Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Homolytic cleavage of Lawesson's reagent: *N*-hetercyclic carbene complexes of $ArPS_2$ (Ar = 4-CH_3O-C6H_4)

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Materials and Methods

General

All preparations and manipulations were carried out under an anhydrous nitrogen atmosphere using standard Schlenk and glovebox techniques. All glassware was oven-dried and cooled under vacuum before use. Commercially-available reagents such as 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene, 2,4-Diphenyl-1,3,2,4-diselenadiphosphetan-2,4-diselenide (Woollins' reagent) and 2,4-Bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-dithione (Lawesson's reagent) were purchased from Sigma Aldrich and used without further purification unless otherwise indicated. 1,3-Bis(2,6-di-iso-propylphenyl)imidazolidin-2-ylidene was prepared according to literature methods [1]. $CDCl_3$ and CD_2Cl_2 were purchased from Sigma Aldrich.

^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker Ultrashield 300 MHz spectrometer at 300.26, 75.50 and 121.54 MHz, respectively. ^{1}H and ^{13}C spectral shifts are reported in relation to either known residual solvent peaks or TMS, when available. ^{31}P spectral shifts are reported without internal calibration. Data was processed using Bruker Topspin software and prepared for publication using ACD software. Values are reported as follows: chemical shift (δ ppm), integration, multiplicity (s = singlet, d = doublet, t = triplet, dd=doublet of doublets, sep = septet), coupling constant (Hz) and assignment. High resolution mass spectra (HR-MS) were recorded on a micrOTOF Bruker Daltonics instrument and the ionization method used was positive electrospray ionization (ESI). Melting points were measured using an Electrothermal Mel-Temp apparatus and are uncorrected. IR spectra were prepared as potassium bromide pellets and recorded on a Bruker Vertex 70 FTIR spectrometer. Infrared data processing was completed using the Bruker OPUS 6.0 software package.

X-ray Diffraction Studies

The crystal chosen was attached to the tip of a MicroLoop with Paratone-N oil. Measurements were made on a Bruker APEXII CCD equipped diffractometer (30 mA, 50 kV) using monochromated Mo Kα radiation (λ = 0.71073 Å) at 125 K [2]. The initial orientation and unit cell were indexed using a least-squares analysis of a random set of reflections collected from three series of 0.5° ω-scans, 10 seconds per frame and 12 frames per series, that were well distributed in reciprocal space. For the data collection of compound **4**, five ω-scan frame series were collected with 0.5° wide scans, 20

second frames and 366 frames per series at varying φ angles (φ = 0°, 90°, 180°, 270° and 0°). The crystal to detector distance was set to 6 cm and an over-complete sphere of data was collected. In addition, a separate φ-scan was carried out, collecting 720 frames for a complete 360° rotation. For the compound **5** data collection, the crystal was much smaller, so four ω-scan frame series were collected with 0.5° wide scans, 60 second frames and 366 frames per series at varying φ angles (φ = 0°, 90°, 180°, 270°). The crystal to detector distance was set to 6 cm and a complete sphere of data was collected.

Cell refinement and data reduction were performed with the Bruker SAINT [3] software, which corrects for beam inhomogeneity, possible crystal decay, Lorentz and polarisation effects. A multi-scan absorption correction was applied to each data set (SADABS [4]). The structures were solved using SHELXT-2014 [5] and were refined using a full-matrix least-squares method on F^2 with SHELXL-2014 [5]. The refinements were unremarkable. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms bonded to carbon were included at geometrically idealized positions and were not refined. Their isotropic thermal parameters were fixed at $1.2U_{eq}$ of the parent carbon atom or $1.5U_{eq}$ for methyl hydrogens.

Structure **4** was found to contain one dichloromethane solvent molecule in the asymmetric unit. Structure **5** was found to contain one half of a toluene solvent molecule in the asymmetric unit. The solvent molecules were not disordered and were well-behaved during the refinements.

All structural diagrams were prepared using the program Mercury CSD 3.9 [6].

Computational Studies

Calculations were performed using Gaussian 03 software [7], and the MP2 calculations used the frozen core approximation. The geometries were optimized using a stepping stone approach, in which the geometries at the levels HF/6-31G*, HF/6-31+G*, HF/6-311+G*, B3LYP/6-31G*, B3LYP/6-31+G*, B3LYP/6-311+G*, MP2/6-31G*, MP2/6-31+G* and MP2/6-311+G* were sequentially optimized, with the geometry and molecular orbital reused for the subsequent level. Default optimization specifications were normally used. After each level, where possible, a frequency calculation was performed at the same level and the resulting Hessian was used in the next optimization. Z-matrix coordinates constrained to the appropriate symmetry were used as required to speed up the optimizations. Because frequency calculations are done at each level, any problems with the Z-matrix coordinates would manifest themselves by

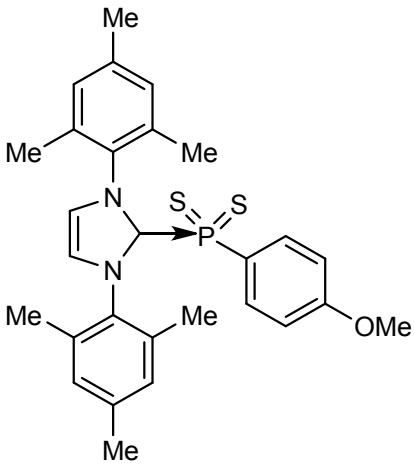
giving imaginary frequencies corresponding to modes orthogonal to the spanned Z-matrix space. The Hessian was evaluated at the first geometry (Opt = CalcFC) for the first level in a series in order to aid geometry convergence. In some cases, MP2 calculations with diffuse functions on species with aromatic rings gave imaginary frequencies which were believed to be an artifact of the computational model. This prevents accurate estimation of entropic and thermal corrections to the energy.

Electrostatic Potential Plots

The Spartan 14 semi-empirical and DFT calculations were carried out on a Microsoft Windows 7 professional version computer system. For compound **2**, density functional theory (DFT) was used for the geometry optimization and calculations were performed using the B3LYP method of DFT and a 6-31G* basis set. For the $ArPS_2$-IMes adduct (**4**) initial coordinates were taken from the X-ray crystallographic results. The heavy atom positions were frozen and the geometry optimised. Electrostatic potential plots were created from the optimized wavefunctions using the program Spartan 14 [8].

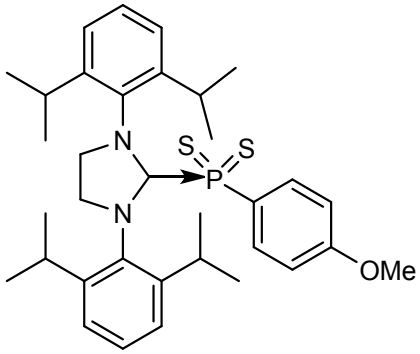
Syntheses and Spectroscopic Data of Compounds 4 and 5

Compound 4

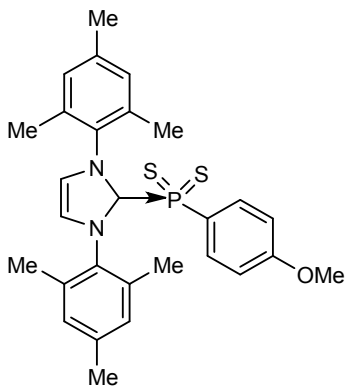


To a stirred solution of 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (1.0 mmol, 304 mg) in 15 mL THF was added 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-dithione (Lawesson's reagent) (0.5 mmol, 202 mg) and the mixture was left to stir under ambient temperature for 12 h. Then, the solvent was removed under vacuum and the residue was crystallized from dichloromethane. The product was obtained in the form of colourless crystals (460 mg, yield 91%); mp 224-227 ºC (dec). IR (KBr) (ν_{max}/cm^{-1}): 3449, 3164, 2917, 1636, 1623, 1592, 1492, 1250, 1092, 690. HRMS (ESI) calcd for $C_{28}H_{31}N_2NaOPS_2$ [M + Na] 529.1508, found 529.1498. ^{1}H NMR (300 MHz, CD_2Cl_2): δ_H (ppm) 2.14 (12H, s, 4CH_3), 2.32 (6H, s, 2CH_3), 3.77 (3H, s, OCH_3), 6.50 (2H, dd, $^3J_{HH}$ = 9.0 Hz, $^4J_{HP}$ = 3.0 Hz, H-Ar), 6.83 (4H, s, H-Ar), 6.99 (2H, s, H-Imidazole), 7.81 (2H, dd, $^3J_{HP}$ = 12.0 Hz, $^3J_{HH}$ = 9.0 Hz, H-Ar). ^{13}C NMR (75 MHz, CD_2Cl_2): δ_C (ppm) 19.2 (4CH_3), 21.4 (2CH_3), 55.8 (OCH_3), 112.4 (d, $^3J_{PC}$ = 15.1 Hz, C-Ar), 124.2 (CH-Imidazole), 129.7 (C-Ar), 131.0 (d, $^1J_{PC}$ = 97.4 Hz, C-Ar), 133.7 (C-Ar), 135.2 (d, $^2J_{PC}$ = 14.3 Hz, C-Ar), 135.6 (C-Ar), 140.8 (C-Ar), 148.8 (d, $^1J_{PC}$ = 26.4 Hz, C-Imidazole), 161.9 (d, $^4J_{PC}$ = 3.0 Hz, C-Ar). ^{31}P NMR (121 MHz, CD_2Cl_2): δ_P (ppm) 52.6 (t, $^3J_{HP}$ = 15.7 Hz). ^{31}P {1H} NMR (121 MHz, CD_2Cl_2): δ_P (ppm) 52.6.

Compound 5



To a stirred solution of 1,3-bis(2,6-di-*iso*-propylphenyl)imidazolidin-2-ylidene (1.0 mmol, 390 mg) in 15 mL THF was added 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-dithione (Lawesson's reagent) (0.5 mmol, 202 mg) and the mixture was stirred at ambient temperature for 12 h. Then, the solvent was removed under vacuum and the residue was crystallized from dichloromethane. The product was obtained in the form of colourless crystals (414 mg, yield 70%); mp 182-185 ºC. IR (KBr) (ν_{max}/cm^{-1}): 3415, 2961, 2867, 1654, 1637, 1592, 1490, 1459, 1273, 1254, 1181, 1090, 1031, 925, 801, 693, 574. HRMS (ESI) calcd for $C_{34}H_{45}N_2NaOPS_2$ [M + Na] 615.2603, found 615.2596. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H (ppm) 1.15 (12H, d, $^3J_{HH}$ = 6.0 Hz, 4CH_3), 1.38 (12H, d, $^3J_{HH}$ = 6.0 Hz, 4CH_3), 3.19 (4H, sep, $^3J_{HH}$ = 6.0 Hz, 4CH), 3.60 (3H, s, OCH_3), 4.00 (4H, s, 2CH_2), 6.31 (2H, dd, $^3J_{HH}$ = 9.0 Hz, $^4J_{HP}$ = 3.0 Hz, H-Ar), 6.99 (4H, d, $^3J_{HH}$ = 6.0 Hz, H-Ar), 7.2 (2H, t, $^3J_{HH}$ = 6.0 Hz, H-Ar), 7.59 (2H, dd, $^3J_{HP}$ = 15.0 Hz, $^3J_{HH}$ = 9.0 Hz, H-Ar). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C (ppm) 23.5 (CH_3 of isopropyl), 26.2 (CH_3 of isopropyl), 29.2 (CH of isopropyl), 53.8 (CH_2-Imidazole), 55.2 (OCH_3), 112.2 (d, $^3J_{PC}$ = 15.1 Hz, C-Ar), 124.5 (C-Ar), 128.3 (C-Ar), 130.1 (C-Ar), 131.0 (d, $^1J_{PC}$ = 95.1 Hz, C-Ar), 134.1 (C-Ar), 135.5 (d, $^2J_{PC}$ = 14.2 Hz, C-Ar), 146.0 (C-Ar), 160.4 (d, $^4J_{PC}$ = 3.0 Hz, C-Ar), 170.5 (d, $^1J_{PC}$ = 13.6 Hz, C- Imidazole). ^{31}P NMR (121 MHz, $CDCl_3$): δ_P (ppm) 62.9 (t, $^3J_{HP}$ = 14.6 Hz). ^{31}P {1H} NMR (121 MHz, $CDCl_3$): δ_P (ppm) 62.9.



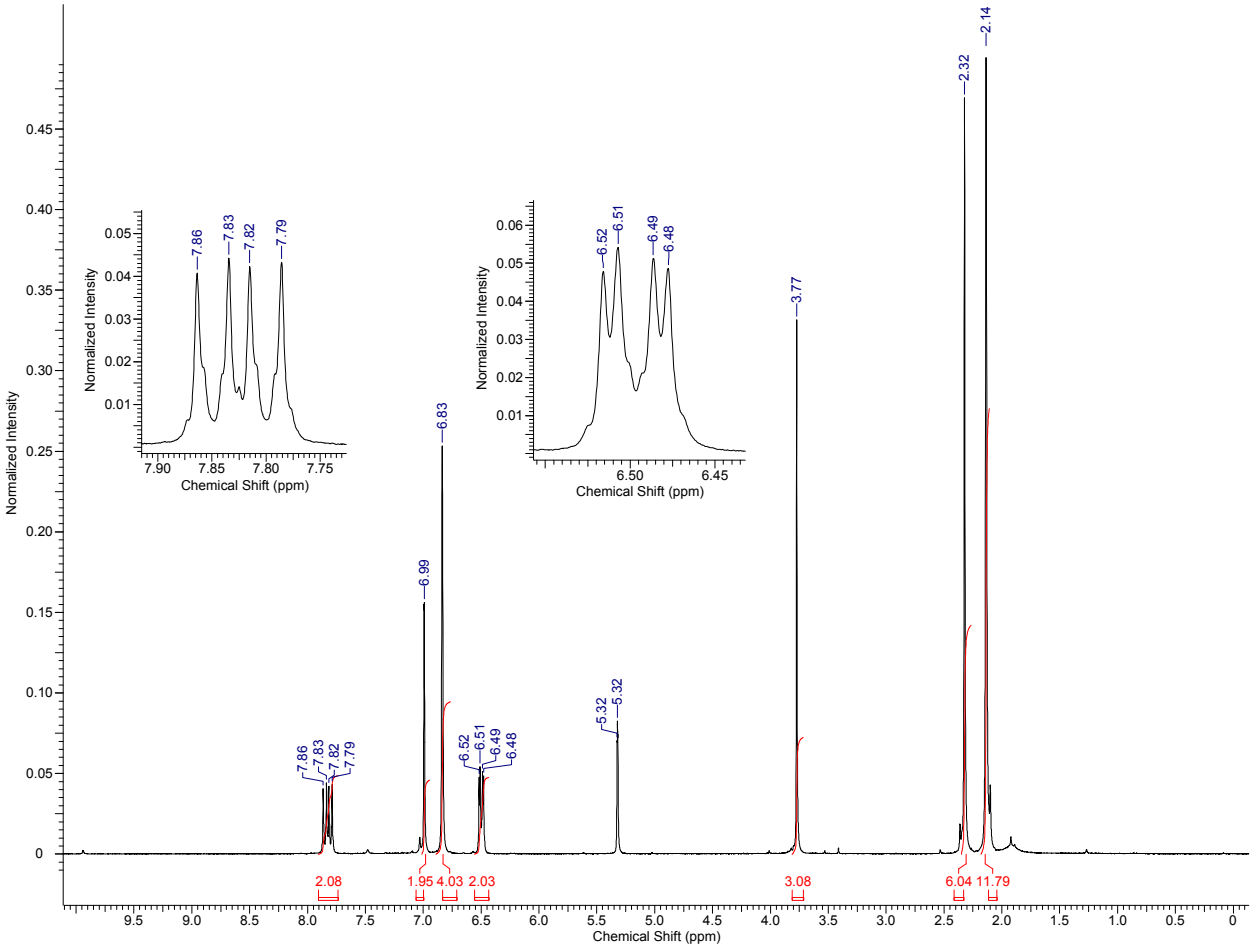


Figure S1. The ^{1}H NMR spectrum of compound **4** (CD_2Cl_2).

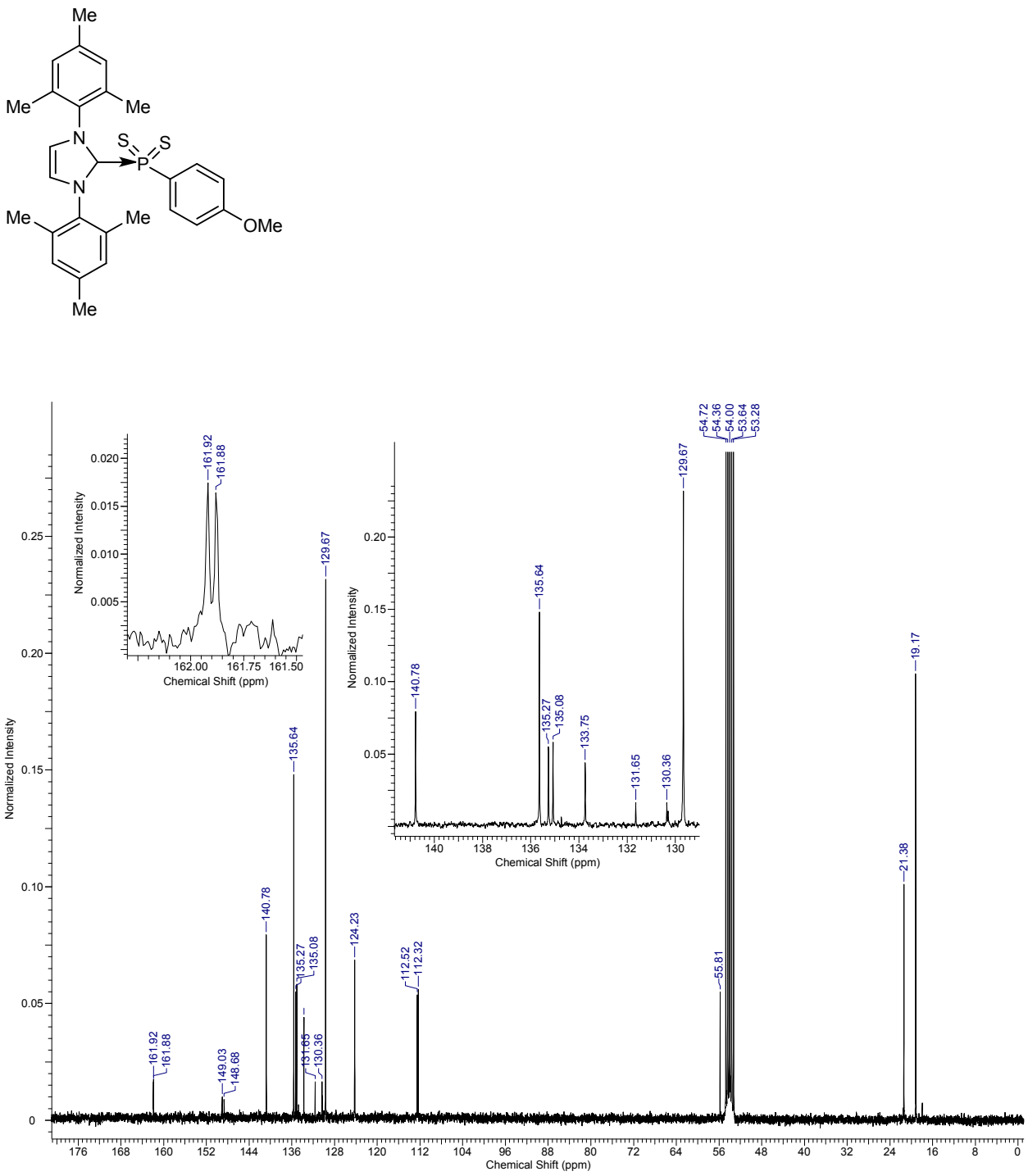


Figure S2. The ^{13}C NMR spectrum of compound **4** (CD_2Cl_2).

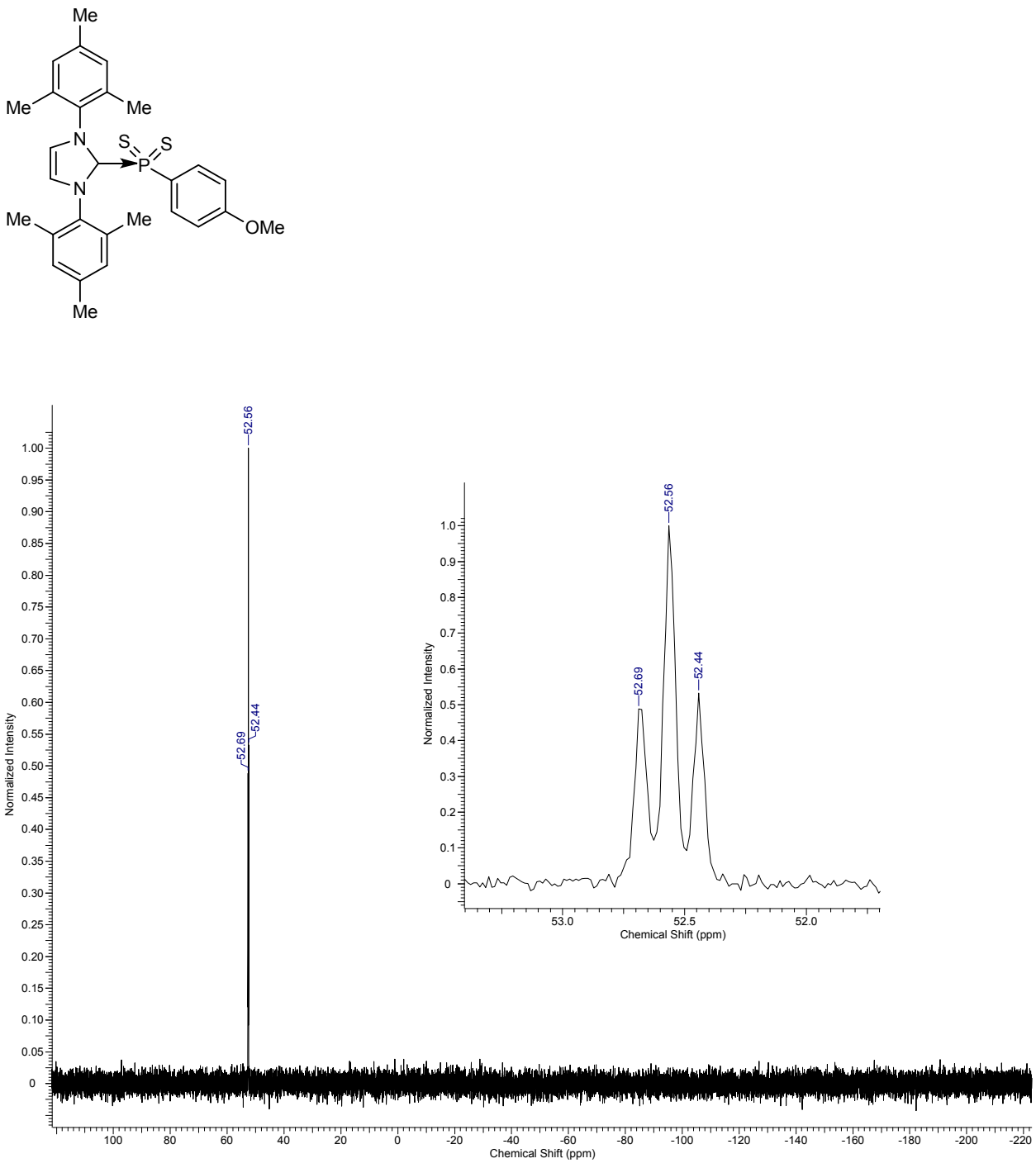


Figure S3. The ^{31}P NMR spectrum of compound **4** (CD_2Cl_2).

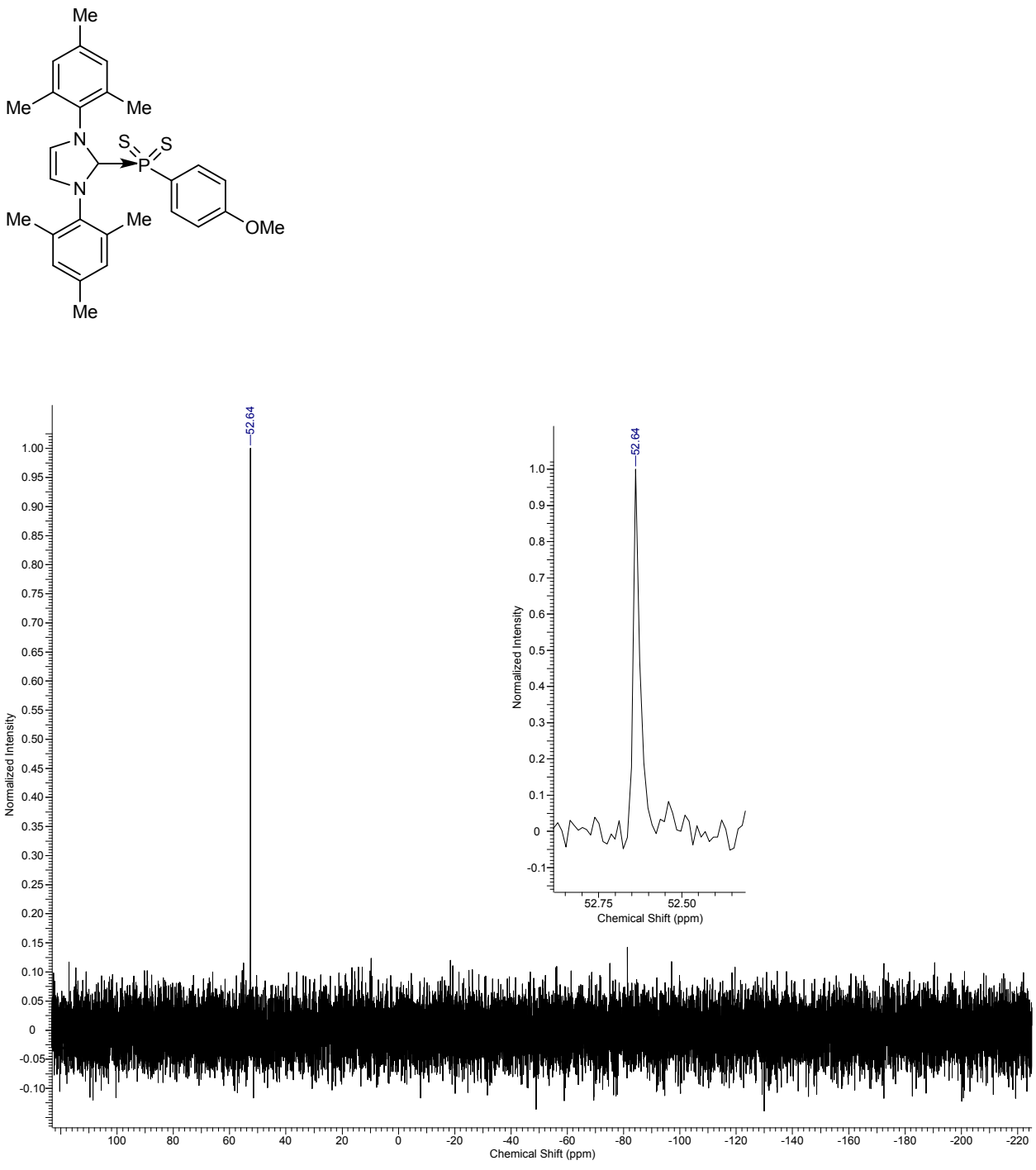
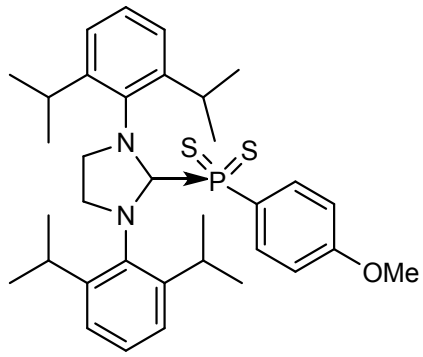


Figure S4. The ^{31}P $\{^{1}H\}$ NMR spectrum of compound **4** (CD_2Cl_2).



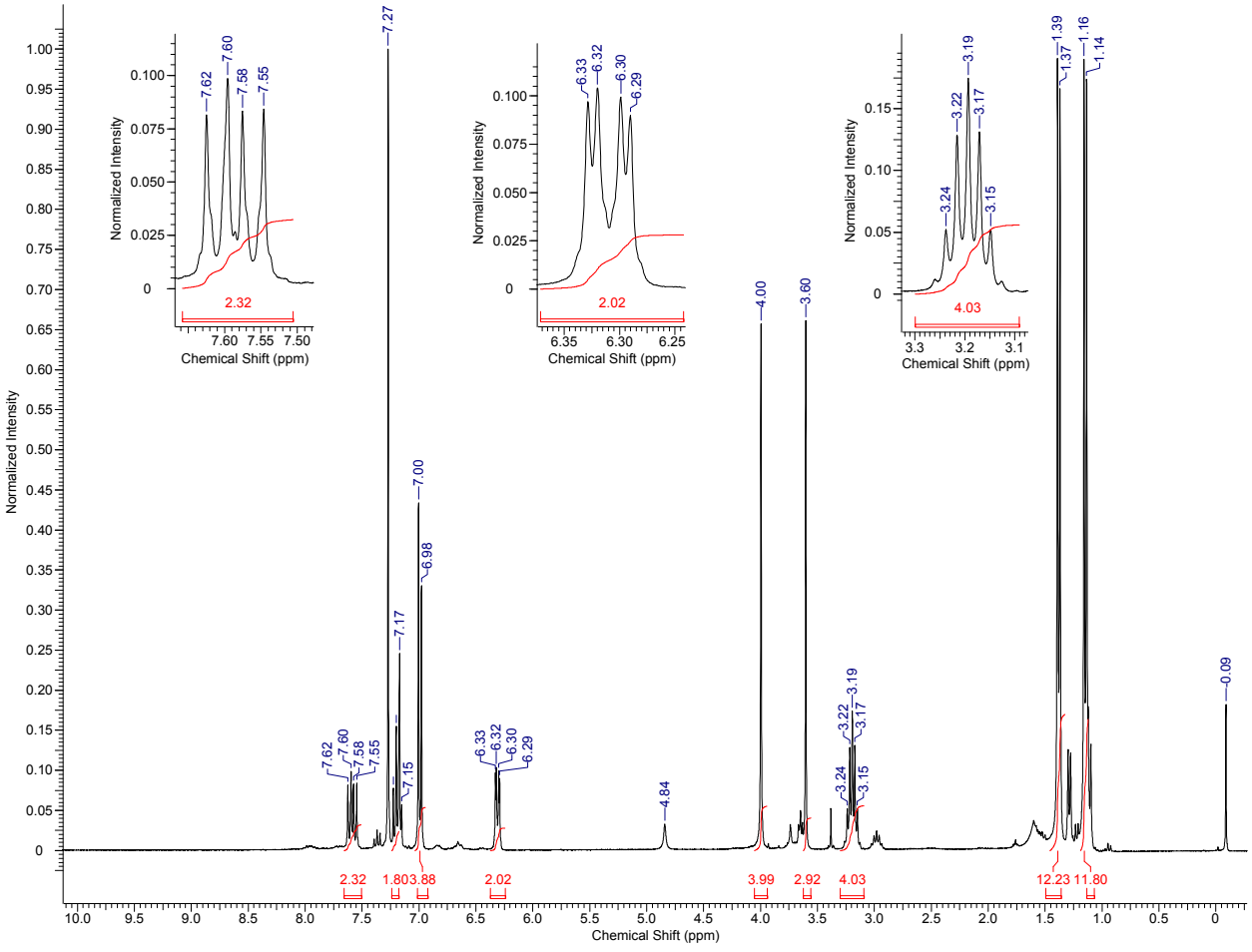


Figure S5. The ^{1}H NMR spectrum of compound **5** ($CDCl_3$).

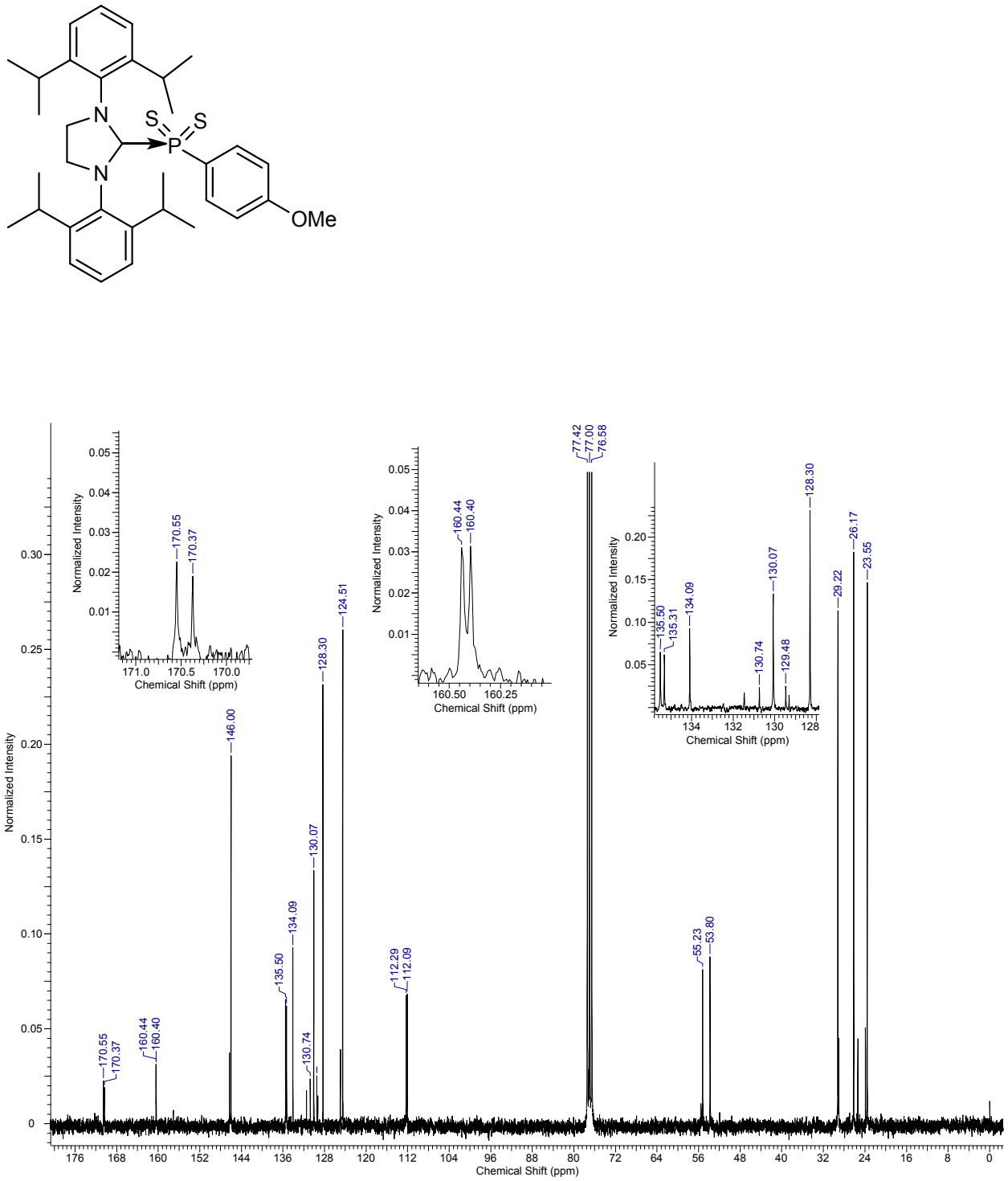
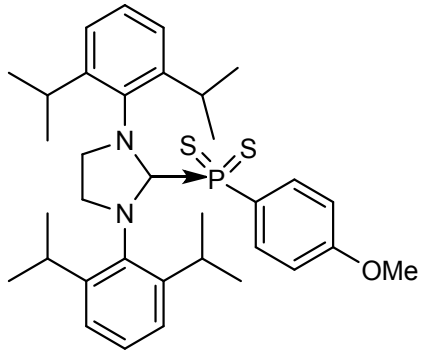


Figure S6. The ^{13}C NMR spectrum of compound **5** ($CDCl_3$).



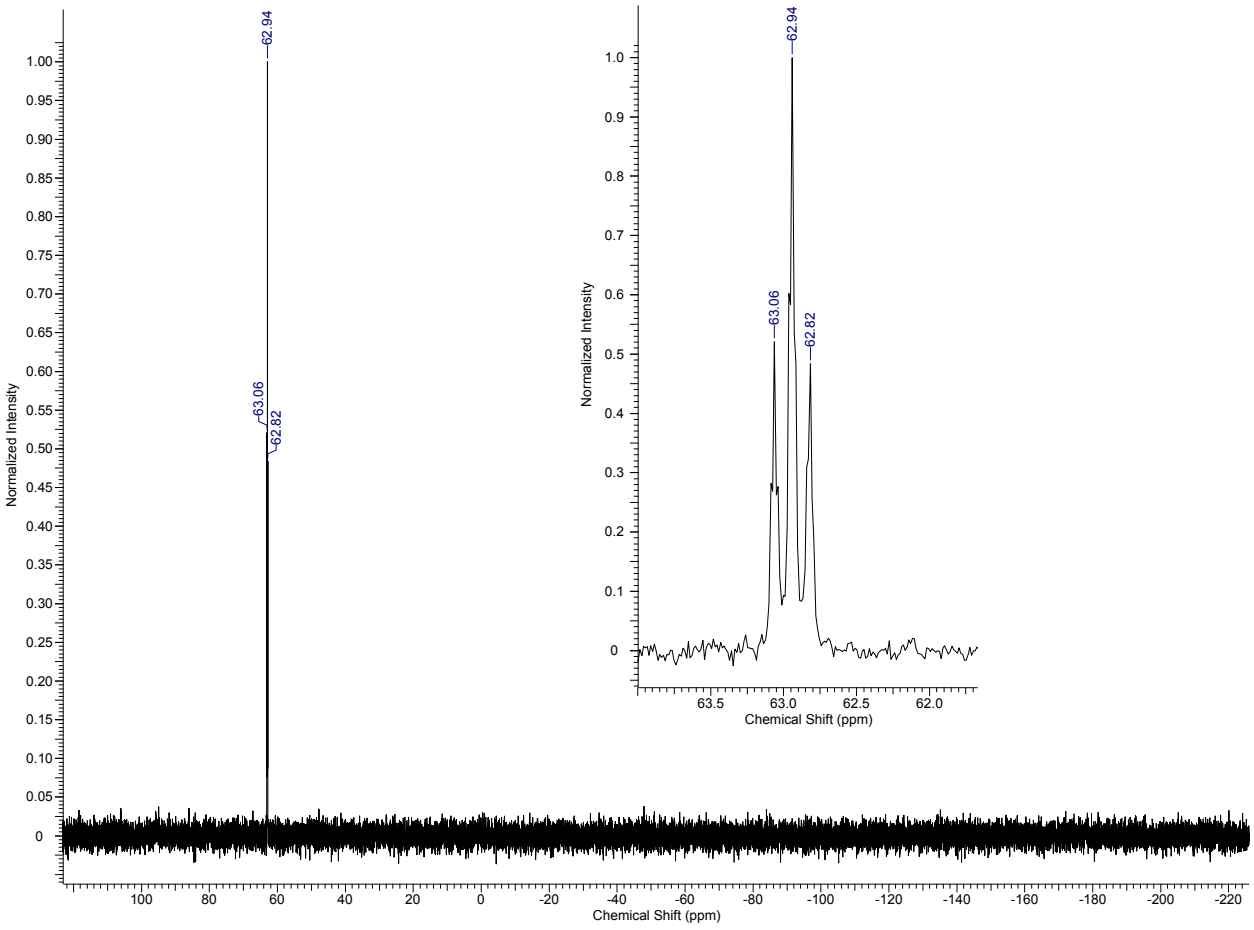
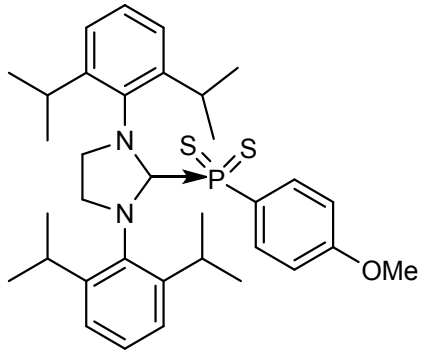


Figure S7. The ^{31}P NMR spectrum of compound **5** ($CDCl_3$).



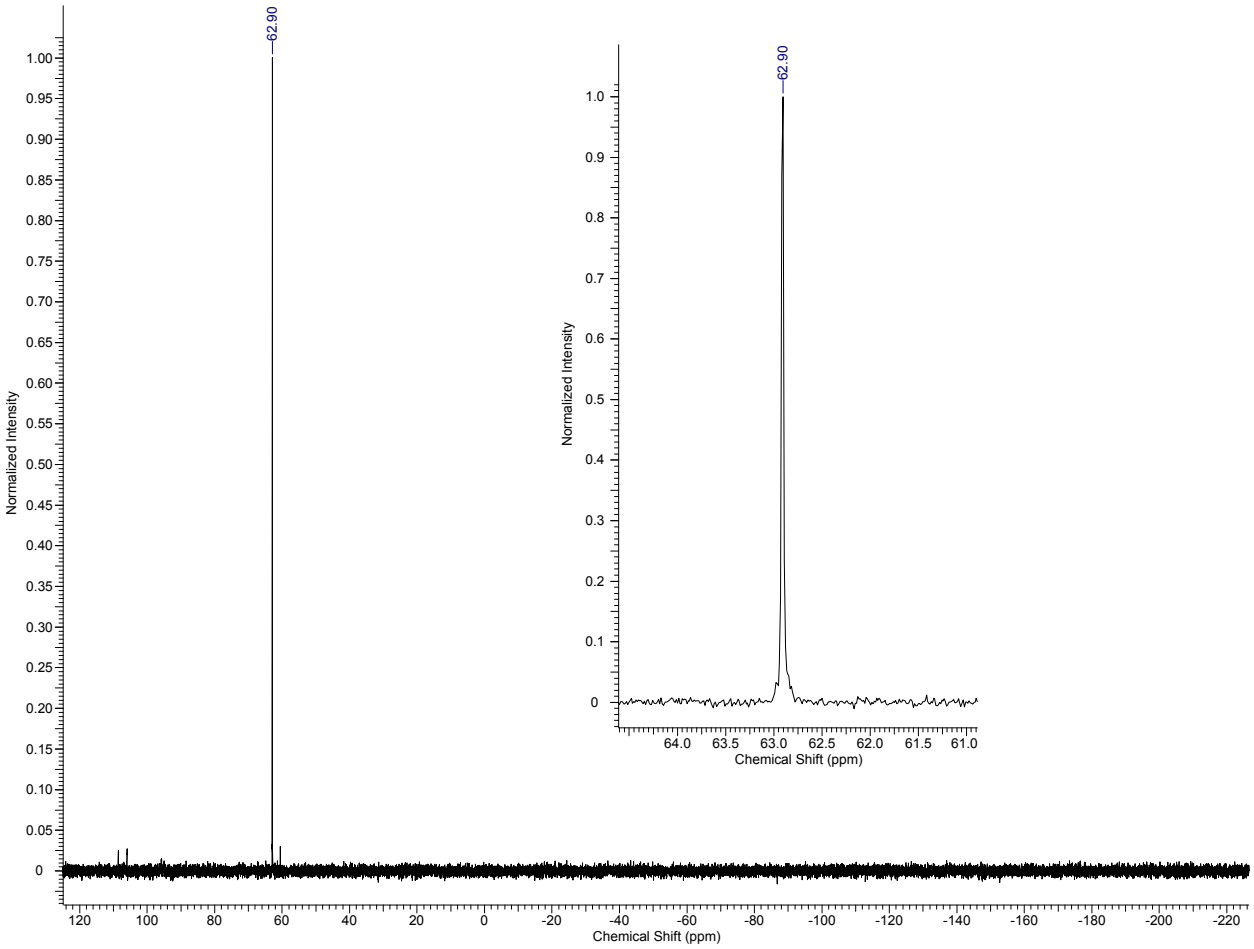


Figure S8. The ^{31}P $\{^{1}H\}$ NMR spectrum of compound **5** ($CDCl_3$).

Table S1. Details of the crystal data and structure refinements.

Identification code	**4**	**5**
Empirical formula	$C_{29}H_{33}Cl_2N_2OPS_2$	$C_{75}H_{98}N_4O_2P_2S_4$
Formula weight	591.56	1277.75
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$
Unit cell dimensions (Å and °)	a = 14.3251(3)	34.664(5)
	b = 13.4264(3)	13.266(2)
	c = 15.3146(3)	15.692(3)
	α = 90	90
	β = 99.1770(10)	105.515(2)
	γ = 90°	90
Volume (Å^3)	2907.82(11)	6953.1(19)
Z	4	4
Density (calculated, Mg/m^3)	1.351	1.221
Absorption coefficient (mm^{-1})	0.448	0.231
F(000)	1240	2744
Crystal size (mm3)	0.325x0.190x0.100	0.575x0.050x0.030
Theta range for data collection (°)	1.440 to 28.967	1.219 to 26.958
Reflections collected	51144	38530
Independent reflections	7287 [R(int) = 0.0327]	7542 [R(int) = 0.1101]
Completeness to theta = 25.242°	100.0 %	100.0 %
Max. and min. transmission	0.7458 and 0.6983	0.7454 and 0.6896
Data / restraints / parameters	7287 / 0 / 341	7542 / 0 / 403
Goodness-of-fit on F^2	1.033	1.011
Final R indices [I>2sigma(I)]	R1=0.0339, wR2=0.0820	R1=0.0515, wR2=0.0982
R indices (all data)	R1=0.0460, wR2=0.0884	R1=0.1089, wR2=0.1169
Largest diff. peak and hole (e.Å^{-3})	0.389 and -0.246	0.361 and -0.362

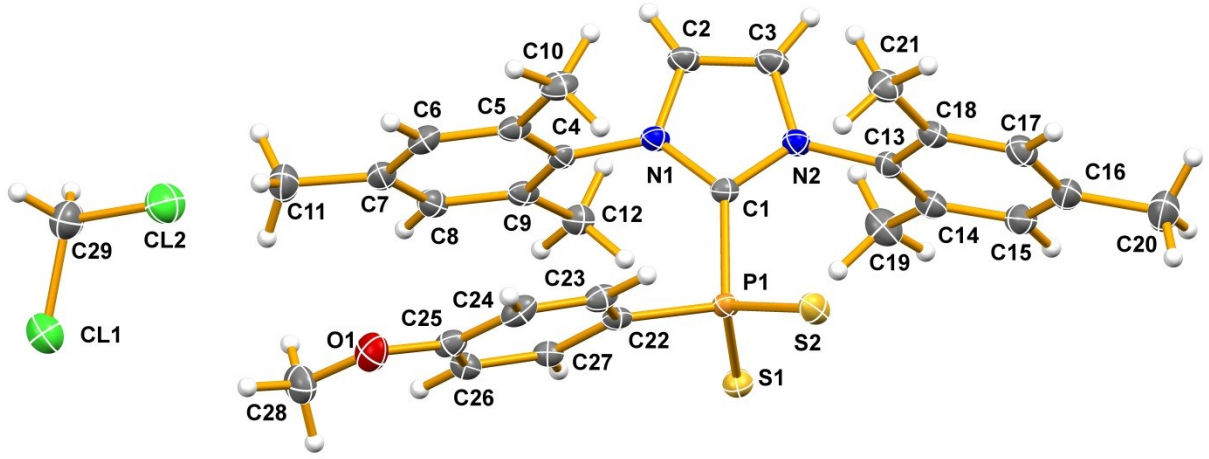


Figure S9. Structural diagram of compound **4**. Ellipsoids are drawn at the 50% probability level.

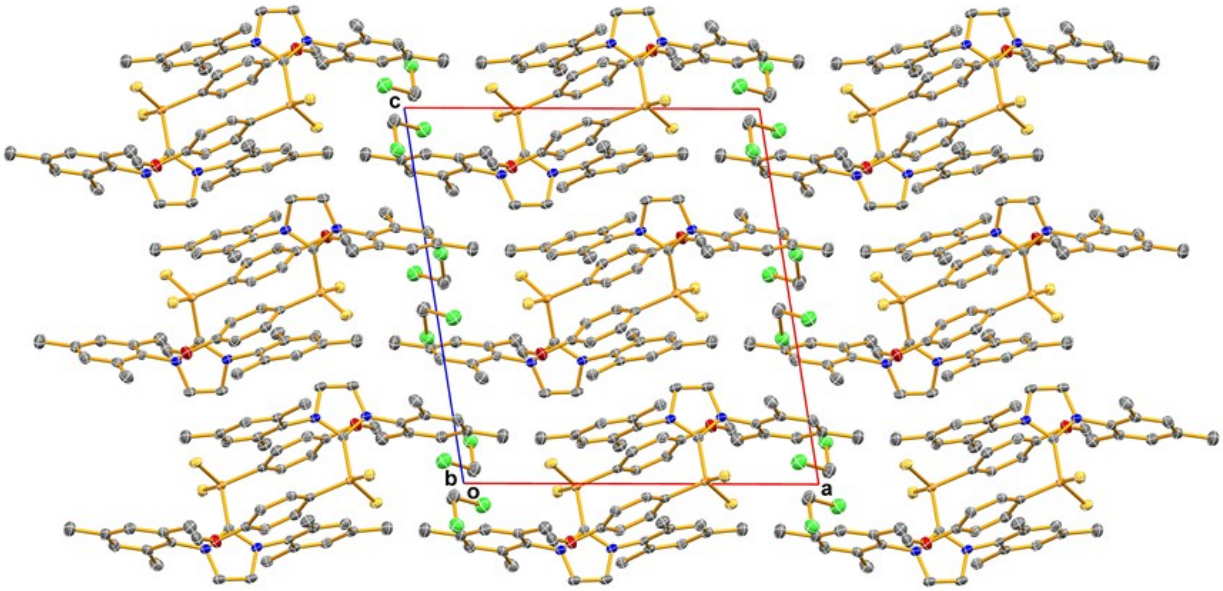


Figure S10. Packing diagram of compound **4** viewed down the *Y* axis. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Table S2. Contact distances less than the sum of the van der Waal radii for compound **4** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(2)-H(2)...C(22)#1	0.95	2.73	3.591(2)	151.0
C(3)-H(3)...Cl(1)#2	0.95	2.92	3.7560(17)	147.1
C(6)-H(6)...H(20B)#3	0.95	2.39	3.120(6)	133.7
C(10)-H(10B)...H(12B)#4	0.98	2.41	3.157(11)	132.8
C(10)-H(10C)...H(23)	0.98	2.52	3.425(2)	154.1
C(10)-H(10C)...C(23)	0.98	2.63	3.378(2)	133.7
C(11)-H(11B)...S(1)#5	0.98	2.90	3.8166(19)	157.0
C(12)-H(12C)...S(1)	0.98	2.93	3.8860(16)	166.4
C(12)-H(12C)...N(1)	0.98	2.74	2.8388(19)	85.9
C(17)-H(17)...Cl(2)#6	0.95	2.87	3.7858(17)	161.8
C(19)-H(19A)...S(1)	0.98	2.72	3.6525(17)	158.1
C(21)-H(21A)...N(2)	0.98	2.72	2.859(2)	87.8
C(21)-H(21C)...S(2)	0.98	2.86	3.5665(17)	129.9
C(23)-H(23)...S(2)	0.95	2.85	3.3186(17)	111.5
C(27)-H(27)...S(1)	0.95	2.81	3.2986(15)	112.9
C(29)-H(29B)...S(1)#3	0.99	2.89	3.5786(19)	127.1
C(29)-H(29B)...S(2)#3	0.99	3.01	3.956(2)	160.6

Symmetry transformations used to generate equivalent atoms:
#1 x,-y+3/2,z+1/2 #2 x+1,-y+3/2,z+1/2 #3 x-1,y,z
#4 -x+1,y-1/2,-z+3/2 #5 -x+1,-y+2,-z+1 #6 -x+1,-y+1,-z+1

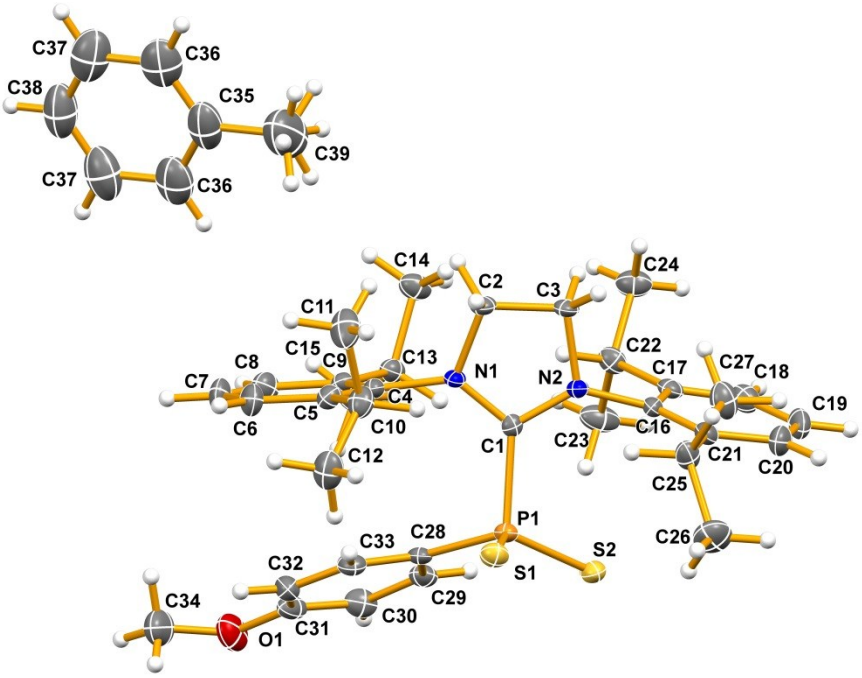


Figure S11. Structural diagram of compound **5**. Ellipsoids are drawn at the 50% probability level.

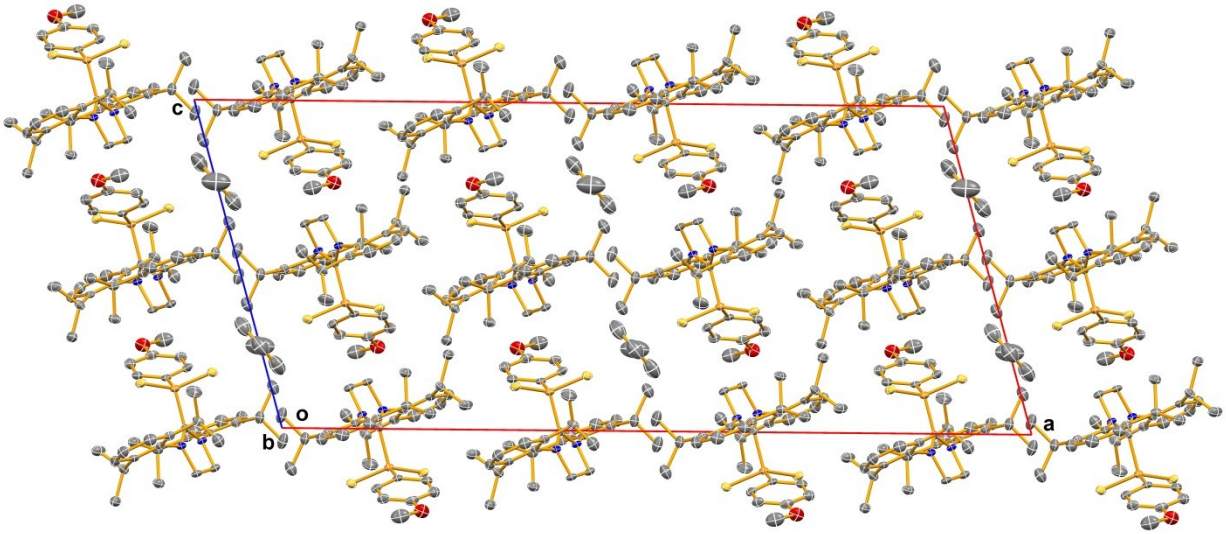


Figure S12. Packing diagram of compound **5** viewed down the *Y* axis. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Table S3. Contact distances less than the sum of the van der Waal radii for compound **5** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(23)-H(23C)...S(2)	0.98	2.99	3.854(3)	148.1
C(29)-H(29)...S(2)	0.95	2.78	3.256(3)	111.6
C(33)-H(33)...S(1)	0.95	2.85	3.320(3)	111.9
C(10)-H(10)...N(1)	1.00	2.48	2.942(3)	107.8
C(13)-H(13)...N(1)	1.00	2.61	2.912(3)	97.6
C(22)-H(22)...N(2)	1.00	2.41	2.912(3)	110.5
C(25)-H(25)...N(2)	1.00	2.46	2.935(3)	108.7
C(14)-H(14C)...C(2)	0.98	2.74	3.584(4)	145.1
C(15)-H(15A)...C(29)	0.98	2.97	3.632(4)	125.7
C(15)-H(15A)...C(30)	0.98	2.81	3.700(4)	151.9
C(26)-H(26B)...C(35)#1	0.98	2.82	3.781(3)	167.9
C(26)-H(26B)...C(39)#1	0.98	2.90	3.804(4)	153.4
C(27)-H(27C)...C(31)#2	0.98	3.10	3.788(4)	128.9
C(27)-H(27C)...C(32)#2	0.98	2.90	3.757(4)	147.2
C(2)-H(2A)...H(11A)	0.99	2.25	2.974(6)	129.1
C(6)-H(6)...H(12A)	0.95	2.27	2.794(13)	114.3
C(8)-H(8)...H(15C)	0.95	2.20	2.795(14)	119.9
C(10)-H(10)...H(2A)	1.00	2.32	2.847(4)	112.1
C(11)-H(11B)...H(10)#1	0.98	2.20	3.105(4)	152.9
C(14)-H(14C)...H(2B)	0.98	2.17	3.050(4)	149.2
C(22)-H(22)...H(3A)	1.00	2.39	2.913(4)	111.6
C(22)-H(22)...H(13)	1.00	2.34	3.171(4)	139.6
C(24)-H(24C)...H(18)	0.98	2.36	2.893(4)	113.6
C(26)-H(26B)...H(39C)#1	0.98	2.27	3.054(4)	136.7
C(34)-H(34A)...H(27A)#3	0.98	2.37	3.111(9)	131.8
C(32)-H(32)...H(34A)	0.95	2.34	2.811(17)	109.8
C(32)-H(32)...H(34C)	0.95	2.29	2.690(16)	104.8
C(39)-H(39B)...H(11A)	0.98	2.20	3.094(10)	151.5

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z+1 #2 x,-y+1,z+1/2 #3 x,-y+1,z-1/2

Table S4. Total Electronic Energies

		HF			B3LYP			MP2		
Species	Sym.	6-31G*	6-31+G*	6-311+G*	6-31G*	6-31+G*	6-311+G*	6-31G*	6-31+G*	6-311+G*
NHCunsat	C_{2v}	-302.8365319	-302.8481781	-302.9033273	-304.7924667	-304.8090816	-304.8691303	-303.7954105	-303.8184571	-303.9164857
pyridine	C_{2v}	-246.6958199	-246.7034912	-246.7446909	-248.2849730	-248.2958027	-248.3429437	-247.4825325	-247.4983885	-247.5733257
HPS_2	C_{2v}	-1136.3228389	-1136.3239690	-1136.3877267	-1138.3422030	-1138.3447926	-1138.4189334	-1136.6766806	-1136.6812556	-1136.7565667
$H(NHC)PS_2$	C_s #1	-1439.2149949	-1439.2222576	-1439.3413969	-1443.1861106	-1443.1973462	-1443.3308317	-1440.5371600	-1440.5613062	-1440.7388257
	C_1 #1	-1439.2260166	-1439.2333559	-1439.3525426	C_s #2	C_s #2	-1443.3406146	-1440.5451184	-1440.5707382	-1440.7478531
	C_s #2	-1439.2259187	-1439.2332112	-1439.3522134	-1443.1958998	-1443.2072026	-1443.3406037	-1440.5450787	-1440.5704303	-1440.7470197
	C_s #3	-1439.2251712	-1439.2326024	-1439.3516515	-1443.1941908	-1443.2057657	-1443.3392079	-1440.5432815	-1440.5688200	-1440.7455410
$HPyPS_2$	C_s #1	-1383.0455686	-1383.0534583	-1383.1592381	-1386.6503274	-1386.6611570	-1386.7827790	-1384.1905276	-1384.2134558	-1384.3654134
	C_s #2	-1383.0424916	-1383.0496158	-1383.1548230	-1386.6465255	-1386.6569261	-1386.7783387	-1384.1861293	-1384.2099271	-1384.3607927
$MeNHCPS_2$	C_s #1	-1478.2638509	-1478.2715847	-1478.3980629	-1482.5139136	-1482.5264612	-1482.6678926	-1479.7229828	-1479.7501012	-1479.9435923
	C_1 #1	-1478.2647022	-1478.2725419	-1478.3990111	-1482.5175689	-1482.5300677	-1482.6715313	-1479.7259755	-1479.7536704	-1479.9474119
$MePyPS_2$	C_s #1	-1422.0950345	-1422.1031134	-1422.2158601	-1425.9782563	-1425.9900341	-1426.1195746	-1423.3760752	-1423.4012347	-1423.5688071
$PhNHCPS_2$	C_s #1	-1668.7692335	-1668.7835387	-1668.9388797	-1674.2468244	-1674.2663422	-1674.4417835	-1670.8608088	-1670.9051943	-1671.1531005
	C_1 #1	-1668.7761560	-1668.7901133	-1668.9456956	-1674.2529563	-1674.2726400	-1674.4485973	-1670.8683033	-1670.9139415	-1671.1627332
$PhPyPS_2$	C_s #1	-1612.6011383	-1612.6159405	-1612.7571848	-1617.7116246	-1617.7308241	-1617.8941672	-1614.5135610	-1614.5566403	-1614.7783100
	C_1 #1	-1612.6013568	-1612.6159518	-1612.7572824	n/a	n/a	n/a	n/a	n/a	n/a
$(HPS_2)_2$	C_{2v}	-2272.6834123	-2272.6880311	-2272.8199834	-2276.7133866	-2276.7192820	-2276.8670441	-2273.3853753	-2273.3984018	-2273.5523297
	C_{2h}	-2272.6836784	-2272.6883821	-2272.8201566	-2276.7130567	-2276.7189363	-2276.8665644	-2273.3847583	-2273.3977693	-2273.5515184
$MePS_2$	C_s #1	-1175.3755553	-1175.3772225	-1175.4480962	-1177.6728756	-1177.6767166	-1177.7585403	-1175.8606564	-1175.8675877	-1175.9586671
	C_s #2	-1175.3755538	-1175.3772241	-1175.4480654	-1177.6728705	-1177.6767108	-1177.7585182	-1175.8606541	-1175.8676183	-1175.9586882
$(MePS_2)_2$	C_{2v} #1	-2350.7890877	-2350.7945763	-2350.9413044	-2355.3760900	-2355.3842857	-2355.5483199	-2351.7639895	-2351.7823021	-2351.9692522
	C_{2v} #2	-2350.7805140	-2350.7860189	-2350.9328456	-2355.3686125	-2355.3767818	-2355.5408225	-2351.7546650	-2351.7725974	-2351.9599810
	C_{2h} #1	-2350.7928865	-2350.7983373	-2350.9453373	-2355.3789707	-2355.3870561	-2355.5511814	-2351.7671247	-2351.7857318	-2351.9727302
	C_{2h} #2	-2350.7839649	-2350.7893046	-2350.9362390	-2355.3711370	-2355.3791523	-2355.5431894	-2351.7571430	-2351.7750685	-2351.9623203
$PhPS_2$	C_{2v} #1	-1365.8884145	-1365.8964642	-1365.9960089	-1369.4109791	-1369.4217122	-1369.5377547	-1366.9985182	-1367.0198465	-1367.1655585
	C_{2v} #2	-1365.8780816	-1365.8851494	-1365.9842191	-1369.4020441	-1369.4121784	-1369.5281124	-1366.9917448	-1367.0129418	-1367.1586949
$(PhPS_2)_2$	C_{2v} #1	-2731.7956961	-2731.8131218	-2732.0175811	-2738.8354450	-2738.8572203	-2739.0905091	-2734.0365471	-2734.0896929	-2734.3891432
	C_{2v} #2	-2731.7958343	-2731.8145489	-2732.0191242	-2738.8365901	-2738.8591227	-2739.0922183	-2734.0325603	-2734.0825247	-2734.3790083
	C_{2h} #1	-2731.7953237	-2731.8123936	-2732.0172816	-2738.8357116	-2738.8569165	-2739.0903720	-2734.0325578	-2734.0830725	-2734.3810299
	C_{2h} #2	-2731.8067816	-2731.8254030	-2732.0299876	-2738.8443189	-2738.8667606	-2739.0999886	-2734.0412429	-2734.0914585	-2734.3879643
$PhOMePS_2$	C_s #1	-1479.7732982	-1479.7833326	-1479.9099735	-1483.9376253	-1483.9520362	-1484.0958248	-1481.1891739	-1481.2177526	-1481.4127112
$(PhOMePS_2)_2$	C_{2h} #1	-2959.5739958	-2959.5964725	-2959.8553585	-2967.8951879	-2967.9250064	-2968.2139030	-2962.4213900	-2962.4855584	-2962.8808603
	C_{2h} #2	-2959.5736168	-2959.5961649	-2959.8549780	-2967.8950544	-2967.9249676	-2968.2138412	-2962.4212257	-2962.4857524	-2962.8806947

Cartesian Coordinates (MP2/6-31G*) (Atomic number, x, y, z) of the Important Species in Table S4.

NHCunsat (1,3-dimethylimidazol-2-ylidene) C_{2v}

6	0.000000	0.000000	0.992102
7	0.000000	1.059021	0.115836
7	0.000000	-1.059021	0.115836
6	0.000000	0.683120	-1.214542
6	0.000000	-0.683120	-1.214542
1	0.000000	1.390396	-2.032340
1	0.000000	-1.390396	-2.032340
6	0.000000	2.438126	0.572690
6	0.000000	-2.438126	0.572690
1	0.000000	2.408960	1.661204
1	0.891750	2.961544	0.217542
1	-0.891750	2.961544	0.217542
1	0.000000	-2.408960	1.661204
1	-0.891750	-2.961544	0.217542
1	0.891750	-2.961544	0.217542

pyridine C_{2v}

7	0.000000	0.000000	1.426615
6	0.000000	1.145533	0.720997
6	0.000000	-1.145533	0.720997
6	0.000000	1.197712	-0.673752
6	0.000000	-1.197712	-0.673752
6	0.000000	0.000000	-1.387838
1	0.000000	2.061983	1.308623
1	0.000000	-2.061983	1.308623
1	0.000000	2.156858	-1.184201
1	0.000000	-2.156858	-1.184201
1	0.000000	0.000000	-2.475052

HPS_2 C_{2v}

15	0.000000	0.000000	0.475534
1	0.000000	0.000000	1.884015

16	0.000000	1.760783	-0.281782
16	0.000000	-1.760783	-0.281782

$(HPS_2)_2$ C_{2h}

15	0.000000	1.465526	0.000000
15	0.000000	-1.465526	0.000000
16	0.000000	0.000000	1.549490
16	0.000000	0.000000	-1.549490
16	1.319795	2.852464	0.000000
16	-1.319795	-2.852464	0.000000
1	-1.334138	1.902593	0.000000
1	1.334138	-1.902593	0.000000

H(NHC)PS_2 C_1 #1

15	-1.163955	-0.588528	-0.124038
1	-0.875935	-1.924548	-0.486932
6	0.616239	-0.054788	-0.060611
16	-1.951404	0.383786	-1.638382
16	-1.780422	-0.496207	1.741332
7	1.030855	1.212613	0.172121
7	1.741188	-0.804126	-0.174493
6	2.402393	1.263509	0.197252
6	2.854217	-0.010606	-0.021337
1	2.938952	2.185009	0.367249
1	3.856847	-0.407738	-0.076605
6	0.137015	2.360537	0.369748
6	0.772555	-2.251005	-0.398819
1	-0.349670	2.602829	-0.574693
1	-0.616627	2.083635	1.108028
1	0.742836	3.191517	0.730588
1	1.319665	-2.487534	-1.361787
1	1.237379	-2.757463	0.404800
1	2.816285	-2.564338	-0.398065

$HPyPS_2$ C_s #1

15	-0.539618	-1.351892	0.000000
1	-1.903206	-0.991308	0.000000
7	-0.089687	0.645378	0.000000
16	0.052756	-1.956622	1.742543
16	0.052756	-1.956622	-1.742543
6	0.052756	1.287700	1.172941
6	0.052756	1.287700	-1.172941
6	0.331879	2.649731	1.201563
6	0.331879	2.649731	-1.201563
6	0.473247	3.343830	0.000000
1	-0.050904	0.671342	2.061981
1	-0.050904	0.671342	-2.061981
1	0.444082	3.150894	2.157865
1	0.444082	3.150894	-2.157865
1	0.695628	4.407327	0.000000

$(MePS_2)_2$ C_{2h} #1

15	0.000000	1.458572	0.000000
15	0.000000	-1.458572	0.000000
16	0.000000	0.000000	1.562449
16	0.000000	0.000000	-1.562449
16	1.385694	2.790157	0.000000
16	-1.385694	-2.790157	0.000000
6	-1.705550	2.079812	0.000000
6	1.705550	-2.079812	0.000000
1	-2.408234	1.243894	0.000000
1	-1.855795	2.695969	0.890708
1	-1.855795	2.695969	-0.890708
1	2.408234	-1.243894	0.000000
1	1.855795	-2.695969	0.890708
1	1.855795	-2.695969	-0.890708

$MePS_2$ C_s #1

15	0.000000	0.148630	0.000000
6	0.069420	1.976598	0.000000
16	-1.765339	-0.612583	0.000000
16	1.721399	-0.705610	0.000000
1	-0.941977	2.384637	0.000000
1	0.614250	2.308701	0.886898
1	0.614250	2.308701	-0.886898

$MeNHCPS_2$ C_1 #1

15	1.176985	-0.153211	0.112780
6	1.371957	-1.041985	1.704027
6	-0.701841	0.075465	0.115457
16	2.021308	1.612060	0.296921
16	1.504038	-1.335167	-1.433156
7	-1.426147	1.206020	-0.120555
7	-1.622390	-0.928425	0.198560
6	-2.765657	0.909980	-0.172290
6	-2.890027	-0.436147	0.031810
1	-3.511626	1.668859	-0.354346
1	-3.762590	-1.071490	0.065291
6	-0.930239	2.573838	-0.344565
6	-1.336242	-2.356994	0.363390
1	-0.421451	2.931141	0.546782
1	-0.227878	2.577146	-1.174065
1	-1.802837	3.186996	-0.572420
1	-1.232762	-2.599591	1.421337
1	-0.421376	-2.580849	-0.188315
1	-2.172436	-2.911206	-0.063451
1	2.450049	-1.099650	1.877899
1	0.922218	-0.465000	2.517043
1	0.972438	-2.056596	1.679302

$MePyPS_2$ C_s #1

15	-0.283938	-1.287847	0.000000
6	-2.091288	-1.013414	0.000000
7	0.064260	0.729045	0.000000
16	0.383578	-1.863535	1.731941
16	0.383578	-1.863535	-1.731941
6	0.174151	1.378562	1.172691
6	0.174151	1.378562	-1.172691
6	0.383578	2.753074	1.201578
6	0.383578	2.753074	-1.201578
6	0.488612	3.453849	0.000000
1	0.109095	0.754595	2.060573
1	0.109095	0.754595	-2.060573
1	0.471917	3.258934	2.157989
1	0.471917	3.258934	-2.157989
1	0.657648	4.527141	0.000000
1	-2.578711	-1.991884	0.000000
1	-2.391434	-0.468521	0.898353
1	-2.391434	-0.468521	-0.898353

$PhPS_2$ C_{2v} #1

15	0.000000	0.000000	1.222911
6	0.000000	0.000000	-0.591086
16	0.000000	1.737328	2.047591
16	0.000000	-1.737328	2.047591
6	0.000000	1.217602	-1.287802
6	0.000000	-1.217602	-1.287802
6	0.000000	1.209616	-2.682041
6	0.000000	-1.209616	-2.682041
6	0.000000	0.000000	-3.381075
1	0.000000	2.156012	-0.740204
1	0.000000	-2.156012	-0.740204
1	0.000000	2.152352	-3.223361
1	0.000000	-2.152352	-3.223361
1	0.000000	0.000000	-4.468353

$(PhPS_2)_2$ C_{2h} #2

15	0.000000	1.466743	0.000000
15	0.000000	-1.466743	0.000000
16	0.000000	0.000000	1.552202
16	0.000000	0.000000	-1.552202
16	1.444896	2.741475	0.000000
16	-1.444896	-2.741475	0.000000
6	-1.672126	2.161493	0.000000
6	1.672126	-2.161493	0.000000
6	-2.790605	1.313834	0.000000
6	-1.831831	3.552370	0.000000
6	2.790605	-1.313834	0.000000
6	1.831831	-3.552370	0.000000
6	-4.068278	1.869776	0.000000
6	-3.117810	4.095319	0.000000
6	4.068278	-1.869776	0.000000
6	3.117810	-4.095319	0.000000
6	-4.234716	3.258265	0.000000
6	4.234716	-3.258265	0.000000
1	-2.671436	0.231955	0.000000
1	-0.956533	4.196509	0.000000
1	2.671436	-0.231955	0.000000
1	0.956533	-4.196509	0.000000
1	-4.936652	1.215791	0.000000
1	-3.244620	5.175025	0.000000
1	4.936652	-1.215791	0.000000
1	3.244620	-5.175025	0.000000
1	-5.234709	3.685035	0.000000
1	5.234709	-3.685035	0.000000

PhNHCPS$_2$ C$_1$ #1

15	-0.171765	-1.065332	0.254525
6	1.445175	-0.311421	-0.164815
6	-1.212536	0.477257	-0.010407
16	-0.650418	-2.391596	-1.111806
16	-0.343822	-1.397342	2.190089
7	-2.464902	0.566127	-0.537131
7	-0.938454	1.715801	0.488363
6	-2.952443	1.840368	-0.386785
6	-1.988706	2.565717	0.259405
1	-3.931904	2.123632	-0.742000
1	-1.969822	3.599481	0.571053
6	-3.257666	-0.515225	-1.140765
6	0.253651	2.090849	1.256783
1	-2.792367	-0.840007	-2.068343
1	-3.302946	-1.358746	-0.455654
1	-4.254575	-0.111055	-1.320036
1	1.107342	2.213086	0.590870
1	0.447434	1.302793	1.986056
1	0.027585	3.028587	1.765561
6	2.514188	-0.378994	0.734867
6	1.616315	0.321473	-1.405410
6	3.741954	0.198966	0.403955
6	2.838668	0.913968	-1.723872
6	3.903640	0.855881	-0.818364
1	2.365081	-0.870813	1.693868
1	0.800088	0.329946	-2.126199
1	4.573029	0.138431	1.103200
1	2.967146	1.409559	-2.683843
1	4.858289	1.311563	-1.071117

$PhPyPS_2$ C_s #1

15	-1.335287	0.120434	0.000000
6	-0.019729	1.390667	0.000000
7	0.096369	-1.346418	0.000000
16	-2.198825	-0.088389	1.727730
16	-2.198825	-0.088389	-1.727730
6	0.576989	-1.795671	1.172486
6	0.576989	-1.795671	-1.172486
6	1.601163	-2.735794	1.201574
6	1.601163	-2.735794	-1.201574
6	2.124621	-3.213534	0.000000
1	0.100494	-1.388222	2.060481
1	0.100494	-1.388222	-2.060481
1	1.974004	-3.089061	2.157987
1	1.974004	-3.089061	-2.157987
1	2.923459	-3.950020	0.000000
6	0.504070	1.859471	-1.212988
6	0.504070	1.859471	1.212988
6	1.542717	2.791426	-1.208659
6	1.542717	2.791426	1.208659
6	2.069611	3.253282	0.000000
1	0.072372	1.515952	-2.149914
1	0.072372	1.515952	2.149914
1	1.938786	3.160516	-2.151995
1	1.938786	3.160516	2.151995
1	2.876059	3.982849	0.000000

$PhOMePS_2$ C_s #1

15	-0.733369	1.887544	0.000000
6	0.000000	0.240412	0.000000
16	-2.657226	1.939550	0.000000
16	0.517372	3.349622	0.000000
6	-0.821362	-0.893704	0.000000
6	1.398205	0.085708	0.000000
6	-0.265518	-2.171944	0.000000
6	1.953504	-1.183793	0.000000
6	1.127798	-2.319605	0.000000
1	-1.901991	-0.777769	0.000000
1	2.041383	0.961440	0.000000
1	-0.926209	-3.032030	0.000000
1	3.030354	-1.328254	0.000000
8	1.785081	-3.511346	0.000000
6	0.988639	-4.698154	0.000000
1	1.701939	-5.520784	0.000000
1	0.362235	-4.752639	0.895960
1	0.362235	-4.752639	-0.895960

$(PhOMePS_2)_2$ C_{2h} #1

15	0.000000	1.468798	0.000000
15	0.000000	-1.468798	0.000000
16	0.000000	0.000000	1.551243
16	0.000000	0.000000	-1.551243
16	1.452747	2.737256	0.000000
16	-1.452747	-2.737256	0.000000
6	-1.661073	2.167133	0.000000
6	1.661073	-2.167133	0.000000
6	-2.792271	1.330660	0.000000
6	-1.822572	3.554639	0.000000
6	2.792271	-1.330660	0.000000
6	1.822572	-3.554639	0.000000
6	-4.060212	1.888978	0.000000
6	-3.099218	4.120025	0.000000
6	4.060212	-1.888978	0.000000

6	3.099218	-4.120025	0.000000
6	-4.221901	3.284800	0.000000
6	4.221901	-3.284800	0.000000
1	-2.686590	0.247285	0.000000
1	-0.946642	4.198347	0.000000
1	2.686590	-0.247285	0.000000
1	0.946642	-4.198347	0.000000
1	-4.949990	1.265442	0.000000
1	-3.195752	5.200242	0.000000
1	4.949990	-1.265442	0.000000
1	3.195752	-5.200242	0.000000
8	-5.515588	3.714565	0.000000
8	5.515588	-3.714565	0.000000
6	-5.731137	5.126191	0.000000
6	5.731137	-5.126191	0.000000
1	-6.812934	5.250921	0.000000
1	-5.306170	5.590890	0.895606
1	-5.306170	5.590890	-0.895606
1	6.812934	-5.250921	0.000000
1	5.306170	-5.590890	0.895606
1	5.306170	-5.590890	-0.895606

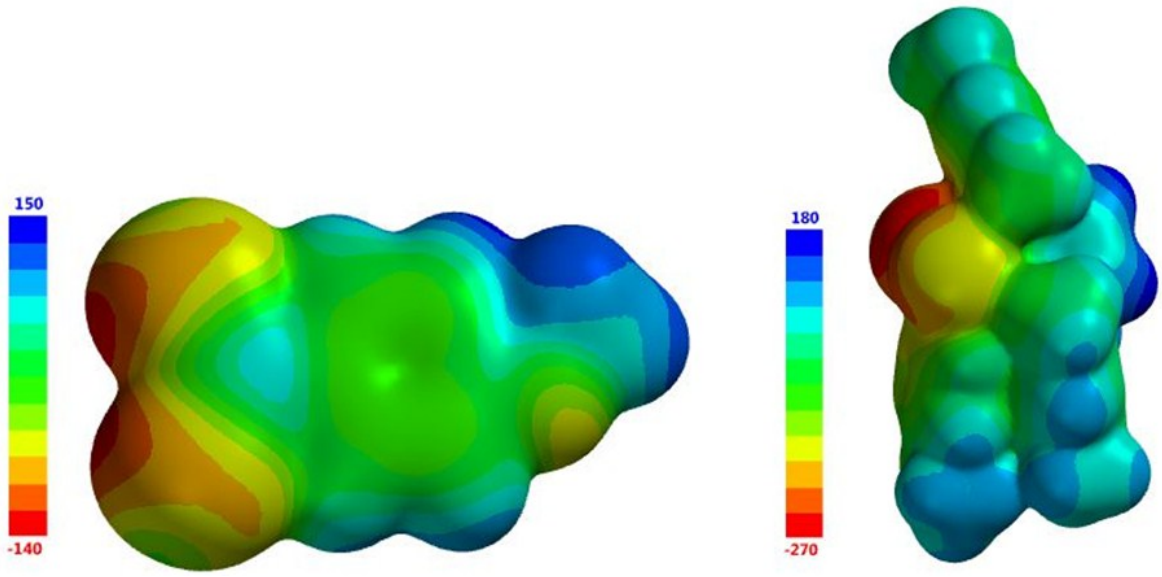


Figure S13. Electrostatic potentials [atomic units (au)] superimposed on the total electron density isosurface ($3x10^{-3}$ au) of (left) **2** and (right) **4** calculated using DFT [B3LYP/6-31G*].

$ArPS_2$

Cartesian Coordinates (Angstroms)

Atom X Y Z

--- --- --- ---

1 P P1 2.0218292 -0.0656068 0.0000096
2 S S1 3.0034207 1.6086801 0.0006010
3 S S2 2.7279810 -1.8747825 -0.0004006
4 C C1 0.2256200 0.0789111 -0.0001548
5 C C4 -2.5706183 0.2954992 -0.0001715
6 C C2 -0.3923397 1.3476981 -0.0006683
7 C C6 -0.5790014 -1.0723148 0.0003176
8 C C5 -1.9656754 -0.9721611 0.0003370
9 C C3 -1.7706142 1.4536911 -0.0006906
10 H H2 0.2201291 2.2432972 -0.0010121
11 H H6 -0.1127975 -2.0521742 0.0006706
12 H H5 -2.5634503 -1.8761313 0.0007520
13 H H3 -2.2609683 2.4216497 -0.0010949
14 O O1 -3.9050854 0.5085465 -0.0002028
15 C C7 -4.7815300 -0.6148612 0.0005111
16 H H1 -4.6383698 -1.2309702 -0.8952975
17 H H4 -5.7906009 -0.2011156 0.0003883
18 H H7 -4.6381678 -1.2299603 0.8969809

$ArPS_2$-IMes

Cartesian Coordinates (Angstroms)

Atom X Y Z

--- --- --- ---

1 S S1 0.7659126 -0.6377634 -2.6565335
2 S S2 1.6694799 -2.4250491 0.0975799
3 P P1 0.5324479 -1.0652345 -0.7431936
4 O O1 -5.1866872 -2.3994597 0.3574217
5 N N1 -0.0678450 1.4756322 0.6006019
6 N N2 2.0459903 1.0481705 0.5159421
7 C C1 0.8286354 0.5489705 0.1784443
8 C C2 0.5898974 2.5366450 1.1949992
9 H H2 0.0419285 3.3766181 1.5914162
10 C C3 1.9009222 2.2716006 1.1400210
11 H H3 2.7618051 2.8252508 1.4795939
12 C C4 -1.5072071 1.5270843 0.4448627
13 C C5 -2.3068863 1.0812960 1.4946705
14 C C6 -3.6759094 1.2528790 1.3599063
15 H H6 -4.3260848 0.9023508 2.1584376
16 C C7 -4.2381930 1.8697554 0.2456972
17 C C8 -3.3935195 2.2973504 -0.7758524
18 H H8 -3.8158509 2.7811104 -1.6542676
19 C C9 -2.0122931 2.1513603 -0.6947174
20 C C10 -1.7134742 0.4603291 2.7352136
21 H H10A -2.4979090 0.0144744 3.3524930
22 H H10B -1.1930588 1.2077095 3.3489587
23 H H10C -0.9926517 -0.3251345 2.4923013
24 C C11 -5.7237211 2.1050594 0.1613731
25 H H11A -6.2726997 1.4707085 0.8646466
26 H H11B -6.1065881 1.9086597 -0.8466472
27 H H11C -5.9737649 3.1475332 0.3991621
28 C C12 -1.0918225 2.6573720 -1.7680320
29 H H12A -0.3143103 3.3148164 -1.3606284
30 H H12B -1.6514358 3.2298570 -2.5142439
31 H H12C -0.5808094 1.8357283 -2.2867658
32 C C13 3.3670633 0.4813925 0.3170196
33 C C14 4.0636208 0.8082207 -0.8428582
34 C C15 5.3632379 0.3118491 -0.9536184

35 H H15 5.9304067 0.5425384 -1.8526953
36 C C16 5.9534888 -0.4402711 0.0498302
37 C C17 5.2333433 -0.6821037 1.2152168
38 H H17 5.6963682 -1.2417304 2.0250235
39 C C18 3.9331351 -0.2199626 1.3837950
40 C C19 3.4759510 1.6955130 -1.9082333
41 H H19A 2.6555083 1.1908207 -2.4311407
42 H H19B 4.2407595 1.9587667 -2.6449285
43 H H19C 3.0813576 2.6300041 -1.4896621
44 C C20 7.3566845 -0.9767905 -0.0873242
45 H H20A 7.9351111 -0.8265728 0.8315953
46 H H20B 7.8945935 -0.4949889 -0.9101733
47 H H20C 7.3457236 -2.0557082 -0.2887360
48 C C21 3.1831677 -0.4603581 2.6610770
49 H H21A 2.7754238 0.4655810 3.0851381
50 H H21B 3.8392602 -0.9083652 3.4135394
51 H H21C 2.3485707 -1.1491590 2.4874396
52 C C22 -1.2157960 -1.4286397 -0.4218556
53 C C23 -1.5914353 -2.2156476 0.6763193
54 H H23 -0.8207367 -2.6097411 1.3321860
55 C C24 -2.9148457 -2.5316556 0.9024366
56 H H24 -3.2109023 -3.1499292 1.7448864
57 C C25 -3.9029469 -2.0636262 0.0398482
58 C C26 -3.5490659 -1.2973534 -1.0722779
59 H H26 -4.2945804 -0.9463535 -1.7747376
60 C C27 -2.2163399 -1.0007703 -1.2948051
61 H H27 -1.9333273 -0.4369606 -2.1770207
62 C C28 -6.2170205 -1.9031644 -0.5000197
63 H H28A -6.2296353 -0.8070010 -0.5221379
64 H H28B -7.1542350 -2.2687183 -0.0761963
65 H H28C -6.1082759 -2.2871685 -1.5217196

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