Supplementary Material for

Diphosphination of CO_2 and CS_2 mediated by frustrated Lewis pairs – catalytic route to phosphanyl derivatives of formic and dithioformic acid

*Natalia Szynkiewicz, Łukasz Ponikiewski, Rafał Grubba**

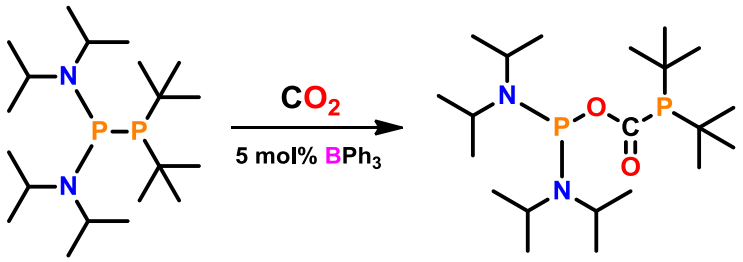
*Department of Inorganic Chemistry, Faculty of Chemistry, Gdańsk University of Technology, G. Narutowicza St. 11/12. PL-80-233, Gdansk, Poland.

CONTENTS:

Experimental section

All manipulations were carried out under a dry argon atmosphere by using of flame-dried Schlenk-type glassware on a vacuum line or in a glove-box. Solvents were dried by standard procedures over Na(K)/K/Na /benzophenone and distilled under argon. 1D (^{31}P, ^{13}C, ^{11}B and ^{1}H) and 2D NMR spectra in C_6D_6 solution were recorded on a Bruker AV400 MHz spectrometer (external standard TMS for ^{1}H and ^{13}C; 85% H_3PO_4 for ^{31}P) at ambient temperature. Low-temperature ^{31}P, ^{31}P{^{1}H} and ^{1}H NMR experiments were performed for toluene-d_8 solutions of **1, 2** and **3** under CO_2 atmosphere with data collected at 298 K, 273 K, 248 K and 223 K. Synthesis and specification of diphosphanes **1** and **3** was described in [1]. Diphosphane **2** was synthezied via method described for **1** and **3**. BPh_3 and CS_2 were purchased from Aldrich. CS_2 was dried over P_2O_5 and distilled prior to use. Reaction progress was monitored by ^{31}P{^{1}H} NMR spectra of reaction mixtures.

Preparation of 1a



1 **1a**

(a) A solution of BPh_3 (6 mg, 0.025 mmol, 5%mol) and **1** (188 mg, 0.5 mmol) in toluene (4 mL) was slowly frozen in a liquid nitrogen bath, evacuated to 0.01 Torr and backfilled with CO_2 (1 atm). The solution was allowed to warm to room temperature and stirred for 2 days. ^{31}P{^{1}H} of the colourless reaction mixture revealed complete conversion of **1** into **1a**. The volume of the reaction mixture was reduced to 1 ml under reduced pressure. The solution was left at -20^{o}C overnight to afford colorless X-ray quality crystals of **1a**, which were dried in vacuum. Yield 90% (190 mg, 0.452 mmol). Product 1a was also obtained in the reaction of **1** (188 mg, 0.5 mmol) with (b) 25%mol (30 mg, 0.125 mmol) and (c) 100%mol (121 mg, 0.5 mmol) of BPh_3. In the case of (c) complete conversion into **1a** proceeded after 24 hours at room temperature. Crystals obtained from reactions (b) and (c) were contaminated with BPh_3 that co-crystalize with **1a** (~10%mol).Yield (b) 71% (150 mg, 0.357 mmol), (c) 55% (115 mg, 0.273 mmol).

NMR:

^{31}P{^{1}H} NMR (C_6D_6): δ = 113.4 (d, $^{3}J_{PP}$ = 14.5 Hz, P(*i*Pr$_2$N)$_2$) , 47.4 (d, $^{3}J_{PP}$ = 14.5 Hz, P*t*Bu$_2$).

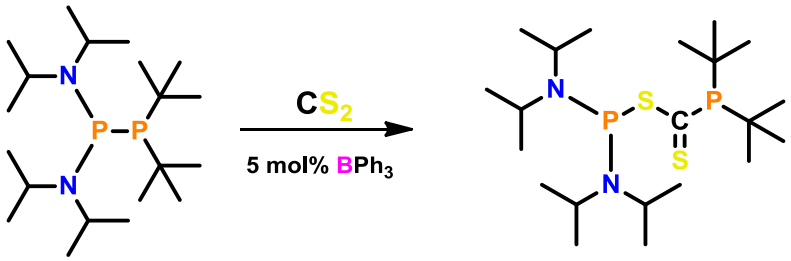
^{1}H NMR (C_6D_6): δ 3.48 (two overlapped signals, 4H, *CH*CH$_3$), 1.38 (d, $^{3}J_{PH}$ = 11.4 Hz, 18H, C(*CH$_3$)$_3$*), 1.31 (d, $^{3}J_{HH}$ = 6.6 Hz, 12H, CH*CH$_3$*), 1.35 (d, $^{3}J_{HH}$ = 6.7 Hz, 12H, CH*CH$_3$*).

^{13}C{^{1}H} NMR (C_6D_6): δ 178.2 (dd, $^{1}J_{PC}$ = 29.4 Hz, $^{2}J_{PC}$ = 4.4 Hz, *C*=O), 45.9 (d, $^{2}J_{PC}$ = 14.2 Hz, *CH*CH$_3$), 32.8 (d, $^{1}J_{PC}$ = 21.8 Hz, *C*(CH$_3$)$_3$), 30.1 (d, $^{2}J_{PC}$ = 13.1 Hz, C*(CH$_3$)$_3$*), 24.1 (d, $^{3}J_{PC}$ = 6.5 Hz, CH*CH$_3$*), 23.5 (d, $^{3}J_{PC}$ = 9.8 Hz, CH*CH$_3$*).

Elemental analysis: calcd. for $C_{21}H_{46}N_2O_2P_2$: C, 59.98; H, 11.02; N, 6.66. Found: C, 59.99; H, 10.91; N, 6.57.

IR (solid): $\tilde{\upsilon}$ = 2969, 2938, 2866, **1667 (C=O),** 1461,1392, 1363, 1183, 1105 1022, 957, 872, 814, 631, 594, 515 cm^{-1}

Preparation of 1b



1 **1b**

(a) To a stirred solution of BPh_3 (6 mg, 0.025 mmol, 5%mol) and **1** (188 mg, 0.5 mmol) in toluene (4 ml), 0.1 ml of CS_2 (126 mg, 1.65 mmol) was added dropwise at room temperature. The solution was allowed to stirred for 3 days. $^{31}P\{^1H\}$ NMR of deep green reaction mixture revealed complete conversion of **1** into **1b**. The volume of the reaction mixture was reduced to 1 ml under reduced pressure. The solution was left at -20°C overnight to afford deep red X-ray quality crystals of **1b**, which were dried in vacuum. Yield 84% (190 mg, 0.42 mmol). Product **1b** was also obtained in the reaction of **1** (188 mg, 0.5 mmol) with (b) 25%mol (30 mg, 0.125 mmol) and (c) 100%mol (121 mg, 0.5 mmol) of BPh_3. In the case of (c) complete conversion into **1b** proceeded after 24 hours at room temperature. Crystals obtained from reactions (b) and (c) were contaminated with BPh_3 that co-crystalize with **1b** (~10%mol). Yield (b) 81% (183 mg, 0.404 mmol), (c) 76% (172mg, 0.380 mmol).

NMR:

$^{31}P\{^1H\}$ NMR (C_6D_6): δ = 106.6 (d, $^3J_{PP}$ = 14.5 Hz, P(*i*$Pr_2N)_2$), 75.0 (d, $^3J_{PP}$ = 14.5 Hz, P*t*Bu_2).

^1H NMR (C_6D_6): δ 3.40 (m, 4H, *CH*CH_3), 1.39 (d, $^3J_{PH}$ = 11.6 Hz, 18H, C(*CH₃*)₃), 1.24 (d, $^3J_{HH}$ = 6.7 Hz, 12H, CH*CH₃*), 1.07 (d, $^3J_{HH}$ = 6.7 Hz, 12H, CH*CH₃*).

$^{13}C\{^1H\}$ NMR (C_6D_6): δ 250.8 (dd, $^1J_{PC}$ = 64.5 Hz, $^2J_{PC}$ = 20.9 Hz, *C*=S), 49.1 (d, $^2J_{PC}$ = 11.8 Hz, *CH*CH_3), 34.9 (d, $^1J_{PC}$ = 30.9 Hz, *C*$(CH_3)_3$), 29.8 (d, $^2J_{PC}$ = 14.5 Hz, C*(CH₃)₃*), 23.8 (d, $^3J_{PC}$ = 4.5 Hz, CH*CH₃*), 23.5 (d, $^3J_{PC}$ = 9.1 Hz, CH*CH₃*).

Elemental analysis: calcd. for $C_{21}H_{46}N_2S_2P_2$: C, 55.72; H, 10.24; N, 6.19; S, 14.17. Found: C ,55.72; H, 10.27; N, 6.19; S, 13.97.

IR (solid): $\tilde{\upsilon}$ = 2962, 2941, 2860, 1456, 1388, 1363, 1196, 1174, 1113, 1045 (**C=S**), 1016, 951, 867, 796, 510 cm^{-1}

Preparation of 2

To a solution of tBu$_2$PLi (1.173 g, 7.710 mmol) in 40 cm^3 of THF cooled to -50°C, (Et$_2$N)(iPr$_2$N)PCl (1.841 g, 7.71 mmol) was added dropwise. The reaction mixture was stirred at -50°C for 30 minutes and then allowed to warm to room temperature for further 30 minutes. The solvent was evaporated and the residue was dried under vacuum (0.01 Torr) for 30 minutes at 50°C to remove all volatiles. The crude product was dissolved in 10 cm^3 of petroleum ether and filtered. Removal of the solvent under vacuum afforded 2.517 g (7.223 mmol) of **2** as a yellowish oil in 94% yield.

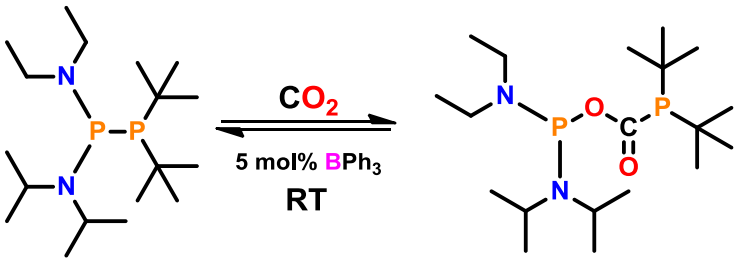
NMR :

^{31}P{^{1}H} NMR (C_6D_6): δ 98.9 (d, $^1J_{PP}$ = 247.0 Hz, P(Et$_2$N)(iPr$_2$N)), 35.3 (d, $^1J_{PP}$ = 247.0 Hz, PtBu$_2$).

^{1}H NMR (C_6D_6): δ 3.59 (m, 2H, C*H*), 3.29 (m, 2H, CH_2), 3.07 (m, 2H, CH_2), 1.42 (d, $^3J_{PH}$ = 10.8, 9H, C(CH_3)$_3$), 1.40 (d, $^3J_{PH}$ =10.3, 9H, C(CH_3)$_3$), 1.21 (d, $^3J_{HH}$ =6.1 Hz, 6H, CHCH_3), 1.20 (d, $^3J_{HH}$ = 6.1 Hz, 6H, CHCH_3), 1.07 (t, $^3J_{HH}$ = 7.0 Hz, 6H, CH$_2$CH_3).

^{13}C{^{1}H} NMR (C_6D_6): δ 50.3 (br, *C*HCH$_3$), 45.6 (dd, $^2J_{PC}$ = 17.6 Hz, $^3J_{PC}$ = 6.6 Hz, *C*H$_2$CH$_3$), 34.2 (dd, $^2J_{PC}$ = 32.3 Hz, $^3J_{PC}$ = 11.7 Hz, *C*(CH$_3$)$_3$), 33.6 (dd, $^2J_{PC}$ = 30.8 Hz, $^3J_{PC}$ = 13.2 Hz, *C*(CH$_3$)$_3$), 32.0 (dd, $^2J_{PC}$ = 13.2 Hz, $^3J_{PC}$ = 5.9 Hz, C*(CH$_3$)$_3$*), 31.8 (dd, $^2J_{PC}$ = 13.2 Hz, $^3J_{PC}$ = 5.9 Hz, C*(CH$_3$)$_3$*), 24.2 (d, $^3J_{PC}$ = 8.8 Hz, CH*C*H$_3$), 23.8 (d, $^3J_{PC}$ = 6.6 Hz, CH*C*H$_3$), 14.4 (br, CH$_2$*C*H$_3$).

Preparation of 2a



2 **2a**

A solution of BPh$_3$ (6 mg, 0.025 mmol, 5%mol) and **2** (174 mg, 0.5 mmol) in toluene (4 mL) was slowly frozen in a liquid nitrogen bath, evacuated to 0.01 Torr and backfilled with CO$_2$ (1 atm). The solution was allowed to warm to room temperature and stirred for 24 hours. ^{31}P{^{1}H} NMR spectra of the colourless reaction mixture revealed complete conversion of **2** into **2a**. Pure product was not isolated as the formation of **2a** turned out to be reversible in absence of CO$_2$ – ^{31}P NMR spectra of crude oil, after evaporation of solvent, revealed presence of **2** (9mol% of **2** and 91mol% of **2a** based on ^{1}H NMR spectra). Product **2a** was also obtained in the reaction of **2** (174 mg, 0.5 mmol) with (b) 25%mol (30 mg, 0.125 mmol) and (c) 100%mol (121 mg, 0.5 mmol) of BPh$_3$ in quantitative yield based on ^{31}P NMR spectra. In each attempt (a-c) complete conversion into **2a** proceeded after 24 hours at room temperature.

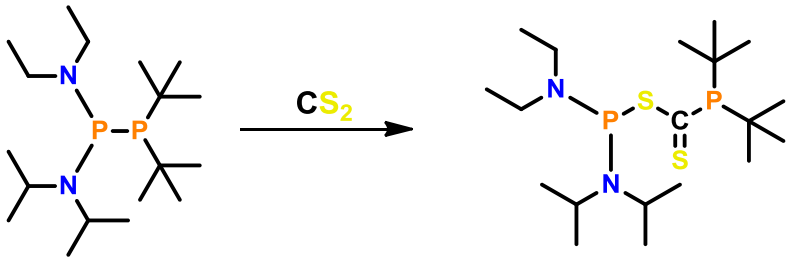
NMR:

^{31}P{^{1}H} NMR (C_6D_6): δ 119.4 (d, $^3J_{PP}$ = 14.5 Hz, P(Et$_2$N)(iPr$_2$N)) , 46.1 (d, $^3J_{PP}$ = 14.5 Hz, PtBu$_2$).

^{1}H NMR (C_6D_6): δ 3.51 (m, 2H, C*H*), 3.14 (m, 2H, CH_2), 3.03 (m, 2H, CH_2), 1.35 (d, $^{3}J_{PH}$ = 11.6 Hz, 9H, C(CH_3)$_3$), 1.36 (d, $^{3}J_{PH}$ = 11.6 Hz, 9H, C(CH_3)$_3$), 1.27 (d, $^{3}J_{HH}$ = 6.7 Hz, 6H, CHCH_3), 1.14 (d, $^{3}J_{HH}$ = 6.8 Hz, 6H, CHCH_3), 1.06 (t, $^{3}J_{HH}$ = 7.2 Hz, 6H, CH$_2$CH_3).

^{13}C{^{1}H} NMR (C_6D_6): δ 178.6 (dd, $^{1}J_{PC}$ = 29.1.4 Hz, $^{2}J_{PC}$ = 4.5 Hz, *C*=O), 45.2 (d, $^{2}J_{PC}$ = 14.5 Hz, *C*HCH$_3$), 40.2 (d, $^{2}J_{PC}$ = 19.1 Hz, *C*H$_2$CH$_3$), 32.8 (d, $^{1}J_{PC}$ =21.8 Hz, *C*(CH$_3$)$_3$), 32.7 (d, $^{1}J_{PC}$ =22.7 Hz, *C*(CH$_3$)$_3$), 30.0 (d, $^{2}J_{PC}$ = 12.7 Hz, C(*CH$_3$*)$_3$), 29.9 (d, $^{2}J_{PC}$ = 12.7 Hz, C(*CH$_3$*)$_3$), 24.1 (d, $^{3}J_{PC}$ = 7.3 Hz, CH*CH$_3$*), 23.5 (d, $^{3}J_{PC}$ = 9.1 Hz, CH*CH$_3$*), 14.4 (bd, $^{3}J_{PC}$ = 3.6 Hz CH$_2$*CH$_3$*).

Preparation of 2b



2 **2b**

To a stirred solution of **2** (174 mg, 0.5 mmol) in toluene (4 ml), 0.2 ml of CS_2 (252 mg, 3.33 mmol) was added dropwise at room temperature. The solution was allowed to stirred for 1 hour. ^{31}P{^{1}H} NMR of deep green reaction mixture revealed complete conversion of **2** into **2b**. The solution was removed in vacuo and 1 cm^3 of pentane was added to deep green oily residue. The solution was left at -80^{o}C overnight to afford deep green X-ray quality crystals of **2b**, which were dried in vacuum at -10°C. Elemental analysis was not performed as crystals of **2b** slowly melt at room temperature. Yield 89% (190 mg, 0.447 mmol).

NMR:

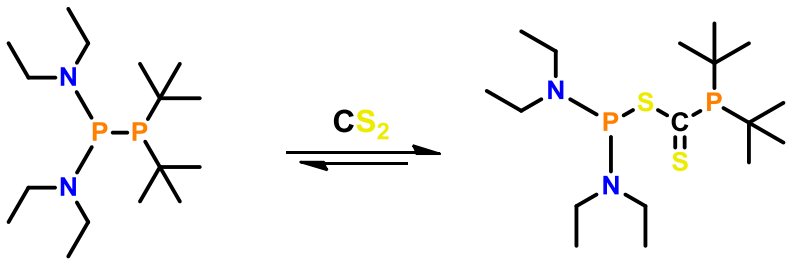
^{31}P{^{1}H} NMR (C_6D_6): δ 112.6 (d, $^{3}J_{PP}$ = 10.5 Hz, P(Et$_2$N)(*i*Pr$_2$N)), 74.9 (d, $^{3}J_{PP}$ = 10.5 Hz, P*t*Bu$_2$).

^{1}H NMR (C_6D_6): δ 3.11 (m, 2H, C*H*), 2.85 (m, 4H, CH_2), 1.21 (d, $^{3}J_{PH}$ = 11.7 Hz, 9H, C(CH_3)$_3$), 1.20 (d, $^{3}J_{PH}$ = 11.7 Hz, 9H, C(CH_3)$_3$), 0.96 (d, $^{3}J_{HH}$ = 6.7 Hz, 6H, CHCH_3), 0.88 (d, $^{3}J_{HH}$ = 6.7 Hz, 6H, CHCH_3), 0.79 (t, $^{3}J_{HH}$ = 7.0 Hz, 6H, CH$_2$CH_3).

^{13}C{^{1}H} NMR (C_6D_6): δ 253.2 (dd, $^{1}J_{PC}$ = 65.4 Hz, $^{2}J_{PC}$ = 20.0 Hz, *C*=S), 48.7 (d, $^{2}J_{PC}$ = 12.7 Hz, *C*HCH$_3$), 44.0 (d, $^{2}J_{PC}$ = 19.1 Hz, *C*H$_2$CH$_3$), 34.9 (d, $^{1}J_{PC}$ = 30.9 Hz, *C*(CH$_3$)$_3$), 34.4 (dd, $^{1}J_{PC}$ = 30.0 Hz, $^{2}J_{PC}$ = 2.7 Hz, *C*(CH$_3$)$_3$), 29.9 (d, $^{2}J_{PC}$ = 13.6 Hz, C*(CH$_3$)$_3$*), 29.7 (d, $^{2}J_{PC}$ = 13.6 Hz, C*(CH$_3$)$_3$*), 23.6 (d, $^{3}J_{PC}$ = 5.4 Hz, CH*CH$_3$*), 23.5 (d, $^{3}J_{PC}$ = 8.2 Hz, CH*CH$_3$*), 14.7 (bs, CH$_2$*CH$_3$*).

IR (solid): $\tilde{\upsilon}$ = 2962, 2925, 2860, 1454, 1386, 1361, 1195, 1195, 1176, 1117, 1050 (**C=S**), 1016, 956, 928, 802, 506 cm^{-1}

Preparation of 3b



3 **3b**

To a stirred solution of **3** (160 mg, 0.5 mmol) in toluene (4 ml), 0.2 ml of CS_2 (252 mg, 3.33 mmol) was added dropwise at room temperature. The solution was allowed to stirred for 30 minutes. $^{31}P\{^1H\}$ NMR of deep green reaction mixture revealed complete conversion of **3** into **3b**. Product was not isolated as the formation of **3b** turned out to be reversible in absence of CS_2 – ^{31}P NMR spectra of crude green oil, after evaporation of solvent, revealed presence of **3** (84 mol% of **3b** and 16mol% **3** based on ^1H NMR spectra). Complete conversion into **3b** proceeded after 30 minutes at room temperature and further stirring and/or storing reaction mixture caused formation of further rearrangement products.

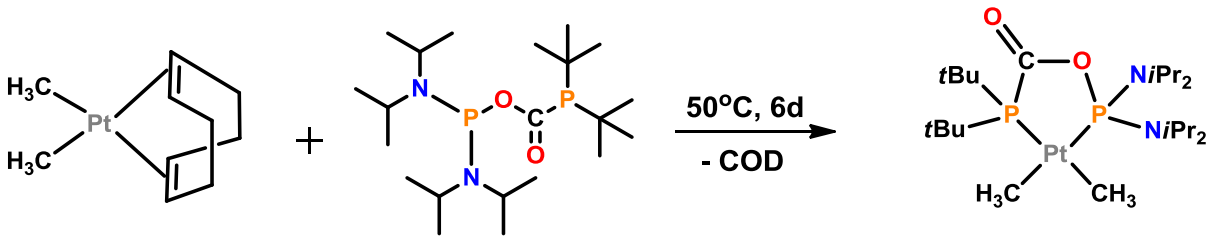
NMR:

$^{31}P\{^1H\}$ NMR (C_6D_6): δ 128.9 (d, $^3J_{PP}$ = 14.5 Hz, $P(Et_2N)_2$) , 75.9 (d, $^3J_{PP}$ = 14.5 Hz, $PtBu_2$).

^1H NMR (C_6D_6): δ 3.12 (m, 4H, CH_2), 2.94 (m, 4H, CH_2), 1.39 (d, $^3J_{PH}$ = 11.6 Hz, 18H, $C(CH_3)_3$), 1.02 (t, $^3J_{HH}$ = 7.2 Hz, 12H, CH_2CH_3).

$^{13}C\{^1H\}$ NMR (C_6D_6): δ 254.56 (dd, $^1J_{PC}$ = 66.3 Hz, $^2J_{PC}$ = 18.2 Hz, *C*=*S*), 43.5 (d, $^2J_{PC}$ = 18.2 Hz, CH_2CH_3), 34.6 (d, $^1J_{PC}$ = 30.9 Hz, $C(CH_3)_3$), 29.8 (d, $^2J_{PC}$ = 14.5 Hz, $C(CH_3)_3$), 14.4 (d, $^3J_{PC}$ = 3.6 Hz, CH_2CH_3).

Preparation of 4



A solution of **1a** (110 mg, 0.262 mmol) and (1,5-COD)$PtMe_2$ (87 mg, 0.262 mmol) in toluene (4 mL) was stirred at 50°C. After six days $^{31}P\{^1H\}$ NMR spectra revealed complete conversion of substrates into **1a**. The solvent was evaporated and oily residue was dried *in vacuo* at 50°C to remove all volatiles (crude oily product solidifies). **4** was obtained as crystalline yellowish solid in 98% yield (166 mg, 0.257 mmol). X-ray quality crystals of **4** were obtained by slow evaporation of toluene solution under reduced pressure.

NMR:

^{31}P{^{1}H} NMR (C_6D_6): δ = 135.1 (d, $^{2}J_{PP}$ = 21.8 Hz, $^{1}J_{PPt}$ = 2688.4 Hz, P(*i*Pr$_2$N)$_2$) , 86.2 (d, $^{2}J_{PP}$ = 21.8 Hz, $^{1}J_{PPt}$ = 1707.5 Hz, P*t*Bu$_2$).

^{1}H NMR (C_6D_6): δ 4.25 (m, 4H, *CH*CH$_3$), 1.36 (d, $^{3}J_{PH}$ = 13.8 Hz, 18H, C(*CH$_3$)$_3$*), 1.29-1.12 (two overlapped m, 6H, PtC*H$_3$*), 1.22 (d, $^{3}J_{HH}$ = 6.8 Hz, 12H, CH*CH$_3$*), 1.15 (d, $^{3}J_{HH}$ = 7.0 Hz, 12H, CH*CH$_3$*).

^{13}C{^{1}H} NMR (C_6D_6): δ 175.9 (dd, $^{1}J_{PC}$ = 33.6 Hz, $^{2}J_{PC}$ = 22.4 Hz, *C*=O), 47.6 (d, $^{2}J_{PC}$ = 12.4 Hz, $^{3}J_{CPt}$ = 12.4 Hz, *CH*CH$_3$), 37.2 (dd, $^{1}J_{PC}$ = 9.9 Hz, $^{3}J_{PC}$ = 2.5 Hz, $^{2}J_{CPt}$ = 24.9 Hz, *C*(CH$_3$)$_3$), 29.7 (d, $^{2}J_{PC}$ = 6.2 Hz, $^{3}J_{CPt}$ = 10.0 Hz C*(CH$_3$)$_3$*), 25.1 (d, $^{3}J_{PC}$ = 2.5 Hz, CH*CH$_3$*), 23.9 (d, $^{3}J_{PC}$ = 5.0 Hz, CH*CH$_3$*), 3.5 (dd, $^{2}J_{PC}$ = 95.8 Hz, $^{2}J_{PC}$ = 7.5 Hz, $^{1}J_{CPt}$ = 609.5 Hz, Pt*C*H$_3$), -0.8 (dd, $^{2}J_{PC}$ = 134.3 Hz, $^{1}J_{PC}$ = 7.5 Hz, $^{2}J_{CPt}$ = 577.2 Hz, Pt*C*H$_3$).

Elemental analysis: calcd. for $C_{23}H_{52}N_2O_2P_2Pt$: C, 42.78; H, 8.12; N, 4.34. Found: C, 42.77; H, 8.01; N, 4.09.

IR (solid): $\tilde{\upsilon}$ = 2969, 2933, 2872, 1712 (**C=O**), 1471, 1457, 1362, 1184, 1124, 1078, 986, 972, 869, 844, 809, 641, 611, 590, 553, 476.

X-ray structures analysis

Diffraction data of compounds **1a**, **1b**, **2b** and **4** were collected on diffractometer equipped with a STOE image plate detector system IPDS2T using MoKα (λ = 0.71073 Å) radiation with graphite monochromatization (λ = 0.71073 Å). Good quality single-crystal specimens were selected for the X-ray diffraction experiments at 120 K. The structures were solved by direct methods and refined against F2 using the Shelxs-97 and Shelxl-97[2] programs run under WinGX[3]. Non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms were usually refined using the isotropic model with U_{iso}(H) values fixed to be 1.5 times U_{eq} of C atoms for $-CH_3$ or 1.2 times U_{eq} for –CH, $-CH_2$ groups and aromatic H.

Crystallographic data for structures of **1a, 1b, 2b** and **4** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-1857357 (**1a**), CCDC- 1857359 (**1b**), CCDC- 1857358 (**2b**) CCDC- 1857360 (**4**). Copies of the data can be obtained free of charge on *via* www.ccdc.cam.uk/data_request/cif (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

TABLE S1. CRYSTALLOGRAPHIC PARAMETERS OF DETERMINED STRUCTES **1A**, **1B**, **2B** AND **4**

	1a	**1b**	**2b**	**4**
Empirical formula	$C_{21}H_{46}N_2O_2P_2$	$C_{21}H_{46}N_2P_2S_2$	$C_{19}H_{42}N_2P_2S_2$	$C_{23}H_{52}N_2O_2P_2Pt$
M_r [g mol^{-1}]	420.54	452.66	424.6	645.69
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1$	$P2_1$	P-1	$P2_1/c$
a [Å]	10.3569(7)	10.7172(5)	12.6968(4)	18.1821(10)
b [Å]	11.0026(4)	10.5593(6)	13.8758(6)	17.6525(7)
c [Å]	12.2025(7)	12.6782(6)	14.6351(5)	17.7026(10)
α [°]	90	90	94.762(3)	90
β [°]	114.816(4)	113.193(3)	100.840(3)	97.794(4)
γ [°]	90	90	90.497(3)	90
V [Å^3]	1262.11(13)	1318.8(12)	2522.86(16)	5629.3(5)
Z	2	2	4	8
Calculated density [g cm^{-3}]	1.107	1.14	1.118	1.524
T [K]	120	120	120	120
μ [mm^{-1}]	0.19	0.33	0.34	5.119
Crystal size/mm^3	0.22 × 0.22 × 0.1	0.22 × 0.21 × 0.17	0.23 × 0.21 × 0.20	0.22 × 0.21 × 0.21
F(000)	464	496	928	2624
λ [Å] (MoKα)	0.71073	0.71073	0.71073	0.71073
Final R indices	R_1 = 0.0338	R_1 = 0.0443	R_1 = 0.0445	R_1 = 0.0516
[*I>2σ(I)*]	wR_2 = 0.0828	wR_2 = 0.0922	wR_2 = 0.1139	wR_2 = 0.1312
R indices (all data)	R_1 = 0.0.0407	R_1 = 0.0674	R_1 = 0.0679	R_1 = 0.0641
	wR_2 = 0.0889	wR_2 = 0.1018	wR_2 = 0.1230	wR_2 = 0. 0.1383
Largest diff. peak/hole/ e Å^{-3}	0.32/-0.18	0.42/-0.26	0.39/-0.33	3.234/ -4.021
CCDC	1857357	1857359	1857358	1857360

Single X-ray structure analysis of 1a

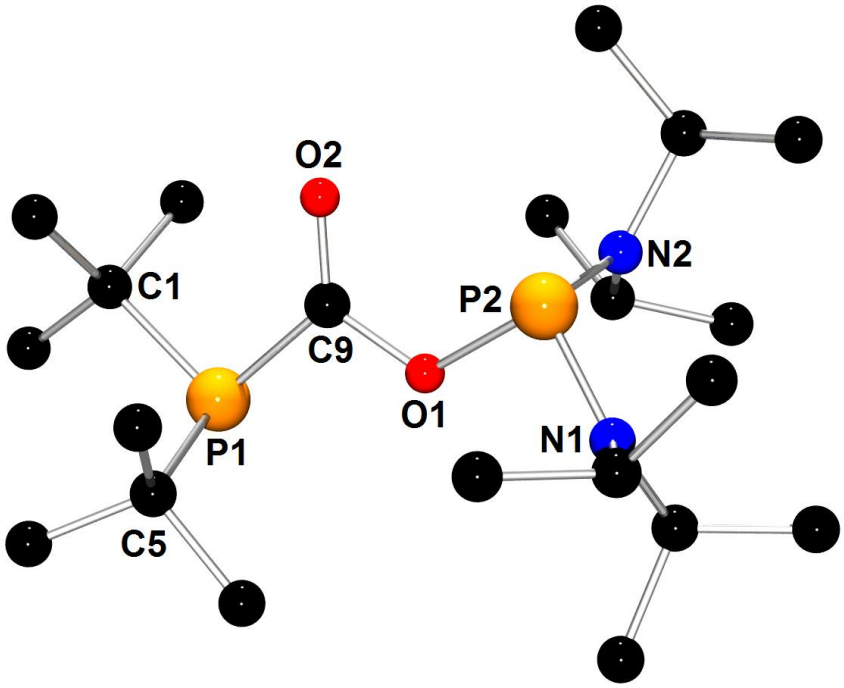


FIG. S1. SINGLE CRYSTAL X-RAY STRUCTURE **1A**

TABLE S2. SELECTED STRUCTURAL PARAMETERS OF **1A**

Bond lengths [Å]		**Bond angles [°]**		**Dihedrals [°]**	
P1-C9	1.870(2)	P1-C9-O2	109.3(2)	P1-C9-O1-P2	-176.0(1)
C9-O2	1.205(3)	O2-C9-O1	123.0(2)	O2-C9-O1-P2	5.9(3)
C9-O1	1.348(3)	C9-O1-P2	118.3(2)		
P2-O1	1.736(2)	N1-P2-N2	108.9(1)		
P2-N1	1.667(2)	C1-P1-C5	110.9(1)		
P2-N2	1.674(2)				
P1-C1	1.877(2)				
P1-C5	1.892(3)				

Single X-ray structure analysis of 1b

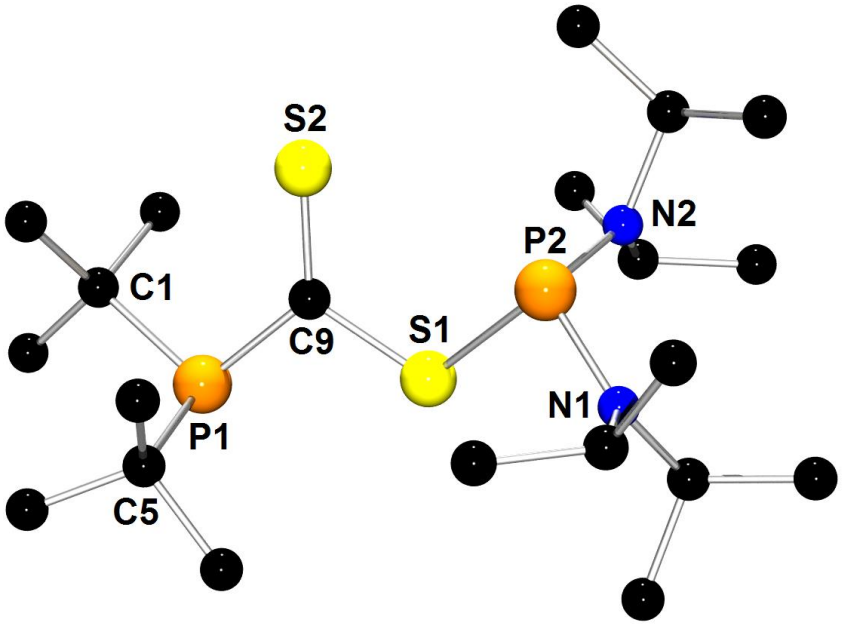


FIG. S2. SINGLE CRYSTAL X-RAY STRUCTURE OF **1B**

TABLE S3. SELECTED STRUCTURAL PARAMETERS OF **1B**

Bond lengths [Å]		**Bond angles [°]**		**Dihedrals [°]**	
P1-C9	1.851(4)	P1-C9-S2	129.3(3)	P1-C9-S1-P2	-164.8(1)
C9-S2	1.640(4)	S2-C9-S1	123.6(3)	S2-C9-S1-P2	16.2(3)
C9-S1	1.730(4)	C9-S1-P2	105.2(1)		
P2-S1	2.193(1)	N1-P2-N2	108.6(2)		
P2-N1	1.680(3)	C1-P1-C5	110.5(2)		
P2-N2	1.673(4)				
P1-C1	1.886(4)				
P1-C5	1.911(5)				

Single X-ray structure analysis of 2b

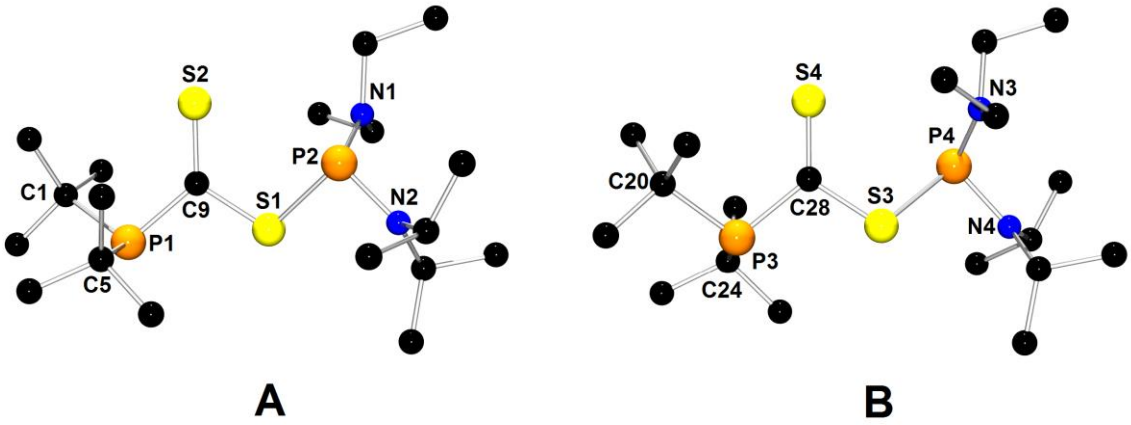


FIG. S3. SINGLE CRYSTAL X-RAY STRUCTURE OF **2B**

TABLE S4. SELECTED STRUCTURAL PARAMETERS OF **2B** (A)

Bond lengths [Å]		**Bond angles [°]**		**Dihedrals [°]**	
P1-C9	1.859(2)	P1-C9-S2	129.7(1)	P1-C9-S1-P2	-158.77(8)
C9-S2	1.636(2)	S2-C9-S1	123.8(1)	S2-C9-S1-P2	20.2(1)
C9-S1	1.745(2)	C9-S1-P2	101.27(7)		
P2-S1	2.1735(8)	N1-P2-N2	110.04(9)		
P2-N1	1.668(2)	C1-P1-C5	111.6(1)		
P2-N2	1.684(2)				
P1-C1	1.908(2)				
P1-C5	1.884(2)				

TABLE S5. SELECTED STRUCTURAL PARAMETERS OF **2B** (B)

Bond lengths [Å]		**Bond angles [°]**		**Dihedrals [°]**	
P3-C28	1.857(2)	P3-C28-S4	129.3(1)	P3-C28-S3-P4	158.83(7)
C28-S4	1.641(2)	S4-C28-S3	124.3(1)	S4-C28-S3-P4	-20.0(1)
C28-S3	1.741(2)	C28-S3-P4	101.72(7)		
P4-S3	2.1756(7)	N3-P4-N4	110.03(9)		
P4-N3	1.668(2)	C20-P3-C24	111.5(1)		
P4-N4	1.681(2)				
P3-C20	1.886(3)				
P3-C24	1.899(2)				

Single X-ray structure analysis of 4

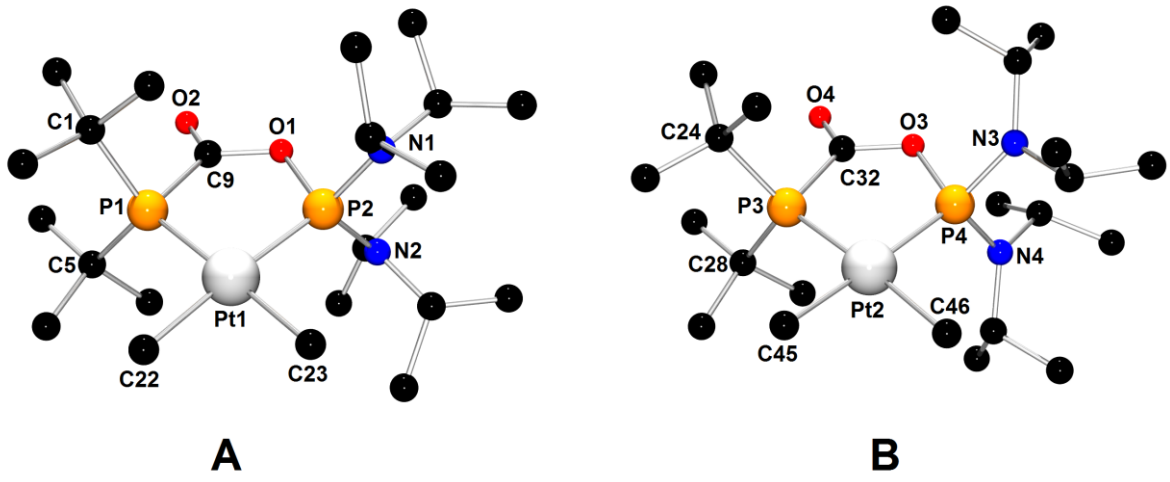


FIG. S4. SINGLE CRYSTAL X-RAY STRUCTURE OF **4**

TABLE S6. SELECTED STRUCTURAL PARAMETERS OF **4**(A)

Bond lengths [Å]		**Bond angles [°]**		**Dihedrals [°]**	
Pt1-P1	2.275(2)	P1-Pt1-P2	86.06(5)	P1-Pt1-P2-O1	1.5(2)
Pt1-P2	2.260(2)	Pt1-P1-C9	105.6(2)	P1-C9-O1-P2	13.9(6)
Pt1-C22	2.131(6)	Pt1-P2-O1	109.7(2)	O2-C9-O1-P2	-167.2(5)
Pt1-C23	2.116(6)	C22-Pt1-C23	81.4(2)		
P1-C9	1.896(6)	P1-C9-O1	115.1(4)		
C9-O1	1.354(6)	O2-C9-O1	119.8(6)		
C9-O2	1.202(9)	C9-O1-P2	122.3(4)		
P2-O1	1.687(6)	N1-P2-N2	105.9(3)		
P2-N1	1.661(5)	C1-P1-C5	113.1(2)		
P2-N2	1.676(5)				
P1-C1	1.887(5)				
P1-C5	1.886(5)				

TABLE S7. SELECTED STRUCTURAL PARAMETERS OF **4**(B)

Bond lengths [Å]		**Bond angles [°]**		**Dihedrals [°]**	
Pt2-P3	2.272(1)	P3-Pt2-P4	85.49(5)	P3-Pt2-P4-O3	7.8(1)
Pt2-P4	2.268(1)	Pt2-P3-C32	106.1(2)	P3-C32-O3-P4	15.2(5)
Pt2-C45	2.110(6)	Pt2-P4-O3	109.7(1)	O4-C32-O3-P4	-165.1(4)
Pt2-C46	2.141(5)	C45-Pt2-C46	82.0(2)		
P3-C32	1.901(6)	P3-C32-O3	114.4(4)		
C32-O3	1.354(7)	O4-C32-O3	120.2(5)		
C32-O4	1.199(7)	C32-O3-P4	122.5(3)		
P4-O3	1.672(4)	N3-P4-N4	112.0(3)		
P4-N3	1.661(5)	C24-P3-C28	106.2(3)		
P4-N4	1.674(5)				
P3-C24	1.904(7)				
P3-C28	1.883(7)				

Spectroscopic data

NMR spectra of isolated compounds

NMR spectra of 2

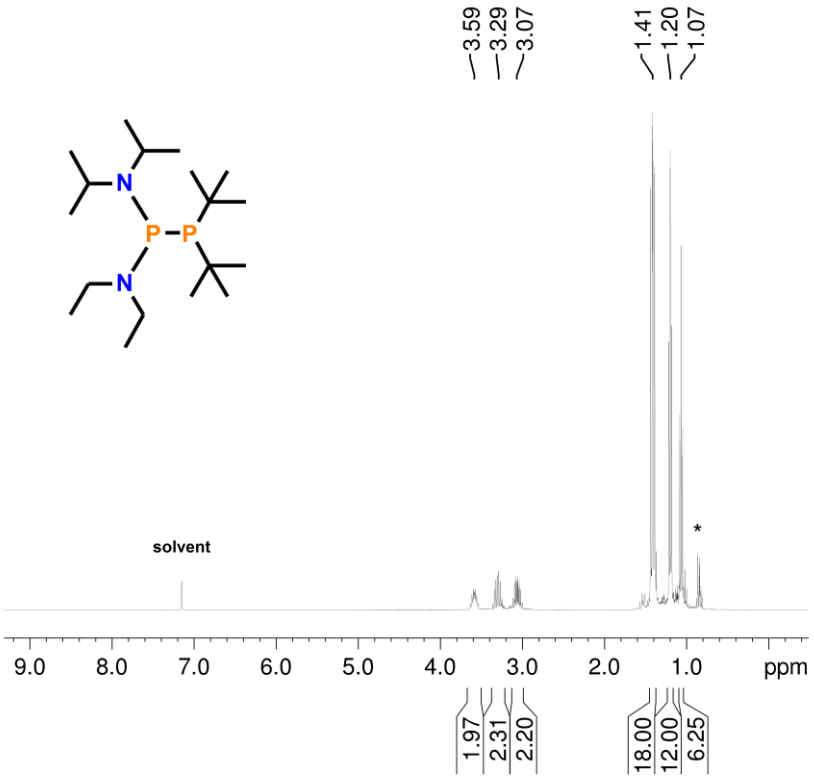


FIG. S5. ^{1}H NMR (C_6D_6) SPECTRUM OF **2.**(* - IMPURITIES)

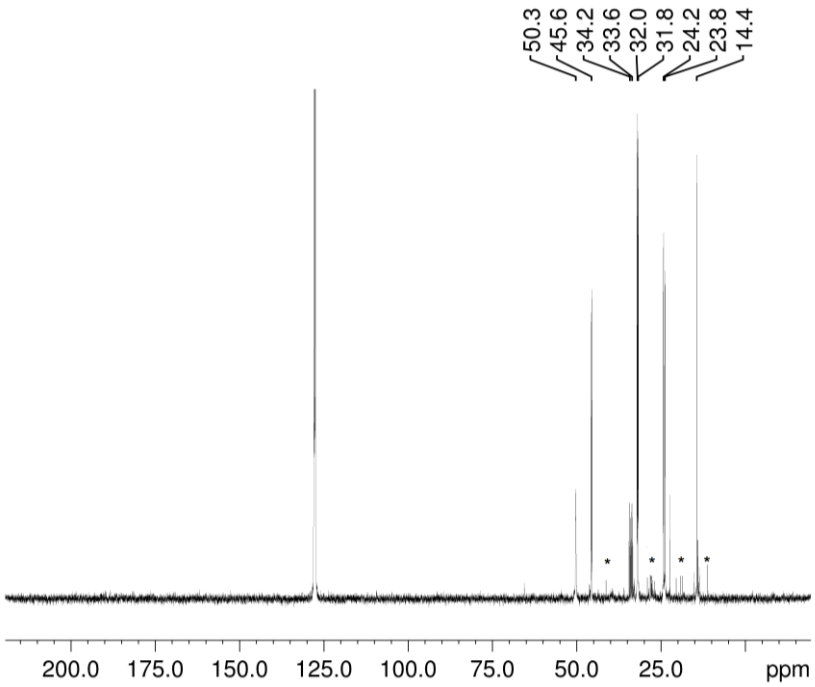


FIG. S6. $^{13}C\{^{1}H\}$ NMR (C_6D_6) SPECTRUM OF **2.** (* - IMPURITIES)

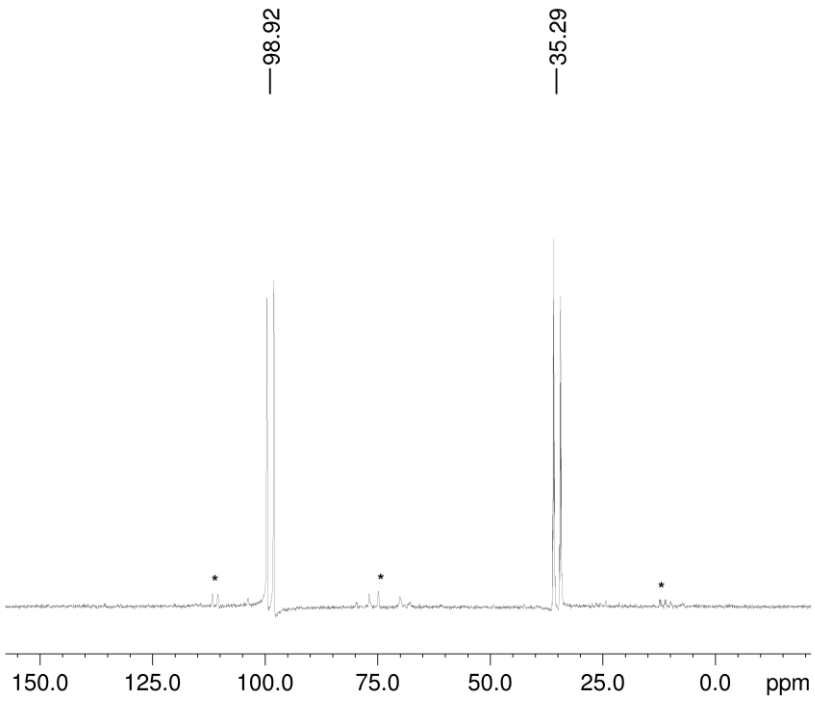


FIG. S7. ^{31}P NMR (C_6D_6) SPECTRUM OF **2.** (* - IMPURITIES)

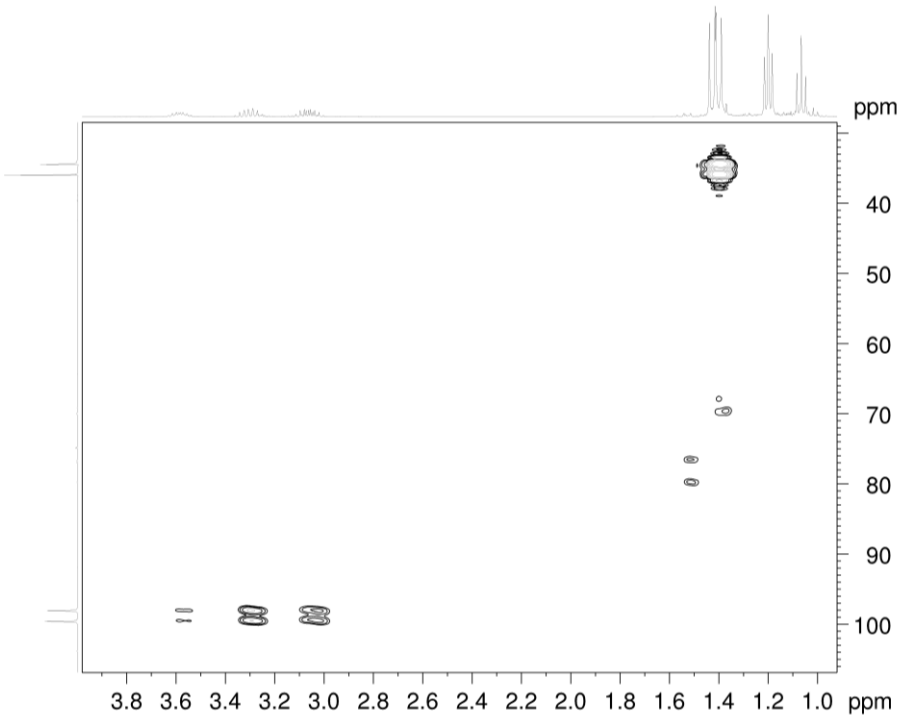


FIG. S8. ^{31}P-^{1}H 2D NMR (C_6D_6) SPECTRUM OF **2**

NMR spectra of 1a

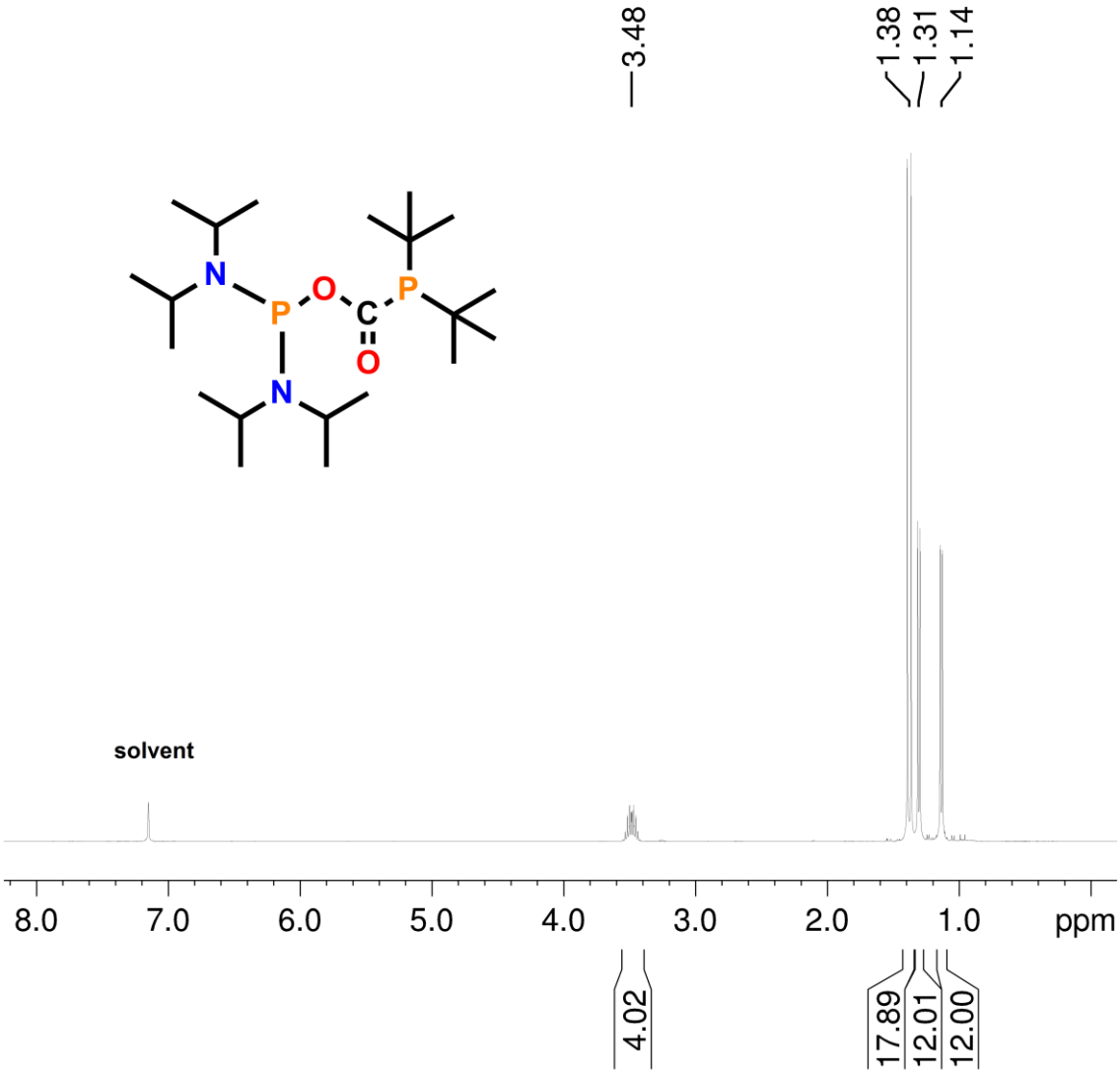


FIG. S9. ^{1}H NMR (C_6D_6) SPECTRUM OF **1A**

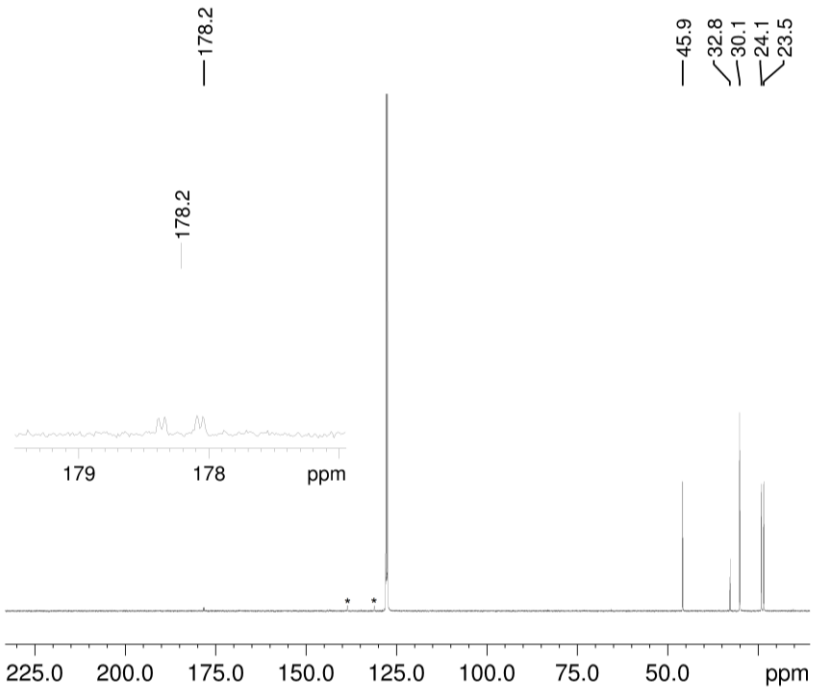


FIG. S10. $^{13}C\{^{1}H\}$ NMR (C_6D_6) SPECTRUM OF **1A**

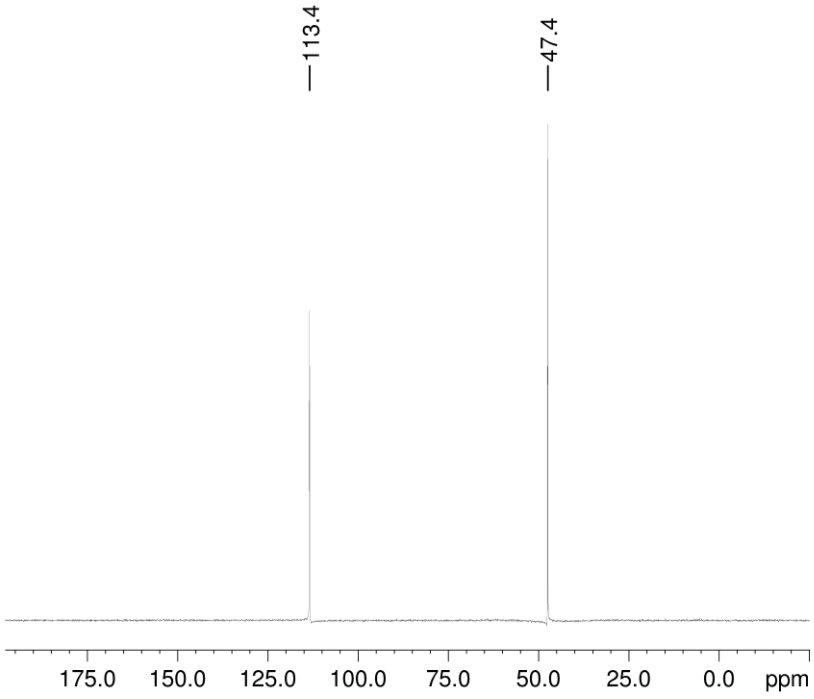


FIG. S11. $^{31}P\{^{1}H\}$ NMR (C_6D_6) SPECTRUM OF **1A**

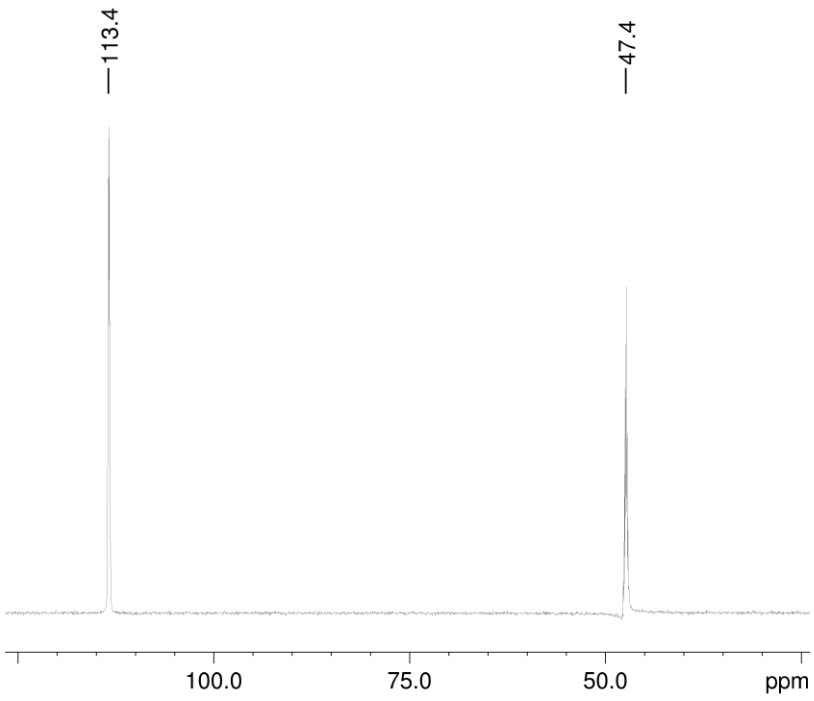


FIG. S12. ^{31}P NMR (C_6D_6) SPECTRUM OF **1A**

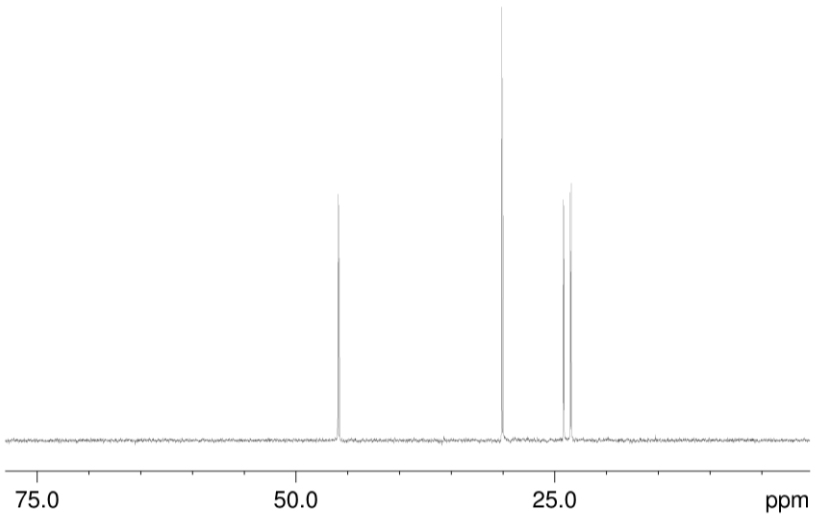


FIG. S13. ^{13}C(DEPT) NMR (C_6D_6) SPECTRUM OF **1A**

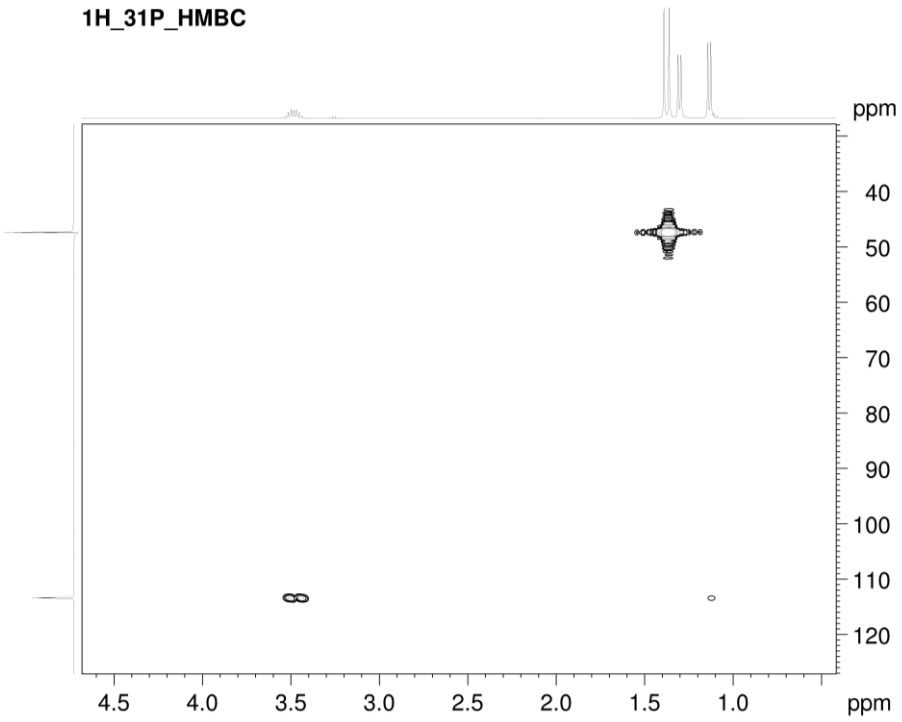


FIG. S14. ^{31}P-^{1}H HMBC NMR (C_6D_6) SPECTRUM OF **1A**

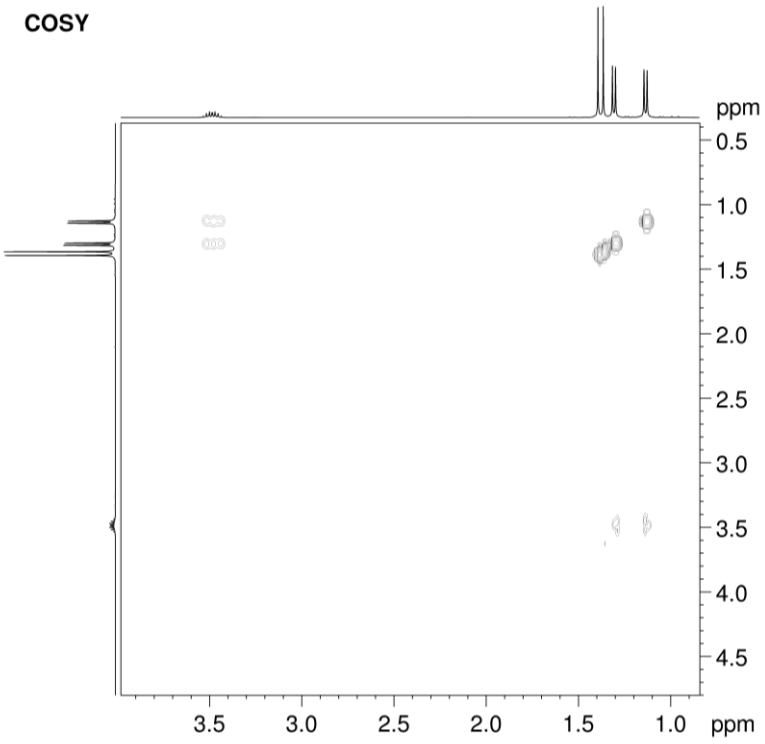


FIG. S15. COSY NMR (C_6D_6) SPECTRUM OF **1A**

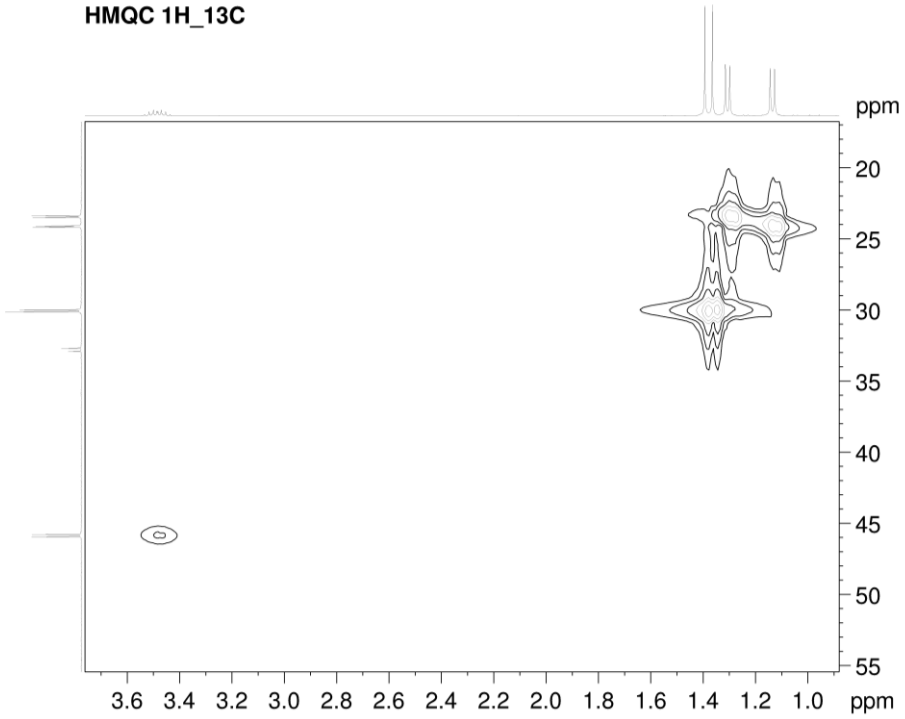


FIG. S16. ^{13}C-^{1}H HMQC NMR (C_6D_6) SPECTRUM OF **1A**

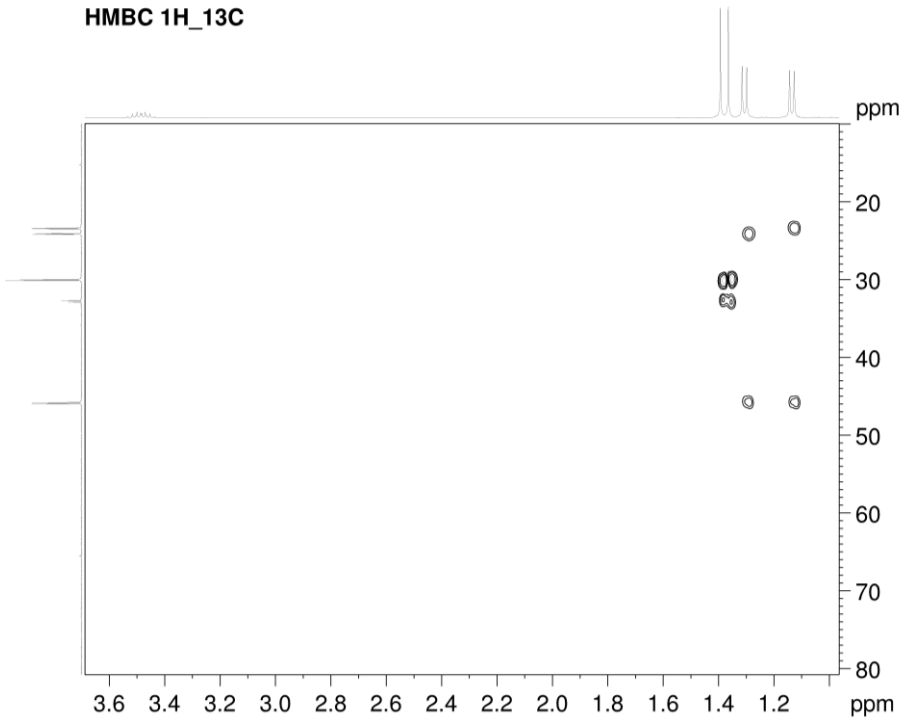


FIG. S17. ^{13}C-^{1}H HMBC NMR (C_6D_6) SPECTRUM OF **1A**

NMR spectra of 1b

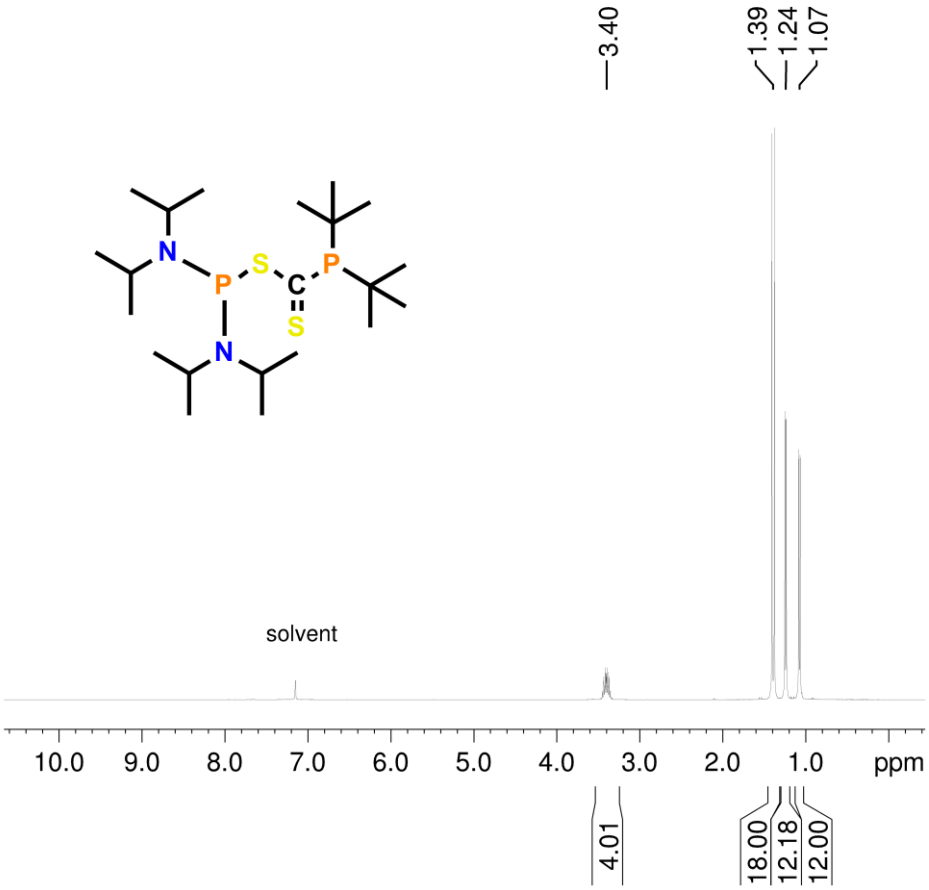


FIG. S18. ^{1}H NMR (C_6D_6) SPECTRA OF **1B**

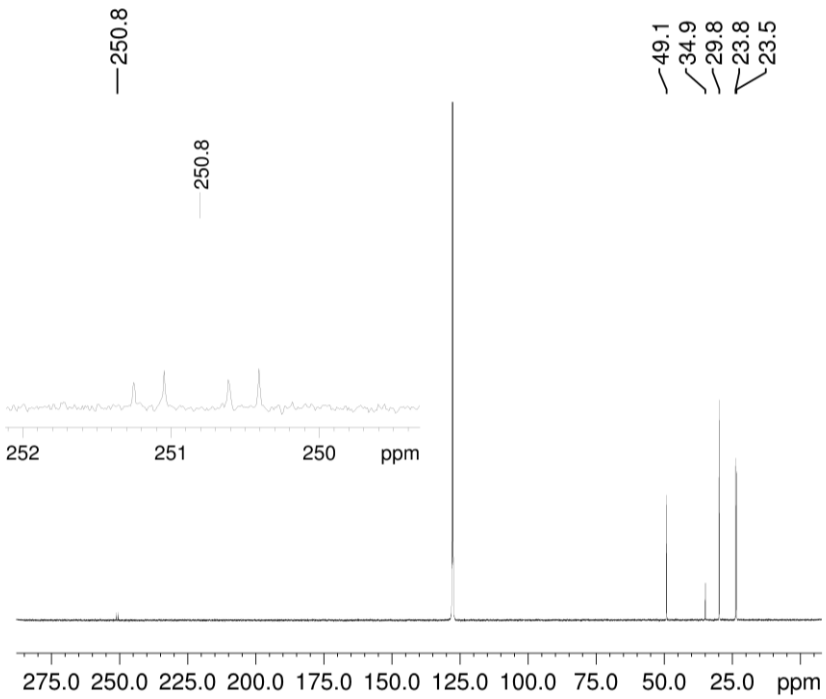


FIG. S19. $^{13}C\{^{1}H\}$ NMR (C_6D_6) SPECTRA OF **1B**

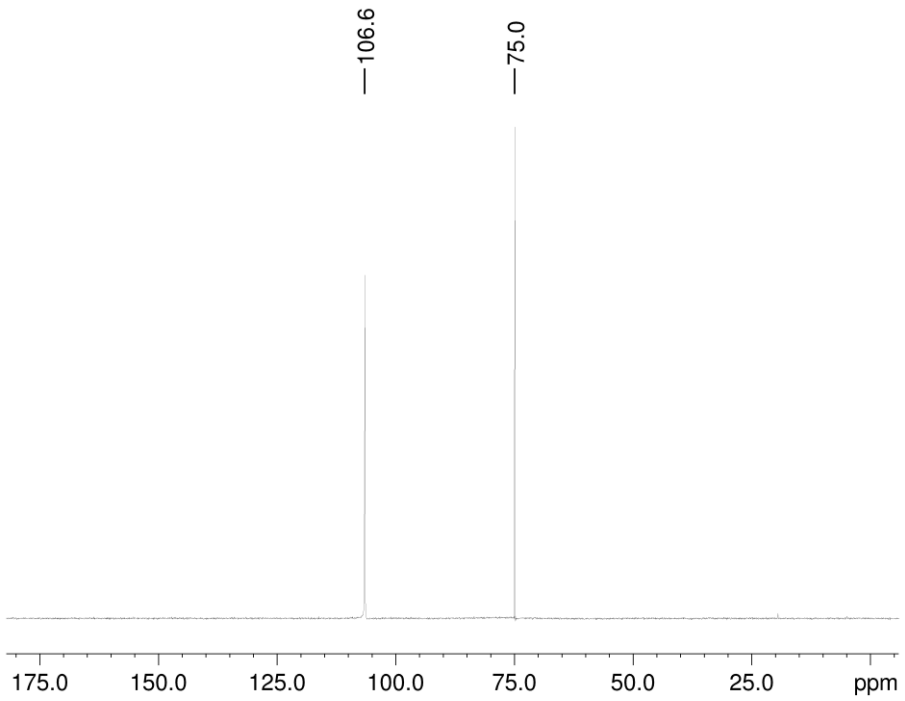


FIG. S20. $^{31}P\{^{1}H\}$ NMR (C_6D_6) SPECTRA OF **1B**

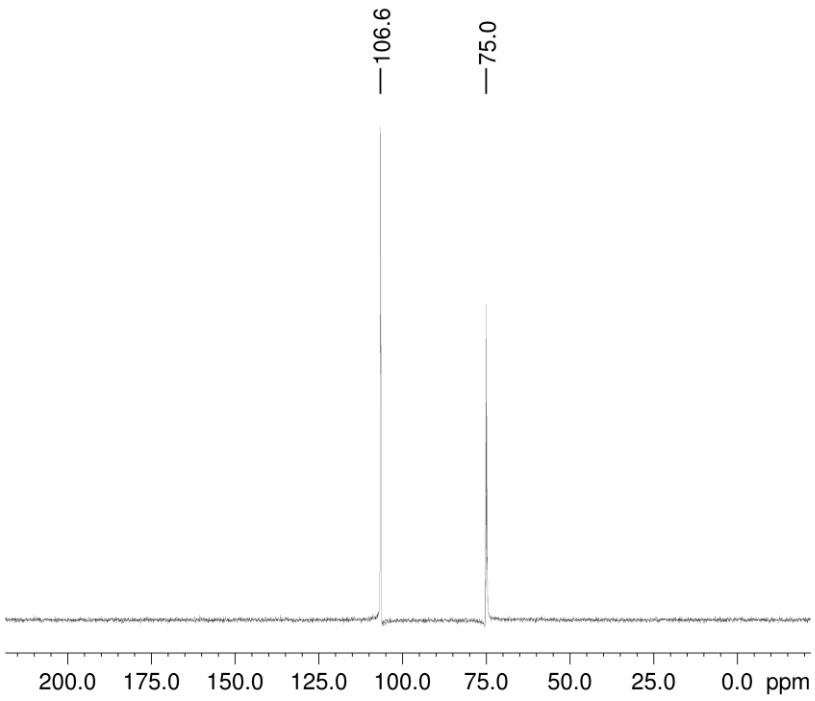


FIG. S21. ^{31}P NMR (C_6D_6) SPECTRA OF **1B**

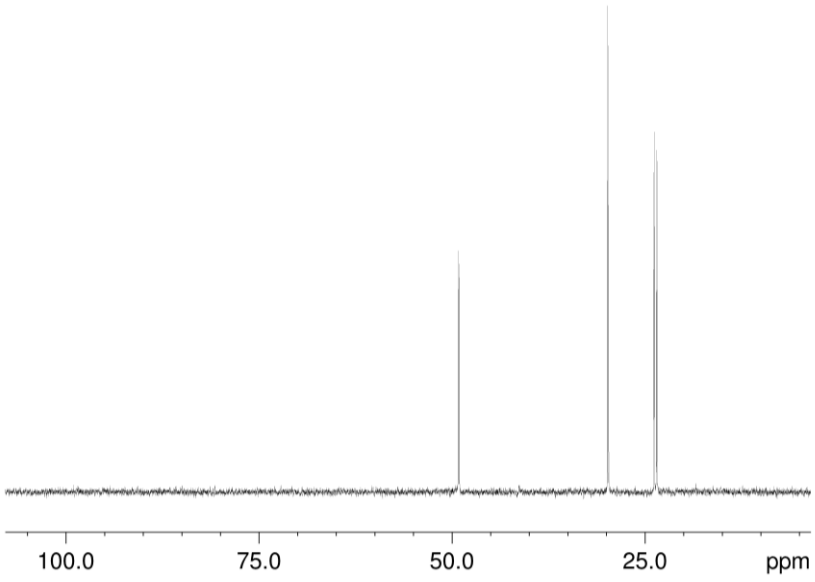


FIG. S22. ^{13}C(DEPT) NMR (C_6D_6) SPECTRA OF **1B**

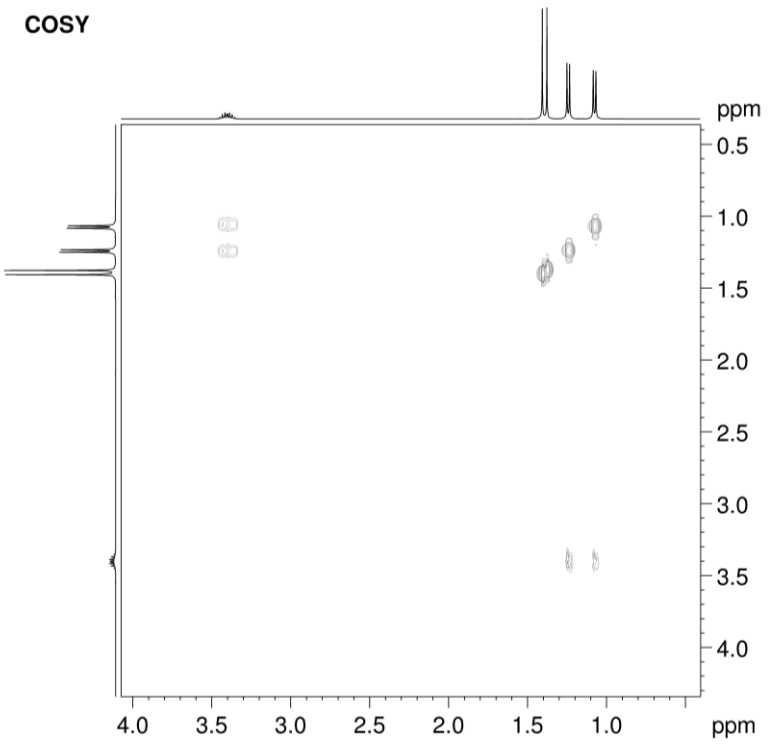


FIG. S23. COSY NMR (C_6D_6) SPECTRA OF **1B**

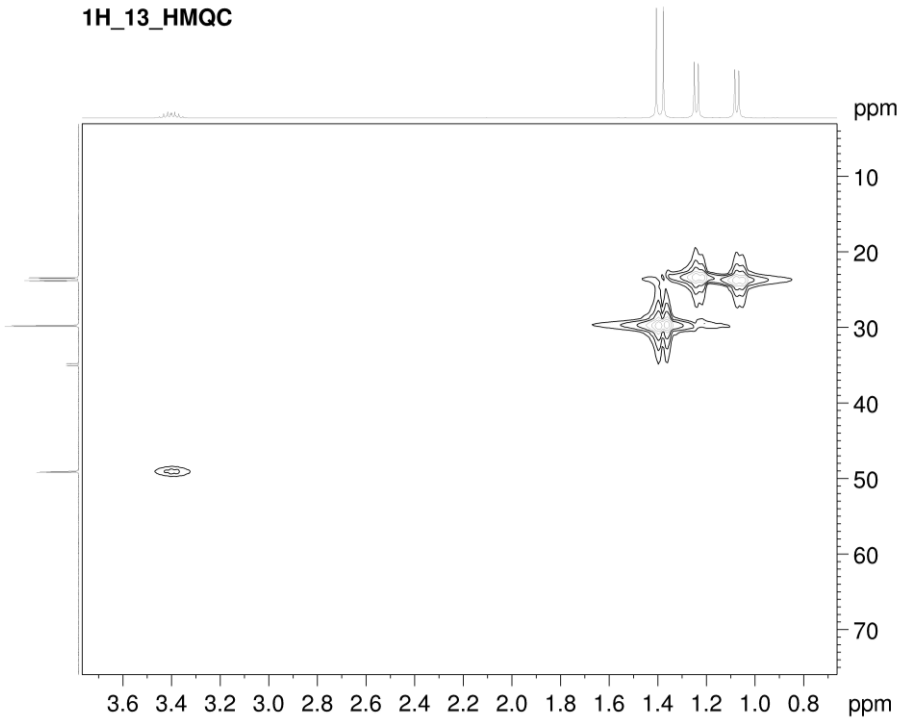


FIG. S24. ^{13}C-^{1}H HMQC NMR (C_6D_6) SPECTRA OF **1B**

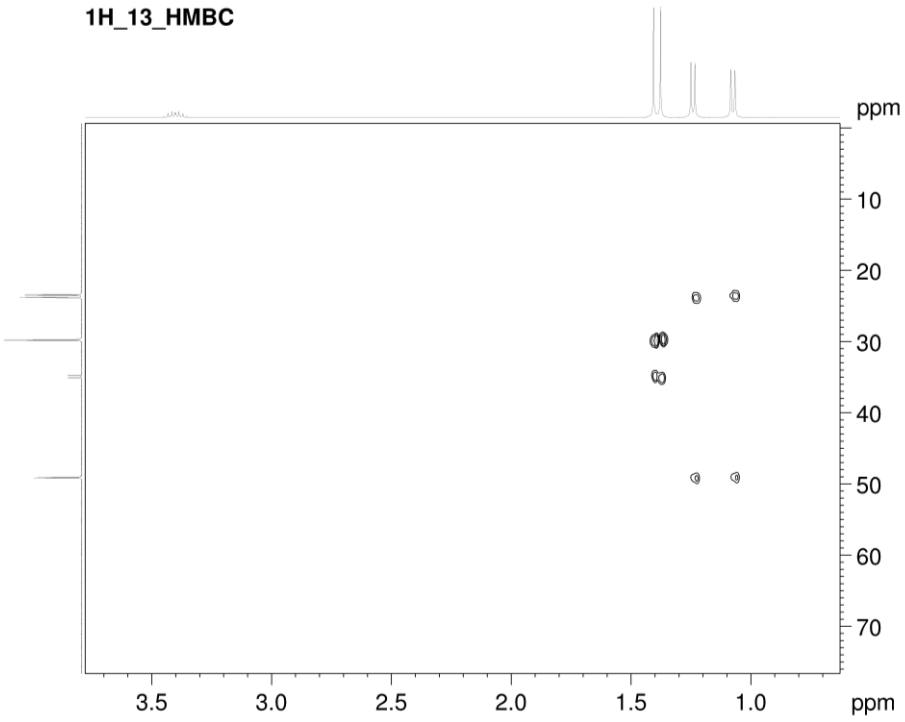


FIG. S25. ^{13}C-^{1}H HMBC NMR (C_6D_6) SPECTRA OF **1B**

NMR spectra of 2a

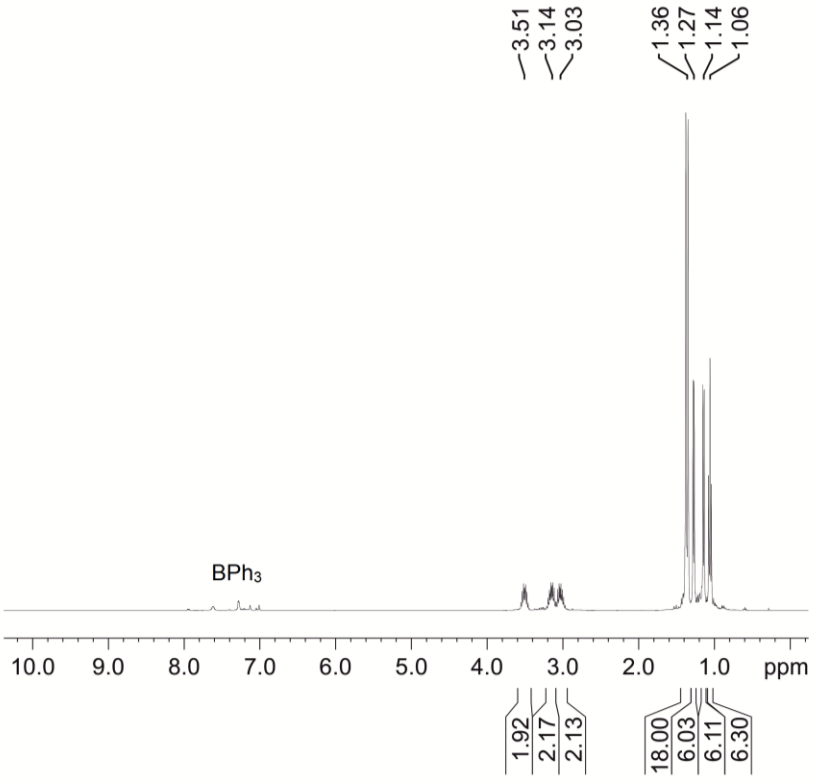


FIG. S26. ^{1}H NMR (C_6D_6) SPECTRA OF **2A**

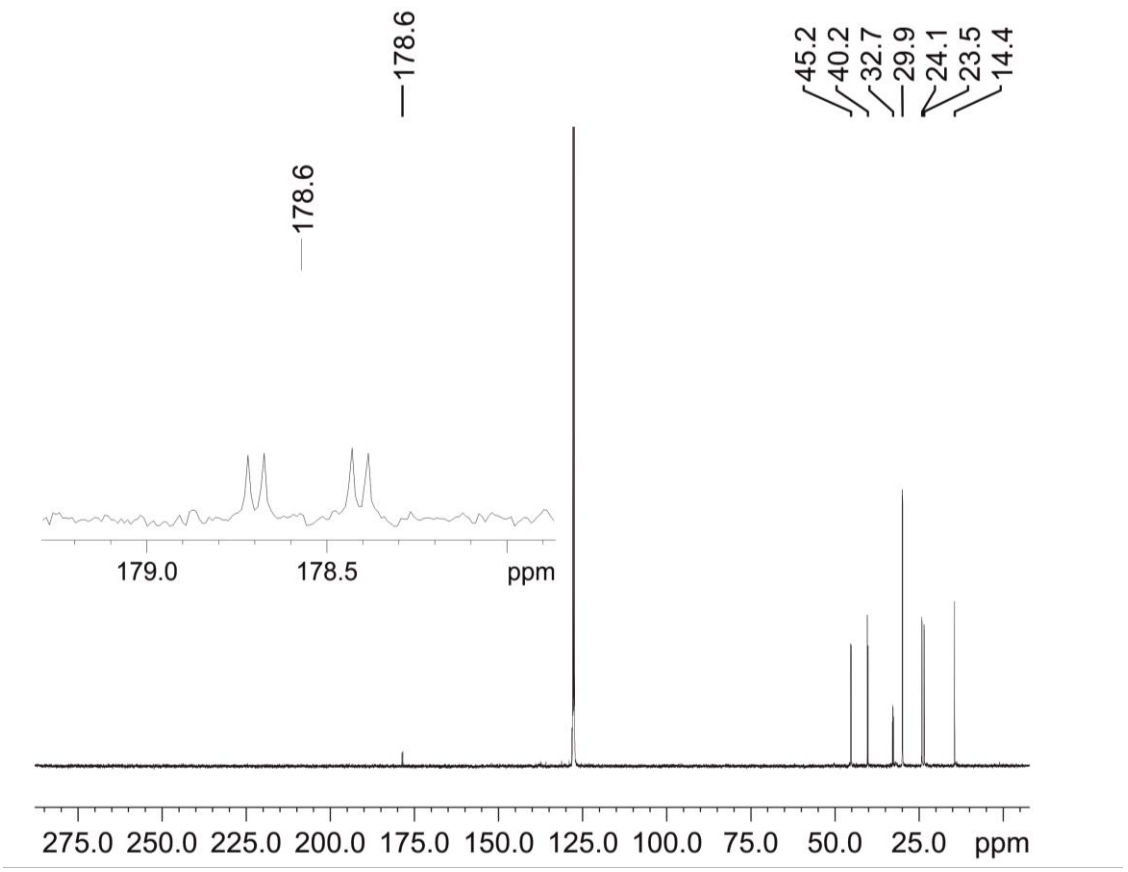


FIG. S27. $^{13}C\{^{1}H\}$ NMR (C_6D_6) SPECTRA OF **2A**

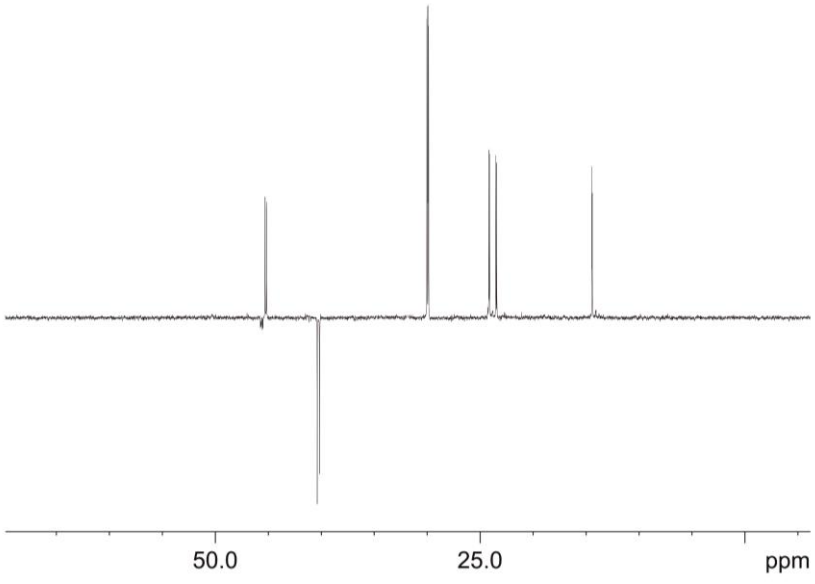


FIG. S28. ^{13}C(DEPT) NMR (C_6D_6) SPECTRA OF **2A**

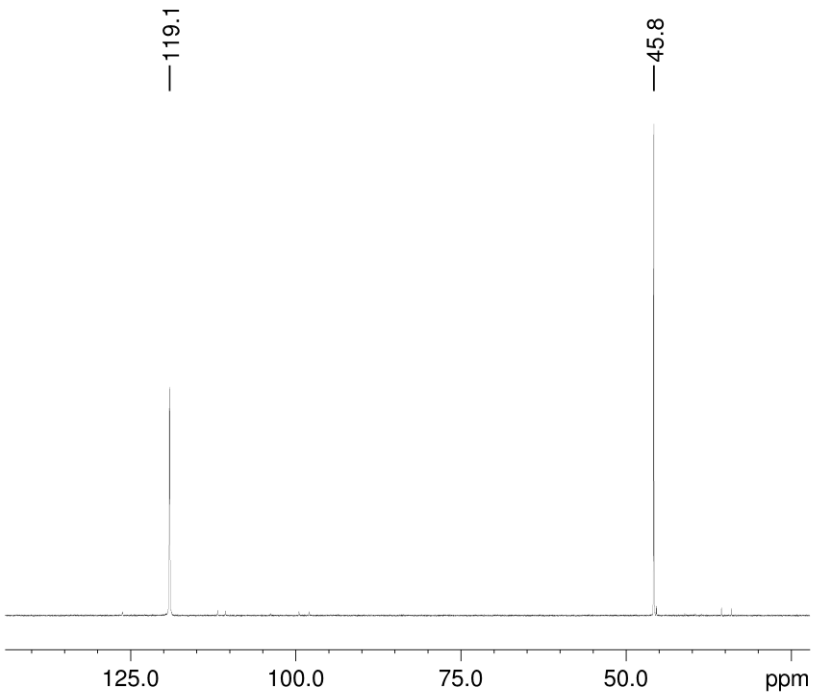


FIG. S29. $^{31}P\{^{1}H\}$ NMR (C_6D_6) SPECTRA OF **2A**

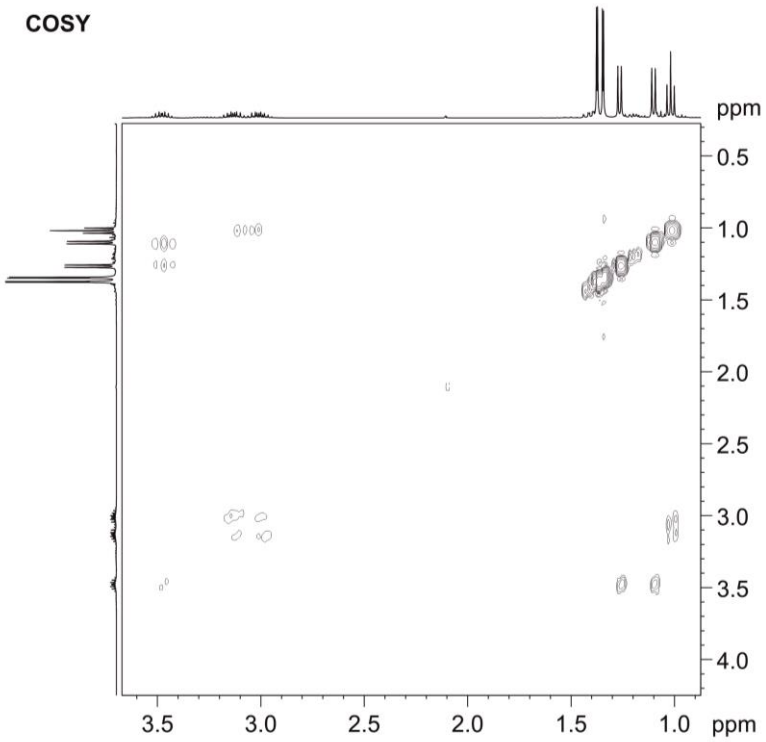


FIG. S30. COSY NMR (C_6D_6) SPECTRA OF **2A**

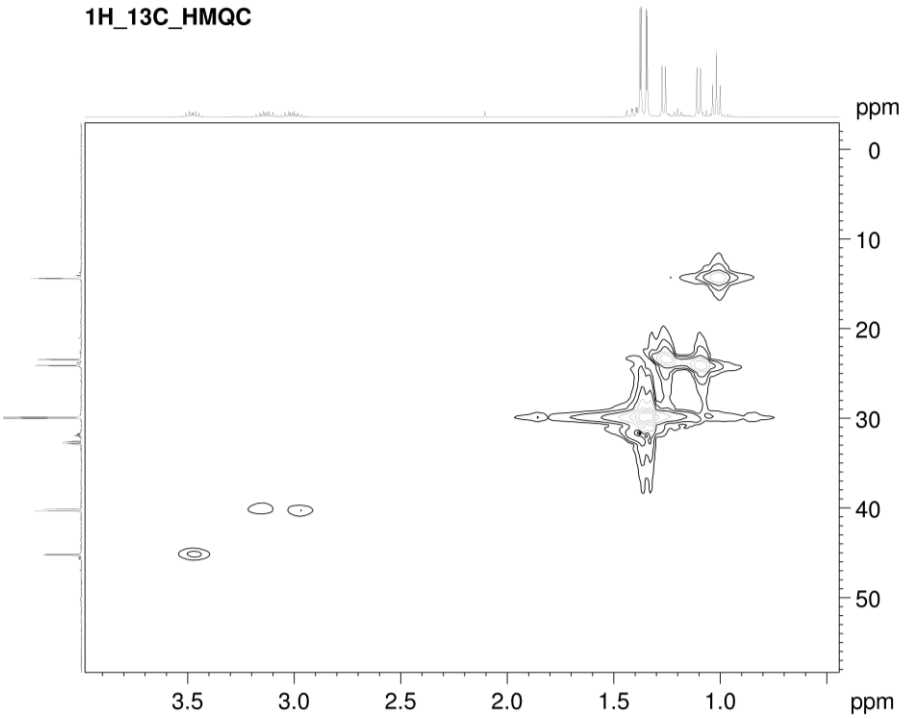


FIG. S31. ^{13}C-^{1}H HMQC NMR (C_6D_6) SPECTRA OF **2A**

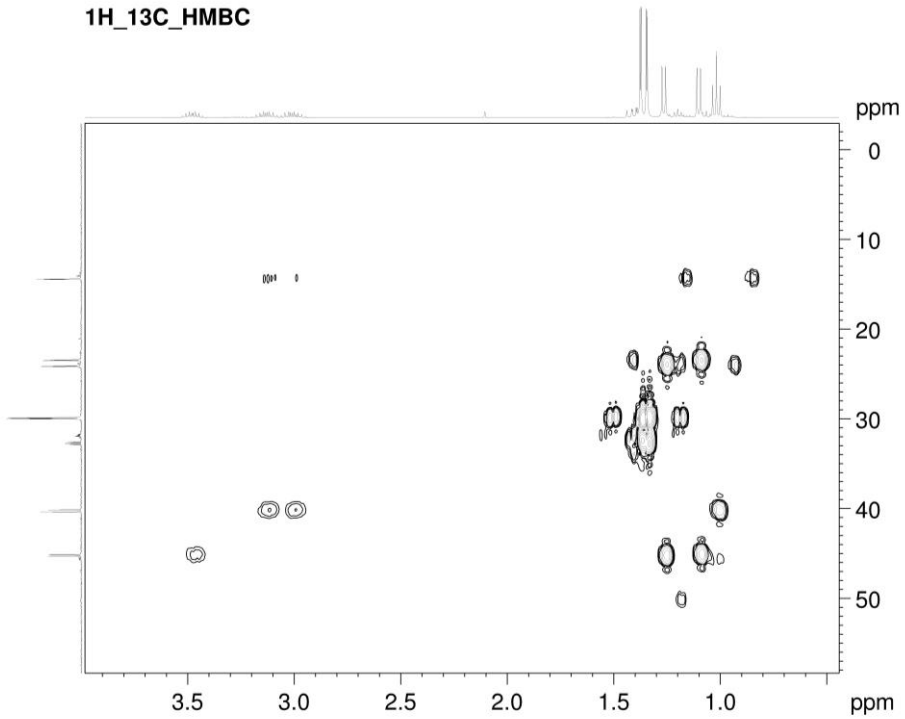


FIG. S32. ^{13}C-^{1}H HMBC NMR (C_6D_6) SPECTRA OF **2A**

NMR spectra of 2b

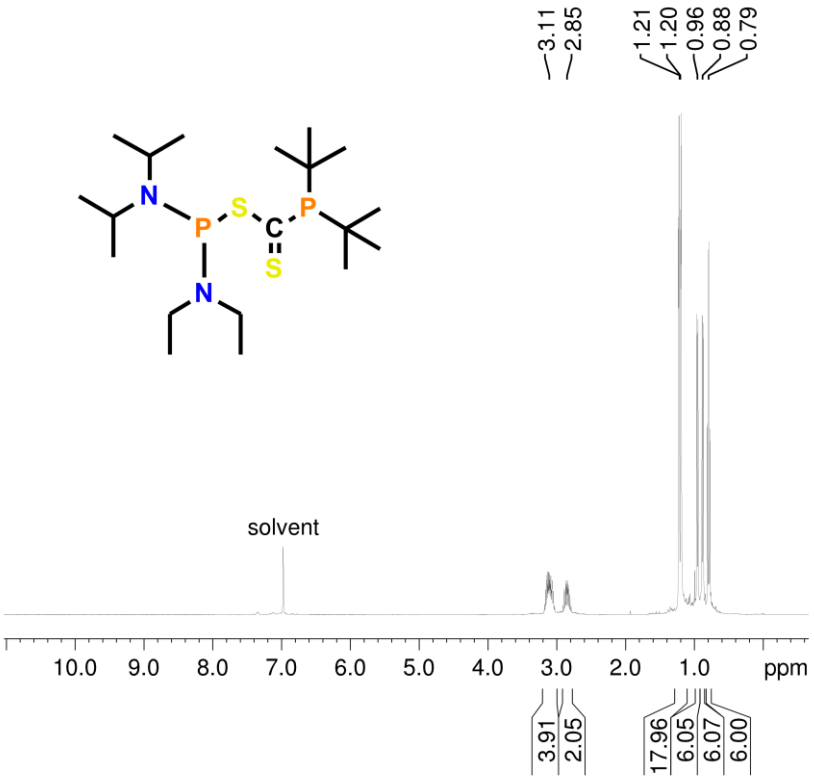


FIG. S33. ^{1}H NMR (C_6D_6) SPECTRA OF **2B**

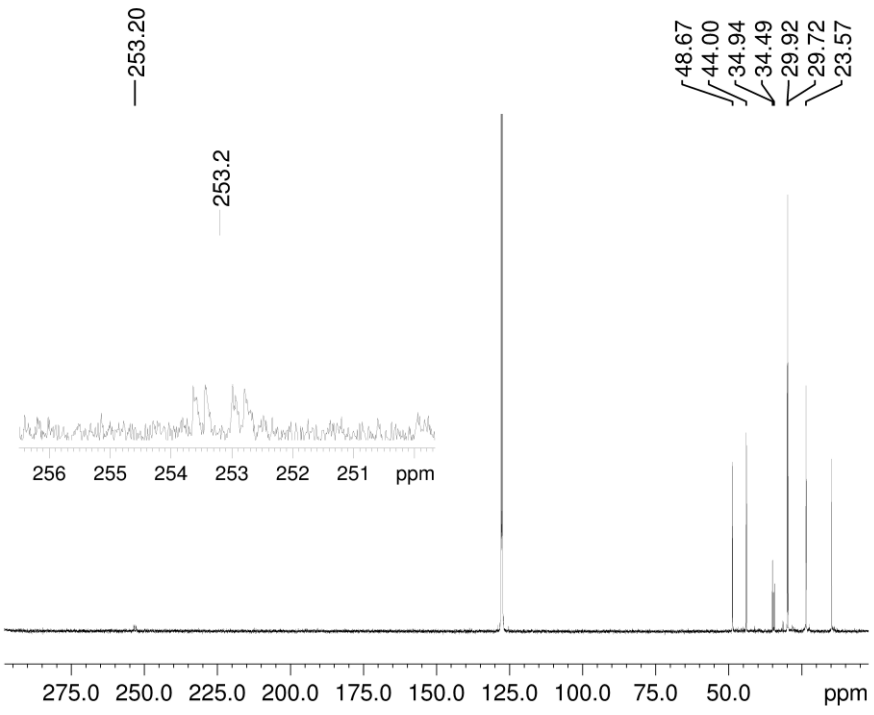


FIG. S34. $^{13}C\{^{1}H\}$ NMR (C_6D_6) SPECTRA OF **2B**

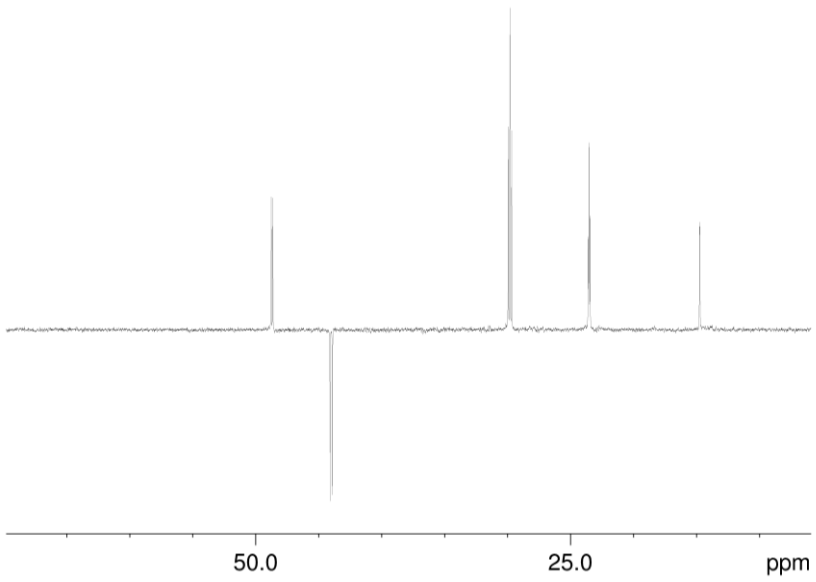


FIG. S35. ^{13}C(DEPT) NMR (C_6D_6) SPECTRA OF **2B**

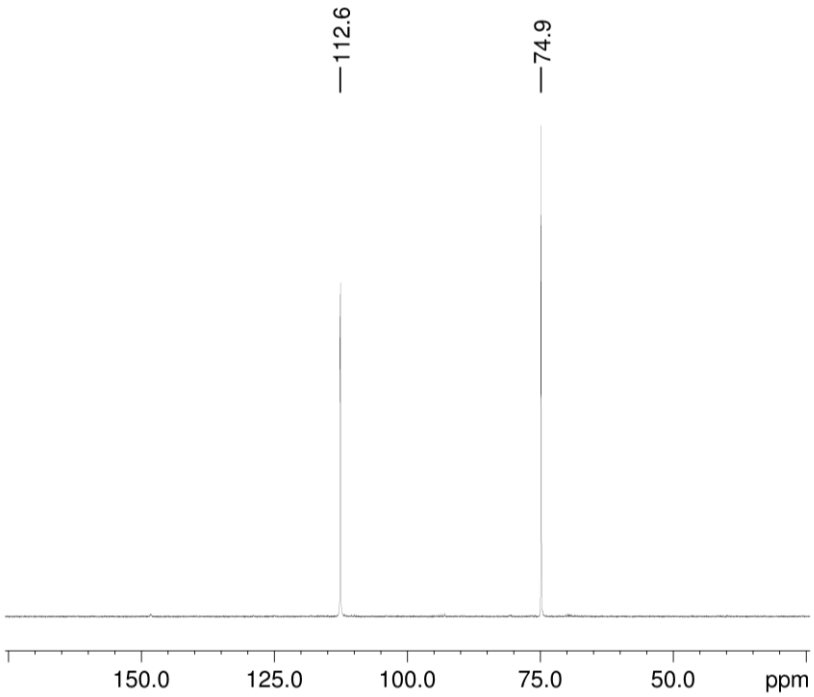


FIG. S36. $^{31}P\{^{1}H\}$ NMR (C_6D_6) SPECTRA OF **2B**

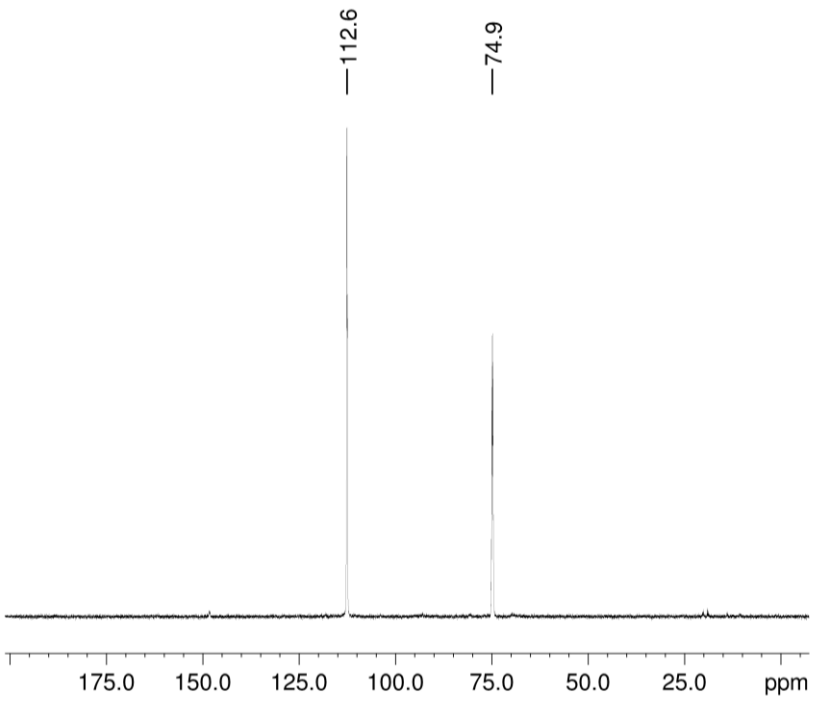


FIG. S37. ^{31}P NMR (C_6D_6) SPECTRA OF **2B**

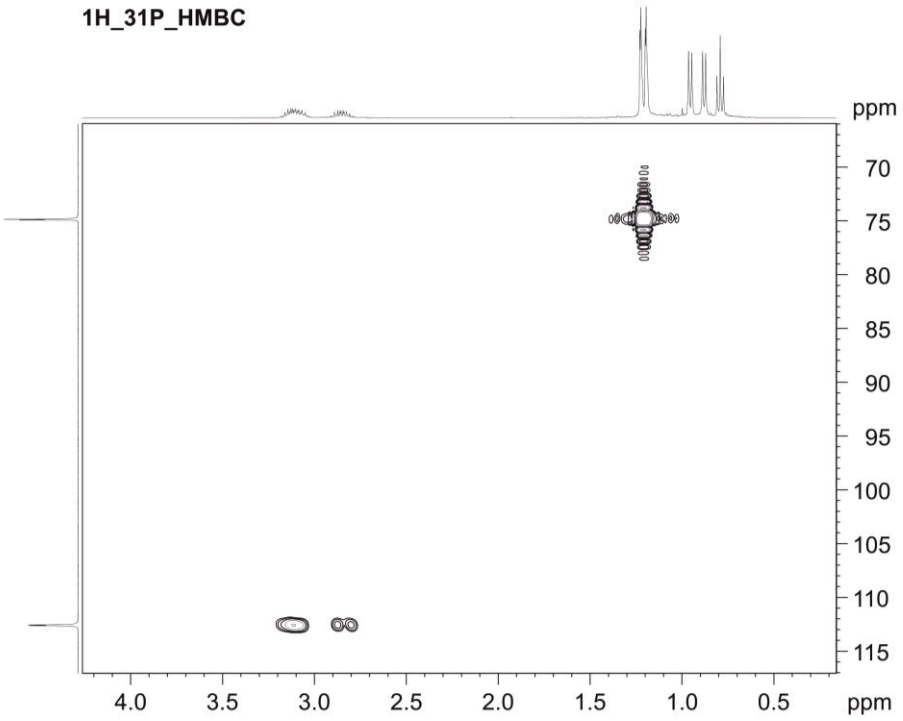


FIG. S38. ^{31}P-^{1}H NMR (C_6D_6) SPECTRA OF **2B**

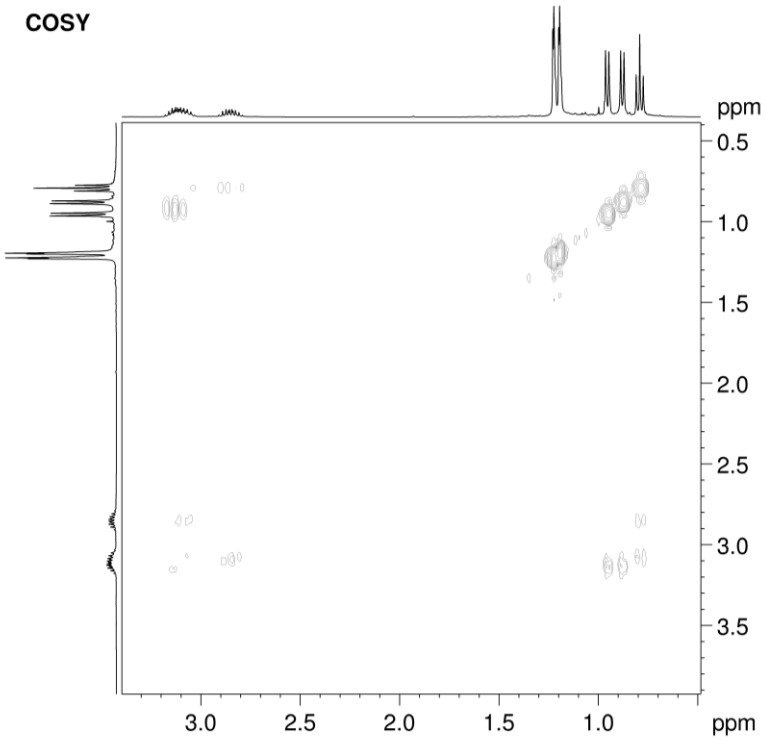


FIG. S39. COSY NMR (C_6D_6) SPECTRA OF **2B**

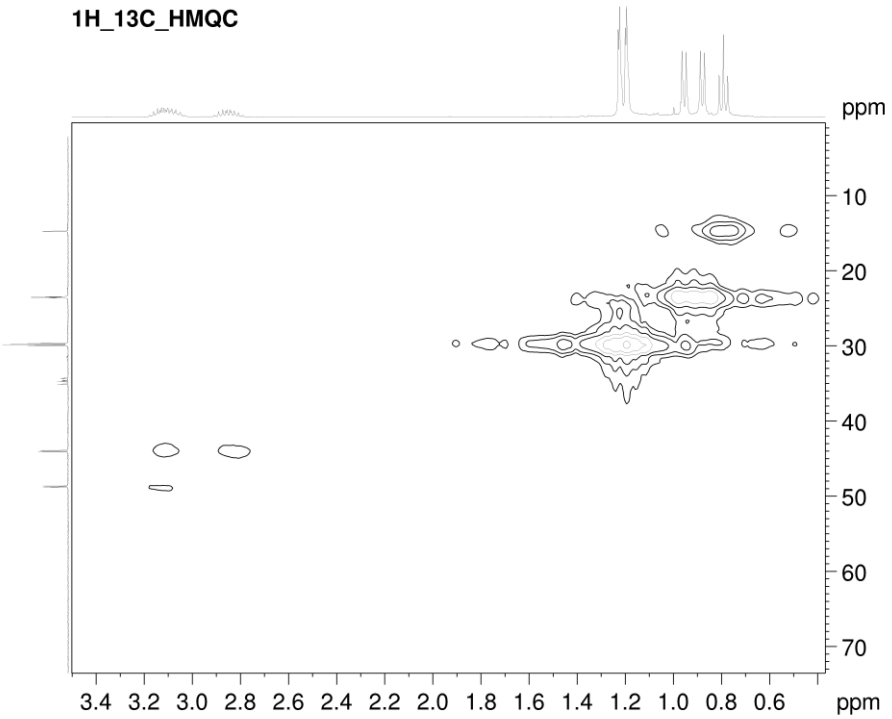


FIG. S40. ^{13}C-^{1}H HMQC NMR (C_6D_6) SPECTRA OF **2B**

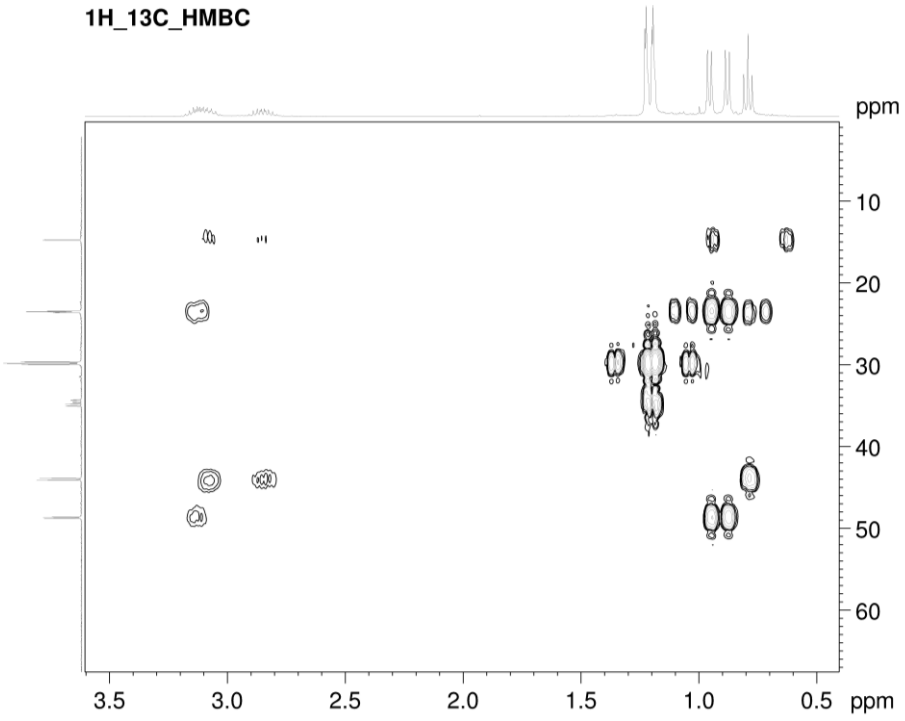


FIG. S41. ^{13}C-^{1}H HMBC NMR (C_6D_6) SPECTRA OF **2B**

NMR spectra of 3b

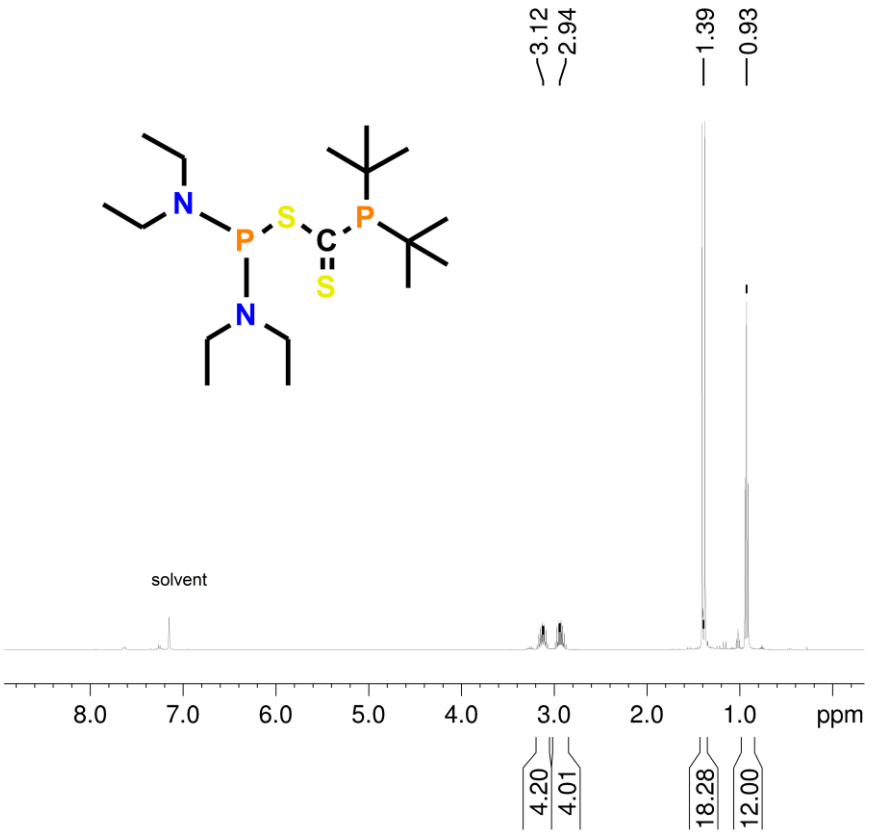


FIG. S42. ^{1}H NMR (C_6D_6) SPECTRA OF **3B**

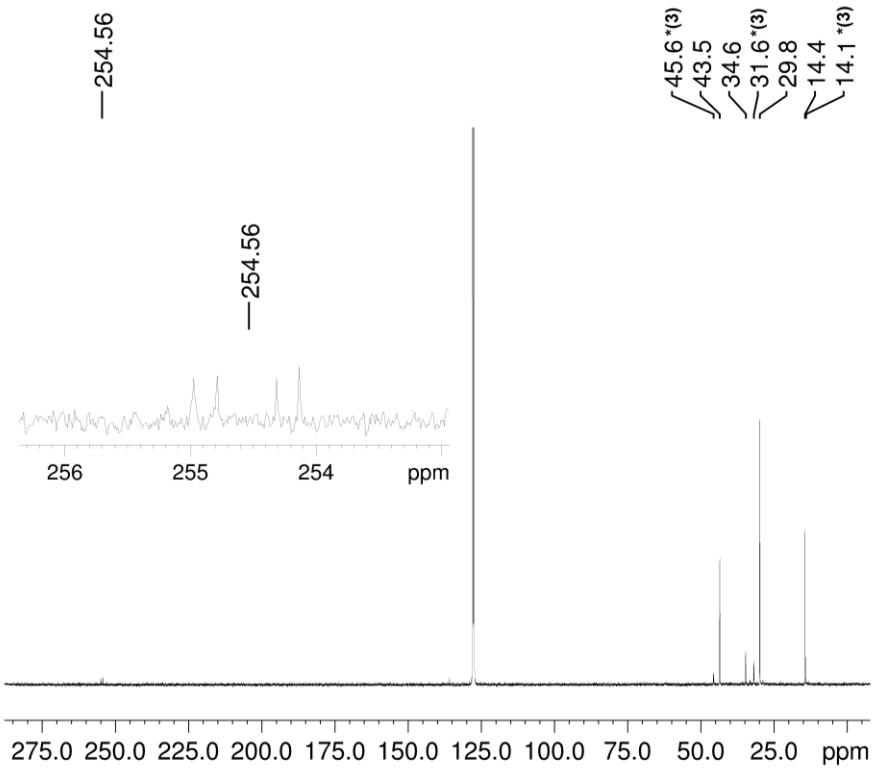


FIG. S43. ^{13}C{^{1}H} NMR (C_6D_6) SPECTRA OF **3B**

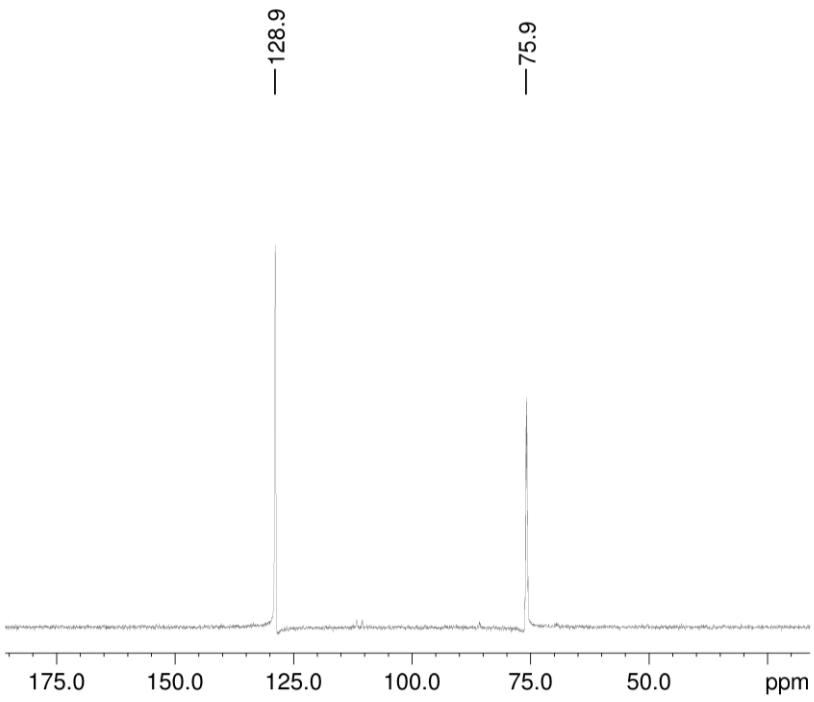


FIG. S44. $^{31}P\{^{1}H\}$ NMR (C_6D_6) SPECTRA OF **3B**

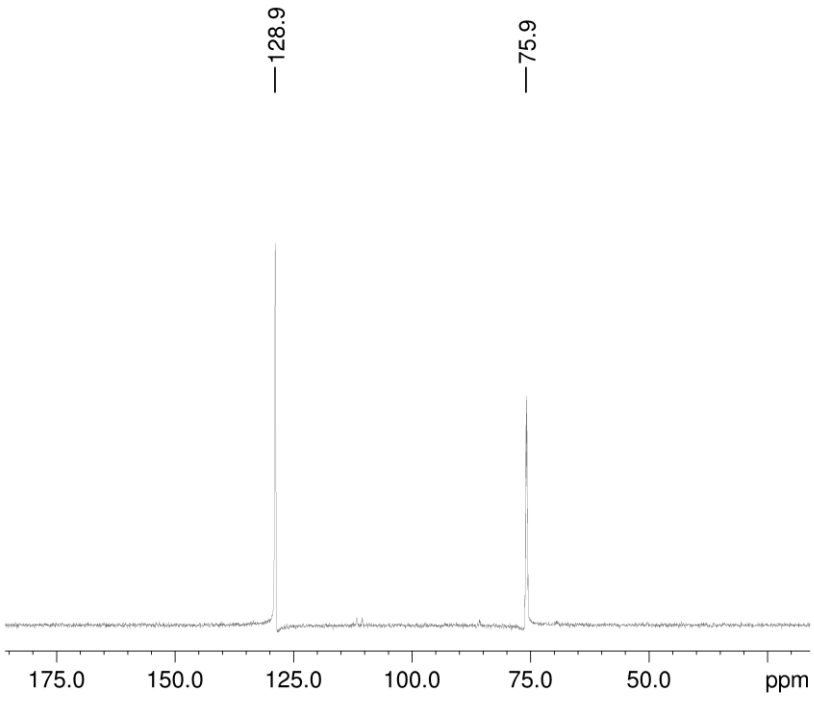


FIG. S45. ^{31}P NMR (C_6D_6) SPECTRA OF **3B**

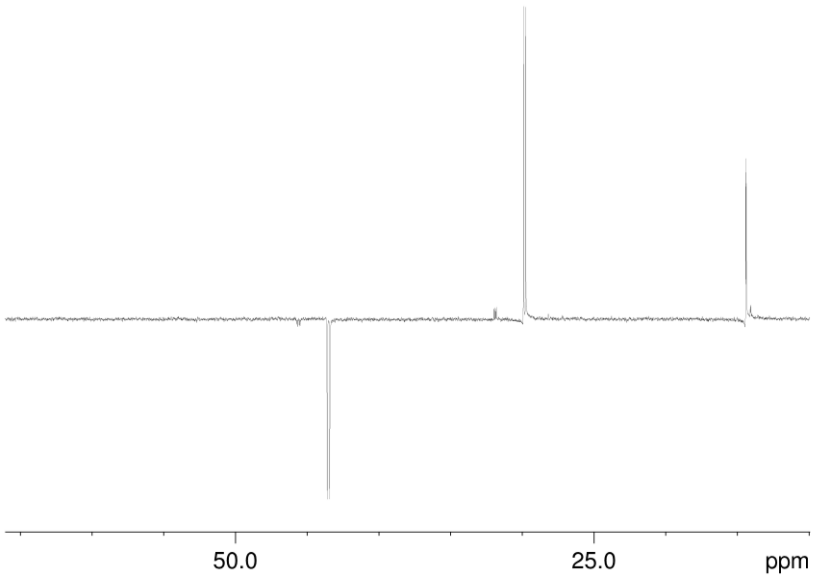


FIG. S46. ^{13}C(DEPT) NMR (C_6D_6) SPECTRA OF **3B**

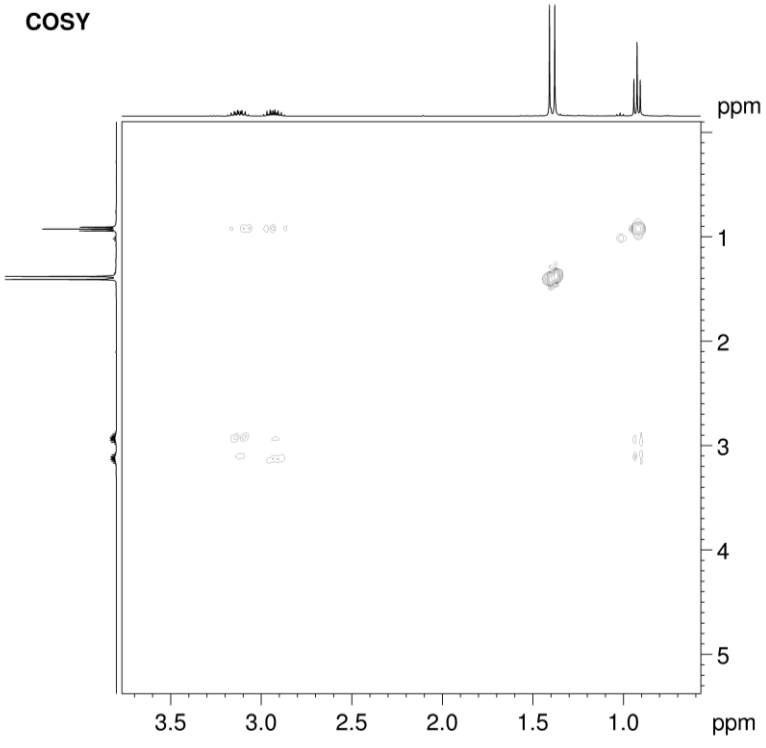


FIG. S47. COSY NMR (C_6D_6) SPECTRA OF **3B**

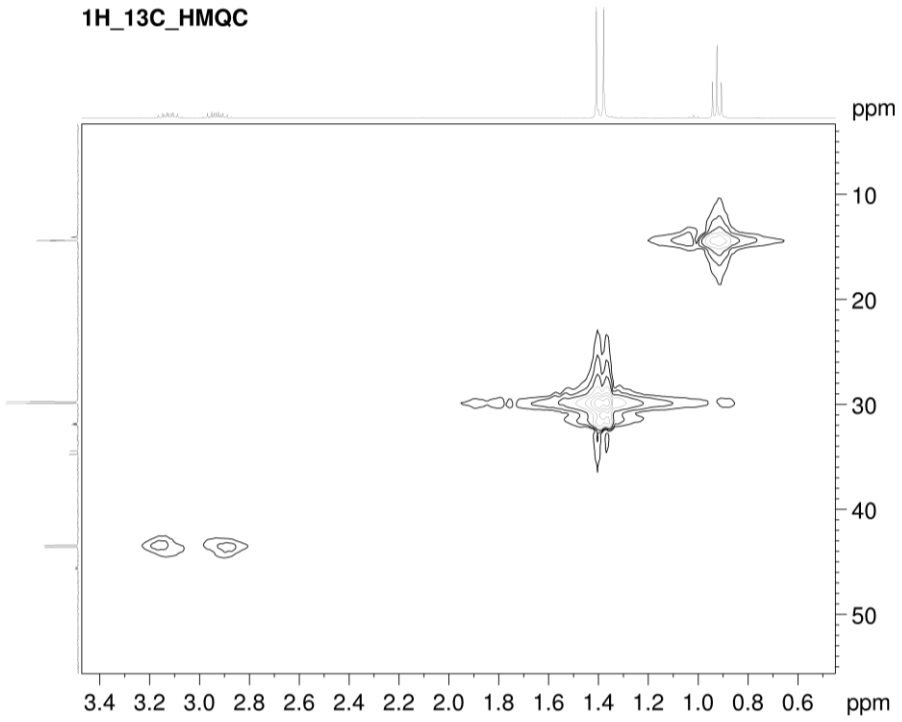


FIG. S48. ^{13}C-^{1}H HMQC NMR (C_6D_6) SPECTRA OF **3B**

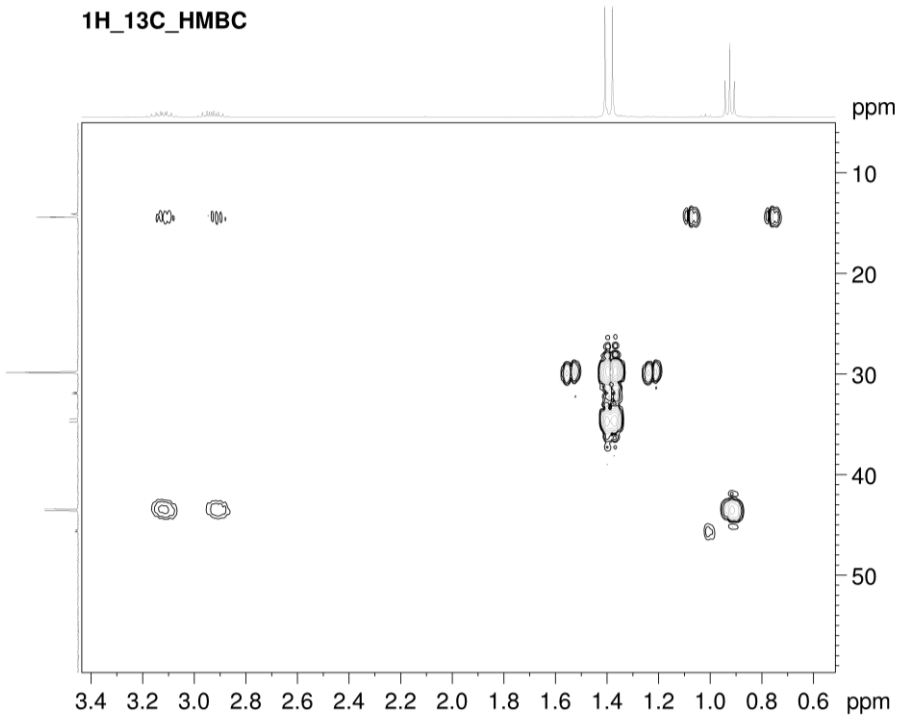


FIG. S49. ^{13}C-^{1}H HMBC NMR (C_6D_6) SPECTRA OF **3B**

NMR spectra of 4

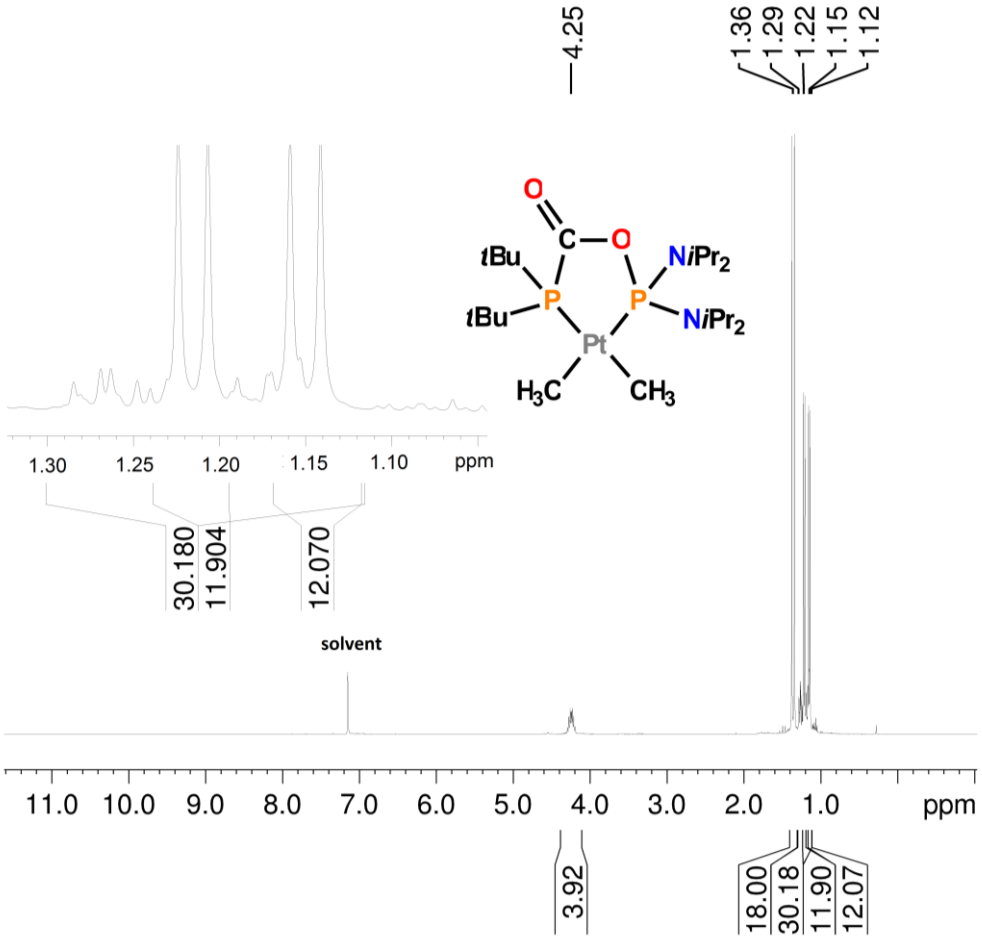


FIG. S50. ^{1}H NMR (C_6D_6) SPECTRA OF **4**

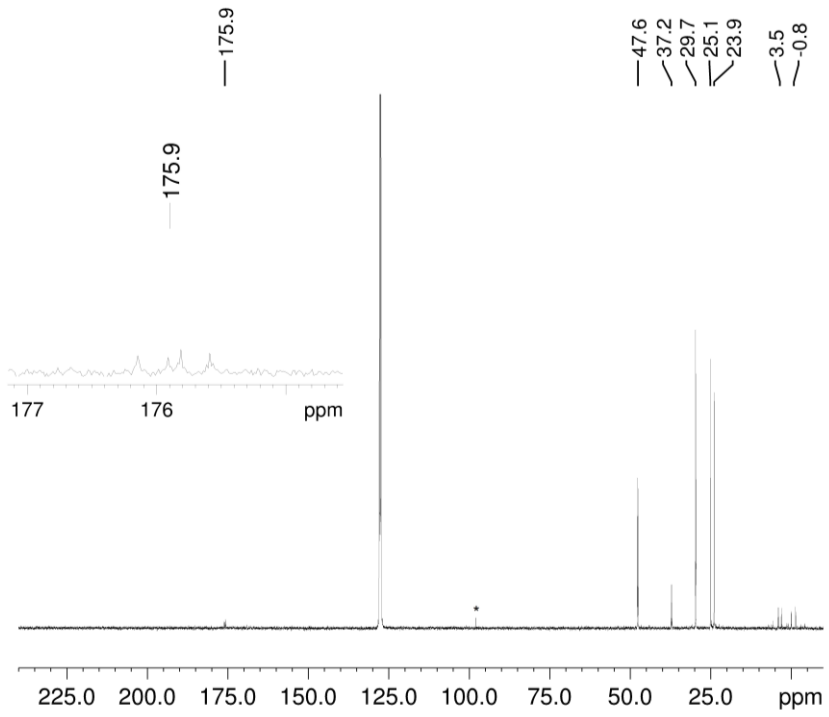


FIG. S51. $^{13}C\{^{1}H\}$ NMR (C_6D_6) SPECTRA OF **4**

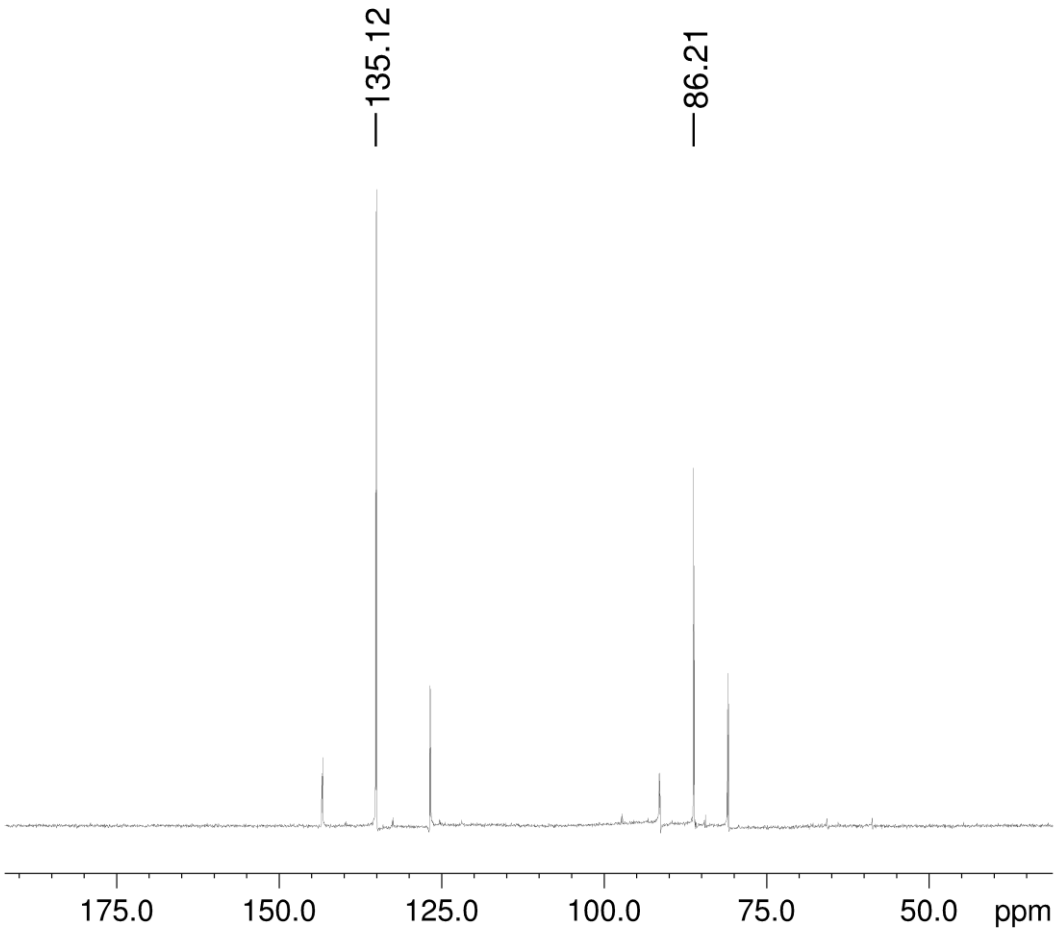


FIG. S52. $^{31}P\{^{1}H\}$ NMR (C_6D_6) SPECTRA OF **4**

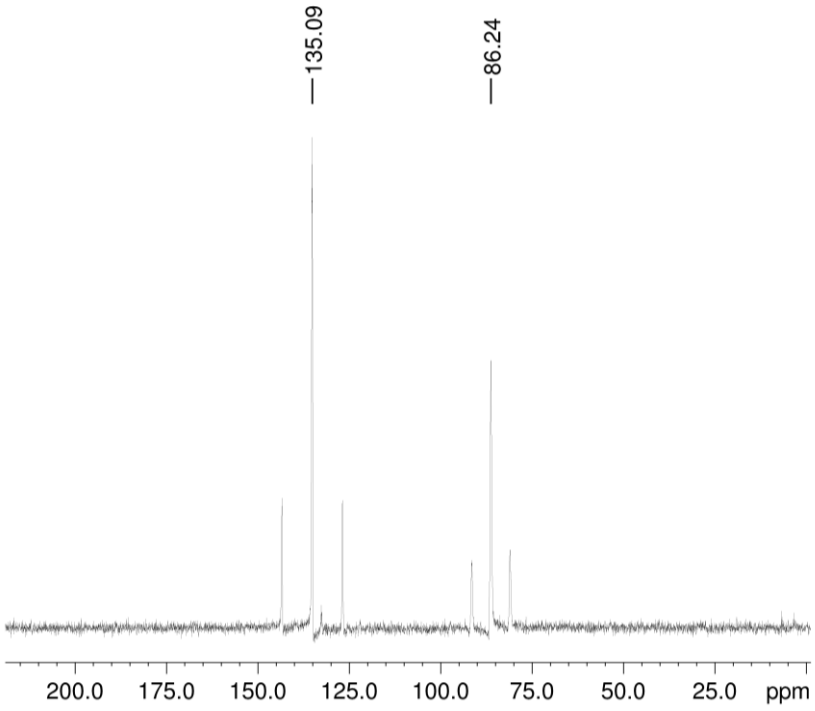


FIG. S53. ^{31}P NMR (C_6D_6) SPECTRA OF **4**

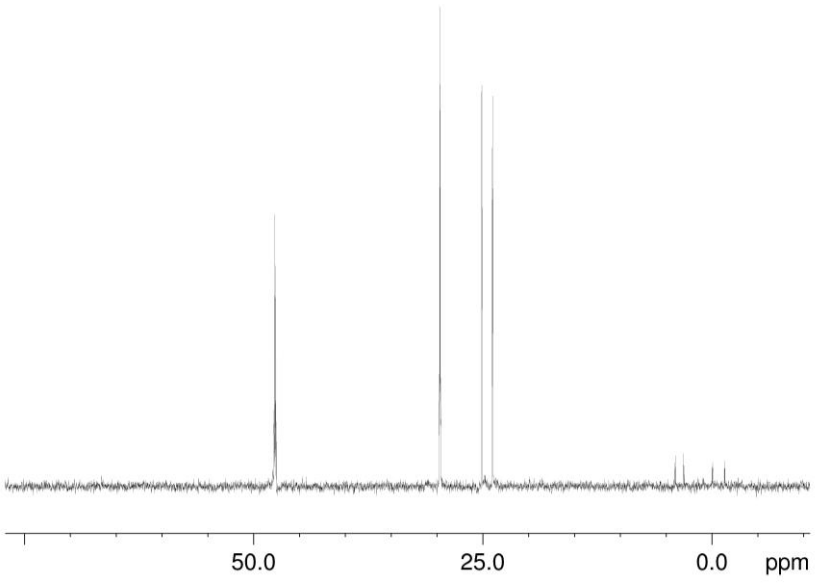


FIG. S54. ^{13}C(DEPT) NMR (C_6D_6) SPECTRA OF **4**

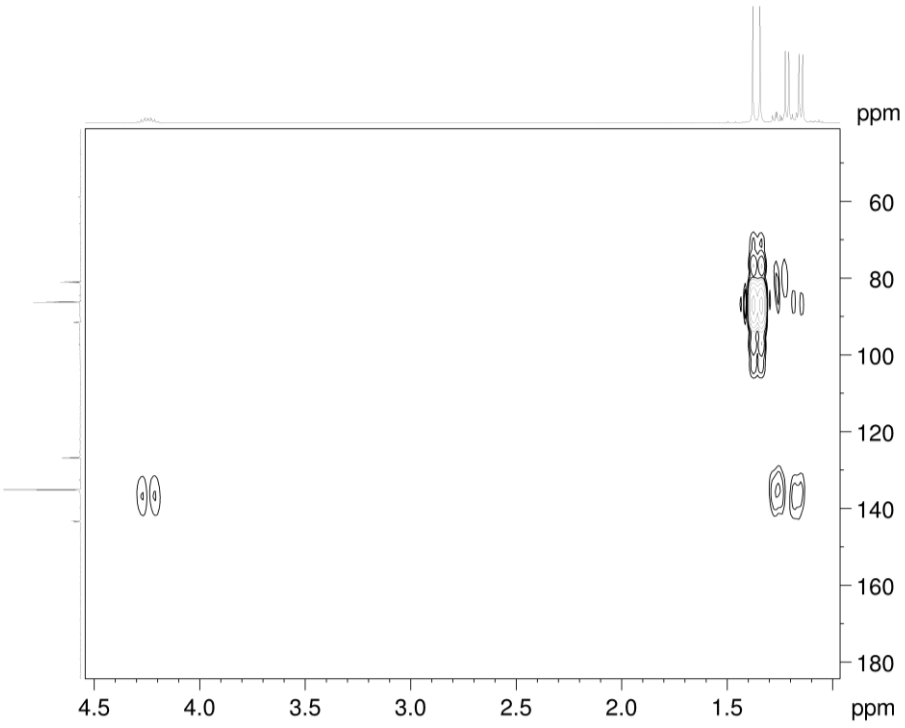


FIG. S55. ^{31}P-^{1}H HMBC NMR (C_6D_6) SPECTRA OF **4**

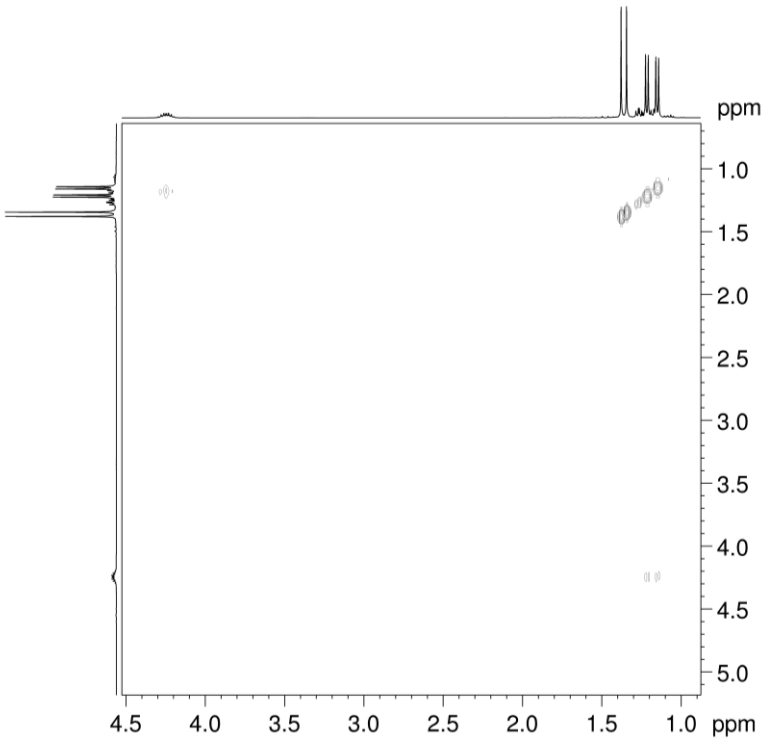


FIG. S56. COSY NMR (C_6D_6) SPECTRA OF **4**

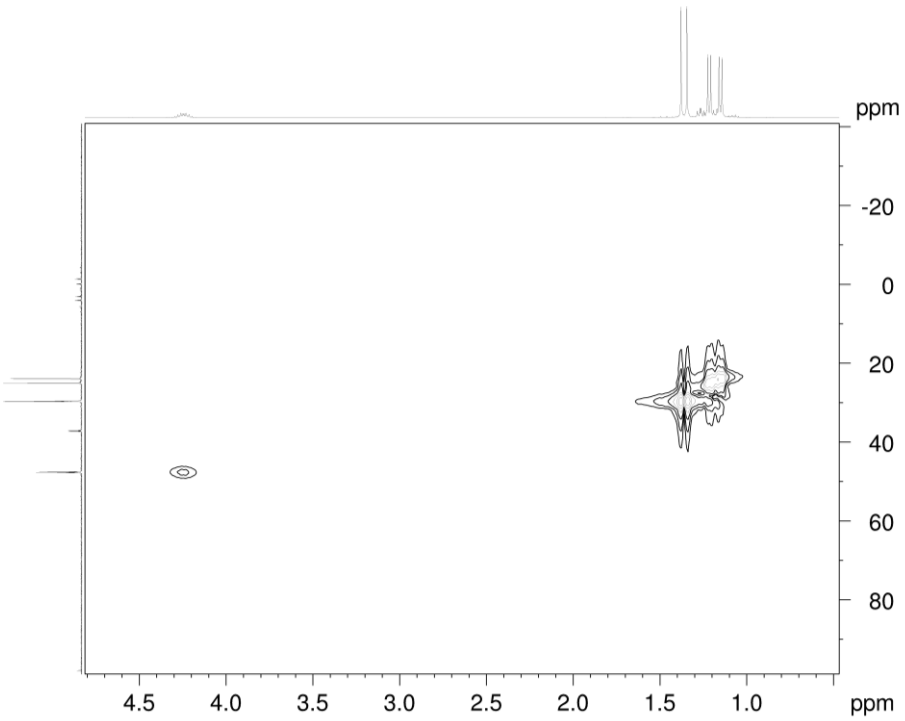


FIG. S57. ^{13}C-^{1}H HMQC NMR (C_6D_6) SPECTRA OF **4**

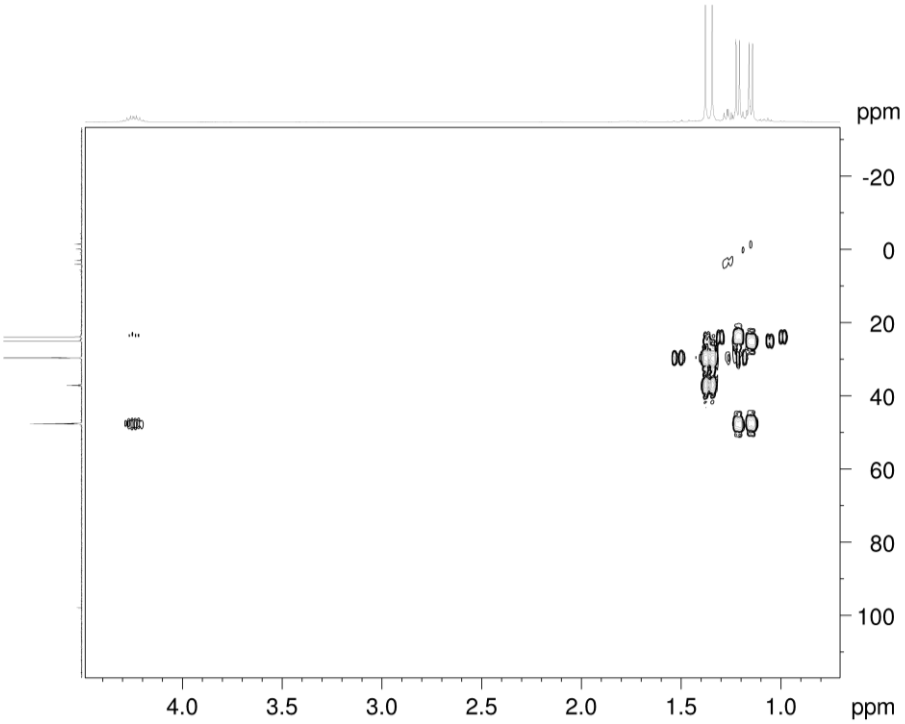


FIG. S58. ^{13}C-^{1}H HMBC NMR (C_6D_6) SPECTRA OF **4**

IR spectra of isolated compounds

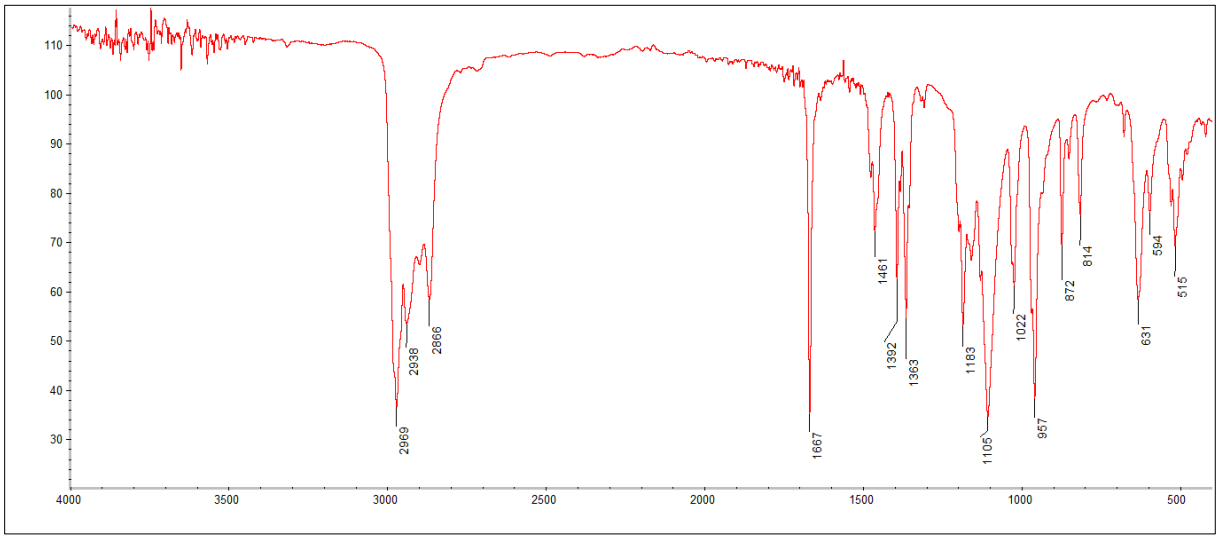


FIG. S59. IR SPECTRA OF SOLID **1A**

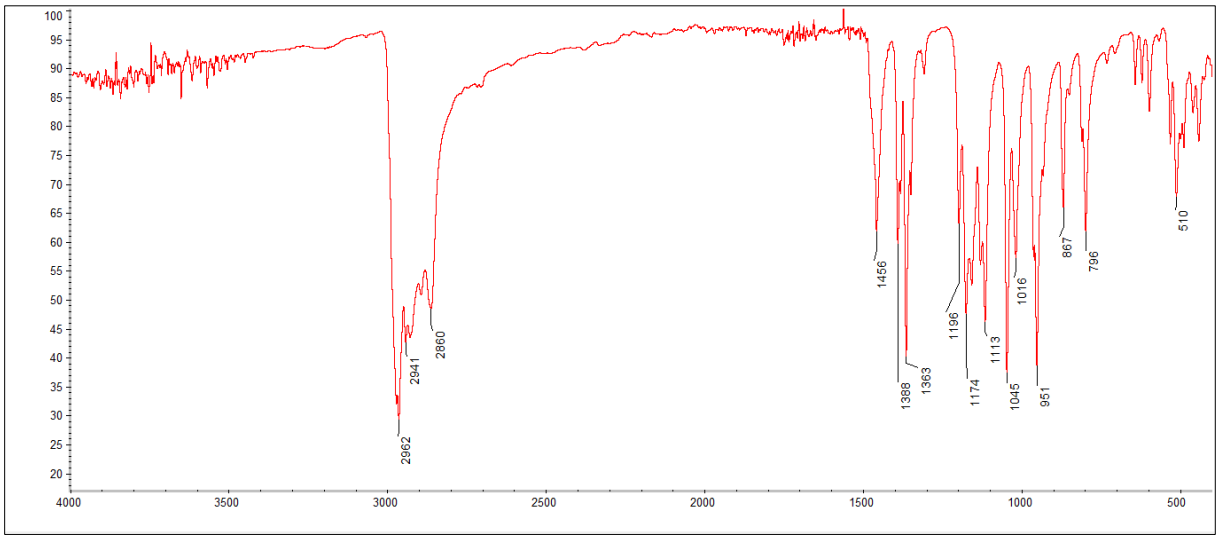


FIG. S60. IR SPECTRA OF SOLID **1B**

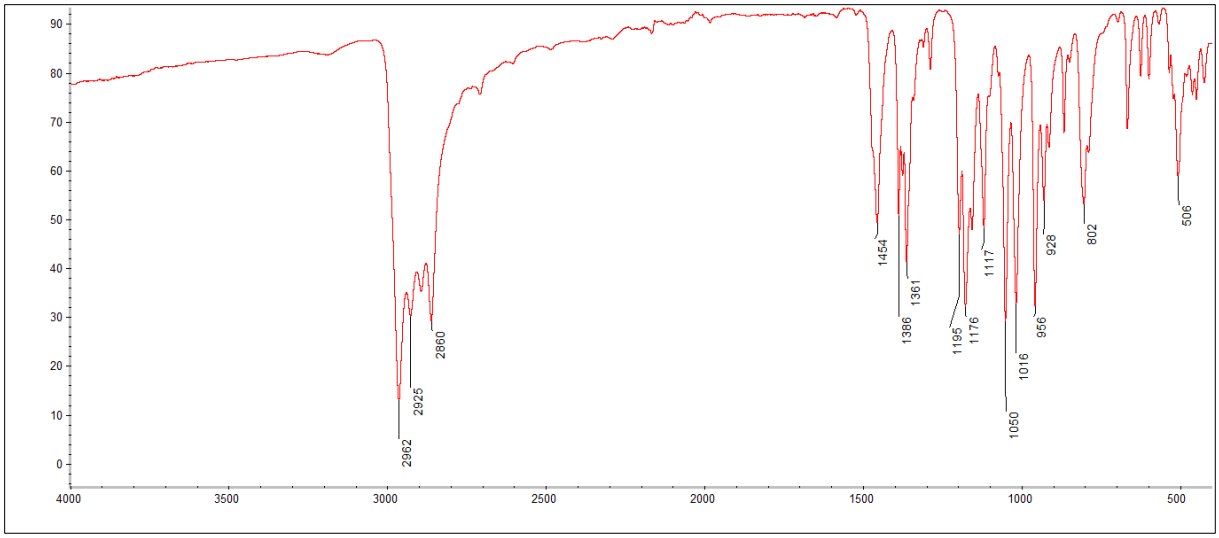


FIG. S61. IR SPECTRA OF SOLID **2B**

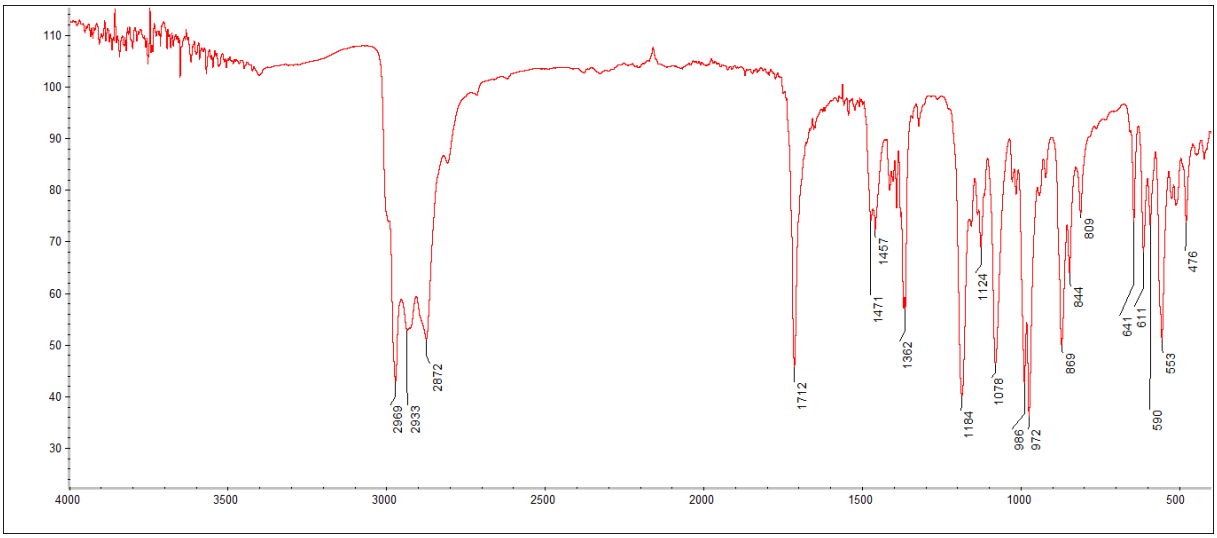


FIG. S62. IR SPECTRA OF SOLID **4**

Vis spectra of isolated compounds

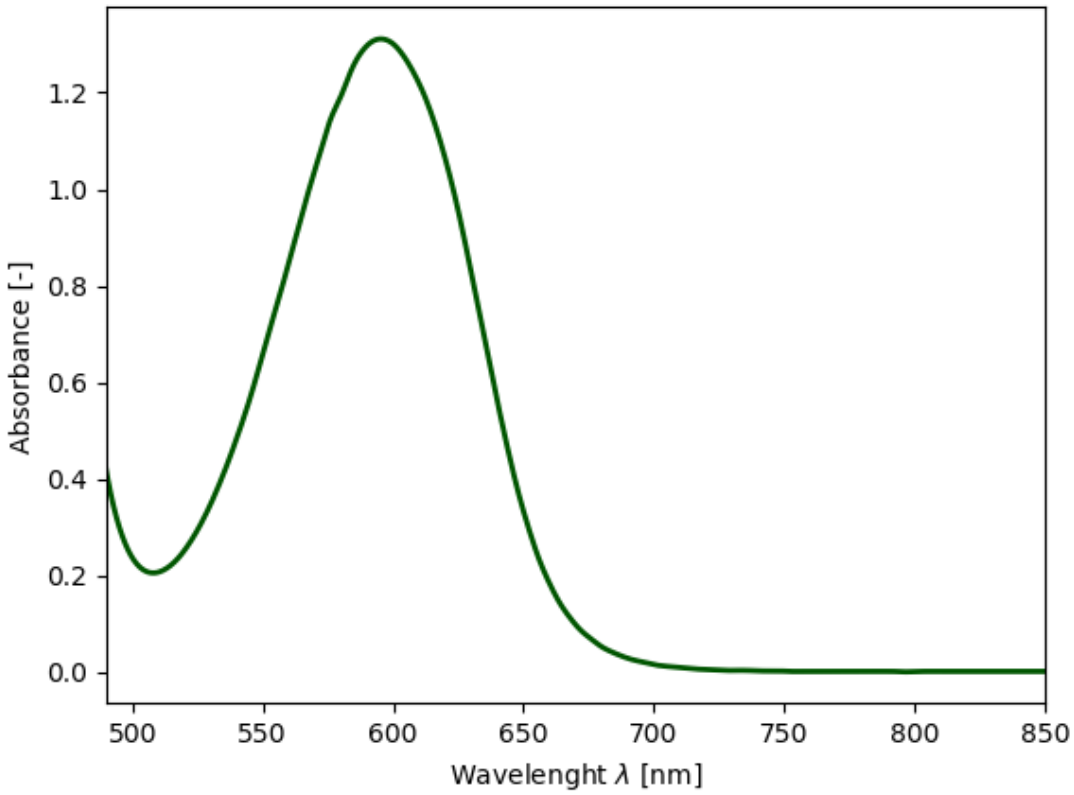


FIG. S63. VIS SPECTRA OF **1B**

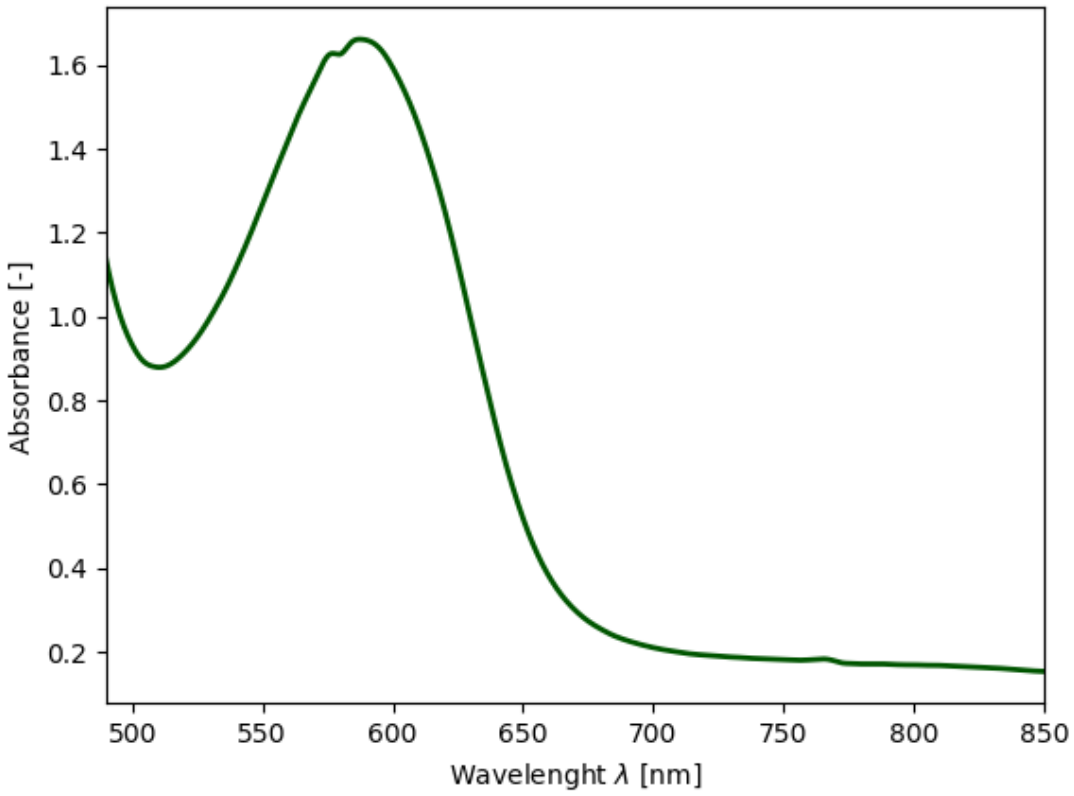


FIG. S64. VIS SPECTRA OF **2B**

NMR study of formation and stability of obtained compounds

Reversible formation of 2a

A solution of **2** (87 mg, 0.25 mmol) and BPh_3 (3 mg, 0.0125 mmol, 5%mol) in toluene-d_8 (2 mL) was slowly frozen, evacuated to 0.01 Torr and backfilled with CO_2 (1 atm). The solution was allowed to warm to room temperature and stirred for 24 hours. $^{31}P\{1H\}$ NMR spectra of the colourless reaction mixture revealed complete conversion of **2** into **2a**. Then, reaction mixture was cooled to 0°C, subjected to three pump-thaw cycles to remove CO_2 and backfilled with argon. An equilibrium between **2** and **2a** in stirred reaction mixture was controlled by ^{1}H and ^{31}P NMR spectra that was recorded after: 3 and 24 h at 0°C; 3 h at 10°C; 3, 24, 48 and 96 h at RT; 3 and 24 h at 35°C; 3 and 24 h at 45°C. Composition of the reaction mixture (including only phosphorus reagents) in each attempt was determined based on ^{1}H NMR spectra.

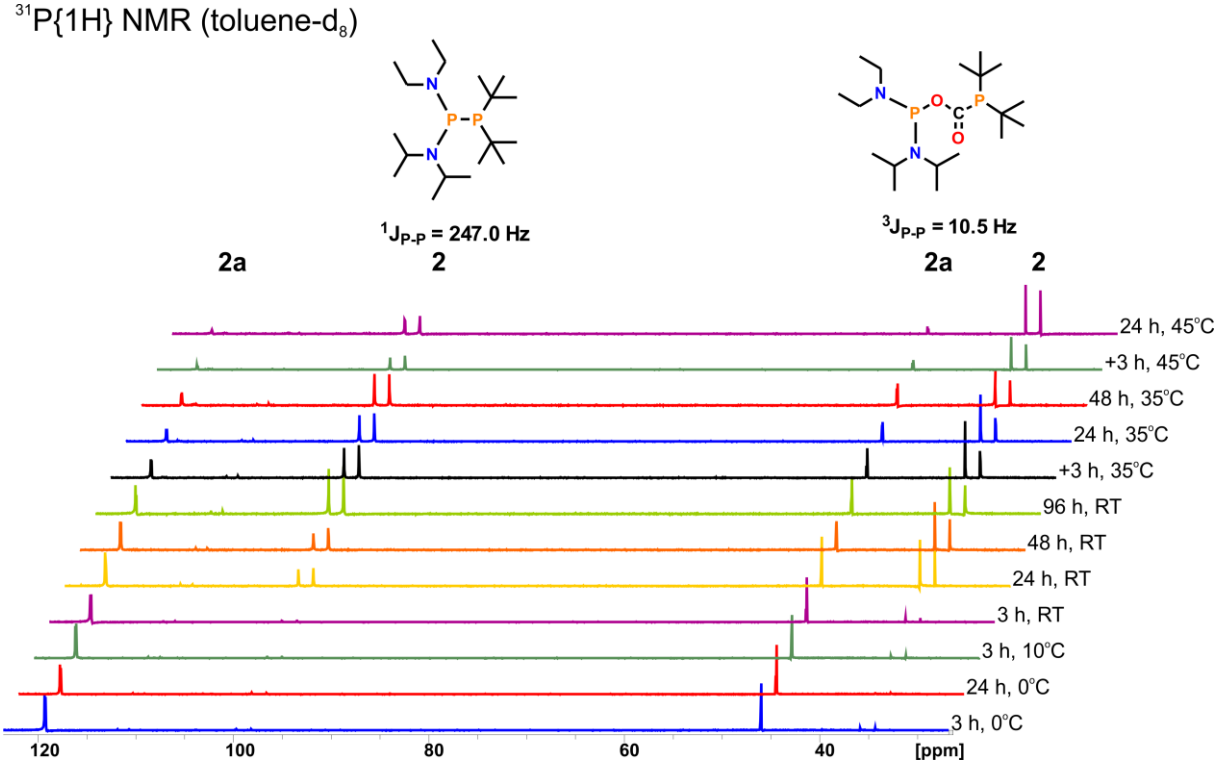


FIG. S65. EQUILIBRIUM BETWEEN **2** AND **2A** MEASURED AT SELECTED TIME INTERVALS

TABLE S8. COMPOSITION OF THE REACTION MIXTURE AT SELECTED TIME INTERVALS

Temperature [°C]	Time [h]	Composition of the reaction mixture [%mol]	
		2	**2a**
0	3	7.79	92.21
0	24	8.86	91.14
10	3	9.27	90.73
RT	3	9.5	90.5
RT	24	38.66	61.34
RT	48	51.83	48.17
RT	96	66.16	33.84
35	3	66.31	33.69
35	24	69.74	30.26
35	48	71.08	28.92
45	3	72.37	27.63
45	24	78.73	21.27

Formation of 1b

To a stirred solution of **1** (94 mg, 0.25 mmol) and BPh_3 (3 mg, 0.0125 mmol, 5%mol) in 2 cm^3 of C_6D_6 0.1 ml (1.65 mmol) (**A**); 0.015 ml (0.25 mmol) (**B**) of CS_2 was added dropwise at room temperature and stirred for 48 hours at RT, 48 hours at 35°C and 72 hours at 45°C. Reaction progress was controlled by ^1H and ^{31}P NMR spectra that was recorded after 0.5 h, 1.5 h, 4.5 h, 24 h and 48 h at room temperature, 3 h, 24 h and 48 h at 35°C and 3 h, 24 h and 72 h at 45°C. Composition of the reaction mixture (including only phosphorus reagents) in each attempt was determined based on ^1H NMR spectra.

Experiment A – excess of CS_2

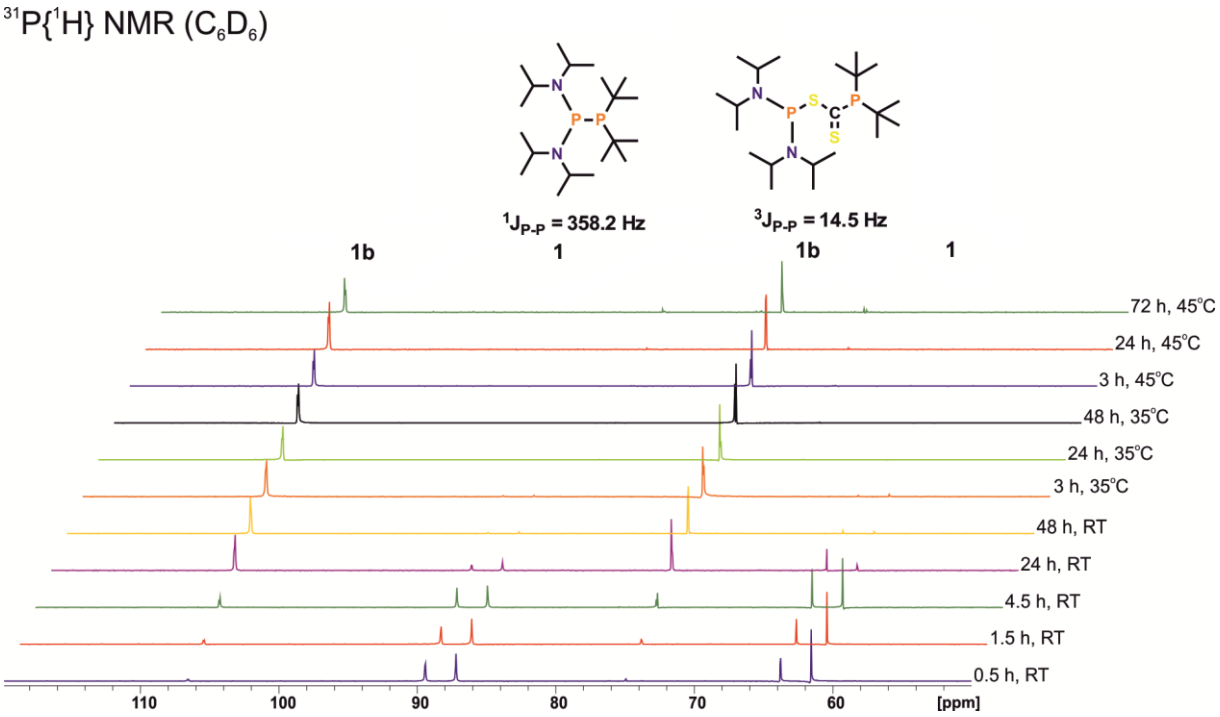


FIG. S66. DEGREE OF CONVERSION OF **1** INTO **1B** MEASURED AT SELECTED TIME INTERVALS (**A**)

TABEL S9. COMPOSITION OF THE REACTION MIXTURE (**A**) AT SELECTED TIME INTERVALS

Temperature [°C]	Time [h]	Composition of the reaction mixture [mol%]	
		1	**1b**
RT	0.5	94.0	6.0
RT	1.5	87.3	12.7
RT	4.5	77.1	22.9
RT	24	30.4	69.6
RT	48	6.4	93.6
35	3	0.0	100.0
35	24	0.0	100.0
35	48	0.0	100.0
45	3	0.0	100.0
45	24	0.0	100.0
45	72	0.0	100.0

Experiment B – equimolar amount of CS_2

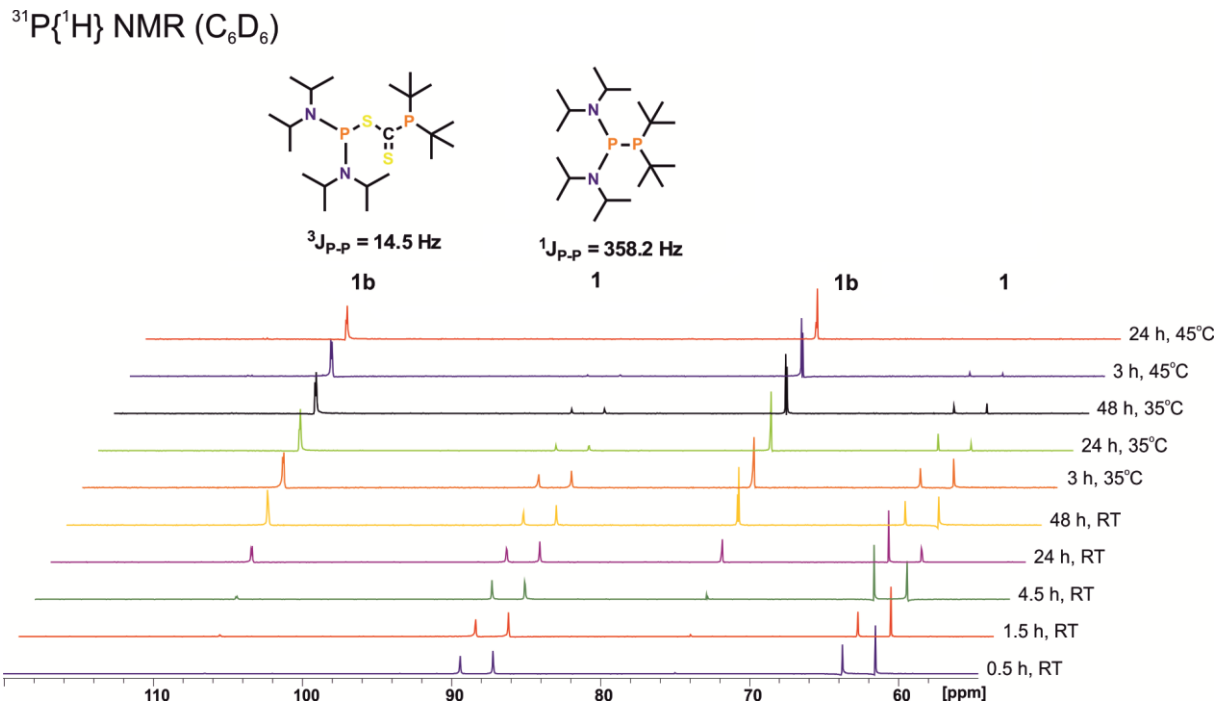


FIG. S67. DEGREE OF CONVERSION OF **1** INTO **1B** MEASURED AT SELECTED TIME INTERVALS (**B**)

TABLE S10. COMPOSITION OF THE REACTION MIXTURE (**B**) AT SELECTED TIME INTERVALS

Temperature [°C]	**Time [h]**	**Composition of the reaction mixture [%mol]**	
		1	**1b**
RT	0.5	96.9	3.1
RT	1.5	94.4	5.6
RT	4.5	89.2	10.8
RT	24	64.5	35.5
RT	48	43.4	56.6
35	3	42.8	57.2
35	24	19.9	80.1
35	48	14.6	85.4
45	3	6.0	94.0
45	24	0.0	100.0

DFT calculations

General methods

All calculations presented in the paper were performed using the Gaussian 09[4] program package. Molecular geometries of all compounds were optimized using density functional theory at the ωB97XD functional by Head-Gordon[5,6] with 6-31+G(d,p) basis set. The ωB97XD exchange-correlation functional has been chosen, as it has good overall performance for the description of main-group element compounds, and it also accounts well for long-range and dispersion interactions. Molecular geometries were energy optimized and the most stable (the lowest energy) conformer was identified during the potential energy surface scanning**.** Nature of the final gas phase geometries as a local minima (no imaginary frequencies) on the potential energy surface was then validated by harmonic frequency calculations at the same level of theory. Values of calculated energies, enthalpies and free energies derived from thermochemical calculations were corrected for the zero-point energy (ZPE).

Condensed Fukui functions[7] and dual descriptors[7,8] were determined using optimized structures to single point calculations on diphosphanes **1-3** and products **1a**, **1b**, **2a**, **2b**, **2c**, **3a**, **3b** for *N*, *N-1* and *N+1* electron states at ωB97XD/6-31G+(d,p) level of theory. Condensed to atom parameters were calculated using partial charges derived *via* Hirshfeld population analysis.

TABLE S11. Selected computational parameters obtained for systems involved in mechanism supported by BPh_3 (in atomic units A.U.): $\boldsymbol{\varepsilon_0}$ - electronic energy; $\boldsymbol{\varepsilon_0 + \ldots}$ - sum of electronic and: $\mathbf{E_{zpe}}$ - zero-point energies, $\mathbf{E_{therm}}$ - thermal energies, **H –** thermal enthalpies, **G -** thermal free energies calculated in the gas phase at ωB97XD//6-31+G(d,p) level of theory

Compound	E_{electr} [A.U.]	$\varepsilon_0 + E_{ZPE}$ [A.U.]	$\varepsilon_0 + E_{therm}$ [A.U.]	ε_0 + H [A.U.]	ε_0 + G [A.U.]
1	-1581.854588	-1581.206485	-1581.174174	-1581.173229	-1581.263890
1a	-1770.402377	-1769.742215	-1769.706130	-1769.705185	-1769.806963
1b	-2416.301937	-2415.646561	-2415.609587	-2415.608643	-2415.713090
2	-1503.244179	-1502.653508	-1502.623530	-1502.622586	-1502.709932
2a	-1691.783538	-1691.179743	-1691.146279	-1691.145335	-1691.243146
2b	-2337.685609	-2337.087199	-2337.052603	-2337.051658	-2337.152913
3	-1424.631215	-1424.097280	-1424.069799	-1424.068855	-1424.152057
3a	-1613.168165	-1612.620794	-1612.590090	-1612.589146	-1612.682537
3b	-2259.067648	-2258.524974	-2258.493460	-2258.492516	-2258.585839
CO_2	-188.526945	-188.515158	-188.515158	-188.511588	-188.535860
CS_2	-834.426915	-834.419915	-834.416831	-834.415887	-834.442831

Nucleophicility of phosphorus centers

TABLE S12. VALUES OF NUCLEOPHILIC (f_N), ELECTROPHILIC (f_E) FUKUI FUNCTIONS AND DUAL DESCRIPTOR (Δf) CALCULATED USING PARTIAL CHARGES DERIVED *VIA* HIRSHFELD POPULATION ANALYSIS

Compound	**P**(RR'N)$_2$			**P***t*Bu$_2$		
	f_N	f_E	Δf	f_N	f_E	Δf
1	0.130	-0.002	-0.132	0.152	-0.009	-0.162
1a	0.099	-0.010	-0.110	0.013	-0.035	-0.048
1b	0.017	-0.027	-0.045	0.108	-0.051	-0.159
2	0.134	0.000	-0.134	0.156	-0.010	-0.166
2a	0.111	-0.013	-0.123	0.014	-0.030	-0.044
2b	0.022	-0.031	-0.052	0.110	-0.050	-0.160
2c	0.012	-0.021	-0.033	0.098	-0.040	-0.138
3	0.159	-0.024	-0.183	0.203	-0.070	-0.273
3a	0.062	-0.039	-0.101	0.021	-0.112	-0.133
3b	0.035	-0.039	-0.074	0.108	-0.051	-0.159

Optimized structures, Hirshfeld atomic charges and Cartesian coordinates

Hirshfeld atomic charges for all optimized structures of substrates, intermediates, transition states and products were presented in Figures S77-S114 . Hydrogen atoms are omitted for clarity.

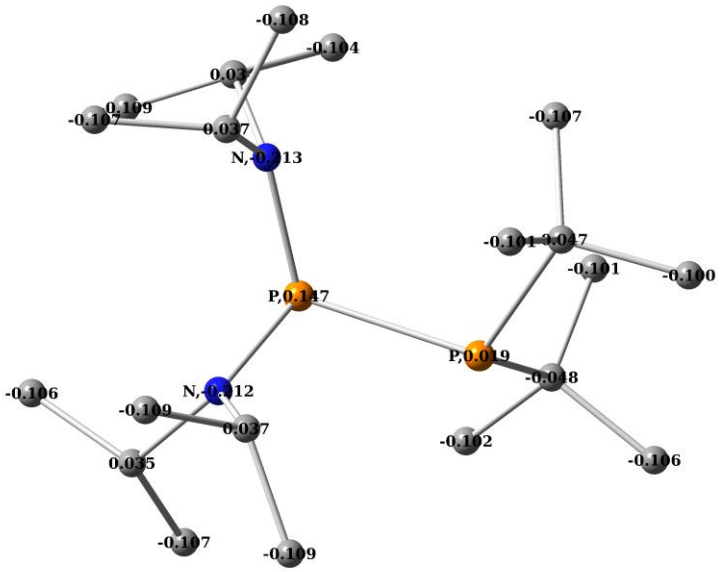


FIG. S68. OPTIMIZED STRUCTURE **1**

C	2.72462200	-0.94449200	-1.07981200
C	1.96812500	-1.88742600	-2.03126200
H	1.54535300	-2.74459700	-1.49735800
H	2.67150400	-2.27512300	-2.77868200
H	1.15645800	-1.38007400	-2.55679200
C	3.93334900	-1.74045500	-0.54667000
H	3.60877600	-2.64071200	-0.01584500
H	4.56337900	-1.15982900	0.12876600
H	4.56008900	-2.05262100	-1.39227700
C	3.22300000	0.26337300	-1.88071600
H	3.92144400	0.87560300	-1.30433400
H	2.39903200	0.90132200	-2.20926200
H	3.75697700	-0.08416500	-2.77472700
C	2.24784500	0.96438200	1.33156600
C	3.71014000	0.72547000	1.74473400
H	3.84425300	-0.24103400	2.24183900
H	4.01367500	1.51111600	2.44835000
H	4.39198100	0.77579300	0.89242800
C	1.42366100	1.05044100	2.62917300
H	1.49945600	0.12563600	3.21041600
H	0.36772300	1.24750400	2.43607600
H	1.79907700	1.87404400	3.24940700
C	2.15617500	2.29981200	0.58431600
H	2.84935500	2.34782900	-0.25713300
H	2.41118400	3.12152400	1.26741900
H	1.14939600	2.46407100	0.20431200
C	-1.27721000	2.19992400	-1.60081700
H	-1.67195900	3.15910300	-1.25043800
C	-0.01009900	2.51005500	-2.40091300
H	0.74338700	3.01102500	-1.78986800
H	-0.25284900	3.15876300	-3.24923200

H	0.42263500	1.58797700	-2.80245100
C	-2.33060200	1.59116800	-2.53689600
H	-3.24264300	1.31798000	-2.00284300
H	-1.93671500	0.69570800	-3.02702700
H	-2.59302000	2.31302200	-3.31790600
C	-1.71571100	1.86098800	0.83668400
H	-1.45654900	1.14353100	1.61698400
C	-1.28461000	3.24727300	1.33516100
H	-0.21128300	3.30035100	1.52016600
H	-1.80206400	3.47474300	2.27311600
H	-1.54623200	4.03569500	0.62192000
C	-3.24246800	1.81949900	0.68530000
H	-3.56732100	0.83592500	0.34110500
H	-3.59430000	2.57277000	-0.02754900
H	-3.72347600	2.02814100	1.64705000
C	-2.18920900	-2.27107500	-0.42043400
H	-2.68776200	-2.86291100	0.35320000
C	-1.33896800	-3.24218000	-1.24556700
H	-0.54615600	-3.68088100	-0.63373200
H	-0.87541900	-2.73065000	-2.09419900
H	-1.96264700	-4.05287300	-1.63798600
C	-3.29916600	-1.66235900	-1.27595700
H	-3.93963200	-1.00833700	-0.67808000
H	-3.92237600	-2.45470700	-1.70436300
H	-2.88312800	-1.08051400	-2.10154800
C	-1.27740800	-1.48777900	1.76074500
H	-0.57366700	-0.73783700	2.12910000
C	-0.67627100	-2.85467800	2.11546300
H	0.28890400	-2.98398700	1.62163300
H	-1.33877700	-3.67926400	1.83084400
H	-0.52004300	-2.92061400	3.19752800
C	-2.60672500	-1.27892300	2.49736100
H	-3.01950900	-0.28616900	2.30898000
H	-2.45879700	-1.39345900	3.57633900
H	-3.35590100	-2.01713500	2.19129200
N	-1.39564600	-1.25806400	0.30879700
N	-0.99956300	1.41877000	-0.37149500
P	1.59003200	-0.57944900	0.42241000
P	-0.41311000	-0.18820000	-0.60737800

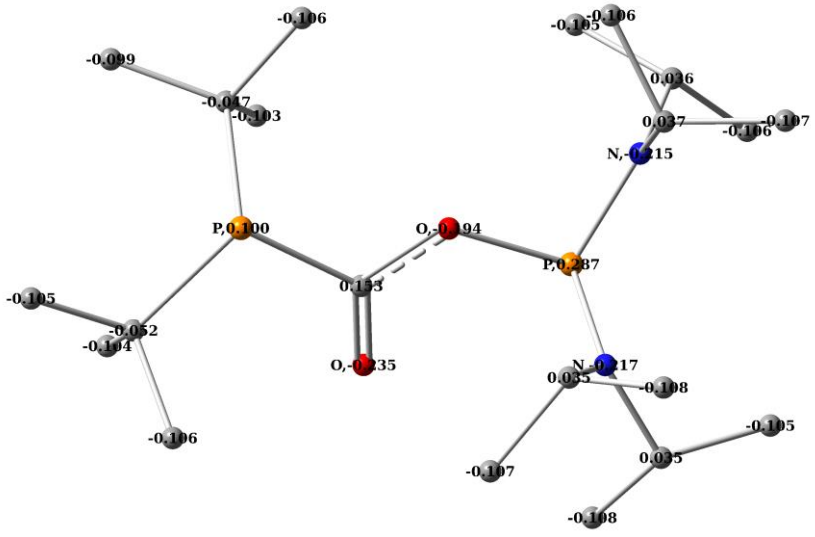


FIG. S69. OPTIMIZED STRUCTURE **1A**

C	-3.99634000	-1.08963200	0.00922000
C	-3.48893800	-2.52247900	0.27435300
H	-3.18277400	-2.65616500	1.31833400
H	-4.30239700	-3.23069800	0.07493700
H	-2.65043700	-2.77885400	-0.37511900
C	-4.33402300	-0.93930100	-1.47900300
H	-3.44182400	-1.04178400	-2.10074500
H	-5.04413200	-1.72423100	-1.76913700
H	-4.81090400	0.02149000	-1.69356500
C	-5.26856300	-0.89332900	0.85645400
H	-5.06348500	-1.02036800	1.92466500
H	-5.72859400	0.08653500	0.71274900
H	-6.00941200	-1.64790800	0.56540800
C	-2.87324100	1.83832900	0.03101100
C	-4.31555700	2.31162900	0.26433500
H	-4.63718300	2.14975200	1.29863300
H	-4.37477100	3.38812400	0.06282100
H	-5.02538300	1.81593300	-0.40262300
C	-2.50710200	2.01486700	-1.45006300
H	-1.45183700	1.79258700	-1.63344200
H	-3.10565300	1.38139500	-2.10689100
H	-2.67619300	3.05942700	-1.74125500
C	-1.93542100	2.71611400	0.87888100
H	-2.18607900	2.66245100	1.94309700
H	-0.89491200	2.40888500	0.75448100
H	-2.02459200	3.76116100	0.55598600
C	-1.16733300	-0.41714500	-0.31067100
C	2.66967300	2.38708200	-0.79813000
H	3.24154100	3.04846500	-0.14015200
C	1.45547600	3.17833000	-1.29420800
H	1.77354600	4.08742000	-1.81569400
H	0.86197200	2.57972300	-1.99386300
H	0.81000300	3.46459000	-0.45928800
C	3.60197900	2.00002600	-1.94971800
H	3.95551000	2.89662900	-2.46959100
H	4.46906300	1.45244800	-1.56910100
H	3.08657700	1.36747200	-2.67891200
C	2.59813300	1.29819400	1.46744200
H	2.17944800	0.39685300	1.91415400
C	1.92619800	2.48294400	2.16856000
H	2.13462400	2.44861300	3.24279700
H	2.29246400	3.44458500	1.79333000
H	0.84367500	2.44474100	2.02852300
C	4.10968000	1.26510100	1.71321400
H	4.32286300	1.21274700	2.78606100
H	4.55108700	0.39122800	1.22556800
H	4.60388200	2.16075700	1.32121300
C	2.58696100	-2.44956600	-0.84403400
H	2.79943800	-3.31211800	-0.20512000
C	3.93925400	-1.91241400	-1.32159500
H	4.49507000	-2.69272000	-1.85214700
H	3.80999400	-1.06964100	-2.00907100
H	4.53787300	-1.57067300	-0.47189800
C	1.44892000	-1.95482800	1.34364700
H	0.89154000	-1.13255600	1.79906000
C	1.72909200	-2.94780900	-2.01140300
H	2.25433000	-3.74249200	-2.55262900
H	0.77423800	-3.33643600	-1.65074800
H	1.51104900	-2.13971100	-2.71579100
C	2.63556400	-2.28740000	2.25673100
H	2.28129200	-2.52192700	3.26584000
H	3.18906600	-3.15976800	1.89335000
H	3.33473600	-1.44946200	2.31974500
C	0.47995600	-3.14069900	1.25180900
H	0.08742200	-3.38009800	2.24532500

H	-0.35938300	-2.90737600	0.59350900
H	0.97486300	-4.03879000	0.86651000
O	-0.08012100	0.21889000	0.14159100
O	-1.13578600	-1.20872700	-1.23033700
P	-2.66608900	0.06456800	0.70976100
P	1.44125800	-0.01916400	-0.71729400
N	2.29103200	1.22594000	0.03367400
N	1.88557800	-1.47746600	0.02099000

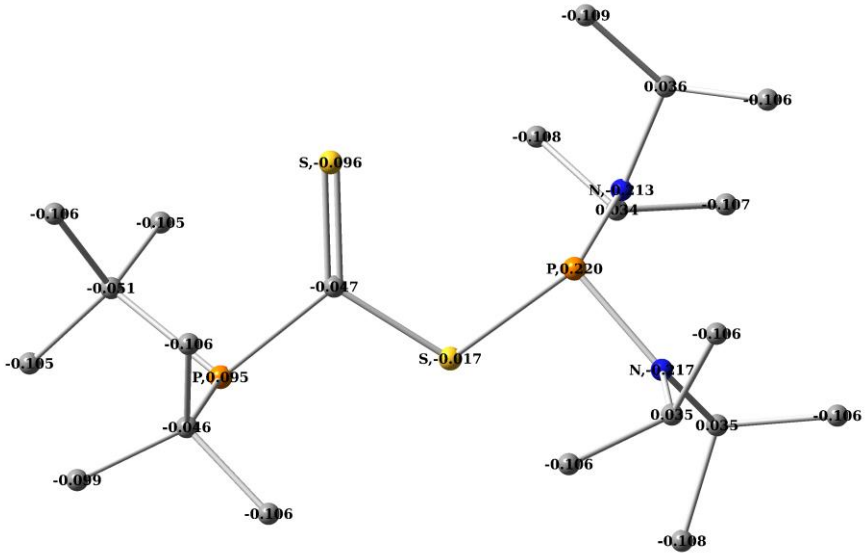


FIG. 70. OPTIMIZED STRUCTURE **1B**

S	0.09924600	0.27290700	-0.79658200
P	-1.63290800	0.10168200	0.55845500
P	3.01407700	0.21867800	-0.74683500
S	1.30346800	-1.30631000	1.44625400
N	-2.26392200	-1.40743600	0.11525200
N	-2.60549500	1.29305600	-0.16270400
C	-2.10659200	-2.09774100	-1.17536900
H	-1.62285200	-1.38850600	-1.85129200
C	-2.97589000	-2.15497100	1.17791100
H	-3.24828500	-3.11278100	0.72602500
C	3.41466500	1.76660700	0.30713000
C	-3.44799400	-2.48689900	-1.80877500
H	-3.95542800	-3.27729500	-1.24602300
H	-3.28365000	-2.86548400	-2.82262700
H	-4.12317700	-1.62803700	-1.86541500
C	3.65419500	-2.46557900	-0.92287400
H	2.90541700	-2.82791500	-0.21642100
H	4.43215200	-3.23342400	-1.01174500
H	3.18140700	-2.35521400	-1.90557000
C	2.48580000	2.88400700	-0.20176600
H	2.61398200	3.05696000	-1.27480600
H	2.72280800	3.81566400	0.32715300
H	1.43285300	2.65668200	-0.01906200
C	-2.74205200	2.57569200	0.55916100
H	-3.38275400	3.20375700	-0.06755500
C	4.30260000	-1.14817300	-0.45276000
C	-1.16193300	-3.29765300	-1.05704300
H	-0.19615100	-2.97680300	-0.65709400
H	-1.00340300	-3.75871800	-2.03748500
H	-1.56816900	-4.06536400	-0.38923500
C	-3.17023000	1.22130000	-1.51563800

H	-2.91030100	0.23390400	-1.90030900
C	4.86249800	2.18900100	0.00632000
H	5.59457500	1.50352400	0.43969400
H	5.03986100	3.17713100	0.44782800
H	5.05047700	2.26818100	-1.06967900
C	-2.56812500	2.25061500	-2.47997100
H	-2.81223100	3.27701400	-2.18595100
H	-2.96609800	2.09508300	-3.48797300
H	-1.47967400	2.15545800	-2.52157700
C	3.22444300	1.62030200	1.82159600
H	2.17450500	1.46224200	2.08023300
H	3.55469100	2.54451500	2.31279700
H	3.79725500	0.79102900	2.24059600
C	5.45938600	-0.84442500	-1.42844000
H	5.10045800	-0.75053300	-2.45838300
H	6.18016700	-1.67047100	-1.39450500
H	5.99955400	0.06999700	-1.17387200
C	1.44851900	-0.36701500	0.10635000
C	-2.10574400	-2.47716100	2.39450000
H	-1.19971700	-3.00547200	2.08991100
H	-2.66810100	-3.10590800	3.09299700
H	-1.80009700	-1.56858600	2.92142600
C	-3.46096900	2.40313500	1.89950100
H	-4.43350400	1.92469700	1.75136100
H	-3.61925000	3.37618400	2.37604400
H	-2.87098900	1.78386500	2.58268900
C	-4.28033400	-1.46232900	1.58136700
H	-4.08048400	-0.50526300	2.07438000
H	-4.84942000	-2.08764000	2.27730500
H	-4.90005900	-1.26761500	0.70134600
C	-1.40873600	3.31377600	0.72236200
H	-0.73167700	2.75705400	1.37974700
H	-1.56936300	4.30211400	1.16571200
H	-0.91529400	3.44147100	-0.24533300
C	-4.70000600	1.29434300	-1.48423900
H	-5.10038000	0.52276200	-0.82088700
H	-5.11275900	1.14385200	-2.48717800
H	-5.05270100	2.26706900	-1.12476200
C	4.86580300	-1.33016700	0.96180000
H	5.43575400	-0.45710000	1.29133300
H	5.55422700	-2.18525700	0.96435600
H	4.07496100	-1.52709400	1.68819300

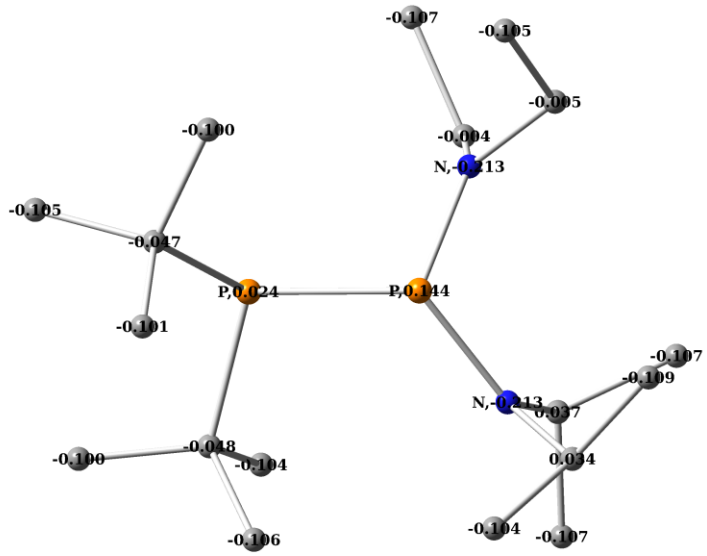


FIG. S71. OPTIMIZED STRUCTURE **2**

C	-1.92623100	-1.80059200	-0.64044500
C	-1.33547300	-2.26206800	-1.98665500
H	-1.82243900	-1.75510200	-2.82566200
H	-1.48613900	-3.34267600	-2.10596700
H	-0.26366600	-2.07073500	-2.05734400
C	-3.44333900	-2.03443400	-0.71958400
H	-3.91919900	-1.40603500	-1.47940100
H	-3.93928900	-1.86385000	0.23869900
H	-3.62130300	-3.08172800	-0.99451000
C	-1.34770200	-2.66069600	0.48713200
H	-1.71440100	-2.35587600	1.47041100
H	-0.26084700	-2.59403400	0.49919600
H	-1.62996100	-3.71074600	0.33233600
C	-2.64236500	0.88093300	0.77586700
C	-4.05502300	1.07976500	0.19417200
H	-4.01573400	1.59678700	-0.77005400
H	-4.64319000	1.69816700	0.88405500
H	-4.59676600	0.14386800	0.05574900
C	-2.06837500	2.28744900	1.02781000
H	-1.92597400	2.84187600	0.09478100
H	-1.11050500	2.24832000	1.54883500
H	-2.76758000	2.85225700	1.65672000
C	-2.72476700	0.13808700	2.11491300
H	-3.22139200	-0.83108600	2.01905000
H	-3.30685000	0.73399400	2.83001900
H	-1.73026500	-0.02217100	2.54336300
C	1.93980400	2.60539400	0.06554000
H	2.42232500	3.14162900	-0.75925800
C	1.33694400	3.61766000	1.03458200
H	0.52855900	4.17674600	0.55414400
H	2.10269600	4.32386700	1.37307200
H	0.92713800	3.11665200	1.91634800
C	0.86949900	1.74185400	-1.97675800
H	0.27482500	0.89684100	-2.32846200
C	0.20244100	3.02617500	-2.46158800
H	-0.82735900	3.06996300	-2.09506600
H	0.18495000	3.05993000	-3.55607200
H	0.73018800	3.91771900	-2.10696200
C	2.33056600	-1.34509800	1.44570000
H	3.02394400	-2.11393000	1.09007100
C	1.46799300	-1.99171100	2.53251000
H	0.99056700	-2.90466800	2.17018900
H	0.68559200	-1.30219900	2.86606800
H	2.08470600	-2.25016600	3.39963400
C	3.18496000	-0.21915600	2.04514300
H	3.83506900	0.23148600	1.29101900
H	3.81920300	-0.61360000	2.84635400
H	2.55038700	0.56519100	2.47061200
C	2.10364200	-1.29645600	-1.04994900
H	1.39694700	-0.91357700	-1.79156100
C	2.20967100	-2.81315400	-1.26077200
H	1.27747800	-3.31752700	-0.99652900
H	3.01636000	-3.25366000	-0.66599300
H	2.42980700	-3.02674400	-2.31199000
C	3.45503900	-0.62481100	-1.33054700
H	3.39031800	0.45636000	-1.18486900
H	3.76745500	-0.81762700	-2.36221300
H	4.23638300	-1.01540000	-0.66956500
N	1.53351900	-0.94496000	0.25918700
N	0.96551300	1.67685300	-0.51939700
P	-1.54483600	0.06717200	-0.56601800
P	0.45661300	0.37907100	0.48659800
H	2.74493000	2.05599400	0.57117100
H	1.86944300	1.64375500	-2.43007700

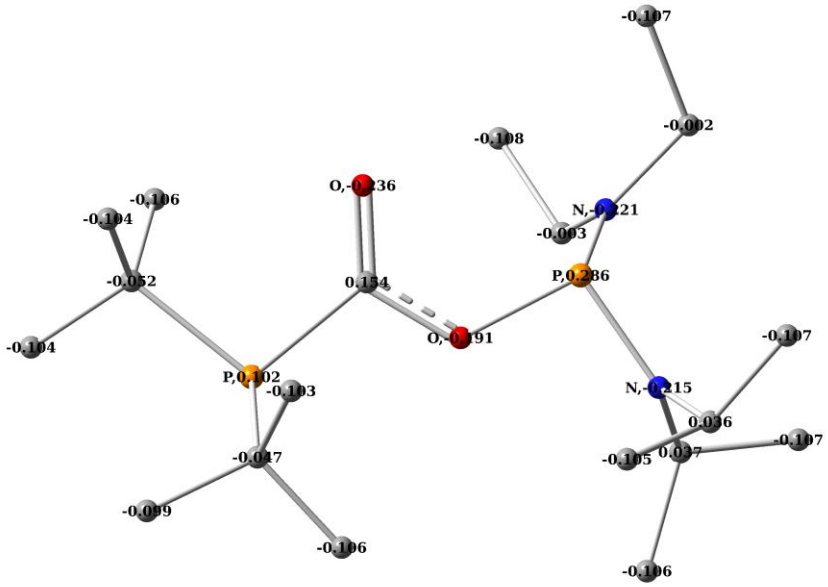


FIG. S72. OPTIMIZED STRUCTURE **2A**

C	2.47410900	-1.91080500	-0.09893400
C	3.85613200	-2.56194700	0.06068000
H	4.60552500	-2.10536800	-0.59086500
H	3.78326800	-3.62091700	-0.21504900
H	4.21580300	-2.51276600	1.09396600
C	2.06500200	-1.92988000	-1.57935400
H	2.71255100	-1.30774100	-2.19993500
H	1.03445400	-1.58998000	-1.71848000
H	2.12210400	-2.95840900	-1.95787800
C	1.45683100	-2.73975000	0.70654200
H	0.45866600	-2.30065200	0.64868000
H	1.74173900	-2.81274200	1.76098400
H	1.40821800	-3.75474100	0.29191100
C	3.94046800	0.85817600	0.07235400
C	5.18985300	0.44797200	0.87576400
H	5.01008300	0.50631700	1.95440300
H	6.00900500	1.13623000	0.63437700
H	5.53236900	-0.56206500	0.64163400
C	3.60996900	2.31605600	0.45550600
H	3.35899300	2.40624500	1.51859300
H	2.78384000	2.71243100	-0.13691500
H	4.49316200	2.93952400	0.27032400
C	4.23966800	0.78322500	-1.42953300
H	4.58978200	-0.20967400	-1.72654200
H	5.03834700	1.49493100	-1.67463900
H	3.36156200	1.04428800	-2.02470000
C	-2.97726300	2.53871900	-0.57997100
H	-3.44655600	3.17566200	0.17995100
C	-2.47993600	3.38885500	-1.74947400
H	-1.72907900	4.11124700	-1.42062900
H	-3.31284500	3.93226400	-2.20899600
H	-2.01884900	2.75397200	-2.51139200
C	-1.41055700	2.26515700	1.34146800
H	-0.71866900	1.52633600	1.75110800
C	-0.67753500	3.59923500	1.20244800
H	0.12162900	3.51385500	0.46079500
H	-0.24081100	3.88951900	2.16364000
H	-1.35517400	4.40006900	0.89015100
C	-3.10624500	-1.96599000	-0.72804600
H	-3.70835100	-2.56522100	-0.03794300
C	-2.04846300	-2.89413400	-1.33201100
H	-1.38855600	-3.28476400	-0.55231000
H	-1.43263900	-2.35663700	-2.06142400
H	-2.52063900	-3.73842100	-1.84567800
C	-4.06501500	-1.42423300	-1.79332900
H	-4.81945200	-0.77876400	-1.33336500
H	-4.57586000	-2.24864200	-2.30208900
H	-3.52718700	-0.84226500	-2.54823500

C	-2.77854700	-0.89152000	1.53232000
H	-2.17352200	-0.08639400	1.95312500
C	-2.32895000	-2.18242800	2.22234400
H	-1.26788100	-2.36530300	2.03626100
H	-2.89659700	-3.05388200	1.87912400
H	-2.47889000	-2.09852200	3.30336500
C	-4.24499800	-0.55725900	1.82023300
H	-4.50666000	0.40030500	1.36014300
H	-4.42195400	-0.48660400	2.89839800
H	-4.91848900	-1.32474300	1.42232700
N	-2.50696500	-0.89335200	0.08834600
N	-1.93301300	1.75565000	0.08024000
P	2.48906000	-0.17807900	0.71010800
P	-1.57724000	0.28142300	-0.68058200
H	-3.77204000	1.86599900	-0.93282200
H	-2.23235800	2.36831900	2.06903800
O	-0.08892200	-0.03523100	0.16767800
C	1.04861300	0.54812400	-0.24358700
O	1.07713200	1.41973600	-1.08491700

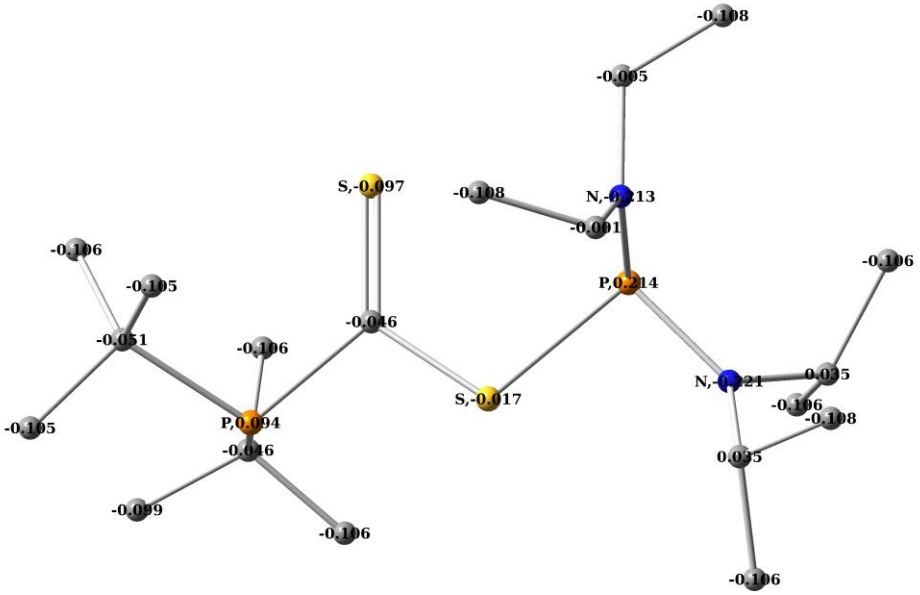


FIG. S73. OPTIMIZED STRUCTURE **2B**

S	0.08088500	-0.48777100	0.68620200
P	-2.83156700	-0.42152700	0.66881200
P	1.79609300	-0.02249700	-0.59351400
S	-1.14677100	1.24147600	-1.44071300
N	2.87510500	-1.02714200	0.25125300
N	2.12395200	1.60038200	-0.24674100
C	-1.27162200	0.21502600	-0.16277400
C	4.46702200	-0.31281500	2.03536200
H	5.32505600	-0.87978800	1.65810600
H	4.58522300	-0.21624200	3.11948400
H	4.49796000	0.68578600	1.59009500
C	-3.31564300	-1.82877200	-0.53163400
C	2.09714800	2.24970900	1.06069300
H	3.03528300	2.80169100	1.20947600
H	2.07715800	1.47878400	1.83145700
C	3.10449100	-2.87703200	-1.40178700
H	2.51502600	-3.51905600	-0.74119800
H	3.82917600	-3.49660900	-1.94069100
H	2.42785200	-2.43059000	-2.13750600
C	3.81963300	-1.79446300	-0.59076800
H	4.49068600	-2.30515600	0.10605800
C	-4.75400500	-2.25715300	-0.19394700
H	-4.88782200	-2.43466400	0.87847700
H	-4.97643100	-3.19543600	-0.71624300
H	-5.49195600	-1.51982100	-0.51979200
C	-4.68945100	1.35582700	-0.78946400
H	-3.92165400	1.59606000	-1.52733500
H	-5.34197400	2.23141100	-0.67708100
H	-5.30720400	0.54077200	-1.17695200

C	2.24632100	2.48437300	-1.40643700
H	1.46913100	3.25791800	-1.37644700
H	2.03972500	1.88788900	-2.30005500
C	3.14495100	-1.00961400	1.69628300
H	2.33937400	-0.42781800	2.15265500
C	-4.07674300	1.01176300	0.57308900
C	3.05180200	-2.40870700	2.31390700
H	2.08260000	-2.85970700	2.08479400
H	3.15719100	-2.34351500	3.40156100
H	3.83865900	-3.07674900	1.94868800
C	3.62755000	3.12547200	-1.52727400
H	3.68407100	3.72849000	-2.43922900
H	4.40468100	2.35621000	-1.57066000
H	3.84770900	3.78598500	-0.68254000
C	4.69475300	-0.89980100	-1.47630000
H	4.09457100	-0.39574200	-2.24165100
H	5.45713100	-1.49643800	-1.98832200
H	5.19529800	-0.13469900	-0.87567300
C	-3.36008100	2.25162000	1.14316800
H	-2.84996900	2.02681600	2.08707500
H	-4.10399900	3.03150700	1.34555100
H	-2.62929400	2.65921200	0.44200900
C	-3.20974400	-1.52593400	-2.03099400
H	-3.79159900	-0.65173300	-2.32834400
H	-3.58548600	-2.39021400	-2.59353000
H	-2.17453500	-1.35641300	-2.33575300
C	-5.20423700	0.64619700	1.56142100
H	-5.77776700	-0.22735600	1.24348500
H	-5.90297200	1.48874300	1.63209100
H	-4.80954000	0.44759600	2.56288000
C	0.90656500	3.18363700	1.27938400
H	0.91678600	4.03317700	0.59080200
H	0.93594800	3.58365700	2.29793800
H	-0.03586400	2.64662600	1.14365400
C	-2.38089200	-3.00642600	-0.19828900
H	-1.33417200	-2.77479700	-0.41437900
H	-2.66429500	-3.87254400	-0.80929900
H	-2.45379700	-3.29226700	0.85564900

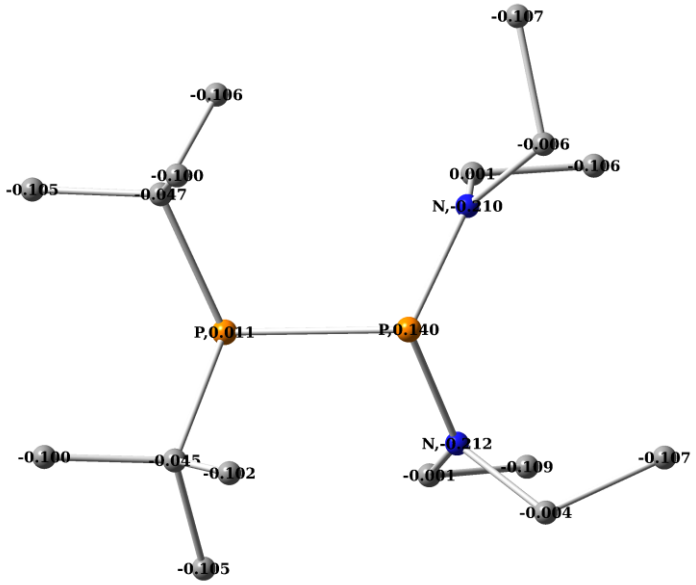


FIG. S74. OPTIMIZED STRUCTURE **3**

P	0.46447100	-0.12941000	0.66171100
P	-1.36356100	-0.13303600	-0.67295100
N	1.19562800	-1.56232000	0.07090800
C	-2.35197900	-1.49928600	0.26402700
C	-2.19105800	-1.54634300	1.79196000
H	-1.16680600	-1.78557300	2.08802700
H	-2.45922600	-0.60341300	2.27286400
H	-2.84691600	-2.32947800	2.19445400
C	-3.84877200	-1.37922300	-0.06239700

H	-4.31876500	-0.55089500	0.47335100
H	-4.03017900	-1.25259000	-1.13460600
H	-4.35563700	-2.29849600	0.25612300
C	3.27628700	-1.76671300	1.47790100
H	3.94166300	-1.66170800	0.61629500
H	3.14523700	-0.77631200	1.92594800
H	3.76551900	-2.41136700	2.21622500
C	2.69558100	-2.08592900	-1.90657200
H	3.15721100	-1.09687900	-1.92920800
H	3.35369600	-2.75760400	-1.34671100
H	2.63940000	-2.46175200	-2.93372900
C	-1.86415300	-2.84476600	-0.30609500
H	-1.95556500	-2.88006900	-1.39654800
H	-0.82325400	-3.03530800	-0.03778000
H	-2.47223500	-3.65625900	0.11347700
C	1.29073300	-2.04371400	-1.30525000
H	0.63901400	-1.42550300	-1.92737900
C	1.92020000	-2.34761800	1.07063600
H	2.05232100	-3.36078600	0.66948300
N	1.40476500	1.22039000	0.19951100
C	3.45405600	1.44532200	-1.23069200
H	3.89904000	2.32785900	-0.76118400
H	3.86715900	0.55893500	-0.74023300
H	3.76524900	1.43945600	-2.28004200
C	1.79434600	3.49544800	1.18705400
H	2.18043200	3.90513400	0.24774400
H	0.73104800	3.74324600	1.25430600
H	2.31499600	4.00076100	2.00673900
C	1.92681600	1.46351100	-1.14088800
H	1.50855900	0.70435700	-1.80693900
C	2.01444400	1.98682000	1.28578800
H	3.09467100	1.78205000	1.34210500
H	1.29627900	-2.44667800	1.96785500
H	0.87273500	-3.06123800	-1.35238300
H	1.56275300	2.42891000	-1.52367100
H	1.58313700	1.62007500	2.22183300
C	-2.18247900	1.56672900	-0.35375600
C	-3.49217500	1.65287200	-1.16264800
C	-2.45420400	1.91550500	1.11397600
C	-1.24356000	2.62508700	-0.96009300
H	-3.33735300	1.35162000	-2.20392900
H	-4.29763200	1.04814600	-0.74836100
H	-3.83718000	2.69465500	-1.16405000
H	-1.54654600	1.84493600	1.72225000
H	-2.83211700	2.94379500	1.18726300
H	-3.21069400	1.25907700	1.55278200
H	-1.74258800	3.60185900	-0.93593900
H	-0.31237300	2.70430100	-0.40339600
H	-1.00594000	2.39672000	-2.00507800

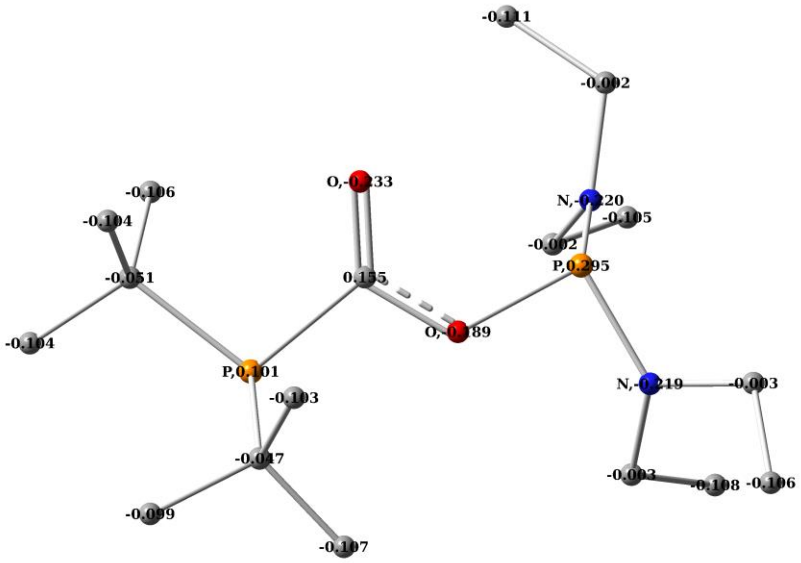


FIG. S75. OPTIMIZED STRUCTURE **3A**

P	-1.79908700	0.08645500	-0.97541300
P	2.17133400	-0.18076900	0.73018300
N	-2.59552400	-1.20600900	-0.22562800
C	2.37499800	-1.94415300	0.02026500
C	2.15020500	-2.06391600	-1.49436000
H	1.11995900	-1.81849700	-1.76846900
H	2.81800600	-1.41957300	-2.06929900
H	2.33237100	-3.10060500	-1.80478200
C	3.77262200	-2.47361600	0.37552000
H	4.55909600	-1.98620900	-0.20619100
H	3.99829000	-2.35020300	1.44004400
H	3.81575900	-3.54590000	0.14949100
C	-3.74818100	-3.27078800	-1.03265200
H	-2.79872800	-3.65016900	-1.42256500
H	-4.55403000	-3.60650500	-1.69233600
C	-3.69533200	-1.24582400	2.03390900
H	-3.91061500	-0.17582900	1.96332100
H	-4.59484300	-1.79054000	1.73051500
H	-3.49843300	-1.49036000	3.08243400
C	1.33383900	-2.81698200	0.74714600
H	1.48650600	-2.80105600	1.83108800
H	0.31411900	-2.48615300	0.53667800
H	1.43318800	-3.85429600	0.40313200
C	-2.48775100	-1.61747300	1.17240600
H	-1.57744300	-1.17954700	1.58485200
C	-3.73130900	-1.74521500	-0.97312600
H	-3.66969900	-1.34795700	-1.99191500
N	-2.19790300	1.54909600	-0.22177400
C	-3.06215700	2.64486500	1.84451400
H	-3.14989300	3.65048200	1.42247400
H	-4.02500500	2.14076400	1.71545400
H	-2.86543200	2.75142000	2.91546800
C	-1.31984100	3.75725400	-1.06755800
H	-1.25857400	4.24897100	-0.09107200
H	-0.35028700	3.30639400	-1.29250500
H	-1.53056100	4.53198200	-1.81149000
C	-1.94100500	1.84730800	1.18427400
H	-1.80953700	0.90362900	1.71510500
C	-2.42029300	2.69804400	-1.10553300
H	-3.38826700	3.15580200	-0.86178200
H	-4.68212400	-1.38022000	-0.55709900
H	-2.33464600	-2.70398800	1.20936500
H	-0.98795300	2.38681600	1.29061400
H	-2.51172300	2.30776500	-2.12407700
C	3.61379500	0.93517700	0.21806500
C	4.78456500	0.65216400	1.17925700
C	4.09282900	0.82644200	-1.23438300
C	3.13820500	2.37737600	0.49410800

H	4.47131800	0.72725500	2.22599700
H	5.23172600	-0.33228400	1.02748400
H	5.57095200	1.39818400	1.01126200
H	3.27534100	0.99854200	-1.93834200
H	4.86414500	1.58544000	-1.41800100
H	4.54303400	-0.14844200	-1.44305200
H	3.99267900	3.05839100	0.39848800
H	2.37165400	2.69313300	-0.21522100
H	2.74330000	2.48320700	1.51111700
C	0.80827900	0.39651300	-0.41895000
H	-3.92017500	-3.72079200	-0.04998000
O	-0.31439500	-0.26623800	-0.12302900
O	0.87264400	1.24511100	-1.28363900

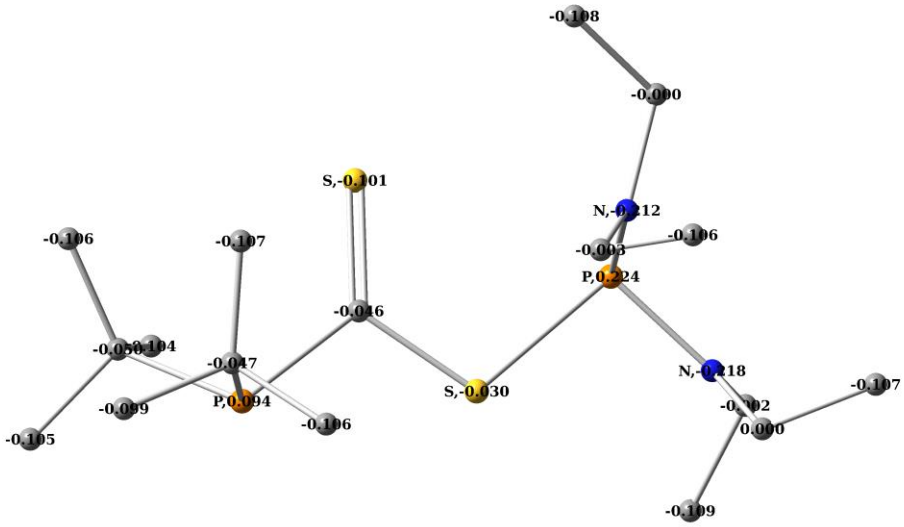


FIG. S76. OPTIMIZED STRUCTURE **3B**

P	2.12906300	0.53886300	0.82396800
P	-2.51341500	0.62560900	-0.68233000
N	2.27779500	-1.13684300	0.62538800
C	-2.72057900	-1.15553000	-1.35046200
C	-2.56015300	-2.29705400	-0.33920900
H	-1.54684100	-2.33915300	0.06748100
H	-3.25081100	-2.21553000	0.50169800
H	-2.75559200	-3.25072400	-0.84638000
C	-4.10452000	-1.25247000	-2.01404800
H	-4.91345600	-1.26047500	-1.27954600
H	-4.27947900	-0.43235500	-2.71848000
H	-4.16433500	-2.19270700	-2.57547200
C	1.72867800	-2.92842000	2.30945500
H	0.74466600	-2.48392100	2.47936300
H	2.08883800	-3.35343900	3.25118800
C	2.92299400	-2.90639500	-1.02874800
H	3.82115900	-2.36256400	-1.33479200
H	3.21387200	-3.64473500	-0.27571500
H	2.53792900	-3.45208300	-1.89561000
C	-1.65643500	-1.31988300	-2.45105500
H	-1.75044500	-0.55020300	-3.22321800
H	-0.64277400	-1.26866800	-2.04549400
H	-1.77827200	-2.30133900	-2.92610400
C	1.85173900	-1.95031800	-0.50957400
H	1.54361700	-1.28429400	-1.31628400
C	2.71523900	-1.87141600	1.81796200
H	2.87657100	-1.13600700	2.61257300
N	3.31076100	1.25565700	-0.15802900
C	5.20776700	0.12305200	-1.28296900
H	5.94060700	0.86813300	-0.95883300
H	5.18854400	-0.67699100	-0.53764500
H	5.54981100	-0.29058000	-2.23760400

C	3.06472700	3.73375200	-0.49519500
H	3.18104200	3.65399100	-1.58062600
H	1.99427900	3.73241100	-0.27002000
H	3.48337500	4.69621300	-0.18353900
C	3.81613400	0.73897700	-1.42510800
H	3.12197500	-0.00964700	-1.81278000
C	3.77340000	2.58792200	0.22899800
H	4.85474700	2.64655200	0.05041600
H	3.69248900	-2.33704900	1.62486100
H	0.95110100	-2.51951300	-0.23628300
H	3.83491800	1.54480200	-2.17036900
H	3.63045000	2.69563100	1.30970000
C	-3.93509200	1.06964200	0.50018200
C	-5.06984500	1.60291000	-0.39941500
C	-4.49012400	-0.02260500	1.42214400
C	-3.43737900	2.25555000	1.34980400
H	-4.72362800	2.41920000	-1.04129200
H	-5.50224700	0.82983300	-1.03839000
H	-5.87473100	1.99022700	0.23721500
H	-3.71026500	-0.44798200	2.05675200
H	-5.25776700	0.41627600	2.07259500
H	-4.96788300	-0.83060200	0.86045200
H	-4.29263400	2.70553200	1.86814000
H	-2.71297800	1.94354000	2.10417800
H	-2.97872400	3.03331600	0.72863100
C	-0.99891200	0.39393500	0.40712300
S	-0.93638000	-0.20151200	1.93903700
S	0.38845100	0.95835700	-0.48620200
H	1.61927200	-3.75330600	1.59847800

FIG. S77. OPTIMIZED STRUCTURE CO_2

C	0.00000000	0.00000000	0.00000000
O	0.00000000	0.00000000	1.16478300
O	0.00000000	0.00000000	-1.16478300

FIG. S78. OPTIMIZED STRUCTURE CS_2

C	0.00000000	0.00000000	0.00000000
S	0.00000000	0.00000000	1.55606900
S	0.00000000	0.00000000	-1.55606900

References

(1) Szynkiewicz, N.; Ponikiewski, Ł.; Grubba, R. Symmetrical and Unsymmetrical Diphosphanes with Diversified Alkyl, Aryl, and Amino Substituents. *Dalt. Trans.* **2018**, *47* (47), 16885–16894 DOI: 10.1039/C8DT03775B.

(2) Sheldrick, G. M. A Short History of SHELX. *Acta Crystallographica Section A: Foundations of Crystallography*. International Union of Crystallography 2008, pp 112–122.

(3) Farrugia, L. J. WinGX and ORTEP for Windows: An Update. *J. Appl. Crystallogr.* **2012**, *45* (4), 849–854 DOI: 10.1107/S0021889812029111.

(4) M. J. Frisch; G. W. Trucks; H. B. Schlegel; G. E. Scuseria; M. A. Robb; J. R. Cheeseman; G. Scalmani; V. Barone; G. A. Petersson; H. Nakatsuji; X. Li; M. Caricato; A. Marenich; J. Bloino; B. G. Janesko; R. Gomperts; B. Mennucci; H. P. Hratchian; J. V. Ortritz; Izmaylov, A. F.; J. L. Sonnenberg; D. Williams-Young, F. Ding, F. L.; F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throsse, J. B. F.; Fox, D. J. Gaussian 09. Gaussian, Inc.: Wallingford CT 2016.

(5) Chai, J.-D.; Head-Gordon, M. Long-Range Corrected Hybrid Density Functionals with Damped Atom–atom Dispersion Corrections. *Phys. Chem. Chem. Phys.* **2008**, *10* (44), 6615 DOI: 10.1039/b810189b.

(6) Grimme, S. Density Functional Theory with London Dispersion Corrections. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2011**, *1* (2), 211–228 DOI: 10.1002/wcms.30.

(7) Parr, R. G.; Yang, W. Density Functional Approach to the Frontier-Electron Theory of Chemical Reactivity. *J. Am. Chem. Soc.* **1984**, *106* (14), 4049–4050 DOI: 10.1021/ja00326a036.

(8) Morell, C.; Grand, A.; Toro-Labbé, A. New Dual Descriptor for Chemical Reactivity. *J. Phys. Chem. A* **2005**, *109* (1), 205–212 DOI: 10.1021/jp046577a.