Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

For

Rhodium-Catalyzed P–P Bond Exchange Reaction of Diphosphines

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Contents

Page S2	Supplementary Materials
Page S2-S16	Typical procedures and The Spectral and Analytical Data
Page S3-S6, S14	Crystal Data
Page S17	References
Page S18-S59	NMR Spectra

Supplimentary Materials

^{1}H-, ^{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 μ m) was employed for flash column chromatography. $RhH(dppe)_2$[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 $RhH(dppe)_2$ (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, Rf = 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.

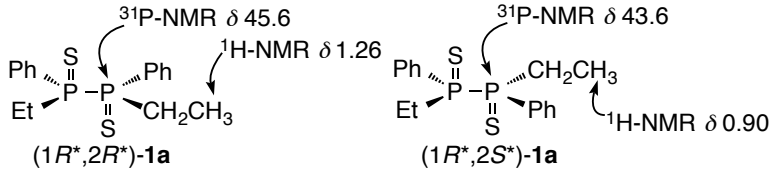
Crystal data and structure refinement

Compound: (1*R**,2*S**)-**1a**
Formula: C16 H20 P2 S2
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) Å α = 90.00 °
b = 7.1672(4) Å β = 101.490(2) °
c = 13.3103(8) Å γ = 90.00 °
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/a
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. ^{1}H-NMR (400 MHz, $CDCl_3$) 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). ^{13}C-NMR (100 MHz, $CDCl_3$) 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). ^{31}P-NMR (162 MHz, $CDCl_3$) 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 $C_{16}H_{20}P_2S_2$: 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. ^{1}H-NMR (400 MHz, $CDCl_3$) 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}P{^{1}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 Cacld for $C_{16}H_{20}P_2S_2$: 338.0482. Found: 338.0472.



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

In a two-necked flask equipped with a magnetic stirrer bar were placed $RhH(dppe)_2$ (10.0 mol%, 22.5 mg), 1,2-dimethyl-1,2-diphenyldiphosphine disulfide **1b** [(1*R**,2*R**)-**1b**, 0.75 mmol, 232.5 mg, Rf = 0.4 (toluene)], and 1,2-diethyl-1,2-diphenyldiphosphine disulfide **1a** [(1*R**,2*R**)-**1a**:(1*R**,2*S**)-**1a** = 1:2, 0.25 mmol, 84.5 mg, Rf = 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 (1*R**,2*R**)-1-ethyl-2-methyl-1,2-diphenyldiphosphine disulfide [(1*R**,2*R**)-**2ab**] and (1*R**,2*S**)-1-ethyl-2-methyl-1,2-diphenyldiphosphine disulfide [(1*R**,2*S**)-**2ab**] [93.9 mg, 58%, (1*R**,2*R**)-**2ab**:(1*R**,2*S**)-**2ab** = 2:1 mixture, Rf = 0.6 (toluene)]. The (1*R**,2*R**)-**2ab** and (1*R**,2*S**)-**2ab** were isolated by recrystallization. (1*R**,2*S**)-**2ab** (23 mg) was isolated by recrystallization twice from hexane, and (1*R**,2*R**)-**2ab** (43 mg) was isolated by recrystallization twice of the residue. The structure of (1*R**,2*S**)-**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/a
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)

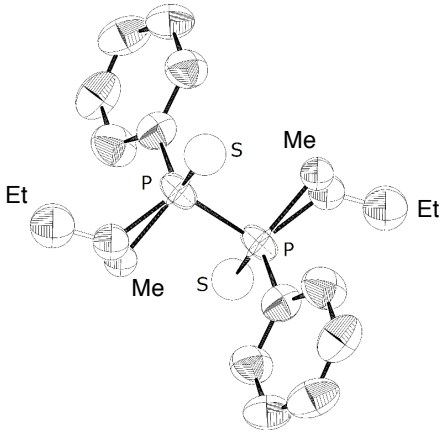
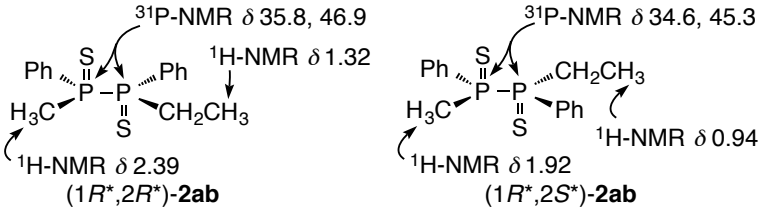


Figure S1. ORTEP view of (1*R**,2*S**)-**2ab**. The methyl and ethyl groups on the phosphorous atom were disordered in two positions (the occupancy factor 50% for each).

(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). ^{1}H-NMR (400 MHz, $CDCl_3$) 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). ^{13}C-NMR (100 MHz, $CDCl_3$) 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). ^{31}P{^{1}H}-NMR (162 MHz, $CDCl_3$) 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 $C_{15}H_{18}P_2S_2$: 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). ^{1}H-NMR (400 MHz, $CDCl_3$) 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). ^{13}C-NMR (100 MHz, $CDCl_3$) 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). ^{31}P{^{1}H}-NMR (162 MHz, $CDCl_3$) δ 34.6 (d, J = 29.2 Hz), 45.3 (d, J = 29.2 Hz). IR (KBr) 3054,

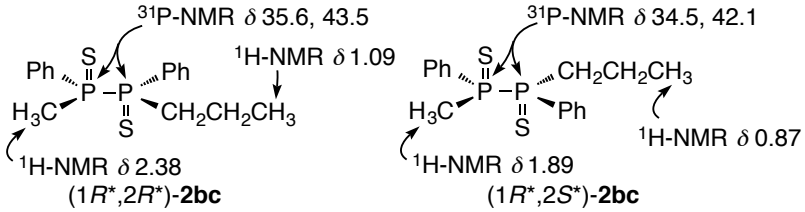
2975, 1436, 1100 cm^{-1}. MS (EI) m/z 324 (M^+, 48%), 169 (M^+-155, 100%). HRMS Calcd for $C_{15}H_{18}P_2S_2$: 324.0325. Found: 324.0332.



2bc, **2ac**, **2ad**, and **2cd** were used as a mixture of (1*R**,2*R**)- and (1*R**,2*S**)-isomers. The ^{31}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}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}P- and ^{1}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.

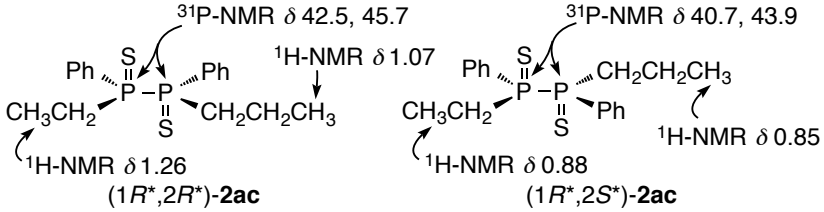
(1*R,2*R**)-1-Methyl-2-propyl-1,2-diphenyldiphosphine disulfide [(1*R**,2*R**)-2bc] and (1*R**,2*S**)-1-methyl-2-propyl-1,2-diphenyldiphosphine disulfide [(1*R**,2*S**)-2bc] [(1*R**,2*R**)-2bc:(1*R**,2*S**)-2bc = 3:2 mixture]:** Colorless oil. The data (a) are those of (1*R**,2*R**)-**2bc**, and the data (b) (1*R**,2*S**)-**2bc**. ^{1}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}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}P{^{1}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 (1*R**,2*S**)-**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): **(1*R**,2*R**)-2bc** and **(1*R**,2*S**)-2bc** Rf = 0.6, **1b** Rf = 0.4, **1c** Rf = 0.7.



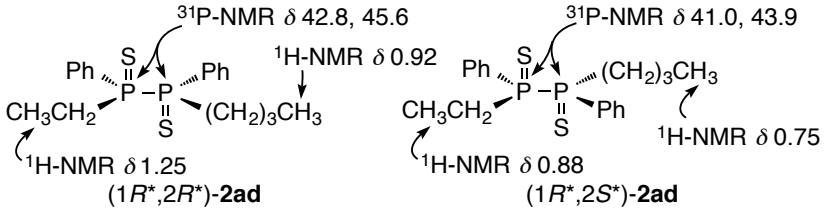
(1*R,2*R**)-1-Ethyl-2-propyl-1,2-diphenyldiphosphine disulfide [(1*R**,2*R**)-2ac] and (1*R**,2*S**)-1-ethyl-2-propyl-1,2-diphenyldiphosphine disulfide [(1*R**,2*S**)-2ac] [(1*R**,2*R**)-2ac:(1*R**,2*S**)-2ac = 2:1 mixture]:** Colorless oil. The data (a) are those of (1*R**,2*R**)-**2ac**, and the data (b) (1*R**,2*S**)-**2ac**. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.85 (3H, t, J = 7.6Hz)[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}P{^{1}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.



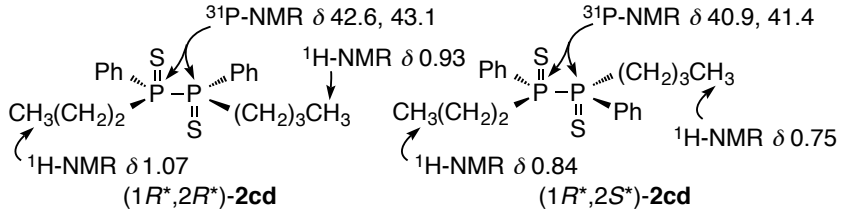
(1*R,2*R**)-1-Butyl-2-ethyl-1,2-diphenyldiphosphine disulfide [(1*R**,2*R**)-2ad] and (1*R**,2*S**)-1-butyl-2-ethyl-1,2-diphenyldiphosphine disulfide [(1*R**,2*S**)-2ad] [(1*R**,2*R**)-2ad:(1*R**,2*S**)-2ad = 2:1 mixture]:** Yellow oil. The data (a) are those of (1*R**,2*R**)-**2ad**, and the data (b) (1*R**,2*S**)-**2ad**. ^{1}H-NMR (400 MHz, $CDCl_3$) 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]. ^{13}C-NMR (100 MHz, $CDCl_3$) 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]. ^{31}P{^{1}H}-NMR (162 MHz, $CDCl_3$) 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): **(1*R**,2*R**)-2ad** and **(1*R**,2*S**)-2ad** Rf = 0.6, **1a** Rf = 0.5, **1d** Rf = 0.7.



(1*R,2*R**)-1-Butyl-2-propyl-1,2-diphenyldiphosphine disulfide [(1*R**,2*R**)-2cd] and (1*R**,2*S**)-1-butyl-2-propyl-1,2-diphenyldiphosphine disulfide [(1*R**,2*S**)-2cd] [(1*R**,2*R**)-2cd:(1*R**,2*S**)-2cd = 2:1 mixture]:** Colorless oil. The data (a) are those of (1*R**,2*R**)-**2cd**, and the data (b) (1*R**,2*S**)-**2cd**. ^{1}H-NMR (400 MHz, $CDCl_3$) 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]. ^{13}C-NMR (100 MHz, $CDCl_3$) 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]. ^{31}P{^{1}H}-NMR (162 MHz, $CDCl_3$) 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 $C_{19}H_{28}P_2S_2$: 380.0951. Found: 380.0956. The aromatic carbons of (1*R**,2*R**)-**2cd** at δ 127.8, 131.7, and 131.8 were overlapped in two phenyl groups. The aromatic carbon of (1*R**,2*S**)-**2cd** at δ 128.3, 132.5, and 133.3 were also overlapped in two phenyl groups. Rf values (hexane:toluene = 2:1): **(1*R**,2*R**)-2cd** and **(1*R**,2*S**)-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}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}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}P{^{1}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 (M^+-93, 100%). HRMS Calcd for $C_{12}H_{20}P_2S_2$: 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 °C (MeOH). ^{1}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}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}P{^{1}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 (M^+-C_2H_5PS, 100%). HRMS Calcd for $C_{16}H_{20}P_2S_2$: 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). ^{1}H-NMR (400 MHz, $CDCl_3$) 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). ^{13}C-NMR (100 MHz, $CDCl_3$) 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). ^{31}P{^{1}H}-NMR (162 MHz, $CDCl_3$) 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 $C_6H_{16}P_2S_2$: 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). ^{1}H-NMR (400 MHz, $CDCl_3$) 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). ^{13}C-NMR (100 MHz, $CDCl_3$) 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). ^{31}P{^{1}H}-NMR (162 MHz, $CDCl_3$) 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 $C_8H_{20}P_2S_2$: 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). ^{1}H-NMR (400 MHz, $CDCl_3$) 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). ^{13}C-NMR (100 MHz, $CDCl_3$) 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). ^{31}P{^{1}H}-NMR (162 MHz, $CDCl_3$) 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 $C_{10}H_{24}P_2S_2$: 270.0795. Found: 270.0759. Rf values (toluene): **2gi** 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). ^{1}H-NMR (400 MHz, $CDCl_3$) 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}P{^{1}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 (M^+-29, 80%). HRMS Calcd for $C_{10}H_{24}P_2S_2$: 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. ^{1}H-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}P{^{1}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 $C_{14}H_{32}P_2S_2$: 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 °C (Hexane). ^{1}H-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}P{^{1}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 (M^+-$C_{12}H_{10}PS$, 100%). HRMS Calcd for $C_{24}H_{20}OP_2S$: 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. ^{1}H-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}P{^{1}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 (M^+-201, 100%). HRMS Calcd for $C_{14}H_{16}OP_2S$: 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. ^{1}H-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}P{^{1}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 (M^+-156, 100%). HRMS Calcd for $C_{16}H_{20}OP_2S$: 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 Aldehydes[9)]

In a two-necked flask equipped with a magnetic stirrer bar were placed $RhH(dppe)_2$ (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 °C (Hexane). ^{1}H-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}P{^{1}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 (M^+-121, 100%). HRMS Calcd for $C_{14}H_{24}OP_2S_2$: 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: C14 H24 O P2 S2
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 α = 90.00 °
b = 12.3783(6) Å β = 90.00 °
c = 22.5131(13) Å γ = 90.00 °
Temperature of data collection: 173(K)
Values of Z, R, GOF: Z = 4,
R(reflections) = 0.0606 (2694), wR2(reflections) = 0.1536 (4104)
GOF = 1.061
Radiation type: Mo K/a
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). ^{1}H-NMR (400 MHz, $CDCl_3$) 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). ^{13}C-NMR (100 MHz, $CDCl_3$) 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). ^{31}P{^{1}H}-NMR (162 MHz, $CDCl_3$) 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 $C_{12}H_{20}OP_2S_2$: 306.0431. Found: 306.0438.

[1-(Diethylthiophosphinoyloxy)-4-methylbenzyl]diethylphosphine sulfide (14): Colorless solid. Mp. 73.0-74.0 °C (Hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) 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). ^{13}C-NMR (100 MHz, $CDCl_3$) 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). ^{31}P{^{1}H}-NMR (162 MHz, $CDCl_3$) 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 $C_{16}H_{28}OP_2S_2$: 362.1057. Found: 362.1074.

References

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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.

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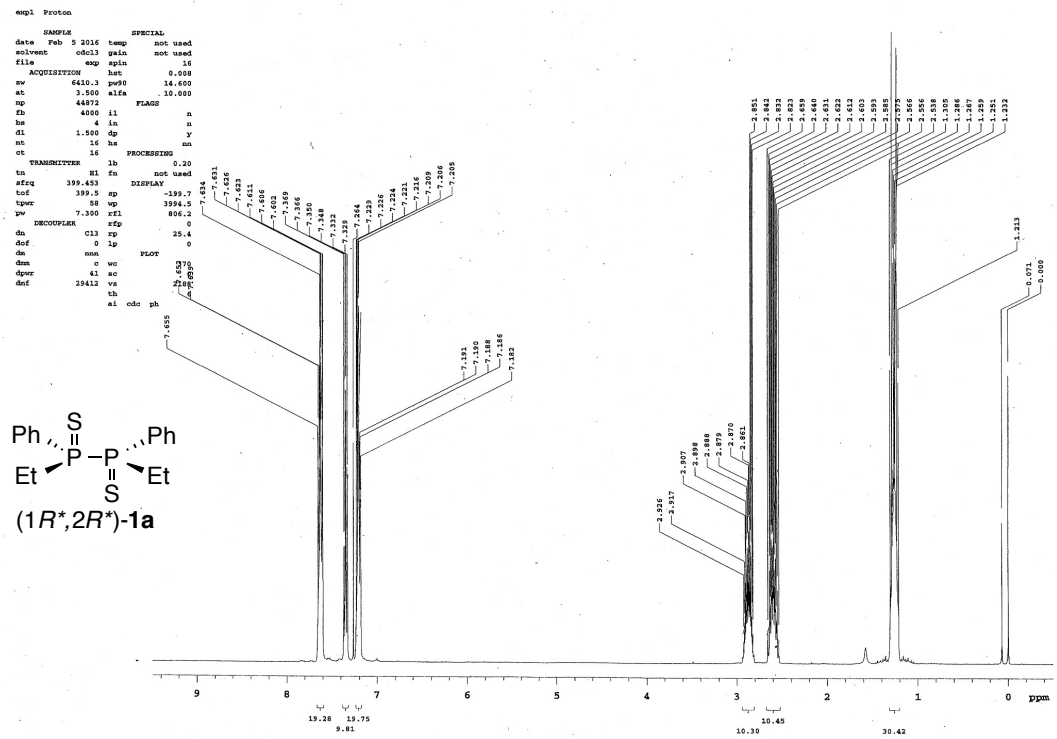
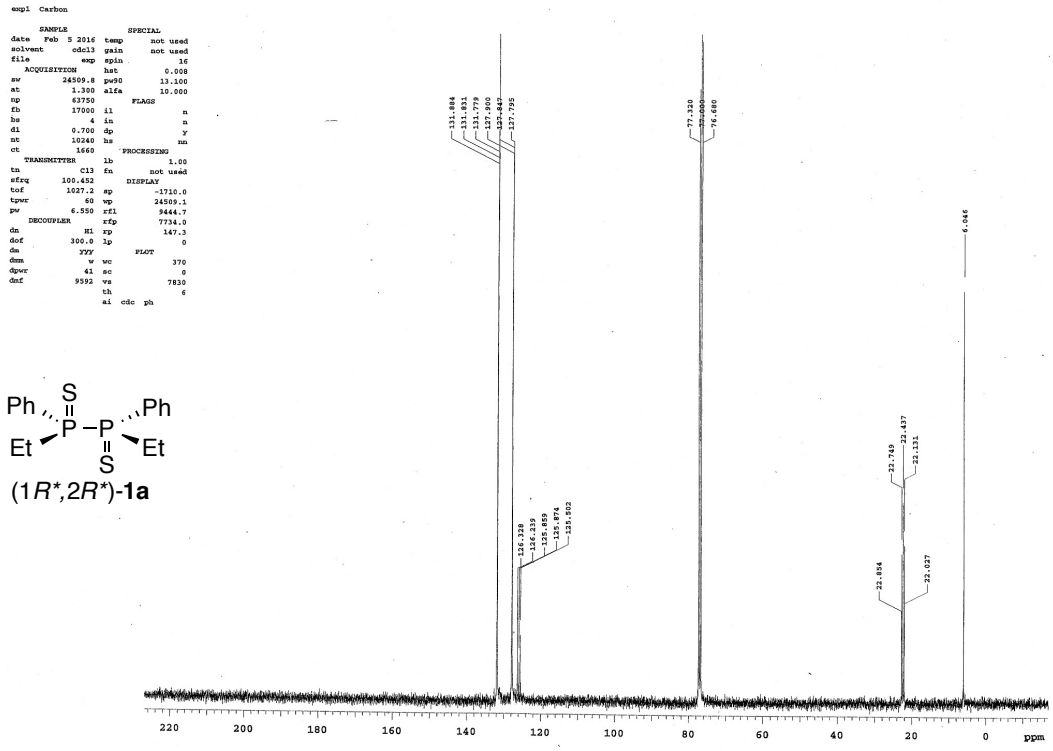
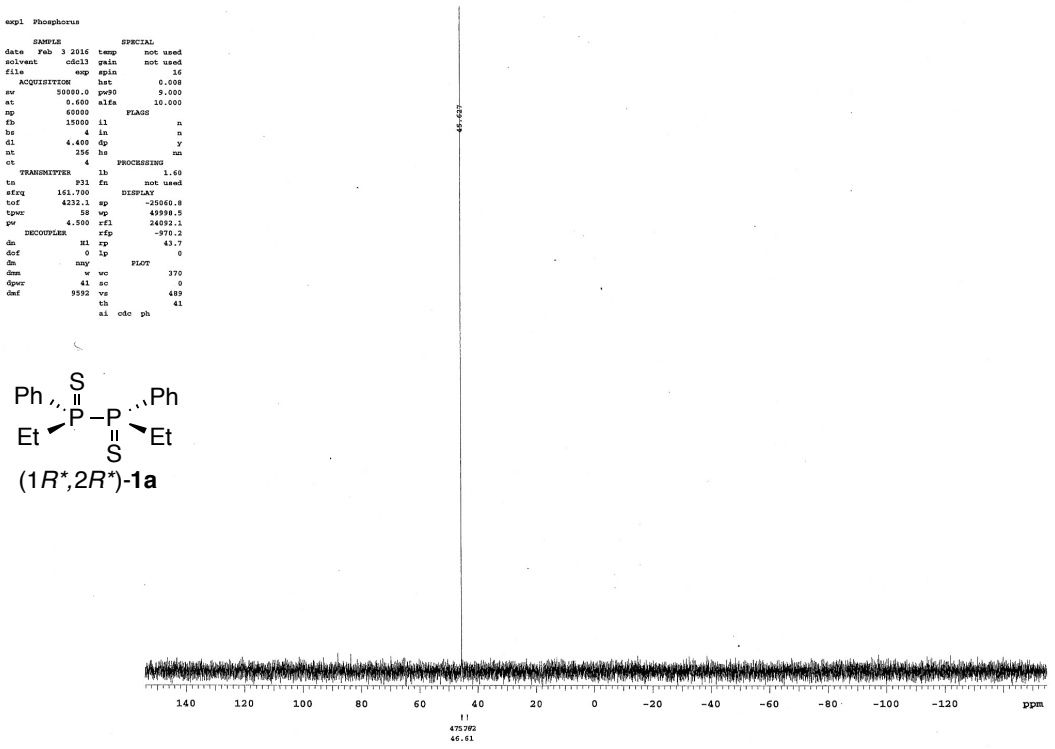
(1*R,2*R**)-1,2-diethyl-1,2-diphenyldiphosphine disulfide (1*R**,2*R**)-1a**



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80
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20
0
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-40
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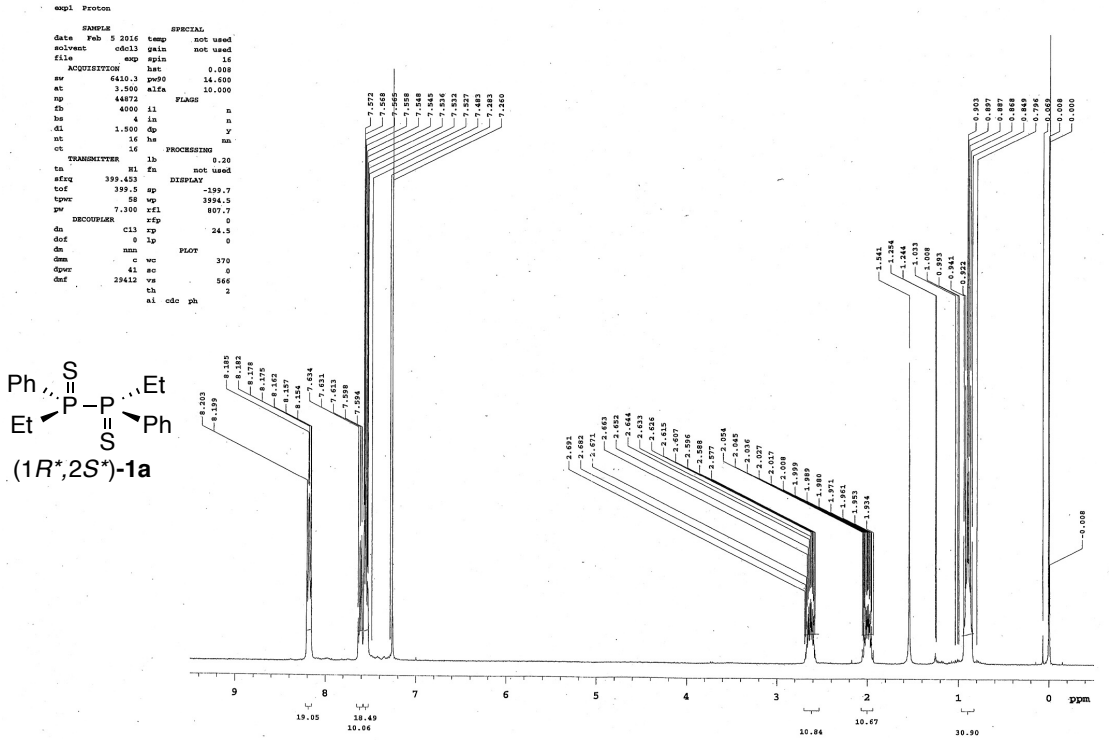
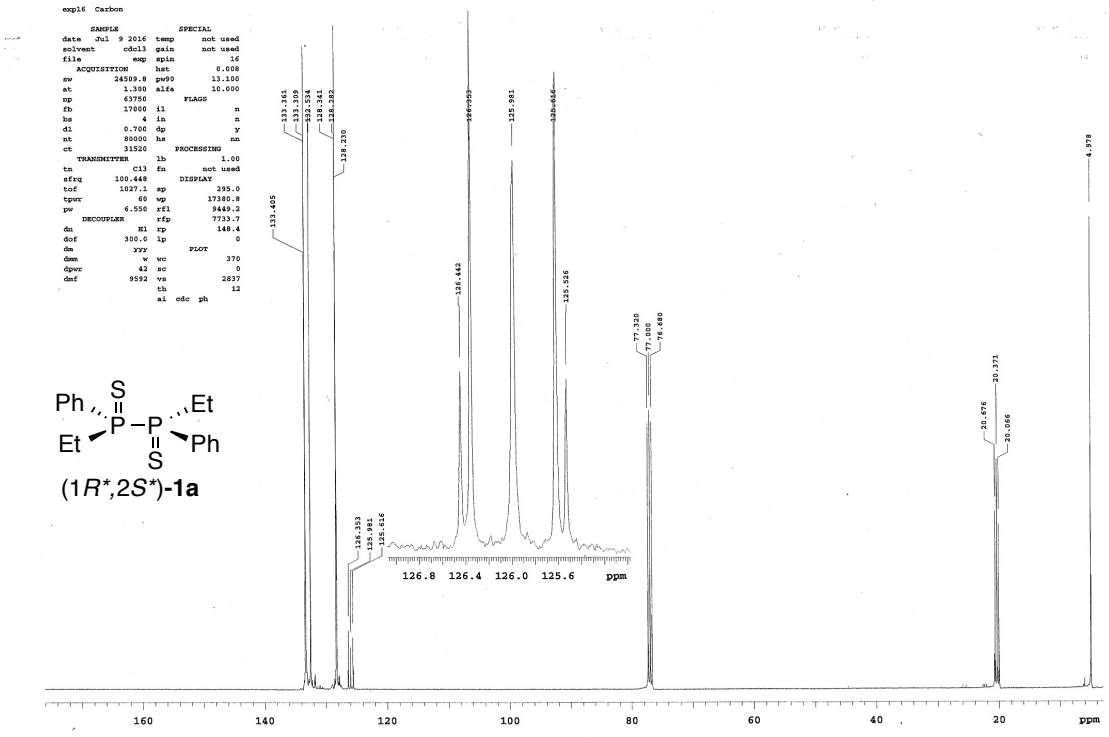
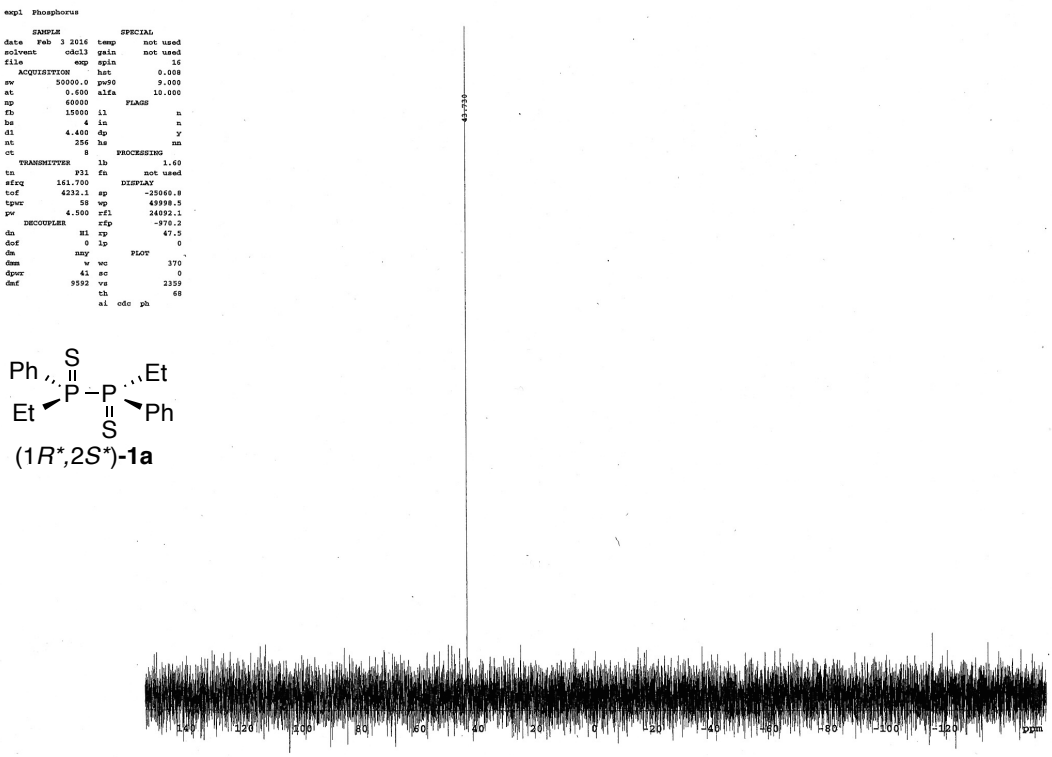
46.61

(1*R**,2*R**)-**1a**

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



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al odc ph
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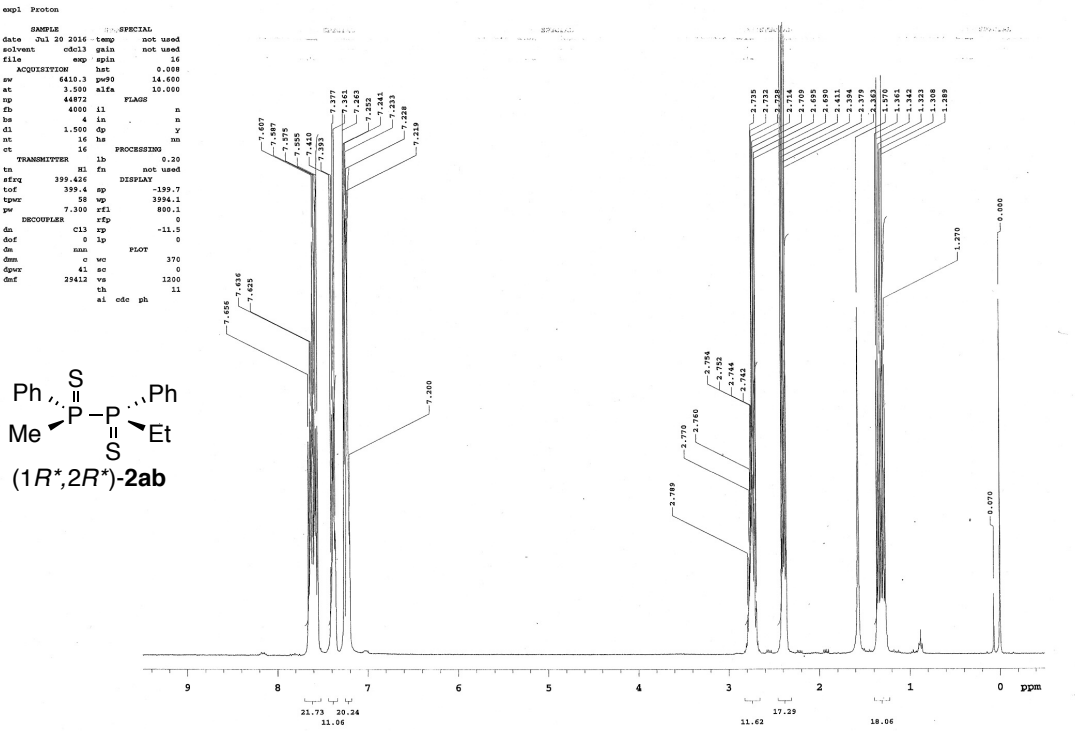
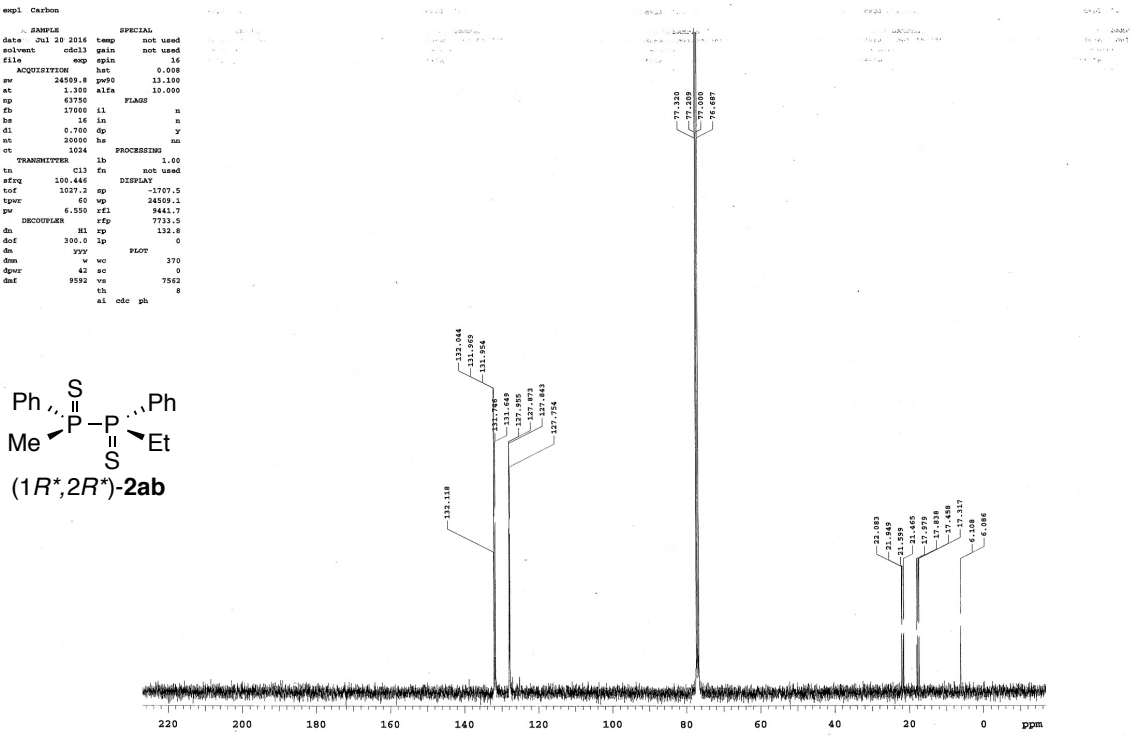
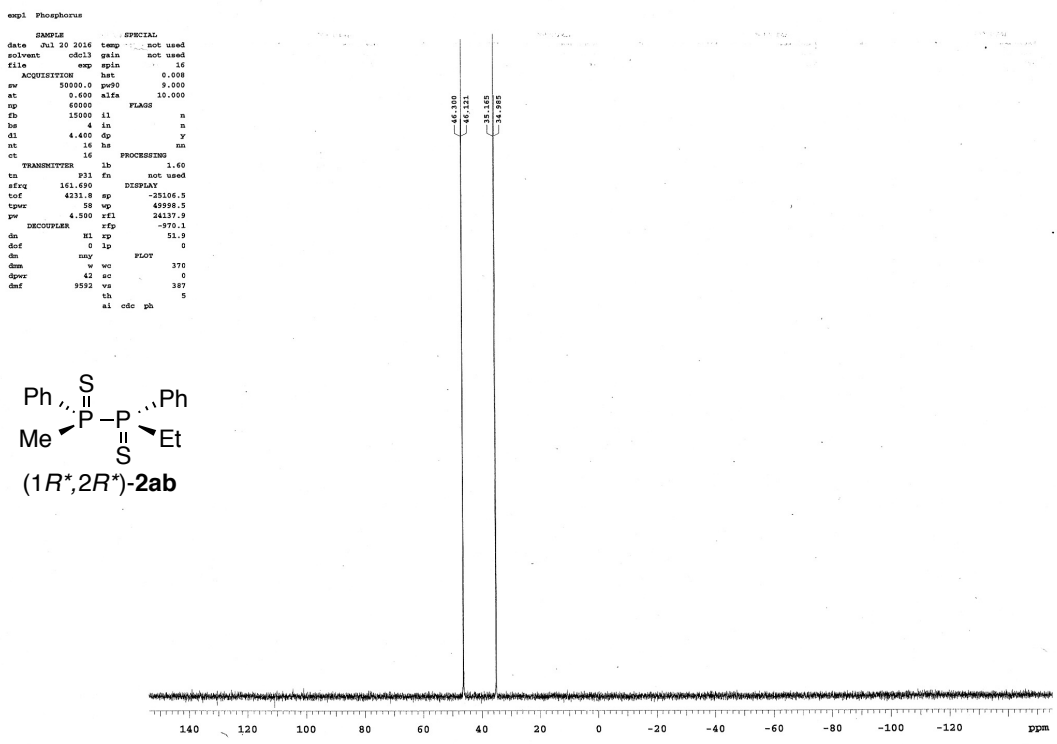
Ph
Et
Et
Ph
S
S
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
ppm

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

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



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ai cdc ph
Ph
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P
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P
S
Et
Ph
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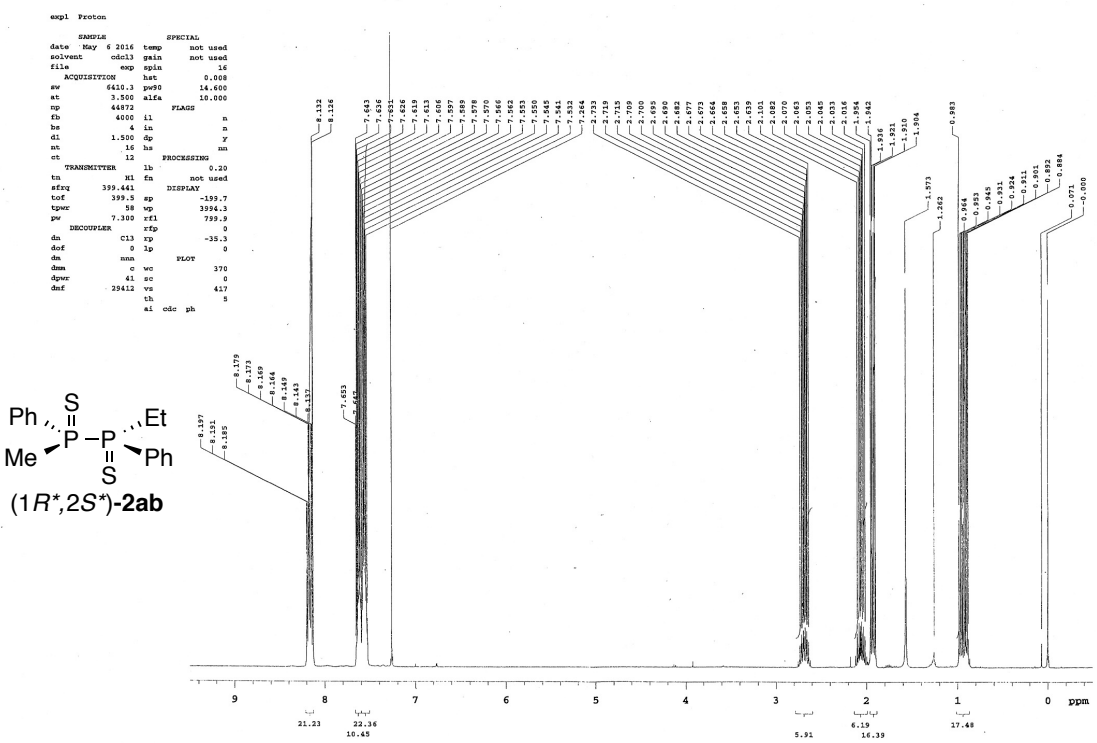
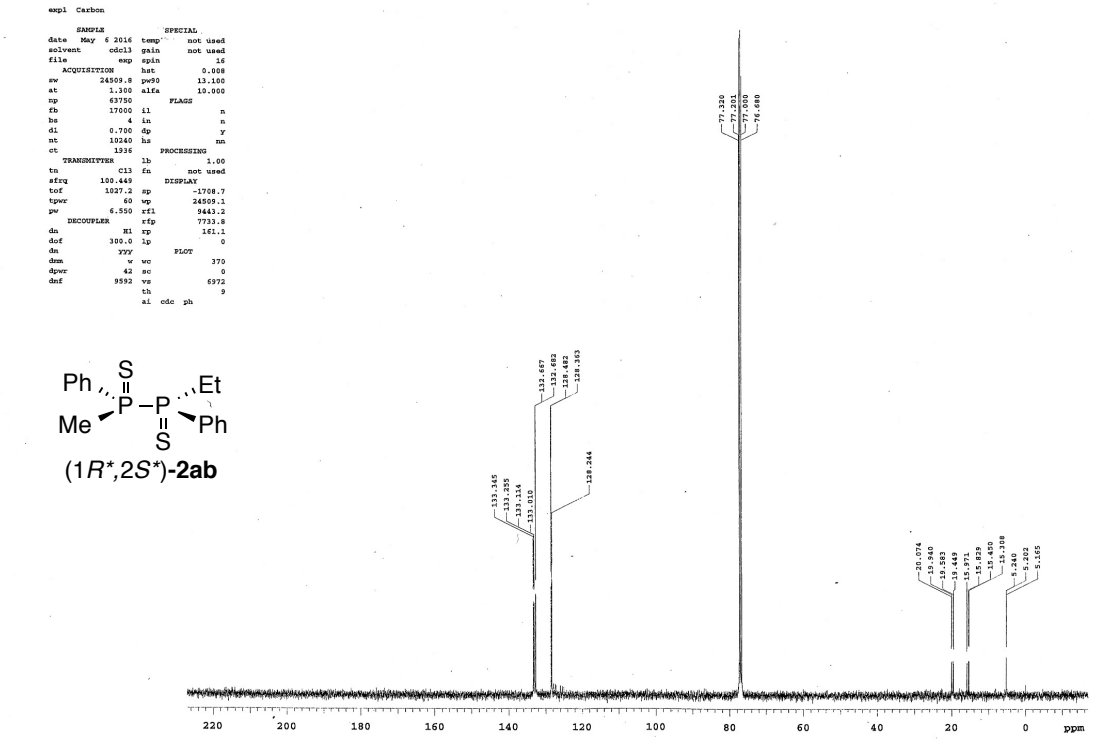
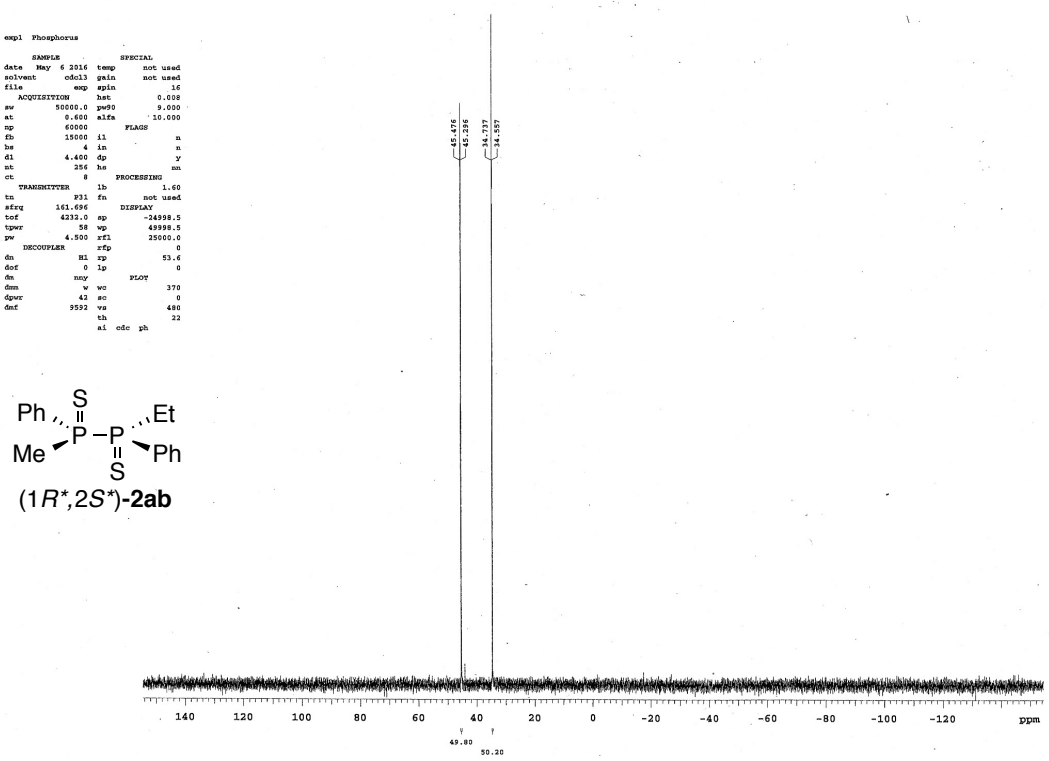
46.121
35.165
34.985
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
ppm

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



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-80
-100
-120
ppm
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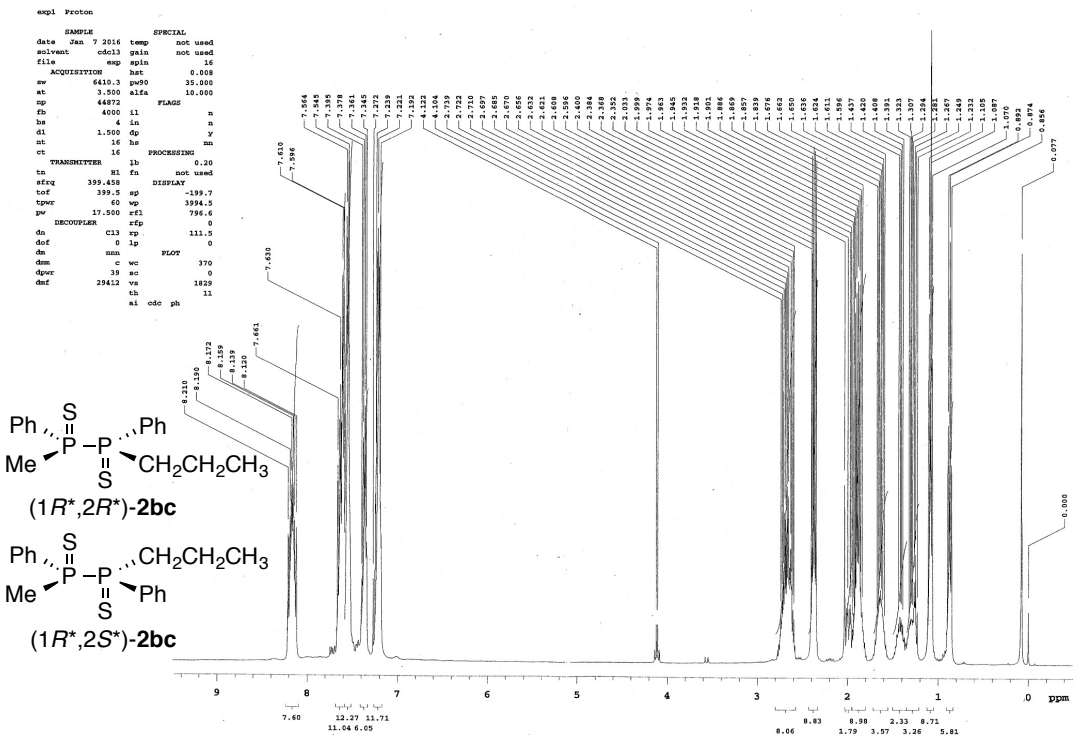
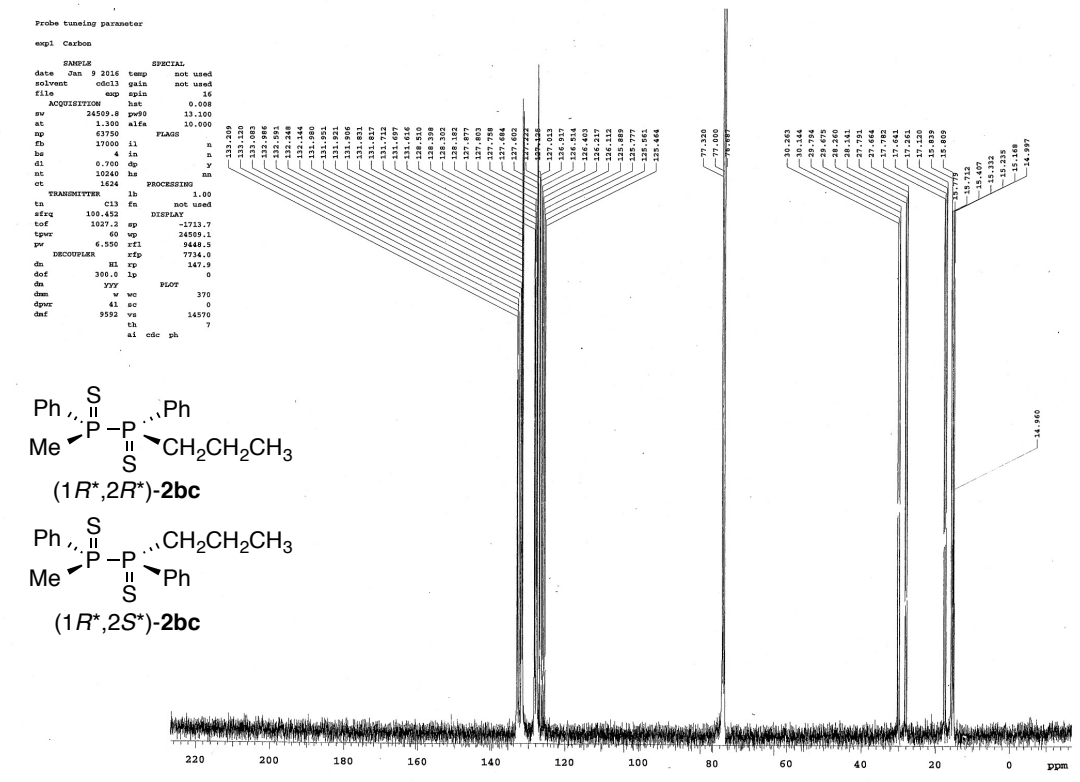
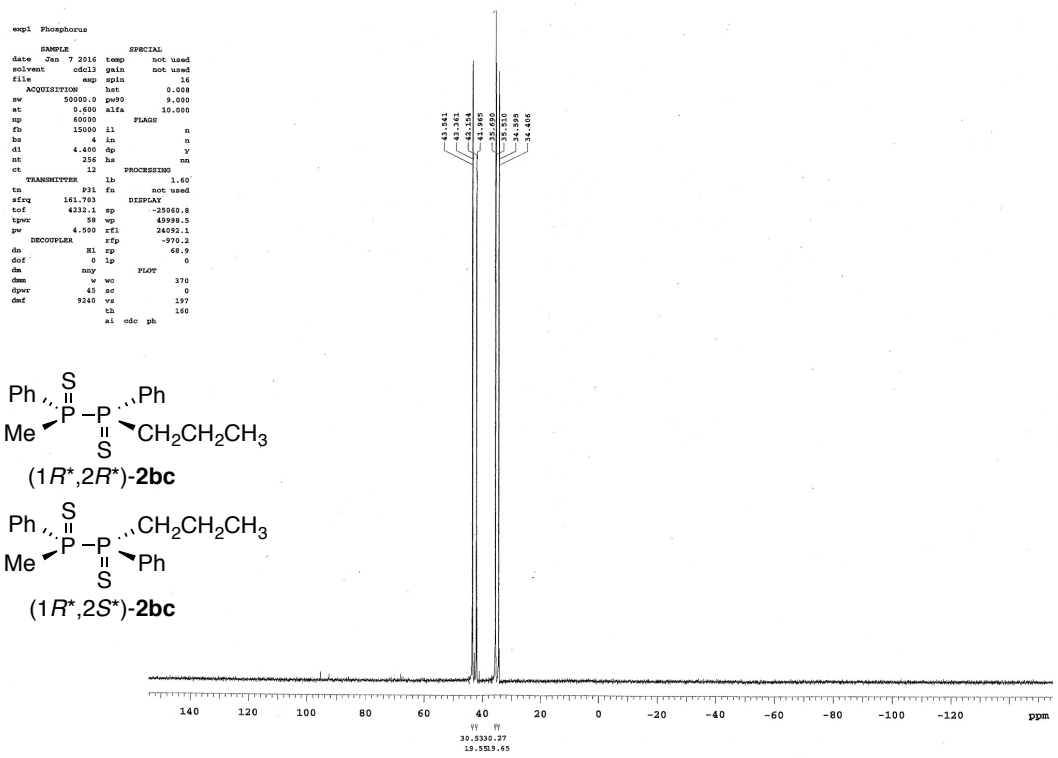
1-Methyl-2-propyl-1,2-diphenyldiphosphine disulfide [(1*R,2*R**)-2bc:(1*R**,2*S**)-2bc = 3:2]**



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P
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Ph
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S
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60
40
20
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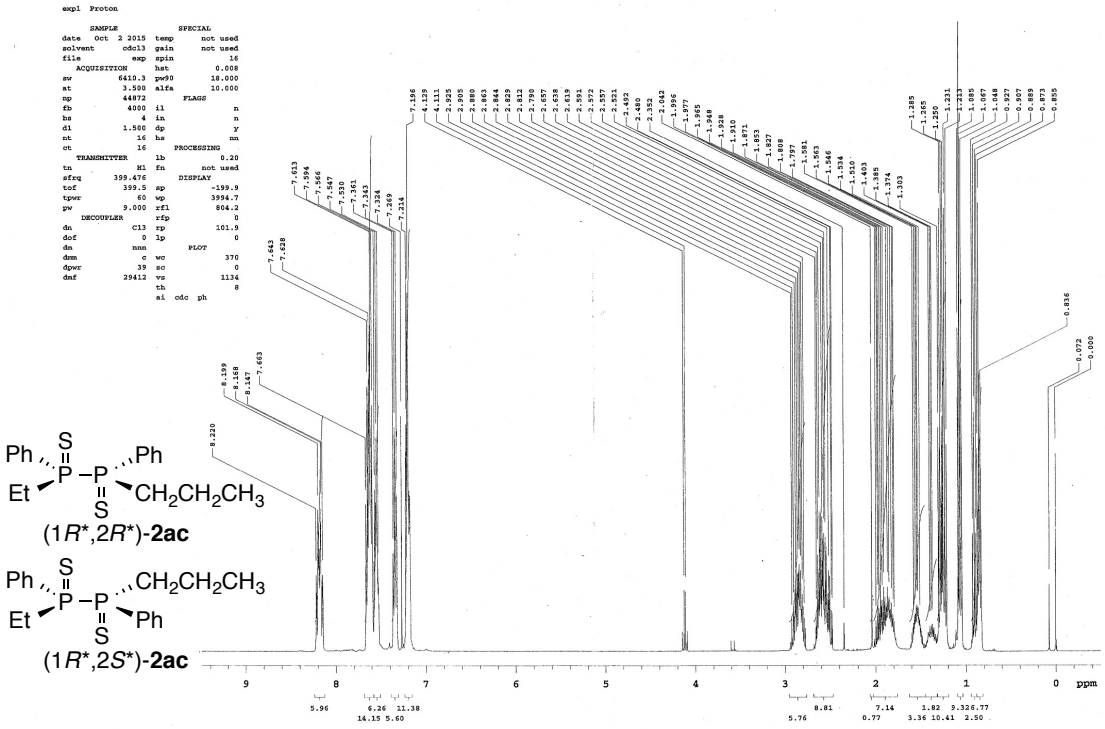
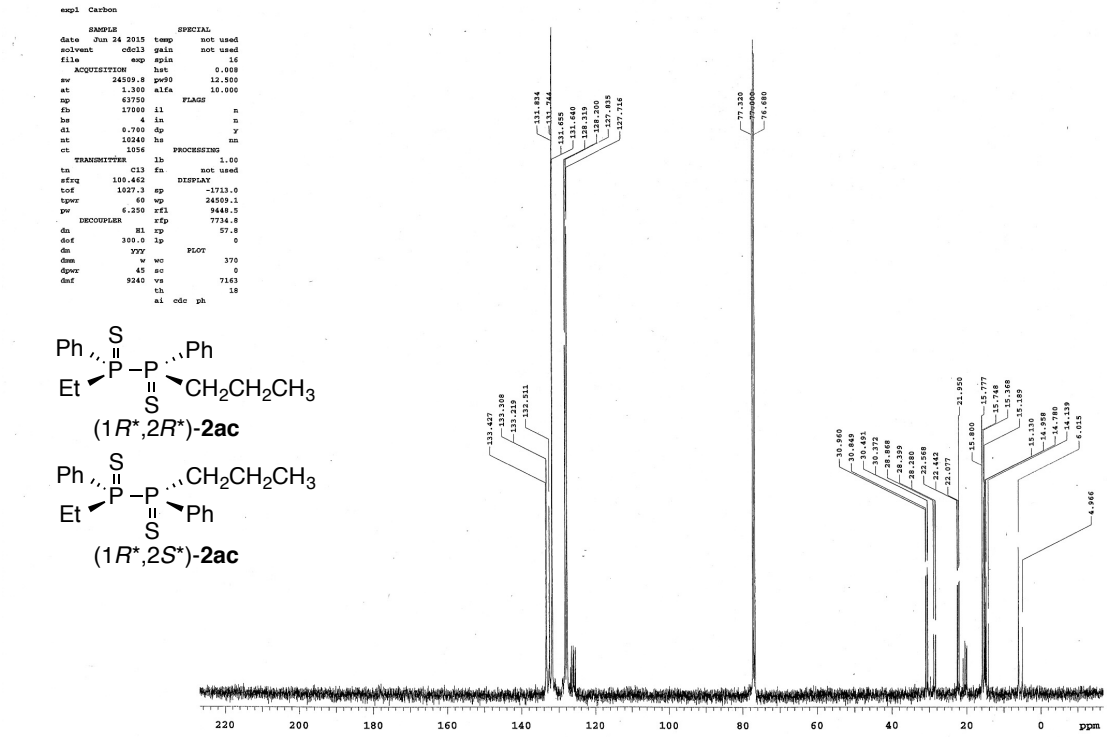
1-Ethyl-2-propyl-1,2-diphenyldiphosphine disulfide [(1*R,2*R**)-2ac:(1*R**,2*S**)-2ac = 2:1]**



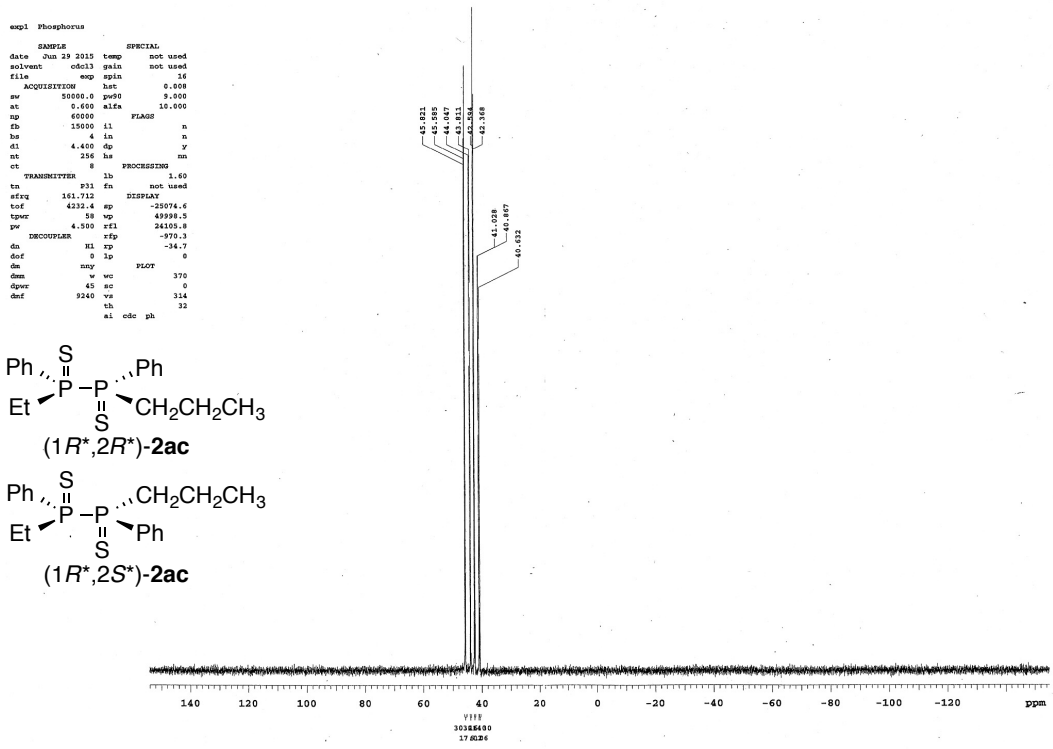
(1*R**,2*R**)-**2ac**

(1*R**,2*S**)-**2ac**



(1*R**,2*R**)-**2ac**

(1*R**,2*S**)-**2ac**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P
P
Ph
Et
CH2CH2CH3
S
(1R*,2R*)-2ac
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S
P
P
CH2CH2CH3
Et
Ph
S
(1R*,2S*)-2ac
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
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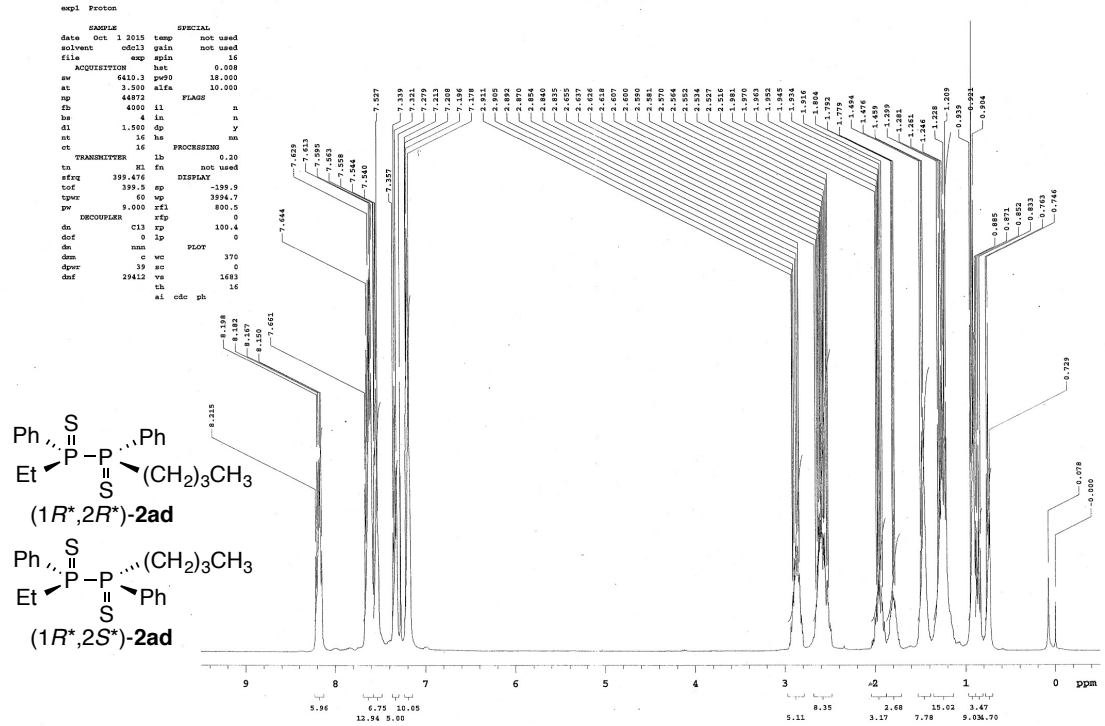
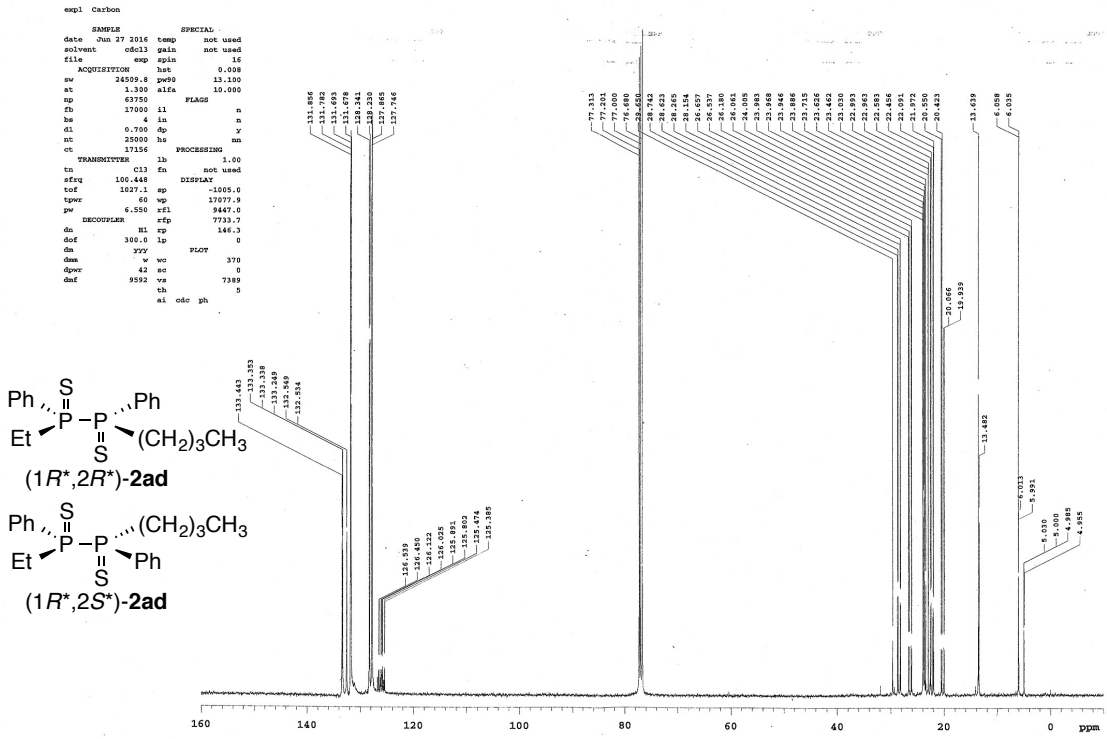
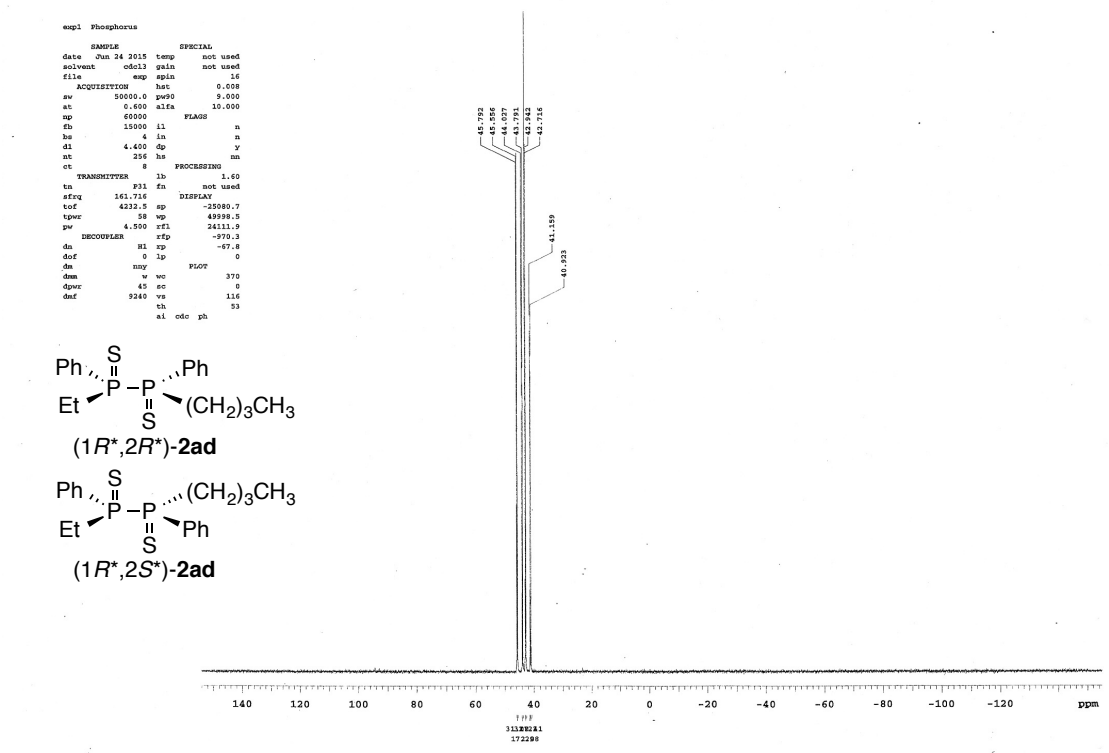
ppm

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



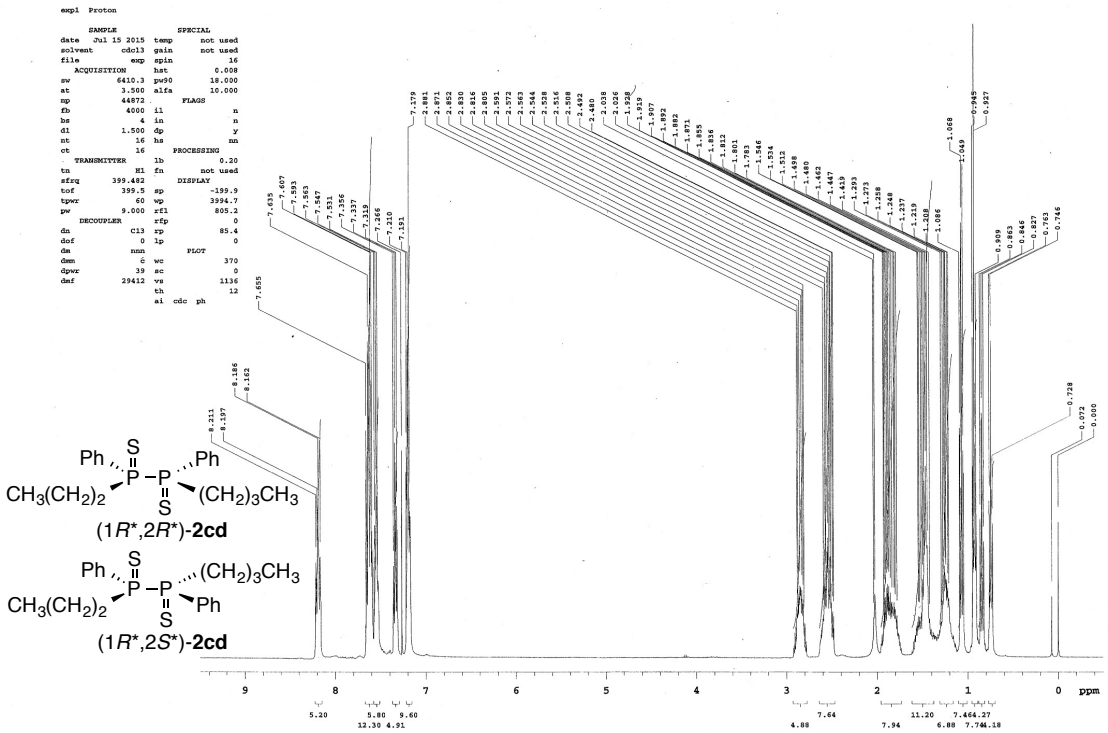


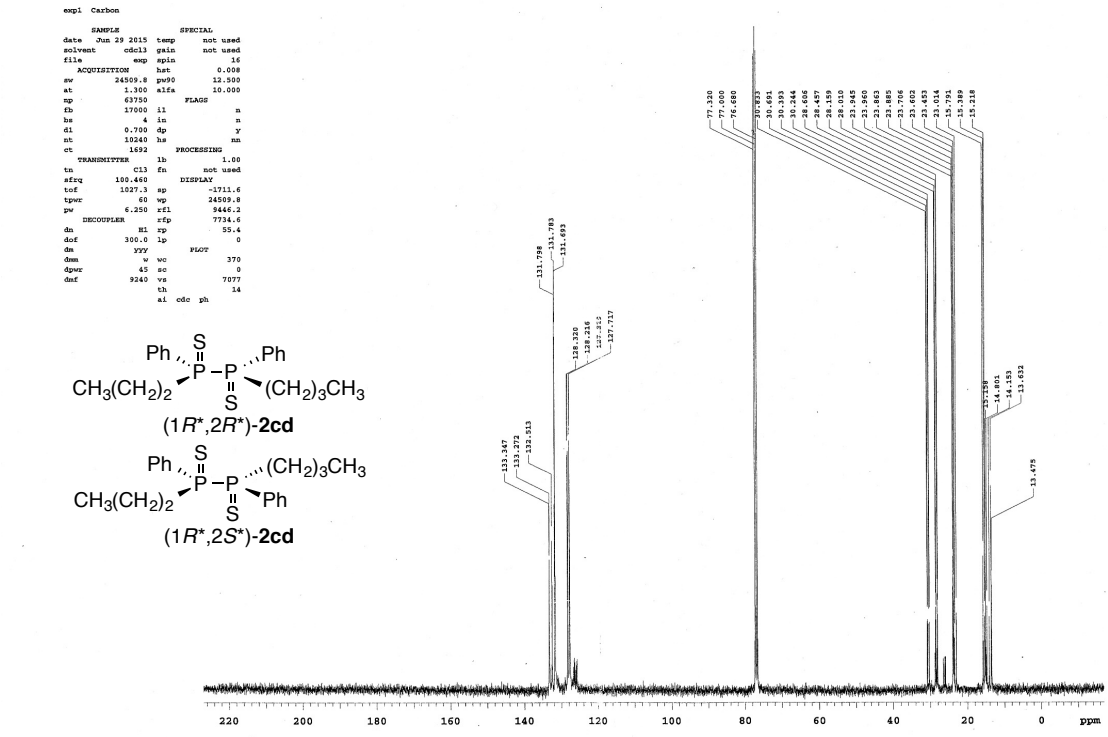


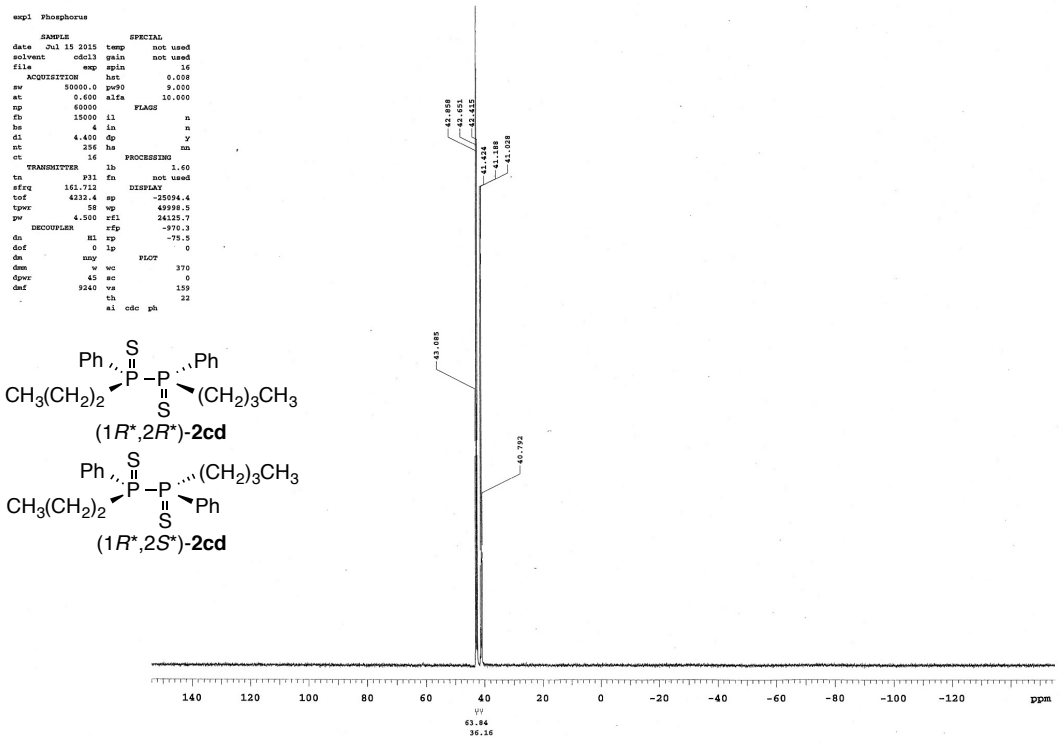
(1*R**,2*R**)-**2ad**

(1*R**,2*S**)-**2ad**

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



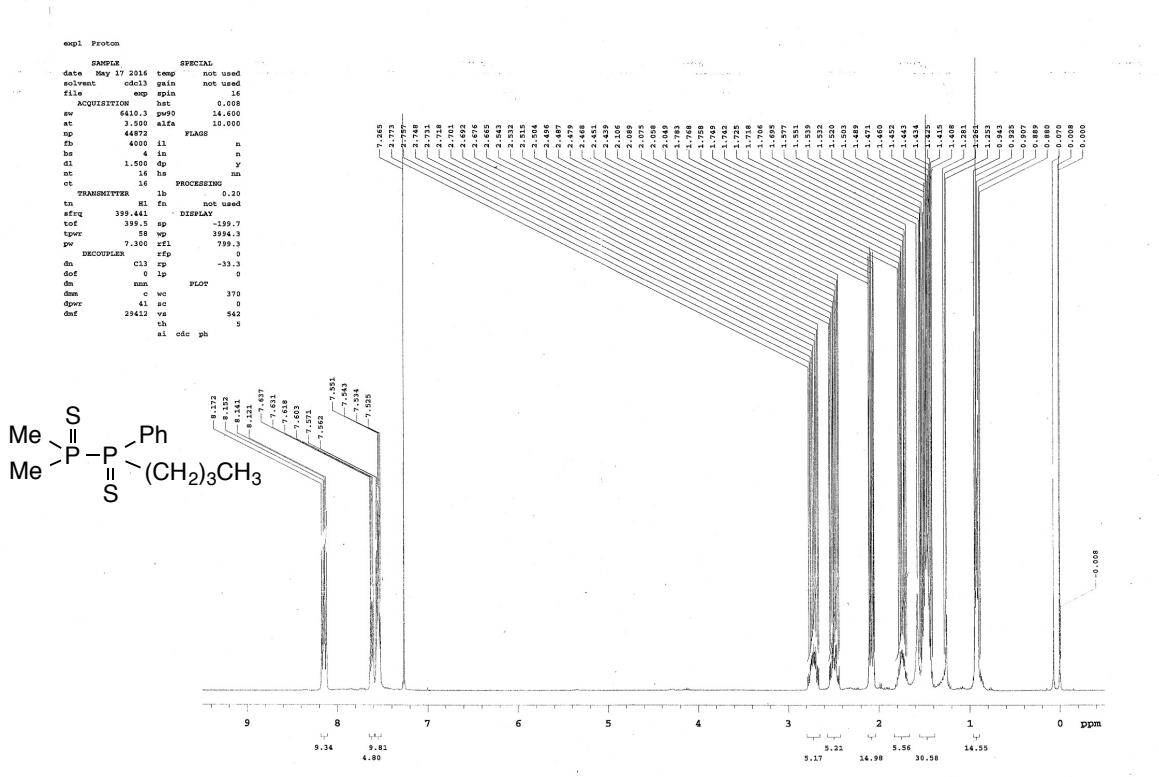


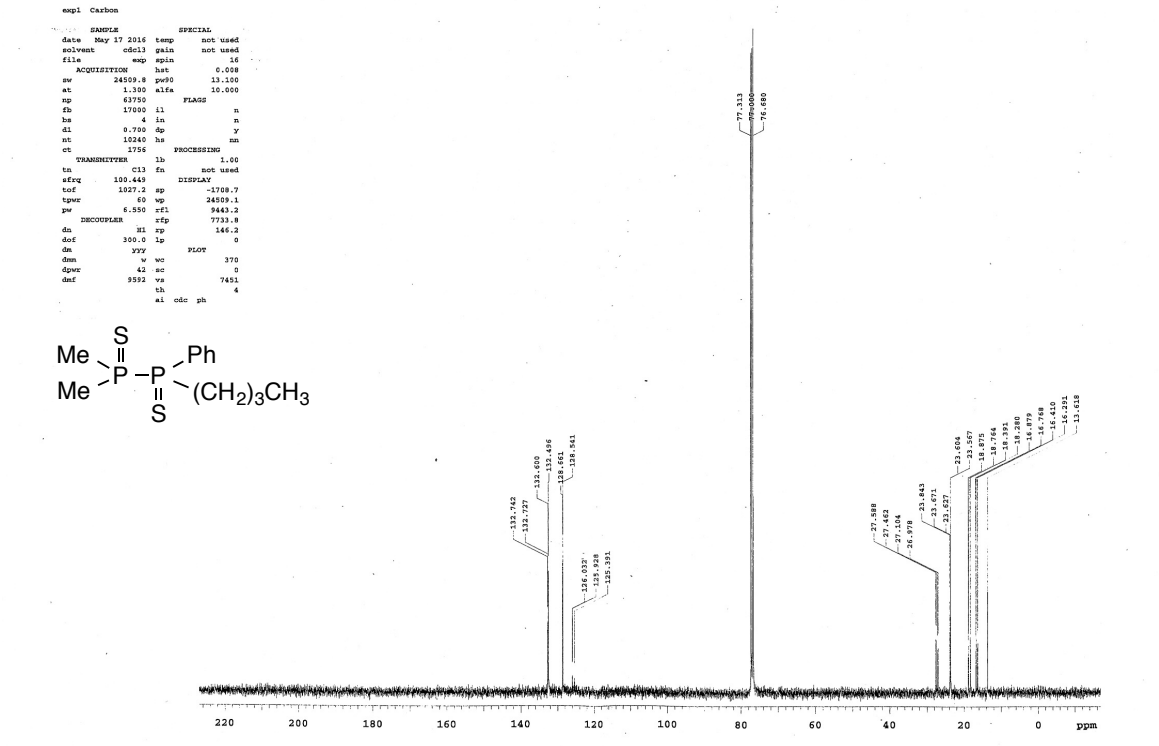


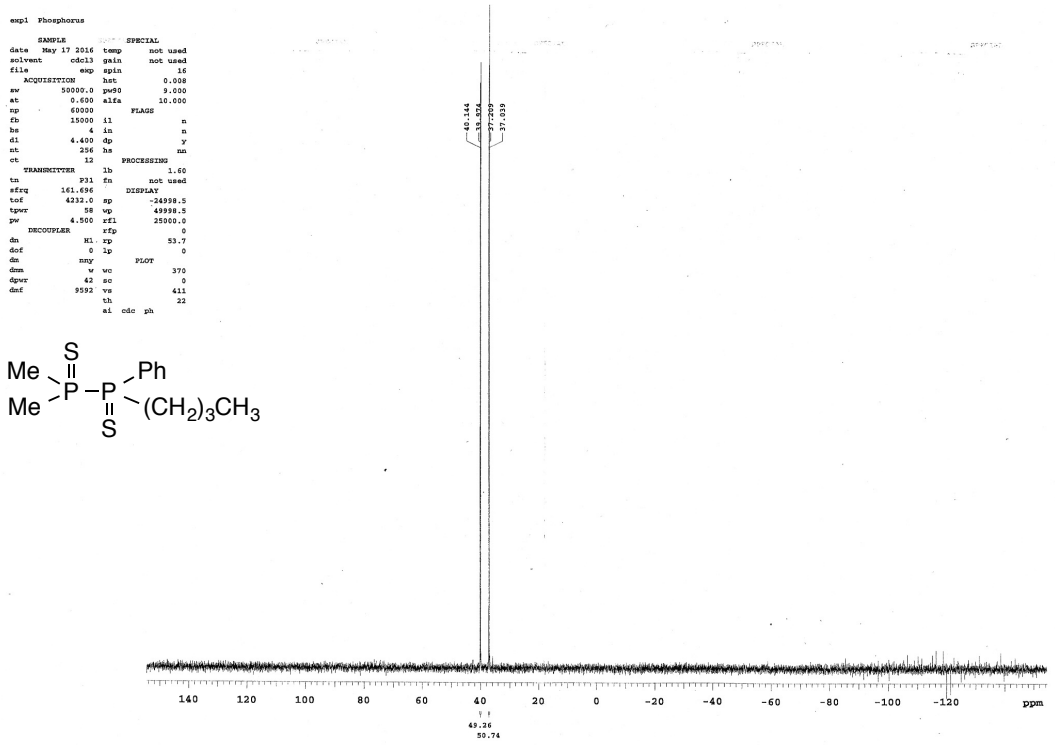
(1*R**,2*R**)-**2cd**

(1*R**,2*S**)-**2cd**

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



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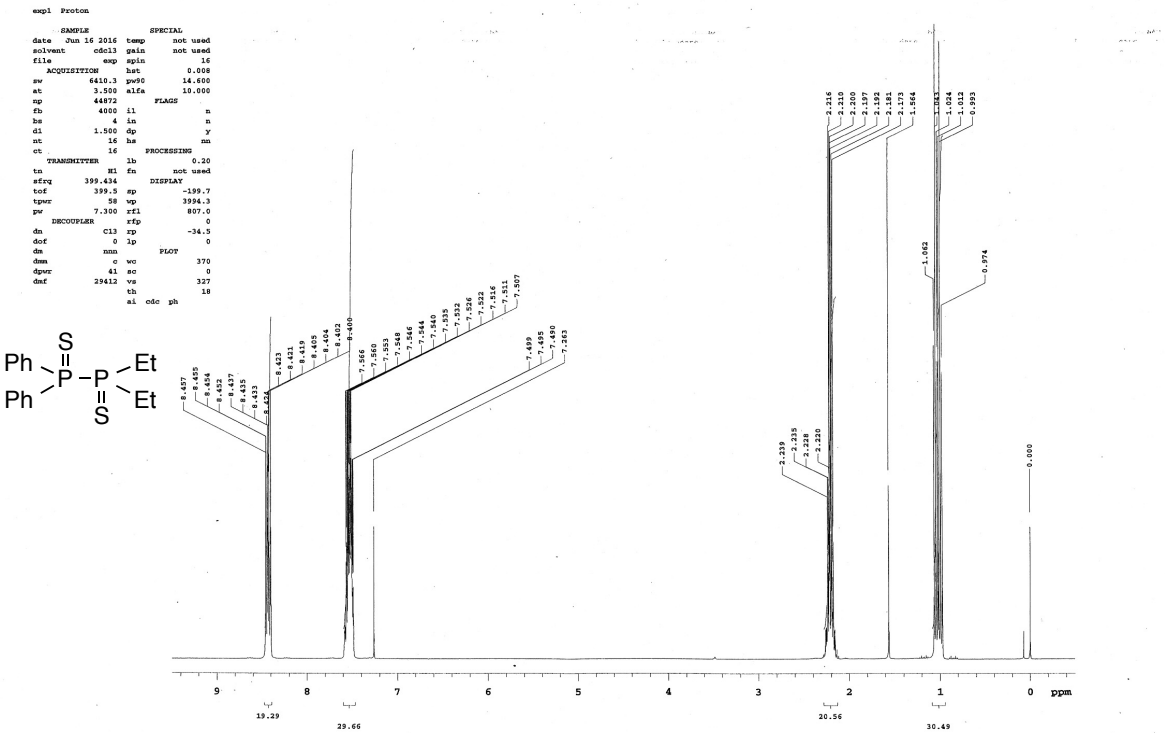
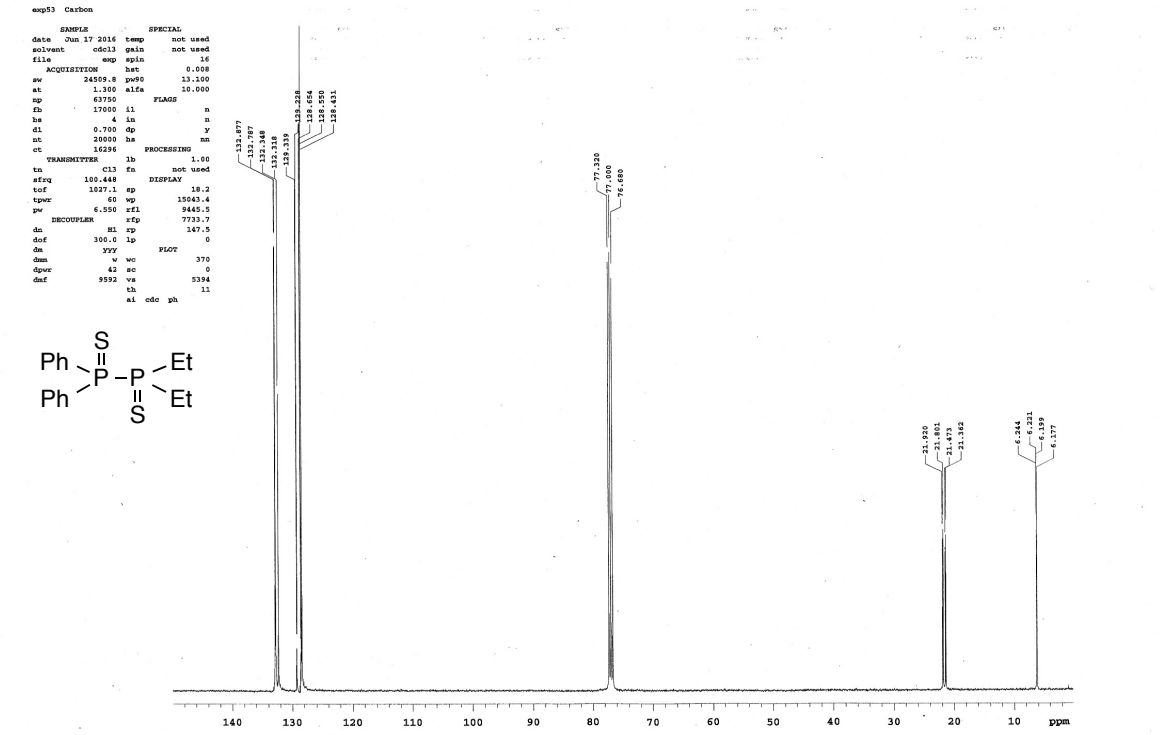
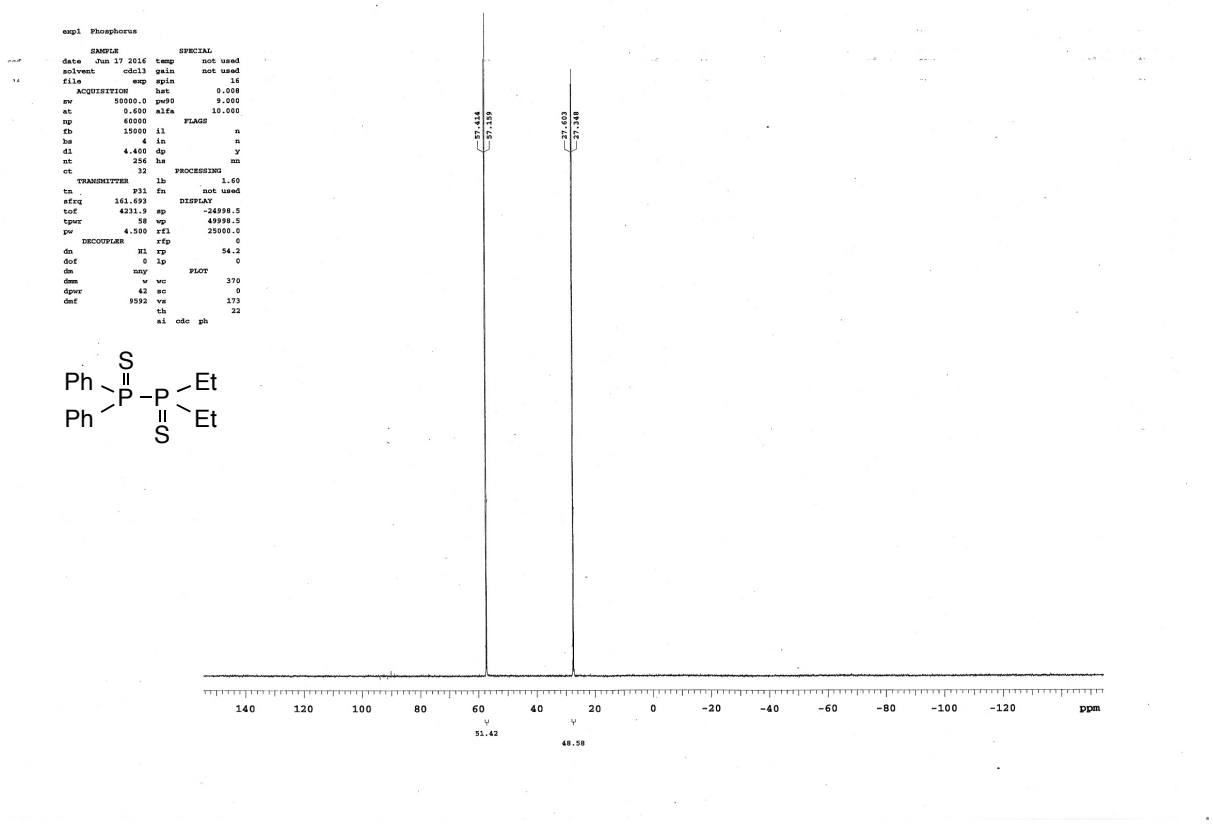
PLOT
wc 370
sc 0
vs 411
th 22
ai cdc ph
Me
Me
S
P
P
S
Ph
(CH2)3CH3
40.144
39.824
37.269
37.039
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
ppm
49.26
50.74

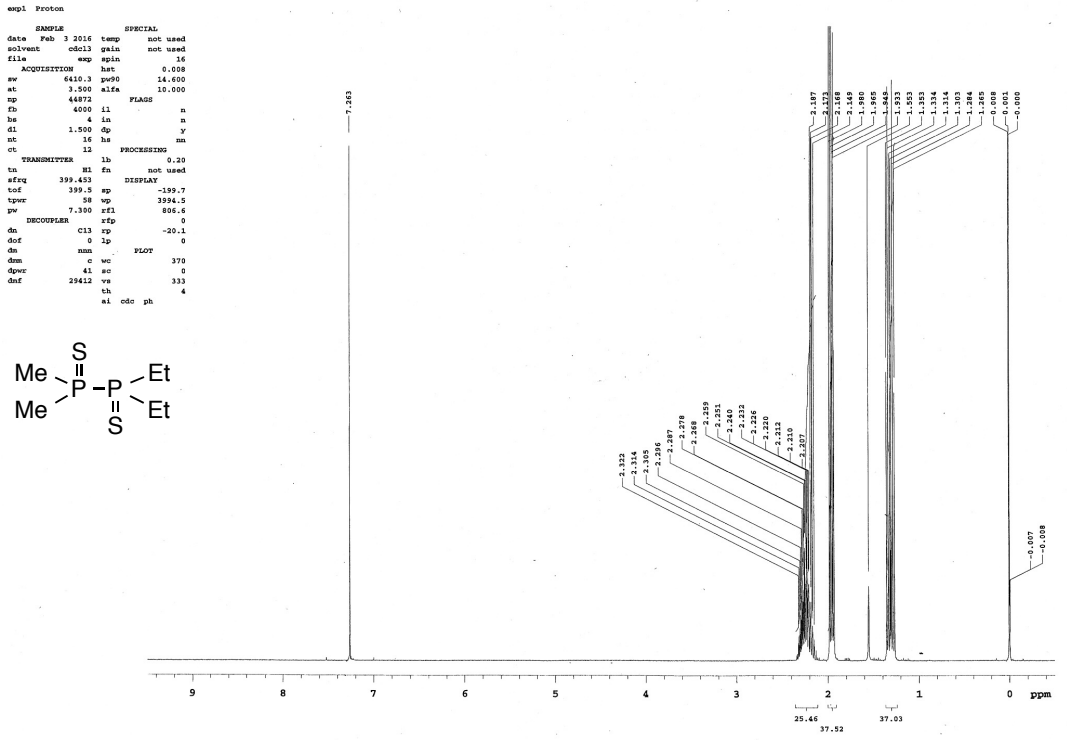
1,1-Diethyl-2,2-diphenyldiphosphine disulfide (2af)

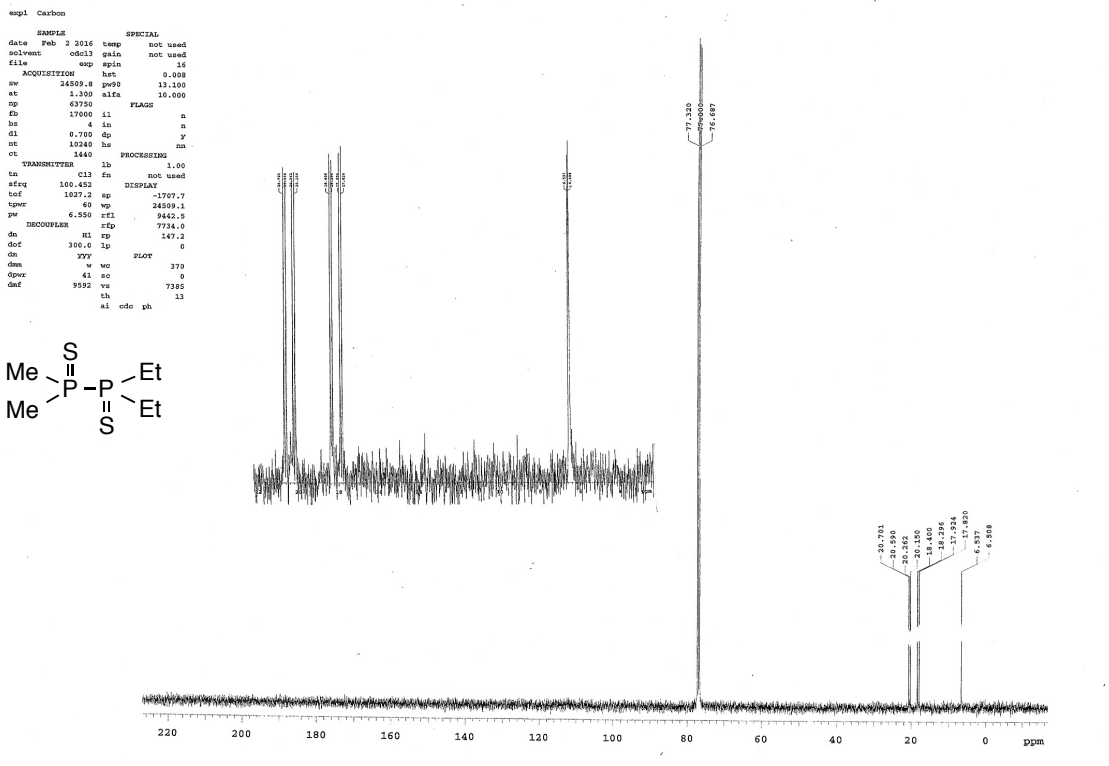


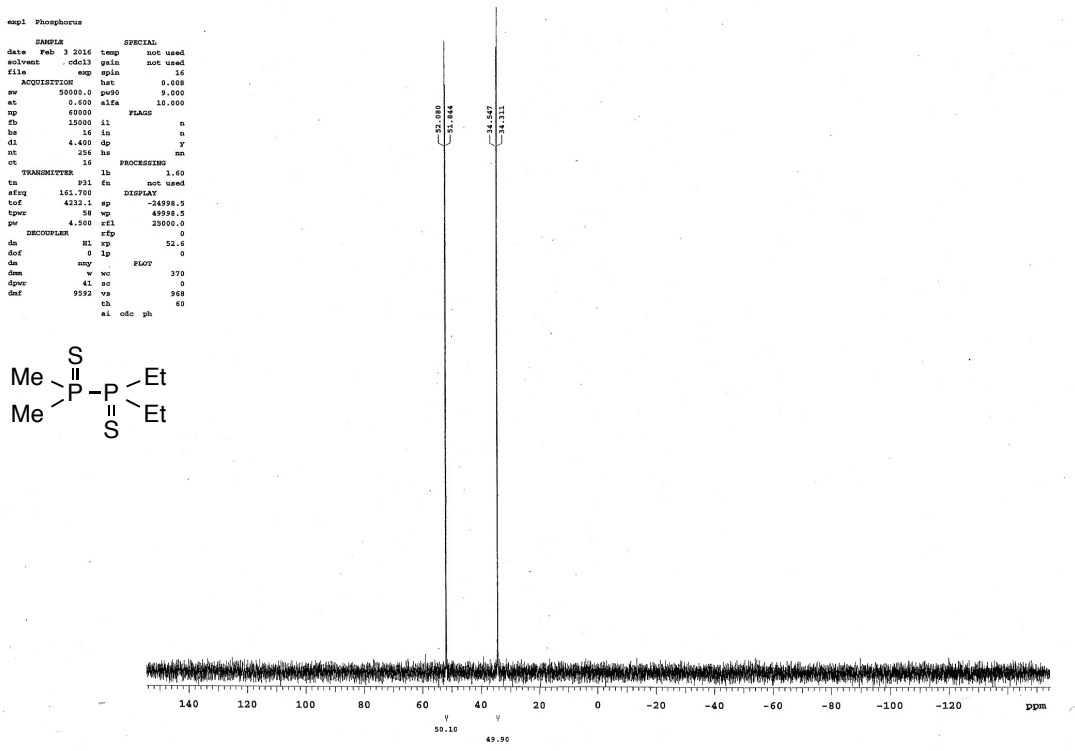



exp1 Phosphorus
SAMPLE
date Jun 17 2016
solvent cdcl3
file exp
ACQUISITION
sw 50000.0
at 0.600
np 60000
fb 15000
bs 4
d1 4.400
nt 256
ct 32
TRANSMITTER
tn P31
sfrq 161.693
tof 4231.9
tpwr 58
pw 4.500
DECOUPLER
dn H1
dof 0
dm nny
dmm w
dpwr 42
dmf 9592
SPECIAL
temp not used
gain not used
spin 16
hst 0.008
pw90 9.000
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 1.60
fn not used
DISPLAY
sp -24998.5
wp 49998.5
rfl 25000.0
rfp 0
rp 54.2
lp 0
PLOT
wc 370
sc 0
vs 173
th 22
ai cdc ph
Ph
Ph
S
P
P
S
Et
Et
57.414
57.159
27.603
27.348
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
ppm
51.42
48.58

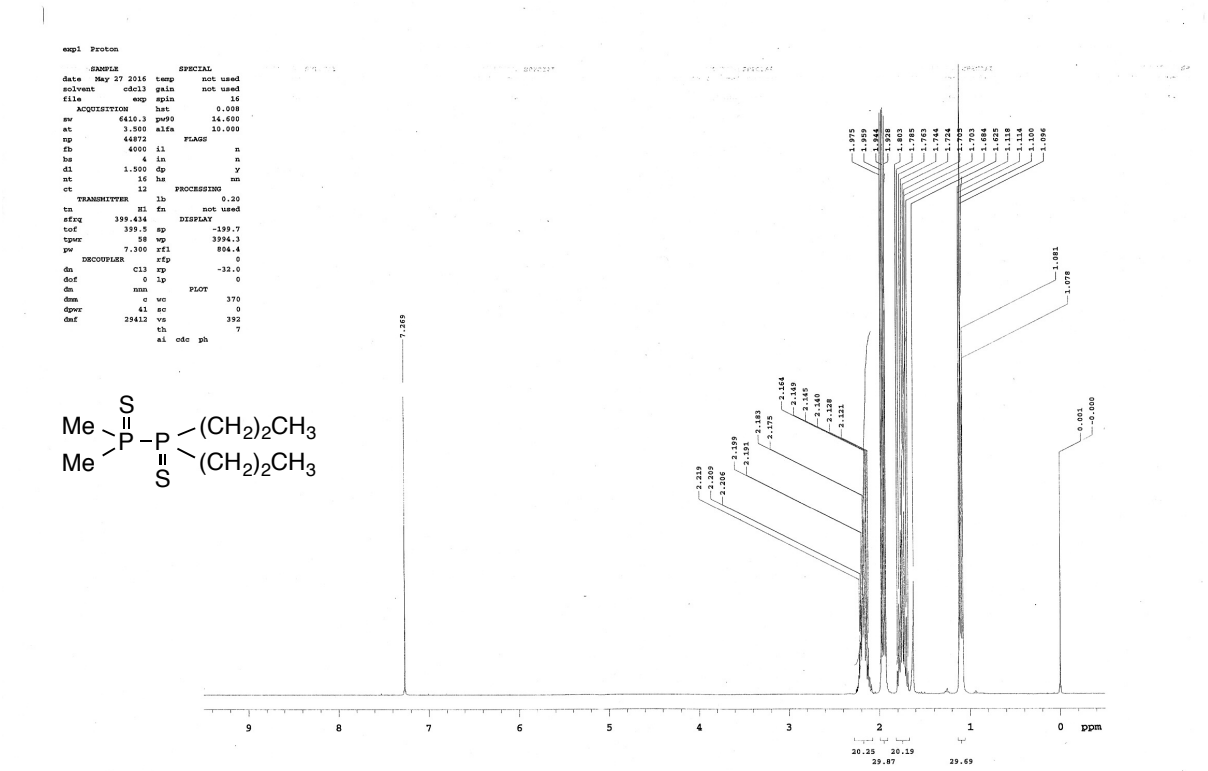
1,1-diethyl-2,2-dimethyldiphosphine disulfide (2gh)

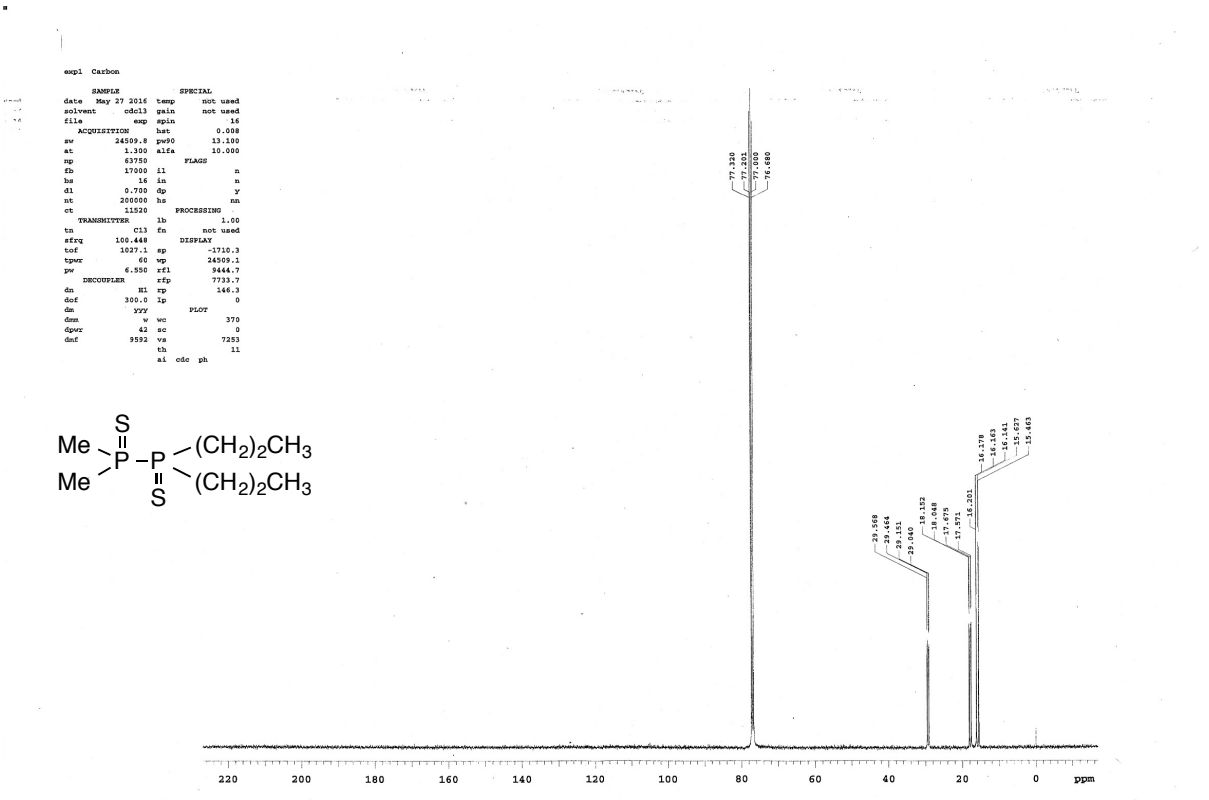


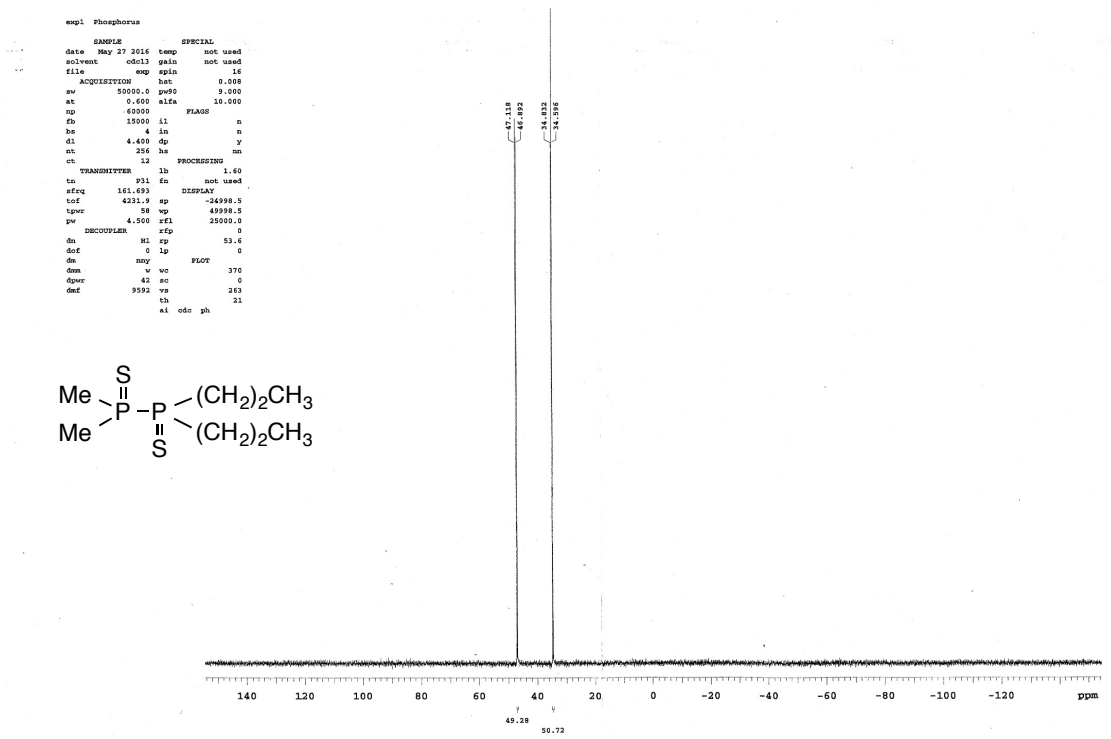



expl Phosphorus
SAMPLE
date Feb 3 2016
solvent cdcl3
file exp
ACQUISITION
sw 50000.0
at 0.600
np 60000
fb 15000
bs 16
d1 4.400
nt 256
ct 16
TRANSMITTER
tn P31
sfrq 161.700
tof 4232.1
tpwr 58
pw 4.500
DECOUPLER
dn H1
dof 0
dn nny
dmm w
dpwr 41
dmf 9592
SPECIAL
temp not used
gain not used
spin 16
hst 0.008
pw90 9.000
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 1.60
fn not used
DISPLAY
sp -24998.5
wp 49998.5
rfl 25000.0
rfp 0
rp 52.6
lp 0
PLOT
wc 370
sc 0
vs 968
th 60
ai cdc ph
Me
Me
S
P
P
S
Et
Et
52.080
51.844
34.547
34.311
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
ppm
50.10
49.90

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

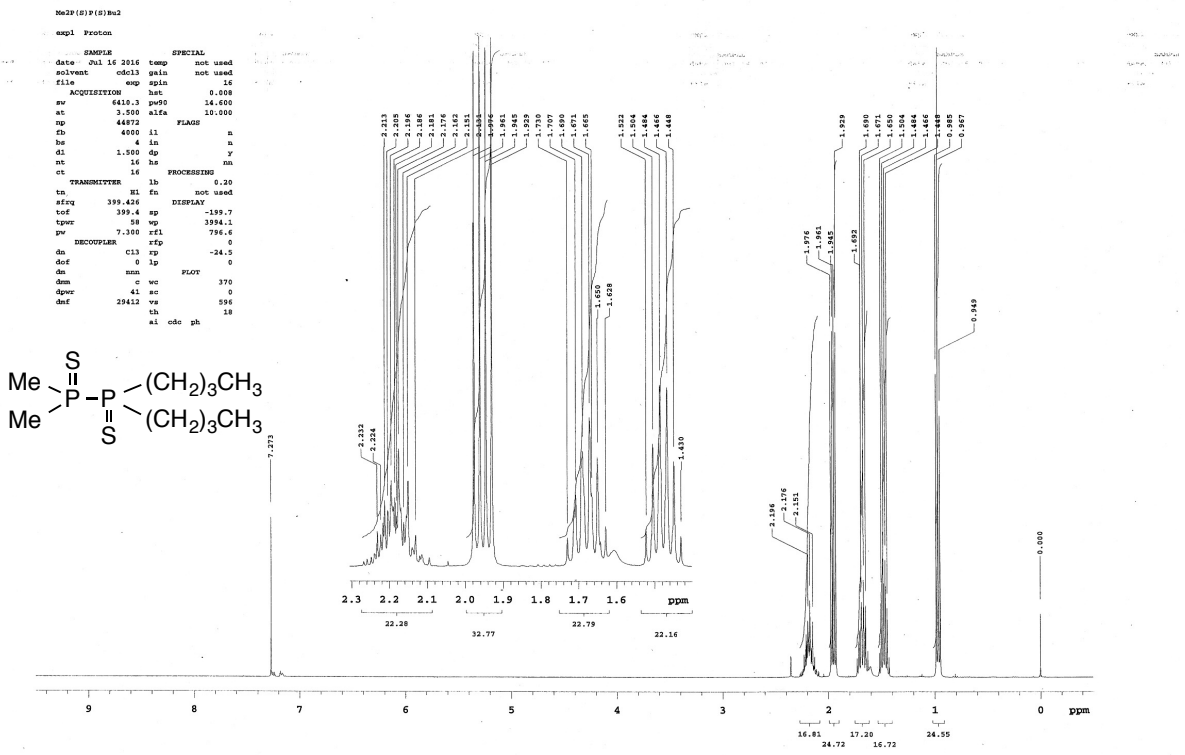





exp1 Phosphorus
SAMPLE
date May 27 2016
solvent cdcl3
file exp
ACQUISITION
sw 50000.0
at 0.600
np 60000
fb 15000
bs 4
d1 4.400
nt 256
ct 12
TRANSMITTER
tn P31
sfrq 161.693
tof 4231.9
tpwr 58
pw 4.500
DECOUPLER
dn H1
dof 0
dm nny
dmm w
dpwr 42
dmf 9592
SPECIAL
temp not used
gain not used
spin 16
hst 0.008
pw90 9.000
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 1.60
fn not used
DISPLAY
sp -24998.5
wp 49998.5
rfl 25000.0
rfp 0
rp 53.6
lp 0
PLOT
wc 370
sc 0
vs 263
th 21
ai cdc ph
47.118
46.892
34.853
34.596
Me
Me
S
P
P
S
(CH2)2CH3
(CH2)2CH3
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
ppm
49.28
50.72

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

-



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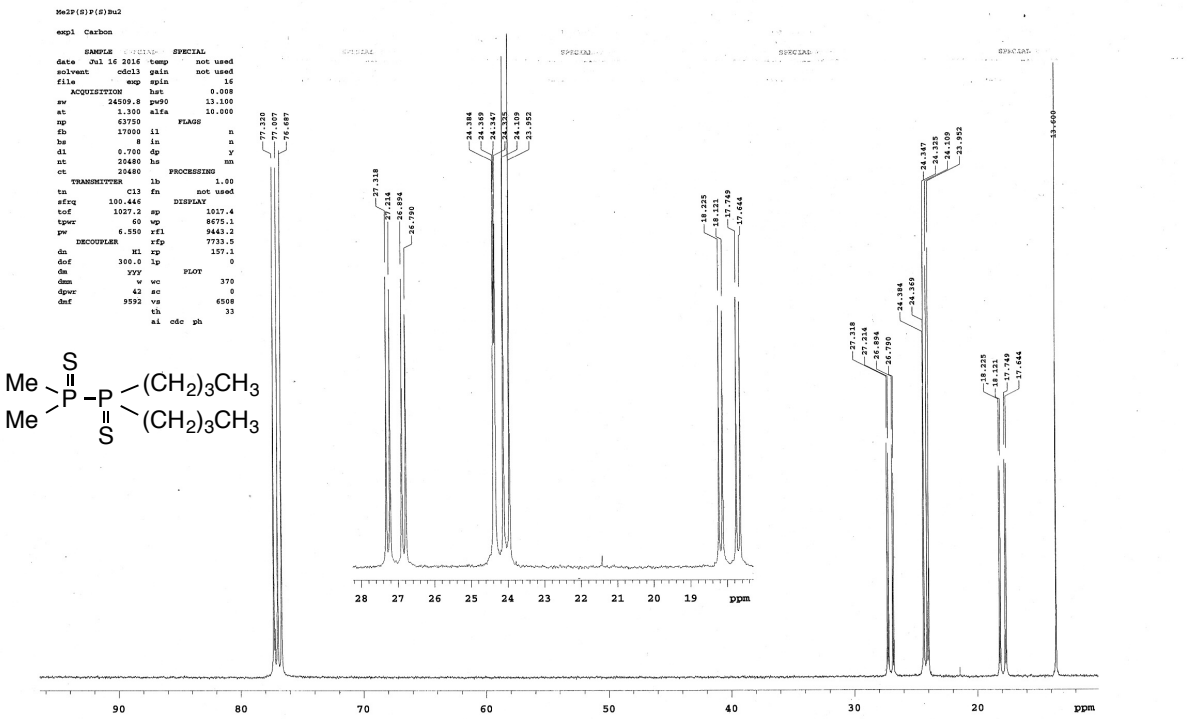
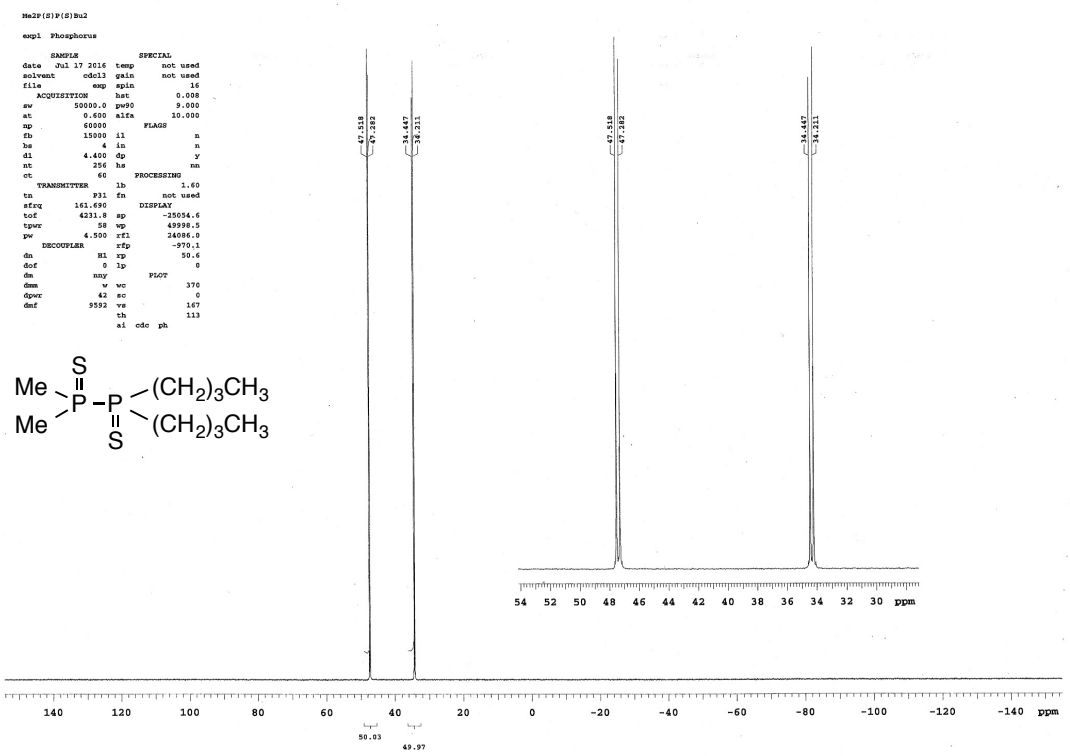
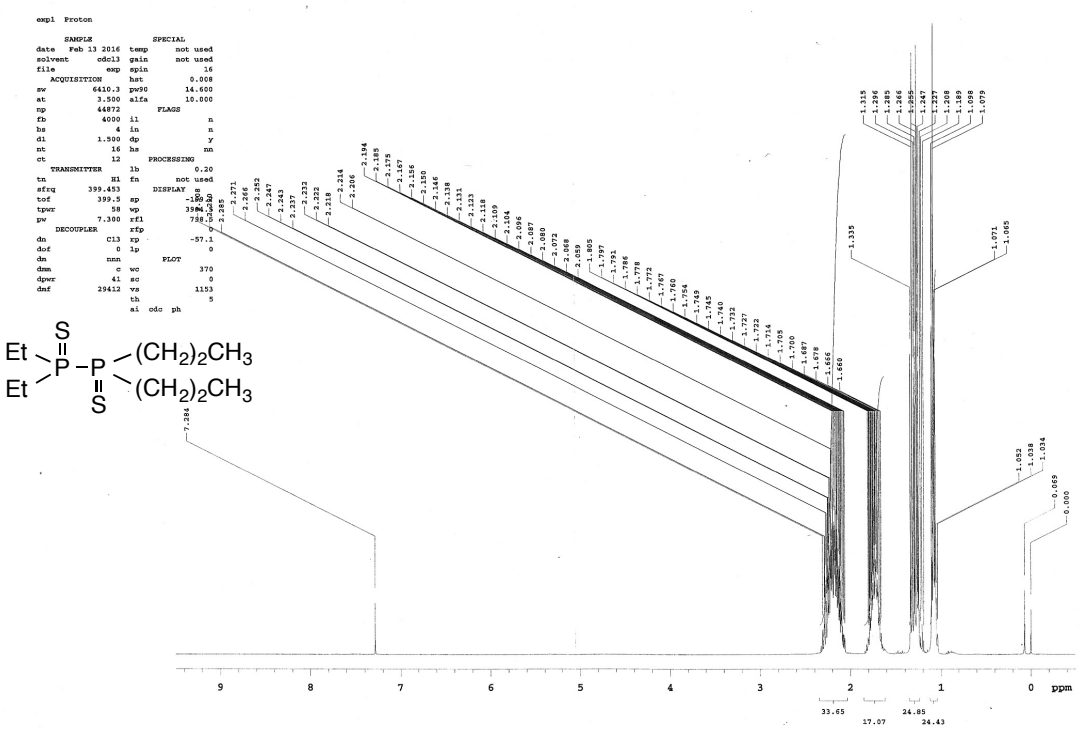
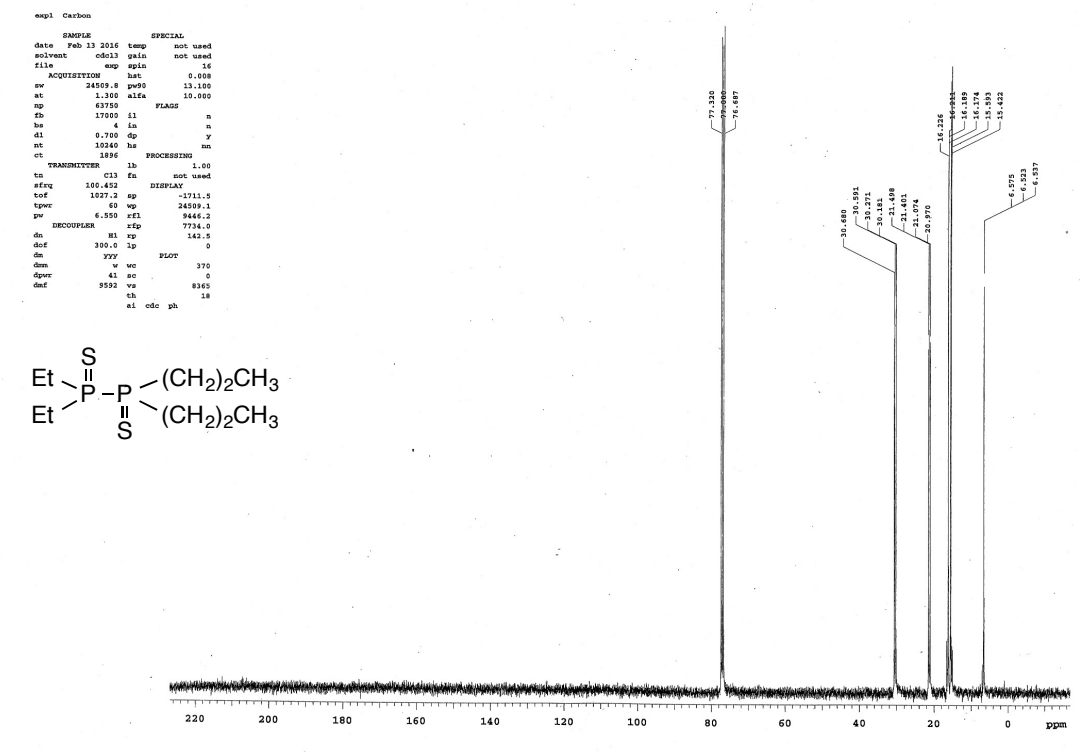
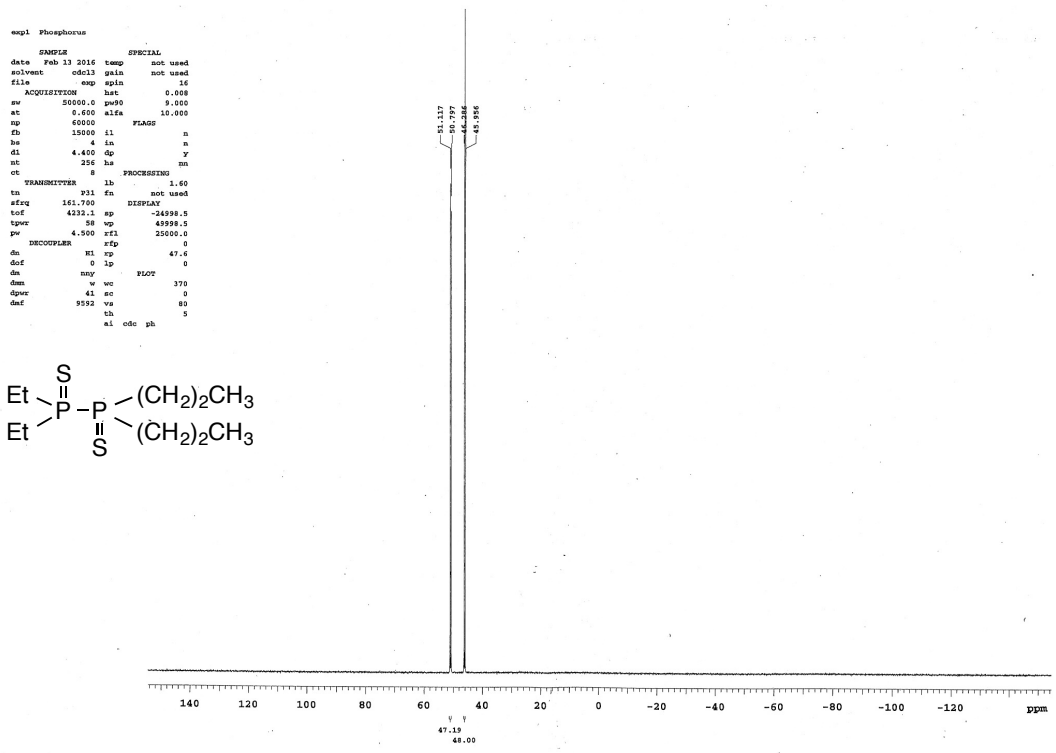



Me2P(S)P(S)Bu2
expl Phosphorus
SAMPLE
date Jul 17 2016
solvent cdcl3
file exp
ACQUISITION
sw 50000.0
at 0.600
np 60000
fb 15000
bs 4
d1 4.400
nt 256
ct 60
TRANSMITTER
tn P31
sfrq 161.690
tof 4231.8
tpwr 58
pw 4.500
DECOUPLER
dn H1
dof 0
dm nny
dmm w
dpwr 42
dmf 9592
SPECIAL
temp not used
gain not used
spin 16
hst 0.008
pw90 9.000
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 1.60
fn not used
DISPLAY
sp -25054.6
wp 49998.5
rfl 24086.0
rfp -970.1
rp 50.6
lp 0
PLOT
wc 370
sc 0
vs 167
th 113
si cdc ph
Me
Me
S
P
P
S
(CH2)3CH3
(CH2)3CH3
47.518
47.282
34.447
34.211
54 52 50 48 46 44 42 40 38 36 34 32 30 ppm
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 ppm
50.03
49.97

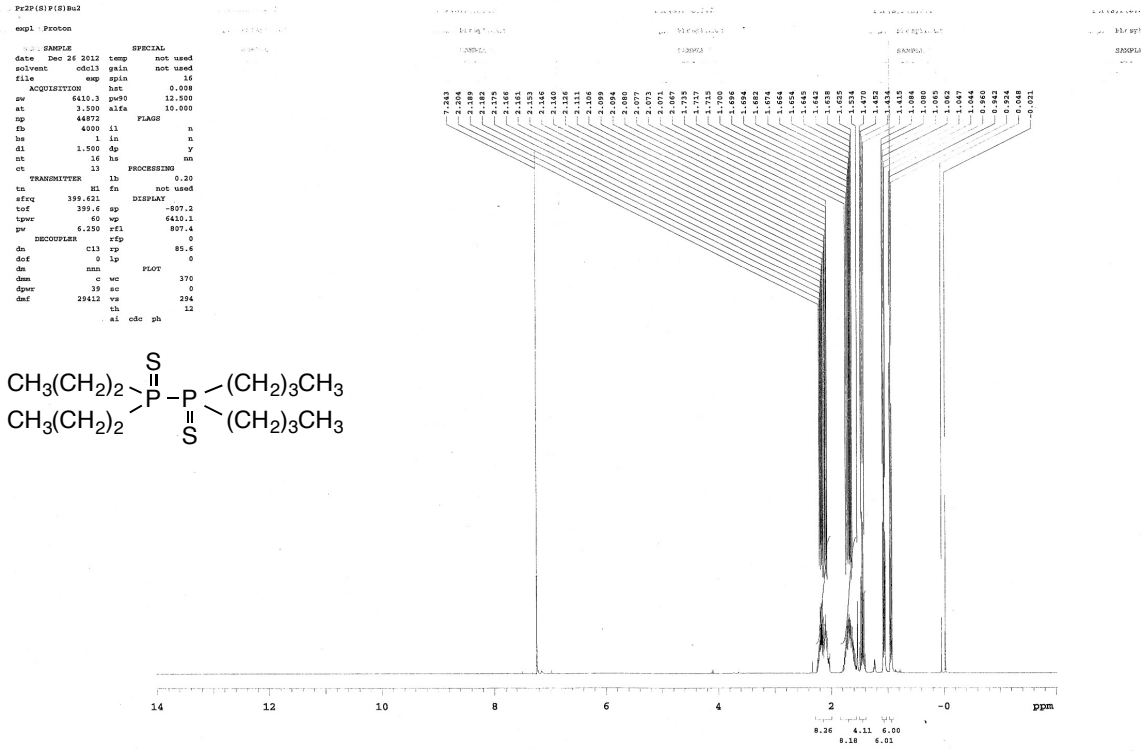
1,1-Diethyl-2,2-dipropyldiphosphine Disulfide (2hi)

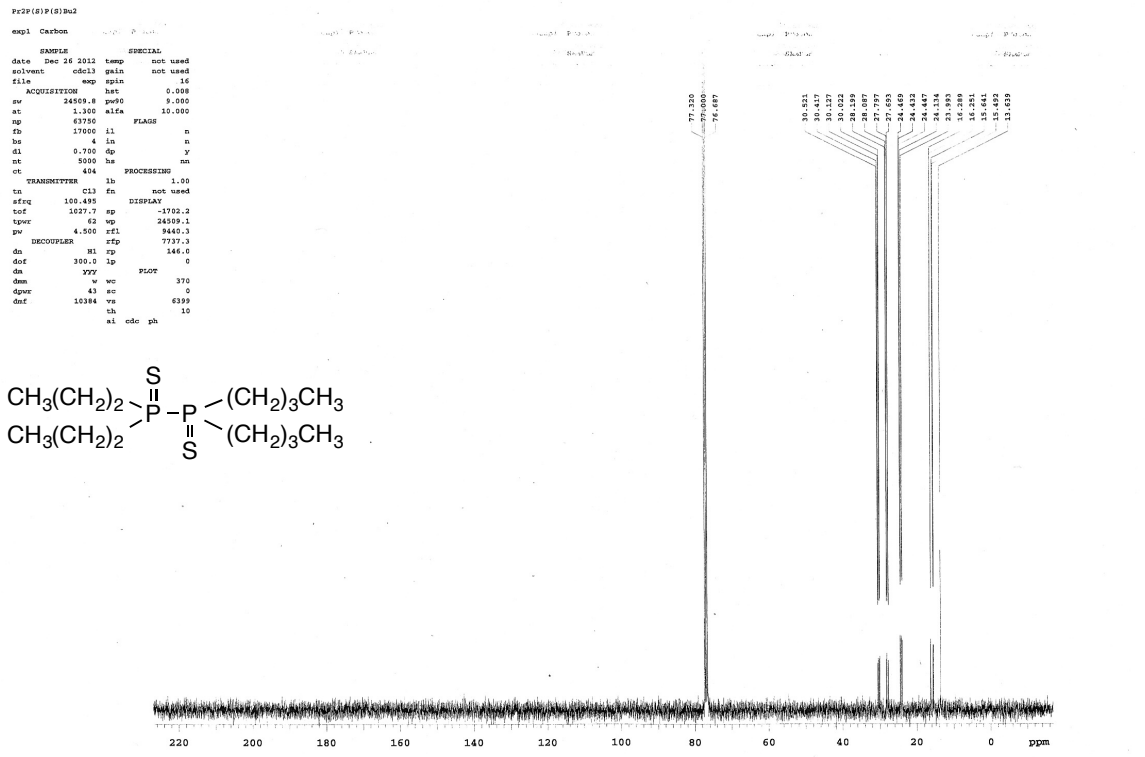





expl Phosphorus
SAMPLE
date Feb 13 2016
solvent cdcl3
file exp
ACQUISITION
sw 50000.0
at 0.600
np 60000
fb 15000
hs 4
di 4.400
nt 256
ct 8
TRANSMITTER
tn P31
sfrq 161.700
tof 4232.1
tpwr 58
pw 4.500
DECOUPLER
dn H1
dof 0
dn nny
dmm w
dpwr 41
daf 9592
SPECIAL
temp not used
gain not used
spin 16
hst 0.008
pw90 9.000
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 1.60
fn not used
DISPLAY
sp -24998.5
wp 49998.5
rfl 25000.0
rfp 0
rp 47.6
lp 0
PLOT
wc 370
sc 0
vs 80
th 5
ai cdc ph
51.117
50.797
46.286
45.956
Et
Et
S
P
P
S
(CH2)2CH3
(CH2)2CH3
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
ppm
47.19
48.00

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

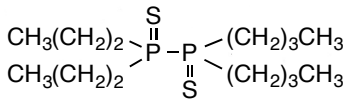




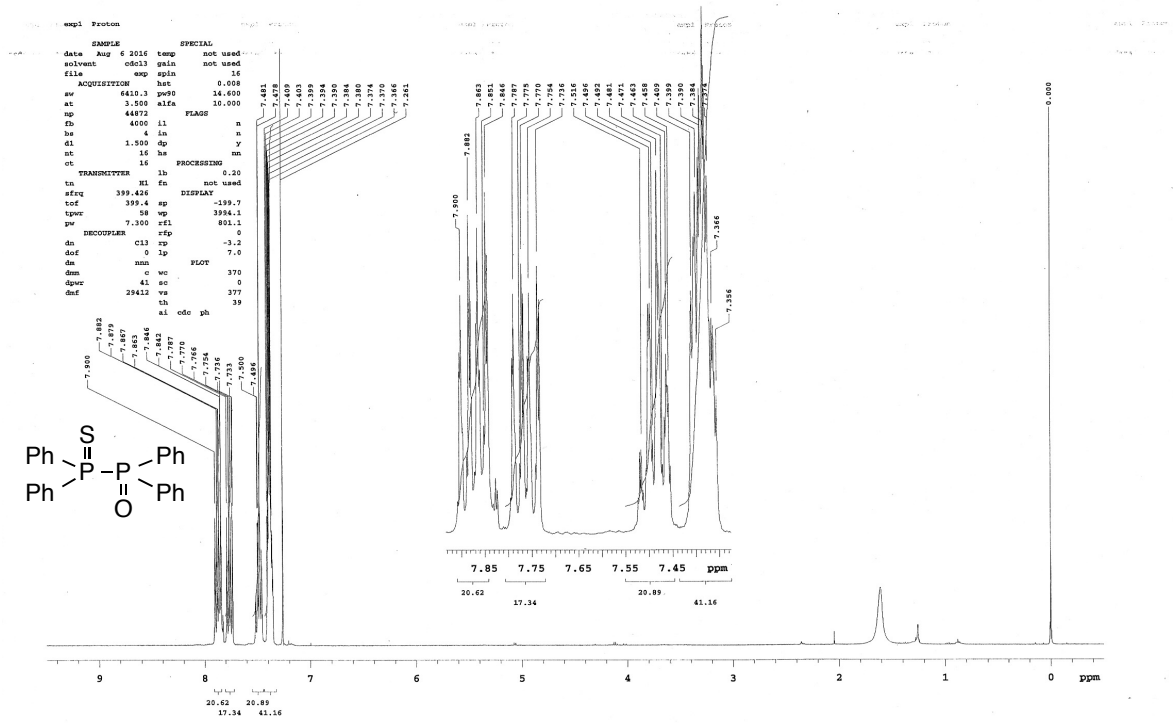
Pr2P(S)P(S)Br2

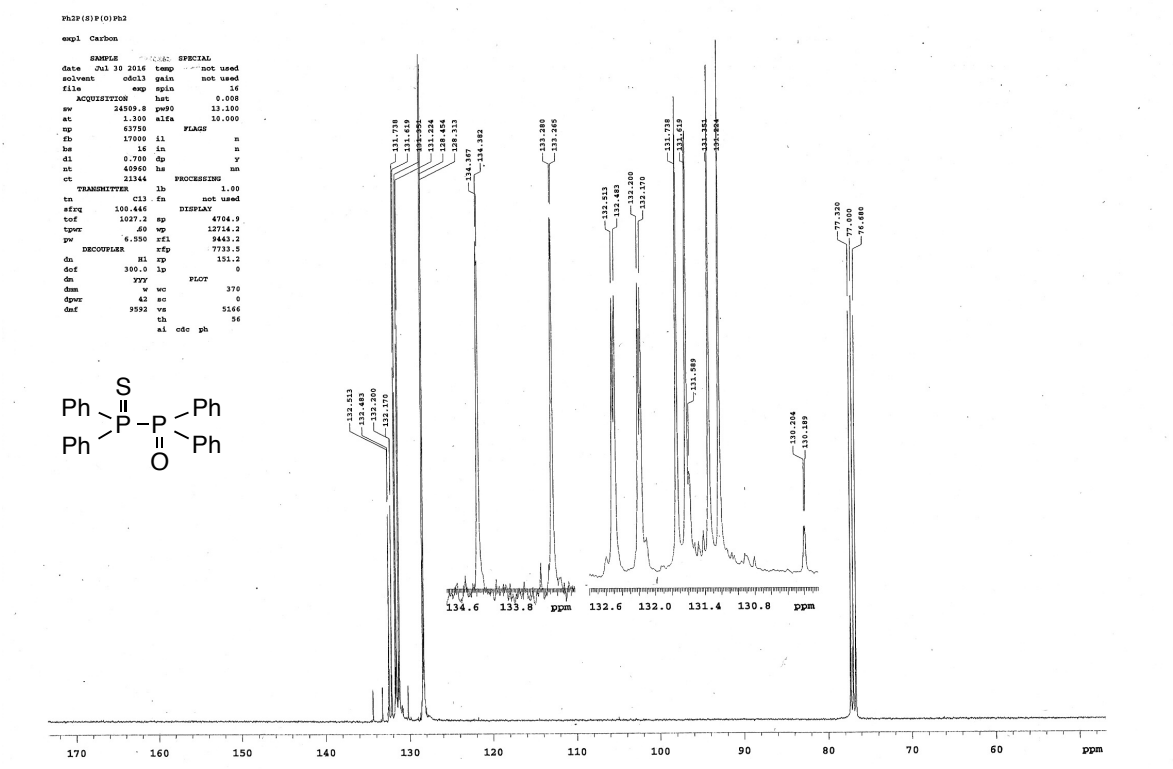
expl Phosphorus

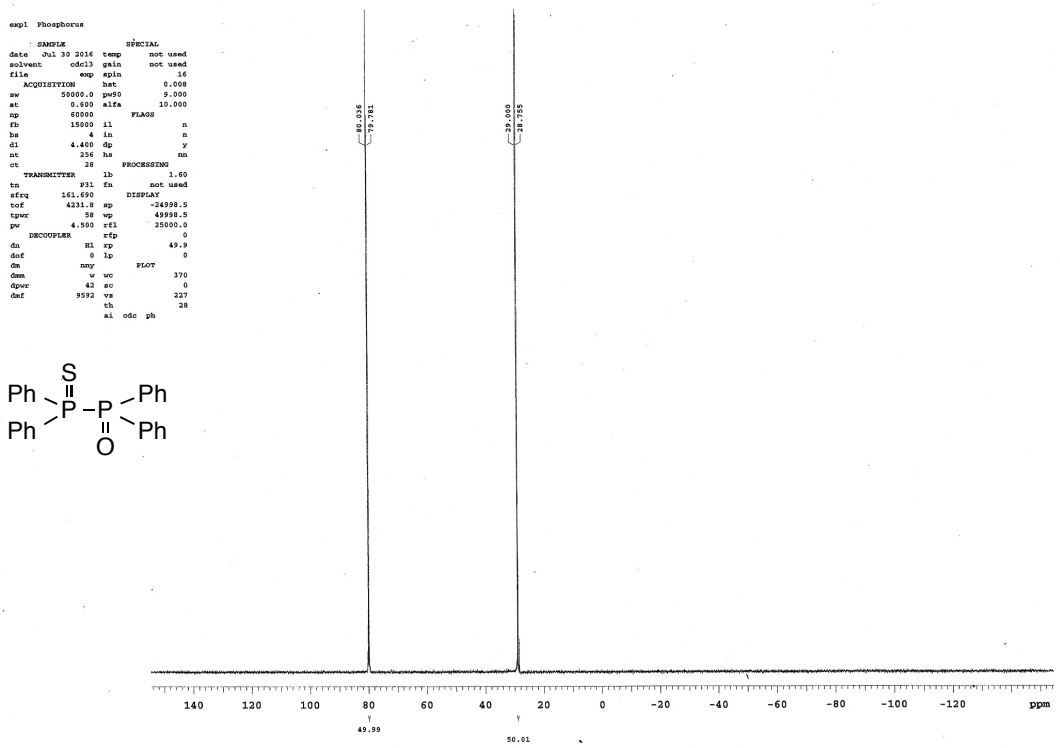
SAMPLE		SPECIAL	
date	Dec 26 2012	temp	not used
solvent	cdcl3	gain	not used
file	exp	spin	16
ACQUISITION		hst	0.008
sw	50000.0	pw90	9.000
at	0.600	alfa	10.000
np	60000	FLAGS	
fb	15000	il	n
bs	1	in	n
d1	4.400	dp	y
nt	256	hs	nn
ct	8	PROCESSING	
TRANSMITTER		lb	1.60
tn	P31	fn	not used
sfrq	161.768	DISPLAY	
tof	4233.9	sp	-25035.2
tpwr	58	wp	49998.5
pw	4.500	rfl	24066.2
DECOUPLER		rfp	-970.6
dn	H1	rp	148.1
dof	0	lp	0
dm	nny	PLOT	
dmm	w	wc	370
dpwr	43	sc	0
dmf	10384	vs	515
		th	8
		ai	cdc ph



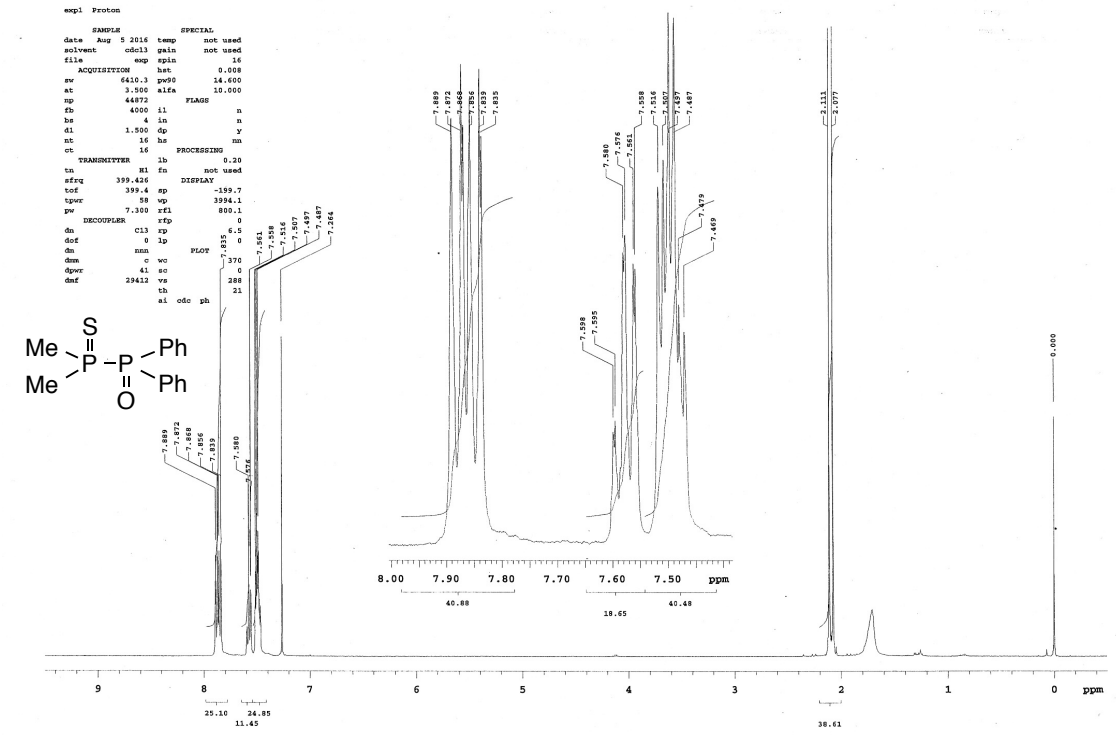
Tetraphenyldiphosphine 1-oxide 2-sulfide (4)

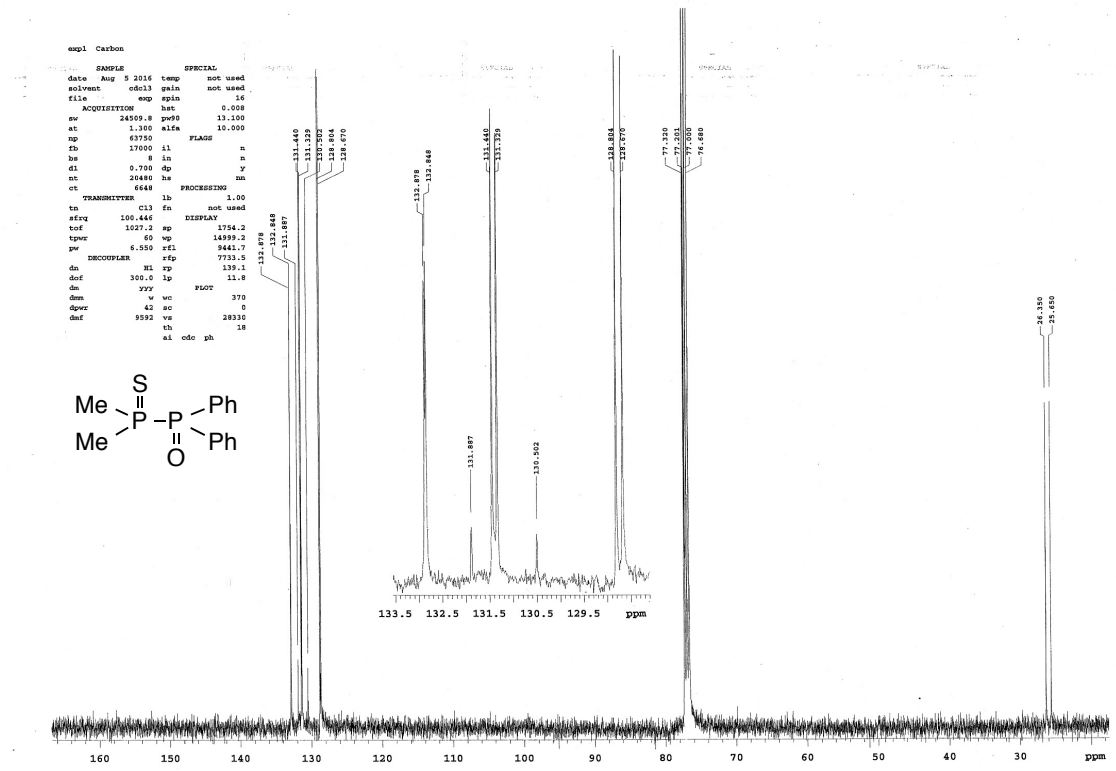


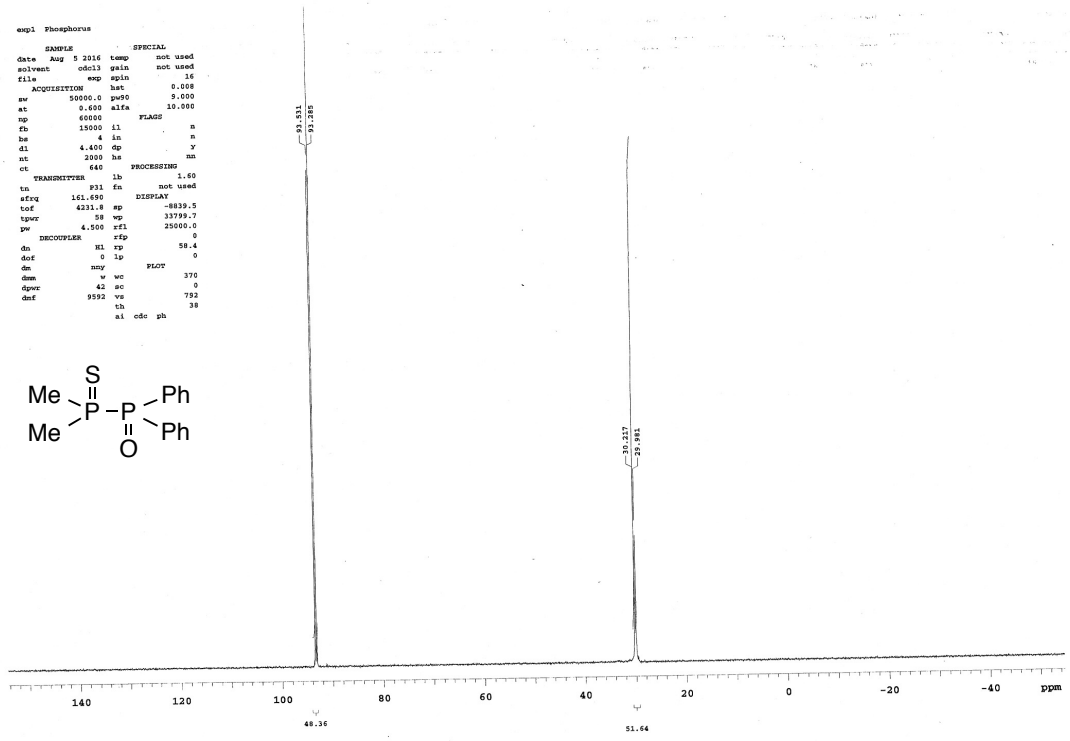



expl Phosphorus
SAMPLE
date Jul 30 2016
solvent cdcl3
file exp
ACQUISITION
sw 50000.0
at 0.600
np 60000
fb 15000
bs 4
d1 4.400
nt 256
ct 28
TRANSMITTER
tn P31
sfrq 161.690
tof 4231.8
tpwr 58
pw 4.500
DECOUPLER
dn H1
dof 0
dm nny
dmm w
dpwr 42
dmf 9592
SPECIAL
temp not used
gain not used
spin 16
hst 0.008
pw90 9.000
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 1.60
fn not used
DISPLAY
sp -24998.5
wp 49988.5
rfl 25000.0
rfp 0
rp 49.9
lp 0
PLOT
wc 370
sc 0
vs 227
th 28
ai cdc ph
Ph
Ph
S
P
P
O
Ph
Ph
80.036
79.781
29.006
28.755
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
ppm
49.99
50.01

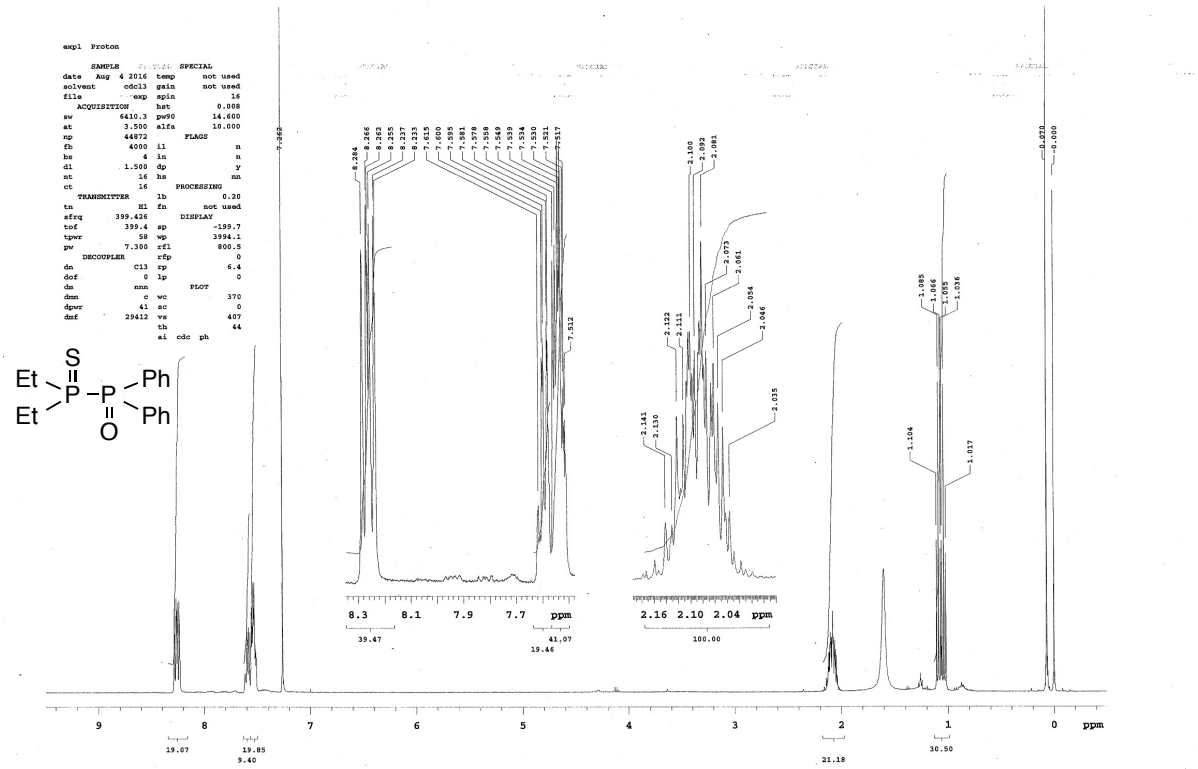
1,1-Dimethyl-2,2-diphenyldiphosphine 2-oxide 1-sulfide (6g)

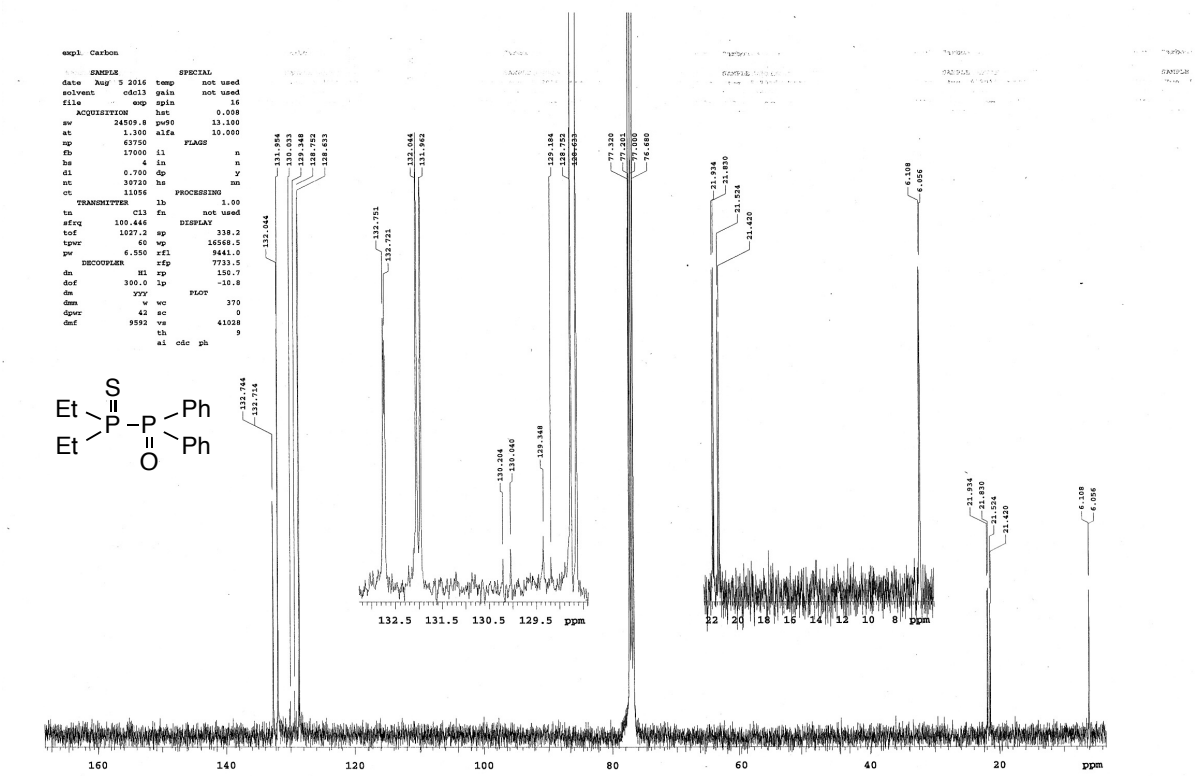


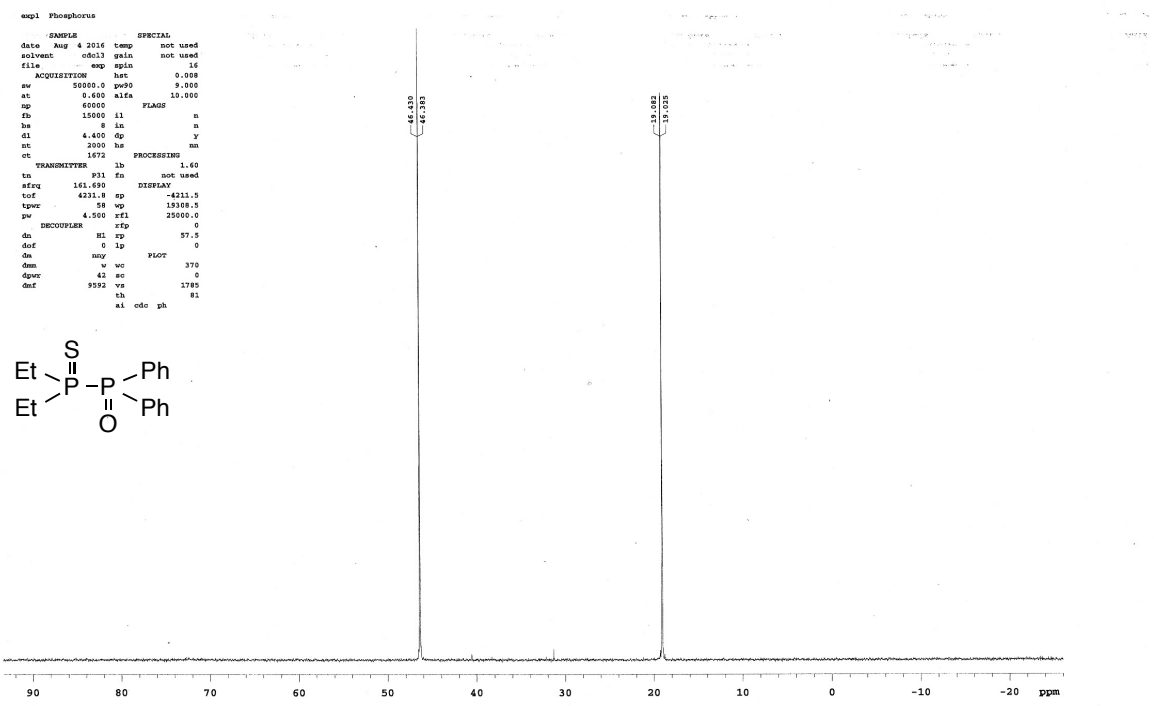



expl Phosphorus
SAMPLE
date Aug 5 2016
solvent cdcl3
file exp
ACQUISITION
sw 50000.0
at 0.600
np 60000
fb 15000
bs 4
d1 4.400
nt 2000
ct 640
TRANSMITTER
tn P31
sfrq 161.690
tof 4231.8
tpwr 58
pw 4.500
DECOUPLER
dn H1
dof 0
dm nny
dmm w
dpwr 42
dmf 9592
SPECIAL
temp not used
gain not used
spin 16
hst 0.008
pw90 9.000
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 1.60
fn not used
DISPLAY
sp -8839.5
wp 33799.7
rf1 25000.0
rfp 0
rp 58.4
lp 0
PLOT
wc 370
sc 0
vs 792
th 38
ai cdc ph
S
Me
P
P
Ph
Me
O
Ph
93.531
93.285
30.217
29.981
140
120
100
80
60
40
20
0
-20
-40
ppm
48.36
51.64

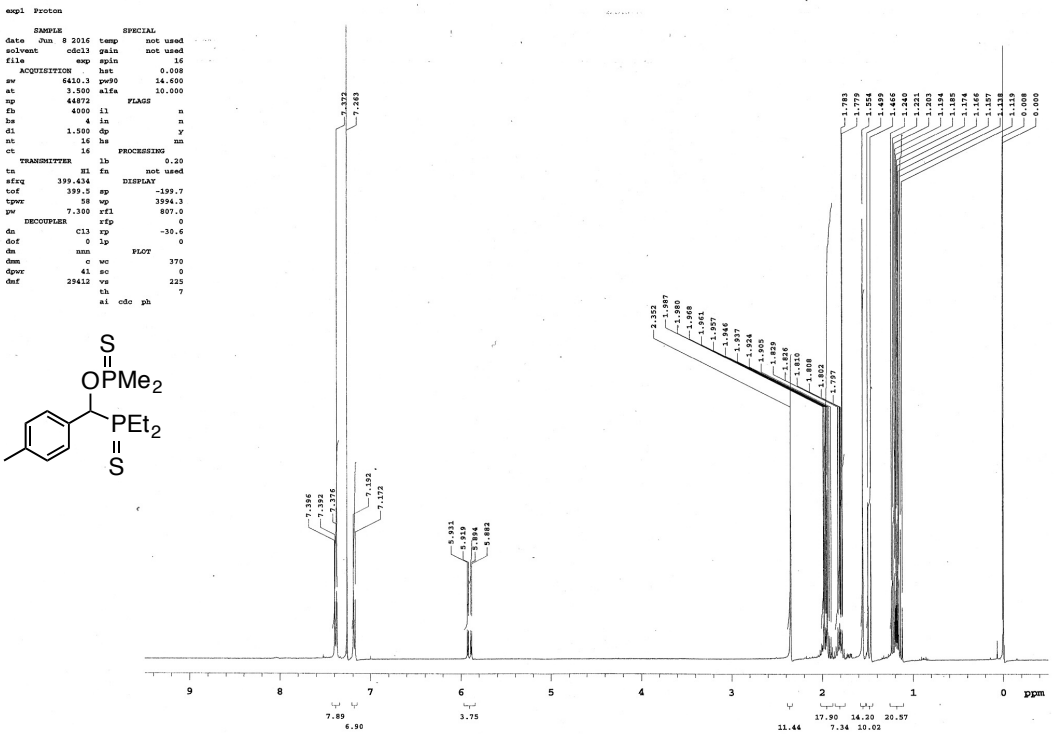
1,1-Diethyl-2,2-diphenyldiphosphine 2-oxide 1-sulfide (6h)

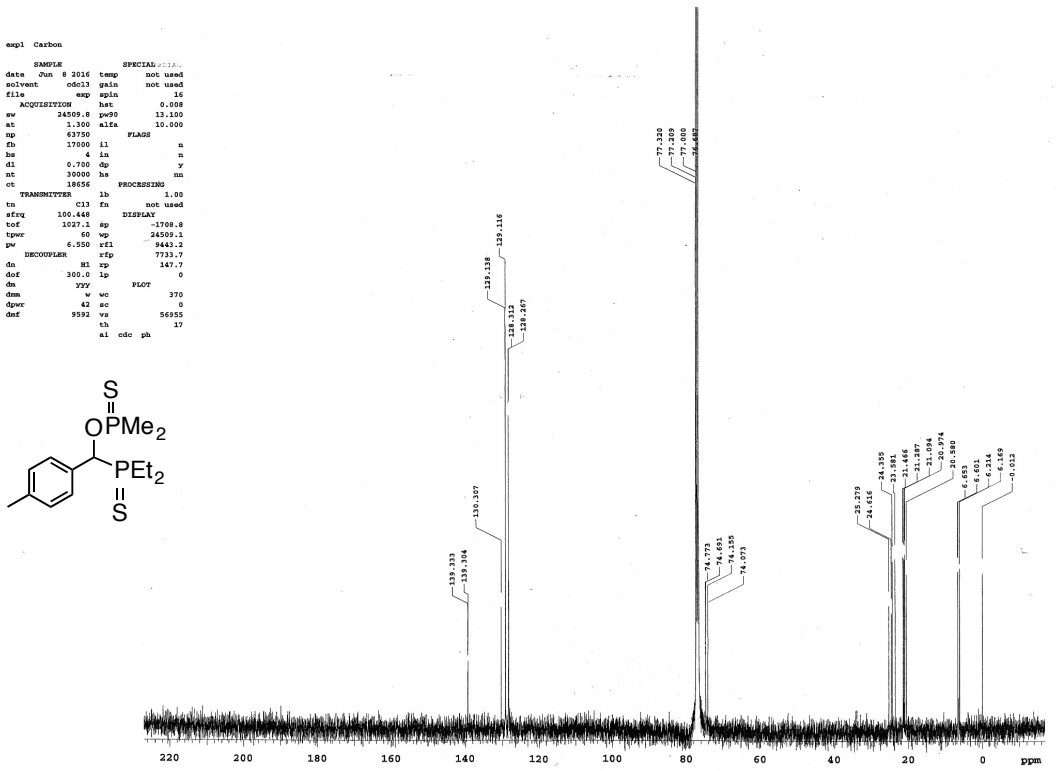


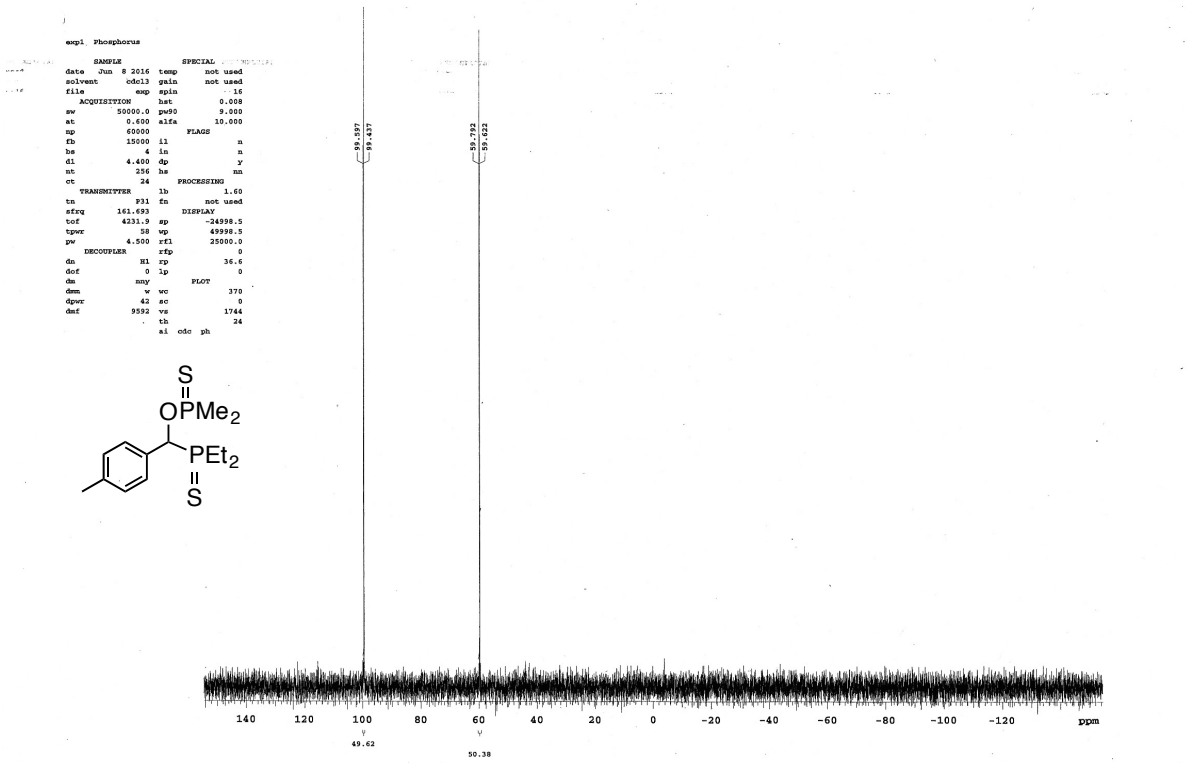



expl Phosphorus
SAMPLE
date Aug 4 2016
solvent cdcl3
file exp
ACQUISITION
sw 50000.0
at 0.600
np 60000
fb 15000
bs 8
d1 4.400
nt 2000
ct 1672
TRANSMITTER
tn P31
sfrq 161.690
tof 4231.8
tpwr 58
pw 4.500
DECOUPLER
dn H1
dof 0
dm nny
dmm w
dpwr 42
dmf 9592
SPECIAL
temp not used
gain not used
spin 16
hst 0.008
pw90 9.000
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 1.60
fn not used
DISPLAY
sp -4211.5
wp 19308.5
rfl 25000.0
rfp 0
rp 57.5
lp 0
PLOT
wc 370
sc 0
vs 1785
th 81
ai cdc ph
S
Et
P
P
Ph
Et
O
Ph
46.430
46.383
19.082
19.035
90
80
70
60
50
40
30
20
10
0
-10
-20
ppm

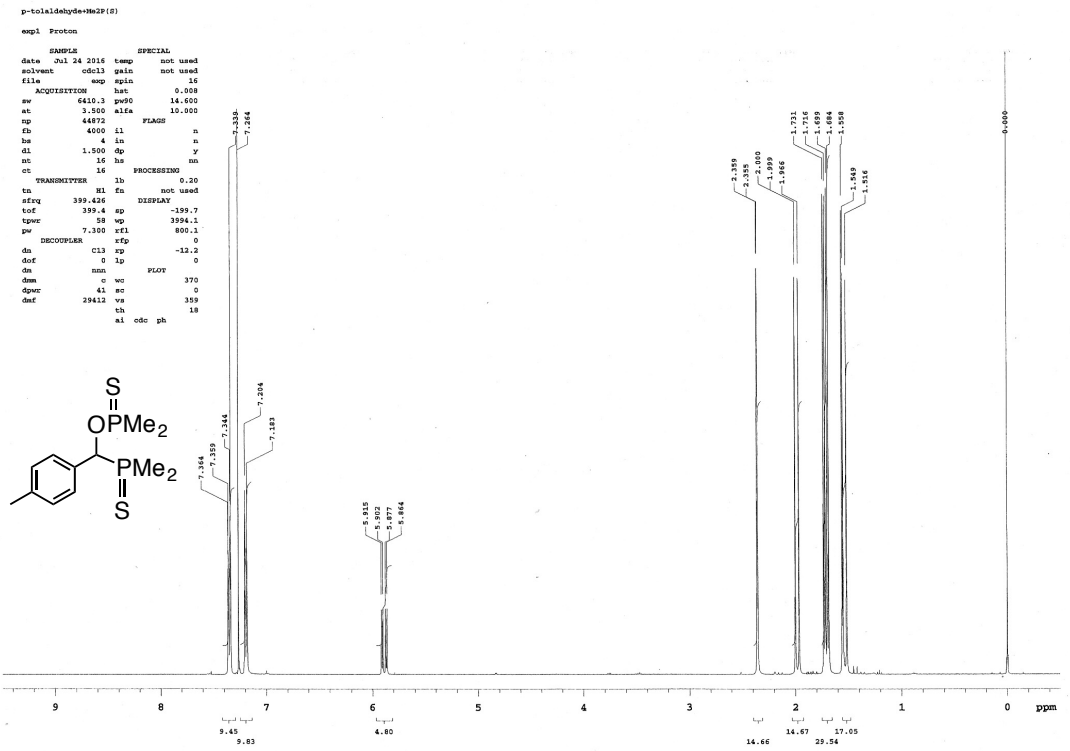
[1-(Dimethylthiophosphinoyloxy)-4-methylbenzyl]diethylphosphine sulfide (11)

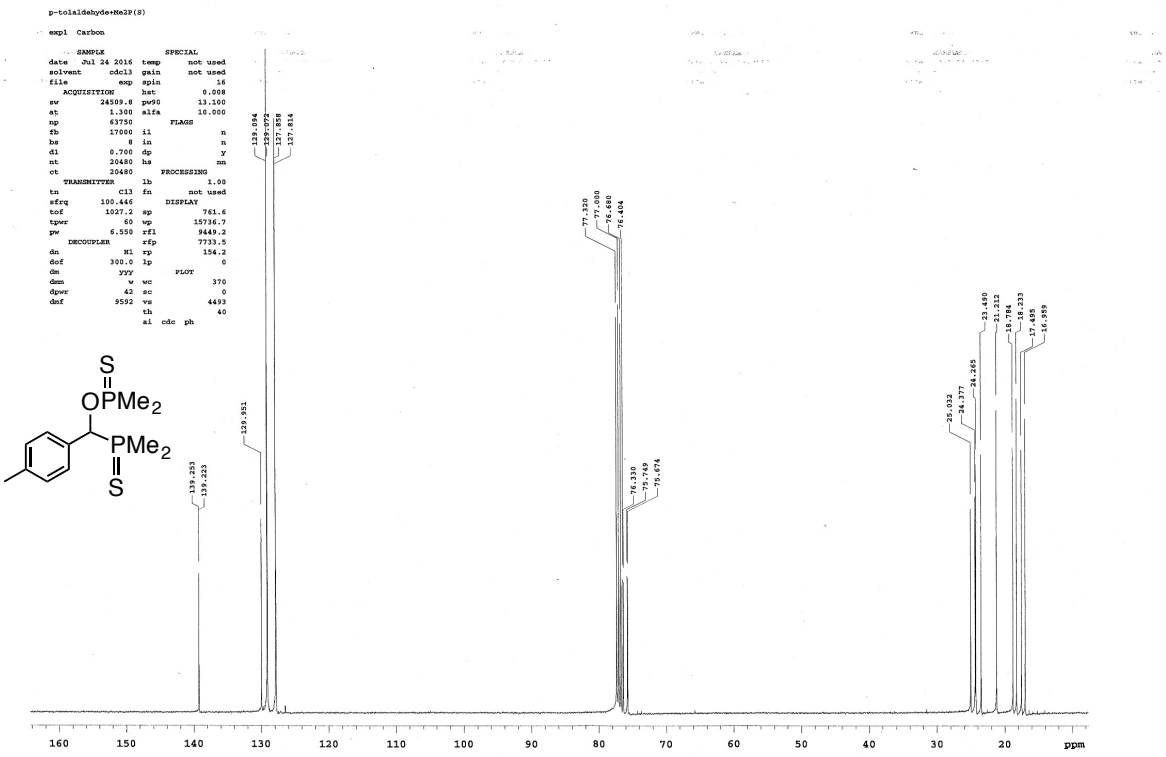


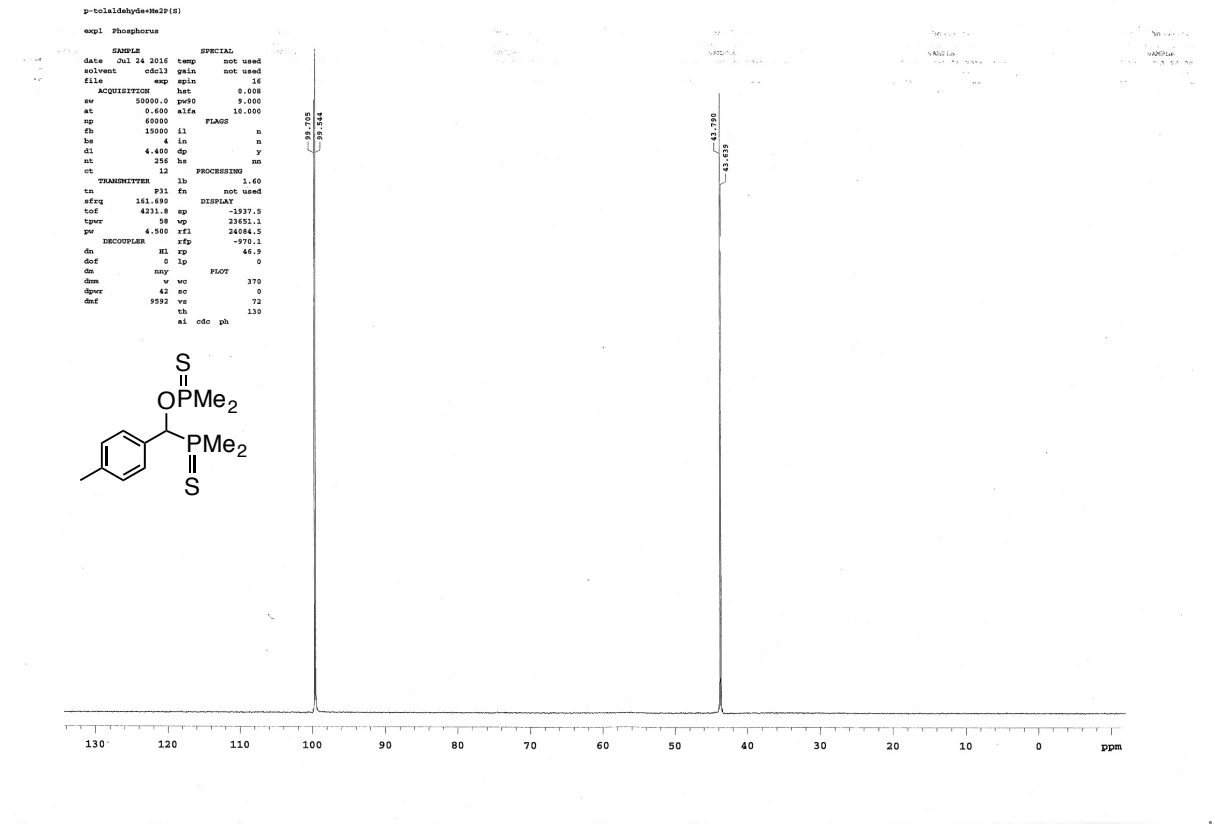



exp1 Phosphorus
SAMPLE
date Jun 8 2016
solvent cdcl3
file exp
ACQUISITION
sw 50000.0
at 0.600
np 60000
fb 15000
bs 4
d1 4.400
nt 256
ct 24
TRANSMITTER
tn P31
sfrq 161.693
tof 4231.9
tpwr 58
pw 4.500
DECOUPLER
dn H1
dof 0
dm nny
dmm w
dpwr 42
dmf 9592
SPECIAL
temp not used
gain not used
spin 16
hst 0.008
pw90 9.000
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 1.60
fn not used
DISPLAY
sp -24998.5
wp 49998.5
rfl 25000.0
rfp 0
rp 36.6
lp 0
PLOT
wc 370
sc 0
vs 1744
th 24
ai cdc ph
S
OPMe2
PEt2
S
99.597
99.437
59.792
59.622
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
ppm
49.62
50.38

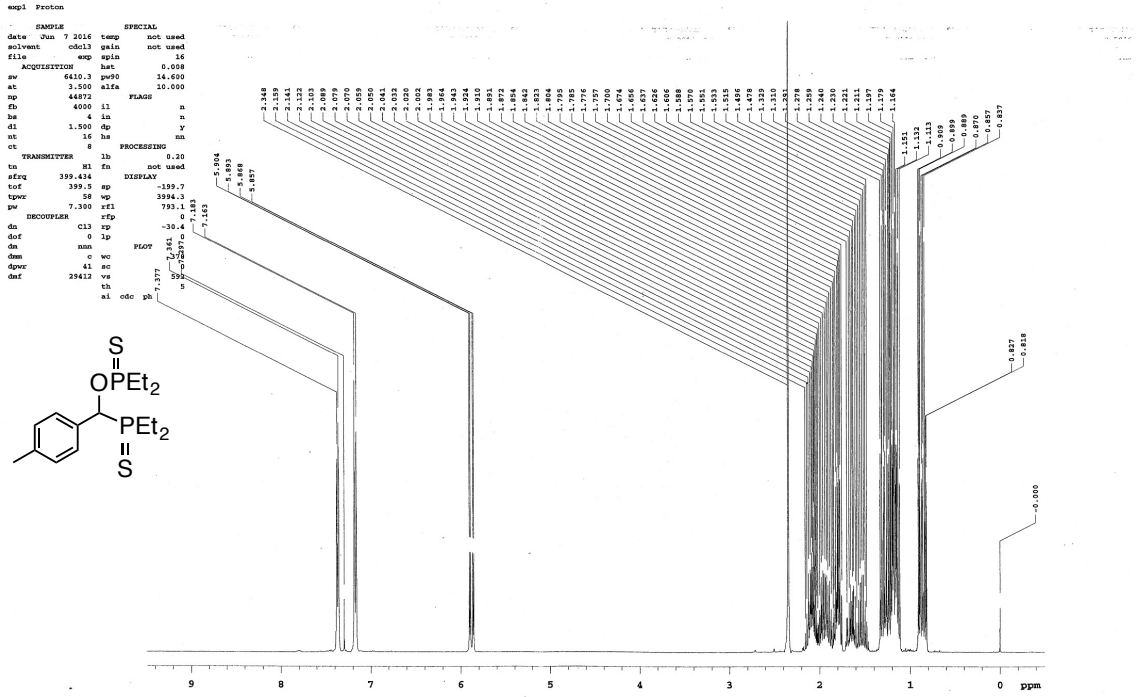
[1-(Dimethylthiophosphinoyloxy)-4-methylbenzyl]dimethylphosphine sulfide (13)

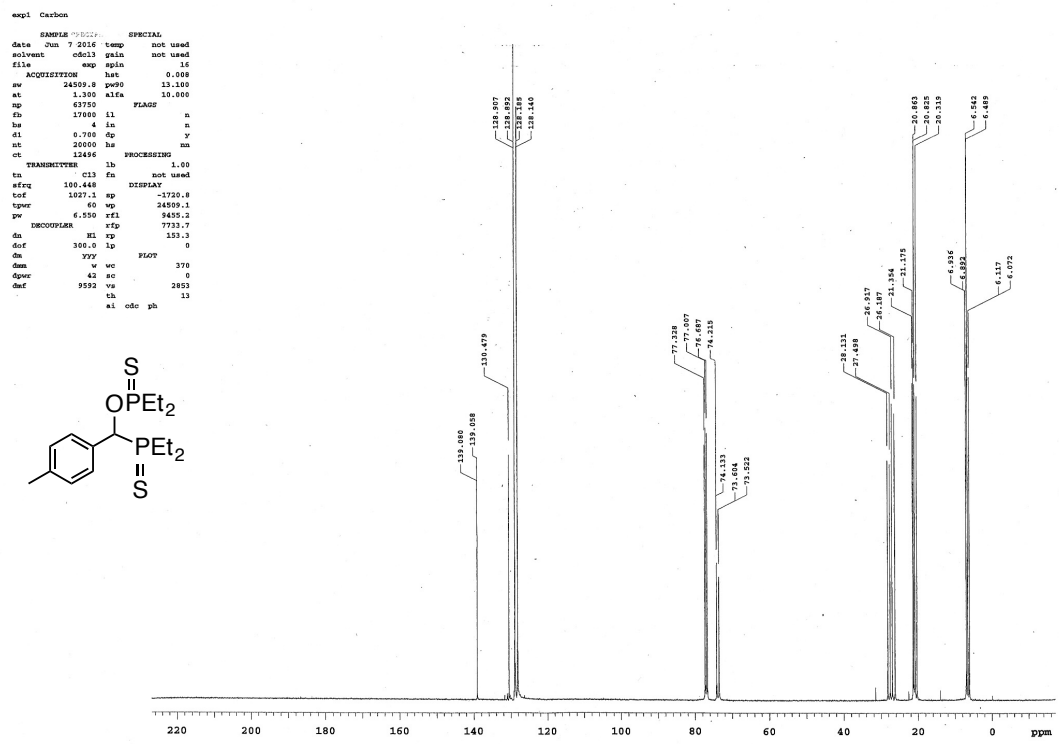


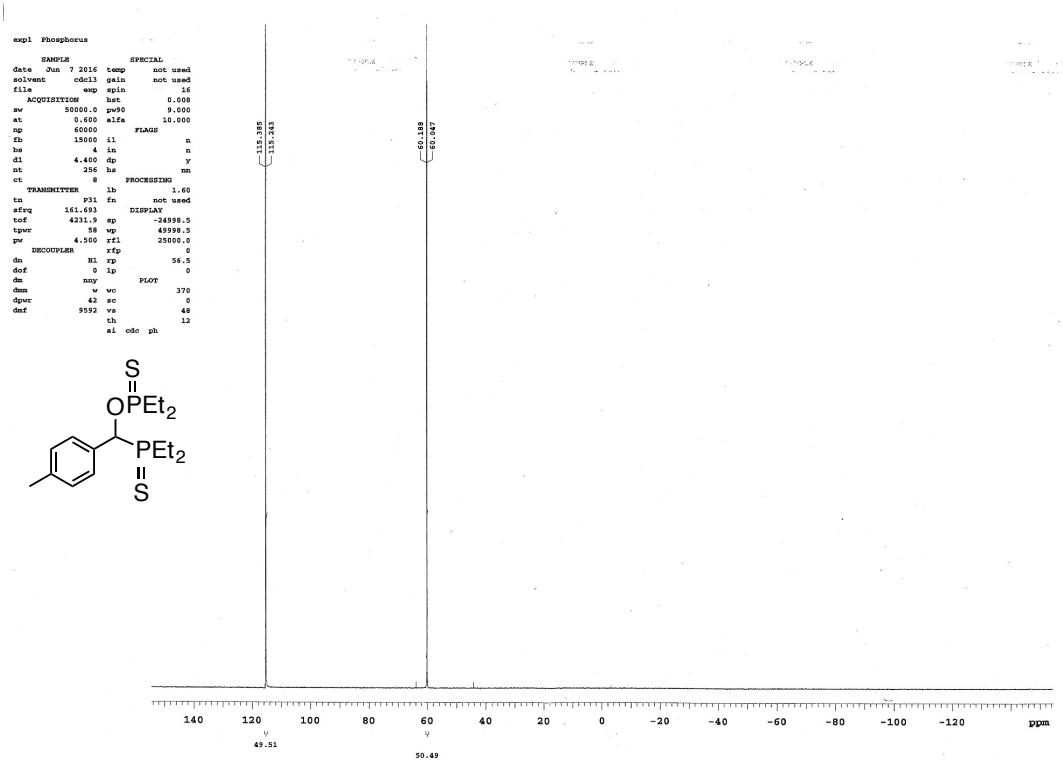



p-tolaldehyde+Me2P(S)
expl Phosphorus
SAMPLE
date Jul 24 2016
solvent cdcl3
file exp
ACQUISITION
sw 50000.0
at 0.600
np 60000
fb 15000
bs 4
d1 4.400
nt 256
ct 12
TRANSMITTER
tn P31
sfrq 161.690
tof 4231.8
tpwr 58
pw 4.500
DECOUPLER
dn H1
dof 0
dm nny
dmm w
dpwr 42
dmf 9592
SPECIAL
temp not used
gain not used
spin 16
hst 0.008
pw90 9.000
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 1.60
fn not used
DISPLAY
sp -1937.5
wp 23651.1
rfl 24084.5
rfp -970.1
rp 46.9
lp 0
PLOT
wc 370
sc 0
vs 72
th 130
ai cdc ph
99.705
99.544
43.790
43.639
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

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






expl Phosphorus
SAMPLE
date Jun 7 2016
solvent cdcl3
file exp
ACQUISITION
sw 50000.0
at 0.600
np 60000
fb 15000
bs 4
d1 4.400
nt 256
ct 8
TRANSMITTER
tn P31
sfrq 161.693
tof 4231.9
tpwr 58
pw 4.500
DECOUPLER
dn H1
dof 0
dm nny
dmm w
dpwr 42
dmf 9552
SPECIAL
temp not used
gain not used
spin 16
hst 0.008
pw90 9.000
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 1.60
fn not used
DISPLAY
sp -24998.5
wp 49998.5
rfl 25000.0
rfp 0
rp 56.5
lp 0
PLOT
wc 370
sc 0
vs 48
th 12
ai cdc ph
S
OPEt2
PEt2
S
115.385
115.243
60.188
60.047
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
ppm
49.51
50.49