Electronic supporting information

Homolytic dissociation of a Ge(I) dimer to a monomeric Ge(I) radical

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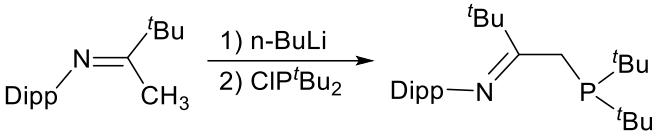
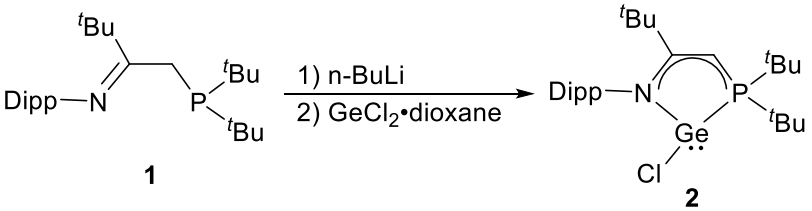
General Procedure. All operations were carried out under atmosphere of dry nitrogen with standard Schlenk and glove box techniques. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker Avance III HD spectrometer at 600, 151, and 243 MHz at ambient temperature, respectively. All chemical shifts were reported in δ units with references to the residual solvent resonances of the deuterated solvents for proton and carbon chemical shifts. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, m = multiplet, and br = broad signal. Mass spectra were measured on a Waters Q-Tof Premier Mass spectrometer. EPR spectrum was measured on a Bruker EMXplus-9.5/12 electron paramagnetic resonance spectrometer. UV-vis spectrum was measured on a Shimadzu UV-2600 spectrophotometer. All organic solvents were distilled from sodium benzophenone ketyl and stored over 4 Å molecular sieves in a nitrogen-filled glove box. Compound DippNC(^{t}Bu)CH_3 (Dipp = 2,6-$^{i}Pr_2$-C_6H_3)[1] was prepared according to literature procedures. All other chemicals were purchased from either J&K, Mayer, Energy Chemical or TCI, and used as received unless otherwise specified.



1

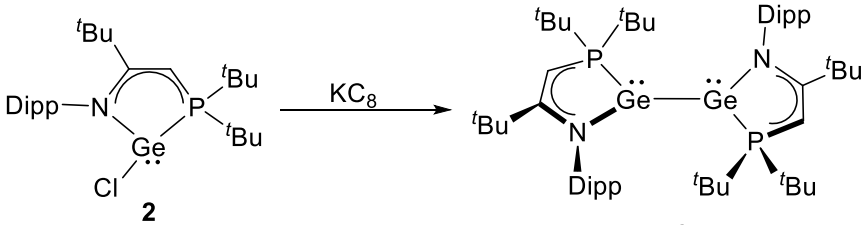
Preparation of 1. To a diethylether solution (15 mL) of DippNC(^{t}Bu)CH_3 (2.59 g, 10.0 mmol) was added via syringe n-BuLi (1.6 M in n-hexane, 6.3 mL, 10.1 mmol) at -78 ºC under stirring. The resulting mixture was allowed to warm up to room temperature and stirred overnight. All volatiles were removed in vacuo, and the residue was washed with n-hexane (3 x 5 mL) to give DippNC(^{t}Bu)CH_2Li as a white solid. To a THF solution (18 mL) of DippNC(^{t}Bu)CH_2Li (1.33 g, 5.0 mmol) was added via syringe di-*tert*-butylchlorophosphine (0.95 mL, 5.0 mmol) at -78 ºC under stirring. The resulting mixture was allowed to warm up to room temperature and stirred for 24 h. All volatiles were removed in vacuo, and the residue was extracted with toluene (18 mL). After filtration, the colorless filtrate was concentrated to about 3 mL. Compound **1** was isolated as colorless crystals after standing the solution for 2 days at room temperature (1.51 g, 75%). ^{1}H NMR (600 MHz, C_6D_6, 298K): δ = 7.18-7.17 (m, 2H; Ar-*H*), 7.10-7.07 (m, 1H; Ar-*H*), 2.95-2.89 (m, 2H; C*H*Me_2), 2.55 (d, *J* = 3.0 Hz, 2H; CH_2), 1.60 (s, 9H; CMe_3), 1.33 (d, *J* = 6.6 Hz, 6H; CHMe_2), 1.25 (d, *J* = 6.6 Hz, 6H; CHMe_2), 0.96 (d, *J* = 10.8 Hz, 18H; CMe_3). $^{13}C\{^{1}H\}$ NMR (151 MHz, C_6D_6, 298K): δ = 176.5 (d, *J* = 9.1 Hz, N*C*), 145.2, 136.4, 123.7, 123.0 (Ar-*C*), 42.7 (d, *J* = 1.5 Hz, *C*Me_3), 32.2 (d, *J* = 25.7 Hz, *C*Me_3), 30.4 (d, *J* = 9.1 Hz, CMe_3), 29.7 (d, *J* = 13.6 Hz, CMe_3), 29.1 (*C*HMe_2), 25.6 (d, *J* = 36.2 Hz, *C*H_2), 24.6 (CHMe_2), 21.3 (CMe_3). $^{31}P\{^{1}H\}$ NMR (243 MHz, C_6D_6, 298K): δ = 26.4. HRMS (ESI): *m/z* calcd for $C_{26}H_{46}NP+H^{+}$: 404.3446 $[M+H]^{+}$; found: 404.3443.



1 **2**

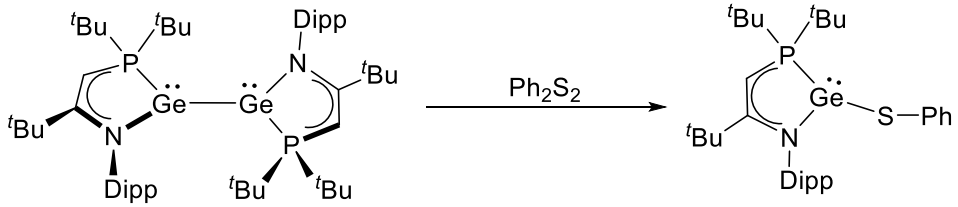
Preparation of 2. To a diethylether solution (20 mL) of **1** (2.02 g, 5.0 mmol) was added via syringe n-BuLi (1.6 M in n-hexane, 4.1 mL, 6.6 mmol) at -30 ºC under stirring. The resulting

mixture was allowed to warm up to room temperature and heated at 70 ºC for 24 h. The resulting mixture was added to a diethylether suspension (12 mL) of $GeCl_2$·dioxane (1.16 g, 5.0 mmol) at room temperature and stirred for 12 h. All volatiles were removed in vacuo, and the residue was extracted with toluene (30 mL). After filtration, the filtrate was concentrated to about 3 mL. Compound **2** was isolated as colorless crystals after this solution stood at -30 ºC overnight (1.63 g, 64%). ^{1}H NMR (600 MHz, C_6D_6, 298K): δ = 7.14-7.13 (m, 2H; Ar-*H*), 7.05-7.03 (m, 1H; Ar-*H*), 4.38 (s, 1H; CC*H*), 3.86-3.80 (m, 1H; C*H*Me$_2$), 3.41-3.34 (m, 1H; C*H*Me$_2$), 1.62 (d, *J* = 6.6 Hz, 3H; CH*Me*$_2$), 1.39 (d, *J* = 6.6 Hz, 6H; CH*Me*$_2$), 1.34 (d, *J* = 14.4 Hz, 9H; C*Me*$_3$), 1.31 (d, *J* = 6.6 Hz, 3H; CH*Me*$_2$), 1.11 (s, 9H; C*Me*$_3$), 1.09 (d, *J* = 14.4 Hz, 9H; C*Me*$_3$). ^{13}C{^{1}H} NMR (151 MHz, C_6D_6, 298K): δ = 181.0 (d, *J* = 13.6 Hz, N*C*), 148.5, 146.3 (Ar-*C*), 141.9 (d, *J* = 4.6 Hz, Ar-*C*), 126.8, 124.9, 124.3 (Ar-*C*), 70.3 (d, *J* = 48.3 Hz, C*C*H), 41.3 (d, *J* = 10.6 Hz, *C*Me$_3$), 39.5 (d, *J* = 6.0 Hz, *C*Me$_3$), 34.4 (d, *J* = 25.7 Hz, *C*Me$_3$), 33.3, 29.6 (*C*HMe$_2$), 28.9 (d, *J* = 3.0 Hz, C*Me*$_3$), 28.8, 28.0 (CH*Me*$_2$), 27.8 (d, *J* = 3.0 Hz, C*Me*$_3$), 27.2, 25.1, 24.3 (C*Me*$_3$). ^{31}P{^{1}H} NMR (243 MHz, C_6D_6, 298K): δ = 21.5. HRMS (ESI): *m/z* calcd for $C_{26}H_{45}NPGeCl+H^+$: 512.2268 [*M*+H]$^+$; found: 512.2248.



2 **3**

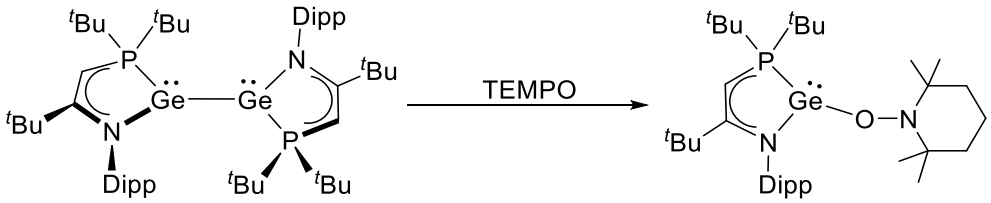
Preparation of 3. Toluene (10 mL) was added to a flask containing **2** (2.55 g, 5.0 mmol) and KC_8 (878 mg, 6.5 mmol) at room temperature. The resulting mixture was stirred at room temperature for 14 days. After filtration, the dark red filtrate was concentrated to about 6 mL. Compound **3** was obtained as dark purple crystals after this solution stood at -30 ºC overnight (1.45 g, 61%). Magnetic susceptibility (Evans method, C_6D_6, 298 K): μ_{eff} = 2.06 μ_B. UV-vis (toluene) λ = 495 nm (ε = 4317 L·mol^{-1}·cm^{-1}). HRMS (ESI): *m/z* calcd for $C_{26}H_{45}NPGe+H^+$: 477.2580 [0.5*M*+H]$^+$; found: 477.2561. (The absence of a peak assignable to Ge(I) dimer **3** in the mass spectrum may be attributed to dissociation of this species into the monomeric Ge(I) radical, potentially occurring in solution.)



3 **5**

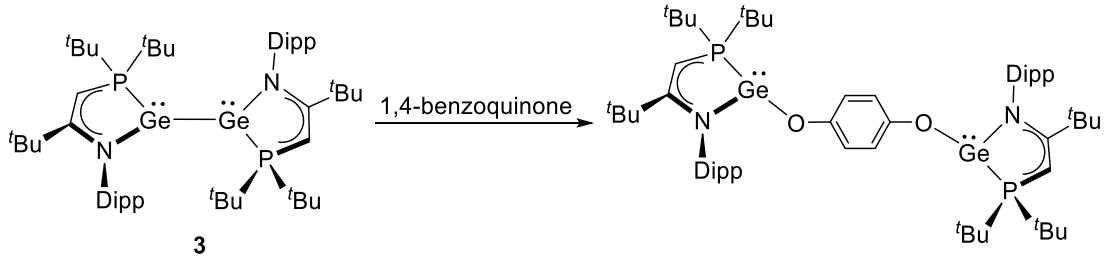
Preparation of 5. Toluene (10 mL) was added to a flask containing **3** (1.90 g, 2.0 mmol) and diphenyl disulfide (437 mg, 2.0 mmol) at room temperature. The resulting mixture was stirred at room temperature overnight. All volatiles were removed in vacuo, and the residue was washed with n-hexane (3 x 2 mL). Compound **5** was obtained as a white solid (1.35 g, 58%). ^{1}H NMR (600 MHz, C_6D_6, 298K): δ = 7.20-7.19 (m, 2H; Ar-*H*), 7.10-7.08 (m, 1H; Ar-*H*), 7.01-7.00 (m, 2H; Ar-*H*), 6.92 (t, *J* = 6.6 Hz, 2H; Ar-*H*), 6.89-6.86 (m, 1H; Ar-*H*), 4.30 (s, 1H; CC*H*), 3.64-3.58 (m,

1H; C*H*Me$_2$), 3.53-3.47 (m, 1H; C*H*Me$_2$), 1.66 (d, *J* = 6.6 Hz, 3H; CH*Me$_2$*), 1.39 (d, *J* = 6.6 Hz, 3H; CH*Me$_2$*), 1.36-1.31 (m, 15H; CH*Me$_2$*+C*Me$_3$*), 1.17 (d, *J* = 14.4 Hz, 9H; C*Me$_3$*), 1.15 (s, 9H; C*Me$_3$*). ^{13}C{^{1}H} NMR (151 MHz, C_6D_6, 298K): δ = 179.2 (d, *J* = 13.6 Hz, N*C*), 148.0, 145.9, 143.1 (Ar-*C*), 141.6 (d, *J* = 12.1 Hz, Ar-*C*), 134.3, 128.4, 126.1, 125.2 (Ar-*C*), 124.7 (d, *J* = 9.1 Hz, Ar-*C*), 67.4 (d, *J* = 51.3 Hz, C*C*H), 41.5 (d, *J* = 10.6 Hz, *C*Me$_3$), 39.4 (d, *J* = 4.5 Hz, *C*Me$_3$), 34.4 (d, *J* = 28.7 Hz, *C*Me$_3$), 33.2, 29.9 (*C*HMe$_2$), 29.0 (CH*Me$_2$*), 28.6 (d, *J* = 3.0 Hz, C*Me$_3$*), 27.9, 27.6, 26.7, 25.2, 24.8 (C*Me$_3$*). ^{31}P{^{1}H} NMR (243 MHz, C_6D_6, 298K): δ = 26.3. HRMS (ESI): *m/z* calcd for $C_{32}H_{50}NPGeS+H^+$: 586.2692 [*M*+H]$^+$; found: 586.2700.



3 **6**

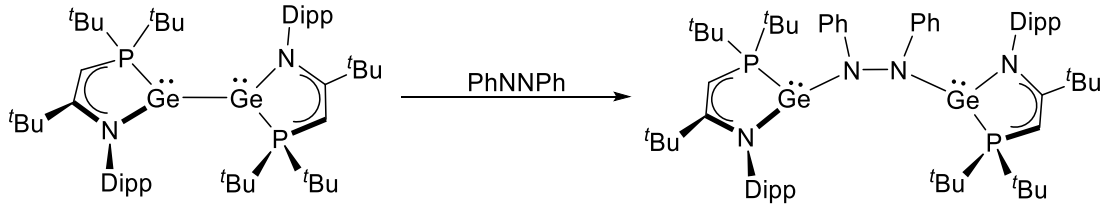
Preparation of 6. Toluene (10 mL) was added to a flask containing **3** (1.90 g, 2.0 mmol) and 2,2,6,6-tetramethylpiperidinyl-1-oxide (625 mg, 4.0 mmol) at room temperature. The resulting mixture was stirred overnight at room temperature. All volatiles were removed in vacuo, and the residue was washed with n-hexane (3 x 2 mL). Compound **6** was obtained as a white solid (1.72 g, 68%). ^{1}H NMR (600 MHz, C_6D_6, 298K): δ = 7.13-7.12 (m, 2H; Ar-*H*), 7.06-7.04 (m, 1H; Ar-*H*), 4.41 (s, 1H; CC*H*), 3.64-3.58 (m, 1H; C*H*Me$_2$), 3.56-3.52 (m, 1H; C*H*Me$_2$), 1.68 (d, *J* = 6.6 Hz, 3H; CH*Me$_2$*), 1.62 (d, *J* = 6.6 Hz, 3H; CH*Me$_2$*), 1.49 (br, 6H; C*H$_2$*), 1.40 (d, *J* = 6.6 Hz, 3H; CH*Me$_2$*), 1.32-1.28 (overlap, 18H; CH*Me$_2$*+NC*Me$_2$*+C*Me$_3$*), 1.25 (d, *J* = 12.6 Hz, 9H; C*Me$_3$*), 1.21 (s, 9H; C*Me$_3$*), 1.02 (br, 3H; NC*Me*), 0.41 (br, 3H; NC*Me*). ^{13}C{^{1}H} NMR (151 MHz, C_6D_6, 298K): δ = 175.9 (d, *J* = 15.1 Hz, N*C*), 147.9, 145.5 (Ar-*C*), 144.8 (d, *J* = 3.0 Hz, Ar-*C*), 125.7, 124.8, 123.9 (Ar-*C*), 69.7 (d, *J* = 45.3 Hz, C*C*H), 59.0 (N*C*Me$_2$), 41.7 (d, *J* = 10.6 Hz, *C*Me$_3$), 38.4 (d, *J* = 6.0 Hz, *C*Me$_3$), 34.4 (d, *J* = 21.1 Hz, *C*Me$_3$), 33.5, 30.1 (*C*HMe$_2$), 29.2, 28.4 (CH*Me$_2$*), 28.3 (d, *J* = 6.0 Hz, C*Me$_3$*), 27.8 (d, *J* = 4.5 Hz, C*Me$_3$*), 25.7, 25.4 (NC*Me$_2$*), 24.4 (*C*H$_2$), 17.7 (C*Me$_3$*). ^{31}P{^{1}H} NMR (243 MHz, C_6D_6, 298K): δ = 8.5. HRMS (ESI): *m/z* calcd for $C_{35}H_{63}N_2PGeO+H^+$: 633.3968 [*M*+H]$^+$; found: 633.3943.



3 **7**

Preparation of 7. Toluene (10 mL) was added to a flask containing **3** (1.90 g, 2.0 mmol) and 1,4-benzoquinone (216 mg, 2.0 mmol) at room temperature. The resulting mixture was stirred at room temperature overnight. All volatiles were removed in vacuo, and the residue was washed with n-hexane (3 x 2 mL). Compound **7** was obtained as a white solid (1.14 g, 54%). ^{1}H NMR (600 MHz, C_6D_6, 298K): δ = 7.19-7.18 (m, 2H; Ar-*H*), 7.13-7.09 (m, 4H; Ar-*H*), 6.39 (s, 4H; Ar-*H*), 4.33 (s, 2H; CC*H*), 3.73-3.60 (m, 2H; C*H*Me$_2$), 3.59-3.53 (m, 2H; C*H*Me$_2$), 1.47-1.45 (m,

6H; CH*Me*$_2$), 1.36-1.32 (m, 18H; CH*Me*$_2$), 1.26 (d, *J* = 13.8 Hz, 18H; C*Me*$_3$), 1.17 (s, 18H; C*Me*$_3$), 1.11 (d, *J* = 13.8 Hz, 18H; C*Me*$_3$). ^{13}C{^{1}H} NMR (151 MHz, C_6D_6, 298K): δ = 180.0 (d, *J* = 15.1 Hz, N*C*), 155.1 (d, *J* = 4.5 Hz, Ar-*C*), 155.0 (d, *J* = 4.5 Hz, Ar-*C*), 148.6 (d, *J* = 3.0 Hz, Ar-*C*), 145.8 (d, *J* = 4.5 Hz, Ar-*C*), 143.1 (d, *J* = 4.5 Hz, Ar-*C*), 126.0 (Ar-*C)*, 124.6 (d, *J* = 4.5 Hz, Ar-*C*), 124.3 (d, *J* = 1.5 Hz, Ar-*C*), 120.5, 120.4 (Ar-*C),* 68.8 (d, *J* = 9.1 Hz, C*C*H), 68.5 (d, *J* = 9.1 Hz, C*C*H), 41.2 (d, *J* = 9.1 Hz, *C*Me$_3$), 37.9 (d, *J* = 6.0 Hz, *C*Me$_3$), 33.8 (d, *J* = 25.7 Hz, *C*Me$_3$), 33.3, 29.4 (*C*HMe$_2$), 29.0, 28.8, 28.0, 27.5 (CH*Me*$_2$), 26.2 (d, *J* = 4.5 Hz, C*Me*$_3$), 24.9 (d, *J* = 4.5 Hz, C*Me*$_3$), 24.6 (C*Me*$_3$). ^{31}P{^{1}H} NMR (243 MHz, C_6D_6, 298K): δ = 13.5, 13.4. HRMS (ESI): *m/z* calcd for $C_{58}H_{94}N_2P_2Ge_2O_2$+H$^+$: 1061.5292 [*M*+H]$^+$; found: 1061.5300.



3 **8**

Preparation of 8. Toluene (10 mL) was added to a flask containing **3** (1.90 g, 2.0 mmol) and azobenzene (364 mg, 2.0 mmol) at room temperature. The resulting mixture was stirred at room temperature overnight. All volatiles were removed in vacuo, and the residue was washed with n-hexane (3 x 2 mL). Compound **8** was obtained as a yellow solid (1.61 g, 71%). ^{1}H NMR (600 MHz, C_6D_6, 298K): δ = 7.27 (d, *J* = 7.2 Hz, 4H; Ar-*H*), 7.17-7.12 (m, 2H; Ar-*H*), 7.06-7.02 (m, 4H; Ar-*H*), 6.98 (d, *J* = 7.2 Hz, 2H; Ar-*H*), 6.89 (d, *J* = 7.2 Hz, 2H; Ar-*H*), 6.80 (t, *J* = 7.2 Hz, 2H; Ar-*H*), 4.67 (s, 2H; CC*H*), 3.94-3.88 (m, 2H; C*H*Me$_2$), 3.20-3.13 (m, 2H; C*H*Me$_2$), 1.29-1.27 (overlap, 30H; CH*Me*$_2$+C*Me*$_3$), 1.22-1.21 (overlap, 36H; CH*Me*$_2$+C*Me*$_3$), 0.89 (d, *J* = 6.0 Hz, 6H; CH*Me*$_2$), 0.72 (d, *J* = 6.0 Hz, 6H; CH*Me*$_2$). ^{13}C{^{1}H} NMR (151 MHz, C_6D_6, 298K): δ = 179.3 (d, *J* = 18.1 Hz, N*C*), 153.6, 148.9, 148.4, 142.9, 126.6, 124.6, 124.3, 118.8, 117.2 (Ar-*C),* 75.8 (d, *J* = 30.2 Hz, C*C*H), 42.5 (d, *J* = 10.6 Hz, *C*Me$_3$), 37.9 (d, *J* = 6.0 Hz, *C*Me$_3$), 36.4 (d, *J* = 10.6 Hz, *C*Me$_3$), 33.6 (*C*HMe$_2$), 31.7 (d, *J* = 4.5 Hz, C*Me*$_3$), 30.8 (CH*Me*$_2$), 29.3, 28.2, 27.8, 27.5, 24.2, 24.1 (C*Me*$_3$). ^{31}P{^{1}H} NMR (243 MHz, C_6D_6, 298K): δ = 13.4. HRMS (ESI): *m/z* calcd for $C_{64}H_{100}N_4P_2Ge_2$+Na$^+$: 1157.5744 [*M*+Na]$^+$; found: 1157.5780.

Evans Method. The magnetic susceptibility of compound **3** was determined using the Evans method.[2-4] The NMR experiments were performed using a Bruker Avance III HD spectrometer, operating compound **3** at a proton frequency of 600 MHz and a 5mm NMR tube with capillary insert. Tetrakis(trimethylsilyl)silane in C_6D_6 solution was used as the reference. The compound **3** solution was prepared under N_2 atmosphere and 400 µl of the solution was put into the 5 mm NMR tube. The acquired FID data was processed by a Bruker topspin software.

X-band EPR spectroscopy. 9 GHz (X-band) continuous wave (CW) EPR spectra were collected on a Bruker EMX plus 6/1 spectrometer equipped with an Oxford Instrument ESR900 liquid He cryostat using an Oxford ITC 503 temperature controller. The sample solutions were charged with EPR tubes made of quartz glass. All preparations were done under N_2 atmosphere. Spectra were collected for compound **3** at 298 K and 100 K. Simulations were performed with

EasySpin.[5]

X-ray Structure Determination. Single-crystal X-ray diffraction data for complexes **2**, **3**, **5**, **6**, **7** and **8** were collected at 193 K on a Bruker D8 Venture with TXS detectors using Mo-Kα radiation. An empirical absorption correction was applied using the SADABS program.[6] All structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms by full-matrix least squares calculations on F^2 using the SHELXTL program package within OLEX2.[7,8] All hydrogen atoms were geometrically fixed using the riding model. Crystal data and details of data collection and refinement are given in Table S1 and S2. Details of the crystal structures were deposited in the Cambridge Crystallographic Data Centre with CCDC 2414423 for **2**, CCDC 2414424 for **3**, CCDC 2414425 for **5**, CCDC 2414426 for **6**, CCDC 2414427 for **7**, and CCDC 2414428 for **8**.

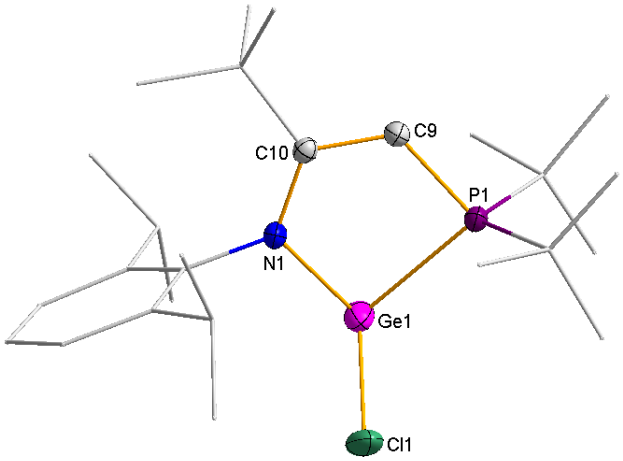


Fig. S1 Molecular structure of **2** with ellipsoids set at the 30% probability level.

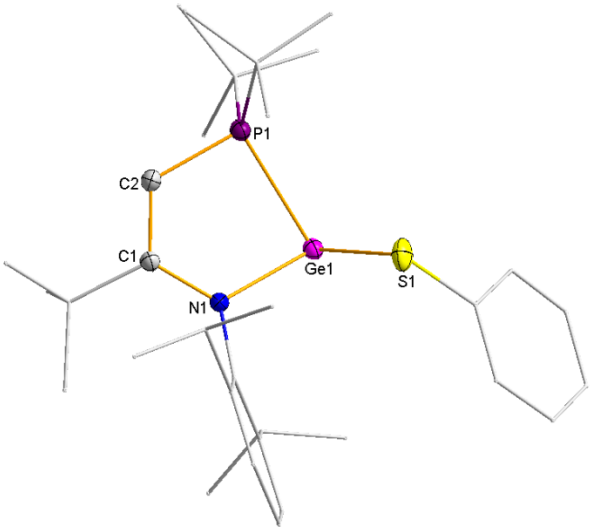


Fig. S2 Molecular structure of **5** with ellipsoids set at the 30% probability level.

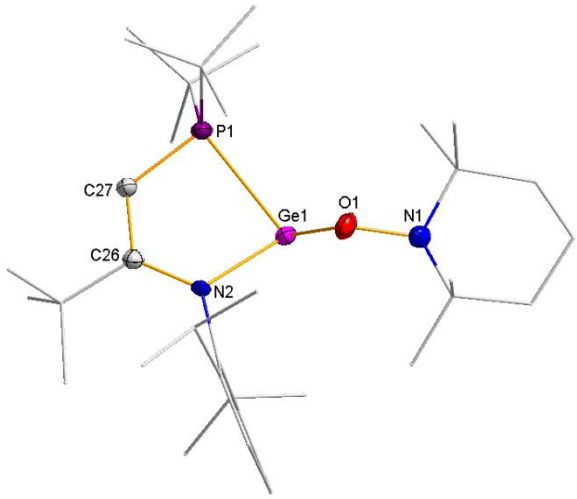


Fig. S3 Molecular structure of **6** with ellipsoids set at the 30% probability level.

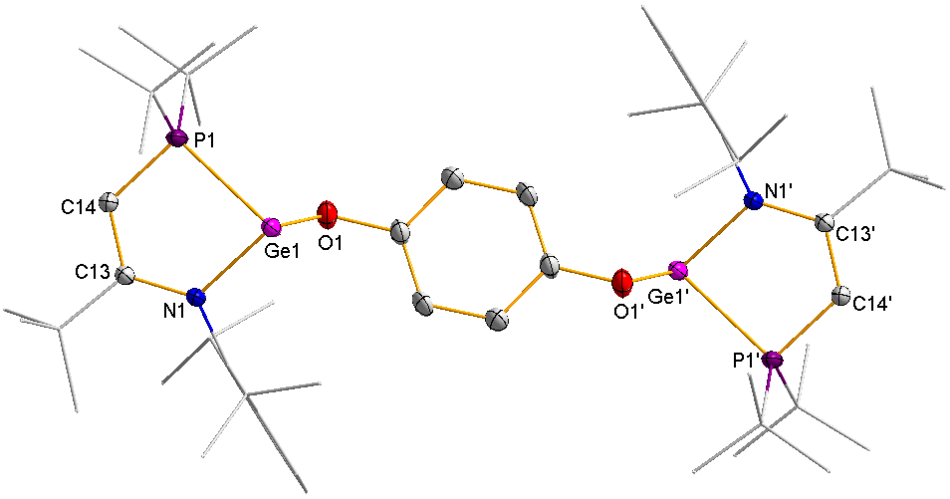


Fig. S4 Molecular structure of **7** with ellipsoids set at the 30% probability level.

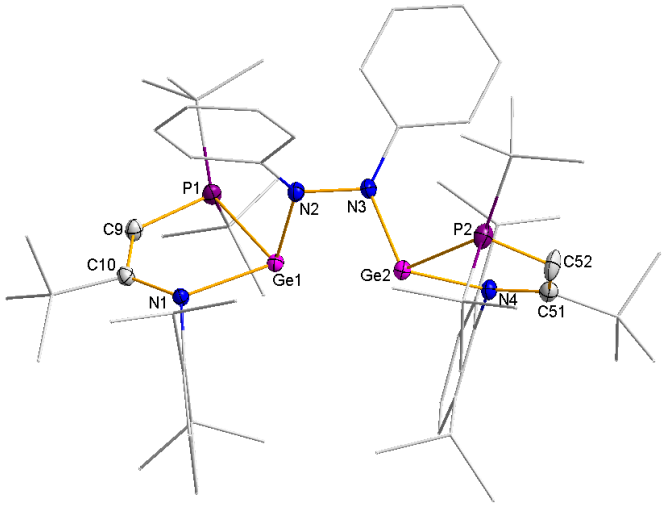


Fig. S5 Molecular structure of **8** with ellipsoids set at the 30% probability level.

Table S1 Crystal Data and Summary of Data Collection and Refinement for **2**, **3**, and **5**.

compound	**2**	**3**·0.5(C_7H_8)	**5**
formula	$C_{26}H_{45}ClGeNP$	$C_{55.5}H_{94}Ge_2N_2P_2$	$C_{32}H_{50}GeNPS$
Mw	510.64	996.44	584.35
crystal system	Monoclinic	Monoclinic	Triclinic
space group	$P2_1/n$	P2/n	P-1
a, Å	10.0595(8)	13.7277(3)	10.0203(10)
b, Å	17.6018(14)	14.7353(4)	10.4835(10)
c, Å	15.6334(11)	14.6668(4)	17.3506(15)
α, deg	90	90	86.887(3)
β,deg	92.688(4)	92.4980(10)	75.127(3)
γ, deg	90	90	64.355(3)
V, $Å^3$	2765.1(4)	2964.01(13)	1584.7(3)
Z	4	2	2
D_{calcd}, g/cm^3	1.227	1.116	1.225
Radiation (Å)	0.71073	0.71073	0.71073
2θ range, deg	3.486 to 50.71	4.844 to 55.046	4.818 to 55.038
μ, mm^{-1}	1.275	1.101	1.103
F(000)	1088.0	1070.0	624.0
No. of obsd reflns	4993	6799	7164
No. of params refnd	330	415	332
Goodness of fit	1.059	1.049	1.063
R1	0.0683	0.0426	0.0379
wR2	0.1853	0.1211	0.0832

Table S2 Crystal Data and Summary of Data Collection and Refinement for **6**, **7**, and **8**.

compound	**6**	**7**·2(C_4H_8O)	**8**
formula	$C_{35}H_{63}GeN_2OP$	$C_{66}H_{110}Ge_2N_2O_4P_2$	$C_{64}H_{100}Ge_2N_4P_2$
Mw	631.43	1202.67	1132.59
crystal system	Triclinic	Triclinic	Monoclinic
space group	P-1	P-1	$P2_1/n$
a, Å	11.1758(15)	10.6889(11)	22.036(2)
b, Å	12.5354(16)	13.1575(13)	15.8826(12)
c, Å	13.4623(16)	15.7892(14)	22.4630(19)
α, deg	90.209(4)	104.271(3)	90
β,deg	109.976(3)	95.656(4)	118.866(3)
γ, deg	90.517(4)	106.021(3)	90
V, $Å^3$	1772.4(4)	2035.1(3)	6884.9(11)
Z	2	1	4
D_{calcd}, g/cm^3	1.183	0.981	1.093
Radiation (Å)	0.71073	0.71073	0.71073
2θ range, deg	3.878 to 55.248	4.37 to 55.024	3.6 to 55.008
μ, mm^{-1}	0.937	0.815	0.956
F(000)	684.0	646.0	2424.0
No. of obsd reflns	8118	9194	15787
No. of params refnd	581	356	675
Goodness of fit	1.107	1.023	1.024
R1	0.0642	0.0491	0.0466
wR2	0.1732	0.1307	0.0932

Computational Detail: In the optimization and single point energy calculations, the Becke three-parameter hybrid functional (B3LYP) method was employed.[9-11] The 6-311G(d) basis set was used for all atoms.[12,13] Frequency calculations were made to determine the characteristics of all stationary points as energy minima. Natural bond orbital (NBO) analysis[14] which was performed using NBO 7.0 program[15] at the B3LYP-D3(BJ)[16]/6-311G(d) level of density functional theory. Quantum theory of atoms in molecules (QTAIM)[17] and the electron localization function (ELF)[18] analysis were calculated in Multiwfn software.[19] Time-Dependent Density Functional Theory (TD-DFT) calculations were performed using the BP86[20]-D3(BJ) /Def2-TZVP[21](SMD[22]) level of theory with toluene as the solvent. All the calculations were performed in the Gaussian 16 program.[23] The molecular orbital graphics were plotted using VMD program.[24]

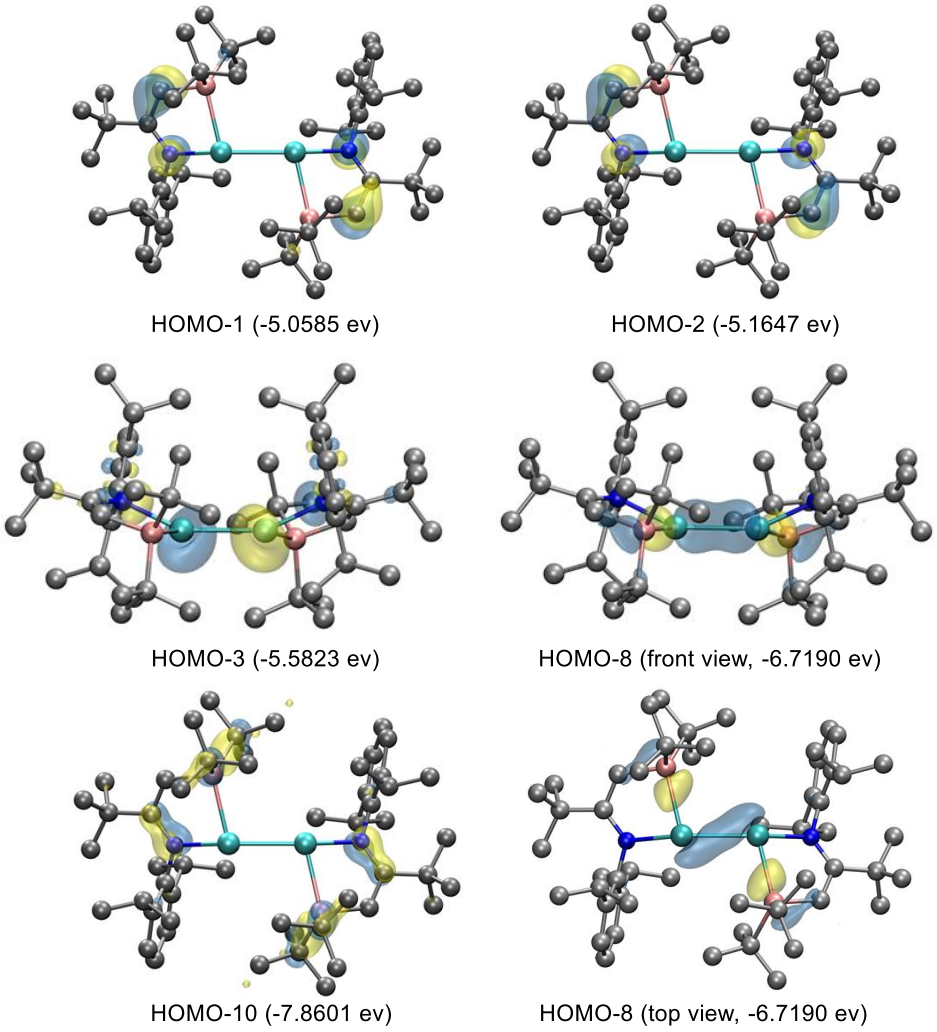
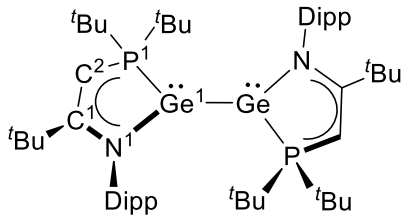


Fig. S6 Selected molecular orbitals calculated for **3**.



Ge^1	0.34
P^1	1.00
N^1	-0.81
C^1	0.29
C^2	-0.80

Fig. S7 Natural population analysis calculated for **3**.

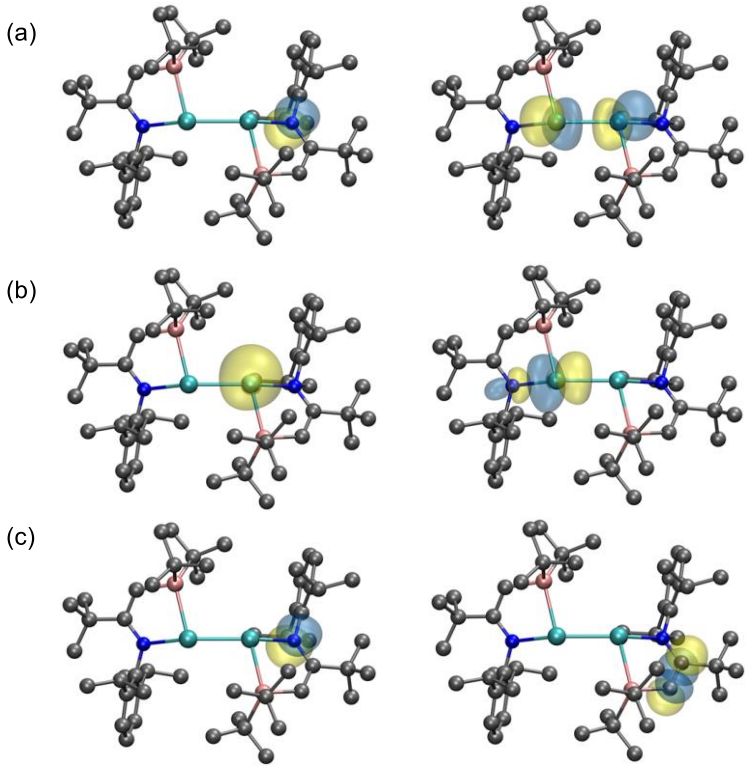


Fig. S8 NBO plots showing the donor (LP) and acceptor (BD*) orbitals in compound **3** for three selected interactions (E(2) in kcal mol^{-1}): (a) LP(N) and BD*(Ge-Ge) (4.05), (b) LP(Ge) and BD*(Ge-N) (31.66), and (c) LP(N) and BD*(C=C) (70.61). For each pair, the two orbitals are displayed side by side to illustrate their spatial overlap.

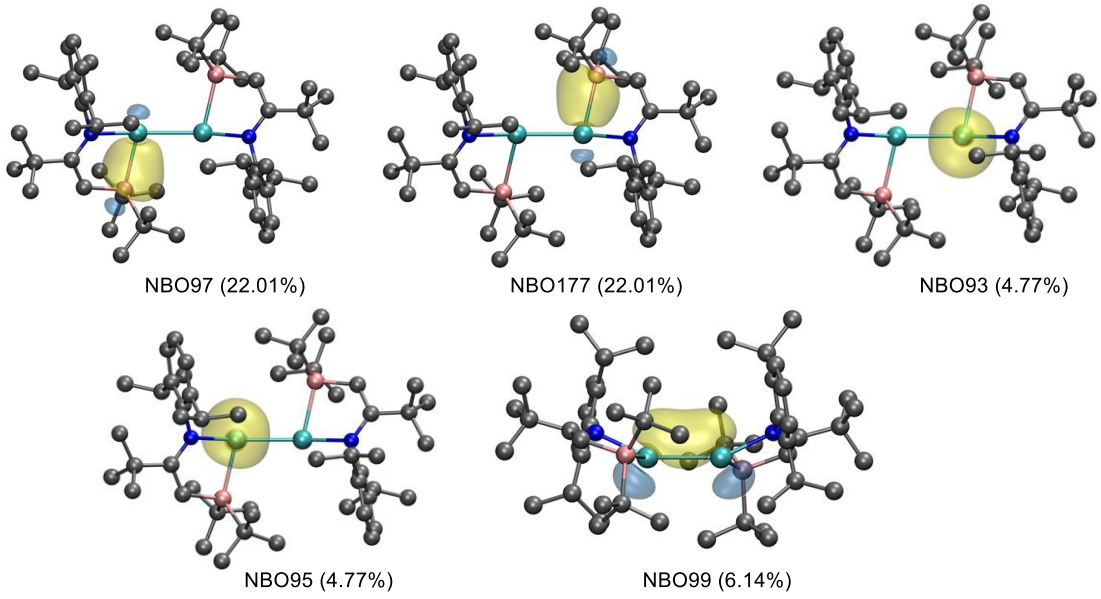


Fig. S9 NBO composition of the HOMO-8. Contributions below 3% are omitted.

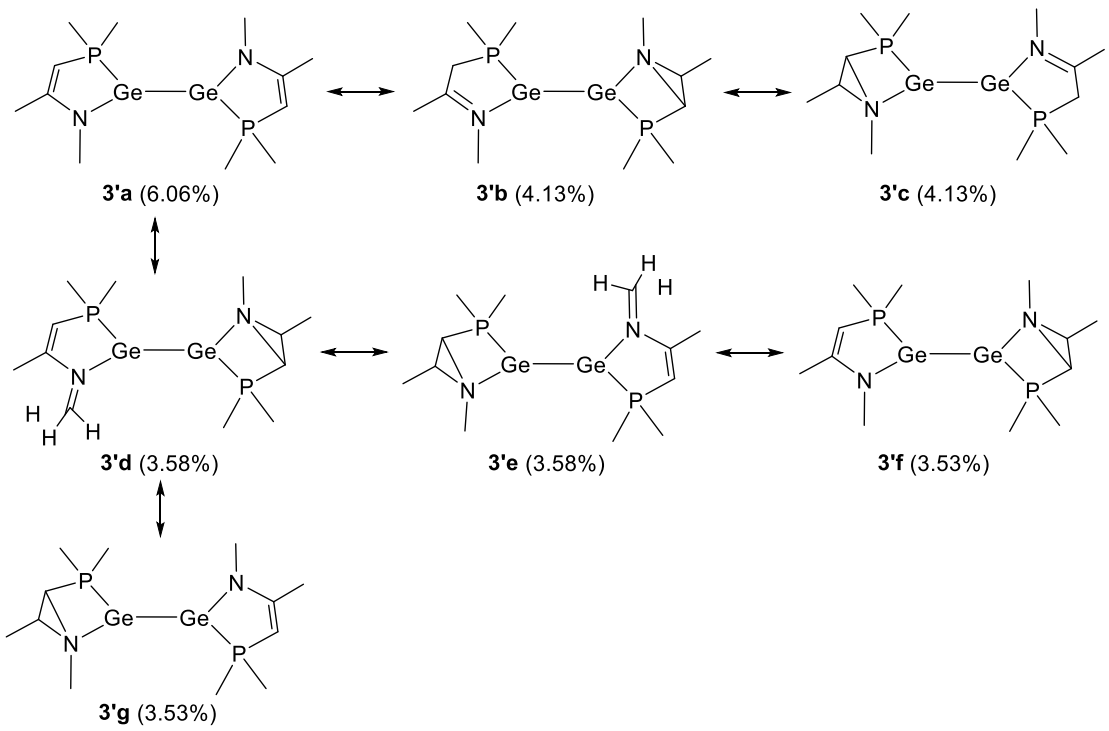
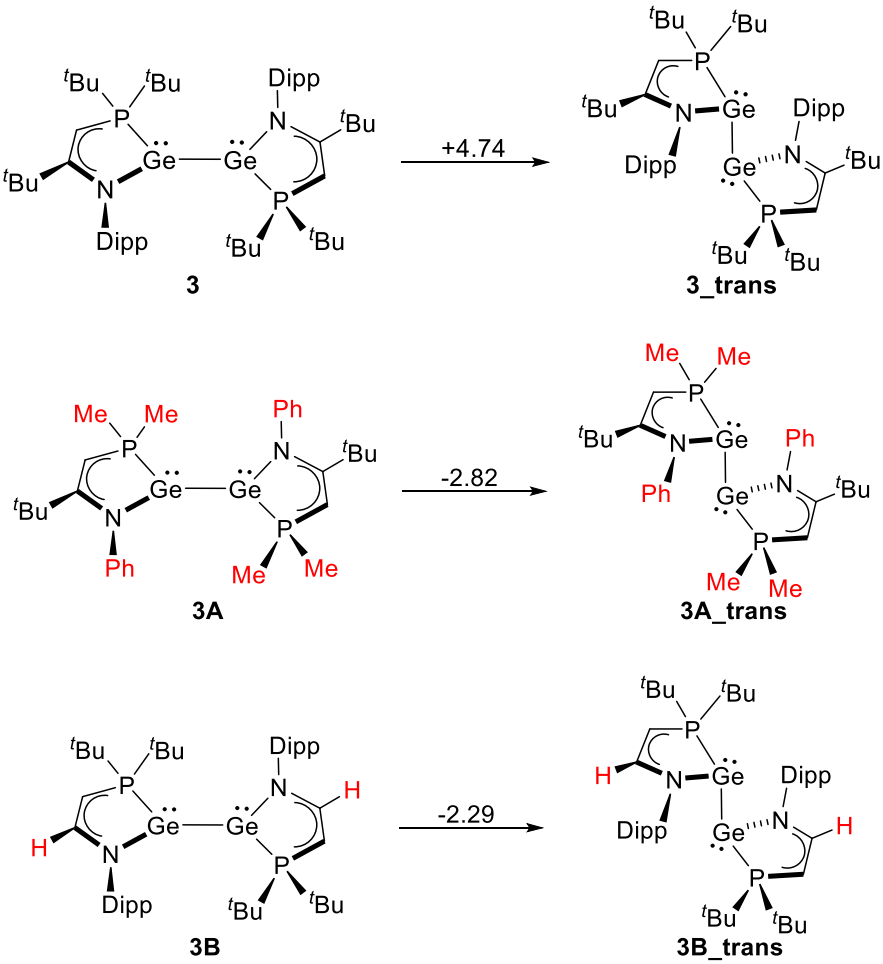


Fig. S10 Natural resonance theory (NRT) analysis calculated for **3**'. Structures contributing less than 3% are not shown.



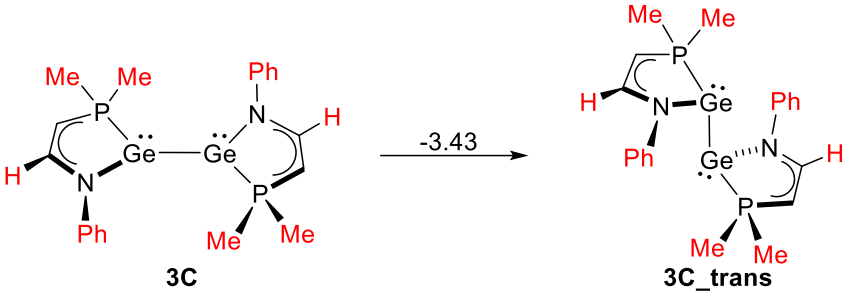


Fig. S11 Calculated Gibbs free energy (ΔG) for the transformation of **3**, **3A**, **3B** and **3C** to their *trans*-bent isomers (in kcal mol^{-1}).

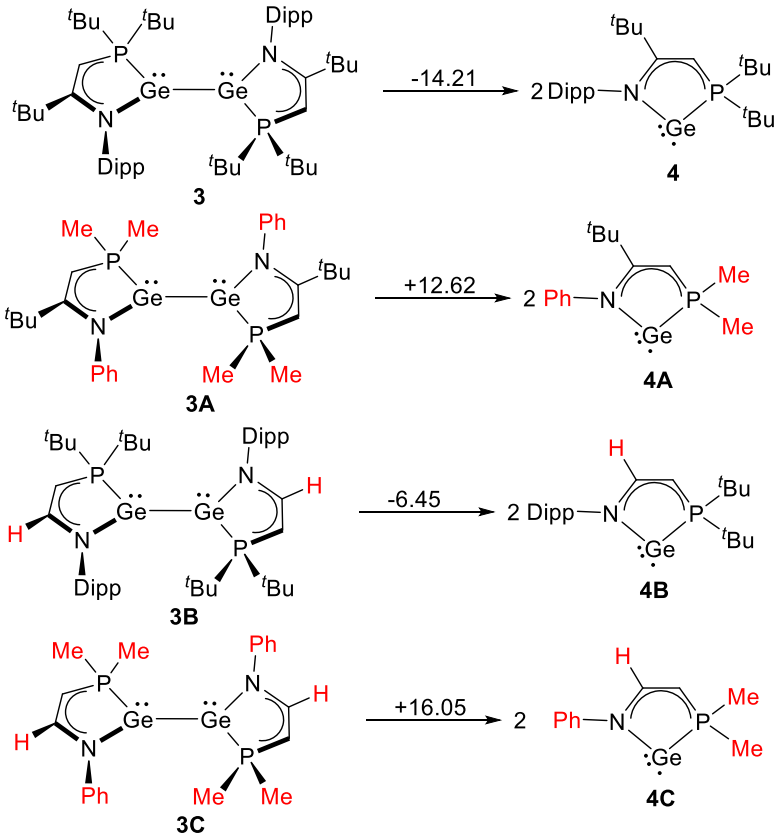


Fig. S12 Calculated Gibbs free energy (ΔG) for the dissociation of **3**, **3A**, **3B** and **3C** to their corresponding monomeric Ge(I) radicals (in kcal mol^{-1}).

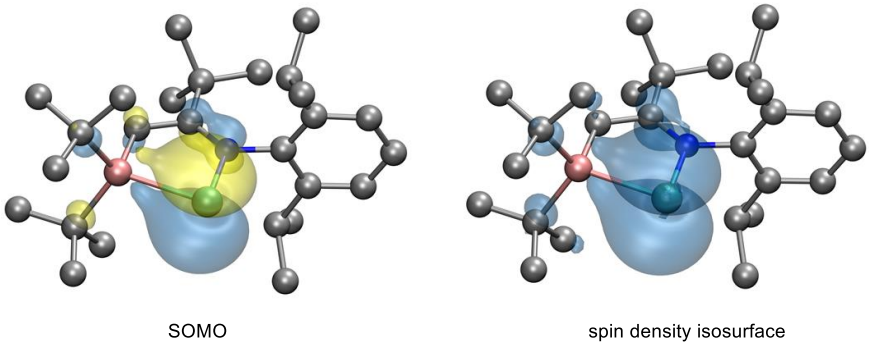


Fig. S13 SOMO and spin density isosurface calculated for **4**.

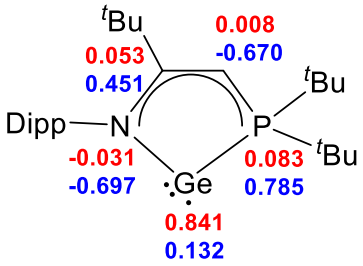


Fig. S14 Selected Mulliken charges (blue) and spin densities population (red) calculated for **4**.

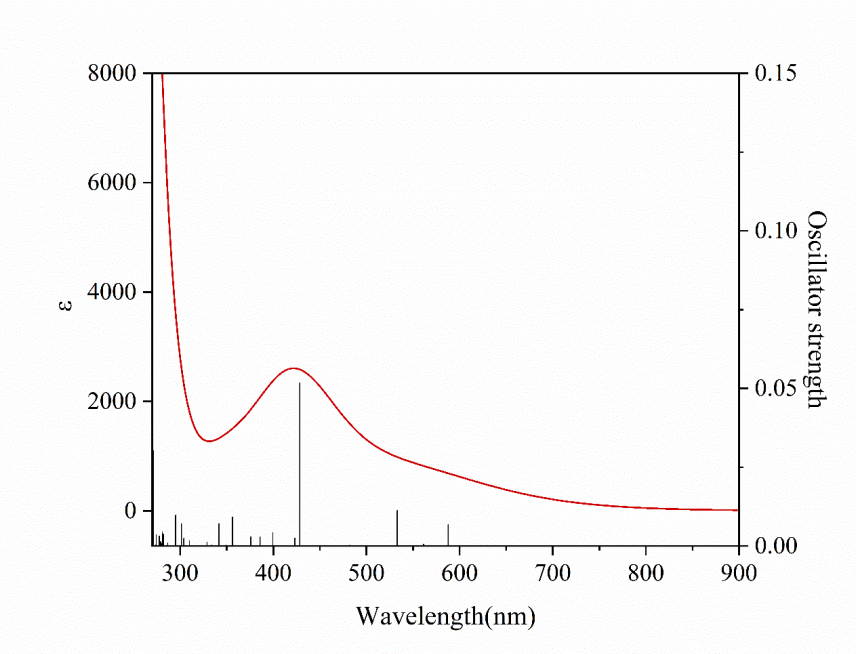


Fig.S15 Calculated UV/vis spectrum for **4**.

Cartesian Coordinates for the optimized structure of 3.

Ge	-1.34236600	-0.03549300	-0.59832000
P	-1.83028000	-2.45195100	-0.78075300
C	-2.87682300	-1.99277900	-3.32515500
H	-3.88293300	-2.07788300	-2.91194000
H	-2.92341500	-2.23170000	-4.39338800
H	-2.55757100	-0.95261400	-3.23015300
C	-1.89045700	-2.95776700	-2.64036400
C	-0.51002000	-2.78739000	-3.29348900
H	-0.11469900	-1.77957000	-3.14572100
H	-0.59652000	-2.95348700	-4.37310900
H	0.22550600	-3.49673700	-2.91497200
C	-2.39327500	-4.39585600	-2.84594500
H	-1.68090300	-5.14263600	-2.49263700
H	-2.53915100	-4.57510400	-3.91706500
H	-3.35371100	-4.57400800	-2.35569200
C	0.37305400	-4.22907600	-0.24889100
H	0.29167600	-4.80100600	-1.17531800

H	0.87724900	-4.86918200	0.48228600
H	1.02935200	-3.37492800	-0.42611900
C	-0.99548300	-3.80792100	0.30213100
C	-0.80771900	-3.15807900	1.68341200
H	-0.13468700	-2.30297200	1.63857900
H	-0.37565400	-3.89114100	2.37300300
H	-1.75949200	-2.82190900	2.10152300
C	-1.89845600	-5.04292900	0.47693600
H	-2.86650600	-4.77826400	0.90598100
H	-1.41441600	-5.73556300	1.17458500
H	-2.07005200	-5.58820100	-0.45052600
N	-3.25396000	-0.02163600	0.30629700
C	-3.49582700	-2.32838000	-0.20362700
H	-4.11225500	-3.21493200	-0.23127400
C	-4.03314000	-1.14091000	0.25855300
C	-5.54735200	-1.23340100	0.68042600
C	-5.68744700	-2.29498700	1.79926400
H	-5.36222300	-3.28604300	1.48247600
H	-6.73481100	-2.37189400	2.10777200
H	-5.10199300	-2.01951000	2.68028600
C	-6.37361200	-1.68318100	-0.55004500
H	-6.28337400	-0.96574700	-1.36981500
H	-7.43289800	-1.74944200	-0.28238900
H	-6.06520100	-2.65816100	-0.92797800
C	-6.21882700	0.04669800	1.21195400
H	-5.76374900	0.41782700	2.12631100
H	-7.26229300	-0.18968100	1.44252400
H	-6.22358100	0.86062100	0.49166600
C	-1.60712200	0.86776100	3.61523300
H	-1.45701600	1.86309800	4.04509600
H	-0.91715100	0.75336600	2.77943800
H	-1.33499500	0.13061800	4.37652200
C	-3.06169100	0.66801800	3.16399200
H	-3.12697300	-0.32875600	2.72353700
C	-3.99379500	0.70170500	4.39016000
H	-3.73833500	-0.11032200	5.07770800
H	-5.04554400	0.58792900	4.11892000
H	-3.89888700	1.63672600	4.94955900
C	-3.46073500	1.67216400	2.08440700
C	-3.68962200	3.00148500	2.44642100
H	-3.56013400	3.30190700	3.48140700
C	-4.08763300	3.94895200	1.51139400
H	-4.26044200	4.97744600	1.81363400
C	-4.27608100	3.56630400	0.19074300

H	-4.60453000	4.30624100	-0.53265800
C	-4.05792000	2.24969800	-0.22731500
C	-3.62953000	1.29258900	0.72835700
C	-4.33506100	1.89321000	-1.68832700
H	-4.16741000	0.82066900	-1.80352700
C	-5.79303500	2.18634900	-2.09424300
H	-6.51377700	1.68393200	-1.44629600
H	-5.97549000	1.84750300	-3.11873700
H	-6.01455600	3.25703100	-2.06207600
C	-3.37854300	2.61184600	-2.65519800
H	-3.48201800	3.69947600	-2.58917500
H	-3.59055600	2.32304200	-3.68963100
H	-2.34021300	2.35498400	-2.44485500
Ge	1.34237900	0.03550400	-0.59832700
P	1.83031300	2.45195700	-0.78076600
C	2.87683600	1.99279400	-3.32517500
H	3.88294900	2.07789900	-2.91196800
H	2.92341800	2.23171600	-4.39340800
H	2.55758700	0.95262800	-3.23017200
C	1.89047300	2.95777800	-2.64037400
C	0.51003100	2.78739900	-3.29348600
H	0.11471100	1.77957900	-3.14571400
H	0.59651900	2.95349700	-4.37310700
H	-0.22549200	3.49674600	-2.91496200
C	2.39328300	4.39587000	-2.84595600
H	1.68090700	5.14264500	-2.49264600
H	2.53915500	4.57511900	-3.91707700
H	3.35371900	4.57402800	-2.35570600
C	-0.37303900	4.22903400	-0.24883700
H	-0.29170500	4.80095700	-1.17527100
H	-0.87722200	4.86913500	0.48235200
H	-1.02932400	3.37486900	-0.42603500
C	0.99552900	3.80791600	0.30213900
C	0.80783900	3.15807000	1.68342900
H	0.13488500	2.30290200	1.63861000
H	0.37571800	3.89110000	2.37302000
H	1.75964900	2.82198800	2.10152700
C	1.89847500	5.04295000	0.47690900
H	2.86656000	4.77830900	0.90589200
H	1.41445600	5.73555800	1.17459800
H	2.06999700	5.58824100	-0.45055500
N	3.25396400	0.02163800	0.30629500
C	3.49586300	2.32837400	-0.20365000
H	4.11229800	3.21492000	-0.23129400

C	4.03315700	1.14090300	0.25854900
C	5.54736100	1.23338300	0.68045300
C	5.68743800	2.29495800	1.79930100
H	5.36222700	3.28601900	1.48251300
H	6.73479600	2.37185700	2.10783400
H	5.10196300	2.01947800	2.68030900
C	6.37365000	1.68316700	-0.54999800
H	6.28342600	0.96574000	-1.36977500
H	7.43293000	1.74942100	-0.28231800
H	6.06525300	2.65815200	-0.92793100
C	6.21881600	-0.04672600	1.21198200
H	5.76371700	-0.41785900	2.12632900
H	7.26227900	0.18964100	1.44257300
H	6.22357500	-0.86064300	0.49168700
C	1.60704600	-0.86764600	3.61516900
H	1.45685800	-1.86298100	4.04500700
H	0.91711000	-0.75318600	2.77935300
H	1.33494200	-0.13049900	4.37646400
C	3.06164600	-0.66799000	3.16398800
H	3.12700300	0.32878100	2.72353800
C	3.99369800	-0.70173300	4.39019300
H	3.73826500	0.11031600	5.07772600
H	5.04546600	-0.58802900	4.11899500
H	3.89870500	-1.63674300	4.94959500
C	3.46068200	-1.67215400	2.08441700
C	3.68953400	-3.00147900	2.44644000
H	3.56002100	-3.30189500	3.48142500
C	4.08754300	-3.94895800	1.51142300
H	4.26032500	-4.97745400	1.81367100
C	4.27602700	-3.56631800	0.19077500
H	4.60447600	-4.30626400	-0.53261700
C	4.05790100	-2.24970900	-0.22729300
C	3.62951000	-1.29258900	0.72836800
C	4.33508200	-1.89322900	-1.68829900
H	4.16746300	-0.82068300	-1.80350300
C	5.79305500	-2.18640800	-2.09418600
H	6.51379900	-1.68401700	-1.44622100
H	5.97554200	-1.84756200	-3.11867400
H	6.01454500	-3.25709700	-2.06202000
C	3.37856400	-2.61183800	-2.65519200
H	3.48200800	-3.69947100	-2.58916600
H	3.59060900	-2.32304100	-3.68961900
H	2.34023700	-2.35494800	-2.44487100

Cartesian Coordinates for the optimized structure of 3'.

Ge	0.84280200	-0.73463300	1.02797100
P	2.82778800	-0.96858300	-0.38320700
C	2.80979500	-1.55940200	-2.13481700
N	1.39384900	1.20514500	0.99110000
C	3.33918900	0.71511900	-0.30780600
H	4.24917800	1.05755600	-0.78669800
C	2.54529400	1.59538100	0.41077600
C	0.59824300	2.12482100	1.78809900
Ge	-0.84268900	-0.73441700	-1.02784500
P	-2.82781900	-0.96862200	0.38307600
N	-1.39374100	1.20531300	-0.99088100
C	-3.33946900	0.71498500	0.30733900
H	-4.24968600	1.05730000	0.78588800
C	-2.54540100	1.59539400	-0.41087300
H	2.55719400	-2.62124900	-2.17983600
H	2.06241000	-1.00449400	-2.70102400
H	3.79038500	-1.41173200	-2.59619200
C	2.98335200	3.03774500	0.54134600
H	2.25442700	3.71946300	0.09237500
H	3.08783900	3.32818000	1.59106500
H	3.94167500	3.19898000	0.04911000
C	4.12148400	-2.06502400	0.35217800
H	4.26370900	-1.79068000	1.39756600
H	3.80560700	-3.11078300	0.30705100
H	5.07385200	-1.96084200	-0.17520900
C	-4.12111200	-2.06540400	-0.35249200
H	-4.26319900	-1.79117500	-1.39792700
H	-3.80501900	-3.11109000	-0.30721600
H	-5.07360500	-1.96139800	0.17470600
C	-2.81030100	-1.55915600	2.13481300
H	-3.79100400	-1.41132100	2.59589600
H	-2.55777800	-2.62100900	2.18008900
H	-2.06303800	-1.00417800	2.70111500
C	-2.98366000	3.03767600	-0.54162700
H	-2.25466000	3.71963300	-0.09316600
H	-3.08859200	3.32777300	-1.59140600
H	-3.94181600	3.19893600	-0.04907400
C	-0.59790900	2.12518100	-1.78744200
H	0.36401900	1.66195600	-2.01246700
H	-1.07281100	2.38068400	-2.74448500
H	-0.38334500	3.05931000	-1.25757800
H	1.07313000	2.37963500	2.74534000
H	0.38403500	3.05931200	1.25873400

H	-0.36386400	1.66178300	2.01277700

Cartesian Coordinates for the optimized structure of 3_trans.

Ge	1.08977200	-0.47152500	0.79975500
P	1.80845400	-2.66740700	-0.20140500
C	2.43924400	-3.48198000	2.40150600
H	3.48898600	-3.25564200	2.20789100
H	2.39210800	-4.23390000	3.19738500
H	1.96523600	-2.57054000	2.76971700
C	1.73189700	-4.03627900	1.14993300
C	0.27116500	-4.35038600	1.50755400
H	-0.27689800	-3.45499700	1.79833000
H	0.24392500	-5.04175300	2.35782100
H	-0.27612000	-4.81912100	0.69099700
C	2.45006800	-5.32873800	0.72595600
H	1.93367200	-5.85110400	-0.08010500
H	2.48361900	-6.01399700	1.58043300
H	3.48274800	-5.15016300	0.41653200
C	0.06387700	-4.19187600	-1.92399900
H	0.17124800	-5.15221800	-1.41618800
H	-0.24420400	-4.40760800	-2.95290700
H	-0.75379900	-3.64769600	-1.44878300
C	1.37563700	-3.39726800	-1.93982000
C	1.23435000	-2.16605800	-2.85276200
H	0.44071700	-1.49232000	-2.52759500
H	1.00246300	-2.49170800	-3.87286700
H	2.16444900	-1.59480000	-2.88909300
C	2.50892600	-4.26879800	-2.51142300
H	3.45303400	-3.72314100	-2.55606400
H	2.25070900	-4.55340200	-3.53807000
H	2.66978900	-5.19052000	-1.95322300
N	2.98958500	0.11350200	0.08819200
C	3.49943800	-2.17017100	-0.32492500
H	4.23419000	-2.93853600	-0.51516300
C	3.91171700	-0.86198000	-0.17680200
C	5.47564000	-0.66968800	-0.27776200
C	5.97961700	-1.26762000	-1.61505300
H	5.77997300	-2.33490200	-1.70833600
H	7.06227500	-1.12921500	-1.69472700
H	5.51835400	-0.76807500	-2.47067800
C	6.12124700	-1.44709900	0.89713800
H	5.77225800	-1.06699800	1.86061400
H	7.20953800	-1.33184600	0.86861700
H	5.89697700	-2.51348100	0.86159700

C	6.04578600	0.76138400	-0.21662400
H	5.71331000	1.39102700	-1.03799200
H	7.13579400	0.69009400	-0.28489600
H	5.81533200	1.27951800	0.70929600
C	1.71488700	1.84313400	-3.04728900
H	1.56225000	2.90517800	-3.25937700
H	0.92121700	1.51291300	-2.37425500
H	1.59458800	1.29755100	-3.98830800
C	3.10444300	1.59075200	-2.44433600
H	3.19552700	0.51512900	-2.28892100
C	4.18635800	2.00771900	-3.45836400
H	4.09058500	1.41520500	-4.37330300
H	5.19732000	1.86068300	-3.07299600
H	4.09428000	3.05866500	-3.74690800
C	3.26700100	2.26253000	-1.08079600
C	3.46898800	3.64265300	-1.01924100
H	3.48104100	4.22260700	-1.93678300
C	3.67870100	4.28973100	0.19318500
H	3.84123100	5.36298500	0.21911100
C	3.68884400	3.55241300	1.36841500
H	3.86596200	4.06231600	2.31032700
C	3.48059800	2.16931300	1.36731300
C	3.26051000	1.51656900	0.12709400
C	3.55163100	1.41796000	2.69862000
H	3.45757600	0.35246600	2.47977500
C	4.89285900	1.63235300	3.42788600
H	5.75128200	1.36119000	2.81081100
H	4.92989700	1.01887900	4.33325700
H	5.02627800	2.67321500	3.73676800
C	2.39604500	1.79310100	3.64329100
H	2.42416100	2.85434800	3.91000300
H	2.46214400	1.21714000	4.57159200
H	1.42527400	1.58322100	3.19374100
Ge	-1.15178700	0.35375100	-0.90659100
P	-1.82712900	2.68224700	-0.22605900
C	-1.46459200	2.59416400	2.50864900
H	-2.52030400	2.34557300	2.62547300
H	-1.11013600	3.02988000	3.44890500
H	-0.91379600	1.66500800	2.34591300
C	-1.24179600	3.60342000	1.36733900
C	0.25049300	3.94347700	1.29422400
H	0.85415400	3.08022200	1.01292700
H	0.59898300	4.27328100	2.27846400
H	0.47168800	4.74476100	0.59161000

C	-2.05992700	4.86948400	1.66761600
H	-1.86285500	5.67442000	0.95753900
H	-1.78695800	5.24642300	2.66021600
H	-3.13524500	4.67504900	1.68322800
C	-0.65074200	4.76698800	-1.83814500
H	-0.60556400	5.53405000	-1.06374300
H	-0.65813400	5.28675200	-2.80266900
H	0.26792300	4.18105000	-1.78834200
C	-1.91509500	3.89960400	-1.72366000
C	-2.06272000	3.05222700	-3.00118900
H	-1.18297600	2.44109000	-3.20194500
H	-2.21030900	3.72257300	-3.85598000
H	-2.92484300	2.38490900	-2.94624900
C	-3.15083800	4.81622100	-1.63362600
H	-4.07855600	4.24355200	-1.66783700
H	-3.15230100	5.49142700	-2.49677400
H	-3.16460000	5.43737600	-0.73822100
N	-2.97434400	-0.11731000	0.05421200
C	-3.49896100	2.19813700	0.08329100
H	-4.22701700	2.98227400	0.22572500
C	-3.89427400	0.88161200	0.20787300
C	-5.43871800	0.70191900	0.47582600
C	-6.20625000	1.31100000	-0.72511900
H	-6.00006200	2.37317400	-0.85684100
H	-7.28449500	1.19497400	-0.57553900
H	-5.94404500	0.80496200	-1.65778700
C	-5.82250500	1.47408300	1.76269000
H	-5.28026800	1.09182400	2.63096400
H	-6.89200200	1.35245000	1.96068600
H	-5.62184700	2.54308400	1.69173500
C	-5.98688400	-0.72702700	0.65408500
H	-5.83033200	-1.35767000	-0.21516900
H	-7.06759900	-0.65514500	0.81160500
H	-5.57096200	-1.24495500	1.51282900
C	-2.71578400	-2.18883000	-3.33102100
H	-2.69474400	-3.27535100	-3.45964200
H	-1.71793800	-1.86038000	-3.04473500
H	-2.94201500	-1.74554000	-4.30587100
C	-3.77075200	-1.76342800	-2.29624900
H	-3.72763000	-0.67512900	-2.21959800
C	-5.16687500	-2.14614700	-2.83022700
H	-5.34909700	-1.64993600	-3.78836600
H	-5.97223200	-1.85901800	-2.15291100
H	-5.25240200	-3.22286400	-3.00284100

C	-3.50303500	-2.33431100	-0.89935700
C	-3.62445700	-3.71499500	-0.71079500
H	-3.84449100	-4.35036900	-1.56318800
C	-3.49361000	-4.29125300	0.54521800
H	-3.59764900	-5.36501400	0.66839300
C	-3.24847300	-3.48081800	1.64676900
H	-3.17166900	-3.93502300	2.62979700
C	-3.10454400	-2.09762000	1.51859200
C	-3.21349900	-1.51695500	0.22623700
C	-2.89227300	-1.26024300	2.78268500
H	-2.92671800	-0.21072600	2.48742600
C	-3.99078800	-1.49156000	3.84046100
H	-4.99637200	-1.32798500	3.45071200
H	-3.84809100	-0.80842600	4.68334000
H	-3.95668500	-2.50856800	4.24167800
C	-1.52329900	-1.50571500	3.43759200
H	-1.42023400	-2.54214300	3.77306200
H	-1.40252100	-0.86475300	4.31662300
H	-0.69505200	-1.28561400	2.76145500

Cartesian Coordinates for the optimized structure of 3A.

Ge	-1.23332700	0.45906000	-1.77853800
P	-2.28387600	-1.71963900	-1.69320500
N	-1.99753400	0.58870000	0.12386900
C	-3.04969800	-1.52427400	-0.11457300
H	-3.66257100	-2.32700000	0.26440000
C	-2.84340400	-0.36710400	0.61476300
C	-3.57655800	-0.21401000	1.98427200
C	-2.58000700	0.07694000	3.12856900
H	-1.81123100	-0.69862600	3.18924300
H	-3.11354300	0.08578400	4.08395600
H	-2.08362900	1.03848400	3.02396700
C	-4.32940200	-1.50417500	2.37820400
H	-5.12797600	-1.75050600	1.67523000
H	-4.79442900	-1.35634100	3.35640400
H	-3.66157800	-2.36472600	2.45977800
C	-4.63854800	0.90831500	1.91589500
H	-4.19823500	1.89831000	1.82237100
H	-5.23809800	0.90098500	2.83158800
H	-5.31785000	0.75294900	1.07299700
C	-0.63049000	2.20832600	1.35244900
C	-0.36254800	3.51399000	1.75972700
H	0.53352300	3.72075600	2.33645700
C	-1.22946200	4.55005500	1.41790100

H	-1.01981500	5.56695500	1.73384400
C	-2.35761300	4.27155600	0.64770500
H	-3.02740600	5.07348500	0.35280500
C	-2.62673000	2.96640700	0.24210100
C	-1.78530600	1.90879200	0.61810300
Ge	1.23320200	-0.45924000	-1.77842700
P	2.28385400	1.71940500	-1.69345500
N	1.99737900	-0.58860900	0.12402900
C	3.04976400	1.52421400	-0.11483900
H	3.66269200	2.32697200	0.26398000
C	2.84338400	0.36720100	0.61471400
C	3.57660000	0.21430200	1.98421500
C	2.58006600	-0.07644800	3.12857700
H	1.81132000	0.69915600	3.18916500
H	3.11361300	-0.08519100	4.08395900
H	2.08364700	-1.03798500	3.02410400
C	4.32944600	1.50454400	2.37791100
H	5.12798600	1.75076700	1.67485900
H	4.79452500	1.35687100	3.35611100
H	3.66162600	2.36510700	2.45937700
C	4.63860200	-0.90802600	1.91602600
H	4.19830700	-1.89805300	1.82276100
H	5.23819800	-0.90046300	2.83168700
H	5.31785700	-0.75283400	1.07305700
C	0.63040100	-2.20837800	1.35248600
C	0.36256000	-3.51406600	1.75975100
H	-0.53357400	-3.72093000	2.33634700
C	1.22965600	-4.55003000	1.41808500
H	1.02009300	-5.56695000	1.73401900
C	2.35787700	-4.27140800	0.64803700
H	3.02780400	-5.07326300	0.35323800
C	2.62688500	-2.96623400	0.24244000
C	1.78529200	-1.90870700	0.61831700
H	0.05822100	1.40590500	1.58811200
H	-3.49153700	2.75239200	-0.37597400
H	3.49173000	-2.75213600	-0.37555200
H	-0.05846100	-1.40604900	1.58800400
C	1.40534700	3.34083000	-1.77151800
H	0.93043200	3.46799500	-2.74657700
H	0.63783600	3.37824200	-1.00000200
H	2.10965600	4.16280900	-1.61293600
C	3.58577800	1.94632600	-2.98496400
H	3.12518800	2.08732400	-3.96640800
H	4.21354300	2.81366300	-2.76224700

H	4.21191900	1.05477500	-3.02021000
C	-3.58586400	-1.94676700	-2.98461800
H	-3.12532400	-2.08771500	-3.96609500
H	-4.21349600	-2.81418800	-2.76184900
H	-4.21213100	-1.05530200	-3.01983900
C	-1.40530600	-3.34103200	-1.77113100
H	-0.93048600	-3.46830900	-2.74622100
H	-0.63771700	-3.37831500	-0.99968500
H	-2.10957000	-4.16301300	-1.61236500

Cartesian Coordinates for the optimized structure of 3A_trans.

Ge	-0.67838500	-0.41130800	-1.07128100
P	-1.03121100	-2.66864500	-0.23002800
N	-2.57888900	-0.15525100	-0.29857800
C	-2.75479800	-2.48145300	0.10810900
H	-3.32240700	-3.36272400	0.36333300
C	-3.34168600	-1.23311400	0.06029000
C	-4.87090700	-1.12239900	0.35383500
C	-5.15265100	-0.29769500	1.63126100
H	-4.57865000	-0.68070200	2.47980400
H	-6.21389400	-0.37403000	1.88786800
H	-4.92290800	0.75828100	1.51243800
C	-5.51013100	-2.50977900	0.58574700
H	-5.39299700	-3.16850100	-0.27731600
H	-6.58215000	-2.37969100	0.75579500
H	-5.10237100	-3.01278700	1.46542400
C	-5.60712000	-0.49733800	-0.85282300
H	-5.34176200	0.54486100	-1.01473700
H	-6.68776400	-0.53789400	-0.68462400
H	-5.39239300	-1.05093800	-1.77125300
C	-2.84816500	1.94287800	0.95691300
C	-3.15551600	3.30135000	0.99438400
H	-3.10048300	3.83728700	1.93720100
C	-3.53471300	3.97098800	-0.16924100
H	-3.77800700	5.02813100	-0.13871800
C	-3.58606100	3.27088800	-1.37323900
H	-3.86379500	3.78324200	-2.28919100
C	-3.28516800	1.91051000	-1.41009000
C	-2.94328100	1.21574700	-0.24000600
Ge	0.67905500	0.40985600	1.07267500
P	1.03019700	2.66767400	0.23177300
N	2.57952500	0.15531300	0.29944000
C	2.75390200	2.48172500	-0.10660300
H	3.32104100	3.36352300	-0.36107900

C	3.34158200	1.23376000	-0.05921100
C	4.87096200	1.12408800	-0.35225000
C	5.60673300	0.49815100	0.85422800
H	5.39134900	1.05085400	1.77304100
H	6.68745700	0.53914200	0.68664300
H	5.34154000	-0.54426700	1.01503900
C	5.50957500	2.51203100	-0.58242300
H	5.10215100	3.01562800	-1.46192200
H	6.58178700	2.38271000	-0.75183800
H	5.39144300	3.16988700	0.28116500
C	5.15388300	0.30079200	-1.63032200
H	4.92470400	-0.75543900	-1.51266500
H	6.21522100	0.37801500	-1.88626800
H	4.58013100	0.68428500	-2.47881700
C	3.28562700	-1.91257900	1.40694300
C	3.58633800	-3.27293300	1.36751600
H	3.86390800	-3.78707100	2.28251800
C	3.53502000	-3.97072100	0.16218400
H	3.77809700	-5.02785500	0.12967000
C	3.15620500	-3.29876400	-1.00024000
H	3.10118000	-3.83290800	-1.94407200
C	2.84909300	-1.94032300	-0.96022600
C	2.94394100	-1.21553800	0.23815600
H	-2.54261900	1.42512600	1.85972900
H	-3.32684500	1.36319800	-2.34531600
H	2.54373100	-1.42082700	-1.86209600
H	3.32727400	-1.36706300	2.34322000
C	0.81149200	3.96535000	1.52391500
H	-0.25161800	4.13823600	1.70517700
H	1.27868000	3.63074400	2.45017500
H	1.27315800	4.90645300	1.21257100
C	0.23280700	3.45579300	-1.23604800
H	-0.81999400	3.66436800	-1.04269400
H	0.74595600	4.39072700	-1.48095500
H	0.30703900	2.78029100	-2.08831300
C	-0.81293700	-3.96642500	-1.52214000
H	0.25013000	-4.13971200	-1.70329400
H	-1.27502700	-4.90735400	-1.21090000
H	-1.27987000	-3.63157200	-2.44843700
C	-0.23449700	-3.45720900	1.23793100
H	0.81835600	-3.66571700	1.04479500
H	-0.30889800	-2.78186600	2.09030700
H	-0.74775600	-4.39217100	1.48246700

Cartesian Coordinates for the optimized structure of 3B.

Ge	-1.26407100	-0.33611000	-0.80160900
P	-1.07233900	-2.82009400	-0.91375200
C	-2.74647800	-2.79591700	-3.14815600
H	-3.55661100	-3.20208300	-2.54008700
H	-2.93772600	-3.05960600	-4.19422700
H	-2.77504600	-1.70759800	-3.06771300
C	-1.37589600	-3.36313900	-2.73352300
C	-0.29638500	-2.74711900	-3.64171100
H	-0.25667800	-1.65993400	-3.53941300
H	-0.53149700	-2.97103900	-4.68804600
H	0.70130000	-3.13846800	-3.44099600
C	-1.40914100	-4.88939100	-2.91474600
H	-0.43573900	-5.35384600	-2.75318100
H	-1.70688600	-5.12128600	-3.94335900
H	-2.13527500	-5.36877800	-2.25330600
C	1.60703900	-3.86749900	-0.94005500
H	1.50109100	-4.45825700	-1.85193500
H	2.42233000	-4.31187900	-0.35965500
H	1.92159900	-2.85890500	-1.21797200
C	0.32559100	-3.85717400	-0.09355700
C	0.61011900	-3.16451900	1.24963300
H	0.98335400	-2.14871000	1.11658000
H	1.37419300	-3.73098100	1.79150600
H	-0.28536100	-3.11812600	1.87345300
C	-0.12942300	-5.29743900	0.20750400
H	-1.02776300	-5.31425200	0.82787300
H	0.66096500	-5.80668200	0.77020700
H	-0.31862400	-5.88775100	-0.68803300
N	-2.69396900	-0.77097200	0.61968600
C	-2.53913900	-3.12035800	0.04266300
H	-2.96182900	-4.10952500	0.17065100
C	-3.13526700	-2.04856900	0.65337700
C	-1.65912100	1.18411800	4.31193000
H	-2.36622300	1.48669700	5.08988900
H	-1.32416100	2.08489600	3.79413700
H	-0.79558700	0.75329400	4.82396000
C	-2.26598400	0.15672700	3.34377400
H	-1.46793400	-0.20267200	2.68816100
C	-2.79493800	-1.05624000	4.13566500
H	-2.00512800	-1.48531900	4.76028800
H	-3.15950300	-1.84435800	3.47452400
H	-3.61975600	-0.76272900	4.79280100
C	-3.35667600	0.73633000	2.44917300

C	-4.21308400	1.72615300	2.93839200
H	-4.07197800	2.10936000	3.94260900
C	-5.25178900	2.22998400	2.16466300
H	-5.90542900	2.99955500	2.56429400
C	-5.45532100	1.73677200	0.88435400
H	-6.27823000	2.12322700	0.29124400
C	-4.62917000	0.74332300	0.34767400
C	-3.56488200	0.24689200	1.13742200
C	-4.94230000	0.19961500	-1.04330600
H	-4.13627600	-0.47804000	-1.32638000
C	-6.24993100	-0.61493600	-1.03908500
H	-6.20826500	-1.43586300	-0.31885300
H	-6.43905500	-1.04548300	-2.02741100
H	-7.11064500	0.00866800	-0.77863400
C	-4.99462600	1.30390200	-2.11251000
H	-5.81138500	2.01009000	-1.93656800
H	-5.15022800	0.86628900	-3.10337100
H	-4.06187700	1.87129100	-2.14170400
Ge	1.26405600	0.33604800	-0.80160300
P	1.07225900	2.82003300	-0.91369700
C	2.74653300	2.79610000	-3.14800000
H	3.55657400	3.20235700	-2.53987100
H	2.93781300	3.05983800	-4.19405200
H	2.77523600	1.70778400	-3.06758000
C	1.37585100	3.36313800	-2.73344200
C	0.29647800	2.74699500	-3.64171100
H	0.25688800	1.65980400	-3.53941500
H	0.53164400	2.97094000	-4.68802800
H	-0.70126700	3.13822800	-3.44107500
C	1.40891200	4.88939900	-2.91462000
H	0.43544700	5.35372800	-2.75307200
H	1.70666400	5.12136300	-3.94321500
H	2.13496200	5.36885800	-2.25313800
C	-1.60722700	3.86718900	-0.93993300
H	-1.50139800	4.45787900	-1.85187000
H	-2.42251900	4.31154400	-0.35951600
H	-1.92171100	2.85854100	-1.21774000
C	-0.32572000	3.85706400	-0.09352000
C	-0.61009900	3.16452000	1.24976000
H	-0.98325600	2.14866600	1.11683500
H	-1.37418700	3.73097200	1.79162500
H	0.28542600	3.11826900	1.87352700
C	0.12919000	5.29740100	0.20735300
H	1.02754100	5.31436200	0.82770200

H	-0.66122700	5.80665500	0.77000700
H	0.31832800	5.88761200	-0.68826500
N	2.69394400	0.77092300	0.61970400
C	2.53902800	3.12032200	0.04275500
H	2.96168300	4.10949900	0.17078000
C	3.13518600	2.04853800	0.65344600
C	1.65932700	-1.18416500	4.31206100
H	2.36649900	-1.48662000	5.09000300
H	1.32442100	-2.08501300	3.79435500
H	0.79578100	-0.75338300	4.82410600
C	2.26604300	-0.15678500	3.34379900
H	1.46792800	0.20249900	2.68820100
C	2.79492800	1.05628200	4.13558100
H	2.00511300	1.48532500	4.76022300
H	3.15938000	1.84439400	3.47437100
H	3.61981100	0.76288900	4.79268900
C	3.35674200	-0.73634900	2.44918200
C	4.21322100	-1.72610800	2.93840400
H	4.07214900	-2.10931300	3.94262800
C	5.25195300	-2.22987600	2.16467200
H	5.90565000	-2.99939700	2.56430700
C	5.45545300	-1.73664800	0.88436300
H	6.27839800	-2.12303700	0.29125800
C	4.62923400	-0.74325600	0.34768300
C	3.56490200	-0.24691000	1.13742600
C	4.94236200	-0.19948600	-1.04327400
H	4.13626500	0.47807100	-1.32637600
C	6.24988600	0.61523500	-1.03897400
H	6.20807600	1.43614300	-0.31872700
H	6.43900000	1.04582700	-2.02728200
H	7.11066900	-0.00826000	-0.77849300
C	4.99488700	-1.30374700	-2.11249600
H	5.81172200	-2.00983800	-1.93651900
H	5.15049300	-0.86609600	-3.10333900
H	4.06221000	-1.87125100	-2.14175700
H	-4.05393700	-2.21879900	1.21677400
H	4.05384500	2.21878500	1.21685800

Cartesian Coordinates for the optimized structure of 3B_trans.

Ge	-0.28411400	-1.05730900	0.56684000
P	0.51739800	-3.00452200	-0.87206900
C	0.29620900	-1.86640500	-3.38801400
H	-0.76865200	-2.10081700	-3.32473900
H	0.56475000	-1.82139600	-4.44944200

H	0.45670800	-0.87364700	-2.96440900
C	1.15258500	-2.94270800	-2.69515500
C	2.62930200	-2.53235100	-2.76448000
H	2.82610600	-1.62379400	-2.19136700
H	2.90392300	-2.32743900	-3.80530000
H	3.29993300	-3.31413000	-2.40316000
C	0.92656400	-4.27074500	-3.44013800
H	1.53353800	-5.09020600	-3.05831500
H	1.19167600	-4.13500800	-4.49500800
H	-0.12170700	-4.57506500	-3.40909000
C	2.89516300	-3.33789800	0.63188500
H	3.54532400	-3.10187300	-0.21071700
H	3.48258700	-3.93660800	1.33666200
H	2.64950700	-2.40006300	1.13230500
C	1.63718700	-4.12016800	0.21779900
C	0.83012100	-4.47173400	1.48247900
H	0.50731200	-3.57996000	2.02243600
H	1.46297400	-5.06312400	2.15355700
H	-0.05986800	-5.05770000	1.24675900
C	2.04374300	-5.43421300	-0.46985400
H	1.18030900	-6.00291100	-0.82396300
H	2.57154900	-6.06543400	0.25373900
H	2.72264600	-5.27781300	-1.30903700
N	-2.12387400	-1.72746000	-0.09826300
C	-1.09462400	-3.74614200	-0.95625500
H	-1.25568400	-4.74898200	-1.33359100
C	-2.16902500	-2.99512800	-0.56564900
C	-2.93059300	-1.03957600	3.93347500
H	-3.87273500	-0.74202700	4.40366200
H	-2.36446700	-0.13193600	3.71431100
H	-2.36583500	-1.61290900	4.67468000
C	-3.15193000	-1.88335300	2.66804900
H	-2.16580900	-2.17123000	2.30045700
C	-3.91250400	-3.18039000	3.00647600
H	-3.37273400	-3.75676000	3.76434600
H	-4.03111900	-3.81535300	2.12484200
H	-4.91225100	-2.96834100	3.39821700
C	-3.86334700	-1.12471200	1.55039700
C	-5.08910300	-0.50748000	1.82209900
H	-5.47416100	-0.51245700	2.83693500
C	-5.83978600	0.08453600	0.81580800
H	-6.79236500	0.55151800	1.04743800
C	-5.37780900	0.05317600	-0.49423200
H	-5.98547600	0.49071400	-1.27956200

C	-4.15294000	-0.53663200	-0.81833900
C	-3.37807100	-1.11037300	0.22097000
C	-3.71776500	-0.61819700	-2.27927100
H	-2.64892600	-0.84090200	-2.28525200
C	-4.44297900	-1.76705900	-3.00891400
H	-4.26533900	-2.73236400	-2.53178600
H	-4.10276000	-1.84092800	-4.04674500
H	-5.52447300	-1.59928000	-3.02360800
C	-3.92239800	0.69187400	-3.05549800
H	-4.98088300	0.93175300	-3.19228800
H	-3.48148600	0.61120300	-4.05344000
H	-3.45136500	1.53680000	-2.55269600
Ge	0.64717200	1.05284500	-0.89236000
P	-0.45290500	3.21332100	-0.12610200
C	0.85005000	4.45321500	-2.27008600
H	1.54946400	4.91441900	-1.57125300
H	0.81078800	5.07109800	-3.17423100
H	1.24752800	3.47562300	-2.54891700
C	-0.56823700	4.34843400	-1.67768800
C	-1.48965700	3.70709700	-2.72791700
H	-1.15932100	2.69781000	-2.98643900
H	-1.46840900	4.30256100	-3.64734900
H	-2.52825400	3.65524800	-2.40070000
C	-1.05492600	5.76869100	-1.34602100
H	-2.09343200	5.79369700	-1.01406500
H	-0.99160400	6.38839700	-2.24748200
H	-0.43632400	6.24717400	-0.58272400
C	-3.30984200	3.30889000	0.25219700
H	-3.48198600	4.14476600	-0.42832300
H	-4.14184800	3.29558000	0.96395900
H	-3.36919500	2.37884100	-0.31586500
C	-1.98703200	3.43322400	1.01991100
C	-1.89034900	2.28618900	2.04045400
H	-2.00439900	1.31081200	1.56619200
H	-2.69265600	2.38908100	2.77848200
H	-0.93736600	2.29984500	2.57437400
C	-1.94202600	4.76350700	1.79417600
H	-1.02810400	4.85611100	2.38368500
H	-2.78331500	4.79178700	2.49586500
H	-2.02769900	5.63967000	1.15239500
N	2.06856000	1.62720700	0.49790100
C	0.94306200	3.74642800	0.83100800
H	0.99466700	4.73039800	1.28098500
C	1.98818000	2.87901100	0.99539100

C	1.88571900	-0.78518600	3.94981600
H	2.71422400	-1.20436700	4.52818600
H	1.53502800	-1.54640100	3.25135100
H	1.07092000	-0.58494200	4.65195500
C	2.28050600	0.50982700	3.22084700
H	1.38344300	0.88987800	2.72863300
C	2.73982800	1.56475700	4.24753100
H	1.95844500	1.74161500	4.99327700
H	2.97291100	2.52200000	3.77662300
H	3.63714400	1.23248100	4.77886300
C	3.34176500	0.29802500	2.14243400
C	4.49695000	-0.42478900	2.46018800
H	4.59980700	-0.85561800	3.45066600
C	5.51538700	-0.60422000	1.53563900
H	6.39948800	-1.17614400	1.80088100
C	5.40777500	-0.03044600	0.27445600
H	6.22317400	-0.15038500	-0.43021600
C	4.28629600	0.71943900	-0.08974200
C	3.23008300	0.85983500	0.84639400
C	4.27407800	1.46749900	-1.42139900
H	3.23168200	1.58828400	-1.72584300
C	4.86731400	2.88022900	-1.24507300
H	4.31846000	3.45959500	-0.50065300
H	4.83318100	3.43357300	-2.18897400
H	5.91277400	2.82668400	-0.92481500
C	5.00105600	0.73917600	-2.56196700
H	6.08568500	0.72120700	-2.41904300
H	4.81497700	1.25398000	-3.50885100
H	4.66212300	-0.29287100	-2.67324800
H	-3.16160100	-3.44270200	-0.62553100
H	2.84692300	3.21341500	1.57794200

Cartesian Coordinates for the optimized structure of 3C.

Ge	1.26754400	-0.39613600	-1.30284300
P	2.13472400	1.90163700	-1.51230700
C	1.09540400	3.40468600	-1.77880200
N	1.98046100	-0.18325900	0.60382000
C	2.90290400	1.98364400	0.08167800
H	3.46921000	2.84523500	0.41662400
C	2.72822400	0.90117100	0.90371900
C	0.83862300	-2.04367300	1.67707900
C	0.85260100	-3.17496900	2.48709800
H	-0.07336100	-3.71496400	2.65968100
C	2.03497500	-3.60205000	3.09000100

H	2.04157400	-4.48126400	3.72587100
C	3.20940600	-2.88750300	2.86336600
H	4.14113900	-3.21553300	3.31434800
C	3.20729500	-1.76488600	2.03994800
C	2.01653100	-1.31846800	1.44546600
Ge	-1.26743900	0.39613100	-1.30303900
P	-2.13464900	-1.90162000	-1.51261200
N	-1.98063100	0.18327600	0.60352100
C	-2.90313500	-1.98356200	0.08123000
H	-3.46953200	-2.84512700	0.41609200
C	-2.72853600	-0.90109300	0.90329300
C	-0.83868100	2.04349700	1.67698100
C	-0.85260300	3.17476800	2.48703600
H	0.07341100	3.71462900	2.65975300
C	-2.03499400	3.60199100	3.08980500
H	-2.04155100	4.48118500	3.72570300
C	-3.20949500	2.88761300	2.86300200
H	-4.14123900	3.21575600	3.31387900
C	-3.20743700	1.76502100	2.03954900
C	-2.01666100	1.31846100	1.44519800
H	4.13736700	-1.24649800	1.83176700
H	-0.09160200	-1.68764200	1.25044200
H	0.61715800	3.37090600	-2.75982100
H	0.31770100	3.45127900	-1.01695600
H	1.70944000	4.30755800	-1.71671800
C	3.41274900	2.08641200	-2.83098500
H	4.12443000	1.26442900	-2.75352300
H	2.94513200	2.05043600	-3.81831900
H	3.94912300	3.03365300	-2.72904100
C	-3.41243400	-2.08638400	-2.83152400
H	-4.12410200	-1.26437500	-2.75421400
H	-2.94463200	-2.05044600	-3.81877100
H	-3.94885900	-3.03360500	-2.72965900
C	-1.09532800	-3.40470800	-1.77887600
H	-1.70940700	-4.30755800	-1.71688800
H	-0.61689400	-3.37096700	-2.75980400
H	-0.31777300	-3.45131000	-1.01687900
H	-4.13755500	1.24676900	1.83123500
H	0.09154900	1.68735000	1.25044800
H	3.19179700	0.90800300	1.89014800
H	-3.19224200	-0.90790900	1.88965900

Cartesian Coordinates for the optimized structure of 3C_trans.

Ge	-0.28851100	-0.82987800	0.98479800

P	0.92870400	-2.71752100	-0.05115700
C	1.61040200	-3.89381700	1.19777800
N	-1.86502600	-1.69982700	-0.02286900
C	-0.45170600	-3.45001200	-0.88316500
H	-0.36630100	-4.36331900	-1.46099800
C	-1.65839700	-2.81752600	-0.75142300
C	-3.73598500	-0.76285000	1.22789500
C	-5.00261600	-0.18765900	1.26780900
H	-5.44251400	0.06761000	2.22711400
C	-5.71354100	0.04461200	0.09071500
H	-6.70408300	0.48619700	0.12545400
C	-5.13774200	-0.30037500	-1.13125700
H	-5.67643900	-0.11928500	-2.05654400
C	-3.86582000	-0.86517800	-1.17903900
C	-3.14842800	-1.11514200	0.00290900
Ge	0.32112400	0.82324400	-1.01681000
P	-0.93822900	2.70912800	-0.03392700
N	1.86280100	1.71186200	0.02865800
C	0.41253700	3.46024800	0.82935400
H	0.30427500	4.37919900	1.39426600
C	1.62675600	2.83465900	0.74015100
C	3.82294400	0.90371100	1.27093100
C	5.09457300	0.33667000	1.27882100
H	5.60166900	0.17705300	2.22565000
C	5.70984000	-0.03887200	0.08547500
H	6.70017900	-0.48217900	0.09423800
C	5.03827700	0.16502300	-1.11965400
H	5.50906700	-0.11375900	-2.05754900
C	3.77208000	0.74256500	-1.13566100
C	3.14508800	1.12580900	0.06022200
H	-3.40994600	-1.10101300	-2.13504200
H	-3.19675500	-0.97030000	2.14593600
H	2.47353100	-3.44875000	1.69919400
H	0.84507500	-4.10530800	1.94475000
H	1.91880700	-4.83193600	0.72842000
C	2.33130200	-2.57959500	-1.24036800
H	2.03832500	-1.93729300	-2.07025200
H	3.21037700	-2.14904900	-0.75914700
H	2.58577000	-3.56904300	-1.63133900
C	-1.58653600	3.86439100	-1.31987900
H	-0.79896400	4.07061700	-2.04483700
H	-2.43062200	3.40740200	-1.84257900
H	-1.91532500	4.80672400	-0.87334900
C	-2.37723100	2.57906000	1.11140800

H	-2.64988400	3.57216200	1.48031400
H	-3.23813800	2.13724900	0.60807000
H	-2.10862800	1.94954100	1.95889400
H	3.26419600	0.92846200	-2.07593900
H	3.33606800	1.16133600	2.20569600
H	2.48737800	3.27685600	1.24325500
H	-2.53707800	-3.24954100	-1.23170000

Cartesian Coordinates for the optimized structure of 4.

Ge	0.37271700	-0.07677300	-1.68523600
P	2.26493200	-0.00326200	-0.13882000
C	2.38509500	-2.75548000	0.22291600
H	2.02468100	-2.64262700	1.24641600
H	2.92619300	-3.70542700	0.15178400
H	1.51499200	-2.81752200	-0.43500500
C	3.32729000	-1.60742700	-0.18437200
C	3.80944100	-1.86326800	-1.62462200
H	2.97100000	-1.90799400	-2.32477200
H	4.32541200	-2.82867500	-1.67056700
H	4.50820300	-1.10585200	-1.98101600
C	4.52337900	-1.58738900	0.78027800
H	5.28943500	-0.86839300	0.48588300
H	4.99832400	-2.57502100	0.78873400
H	4.22070700	-1.36684000	1.80720200
C	4.39165800	1.54882400	-1.28738300
H	5.17588100	0.80616700	-1.13152700
H	4.88387100	2.52505700	-1.35668800
H	3.92212300	1.35400600	-2.25547500
C	3.36547600	1.57539000	-0.14411200
C	2.39934700	2.75366300	-0.37215100
H	1.90396100	2.69565800	-1.34351800
H	2.96068700	3.69378200	-0.33336300
H	1.62652200	2.79303900	0.39833900
C	4.07278500	1.79107700	1.20558400
H	3.35674100	1.83931700	2.02859700
H	4.60618300	2.74820300	1.18401900
H	4.80589500	1.01798800	1.43442000
N	-0.69395700	-0.00269800	0.02947000
C	1.28778200	0.03608800	1.33333700
H	1.77640900	0.05327900	2.29716300
C	-0.09569500	0.03278000	1.26025800
C	-0.83825900	0.06936400	2.64109200
C	-0.39719100	1.34112600	3.40708400
H	0.67618100	1.36529300	3.59667300

H	-0.90737800	1.38784600	4.37424700
H	-0.65633800	2.24578900	2.85086700
C	-0.42332500	-1.18119000	3.45510500
H	-0.70207300	-2.10096300	2.93434900
H	-0.93252100	-1.18018900	4.42393400
H	0.64997300	-1.21946800	3.64393000
C	-2.37866000	0.08664100	2.61694100
H	-2.78862800	0.95838600	2.11159600
H	-2.73251600	0.11455800	3.65212700
H	-2.80924500	-0.79730900	2.15213700
C	-1.87786400	3.23774100	-1.82247500
H	-2.85072200	3.47078000	-2.26604900
H	-1.34302300	2.58220000	-2.51296800
H	-1.31686400	4.17446300	-1.74315900
C	-2.03390500	2.58110900	-0.43766000
H	-1.03004300	2.39103200	-0.05345300
C	-2.72985200	3.55258500	0.53347100
H	-2.14833000	4.47467500	0.62947000
H	-2.84141500	3.12529400	1.53268500
H	-3.72726700	3.83383600	0.18360900
C	-2.74890500	1.23612700	-0.54325000
C	-4.09092100	1.21387800	-0.93258700
H	-4.60398300	2.15002600	-1.12929800
C	-4.78102000	0.01858200	-1.08309200
H	-5.82332800	0.02341200	-1.38697400
C	-4.12330900	-1.18354800	-0.85985100
H	-4.66169300	-2.11566400	-0.99979200
C	-2.78238600	-1.21843800	-0.46752800
C	-2.09695500	0.00673100	-0.28123000
C	-2.10551900	-2.57365400	-0.27489400
H	-1.10216300	-2.38813300	0.11305800
C	-2.83938500	-3.46994200	0.73976900
H	-2.95627200	-2.98224600	1.71025300
H	-2.28103400	-4.39749000	0.89931500
H	-3.83750100	-3.74918300	0.39040700
C	-1.95004500	-3.31339100	-1.61732700
H	-2.92350300	-3.54385500	-2.06095800
H	-1.41783700	-4.25966500	-1.47610800
H	-1.38728000	-2.71488300	-2.33675500

Cartesian Coordinates for the optimized structure of 4A.

Ge	0.73846400	-1.89453400	-0.00012100
P	2.65530100	-0.39532000	-0.00000600
N	-0.25350300	-0.13765900	0.00000700

C	1.75191800	1.12158000	-0.00000300
H	2.29514300	2.05359900	0.00001000
C	0.37147300	1.08546200	0.00002600
C	-0.41429700	2.42913800	0.00003700
C	-1.29121200	2.55726500	-1.26681400
H	-0.69238600	2.42391300	-2.17234300
H	-1.73350500	3.55750800	-1.30573000
H	-2.10717300	1.83884100	-1.28899700
C	0.53693100	3.64587500	0.00022800
H	1.17378100	3.67335300	0.88721000
H	-0.06071000	4.56110300	0.00027700
H	1.17391300	3.67356700	-0.88665600
C	-1.29166900	2.55714900	1.26659000
H	-2.10758100	1.83866200	1.28853100
H	-1.73406100	3.55735100	1.30539200
H	-0.69315400	2.42384000	2.17233300
C	-2.33500800	-0.64206600	-1.20384100
C	-3.67173300	-1.03417400	-1.20347300
H	-4.18176000	-1.20153400	-2.14700300
C	-4.34752600	-1.22505400	0.00004500
H	-5.38734900	-1.53551800	0.00008100
C	-3.67156400	-1.03452200	1.20355600
H	-4.18149600	-1.20215300	2.14708900
C	-2.33486900	-0.64242300	1.20386400
C	-1.65588500	-0.41279400	-0.00001300
H	-1.79915600	-0.51440200	-2.13799800
H	-1.79888600	-0.51488500	2.13796500
C	3.82593700	-0.41710600	1.43248200
H	4.41448100	-1.33786600	1.43053000
H	4.50802800	0.43696900	1.39261000
H	3.25503800	-0.36996200	2.35970500
C	3.82622400	-0.41713000	-1.43222000
H	4.41435400	-1.33816100	-1.43032600
H	3.25561700	-0.36953600	-2.35959900
H	4.50871100	0.43660900	-1.39197000

Cartesian Coordinates for the optimized structure of 4B.

Ge	0.25032700	-0.02365300	-1.46808000
P	2.14760700	0.00310700	0.14331200
C	2.26678500	-2.75693000	0.41374000
H	1.89319000	-2.67990700	1.43590500
H	2.81105600	-3.70270400	0.31738000
H	1.40530500	-2.79863700	-0.25705400
C	3.21190300	-1.59418000	0.05676700

C	3.71141800	-1.79890300	-1.38572700
H	2.88137000	-1.82235300	-2.09670200
H	4.23125700	-2.76044700	-1.45806500
H	4.41168600	-1.02738700	-1.70735300
C	4.39611800	-1.60290600	1.03610800
H	5.16302000	-0.87212400	0.77487000
H	4.87393000	-2.58887400	1.01668900
H	4.08048200	-1.41787900	2.06606600
C	4.27045100	1.61012800	-0.92708600
H	5.05949800	0.86878300	-0.78963300
H	4.75483700	2.59214700	-0.95682200
H	3.81194900	1.44601300	-1.90608500
C	3.23299400	1.58831200	0.20618900
C	2.25813800	2.76558900	0.01056900
H	1.77214800	2.73675800	-0.96687700
H	2.81122900	3.70819600	0.08662600
H	1.47834700	2.77301000	0.77507300
C	3.92377200	1.75896100	1.57079500
H	3.19878900	1.76840000	2.38737900
H	4.44756600	2.72130000	1.59122500
H	4.66220700	0.98469900	1.77747500
N	-0.81485400	0.00302800	0.22512800
C	1.15209200	-0.01331300	1.61721000
H	1.56656300	-0.02920600	2.61785000
C	-0.20581100	-0.01087400	1.43442800
C	-2.50553600	3.41457600	-1.15392500
H	-3.56058200	3.69695200	-1.21857200
H	-2.25121600	2.86387200	-2.06275200
H	-1.91896000	4.33852500	-1.14616100
C	-2.20909600	2.57867900	0.10322900
H	-1.13867000	2.36743000	0.10365200
C	-2.52363700	3.37503400	1.38287800
H	-1.95089200	4.30744500	1.40782900
H	-2.27286500	2.80330700	2.28038300
H	-3.58414200	3.63734700	1.44508200
C	-2.93852900	1.24021300	0.08502700
C	-4.33424400	1.21913200	0.00978900
H	-4.88002800	2.15604400	-0.04282800
C	-5.03792000	0.02180000	0.00316900
H	-6.12211100	0.02678900	-0.05544300
C	-4.34864900	-1.18188400	0.07076800
H	-4.90553700	-2.11373600	0.06446300
C	-2.95306500	-1.21589400	0.14630000
C	-2.24851000	0.00919500	0.15970800

C	-2.24048600	-2.56156300	0.22408900
H	-1.16728300	-2.36506600	0.22230100
C	-2.57149600	-3.30232800	1.53257300
H	-2.31886300	-2.69831000	2.40810100
H	-2.00988100	-4.23944500	1.59815700
H	-3.63531000	-3.54965800	1.59904300
C	-2.54182100	-3.44351200	-1.00023000
H	-3.60039400	-3.71352000	-1.05935500
H	-1.96829800	-4.37446400	-0.95192600
H	-2.27544000	-2.93350700	-1.92915100
H	-0.86378000	-0.01669800	2.30402100

Cartesian Coordinates for the optimized structure of 4C.

Ge	-0.65327100	-1.29139700	-0.40306900
P	-2.51721400	0.25350500	0.05366800
N	0.42237800	0.30561800	0.20768400
C	-1.54678400	1.65000000	0.54977400
H	-1.98172500	2.59005300	0.86890000
C	-0.19160500	1.46646100	0.54873200
C	2.51368500	-0.88442200	0.59239400
C	3.89984000	-0.96494800	0.50583500
H	4.40531900	-1.85376000	0.87058900
C	4.63901300	0.08972100	-0.02689200
H	5.72044300	0.02701300	-0.08772300
C	3.97155400	1.22338700	-0.48613000
H	4.53227000	2.04699800	-0.91762400
C	2.58366900	1.30304300	-0.42071000
C	1.83365300	0.25312500	0.13230200
C	-3.64197000	0.72762900	-1.33436300
H	-3.04164100	1.04684800	-2.18612900
H	-4.25257300	-0.12629000	-1.63743000
H	-4.30355500	1.54662200	-1.03894700
C	-3.72160400	-0.17361700	1.38897600
H	-4.38490200	0.66901600	1.60312900
H	-4.32812200	-1.03268300	1.09220600
H	-3.17250700	-0.43090700	2.29461000
H	2.07284500	2.16895300	-0.82834300
H	1.94616700	-1.69309400	1.04088200
H	0.45749900	2.28175700	0.86578900

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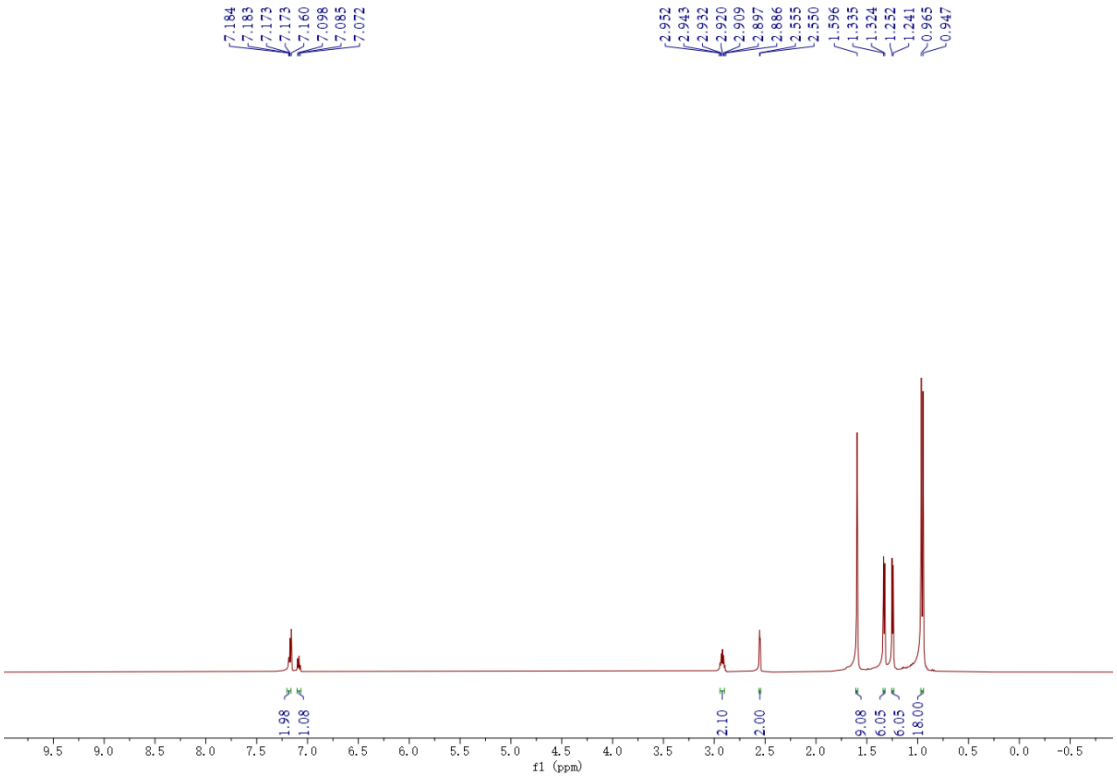

Fig. S16 ^{1}H NMR spectrum of **1** in C_6D_6 at 298 K.

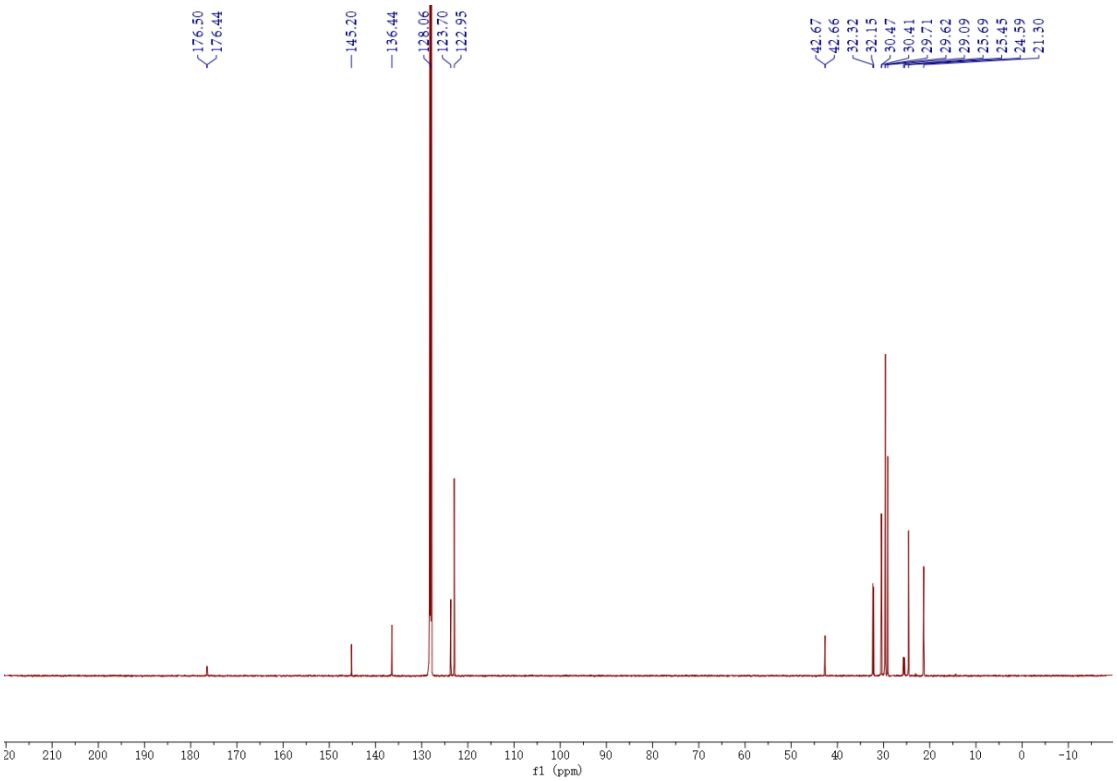

Fig. S17 ^{13}C{^{1}H} NMR spectrum of **1** in C_6D_6 at 298 K.

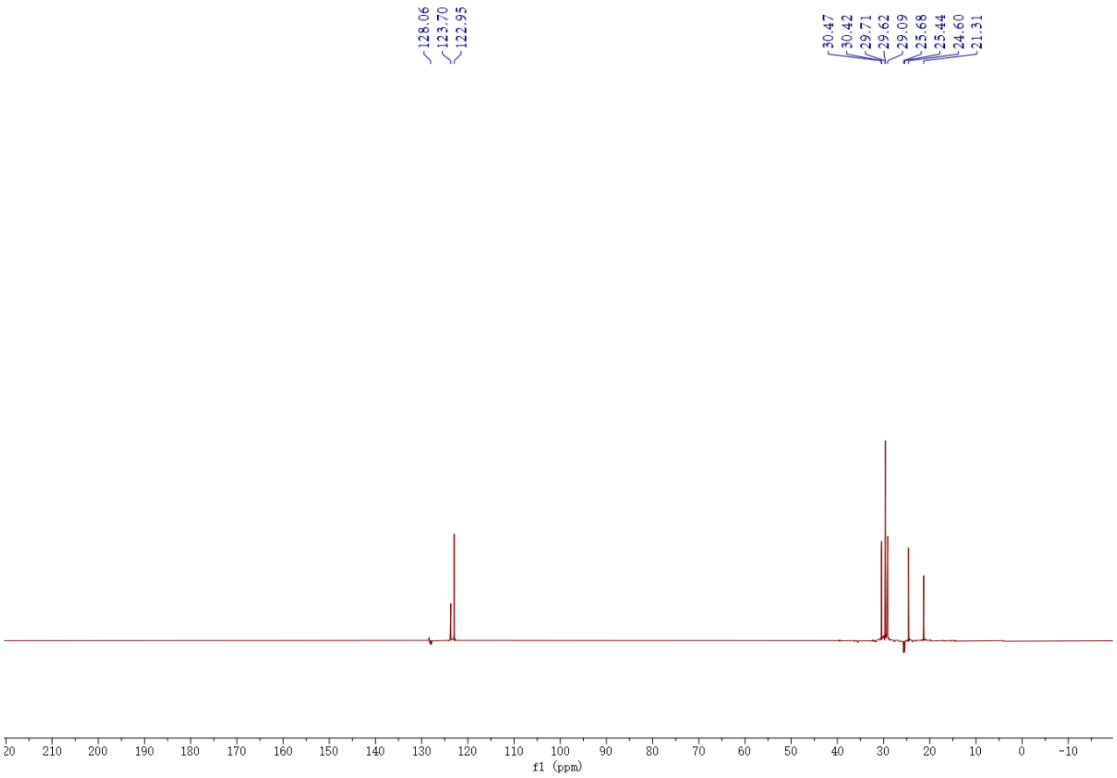

Fig. S18 $^{13}C\{^{1}H\}$ NMR (DEPT 135) spectrum of **1** in C_6D_6 at 298 K.

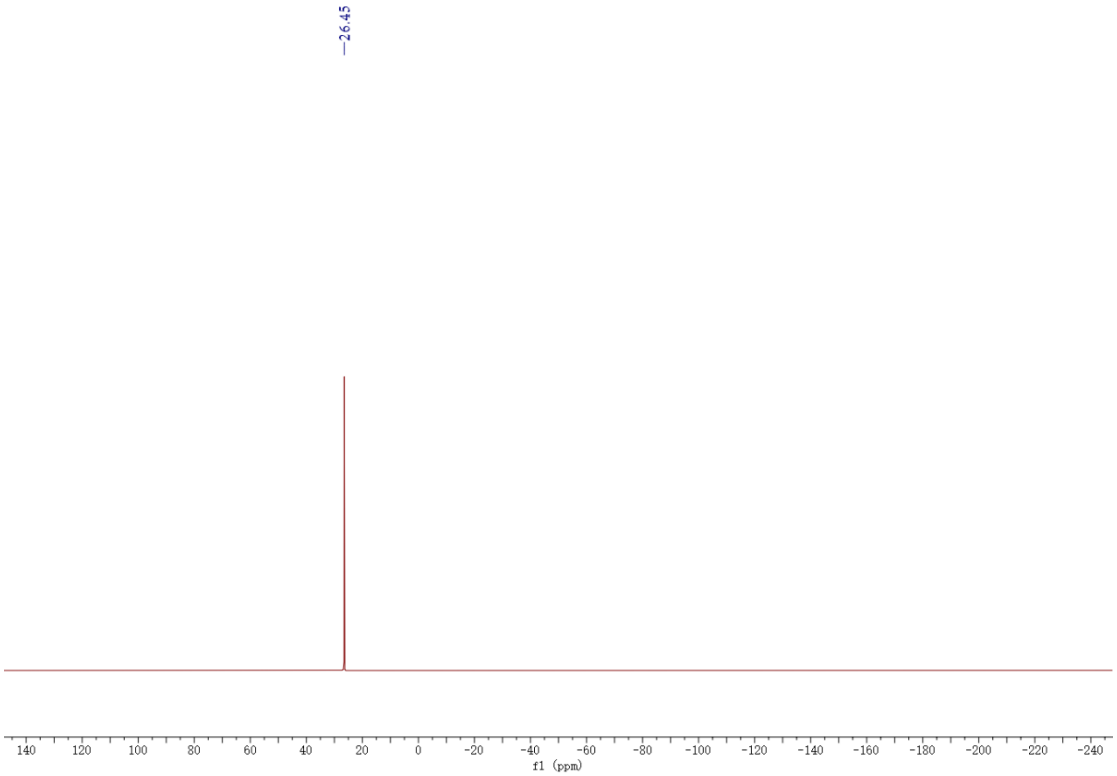

Fig. S19 $^{31}P\{^{1}H\}$ NMR spectrum of **1** in C_6D_6 at 298 K.

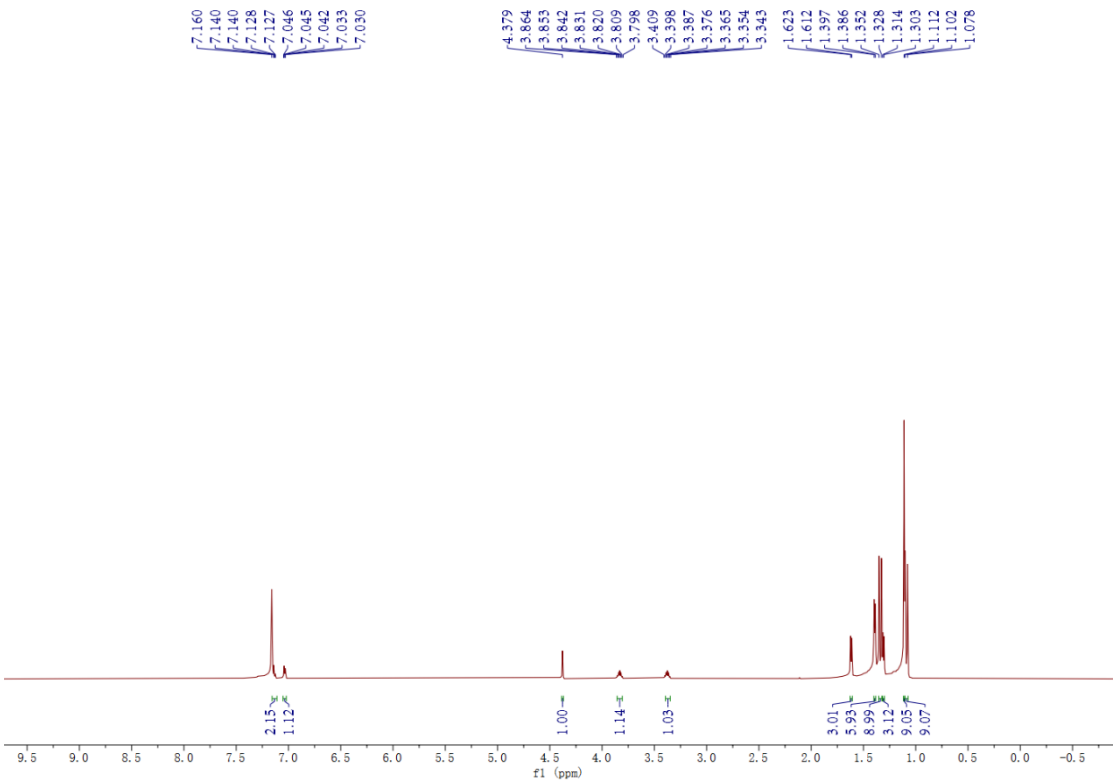

Fig. S20 ^{1}H NMR spectrum of **2** in C_6D_6 at 298 K.

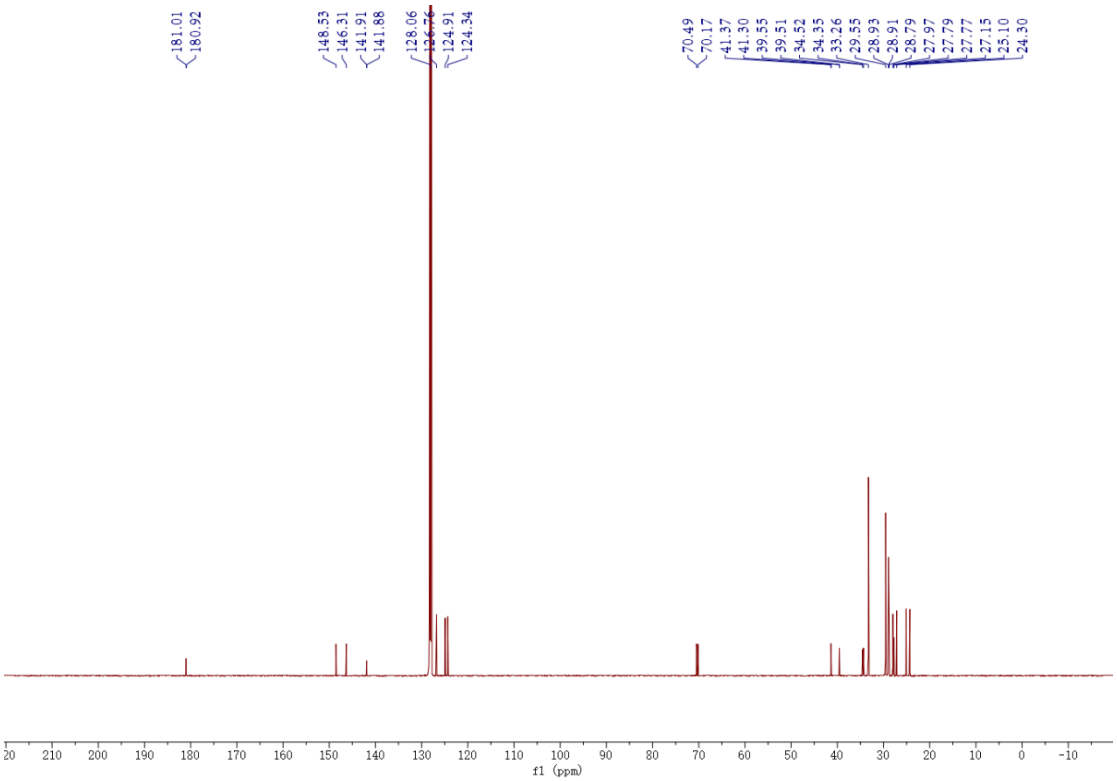

Fig. S21 ^{13}C{^{1}H} NMR spectrum of **2** in C_6D_6 at 298 K.

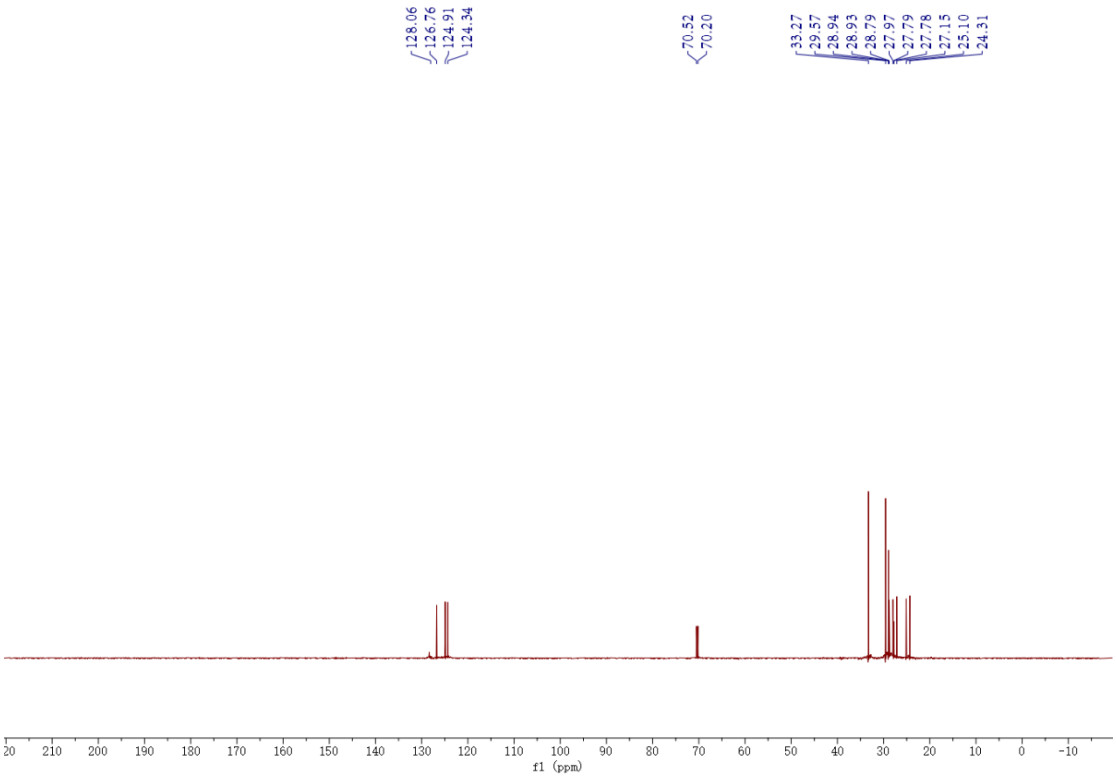

Fig. S22 $^{13}C\{^{1}H\}$ NMR (DEPT 135) spectrum of **2** in C_6D_6 at 298 K.

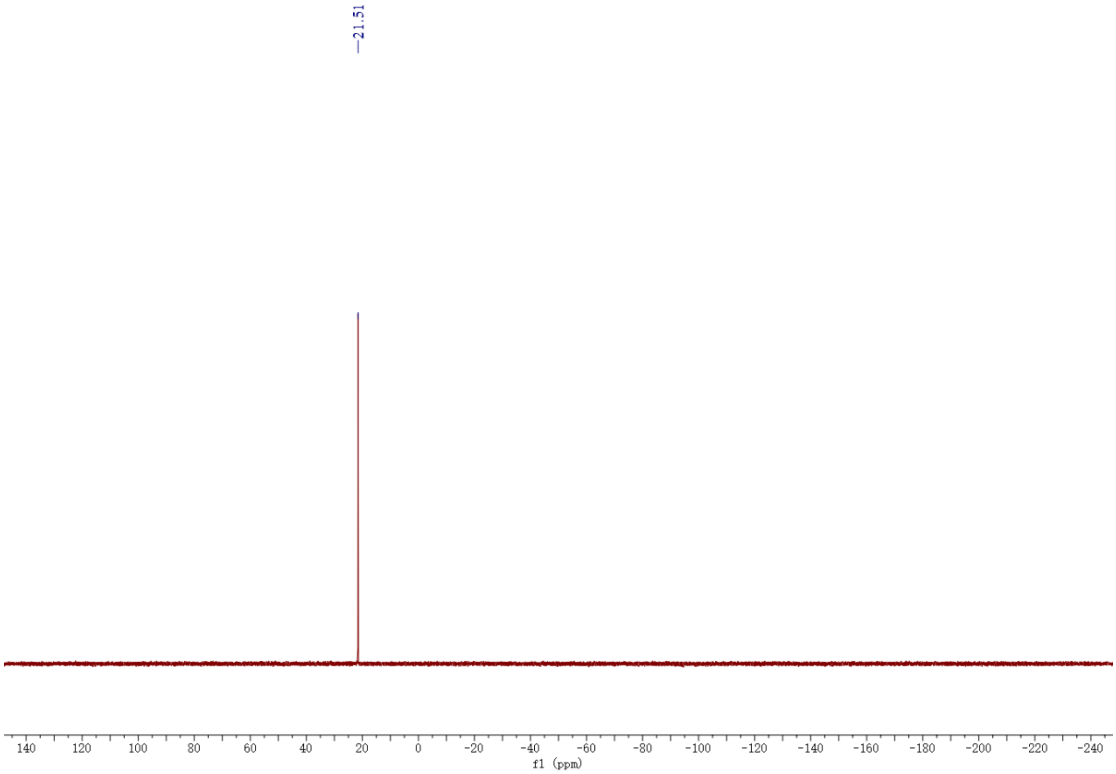

Fig. S23 $^{31}P\{^{1}H\}$ NMR spectrum of **2** in C_6D_6 at 298 K.

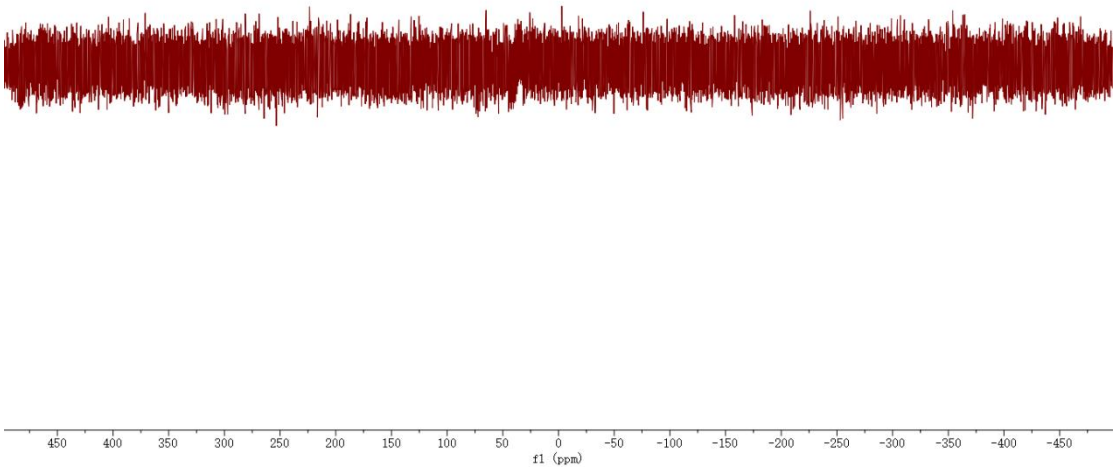

Fig. S24 $^{31}P\{^{1}H\}$ NMR spectrum of **3** in THF-d8 at 293 K.

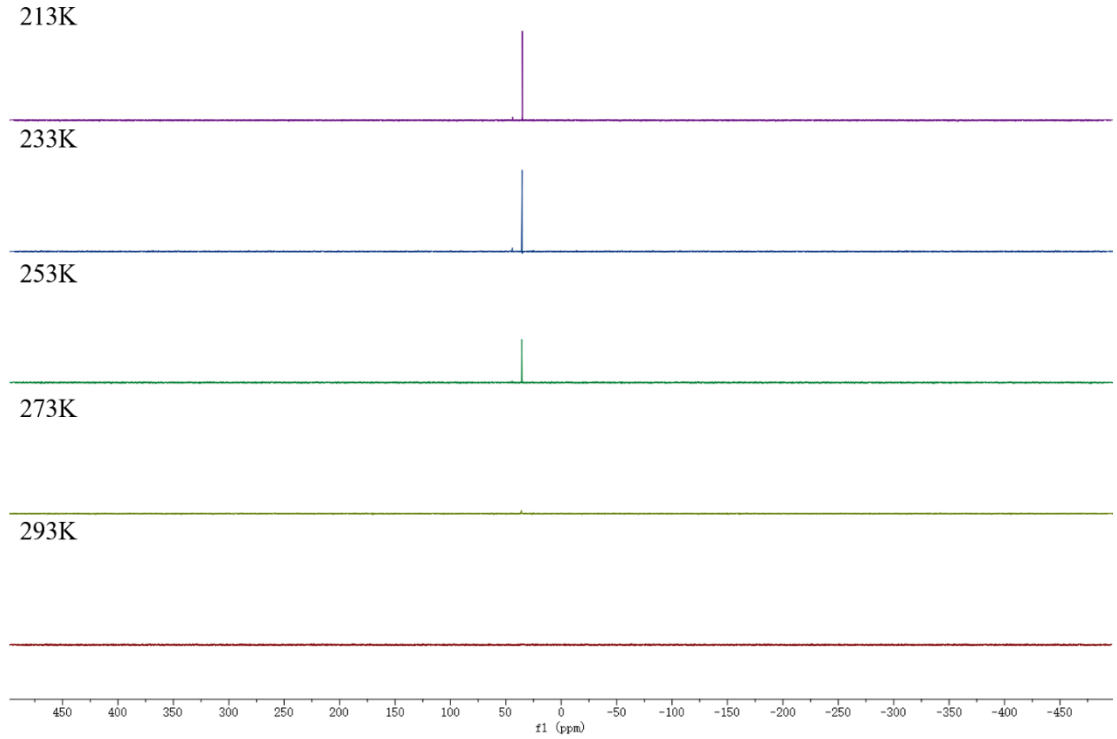

Fig. S25 Temperature-dependent $^{31}P\{^{1}H\}$ NMR spectra of **3** in THF-d_8.

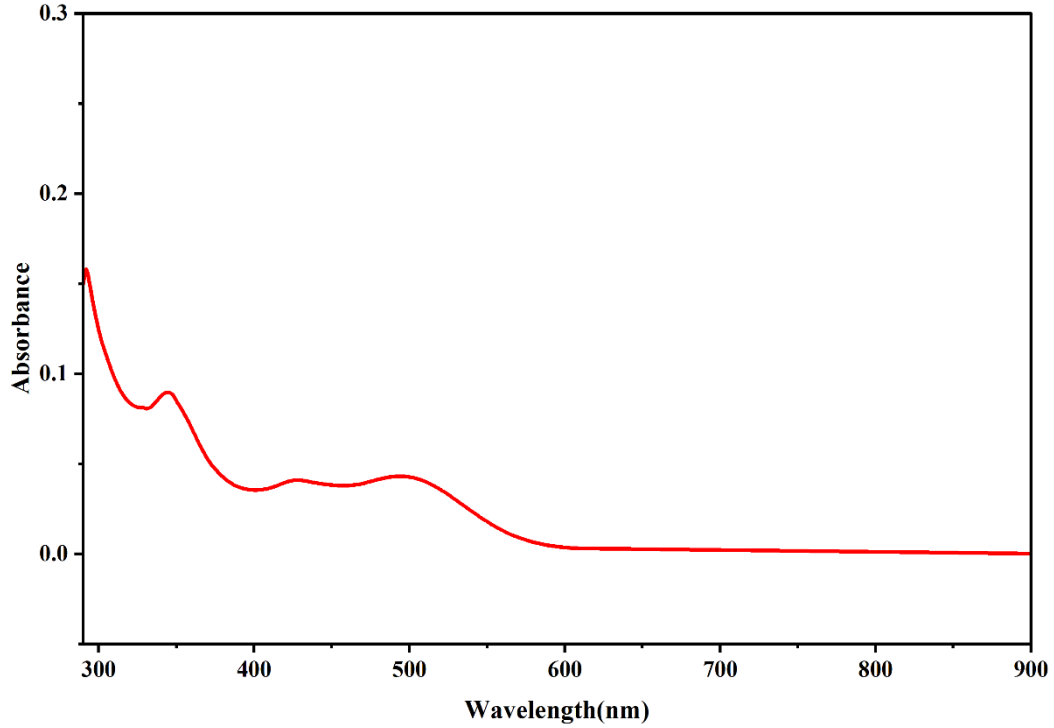

Fig. S26 UV-vis spectrum of **3** in toluene at 298 K.

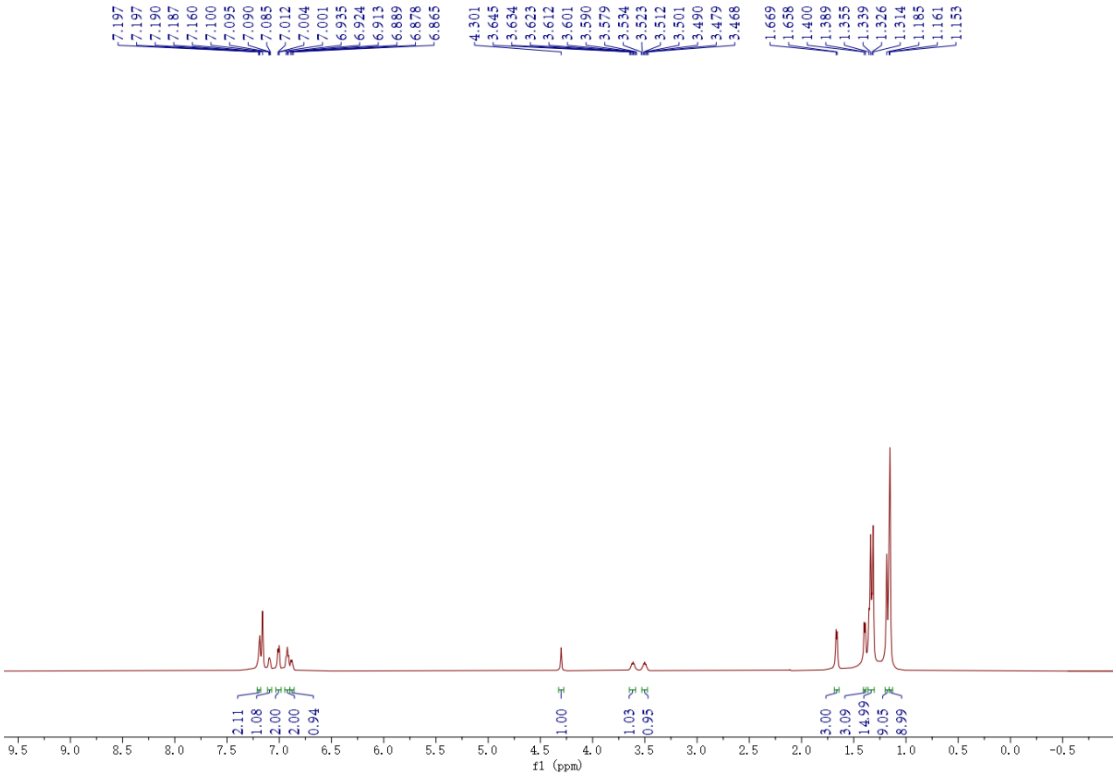

Fig. S27 ^{1}H NMR spectrum of **5** in C_6D_6 at 298 K.

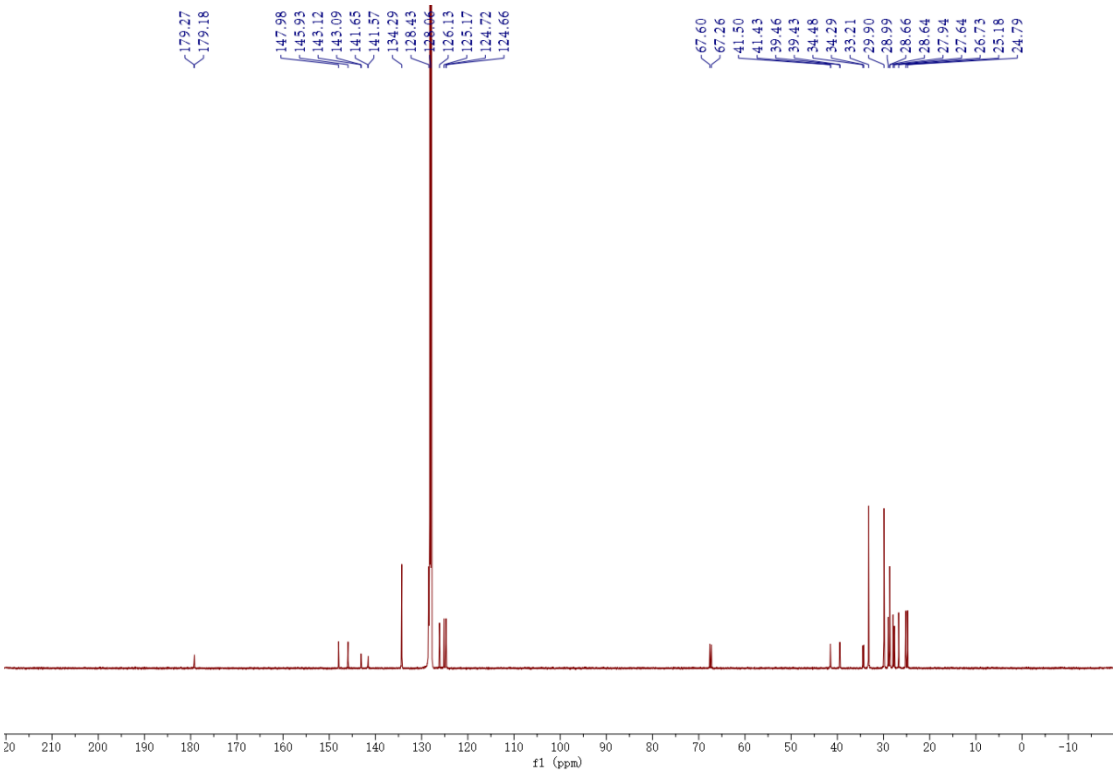

Fig. S28 $^{13}C\{^{1}H\}$ NMR spectrum of **5** in C_6D_6 at 298 K.

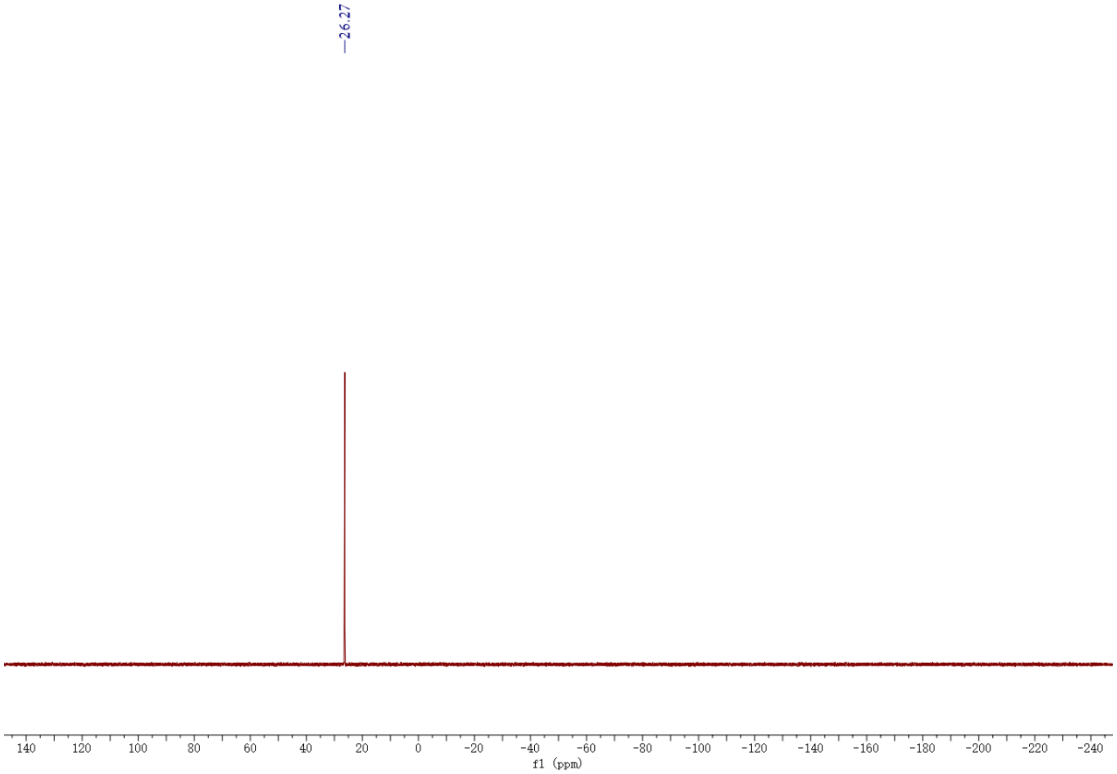

Fig. S29 $^{31}P\{^{1}H\}$ NMR spectrum of **5** in C_6D_6 at 298 K.

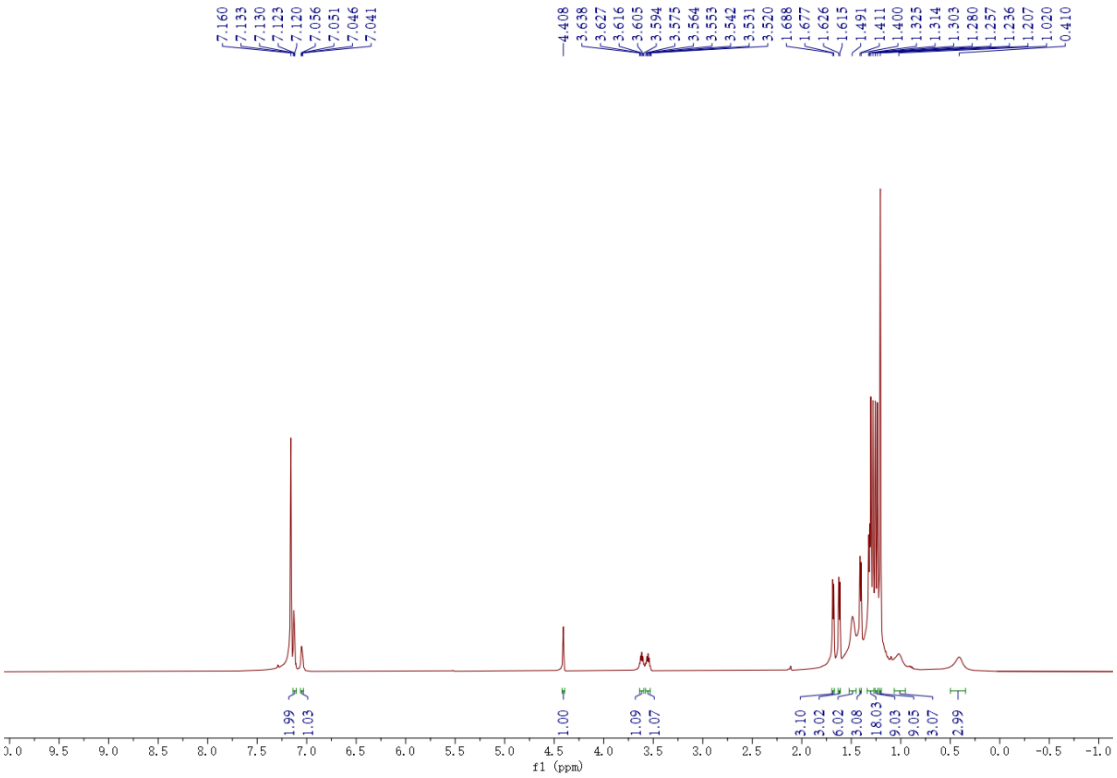

Fig. S30 ^{1}H NMR spectrum of **6** in C_6D_6 at 298 K.

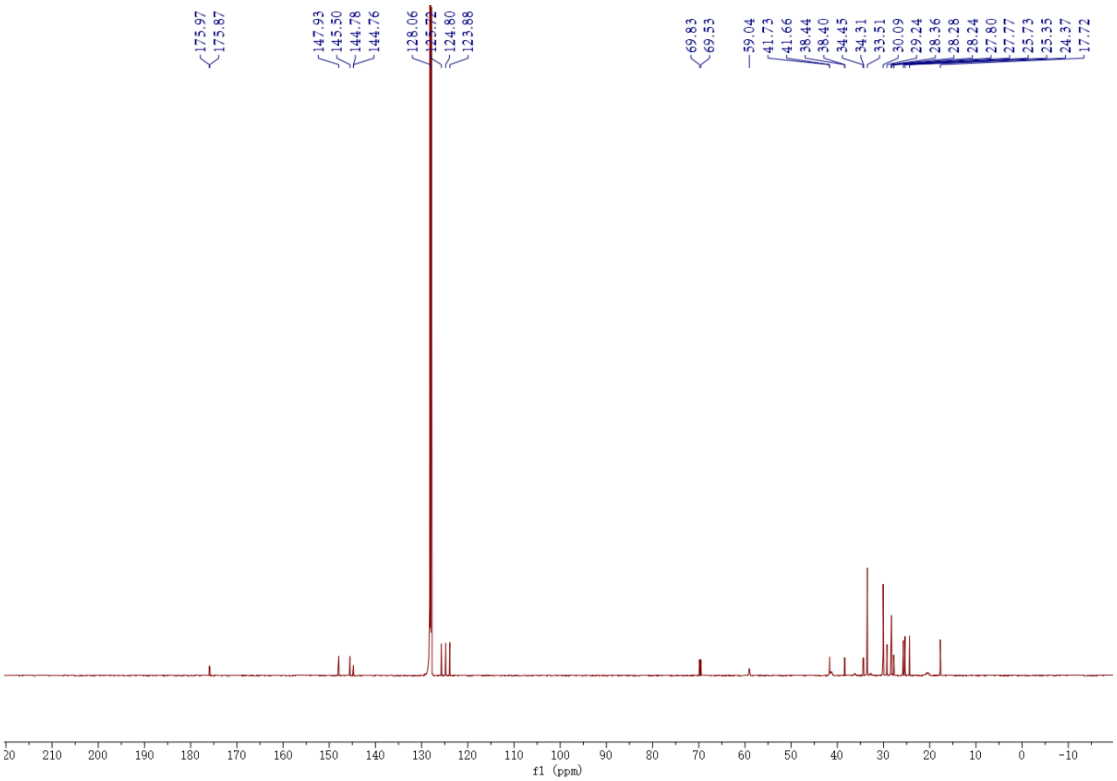

Fig. S31 ^{13}C{^{1}H} NMR spectrum of **6** in C_6D_6 at 298 K.

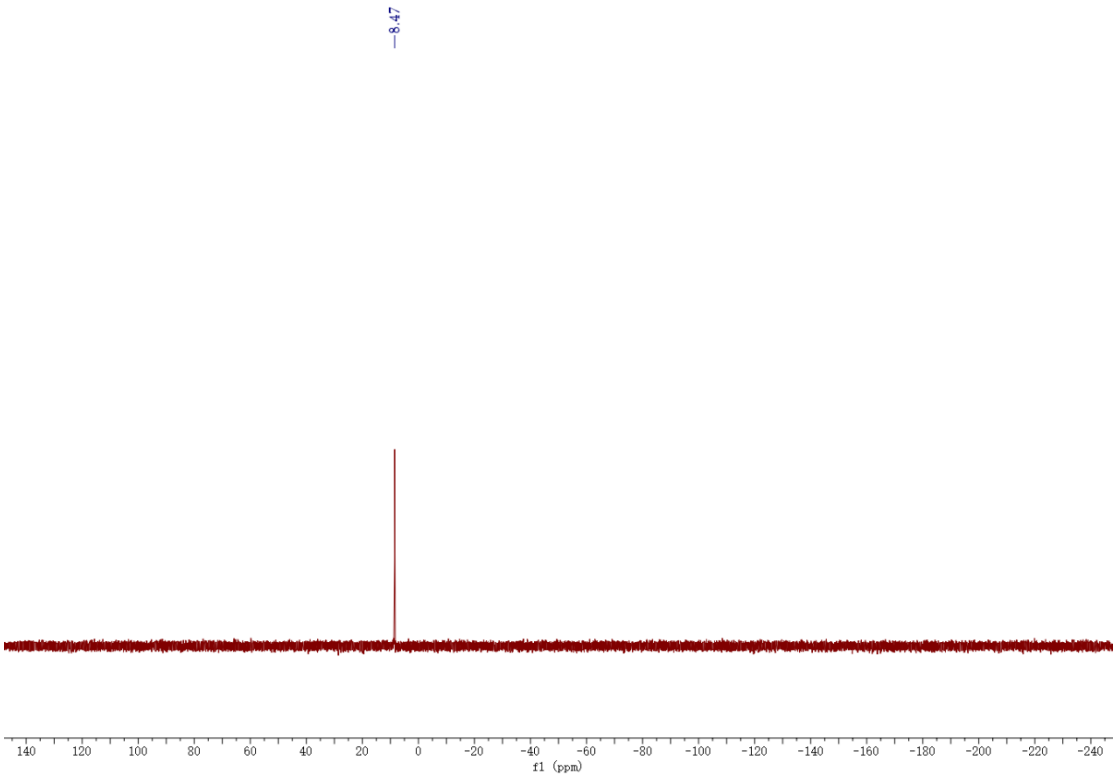

Fig. S32 $^{31}P\{^{1}H\}$ NMR spectrum of **6** in C_6D_6 at 298 K.

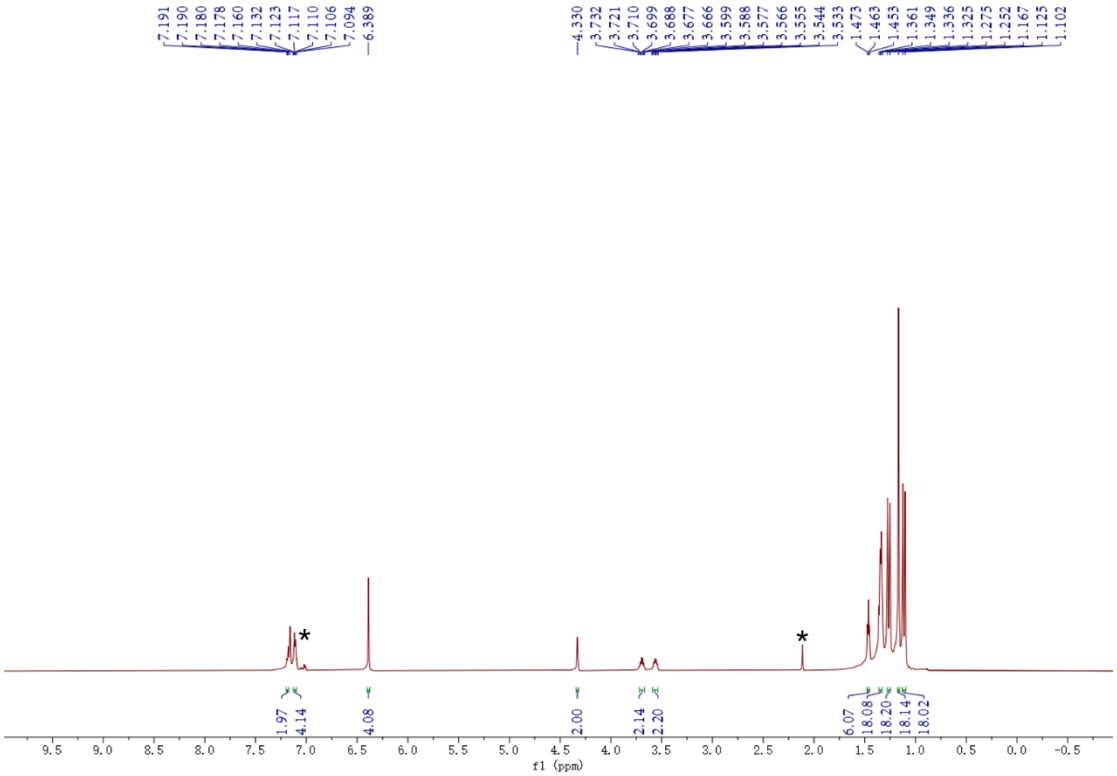

Fig. S33 ^{1}H NMR spectrum of **7** in C_6D_6 at 298 K (* toluene).

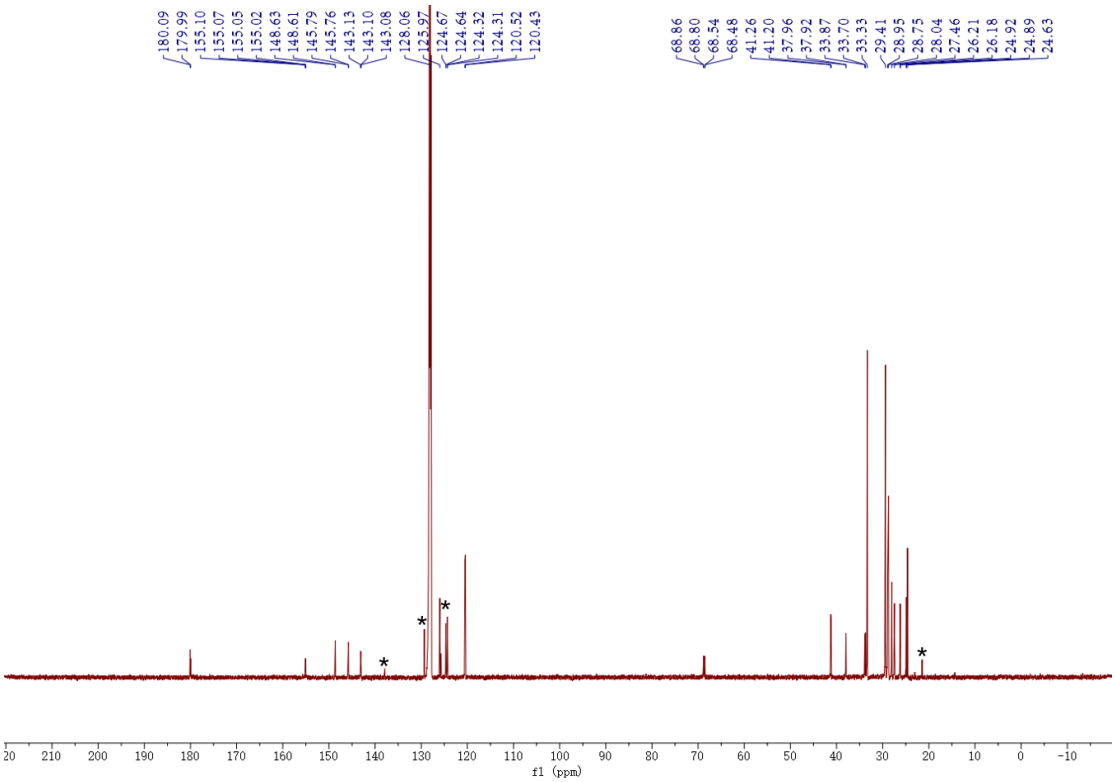

Fig. S34 $^{13}C\{^{1}H\}$ NMR spectrum of **7** in C_6D_6 at 298 K (* toluene).

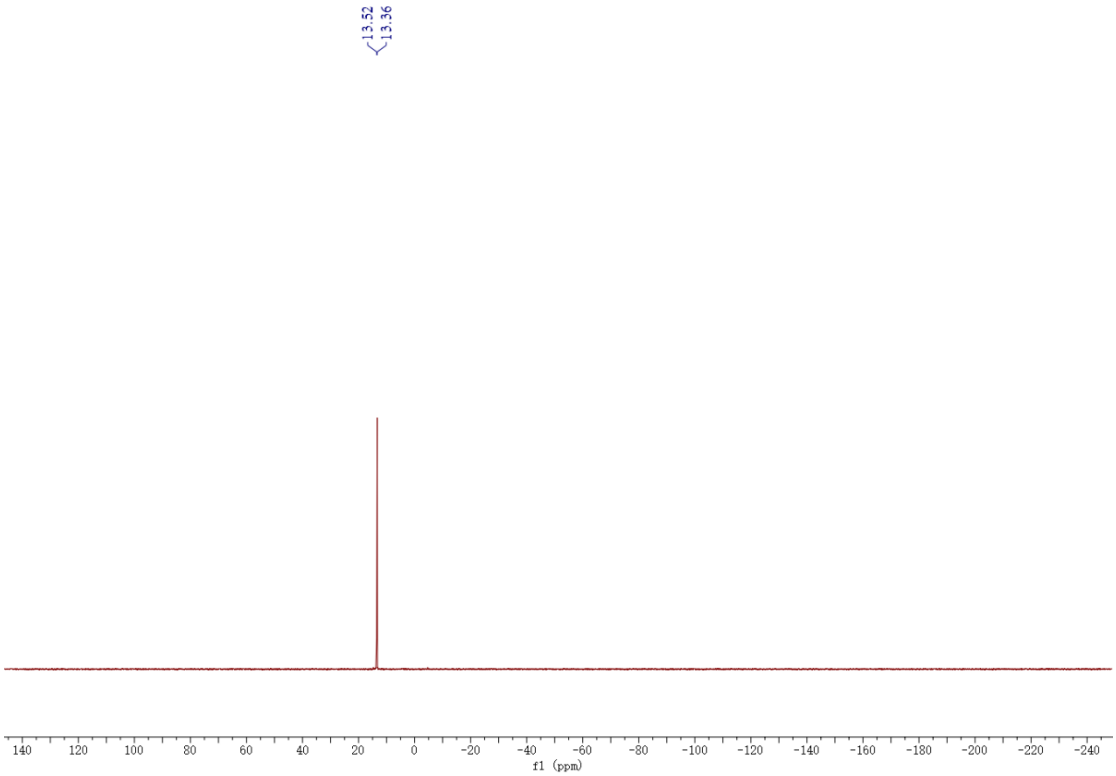

Fig. S35 $^{31}P\{^{1}H\}$ NMR spectrum of **7** in C_6D_6 at 298 K.

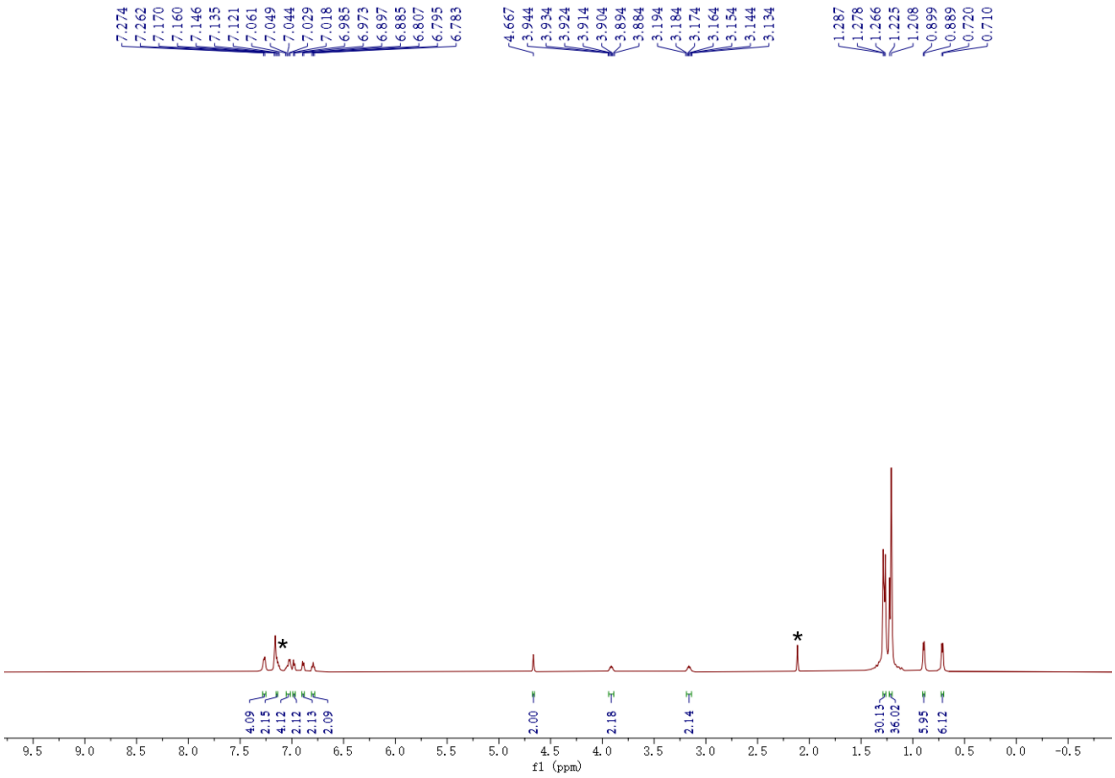

Fig. S36 ^{1}H NMR spectrum of **8** in C_6D_6 at 298 K (* toluene).

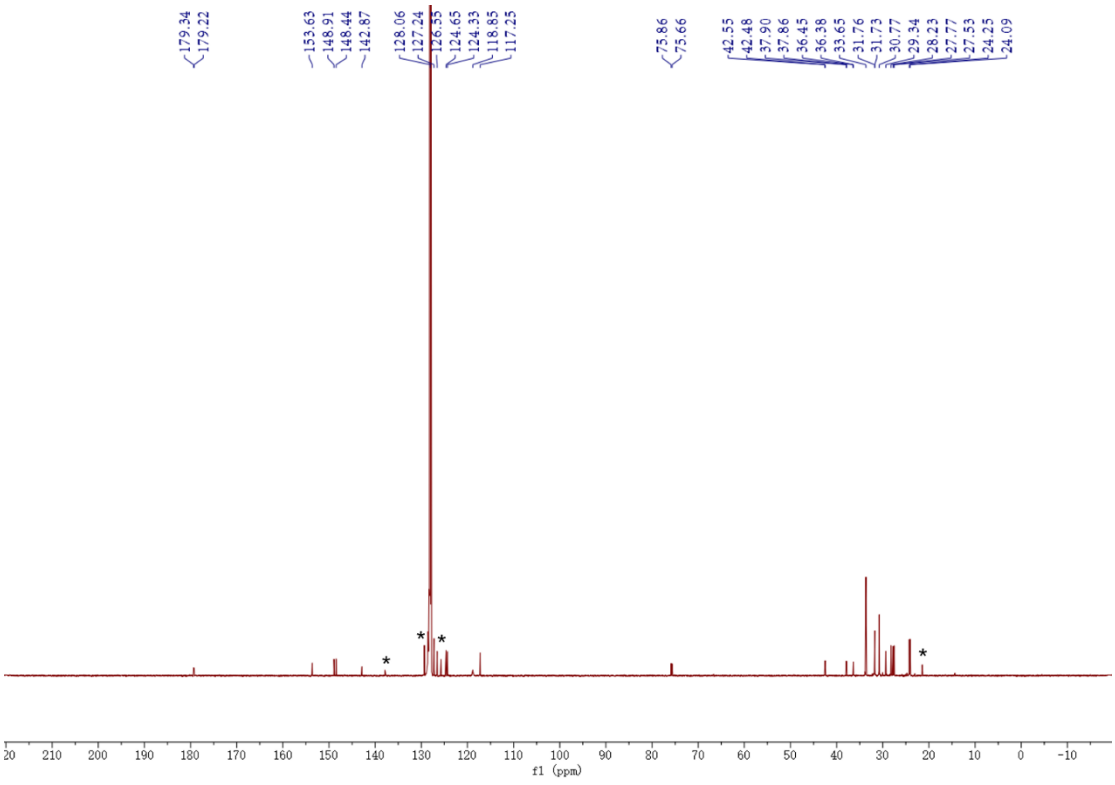

Fig. S37 $^{13}C\{^{1}H\}$ NMR spectrum of **8** in C_6D_6 at 298 K (* toluene).

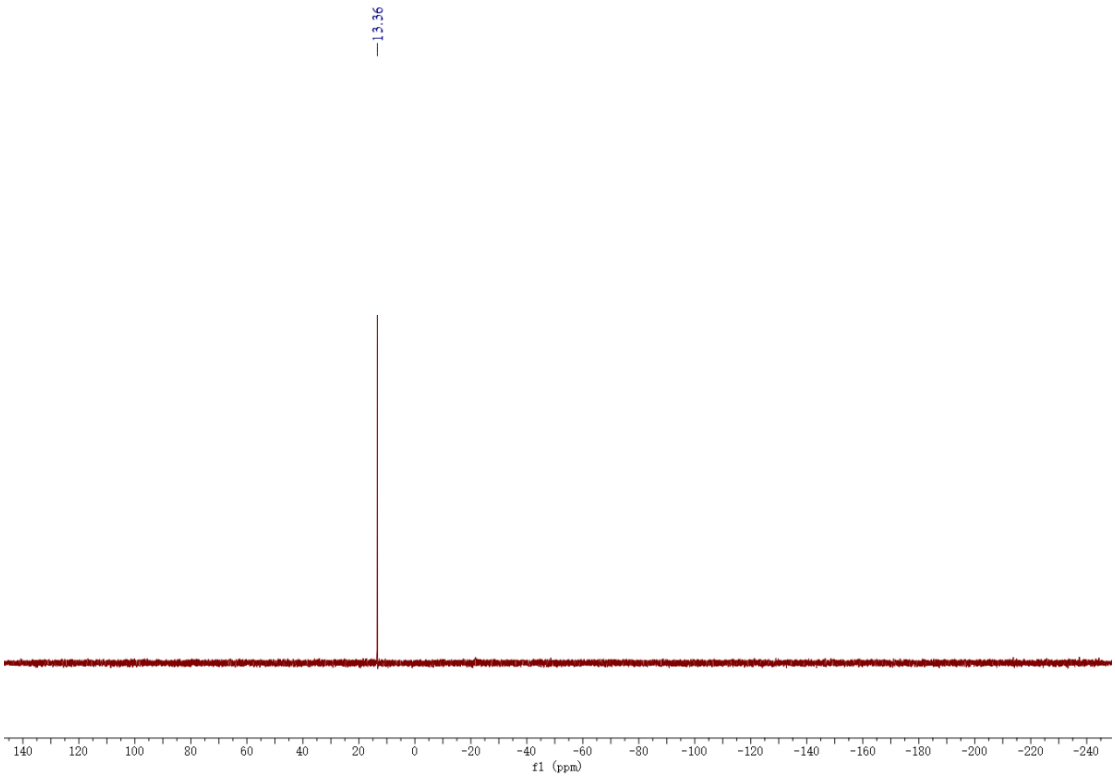

Fig. S38 $^{31}P\{^{1}H\}$ NMR spectrum of **8** in C_6D_6 at 298 K.