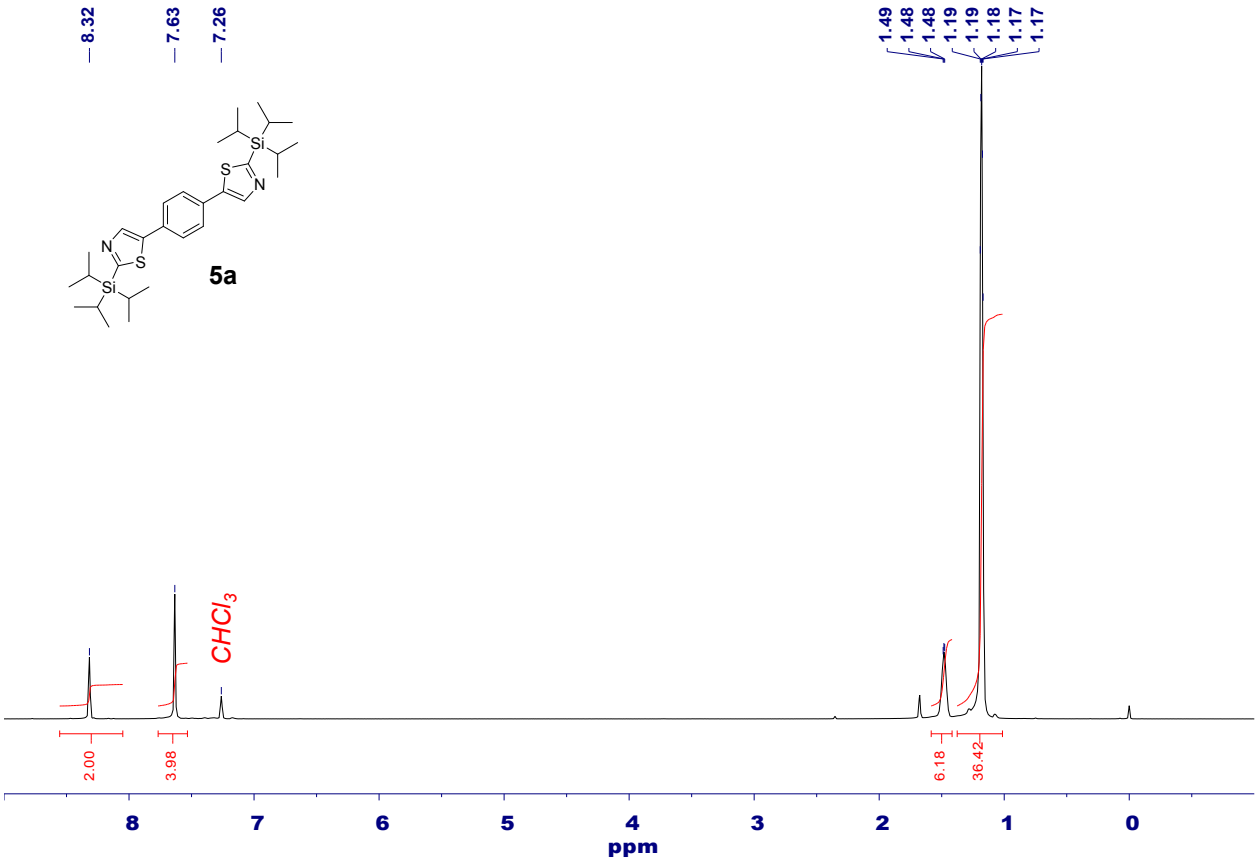

Figure S19. ^{1}H NMR spectrum of 1,4-di(2-(triisopropylsilyl)thiazol-5-yl)benzene **5a** ($CDCl_3$, 400 MHz, 298 K).

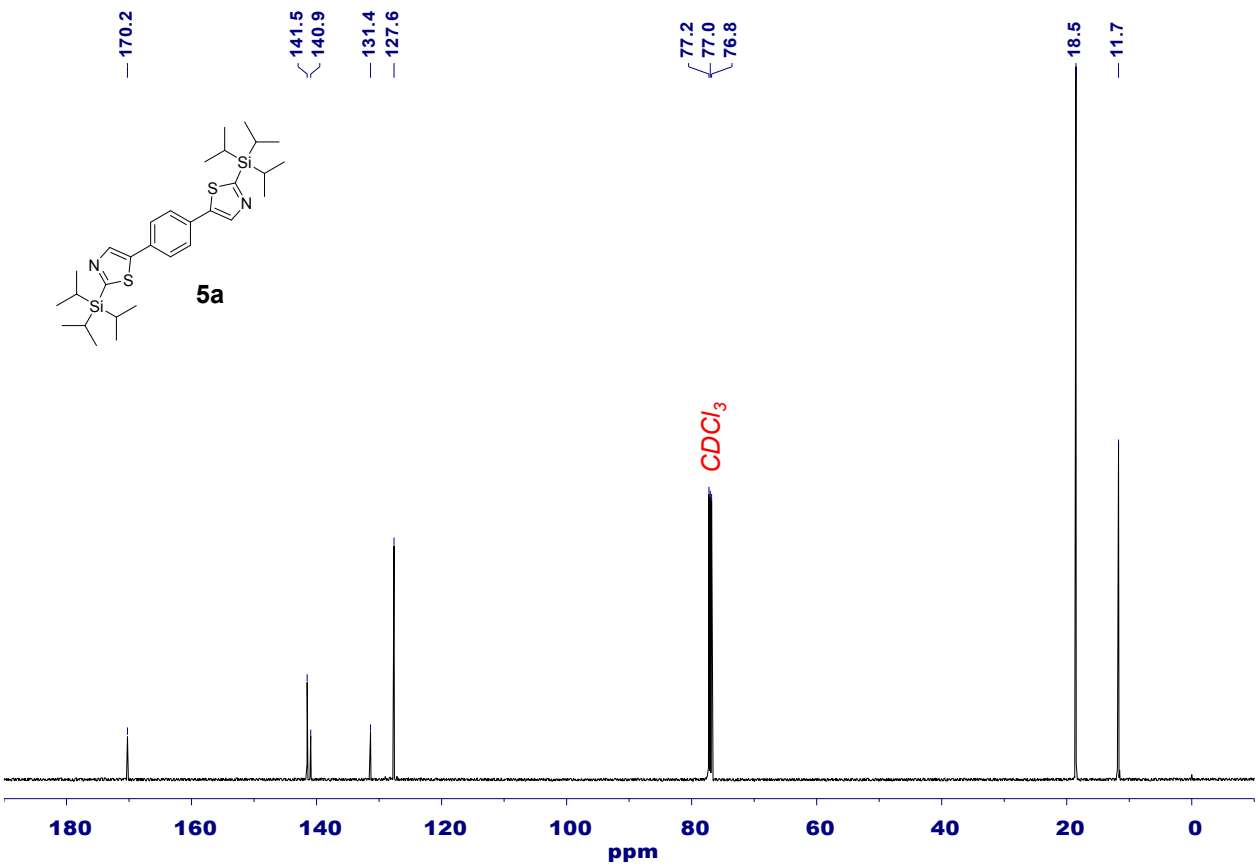

Figure S20. $^{13}C\{^{1}H\}$ NMR spectrum of 1,4-di(2-(triisopropylsilyl)thiazol-5-yl)benzene **5a** ($CDCl_3$, 100 MHz, 298 K).

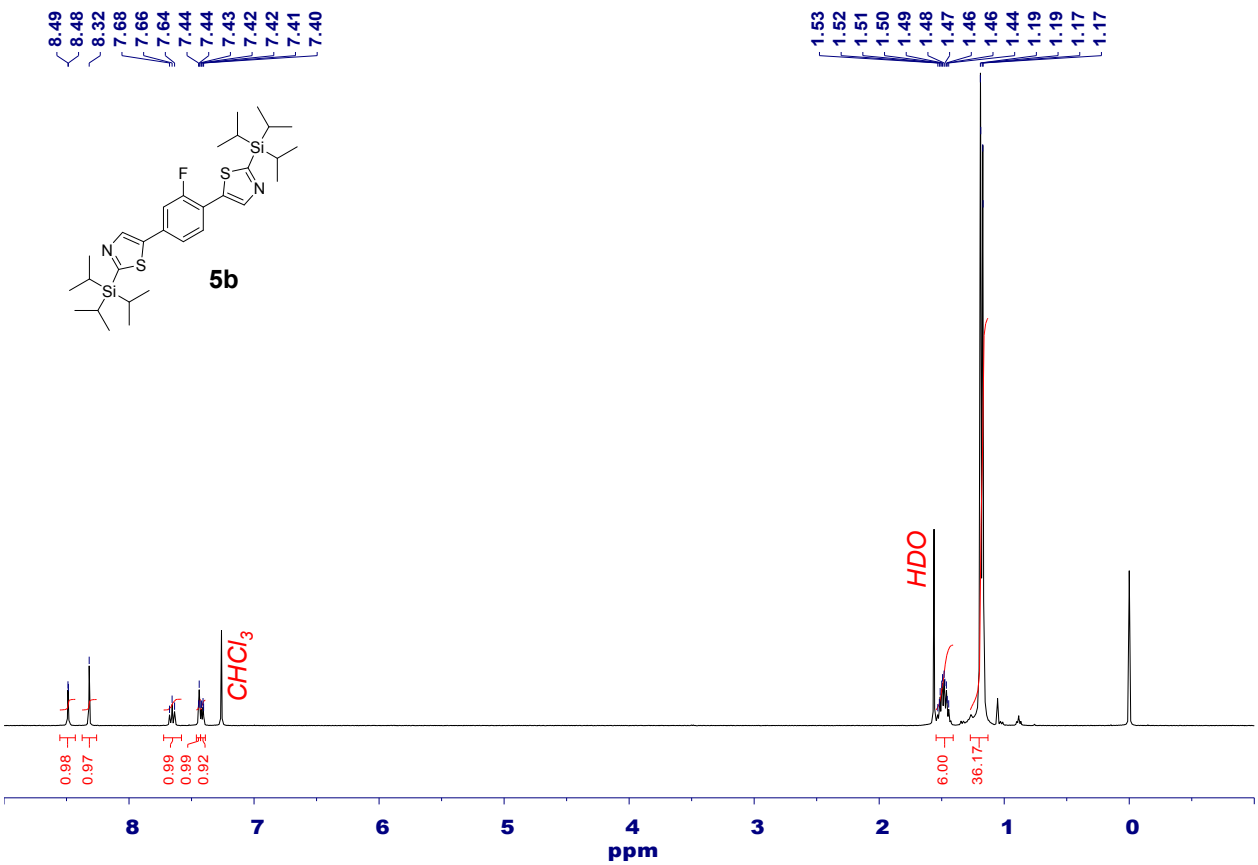

Figure S21. ^{1}H NMR spectrum of 1,4-di(2-(triisopropylsilyl)thiazol-5-yl)-2-fluorobenzene **5b** ($CDCl_3$, 400 MHz, 298 K).

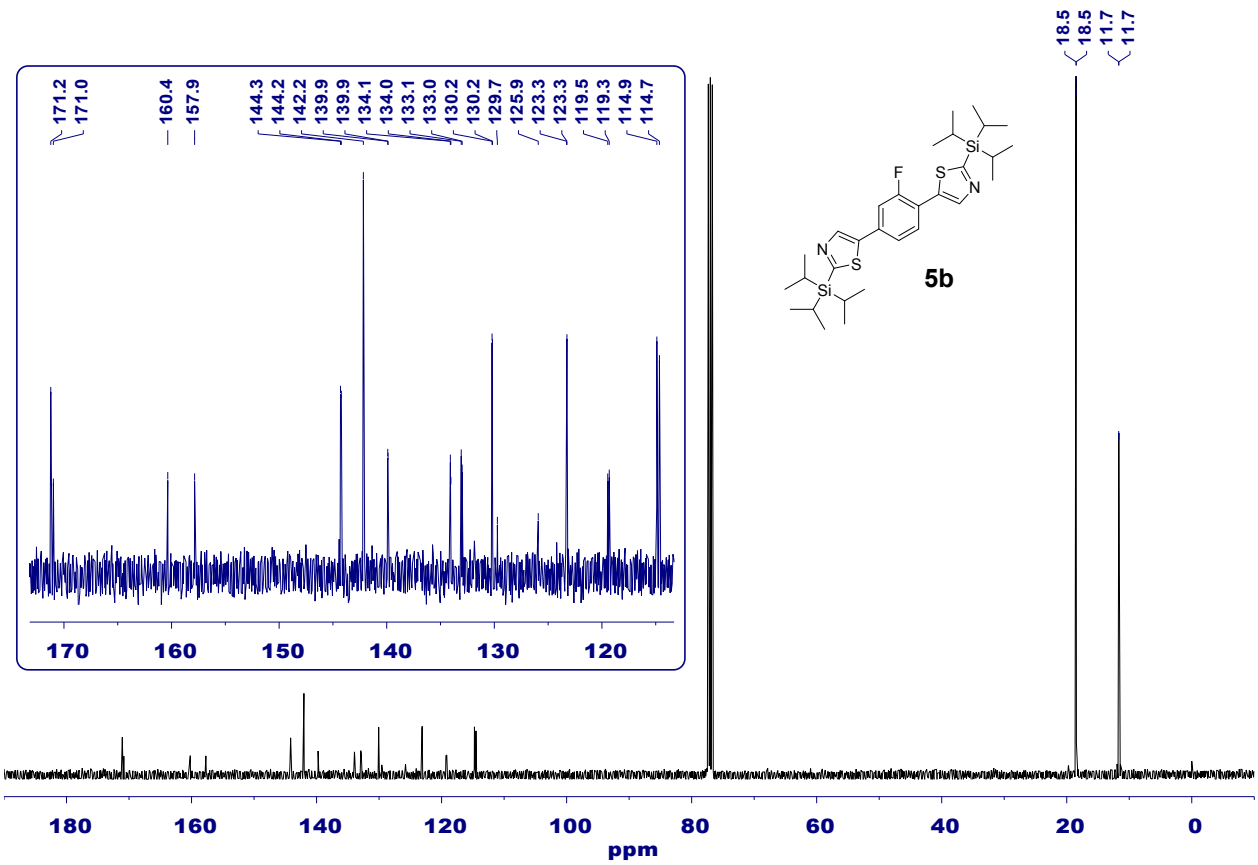

Figure S22. $^{13}C\{^{1}H\}$ NMR spectrum of 1,4-di(2-(triisopropylsilyl)thiazol-5-yl)-2-fluorobenzene **5b** ($CDCl_3$, 150 MHz, 298 K).

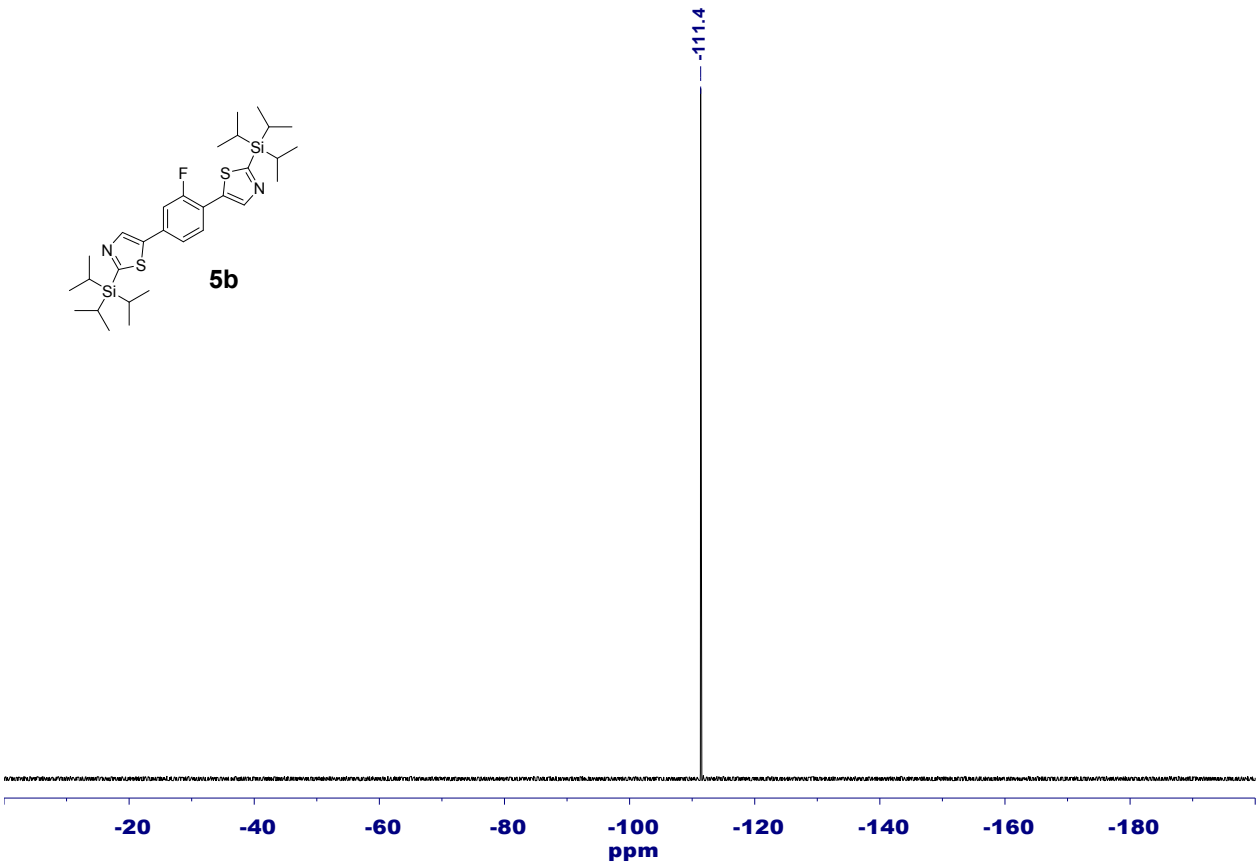

Figure S23. $^{19}F\{^{1}H\}$ NMR spectrum of 1,4-di(2-(triisopropylsilyl)thiazol-5-yl)-2-fluorobenzene **5b** ($CDCl_3$,376 MHz, 298 K).

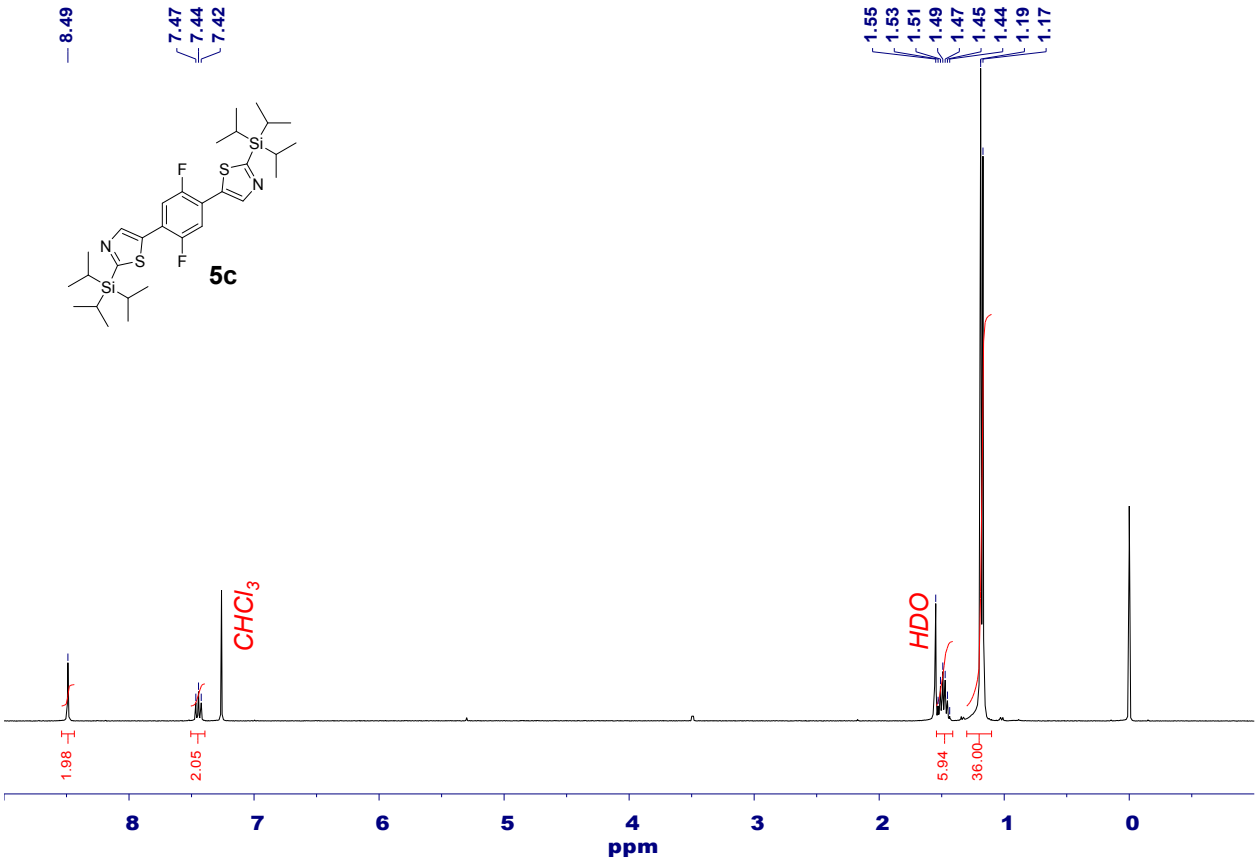

Figure S24. ^{1}H NMR spectrum of 1,4-di(2-(triisopropylsilyl)thiazol-5-yl)-2,5-difluorobenzene **5c** ($CDCl_3$, 400 MHz, 298 K).

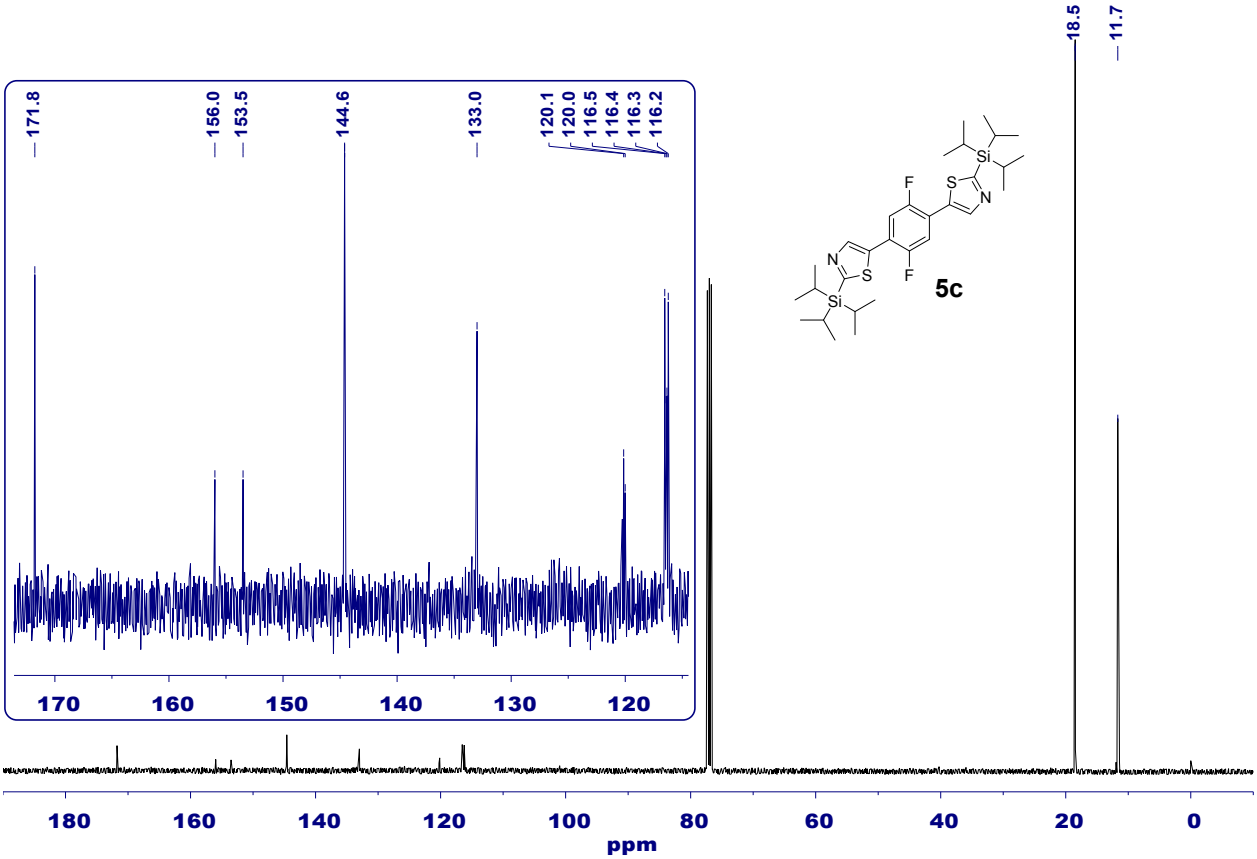

Figure S25. $^{13}C\{^{1}H\}$ NMR spectrum of 1,4-di(2-(triisopropylsilyl)thiazol-5-yl)-2,5-difluorobenzene **5c** ($CDCl_3$, 150 MHz, 298 K).

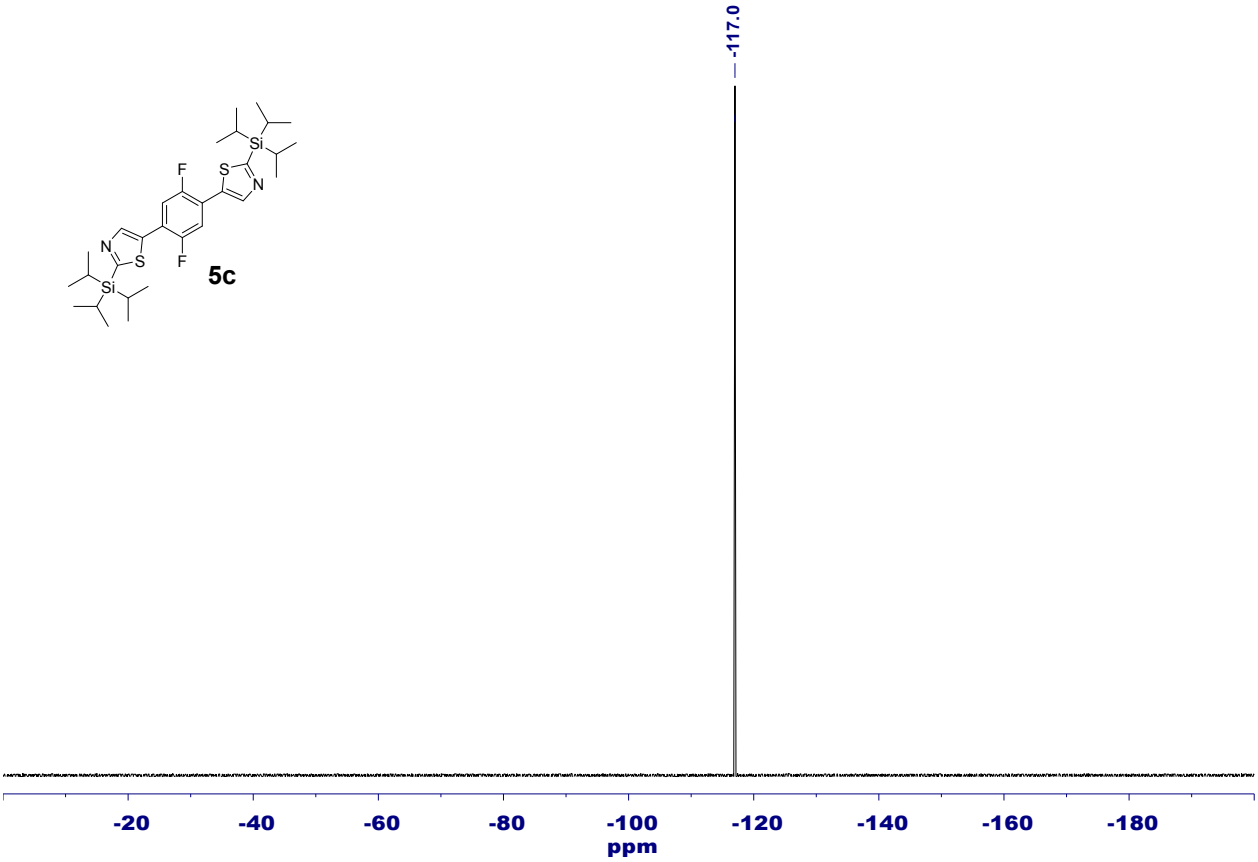

Figure S26. $^{19}F\{^{1}H\}$ NMR spectrum of 1,4-di(2-(triisopropylsilyl)thiazol-5-yl)-2,5-difluorobenzene **5c** ($CDCl_3$, 376 MHz, 298 K).

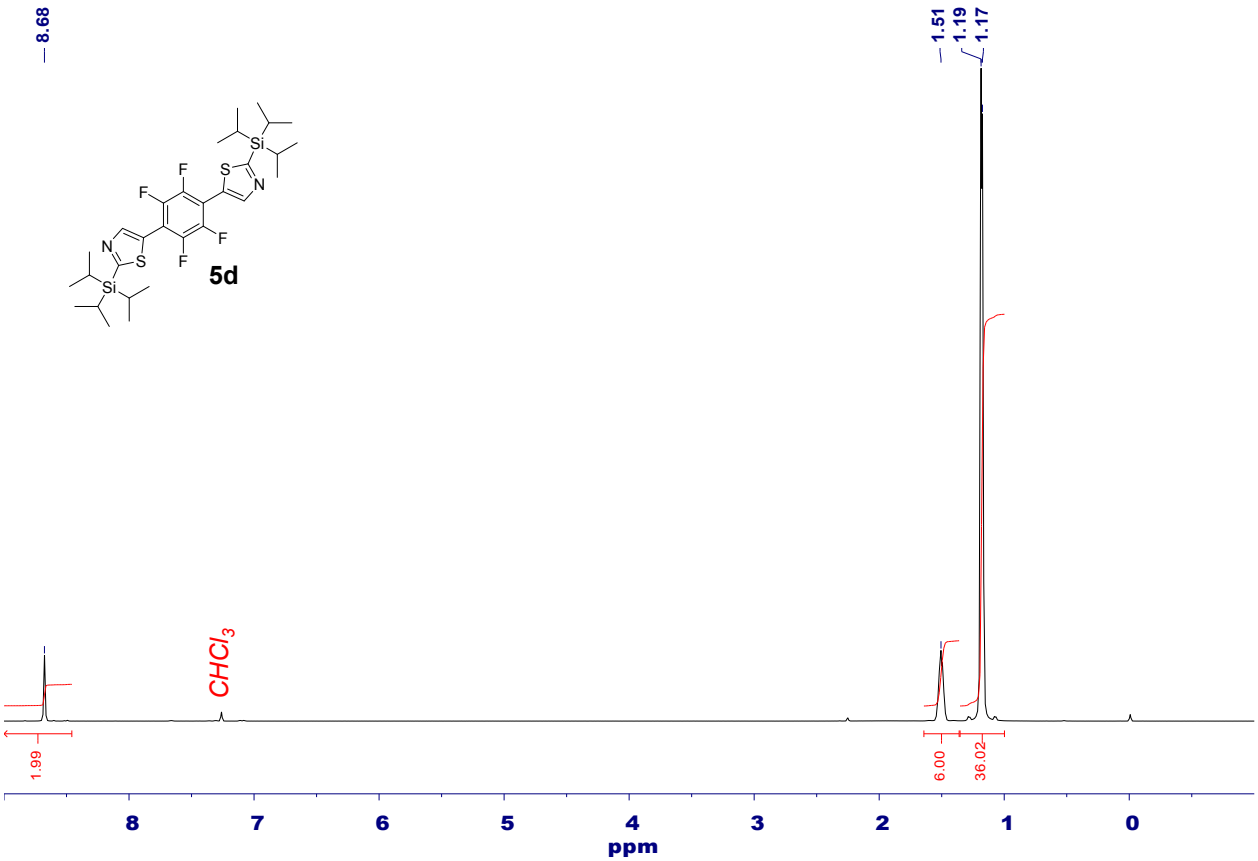

Figure S27. ^{1}H NMR spectrum of 1,4-di(2-(triisopropylsilyl)thiazol-5-yl)-tetrafluorobenzene **5d** ($CDCl_3$, 600 MHz, 298 K).

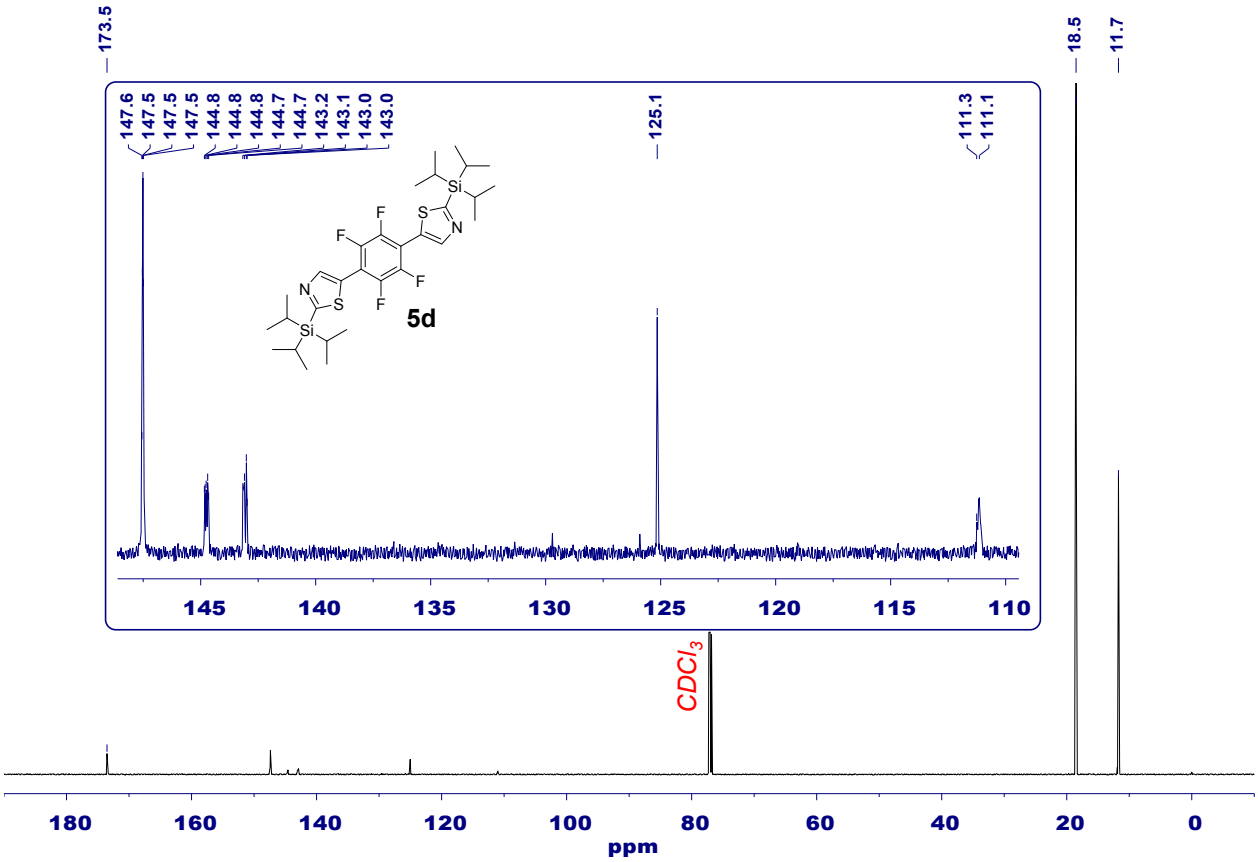

Figure S28. $^{13}C\{^{1}H\}$ NMR spectrum of 1,4-di(2-(triisopropylsilyl)thiazol-5-yl)-tetrafluorobenzene **5d** ($CDCl_3$, 150 MHz, 298 K).

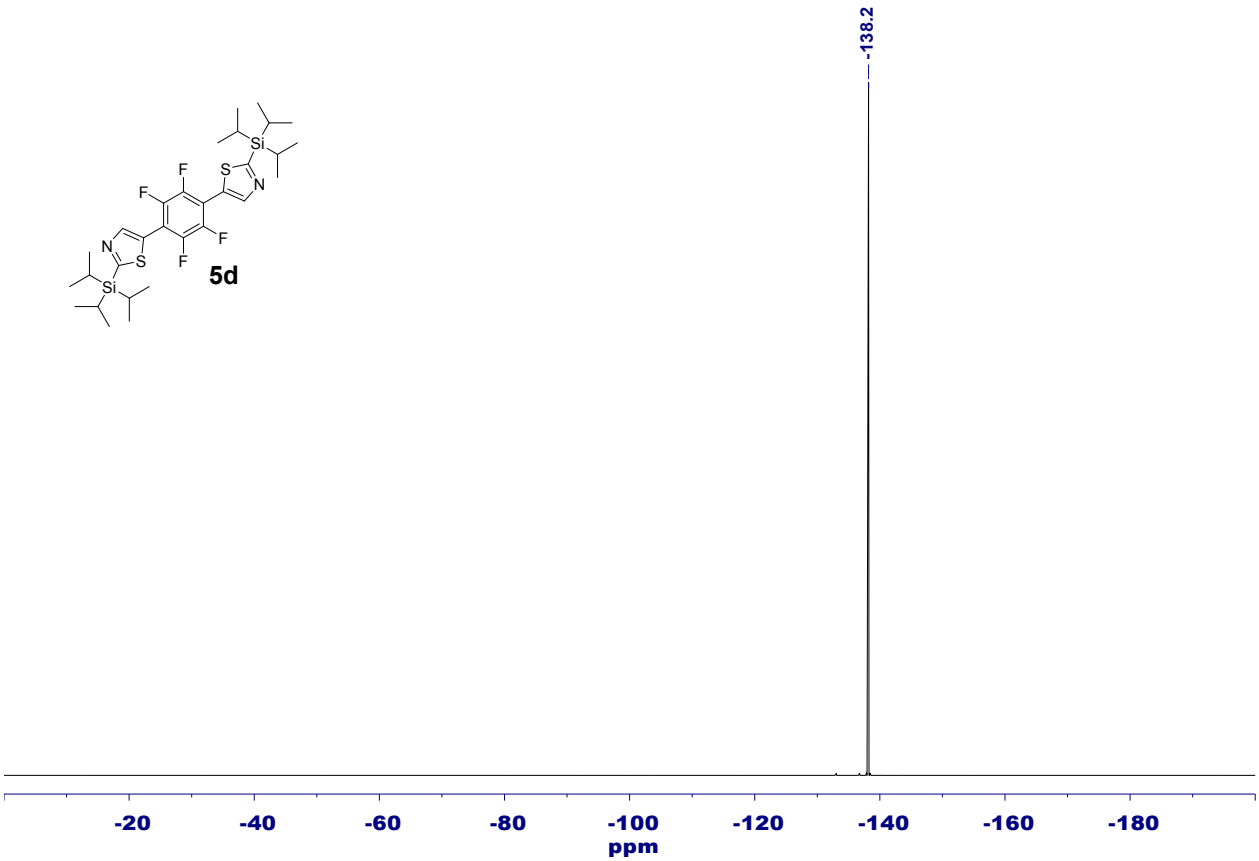

Figure S29. $^{19}F\{^{1}H\}$ NMR spectrum of 1,4-di(2-(triisopropylsilyl)thiazol-5-yl)-tetrafluorobenzene **5d** ($CDCl_3$, 564 MHz, 298 K).

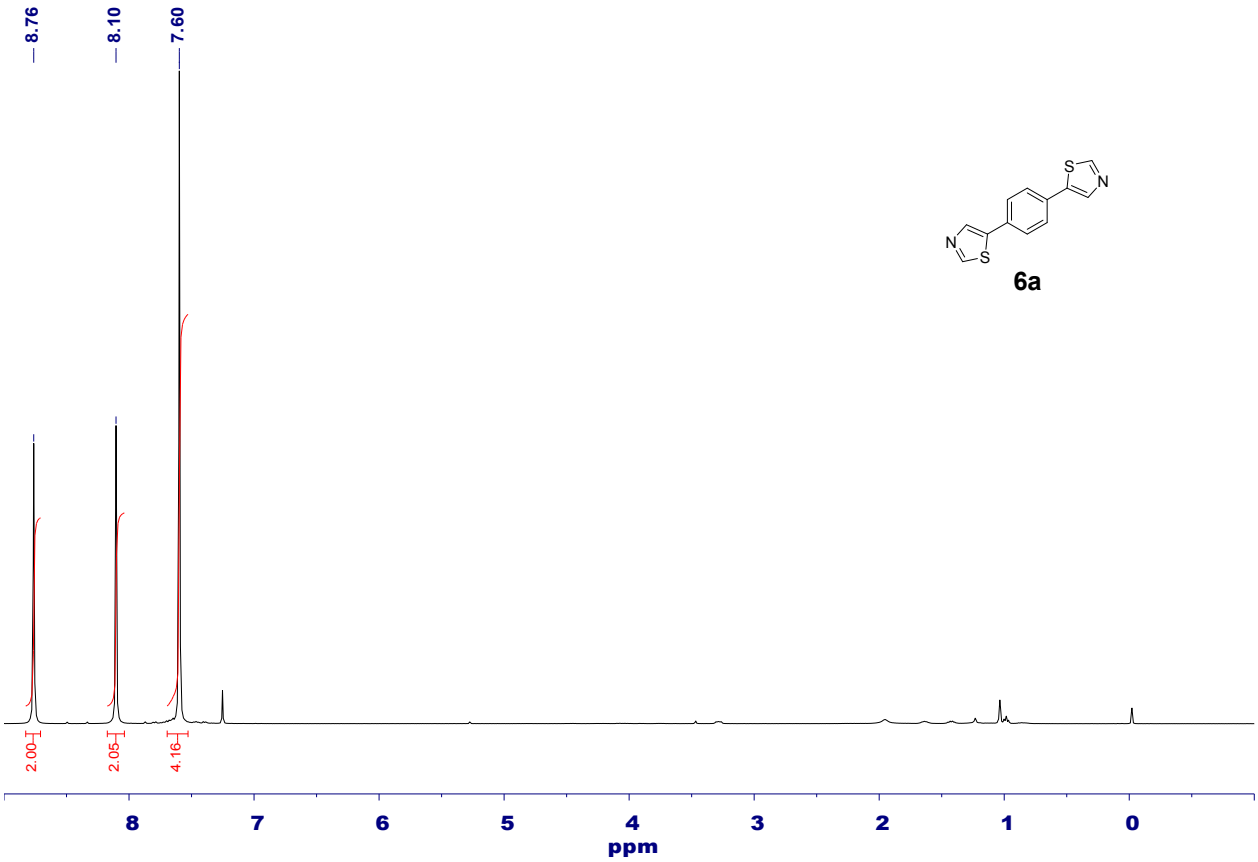

Figure S30. ^{1}H NMR spectrum of 1,4-di(thiazol-5-yl)-benzene **6a** ($CDCl_3$, 400 MHz, 298 K).

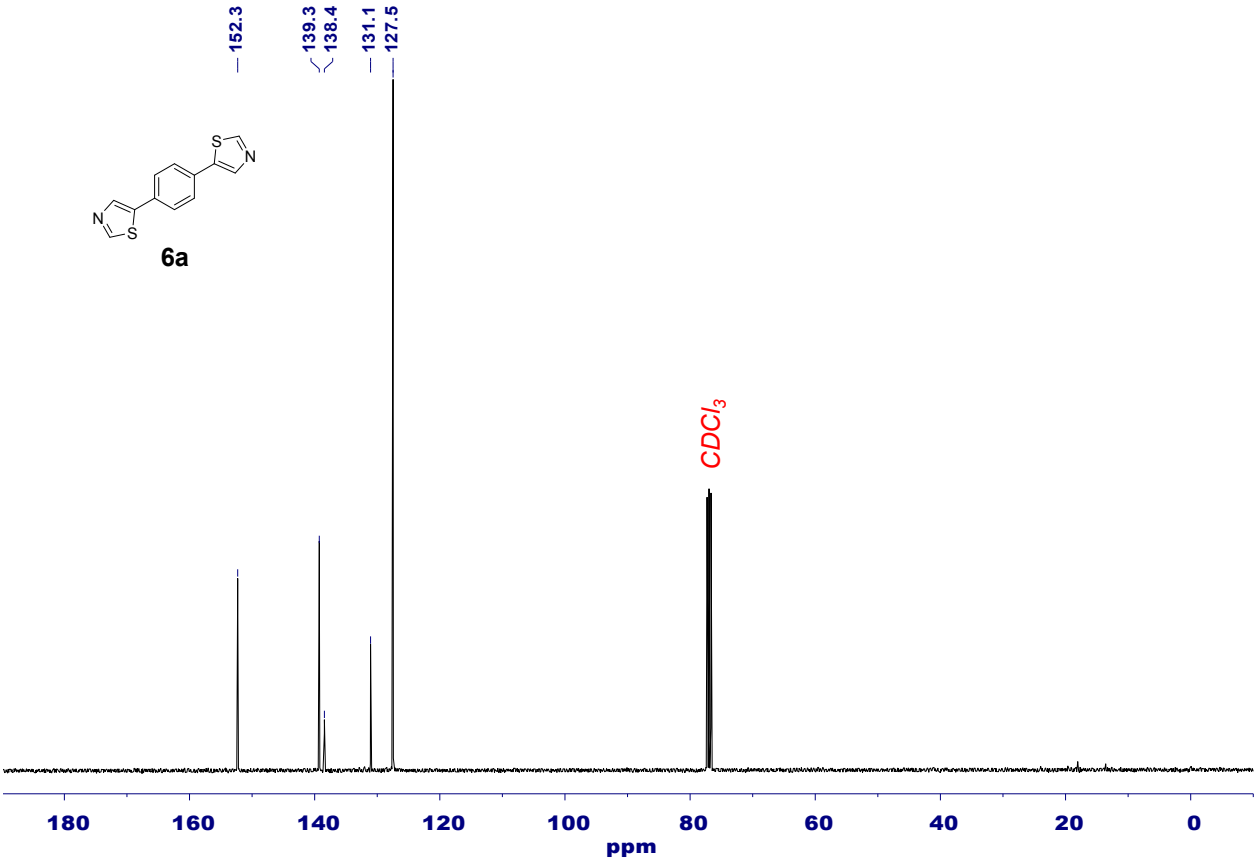

Figure S31. $^{13}C\{^{1}H\}$ NMR spectrum of 1,4-di(thiazol-5-yl)-benzene **6a** ($CDCl_3$, 150 MHz, 298 K).

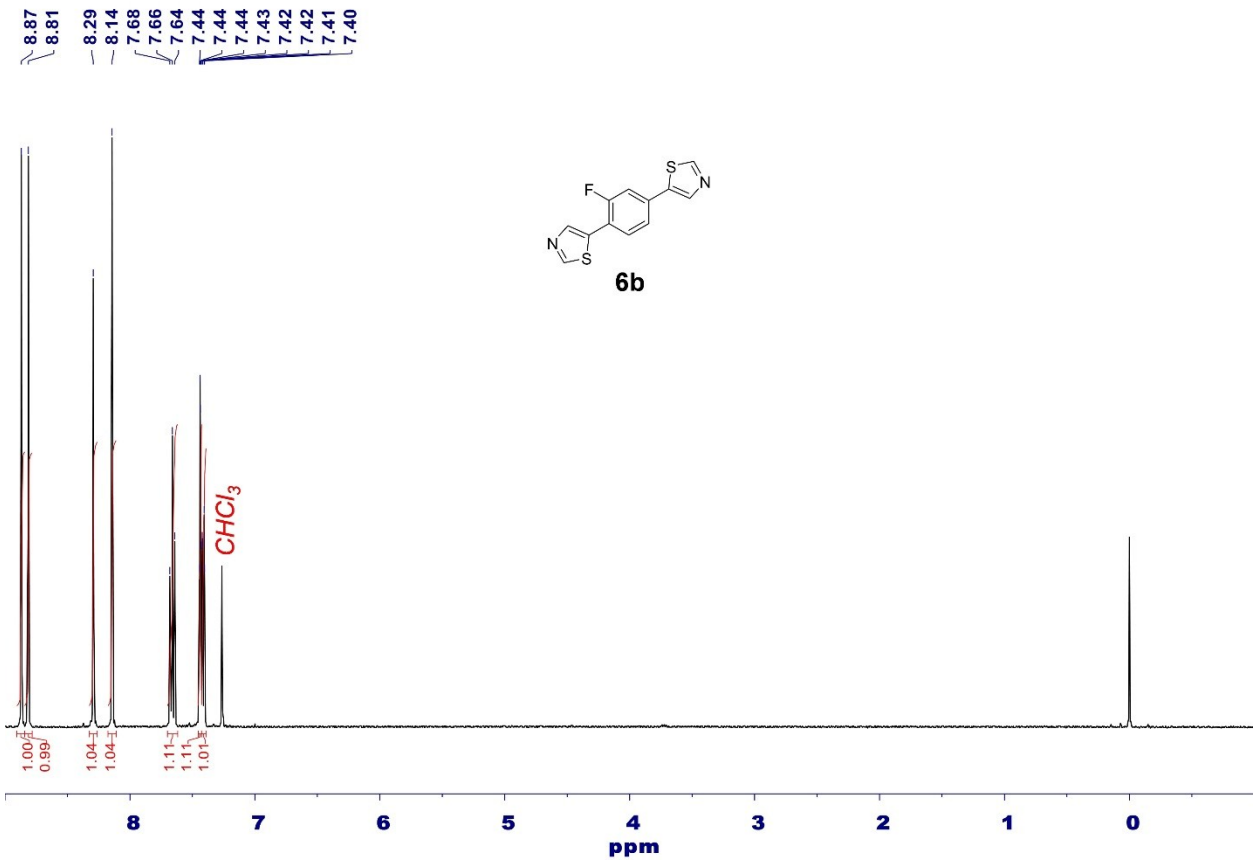

Figure S32. ^{1}H NMR spectrum of 1,4-di(thiazol-5-yl)-2-fluorobenzene **6b** ($CDCl_3$, 400 MHz, 298 K).

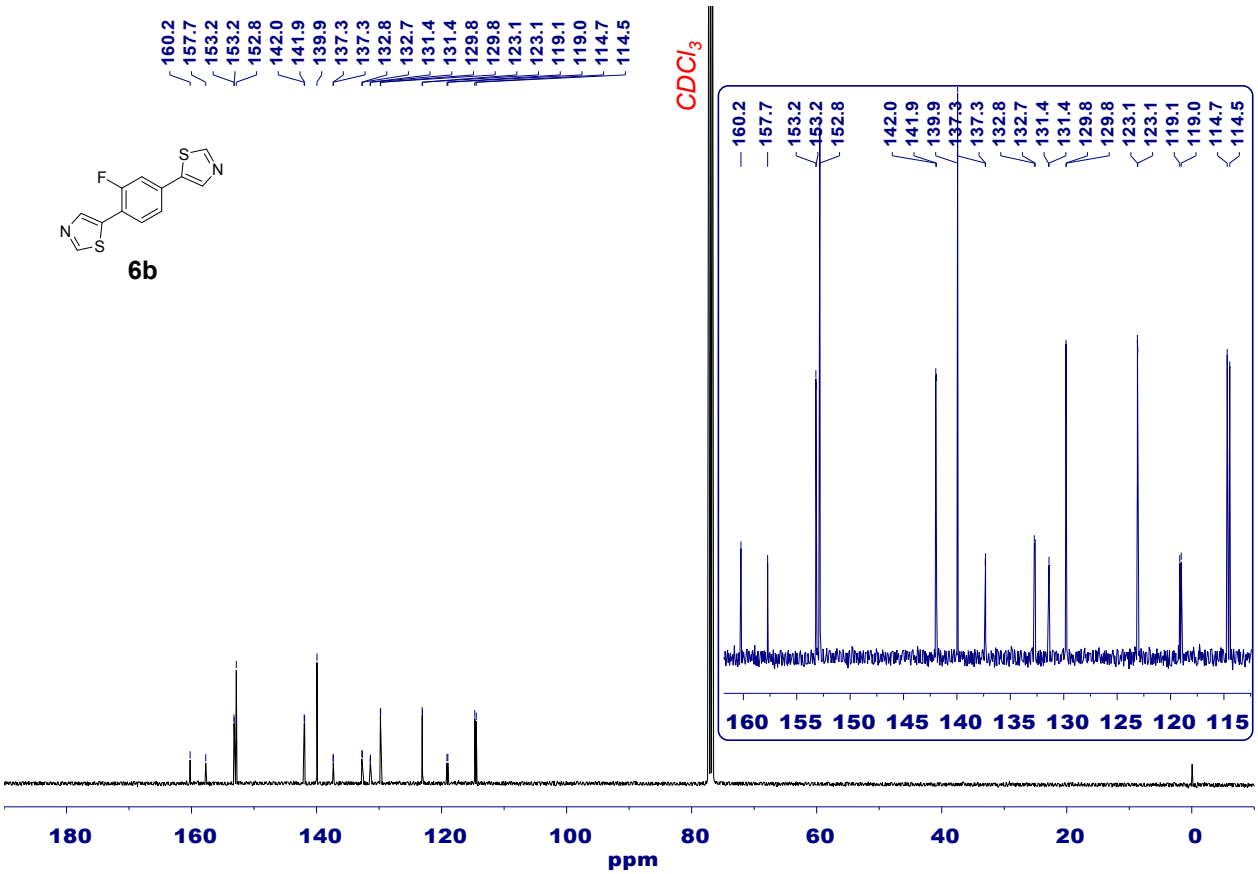

Figure S33. $^{13}C\{^{1}H\}$ NMR spectrum of 1,4-di(thiazol-5-yl)-2-fluorobenzene **6b** ($CDCl_3$, 150 MHz, 298 K).

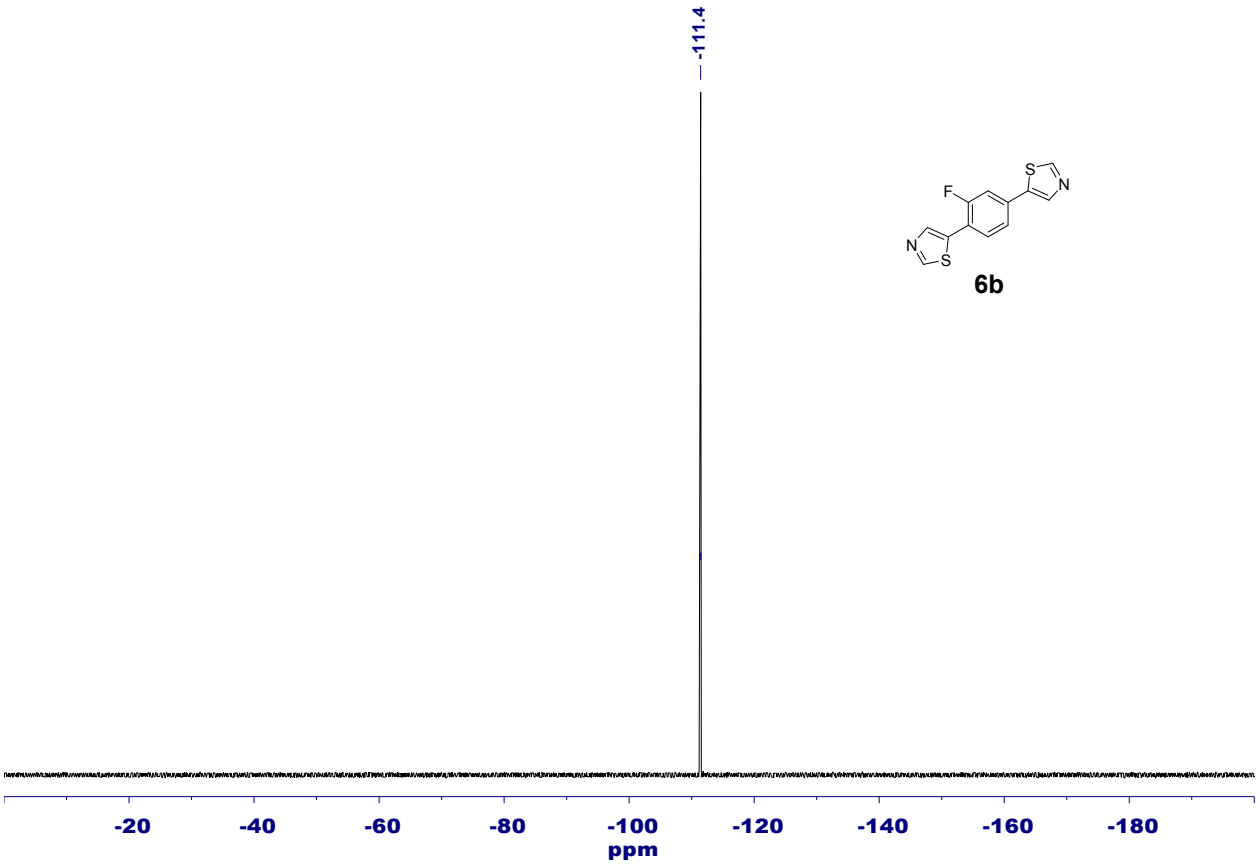

Figure S34. $^{19}F\{^{1}H\}$ NMR spectrum of 1,4-di(thiazol-5-yl)-2-fluorobenzene **6b** ($CDCl_3$, 376 MHz, 298 K).

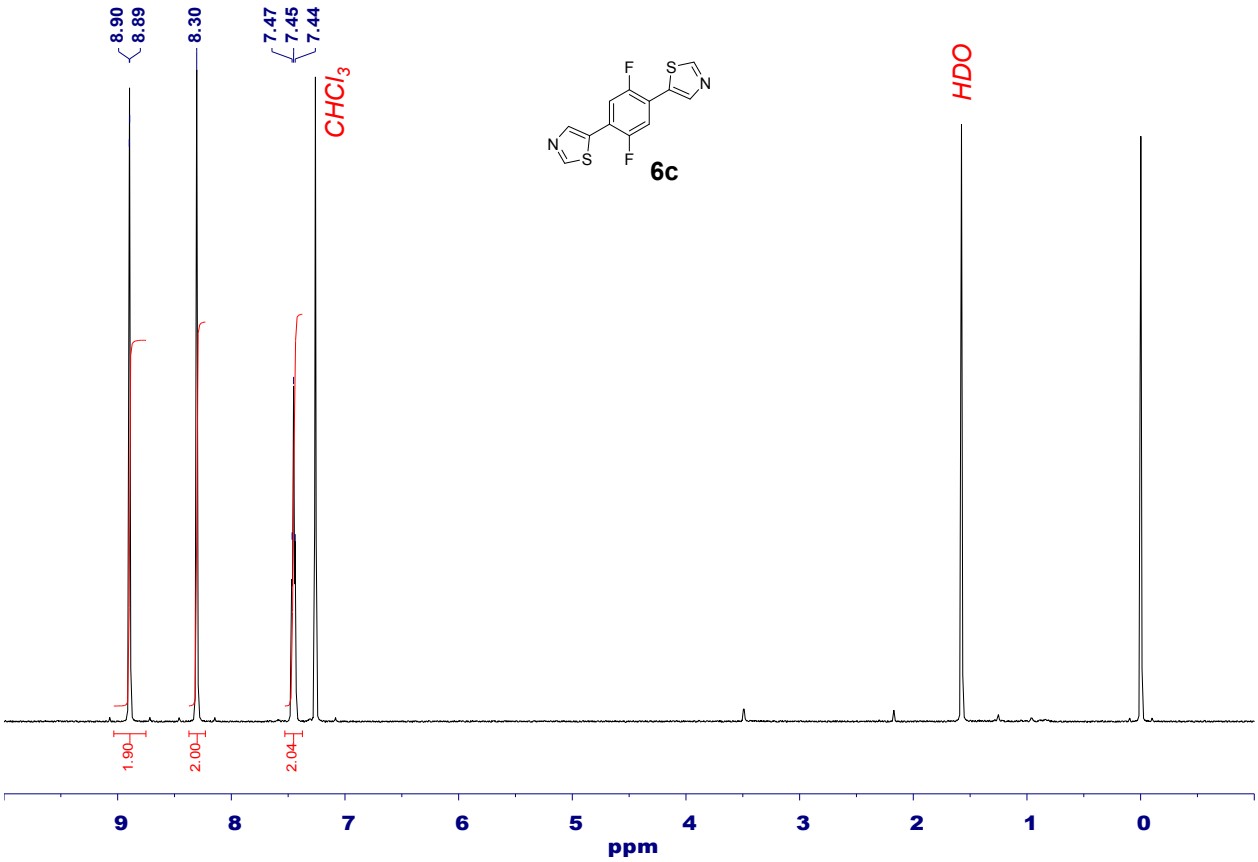

Figure S35. ^{1}H NMR spectrum of 1,4-di(thiazol-5-yl)-2,5-difluorobenzene **6c** ($CDCl_3$, 600 MHz, 298 K).

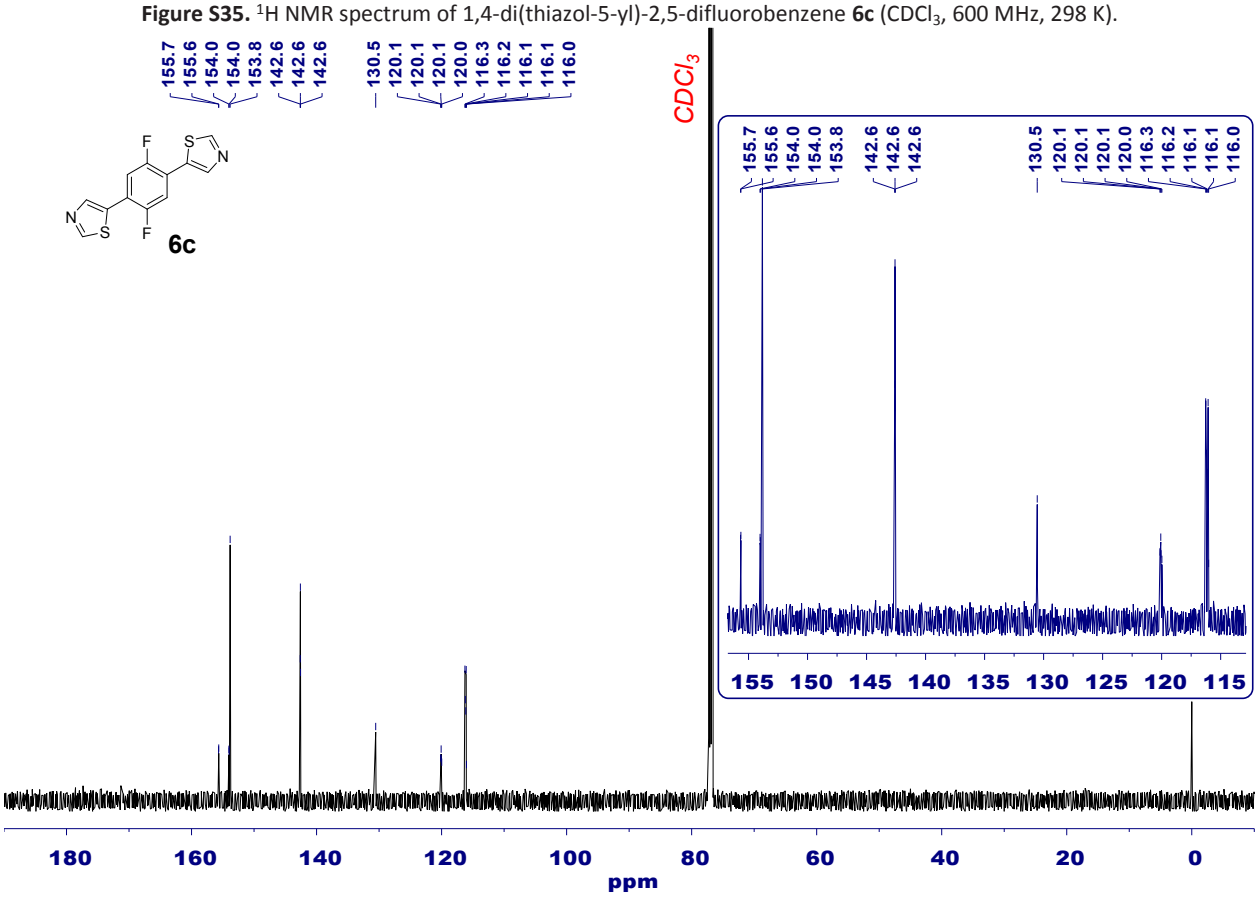

Figure S36. $^{13}C\{^{1}H\}$ NMR spectrum of 1,4-di(thiazol-5-yl)-2,5-difluorobenzene **6c** ($CDCl_3$, 150 MHz, 298 K).

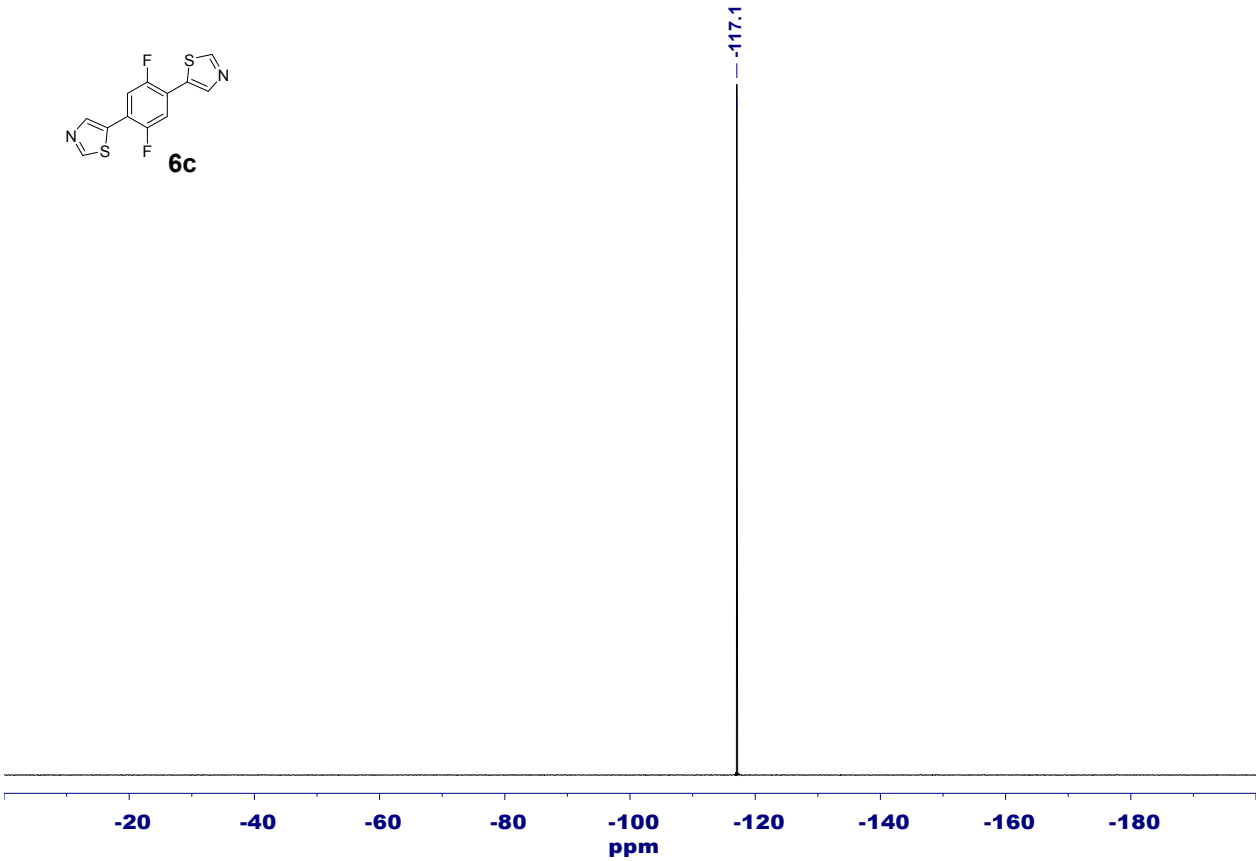

Figure S37. $^{19}F\{^{1}H\}$ NMR spectrum of 1,4-di(thiazol-5-yl)-2,5-difluorobenzene **6c** ($CDCl_3$, 564 MHz, 298 K).

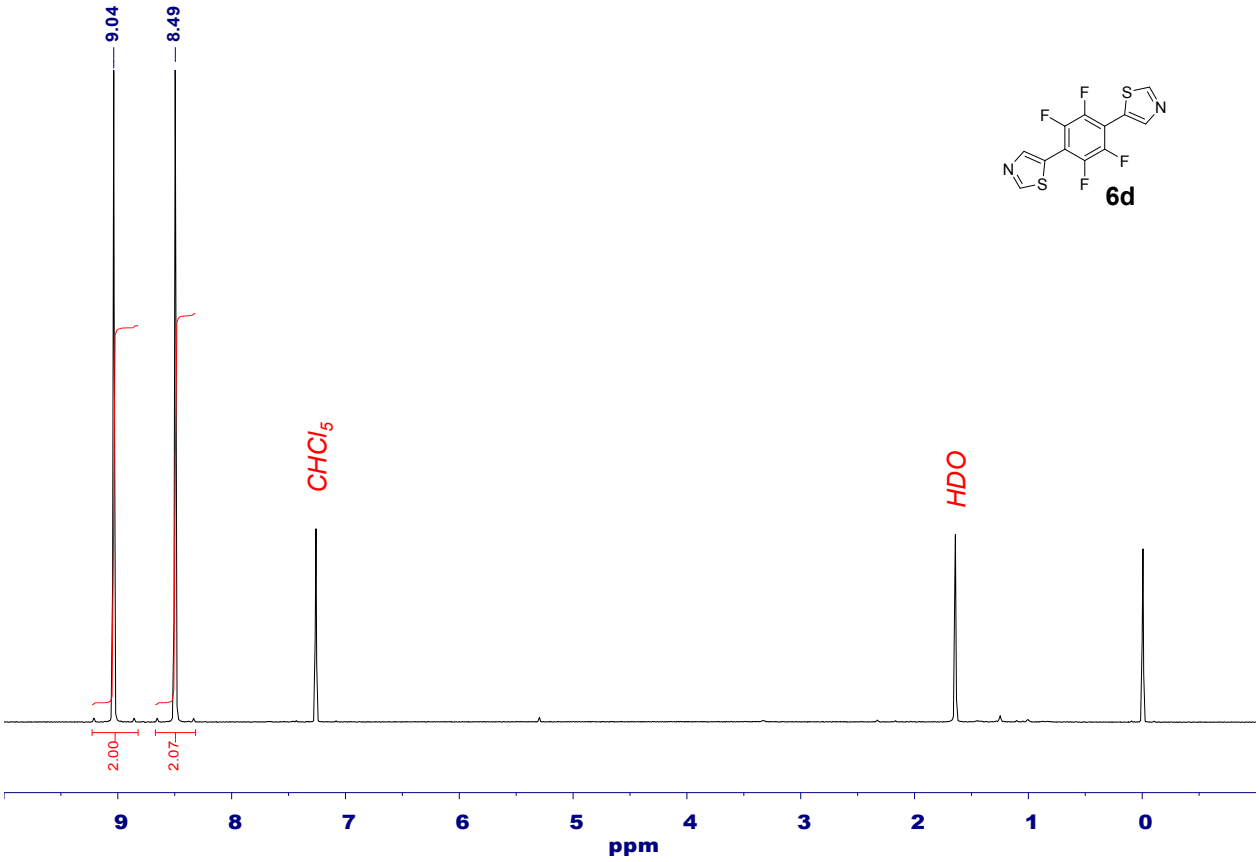

Figure S38. ^{1}H NMR spectrum of 1,4-di(thiazol-5-yl)-tetrafluorobenzene **6d** ($CDCl_3$, 600 MHz, 298 K).

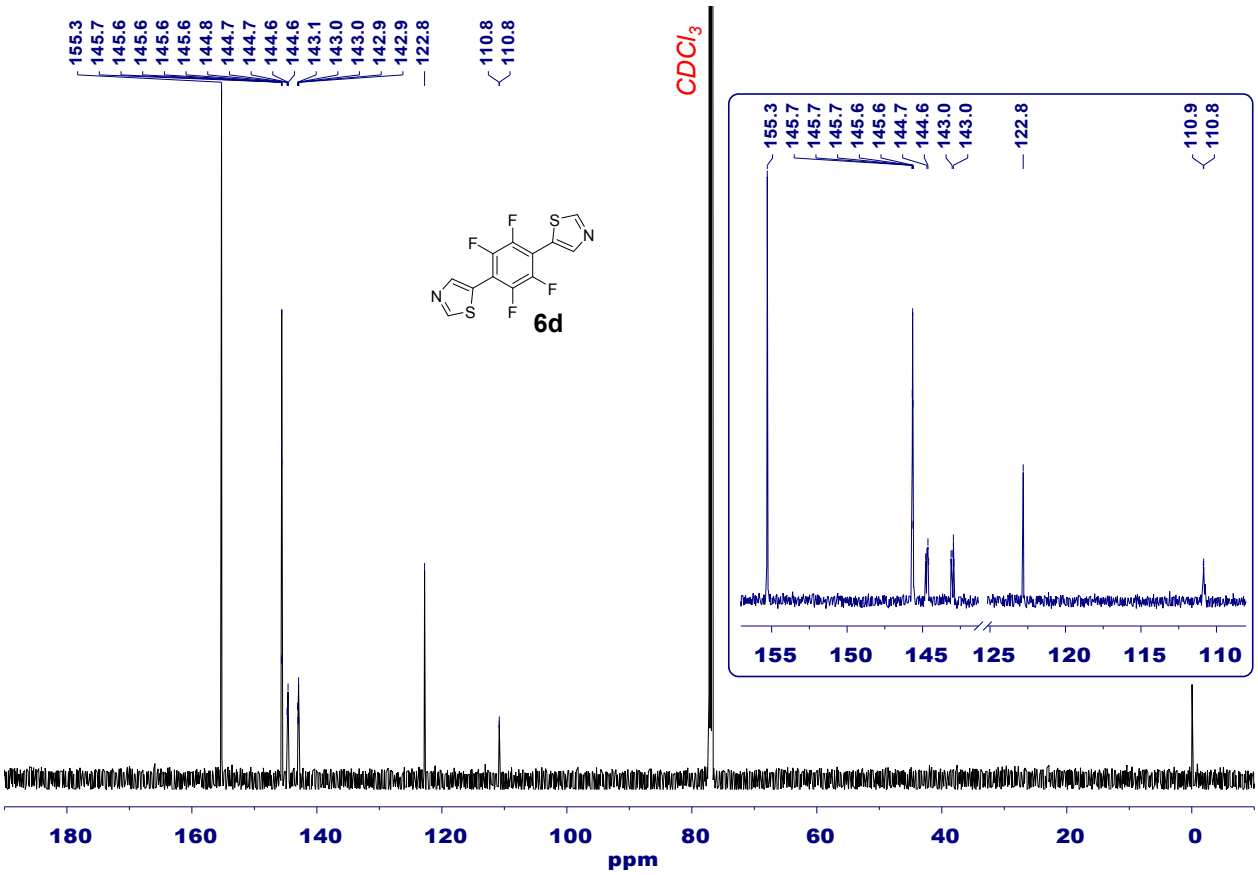

Figure S39. $^{13}C\{^{1}H\}$ NMR spectrum of 1,4-di(thiazol-5-yl)-tetrafluorobenzene **6d** ($CDCl_3$, 150 MHz, 298 K).

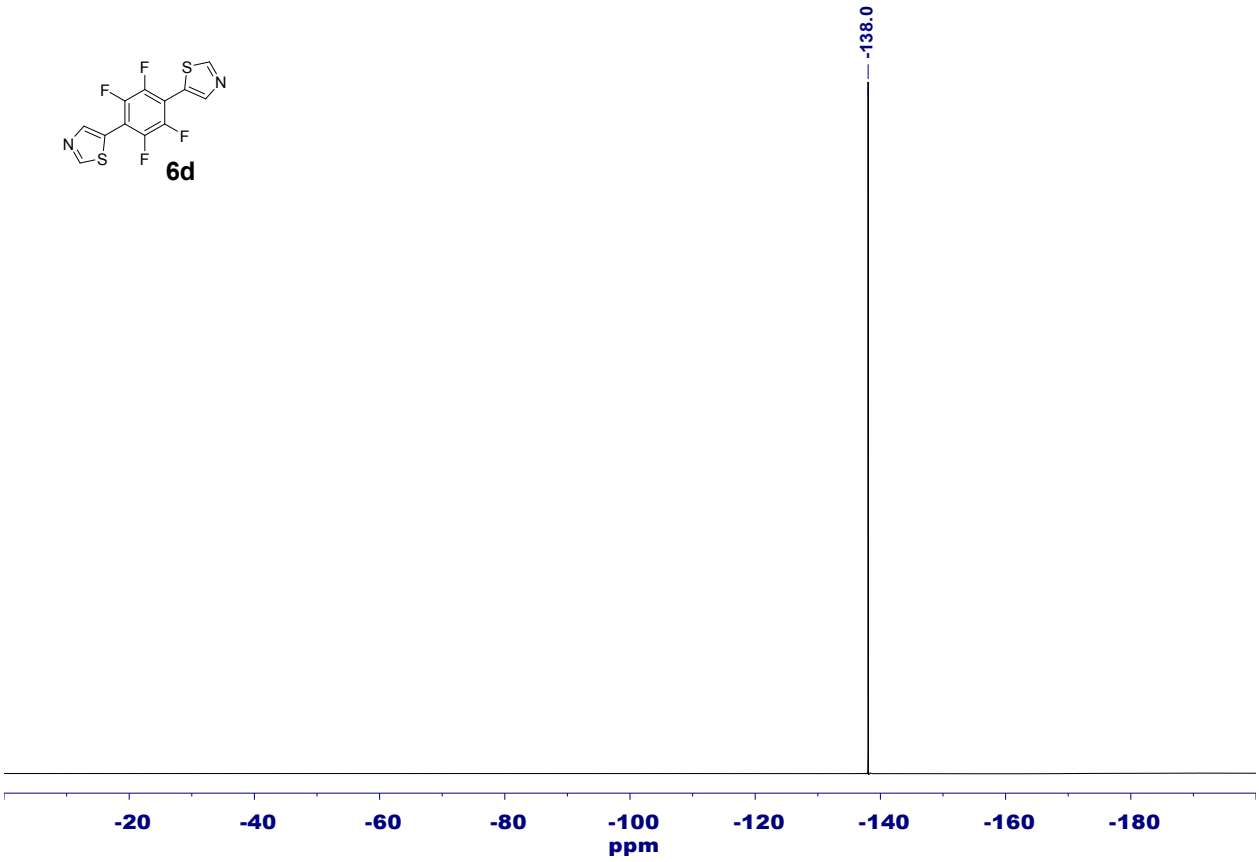

Figure S40. $^{19}F\{^{1}H\}$ NMR spectrum of 1,4-di(thiazol-5-yl)-tetrafluorobenzene **6d** ($CDCl_3$, 564 MHz, 298 K).

Table S1. Key crystallographic data

Compound	3b	3c	4a	4b	4c	5a	5b	5c	5d	6a	6b	6c	6d
CCDC entry	**1856883**	**1856884**	**1856885**	**1856886**	**1856887**	**1856895**	**1856896**	**1856897**	**1856898**	**1856899**	**1856900**	**1856901**	**1856902**
Formula	$C_{14}H_8F_2S_2$	$C_{14}H_6F_4S_2$	$C_{12}H_6FN_2S_2$	N/A	$C_{12}H_4F_4N_2S_2$	$C_{30}H_{48}N_2S_2Si_2$	$C_{30}H_{46}FN_2S_2Si_2$	$C_{30}H_{46}F_2N_2S_2Si_2$	$C_{30}H_{44}F_4N_2S_2Si_2$	$C_{12}H_8N_2S_2$	$C_{12}H_7FN_2S_2$	$C_{12}H_6F_2N_2S_2$	$C_{12}H_4F_4N_2S_2$
M, g mol^{-1}	278.32	314.31	261.31	280.31	316.29	557	573.99	592.99	628.97	244.32	262.30	280.31	316.29
Size, µm^3	512×423×70	244×53×21	222×135×94	150×90×20	512×437×150	695×288×76	386×220×105	337×50×47	822×321×70	113×73×35	49×42×35	184×128×15	900×755×66
Appearance	yellow plate	colorless needle	yellow block	colorless plate	colorless block	colorless block	colorless block	colorless block	colorless plate	yellow plate	colorless block	colorless plate	colorless plate
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	monoclinic	monoclinic	orthorhombic	orthorhombic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/n$	P-1	$P2_1/c$	$P2_1/c$	$P2_1/c$	$Pna2_1$	Fdd2	$P2_1/c$	$P2_1/n$	$P2_1/n$
T, K	110	100	100	100	110	100	100	100	100	100	100	110	110
λ, Å	0.71073 ($Mo_{K\alpha}$)	1.54178 ($Cu_{K\alpha}$)	0.71073 ($Mo_{K\alpha}$)	1.54178 ($Cu_{K\alpha}$)	0.71073 ($Mo_{K\alpha}$)	1.54178 ($Cu_{K\alpha}$)	1.54178 ($Cu_{K\alpha}$)	1.54178 ($Cu_{K\alpha}$)	1.54178 ($Cu_{K\alpha}$)	1.54178 ($Cu_{K\alpha}$)	1.54178 ($Cu_{K\alpha}$)	1.54178 ($Cu_{K\alpha}$)	0.71073 ($Mo_{K\alpha}$)
***a*, Å**	7.4893(9)	6.2999(3)	5.9315(6)	5.7427(3)	5.0225(8)	9.2882(2)	9.3302(4)	9.3622(3)	19.9633(7)	15.9825(7)	3.8093(3)	6.6214(4)	3.8531(6)
***b*, Å**	3.8493(4)	5.0655(3)	4.9497(5)	5.5541(3)	7.1949(14)	12.3511(3)	12.3529(5)	12.3591(4)	12.2859(4)	9.7302(4)	6.6644(4)	25.6046(15)	23.868(3)
***c*, Å**	19.835(2)	18.6515(11)	18.794(2)	17.1753(8)	17.290(3)	14.5307(4)	14.5826(5)	14.6437(4)	13.3676(5)	13.6524(4)	21.5126(15)	7.2049(4)	6.1210(9)
***α*, °**	90	90	90	90	84.549(3)	90	90	90	90	90	90	90	90
***β*, °**	94.273(4)	90.341(2)	95.890(4)	90.509(2)	83.096(2)	105.8260(10)	106.1850(10)	106.6740(10)	90	90	94.338(4)	116.456(4)	95.290(3)
***γ*, °**	90	90	90	90	70.873(2)	90	90	90	90	90	90	90	90
V, Å^3	570.23(11)	595.20(6)	548.85(10)	547.79(5)	584.98(18)	1603.77(7)	1614.11(11)	1623.15(9)	3278.6(2)	2123.12(14)	544.57(7)	1093.59(12)	560.53(14)
Z	2	2	2	2	2	2	2	2	4	8	2	4	2
ρ_{calc}, g cm^{-3}	1.621	1.754	1.581	1.699	1.796	1.153	1.181	1.213	1.274	1.529	1.587	1.703	1.874
μ, mm^{-1}	0.468	4.434	0.472	4.514	0.496	2.364	2.41	2.458	2.555	4.284	4.358	4.523	0.517
Θ_{min}, °	2.727	4.742	2.179	5.150	1.188	4.777	4.773	4.768	4.225	6.234	4.122	3.452	3.414
Θ_{max}, °	24.977	70.09	22.487	78.795	27.48	70.133	70.091	70.187	64.996	65.259	70.212	62.519	27.499
Collected refl.	976	1110	1289	3760	6854	15613	18663	26658	56562	10935	8852	16240	7415
Independent	976	1110	1289	1047	2659	3032	3060	3087	5565	904	1034	1694	1261
Used	976	1110	1289	964	2659	3032	3060	3087	5565	904	1034	1694	1261
R_{int}	0.079	0.0724	0.0586	0.0375	0.0140	0.0410	0.0350	0.0409	0.0490	0.0289	0.0605	0.0675	0.0496
Parameters	107	91	130	82	181	169	178	178	373	126	86	163	91
Restraints	220	0	468	0	0	0	0	0	1	510	1	0	0
Largest peak, e Å^{-3}	0.41	0.325	0.352	0.362	0.393	0.358	0.339	0.307	0.252	0.166	0.429	0.455	0.294
Deepest hole, e Å^{-3}	-0.493	-0.332	-0.333	-0.302	-0.211	-0.333	-0.218	-0.236	-0.179	-0.156	-0.567	-0.313	-0.254
GooF	1.342	1.147	1.174	1.092	1.04	1.056	1.085	1.075	1.068	1.104	1.314	1.244	1.079
wR_2 (all data)	0.1703	0.1070	0.1590	0.0850	0.0681	0.0915	0.0757	0.0738	0.0563	0.0621	0.1609	0.1468	0.0773
wR_2	0.1626	0.1048	0.1515	0.0832	0.0660	0.0877	0.0737	0.0717	0.0557	0.0616	0.1564	0.1451	0.0761
R_1 (all data)	0.0902	0.0472	0.0928	0.0350	0.0294	0.0422	0.0331	0.0311	0.0235	0.0265	0.0979	0.0631	0.0320
R_1	0.0787	0.0429	0.0818	0.0315	0.0266	0.0363	0.0296	0.0282	0.0222	0.0256	0.0864	0.0591	0.0301

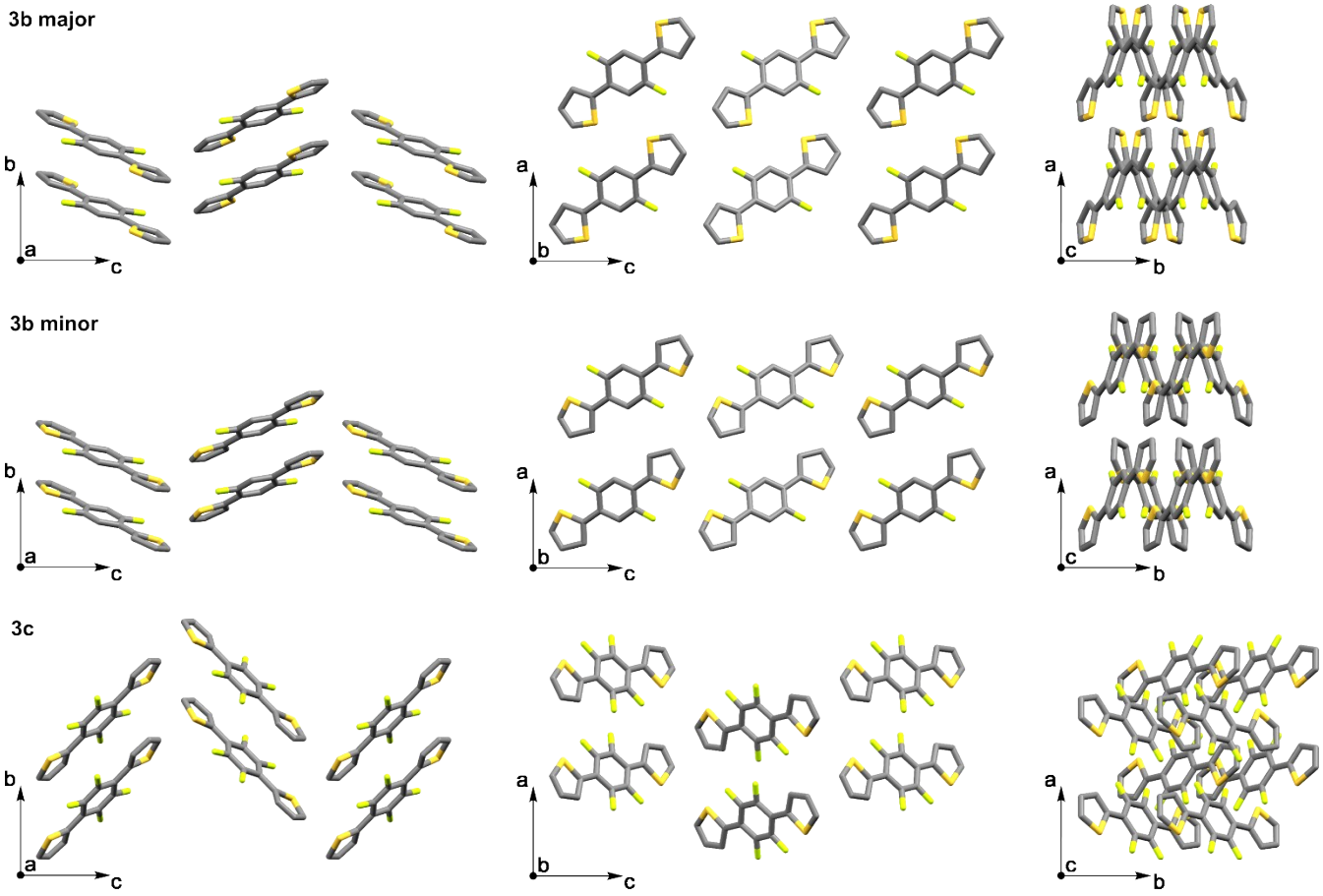

Figure S41. Crystal structures of 1,4-di(thien-2-yl)benzenes **3b,c**.

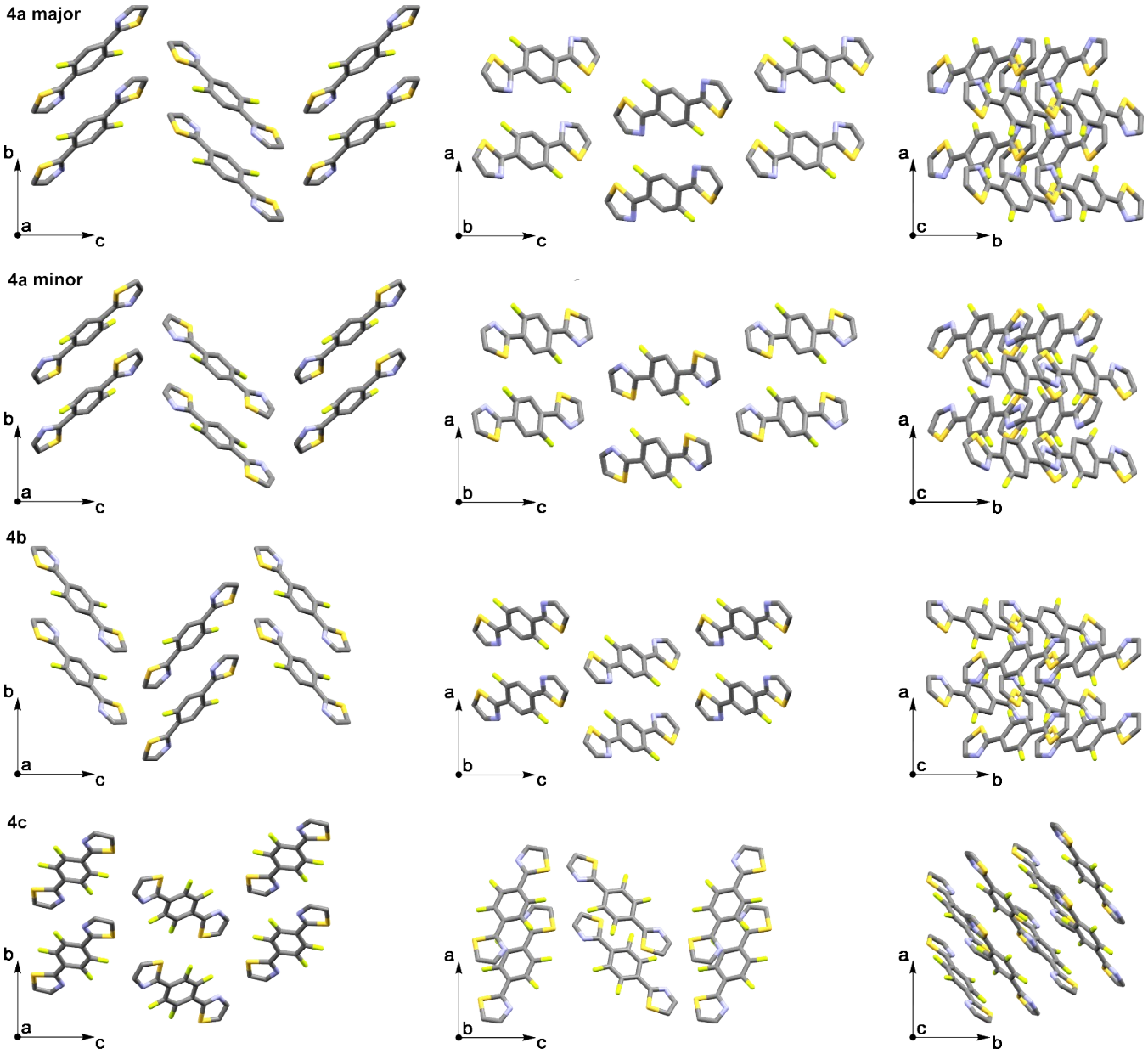

Figure S42. Crystal structures of 1,4-di(thiazol-2-yl)benzenes **4a-c**.

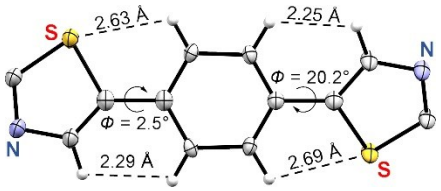

Figure S43. Molecular structure of di(thiazol-5-yl)benzene **6a**. The thermal ellipsoids are scaled to the 50% probability level. Hydrogen atoms irrelevant to discussion are omitted for clarity.

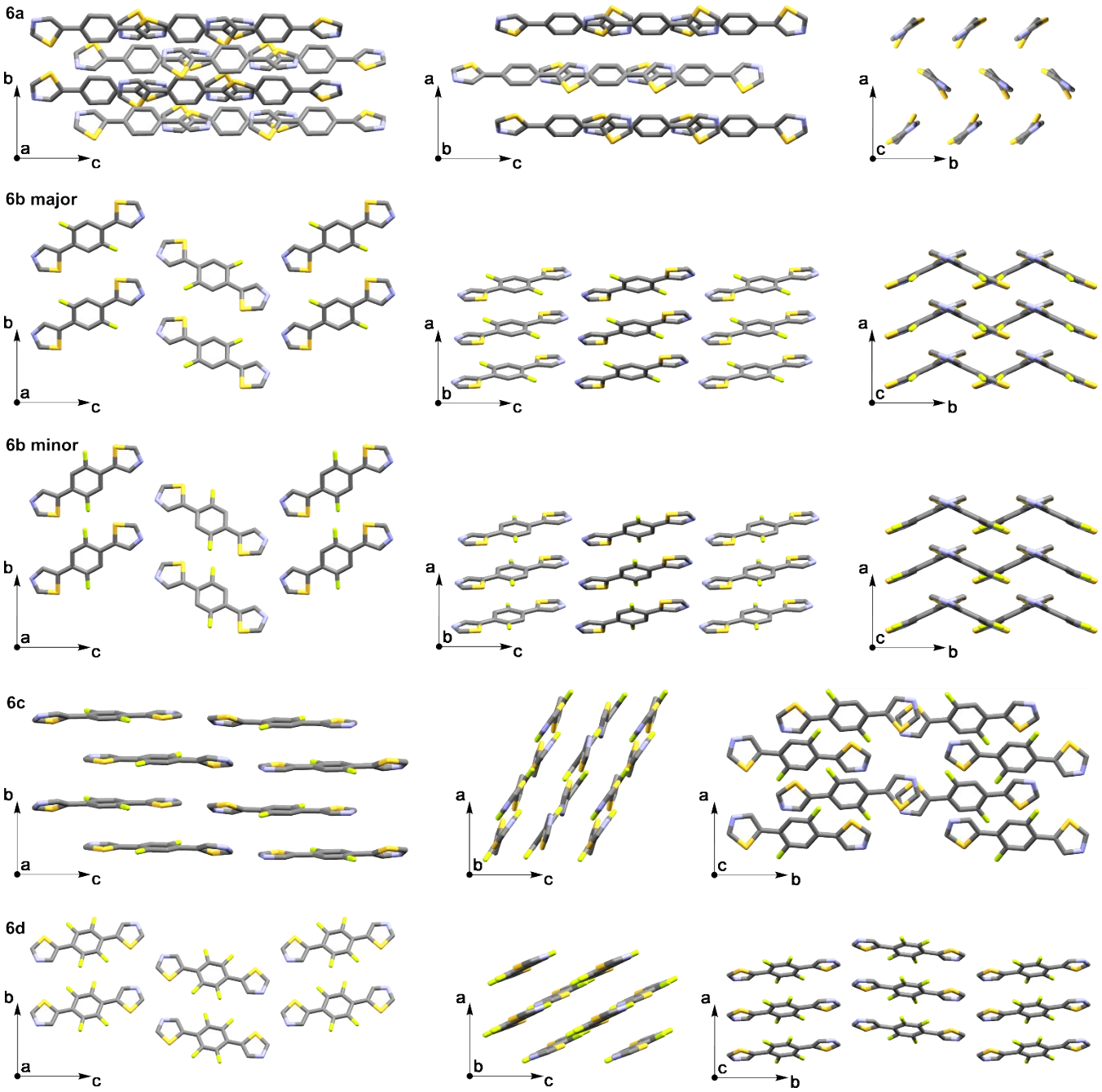

Figure S44. Crystal structures of 1,4-di(thiazol-5-yl)benzenes **6a-d**.

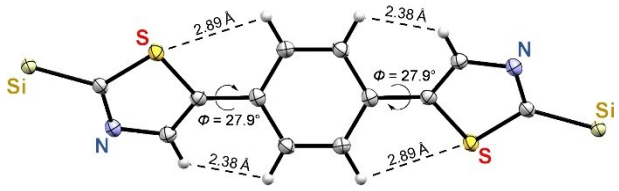

Figure S45. Molecular structure of 1,4-di(2-(triisopropylsilyl)thiazol-5-yl)benzene **5a**.

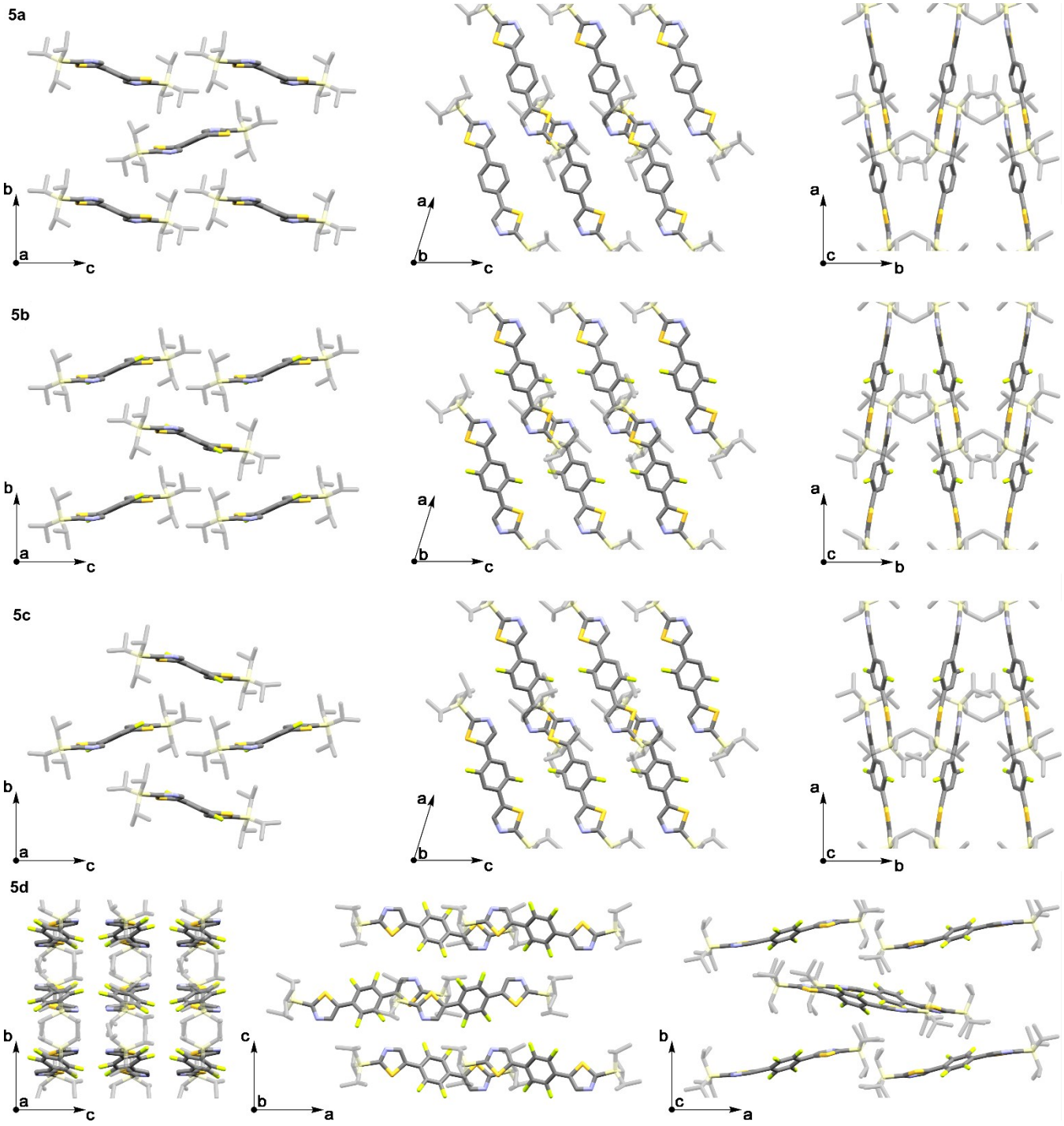

Figure S46. Crystal structures of 1,4-di(2-(triisopropylsilyl)thiazol-5-yl)benzenes **5a-d**. TIPS groups are dashed for clarity.

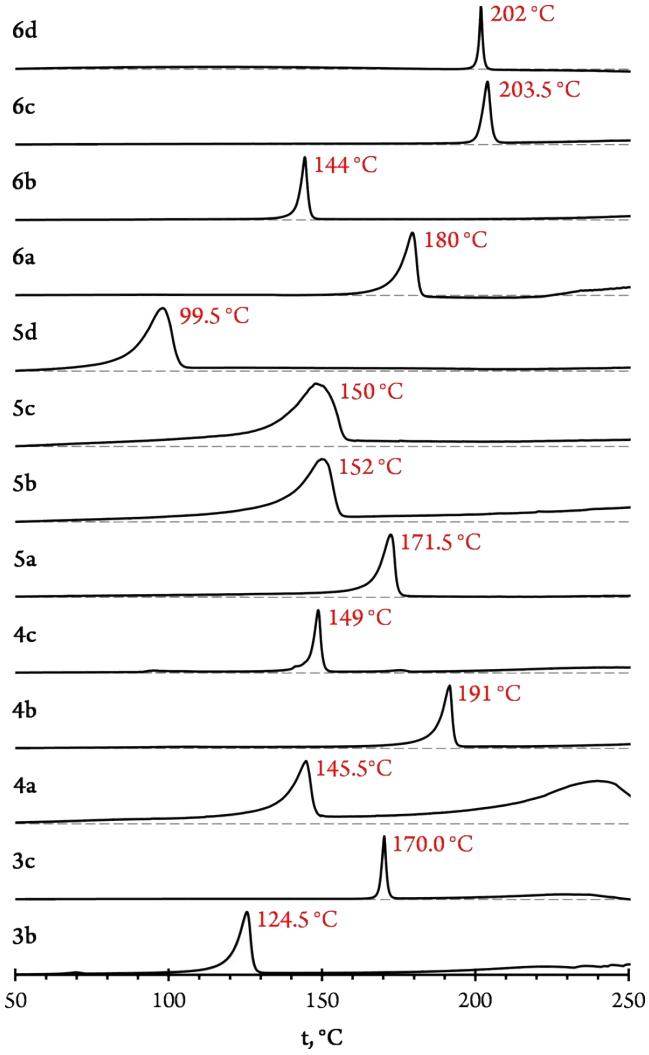

Figure S47. Normalized DSC curves for compounds **3b,c**, **4a-c**, **5a-d** and **6a-d**.