Supporting Information

2,2′-Bipyridine derived doubly B←N fused bisphosphine-chalcogenides, $[C_5H_3N(BF_2)\{NCH_2P(E)Ph_2\}]_2$ (E = O, S, Se): tuning of structural features and photophysical studies

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Crystal Structure Determination of Compounds 1-7.

Single crystals of all compounds were mounted on a Cryoloop with a drop of Paratone oil and positioned in the cold nitrogen stream on a Rigaku Saturn724+ (2x2 bin mode) diffractometer. The data collections were performed at 150 K using a graphite monochromated Mo-Kα (λ = 0.71073) radiation source for compounds **1-7**, and a Cu-Kα (λ = 1.54184) radiation source was used for **6·CH_2Cl_2** with the ω-scan technique. The data were reduced using CrysalisPro Red 171.41_64.93a software. The structures were solved using Olex2[1] with the ShelXT[2] structure solution program using intrinsic phasing and refined with the SHELXL[3] refinement package using least-squares minimization. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and included as riding contributions with isotropic displacement parameters tied to those of the attached non-hydrogen atoms. In compound **5** the disordered solvent molecule could not be recognized or modelled to a known solvent; hence, it was SQUEEZED using PLATON.[4] The results indicated 93 electrons and a volume of 316 $Å^3$ for **5**. The given chemical formula and other crystal data do not take into account the unknown solvent molecule(s). The reflections with error/esd more than 10 were excluded in order to avoid problems related to better refinement of the data. The data completeness is more than 99.8% in most of the cases, which is enough to guarantee a very good refinement of data. The details of X-ray structural determinations are given in Tables S1 and S2. All types of interaction images are visualised by Mercury 2020.3.0 software and all dihedral angles are visualised by Diamond 3.2 software.

Table S1 Crystallography details.

	1	**2**	**3**	**4**
Empirical formula	$C_{36}H_{32}N_4P_2$	$C_{36}H_{32}N_4O_2P_2$	$C_{144}H_{128}N_{16}P_8S_8$	$C_{144}H_{128}N_{16}P_8Se_8$
Formula weight	582.59	614.59	2586.86	2962.06
Temperature (K)	150.00	150.00	150	150.00
Crystal system	triclinic	monoclinic	monoclinic	monoclinic
Space group	P-1	$P2_1/c$	$P2_1$	$P2_1$
a, Å	8.9408(5)	19.2473(6)	20.1925(8)	20.4030(6)
b, Å	9.5762(5)	14.8930(5)	18.0964(4)	18.0437(4)
c, Å	10.2682(6)	10.3914(4)	20.5065(7)	20.5579(5)
α, °	62.279(5)	90	90	90
β, °	74.450(5)	90.335(3)	118.817(5)	117.871(3)
γ, °	81.103(4)	90	90	90
V, $Å^3$	749.30(8)	2978.64(18)	6565.4(5)	6690.4(3)
Z	1	4	2	2
$\rho_{calc,}$ (g cm^{-3})	1.291	1.371	1.309	1.470
M (Mo K_α), mm^{-1}	0.178	0.188	0.292	2.338
F(000)	306.0	1288.0	2704.0	2992.0
Crystal size (mm^3)	0.275 × 0.129 × 0.124	0.156 × 0.089 × 0.043	0.294 × 0.152 × 0.065	0.38 × 0.161 × 0.083
2θ range, °	4.598 to 49.998	4.232 to 53.998	3.22 to 50	3.238 to 50
Reflections collected	6241	15831	68679	68419
Independent reflections	2628 [R_{int} = 0.0328]	6484 [R_{int} = 0.0397]	22464 [R_{int} = 0.0910]	22821 [R_{int} = 0.0608]
Goodness-of-fit on F^2	1.105	1.030	1.048	1.052
R_1	0.0370	0.0494	0.0604	0.0434
wR_2	0.0938	0.1233	0.1305	0.0977

Table S2 Crystallography details.

	5	**6**	**6·CH_2Cl_2**	**7**
Empirical formula	$C_{36}H_{30}B_2F_4N_4O_2P_2$	$C_{36}H_{30}B_2F_4N_4P_2S_2$	$C_{37}H_{32}B_2Cl_2F_4N_4P_2S_2$	$C_{36}H_{30}B_2F_4N_4P_2Se_2$
Formula weight	710.20	742.32	827.24	836.12
Temperature (K)	150.00	150.00	150.00	150.00
Crystal system	triclinic	triclinic	triclinic	orthorhombic
Space group	P-1	P-1	P-1	$Pca2_1$
a, Å	12.2600(5)	8.8004(3)	9.3602(7)	25.0141(6)
b, Å	12.3283(5)	13.4350(5)	13.5014(9)	16.0868(3)
c, Å	14.7477(6)	15.5523(4)	16.0901(16)	17.0784(4)
α, °	113.820(4)	108.367(3)	108.010(7)	90
β, °	90.964(3)	96.762(3)	103.978(7)	90
γ, °	112.284(4)	90.049(3)	92.449(6)	90
V, $Å^3$	1848.43(15)	1731.58(10)	1861.3(3)	6872.3(3)
Z	2	2	2	8
$\rho_{calc,}$ (g cm^{-3})	1.276	1.424	1.476	1.616
M (Mo K_α), mm^{-1}	0.175	0.302	3.900	2.301
F(000)	732.0	764.0	848.0	3344.0
Crystal size (mm^3)	0.245 × 0.085 × 0.061	0.165 × 0.113 × 0.098	0.103 × 0.098 × 0.02	0.295 × 0.28 × 0.175
2θ range, °	4.486 to 50	4.664 to 49.998	5.996 to 137.992	4.766 to 49.998
Reflections collected	29048	24915	23924	79486
Independent reflections	6502 [R_{int} = 0.0840]	6106 [R_{int} = 0.0652]	6771 [R_{int} = 0.1264]	12071 [R_{int} = 0.0823]
Goodness-of-fit on F^2	1.024	1.047	1.017	1.039
R_1	0.0585	0.0460	0.1064	0.0419
wR_2	0.1544	0.1086	0.3294	0.0990

Table S3 Important bond lengths and bond angles of compounds **1-4**

Selected bond distances (Å)					
	1		**2** (E = O)	**3** (E = S)[a]	**4** (E = Se)[a]
C1–C1′	1.486(3)	C1–C6	1.490(3)	1.475(8)	1.489(8)
C6–N2	1.449(2)	C11–N3	1.452(3)	1.438(8)	1.440(8)
		C24–N4	1.444(2)	1.438(8)	1.454(8)
P1–C6	1.8502(17)	P1–C11	1.821(2)	1.824(6)	1.824(6)
		P2–C24	1.808(2)	1.832(6)	1.820(6)
		P1–E1	1.4842(15)	1.951(2)	2.1039(19)
		P2–E2	1.4876(15)	1.950(2)	2.0995(18)
N2–H2···N1′	1.967	N3–H3···N2	1.960	2.068	2.033
		N4–H4···N1	1.983	2.104	2.033
Selected bond angles (deg.)					
N2–C6–P1	111.03(11)	N3–C11–P1	107.85(15)	109.5(4)	108.7(4)
		N4–C24–P2	109.86(14)	107.6(4)	109.7(4)
		E1–P1–C11	112.78(10)	111.2(2)	110.4(2)
		E2–P2–C24	113.22(9)	110.6(2)	112.6(2)
N2–H2···N1′	132.2	N3–H3···N2	132.2	127.6	127.9
		N4–H4···N1	133.1	125.8	128.5
Δ^b			13.41	26.21	22.35

[a] For compounds **3** and **4** only one molecule is considered from the asymmetric unit cell. [b] dihedral angle measured between the two mean planes: *plane 1* contains N1-C1-C2-N3 and *plane 2* contains N2-C6-C7-N4 atoms, respectively.

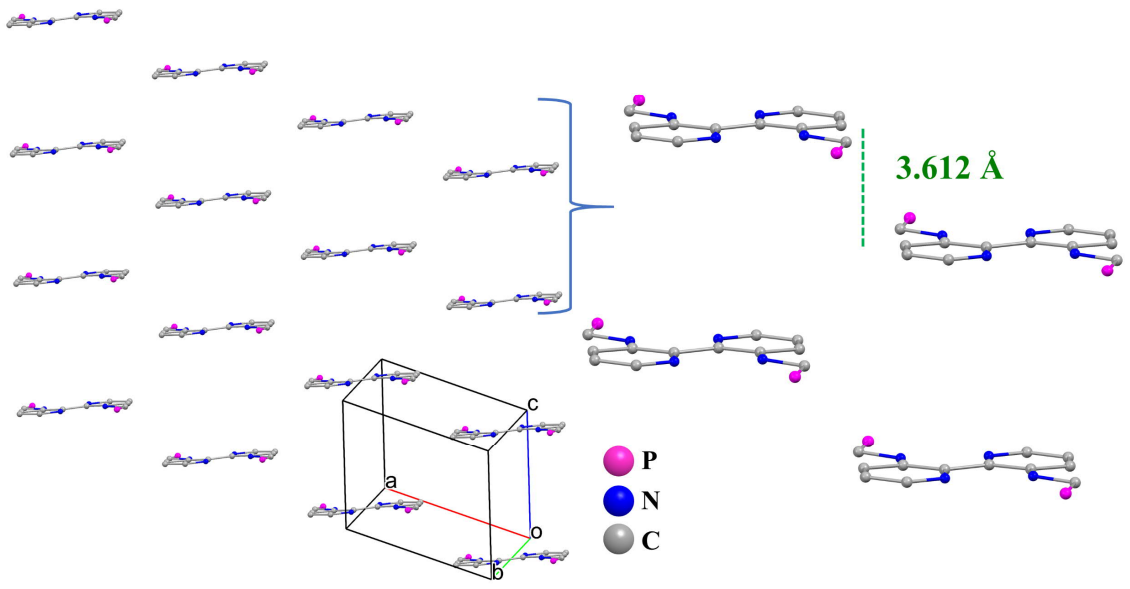

Fig. S1 Stair case stacking of bisphosphine ligand **1**.

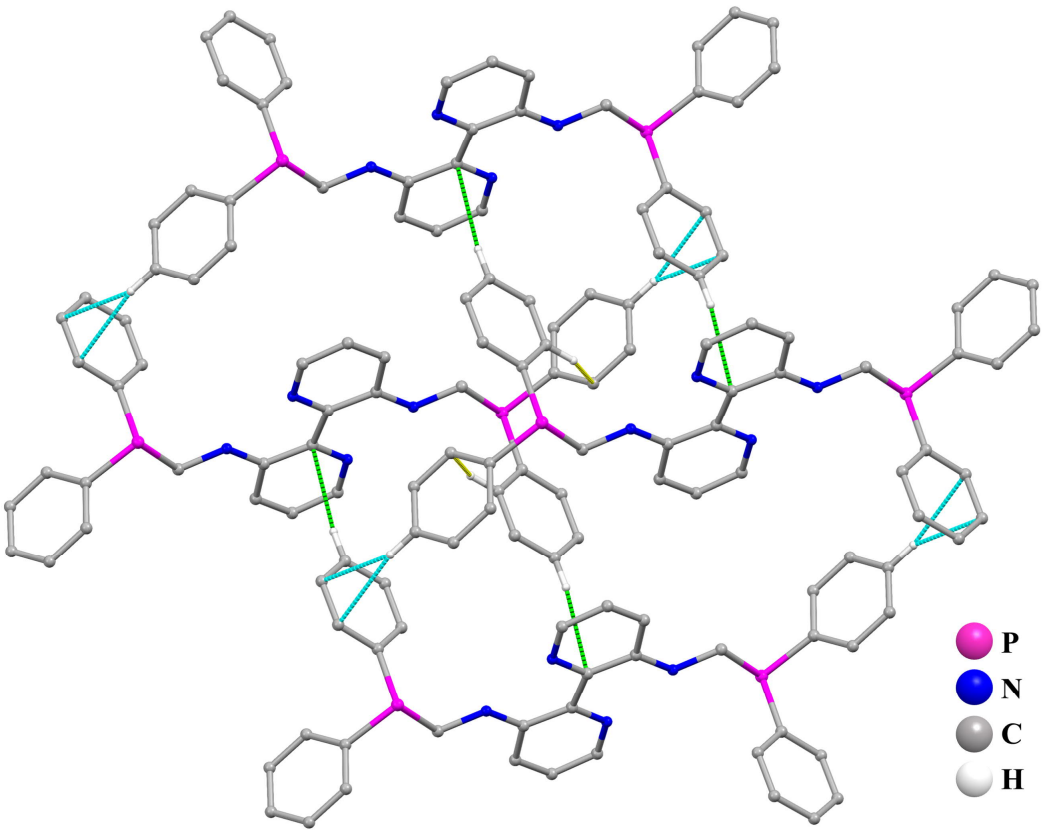

Fig. S2 Intermolecular C–H···π interactions occur in crystal packing of ligand **1** and are depicted by dashed line; *green lines*: H10···C1 = 2.686 Å, C10–H10···C1 = 173°; *light blue line*: H16··· centroid (C8–C9) = 2.697 Å, C16–H16···centroid = 150°; *yellow line*: H12···C18 = 2.894 Å, C12–H12···C18 = 129°.

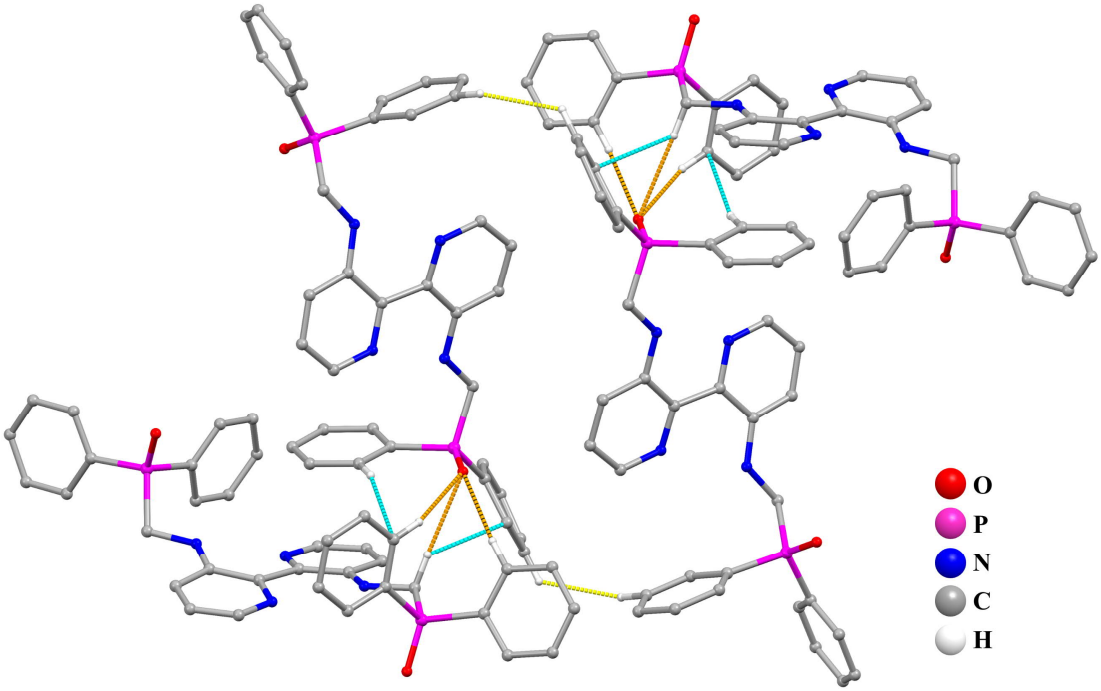

Fig. S3 Dash line represents various intermolecular interactions occur in **2**; *yellow line*, H···H interactions: H20···H35 = 2.358 Å; *orange line*, O···H interactions: O2···H24A/H26/H32 2.336

to 2.633Å; *light blue lines*, C–H···π interactions: H30···C26 = 2.850 Å, C30–H30···C26 = 161°, H24A···C36 = 2.873 Å, C24–H24A···C36 = 121°.

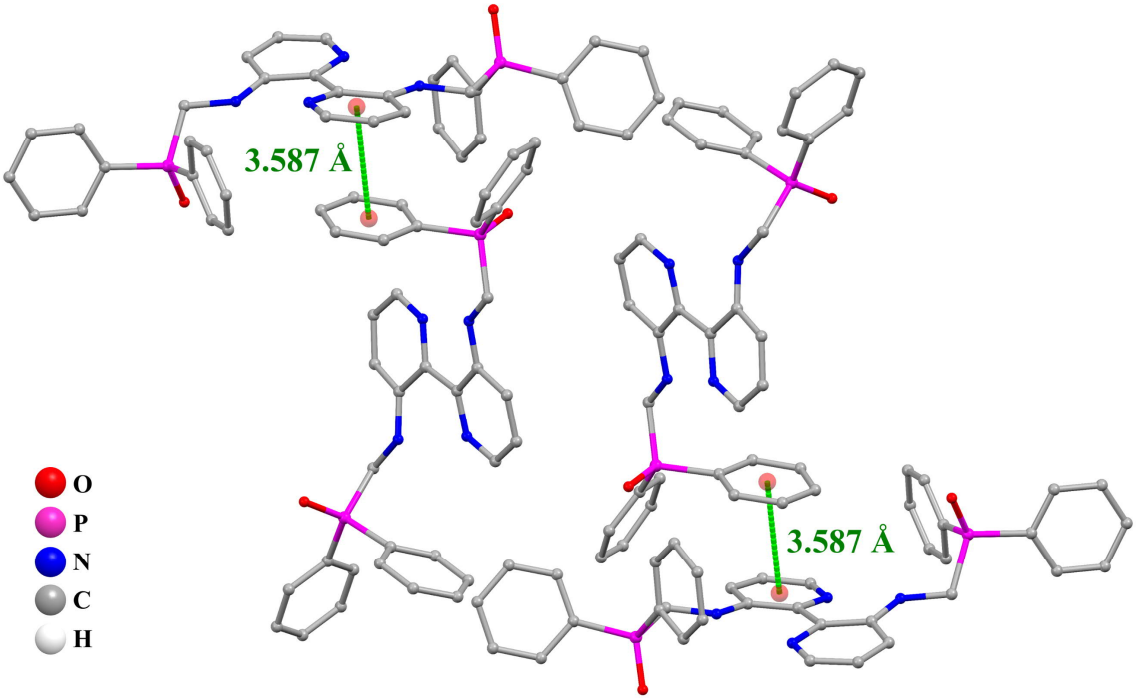

Fig. S4 Sandwich type π -stacking or π–π stacking occurs in crystal packing of compound **2**.

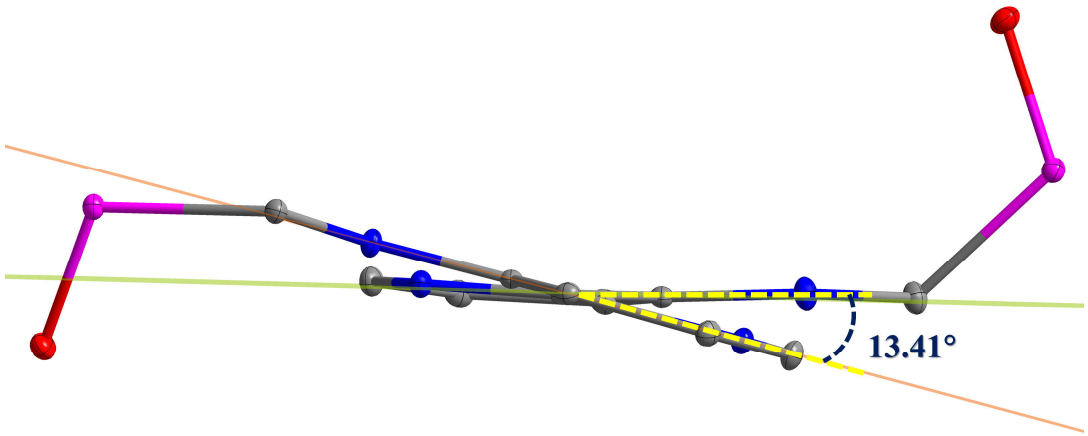

Fig. S5 Dihedral angle between two mean planes: N1-C1-C2-N3 (green) and N2-C6-C7-N4 (orange) in **2** (P: magenta, N: blue, O: red, C: grey, phenyl rings and H atoms are omitted for clarity).

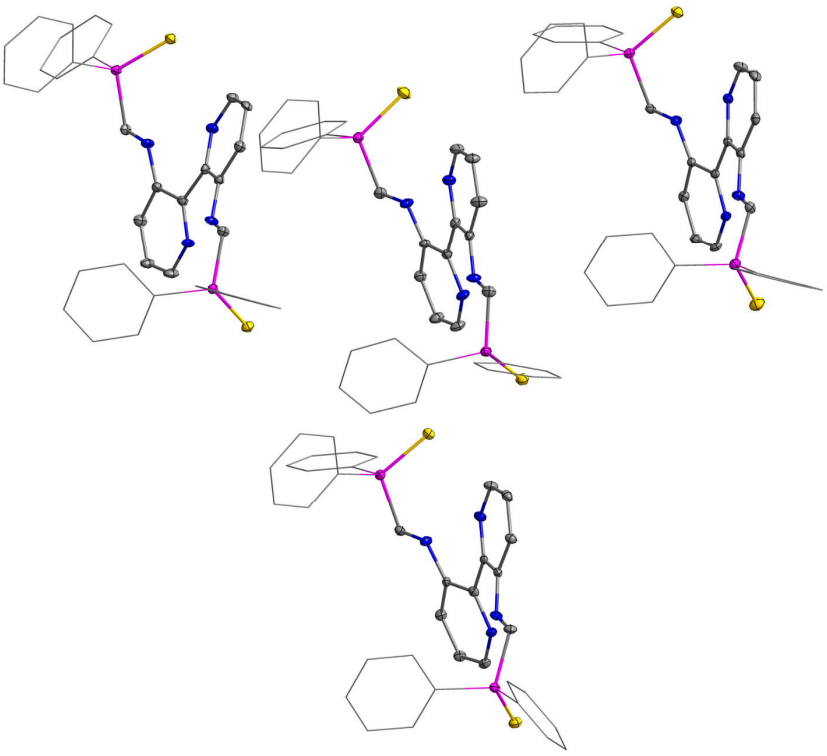

Fig. S6 Asymmetric unit of compound **3** (P: magenta, N: blue, S: dark yellow, C: grey, H atoms are omitted for clarity).

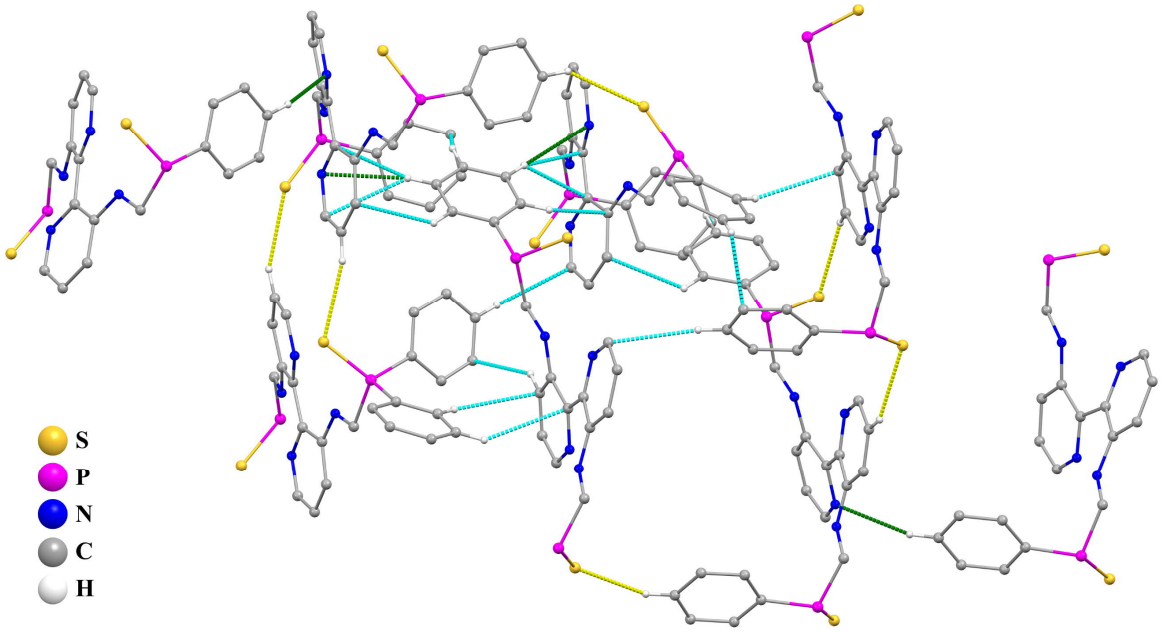

Fig. S7 Dash line represents various intermolecular interactions occur in **3**: *green line*, N···H interactions: N1···H51 = 2.656 Å, N4···H137 = 2.637 Å, N2···H135 = 2.731 Å; *yellow lines*, S···H interactions: S1···H81 = 2.871 Å, S5···H9 = 2.876 Å, S7···H34 = 2.949 Å; *light blue lines*, C–H···π interactions: distances = 2.730 to 2.899 Å, angles = 124° to 171°.

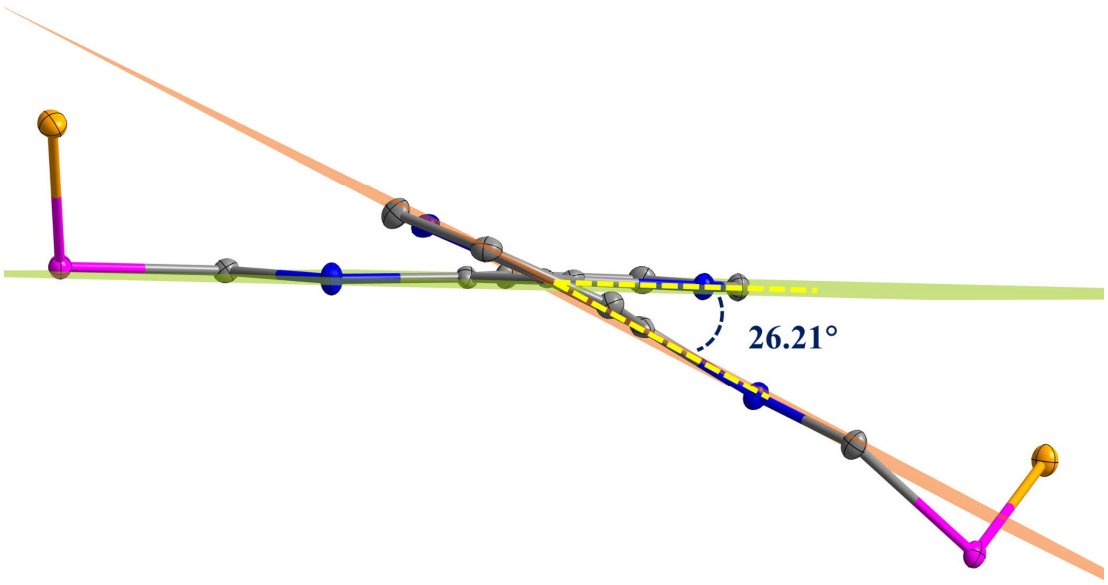

Fig. S8 Dihedral angle between two mean planes: N1-C1-C2-N3 (green) and N2-C6-C7-N4 (orange) in **3** (P: magenta, N: blue, O: red, C: grey, phenyl rings and H atoms are omitted for clarity).

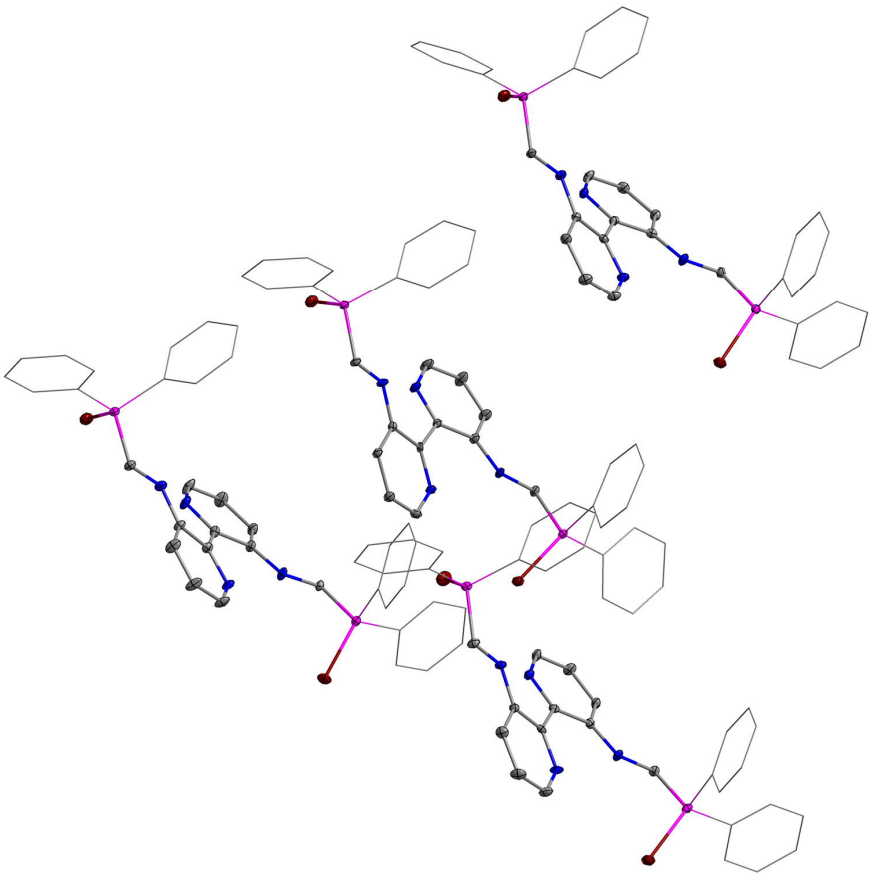

Fig. S9 Asymmetric unit of compound **4** (P: magenta, N: blue, Se: dark brown, C: grey, H atoms are omitted for clarity).

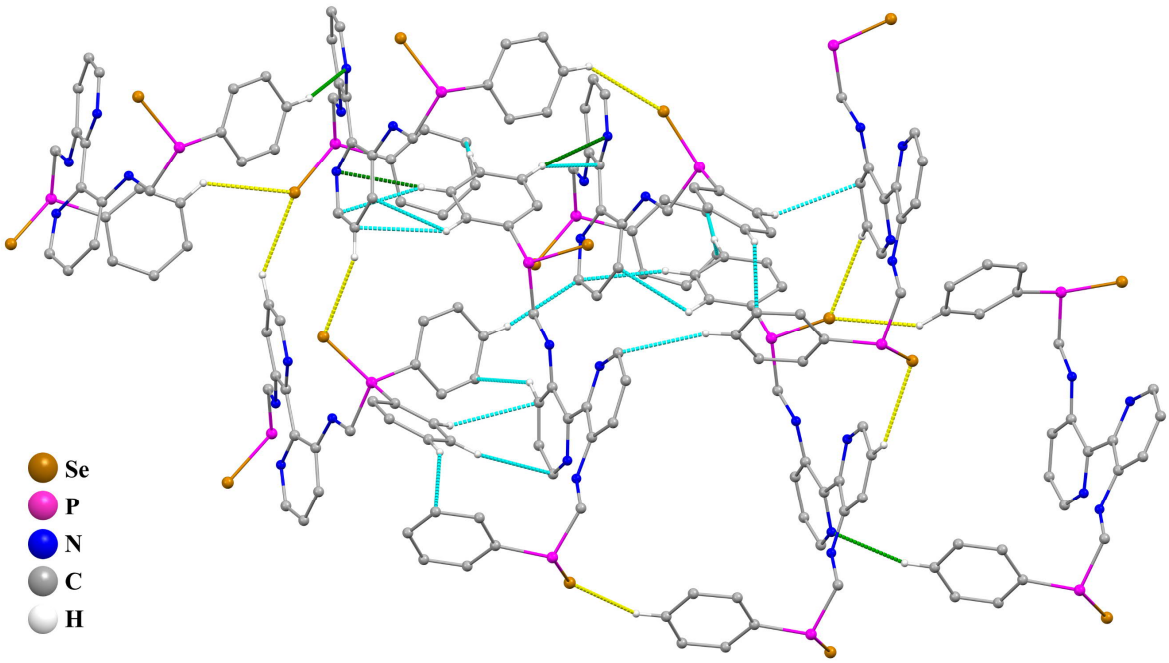

Fig. S10 Dash line represents various intermolecular interactions occur in **4**: *green line*, N···H interactions: N1···H16A = 2.610 Å, N5···H100 = 2.647 Å, N7···H14A = 2.749 Å; *yellow lines*, Se···H interactions: distances = 2.957 to 3.089 Å; *light blue lines*, C–H···π interactions: distances = 2.757 to 2.891 Å, angles = 124° to 164°.

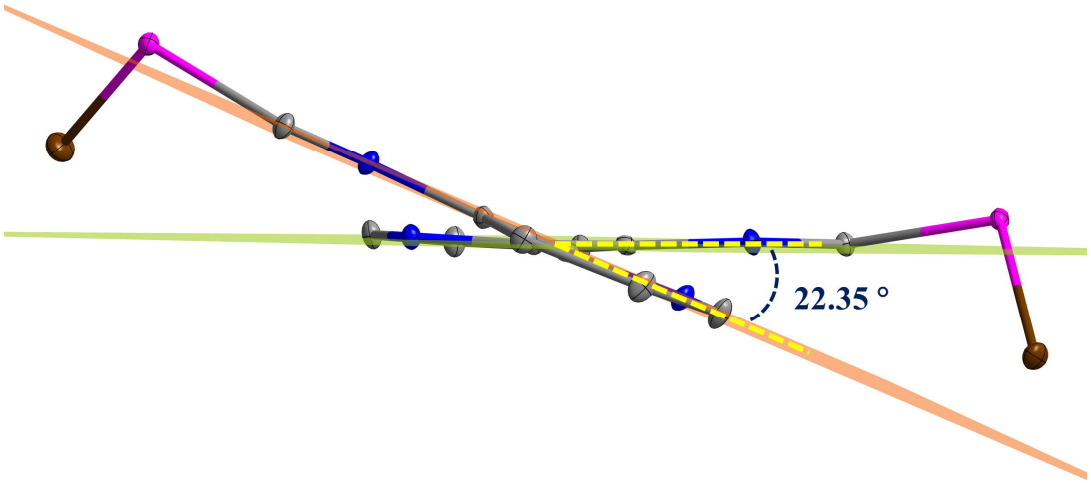

Fig. S11 Dihedral angle between two mean planes: N1-C1-C2-N3 (green) and N2-C6-C7-N4 (orange) in **4** (P: magenta, N: blue, Se: dark brown, C: grey, phenyl rings and H atoms are omitted for clarity).

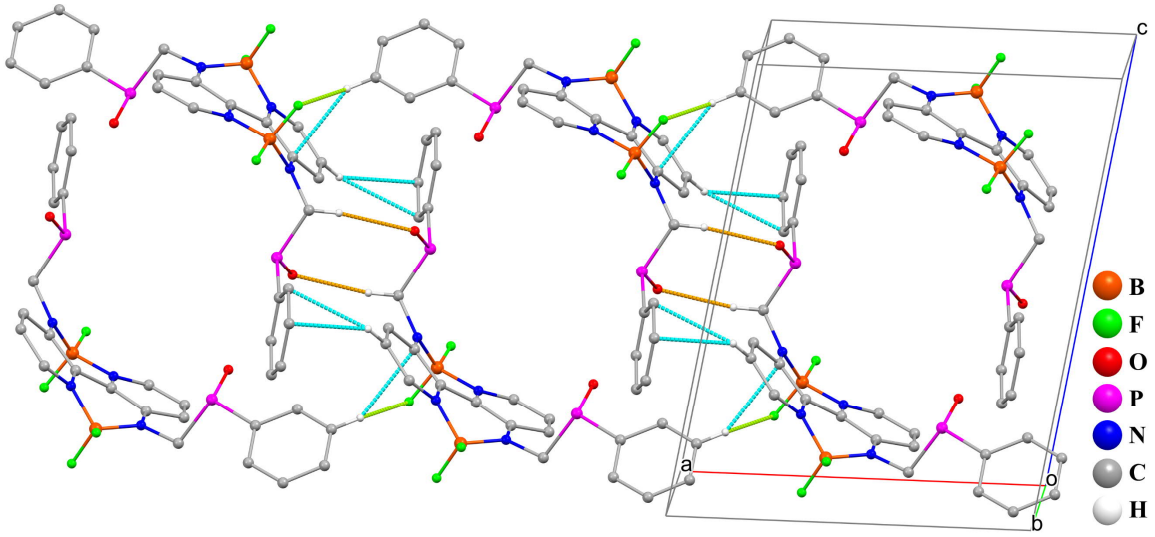

Fig. S12 Dash line represents various intermolecular interactions occur in **5**: *light green line*, F···H interactions: F4···H35 = 2.527 Å; *orange lines*, O···H interactions: O1···H11A = 2.570 Å; *light blue line*, C–H···π interactions: H35···C2 = 2.774 Å, C35–H35···C2 = 144º, H4··· centroid(C13–C14) = 2.737 Å, C4–H4···centroid(C13–C14) = 153º.

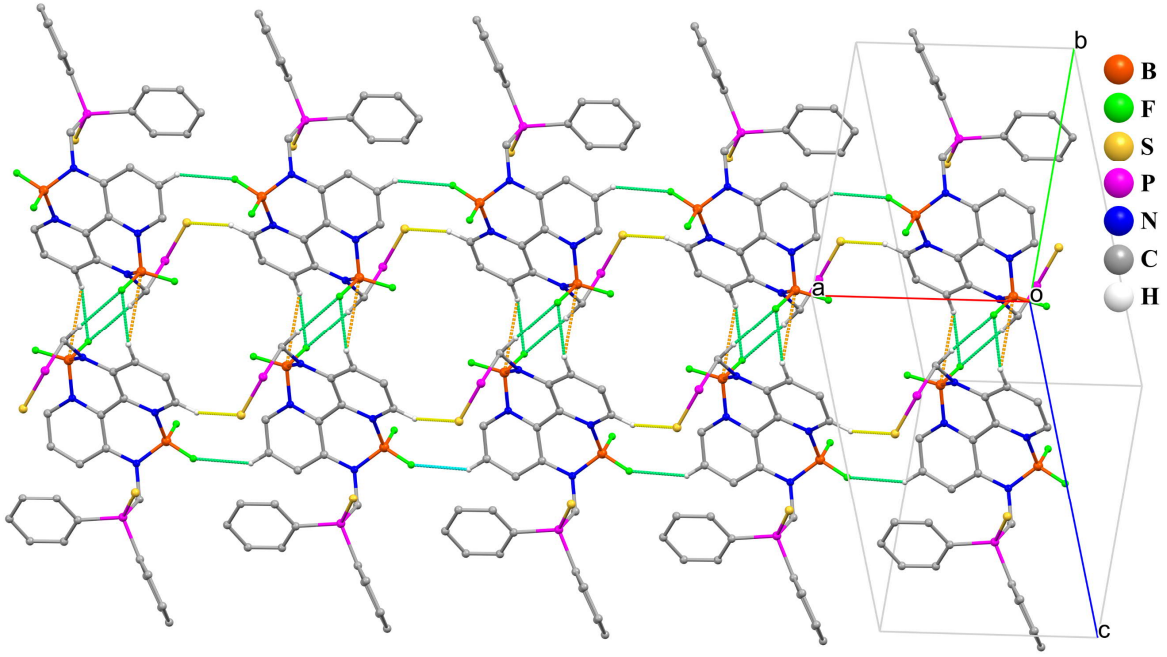

Fig. S13 Dash line represents various intermolecular interactions occur in **6**: *yellow line*, S···H interactions: S2···H10 = 2.834 Å; *light green line*, F···H interactions: F2···H8 = 2.405 Å, F2···H24B = 2.548 Å, F3···H4 = 2.516 Å; *orange lines*, B···H interactions: B1···H8 = 2.971 Å.

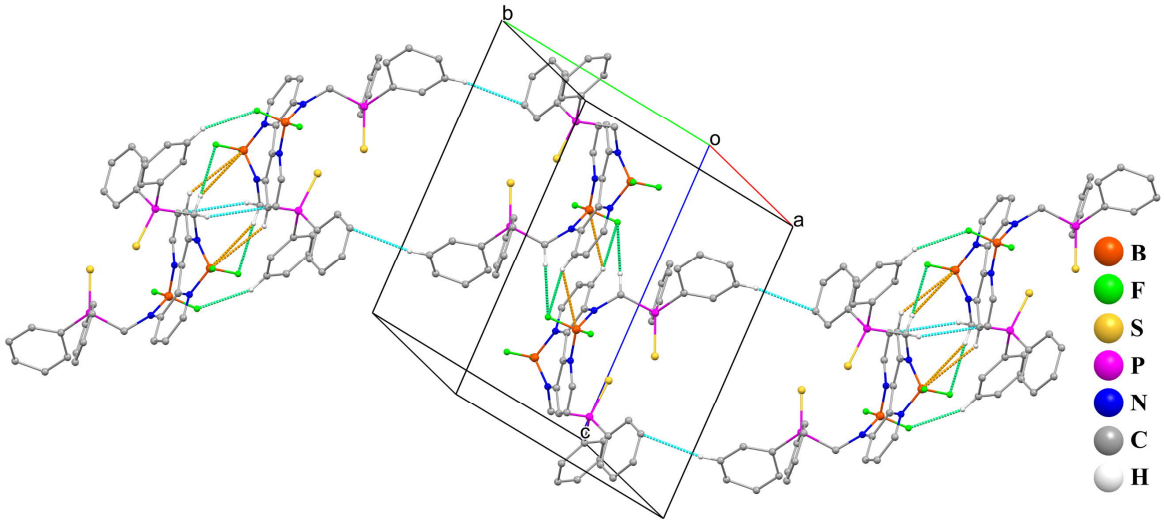

Fig. S14 Dash line represents various intermolecular interactions occur in **6**: *green line*, F···H interactions: F2···H8 = 2.405 Å, F2···H24B = 2.548 Å, F2···H14 = 2.588 Å, F4···H11B = 2.499 Å; *orange lines*, B···H interactions: B1···H8 = 2.971 Å, B2···H3 = 3.171 Å, B2···H11B = 3.104 Å; *light blue line*, C–H···π interactions: H11A···C3 = 2.778 Å, C11–H11A···C3 = 124°, H33···C22 = 2.885 Å, C33–H33··· C22 = 164°.

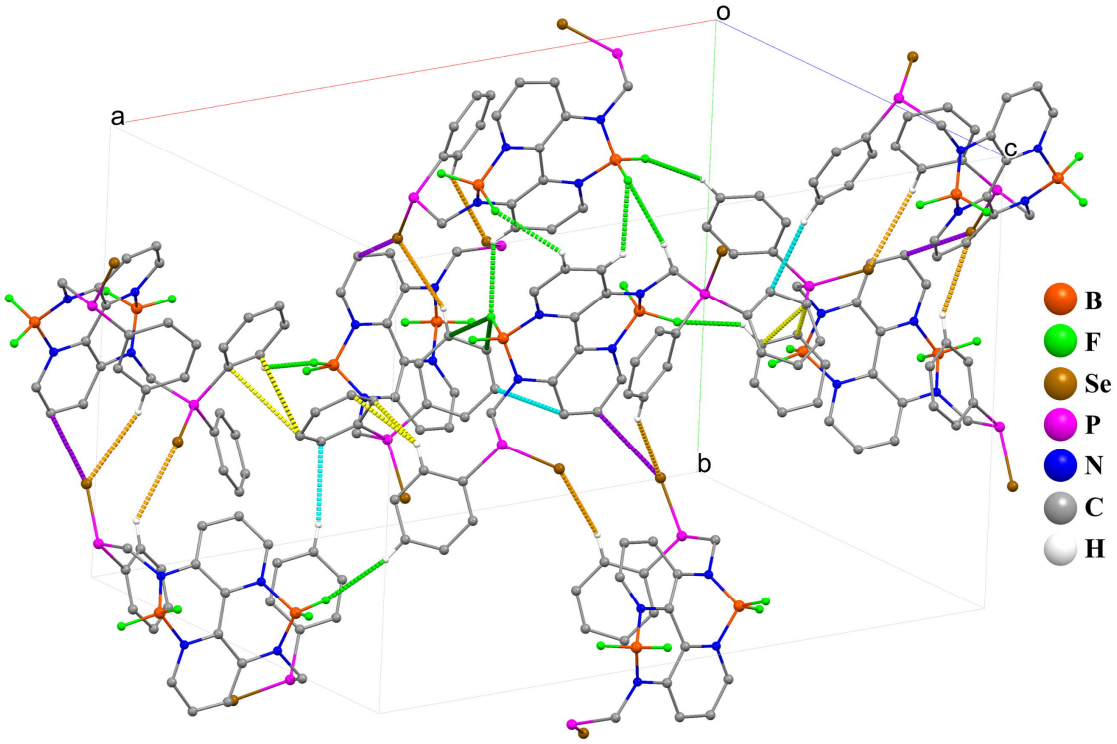

Fig. S15 Dash line represents various intermolecular interactions occur in **7**: *orange line*, Se···H interactions: Se1···H66 = 3.050 Å, Se4···H35 = 3.047 Å; pink lines, Se···C_{arene} interactions: Se4···C4 = 3.472 Å; *light green line*, F···H interactions: distances = 2.451 to 2.668 Å; *dark green line*, F···C_{arene} interactions: F4···centroid(C34–C35) = 3.035 Å; *light blue line*, C–H···π interactions: H52···C30 = 2.858 Å, C52–H52···C30 = 168°, H19···centroid(C26–C27) = 2.733

Å, C19–H19···centroid(C26–C27) = 140°; *yellow line*, π-π interaction: C29···centroid(C12-C17) = 3.278 Å.

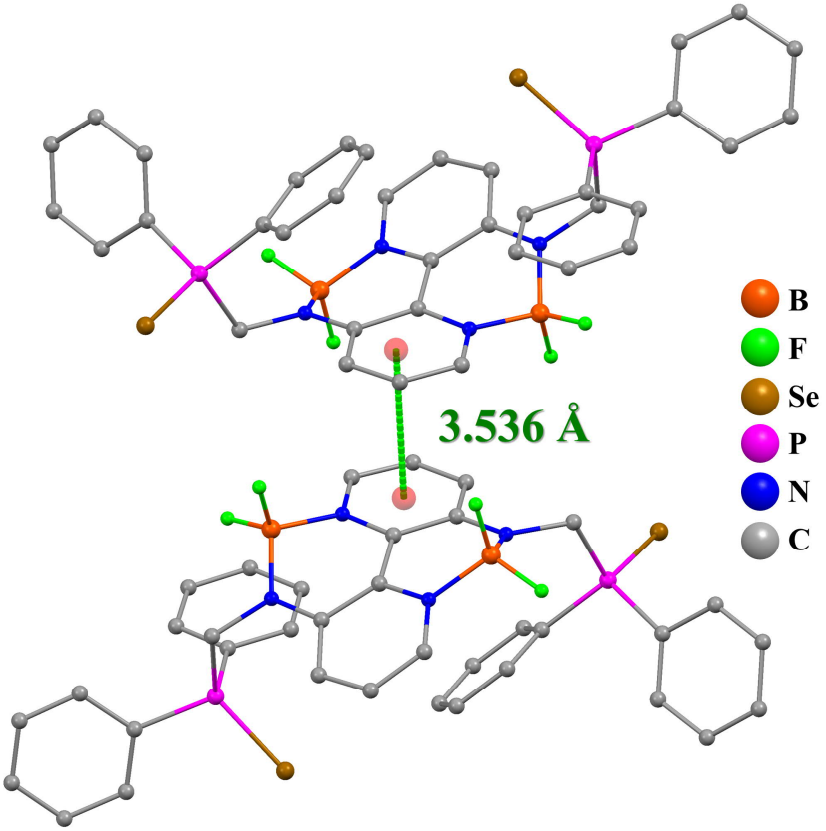

Fig. S16 Sandwich type pi-stacking or π–π stacking occurs in crystal packing of compound **7**.

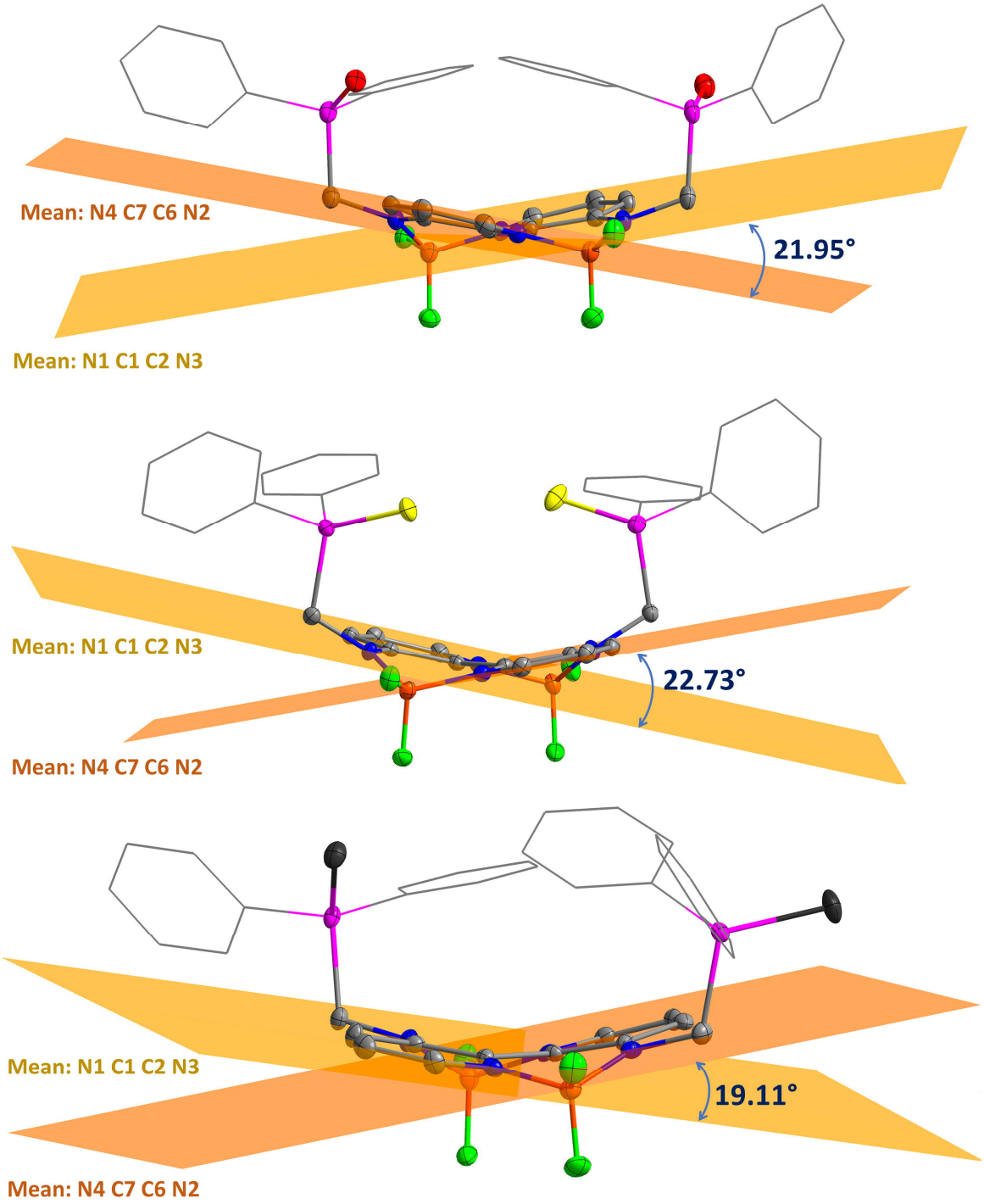

Fig. S17 Dihedral angled of **5** (top), **6** (middle) and **7** (bottom).

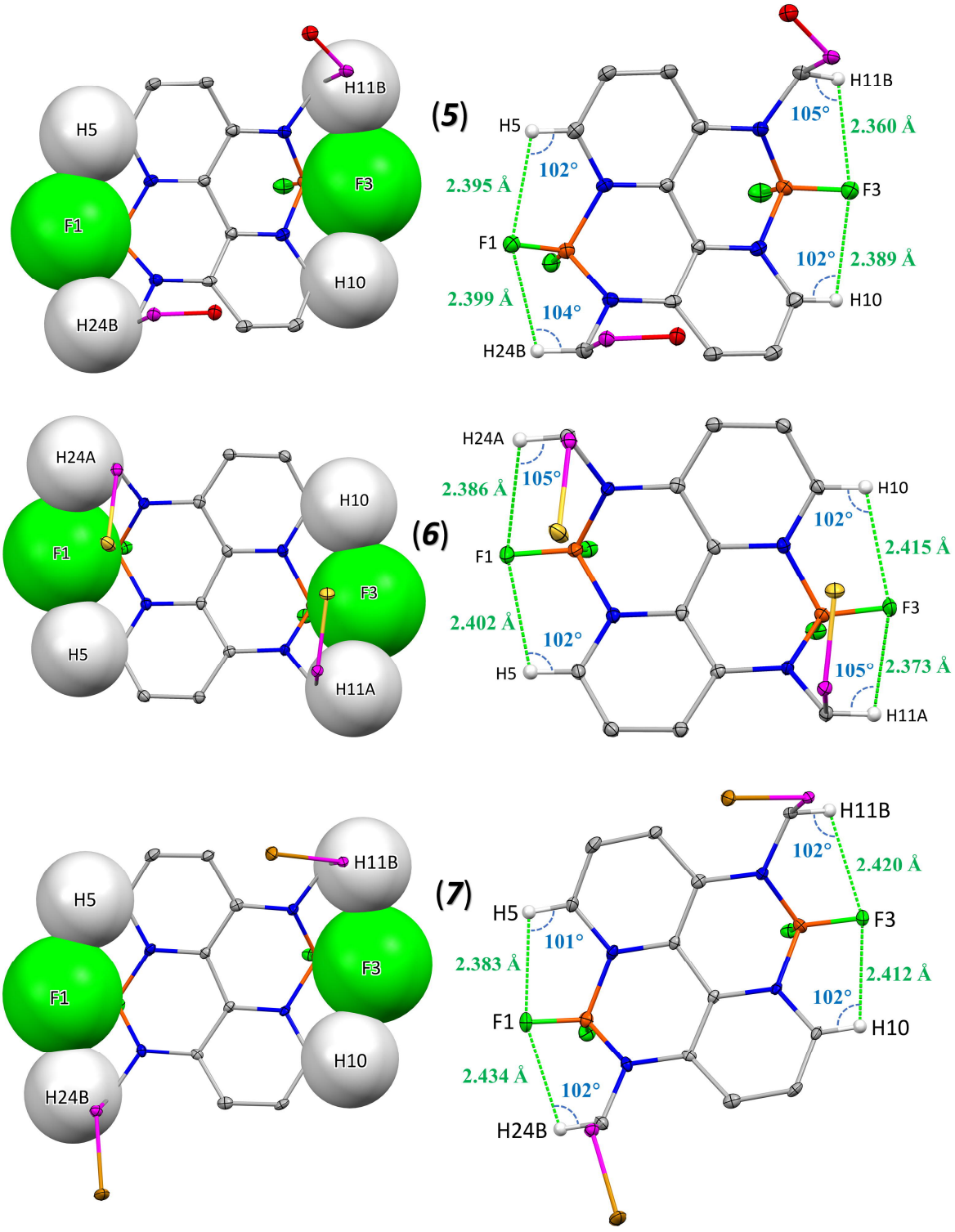

Fig. S18 Intramolecular F···H–C interaction of **5** (top), **6** (middle) and **7** (bottom); left-side images showing space filling models and right-side images showing thermal ellipsoid models of respective compounds.

Table S4 Bond distances (Å) and bond angles (°) of intramolecular F···H–C interaction of compounds **5-7**.

	5		**6**		**6·CH_2Cl_2**		**7**	
	F···H	angle	F···H	angle	F···H	angle	F···H	angle
F1···H5	2.395	102	2.402	102	2.424	101	2.383	101
F1···H24	2.399	104	2.386	105	2.384	103	2.434	102
F3···H10	2.389	102	2.415	102	2.420	102	2.412	102
F3···H11	2.360	105	2.373	105	2.460	100	2.420	102

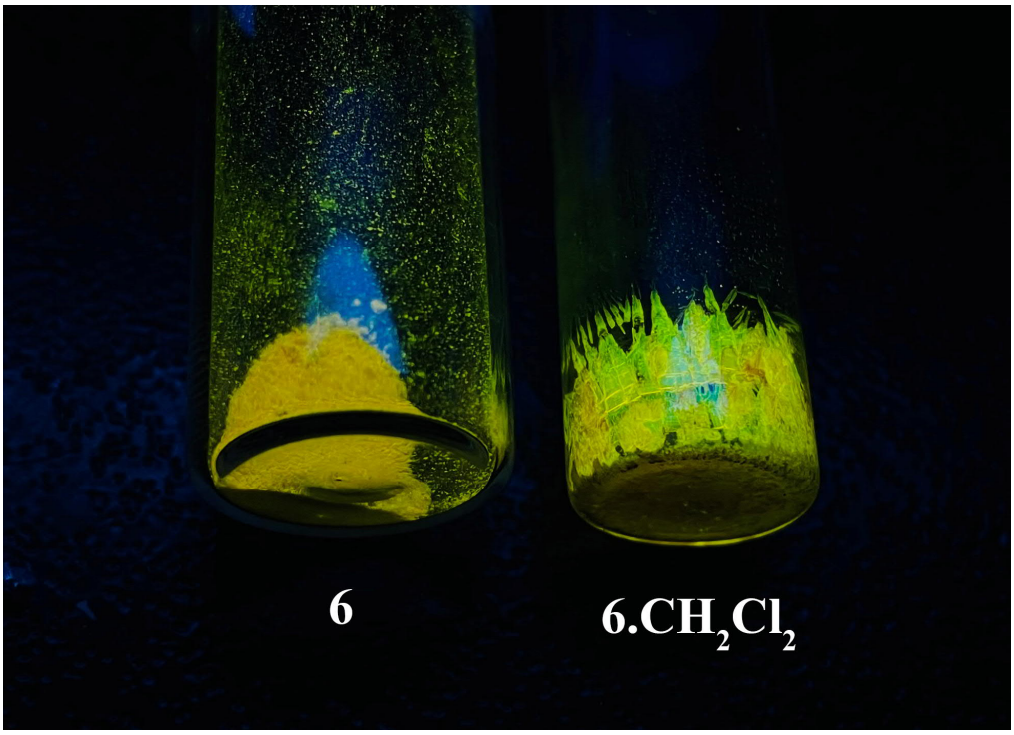

Fig. S19 Images of solid compounds **6** and **6·CH_2Cl_2** under UV light (at 365 nm).

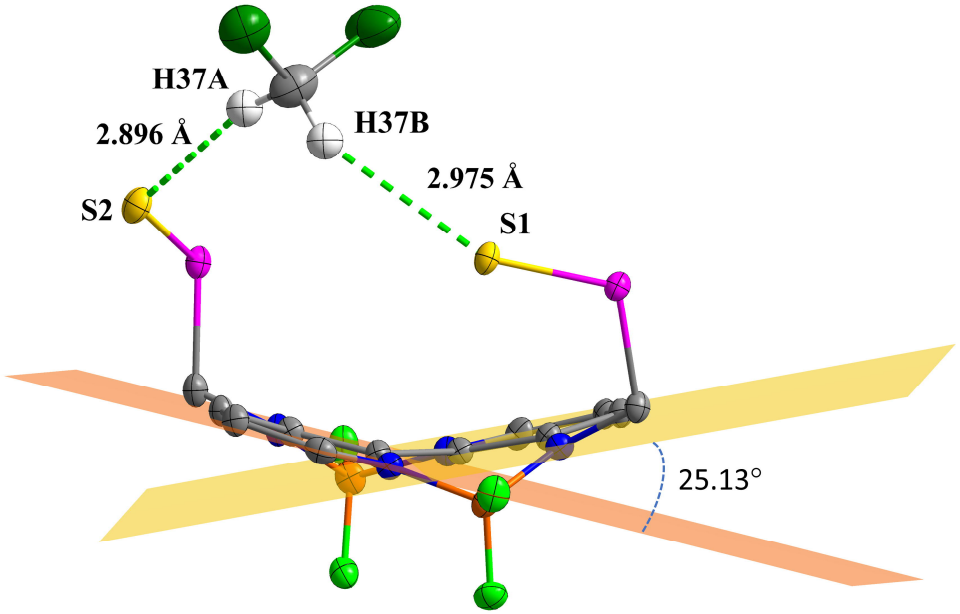

Fig. S20 Dihedral angled and S···H–C interactions of compound **6·CH₂Cl₂**.

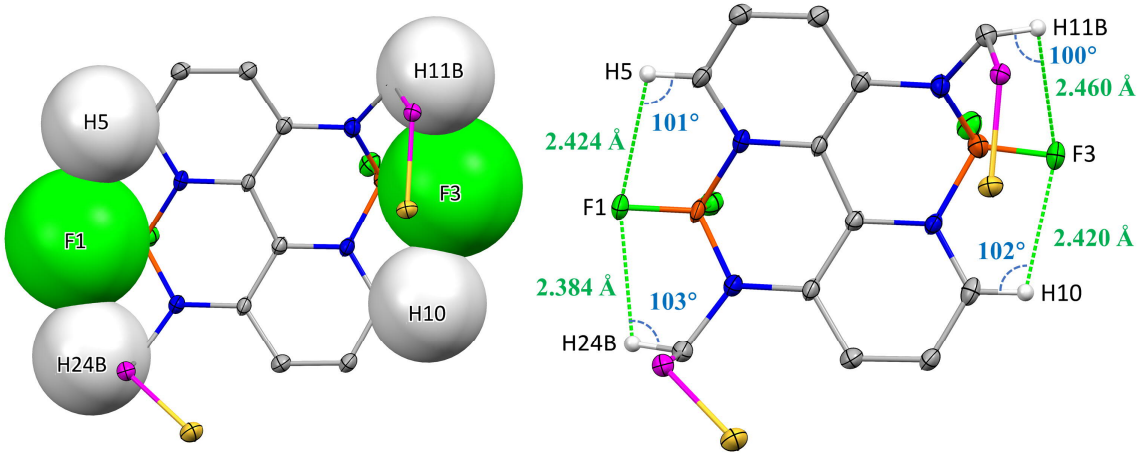

Fig. S21 Intramolecular F···H–C interaction of compound **6·CH₂Cl₂**.

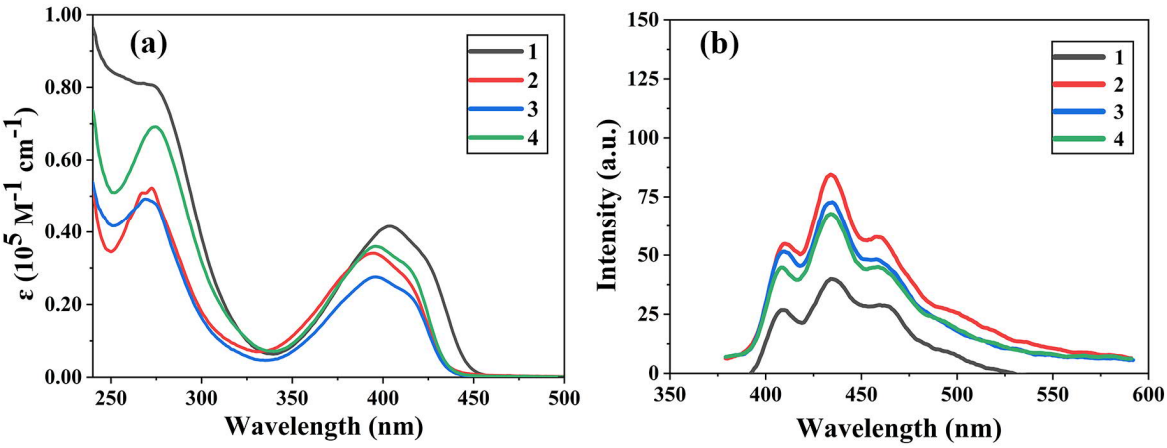

Fig. S22 (a) UV−vis absorption and (b) emission spectra of **1-4** recorded in chloroform (1 x 10^{-5} M) at room temperature.

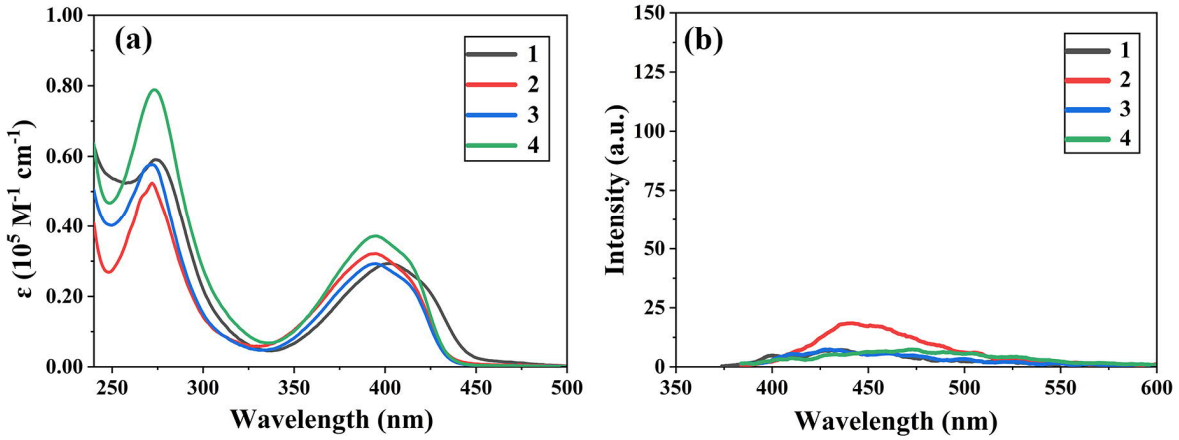

Fig. S23 (a) UV−vis absorption and (b) emission spectra of **1-4** recorded in acetonitrile (1 x 10^{-5} M) at room temperature.

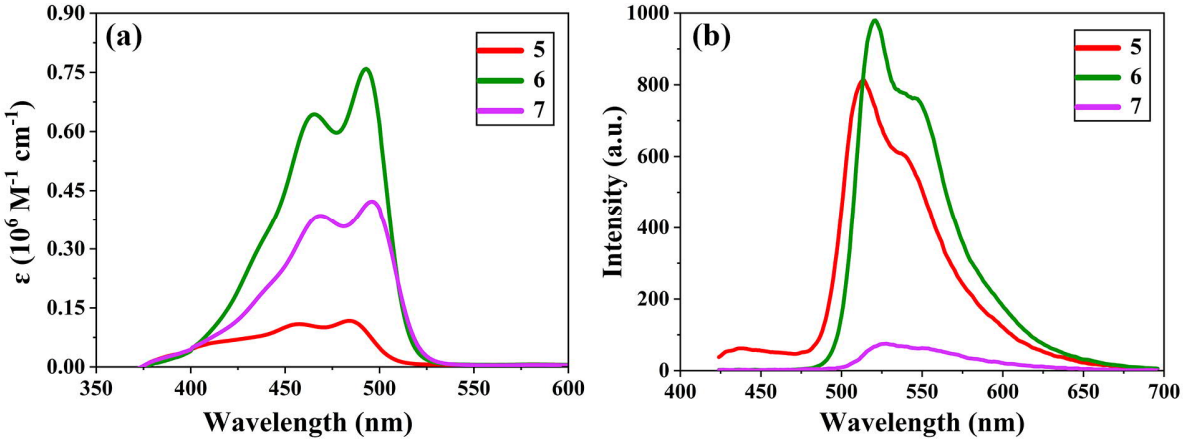

Fig. S24 (a) UV−vis absorption and (b) emission spectra of **5-7** recorded in chloroform (1 x 10^{-6} M) at room temperature.

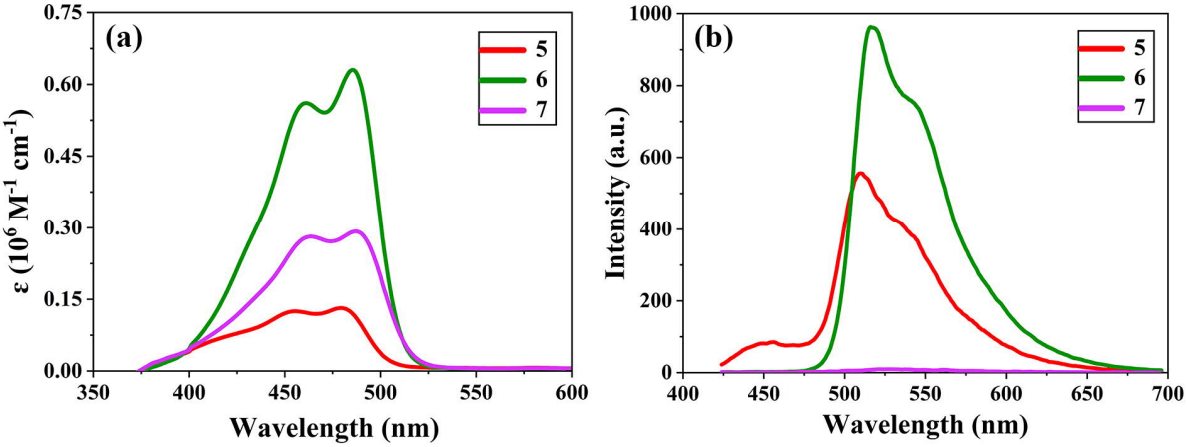

Fig. S25 (a) UV−vis absorption and (b) emission spectra of **5-7** recorded in acetonitrile (1 x 10^{-6} M) at room temperature.

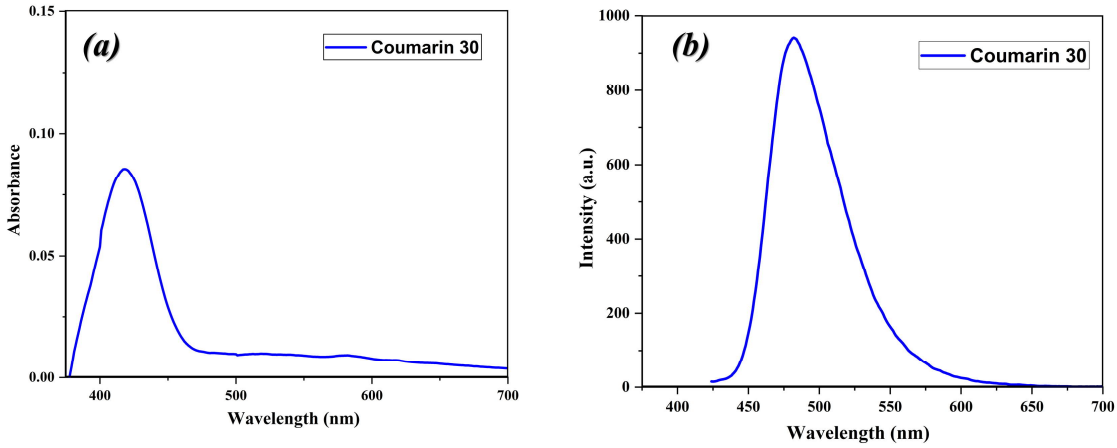

Fig. S26 UV-vis absorption (a) and fluorescence (b) spectra of Coumarin 30 in 90% ethanol at room temperature.

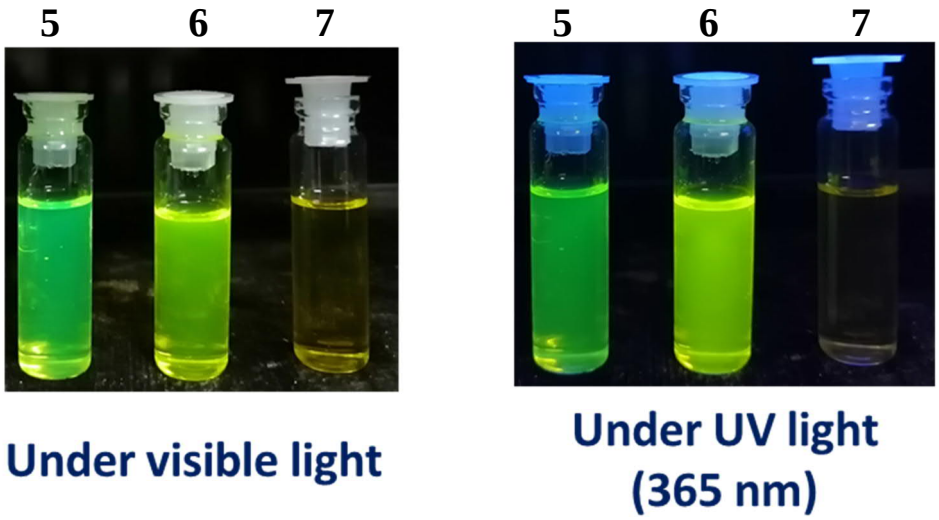

Fig. S27 Images of compounds **5-7** in CH_2Cl_2 taken under visible light (left) and UV light at 365 nm (right).

Molecular orbitals and TD-DFT calculations

All DFT calculations were performed with the Gaussian09 (Rev. D.01) suite of programs.[5] The input files were generated from GaussView 6.0 program.[6] Ground state geometries were optimized using the hybrid density functional B3LYP with split valence polarised (SVP) basis set. Frequency calculations were performed subsequently to confirm the presence of local minima (only positive frequencies). Vertical excitations (40 singlet excited states) were calculated by TD-DFT method at the B3LYP/TZVP level.[7, 8] Solvent (Chloroform) effects were incorporated using polarizable continuum model (PCM) during both optimization and TD-DFT calculations. Molecular orbitals were visualised using Chemcraft software with countor value: 0.030.

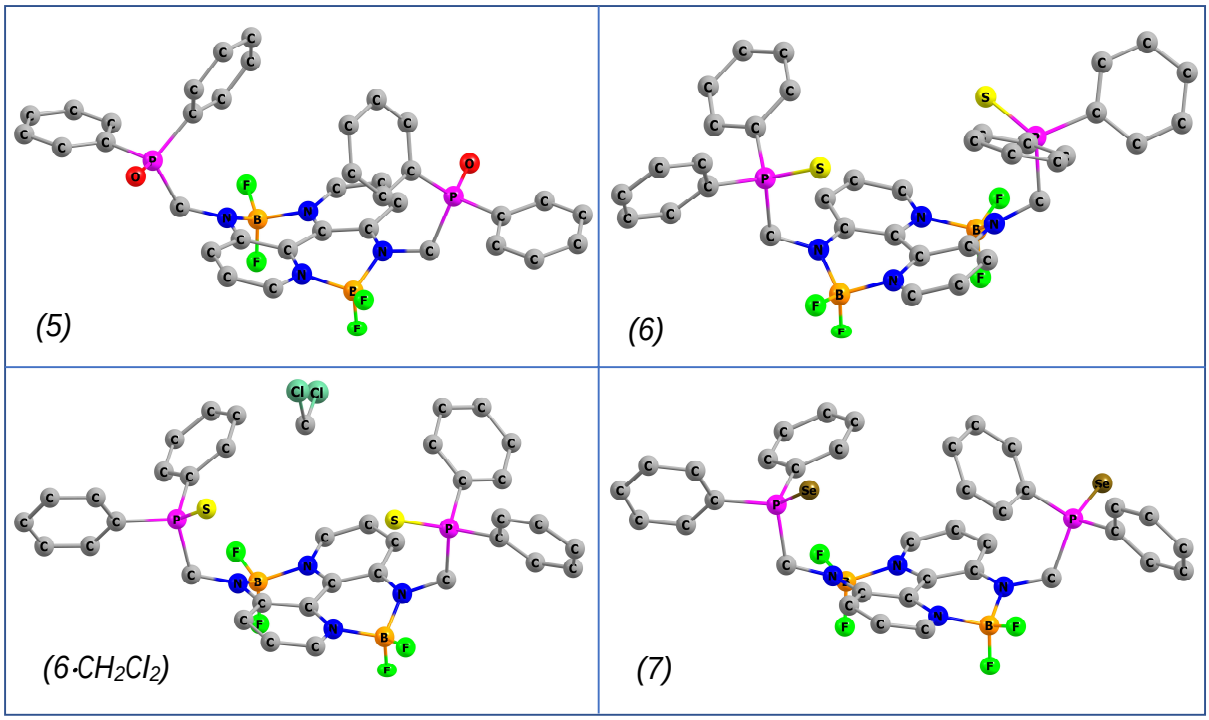

Fig. S28 Optimized structures of compounds **5-7** (Gaussian 09; B3LYP/TZVP).

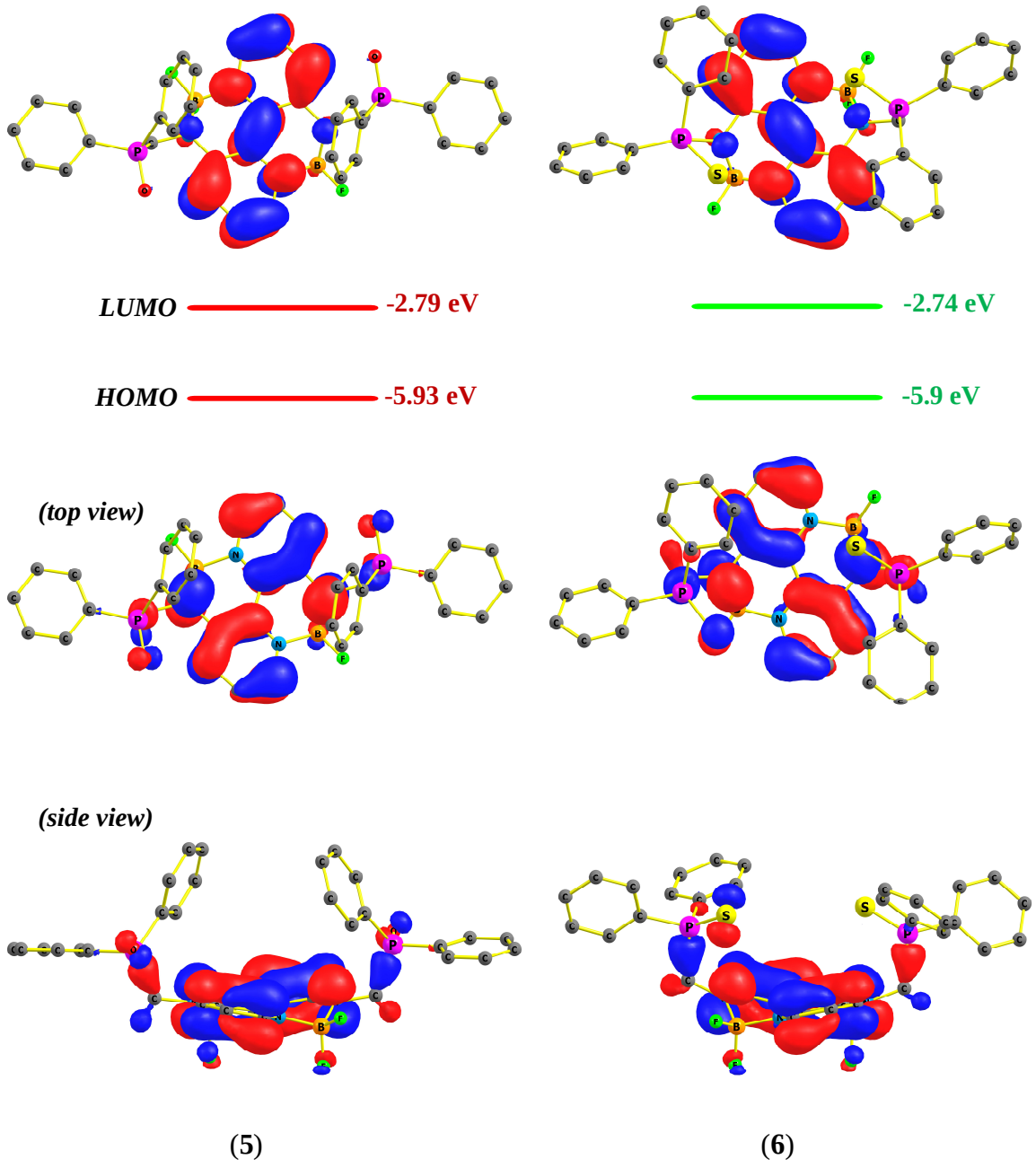

Fig. S29 Pictographic drawings of LUMO/HOMO and energy levels of **5** and **6** (Gaussian 09; B3LYP/TZVP).

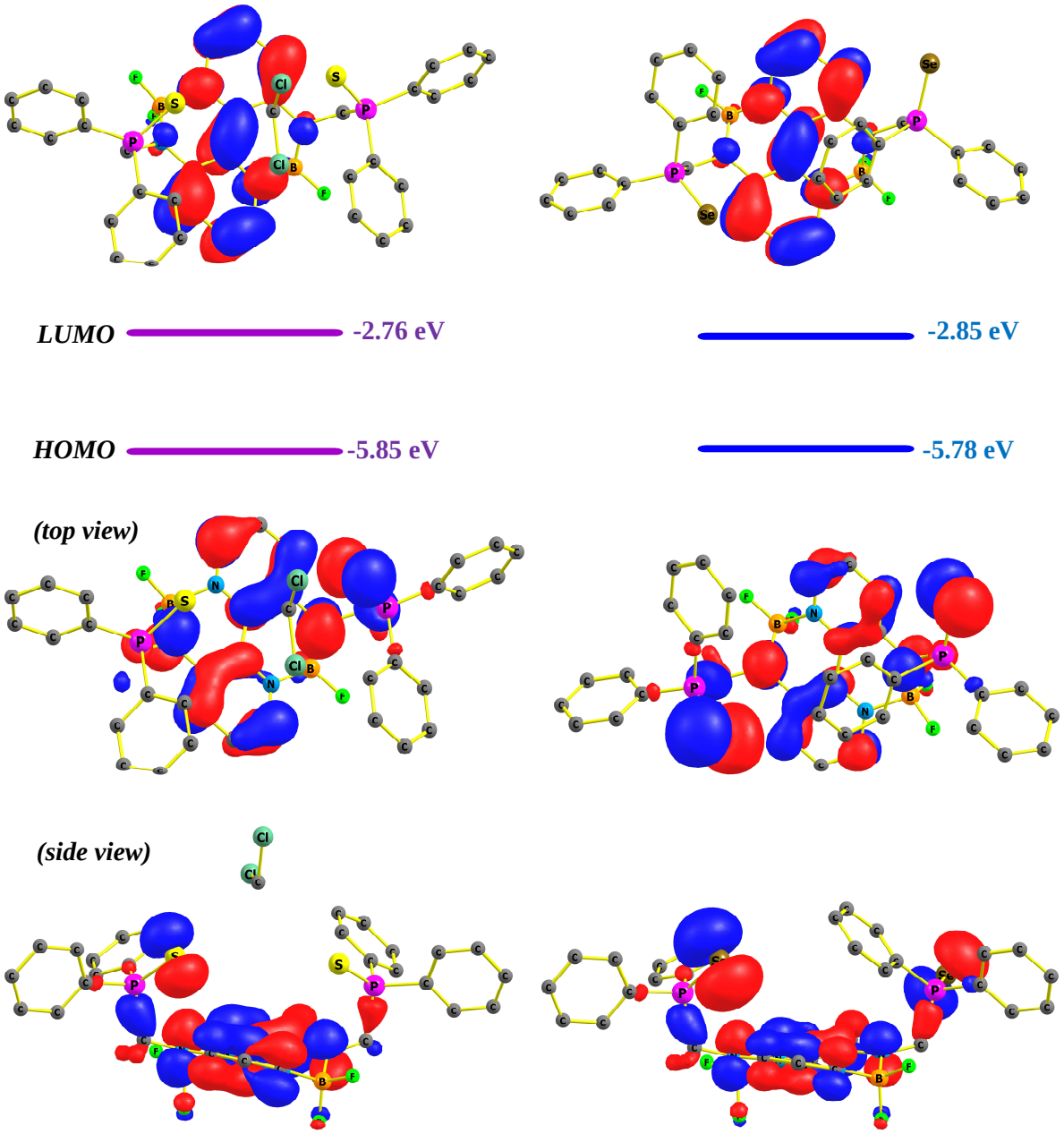

Fig. S30 Pictographic drawings of LUMO/HOMO and energy levels of **6·CH$_2$Cl$_2$** and **7** (Gaussian 09; B3LYP/TZVP).

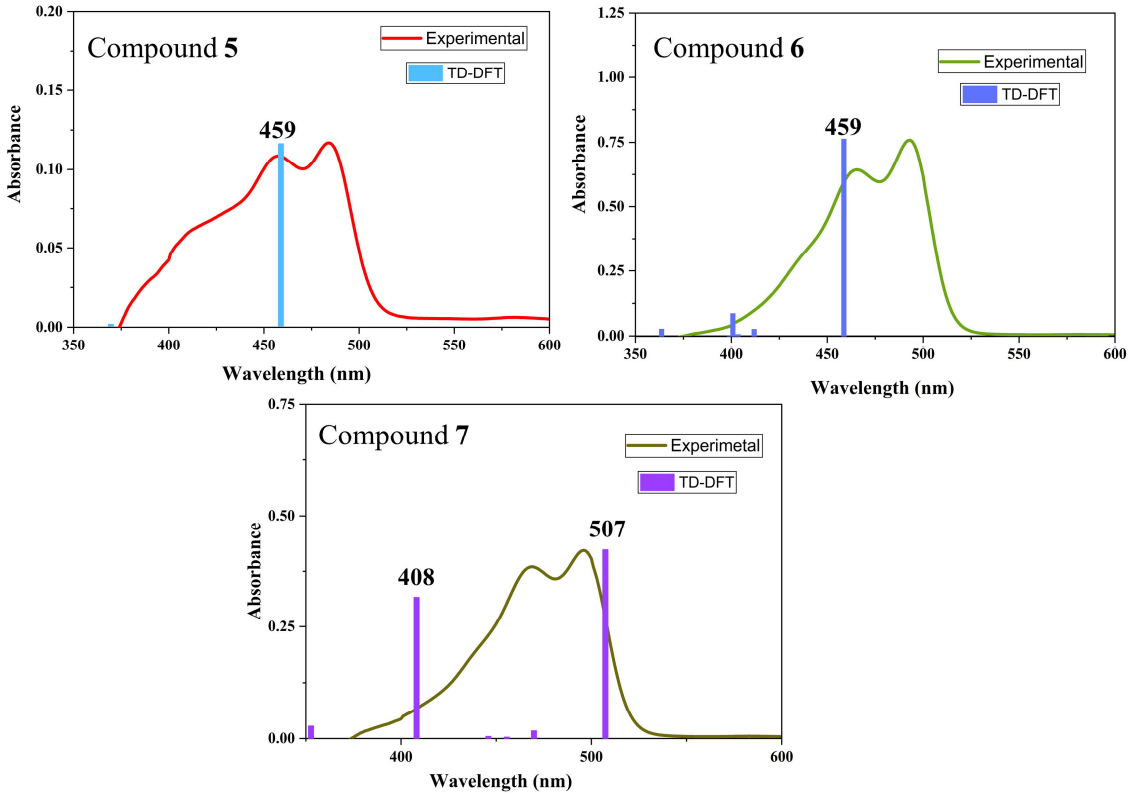

Fig. S31 Calculated absorption spectrum of **5-7** based on the TDDFT method at the B3LYP/TZVP level (aqua bars) overlaid on the UV/Vis absorption spectrum of **5-7** in chloroform.

Table S5 TD-DFT data for compounds **5-7** (Gaussian 09; B3LYP/TZVP).

Comp	Transition	E_{ex} (eV)	λ (nm)	Oscillator strength *f*	Assignment
5	$S_0 \rightarrow S_1$	2.7015	458.9	0.3195	H → L (0.70)
6	$S_0 \rightarrow S_1$	2.7029	458.71	0.2911	H → L (0.70)
7	$S_0 \rightarrow S_1$	2.4437	507.37	0.1875	H → L (0.70)
	$S_0 \rightarrow S_5$	3.0375	408.18	0.1401	H-4 → L (0.70)

Table S6 Selected bond length and bond angles of **5-7** obtained from X-ray diffraction analysis and DFT calculation (B3LYP/TZVP).

Selected bond distances (Å)								
	5 (E = O)		**6** (E = S)		**6·CH_2Cl_2** (E= S)		**7**(E = Se)	
	X-ray	***DFT***	***X-ray***	***DFT***	***X-ray***	***DFT***	***X-ray***	***DFT***
P1–E1	1.491(2)	1.517	1.9418(10)	1.977	1.949(3)	1.978	2.1097(19)	2.145
P2–E2	1.4939(19)	1.517	1.9453(10)	1.977	1.958(3)	1.984	2.101(2)	2.148
B1–F1	1.373(4)	1.393	1.375(3)	1.382	1.381(8)	1.369	1.381(9)	1.384
B1–F2	1.400(4)	1.394	1.403(3)	1.395	1.372(10)	1.382	1.398(9)	1.395
B2–F3	1.378(3)	1.393	1.378(3)	1.379	1.383(9)	1.384	1.377(9)	1.391
B2–F4	1.403(4)	1.394	1.402(3)	1.396	1.388(10)	1.395	1.395(10)	1.393
C1–C6	1.447(4)	1.450	1.450(3)	1.452	1.445(9)	1.451	1.458(9)	1.451
B1-$N1_{coord.}$	1.587(4)	1.597	1.582(4)	1.597	1.578(10)	1.595	1.566(10)	1.594
B1-$N4_{covalent}$	1.511(4)	1.527	1.510(4)	1.529	1.548(10)	1.529	1.517(10)	1.530
B2-$N2_{coord.}$	1.590(4)	1.597	1.581(4)	1.599	1.566(10)	1.595	1.582(10)	1.594
B2-$N3_{covalent}$	1.498(4)	1.527	1.505(3)	1.530	1.530(10)	1.529	1.513(10)	1.528
F1···H5	2.395	2.274	2.402	2.284	2.424	2.282	2.383	2.284
F1···H24	2.399	2.260	2.386	2.264	2.384	2.263	2.434	2.311
F3···H10	2.389	2.274	2.415	2.290	2.420	2.281	2.412	2.278
F3···H11	2.360	2.260	2.373	2.297	2.460	2.337	2.420	2.309
Selected bond angles (deg.)								
N1–B1–N4	106.0(2)	107.4	107.3(2)	106.1	106.1(6)	106.6	108.5(6)	107.6
N2–B2–N3	107.5(2)	107.4	107.7(2)	106.6	107.3(6)	106.9	107.1(6)	106.6
F1–B1–F2	110.1(2)	110.02	110.5(2)	110.9	111.7(6)	110.8	109.8(6)	110.7
F3–B2–F4	108.9(2)	110.02	109.5(2)	110.9	109.7(6)	110.6	109.6(6)	110.4
Δ	21.97	18.39	22.73	22.86	25.13	21.21	19.11	18.83

OLED fabrication and characterization:

The ITO coated glass substrates were sequentially cleaned with soap solution, deionized water, acetone, and isopropanol for 10 minutes each and treated with oxygen plasma for 10 minutes. The devices were fabricated by first spincoating the hole-injection layer from PEDOT:PSS solution following annealing at 150 °C for 30 minutes. A thin layer of TFB was deposited by spincoating 2 mg/ml TFB solution on it, annealing at 180°C for 30 minutes, and then cooling the film rapidly. Solutions of compounds **5** and 6 were prepared from chlorobenzene and spin coated on the TFB coated substrates inside a nitrogen gas-filled glove box following annealing at 80 °C for 30 minutes. After that Ca (20 nm)/ Ag (100 nm) were deposited on the active layer as electron-injector in an evaporation chamber at ~3×10^{-6} mbar without exposing the samples to air. Finally, the OLEDs were encapsulated inside the glove box. The J-V-L characteristics of the diodes were measured using Keithley 2400 source meter, 2000 multimeter and a calibrated Si photodetector (from RS components).

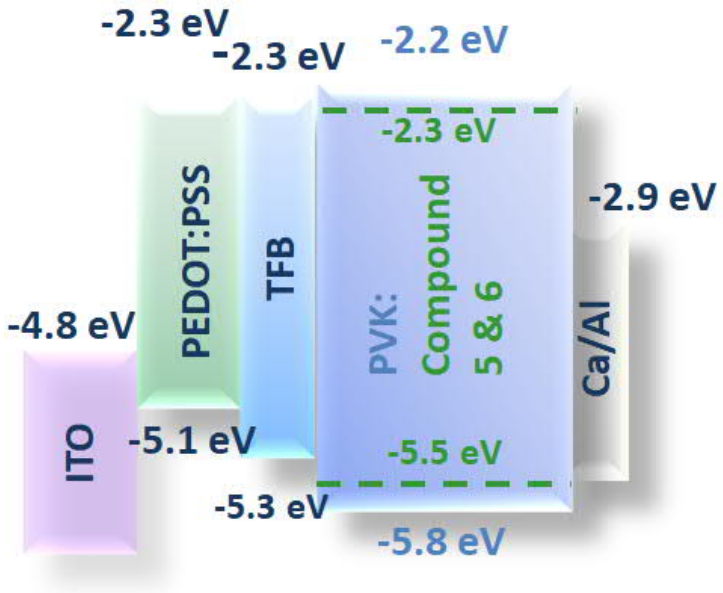

Fig. S32 Typical OLED structure with energy levels at zero-bias condition.

Spectral Data for Isolated Compounds (1-7)

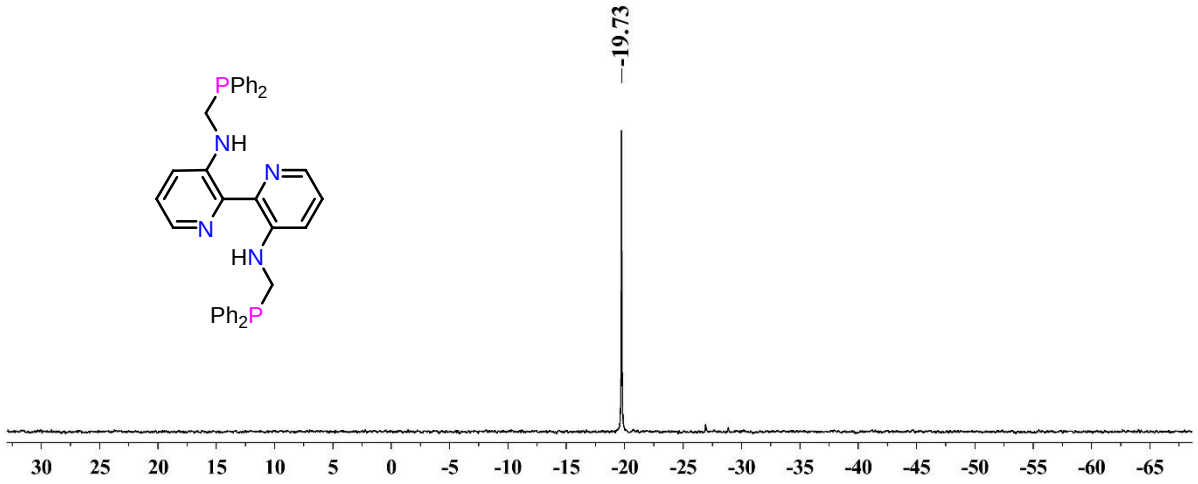

Fig. S33 $^{31}P\{^{1}H\}$ NMR spectrum of compound **1** in $CDCl_3$.

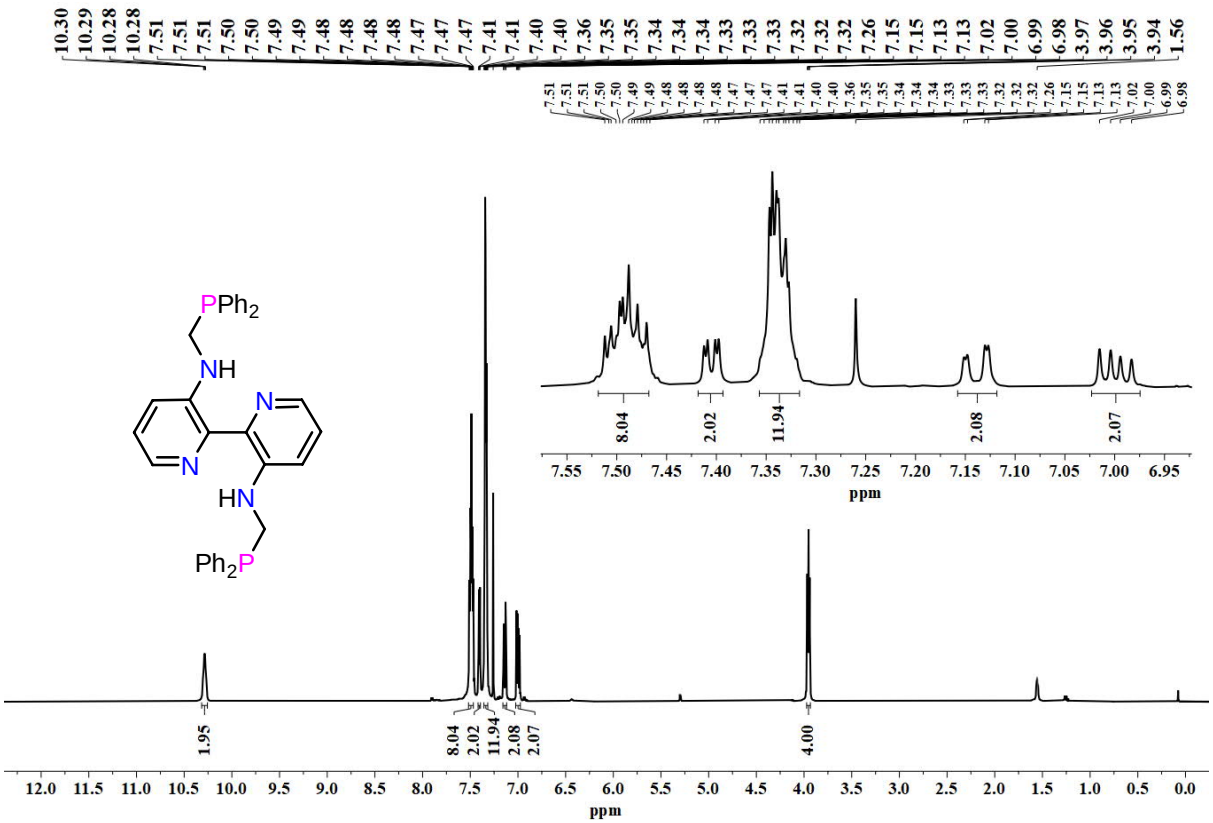

Fig. S34 ^{1}H NMR spectrum of compound **1** in $CDCl_3$.

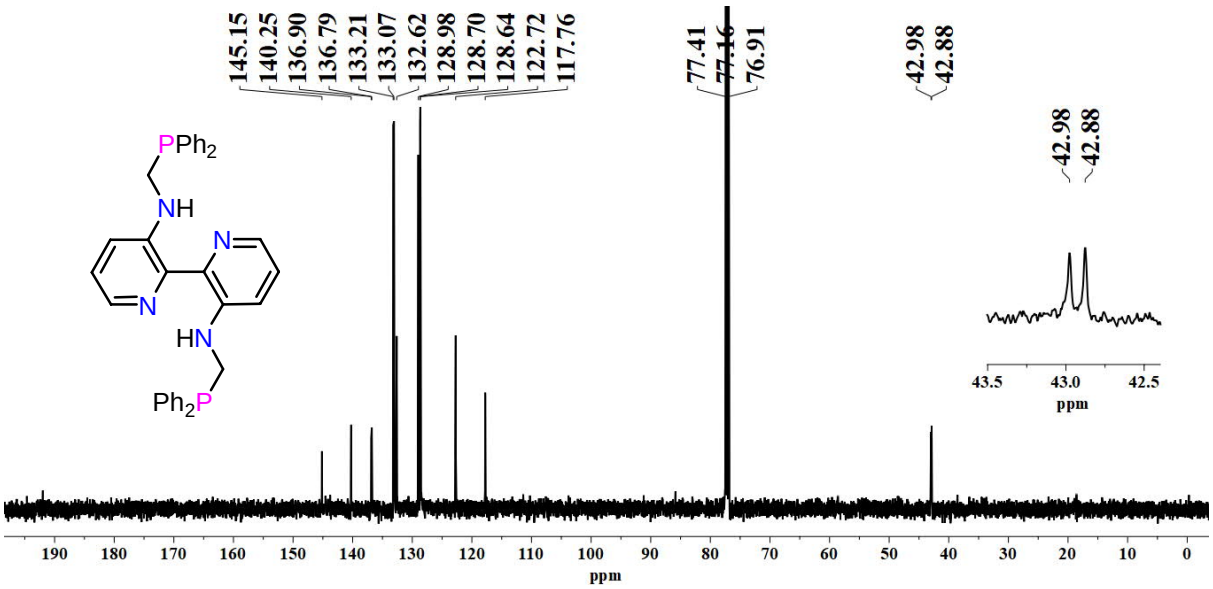

Fig. S35 $^{13}C\{^{1}H\}$ NMR spectrum of compound **1** in $CDCl_3$.

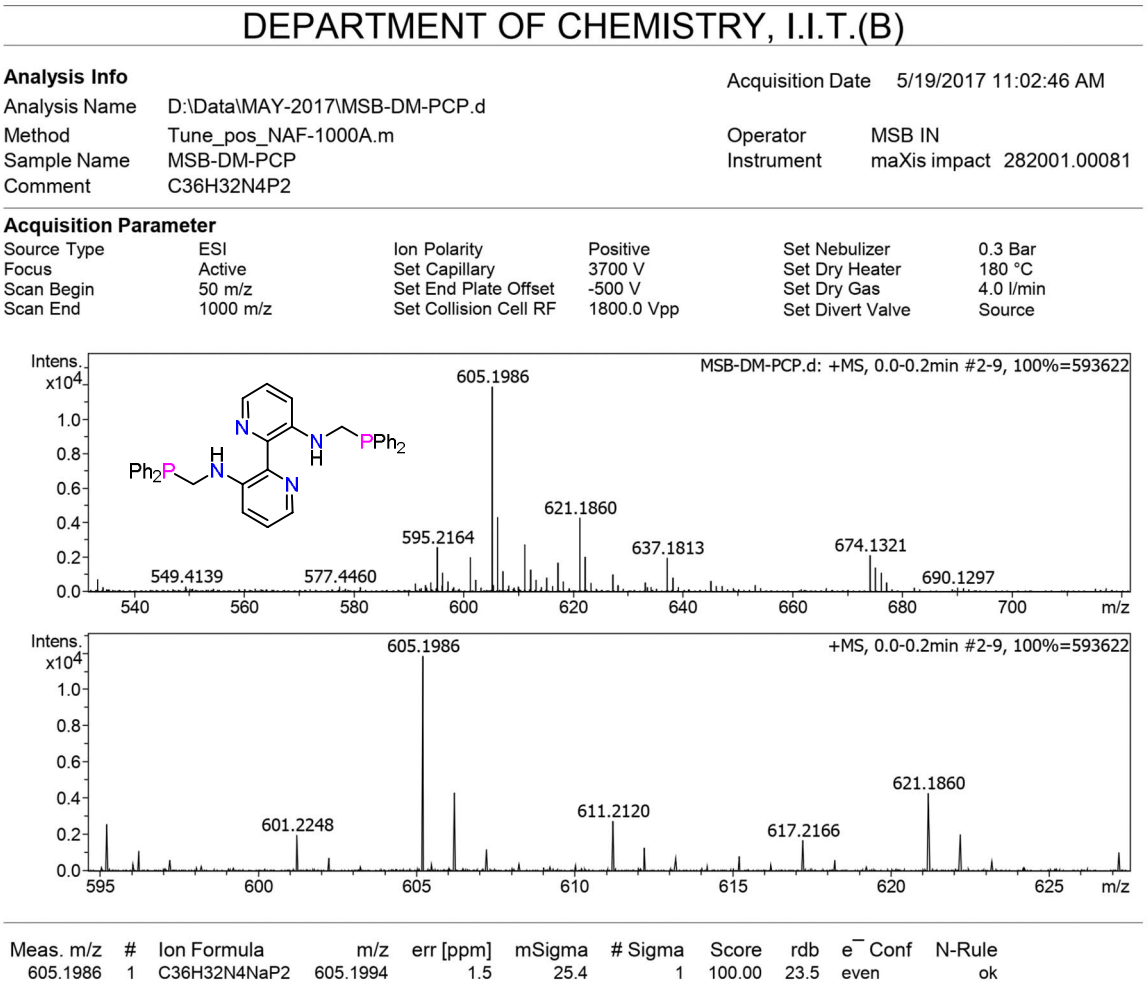

Fig. S36 Mass spectrum of compound **1**.

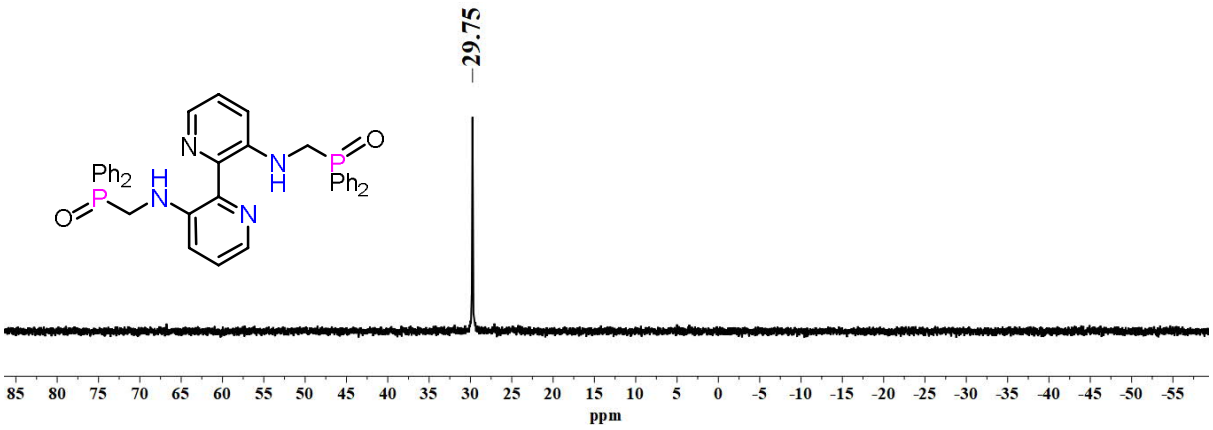

Fig. S37 $^{31}P\{^{1}H\}$ NMR spectrum of compound **2** in $CDCl_3$.

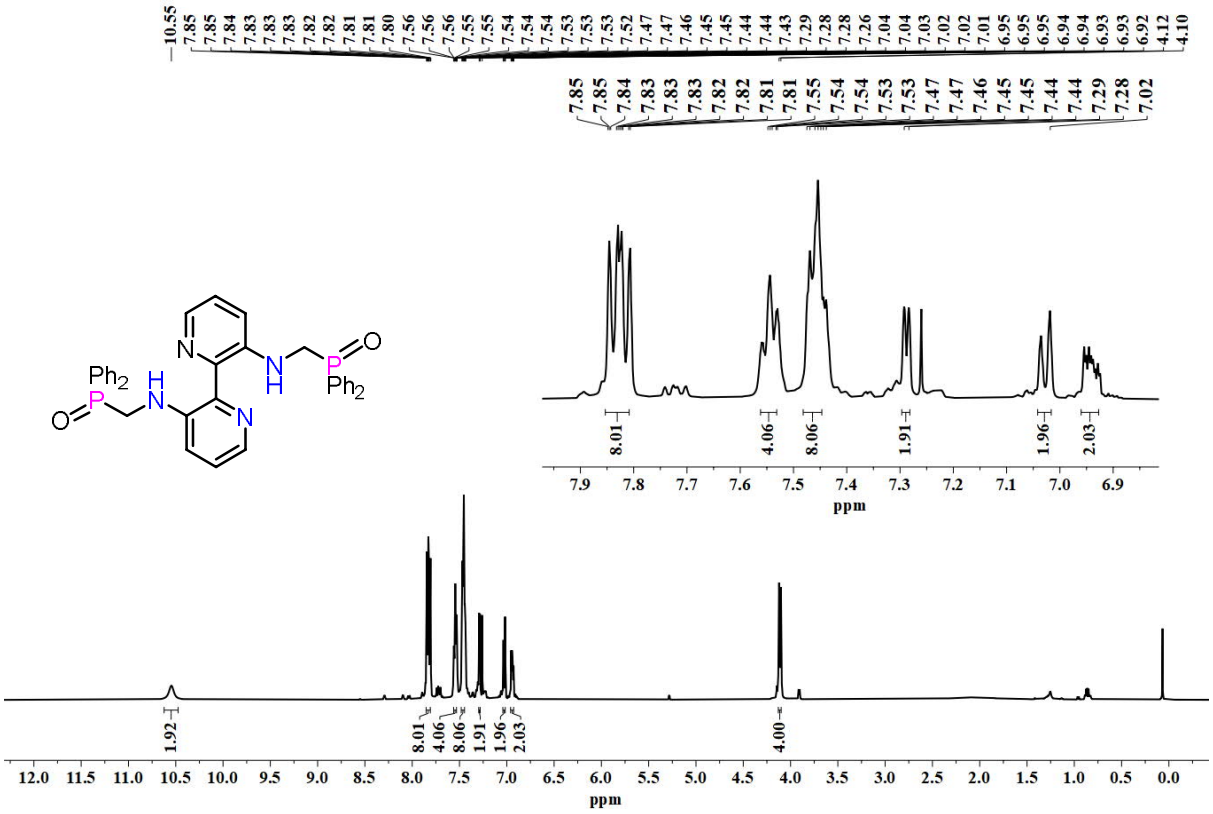

Fig. S38 ^{1}H NMR spectrum of compound **2** in $CDCl_3$.

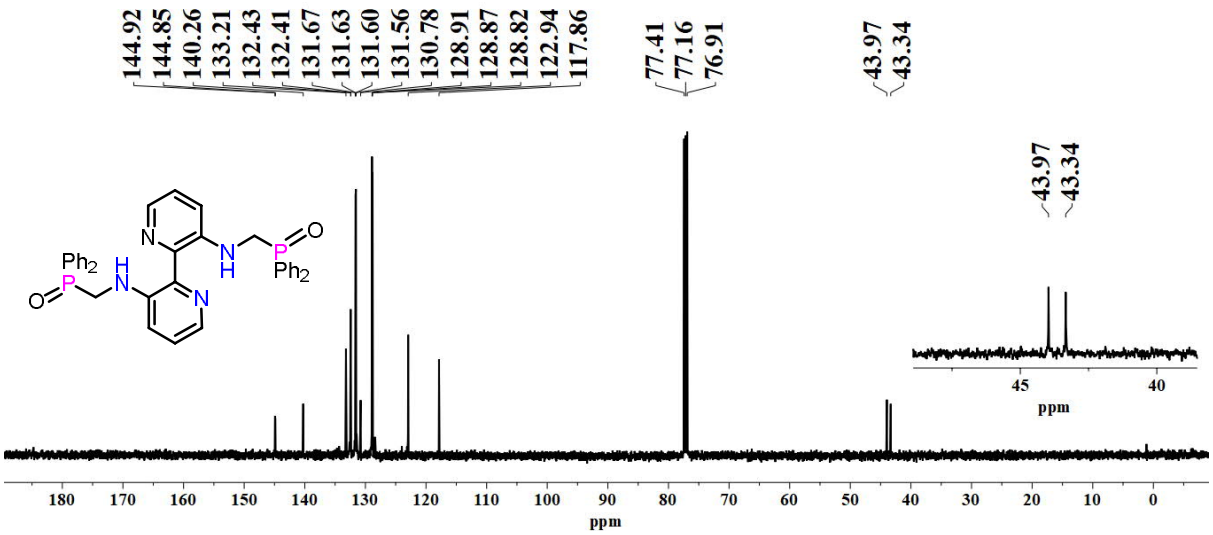

Fig. S39 $^{13}C\{^{1}H\}$ NMR spectrum of compound **2** in $CDCl_3$.

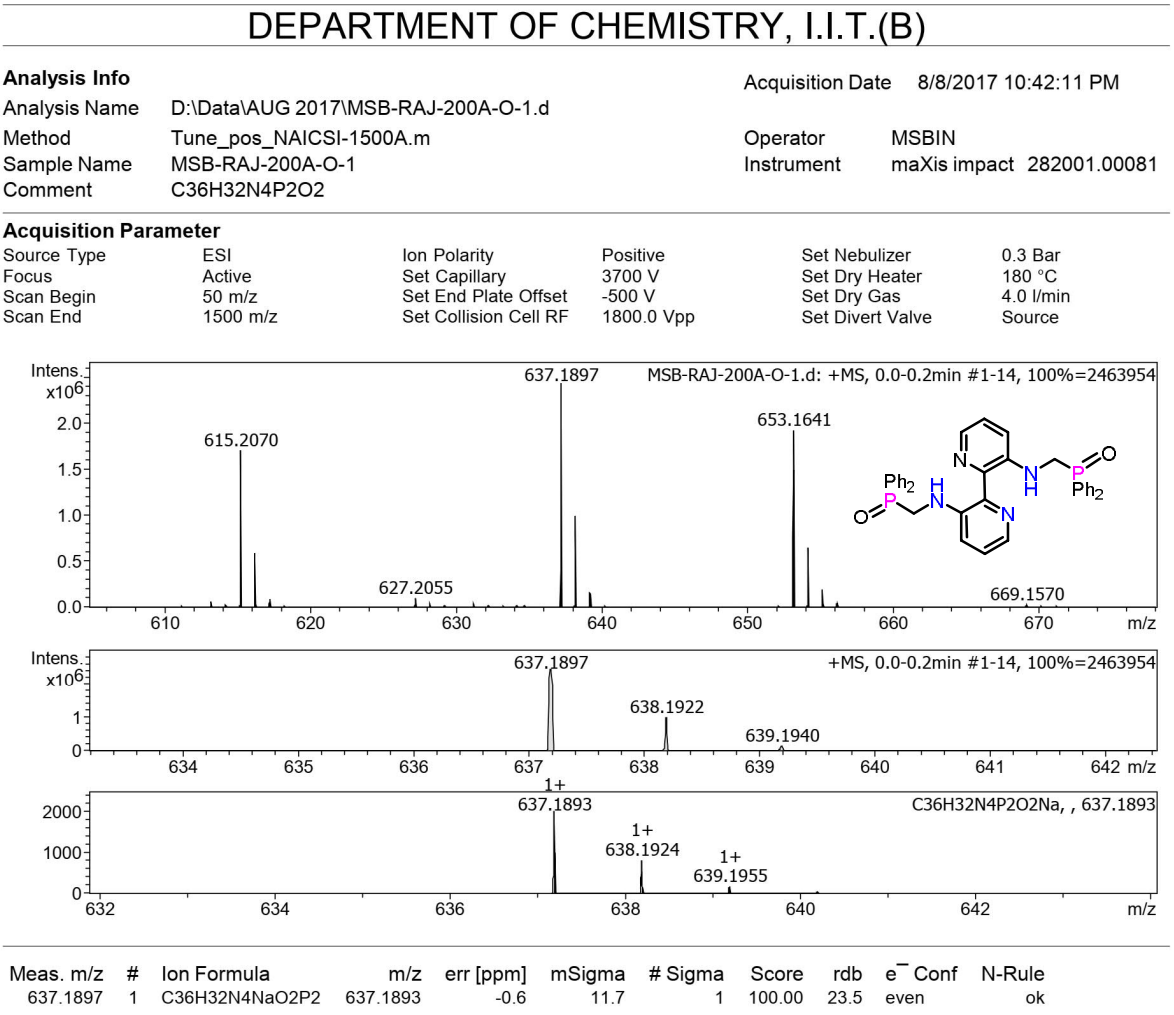

Fig. S40 Mass spectrum of compound **2**.

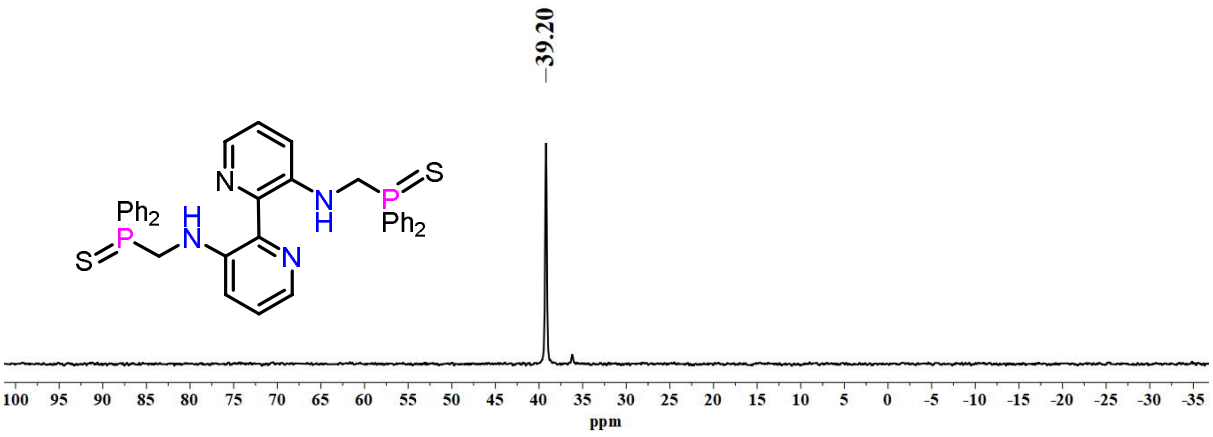

Fig. S41 $^{31}P\{^{1}H\}$ NMR spectrum of compound **3** in $CDCl_3$.

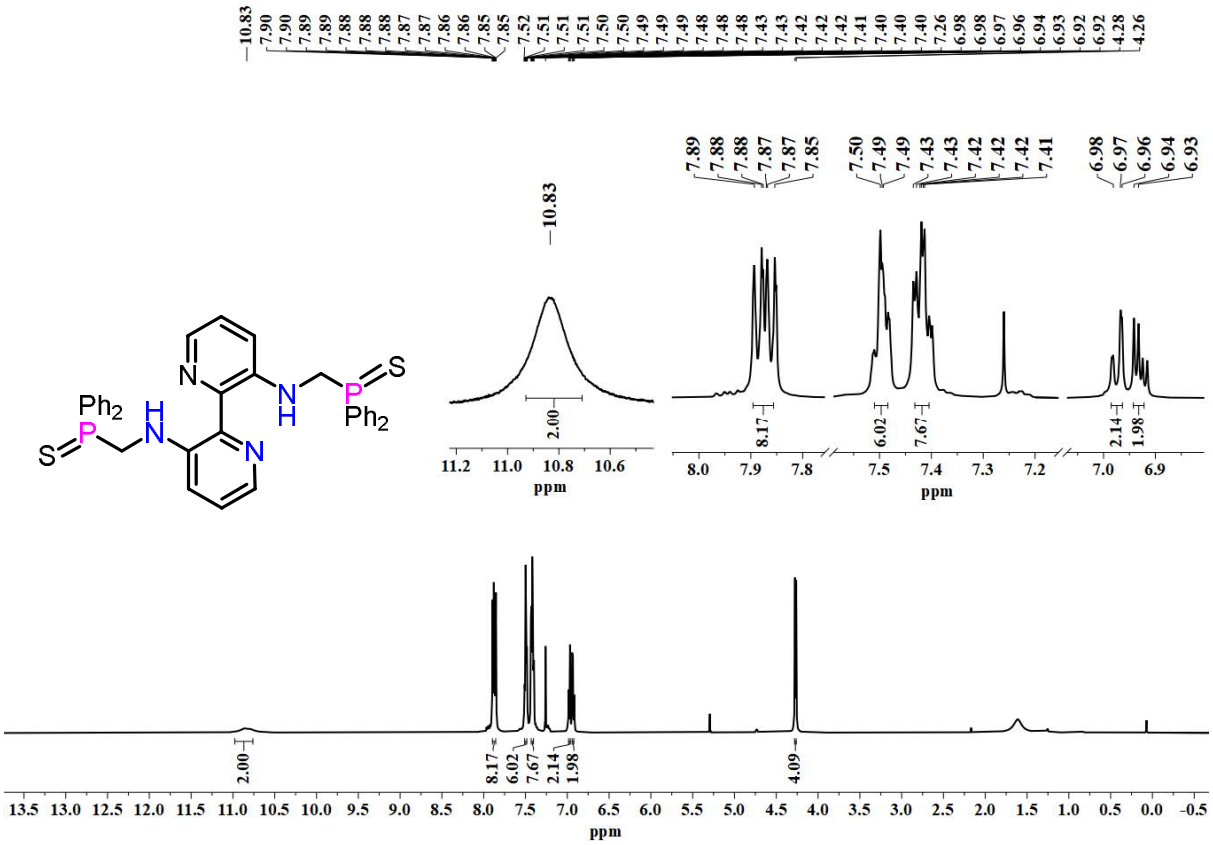

Fig. S42 ^{1}H NMR spectrum of compound **3** in $CDCl_3$.

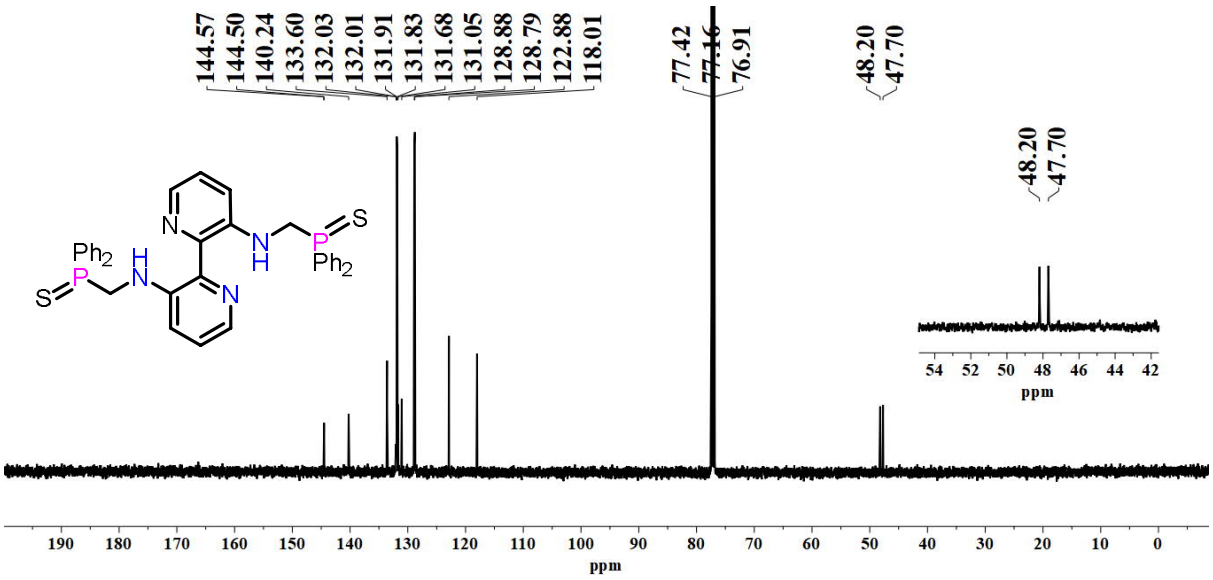

Fig. S43 $^{13}C\{^{1}H\}$ NMR spectrum of compound **3** in $CDCl_3$.

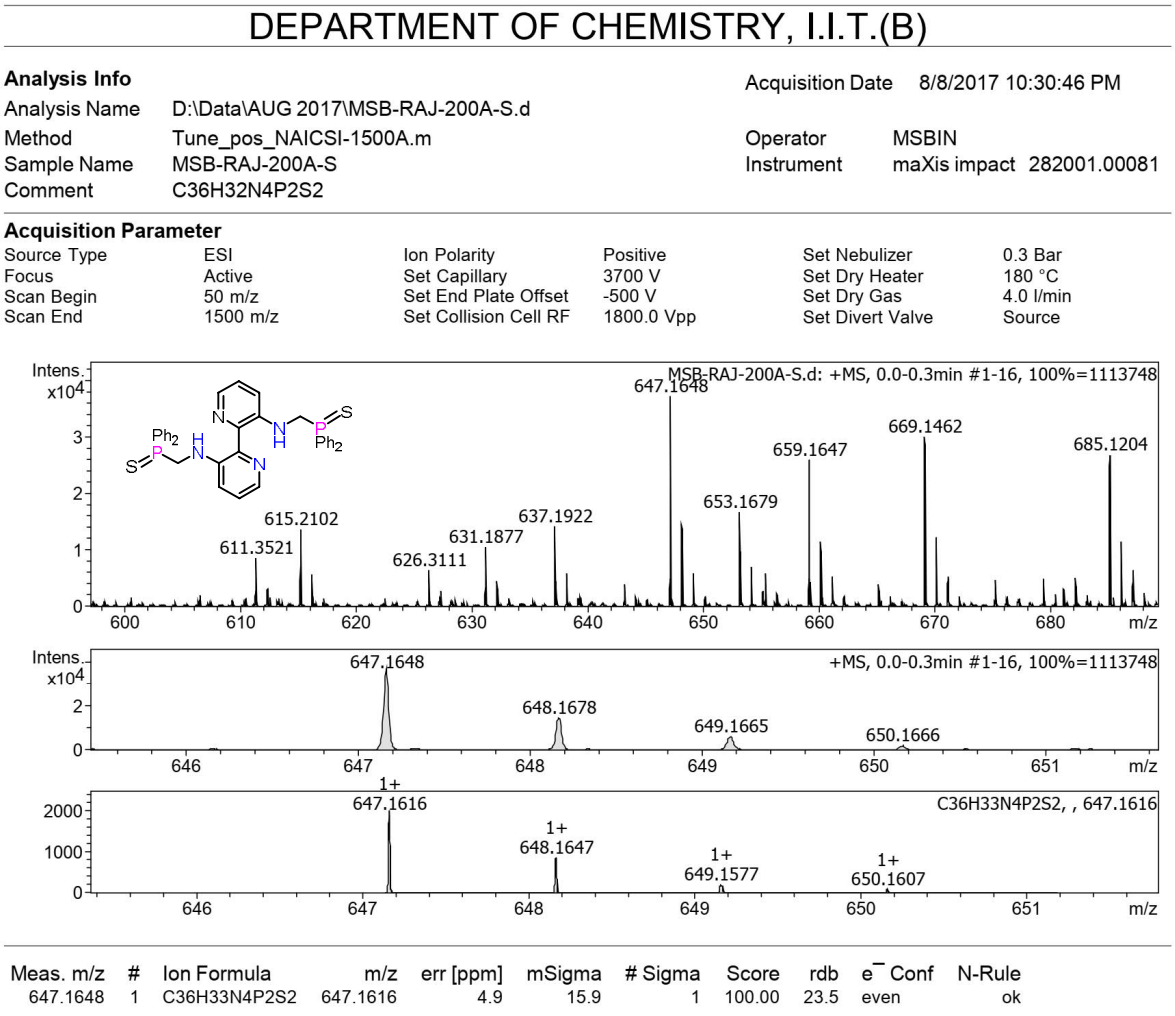

Fig. S44 Mass spectrum of compound **3**.

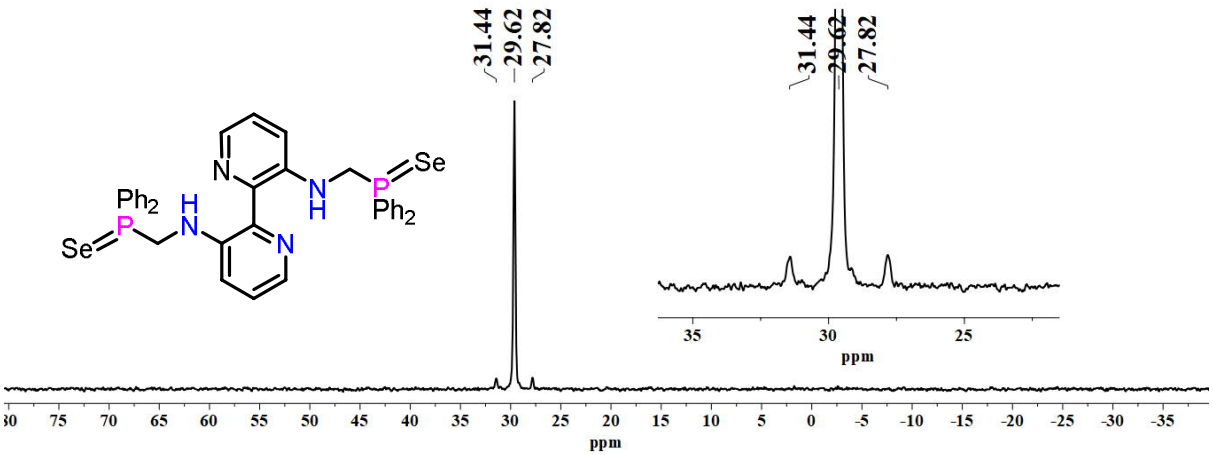

Fig. S45 $^{31}P\{^{1}H\}$ NMR spectrum of compound **4** in $CDCl_3$.

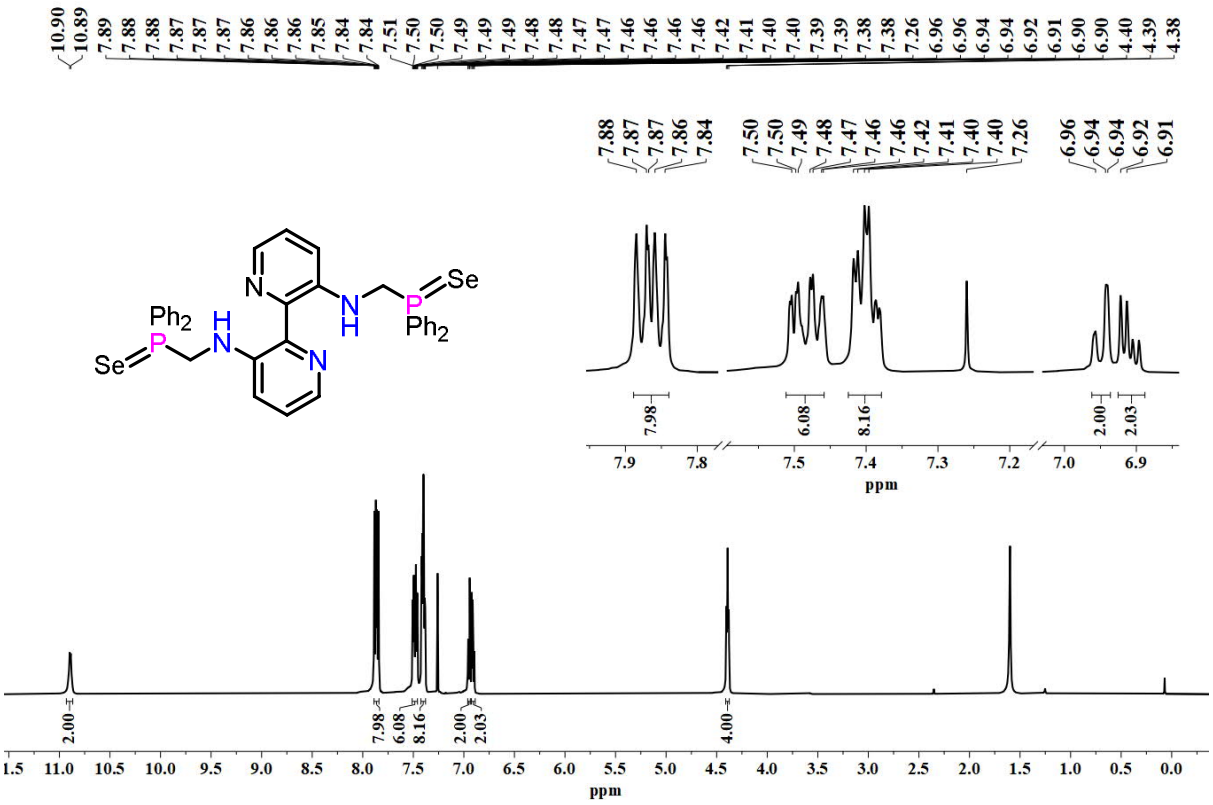

Fig. S46 ^{1}H NMR spectrum of compound **4** in $CDCl_3$.

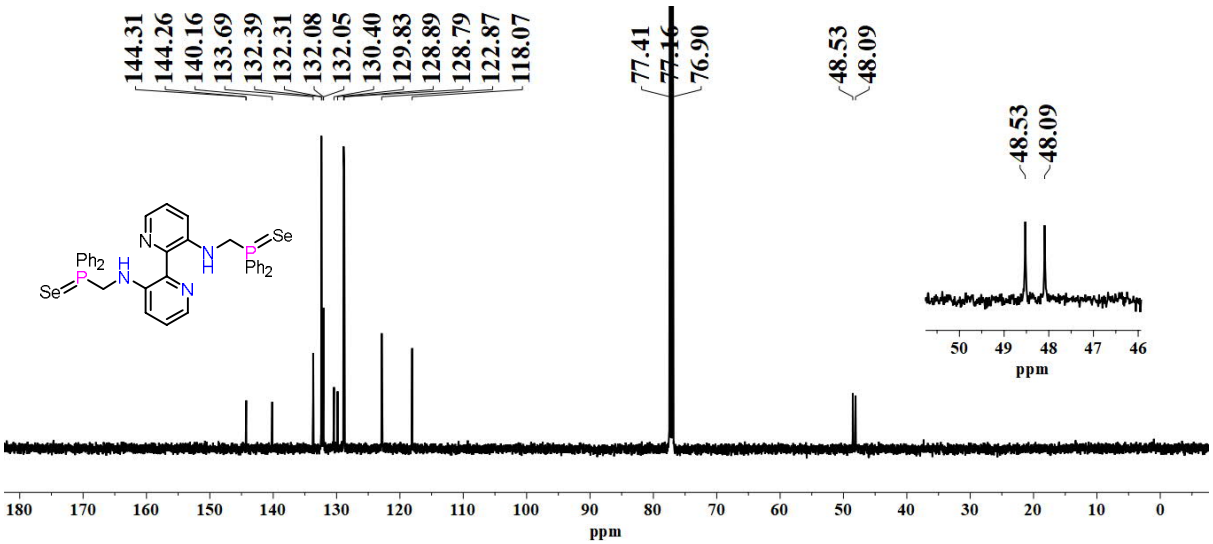

Fig. S47 $^{13}C\{^{1}H\}$ NMR spectrum of compound **4** in $CDCl_3$.

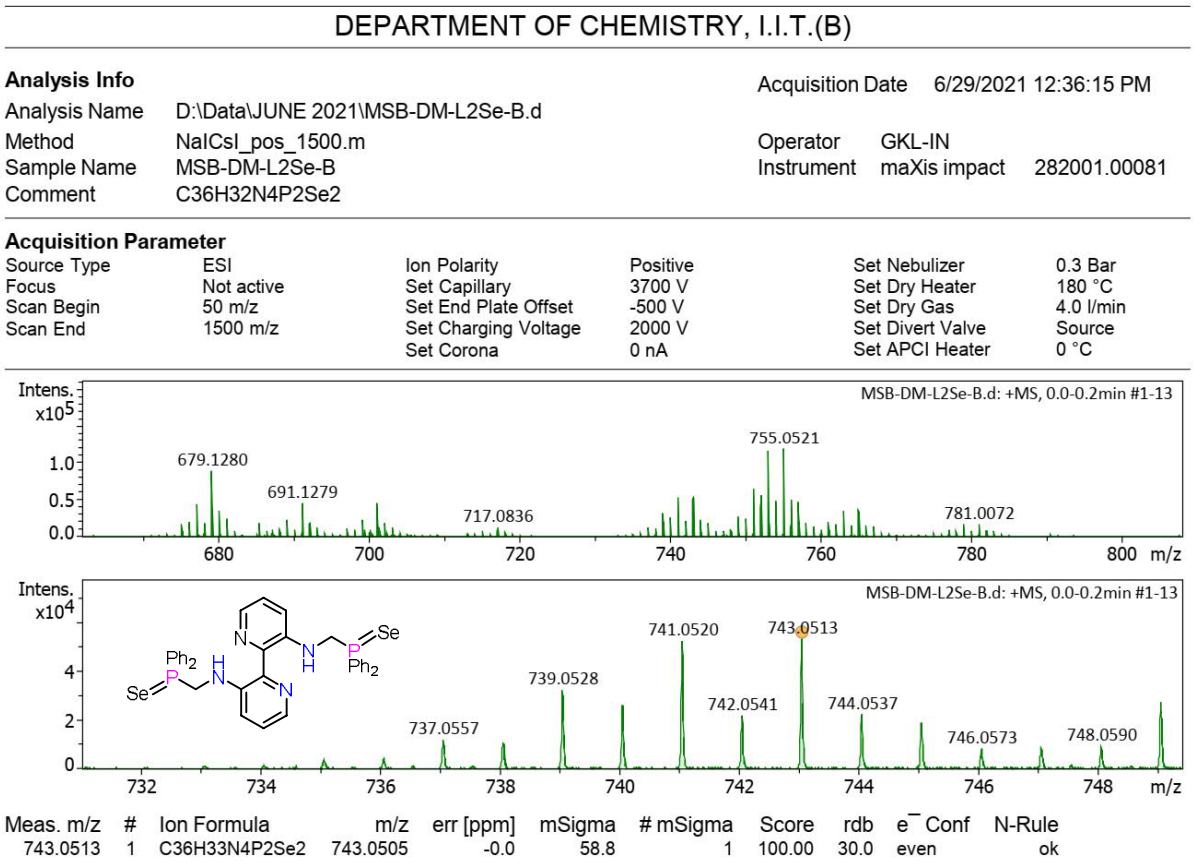

Fig. S48 Mass spectrum of compound **4**.

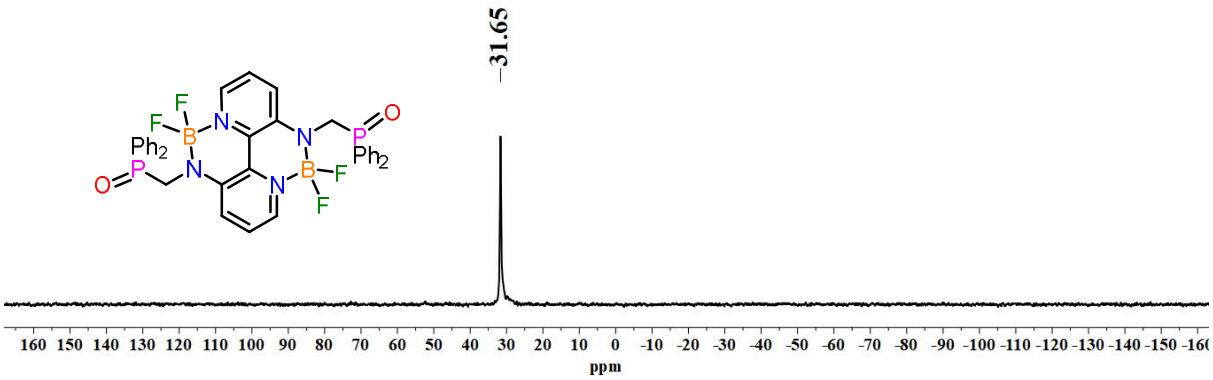

Fig. S49 $^{31}P\{^{1}H\}$ NMR spectrum of compound **5** in $CDCl_3$.

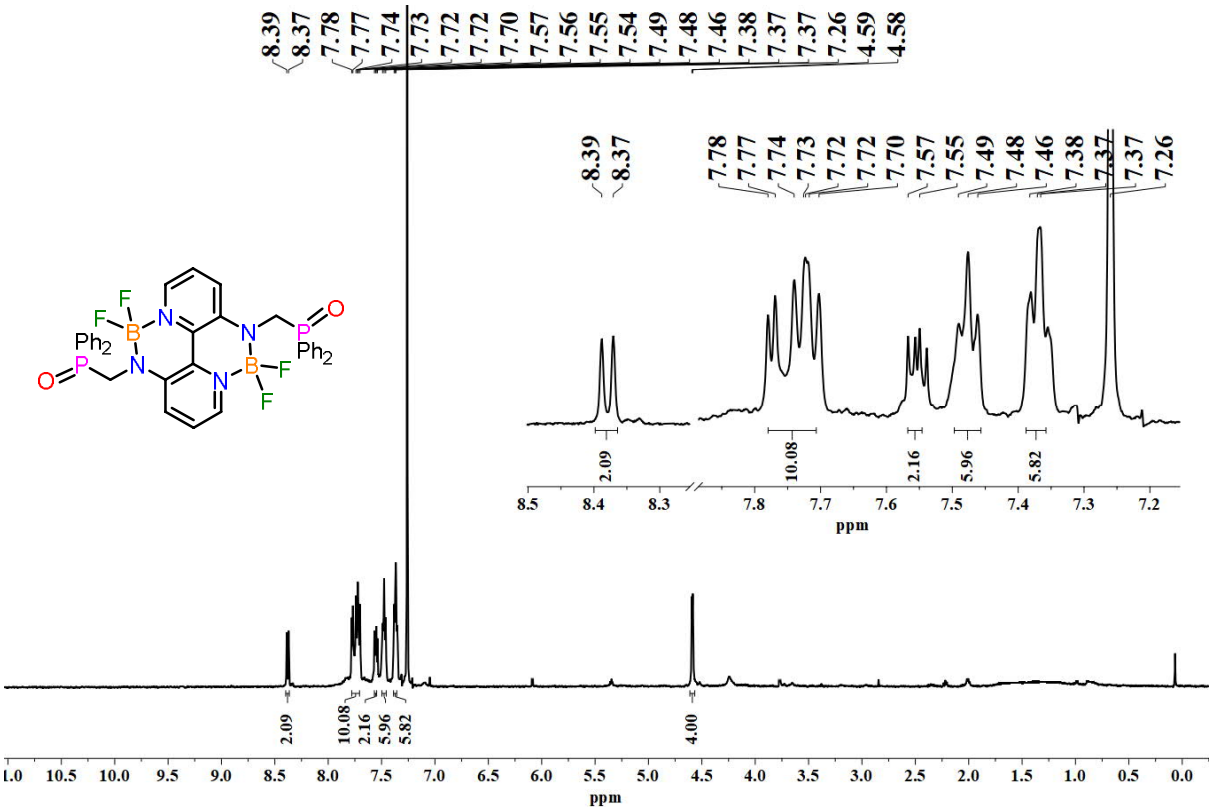

Fig. S50 ^{1}H NMR spectrum of compound **5** in $CDCl_3$.

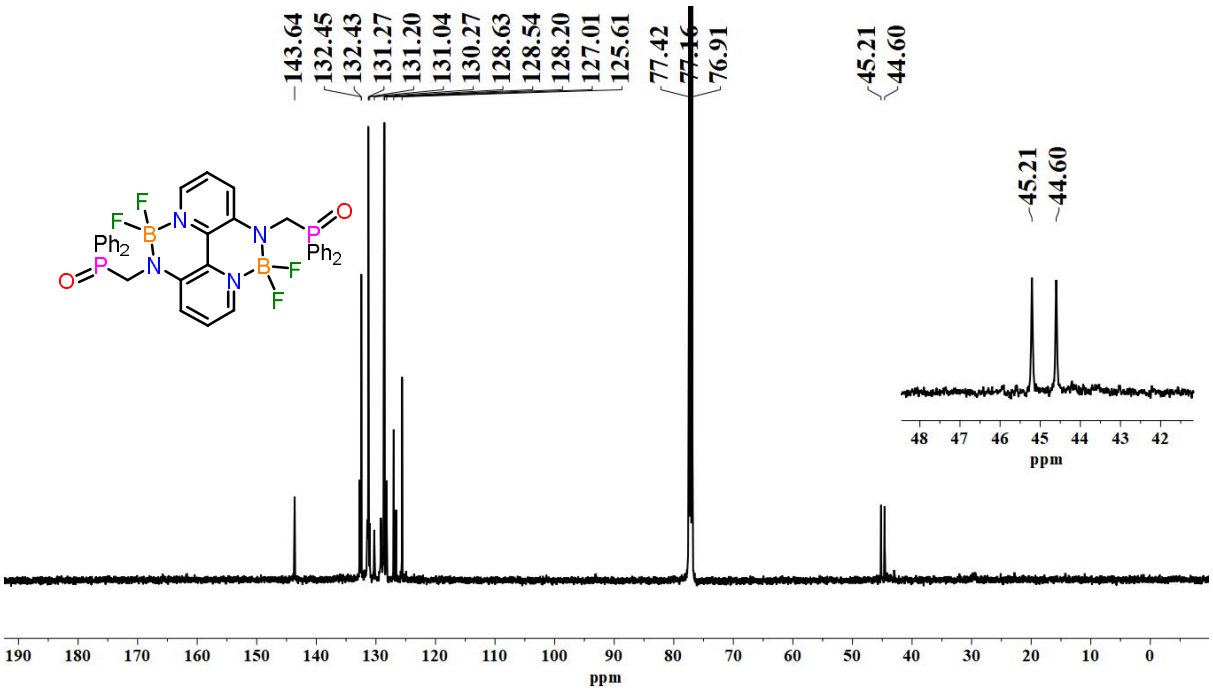

Fig. S51 $^{13}C\{^{1}H\}$ NMR spectrum of compound **5** in $CDCl_3$.

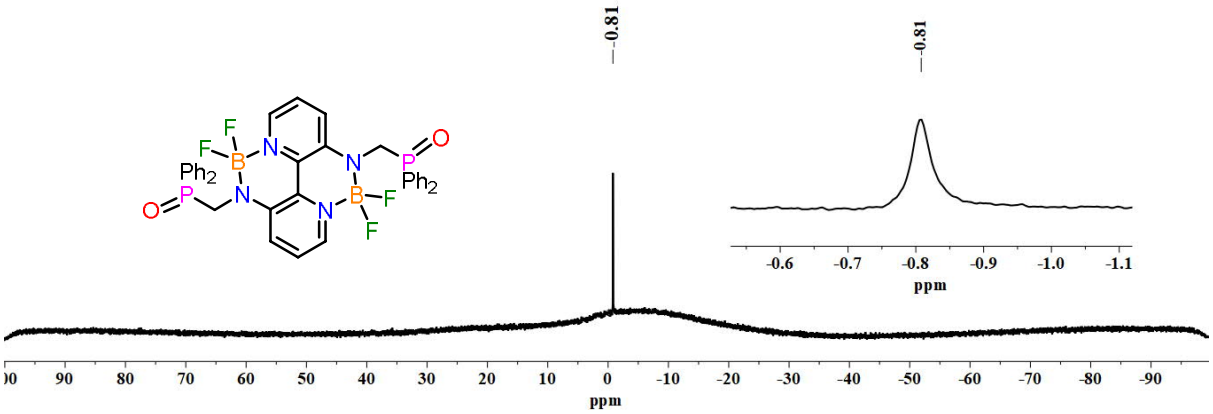

Fig. S52 $^{11}B\{^{1}H\}$ NMR spectrum of compound **5** in $CDCl_3$.

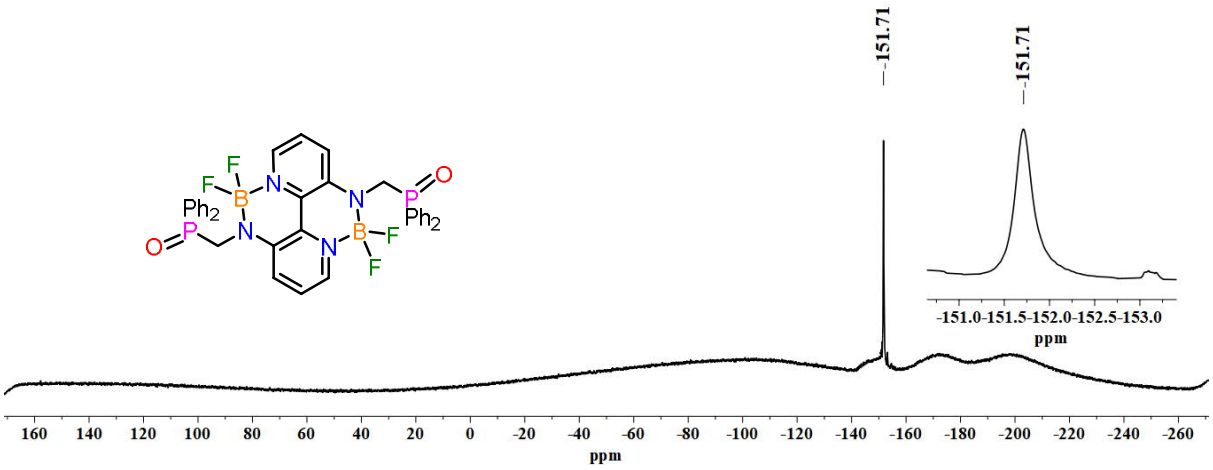

Fig. S53 ^{19}F NMR spectrum of compound **5** in $CDCl_3$.

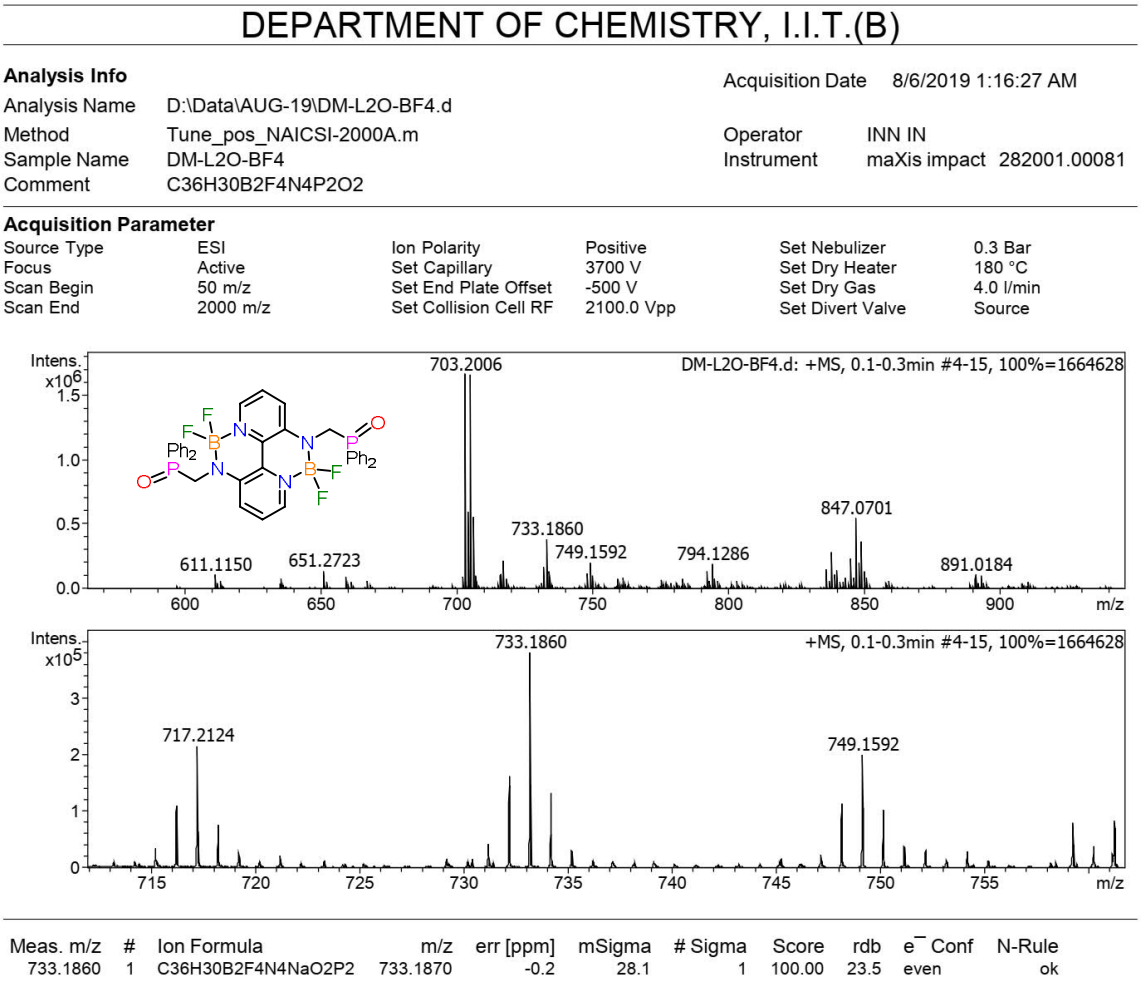

Fig. S54 Mass spectrum of compound **5**.

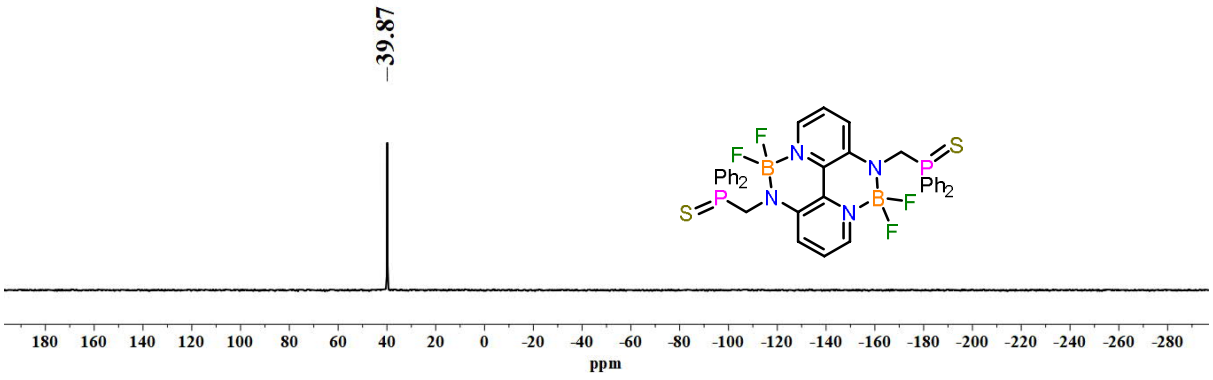

Fig. S55 $^{31}P\{^{1}H\}$ NMR spectrum of compound **6** in $CDCl_3$.

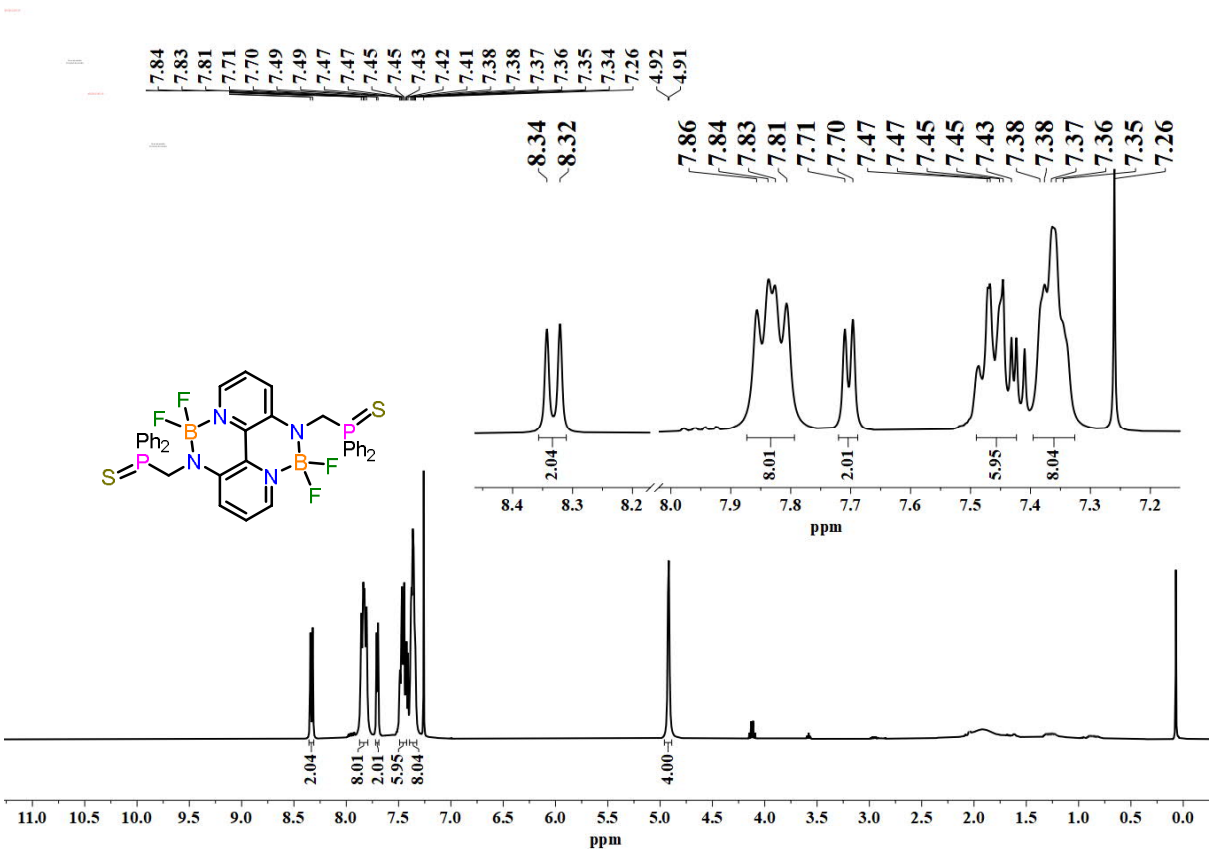

Fig. S56 ^{1}H NMR spectrum of compound **6** in $CDCl_3$.

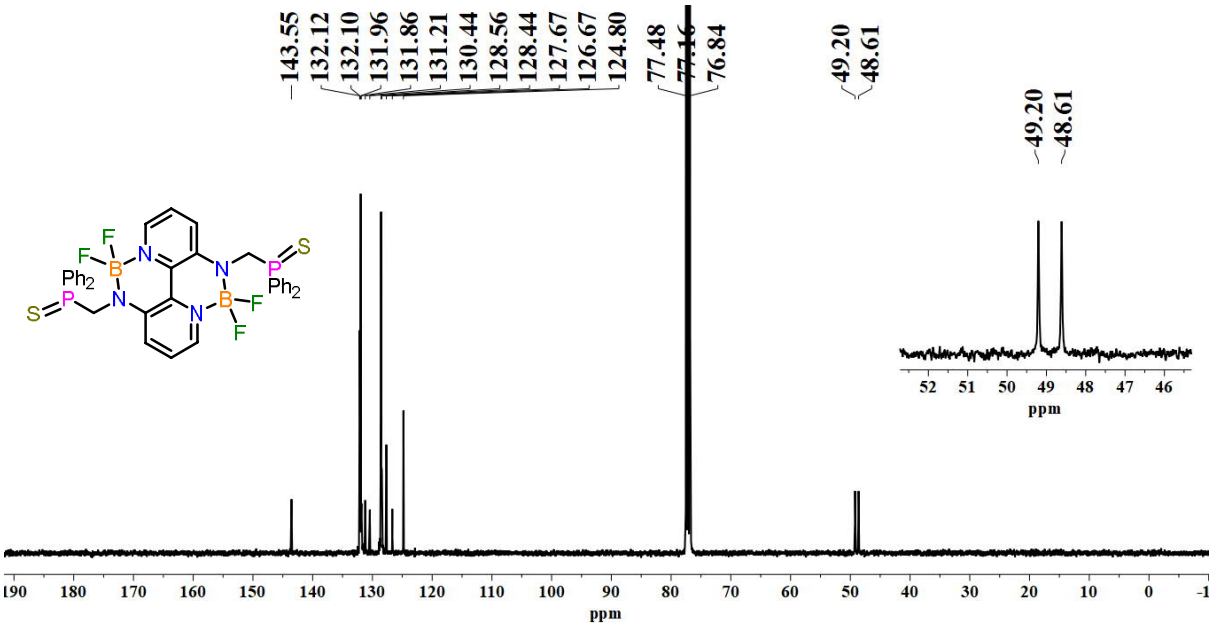

Fig. S57 $^{13}C\{^{1}H\}$ NMR spectrum of compound **6** in $CDCl_3$.

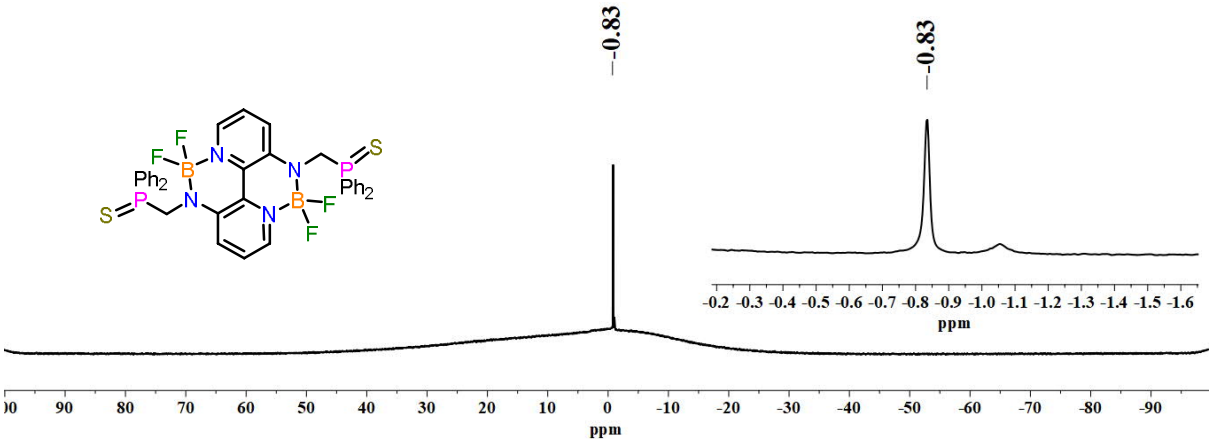

Fig. S58 $^{11}B\{^{1}H\}$ NMR spectrum of compound **6** in $CDCl_3$.

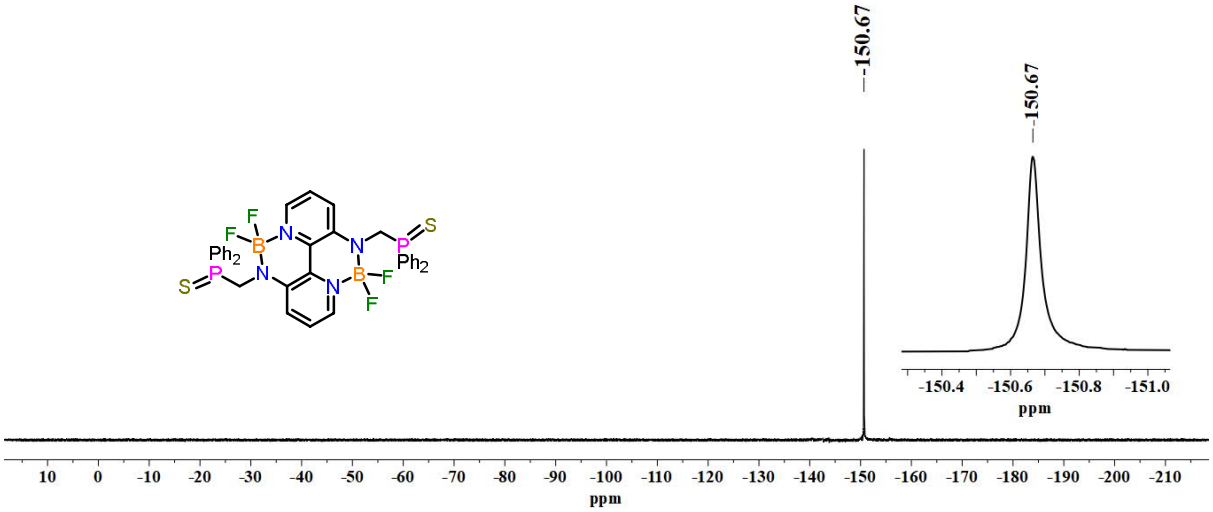

Fig. S59 ^{19}F NMR spectrum of compound **6** in $CDCl_3$.

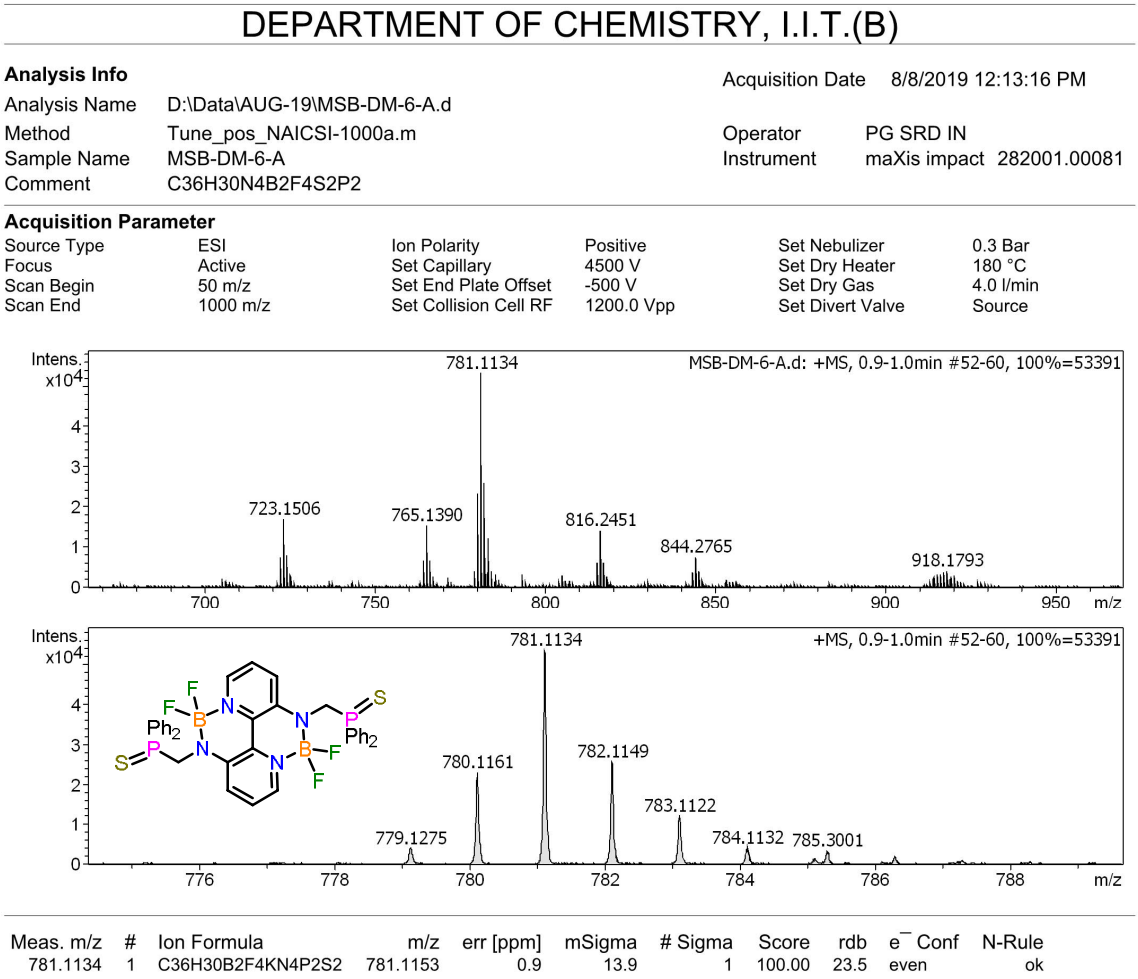

Fig. S60 Mass spectrum of compound **6**.

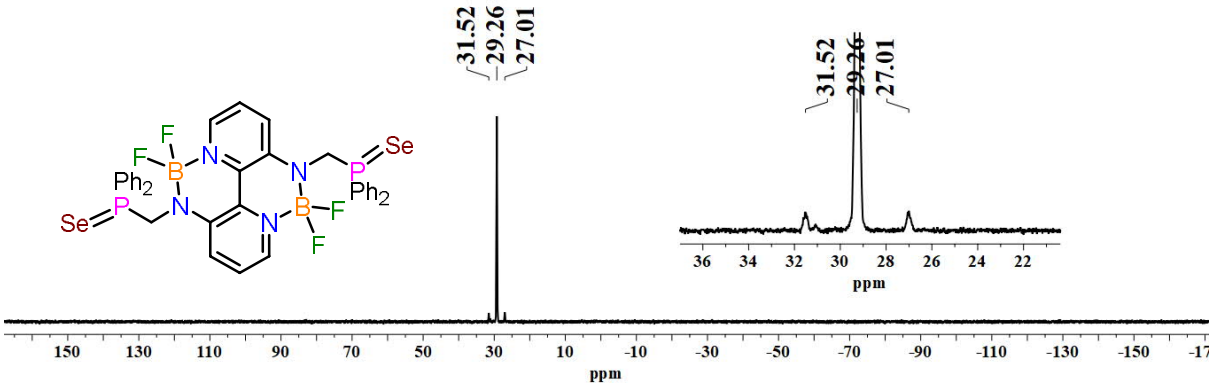

Fig. S61 $^{31}P\{^{1}H\}$ NMR spectrum of compound **7** in $CDCl_3$.

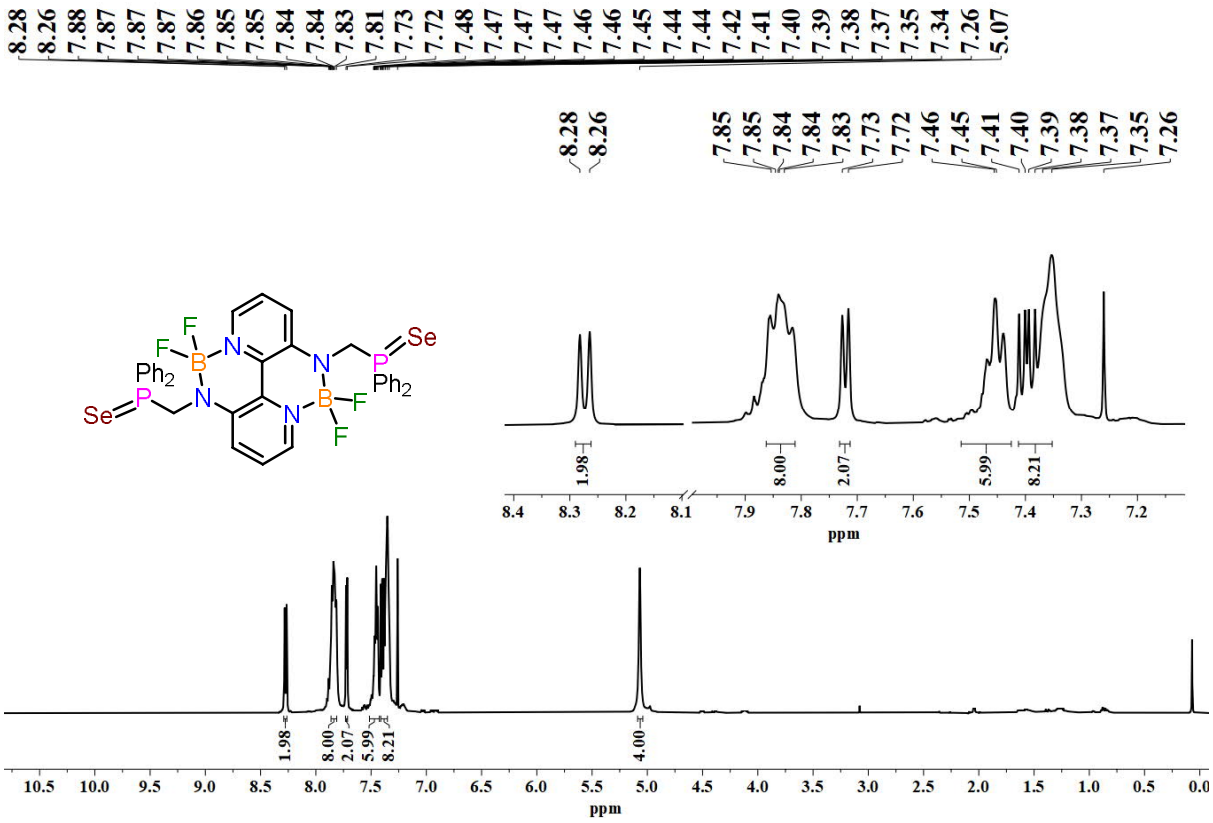

Fig. S62 ^{1}H NMR spectrum of compound **7** in $CDCl_3$.

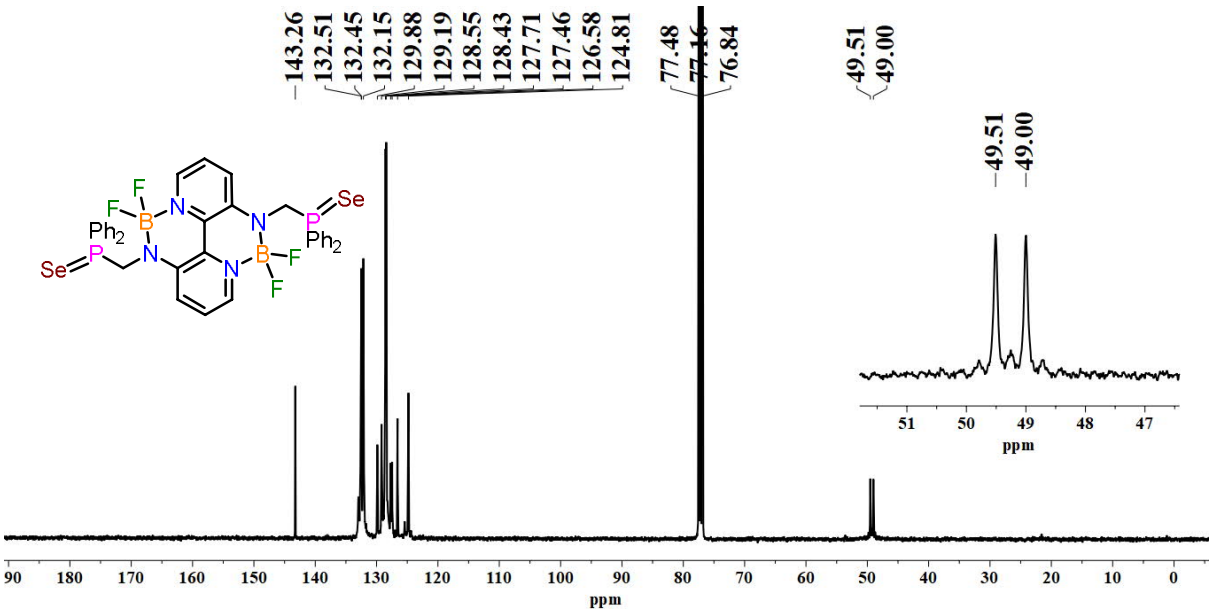

Fig. S63 $^{13}C\{^{1}H\}$ NMR spectrum of compound **7** in $CDCl_3$.

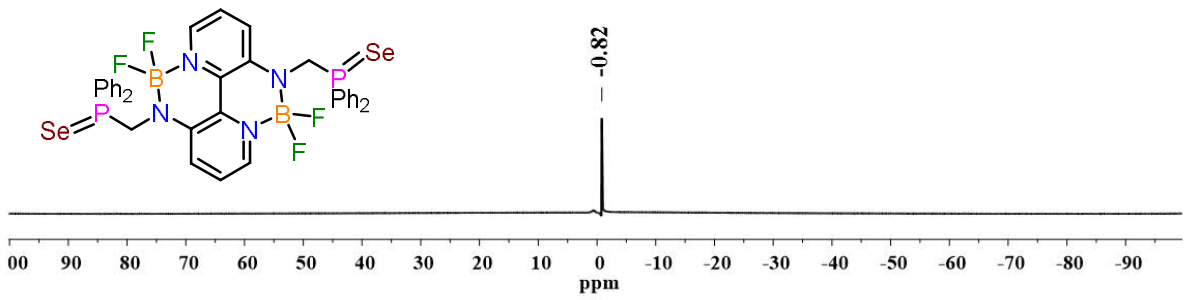

Fig. S64 $^{11}B\{^{1}H\}$ NMR spectrum of compound **7** in $CDCl_3$.

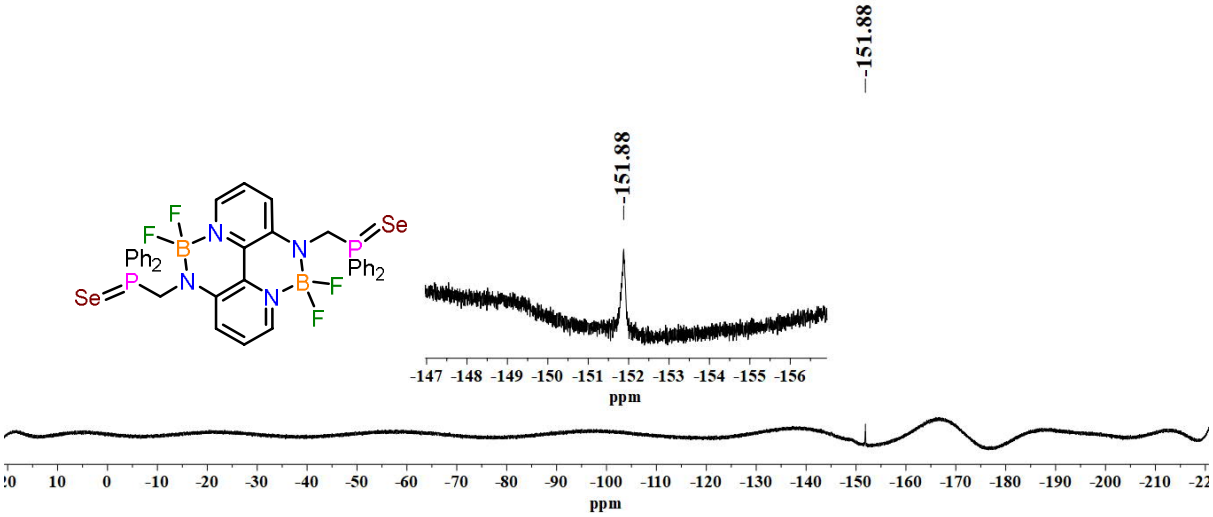

Fig. S65 ^{19}F NMR spectrum of compound **7** in $CDCl_3$.

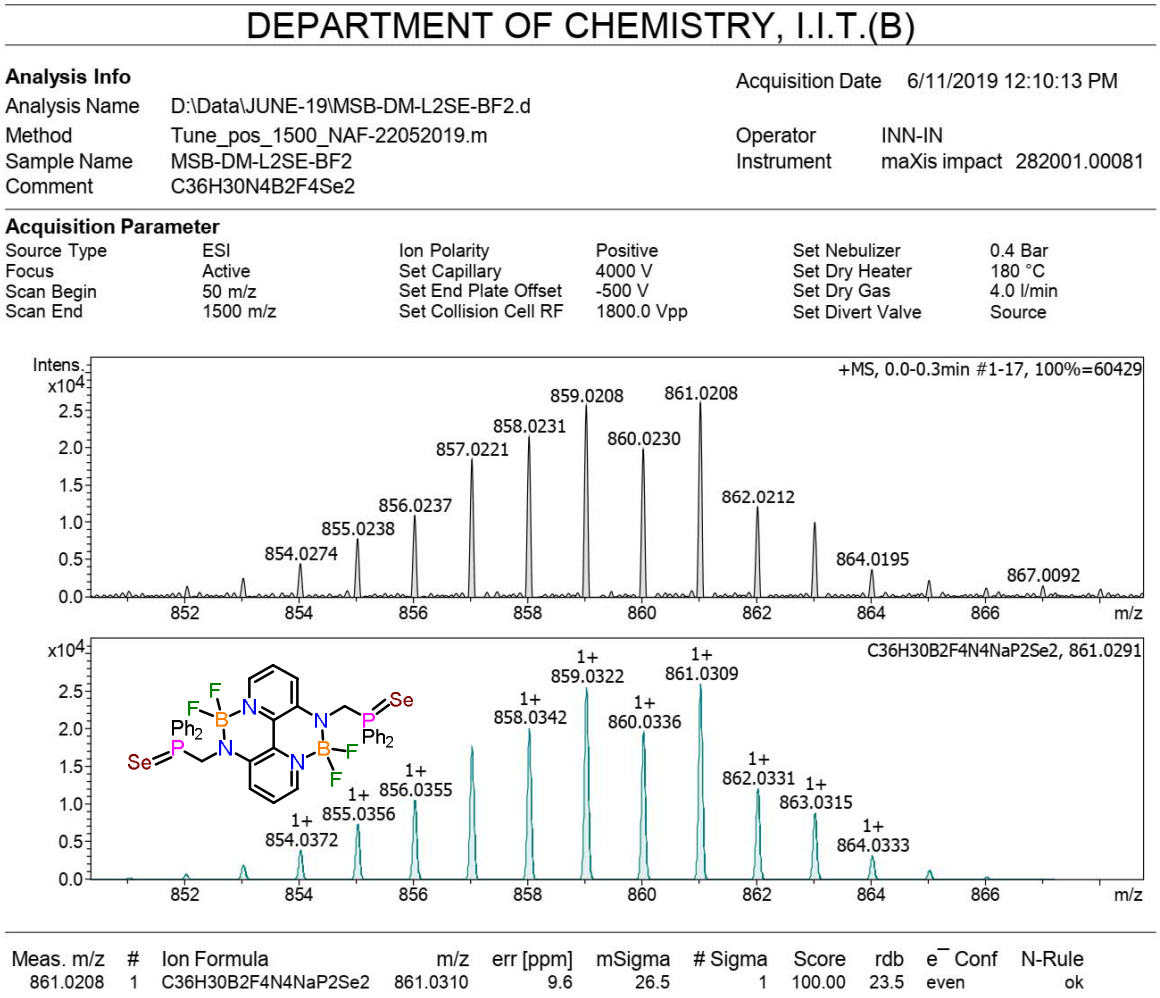

Fig. S66 Mass spectrum of compound **7**.

Optimized Cartesian Coordinates of compounds 5-7 (TD-DFT**;** Gaussian 09; B3LYP/TZVP**).**

Compound **5**			
P	-4.544809000	0.419912000	0.807700000
P	4.544833000	0.419793000	-0.807791000
F	-2.237026000	-3.542330000	-1.201148000
F	-3.049017000	-1.720595000	-2.313527000
F	3.049178000	-1.720433000	2.313768000
F	2.236873000	-3.542193000	1.201649000

O	-4.368821000	0.709898000	2.285965000
O	4.368878000	0.709550000	-2.286100000
N	0.708851000	-1.742558000	1.670116000
N	-2.541070000	-1.474264000	0.030515000
N	2.541237000	-1.474361000	-0.030325000
N	-0.708687000	-1.742995000	-1.669853000
C	-1.607241000	-1.458925000	1.022224000
C	0.229137000	-1.670186000	-0.687885000
C	-0.228965000	-1.669980000	0.688121000
C	1.607422000	-1.459260000	-1.022046000
C	-1.908185000	-1.225885000	2.386570000
H	-2.920110000	-0.947851000	2.681227000
C	-6.319774000	0.401985000	0.351928000
C	-0.400057000	-1.573406000	-2.965154000
H	-1.224690000	-1.659751000	-3.670259000
C	-0.907422000	-1.291670000	3.345591000
H	-1.137967000	-1.126701000	4.398982000
C	0.400235000	-1.572585000	2.965367000
H	1.224870000	-1.658769000	3.670490000
C	1.908371000	-1.226579000	-2.386453000
H	2.920301000	-0.948626000	-2.681172000
C	-3.953101000	-1.282445000	0.308281000
H	-4.319478000	-1.938763000	1.120153000
H	-4.509264000	-1.559160000	-0.595988000

C	-6.781794000	0.228409000	-0.963669000
H	-6.079079000	0.107899000	-1.791864000
C	0.907609000	-1.292628000	-3.345456000
H	1.138151000	-1.127967000	-4.398895000
C	3.423257000	1.461761000	1.607235000
H	3.675727000	0.524018000	2.105118000
C	3.953269000	-1.282511000	-0.308086000
H	4.319717000	-1.938998000	-1.119790000
H	4.509417000	-1.559007000	0.596263000
C	-3.696127000	1.650232000	-0.241775000
C	-7.243393000	0.567026000	1.395749000
H	-6.871567000	0.705124000	2.413395000
C	-3.315531000	2.848320000	0.384820000
H	-3.513536000	2.976052000	1.451337000
C	-8.615451000	0.557434000	1.126478000
H	-9.330186000	0.687207000	1.943081000
C	-8.153404000	0.218607000	-1.228232000
H	-8.507314000	0.084384000	-2.253319000
C	2.791518000	2.473169000	2.336839000
H	2.577447000	2.321594000	3.397712000
C	3.695958000	1.650172000	0.241448000
C	2.425546000	3.670195000	1.711678000
H	1.930658000	4.457116000	2.286568000
C	-9.070969000	0.382553000	-0.183699000

H	-10.143530000	0.374965000	-0.393791000
C	3.315174000	2.848081000	-0.385370000
H	3.513100000	2.975592000	-1.451928000
C	-2.685348000	3.855650000	-0.350670000
H	-2.393257000	4.786425000	0.142059000
C	2.684903000	3.855481000	0.349949000
H	2.392630000	4.786105000	-0.142959000
B	-2.201380000	-2.151646000	-1.295157000
C	-3.423337000	1.461583000	-1.607508000
H	-3.675720000	0.523730000	-2.105218000
C	-2.425869000	3.670109000	-1.712342000
H	-1.931034000	4.456964000	-2.287368000
B	2.201478000	-2.151486000	1.295476000
C	-2.791660000	2.472910000	-2.337277000
H	-2.577484000	2.321134000	-3.398100000
C	6.319778000	0.402090000	-0.351914000
C	7.243458000	0.566834000	-1.395736000
H	6.871699000	0.704636000	-2.413448000
C	6.781723000	0.228947000	0.963760000
H	6.078952000	0.108701000	1.791946000
C	9.070941000	0.382894000	0.183886000
H	10.143489000	0.375392000	0.394045000
C	8.153320000	0.219265000	1.228415000
H	8.507166000	0.085386000	2.253568000

C	8.615497000	0.557353000	-1.126376000
H	9.330280000	0.686884000	-1.942975000

Compound **6**

P	-3.830326000	0.204224000	-0.638205000
S	-2.376802000	1.418092000	-1.206842000
P	3.927399000	-0.141485000	-0.711361000
S	2.751490000	-1.505136000	-1.527530000
F	-2.097812000	0.589495000	4.060093000
F	3.022283000	-2.708428000	1.942555000
F	2.189304000	-1.613181000	3.768482000
F	-2.899108000	2.081626000	2.522811000
N	0.699779000	-1.985476000	1.921190000
N	-0.579570000	1.376582000	2.371798000
N	-2.460977000	-0.174896000	1.792607000
N	2.576008000	-0.340818000	1.747662000
C	-1.917640000	-2.504259000	1.223722000
H	-2.940917000	-2.732192000	0.930071000
C	-3.779616000	-0.207935000	1.217934000
H	-4.376952000	0.580034000	1.692159000
H	-4.298431000	-1.167303000	1.377664000
C	-0.958700000	-3.506841000	1.179599000
H	-1.224745000	-4.516738000	0.865046000
C	-1.576103000	-1.201912000	1.656266000
C	0.352515000	-3.225921000	1.551025000

H	1.149057000	-3.967891000	1.552451000
C	-0.195546000	-0.965178000	1.958021000
C	-5.522021000	0.887017000	-0.886014000
C	-3.825146000	-1.412548000	-1.532046000
C	-0.228130000	2.669977000	2.352872000
H	-1.024057000	3.386551000	2.547775000
C	0.315095000	0.381434000	2.139734000
C	3.889963000	-0.159800000	1.184891000
H	4.507868000	-1.024529000	1.458925000
H	4.395632000	0.746028000	1.556262000
C	1.086608000	3.037998000	2.085175000
H	1.356573000	4.094482000	2.064175000
C	-2.729034000	-1.746002000	-2.340137000
H	-1.906986000	-1.033672000	-2.442046000
C	1.695889000	0.688745000	1.908969000
C	3.498299000	1.576932000	-1.231504000
C	-5.721312000	1.806293000	-1.928427000
H	-4.869955000	2.111975000	-2.541050000
C	2.211402000	1.832017000	-1.729727000
H	1.500850000	1.007970000	-1.826475000
C	-4.891257000	-2.320185000	-1.401952000
H	-5.766806000	-2.072424000	-0.797244000
C	2.042362000	2.058441000	1.856780000
H	3.067766000	2.354012000	1.642857000

C	-6.990564000	2.338891000	-2.165486000
H	-7.133701000	3.053843000	-2.979490000
C	-4.850374000	-3.549862000	-2.064817000
H	-5.684207000	-4.248624000	-1.961054000
C	4.419565000	2.633183000	-1.122038000
H	5.434226000	2.452974000	-0.760378000
C	1.844812000	3.129215000	-2.098661000
H	0.838239000	3.316902000	-2.480119000
C	-6.611123000	0.517699000	-0.076756000
H	-6.489772000	-0.185132000	0.750246000
C	-3.751014000	-3.880107000	-2.865626000
H	-3.722920000	-4.840763000	-3.386014000
C	-8.071520000	1.965940000	-1.359713000
H	-9.063039000	2.387590000	-1.542447000
C	-2.693576000	-2.975963000	-3.003996000
H	-1.834943000	-3.226424000	-3.631861000
C	2.760932000	4.179109000	-1.980393000
H	2.474570000	5.192412000	-2.273278000
C	-7.879109000	1.057870000	-0.314588000
H	-8.717356000	0.768593000	0.323918000
C	4.049103000	3.928555000	-1.494622000
H	4.773184000	4.743035000	-1.412477000
B	-2.087358000	0.981223000	2.720815000
B	2.203468000	-1.686267000	2.374812000

C	5.713743000	-0.356523000	-1.102855000
C	6.056665000	-0.990800000	-2.307868000
H	5.261985000	-1.356154000	-2.962411000
C	7.397828000	-1.169981000	-2.654253000
H	7.652287000	-1.664219000	-3.595098000
C	8.410527000	-0.727135000	-1.796885000
H	9.459672000	-0.872889000	-2.065904000
C	6.735978000	0.083748000	-0.242814000
H	6.506041000	0.571010000	0.706769000
C	8.077621000	-0.104065000	-0.590693000
H	8.863787000	0.236760000	0.087375000

Compound **6·CH_2Cl_2**

P	-4.146776000	0.066360000	-0.276260000
S	-2.734832000	0.488609000	-1.595698000
P	4.220740000	0.066279000	-0.553144000
S	2.999839000	0.668626000	-1.996621000
F	2.235269000	-3.497389000	2.250712000
F	-2.124379000	-4.478184000	0.306779000
F	-3.061159000	-3.364442000	-1.457080000
F	3.063324000	-1.410267000	2.674958000
N	-2.542513000	-2.104711000	0.530947000
N	-0.716302000	-2.990307000	-0.946537000
N	2.518964000	-1.963409000	0.394649000
N	0.713794000	-1.641564000	2.100952000

C	-1.609261000	-1.666529000	1.419097000
C	-3.901190000	-1.632845000	0.545427000
H	-4.336764000	-1.598062000	1.557798000
H	-4.503423000	-2.322071000	-0.057943000
C	-1.900710000	-0.905463000	2.574729000
H	-2.922578000	-0.589645000	2.778223000
C	-3.335469000	2.325676000	1.195185000
H	-2.534790000	2.396890000	0.456447000
C	-5.839546000	-0.030003000	-0.993763000
C	-0.893598000	-0.560462000	3.466730000
H	-1.121008000	0.010252000	4.367971000
C	-0.228839000	-1.977101000	1.182512000
C	-4.437282000	3.159953000	3.186932000
H	-4.500202000	3.887678000	3.999899000
C	1.585062000	-2.365043000	-0.515784000
C	-6.124859000	0.741337000	-2.131492000
H	-5.333257000	1.346810000	-2.579002000
C	-4.280144000	1.295058000	1.095816000
C	-6.849089000	-0.833929000	-0.435570000
H	-6.657430000	-1.456226000	0.441270000
C	1.861413000	-2.666028000	-1.871629000
H	2.860544000	-2.512591000	-2.272985000
C	0.222744000	-2.500374000	-0.093158000
C	-0.428803000	-3.310684000	-2.214429000

H	-1.253958000	-3.693158000	-2.812641000
C	3.889302000	-1.696677000	0.024327000
H	4.254966000	-2.360315000	-0.774657000
H	4.522955000	-1.861670000	0.905337000
C	0.862591000	-3.141746000	-2.706566000
H	1.078890000	-3.388305000	-3.746787000
C	-5.383890000	2.133273000	3.091763000
H	-6.188763000	2.058123000	3.827100000
C	0.414748000	-0.958661000	3.217537000
H	1.247417000	-0.741367000	3.884028000
C	-7.402521000	0.718129000	-2.695687000
H	-7.613247000	1.321787000	-3.581898000
C	-8.404810000	-0.079981000	-2.134399000
H	-9.402508000	-0.101271000	-2.579802000
C	6.407026000	0.890504000	-2.086165000
H	5.674923000	1.549893000	-2.558121000
C	3.059486000	1.984962000	1.130847000
H	2.284512000	2.042362000	0.364979000
C	-3.416555000	3.255132000	2.236541000
H	-2.676600000	4.056826000	2.298929000
C	5.061086000	1.855907000	3.079507000
H	5.848066000	1.806649000	3.836076000
C	3.971404000	2.716754000	3.253112000
H	3.905670000	3.341787000	4.147381000

C	2.972667000	2.780015000	2.277567000
H	2.121548000	3.454304000	2.398940000
C	-5.309955000	1.205484000	2.049310000
H	-6.070040000	0.423552000	1.981298000
C	4.147241000	1.119046000	0.954627000
B	-2.185555000	-3.270893000	-0.391553000
C	6.923723000	-0.855733000	-0.484593000
H	6.632502000	-1.555603000	0.300968000
C	-8.125451000	-0.857186000	-1.006550000
H	-8.901396000	-1.489505000	-0.568343000
C	5.151010000	1.059444000	1.935997000
H	6.013550000	0.401049000	1.814474000
C	8.256096000	-0.846032000	-0.909900000
H	8.972984000	-1.532035000	-0.452290000
C	5.988229000	0.017520000	-1.068829000
C	7.740205000	0.901464000	-2.502325000
H	8.054213000	1.586895000	-3.293365000
B	2.207912000	-2.152963000	1.879581000
C	8.667091000	0.033684000	-1.915393000
H	9.708890000	0.039071000	-2.245411000
Cl	-0.043075000	4.518434000	-3.115474000
Cl	-0.031308000	4.002129000	-0.178514000
C	-0.010574000	3.281770000	-1.827206000
H	0.912417000	2.699349000	-1.923636000

H	-0.901521000	2.651595000	-1.921552000

Compound **7**

Se	3.181565000	-1.647760000	-1.878588000
Se	-5.177366000	2.645467000	-0.498530000
P	4.228995000	-0.360112000	-0.520688000
P	-4.510689000	0.606941000	-0.385416000
F	3.044770000	1.797350000	2.293683000
F	2.088091000	0.456509000	3.877624000
F	-3.207433000	-2.546699000	1.573866000
F	-2.441899000	-1.690473000	3.550925000
N	0.680717000	1.264894000	2.106523000
N	-2.618040000	-0.217327000	1.631378000
N	-0.851466000	-2.007715000	1.770826000
N	2.449587000	-0.451021000	1.660443000
C	-0.857916000	3.035861000	1.769225000
H	-1.047182000	4.107527000	1.694833000
C	-1.647505000	0.734887000	1.721811000
C	8.847587000	-0.843033000	-0.820685000
H	9.930883000	-0.959063000	-0.905750000
C	0.427343000	2.581247000	2.042196000
H	1.277212000	3.241246000	2.206393000
C	2.628676000	1.783122000	-1.358638000
H	1.930065000	1.002403000	-1.667294000
C	3.217260000	4.126321000	-1.169109000

H	2.968198000	5.180068000	-1.318011000
C	-1.452477000	0.830907000	-3.131401000
H	-1.032984000	1.588754000	-3.797676000
C	6.061057000	-0.549595000	-0.599533000
C	8.022768000	-1.124346000	-1.914798000
H	8.458355000	-1.461197000	-2.858646000
C	-0.287777000	0.329903000	1.920092000
C	4.773787000	2.424114000	-0.424636000
H	5.742178000	2.164915000	0.007064000
C	4.450808000	3.770097000	-0.614359000
H	5.168969000	4.542936000	-0.329673000
C	2.307214000	3.131196000	-1.539549000
H	1.343939000	3.402546000	-1.978518000
C	0.717901000	-3.699008000	1.219679000
H	0.918014000	-4.746078000	0.989200000
C	8.281859000	-0.418194000	0.384578000
H	8.918811000	-0.201659000	1.245548000
C	-0.583083000	-3.293292000	1.499487000
H	-1.432524000	-3.974009000	1.509485000
C	3.862014000	1.422391000	-0.795319000
C	0.122012000	-1.056825000	1.797438000
C	-1.892224000	2.123770000	1.605734000
H	-2.893632000	2.488768000	1.371447000
C	-6.946977000	-0.689503000	0.080986000

H	-6.975560000	-0.106955000	1.005389000
C	6.895925000	-0.268214000	0.497753000
H	6.486151000	0.068188000	1.451410000
C	1.489696000	-1.416488000	1.559774000
C	-5.856633000	-0.575393000	-0.800608000
C	1.746355000	-2.769650000	1.235847000
H	2.756313000	-3.089290000	0.989638000
C	-5.866010000	-1.299468000	-2.002950000
H	-5.037144000	-1.212285000	-2.707323000
C	-0.898840000	-0.452190000	-3.089928000
H	-0.038311000	-0.698872000	-3.716249000
C	-8.014830000	-1.534411000	-0.225511000
H	-8.853448000	-1.620020000	0.469716000
C	-3.995783000	0.140356000	1.399696000
H	-4.321200000	0.998314000	2.009245000
H	-4.619629000	-0.721788000	1.662382000
C	6.637634000	-0.984233000	-1.804376000
H	5.989620000	-1.225283000	-2.650420000
C	-2.544445000	1.150200000	-2.317989000
H	-2.980762000	2.152134000	-2.336834000
C	-6.942575000	-2.138939000	-2.308687000
H	-6.939805000	-2.697927000	-3.247683000
C	3.827735000	-0.682111000	1.295399000
H	4.174783000	-1.703939000	1.514944000

H	4.451146000	0.011325000	1.873122000
C	-8.014463000	-2.262064000	-1.421092000
H	-8.852642000	-2.920713000	-1.661507000
C	-2.539827000	-1.112846000	-1.431719000
H	-2.962501000	-1.879437000	-0.779610000
C	-1.444674000	-1.422543000	-2.241054000
H	-1.011699000	-2.424932000	-2.206092000
C	-3.092761000	0.181315000	-1.466335000
B	-2.348640000	-1.624035000	2.162572000
B	2.139980000	0.775603000	2.520921000

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