Electronic Supplementary Material (ESI) for Nanoscale Advances.

Supporting Information

Access to and reactions of P-functional 1,4-dihydro-1,4-diphosphinines being fused to two TTF units

Shahriar Kermanshahian,[a] Tim Kalisch,[a] Zsolt Kelemen,[b] Gregor Schnakenburg,[a] László Nyulászi,*[b] René T. Boeré*[c] and Rainer Streubel*[a]

[a]Institut Für Anorganische Chemie, Rheinische Friedrich-Wilhelms-Universität Bonn, Bonn (Germany). E-mail: r.streubel@uni-bonn.de

[b]Department of Inorganic and Analytical Chemistry, Budapest University of Technology and Economics, Budapest (Hungary). E-mail: nyulaszi@mail.bme.hu

[c]Department of Chemistry and Biochemistry, University of Lethbridge, Lethbridge (Canada). E-mail: boere@uleth.ca

Contents

Experimental

General procedure

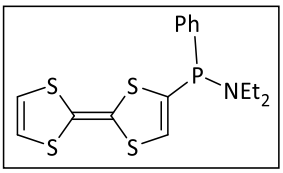
All reactions and manipulations were carried out under an atmosphere of deoxygenated (preheated BTS catalyst at 100–130 °C) and dried (phosphorus pentoxide and silica gel) argon gas, using standard Schlenk techniques or glove box techniques with conventional glassware. All air and/or moister sensitive chemicals were stored in either Schlenk flasks/tubes or handled in the glovebox. Solvents were dried and distilled according to standard procedures[1] and were used freshly from distills. Tetrathiafulvalene (**1a**)[2], 2-(1,3-Dithiol-2-ylidene)-4,5-dimethyl-1,3-dithiole (**1b**)[3,4] and 2-(1,3-Dithiol-2-ylidene)-4,5-dipropyl-1,3-dithiole (**1c**)[3] were synthesised following the literature protocol. Also chloro(diethylamino)phenylphosphne **2a**[5] and bis(diethylamino)chlorophosphane **2b**[6] were synthesised and distilled before use and were stored under argon atmosphere. The progress of all reactions was monitored via $^{31}P\{^{1}H\}$ NMR spectroscopy. NMR spectra of all the compounds were recorded on Bruker Avance DMX-300, DPX-300, DPX-400 or DMX-500 spectrometers. Deuterated solvent ($CDCl_3$) were dried using literature procedures and used for the multinuclear NMR characterizations. The chemical resonances are given relative to the residual protons of the deuterated solvents (^{1}H, ^{13}C) or 85% H_3PO_4 (^{31}P NMR). All the measurements were recorded at 298K unless some specific temperature is given. HSQC and HMBC experiments were used for purpose of assigning the ^{1}H NMR and ^{13}C NMR signals of all compounds. The melting points (or decomposition temperatures) were recorded on a Büchi 535 Type S melting point apparatus, where the samples were placed inside both-sided closed glass capillary tubes; the values are not corrected. The samples for the elemental analyses were prepared in a tin or silver (for halogen containing compounds) boat using a glove box. Elemental analyses were performed using an elementary vario EL analytical gas chromatograph. The mean values of three or four independent measurements are given in each case. Despite considerable effort, EA agreement remained poor, which probably reflects that column chromatography could not be performed with full efficiency. Importantly, the $CDCl_3$ NMR purity is high for most compounds. Electron ionization mass spectra were recorded on a MAT 95 XL Finnigan using EI (70 eV). For ESI mass spectra a Thermo Fisher Scientific Orbitrap XL Mass spectrometer was used. LIFDI mass spectra were recorded on a Thermo Finnigan MAT 90 sector instrument equipped with a LIFDI ion source (Linden CMS). MALDI mass spectra were acquired from a

Bruker Daltonik ultrafleXtreme TOF/TOF time-of-flight spectrometer. Only selected data are given for the detected ions (mass to charge ratio, relative intensity in percent). Single crystals were grown by evaporation of saturated solutions of the compounds or by diffusion technique. After crystal growing the single crystals were separated from the supernatant solution and were covered with fomblin for protection from further decomposition. A suitable single crystal was selected under the microscope and loaded onto the diffractometer. The crystallographic data were collected on Brucker D8-Venture diffractometer, Bruker X8-KappaApexII, Bruker APEX-II CCD, Nonius KappaCCD or STOE IPDS 2T diffractometer equipped with a low-temperature device at 100.0 K using graphite monochromated Cu-Kα radiation (λ = 1.54178 Å) or Cu-K_α radiation (λ = 1.54178). The structures were solved by Patterson methods or Direct Methods (SHELXS-97)[7,8] and refined by full-matrix least squares on F2 (SHELXL-97).[8,9] All non-hydrogen atoms were refined anisotropically, the hydrogen atoms were included isotropically using the riding model on the bound carbon atoms. Data analyses and the picture preparation of the molecular structure for all the compounds were done using the Olex-2 program. CCDC 2087015-2087016 and 2252852-2252853 contain the supplementary crystallographic data (see ESI p.34).

Synthesis of *C*-Phosphanylated tetrathiafulvalenes 3a–f

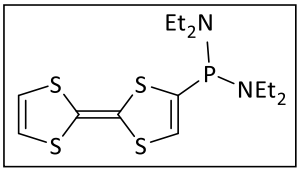
1 was dissolved in dry THF in a Schlenk flask and cooled to −95 °C. A solution of LDA (1.05 eq for **1a,b**, 1.1 eq for **1c**–**f**) in dry THF was prepared and cooled to −95 °C, then added dropwise to the TTF's solution and the reaction mixture was stirred for 90 minutes (**1a,b**), 3 hours (**1c,d**) or 105 minutes (**1e,f**). During this time temperature was kept between −95 °C and −75 °c. Then **2a,b** (1.05–1.1 eq) was added dropwise (T = −95 °C) and the reaction mixture was warmed up slowly and stirred for 3 hours. Then the solution was concentrated in *vacuo* (8×10^{-3} mbar) and the residue was taken up in dry dichloromethane and filtered over a 3G-frit having a celite® pad and silica gel to remove the formed lithium chloride. The filtrate was collected and the solvent was removed in *vacuo* (8×10^{-3} mbar) and then dried. In the case of **3a** and **3b** the residue was subjected to a low temperature column chromatography to remove doubly substituted side-products. The unreacted TTF was partially removed via sublimation using an ultrahigh vacuum pump (1×10^{-5} mbar). However, in these cases the pure product couldn't be obtained.

4-Diethylamino(phenyl)phosphanyl-2,2'-bis(1,3-dithiolyl-idene) (3a)



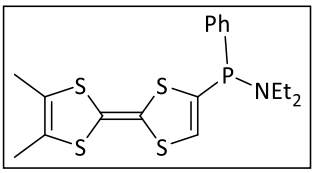
Product: Orange-yellow oil of the raw product (content of **3a**: 82%), ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 1.09 (*t*, 6H, $^{3}J_{H,H}$ = 7.0 Hz, N-CH_2-$\underline{CH_3}$), 3.12 (*m*, 4H, N-$\underline{CH_2}$-CH_3), 6.28 and 6.30 (*d*, 2H, $^{3}J_{H,H}$ = 6.4 Hz, $C^{4'}$,$C^{5'}$-H), 6.31 (*s*, s.m.), 6.63 (*d*, 1H, $^{3}J_{P,H}$ = 9 Hz, C^{5}-H), 7.31 (*m*, 1H, *para*-C_6H_5), 7.37 (*m*, 2H, *meta*-C_6H_5), 7.43 (*m*, 2H, *ortho*-C_6H_5).^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 14.5 (*d*, $^{3}J_{P,C}$ = 3.4 Hz, N-CH_2-$\underline{CH_3}$), 44.6 (*d*, $^{2}J_{P,C}$ = 15 Hz, N-$\underline{CH_2}$-CH_3) , 109.8 and 112.6 (*s*, C^{2},$C^{2'}$), 119.1 and 119.2 (*s*, $C^{4'}$and $C^{5'}$), 119.3 (*s*, s.m.), 127.5 (*d*, $^{2}J_{P,C}$ = 42 Hz, C^{5}), 128.5-128.6 (*para, meta*-C_6H_5), 130.7 (*d*, $^{2}J_{P,C}$ = 18 Hz, *ortho*-C_6H_5), 138.4 (*d*, $^{1}J_{P,C}$ = 13.2 Hz, *ipso*-C_6H_5), 138.6 (*d*, $^{1}J_{P,C}$ = 48.2 Hz, C^{4}). $^{31}P\{^{1}H\}$ NMR (202.5 MHz, $CDCl_3$): δ = 52.9 (*s*). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ = 52.9 (*m*). MS (EI, 70 eV): m/z (%) = 415 (38) $[M+O_2]^{\cdot+}$, 383.1 (88) $[M]^{\cdot+}$, 312 (34) $[M-NEt_2+H]^{\cdot+}$, 204 (25) $[M-PPh(NEt_2)+H]^{\cdot+}$, 180 (54) $[PPh(NEt_2)]^{\cdot+}$, 109 (38) $[P-C_6H_5+H]^{\cdot+}$. HR-MS: Calculated: 383.0059, Found: 383.0058.

4-Bis(diethylamino)phosphanyl-2,2'-bis(1,3-dithiolylidene) (3b)



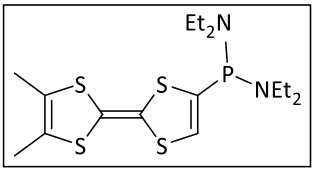
product: Yellow-orange oil of the raw product (content of **3b**: 78%). ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 1.08 (*t*, 12H, $^{3}J_{H,H}$ = 7.2 Hz, N-CH_2-$\underline{CH_3}$), 3.10 (*m*, 8H, N-$\underline{CH_2}$-CH_3), 6.10 (*d*, 1H, $^{3}J_{P,H}$ = 1.7 Hz, C^{5}-H), 6.28 and 6.29 (*d*, 2H, $^{3}J_{H,H}$ = 6.5 Hz, $C^{4'}$,$C^{5'}$-H), 6.31 (*s*, s.m.). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 14.7 (*d*, $^{3}J_{P,C}$ = 3.3 Hz, N-CH_2-$\underline{CH_3}$), 42.9 (*d*, $^{2}J_{P,C}$ = 17.7 Hz, N-$\underline{CH_2}$-CH_3), 109 and 113.4 (*s*, C^{2},$C^{2'}$), 119.1 (*d*, $^{2}J_{P,C}$ = 17.9 Hz, C^{5}), 119.3 and 119.4 (*s*, $C^{4'}$and $C^{5'}$), 119.5 (*s*, s.m.), 140.3 (*d*, $^{1}J_{P,C}$ = 18.3 Hz, C^{4}). $^{31}P\{^{1}H\}$ NMR (202.5 MHz, $CDCl_3$): δ = 84.4 (*s*). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ = 84.4 (*m*). MS (EI, 70 eV): m/z (%) = 410 (8) $[M+O_2]^{\cdot+}$, 378.1 (6) $[M]^{\cdot+}$, 204 (100) $[M-P(NEt_2)_2+H]^{\cdot+}$. HR-MS: Calculated: 378.0481, Found: 378.0480.

4-Diethylamino(phenyl)phosphanyl-4',5'-dimethyl-2,2'-bis(1,3-dithiolylidene) (3c)



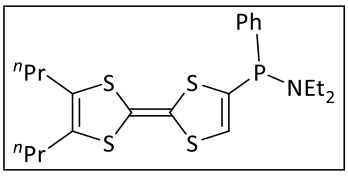
Product: Orange oil, Yield: 427 mg (1.04 mmol, 80%). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.08 (*t*, 6H, $^{3}J_{H,H}$ = 7.3 Hz, N-CH_2-$\underline{CH_3}$), 1.92 and 1.93 (*br*, 6H, $C^{4'}$, $C^{5'}$-Me), 3.10 (*m*, 4H, N-$\underline{CH_2}$-CH_3), 6.61 (*d*, 1H, $^{3}J_{P,H}$ = 8.9 Hz, C^{5}-H), 7.30 (*m*, 1H, *para*-C_6H_5), 7.36 (*m*, 2H, *meta*-C_6H_5), 7.42 (*m*, 2H, *ortho*-C_6H_5). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 13.8 (*s*, $C^{4'}$, $C^{5'}$-Me), 14.5 (*d*, $^{3}J_{P,C}$ = 3.5 Hz, N-CH_2-$\underline{CH_3}$), 44.6 (*d*, $^{2}J_{P,C}$ = 14.9 Hz, N-$\underline{CH_2}$-CH_3), 108.4 and 111.7 (*s*, C^{2},$C^{2'}$), 122.9 and 123.1 (*s*, $C^{4'}$and $C^{5'}$), 127.6 (*d*, $^{2}J_{P,C}$ = 42.2 Hz, C^{5}), 128.4-128.5 (*para, meta*-C_6H_5), 130.7 (*d*, $^{2}J_{P,C}$ = 18.1 Hz, *ortho*-C_6H_5), 138.4 (*d*, $^{1}J_{P,C}$ = 39.1 Hz, C^{4}), 138.6 (*d*, $^{1}J_{P,C}$ = 22.2 Hz, *ipso*-C_6H_5). ^{31}P{^{1}H} NMR (162.0 MHz, $CDCl_3$): δ = 52.9 (*s*). ^{31}P NMR (162.0 MHz, $CDCl_3$): δ = 52.9 (*m*). MS (EI, 70 eV): m/z (%) = 411 (27) $[M]^{\cdot+}$, 339.9 (8) $[M-NEt_2+H]^{\cdot+}$, 231.9 (54) $[M-PPh(NEt_2)+H]^{\cdot+}$. HR-MS: Calculated: 411.0372, Found: 411.0368. EA (%): Calculated/Found C: 52.53/51.15, H: 5.39/5.67, N: 3.40/2.92, S: 31.16/28.90.

4-Bis(diethylamino)phosphanyl-4',5'-dimethyl-2,2'-bis(1,3-dithiolylidene) (3d)



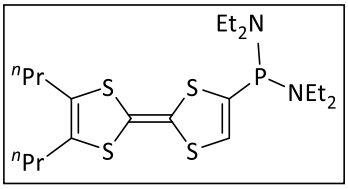
Product: Orange oil, Yield: 579 mg (1.4 mmol, 50%). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.07 (*t*, 12H $^{3}J_{H,H}$ = 7.1 Hz, N-CH_2-$\underline{CH_3}$,), 1.93 (*s*, 6H, $C^{4'}$, $C^{5'}$-Me), 3.09 (*m*, 8H, N-$\underline{CH_2}$-CH_3), 6.09 (*d*, 1H, $^{3}J_{P,H}$ = 1.7 Hz, C^{5}-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 13.8 and 13.9(*s*, $C^{4'}$, $C^{5'}$-Me), 14.7 (*d*, $^{3}J_{P,C}$ = 3.2 Hz, N-CH_2-$\underline{CH_3}$), 43 (*d*, $^{2}J_{P,C}$ = 17.7 Hz, N-$\underline{CH_2}$-CH_3), 107.5 and 112.5 (*s*, C^{2},$C^{2'}$), 119.5 (*d*, $^{2}J_{P,C}$ = 14.5 Hz, C^{5}), 122.8 and 123.1 (*s*, $C^{4'}$and $C^{5'}$), 140.4 (*d*, $^{1}J_{P,C}$ = 18.4 Hz, C^{4}). ^{31}P{^{1}H} NMR (162.0 MHz, $CDCl_3$): δ = 84.7 (*s*). ^{31}P NMR (162.0 MHz, $CDCl_3$): δ = 84.7 (*m*). MS (EI, 70 eV): m/z (%) = 438 (6) $[M+O_2]^{\cdot+}$, 406.0 (36) $[M]^{\cdot+}$, 231.9 (100) $[M-P(NEt_2)_2+H]^{\cdot+}$. HR-MS: Calculated: 406.0794, Found: 406.0791. EA (%): Calculated/Found C: 47.26/46.35, H: 6.69/6.73, N: 6.89/5.84, S: 31.54/29.98.

4-Diethylamino(phenyl)phosphanyl-4',5'-dipropyl-2,2'-bis(1,3-dithiolylidene) (3e)



Product: Orange oil, Yield: 497 mg (1.06 mmol, 88%). ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 0.93 (*t*, 6H, $^{3}J_{H,H}$ = 7.35 Hz, $C^{4'}$, $C^{5'}$-CH_2-CH_2-$\underline{CH_3}$), 1.09 (*t*, 6H, $^{3}J_{H,H}$ = 7.08 Hz, N-CH_2-$\underline{CH_3}$), 1.53 (*m*, 4H, $C^{4'}$, $C^{5'}$-CH_2-$\underline{CH_2}$-CH_3), 2.31 (*m*, 4H, $C^{4'}$, $C^{5'}$-$\underline{CH_2}$-CH_2-CH_3), 3.11 (*m*, 4H, N-$\underline{CH_2}$-CH_3), 6.60 (*d*, 1H, $^{3}J_{P,H}$ = 9 Hz, C^{5}-H), 7.30 (*m*, 1H, *para*-C_6H_5), 7.36 (*m*, 2H, *meta*-C_6H_5), 7.42 (*m*, 2H, *ortho*-C_6H_5). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 13.8 (2*s*, $C^{4'}$, $C^{5'}$-CH_2-CH_2-$\underline{CH_3}$,), 14.6 (*d*, $^{3}J_{P,C}$ = 3.37 Hz, N-CH_2-$\underline{CH_3}$), 23.1 (2*s*, $C^{4'}$, $C^{5'}$-CH_2-$\underline{CH_2}$-CH_3), 30.9 (*s*, $C^{4'}$, $C^{5'}$-$\underline{CH_2}$-CH_2-CH_3), 44.6 (*d*, $^{2}J_{P,C}$ = 14.79 Hz, N-$\underline{CH_2}$-CH_3), 108.6 and 110.8 (*s*, C^{2},$C^{2'}$), 119.2 (*s*, $C^{4'}$and $C^{5'}$), 127.6 (*d*, $^{2}J_{P,C}$ = 42.22 Hz, C^{5}), 128.4-129 (*para, meta*-C_6H_5), 130.7 (*d*, $^{2}J_{P,C}$ = 17.91 Hz, *ortho*-C_6H_5), 138.4 (*d*, $^{1}J_{P,C}$ = 40.7 Hz, C^{4}), 138.6 (*d*, $^{1}J_{P,C}$ = 19.5 Hz, *ipso*-C_6H_5). $^{31}P\{^{1}H\}$ NMR (202.5 MHz, $CDCl_3$): δ = 52.9 (*s*). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ = 52.9 (*m*). MS (EI, 70 eV): m/z (%) = 499.1 (8) $[M+O_2]^{\cdot+}$, 467.1 (30) $[M]^{\cdot+}$, 396.0 (5) $[M-NEt_2]^{\cdot+}$, 288 (100) $[M-P(NEt_2)Ph+H]^{\cdot+}$, 230.0 (30) $[M-P(NEt_2)Ph-2C_2H_5+2H]^{\cdot+}$, 180.1 (10) $[P(NEt_2)Ph]^{\cdot+}$. HR-MS: Calculated: 467.0999, Found: 467.1008. EA (%): Calculated/Found C: 56.50/56.44, H: 6.47/6.21, N: 2.99/3.30, S: 27.42/30.13.

4-Bis(diethylamino)phosphanyl-4',5'-dipropyl-2,2'-bis(1,3-dithiolylidene) (3f)



Product: Orange oil, Yield: 1.718 gr (3.71 mmol, 70%). ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 0.93 (*t*, 6H, $^{3}J_{H,H}$ = 7.36 Hz, $C^{4'}$, $C^{5'}$-CH_2-CH_2-$\underline{CH_3}$), 1.07 (*t*, 12H, $^{3}J_{H,H}$ = 7.05 Hz, N-CH_2-$\underline{CH_3}$), 1.53 (*m*, 4H, $C^{4'}$, $C^{5'}$-CH_2-$\underline{CH_2}$-CH_3), 2.31 (*t*, 4H, $^{3}J_{H,H}$ = 7.52 Hz, $C^{4'}$, $C^{5'}$-$\underline{CH_2}$-CH_2-CH_3), 3.09 (*m*, 8H, N-$\underline{CH_2}$-CH_3), 6.09 (*d*, 1H, $^{3}J_{P,H}$ = 1.8 Hz, C^{5}-H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 13.8 (*s*, $C^{4'}$, $C^{5'}$-CH_2-CH_2-$\underline{CH_3}$), 14.7 (*d*, $^{3}J_{P,C}$ = 3.22 Hz, N-CH_2-$\underline{CH_3}$), 23.1 (2*s*, $C^{4'}$, $C^{5'}$-CH_2-$\underline{CH_2}$-CH_3), 30.9 (2*s*, $C^{4'}$, $C^{5'}$-$\underline{CH_2}$-CH_2-CH_3), 43 (*d*, $^{2}J_{P,C}$ = 17.59 Hz, N-$\underline{CH_2}$-CH_3), 107.9 (*s*, $C^{2'}$), 111.7 (*d*, $^{3}J_{P,C}$ = 2.93 Hz, C^{2}), 119.6 (*d*, $^{2}J_{P,C}$ = 14.61 Hz, C^{5}), 128.7 and 129 (*s*, $C^{4'}$and $C^{5'}$), 140.4 (*d*, $^{1}J_{P,C}$ = 18.13 Hz, C^{4}). $^{31}P\{^{1}H\}$ NMR (202.5 MHz, $CDCl_3$): δ = 84.7 (*s*).

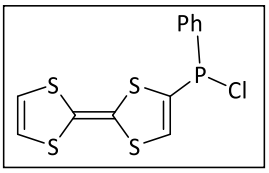
^{31}P NMR (202.5 MHz, $CDCl_3$): δ = 84.7 (*m*). MS (EI, 70 eV): m/z (%) = 494.1 (35) $[M+O_2]^{\cdot+}$, 462.1 (92) $[M]^{\cdot+}$, 390.0 (10) $[M-NEt_2]^{\cdot+}$, 319.0 (5) $[M-2(NEt_2)+H]^{\cdot+}$, 287 (10) $[M-P(NEt_2)_2]^{\cdot+}$, 230.0 (95) $[M-P(NEt_2)_2-2C_2H_5+2H]^{\cdot+}$, 175.1 (100) $[P(NEt_2)_2]^{\cdot+}$. HR-MS: Calculated: 462.1421, Found: 462.1435. EA (%): Calculated/Found C: 51.91/52.09, H: 7.62/7.23, N: 6.05/6.06, S: 27.71/36.00.

Synthesis of 4-Chlorophosphanyltetrathiafulvalenes 4a–h

General protocol (I): 3a,c,e were each dissolved in dry dichloromethane in a Schlenk tube, then PCl_3 (1 eq) was added dropwise, and the reaction mixture was stirred for 1 hour (**3a**), 2 (**3c**) or 3 hours (**3e**) at r.t. The reaction mixture was concentrated in *vacuo* (8×10^{-3} mbar), and the residue was then dissolved in dry diethylether. The solution was filtered, concentrated and dried in *vacuo* (8×10^{-3} mbar).

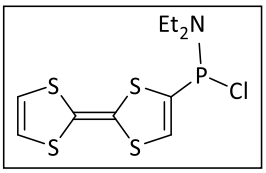
General protocol (II): 3b,d,f were each dissolved in dry diethylether in a Schlenk tube and cooled to −90 °C, then PCl_3 (1 eq) was added dropwise, and the reaction mixture was warmed up slowly and stirred for 1 h. The reaction mixture was concentrated in *vacuo* (8×10^{-3} mbar), and the residue was then dissolved in dry diethylether. The solution was filtered, concentrated and dried in *vacuo* (8×10^{-3} mbar).

4-Chloro(phenyl)phosphanyl-2,2'-bis(1,3-dithiolylidene) (4a)



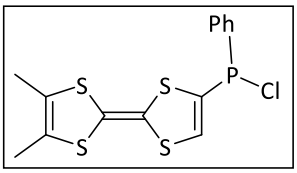
Product: Red oil of the raw product (content of **4a**: 85%). ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 6.28 and 6.29 (*d*, 2H, $^3J_{H,H}$ = 6.8 Hz, $C^{4'}$,$C^{5'}$-H), 6.31 (*s*, TTF), 6.96 (*d*, 1H, $^3J_{P,H}$ = 10.8 Hz, C^5-H), 7.46 (*m*, 3H, *para, meta*-C_6H_5), 7.71 (*m*, 2H, *ortho*-C_6H5). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 109.4 and 113.2 (*s*, C^2,$C^{2'}$), 119 and 119.2 (*s*, $C^{4'}$ and $C^{5'}$), 119.3 (*s*, $C^{4,4'}$,$C^{5,5'}$-TTF), 128.9, 129 and 130.7 (*para,meta*- C_6H_5), 131 (*d*, $^2J_{P,C}$ = 13.1 Hz, *ortho*-C_6H_5), 132.3 (*d*, $^2J_{P,C}$ = 52 Hz, C^5), 135.9 (*d*, $^1J_{P,C}$ = 28.9 Hz, *ipso*-C_6H_5), 136.7 (*d*, $^1J_{P,C}$ = 61.2 Hz, C^4). ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$): δ = 63.9 (*s, with chlorine shoulder*). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ = 63.9 (*m*). MS (EI, 70 eV): m/z (%) = 345.8 (4) $[M]^{\cdot+}$, 311.8 (16) $[M-Cl+H]^{\cdot+}$, 203.8 (100) $[M-PhPCl+H]^{\cdot+}$. HR-MS: Calculated: 345.8935, Found: 345.8935.

4-Chloro(diethylamino)phosphanyl-2,2'-bis(1,3-dithiolylidene) (4b)



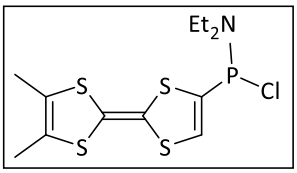
Product: Yellow-orange oil of the raw product (content of **4b**: 95%). ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 1.17 (*t*, 6H, $^{3}J_{H,H}$ = 7.4 Hz, N-CH_2-$\underline{CH_3}$), 3.20 (*m*, 4H, N-$\underline{CH_2}$-CH_3), 6.30 and 6.32 (*d*, 2H, $^{3}J_{H,H}$ = 6.5 Hz, $C^{4'}$,$C^{5'}$-H), 6.31 (*s*, TTF) , 6.73 (*d*, 1H, $^{3}J_{P,H}$ = 2.6 Hz, C^{5}-H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 14.1 (*d*, $^{3}J_{P,C}$ = 6.2 Hz, N-CH_2-$\underline{CH_3}$), 43.9 (*d*, $^{2}J_{P,C}$ = 14.8 Hz, N-$\underline{CH_2}$-CH_3), 110.6 and 112.1 (*s*, C^{2},$C^{2'}$), 119.1 and 119.3 (*s*, $C^{4'}$and $C^{5'}$), 126.4 (*d*, $^{2}J_{P,C}$ = 18.5 Hz, C^{5}), 136.9 (*d*, $^{1}J_{P,C}$ = 50.9 Hz, C^{4}). ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$): δ = 117.9 (*s*). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ = 117.9 (*s*). MS (EI, 70 eV): m/z (%) = 372.9 (30) $[M+O_2]^{\cdot+}$, 340.9 (90) $[M]^{\cdot+}$, 203.9 (78) $[M-P(NEt_2)_2+H]^{\cdot+}$. HR-MS: Calculated: 340.9357, Found: 340.9352.

4-Chloro(phenyl)phosphanyl-4',5'-dimethyl-2,2'-bis(1,3-dithiolylidene) (4c)



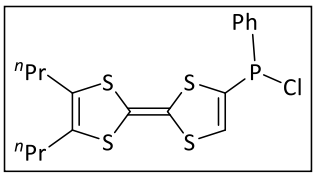
Product: Red powder, Yield: 271 mg (0.72 mmol, 90%), Melting point: 104 °C. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 1.91 (*m*, 6H, $C^{4'}$, $C^{5'}$-Me), 6.95 (*d*, 1H, $^{3}J_{P,H}$ = 10.7 Hz, C^{5}-H), 7.46 (*m*, 3H, *para, meta*-C_6H_5), 7.71 (*m*, 2H, *ortho*-C_6H_5). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 13.8 (*s*, $C^{4'}$, $C^{5'}$-Me), 108.4 and 111.9 (*s*, C^{2},$C^{2'}$), 122.8 and 123.1 (*s*, $C^{4'}$and $C^{5'}$), 128.9, 130 and 130.7 (*para,meta*-C_6H_5), 131 (*d*, $^{2}J_{P,C}$ = 6.2 Hz, *ortho*-C_6H_5), 132.5 (*d*, $^{2}J_{P,C}$ = 52.1 Hz, C^{5}), 136 (*d*, $^{1}J_{P,C}$ = 27.8 Hz, *ipso*-C_6H_5), 136.6 (*d*, $^{1}J_{P,C}$ = 60.6 Hz, C^{4}). ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$): δ = 64 (*s, with chlorine shoulder*). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ = 64 (*m*). MS (EI, 70 eV): m/z (%) = 373.9 (100) $[M]^{\cdot+}$, 339.9 (38) $[M-Cl+H]^{\cdot+}$, 231.9 (62) $[M-PhPCl+H]^{\cdot+}$. HR-MS: Calculated: 373.9248, Found: 373.9243. EA (%): Calculated/Found C: 44.85/45.96, H: 3.23/3.89, S: 34.21/32.69.

4-Chloro(diethylamino)phosphanyl-4',5'-dimethyl-2,2'-bis(1,3-dithiolylidene) (4d)



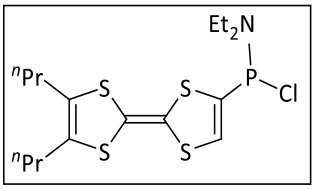
Product: Orange-red oil, Yield: 410 mg (1.1 mmol, 95%). ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 1.17 (*t*, 6H, $^{3}J_{H,H}$ = 7.2 Hz, N-CH_2-$\underline{CH_3}$), 1.94 (*s*, 6H, $C^{4'}$,$C^{5'}$-Me), 3.20 (*m*, 4H, N-$\underline{CH_2}$-CH_3), 6.72 (*d*, 1H, $^{3}J_{P,H}$ = 2.7 Hz, C^{5}-H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 13.9 (*s*, $C^{4'}$, $C^{5'}$-Me), 14.1 (*d*, $^{3}J_{P,C}$ = 5.9 Hz, N-CH_2-$\underline{CH_3}$), 43.9 (*d*, $^{2}J_{P,C}$ = 15 Hz, N-$\underline{CH_2}$-CH_3), 109.6 and 110.8 (*s*, C^{2},$C^{2'}$), 122.9 and 123.1 (*s*, $C^{4'}$and $C^{5'}$), 126.5 (*d*, $^{2}J_{P,C}$ = 18.6 Hz, C^{5}), 136.8 (*d*, $^{1}J_{P,C}$ = 51 Hz, C^{4}). ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$): δ = 118.2 (*s*). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ = 118.2 (*m*). MS (EI, 70 eV): m/z (%) = 368.9 (26) $[M]^{\cdot+}$, 231.9 (86) $[M-(Et_2N)PCl+H]^{\cdot+}$. HR-MS: Calculated: 368.9670, Found: 368.9663.

4-Chloro(phenyl)phosphanyl-4',5'-dipropyl-2,2'-bis(1,3-dithiolylidene) (4e)



Product: Red oil, Yield: 362 mg (0.84 mmol, 98%). ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 0.92 (*m*, 6H, $C^{4'}$, $C^{5'}$-CH_2-CH_2-$\underline{CH_3}$), 1.51 (*m*, 4H, $C^{4'}$, $C^{5'}$-CH_2-$\underline{CH_2}$-CH_3), 2.30 (*m*, 4H, $C^{4'}$, $C^{5'}$-$\underline{CH_2}$-CH_2-CH_3), 6.95 (*d*, 1H, $^{3}J_{P,H}$ = 10.73 Hz, C^{5}-H), 7.46 (*m*, 3H, *para, meta*-C_6H_5), 7.71 (*m*, 2H, *ortho*-C_6H_5). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 13.8 (*s*, $C^{4'}$, $C^{5'}$-CH_2-CH_2-$\underline{CH_3}$), 23.1 (2*s*, $C^{4'}$, $C^{5'}$-CH_2-$\underline{CH_2}$-CH_3), 30.8 (2*s*, $C^{4'}$, $C^{5'}$-$\underline{CH_2}$-CH_2-CH_3), 107.7 and 112.2 (*s*, C^{2},$C^{2'}$), 129 (*s*, $C^{4'}$and $C^{5'}$), 128.8 - 131 (*para,meta- ortho*-C_6H_5), 132.6 (*d*, $^{2}J_{P,C}$ = 52.24 Hz, C^{5}), 136 (*d*, $^{1}J_{P,C}$ = 28.08 Hz, *ipso*-C_6H_5), 136.6 (*d*, $^{1}J_{P,C}$ = 60.43 Hz, C^{4}). ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$): δ = 64.1 (*s, with chlorine shoulder*). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ = 64.1 (*m*). MS (LIFDI): m/z (%) = 430.0 (100) $[M]^{\cdot+}$ HR-MS (ESI-pos): $[M-Cl+OH]^{\cdot+}$ (100%) Calculated: 412.0207, Found: 412.0207. EA (%): Calculated/Found C: 50.16/51.01, H: 4.68/4.99, S: 29.75/30.48.

4-Chloro(diethylamino)phosphanyl-4',5'-dipropyl-2,2'-bis(1,3-dithiolylidene) (4f)

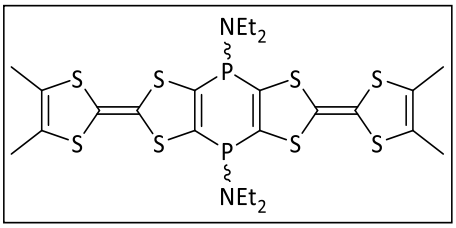


Product: Red oil, Yield: 1.487 gr (3.49 mmol, 100%). ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 0.94 (2*t*, 6H, $^{3}J_{H,H}$ = 7.34 Hz, $C^{4'}$, $C^{5'}$-CH_2-CH_2-$\underline{CH_3}$), 1.16 (*t*, 6H, $^{3}J_{H,H}$ = 7.16 Hz, N-CH_2-$\underline{CH_3}$), 1.53 (*m*, 4H, $C^{4'}$, $C^{5'}$-CH_2-$\underline{CH_2}$-CH_3), 2.32 (*m*, 4H, $C^{4'}$, $C^{5'}$-$\underline{CH_2}$-CH_2-CH_3), 3.20 (*m*, 4H, N-$\underline{CH_2}$-CH_3), 6.72 (*d*, 1H, $^{3}J_{P,H}$ = 2.61 Hz, C^{5}-H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 13.8 (*s*, $C^{4'}$, $C^{5'}$-CH_2-CH_2-$\underline{CH_3}$), 14.1 (*d*, $^{3}J_{P,C}$ = 6.08 Hz, N-CH_2-$\underline{CH_3}$), 23.1 (2*s*, $C^{4'}$, $C^{5'}$-CH_2-$\underline{CH_2}$-CH_3), 30.9 (*s*, $C^{4'}$, $C^{5'}$-$\underline{CH_2}$-CH_2-CH_3), 43.9 (*d*, $^{2}J_{P,C}$ = 14.7 Hz, N-$\underline{CH_2}$-CH_3), 108.9 (*d*, $^{4}J_{P,C}$ = 2.88 Hz, $C^{2'}$), 111.2 (*s*, C^{2}), 126.6 (*d*, $^{2}J_{P,C}$ = 18.57 Hz, C^{5}), 128.9 and 129 (*s*, $C^{4'}$and $C^{5'}$), 136.8 (*d*, $^{1}J_{P,C}$ = 50.81 Hz, C^{4}). ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$): δ = 118.4 (*s*). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ = 118.4 (*p,* $^{3}J_{P,H}$ = 12.29 Hz) MS (LIFDI): m/z (%) = 425.1 (100) $[M]^{\cdot+}$ HR-MS (ESI-pos): $[M-Cl]^{\cdot+}$ (5%) Calculated: 390.0602, Found: 390.0598, $[M-Cl+OH]^{\cdot+}$ (100%) Calculated: 407.0629, Found: 407.0625. EA (%): Calculated/Found C: 45.11/45.06, H: 5.91/6.02, N: 3.29/3.54, S: 30.10/31.89.

Synthesis of 1,4-bis(diethylamino)-1,4*H*-1,4-diphosphinines 5d–f

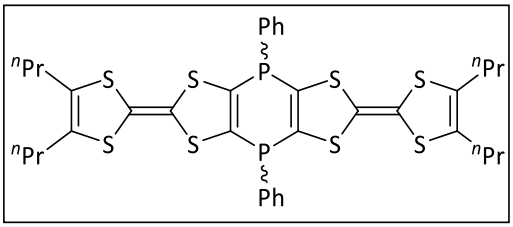
4d,e,f were each dissolved in dry THF and cooled down to −95 °C. A solution of LDA (1.1 eq) in dry THF was prepared and cooled down to −95 °C, then it was added dropwise to starting material. Then the reaction mixture was allowed to warm up slowly and stirred for 3 hours. After that the solvent was evaporated in *vacuo* (8×10^{-3} mbar). Then the residue was taken up in dry diethylether and filtered, the solution was concentrated and dried in *vacuo* (8×10^{-3} mbar).

2,6-Bis(4,5-dimethyl-1,3-dithiol-2-ylidene)-bis(1,3-dithiole)[2,3-d:5,6-d']-4,8-bis(diethylamino)-4,8*H*-4,8-diphosphinine (5d)



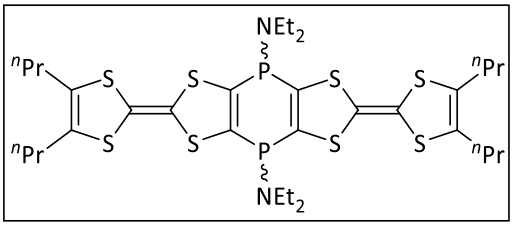
Product: Brown powder, Yield: 162 mg (0.24 mmol, 60%), Melting point: 182 °C (decomp.). ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 1.11 and 1.16 (*t*, 12H, $^{3}J_{H,H}$ = 7.1 Hz, N-CH_2-$\underline{CH_3}$), 1.93 (*s*, 12H, C^4,C^4-Me), 2.98 and 3.05 (*m*, 8H, N-$\underline{CH_2}$-CH_3). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 13.9 (*s*, C^4, C^5-Me), 14.9 (*br*, N-CH_2-$\underline{CH_3}$), 44.8 (*br*, N-$\underline{CH_2}$-CH_3), 110.8 and 111 (*s*, C^2,$C^{2'}$), 123.1 and 123.1 (*s*, C^4 and C^5), 133.5 and 139 (*m*, $C^{2,3,5,6}$, central ring). ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$): δ = 29.4 (*s*), 32.3 (*s*). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ = 29.4 (*m*), 32.3 (*m*). MS (EI, 70 eV): m/z (%) = 698 (8) $[M+O_2]^{\cdot+}$, 666 (80) $[M]^{\cdot+}$, 521.8 (35) $[M-(Et_2N)_2PCl]^{\cdot+}$. HR-MS: Calculated: 665.9806, Found: 665.9819. EA (%): Calculated/Found C: 43.22/44.49, H: 4.84/5.99, N: 4.20/3.09, S: 38.45/29.82.

2,6-Bis(4,5-dipropyl-1,3-dithiol-2-ylidene)-bis(1,3-dithiole)[2,3-d:5,6-d']-4,8-diphenyl-4,8*H*-4,8-diphosphinine (5e)



Product: Brown powder, Yield: 251 mg (0.31 mmol, 97%), Melting point: 131 °C. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 0.9 (*m*, 12H, $C^{4'}$, $C^{5'}$-CH_2-CH_2-$\underline{CH_3}$), 1.46 (*m*, 8H, $C^{4'}$, $C^{5'}$-CH_2-$\underline{CH_2}$-CH_3), 2.26 (*m*, 8H, $C^{4'}$, $C^{5'}$-$\underline{CH_2}$-CH_2-CH_3), 7.39-7.73 (*m*, 5H, *para, meta, ortho* -C_6H_5). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 13.7 (*s*, $C^{4'}$, $C^{5'}$-CH_2-CH_2-$\underline{CH_3}$), 23.1 (*s*, $C^{4'}$, $C^{5'}$-CH_2-$\underline{CH_2}$-CH_3), 30.8 (*s*, $C^{4'}$, $C^{5'}$-$\underline{CH_2}$-CH_2-CH_3), 113.6 and 114 (*s*, C^2,$C^{2'}$), 128.7-135.1 (*m*, *para, meta, ortho, ipso* -C_6H_5), 134.2 (*m*, $C^{2,3,5,6}$, central ring). ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$): δ = −21.9 (*s*), −26.2 (*s*). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ = −21.9 (*m*), −26.2 (*m*). MS (EI, 70 eV): m/z (%) = 788.2 (5) $[M]^{\cdot+}$, 287.0 (32) [$^{n}Pr_2$TTF], 230.1 (80) [DimethylTTF]. HR-MS: Calculated: 788.0214, Found: 788.0220. EA (%): Calculated/Found C: 54.79/55.50, H: 4.85/5.36, S: 32.5/31.47.

2,6-Bis(4,5-dipropyl-1,3-dithiol-2-ylidene)-bis(1,3-dithiole)[2,3-d:5,6-d']-4,8-bis(diethylamino)-4,8*H*-4,8-diphosphinine (5f)

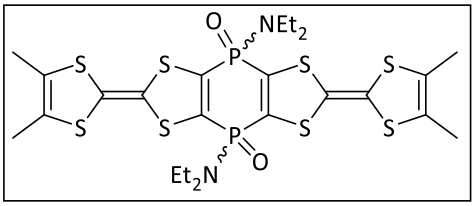


Product: Brown powder, Yield: 1.253 mg (3.21 mmol, 100%), Melting point: 118 °C. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 0.93 (*t*, 12H, $^{3}J_{H,H}$ = 7.35 Hz, $C^{4'}$, $C^{5'}$-CH_2-CH_2-$\underline{CH_3}$), 1.12 (*m (2t)*, 12H, N-CH_2-$\underline{CH_3}$), 1.53 (*m*, 8H, $C^{4'}$, $C^{5'}$-CH_2-$\underline{CH_2}$-CH_3), 2.31 (*m*, 8H, $C^{4'}$, $C^{5'}$-$\underline{CH_2}$-CH_2-CH_3), 2.99 (*m*, 8H, N-$\underline{CH_2}$-CH_3). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 13.8 (*s*, $C^{4'}$, $C^{5'}$-CH_2-CH_2-$\underline{CH_3}$), 14.9 (*s*, N-CH_2-$\underline{CH_3}$), 23.1 (2*s*, $C^{4'}$, $C^{5'}$-CH_2-$\underline{CH_2}$-CH_3), 30.9 (*s*, $C^{4'}$, $C^{5'}$-$\underline{CH_2}$-CH_2-CH_3), 44.8 (*m (2d)*, N-$\underline{CH_2}$-CH_3), 110.9 and 111.3 (*s*, C^{2}, $C^{2'}$), 129 (2*s*, $C^{4'}$ and $C^{5'}$), 133.5 and 139.1 (*m*, $C^{2,3,5,6}$, central ring). ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$): δ = 29.7 (*s*), 32.5 (*s*). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ = 29.7 (*m*), 32.5 (*m*). MS (EI, 70 eV): m/z (%) = 778.1 (75) $[M]^{\cdot+}$, 634.0 (10) $[M-2NEt_2]^{+}$, 230.0 (100) [DimethylTTF]. HR-MS: Calculated: 778.1058, Found: 778.1079. EA (%): Calculated/Found C: 49.33/49.46, H: 6.21/6.08, N: 3.60/3.63, S: 32.92/41.50.

Oxidation of the 1,4-bis(diethylamino)-1,4*H*-1,4-diphosphinines with hydrogen peroxide-urea adduct 6

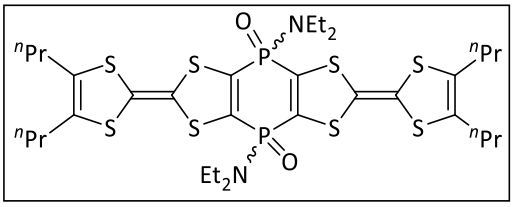
hydrogen peroxide-urea adduct was added to a Schlenk tube, containing starting material, then DCM was added and the reaction mixture was stirred overnight at r.t. After this time, solvent was removed in *vacuo* (8×10^{-3} mbar). The residue was extracted with DCM (2x20 mL) and the solution was concentrated and dried in *vacuo* (8×10^{-3} mbar). In the case of **6d**, the product was washed with ^{n}Pentane (2x10 mL) and dried in *vacuo* (8×10^{-3} mbar).

2,6-Bis(4,5-dimethyl-1,3-dithiol-2-ylidene)-bis(1,3-dithiole)[2,3-d:5,6-d']-4,8-bis(diethyl-amino)-4,8*H*-4,8-dioxide-4,8-diphosphinine (6d)



Product: Brown powder, Yield: 31 mg (0.044 mmol, 74%), Melting point: 207 °C. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 1.17 (*m(2t)*, 12H, N-CH_2-$\underline{CH_3}$), 1.94 (*s*, 12H, $C^{4'}$, $C^{5'}$-$\underline{CH_3}$), 3.14 (*m*, 8H, N-$\underline{CH_2}$-CH_3). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 13.8 (*s*, N-CH_2-$\underline{CH_3}$), 14.1 (*s*, $C^{4'}$, $C^{5'}$-$\underline{CH_3}$), 38.2 (*d*, $^{2}J_{P,C}$ = 10.76 Hz, N-$\underline{CH_2}$-CH_3), 118.1 and 118.4 (*s*, C^{2},$C^{2'}$), 123.1 and 123.2 (*s*, $C^{4'}$ and $C^{5'}$), 140.6 (*m*, $C^{2,3,5,6}$, central ring). ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$): δ = −2.1 (*s*), −0.8 (*s*). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ = −2.1 (*m*), −0.8 (*m*). MS (ESI-pos): m/z (%) = 730.967 (30) $[M+O_2+H]^{\cdot+}$, 713.965 (76) $[M+O]^{\cdot+}$, 697.970 (100) $[M]^{\cdot+}$. HR-MS: Calculated: 697.9699, Found: 697.9700. EA (%): Calculated/Found C: 41.24/42.31, H: 4.61/5.21, N: 4.01/4.37, S: 36.96/35.30.

2,6-Bis(4,5-dipropyl-1,3-dithiol-2-ylidene)-bis(1,3-dithiole)[2,3-d:5,6-d']-4,8-bis(diethylamino)-4,8*H*-4,8-dioxide-4,8-diphosphinine (6f)



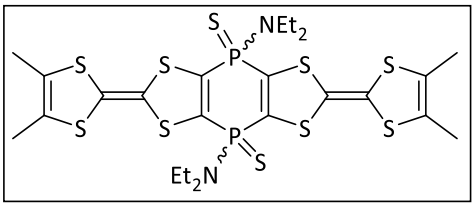
Product: Brown powder, Yield: 42 mg (0.052 mmol, 86%), Melting point: 151 °C. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 0.93 (2*t*, 12H, $^{3}J_{H,H}$ = 7.34 Hz, $C^{4'}$, $C^{5'}$-CH_2-CH_2-$\underline{CH_3}$), 1.18 (*m(2t)*, 12H, N-CH_2-$\underline{CH_3}$), 1.52 (*m*, 8H, $C^{4'}$, $C^{5'}$-CH_2-$\underline{CH_2}$-CH_3), 2.32 (*m*, 8H, $C^{4'}$, $C^{5'}$-$\underline{CH_2}$-CH_2-CH_3), 3.15 (*m*, 8H, N-$\underline{CH_2}$-CH_3). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 13.7 (*s*, $C^{4'}$, $C^{5'}$-CH_2-CH_2-$\underline{CH_3}$), 14.1 (*s*, N-CH_2-$\underline{CH_3}$), 23.1 (*s*, $C^{4'}$, $C^{5'}$-CH_2-$\underline{CH_2}$-CH_3), 30.8 (*s*, $C^{4'}$, $C^{5'}$-$\underline{CH_2}$-CH_2-CH_3), 38.2 (*m*, N-$\underline{CH_2}$-CH_3), 118.3 and 118.9 (*s*, C^{2}, $C^{2'}$), 129.1 (*s*, $C^{4'}$ and $C^{5'}$), 140.6 (*m*, $C^{2,3,5,6}$, central ring). ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$): δ = −2.1 (*s*), −0.7 (*s*). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ = −2.2 (*m*), −0.7 (*m*). MS (ESI-pos): m/z (%) = 843.092 (29) $[M+O_2+H]^{\cdot+}$, 826.090 (65) $[M+O]^{\cdot+}$, 810.095 (100) $[M]^{\cdot+}$. HR-MS: Calculated: 810.0951,

Found: 810.0953. EA (%): Calculated/Found C: 47.38/47.68, H: 5.96/6.35, N: 3.45/4.09, S: 31.62/28.70.

Oxidation of the 1,4-bis(diethylamino)-1,4*H*-1,4-diphosphinines with elemental sulfur 7

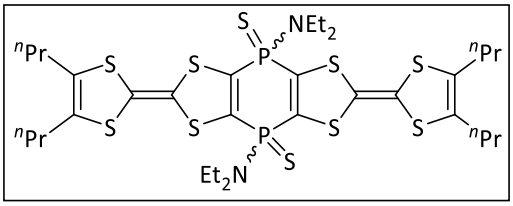
Elemental sulfur was added to a Schlenk tube, containing starting material, then Toluene was added and the reaction mixture was stirred for 3 hours at 100 °C. After this time, solvent was removed in *vacuo* (8×10^{-3} mbar). The residue was extracted with DCM (2x20 mL) and the solution was concentrated and dried in *vacuo* (8×10^{-3} mbar). In the case of **7d**, the product was washed with ^{n}Pentane (2x10 mL) and dried in *vacuo* (8×10^{-3} mbar).

2,6-Bis(4,5-dimethyl-1,3-dithiol-2-ylidene)-bis(1,3-dithiole)[2,3-d:5,6-d']-4,8-bis(diethylamino)-4,8*H*-4,8-diphosphinine-4,8-disulfide (7d)



Product: Brown powder, Yield: 26 mg (0.035 mmol, 58%), Melting point: 238 °C. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 1.17 (*m*, 12H, N-CH_2-$\underline{CH_3}$), 1,94 (*s*, 12H, $C^{4'}$, $C^{5'}$-$\underline{CH_3}$), 3.27 (*m*, 8H, N-$\underline{CH_2}$-CH_3). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 13.8 (*s*, N-CH_2-$\underline{CH_3}$), 14.2 (*s*, $C^{4'}$, $C^{5'}$-$\underline{CH_3}$), 39.3 (*s*, N-$\underline{CH_2}$-CH_3), 117.7 (2*s*, C^{2},$C^{2'}$), 123.2 (2*s*, $C^{4'}$ and $C^{5'}$), 139.8 (*m*, $C^{2,3,5,6}$, central ring). ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$): δ = 25.2 (2*s*). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ = 25.2 (*m*). MS (ESI-pos): m/z (%) = 762.921 (10) $[M+O_2+H]^{\cdot+}$, 745.919 (48) $[M+O]^{\cdot+}$, 729.924 (100) $[M]^{\cdot+}$. HR-MS: Calculated: 729.9242, Found: 729.9243. EA (%): Calculated/Found C: 39.43/38.48, H: 4.41/4.83, N: 3.83/3.15, S: 43.85/41.68.

2,6-Bis(4,5-dipropyl-1,3-dithiol-2-ylidene)-bis(1,3-dithiole)[2,3-d:5,6-d']-4,8-bis(diethylamino)-4,8*H*-4,8-diphosphinine-4,8-disulfide (7f)

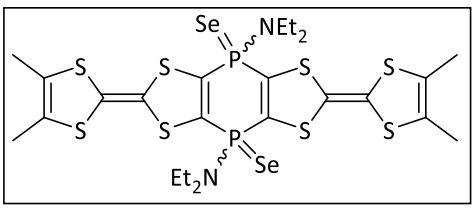


Product: Brown powder, Yield: 41 mg (0.049 mmol, 81%), Melting point: 183 °C. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 0.93 (*t*, 12H, $^{3}J_{H,H}$ = 7.40 Hz, $C^{4'}$, $C^{5'}$-CH_2-CH_2-$\underline{CH_3}$), 1.16 and 1.19 (*t*, 12H, $^{3}J_{H,H}$ = 7.1 Hz, N-CH_2-$\underline{CH_3}$), 1.52 (*m*, 8H, $C^{4'}$, $C^{5'}$-CH_2-$\underline{CH_2}$-CH_3), 2.32 (*m*, 8H, $C^{4'}$, $C^{5'}$-$\underline{CH_2}$-CH_2-CH_3), 3.27 (*m*, 8H, N-$\underline{CH_2}$-CH_3). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 13.7 (*s*, $C^{4'}$, $C^{5'}$-CH_2-CH_2-$\underline{CH_3}$), 14.2 (*s*, N-CH_2-$\underline{CH_3}$), 23.1 (2*s*, $C^{4'}$, $C^{5'}$-CH_2-$\underline{CH_2}$-CH_3), 30.8 (*s*, $C^{4'}$, $C^{5'}$-$\underline{CH_2}$-CH_2-CH_3), 39.4 (*s*, N-$\underline{CH_2}$-CH_3), 117.6 and 117.9 (*s*, C^{2}, $C^{2'}$), 129.1 (*s*, $C^{4'}$ and $C^{5'}$), 139.9 (*m*, $C^{2,3,5,6}$, central ring). ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$): δ = 25.2 (*s*), 25.4 (*s*). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ = 25.3 (*m*). MS (ESI-pos): m/z (%) = 875.046 (15) $[M+O_2+H]^{\cdot+}$, 858.044 (51) $[M+O]^{\cdot+}$, 842.049 (100) $[M]^{\cdot+}$. HR-MS: Calculated: 842.0494, Found: 842.0491. EA (%): Calculated/Found C: 45.58/43.85, H: 5.74/5.72, N: 3.33/3.07, S: 38.02/40.80.

Oxidation of the 1,4-bis(diethylamino)-1,4*H*-1,4-diphosphinines with elemental selenium 8

Selenium was added to a Schlenk tube, containing starting material, then Toluene was added and the reaction mixture was stirred for 3 hours at 100 °C. After this time, solvent was removed in *vacuo* (8×10^{-3} mbar). The residue was extracted with DCM (2x20 mL) and the solution was concentrated and dried in *vacuo* (8×10^{-3} mbar). In the case of **8d**, the product was washed with n-Pentane (2x10 mL) and dried in *vacuo* (8×10^{-3} mbar).

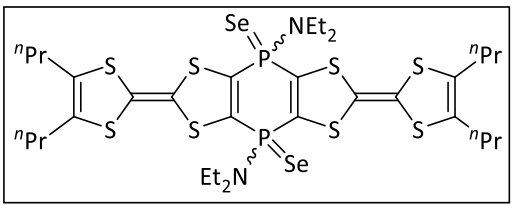
2,6-Bis(4,5-dimethyl-1,3-dithiol-2-ylidene)-bis(1,3-dithiole)[2,3-d:5,6-d']-4,8-bis(diethylamino)-4,8*H*-4,8-diphosphinine-4,8-diselenide (8d)



Product: Brown powder, Yield: 30 mg (0.036 mmol, 61%), Melting point: 264 °C (decomp.) ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 1.16 and 1.19 (*t*, 12H, $^{3}J_{H,H}$ = 7.1 Hz, N-CH_2-$\underline{CH_3}$), 1.94 (*s*, 12H, $C^{4'}$, $C^{5'}$-$\underline{CH_3}$), 3.32 (*m*, 8H, N-$\underline{CH_2}$-CH_3). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 13.8 (*s*, N-CH_2-$\underline{CH_3}$), 14.2 (*s*, $C^{4'}$, $C^{5'}$-$\underline{CH_3}$), 40.2 (*d*, $^{2}J_{P,C}$ = 16.72 Hz, N-$\underline{CH_2}$-CH_3), 117.8 (*s*, C^{2},$C^{2'}$), 123.2 (2*s*, $C^{4'}$ and $C^{5'}$), 138.5 (*m*, $C^{2,3,5,6}$, central ring). ^{31}P{^{1}H} NMR (202.5 MHz,

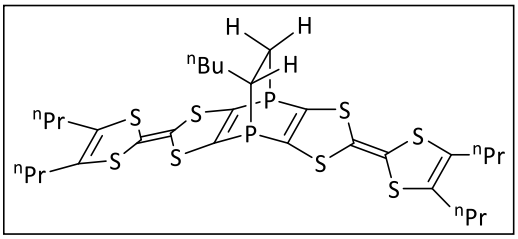
$CDCl_3$): δ = 15.7 (s_{sat}, $^1J_{P,Se}$ = 816 Hz), 15.8 (s_{sat}, $^1J_{P,Se}$ = 804 Hz). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ = 15.7 (*m*). MS (ESI-pos): m/z (%) = 841.807 (27) $[M+O]^{\cdot+}$, 825.812 (100) $[M]^{\cdot+}$. HR-MS: Calculated: 825.8127, Found: 825.8127. EA (%): Calculated/Found C: 34.95/37.67, H: 3.91/4.52, N: 3.40/3.08, S: 31.09/30.18.

2,6-Bis(4,5-dipropyl-1,3-dithiol-2-ylidene)-bis(1,3-dithiole)[2,3-d:5,6-d']-4,8-bis(diethylamino)-4,8*H*-4,8-diphosphinine-4,8-diselenide (8f)



Product: Brown powder, Yield: 52 mg (0.055 mmol, 92%), Melting point: 209 °C. ^1H NMR (500.1 MHz, $CDCl_3$): δ = 0.93 (*t*, 12H, $^3J_{H,H}$ = 7.34 Hz, $C^{4'}$, $C^{5'}$-CH_2-CH_2-$\underline{CH_3}$), 1.16 and 1.19 (*t*, 12H, $^3J_{H,H}$ = 7.1 Hz, N-CH_2-$\underline{CH_3}$), 1.52 (*h*, 8H, $^3J_{H,H}$ = 7.41 Hz, $C^{4'}$, $C^{5'}$-CH_2-$\underline{CH_2}$-CH_3), 2.32 (*m*, 8H, $C^{4'}$, $C^{5'}$-$\underline{CH_2}$-CH_2-CH_3), 3.33 (*m*, 8H, N-$\underline{CH_2}$-CH_3). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 13.7 (*s*, $C^{4'}$, $C^{5'}$-CH_2-CH_2-$\underline{CH_3}$), 14.2 (*d*, $^3J_{P,C}$ = 3.59 Hz, N-CH_2-$\underline{CH_3}$), 23.1 (*s*, $C^{4'}$, $C^{5'}$-CH_2-$\underline{CH_2}$-CH_3), 30.8 (*s*, $C^{4'}$, $C^{5'}$-$\underline{CH_2}$-CH_2-CH_3), 40.2 (*d*, $^2J_{P,C}$ = 21.51 Hz, N-$\underline{CH_2}$-CH_3), 117.7 and 117.9 (*s*, C^2,$C^{2'}$), 129.1 (*s*, $C^{4'}$ and $C^{5'}$), 138.5 (*m*, $C^{2,3,5,6}$, central ring). $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$): δ = 15.7 (s_{sat}, $^1J_{P,Se}$ = 804 Hz), 15.9 (s_{sat}, $^1J_{P,Se}$ = 812 Hz). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ = 15.7 (*m*), 15.9 (*m*). MS (ESI-pos): m/z (%) = 970.936 (18) $[M+O_2+H]^{\cdot+}$, 953.934 (33) $[M+O]^{\cdot+}$, 937.938 (100) $[M]^{\cdot+}$. HR-MS: Calculated: 937.9381, Found: 937.9384. EA (%): Calculated/Found C: 41.01/41.88, H: 5.16/5.45, N: 2.99/2.96, S: 27.37/26.23.

Synthesis of 10-butyl-2,6-bis(4,5-dipropyl-1,3-dithiol-2-ylidene)-4 ,8-ethano[1,4]diphosphinino[2,3-d:5,6-d']bis([1,3]dithiole) 11f



Starting material was dissolved in dry DCM, then PCl_3 (2.5 eq) was slowly added and the reaction mixture was stirred for 3 hours at r.t. After this time, all volatiles were

evaporated in *vacuo* (8×10^{-3} mbar) and the residue was dissolved in dry DCM. Then first 1-hexene (200 eq) and after that PMe_3 (1.3 eq) were added to the reaction mixture and it was stirred for 3 days. After that, all volatiles were evaporated in *vacuo* (8×10^{-3} mbar). Then the product was extracted from the residue using dry n-Pentane (3x30 mL) and the solution was concentrated and dried in *vacuo* (8×10^{-3} mbar). Product: Orange-red oily/sticky solid, Yield: 63 mg (0.088 mmol, 38%). ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 0.89 *(t*, 3H, $^{3}J_{H,H}$ = 7.31 Hz, P-CH-CH_2-CH_2-CH_2-$\underline{CH_3}$), 0.93 (*m*, 12H, $C^{4'}$, $C^{5'}$-CH_2-CH_2-$\underline{CH_3}$), 1.18-1.46 (*m*, 7H, P-$\underline{CH}$-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-CH_3), 1.52 (*m*, 8H, $C^{4'}$, $C^{5'}$-CH_2-$\underline{CH_2}$-CH_3), 1.99 (*m*, 2H, P-$\underline{CH_2}$) 2.31 (*t*, 8H, $^{3}J_{H,H}$ = 6.46 Hz, $C^{4'}$, $C^{5'}$-$\underline{CH_2}$-CH_2-CH_3). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 13.8 (*s*, P-CH-CH_2-CH_2-CH_2-$\underline{CH_3}$), 14.1 (*s*, $C^{4'}$, $C^{5'}$-CH_2-CH_2-$\underline{CH_3}$), 22.6 and 22.8 (*s*, P-CH-CH_2-$\underline{CH_2}$-$\underline{CH_2}$-CH_3), 23.1 (*s*, $C^{4'}$, $C^{5'}$-CH_2-$\underline{CH_2}$-CH_3), 29.8 (*s*, P-CH-$\underline{CH_2}$-CH_2-CH_2-CH_3), 30.8 (*s*, $C^{4'}$, $C^{5'}$-$\underline{CH_2}$-CH_2-CH_3), 31.3 (*d*, $^{1}J_{P,C}$ = 15.21 Hz, P-$\underline{CH}$-CH_2-CH_2-CH_2-CH_3), 34.9 (*d*, $^{1}J_{P,C}$ = 17.04 Hz, P-$\underline{CH_2}$), 110.9 and 111.9 (*s*, C^{2},$C^{2'}$), 129 (2*s*, $C^{4'}$ and $C^{5'}$), 140-143.6 (*m*, $C^{2,3,5,6}$, central ring). ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$): δ = -71.7 (*d*, $^{3}J_{P,P}$ = 32.39 Hz), -67.70 (*d*, $^{3}J_{P,P}$ = 32.30 Hz). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ = -71.7 (*dt*, $^{3}J_{P,P}$ = 32.39 Hz and $^{2}J_{P,H}$ = 8.14), -67.70 (*m*). MS (ESI-pos): m/z (%) = 734.030 (3) $[M+O]^{\cdot+}$, 718.036 (16) $[M]^{\cdot+}$, 633.942 (3) $[M-C_6H_{12}]^{\cdot+}$. HR-MS: Calculated: 718.0365, Found: 718.0363. EA (%): Calculated/Found C: 50.11/53.77, H: 5.61/6.30, S: 35.67/39.76.

NMR Spectra

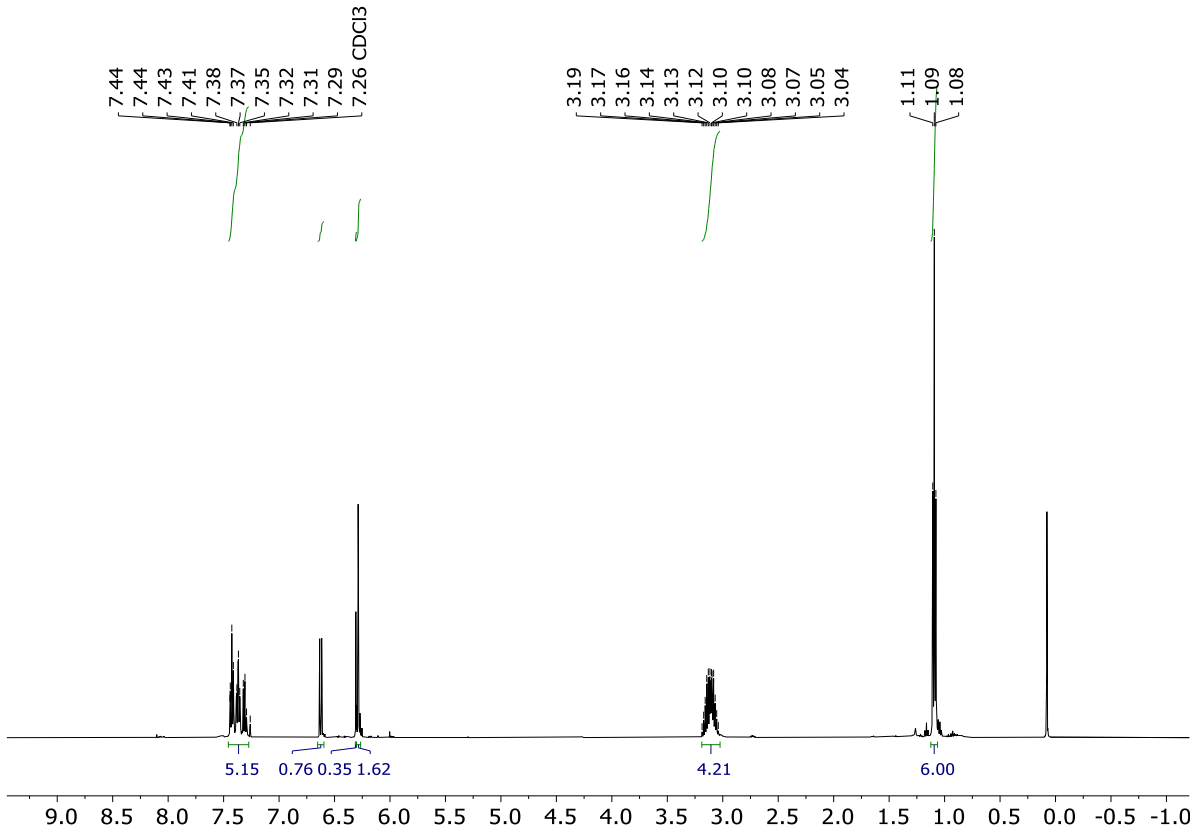


Figure S1: ^{1}H NMR spectrum of compound **3a** in $CDCl_3$.

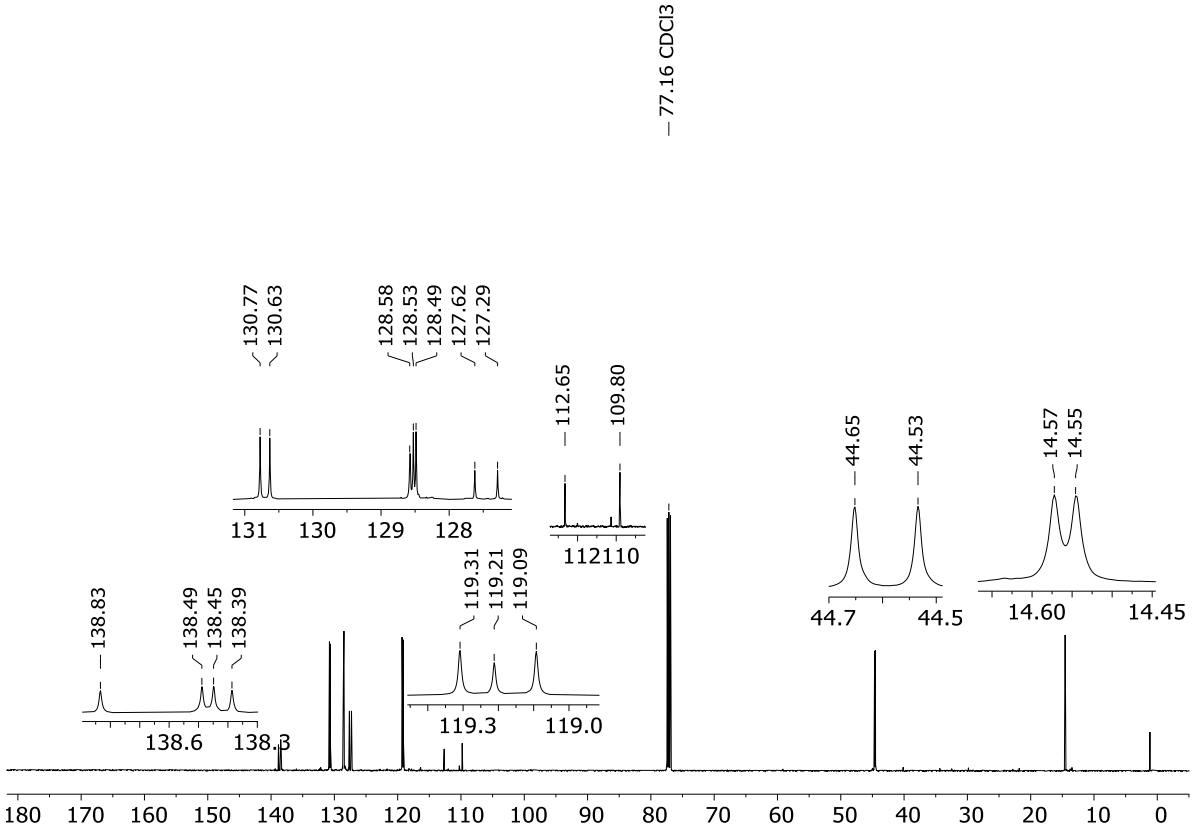


Figure S2: $^{13}C\{^{1}H\}$ NMR spectrum of compound **3a** in $CDCl_3$.

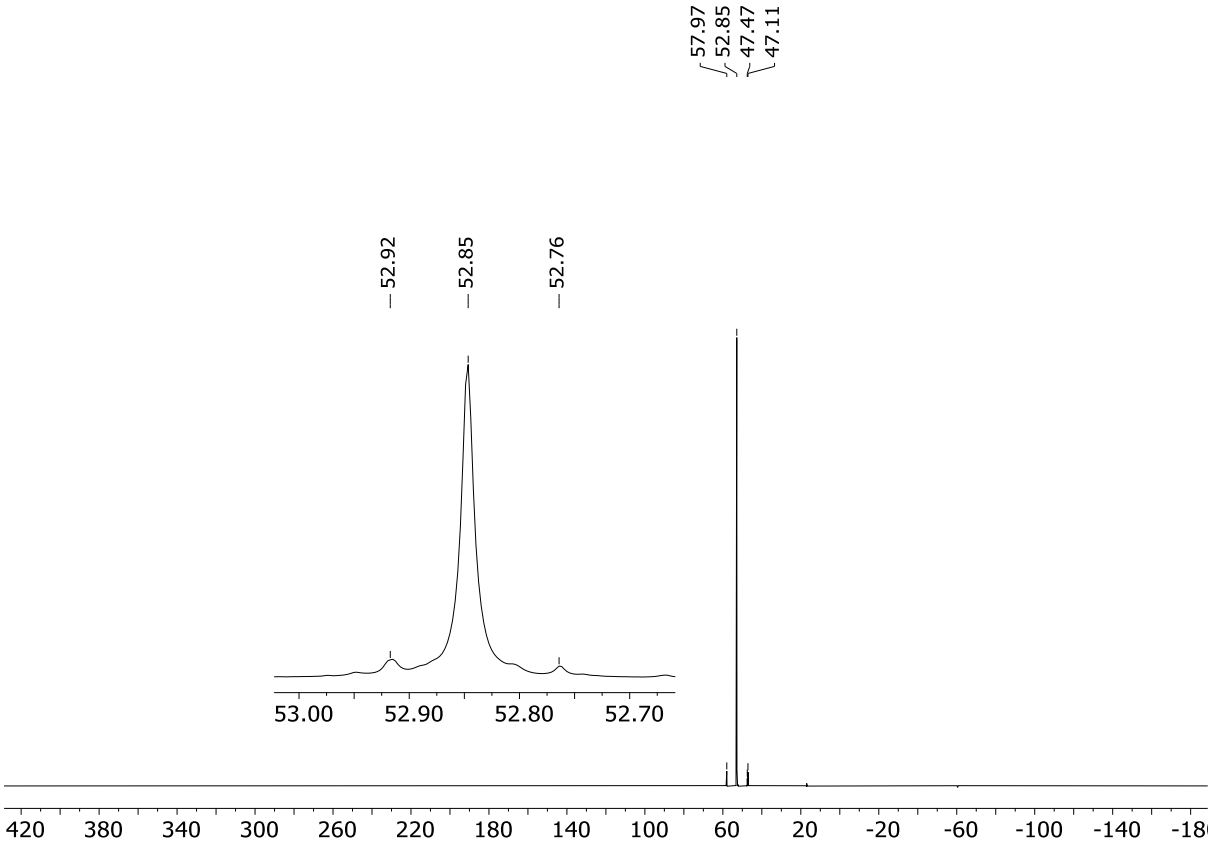


Figure S3: $^{31}P\{^{1}H\}$ NMR spectrum of compound **3a** in $CDCl_3$.

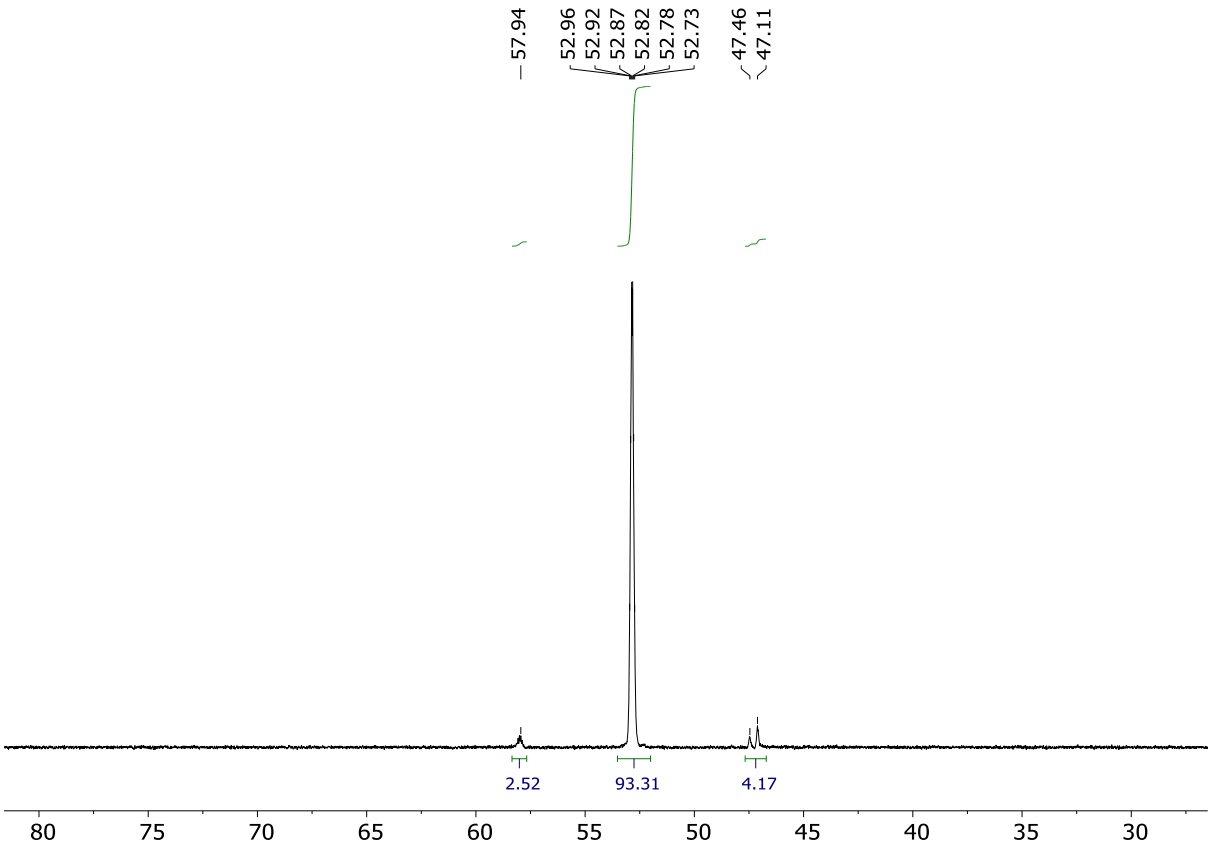


Figure S4: ^{31}P NMR spectrum of compound **3a** in $CDCl_3$.

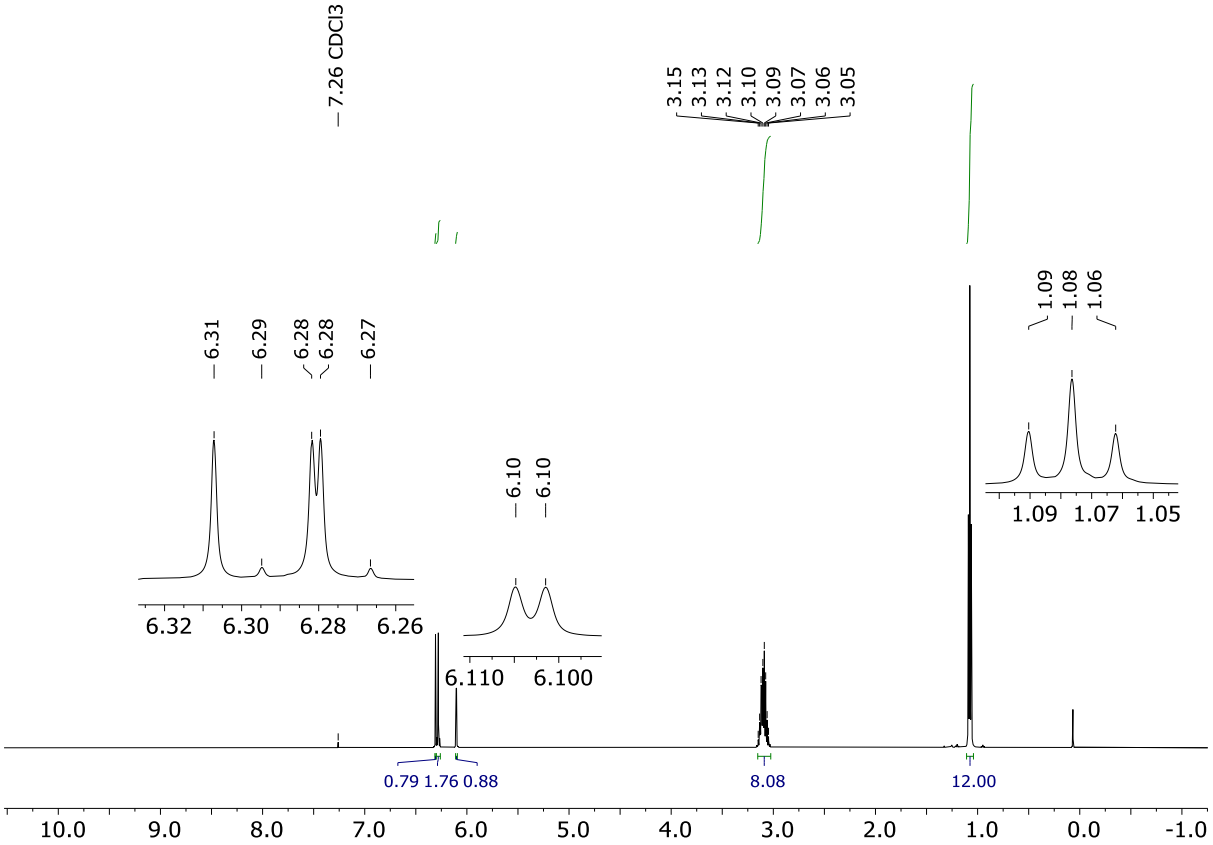


Figure S5: ^{1}H NMR spectrum of compound **3b** in $CDCl_3$.

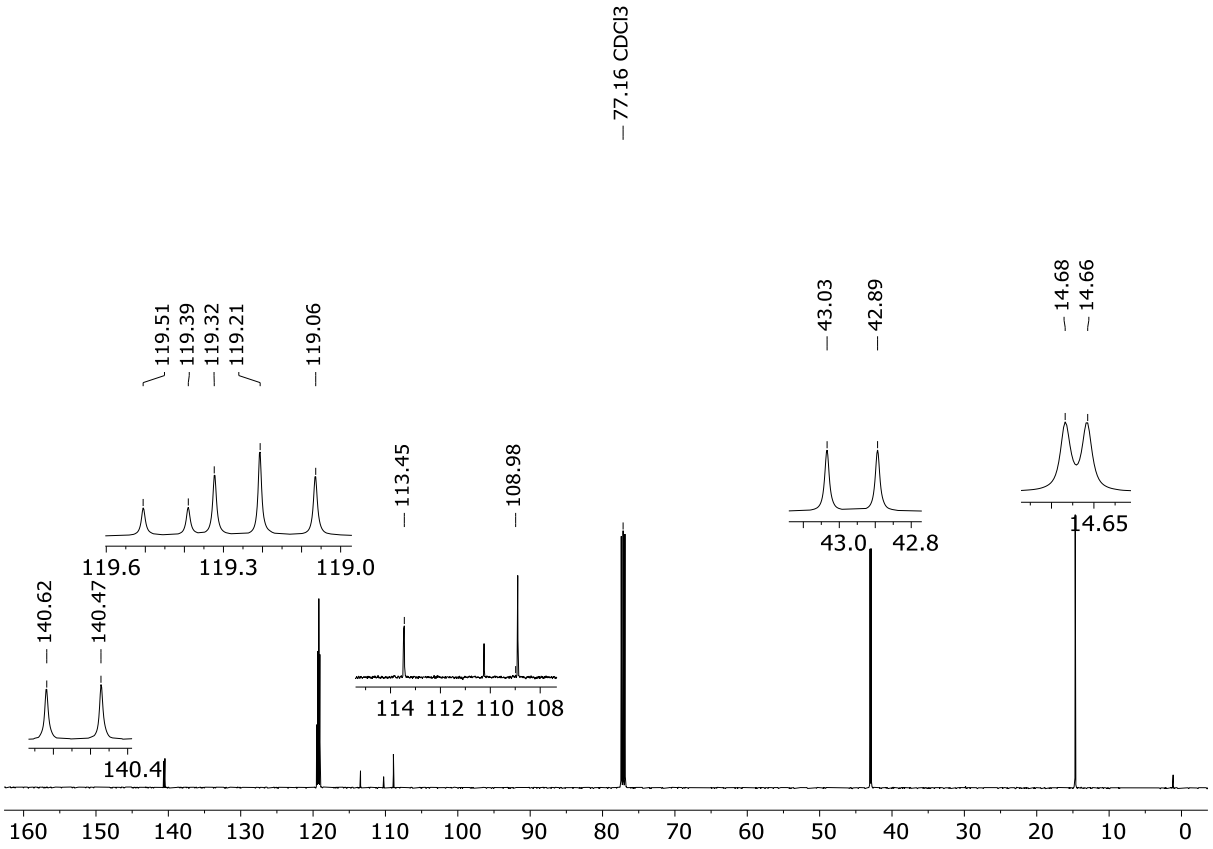


Figure S6: $^{13}C\{^{1}H\}$ NMR spectrum of compound **3b** in $CDCl_3$.

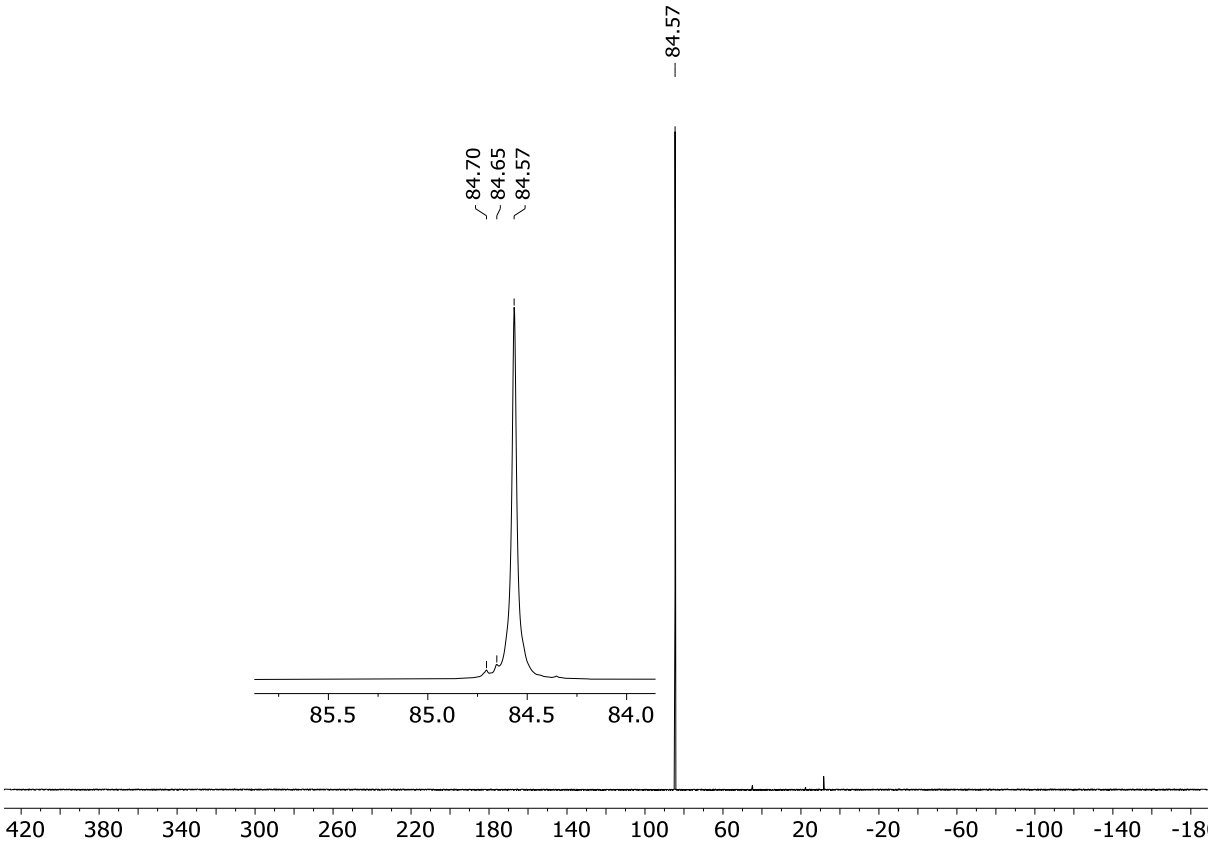


Figure S7: $^{31}P\{^{1}H\}$ NMR spectrum of compound **3b** in $CDCl_3$.

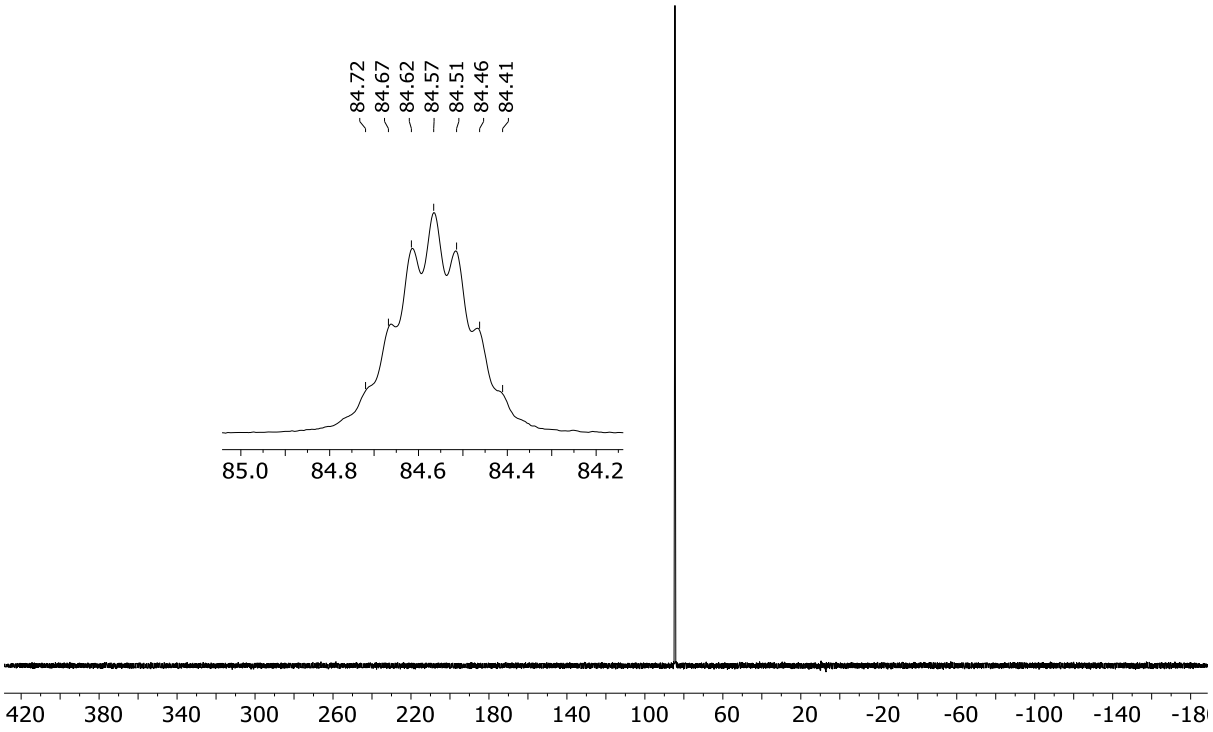


Figure S8: ^{31}P NMR spectrum of compound **3b** in $CDCl_3$.

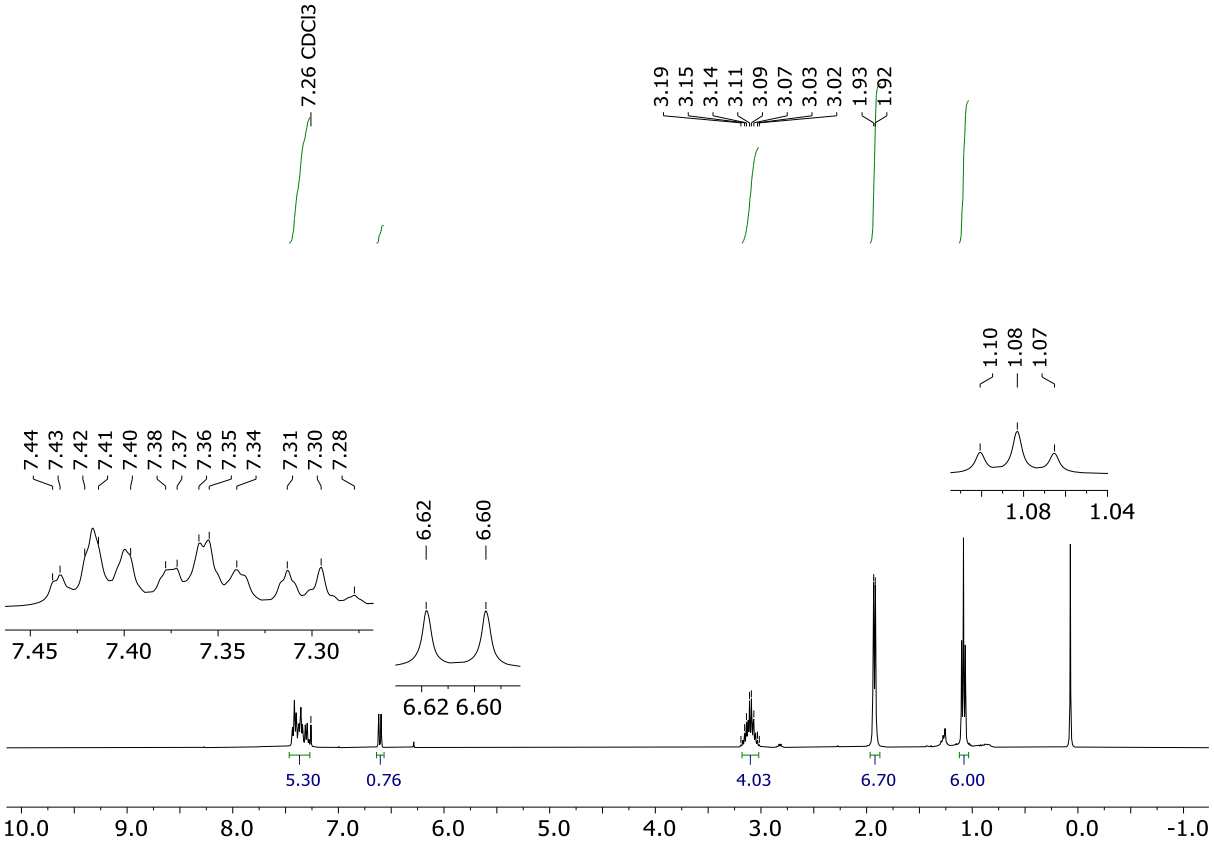


Figure S9: ^{1}H NMR spectrum of compound **3c** in $CDCl_3$.

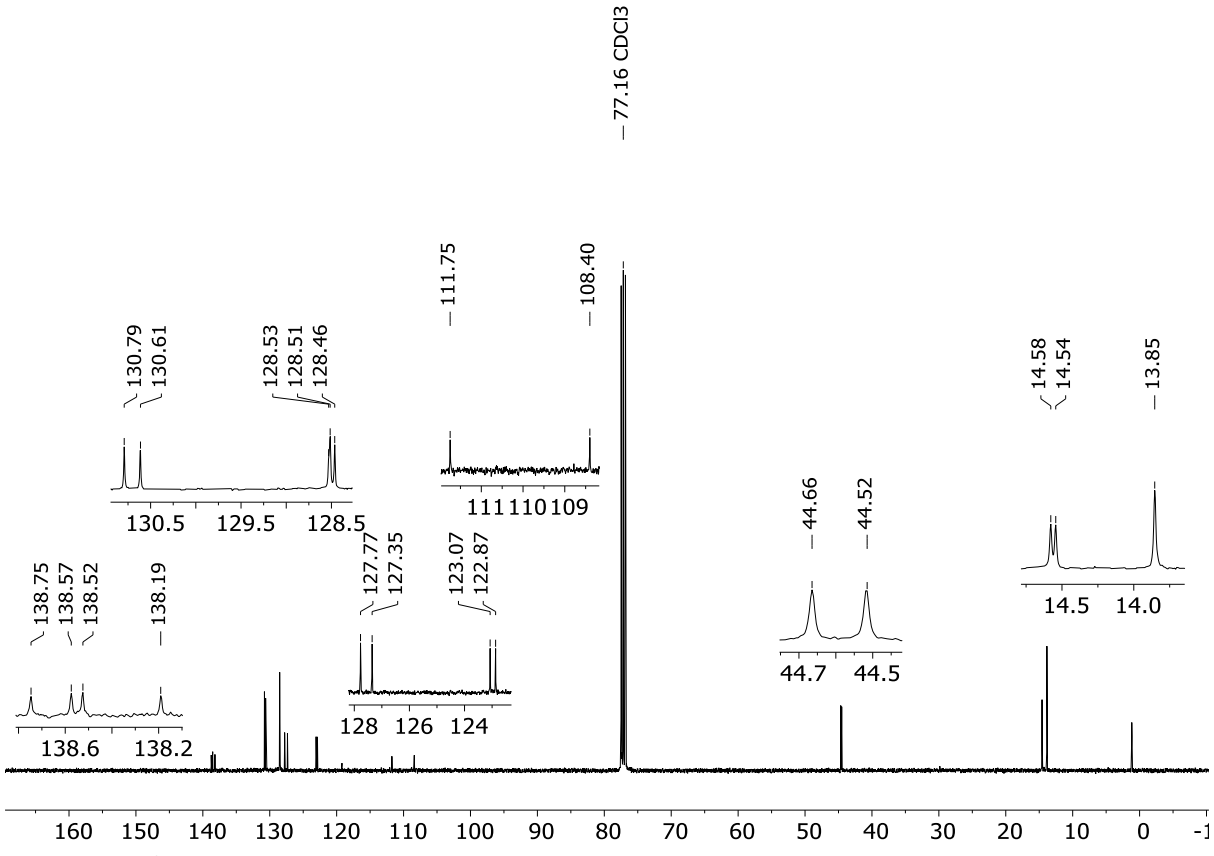


Figure S10: $^{13}C\{^{1}H\}$ NMR spectrum of compound **3c** in $CDCl_3$.

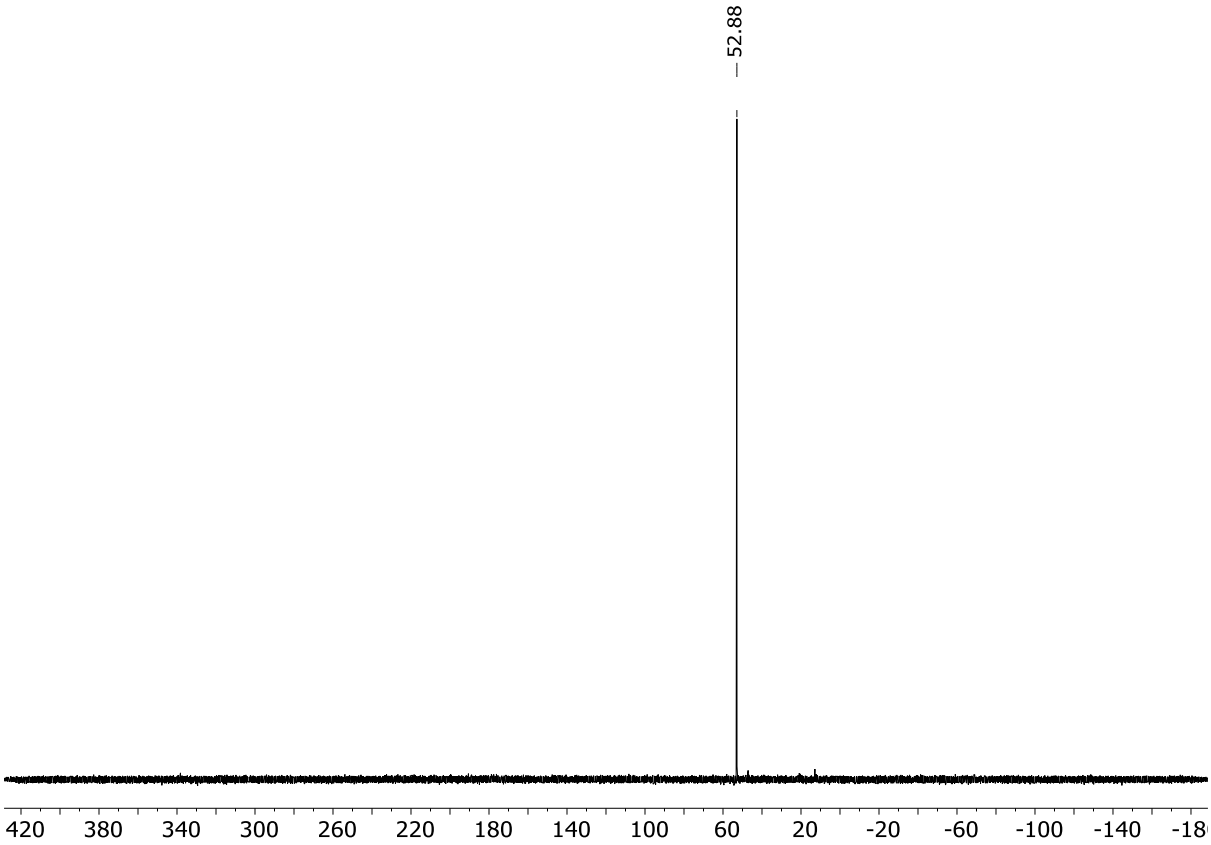


Figure S11: $^{31}P\{^{1}H\}$ NMR spectrum of compound **3c** in $CDCl_3$.

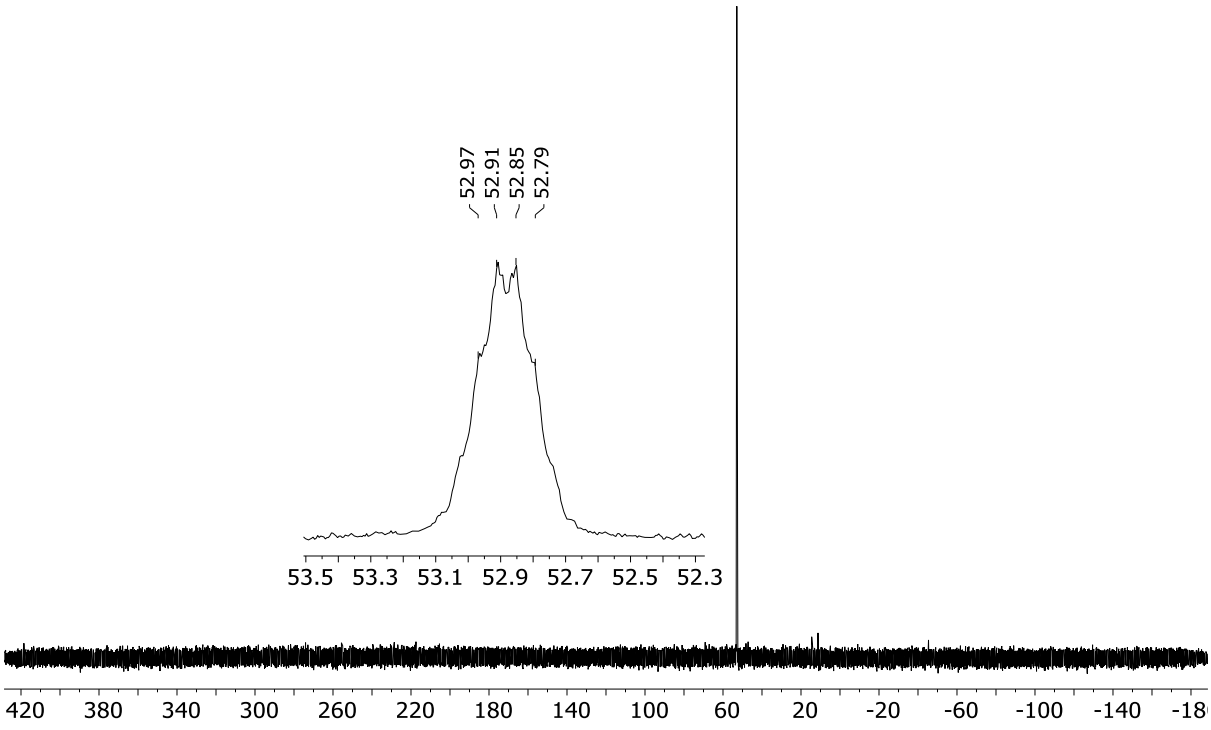


Figure S12: ^{31}P NMR spectrum of compound **3c** in $CDCl_3$.

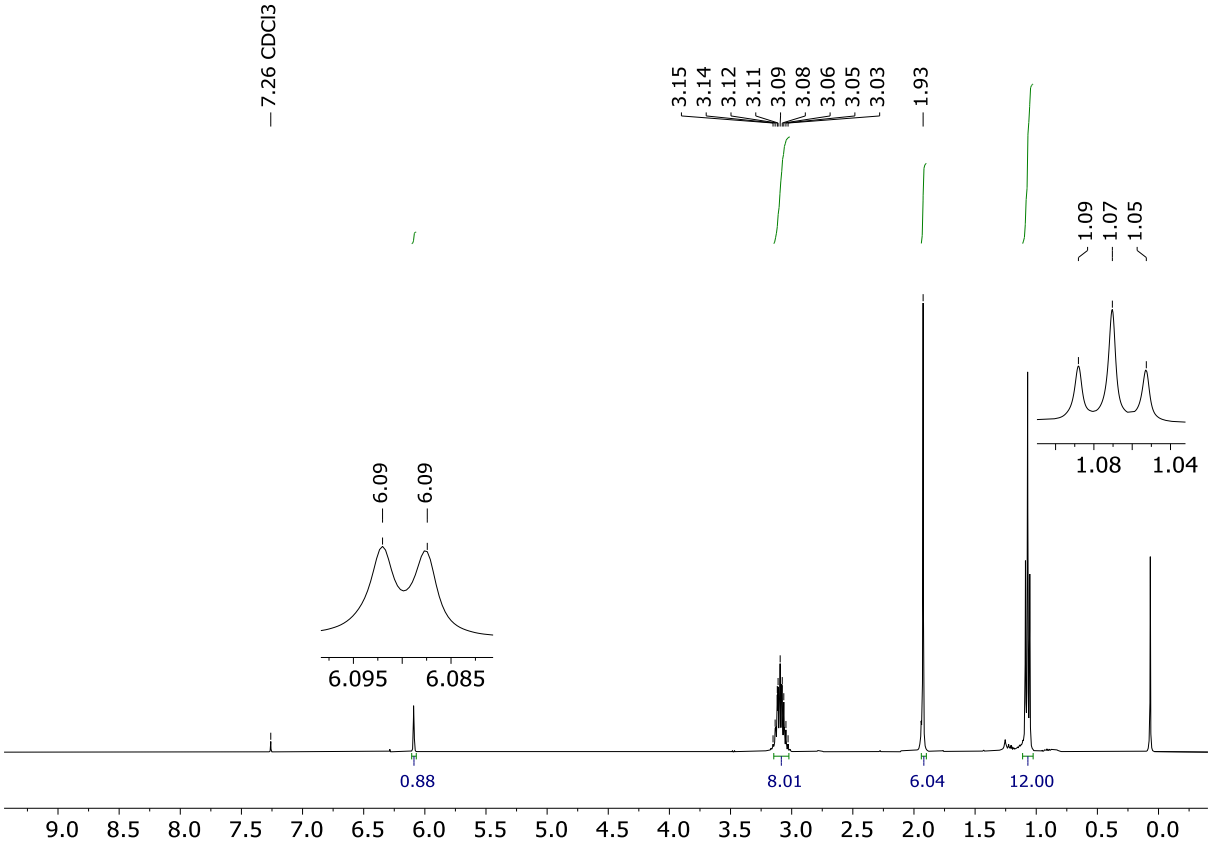


Figure S13: ^{1}H NMR spectrum of compound **3d** in $CDCl_3$.

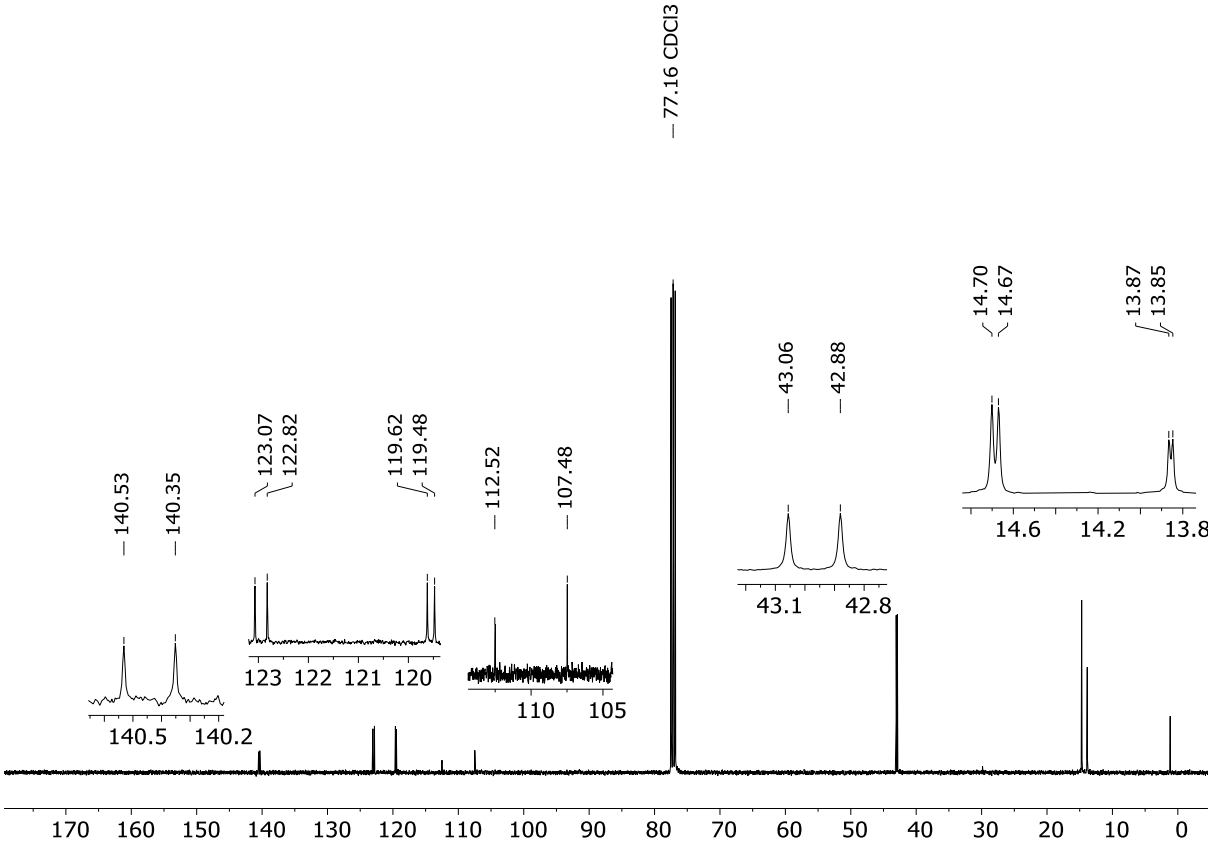


Figure S14: $^{13}C\{^{1}H\}$ NMR spectrum of compound **3d** in $CDCl_3$.

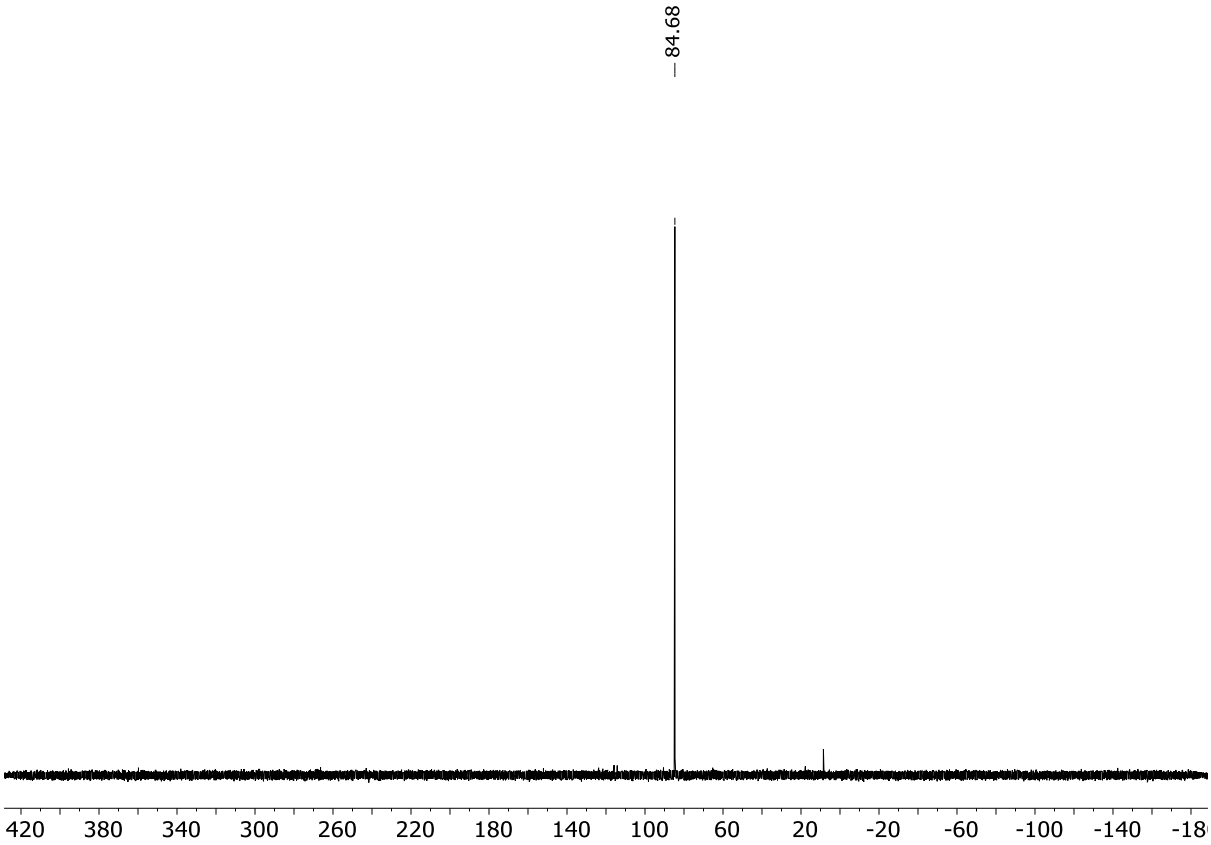


Figure S15: $^{31}P\{^{1}H\}$ NMR spectrum of compound **3d** in $CDCl_3$.

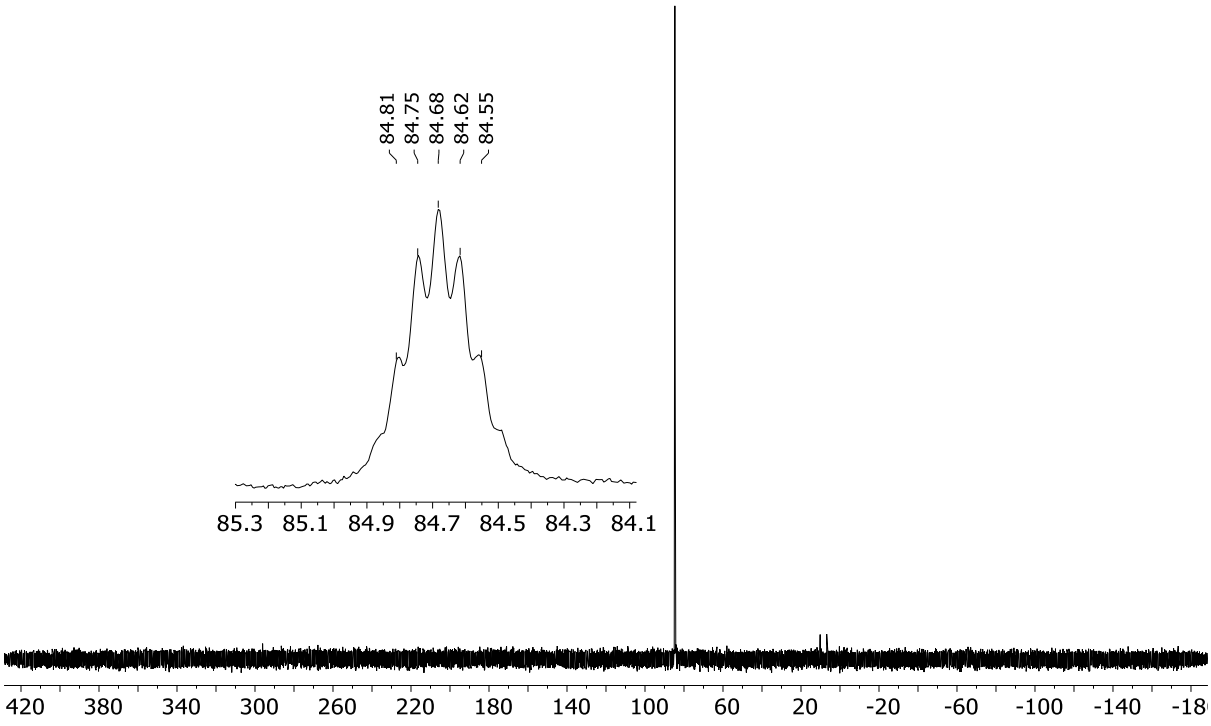


Figure S16: ^{31}P NMR spectrum of compound **3d** in $CDCl_3$.

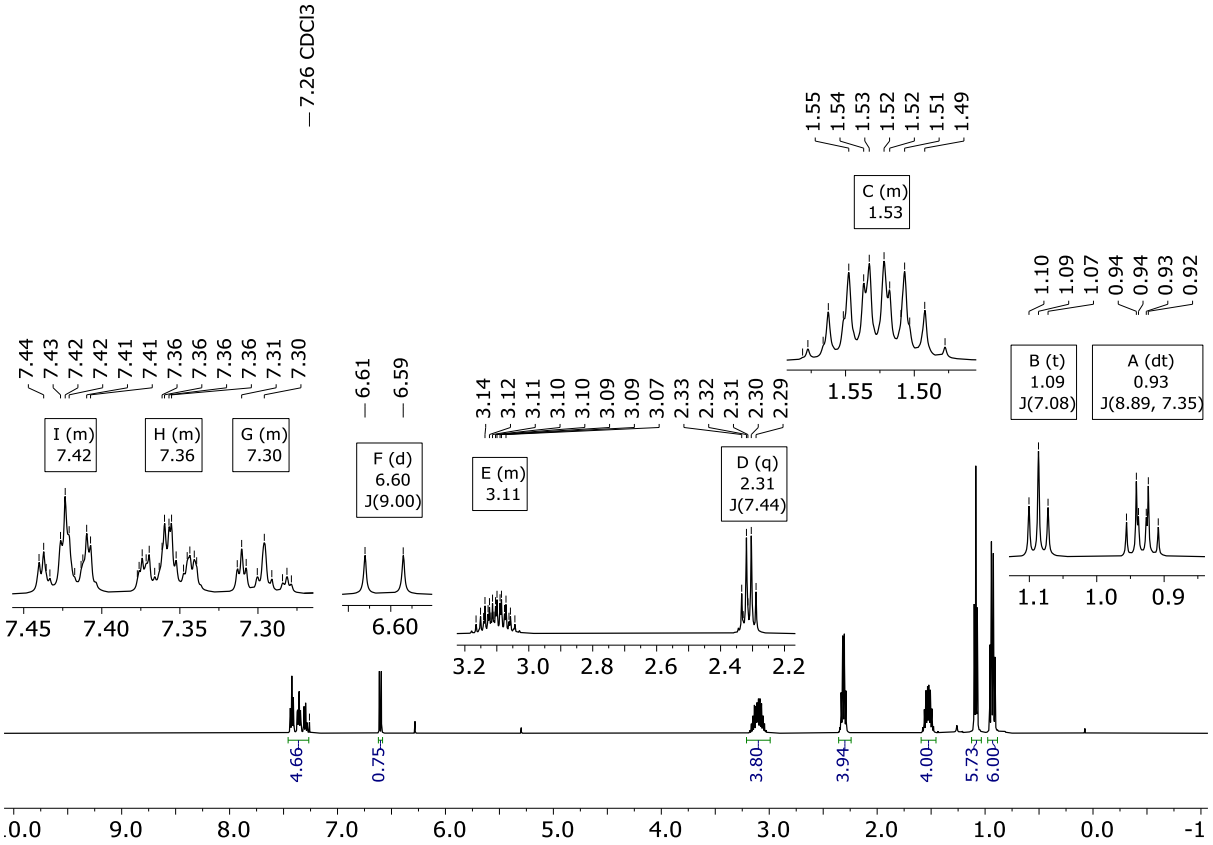


Figure S17: ^{1}H NMR spectrum of compound **3e** in $CDCl_3$.

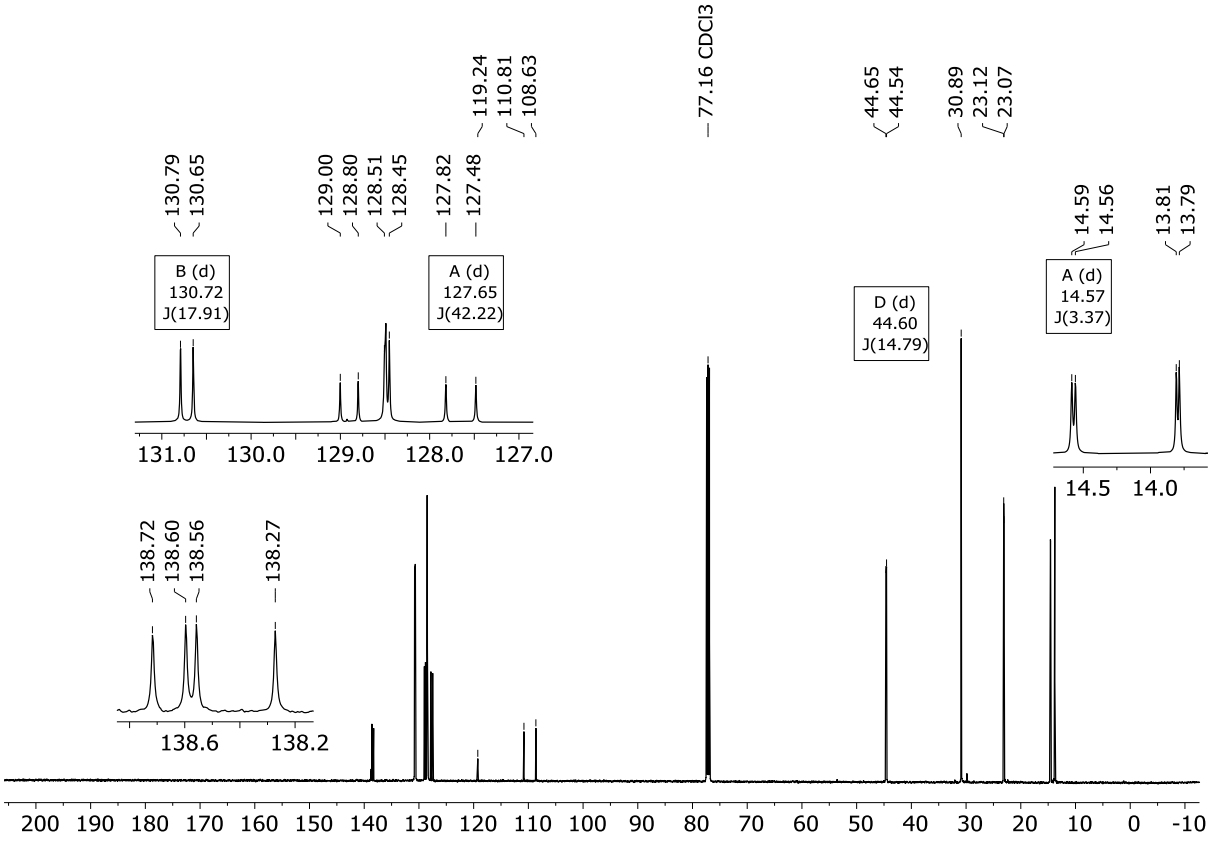


Figure S18: $^{13}C\{^{1}H\}$ NMR spectrum of compound **3e** in $CDCl_3$.

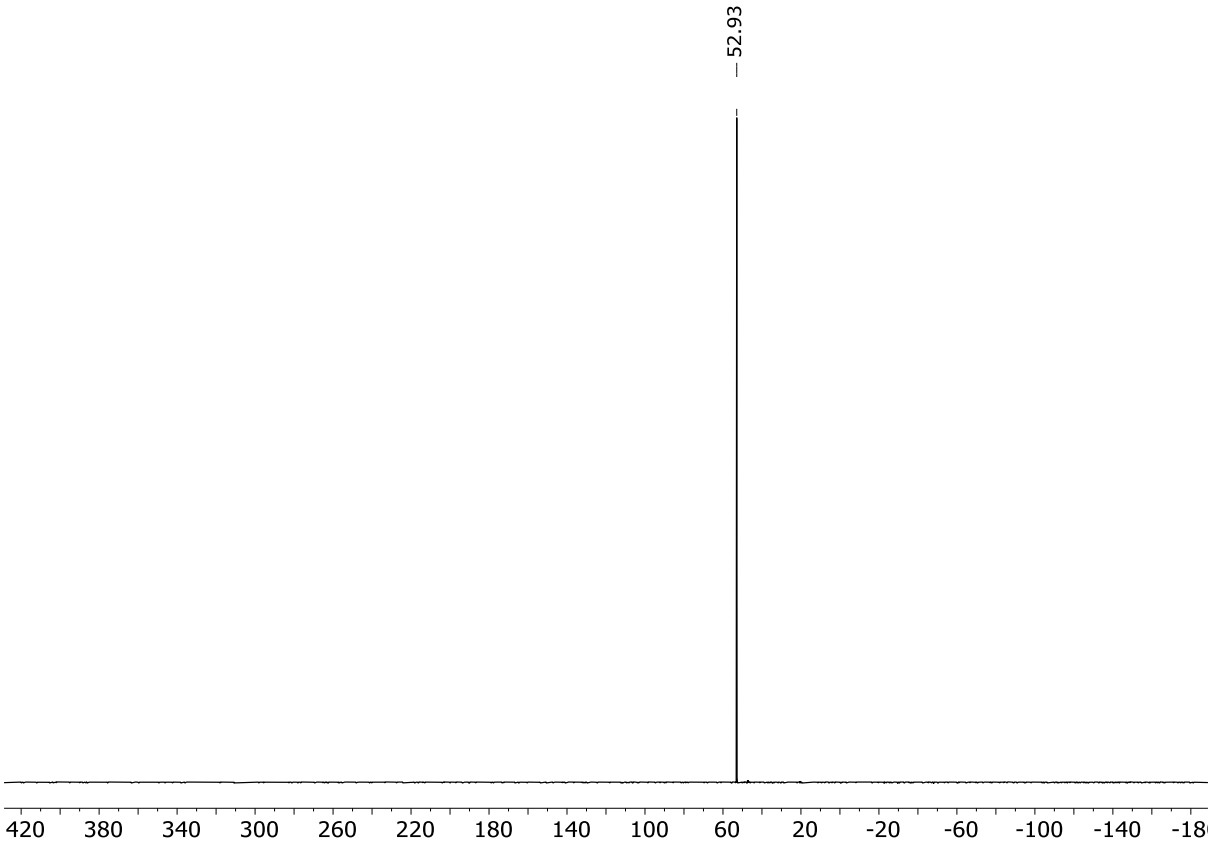


Figure S19: $^{31}P\{^{1}H\}$ NMR spectrum of compound **3e** in $CDCl_3$.

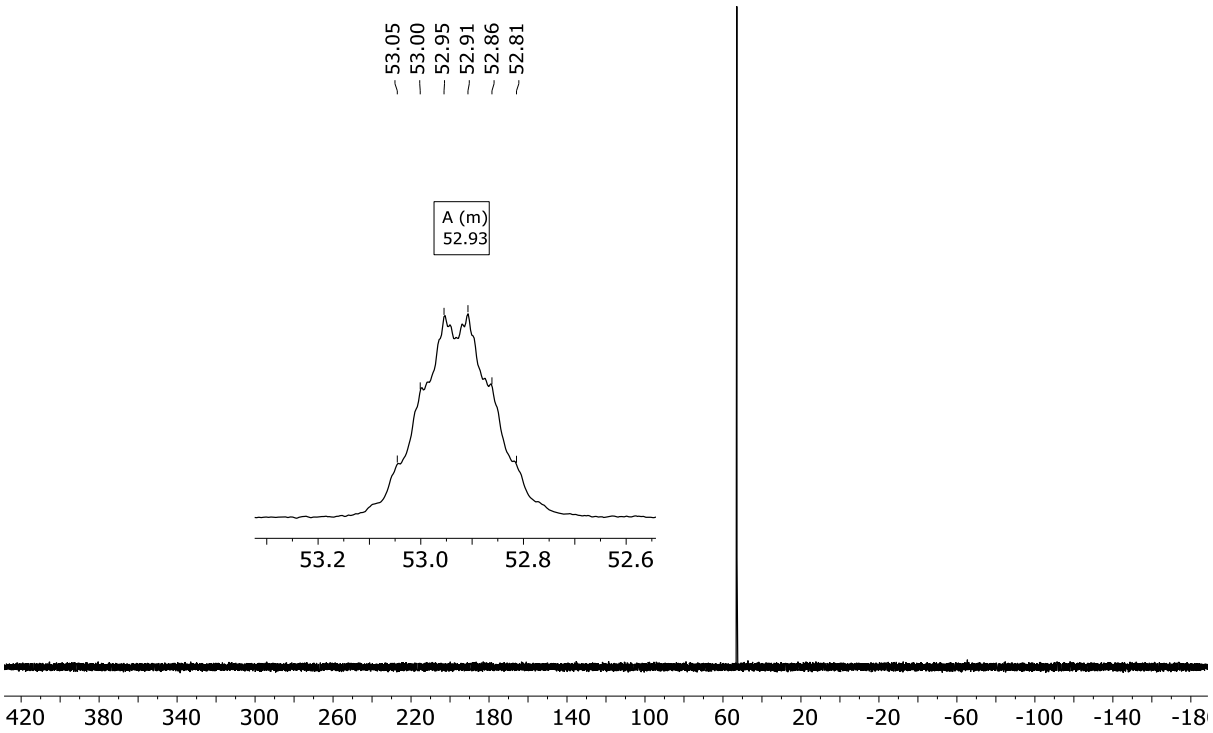


Figure S20: ^{31}P NMR spectrum of compound **3e** in $CDCl_3$.

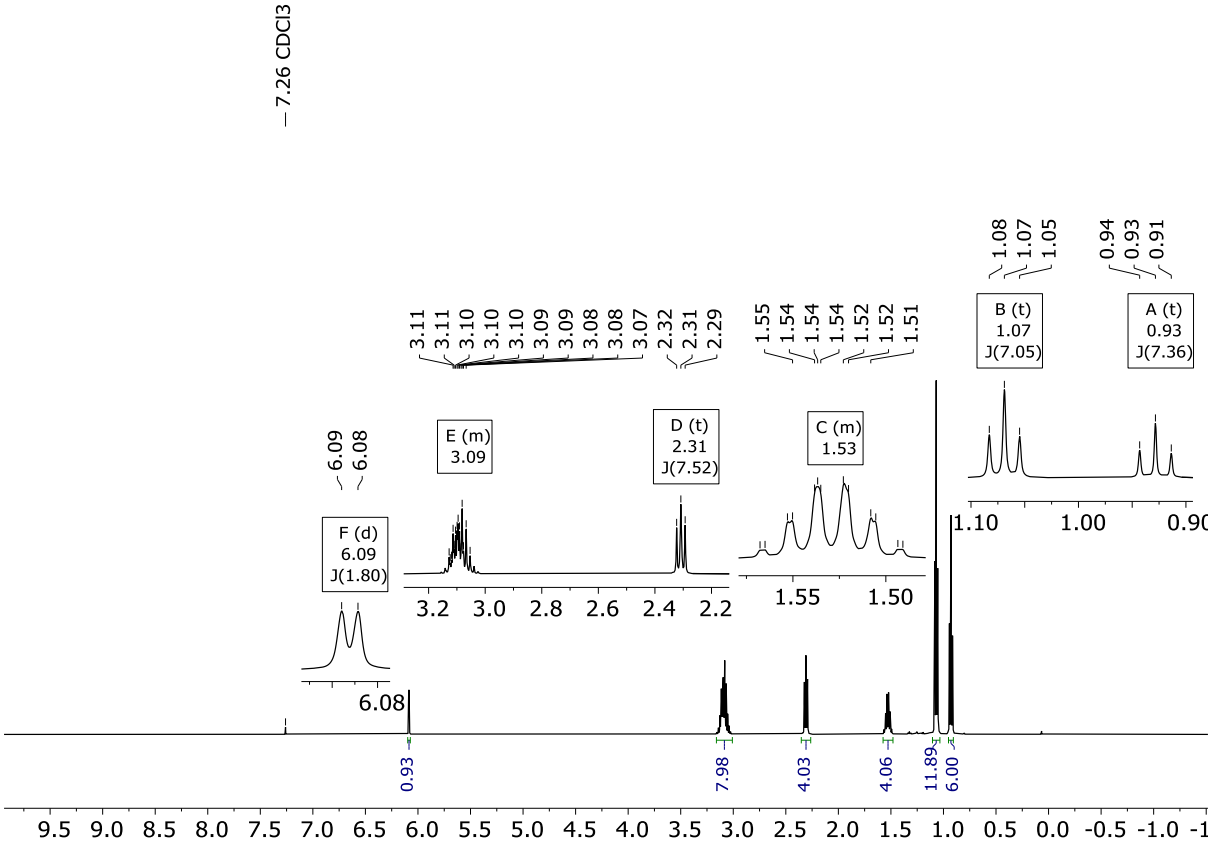


Figure S21: ^{1}H NMR spectrum of compound **3f** in $CDCl_3$.

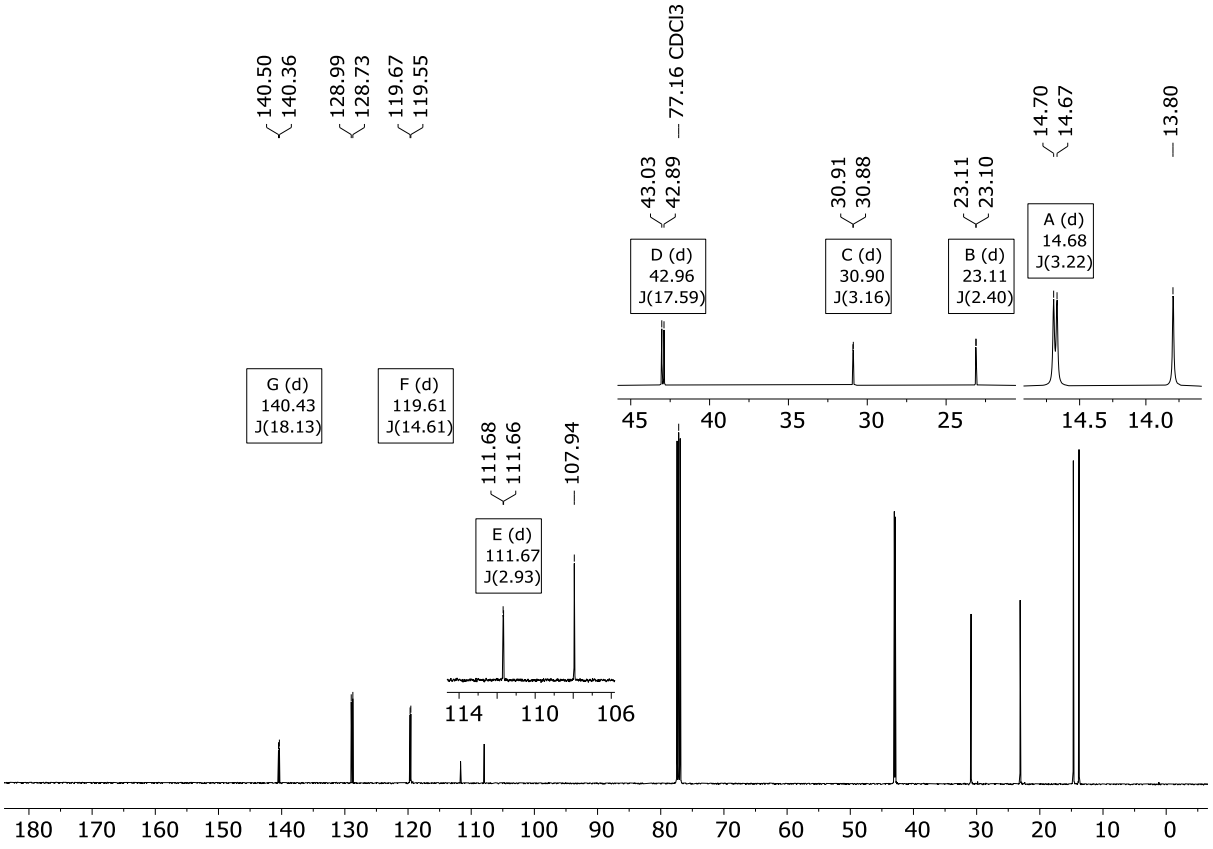


Figure S22: $^{13}C\{^{1}H\}$ NMR spectrum of compound **3f** in $CDCl_3$.

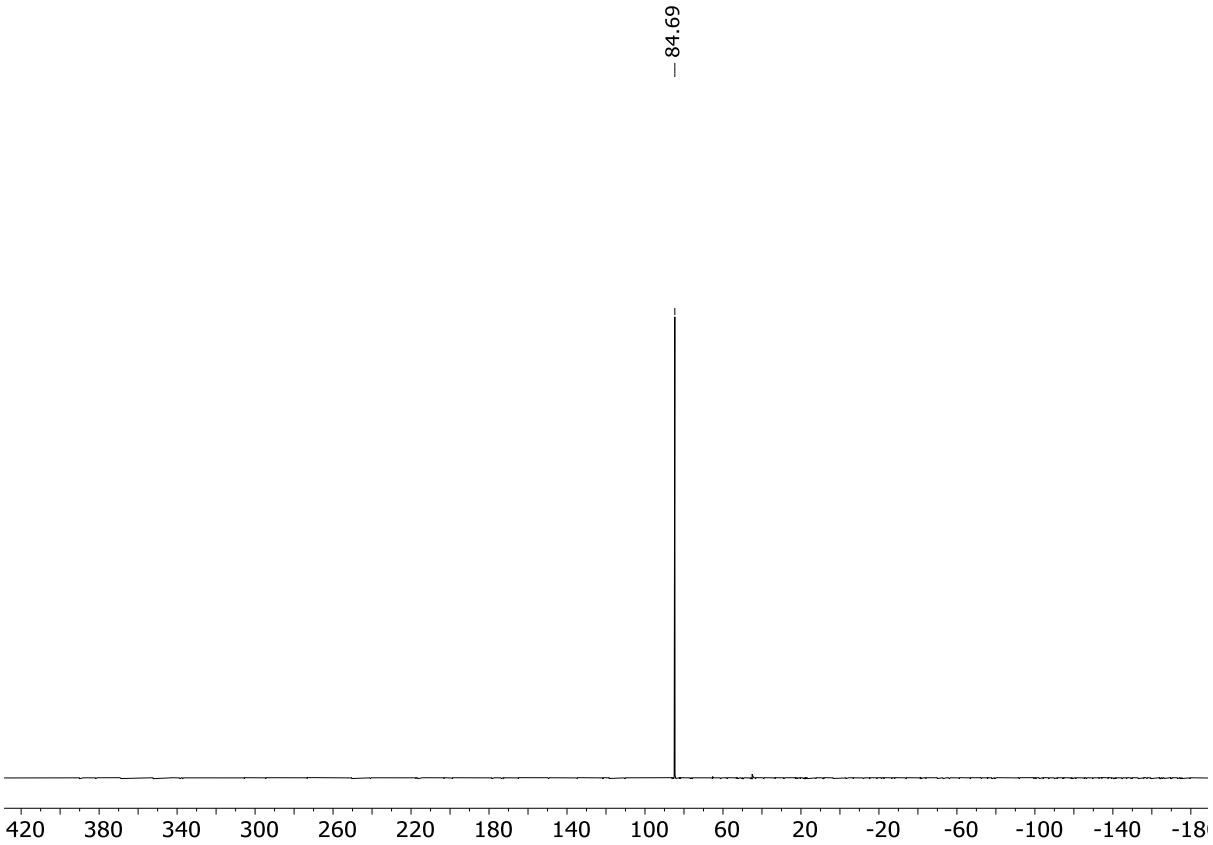


Figure S23: $^{31}P\{^{1}H\}$ NMR spectrum of compound **3f** in $CDCl_3$.

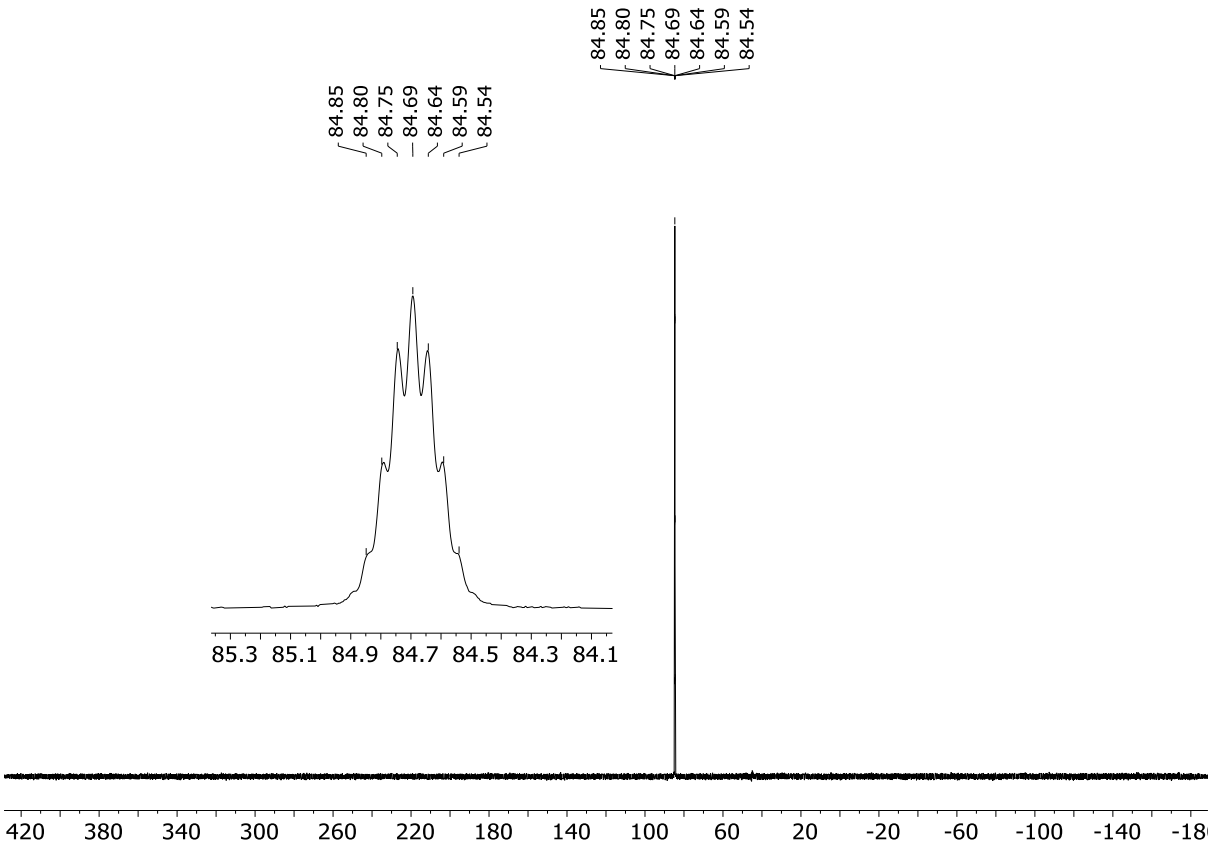


Figure S24: ^{31}P NMR spectrum of compound **3f** in $CDCl_3$.

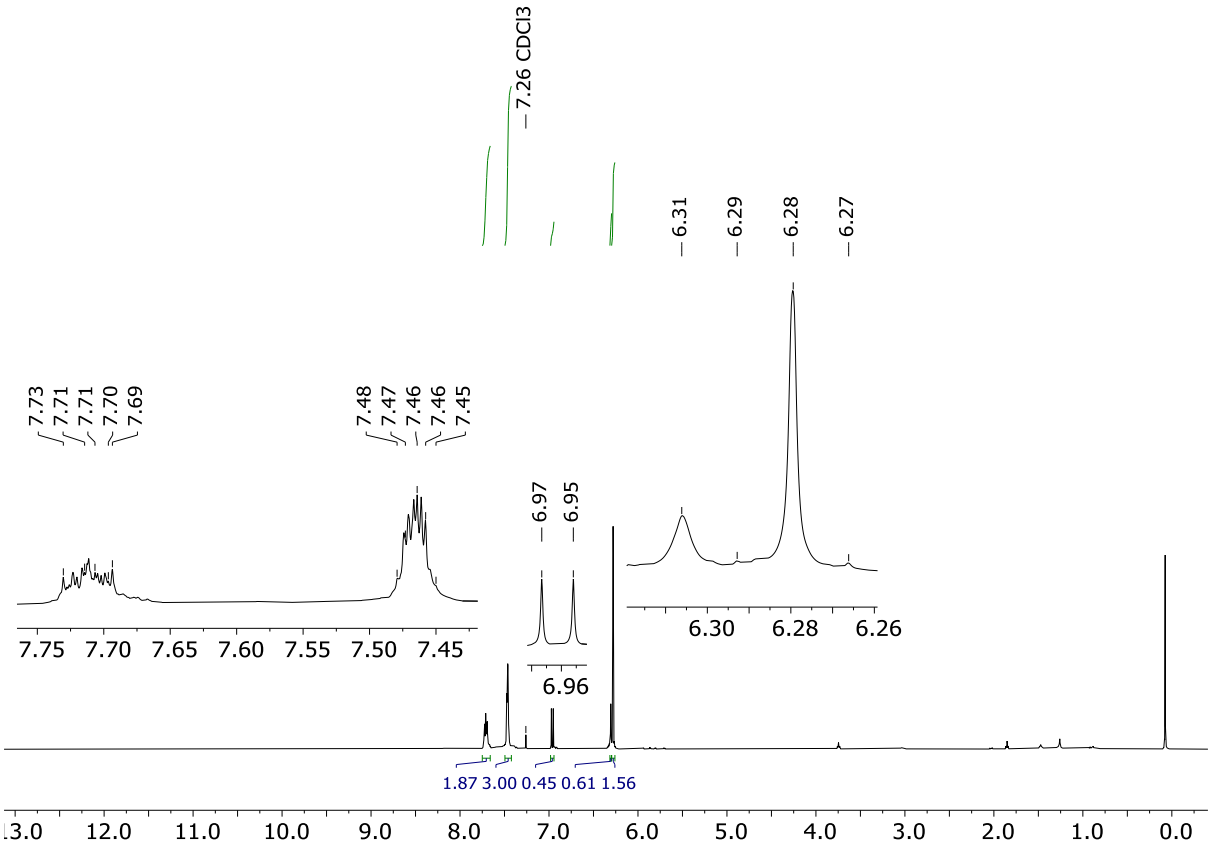


Figure S25: ^{1}H NMR spectrum of compound **4a** in $CDCl_3$.

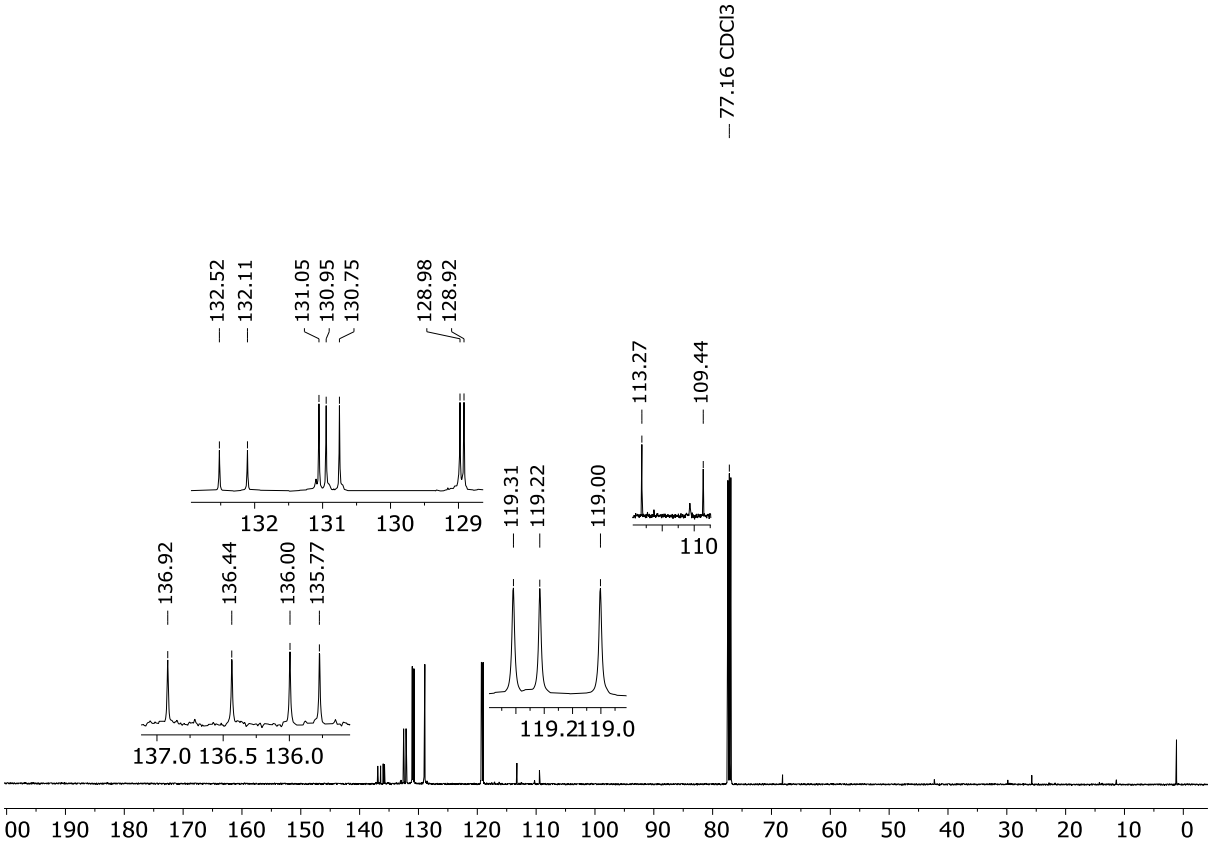


Figure S26: $^{13}C\{^{1}H\}$ NMR spectrum of compound **4a** in $CDCl_3$.

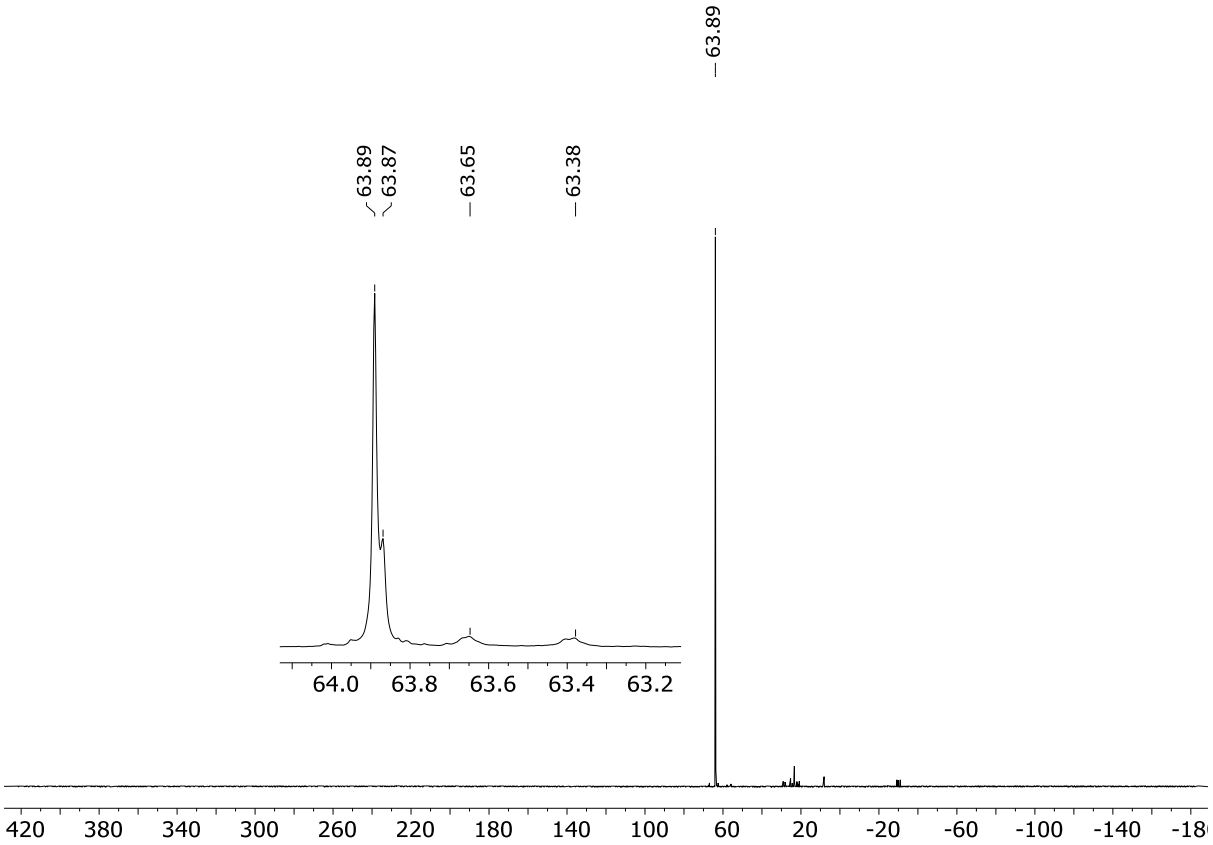


Figure S27: $^{31}P\{^{1}H\}$ NMR spectrum of compound **4a** in $CDCl_3$.

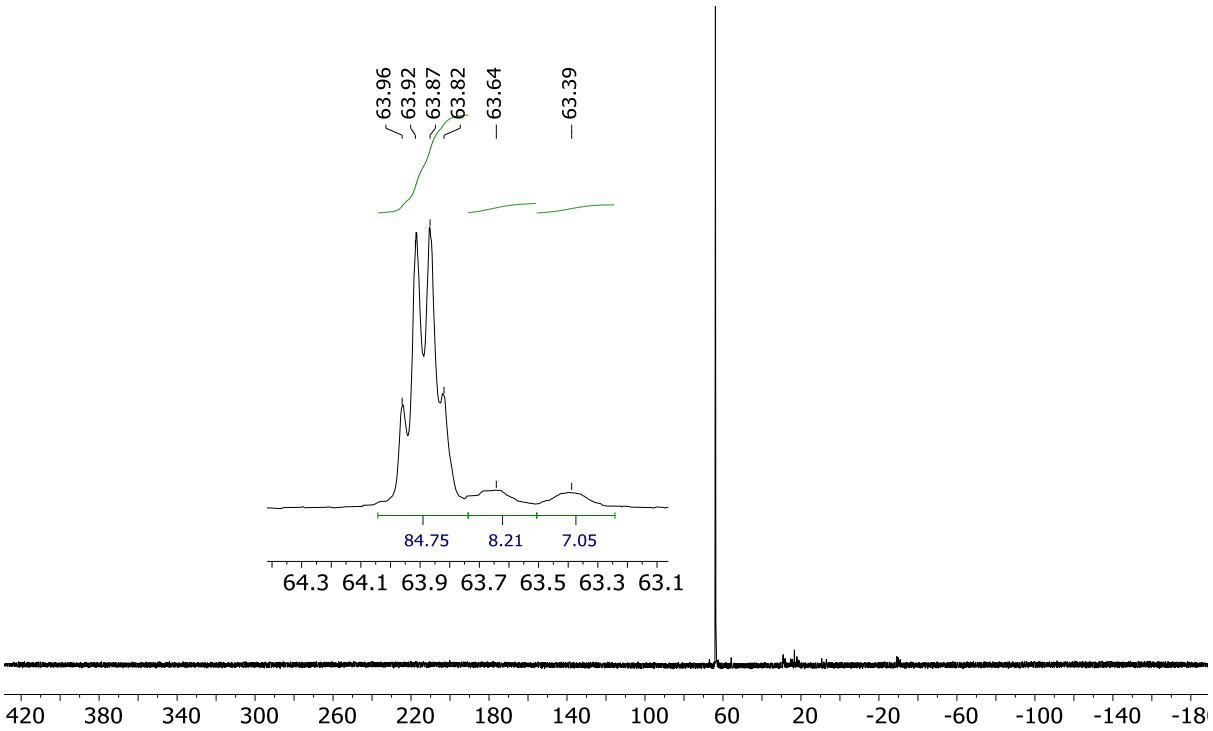


Figure S28: ^{31}P NMR spectrum of compound **4a** in $CDCl_3$.

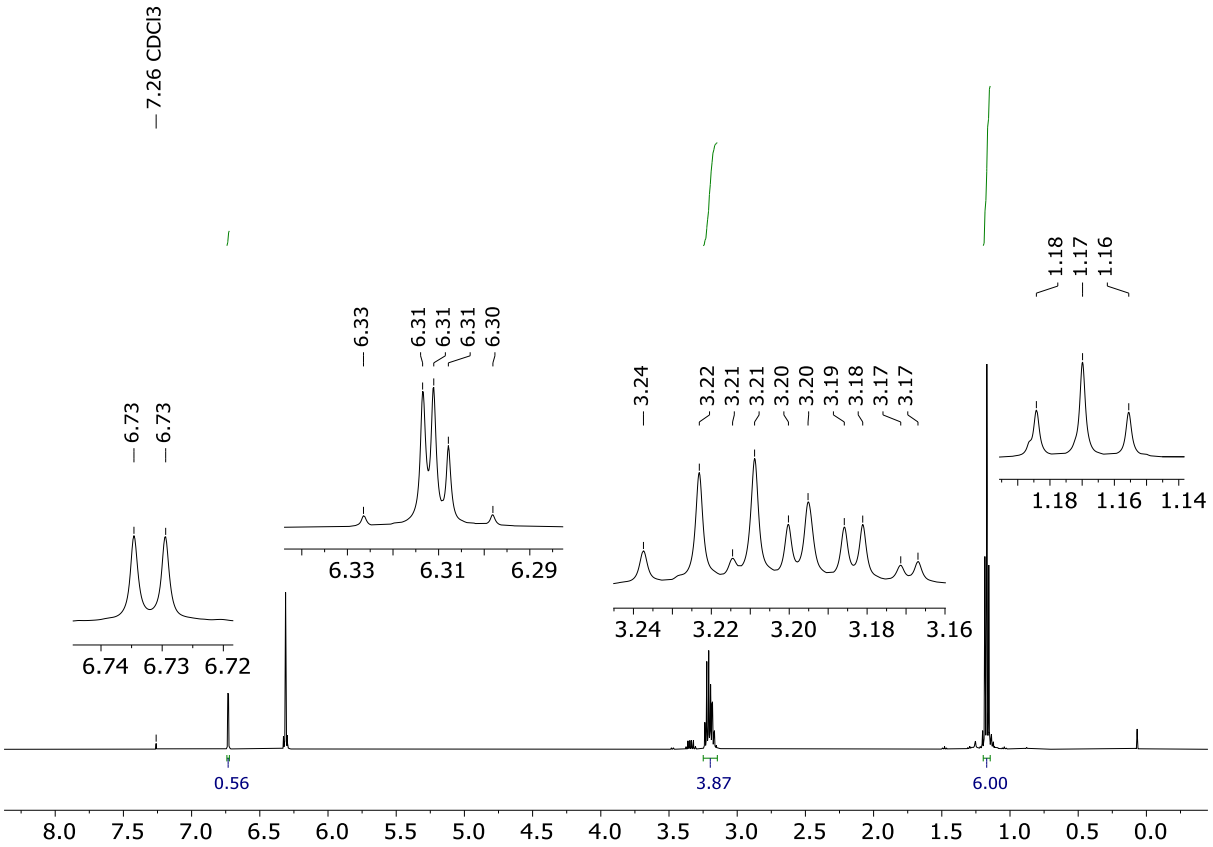


Figure S29: ^{1}H NMR spectrum of compound **4b** in $CDCl_3$.

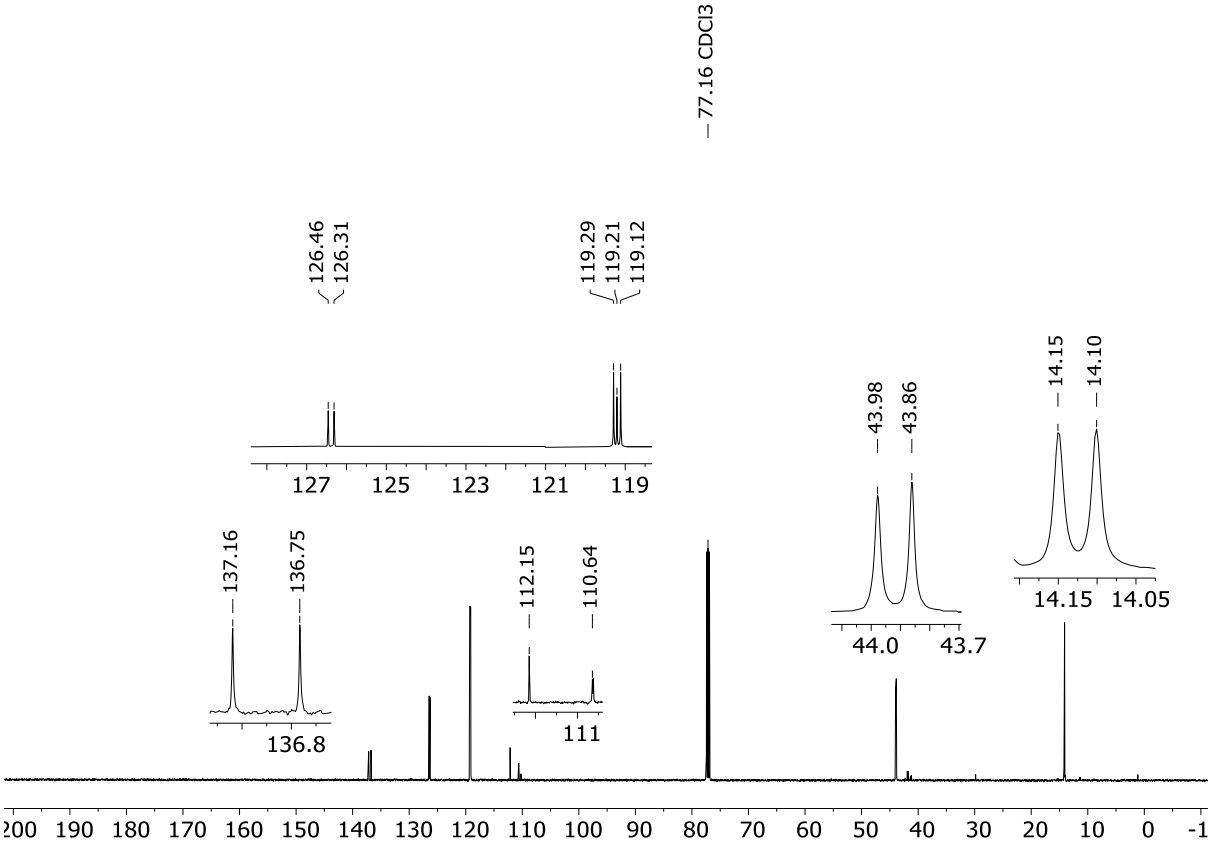


Figure S30: $^{13}C\{^{1}H\}$ NMR spectrum of compound **4b** in $CDCl_3$.

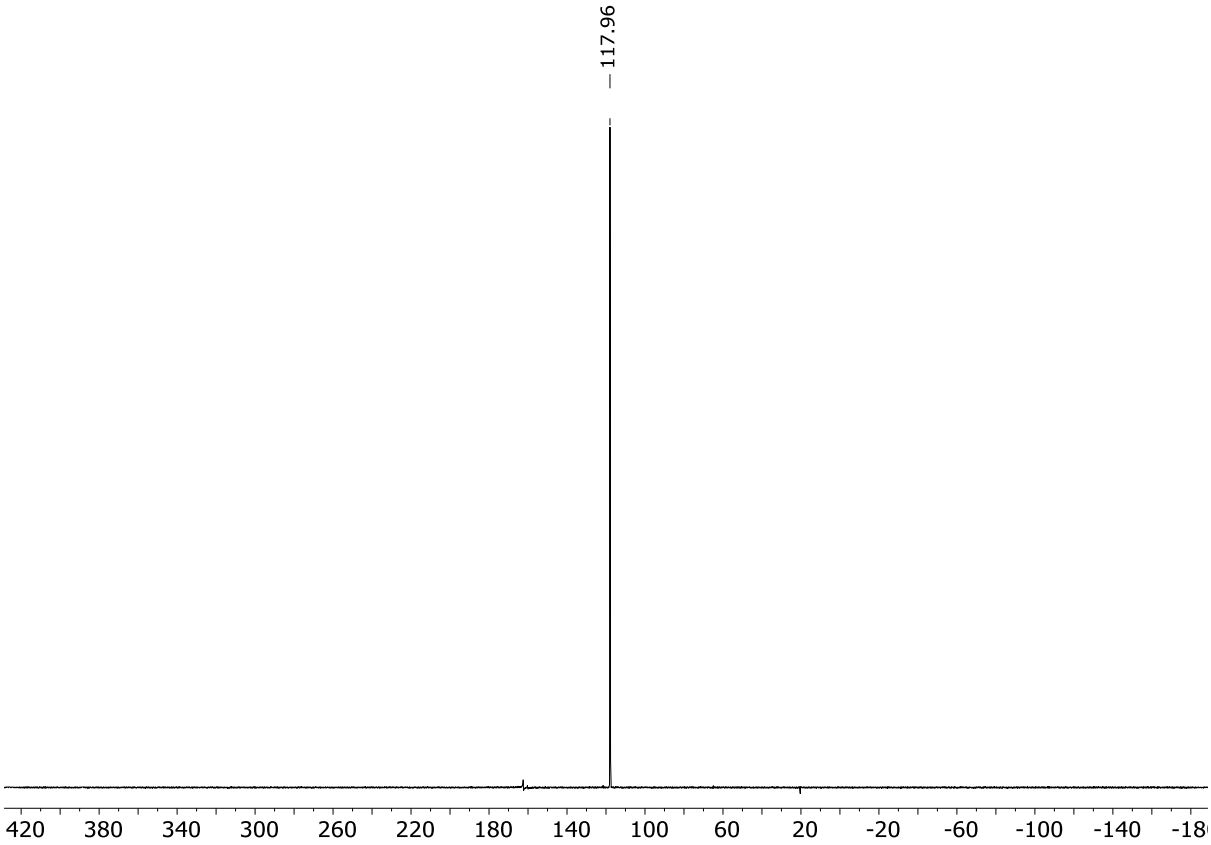


Figure S31: $^{31}P\{^{1}H\}$ NMR spectrum of compound **4b** in $CDCl_3$.

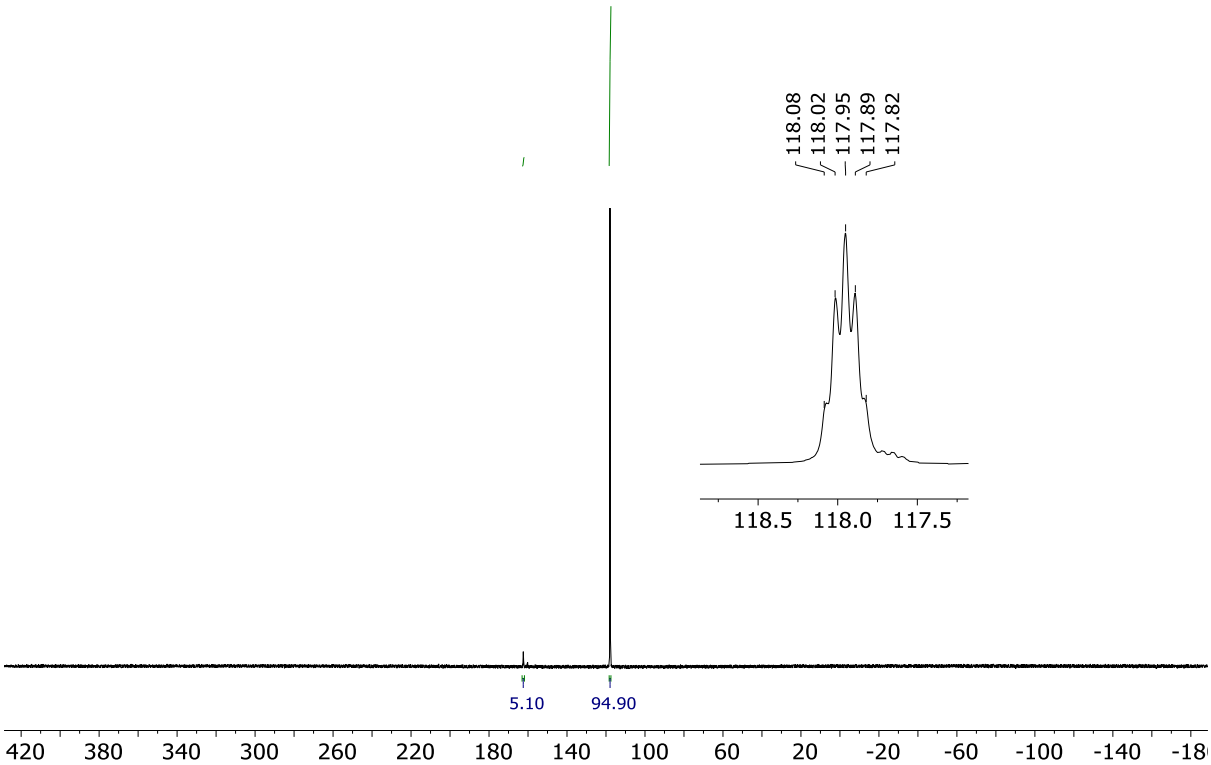


Figure S32: ^{31}P NMR spectrum of compound **4b** in $CDCl_3$.

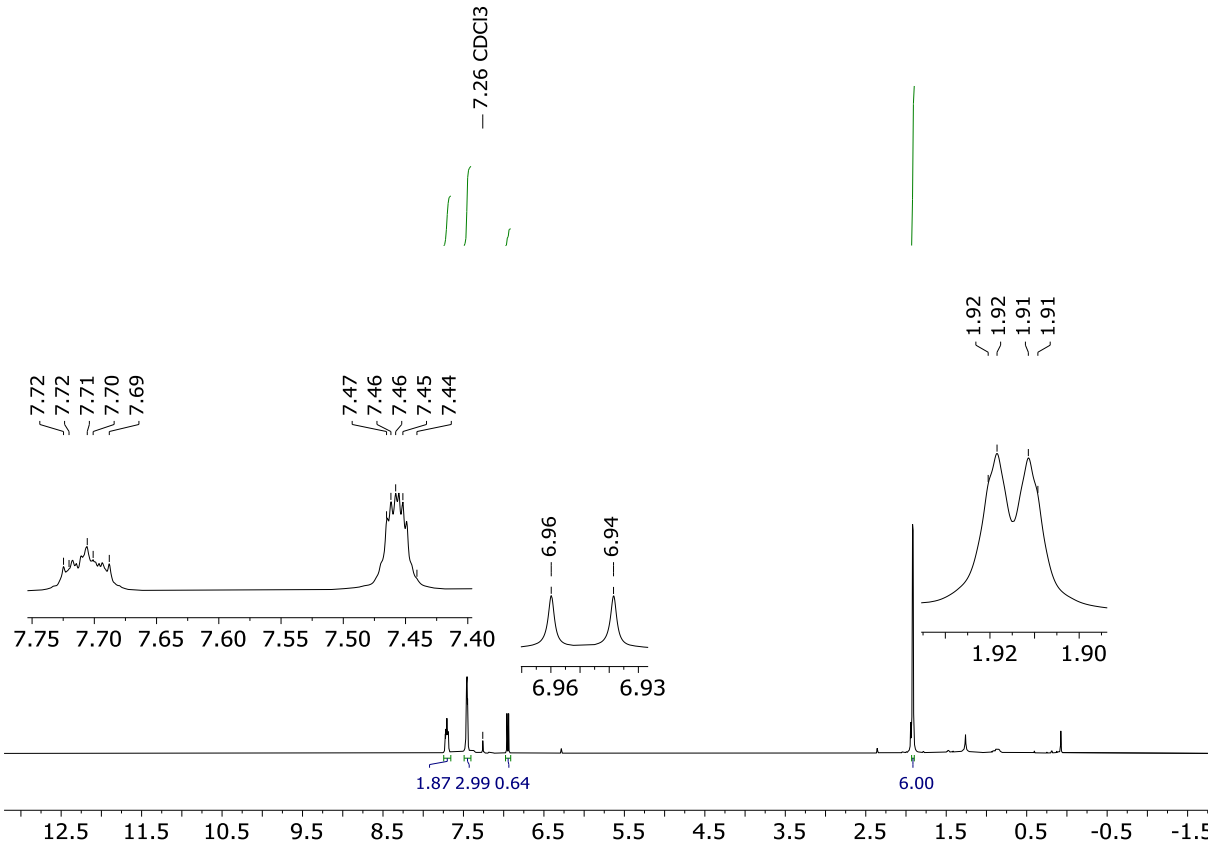


Figure S33: ^{1}H NMR spectrum of compound **4c** in $CDCl_3$.

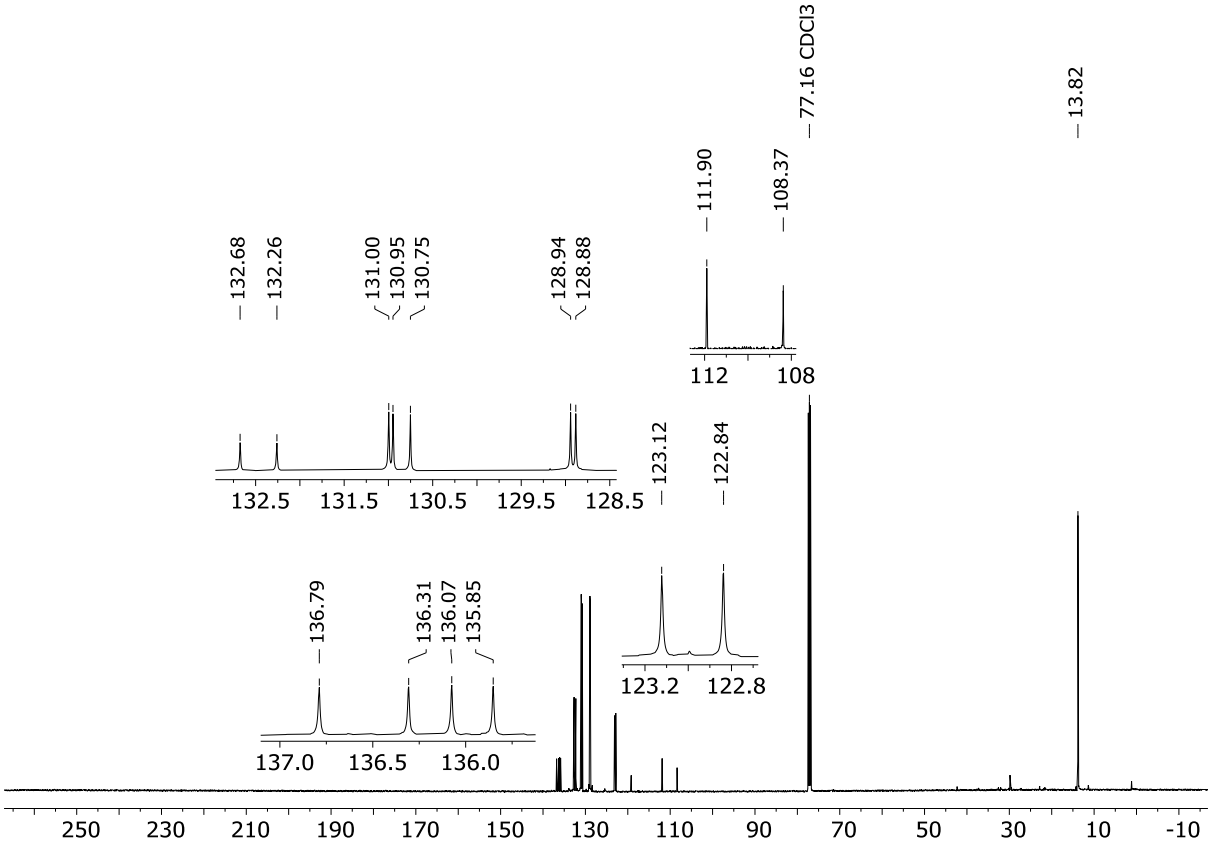


Figure S34: $^{13}C\{^{1}H\}$ NMR spectrum of compound **4c** in $CDCl_3$.

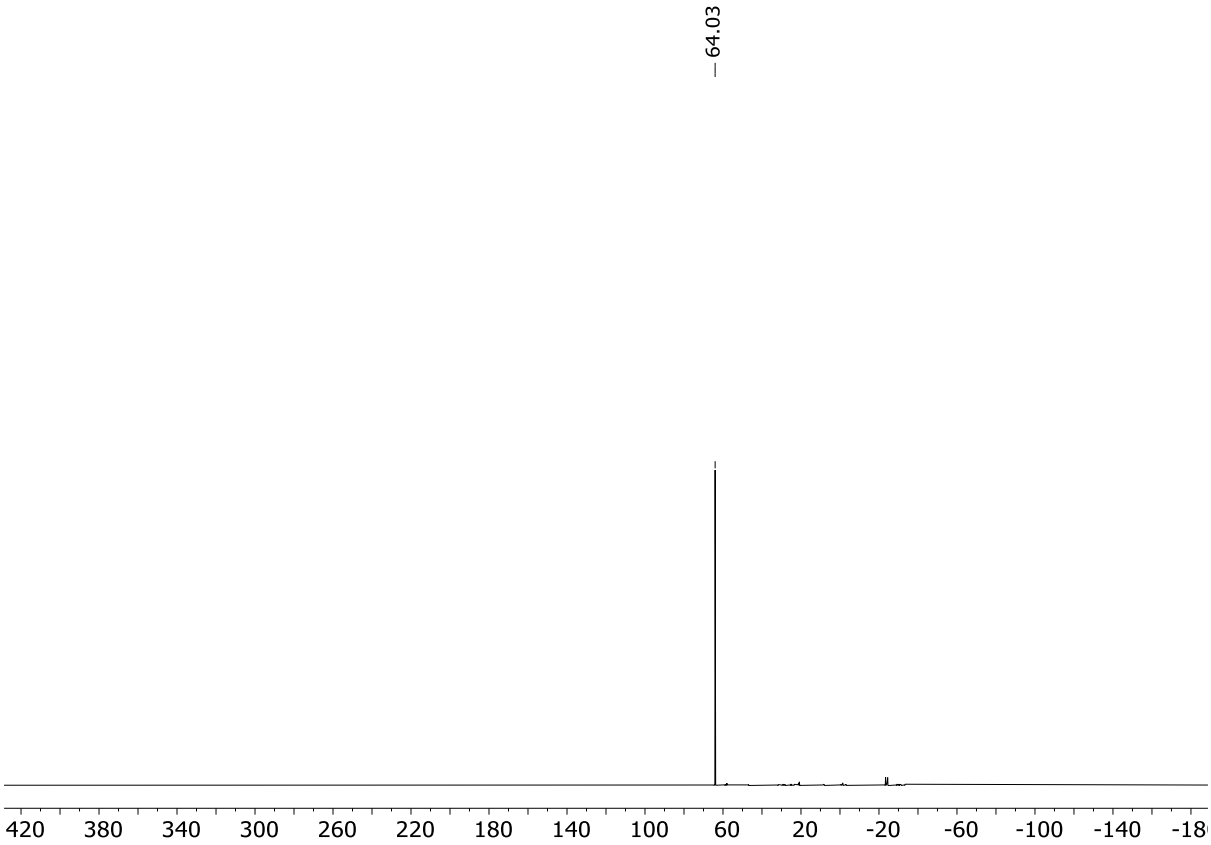


Figure S35: $^{31}P\{^{1}H\}$ NMR spectrum of compound **4c** in $CDCl_3$.

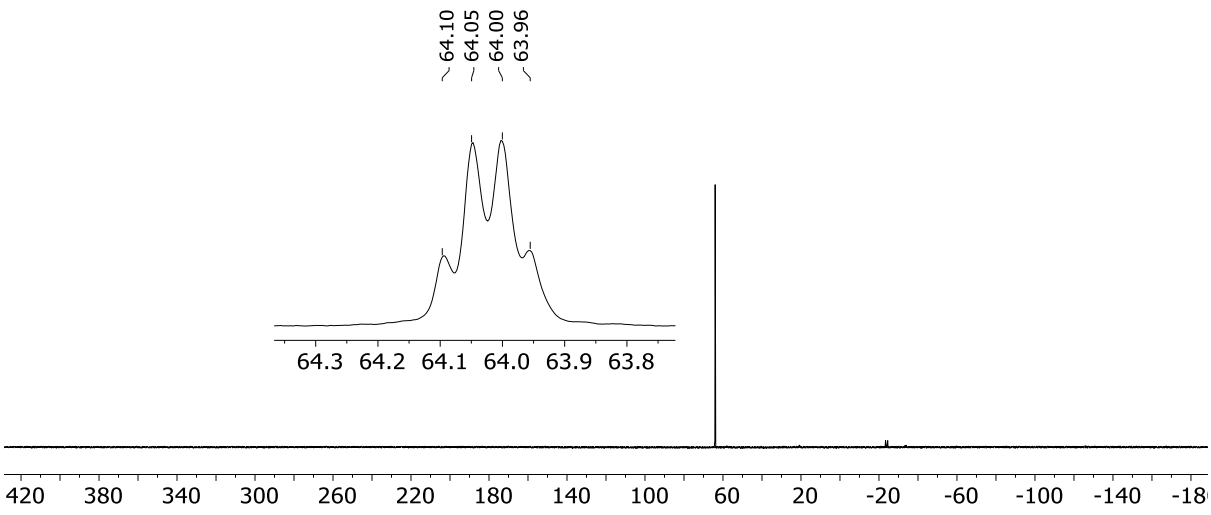


Figure S36: ^{31}P NMR spectrum of compound **4c** in $CDCl_3$.

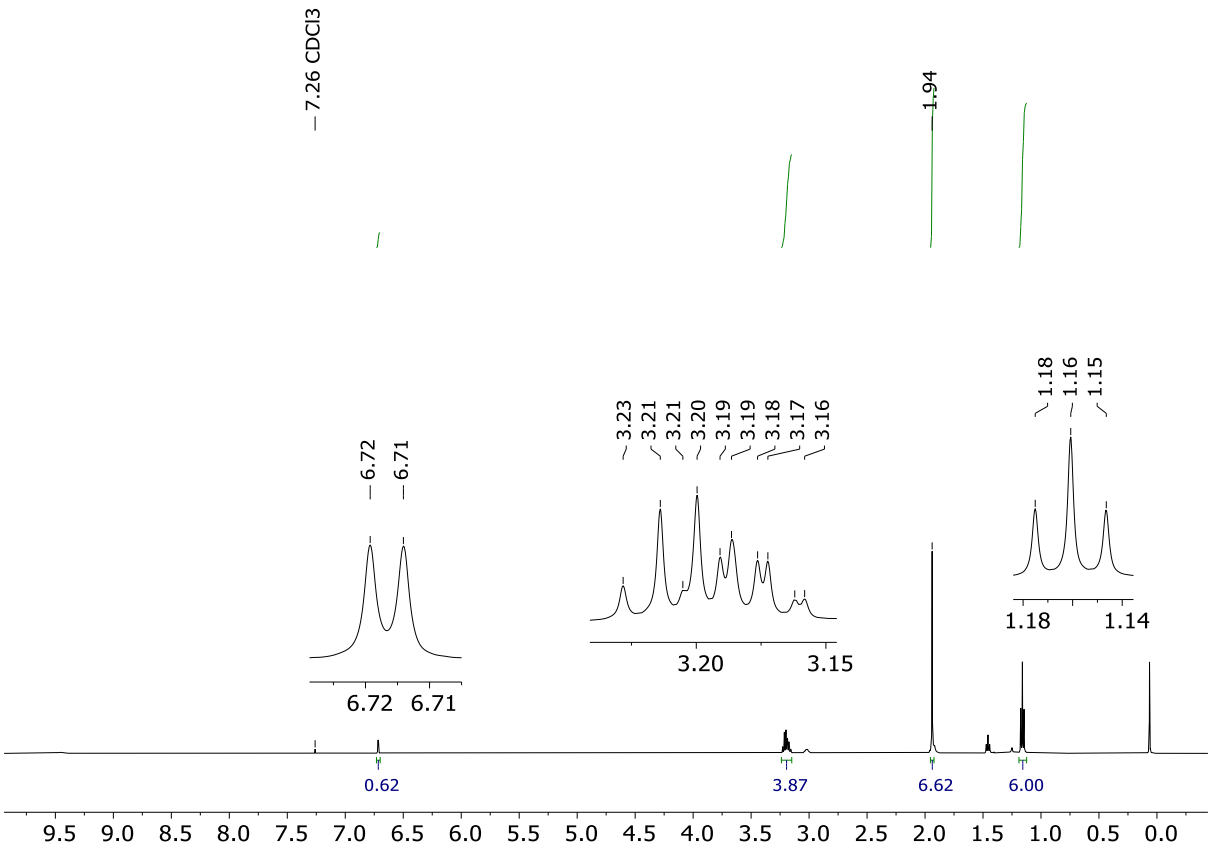


Figure S37: ^{1}H NMR spectrum of compound **4d** in $CDCl_3$.

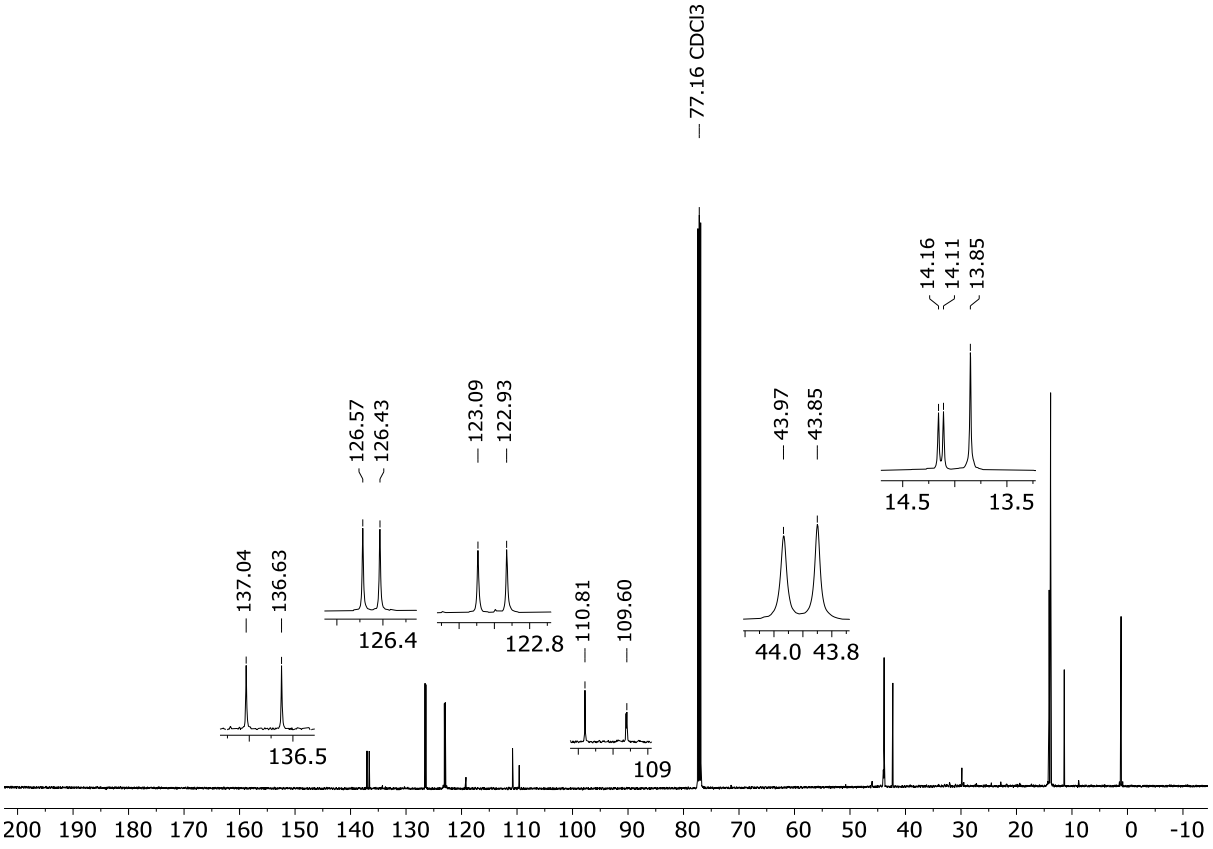


Figure S38: $^{13}C\{^{1}H\}$ NMR spectrum of compound **4d** in $CDCl_3$.

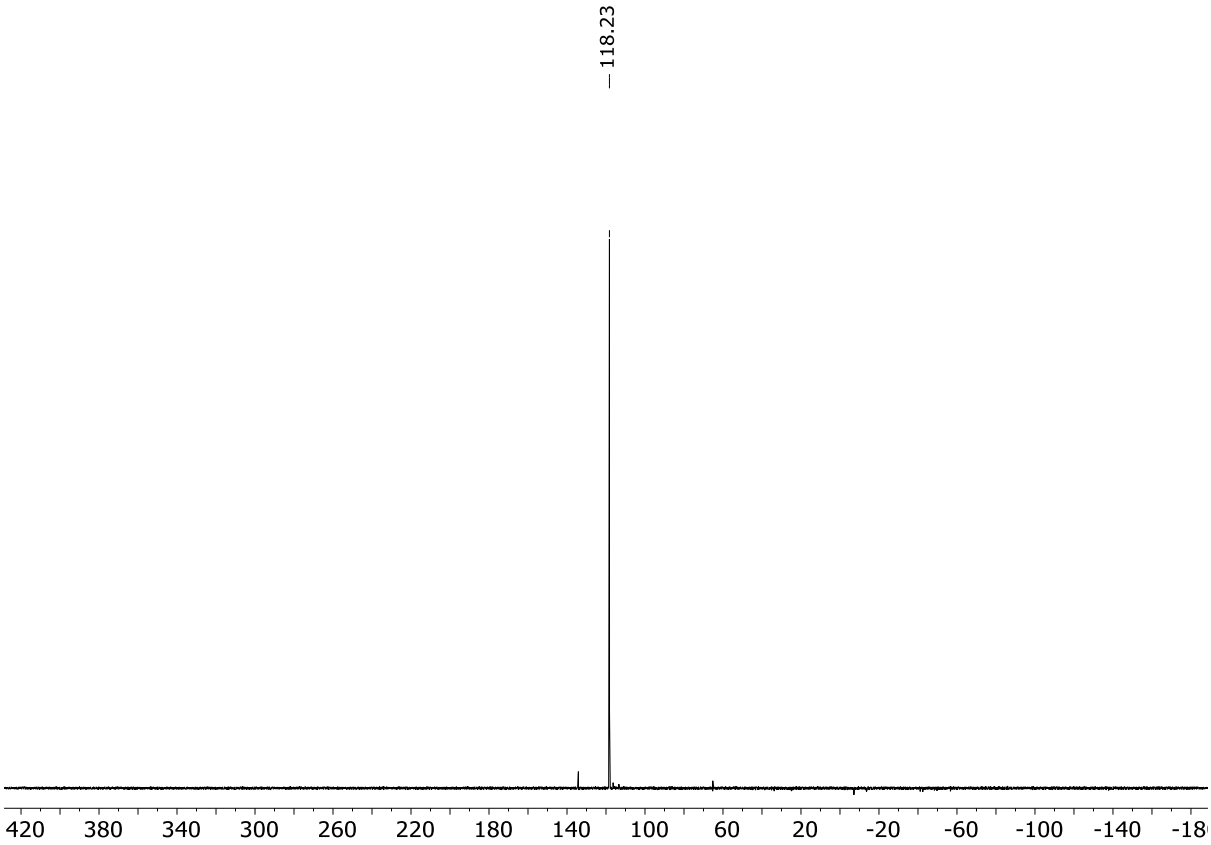


Figure S39: $^{31}P\{^{1}H\}$ NMR spectrum of compound **4d** in $CDCl_3$.

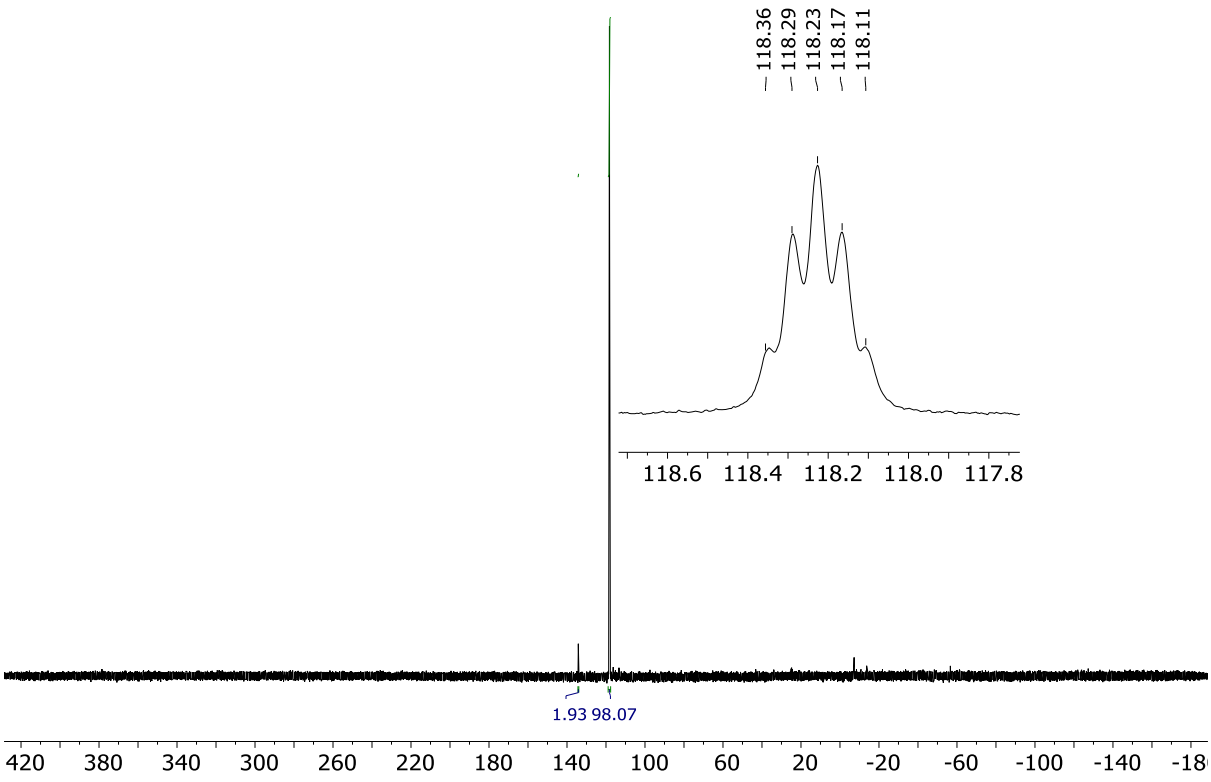


Figure S40: ^{31}P NMR spectrum of compound **4d** in $CDCl_3$.

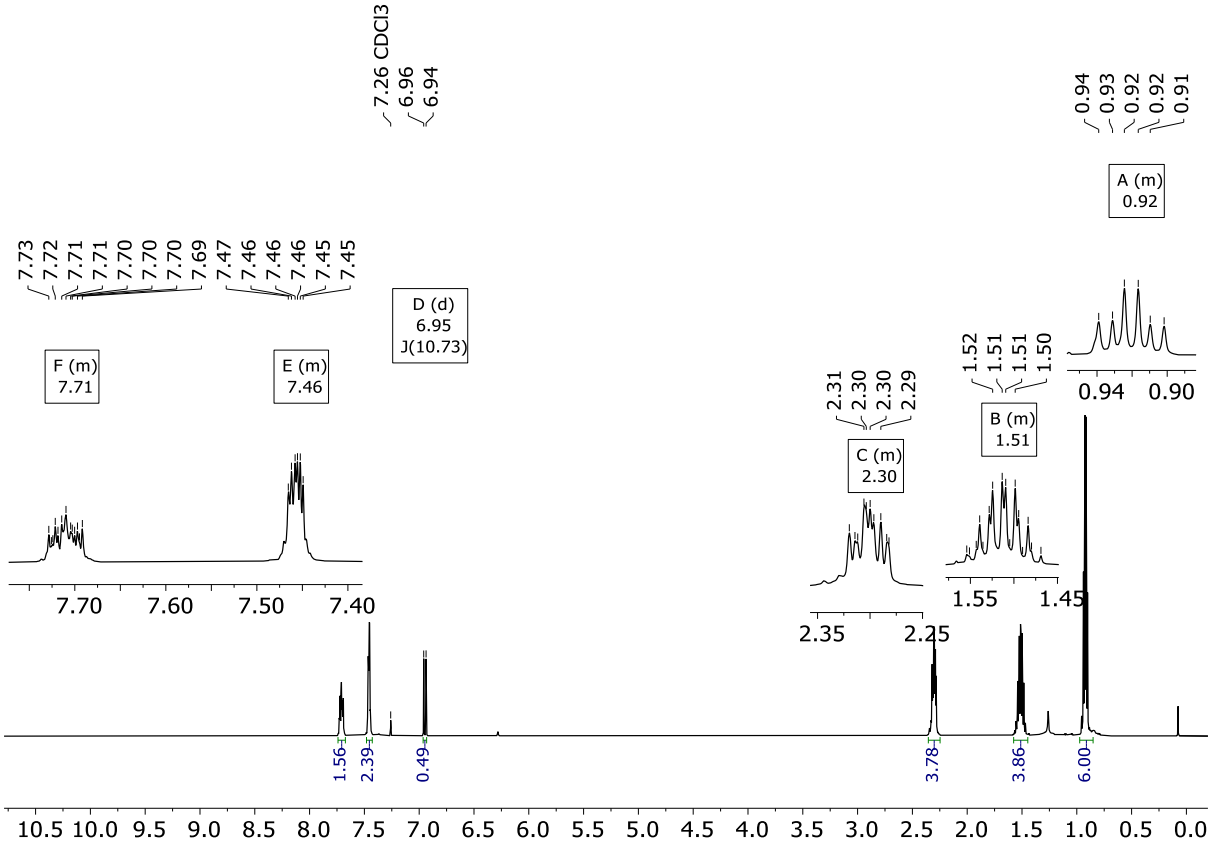


Figure S41: ^{1}H NMR spectrum of compound **4e** in $CDCl_3$.

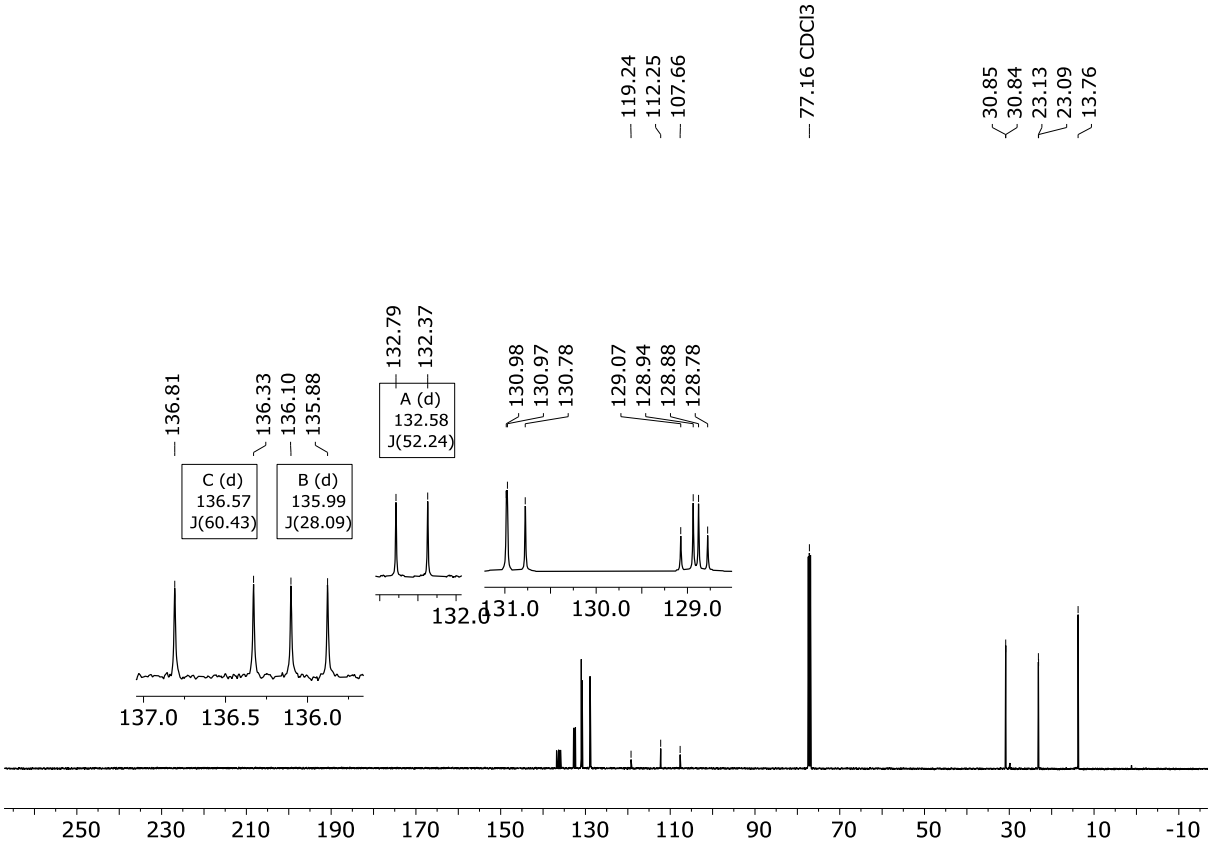


Figure S42: $^{13}C\{^{1}H\}$ NMR spectrum of compound **4e** in $CDCl_3$.

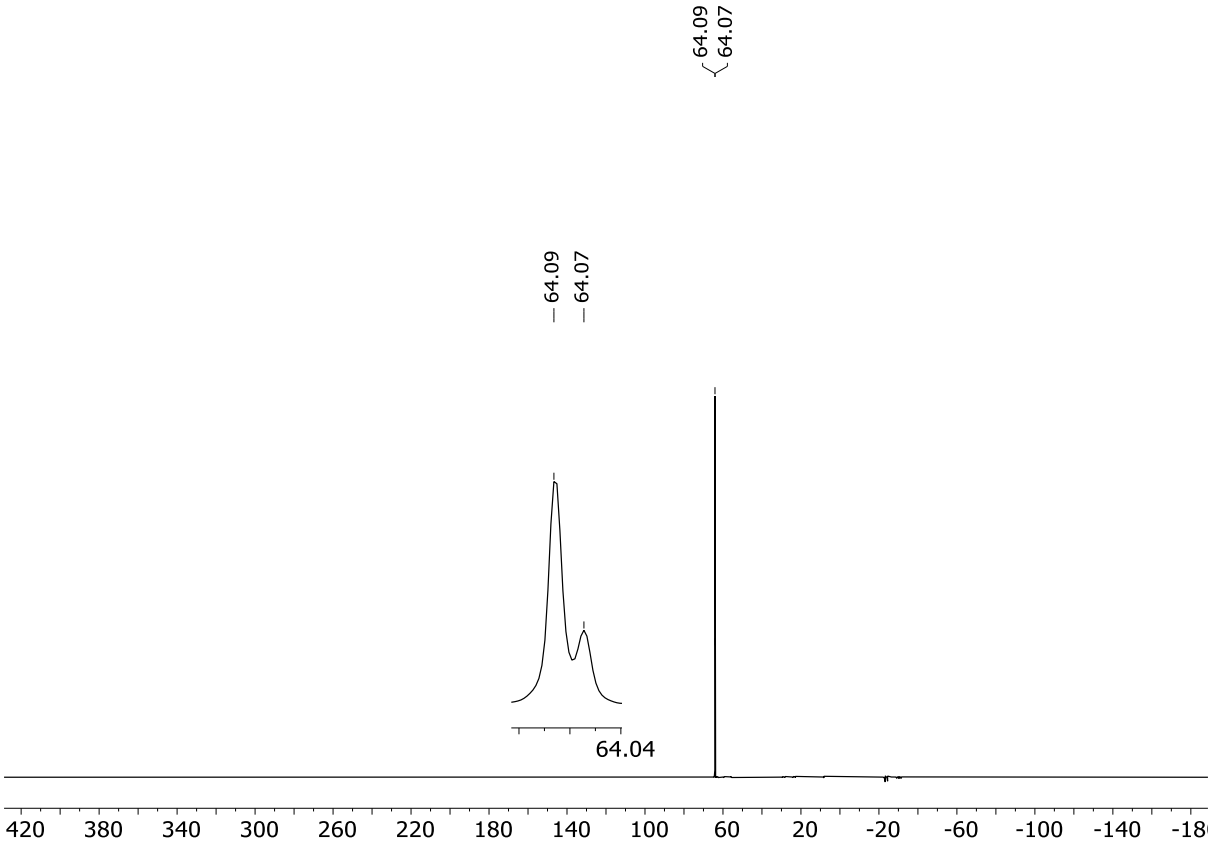


Figure S43: $^{31}P\{^{1}H\}$ NMR spectrum of compound **4e** in $CDCl_3$.

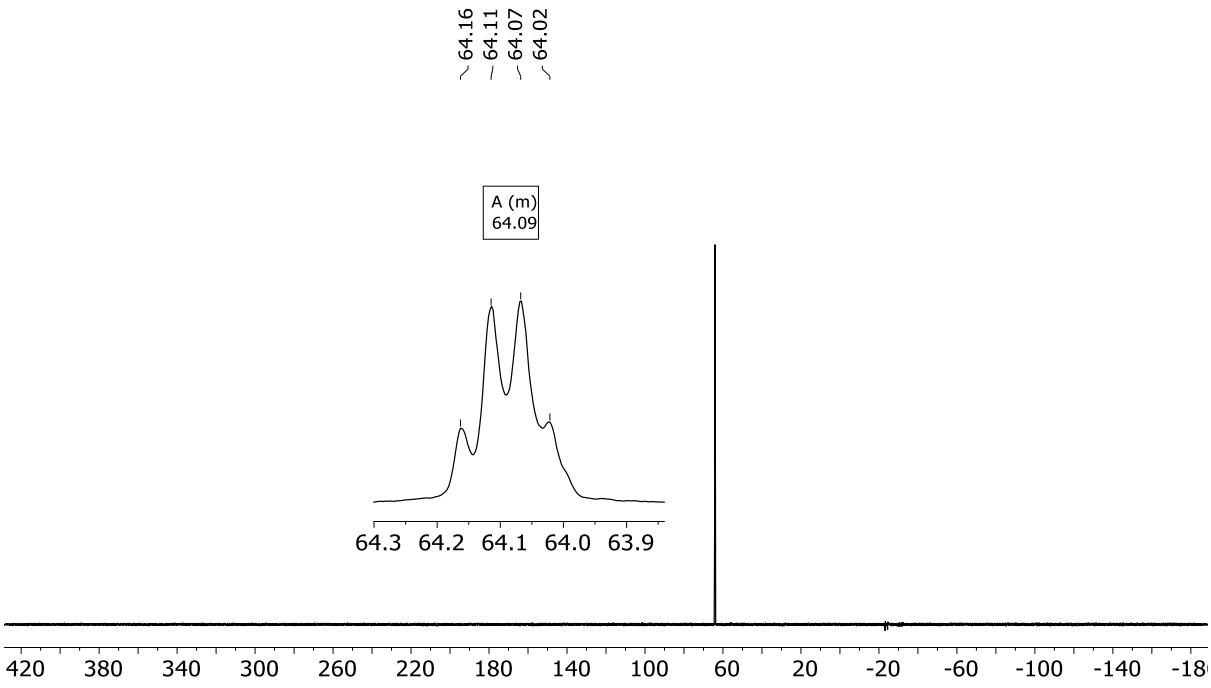


Figure S44: ^{31}P NMR spectrum of compound **4e** in $CDCl_3$.

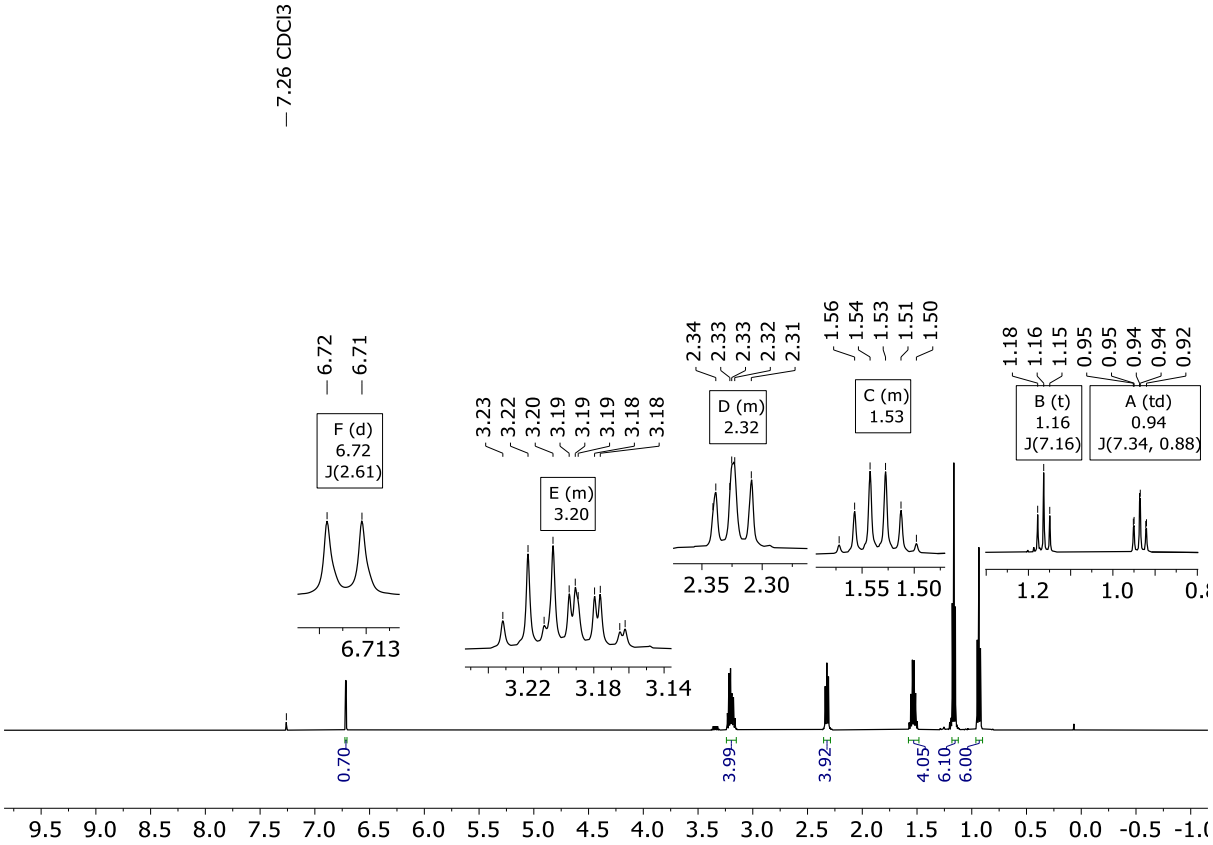


Figure S45: ^{1}H NMR spectrum of compound **4f** in $CDCl_3$.

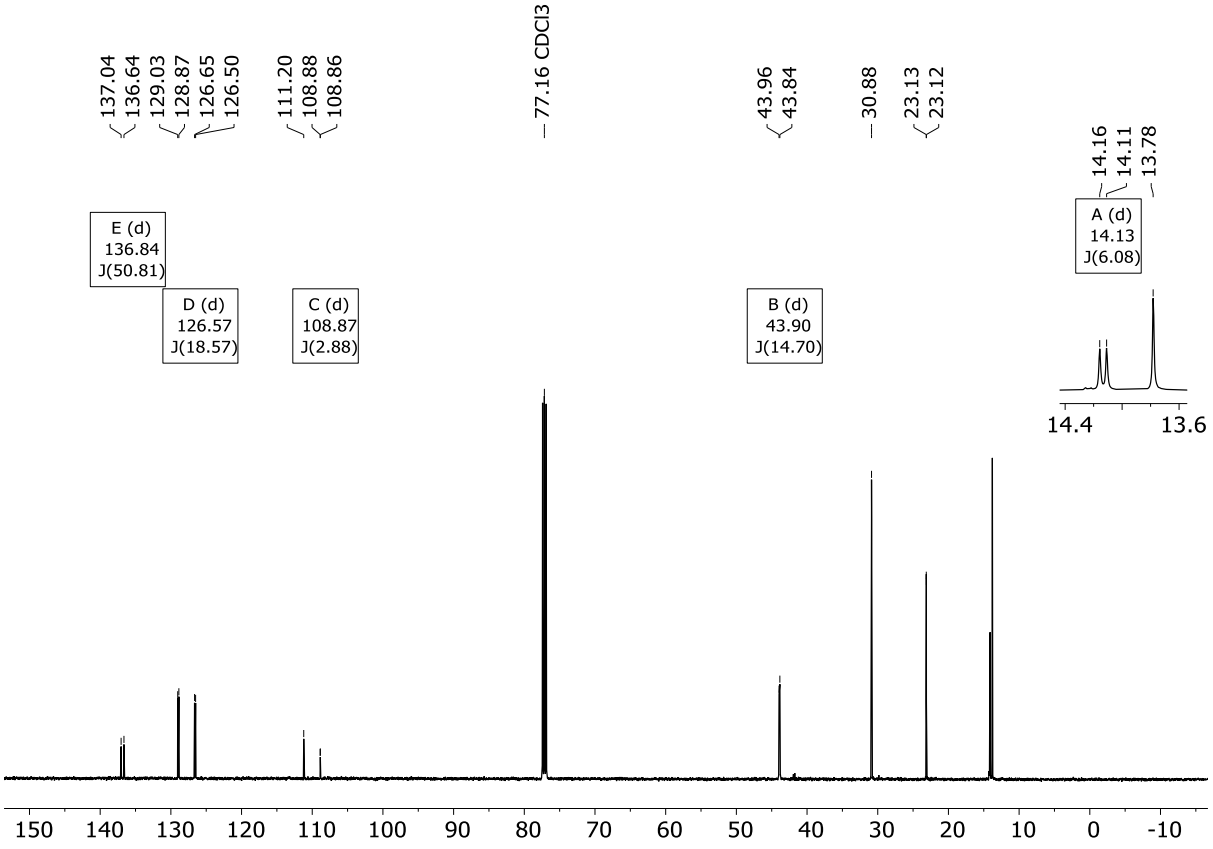


Figure S46: $^{13}C\{^{1}H\}$ NMR spectrum of compound **4f** in $CDCl_3$.

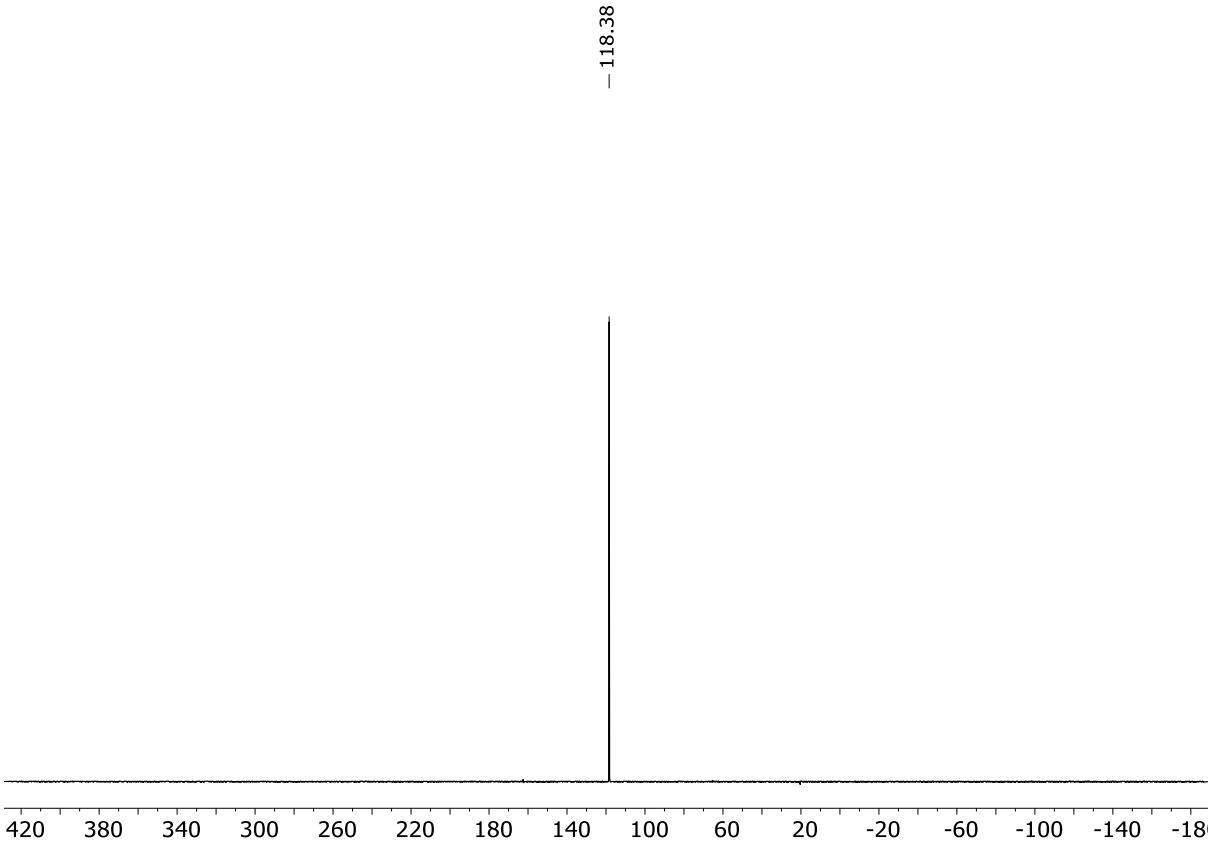


Figure S47: $^{31}P\{^{1}H\}$ NMR spectrum of compound **4f** in $CDCl_3$.

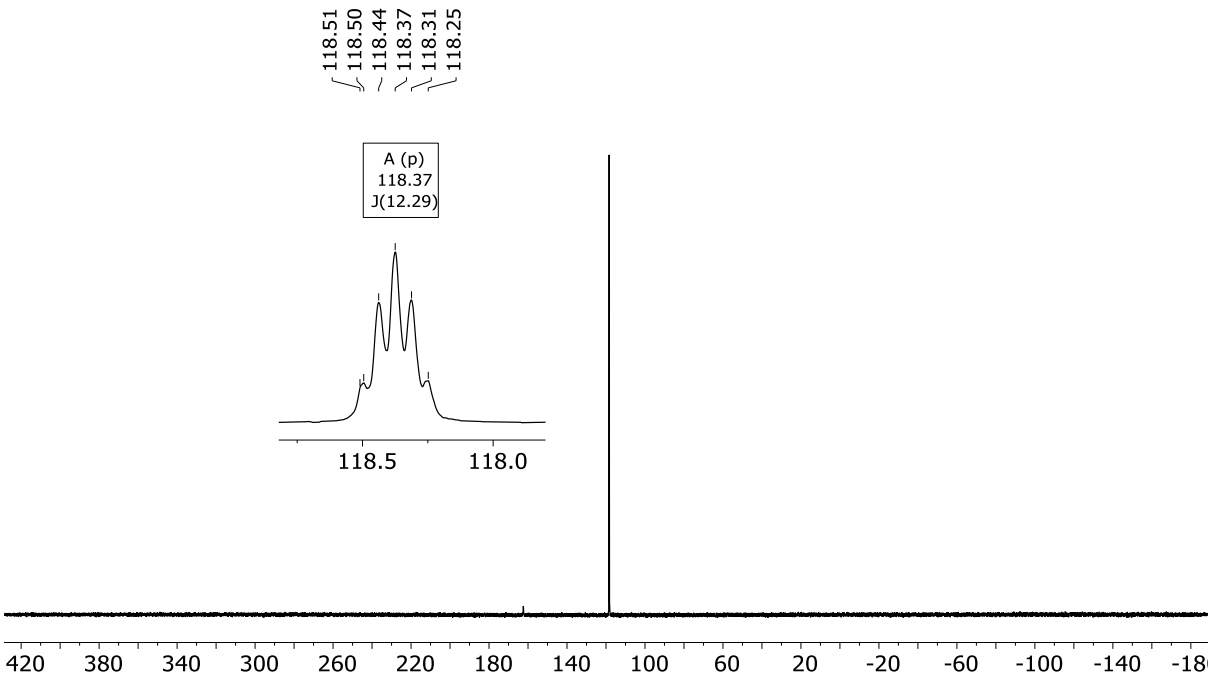


Figure S48: ^{31}P NMR spectrum of compound **4f** in $CDCl_3$.

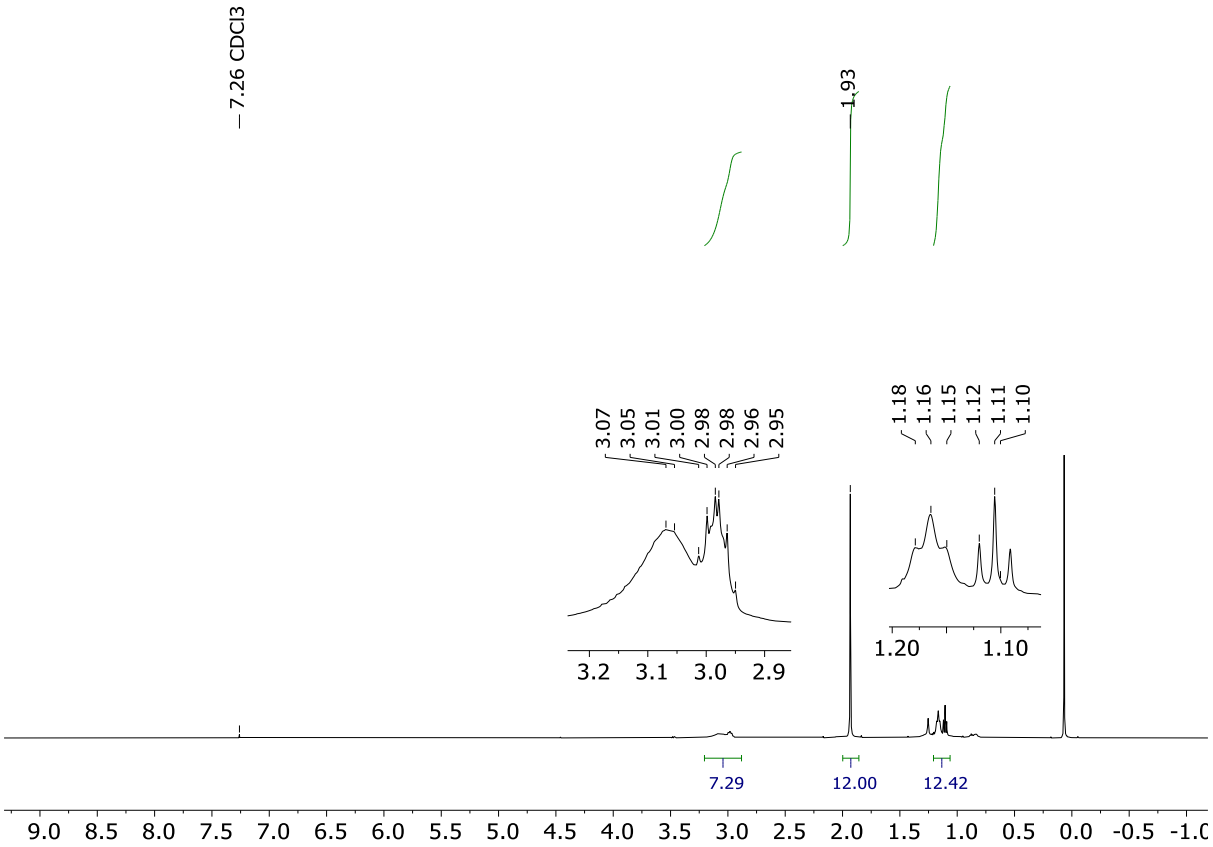


Figure S49: ^{1}H NMR spectrum of compound **5d** in $CDCl_3$.

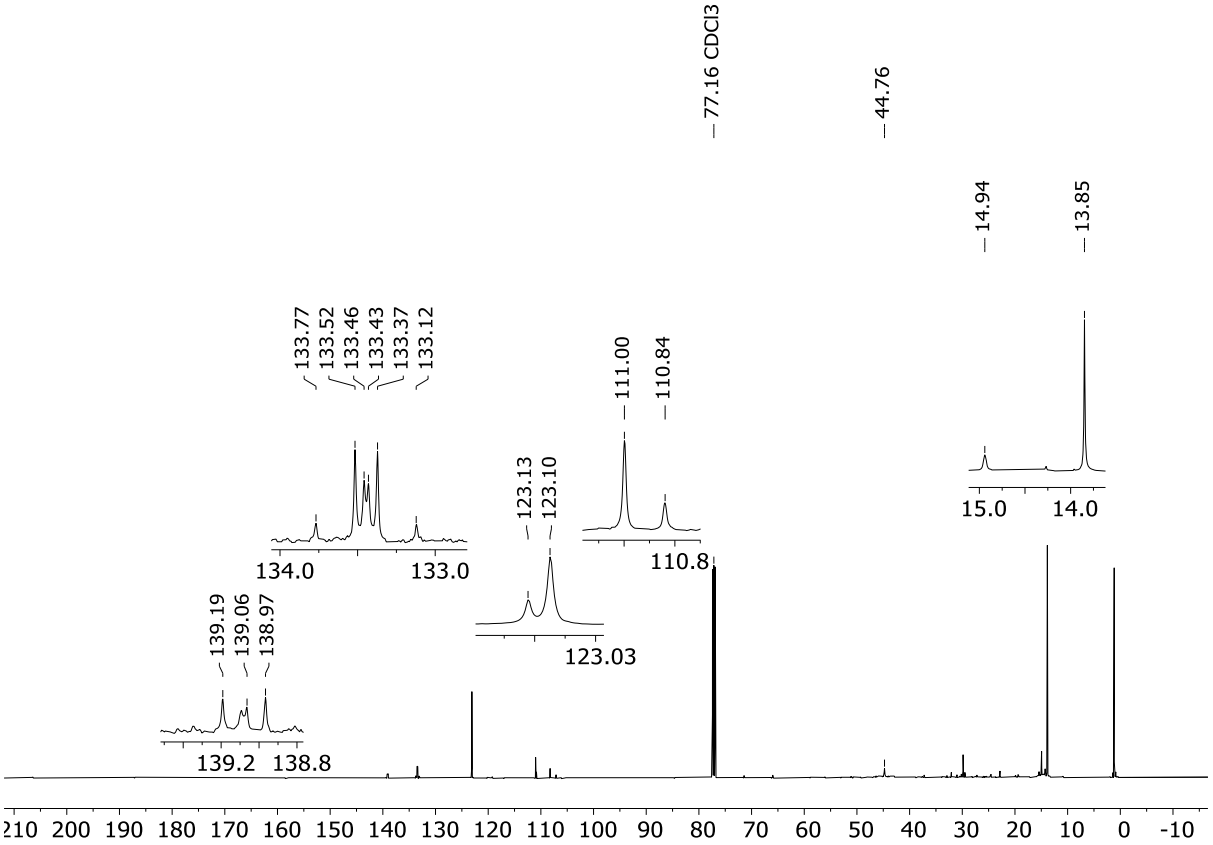


Figure S50: $^{13}C\{^{1}H\}$ NMR spectrum of compound **5d** in $CDCl_3$.

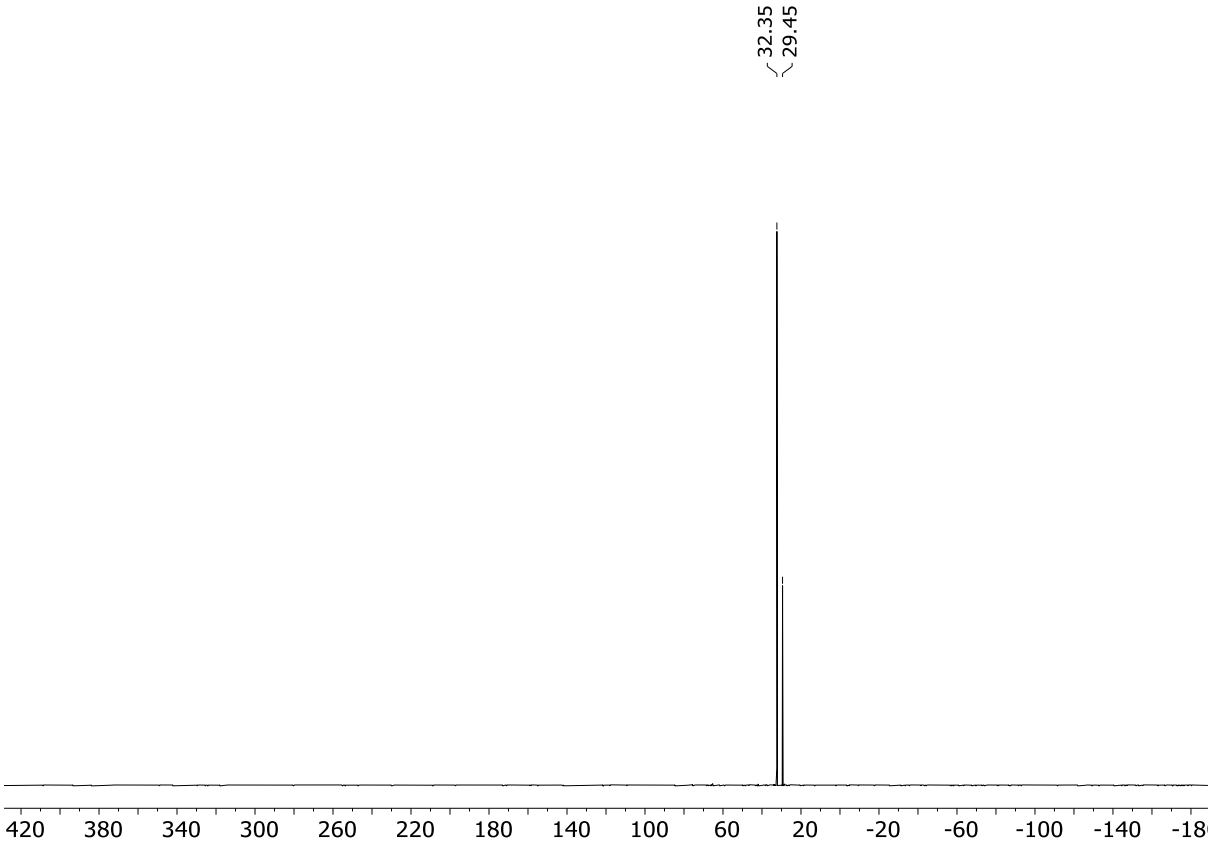


Figure S51: $^{31}P\{^{1}H\}$ NMR spectrum of compound **5d** in $CDCl_3$.

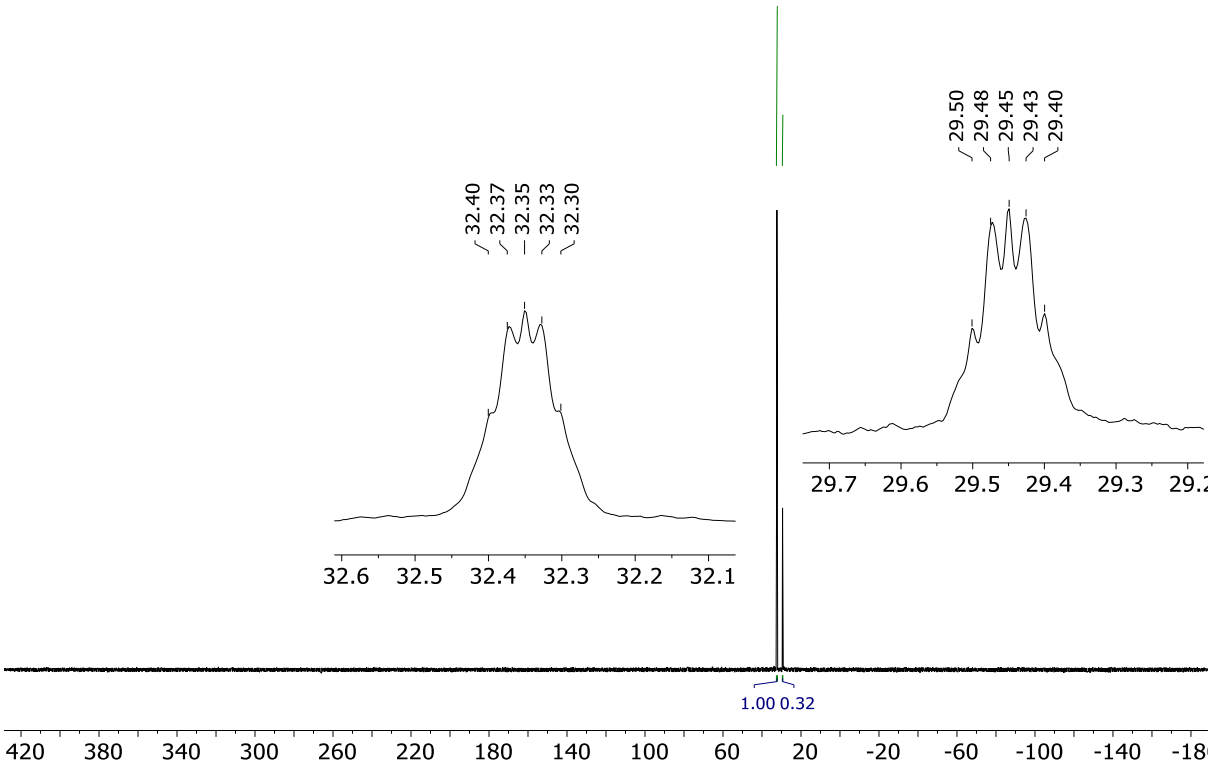


Figure S52: ^{31}P NMR spectrum of compound **5d** in $CDCl_3$.

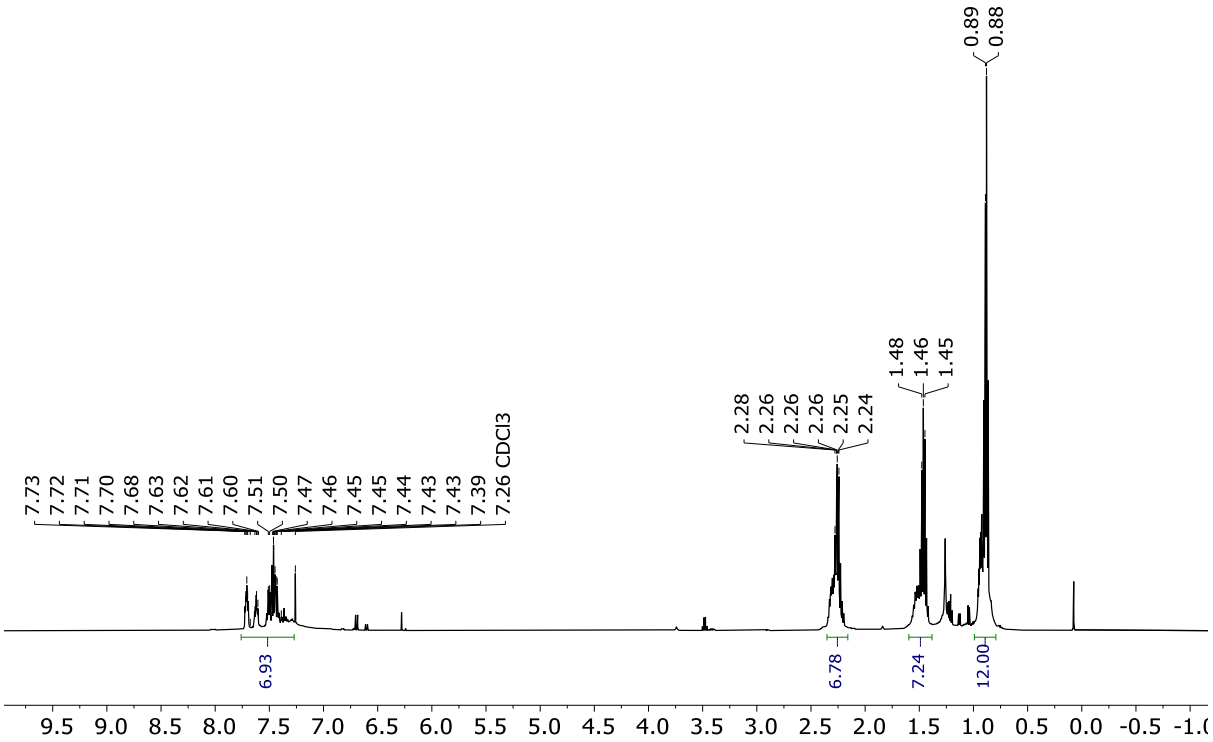


Figure S53: ^{1}H NMR spectrum of compound **5e** in $CDCl_3$.

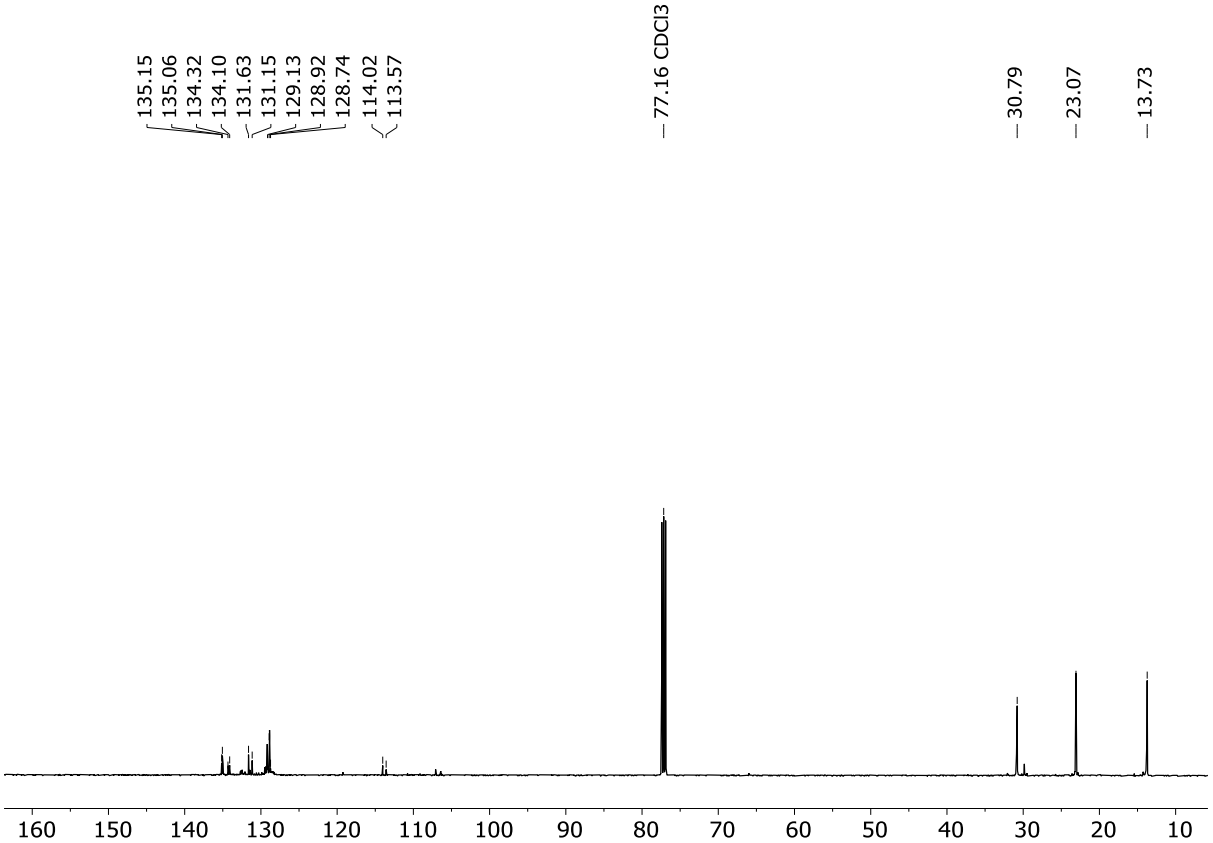


Figure S54: $^{13}C\{^{1}H\}$ NMR spectrum of compound **5e** in $CDCl_3$.

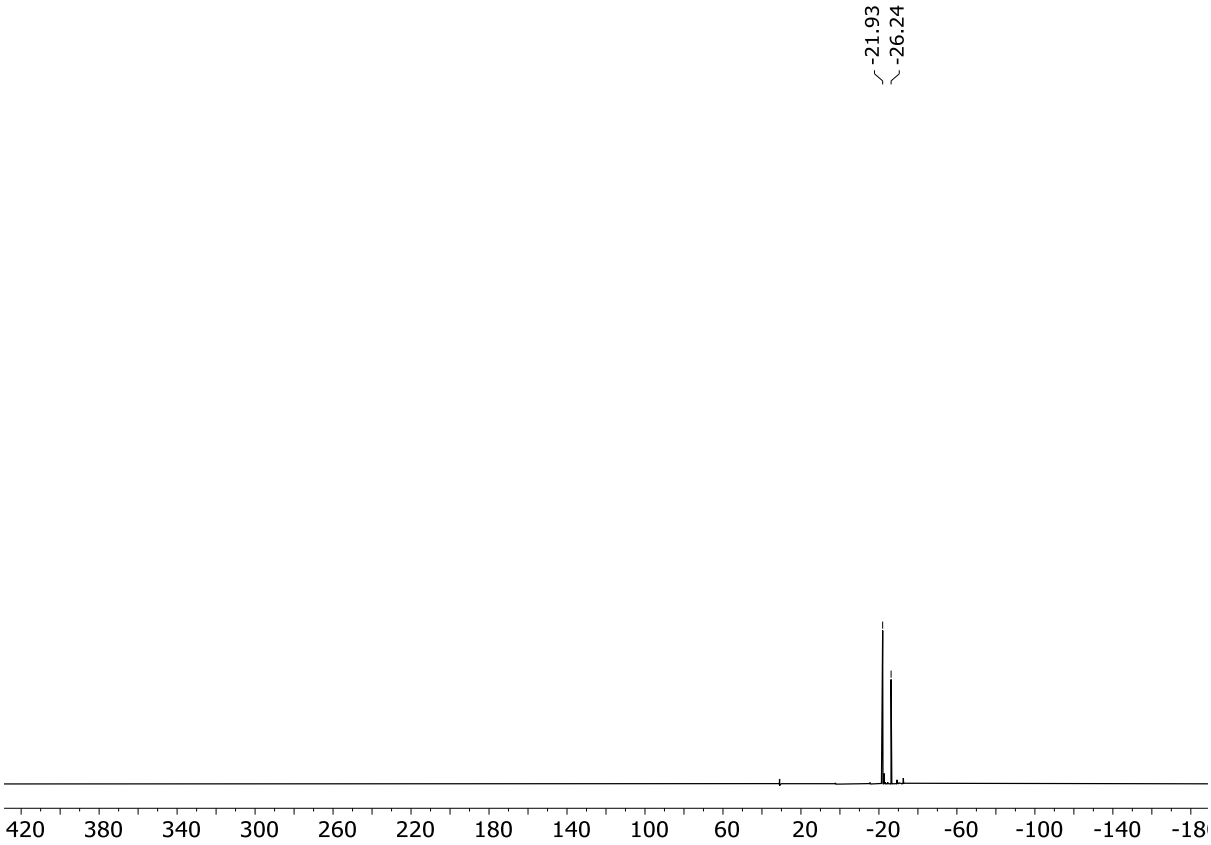


Figure S55: $^{31}P\{^{1}H\}$ NMR spectrum of compound **5e** in $CDCl_3$.

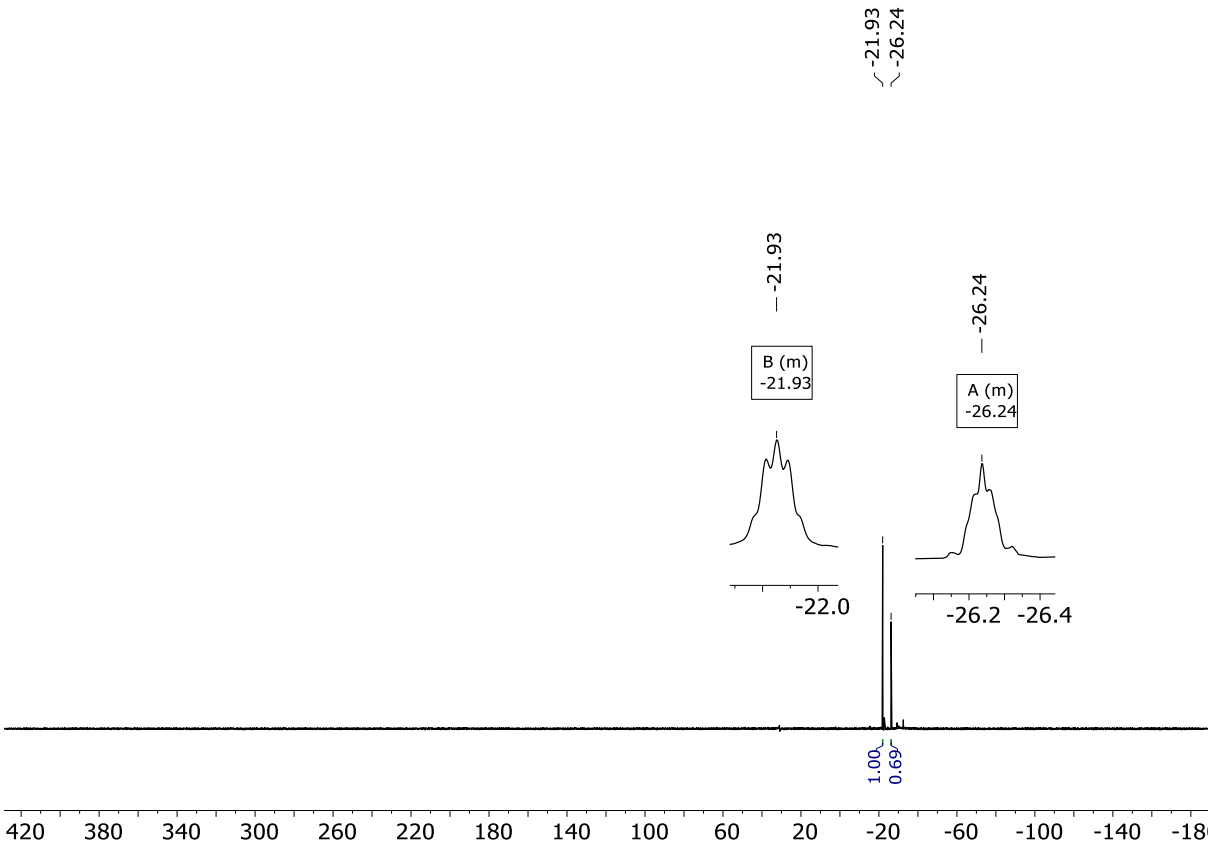


Figure S56: ^{31}P NMR spectrum of compound **5e** in $CDCl_3$.

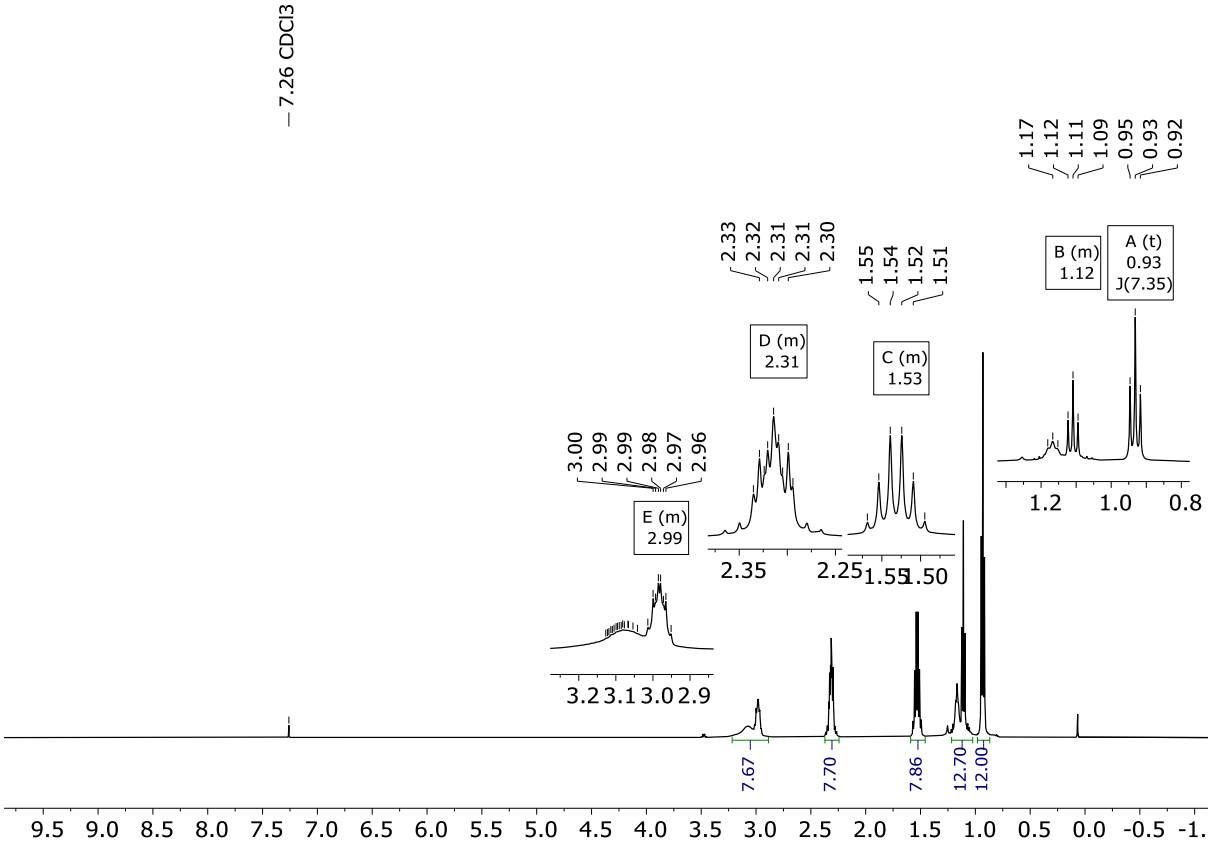


Figure S57: ^{1}H NMR spectrum of compound **5f** in $CDCl_3$.

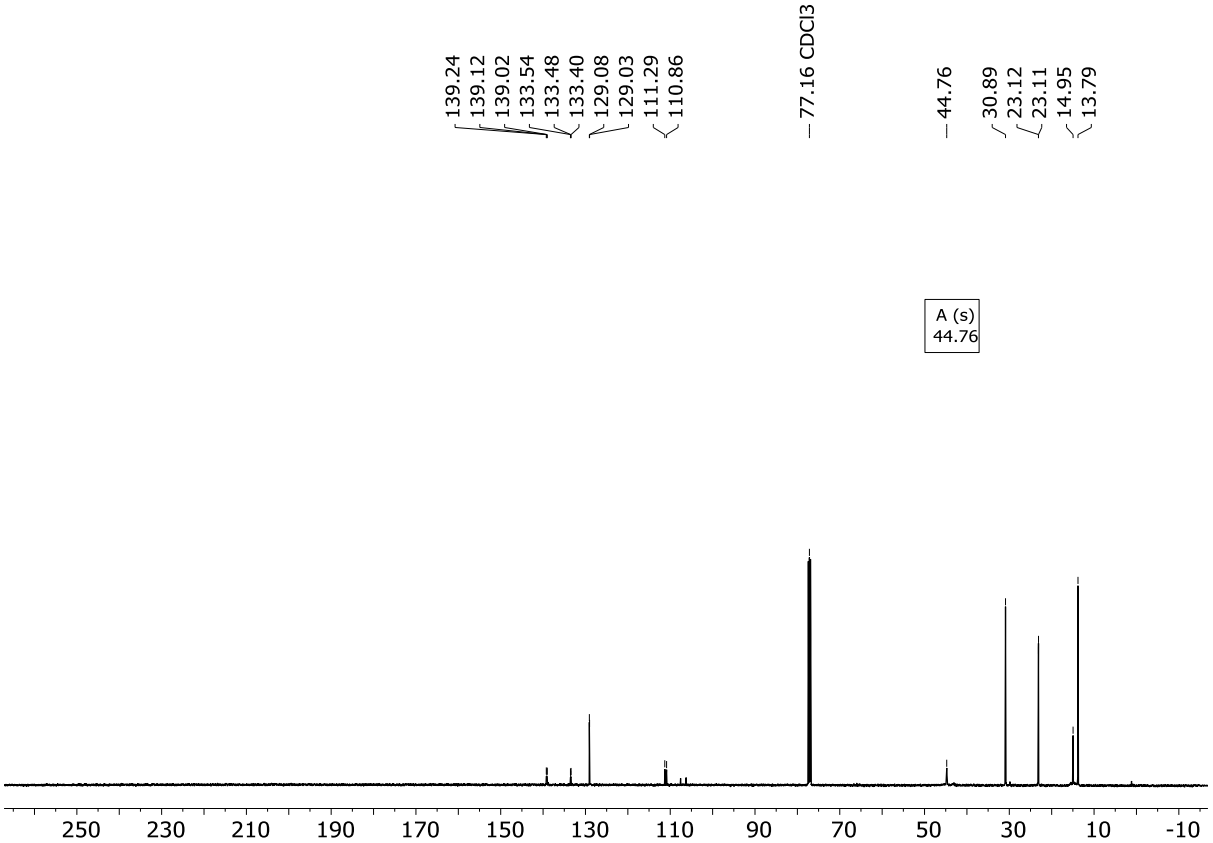


Figure S58: $^{13}C\{^{1}H\}$ NMR spectrum of compound **5f** in $CDCl_3$.

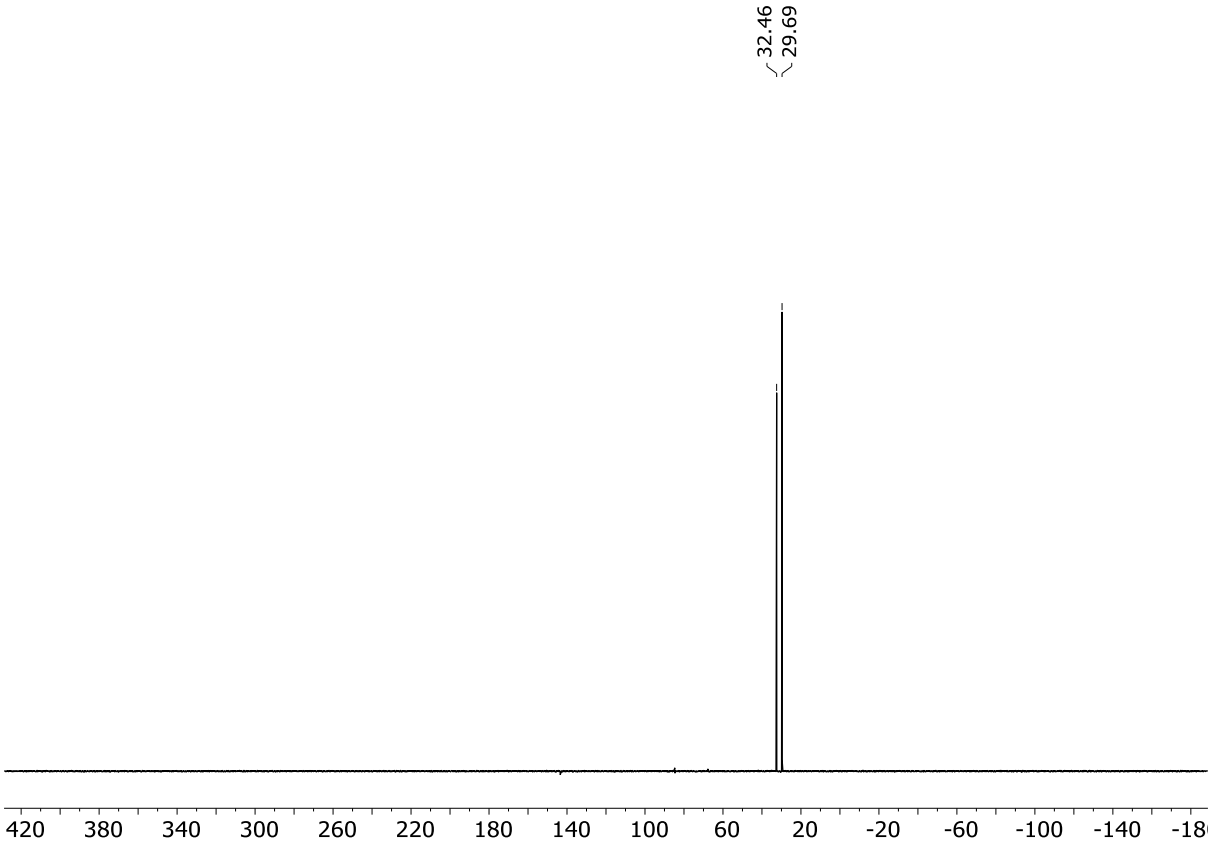


Figure S59: $^{31}P\{^{1}H\}$ NMR spectrum of compound **5f** in $CDCl_3$.

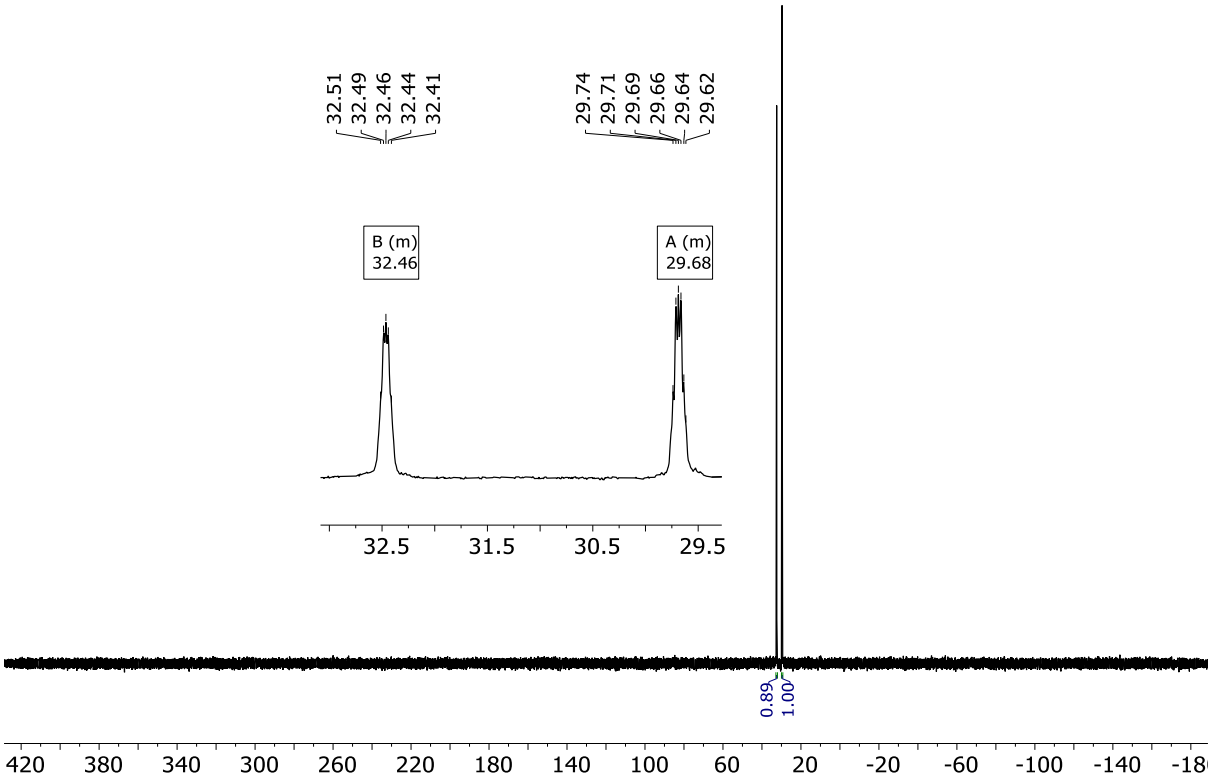


Figure S60: ^{31}P NMR spectrum of compound **5f** in $CDCl_3$.

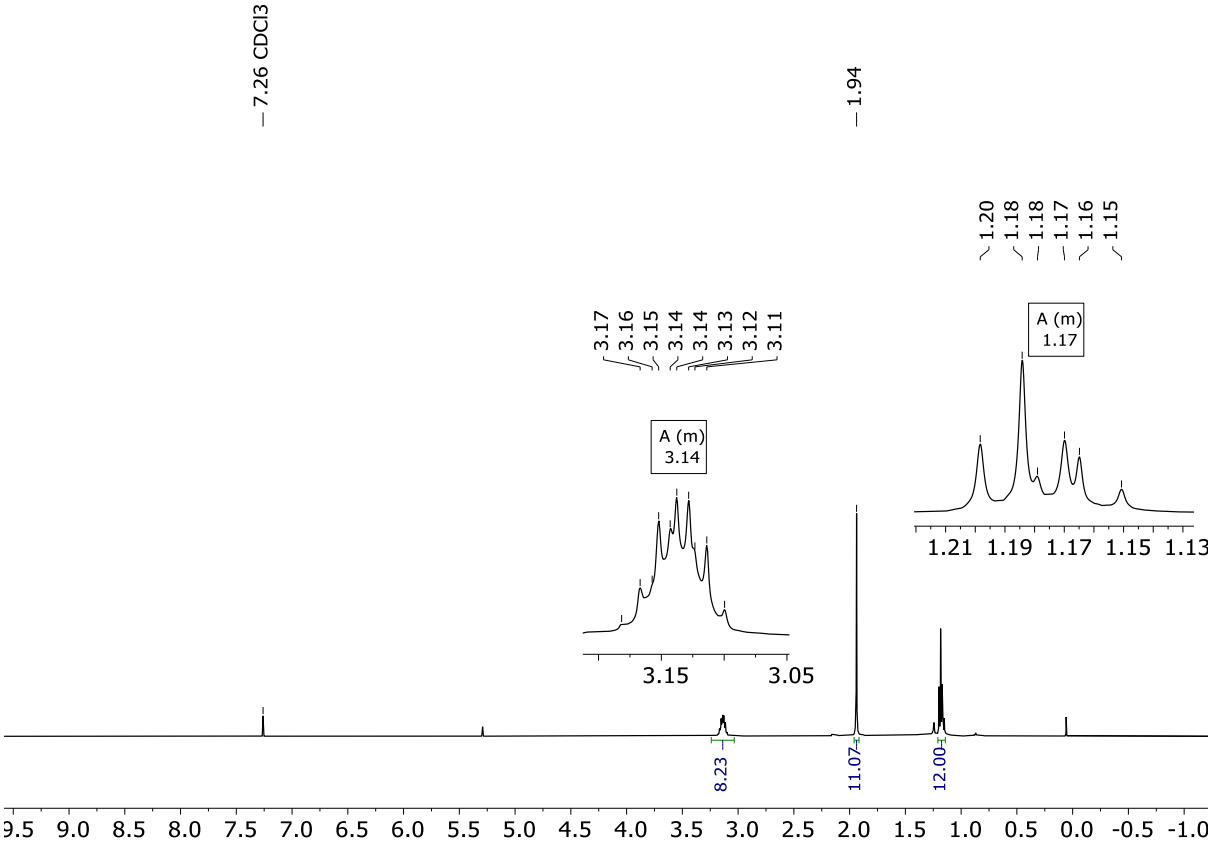


Figure S61: ^{1}H NMR spectrum of compound **6d** in $CDCl_3$.

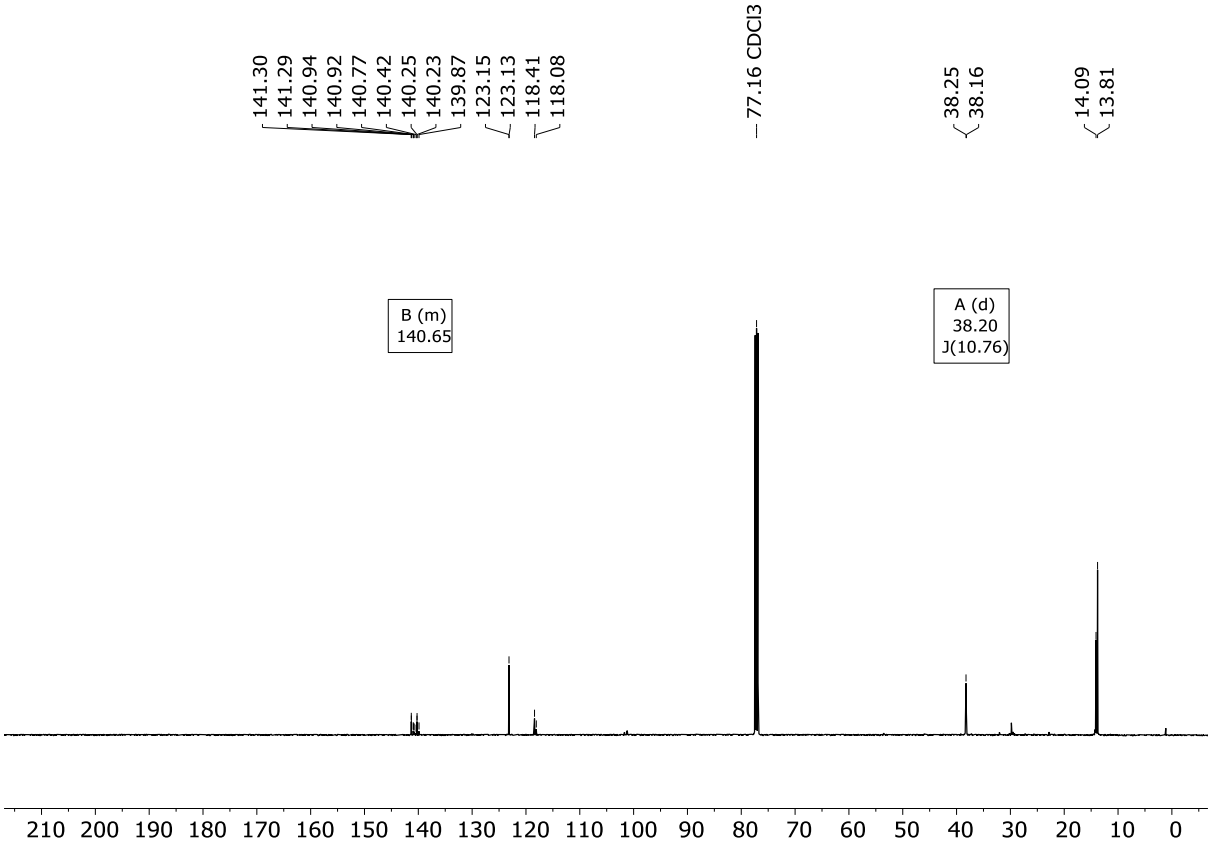


Figure S62: $^{13}C\{^{1}H\}$ NMR spectrum of compound **6d** in $CDCl_3$.

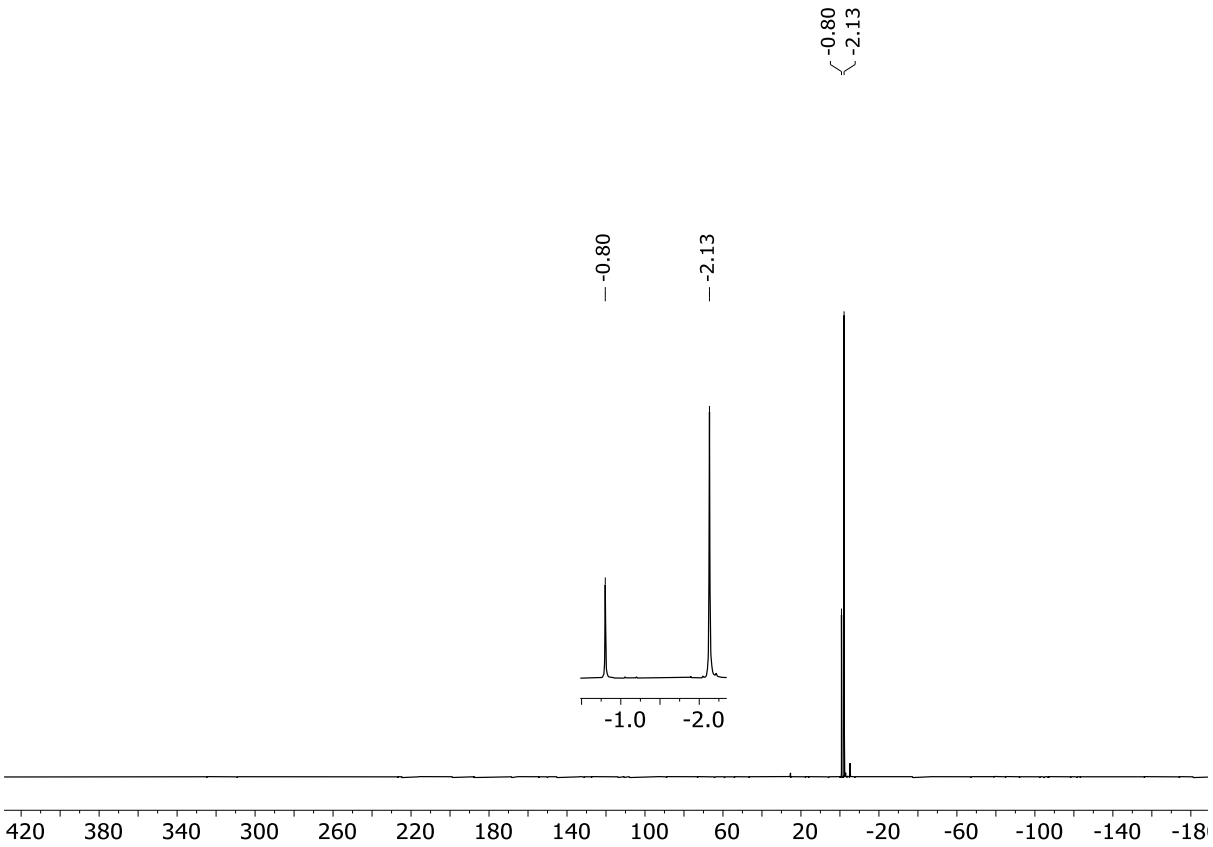


Figure S63: $^{31}P\{^{1}H\}$ NMR spectrum of compound **6d** in $CDCl_3$.

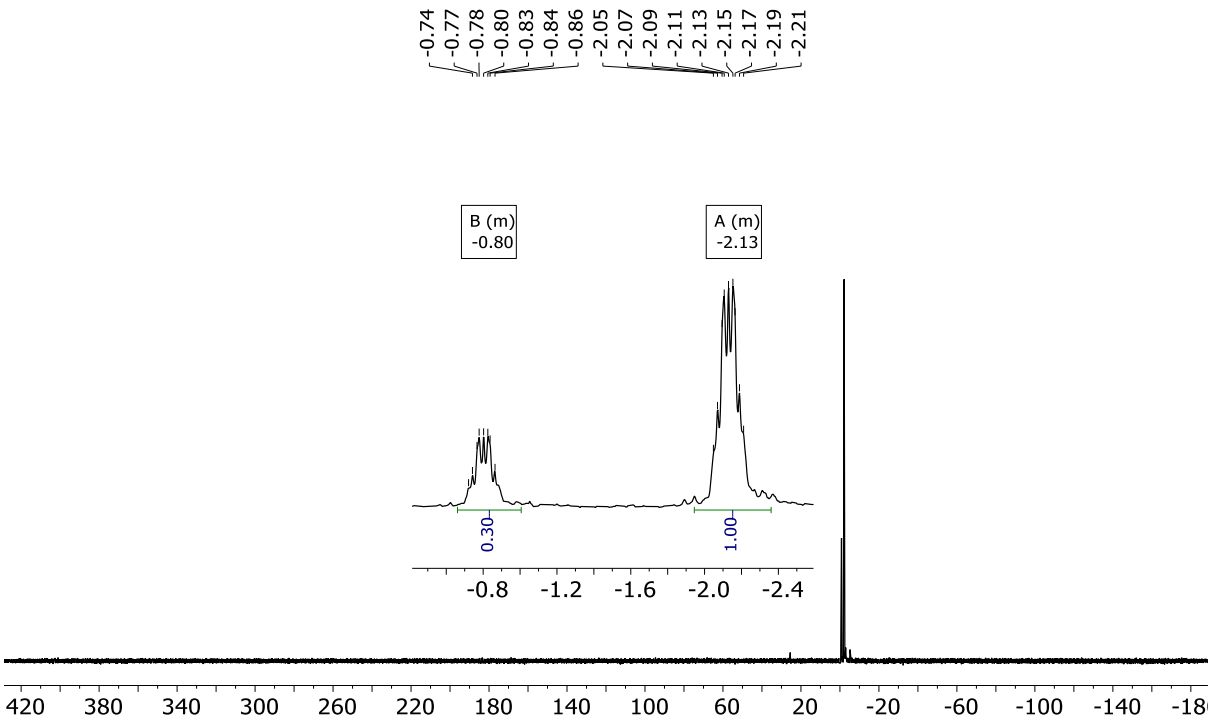


Figure S64: ^{31}P NMR spectrum of compound **6d** in $CDCl_3$.

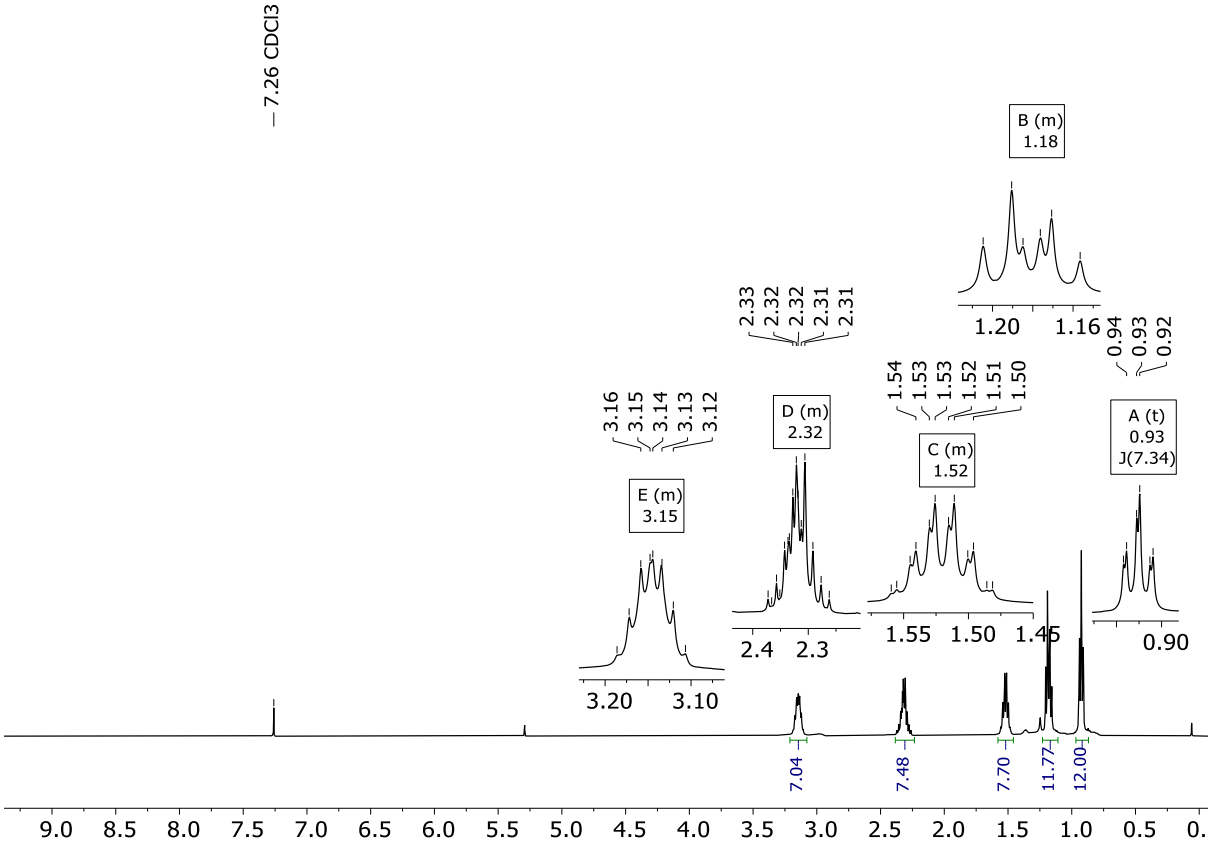


Figure S65: ^{1}H NMR spectrum of compound **6f** in $CDCl_3$.

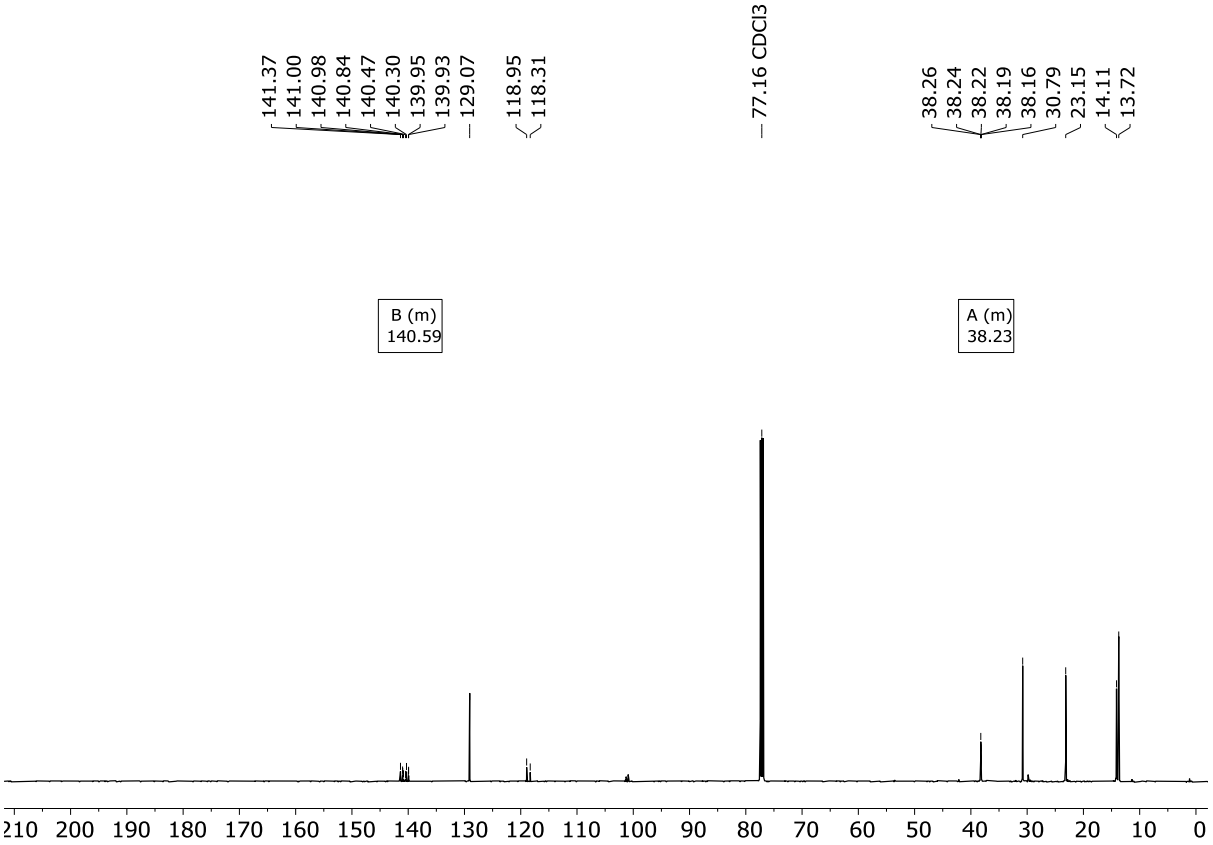


Figure S66: $^{13}C\{^{1}H\}$ NMR spectrum of compound **6f** in $CDCl_3$.

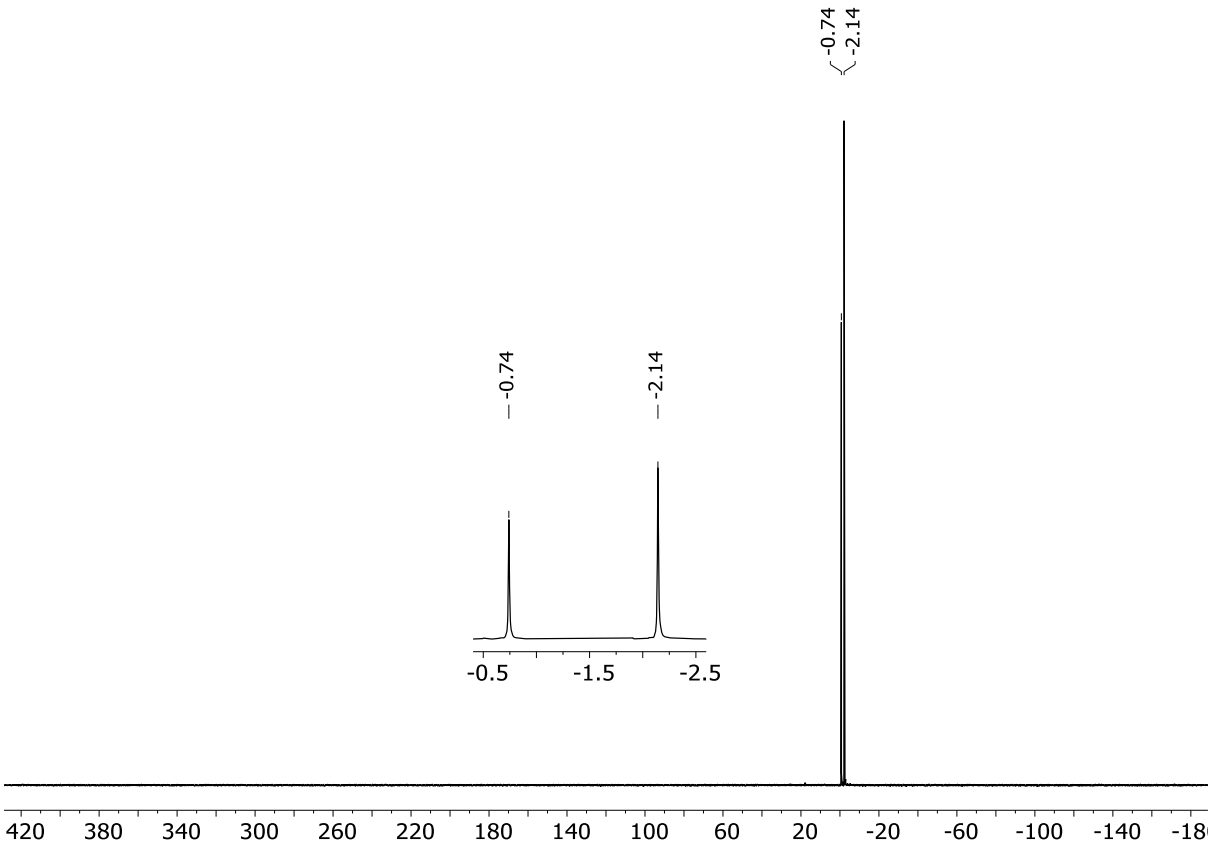


Figure S67: $^{31}P\{^{1}H\}$ NMR spectrum of compound **6f** in $CDCl_3$.

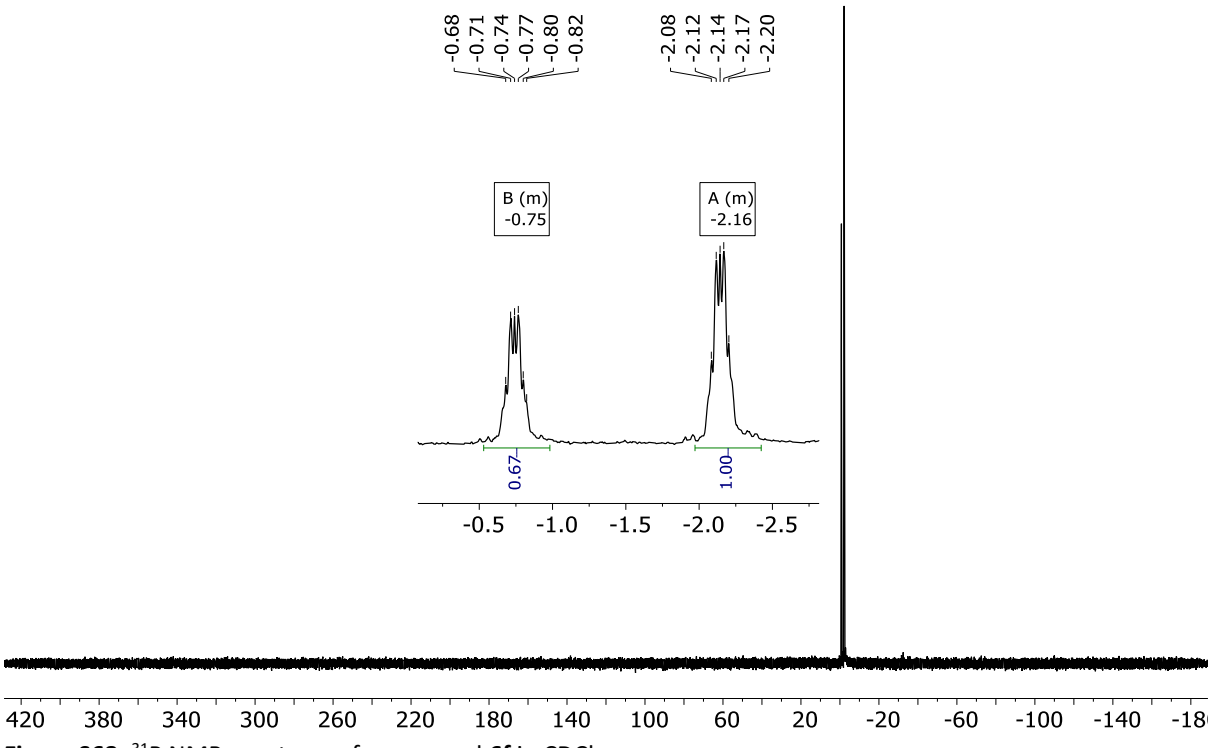


Figure S68: ^{31}P NMR spectrum of compound **6f** in $CDCl_3$.

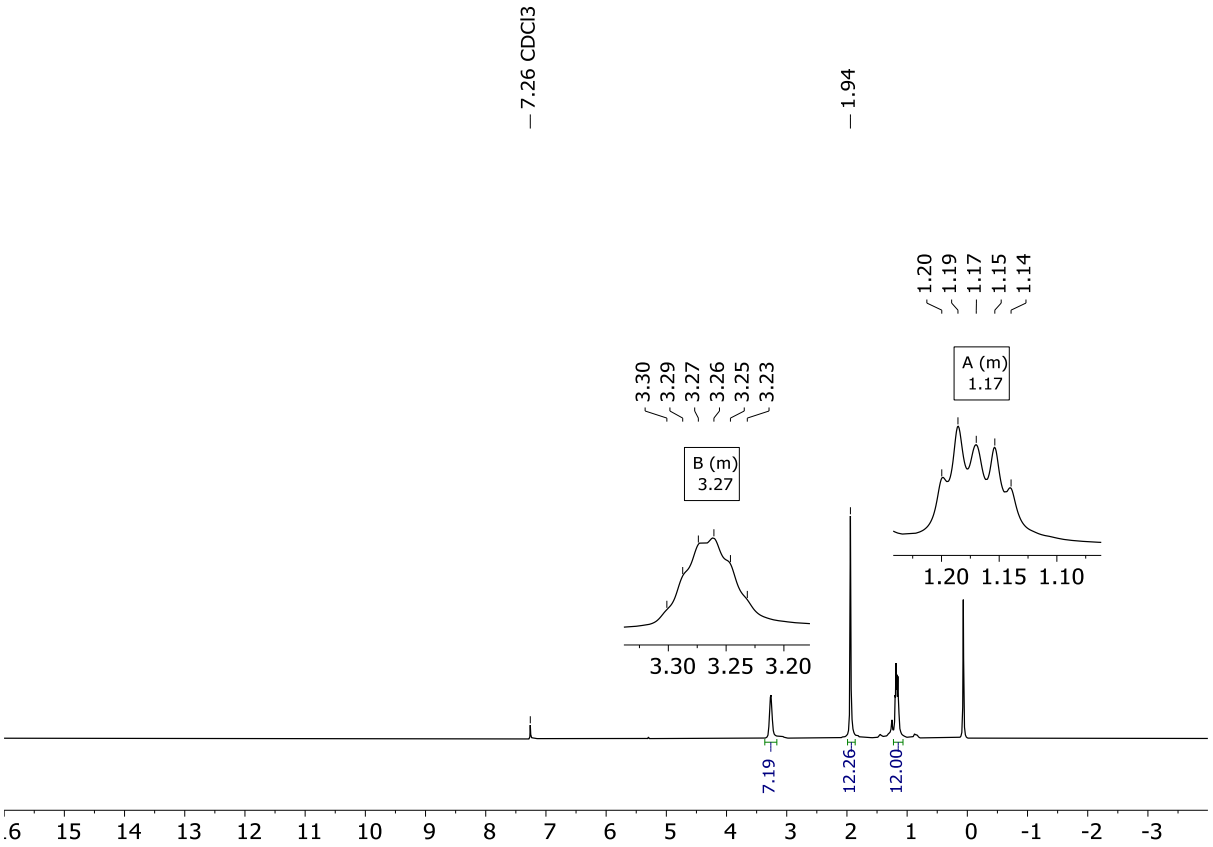


Figure S69: ^{1}H NMR spectrum of compound **7d** in $CDCl_3$.

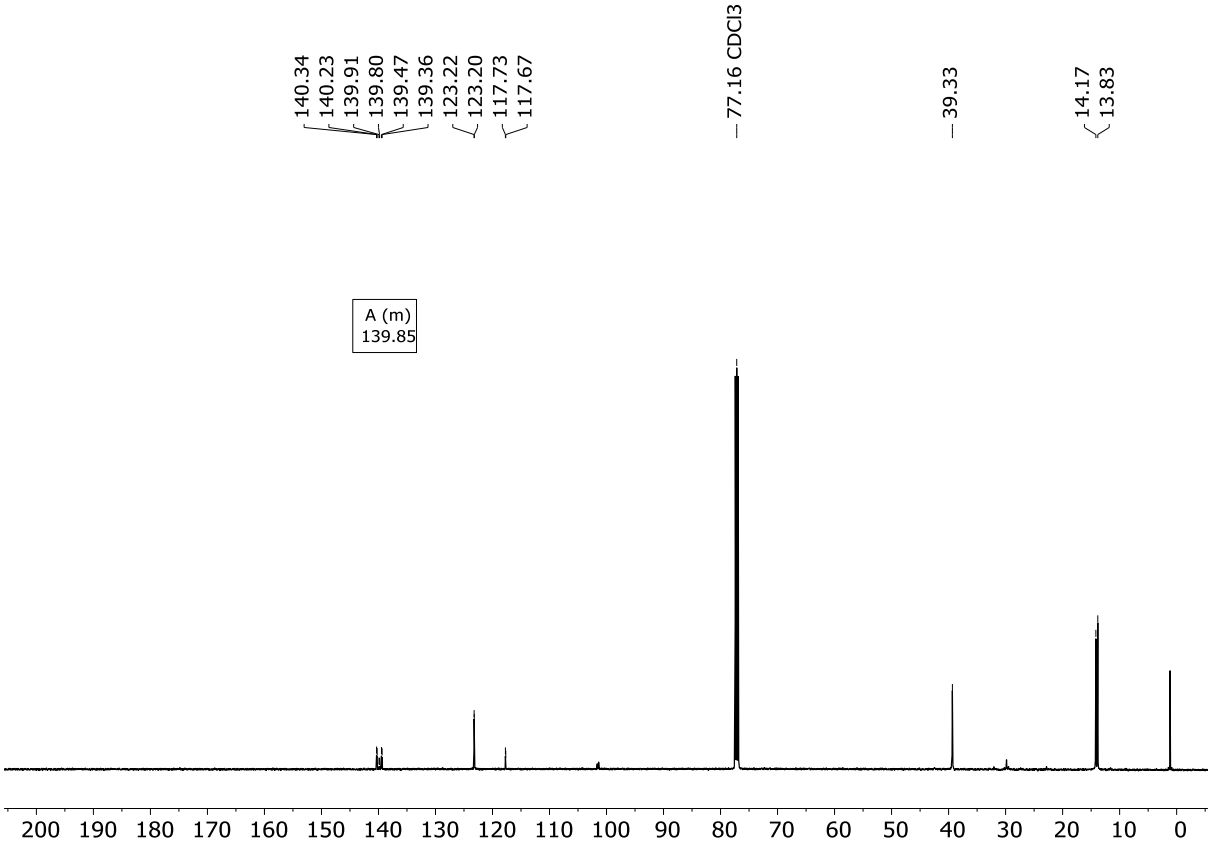


Figure S70: $^{13}C\{^{1}H\}$ NMR spectrum of compound **7d** in $CDCl_3$.

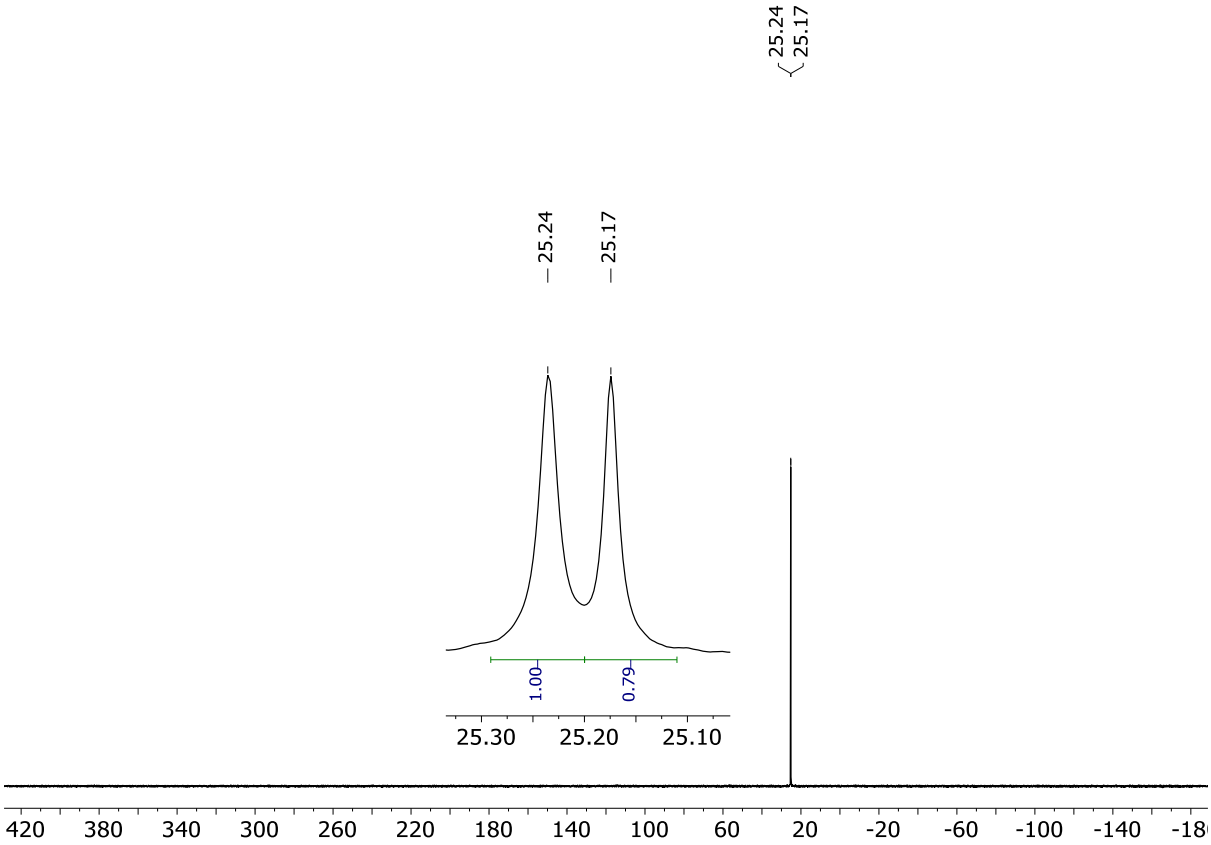


Figure S71: $^{31}P\{^{1}H\}$ NMR spectrum of compound **7d** in $CDCl_3$.

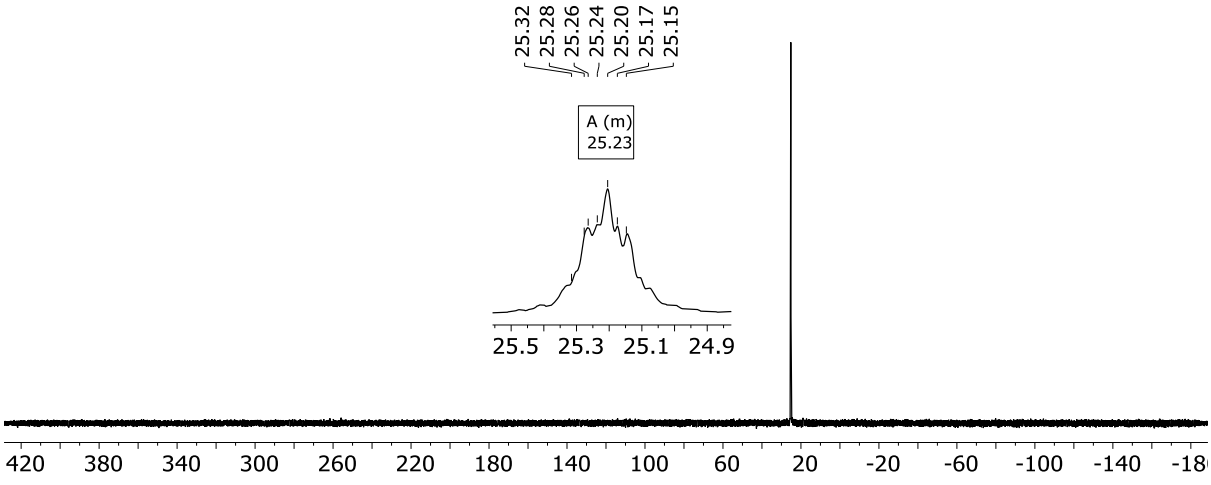


Figure S72: ^{31}P NMR spectrum of compound **7d** in $CDCl_3$.

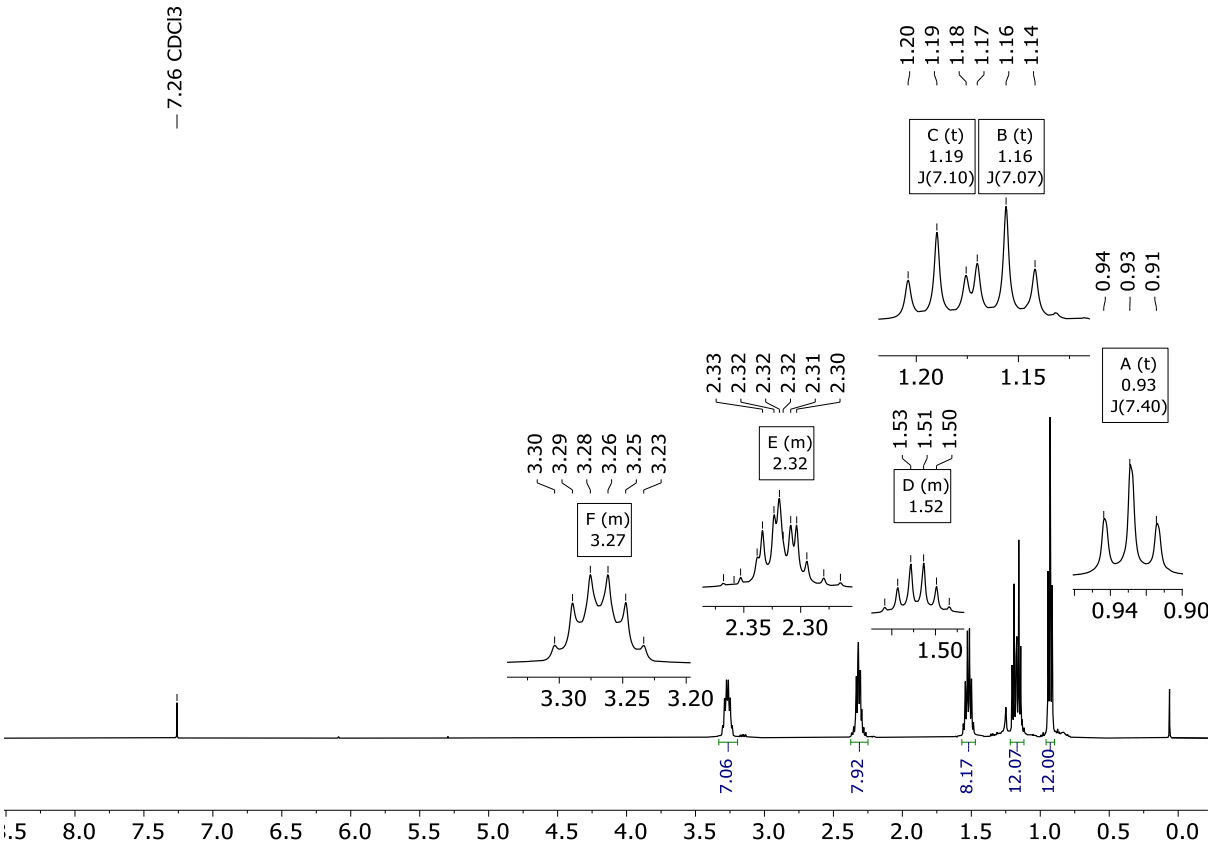


Figure S73: ^{1}H NMR spectrum of compound **7f** in $CDCl_3$.

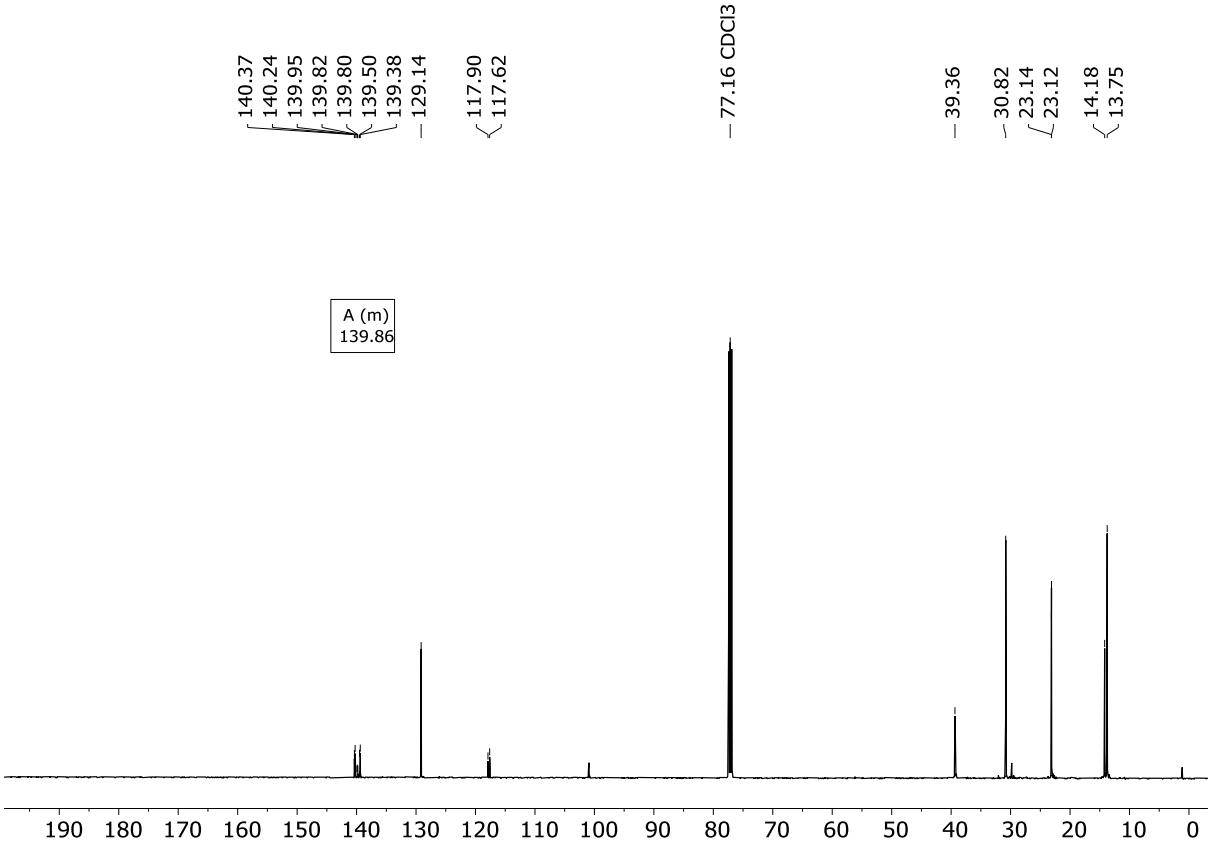


Figure S74: $^{13}C\{^{1}H\}$ NMR spectrum of compound **7f** in $CDCl_3$.

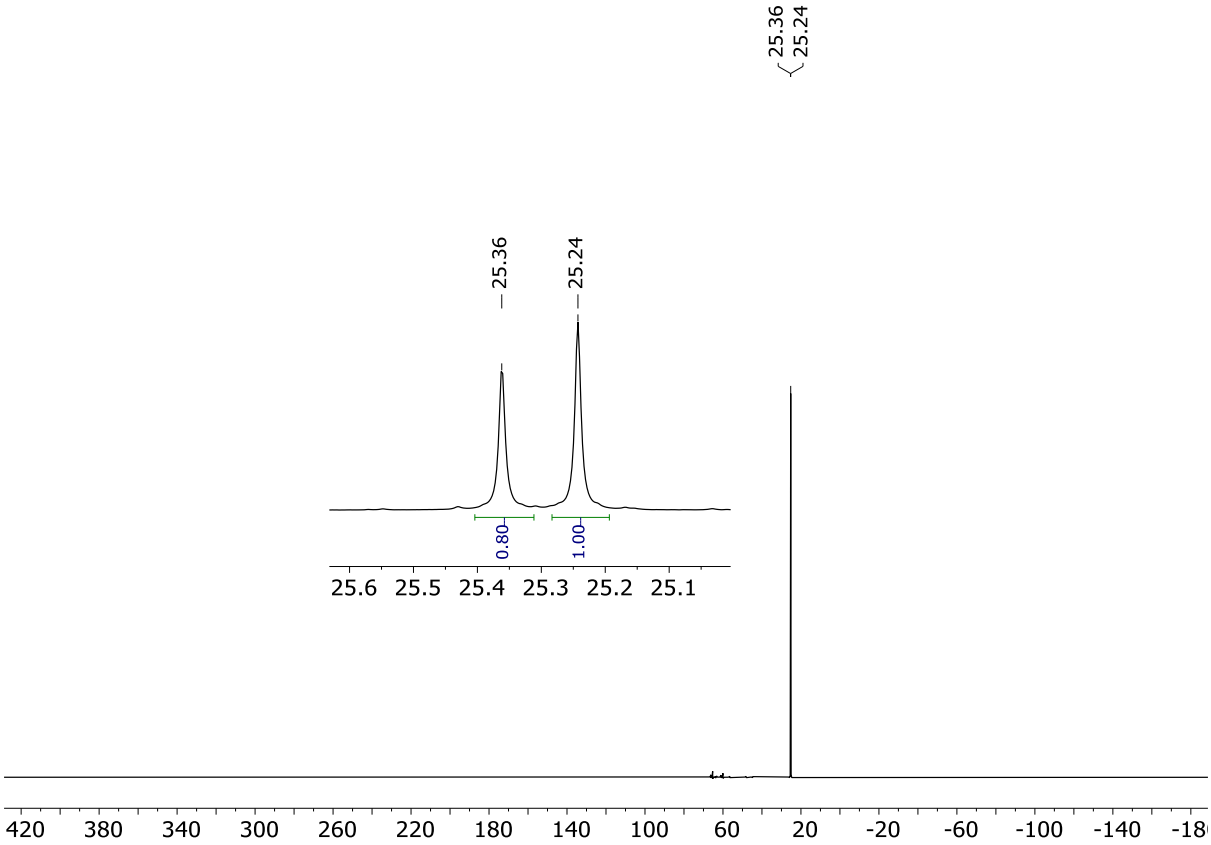


Figure S75: $^{31}P\{^{1}H\}$ NMR spectrum of compound **7f** in $CDCl_3$.

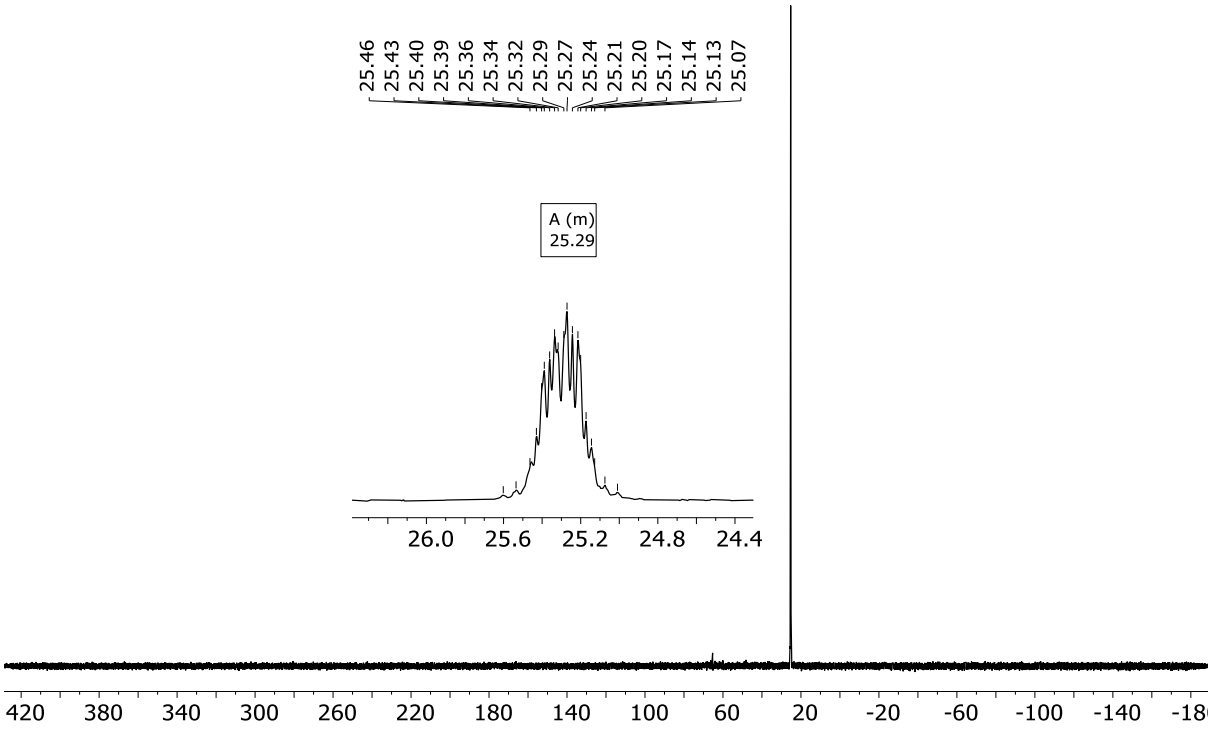


Figure S76: ^{31}P NMR spectrum of compound **7f** in $CDCl_3$.

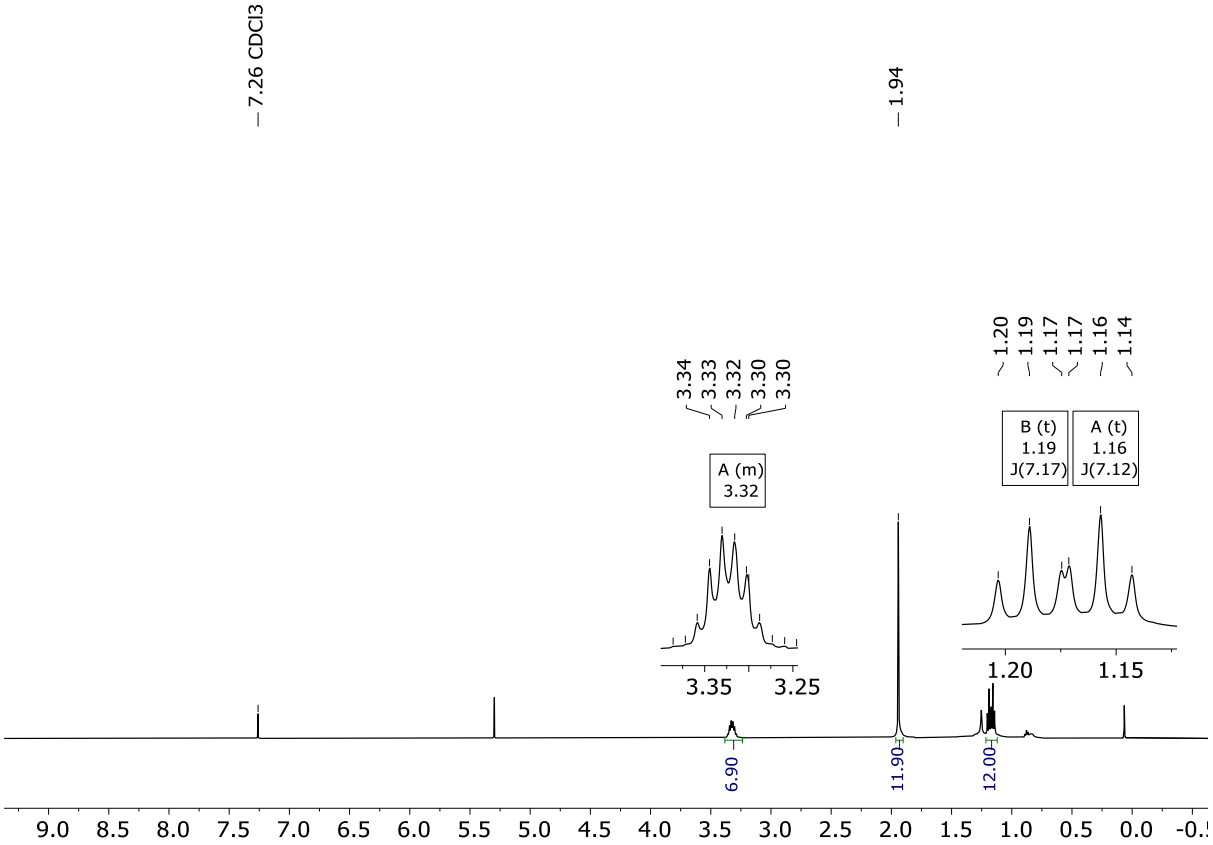


Figure S77: ^{1}H NMR spectrum of compound **8d** in $CDCl_3$.

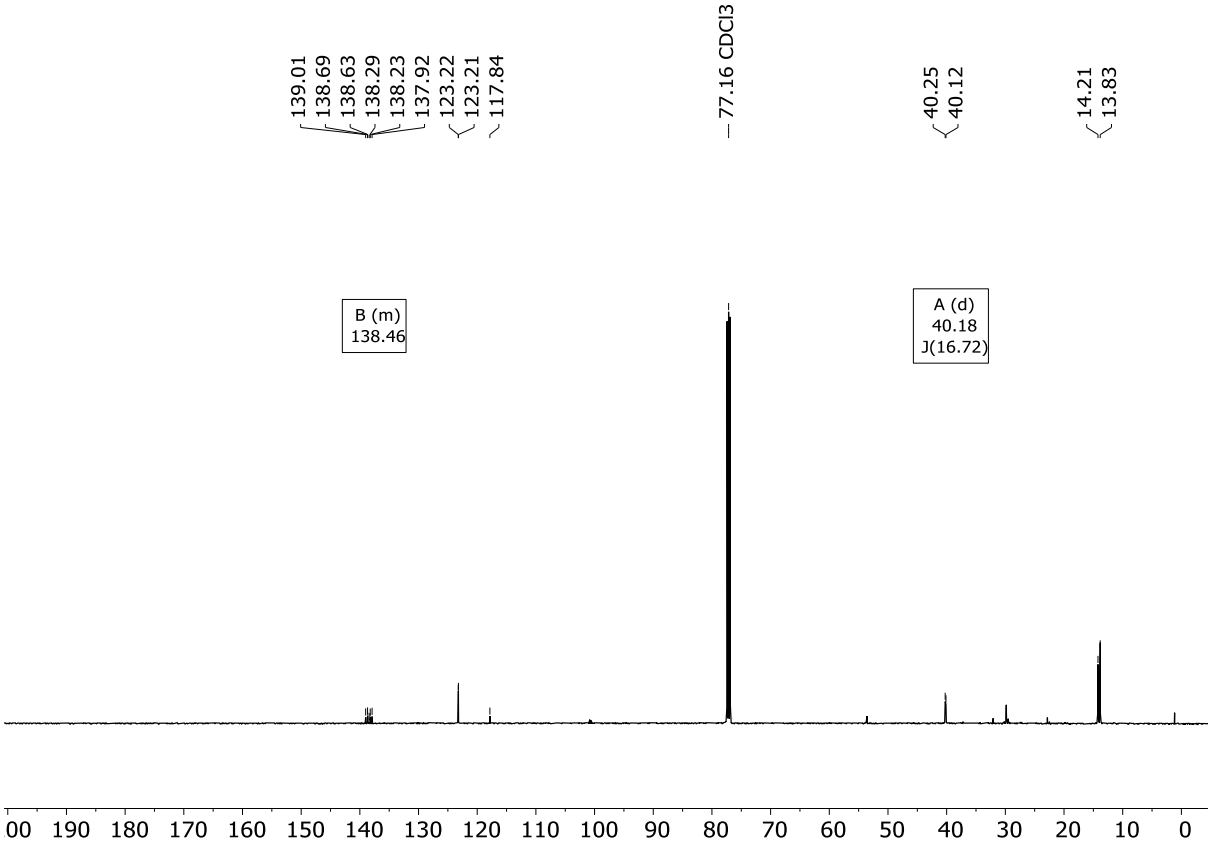


Figure S78: $^{13}C\{^{1}H\}$ NMR spectrum of compound **8d** in $CDCl_3$.

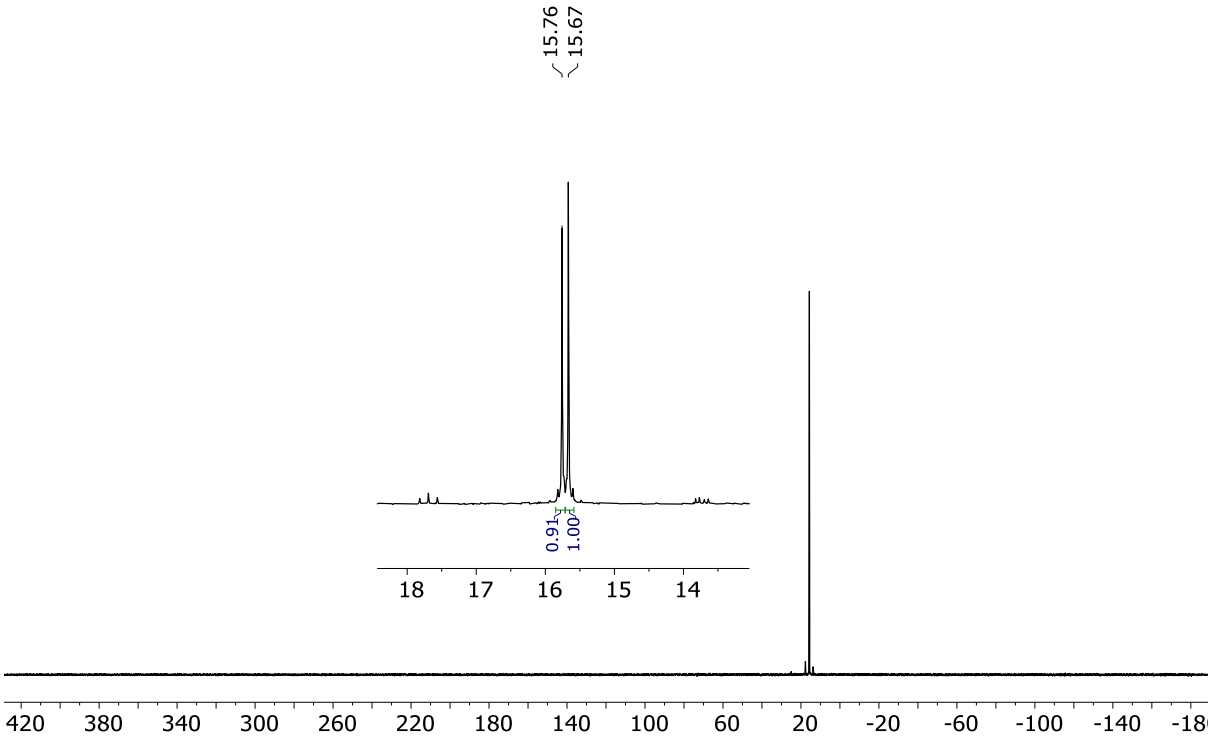


Figure S79: $^{31}P\{^{1}H\}$ NMR spectrum of compound **8d** in $CDCl_3$.

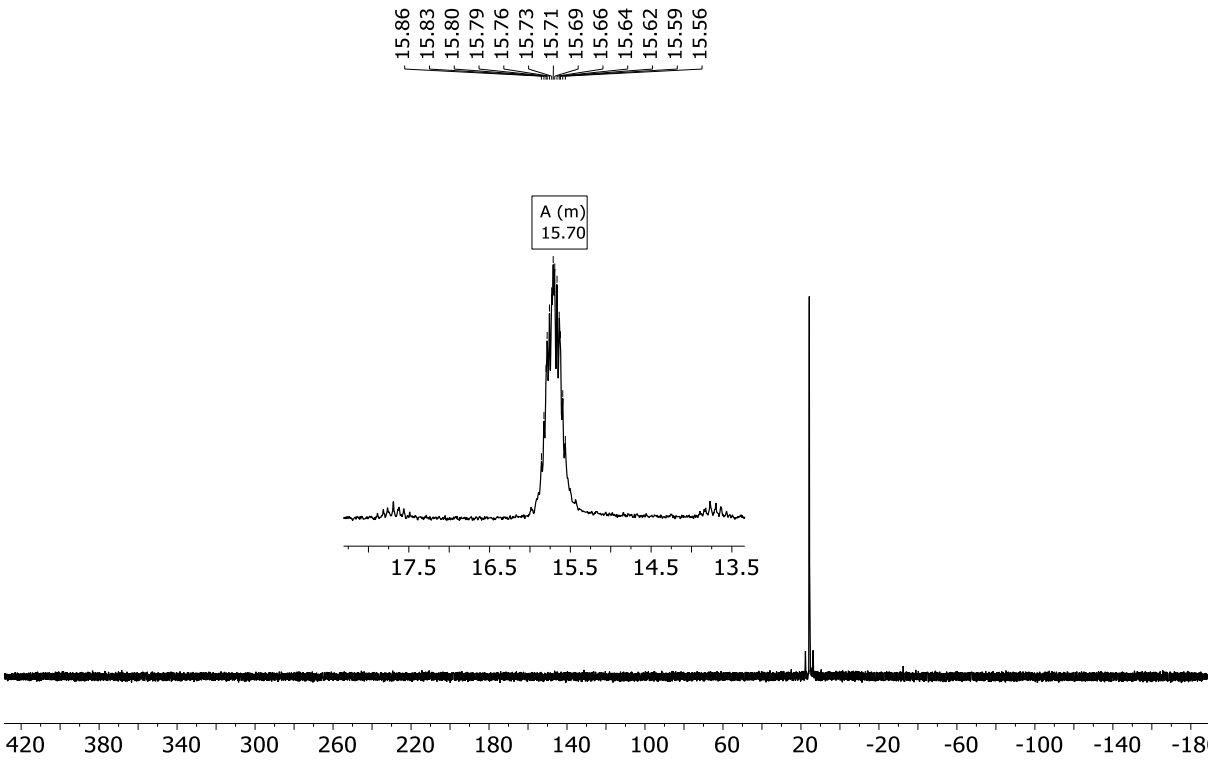


Figure S80: ^{31}P NMR spectrum of compound **8d** in $CDCl_3$.

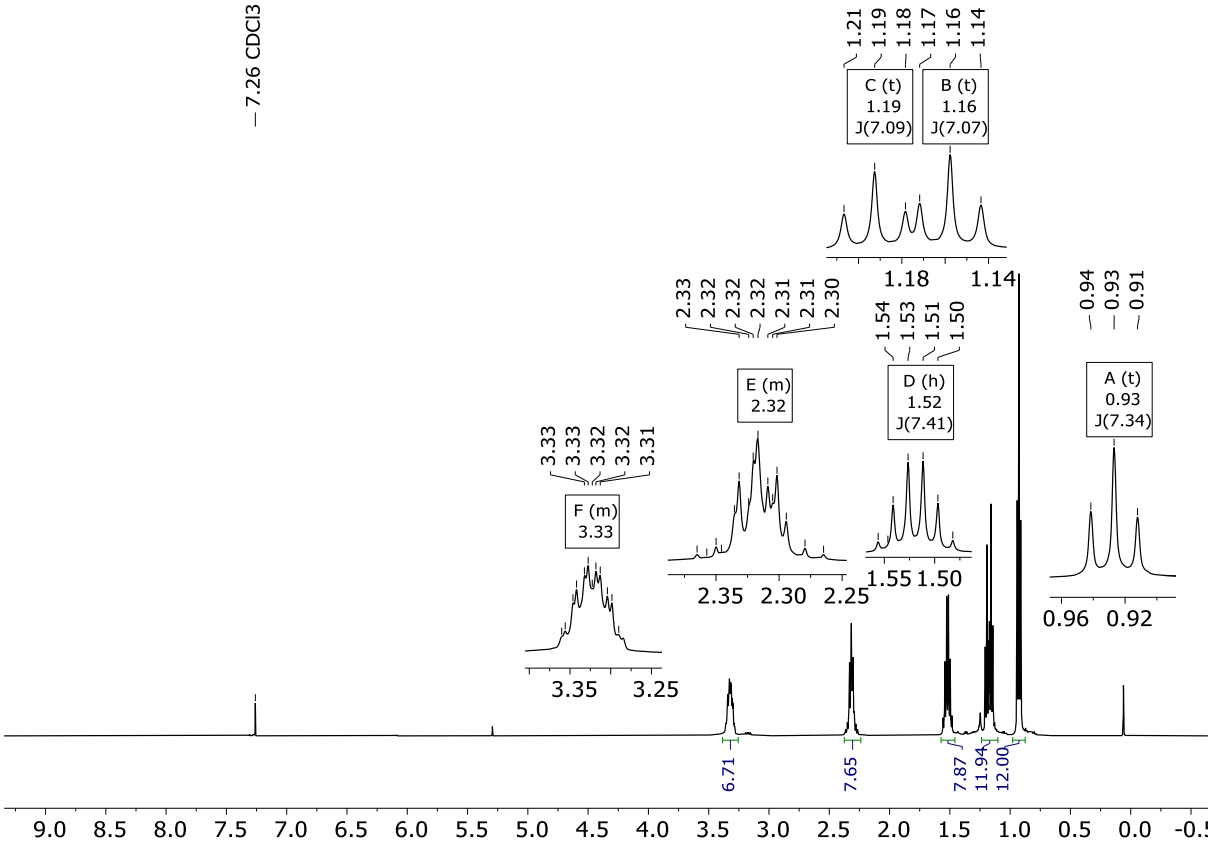


Figure S81: ^{1}H NMR spectrum of compound **8f** in $CDCl_3$.

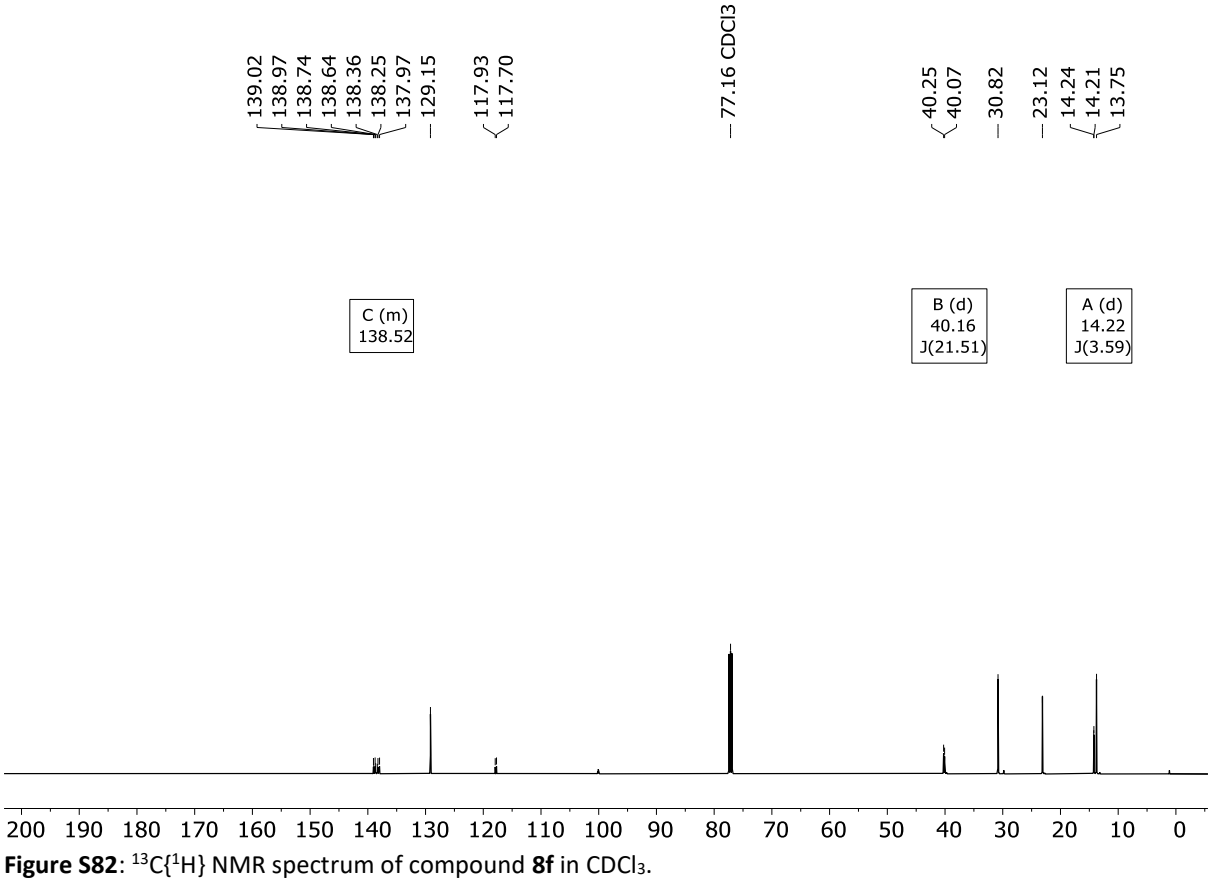


Figure S82: $^{13}C\{^{1}H\}$ NMR spectrum of compound **8f** in $CDCl_3$.

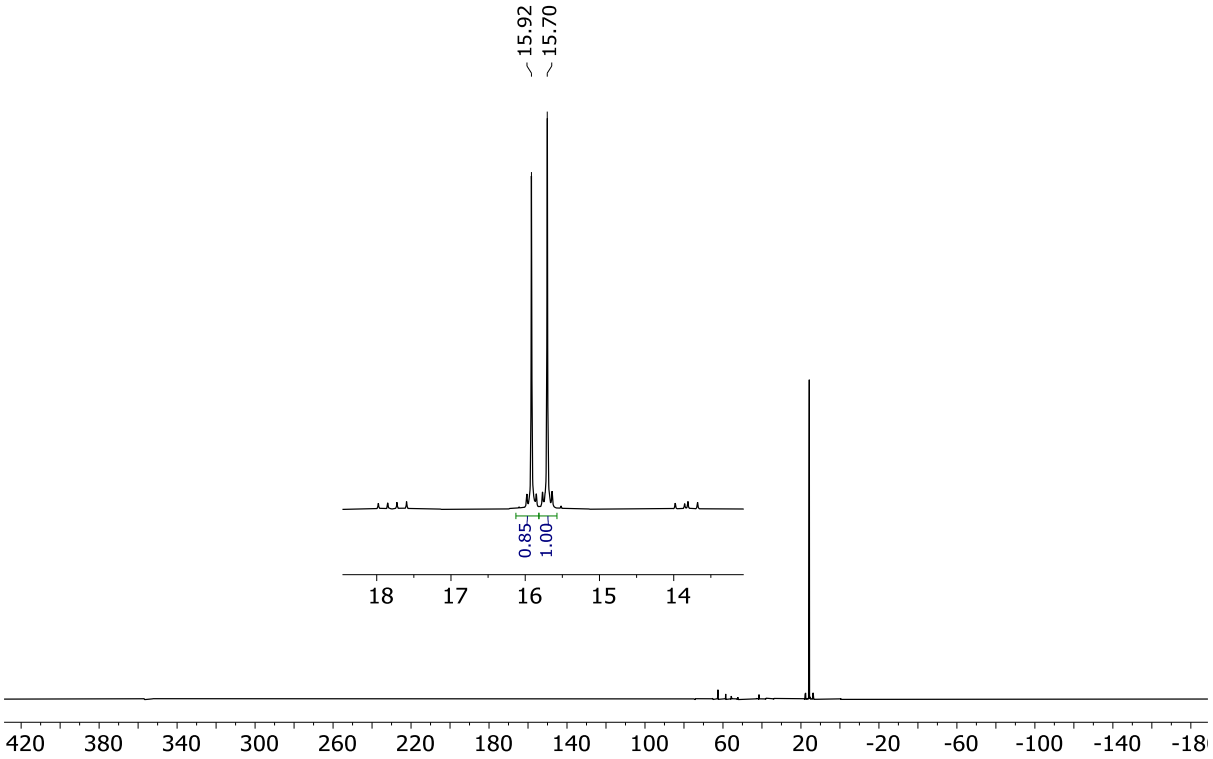


Figure S83: $^{31}P\{^{1}H\}$ NMR spectrum of compound **8f** in $CDCl_3$.

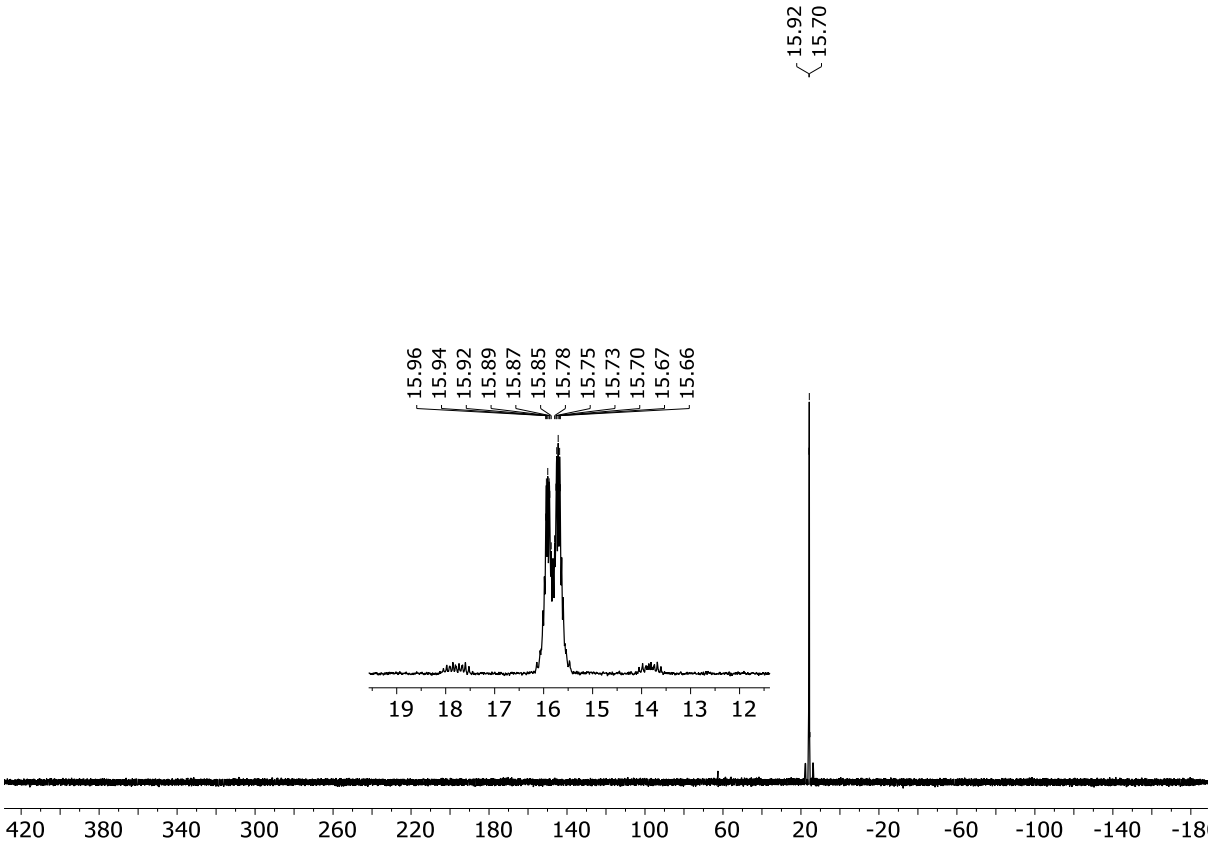


Figure S84: ^{31}P NMR spectrum of compound **8f** in $CDCl_3$.

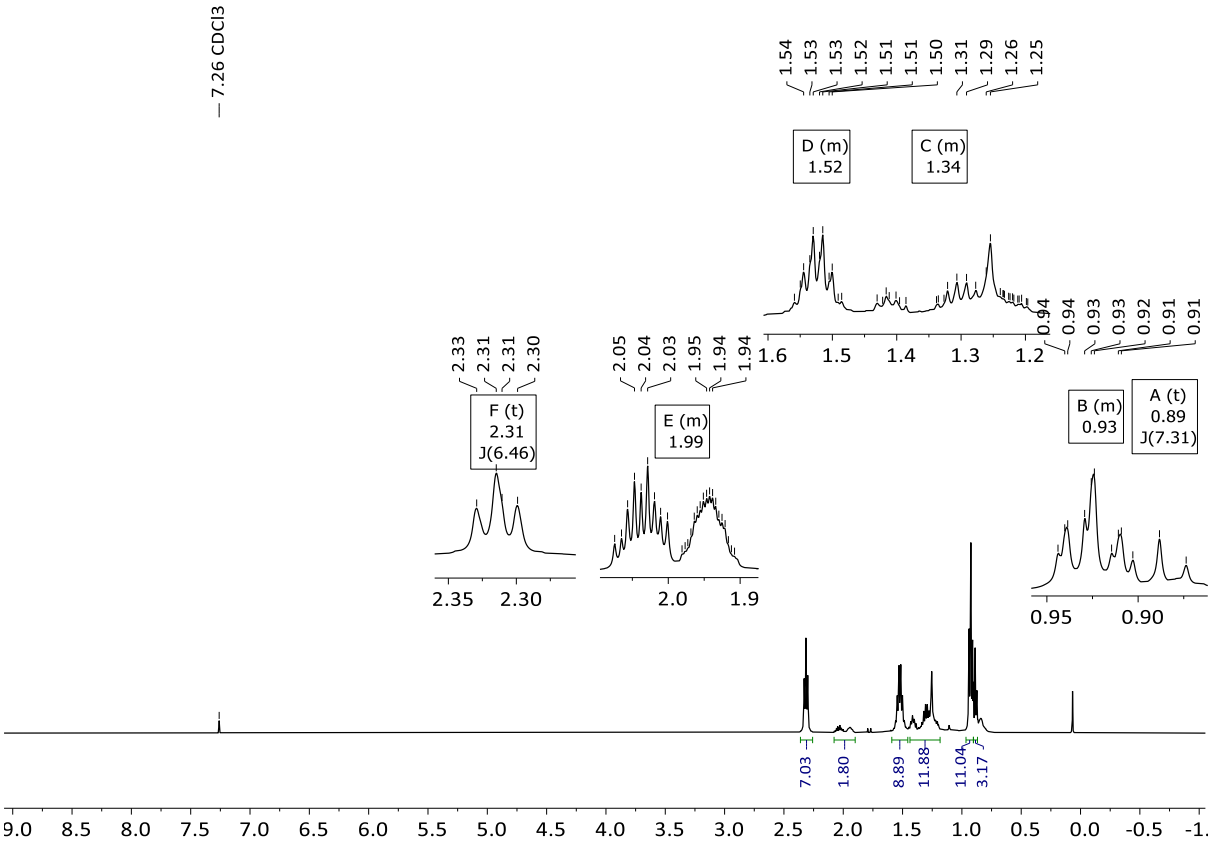


Figure S85: ^{1}H NMR spectrum of compound **11f** in $CDCl_3$.

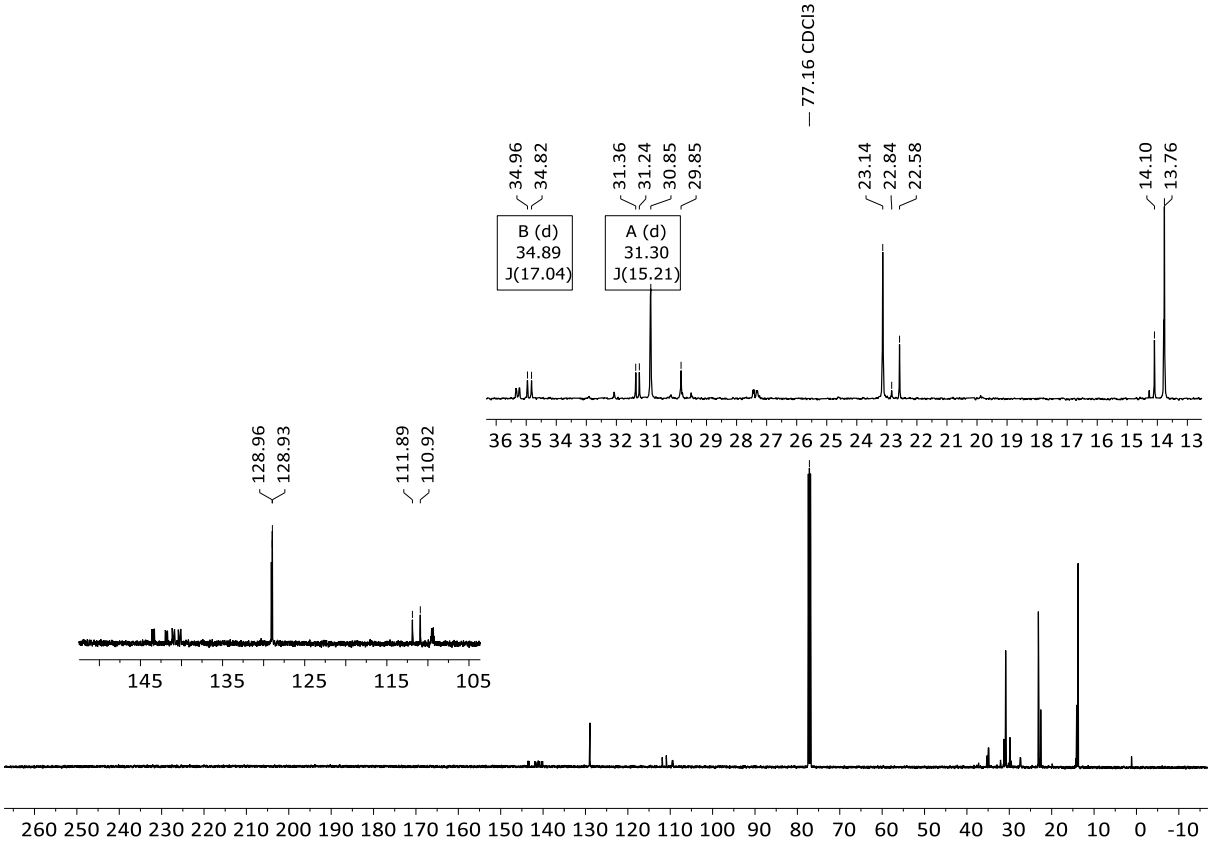


Figure S86: $^{13}C\{^{1}H\}$ NMR spectrum of compound **11f** in $CDCl_3$.

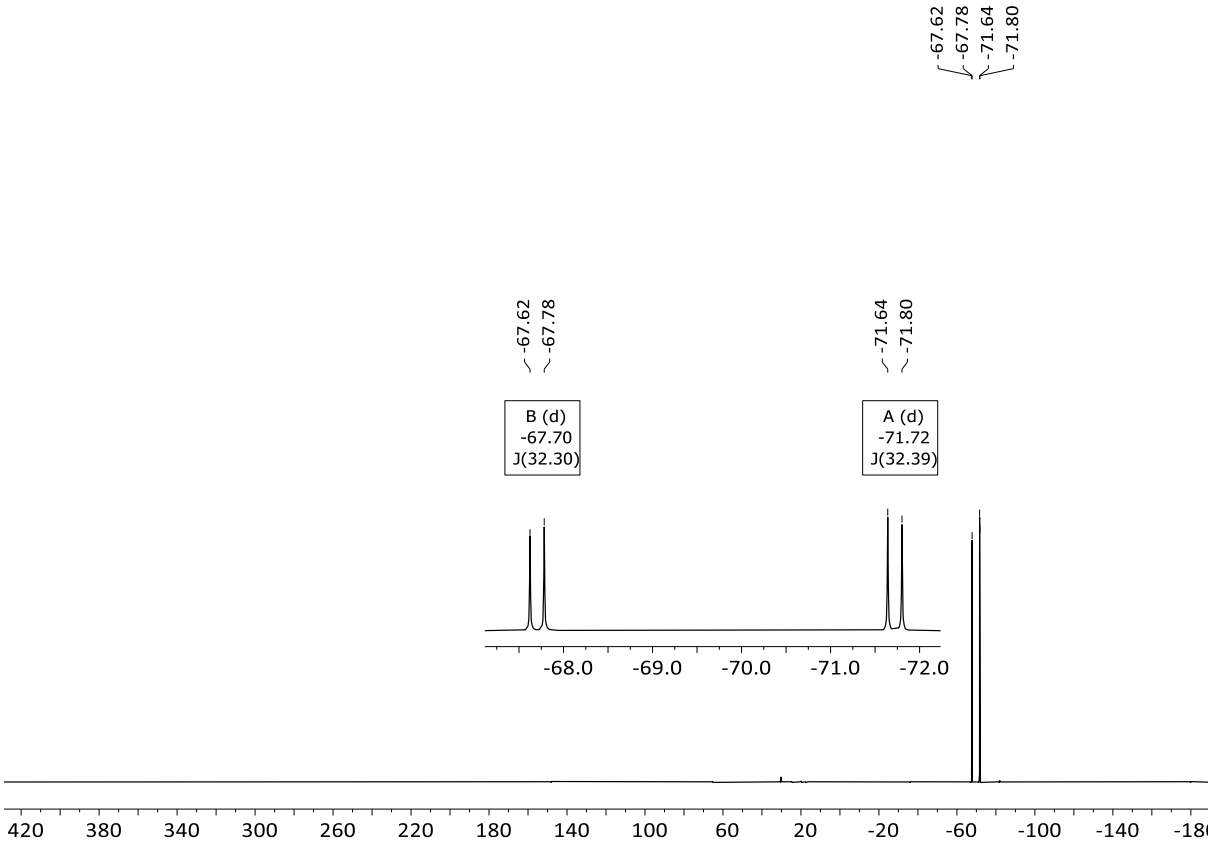


Figure S87: $^{31}P\{^{1}H\}$ NMR spectrum of compound **11f** in $CDCl_3$.

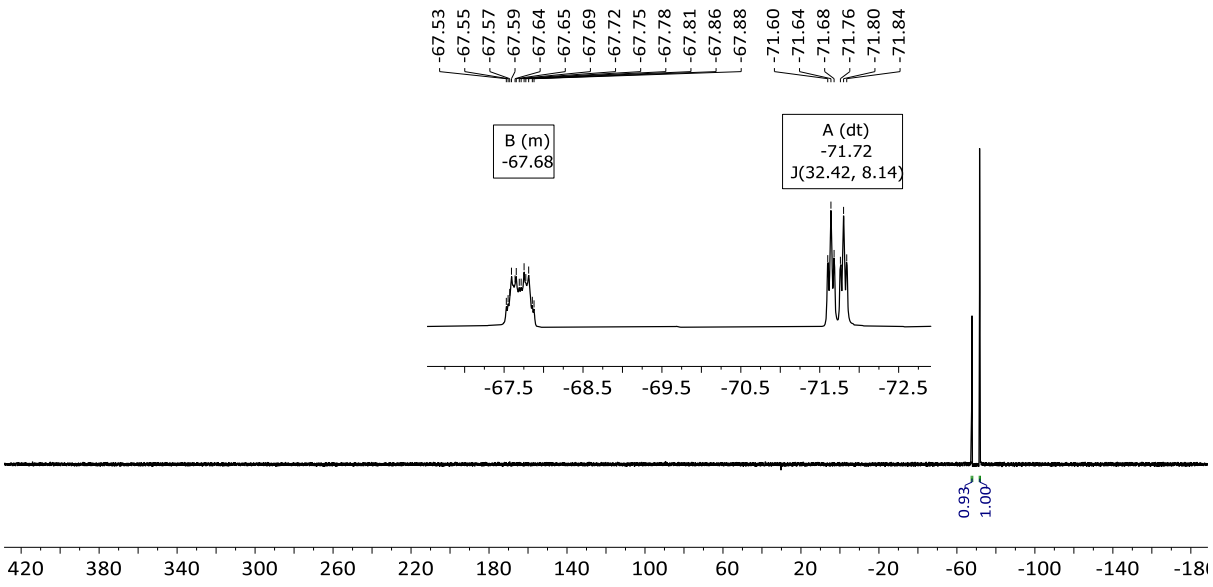


Figure S88: ^{31}P NMR spectrum of compound **11f** in $CDCl_3$.

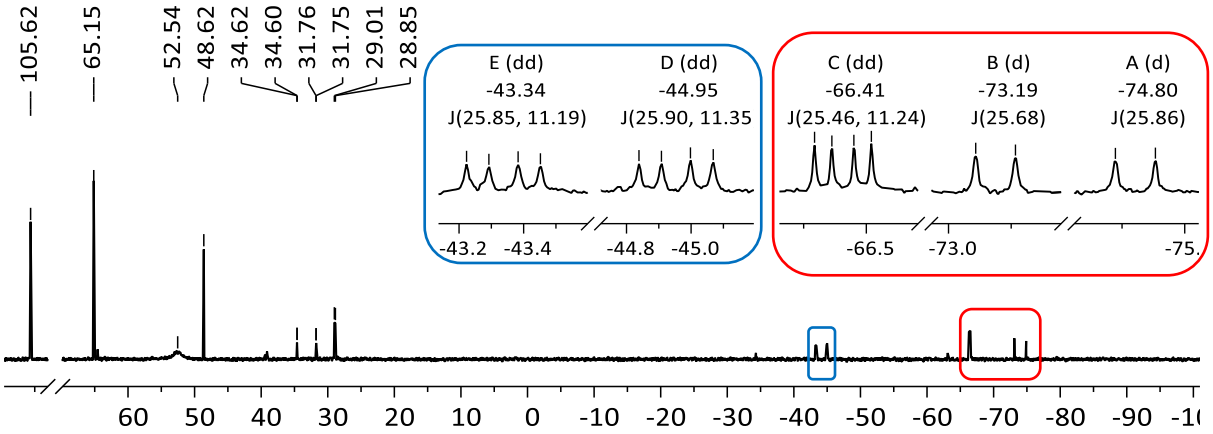


Figure S89. $^{31}P\{^{1}H\}$ NMR spectrum of the reaction of **9f** with $^{n}Bu_3P$.

Cyclic voltammetry studies

Cyclic voltammograms (CVs) were measured under rigorous exclusion of the atmosphere by working in an argon-filled glove box. Voltammograms were obtained using a Pine Instruments, Inc., WaveNano potentiostat/galvanostat connected to platinum (Pt) or gold (Au) screen-printed electrodes on rugged ceramic substrates. The patterned electrodes formed an inner working disk and outer auxiliary ring separated by an Ag/AgCl spot (for further information, consult the website at https://www.pineresearch.com/shop/products/electrodes/screen-printedelectrodes/ceramic/). Experiments were controlled and data were processed using AfterMath software (https://pineresearch.com/shop/kb/knowledge-category/downloads/). The solvent dichloromethane was first distilled over CaH_2, under Ar atmosphere and then collected into a Young-valve-Schlenk over P_2O_5 and freeze-thaw degassed with 5 cycles of freezing and thawing, using a high vacuum source ($8x10^{-3}$ mbar). Pure solvent was then vacuum transferred to a second Young-valve-Schlenk of similar volume and taken directly into the glove box. All solution and sample preparations were undertaken within the same glove box. The commercial $[^nBu_4N]PF_6$ was dried by heating for 24h at +80 °C in *vacuo* (8×10^{-3} mbar) and used as electrolyte. After background scans were obtained, using electrolyte solutions (0.4 M solution in DCM), the analytes were added to make a 1 mM (in the cases of **3c,d**, **4c**, **5d** and **11f**) or 2mM (in the cases of **3e,f**, **4d–f**, **5e,f** and **6–8**) solutions (with ±50% accuracy). The starting potentials were determined from an open circuit potential (OCP) experiment and electrochemical samples were recorded with scan rates of 50–800 mVs^{-1} at r.t. Cobaltocenium hexafluorophosphate was used as an internal reference to determine the potential, set to −1.350 V;[10] all reported potentials are corrected to the ferrocene/ferrocenium ($Fc^{+/0}$) redox couple set to 0 V.

For compounds with multi-stage redox properties, the nature of the cyclic voltammogram depends on $\Delta E_m = (E_m^2 - E_m^1)$, the reversibility and the number of transferred electrons in each step.[11] Calculated cyclic voltammograms for different values of ΔE_m in a system with two one-electron steps were reported by Polcyn and Shain.[12] These calculations show when $\Delta E_{1/2} \geq 180$ mV, two well-separated waves are observed, while for ΔE_m between 0 and 100 mV, the individual waves are merged into a broad one. For $\Delta E_m = 0$, a single peak with a current between those of single-step one and two electrons transfer was found with $E_p^a - E_p^c$

= 21 mV.[12] Considering this background, the redox behavior of compounds with two TTFs in their structure, depending on the degree of communication between two redox-active units can be divided into three main categories. i) If two TTF units have no interaction, i.e. oxidation of one TTF molecule does not affect the oxidation potential of the other TTF unit, the cyclic voltammogram shows only two redox waves, each representing a two-electron transfer process[13]; ii) For compounds with strong communication between TTF units, four sperate one-electron transfer processes are expected[14,15]; iii) In weakly interacting systems, the separation between oxidation potentials are smaller and hence broad waves, sometimes with no clear separation, in cyclic voltammograms are expected. In these cases, it is also possible that the third and fourth oxidations occur in a single potential together with an enlarged current and narrow peak.[16–18]

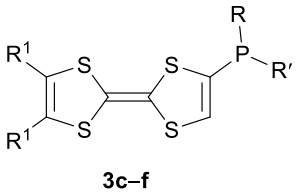
For consistency in the conceptual presentation of data between the mono-TTF (**3**,**4**) and bis-TTF (**5**-**11**) species, the processes for the bis species are designated E1/E1' for the first electron removals from the (weakly interacting) TTF species, reflecting the closely spaced HOMO and HOMO-1 of the neutral molecules. Similarly, the second electron removals from the TTFs are indicated by E2/E2' to again emphasize the weak interactions between TTF moieties. In this notation, we differ from most of the other bis-TTF papers where E1 – E4 have routinely been employed. The latter, in our opinion, would only be helpful when a full delocalization is achieved, as was the goal but not the achievement of this work.

CVs were recorded at various scan rates (50, 100, 200, 400 and 800 mVs^{-1}) and the plot of the anodic peak current versus the square root of the scan rates is depicted. The linear increase of the peak current with respect to the square root of the scan rate based on the Randles–Ševčik equation (Equation 1), indicating the redox processes are diffusion controlled as another proof of electrochemical reversibility.

$$I_p = 0.4463 \cdot A \cdot C \sqrt{\frac{n^3 F^3 D v}{RT}} \quad \text{(Equation 1)}$$

Where I_p is the peak current, A is the surface of the electrode, C is the concentration of the analyte, n is the number of transferred electrons in the redox process, *F* is Faraday coefficient, *D* is the diffusion coefficient, *v* is the scan rate, R is the ideal rate constant and T is temperature.

Cyclic voltammograms



3c–f

3c: R^1 = Me, R = Ph, R′ = NEt_2
3d: R^1 = Me, R = R′ = NEt_2
3e: R^1 = ^{n}Pr, R = Ph, R′ = NEt_2
3f: R^1 = ^{n}Pr, R = R′ = NEt_2

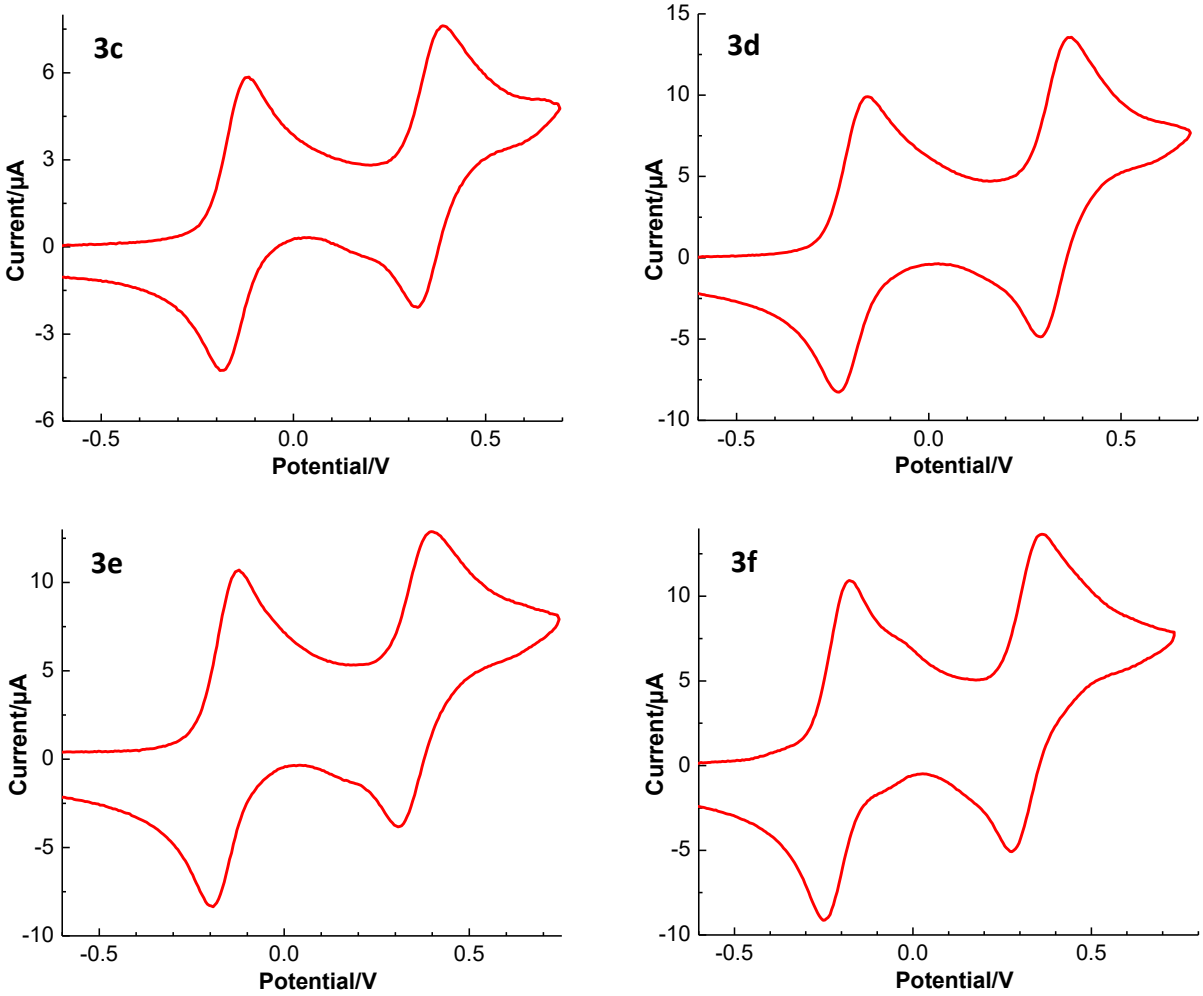


Figure S90. Cyclic voltammograms of **3c** (top left, 1 mM in DCM), **3d** (top right, 1 mM in DCM), **3e** (bottom left, 2 mM in DCM) and **3f** (bottom right, 2 mM in DCM) vs. $Fc^{+/0}$ (0.4 M ^{n}Bu$_4$PF$_6$ in DCM, 100 mVs^{-1}).

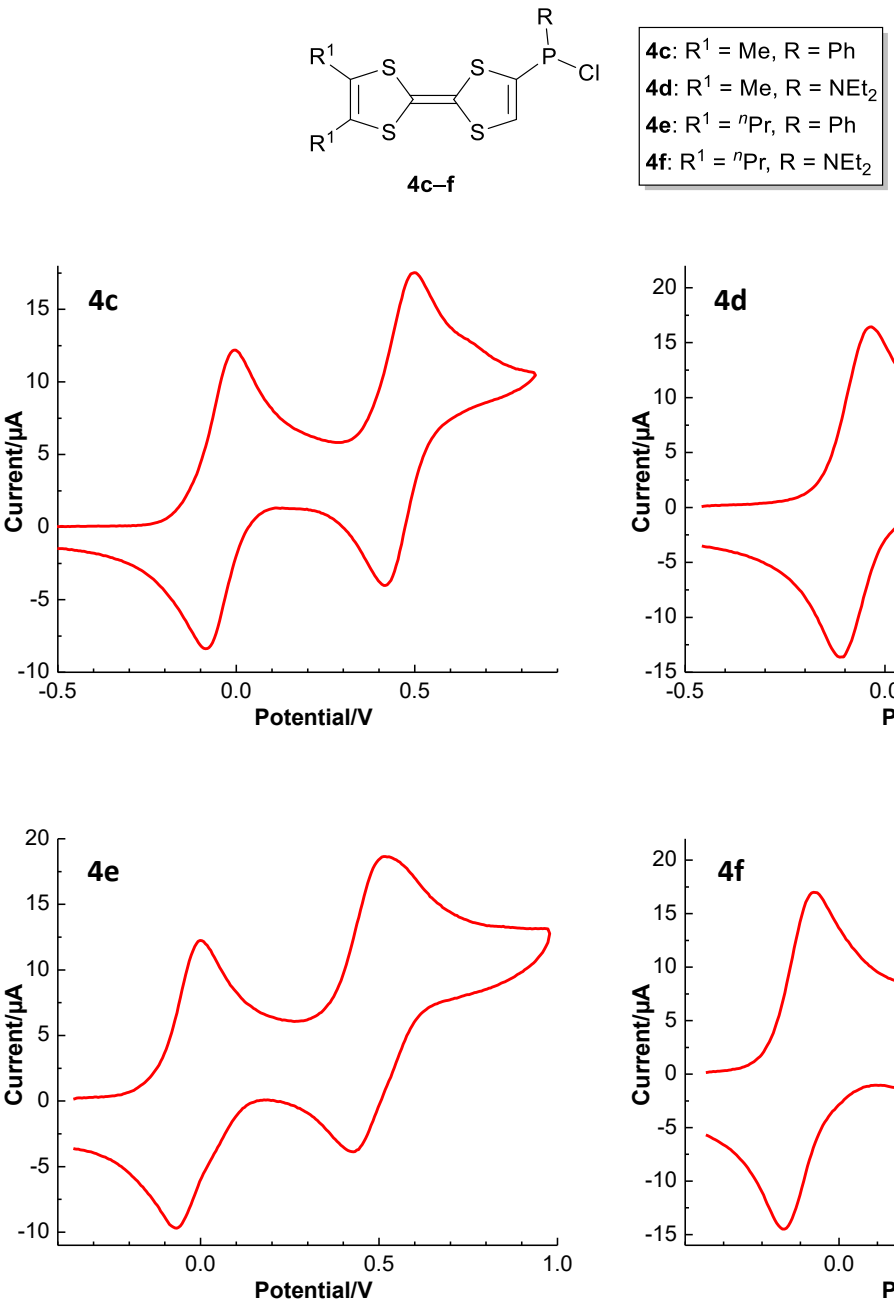


Figure S91. Cyclic voltammograms (oxidation processes) of **4c** (top left, 1 mM in DCM), **4d** (top right, 2 mM in DCM), **4e** (bottom left, 2 mM in DCM) and **4f** (bottom right, 2 mM in DCM) vs. $Fc^{+/0}$ (0.4 M $^{n}Bu_4PF_6$ in DCM, 200 mVs^{-1}).

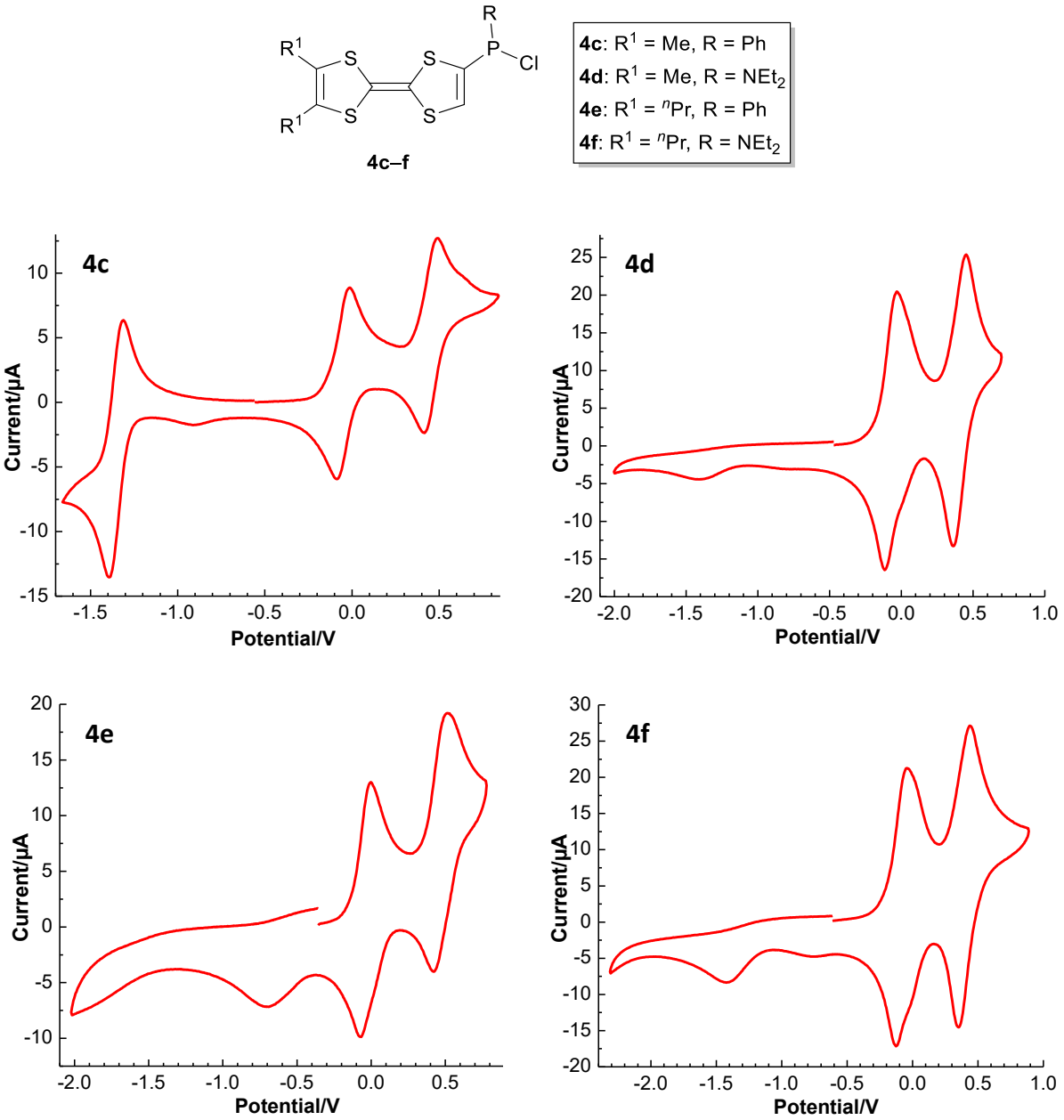
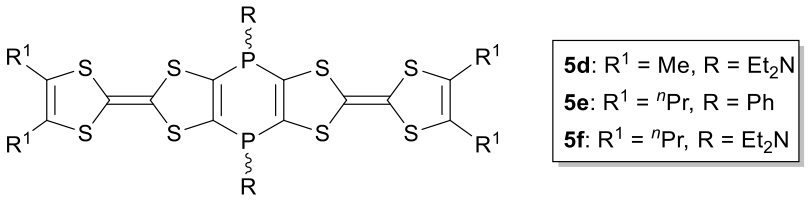


Figure S92. Cyclic voltammograms (wide range) of **4c** (top left), **4d** (top right), **4e** (bottom left) and **4f** (bottom right) vs. $Fc^{+/0}$ (0.4 M $^{n}Bu_4PF_6$ and 2mM solutions of analytes in DCM, 200 mVs^{-1}).



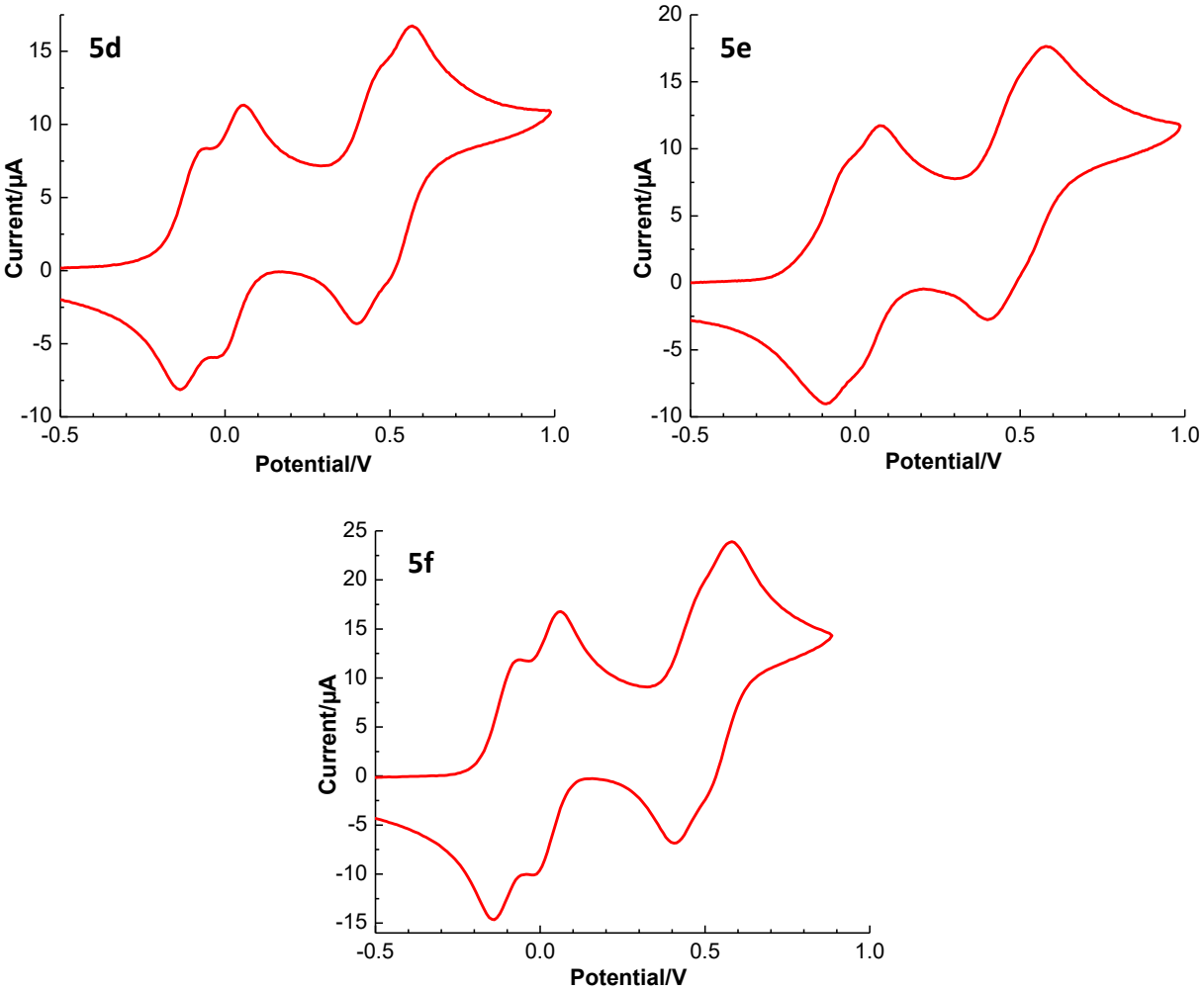


Figure S93. Cyclic voltammograms of **5d** (top left, 1 mM in DCM), **5e** (top right, 2 mM in DCM) and **5f** (bottom, 2 mM in DCM) vs. $Fc^{+/0}$ (0.4 M $^{n}Bu_4PF_6$ in DCM, 100 mVs^{-1}).

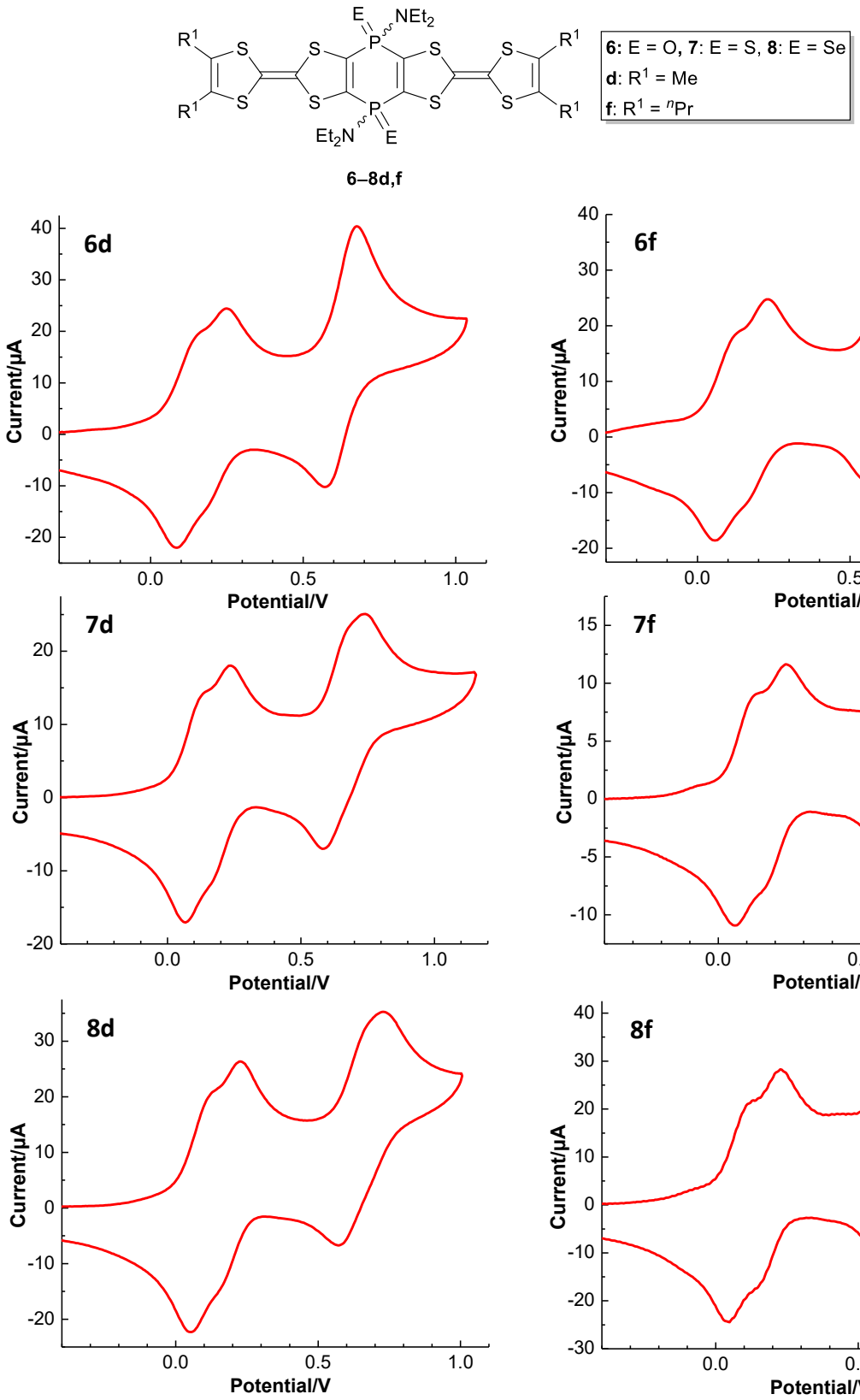


Figure S94. Cyclic voltammograms (oxidation) of **6d** (top left), **6f** (top right), **7d** (middle left), **7f** (middle right), **8d** (bottom left) and **8f** (bottom right) vs. $Fc^{+/0}$ (0.4 M $^{n}Bu_4PF_6$ and 2mM solutions of analytes in DCM, 200 mVs^{-1}).

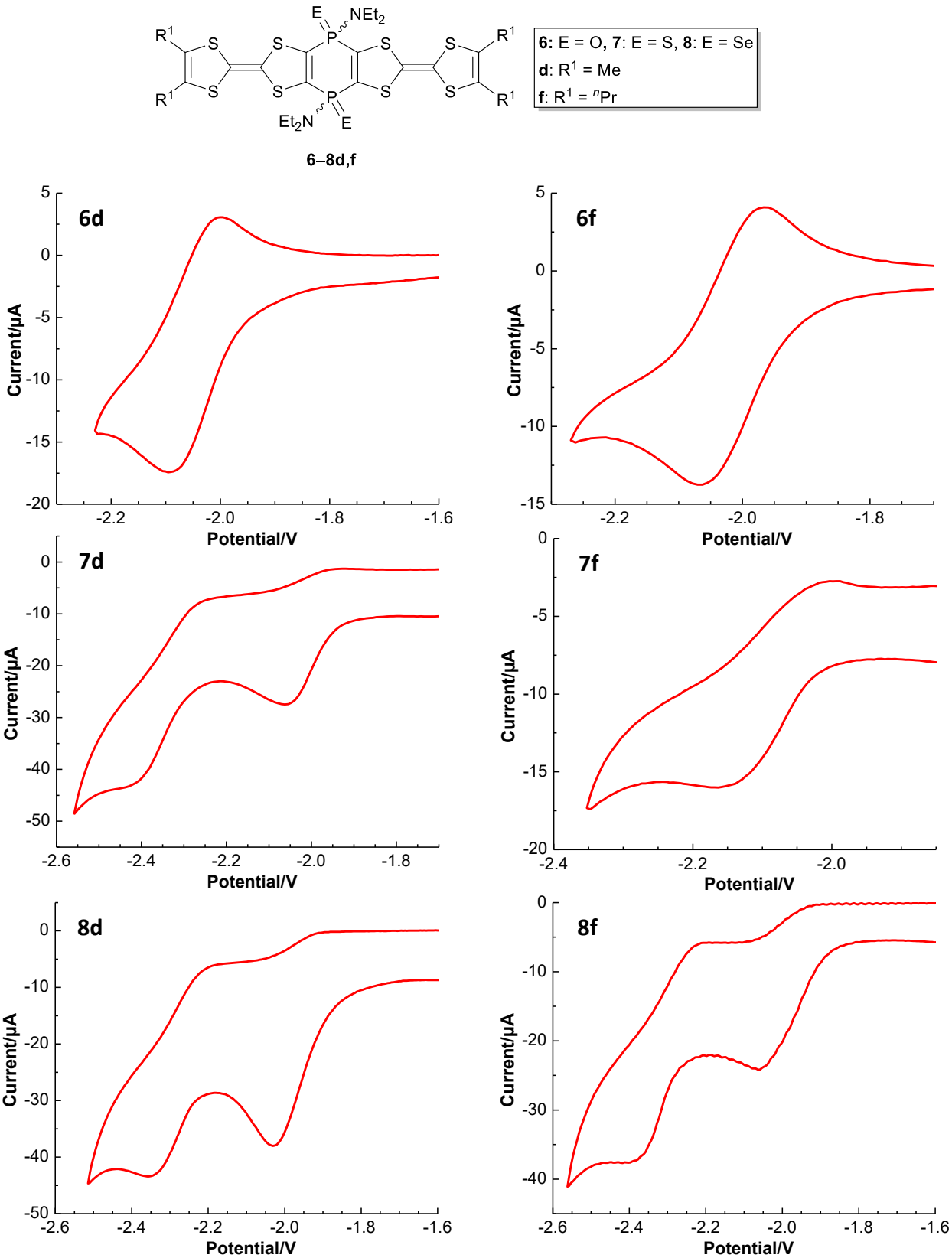


Figure S95. Cyclic voltammograms (reduction) of **6d** (top left), **6f** (top right), **7d** (middle left), **7f** (middle right), **8d** (bottom left) and **8f** (bottom right) vs. $Fc^{+/0}$ (0.4 M $^{n}Bu_4PF_6$ and 2mM solutions of analytes in DCM, 200 mVs^{-1}).

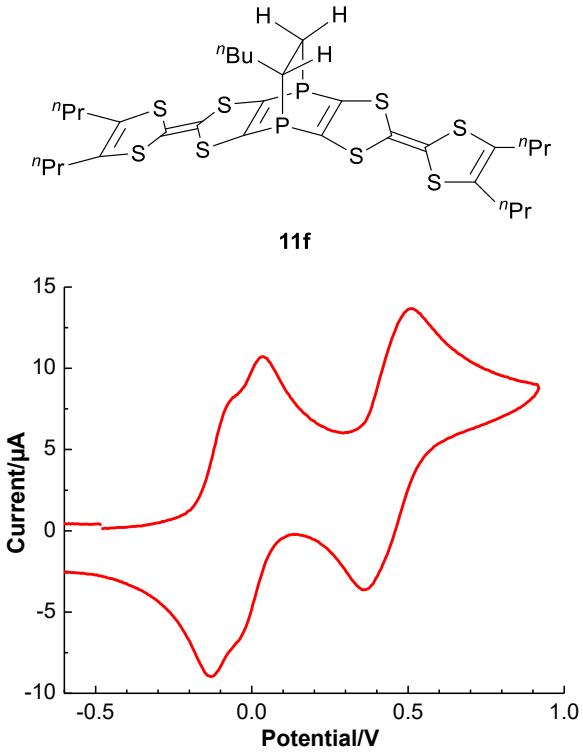


Figure S96. Cyclic voltammograms of **11f** (1 mM in DCM) vs. $Fc^{+/0}$ (0.4 M $^{n}Bu_4PF_6$ in DCM, 100 mVs^{-1}).

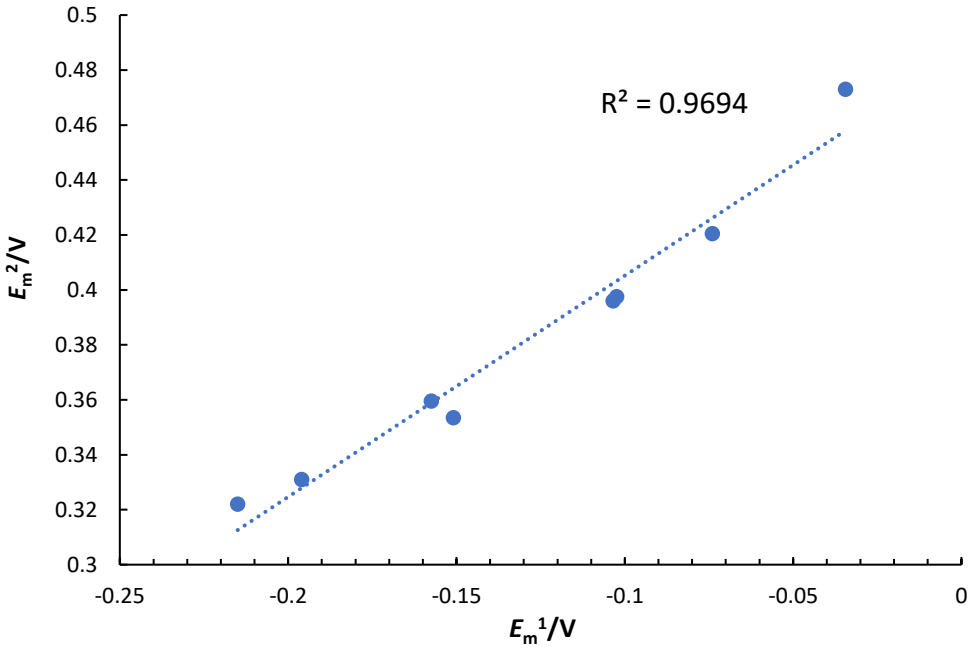


Figure S97. Correlation of all the substituent inductive effects in **3d**–**4f** on the first and second anodic mid-point potentials.

Table S1. Voltammetric data (potentials) for **3c–f** and **4c–f** (vs. $Fc^{+/0}$,0.4 M $^{n}Bu_4PF_6$ in DCM, 200 mVs^{-1}).

Compound	E_P^{a1}/V	E_P^{c1}/V	$E_{1/2}^{1}$/V	ΔE_P^{1}/mV	E_P^{a2}/V	E_P^{c2}/V	$E_{1/2}^{2}$/V	ΔE_P^{2}/mV	$\Delta E_{1/2}^{1,2}$/mV
3c	−0.115	−0.187	−0.151	72	0.389	0.318	0.354	71	505
3d	−0.158	−0.234	−0.196	76	0.371	0.291	0.331	80	527
3e	−0.120	−0.195	−0.158	75	0.409	0.310	0.360	99	517
3f	−0.180	−0.250	−0.215	70	0.369	0.275	0.322	94	537
4c	−0.062	−0.143	−0.103	81	0.438	0.357	0.398	81	500
4d	−0.034	−0.114	−0.074	80	0.461	0.380	0.421	81	495
4e	−0.002	−0.067	−0.035	65	0.518	0.428	0.473	90	508
4f	−0.066	−0.141	−0.104	75	0.444	0.348	0.396	96	500

E_p^a: Oxidation peak potentials; E_p^c: Reduction peak potentials; E_m: The mid-point of the oxidation and reduction peak potentials; I_p^a: Oxidation current; I_p^c: Reduction current; $\Delta E_P^{(a-c)}$: Difference between oxidation and reduction potentials; ΔE_m: Difference between mid-point potentials.

Table S2. Voltammetric data (currents) for **3c–f** and **4c–f** (0.4 M $^{n}Bu_4PF_6$ in DCM, 200 mVs^{-1}).

Compound	I_P^{a1}/µA	I_P^{c1}/µA	I_P^{a1}/µA corr.*	I_P^{c1}/µA corr.*	I_P^{c1}/I_P^{a1}	I_P^{c1}/I_P^{a1} corr.	I_P^{a2}/µA	I_P^{c2}/µA	I_P^{a2}/µA corr.*	I_P^{c2}/µA corr.*	I_P^{c2}/I_P^{a2}	I_P^{c2}/I_P^{a2} corr.
3c	7.346	6.034	4.7	4.7	0.82	1.00	9.718	3.218	4.6	4.55	0.33	0.99
3d	11.37	11.9	7.6	7.6	1.05	1.00	16.75	7.584	8	8	0.45	1.00
3e	13.15	11.23	8	8	0.85	1.00	16.2	5.244	7.2	7.5	0.32	1.04
3f	12.76	12.69	9.5	10.5	0.99	1.11	16.8	7.541	8	8	0.45	1.00
4c	9.46	8.882	10	9.8	0.94	0.98	14.42	4.778	10.2	10	0.33	0.98
4d	16.44	13.63	13	13	0.83	1.00	21.03	7.648	13	13	0.36	1.00
4e	12.24	9.699	12	12	0.79	1.00	18.65	3.867	12.5	10	0.21	0.80
4f	17.01	14.49	15	15	0.85	1.00	20.92	7.939	15	13	0.38	0.87

* To obtain the corrected values for currents, the anodic currents of the second processes were corrected back to the first anodic values, which enables to find the true zero and cathodic currents of the second peaks.

E_p^a: Oxidation peak potentials; E_p^c: Reduction peak potentials; E_m: The mid-point of the oxidation and reduction peak potentials; I_p^a: Oxidation current; I_p^c: Reduction current; $\Delta E_P^{(a-c)}$: Difference between oxidation and reduction potentials; ΔE_m: Difference between mid-point potentials.

Table S3. Voltammetric data (potentials) for **5–8** and **11f** (vs. $Fc^{+/0}$,0.4 M $^{n}Bu_4PF_6$ in DCM, 100 mVs^{-1}).

Compound	E_P^{a1}/V	E_P^{c1}/V	ΔE_P^{1}/ mV	$E_P^{a1'}$/V	$E_P^{c1'}$/V	$\Delta E_P^{1'}$/ mV	$\Delta E_{1/2}^{1,1'}$/ mV	E_P^{a2}/V	E_P^{c2}/V	ΔE_P^{2}/ mV	$E_P^{a2'}$/V	$E_P^{c2'}$/V	$\Delta E_P^{2'}$/ mV	$\Delta E_{1/2}^{2,2'}$/ mV
5d	–0.057	–0.137	80	0.053	–0.022	75	112	0.458	0.398	60	0.568	0.503	65	107
5e	–0.028	–0.088	60	0.077	0.016	61	104	0.466	0.401	65	0.581	0.516	65	115
5f	–0.066	–0.139	73	0.062	–0.019	81	124	0.477	0.405	72	0.581	0.509	72	104
6d	0.154	0.081	73	0.249	0.181	68	97	0.674	0.571	103	—	—	—	—
6f	0.130	0.057	73	0.226	0.153	73	96	0.650	0.545	105	—	—	—	—
7d	0.141	0.068	73	0.237	0.164	73	96	0.742	0.579	163	—	—	—	—
7f	0.141	0.060	81	0.236	0.155	81	95	0.746	0.575	171	—	—	—	—
8d	0.133	0.051	82	0.228	0.151	77	97	0.728	0.571	157	—	—	—	—
8f	0.126	0.048	78	0.232	0.153	79	105	0.732	0.587	145	—	—	—	—
11f	–0.061	–0.132	71	0.034	–0.036	70	95	0.514	0.353	161	—	—	—	—

E_p^a: Oxidation peak potentials; E_p^c: Reduction peak potentials; E_m: The mid-point of the oxidation and reduction peak potentials; I_P^a: Oxidation current; I_P^c: Reduction current; $\Delta E_P^{(a-c)}$: Difference between oxidation and reduction potentials; ΔE_m: Difference between mid-point potentials.

Table S4. Voltammetric data (currents) for **5–8** and **11f** (0.4 M $^{n}Bu_4PF_6$ in DCM, 100 mVs^{-1}).

Compound	I_P^{a1}/µA	I_P^{c1}/µA	I_P^{c1}/I_P^{a1}	$I_P^{a1'}$/µA (corr.)*	$I_P^{c1'}$/µA (corr.)*	$I_P^{c1'}/I_P^{a1'}$ corr.	I_P^{a2}/µA (corr.)*	I_P^{c2}/µA (corr.)*	I_P^{c2}/I_P^{a2} corr.	$I_P^{a2'}$/µA (corr.)*	$I_P^{c2'}$/µA (corr.)*	$I_P^{c2'}/I_P^{a2'}$ corr.
5d	8.376	8.157	0.97	11.320 (8.376)	5.928 (8.872)	0.97	13.440 (8.376)	3.632 (8.696)	0.97	16.750 (8.376)	0.477 (8.851)	0.97
5e	8.869	9.028	1.02	11.730 (8.869)	6.409 (9.270)	1.02	13.870 (8.869)	2.753 (7.754)	1.02	17.64 (8.869)	1.167 (9.938)	1.02
5f	11.860	14.650	1.24	16.790 (11.860)	10.090 (15.020)	1.24	18.510 (11.860)	6.831 (13.481)	1.24	23.900 (11.860)	1.944 (13.984)	1.24
6d	19.400	21.990	1.13	24.450 (19.400)	14.570 (19.620)	1.13	40.400 (19.400)	10.230 (31.230)	1.13	—	—	—
6f	18.720	18.620	0.99	24.760 (18.720)	12.480 (18.520)	0.99	35.050 (18.720)	7.623 (23.953)	0.99	—	—	—
7d	14.420	17.060	1.18	18.040 (14.420)	11.790 (15.410)	1.18	25.080 (14.420)	6.999 (17.659)	1.18	—	—	—
7f	9.123	10.920	1.20	11.640 (9.123)	7.936 (10.453)	1.20	16.500 (9.123)	3.847 (11.224)	1.20	—	—	—
8d	20.960	22.320	1.06	26.350 (20.960)	15.040 (20.430)	1.06	35.280 (20.960)	6.723 (21.043)	1.06	—	—	—
8f	19.980	23.070	1.15	26.920 (19.980)	16.320 (23.260)	1.15	39.010 (19.980)	10.530 (29.560)	1.15	—	—	—
11f	8.199	8.979	1.10	10.720 (8.199)	6.595 (9.116)	1.10	13.680 (8.199)	3.631 (9.112)	1.10	—	—	—

* To obtain the corrected values for currents, the anodic currents of the second, third and fourth processes were corrected back to the first anodic values, which enables to find the true zero and cathodic currents of the remaining peaks.

E_p^a: Oxidation peak potentials; E_p^c: Reduction peak potentials; I_P^a: Oxidation current; I_P^c: Reduction current; $\Delta E_P^{(a-c)}$: Difference between oxidation and reduction peak potentials.

Table S5. Voltammetric data (potentials and currents) for reduction processes of compounds **4d–f** and **6–8** (vs. $Fc^{+/0}$,0.4 M $^{n}Bu_4PF_6$ in DCM, 200 mVs^{-1}).

Compound	E_P^{c3}/V	I_P^{c3}/µA	E_P^{a3}/V	I_P^{a3}/µA	E_P^{c4}/V	I_P^{c4}/µA	E_P^{a4}/V	I_P^{a4}/µA
4d	−0.78	2.00	—	—	−1.402	4.44	—	—
4e	−0.71	7.18	—	—	—	—	—	—
4f	−0.75	4.77	—	—	−1.423	8.36	—	—
6d	−2.10	17.43	−2.001	3.07	−2.36	15.30	—	—
6f	−2.06	13.75	−1.967	6.5	—	—	—	—
7d	−2.06	27.46	−1.919	1.28	−2.405	42.15	—	—
7f	−2.14	27.12	−2.026	10.70	—	—	—	—
8d	−2.03	38.00	−1.915	0.44	−2.360	43.42	—	—
8f	−2.06	24.20	−1.938	0.69	−2.417	37.67	—	—

E_p^a: Oxidation peak potentials; E_p^c: Reduction peak potentials; I_P^a: Oxidation current; I_P^c: Reduction current; $\Delta E_P^{(a-c)}$: Difference between oxidation and reduction peak potentials; ΔE_m: Difference between mid-point potentials.

Scan rate dependency studies

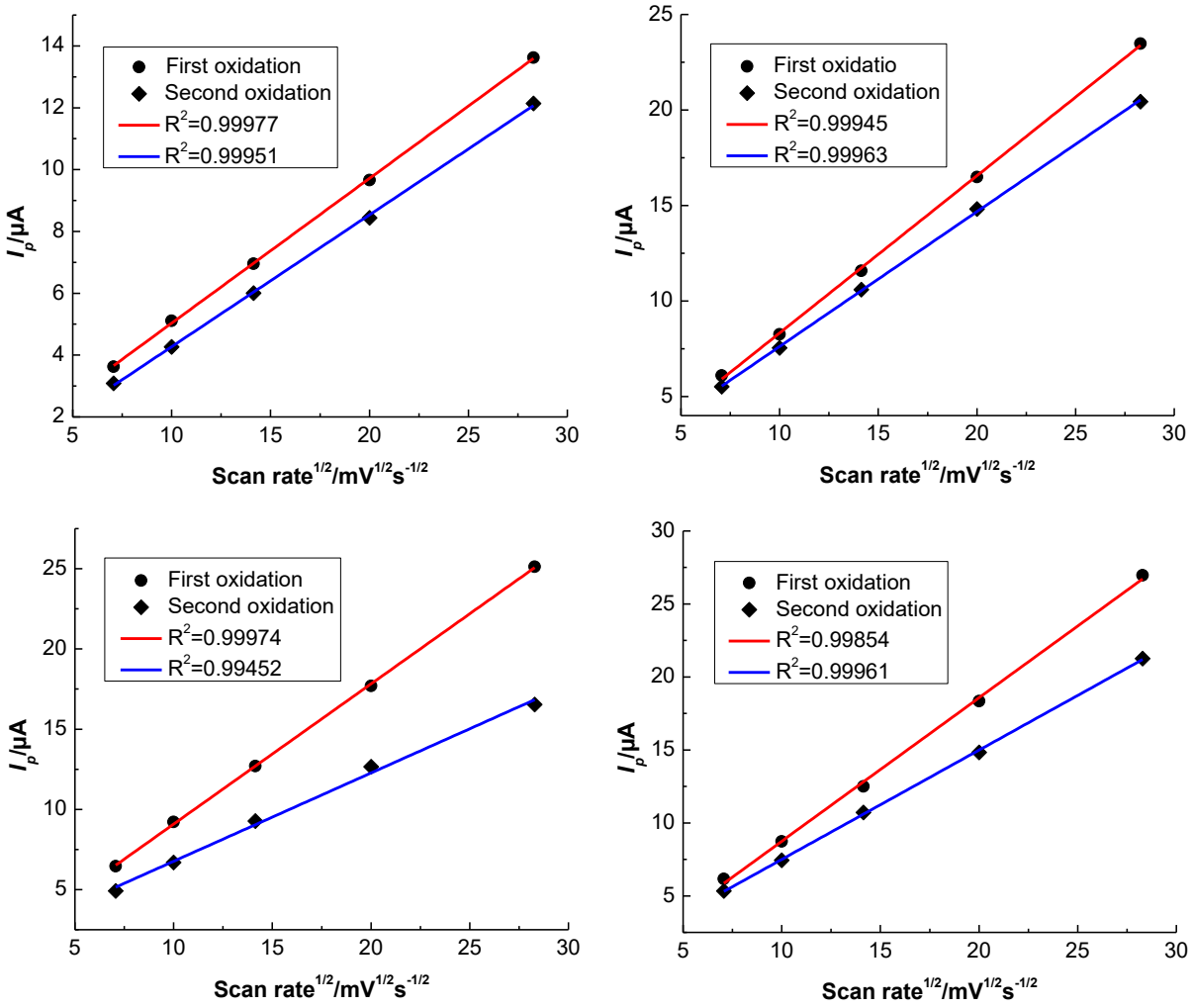


Figure S98. Dependency of the anodic peak currents on the scan rate for **3c** (top left), **3d** (top right), **3e** (bottom left) and **3f** (bottom right).

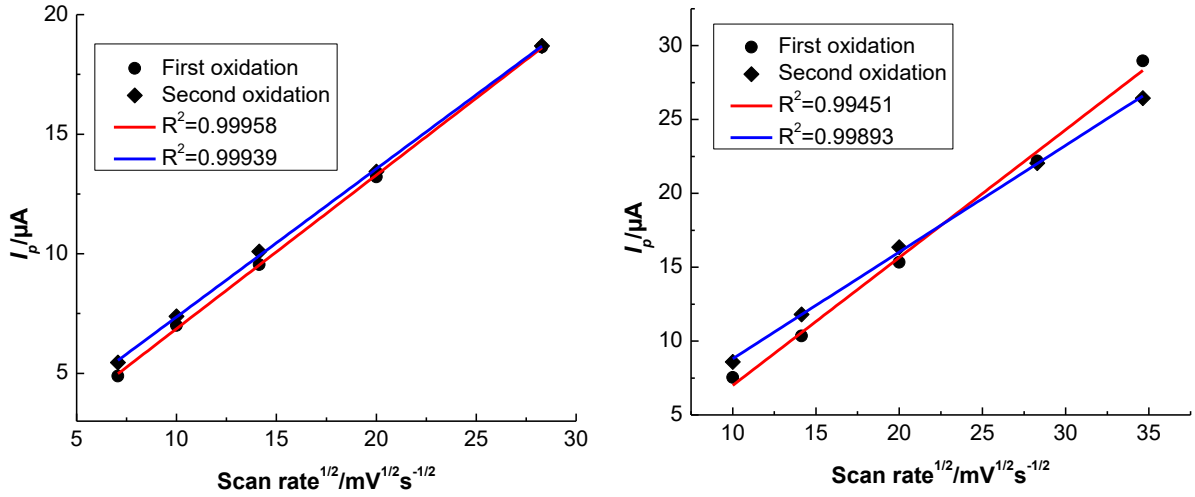


Figure S99. Dependency of the anodic peak currents on the scan rate for **4c** (left) and **4e** (right).

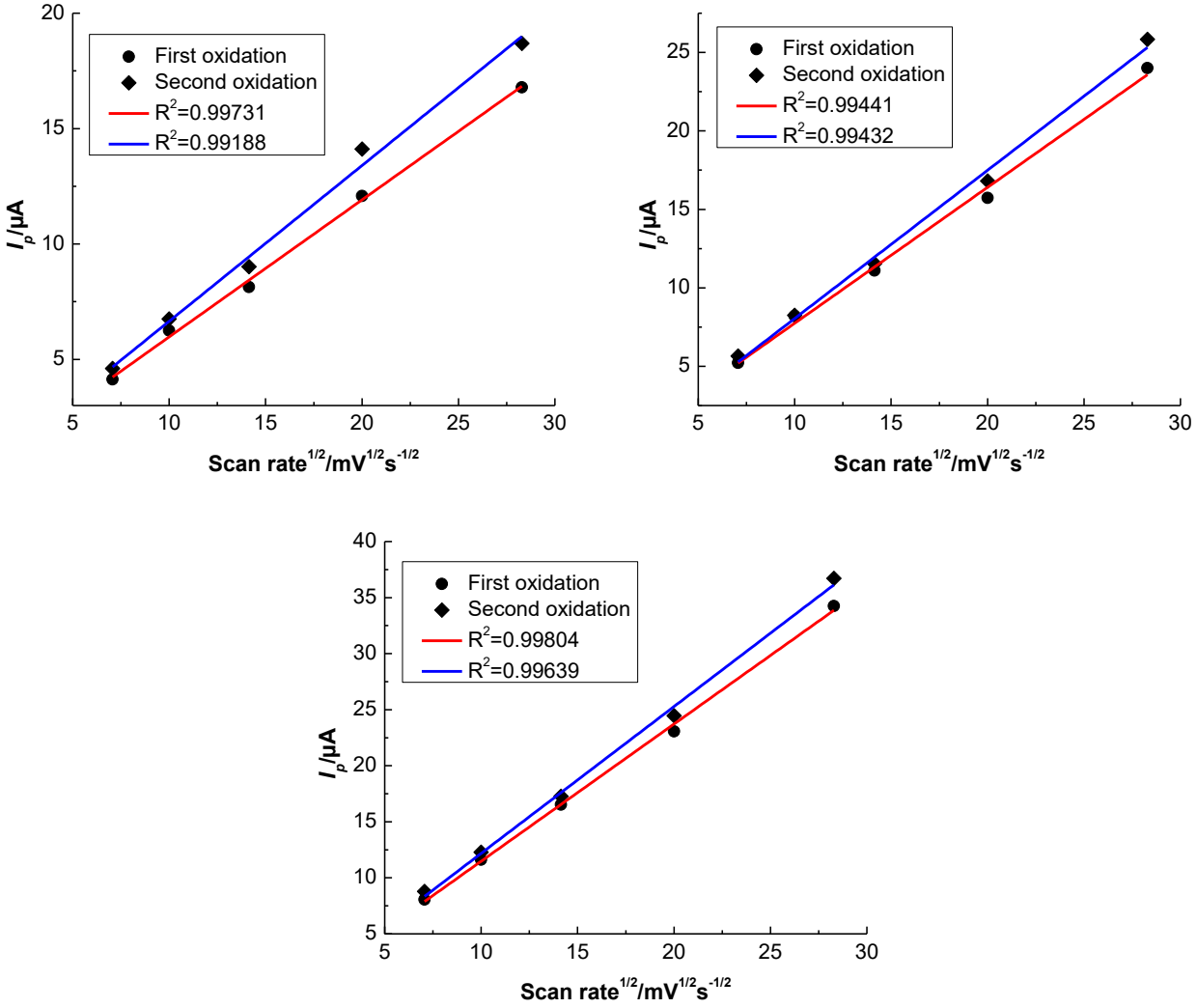


Figure S100. Dependency of the anodic peak currents (first and second redox processes) on the scan rate for **5d** (top left), **5e** (top right) and **5f** (bottom).

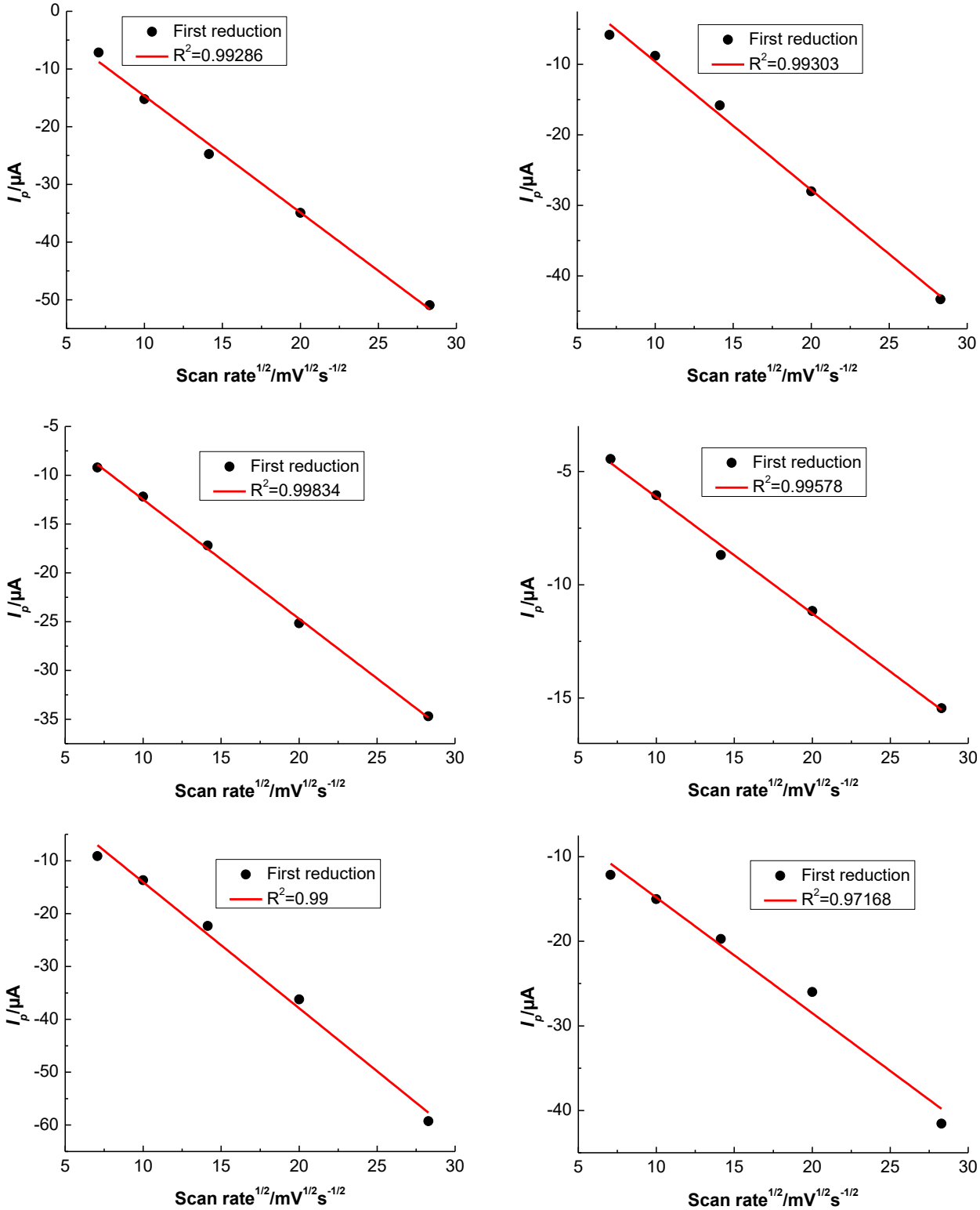


Figure S101. Dependency of the cathodic peak current (first reduction process) on the scan rate for **6d** (top left), **6f** (top right), **7d** (middle left), **7f** (middle right), **8d** (bottom left) and **8f** (bottom right).

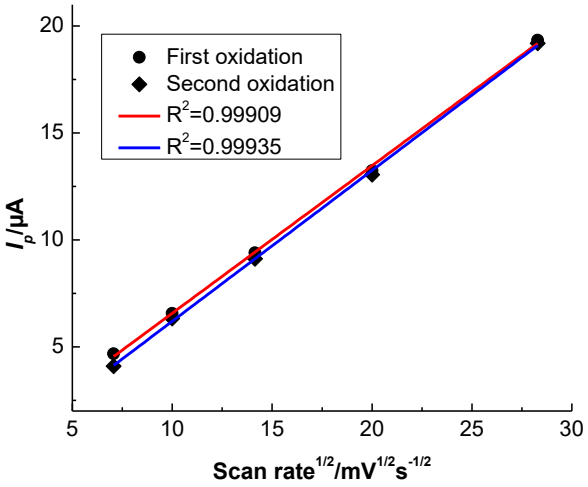
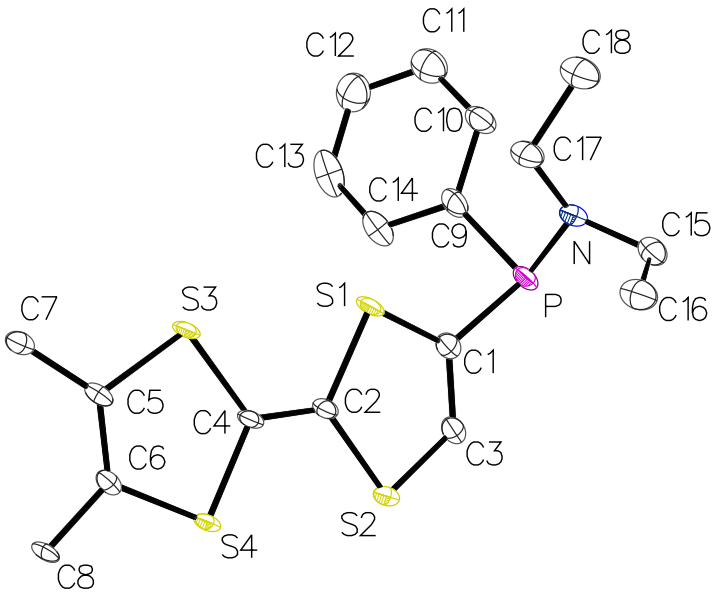


Figure S102. dependency of the anodic peak currents (first and second redox processes) on the scan rate for **11f**.

Crystallographic data

CCDC numbers 2087015 (*cis*-**5d**), 2087016 (**3c**), 2252852 (*trans*-**6d**), and 2252853 (*cis*-**8f**) contain the supplementary crystallographic data for this paper, which can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

Crystal data and structure refinement for compound 3c



Identification code	GSTR711, SHK-297 // GXraycu_6477f
Crystal Habitus	clear yellow plate
Device Type	Bruker D8 Venture
Empirical formula	$C_{18}H_{22}NPS_4$
Moiety formula	C18 H22 N P S4
Formula weight	411.57
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	6.8055(3)
b/Å	7.6486(4)
c/Å	37.8273(16)
α/°	90
β/°	92.938(2)

γ/°	90
Volume/Å^3	1966.42(16)
Z	4
ρ_{calc}g/cm^3	1.390
μ/mm^{-1}	5.200
F(000)	864.0
Crystal size/mm^3	0.12 × 0.09 × 0.05
Absorption correction	empirical
Tmin; Tmax	0.4144; 0.7536
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	4.678 to 135.438°
Completeness to theta	0.984
Index ranges	-7 ≤ h ≤ 8, -9 ≤ k ≤ 9, -40 ≤ l ≤ 45
Reflections collected	15066
Independent reflections	3506 [R_{int} = 0.0683, R_{sigma} = 0.0534]
Data/restraints/parameters	3506/6/221
Goodness-of-fit on F^2	1.066
Final R indexes [I>=2σ (I)]	R_1 = 0.0620, wR_2 = 0.1725
Final R indexes [all data]	R_1 = 0.0720, wR_2 = 0.1852
Largest diff. peak/hole / e Å^{-3}	0.63/-0.78

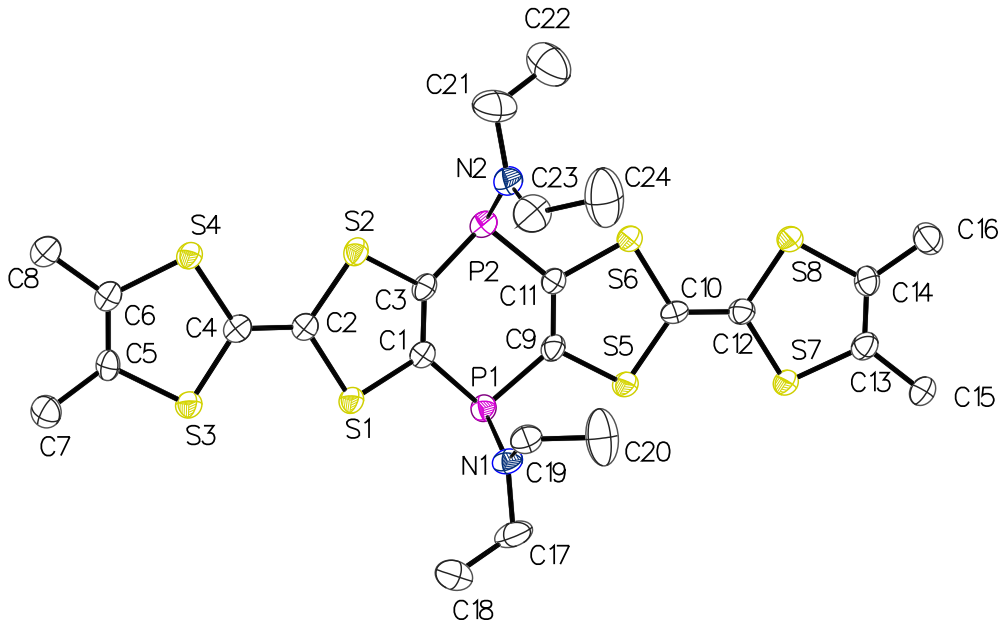
Bond Lengths

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	C1	1.765(4)	C1	C3	1.329(6)
S1	C2	1.762(4)	C2	C4	1.340(6)
S2	C2	1.770(4)	C5	C6	1.336(6)
S2	C3	1.752(4)	C5	C7	1.501(6)
S3	C4	1.754(4)	C6	C8	1.493(5)
S3	C5	1.763(4)	C9	C10	1.410(6)
S4	C4	1.756(4)	C9	C14	1.399(6)
S4	C6	1.763(4)	C10	C11	1.388(7)
P	N	1.695(4)	C11	C12	1.386(7)
P	C1	1.833(4)	C12	C13	1.386(7)
P	C9	1.832(5)	C13	C14	1.374(7)
N	C15	1.479(6)	C15	C16	1.514(7)
N	C17	1.458(6)	C17	C18	1.523(6)

Bond Angles

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C2	S1	C1	95.58(19)	C2	C4	S3	122.5(3)
C3	S2	C2	94.06(19)	C2	C4	S4	123.2(3)
C4	S3	C5	95.56(19)	C6	C5	S3	117.3(3)
C4	S4	C6	95.64(19)	C6	C5	C7	127.5(4)
N	P	C1	107.0(2)	C7	C5	S3	115.2(3)
N	P	C9	101.15(19)	C5	C6	S4	117.1(3)
C9	P	C1	100.58(18)	C5	C6	C8	127.7(4)
C15	N	P	115.5(3)	C8	C6	S4	115.2(3)
C17	N	P	123.9(3)	C10	C9	P	120.7(3)
C17	N	C15	113.9(4)	C14	C9	P	121.1(3)
S1	C1	P	123.6(2)	C14	C9	C10	117.9(4)
C3	C1	S1	115.7(3)	C11	C10	C9	120.6(4)
C3	C1	P	120.3(3)	C12	C11	C10	120.6(5)
S1	C2	S2	114.0(2)	C13	C12	C11	118.8(5)
C4	C2	S1	123.1(3)	C14	C13	C12	121.5(4)
C4	C2	S2	122.9(3)	C13	C14	C9	120.5(4)
C1	C3	S2	119.7(3)	N	C15	C16	113.9(4)

Crystal data and structure refinement for compound *cis*-5d



Identification code	GSTR689, SHK-150 // GXray6209f
Crystal Habitus	clear orange plate

Device Type	Bruker X8-KappaApexII
Empirical formula	$C_{49}H_{66}Cl_2N_4P_4S_{16}$
Moiety formula	C H2 Cl2, 2(C24 H32 N2 P2 S8)
Formula weight	1418.79
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	15.909(2)
b/Å	11.9462(15)
c/Å	17.630(2)
α/°	90
β/°	107.950(3)
γ/°	90
Volume/Å^3	3187.4(7)
Z	2
ρ_{calc}g/cm^3	1.478
μ/mm^{-1}	0.765
F(000)	1476.0
Crystal size/mm^3	0.18 × 0.1 × 0.05
Absorption correction	empirical
Tmin; Tmax	0.5748; 0.7461
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.554 to 55.996°
Completeness to theta	0.997
Index ranges	-19 ≤ h ≤ 21, -15 ≤ k ≤ 15, -23 ≤ l ≤ 14
Reflections collected	33038
Independent reflections	7663 [R_{int} = 0.1087, R_{sigma} = 0.1051]
Data/restraints/parameters	7663/6/360
Goodness-of-fit on F^2	1.060
Final R indexes [I>=2σ (I)]	R_1 = 0.0826, wR_2 = 0.1757
Final R indexes [all data]	R_1 = 0.1361, wR_2 = 0.2018
Largest diff. peak/hole / e Å^{-3}	1.00/-0.50

Bond Lengths

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl1	C25	1.726(17)	P2	N2	1.657(5)

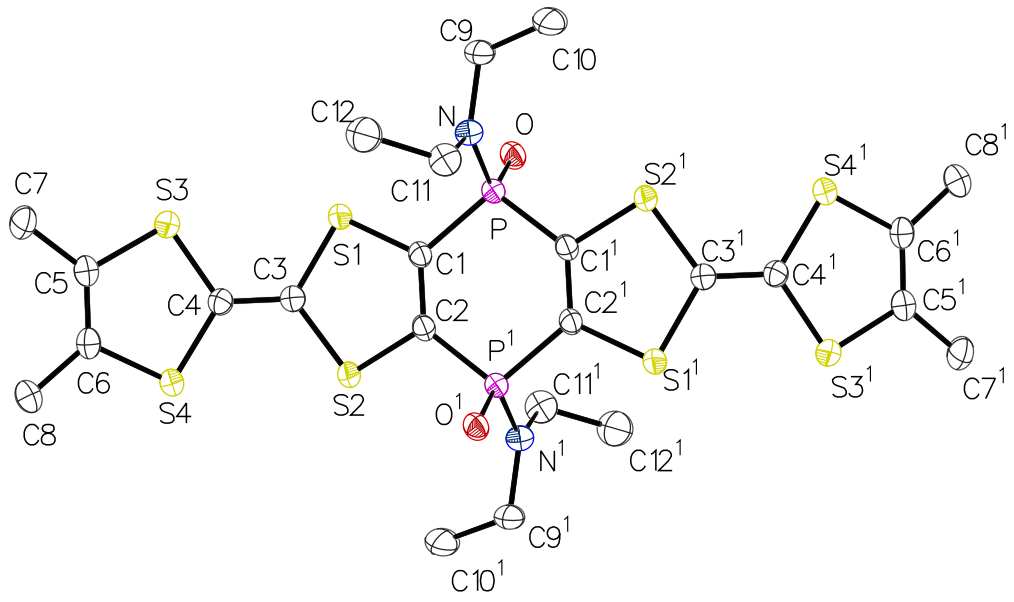
Cl2	C25	1.722(18)	P2	C3	1.819(5)
S1	C1	1.762(5)	P2	C11	1.816(5)
S1	C2	1.763(5)	N1	C17	1.466(7)
S2	C2	1.760(5)	N1	C19	1.451(7)
S2	C3	1.769(5)	N2	C21	1.479(8)
S3	C4	1.751(5)	N2	C23	1.465(8)
S3	C5	1.750(5)	C1	C3	1.342(7)
S4	C4	1.751(5)	C2	C4	1.338(8)
S4	C6	1.753(6)	C5	C6	1.353(8)
S5	C9	1.753(5)	C5	C7	1.501(8)
S5	C10	1.750(5)	C6	C8	1.498(7)
S6	C10	1.759(5)	C9	C11	1.343(7)
S6	C11	1.770(5)	C10	C12	1.358(8)
S7	C12	1.749(5)	C13	C14	1.338(8)
S7	C13	1.759(6)	C13	C15	1.503(7)
S8	C12	1.747(5)	C14	C16	1.501(8)
S8	C14	1.758(6)	C17	C18	1.473(10)
P1	N1	1.684(5)	C19	C20	1.474(8)
P1	C1	1.821(5)	C21	C22	1.429(10)
P1	C9	1.827(5)	C23	C24	1.455(10)

Bond Angles

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
Cl2	C25	Cl1	111.2(8)	C2	C4	S3	122.8(4)
C1	S1	C2	95.3(3)	C2	C4	S4	123.7(4)
C2	S2	C3	95.0(2)	C6	C5	S3	116.5(4)
C5	S3	C4	96.1(3)	C6	C5	C7	126.8(5)
C4	S4	C6	95.8(3)	C7	C5	S3	116.5(4)
C10	S5	C9	95.0(3)	C5	C6	S4	116.9(4)
C10	S6	C11	95.0(2)	C5	C6	C8	126.2(5)
C12	S7	C13	94.7(3)	C8	C6	S4	116.8(4)
C12	S8	C14	95.1(3)	S5	C9	P1	112.3(3)
N1	P1	C1	100.3(2)	C11	C9	S5	118.0(4)
N1	P1	C9	104.0(2)	C11	C9	P1	129.5(4)
C1	P1	C9	98.5(2)	S5	C10	S6	114.4(3)
N2	P2	C3	103.2(2)	C12	C10	S5	123.6(4)
N2	P2	C11	104.2(2)	C12	C10	S6	122.0(4)

C11	P2	C3	97.7(2)	S6	C11	P2	113.5(3)
C17	N1	P1	119.2(4)	C9	C11	S6	116.3(4)
C19	N1	P1	124.1(4)	C9	C11	P2	129.4(4)
C19	N1	C17	116.6(5)	S8	C12	S7	114.5(3)
C21	N2	P2	119.3(5)	C10	C12	S7	122.7(4)
C23	N2	P2	123.8(4)	C10	C12	S8	122.8(4)
C23	N2	C21	115.9(5)	C14	C13	S7	117.5(4)
S1	C1	P1	113.2(3)	C14	C13	C15	126.8(5)
C3	C1	S1	117.1(4)	C15	C13	S7	115.6(4)
C3	C1	P1	129.7(4)	C13	C14	S8	116.7(4)
S2	C2	S1	113.4(3)	C13	C14	C16	127.4(5)
C4	C2	S1	122.8(4)	C16	C14	S8	115.9(4)
C4	C2	S2	123.8(4)	N1	C17	C18	113.8(6)
S2	C3	P2	113.8(3)	N1	C19	C20	114.9(5)
C1	C3	S2	116.8(4)	C22	C21	N2	114.9(7)
C1	C3	P2	129.2(4)	C24	C23	N2	115.6(7)
S3	C4	S4	113.5(3)				

Crystal data and structure refinement for compound *trans*-6d



Identification code	GSTR782, SHK-499 // GXray7037
Crystal Habitus	clear brown plate
Device Type	STOE STADIVARI
Empirical formula	$C_{25}H_{32}Cl_2N_2O_2P_2S_8$

Moiety formula	C H2 Cl2, C24 H32 N2 O2 P2 S8
Formula weight	781.84
Temperature/K	100
Crystal system	monoclinic
Space group	C2/c
a/Å	23.9063(4)
b/Å	7.61506(10)
c/Å	19.2661(3)
α/°	90
β/°	102.0920(10)
γ/°	90
Volume/Å^3	3429.53(9)
Z	4
ρ_{calc}g/cm^3	1.514
μ/mm^{-1}	7.374
F(000)	1616.0
Crystal size/mm^3	0.075 × 0.07 × 0.02
Absorption correction	multi-scan
Tmin; Tmax	0.4930; 0.6081
Radiation	CuKα (λ = 1.54186)
2Θ range for data collection/°	7.564 to 135.468°
Completeness to theta	1.000
Index ranges	-26 ≤ h ≤ 28, -7 ≤ k ≤ 9, -22 ≤ l ≤ 22
Reflections collected	87125
Independent reflections	3093 [R_{int} = 0.0524, R_{sigma} = 0.0121]
Data/restraints/parameters	3093/238/231
Goodness-of-fit on F^2	1.038
Final R indexes [I>=2σ (I)]	R_1 = 0.0352, wR_2 = 0.0917
Final R indexes [all data]	R_1 = 0.0400, wR_2 = 0.0954
Largest diff. peak/hole / e Å^{-3}	0.70/-0.46

Bond Lengths

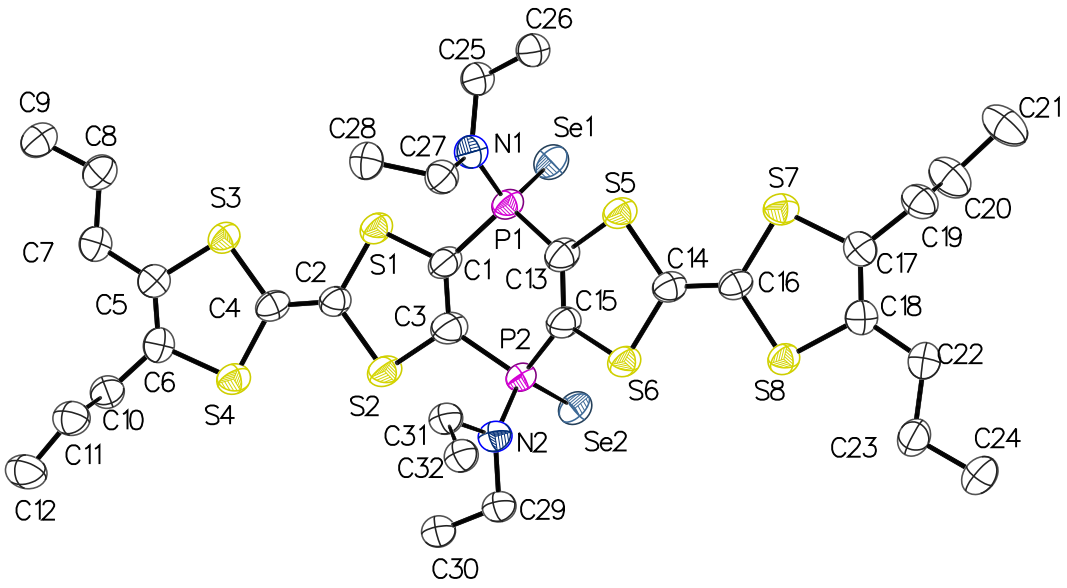
Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl1	C13	1.708(8)	P	N	1.629(2)
Cl2	C13	1.728(9)	P	C1	1.800(2)
Cl1S	C13S	1.702(10)	P	C2^1	1.802(2)
Cl2S	C13S	1.703(10)	N	C9	1.476(3)
S1	C1	1.761(2)	N	C11	1.481(3)
S1	C3	1.760(2)	C1	C2	1.347(3)
S2	C2	1.770(2)	C3	C4	1.345(3)
S2	C3	1.757(2)	C5	C6	1.332(4)
S3	C4	1.749(2)	C5	C7	1.500(4)

S3	C5	1.767(2)	C6	C8	1.492(3)
S4	C4	1.750(2)	C9	C10	1.502(4)
S4	C6	1.766(2)	C11	C12	1.525(4)
P	O	1.4905(17)			

Bond Angles

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
Cl1	C13	Cl2	110.4(6)	S2	C2	P^1	115.06(13)
Cl1S	C13S	Cl2S	98.6(18)	C1	C2	S2	116.59(18)
C3	S1	C1	93.39(11)	C1	C2	P^1	128.34(18)
C3	S2	C2	93.08(11)	S2	C3	S1	113.39(13)
C4	S3	C5	95.53(12)	C4	C3	S1	122.41(19)
C4	S4	C6	95.39(12)	C4	C3	S2	124.07(19)
O	P	N	113.18(10)	S3	C4	S4	113.89(13)
O	P	C1	111.10(11)	C3	C4	S3	122.43(19)
O	P	$C2^1$	112.67(10)	C3	C4	S4	123.68(19)
N	P	C1	108.28(11)	C6	C5	S3	116.73(19)
N	P	$C2^1$	107.61(11)	C6	C5	C7	128.7(2)
C1	P	$C2^1$	103.45(11)	C7	C5	S3	114.51(19)
C9	N	P	121.18(18)	C5	C6	S4	117.14(19)
C9	N	C11	118.2(2)	C5	C6	C8	128.4(2)
C11	N	P	119.98(17)	C8	C6	S4	114.46(19)
S1	C1	P	115.20(13)	N	C9	C10	114.2(2)
C2	C1	S1	117.00(18)	N	C11	C12	112.5(2)
C2	C1	P	127.13(18)				

Crystal data and structure refinement for compound *cis*-8f



Identification code	GSTR783, SHK-474 // GXray7038
Crystal Habitus	clear dark red block
Device Type	STOE STADIVARI
Empirical formula	$C_{32}H_{48}N_2P_2S_8Se_2$
Moiety formula	C32 H48 N2 P2 S8 Se2
Formula weight	937.06
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	25.4912(5)
b/Å	7.70630(10)
c/Å	21.8491(5)
α/°	90.00
β/°	108.0643(16)
γ/°	90.00
Volume/Å^3	4080.54(14)
Z	4
ρ_{calc}g/cm^3	1.525
μ/mm^{-1}	7.03
F(000)	1920.0
Crystal size/mm^3	0.15 × 0.13 × 0.1
Absorption correction	multi-scan
Tmin; Tmax	0.1542; 0.3100
Radiation	CuKα (λ = 1.54186)
2Θ range for data collection/°	7.296 to 135.474°

Completeness to theta	0.999
Index ranges	-30 ≤ h ≤ 28, -8 ≤ k ≤ 9, -26 ≤ l ≤ 24
Reflections collected	63776
Independent reflections	7388 [R_{int} = 0.0543, R_{sigma} = 0.0255]
Data/restraints/parameters	7388/230/561
Goodness-of-fit on F^2	1.183
Final R indexes [I>=2σ (I)]	R_1 = 0.0697, wR_2 = 0.1759
Final R indexes [all data]	R_1 = 0.0748, wR_2 = 0.1790
Largest diff. peak/hole / e $Å^{-3}$	1.00/-0.72

Bond Lengths

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Se1	P1	2.081(2)	N1	C27	1.461(10)
Se1S	P1S	2.07(2)	N1S	C25S	1.482(10)
Se2	P2	2.079(2)	N1S	C27S	1.484(10)
Se2S	P2S	2.084(10)	N2	C29	1.477(7)
S1	C1	1.753(6)	N2	C31	1.487(8)
S1	C2	1.745(6)	N2S	C29S	1.485(10)
S2	C2	1.778(6)	N2S	C31S	1.52(3)
S2	C3	1.759(7)	C1	C3	1.344(9)
S3	C4	1.759(6)	C2	C4	1.334(8)
S3	C5	1.762(6)	C5	C6	1.344(8)
S4	C4	1.748(6)	C5	C7	1.502(8)
S4	C6	1.758(6)	C6	C10	1.504(8)
S5	C13	1.739(7)	C7	C8	1.510(9)
S5	C14	1.780(6)	C8	C9	1.523(9)
S6	C14	1.744(6)	C10	C11	1.530(9)
S6	C15	1.772(6)	C11	C12	1.523(9)
S7	C16	1.740(6)	C13	C15	1.357(9)
S7	C17	1.757(7)	C14	C16	1.338(8)
S8	C16	1.756(6)	C17	C18	1.345(9)
S8	C18	1.753(6)	C17	C19	1.507(8)
P1	N1	1.651(6)	C18	C22	1.507(8)
P1	C1	1.806(7)	C19	C20	1.522(10)
P1	C13	1.813(6)	C20	C21	1.526(10)
P1S	N1S	1.65(5)	C22	C23	1.515(9)
P1S	C1	1.963(17)	C23	C24	1.507(9)
P1S	C13	2.074(18)	C25	C26	1.481(11)
P2	N2	1.652(7)	C25S	C26S	1.63(9)
P2	C3	1.824(7)	C27	C28	1.526(11)

P2	C15	1.793(6)	C27S	C28S	1.495(10)
P2S	N2S	1.60(2)	C29	C30	1.507(12)
P2S	C3	2.019(10)	C29S	C30S	1.45(4)
P2S	C15	2.020(10)	C31	C32	1.516(8)
N1	C25	1.480(9)	C31S	C32S	1.511(10)

Bond Angles

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C2	S1	C1	95.3(3)	S2	C3	P2	115.4(4)
C3	S2	C2	93.9(3)	S2	C3	P2S	106.4(4)
C4	S3	C5	95.8(3)	C1	C3	S2	117.9(5)
C4	S4	C6	95.6(3)	C1	C3	P2	126.2(5)
C13	S5	C14	93.6(3)	C1	C3	P2S	125.8(6)
C14	S6	C15	93.0(3)	S4	C4	S3	114.4(3)
C16	S7	C17	95.5(3)	C2	C4	S3	122.5(5)
C18	S8	C16	95.4(3)	C2	C4	S4	123.1(4)
N1	P1	Se1	115.2(2)	C6	C5	S3	116.5(5)
N1	P1	C1	105.0(3)	C6	C5	C7	125.5(5)
N1	P1	C13	105.7(3)	C7	C5	S3	118.0(4)
C1	P1	Se1	112.8(2)	C5	C6	S4	117.7(5)
C1	P1	C13	101.5(3)	C5	C6	C10	127.0(5)
C13	P1	Se1	115.1(2)	C10	C6	S4	115.3(4)
Se1S	P1S	C13	132.6(8)	C5	C7	C8	117.0(5)
N1S	P1S	Se1S	118.9(16)	C7	C8	C9	112.6(5)
N1S	P1S	C1	85.4(17)	C6	C10	C11	113.5(5)
N1S	P1S	C13	83.4(18)	C12	C11	C10	111.0(6)
C1	P1S	Se1S	131.8(9)	S5	C13	P1	117.0(4)
C1	P1S	C13	87.9(7)	S5	C13	P1S	110.9(5)
N2	P2	Se2	115.5(2)	C15	C13	S5	116.6(5)
N2	P2	C3	106.0(4)	C15	C13	P1	126.4(5)
N2	P2	C15	102.0(3)	C15	C13	P1S	115.2(6)
C3	P2	Se2	115.8(3)	S6	C14	S5	113.4(3)
C15	P2	Se2	115.1(3)	C16	C14	S5	122.9(5)
C15	P2	C3	100.5(3)	C16	C14	S6	123.7(5)
N2S	P2S	Se2S	115.6(8)	S6	C15	P2	114.8(3)
N2S	P2S	C3	92.8(8)	S6	C15	P2S	104.9(4)
N2S	P2S	C15	97.3(8)	C13	C15	S6	117.2(5)
C3	P2S	Se2S	131.5(5)	C13	C15	P2	127.4(5)

C3	P2S	C15	87.1(4)	C13	C15	P2S	128.6(5)
C15	P2S	Se2S	123.9(4)	S7	C16	S8	114.8(3)
C25	N1	P1	123.3(5)	C14	C16	S7	123.8(5)
C27	N1	P1	119.0(5)	C14	C16	S8	121.5(5)
C27	N1	C25	116.5(6)	C18	C17	S7	117.3(5)
C25S	N1S	P1S	114(4)	C18	C17	C19	126.9(6)
C25S	N1S	C27S	129(5)	C19	C17	S7	115.8(5)
C27S	N1S	P1S	117(4)	C17	C18	S8	117.0(5)
C29	N2	P2	121.5(5)	C17	C18	C22	125.0(6)
C29	N2	C31	117.2(7)	C22	C18	S8	118.0(5)
C31	N2	P2	117.9(6)	C17	C19	C20	113.7(6)
C29S	N2S	P2S	121.3(18)	C19	C20	C21	112.0(6)
C29S	N2S	C31S	116(2)	C18	C22	C23	116.7(5)
C31S	N2S	P2S	121.6(15)	C24	C23	C22	111.8(6)
S1	C1	P1	114.9(3)	N1	C25	C26	113.0(6)
S1	C1	P1S	109.9(5)	N1S	C25S	C26S	109(5)
C3	C1	S1	116.6(5)	N1	C27	C28	114.0(6)
C3	C1	P1	127.8(5)	N1S	C27S	C28S	119(5)
C3	C1	P1S	120.4(7)	N2	C29	C30	114.0(7)
S1	C2	S2	113.8(3)	C30S	C29S	N2S	111(2)
C4	C2	S1	124.1(5)	N2	C31	C32	111.1(7)
C4	C2	S2	122.0(5)	C32S	C31S	N2S	111(2)

Theoretical calculations

Frontier molecular orbitals

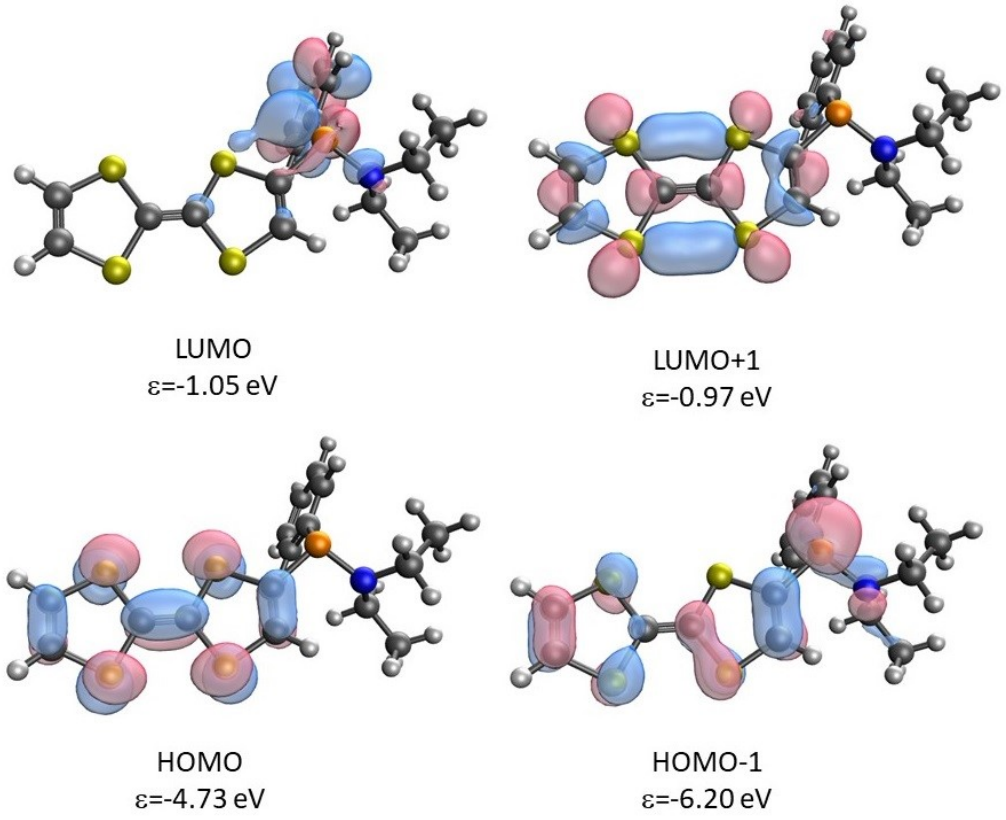


Figure S103. Kohn-Sahm molecular orbitals of **3a** at B3LYP/6-311+G**//M06-2X/6-311+G** level of theory.

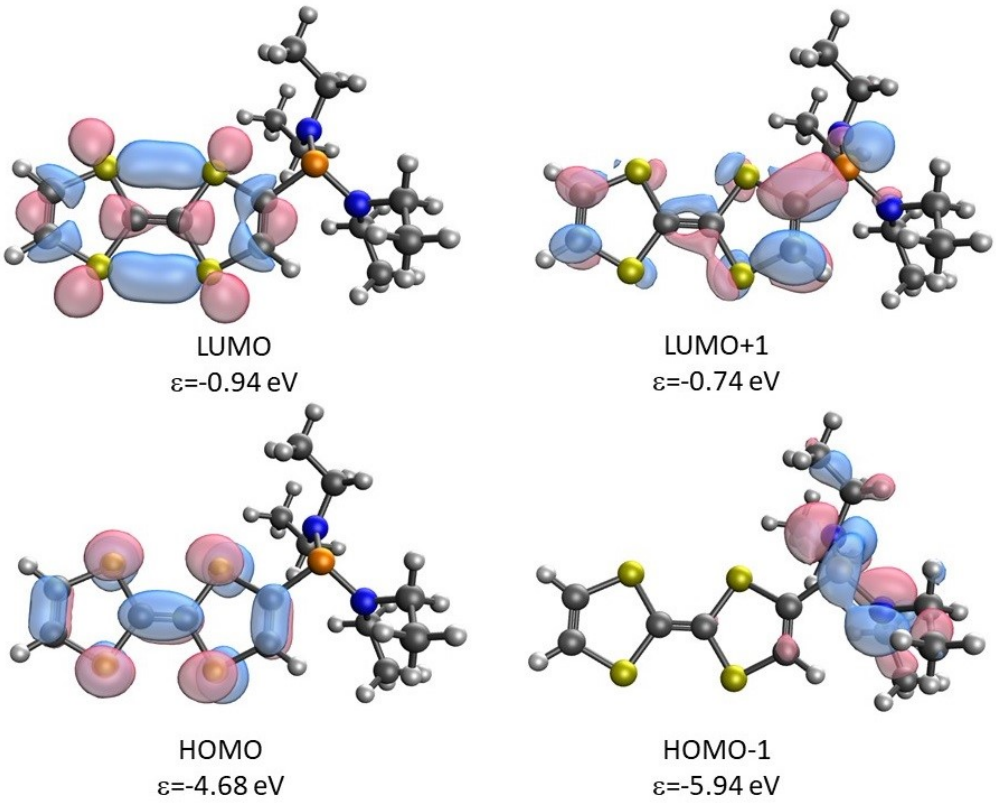


Figure S104. Kohn-Sham molecular orbitals of **3b** at B3LYP/6-311+G**//M06-2X/6-311+G** level of theory.

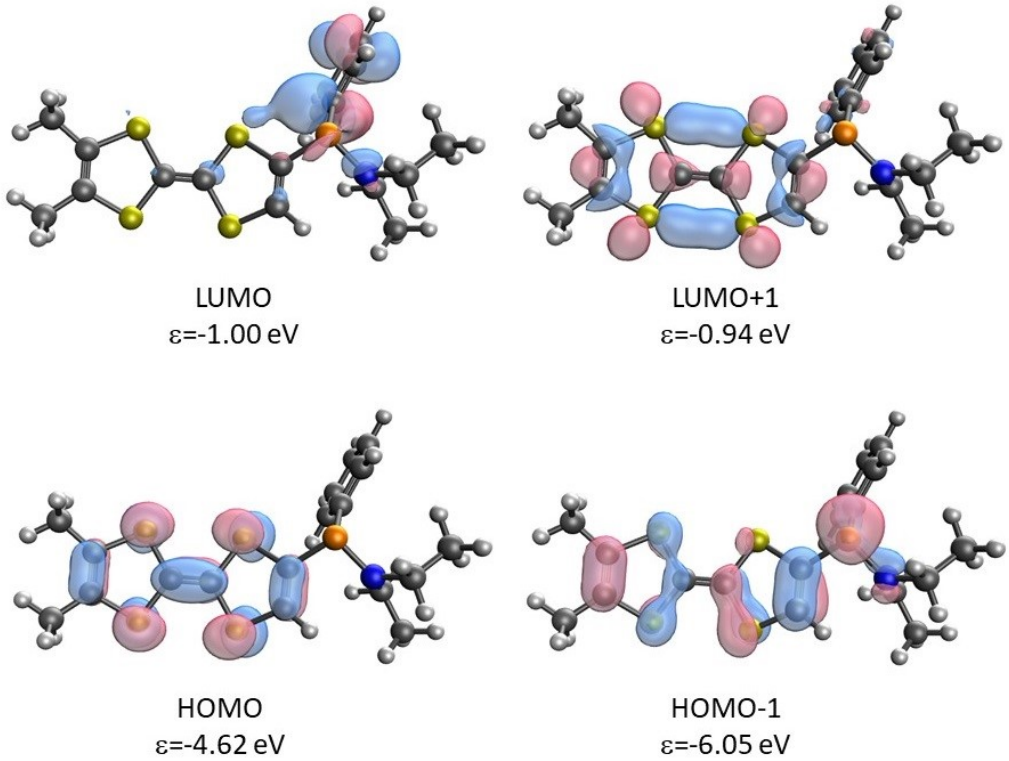


Figure S105. Kohn-Sahm molecular orbitals of **3c** at B3LYP/6-311+G**//M06-2X/6-311+G** level of theory.

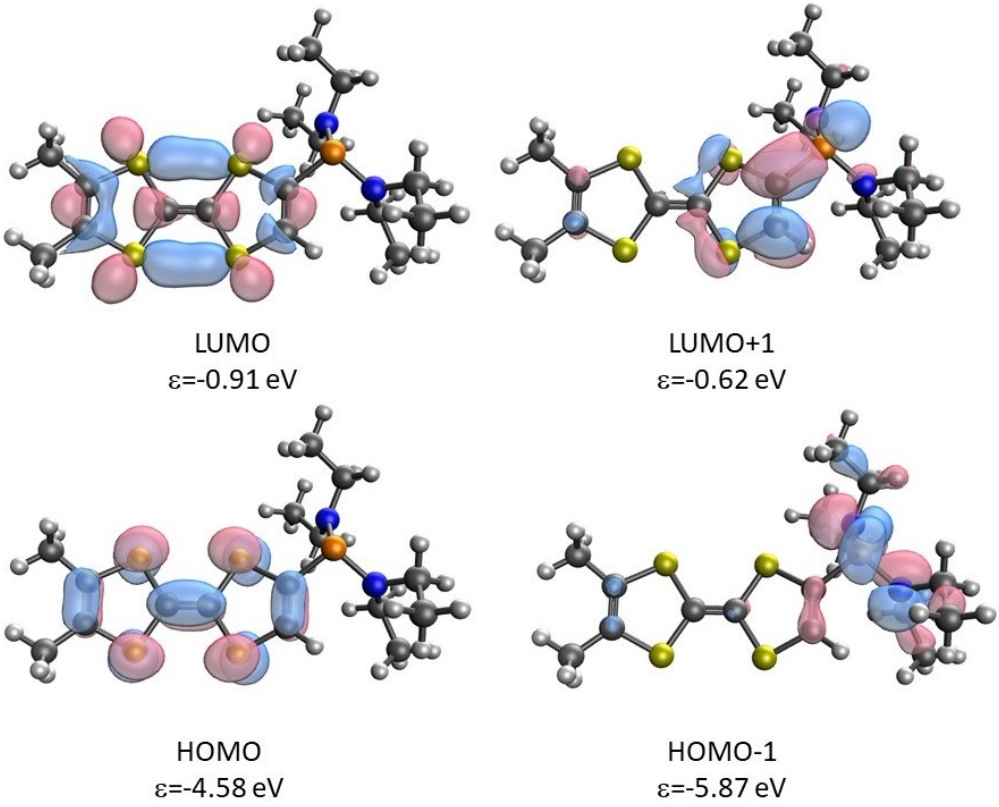


Figure S106. Kohn-Sham molecular orbitals of **3d** at B3LYP/6-311+G**//M06-2X/6-311+G** level of theory.

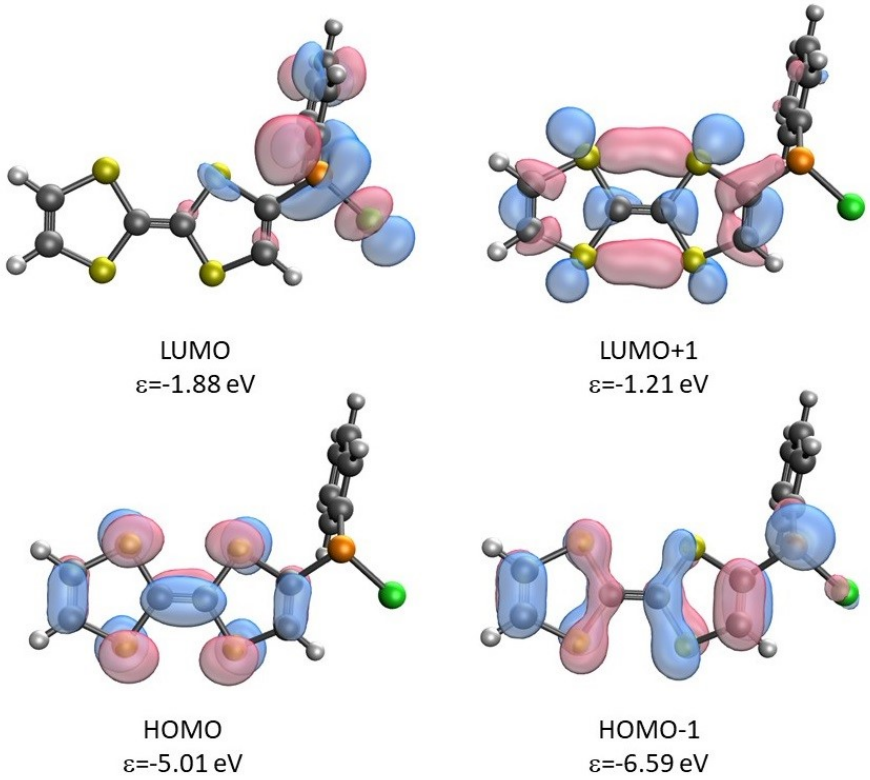


Figure S107. Kohn-Sham molecular orbitals of **4a** at B3LYP/6-311+G**//M06-2X/6-311+G** level of theory.

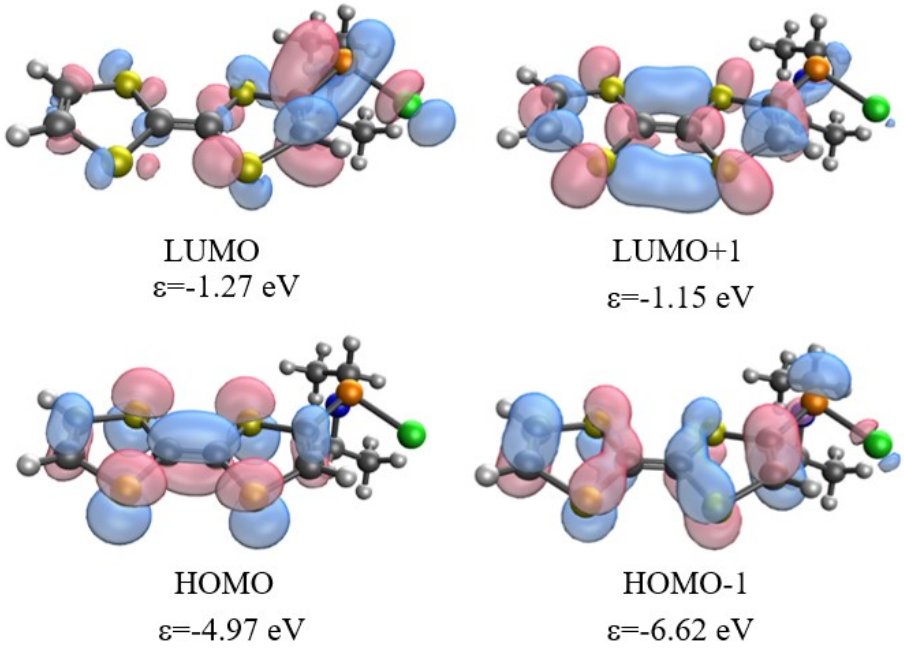


Figure S108. Kohn-Sham molecular orbitals of **4b** at B3LYP/6-311+G**//M06-2X/6-311+G** level of theory.

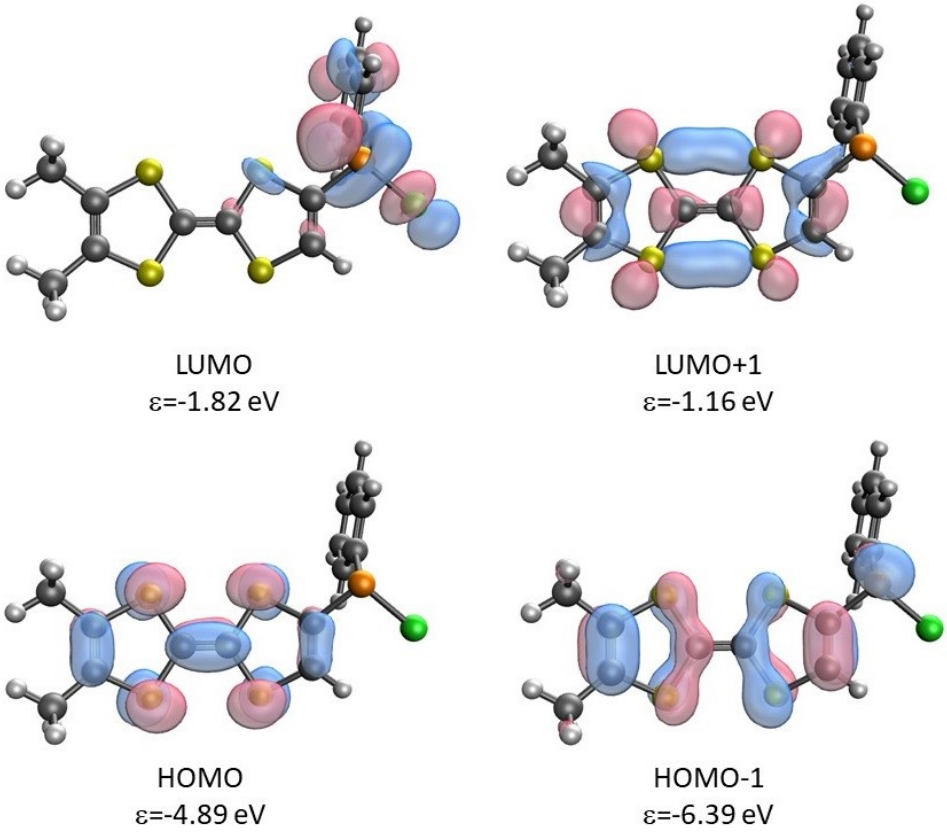


Figure S109. Kohn-Sham molecular orbitals of **4c** at B3LYP/6-311+G**//M06-2X/6-311+G** level of theory.

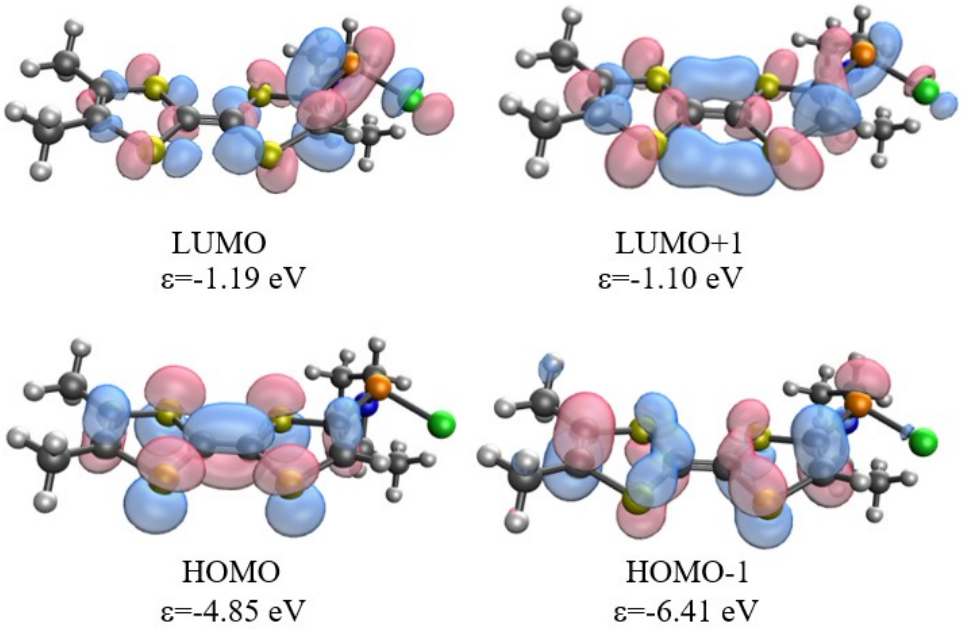


Figure S110. Kohn-Sham molecular orbitals of **4d** at B3LYP/6-311+G**//M06-2X/6-311+G** level of theory.

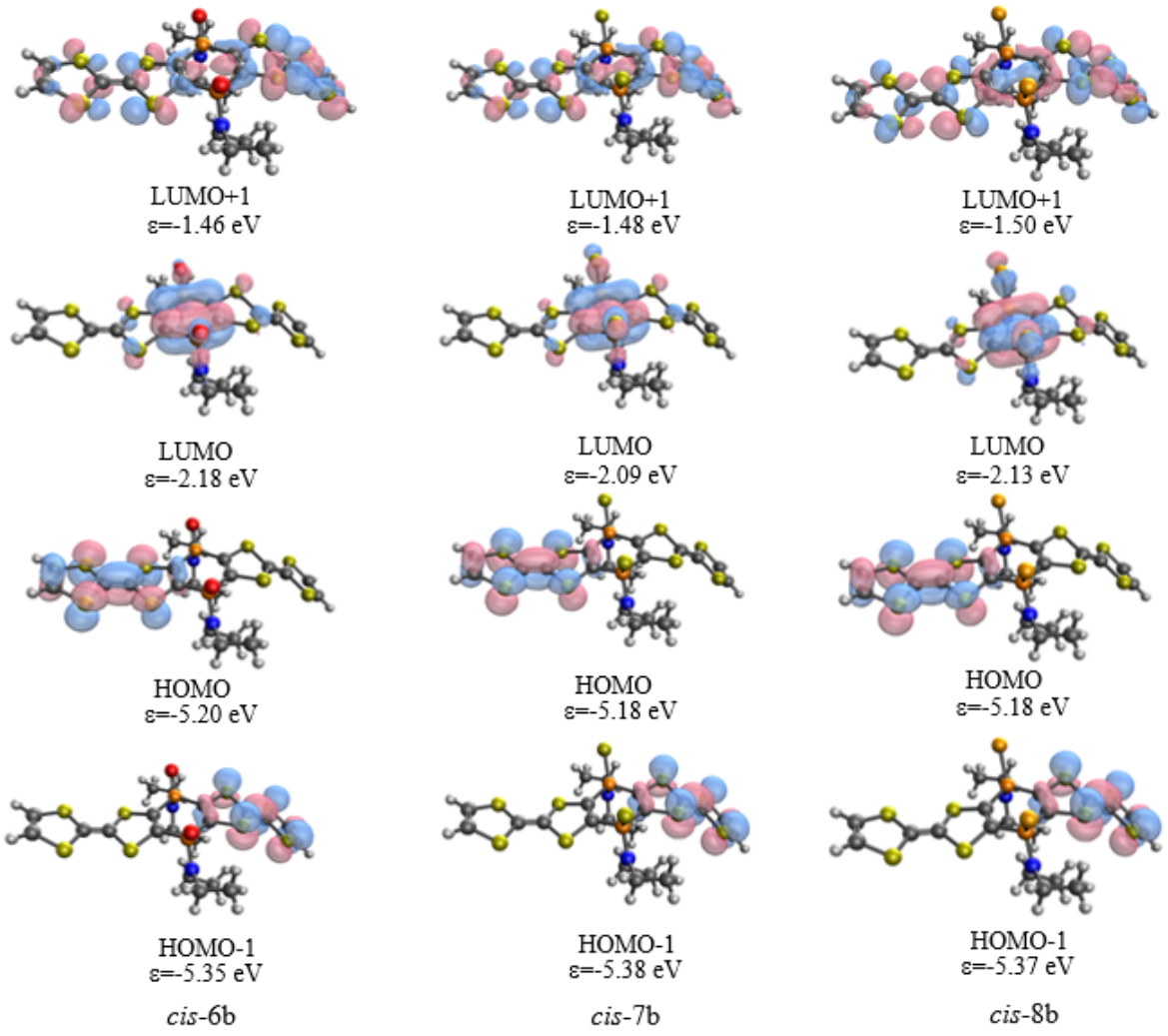


Figure S111. Kohn-Sham molecular orbitals of ***cis*-6b, *cis*-7b** and ***cis*-8b** at B3LYP/6-311+G**//M06-2X/6-311+G** level of theory.

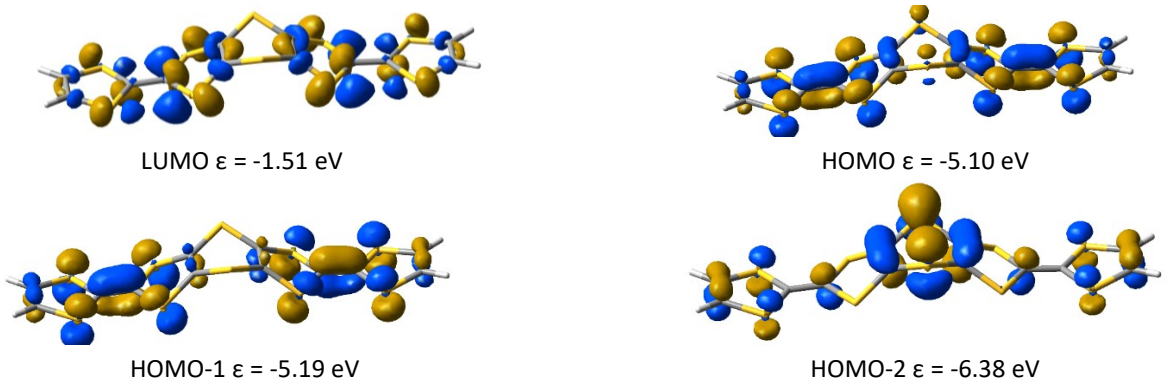


Figure S112. Kohn-Sham molecular orbitals of **IVa-H$_4$** as computed at B3LYP/6-31++G** level of theory.

Details of DFT calculations

All calculations have been carried out with the Gaussian16.[19] For visualization, MOLDEN[20] and IQmol[21] programs were used. Full geometry optimization was performed at the M06-2X/6-311+G** level of theory for each molecule. Minima are characterized by only positive eigenvalues, and transition states by a single negative eigenvalue of the Hessian.

XYZ coordinates of the investigated systems at M06-2X/6-311+G level of theory**

benzene

12
scf done: -232.198347

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.400000
C	1.212436	0.000000	2.100000
C	2.424871	0.000000	1.400000
C	2.424871	0.000000	0.000000
C	1.212436	0.000000	-0.700000
H	-0.943102	0.000000	1.944500
H	1.212436	0.000000	3.189000
H	3.367973	0.000000	1.944500
H	3.367973	0.000000	-0.544500
H	1.212436	0.000000	-1.789000
H	-1.026719	0.000000	-0.363000

3a

40
scf done: -2609.204794

S	0.122533	0.105760	0.099644
C	0.059791	0.035705	1.868947
S	1.649475	-0.046361	2.646812
C	2.506713	-0.388703	1.153398
C	1.823292	-0.320319	0.014088
C	-1.090296	0.049601	2.558329
S	-2.679106	0.165082	1.784103
C	-3.578341	-0.319252	3.229761
C	-2.877901	-0.392799	4.363861
S	-1.163448	-0.013246	4.325073
P	-5.322650	-0.864567	3.038382
N	-5.846872	-0.735506	4.663672
C	-6.016802	0.623512	2.180606
C	-5.520016	1.924571	2.307559
C	-6.147599	2.985463	1.664343
C	-7.280266	2.760769	0.886984
C	-7.781154	1.470960	0.747846
C	-7.148075	0.410203	1.387637
H	2.245501	-0.480997	-0.967815

H	3.561581	-0.612264	1.227067
H	-3.311868	-0.676535	5.314272
C	-5.960133	0.577738	5.305814
C	-6.831255	-1.738156	5.086455
H	-7.529053	-0.599011	1.263385
H	-8.655997	1.289422	0.134713
H	-7.766145	3.589075	0.384748
H	-5.750105	3.988379	1.767057
H	-4.632264	2.110925	2.902451
H	-6.681014	-1.945820	6.149887
C	-8.283029	-1.339269	4.829578
H	-6.601795	-2.663339	4.554146
C	-5.984484	0.490122	6.827833
H	-5.092651	1.166450	5.001759
H	-6.846588	1.117732	4.945498
H	-8.958208	-2.142492	5.132641
H	-8.558552	-0.441849	5.388347
H	-8.442868	-1.136545	3.767244
H	-5.920022	1.493303	7.253228
H	-6.903077	0.032215	7.199957
H	-5.137892	-0.095213	7.195253

3b

44

scf done: -2590.7564057

S	0.753526	0.761610	-0.050776
C	1.996876	-0.489945	0.120108
S	1.348634	-2.101794	0.459476
C	-0.300283	-1.664265	0.046015
C	-0.589271	-0.381062	-0.181518
C	3.309581	-0.234996	0.021740
S	3.952275	1.383101	-0.310060
C	5.582721	0.813626	-0.624830
C	5.851735	-0.467682	-0.388895
S	4.553942	-1.481666	0.218661
P	-2.185521	0.263513	-0.811998
N	-2.257583	1.687095	0.129831
C	-2.044001	1.763002	1.576702
C	-1.326808	3.037748	2.010958
N	-3.235690	-0.942769	-0.207512
C	-4.374114	-1.294627	-1.067060
C	-4.130668	-2.569990	-1.868527
C	-3.396571	-1.249880	1.214126

C	-3.690121	-2.721698	1.493274
C	-3.024369	2.795170	-0.457266
C	-2.137042	3.782507	-1.208532
H	6.303452	1.540299	-0.972286
H	6.821337	-0.927419	-0.518155
H	-1.033225	-2.458763	-0.009209
H	-3.576558	3.299566	0.342147
H	-3.779722	2.396408	-1.141743
H	-3.004259	1.681357	2.106859
H	-1.436660	0.906720	1.875964
H	-5.268461	-1.394043	-0.442434
H	-4.574114	-0.472249	-1.759961
H	-2.473271	-0.976607	1.725949
H	-4.200198	-0.633226	1.642974
H	-1.159309	3.017080	3.090115
H	-0.359530	3.117360	1.511599
H	-1.912118	3.931145	1.783039
H	-2.730196	4.594712	-1.636894
H	-1.382790	4.210409	-0.546321
H	-1.618533	3.266094	-2.019563
H	-4.993314	-2.808540	-2.496161
H	-3.259982	-2.436467	-2.514788
H	-3.935725	-3.417805	-1.209433
H	-3.767855	-2.884864	2.570406
H	-4.630717	-3.041511	1.040405
H	-2.892546	-3.360091	1.106641

3c

46

scf done: -2687.822176

S	0.095673	0.156157	0.095926
C	0.029883	0.098866	1.858590
S	1.622125	0.049724	2.618591
C	2.497426	-0.347730	1.128277
C	1.806031	-0.298957	-0.014088
C	-1.117430	0.107486	2.552197
S	-2.711229	0.198285	1.783437
C	-3.597988	-0.288948	3.236356
C	-2.892158	-0.343600	4.368325
S	-1.184136	0.062206	4.320402
P	-5.334782	-0.859946	3.056888
N	-5.854326	-0.727767	4.683672
C	-6.055207	0.613446	2.194899

C	-5.574004	1.921404	2.310074
C	-6.220335	2.970491	1.666027
C	-7.356543	2.726991	0.899586
C	-7.842173	1.430109	0.772300
C	-7.190285	0.381226	1.412805
C	2.300833	-0.555867	-1.405695
C	3.948788	-0.671774	1.317575
H	-3.318426	-0.626185	5.322559
C	-5.981514	0.587268	5.319017
C	-6.821902	-1.741176	5.118446
H	-7.559569	-0.633438	1.297745
H	-8.719847	1.233869	0.167783
H	-7.857112	3.546110	0.396693
H	-5.834652	3.978914	1.759566
H	-4.683777	2.122337	2.896449
H	-6.661523	-1.941629	6.181886
C	-8.280806	-1.363050	4.870265
H	-6.584013	-2.665819	4.588923
C	-5.993413	0.508282	6.841688
H	-5.124556	1.186304	5.005586
H	-6.878097	1.112730	4.962150
H	-8.942817	-2.174714	5.179894
H	-8.564922	-0.468006	5.428569
H	-8.450315	-1.165285	3.808515
H	-5.940586	1.514811	7.260784
H	-6.902219	0.038987	7.223597
H	-5.135452	-0.062266	7.205987
H	2.074729	0.295021	-2.053663
H	3.377289	-0.716135	-1.421053
H	1.814582	-1.436844	-1.831426
H	4.454228	-0.801152	0.362340
H	4.451239	0.132129	1.861945
H	4.066510	-1.590549	1.897060

3d

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scf done: -2669.373754

S	-0.115316	0.010884	-0.007899
C	-0.135463	0.052477	1.756828
S	1.476276	0.048247	2.476901
C	2.315017	-0.426420	0.987920
C	1.594646	-0.441673	-0.137336
C	-1.265200	0.097887	2.477306

S	-1.281991	0.153197	4.247235
C	-2.997023	-0.201537	4.367635
C	-3.733848	-0.207489	3.254410
S	-2.879267	0.137053	1.745099
P	-5.484787	-0.734846	3.130189
N	-5.998872	-0.379824	4.722939
N	-6.018769	0.452972	2.025203
C	2.055276	-0.774057	-1.524792
C	3.772298	-0.735146	1.155898
H	-3.402385	-0.403265	5.350778
C	-7.161002	0.067382	1.185523
C	-5.757375	1.890662	2.117751
C	-5.980670	0.965357	5.298332
C	-6.977072	-1.306990	5.306779
H	-7.804861	0.942221	1.049915
C	-6.727819	-0.498909	-0.162925
H	-7.768810	-0.676437	1.710632
C	-5.512379	2.545012	0.761231
H	-6.592622	2.396002	2.624550
H	-4.869911	2.036130	2.736489
H	-7.756087	-0.725578	5.812282
H	-7.477206	-1.858533	4.505454
C	-6.337515	-2.303978	6.268671
C	-5.725919	0.984843	6.803319
H	-5.190812	1.533172	4.805468
H	-6.930474	1.477932	5.085339
H	-5.288939	3.605344	0.898785
H	-4.664401	2.074446	0.260592
H	-6.386806	2.471740	0.111025
H	-7.595121	-0.774922	-0.768516
H	-6.130008	0.227284	-0.715903
H	-6.115444	-1.390033	-0.007192
H	-7.088689	-2.975873	6.692165
H	-5.597642	-2.905305	5.735261
H	-5.829409	-1.791328	7.087276
H	-5.690807	2.017126	7.158328
H	-6.514388	0.470211	7.356142
H	-4.773874	0.506700	7.044621
H	4.251382	-0.921284	0.196423
H	4.286751	0.100972	1.636823
H	3.909266	-1.617241	1.785952
H	1.784306	0.026142	-2.218434
H	3.135370	-0.903318	-1.564147
H	1.583662	-1.694338	-1.877602

4a

26
scf done: -2856.263612

C	0.377147	-0.544087	0.287411
S	0.767787	-0.460383	2.012302
C	2.341418	0.273428	1.754367
C	2.656772	0.650628	0.518472
S	1.473627	0.381281	-0.749835
H	3.580397	1.137346	0.238906
H	2.972235	0.410122	2.621254
C	-0.664642	-1.240173	-0.190632
S	-1.092707	-1.287783	-1.906945
C	-2.085927	-2.749668	-1.744590
C	-2.393450	-3.122940	-0.500409
S	-1.770921	-2.167397	0.833915
H	-3.020747	-3.969460	-0.254587
P	-2.426863	-3.647986	-3.303131
Cl	-4.131581	-4.708054	-2.678710
C	-3.210064	-2.279749	-4.238167
C	-2.860144	-2.142629	-5.581199
C	-3.410403	-1.115832	-6.344616
C	-4.311208	-0.231505	-5.765422
C	-4.665492	-0.366788	-4.423055
C	-4.116191	-1.385738	-3.659989
H	-2.157774	-2.837260	-6.029935
H	-3.135544	-1.010068	-7.387048
H	-4.740116	0.568047	-6.357938
H	-5.366403	0.326703	-3.974281
H	-4.383106	-1.493398	-2.613385

4b

30
scf done: -2837.825998

S	0.012955	-0.029593	0.003106
C	0.006587	-0.034707	1.774112
S	1.620119	-0.017350	2.504147
C	2.440144	0.360955	0.998969
C	1.720871	0.356613	-0.119960
C	-1.120507	-0.056525	2.500200
S	-1.130569	-0.101425	4.269919
C	-2.834331	0.374432	4.402610
C	-3.543557	0.373291	3.271885

S	-2.738528	-0.072909	1.780369
P	-3.326137	0.962499	6.065978
Cl	-5.443813	0.662627	5.815834
N	-2.796563	-0.344690	6.961213
C	-2.469745	-0.098714	8.372692
C	-1.221138	-0.857695	8.804320
C	-3.061535	-1.744302	6.592989
C	-4.125898	-2.405699	7.463967
H	2.116145	0.545613	-1.107992
H	3.502330	0.554593	1.048381
H	-4.599167	0.603908	3.216379
H	-2.304015	0.974468	8.487978
H	-3.317919	-0.364110	9.013613
H	-2.121347	-2.301939	6.640403
H	-3.383306	-1.757033	5.550650
H	-0.943153	-0.567800	9.819184
H	-1.382227	-1.937614	8.799918
H	-0.389042	-0.629861	8.134765
H	-4.349414	-3.399589	7.071671
H	-3.792320	-2.525519	8.496974
H	-5.044652	-1.816602	7.458095

4c

32

scf done: -2934.881297

C	0.002704	-0.004658	0.020457
C	0.000114	-0.006574	1.418490
C	1.207941	-0.036465	2.115103
C	2.414446	-0.063236	1.419896
C	2.410979	-0.062880	0.030951
C	1.205057	-0.034553	-0.669379
P	-1.540213	0.038975	2.411531
Cl	-2.468147	-1.728878	1.750607
C	-2.483810	1.233423	1.394987
S	-1.717006	2.818215	1.168923
C	-3.222142	3.611990	0.681339
S	-4.461146	2.478271	0.119369
C	-3.716940	1.095130	0.902554
C	-3.393791	4.941519	0.707331
S	-4.871940	5.735006	0.163631
C	-4.466789	7.319183	0.849418
C	-3.235537	7.469543	1.345916
S	-2.154325	6.066714	1.262125

C	-2.626599	8.697685	1.952720
C	-5.563277	8.338296	0.769567
H	-4.286907	0.176132	0.935135
H	1.205385	-0.038213	3.200109
H	3.351403	-0.084479	1.963118
H	3.348817	-0.083004	-0.511645
H	1.206730	-0.031179	-1.752724
H	-0.939245	0.023131	-0.518175
H	-5.220244	9.316108	1.102379
H	-5.919899	8.435434	-0.259127
H	-6.411957	8.041050	1.390128
H	-1.695912	8.955163	1.440505
H	-3.299521	9.550076	1.880976
H	-2.392226	8.531513	3.006835

4d

36

scf done: -2916.443611

S	0.011969	-0.057646	-0.000170
C	0.007101	-0.053467	1.763895
S	1.623033	-0.048257	2.471509
C	2.459719	0.355092	0.961108
C	1.729947	0.352516	-0.158057
C	-1.115307	-0.069581	2.497044
S	-1.115554	-0.115515	4.267211
C	-2.813158	0.379982	4.408988
C	-3.529687	0.382271	3.282734
S	-2.739029	-0.079472	1.788378
P	-3.287154	0.977622	6.073270
Cl	-5.411303	0.707366	5.837811
C	3.925023	0.634780	1.109199
C	2.184725	0.627896	-1.559692
N	-2.771960	-0.335220	6.968771
C	-2.432215	-0.092444	8.377318
C	-1.186175	-0.861490	8.798583
C	-3.054837	-1.731582	6.602637
C	-4.122381	-2.380230	7.479355
H	-4.583111	0.623984	3.233485
H	-2.257466	0.979366	8.491989
H	-3.277216	-0.351635	9.024918
H	-2.121044	-2.300244	6.645106
H	-3.381996	-1.740959	5.562033
H	-0.897109	-0.574262	9.811106

H	-1.356169	-1.940051	8.795247
H	-0.358214	-0.640452	8.121682
H	-4.361572	-3.370510	7.087200
H	-3.784237	-2.505904	8.510182
H	-5.033152	-1.778850	7.479897
H	3.263271	0.765965	-1.606454
H	1.919745	-0.204060	-2.217304
H	1.704676	1.528011	-1.950913
H	4.401941	0.772913	0.140701
H	4.087239	1.536193	1.704894
H	4.422415	-0.195197	1.617706

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scf done: -4753.994643

C	7.064724	0.396488	0.978873
S	5.864490	1.283825	0.053924
C	4.938295	-0.162347	-0.377088
S	5.772438	-1.685826	-0.036634
C	7.023635	-0.932354	0.937894
C	3.712791	-0.106841	-0.920899
S	2.759200	-1.530681	-1.340681
C	1.212264	-0.684283	-1.110913
C	1.255711	0.654209	-1.066925
S	2.859890	1.403963	-1.246822
P	-0.230496	-1.827393	-1.115014
C	-1.509647	-0.633402	-0.571530
S	-2.987343	-1.411587	0.034882
C	-3.906648	0.096486	0.090875
S	-2.880296	1.533279	0.151741
C	-1.463832	0.702625	-0.523866
C	-5.246432	0.143420	0.117731
S	-6.260574	-1.308582	0.087216
C	-7.744836	-0.423048	-0.220782
C	-7.698499	0.905383	-0.172099
S	-6.156881	1.660719	0.195857
P	-0.133133	1.856769	-1.039981
N	0.091705	2.702112	0.404957
C	0.285582	2.050127	1.699737
C	1.684516	2.216956	2.285375
H	-8.638004	-1.002864	-0.408978
H	-8.548687	1.558125	-0.315202
H	7.724712	-1.587214	1.436933

H	7.804004	0.974848	1.515828
N	-0.045441	-2.719591	0.306695
C	0.085065	-2.134602	1.641716
C	1.519037	-1.788947	2.041444
C	0.080529	-4.175540	0.225958
C	-1.229039	-4.890321	0.540548
C	0.214601	4.160846	0.357739
C	1.559873	4.657344	-0.164614
H	0.871223	-4.492869	0.914553
H	0.420927	-4.446164	-0.776347
H	-1.611697	-4.600306	1.521794
H	-1.095319	-5.974878	0.535354
H	-1.986601	-4.632886	-0.203362
H	-0.339479	-2.848082	2.355378
H	-0.547121	-1.244389	1.701526
H	1.554646	-1.504561	3.096581
H	1.909368	-0.954661	1.455193
H	2.187700	-2.640448	1.895555
H	-0.590962	4.567943	-0.260923
H	0.039182	4.530138	1.372752
H	1.699418	4.355171	-1.206179
H	2.388628	4.247461	0.414940
H	1.609670	5.748657	-0.125650
H	-0.465453	2.437186	2.399446
H	0.069391	0.986188	1.573383
H	1.760678	1.670160	3.228648
H	1.908691	3.265852	2.494232
H	2.444739	1.834372	1.601153

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scf done: -4911.253570

S	-2.925457	-1.451112	0.115727
S	-2.851711	1.493838	0.244628
S	-6.201184	-1.379380	0.299742
S	-6.131989	1.566663	0.420182
S	2.753552	-1.486127	-1.527381
S	2.817536	1.448760	-1.433174
S	5.832834	-1.587685	-0.359912
S	5.884003	1.360371	-0.271648
P	-0.219588	-1.823430	-1.164680
P	-0.167235	1.859607	-1.072915
N	0.041149	-2.725446	0.239385

N	0.119222	2.699625	0.364805
C	-1.486641	-0.650550	-0.552488
C	-3.862466	0.044420	0.215400
C	-1.456320	0.685849	-0.499775
C	-5.200580	0.073693	0.293469
C	-7.726600	-0.524169	0.005955
C	-7.695359	0.810437	0.060656
C	-8.907541	-1.412165	-0.247593
H	-8.781385	-1.964465	-1.181825
H	-9.829583	-0.837218	-0.310357
H	-9.016319	-2.141967	0.558964
C	-8.832928	1.770576	-0.116368
H	-8.909552	2.434633	0.748586
H	-9.780628	1.246615	-0.225806
H	-8.678672	2.392522	-1.001302
C	1.207546	-0.662497	-1.220570
C	3.705507	-0.049906	-1.145392
C	1.234415	0.676658	-1.175562
C	4.954379	-0.088150	-0.656291
C	7.131315	-0.830933	0.581220
C	7.154743	0.504274	0.621439
C	8.091739	-1.792575	1.213927
H	7.589744	-2.394746	1.974976
H	8.923987	-1.270949	1.682815
H	8.498066	-2.475130	0.463029
C	8.147419	1.392290	1.309457
H	8.580262	2.102106	0.599746
H	8.958935	0.814432	1.747780
H	7.665599	1.967139	2.103951
C	0.188820	-4.178248	0.138687
H	1.020100	-4.486950	0.781956
H	0.477555	-4.432963	-0.883822
C	-1.090095	-4.919214	0.516397
H	-1.420978	-4.643494	1.520271
H	-0.936901	-6.000776	0.491327
H	-1.889375	-4.664592	-0.183424
C	0.227192	-2.149813	1.572141
H	-0.158501	-2.872816	2.298219
H	-0.407126	-1.263959	1.665685
C	1.676183	-1.796714	1.908988
H	1.754245	-1.513120	2.961965
H	2.033536	-0.960484	1.304436
H	2.339561	-2.646504	1.732023
C	0.214575	4.160796	0.322474

H	-0.628275	4.557924	-0.251488
H	0.088356	4.519152	1.348593
C	1.522680	4.683523	-0.266720
H	1.610793	4.383891	-1.314572
H	2.385526	4.285007	0.269446
H	1.552801	5.775375	-0.225938
C	0.389633	2.041452	1.643030
H	-0.328451	2.413787	2.384239
H	0.184181	0.975086	1.518051
C	1.815699	2.225392	2.155899
H	1.945791	1.675973	3.091634
H	2.032992	3.277578	2.355308
H	2.542230	1.855171	1.429228

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scf done: -4904.515185

C	-7.155216	-0.418639	0.796745
S	-5.894148	-1.305989	-0.042384
C	-4.957160	0.141041	-0.441285
S	-5.810482	1.662456	-0.148791
C	-7.117711	0.909893	0.749045
C	-3.709012	0.087185	-0.930937
S	-2.745514	1.516397	-1.326239
C	-1.220972	0.675483	-1.004447
C	-1.261931	-0.663109	-0.949574
S	-2.840244	-1.425480	-1.221423
P	0.209425	1.776309	-0.792600
C	1.553700	0.644413	-0.351864
S	3.034551	1.431416	0.203990
C	3.961859	-0.075319	0.200431
S	2.949395	-1.521867	0.303450
C	1.515270	-0.695521	-0.311258
C	5.300706	-0.116290	0.127432
S	6.301890	1.338675	0.029887
C	7.768811	0.462853	-0.371595
C	7.731307	-0.865761	-0.327353
S	6.217973	-1.628631	0.129176
P	0.130484	-1.804920	-0.717199
N	-0.136332	-2.636589	0.688655
C	-0.390045	-1.947981	1.952942
C	-1.819980	-2.099547	2.462021
H	8.644381	1.048721	-0.612792

H	8.571969	-1.514863	-0.527256
H	-7.851659	1.565127	1.196436
H	-7.923957	-0.997607	1.288650
N	-0.008473	2.651537	0.597617
C	-0.122279	2.037883	1.921044
C	-1.544234	1.609670	2.283257
C	-0.338041	4.081828	0.502429
C	0.870599	4.952296	0.822055
C	-0.235858	-4.104454	0.658058
C	-1.551535	-4.624825	0.088345
H	-1.167840	4.284601	1.186565
H	-0.689008	4.295347	-0.507711
H	1.278555	4.717129	1.808092
H	0.598125	6.009932	0.808532
H	1.649473	4.783594	0.076128
H	0.248283	2.767715	2.646736
H	0.564808	1.188246	1.977314
H	-1.577547	1.244163	3.312671
H	-1.901931	0.812849	1.626289
H	-2.238012	2.448569	2.196438
H	0.595965	-4.499221	0.071731
H	-0.095542	-4.440399	1.689526
H	-1.625529	-4.361223	-0.968617
H	-2.409430	-4.202998	0.615071
H	-1.591167	-5.713813	0.168757
H	0.323566	-2.319689	2.697135
H	-0.162581	-0.887069	1.812480
H	-1.950396	-1.530870	3.385582
H	-2.050400	-3.145197	2.676937
H	-2.537170	-1.735528	1.722197
O	0.413215	2.639058	-1.977763
O	0.352739	-2.702960	-1.872165

cis-7b

58
scf done: -5550.443402

C	7.041207	-0.407806	-1.137658
S	5.848998	-1.287560	-0.196016
C	4.934292	0.161475	0.245558
S	5.758476	1.681616	-0.126248
C	7.000878	0.921118	-1.105867
C	3.722652	0.109407	0.819908
S	2.775003	1.537366	1.253846

C	1.245542	0.690027	0.954383
C	1.290992	-0.648811	0.913091
S	2.877244	-1.401337	1.179123
P	-0.195708	1.783673	0.767515
C	-1.510549	0.637279	0.262865
S	-2.973674	1.417601	-0.349867
C	-3.890045	-0.094953	-0.389196
S	-2.868483	-1.537328	-0.446936
C	-1.464503	-0.701602	0.224587
C	-5.230549	-0.142464	-0.378077
S	-6.241805	1.308016	-0.327269
C	-7.719361	0.425848	0.017714
C	-7.673984	-0.902645	-0.023640
S	-6.140304	-1.658824	-0.419908
P	-0.096029	-1.804798	0.707001
N	0.211149	-2.657709	-0.688333
C	0.445715	-1.945153	-1.948332
C	1.868706	-2.074898	-2.481632
H	-8.606453	1.007878	0.223506
H	-8.518878	-1.555475	0.143669
H	7.697539	1.572652	-1.614149
H	7.775445	-0.990861	-1.675317
N	0.035409	2.682205	-0.615492
C	0.180681	2.050714	-1.931856
C	1.616369	1.657548	-2.277257
C	0.296860	4.127901	-0.568564
C	-0.961710	4.931058	-0.869802
C	0.344844	-4.121480	-0.701230
C	1.696578	-4.632864	-0.211863
H	1.088533	4.342805	-1.292504
H	0.683761	4.391499	0.415564
H	-1.394110	4.639321	-1.830104
H	-0.738585	5.999795	-0.904508
H	-1.703520	4.754310	-0.088586
H	-0.203526	2.763022	-2.667712
H	-0.481905	1.182711	-1.987138
H	1.670291	1.309354	-3.311830
H	1.981089	0.857008	-1.629119
H	2.291609	2.508792	-2.167253
H	-0.452621	-4.551509	-0.092980
H	0.163595	-4.430597	-1.734915
H	1.817220	-4.414143	0.850520
H	2.521492	-4.168992	-0.754584
H	1.754760	-5.716130	-0.343874

H	-0.276358	-2.311732	-2.687038
H	0.215378	-0.888245	-1.790400
H	1.979585	-1.472579	-3.386280
H	2.101933	-3.110002	-2.738782
H	2.595205	-1.730943	-1.741372
S	-0.526773	2.829764	2.366834
S	-0.428619	-2.894360	2.274906

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58

scf done: -9557.182015

S	-6.077262	-1.666949	-0.730321
C	-5.170152	-0.149301	-0.679817
S	-6.183910	1.299943	-0.645776
C	-7.665219	0.416621	-0.320879
C	-7.617512	-0.911878	-0.358584
C	-3.829659	-0.099890	-0.673514
S	-2.916487	1.414327	-0.626282
C	-1.459150	0.637520	0.004838
C	-1.410737	-0.701741	-0.029712
S	-2.805737	-1.541101	-0.715692
P	-0.153000	1.785358	0.526005
Se	-0.535385	2.888556	2.264119
P	-0.046397	-1.799421	0.473285
Se	-0.425206	-2.946302	2.181889
C	1.288758	0.696993	0.727831
S	2.813754	1.546306	1.046026
C	3.765540	0.120227	0.614487
S	2.921584	-1.391538	0.973534
C	1.336652	-0.642400	0.689269
C	4.979513	0.174296	0.045294
S	5.899648	-1.273094	-0.390361
C	7.096590	-0.391566	-1.324212
C	7.053200	0.937285	-1.293822
S	5.802144	1.695970	-0.323922
N	0.088623	2.692465	-0.851002
C	0.338330	4.140519	-0.806340
C	-0.918302	4.933523	-1.140385
N	0.278919	-2.662969	-0.912861
C	0.414195	-4.126843	-0.925538
C	1.769255	-4.636432	-0.443936
C	0.517757	-1.950770	-2.173934
C	1.943134	-2.076861	-2.701623

C	0.255112	2.058274	-2.165146
C	1.696333	1.668849	-2.491248
H	-8.555944	0.997978	-0.129395
H	-8.463895	-1.565482	-0.202161
H	7.751956	1.589920	-1.797800
H	7.835743	-0.973536	-1.856282
H	1.145157	4.356585	-1.513079
H	0.700397	4.411696	0.185156
H	-1.328908	4.633302	-2.107614
H	-0.699753	6.003111	-1.177758
H	-1.675377	4.758681	-0.373392
H	-0.121000	2.769090	-2.906422
H	-0.403875	1.188124	-2.228342
H	1.764055	1.325275	-3.526572
H	2.053603	0.865725	-1.842213
H	2.368829	2.520581	-2.368981
H	-0.379049	-4.557116	-0.311809
H	0.226574	-4.436438	-1.958003
H	1.897954	-4.411508	0.616233
H	2.591233	-4.177920	-0.995420
H	1.824215	-5.720630	-0.569707
H	-0.200507	-2.320867	-2.914543
H	0.284339	-0.894223	-2.018579
H	2.055575	-1.470306	-3.603284
H	2.179064	-3.110269	-2.962687
H	2.666304	-1.734320	-1.957405

cis-1,4-dichloro-1,4-dihydro-1,4-diphosphinines

40

scf done: -5405.353394

C	3.919294	7.124534	1.205395
C	2.598308	7.352075	1.256104
P	1.394217	6.869774	-0.029802
C	2.457566	7.146704	-1.488777
C	3.778553	6.919172	-1.539490
P	4.793755	6.284178	-0.160302
S	4.556125	7.045751	-3.123953
C	3.019513	7.014728	-3.999552
S	1.651278	7.546103	-3.012444
S	1.948166	7.979314	2.777637
C	3.413710	7.589922	3.688334
S	4.853011	7.478943	2.666125

C	3.437789	7.432879	5.020217
C	2.909194	6.661568	-5.288840
Cl	6.443699	7.573876	-0.341391
S	4.283918	6.170771	-6.275645
S	1.380067	6.670952	-6.164181
S	4.909448	7.083522	5.923934
S	2.005601	7.583723	6.035410
C	2.765926	6.919130	7.492384
C	4.081496	6.692515	7.441879
C	4.973298	6.167179	8.526366
H	4.428957	6.044539	9.460737
H	5.803893	6.854967	8.704460
H	5.395316	5.199829	8.244009
C	1.833229	6.708062	8.646908
H	1.295770	7.631451	8.877442
H	2.373297	6.398748	9.539683
H	1.092564	5.940916	8.409226
C	1.993297	5.791717	-7.576073
C	3.308869	5.565111	-7.626571
C	4.089714	4.877867	-8.706097
H	3.454114	4.622073	-9.551661
H	4.545596	3.959944	-8.327706
H	4.892641	5.525257	-9.067830
C	0.949643	5.418731	-8.585563
H	0.384510	6.301739	-8.894720
H	0.242854	4.701017	-8.162565
H	1.398444	4.976234	-9.472789
Cl	0.261391	8.638848	-0.104080

trans-1,4-dichloro-1,4-dihydro-1,4-diphosphinines

40

scf done: -5405.354451

C	3.812196	6.990922	1.202689
C	2.485681	7.189546	1.260759
P	1.247067	6.932589	-0.050999
C	2.347197	6.978566	-1.503062
C	3.674384	6.780970	-1.547728
P	4.656146	6.119538	-0.159756
S	4.466121	6.957607	-3.114235
C	2.942241	6.936263	-4.015044
S	1.546966	7.387117	-3.027394
S	1.837835	7.830205	2.777560
C	3.327749	7.523524	3.678466

S	4.754345	7.396669	2.637860
C	3.379712	7.425080	5.014897
C	2.861863	6.636192	-5.319628
Cl	6.354109	7.341602	-0.338121
Cl	0.989299	4.848529	0.121005
S	4.260325	6.200172	-6.298694
S	1.349143	6.661825	-6.222418
S	4.871825	7.131675	5.904782
S	1.964045	7.598567	6.049206
C	2.756300	6.988564	7.513489
C	4.073816	6.777361	7.448108
C	4.989597	6.296095	8.532981
H	4.462946	6.198942	9.480387
H	5.816270	6.997110	8.673848
H	5.416135	5.324084	8.274457
C	1.845188	6.799980	8.688852
H	1.298144	7.722362	8.900104
H	2.403632	6.525507	9.581713
H	1.112101	6.015685	8.486284
C	1.996501	5.830851	-7.648702
C	3.315561	5.622022	-7.683380
C	4.122482	4.974489	-8.768185
H	3.505702	4.741985	-9.634163
H	4.576948	4.047873	-8.409810
H	4.927991	5.638092	-9.092872
C	0.974518	5.472855	-8.685309
H	0.400690	6.356141	-8.977185
H	0.272503	4.732403	-8.294819
H	1.443676	5.063721	-9.578005

trans-10

38

scf done: -4484.921523

C	0.115220	0.026220	0.215820
S	0.122319	-0.092104	1.984253
C	1.878164	-0.096799	2.141826
S	2.721914	-0.333747	0.612191
C	1.292707	-0.083235	-0.405656
C	2.510783	0.039208	3.316468
S	1.677182	0.237884	4.856879
C	3.048823	1.038091	5.657579
C	4.276968	0.923928	5.009378
S	4.264328	-0.002534	3.491370

P	5.839882	1.507940	5.512126
C	5.471003	2.271633	7.034352
C	4.242818	2.385935	7.682477
S	4.255458	3.312532	9.200412
C	6.008969	3.270482	9.375491
S	6.842683	3.071678	7.835153
P	2.679932	1.801849	7.179786
C	6.641503	3.406342	10.550197
S	5.797662	3.643321	12.079776
C	7.226708	3.392301	13.097720
C	8.404235	3.282710	12.476341
S	8.397330	3.401373	10.707933
C	9.759750	3.092927	13.087911
C	6.949984	3.354445	14.570625
C	1.569276	-0.045587	-1.878595
C	-1.240401	0.215547	-0.395656
H	7.872714	3.299504	15.145067
H	6.333806	2.488872	14.825096
H	6.409164	4.252202	14.880913
H	10.443562	3.876666	12.751924
H	10.184461	2.130443	12.793135
H	9.711789	3.128394	14.174592
H	-1.192507	0.180069	-1.482339
H	-1.665402	1.177902	-0.100878
H	-1.923935	-0.568404	-0.059594
H	2.110401	-0.943206	-2.188746
H	2.185109	0.820162	-2.133305
H	0.646472	0.008885	-2.452963

cis-10

38

scf done: -4484.921828

S	-0.166543	-0.020699	0.161773
C	-0.163834	-0.100032	1.922658
S	1.449211	-0.020772	2.628930
C	2.260376	0.476985	1.133516
C	1.528455	0.477018	0.015918
C	-1.280131	-0.233915	2.653723
S	-1.288867	-0.354671	4.412489
C	-2.958956	0.229350	4.586035
C	-3.722372	0.229385	3.420347
S	-2.895810	-0.354598	1.958787
P	-5.379353	0.722161	3.196909

C	-5.876391	1.069828	4.831051
C	-5.112976	1.069792	5.996739
S	-5.987383	1.478567	7.489627
C	-7.387069	2.148857	6.653261
S	-7.594325	1.478642	5.035925
C	-8.222316	3.044185	7.200296
S	-8.025414	3.675990	8.834024
C	-9.233433	4.961592	8.661008
C	-9.965353	4.961627	7.543410
S	-9.641168	3.676066	6.366867
C	-9.315071	5.907342	9.821354
C	-11.061595	5.907422	7.154522
P	-3.416385	0.722070	6.194241
C	3.709998	0.825268	1.291012
C	1.963475	0.825346	-1.375820
H	4.175557	1.025203	0.327837
H	4.251052	0.002884	1.765979
H	3.827672	1.710234	1.920802
H	1.433230	1.710342	-1.735363
H	1.744319	0.002998	-2.061648
H	3.032455	1.025255	-1.417610
H	-10.137621	6.609868	9.701783
H	-8.387760	6.476407	9.920894
H	-9.470803	5.356833	10.752662
H	-11.977544	5.356947	6.925039
H	-10.782205	6.476510	6.264730
H	-11.280718	6.609927	7.956332

triplet 10

38

scf done: -4484.859922

S	-0.000646	0.010380	0.000281
C	-0.000484	0.011437	1.738089
S	1.583301	0.010076	2.453349
C	2.475740	0.009014	0.938087
C	1.747616	0.009153	-0.189560
C	-1.160534	0.018224	2.487133
S	-1.161016	0.006502	4.211261
C	-2.900802	0.056807	4.431914
C	-3.649156	0.056899	3.272947
S	-2.732117	0.006738	1.778077
P	-5.426773	0.137752	3.032405
C	-5.895449	-0.188948	4.726404

C -5.149849 -0.188910 5.881140
S -6.026901 -0.558233 7.373732
C -7.633088 -0.476132 6.666455
S -7.616700 -0.558358 4.911526
C -8.761949 -0.409858 7.395341
S -8.772177 -0.374477 9.157343
C -10.493448 0.010986 9.308987
C -11.218617 0.010939 8.185883
S -10.372046 -0.374580 6.679548
C -10.957752 0.281391 10.708755
C -12.685445 0.281287 8.033000
P -3.413042 0.137667 6.151049
C 3.969420 0.008837 1.075097
C 2.237407 0.009163 -1.607290
H 4.451911 0.007366 0.100192
H 4.305008 -0.874194 1.623327
H 4.305483 0.893135 1.620989
H 1.878235 0.893569 -2.138081
H 1.875782 -0.873759 -2.138887
H 3.324490 0.007621 -1.645850
H -12.036623 0.419154 10.748756
H -10.480759 1.180674 11.105770
H -10.696712 -0.552302 11.365661
H -13.176691 -0.552430 7.524761
H -12.851024 1.180557 7.434879
H -13.165893 0.419038 8.999818

closed-shell dicationic 10

38
scf done: -4484.349587
S 0.000034 -0.000169 -0.000036
C 0.000006 -0.000312 1.720392
S 1.570417 -0.000151 2.423519
C 2.465031 -0.003078 0.928133
C 1.729167 -0.000283 -0.206713
C -1.170613 -0.003831 2.479263
S -2.741208 0.059062 1.773136
C -3.658105 0.006417 3.250776
C -2.890003 -0.038941 4.435026
S -1.166569 -0.079613 4.200758
P -3.409263 -0.059027 6.110721
C -5.150836 -0.021996 5.901955
C -5.919215 0.005038 4.717334

S -7.643244 -0.009963 4.950591
C -7.638178 -0.020851 6.673706
S -6.066887 -0.019560 7.381003
C -8.808555 -0.023830 7.433015
S -8.807999 -0.098074 9.152031
C -10.537434 -0.054814 9.360096
C -11.272685 0.012100 8.226809
S -10.378391 0.050783 6.733075
C -12.771436 0.041389 8.136508
C -11.062579 -0.084870 10.764386
P -5.399825 0.034818 3.041796
C 3.961479 -0.017499 1.022205
C 2.257302 0.017004 -1.612525
H 3.143988 -0.611812 -1.688793
H 2.522024 1.035301 -1.907096
H 1.518604 -0.360456 -2.319531
H 4.323599 -1.024265 1.244205
H 4.313232 0.654105 1.806595
H 4.398087 0.309547 0.079816
H -13.185121 0.640558 8.947221
H -13.176763 -0.970939 8.205339
H -13.104653 0.478003 7.195028
H -10.997729 0.905949 11.220595
H -10.497094 -0.784123 11.381790
H -12.104339 -0.401921 10.766854

open-shell dicationic 10
38
scf done: -4484.378979
S 0.000182 -0.000887 0.000231
C 0.000166 -0.000829 1.723812
S 1.571747 -0.000373 2.431545
C 2.460247 0.000922 0.941135
C 1.723967 0.000352 -0.197925
C -1.168163 0.002355 2.478979
S -1.150624 0.031051 4.208457
C -2.899329 0.015191 4.429672
C -3.657672 -0.001508 3.256596
S -2.738069 -0.014491 1.752815
P -5.392902 -0.025734 3.048196
C -5.915077 -0.023539 4.716238
C -5.156732 -0.007069 5.889315
S -6.076326 0.005365 7.393102
C -7.646234 -0.010935 6.666938

S -7.663785 -0.038900 4.937449
C -8.814558 -0.007939 7.422119
S -8.814543 -0.007398 9.145695
C -10.538348 -0.009432 9.343884
C -11.274636 -0.010525 8.204835
S -10.386143 -0.009269 6.714414
C -12.773578 -0.028139 8.134062
C -11.089289 0.006826 10.739694
P -3.421502 0.017277 6.097713
C 3.959179 0.018001 1.011824
C 2.275064 -0.015762 -1.593693
H 4.332117 1.040272 0.909726
H 4.377571 -0.586792 0.207139
H 4.319799 -0.383565 1.958657
H 1.558356 0.382536 -2.311649
H 2.525183 -1.037331 -1.890976
H 3.178283 0.592441 -1.645210
H -11.994186 -0.598898 10.790666
H -11.336515 1.028782 11.038077
H -10.373618 -0.394256 11.457146
H -13.146227 -1.050351 8.237755
H -13.134225 0.371797 7.186553
H -13.192227 0.577847 8.937716

triplet dicationic 10
38
scf done: -4484.378345
S -0.006663 -0.037989 0.000291
C -0.005740 -0.013822 1.724008
S 1.566410 0.005760 2.430911
C 2.453704 -0.010510 0.940347
C 1.716677 -0.030826 -0.198526
C -1.173359 -0.013861 2.479618
S -2.743698 -0.018972 1.752738
C -3.662393 -0.014482 3.259267
C -2.904108 -0.008537 4.430928
S -1.153473 -0.016053 4.209933
P -3.425444 0.010362 6.098862
C -5.160651 0.020009 5.891208
C -5.918933 0.014305 4.719544
S -7.669570 0.022374 4.940528
C -7.649702 0.019384 6.670844
S -6.079356 0.023859 7.397735
C -8.817322 0.019194 7.426446

S	-10.389460	-0.001557	6.719507
C	-11.276778	0.015109	8.210034
C	-10.539754	0.036238	9.348911
S	-8.816484	0.044225	9.150152
C	-11.090626	0.036555	10.744818
C	-12.775813	0.020682	8.140571
P	-5.397602	-0.004788	3.051615
C	3.952762	-0.016834	1.009937
C	2.267246	-0.030779	-1.594525
H	-13.155713	1.041699	8.228805
H	-13.189356	-0.575642	8.954048
H	-13.134407	-0.396475	7.199738
H	-10.376317	0.449398	11.456911
H	-11.334328	-0.982280	11.056530
H	-11.997695	0.639678	10.787909
H	3.176112	-0.631175	-1.637296
H	2.507770	0.988471	-1.907327
H	1.553994	-0.446502	-2.306038
H	4.332218	-1.037863	0.919873
H	4.311423	0.398402	1.951585
H	4.366675	0.580833	0.197647

TS (changing axial and equatorial positions of P) in case of 9a

40

scf done: -5404.838128

S	6.007133	1.522662	-0.107302
C	5.113307	0.019525	0.127053
S	6.009271	-1.206878	1.023689
C	7.302071	-0.113877	1.548841
C	7.300862	1.122842	1.036986
C	3.872363	-0.178721	-0.346132
S	2.981462	-1.689972	-0.131249
C	1.403824	-0.969442	-0.487762
C	1.402500	0.277668	-0.994886
S	2.971165	1.053701	-1.240303
P	0.000000	1.185001	-1.723989
Cl	0.000000	2.897212	-0.525155
P	0.000000	-2.059241	-0.076582
Cl	0.000000	-3.282430	-1.785425
C	8.286005	-0.715679	2.507629
C	8.282109	2.229028	1.291126
C	-1.402500	0.277668	-0.994886
C	-1.403824	-0.969442	-0.487762
S	-2.981462	-1.689972	-0.131249

C	-3.872363	-0.178721	-0.346132
S	-2.971165	1.053701	-1.240303
C	-5.113307	0.019525	0.127053
S	-6.009271	-1.206878	1.023689
C	-7.302071	-0.113877	1.548841
C	-7.300862	1.122842	1.036986
S	-6.007133	1.522662	-0.107302
C	-8.286005	-0.715679	2.507629
C	-8.282109	2.229028	1.291126
H	9.102015	-0.024845	2.724779
H	8.719334	-1.631050	2.090475
H	7.797951	-0.978036	3.451423
H	8.712755	2.585511	0.349840
H	9.099169	1.894029	1.931289
H	7.791923	3.078399	1.777151
H	-9.102014	-0.024845	2.724779
H	-7.797951	-0.978036	3.451423
H	-8.719334	-1.631050	2.090475
H	-8.712755	2.585511	0.349840
H	-7.791923	3.078399	1.777151
H	-9.099169	1.894029	1.931289

IVa-H$_4$ geometry optimized at computed at B3LYP/6-31++G** level of theory.

C	-7.513900	0.669600	-0.219300
S	-5.971300	1.493300	-0.438600
C	-5.005300	-0.000000	-0.366800
S	-5.971300	-1.493300	-0.438500
C	-7.513900	-0.669600	-0.219300
C	-3.657500	-0.000000	-0.278600
S	-2.676100	-1.485600	-0.216800
C	-1.339500	-0.674200	0.622000
C	-1.339500	0.674300	0.621900
S	-2.676100	1.485600	-0.216800
C	1.339500	-0.674200	0.622000
S	2.676100	-1.485600	-0.216800
C	3.657500	-0.000000	-0.278600
S	2.676100	1.485600	-0.216800
C	1.339500	0.674300	0.621900
C	5.005200	-0.000000	-0.366800
S	5.971300	-1.493300	-0.438500
C	7.513900	-0.669600	-0.219300
C	7.513900	0.669600	-0.219300
S	5.971300	1.493300	-0.438600
H	8.397000	-1.288400	-0.120500

H	8.397000	1.288400	-0.120500
H	-8.397000	-1.288400	-0.120500
H	-8.397000	1.288400	-0.120500
S	0.000000	1.641000	1.265700
S	0.000000	-1.641000	1.265700

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