

Supporting Information
For
Rhodium-Catalyzed P–P Bond Exchange Reaction of Diphosphines

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Supplimentary Materials

^1H -, ^{13}C - and ^{31}P -NMR spectra were recorded on a Varian Mercury (400 MHz) and tetramethylsilane were used as standard. The ^{31}P -NMR spectrum decoupled a proton. IR spectra were measured on a JASCO FT/IR-410 spectrophotomer. Melting points were determined with a Yanagimoto micro melting point apparatus without correction. High- and low-resolution mass spectra were measured on a JEOL JMS-DX-303, a JEOL JMS-700, or a JMS-T100GC spectrometer. X-ray diffraction data were recorded on Rigaku R-AXIS RAPID. Kanto Chemical. CO. INC. silica gel 60 (63-210 μm) was employed for flash column chromatography. $\text{RhH}(\text{dppe})_2$ ¹⁾, tetralkyldiphosphine disulfides **1g-1j**²⁾, 1,2-dialkyl-1,2-diphenyldiphosphine disulfides **1a-1d**³⁾, **1f**⁴⁾, **3**⁵⁾, and **5**⁶⁾ were synthesized by the literature methods.

Rhodium-catalyzed isomerization of (1*R**,2*R**)-1,2-diethyl-1,2-diphenyldiphosphine disulfide (1*R**,2*R**)-1a to (1*R**,2*S**)-1,2-diethyl-1,2-diphenyldiphosphine disulfide (1*R**,2*S**)-1a (Scheme 1)

In a two-necked flask equipped with a magnetic stirrer bar were placed $\text{RhH}(\text{dppe})_2$ (10.0 mol%, 22.5 mg), (1*R**,2*R**)-1,2-diethyl-1,2-diphenyldiphosphine disulfide (1*R**,2*R**)-**1a** (0.25 mmol, 84.5 mg) in THF (0.25 mL) under an argon atmosphere, and the solution was heated at reflux for 6 h. Then, the solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel using toluene giving mixture of (1*R**,2*R**)-**1a** and (1*R**,2*S**)-1,2-diethyl-1,2-diphenyldiphosphine disulfide (1*R**,2*S**)-**1a** [82.1 mg, 97%, (1*R**,2*R**)-**1a**:(1*R**,2*S**)-**1a** = 2:3, $R_f = 0.7$ (toluene)].

The starting material (1*R**,2*R**)-**1a** and (1*R**,2*S**)-**1a** were isolated by recrystallization according to literature.³⁾ A crystal of (1*R**,2*R**)-**1a** was obtained by recrystallization from ethanol, and that of (1*R**,2*S**)-**1a** from methanol. The structure of (1*R**,2*S**)-**1a** was determined by X-ray crystal structure analysis. X-Ray crystallography: CCDC 1486721 contains the supplementary

crystallographic data for this paper. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal data and structure refinement

Compound: (1*R**,2*S**)-1a

Formula: C₁₆H₂₀P₂S₂

Formula weight: 338.38

Wave length: 0.71075

Crystal system: monoclinic

Space group: P 21/c

Color of crystal: Colorless

Unit cell parameters: $a = 9.3474(7) \text{ \AA}$ $\alpha = 90.00^\circ$
 $b = 7.1672(4) \text{ \AA}$ $\beta = 101.490(2)^\circ$
 $c = 13.3103(8) \text{ \AA}$ $\gamma = 90.00^\circ$

Temperature of data collection: 173(K)

Values of Z, R, GOF: Z = 2

R(reflections) = 0.0391(1658), wR₂(reflections) = 0.1213(1989)

GOF = 1.268

Radiation type: Mo K α

Radiation source: sealed X-ray tube

Radiation monochromator: graphite

Measurement device type: Rigaku R-AXIS RAPID

Computing structure solution: SHELX

Computing structure refinement: SHELXL-97 (Sheldrick, 1997)

(1*R,2*R**)-1,2-diethyl-1,2-diphenyldiphosphine disulfide (1*R**,2*R**)-1a:** colorless solid. Mp.

92.0-92.6 °C (MeOH). Lit.³⁾ 85-87 °C. ¹H-NMR (400 MHz, CDCl₃) δ 1.26 (6H, dt, $J = 21.6, 7.6$

Hz), 2.54-2.66 (2H, m), 2.82-2.93 (2H, m), 7.21 (4H, bt, $J = 7.6$ Hz), 7.35 (2H, dt, $J = 7.6, 1.2$ Hz),

7.60-7.66 (4H, m). ¹³C-NMR (100 MHz, CDCl₃) δ 6.0, 22.4 (t, $J = 31.0$ Hz), 125.8 (dd, 38.0, 36.5

Hz), 127.8 (t, $J = 5.2$ Hz), 131.8, 131.9 (d, $J = 5.3$ Hz). ³¹P-NMR (162 MHz, CDCl₃) δ 45.6. IR

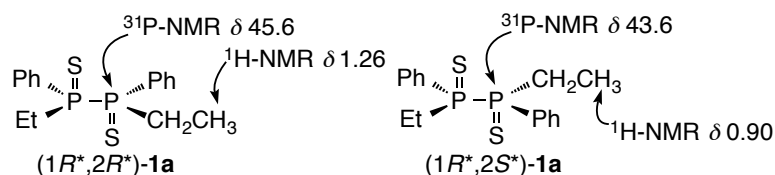
(KBr) 3053, 2969, 1435, 1100, 1027 cm⁻¹. MS (EI) m/z 338 (M⁺, 46%), 214 (M⁺-124, 100%).

HRMS Calcd for C₁₆H₂₀P₂S₂: 338.0482. Found: 338.0472.

(1*R,2*S**)-1,2-diethyl-1,2-diphenyldiphosphine disulfide (1*R**,2*S**)-1a:** Colorless solid. Mp.

152.8-153.2 °C (EtOH). Lit.³⁾ 156-157 °C. ¹H-NMR (400 MHz, CDCl₃) δ 0.90 (6H, dt, $J = 21.6, 7.6$

Hz), 1.93-2.06 (2H, m), 2.58-2.68 (2H, m), 7.55 (4H, bt, $J = 7.2$ Hz), 7.61 (2H, dt, $J = 7.2, 1.2$ Hz), 8.15-8.21 (4H, m). ^{13}C -NMR (100 MHz, CDCl_3) δ 5.0, 20.4 (t, $J = 30.5$ Hz), 126.0 (m), 128.3 (t, $J = 5.2$ Hz), 132.5, 133.4 (t, 5.2 Hz). $^{31}\text{P}\{^1\text{H}\}$ -NMR (162 MHz, CDCl_3) δ 43.7. IR (KBr) 2974, 2932, 1435, 1102, 1016 cm^{-1} . MS (EI) m/z 338 (M^+ , 39%), 214 (M^+-124 , 100%). HRMS Calcd for $\text{C}_{16}\text{H}_{20}\text{P}_2\text{S}_2$: 338.0482. Found: 338.0472.



Typical procedures for synthesis of the $(1R^*,2R^*)\text{-1-ethyl-2-methyl-1,2-diphenyldiphosphine disulfide [(1R^*,2R^*)\text{-2ab}]$ and $(1R^*,2S^*)\text{-1-ethyl-2-methyl-1,2-diphenyldiphosphine disulfide [(1R^*,2S^*)\text{-2ab}]$ [($1R^*,2R^*)\text{-2ab}:(1R^*,2S^*)\text{-2ab} = 2:1$ mixture]

In a two-necked flask equipped with a magnetic stirrer bar were placed $\text{RhH}(\text{dppe})_2$ (10.0 mol%, 22.5 mg), 1,2-dimethyl-1,2-diphenyldiphosphine disulfide **1b** [($1R^*,2R^*)\text{-1b}$, 0.75 mmol, 232.5 mg, $R_f = 0.4$ (toluene)], and 1,2-diethyl-1,2-diphenyldiphosphine disulfide **1a** [($1R^*,2R^*)\text{-1a}:(1R^*,2S^*)\text{-1a} = 1:2$, 0.25 mmol, 84.5 mg, $R_f = 0.7$ (toluene)] in THF (0.25 mL) under an argon atmosphere, and the solution was heated at reflux for 6 h. Then, the solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel using toluene:hexane = 3:1 giving $(1R^*,2R^*)\text{-1-ethyl-2-methyl-1,2-diphenyldiphosphine disulfide [(1R^*,2R^*)\text{-2ab}]$ and $(1R^*,2S^*)\text{-1-ethyl-2-methyl-1,2-diphenyldiphosphine disulfide [(1R^*,2S^*)\text{-2ab}]$ [93.9 mg, 58%, ($1R^*,2R^*)\text{-2ab}:(1R^*,2S^*)\text{-2ab} = 2:1$ mixture, $R_f = 0.6$ (toluene)].

The $(1R^*,2R^*)\text{-2ab}$ and $(1R^*,2S^*)\text{-2ab}$ were isolated by recrystallization. $(1R^*,2S^*)\text{-2ab}$ (23 mg) was isolated by recrystallization twice from hexane, and $(1R^*,2R^*)\text{-2ab}$ (43 mg) was isolated by recrystallization twice of the residue. The structure of $(1R^*,2S^*)\text{-2ab}$ was determined by X-ray crystal structure analysis (Figure S1). X-Ray crystallography: The methyl and ethyl groups on the phosphorous atom were refined with isotropic thermal parameters because of a disorder of these

groups in two positions with the occupancy factor 50% for each. The refinement of the structure of (1*R**,2*S**)-**2ab** was achieved only with the *R* value of 0.14, because the recrystallization of (1*R**,2*S**)-**2ab** with various solvents always gave thin scales. The analysis, however, was sufficient for assigning atom connectivity and the structural characteristics of (1*R**,2*S**)-**2ab**. CCDC 1498142 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal data and structure refinement

Compound: (1*R**,2*S**)-**2ab**

Formula: C₁₅ H₁₈ P₂ S₂

Formula weight: 324.35

Wave length: 0.71075

Crystal system: orthorhombic

Space group: P b c a

Color of crystal: Colorless

Unit cell parameters: a = 9.1542(14) Å α = 90.00 °
 b = 16.9650(15) Å β = 90.00 °
 c = 10.682(2) Å γ = 90.00 °

Temperature of data collection: 173(K)

Values of Z, R, GOF: Z = 4

 R(reflections)= 0.1403(967)

 wR₂(reflections)= 0.4216(1880)

 GOF = 1.310

Radiation type: Mo K/α

Radiation source: sealed X-ray tube

Radiation monochromator: graphite

Measurement device type: Rigaku R-AXIS RAPID

Computing structure solution: SHELX

Computing structure refinement: SHELXL-97 (Sheldrick, 1997)

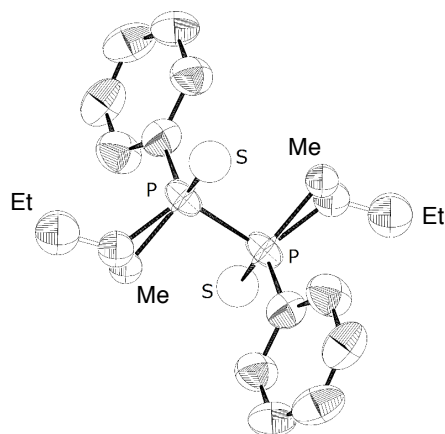
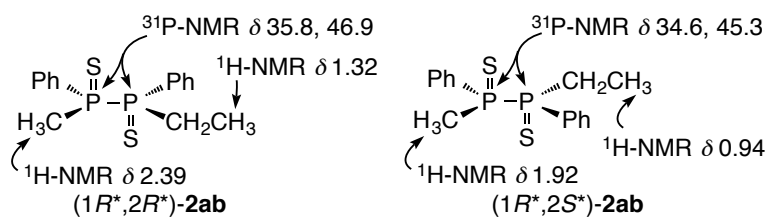


Figure S1. ORTEP view of (1*R**,2*S**)-**2ab**. The methyl and ethyl groups on the phosphorous atom were disordered in two positions (the occupancy factor 50% for each).

(1*R,2*R**)-1-ethyl-2-methyl-1,2-diphenyldiphosphine disulfide [(1*R**,2*R**)-**2ab**]:** Colorless solid. Mp. 95.0-96.0 °C (Hexane). ¹H-NMR (400 MHz, CDCl₃) δ 1.32 (3H, dt, *J* = 21.2, 7.6 Hz), 2.39 (6H, dd, *J* = 13.2, 6.8 Hz), 2.68-2.80 (4H, m), 7.20-7.25 (4H, m), 7.36-7.42 (2H, m), 7.58 (2H, ddd, *J* = 12.8, 8.0, 0.8 Hz), 7.63 (2H, ddd, *J* = 12.0, 8.0, 0.8 Hz). ¹³C-NMR (100 MHz, CDCl₃) δ 6.1 (dd, *J* = 4.5, 2.3 Hz), 17.6 (dd, *J* = 52.2, 13.4 Hz), 21.8 (dd, *J* = 48.5, 13.5 Hz), 125.5 (dd, *J* = 65.5, 9.7 Hz), 127.4 (dd, *J* = 68.5, 9.7 Hz), 127.8 (d, *J* = 12.7 Hz), 127.9 (d, *J* = 11.2 Hz), 131.7 (d, *J* = 9.6 Hz), 132.00 (d, *J* = 10.0 Hz), 132.01 (d, *J* = 8.9 Hz). ³¹P{¹H}-NMR (162 MHz, CDCl₃) δ 35.8 (d, *J* = 30.6 Hz), 46.9 (d, *J* = 29.0 Hz). IR (KBr) 3055, 2973, 1435, 1099 cm⁻¹. MS (EI) *m/z* 324 (M⁺, 47%), 169 (M⁺-155, 100%). HRMS Calcd for C₁₅H₁₈P₂S₂: 324.0325. Found: 324.0334.

(1*R,2*S**)-1-ethyl-2-methyl-1,2-diphenyldiphosphine disulfide [(1*R**,2*S**)-**2ab**]:** Colorless solid. Mp. 165.0-166.0 °C (Hexane). ¹H-NMR (400 MHz, CDCl₃) δ 0.94 (3H, dt, *J* = 21.2, 7.6 Hz), 1.92 (3H, dd, *J* = 12.8, 7.2 Hz), 1.99-2.12 (1H, m), 2.62-2.75 (1H, m), 7.53-7.59 (4H, m), 7.59-7.66 (2H, m), 8.12-8.20 (4H, m). ¹³C-NMR (100 MHz, CDCl₃) δ 5.2 (t, *J* = 3.8 Hz), 15.6 (dd, *J* = 52.1, 14.2 Hz), 19.8 (dd, *J* = 49.1, 13.4 Hz), 125.5 (dd, *J* = 63.3, 10.4 Hz), 127.5 (dd, *J* = 67.7, 10.4 Hz), 128.3 (d, *J* = 11.9 Hz), 128.4 (d, *J* = 11.9 Hz), 132.67, 132.68, 133.0 (d, *J* = 10.4 Hz), 133.3 (d, *J* = 9.0 Hz). ³¹P{¹H}-NMR (162 MHz, CDCl₃) δ 34.6 (d, *J* = 29.2 Hz), 45.3 (d, *J* = 29.2 Hz). IR (KBr) 3054,

2975, 1436, 1100 cm^{-1} . MS (EI) m/z 324 (M^+ , 48%), 169 (M^+-155 , 100%). HRMS Calcd for $C_{15}H_{18}P_2S_2$: 324.0325. Found: 324.0332.

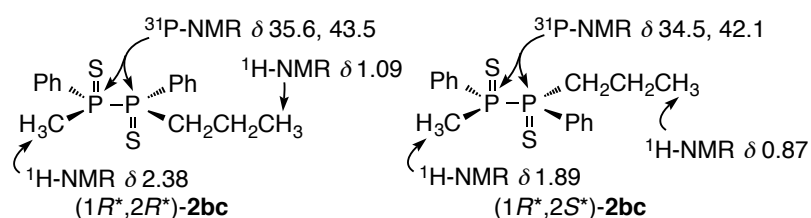


2bc, **2ac**, **2ad**, and **2cd** were used as a mixture of (1*R**,2*R**)- and (1*R**,2*S**)-isomers. The $^{31}\text{P-NMR}$ of (1*R**,2*R**)-**2ab** was observed downfield than (1*R**,2*S**)-**2ab**. The terminal methyl protons of (1*R**,2*R**)-**2ab** by $^1\text{H-NMR}$ was also observed downfield compared with (1*R**,2*S**)-**2ab**. Then, the stereo-structures of **2bc**, **2ac**, **2ad**, and **2cd** were determined by $^{31}\text{P-}$ and $^1\text{H-NMR}$ studies in analogy to **2ab**. In all cases, (1*R**,2*R**)-**2** was obtained as a main product compared with (1*R**,2*S**)-**2** under the condition.

(1*R,2*R**)-1-Methyl-2-propyl-1,2-diphenyldiphosphine disulfide [(1*R**,2*R**)-2bc]** and **(1*R**,2*S**)-1-methyl-2-propyl-1,2-diphenyldiphosphine disulfide [(1*R**,2*S**)-2bc]**

[(1*R,2*R**)-2bc:(1*R**,2*S**)-2bc = 3:2 mixture]:** Colorless oil. The data (a) are those of (1*R**,2*R**)-**2bc**, and the data (b) (1*R**,2*S**)-**2bc**. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 0.87 (3H, t, $J = 7.2$ Hz)^b, 1.09 (3H, t, 7.2Hz)^a, 1.23-1.35 (1H, m)^b, 1.35-1.48 (1H, m)^b, 1.56-1.70 (1H, m)^a, 1.79-1.83 (1H, m)^a, 1.89 (3H, dd, $J = 12.8, 6.8$ Hz)^b, 1.88-2.20 (1H, m)^b, 2.38 (3H, dd, $J = 12.8, 6.4$ Hz)^a, 2.59-2.76 (3H, m)^{a,b}, 7.18-7.24 (4H, m)^a, 7.34-7.40 (2H, m)^a, 7.54-7.66 (10H, m)^{a,b}, 8.12-8.21 (4H, m)^b. $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 15.0^b, 15.1 (d, $J = 15.3$ Hz)^b, 15.3 (d, $J = 17.2$ Hz)^a, 15.6 (dd, $J = 38.0, 7.5$ Hz)^b, 15.8^a, 17.4 (dd, $J = 52.1, 14.1$ Hz)^a, 27.9 (dd, $J = 47.3, 11.9$ Hz)^b, 29.9 (dd, $J = 46.9, 11.9$ Hz)^a, 125.8 (dd, $J = 64.8, 10.5$ Hz)^a, 126.1 (dd, $J = 62.6, 11.1$ Hz)^b, 127.2 (dd, $J = X, 9.7$ Hz)^b, 127.3 (dd, $J = 68.5, 9.6$ Hz)^a, 127.7 (d, $J = 7.4$ Hz)^a, 127.8 (d, $J = 7.4$ Hz)^a, 128.2 (d, $J = 12.0$ Hz)^b, 128.3 (d, $J = 9.6$ Hz)^b, 131.6 (dd, $J = 8.1, 1.5$ Hz)^a, 131.8 (dd, $J = 8.9, 1.4$ Hz)^a, 131.9^a, 132.0^a, 132.59^b, 132.60^b, 133.0 (d, $J = 9.7$ Hz)^b, 133.2 (d, $J = 8.9$ Hz)^b. $^{31}\text{P}\{^1\text{H}\}$ -NMR (162 MHz, CDCl_3) δ

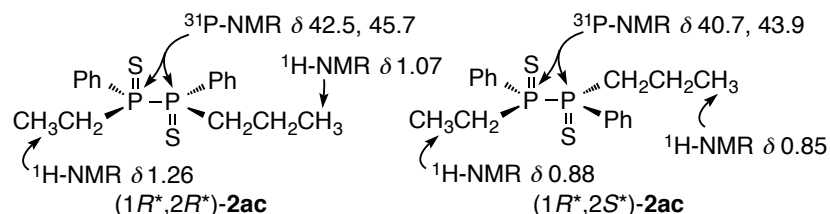
34.5 (d, $J = 30.6$ Hz)^b, 35.6 (d, $J = 29.2$ Hz)^a, 42.1 (d, $J = 30.6$ Hz)^b, 43.5 (d, $J = 29.2$ Hz)^a. IR (neat) 3054, 2962, 1436, 1097 cm^{-1} . MS (EI) m/z 338 (M^+ , 41%), 183 ($M^+ - 155$, 100%). HRMS Calcd for $C_{16}H_{20}P_2S_2$: 338.04816. Found: 338.0478. The aromatic carbon of ($1R^*$, $2S^*$)-**2bc** at δ 127.2 was not assigned precisely, because a part of the peak was overlapped aromatic carbon at δ 127.7 and 127.8 in ^{13}C -NMR. Rf values (toluene): ($1R^*$, $2R^*$)-**2bc** and ($1R^*$, $2S^*$)-**2bc** Rf = 0.6, **1b** Rf = 0.4, **1c** Rf = 0.7.



($1R^*$, $2R^*$)-1-Ethyl-2-propyl-1,2-diphenyldiphosphine disulfide [($1R^*$, $2R^*$)-2ac**] and ($1R^*$, $2S^*$)-1-ethyl-2-propyl-1,2-diphenyldiphosphine disulfide [($1R^*$, $2S^*$)-**2ac**]**

[($1R^*$, $2R^*$)-2ac**:($1R^*$, $2S^*$)-**2ac** = 2:1 mixture]:** Colorless oil. The data (a) are those of ($1R^*$, $2R^*$)-**2ac**, and the data (b) ($1R^*$, $2S^*$)-**2ac**. ^1H -NMR (400 MHz, CDCl_3) δ 0.85 (3H, t, $J = 7.6\text{Hz}$)^b, 0.88 (3H, dt, $J = 20.8, 7.6$ Hz)^b, 1.07 (3H, t, $J = 7.2$ Hz)^a, 1.26 (3H, dt, $J = 21.6, 7.6$ Hz)^a, 1.32-1.43 (1H, m)^b, 1.46-1.60 (1H, m)^a, 1.78-2.00 (3H, m)^{a,b}, 2.48-2.68 (4H, m)^{a,b}, 2.77-2.93 (2H, m)^a, 7.20 (4H, dt, $J = 7.2, 3.2$ Hz)^a, 7.34 (2H, bt, $J = 7.6$ Hz)^a, 7.52-7.58 (4H, m)^b, 7.58-7.67 (6H, m)^{a,b}, 8.14-8.22 (4H, m)^b. ^{13}C -NMR (100 MHz, CDCl_3) δ 5.0^b, 6.0^a, 14.8 (t, $J = 12.6$ Hz)^b, 15.0 (d, $J = 17.2$ Hz)^b, 15.2 (d, $J = 17.9$ Hz)^a, 15.8 (t, $J = 12.6$ Hz)^a, 20.3 (dd, $J = 48.4, 12.6$ Hz)^b, 22.3 (dd, $J = 49.5, 12.6$ Hz)^a, 28.5 (dd, $J = 46.9, 11.9$ Hz)^b, 30.7 (dd, $J = 46.9, 11.1$ Hz)^a, 125.7 (dd, $J = 49.1, 9.7$ Hz)^a, 125.9 (dd, $J = 49.0, 8.9$ Hz)^b, 126.2 (dd, $J = 64.1, 9.0$ Hz)^a, 126.5 (dd, $J = 57.0, 11.5$ Hz)^b, 127.8 (2C, d, $J = 11.9$ Hz)^a, 128.2 (2C, d, $J = 11.9$ Hz)^b, 131.6 (2C, d, $J = 1.5$ Hz)^a, 131.8 (2C, d, $J = 9.0$ Hz)^a, 132.5 (2C, s)^b, 133.3 (d, $J = 8.9$ Hz)^b, 133.4 (d, $J = 10.9$ Hz)^b. $^{31}\text{P}\{^1\text{H}\}$ -NMR (162 MHz, CDCl_3) δ 40.7 (d, $J = 38.2$ Hz)^b, 42.5 (d, $J = 36.6$ Hz)^a, 43.9 (d, $J = 38.2$ Hz)^b, 45.7 (d, $J = 38.2$ Hz)^a. IR (neat) 2931, 1463, 1436, 1097 cm^{-1} . MS (EI) m/z 352 (M^+ , 54%), 183 ($M^+ - 169$, 100%). HRMS

Calcd for $C_{17}H_{22}P_2S_2$: 352.0638. Found: 352.0642. The aromatic carbons of (1*R**,2*R**)-**2ac** at δ 127.8, 131.6, and 131.8 were overlapped in two phenyl groups. The aromatic carbon of (1*R**,2*S**)-**2ac** at δ 128.2 and 132.5 were also overlapped in two phenyl groups. Rf values (hexane:toluene = 1:1): (1*R**,2*R**)-**2ac** and (1*R**,2*S**)-**2ac** Rf = 0.57, **1a** Rf = 0.5, **1c** Rf = 0.65.

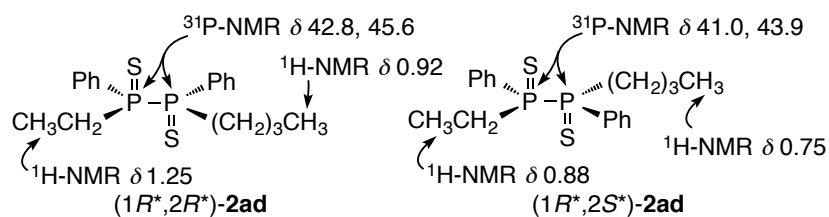


(1*R**,2*R**)-1-Butyl-2-ethyl-1,2-diphenyldiphosphine disulfide [(1*R**,2*R**)-**2ad**] and

(1*R**,2*S**)-1-butyl-2-ethyl-1,2-diphenyldiphosphine disulfide [(1*R**,2*S**)-**2ad**]

[(1*R**,2*R**)-**2ad**:(1*R**,2*S**)-**2ad** = 2:1 mixture]: Yellow oil. The data (a) are those of (1*R**,2*R**)-**2ad**, and the data (b) (1*R**,2*S**)-**2ad**. ¹H-NMR (400 MHz, CDCl₃) δ 0.75 (3H, t, J = 6.8 Hz)^b, 0.88 (3H, dt, J = 20.8, 7.6 Hz)^b, 0.92 (3H, t, J = 7.2 Hz)^a, 1.14-1.21 (2H, m)^a, 1.25 (3H, dt, J = 21.2, 7.2 Hz)^a, 1.45-1.50 (4H, m)^{a,b}, 1.72-1.84 (2H, m)^b, 1.92-2.02 (2H, m)^b, 2.52-2.66 (4H, m)^{a,b}, 2.80-2.93 (2H, m)^a, 7.17-7.23 (4H, m)^a, 7.34 (2H, bt, J = 7.6 Hz)^a, 7.54 (4H, dt, J = 7.6, 2.4 Hz)^b, 7.59-7.66 (6H, m)^{a,b}, 8.15-8.21 (4H, m)^b. ¹³C-NMR (100 MHz, CDCl₃) δ 5.0^b, 6.0^a, 13.4^b, 13.6^a, 20.2 (dd, J = 48.4, 12.6 Hz)^b, 22.2 (dd, J = 48.4, 12.7 Hz)^a, 23.0^b, 23.5 (d, J = 16.4 Hz)^b, 23.7 (d, J = 17.1 Hz)^a, 23.9^a, 26.3 (dd, J = 47.3, 17.6 Hz)^b, 28.4 (dd, J = 47.4, 11.6 Hz)^a, 125.6 (dd, J = 41.7, 8.9 Hz)^a, 125.9 (dd, J = 49.9, 10.5 Hz)^b, 126.3 (dd, J = 42.5, 8.9 Hz)^a, 126.5 (dd, J = 49.8, 10.5 Hz)^b, 127.8 (2C, d, J = 11.9 Hz)^a, 128.3 (2C, d, J = 11.1 Hz)^b, 131.7 (2C, d, J = 1.5 Hz)^a, 131.8 (d, J = 7.4 Hz)^a, 132.5 (2C, d, J = 1.5 Hz)^b, 133.2 (d, J = 11.2 Hz)^b, 133.3 (d, J = 8.9 Hz)^b. ³¹P{¹H}-NMR (162 MHz, CDCl₃) δ 41.0 (d, J = 38.2 Hz)^b, 42.8 (d, J = 38.2 Hz)^a, 43.9 (d, J = 38.2 Hz)^b, 45.6 (d, J = 38.2 Hz)^a. IR (neat) 2930, 1435, 1097 cm⁻¹. MS (EI) m/z 366 (M⁺, 81%), 197 (M⁺-169, 100%). HRMS Calcd for $C_{18}H_{24}P_2S_2$: 366.0795. Found: 366.0786. The aromatic carbons of (1*R**,2*R**)-**2ad** at δ 127.8, 131.7, and 131.8 were overlapped in two phenyl groups. The aromatic carbon of (1*R**,2*S**)-**2ad** at δ

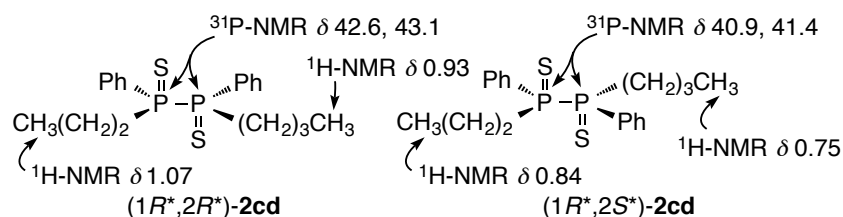
128.3 and 132.5 were also overlapped in two phenyl groups. Rf values (hexane:toluene = 1:1): **(1R*,2R*)-2ad** and **(1R*,2S*)-2ad** Rf = 0.6, **1a** Rf = 0.5, **1d** Rf = 0.7.



(1R*,2R*)-1-Butyl-2-propyl-1,2-diphenyldiphosphine disulfide [(1R*,2R*)-2cd] and **(1R*,2S*)-1-butyl-2-propyl-1,2-diphenyldiphosphine disulfide [(1R*,2S*)-2cd]**

[(1R*,2R*)-2cd:(1R*,2S*)-2cd = 2:1 mixture]: Colorless oil. The data (a) are those of **(1R*,2R*)-2cd**, and the data (b) **(1R*,2S*)-2cd**. ¹H-NMR (400 MHz, CDCl₃) δ 0.75 (3H, t, *J* = 7.2 Hz)^b, 0.84 (3H, dt, *J* = 7.2, 1.2 Hz)^b, 0.93 (3H, t, *J* = 7.2 Hz)^a, 1.07 (3H, dt, *J* = 7.2, 1.2 Hz)^a, 1.16-1.32 (4H, m)^{a,b}, 1.41-1.60 (6H, m)^{a,b}, 1.73-1.92 (4H, m)^{a,b}, 2.47-2.64 (4H, m)^{a,b}, 2.77-2.93 (2H, m)^a, 7.19 (4H, dt, *J* = 7.6, 2.8 Hz)^a, 7.34 (2H, bt, *J* = 7.6 Hz)^a, 7.55 (4H, bt, *J* = 8.0 Hz)^b, 7.58-7.66 (6H, m)^{a,b}, 8.19 (4H, bt, *J* = 8.0 Hz)^b. ¹³C-NMR (100 MHz, CDCl₃) δ 13.5^b, 13.6^a, 14.8 (bs)^b, 15.0 (dd, *J* = 14.8, 3.1 Hz)^b, 15.3 (bd, *J* = 17.1 Hz)^a, 15.8 (bs)^a, 23.0 (bs)^b, 23.5 (dd, *J* = 14.9, 1.1 Hz)^b, 23.8 (dd, *J* = 15.7, 2.2 Hz)^a, 23.9 (bs)^a, 26.2 (dd, *J* = 43.2, 15.6 Hz)^b, 28.3 (dd, *J* = 44.7, 14.9 Hz)^a, 28.5 (dd, *J* = 43.2, 13.4 Hz)^b, 30.5 (dd, *J* = 47.5, 14.2 Hz)^a, 126.1 (dd, *J* = 57.0, 9.0 Hz)^a, 126.2 (dd, *J* = 59.0, 7.5 Hz)^a, 126.3 (dd, *J* = 58.0, 9.0 Hz)^b, 126.5 (dd, *J* = 59.0, 3.0 Hz)^b, 127.8 (2C, d, *J* = 11.2 Hz)^a, 128.3 (2C, d, *J* = 10.4 Hz)^b, 131.7 (2C, d, *J* = 9.0 Hz)^a, 131.8 (2C, d, *J* = 1.5 Hz)^a, 132.5 (2C)^b, 133.3 (2C, d, *J* = 7.5 Hz)^b. ³¹P{¹H}-NMR (162 MHz, CDCl₃) δ 40.9 (d, *J* = 38.2 Hz)^b, 41.3 (d, *J* = 38.2 Hz)^b, 42.5 (d, *J* = 38.2 Hz)^a, 43.1 (d, *J* = 38.2 Hz)^a. IR (neat) 2929, 1436, 1096 cm⁻¹. MS (EI) *m/z* 380 (M⁺, 61%), 197 (M⁺-183, 100%). HRMS Calcd for C₁₉H₂₈P₂S₂: 380.0951. Found: 380.0956. The aromatic carbons of **(1R*,2R*)-2cd** at δ 127.8, 131.7, and 131.8 were overlapped in two phenyl groups. The aromatic carbon of **(1R*,2S*)-2cd** at δ 128.3, 132.5, and 133.3 were also overlapped in two phenyl groups. Rf values (hexane:toluene = 2:1): **(1R*,2R*)-2cd** and **(1R*,2S*)-2cd** Rf = 0.3,

1c Rf = 0.2, **1d** Rf = 0.4.



1-Butyl-2,2-dimethyl-1-phenyldiphosphine disulfide (2de): Pale brown oil. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 0.93 (3H, t, $J = 7.2$ Hz), 1.40-1.54 (3H, m), 1.50 (3H, dd, $J = 12.6, 7.2$ Hz), 1.69-1.81 (1H, m), 2.08 (3H, dd, $J = 12.4, 6.8$ Hz), 2.44-2.54 (1H, m), 2.67-2.78 (1H, m), 7.55 (2H, bdt, $J = 7.2, 3.6$ Hz), 7.62 (1H, bt, $J = 7.2$ Hz), 8.14 (2H, dd, $J = 12.4, 8.0$ Hz). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 13.6, 16.6 (dd, $J = 47.7, 11.9$ Hz), 18.6 (dd, $J = 48.4, 11.1$ Hz), 23.6 (t, $J = 2.3$ Hz), 23.7 (d, $J = 17.2$ Hz), 27.3 (dd, $J = 48.4, 12.6$ Hz), 125.7 (dd, $J = 64.1, 10.4$ Hz), 128.6 (d, $J = 12.0$ Hz), 132.5 (d, $J = 10.4$ Hz), 132.7 (t, $J = 1.5$ Hz). $^{31}\text{P}\{^1\text{H}\}$ -NMR (162 MHz, CDCl_3) δ 37.1 (d, $J = 27.5$ Hz), 40.1 (d, $J = 27.5$ Hz). IR (KBr) 2957, 2928, 1436, 1096 cm^{-1} . MS (EI) m/z 290 (M^+ , 74%), 197 ($\text{M}^+ - 93$, 100%). HRMS Calcd for $\text{C}_{12}\text{H}_{20}\text{P}_2\text{S}_2$: 290.0482. Found: 290.0480. Rf values (hexane:ethyl acetate = 4:1): **2de** Rf = 0.63, **1d** Rf = 0.80, **1e** Rf = 0.57, **2ad** Rf = 0.73.

1,1-Diethyl-2,2-diphenyldiphosphine disulfide (2af)⁷: Colorless solid. Mp. 117.1-118.0 $^\circ\text{C}$ (MeOH). $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 1.02 (6H, dt, $J = 20.0, 7.6$ Hz), 2.15-2.26 (4H, m), 7.49-7.59 (6H, m), 8.43 (4H, ddd, $J = 13.2, 8.0, 0.8$ Hz). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 6.2, 21.7 (dd, $J = 12.0, 44.0$ Hz), 128.5 (d, $J = 12.6$ Hz), 128.9 (dd, $J = 68.5, 11.1$ Hz), 132.3 (d, $J = 3.0$ Hz), 132.9 (d, $J = 9.7$ Hz). $^{31}\text{P}\{^1\text{H}\}$ -NMR (162 MHz, CDCl_3) δ 27.0 (d, $J = 41.2$ Hz), 56.8 (d, $J = 41.3$ Hz). IR (KBr) 3052, 1435, 1092 cm^{-1} . MS (EI) m/z 338 (M^+ , 46%), 217 ($\text{M}^+ - \text{C}_2\text{H}_5\text{PS}$, 100%). HRMS Calcd for $\text{C}_{16}\text{H}_{20}\text{P}_2\text{S}_2$: 338.0482. Found: 338.0492. Rf values (toluene): **2af** Rf = 0.6, **1a** Rf = 0.4, **1f** Rf = 0.8.

1,1-Diethyl-2,2-dimethyldiphosphine disulfide (2gh): Colorless solid. Mp. 100.5-101.0 °C (Hexane). ¹H-NMR (400 MHz, CDCl₃) δ 1.31 (6H, dt, *J* = 20.0, 7.6 Hz), 1.95 (6H, dd, *J* = 12.8, 6.4 Hz), 2.15-2.32 (4H, m). ¹³C-NMR (100 MHz, CDCl₃) δ 6.5 (d, *J* = 2.9 Hz), 18.1 (dd, *J* = 47.6, 10.4 Hz), 20.4 (dd, *J* = 44.0, 11.1 Hz). ³¹P{¹H}-NMR (162 MHz, CDCl₃) δ 34.4 (d, *J* = 38.2 Hz), 51.9 (d, *J* = 38.2 Hz). IR (KBr) 2982, 1397, 1281, 1041, 946 cm⁻¹. MS (EI) *m/z* 214 (M⁺, 76%), 93 (M⁺-121, 100%). HRMS Calcd for C₆H₁₆P₂S₂: 214.0169. Found: 214.0192. Rf values (hexane:ethyl acetate = 4:1): **2gh** Rf = 0.5, **1g** Rf = 0.3, **1h** Rf = 0.6.

1,1-Dimethyl-2,2-dipropyldiphosphine disulfide (2gi): Colorless solid. Mp. 65.0-66.0 °C (Hexane). ¹H-NMR (400 MHz, CDCl₃) δ 1.10 (6H, dt, *J* = 7.6, 1.6 Hz), 1.74 (4H, dseptet, *J* = 7.6, 1.2 Hz), 1.95 (6H, dd, *J* = 12.6, 6.4 Hz), 2.08-2.26 (4H, m). ¹³C-NMR (100 MHz, CDCl₃) δ 15.5 (d, *J* = 16.4 Hz), 16.2, 17.8 (dd, *J* = 47.7, 10.4 Hz), 29.3 (dd, *J* = 42.1, 10.4 Hz). ³¹P{¹H}-NMR (162 MHz, CDCl₃) δ 34.7 (d, *J* = 38.2 Hz), 47.0 (d, *J* = 36.7 Hz). IR (KBr) 2962, 1405, 1278, 1079 cm⁻¹. MS (EI) *m/z* 242 (M⁺, 100%), 149 (M⁺-93, 97%). HRMS Calcd for C₈H₂₀P₂S₂: 242.0482. Found: 242.0512. Rf values (hexane:ethyl acetate = 4:1): **2gi** Rf = 0.5, **1g** Rf = 0.3, **1i** Rf = 0.8.

1,1-Dimethyl-2,2-dibutyldiphosphine disulfide (2gj): Colorless solid. Mp. 66.5-67.5 °C (Hexane). ¹H-NMR (400 MHz, CDCl₃) δ 0.97 (6H, t, *J* = 7.2 Hz), 1.48 (4H, sextet, *J* = 7.2 Hz), 1.63-1.73 (4H, m), 1.96 (6H, dd, *J* = 12.8, 6.4 Hz), 2.13-2.23 (4H, m). ¹³C-NMR (100 MHz, CDCl₃) δ 13.6, 17.9 (dd, *J* = 47.7, 10.5 Hz), 24.0 (d, *J* = 15.7 Hz), 24.3 (dd, *J* = 3.7, 1.5 Hz), 27.1 (dd, *J* = 42.4, 10.4 Hz). ³¹P{¹H}-NMR (162 MHz, CDCl₃) δ 34.3 (d, *J* = 38.2 Hz), 47.4 (d, *J* = 38.2 Hz). IR (KBr) 2953, 2870, 1464, 1406, 952 cm⁻¹. MS (EI) *m/z* 270 (M⁺, 87%), 177 (M⁺-93, 100%). HRMS Calcd for C₁₀H₂₄P₂S₂: 270.0795. Found: 270.0759. Rf values (toluene): **2gj** Rf = 0.5, **1g** Rf = 0.2, **1j** Rf = 0.8.

1,1-Diethyl-2,2-dipropyldiphosphine disulfide (2hi): Colorless solid. Mp. 43.1-44.1 °C (Hexane). ¹H-NMR (400 MHz, CDCl₃) δ 1.08 (6H, dt, *J* = 7.2, 1.2 Hz), 1.29 (6H, dt, 12.0, 7.6 Hz), 1.66-1.81

(4H, m), 2.06-2.30 (8H, m). ^{13}C -NMR (100 MHz, CDCl_3) δ 6.5 (dd, $J = 3.8, 1.4$ Hz), 15.5 (d, $J = 17.1$ Hz), 16.2 (dd, $J = 3.7, 1.5$ Hz), 21.2 (dd, $J = 41.6, 9.7$ Hz), 30.4 (dd, $J = 41.0, 9.0$ Hz). $^{31}\text{P}\{^1\text{H}\}$ -NMR (162 MHz, CDCl_3) δ 46.1 (d, $J = 53.5$ Hz), 51.0 (d, $J = 51.8$ Hz). IR (KBr) 2961, 2933, 2872, 1456, 1080, 1028 cm^{-1} . MS (EI) m/z 270 (M^+ , 100%), 241 ($\text{M}^+ - 29$, 80%). HRMS Calcd for $\text{C}_{10}\text{H}_{24}\text{P}_2\text{S}_2$: 270.0795. Found: 270.0798. Rf values (hexane:ethyl acetate = 4:1): **2hi** Rf = 0.8, **1h** Rf = 0.7, **1i** Rf = 0.9.

1,1-Dibutyl-2,2-dipropyldiphosphine disulfide (2ij): Colorless oil. ^1H -NMR (400 MHz, CDCl_3) δ 0.94 (3H, t, $J = 7.2$ Hz), 1.06 (3H, dt, $J = 7.2, 1.2$ Hz), 1.44 (2H, sextet, $J = 7.2$ Hz), 1.59-1.76 (4H, m), 2.15-2.21 (4H, m). ^{13}C -NMR (100 MHz, CDCl_3) δ 13.6, 15.6 (d, $J = 14.9$ Hz), 16.3 (d, $J = 15.2$ Hz), 24.1 (d, $J = 14.1$ Hz), 24.5 (dd, $J = 3.7, 1.5$ Hz), 27.9 (dd, $J = 39.4, 10.4$ Hz), 30.3 (dd, $J = 39.5, 10.5$ Hz). $^{31}\text{P}\{^1\text{H}\}$ -NMR (162 MHz, CDCl_3) δ 46.0 (d, $J = 52.0$ Hz), 46.8 (d, $J = 53.6$ Hz). IR (neat) 2957, 2930, 2871, 1464, 1089, 902 cm^{-1} . MS (EI) m/z 326 (M^+ , 100%). HRMS Calcd for $\text{C}_{14}\text{H}_{32}\text{P}_2\text{S}_2$: 326.1421. Found: 326.1423. Rf values (toluene): **2ij** Rf = 0.75, **1i** Rf = 0.7, **1j** Rf = 0.8.

Tetraphenyldiphosphine-1-oxide-2-sulfide (4)⁸: Colorless solid. Mp. 96.8-98.0 $^\circ\text{C}$ (Hexane). ^1H -NMR (400 MHz, CDCl_3) δ 7.36-7.41 (8H, m), 7.46-7.52 (4H, m), 7.76 (4H, ddd, $J = 13.6, 6.8, 2.0$ Hz), 7.87 (4H, ddd, $J = 14.8, 7.2, 2.0$ Hz). ^{13}C -NMR (100 MHz, CDCl_3) δ 128.3, 128.5, 130.9 (dd, $J = 140.0, 1.5$ Hz), 131.3 (d, $J = 12.7$ Hz), 131.7 (d, $J = 11.9$ Hz), 132.2 (d, $J = 3.0$ Hz), 132.5 (d, $J = 3.0$ Hz), 133.8 (dd, $J = 108.7, 1.5$ Hz). $^{31}\text{P}\{^1\text{H}\}$ -NMR (162 MHz, CDCl_3) δ 28.9 (d, $J = 39.7$ Hz), 79.9 (d, $J = 41.3$ Hz). IR (KBr) 3056, 1437, 1130, 1110, 916 cm^{-1} . MS (EI) m/z 418 (M^+ , 12%), 201 ($\text{M}^+ - \text{C}_{12}\text{H}_{10}\text{PS}$, 100%). HRMS Calcd for $\text{C}_{24}\text{H}_{20}\text{OP}_2\text{S}$: 418.0710. Found: 418.0749. Rf values (hexane:ethyl acetate = 4:1): **4** Rf = 0.5, **1f** Rf = 0.6, **3** Rf = 0.02.

1,1-Dimethyl-2,2-diphenyldiphosphine-2-oxide-1-sulfide (6g): Colorless oil. ^1H -NMR (400 MHz, CDCl_3) δ 2.09 (6H, d, $J = 13.6$ Hz), 7.49 (4H, dt, $J = 7.6, 3.6$ Hz), 7.58 (2H, dt, $J = 7.6, 1.6$ Hz),

7.86 (4H, ddd, $J = 13.2, 6.8, 1.6$ Hz). ^{13}C -NMR (100 MHz, CDCl_3) δ 26.0 (d, $J = 70.0$ Hz), 128.7 (d, $J = 13.4$ Hz), 131.2 (d, $J = 138.5$ Hz), 131.4 (d, $J = 11.1$ Hz), 132.8 (d, $J = 3.0$ Hz). $^{31}\text{P}\{^1\text{H}\}$ -NMR (162 MHz, CDCl_3) δ 30.1 (d, $J = 38.2$ Hz), 93.4 (d, $J = 39.8$ Hz). IR (neat) 2914, 1439, 1233, 1130, 953, 905 cm^{-1} . MS (EI) m/z 294 (M^+ , 10%), 93 ($\text{M}^+ - 201$, 100%). HRMS Calcd for $\text{C}_{14}\text{H}_{16}\text{OP}_2\text{S}$: 294.0397. Found: 294.0369. Rf values (hexane:ethyl acetate = 4:1): **6g** Rf = 0.1, **1g** Rf = 0.3, **3** Rf = 0.02.

1,1-Diethyl-2,2-diphenyldiphosphine-2-oxide-1-sulfide (6h): Colorless oil. ^1H -NMR (400 MHz, CDCl_3) δ 1.06 (6H, dt, $J = 19.6, 7.6$ Hz), 2.04-2.14 (4H, m), 7.51-7.56 (4H, m), 7.60 (2H, dt, $J = 8.0, 1.2$ Hz), 7.26 (4H, ddd, $J = 11.6, 7.2, 1.6$ Hz). ^{13}C -NMR (100 MHz, CDCl_3) δ 6.1 (d, $J = 5.2$ Hz), 21.7 (dd, $J = 41.0, 10.4$ Hz), 128.7 (d, $J = 11.9$ Hz), 129.7 (dd, $J = 85.6, 16.4$ Hz), 132.0 (d, $J = 8.2$ Hz), 132.7 (d, $J = 3.0$ Hz). $^{31}\text{P}\{^1\text{H}\}$ -NMR (162 MHz, CDCl_3) δ 19.1 (d, $J = 9.2$ Hz), 46.4 (d, $J = 7.6$ Hz). IR (neat) 3057, 2935, 1438, 1261, 1180, 1108, 1027, 803 cm^{-1} . MS (EI) m/z 322 (M^+ , 57%), 166 ($\text{M}^+ - 156$, 100%). HRMS Calcd for $\text{C}_{16}\text{H}_{20}\text{OP}_2\text{S}$: 322.0710. Found: 322.0712. Rf values (hexane:ethyl acetate = 4:1): **6h** Rf = 0.2, **1h** Rf = 0.6, **3** Rf = 0.02.

Addition Reaction of Diphosphine Disulfide to Aldehydes⁹⁾

In a two-necked flask equipped with a magnetic stirrer bar were placed $\text{RhH}(\text{dppe})_2$ (5 mol%, 11.3 mg), **2gh** (0.25 mmol, 53.5 mg), and 4-tolaldehyde **10** (0.25 mmol, 29.5 μL) in THF (1.0 mL) under an argon atmosphere, and the solution was heated at reflux for 1 h. Then, the solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel giving [1-(dimethylthiophosphinoyloxy)-4-methylbenzyl]diethylphosphine sulfide **11** (57.8 mg, 69%), [1-(dimethylthiophosphinoyloxy)-4-methylbenzyl]dimethylphosphine sulfide **13** (7.8 mg, 10%), and [1-(diethylthiophosphinoyloxy)-4-methylbenzyl]diethylphosphine sulfide **14** (7.9 mg, 9%). **11**: Colorless solid. Mp. 138.5-139.0 $^\circ\text{C}$ (Hexane). ^1H -NMR (400 MHz, CDCl_3) δ 1.16 (3H, dt, $J = 14.4, 7.6$ Hz), 1.20 (3H, dt, $J = 14.4, 7.6$ Hz), 1.48 (3H, d, $J = 13.2$ Hz), 1.76-1.86

(2H, m), 1.90-1.99 (2H, m), 1.96 (3H, d, $J = 13.2$ Hz), 2.35 (3H, s), 5.91 (1H, dd, $J = 14.8, 4.8$ Hz), 7.18 (2H, d, $J = 8.0$ Hz), 7.38 (2H, $J = 8.0$ Hz). ^{13}C -NMR (100 MHz, CDCl_3) δ 6.2 (d, $J = 4.5$ Hz), 6.6 (d, $J = 5.2$ Hz), 20.6, 21.0 (d, $J = 12.0$ Hz), 21.3 (d, $J = 17.9$ Hz), 23.9 (d, $J = 77.4$ Hz), 24.9 (d, $J = 66.3$ Hz), 74.4 (dd, $J = 61.8, 8.2$ Hz), 128.3 (d, $J = 4.5$ Hz), 129.1 (d, $J = 2.2$ Hz), 130.3, 139.3 (d, $J = 2.9$ Hz). $^{31}\text{P}\{^1\text{H}\}$ -NMR (162 MHz, CDCl_3) δ 59.7 (d, $J = 27.5$ Hz), 99.5 (d, $J = 25.9$ Hz). IR (KBr) 2907, 2883, 1411, 1003, 924 cm^{-1} . MS (EI) m/z 334 (M^+ , 17%), 213 ($\text{M}^+ - 121$, 100%). HRMS Calcd for $\text{C}_{14}\text{H}_{24}\text{O}_2\text{S}_2$: 334.0744. Found: 334.0762. The structure of **11** was determined by X-ray crystal structure analysis. X-Ray crystallography: CCDC 1483048 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal data and structure refinement

Compound: **11**

Formula: $\text{C}_{14}\text{H}_{24}\text{O}_2\text{S}_2$

Formula weight: 334.39

Wave length: 0.71075

Crystal system: orthorhombic

Space group: P 21 21 21

Color of crystal: Colorless

Unit cell parameters: $a = 6.4559(4)$ Å $\alpha = 90.00^\circ$
 $b = 12.3783(6)$ Å $\beta = 90.00^\circ$
 $c = 22.5131(13)$ Å $\gamma = 90.00^\circ$

Temperature of data collection: 173(K)

Values of Z, R, GOF: $Z = 4$,

$R(\text{reflections}) = 0.0606$ (2694), $wR2(\text{reflections}) = 0.1536$ (4104)

GOF = 1.061

Radiation type: Mo K α

Radiation source: sealed X-ray tube

Radiation monochromator: graphite

Measurement device type: Rigaku R-AXIS RAPID

Computing structure solution: SHELX

Computing structure refinement: SHELXL-97 (Sheldrick, 1997)

[1-(Dimethylthiophosphinoyloxy)-4-methylbenzyl]dimethylphosphine sulfide (13): Colorless solid. Mp. 194.0-195.0 °C (Hexane/AcOEt = 1/3). ¹H-NMR (400 MHz, CDCl₃) δ 1.53 (3H, d, *J* = 13.2 Hz), 1.70 (3H, d, *J* = 12.8 Hz), 1.72 (3H, d, *J* = 12.8 Hz), 1.98 (3H, d, *J* = 13.6 Hz), 2.35 (3H, s), 5.89 (1H, dd, *J* = 15.2, 4.8 Hz), 7.19 (2H, d, *J* = 8.0 Hz), 7.35 (2H, dd, *J* = 8.0, 1.6 Hz). ¹³C-NMR (100 MHz, CDCl₃) δ 17.4 (d, *J* = 53.6 Hz), 18.6 (d, *J* = 54.3 Hz), 21.3, 23.9 (d, *J* = 77.4 Hz), 24.8 (d, *J* = 66.2 Hz), 76.1 (dd, *J* = 65.6, 7.5 Hz), 127.9 (d, *J* = 4.5 Hz), 129.1 (d, *J* = 2.2 Hz), 130.1, 139.3 (d, *J* = 3.0 Hz). ³¹P{¹H}-NMR (162 MHz, CDCl₃) δ 43.8 (d, *J* = 25.9 Hz), 99.7 (d, *J* = 25.9 Hz). IR (KBr) 2980, 2904, 1514, 1413, 1289, 1011, 947, 913 cm⁻¹. MS (EI) *m/z* 306 (M⁺, 21%), 213 (M⁺-93, 100%). HRMS Calcd for C₁₂H₂₀OP₂S₂: 306.0431. Found: 306.0438.

[1-(Diethylthiophosphinoyloxy)-4-methylbenzyl]diethylphosphine sulfide (14): Colorless solid. Mp. 73.0-74.0 °C (Hexane). ¹H-NMR (400 MHz, CDCl₃) δ 0.86 (3H, dt, *J* = 20.8, 7.6 Hz), 1.16 (3H, dt, *J* = 18.8, 7.6 Hz), 1.19 (3H, dt, *J* = 18.8, 7.6 Hz), 1.28 (3H, dt, *J* = 20.4, 7.6 Hz), 1.44-1.56 (1H, m), 1.60-1.72 (1H, m), 1.78-1.84 (2H, m), 1.86-2.01 (2H, m), 2.35 (3H, s), 5.88 (1H, dd, *J* = 14.4, 4.4 Hz), 7.17 (2H, d, *J* = 8.0 Hz), 7.37 (2H, dd, *J* = 8.0, 1.6 Hz). ¹³C-NMR (100 MHz, CDCl₃) δ 6.1 (d, *J* = 4.5 Hz), 6.5 (d, *J* = 5.3 Hz), 6.5 (d, *J* = 5.3 Hz), 6.9 (d, *J* = 4.4 Hz), 20.6 (d, *J* = 54.4 Hz), 21.1 (d, *J* = 52.9 Hz), 21.2, 26.6 (d, *J* = 73.0 Hz), 27.8 (d, *J* = 63.3 Hz), 73.8 (dd, *J* = 61.1, 8.2 Hz), 128.1 (d, *J* = 3.5 Hz), 128.9 (d, *J* = 1.5 Hz), 130.5, 139.1 (d, *J* = 2.2 Hz). ³¹P{¹H}-NMR (162 MHz, CDCl₃) δ 60.1 (d, *J* = 22.8 Hz), 115.3 (d, *J* = 23.0 Hz). IR (KBr) 3022, 2974, 1454, 1048, 989 cm⁻¹. MS (EI) *m/z* 362 (M⁺, 21%), 241 (M⁺-121, 100%). HRMS Calcd for C₁₆H₂₈OP₂S₂: 362.1057. Found: 362.1074.

References

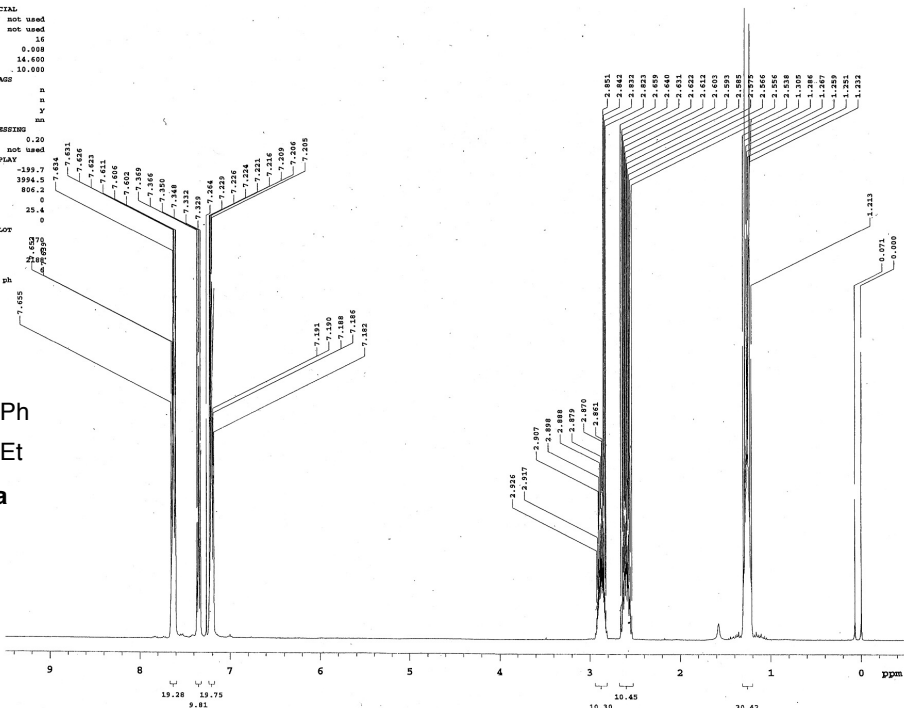
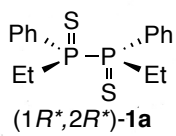
- 1) M. Arisawa, T. Ichikawa and M. Yamaguchi, *Chem. Commun.* 2015, **51**, 8821.
- 2) G. W. Parshall, *Org. Synth.*, V, 1973, 1016.
- 3) K. A. Pollart and H. J. Harwood, *J. Org. Chem.* 1962, **27**, 4444.

- 4) H. Klaus, K. Olaf, B. Ingo, S. Patrick, F. Sabine, D. Peter, M. Klemens, D. Hartmut, F. Christoph and J. Geert, *PCT Int. Appl.* 2011, WO 2011029901.
- 5) J. E. Nycz, *Phosphorus, sulfur, and silicon and the related elements*, 2012, **187**, 564-572.
- 6) C. Dorken, *Chem. Ber.* 1888, **21**, 1505.
- 7) F. Ekkehard, I. Kurt, *Chem. Ber.* 1965, **98**, 2674.
- 8) J. McKechnie, D. S. Payne and W. Sim, *J. Chem. Soc.* 1965, 3500.
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(1*R,2*R**)-1,2-diethyl-1,2-diphenyldiphosphine disulfide (1*R**,2*R**)-1a**

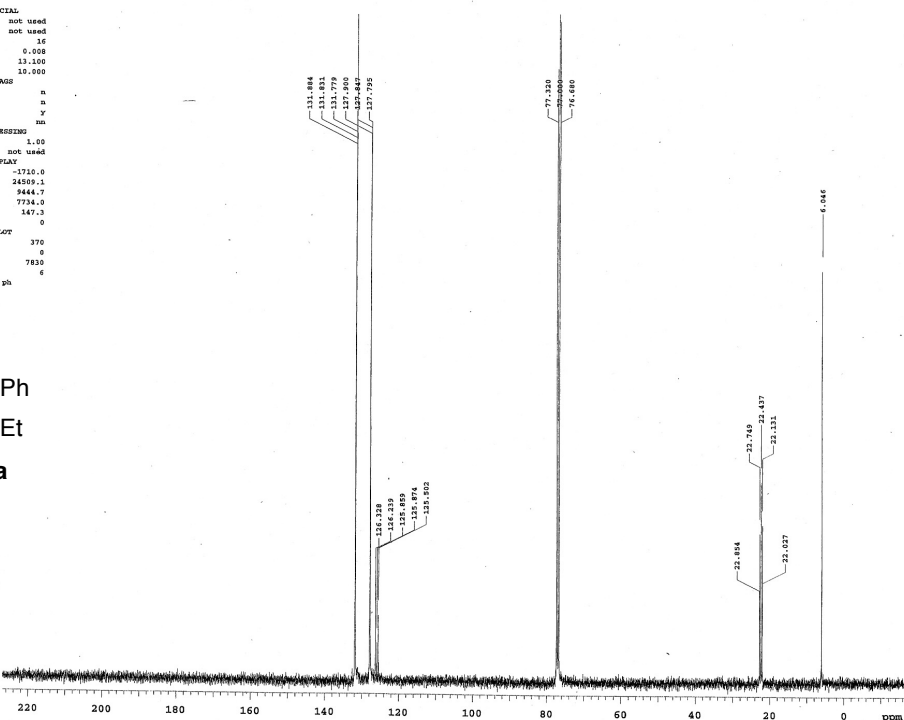
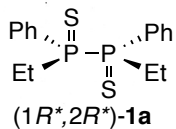
expt Proton

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solvent	cdcl3	gain	not used
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sv	6410.3	pw50	14.600
nt	2.500	alfa	10.000
sp	14812	PLANS	
fb	4090	il	n
ba	4	in	n
dl	1.500	op	y
nt	16	hs	mn
cc	16		
TRANSMITTER	lb	fn	not used
seq	399.453	sp	not used
tof	399.5	sp	-189.7
tpwr	88	wp	3994.5
pw	7.300	rl	606.2
DECOUPLER	cl3	rfd	0
da	0	ip	25.4
dof	0		
dm	mm	PLOT	
dm	c	wc	370
dpwr	41	sc	0
dnf	28412	va	0
	sh	sh	7830
	ai	oda	ph



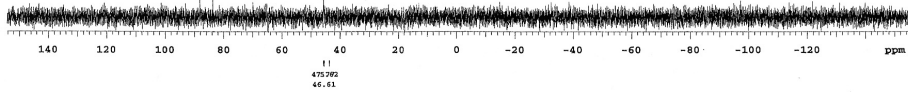
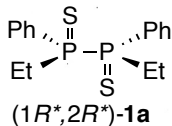
expt Carbon

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solvent	cdcl3	gain	not used
file	exp	spin	16
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nt	1.300	alfa	10.000
sp	63750	PLANS	
fb	17000	il	n
ba	4	in	n
dl	0.700	op	y
nt	10240	hs	mn
cc	1660		
TRANSMITTER	lb	fn	not used
seq	100.452	sp	not used
tof	1027.2	sp	-1710.0
tpwr	80	wp	24509.1
pw	6.550	rl	8484.7
DECOUPLER	cl3	rfd	7734.0
da	0	ip	147.3
dof	300.0		
dm	xyy	PLOT	
dm	w	wc	370
dpwr	41	sc	0
dnf	9592	va	0
	sh	sh	7830
	ai	oda	ph

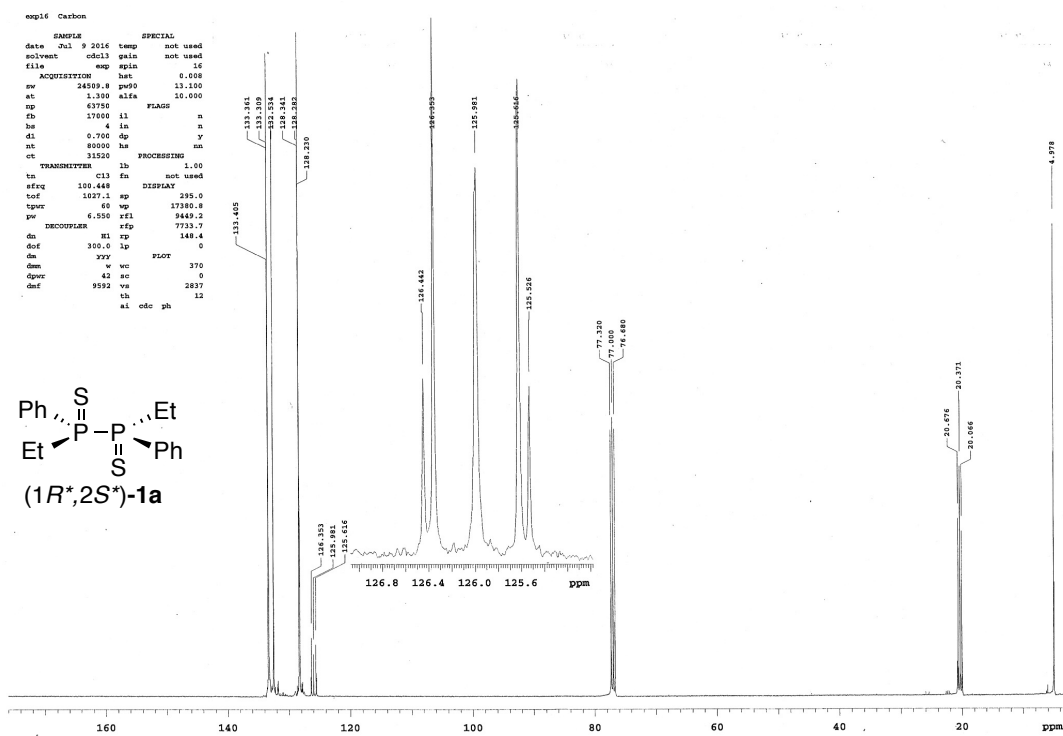
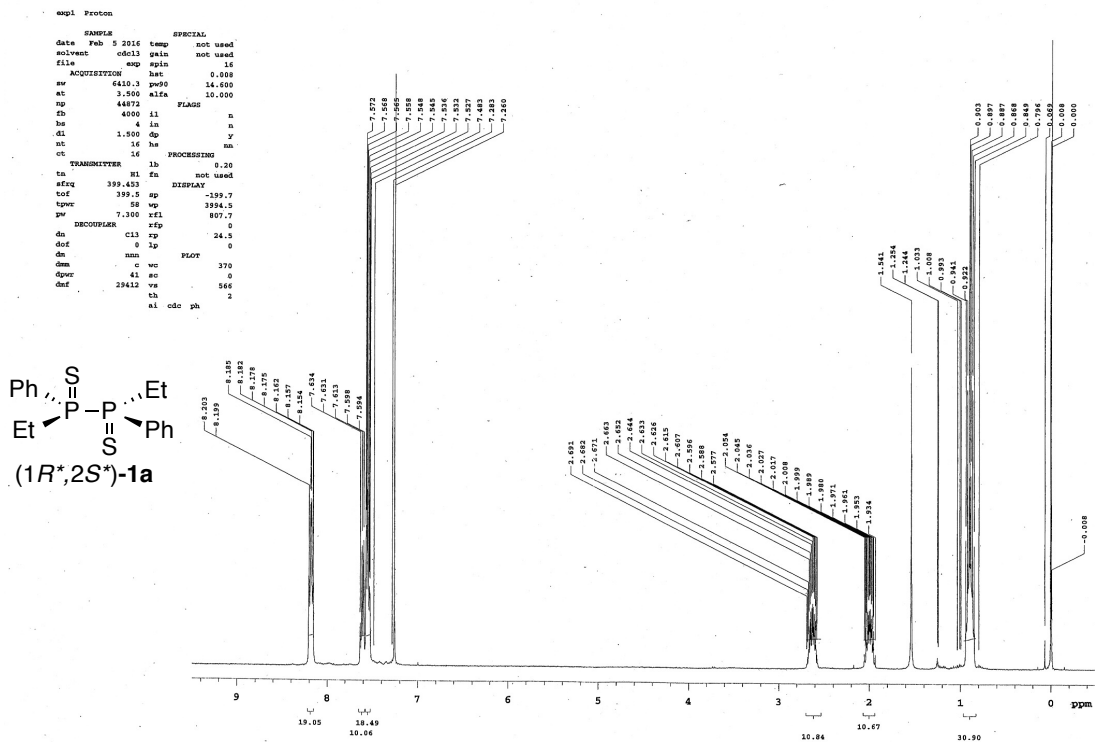


expt Phosphorus

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solvent cdcl3 gain not used
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ACQUISITION  exp  gain 0.008
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st 0.650 alic 10.000
mp 60000 FLAG 0
fb 15000 il n
bc 4 in n
dl 4.400 sp Y
nt 256 hs nm
ct 4 PROCESSING
TRANSMITTER lb 1.60 not used
ts 821 fn not used
sfreq 161.700 DISPLAY
tof 4232.1 sp -25060.8
tproc 80 sp 49390.5
pw 4.500 rfl 24092.1
DECOUPLEX m1 rfp -970.2
dm 0 ip 43.7
dof 0 ip 0
dm nny PLAT 370
dwm w wc 0
dprc 41 sc 0
dof 9332 vr 489
dof th 41
ai odo ph
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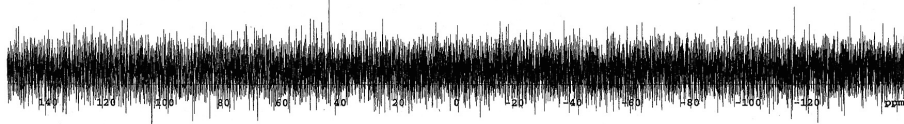
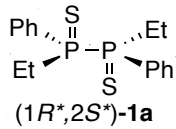


(1R*,2S*)-1,2-diethyl-1,2-diphenyldiphosphine disulfide (1R*,2S*)-1a



expt Phosphorus

```
SAMPLE          SPECIAL
date Feb 3 2016 temp not used
solvent c6d13 gain not used
file exp sp1a 15
ACQUISITION    hnt 0.008
sv 50000.0 pu50 9.000
at 0.600 a1fa 10.000
sp 60000 FLANG
fb 15000 il n
ds 4 in n
dl 4.460 sp y
nt 256 hs nn
oc 8
TRANSMITTER    lb 1.60
tn P31 fn not used
rfcq 161.700 DISPLAY
tof 4232.1 sp -23066.8
tprv 50 sp 49998.5
pw 4.500 rrl 24032.1
DECOUPLER     rfp -970.2
ds r1 rp 47.5
dof 0 lp 0
dm mny PLOT 370
dm w wc
dprv 41 ec 0
dof 9592 vs 2329
ch 68
al odo ph
```

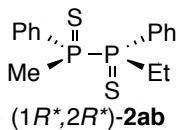
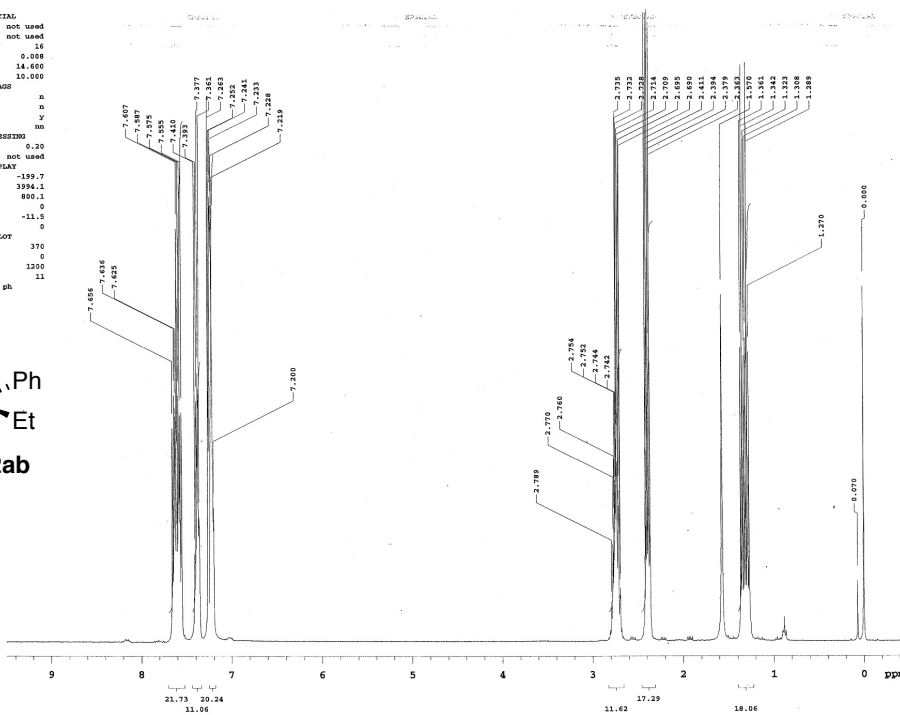


(1R*,2R*)-1-ethyl-2-methyl-1,2-diphenyldiphosphine disulfide [(1R*,2R*)-2ab]

expt1 Proton

```

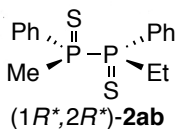
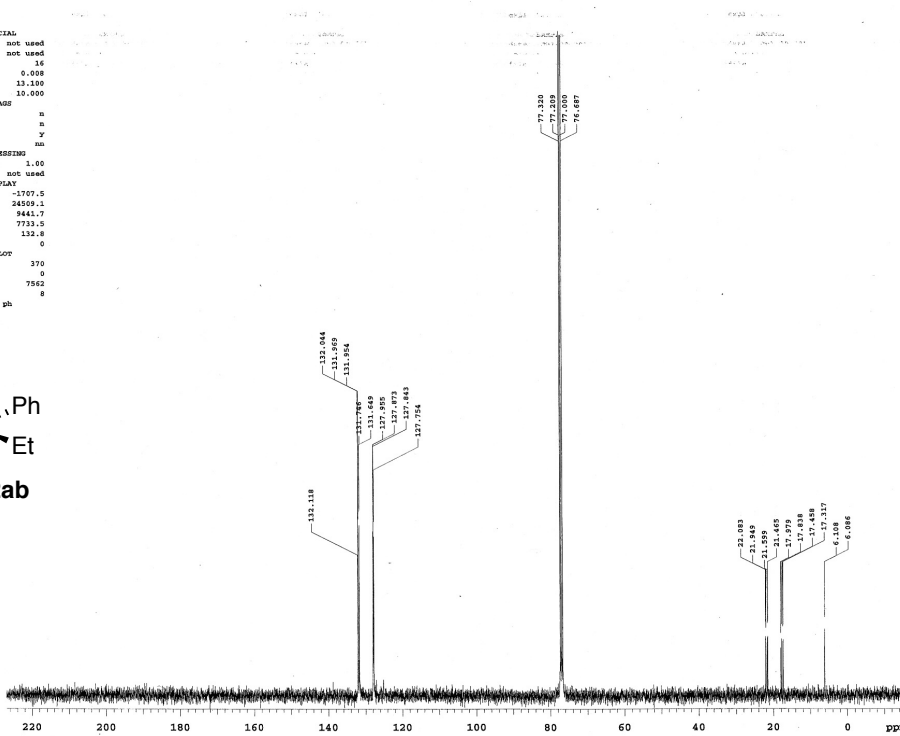
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solvent cdcl3 gain not used
file             exp spin 16
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at 3.500 aifa 10.000
sp 44872          FLAGS
fb 4600 il n
hs 4 in n
dl 1.500 sp y
nt 16 ha nm
ct          PROCESSED 0.20
TRANSMITTER lb fn not used
tn          not used
rfcq 399.446 DISPLAY 199.7
tof 399.4 sp 3994.1
tpwr 58 wp 3994.1
pw 7.100 rfi 800.1
DECOUPLER xfp 0
dn c13 xp -11.5
dof 0 ip 0
dm          woc PLOT 370
dpr 41 so 0
dnf 29412 ve 1200
          th ai cdc ph 11
    
```



expt1 Carbon

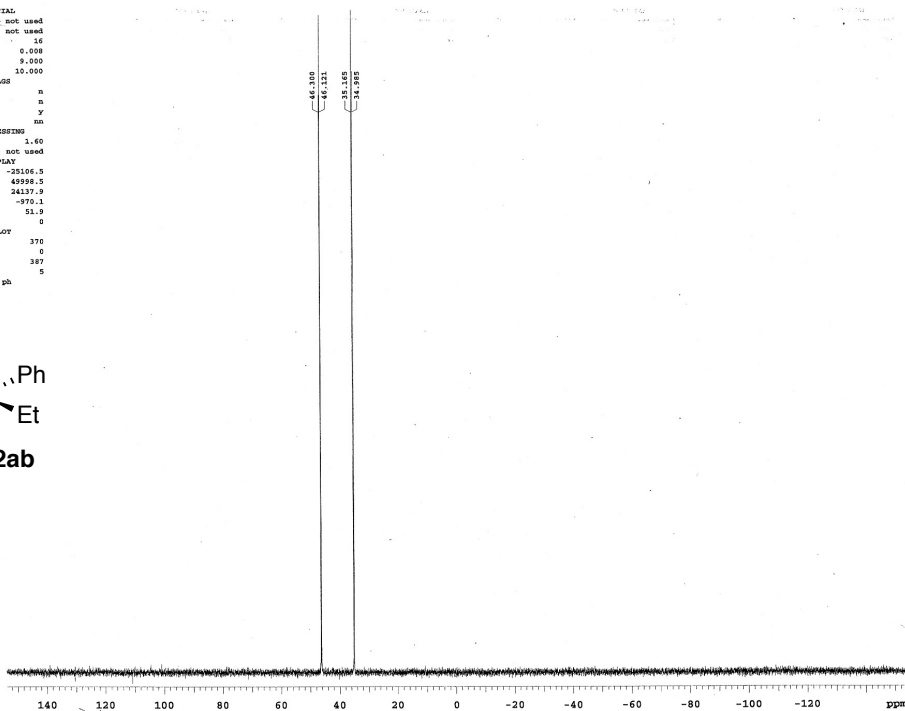
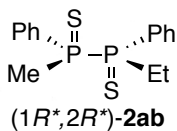
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SAMPLE          SPECIAL
date Jul 20 2016 temp not used
solvent cdcl3 gain not used
file             exp spin 16
ACQUISITION    hst 0.088
av 24509.8 pw90 13.100
at 1.100 aifa 10.000
sp 63750          FLAGS
fb 17000 il n
hs 16 in n
dl 0.700 sp y
nt 20000 hs nm
ct 1004          PROCESSED 1.00
TRANSMITTER lb fn not used
tn          not used
rfcq 100.446 DISPLAY 100.446
tof 1027.2 sp -1707.5
tpwr 60 wp 24509.1
pw 6.550 rfi 9441.7
DECOUPLER xfp 7733.5
dn c13 xp 132.8
dof 300.0 ip 0
dm          woc PLOT 370
dpr 42 so 0
dnf 9332 ve 7562
          th ai cdc ph 8
    
```



expl Phosphorus

```
NAME          SPECIAL
date  Jul 20 2016 temp      not used
solvent  cdcl3 gain      not used
file      exp  gain      16
ACQUISITION
av      50000.0 pw90      9.000
ac      0.400  afa      10.000
ap      60000          FLAGS
fb      15000  f1          n
hs      4       in          n
dl      4.400  dp          y
nt      16     hs          mm
ct      16     PROCESSING
TRANSMITTER
tn      931  fm      not used
afreq  161.690  DISPLAY
tof     4231.8  ap     -25106.5
tprc    58     wp     49298.5
pw      4.500  rfl    24137.9
DECOUPLER
dn      81  ap     -370.1
dof     0    lp     51.9
dm      0
dmw     w  wo     FLOW  370
dprc    42  ac     0
dwd     9592  wa     387
          th     5
          ai  odc  ph  5
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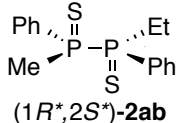
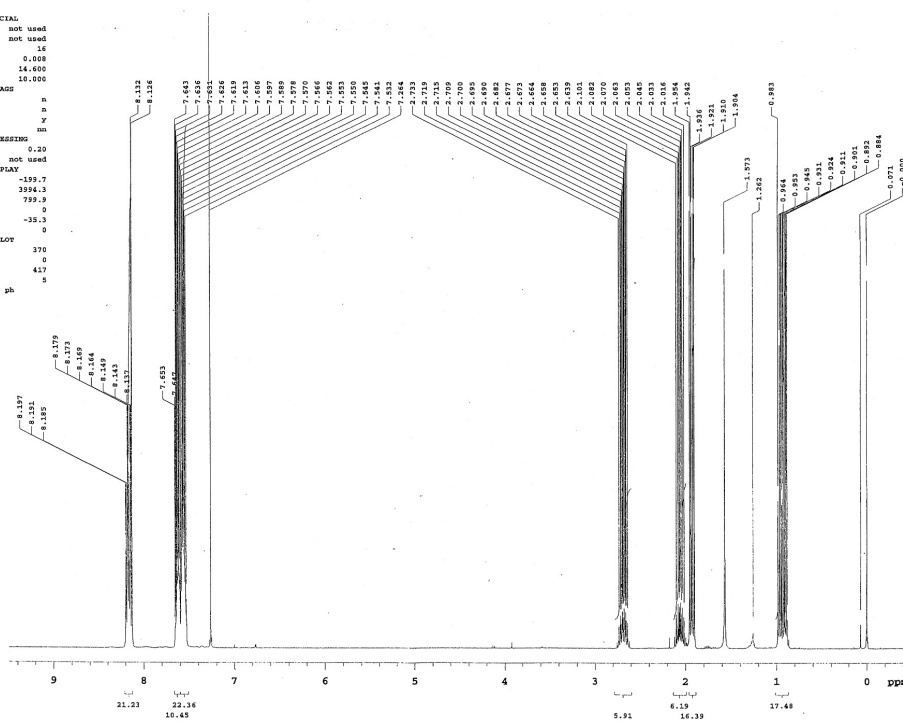


(1R*,2S*)-1-ethyl-2-methyl-1,2-diphenyldiphosphine disulfide [(1R*,2S*)-2ab]

expt Proton

```

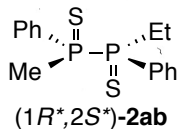
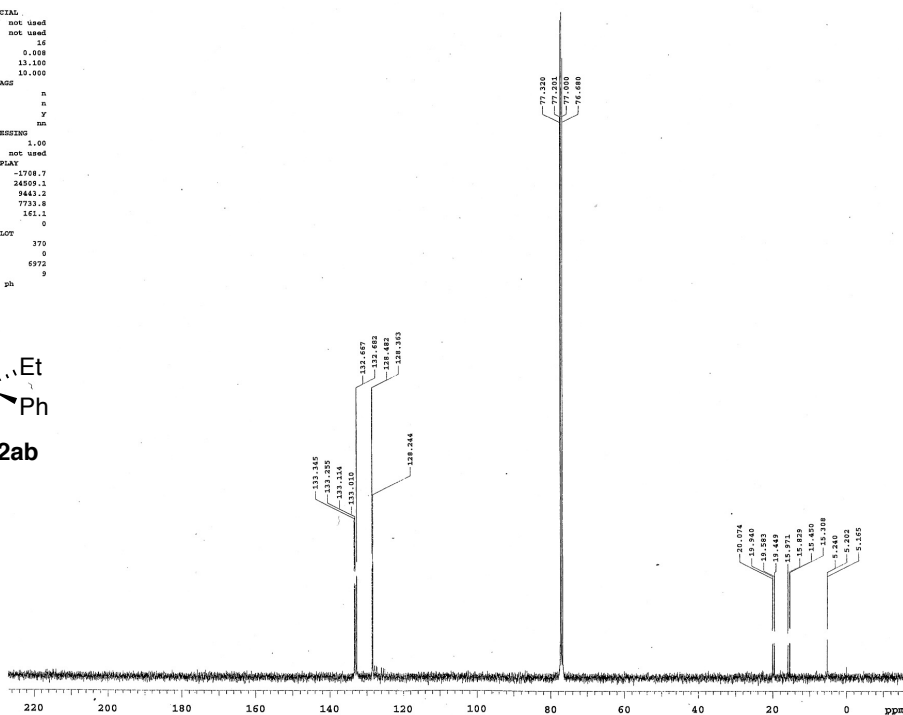
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solvent cdc13  prin      not used
file          exp spin    16
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sv            pw90       14.600
nt            a1a       10.000
sp            FLAG      1
ft            ll        n
bs            4 in       n
dl            1.550 dp    y
nt            16 hs      nm
ct            12
TRANSMITTER    lb        0.20
tn            ml        not used
rfreq 191.441  DISPLAY  -199.7
tof        399.5  sp      3994.3
tpwr       18  wp      399.9
pw         7.383  r11    398.9
DECOUPLER     rfp       0
ds          C13  rp      -35.3
dn          mn      0
dm          w  wo      370
dpr         41  sc      0
dnt        29412 vs     417
                   lb
                   ai odc ph  9
    
```



expt Carbon

```

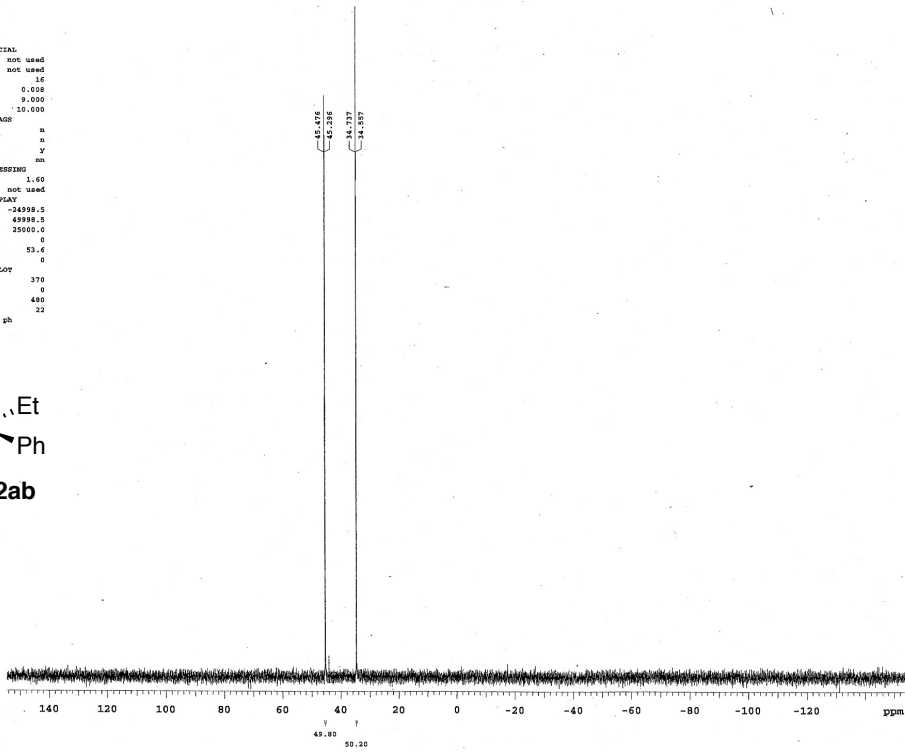
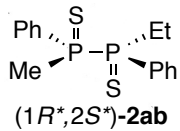
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solvent cdc13  prin      not used
file          exp spin    16
ACQUISITION    hat       0.008
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nt            a1a       10.000
sp            FLAG      1
ft            ll        n
bs            4 in       n
dl            0.750 dp    y
nt            10240 hs    nm
ct            1936
TRANSMITTER    lb        1.00
tn            ml        not used
rfreq 100.449  DISPLAY  -1708.7
tof        1027.2  sp      24509.1
tpwr       60  wp      9443.2
pw         6.550  r11    7733.8
DECOUPLER     rfp       0
ds          C13  rp      161.1
dn          mn      0
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                   lb
                   ai odc ph  9
    
```



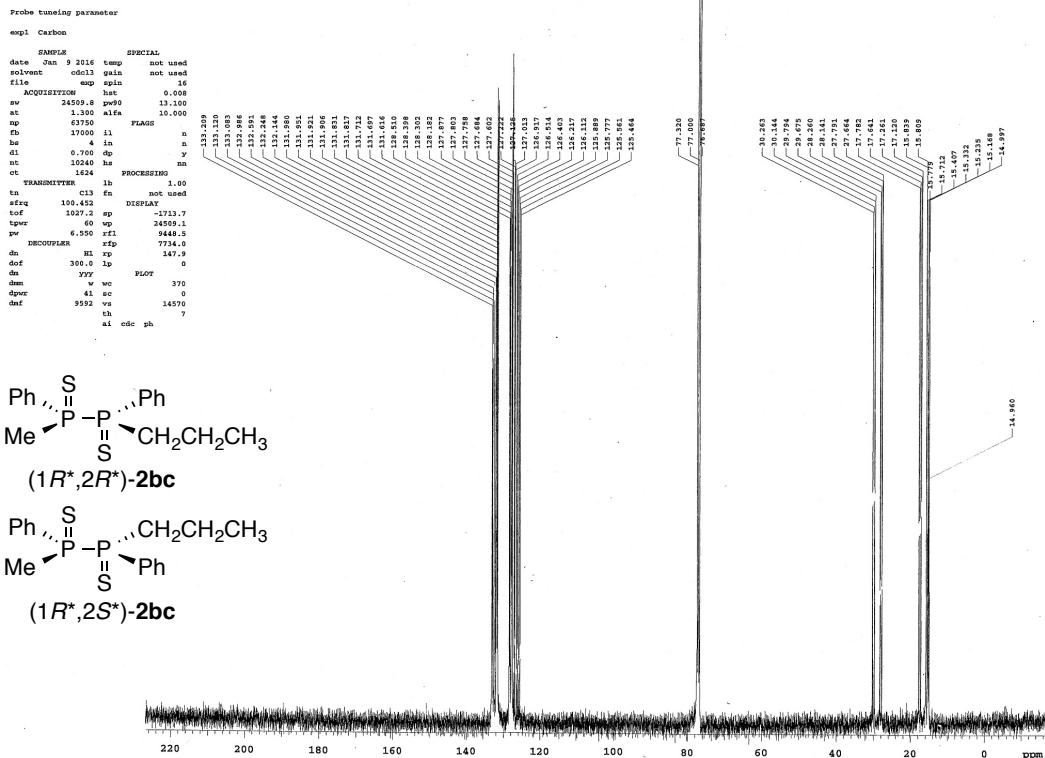
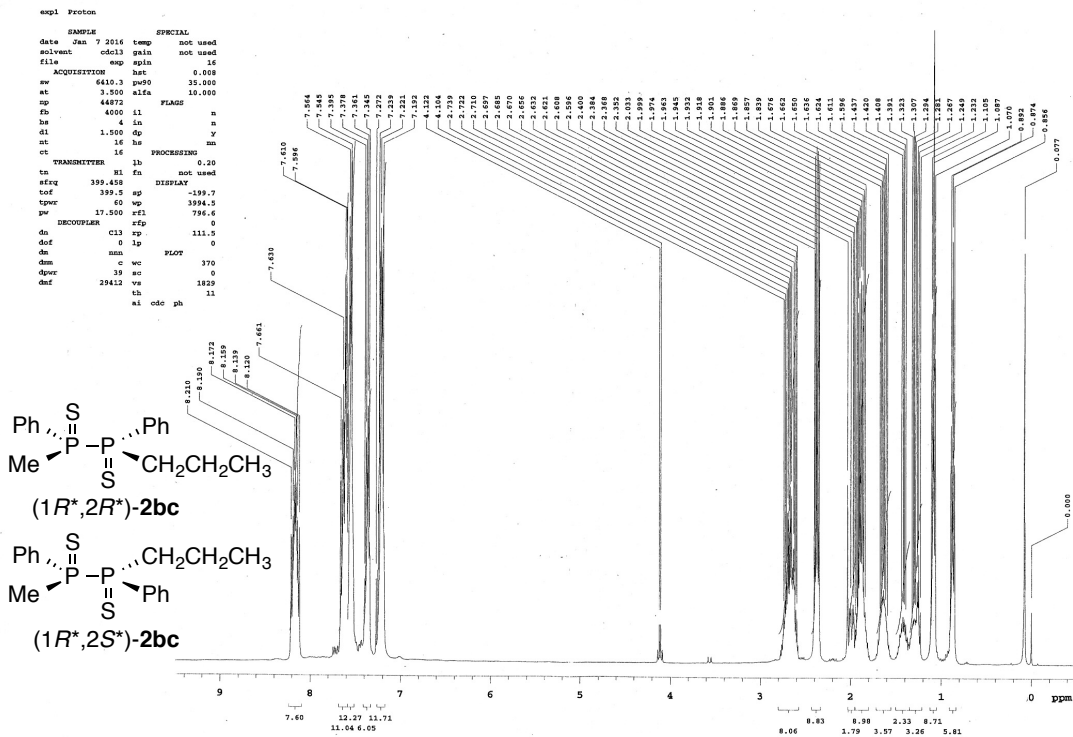

```

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solvent  cdcl3   gain   not used
file    exp   spin   16
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ACQUISITION
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at      9.450   n1a    10.000
=====
sp      60000   f1     FLAGS   n
f2     15000   f2     n
h2     4     in     n
d1     4.400   d2     y
at     256   h2     m
ct      8     PROCESSING
=====
TRANSMITTER
tr      931   fr     not used
=====
freq    161.496   DISPLAY
tod     4231.0   sp     -24998.5
tpr     58     up     49998.5
pw      4.500   rfd    25000.0
=====
DECOUPLER
dn      H1   sp     53.6
dof     0   lp     0
dn      none
=====
dms     w   wo     370
dpr     42   ac     0
dnt     9592  va     480
          th     22
          nl   cdc   ph

```



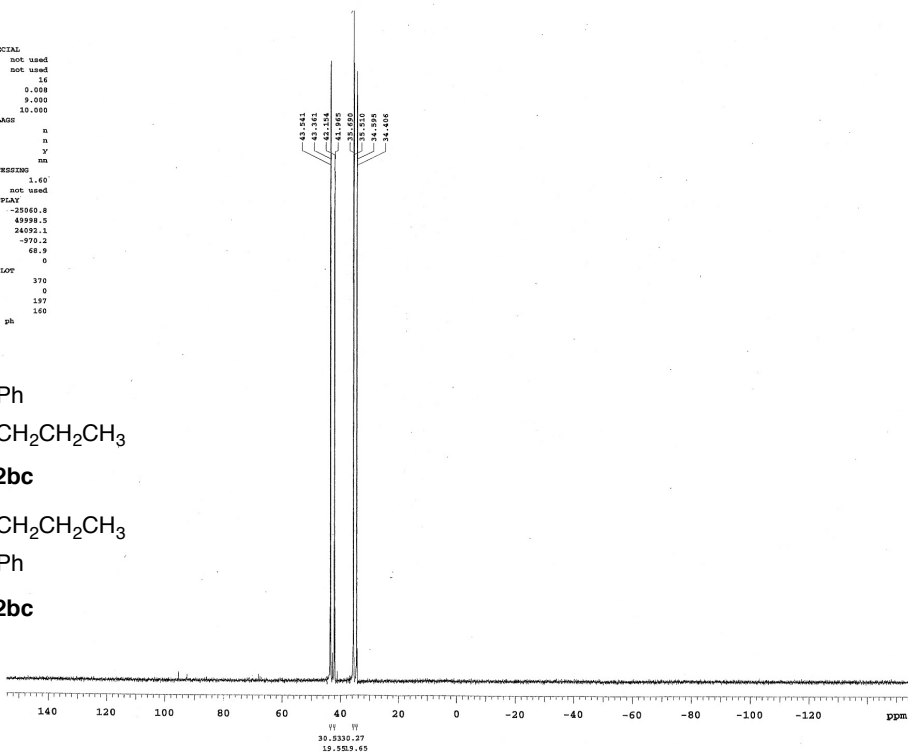
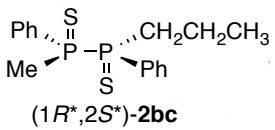
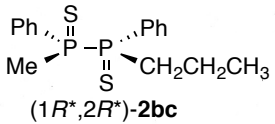
1-Methyl-2-propyl-1,2-diphenyldiphosphine disulfide [(1*R,2*R**)-2bc:(1*R**,2*S**)-2bc = 3:2]**



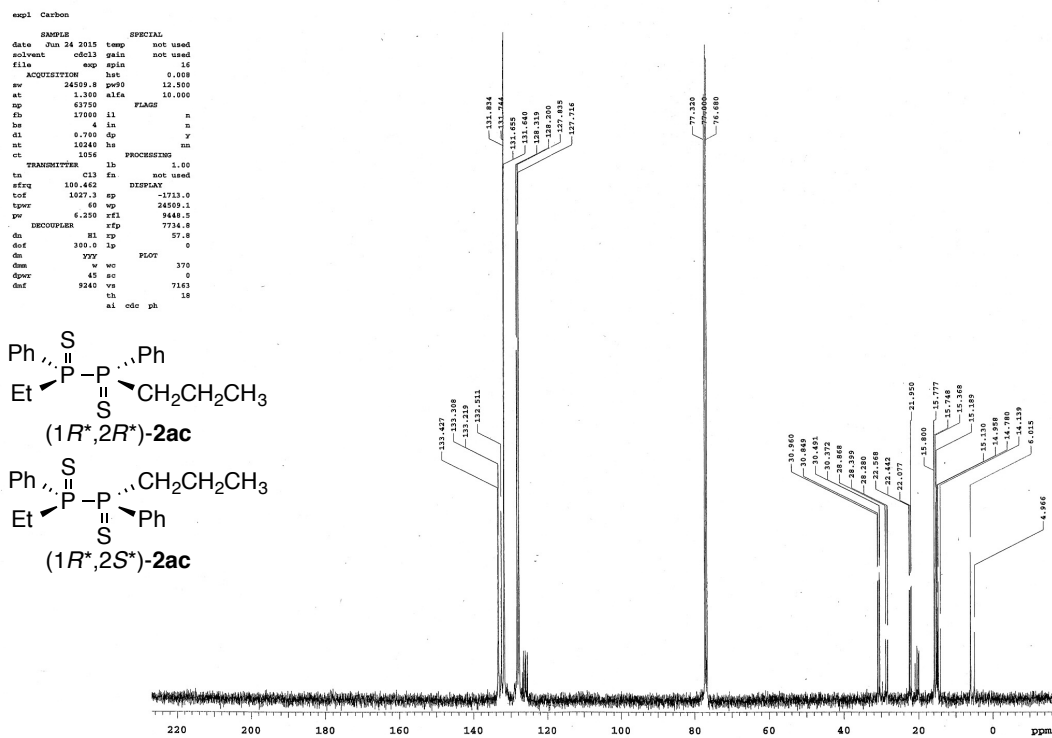
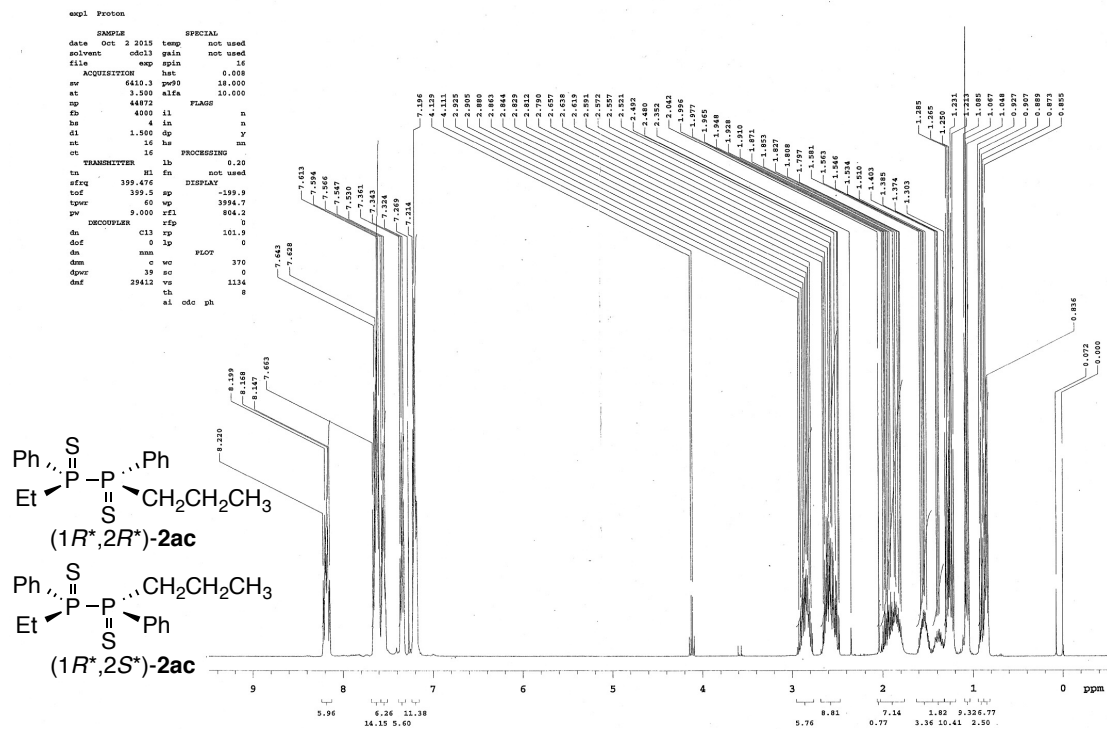
```

expi Phosphorus
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solvent cdcl3 gain not used
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at 0.600 alfa 10.000
sp 60000
ft 15000 ii n
ba 4 an n
dt 4.400 qp y
nt 256 ha mn
ct
TRANSMITTER
lb 1b 1.60
to 931 fn not used
rfcw 161.703 DISPLAY
tof 4232.1 sp -25060.8
tpwr 58 wp 49998.5
sw 4.500 rfi 24092.1
DECOUPLER
dl rfp -970.2
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dof 0
dm nuy PLOT 370
dms w wc 0
dpwr 45 ec 0
dmf 9240 va 197
sh 140
al odo ph 140

```

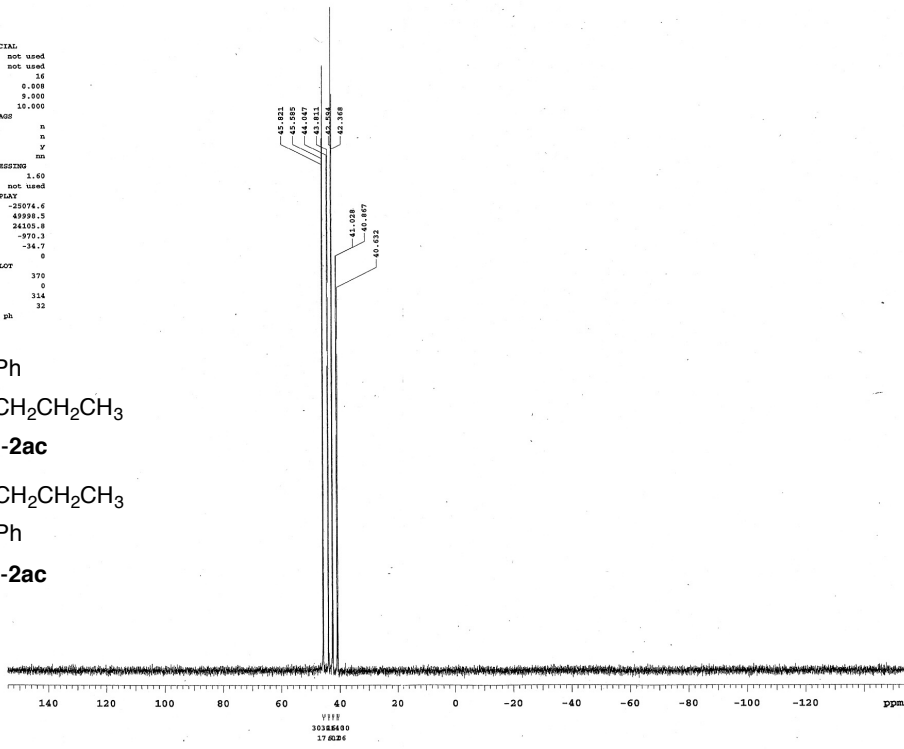
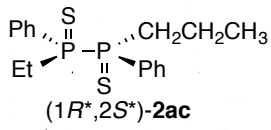
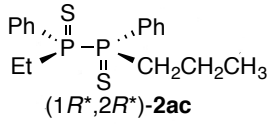


1-Ethyl-2-propyl-1,2-diphenyldiphosphine disulfide [(1*R**,2*R**)-2ac:(1*R**,2*S**)-2ac = 2:1]

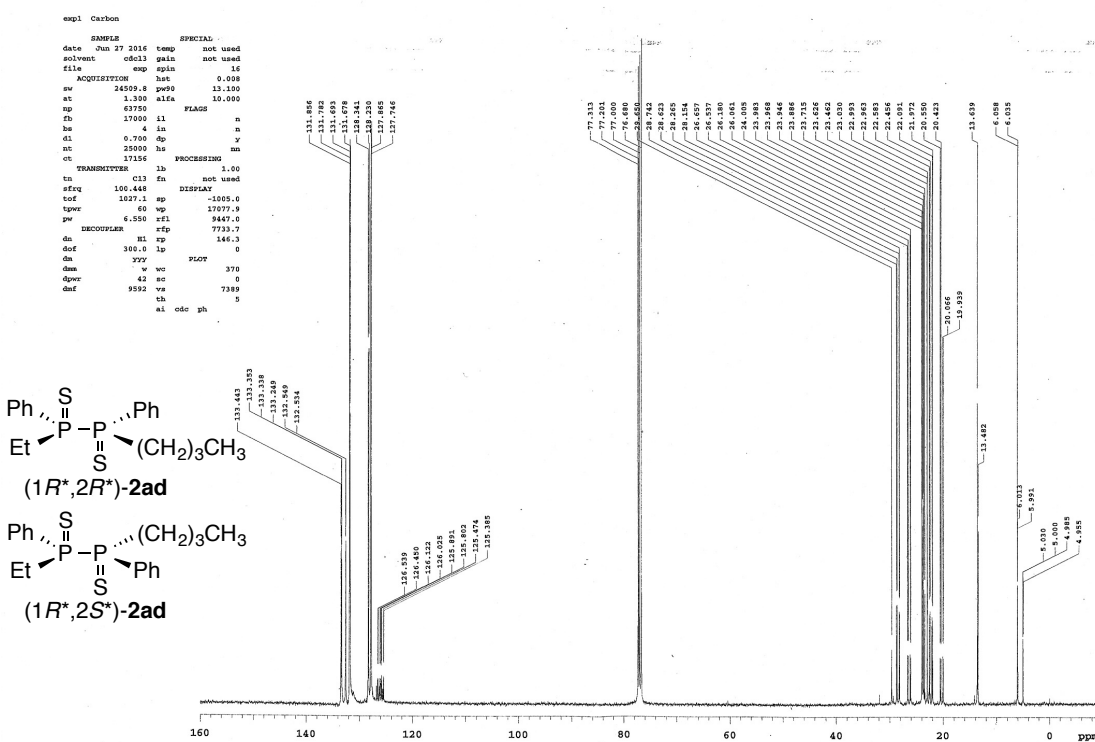
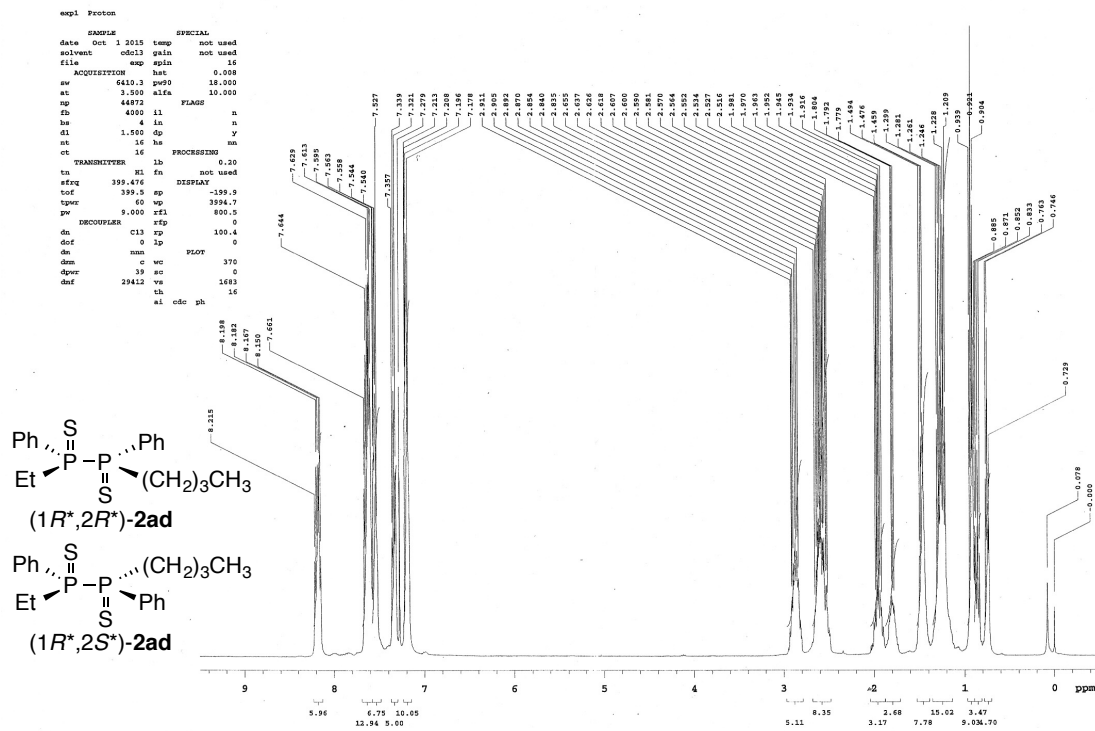


exp1 Phosphorus

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file		exp	spin 16
ACQUISITION			
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sv	50000.0	pw90	5.000
at	0.400	alfa	10.000
ap	60000	PLANS	
cb	15000	il	n
be	4	in	n
dl	4.400	gp	y
nt	256	hs	m
ct	8	PROCESSING	
TRANSMITTER			
tn	931	fn	not used
freq	161.712	DISPLAY	
tof	4232.4	sp	-25074.6
tpwr	58	wp	49998.9
pw	4.500	rfl	24500.0
DECOUPLER			
dm		rfl	-970.3
dof	xl	sp	-34.7
dof	0	ip	0
dm	noy	PLOT	
dm	w	uc	370
dpwr	45	ac	0
def	9240	vs	314
	th	th	32
	ai	ode	ph



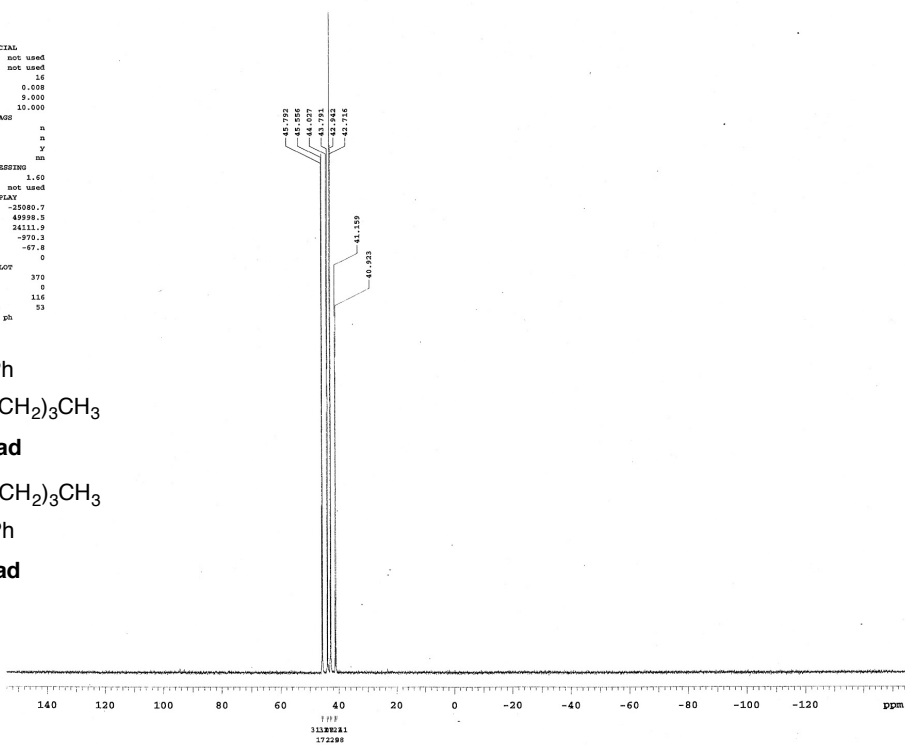
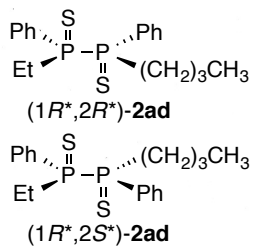
1-Butyl-2-ethyl-1,2-diphenyldiphosphine disulfide [(1*R**,2*R**)-2ad:(1*R**,2*S**)-2ad = 2:1]



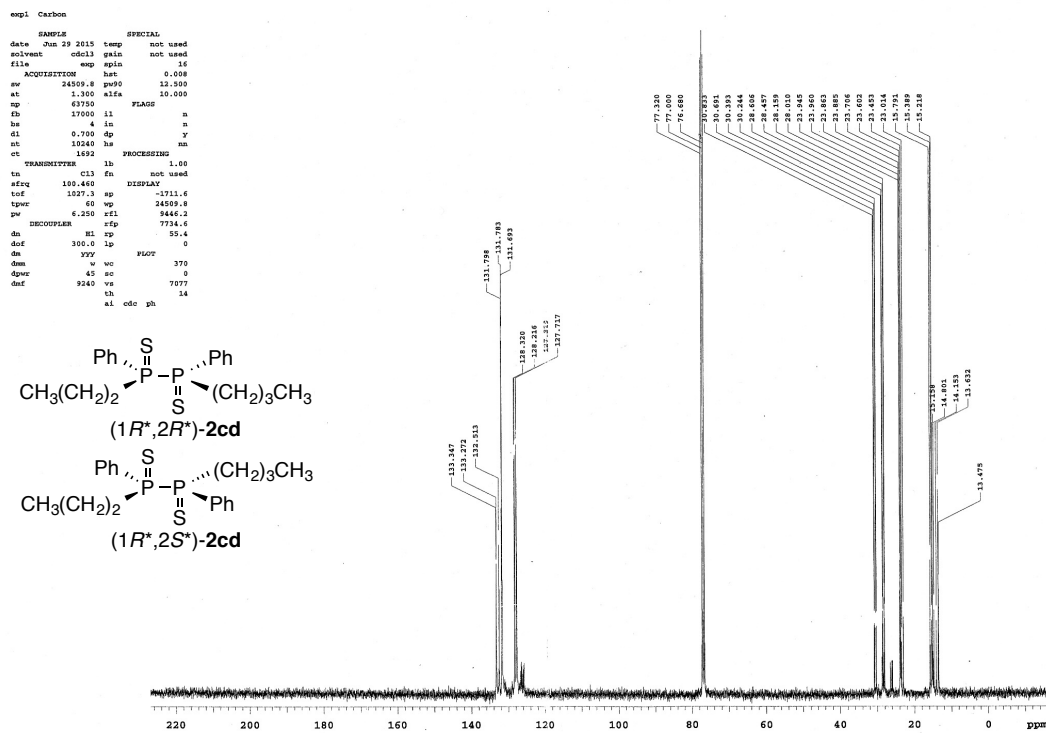
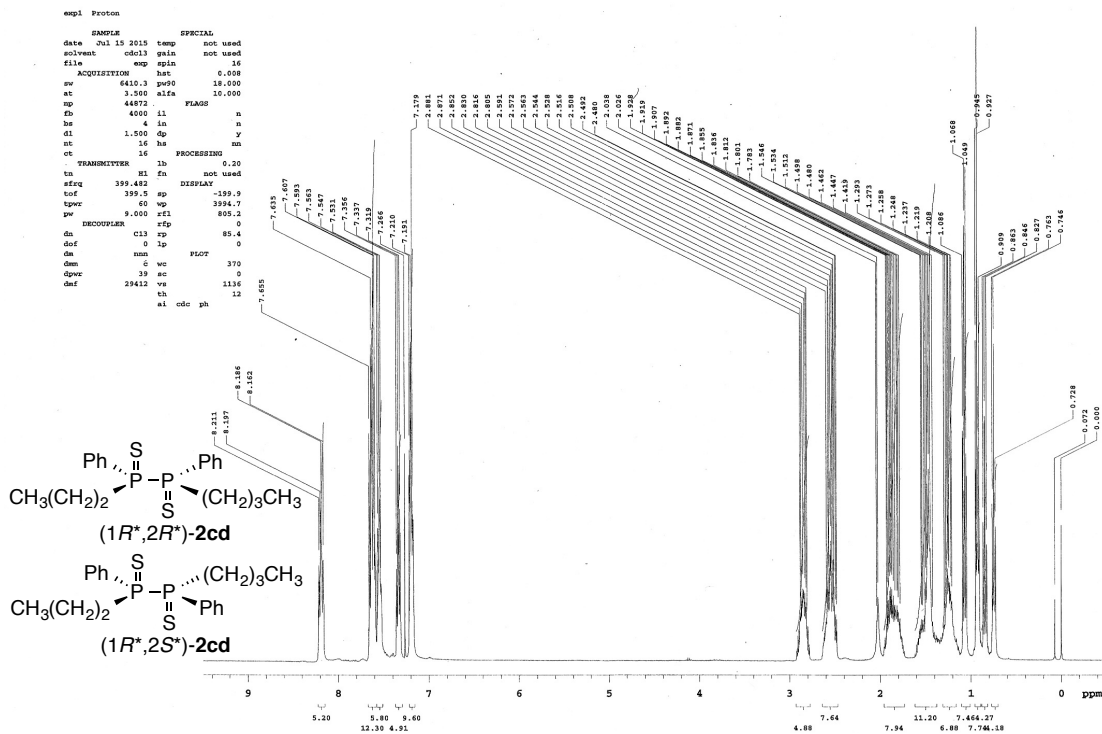
```

expt Phosphorus
SAMPLE          SPECIAL
date   Jun 24 2015  temp  not used
solvent cdcl3  gain    not used
file   exp  spin     16
ACQUISITION  hsc      0.608
av      50000.0  pw90    9.000
at      0.6000  a1fa    10.000
ap      60000
sp      15000  il
hs      4      in      n
dl      4.600  dp      v
nt      256   hs      mn
cc      8      PROCESSING
TRANSMITTER  lb      1.60
ta      f31   fn      not used
rfcq    161.716  DISPLAY
tof     4332.5  sp      -25080.7
tqwr    50     sp      43598.5
pw      4.500  rfl     24111.9
DECOUPLER  rl     rfp     -970.3
ds      81     sp      -87.8
dof     0      lp      0
dm      mny   wv     PLOT  370
dmm     w     wv     0
dprc    45    sc     0
dnt     9240  vs     116
          th     53
          al     odc  ph

```



1-Butyl-2-propyl-1,2-diphenyldiphosphine disulfide [(1*R**,2*R**)-2cd:(1*R**,2*S**)-2cd = 2:1]

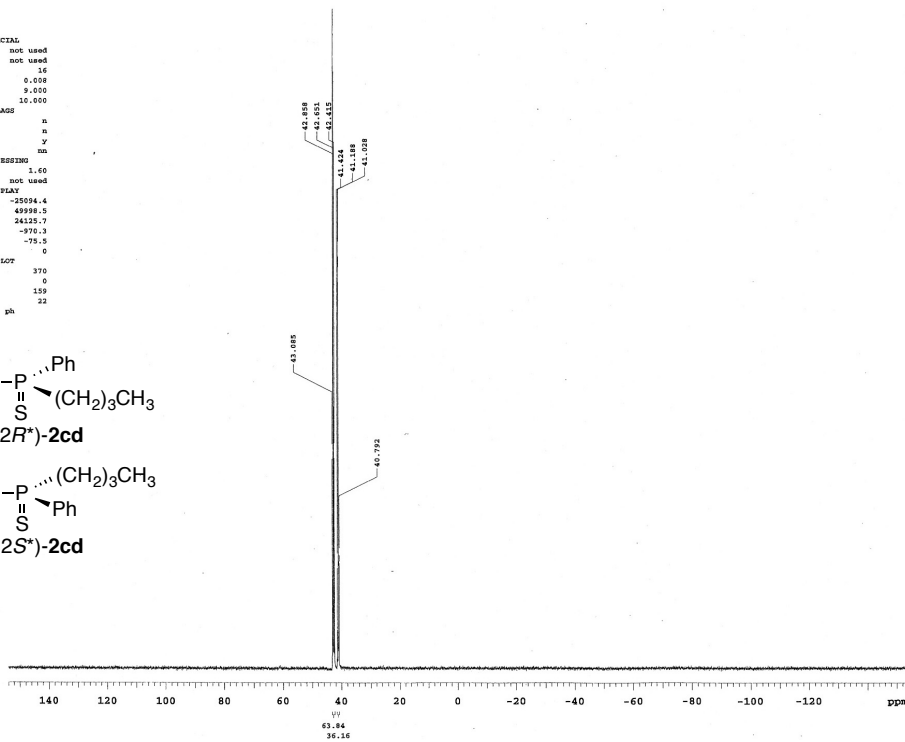
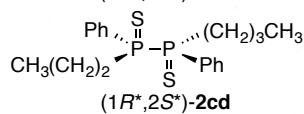
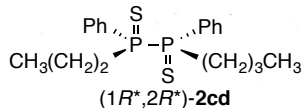


expt Phosphorus

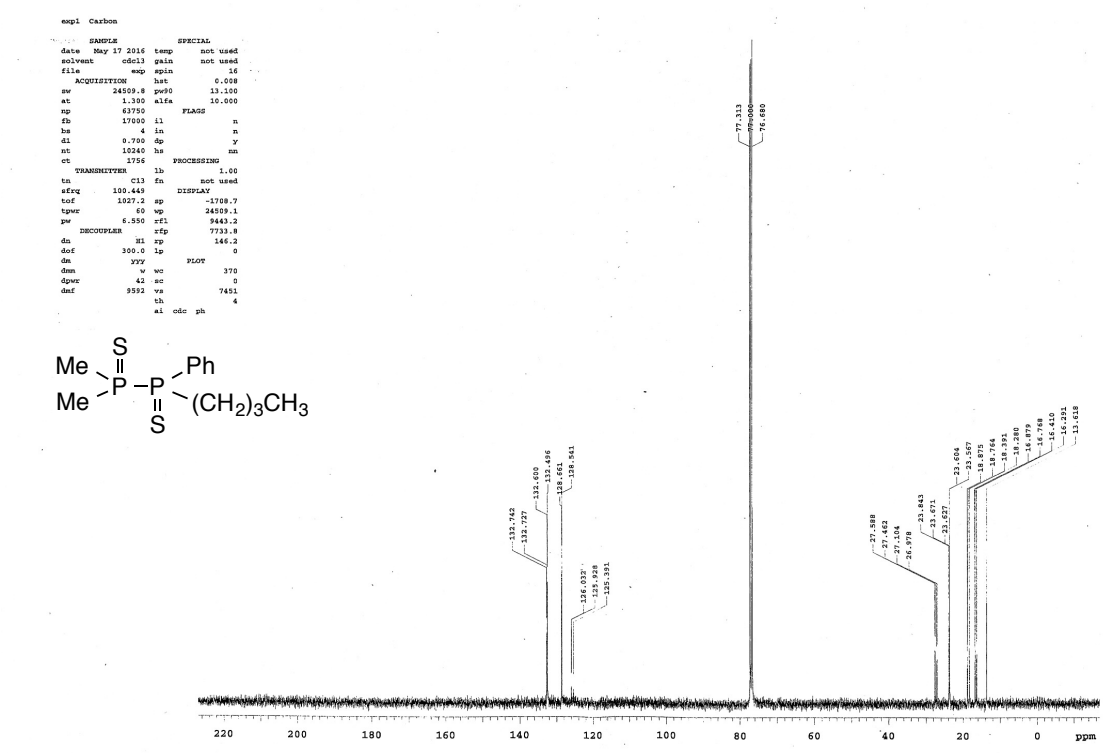
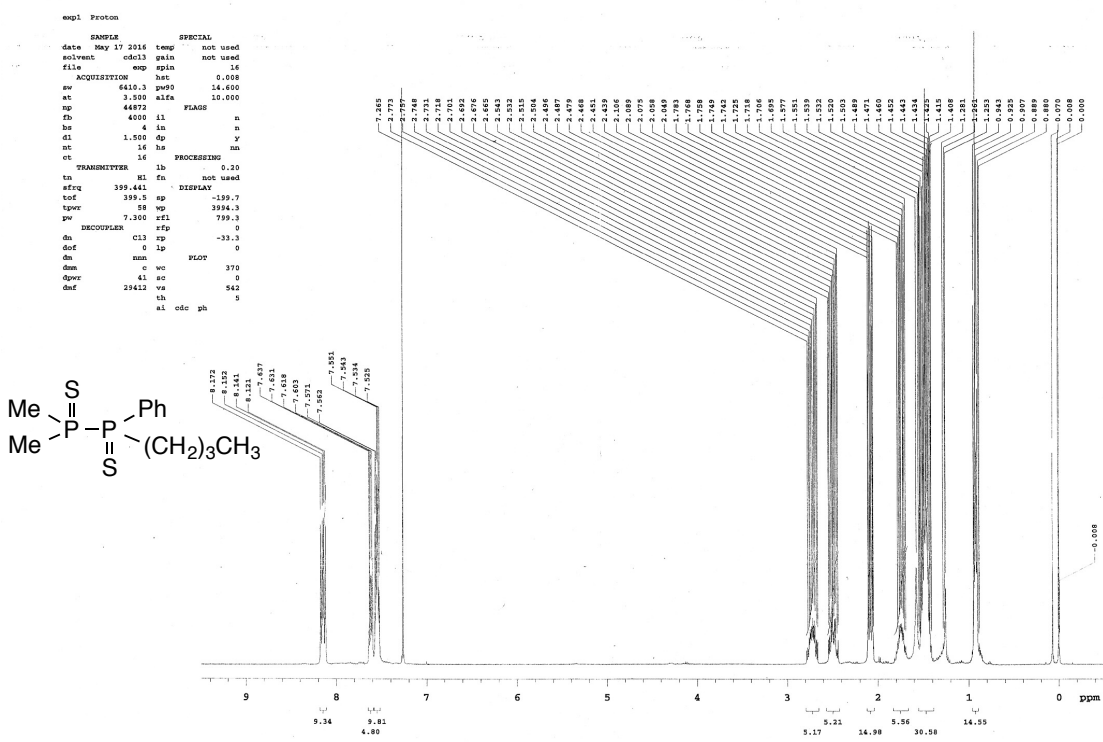
```

SAMPLE          SPECIAL
date Jul 15 2015 temp not used
solvent cdcl3 gain not used
file exp apin 16
ACQUISITION    het 0.008
sv 50000.0 pw90 9.000
at 0.600 aiaa 10.000
rp 60000
fb 15000 li n
hs 4 la n
dl 4.400 dp y
nt 296 hs mn
ct 16 PROCESSING 1.60
TRANSMITTER    lb not used
ts 211 fn DISPLAY
freq 161.712
tof 4332.4 ap -25094.4
tprc 50 sp 45998.5
pw 4.500 rfl 24125.7
DECOUPLER      rfp -270.3
dn 81 sp -75.5
dof 0 lp 0
dn smy PLOT 370
dnn w wc 0
dpwr 45 ac 0
dncf 9240 ve 159
ai edc ph 22

```

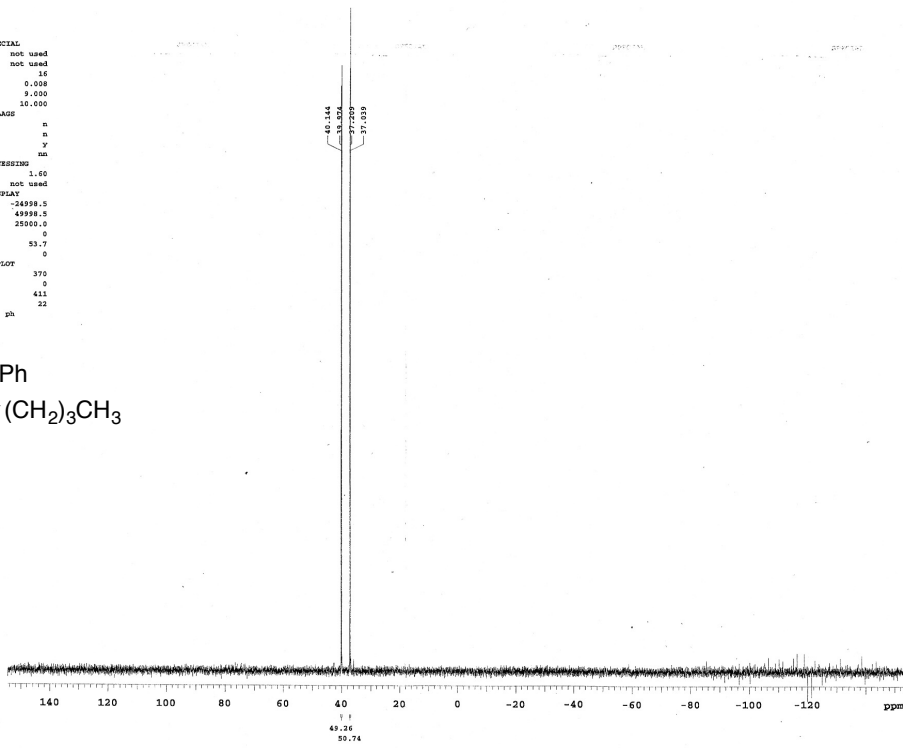
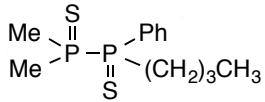


1-Butyl-2,2-dimethyl-1-phenyldiphosphine disulfide (2de)

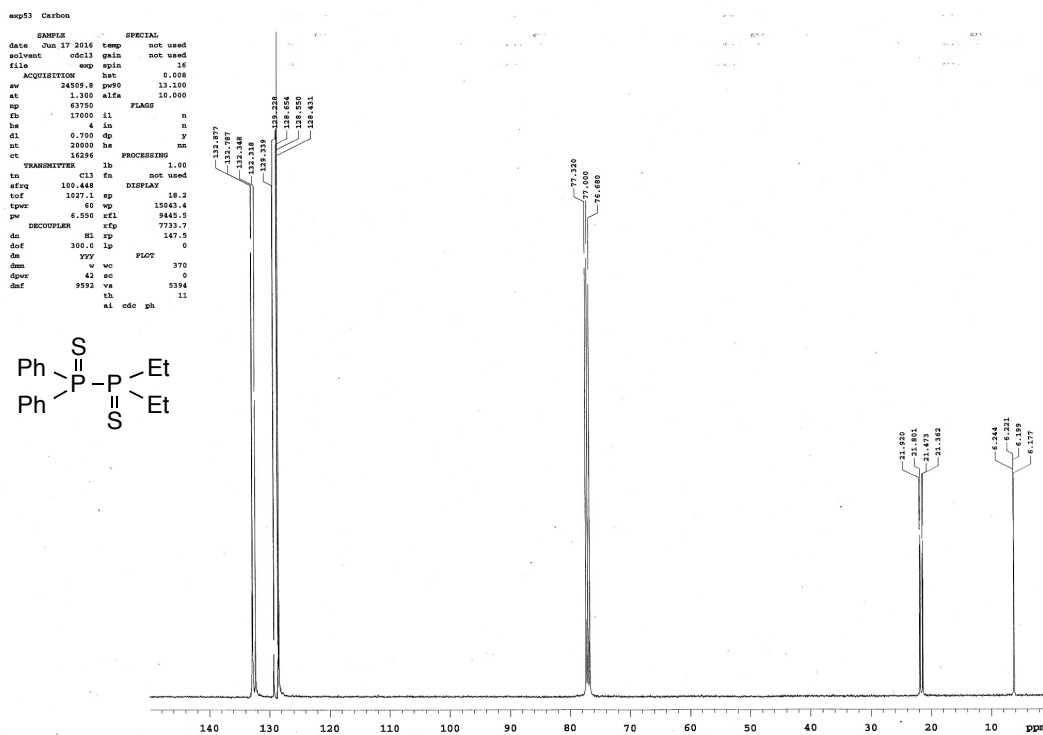
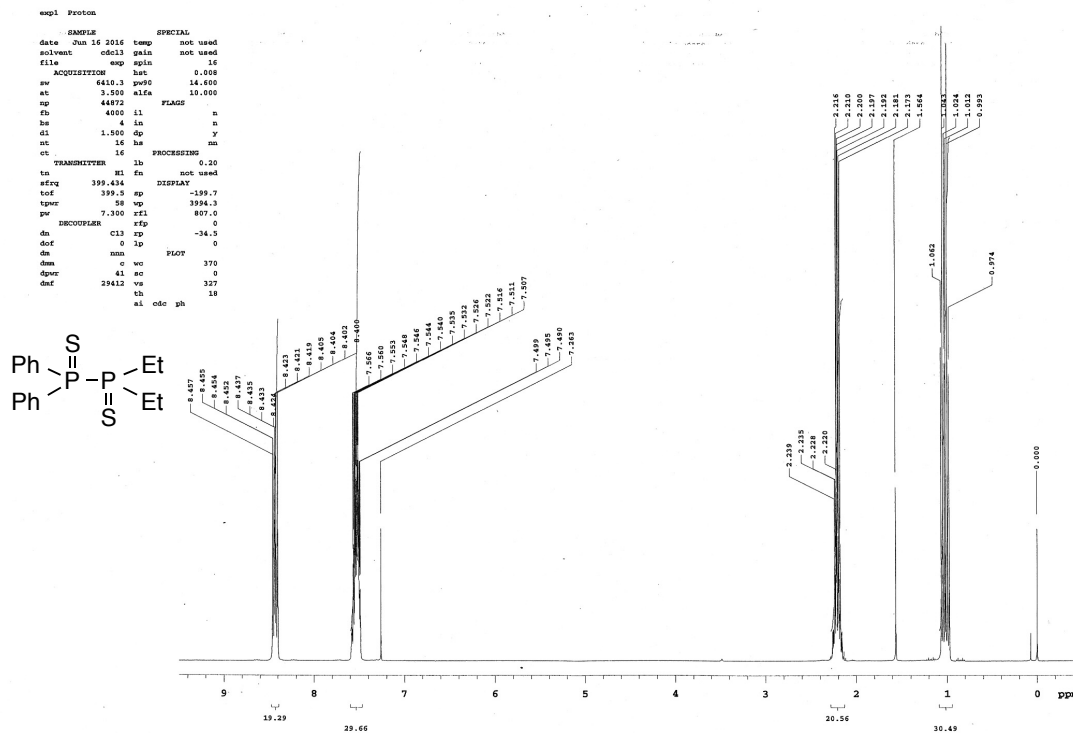


expt Phosphorus

SAMPLE		SPECIAL	
date	May 17 2016	temp	not used
solvent	cdcl3	gain	not used
file		spin	16
ACQUISITION		hst	0.008
av	50000.0	ps90	9.000
at	0.400	alta	10.000
ap	60000	FLAGS	
fb	15000	il	n
bs	4	in	n
dl	4.400	dp	y
nt	256	hs	nn
ct	12	PROCESSING	
tn		lb	1.60
ts	231	fn	not used
frq	161.496	DISPLAY	
tof	4232.0	sp	-24998.5
tpwr	50	vp	49998.5
pw	4.500	xf1	25000.0
DECOUPLER		rfp	0
dn	81	rp	53.7
dof	0	lp	0
dm	any	PLOT	
dsm	w	vc	370
dpwr	42	sc	0
dnd	5592	vp	411
		th	22
ai	cdc	ph	22



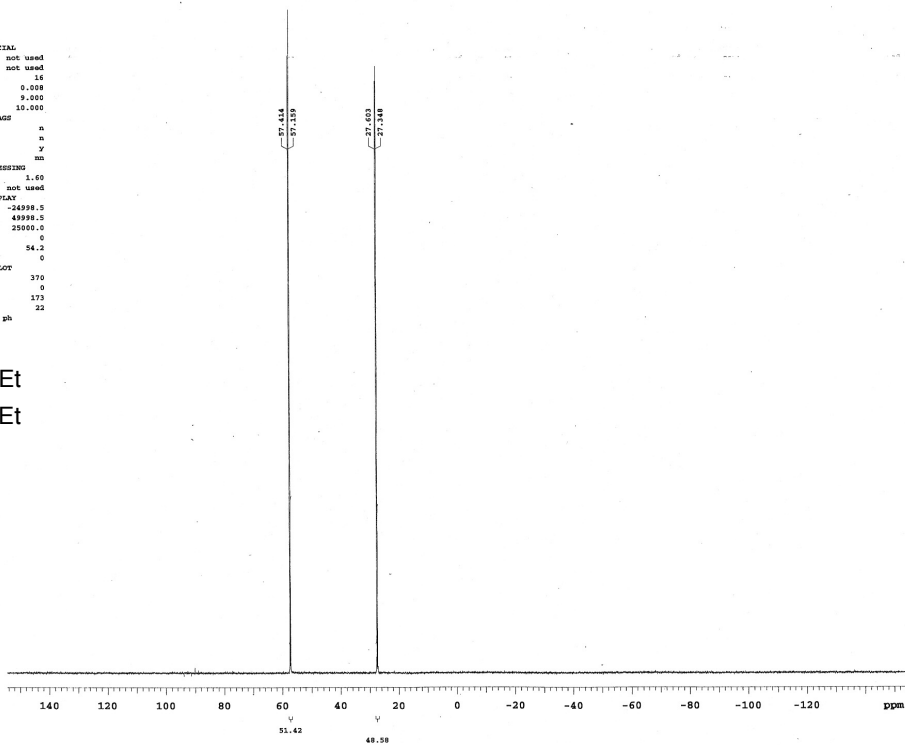
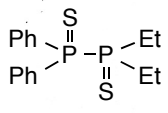
1,1-Diethyl-2,2-diphenyldiphosphine disulfide (2af)



```

exp1 Phosphorus
SAMPLE
data Jan 17 2016 temp not used
solvent cdcl3 gain not used
file exp spin 16
ACQUISITION hnt 0.038
sv 50000.0 pps0 9.000
at 0.600 a1fa 10.000
ap 60000
fb 15000 il
ha 4 in n
dl 4.400 dp y
nt 256 ha mn
cc 32 PROCESSING
TRANSMITTER lb 1.60
tn 931 fn not used
frc 161.692 DISPLAY
tof 4231.9 ap -24998.5
tpr 50 vp 49998.5
pw 4.500 rfi 25000.0
DECOUPLER rfp 0
ds 01 xp 54.2
dof 0 lp 0
dm may w uc PLOT 370
dmm 42 ac 0
dpr 9992 va 173
dnt th 22
al cdc ph

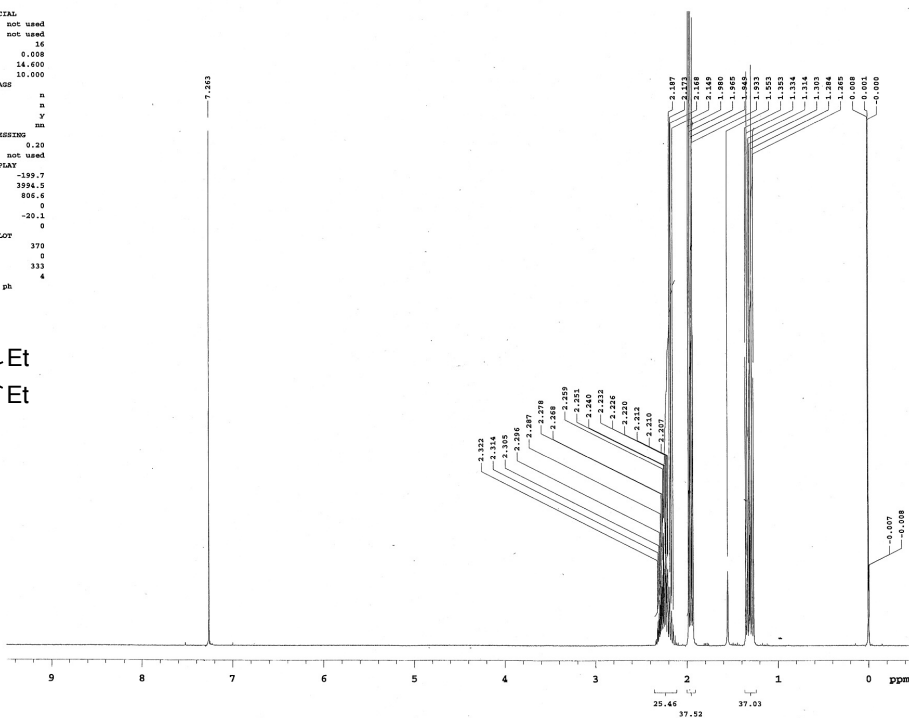
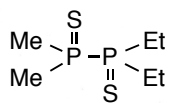
```



1,1-diethyl-2,2-dimethyldiphosphine disulfide (2gh)

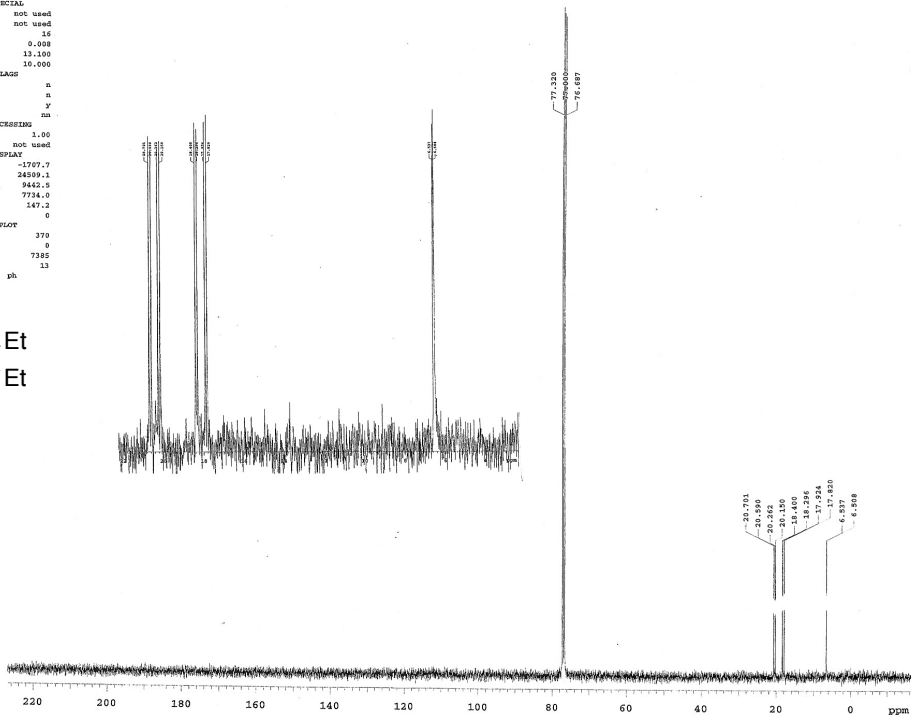
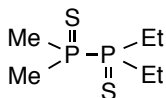
exp1 Proton

SAMPLE		SPECIAL	
date	Feb 3 2016	temp	not used
solvent	CDCl3	gain	not used
file		exp	spin 16
ACQUISITION	hut	0.008	
sv	6410.3	ppm	14.600
at	3.500	alpha	10.000
ap	44872	FLAGS	
fb	4000	il	n
bs	4	in	n
dl	1.500	sp	y
nt	16	hs	nm
ct		PROCESSING	
TRANSMITTER	12	lb	0.20
tn	H1	fn	not used
refrq	399.453	DISPLAY	-199.7
tof	399.5	sp	
tpwr	58	wp	3994.5
rw	7.300	rfl	806.6
DECOUPLER	rfd	0	
dn	C13	rp	-20.1
dof	0	lp	0
dm	nm	PLOT	
dm	4	uc	370
dpwr	41	sc	0
dnf	29412	vs	333
sh		hh	4
ai	edo	ph	



exp1 Carbon

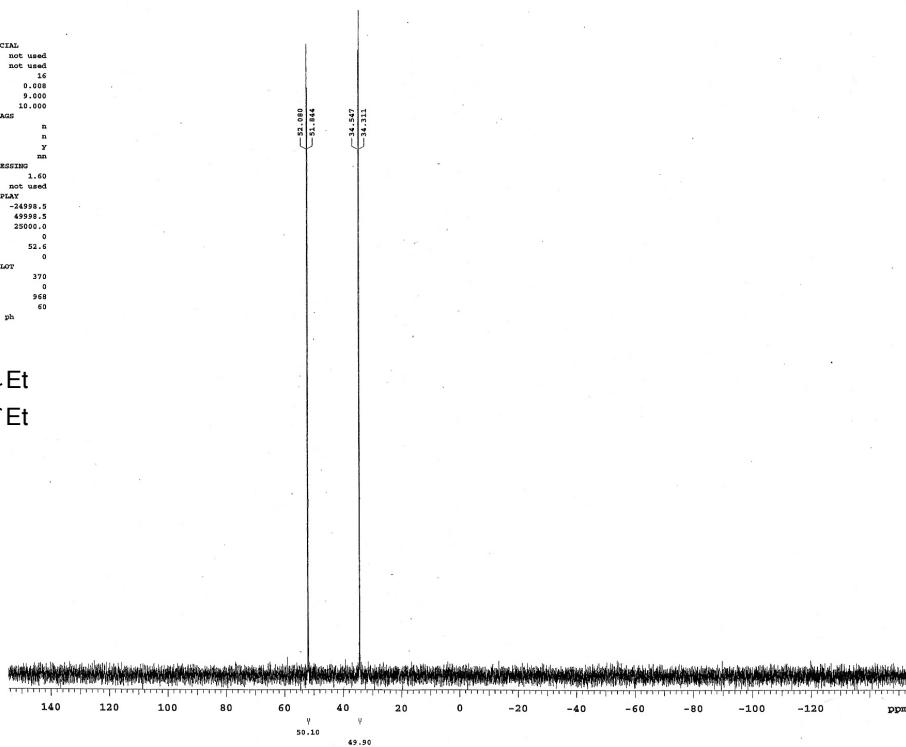
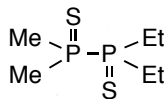
SAMPLE		SPECIAL	
date	Feb 3 2016	temp	not used
solvent	CDCl3	gain	not used
file		exp	spin 16
ACQUISITION	hut	0.008	
sv	24509.8	ppm	13.100
at	1.300	alpha	10.000
ap	43730	FLAGS	
fb	17000	il	n
bs	4	in	n
dl	0.700	sp	y
nt	10240	hs	nm
ct	1460	PROCESSING	
TRANSMITTER	12	lb	1.00
tn	C13	fn	not used
refrq	100.453	DISPLAY	-1707.7
tof	1007.2	sp	
tpwr	60	wp	24509.1
rw	6.950	rfl	9462.3
DECOUPLER	rfd	0	
dn	H1	rp	7734.0
dof	0	lp	147.2
dm	yyy	PLOT	
dm	4	uc	370
dpwr	41	sc	0
dnf	9592	vs	7385
sh		hh	33
ai	edo	ph	



```

exp1 Phosphorus
=====
SINGLE SPECIAL
date Feb 3 2016 temp not used
solvent cdcl3 gain not used
file exp spin 16
=====
ACQUISITION
sv 50000.0 pw90 9.000
st 0.600 sfile 10.000
np 60000
fb 15000 il n
hs 16 ia n
d1 4.400 sp y
nt 256 hs nm
ot 16 PROCESSING
=====
TRANSMITTER
tn 931 fm not used
sfrq 161.760 DISPLAY
tof 4232.1 sp -24998.5
kpcr 58 wp 49298.5
pw 4.500 rfl 25000.0
=====
DECOUPLER
ds H1 rp 52.6
dof 0 lp 0
ds mvy
dm w wo 370
dprc 41 sp 0
dof 2502 ve 968
th 60
al odc ph

```

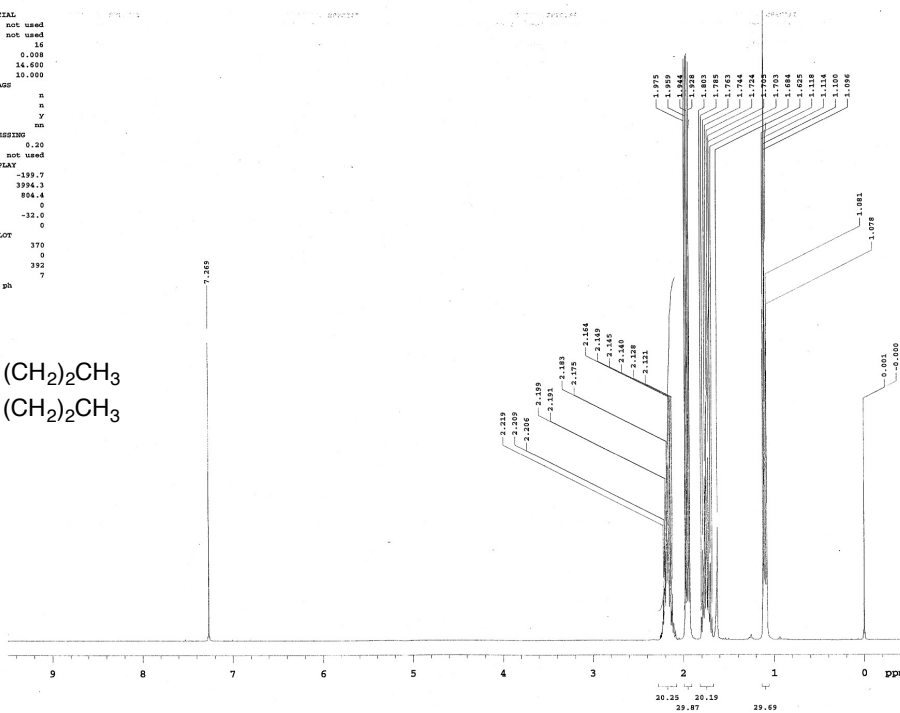
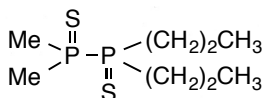


1,1-Dimethyl-2,2-dipropyldiphosphine disulfide (2gi)

expt Proton

```

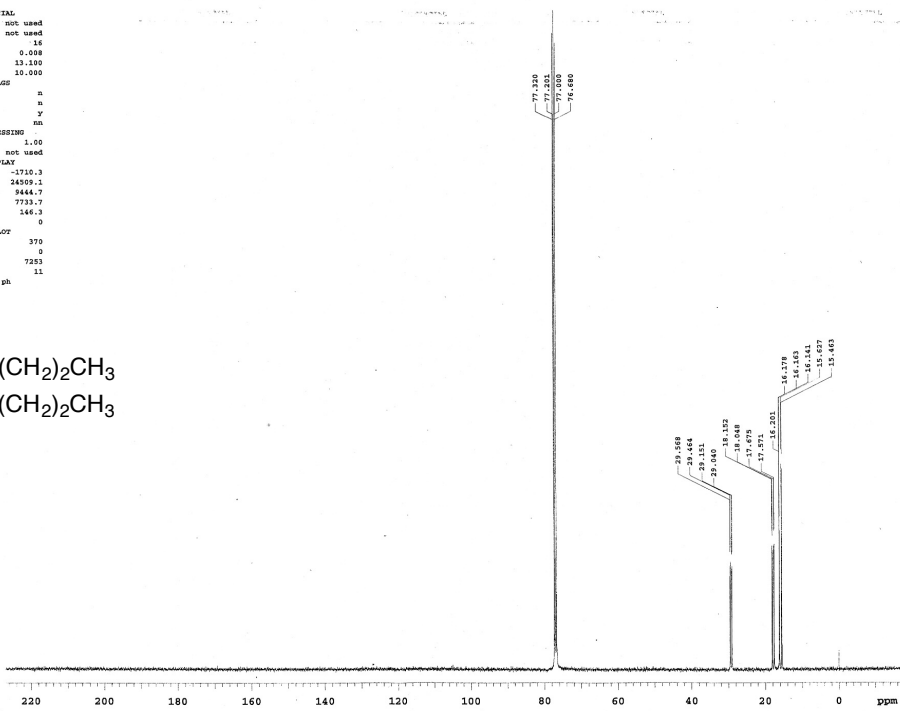
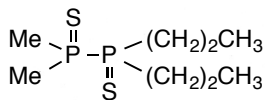
SAMPLE          SPECIAL
date May 27 2016 temp not used
solvent cdcl3 gain not used
file exp spm 16
ACQUISITION bat 0.008
av 6416.3 ppsf 14.000
at 3.500 alfa 10.000
ap 44872
cb 4000 li FLAGS n
ba 4 in n
dl 1.500 dp y
nt 16 ha nu
ct TRANSMITTER 13 PROCESSING 0.20
tn MI fn not used
strq 399.434 DISPLAY -199.7
tcf 399.5 sp -199.7
tpwr 58 wp 3994.3
pw 7.300 rfi 804.4
DISCOUPLER rfd 0
dn C13 rp -32.0
dnc 0 lp 0
dm nmn lp PLOT 0
dmn c wc 370
dpcr 41 sc 0
dnf 29412 vs 392
nl odc ph 7
    
```



expt Carbon

```

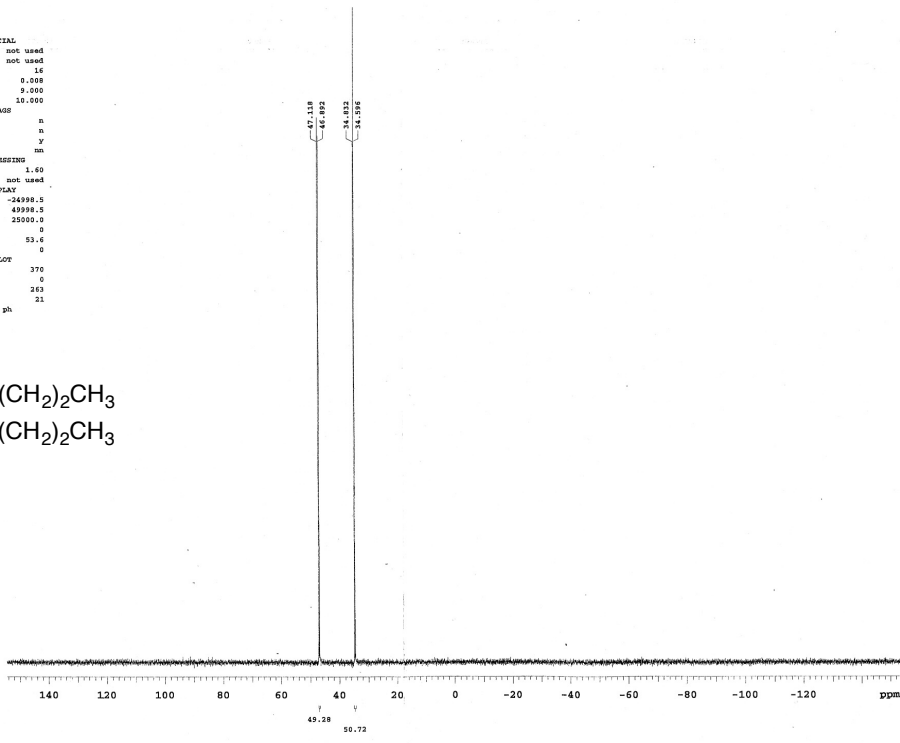
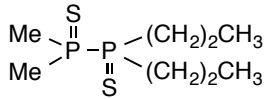
SAMPLE          SPECIAL
date May 27 2016 temp not used
solvent cdcl3 gain not used
file exp spm 16
ACQUISITION bat 0.008
av 24599.8 ppsf 13.300
at 1.300 alfa 10.000
ap 63750
cb 17000 li FLAGS n
ba 16 in n
dl 0.500 dp y
nt 30000 ha nu
ct TRANSMITTER 13 PROCESSING 1.00
tn MI fn not used
strq 100.448 DISPLAY -170.3
tcf 1007.1 sp -170.3
tpwr 60 wp 24599.1
pw 6.350 rfi 9444.7
DISCOUPLER rfd 7733.7
dn C13 rp 146.3
dnc 300.0 lp 0
dm xyy lp PLOT 0
dmn w wc 370
dpcr 42 sc 0
dnf 9592 vs 7253
nl odc ph 11
    
```



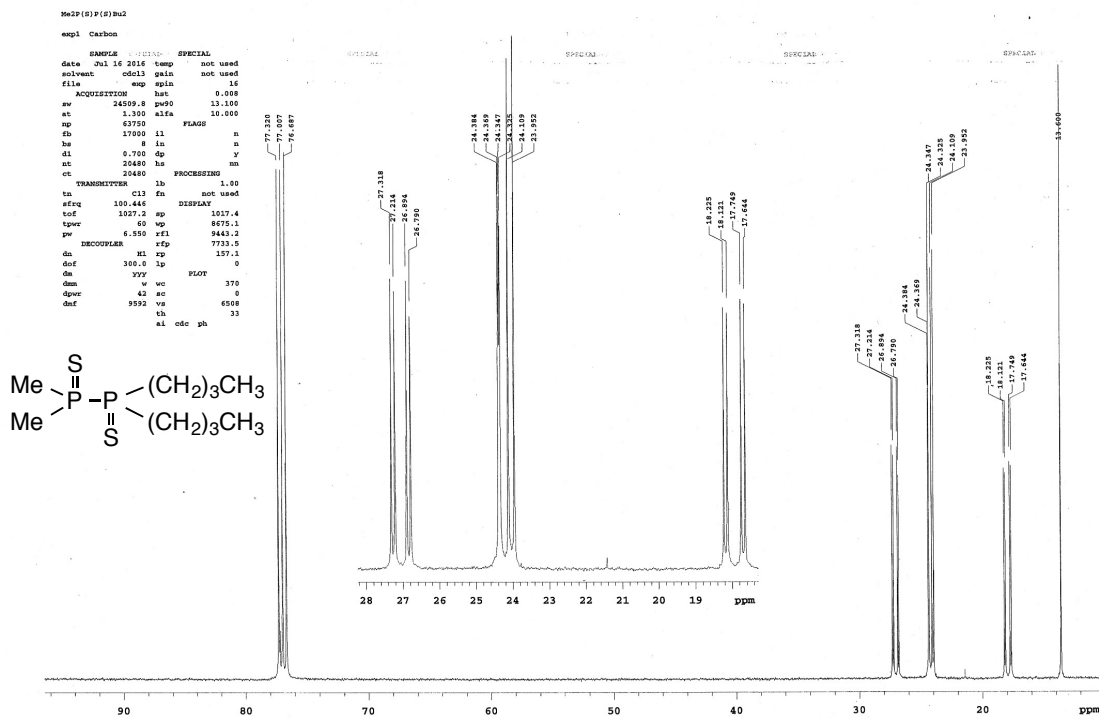
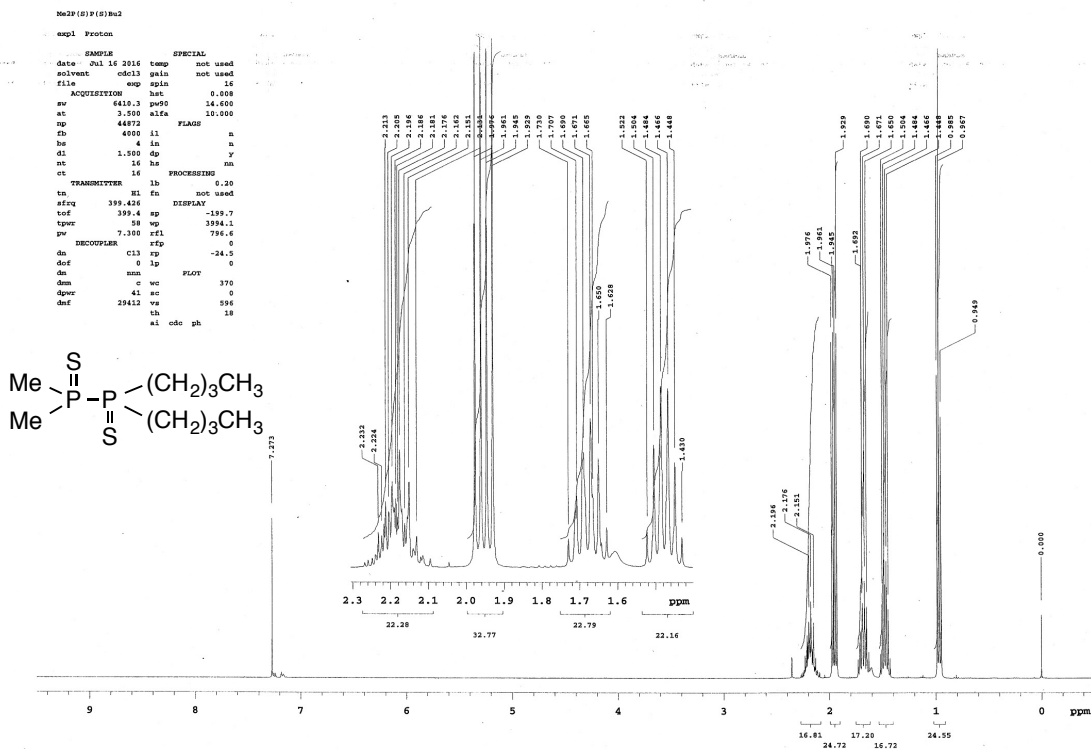

```

expt Phosphorus
SAMPLE
date May 27 2016 temp not used
solvent CDCl3 gain not used
file exp spln 16
ACQUISITION hst 0.000
sv 50000.0 pu50 9.000
ap 40000 alfa 10.000
fb 15000 il n
bs 4 in n
sl 4.400 sp y
nt 256 hs nm
ct 12 PROCESSING 1.60
TRANSMITTER lb 1b not used
ts 931 en not used
rfreq 161.490 DIEPMAN
tof 4231.9 ap -24998.5
tpwr 58 wp 49998.5
pw 4.150 rfi 25000.0
DECOUPLER ml zp 53.6
ds 0 lp 0
dm hny w PLOT 370
dcm w wc 263
dpr 42 so 0
dof 9592 th 21
at edo ph 21

```



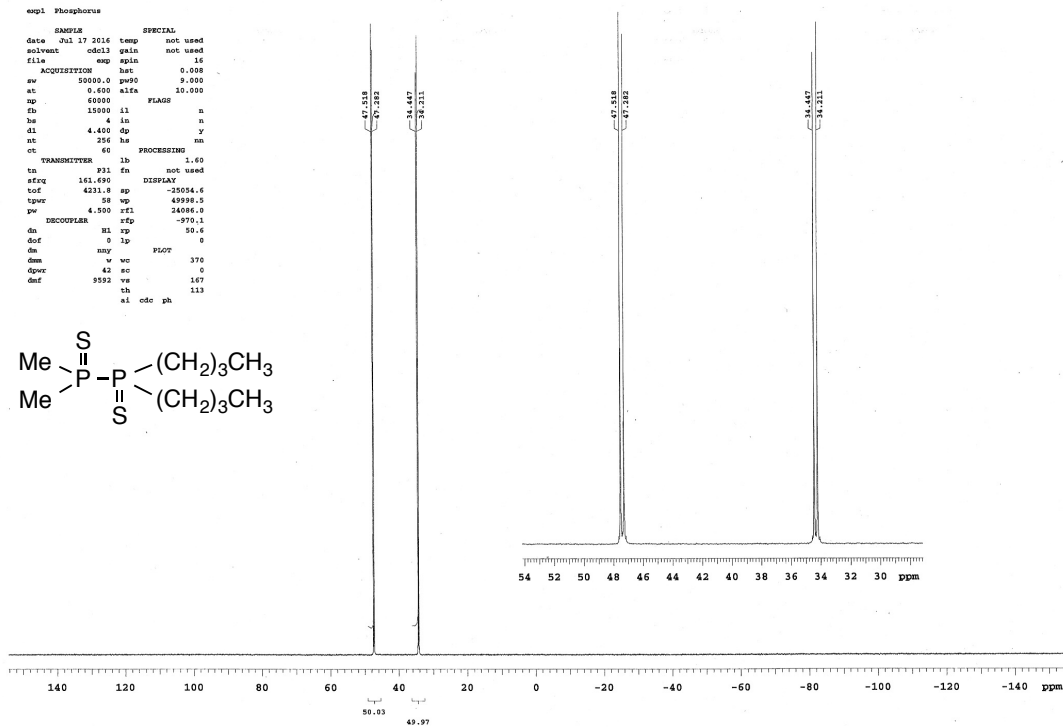
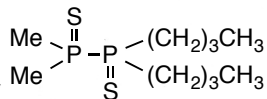
1,1-Dimethyl-2,2-dibutyldiphosphine disulfide (2gj)



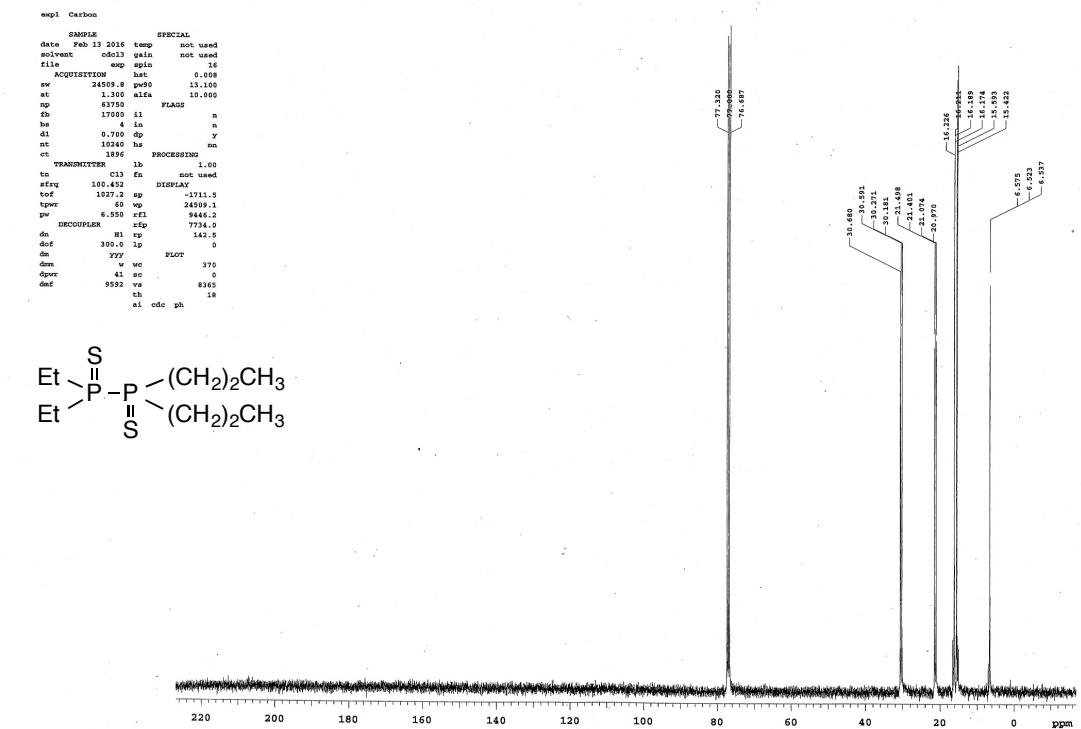
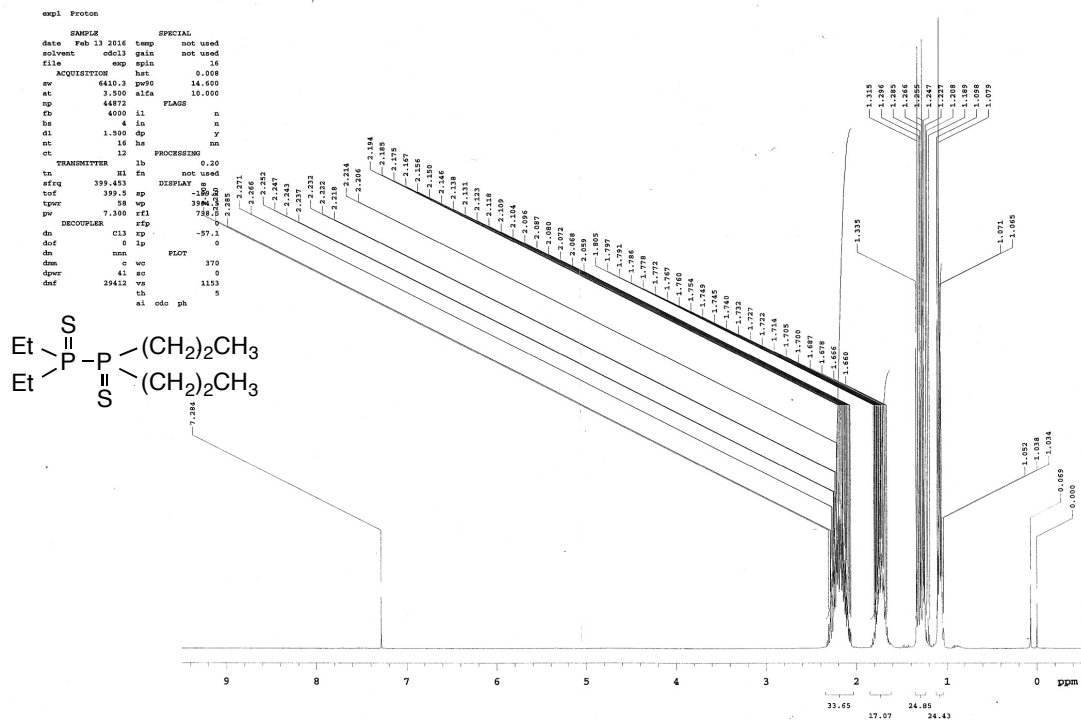
Me2P(S)P(S)Bu2

expt Phosphorus

SAMPLE		SPECIAL	
date	Jul 17 2016	temp	not used
solvent	cdcl3	gain	not used
file		spin	16
ACQUISITION		bat	0.008
sv	50000.0	pw90	9.000
at	0.400	alta	10.000
rg	60000	FLAGS	
fb	15000	il	n
ba	4	in	n
dl	4.400	dp	y
nt	256	hs	nm
ct	60	PROCESSING	
ts		lb	1.60
tn	231	fn	not used
stfq	161.690	DISPLAY	
tof	4231.8	sp	-25054.6
lgr	50	wp	45998.5
pw	4.500	rfl	24086.0
DECOUPLER		rfd	-970.1
dn		rl	92.4
do		lp	0
dm		wp	370
dpr		sc	0
def	9392	ve	167
		th	113
		sl	odo ph



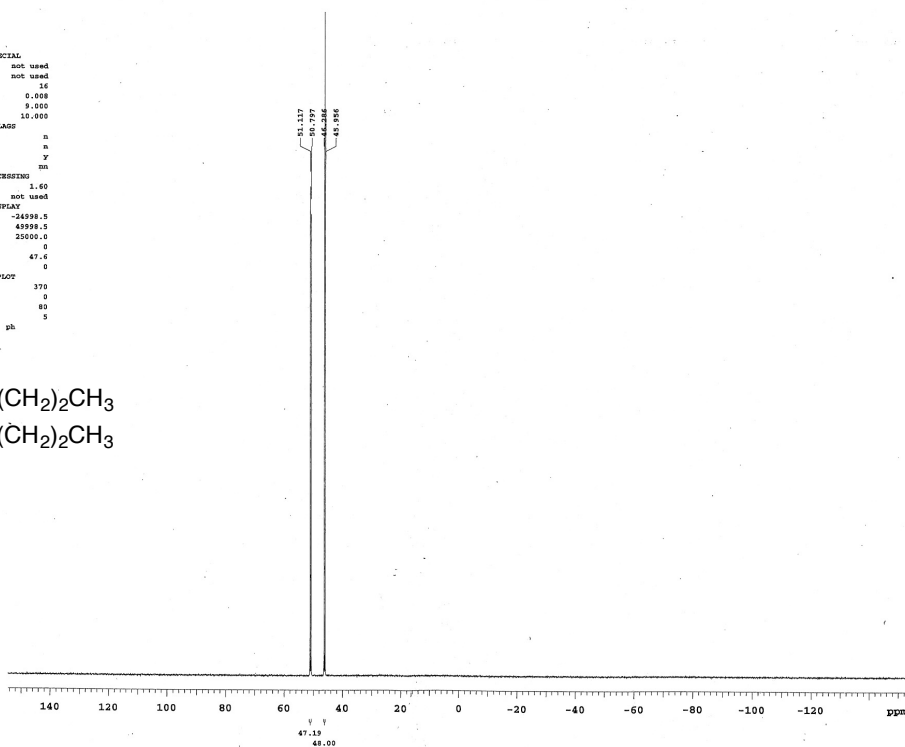
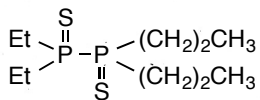
1,1-Diethyl-2,2-dipropyldiphosphine Disulfide (2hi)



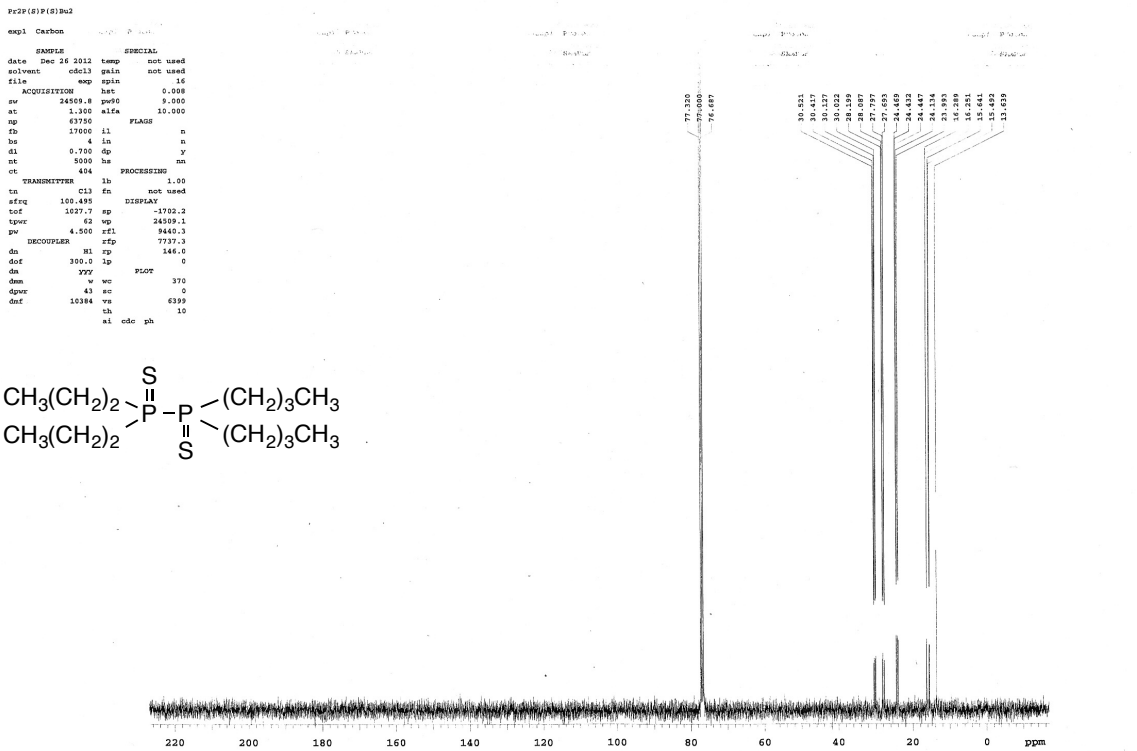
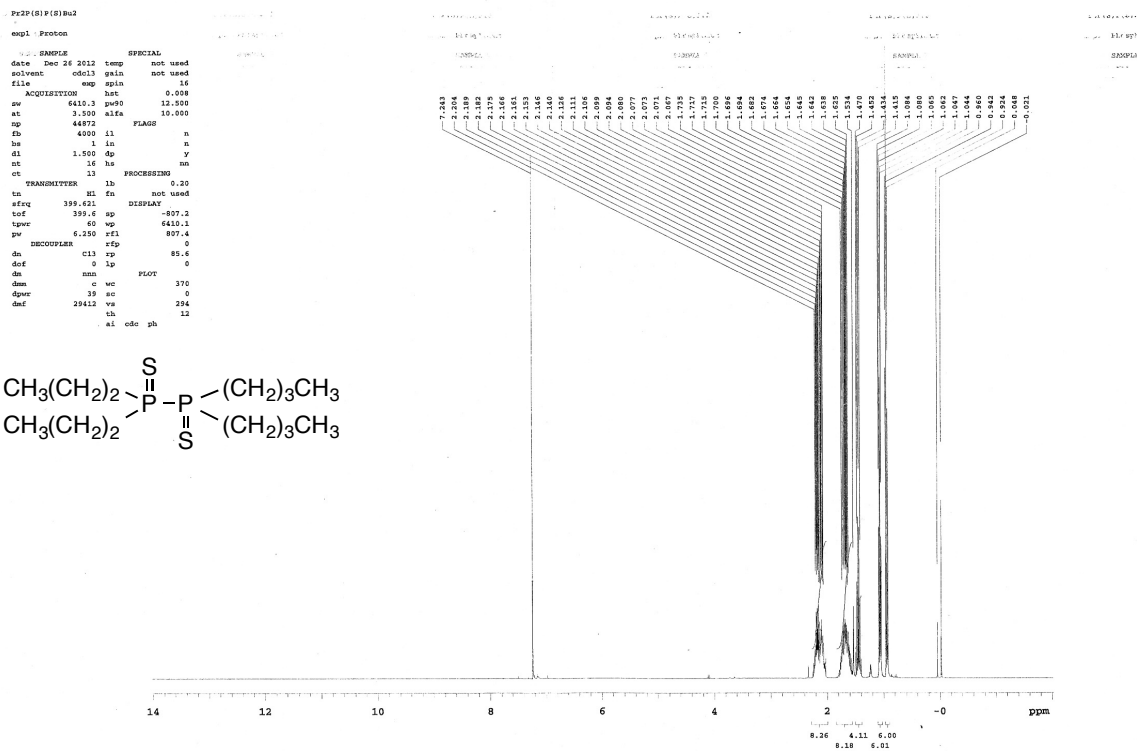
```

expt Phosphorus
NAME
date Feb 12 2016 temp not used
solvent cdcl3 gain not used
file          emp spin    16
ACQUISITION  lat      0.008
sv          50000.0 pw90    9.000
at          0.600 aia     10.000
ap          60000          FLAGS
fb          15000 il       n
hs          4 in         n
dl          4.400 qp       y
st          258 ha       nn
ot          8          PROGRESSING
TRANSMITTER lb          1.60
tn          731 fn       not used
sfreq      161.700 DISPLAY
tof        4232.1 sp     -24998.5
tprc       58 sp       45598.5
pw         4.500 rf1    25000.0
DECOUPLER  rf2         0
dn         81 rp       47.6
dof        0 lp         0
dm         mny          PLOT
dmn         w wc       370
dprc       41 ec         0
dof       9552 va       80
dof        th          5
          al odc ph    5

```



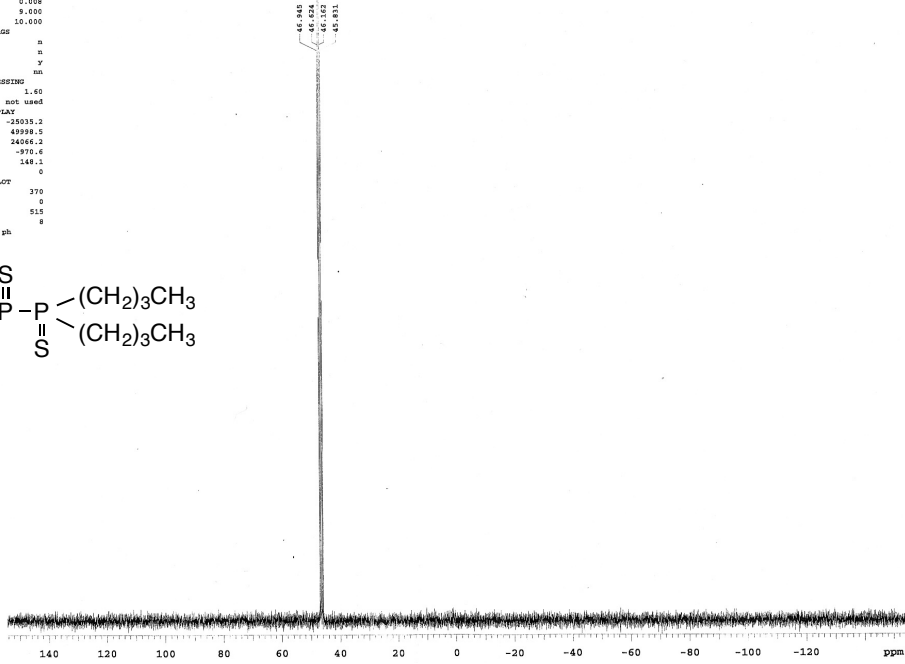
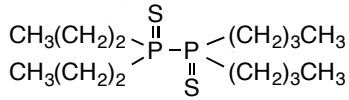
1,1-Dibutyl-2,2-dipropyldiphosphine Disulfide (2hi)



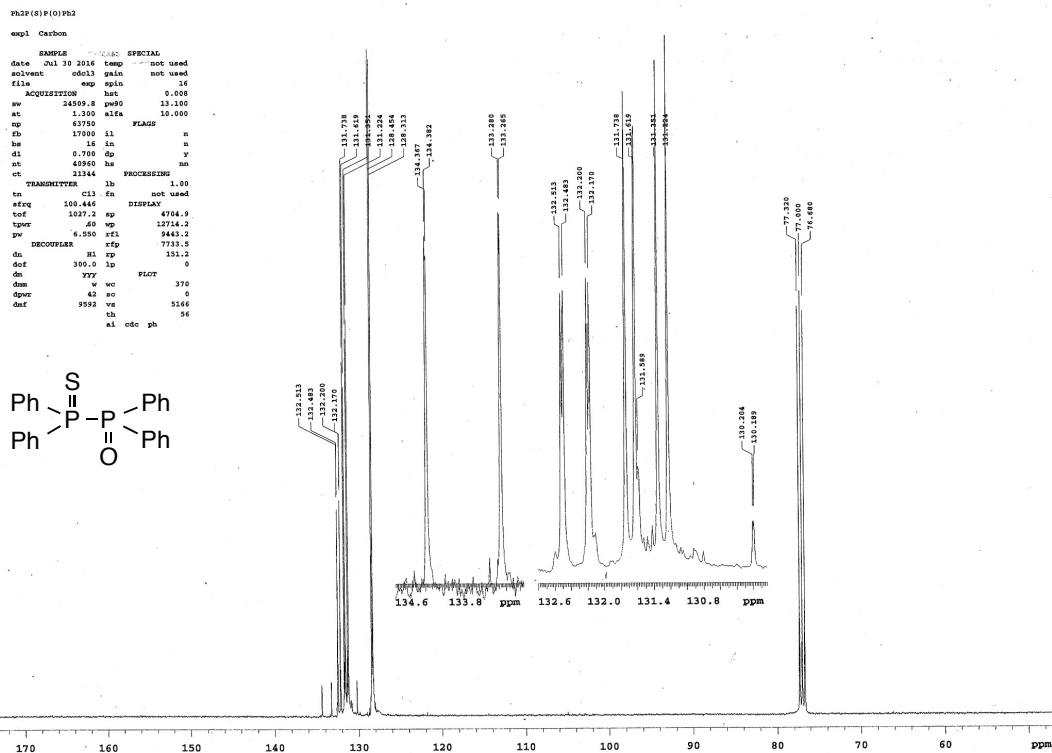
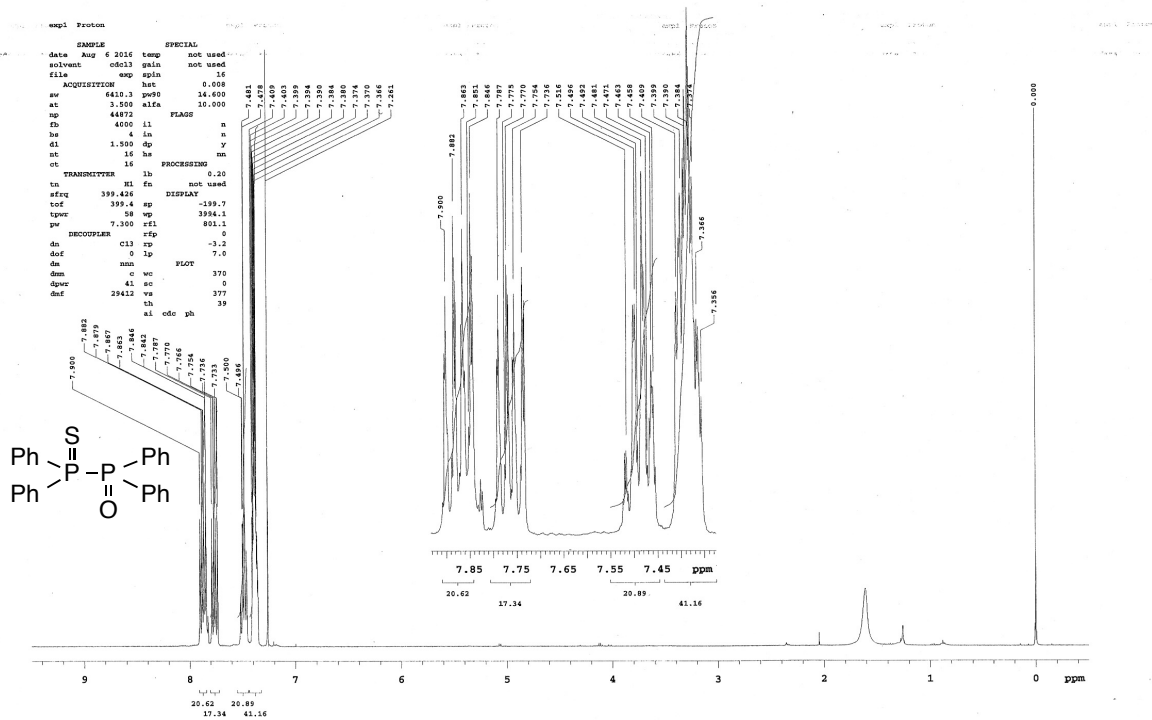
Pr2P(S)(S)Br2

expt1 Phosphorus

```
SAMPLE          SPECIAL
data   Dec 26 2012  temp      not used
solvent  cdcl3  gain      not used
file          exp  apin      18
ACQUISITION  exp  hst       0.008
pu       50000.0  pw90      9.000
at       0.400  a1ca      10.000
ap       60000
fb       15000  il
hs       1      in
dl       4.400  dp
nt       256   hs
ct       8      PROCESSING
ts       931   fn      not used
efrq    161.768  DISPLAY
tof     4233.9  ap      -25033.2
tprc    58     ap      42938.5
pu       4.500  efl     24066.2
ds       0     rfp     -970.6
ds       0     rfp     148.1
ds       0     ip
ds       0     PLOT
ds       0     w  wc     370
dpr     43     ac     0
cdf     10384  ve     515
          th     8
          ak     odc  ph
```

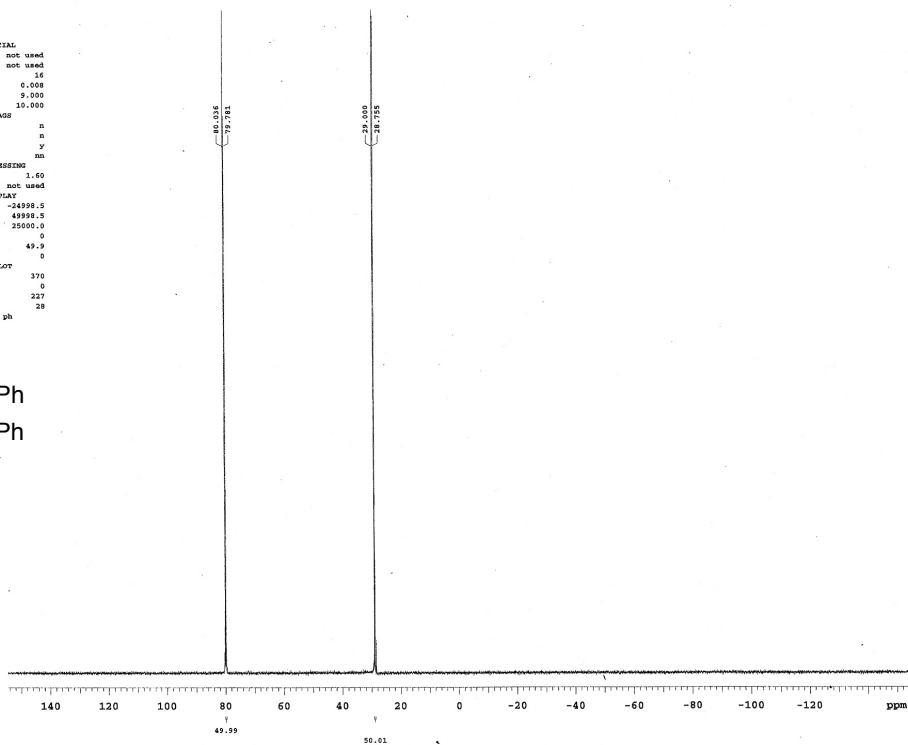
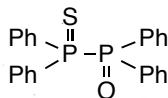


Tetraphenyldiphosphine 1-oxide 2-sulfide (4)

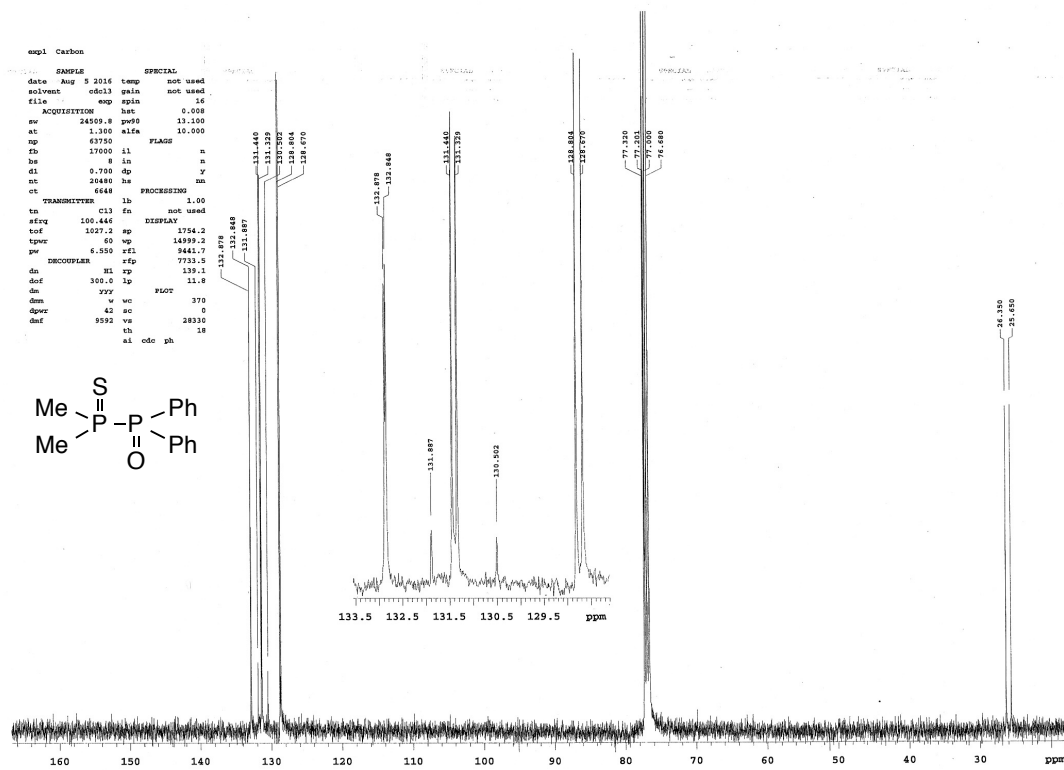
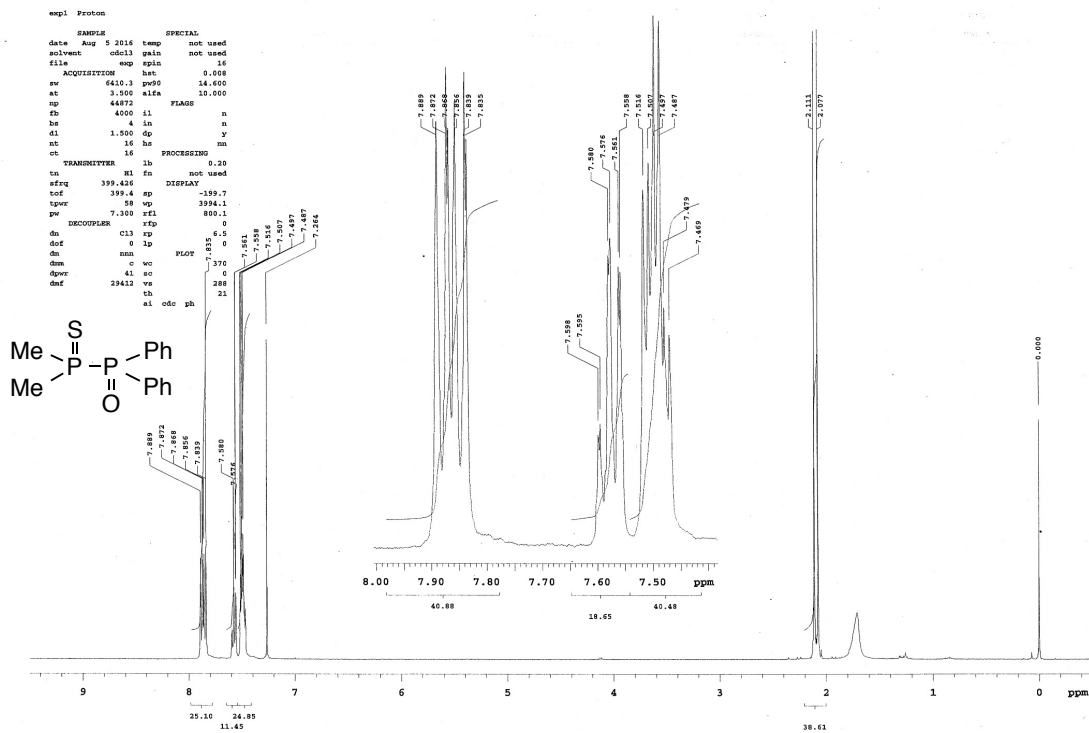


ex01 Phosphorus

```
SAMPLE SPECIAL
Date Jul 30 2016 temp not used
solvent c6d13 gain not used
file exp gain 16
ACQUISITION bat 0.008
aw 50000.0 pw90 9.000
at 3.600 sifa 10.000
sp 60000 FLAGS
fb 15000 il n
hs 4 lu n
dl 4.400 qp y
sc 256 hs nm
ot 28 PROCESSING nm
TRANSMITTE 931 fb not used
tn
sfreq 161.690 DISPLAY
tof 4231.8 sp -24998.5
tprc 58 sp 49998.5
pw 4.500 rfl 25000.0
DECOUPLER rfp 0
dn H1 rfp 49.9
dof 0 lp 0
dm
dmz mny PLOT 370
dmz w wc 0
dprc 42 eo 0
dof 9592 ve 227
th 28
al odc ph
```



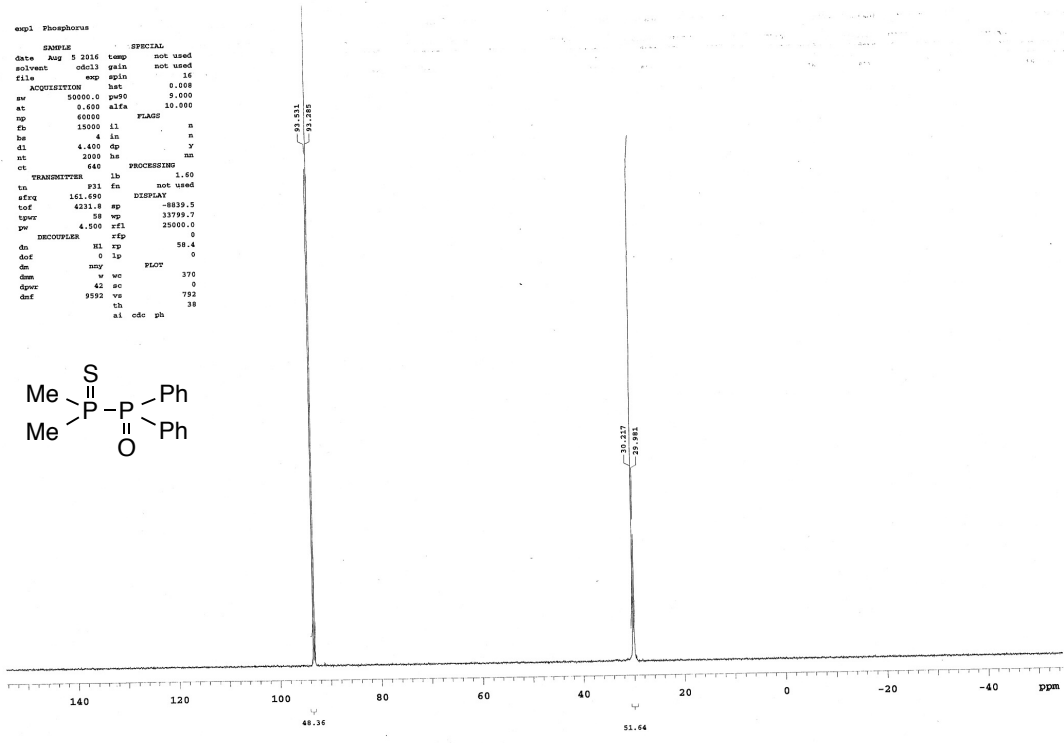
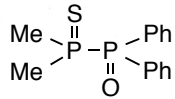
1,1-Dimethyl-2,2-diphenyldiphosphine 2-oxide 1-sulfide (6g)



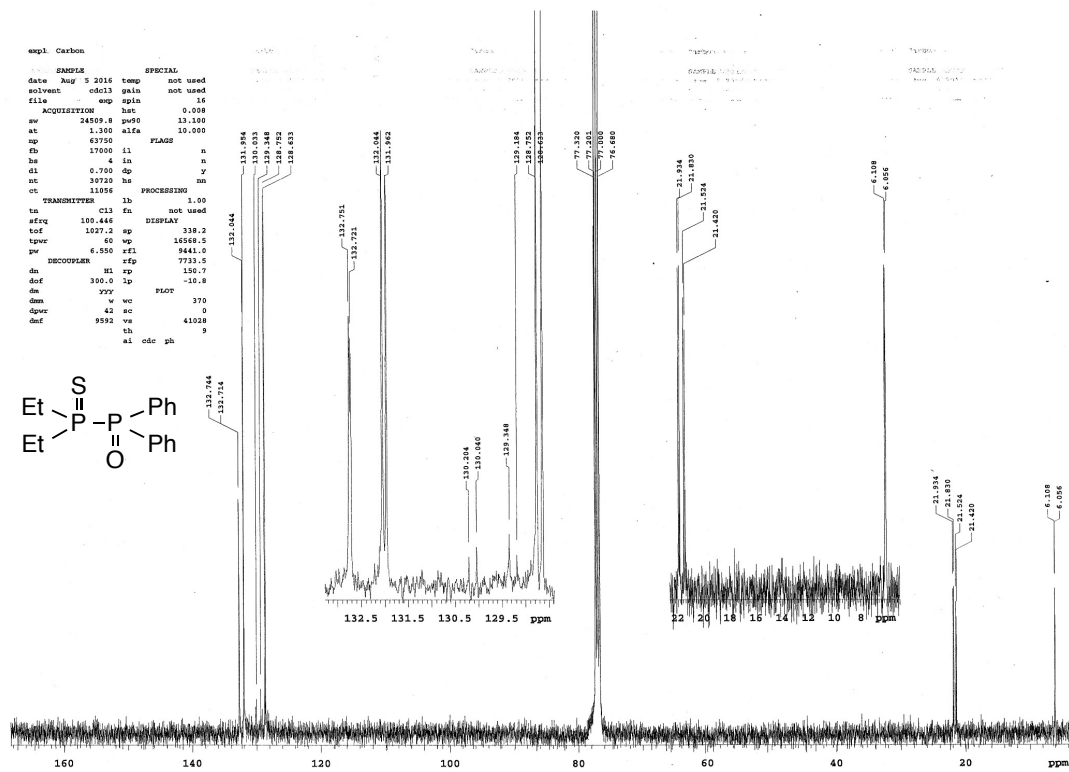
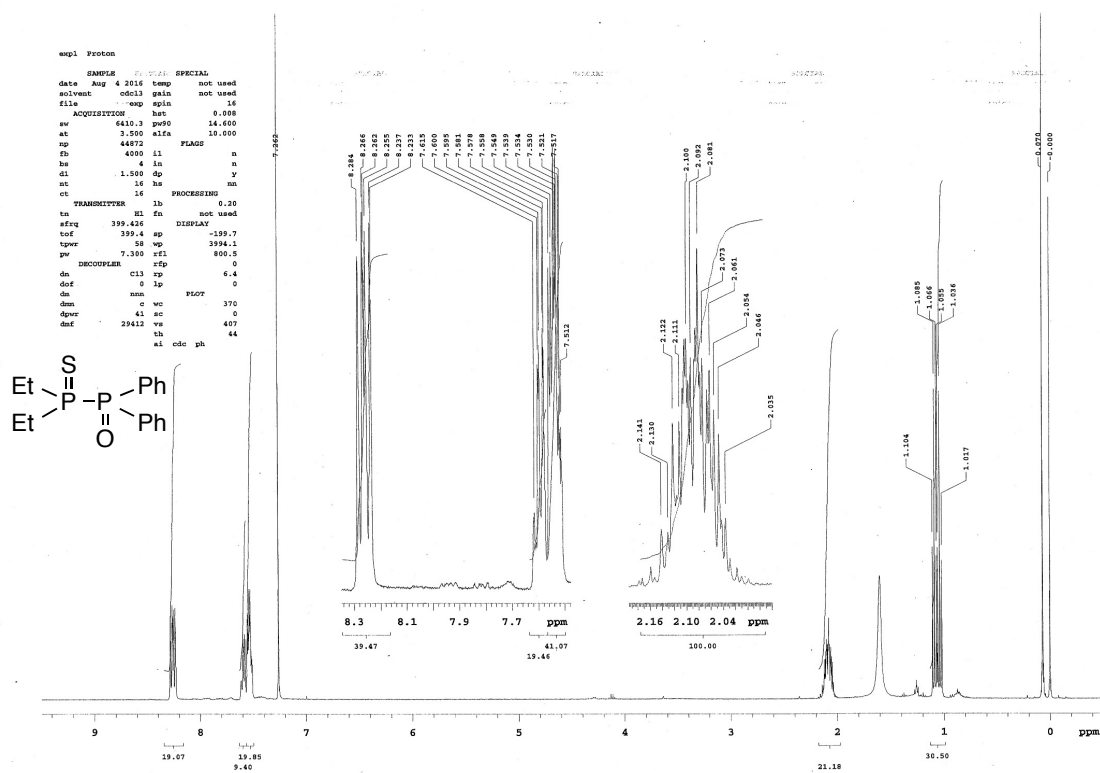
```

exp1 Phosphorus
SAMPLE SPECIAL
date Aug 5 2016 temp not used
solvent odcl3 gain not used
file exp gain 16
ACQUISITION hsc 0.008
sw 20000.0 pufo 2.000
at 0.600 alfa 10.000
ap 60000 FLAG n
fo 15000 ll n
hs 4 in n
dl 4.000 op y
st 2000 hs nm
ct
TRANSMITTER lb 1.60
tn f31 fn not used
sfrq 161.690 DISPLAY
tcf 4231.8 sp -8939.5
tprc 58 wp 13799.7
pw 4.500 rfi 25000.0
DECOUPLER rfp 0
dn hl rp 58.4
dnc 0 sp 0
dm nuy PLOT
dm w wc 370
dpcr 43 ac 0
dnf 9552 vs 792
ch
al odo ph 38

```

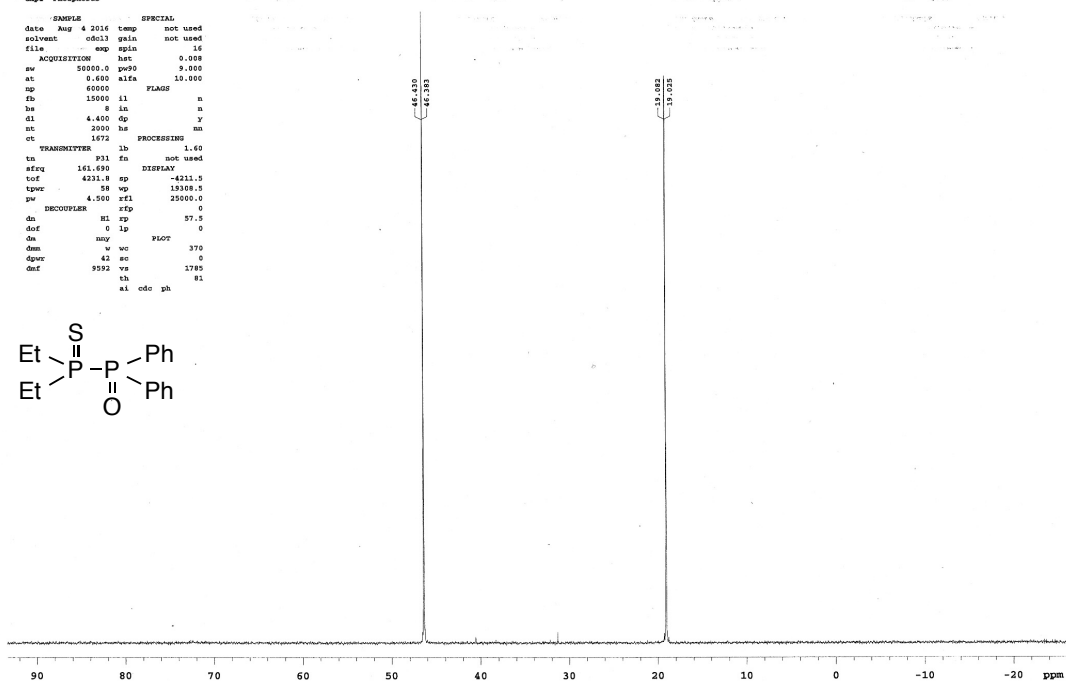
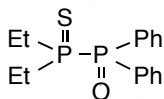


1,1-Diethyl-2,2-diphenyldiphosphine 2-oxide 1-sulfide (6h)



expt Phosphorus

```
SAMPLE
date Aug 4 2016 temp not used
solvent cdcl3 gain not used
file exp spin 16
ACQUISITION
aw 50000.0 pw90 9.000
ax 0.600 rfa 10.000
ap 60000
fb 15000 il n
hs 8 ln n
dl 4.400 op Y
sc 2000 hc mm
ct 1672 PROCESSING
TRANSMITTER
tn 931 fb not used
afreq 161.690 DISPLAY
tof 4231.8 op -4231.5
tprc 58 wp 15308.5
pv 4.500 rfl 25000.0
DECOUPLER
dn 0 rfp 0
dof 0 lp 0
ds any plot 370
dm w wc 0
dprc 42 ac 0
dcr 9392 vs 1785
sh 01
nl cdo ph 01
```

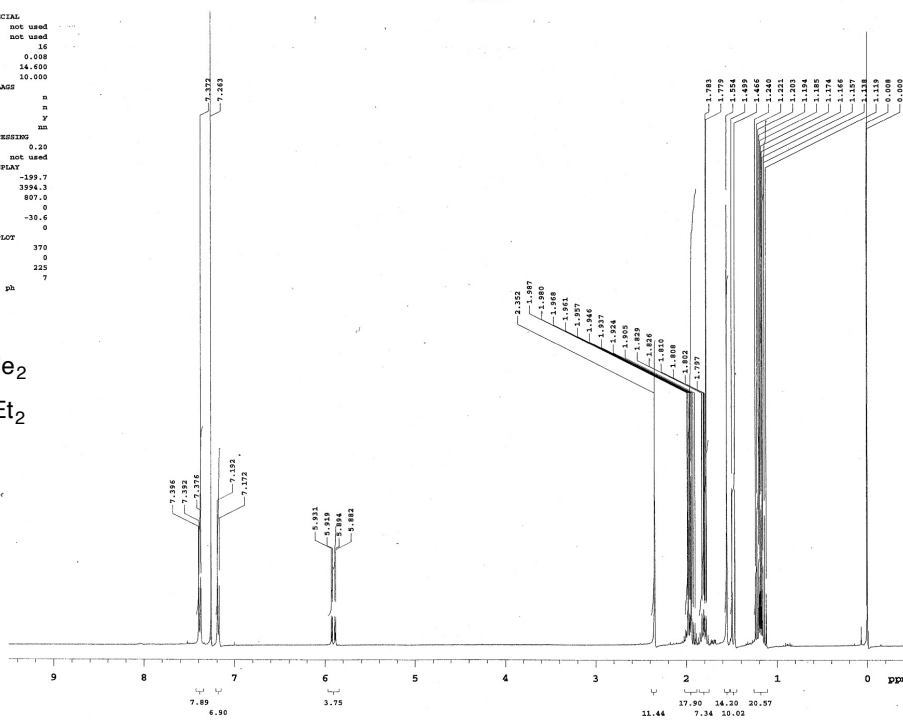
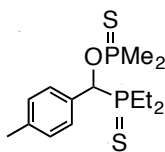


[1-(Dimethylthiophosphinoyloxy)-4-methylbenzyl]diethylphosphine sulfide (11)

expt Proton

```

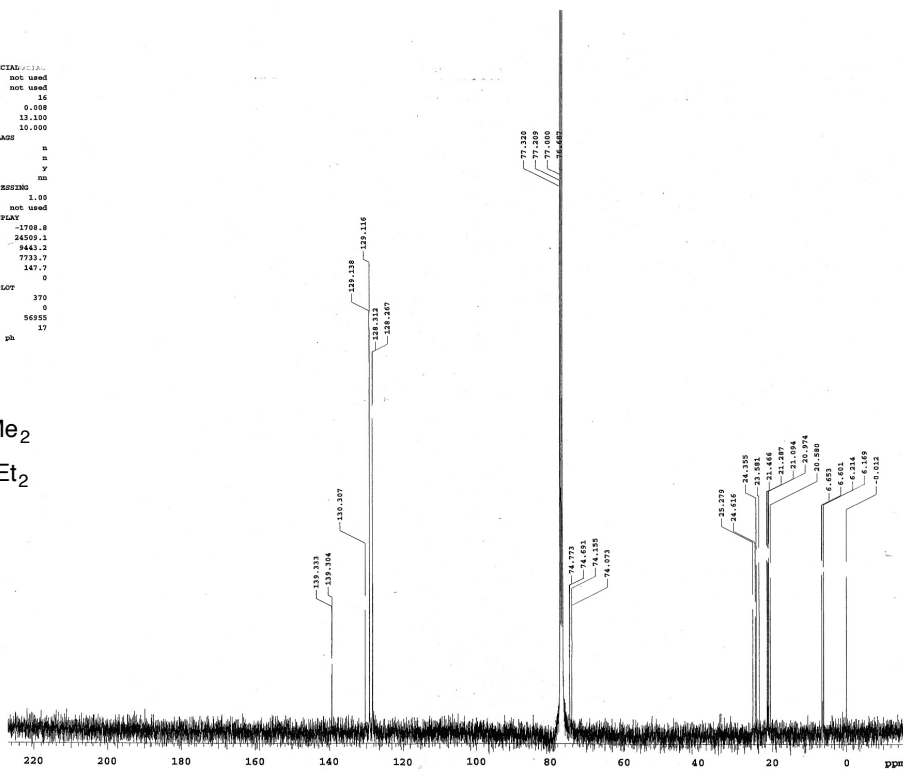
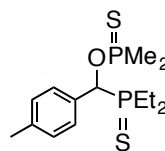
SAMPLE
date 08 2016 temp not used
solvent cdcl3 gain not used
file exp sgin 16
ACQUISITION hnt 0.008
sw 6411.3 ppp0 14.000
at 3.500 aifa 10.000
sp 44872
fn 4000 l1 FLAGS n
hs 4 in n
hl 1.500 sp y
nt 16 ha nm
ct 16
TRANSMITTER lb 0.20
tn hl fn not used
afreq 399.434 DISPLAY
tof 399.5 -199.7
tpwr 58 wp 3994.3
pw 7.300 rfi 807.0
DECOUPLER rfp 0
ds C13 rp -30.6
dnt 0
dm nm PLOT
dmw c wc 370
dpr 41 ac 0
dnf 29412 vs 225
al odc ph 7
    
```



expt Carbon

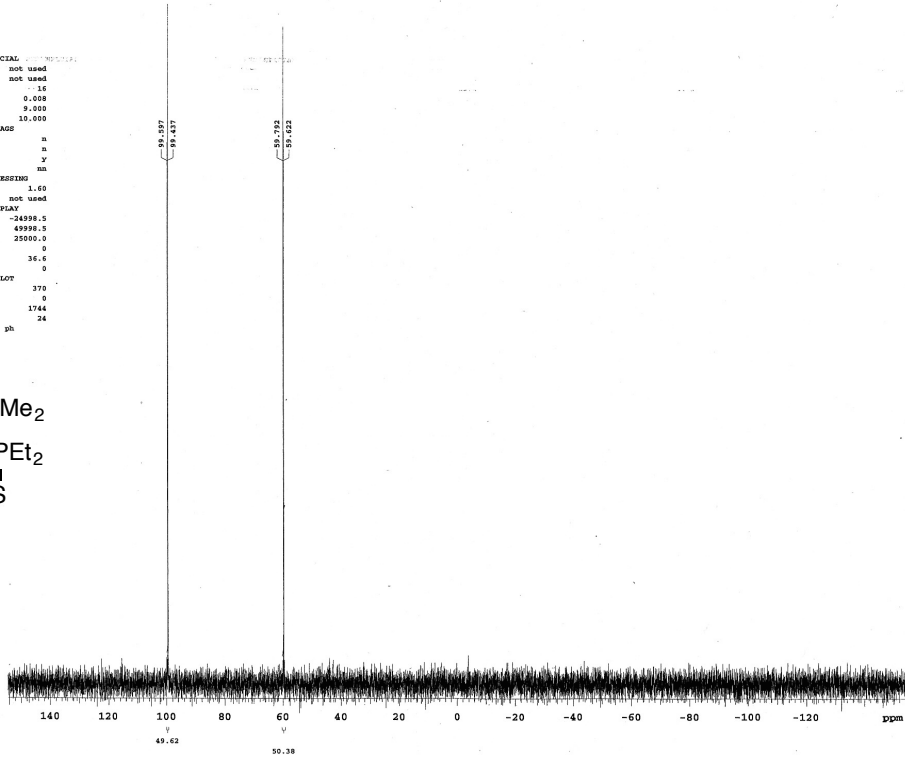
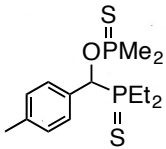
```

SAMPLE
date 08 2016 temp not used
solvent cdcl3 gain not used
file exp sgin 16
ACQUISITION hnt 0.008
sw 24509.8 ppp0 12.100
at 1.300 aifa 10.000
sp 63700
fn 12000 l1 FLAGS n
hs 4 in n
hl 0.700 sp y
nt 30000 ha nm
ct 18556
TRANSMITTER lb 1.00
tn C13 fn not used
afreq 100.448 DISPLAY
tof 1007.1 sp -1708.8
tpwr 60 wp 24509.1
pw 6.550 rfi 9440.2
DECOUPLER rfp 7933.7
ds hl rp 147.7
dnt 100.0 lp 0
dm yyy PLOT
dmw w wc 370
dpr 42 ac 0
dnf 9592 vs 56955
al odc ph 17
    
```

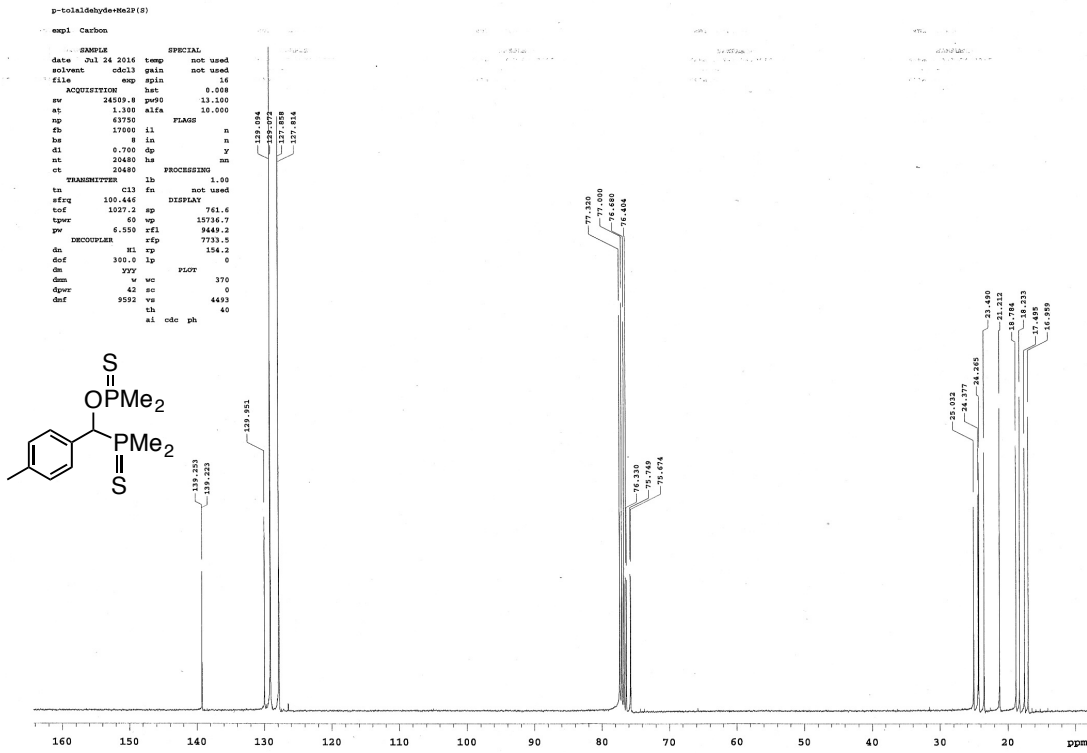
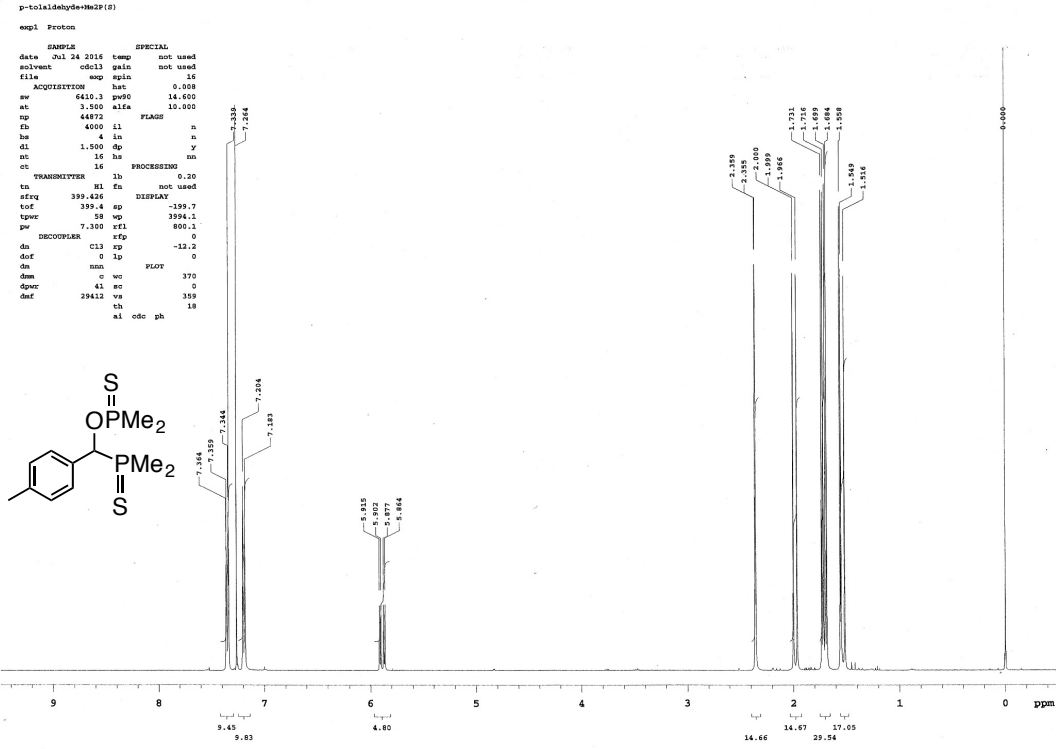


exp1. Phosphorus

SAMPLER		SPECIAL		MULTIPLI	
date	Jun 8 2016	temp	not used		
solvent	cdcl3	gain	not used		
file		spin	16		
ACQUISITION		bat	0.008		
sv	50000.0	pu90	9.000		
at	0.400	alfa	10.000		
ap	60000				
fb	15000	l1	n		
ba	4	la	n		
dl	4.400	dp	y		
nt	236	he	mm		
ct	24				
TRANSMITTER		lb	1.60		
ts	231	fu	not used		
efrq	161.693				
tof	4231.9	sp	-24898.5		
tpwr	300	wp	48998.5		
pw	4.500	rfl	25000.0		
DECOUPLER		rfd	0		
ds	31	rp	36.6		
dof	0	lp	0		
ds	any				
dm	v	wc	370		
dpr	42	sc	0		
daf	932	ve	1944		
		th	24		
		sl	ode	ph	24



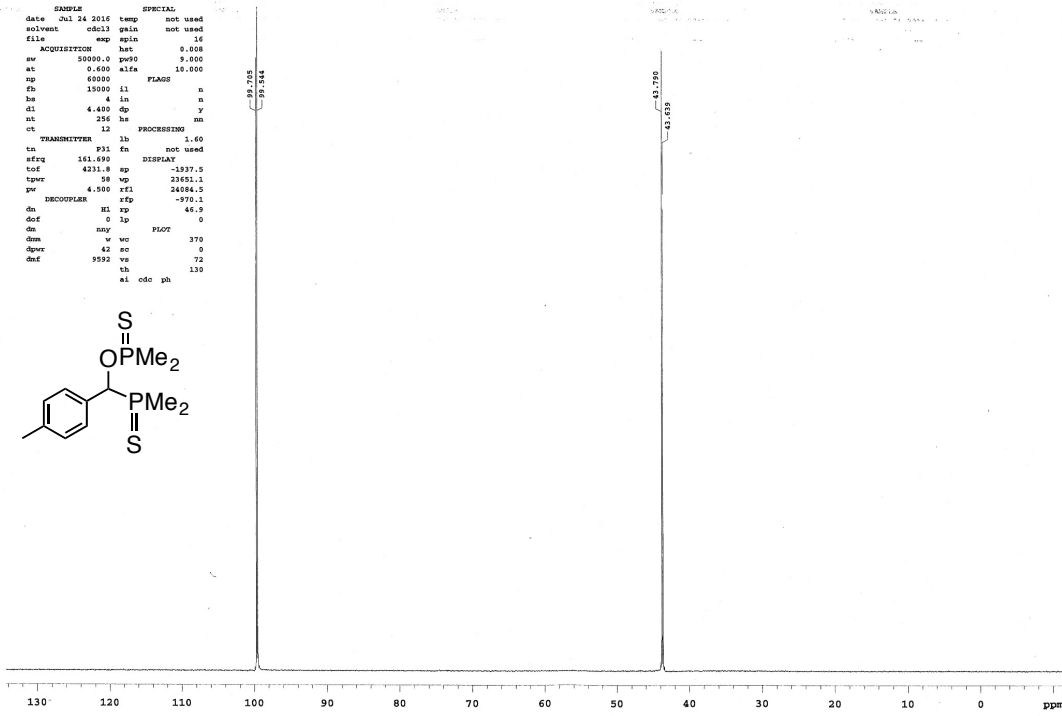
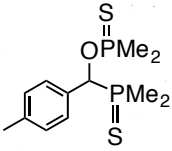
[1-(Dimethylthiophosphinoyloxy)-4-methylbenzyl]dimethylphosphine sulfide (13)



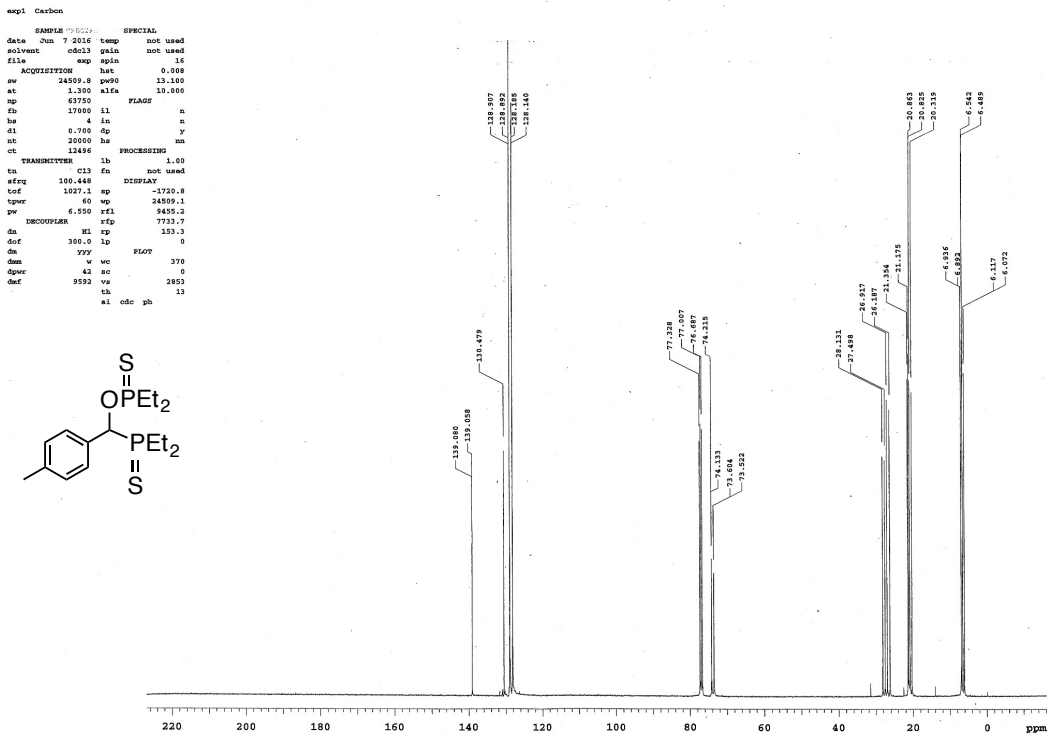
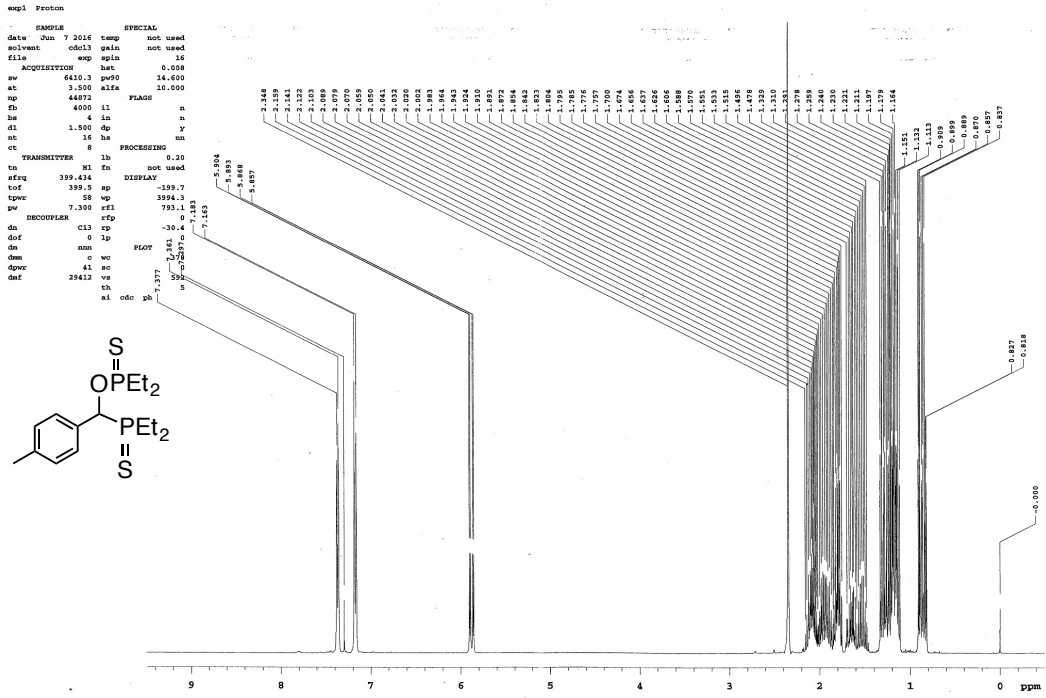
p-tolaldehyde+Me2P(S)

exp1 Phosphorus

```
SAMPLE SPECIAL
date Jul 14 2016 temp not used
solvent cdcl3 gain not used
file          exp spin 16
ACQUISITION  het 0.008
sw 5000.0 pw90 9.000
at 0.400 aifa 10.000
np 60000
fb 15000 il n
hs 4 in n
dl 4.400 dp y
nl 256 ht mn
ct 10 PROCESSING 1.60
TRANSMITTER 3b not used
ts p31 fa
sfrq 161.690 DISPLAY
tof 4231.8 sp -1937.5
tqwr 58 wv 23651.1
pw 4.500 xfl 24084.5
DECOUPLER H1 xp -970.1
dm 45.0
dof 0 lp 0
dm any wv PLOT 370
dprv 42 sc 0
dnt 1020 vs 72
th 130
al cdc ph
```



[1-(Diethylthiophosphinoyloxy)-4-methylbenzyl]diethylphosphine sulfide (14)



exp1 Phosphorus

```
SAMPLE          SPECIAL
date 08m 7 2016 temp not used
solvent cdcl3 gain not used
file          exp spin 16
ACQUISITION   hsc 0.000
sv 50000.0 pu90 9.000
at 0.000 alfa 10.000
rg 60000          FLAGS
fb 15000 il      n
hs 4 in         n
dl 4.400 dp     Y
nt 256 ha      nn
ct 0          PROCESSING
TRANSMITTER   lb 1.60
ts          p31 fn not used
sfreq 161.053 DSIEMAN
tof 4231.9 sp -24999.5
tpr 58 vp 49999.5
pr 4.500 rfl 25000.0
DECOUPLER    xl xp 0
ds 0 ip 56.5
dof          0
dm          any PLOT 370
dum          w wo 48
dpr 42 so 0
daf 9592 va 48
          ls 12
          al cdc ph
```

