Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.
This journal is © the Partner Organisations 2023

Atom-economic synthesis of 1,2-bis(phosphine oxide)ethanes from calcium carbide with straightforward access to deuterium- and ^{13}C-labeled bidentate phosphorus ligands and metal complexes

Kristina A. Lotsman,[a] Konstantin S. Rodygin,[a] Irina Skvortsova,[a] Anastasia M. Kutskaya,[a] Mikhail E. Minyaev [b] and Valentine P. Ananikov*[a, b]

[a] Saint Peterburg State University, Universitetskiy pr. 26, Stary Petergof 198504, Russia. E-mail: k.rodygin@spbu.ru

[b] N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Leninsky pr. 47, Moscow 119991, Russia. E-mail: val@ioc.ac.ru.

Contents

S1. Materials and methods

Materials. Calcium carbide (granulated, particle size 0.1-1 mm, 75 % of acetylene (gas-volumetric as indicated by the supplier)), isobutyl bromide (99%), carbon-13 and $PdCl_2$ were purchased from Sigma Aldrich and used without further purification. 4-Bromotoluene (99%) and di-*tert*-butylphosphine 0.5 M (10 wt.%) solution in hexanes were purchased from Acros Organics and used as received. o-Bromotoluene (99%) and 3-bromotoluene (98%) were purchased from Macklin. 4-Bromoanisole (99%), *n*-butyl bromide (99%), dicyclohexylphosphine (98%), diethyl phosphite (99%), diphenylphosphineoxide (97%), and nickel(II) bromide anhydrous (99%) were purchased from Alfa Aesar, Chemical Line, abcr GmbH&Co, Energy-chemical and Bide Pharmatech Ltd., respectively. KF, *n*-butyl bromide, and magnesium (turnings) were purchased from Vekton, Reakhim and Ruskhim (Russia).

K_2PdCl_4 was prepared from $PdCl_2$ and KCl.[1] A solution of 6.72 g of KCl was mixed with a solution of 4 g of $PdCl_2$. The mixture was heated and cooled. As a result, 5.9 g of K_2PdCl_4 was isolated. KF was dried and grinded before use. $^{13}C_2Ca$ was prepared from carbon-13 and calcium metal according to previous procedure.[2] All the solvents were purified by standard procedures. THF was predried over 4 Å molecular sieves and distilled from sodium/benzophenone. Toluene was distilled from sodium and stored over 4 Å molecular sieves.

Instrumentation. The NMR spectra were recorded on Bruker Avance III 400 and Bruker Avance III 500 NMR spectrometers at 25 °C (at 400 or 500, 100 or 126, 162, and 61 or 77 MHz for ^{1}H, ^{13}C, ^{31}P, and ^{2}H NMR spectra, respectively). Chemical shifts are given in δ values [ppm] referenced to the residual signals of deuterated solvent ($CHCl_3$): δ 7.26 (^{1}H), 77.2 (^{13}C); deuterated solvent ($CDCl_3$): δ 7.26 (^{2}H); or 85% H_3PO_4 δ 0.0 ppm (^{31}P). The deuterium incorporation (DI) was calculated using ^{1}H NMR spectroscopy by decrease the intensity of the signal of the corresponding hydrogen atom. The data were processed using MestReNova (version 6.0.2) desktop NMR data processing software. High-resolution mass spectra were registered on a Bruker Micro-TOF mass spectrometer (ESI-MS).

Computational details. Quantum chemical, spin restricted calculations were performed using the ORCA 5.0.1 software package. The molecular structures of the reactants, transition states, intermediates and products were optimized by DFT calculations at the B3LYP/6-31+G* level of theory. Calculations of vibrational frequencies were performed at the same level of theory. A tight convergence criterion for the Kohn-Sham self-consistent field procedure (TightSCF) was selected. An integration grid (DefGRID3) with disabled double integration grid procedure (NOFINALGRID) was used to calculate the energies.

A search for the geometry of the transition state was performed by scanning a potential energy surface (geom scan option) of a structure prereaction complex. Received transition states are located on first-order saddle points on the potential energy surface, which is local maxima in exactly one direction. Each found transition state is characterized by having exactly one vibrational mode with an imaginary frequency.

A continuum model CPCM was used to simulate the reaction medium; the model solvent was DMSO. The cavity was built using the GEPOL approach[3] with an electrostatic scale factor $\alpha = 1.1$.[4] For the calculation, the dielectric constant for DMSO $\varepsilon = 46.8$ was used. The calculations of the Gibbs free energy of solvation $\Delta G^{\mathrm{A}}_{\mathrm{solv}}$ were performed as a separate optimization of the

geometry of the molecule, preoptimized at the B3LYP/6-31+G* theory level, and calculated as the difference of the Gibbs energy of the molecule in the solvent medium and in the gas phase.

The standard Gibbs free energy of species A in solution was calculated according to the equation:

$$G^A = H^A - T \cdot S_{\text{sol}} + \Delta G^{\text{A}}_{\text{solv}},$$

where S_{sol} is entropy in the DMSO solution, according to the Wertz approach,[5, 6] which takes into account the change of state of the system from an ideal gas at 1 atm pressure and temperature 298.15 K (or 403.15 K) to 1 M DMSO solution at the same temperature as follows:

$$S_{\text{sol}} = 0{,}74 S_{\text{harm}} - 3{,}21 \text{ cal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}.$$

S2. General procedures

Preparation of phosphine oxides:

Synthetic procedure for phosphine oxides (1a-d, g).

Phosphine oxides (**1a-d, g**) were obtained using Grignard reagents from the corresponding bromides and diethyl phosphite according to the procedure.[7] The procedure was carried out under argon atmosphere. Magnesium turnings (0.367 g, 15.1 mmol) were loaded into a flask, and activated with iodine. Then, a solution of the corresponding bromide (15.1 mmol) in 2 ml of anhydrous THF was added dropwise. The reaction mixture was stirred at 65 °C for 15 hours. After that, the mixture was cooled to 0 °C and a solution of diethyl phosphite (593 µl, 4.6 mmol) in 2 ml of anhydrous THF was slowly added dropwise. The reaction was continued for 2 hours at room temperature. Then, 10 ml of 0.1 N HCl solution was added to the mixture and filtered through Celite. The organic layer was separated, and the aqueous layer was additionally extracted with CH_2Cl_2 (3 × 10 ml). The combined organic layers were dried over $MgSO_4$ and the solvent was evaporated. The resulting crude product was further purified.
Crude di-*n*-hexyl and di-*n*-butyl phosphine oxides (**1b** and **1c**) were recrystallized from hexane.
Di-*i*-butyl phosphine oxide (**1d**) was purified on silica gel (Et_2O:MeOH (97:3)).
Di-*p*-tolyl phosphine oxide (**1g**) was purified on silica gel (DCM:MeOH = 40:1-20:1)).

Synthetic procedure for phosphine oxide (1e).

Di-*o*-tolyl phosphine oxide (**1e**) was obtained using Grignard reagents from the corresponding bromides and diethyl phosphite according to the procedure.[8] The procedure was carried out under argon atmosphere. Magnesium turnings (0.345 g, 14.2 mmol) and anhydrous THF (10 mL) were loaded into a flask, and Mg was activated with iodine. Then, *o*-bromotoluene (2.5 g, 14.2 mmol) was added dropwise. The reaction mixture was refluxed for 30 minutes. After that, the mixture was cooled to 0 °C and a solution of diethyl phosphite (554 µl, 4.3 mmol) in 2 ml of anhydrous THF was slowly added dropwise. The reaction was continued for 2 hours at room temperature. Then, 10 ml of 0.1 N HCl solution was slowly added to the mixture at 0 °C followed by additionally stirring for 20 min. After that, 10 ml of MTBE was added to the reaction mixture, followed by additionally stirring for 5 minutes. The organic layer was separated (decantation), and 15 ml of CH_2Cl_2 was added to the remaining gel and stirred for 5 minutes. The resulting mixture was filtered through a Celite pad and washed with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$ and the solvent was evaporated. The crude product was triturated with hexane.

Synthetic procedure for phosphine oxide (1f, h).

Phosphine oxides (**1f, h**) were obtained using Grignard reagents from the corresponding bromides and diethyl phosphite according to the procedure.[9] The procedure was carried out under argon atmosphere. Magnesium (0.306 g, 12.6 mmol) and anhydrous THF (5 mL) were loaded into a flask, and Mg was activated with iodine. Then, a solution of the corresponding bromide (2.35 g, 12.6 mmol) in 5 ml of anhydrous THF was added dropwise. The reaction mixture was stirred at room temperature for 1 hours. If the reaction with bromide does not start spontaneously, then the reaction mixture (with a small amount of bromide) is shortly heated,

followed by cooling and addition of the residue. After the completion, the mixture was cooled to 0 °C and a solution of diethyl phosphite (491 µl, 3.8 mmol) in 2 ml of anhydrous THF was slowly added dropwise. The reaction was continued for 2 hours at room temperature. Then, 10 ml of 10% $NaHCO_3$ solution was slowly added to the mixture at 0 °C and stirred for 20 min. The resulting mixture was filtered and extracted with EtOAc (3 × 10 ml). The organic layer was dried over $MgSO_4$ and the solvent was evaporated. The resulting crude product was further purified.
Di-*m*-tolylphosphine oxide (**1f**) was purified on silica gel (DCM:MeOH (99:1)).
Bis-(4-methoxyphenyl)-phosphine oxide (**1h**) was purified on silica gel (DCM:MeOH = 40:1-20:1).

Synthetic procedure for phosphine oxide (1i-j).

Phosphine oxides (**1i-j**) were obtained after oxidation of the corresponding phosphines according to the procedure (method A).[10] A phosphine (5 mmol) was stirred in air at room temperature for 15 hours. Then, the resulting crude product was further purified.
Di-*t*-butyl phosphine oxide (**1i**) was purified on silica gel (Et_2O:MeOH (97:3)).
Di-cyclohexyl phosphine oxide (**1j**) was triturated with hexane.

General procedure for double addition of phosphine oxides to acetylene (Scheme 1):

Phosphine oxide (0.25 mmol), DMSO (0.5 mL), KF (17 mg, 0.3 mmol), CaC_2 (64 mg, 1 mmol) and H_2O (36 µL, 2 mmol) were loaded in a 5 mL pressure tube. Then, the tube was sealed, and the mixture was heated at 130 °C for 2 h with vigorous stirring. After cooling to 25 °C, the mixture was filtered, diluted with water (2 mL), extracted with DCM (3 × 2 mL), and treated with brine (3 × 2 mL), and the organic layer was dried over Na_2SO_4. After solvent evaporation, the crude product was washed with diethyl ether (3 × 0.5 mL).

General procedure for preparation of d_4-ligands ((2a-c, e, h, j)-d_4) (Scheme 5):

Phosphine oxide (0.5 mmol), DMSO-d_6 (1 mL) (or 0.05 mL of DMSO-d_6 and 0.45 mL of dioxane), KF (35 mg, 0.6 mmol), CaC_2 (128 mg, 2 mmol) and D_2O (80 µL, 4 mmol) were loaded in a 5 mL pressure tube. Then, the tube was sealed, and the mixture was heated at 130 °C for 5 h with vigorous stirring. After cooling to 25 °C, the mixture was filtered, diluted with water (2 mL), extracted with DCM (3 × 2 mL), treated with brine (3 × 2 mL), and the organic layer was dried over Na_2SO_4. After solvent evaporation, the crude product was washed with diethyl ether (3 × 0.5 mL).

Preparation of ^{13}C-DPPEO$_2$ ($^{13}C_2$-2a):

Diphenylphosphine oxide (2.5 mmol) with $Ca^{13}C_2$ (10 mmol) were placed into a 20 ml pressure tube followed by the addition of 5 ml of DMSO as a solvent and 0.02 mmol of H_2O and heated up to 130 °C at constant stirring. After 20 h, the mixture was filtered to dispose of inorganic precipitates. The organic phase was separated, and to extract the product from the aqueous layer, 30 ml of $CHCl_3$ was used. The organic extracts were dried over Na_2SO_4.

General procedure for reduction of the prepared ligands:

The reduction was carried out according to the modified procedure.[11] A phosphine oxide (1 mmol), toluene (3.5 ml) and $HSiCl_3$ (2 ml, 20 mmol) were placed under argon in a pressure

flask. The reaction mass was stirred for 5 hours at 100 °C. After that, 20 ml of 25% NaOH solution was added while cooling in an ice bath. The resulting mixture was left to stir overnight. Then, the organic layer was separated and the aqueous layer was extracted with diethyl ether and washed with brine. The organic layers were combined, dried over $MgSO_4$, and the solvent was evaporated. The crude product was purified on silica gel (eluent DCM:MeOH (80:1) for **3a**, DCM – for **3e**).

Synthesis of Ni complexes:

Complexes with $NiBr_2$ were prepared according to the procedure[12] from anhydrous $NiBr_2$ and the corresponding reduced phosphorus ligands. $NiBr_2$ (82 mg, 0.375 mmol) was dissolved on heating in a minimal amount in methanol (3–4 ml). After that, the hot solution was added through a filter to a warm solution of the corresponding ligand (0.25 mmol) in 1 ml of toluene; in this case, change in the color of the solution from colorless to dark brown was observed. The resulting mixture was refluxed for 2 hours, while the growth of red crystals was observed. After cooling to 25 °C, the precipitate was filtered, washed with methanol, and dried in vacuum. Crystals suitable for XRD were obtained by slow evaporation of the solvent (a mixture of methylene chloride and diethyl ether).

Synthesis of Pd complexes:

Complexes with $PdCl_2$ were prepared according to the procedure[13] from K_2PdCl_4 and the corresponding reduced phosphorus ligands. K_2PdCl_4 (20 mg, 0.06 mmol) was dissolved with heating in DMF (1.25 ml). After that, the hot salt solution was added through a filter to a warm solution of DPPE (25 mg, 0.0625 mmol) in 2 ml of DCM, and color change of the solution from colorless to yellow was observed. The resulting mixture was refluxed for 2 hours, and the growth of white crystals was observed. After cooling to 25 °C, the precipitate was filtered, washed with water, diethyl ether, and dried in vacuum. Crystals suitable for XRD were obtained by slow evaporation from methylene chloride.

S3. Spectral data and characterization

DPPEO$_2$ (2a)

Yield 105 mg (98%), white solid, m.p. 272-273 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.62 (m, 8H), 7.50 (t, *J* = 7.2 Hz, 4H), 7.43 (t, *J* = 7.2 Hz, 8H), 2.51 (d, *J* = 2.2 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.2, 132.9 – 131.3 (m), 130.9 (t, *J* = 4.8 Hz), 128.9 (t, *J* = 5.9 Hz), 22.7 – 21.0 (m). ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.5.

Cf. lit. data.[14]

DHHEO$_2$ (2b)

Yield 106 mg (92%), white solid, m.p. 163-164 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.90 (d, *J* = 2.1 Hz, 4H), 1.81 – 1.62 (m, 8H), 1.63 – 1.47 (m, 8H), 1.45 – 1.34 (m, 8H), 1.35 – 1.20 (m, 16H), 0.97 – 0.76 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 31.4, 31.0 (t, *J* = 7.0 Hz), 28.8 – 27.5 (m), 22.5, 21.9, 20.6 – 19.5 (m), 14.1. ^{31}P NMR (162 MHz, $CDCl_3$) δ 48.4. HRMS exact mass calculated for $[M+H]^+$ ($C_{26}H_{57}O_2P_2^+$): m/z 463.3828, found m/z 463.3830.

The compound has been previously synthesized.[15] However, NMR spectra were not presented in the work.

DBBEO$_2$ (2c)

Yield 70 mg (80%), white solid, m.p. 173-174 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.89 (s, 4H), 1.80 – 1.60 (m, 8H), 1.59 – 1.46 (m, 8H), 1.45 – 1.31 (m, 8H), 0.90 (t, *J* = 7.2 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 28.6 – 27.1 (m), 24.3 (t, *J* = 7.1 Hz), 23.9, 20.7 – 19.1 (m), 13.7. ^{31}P NMR (162 MHz, $CDCl_3$) δ 48.7. HRMS exact mass calculated for $[M+H]^+$ ($C_{18}H_{41}O_2P_2^+$): m/z 251.2576, found m/z 251.2578.

The compound has been previously synthesized.[16] However, NMR spectra were not presented in the work.

D(*i*-Bu)$_2$EO$_2$ (2d)

Yield 61 mg (70%), white solid, m.p. 155-157 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.21 – 2.02 (m, 4H), 1.92 (d, *J* = 2.4 Hz, 4H), 1.70 – 1.58 (m, 8H), 1.09 (d, *J* = 6.6 Hz, 12H), 1.08 (d, *J* = 6.6 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 39.2 – 37.4 (m), 25.2 – 24.8 (m), 23.8 (t, *J* = 1.7 Hz), 22.9 – 21.4 (m). ^{31}P NMR (162 MHz, $CDCl_3$) δ 46.4. HRMS exact mass calculated for $[M+H]^+$ ($C_{18}H_{41}O_2P_2^+$): m/z 351.2576, found m/z 351.2577.

Cf. lit. data.[17]

D(*o*-Tol)$_2$EO$_2$ (2e)

Yield 89 mg (73%), white solid, m.p. 228-233 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.62 (m, 4H), 7.39 (t, *J* = 7.5 Hz, 4H), 7.32 – 7.20 (m, 4H), 7.17 (d, *J* = 7.4 Hz, 4H), 2.63 (d, *J* = 2.4 Hz, 4H), 2.23 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.8 (t, *J* = 4.4 Hz), 132.5 – 131.8 (m), 131.5 – 129.7 (m), 125.9 (t, *J* = 5.9 Hz), 21.2 (t, *J* = 2.0 Hz), 21.6 – 20.4 (m). ^{31}P NMR (162

MHz, $CDCl_3$) δ 34.6. HRMS exact mass calculated for $[M+H]^+$ ($C_{30}H_{33}O_2P_2^+$): m/z 487.1950, found m/z 487.1953.

D(*m*-Tol)$_2$EO$_2$ (2f)

Yield 118 mg (97%), white solid, m.p. 174-178 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.53 (m, 4H), 7.47 – 7.42 (m, 4H), 7.32 – 7.27 (m, 8H), 2.49 (s, 4H), 2.33 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.9 (t, *J* = 5.8 Hz), 132.9, 132.7 – 131.5 (m), 131.4 (t, *J* = 4.6 Hz), 128.8 (t, *J* = 6.2 Hz), 127.8 (t, *J* = 4.8 Hz), 22.5 – 21.7 (m), 21.5. ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.9. HRMS exact mass calculated for $[M+H]^+$ ($C_{30}H_{33}O_2P_2^+$): m/z 487.1950, found m/z 487.1950.

D(*p*-Tol)$_2$EO$_2$ (2g)

Yield 101 mg (83%), white solid, m.p. 237-238 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.44 (m, 8H), 7.28 – 7.09 (m, 8H), 2.46 (s, 4H), 2.34 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.5, 130.9 (t, *J* = 4.8 Hz), 129.6 (t, *J* = 6.0 Hz), 129.1 – 128.5 (m), 23.3 – 21.2 (m), 21.7. ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.1. HRMS exact mass calculated for $[M+Na]^+$ ($C_{30}H_{32}O_2P_2Na^+$): m/z 509.1770, found m/z 509.1770.

D(*p*-OMe(C$_6$H$_4$))$_2$EO$_2$ (2h)

Yield 118 mg (86%), white solid, m.p. 179-180 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.39 (m, 8H), 6.91 (d, *J* = 7.5 Hz, 8H), 3.79 (s, 12H), 2.41 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5, 132.7 (t, *J* = 5.2 Hz), 125.1 – 121.9 (m), 114.4 (t, *J* = 6.3 Hz), 55.4, 23.9 – 20.0 (m). ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.7. HRMS exact mass calculated for $[M+H]^+$ ($C_{30}H_{33}O_6P_2^+$): m/z 551.1747, found m/z 551.1747.

Cf. lit. data.[18]

D(*t*-Bu)$_2$EO$_2$ (2i)

Yield 60 mg (69%), white solid, m.p. 134-136 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.01 (s, 4H), 1.29 – 1.18 (m, 36H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 36.6 – 35.6 (m), 26.6, 14.6 – 13.7 (m). ^{31}P NMR (162 MHz, $CDCl_3$) δ 60.7. HRMS exact mass calculated for $[M+H]^+$ ($C_{18}H_{41}O_2P_2^+$): m/z 351.2576, found m/z 351.2579.

Cf. lit. data.[17]

D(Cy)$_2$EO$_2$ (2j)

Yield 76 mg (67%), white solid, m.p. 184-188 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.23 – 1.46 (m, 14H), 1.47 – 1.10 (m, 10H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 37.5 – 35.8 (m), 27.0 – 26.5 (m), 26.0, 25.8 (d, *J* = 22.0 Hz), 16.2 – 14.8 (m). ^{31}P NMR (162 MHz, $CDCl_3$) δ 51.8. HRMS exact mass calculated for $[M+H]^+$ ($C_{26}H_{49}O_2P_2^+$): m/z 455.3202, found m/z 455.3201.

Cf. lit. data.[19]

DPPEO$_2$-d$_4$ (2a-d$_4$)

Yield 107 mg (99%), white solid, m.p. 264-266 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.57 (m, 8H), 7.57 – 7.47 (m, 4H), 7.44 (t, *J* = 7.1 Hz, 8H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 132.1,

133.1 – 131.1 (m), 130.8 (t, J = 4.4 Hz), 128.9 (t, J = 5.7 Hz), 22.1 – 19.9 (m). ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.5. ^{2}H NMR (77 MHz, $CHCl_3$) δ 2.48 (s). HRMS exact mass calculated for $[M+H]^+$ ($C_{26}H_{21}D_4O_2P_2^+$): m/z 435.1575, found m/z 435.1575.

DHHEO$_2$-d$_{12}$ (2b-d$_{12}$)

Yield 107 mg (90%), white solid, m.p. 163-164 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.50 (s, 8H), 1.43 – 1.06 (m, 24H), 1.02 – 0.65 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 31.4, 30.8 (t, J = 6.8 Hz), 28.6 – 26.5 (m), 22.5, 21.6, 20.2 – 18.0 (m), 14.1. ^{31}P NMR (162 MHz, $CDCl_3$) δ 48.3. ^{2}H NMR (61 MHz, $CHCl_3$) δ 1.83 (s, 4D), 1.66 (s, 8D). HRMS exact mass calculated for $[M+Na]^+$ ($C_{26}H_{44}D_{12}O_2P_2Na^+$): m/z 497.4394, found m/z 497.4389.

DBBEO$_2$-d$_{12}$ (2c-d$_{12}$)

Yield 55 mg (61%), white solid, m.p. 174-175 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.45 (s, 8H), 1.41 – 1.28 (m, 8H), 0.93 – 0.77 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 28.1 – 26.2 (m), 24.4 – 24.0 (m), 23.6, 20.1 – 18.0 (m), 13.6. ^{31}P NMR (162 MHz, $CDCl_3$) δ 48.5. ^{2}H NMR (77 MHz, $CHCl_3$) δ 1.83 (s, 4D), 1.65 (s, 8D). HRMS exact mass calculated for $[M+H]^+$ ($C_{18}H_{29}D_{12}O_2P_2^+$): m/z 363.3330, found m/z 463.3329.

D(*o*-Tol)$_2$EO$_2$-d$_{16}$ (2e-d$_{16}$)

Yield 93 mg (74%), white solid, m.p. 228-233 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, J = 12.7, 6.8 Hz, 4H), 7.49 – 7.34 (m, 4H), 7.31 – 7.23 (m, 4H), 7.17 (d, J = 7.1 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.6, 132.2 – 132.0 (m), 131.4 – 129.9 (m), 125.9 (t, J = 5.9 Hz), 20.8 – 20.0 (m). ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.5. ^{2}H NMR (61 MHz, $CHCl_3$) δ 2.60 (s, 4D), 2.18 (s, 12D). HRMS exact mass calculated for $[M+H]^+$ ($C_{30}H_{17}D_{16}O_2P_2^+$): m/z 503.2944, found m/z 503.2949.

D(*o*-Tol)$_2$EO$_2$-d$_4$ (2e-d$_4$)

Yield 98 mg (80%), white solid, m.p. 226-230 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, J = 13.0, 6.6 Hz, 4H), 7.39 (t, J = 7.5 Hz, 4H), 7.31 – 7.22 (m, 4H), 7.17 (d, J = 7.4 Hz, 4H), 2.23 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.7 (t, J = 4.4 Hz), 132.8 – 131.7 (m), 131.4 – 129.7 (m), 125.9 (t, J = 5.8 Hz), 22.0 – 20.9 (m). ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.5. ^{2}H NMR (77 MHz, $CHCl_3$) δ 2.61 (s). HRMS exact mass calculated for $[M+Na]^+$ ($C_{30}H_{28}D_4O_2P_2Na^+$): m/z 513.2021, found m/z 513.2018.

D(*p*-OMe(C$_6$H$_4$))$_2$EO$_2$-d$_4$ (2h-d$_4$)

Yield 102 mg (74%), white solid, m.p. 181-182 °C. The intensity of integrals may be variable due to partial deuteration. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 8H), 6.90 (d, J = 7.4 Hz, 5H), 3.78 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5, 133.2 – 132.2 (m), 124.8 – 122.3 (m), 114.5 – 114.2 (m), 55.4, 22.1 – 21.5 (m). ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.8. ^{2}H NMR (61 MHz, $CHCl_3$) δ 7.63 (s, 1D), 6.96 (s, 2D), 2.40 (s, 4D). HRMS exact mass calculated for $[M+Na]^+$ ($C_{30}H_{25}D_7O_6P_2Na^+$): m/z 580.2004, found m/z 580.1975.

DCy$_2$EO$_2$-d$_4$ (2j-d$_4$)

Yield 48 mg (42%), white solid, m.p. 198-199 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.03 – 1.56 (m, 24H), 1.45 – 1.09 (m, 20H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 38.4 – 34.9 (m), 27.37 – 26.24 (m), 26.0, 25.7 (d, *J* = 23.6 Hz), 16.1 – 13.3 (m). ^{31}P NMR (162 MHz, $CDCl_3$) δ 50.8. ^{2}H NMR (77 MHz, $CHCl_3$) δ 1.84 (s). HRMS exact mass calculated for $[M+H]^+$ ($C_{26}H_{45}D_4O_2P_2^+$): m/z 459.3453, found m/z 459.3454.

Cf. lit. data.[20]

^{13}C-DPPEO$_2$ ($^{13}C_2$-2a)

Yield 0.513 g (96%), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 77.82 – 7.61 (m, 8H), 7.52 (t, *J* = 7.1 Hz, 4H), 7.46 (t, *J* = 7.1 Hz, 8H), 2.83 – 2.24 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.3, 131.9 – 131.1 (m), 131.0 – 130.9 (m), 129.1 – 128.9 (m), 22.7 – 20.8 (m). ^{31}P NMR (162 MHz, $CDCl_3$) δ 38.8 – 28.8 (m). HRMS exact mass calculated for $[M+Na]^+$ ($C_{24}{}^{13}C_2H_{24}O_2P_2Na^+$): m/z 455.1211, found m/z 455.1213.

DPPE (3a)

Yield 0.295 g (74%), white solid, m.p. 139-140 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.22 (m, 20H), 2.10 (t, *J* = 3.7 Hz, 4H). ^{31}P NMR (162 MHz, $CDCl_3$) δ -12.5.

Cf. lit. data.[14]

DPPE-d$_4$ (3a-d$_4$)

Yield 0.302 g (75%), white solid, m.p. 139-140 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.28 (m, 10H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.3 – 138.2 (m), 132.9 (t, *J* = 9.3 Hz), 128.8, 128.6 (t, *J* = 3.0 Hz), 24.0 – 22.2 (m). ^{31}P NMR (162 MHz, $CDCl_3$) δ -13.2. ^{2}H NMR (61 MHz, $CHCl_3$) δ 2.08 (s). HRMS exact mass calculated for $[M+H]^+$ ($C_{26}H_{21}D_4P_2^+$): m/z 403.1677, found m/z 403.1677.

The compound has been previously synthesized.[21] However, NMR spectra were not presented in the work.

^{13}C-DPPE ($^{13}C_2$-3a)

Yield 0.312 g (78%), white solid, m.p. 141-142 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.27 (m, 20H), 2.36 – 1.79 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.5 – 138.0 (m), 132.9 (t, *J* = 9.4 Hz), 128.8, 128.6 (t, *J* = 3.3 Hz), 25.1 – 23.2 (m). ^{31}P NMR (162 MHz, $CDCl_3$) δ -11.9 – -13.2 (m). HRMS exact mass calculated for $[M+H]^+$ ($C_{24}{}^{13}C_2H_{25}P_2$): m/z 401.1493, found m/z 401.1489.

DHHE (3b)

Yield 46 mg (72%), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.83 – 1.07 (m, 44H), 0.88 (t, *J* = 6.7 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 31.7, 31.3 (t, *J* = 5.3 Hz), 27.3 – 26.7 (m), 26.0 (t, *J* = 6.3 Hz), 22.7, 22.7 – 22.3 (m), 14.2. ^{31}P NMR (162 MHz, $CDCl_3$) δ -26.1. HRMS exact mass calculated for $[M+H]^+$ ($C_{26}H_{57}P_2^+$): m/z 431.3930, found m/z 431.3922.

DHHE-d$_{12}$ (3b-d$_{12}$)

Yield 46 mg (70%), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.65 – 1.11 (m, 32H), 0.87 (t, *J* = 6.9 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 31.7, 31.3 – 31.2 (m), 26.4 – 25.9 (m), 25.9 – 25.6 (m), 22.7, 22.6 – 21.4 (m), 14.2. ^{31}P NMR (162 MHz, $CDCl_3$) δ -28.2. ^{2}H NMR (61 MHz, $CHCl_3$) δ 1.69 (s, 4D), 1.36 (s, 8D). HRMS exact mass calculated for $[M+H]^+$ ($C_{26}H_{45}D_{12}P_2^+$): m/z 443.4683, found m/z 443.4677.

D(*o*-Tol)$_2$E (3e)

Yield 35 mg (78%), white solid, m.p. 150-152 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.18 (m, 4H), 7.18 – 7.12 (m, 4H), 7.09 (t, *J* = 7.4 Hz, 4H), 7.06 – 6.99 (m, 4H), 2.40 (s, 12H), 2.06 (t, *J* = 4.4 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.8 – 142.3 (m), 136.7 – 136.3 (m), 131.2, 130.2 (t, *J* = 2.3 Hz), 128.6, 126.2, 22.8 (d, *J* = 3.7 Hz), 21.6 – 21.0 (m). ^{31}P NMR (162 MHz, $CDCl_3$) δ -33.6. HRMS exact mass calculated for $[M+H]^+$ ($C_{30}H_{33}P_2^+$): m/z 455.2052, found m/z 455.2051.

Cf. lit. data.[22]

D(*o*-Tol)$_2$E-d$_4$ (3e-d$_4$)

Yield 28 mg (61%), white solid, m.p. 147-152 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.18 (m, 4H), 7.18 – 7.12 (m, 4H), 7.09 (t, *J* = 7.4 Hz, 4H), 7.05 – 6.99 (m, 4H), 2.41 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.8 – 142.3 (m), 136.9 – 136.4 (m), 131.2, 130.4 – 130.0 (m), 128.6, 126.2, 21.6 – 21.1 (m). ^{31}P NMR (162 MHz, $CDCl_3$) δ -34.1. ^{2}H NMR (61 MHz, $CHCl_3$) 2.02 (s). HRMS exact mass calculated for $[M+H]^+$ ($C_{30}H_{29}D_4P_2^+$): m/z 459.2303, found m/z 459.2302.

D(*o*-Tol)$_2$E-d$_{16}$ (3e-d$_{16}$)

Yield 36 mg (77%), white solid, m.p. 151-152 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.18 (m, 4H), 7.18 – 7.12 (m, 4H), 7.10 (t, *J* = 7.4 Hz, 4H), 7.06 – 6.97 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.8 – 142.1 (m), 136.7 – 136.2 (m), 131.2, 130.2, 128.6, 126.2, 22.3 – 22.0 (m), 21.0 – 20.3 (m). ^{31}P NMR (162 MHz, $CDCl_3$) δ -34.1. ^{2}H NMR (61 MHz, $CHCl_3$) δ 2.38 (s, 12D), 2.03 (s, 4D). HRMS exact mass calculated for $[M+H]^+$ ($C_{30}H_{17}D_{16}P_2^+$): m/z 503.2944, found m/z 503.2949.

Ni(DPPE)Br$_2$ (NiBr$_2$(3a))

Yield 123 mg (80%), red crystals, decompose at 280 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.94 (m, 8H), 7.57 (t, *J* = 7.3 Hz, 4H), 7.50 (t, *J* = 6.9 Hz, 8H), 2.16 – 2.06 (m, 4H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 65.6. HRMS exact mass calculated for $[M-Br]^+$ ($C_{26}H_{24}P_2NiBr^+$): m/z 536.9863, found m/z 536.9852.

Ni(DPPE-d$_4$)Br$_2$ (NiBr$_2$(3a-d$_4$))

Yield 128 mg (83%), red crystals, decompose at 280 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 7.90 (m, 8H), 7.57 (t, *J* = 7.3 Hz, 4H), 7.50 (t, *J* = 7.4 Hz, 8H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 65.0. HRMS exact mass calculated for $[M-Br]^+$ ($C_{26}H_{20}D_4P_2NiBr^+$): m/z 541.0114, found m/z 541.0100.

Ni(D(oTol)$_2$E)Br$_2$ (NiBr$_2$(3e))

Yield 162 mg (96%), red crystals poorly soluble, decompose at 280 °C. The experimental diffraction patterns of the samples (Fig. S110) are in a good agreement with those simulated from the single-crystal data and this indicates that the powders exhibit the same packing features as the corresponding crystal.

$Ni(D(oTol)_2E\text{-}d_{16})Br_2$ ($NiBr_2(3e\text{-}d_{16})$)

Yield 158 mg (92%), poorly soluble red crystals, decompose at 280 °C. The experimental diffraction patterns of the samples (Fig. S111) are in a good agreement with those simulated from the single-crystal data and this indicates that the powders exhibit the same packing features as the corresponding crystal.

$Ni(D(oTol)_2E\text{-}d_4)Br_2$ ($NiBr_2(3e\text{-}d_4)$)

Yield 151 mg (89%), poorly soluble red crystals, decompose at 280 °C. The experimental diffraction patterns of the samples (Fig. S112) are in a good agreement with those simulated from the single-crystal data and this indicates that the powders exhibit the same packing features as the corresponding crystal.

$Pd(DPPE)Cl_2$ ($PdCl_2(3a)$)

Yield 30 mg (87%), white crystals, decompose at 270 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.83 (m, 8H), 7.62 – 7.53 (m, 4H), 7.53 – 7.44 (m, 8H), 2.50 – 2.40 (m, 4H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 63.7. HRMS exact mass calculated for $[M+Na]^+$ ($C_{26}H_{24}P_2PdCl_2Na^+$): m/z 596.9661, found m/z 596.9672

$Pd(DPPE\text{-}d_4)Cl_2$ ($PdCl_2(3a\text{-}d_4)$)

Yield 31 mg (89%), white crystals, decompose at 270 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.76 (m, 8H), 7.60 – 7.52 (m, 4H), 7.52 – 7.44 (m, 8H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 63.1. HRMS exact mass calculated for $[M+Na]^+$ ($C_{26}H_{20}D_4P_2PdCl_2Na^+$): m/z 600.9913, found m/z 600.9920

S4. NMR spectra

DPPEO$_2$ (**2a**)

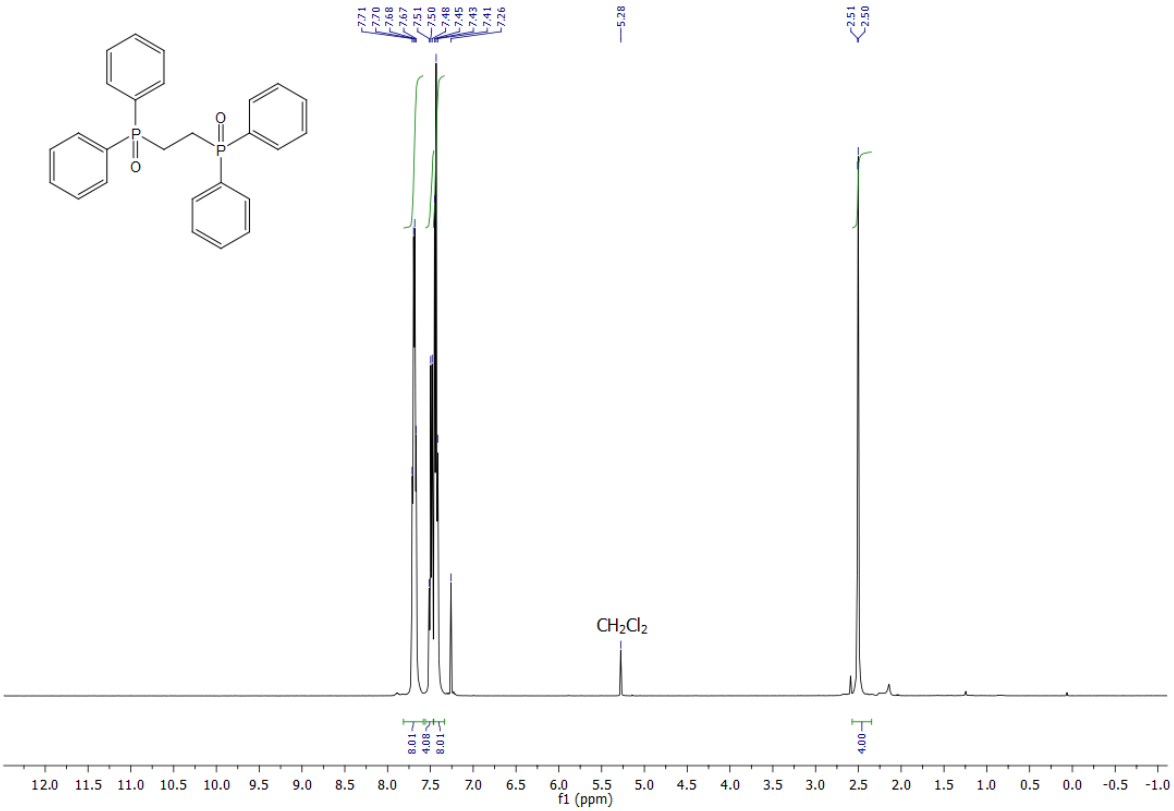


Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of DPPEO$_2$ (**2a**).

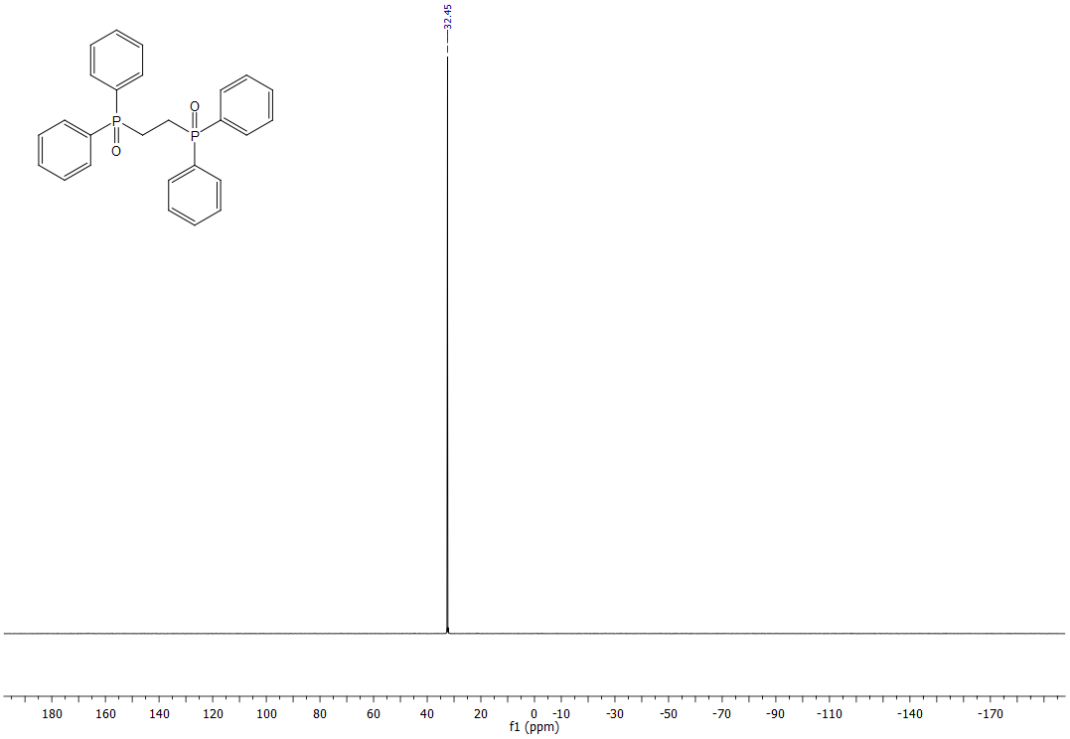


Figure S2. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of DPPEO$_2$ (**2a**).

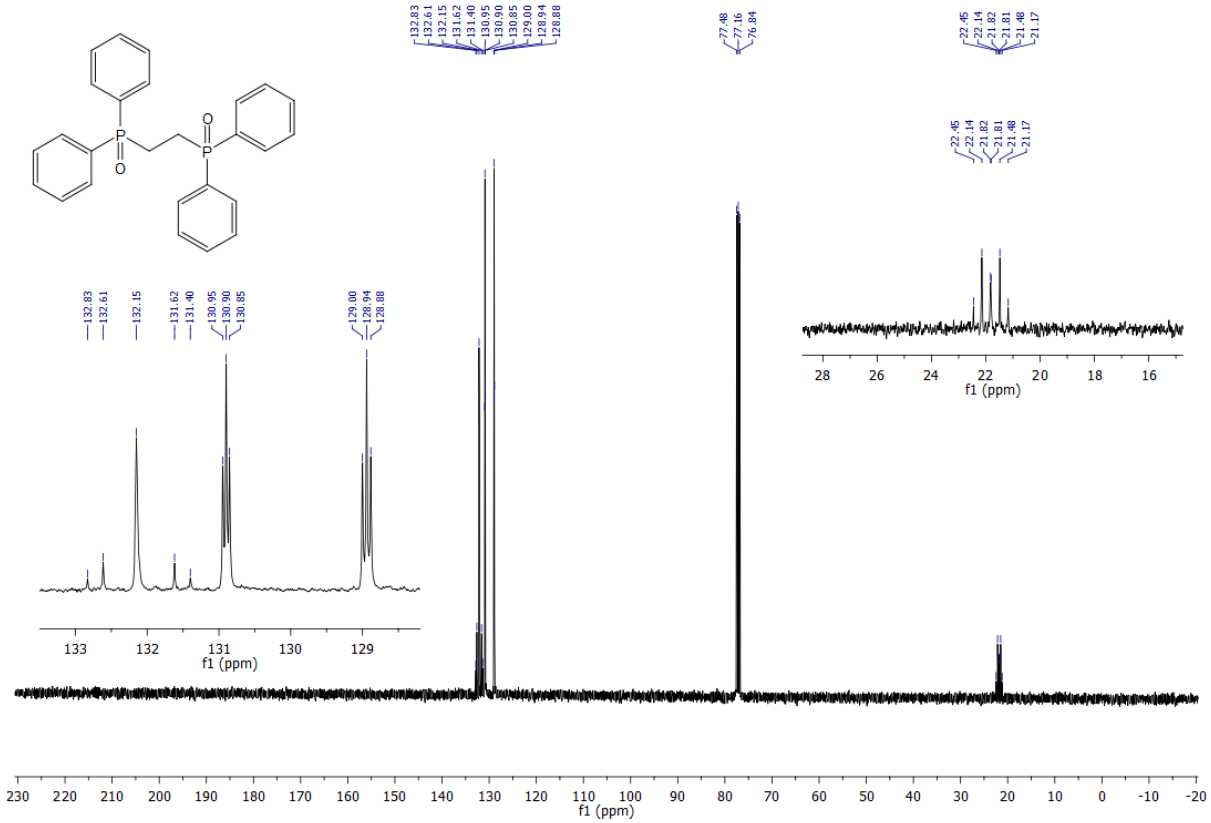


Figure S3. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of $DPPEO_2$ (**2a**).

$DHHEO_2$ (**2b**)

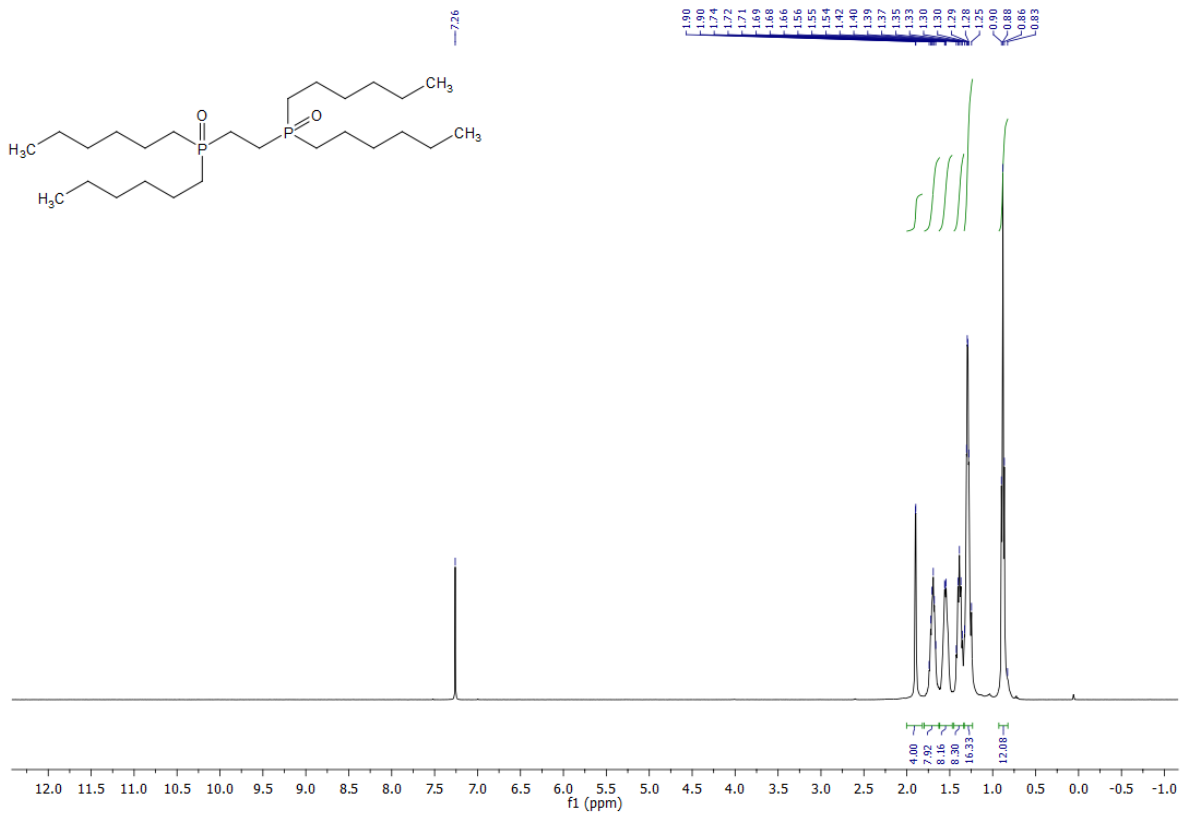


Figure S4. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of $DHHEO_2$ (**2b**).

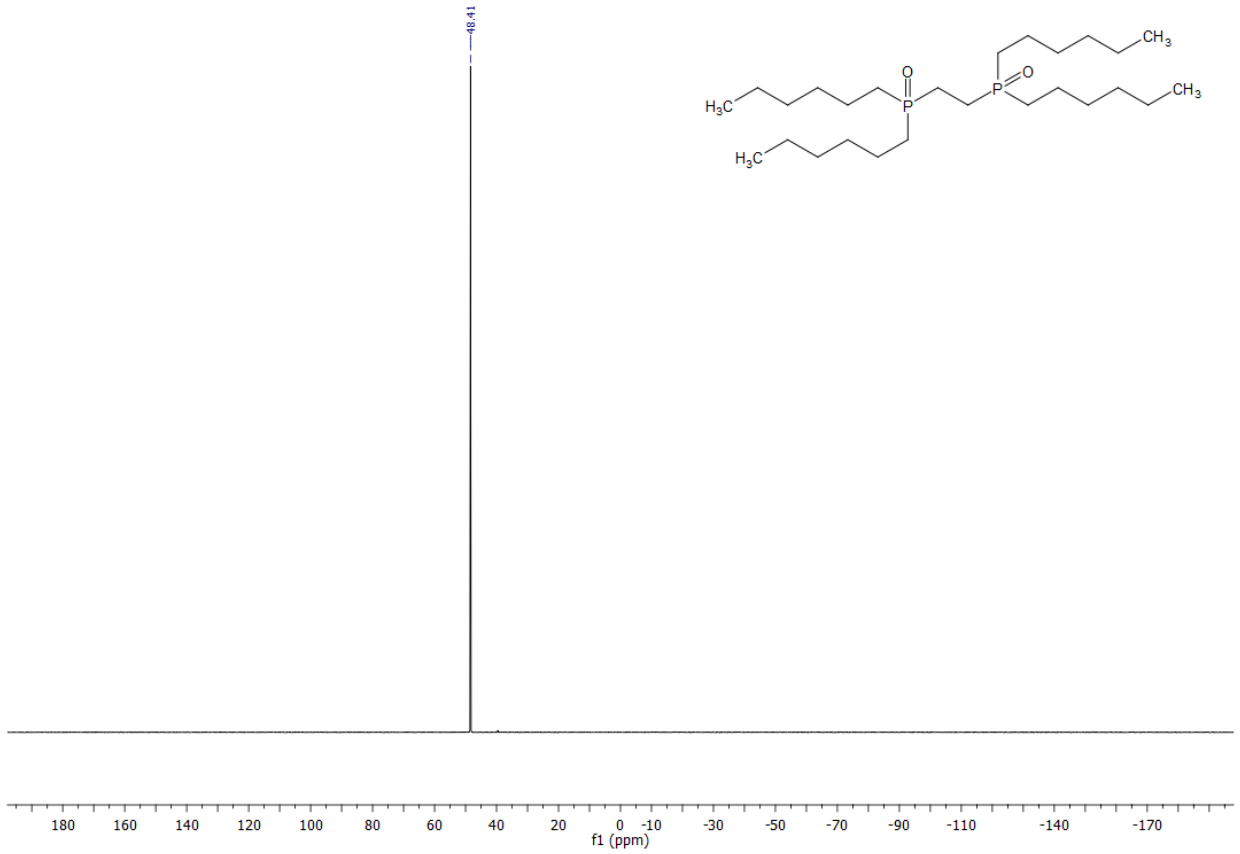


Figure S5. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of $DHHEO_2$ (**2b**).

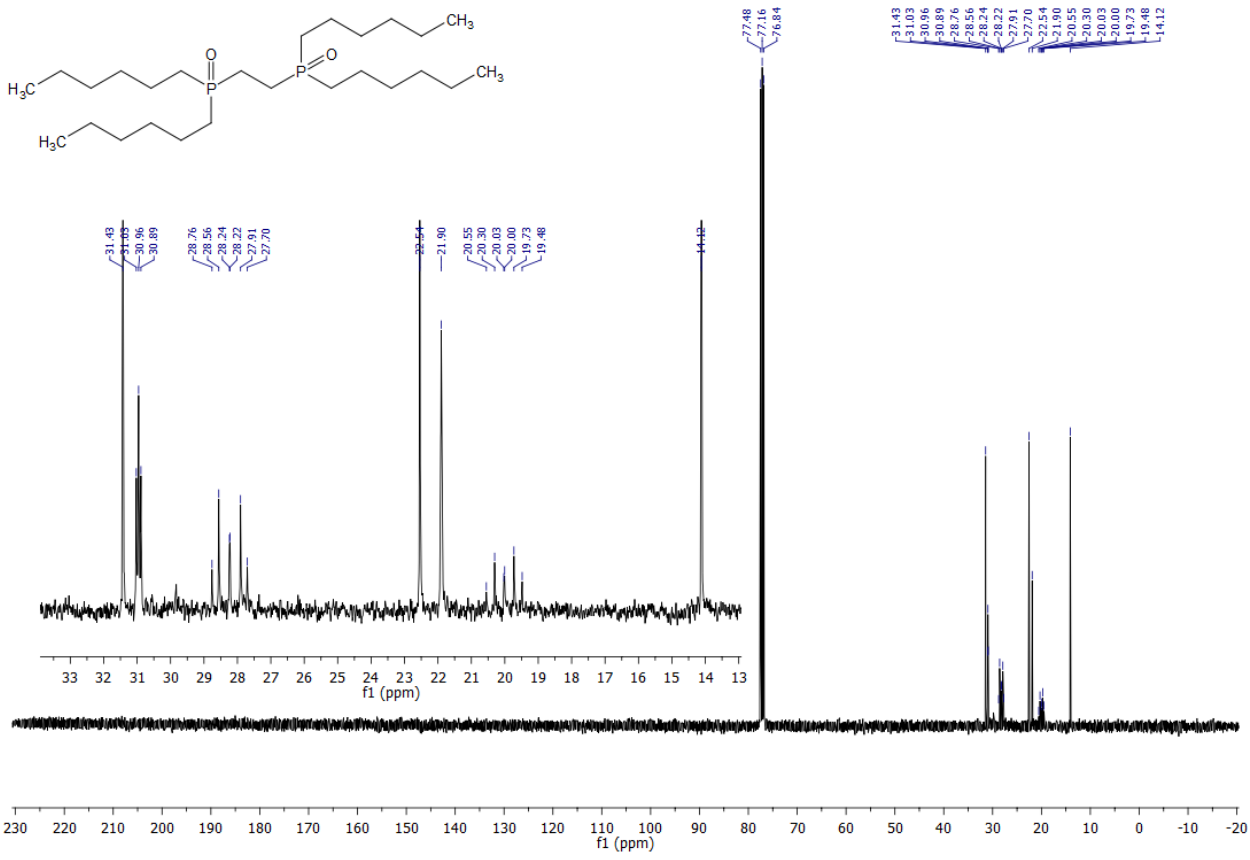


Figure S6. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of $DHHEO_2$ (**2b**).

DBBEO$_2$ (**2c**)

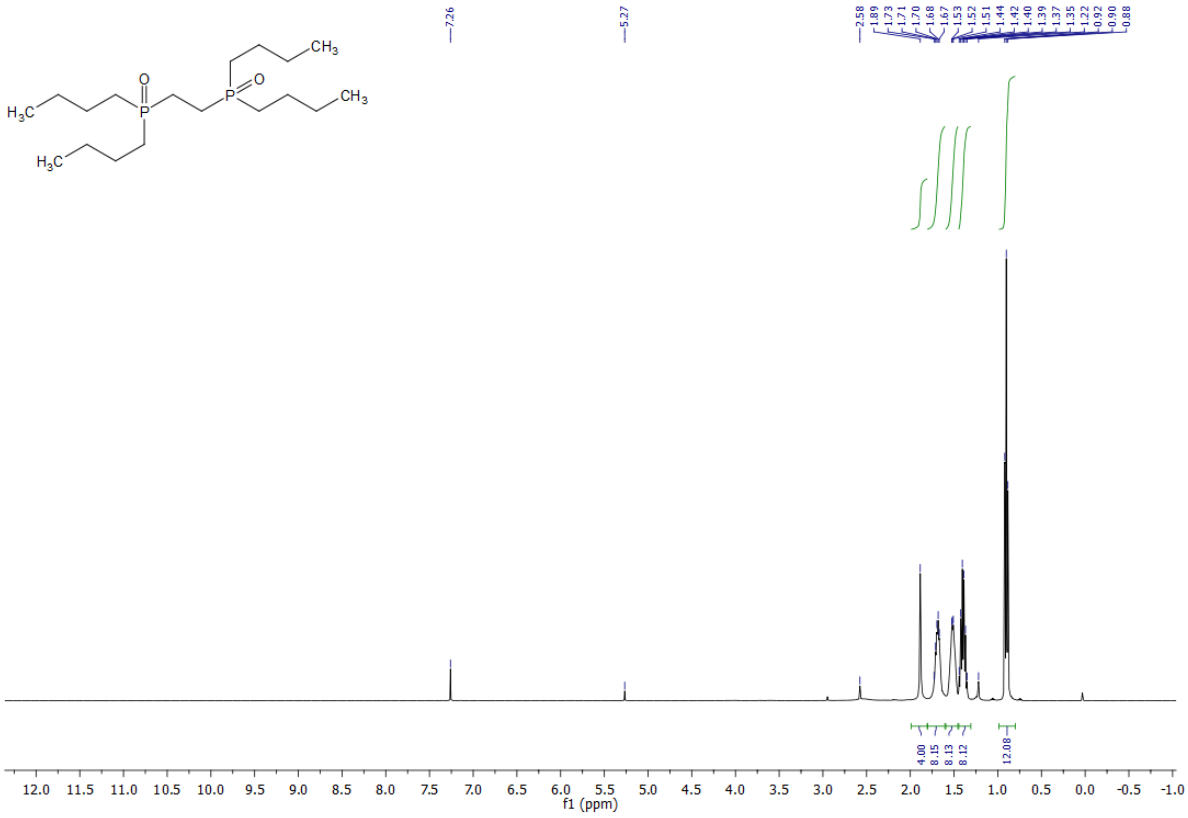


Figure S7. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of DBBEO$_2$ (**2c**).

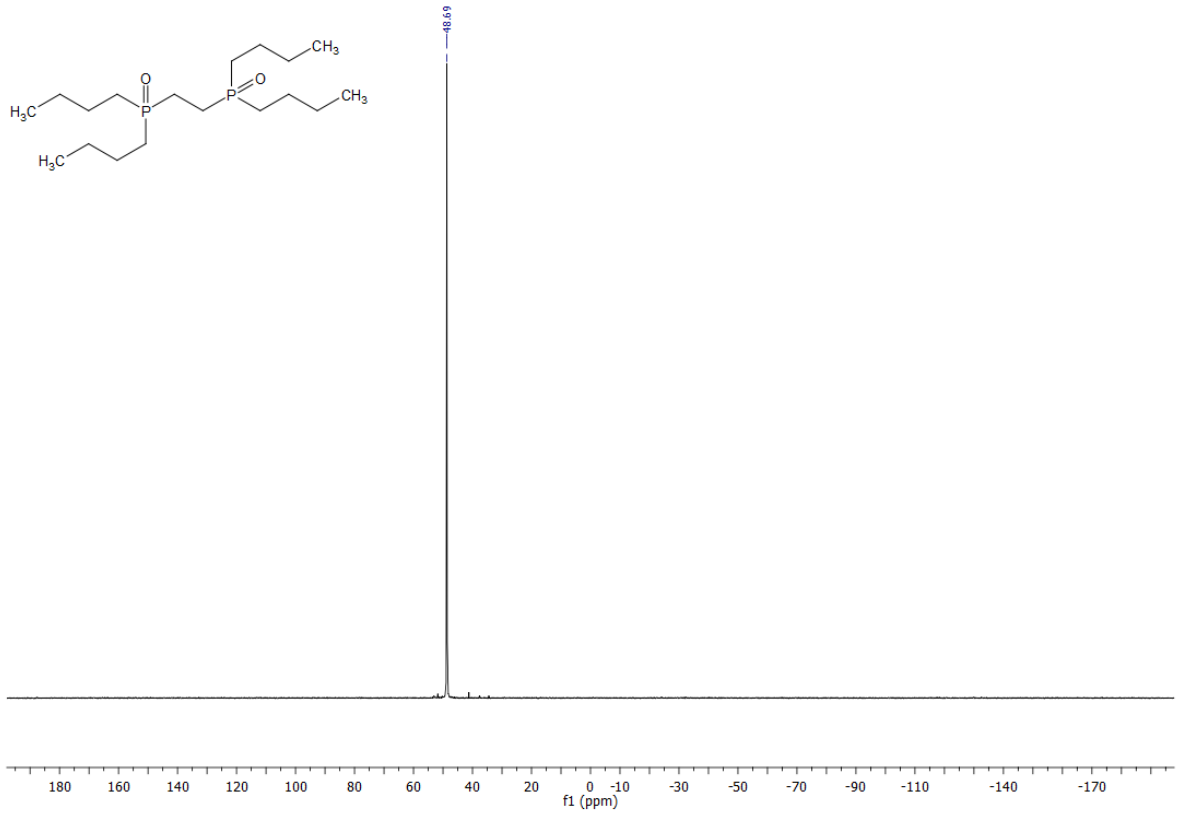


Figure S8. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of DBBEO$_2$ (**2c**).

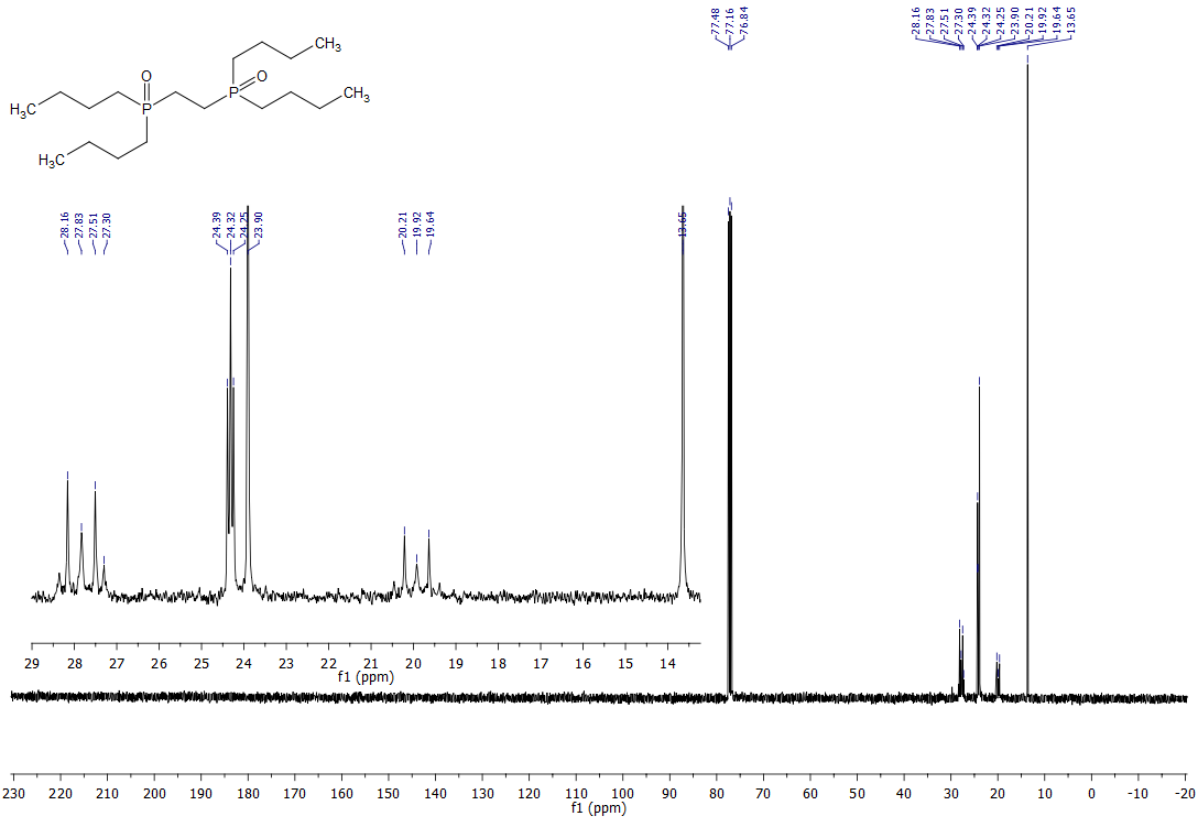


Figure S9. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of $DBBEO_2$ (**2c**).

D(*i*-Bu)$_2$EO$_2$ (**2d**)

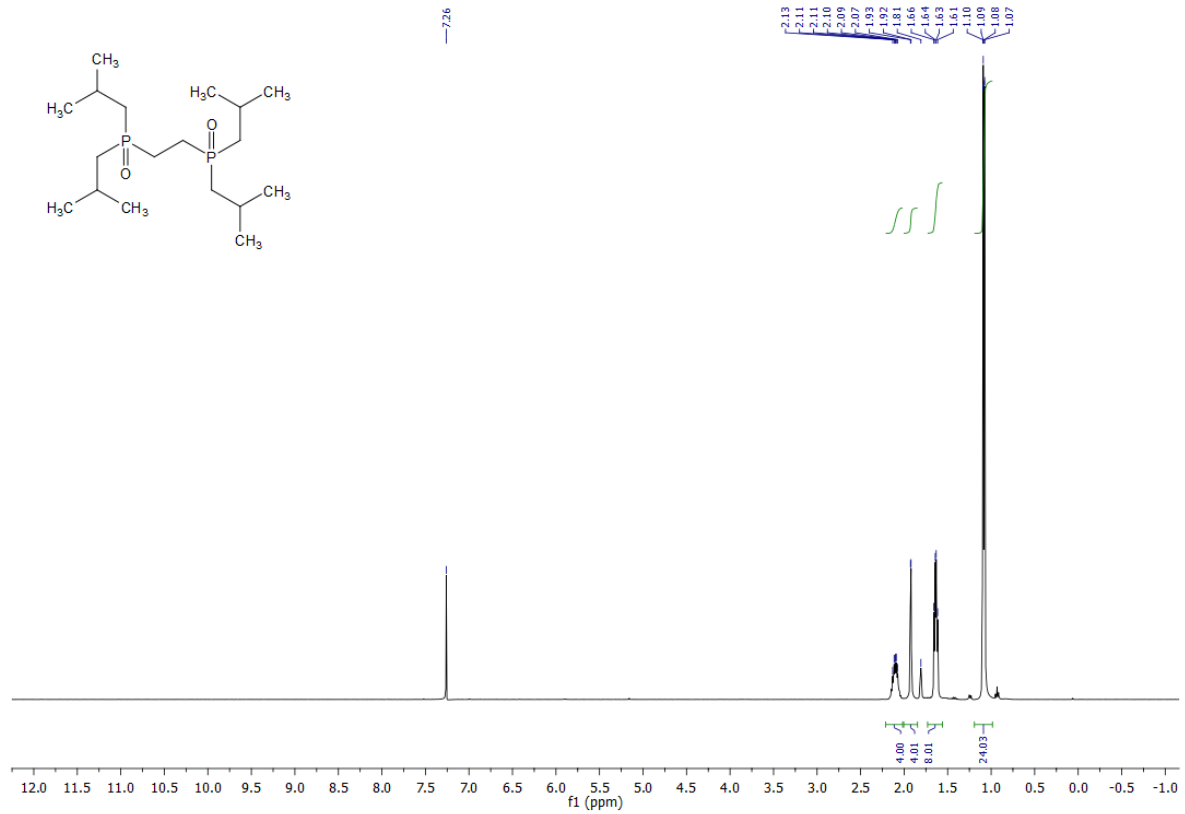


Figure S10. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of D(*i*-Bu)$_2$EO$_2$ (**2d**).

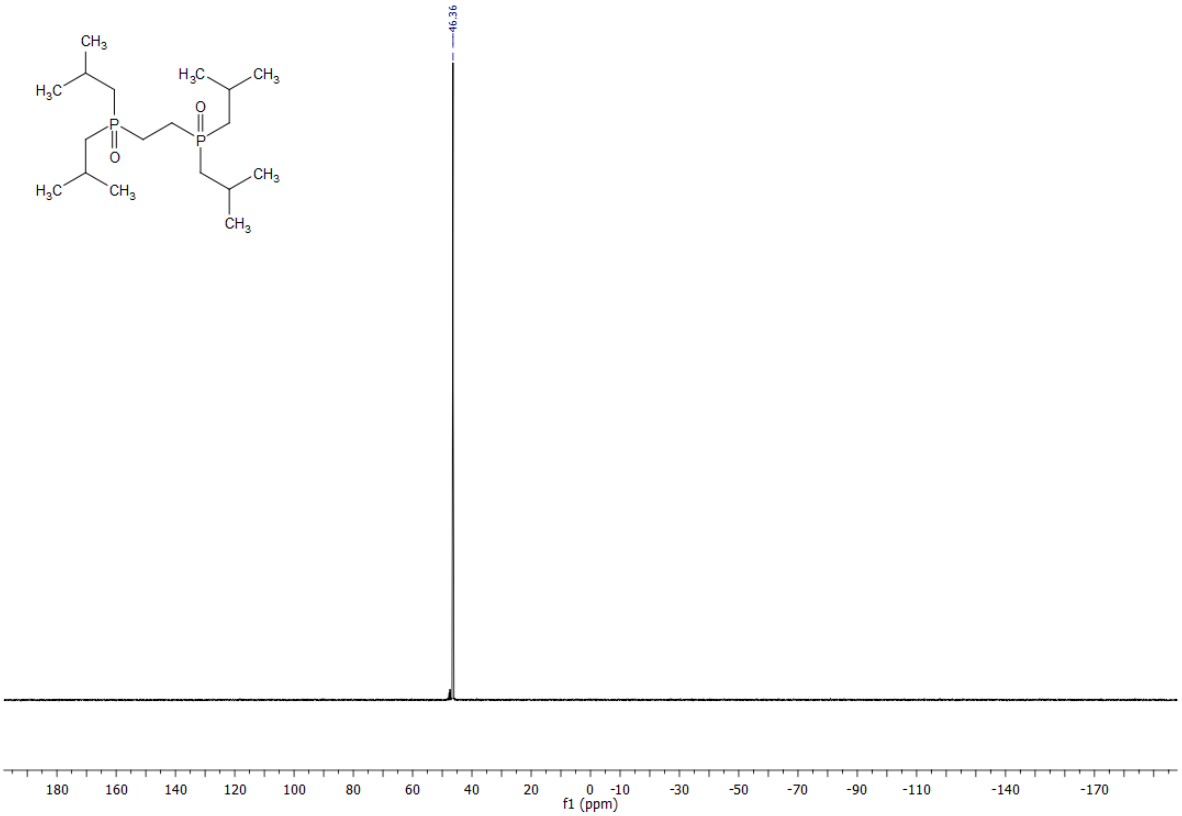


Figure S11. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of D(*i*-Bu)$_2$EO$_2$ (**2d**).

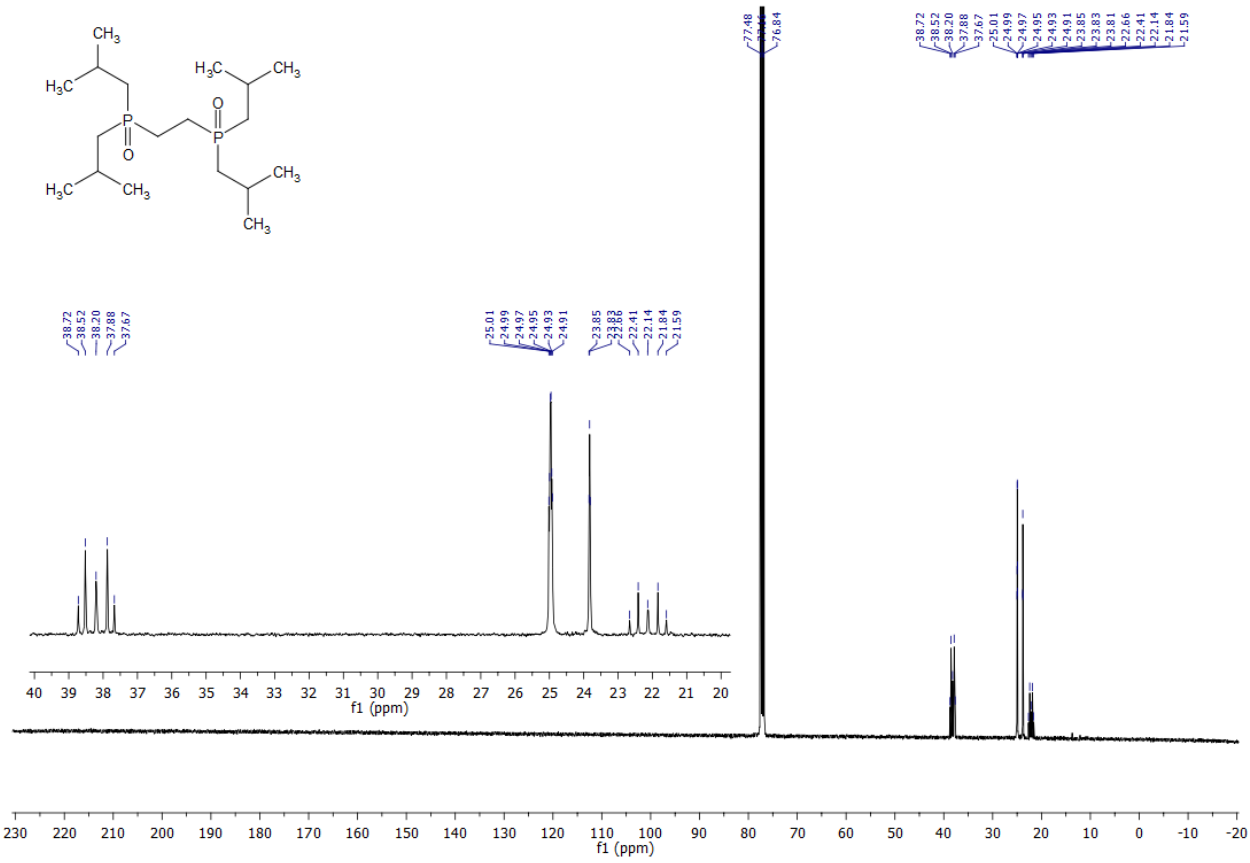


Figure S12. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of D(*i*-Bu)$_2$EO$_2$ (**2d**).

D(*o*-Tol)$_2$EO$_2$ (**2e**)

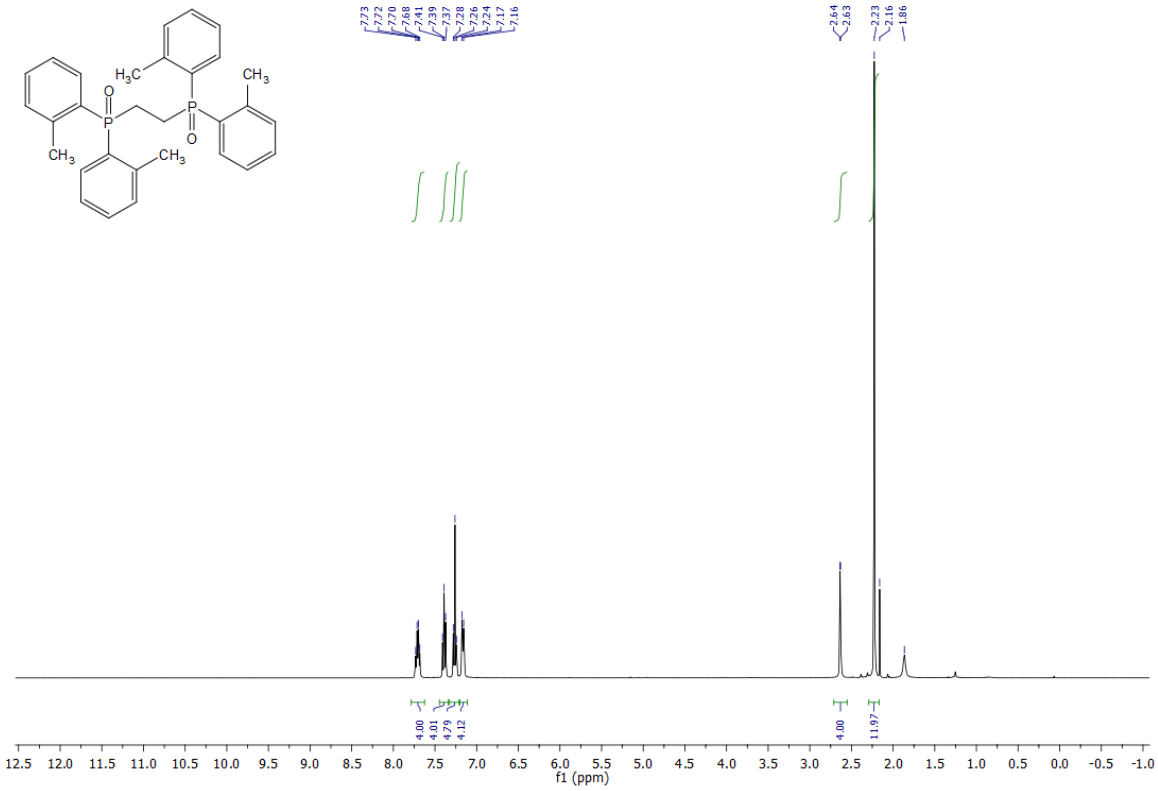


Figure S13. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of D(*o*-Tol)$_2$EO$_2$ (**2e**).

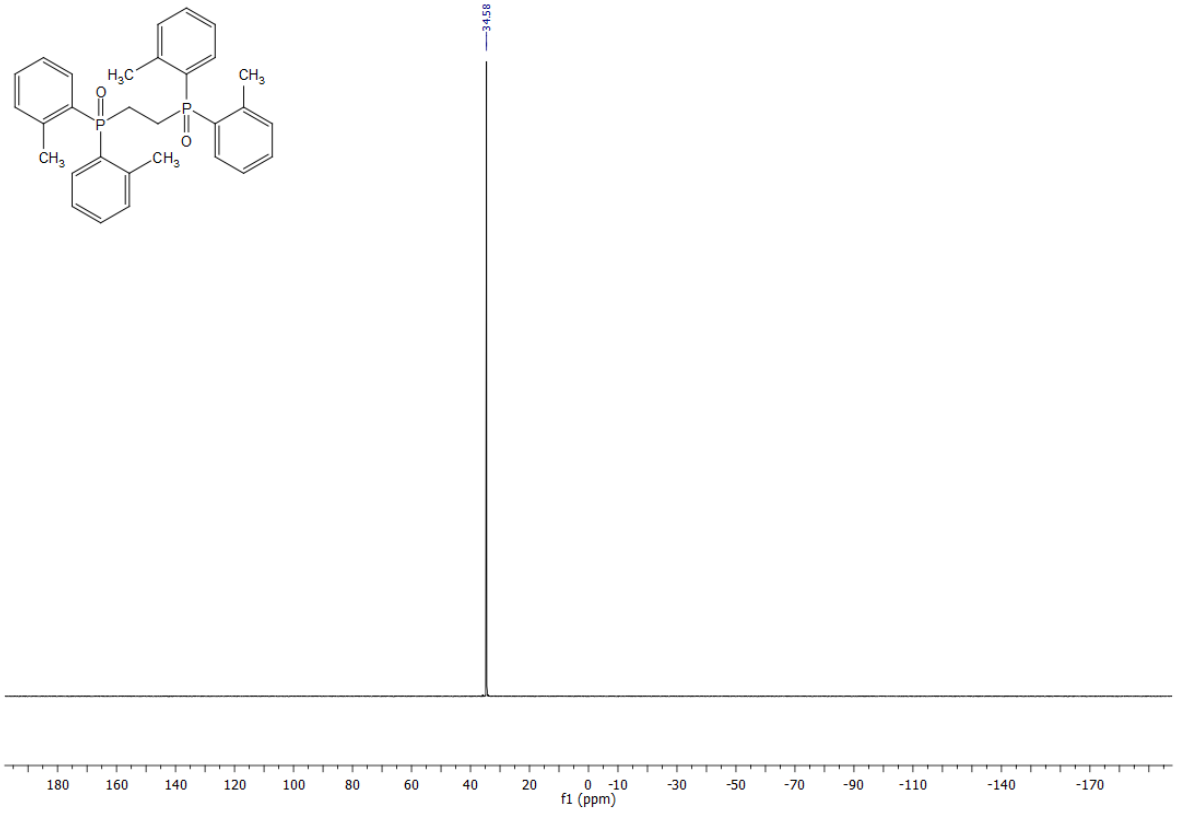


Figure S14. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of D(*o*-Tol)$_2$EO$_2$ (**2e**).

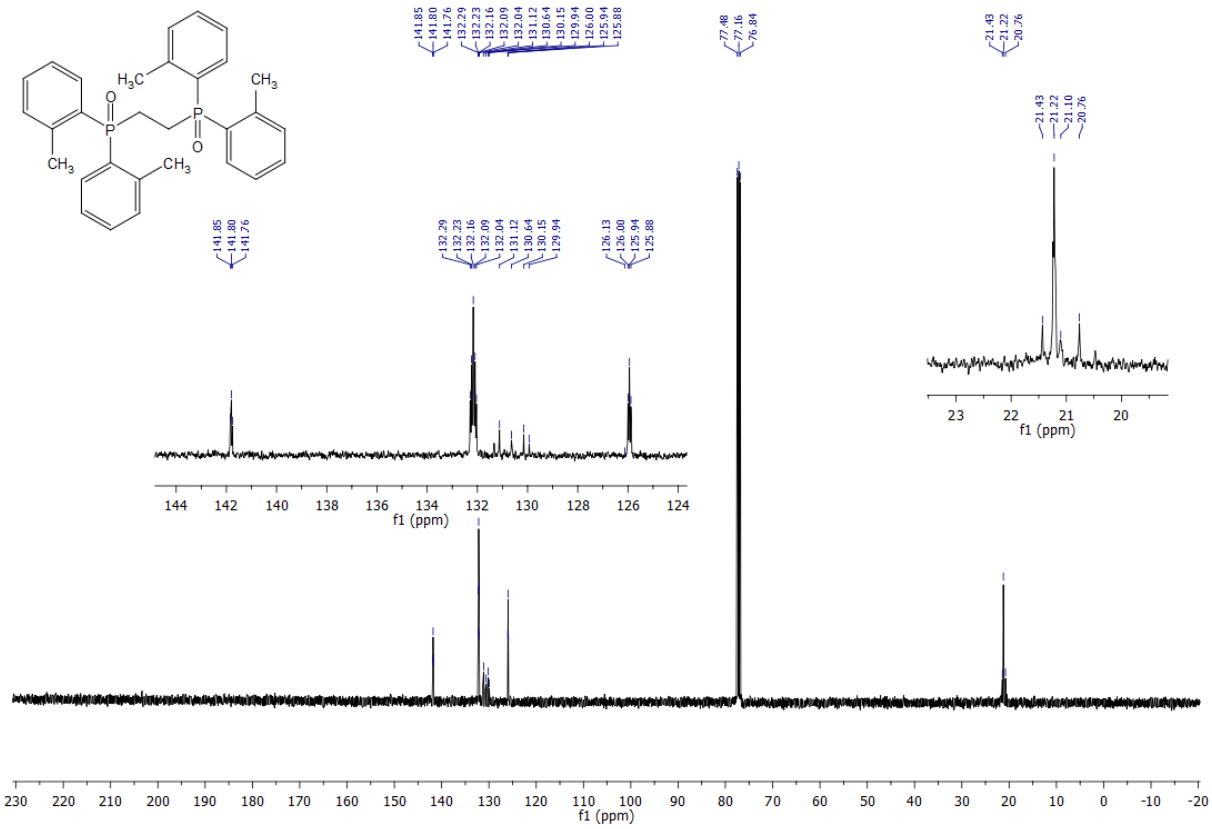


Figure S15. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of D(*o*-Tol)$_2$EO$_2$ (**2e**).

D(*m*-Tol)$_2$EO$_2$ (**2f**)

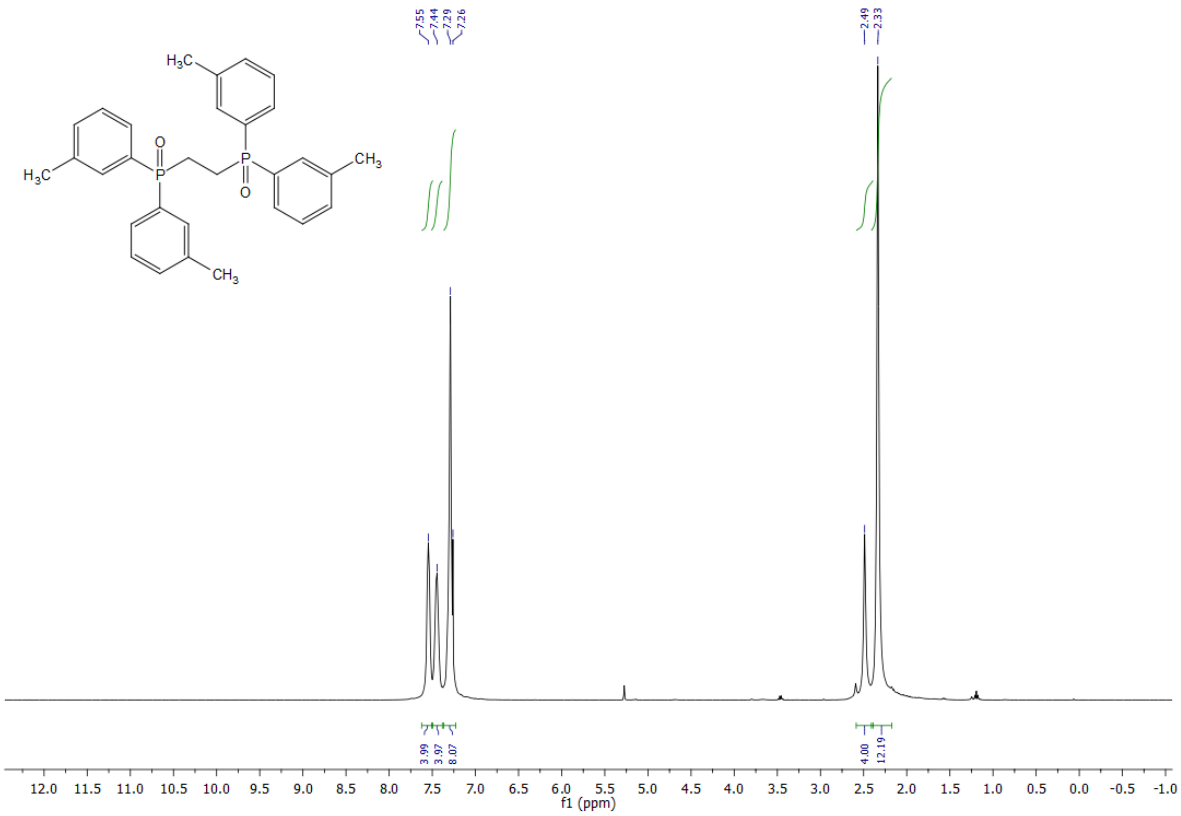


Figure S16. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of D(*m*-Tol)$_2$EO$_2$ (**2f**).

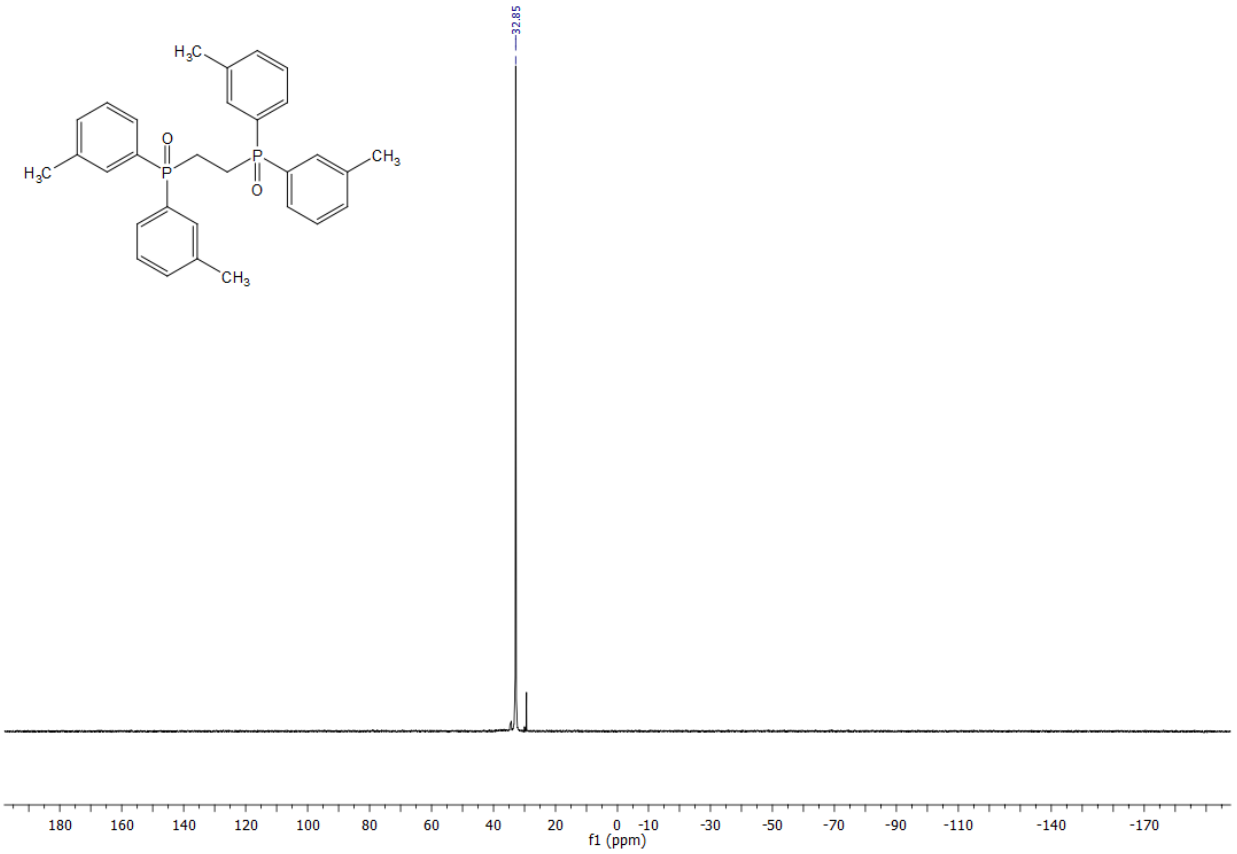


Figure S17. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of D(*m*-Tol)$_2$EO$_2$ (**2f**).

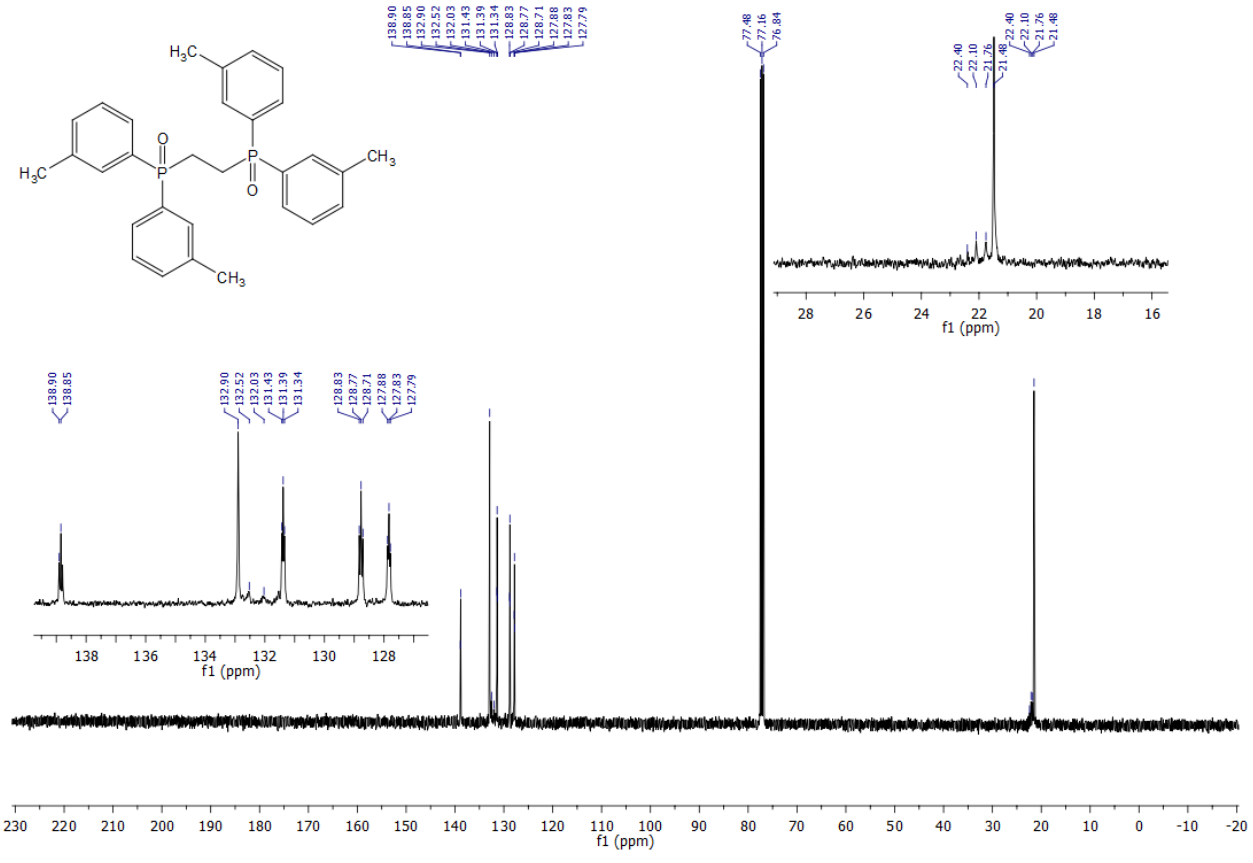


Figure S18. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of D(*m*-Tol)$_2$EO$_2$ (**2f**).

D(*p*-Tol)$_2$EO$_2$ (**2g**)

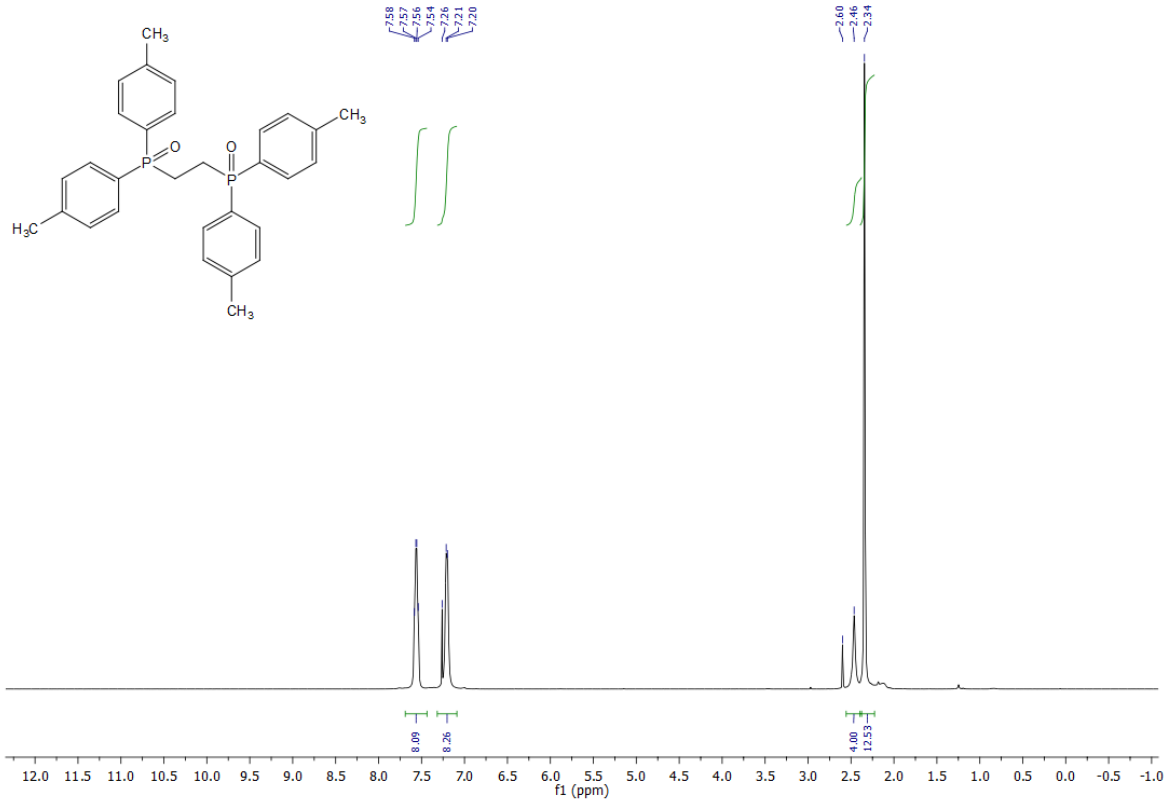


Figure S19. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of D(*p*-Tol)$_2$EO$_2$ (**2g**).

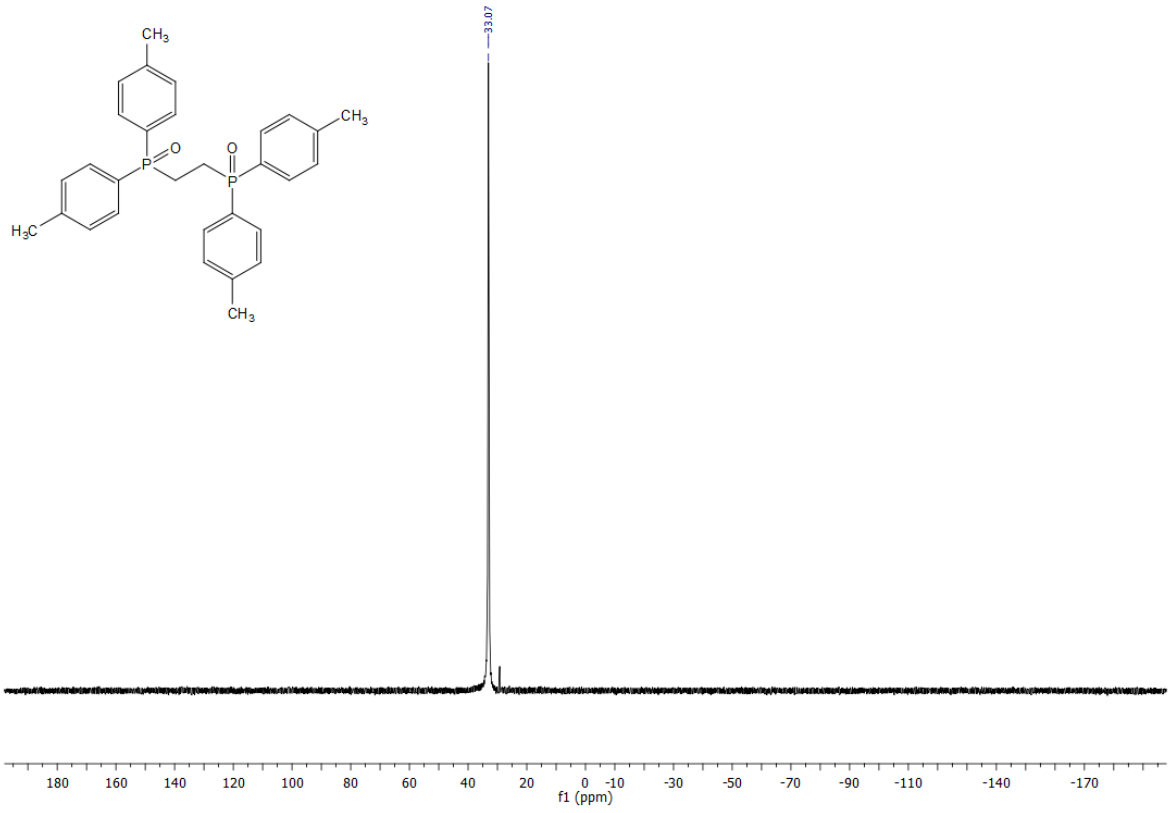


Figure S20. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of D(*p*-Tol)$_2$EO$_2$ (**2g**).

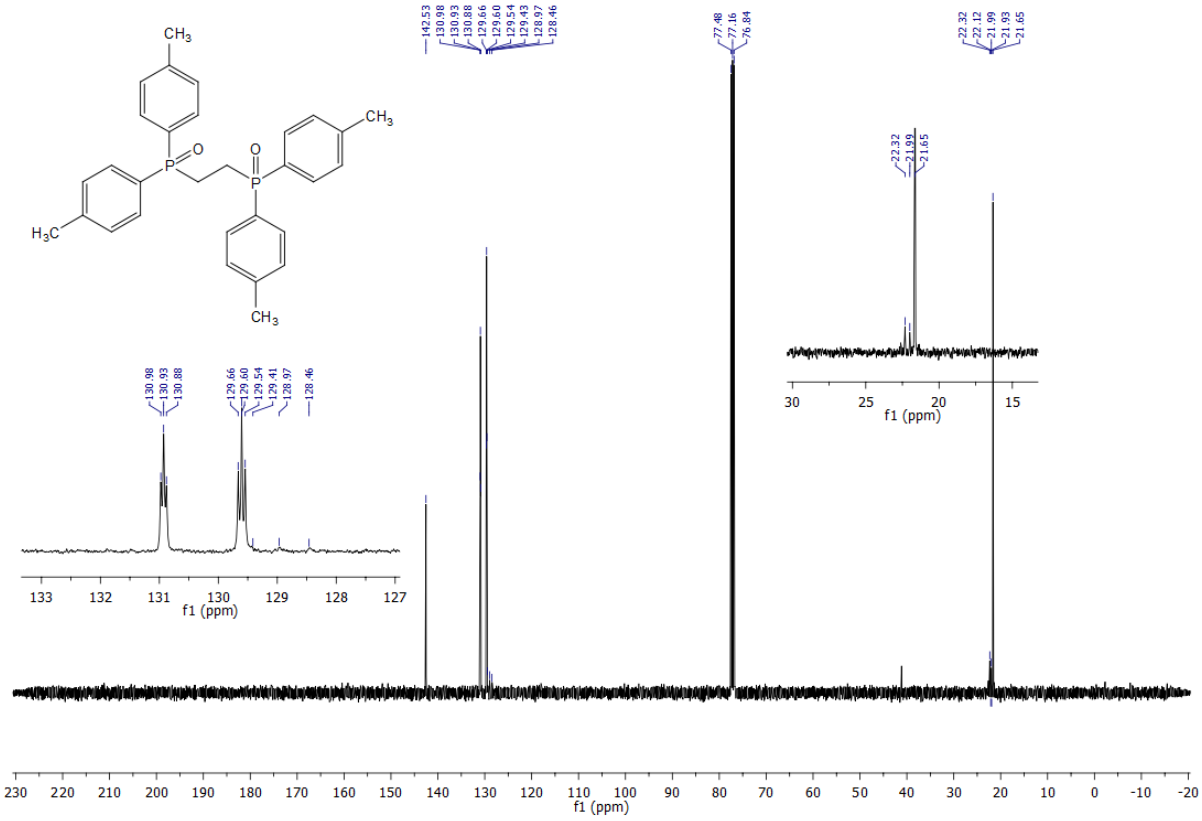


Figure S21. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of D(*p*-Tol)$_2$EO$_2$ (**2g**).

D(*p*-OMe(C_6H_4))$_2$EO$_2$ (**2h**)

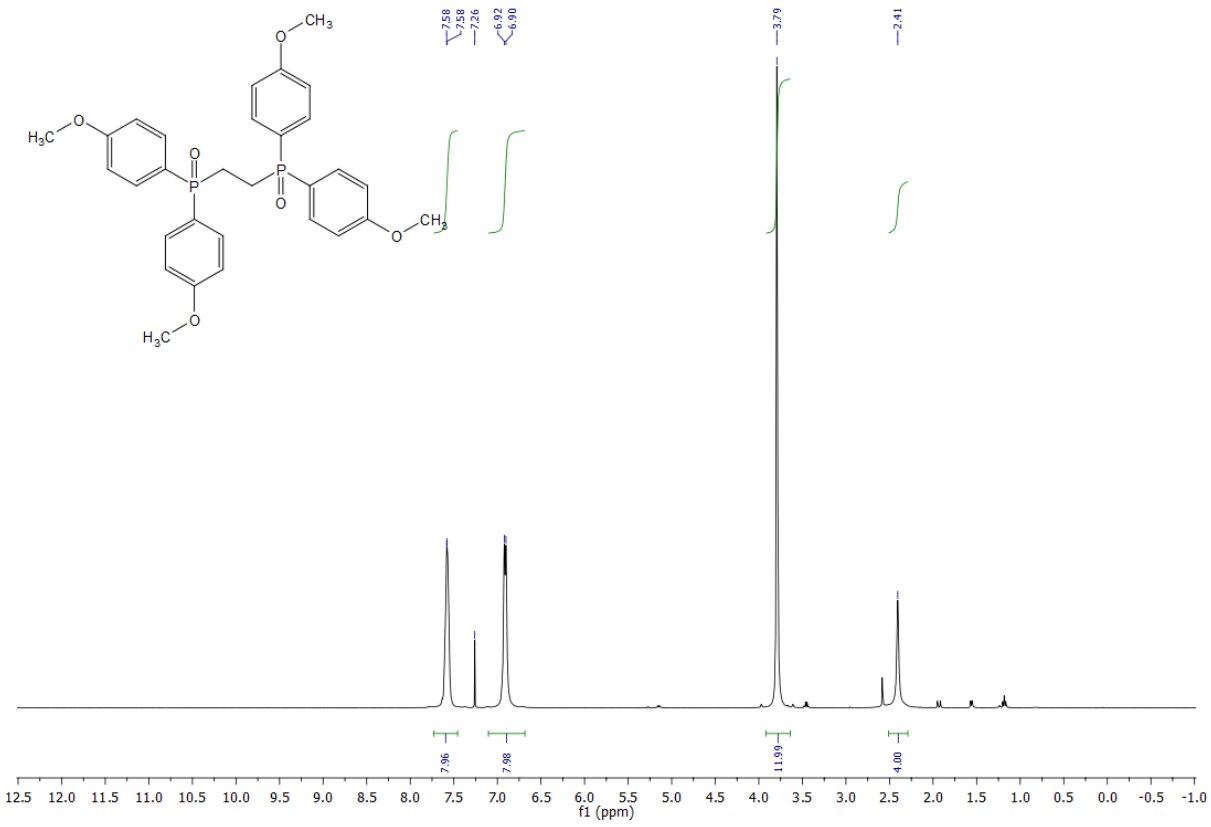


Figure S22. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of D(*p*-OMe(C_6H_4))$_2$EO$_2$ (**2h**).

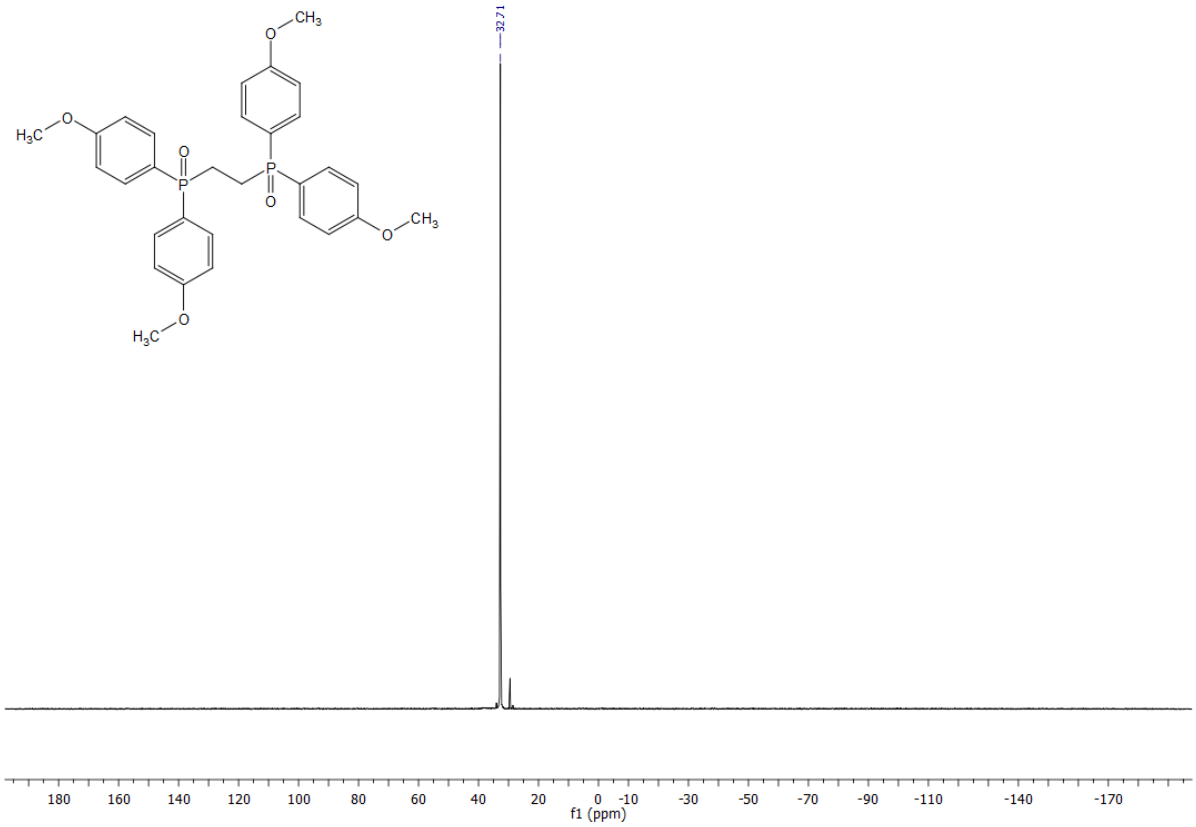


Figure S23. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of D(*p*-OMe(C_6H_4))$_2$EO$_2$ (**2h**).

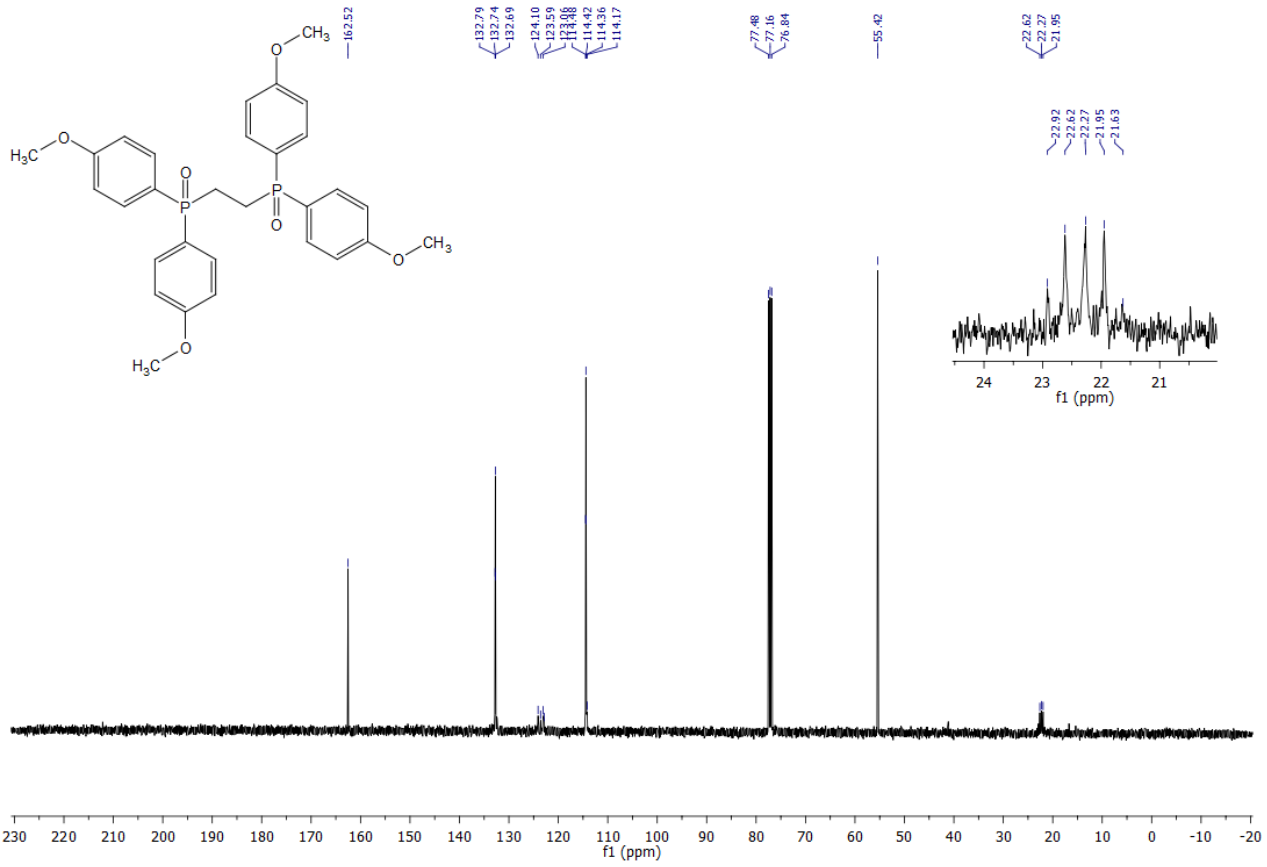


Figure S24. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of D(*p*-OMe(C_6H_4))$_2$EO$_2$ (**2h**).

D(*t*-Bu)$_2$EO$_2$ (**2i**)

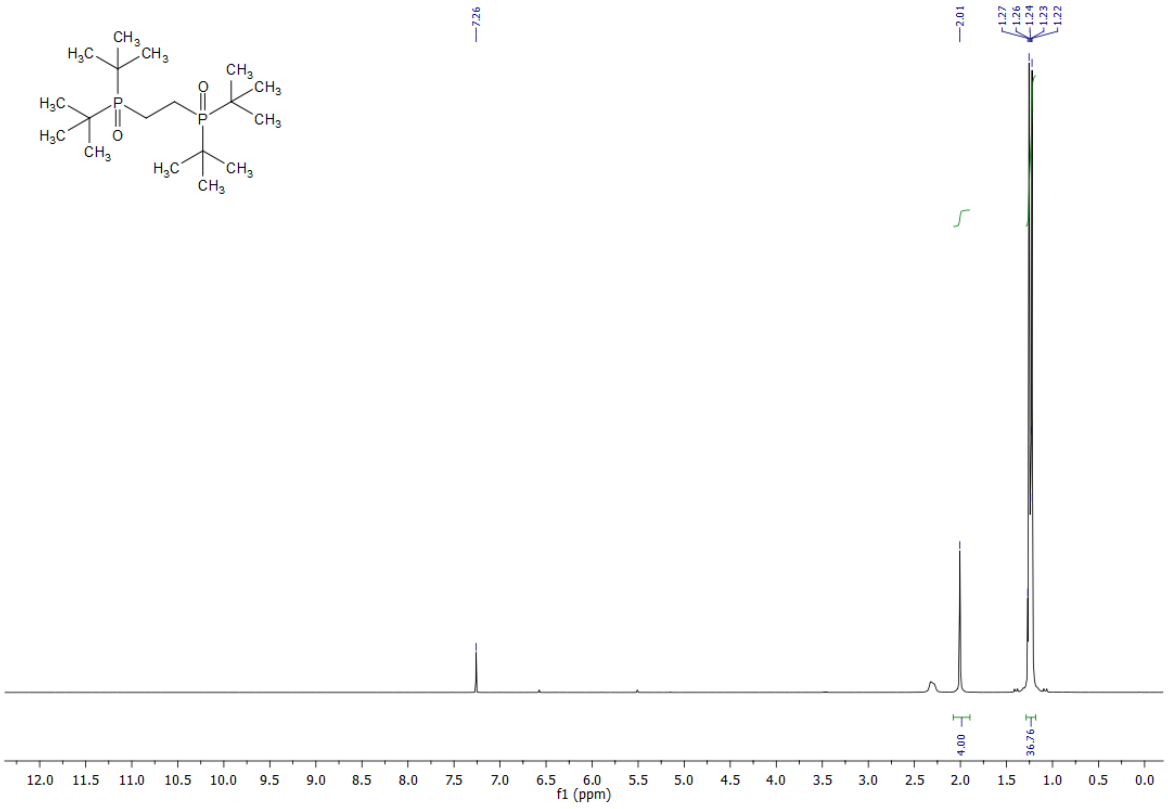


Figure S25. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of D(*t*-Bu)$_2$EO$_2$ (**2i**).

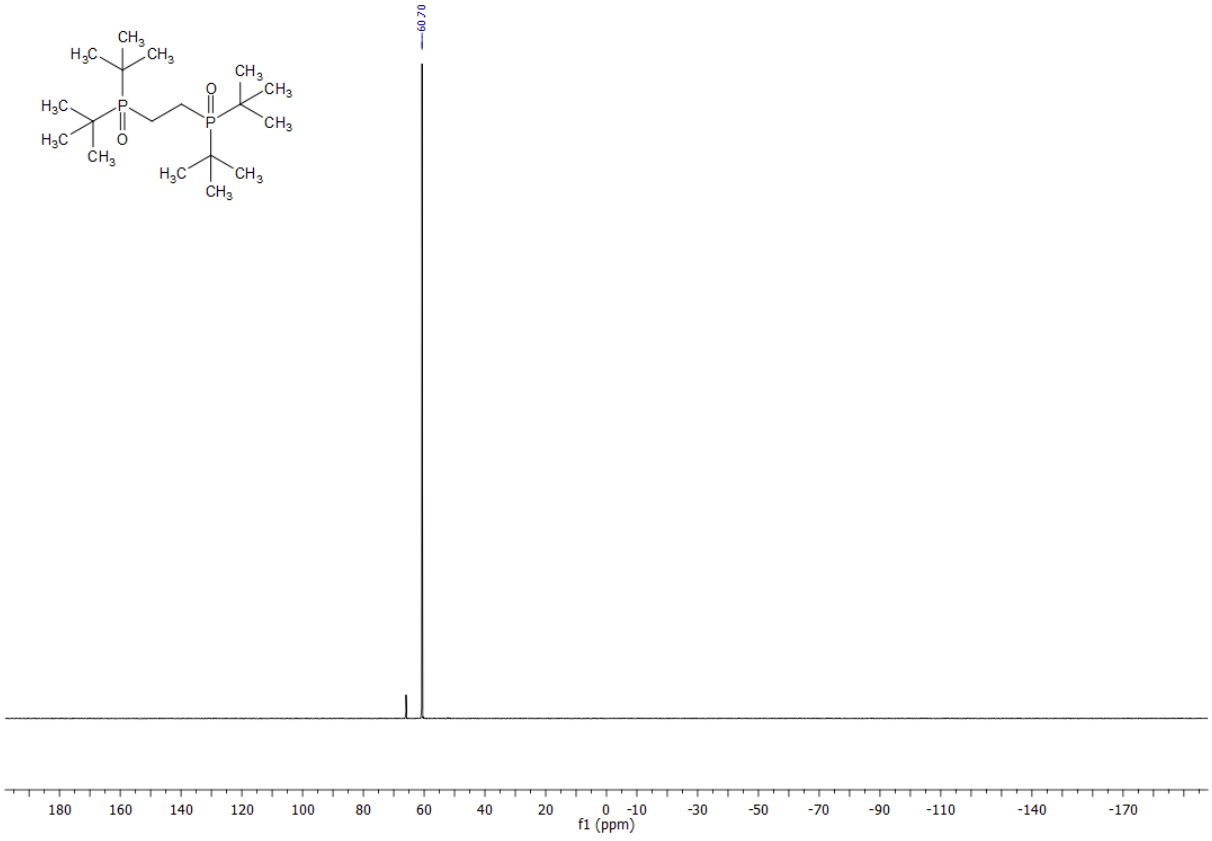


Figure S26. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of D(*t*-Bu)$_2$EO$_2$ (**2i**).

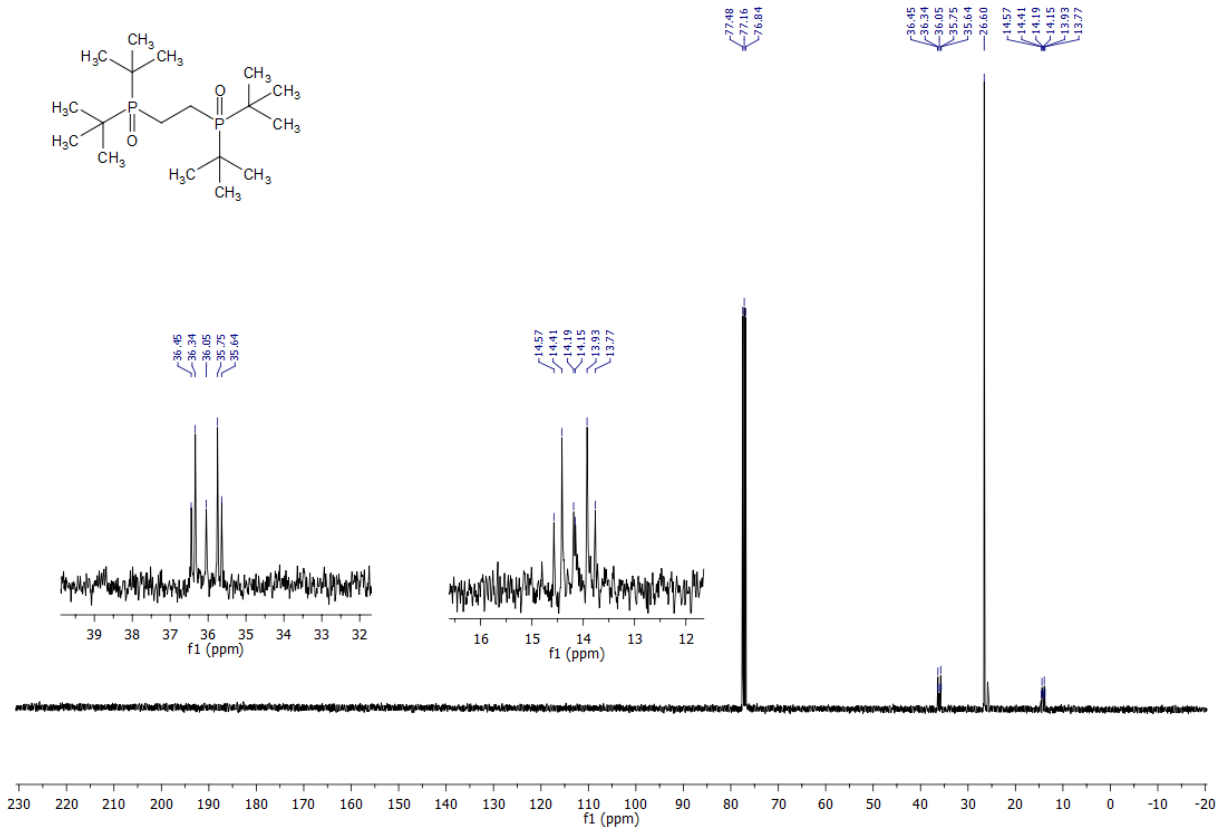


Figure S27. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of D(*t*-Bu)$_2$EO$_2$ (**2i**).

D(Cy)$_2$EO$_2$ (**1j**)

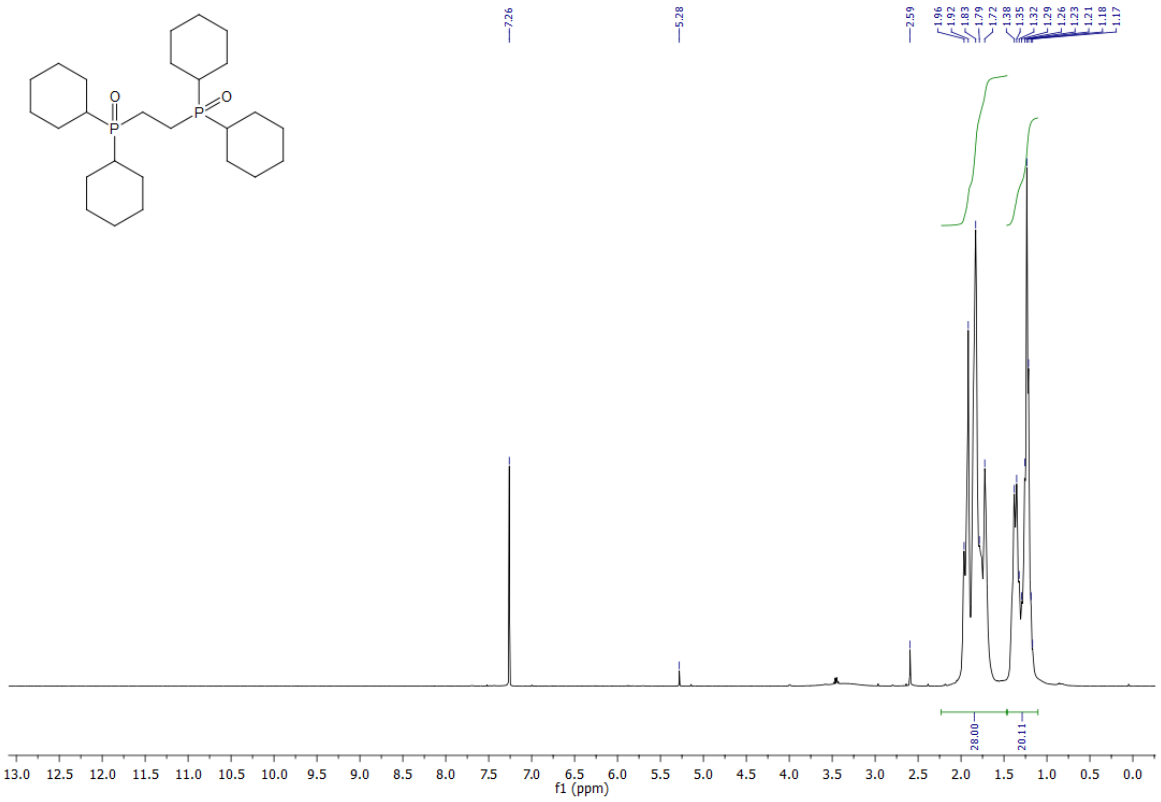


Figure S28. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of D(Cy)$_2$EO$_2$ (**1j**).

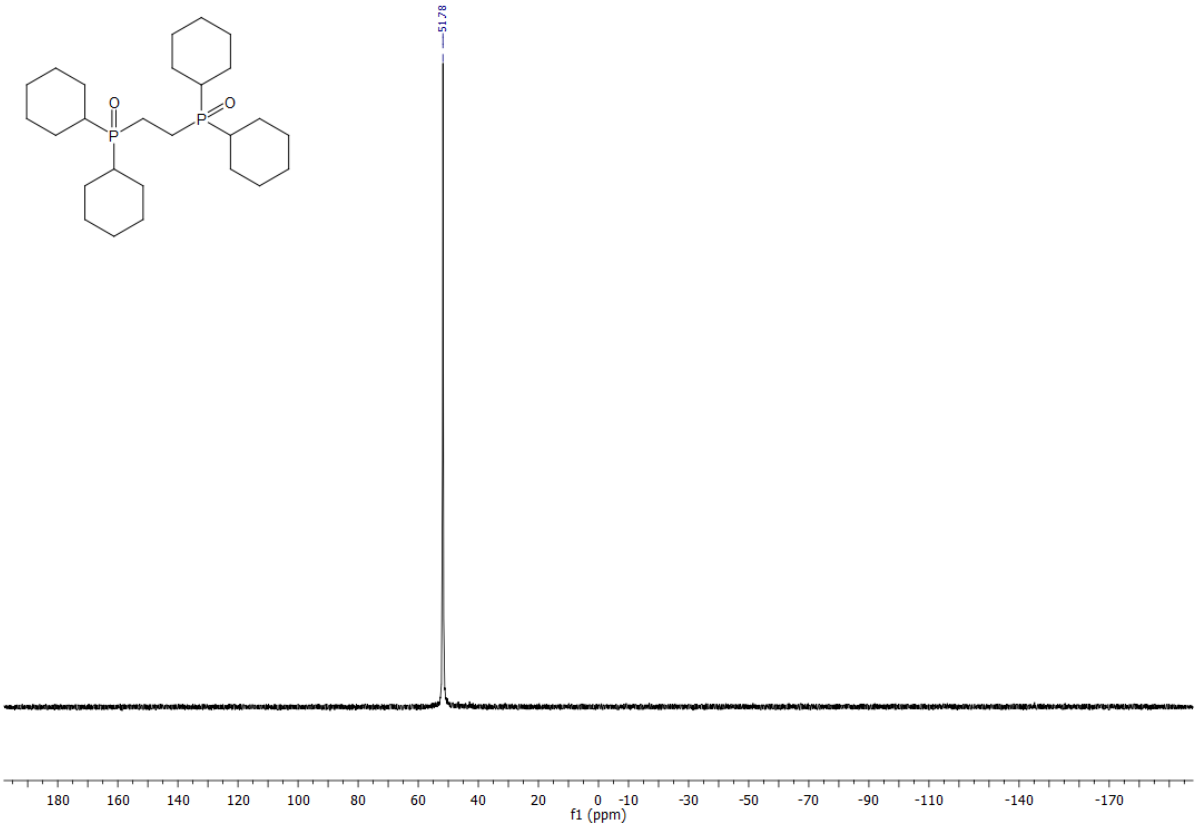


Figure S29. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of $D(Cy)_2EO_2$ (**1j**).

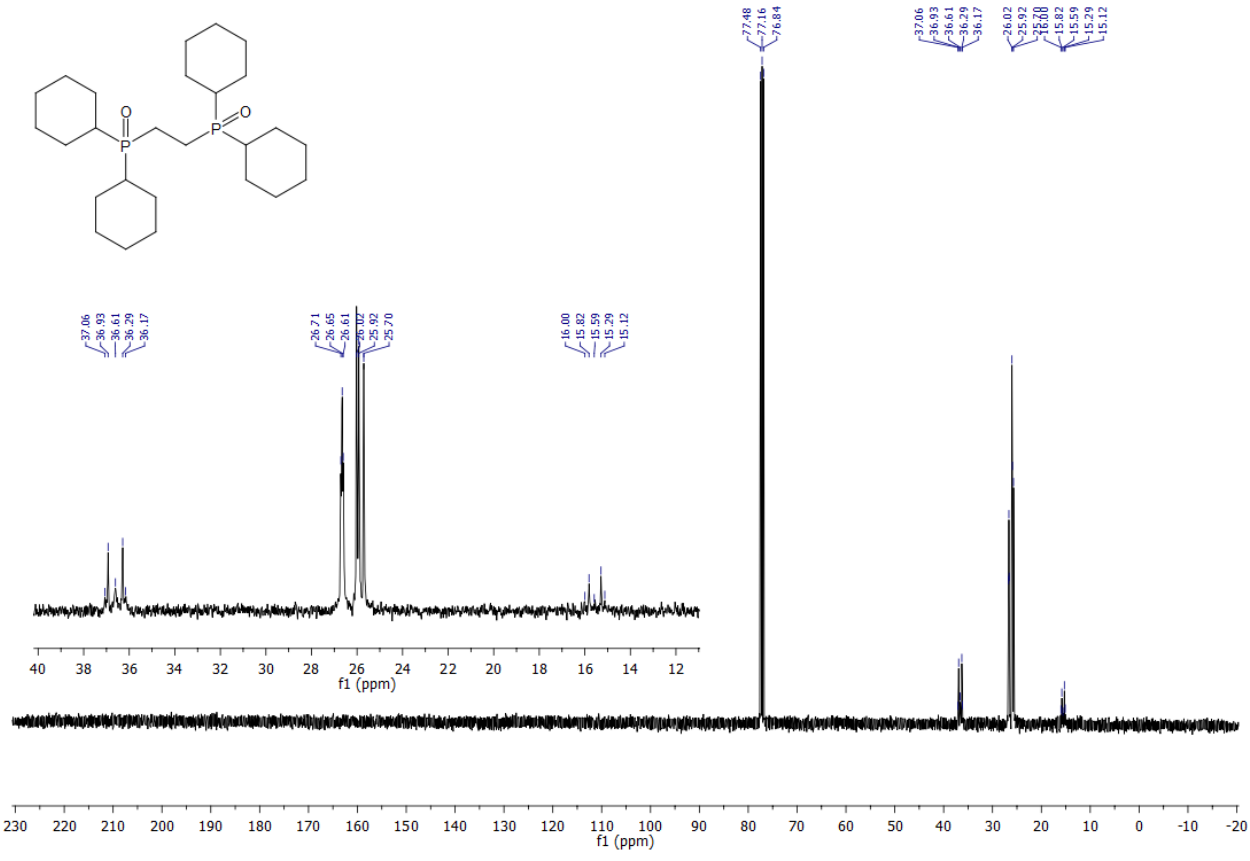


Figure S30. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of $D(Cy)_2EO_2$ (**1j**).

DPPEO$_2$-d$_4$ (**2a-d$_4$**)

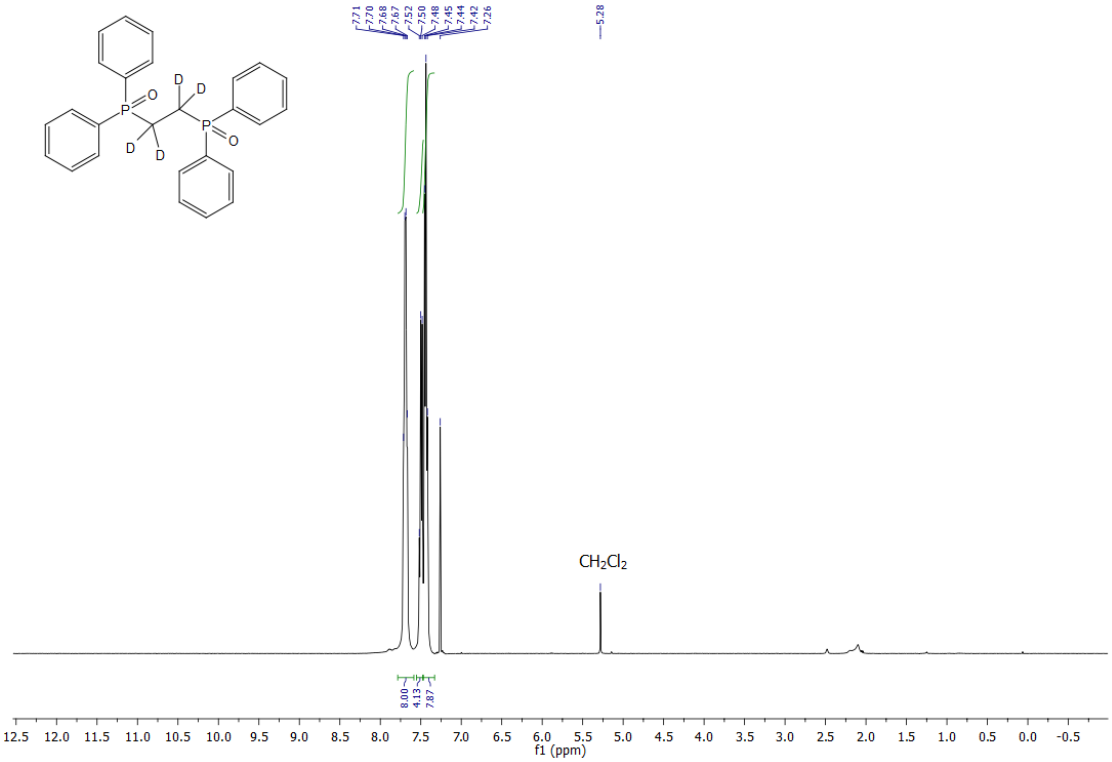


Figure S31. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of DPPEO$_2$-d$_4$ (**2a-d$_4$**).

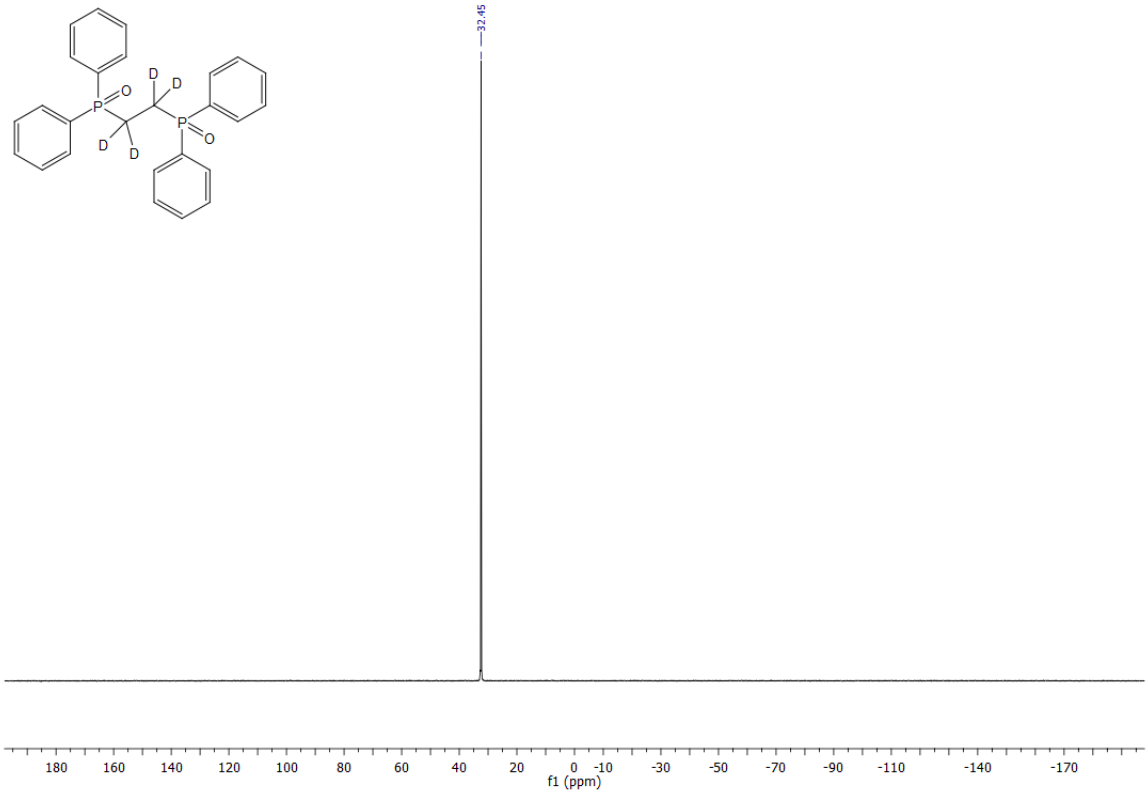


Figure S32. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of DPPEO$_2$-d$_4$ (**2a-d$_4$**).

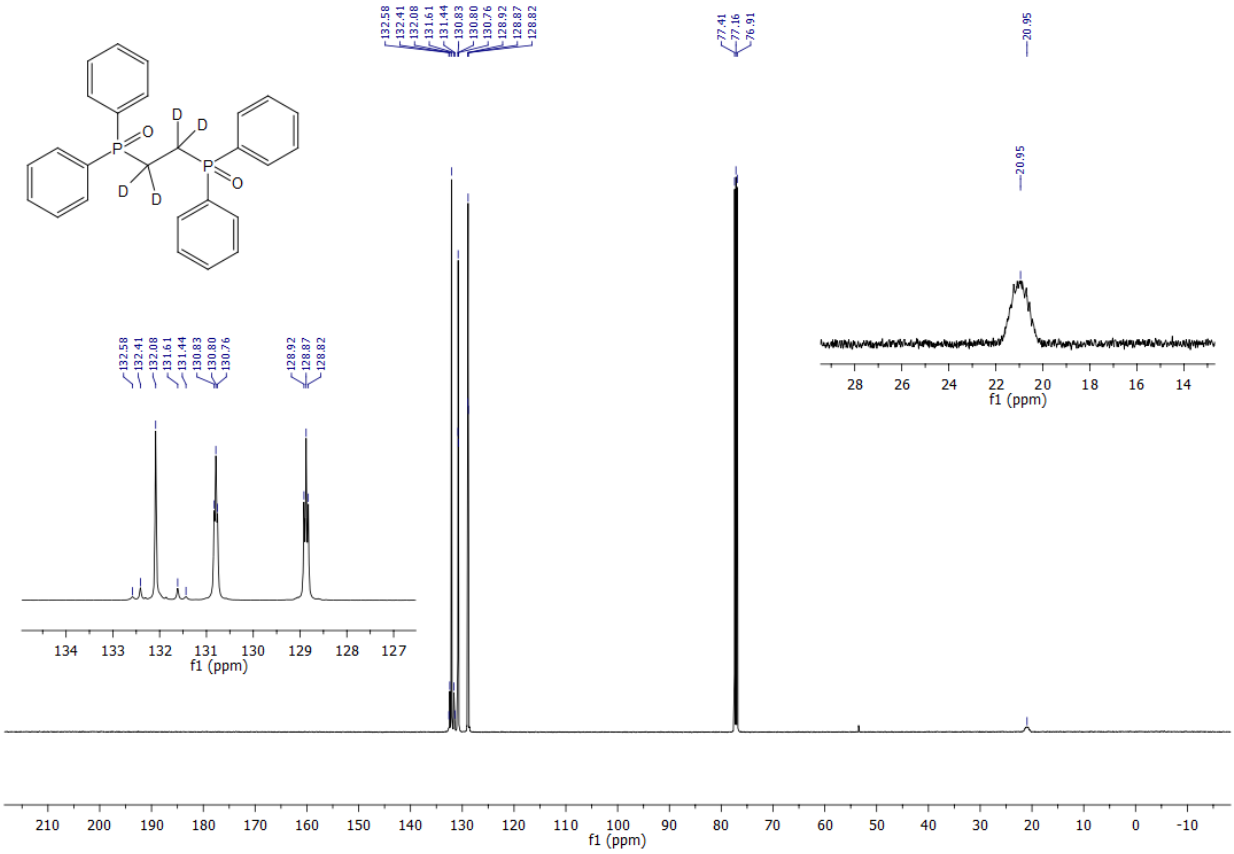


Figure S33. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of $DPPEO_2$-d_4 (**2a-d$_4$**).

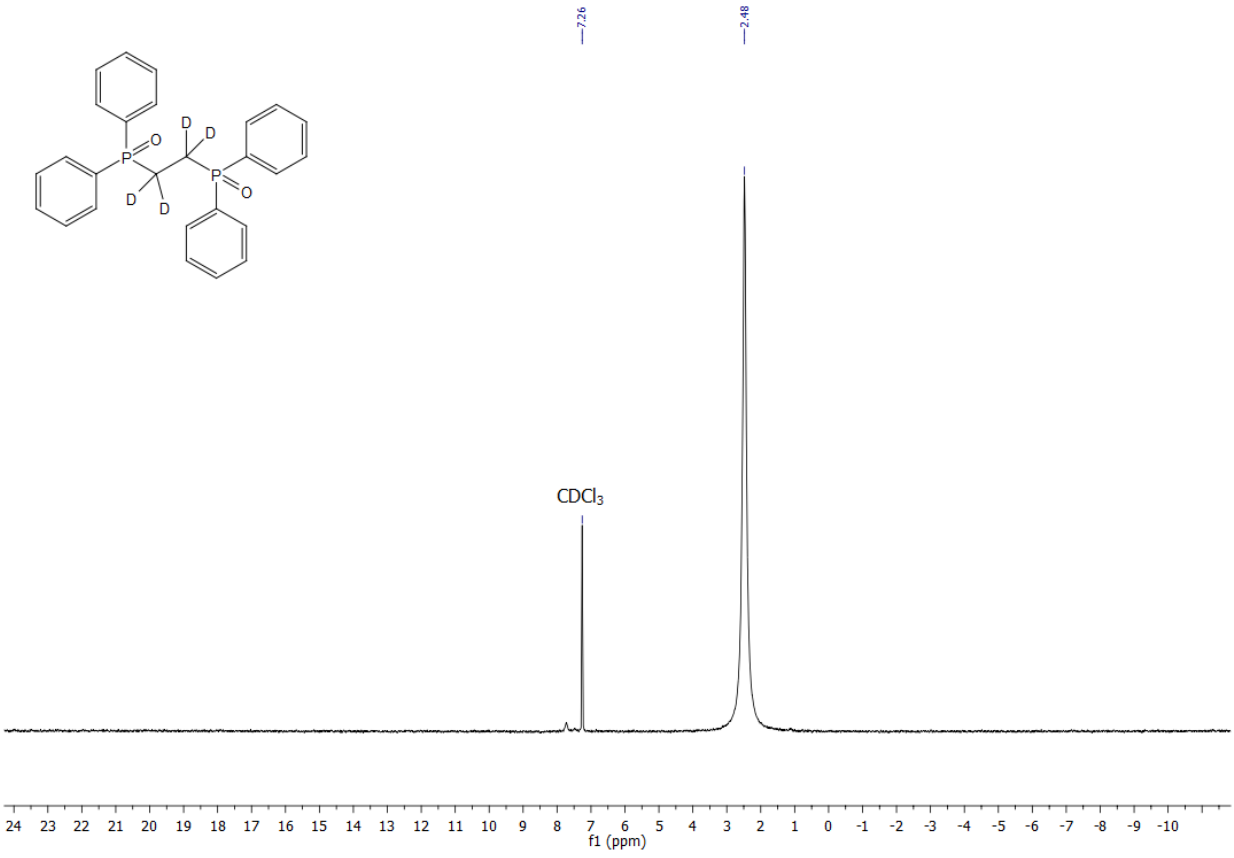


Figure S34. ^{2}H NMR (77 MHz, $CHCl_3$) spectrum of $DPPEO_2$-d_4 (**2a-d$_4$**).

DHHEO$_2$-d$_{12}$ (**2b-d$_{12}$**)

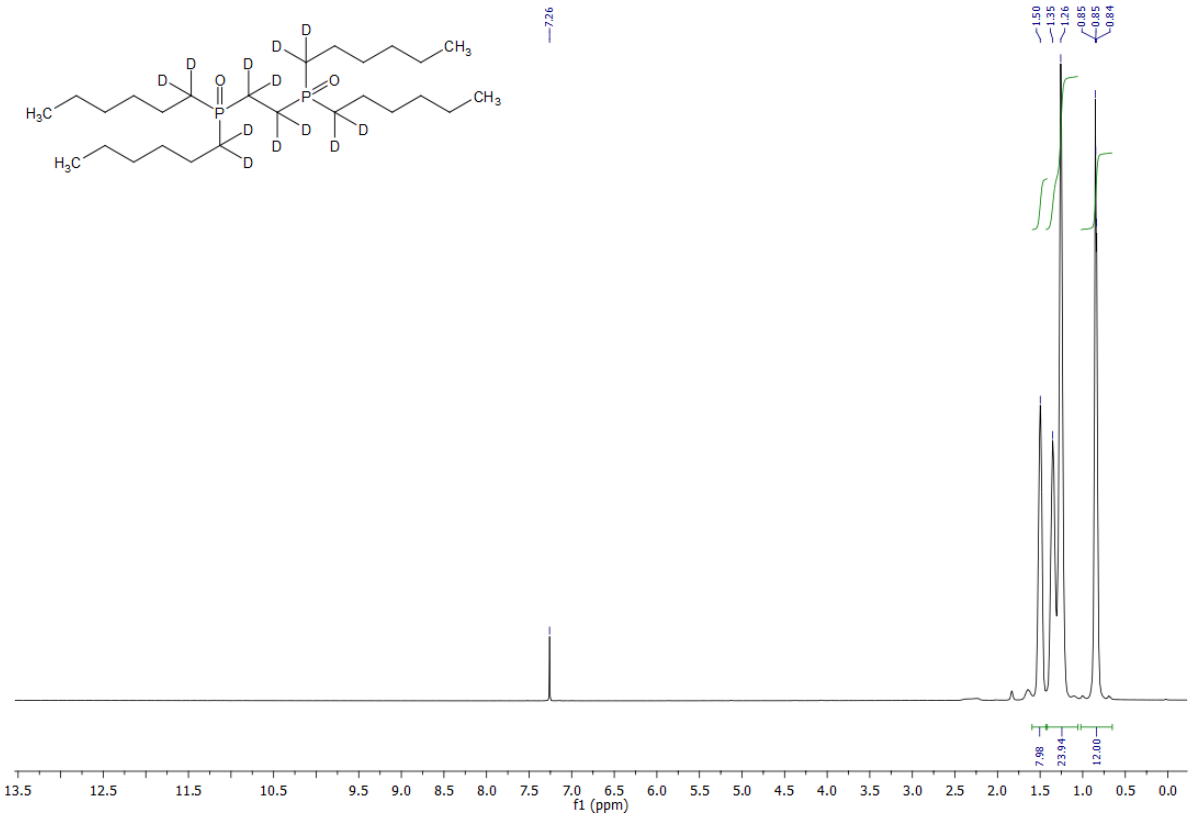


Figure S35. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of DHHEO$_2$-d$_{12}$ (**2b-d$_{12}$**).

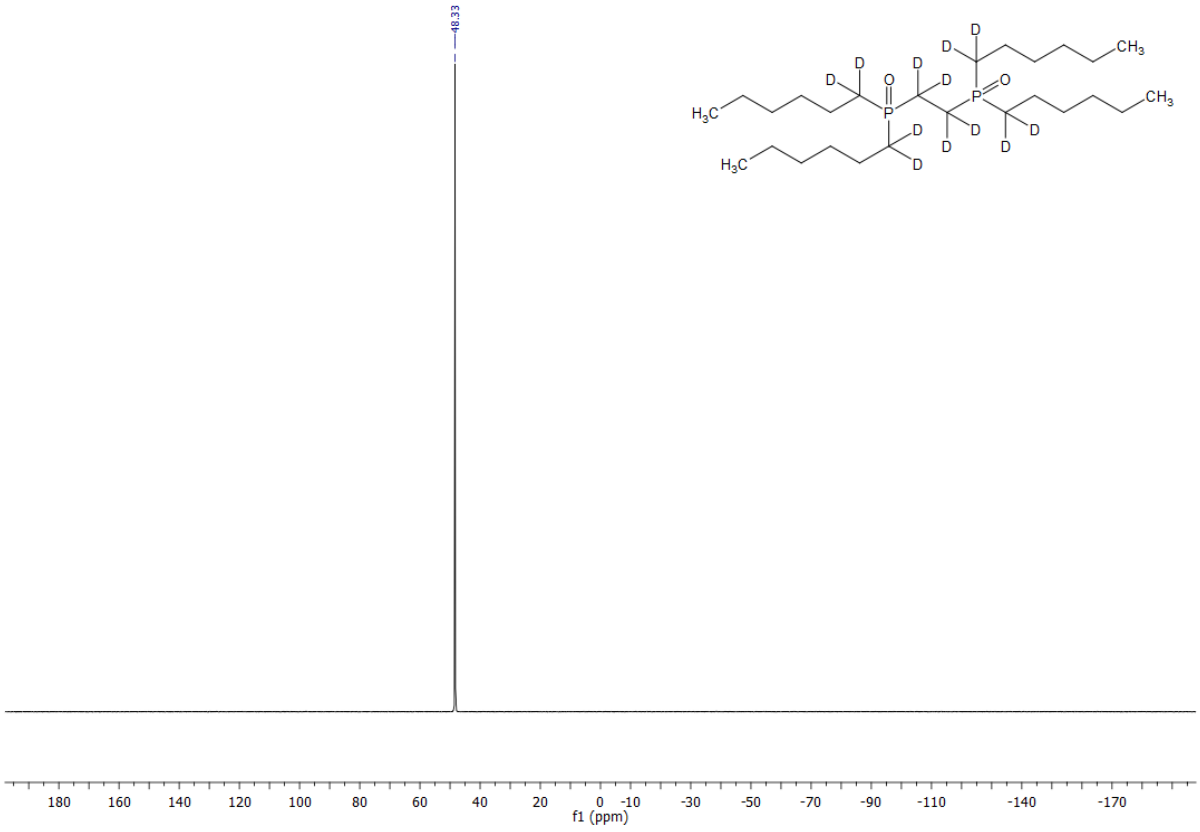


Figure S36. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of DHHEO$_2$-d$_{12}$ (**2b-d$_{12}$**).

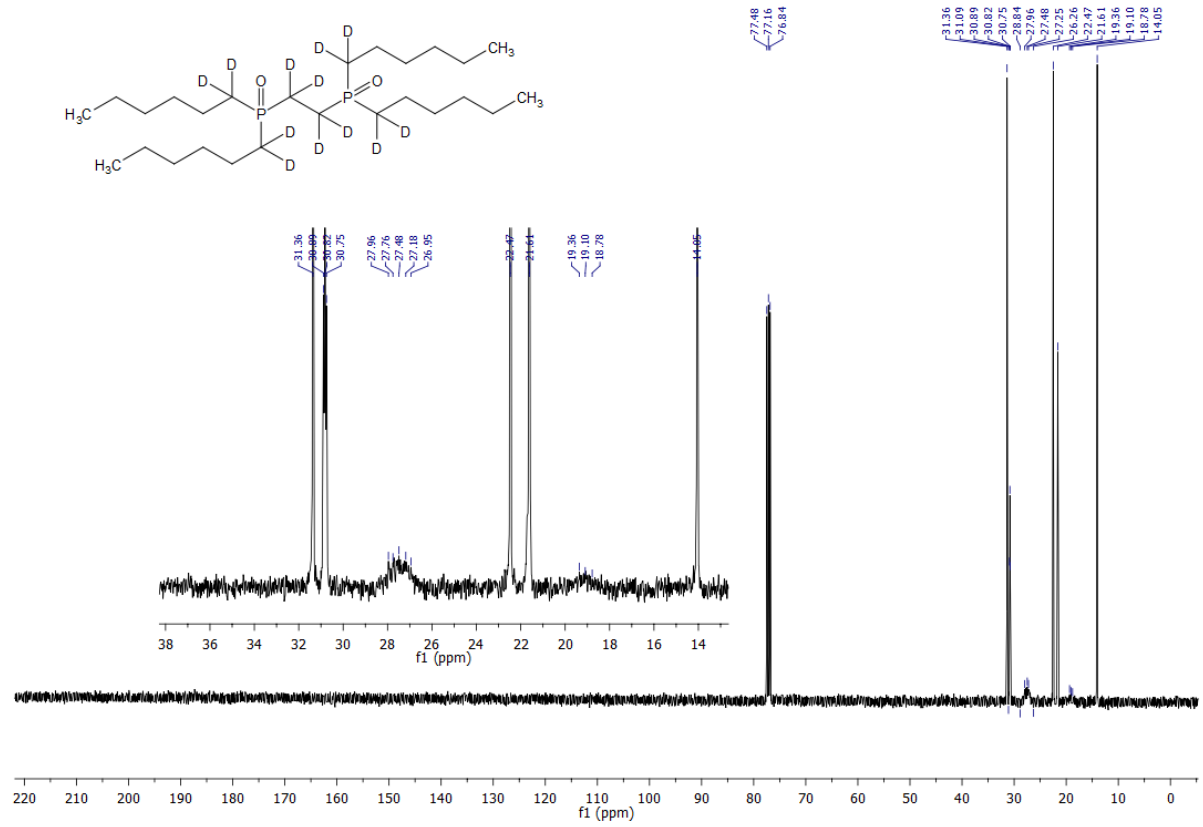


Figure S37. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of $DHHEO_2$-d_{12} (**2b-d_{12}**).

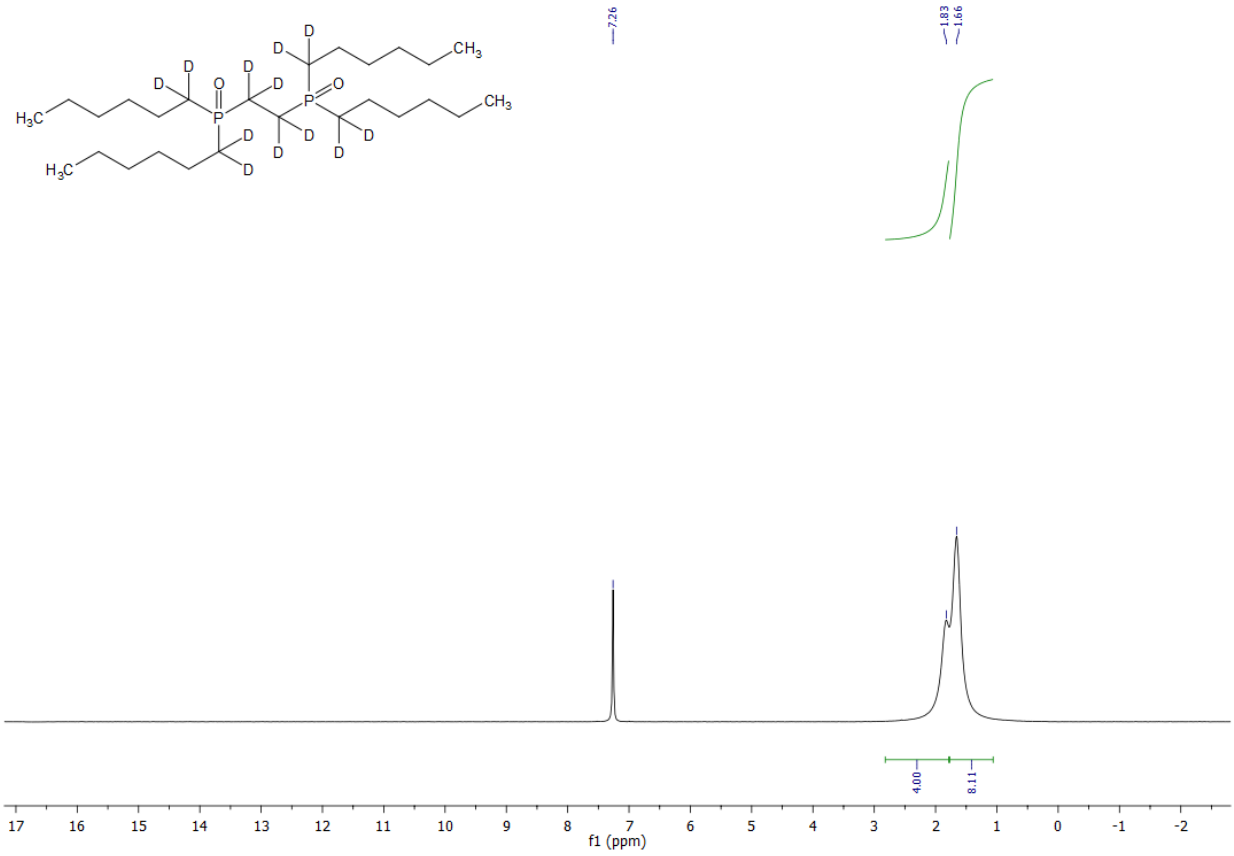


Figure S38. ^{2}H NMR (61 MHz, $CHCl_3$) spectrum of $DHHEO_2$-d_{12} (**2b-d_{12}**).

DBBEO$_2$-d$_{12}$ (**2c-d$_{12}$**)

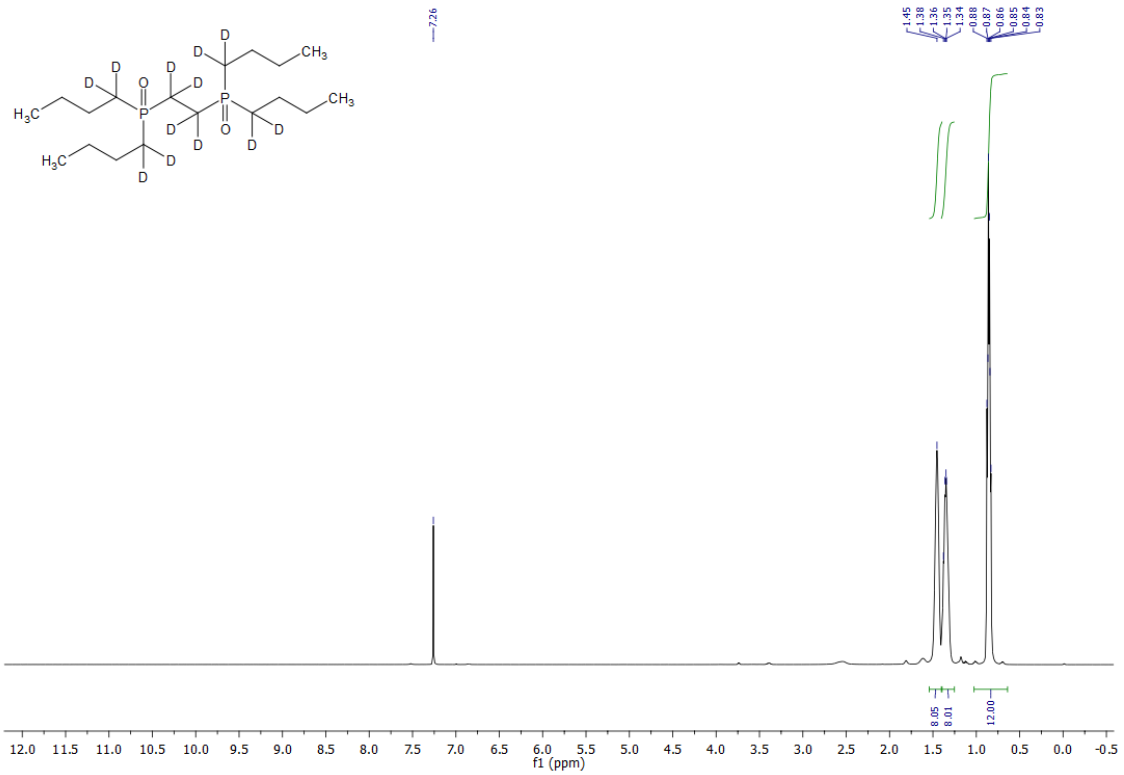


Figure S39. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of DBBEO$_2$-d$_{12}$ (**2c-d$_{12}$**).

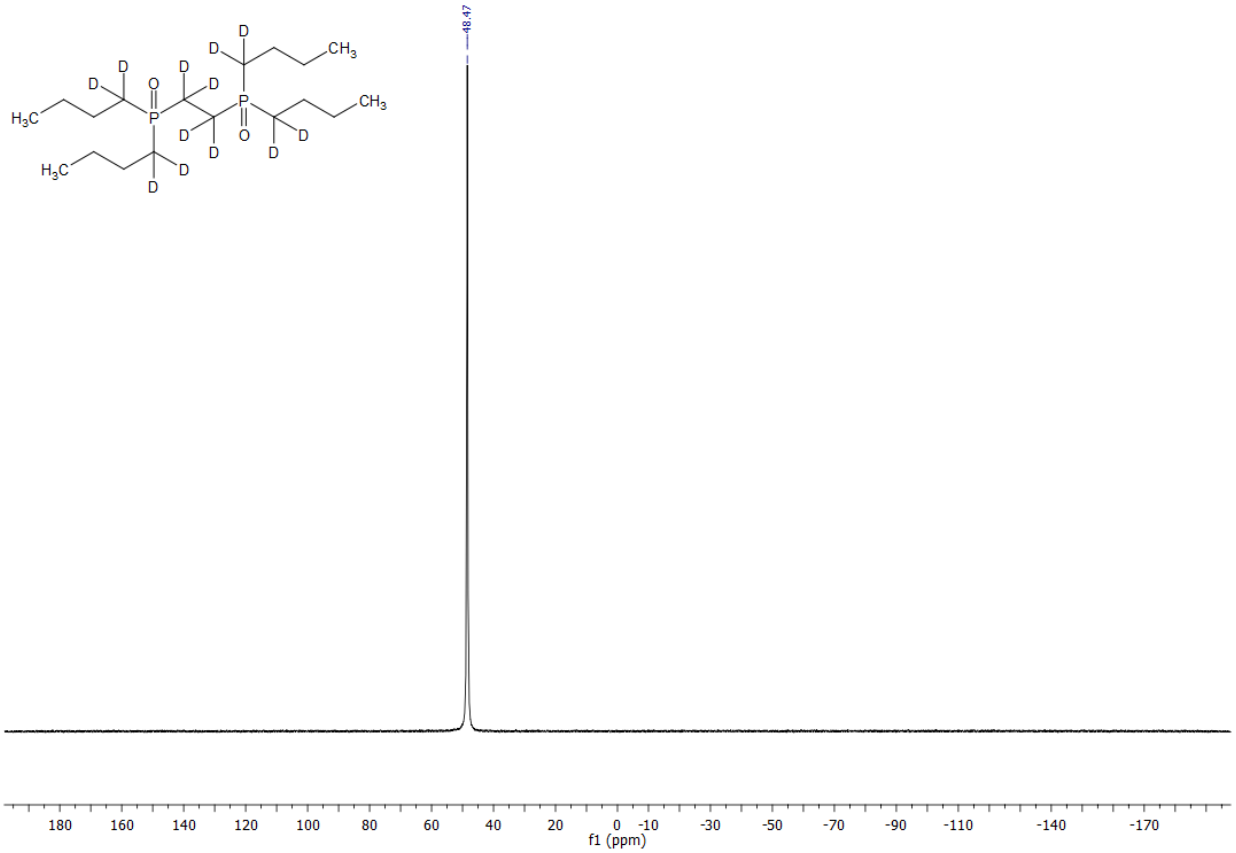


Figure S40. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of DBBEO$_2$-d$_{12}$ (**2c-d$_{12}$**).

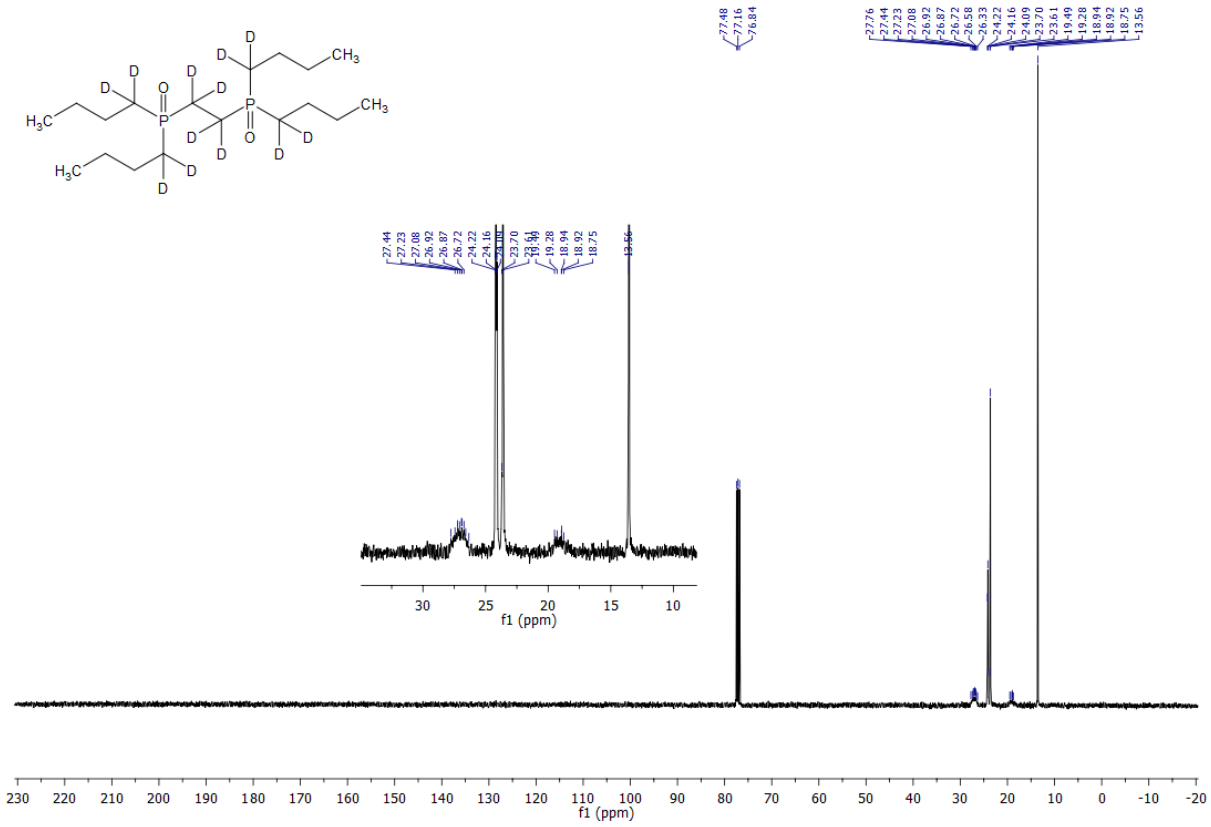


Figure S41. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of $DBBEO_2$-d_{12} (**2c-d_{12}**).

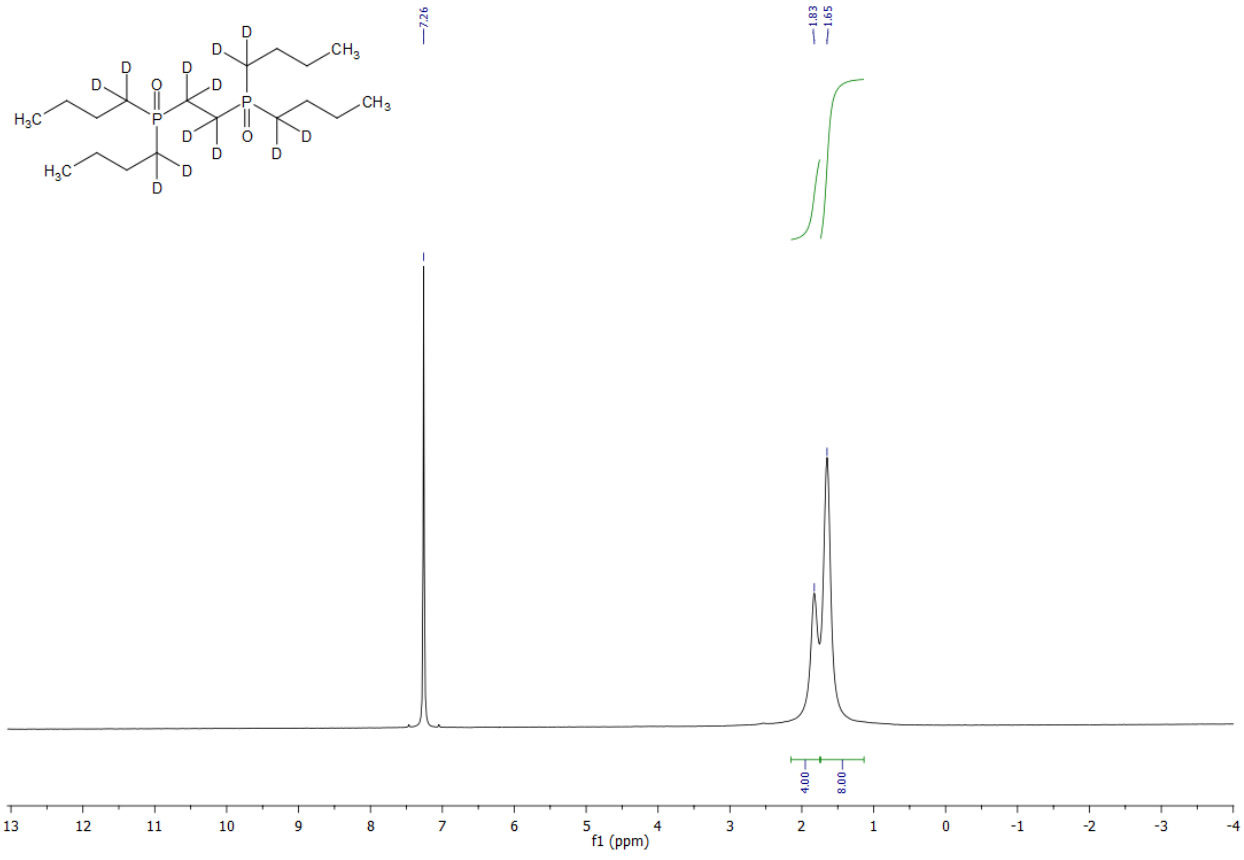


Figure S42. ^{2}H NMR (77 MHz, $CHCl_3$) spectrum of $DBBEO_2$-d_{12} (**2c-d_{12}**).

D(*o*-Tol)$_2$EO$_2$-d$_{16}$ (**2e-d$_{16}$**)

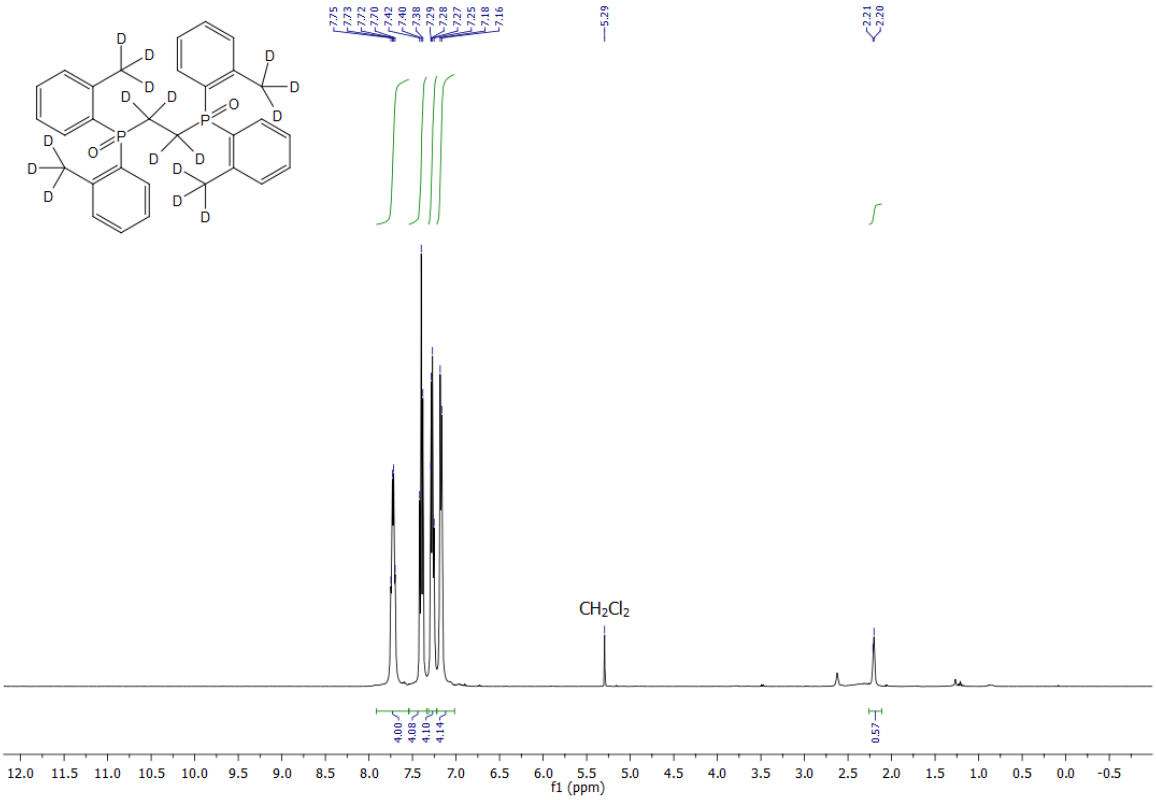


Figure S43. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of D(*o*-Tol)$_2$EO$_2$-d$_{16}$ (**2e-d$_{16}$**).

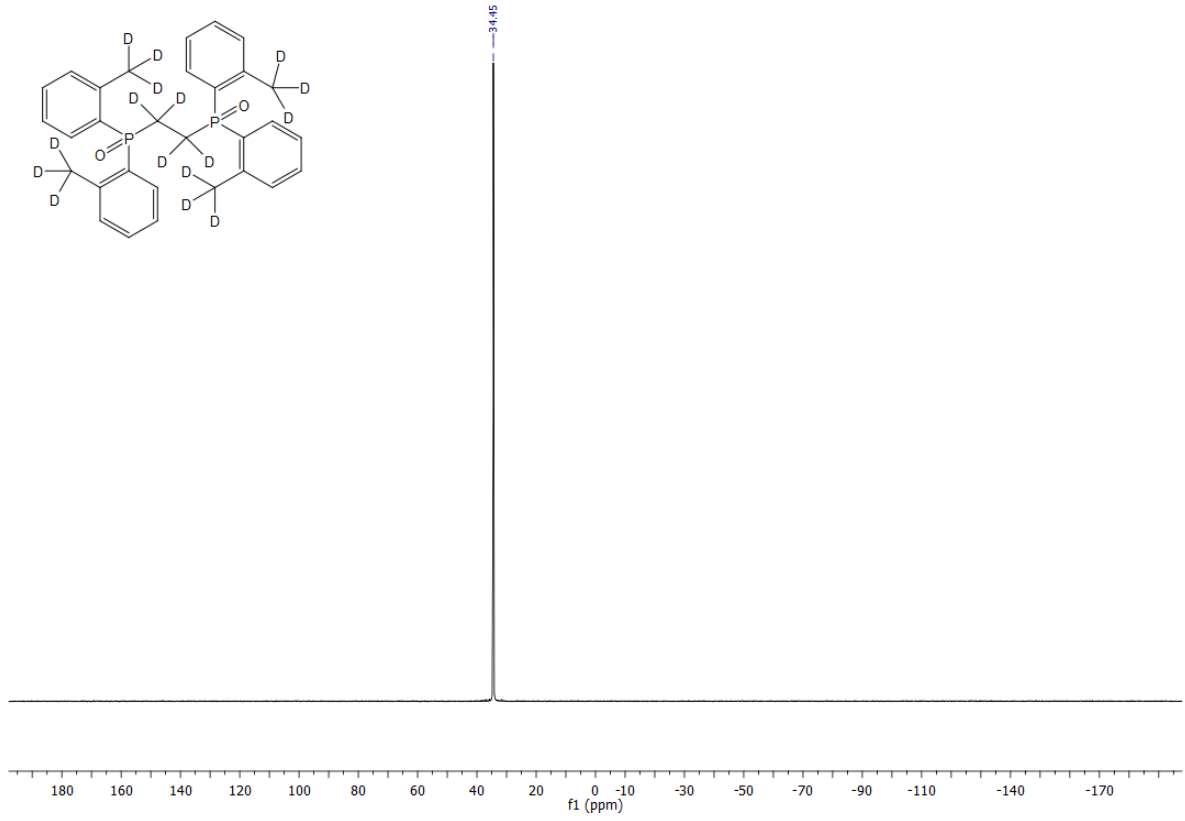


Figure S44. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of D(*o*-Tol)$_2$EO$_2$-d$_{16}$ (**2e-d$_{16}$**).

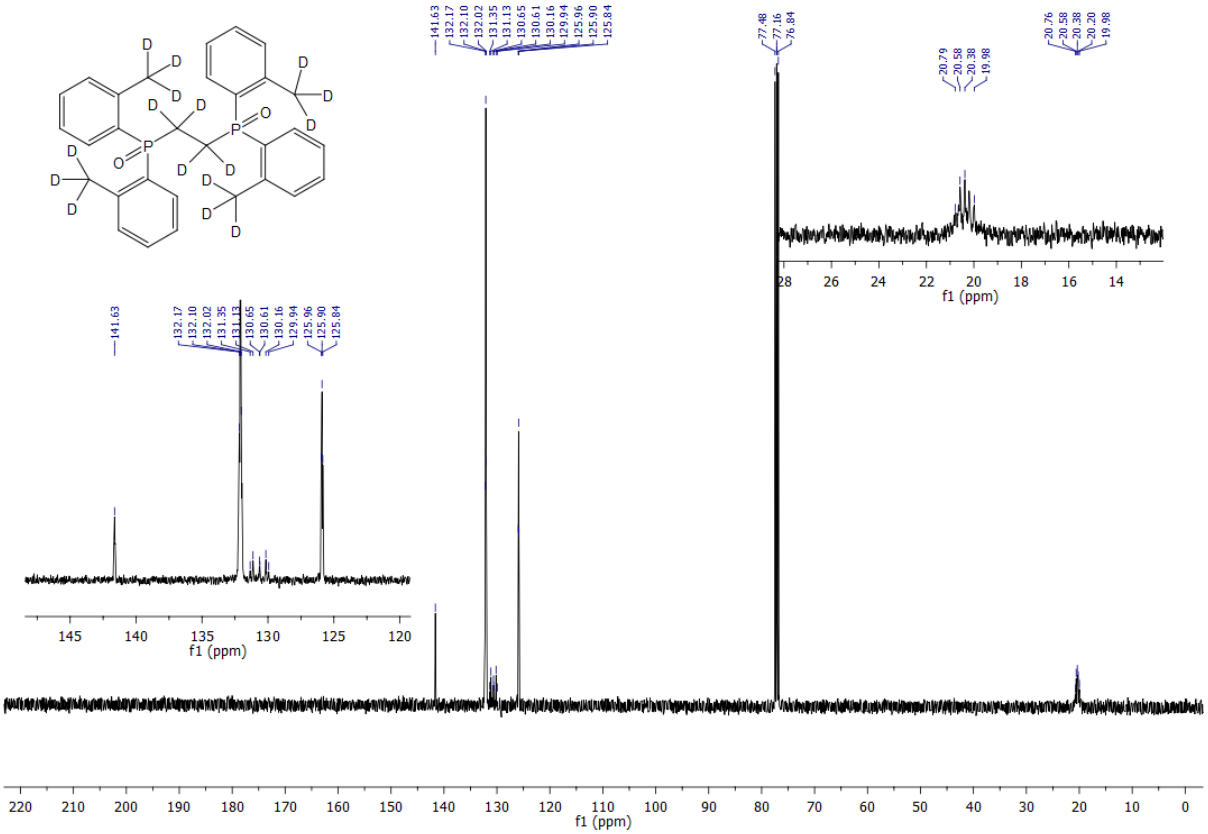


Figure S45. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of D(*o*-Tol)$_2$EO$_2$-d$_{16}$ (**2e-d$_{16}$**).

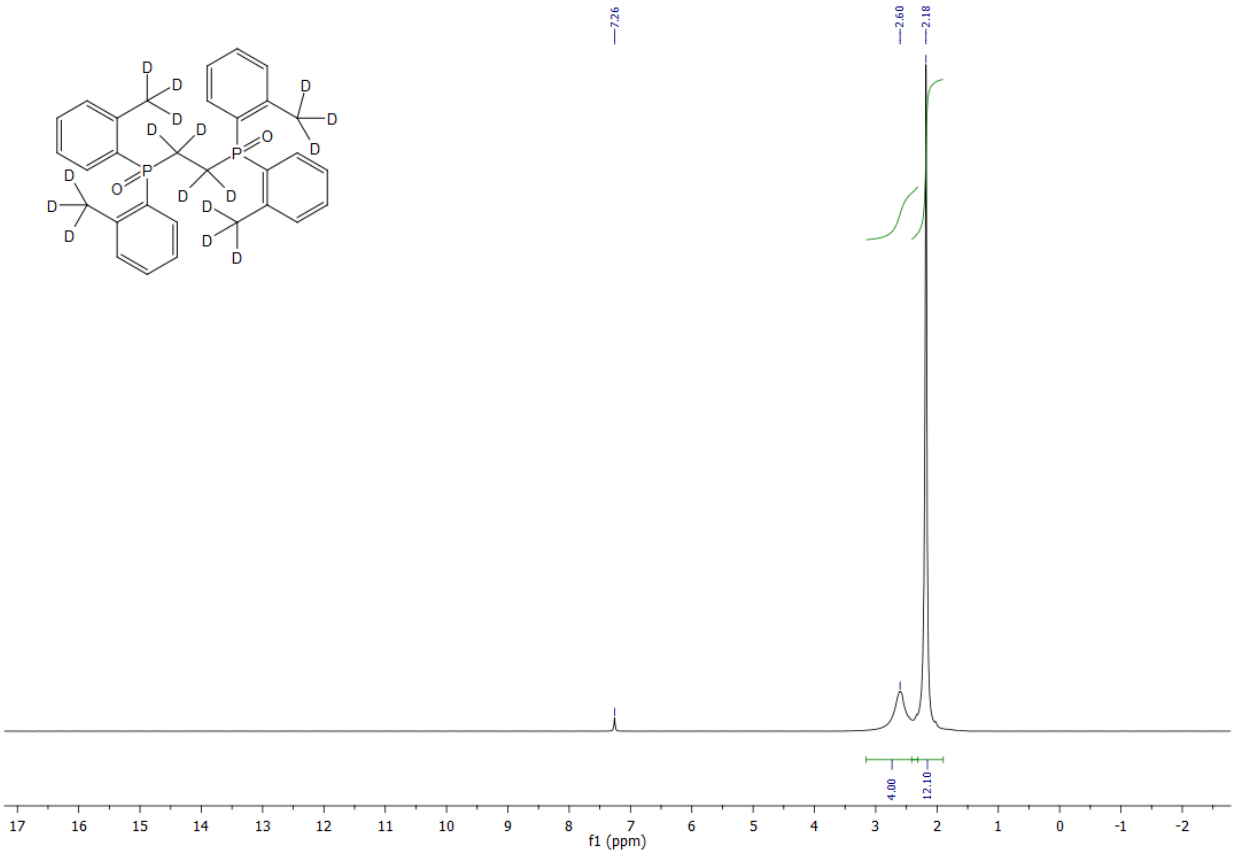


Figure S46. ^{2}H NMR (61 MHz, $CHCl_3$) spectrum of D(*o*-Tol)$_2$EO$_2$-d$_{16}$ (**2e-d$_{16}$**).

D(*o*-Tol)$_2$EO$_2$-d$_4$ (**2e-d$_4$**)

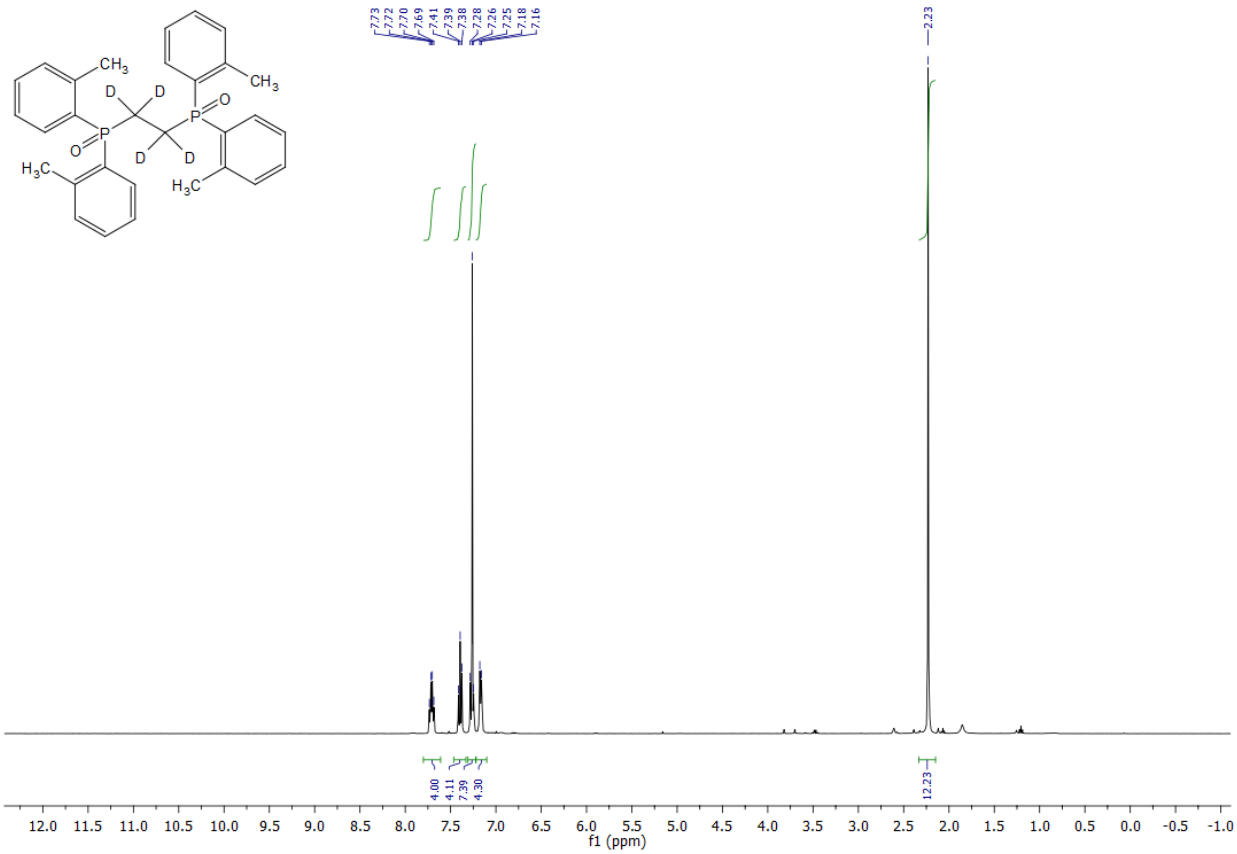


Figure S47. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of D(*o*-Tol)$_2$EO$_2$-d$_4$ (**2e-d$_4$**).

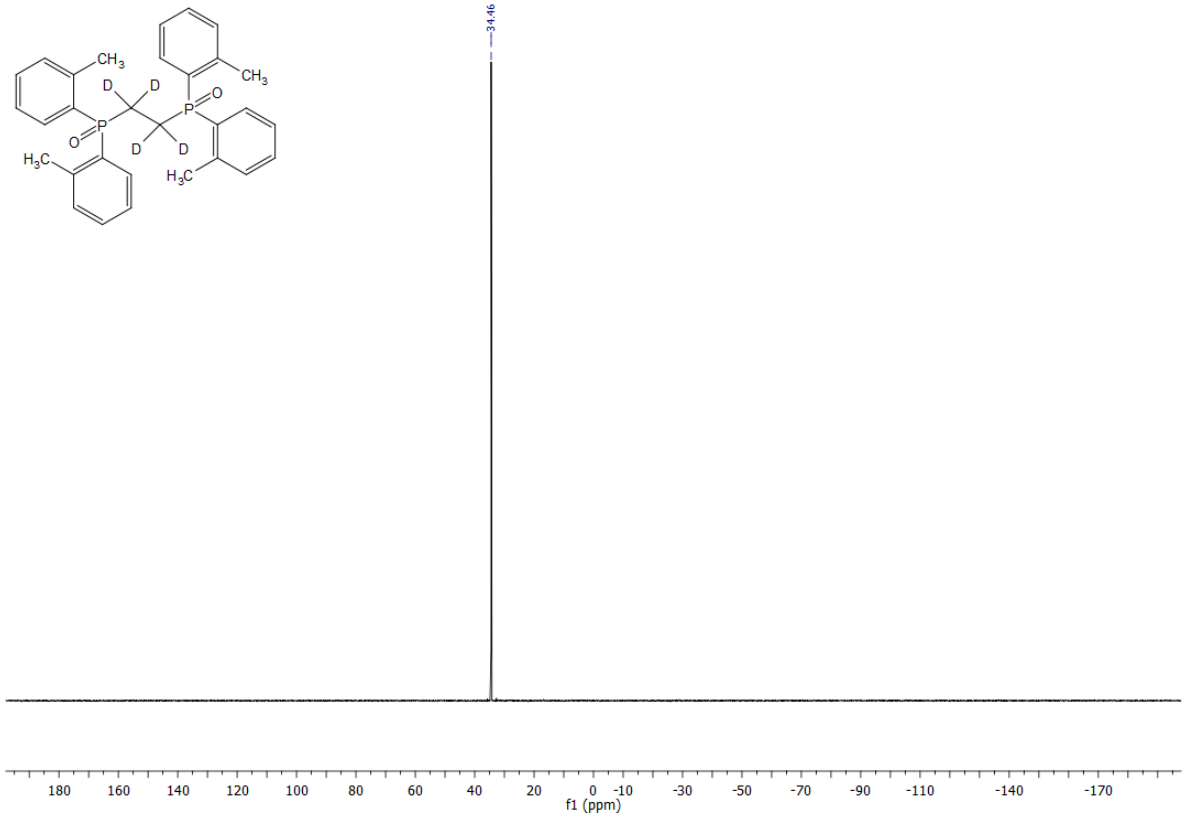


Figure S48. ^{31}P NMR (162 MHz, CDCl$_3$) spectrum of D(*o*-Tol)$_2$EO$_2$-d$_4$ (**2e-d$_4$**).

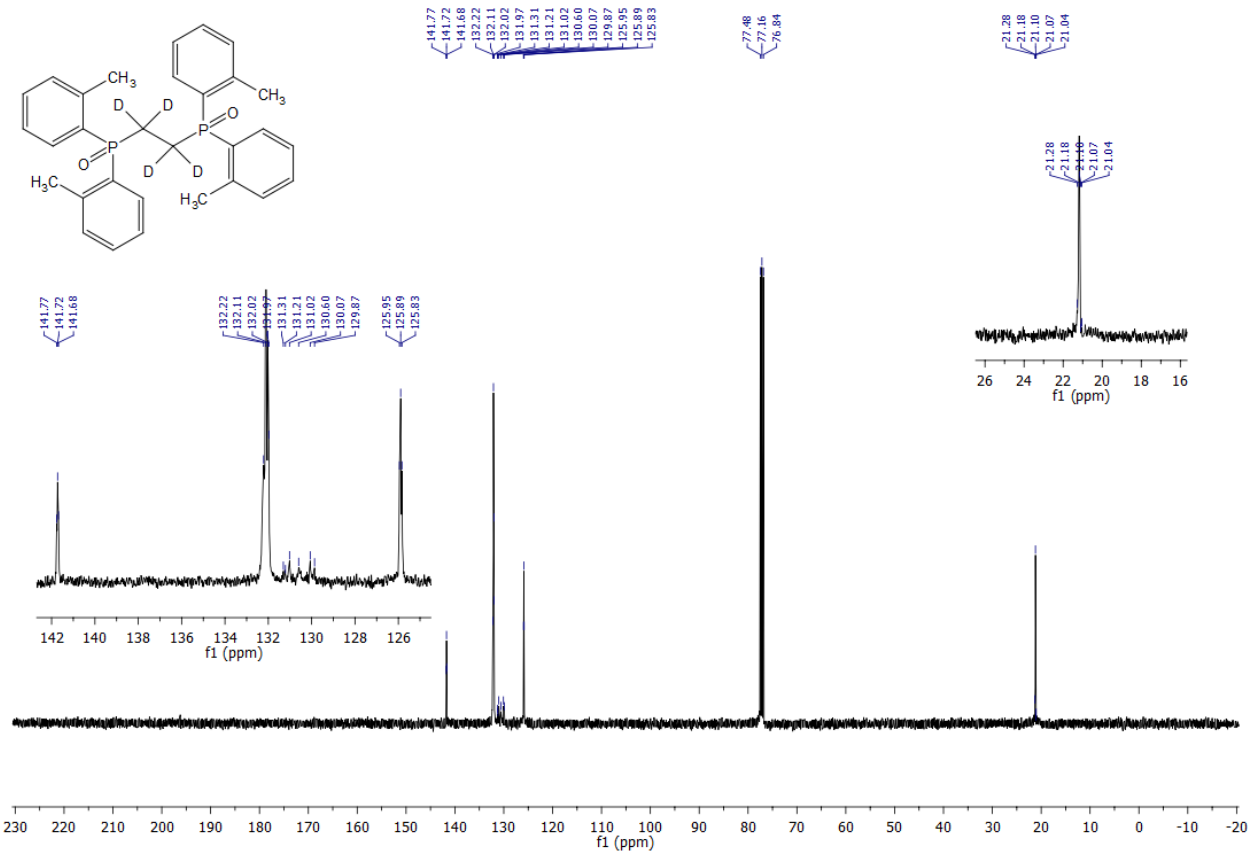


Figure S49. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of D(*o*-Tol)$_2$EO$_2$-d$_4$ (**2e-d$_4$**).

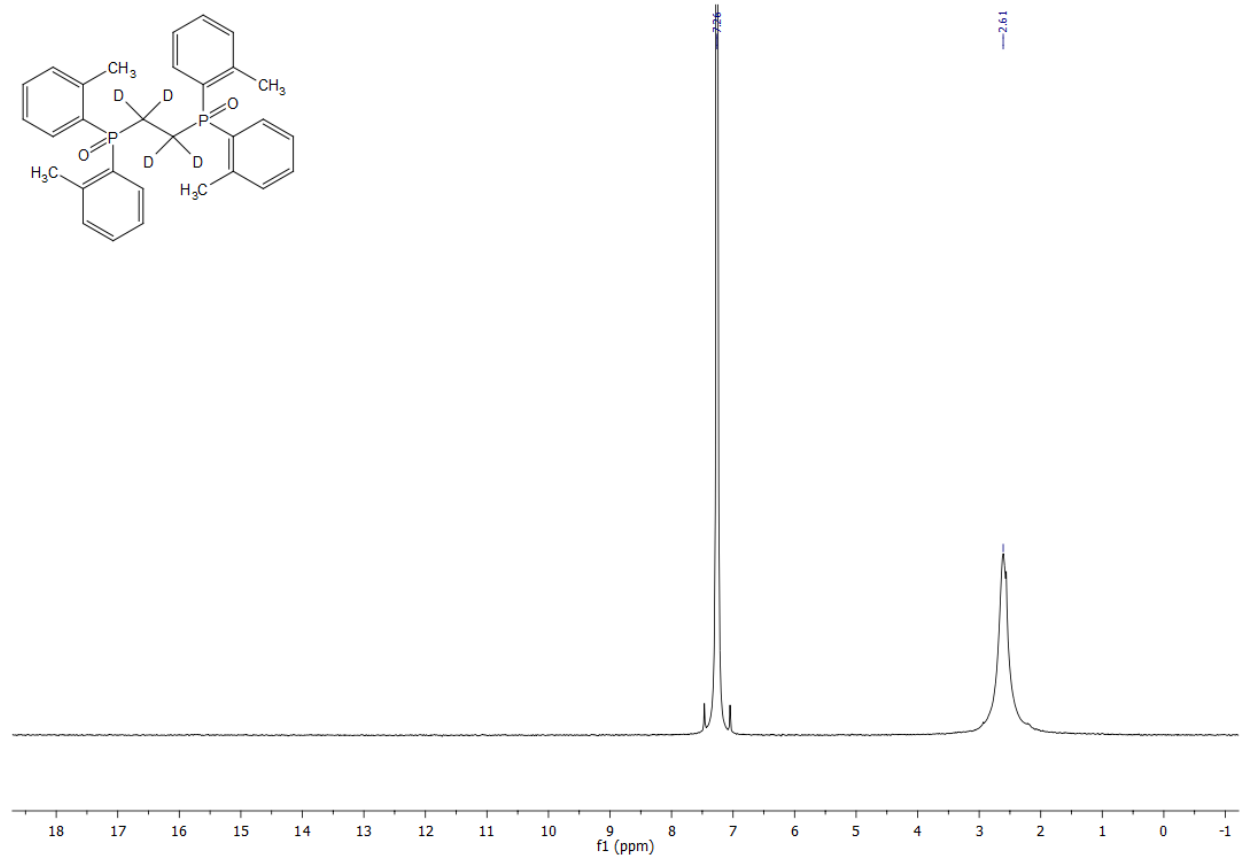


Figure S50. ^{2}H NMR (77 MHz, $CHCl_3$) spectrum of D(*o*-Tol)$_2$EO$_2$-d$_4$ (**2e-d$_4$**).

D(*p*-OMe(C_6H_4))$_2$EO$_2$-d$_4$ (**2h-d$_4$**)

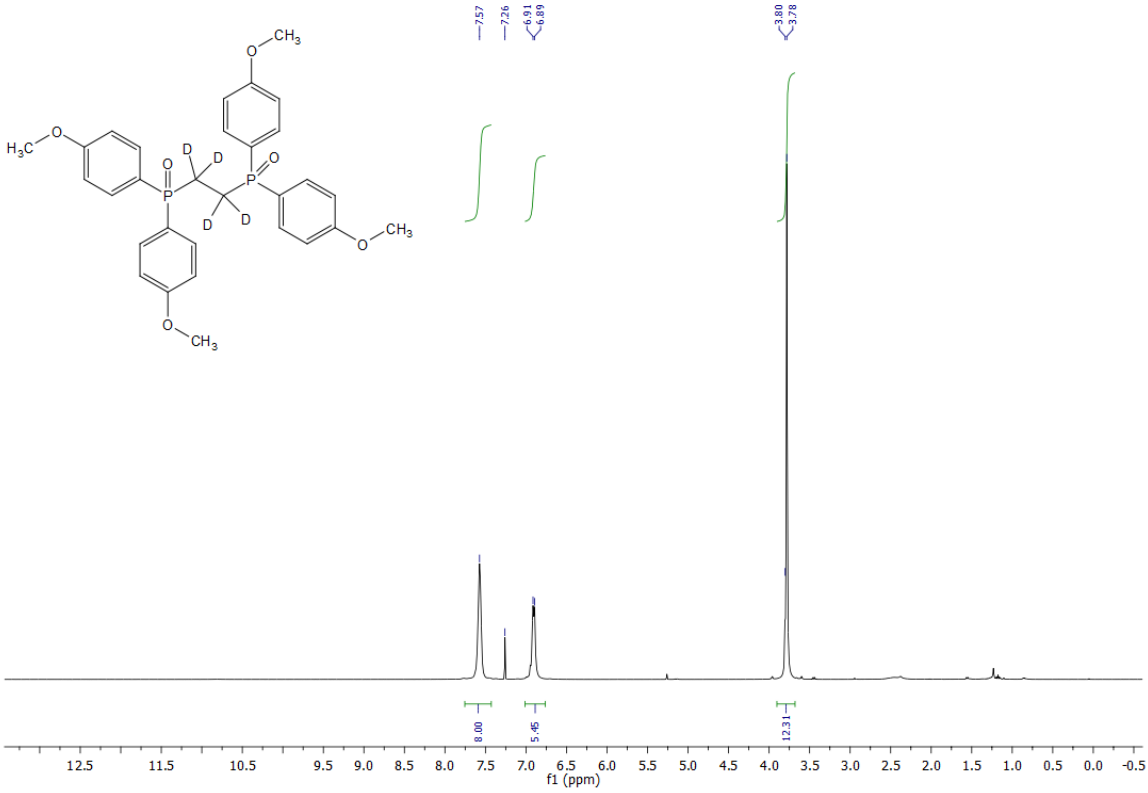


Figure S51. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of D(*p*-OMe(C_6H_4))$_2$EO$_2$-d$_4$ (**2h-d$_4$**).

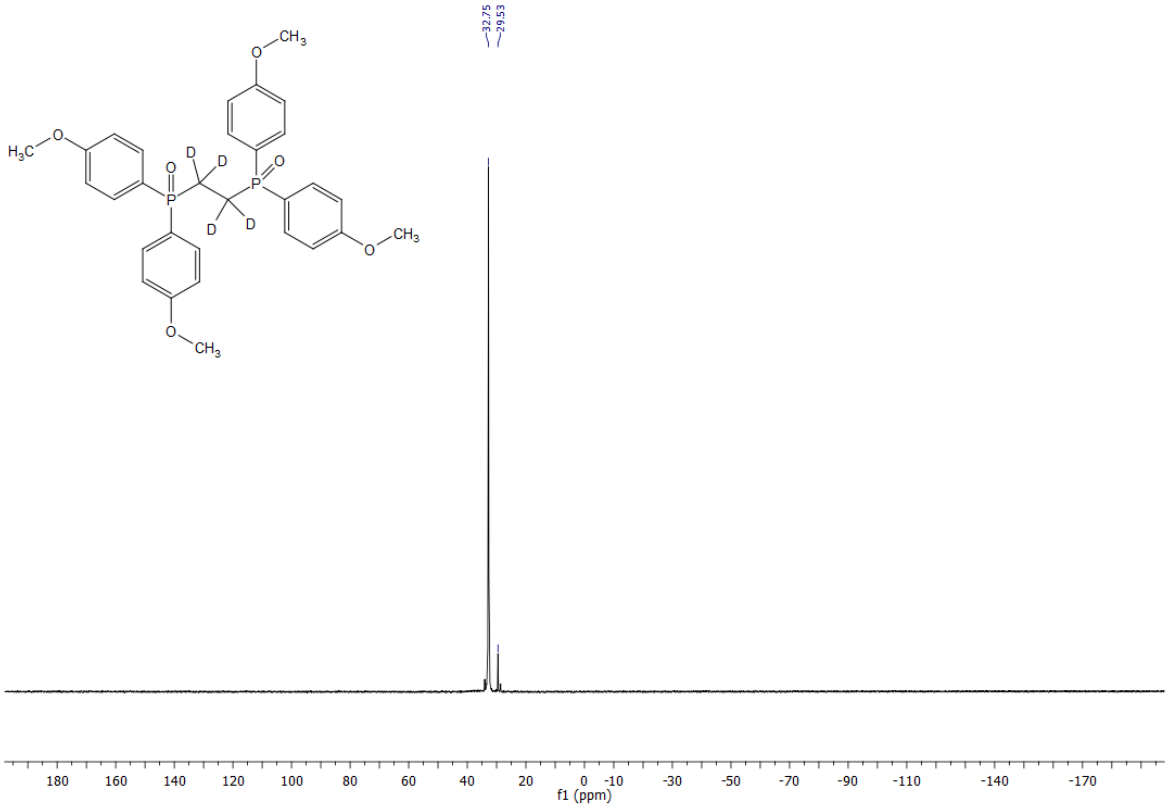


Figure S52. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of D(*p*-OMe(C_6H_4))$_2$EO$_2$-d$_4$ (**2h-d$_4$**).

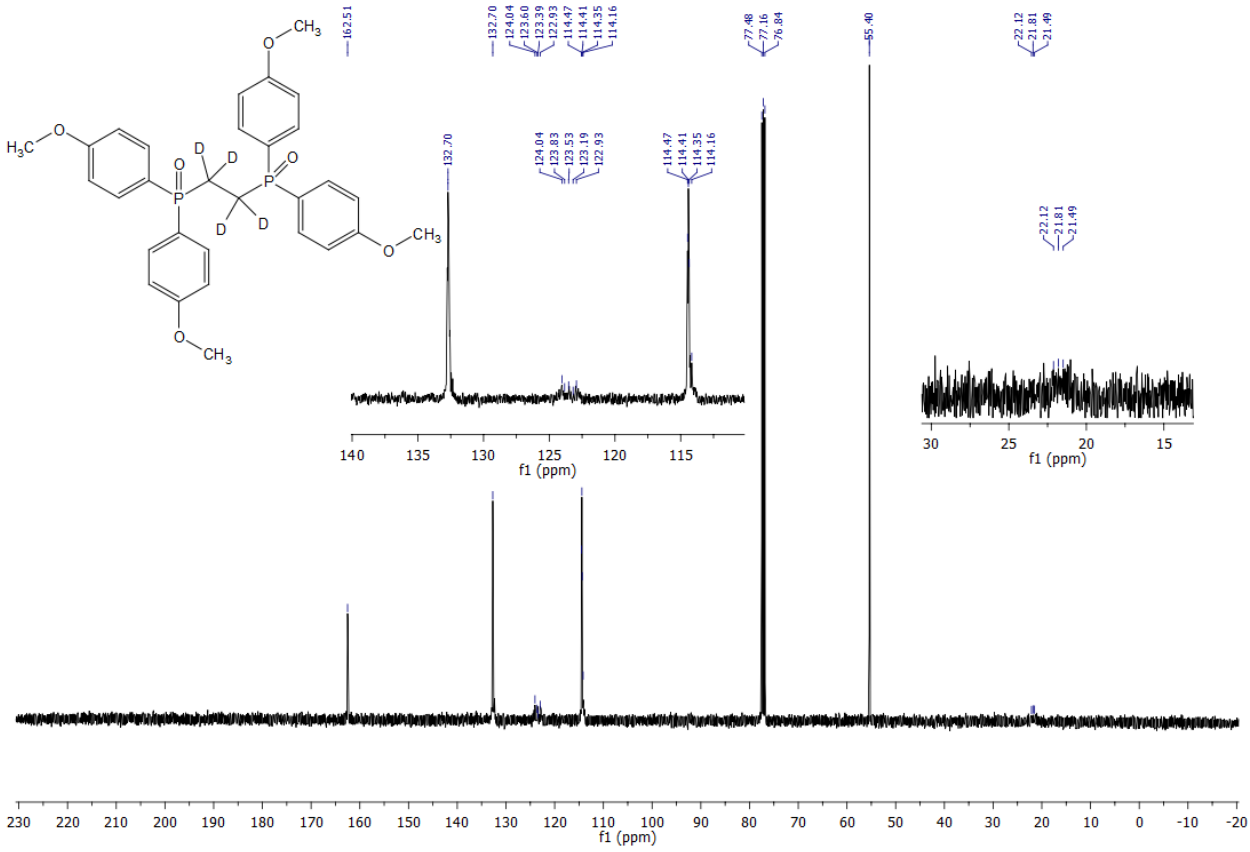


Figure S53. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of D(*p*-OMe(C_6H_4))$_2EO_2$-d_4 (**2h-d$_4$**).

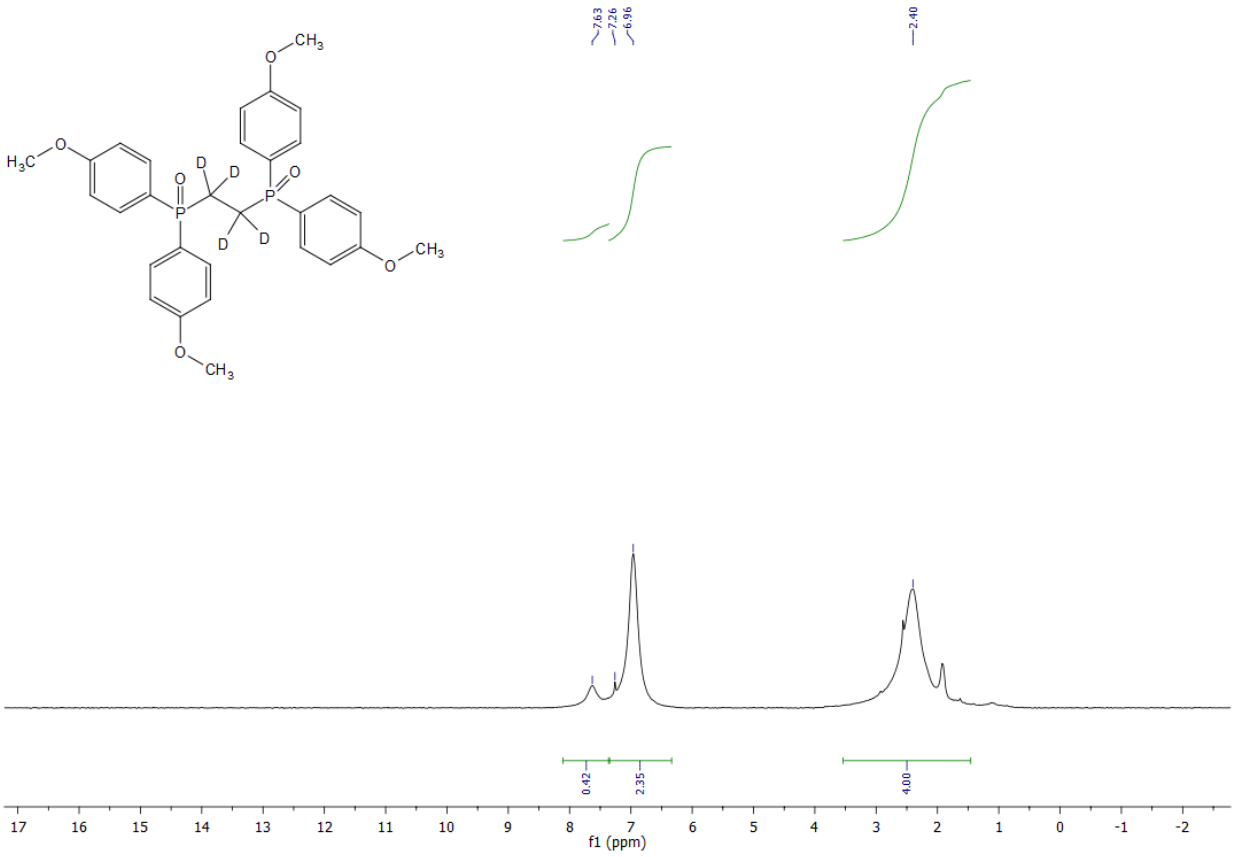


Figure S54. ^{2}H NMR (61 MHz, $CHCl_3$) spectrum of D(*p*-OMe(C_6H_4))$_2EO_2$-d_4 (**2h-d$_4$**).

DCy_2EO_2-d_4 (**2j-d$_4$**)

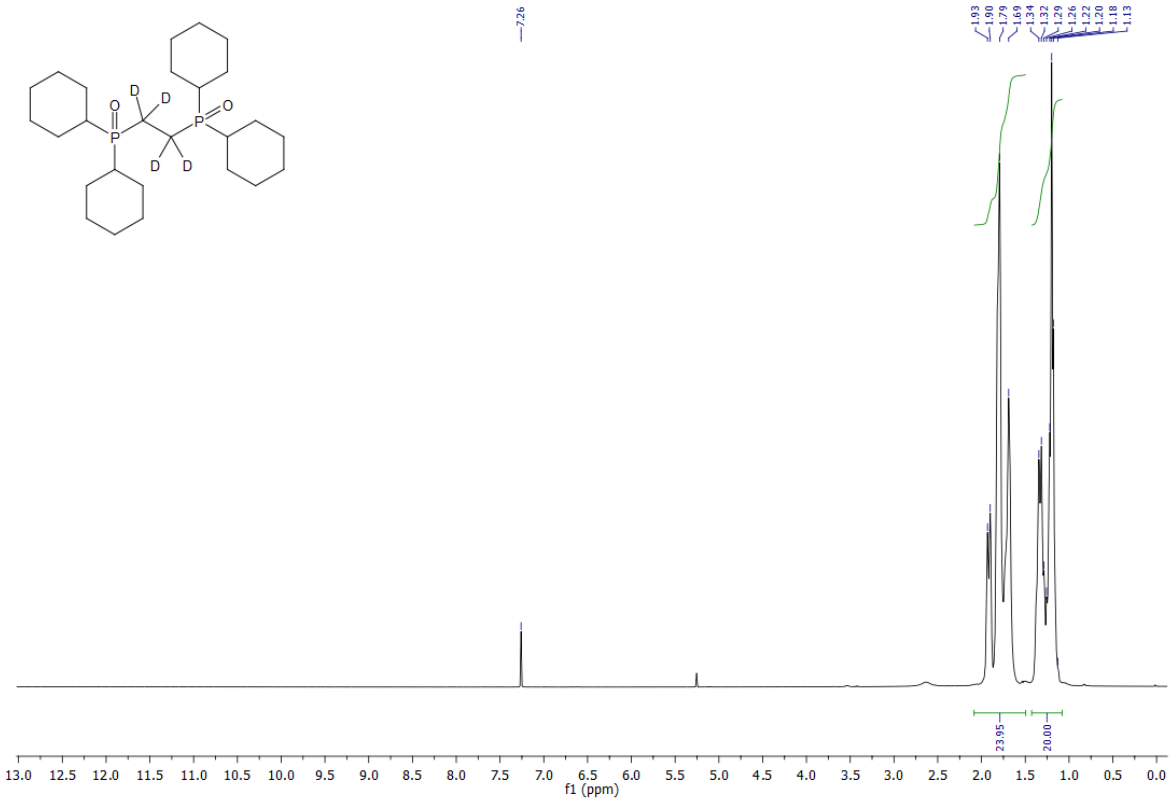


Figure S55. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of DCy_2EO_2-d_4 (**2j-d$_4$**).

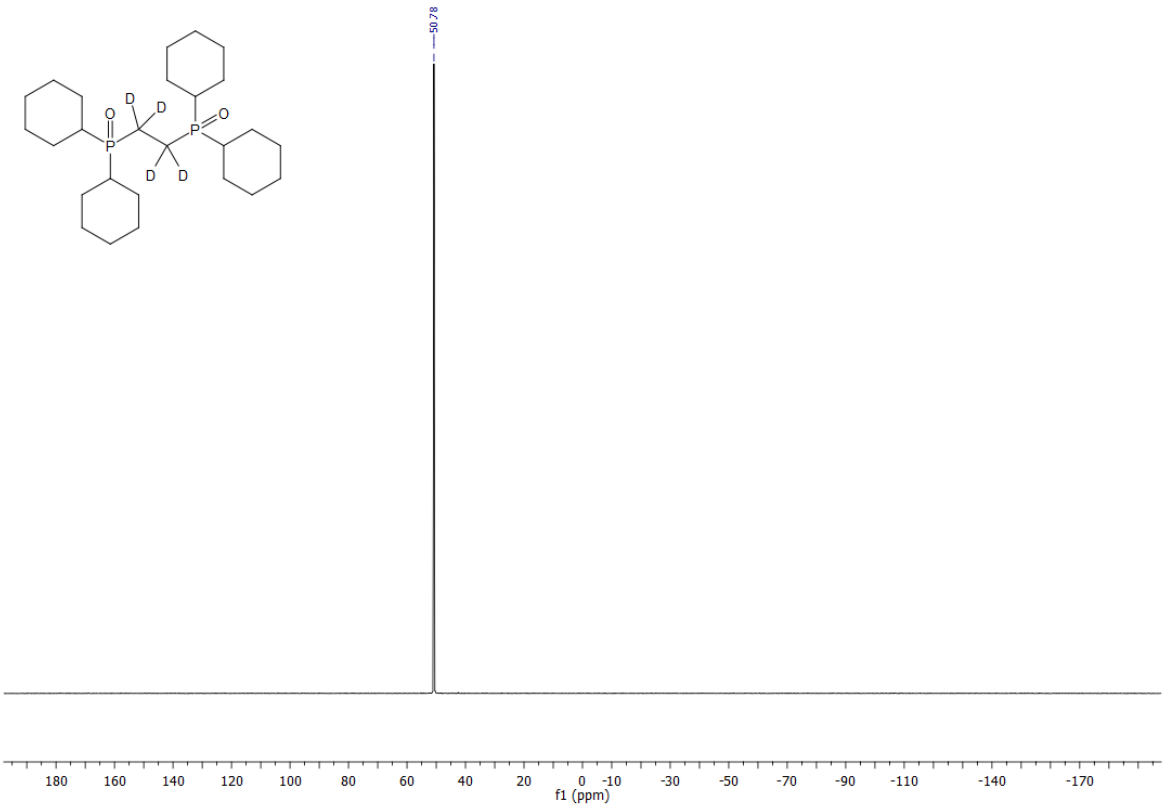


Figure S56. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of DCy_2EO_2-d_4 (**2j-d$_4$**).

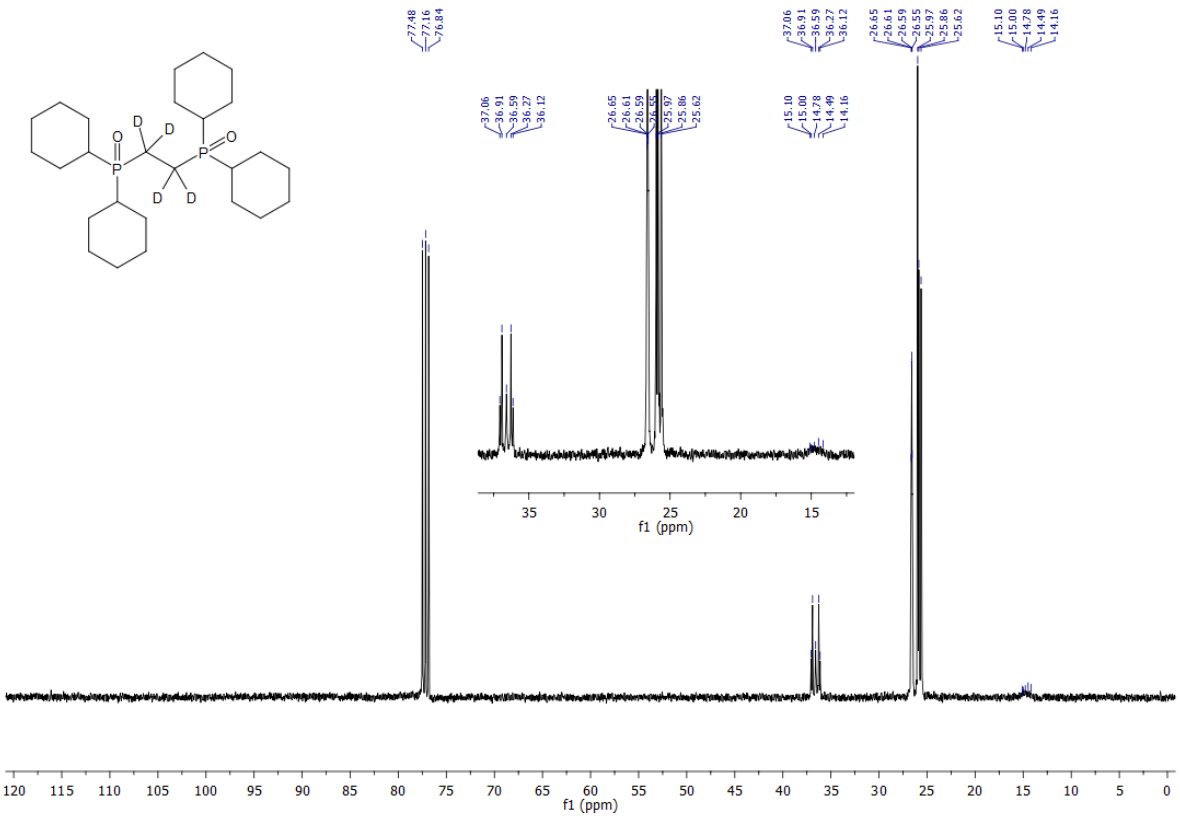


Figure S57. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of DCy_2EO_2-d_4 (**2j-d$_4$**).

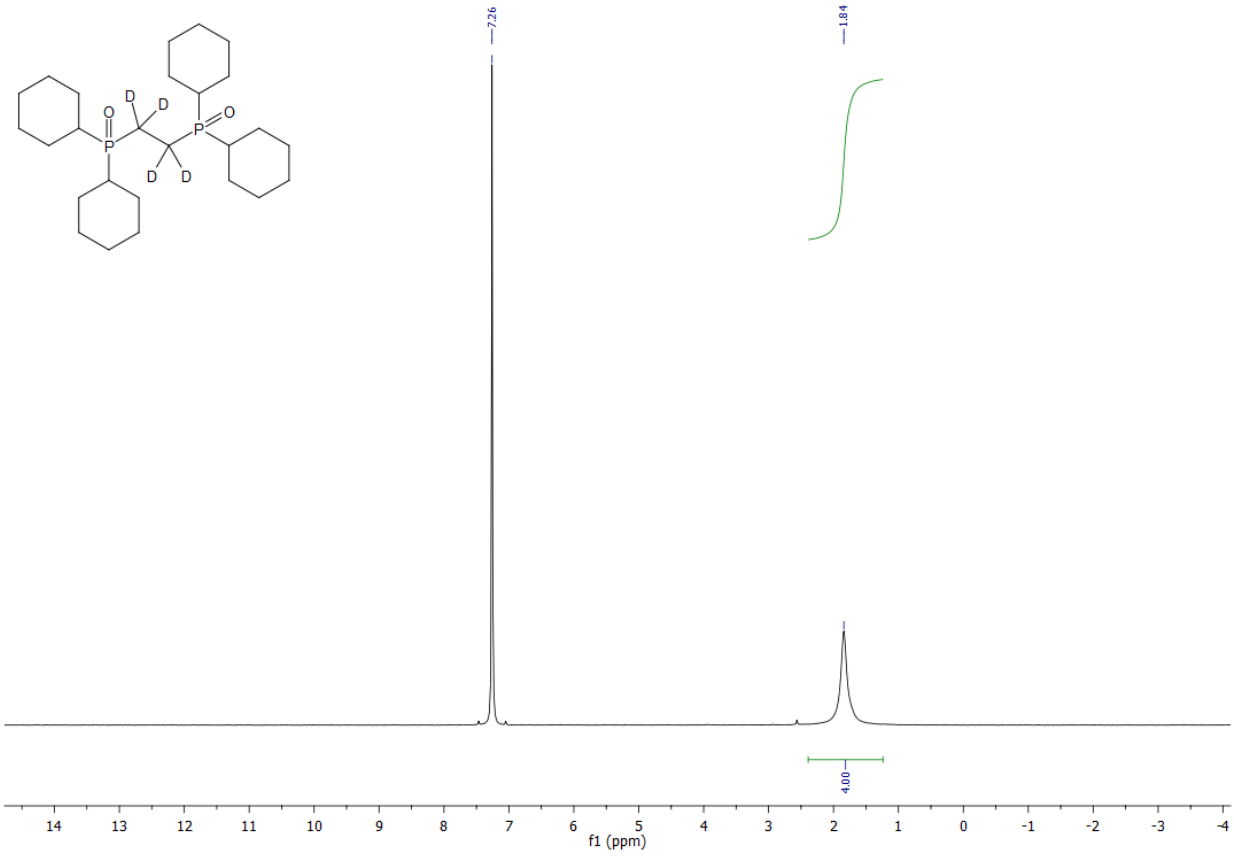


Figure S58. ^{2}H NMR (77 MHz, $CHCl_3$) spectrum of DCy_2EO_2-d_4 (**2j-d$_4$**).

^{13}C-DPPEO$_2$ (**^{13}C$_2$-2a**)

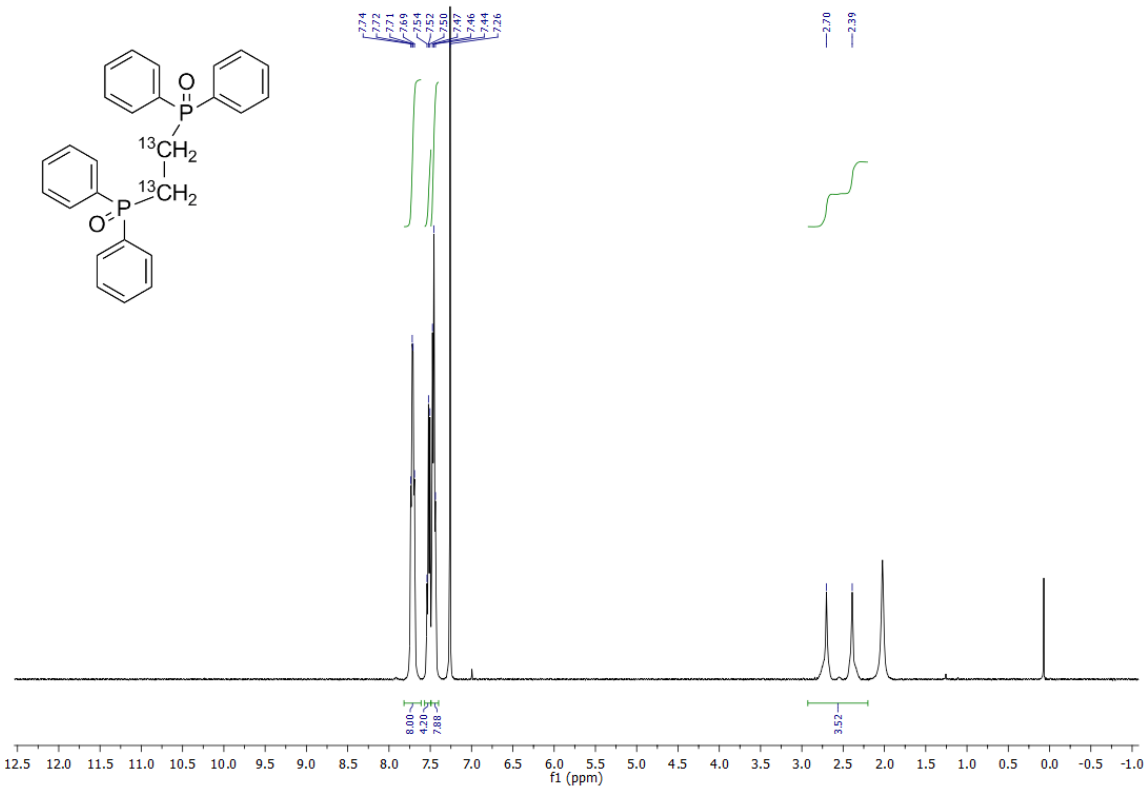


Figure S59. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of ^{13}C-DPPEO$_2$ (**^{13}C$_2$-2a**).

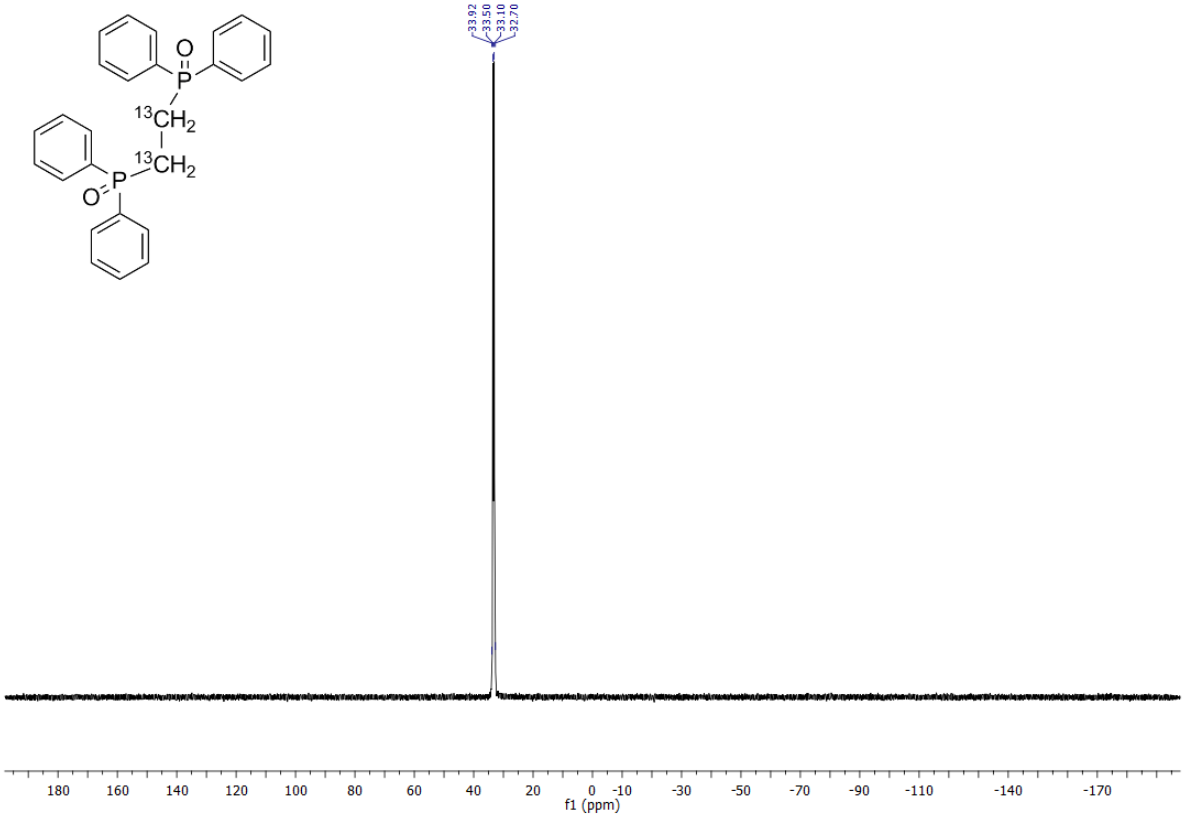


Figure S60. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of ^{13}C-DPPEO$_2$ (**^{13}C$_2$-2a**).

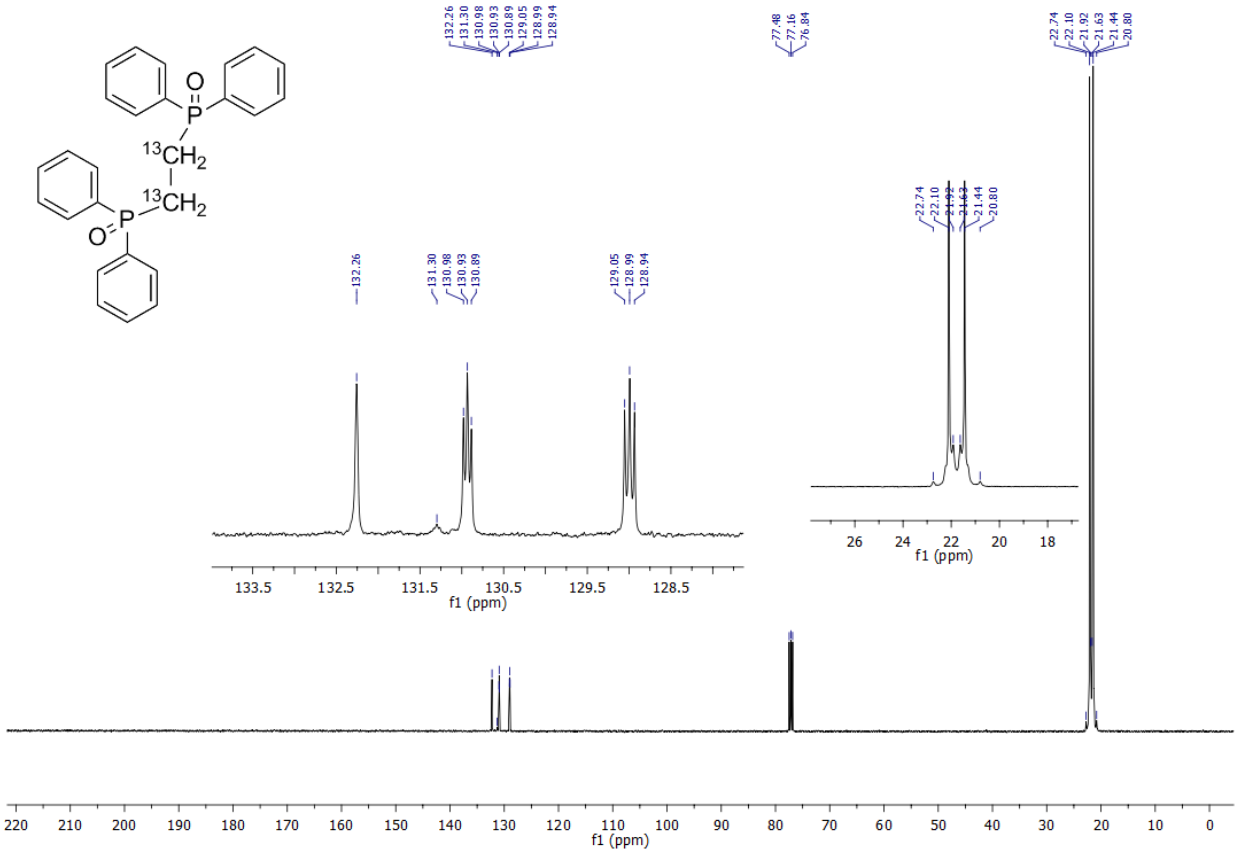


Figure S61. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of ^{13}C-DPPEO$_2$ (**$^{13}C_2$-2a**).

DPPE-d_4 (**3a-d_4**)

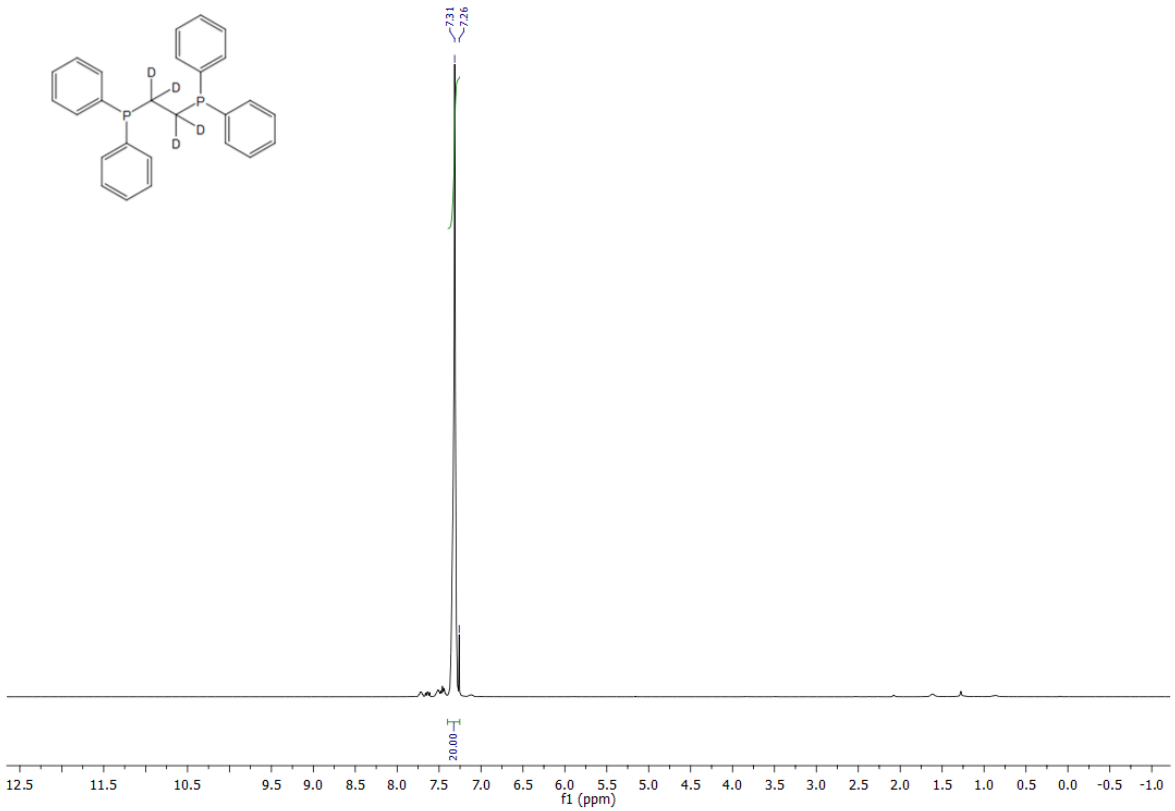


Figure S62. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of DPPE-d_4 (**3a-d_4**).

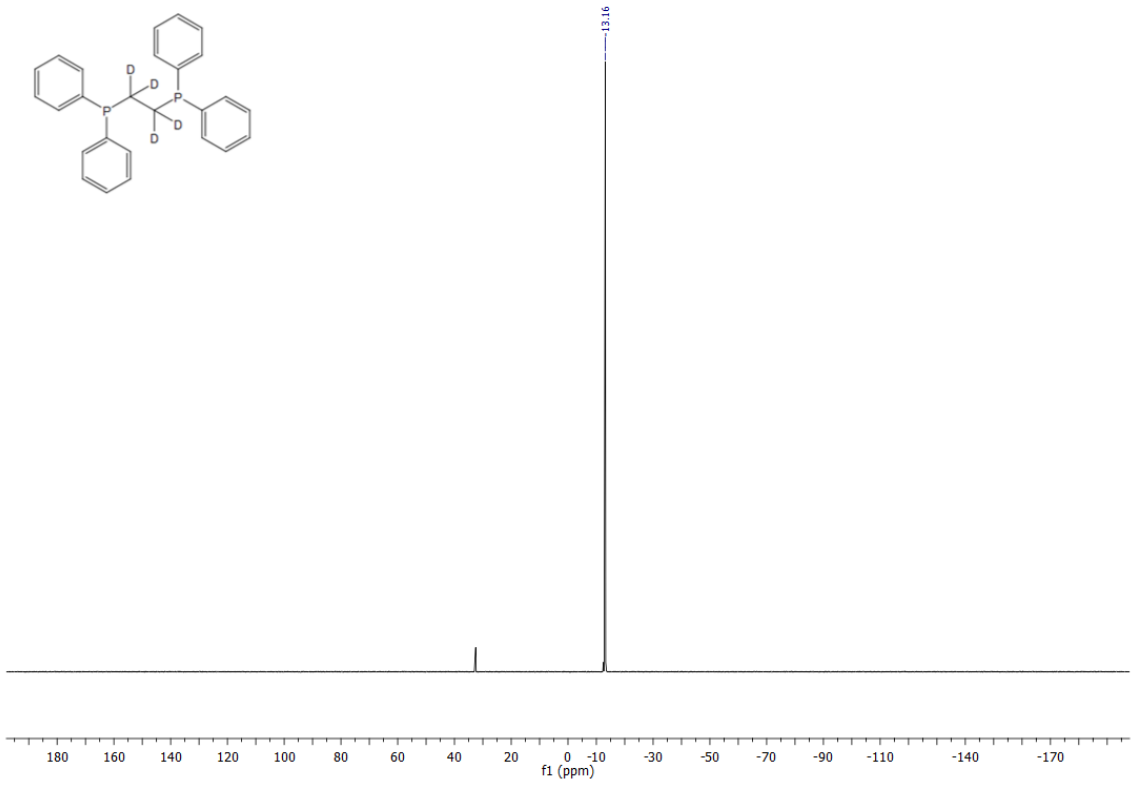


Figure S63. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of DPPE-d_4 (**3a-d_4**).

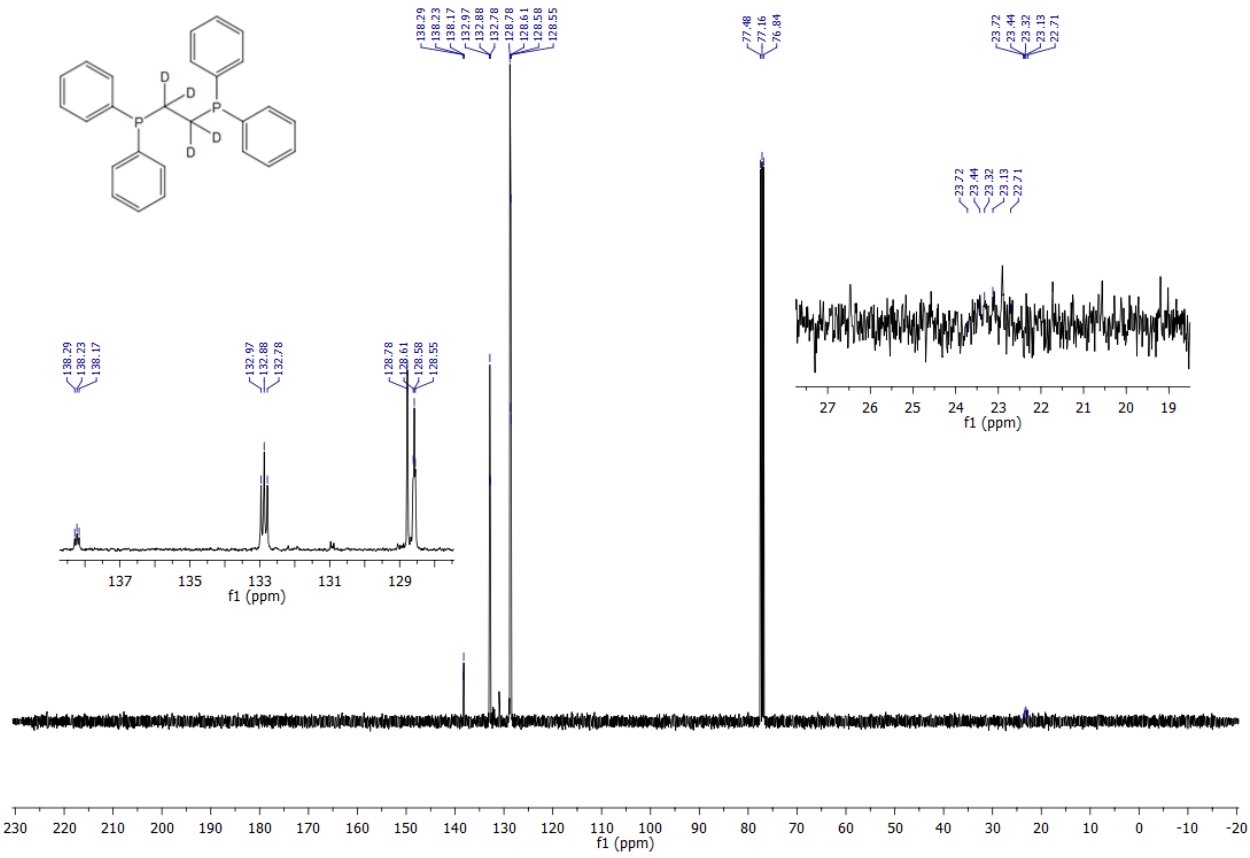


Figure S64. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of DPPE-d_4 (**3a-d_4**).

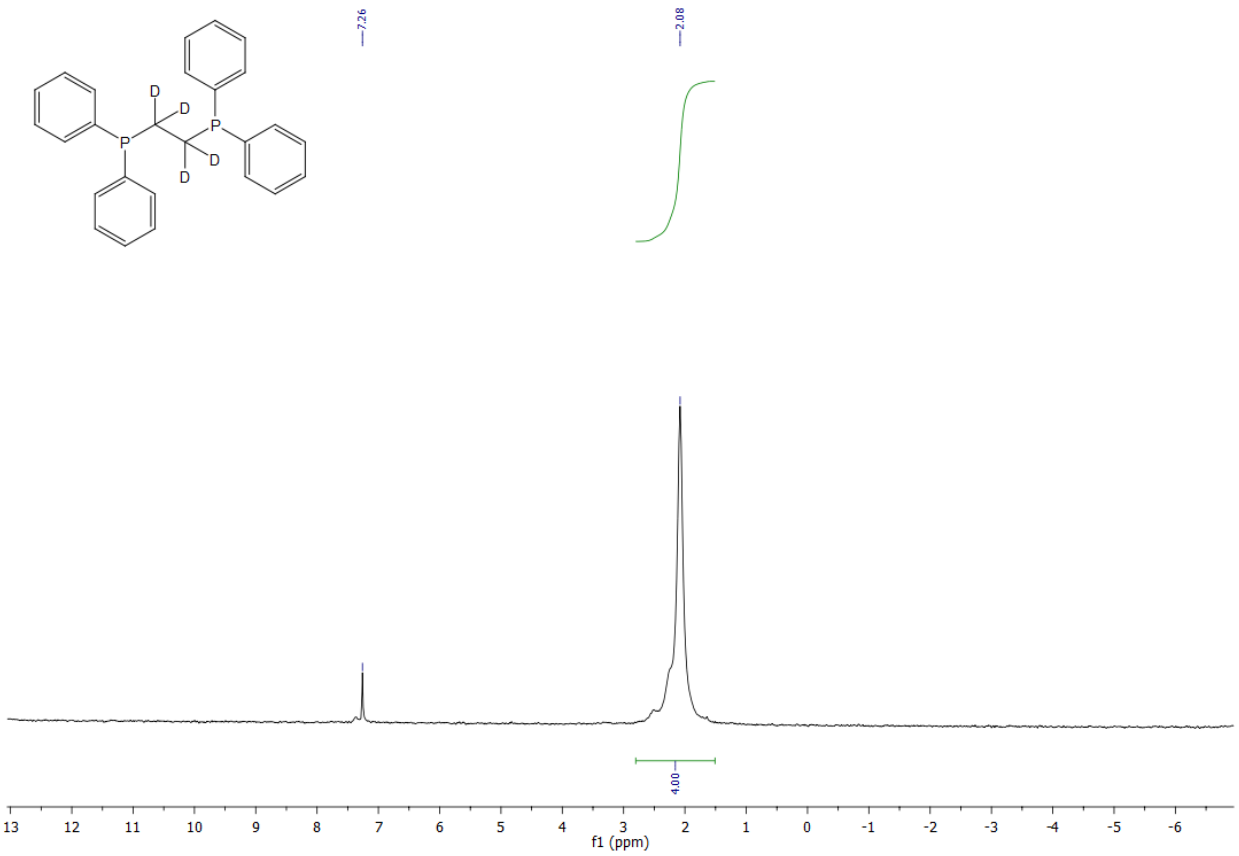


Figure S65. ^{2}H NMR (61 MHz, $CHCl_3$) spectrum of DPPE-d_4 (**3a-d$_4$**).

^{13}C-DPPE (**$^{13}C_2$-3a**)

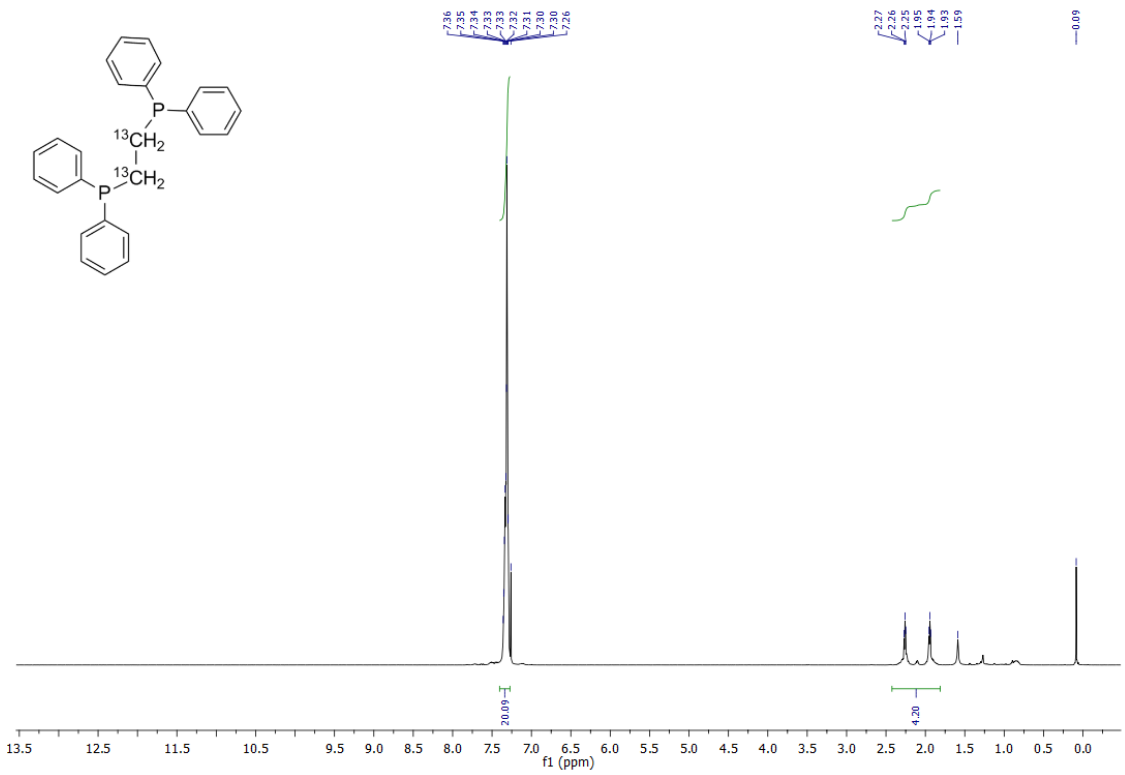


Figure S66. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of ^{13}C-DPPE (**$^{13}C_2$-3a**).

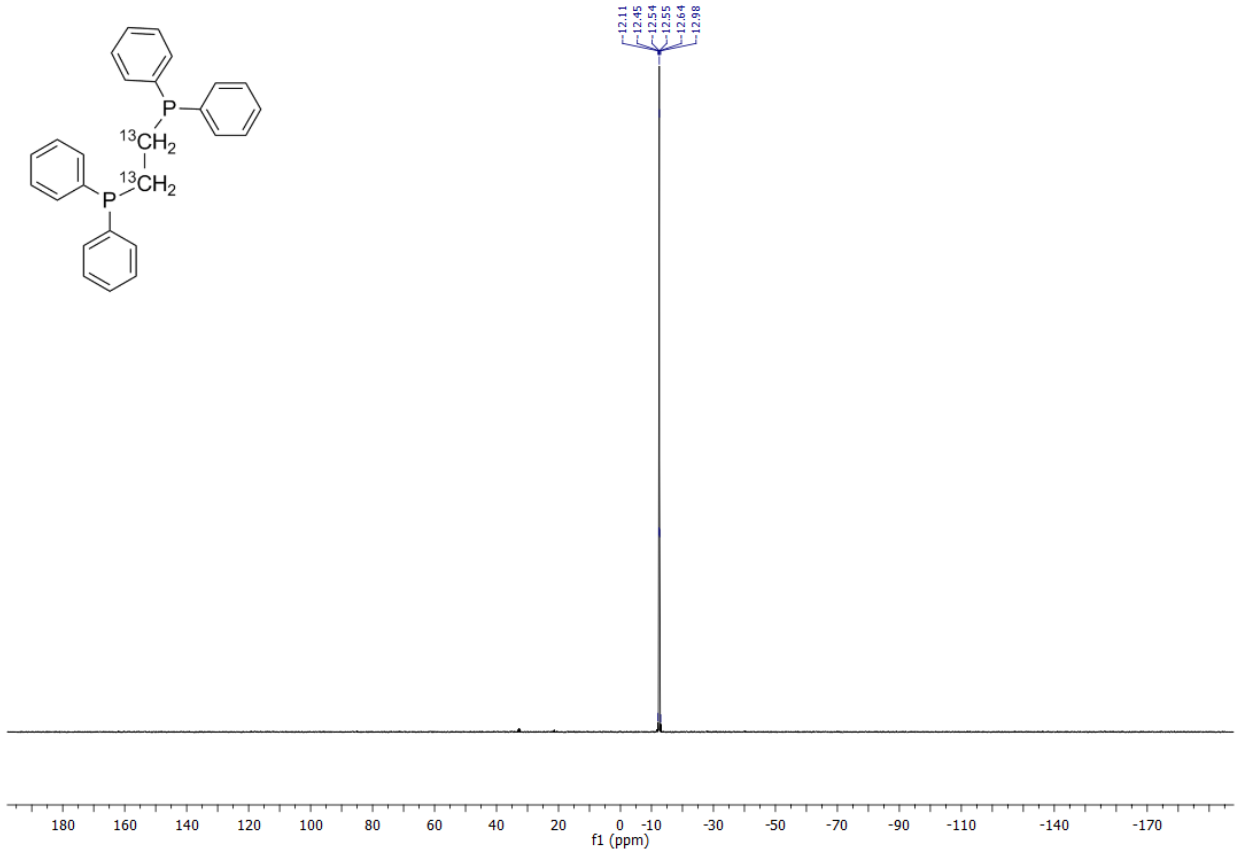


Figure S67. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of ^{13}C-DPPE (**$^{13}C_2$-3a**).

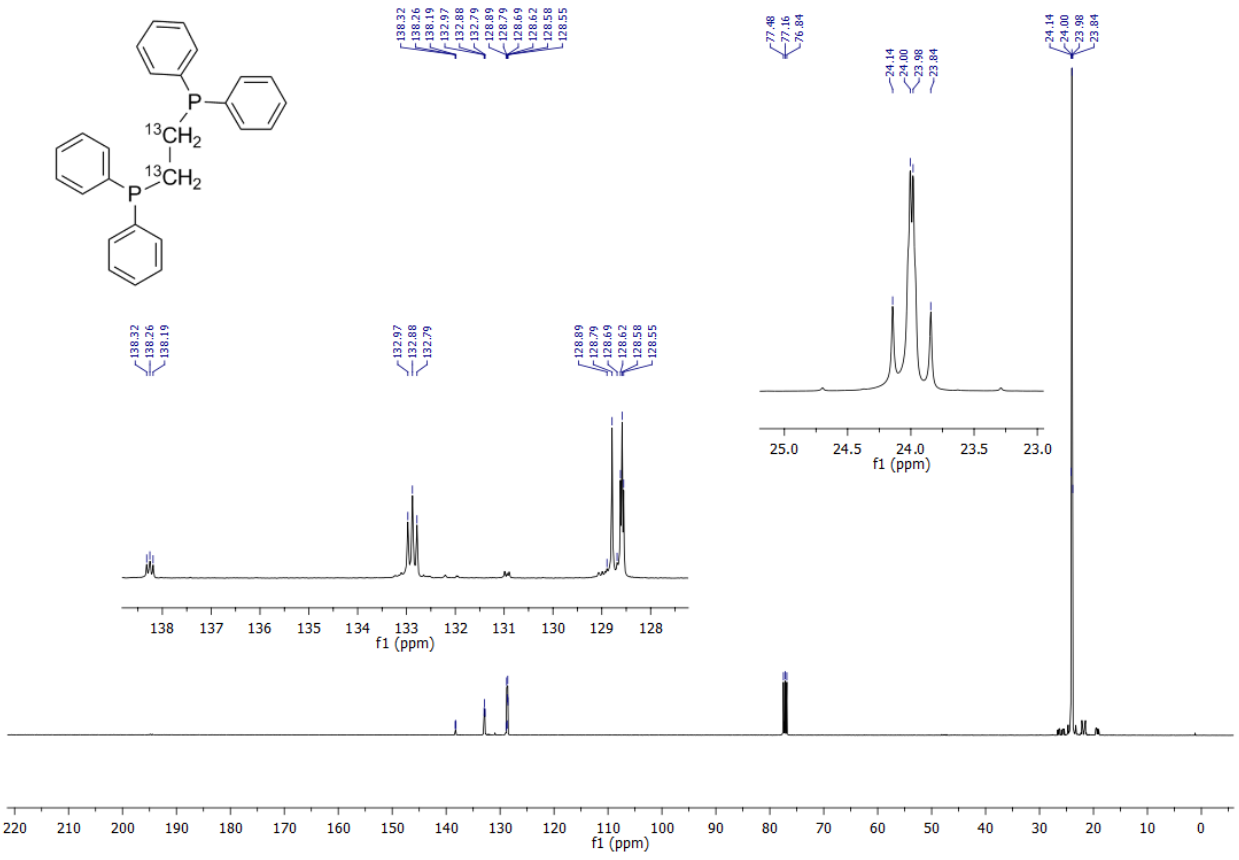


Figure S68. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of ^{13}C-DPPE (**$^{13}C_2$-3a**).

DHHE (**3b**)

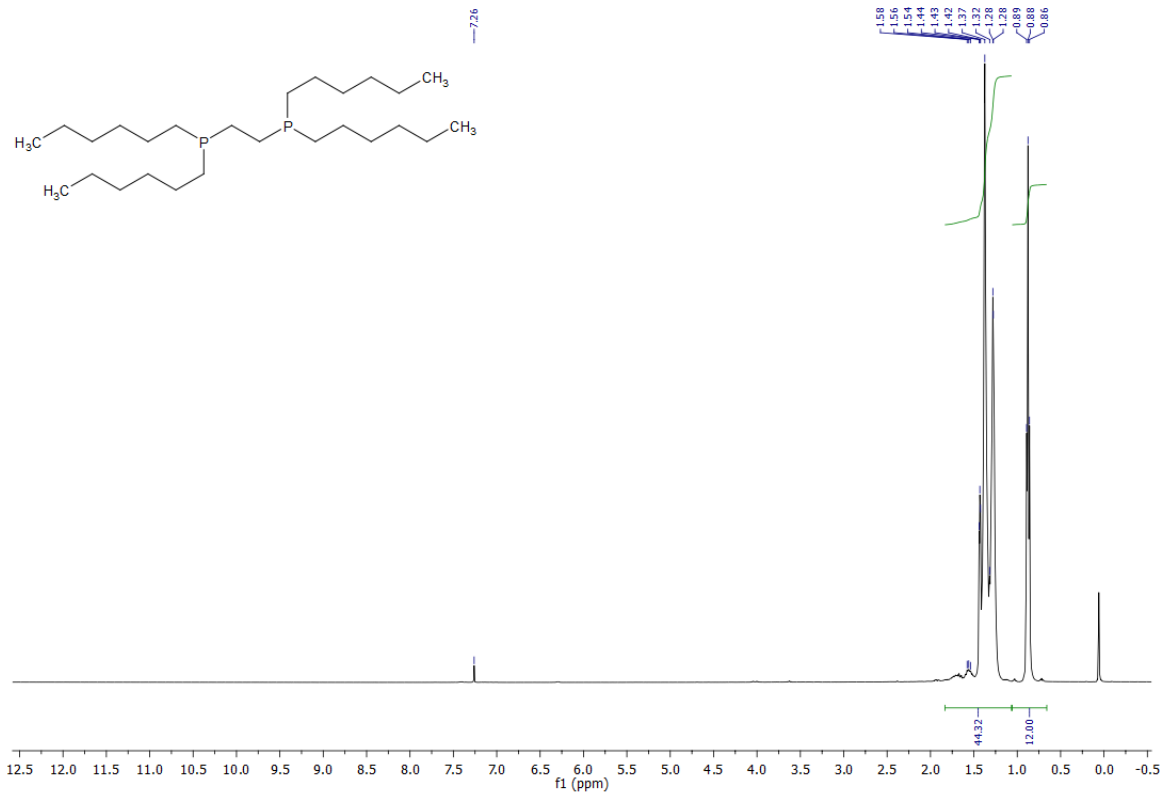


Figure S69. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of DHHE (**3b**).

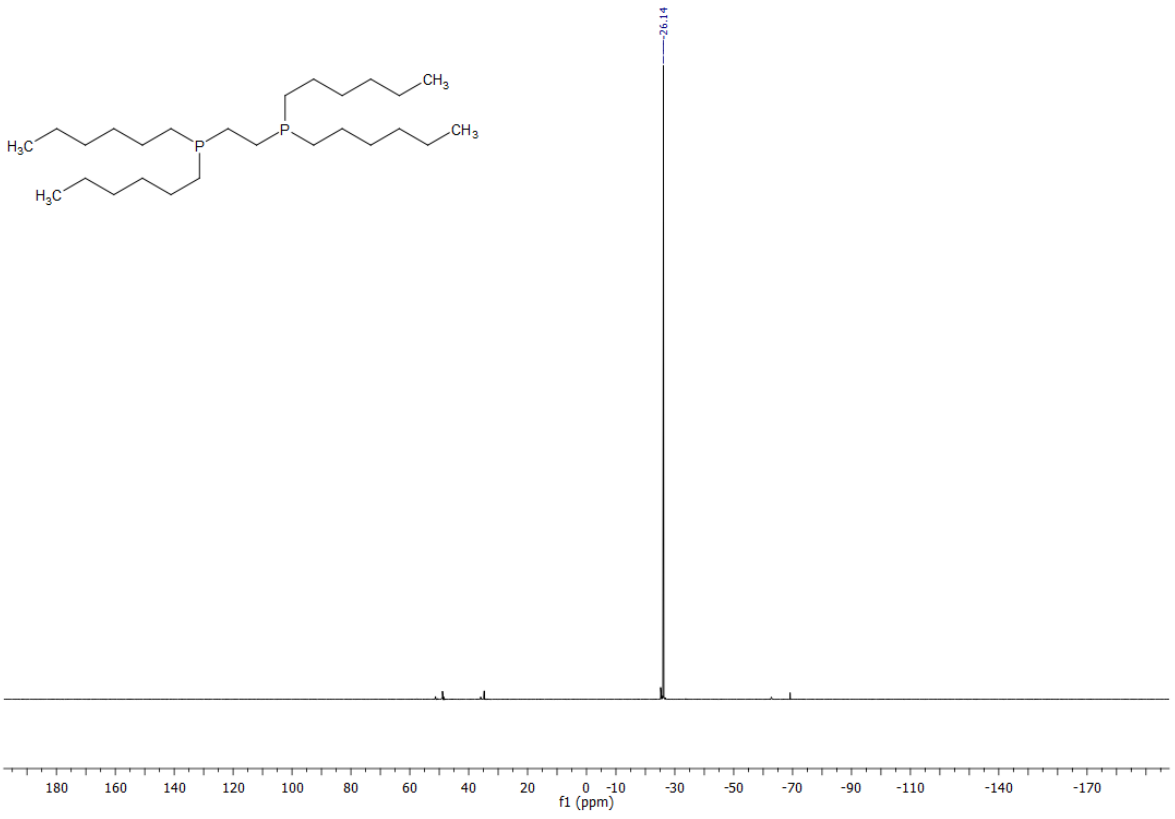


Figure S70. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of DHHE (**3b**).

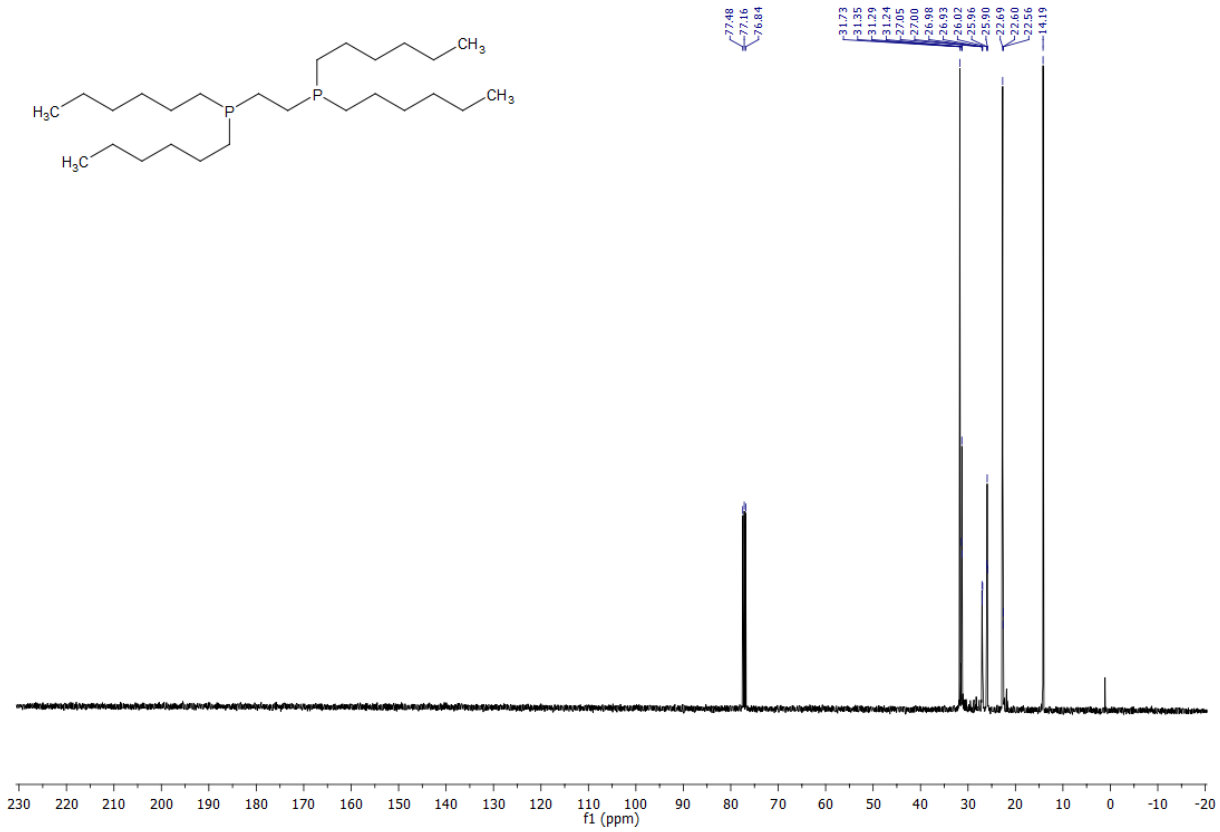


Figure S71. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of DHHE (**3b**).

DHHE-d_{12} (**3b-d_{12}**)

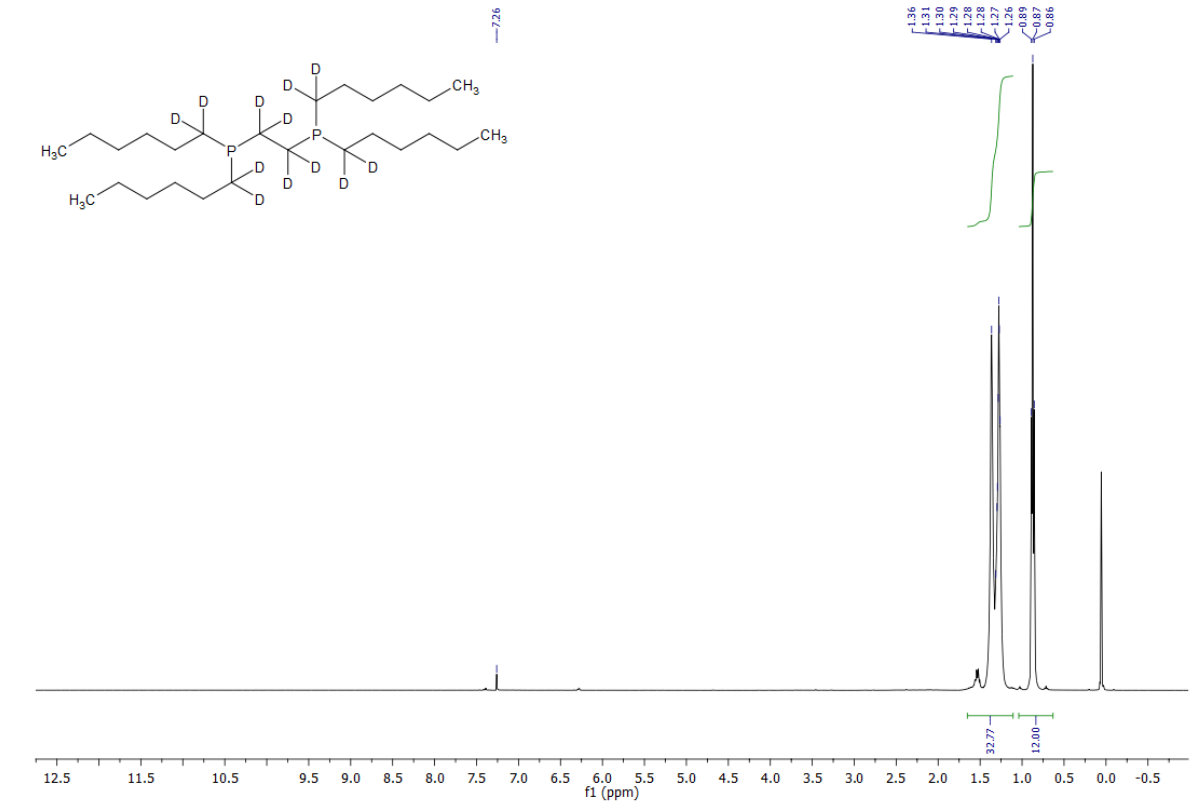


Figure S72. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of DHHE-d_{12} (**3b-d_4**).

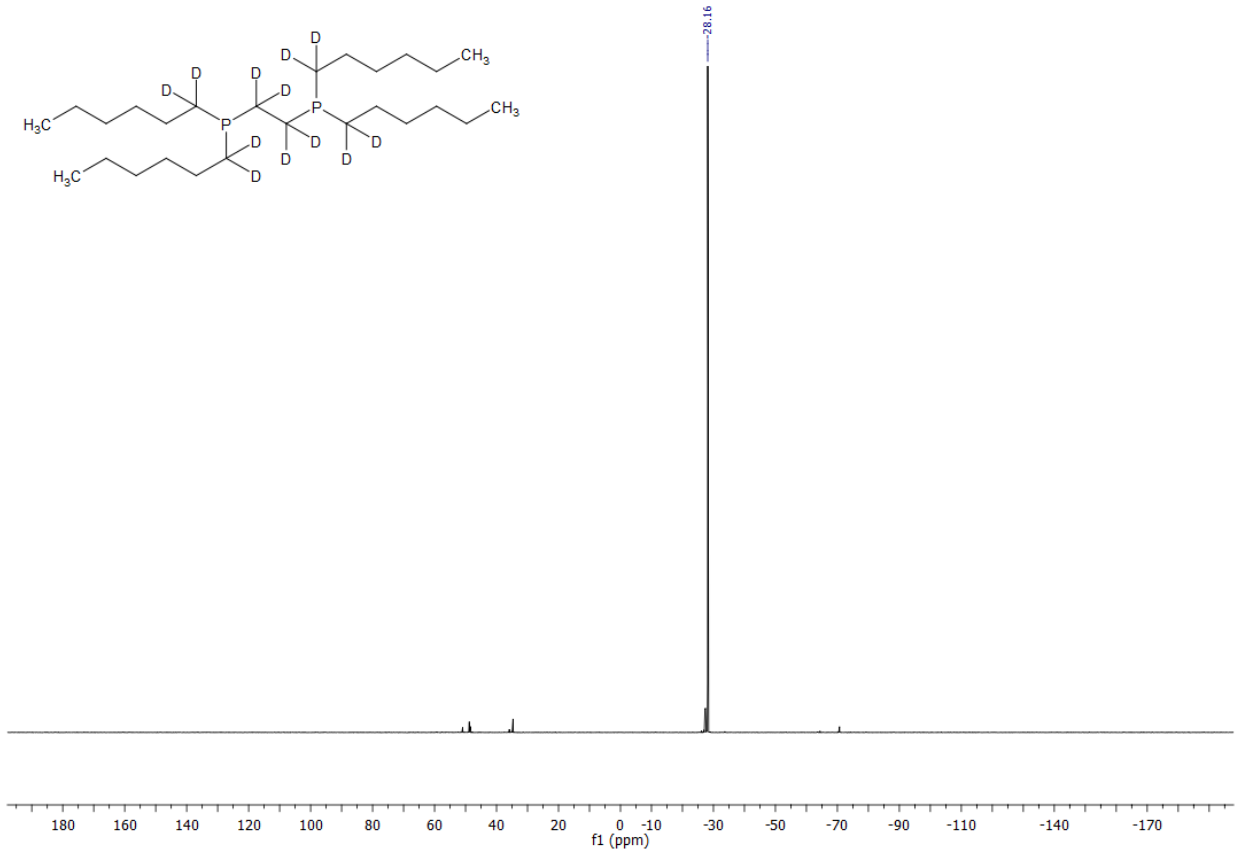


Figure S73. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of DHHE-d_{12} (**3b-d$_{12}$**).

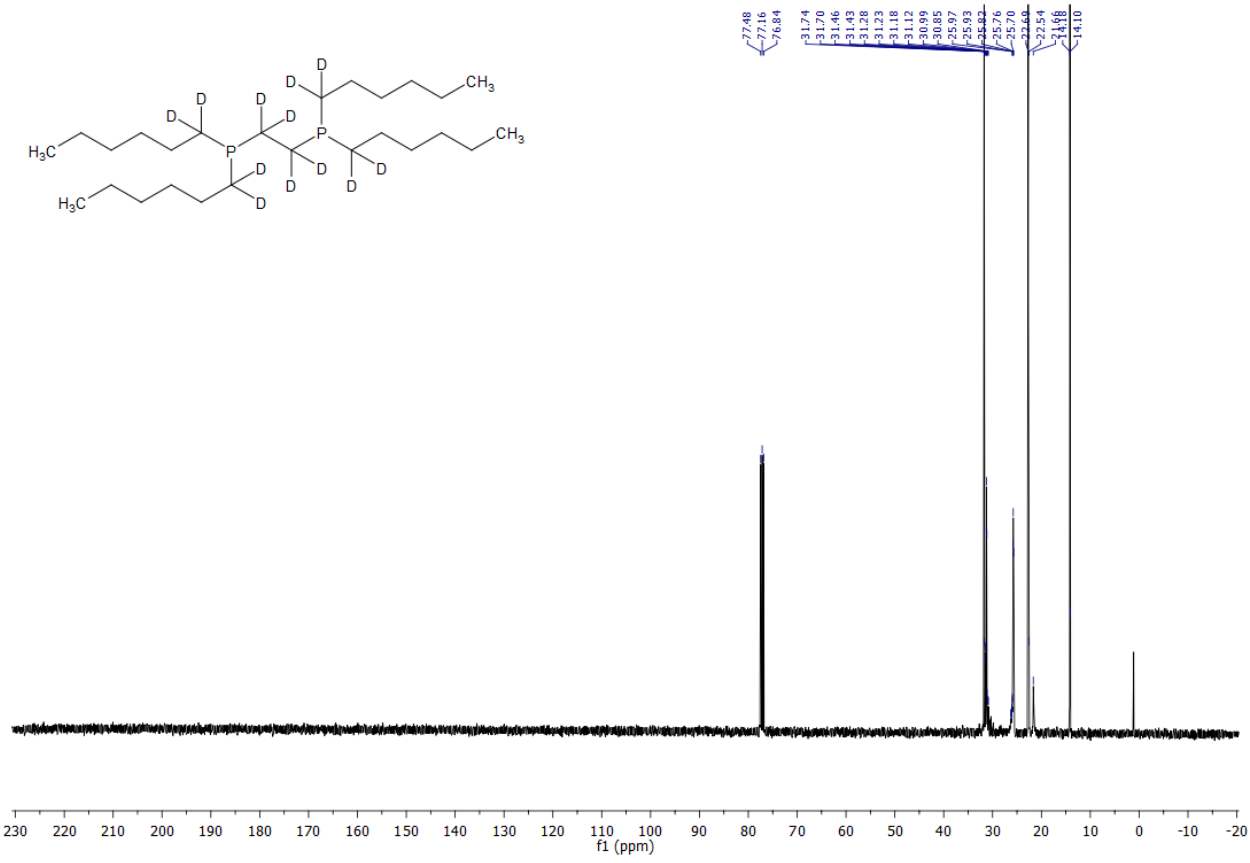


Figure S74. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of DHHE-d_{12} (**3b-d$_{12}$**).

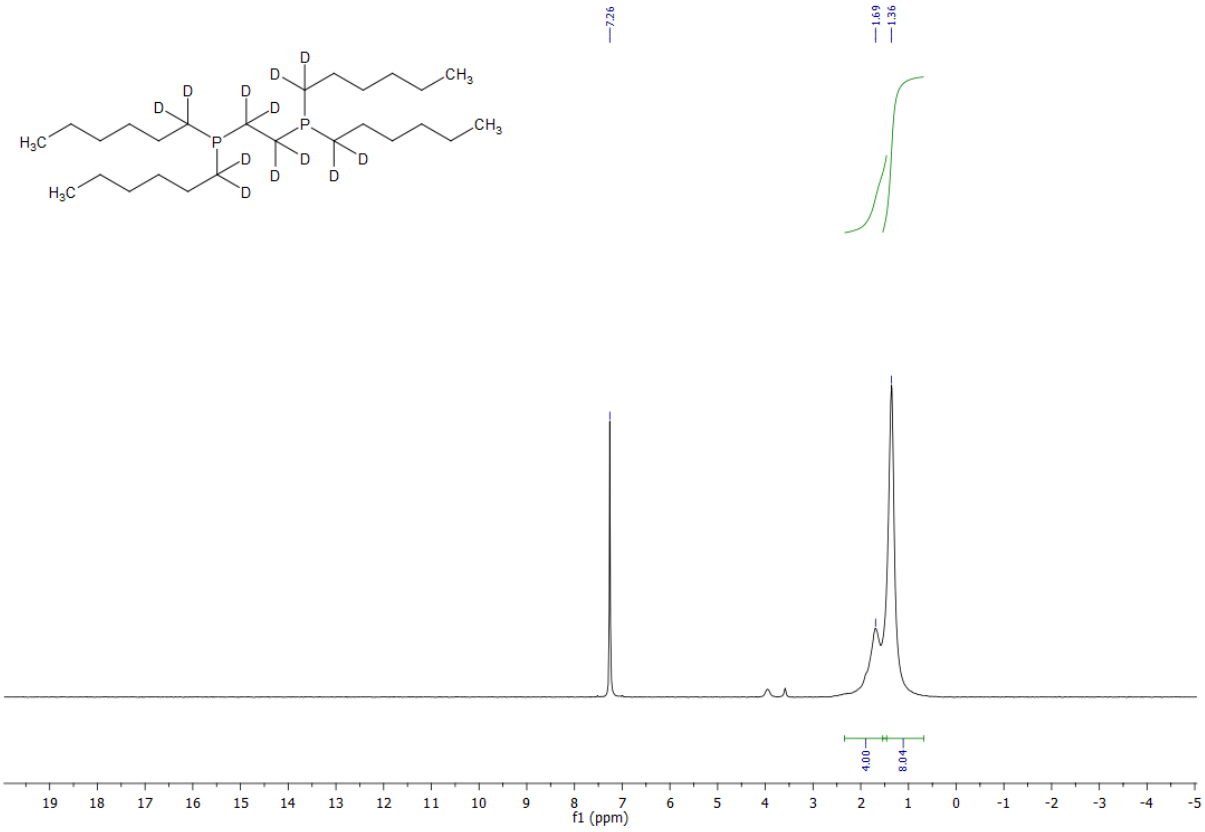


Figure S75. ^{2}H NMR (61 MHz, $CHCl_3$) spectrum of DHHE-d_{12} (**3b-d$_{12}$**).

D(*o*-Tol)$_2$E (**3e**)

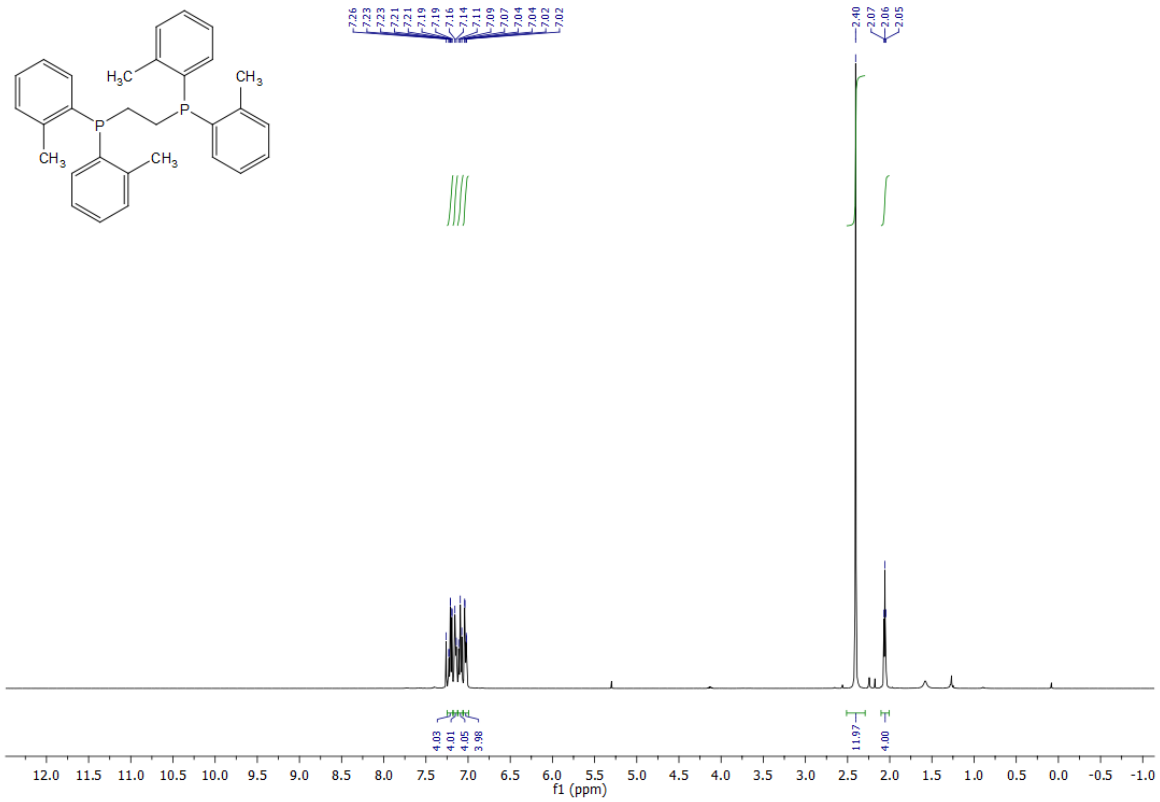


Figure S76. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of D(*o*-Tol)$_2$E (**3e**).

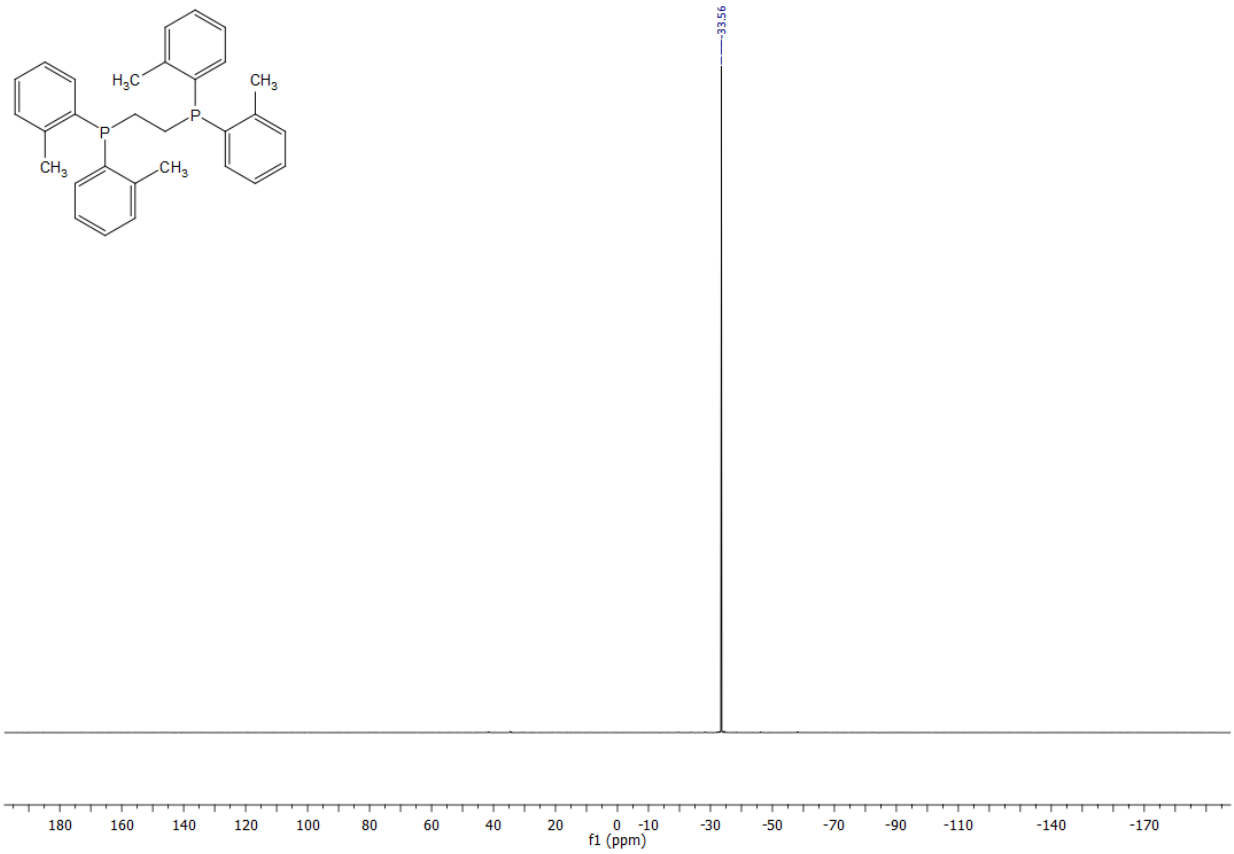


Figure S77. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of D(*o*-Tol)$_2$E (**3e**).

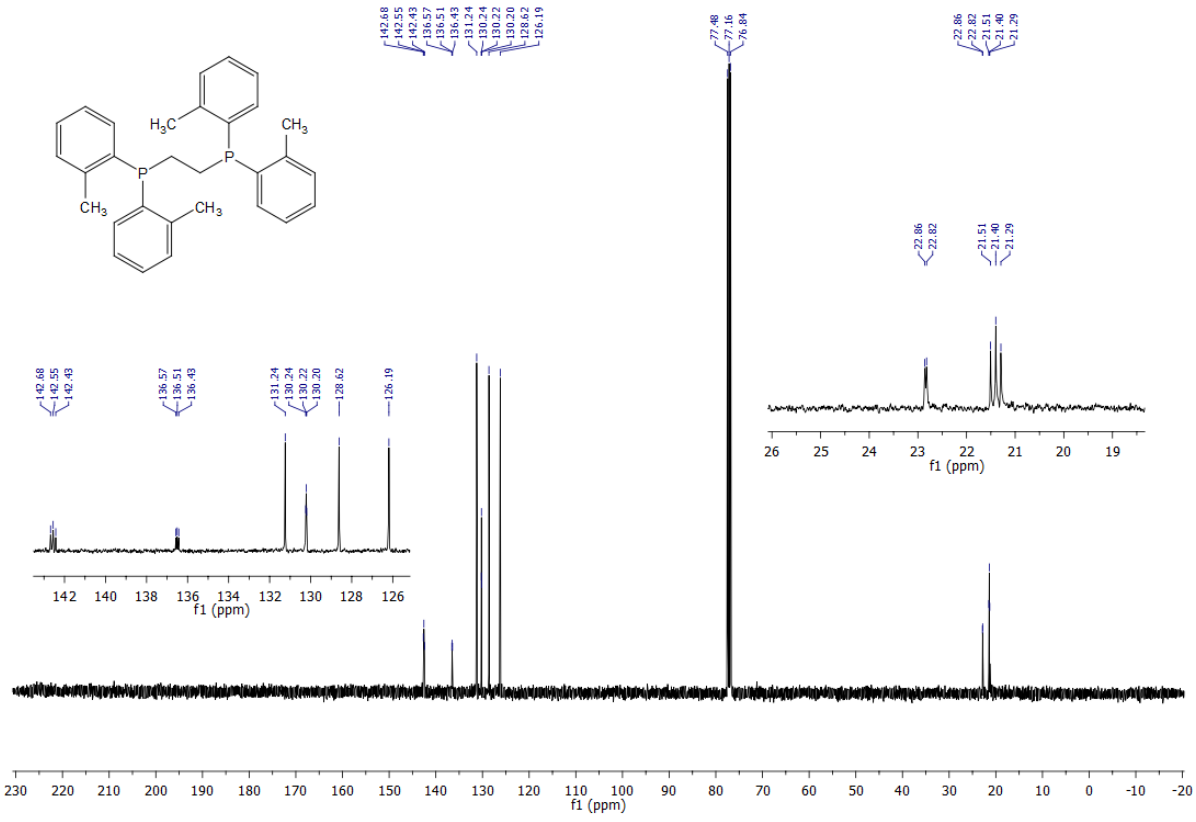


Figure S78. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of D(*o*-Tol)$_2$E (**3e**).

D(*o*-Tol)$_2$E-d$_4$ (**3e-d$_4$**)

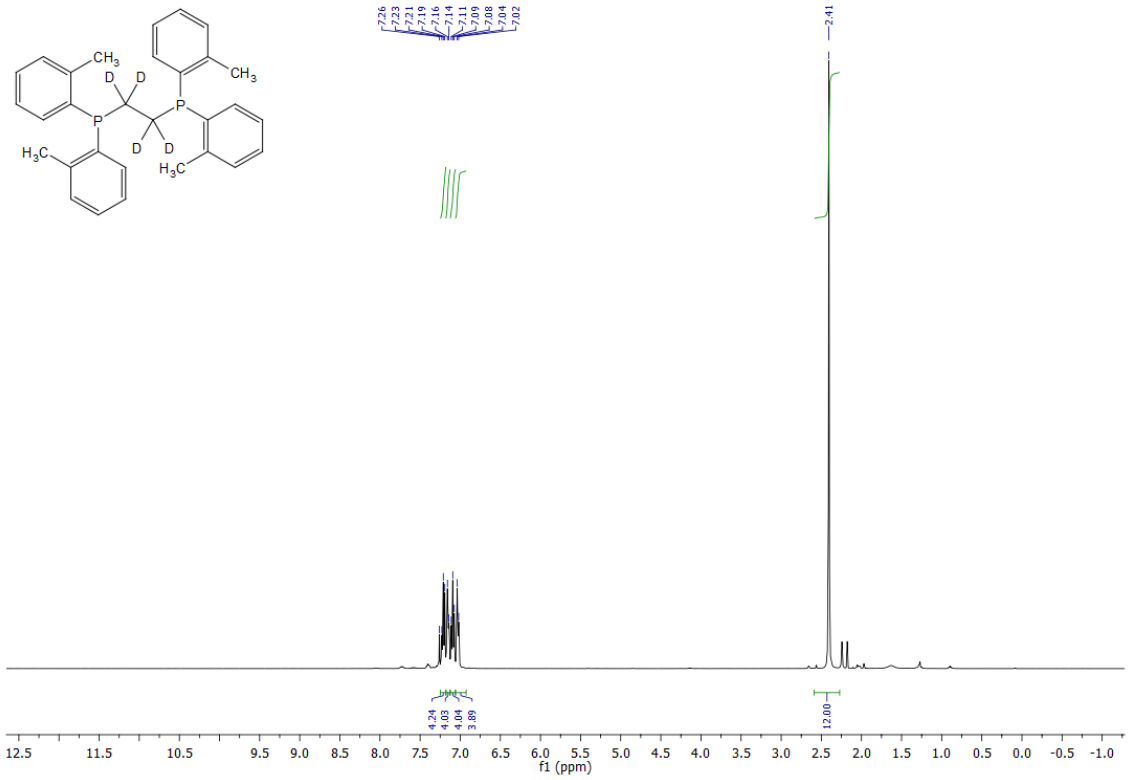


Figure S79. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of D(*o*-Tol)$_2$E-d$_4$ (**3e-d$_4$**).

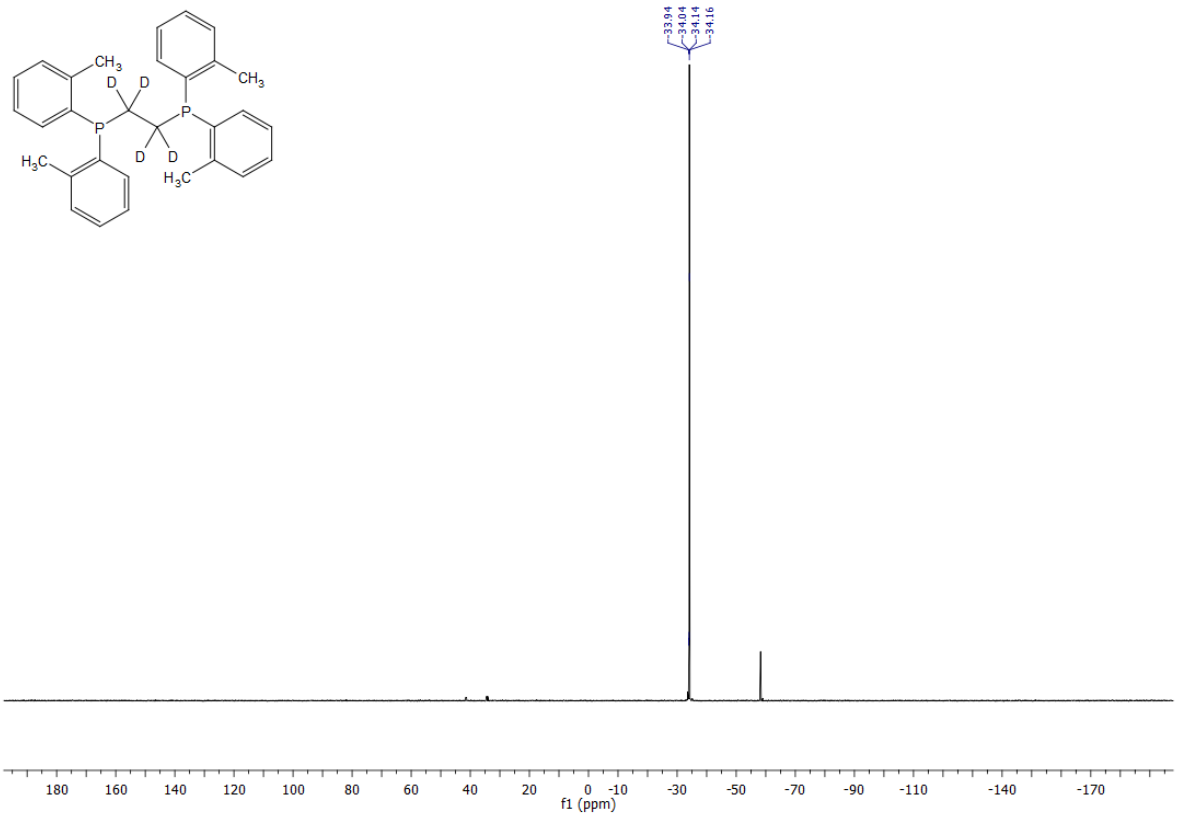


Figure S80. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of D(*o*-Tol)$_2$E-d$_4$ (**3e-d$_4$**).

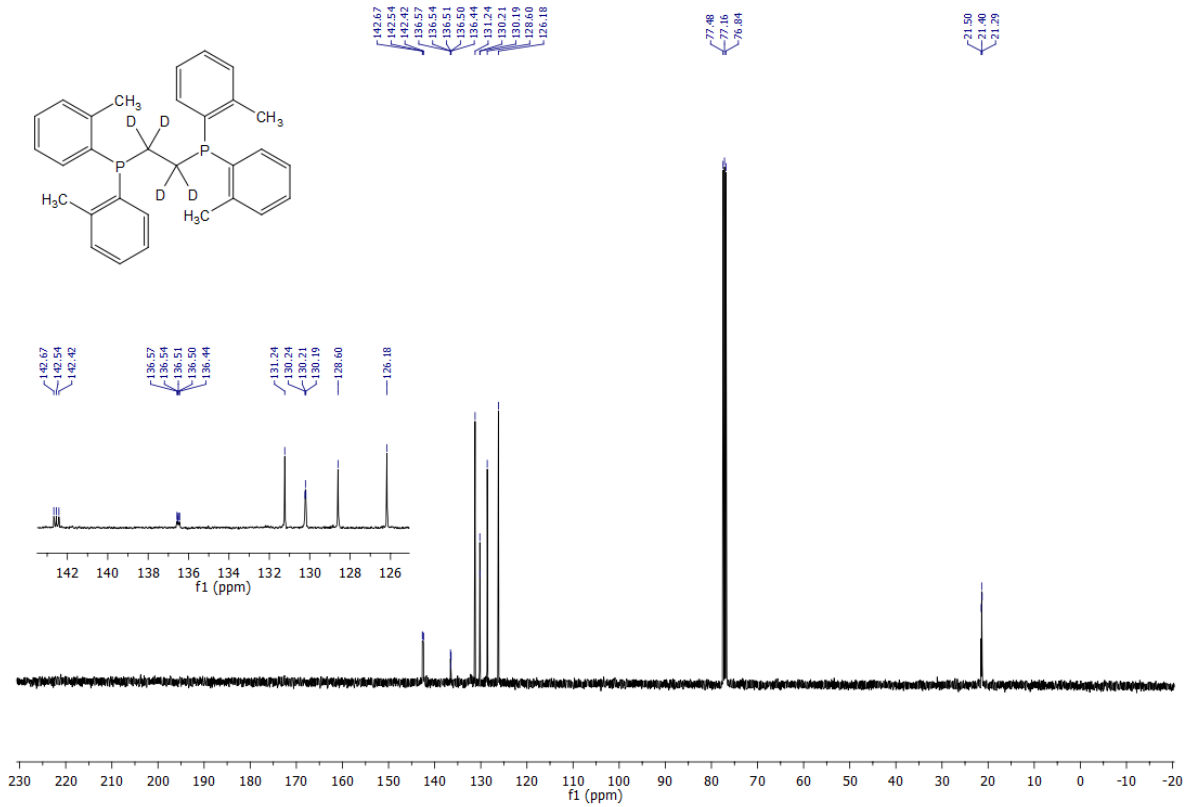


Figure S81. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of D(*o*-Tol)$_2$E-d$_4$ (**3e-d$_4$**).

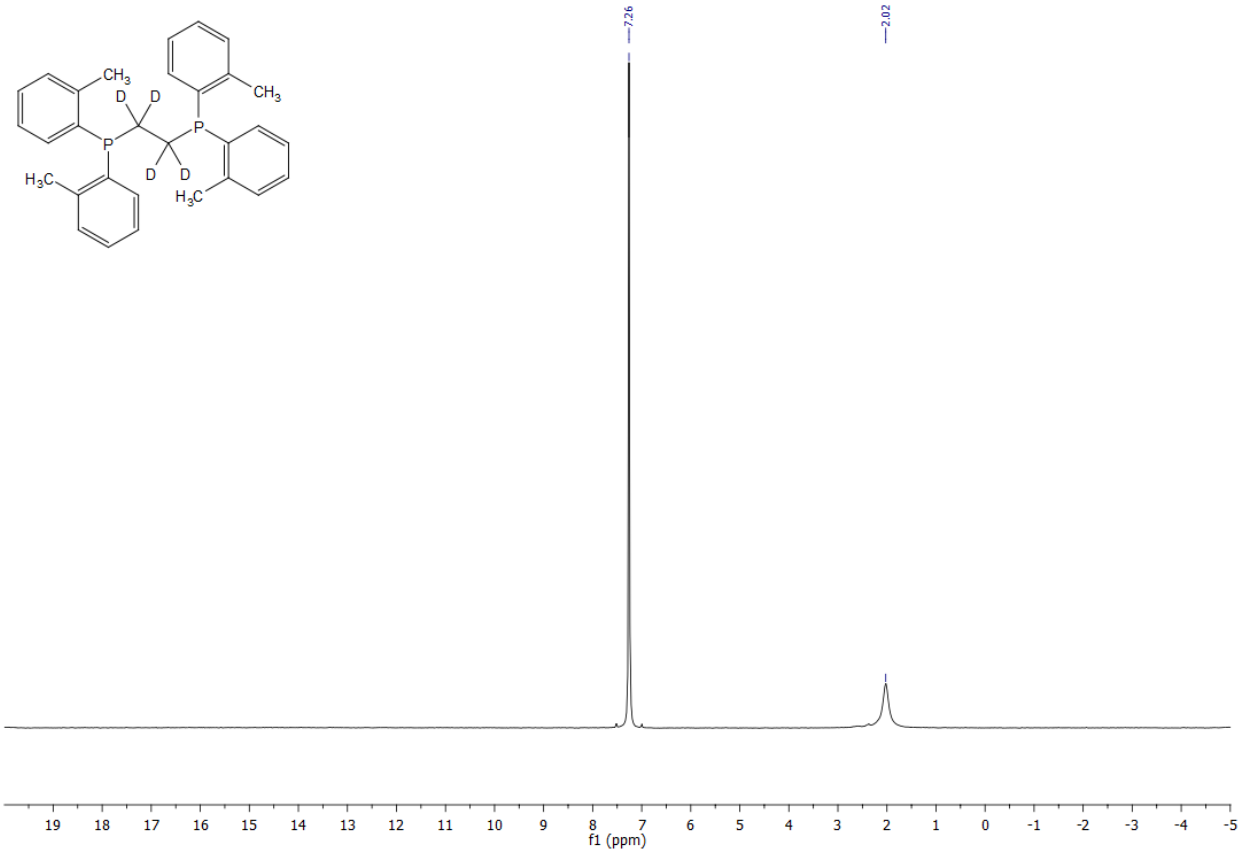


Figure S82. ^{2}H NMR (61 MHz, $CHCl_3$) spectrum of D(*o*-Tol)$_2$E-d$_4$ (**3e-d$_4$**).

D(*o*-Tol)$_2$E-d$_{16}$ (**3e-d$_{16}$**)

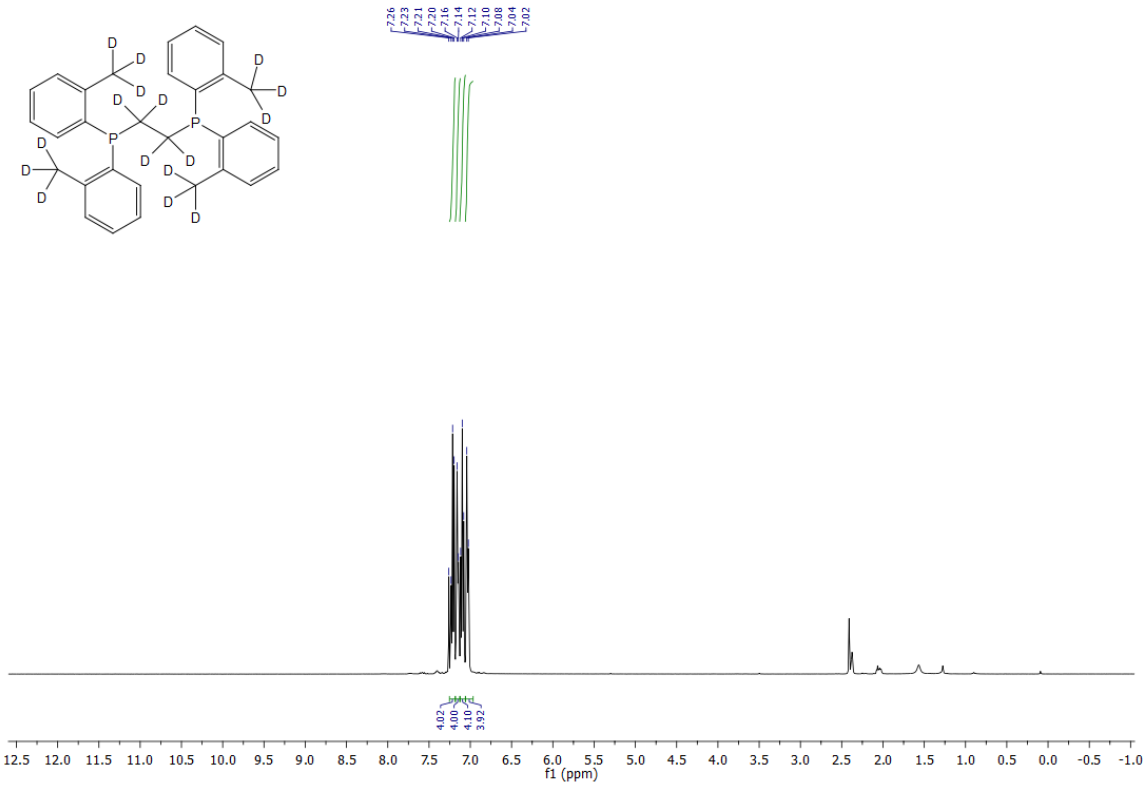


Figure S83. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of D(*o*-Tol)$_2$E-d$_{16}$ (**3e-d$_{16}$**).

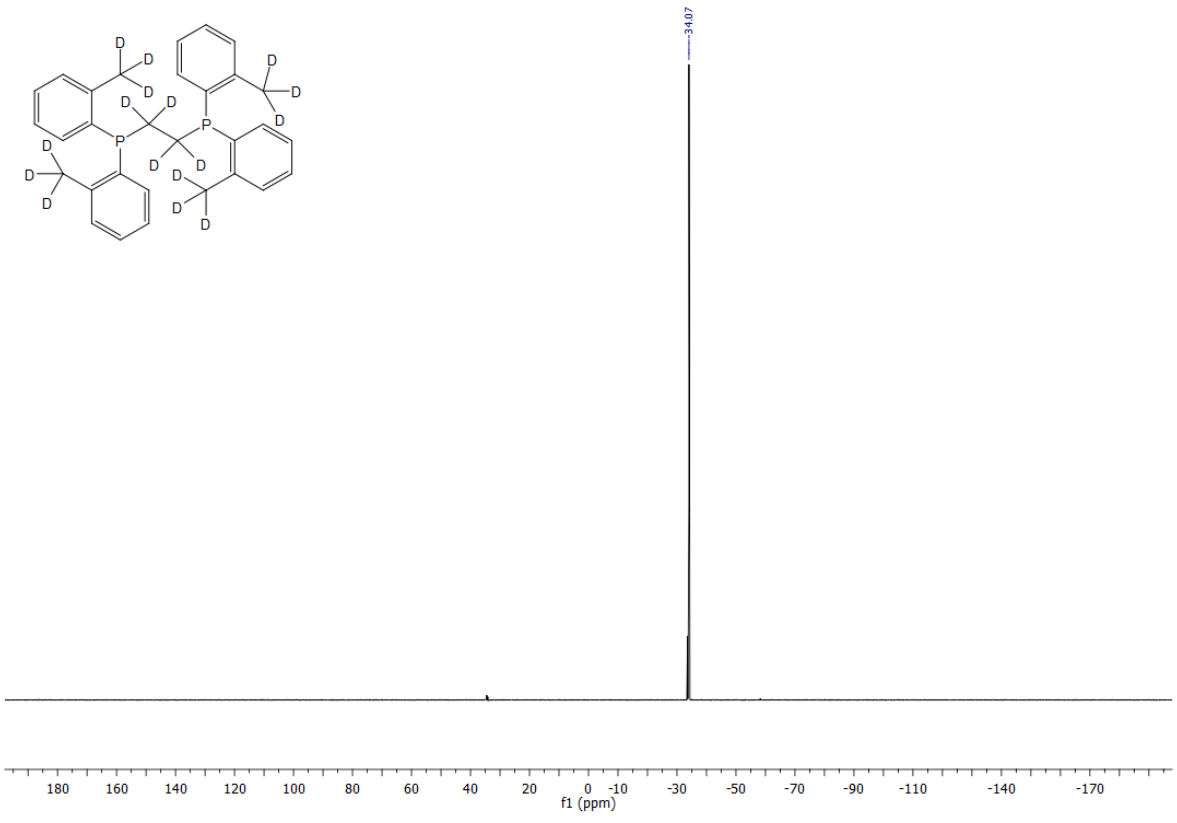


Figure S84. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of D(*o*-Tol)$_2$E-d$_{16}$ (**3e-d$_{16}$**).

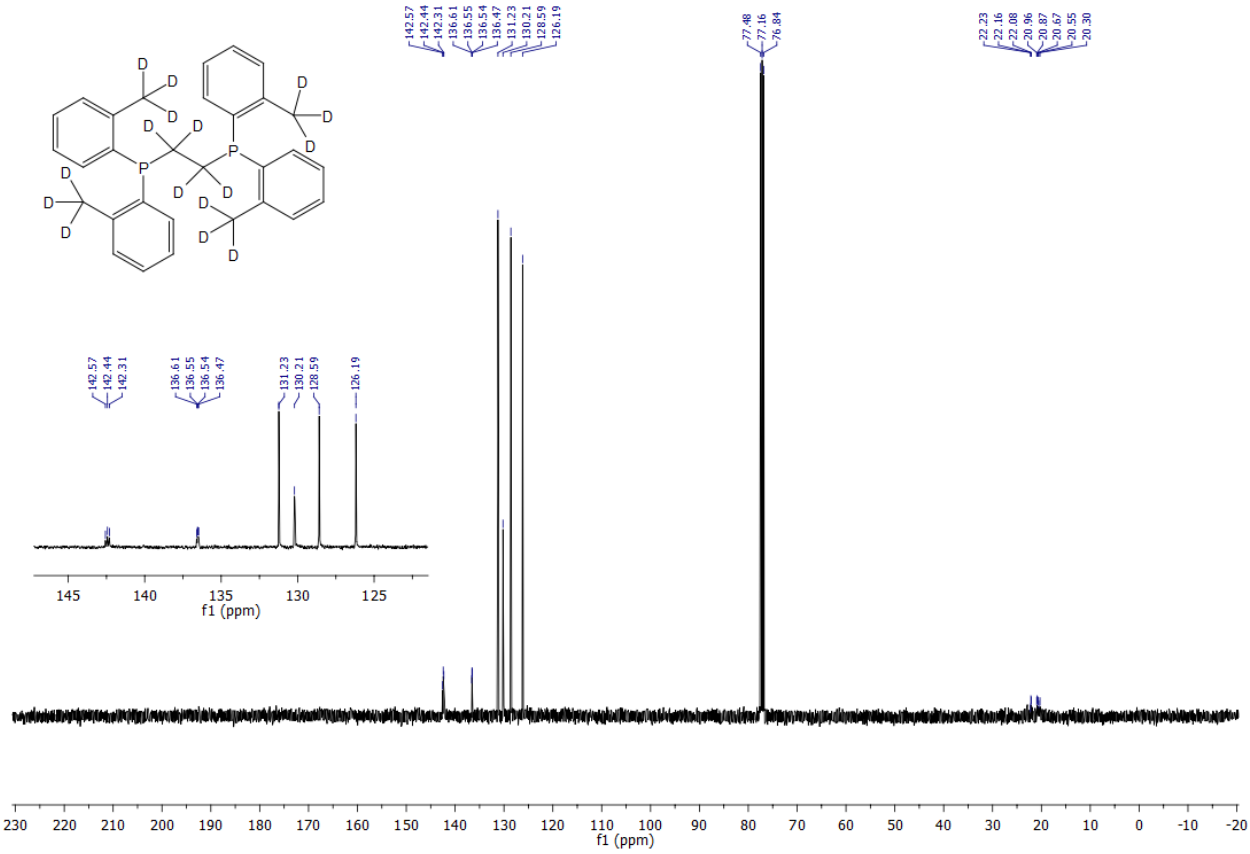


Figure S85. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of D(*o*-Tol)$_2$E-d$_{16}$ (**3e-d$_{16}$**).

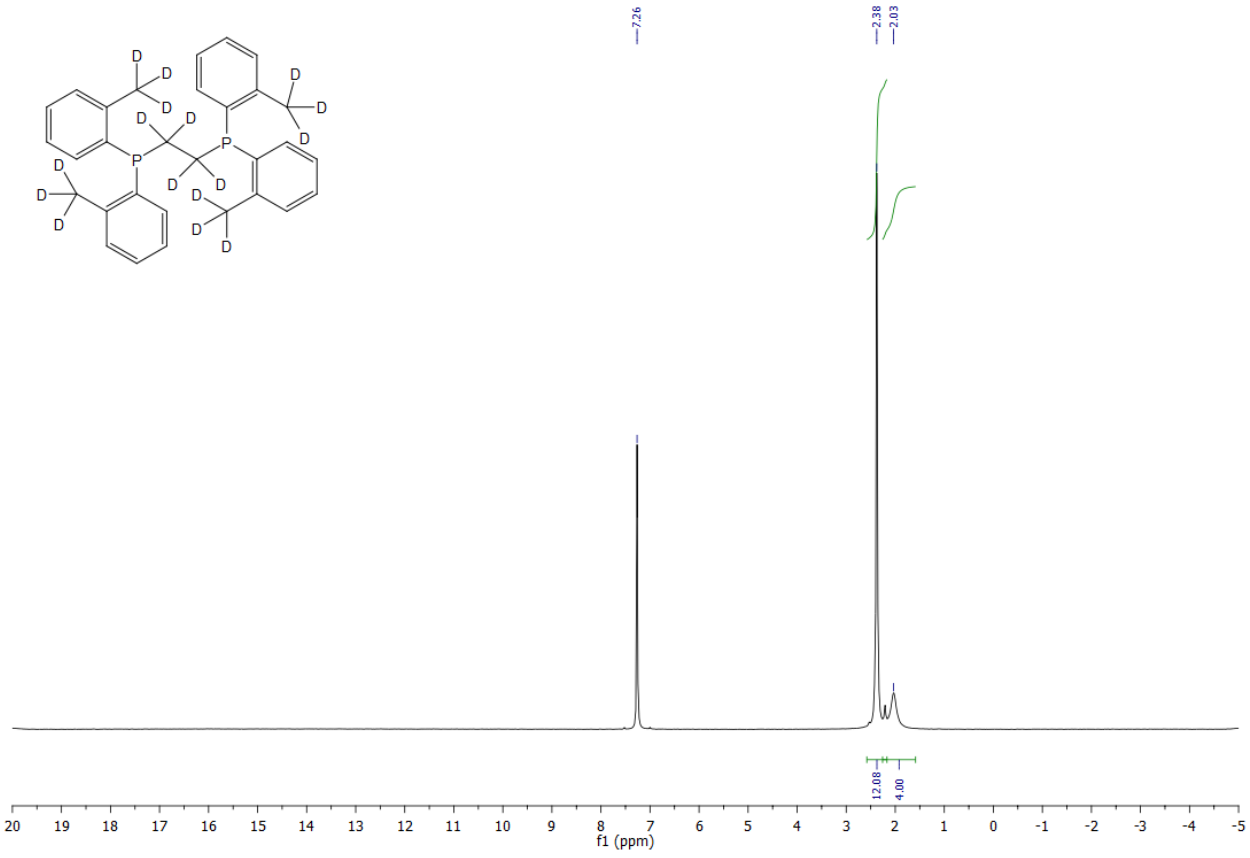


Figure S86. ^{2}H NMR (61 MHz, $CHCl_3$) spectrum of D(*o*-Tol)$_2$E-d$_{16}$ (**3e-d$_{16}$**).

Ni(DPPE)Br_2 (**$NiBr_2$(3a)**)

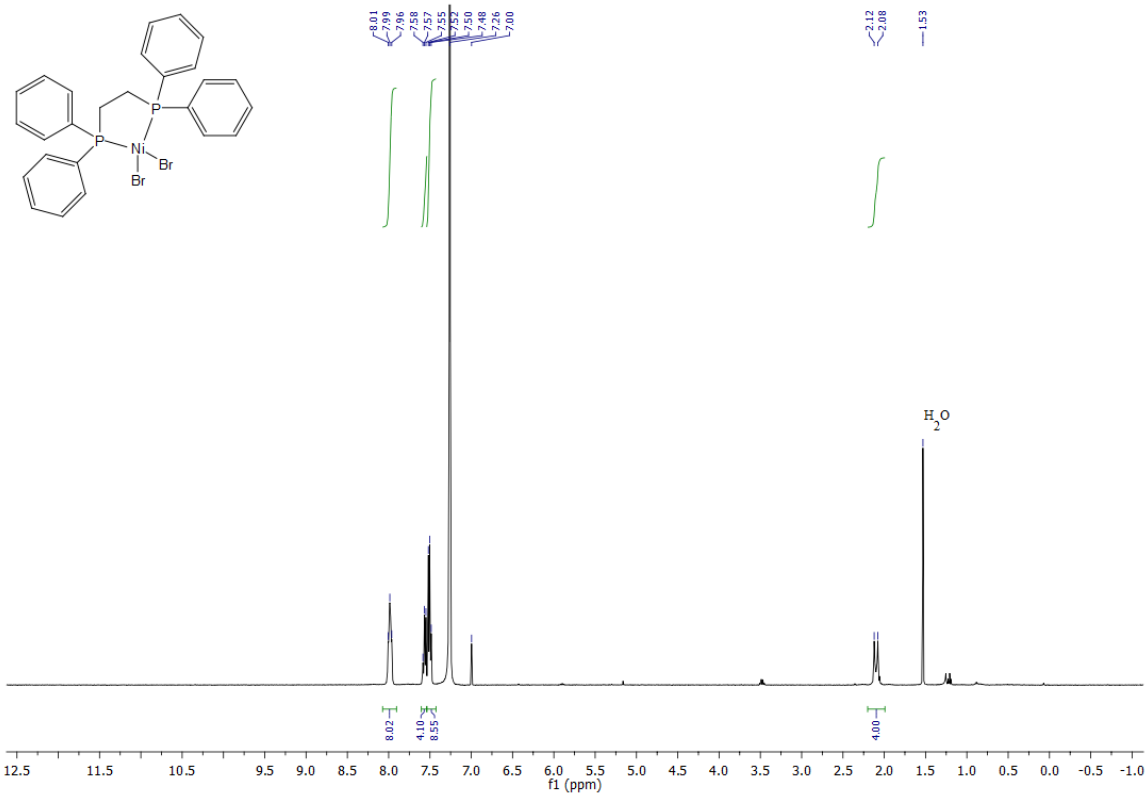


Figure S87. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of Ni(DPPE)Br_2 (**$NiBr_2$(3a)**).

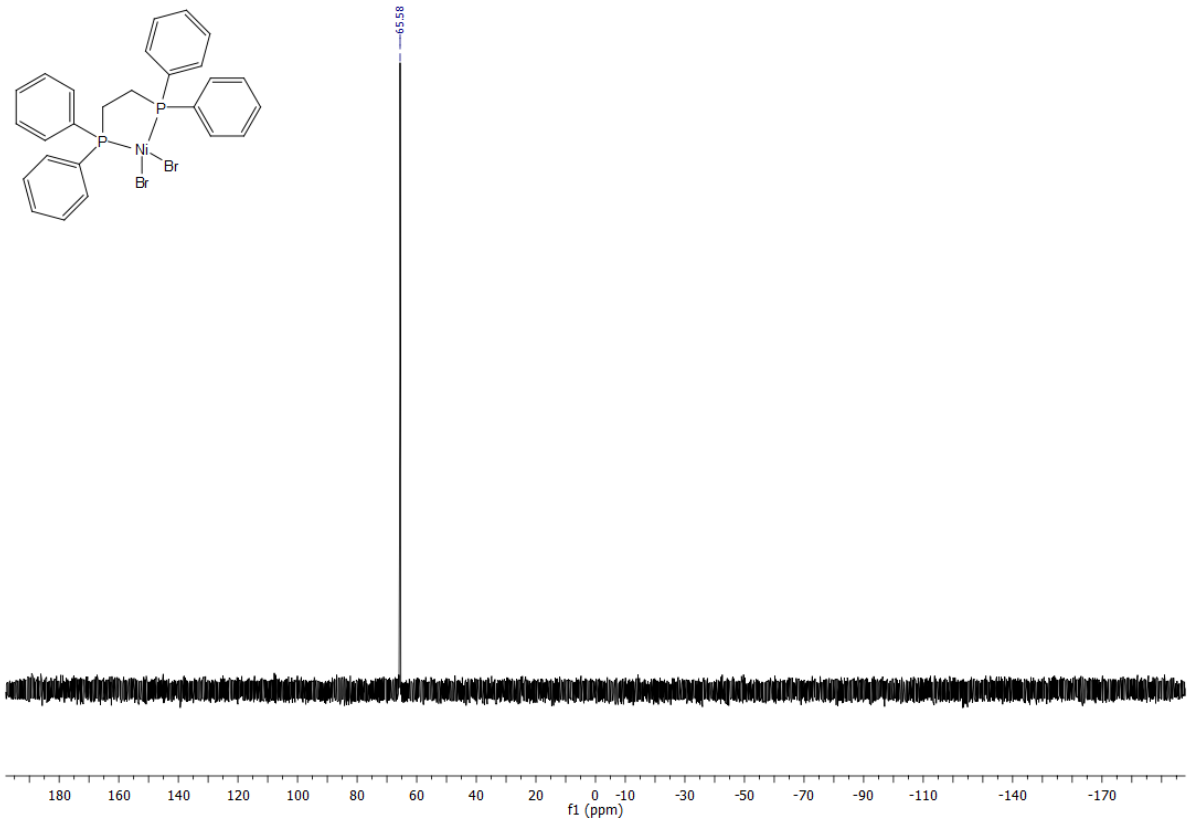


Figure S88. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of Ni(DPPE)Br_2 (**$NiBr_2$(3a)**).

Ni(DPPE-d_4)Br_2 (**$NiBr_2$(3a-d_4)**)

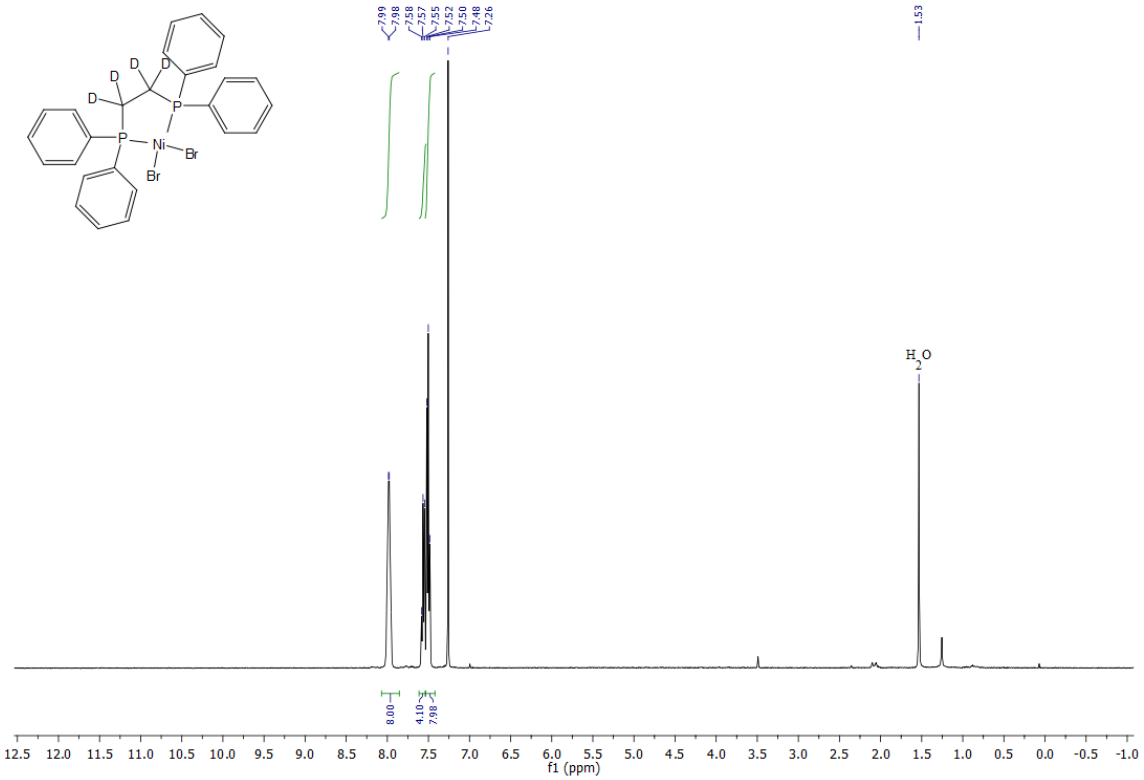


Figure S89. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of Ni(DPPE-d_4)Br_2 (**$NiBr_2$(3a-d_4)**).

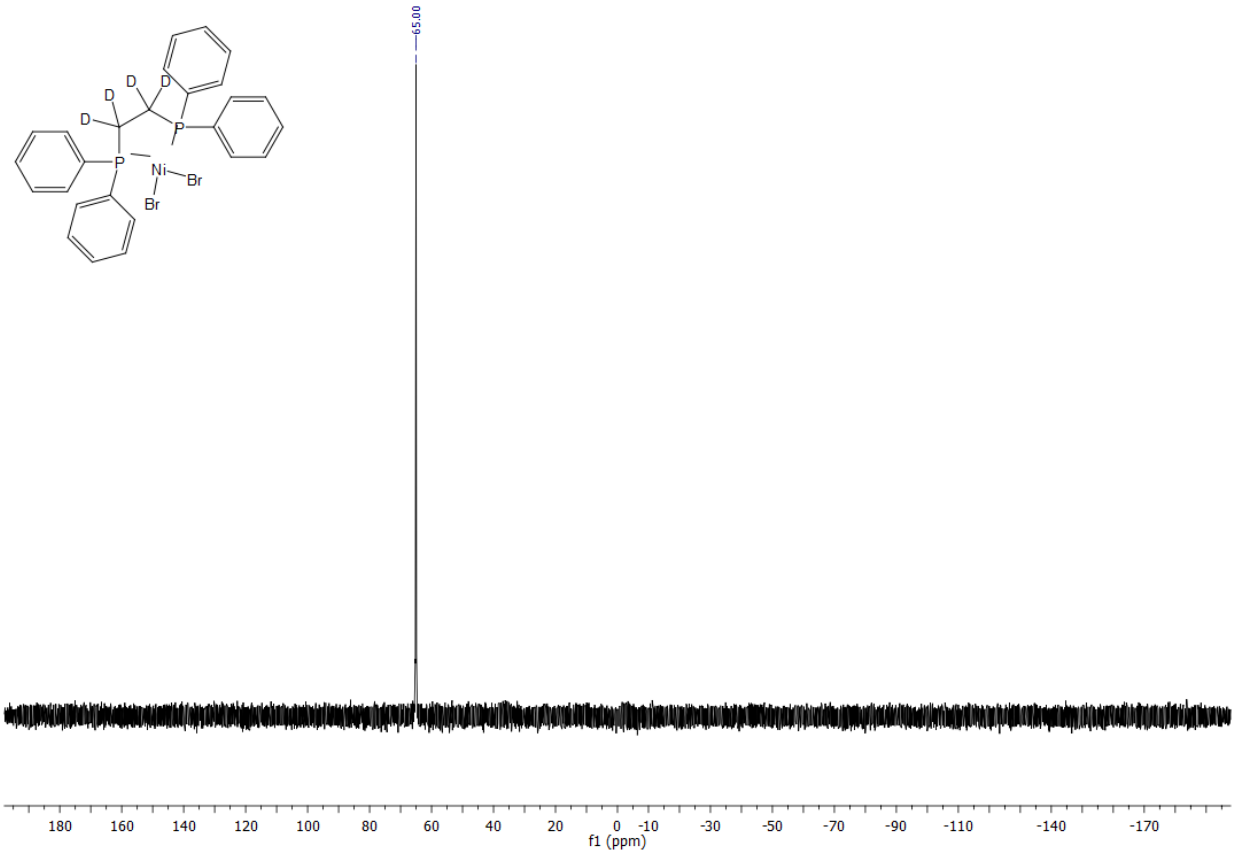


Figure S90. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of Ni(DPPE-d_4)Br_2 (**$NiBr_2$(3a-d_4)**).

Pd(DPPE)Cl_2 (**$PdCl_2$(3a)**)

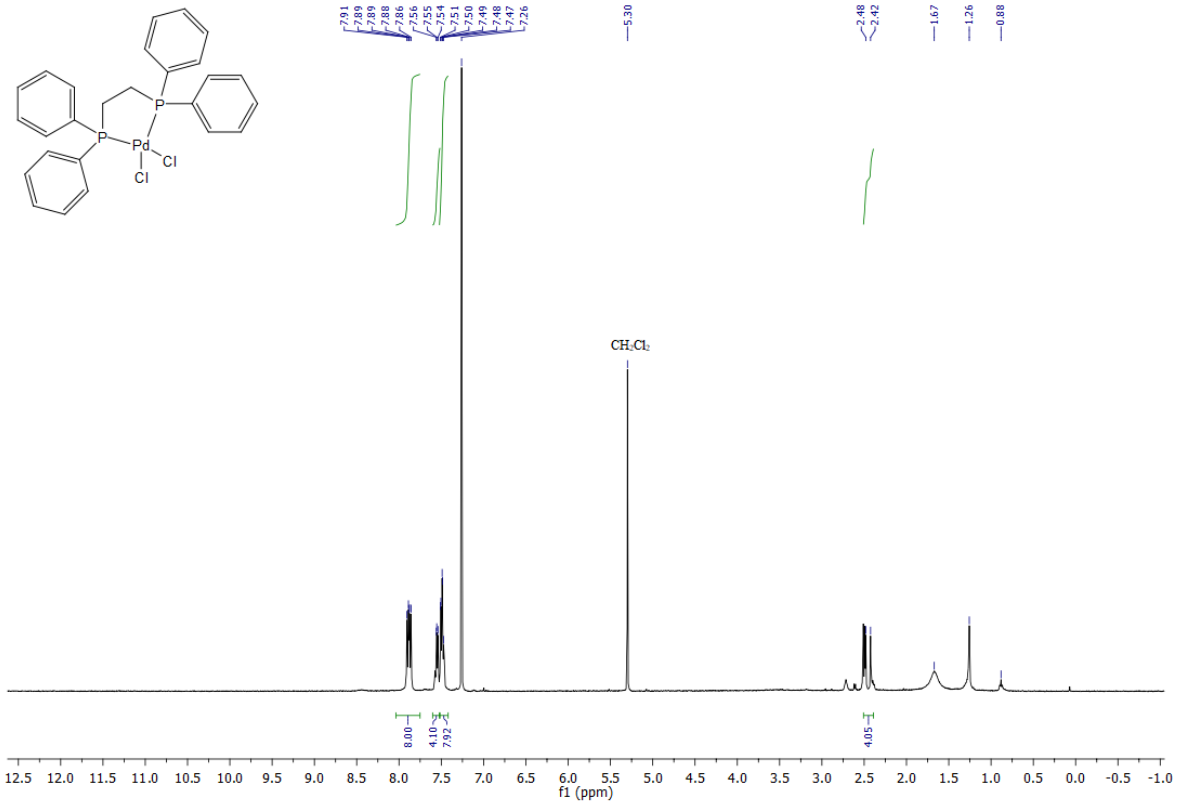


Figure S91. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of Pd(DPPE)Cl_2 (**$PdCl_2$(3a)**).

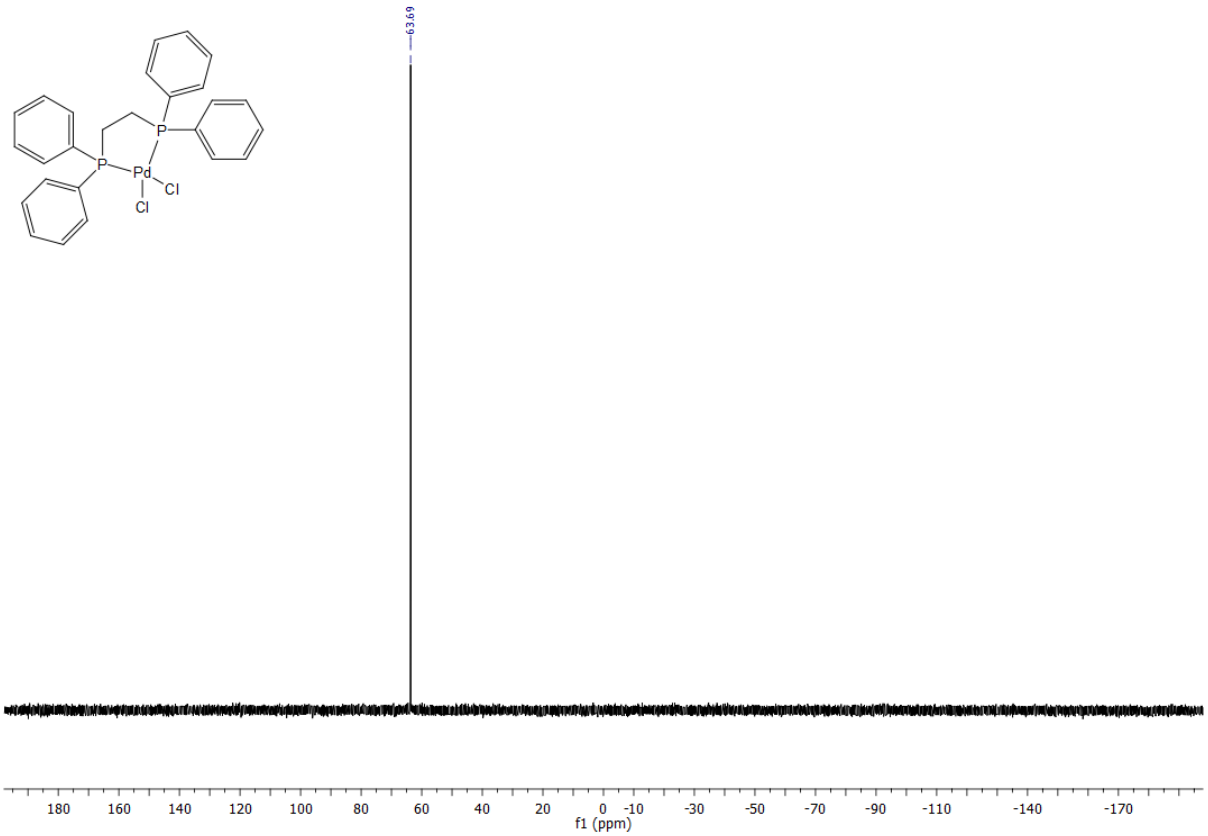


Figure S92. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of Pd(DPPE)Cl_2 (**$PdCl_2$(3a)**).

Pd(DPPE-d_4)Cl_2 (**$PdCl_2$(3a-d_4)**)

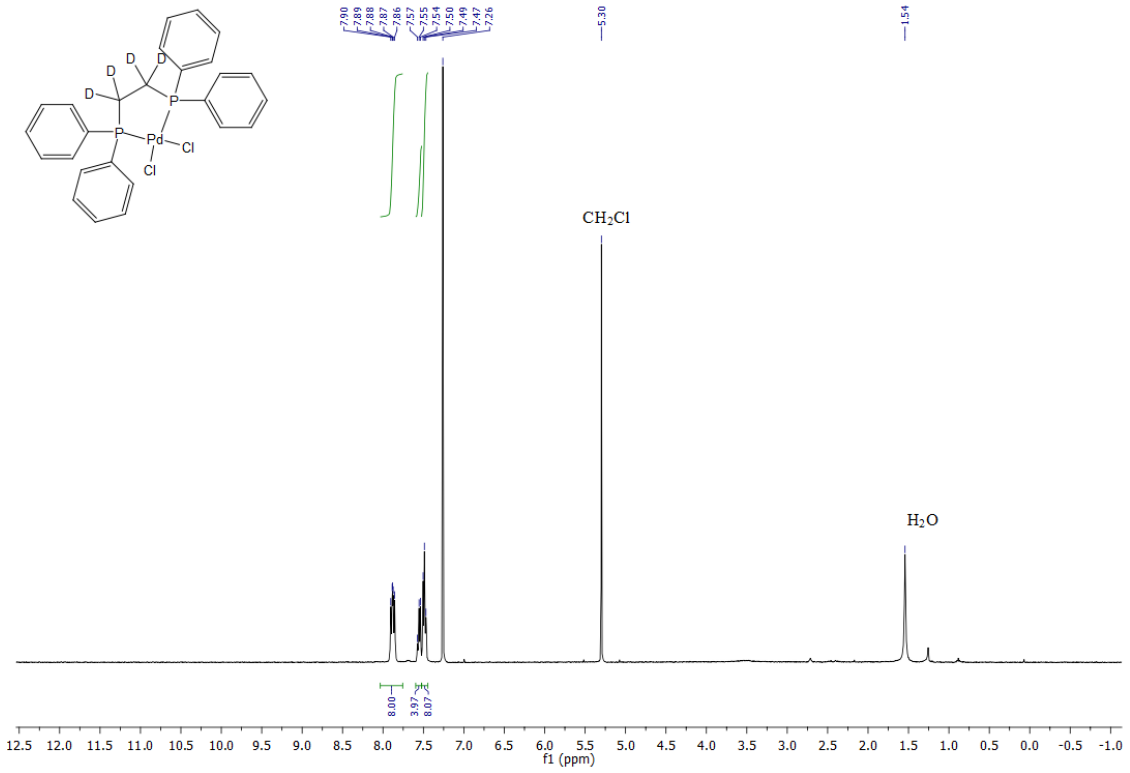


Figure S93. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of Pd(DPPE-d_4)Cl_2 (**$PdCl_2$(3a-d_4)**).

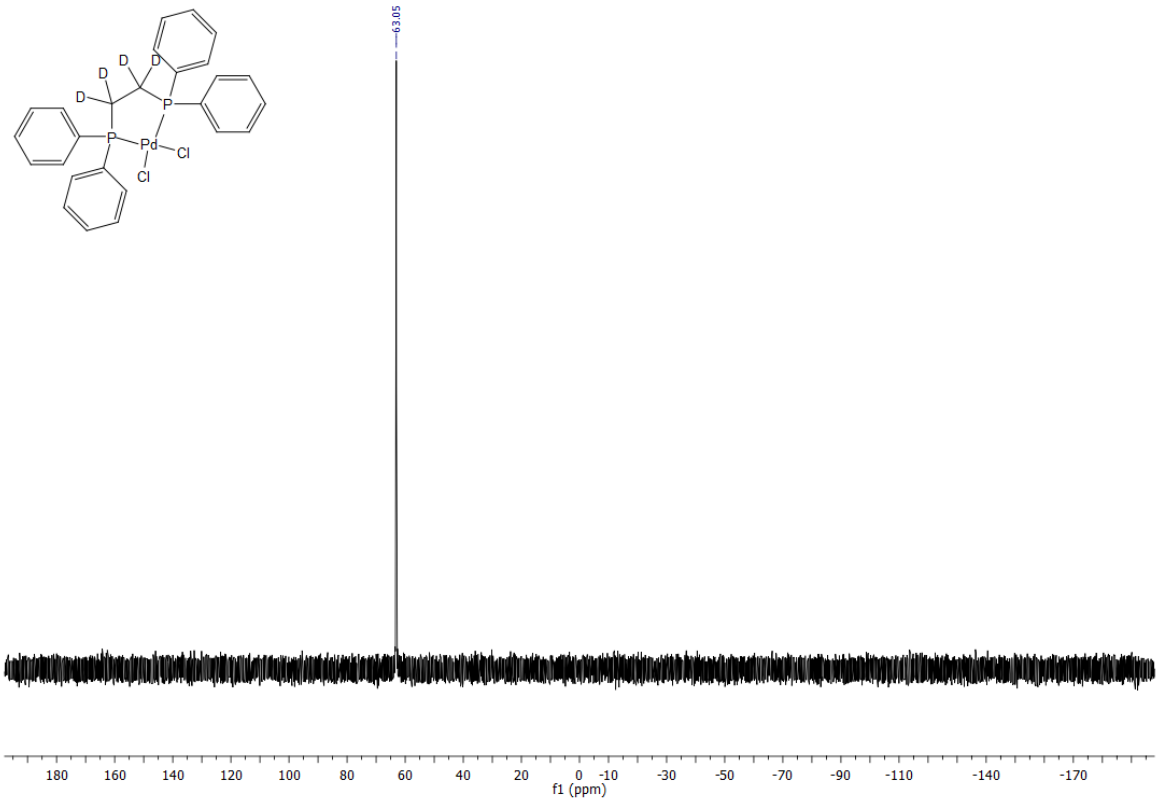
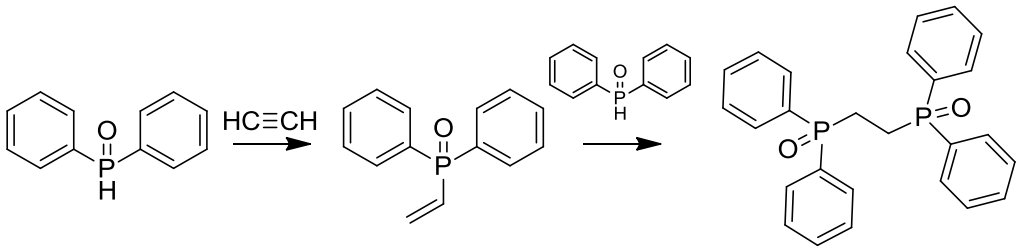
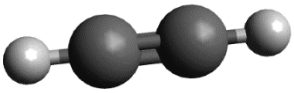
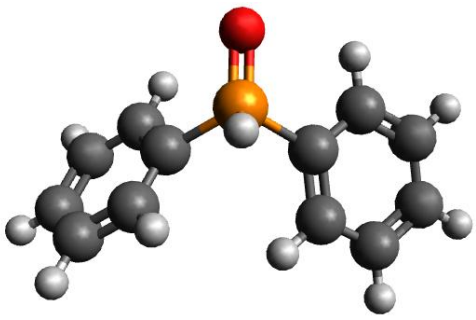


Figure S94. ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of Pd(DPPE-d_4)Cl_2 (**$PdCl_2$(3a-d_4)**).

S5. Calculations

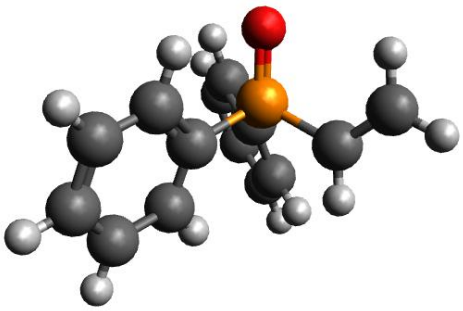
Please, see Table 2 in the manuscript.

Cartesian coordinates	Structure
	
4 C 0.00000000148990 0.00000000384130 0.60402181301688 C 0.00000000425352 0.00000000034731 -0.60402181676118 H -0.00000000241113 -0.00000000267650 1.67171107864566 H -0.00000000333230 -0.00000000151212 -1.67171107490136	 **Acetylene**
25 P -0.54962647580488 1.49841001826577 -0.09508173668755 O 0.81214771988956 2.04606442262290 -0.42299349790036 C -1.73084589197820 -0.60638218242415 3.26430734727647 C -0.57021361584297 -0.57133914888865 4.04642289075658 C -1.74387335782998 -0.00129991753088 2.00555699308148 H -2.62216975880842 -1.10806082350035 3.63313573633374 C 0.57644943758119 0.06926011730239 3.56833784954489 H -0.56187171171298 -1.04384732135971 5.02569780174155 C -0.59531192348996 0.64609232564464 1.52329980045008 C 0.56548742993587 0.67888888992754 2.30966384567992 H -2.64736402583785 -0.04410374518739 1.40089579109523 H 1.47917309498413 0.09696036229941 4.17363718474995 H 1.44880178581825 1.18298474451967 1.92668099591794 C -3.12445985288466 -0.53474887043534 -2.59258061827467 C -2.26308320656283 -1.41615746990837 -3.25260164561360 C -2.61617384896082 0.35543954364609 -1.64117247265803	 **$(C_6H_5)_2PHO$** (N)

H	-4.18669204532232	-0.53244808675246	-2.82433193347946
C	-0.89301948392977	-1.40363270638681	-2.96611410702686
H	-2.65641136933608	-2.10459153444955	-3.99658729939801
C	-1.24677360639432	0.35965880792021	-1.33795104620467
C	-0.38441423674345	-0.51902214069626	-2.01279121657641
H	-3.28997089748765	1.05347365722193	-1.14710448709864
H	-0.22093355464456	-2.07898684770480	-3.48968793819957
H	0.68162988425663	-0.49330397415006	-1.80153956739731
H	-1.59346048889385	2.45731188000416	0.01313132988725

29

P	-0.69339898254853	1.49777794001222	0.00154544731726
O	0.68801516660868	2.04032474952291	-0.25799432227617
C	-2.07576933549731	-0.10580584815486	3.57393435746921
C	-0.90009473030816	-0.63546138533668	4.11471903467143
C	-2.04615493118812	0.54528675385625	2.33722784404634
H	-3.01429122663499	-0.19291304587196	4.11610173817873
C	0.30690153991018	-0.50603317459504	3.42003584567681
H	-0.92370771874385	-1.13971839770433	5.07776349921655
C	-0.83979428398628	0.66889024445548	1.62942484592012
C	0.33888692572007	0.14536426913721	2.18439878750674
H	-2.96649536794839	0.96677709202956	1.94075132299518
H	1.22514632912636	-0.90616372533900	3.84289248441036
H	1.27694325179909	0.26813799365995	1.64968982942720
C	-2.63179365101587	-1.51251567902859	-2.09867870458449
C	-1.93130996510674	-1.50765482886566	-3.30961514367549
C	-2.27134965744765	-0.62857148592696	-1.07805579909229
H	-3.45344552736879	-2.20819921891902	-1.94595220861559
C	-0.86622223443490	-0.62069905889865	-3.49579027440868
H	-2.21094090354411	-2.19802766428966	-4.10184752337741
C	-1.20894140126797	0.26982873963014	-1.26237048442987
C	-0.50486815609692	0.26557990684179	-2.47700705046129



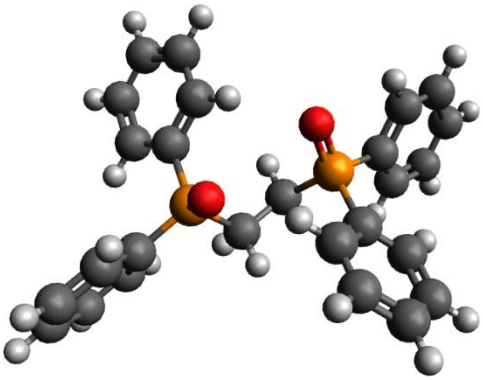
$(C_6H_5)_2P(O)Vy$

(VE)

H	-2.81180167986957	-0.65689017398096	-0.13502847141484
H	-0.31350623664555	-0.62051434270557	-4.43216890790743
H	0.32911622662707	0.95000225741310	-2.60737389547713
C	-1.99037724492384	2.77645405426465	-0.03849889833662
C	-1.65903223846995	4.06044981175681	-0.21331909463628
H	-3.03438193066206	2.47359601176322	0.04302005474219
H	-0.61774839531201	4.35930737841065	-0.31393243405527
H	-2.41379364076986	4.84293082686294	-0.26523187882928

54

P	-1.30571398063995	1.39450325359797	-0.51584532429635
O	-0.24027827219055	1.89851390785302	-1.45561161691044
C	-0.48496966504297	-0.38105106766631	3.14750433502252
C	0.43861956388563	0.51478641027553	3.69448491131960
C	-1.03457286365813	-0.13615852485150	1.88542993070498
H	-0.77126540905433	-1.27549900207059	3.69583616469548
C	0.81373763019183	1.65404031107794	2.97468920982910
H	0.86856714013387	0.32233290955843	4.67479809970235
C	-0.66826453587235	1.01078241439668	1.16166086436867
C	0.27173427251106	1.90334335904799	1.71071545101193
H	-1.73386062171268	-0.85270283467969	1.46506766209521
H	1.53597177255286	2.35120195636978	3.39238357602573
H	0.56703444120931	2.79054388654935	1.15498339330109
C	-3.80125057103596	-1.86725948044702	-1.23155132724767
C	-3.11620471227313	-2.50854511092113	-2.26894507469009
C	-3.29198202732750	-0.68783978128850	-0.68089427652273
H	-4.73116662399298	-2.28348584976752	-0.85156393261935
C	-1.92403051478115	-1.96491398440553	-2.75650823409516
H	-3.51303509146081	-3.42605664887701	-2.69676436905278
C	-2.09147875984594	-0.13736459916196	-1.16126371210831
C	-1.41473134785549	-0.78424248584107	-2.20817499180983
H	-3.83852078841233	-0.20834566629857	0.12792662378077

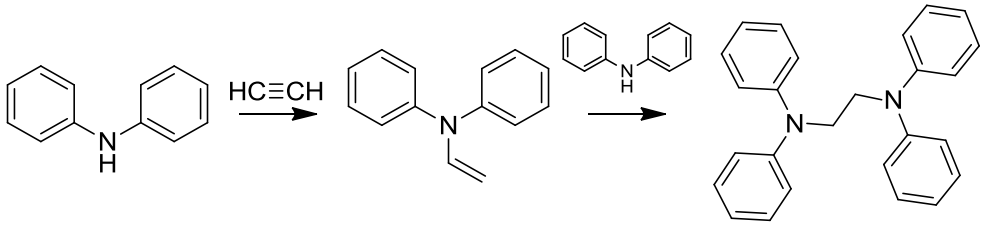


$(C_6H_5)_2P(O)CH_2CH_2P(O)(C_6H_5)_2$

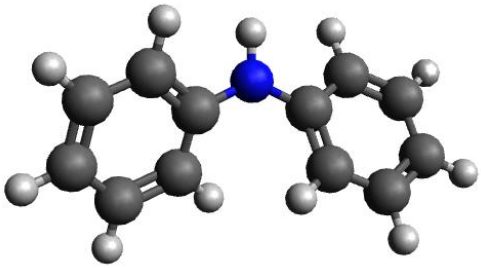
(DA)

H	-1.39094432057638	-2.45743973878850	-3.56609003724343
H	-0.49530869434655	-0.34674148666639	-2.58752326762933
C	-2.73354112954494	2.56475198240738	-0.30984247480836
C	-2.57400923496043	3.81374616195612	0.58192157060498
H	-0.58082827506530	4.49281932273450	-4.73985056220024
C	-1.16275459113920	5.05557684775405	-4.01407002314547
H	-2.20861604884657	6.21631773741678	-5.50517324035601
C	-2.07785398607883	6.02204288671515	-4.44309293964706
C	-0.98387895476158	4.80740496495884	-2.65028942062168
H	-0.27997479086492	4.04900866560257	-2.31821614814509
O	0.04208122260196	4.85326493495411	0.34017916881013
C	-2.82047221648918	6.74426399216719	-3.50380472719660
C	-1.73364516261430	5.52728372472236	-1.70264919009875
C	-2.64827195890131	6.50040703383917	-2.13805119799520
P	-1.40726045492692	5.16401993429609	0.06444211617054
H	-3.52505162166243	7.50505544019524	-3.83129510348110
H	-3.21400206052949	7.08590298033042	-1.41878449822801
H	0.08868305224265	7.18482793178148	1.33905369793565
C	-1.96604857106231	6.62591273908941	1.03061233722752
C	-0.94662372138013	7.45340954809325	1.53028254866214
C	-3.30480828214202	6.95588426857210	1.30011972338120
H	-4.11670374270909	6.33495845971466	0.92901919537355
C	-1.26092680654421	8.59285210036457	2.27595425723520
H	-0.46290163534873	9.22491855215045	2.65770536773261
C	-3.61820131272656	8.09383076919704	2.04939923088631
C	-2.59637572265525	8.91486838069730	2.53677329984018
H	-4.65853325536561	8.33618498253792	2.25278166582982
H	-2.84125512648084	9.79893445808037	3.12052382756393
H	-3.57341431145188	1.98225064592179	0.08888369690673
H	-3.01082197670313	2.85196473105710	-1.33246035712883
H	-3.56749653314906	4.26684181129721	0.68599905167858

H	-2.25289881114549	3.53251186439961	1.59318506958144



24



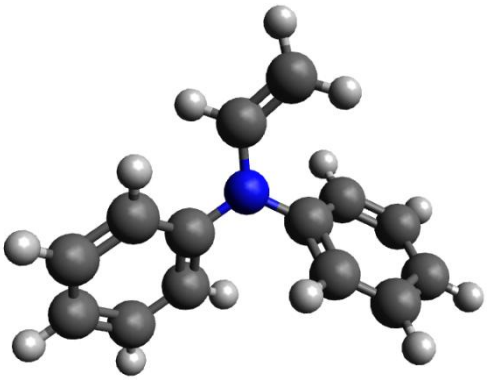
$(C_6H_5)_2NH$

(N)

C	3.81516315237673	-2.45319141441294	-2.53138372390217
C	3.87098967606873	-1.18125229581686	-1.95227390188626
H	4.47156872629969	-2.71319288988568	-3.35740153887512
H	4.56722161671351	-0.43911440389387	-2.33651827554048
C	2.89671610795827	-3.38360407016067	-2.03330608678713
C	3.02934708922910	-0.83521567641701	-0.89304296757490
H	2.83453563811617	-4.37752088763413	-2.47050862401984
H	3.06172779653963	0.16911333693503	-0.48336302604802
C	2.06404528887125	-3.05476533716731	-0.96347730622479
C	2.11863658344213	-1.77575960724412	-0.37599778036649
N	1.22601238049003	-1.47371315773003	0.66206475596033
H	1.36757057105333	-3.79301276272038	-0.56951749356423
C	1.37563184672112	-0.57893659081476	1.73039571263348
C	2.63069167097315	-0.13968351026054	2.19158843044205
H	3.53886466954071	-0.49065013239390	1.71316695374716
C	0.21884433670989	-0.14185952633136	2.40660431278792
C	2.71375543634963	0.72193258478639	3.28785904448732
H	-0.75877222869958	-0.46868886966025	2.05614337772838
C	0.31527217310177	0.70629114636326	3.50912706961719
C	1.56369943888065	1.15340598778711	3.95611091287115
H	3.69456848334463	1.04519027629407	3.62948470842506
H	-0.59307956808825	1.02718764655922	4.01388277116388
H	1.63817700014363	1.82157907049286	4.80977673024211
H	0.38204211386405	-2.02987891667413	0.68115594468339

28

H	-0.89592903180463	-3.61140355901083	3.10563824463676
C	3.22728208962981	-2.25231188031641	-2.45245083889846
C	3.09162613589152	-0.98107463257596	-1.88092286431798
H	3.69682796720909	-2.37144969868882	-3.42527415095112
H	3.45027394630771	-0.10330509933688	-2.41349793298634
C	2.75570102908975	-3.36511472791628	-1.75195968199238
C	2.48323441468053	-0.82043967590837	-0.63676857226804
H	2.86561898708046	-4.36190482784138	-2.17279747595661
H	2.36852400969680	0.17191525284033	-0.21107910203448
C	2.16094461460276	-3.21754783958888	-0.49556648537796
C	2.00736996644027	-1.93977235917493	0.07226012356012
N	1.36626347414097	-1.77240974775197	1.32672962794576
H	1.83864994868595	-4.09630823597965	0.05495125892808
C	1.84590534826175	-0.77963279713616	2.23926242538358
C	3.20339165216783	-0.73585822479154	2.58877236359589
H	3.88738234495342	-1.46578646508196	2.16465083474183
C	0.96100526470251	0.15910265543142	2.78924100103734
C	3.67037330975903	0.24279487877585	3.47018947697907
H	-0.09011642181215	0.12176636628657	2.51828841733781
C	1.43063029318804	1.12696700924464	3.67941818540417
C	2.78695014197770	1.17589463866409	4.02147178321702
H	4.72538423488230	0.26795795316303	3.73236851948166
H	0.73635654019348	1.85168575822501	4.09801150748751
H	3.15066838919173	1.93352725754448	4.71091004491143
C	0.36472232213214	-2.67042128773346	1.71614579471631
H	-0.09267131940343	-3.17856242345582	0.87092313136234
C	-0.07167028055936	-2.92080214212278	2.96319775070880
H	0.34810062871402	-2.44840614576334	3.84535661334787

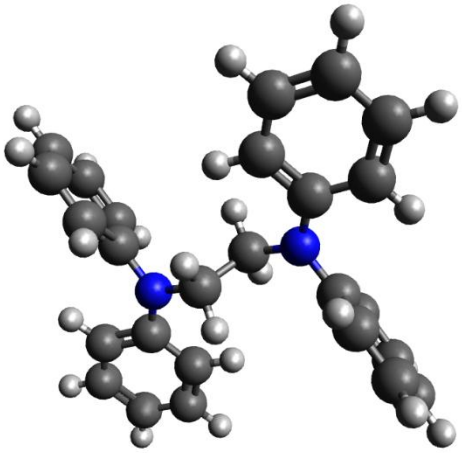


$(C_6H_5)_2NVy$

(VE)

52

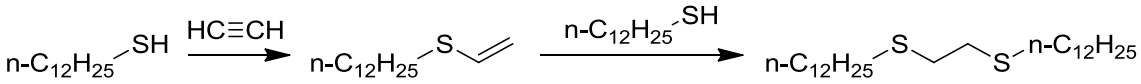
C	3.89990241713622	-2.86070043111102	-1.85632504816593
C	3.81678557049803	-1.50203713648495	-1.52875071679392
H	4.52633206201876	-3.19636559335224	-2.67824133196578
H	4.37413328575481	-0.76709115805182	-2.10544658256074
C	3.15565745633942	-3.77371967370095	-1.10695330059699
C	3.01088470018324	-1.06523213551860	-0.47965136161977
H	3.20056927535989	-4.83548437938118	-1.33910686376568
H	2.94624616397965	-0.00422019071455	-0.26098503284821
C	2.35354963762312	-3.35025467784081	-0.04333470736070
C	2.26602735700821	-1.98345183917396	0.29406783597005
N	1.43311502416054	-1.52526015416298	1.33178434338743
H	1.80624411190511	-4.09665903589267	0.52213979706722
C	1.70541474251586	-0.29774324057456	2.00681610563339
C	2.97650040549280	-0.03647306225562	2.54753917668265
H	3.76720166104239	-0.77184535927086	2.42578498197876
C	0.69114702002624	0.65994330737409	2.16949442034230
C	3.22386004201799	1.15578499576452	3.23022355684792
H	-0.28879493415915	0.48155326416901	1.73416180068038
C	0.93771463618439	1.84372449136232	2.87060269028127
C	2.20515735302470	2.10000270665890	3.40173409748131
H	4.21347806883242	1.34063444528069	3.64154516246709
H	0.13961579121052	2.57327351535038	2.98655337005467
H	2.39811026504561	3.02371176040132	3.94106326621148
C	0.38473867118274	-2.37816622643878	1.89315810797268
C	0.85027270238872	-3.18290362725052	3.13196507659692
H	-3.18559112448498	-4.77745021351975	7.09408172918585
H	-1.73974722762365	-5.54826665176718	5.26740250895084
C	-2.61691217255503	-4.04555451893949	6.52459856471976
C	-1.80069405430032	-4.48691998404619	5.48536705445513
C	-2.69657543391587	-2.68654553835051	6.85144320849168



$(C_6H_5)_2NCH_2CH_2N(C_6H_5)_2$

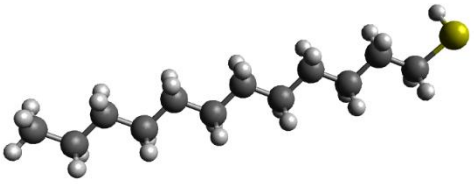
(DA)

H	-2.94060136888858	-6.91287104911270	1.35164312725839
C	-1.95927615604376	-6.72746111118957	1.78211643052563
C	-1.72206385616212	-5.52981838054033	2.45912063814052
H	-2.51247672529073	-4.79066602498480	2.55801892944362
H	-3.33124094492243	-2.34751606630644	7.66561494789602
C	-0.94042682160968	-7.67650391672731	1.64097757537442
C	-1.04105211507173	-3.57285313751943	4.72096742075939
C	-0.46182265902365	-5.26820466777316	3.02393065781115
N	-0.19848523734742	-4.03521575886638	3.69339106433355
H	-1.12523730450696	-8.60450644604669	1.10616506571548
C	0.31647288346369	-7.41985554250986	2.19644371868452
C	-1.93792146256338	-1.77776845300173	6.11141951833793
C	0.55231495996203	-6.23045307035438	2.89174147856722
C	-1.12518243340530	-2.20552990644669	5.05765332850027
H	1.11415083857572	-8.15319175899828	2.10392115714603
H	1.52333543119304	-6.05031379688663	3.34605288166403
H	-1.97937784167774	-0.71577440427155	6.34320759322148
H	-0.56630287619102	-1.46190565810228	4.49998062596352
H	1.70314344276982	-3.80970360415431	2.85336559451286
H	1.20860484563325	-2.50083273849291	3.90874952169940
H	0.02811239476844	-3.06038912078251	1.11586476008167
H	-0.46961046755393	-1.75316904549382	2.17124205458155



39

S	6.41660941763706	5.54702497016820	6.04035073441257
C	7.86104843152543	5.68322367189096	4.90120751583568
C	8.58337336288680	4.36130779685664	4.62639611156274
C	9.83205308895397	4.53884524247609	3.74627436551573
C	10.55776232129982	3.21461839595013	3.46383713125634
C	11.84923143028887	3.37554320934684	2.64919941326530



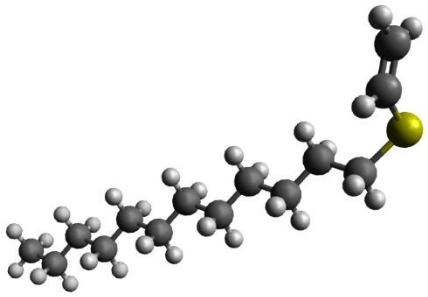
$C_{12}H_{25}SH$

(N)

C	12.56769149855334	2.04442029020002	2.38171427947447
C	13.89174486028782	2.19790734252499	1.62013556556707
C	14.61417030268941	0.86561899204635	1.37096073592253
C	15.94575312534888	1.01870956764185	0.62173117383513
C	16.67319502724827	-0.31163158774066	0.37801173664474
C	17.99922883897528	-0.15808523074948	-0.38131182734991
C	18.72440490448695	-1.49018926921229	-0.61278825934145
H	8.86507865189418	3.90143316917555	5.58314704846747
H	7.88841203815498	3.66162041418058	4.13887399178537
H	10.52698769724772	5.23527420616709	4.24017495834679
H	9.54892078826856	5.01141624933230	2.79326819050572
H	10.79572989795153	2.72456430809099	4.42049371199960
H	9.87482872236473	2.53263835558292	2.93422503183682
H	11.61948010023729	3.86589969718468	1.69049274350995
H	12.53145116262422	4.05449832852034	3.18383668384729
H	11.89809609486923	1.37678261023719	1.81767455625253
H	12.76097889776362	1.54095410554148	3.34180718104722
H	13.70202938038915	2.69433341597082	0.65567452679405
H	14.55720356323657	2.87060963277839	2.18319545626089
H	13.95252290297837	0.19428753908499	0.80182445421255
H	14.79652188321622	0.36730385582886	2.33583205016857
H	16.60557134459429	1.69358529831809	1.18886768163336
H	15.76265185694968	1.51357513050666	-0.34486732379531
H	16.86469051448924	-0.80329705529174	1.34464276935930
H	16.01207970010368	-0.99048744320303	-0.18311595529113
H	18.65830578802034	0.52482104216103	0.17536380668646
H	17.80694899930399	0.32646064030738	-1.35029620942829
H	18.96415305379790	-1.98215722523728	0.33923449831217
H	19.66506423824326	-1.34491231918404	-1.15856836767238
H	18.10426358083935	-2.18348381778125	-1.19648090968380
H	7.53552706133930	6.15697686676293	3.96818899793929

H	8.53174678424657	6.39036947018932	5.40369990886327
H	5.68692868669397	4.70819013337612	5.27145184144123

43



$C_{12}H_{25}SVy$

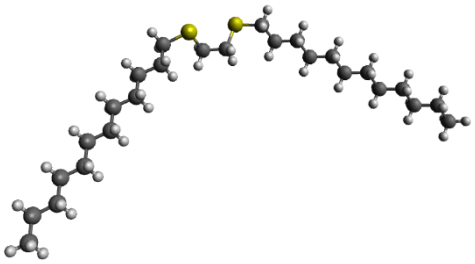
(VE)

S	5.55070586971723	5.79739092377232	4.16733762945174
C	7.24051231610630	5.88046300984742	3.44338066738428
C	7.99225442522515	4.54608041950432	3.41455635528569
C	9.38718550268092	4.67100782255745	2.78047246006421
C	10.15127027660136	3.33910697369721	2.73427850523183
C	11.54448044611683	3.45327965148148	2.09850850288989
C	12.30668613702563	2.12094614910008	2.04699664995177
C	13.69779782301234	2.23357561767817	1.40638331275685
C	14.46274583468645	0.90275490480029	1.35664194723535
C	15.85041404810473	1.01628794175412	0.70853191415770
C	16.61794118338961	-0.31275424401737	0.65741695828027
C	18.00331120202247	-0.19888848039395	0.00436220655070
C	18.76401546585969	-1.53051417098625	-0.04061341648304
H	7.80951990911909	6.64433392148348	3.98921136830225
H	7.08667717063440	6.26149380898727	2.42680097057860
H	8.08593058727220	4.15887811694705	4.43860391367748
H	7.39442406509644	3.81033504828863	2.85953587410953
H	9.97975701747425	5.41040421886123	3.34100966319743
H	9.28954662457021	5.06818592284245	1.75829053381103
H	10.24920143801294	2.94223204910440	3.75638706746953
H	9.55657943449554	2.60026692742697	2.17565463277292
H	11.44531710689655	3.85346758089961	1.07755346704540
H	12.14006582835751	4.19071696859865	2.65864801687927
H	11.70936971183193	1.38282920105970	1.48968928272137
H	12.40860017683480	1.72201151142504	3.06817614386845
H	13.59491490422606	2.63041607467475	0.38444039469021
H	14.29421450408095	2.97385998750888	1.96195204909414
H	13.86461343479774	0.16078730687359	0.80526351653394

H	14.57082768411238	0.50818154680483	2.37889722222290
H	16.44826019449730	1.75899360632272	1.25936886664378
H	15.74138998494912	1.41080749190591	-0.31370929898638
H	16.73144910212927	-0.70641455752830	1.67960933703520
H	16.01997735585320	-1.05733248180949	0.10906713131854
H	18.60115253966015	0.54545689506144	0.55122430406164
H	17.89032228196855	0.19214058624764	-1.01782331813292
H	18.92310410764372	-1.93077652683437	0.96948984061653
H	19.74820411317956	-1.41424451855288	-0.51135662662422
H	18.20838201485291	-2.28581670079261	-0.61208665158734
C	5.93943024648688	5.62838689392290	5.88756465022362
C	5.15932243746332	5.00211201877502	6.77831848273481
H	6.84763078014794	6.14103040301347	6.20736056125430
H	4.25282856942295	4.47642783061062	6.48779114590014
H	5.40948614338276	5.01634234907598	7.83616376581053

82

S	4.20917947735795	5.47748957061858	2.50600526086313
C	5.94379311690602	5.48497650947005	1.90047027582224
C	6.87737250082881	4.45396575743655	2.54544531971799
C	8.29501935998490	4.49132745172353	1.95116276903918
C	9.26146760614954	3.50304493177487	2.62089615669270
C	10.67914576237561	3.53774713759794	2.03162267916587
C	11.65784883202032	2.57883319598696	2.72542763615710
C	13.07844797148467	2.62611772507495	2.14402121698092
C	14.06528114358694	1.68426510921881	2.84936480257785
C	15.48734312435733	1.74155636881047	2.27247111596708
C	16.47693453111953	0.80139714464253	2.97573509539017
C	17.89786377983060	0.85731019803211	2.39586134440879
C	18.88123259495665	-0.08078693705355	3.10746034602901
H	6.34495182083835	6.50069307307124	2.01510478482671
H	5.85631183883495	5.29687628997042	0.82328700884653



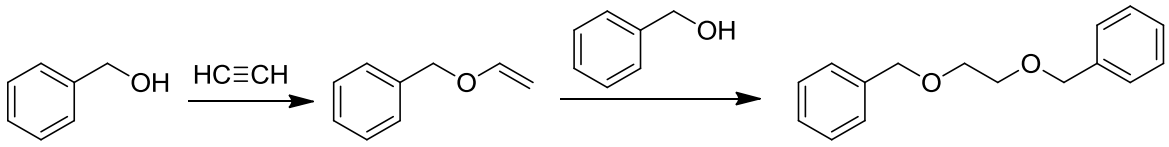
$C_{12}H_{25}SCH_2CH_2SC_{12}H_{25}$

(DA)

H	6.93905445789657	4.63604912415885	3.62751514044522
H	6.44564455124029	3.45135846317562	2.42255157966009
H	8.70154583156793	5.51044323977566	2.04107478675239
H	8.24347243513976	4.27693497643346	0.87264289122593
H	9.31216453607444	3.72259979025799	3.69862919654900
H	8.85622503463714	2.48309430706294	2.53615693915437
H	10.63269460012521	3.29661394751654	0.95842672977339
H	11.07249023491171	4.56411795374938	2.09633605959229
H	11.27047588037623	1.55050687672296	2.65714484342876
H	11.69832360713742	2.81839085444732	3.79939485190375
H	13.04080742139044	2.37590658648878	1.07246201669281
H	13.45877645707935	3.65778923317653	2.20231762160065
H	13.68941379082415	0.65124487137538	2.78719337381933
H	14.09905095087662	1.93190205549802	3.92172656973554
H	15.86243269317041	2.77488253050207	2.33501176599040
H	15.45338496341291	1.49469332085195	1.19992022243429
H	16.51428044590974	1.04941319321560	4.04805000206901
H	16.10219900336193	-0.23233272010614	2.91561045797666
H	18.27159702151125	1.89050956467985	2.45335311887981
H	17.86196416996701	0.60530142915168	1.32547959716243
H	18.96515672848415	0.16725773060854	4.17388404756240
H	19.88543074738147	-0.01541254944197	2.67042489947890
H	18.55412878963379	-1.12659892365387	3.03605869906638
C	4.45888927062142	6.08934806767728	4.22420247770129
C	3.13740680616229	6.47944304207828	4.88850463248693
H	-0.37765443048379	13.18472271657067	17.37997799242644
H	-0.21086377981478	12.09592717793848	15.05049557414688
H	-0.03155657480394	11.01634313779335	12.71375650032308
H	1.69374899772769	13.80225235432837	18.69817123129170
C	0.27881689005323	14.00149395679236	17.04464642829082
H	0.17328832188331	9.93209896043523	10.38657034733775

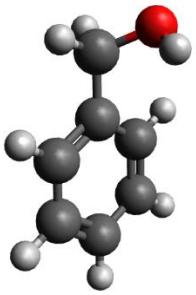
H	0.36210437635914	14.92456147392089	19.02683068859345
H	1.86270510913947	12.70910475961512	16.33680524659275
C	1.04586982026269	14.56577163039485	18.24745358606556
H	0.41931708495345	8.81336927286942	8.08716786467671
C	0.44106599508266	12.91861067308261	14.71792582776034
H	0.68206757772355	7.65627641978680	5.81820571831940
H	2.03408584237635	11.63970287573115	14.00473103077786
C	1.19753586378432	13.48564936665150	15.92785428418706
C	0.61314729127247	11.84668506693945	12.38626662547146
H	2.22722144512683	10.59386356679638	11.67551968868190
C	1.36401294946563	12.41388441780171	13.59969117896599
H	2.45113700765823	9.55369349008905	9.36183424716590
H	2.72467973292388	8.51237853964012	7.08031682416056
C	0.80442949102716	10.77172366182535	10.05639952742374
H	-0.38500506044138	14.77850015778013	16.63709163176432
C	1.54424419936030	11.35570799197983	11.26857866836354
C	1.02349826721280	9.66672229988271	7.74242403395573
C	1.27297341126061	8.51388325730184	5.47059943539112
H	-0.22855540829423	13.69345916131156	14.31339466741355
C	1.74760675886591	10.29074349295695	8.94449293499838
C	1.98834920370337	9.19971947411758	6.64023440675916
S	2.36791359596706	7.95779284089397	4.10005321545921
H	-0.06272155996013	12.61721326063954	11.98408902084017
H	1.68461569168675	15.40824760216683	17.95080529471083
H	0.11682572315833	11.52875375522241	9.64881319075913
H	1.85456973924608	14.30391201008358	15.59397426759044
H	0.31322052637577	10.39538326195969	7.32273753726054
H	2.01571712163015	13.23754994267430	13.26916433708310
H	0.57022311111656	9.20908499889227	4.99541759935305
H	2.18206369934686	12.18948838606505	10.93647711135981
H	2.36208279136150	11.13616946275042	8.59891412244513

H	2.55850786978019	10.05611260369422	6.25591166210286
H	5.13156685803148	6.95500102937226	4.19700609555260
H	4.92999999443632	5.30389834722687	4.82652765411503
H	3.34407932936509	6.71502124355901	5.93807939373595
H	2.43167123554548	5.64014140868603	4.86393497269787



16

C	0.17152516268734	0.44137970494653	-0.80181788311546
C	1.46074568365623	-0.08232301488986	-0.68993483375220
C	1.91075220750543	-0.58972949960766	0.53569836306878
C	1.06473893862959	-0.56576166966804	1.64698044464005
C	-0.22549816862408	-0.03449796117414	1.53235927522717
C	-0.68731627100154	0.47054894569526	0.30965375739115
H	-0.17629691707773	0.83940459288576	-1.75232332571979
H	2.11512715911738	-0.09895188342800	-1.55839644642590
H	2.91462759886599	-0.99858667020867	0.62152091520543
H	1.40725473570022	-0.95440799863366	2.60308873842614
H	-0.87959428881456	-0.01425019279312	2.40252196443980
C	-2.08557087232620	1.04093745379577	0.18237100377713
O	-2.10996893211488	2.37398291483411	-0.33896529295449
H	-2.59783446771809	0.99500299936916	1.15521392719258
H	-2.67973361102248	0.45923865612760	-0.53089970113103
H	-1.53665795746260	2.93018362274894	0.21353909373066



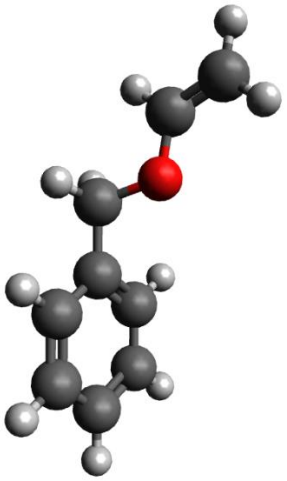
BnOH

(N)

20

H	-2.17222342906075	-2.72821669167259	2.83510087862292
H	-1.67537481024997	-1.70316173309571	0.84437677919442
C	-1.09513989309880	-2.41315973606010	5.36328578953064
C	-0.97419985289680	-2.44012346941234	6.75387144554837
C	-2.29177736072565	-1.71666490272949	3.25174801311425

C	-1.16150901283933	-0.88004562228368	1.34462922878776
H	-0.35220363208569	-2.91037911949494	4.74341681908463
C	-2.16569760856564	-1.74145057560346	4.75367727185528
H	-0.14001523237567	-2.96358295050291	7.21476596775251
C	-1.92705869605195	-1.79780419395350	7.55376558771815
C	-3.11124548023872	-1.09781456794403	5.56134506255258
C	-2.99653953708538	-1.12663340560033	6.95534736771152
O	-1.26790106751813	-0.86817070076196	2.70455008863747
H	-0.36517360088085	-0.04563370300324	-0.40739703531959
C	-0.45285871483364	0.03147261084475	0.67081708483161
H	-1.83504743659743	-1.82217565428241	8.63691290767279
H	-3.94191107269447	-0.56893414484756	5.09822213640411
H	-3.73941286655669	-0.62381413322683	7.56976297714088
H	-3.27834018398889	-1.33627973068280	2.95336849207479
H	0.05204948834450	0.84896242431316	1.17673313708480

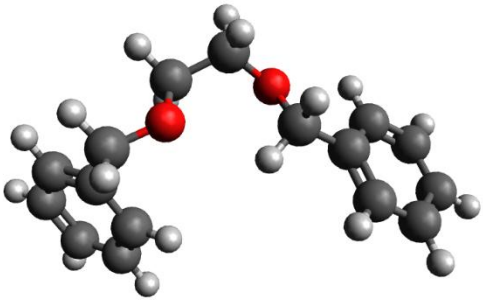


BnOVy

(VE)

36

H	2.01600724518901	-1.01505213873728	1.22835636015580
C	3.85109284399943	-2.29151748734838	3.14154988507111
C	4.90184767749329	-3.16911325175648	3.42034292749492
H	3.87259350465949	-1.28068239026250	3.54676691115375
C	1.67471216195219	-1.69970447067442	2.02525260668225
H	5.73335117318877	-2.83778709664554	4.03825228303434
C	2.76827472427804	-2.69636665426119	2.34671829276472
C	4.87882309087083	-4.47273188198520	2.91260652629110
O	0.50678788417076	-2.38096133965092	1.58192975102620
C	2.75051890259068	-4.00336554605779	1.84324710059343
C	3.79889865571528	-4.88560653410998	2.12690941717482
H	5.69250403428013	-5.16013148506392	3.13158743451044
C	-0.50976302012070	-1.55833243712911	1.03172191802181
H	1.90868319958375	-4.32562404367704	1.23880221584449
H	3.76924079444860	-5.89909853740879	1.73289811670042



BnOCH$_2$CH$_2$OBn

(DA)

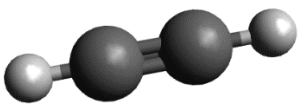
C	-1.44018849452023	-0.92775229296907	2.05993485553971
H	1.45108284676496	-1.08138203927189	2.90425347948043
H	-2.49111132927107	1.24501402030413	3.08563930335782
O	-0.77184288823103	0.13435711668617	2.73303907410315
H	-0.01685746645255	-0.32431019479561	5.48853061567235
C	-1.07252178245101	-0.44474541070614	5.72168906472950
C	-1.60336945971959	0.87568812507540	3.62491932471996
C	-1.45885320209569	-1.14857493614311	6.86381095439532
C	-2.03486684251546	0.10364708740790	4.85905176084252
H	-0.70212705851470	-1.57013067188941	7.52119641179726
C	-2.81724635053448	-1.30926524398148	7.16437166281810
C	-3.39080192506087	-0.06685020116742	5.16616668474912
C	-3.78316341791956	-0.76584461993101	6.31389822855003
H	-3.11811844602975	-1.85595323765809	8.05480845513862
H	-4.14779390618144	0.34969908245677	4.50361657948980
H	-0.99703087764833	1.74321986768487	3.90815406698542
H	-4.84016738949567	-0.88923055403393	6.53770907558384
H	-2.32832843961089	-0.53254646570171	1.53443686031028
H	-1.10966747880451	-2.21906575810031	0.39395899373008
H	-1.77583229005505	-1.69270803742024	2.77487555806242
H	-0.06865667395266	-0.77234034107712	0.39778724342422

Structures of Species from Figure 2.

Cartesian coordinates | Structure

4

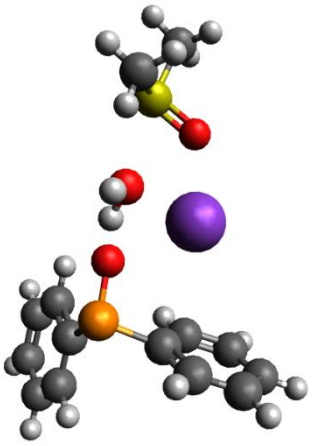
C	-0.00000000467141	-0.00000000442611	0.60403267159474
C	0.00000000311363	-0.00000000991531	-0.60403267415776
H	0.00000000207636	0.00000000625585	1.67170605838722
H	-0.00000000051858	0.00000000808557	-1.67170605582420



Acetylene

38

C	-3.07608236485223	-0.47972225355892	-0.93871872365177
C	-3.75677233911769	-1.68390138289424	-0.73025184294240
C	-4.45270105126117	-1.89947122393928	0.46802174517324
C	-4.46332729262447	-0.90284717027884	1.44761687961326
C	-3.77405495811228	0.29913949158007	1.23203180372015
C	-3.06794419721823	0.53265760950710	0.04124468427820
P	-2.02125334315902	2.10599534893890	-0.11538860880231
O	-0.55022521906777	1.49603926527794	-0.28613104292210
K	0.02387888407303	-0.96341400167044	0.26429935887955
O	2.42033252376815	-1.75317400979893	-0.52399368776135
S	3.61944281153839	-0.87035292568730	-0.90626432458442
C	5.03676410245584	-2.01526629013993	-1.06027441372200
C	4.14073050317586	-0.02178279880962	0.62398152977490
O	1.24252213086293	1.21861177446384	1.54281565969240
H	0.55057922089196	1.54484872249742	0.86628199368513
H	5.01697162041855	0.59838611934145	0.40572569418681
H	3.29527014985540	0.60127898787970	0.93969170397039
H	4.36950473041391	-0.76709854160992	1.39285085568879
H	5.95499131568099	-1.43837260631335	-1.21211245952889
H	5.10270060507404	-2.62887052213690	-0.15646491078633
H	4.84800234759598	-2.64977005022727	-1.92999910718702
H	-3.78380768352749	1.07202828980355	1.99959447827348
H	-2.56308991906131	-0.30869940135492	-1.88461727378249
H	-5.00895035380219	-1.05752121741809	2.37642561481285
H	-3.76555768924593	-2.44619997000808	-1.50773744934226
H	1.17204181857376	1.80962827909419	2.30660394506366
H	-4.99036295477417	-2.83141326723901	0.62808844665519
H	-0.56627480307765	2.10915046607241	-2.66631975035338
H	-1.15660986569106	2.80225309526976	-4.99572923881945
C	-1.56354988315370	2.47573157386545	-2.89953520001637



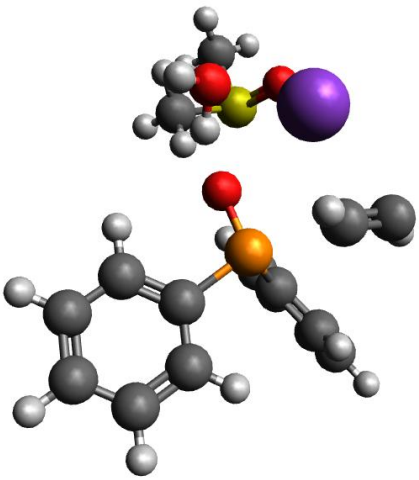
DMSO·$(C_6H_5)_2$POK·HOH

(1a`)

C	-1.89850847927668	2.86804758814704	-4.20158082548612
C	-2.50565653682733	2.55074463574852	-1.86318204787965
C	-3.18113515886424	3.34832436642460	-4.48303802508718
H	-3.44258550281491	3.65610211801515	-5.49322784719538
C	-3.78672530442953	3.05110111616443	-2.15444656922448
C	-4.12621557534846	3.43990464082944	-3.45245482263060
H	-4.52712546485221	3.13639069364861	-1.35929060212837
H	-5.12490682421866	3.81841345051531	-3.66191561963332

42

C	-2.12398051339890	-0.97313420405776	-0.68749604647629
C	-2.63280977688579	-2.27373126094847	-0.64084449637710
C	-3.96497536967604	-2.49290767930845	-0.27084526317563
C	-4.78065893058420	-1.40602010793042	0.05815539556884
C	-4.26678631831889	-0.10525724292270	0.01593767077081
C	-2.93721672916704	0.12619384572684	-0.37170866779588
P	-2.25638855616884	1.84537652899048	-0.39998347774605
O	-0.68558622742269	1.71631788825926	-0.31410729750193
K	0.03429763668162	1.72588548788479	2.40151029506546
O	1.61814633324119	-0.33113008920162	2.02293154095934
S	1.95724244853777	-1.13470069138332	0.75878068367918
C	3.72013885217961	-1.59206822896075	0.93272416456966
C	2.14308608458874	0.07683514846955	-0.59556800526042
O	0.90875074570191	3.58294834761229	0.65723257083491
H	0.29457733650223	3.03203003053645	0.08928181878495
H	2.45034079829844	-0.45255743926606	-1.50425737150089
H	1.16377206250099	0.55025188266844	-0.73859450761886
H	2.88371265163394	0.83122320944239	-0.31089264900258
H	4.06357838741710	-2.07765752891984	0.01335825943038
H	4.30605806896846	-0.69216040462848	1.14372836454667
H	3.79164864142179	-2.28964228166507	1.77122073884759
H	-4.89967458526753	0.73275859095466	0.30055396921571



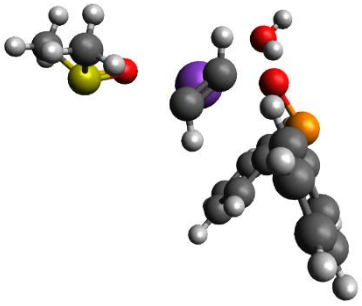
TS2A`

I = - 226.64 cm^{-1}

H	-1.09004588958512	-0.79840286519750	-0.97398000886265
H	-5.81287000804659	-1.57027404701038	0.35960630446388
H	-1.99348645223626	-3.11652131130938	-0.89592919437098
H	1.00810085849681	4.44695337743445	0.23367225390752
H	-4.36175257270412	-3.50479699348227	-0.23183849445091
H	-0.58603566257557	2.79215804864848	-2.61268520332215
H	-1.08398657951213	3.72220511728216	-4.86762258065777
C	-1.61312452680752	2.85688352392189	-2.96335005860455
C	-1.89634432117232	3.37400132913732	-4.23251395756583
C	-2.64538473195554	2.39079366334437	-2.13284884607696
C	-3.21674606492209	3.44066482534760	-4.68650308130895
H	-3.43828904466923	3.84424467390587	-5.67179037431906
C	-3.97128976350681	2.47328302796475	-2.59504250692041
C	-4.25421628305045	2.98607376320643	-3.86217013203808
H	-4.78957788626154	2.12924679973489	-1.96535380854490
H	-5.28462980154651	3.03309303594470	-4.20815228930889
C	-3.10353437745549	1.88884309036836	2.69142189313914
H	-3.27754865142055	0.82044708159356	2.73919603460640
C	-2.85926252293474	2.69854508773050	1.74303920909585
H	-2.72887875891639	3.75515497008088	1.57426715132227

42

C	-2.62987984128332	-0.21379907946761	-1.54072494156677
C	-2.53949322573882	-1.60381988323805	-1.66718902318596
C	-2.74685682051699	-2.43077375694497	-0.55659156005350
C	-3.06218550960394	-1.85566412136416	0.67973301130239
C	-3.16111010544479	-0.46306535948234	0.79756057167901
C	-2.92576890064212	0.38474575371659	-0.30300844833741
P	-3.09691637022520	2.22760766336604	0.04520471367891
O	-1.63250796248423	2.68102840887901	0.64718408404228
K	0.08988065523524	-0.19331204872506	1.38596832334457
O	2.51615597160202	-1.04371762949681	0.93275064278410



TS2B`

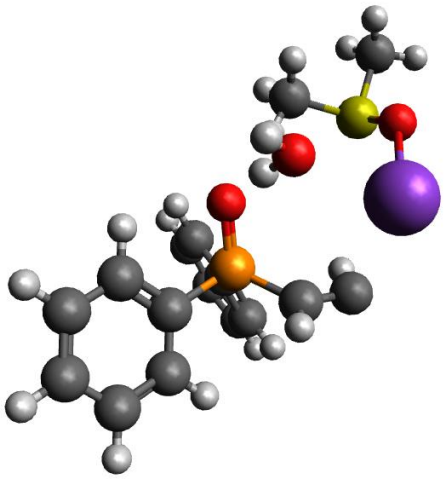
I = -188.71 cm^{-1}

S	3.47111526826695	-0.87225809744270	-0.26277631027907
C	5.13014561971648	-1.28205163448944	0.38852606085291
C	3.70920069672919	0.92009323223097	-0.48968953108779
O	-0.97757105794749	1.62187549793591	3.05938449940555
H	-1.32503499784421	2.16682024917731	2.30179275756596
H	4.43350227614814	1.07875374199341	-1.29675299015082
H	2.72579760524592	1.33550600696205	-0.76930176823394
H	4.06431919439840	1.36075806530022	0.44813514325964
H	5.88293938670271	-1.07553262341000	-0.37946402616801
H	5.31771728503485	-0.69096770739398	1.29034506136005
H	5.12977661075867	-2.34763119341672	0.63297387134846
H	-3.43445145983426	-0.02582341127471	1.75692263376673
H	-2.46393437415264	0.41083348698149	-2.41399975871198
H	-3.25759747593967	-2.48888871483395	1.54318762014012
H	-2.30353774441723	-2.04197757609254	-2.63466760874999
H	-1.23246497971157	2.07662143061092	3.87452860845935
H	-2.68023196710047	-3.51155718501484	-0.65845199383801
H	-1.45324606535104	4.21338875089552	-1.46396164190926
H	-1.78730242190251	5.35010787312151	-3.63827399656214
C	-2.29838384952608	3.94368051043553	-2.08859593035328
C	-2.48757899078702	4.58087331683856	-3.31965958014621
C	-3.18161354395972	2.93993606249405	-1.66068363996610
C	-3.56404521001832	4.23107906572573	-4.13994229921410
H	-3.70960995424055	4.72813938072489	-5.09637478242074
C	-4.27449915451873	2.61047469901648	-2.48469806355535
C	-4.45997654879042	3.24236733053867	-3.71657574310346
H	-4.99104103860172	1.85619997967677	-2.16218934620975
H	-5.30680669433622	2.96820867895461	-4.34234649773529
C	0.34587378131220	1.79615609327851	-0.99434889246788
H	-0.33592405742956	1.27983632283697	-1.66713599415966
C	-0.06837357971075	2.47813702791605	0.02529251254215

H	0.41982955090981	3.09064139247882	0.77396425263528

42

C	-2.04525770305814	-1.05440473748900	-1.61975236214278
C	-2.57680983608955	-2.34703171825360	-1.63164488872682
C	-3.68828010353439	-2.65447075112500	-0.83910097478139
C	-4.26523117549803	-1.66561207331366	-0.03588807463855
C	-3.73707202168633	-0.37098774471695	-0.02664476045292
C	-2.62274616599219	-0.05589513883837	-0.81914019336332
P	-1.92259050525555	1.63812167756611	-0.88314772272164
O	-0.42620422627966	1.54254703668328	-1.25235049362138
K	0.52127574100563	3.03217851125622	2.32422361391669
O	1.87216519494700	0.78589515631323	2.53427246386615
S	1.70605134829196	-0.60100861840401	1.89509612027467
C	3.27032637291013	-1.48381052427731	2.24752133653588
C	1.95087072776410	-0.38408701943224	0.09807785538279
O	1.17321190296339	3.47567277368145	-0.24929957356011
H	0.59671136465844	2.79593041057131	-0.70381974348246
H	1.97530771115572	-1.37274797986018	-0.37355322138482
H	1.10499744042187	0.19309209265122	-0.29343005380603
H	2.88790075504105	0.15580574749298	-0.07242056566728
H	3.26925132759533	-2.44905943235019	1.73055092370164
H	4.11325035867149	-0.86551359276299	1.92331396142356
H	3.31622849702635	-1.64104557231506	3.32819502623735
H	-4.17567789386469	0.38989872669412	0.61278639660640
H	-1.17580680161220	-0.81328237865821	-2.22593990418373
H	-5.12287420631973	-1.90218039060301	0.58942511747565
H	-2.12495952382614	-3.11273918602591	-2.25849704149607
H	1.52308535029643	4.04467488539599	-0.94919378037966
H	-4.10097319668681	-3.66078860901553	-0.84547583519972
H	-1.08451557049602	2.52340943183837	-3.52027077913470
H	-2.22668314374385	3.76607306437723	-5.35728293308709



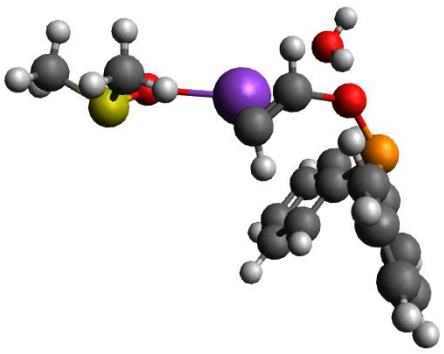
DMSO·H_2O·K^+[CH=CHPO(Ph)$_2$]$^-$

(3A`)

C	-2.12279258932181	2.82759641498979	-3.41720967649354
C	-2.76640641432189	3.52677611702301	-4.44363292483627
C	-2.80985559598133	2.51043456932705	-2.23615394544665
C	-4.10058400613370	3.91863113571572	-4.29531090538149
H	-4.60116345233155	4.46413670812601	-5.09197863467434
C	-4.14721981468848	2.91367658117228	-2.09097450769755
C	-4.79010627103239	3.61170527513622	-3.11650111563437
H	-4.68614162431537	2.68780508534746	-1.17330957736992
H	-5.82590944069361	3.91989287039719	-2.99428740243707
C	-2.05033966532442	1.98474477560738	1.91108027225084
H	-1.83032562572605	0.89490431595605	1.85603241020352
C	-2.25461571766042	2.50124029175692	0.66873585010344
H	-2.49614180127441	3.56105181236451	0.51322024382316

42

C	-2.50958888698480	-0.23892230110865	-1.55071893614676
C	-2.44216050733754	-1.63158465894433	-1.65788951515191
C	-2.67624606832253	-2.44003818992580	-0.53875587462461
C	-2.99489867453610	-1.84300940152741	0.68617771431509
C	-3.07490452128232	-0.44810582247008	0.78456231776520
C	-2.81170160972543	0.37981176831305	-0.32453103677002
P	-2.99563881233222	2.22358549052111	-0.01571049487472
O	-1.56325723221396	2.68298149946447	0.69482589674078
K	0.23767105117154	-0.38004950009670	1.31116932730706
O	2.60055780111757	-1.29650546489744	0.63974364568761
S	3.44005765164379	-0.98469147208166	-0.61447639549008
C	5.14012484793997	-1.50846567438096	-0.18989543062684
C	3.70987561418531	0.81661616345867	-0.63265635971696
O	-1.14670491392924	1.27147833895273	3.04208907231529
H	-1.39296860067945	1.93330669191829	2.34834322715356
H	4.35950931880973	1.06456801729004	-1.47994374228491
H	2.71280006442648	1.27913459364256	-0.76254395752812



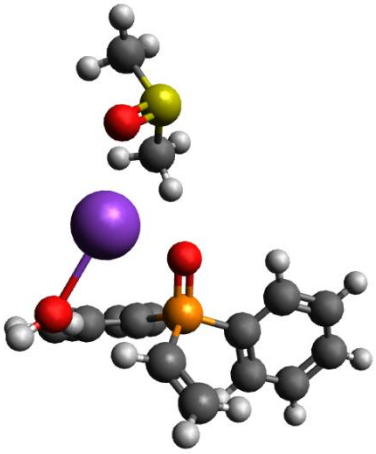
DMSO·H_2O·K^+[CH=CHOP(Ph)$_2$]$^-$

(3B`)

H	4.16692489238270	1.12422002530262	0.31433977516505
H	5.82092786776246	-1.21853615261501	-0.99703405722218
H	5.43407861851387	-1.04235021047113	0.75567105494815
H	5.13036278757735	-2.59642263170421	-0.08327196212602
H	-3.34325759219445	0.00378799665439	1.73725582916171
H	-2.31507192025866	0.37090918349908	-2.42814574640029
H	-3.20629185519744	-2.45992150896295	1.55748060926228
H	-2.20012250345731	-2.08598629049876	-2.61604746254304
H	-1.26162129817577	1.71038687848873	3.89719345234038
H	-2.62525118437291	-3.52297137806770	-0.62483100236117
H	-1.21563184825421	4.16377345563578	-1.46179494013150
H	-1.42881437463916	5.28570814074036	-3.65620446291666
C	-2.04126752605559	3.90907675641065	-2.11785675422209
C	-2.16084881383816	4.53676362061592	-3.36225159700695
C	-2.96596278900542	2.92955259831700	-1.72290078926363
C	-3.20677521406760	4.20279938534873	-4.22752544109434
H	-3.29649228737949	4.69232400146254	-5.19447576187737
C	-4.02940993244624	2.61779982339639	-2.59104515073300
C	-4.14418123439011	3.24011869319194	-3.83622674333017
H	-4.77813609497849	1.88511286657163	-2.29314158743453
H	-4.96858285938911	2.97917612226035	-4.49631467062385
C	0.38220537947140	1.77776375942195	-0.79711560750471
H	-0.34449516506986	1.37596256285540	-1.50990357537588
C	-0.10094774101825	2.43108519173053	0.23763916836141
H	0.43693616653039	2.94638703228667	1.03228796485957

42

C	-2.75868234969281	-1.76140003463000	-0.08792054915472
C	-3.49868727165972	-2.91278135731716	-0.37645064624858
C	-4.77250438428444	-2.80296853432747	-0.94148056540447
C	-5.30855953463881	-1.53917054336681	-1.21546713470390
C	-4.57096383182487	-0.38807533049552	-0.92752701745282
C	-3.28792948770466	-0.49161790742817	-0.36285806265463
P	-2.27073237294208	0.96992833891728	0.06357714652926
O	-0.88918934511686	0.54317289184636	0.55940162355720
K	0.52063136925346	2.33391322442111	2.07382804852428
O	2.77055923540177	1.07236220268519	1.37763820750410
S	3.01597415719777	-0.14692224269655	0.48080895030366
C	4.64406192408418	0.14060464016241	-0.30518094405566
C	1.97964097030731	0.08385053661570	-1.00565929572540
O	-1.08600456281377	4.15768612771229	1.69156064754162
H	2.15341664560296	-0.74967287843030	-1.69515667163871
H	0.93831310609805	0.09161222560062	-0.66379681602028
H	2.22648121254317	1.03992070280271	-1.47881847202756
H	4.83135256335796	-0.63512175486001	-1.05506108456383
H	4.65086339931636	1.13643109076934	-0.75917553306934
H	5.39852722448159	0.08591693559170	0.48389520340556
H	-4.99342098043717	0.58939233014331	-1.14743671236811
H	-1.76794506655415	-1.83429880586465	0.35220768593844
H	-6.29938274105293	-1.45031491475104	-1.65439850296179
H	-3.08022409566413	-3.89310383235395	-0.16107204703746
H	-1.32658637752317	5.07063825201793	1.90471746869058
H	-5.34759151127780	-3.69769855457207	-1.16806872943572
H	-2.68298419447536	0.47132168026876	-2.85514992378997
H	-2.39582540135653	1.92221317532025	-4.83356756358864
C	-2.38717220520807	1.50802260142312	-2.71830034669441
C	-2.22265651992235	2.32698063488315	-3.83898925979216

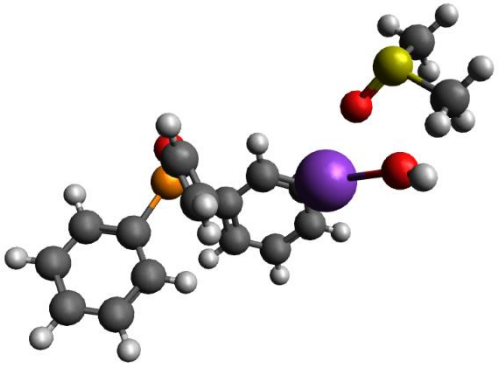


DMSO· KOH· $(C_6H_5)_2P(O)CH=CH_2$

(4A`)

C	-2.17194237913523	2.02281216298343	-1.42820019184223
C	-1.84026782873242	3.66292340651663	-3.67826455701609
H	-1.71709015352822	4.30134672158666	-4.55052499605878
C	-1.77554171635427	3.36587669090728	-1.26546146472388
C	-1.61431013263118	4.17360931364201	-2.39574386155399
H	-1.57248945103375	3.77737288105106	-0.26451322952514
H	-1.31130794038759	5.21024054116279	-2.26652319453700
C	-4.27151182669325	1.57718022501607	1.93137465277778
C	-3.14099109982018	1.94682147084248	1.31596937232833
H	-2.59629773420462	2.87727284539267	1.58089685051334
H	-4.80864224733615	0.65967824350272	1.69678011165904
H	-4.70354706363784	2.20242459730853	2.71173140437221

42



DMSO · KOH · $(C_6H_5)_2POCH=CH_2$

(4B`)

C	-4.48719069303871	-0.10075104025360	-0.69791511926262
C	-5.60616430409466	-0.91529921510110	-0.50747206998158
C	-6.72592665030157	-0.42619250145181	0.17391156776018
C	-6.72660130278713	0.88522750807451	0.65638812225020
C	-5.61055356341858	1.70145405019619	0.45342633834819
C	-4.46867843054172	1.21899424466087	-0.21395918734563
P	-3.10535448707421	2.46404004573674	-0.38003038289936
O	-2.15067432870820	2.24429204584444	1.01689900466065
K	1.48844917805839	-0.38545266184327	-0.18273420591206
O	2.89514778748100	1.82615945562173	-0.70159963732114
S	4.30791774861804	1.93843878420187	-0.08518566323614
C	5.15060471396078	3.21733044029680	-1.08642219105080
C	5.23373362112157	0.47548295861024	-0.63430035087840
O	3.43202215481485	-1.64704388365854	0.45999015308904
H	-1.14309032590309	-0.88843093475846	1.81435835707100
H	6.24304642348394	0.52879202745684	-0.20898830570397
H	4.67923580071071	-0.41220566572888	-0.22910612264657
H	5.27276275444797	0.45982242544378	-1.72951544540972

H	6.20118025274065	3.28053040418081	-0.78423568021679
H	5.06578347888375	2.95474176163428	-2.14567728833977
H	4.64895385467815	4.16992413483884	-0.89544444025387
H	-5.62455935159781	2.72807257191373	0.81427972540700
H	-3.63246322730847	-0.49881119750136	-1.23641343535574
H	-7.59591546293156	1.27664889959708	1.17888964131696
H	-5.60219259840075	-1.93362115788524	-0.88891558078019
H	3.89713961798072	-2.39597159300897	0.85762892492403
H	-7.59452597089173	-1.06320527025013	0.32192208420706
H	-0.19252529663330	2.40270009777372	-0.71876249856249
H	1.28446076367726	1.87048952222187	-2.60154768744203
C	-0.62709018261026	2.00348840674654	-1.63210719218534
C	0.21409419863569	1.70904166244868	-2.70987006342632
C	-2.01833855506218	1.80832591913796	-1.72467414069372
C	-0.32673467095661	1.22883717922111	-3.90869105790608
H	0.32361022451902	1.00332112526413	-4.75032288858847
C	-2.54977241999599	1.35122434283915	-2.94442715215281
C	-1.70942802663752	1.05764758953722	-4.02374367266727
H	-3.62316577390715	1.22477945146819	-3.06235392679857
H	-2.13980703290094	0.69783671161196	-4.95543511930433
C	-1.55200267441766	-0.12511834110631	1.15803838611468
H	-1.92708822921045	-0.43563345572505	0.19123870324821
C	-1.63985573323348	1.13011274946706	1.61743957079111
H	-1.26751328124873	1.39582040222633	2.60523992713349

S6. Single-crystal X-ray structure determination

X-ray diffraction data were collected at 100 K on a four-circle Xtalab Supernova diffractometer equipped with a HyPix3000 area detector using monochromatized Cu K_α radiation (**3a-d$_4$**), on a four-circle Rigaku Synergy S diffractometer equipped with a HyPix6000, using monochromatized Cu K_α radiation (**PdCl$_2$(3a-d$_4$)**), or with a HyPix6000HE area detector using monochromatized Cu K_α (**NiBr$_2$(3a-d$_4$), NiBr$_2$(3e)**, **NiBr$_2$(3e-d$_4$)**, **NiBr$_2$(3e-d$_{16}$)**) or Mo K_α (**NiBr$_2$(3a)**) radiation. Shutterless ω-scan technique were used in all cases. Cu K_α radiation was selected for 5 metal complexes due to small crystal sizes and relatively poor diffraction ability and for complexes **NiBr$_2$(3e)**, **NiBr$_2$(3e-d$_4$)**, and **NiBr$_2$(3e-d$_{16}$)** due to extensive non-merohedral twinning. The intensity data were integrated and semi-empirically corrected for absorption and decay based on measurements of equivalent reflections with the CrysAlisPro program.[23] The structures were solved by dual methods using SHELXT[24] and refined by the full-matrix least-squares method on F^2 using SHELXL-2018[25] within the OLEX2 program.[26] Positions of non-hydrogen atoms were found from the electron density-difference map; these atoms were refined with individual anisotropic displacement parameters. For **3a-d$_4$** and **NiBr$_2$(3a)**, the positions of hydrogen atoms were found from the electron density-difference map; these atoms were refined with individual anisotropic isotropic displacement parameters. For the other structures, all hydrogen atoms were placed in ideal calculated positions and refined as riding atoms (C-H distance = 0.950 Å for aromatic, 0.980 Å for methyl and 0.990 Å for methylene hydrogen atoms) with relative isotropic displacement parameters (U_{iso}(H)=1.5U_{eq}(C) for methyl groups or U_{iso}(H)=1.2U_{eq}(C) otherwise). A rotating group model was applied for methyl groups. Some reflections affected by the beam stop were omitted from the final steps of the refinement.

The absolute structure parameter (Flack) was determined by using quotients [(I+)-(I-)]/[(I+)+(I-)][27] for chiral crystals of **NiBr$_2$(3a)** and **NiBr$_2$(3a-d$_4$)** crystallized in the *I*2 (*C2*) space group and refined as monocrystals. The studied crystals **NiBr$_2$(3a)** and **NiBr$_2$(3a-d$_4$)** are isostructural but possess the opposite chirality.

All the studied crystals of chiral isostructural complexes **NiBr$_2$(3e)**, **NiBr$_2$(3e-d$_4$)** and **NiBr$_2$(3e-d$_{16}$)** contained multiple domains (from 3 to 7 major domains). The structures were refined using 2 to 4 major domains; the number and orientations of the major domains selected for further refinement were optimized to provide better R1 and ωR2 factors, better precision on bond distances and smaller absolute structure parameters. In addition to the found non-merohedral twinning, crystals of **NiBr$_2$(3e)**, **NiBr$_2$(3e-d$_4$)** and **NiBr$_2$(3e-d$_{16}$)** likely exhibit additional racemic twinning. All these obstacles, including omitting some major and all minor crystal domains, led to, on average, a relatively poor bond distance precision, unreliable absolute

structure parameters (calculated either by classical fit or from quotients), and a number of reflections with F_{obs}^2 being much smaller than F_{calcd}^2.

The *Mercury* program[28] was used for molecular graphics.

Crystal data, data collection and structure refinement details are summarized in Table S1. The structures have been deposited at the Cambridge Crystallographic Data Center with the reference CCDC numbers 2164954-2164960; they also contain the supplementary crystallographic data. These data can be obtained free of charge from the CCDC *via* http://www.ccdc.cam.ac.uk/data_request/cif

Table S1. Crystal data, data collection and structure refinement details.

Compound	**3a-d_4**	**$NiBr_2$(3a)**	**$NiBr_2$(3a-d_4)**	**$PdCl_2$(3a-d_4)**
Empirical formula	$C_{26}H_{20}D_4P_2$	$C_{26}H_{24}Br_2NiP_2$	$C_{26}H_{20}D_4Br_2NiP_2$	$C_{26}H_{20}D_4Cl_2P_2Pd{\bullet}CH_2Cl_2$
Formula weight	402.42	616.92	620.95	664.64
Temperature (K)	99.9(6)	100.0(1)	100.0(1)	100(1) K
Wavelength (Å)	1.54184	0.71073	1.54184	1.54184
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	I2 (C2)	I2 (C2)	$P2_1/c$
Unit cell dimensions				
a (Å)	12.9927(2)	14.7357(2)	14.76958(12)	12.23371(15)
b (Å)	5.42935(8)	8.18130(10)	8.13419(6)	15.33669(17)
c (Å)	16.1917(3)	31.1513(4)	31.1623(2)	15.30095(17)
β (°)	111.1377(19)	99.3775(12)	99.6666(8)	105.8845(12)
Volume ($Å^3$)	1065.35(3)	3705.32(8)	3690.64(5)	2761.21(6)
Z / Z'	2 / 0.5	6 / 1.5	6 / 1.5	4 / 1
Calcd. Density (g/cm^3)	1.254	1.659	1.676	1.599
Absorp. coef. (mm^{-1})	1.899	4.162	6.255	10.193
F(000)	420	1848	1848	1328
Crystal size (mm)	0.20×0.14×0.12	0.87×0.12×0.09	0.18×0.03×0.02	0.18×0.08×0.08
θ range (°)	3.764-70.696	2.238-33.499	2.877-79.537	3.757-78.853
Index ranges	-15≤h≤14,	-22≤h≤22,	-18≤h≤18,	-15≤h≤15,
	-6≤k≤6,	-12≤k≤12,	-9≤k≤10,	-19≤k≤18,
	-19≤l≤19	-48≤l≤48	-39≤l≤39	-19≤l≤17
Reflections				
Collected	8374	72208	41465	26319
Independent [R_{int}]	2057 [0.0373]	14530 [0.0575]	7855 [0.0367]	5727 [0.0873]
Observed [I>2σ(I)]	1903	13520	7712	5278
θ_{full} / θ_{max} (°)	67.684 / 70.696	33.499 / 25.242	67.684 / 79.537	67.684 / 78.853
Completeness to θ_{full} / θ_{max}	1.000 / 0.999	0.999 / 1.000	1.000 / 0.994	0.996 / 0.959
Data / restraints / parameters	2057 / 0 / 175	14530 / 1 / 528	7855 / 1 / 420	5727 / 10 / 328
Goodness-of-fit on F^2	1.103	1.047	1.068	1.082
R1 / ωR2 indices [I>2σ(I)]	0.0325 / 0.0851	0.0330 / 0.0827	0.0244 / 0.0646	0.0415 / 0.1133
R1 / ωR2 indices (all data)	0.0346 / 0.0874	0.0363 / 0.0839	0.0250 / 0.0648	0.0438 / 0.1158
Flack parameter	-	-0.003(4)	-0.050(12)	-
Number of quotients	-	5915	3460	-
$\Delta\rho_{max}$ / $\Delta\rho_{max}$ ($\bar{e}{\cdot}Å^{-3}$)	0.325 / -0.245	1.154 / -0.488	0.390 / -0.550	1.713 / -1.442
CCDC number	2164954	2164955	2164956	2164957

Table S1. Crystal data, data collection and structure refinement details (*cont.*).

Compound	**$NiBr_2$(3e)**	**$NiBr_2$(3e-d_4)**	**$NiBr_2$(3e-d_{16})**
Empirical formula	$C_{30}H_{32}Br_2NiP_2$	$C_{30}H_{28}D_4Br_2NiP_2$	$C_{30}H_{16}D_{16}Br_2NiP_2$
Formula weight	673.02	677.05	689.12
Temperature (K)	100.0(1)	100.0(1)	100.0(1)
Wavelength (Å)	1.54184	1.54184	1.54184
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1$	$P2_1$
Unit cell dimensions			
a (Å)	11.39760(19)	11.4120(4)	11.38816(10)
b (Å)	16.6937(3)	16.6991(4)	16.66903(18)
c (Å)	14.8531(3)	14.8765(4)	14.84741(15)
β (°)	91.7332(17)	91.629(3)	91.9150(8)
Volume ($Å^3$)	2824.78(9)	2833.87(14)	2816.90(5)
Z / Z'	4 / 2	4 / 2	4 / 2
Calcd. Density (g/cm^3)	1.583	1.587	1.587
Absorp. coef. (mm^{-1})	5.500	5.482	5.515
F(000)	1360	1360	1360
Crystal size (mm)	0.09×0.08×0.02	0.06×0.05×0.01	0.23×0.12×0.07
θ range (°)	3.985-79.711	3.981-79.461	3.884-79.438
Index ranges	-14≤h≤12	-14≤h≤14	-14≤h≤14
	-21≤k≤21	-21≤k≤21	-21≤k≤21
	-18≤l≤18	-18≤l≤18	-18≤l≤18
Reflections			
Collected	12854*	15002*	13566*
Independent [R_{int}]	12854 [0*]	15002 [0*]	13566 [0*]
Observed [I>2σ(I)]	12450	14242	13509
θ_{full} / θ_{max} (°)	67.684 / 79.711		
Completeness to θ_{full} / θ_{max}	0.984 / 0.967		
Data / restraints / parameters	12854 / 1 / 643	15002 / 1 / 641	13566 / 1 / 640
Goodness-of-fit on F^2	1.035	1.054	1.053
R1 / ωR2 indices [I>2σ(I)]	0.0757 / 0.2064	0.0779 / 0.2235	0.0575 / 0.1539
R1 / ωR2 indices (all data)	0.0768 / 0.2109	0.0864 / 0.2460	0.0578 / 0.1546
$\Delta\rho_{max}$ / $\Delta\rho_{max}$ ($ē·Å^{-3}$)	1.615 / -0.929	2.221 / -0.569	2.071 / -0.910
CCDC number	2164957	2164959	2164960

* Due to processing as multidomain structures, identical reflections were merged, decreasing the number of collected reflections to the number of unique reflections and providing R_{int}=0.

Two polymorphic modifications for 1,2-bis(diphenylphosphino)ethane, **3a**, are known to date: modification I (the CSD codes: DPPETH, DPPETH02 and DPPETH04; the CCDC deposition numbers: 1145364, 161363 and 2113126)[29-31] and modification II (CSD DPPETH01; CCDC 1145365).[29] The crystal structure of **3a-d$_4$** is isostructural with modification I of **3a**, in which the molecule of **3a-d$_4$** (Fig. S95) is located on an inversion center (Z'=0.5).

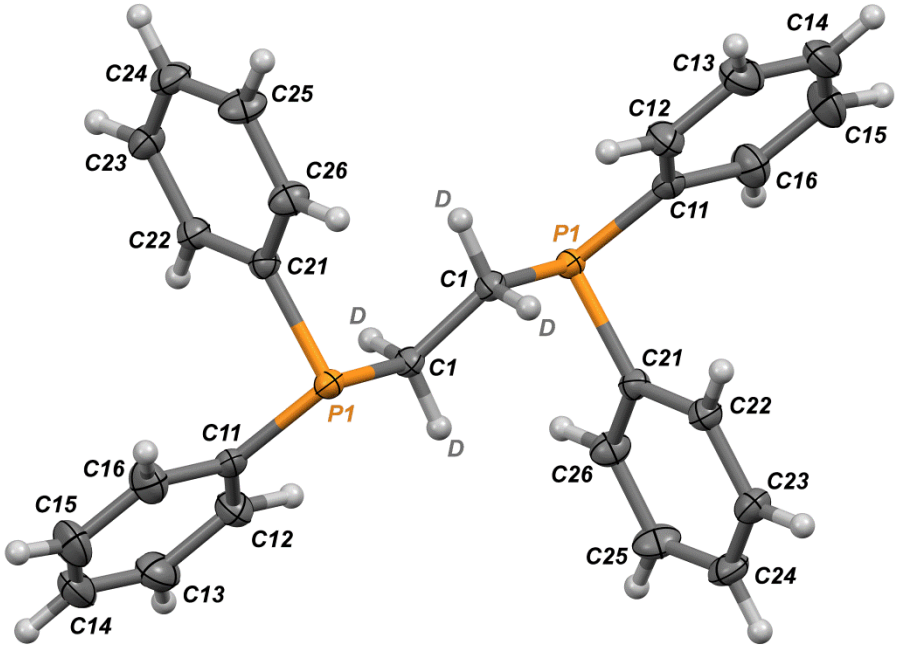


Fig. S95. The structure of **3a-d$_4$** (p=50%).

The crystal structures of **NiBr$_2$(3a)** (Figs. S96, S97) and **NiBr$_2$(3a-d$_4$)** (Figs. S99, S100) are isostructural. Their asymmetric units contain 1.5 molecules. One crystallographically unique molecule of **NiBr$_2$(3a-d$_4$)** (Figs. S96 and S99) is located in a general position, and the second one (Figs. S97 and S100) is situated on a 2-fold proper rotation axis passing through the Ni atom and the middle of the CH_2-CH_2 bond. Both molecules exhibit similar conformations (Fig. S98 for **NiBr$_2$(3a)**. The structure of **NiBr$_2$(3a)**, reported herein, is of better quality than that reported earlier for this chiral polymorphic modification (*C*2 space group, Z'=1.5, CCDC 805341, CSD refcode DAGBIY01).[32] The other known polymorphic modification of **NiBr$_2$(3a)** is centrosymmetric ($P2_1/c$, Z'=1, CCDC numbers 769521 and 1412269, CSD refcodes DAGBIY and DAGBIY02).[33, 34]

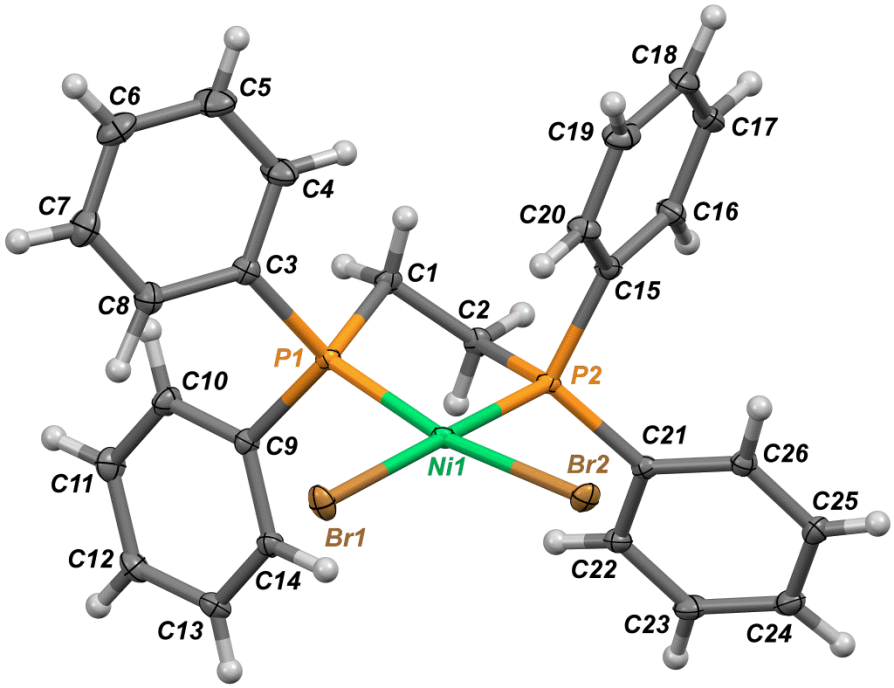


Fig. S96. The molecular structure of **$NiBr_2$(3a)**. The first crystallographically independent molecules is shown (p=50%). Selected bond distances (Å): Br1-Ni1 2.3305(5), Br2-Ni1 2.3428(5), Ni1-P1 2.1611(9), Ni1-P2 2.1425(9).

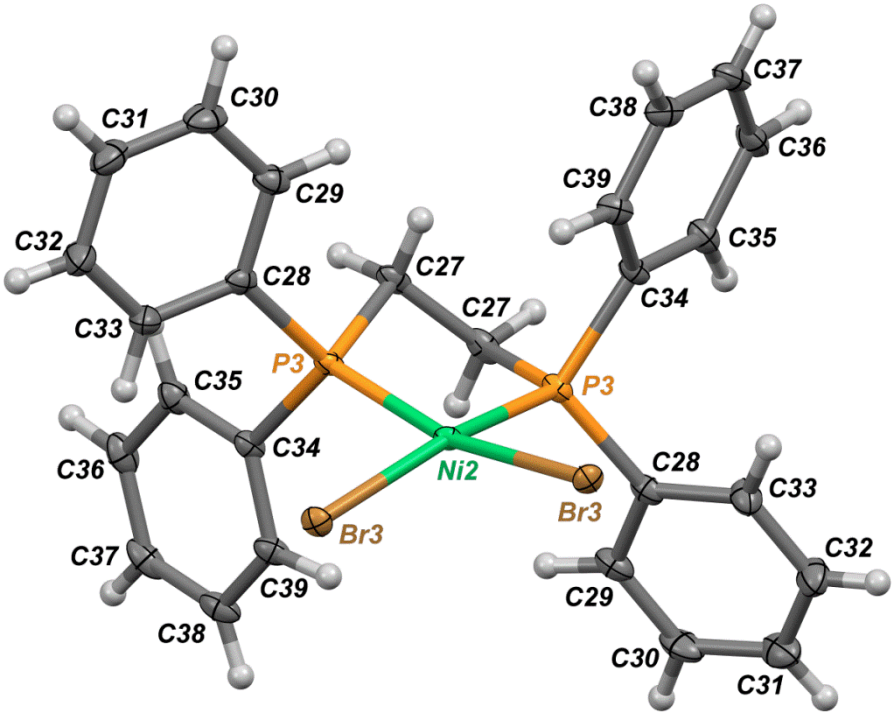


Fig. S97. The molecular structure of **$NiBr_2$(3a)**. The second crystallographically independent molecule is shown (p=50%). A 2-fold rotation axis passes through Ni2 and the middle of the C27-C27 bond. Selected distances (Å): Br3-Ni2 2.3427(5), Ni2-P3 2.1495(9).

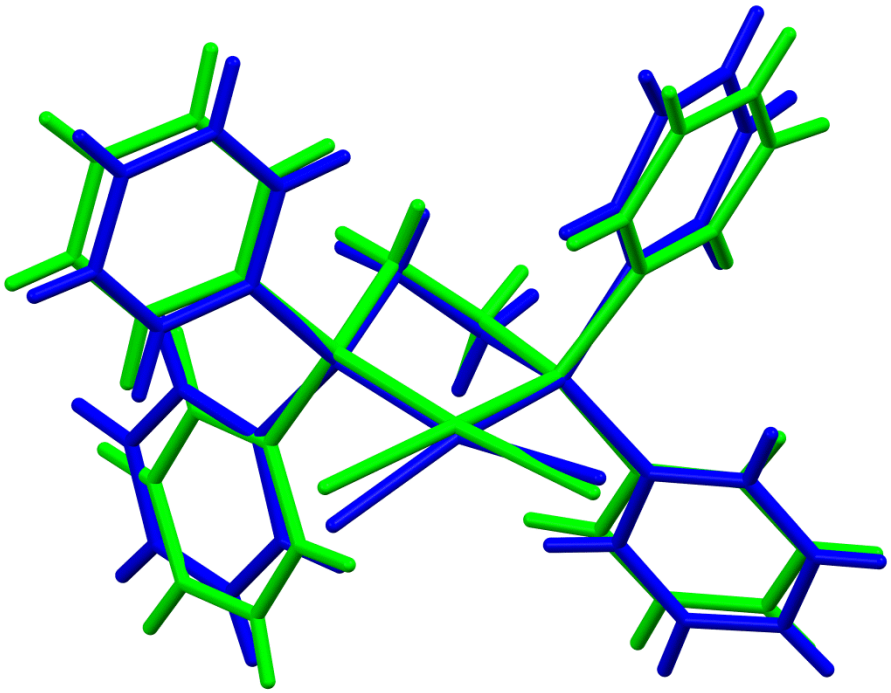


Fig. S98. The overlay of two crystallographically independent molecules exhibiting similar conformations. The first molecule (from Fig. S96) is marked in green, and the second molecule (from Fig. S97) is labeled in blue. The RMSD is 0.4190, and the maximum atom deviation is 0.7262 Å.

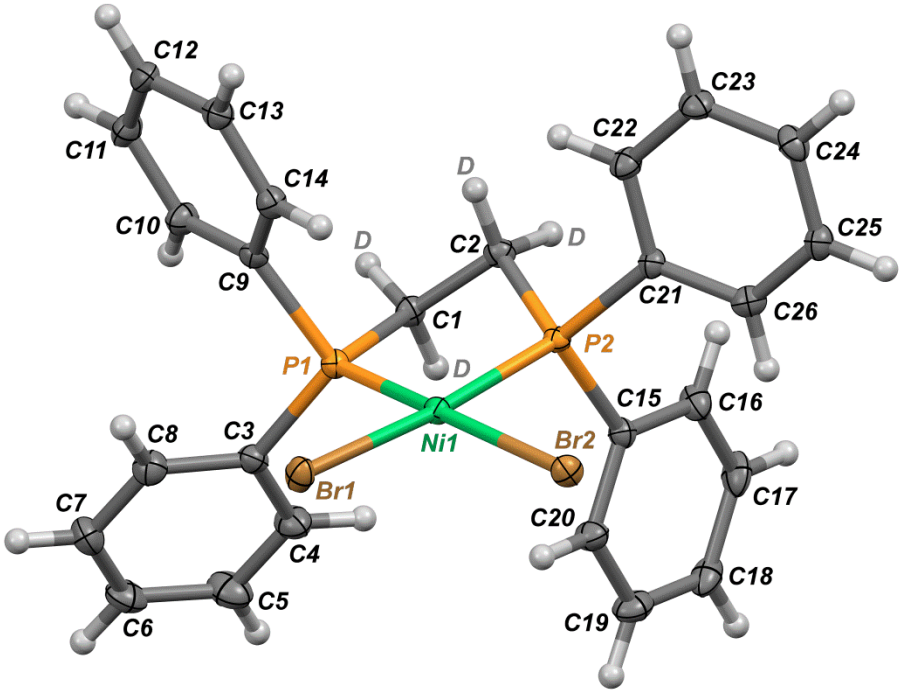


Fig. S99. One of two crystallographically independent molecules of **$NiBr_2$(3a-d_4)** (p=50%). Deuterium atoms are labeled ***D***. Selected bond lengths (Å): Br1-Ni1 2.3296(7), Br2-Ni1 2.3408(7), Ni1-P1 2.1608(11), Ni1-P2 2.1435(11).

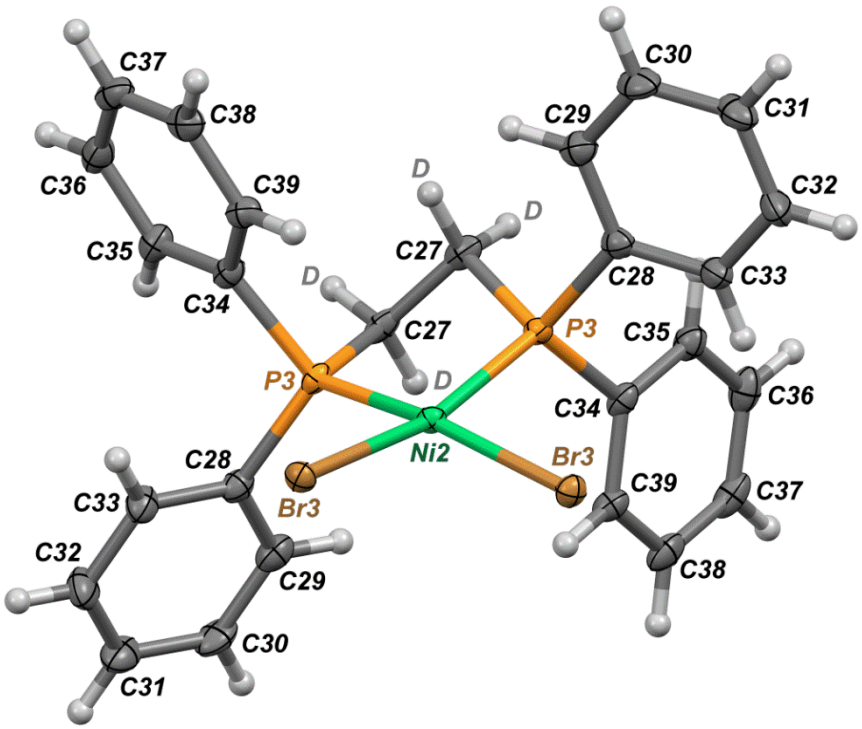


Fig. S100. The second crystallographically independent molecule of **$NiBr_2$(3a-d_4)** (p=50%). A 2-fold rotation axis passes through Ni2 and the middle of the C27-C27 bond. Deuterium atoms are labeled as ***D***. Selected distances (Å): Br3-Ni2 2.3420(7), Ni2-P3 2.1520(11).

The structure of **$PdCl_2$(3a-d_4)**•CH_2Cl_2 (Fig. S101) is isostructural with previously described non-deuterated **$PdCl_2$(3a)**•CH_2Cl_2 (CCDC 1145202, CSD refcode DPEPDC).[35] The conformations of **$NiBr_2$(3a)** (Fig. S96) and complex **$PdCl_2$(3a-d_4)** appeared to be very close (Fig. S102).

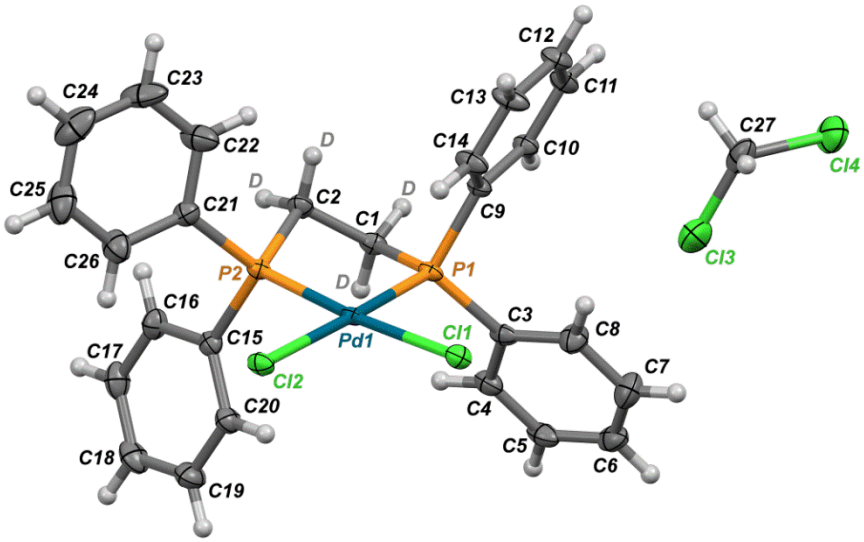


Fig. S101. The crystal structure of **$PdCl_2$(3a-d_4)** (p=50%). Deuterium atoms are labeled ***D***. The disorder of a non-coordinating dichloromethane molecule is omitted. Selected bond lengths (Å): Pd1-Cl1 2.3538(6), Pd1-Cl2 2.3652(6), Pd1-P1 2.2344(7), Pd1-P2 2.2230(7).

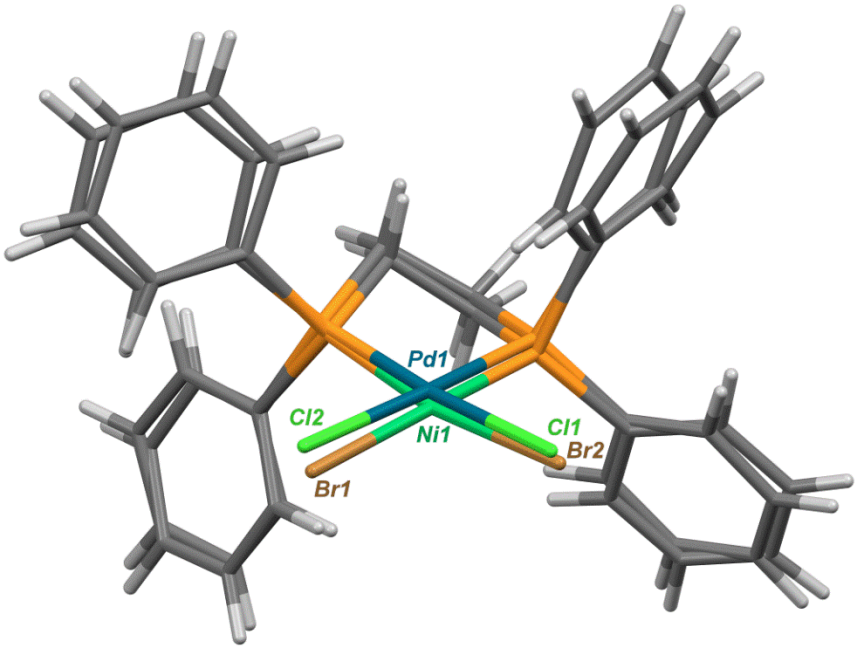


Fig. S102. The overlay of one crystallographically independent molecule of **$NiBr_2$(3a)** (Fig. S96) and complex **$PdCl_2$(3a-d_4)** (Fig. S101). The RMSD is 0.335 (H atoms are not taken into account).

Complexes **$NiBr_2$(3e)** (Figs. S103, S104), **$NiBr_2$(3e-d_4)** (Figs. S106, S107), and **$NiBr_2$(3e-d_{16})** (Figs. S108, S109) are isostructural. They crystalize as multidomain crystals in the $P2_1$ space group with two symmetrically inequivalent molecules, which exhibit very similar conformations (see Fig. S105 for **$NiBr_2$(3e)**).

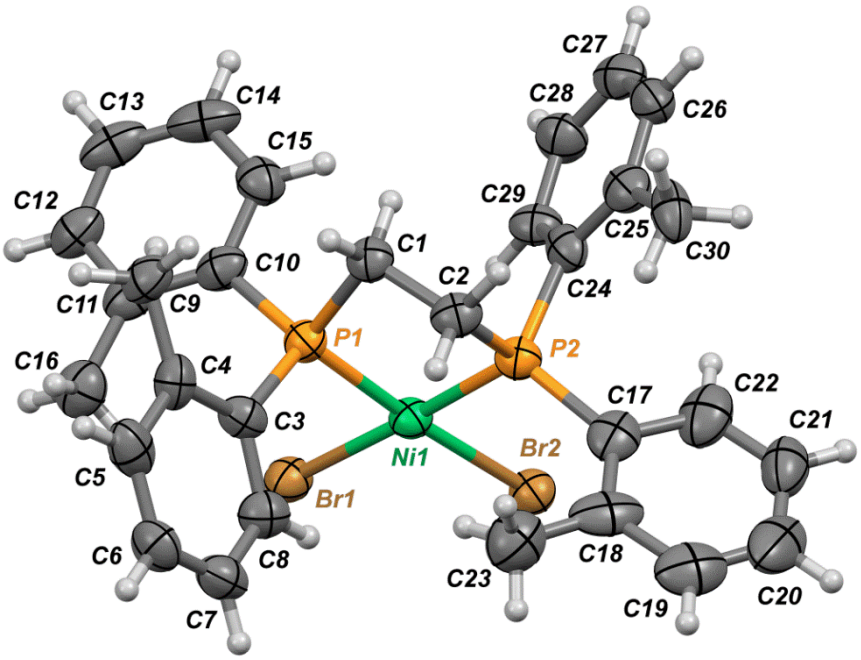


Fig. S103. The first crystallographically independent molecule of **$NiBr_2$(3e)** (p=50%). Selected distances (Å): Br1-Ni1 2.328(2), Br2-Ni1 2.349(2), Ni1-P1 2.182(4), Ni1-P2 2.166(4).

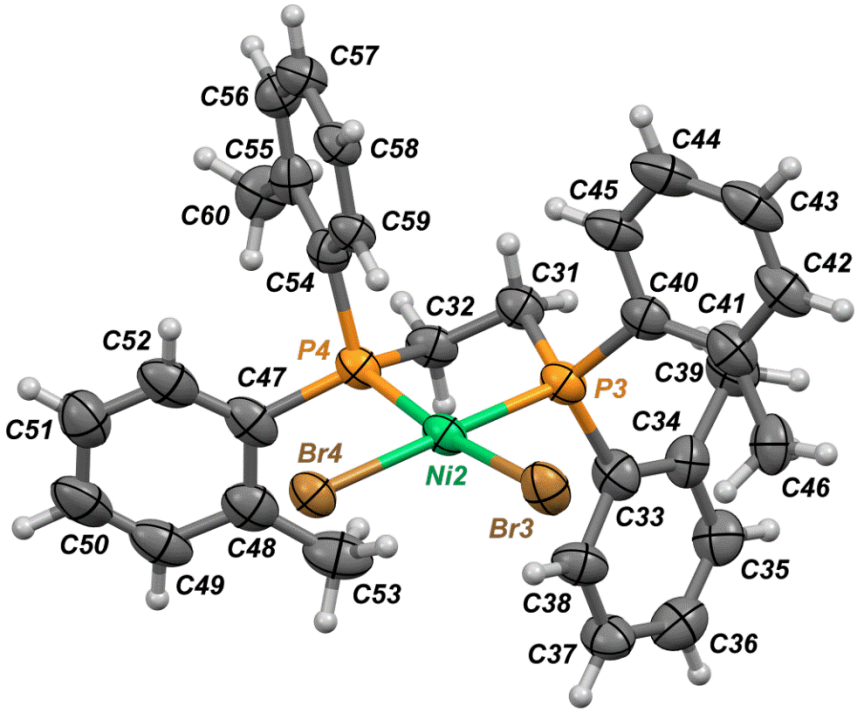


Fig. S104. The second crystallographically independent molecule of **$NiBr_2$(3e)** (p=50%). Selected distances (Å): Br3-Ni2 2.333(2), Br4-Ni2 2.331(2), Ni2-P3 2.178(4), Ni2-P4 2.178(4).

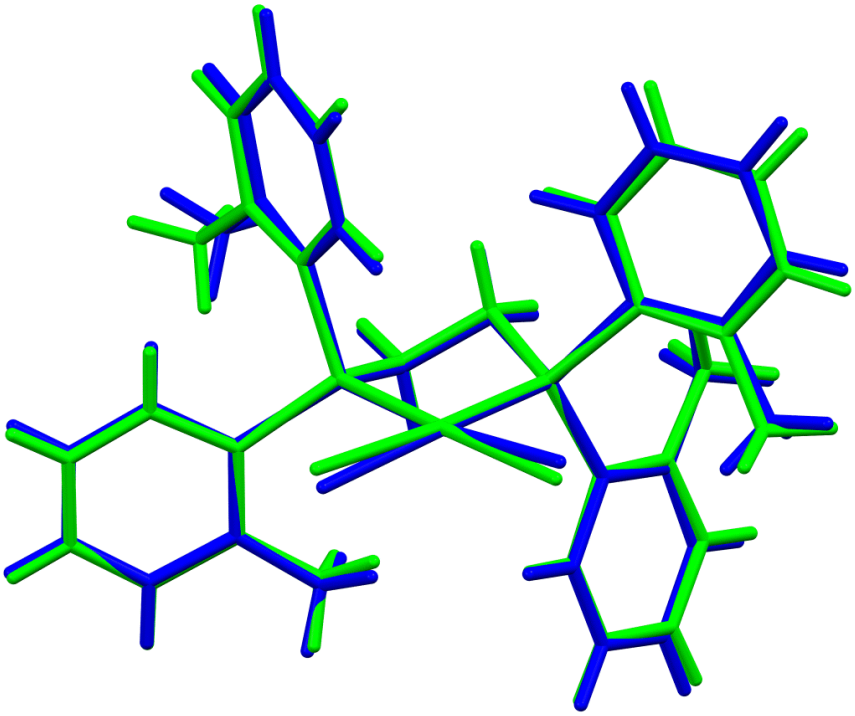


Fig. S105. The overlay of two crystallographically independent molecules of **$NiBr_2$(3e)** exhibiting similar conformations. The first molecule (from Fig. S103) is marked in green, and the second molecule (from Fig. S104) is labeled in blue. The RMSD is 0.1745, and the maximum atom deviation is 0.3532 Å.

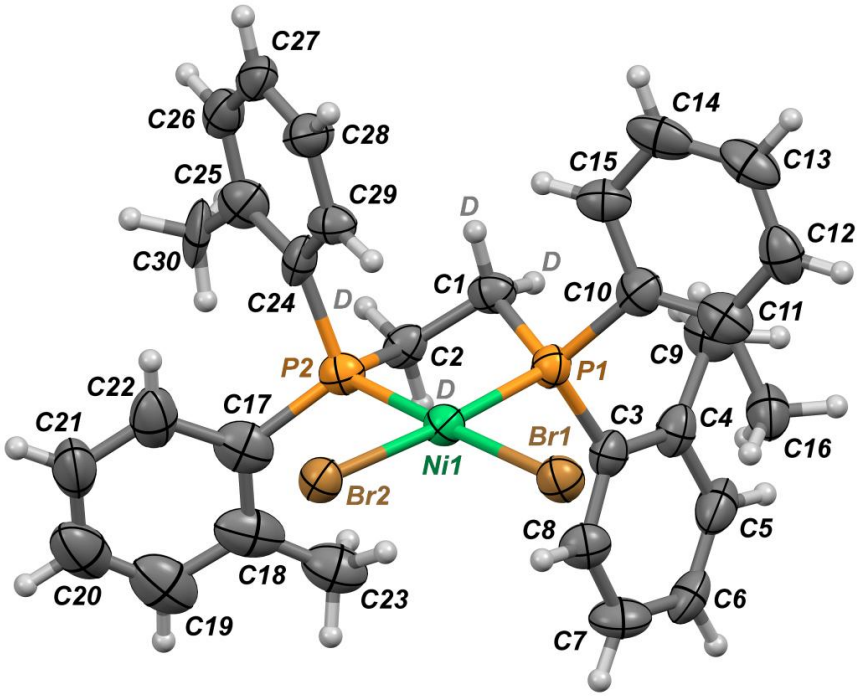


Fig. S106. The first crystallographically independent molecule of **$NiBr_2$(3e-d_4)** (p=50%). Deuterium atoms are labeled as ***D***. Selected distances (Å): Br1-Ni1 2.327(3), Br2-Ni1 2.352(3), Ni1-P1 2.176(5), Ni1-P2 2.173(5).

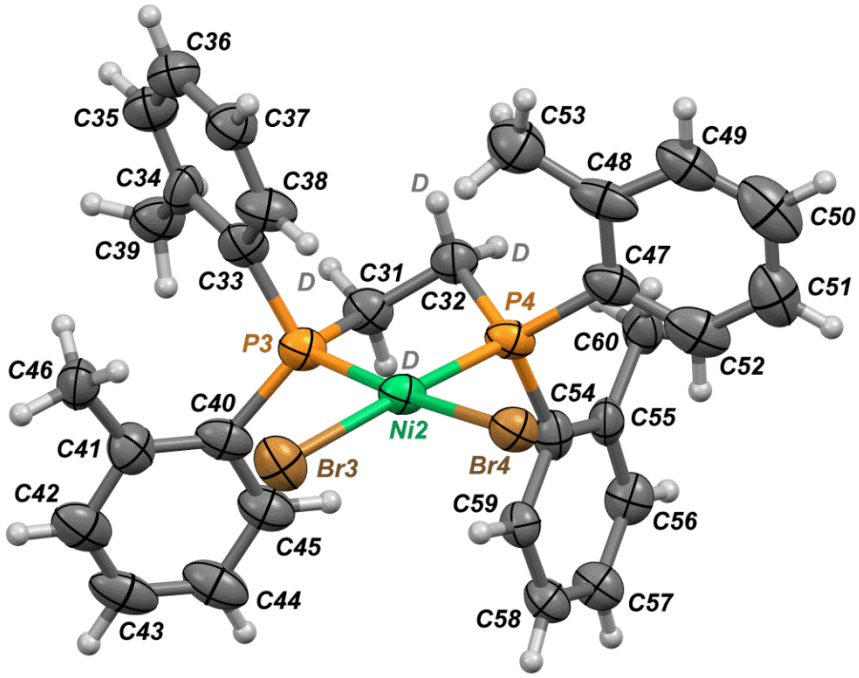


Fig. S107. The second crystallographically independent molecule of **$NiBr_2$(3e-d_4)** (p=50%). Deuterium atoms are labeled as ***D***. Selected distances (Å): Br3-Ni2 2.336(3), Br4-Ni2 2.328(3), Ni2-P3 2.182(5), Ni2-P4 2.179(5).

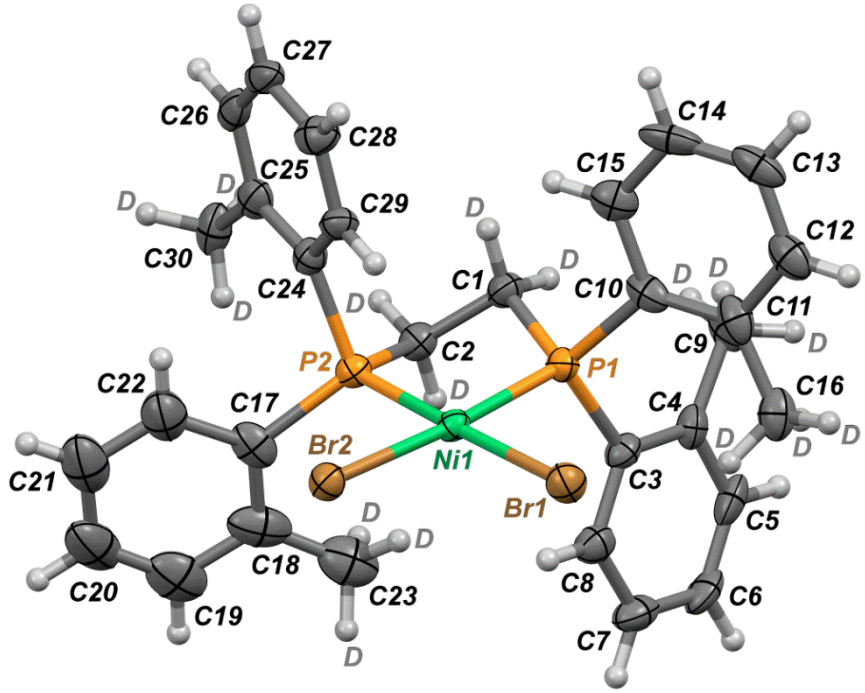


Fig. S108. The first crystallographically independent molecule of **$NiBr_2$(3e-d_{16})** (p=50%). Deuterium atoms are labeled as ***D***. Selected distances (Å): Br1-Ni1 2.3115(17), Br2-Ni1 2.3468(17), Ni1-P1 2.176(3), Ni1-P2 2.164(3).

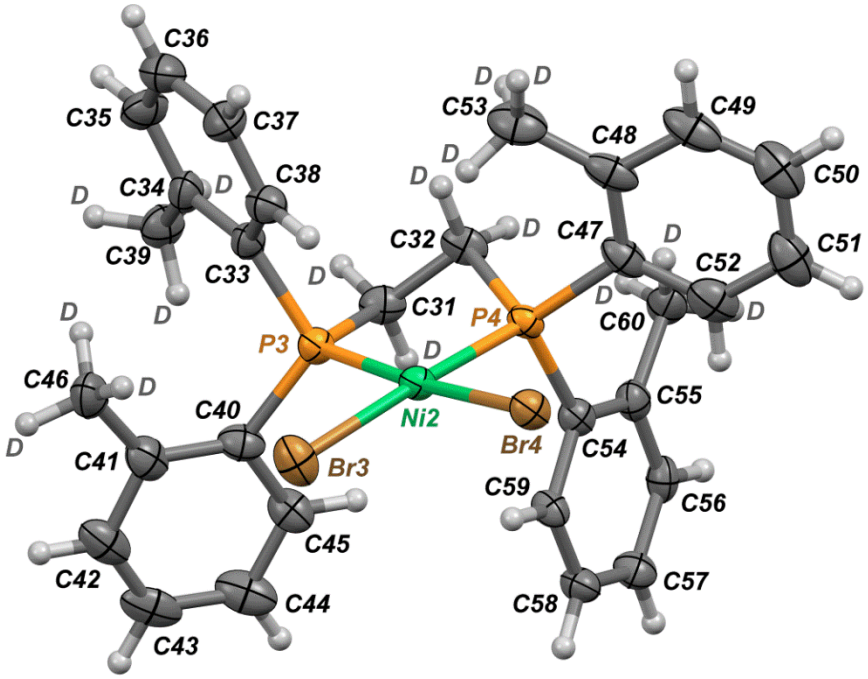


Fig. S109. The second crystallographically independent molecule of **$NiBr_2$(3e-d_{16})** (p=50%). Deuterium atoms are labeled as ***D***. Selected distances (Å): Br3-Ni2 2.3320(19), Br4-Ni2 2.3265(18), Ni2-P3 2.176(3), Ni2-P4 2.173(3).

S7. Powder XRD

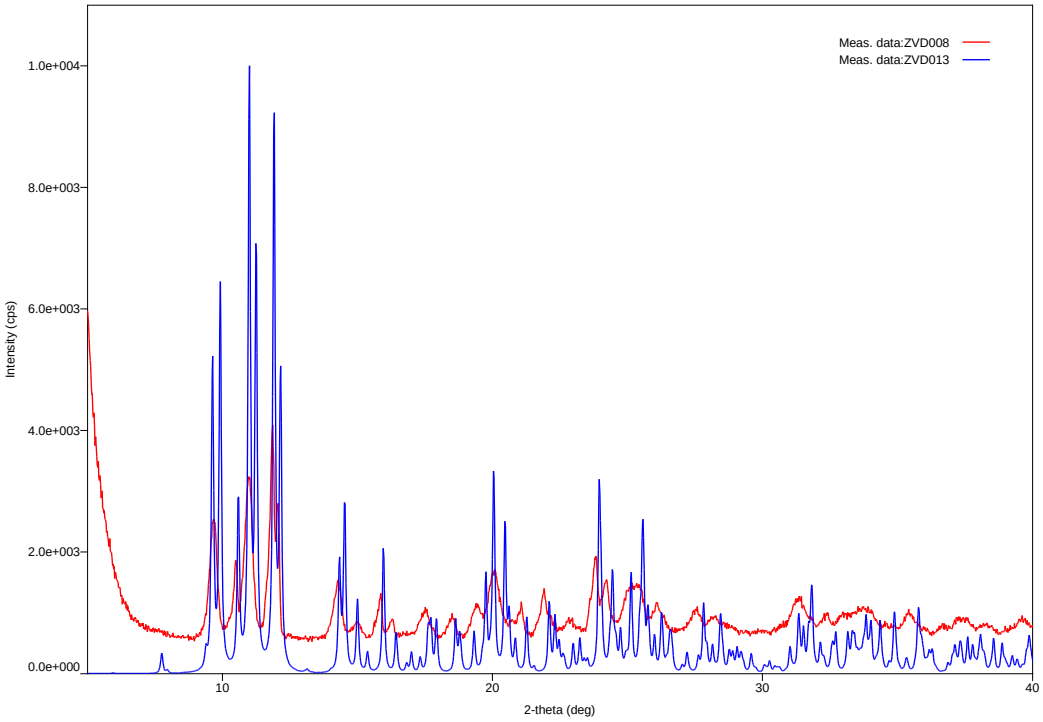


Fig. S110. X-ray patterns for **$NiBr_2$ (3e)**: *red* - obtained, *blue* – simulated from the corresponding single-crystal data. The shift of the diffraction peaks was due to different temperatures of experiments.

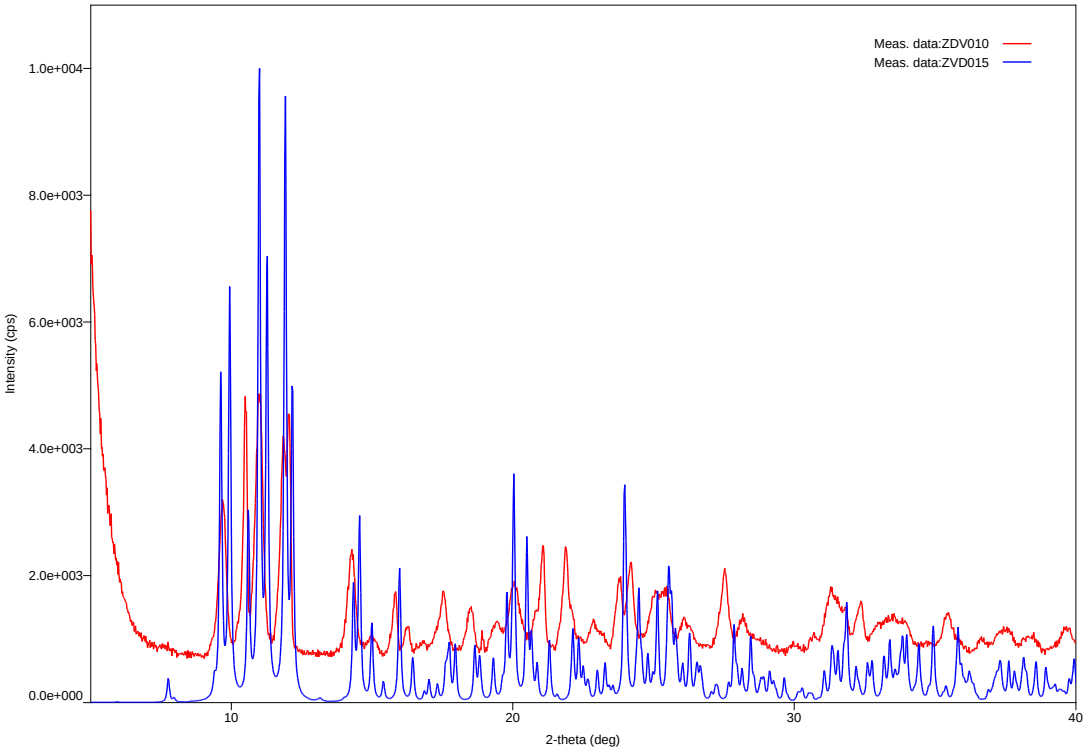


Fig. S111. X-ray patterns for **$NiBr_2$ (3e-d_{16})**: *red* - experimental, *blue* – simulated from the corresponding single-crystal data. The shift of the diffraction peaks was due to different temperatures of experiments.

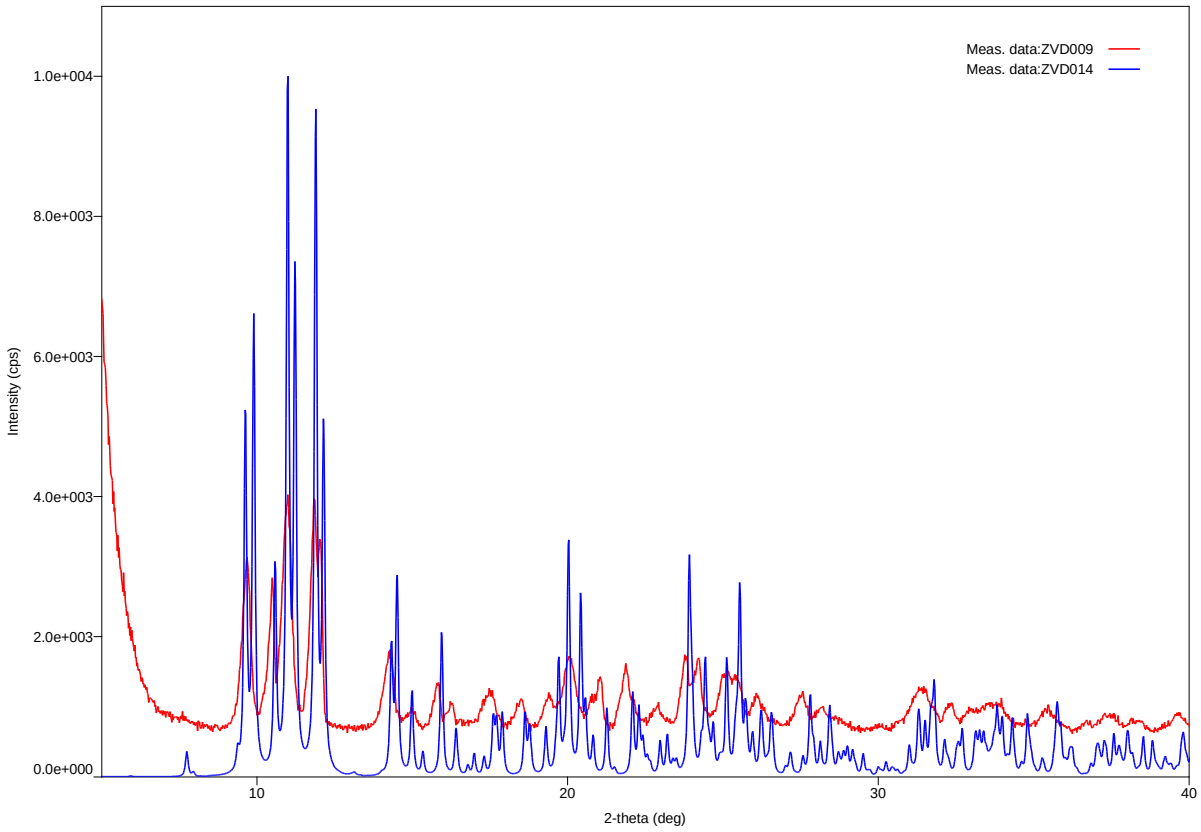


Fig. S112. X-ray patterns for **$NiBr_2$ (3e-d_4)**: *red* - experimental, *blue* – simulated from the corresponding single-crystal data. The shift of the diffraction peaks was due to different temperatures of experiments.

S8. NMR experiment with $^{13}C_2$-DPPE and DPPE

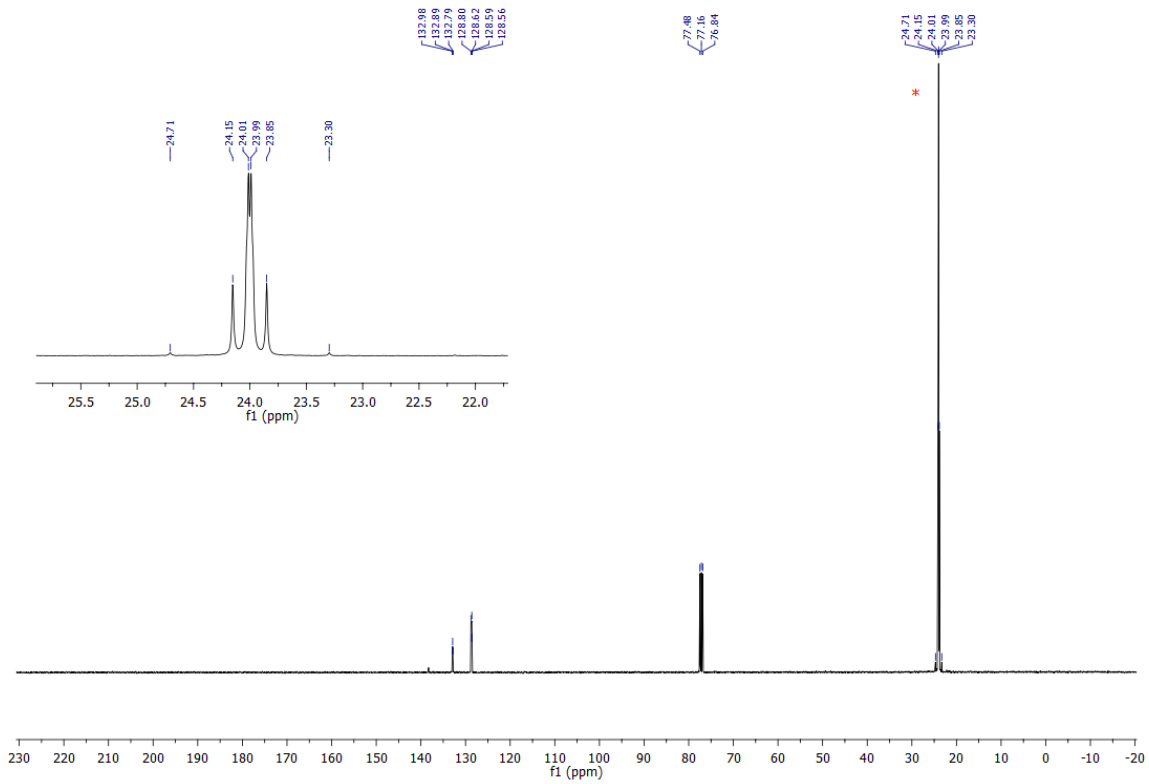


Fig. S113. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of $^{13}C_2$-DPPE (10 mg). The red asterisk indicates the signal of ^{13}C-labeled carbon atoms.

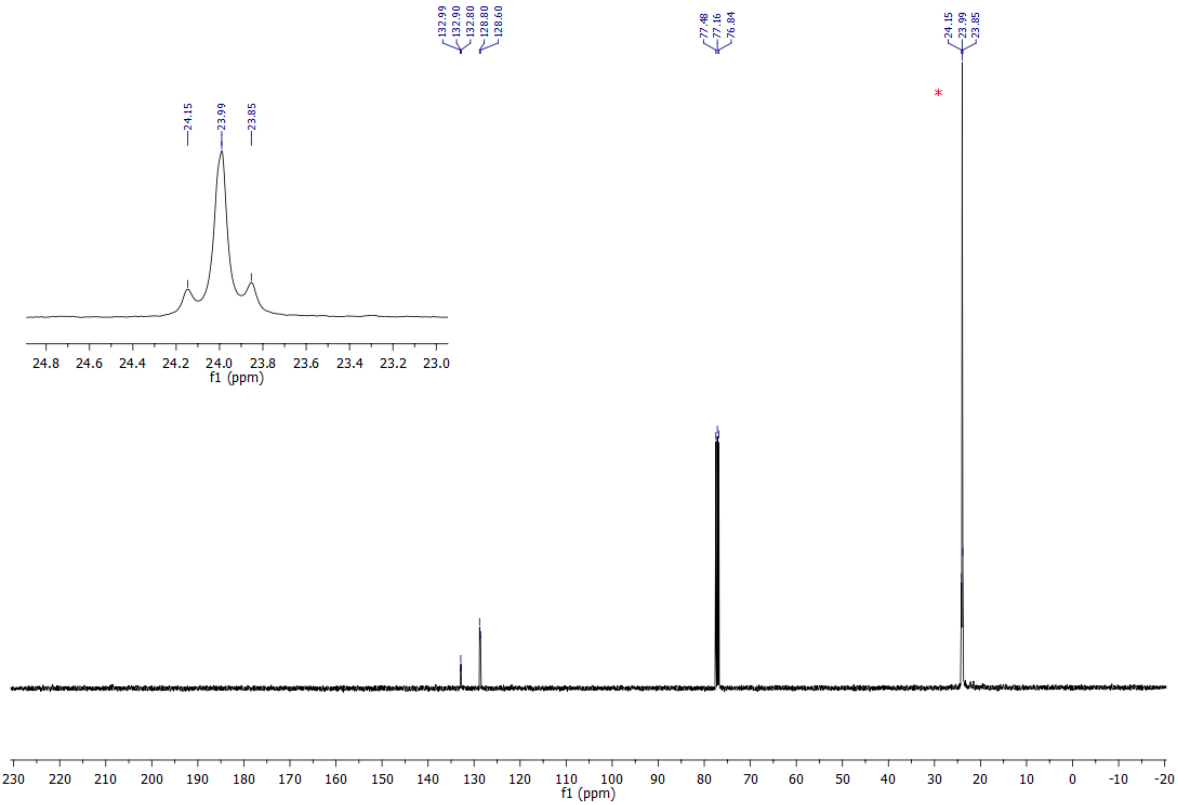


Fig. S114. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of $^{13}C_2$-DPPE (5 mg). The red asterisk indicates the signal of ^{13}C-labeled carbon atoms.

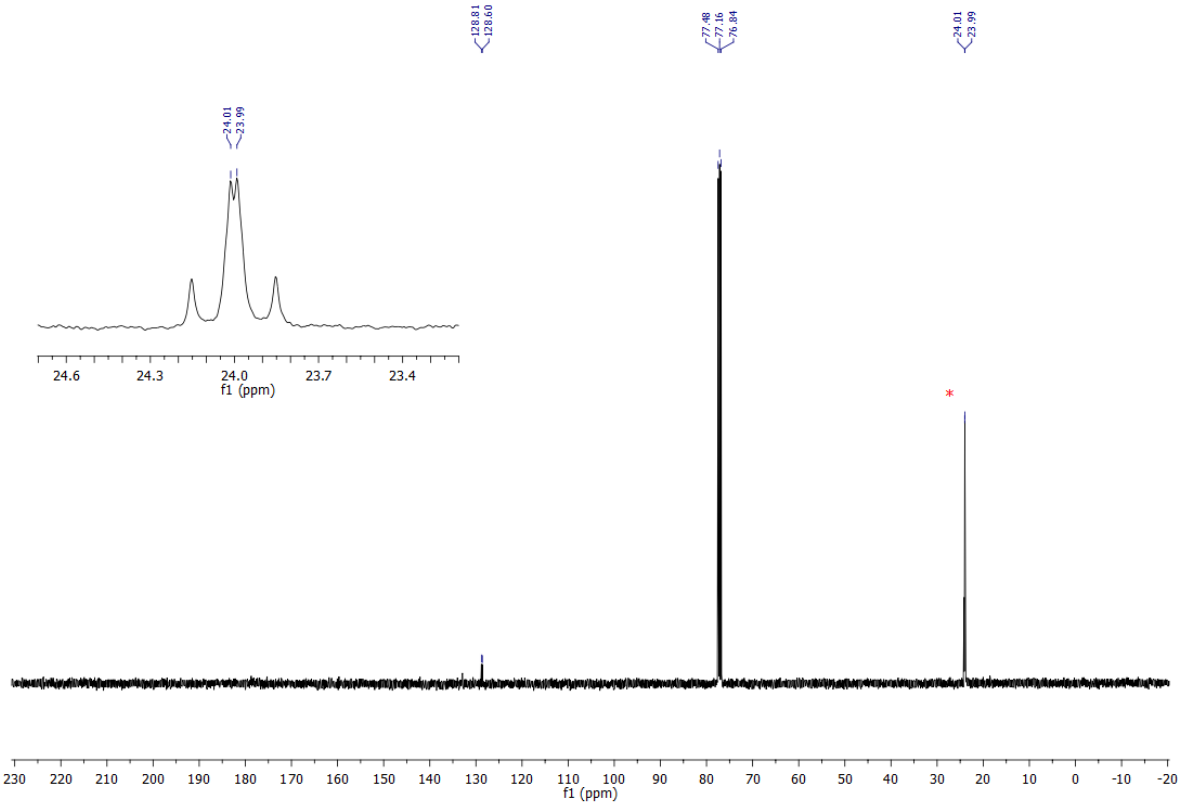


Fig. S115. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of $^{13}C_2$-DPPE (1 mg). The red asterisk indicates the signal of ^{13}C-labeled carbon atoms.

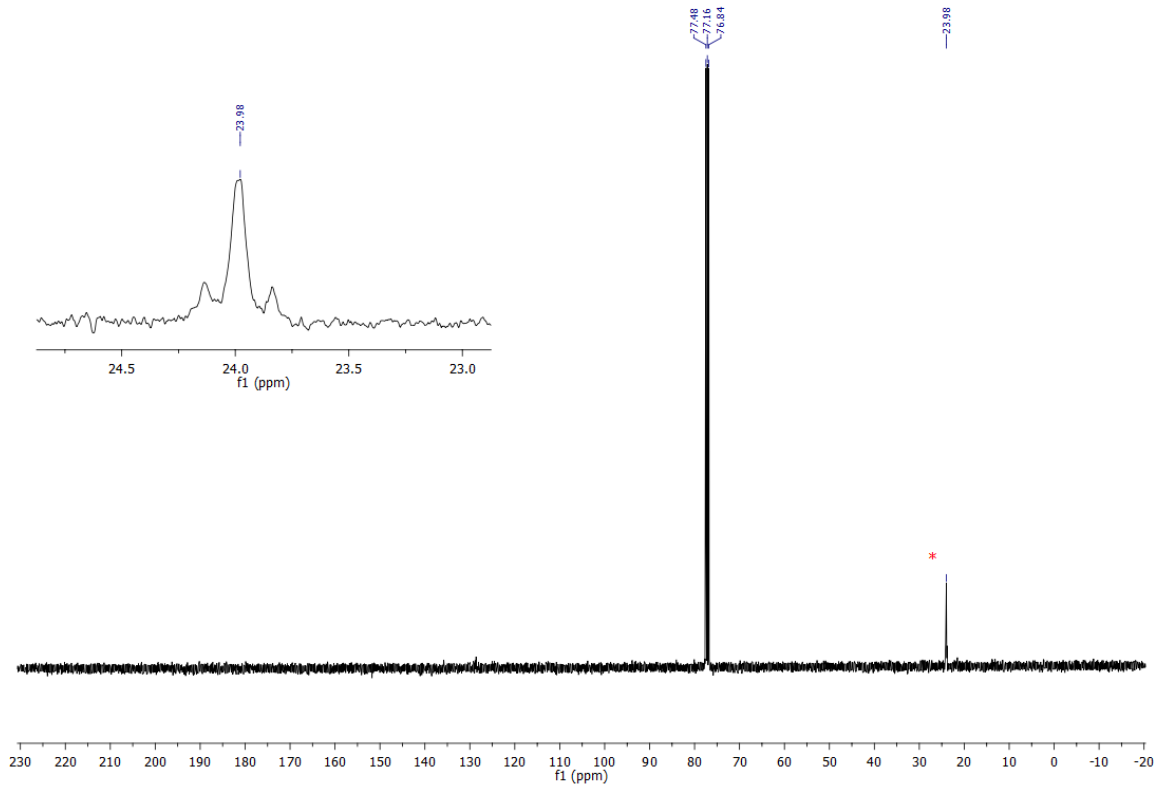


Fig. S116. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of $^{13}C_2$-DPPE (0.5 mg). The red asterisk indicates the signal of ^{13}C-labeled carbon atoms.

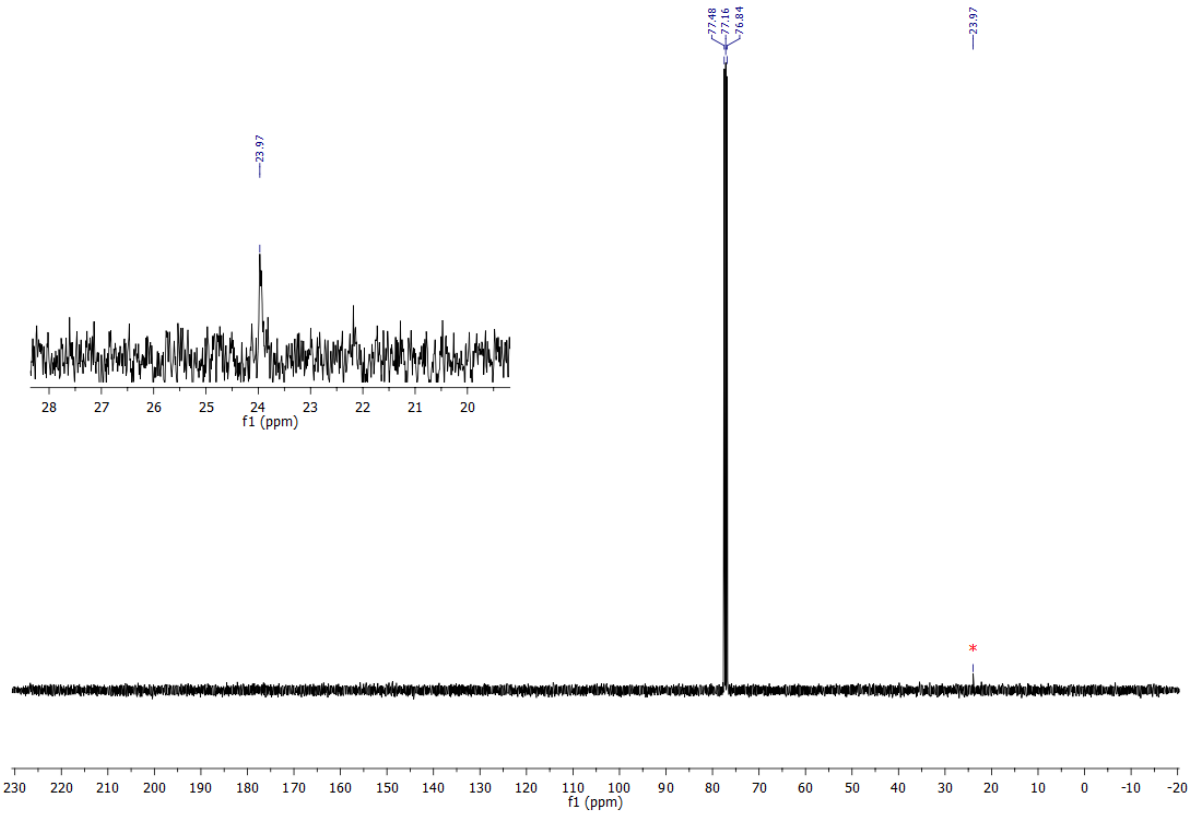


Fig. S117. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of $^{13}C_2$-DPPE (0.1 mg). The red asterisk indicates the signal of ^{13}C-labeled carbon atoms.

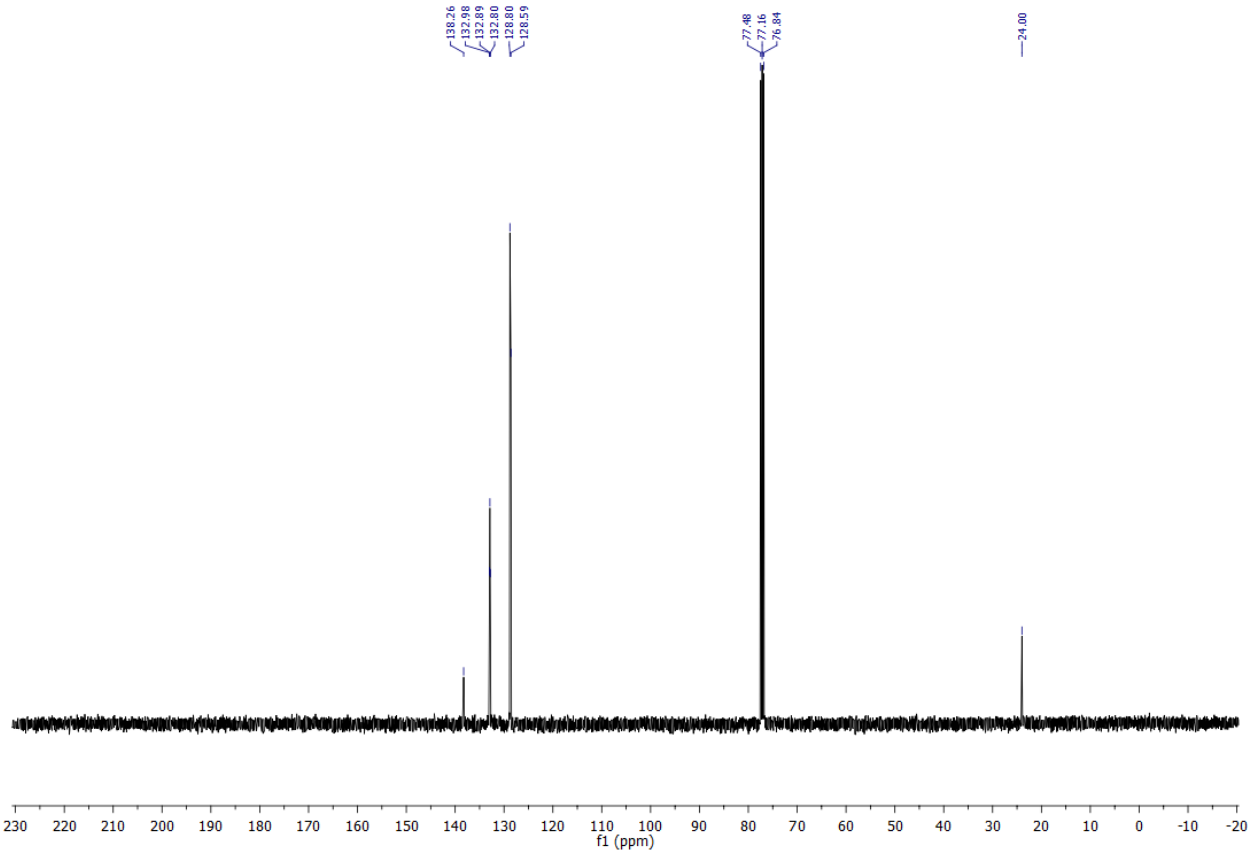


Fig. S118. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of DPPE (10 mg).

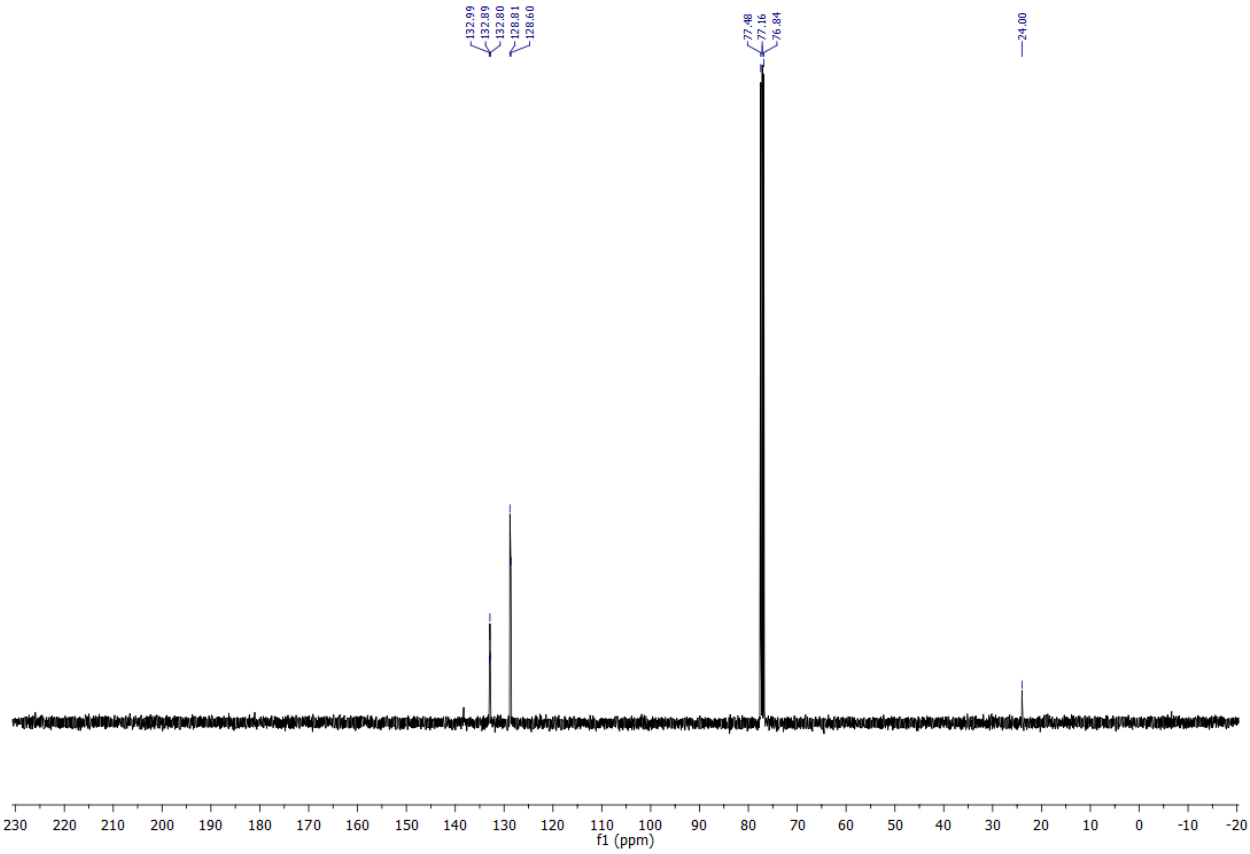


Fig. S119. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of DPPE (5 mg).

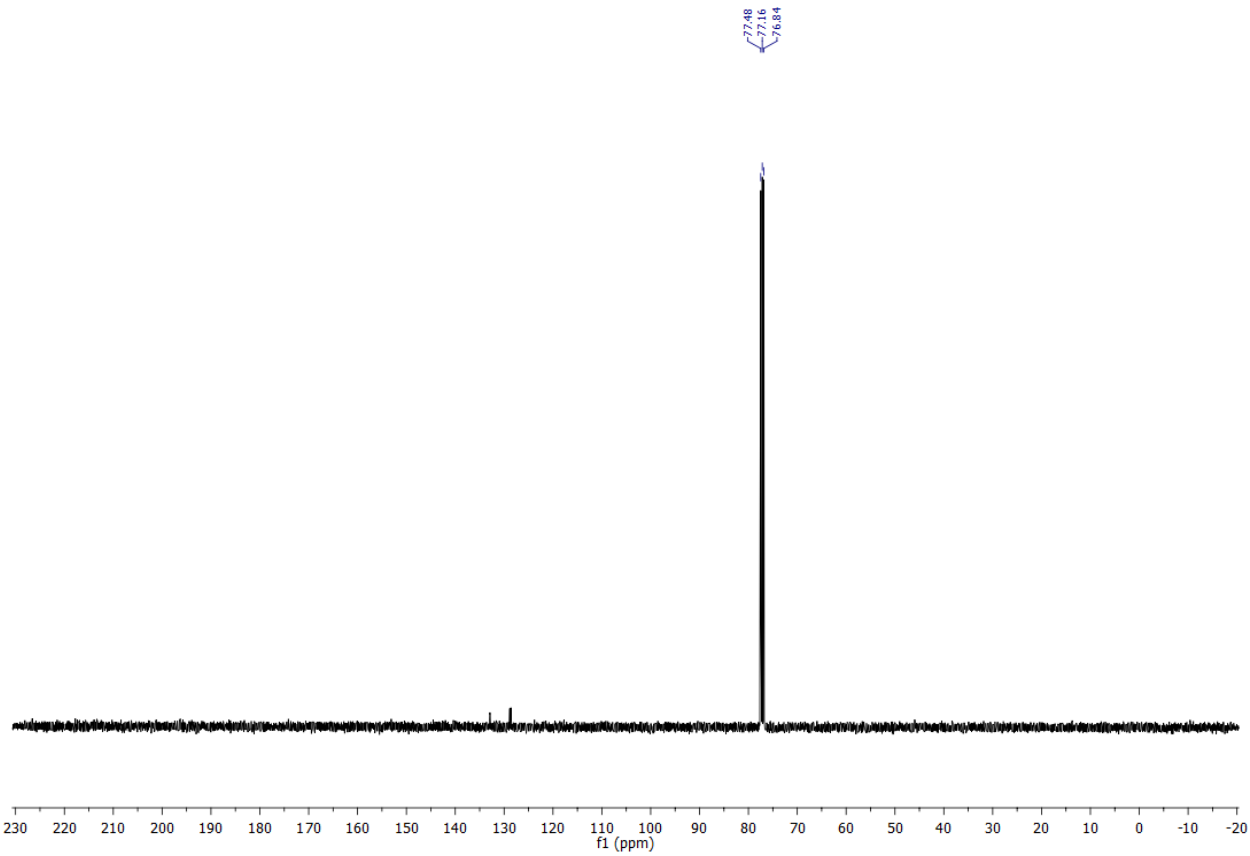


Fig. S120. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of DPPE (1 mg).

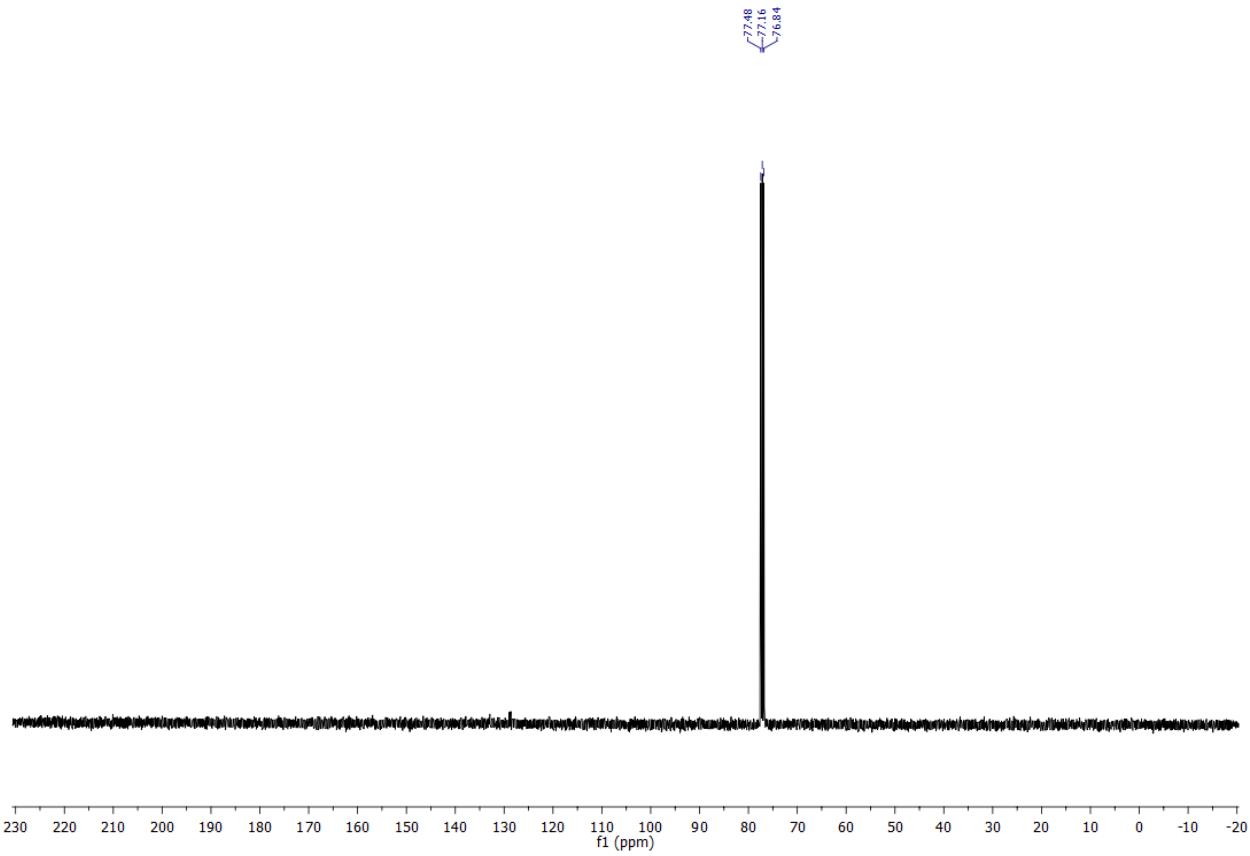


Fig. S121. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of DPPE (0.5 mg).

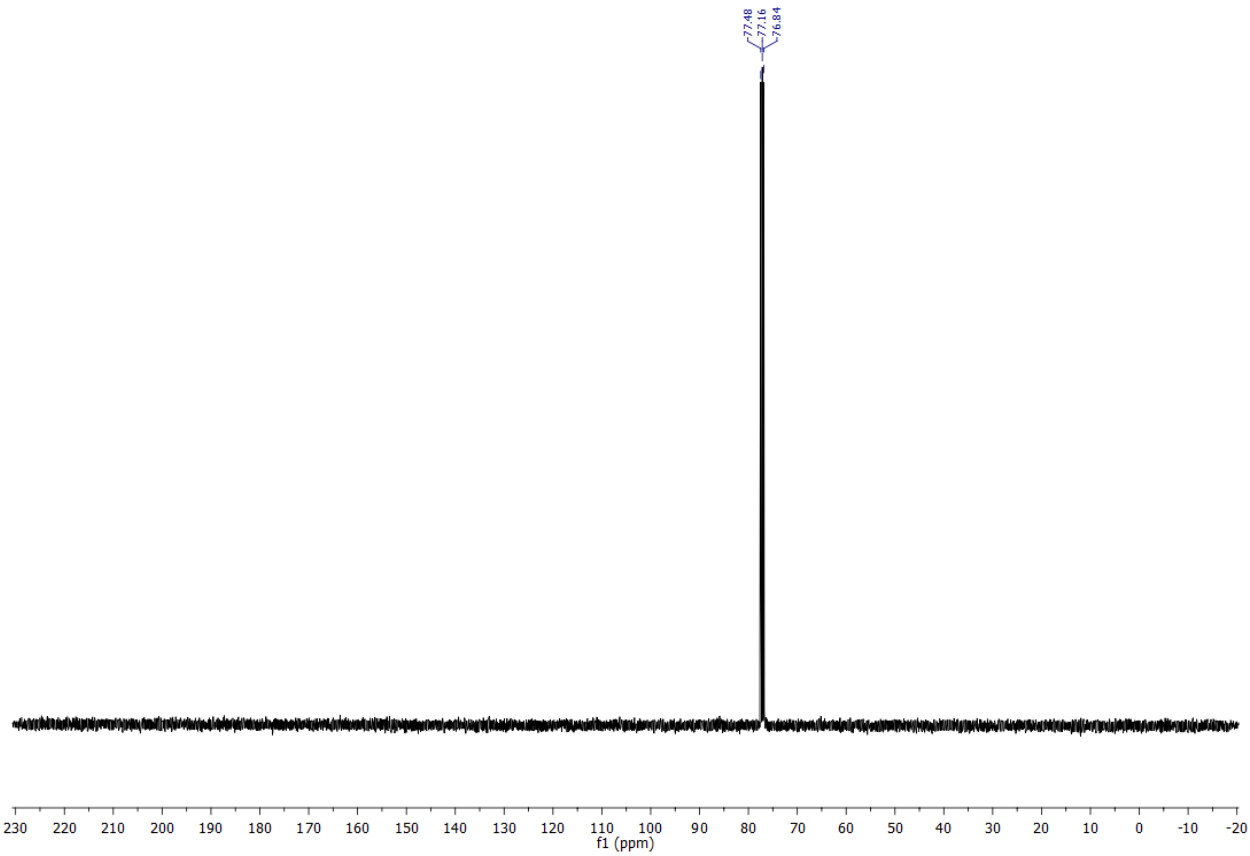


Fig. S122. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of DPPE (0.1 mg).

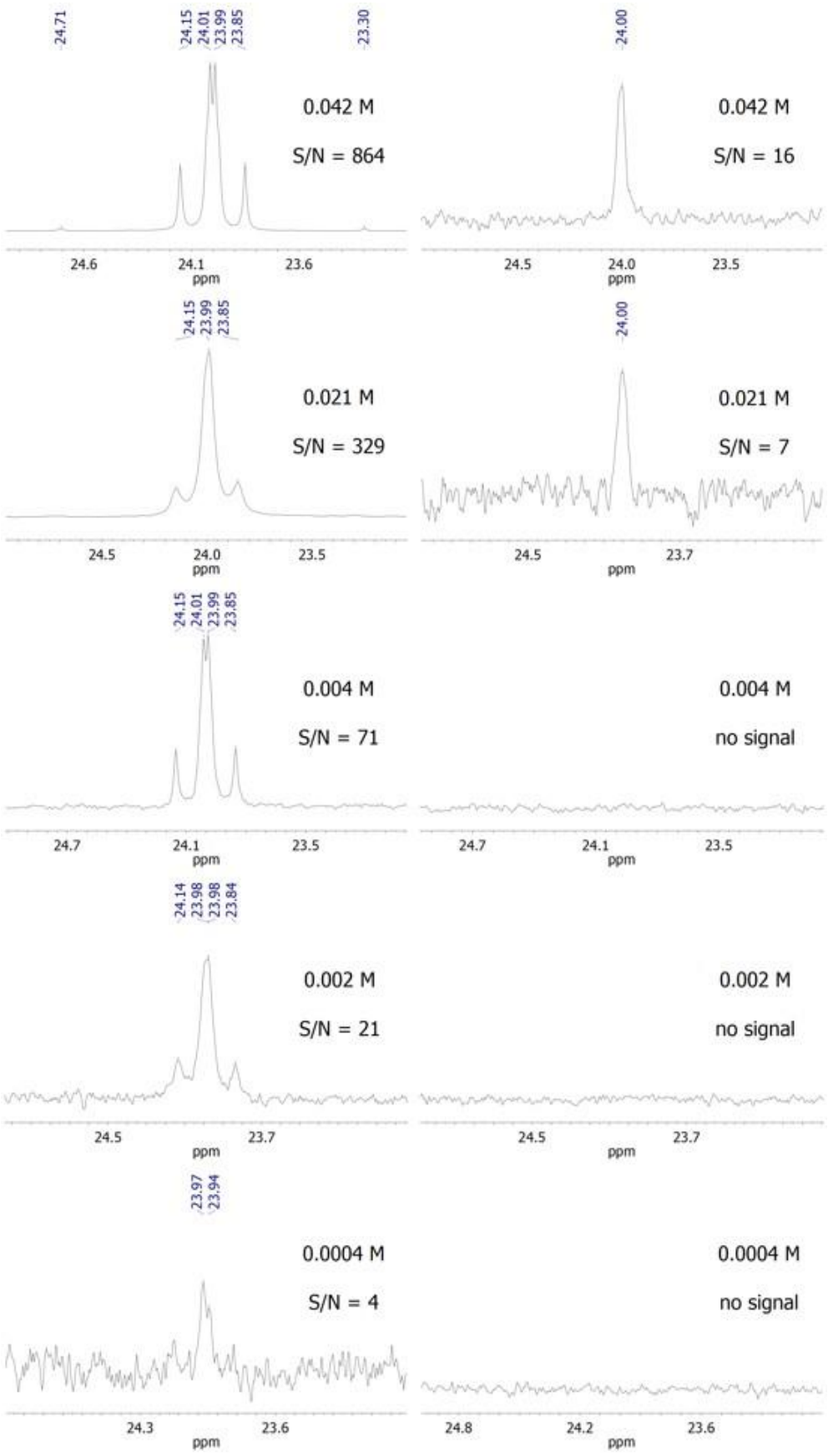


Fig. S123. Comparison of the ^{13}C NMR (101 MHz, $CDCl_3$) spectra of ^{13}C-labeled DPPE (left) and unlabeled DPPE (right) at various concentrations (each recorded with 256 scans for 15 min).

S9. References

1. R. D. Feltham, G. Elbaze, R. Ortega, C. Eck and J. Dubrawski, Synthesis of new carbonyl complexes of palladium, *Inorg. Chem.*, 1985, **24**, 1503-1510.
2. M. S. Ledovskaya, V. V. Voronin, K. S. Rodygin and V. P. Ananikov, Efficient labeling of organic molecules using 13C elemental carbon: universal access to 13C2-labeled synthetic building blocks, polymers and pharmaceuticals, *Org. Chem. Front.*, 2020, **7**, 638-647.
3. J. L. Pascual-ahuir, E. Silla and I. Tuñon, GEPOL: An improved description of molecular surfaces. III. A new algorithm for the computation of a solvent-excluding surface, *J. Comput. Chem.*, 1994, **15**, 1127-1138.
4. A. Bondi, van der Waals Volumes and Radii, *J. Phys. Chem. A*, 1964, **68**, 441-451.
5. J. Cooper and T. Ziegler, A Density Functional Study of SN2 Substitution at Square-Planar Platinum(II) Complexes, *Inorg. Chem.*, 2002, **41**, 6614-6622.
6. D. H. Wertz, Relationship between the gas-phase entropies of molecules and their entropies of solvation in water and 1-octanol, *J. Am. Chem. Soc.*, 1980, **102**, 5316-5322.
7. V. Krishnamurti, C. Barrett and G. K. S. Prakash, Siladifluoromethylation and Deoxo-trifluoromethylation of PV–H Compounds with TMSCF3: Route to PV–CF_2– Transfer Reagents and P–CF_3 Compounds, *Org. Lett.*, 2019, **21**, 1526-1529.
8. C. A. Busacca, J. C. Lorenz, N. Grinberg, N. Haddad, M. Hrapchak, B. Latli, H. Lee, P. Sabila, A. Saha, M. Sarvestani, S. Shen, R. Varsolona, X. Wei and C. H. Senanayake, A Superior Method for the Reduction of Secondary Phosphine Oxides, *Org. Lett.*, 2005, **7**, 4277-4280.
9. D. Zhang, M. Lian, J. Liu, S. Tang, G. Liu, C. Ma, Q. Meng, H. Peng and D. Zhu, Preparation of O-Protected Cyanohydrins by Aerobic Oxidation of α-Substituted Malononitriles in the Presence of Diarylphosphine Oxides, *Org. Lett.*, 2019, **21**, 2597-2601.
10. M. M. Rauhut and H. A. Currier, Oxidation of Secondary Phosphines to Secondary Phosphine Oxides1, *J. Org. Chem.*, 1961, **26**, 4626-4628.
11. M. A. Klingenberg, A. S. Bogachenkov, M. A. Kinzhalov, A. V. Vasilyev and V. P. Boyarskiy, 1,4-Dihydrophosphinolines and their complexes with group 10 metals, *New J. Chem.*, 2016, **40**, 3336-3342.
12. G. R. Van Hecke and W. D. Horrocks, Ditertiary Phosphine Complexes of Nickel. SpeCtral, Magnetic, and Proton Resonance Studies. A Planar-Tetrahedral Equilibrium, *Inorg. Chem.*, 1966, **5**, 1968-1974.
13. A. D. Westland, 562. Five-co-ordinate palladium(II) and platinum(II), *J. Chem. Soc.*, 1965, DOI: 10.1039/JR9650003060, 3060-3067.
14. C. Laye, J. Lusseau, F. Robert and Y. Landais, The Trityl-Cation Mediated Phosphine Oxides Reduction, *Adv. Synth. Catal.*, 2021, **363**, 3035-3043.
15. J. E. Mrochek and C. V. Banks, Bis-(disubstitutedphosphinyl)-alkanes—IV: Extraction of mineral acids, uranium (VI), and some lanthanides, *J. Inorg. Nucl. Chem.*, 1965, **27**, 589-601.
16. L. Maier, Organische Phosphorverbindungen XXXI. Ein einfaches Verfahren zur Herstellung von Alkylen- bzw. Arylen- bzw. diphosphiniten und von Bis-(dialkyl- und diaryl-phosphinyl)-alkanen, *Helv. Chim. Acta*, 1968, **51**, 405-413.
17. L. R. Doyle, A. Heath, C. H. Low and A. E. Ashley, A Convenient Synthetic Protocol to 1,2-Bis(dialkylphosphino)ethanes, *Adv. Synth. Catal.*, 2014, **356**, 603-608.
18. D. Sinou, D. Maillard and G. Pozzi, Synthesis of a Family of Triarylphosphanes with Fluorous Phase Affinity, *Eur. J. Org. Chem.*, 2002, **2002**, 269-275.
19. L. C. Baldwin and M. J. Fink, Synthesis of 1,2-bis[(diorgano)phosphino]ethanes via Michaelis–Arbuzov type rearrangements, *J. Organomet. Chem.*, 2002, **646**, 230-238.
20. P. Boehm, P. Müller, P. Finkelstein, M. A. Rivero-Crespo, M.-O. Ebert, N. Trapp and B. Morandi, Mechanistic Investigation of the Nickel-Catalyzed Metathesis between Aryl Thioethers and Aryl Nitriles, *J. Am. Chem. Soc.*, 2022, **144**, 13096-13108.
21. M. Bacci, Infrared spectra of $(C_6H_5)PCH_2CH_2P(C_6H_5)_2$ and $(C_6H_5)_2PCD_2CD_2P(C_6H_5)_2$, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, 1972, **28**, 2286-2289.

22. A. A. S. W. Tchawou, M. Raducan and P. Chen, Mechanism-Based Design and Optimization of a Catalytic Electrophilic Cyclopropanation without Diazomethane, *Organometallics*, 2017, **36**, 180-191.
23. CrysAlisPro. Version 1.171.41. *Rigaku Oxford Diffraction*, 2022.
24. G. Sheldrick, SHELXT - Integrated space-group and crystal-structure determination, *Acta Crystallogr. A*, 2015, **71**, 3-8.
25. G. Sheldrick, Crystal structure refinement with SHELXL, *Acta Crystallogr. C*, 2015, **71**, 3-8.
26. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program, *J. Appl. Crystallogr.*, 2009, **42**, 339-341.
27. S. Parsons, H. D. Flack and T. Wagner, Use of intensity quotients and differences in absolute structure refinement, *Acta Crystallogr. B*, 2013, **69**, 249-259.
28. C. F. Macrae, I. Sovago, S. J. Cottrell, P. T. A. Galek, P. McCabe, E. Pidcock, M. Platings, G. P. Shields, J. S. Stevens, M. Towler and P. A. Wood, Mercury 4.0: from visualization to analysis, design and prediction, *J. Appl. Crystallogr.*, 2020, **53**, 226-235.
29. C. Pelizzi and G. Pelizzi, Crystal structures of two forms of 1,2-bis(diphenylphosphino)ethane, *Acta Crystallogr. B*, 1979, **35**, 1785-1790.
30. E. R. T. Tiekink, The crystal structure of 1,2-bis(diphenylphosphino)ethane at 173 K, [$Ph_2PCH_2CH_2PPh_2$], *Z. Kristallogr. - New Cryst. Struct.*, 2001, **216**, 69-70.
31. Mengke Li, Xinyi Cai, Zijian Chen, Kunkun Liu, Weidong Qiu, Wentao Xie, Liangying Wang and S.-J. Su, CCDC 2113126: Experimental Crystal Structure Determination, 2021, doi: https://doi.org/10.5517/ccdc.csd.cc28xwcg
32. M. Haddow, G. Owen and M. Slivarichova, CCDC 805341: Experimental Crystal Structure Determination, 2011, doi: https://doi.org/10.5517/ccw10rn
33. M. Haddow, G. Owen and M. Slivarichova, CCDC 769521: Experimental Crystal Structure Determination, 2011, doi: https://doi.org/10.5517/ccttr8m
34. Ali Naghipour, Arash Ghorbani-Choghamarani, Heshmatollah Babaee and B. Notash, CCDC 1412269: Experimental Crystal Structure Determination, 2016, doi: https://doi.org/10.5517/ccdc.csd.cc1jdl2l
35. W. L. Steffen and G. J. Palenik, Crystal and molecular structures of dichloro[bis(diphenylphosphino)methane]palladium(II), dichloro[bis(diphenylphosphino)ethane]palladium(II), and dichloro[1,3-bis(diphenylphosphino)propane]palladium(II), *Inorg. Chem.*, 1976, **15**, 2432-2439.