Electronic Supplementary Information (ESI)

First example of luminescent borasiloxane-based chiral helices assembled through N–B bonds.

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Methods and materials

All chemicals, reagents and solvents were purchased from Sigma Aldrich, TCI, Fluorochem or VWR Chemicals and used as received without any further purification if not otherwise stated. Diethylamine was distilled over $LiAlH_4$ and degassed prior use.

Melting point measurements were carried in capillaries, using FALC melting point device mod. C. (up to 300 °C). Elemental analyses were performed with an EA1108 CHNS-O Fisons instrument.

NMR spectroscopy analysis in solution and in solid-state were performed on samples **1**-**5** in order to investigate the nature and the self-assembly phenomena of the products. The polypyridyl ligand **1** was characterized by ^{1}H, ^{13}C and ^{1}H-^{1}H COSY NMR (Figure S1-S3), the borasiloxanes **2** and **3** were characterized by ^{1}H, ^{11}B, ^{13}C, ^{19}F and ^{29}Si NMR techniques in solution (Figure S4-S14).^{1}H, ^{13}C{^{1}H}, ^{11}B{^{1}H}, ^{19}F{^{1}H}, ^{29}Si{^{1}H} ^{1}H-^{1}H COSY, ^{29}Si-^{1}H HMBC NMR spectra were recorded on Bruker AVANCE III HD 400 MHz spectrometer in $CDCl_3$ or DMSO-d_6 as solvent. The chemical shifts (δ) are reported in ppm and referenced against the solvent residue or by means of external standard such as: $BF_3{\cdot}Et_2O$, $CFCl_3$ and $Si(CH_3)_4$ for ^{11}B, ^{19}F and ^{29}Si nuclei respectively. ^{13}C CPMAS solid-state NMR spectra were recorded on a Bruker Avance III HD 600 MHz (14.1 T) spectrometer at a frequency of 150.9 MHz, using a 2.5 mm probehead with 15.5 kHz spinning frequency.

Single-crystal X-ray diffraction data of **1** and **5** were collected on a Rigaku 007HF diffractometer, equipped with Varimax confocal mirrors, an AFC11 goniometer, a HyPix 6000 detector and an Oxford Cryosystems low temperature device, operating at 100K. **4** was collected on a Rigaku FRE+ diffractometer, equipped with HF Varimax confocal mirrors, an AFC12 goniometer, an HG Saturn 724+ CCD area detector and an Oxford Cryosystems low temperature device, operating at 100K. Data collection and processing for **1**, **4** and **5**, performed using CrysAlisPro (Rigaku Oxford Diffraction).[1] These structures then solved with the ShelXT,[2] structure solution program (using the

Intrinsic Phasing solution method) and by using Olex2,[3] as the graphical interface with their models refined with version 2018/3 of ShelXL,[4] using Least Squares minimisation.

Single-crystal X-ray diffraction data of **2** and **3** were collected on an Oxford Diffraction Xcalibur 3E (Mo K_α radiation, 0.71075 Å). Datasets were processed using Crysalis Pro,[5] solutions then solved and refined using SHELX-97 and SHELX-TL,[6] as well as Olex-2,[3] and WinGX.[7]

Powder X-ray Diffraction analysis performed on a Rigaku Miniflex 600 equipped with CuK_α radiation with a scan step of 0.02 ° and a scan speed of 0.03 °/min in the range from 5 to 30 ° in continuous mode. Experimental patterns were then compared with calculated patterns from single crystal X-ray diffraction analysis by means of CrystalDiffract version 6.8.2.

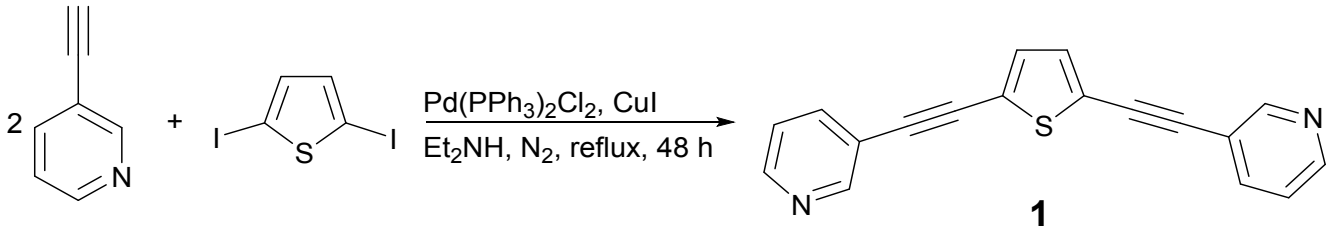
Theoretical calculations

Theoretical calculations performed at the density functional theory (DFT)[8] level with the Gaussian 16 (Rev. B.01)[9] suite of programs on an IBM x3755 server with four 12-core processors and 64 Gb of RAM (OS: SUSE Linux Enterprise Server 11 SP3). The mPW1PW functional[10] was adopted, in combination with the full-electron split valence basis sets (BSs) including polarization functions (def2-SVP),[11,12] obtained from Basis Set Exchange and Basis Set EMSL Library.[13]

Geometry optimizations performed starting from structural data. Fine numerical integration grids (*Integral=ultrafine* keyword) were used, and the nature of the minima of each optimized structure was verified by harmonic frequency calculations (*freq=raman* keyword). PES scans performed on **1** by imposing the rotation of the pyridine rings (between 0 and 180 °, steps of 10 °) and optimizing the resulting geometry at each rotational step (*opt=modredundant* keyword). A natural population analysis was carried out at the optimized geometries using the natural bonding orbital (NBO) partitioning scheme.[14] Investigation of the optimized structures and the shapes of Kohn–Sham molecular orbitals employed the programs GaussView 6.0.16,[15] Molden 5.9,[16] and Chemissian 4.53.[17]

Syntheses

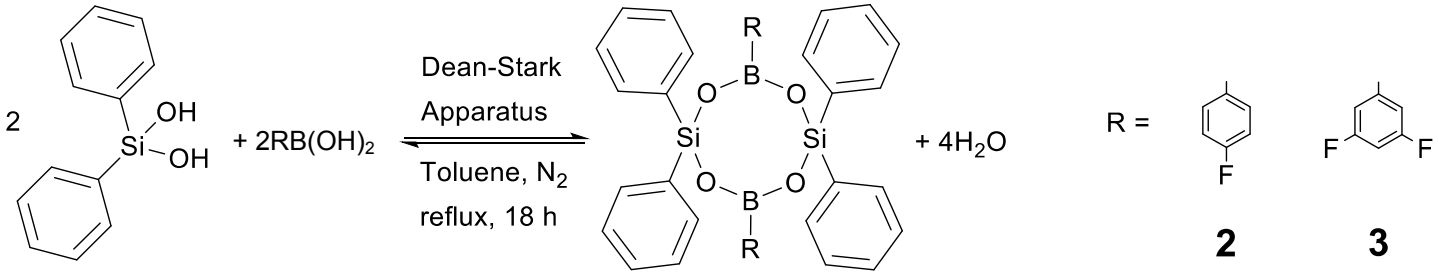
2,5-bis(pyridin-3-ylethynyl)thiophene (1)



3-ethynylpyridine (0.518 g; 5.02 mmol), 2,5-diiodothiophene (0.841 g; 2.50 mmol), copper(I) iodide (0.025 g; 0.13 mmol) and $Pd(PPh_3)_2Cl_2$ (0.089 g; 0.13 mmol) were placed in a three-necked 50 mL round bottom flask, then evacuated and backfilled with nitrogen three times. Freshly distilled and degassed diethylamine (25 mL) was added *via* canula, this mixture then heated to reflux and for 48 h, under a nitrogen atmosphere. A NH_4Cl saturated aqueous solution (100 mL) was added to the mixture and extracted with ethyl acetate (3x 25 mL). The organic phase was dried over $MgSO_4$, filtered and concentrated to give the crude product as a red solid. Purification of the product was achieved by silica gel column chromatography (CH_2Cl_2/EtOAc 2:1). (pale-yellow solid; 501 mg; 1.75 mmol; 70 %) M.p. 98-100 °C. Elemental analysis calculated (%) for $C_{18}H_{10}N_2S$: C 75.50; H 3.52; N 9.78; S 11.20; found C 75.58; H 3.53; N 9.61, S 11.05. FT-IR (KBr, 4000-400 cm^{-1}) 3076w, 3053w, 3024, 2202m, 1581w, 1558m, 1520m, 1471s, 1439w, 1404s, 1327w, 1248w, 1188m, 1120m, 1095w, 1043w, 1022s, 949w, 918w, 802vs, 721w, 700vs, 642m, 615w, 538m, 515w, 461w, 411w cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ 8.78 (dd, *J* = 2.2, 0.9 Hz, 2H, Py), 8.62 (dd, *J* = 4.9, 1.7 Hz, 2H, Py), 8.06 – 7.98 (m, 2H, Py), 7.51 – 7.47 (m, 4H, Py/thiophene). $^{13}C\{^1H\}$ NMR (101 MHz, DMSO-d_6) δ 151.55, 149.51, 138.60, 133.85, 123.69, 123.47, 118.57, 91.30, 84.70.

Electronic Supplementary Information (ESI)

General scheme for the preparation of compounds 2 and 3.



4,8-bis(4-fluorophenyl)-2,2,6,6-tetraphenyl-1,3,5,7,2,6,4,8-tetraoxadisiladiborocane (2)

Diphenylsilanediol (1.007 g; 4.66 mmol), 4-fluorophenylboronic acid (0.650 g; 4.65 mmol) were dissolved in dry toluene (50 mL) in a 100 mL round-bottom flask equipped with a Dean-Stark apparatus, this mixture then heated to reflux for overnight, under nitrogen atmosphere. After discarding the aqueous phase, the solvent removed under reduced pressure, resulting in a white powder (subsequently purified by recrystallization from a 2:1 diethyl ether/dichloromethane mixture). Colourless crystals were collected by filtration and stored under nitrogen atmosphere (1.44 g; 2.25 mmol; 97 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 8.00 (m, 4H, *o*-FC_6H_4B), 7.71 – 7.66 (m, 8H, *o*-C_6H_5Si), 7.45 – 7.38 (m, 4H, *p*-C_6H_5Si), 7.36 – 7.29 (m, 8H, *m*-C_6H_5Si), 7.15 – 7.08 (m, 4H, *m*-FC_6H_4B). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 165.67 (d, $^{1}J_{C\text{-}F}$ = 251 Hz), 138.03 (d, $^{4}J_{H\text{-}F}$ = 8 Hz), 134.20, 133.29, 130.88, 128.28, 115.21 (d, $^{3}J_{H\text{-}F}$ = 20 Hz). $^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$) δ 25.55. $^{19}F\{^{1}H\}$ NMR (377 MHz, $CDCl_3$) δ -107.93. $^{29}Si\{^{1}H\}$ NMR (80 MHz, $CDCl_3$) δ - 44.62.

4,8-bis(3,5-difluorophenyl)-2,2,6,6-tetraphenyl-1,3,5,7,2,6,4,8-tetraoxadisiladiborocane (3)

Diphenylsilanediol (1.371 g; 6.33 mmol) and 3,5-difluorophenylboronic acid (1.002 g; 6.33 mmol) were dissolved in dry toluene (50 mL) in a 100 mL round-bottom flask equipped with a Dean-Stark apparatus, the mixture then heated to reflux for overnight under nitrogen atmosphere. After discarding the aqueous phase, and the solvent removed under reduced pressure to give a white powder (subsequently purified by recrystallization from a 2:1 diethyl ether/dichloromethane mixture). Colourless crystals were collected by filtration and stored under nitrogen atmosphere (1.55 g; 2.29 mmol; 72 %). M.p. 151-152 °C; Elemental analysis calculated (%) for $C_{36}H_{26}B_2F_4O_4Si_2$: C, 63.93; H, 3.87; Found: C, 63.83; H, 4.06. FT-IR (KBr, 4000-400 cm^{-1}) 3072w, 3053w, 3028w, 3005w, 2962w, 1618, 1585ms, 1427vs, 1385s, 1321vs, 1257vs, 1186w, 1119vs, 1018m, 982s, 874m, 852m, 823m, 802m, 739m, 721s, 696vs, 596w, 580ms, 517s, 488ms, 405m cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.64 (m, 8H, *o*-C_6H_5Si), 7.52 – 7.42 (m, 8H, *p*-C_6H_5Si, *o*-$F_2C_6H_3B$), 7.40 – 7.33 (m, 8H, *m*-C_6H_5Si), 6.95 (tt, $^{3}J_{H\text{-}F}$ = 8.9 Hz, $^{4}J_{H\text{-}H}$ = 2.4 Hz, 2H, *p*-$F_2C_6H_3B$). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 163.11 (dd, $^{1}J_{C\text{-}F}$ J = 249.8, $^{3}J_{C\text{-}F}$ 11.0 Hz), 134.48, 134.13, 132.49, 131.20, 128.45, 118.02 – 117.21 (m), 107.29 (t, $^{2}J_{C\text{-}F}$ = 25.0 Hz). $^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$) δ 25.49. $^{19}F\{^{1}H\}$ NMR (377 MHz, $CDCl_3$) δ -110.40. ^{29}Si-^{1}H HMBC NMR (80 MHz, $CDCl_3$) δ - 43.99.

helix-[(μ_2-N,N'-(2,5-bis(pyridin-3-ylethynyl)thiophene))-(μ_2-4,8'-(4,8-bis(4-fluorophenyl)-2,2,6,6-tetraphenyl-1,3,5,7,2,6,4,8-tetraoxadisiladiborocane] (4)

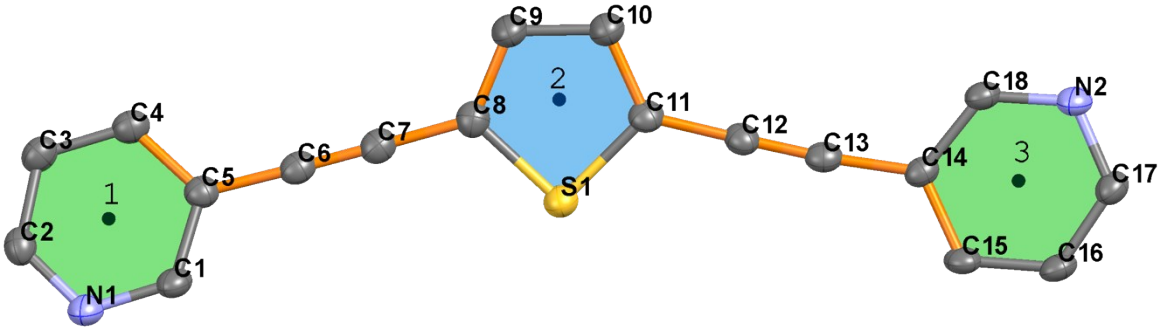
Ligand **1** (11.4 mg; 40 µmol) and compound **2** (25.6 mg; 40 µmol) were dissolved in 3 mL of a dry dichloromethane/diethyl ether (1:2) mixture upon sonication for 10 min. The yellowish clear solution was left to crystallize overnight at room temperature. Colourless crystals suitable for X-ray diffraction were collected by suction filtration and washed with diethyl ether (yield: 32.0 mg; 3.45 mmol; 86 %). Mp: 160 °C. Elemental analysis calculated (%) for $C_{54}H_{38}B_2F_2N_2O_4SSi_2$ C, 69.98; H, 4.13; N, 3.02; S, 3.46. Found: C, 70.01; H, 4.17; N, 2.95; S, 3.38. FT-IR (KBr, 4000–400 cm^{-1}): 3089w, 3051w, 3047w, 3024w, 2220mw, 1587m, 1497m, 1477m, 1429m, 1414m, 1387w, 1329w, 1309w, 1273w, 1188-1178vs (ν_{as}Si-O + ν_{sym}B-O), 1120-1111vs (ν_{sym}Si-O + ν_{as}B-O), 1097s, 1063s, 1016m, 937w, 899w, 877w, 866w, 835m, 816m, 802m, 750ms, 735s, 706s, 677s, 648m, 634w, 563m, 561ms, 534mw,

496ms, 498ms, 428mw cm^{-1}. ^{13}C CP/MAS NMR (151 MHz) δ 164.21, 162.76, 147.74, 145.69, 140.12, 139.38, 134.25, 131.12, 129.22, 127.08, 125.45, 121.74, 114.41, 89.75, 86.85 ppm.

helix-[(μ_2-N,N'-(2,5-bis(pyridin-3-ylethynyl)thiophene))-(μ_2-4,8'-(4,8-bis(3,5-difluorophenyl)-2,2,6,6-tetraphenyl-1,3,5,7,2,6,4,8-tetraoxadisiladiborocane] (5)

Ligand **1** (11.5 mg; 40 µmol) and compound **3** (27.1 mg; 40 µmol) were dissolved in 3 mL of a dry dichloromethane/diethyl ether (1:2) mixture upon sonication for 10 min. The yellowish clear solution was left to crystallize for overnight at room temperature. Colourless crystals suitable for X-ray diffraction were collected by suction filtration and washed with diethyl ether (yield: 33.5 mg; 3.48 mmol; 87 %) Mp: 175 °C. Elemental analysis calculated (%) for $C_{54}H_{36}B_2F_4N_2O_4SSi_2$: C, 67.37; H, 3.77; N, 2.91; S, 3.33. Found: C, 67.41; H, 3.80; N, 2.81; S, 3.28. FT-IR (KBr, 4000–400 cm^{-1}): 3120w, 3089w, 3066w, 3047w, 2212mw, 1612m, 1579ms, 1522w, 1477m, 1416s, 1414s, 1340m, 1325m, 1284vs, 1188s, 1144-1105vs (ν_{as}Si-O + ν_{sym}B-O), 1065s, 976s, 962m, 912w, 839mw, 829m, 806m, 719vs, 706s, 652m, 598m, 553ms, 521m, 498s, 417m cm^{-1}. ^{13}C CP/MAS NMR (151 MHz) δ 164.48, 162.96, 157.12, 145.86, 140.18, 139.45, 138.03, 134.44, 133.35, 129.50, 128.00, 126.87, 125.18, 121.61, 115.50, 102.05, 90.46, 86.82 ppm.

Table S1 Selected bond lengths (Å) and angles (°) for compound **1**. Centroids and planes are identified by numbers (1-3) and letters (a-c), respectively.



1–2–3	155.07
a–b	17.57
a–c	12.05
b–c	5.53
C5–C6–C7	178.17
C8–C7–C6	178.58
C7–C8–S1	121.35
C12–C11–S1	121.67
C14–C13–C12	176.02
C11–C12–C13	178.44
C4–C5–C8–C9	17.49
C10–C11–C14–C15	173.64
$d_{N1–N2}$	14.530

Table S2 Crystal data and structure refinement parameters for compounds 1-5

Compound	**1**	**2**	**3**	**4**	**5**
Formula	$C_{18}H_{10}N_2S$	$C_{36}H_{28}B_2F_2O_4Si_2$	$C_{36}H_{26}B_2F_4O_4Si_2$	$C_{54}H_{36}B_2F_4N_2O_4SSi_2$	$C_{54}H_{38}B_2F_2N_2O_4SSi_2$
$D_{calc.}$/ g cm^{-3}	1.356	1.286	1.380	1.391	1.349
μ/mm^{-1}	1.980	0.157	0.172	1.690	0.183
Formula Weight	286.34	640.38	676.37	962.71	926.72
Colour	colourless	colourless	colourless	pale yellow	colourless
Shape	plate	block	block	block	prism
Size/mm^3	0.15x0.08x0.02	0.30x0.25x0.15	0.30x0.20x0.20	0.19×0.16×0.06	0.06×0.05×0.025
T/K	100(2)	173(2)	173(2)	100(2)	100(2)
Crystal System	orthorhombic	triclinic	triclinic	tetragonal	tetragonal
Flack Parameter	-	-	-	-0.005(7)	-0.06(4)
Hooft Parameter	-	-	-	-0.014(5)	-0.07(4)
Space Group	*Pbcn*	*P*-1	*P*-1	$P4_3$	$P4_32_12$
a/Å	34.6428(11)	8.5686(6)	8.7686(3)	19.62160(10)	13.8634(2)
b/Å	7.5712(2)	9.8331(10)	12.6193(5)	19.62160(10)	13.8634(2)
c/Å	10.6915(2)	11.3579(8)	15.6914(7)	23.8883(2)	23.7340(4)
α/°	90	112.478(8)	71.173(4)	90	90
β/°	90	108.622(6)	82.544(3)	90	90
γ/°	90	91.091(7)	89.851(3)	90	90
V/Å^3	2804.25(13)	827.02(13)	1628.09(12)	9197.17(12)	4561.53(15)
Z	8	1	2	8	4
Z'	1			2	0.5
Wavelength/Å	1.54178	0.71075	0.71075	1.54178	0.71075
Radiation type	CuK_α	MoK_α	MoK_α	CuK_α	MoK_α
Θ_{min}/°	2.551	3.124	2.958	2.252	1.701
Θ_{max}/°	68.235	25.022	25.023	68.246	27.484
Measured Refl.	13192	4382	8704	49836	52919
Independent Refl.	2556	2890	5686	16155	5236
Reflections with I > 2(I)	2277			15953	4550
R_{int}	0.0589	0.0164	0.0201	0.0270	0.0773
Parameters	190	208	433	1312	334
Restraints	-	-	-	444	582
Largest Peak	0.560	0.229	0.462	0.365	0.259
Deepest Hole	-0.555	-0.297	-0.451	-0.219	-0.220
GooF	1.161	1.026	1.048	1.021	1.028
wR_2 (all data)	0.1964	0.1018	0.1209	0.0883	0.0837
wR_2	0.1913	0.0941	0.1085	0.0879	0.0794
R_1 (all data)	0.0848	0.0714	0.0832	0.0330	0.0474
R_1	0.0767	0.0467	0.0498	0.0326	0.0368

Table S3 Selected bond lengths (Å) for compounds 2-5

2		**3**		**4**		**5**	
Si1-O1	1.625(14)	Si1-O1	1.639(19)	Si1-O1	1.6067(17)	Si1-O1	1.6000(3)
Si1-O2	1.618(16)	Si1-O2	1.616(16)	Si1-O2	1.6179(16)	Si1-O2	1.623(3)
						Si2-O3	1.611(3)
						Si2-O4	1.612(3)
						Si61-O61	1.619(3)
						Si61-O62	1.605(3)
						Si62-O63	1.617(3)
						Si62-O64	1.614(3)
Si1–C1	1.849(2)	Si1–C1	1.849(3)	Si1–C7	1.865(2)	Si1–C13	1.857(5)
Si1–C7	1.856(2)	Si1–C7	1.855(3)	Si1–C13	1.877(2)	Si1–C19	1.862(5)
						Si2–C25	1.878(4)
						Si2–C31	1.874(5)
						Si61–C73	1.864(5)
						Si61–C79	1.864(5)
						Si62–C85	1.877(5)
						Si62–C91	1.875(5)
B1–O1	1.367(3)	B1–O1	1.361(3)	B1–O1	1.424(3)	B1–O1	1.415(6)
B1–O2	1.360(3)	B1–O2	1.362(3)	B1–O2	1.440(3)	B1–O4	1.447(6)
						B2–O2	1.415(6)
						B2–O3	1.436(6)
						B61–O61	1.413(6)
						B61–O64	1.439(6)
						B62–O62	1.410(6)
						B62–O63	1.448(6)
B1-C13	1.556(3)	B1-C13	1.561(4)	B1-C1	1.623(4)	B1-C1	1.623(7)
						B2-C7	1.644(7)
						B61-C61	1.636(7)
						B62-C67	1.610(7)
				B1-N21	1.697(3)	B1-N41	1.690(6)
						B2-N102	1.713(6)
						B61-N42	1.704(6)
						B62-N101	1.694(6)
F1–C16	1.368(2)	F1–C15	1.363(3)	F1–C4	1.368(2)	F1–C3	1.356(5)
		F2–C17	1.361(3)			F2–C5	1.363(5)
						F3–C9	1.369(5)
						F4–C11	1.362(5)
						F61–C63	1.376(5)
						F62–C65	1.373(5)
						F63–C69	1.365(5)
						F64–C71	1.344(6)
O1–Si1–O2	113.21(8)	O1–Si1–O2	112.03(10)	O1–Si1–O2	115.65(9)	O1–Si1–O2	115.36(17)
						O3–Si2–O4	115.01(17)
						O61–Si61–O62	114.37(17)

Table S4 Selected bond angles (°) for compounds 2-5

2		**3**		**4**		**5**	
						O63–Si62–O64	114.37(17)
O1–Si1–C1	107.54(9)	O1–Si1–C1	108.11(12)	O1–Si1–C7	108.78(10)	O1–Si1–C13	107.3(2)
O1–Si1–C7	108.89(10)	O1–Si1–C7	106.78(11)	O1–Si1–C13	104.62(9)	O1–Si1–C19	105.87(19)
O2–Si1–C1	108.57(9)	O2–Si1–C1	107.49(12)	O2–Si1–C7	108.11(10)	O2–Si1–C13	109.07(19)
O2–Si1–C7	107.58(10)	O2–Si1–C7	107.24(12)	O2–Si1–C13	107.18(10)	O2–Si1–C19	106.97(19)
						O3–Si2–C25	103.30(18)
						O3–Si2–C31	108.59(18)
						O4–Si2–C25	109.0(2)
						O4–Si2–C31	108.59(18)
						O61–Si61–C73	107.04(19)
						O61–Si61–C79	107.88(19)
						O62–Si61–C73	105.44(18)
						O62–Si61–C79	109.18(19)
						O63–Si62–C85	107.99(18)
						O63–Si62–C91	107.5(2)
						O64–Si62–C85	107.7(2)
						O64–Si62–C91	104.71(18)
C1–Si1–C7	111.0(10)	C1–Si1–C7	115.28(12)	C7–Si1–C13	112.58(10)	C13–Si1–C19	112.3(2)
						C25–Si2–C31	112.68(19)
						C73–Si61–C79	107.88(19)
						C85–Si62–C91	113.0(2)
O1–B1–O2	121.70(2)	O1–B1–O2	121.30(3)	O1–B1–O2	117.6(2)	O1–B1–O4	116.8(4)
						O2–B2–O3	118.7(4)
						O61–B61–O64	118.6(4)
						O62–B62–O63	117.1(4)
O1–B1–C13	119.10(2)	O1–B1–C13	118.90(3)	O1–B1–C1	112.70(19)	O1–B1–C1	113.9(4)
O2–B1–C13	119.20(2)	O2–B1–C13	119.70(19)	O2–B1–C1	110.9(2)	O4–B1–C1	110.5(4)
						O2–B2–C7	111.7(4)
						O3–B2–C7	112.1(4)
						O61–B61–C61	111.4(4)
						O64–B61–C61	111.6(4)
						O62–B62–C67	113.3(4)
						O63–B62–C67	110.0(4)
				O1–B1–N21	102.36(19)	O1–B1–N41	102.6(4)
				O2–B1–N21	104.83(17)	O4–B1–N41	104.8(4)
						O2–B2–N102	106.8(4)
						O3–B2–N102	100.9(3)
						O61–B61–N42	106.6(4)
						O64–B61–N42	101.3(4)
						O62–B62–N101	102.9(3)
						O63–B62–N101	104.8(4)
B1–O1–Si1	143.08(16)	B1–O1–Si1	138.43(19)	B1–O1–Si1	142.59(15)	B1–O1–Si1	145.2(3)
B1–O2–Si1	151.03(16)	B1–O2–Si1	154.50(2)	B1–O2–Si1	141.45(16)	B2–O2–Si1	142.8(3)
						B2–O3–Si2	140.1(3)
						B1–O4–Si2	141.4(3)
						B61–O61–Si61	141.8(3)
						B62–O62–Si61	141.2(3)
						B62–O63–Si62	141.8(3)
						B61–O64–Si62	139.6(3)

Table S5. Optimised geometry calculated for the antiperiplanar conformation of 1 at DFT level in the gas phase (total charge = 0, spin multiplicity = 1) in orthogonal Cartesian coordinate format.

Atom number	*Z*	X	Y	Z
1	6	-1.247285	0.899615	0.000117
2	16	0.009916	-0.298037	0.000057
3	6	1.250487	0.916839	0.000123
4	6	0.695833	2.188207	0.000177
5	6	-0.710506	2.178594	0.000163
6	6	2.609270	0.554879	0.000088
7	6	3.784379	0.227938	0.000043
8	6	5.151256	-0.157869	-0.000017
9	6	5.517310	-1.520372	-0.000144
10	7	6.771856	-1.942566	-0.000207
11	6	7.744324	-1.033369	-0.000153
12	6	7.504217	0.340946	-0.000034
13	6	6.190322	0.788243	0.000039
14	6	-2.601094	0.519513	0.000080
15	6	-3.771459	0.176047	0.000041
16	6	-5.138147	-0.210412	-0.000006
17	6	-5.527304	-1.560756	0.000357
18	6	-6.880797	-1.868133	0.000282
19	6	-7.805397	-0.823396	-0.000140
20	7	-7.453562	0.460599	-0.000493
21	6	-6.163782	0.758207	-0.000434
22	1	4.734058	-2.284683	-0.000196
23	1	5.955920	1.853445	0.000143
24	1	8.335986	1.046499	0.000003
25	1	8.770242	-1.415123	-0.000210
26	1	-8.879232	-1.035802	-0.000202
27	1	-7.219475	-2.904915	0.000548
28	1	-4.769549	-2.345259	0.000696
29	1	-5.897007	1.819565	-0.000732
30	1	1.306596	3.089337	0.000243
31	1	-1.334012	3.070958	0.000198

Table S6. Optimised geometry calculated for the periplanar conformation of 1 at DFT level in the gas phase (total charge = 0, spin multiplicity = 1) in orthogonal Cartesian coordinate format.

Atom number	*Z*	X	Y	Z
1	6	-1.249048	0.000000	-0.880380
2	16	0.000000	0.000000	0.325963
3	6	1.249048	0.000000	-0.880380
4	6	0.703215	0.000000	-2.155481
5	6	-0.703215	0.000000	-2.155481
6	6	2.605390	0.000000	-0.509480
7	6	3.778105	0.000000	-0.174075
8	6	5.147460	0.000000	0.202822
9	6	6.166343	0.000000	-0.772945
10	7	7.458151	0.000000	-0.484295
11	6	7.818995	0.000000	0.797186
12	6	6.901718	0.000000	1.848349
13	6	5.546119	0.000000	1.550387
14	6	-2.605390	0.000000	-0.509480
15	6	-3.778105	0.000000	-0.174075
16	6	-5.147460	0.000000	0.202822
17	6	-5.546119	0.000000	1.550387
18	6	-6.901718	0.000000	1.848349
19	6	-7.818995	0.000000	0.797186
20	7	-7.458151	0.000000	-0.484295
21	6	-6.166343	0.000000	-0.772945
22	1	5.892190	0.000000	-1.832408
23	1	4.793876	0.000000	2.340166
24	1	7.247643	0.000000	2.882739
25	1	8.894295	0.000000	1.002058
26	1	-8.894295	0.000000	1.002058
27	1	-7.247643	0.000000	2.882739
28	1	-4.793876	0.000000	2.340166
29	1	-5.892190	0.000000	-1.832408
30	1	1.320399	0.000000	-3.052227
31	1	-1.320399	0.000000	-3.052227

Table S7. Optimised geometry calculated for 2 at DFT level in the gas phase (total charge = 0, spin multiplicity = 1) in orthogonal Cartesian coordinate format.

Atom number	*Z*	X	Y	Z
1	6	4.404310	-1.744994	-0.555328
2	6	3.484137	-0.763448	-0.957028
3	6	3.691112	-0.120821	-2.187206
4	6	4.776389	-0.455374	-2.995304
5	6	5.675899	-1.437490	-2.583486
6	6	5.489905	-2.082188	-1.361098
7	14	2.014057	-0.354027	0.115257
8	6	2.433864	-0.267882	1.932144
9	6	3.443954	0.601062	2.378110
10	6	3.763214	0.694309	3.730489
11	6	3.078329	-0.085414	4.662740
12	6	2.076375	-0.955971	4.238574
13	6	1.758052	-1.045637	2.884015
14	8	1.465074	1.122049	-0.421085
15	5	0.389143	1.961758	-0.399651
16	6	0.598849	3.470372	-0.766113
17	6	-0.484907	4.361785	-0.819289
18	6	-0.310590	5.703184	-1.144729
19	6	0.973483	6.159257	-1.420410
20	6	2.076375	5.313609	-1.380304
21	6	1.877124	3.975959	-1.053745
22	9	1.152258	7.442189	-1.732252
23	8	-0.856029	1.524970	-0.064197
24	14	-2.014057	0.354027	0.115257
25	8	-1.465074	-1.122049	-0.421085
26	5	-0.389143	-1.961758	-0.399651
27	6	-0.598849	-3.470372	-0.766113
28	6	0.484907	-4.361785	-0.819289
29	6	0.310590	-5.703184	-1.144729
30	6	-0.973483	-6.159257	-1.420410
31	6	-2.076375	-5.313609	-1.380304
32	6	-1.877124	-3.975959	-1.053745
33	9	-1.152258	-7.442189	-1.732252
34	6	-2.433864	0.267882	1.932144
35	6	-3.443954	-0.601062	2.378110
36	6	-3.763214	-0.694309	3.730489
37	6	-3.078329	0.085414	4.662740
38	6	-2.076375	0.955971	4.238574
39	6	-1.758052	1.045637	2.884015
40	6	-3.484137	0.763448	-0.957028
41	6	-3.691112	0.120821	-2.187206
42	6	-4.776389	0.455374	-2.995304
43	6	-5.675899	1.437490	-2.583486
44	6	-5.489905	2.082188	-1.361098
45	6	-4.404310	1.744994	-0.555328
46	8	0.856029	-1.524970	-0.064197
47	1	-1.488511	3.990515	-0.603667
48	1	-1.146893	6.401411	-1.190303
49	1	3.065429	5.714422	-1.604310
50	1	2.734104	3.300513	-1.019703

Atom number	*Z*	X	Y	Z
1	6	3.155545	1.876551	2.174595
51	1	-3.992860	-1.215132	1.659436
52	1	-4.549894	-1.375873	4.059477
53	1	-3.328734	0.014595	5.723058
54	1	-1.538399	1.568024	4.964786
55	1	-0.972340	1.732068	2.562782
56	1	-2.994565	-0.654188	-2.513912
57	1	-4.922178	-0.053992	-3.949785
58	1	-6.527020	1.698984	-3.215239
59	1	-6.196017	2.847368	-1.033093
60	1	-4.277182	2.250893	0.405476
61	1	1.488511	-3.990515	-0.603667
62	1	1.146893	-6.401411	-1.190303
63	1	-3.065429	-5.714422	-1.604310
64	1	-2.734104	-3.300513	-1.019703
65	1	3.992860	1.215132	1.659436
66	1	4.549894	1.375873	4.059477
67	1	3.328734	-0.014595	5.723058
68	1	1.538399	-1.568024	4.964786
69	1	0.972340	-1.732068	2.562782
70	1	2.994565	0.654188	-2.513912
71	1	4.922178	0.053992	-3.949785
72	1	6.527020	-1.698984	-3.215239
73	1	6.196017	-2.847368	-1.033093
74	1	4.277182	-2.250893	0.405476

Table S8. Optimised geometry calculated for 3 at DFT level in the gas phase (total charge = 0, spin multiplicity = 1) in orthogonal Cartesian coordinate format.

2	6	2.645691	2.368018	-0.963164
3	6	2.932341	3.696288	-0.608737
4	6	3.694333	4.511332	-1.442941
5	6	4.188060	4.007546	-2.645871
6	6	3.919632	2.689175	-3.010376
7	14	1.590200	1.309116	0.148272
8	6	2.023213	1.469365	1.955552
9	6	1.056488	1.776380	2.924637
10	6	1.399967	1.873218	4.272429
11	6	2.718604	1.665069	4.672129
12	6	3.694333	1.362182	3.722345
13	6	3.348486	1.267781	2.376617
14	8	-0.000574	1.750474	-0.014256
15	5	-1.299896	1.514026	-0.330624
16	6	-2.236835	2.733716	-0.667689
17	6	-3.598170	2.530738	-0.935152
18	6	-4.409094	3.618062	-1.228573
19	6	-3.915245	4.916717	-1.267989
20	6	-2.563362	5.099228	-1.001257
21	6	-1.721478	4.036891	-0.703216
22	9	-5.702527	3.421661	-1.481416
23	9	-2.070446	6.336469	-1.034822
24	8	1.826417	-0.258973	-0.361789
25	5	1.299896	-1.514026	-0.330624
26	6	2.236835	-2.733716	-0.667689
27	6	1.721478	-4.036891	-0.703216
28	6	2.563362	-5.099228	-1.001257
29	6	3.915245	-4.916717	-1.267989
30	6	4.409094	-3.618062	-1.228573
31	6	3.598170	-2.530738	-0.935152
32	9	2.070446	-6.336469	-1.034822
33	9	5.702527	-3.421661	-1.481416
34	8	0.000574	-1.750474	-0.014256
35	14	-1.590200	-1.309116	0.148272
36	6	-2.023213	-1.469365	1.955552
37	6	-1.056488	-1.776380	2.924637
38	6	-1.399967	-1.873218	4.272429
39	6	-2.718604	-1.665069	4.672129
40	6	-3.694333	-1.362182	3.722345
41	6	-3.348486	-1.267781	2.376617
42	8	-1.826417	0.258973	-0.361789
43	6	-2.645691	-2.368018	-0.963164
44	6	-2.932341	-3.696288	-0.608737
45	6	-3.694333	-4.511332	-1.442941
46	6	-4.188060	-4.007546	-2.645871
47	6	-3.919632	-2.689175	-3.010376
48	6	-3.155545	-1.876551	-2.174595
49	1	0.667181	-4.229175	-0.504824
50	1	4.563731	-5.760464	-1.500003
51	1	4.030168	-1.530218	-0.916301
52	1	-4.030168	1.530218	-0.916301
53	1	-4.563731	5.760464	-1.500003
54	1	-0.667181	4.229175	-0.504824
55	1	-2.561026	-4.101661	0.336259
56	1	-3.906999	-5.541841	-1.152686
57	1	-4.787164	-4.644263	-3.299674

	58			1		-4.309003		-2.291206		-3.949318	
	59			1		-2.954263		-0.843344		-2.465128	
	60			1		-0.020927		-1.945155		2.623264	
	61			1		-0.634147		-2.112478		5.012439	
	62			1		-2.988807		-1.741582		5.727136	
	63			1		-4.728635		-1.201533		4.032065	
Atom number	64	***Z***	**X**	1	**Y**	**Z**	**Atom number**	-1.035946	**X**	1.643700	**Y**
	65			1		0.020927		1.945155		2.623264	**Z**
1	66	6	-14.637321	-6.336178	-0.190191	0.634147	69	2.112478	2.362106	-0.004357	2.292013
2	67	7	-13.364340	-6.368798	-0.578286	2.988807	70	1.741582	3.273357	-0.963594	1.310459
3	68	6	-12.621666	-5.289841	-0.387898	4.728635	71	1.201533	4.327279	-0.954701	4.032065
4	69	6	-13.104704	-4.104392	0.205125	4.125658	72	1.035946	4.692082	0.015212	5.643700
5	70	6	-14.450554	-4.086983	0.608841	2.561026	73	1.101661	3.698365	0.970723	6.336259
6	71	6	-15.225284	-5.220648	0.406831	3.906999	74	0.541811	2.147106	0.958358	5.152686
7	72	6	-12.253733	-2.980927	0.381360	4.787164	75	1.644268	0.064979	1.273437	3.299674
8	73	6	-11.519164	-2.018910	0.530920	4.309003	76	2.291206	0.081645	-1.657282	3.949318
9	74	6	-10.660152	-0.918032	0.697258	2.954263	77	0.843344	0.424642	-2.460504	2.465128
											0.325167

Table S9. Optimised geometry calculated for the antiperiplanar geometry of 1_2·2 at DFT level in the gas phase (total charge = 0, spin multiplicity = 1) in orthogonal Cartesian coordinate format.

10	16	-9.008717	-0.997006	0.169688	78	6	1.105816	-3.665367	0.500940
11	6	-8.699394	0.625487	0.704238	79	6	1.455812	-4.090123	1.781438
12	6	-9.837227	1.188236	1.263530	80	6	1.117164	-3.309117	2.886768
13	6	-10.942119	0.318789	1.259362	81	6	0.433962	-2.108091	2.705598
14	6	-7.425960	1.199873	0.548381	82	6	1.308035	3.477698	1.533739
15	6	-6.312747	1.676748	0.410176	83	6	2.324394	4.311945	1.041736
16	6	-5.015406	2.231253	0.253482	84	6	2.376931	5.672209	1.338157
17	6	-4.021224	1.524404	-0.435864	85	6	1.389675	6.217149	2.149460
18	7	-2.792120	2.010662	-0.601845	86	6	0.361966	5.436742	2.661095
19	6	-2.464437	3.207219	-0.104239	87	6	0.334592	4.077123	2.345984
20	6	-3.389171	3.978576	0.589523	88	9	1.428050	7.521350	2.441907
21	6	-4.675217	3.493612	0.772546	89	1	-2.241300	2.245544	-3.808620
22	5	-1.602033	1.029059	-1.362814	90	1	-3.335570	1.292345	-5.841649
23	6	-2.309558	0.408422	-2.676128	91	1	-3.601715	-2.529285	-3.922134
24	6	-2.548156	1.196513	-3.813020	92	1	-2.508570	-1.578593	-1.875510
25	6	-3.152478	0.680327	-4.957327	93	1	2.566036	-0.733839	-1.107400
26	6	-3.524776	-0.658698	-4.968239	94	1	3.413570	-2.556494	-2.554004
27	6	-3.304827	-1.480784	-3.872119	95	1	3.021447	-2.481066	-5.012721
28	6	-2.699315	-0.936581	-2.738523	96	1	1.784191	-0.564184	-6.007963
29	9	-4.104633	-1.165565	-6.061736	97	1	0.963627	1.265963	-4.569729
30	8	-0.558915	1.971756	-1.650869	98	1	3.786516	2.762621	-2.461982
31	14	1.083397	1.821034	-1.659898	99	1	4.674988	4.892002	-3.343961
32	8	1.672504	1.534504	-0.138000	100	1	3.140394	6.803537	-3.778101
33	5	1.265643	1.891892	1.188393	101	1	0.705784	6.560473	-3.327260
34	7	2.505698	1.209458	2.146898	102	1	-0.185786	4.423754	-2.437683
35	6	2.338831	1.162424	3.473620	103	1	-4.217436	0.546354	-0.874928
36	6	3.320870	0.646853	4.305908	104	1	-5.423442	4.073725	1.313193
37	6	4.499958	0.167464	3.748026	105	1	-3.088809	4.949381	0.982646
38	6	4.669721	0.214916	2.354782	106	1	-1.435722	3.520468	-0.278060
39	6	3.623141	0.756311	1.590092	107	1	-9.851603	2.202448	1.658881
40	6	5.841127	-0.264349	1.712796	108	1	-11.926413	0.569348	1.650922
41	6	6.833414	-0.674597	1.135369	109	1	5.289862	-0.245357	4.376008
42	6	7.974904	-1.147703	0.466037	110	1	1.390125	1.549348	3.844692
43	16	9.357876	-1.715688	1.348169	111	1	3.158574	0.621175	5.383065
44	6	10.216188	-2.074701	-0.116729	112	1	3.665267	0.826679	0.503734
45	6	9.449139	-1.762349	-1.230146	113	1	0.152202	-2.132402	-0.679786
46	6	8.186066	-1.239894	-0.902053	114	1	1.361982	-4.275919	-0.367430
47	6	11.515958	-2.609415	-0.072821	115	1	1.987172	-5.033943	1.920327
48	6	12.643204	-3.072270	-0.023017	116	1	1.379760	-3.643036	3.892879
49	6	13.956038	-3.610679	0.039459	117	1	0.159366	-1.516828	3.583856
50	6	14.573420	-3.865593	1.281973	118	1	-3.256975	-1.734368	1.344150
51	7	15.792848	-4.365278	1.405238	119	1	-5.302413	-1.706469	2.729597
52	6	16.476363	-4.643475	0.297213	120	1	-5.595359	0.023088	4.494014
53	6	15.969530	-4.433908	-0.985683	121	1	-3.820105	1.728903	4.860334
54	6	14.691347	-3.910117	-1.119992	122	1	-1.772234	1.710204	3.456828
55	6	1.709484	0.406809	-2.726590	123	1	3.094996	3.894002	0.390302
56	6	2.404414	-0.684571	-2.185604	124	1	-0.395499	5.900109	3.295286
57	6	2.876789	-1.715433	-2.998340	125	1	-0.476596	3.457957	2.734687
58	6	2.656493	-1.674139	-4.373827	126	1	3.162851	6.317371	0.943812
59	6	1.964317	-0.599332	-4.931720	127	1	14.029557	-3.644251	2.205482
60	6	1.500818	0.429805	-4.115189	128	1	14.254809	-3.729687	-2.103072
61	6	1.732208	3.441648	-2.361140	129	1	16.569683	-4.678365	-1.862948
62	6	3.100635	3.596589	-2.635817	130	1	17.481336	-5.055283	0.433669
63	6	3.607149	4.793834	-3.137480	131	1	7.434818	-0.935151	-1.628937
64	6	2.747338	5.864571	-3.382979	132	1	9.808707	-1.914784	-2.246183
65	6	1.383897	5.727696	-3.129552	133	1	-16.273545	-5.243605	0.707183

66	6	0.884742	4.526861	-2.625532	134	1	-11.578405	-5.338516	-0.714759
67	8	-1.278678	0.027089	-0.389364	135	1	-14.868225	-3.192090	1.071781
68	14	-0.831302	-0.031052	1.193227	136	1	-15.223792	-7.244344	-0.361981

Table S10. Optimised geometry calculated for the periplanar geometry of $1_2 \cdot 2$ at DFT level in the gas phase (total charge = 0, spin multiplicity = 1) in orthogonal Cartesian coordinate format.

Atom number	*Z*	X	Y	Z	Atom number	*Z*	X	Y	Z
1	6	-16.090341	-0.864056	-1.215801	69	6	6.579555	-0.875562	2.766975
2	6	-16.202967	-0.771409	0.171801	70	6	7.969484	-0.673242	2.811041
3	6	-15.056607	-0.540932	0.919327	71	16	8.873453	-0.426452	1.349162
4	6	-13.826996	-0.409629	0.251950	72	6	10.361334	-0.266189	2.227708
5	6	-13.837372	-0.522046	-1.154253	73	6	10.148554	-0.402871	3.592082
6	7	-14.933411	-0.741996	-1.862855	74	6	8.800941	-0.631936	3.920542
7	6	-12.614642	-0.172989	0.953090	75	6	11.571474	-0.031347	1.551211
8	6	-11.571452	0.030363	1.551205	76	6	12.614647	0.172412	0.953205
9	6	-10.361305	0.264711	2.227860	77	6	13.826985	0.409539	0.252202
10	6	-10.148498	0.400320	3.592336	78	6	15.056606	0.540409	0.919646
11	6	-8.800883	0.629156	3.920949	79	6	16.202951	0.771397	0.172255
12	6	-7.969449	0.671367	2.811466	80	6	16.090301	0.864967	-1.215283
13	16	-8.873445	0.425713	1.349409	81	7	14.933360	0.743331	-1.862399
14	6	-6.579525	0.873746	2.767533	82	6	13.837336	0.522898	-1.153926
15	6	-5.373617	1.040724	2.705502	83	6	1.439786	1.920221	-2.628660
16	6	-3.969214	1.229518	2.631999	84	6	1.524018	1.028959	-3.708664
17	6	-3.325496	1.294745	1.388200	85	6	1.530892	1.493487	-5.023974
18	7	-2.010066	1.465812	1.280078	86	6	1.452701	2.860786	-5.281347
19	6	-1.249092	1.583889	2.370912	87	6	1.367982	3.762486	-4.220320
20	6	-1.802894	1.538227	3.645493	88	6	1.364425	3.294176	-2.908667
21	6	-3.171585	1.360018	3.783608	89	1	0.882119	-4.279799	0.152536
22	5	-1.324096	1.540010	-0.310279	90	1	1.974801	-6.277935	-0.867384
23	6	-2.022053	2.837309	-0.979023	91	1	4.392462	-3.723405	-3.314381
24	6	-1.662141	4.139014	-0.597747	92	1	3.303372	-1.711106	-2.292969
25	6	-2.257903	5.266978	-1.157919	93	1	-1.576535	0.046135	-3.514143
26	6	-3.238057	5.090317	-2.127243	94	1	-1.593703	-0.778912	-5.850899
27	6	-3.626376	3.824271	-2.541772	95	1	-1.457017	-3.222261	-6.312437
28	6	-3.013888	2.712803	-1.961591	96	1	-1.303994	-4.831749	-4.419874
29	9	-3.816632	6.165397	-2.672929	97	1	-1.299915	-4.013645	-2.092353
30	8	0.073213	1.692391	-0.027461	98	1	-4.412984	-1.146668	-1.024517
31	14	1.448129	1.302823	-0.859184	99	1	-6.267720	-2.187507	0.233289
32	6	2.844599	2.115981	0.112399	100	1	-5.786737	-3.782595	2.081067
33	6	4.184180	1.835032	-0.205048	101	1	-3.428461	-4.327776	2.660432
34	6	5.234435	2.423403	0.496932	102	1	-1.566136	-3.273455	1.405853
35	6	4.965438	3.317216	1.533777	103	1	3.880132	-1.213948	0.453198
36	6	3.644720	3.619409	1.858958	104	1	3.637001	-1.323877	4.767993
37	6	2.598699	3.023108	1.153622	105	1	1.159441	-1.647906	4.517601
38	8	1.722655	-0.321401	-0.934289	106	1	0.184572	-1.714888	2.174622
39	5	1.324110	-1.539771	-0.311270	107	1	8.427352	-0.766039	4.934242
40	6	2.022037	-2.836651	-0.980852	108	1	10.958049	-0.336366	4.316762
41	6	1.661986	-4.138593	-0.600520	109	1	-0.882384	4.279756	0.155511
42	6	2.257744	-5.266213	-1.161389	110	1	-1.975068	6.278517	-0.863182
43	6	3.238037	-5.088955	-2.130461	111	1	-4.392243	3.725502	-3.312242
44	6	3.626490	-3.822650	-2.544077	112	1	-3.303157	1.712572	-2.292052
45	6	3.013998	-2.711541	-1.963216	113	1	1.577588	-0.043844	-3.514095
46	9	3.816614	-6.163700	-2.676806	114	1	1.594765	0.782631	-5.850349
47	8	-0.073203	-1.692290	-0.028541	115	1	1.456945	3.226190	-6.310426
48	14	-1.448132	-1.302246	-0.860018	116	1	1.302790	4.834451	-4.416909
49	8	-1.722603	0.322035	-0.934081	117	1	1.298703	4.014932	-2.089889

50	6	-1.439840	-1.918535	-2.629878	118	1	4.412987	1.147312	-1.023791
51	6	-1.523447	-1.026576	-3.709354	119	1	6.267731	2.187387	0.234625
52	6	-1.530321	-1.490302	-5.024946	120	1	5.786771	3.781306	2.083418
53	6	-1.452765	-2.857483	-5.283136	121	1	3.428497	4.326132	2.663142
54	6	-1.368679	-3.759871	-4.222643	122	1	1.566162	3.272617	1.407902
55	6	-1.365116	-3.292359	-2.910707	123	1	15.097199	0.459863	2.006593
56	6	-2.844589	-2.116028	0.111068	124	1	17.174824	0.878264	0.655555
57	6	-4.184173	-1.834887	-0.206194	125	1	16.977245	1.046626	-1.830521
58	6	-5.234422	-2.423696	0.495429	126	1	12.897584	0.426055	-1.706263
59	6	-4.965411	-3.318153	1.531714	127	1	-1.159391	1.644790	4.518667
60	6	-3.644690	-3.620545	1.856696	128	1	-3.636955	1.320657	4.768844
61	6	-2.598675	-3.023800	1.151727	129	1	-0.184528	1.713381	2.175720
62	7	2.010095	-1.466647	1.279133	130	1	-3.880113	1.213730	0.453977
63	6	3.325524	-1.295623	1.387368	131	1	-10.957974	0.333227	4.316983
64	6	3.969245	-1.231253	2.631210	132	1	-8.427277	0.762461	4.934749
65	6	3.171628	-1.362573	3.782731	133	1	-17.174833	-0.878578	0.655048
66	6	1.802939	-1.540719	3.644500	134	1	-15.097182	-0.461120	2.006329
67	6	1.249134	-1.585503	2.369890	135	1	-16.977296	-1.045302	-1.831145
68	6	5.373647	-1.042495	2.704838	136	1	-12.897631	-0.424834	-1.706543

Table S11. Optimised geometry calculated for the antiperiplanar geometry of $1_2 \cdot 3$ at DFT level in the gas phase (total charge = 0, spin multiplicity = 1) in orthogonal Cartesian coordinate format.

Atom number	*Z*	X	Y	Z	Atom number	*Z*	X	Y	Z
1	6	14.695711	4.487683	0.519257	69	6	0.527481	-0.433773	-3.998460
2	6	15.133384	3.728860	-0.566712	70	7	-2.353642	-0.163418	1.493588
3	6	14.253540	2.825134	-1.145688	71	6	-3.531539	0.326743	1.108967
4	6	12.956707	2.708152	-0.617399	72	6	-4.717149	-0.411091	1.220938
5	6	12.628199	3.528116	0.482572	73	6	-4.627819	-1.711909	1.749612
6	7	13.470919	4.388691	1.031279	74	6	-3.391447	-2.202586	2.141464
7	6	12.004651	1.804368	-1.159728	75	6	-2.268022	-1.395813	2.004623
8	6	11.183881	1.029860	-1.622038	76	6	-5.953173	0.152643	0.809389
9	6	10.227512	0.141333	-2.144770	77	6	-7.009973	0.647483	0.457223
10	6	10.359682	-0.737277	-3.211091	78	6	-8.230477	1.212220	0.048446
11	6	9.193065	-1.479971	-3.461058	79	16	-9.698401	0.286334	0.091234
12	6	8.157786	-1.176732	-2.588450	80	6	-10.625609	1.619371	-0.521860
13	16	8.641116	0.041554	-1.450129	81	6	-9.816716	2.724609	-0.743522
14	6	6.863282	-1.722006	-2.548967	82	6	-8.467263	2.495368	-0.422353
15	6	5.735697	-2.183352	-2.500913	83	6	-12.010292	1.493071	-0.731754
16	6	4.421452	-2.715074	-2.442940	84	6	-13.210709	1.371950	-0.910135
17	6	3.530601	-2.290016	-1.443241	85	6	-14.608414	1.226421	-1.116451
18	7	2.291541	-2.762781	-1.360066	86	6	-15.401302	2.281024	-1.600026
19	6	1.844906	-3.668948	-2.238322	87	6	-16.761332	2.069373	-1.778216
20	6	2.656746	-4.144793	-3.256302	88	6	-17.290402	0.815708	-1.470070
21	6	3.957589	-3.668168	-3.364597	89	7	-16.553245	-0.193462	-1.011290
22	5	1.241879	-2.244613	-0.135026	90	6	-15.255723	0.003922	-0.839698
23	6	1.039656	-3.544477	0.828346	91	1	2.268711	-4.882917	-3.957608
24	6	-0.227318	-4.123175	0.977185	92	1	-1.079720	-3.732702	0.421379
25	6	-0.411734	-5.187719	1.849960	93	1	0.475689	-6.572902	3.261508
26	6	0.631503	-5.737401	2.580910	94	1	3.109865	-3.671085	1.504402
27	6	1.888098	-5.164880	2.410769	95	1	3.799060	-1.548929	-0.690824
28	6	2.103516	-4.088158	1.561987	96	1	4.619905	-4.022814	-4.154678
29	9	-1.642168	-5.697469	2.004446	97	1	0.814597	-3.995221	-2.098541
30	9	2.912584	-5.672981	3.097343	98	1	-1.093550	1.801021	3.813612
31	8	1.952346	-1.156220	0.463214	99	1	-2.049913	5.895605	2.907319
32	14	1.667793	-0.191931	1.783824	100	1	-1.466735	3.082780	-0.302209
33	6	2.659791	1.373983	1.489300	101	1	4.329732	-1.052443	2.782519
34	6	3.278182	1.642487	0.259369	102	1	5.113316	-2.173421	4.838622
35	6	4.020420	2.807050	0.063638	103	1	3.496087	-2.764559	6.635332
36	6	4.153981	3.730003	1.099279	104	1	1.085330	-2.215093	6.358597
37	6	3.545266	3.482938	2.329604	105	1	0.295996	-1.096305	4.290386
38	6	2.810378	2.314943	2.520840	106	1	3.167524	0.931462	-0.561354
39	8	0.051302	0.074192	1.990955	107	1	4.494370	2.994909	-0.902167
40	5	-0.932018	0.744299	1.194457	108	1	4.732912	4.643522	0.948690
41	6	-1.259312	2.253008	1.690948	109	1	3.645368	4.203307	3.143858
42	6	-1.298235	2.561265	3.058367	110	1	2.346632	2.133553	3.493779
43	6	-1.580632	3.855711	3.470676	111	1	0.887347	2.058166	-1.717083
44	6	-1.832964	4.883669	2.568810	112	1	2.209080	3.030382	-3.577657
45	6	-1.787350	4.563990	1.218422	113	1	2.463552	1.778855	-5.714630
46	6	-1.508641	3.278388	0.769982	114	1	1.373020	-0.442186	-5.984620
47	9	-1.613261	4.136173	4.776444	115	1	0.040605	-1.403096	-4.138776
48	9	-2.021435	5.531991	0.327395	116	1	-2.843222	1.062667	-2.584631
49	6	2.245880	-1.009887	3.373144	117	1	-5.119525	0.500363	-3.362860
50	6	3.604233	-1.314335	3.557815	118	1	-5.939087	-1.845836	-3.244583
51	6	4.053089	-1.942425	4.717303	119	1	-4.456178	-3.629707	-2.341994

52	6	3.147165	-2.272419	5.725344	120	1	-2.173077	-3.063477	-1.550771
53	6	1.796954	-1.966203	5.568619	121	1	-3.526796	1.339189	0.705532
54	6	1.354196	-1.340228	4.403466	122	1	-5.528468	-2.319040	1.843734
55	8	0.026419	-1.910644	-0.819588	123	1	-3.281201	-3.211119	2.539645
56	14	-0.622393	-0.494308	-1.378631	124	1	-1.265828	-1.714274	2.288038
57	6	-2.338754	-0.960827	-1.997996	125	1	-18.359431	0.619927	-1.600637
58	6	-3.190134	0.027767	-2.520100	126	1	-17.407719	2.864632	-2.151470
59	6	-4.473698	-0.284060	-2.963315	127	1	-14.944653	3.244968	-1.827766
60	6	-4.933465	-1.599750	-2.897848	128	1	-14.668892	-0.838873	-0.461579
61	6	-4.103105	-2.597371	-2.390965	129	1	-7.673934	3.234107	-0.523113
62	6	-2.819468	-2.277447	-1.946414	130	1	-10.208312	3.664928	-1.127415
63	8	-0.741801	0.672857	-0.223537	131	1	16.147763	3.847000	-0.949584
64	6	0.380553	0.251197	-2.781100	132	1	14.552257	2.211121	-1.996186
65	6	0.995674	1.505411	-2.652276	133	1	15.367572	5.208388	0.996109
66	6	1.740227	2.051612	-3.698212	134	1	11.626912	3.462992	0.919351
67	6	1.882614	1.351321	-4.894804	135	1	11.282431	-0.825763	-3.781636
68	6	1.273016	0.105431	-5.045029	136	1	9.091091	-2.221396	-4.251674

Table S12. Optimised geometry calculated for the periplanar geometry of $1_2 \cdot 3$ at DFT level in the gas phase (total charge = 0, spin multiplicity = 1) in orthogonal Cartesian coordinate format.

Atom number	*Z*	X	Y	Z	Atom number	*Z*	X	Y	Z
1	6	-7.801876	4.273439	-0.000535	69	6	-1.689586	-5.602043	2.048928
2	16	-6.247935	4.501739	-0.738414	70	7	0.841582	-0.550690	1.961988
3	6	-5.832943	2.831039	-0.512857	71	6	-0.156016	0.228917	2.392637
4	6	-6.864186	2.141008	0.107488	72	6	-0.001120	1.603887	2.508394
5	6	-7.973702	2.954596	0.395895	73	6	1.212621	2.180132	2.159523
6	6	-4.589135	2.329857	-0.932160	74	6	2.254905	1.360145	1.692307
7	6	-3.510607	1.889335	-1.291236	75	6	2.012160	-0.021011	1.617468
8	6	-2.255564	1.361483	-1.690421	76	6	3.509156	1.889432	1.292514
9	6	-2.011338	-0.019438	-1.615989	77	6	4.587038	2.331089	0.932895
10	7	-0.839959	-0.547674	-1.960007	78	6	5.830141	2.833544	0.513018
11	6	0.157071	0.233217	-2.389678	79	16	6.243942	4.504423	0.739408
12	6	0.000727	1.608055	-2.504957	80	6	7.797579	4.277848	0.000353
13	6	-1.213883	2.182806	-2.156642	81	6	7.970109	2.959445	-0.397240
14	5	-0.624360	-2.269678	-1.934924	82	6	6.861424	2.144779	-0.108660
15	6	-1.054788	-2.716040	-3.437352	83	6	8.692050	5.354873	-0.130533
16	6	-0.111977	-2.764536	-4.472721	84	6	9.459324	6.296625	-0.239231
17	6	-0.502082	-3.119213	-5.757525	85	6	10.348875	7.396867	-0.363772
18	6	-1.817635	-3.436195	-6.071763	86	6	9.981393	8.677673	0.099275
19	6	-2.741638	-3.387007	-5.035246	87	7	10.764685	9.740896	0.011312
20	6	-2.384754	-3.035803	-3.739875	88	6	11.965913	9.596163	-0.544036
21	9	0.412961	-3.162068	-6.729720	89	6	12.437908	8.379211	-1.036976
22	9	-4.014024	-3.691084	-5.302964	90	6	11.620115	7.261524	-0.947140
23	6	-8.697214	5.349719	0.130559	91	1	8.998586	8.819119	0.559427
24	6	-9.465256	6.290819	0.239473	92	1	11.947758	6.290044	-1.319211
25	6	-10.355847	7.390195	0.364304	93	1	13.430828	8.312341	-1.483229
26	6	-11.626814	7.253584	0.947962	94	1	12.588897	10.494342	-0.601471
27	6	-12.445662	8.370479	1.038067	95	1	-1.086606	-0.287131	2.625370
28	6	-11.974954	9.587918	0.545107	96	1	-0.831722	2.212906	2.864335
29	7	-10.773987	9.733848	-0.010498	97	1	1.365755	3.256945	2.237024
30	6	-9.989694	8.671389	-0.098726	98	1	2.769081	-0.719383	1.259532
31	8	0.774338	-2.402843	-1.687901	99	1	3.158261	-3.029627	2.967085
32	14	1.805115	-3.130239	-0.626637	100	1	2.116770	-3.720347	7.082693
33	6	1.759233	-4.993789	-0.788540	101	1	-0.935542	-2.551792	4.288177
34	6	1.860457	-5.823590	0.337989	102	1	0.939808	-2.544171	-4.286985
35	6	1.899438	-7.210503	0.205016	103	1	-2.110229	-3.716151	-7.082500
36	6	1.836655	-7.792049	-1.059923	104	1	-3.153262	-3.030005	-2.966514
37	6	1.728370	-6.983558	-2.191011	105	1	4.420464	-3.090240	0.802254
38	6	1.690352	-5.597674	-2.054221	106	1	6.695093	-2.342037	0.206270
39	8	1.540178	-2.721432	0.945731	107	1	7.134955	-1.325719	-2.026713
40	5	0.627918	-2.273112	1.936227	108	1	5.264434	-1.046490	-3.644790
41	6	1.059274	-2.719604	3.438326	109	1	2.983281	-1.797216	-3.046359
42	6	2.389827	-3.037257	3.740510	110	1	1.898883	-5.378201	1.334322
43	6	2.747428	-3.388703	5.035612	111	1	1.971852	-7.839884	1.093860
44	6	1.823598	-3.440199	6.072175	112	1	1.866872	-8.878541	-1.164968
45	6	0.507468	-3.125305	5.758261	113	1	1.671662	-7.434971	-3.183629
46	6	0.116632	-2.770441	4.473729	114	1	1.598908	-4.978219	-2.949632
47	9	4.020367	-3.690763	5.303027	115	1	-1.899240	-5.375515	-1.339089
48	9	-0.407416	-3.170410	6.730510	116	1	-1.975216	-7.837547	-1.103545
49	6	3.520971	-2.487134	-1.072415	117	1	-1.870527	-8.880897	1.153144
50	6	4.591204	-2.630116	-0.174121	118	1	-1.672642	-7.441641	3.174621

51	6	5.878631	-2.211233	-0.506991	119	1	-1.596988	-4.984489	2.945535
52	6	6.124599	-1.639733	-1.755660	120	1	-4.417327	-3.086992	-0.802298
53	6	5.077419	-1.486950	-2.663287	121	1	-6.691462	-2.338653	-0.204812
54	6	3.792700	-1.908058	-2.321337	122	1	-7.130626	-1.326103	2.030073
55	8	-0.770666	-2.408042	1.689803	123	1	-5.259926	-1.051109	3.648603
56	14	-1.801999	-3.131565	0.626508	124	1	-2.979265	-1.802210	3.048768
57	6	-3.517369	-2.487911	1.073463	125	1	-2.767684	-0.718789	-1.258765
58	6	-4.587720	-2.628569	0.174943	126	1	-1.368161	3.259478	-2.233825
59	6	-5.874897	-2.209574	0.508652	127	1	0.830889	2.218152	-2.860077
60	6	-6.120489	-1.640259	1.758387	128	1	1.088380	-0.281736	-2.621958
61	6	-5.073191	-1.489821	2.666267	129	1	-12.598790	10.485494	0.602739
62	6	-3.788739	-1.911072	2.323499	130	1	-13.438408	8.302621	1.484558
63	8	-1.536291	-2.719585	-0.944840	131	1	-11.953435	6.281767	1.320053
64	6	-1.758299	-4.995518	0.784507	132	1	-9.007117	8.813817	-0.559074
65	6	-1.861006	-5.822921	-0.343649	133	1	8.880925	2.613217	-0.882492
66	6	-1.901635	-7.210054	-0.213459	134	1	6.790402	1.083666	-0.343059
67	6	-1.839025	-7.794234	1.050275	135	1	-6.792531	1.079771	0.341104
68	6	-1.729243	-6.988155	2.182940	136	1	-8.884573	2.607302	0.880279

Table S13. Energy *E* (eV), wavelength λ (nm), and oscillator strength *f* of main (*f* ≥ 0.005) electronic transitions calculated for $\mathbf{1_2 \cdot 2}$ in the gas phase (300-400 nm), along with molecular orbital composition of the excited-state functions and molecular fragments where the involved KS-MOs are mainly localized (F-Ph = fluoro-phenyl substituents of 2; PolyPy = polypyridyl ligand 1).

Excited State	*E* (eV)	λ (nm)	*f*	Composition	%	Molecular fragments
S1	3.100	400.0	1.100	HOMO→LUMO	62	F-Ph→PolyPy
				HOMO-1→LUMO+1	35	F-Ph→F-Ph
S3	3.178	390.1	2.076	HOMO-2→LUMO+1	64	F-Ph + PolyPy→PolyPy
				HOMO-3→LUMO+1	33	F-Ph + PolyPy→PolyPy
S4	3.342	382.4	0.059	HOMO-3→LUMO	56	F-Ph + PolyPy→PolyPy
				HOMO-2→LUMO+1	34	F-Ph + PolyPy→PolyPy
S8	3.434	361.1	0.046	HOMO-3→LUMO+1	51	F-Ph + PolyPy→PolyPy
				HOMO-2→LUMO	29	F-Ph + PolyPy→PolyPy
				HOMO-1→LUMO+1	11	F-Ph→F-Ph
S21	3.830	323.7	0.006	HOMO-10→LUMO	56	F-Ph→F-Ph
				HOMO-11→LUMO+1	19	F-Ph→F-Ph
S23	3.857	321.4	0.079	HOMO-2→LUMO+2	34	F-Ph + PolyPy→PolyPy
				HOMO-3→LUMO+3	21	F-Ph + PolyPy→PolyPy
				HOMO→LUMO+2	15	F-Ph→PolyPy

Figure S1: Ellipsoid draw (30%) and numbering scheme for compound 1. H-atoms omitted for clarity.

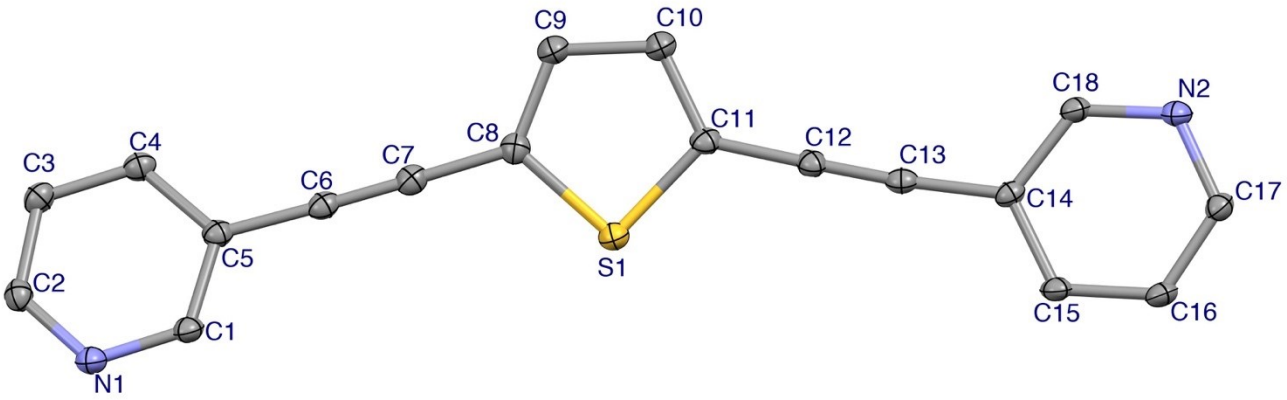


Figure S2: Ellipsoid draw (30%) and numbering scheme for compound 2. H-atoms omitted for clarity.

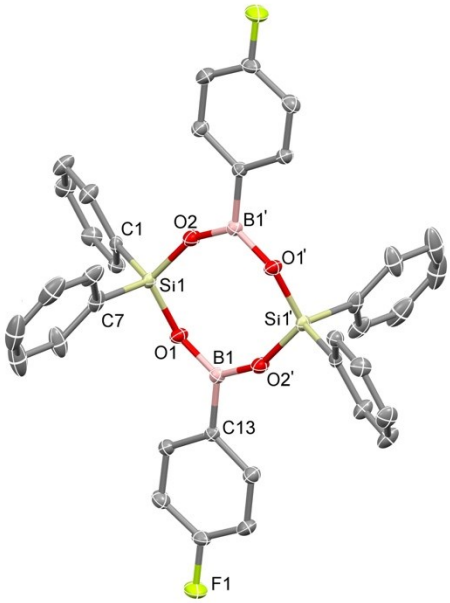


Figure S3: Ellipsoid draw (30%) and numbering scheme for compound 3. H-atoms omitted for clarity.

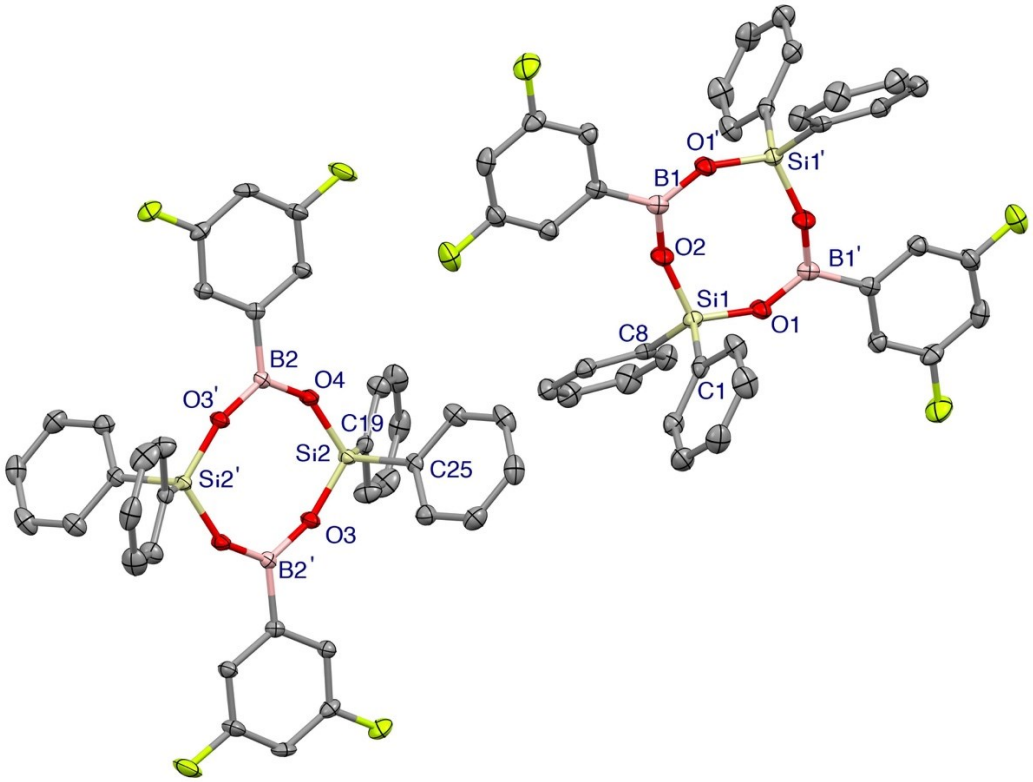


Figure S4: Asymmetric unit and numbering scheme for compound 4. H-atoms omitted for clarity.

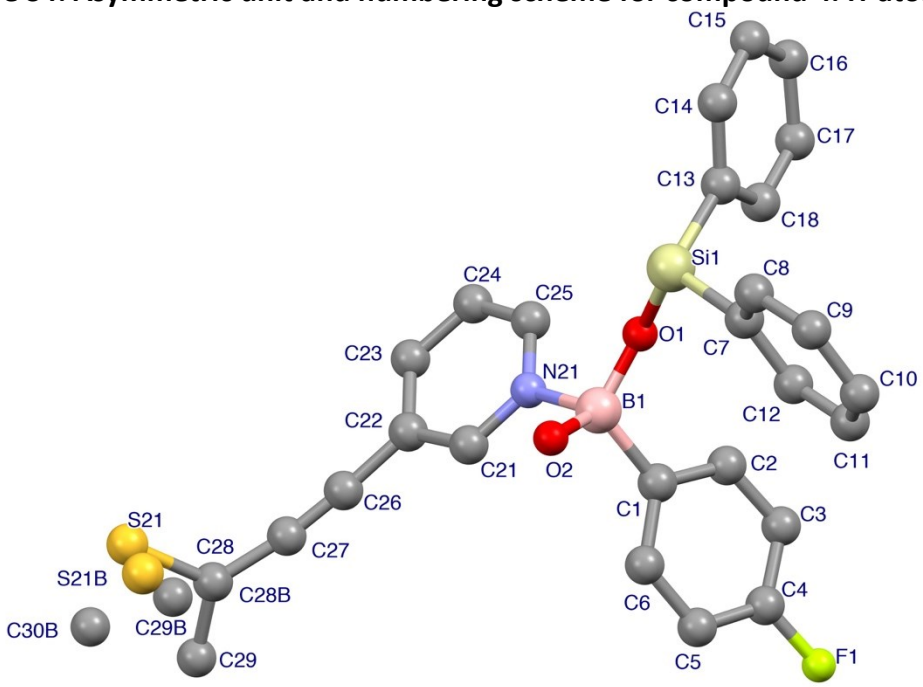
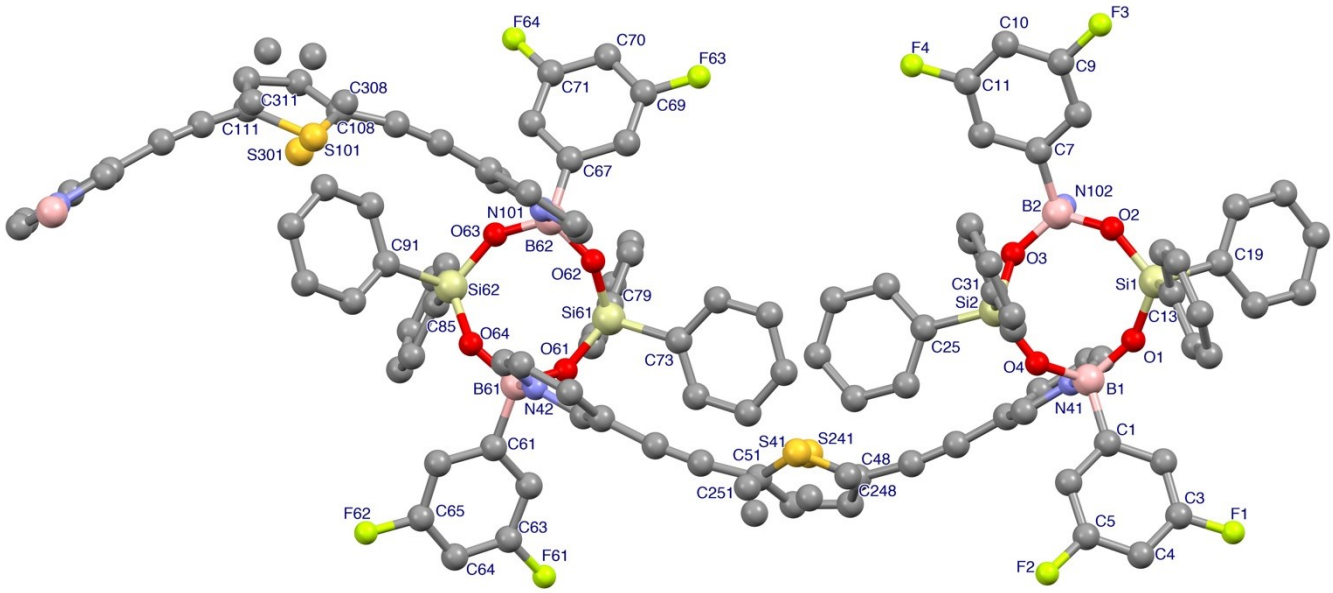


Figure S5: Asymmetric unit and numbering scheme for compound 5. H-atoms omitted for clarity.



FT-IR spectra.

Figure S6: FT-IR spectrum of 1

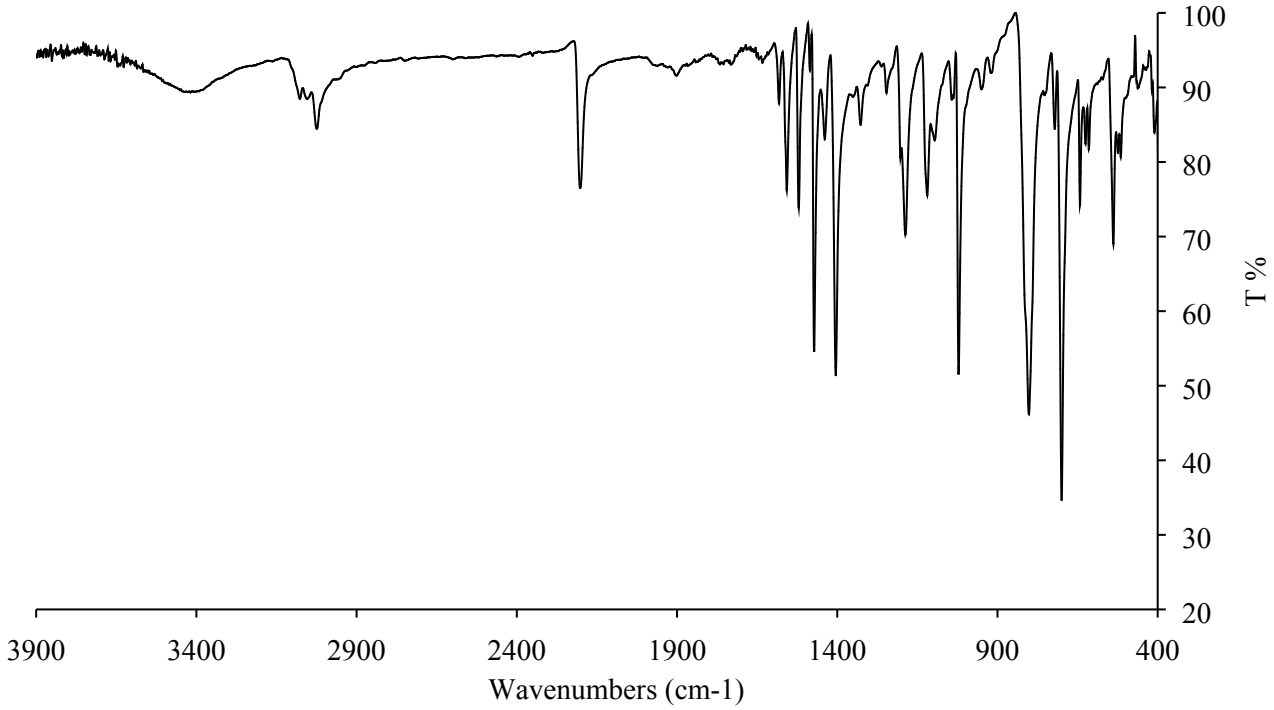


Figure S7: FT-IR spectrum of 2

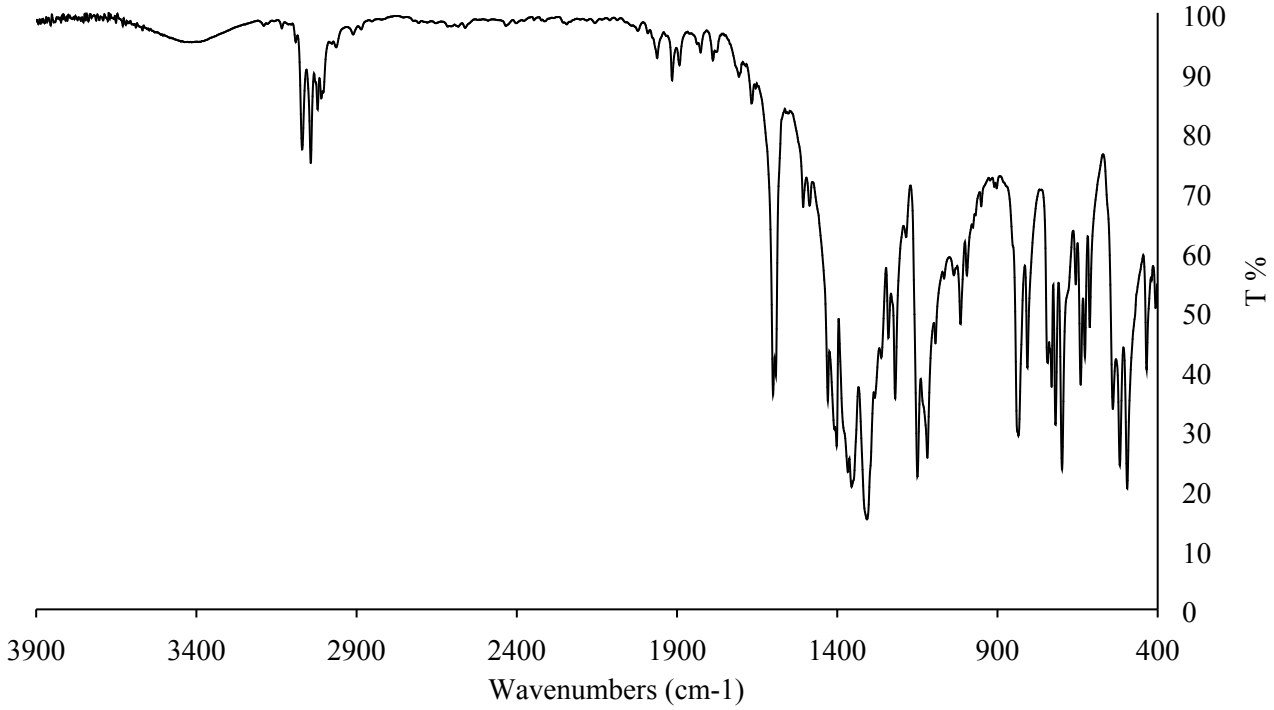


Figure S8: FT-IR spectrum of 3

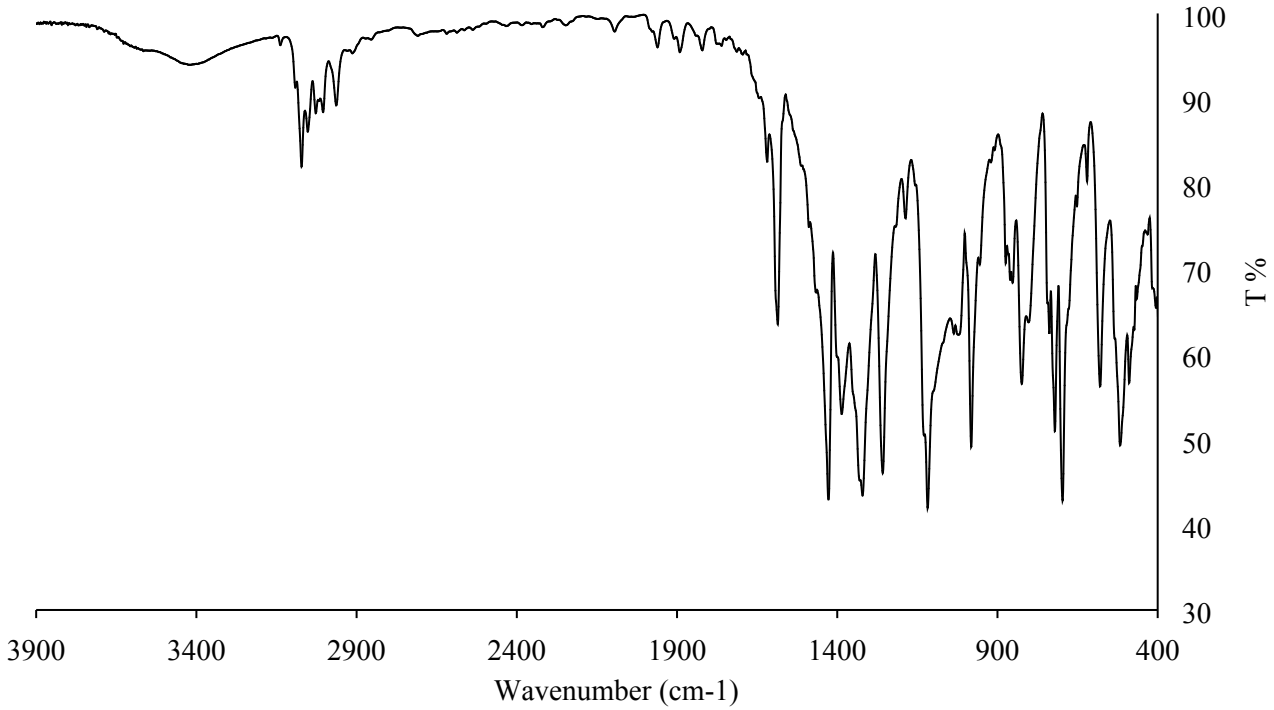


Figure S9: FT-IR spectrum of 4

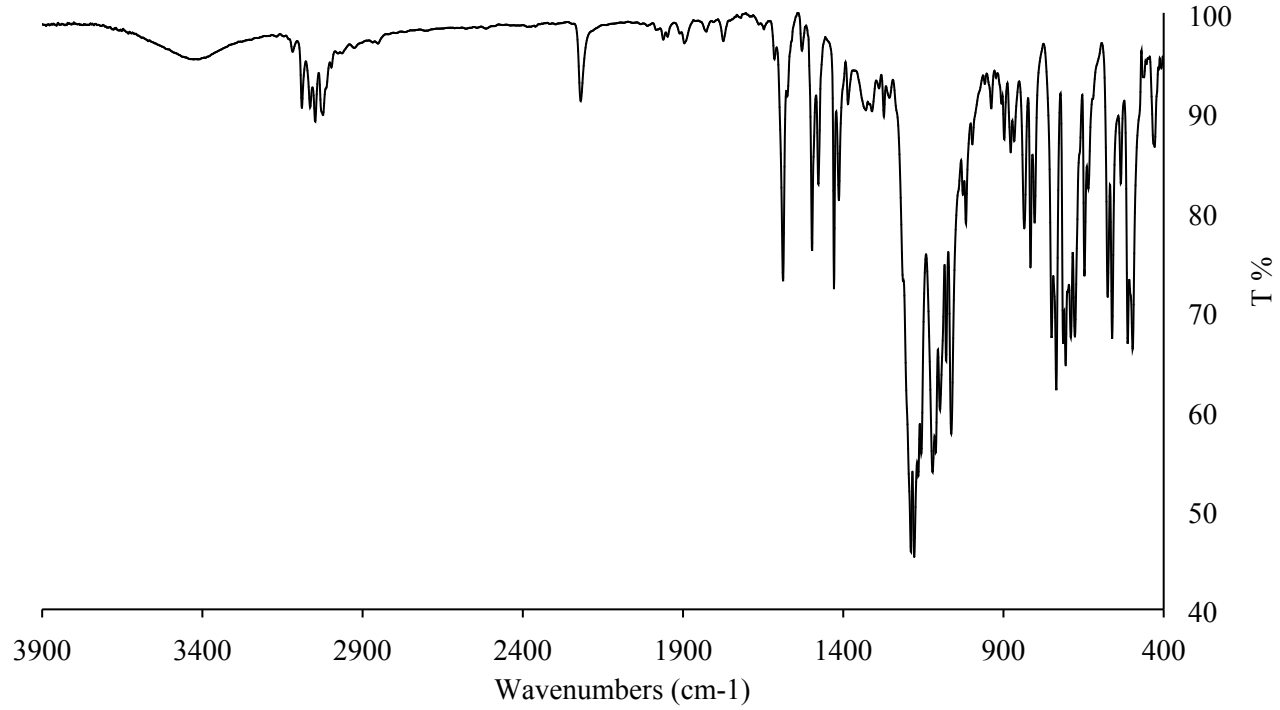


Figure S10: FT-IR spectrum of 5

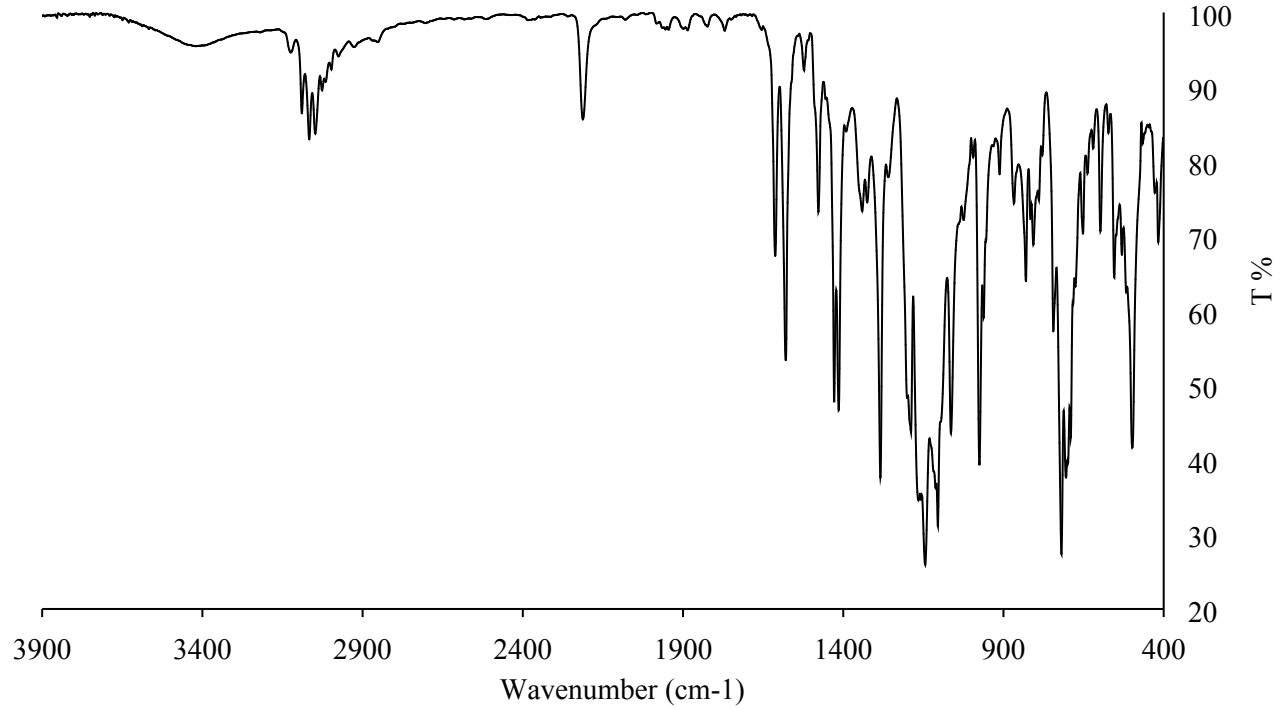
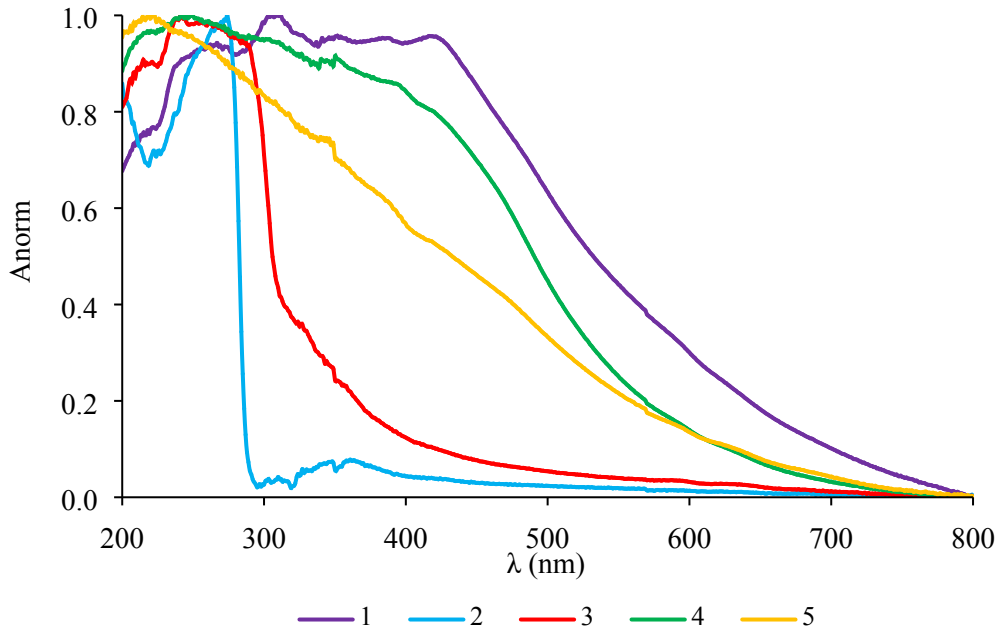


Figure S11. Diffuse reflectance measurements for compounds 1-5



NMR Spectra

Figure S12: ^{1}H-NMR (400 MHz, DMSO-d_6) of 1

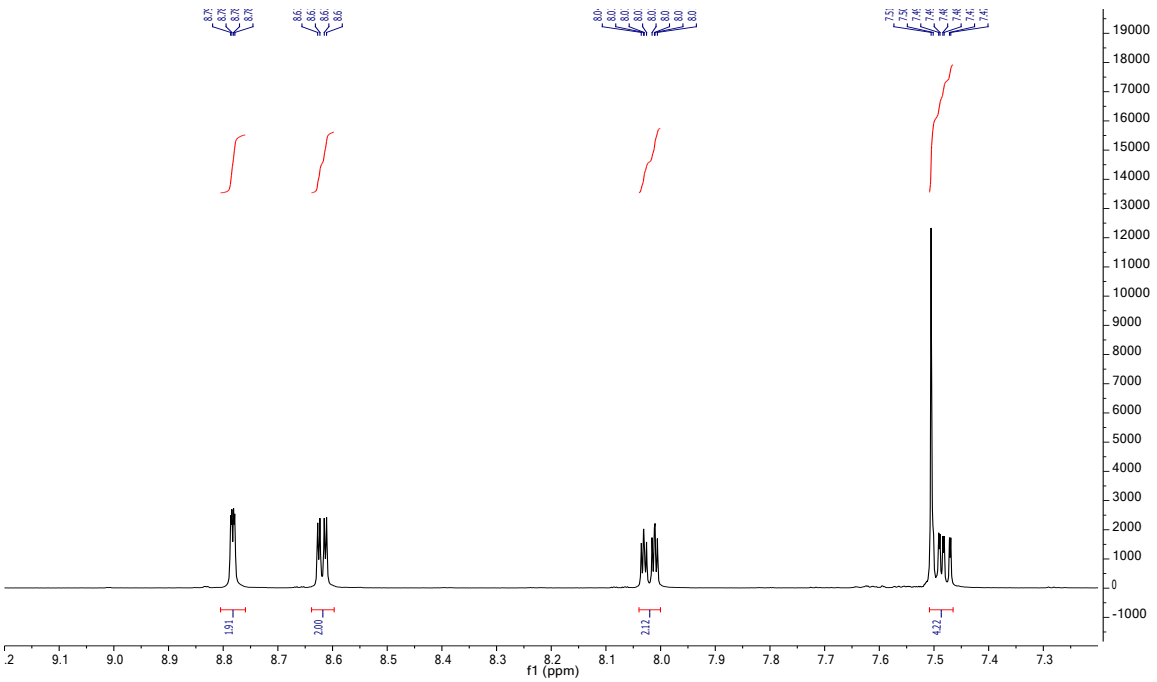


Figure S13: $^{13}C\{^{1}H\}$ NMR (101 MHz, DMSO-d_6) of 1

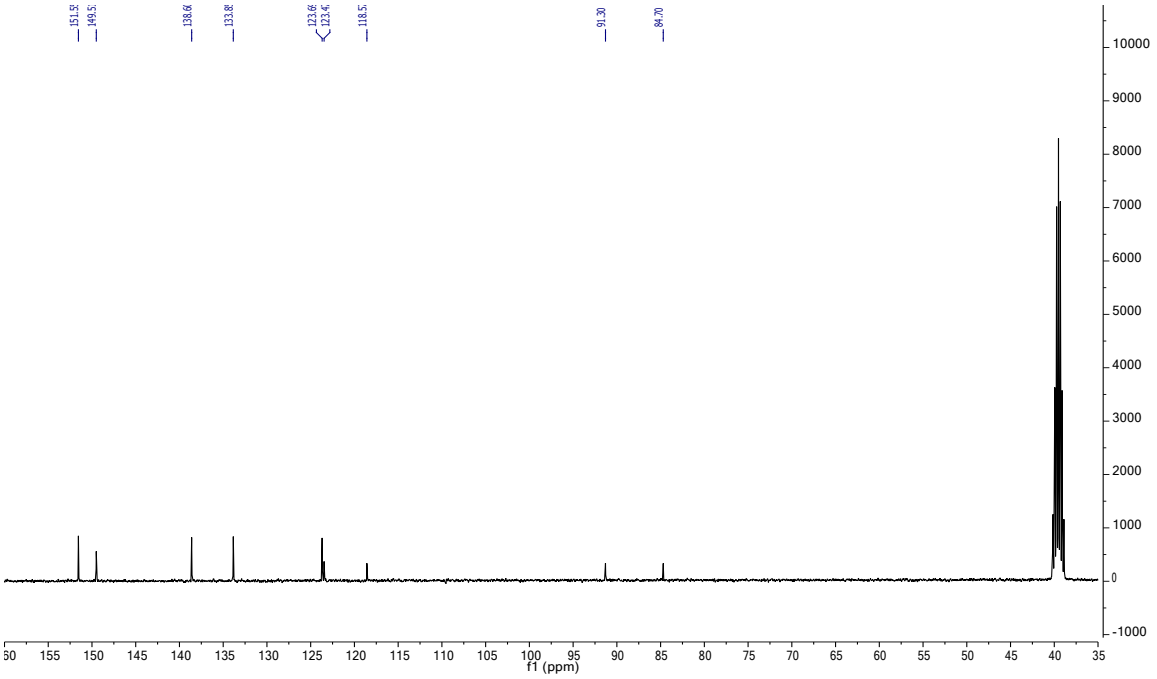


Figure S14: ^{1}H-^{1}H COSY NMR of 1

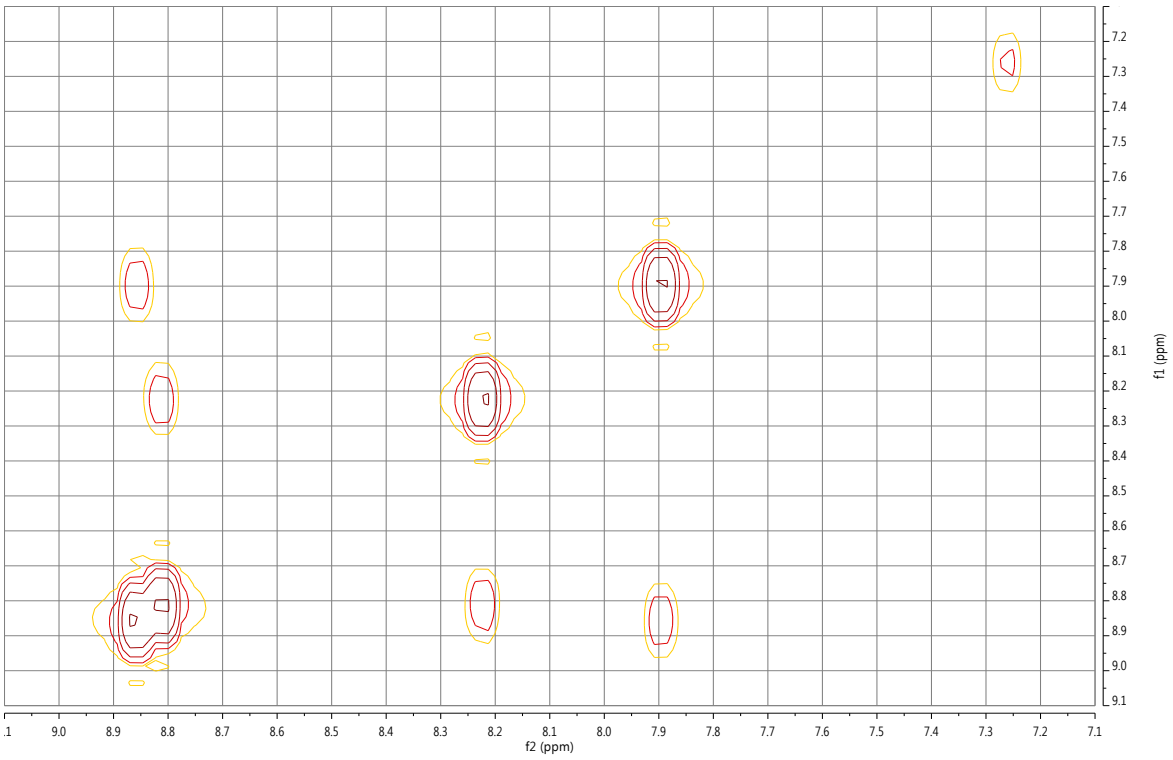


Figure S15: ^{1}H-NMR (400 MHz, $CDCl_3$) of 2

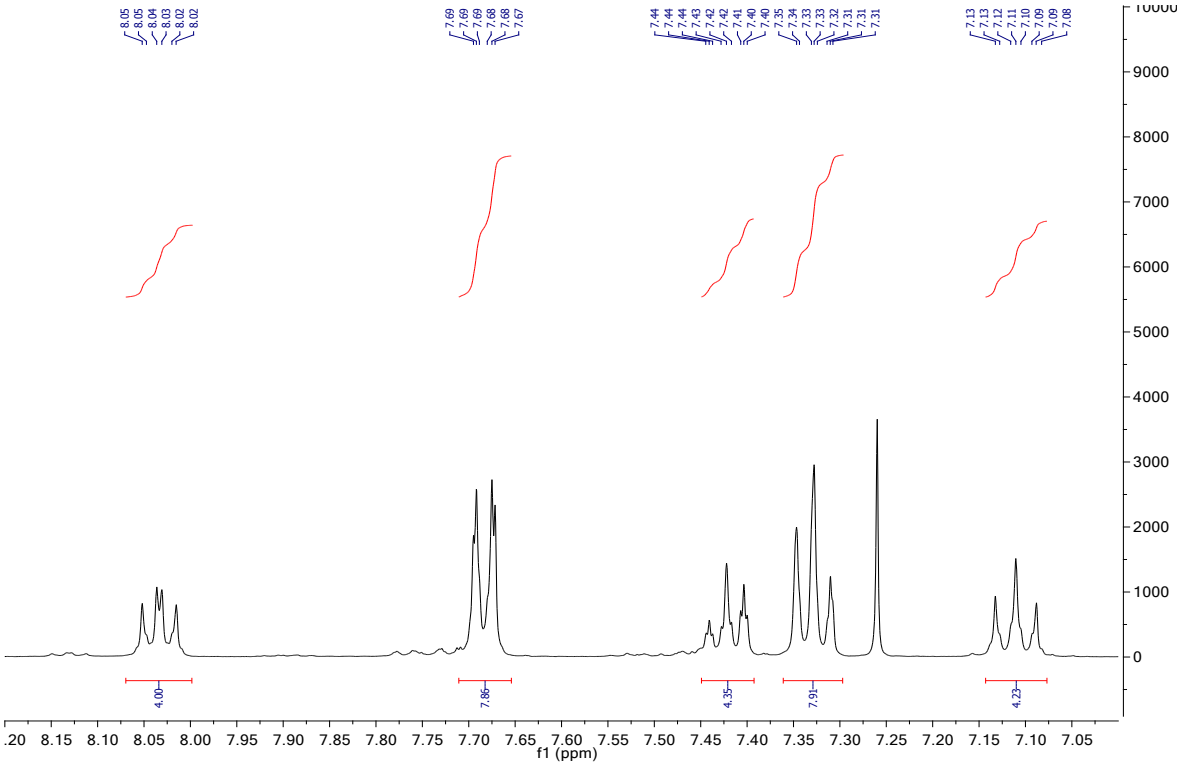


Figure S16: $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 2

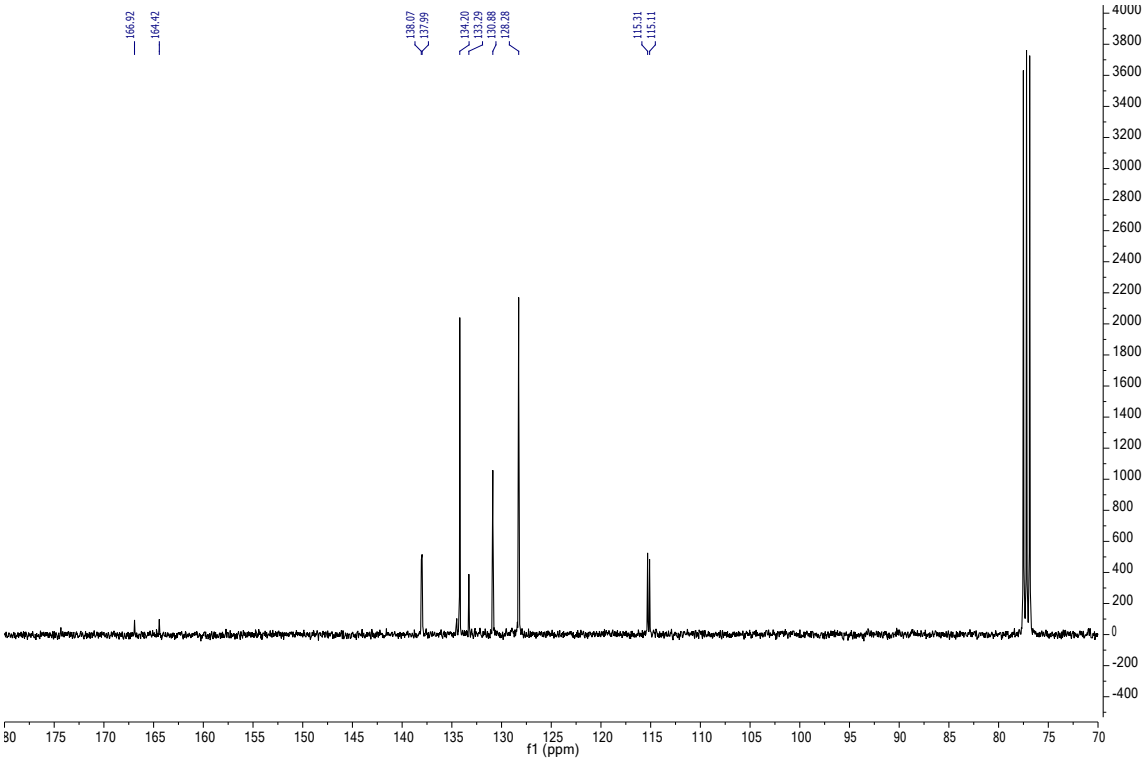


Figure S17: $^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$) of 2

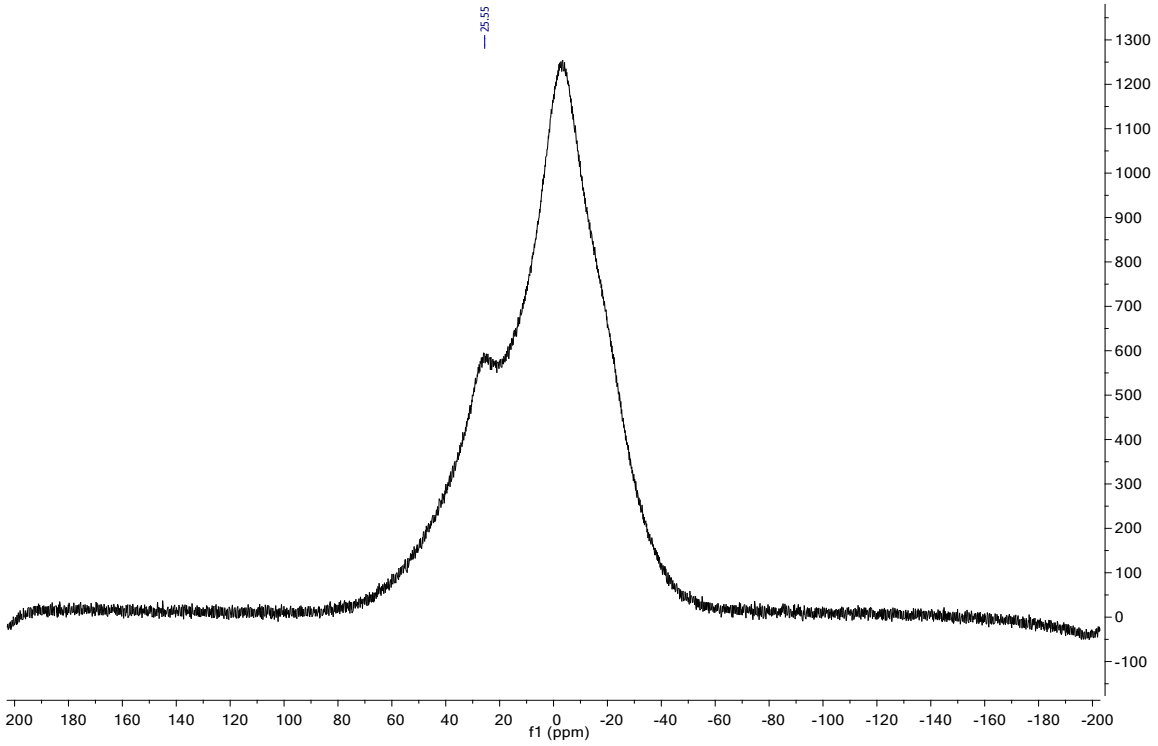


Figure S18: $^{19}F\{^{1}H\}$ NMR (377 MHz, $CDCl_3$) of 2

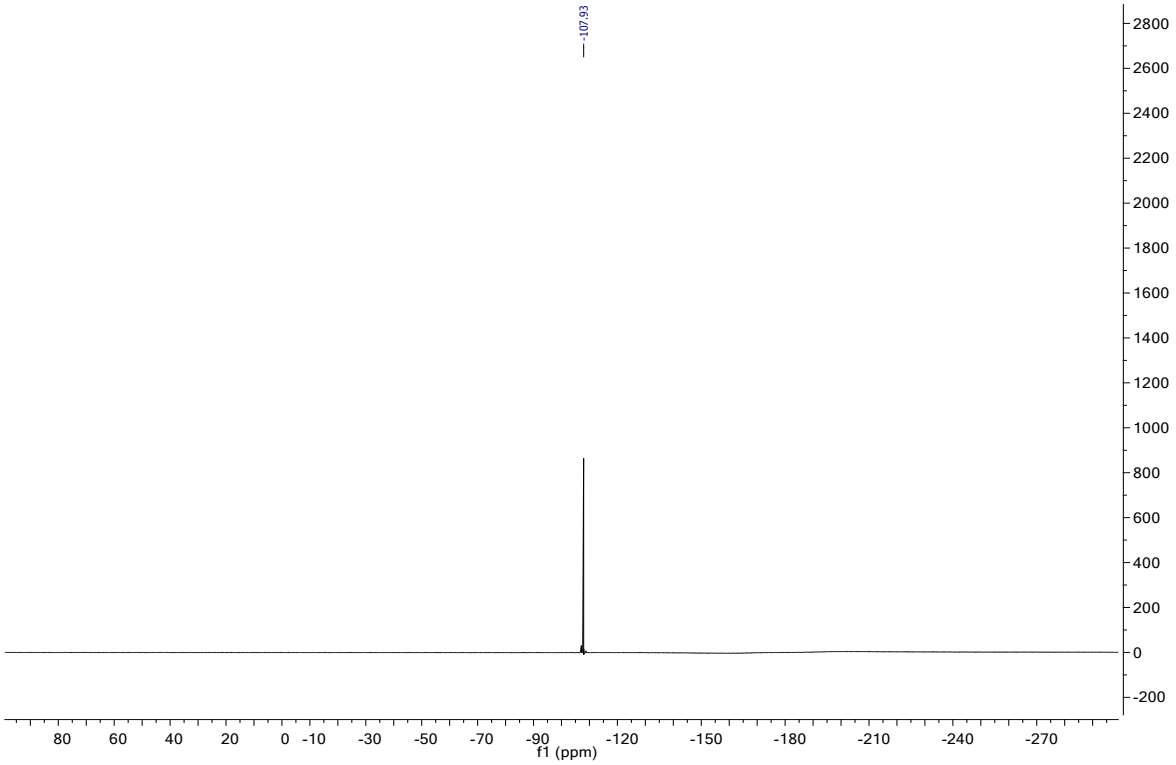


Figure S19. $^{29}Si\{^{1}H\}$ NMR (80 MHz, $CDCl_3$) of 2

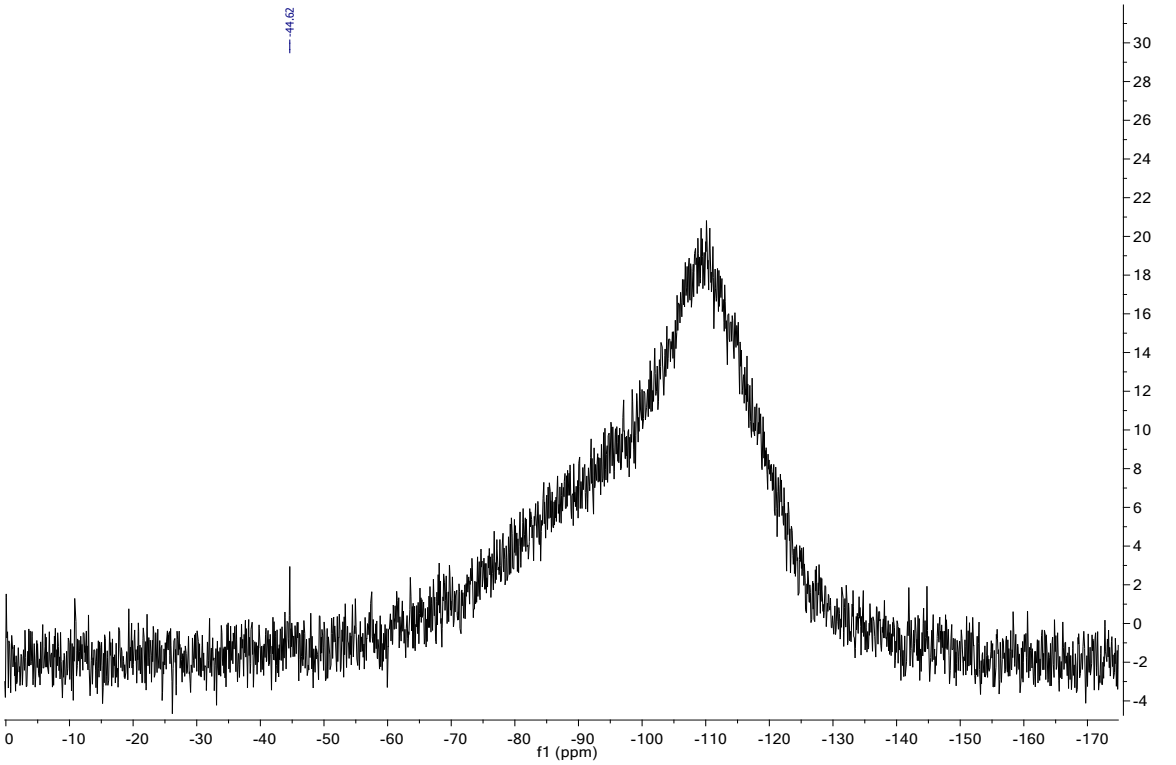


Figure S20: ^{1}H-NMR (400 MHz, $CDCl_3$) of 3

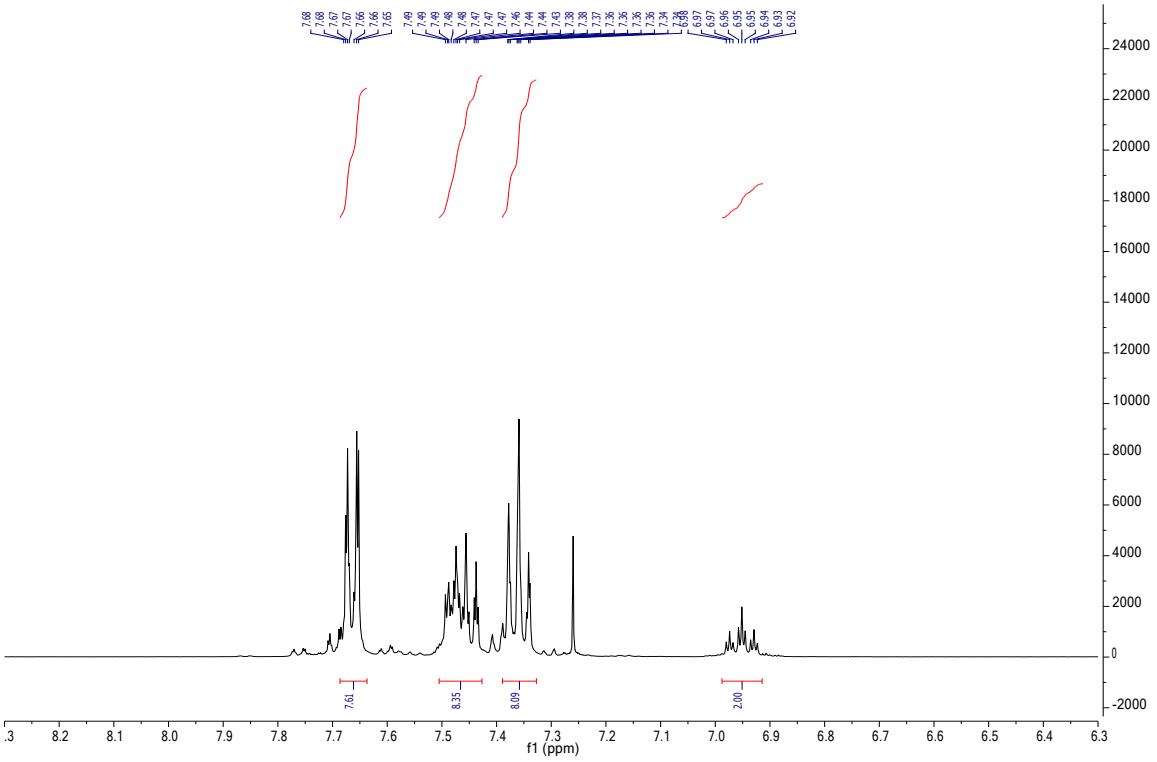


Figure S21 $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 3

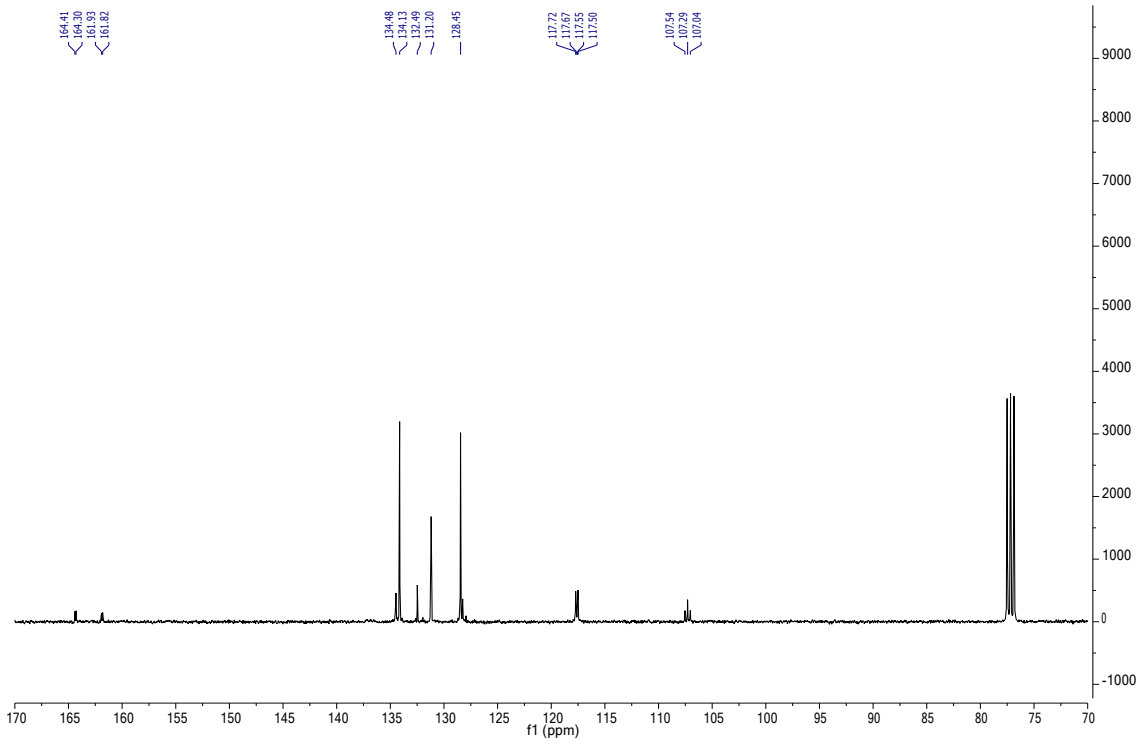


Figure S22: $^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$) of 3

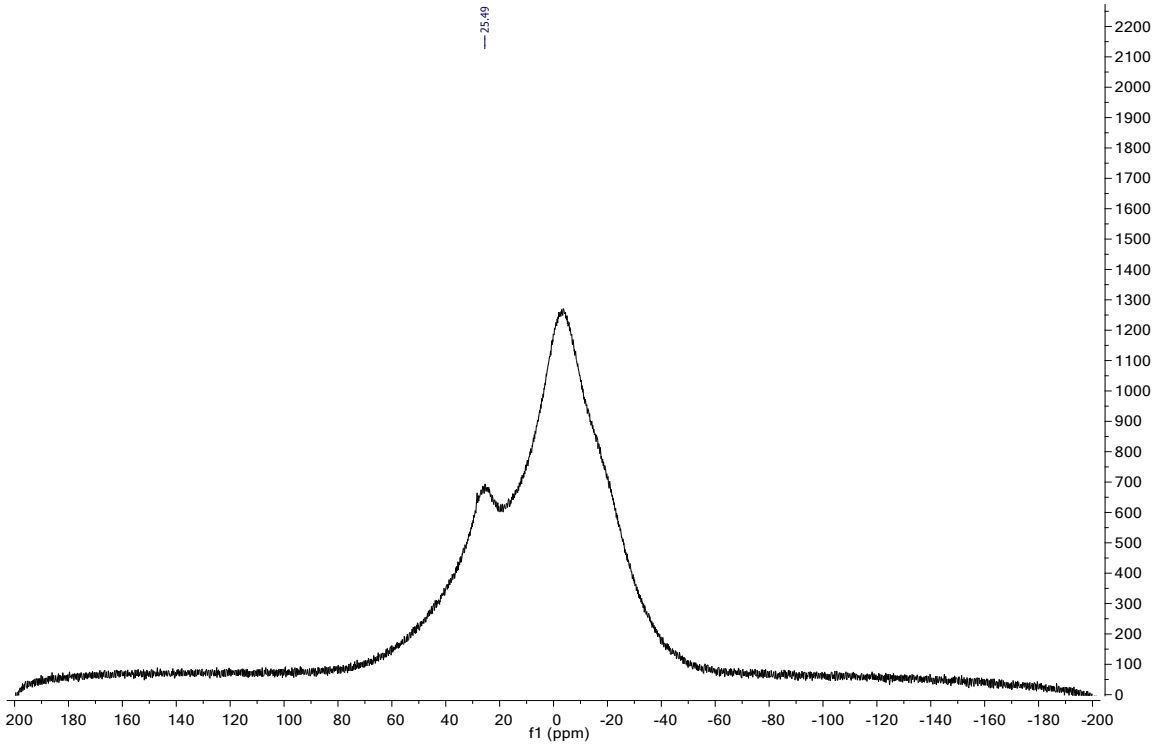


Figure S23: $^{19}F\{^{1}H\}$ NMR (377 MHz, $CDCl_3$) of 3

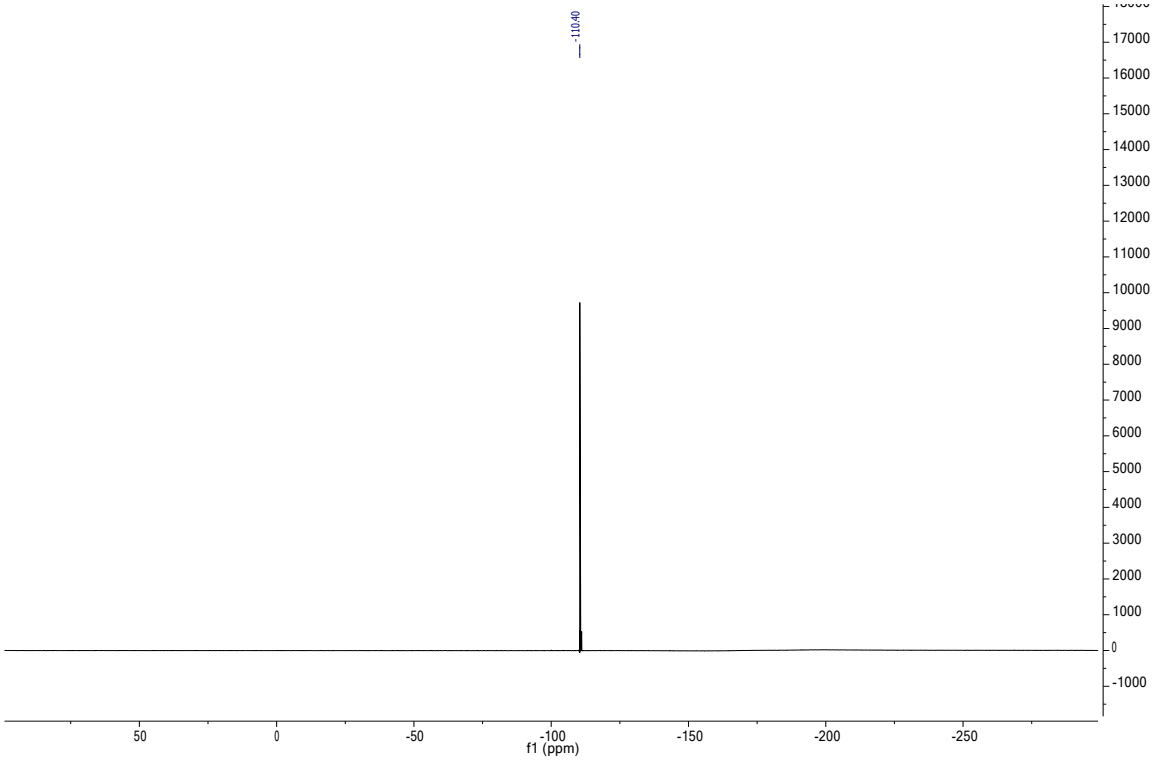


Figure S24: ^{29}Si-^{1}H HMBC of 3

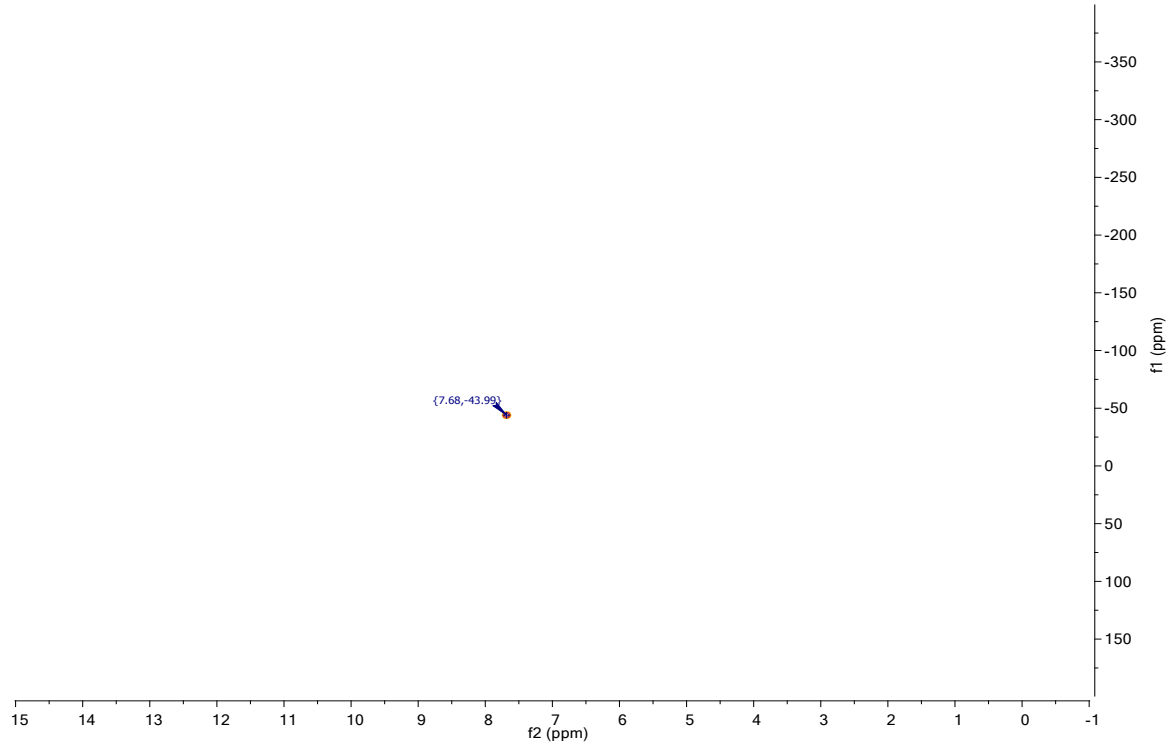


Figure S25: ^{13}C CP MAS of 4

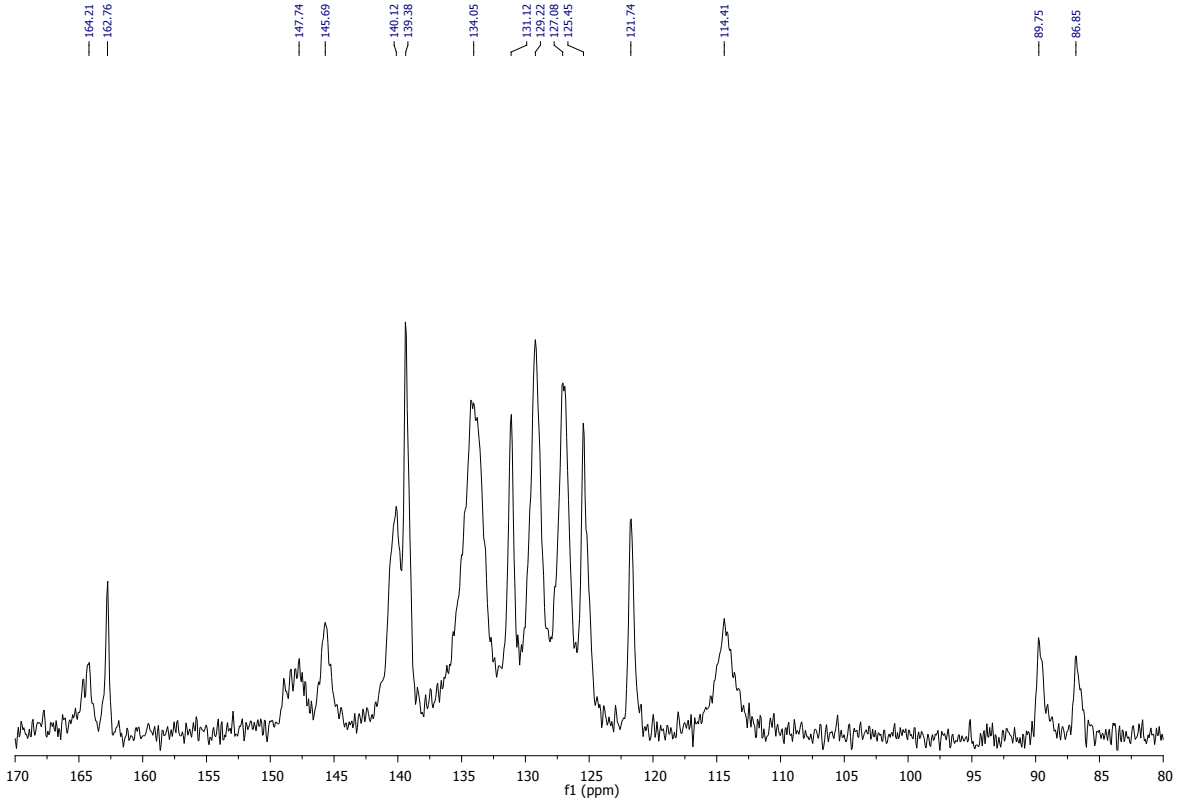
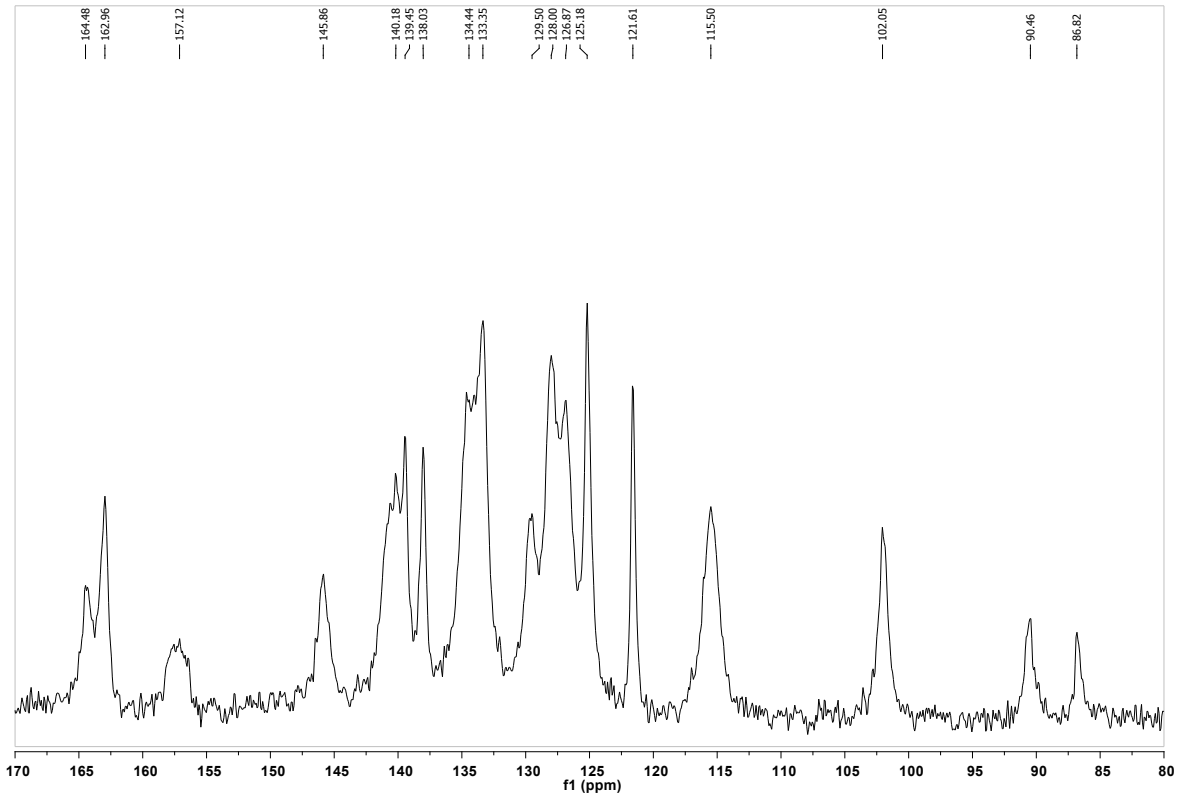
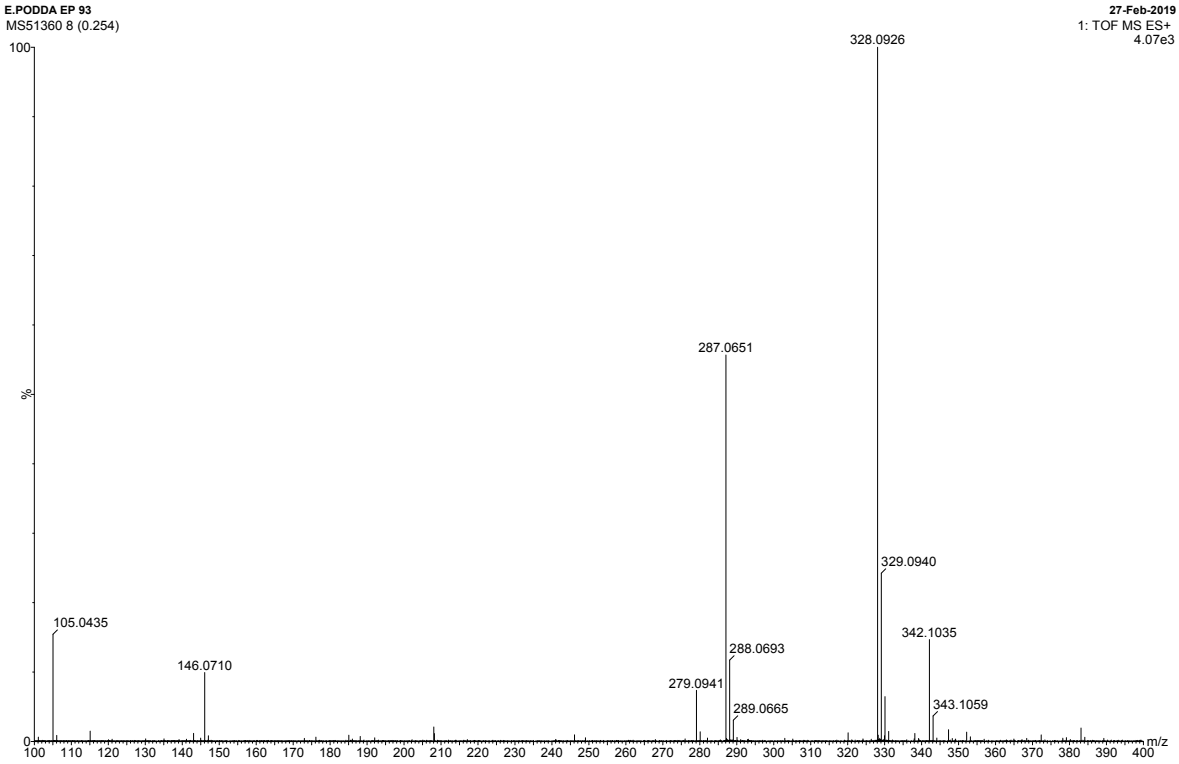


Figure S26: ^{13}C CP MAS of 5



Mass spectra

Figure S27: TOF MS ES+ of 1



Powder X-ray Diffraction analysis

Figure S28: Comparison between the experimental (red) and calculated (blue) PXRD pattern of compound 4

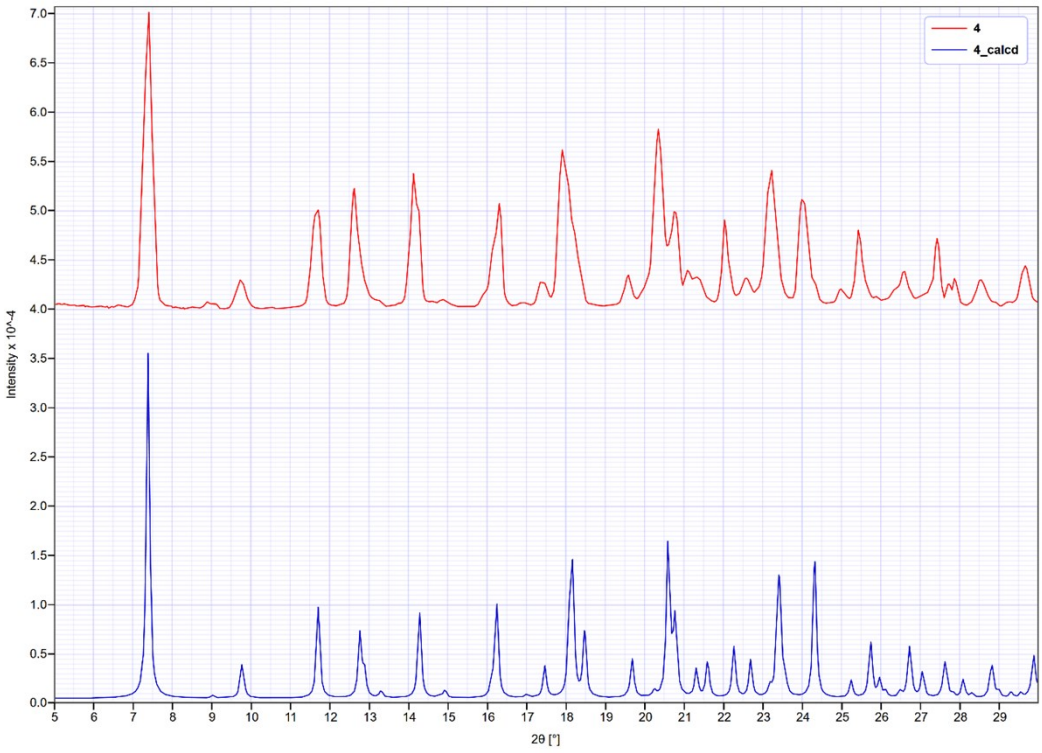


Figure S29: Comparison between the experimental (red) and calculated (blue) PXRD pattern of compound 5

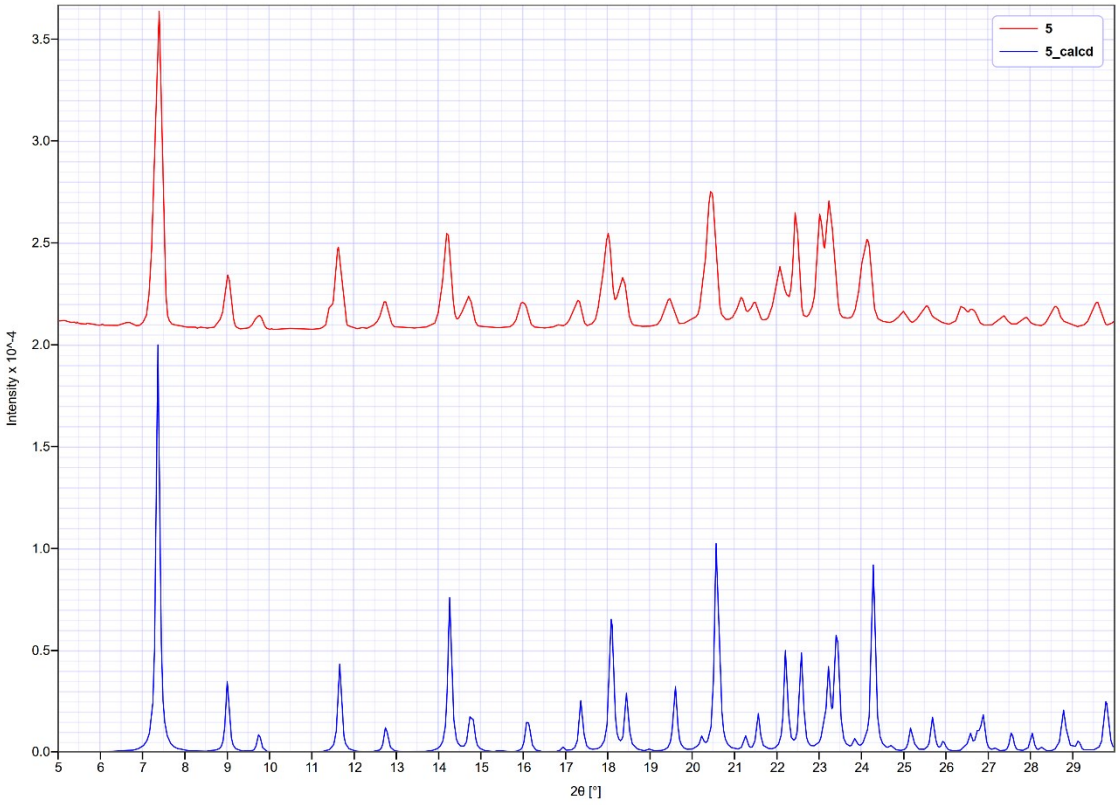
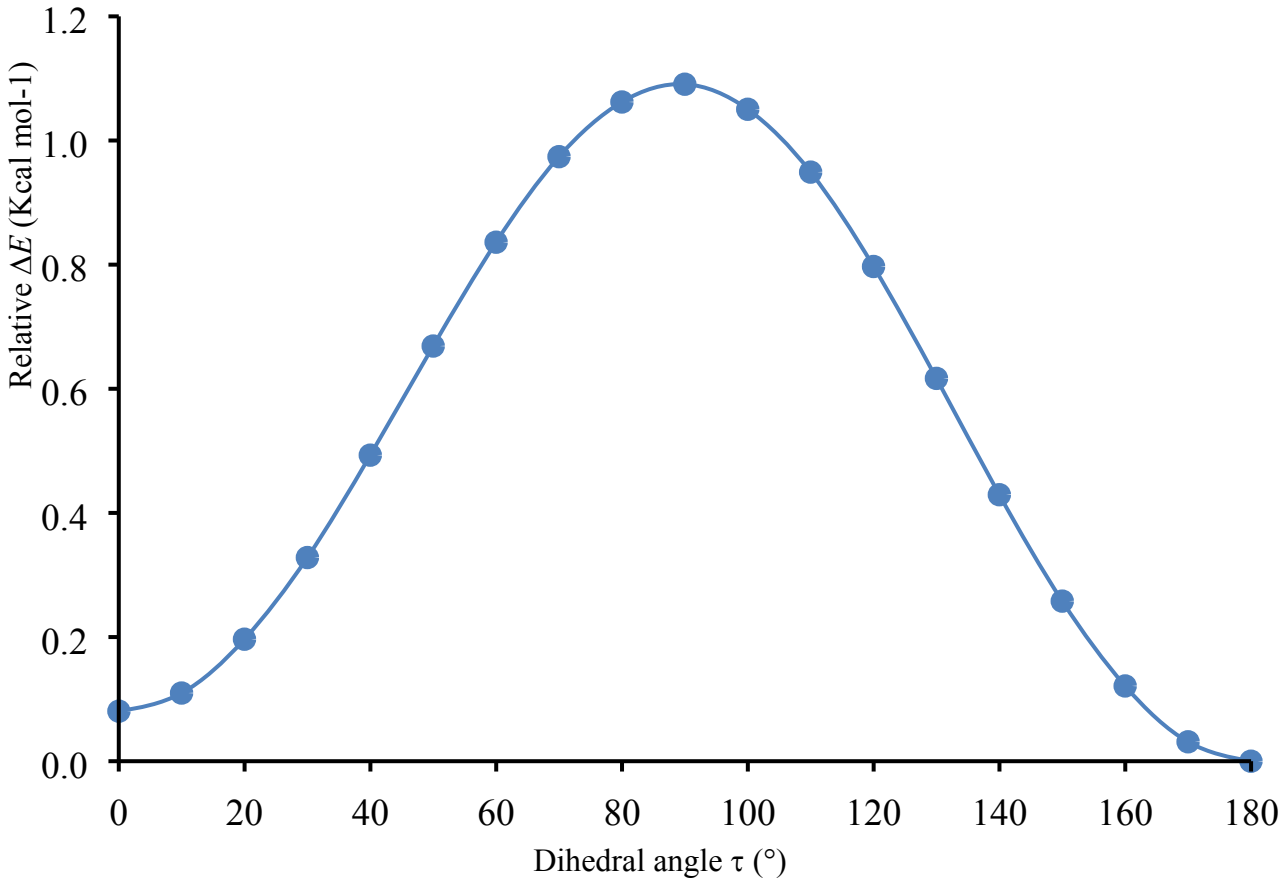
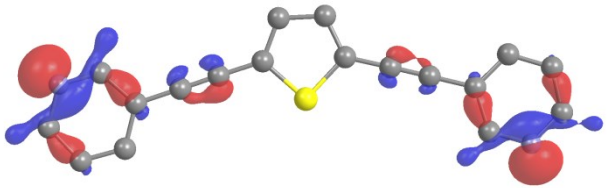


Figure S30: Relative total electronic energy variation (ΔE) calculated as a function of the pyridine ring

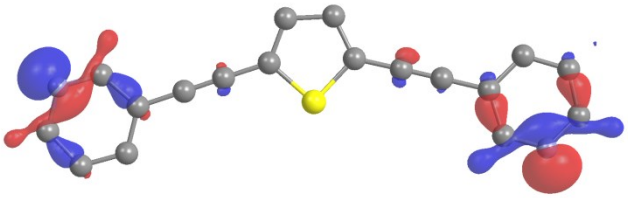


rotation (τ) for 1.

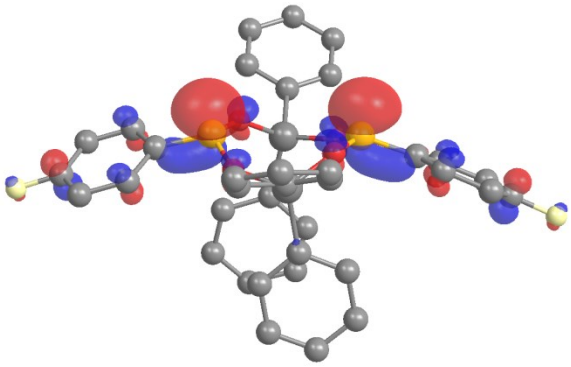
Figure S31: Isosurface drawings of selected frontier Kohn–Sham molecular orbitals calculated for 1, 2, and 3 at the optimized geometry. Hydrogen atoms were omitted for clarity. Cutoff value = 0.05 |e|.



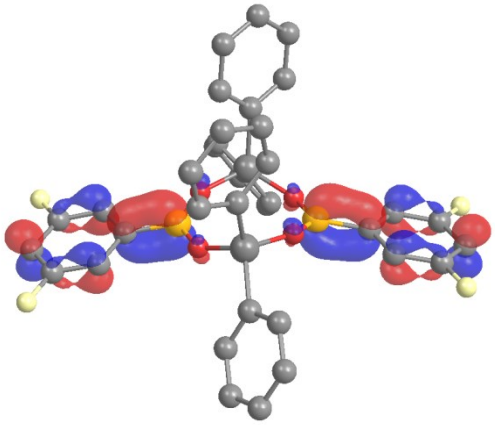
1, HOMO-2



1, HOMO-3



2, LUMO



3, LUMO

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