Electronic Supporting Information

[4+1]- and [4+2]-cycloadditions of a thiazole-2-thione-based 1,4-diphosphinine – broadening the scope and creating perspectives

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Content

1 Experimental methods

If not specified, all reactions were performed in a dried and deoxygenated argon atmosphere using Schlenk or glovebox techniques. The used argon (>99.998%) was purified by a system of three columns (deoxygenation by a BTS copper catalyst (BASF PuriStar® R3-155) at ca. 100 °C, drying with silica gel, phosphorus pentoxide desiccant with indicator (Sicapent®) and calcium chloride). Glassware, spatulas, cannulas and filter papers were dried in a compartment drier at 110 °C for at least 1 h. Additionally, glassware was heated with a heat gun (up to 550 °C) under active vacuum (10^{-2} mbar) and kept under vacuum for 5–10 min. Sterile syringes were purged with argon three times before use. The used solvents were dried using standard procedures[145] by refluxing over proper desiccants (*n*-pentane, petroleum ether 40/65 and toluene over sodium wire (Ø = 2 mm); diethyl ether stabilized with 3,5-di-tert-butyl-4-hydroxytoluene (BHT) and tetrahydrofuran over benzophenone and sodium wire; dichloromethane over calcium hydride) in an argon atmosphere for several days and distilled before use. Alternatively, diethyl ether and toluene were dried using a Mbraun SPS-800 solvent purification system. For filtration Schlenk frits or stainless steel cannulas (Ø = 1–2 mm) with Whatman® glass microfiber filters (grade GF/B) were used. After use, stainless steel cannulas were cleaned with diluted hydrochloric acid, water and acetone, while glassware was stored in a concentrated solution of potassium hydroxide in *i*-propanol for at least 2 d (only overnight for glass frits) and in diluted hydrochloric acid for at least several hours. Afterwards, the glassware was washed with demineralised water and acetone. All glass joints were greased with either OKS 1112 grease of PTFE paste (Carl Roth).

NMR spectra were recorded on a Bruker Avance I 300 MHz, Bruker Avance I 400 MHz, Bruker Avance I 500 Mhz, Bruker Avance III HD Ascend 500 MHz or a Bruker Avance III HD Ascend 700 MHz spectrometer at the NMR department of the University of Bonn and subsequently analysed using the program Mestrenova 14.2 by *Mestrelab Research S.L.* Obtained ^{1}H and ^{13}C{^{1}H} NMR spectra were calibrated using the residual proton/carbon signal of the used deuterated solvents relative to tetramethylsilane[146] (residual peaks given in ppm, C_6D_6: δ(^{1}H) = 7.160, δ(^{13}C) = 128.060, $CDCl_3$: δ(^{1}H) = 7.260, δ(^{13}C) = 77.160, CD_2Cl_2: δ(^{1}H) = 5.320, δ(^{13}C) = 53.840, THF-d8: δ(^{1}H) = 1.730/3.580, δ(^{13}C) = 25.370/67.570, toluene-d8: δ(^{1}H) = 2.090, δ(^{13}C) = 20.400). For heteronuclear NMR spectra the IUPAC recommended method was used, which specifies the chemical shift δ of a compound as

$$\delta = 10^6 \cdot \frac{\Xi_{\text{sample}} - \Xi_{\text{reference}}}{\Xi_{\text{reference}}}$$

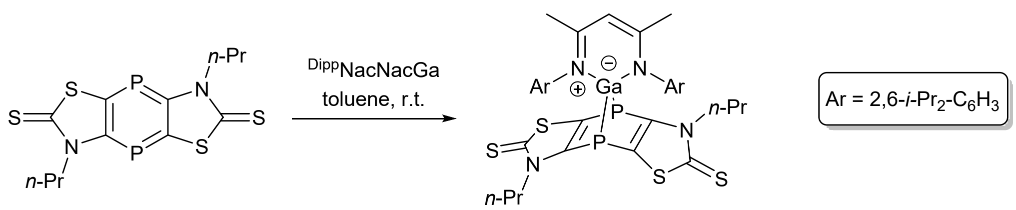
in which Ξ_{sample} denotes the frequency of the respective nucleus relative to the frequency of ^{1}H. Deuterated solvents were stored over 10w% molecular sieve (3 Å) for at least 2 d before use. All chemical shifts δ are given in parts per million (ppm) and scalar coupling constants $^{n}J_{X,Y}$ in Hertz (Hz), with n being the number of covalent bonds between the nuclei X and Y. The multiplicity of a given signal is described as follows: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, hept = heptet, m = multiplet and combinations of these. Broad signals were denotet with "br.". In ^{1}H NMR data, the number of nuclei in a respective signal is given according to integration. Complex NMR spectra were analysed by a combination of 1D and 2D NMR experiments (*i.e.*, COSY, HSQC, HMBC). All NMR measurements were carried out at 298 K if not stated otherwise.

All samples were measured by the analytical department of the University of Bonn. Electron impact ionisation (EI) experiments were performed on a Thermo Finnigan MAT 95 XL sector field instrument using an ionisation energy of 70 eV, calibration and referencing were done using perfluorokerosene (PKF). Electrospray injection (ESI) and atomospheric pressure chemical ionisation (APCI) measurements were done on a Thermo Fisher Scientific Orbitrap XL spectrometer using acetonitrile or dichloromethane as solvents. Air sensitive samples were submitted in sealed glass vials after preparation in a glovebox and only opened shortly before measuring. For all samples, selected data is given, reducing isotopic patterns to the mass-to-charge ratio (m/z) of the isotopomer with the highest relative abundance, which is given in parentheses. As high-resolution mass spectra (HRMS) using ESI or APCI were recorded in a single measurement, no standard deviations were obtained.

ATR-IR spectra of solids were recorded inside a glovebox at ambient temperature in a spectral range from 400–4000 cm^{-1} using a Bruker Alpha FTIR spectrometer with a single-reflection ATR unit (Platinum-ATR Diamond) or a Shimadzu IRSpirit FTIR spectrometer with a single-reflection ATR unit (QATR-S). Apodisation was done using the Happ-Genzel function. The data sets were analysed with the software *EZ Omnic 7.3* from *Fisher Scientific* and *LabSolutions IR 2.26* from *Shimadzu*. Peak intensities are given as very strong (vs), strong (s), medium (m) or weak (w). Only selected peaks at wave numbers >1500 cm^{-1} are given.

2 Experimental procedures and characterisation

2.1 spiro[1',2'-dihydro-1',3'-bis(2',6'-di-*i*-propylphenyl)-4',6'-dimethyl-1',3',2'-diazagallinine-2,9'-[3,7]-di-*n*-propyl-[3,7]-dihydro-[4,8]-gallano[1,4]diphosphinino[2,3-d:5,6-d']bis[1,3]thiazole-[2,6]-dithione] (2a)



In a 10 mL vial a suspension of 51.3 mg (0.136 mmol, 1.00 eq.) **1** in 2 mL of toluene was added to a solution of 73.6 mg (0.151 mmol, 1.11 eq.) ^{Dipp}NacNacGa in 1 mL toluene. The mixture was stirred at ambient temperature for 20 h. The resulting suspension was decanted and the obtained solution was evaporated *in vacuo* (10^{-2} mbar) before addition of diethyl ether. The suspension was cooled to −30 °C and decanted again. The solid residues were combined and dried *in vacuo* to give **7a** as an off-white powder.

Molecular formula: $C_{41}H_{55}GaN_4P_2S_4$

Molecular weight: 863.83 g/mol

Yield: 70 mg (0.081 mmol, 60%)

MS (EI, 70 eV, selected data): m/z (%): 928.2 $[M+3O+H_2O]^{+\bullet}$, 910.1 $[M+3O]^{+\bullet}$, 880.2 $[M+H_2O]^{+\bullet}$ 862.2 $[M]^{+\bullet}$, 486.1 $[C_{29}H_{41}GaN_2]^{+\bullet}$, 375.9 $[M-C_{29}H_{41}GaN_2]^{+\bullet}$, 333.8 $[M-C_{29}H_{41}GaN_2-C_3H_7+H]^{+\bullet}$, 291.9 $[M-C_{29}H_{41}GaN_2-2\ C_3H_7+2\ H]^{+\bullet}$.

HRMS (ESI) for $C_{41}H_{56}GaN_4P_2S_4O_3$ theor./exp. 911.1961/911.1964 $[M+3O+H]^{+\bullet}$.
for $C_{41}H_{56}GaN_4P_2S_4$ theor./exp. 863.211/863.206 $[M+H]^{+\bullet}$.

IR (ATR Diamond, selected data): $\tilde{\nu}$ / cm^{-1} = 2867 (w, *ν*(CH)), 2929 (m, *ν*(CH)), 2959 (w, *ν*(CH)).

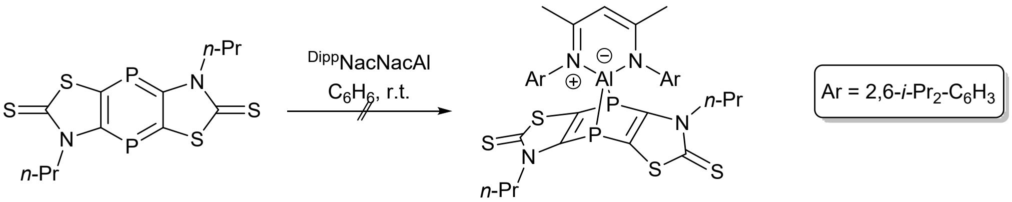
^{1}H NMR (600.2 MHz, 298.1 K, C_6D_6): δ / ppm = 0.58 (t, 6H, $^3J_{H,H}$ = 7.39 Hz, $CH_2CH_2CH_3$), 0.87 (d, 6H, $^3J_{H,H}$ = 6.80 Hz, Ar-CH-CH_3), 0.88 (d, 6H, $^3J_{H,H}$ = 6.82 Hz, Ar-CH-CH_3), 1.40 (d, 6H, $^3J_{H,H}$ = 6.83 Hz, Ar-CH-CH_3), 1.47 (d, 6H, $^3J_{H,H}$ = 6.92 Hz, Ar-CH-CH_3), 1.48 (s, 6H, N-C-CH_3), 1.53−1.69 (m, 4H, $CH_2CH_2CH_3$), 2.84 (hept, 2H, $^3J_{H,H}$ = 6.81 Hz, Ar-*CH*-CH_3), 2.98 (hept, 2H, $^3J_{H,H}$ = 6.81 Hz, Ar-*CH*-CH_3), 3.82−3.89 (m, 2H, CH_2CH$_2$CH$_3$), 4.62–4.69 (m, 2H, CH_2CH$_2$CH$_3$), 4.77 (1H, s, N-C-C*H*), 6.95 (4H, dm, $^3J_{H,H}$ = 7.77 Hz, *m*-Dipp), 7.37 (2H, t, $^3J_{H,H}$ = 7.77 Hz, *p*-Dipp).

^{13}C{^{1}H} NMR (150.9 MHz, 298.4 K, C_6D_6): δ / ppm = 11.3 (s, CH$_2$CH$_2$C*H$_3$*), 20.8 (s, CH$_2$C*H$_2$*CH$_3$), 23.8 (s, Ar-CHC*H$_3$*), 24.3 (s, Ar-CHC*H$_3$*), 24.3 (s, Ar-CHC*H$_3$*), 24.4 (s, Ar-CHC*H$_3$*), 24.4 (s, Ar-CHC*H$_3$*), 25.2 (s, N-C-C*H$_3$*), 25.6 (s, N-C-C*H$_3$*), 28.9 (s, Ar-C*H*-CH$_3$), 29.1 (s, Ar-C*H*-CH$_3$), 53.4 (dd, $^3J_{P,C}$ = 4.16 Hz, $^4J_{P,C}$ = 4.16 Hz, C*H$_2$*CH$_2$CH$_3$), 96.5 (s, N-C-C*H*), 125.1 (s, *m*-Ar), 126.0 (s, *m*-Ar), 128.2 (s, *p*-Ar), 132.7–133.s (s, P*C*S), 140.1 (s, *i*-Ar), 141.3 (s, *o*-Ar), 142.0 (s, *o*-Ar), 160.3–160.8 (m, P*C*N), 170.4 (s, N-*C*-CH$_3$), 190.8 (s, *C*=S).

^{31}P{^{1}H} NMR (243.0 MHz, 298.0 K, C_6D_6): δ / ppm = −81.7 (s).

^{31}P NMR (243.0 MHz, 298.0 K, C_6D_6): δ / ppm = −81.7 (s).

2.2 Targeting spiro[1’,2’-dihydro-1’,3’-bis(2’,6’-di-*i*-propylphenyl)-4’,6’-dimethyl-1’,3’,2’-diazaalu-minine-2,9'-[3,7]-di-*n*-propyl-[3,7]-dihydro-[4,8]-alumano[1,4]diphosphinino[2,3-d:5,6-d']bis[1,3]thiazole-[2,6]-dithione] (2b)



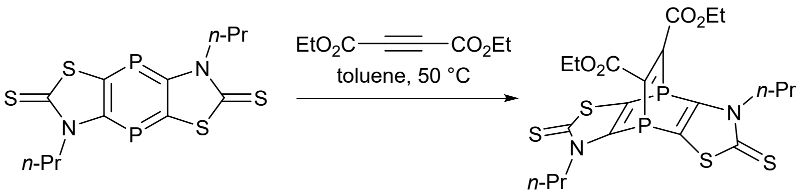
1 2b

In a 10 mL vial a solution of 7.7 mg (0.017 mmol, 0.99 eq.) of ^{Dipp}NacNacAl in 0.5 ml benzene was added dropwise to a suspension of 6.6 mg (0.018, 1.00 eq.) of **1** in 0.5 mL benzene. An immediate colour change from red to dark brown was observed. The reaction was stirred for 3.5 h before the addition of 8.5 mg (0.019 mmol, 1.09 eq.) of ^{Dipp}NacNacAl to the reaction mixture. After stirring for a further 19 h 5.5 mg (0.012 mmol, 0.71 eq.) of ^{Dipp}NacNacAl were added.

^{31}P{^{1}H} NMR (243.0 MHz, 299.1 K, C_6D_6): δ / ppm = −108.4 (d, $^3J_{P,P}$ = 22.3 Hz,), −100.6 (s), −88.2 (d, $^3J_{P,P}$ = 22.3 Hz).

^{31}P NMR (243.0 MHz, 298.0 K, C_6D_6): δ / ppm = −108.5 (dd, $^3J_{P,P}$ = 20.8 Hz, $^nJ_{P,H}$ = 6.25 Hz), −100.6 (s), −88.1 (d, $^3J_{P,P}$ = 20.8 Hz).

2.3 9,10-bis(ethylcarboxy)-3,7-di-*n*-propyl-4,8-etheno[1,4]diphosphinino[2,3-d:5,6-d']bis[1,3]thiazole-2,6-dithione (3a)



1 3a

In a 20 mL Schlenk vessel, 0.07 mL (0.436 mmol, 1.17 eq.) of diethyl acetylene dicarboxylate were added to a suspension of 140 mg (0.371 mmol, 1.00 eq.) of **1** in 6 mL toluene. The mixture was heated to 50 °C and stirred at this temperature for 6.5 h before removing volatiles *in vacuo* (10^{-2} mbar). The residue was washed three times with 4 mL *n*-pentane each before drying *in vacuo* (10^{-2} mbar). The product was obtained as an orange solid.

Molecular formula: $C_{20}H_{24}N_2O_4P_2S_4$

Molecular weight: 546.61 g/mol

Yield: 147.1 mg (0.269 mmol, 72%)

Melting point: 81 °C (dec. to **1**)

Elemental analysis:	calculated / %	C 43.95	H 4.43	N 5.13
	found / %	C 42.20	H 4.81	N 4.31

MS (pos. ESI, selected data): m/z (%): 515.044 (100) $[M-2O+H]^{+\bullet}$.
(neg. ESI, selected data): m/z (%): 579.3 (100) $[M+O+OH]^{-\bullet}$.

IR (ATR Diamond, selected data): ṽ / cm^{-1} = 1719 (s, *ν*(CO)), 2872 (w, *ν*(CH)), 2935 (w, *ν*(CH)), 2966 (w, *ν*(CH)).

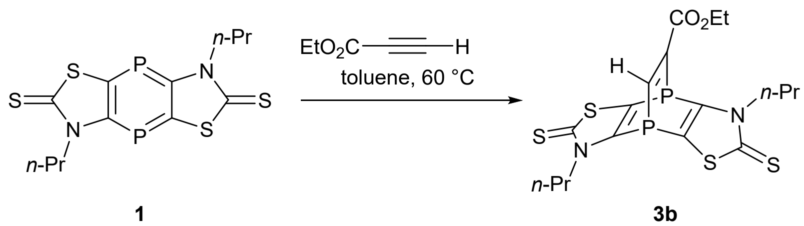
^{1}H NMR (500.0 MHz, 298.0 K, $CDCl_3$): δ / ppm = 1.00 (t, 6H, $^3J_{H,H}$ = 7.38 Hz, $CH_2CH_2CH_3$), 1.33 (t, 6H, $^3J_{H,H}$ = 7.15 Hz, OCH_2CH_3), 1.76–1.89 (m, 4H, $CH_2CH_2CH_3$), 4.26–4.38 (m, 6H, OCH_2CH_3, $CH_2CH_2CH_3$), 4.43–4.53 (m, 2H, $CH_2CH_2CH_3$).

^{13}C{^{1}H} NMR (125.8 MHz, 298.0 K, $CDCl_3$): δ / ppm = 11.3 (s, $CH_2CH_2CH_3$), 14.1 (s, OCH_2CH_3), 22.5 (d, $^4J_{P,C}$ = 1.82 Hz, $CH_2CH_2CH_3$), 51.8 (dd, $^3J_{P,C}$ = 4.84 Hz, $^4J_{P,C}$ = 4.84 Hz, $CH_2CH_2CH_3$), 63.2 (s, OCH_2CH_3), 131.4–132.0 (m, PCS), 157.4–157.9 (m, $PCCO_2Et$), 159.7–160.0 (m, PCN), 164.7–165.4 (m, CCO_2Et), 189.6 (s, C=S).

^{31}P{^{1}H} NMR (202.4 MHz, 298.0 K, $CDCl_3$): δ / ppm = −75.5 (s).

^{31}P NMR (202.4 MHz, 298.0 K, $CDCl_3$): δ / ppm = −75.5 (s).

2.4 3,7-di-*n*-propyl-9-ethylcarboxy-4,8-etheno[1,4]diphosphinino[2,3-d:5,6-d']bis[1,3]thiazole-2,6-dithione (3b)



In a 20 mL Schlenk vessel, 292 mg (0.775 mmol, 1.00 eq.) **1** were dissolved in 12 mL toluene. After addition of 0.40 mL (3.95 mmol, 5.09 eq.) of ethyl propiolate the reaction mixture was stirred at 60 °C for 1.5 h. Volatiles were removed *in vacuo* (10^{-2} mbar) at 50 °C and the dark orange residue was washed three times with 5 mL of *n*-pentane and three times with 5 mL of diethyl ether before drying the residue *in vacuo* (10^{-2} mbar). The product was obtained as an orange solid.

Molecular formula: $C_{17}H_{20}N_2O_2P_2S_4$

Molecular weight: 474.55 g/mol

Yield: 257 mg (0.542 mmol, 70%)

Melting point: 113 °C (dec. to **1**)

MS (pos. ESI, selected data): m/z (%): 474.995 (100) $[M+H]^{+\bullet}$.

IR (ATR Diamond, selected data): ṽ / cm^{-1} = 1702 (s, *v*(CO)), 2870 (w, *v*(CH)), 2928 (w, *v*(CH)), 2958 (w, *v*(CH)).

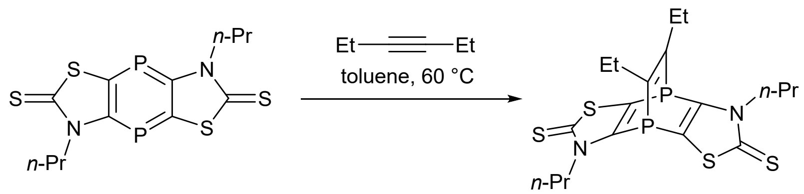
^{1}H NMR (500.1 MHz, 298.0 K, $CDCl_3$): δ / ppm = 0.99 (t, 3H, $^{3}J_{H,H}$ = 7.44 Hz, $CH_2CH_2\mathit{CH_3}$), 0.99 (t, 3H, $^{3}J_{H,H}$ = 7.44 Hz, $CH_2CH_2\mathit{CH_3}$), 1.36 (t, 3H, $^{3}J_{H,H}$ = 7.13 Hz, $OCH_2\mathit{CH_3}$), 1.74–1.86 (m, 4H, $CH_2\mathit{CH_2}CH_3$), 4.29–4.41 (m, 4H, $\mathit{CH_2}CH_2CH_3$), 4.41–4.51 (m, 2H, $O\mathit{CH_2}CH_3$), 8.74 (dd, 1H, $^{2}J_{P,H}$ = 61.6 Hz, $^{3}J_{P,H}$ = 6.77 Hz, C*H*).

^{13}C{^{1}H} NMR (125.8 MHz, 298.0 K, $CDCl_3$): δ / ppm = 11.2 (d, $^{5}J_{P,C}$ = 1.66 Hz, $CH_2CH_2\mathit{CH_3}$), 11.3 (d, $^{5}J_{P,C}$ = 1.66 Hz, $CH_2CH_2\mathit{CH_3}$), 14.2 (s, $OCH_2\mathit{CH_3}$), 22.4 (d, $^{4}J_{P,C}$ = 3.56 Hz, $CH_2\mathit{CH_2}CH_3$), 22.5 (d, $^{4}J_{P,C}$ = 3.40 Hz, $CH_2\mathit{CH_2}CH_3$), 51.4 (d, $^{3}J_{P,C}$ = 9.92 Hz, $\mathit{CH_2}CH_2CH_3$), 62.8 (d, $^{4}J_{P,C}$ = 1.50 Hz, $O\mathit{CH_2}CH_3$), 131.7 (dd, $^{1}J_{P,C}$ = 26.0 Hz, $^{2}J_{P,C}$ = 4.80 Hz, P*C*S), 133.3 (dd, $^{1}J_{P,C}$ = 28.2 Hz, $^{2}J_{P,C}$ = 5.51 Hz, P*C*S), 157.8 (dd, $^{1}J_{P,C}$ = 12.8 Hz, $^{2}J_{P,C}$ = 5.13 Hz, P*C*N), 158.6 (dd, $^{1}J_{P,C}$ = 24.0 Hz, $^{2}J_{P,C}$ = 4.27 Hz, P*CH*), 159.5 (dd, $^{1}J_{P,C}$ = 15.9 Hz, $^{2}J_{P,C}$ = 2.00 Hz, P*C*N), 161.4 (dd, $^{2}J_{P,C}$ = 3.58 Hz, $^{3}J_{P,C}$ = 19.6 Hz, C*C*O_2Et), 163.9 (dd, $^{1}J_{P,C}$ = 34.0 Hz, $^{2}J_{P,C}$ = 3.71 Hz, *C*CO_2Et), 189.0 (d, $^{3}J_{P,C}$ = 2.12 Hz, NS*C*=S), 189.1 (d, $^{3}J_{P,C}$ = 1.95 Hz, NS*C*=S).

^{31}P{^{1}H} NMR (202.5 MHz, 298.0 K, $CDCl_3$): δ / ppm = −87.1 (d, $^{3}J_{P,P}$ = 25.97 Hz), −84.0 (d, $^{3}J_{P,P}$ = 25.97 Hz).

^{31}P NMR (202.5 MHz, 298.0 K, $CDCl_3$): δ / ppm = −87.1 (dd, $^{3}J_{P,P}$ = 25.9 Hz, $^{3}J_{P,H}$ = 6.71 Hz), −84.0 (dd, $^{3}J_{P,P}$ = 25.9 Hz, $^{2}J_{P,H}$ = 61.6 Hz).

2.5 9,10-diethyl-3,7-di-*n*-propyl-4,8-etheno[1,4]diphosphinino[2,3-d:5,6-d']bis[1,3]thiazole-2,6-dithione (3c)



1 **3c**

In a 10 mL Schlenk vessel, 0.05 mL (0.440 mmol, 5.5 eq.) 3-hexyne were added to a suspension of 30 mg (0.080 mmol, 1.00 eq.) of **1** in 2 mL toluene. The mixture was stirred at 60 °C for 22 d before removal of volatiles *in vacuo* (10^{-2} mbar). The residue was washed three times with 2 mL of *n*-pentane each. After drying *in vacuo* (10^{-2} mbar), the product was obtained as a yellow solid.

Molecular formula: $C_{18}H_{24}N_2P_2S_4$

Molecular weight: 458.60 g/mol

Yield: 16.2 mg (0.035 mmol, 57%)

Melting point: 190 °C (dec. to **1**)

MS (EI, 70 eV, selected data): m/z (%): 458.0 (100) $[M]^{+\bullet}$, 375.9 $[M-C_6H_{10}]^{+\bullet}$, 291.8 $[M-C_6H_{10}-2C_3H_7+2H]^{+\bullet}$.

HRMS (pos. ESI) for $C_{18}H_{24}N_2P_2S_4$ theor./exp. 458.0298/458.0296 $[M]^{+\bullet}$.

IR (ATR Diamond, selected data): ṽ / cm^{-1} = 2869 (w, *v*(CH)), 2933 (m, *v*(CH)), 2963 (w, *v*(CH)).

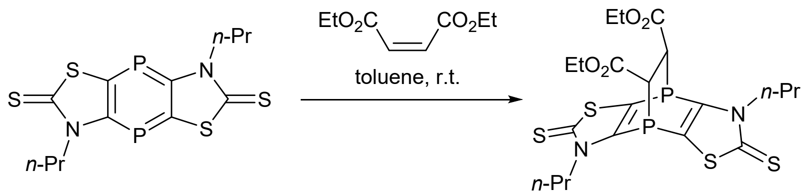
^{1}H NMR (500.0 MHz, 298.0 K, $CDCl_3$): δ / ppm = 1.00 (t, 6H, $^{3}J_{H,H}$ = 7.40 Hz, $CH_2CH_2\mathit{CH_3}$), 1.08 (t, 6H, $^{3}J_{H,H}$ = 7.44 Hz, $CCH_2\mathit{CH_3}$), 1.73–1.90 (m, 4H, $CH_2\mathit{CH_2}CH_2$), 2.43–2.60 (m, 4H, $CC\mathit{H_2}CH_3$), 4.31–4.38 (m, 2H, $C\mathit{H_2}CH_2CH_3$) 4.40–4.47 (m, 2H, $C\mathit{H_2}CH_2CH_3$).

$^{13}C\{^1H\}$ NMR (125.8 MHz, 298.0 K, $CDCl_3$): δ / ppm = 11.3 (s, $CH_2CH_2\mathit{CH_3}$), 13.6 (s, $CCH_2\mathit{CH_3}$), 22.4 (dd, $^4J_{P,C}$ = 1.67 Hz, $^4J_{P,C}$ = 1.67 Hz, $CH_2\mathit{CH_2}CH_3$) 28.1 (m, $C\mathit{CH_2}CH_3$) 31.1 (d, $^4J_{P,C}$ = 15.4 Hz, $CH_2\mathit{CH_2}CH_2CH_3$), 51.6 (dd, $^3J_{P,C}$ = 4.79 Hz, $^4J_{P,C}$ = 4.79 Hz, $\mathit{CH_2}CH_2CH_3$), 133.7 (dd, $^1J_{P,C}$ = 18.2 Hz, $^2J_{P,C}$ = 13.8 Hz, P*C*S), 156.8 (dd, $^1J_{P,C}$ = 9.49 Hz, $^2J_{P,C}$ = 8.51 Hz, $P\mathit{C}CH_2CH_3$), 160.8 (dd, $^1J_{P,C}$ = 12.6 Hz, $^2J_{P,C}$ = 9.08 Hz, P*C*N), 189.3 (s, *C*=S).

$^{31}P\{^1H\}$ NMR (202.4 MHz, 298.0 K, $CDCl_3$): δ / ppm = −71.2 (s).

^{31}P NMR (202.4 MHz, 298.0 K, $CDCl_3$): δ / ppm = −71.2 (m).

2.6 *rel*-(9*S*,10*R*)-9,10-bis(ethylcarboxy)-3,7-di-*n*-propyl-4,8-ethano[1,4]diphosphinino[2,3-d:5,6-d']bis[1,3]thiazole-2,6-dithione (4a)



1 **4a**

In a 10 mL Schlenk vessel, 0.09 mL (0.724 mmol, 5.07 eq.) diethyl maleate were added to a suspension of 53.8 g (0.143 mmol, 1.00 eq.) of **1** in 4 mL toluene. The mixture was stirred for 4 h at ambient temperature and volatiles were removed *in vacuo* (10^{-2} mbar). The residue was washed three times with 1.5 mL of *n*-pentane each and dried *in vacuo* (10^{-2} mbar). The product was obtained as a colourless solid.

Molecular formula: $C_{20}H_{26}N_2O_4P_2S_4$

Molecular weight: 548.63 g/mol

Yield: 49.4 mg (0.090 mmol, 63%)

Melting point: 140 °C (dec. to **1**)

Elemental analysis:					
	calculated / %	C 43.79	H 4.78	N 5.11	S 23.37
	found / %	C 43.45	H 4.74	N 5.00	S 23.30

MS (pos. ESI, selected data): m/z (%): 549.032 (68) $[M+H]^{+\bullet}$, 219.187 (100) $[M-C_8H_{12}O_4-2C_3H_7+2H]^{+\bullet}$.

IR (ATR Diamond, selected data): ṽ / cm^{-1} = 1724 (s, *ν*(CO)), 2871 (w, *ν*(CH)), 2932 (w, *ν*(CH)), 2959 (w, *ν*(CH)).

^1H NMR (300.1 MHz, 298.0 K, $CDCl_3$): δ / ppm = 1.01 (t, 3H, $^3J_{H,H}$ = 7.37 Hz, $CH_2CH_2\mathit{CH_3}$), 1.02 (t, 3H, $^3J_{H,H}$ = 7.39 Hz, $CH_2CH_2\mathit{CH_3}$), 1.20 (t, 3H, $^3J_{H,H}$ = 7.16 Hz, $OCH_2\mathit{CH_3}$), 1.22 (t, 3H, $^3J_{H,H}$ = 7.16 Hz, $OCH_2\mathit{CH_3}$), 1.74–1.92 (m, 4H, $CH_2\mathit{CH_2}CH_3$), 3.37 (ddd, $^2J_{P,H}$ = 2.54 Hz, $^3J_{P,H}$ = 6.32 Hz, $^3J_{H,H}$ = 9.38 Hz, P*CH*), 3.47 (ddd, $^2J_{P,H}$ = 3.08 Hz, $^3J_{P,H}$ = 6.49 Hz, $^3J_{H,H}$ = 9.62 Hz, P*CH*), 3.99–4.14 (m, 4H, $O\mathit{CH_2}CH_3$), 4.22–4.32 (m, 1H, $\mathit{CH_2}CH_2CH_3$), 4.34–4.42 (m, 2H, $\mathit{CH_2}CH_2CH_3$), 4.49–4.57 (m, 1H, $\mathit{CH_2}CH_2CH_3$).

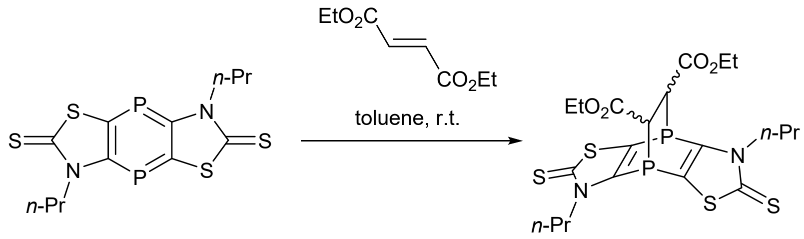
$^{13}C\{^1H\}$ NMR (125.8 MHz, 298.0 K, $CDCl_3$): δ / ppm = 11.3 (d, $^5J_{P,C}$ = 1.16 Hz, $CH_2CH_2\mathit{CH_3}$), 11.3 (d, $^5J_{P,C}$ = 0.87 Hz, $CH_2CH_2\mathit{CH_3}$), 14.1 (s, $OCH_2\mathit{CH_3}$), 14.2 (s, $OCH_2\mathit{CH_3}$), 22.1 (d, $^4J_{P,C}$ = 3.22 Hz, $CH_2\mathit{CH_2}CH_3$), 22.5 (d, $^4J_{P,C}$ = 3.49 Hz, $CH_2\mathit{CH_2}CH_3$), 44.3 (dd, $^1J_{P,C}$ = 18.4 Hz, $^2J_{P,C}$ = 1.99 Hz, P*CH*), 45.2 dd, $^1J_{P,C}$ = 15.8 Hz, $^2J_{P,C}$ = 1.84 Hz, P*CH*), 51.1 (d, $^3J_{P,C}$ = 10.1 Hz, $\mathit{CH_2}CH_2CH_3$), 51.3 (d, $^3J_{P,C}$ = 10.7 Hz, $\mathit{CH_2}CH_2CH_3$), 62.8 (d, $^4J_{P,C}$ = 1.23 Hz, $O\mathit{CH_2}CH_3$), 62.9 (s, $O\mathit{CH_2}CH_3$), 127.0 (dd, $^1J_{P,C}$ = 26.0 Hz, $^2J_{P,C}$ = 4.63 Hz, P*C*S), 128.5 ($^1J_{P,C}$ = 23.4 Hz, $^2J_{P,C}$ = 4.32 Hz,, P*C*S), 152.0 ($^1J_{P,C}$ = 18.6 Hz, $^2J_{P,C}$ = 2.46 Hz, P*C*N), 152.6 ($^1J_{P,C}$ = 16.4 Hz,

$^{2}J_{P,C}$ = 1.92 Hz, P*C*N), 168.6 (d, $^{2}J_{P,C}$ = 9.04 Hz, C*C*O$_2$Et), 169.4 (d, $^{2}J_{P,C}$ = 10.6 Hz, C*C*O$_2$Et), 190.4 (s, *C*=S), 190.8 (d, $^{3}J_{P,C}$ = 2.29 Hz, *C*=S).

^{31}P{^{1}H} NMR (202.5 MHz, 298.0 K, CDCl$_3$): δ / ppm = −75.8 (d, $^{3}J_{P,P}$ = 28.8 Hz), −73.3 (d, $^{3}J_{P,P}$ = 28.8 Hz).

^{31}P NMR (202.5 MHz, 298.0 K, CDCl$_3$): δ / ppm = −75.8 (ddd, $^{3}J_{P,P}$ = 28.8 Hz, $^{2}J_{P,H}$ = 2.53 Hz, $^{3}J_{P,H}$ = 6.06 Hz), −73.3 (dm $^{3}J_{P,P}$ = 25.4 Hz).

2.7 *rel*-(9*R*,10*R*)-9,10-bis(ethylcarboxy)-3,7-di-*n*-propyl-4,8-ethano[1,4]diphosphinino[2,3-d:5,6-d']bis[1,3]thiazole-2,6-dithione (4a')



1 4a'

In a 25 mL Schlenk vessel, 0.3 mL (1.83 mmol, 4.40 eq.) of diethyl fumarate were added to a suspension of 157 mg (0.417 mmol, 1.00 eq.) of **1** in 12 mL toluene. The mixture was stirred for 23 h and volatiles were removed *in vacuo* (10^{-2} mbar). The residue was washed three times with 4 mL of *n*-pentane each and dried *in vacuo* (10^{-2} mbar). The product was obtained as a colourless solid.

Molecular formula: $C_{20}H_{26}N_2O_4P_2S_4$

Molecular weight: 548.63 g/mol

Yield: 154 mg (0.281 mmol, 67%)

Melting point: 118 °C (dec. to **1**)

Elemental analysis:	calculated / %	C 43.79	H 4.78	N 5.11	S 23.37
	found / %	C 43.71	H 4.74	N 5.02	S 23.33

MS (pos. ESI, selected data): m/z (%): 549.032 [M+H]$^{+\bullet}$, 517.060 [M–2 CH$_3$–H]$^{+}$.

IR (ATR Diamond, selected data): ṽ / cm^{-1} = 1714 (s, *v*(CO)), 2904 (w, *v*(CH)), 2941 (w, *v*(CH)), 2974 (w, *v*(CH)).

^{1}H NMR (500.0 MHz, 298.0 K, CDCl$_3$): δ / ppm = 0.99 (t, 6H, $^{3}J_{H,H}$ = 7.41 Hz, CH$_2$CH$_2$C*H$_3$*), 1.03 (t, 6H, $^{3}J_{H,H}$ = 7.42 Hz, CH$_2$CH$_2$C*H$_3$ isomer*), 1.26 (t, 6H, $^{3}J_{H,H}$ = 7.15 Hz, OCH$_2$*CH$_3$*), 1.28 (t, 6H, $^{3}J_{H,H}$ = 7.15 Hz, OCH$_2$*CH$_3$ isomer*), 1.65–1.88 (m, 4+4H, CH$_2$C*H$_2$*CH$_3$, CH$_2$C*H$_2$*CH$_3$ *isomer*), 3.61 (d, $^{2}J_{P,H}$ = 2.20 Hz, P*CH*), 3.82 (d, $^{2}J_{P,H}$ = 2.86 Hz, P*CH isomer*), 4.09–4.20 (m, 4+4H, O*CH$_2$*CH$_3$, O*CH$_2$*CH$_3$ *isomer*), 4.20–4.28 (m, 2H, C*H$_2$*CH$_2$CH$_3$, C*H$_2$*CH$_2$CH$_3$ *isomer*), 4.34–4.51 (m, 6H, C*H$_2$*CH$_2$CH$_3$, C*H$_2$*CH$_2$CH$_3$ *isomer*).

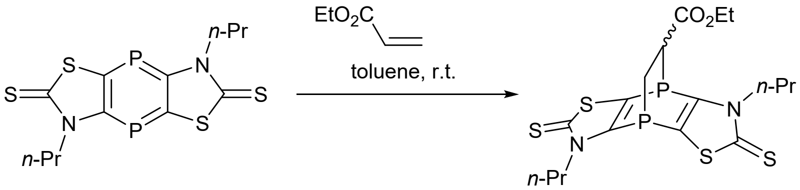
^{13}C{^{1}H} NMR (125.8 MHz, 298.0 K, CDCl$_3$): δ / ppm = 11.2 (s, CH$_2$CH$_2$*CH$_3$ isomer*), 11.2 (s, CH$_2$CH$_2$*CH$_3$*), 14.2 (s, OCH$_2$*CH$_3$*), 14.4 (s, OCH$_2$*CH$_3$ isomer*), 22.2 (dd, $^{4}J_{P,C}$ = 1.63 Hz, $^{5}J_{P,C}$ = 1.63 Hz, CH$_2$*CH$_2$*CH$_3$), 22.4 (dd, $^{4}J_{P,C}$ = 1.78 Hz, $^{5}J_{P,C}$ = 1.78 Hz, CH$_2$*CH$_2$*CH$_3$ isomer), 43.9 (dd, $^{1}J_{P,C}$ = 11.8 Hz, $^{2}J_{P,C}$ = 9.74 Hz, P*CH isomer*), 45.2 (dd, $^{1}J_{P,C}$ = 11.4 Hz, $^{2}J_{P,C}$ = 8.97 Hz, P*CH*), 51.1 (d, $^{3}J_{P,C}$ = 8.96 Hz, *CH$_2$*CH$_2$CH$_3$), 51.1 (d, $^{3}J_{P,C}$ = 9.27 Hz, *CH$_2$*CH$_2$CH$_3$ *isomer*), 63.1 (s, O*CH$_2$*CH$_3$), 63.2 (s, O*CH$_2$*CH$_3$ *isomer*), 127.6 (dd, $^{1}J_{P,C}$ = 13.5 Hz, $^{2}J_{P,C}$ = 1.22 Hz, P*C*S *isomer*), 127.7 (d, $^{1}J_{P,C}$ = 13.7 Hz, P*C*S), 152.1 (dd, $^{1}J_{P,C}$ = 12.4 Hz, $^{2}J_{P,C}$ = 9.29 Hz, P*C*N), 152.4 (dd, $^{1}J_{P,C}$ = 12.4 Hz, $^{2}J_{P,C}$ = 9.66 Hz, P*C*N *isomer*), 169.1 (dd, $^{2}J_{P,C}$ = 3.91 Hz,

$^3J_{P,C}$ = 3.91 Hz, CCO_2Et *isomer*), 170.0 (dd, $^2J_{P,C}$ = 4.71 Hz, $^3J_{P,C}$ = 4.71 Hz, CCO_2Et), 190.5 (s, *C*=S *isomer*), 190.6 (d, $^3J_{P,C}$ = 2.29 Hz, *C*=S).

$^{31}P\{^1H\}$ NMR (202.5 MHz, 298.0 K, $CDCl_3$): δ / ppm = −72.5 (s), −72.3 (s, *isomer*).

^{31}P NMR (202.5 MHz, 298.0 K, $CDCl_3$): δ / ppm = −72.5 (br. s), −72.3 (m, *isomer*); isomeric ratio 53:47.

2.8 3,7-di-*n*-propyl-9-ethylcarboxy-4,8-ethano[1,4]diphosphinino[2,3-d:5,6-d']bis[1,3]thiazole-2,6-dithione (4b)



1 **4b**

In a 20 mL Schlenk vessel, 0.1 mL (0.939 mmol, 2.99 eq.) of ethyl acrylate were added to a suspension of 118.1 mg (0.314 mmol, 1.00 eq.) of **1** in 6 mL toluene. The mixture was stirred for 30 min at ambient temperature and volatiles were removed *in vacuo* (10^{-2} mbar) before washing the off-white residue three times with 1 mL of diethyl ether and three times with 2 mL of *n*-pentane each. After drying *in vacuo* (10^{-2} mbar) the product was obtained as a pale-yellow solid.

Molecular formula: $C_{17}H_{22}N_2O_2P_2S_4$

Molecular weight: 476.56 g/mol

Yield: 57.2 mg (0.120 mmol, 38%)

Melting point: 79 °C

Elemental analysis:	calculated / %	C 42.85	H 4.65	N 5.88	S 26.91
	found / %	C 39.54	H 4.95	N 5.33	S 24.53

MS (pos. ESI, selected data): m/z (%): 461.034 (25) $[M{-}CH_3]^{+\bullet}$, 445.039 (100) $[M{-}S{+}H]^{+\bullet}$, 344.986 (45) $[M{-}CO_2Et{-}2C_2H_5]^{+\bullet}$.

HRMS (pos. ESI) for $C_{17}H_{22}N_2O_2P_2S_4H$ theor./exp. 477.0112/477.0112 $[M{+}H]^{+\bullet}$.

IR (ATR Diamond, selected data): ṽ / cm^{-1} = 1725 (m, *v*(CO), 2870 (w, *v*(CH)), 2934 (w, *v*(CH)), 2962 (w, *v*(CH)).

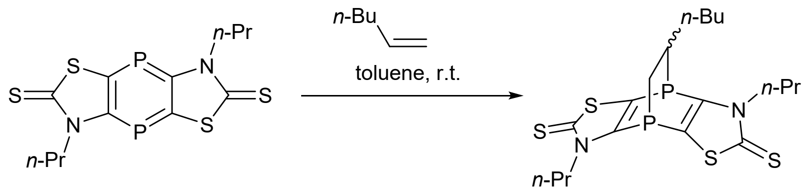
^1H NMR (500.0 MHz, 298.0 K, $CDCl_3$): δ / ppm = 0.96–1.03 (m, 6H, CH_2CH_2*CH_3*), 1.17–1.32 (m, 3H, CO_2CH_2*CH_3*), 1.63–1.87 (m, 4H, CH_2*CH_2*CH_3), 2.05–2.35 (m, 2H, P*CH_2*), 3.13–3.21 (m, 1H, P*CH*CO_2Et),z 4.07–4.28 (m, 2H, CO_2*CH_2*CH_3), 4.30–4.49 (m, 4H, *CH_2*CH_2CH_3).

$^{13}C\{^1H\}$ NMR (125.73 MHz, 298.0 K, $CDCl_3$): δ / ppm = 11.1 (d, $^5J_{P,C}$ = 1.45 Hz CH_2CH_2*CH_3 isomer*), 11.2 (m, CH_2CH_2*CH_3*), 14.2 (s, CO_2CH_2*CH_3 isomer*), 14.4 (s, CO_2CH_2*CH_3*), 22.1 (d, $^4J_{P,C}$ = 3.53 Hz, CH_2*CH_2*CH_3 *isomer*), 22.3 (d, $^4J_{P,C}$ = 3.52 Hz, CH_2*CH_2*CH_3), 22.4 (d, $^4J_{P,C}$ = 3.53 Hz, CH_2*CH_2*CH_3 *isomer*), 22.4 (d, $^4J_{P,C}$ = 3.53 Hz, CH_2*CH_2*CH_3), 24.0 (dd, $^2J_{P,C}$ = 15.3 Hz, $^3J_{P,C}$ = 2.07 Hz, P*CH_2*), 24.4 (dd, $^2J_{P,C}$ = 15.4 Hz, $^3J_{P,C}$ = 2.11 Hz, P*CH_2 isomer*), 40.4 (dd, $^2J_{P,C}$ = 16.9 Hz, $^3J_{P,C}$ = 1.51 Hz, P*CH*), 41.0 (dd $^2J_{P,C}$ = 15.8 Hz, $^3J_{P,C}$ = 1.35 Hz, P*CH isomer*), 51.0 (m, *CH_2*CH_2CH_3), 62.7 (s, CO_2*CH_2*CH_3 *isomer*), 62.8 (s, CO_2*CH_2*CH_3), 125.6 (dd, $^1J_{P,C}$ = 27.6 Hz, $^2J_{P,C}$ = 5.22 Hz, P*C*S), 127.0 (dd, $^1J_{P,C}$ = 24.6 Hz, $^2J_{P,C}$ = 5.85 Hz, P*C*S *isomer*), 128.8 (dd, $^1J_{P,C}$ = 23.8 Hz, $^2J_{P,C}$ = 4.74 Hz, P*C*S *isomer*), 129.5 (dd, $^1J_{P,C}$ = 24.3 Hz, $^2J_{P,C}$ = 4.12 Hz, P*C*S), 150.8 (dd, $^{1}J_{P,C}$ = 19.6 Hz, $^{2}J_{P,C}$ = 3.27 Hz P*C*N *isomer*), 152.1 (dd, $^{1}J_{P,C}$ = 17.7 Hz, $^{2}J_{P,C}$ = 3.64 Hz P*C*N), 153.5 (dd, $^{1}J_{P,C}$ = 16.9 Hz, $^{2}J_{P,C}$ = 2.46 Hz P*C*N), 153.9 (dd, $^{1}J_{P,C}$ = 17.0 Hz, $^{2}J_{P,C}$ = 2.05 Hz, P*C*N *isomer*), 170.2 (d, $^{2}J_{P,C}$ = 8.04 Hz, *C*O_2Et), 171.1 (d, $^{2}J_{P,C}$ = 8.72 Hz, *C*O_2Et *isomer*), 190.3 (m, *C*=S).

^{31}P{^{1}H} NMR (202.4 MHz, 298.0 K, $CDCl_3$): δ / ppm = −80.0 (d, $^{3}J_{P,P}$ = 29.3 Hz, PCH_2 *isomer*), −79.7 (d, $^{3}J_{P,P}$ = 28.8 Hz, PCH_2), −75.4 (d, $^{3}J_{P,P}$ = 29.3 Hz, $PCHCO_2$Et *isomer*), −74.1 (d, $^{3}J_{P,P}$ = 29.0 Hz, $PCHCO_2$Et).

^{31}P NMR (202.4 MHz, 298.0 K, $CDCl_3$): δ / ppm = −79.8 (m, PCH_2, PCH_2 *isomer*), −75.4 (dm, $^{3}J_{P,P}$ = 29.4 Hz, $PCHCO_2$Et *isomer*), −74.1 (dm, $^{3}J_{P,H}$ = 29.0 Hz, $PCHCO_2$Et).

2.9 3,7-di-*n*-propyl-9-*n*-butyl-4,8-ethano[1,4]diphosphinino[2,3-d:5,6-d']bis[1,3]thiazole-2,6-dithione (4c)



1 **4c**

In a 20 mL Schlenk vessel, 0.1 mL (0.796 mmol, 2.08 eq.) of 1-hexene was added to a suspension of 143.8 mg (0.382 mmol, 1.00 eq.) of **1** in 10 mL toluene. The mixture was stirred for 4 h before removing volatiles *in vacuo* (10^{-2} mbar). The residue was washed four times with 5 mL of *n*-pentane each and dried *in vacuo* (10^{-2} mbar). The product was obtained as a colourless solid.

Molecular formula: $C_{18}H_{26}N_2P_2S_4$

Molecular weight: 460.60 g/mol

Yield: 99.5 mg (0.216 mmol, 57%)

Melting point: 130 °C (dec. to **1**)

Elemental analysis:					
	calculated / %	C 46.94	H 5.69	N 6.08	S 27.84
	found / %	C 41.54	H 5.20	N 5.24	S 23.18

MS (EI, 70 eV, selected data): m/z (%): m/z = 460.0 $[M]^{+\bullet}$, 375.9 $[M-C_6H_{12}]^{+\bullet}$, 333.8 $[M-C_6H_{12}-C_3H_7+H]^{+\bullet}$, 291.8 $[M-C_6H_{12}-2\ C_3H_7+2\ H]^{+\bullet}$, 84.0 $[C_6H_{12}]^{+\bullet}$.

IR (ATR Diamond, selected data): ṽ / cm^{-1} = 2868 (w, *v*(CH)), 2921 (m, *v*(CH)), 2955 (w, *v*(CH)).

^{1}H NMR (700.4 MHz, 298.0 K, $CDCl_3$): δ / ppm = 0.92 (td, 6H, $^{3}J_{H,H}$ = 7.34 Hz, $^{4}J_{H,H}$ = 3.74 Hz, $CH_2CH_2CH_2CH_3$), 1.01 (td, 6H, $^{3}J_{H,H}$ = 7.40 Hz, $^{4}J_{H,H}$ = 2.74 Hz, $CH_2CH_2CH_3$), 1.03 (q, 6H, $^{3}J_{H,H}$ = 7.74 Hz, $CH_2CH_2CH_3$), 1.18–1.26 (m, 1H, $CH_2CH_2CH_2CH_3$), 1.28–1.38 (m, PCH_2 (2H), $CH_2CH_2CH_2CH_3$ (4H), $CH_2CH_2CH_2CH_3$ (1H)), 1.41–1.54 (m, 6H, $CH_2CH_2CH_2CH_3$ (4H), $CH_2CH_2CH_2CH_3$ (2H)) 1.70–1.94 (m, 8H, $CH_2CH_2CH_3$), 2.04–2.13 (m, 2H, PCH^{n}Bu, PCH^{n}Bu *isomer*), 2.20–2.28 (m, 2H, PCH_2) 4.28–4.33 (m, 1H, $CH_2CH_2CH_3$), 4.36–4.46 (m, 7H, $CH_2CH_2CH_3$).

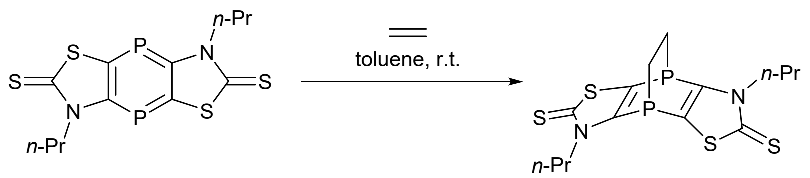
^{13}C{^{1}H} NMR (125.73 MHz, 298.0 K, $CDCl_3$): δ / ppm = (176.1 MHz, 298.0 K, $CDCl_3$): δ / ppm = 11.3 (d, $^{5}J_{P,C}$ = 1.21 Hz, $CH_2CH_2CH_3$), 11.3 (d, $^{5}J_{P,C}$ = 1.40 Hz, $CH_2CH_2CH_3$ *isomer*), 14.0 (s, $CH_2CH_2CH_2CH_3$), 14.0 (s, $CH_2CH_2CH_2CH_3$ *isomer*), 22.3 (d, $^{4}J_{P,C}$ = 3.00 Hz, $CH_2CH_2CH_3$), 22.4 (d, $^{4}J_{P,C}$ = 3.46 Hz, $CH_2CH_2CH_3$ *isomer*), 22.4 (d, $^{4}J_{P,C}$ = 3.48 Hz, $CH_2CH_2CH_3$, $CH_2CH_2CH_3$ *isomer*), 22.5 (s, $CH_2CH_2CH_2CH_3$ *isomer*), 22.6 (s, $CH_2CH_2CH_2CH_3$), 27.4 (dd, $^{1}J_{P,C}$ = 12.3 Hz, $^{2}J_{P,C}$ = 3.62 Hz, PCH_2, isomer), 27.7 (dd, $^{1}J_{P,C}$ = 12.4 Hz, $^{2}J_{P,C}$ = 3.60 Hz, PCH_2), 31.1 (d, $^{4}J_{P,C}$ = 15.4 Hz, $CH_2CH_2CH_2CH_3$), 31.3 (d, $^{4}J_{P,C}$ = 15.4 Hz, $CH_2CH_2CH_2CH_3$

isomer), 34.9 (dd, ${}^4J_{P,C}$ = 17.3 Hz, ${}^4J_{P,C}$ = 1.09 Hz, P*CH*ⁿBu), 35.2 (dd, ${}^4J_{P,C}$ = 10.1 Hz, ${}^4J_{P,C}$ = 1.79 Hz, $CH_2CH_2CH_2CH_3$), 35.4 (dd, ${}^4J_{P,C}$ = 16.1 Hz, ${}^4J_{P,C}$ = 1.14 Hz, P*CH*ⁿBu *isomer*), 35.7 (dd, ${}^4J_{P,C}$ = 10.6 Hz, ${}^4J_{P,C}$ = 1.89 Hz, $CH_2CH_2CH_2CH_3$ *isomer*), 50.9 (d, ${}^3J_{P,C}$ = 10.7 Hz, $CH_2CH_2CH_3$ *isomer*), 51.0 (d, ${}^3J_{P,C}$ = 10.7 Hz, $CH_2CH_2CH_3$), 51.1 (d, ${}^3J_{P,C}$ = 10.5 Hz, $CH_2CH_2CH_3$ *isomer*), 126.2 (dd, ${}^1J_{P,C}$ = 28.7 Hz, ${}^2J_{P,C}$ = 5.67 Hz, P*C*S), 127.2 (dd, ${}^1J_{P,C}$ = 23.8 Hz, ${}^2J_{P,C}$ = 5.30 Hz, P*C*S), 128.9 (dd, ${}^1J_{P,C}$ = 23.5 Hz, ${}^2J_{P,C}$ = 5.40 Hz, P*C*S *isomer*), 129.6 (dd, ${}^1J_{P,C}$ = 24.0 Hz, ${}^2J_{P,C}$ = 6.21 Hz, P*C*S *isomer*), 151.6 (dd, ${}^1J_{P,C}$ = 22.0 Hz, ${}^2J_{P,C}$ = 3.50 Hz, P*C*N *isomer*), 152.6 (dd, ${}^1J_{P,C}$ = 16.8 Hz, ${}^2J_{P,C}$ = 3.24 Hz, P*C*N *isomer*), 153.7 (dd, ${}^1J_{P,C}$ = 16.1 Hz, ${}^2J_{P,C}$ = 3.25 Hz, P*C*N), 154.9 (dd, ${}^1J_{P,C}$ = 16.9 Hz, ${}^2J_{P,C}$ = 3.97 Hz, P*C*N), 190.2 (d, ${}^3J_{P,C}$ = 1.98 Hz, *C*=S *isomer*), 190.3 (d, ${}^3J_{P,C}$ = 2.07 Hz, *C*=S), 190.4 (d, ${}^3J_{P,C}$ = 1.86 Hz, *C*=S *isomer*), 190.5 (d, ${}^3J_{P,C}$ = 2.00 Hz, *C*=S).

$^{31}P\{^1H\}$ NMR (121.5 MHz, 298.0 K, $CDCl_3$): δ / ppm = −77.7 (d, ${}^3J_{P,P}$ = 24.5 Hz, PCH_2, *isomer*), −77.0 (d, ${}^3J_{P,P}$ = 24.2 Hz, PCH_2), −73.6 (d, ${}^3J_{P,P}$ = 24.2 Hz, *P*CHⁿBu), −72.6 (d, ${}^3J_{P,P}$ = 24.5 Hz, *P*CHⁿBu, *isomer*).

^{31}P NMR (121.5 MHz, 298.0 K, $CDCl_3$): δ / ppm = −77.7 (dt, ${}^3J_{P,P}$ = 24.5 Hz, ${}^2J_{P,H}$ = 7.90 Hz, PCH_2, *isomer*), −77.0 (dt, ${}^3J_{P,P}$ = 24.2 Hz, ${}^2J_{P,H}$ = 8.15 Hz, PCH_2), −73.6 (m, *P*CHⁿBu), −72.6 (m, *P*CHⁿBu, *isomer*).

2.10 3,7-di-*n*-propyl-4,8-ethano[1,4]diphosphinino[2,3-d:5,6-d']bis[1,3]thiazole-2,6-dithione (4d)



1 4d

In a 10 mL Schlenk vessel, 7.0 mg (0.0186 mmol) of **1** was stirred in dichloromethane under an atmosphere of ethene. After 2 h, volatiles were removed *in vacuo* (10^{-2} mbar) and the product was obtained as a colourless solid.

Molecular formula: $C_{14}H_{18}N_2P_2S_4$

Molecular weight: 404.50 g/mol

Yield: 7.5 mg (0.0185 mmol, 100%)

Melting point: 183 °C (dec. to **1**)

Elemental analysis:					
	calculated / %	C 41.57	H 4.49	N 6.93	S 31.70
	found / %	C 41.36	H 4.56	N 6.82	S 32.48

MS (pos. ESI, selected data): m/z (%): 403.9 $[M]^{+\bullet}$, 376.0 $[M–C_2H_4]^{+\bullet}$, 333.8 $[M–C_2H_4–C_3H_7+H]^{+\bullet}$, 291.9 $[M–C_2H_4–2\ C_3H_7+2\ H]^{+\bullet}$.

IR (ATR Diamond, selected data): ṽ / cm^{-1} = 2869 (w, *v*(CH)), 2927 (w, *v*(CH)), 2957 (w, *v*(CH)).

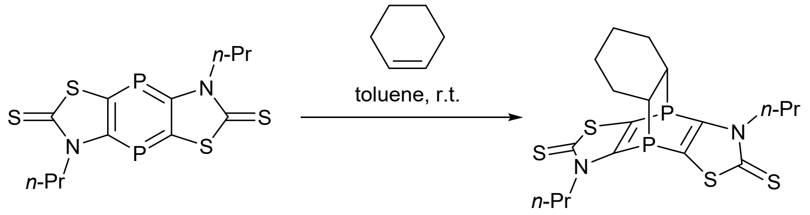
^1H NMR (400.3 MHz, 298.1 K, $CDCl_3$): δ / ppm = 1.00 (t, 6H, ${}^3J_{H,H}$ = 7.39 Hz, $CH_2CH_2CH_3$), 1.69–1.95 (m, 4H, $CH_2CH_2CH_3$), 1.87–1.92 (m, 4H, PCH_2), 4.31-4.44 (m, 4H, $CH_2CH_2CH_3$).

$^{13}C\{^1H\}$ NMR (100.7 MHz, 298.2 K, $CDCl_3$): δ / ppm = 11.3 (s, $CH_2CH_2CH_3$), 19.6 (t, ${}^{1/2}J_{P,C}$ = 7.09 Hz, PCH_2), 22.4 (t, ${}^{4/5}J_{P,C}$ = 1.89 Hz, $CH_2CH_2CH_3$), 50.9 (t, ${}^{3/4}J_{P,C}$ = 5.07 Hz, $CH_2CH_2CH_3$), 127.8 (dd, ${}^1J_{P,C}$ = 16.3 Hz, ${}^2J_{P,C}$ = 13.4 Hz, P*C*S), 153.0 (dd, ${}^1J_{P,C}$ = 11.0 Hz, ${}^2J_{P,C}$ = 9.07 Hz, P*C*N), 190.2 (s, *C*=S).

$^{31}P\{^1H\}$ NMR (162.0 MHz, 298.1 K, $CDCl_3$): δ / ppm = −82.1 (s).

^{31}**P NMR** (121.5 MHz, 298.1 K, $CDCl_3$): δ / ppm = −82.1 (m).

2.11 *rel*-(9*S*,10*R*)-3,7-di-*n*-propyl-4,8-[1′,2′]-cyclohexano[1,4]diphosphinino[2,3-d:5,6-d']bis[1,3]thiazole-2,6-dithione (4e)



In a 25 mL Schlenk vessel, 0.25 mL (2.47 mmol, 11.12 eq.) of cyclohexene were added to a suspension of 83.4 mg (0.222 mmol, 1.00 eq) of **1** in 10 mL toluene. The mixture was stirred for 24 h at ambient temperature and volatiles were removed *in vacuo* (10^{-2} mbar). The residue was washed three times with 3 mL of *n*-pentane each and dried *in vacuo* (10^{-2} mbar). The product was obtained as a colourless solid.

Molecular formula: $C_{18}H_{24}N_2P_2S_4$

Molecular weight: 458.60 g/mol

Yield: 75.1 mg (0.164 mmol, 74%)

Melting point: 79 °C

Elemental analysis:	calculated / %	C 47.14	H 5.28	N 6.11
	found / %	C 42.34	H 5.59	N 5.30

MS (EI, 70 eV, selected data): m/z (%): 475.0 (2) $[M+OH]^{+\bullet}$, 459.0 (1) $[M+H]^{+\bullet}$, 458.0 (1) $[M]^{+\bullet}$, 443.0 (2) $[M-CH_3]^{+\bullet}$, 427.1 (9) $[M-2CH_3-H]^{+\bullet}$, 219.2 (100) $[M-2CS_2-C_3H_7-H]^{+\bullet}$.

HRMS (pos. ESI) for $C_{18}H_{24}N_2P_2S_4$ theor./exp. 459.0370/459.0370 $[M+H]^{+\bullet}$.

IR (ATR Diamond, selected data): ṽ / cm^{-1} = 2871 (w, *ν*(CH)), 2929 (m, *ν*(CH)).

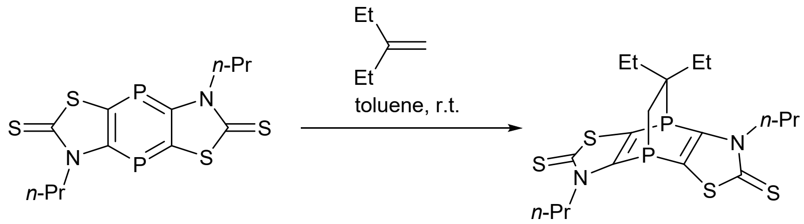
^{1}**H NMR** (700.4 MHz, 298.0 K, $CDCl_3$): δ / ppm = 0.77–0.90 (m, 2H, $PCHCH_2CH_2$), 1.00 (t, 3H, $^3J_{H,H}$ = 7.36 Hz, $CH_2CH_2CH_3$), 1.02 (t, 3H, $^3J_{H,H}$ = 7.40 Hz, $CH_2CH_2CH_3$), 0.94–1.08 (m, 2H, $PCHCH_2CH_2$) 1.67–1.78 (m, 4H, $PCHCH_2$), 1.78–1.92 (m, 4H, $CH_2CH_2CH_2$), 2.08–2.20 (m, 2H, PC*H*), 4.26–4.45 (m, 4H, $CH_2CH_2CH_3$).

^{13}**C{^{1}H} NMR** (176.1 MHz, 298.0 K, $CDCl_3$): δ / ppm = 11.3 (s, $CH_2CH_2CH_3$), 21.4 (d, $^2J_{P,H}$ = 17.7 Hz, $PCHCH_2$), 21.6 (d, $^2J_{P,H}$ = 17.4 Hz, $PCHCH_2$), 22.3 (d, $^4J_{P,C}$ = 3.18 Hz, $CH_2CH_2CH_3$), 22.4 (d, $^4J_{P,C}$ = 3.43 Hz, $CH_2CH_2CH_3$), 25.0 (d, $^3J_{P,H}$ = 19.9 Hz, $PCHCH_2CH_2$), 25.4 (d, $^3J_{P,H}$ = 17.6 Hz, $PCHCH_2CH_2$), 34.8 (dd, $^1J_{P,H}$ = 10.3 Hz, $^2J_{P,H}$ = 3.67 Hz, PC*H*), 35.3 (dd, $^1J_{P,H}$ = 10.9 Hz, $^2J_{P,H}$ = 3.65 Hz, PC*H*), 51.0 (d, $^3J_{P,C}$ = 10.2 Hz, $CH_2CH_2CH_3$), 51.1 (d, $^3J_{P,C}$ = 10.4 Hz, $CH_2CH_2CH_3$), 127.3 (dd, $^1J_{P,C}$ = 27.4 Hz, $^2J_{P,C}$ = 5.67 Hz, P*C*S), 127.6 (dd, $^1J_{P,C}$ = 23.9 Hz, $^2J_{P,C}$ = 5.93 Hz, P*C*S), 152.4 (dd, $^1J_{P,C}$ = 17.0 Hz, $^2J_{P,C}$ = 3.60 Hz P*C*N), 153.3 (dd, $^1J_{P,C}$ = 20.3 Hz, $^2J_{P,C}$ = 3.25 Hz, P*C*N), 190.3 (s, *C*=S), 190.6 (s, *C*=S).

^{31}**P{^{1}H} NMR** (162.0 MHz, 298.0 K, $CDCl_3$): δ / ppm = −69.5 (d, $^3J_{P,H}$ = 20.4 Hz), −68.3 (d, $^3J_{P,H}$ = 20.4 Hz).

^{31}P NMR (202.4 MHz, 298.0 K, $CDCl_3$): δ / ppm = (162.0 MHz, 298.0 K, $CDCl_3$): δ / ppm = −69.5 (m), −68.3 (m).

2.12 9,9-diethyl-3,7-di-*n*-propyl-4,8-ethano[1,4]diphosphinino[2,3-d:5,6-d']bis[1,3]thiazole-2,6-dithione (4f)



1 4f

In a 10 mL Schlenk vessel, 0.05 mL (0.409 mmol, 2.42 eq.) of 2-ethyl-1-butene were added to a suspension of 63.7 mg (0.169 mmol, 1.00 eq.) of **1** in 4 mL toluene. The mixture was stirred for 48 h at ambient temperature and volatiles were removed *in vacuo* (10^{-2} mbar). The residue was washed three times with 2 mL of *n*-pentane each and dried *in vacuo* (10^{-2} mbar). The product was obtained as a colourless solid.

Molecular formula: $C_{18}H_{26}N_2P_2S_4$

Molecular weight: 460.61 g/mol

Yield: 39 mg (0.085 mmol, 80%)

Melting point: 150 °C (dec. to **1**)

Elemental analysis:				
	calculated / %	C 46.94	H 5.69	N 6.08
	found / %	C 47.88	H 6.09	N 5.90

MS (EI, 70 eV, selected data): m/z (%): 460.1 (2) $[M]^{+\bullet}$, 376.0 (71) $[M-C_6H_{12}]^{+\bullet}$, 334.0 (35) $[M-C_6H_{12}-C_3H_7+H]^{+\bullet}$, 291.9 (100) $[M-C_6H_{12}-2\ C_3H_7+2\ H]^{+\bullet}$.

HRMS (neg. ESI) for $C_{18}H_{26}N_2P_2S_4OH$ theor./exp. 477.0476/477.0479 $[M+OH]^{+\bullet}$.
for $C_{12}H_{15}N_2P_2S_4OH$ theor./exp. 392.9537/392.9535 $[M-C_6H_{12}+OH]^{+\bullet}$.
(pos. ESI) for $C_{18}H_{26}N_2P_2S_4H$ theor./exp. 461.0527/461.0531 $[M+H]^{+\bullet}$.
for $C_{12}H_{15}N_2P_2S_4H$ theor./exp. 376.9588/376.9586 $[M-C_6H_{12}+H]^{+\bullet}$.

^{1}H NMR (500.0 MHz, 298.0 K, $CDCl_3$): δ / ppm = 0.92–1.02 (m, 12H, CH_2CH_2, $CCH_2\mathit{CH_3}$), 1.16–1.50 (m, 4H, $C\mathit{CH_2}CH_3$), 1.56 (ddd, 1H, $^2J_{H,H}$ = 14.4 Hz, $^2J_{P,H}$ = 8.01 Hz, $^3J_{P,H}$ = 2.22 Hz $P\mathit{CH_2}$), 1.67 (ddd, 1H, $^2J_{H,H}$ = 14.4 Hz, $^2J_{P,H}$ = 7.19 Hz, $^3J_{P,H}$ = 2.18 Hz $P\mathit{CH_2}$), 1.70–1.92 (m, 4H, $CH_2\mathit{CH_2}CH_3$), 4.18 (dddd, 1H, $^2J_{H,H}$ = 13.1 Hz, $^3J_{H,H}$ = 9.91 Hz, $^3J_{H,H}$ = 6.17 Hz, $^4J_{P,H}$ = 1.93 Hz, $\mathit{CH_2}CH_2CH_3$), 4.38 (td, 2H, $^3J_{H,H}$ = 7.53 Hz, $^4J_{P,H}$ = 1.15 Hz, $\mathit{CH_2}CH_2CH_3$) 4.50 (ddd, 1H, $^2J_{H,H}$ = 13.1 Hz, $^3J_{H,H}$ = 10.0 Hz, $^3J_{H,H}$ = 5.18 Hz, $\mathit{CH_2}CH_2CH_3$).

^{13}C{^{1}H} NMR (125.8 MHz, 298.0 K, $CDCl_3$): δ / ppm = 9.21 (d, $^3J_{P,C}$ = 6.27 Hz, $C(CH_2\mathit{CH_3})_2$), 9.33 (d, $^3J_{P,C}$ = 7.96 Hz, $C(CH_2\mathit{CH_3})_2$), 11.2 (d, $^5J_{P,C}$ = 1.47 Hz, $CH_2CH_2\mathit{CH_3}$), 11.3 (s, $CH_2CH_2\mathit{CH_3}$), 22.1 (d, $^4J_{P,C}$ = 2.75 Hz, $CH_2\mathit{CH_2}CH_3$), , 22.3 (d, $^4J_{P,C}$ = 3.39 Hz, $CH_2\mathit{CH_2}CH_3$), 29.9 (d, $^2J_{P,C}$ = 19.8 Hz, $C(\mathit{CH_2}CH_3)_2$), 30.3 (d, $^2J_{P,C}$ = 20.5 Hz, $C\mathit{CH_2}CH_3$), 34.1 (dd, $^1J_{P,C}$ = 12.8 Hz, $^2J_{P,C}$ = 4.25 Hz, $P\mathit{CH_2}$), 46.3 (dd, $^1J_{P,C}$ = 9.56 Hz, $^2J_{P,C}$ = 2.16 Hz, $\mathit{C}(CH_2CH_3)_2$), 51.1 (dd, $^3J_{P,C}$ = 10.7 Hz, $\mathit{CH_2}CH_2CH_3$), 51.1 (dd, $^3J_{P,C}$ = 10.1 Hz, $\mathit{CH_2}CH_2CH_3$), 128.2 (dd, $^3J_{P,C}$ = 23.1 Hz, $^2J_{P,C}$ = 4.90 Hz, P*C*S), 128.9 (dd, $^3J_{P,C}$ = 27.6 Hz, $^2J_{P,C}$ = 6.03 Hz, P*C*S), 153.0 (dd, $^1J_{P,C}$ = 16.3 Hz, $^2J_{P,C}$ = 2.86 Hz, P*C*N), 154.2 (dd, $^1J_{P,C}$ = 21.1 Hz, $^2J_{P,C}$ = 3.84 Hz, P*C*N), 190.4 (d, $^3J_{P,C}$ = 2.03 Hz, *C*=S), 190.5 (d, $^3J_{P,C}$ = 1.99 Hz, *C*=S).

$^{31}P\{^{1}H\}$ NMR (202.4 MHz, 298.0 K, $CDCl_3$): δ / ppm = −73.4 (d, $^{3}J_{P,P}$ = 23.4 Hz, *P*CH_2), −63.4 (d, $^{3}J_{P,P}$ = 23.4 Hz, *P*Et_2.

^{31}P NMR (202.4 MHz, 298.0 K, $CDCl_3$): δ / ppm = −73.4 (dt, $^{3}J_{P,P}$ = 23.4 Hz, $^{2}J_{P,H}$ = 7.52 Hz, *P*CH_2), −63.4 (m, *P*Et_2).

3 NMR spectra

3.1 2a

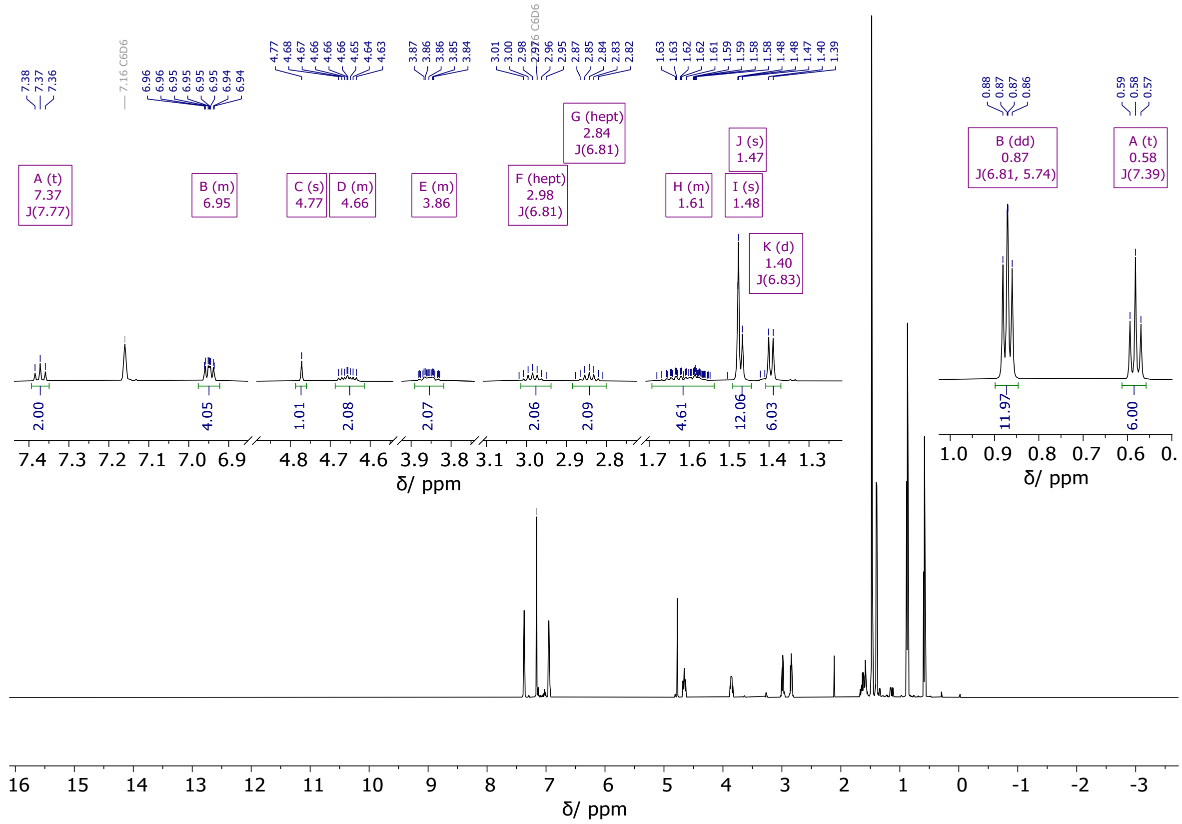


Fig. S1 ^{1}H NMR spectrum of **2a** in C_6D_6.

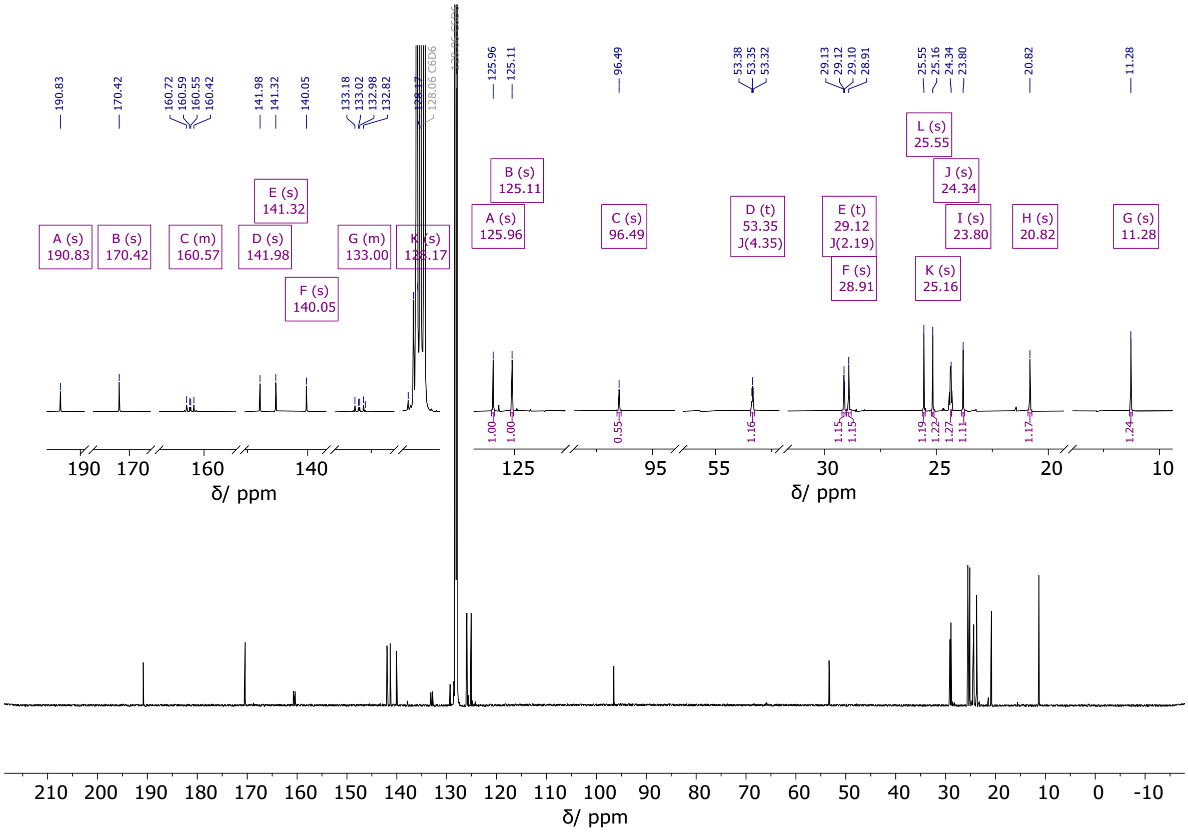


Fig. S2 ^{13}C NMR spectrum of **2a** in C_6D_6.

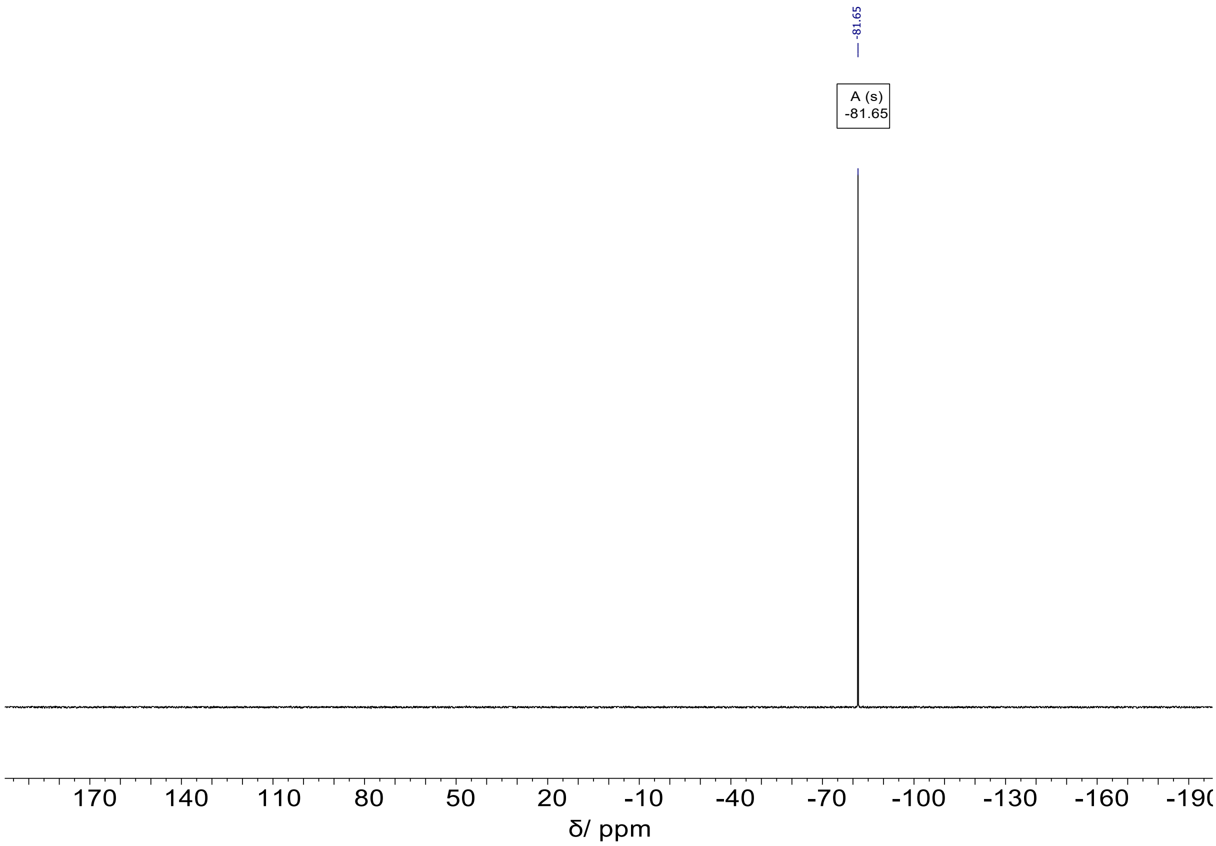


Fig. S3 $^{31}P\{^{1}H\}$ NMR spectrum of **2a** in C_6D_6.

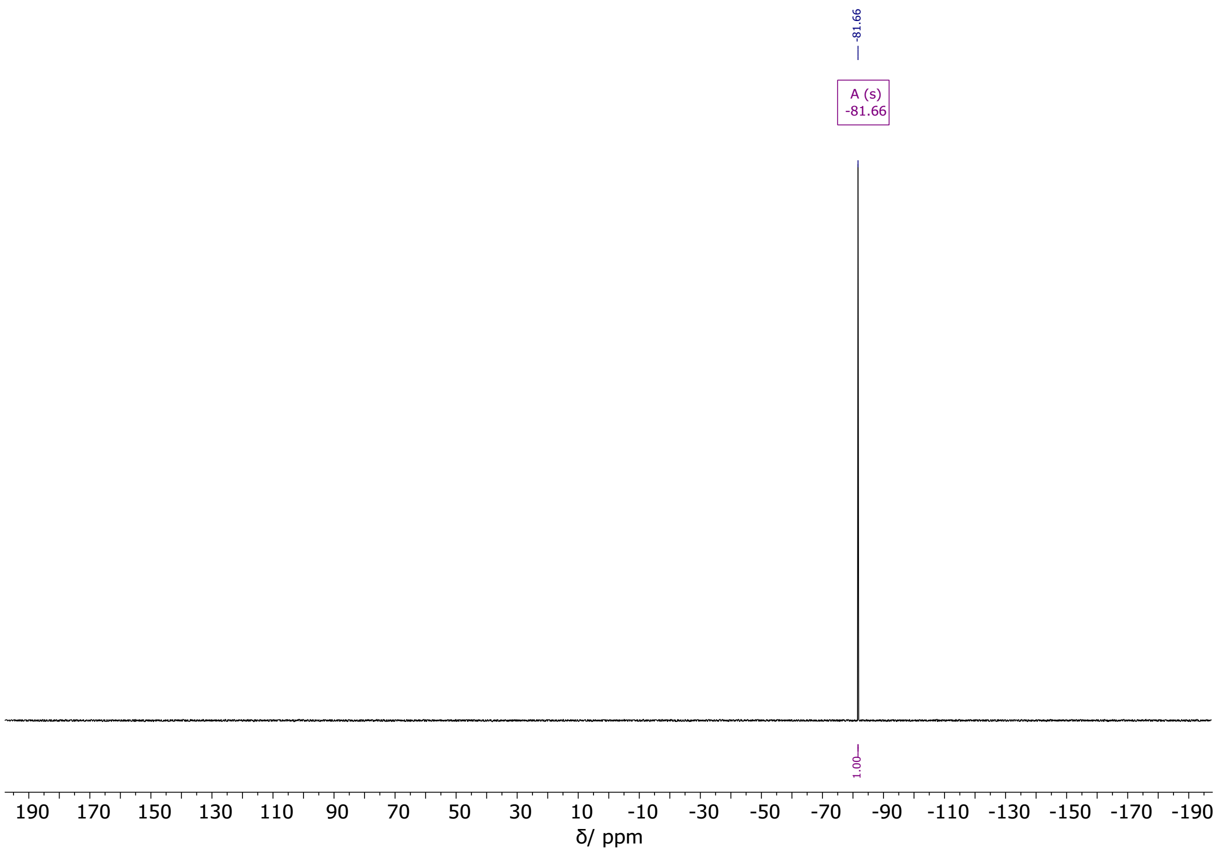


Fig. S4 ^{31}P NMR spectrum of **2a** in C_6D_6.

3.2 2b

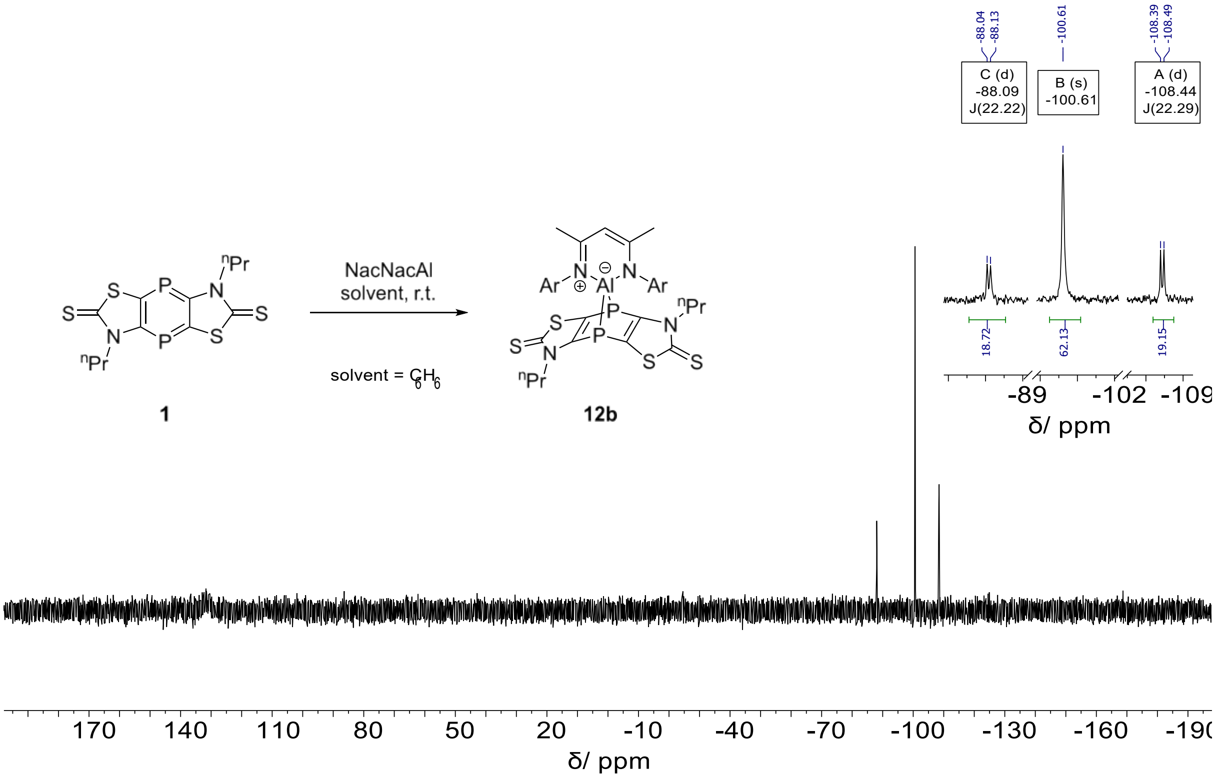


Fig. S5 $^{31}P\{^{1}H\}$ NMR spectrum of **2b** in benzene.

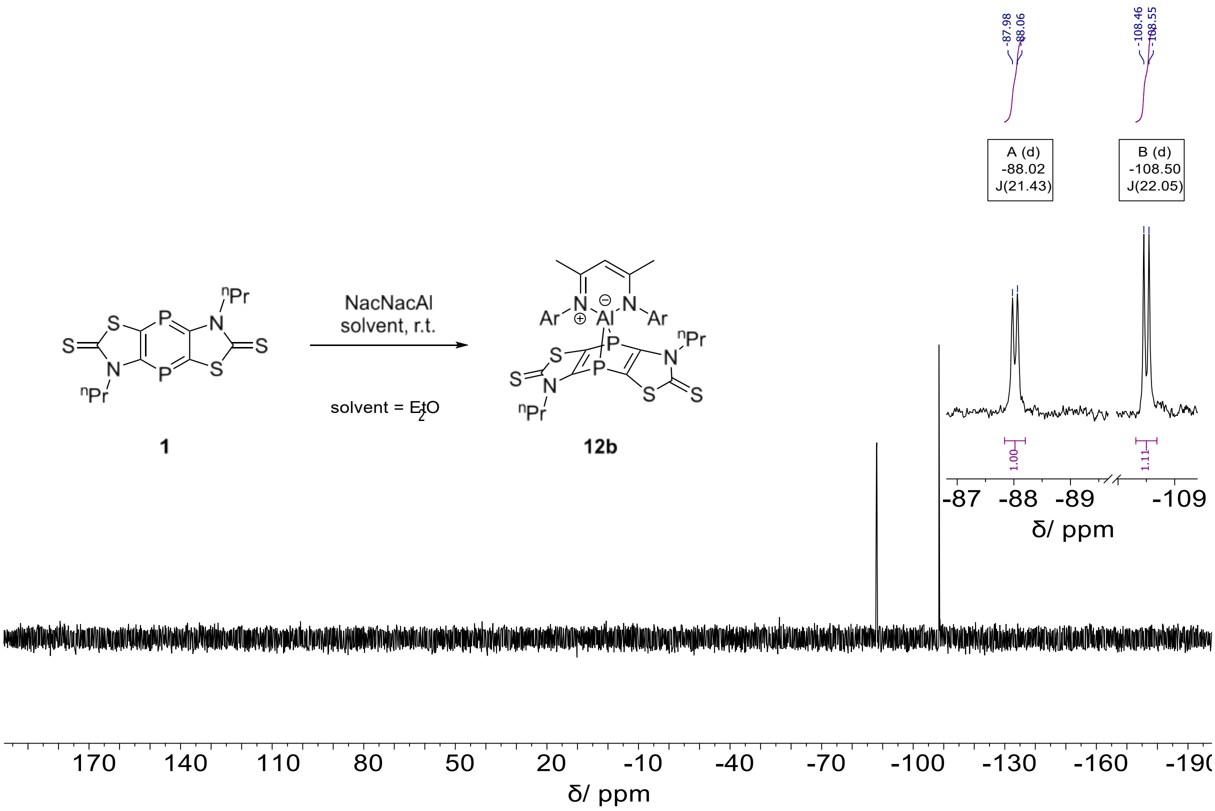


Fig. S6 $^{31}P\{^{1}H\}$ NMR spectrum of **2b** in benzene.

3.3 3a

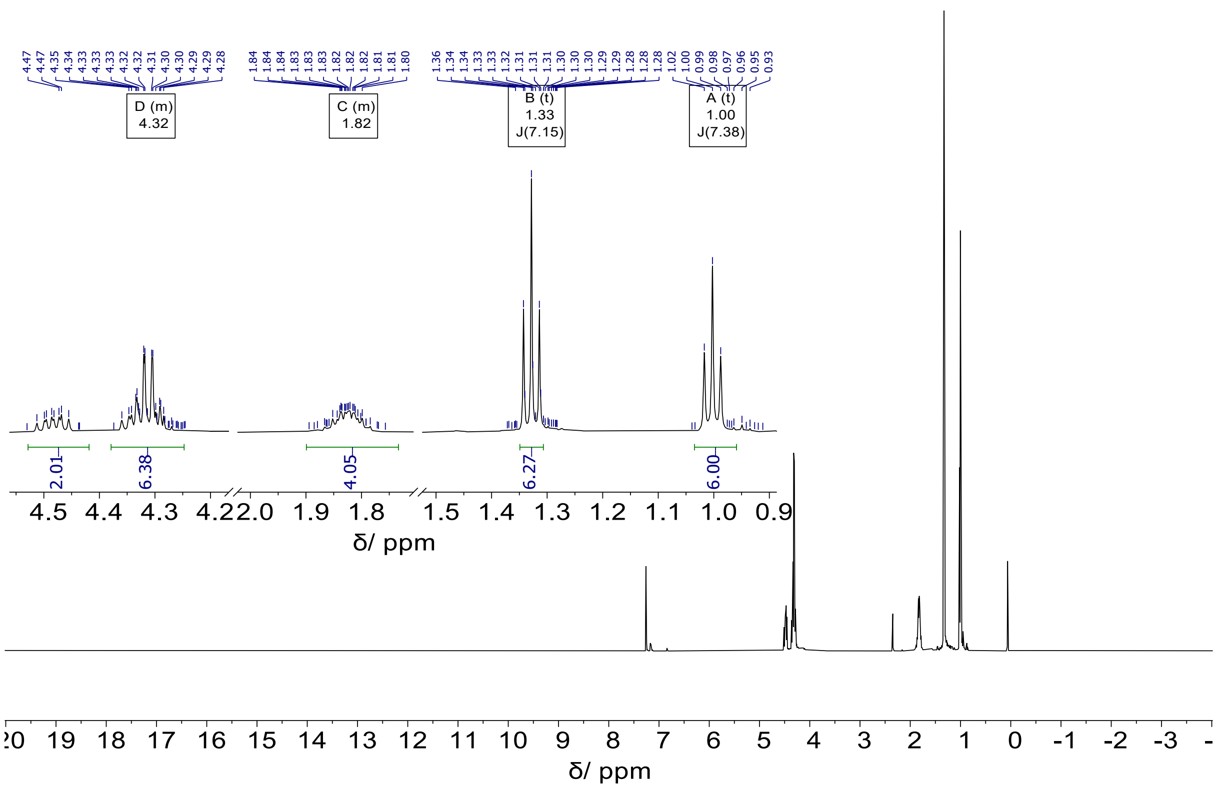


Fig. S7 ^{1}H NMR spectrum of **3a** in $CDCl_3$.

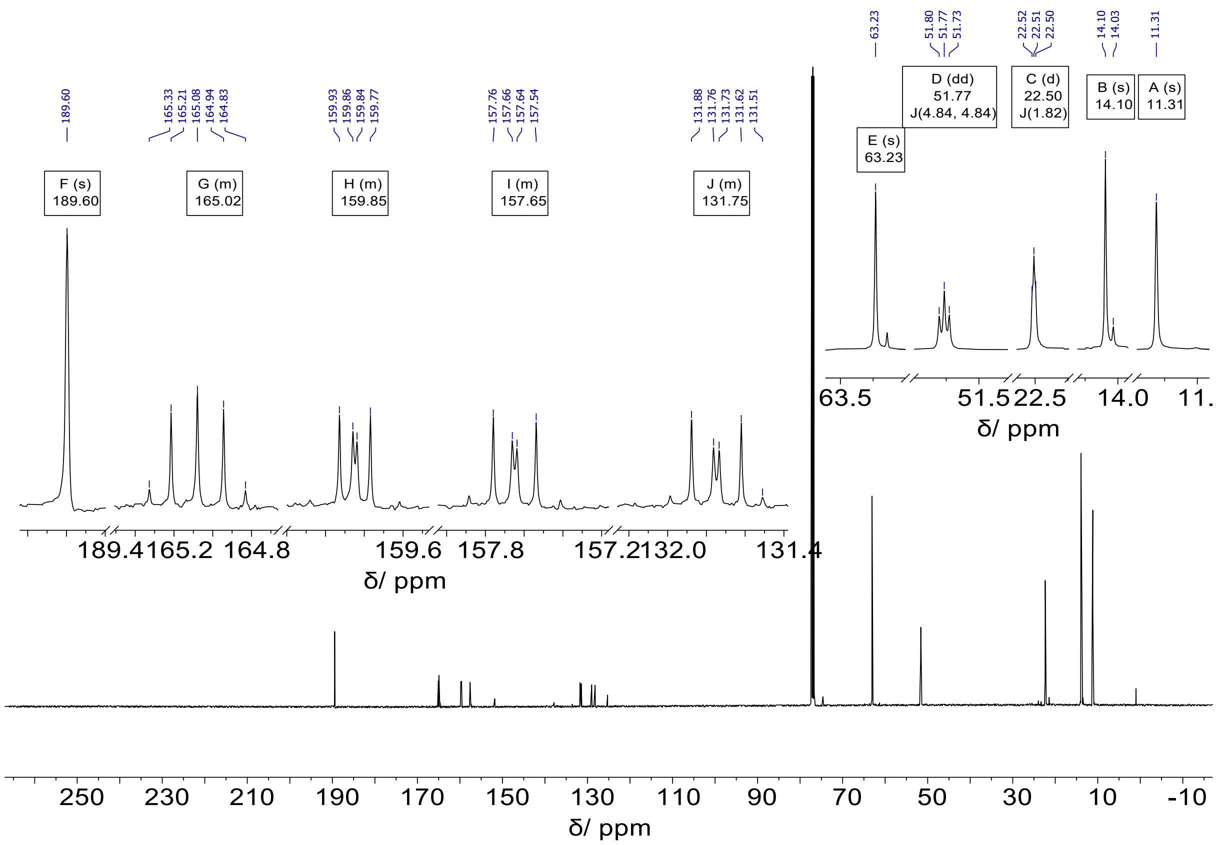


Fig. S8 ^{13}C NMR spectrum of **3a** in $CDCl_3$.

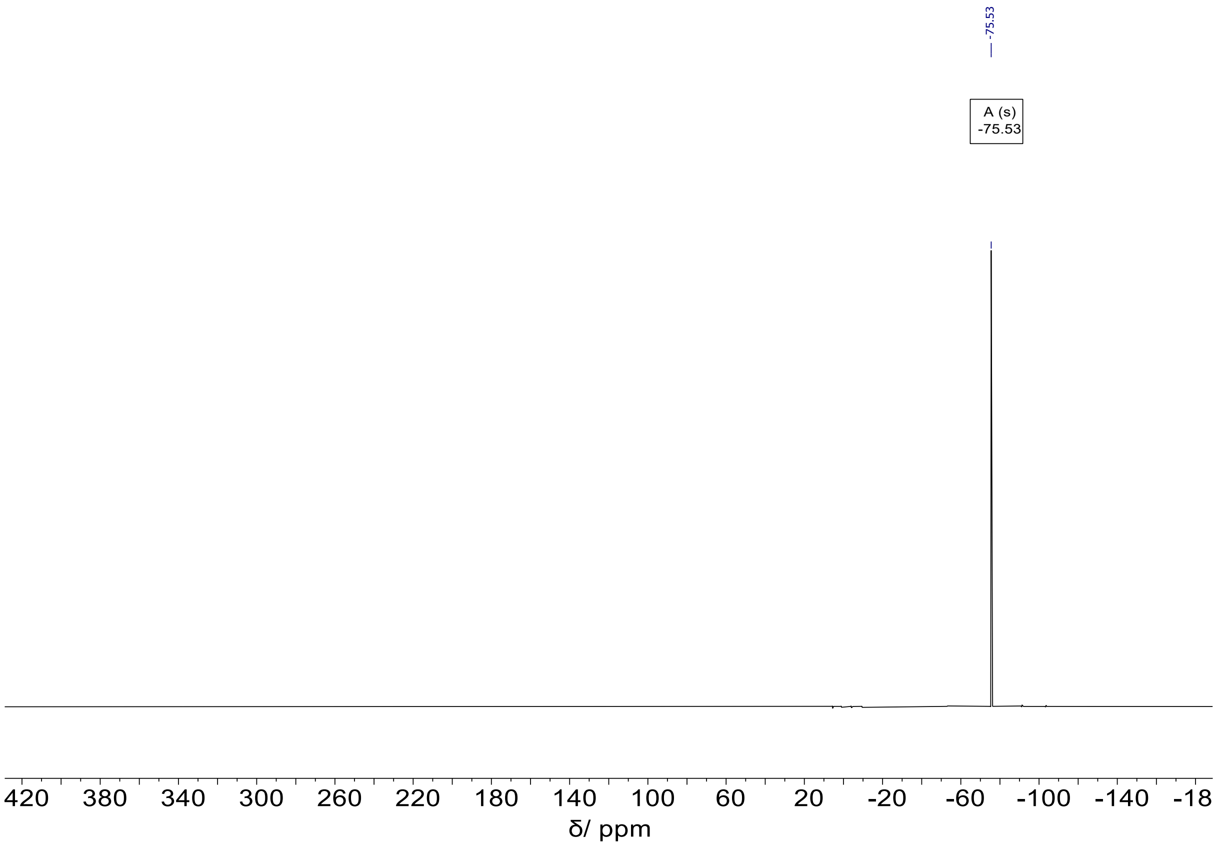


Fig. S9 $^{31}P\{^{1}H\}$ NMR spectrum of **3a** in $CDCl_3$.

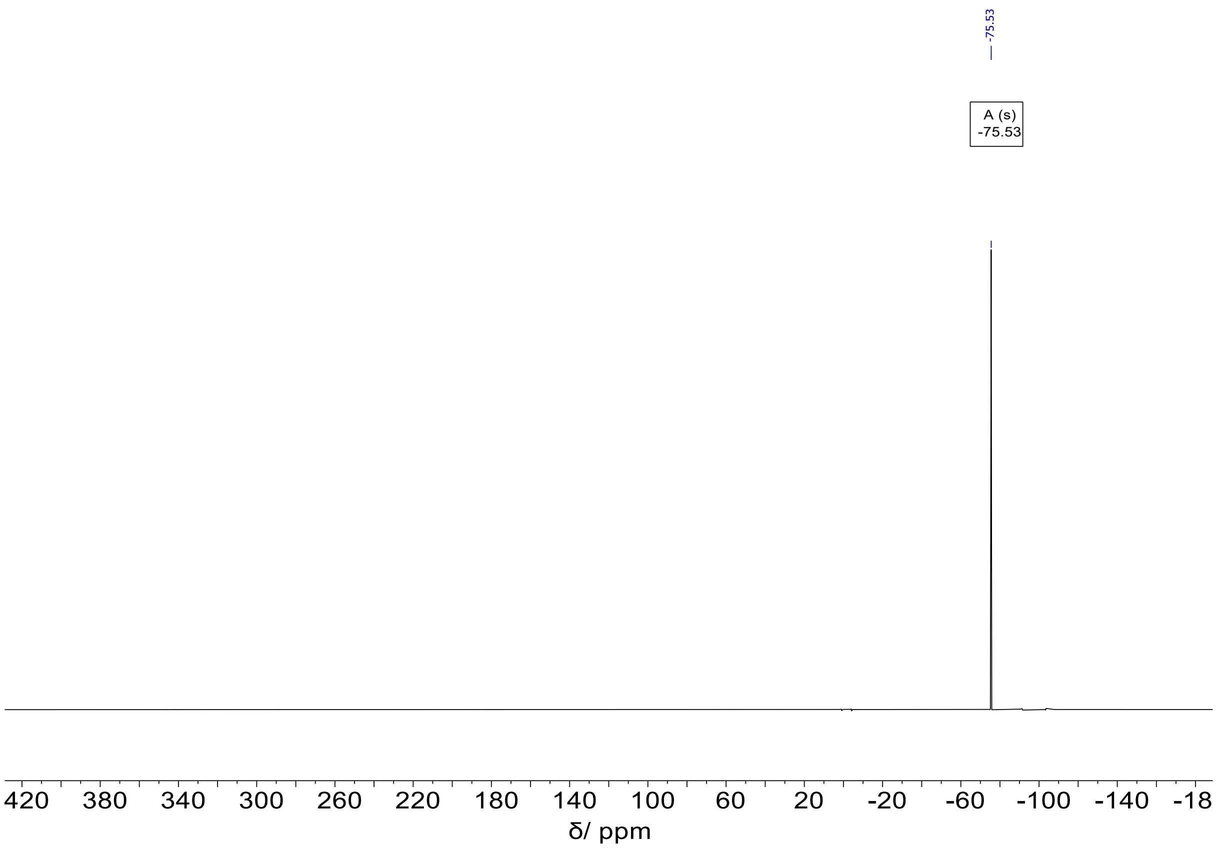


Fig. S10 ^{31}P NMR spectrum of **3a** in $CDCl_3$.

3.4 3b

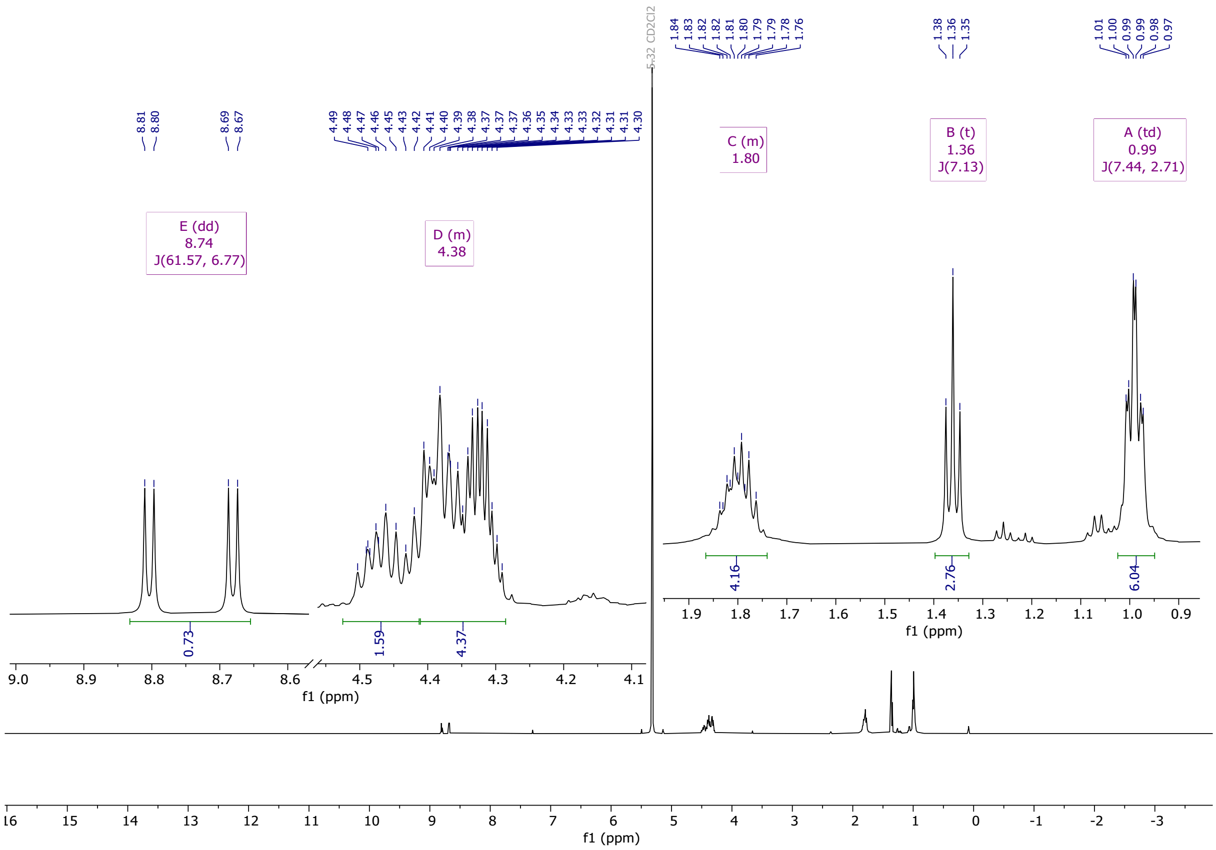


Fig. S11 ^{1}H NMR spectrum of **3b** in $CDCl_3$.

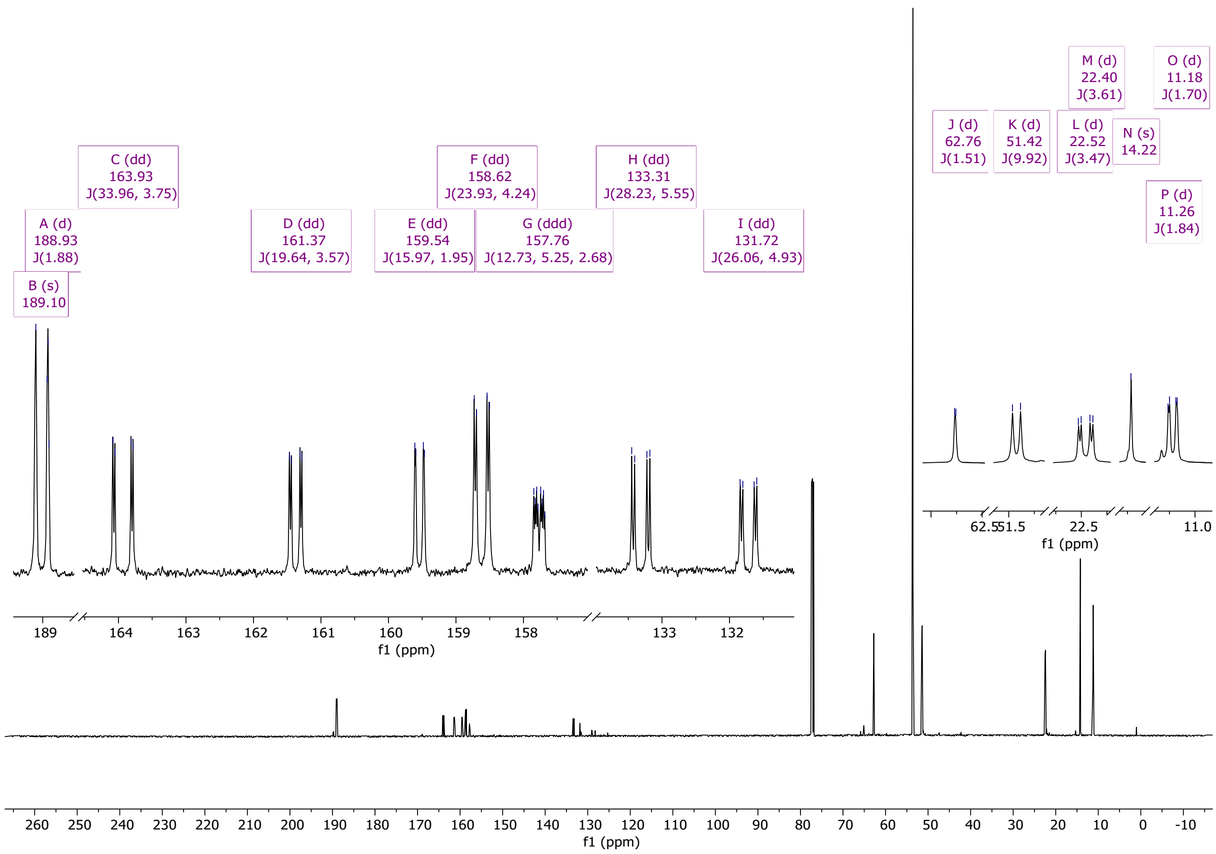


Fig. S12 ^{13}C NMR spectrum of **3b** in C_6D_6.

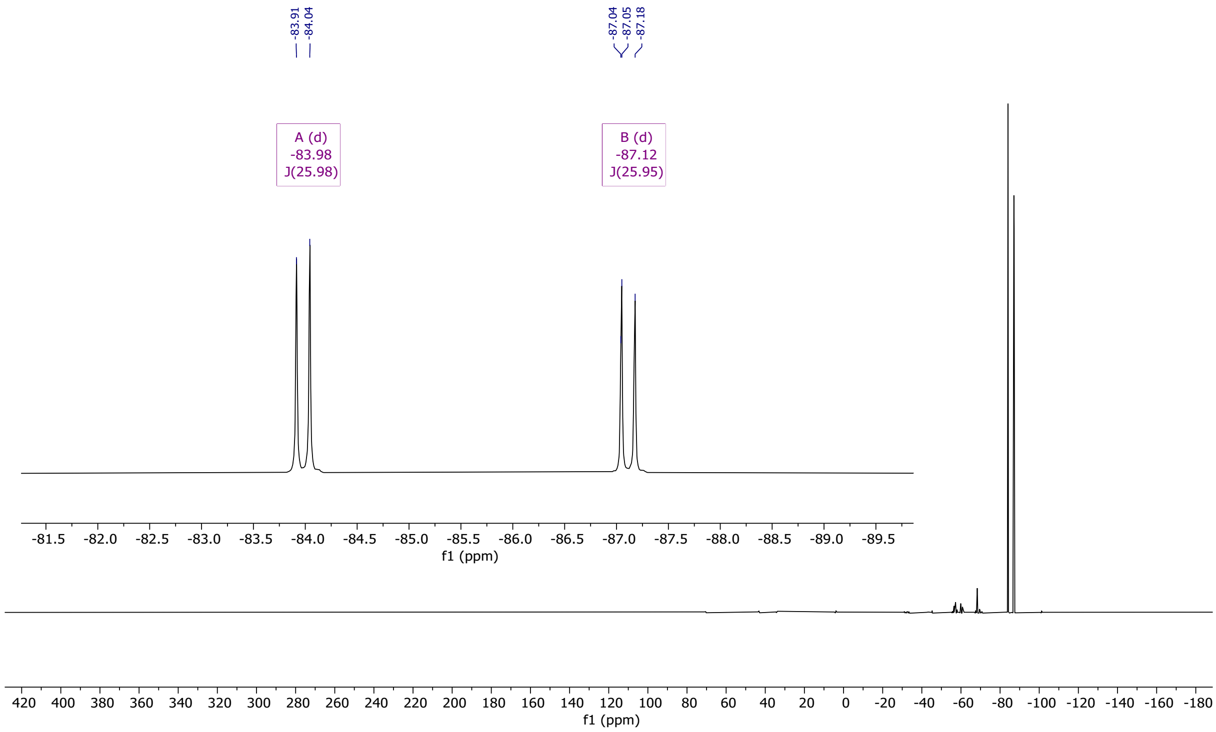


Fig. S13 $^{31}P\{^{1}H\}$ NMR spectrum of **3b** in C_6D_6.

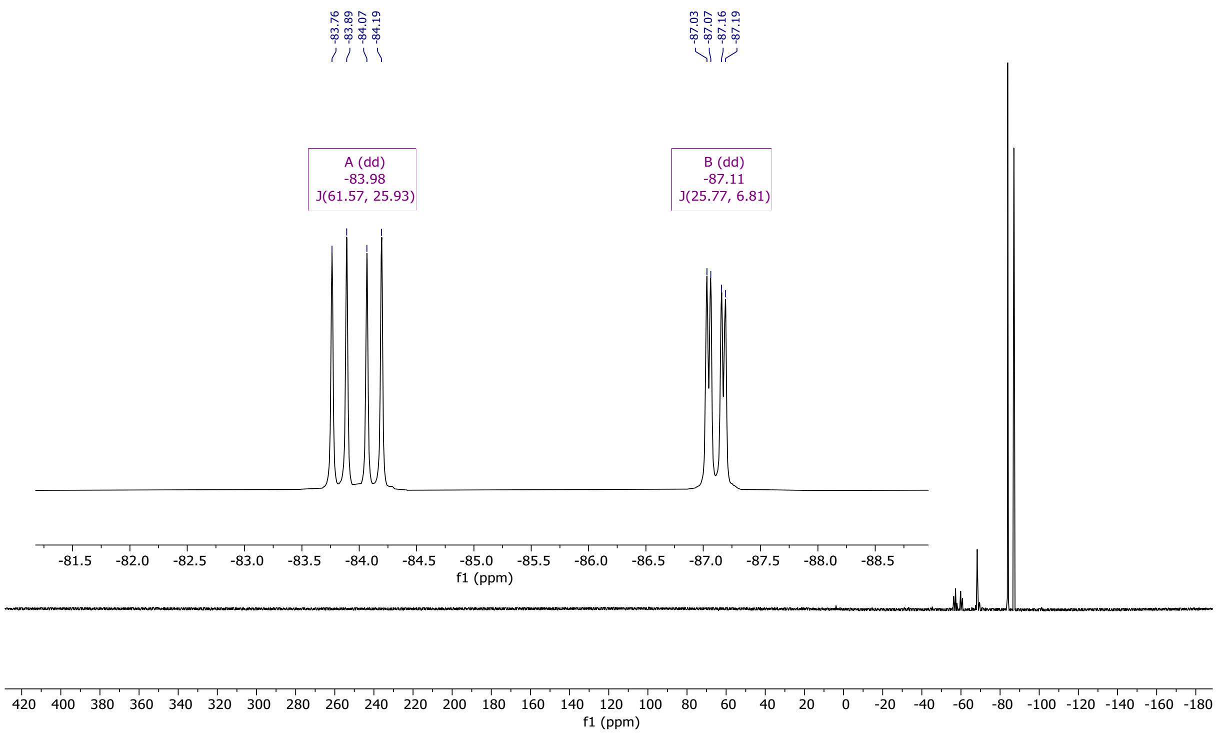


Fig. S14 ^{31}P NMR spectrum of **3b** in $CDCl_3$.

3.5 3c

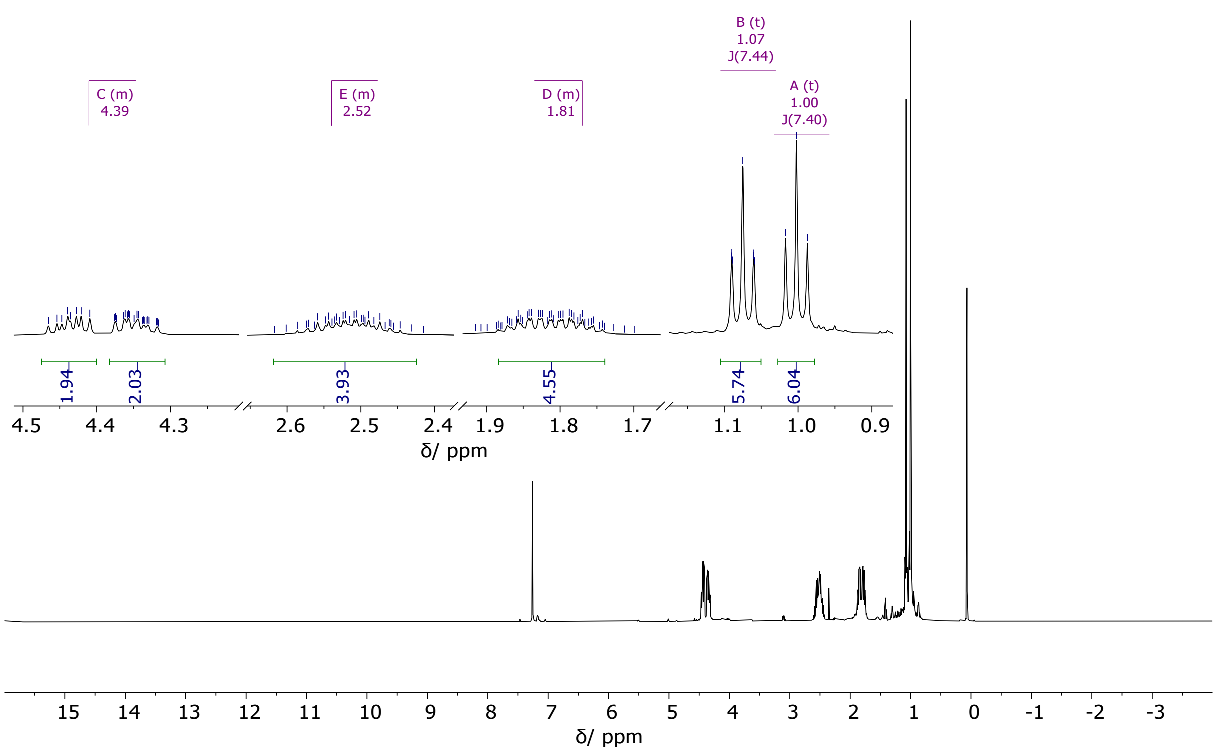


Fig. S15 ^{1}H NMR spectrum of **3c** in $CDCl_3$.

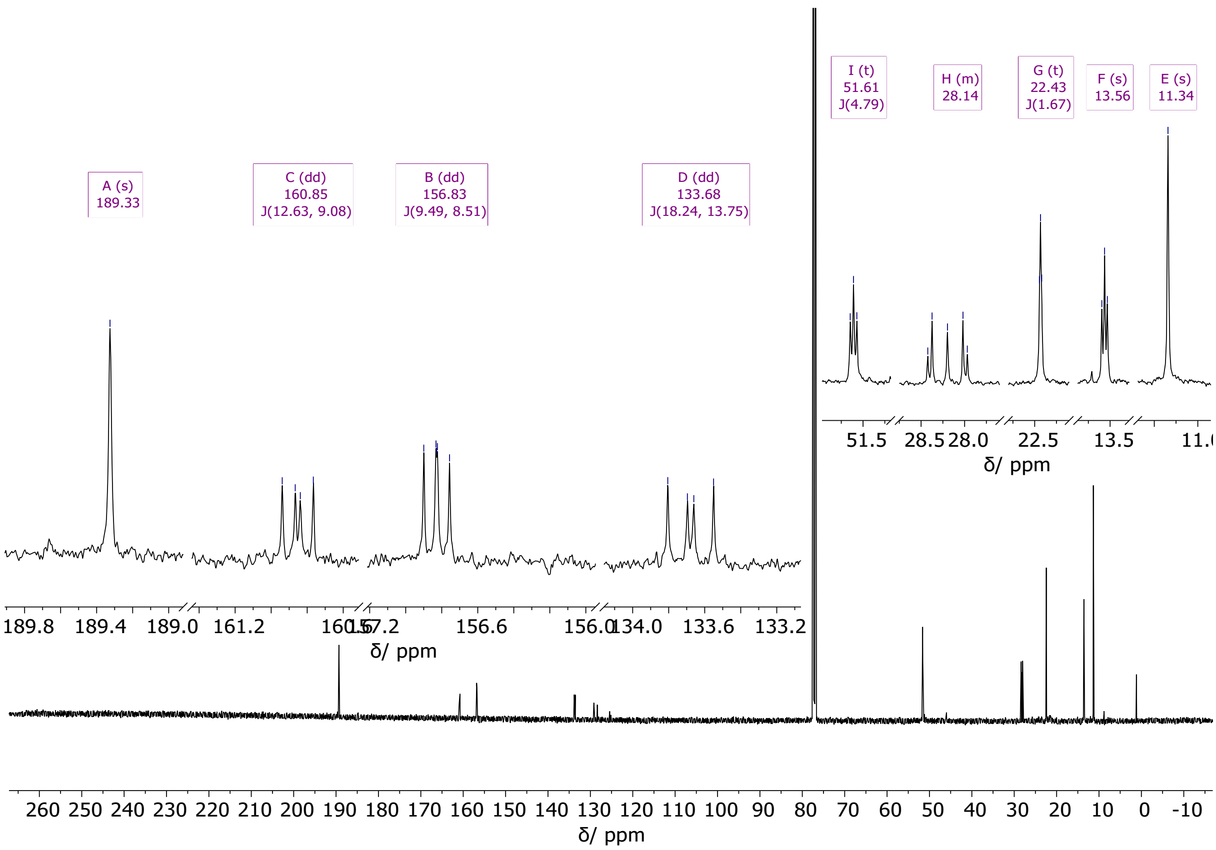


Fig. S16 ^{13}C NMR spectrum of **3c** in $CDCl_3$.

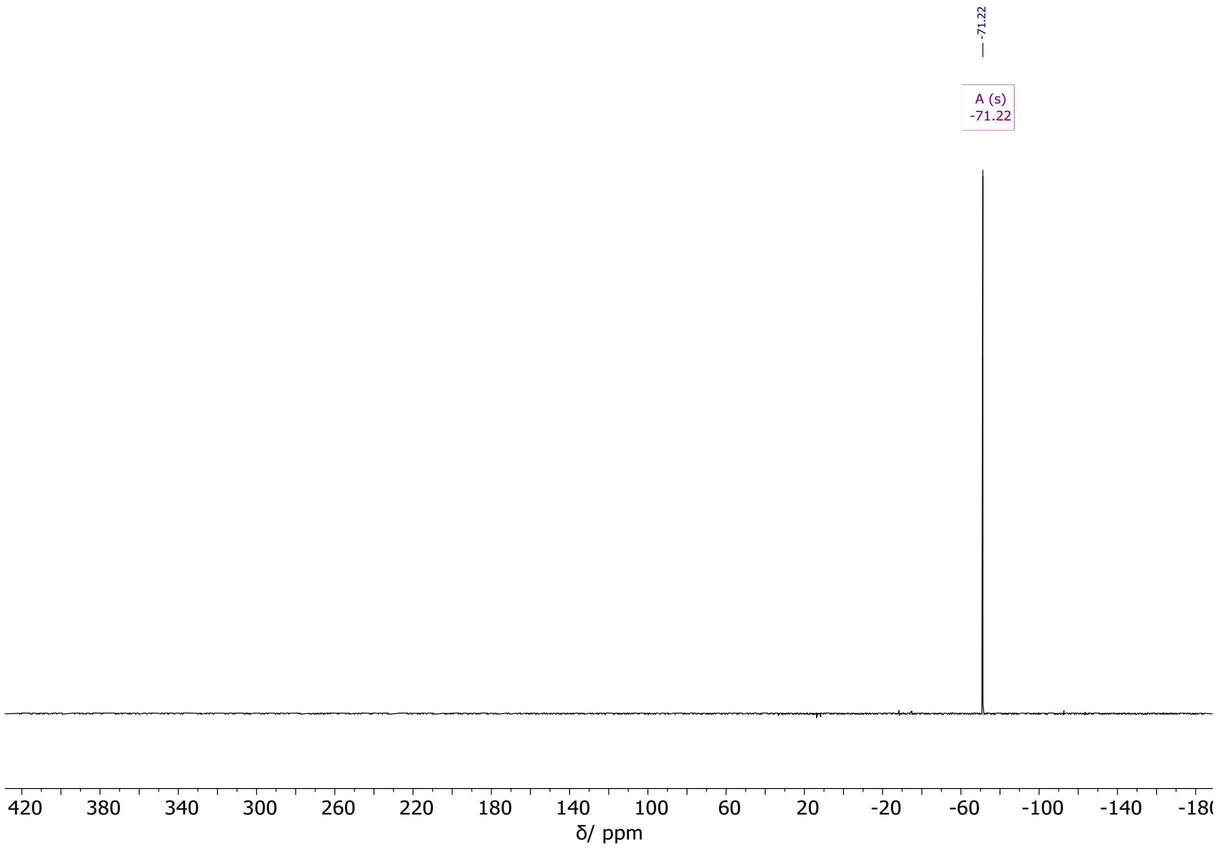


Fig. S17 [31]P{[1]H} NMR spectrum of **3c** in $CDCl_3$.

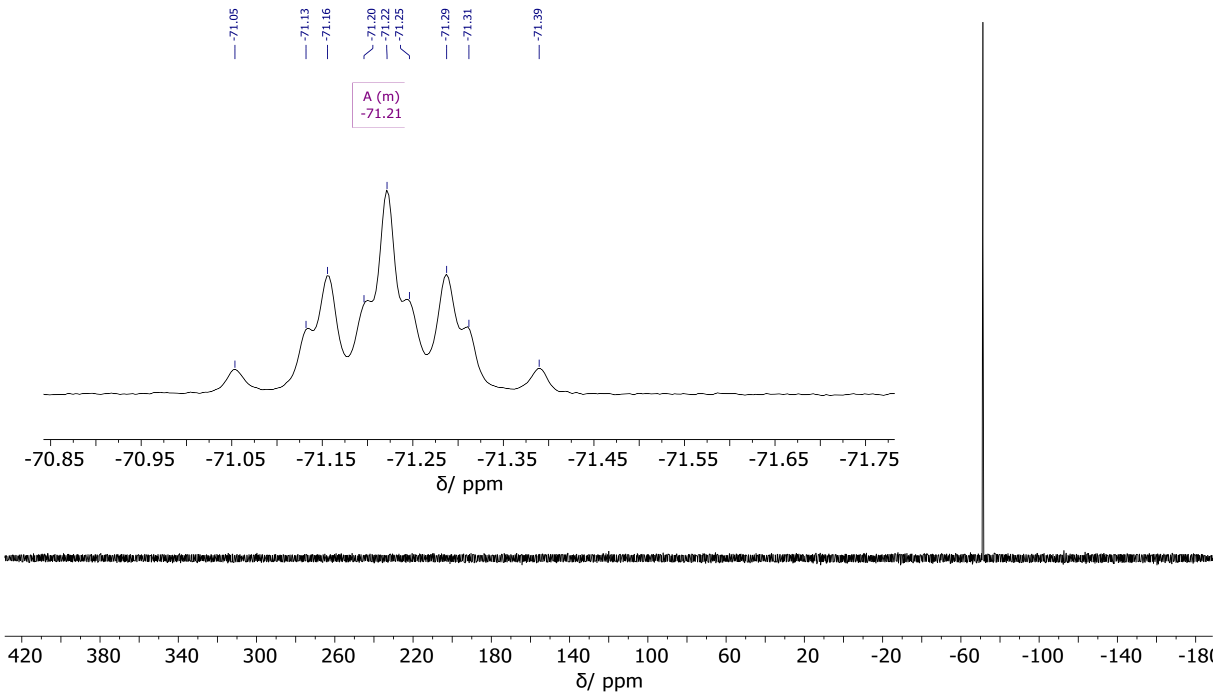


Fig. S18 [31]P NMR spectrum of **3c** in $CDCl_3$.

3.6 4a

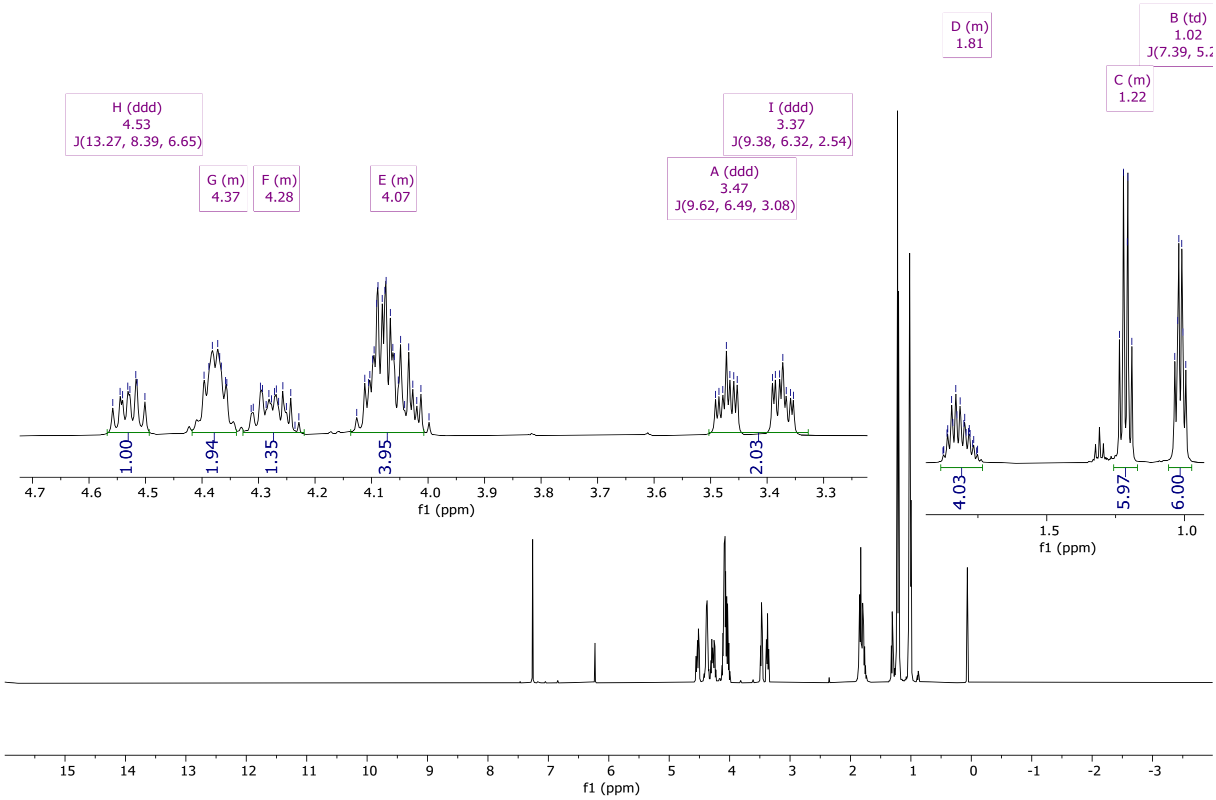


Fig. S19 ^{1}H NMR spectrum of **4a** in $CDCl_3$.

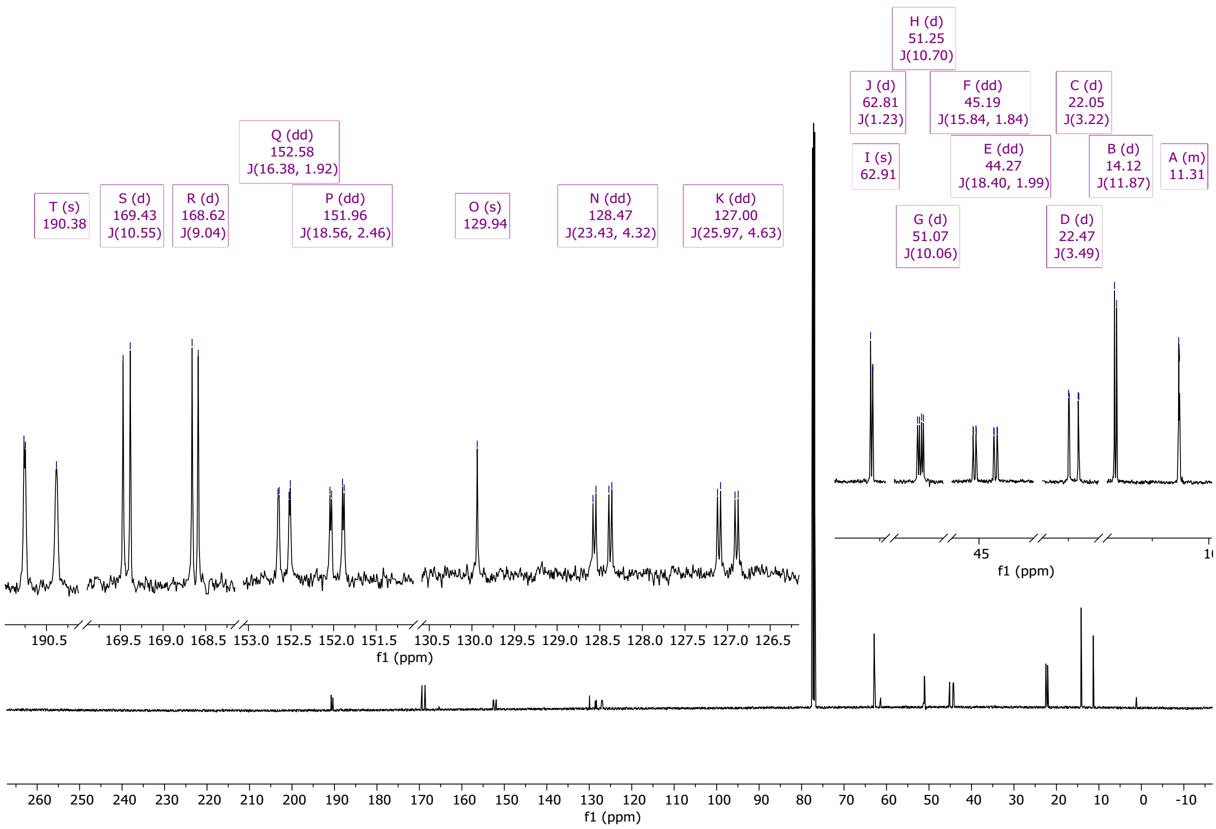


Fig. S20 ^{13}C NMR spectrum of **4a** in C_6D_6.

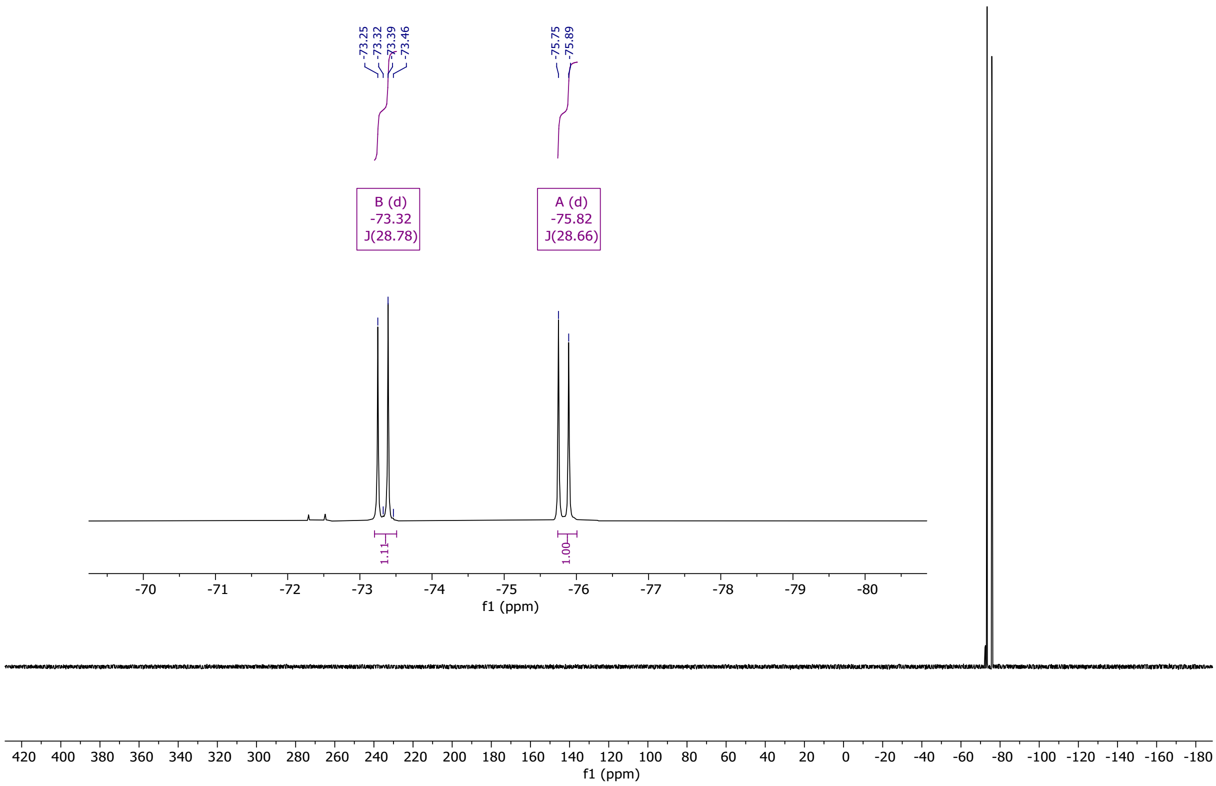


Fig. S21 $^{31}P\{^{1}H\}$ NMR spectrum of **4a** in $CDCl_3$.

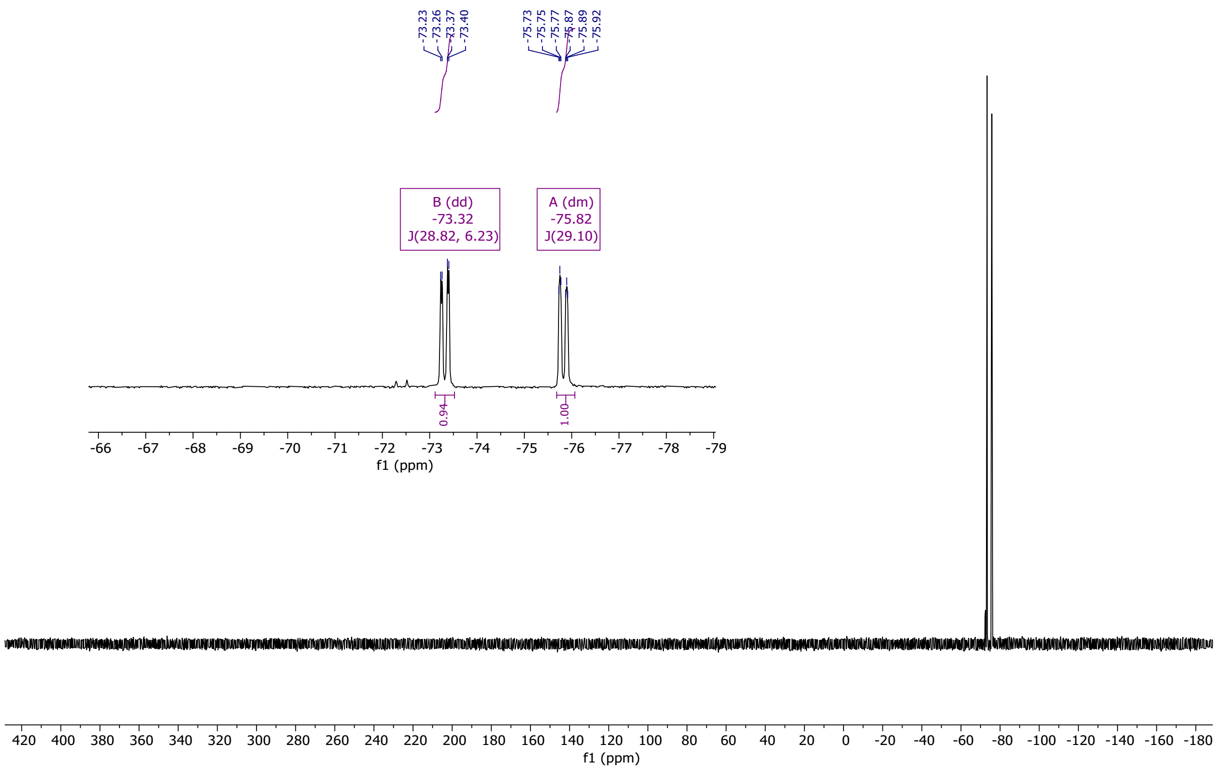


Fig. S22 ^{31}P NMR spectrum of **4a** in $CDCl_3$.

3.7 4a’

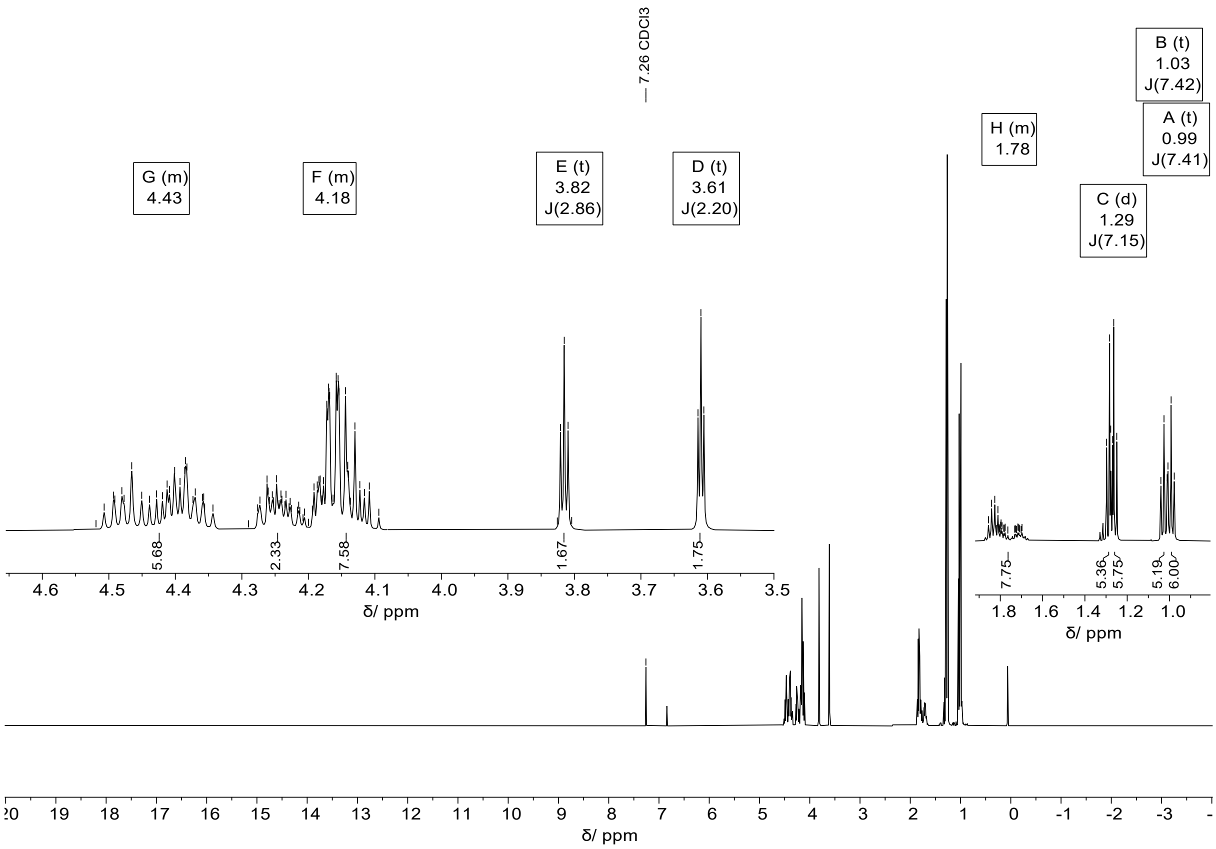


Fig. S23 [1]H NMR spectrum of **4a’** in $CDCl_3$.

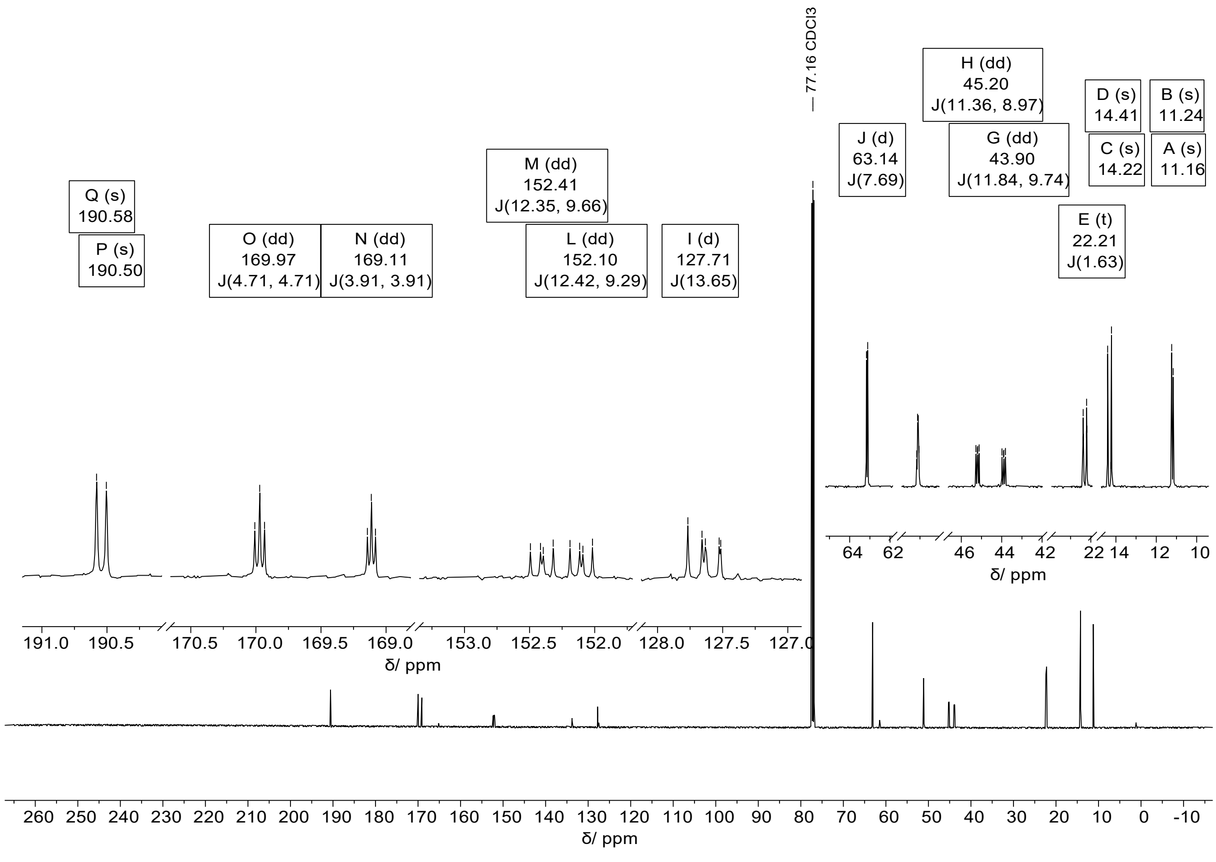


Fig. S24 [13]C NMR spectrum of **4a’** in $CDCl_3$.

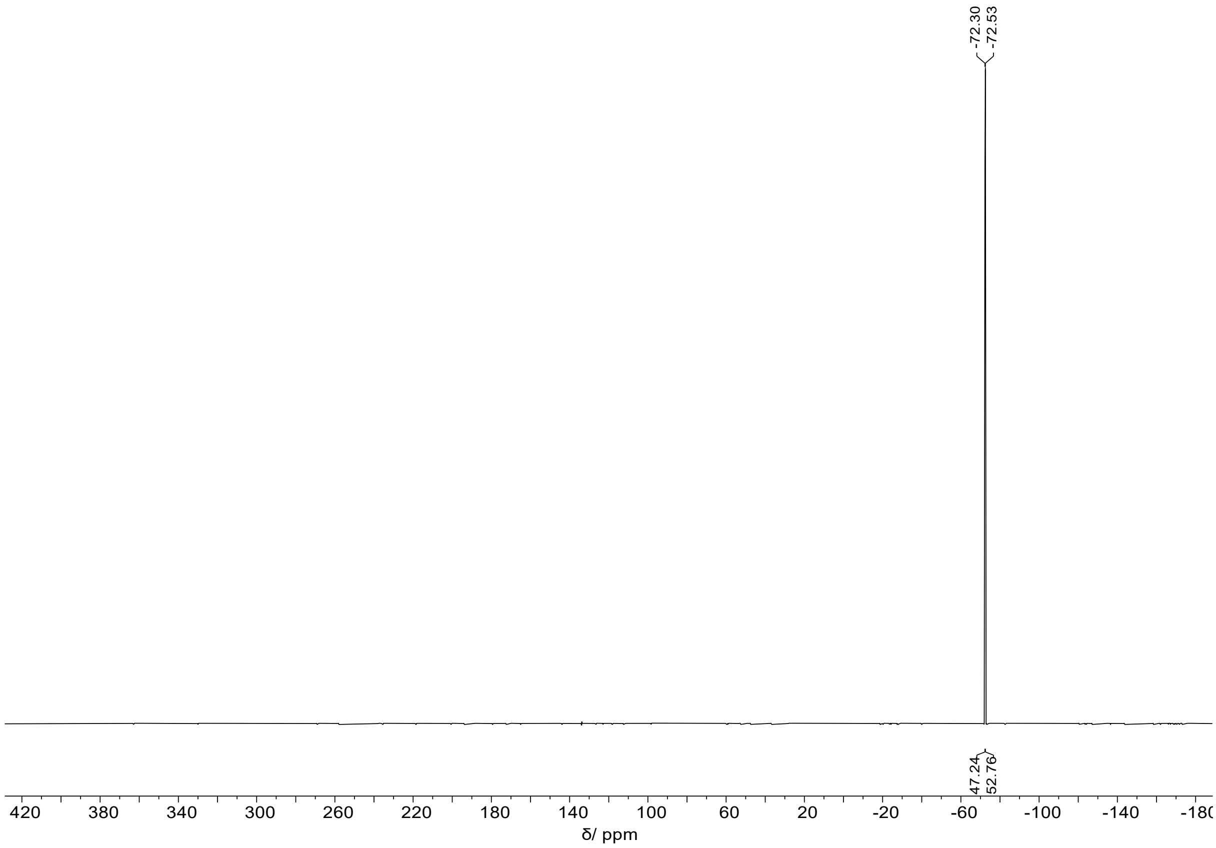


Fig. S25 $^{31}P\{^1H\}$ NMR spectrum of **4a'** in $CDCl_3$.

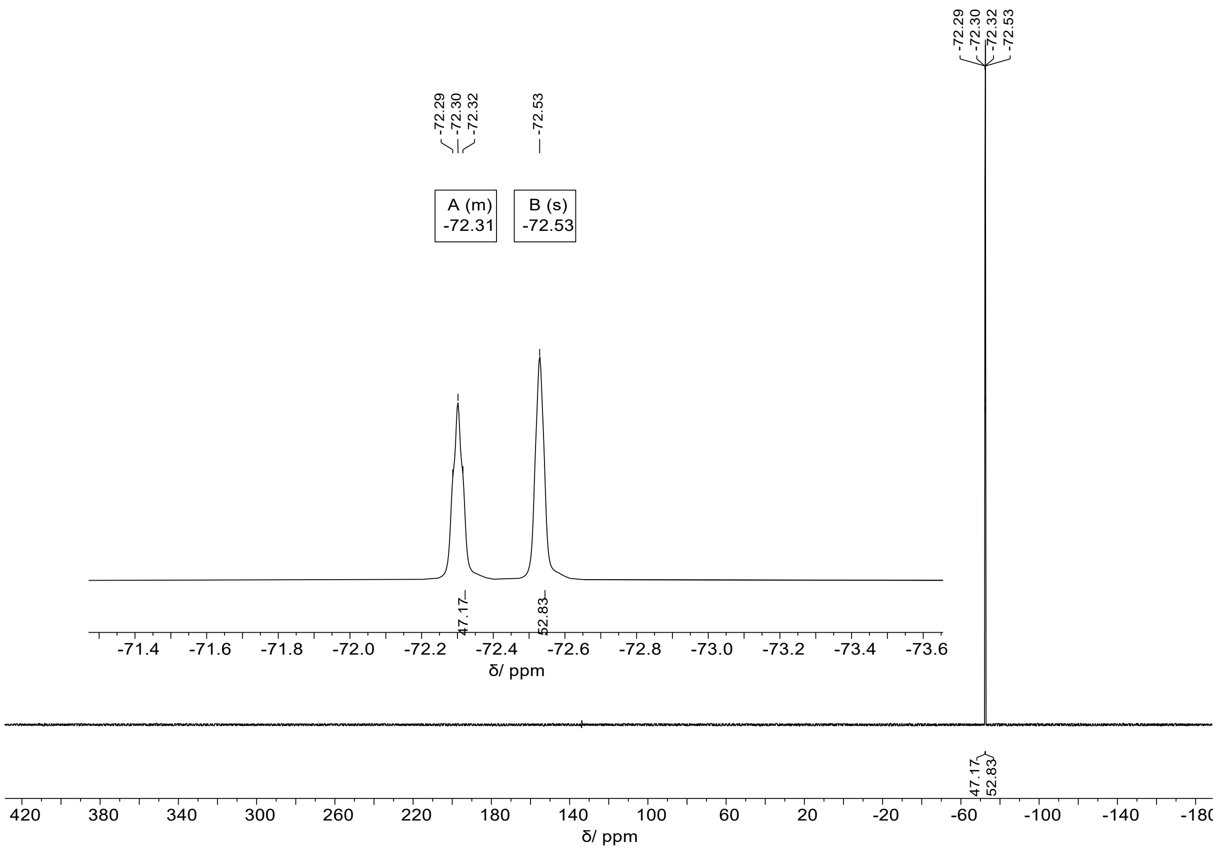


Fig. S26 ^{31}P NMR spectrum of **4b** in $CDCl_3$.

3.8 4b

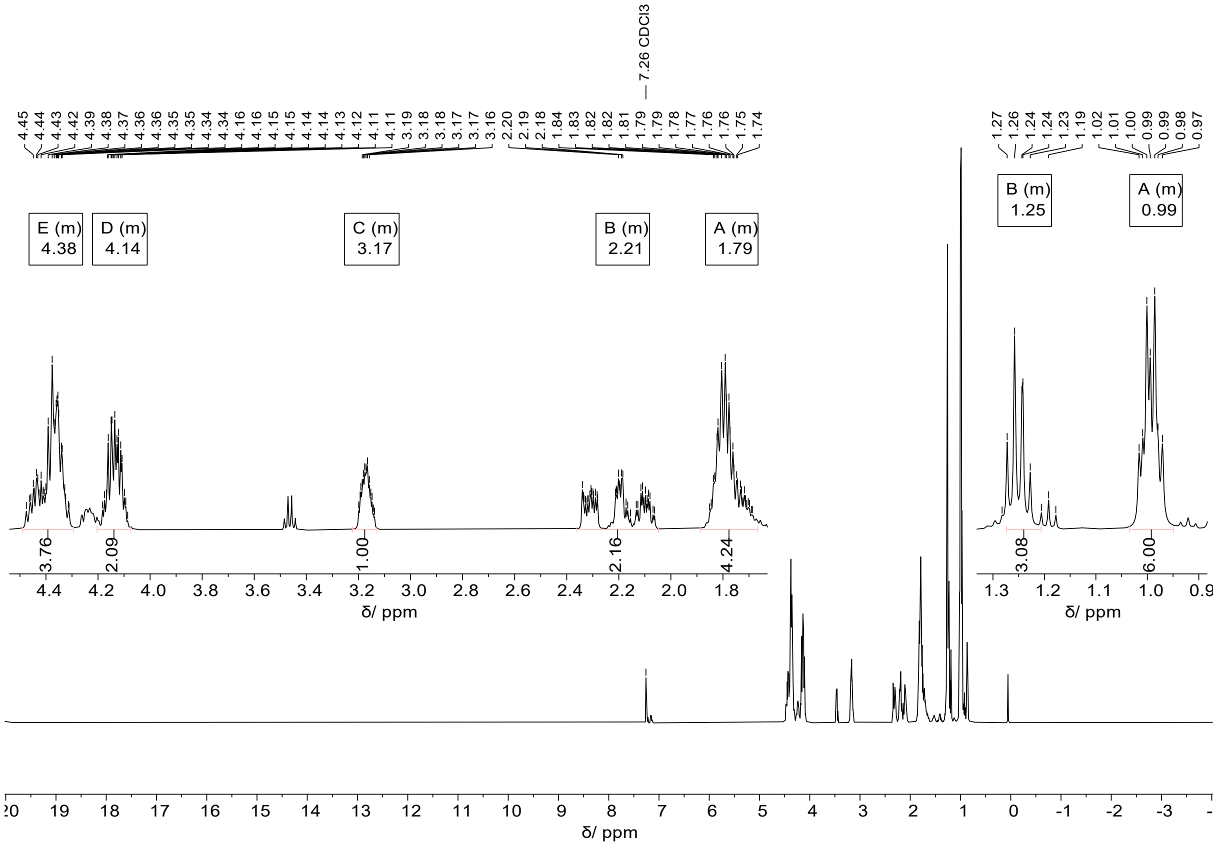


Fig. S27 ^{1}H NMR spectrum of **4b** in $CDCl_3$.

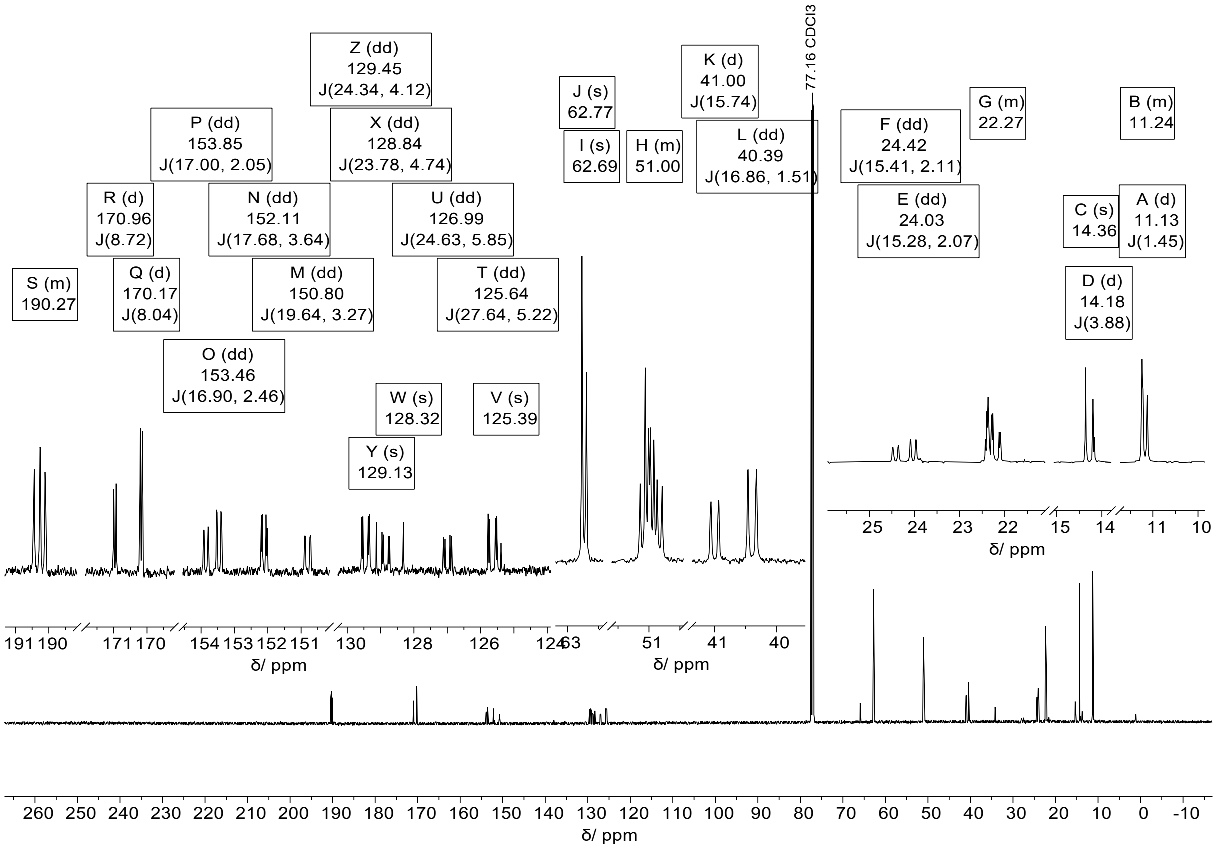


Fig. S28 ^{13}C NMR spectrum of **4b** in $CDCl_3$.

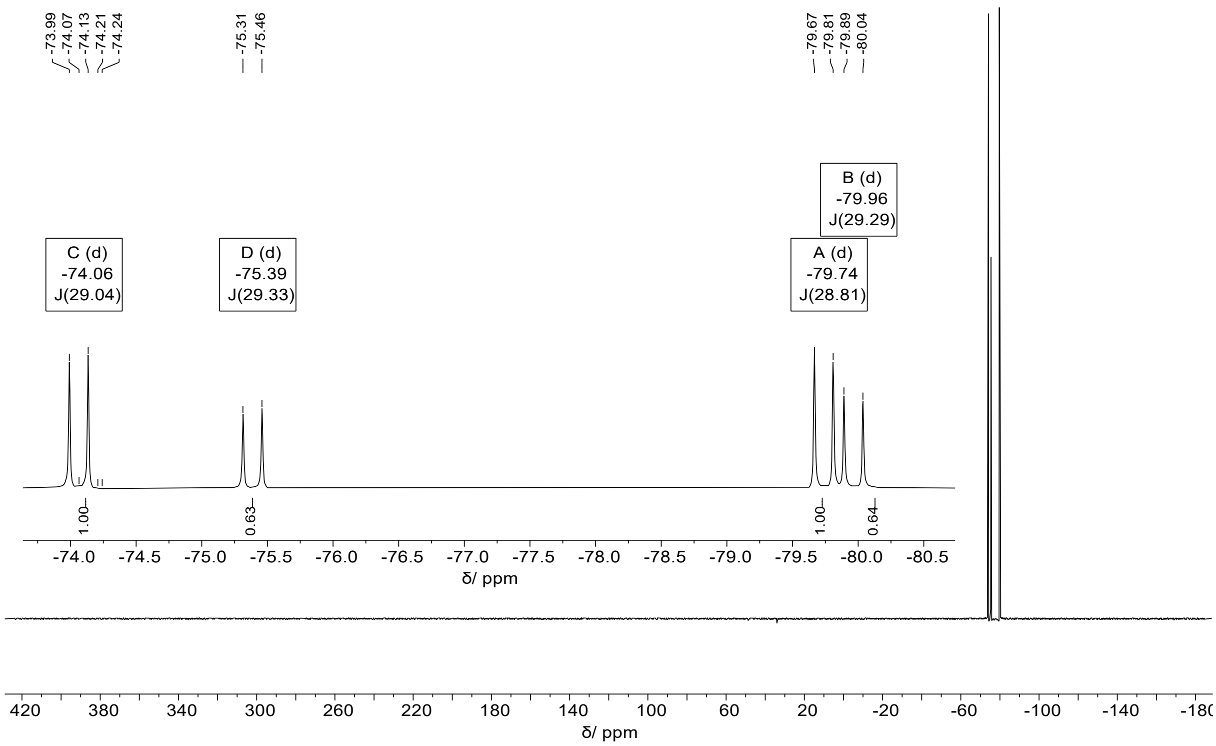


Fig. S29 $^{31}P\{^{1}H\}$ NMR spectrum of **4b** in $CDCl_3$.

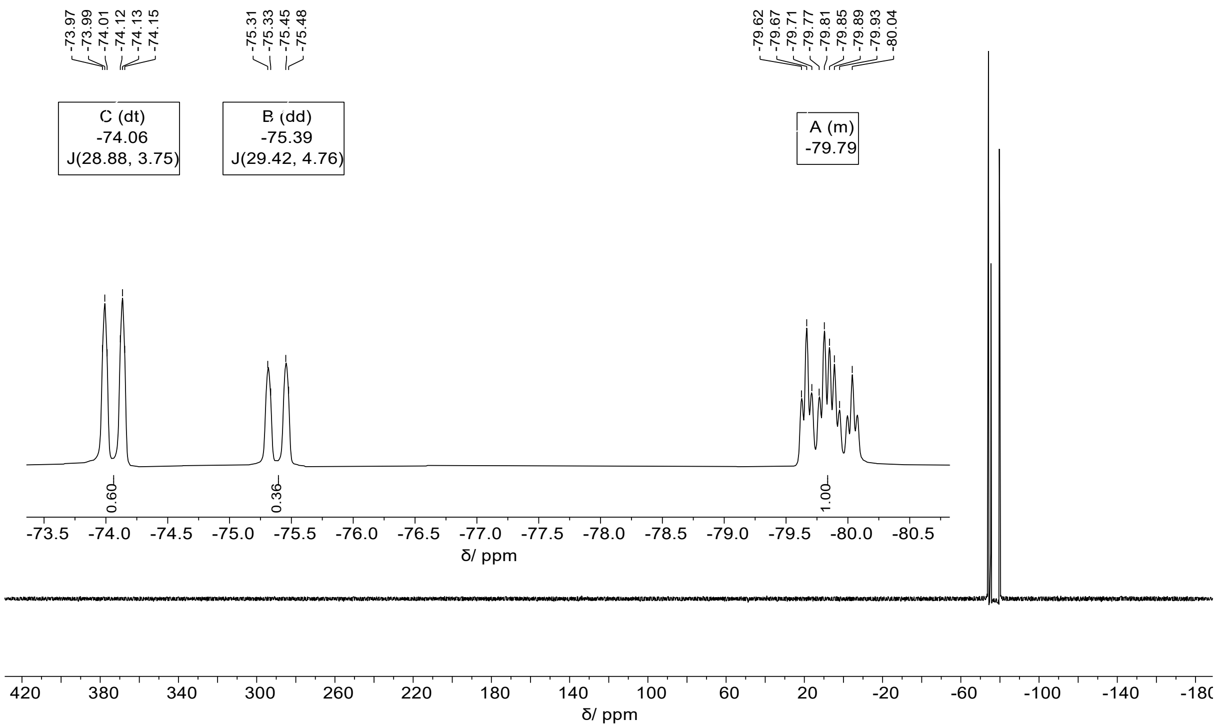


Fig. S30 ^{31}P NMR spectrum of **4b** in $CDCl_3$.

3.9 4c

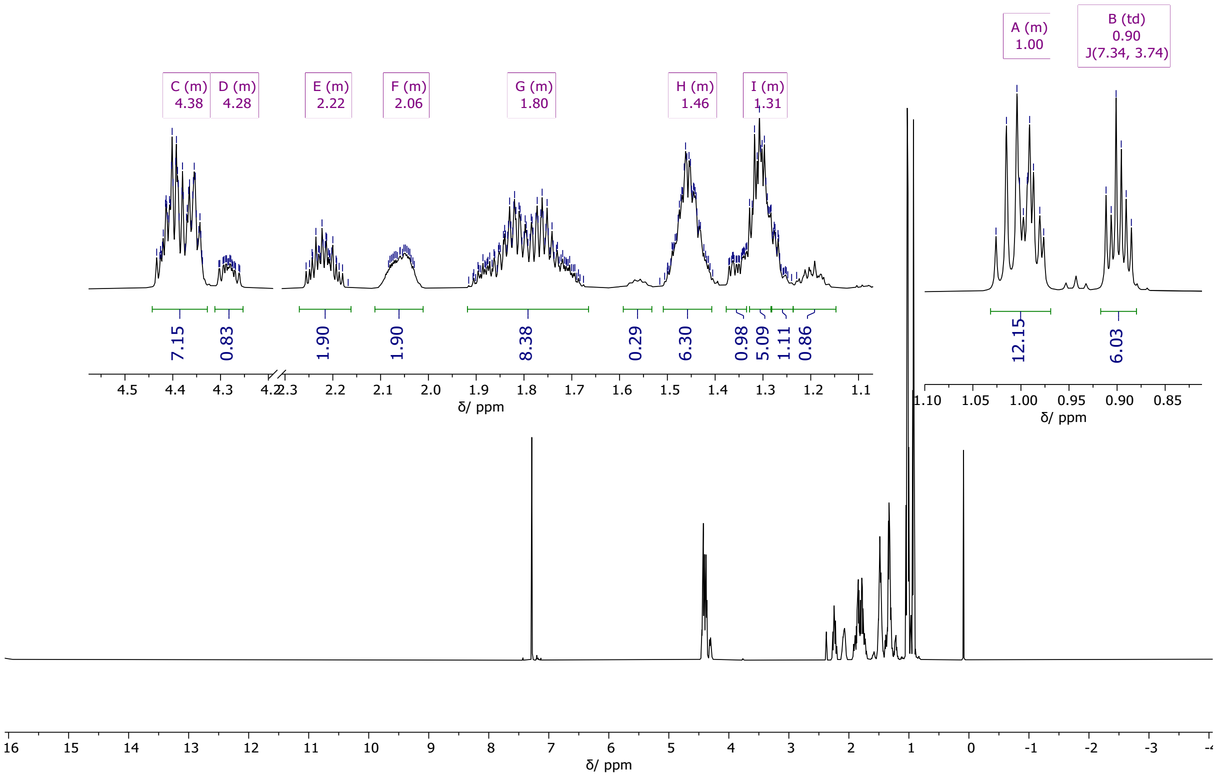


Fig. S31 ^{1}H NMR spectrum of **4c** in $CDCl_3$.

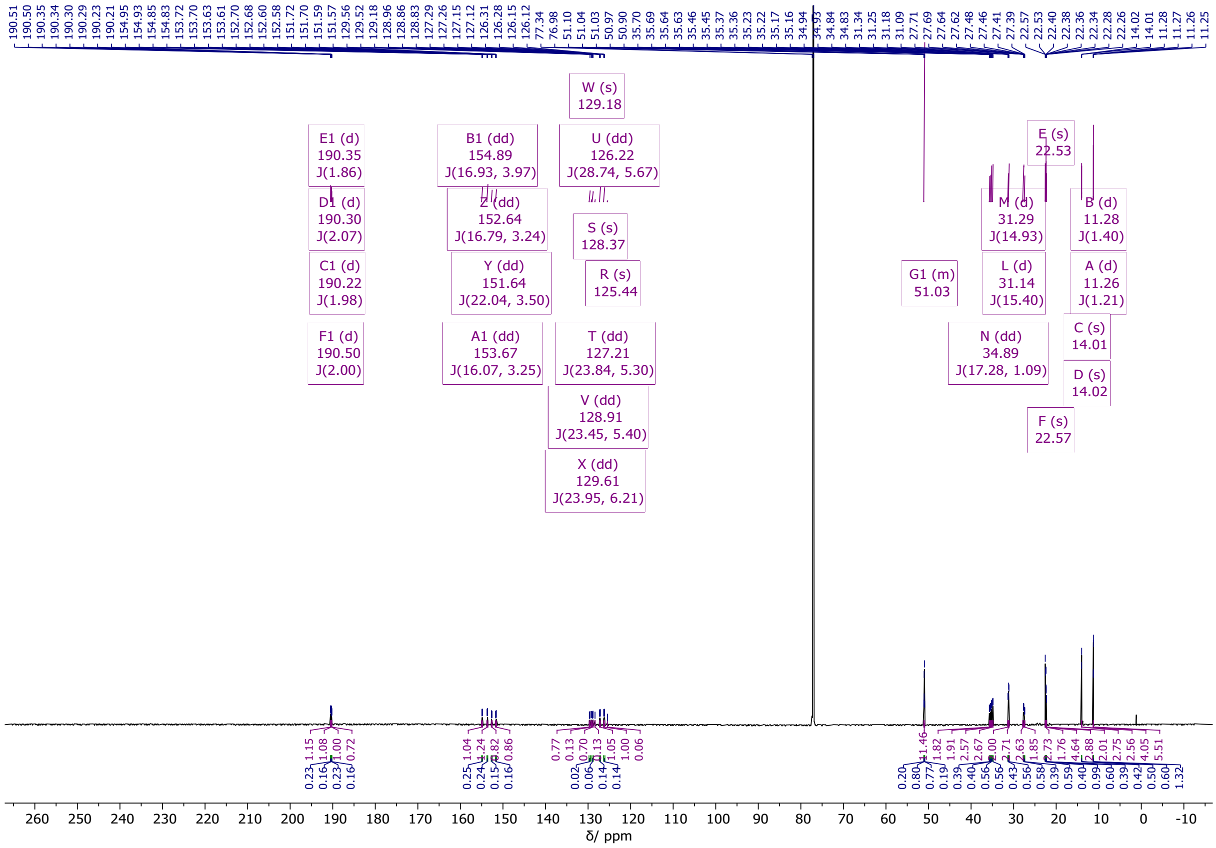


Fig. S32 ^{13}C NMR spectrum of **4c** in $CDCl_3$, for a detailed image see next figures.

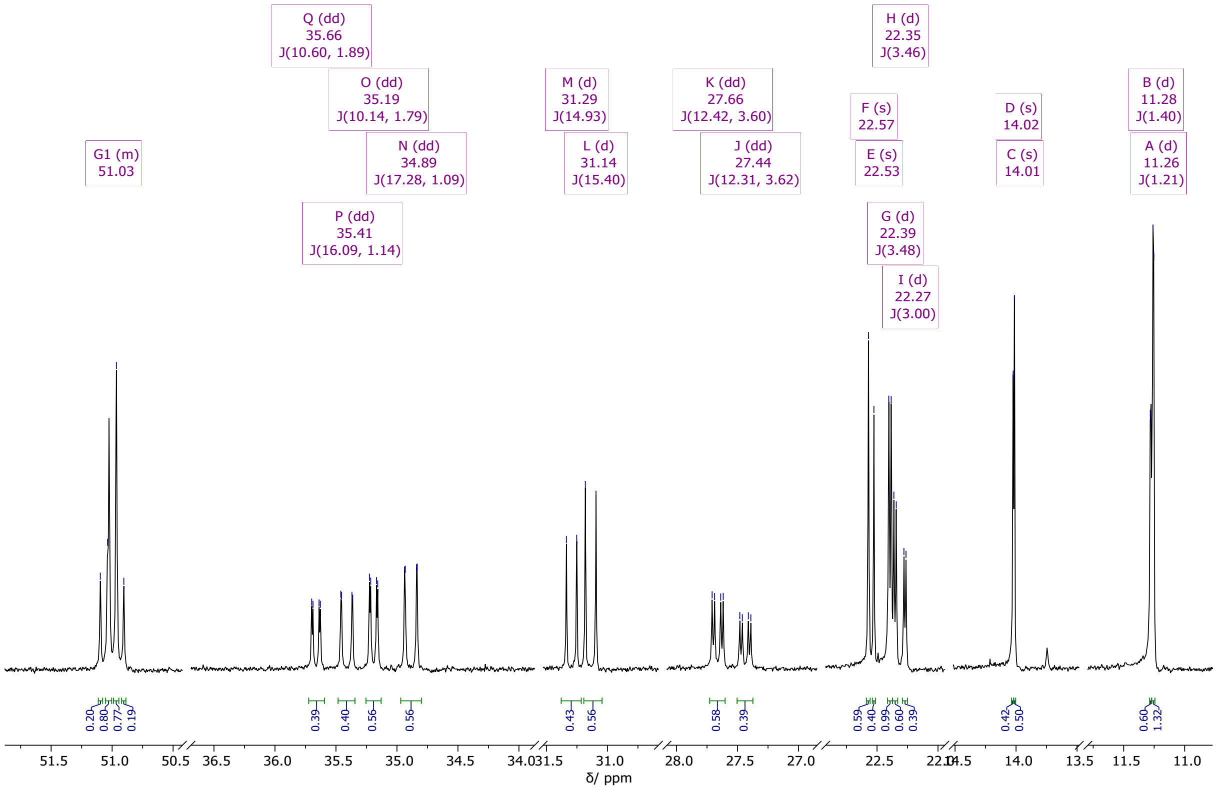


Fig. S33 Part of the ^{13}C NMR spectrum of **4c** in $CDCl_3$.

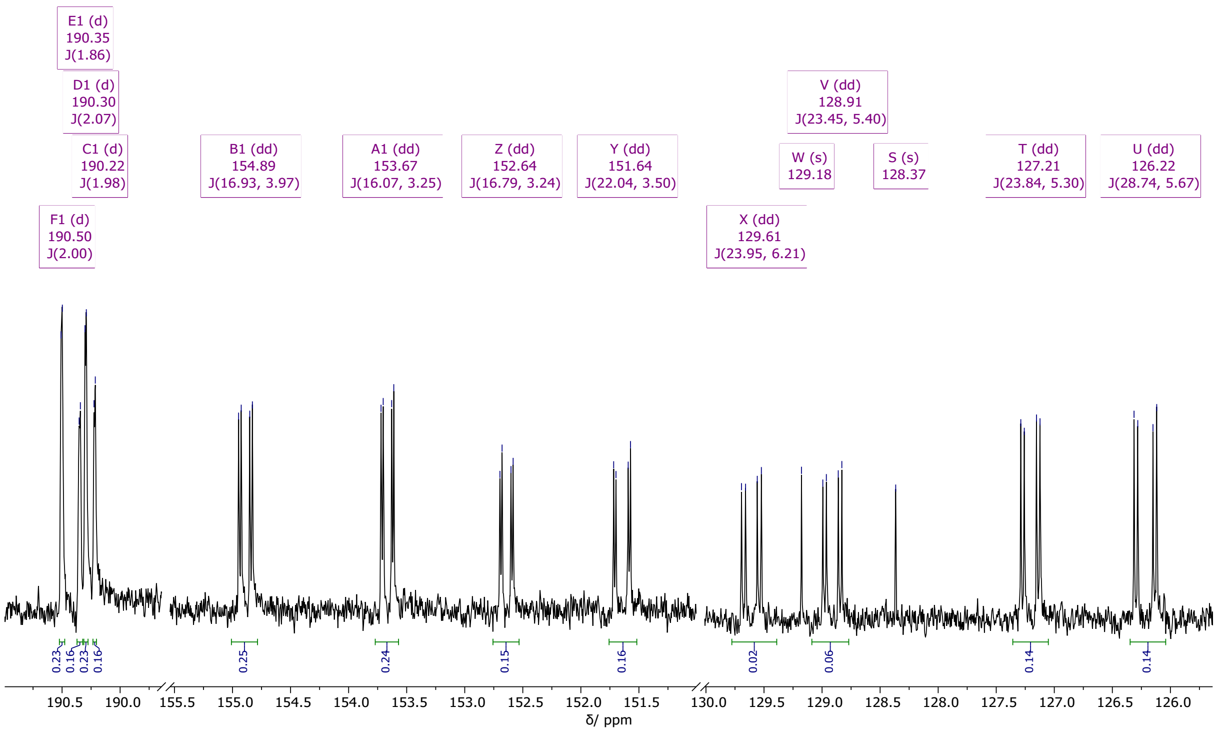


Fig. S34 Part of the ^{13}C NMR spectrum of **4c** in $CDCl_3$.

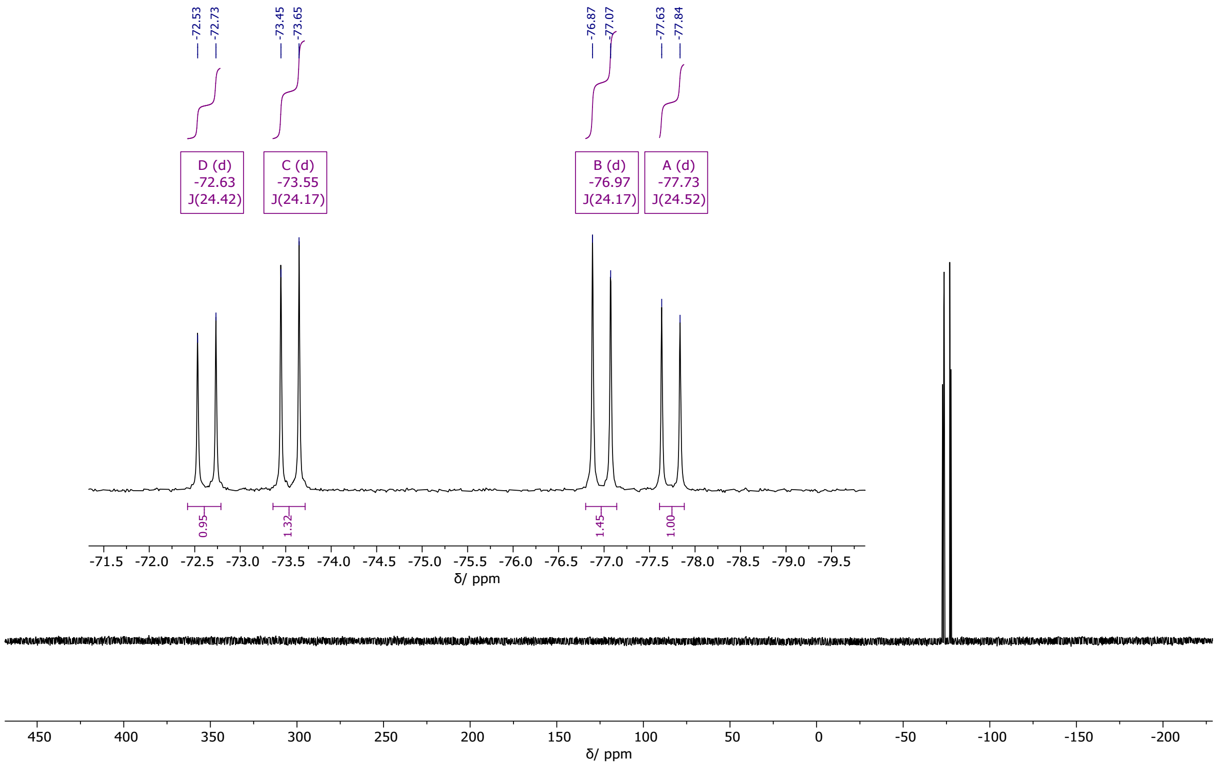


Fig. S35 $^{31}P\{^{1}H\}$ NMR spectrum of **4c** in $CDCl_3$.

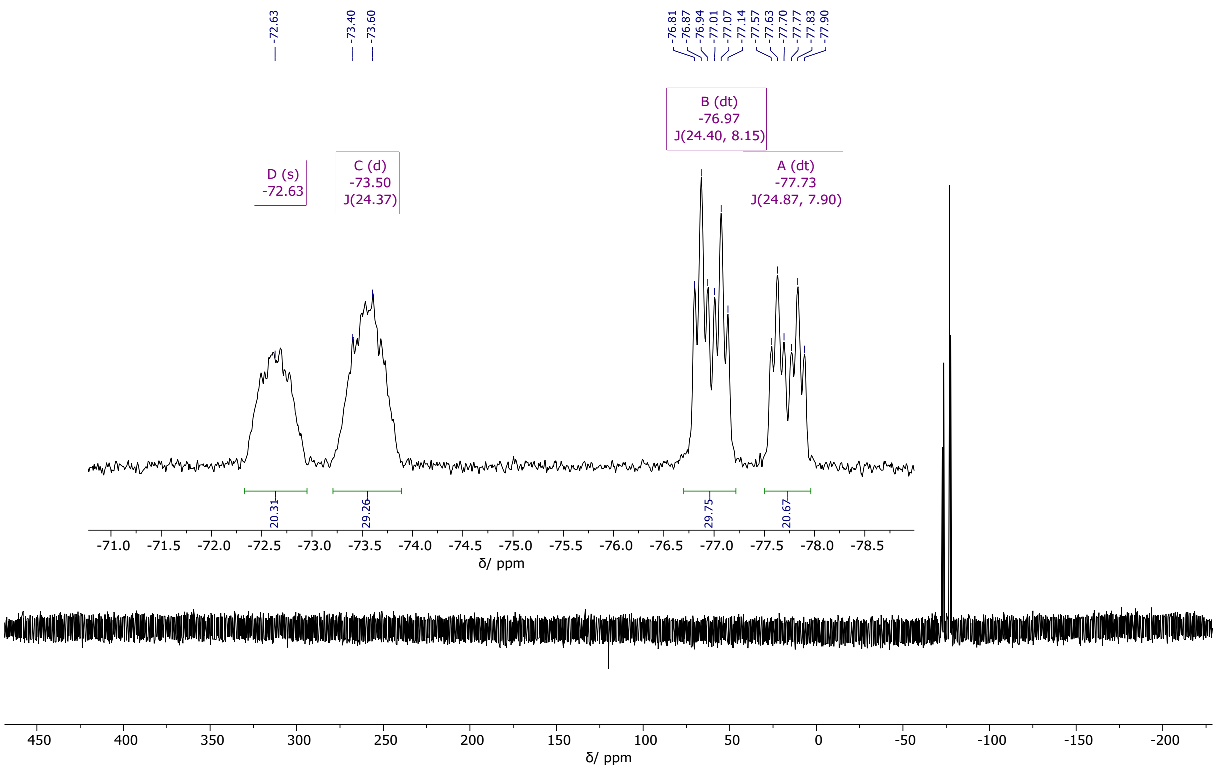


Fig. S36 ^{31}P NMR spectrum of **4c** in $CDCl_3$.

3.10 4d

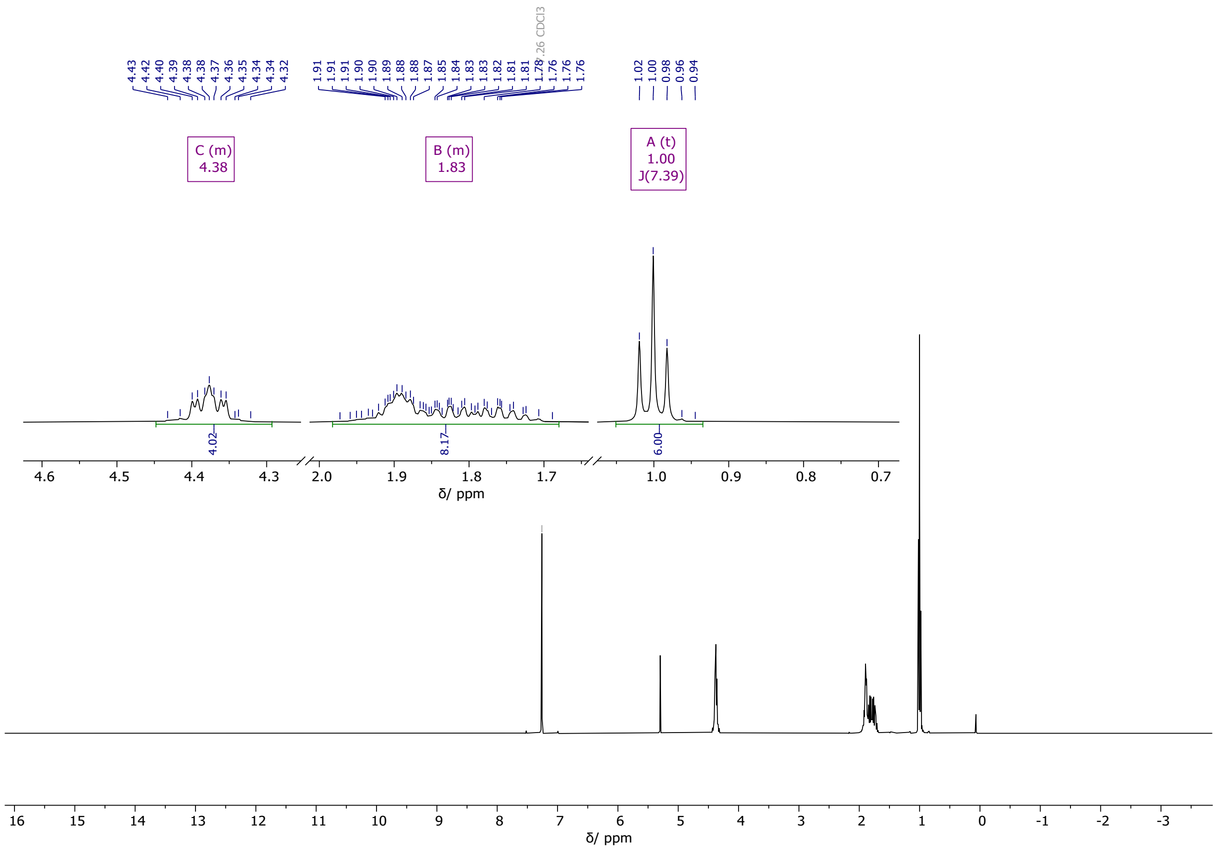


Fig. S37 ^{1}H NMR spectrum of **4d** in $CDCl_3$.

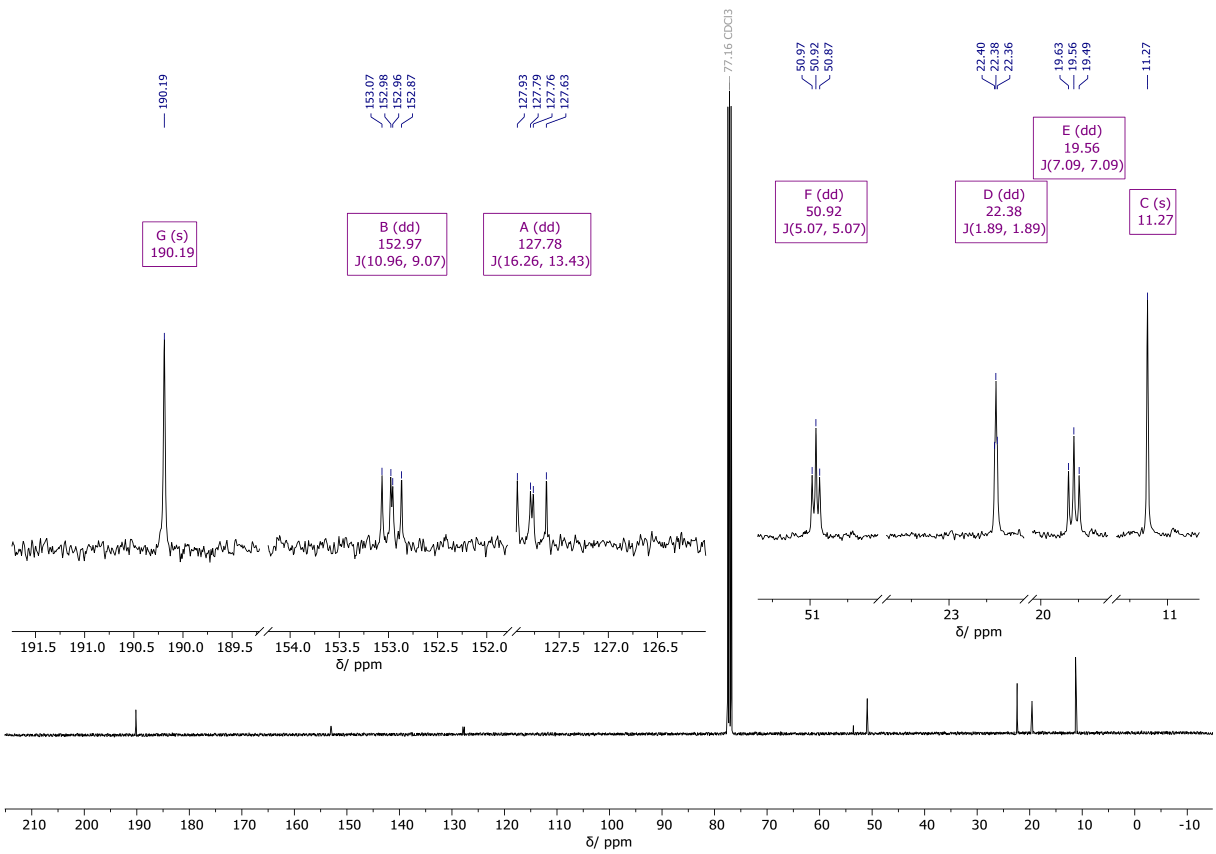


Fig. S38 ^{13}C NMR spectrum of **4d** in $CDCl_3$.

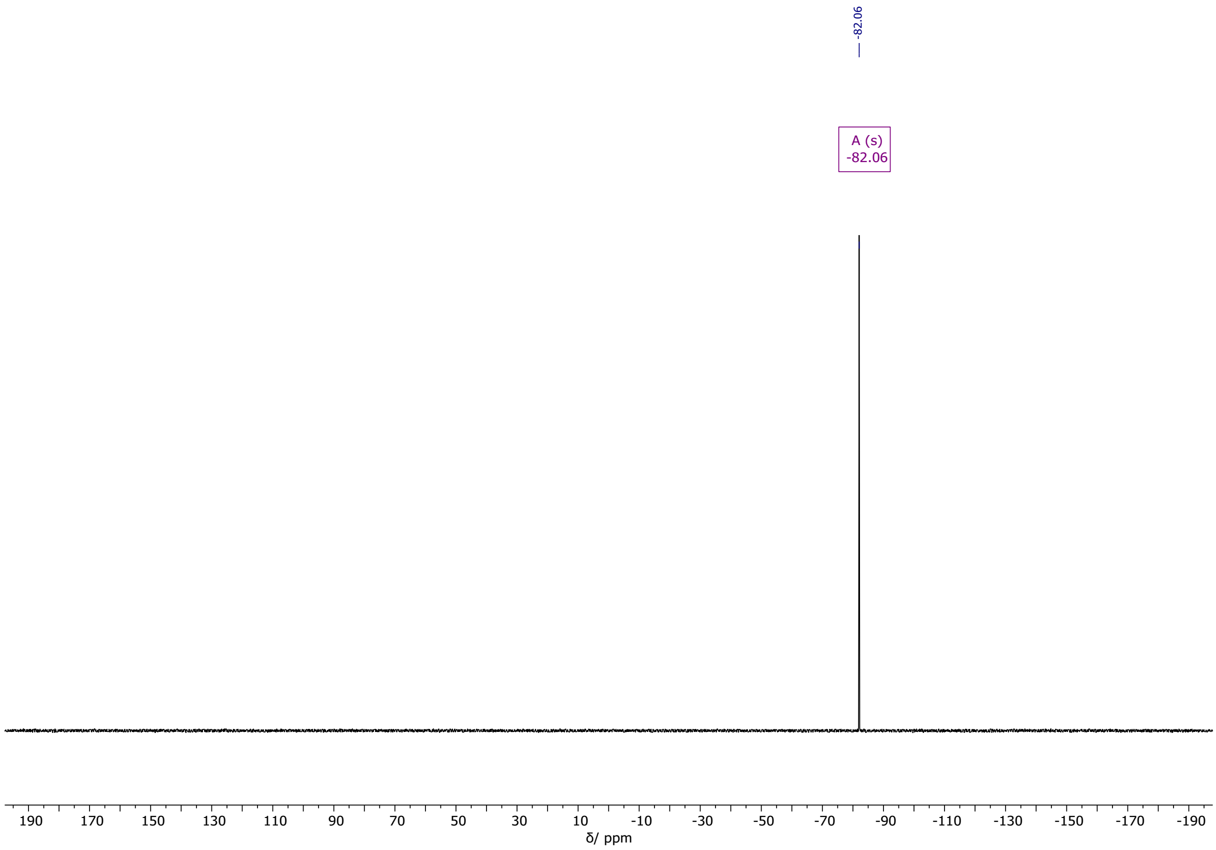


Fig. S39 $^{31}P\{^{1}H\}$ NMR spectrum of **4d** in $CDCl_3$.

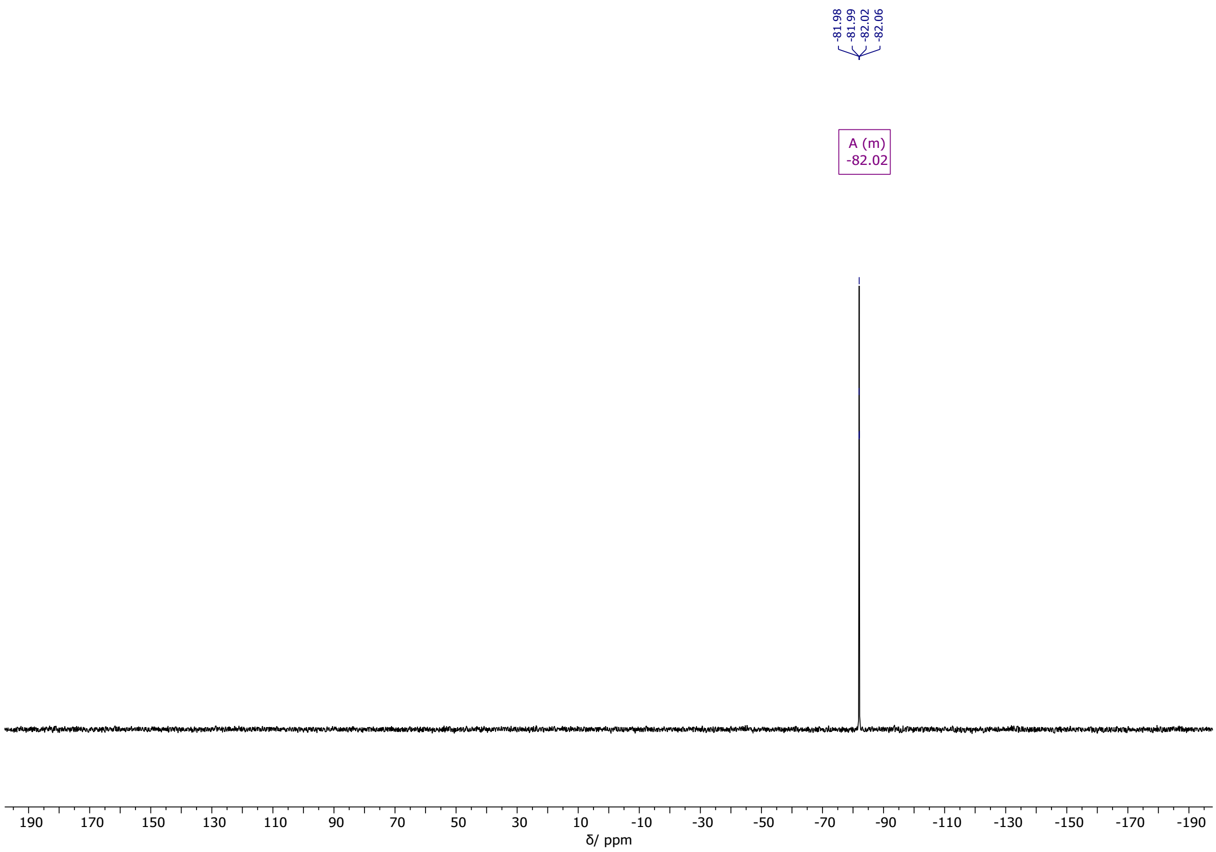


Fig. S40 ^{31}P NMR spectrum of **4d** in $CDCl_3$.

3.11 4e

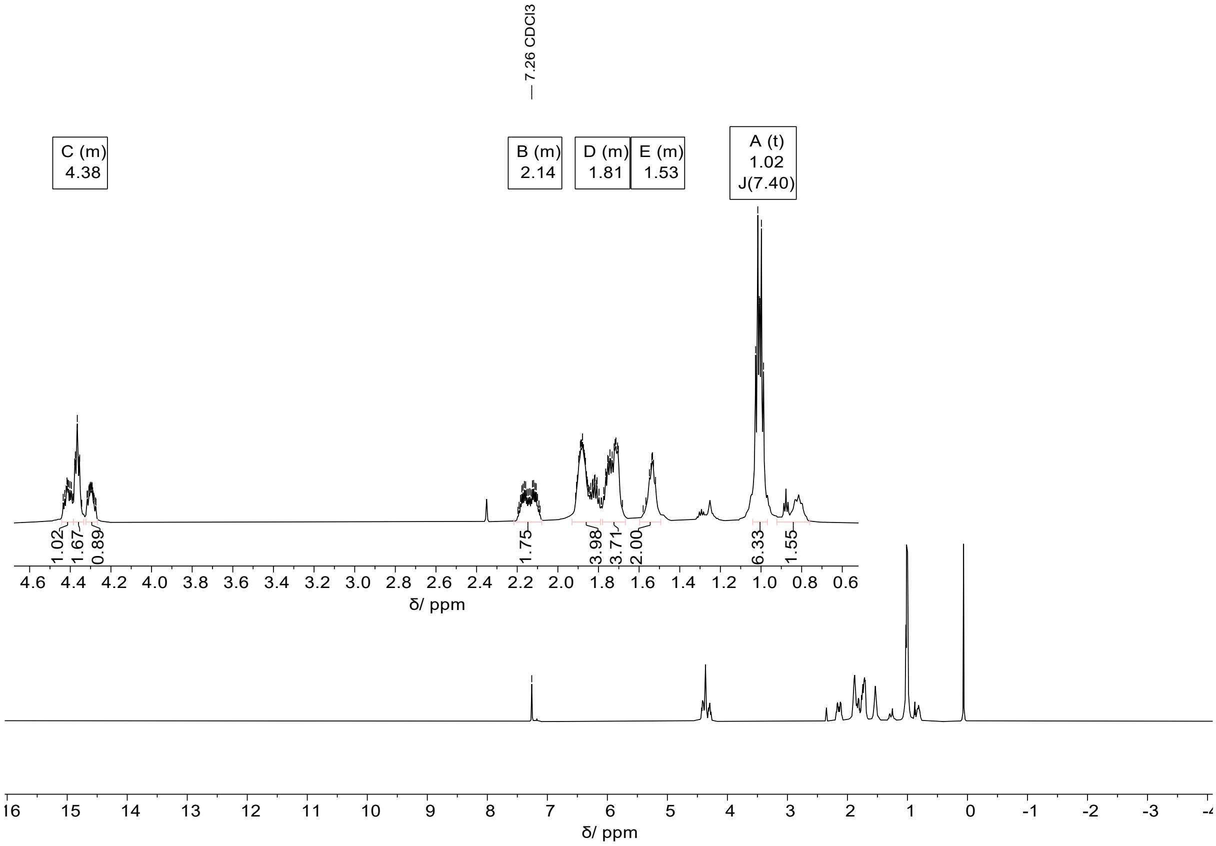


Fig. S41 ^{1}H NMR spectrum of **4e** in $CDCl_3$.

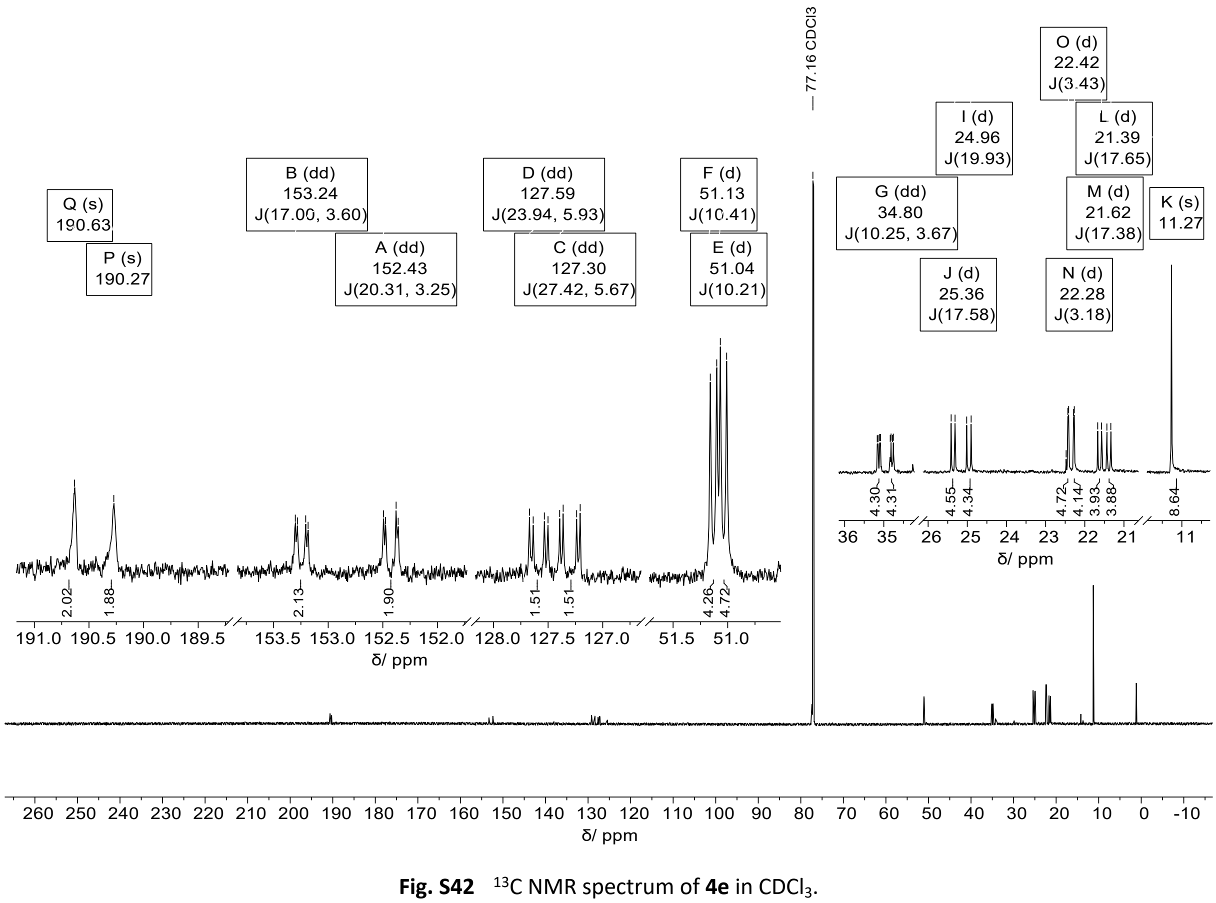


Fig. S42 ^{13}C NMR spectrum of **4e** in $CDCl_3$.

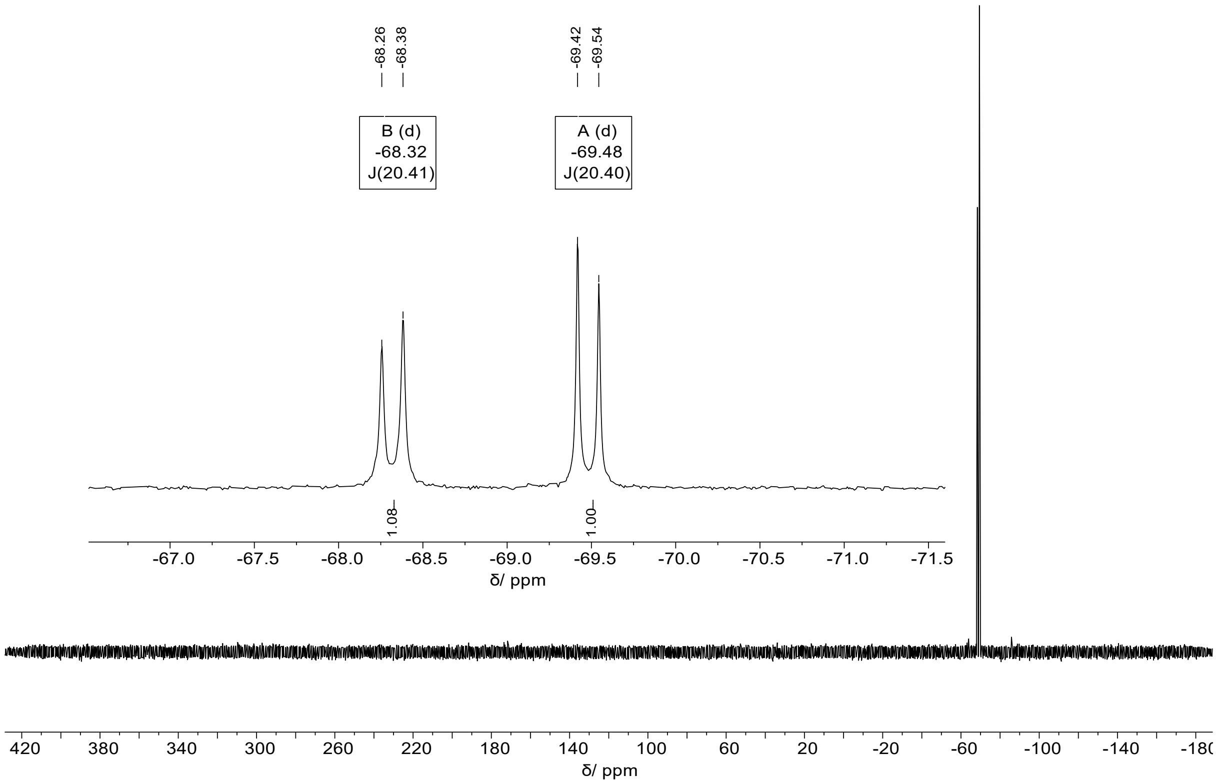


Fig. S43 $^{31}P\{^{1}H\}$ NMR spectrum of **4e** in $CDCl_3$.

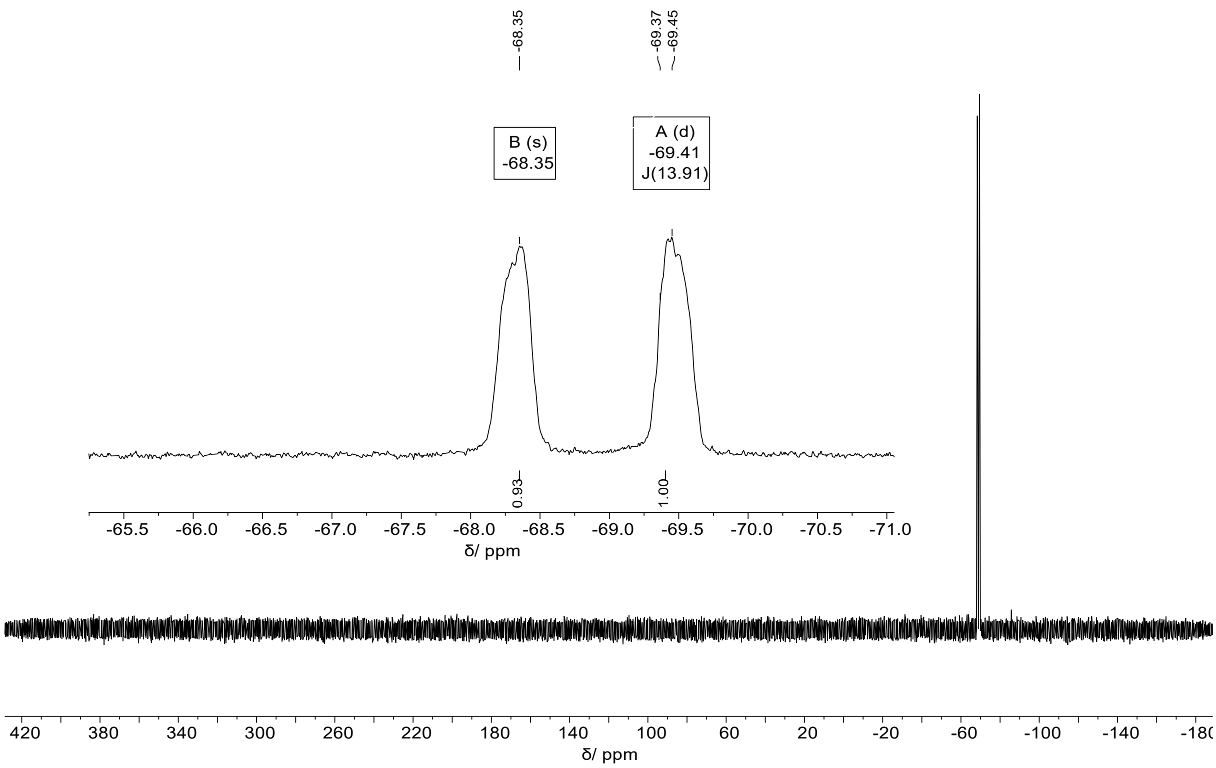


Fig. S44 ^{31}P NMR spectrum of **4e** in $CDCl_3$.

3.12 4f

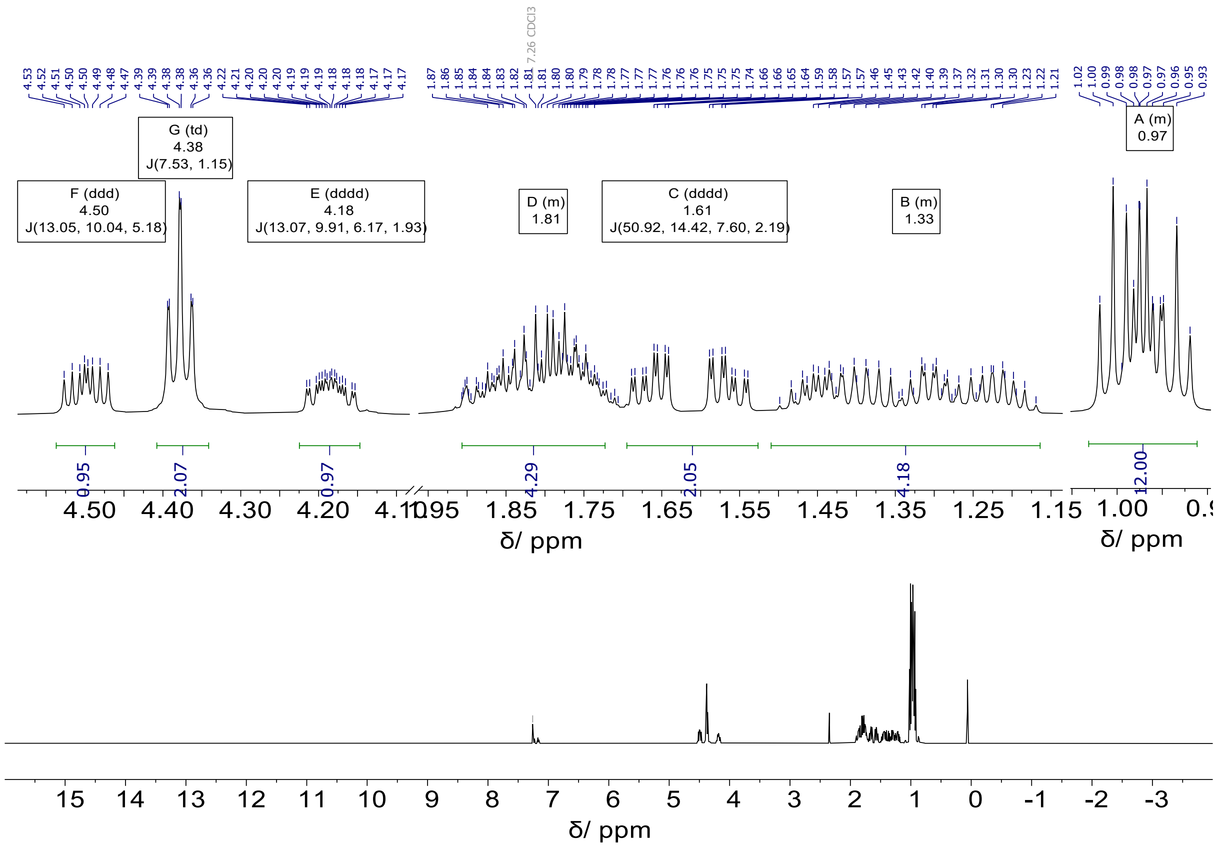


Fig. S45 ^{1}H NMR spectrum of **4f** in $CDCl_3$.

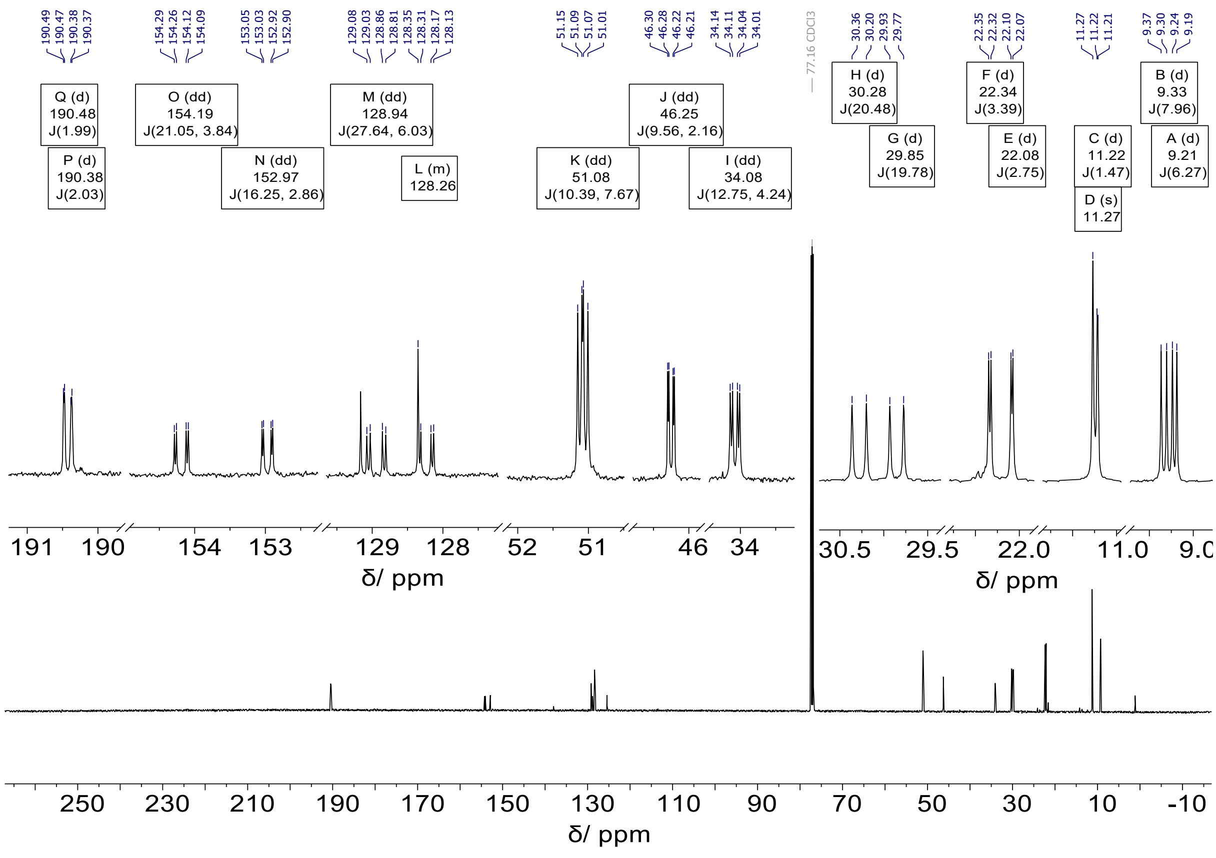


Fig. S46 ^{13}C NMR spectrum of **4f** in $CDCl_3$.

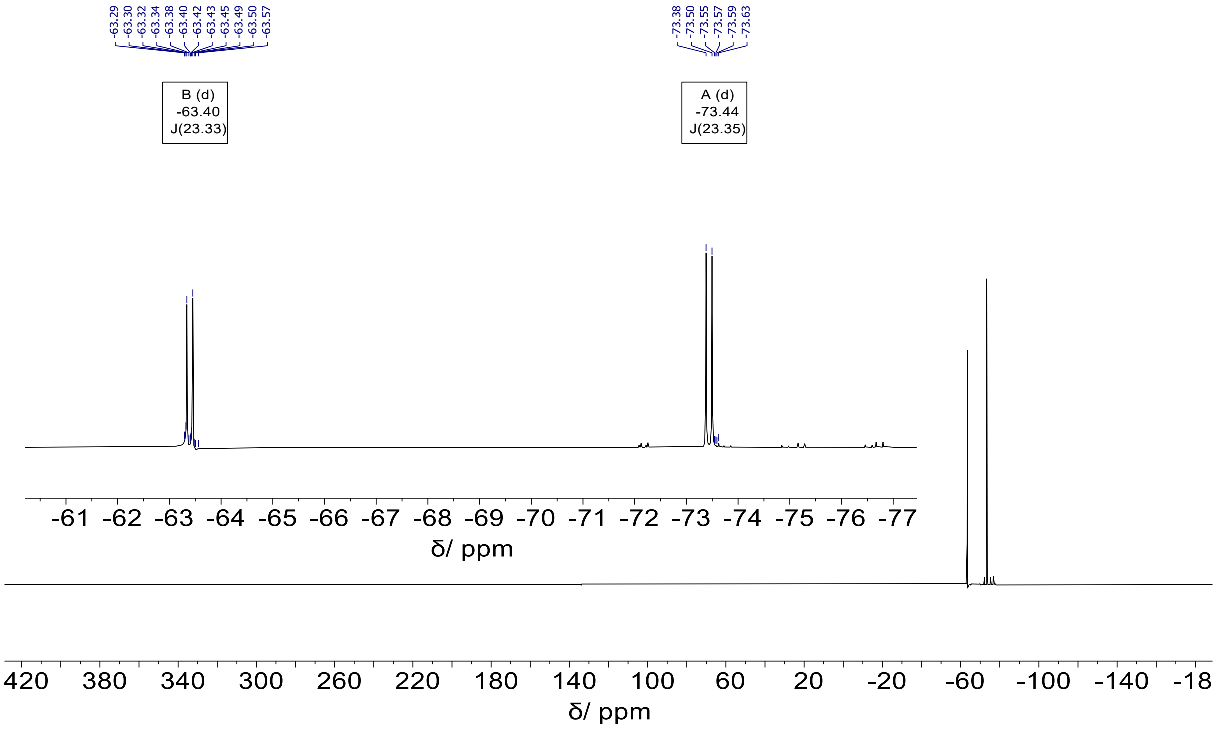


Fig. S47 $^{31}P\{^1H\}$ NMR spectrum of **4f** in $CDCl_3$.

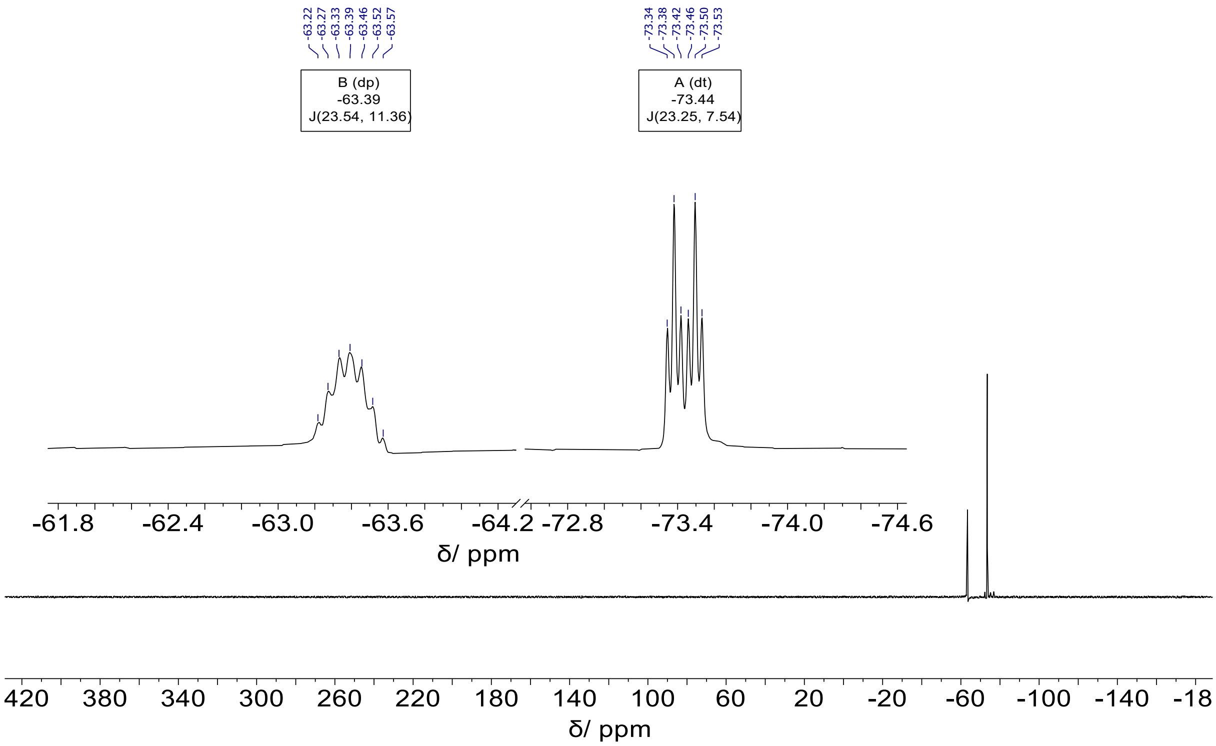


Fig. S48 ^{31}P NMR spectrum of **4f** in $CDCl_3$.

3.13 $^{31}P\{^1H\}$ NMR spectrum of 4c at 100 °C

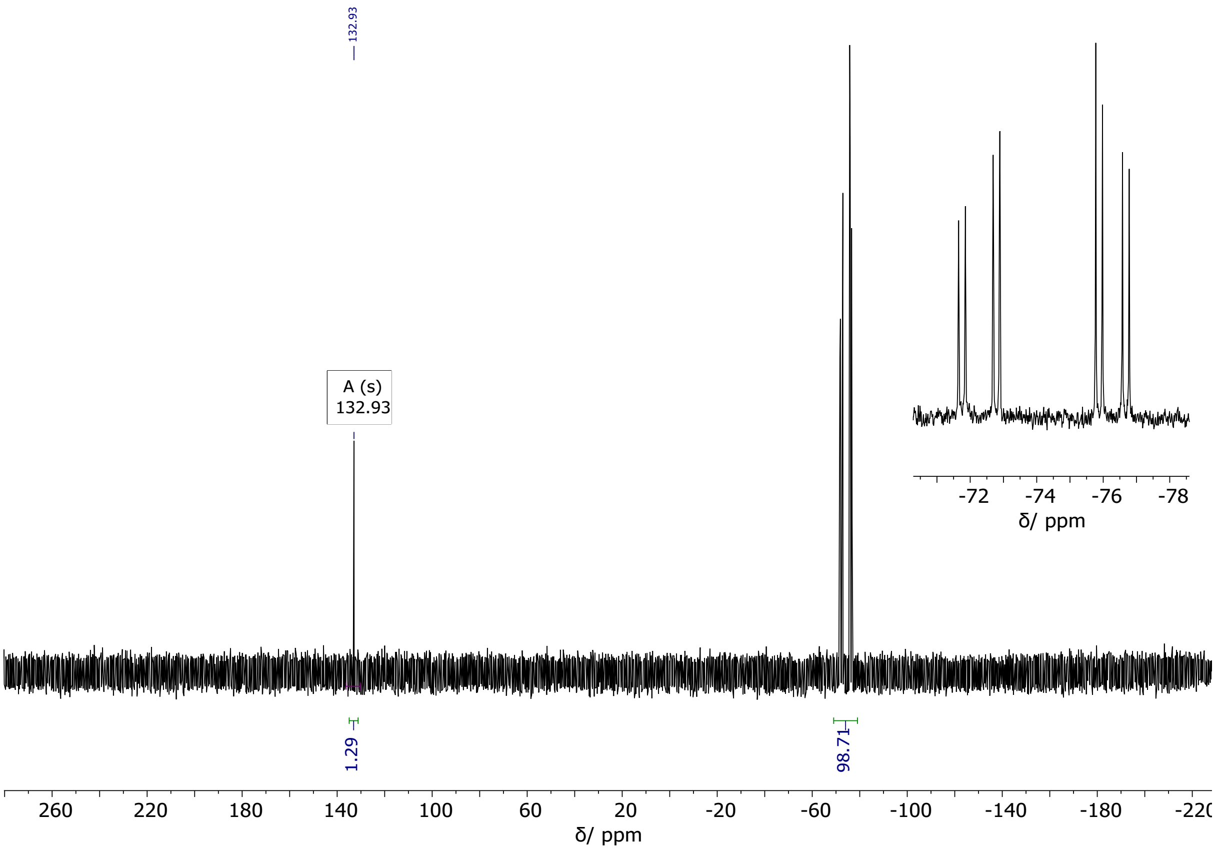


Fig. S49 $^{31}P\{^1H\}$ NMR spectrum of **4c** in toluene at 100 °C.

4 Singel crystal X-ray diffraction studies

4.1 3c

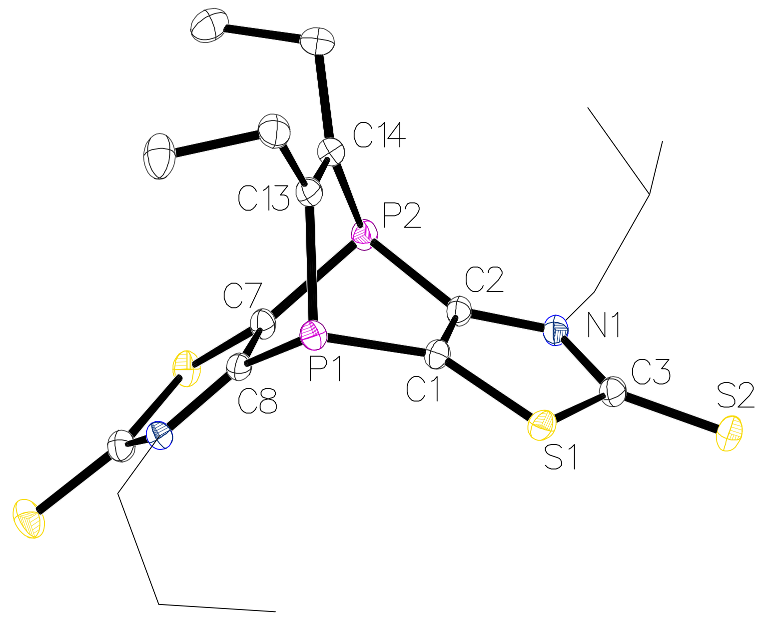


Fig S50: Molecular structure of **3c** in the single crystal lattice at 100 K. Thermal ellipsoids are set at 50% probability level. Hydrogen atoms were omitted and N-*n*-propyl groups are shown as wire-frames for clarity.

Table S1: Crystal data and structure refinement for **3c**.

CCDC Deposition Number	2366202
Crystal Habitus	clear colourless block
Device Type	Bruker D8 Venture
Empirical formula	$C_{18}H_{24}N_2P_2S_4$
Moiety formula	$C_{18}H_{24}N_2P_2S_4$
Formula weight / g/mol	458.57
T / K	100
Crystal system	triclinic
Space group	$P\bar{1}$
a / Å	7.2842(5)
b / Å	9.9259(6)
c / Å	15.0111(9)
α / °	94.948(3)
β / °	94.001(3)
γ / °	96.798(3)
V / Å^3	1070.17(12)
Z	2
ρ_{calc} / g/cm^3	1.423
μ / mm^{-1}	0.600
F(000)	480.0
Crystal size / mm^3	0.24 × 0.22 × 0.1
Absorption correction	empirical
T_{min}; T_{max}	0.6744; 0.7460
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection / °	4.152 to 59.932°
Completeness to Θ	0.996
Index ranges	−10 ≤ h ≤ 10, −13 ≤ k ≤ 13, −21 ≤ l ≤ 21
Reflections collected	20653
Independent reflections	6196 [R_{int} = 0.0426, R_{sigma} = 0.0400]
Data/restraints/parameters	6196/226/250
Goodness-of-fit on F^2	1.023
Final R indexes (I ≥ 2σ (I))	R_1 = 0.0297, ωR_2 = 0.0712
Final R indexes (all data)	R_1 = 0.0354, ωR_2 = 0.0747
Largest diff. peak/hole / e/Å^3	0.46/−0.28

Table S2: Bond lengths for **3c**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	C1	1.7349(13)	N2	C8	1.3886(16)
S1	C3	1.7457(14)	N2	C9	1.3673(16)
S2	C3	1.6664(14)	N2	C10	1.4674(16)
S3	C7	1.7327(13)	C1	C2	1.3491(18)
S3	C9	1.7424(14)	C4	C5	1.523(2)
S4	C9	1.6630(14)	C5	C6	1.496(2)
P1	C1	1.8193(13)	C5	C6A	1.496(3)
P1	C8	1.8458(13)	C7	C8	1.3484(18)
P1	C13	1.8682(14)	C10	C11	1.5292(19)
P2	C2	1.8493(13)	C11	C12	1.524(2)
P2	C7	1.8177(14)	C13	C14	1.338(2)
P2	C14	1.8713(14)	C13	C15	1.5084(19)
N1	C2	1.3907(16)	C14	C17	1.5168(19)
N1	C3	1.3687(17)	C15	C16	1.534(2)
N1	C4	1.4717(17)	C17	C18	1.529(2)

Table S3: Bond angles for **3c**.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C1	S1	C3	92.21(6)	N1	C4	C5	112.61(11)
C7	S3	C9	92.43(6)	C6	C5	C4	115.06(13)

C1	P1	C8	94.52(6)	C6A	C5	C4	114.4(7)
C1	P1	C13	96.19(6)	S3	C7	P2	127.41(8)
C8	P1	C13	96.01(6)	C8	C7	S3	110.13(10)
C2	P2	C14	95.36(6)	C8	C7	P2	122.45(10)
C7	P2	C2	95.05(6)	N2	C8	P1	125.56(9)
C7	P2	C14	96.35(6)	C7	C8	P1	120.35(10)
C2	N1	C4	123.86(11)	C7	C8	N2	114.06(11)
C3	N1	C2	114.66(11)	S4	C9	S3	123.98(8)
C3	N1	C4	121.48(11)	N2	C9	S3	108.71(9)
C8	N2	C10	123.77(11)	N2	C9	S4	127.31(10)
C9	N2	C8	114.66(11)	N2	C10	C11	112.37(11)
C9	N2	C10	121.56(11)	C12	C11	C10	113.97(11)
S1	C1	P1	127.11(8)	C14	C13	P1	121.03(10)
C2	C1	S1	110.41(10)	C14	C13	C15	125.63(13)
C2	C1	P1	122.45(10)	C15	C13	P1	113.28(10)
N1	C2	P2	125.90(10)	C13	C14	P2	120.71(10)
C1	C2	P2	120.21(10)	C13	C14	C17	124.86(13)
C1	C2	N1	113.89(11)	C17	C14	P2	113.93(10)
S2	C3	S1	123.45(8)	C13	C15	C16	111.93(12)
N1	C3	S1	108.82(9)	C14	C17	C18	109.37(12)
N1	C3	S2	127.72(11)				

4.2 4f

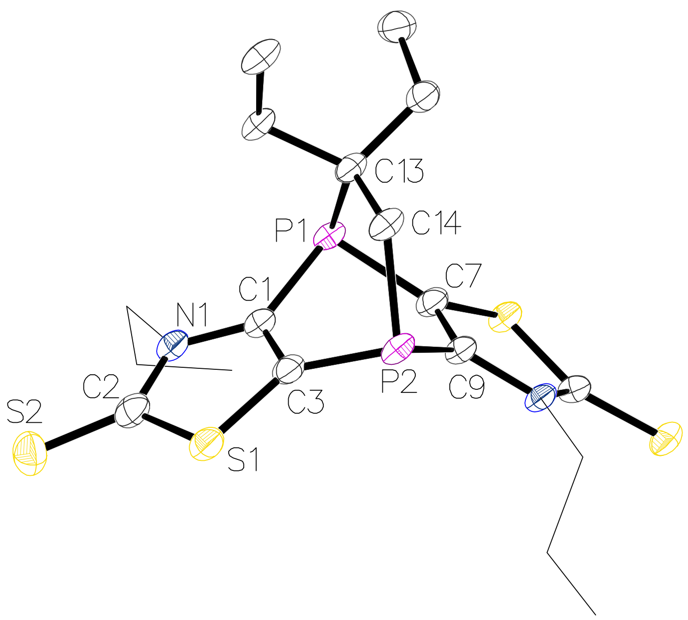


Fig S51: Molecular structure of **4f** in the single crystal lattice at 100 K. Thermal ellipsoids are set at 50% probability level. Hydrogen atoms were omitted and N-*n*-propyl groups are shown as wire-frames for clarity.

Table S4: Crystal data and structure refinement for **4f**.

CCDC Deposition Number	2366203
Crystal Habitus	clear colourless plank
Device Type	STOE Stadivari
Empirical formula	$C_{18}H_{26}N_2P_2S_4$
Moiety formula	
Formula weight / g/mol	$C_{18}H_{26}N_2P_2S_4$
T / K	460.62
Crystal system	100
Space group	triclinic
a / Å	$P\bar{1}$
b / Å	8.3076(3)
c / Å	10.2906(4)

α / °	15.3615(6)
β / °	102.542(3)
γ / °	101.566(3)
V / Å^3	106.023(3)
Z	1183.70(8)
ρ_{calc} / g/cm^3	2
μ / mm^{-1}	1.292
F(000)	5.00
Crystal size / mm^3	484.0
Absorption correction	0.2 × 0.1 × 0.05
T_{min}; T_{max}	multi-scan
Radiation	
2Θ range for data collection / °	0.2631; 0.4032
Completeness to Θ	
Index ranges	CuKα (λ = 1.54186)
Reflections collected	9.342 to 141.228°
Independent reflections	0.994
Data/restraints/parameters	−9 ≤ h ≤ 10, −12 ≤ k ≤ 12, −10 ≤ l ≤ 18
Goodness-of-fit on F^2	27308
Final R indexes (I ≥ 2σ (I))	4455 [R_{int} = 0.0418, R_{sigma} = 0.0251]
Final R indexes (all data)	4455/0/239
Largest diff. peak/hole / e/Å^3	1.051

Table S5: Bond lengths for **4f**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	C2	1.747(2)	N2	C8	1.354(3)
S1	C3	1.729(2)	N2	C9	1.397(3)
S2	C2	1.659(2)	N2	C10	1.473(3)
S3	C7	1.733(2)	C1	C3	1.351(3)
S3	C8	1.744(2)	C4	C5	1.529(3)
S4	C8	1.669(2)	C5	C6	1.516(3)
P1	C1	1.832(2)	C7	C9	1.352(3)
P1	C7	1.818(2)	C10	C11	1.516(3)
P1	C13	1.903(2)	C11	C12	1.525(3)
P2	C3	1.824(2)	C13	C14	1.554(3)
P2	C9	1.837(2)	C13	C15	1.552(3)
P2	C14	1.861(2)	C13	C17	1.543(3)
N1	C1	1.394(3)	C15	C16	1.530(3)
N1	C2	1.362(3)	C17	C18	1.530(3)
N1	C4	1.479(3)			

Table S6: Bond angles for **4f**.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C3	S1	C2	92.36(11)	N1	C4	C5	112.39(17)
C7	S3	C8	92.08(10)	C6	C5	C4	114.9(2)
C1	P1	C13	96.35(10)	S3	C7	P1	126.42(12)
C7	P1	C1	95.11(10)	C9	C7	S3	110.27(16)
C7	P1	C13	98.31(9)	C9	C7	P1	123.28(17)
C3	P2	C9	94.54(10)	S4	C8	S3	123.41(13)
C3	P2	C14	96.38(10)	N2	C8	S3	109.35(15)
C9	P2	C14	96.60(10)	N2	C8	S4	127.24(16)
C1	N1	C4	124.20(18)	N2	C9	P2	125.14(16)
C2	N1	C1	114.85(18)	C7	C9	P2	121.17(16)
C2	N1	C4	120.91(19)	C7	C9	N2	113.68(19)
C8	N2	C9	114.59(17)	N2	C10	C11	111.70(18)
C8	N2	C10	121.75(17)	C10	C11	C12	111.3(2)
C9	N2	C10	123.57(17)	C14	C13	P1	114.38(14)
N1	C1	P1	124.61(16)	C15	C13	P1	104.58(14)
C3	C1	P1	121.70(17)	C15	C13	C14	110.71(17)

C3	C1	N1	113.6(2)	C17	C13	P1	106.59(14)
S2	C2	S1	124.20(14)	C17	C13	C14	108.33(18)
N1	C2	S1	108.71(17)	C17	C13	C15	112.23(17)
N1	C2	S2	127.10(18)	C13	C14	P2	120.95(15)
S1	C3	P2	126.69(13)	C16	C15	C13	114.60(19)
C1	C3	S1	110.44(17)	C18	C17	C13	116.59(19)
C1	C3	P2	122.80(18)				

5 Computational details

5.1 Theoretical methods

All structures were built with the open-source software *Avogadro 1.2.0*.[160] Structures were optimised using the *ORCA*[161] 4.0.1.2 program package at the TPSS-D3BJ/def2-TZVP(CPCM$_{THF}$) level of theory, a combination of the mega-GGA density functional TPSS[162] with BJ-damped DFT-D3[163] dispersion correction and the def2-TZVP[164] basis set, including the conductor-like polarisable continuum model (CPCM)[165] as a solvent model for THF. In order to accelerate the optimisations and following harmonic frequency calculations, the density-fitting RI-J (def2/J) approach was used.[166] The DFT grid was set to 4, with the grid for the final energy being set to 5. Optimised structures were characterised by frequency analyses in order to identify the nature of the respective located stationary point (no imaginary frequency below −30 cm^{-1} for minima and only one imaginary frequency for transition states) and to get access to thermal corrections (for 298.15 K and 1 atm) according to the modified ideal gas-rigid rotor-harmonic oscillator model. Transition states were obtained via relaxed potential energy surface scans along the important bond in *ORCA* 4.0.1.2 or by nudged elastic band calculations[167] using *ORCA* 5.0.4. The transition state vibration was taken from the respective highest energy structure and the structure was optimised, keeping the imaginary frequency. Final single point energies were calculated with *ORCA* 4.0.1.2 on the RI-PW6B95-D3BJ/def2-QZVP(CPCM$_{THF}$)[164,168] level of theory using the density-fitting RI-JK (def2/JK)[169] approach. The final Gibbs free energies G were obtained from the sum of the electronic single point energies and the thermal corrections accessed from the frequency analyses. Distortion energies were calculated by subtracting the energies of the respective dienophile/diphosphinine fragment in the transition state from the energies of the relaxed dienophile/diphosphinine. Calculated structures were visualised using the software *UCSF Chimera 1.17.2*.[170]

5.2 Additional tables/figures

Table S7 $\Delta_r G^\ddagger$ and $\Delta_r G$ of the formation of compounds **3a–c^{Me}** and **4a–f^{Me}**.

	alkyne/alkene	$\Delta_r G^\ddagger$ / kcal/mol	$\Delta_r G$ / kcal/mol
3a^{Me}	DEAD	27.7	−14.4
3b^{Me}	ethyl propiolate	18.5	−23.2
3c^{Me}	3-hexyne	20.3	−11.7
4a^{Me}	diethyl maleate	10.8	−13.0
4a'^{Me}	diethyl fumarate	18.6 14.8	−3.1 −4.4
4b^{Me}	ethyl acrylate	17.8 18.8	−4.9 −6.1
4c^{Me}	1-hexene	21.0 19.5	−6.8 −7.1
4d^{Me}	Ethene	17.8	−11.2
4e^{Me}	Cyclohexene	23.4	−3.0
4f^{Me}	2-ethyl-1-butene	20.6	−5.4

Fig S52 Δ_rG and $\Delta_rG^‡$ of 1,4-diphosphabarrelenes having an unsaturated (**3a–d^{Me}**) or saturated (**4a–f^{Me}**) bridge (left) and Δ_rG of **3a–d^{Me}** and **4a–d^{Me}** (right).

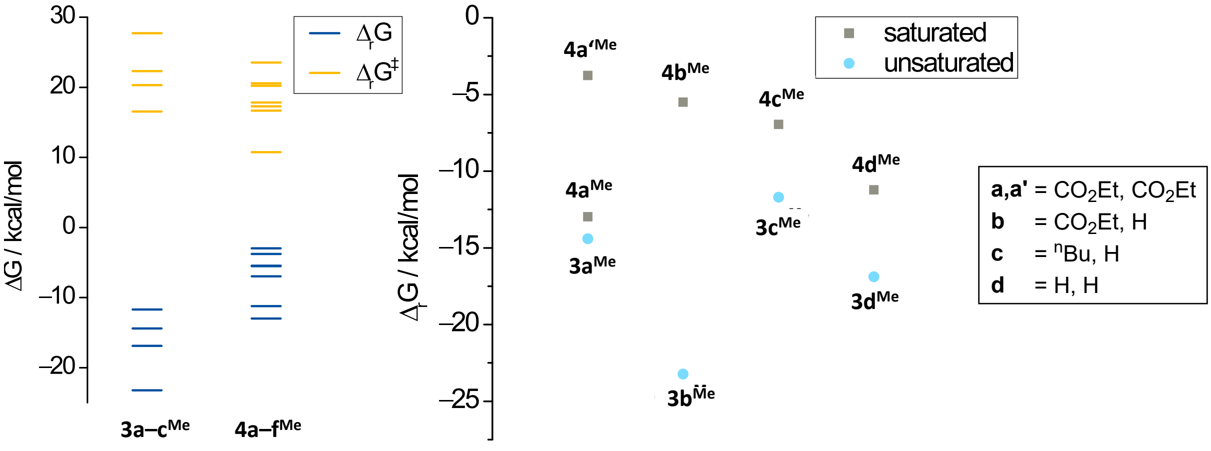


Table S8 $\Delta_rG^‡$ and Δ_rG of the formation of compounds **3a–c^{Me}** and **4a–f^{Me}**.

	alkene/alkyne	Δ_rG_{dist} / kcal/mol		
		alkyne/alkene fragment	diphosphinine fragment	total
3a^{Me}	DEAD	12.4	7.4	19.9
3b^{Me}	ethyl propiolate	5.8	8.1	13.9
3c^{Me}	3-hexyne	16.5	9.7	26.3
3d^{Me}	ethyne	9.2	9.5	18.7
4a^{Me}	diethyl maleate	2.9	10.6	13.4
4a'^{Me}	diethyl fumarate	12.6 10.7	12.1 12.3	24.6 23.0
4b^{Me}	ethyl acrylate	7.9 9.1	9.8 10.0	17.8 19.1
4c^{Me}	1-hexene	12.5 10.7	14.2 10.9	26.7 21.6
4d^{Me}	Ethene	6.7	10.1	16.8
4e^{Me}	Cyclohexene	15.1	10.8	25.9
4f^{Me}	2-ethyl-1-butene	12.7	11.3	23.9

5.3 Coordinates

5.3.1 1^{Me}

E = −2696.235653675209

C	3.972083	6.503908	1.249647
C	2.565938	6.575210	1.320480
P	1.400545	6.515237	0.003816
C	2.475970	6.346970	-1.358836
C	3.882109	6.275521	-1.429660
P	5.047562	6.336801	-0.113112

N	4.338315	6.139387	-2.739973
C	3.379465	6.098055	-3.733366
S	1.802903	6.237618	-2.975836
N	2.109660	6.709924	2.630916
C	3.068453	6.750151	3.624406
S	4.645097	6.612363	2.866722
S	2.837375	6.901697	5.248675
S	3.610511	5.945923	-5.357583
C	5.764815	6.045985	-3.050295
H	5.851238	5.936474	-4.132268
H	6.193954	5.178335	-2.539860
H	6.273266	6.954979	-2.714371
C	0.683148	6.803147	2.941237
H	0.596569	6.909467	4.023515
H	0.174366	5.895420	2.602417
H	0.254488	7.672558	2.433390

5.3.2 2a^{Me}

E = −5006.931003797543

C	4.02475278897753	6.40802738345381	1.32059455141458
C	2.66698873412746	6.59972182756763	1.39234191816411
P	1.56843570258564	6.13814670908466	-0.00474325537492
C	2.62629745620955	6.86170621963828	-1.30205663482201
C	3.98187806350150	6.65532969845691	-1.37534031726600
P	4.85844209589007	5.64983634530337	-0.11322298440008
N	4.56840731170391	7.25009709128418	-2.49388972302703
C	3.70741448359073	7.91299204612130	-3.33043487350230
S	2.09515510180376	7.82854961805499	-2.65227346044413
N	2.25122048164307	7.13328722322069	2.61355701236330
C	3.24624569474207	7.35573880594084	3.53051806981596
S	4.78008264600036	6.92156669660407	2.80594388923020
S	3.05070647740087	7.94945104207396	5.08062868170283
S	4.10912854435923	8.68558014247278	-4.75714566276056
C	6.00046385910380	7.17391774357821	-2.80125433889727
H	6.15433236462938	6.54619340506814	-3.68249737827496
H	6.50524999041684	6.74429029171893	-1.93547468954353
H	6.37181278371757	8.17924081726439	-3.00749172786143
C	0.85272193519396	7.43057526216238	2.94056309356231
H	0.50304408371931	6.74346227616474	3.71497711559795
H	0.26419922525036	7.31010436374402	2.03062131348076
H	0.78571223685242	8.45448515192912	3.31269308475474
Ga	2.94724081504659	4.13494587838222	-0.22321084982517
C	2.46217584359055	1.00414098973337	-0.51723916750210
C	2.50211764415207	1.72406339368218	-1.72276136637992
N	2.69487910891222	3.04810536891816	-1.79703806804114
N	2.82364188528111	2.75427138766433	1.11849881369603
C	2.60891144550370	1.47050034446789	0.79962425992184
C	2.31336015118197	0.95154090122197	-3.00301073150429
H	2.18099622120450	-0.11012503124939	-2.79299663730597
H	3.17889464419822	1.07958146118349	-3.66291445776207
H	1.43575804792795	1.31772646691871	-3.54811920788874

C	2.52065945053692	0.45769220672605	1.91216346702371
H	2.32649357962038	-0.53674564364176	1.50949614143130
H	1.72013349617837	0.72163603506225	2.61243701825240
H	3.45470544778835	0.43268211975122	2.48520520594925
C	2.71832754251840	3.70181142529459	-3.11572561431047
H	2.83849974069539	4.77567846090538	-2.96988517025022
H	1.78366190876362	3.53018898819737	-3.65946408844692
H	3.55333049250686	3.33650500046782	-3.72341672070723
C	2.96340842018669	3.13336068661146	2.53395043389273
H	3.78428896682962	2.58800855576048	3.01076965627152
H	2.03938963625569	2.93745340442227	3.08890229501243
H	3.18218464860074	4.20016787883379	2.58886107110874
H	2.29544380110069	-0.06164444022130	-0.61740396654819

5.3.3 2b^{Me}

E = −3323.791623352091

C	4.04199549810001	6.37112814438846	1.31386142688811
C	2.68454485890242	6.56259352849417	1.39609489586857
P	1.57321255605512	6.09699183218913	0.00606857095339
C	2.62576186797545	6.82241131224260	-1.30060421237631
C	3.98136465289419	6.61836532924965	-1.38373533659069
P	4.86940163808019	5.60952667426282	-0.12729381144056
N	4.55969723167665	7.21965810153630	-2.50402378753246
C	3.69232231080885	7.88403697100211	-3.33290079200986
S	2.08540899064136	7.79667228589250	-2.64310329698630
N	2.27910751066627	7.10298278977937	2.61857145409105
C	3.28130530547304	7.32979032800607	3.52667059039921
S	4.80939003936789	6.89601260626500	2.79031797599078
S	3.09713055456696	7.92766343162252	5.07672770046405
S	4.08421985417031	8.66026057292206	-4.76050167490793
C	5.98985129367221	7.14809457394379	-2.82048103375697
H	6.13837554104371	6.53555118765576	-3.71327084448227
H	6.49824133292919	6.70349197047373	-1.96443204642753
H	6.36128663693290	8.15644059183164	-3.01165951347595
C	0.88334266980878	7.40110637127781	2.95565311543587
H	0.54213818498007	6.72109809091667	3.74009415724711
H	0.28744278176848	7.27037926120721	2.05192932667530
H	0.81755255196955	8.42851230919831	3.31833460958784
Al	2.95753296546474	4.11005902353216	-0.22205865128706
C	2.43124304813621	1.01586338855026	-0.50631513645127
C	2.48726908557036	1.74193301531907	-1.70548318784714
N	2.70962192450718	3.06761852373285	-1.75528330568670
N	2.83437289906030	2.78479810625158	1.09206806526683
C	2.59435380676652	1.49335673982549	0.80281742704787
C	2.28566368353618	0.98794597296528	-2.99228122038105
H	2.12504134713980	-0.07191824110956	-2.79358989546666
H	3.15754087904457	1.10038210762033	-3.64682257287514
H	1.42120048464788	1.38253865076949	-3.53871542940661
C	2.49713543356375	0.49998346701561	1.92921796895630
H	2.27620781780474	-0.49547511103643	1.54343101267695
H	1.71216042016791	0.79211458800166	2.63595735086195
H	3.43753884927437	0.46245115256772	2.49133226170211

C	2.75027727239882	3.72214667989932	-3.07730159814810
H	2.90825156543842	4.79123247664211	-2.93201636884290
H	1.80742774776724	3.58453841576050	-3.61580079865621
H	3.56979932628088	3.32867788247274	-3.68745917752830
C	2.99205679577099	3.16910440187442	2.50812244616110
H	3.80057149049767	2.60524455752627	2.98323846200888
H	2.06541789461696	3.00305334030068	3.06762857230030
H	3.24057407355461	4.22989319467985	2.55569112964483
H	2.24242432650629	-0.04640159751905	-0.60360282766442

5.3.4 3a^{Me}

E = −3309.032275071040

C	3.74105119134508	6.26126491346011	0.58588866717453
C	2.38990597994887	6.41901457005862	0.59983269667995
P	1.37849050145422	5.97962885891949	-0.87481703676052
C	2.46617992638098	6.79937024407936	-2.08276723154829
C	3.81674060113616	6.62897068002108	-2.09100506821728
P	4.65320254095644	5.56432263010779	-0.83622568685325
N	4.45760344741136	7.30840606772400	-3.11290814946405
C	3.62712228152704	8.03287567790746	-3.94092033371283
S	1.97599947132268	7.83246168273285	-3.38862299011400
N	1.89310598834872	6.91289708131052	1.79549754331371
C	2.84479497923542	7.16077965719521	2.75970702204402
S	4.41882886770513	6.74513984822065	2.10724924486915
S	2.56674778595950	7.75664589994397	4.28889704040103
S	4.09659629063249	8.95210435118821	-5.24641883809526
C	5.90800213593385	7.29600291740397	-3.34078701106677
H	6.11261924824472	6.86459434150963	-4.32260469205449
H	6.37015730241314	6.69759325524788	-2.55604559608402
H	6.28029093077361	8.32183314838601	-3.31133097884297
C	0.47319749313500	7.17038148879568	2.06604050063188
H	0.14852523288100	6.54338000882742	2.89887826156868
H	-0.09390830469019	6.93415832161527	1.16590491768540
H	0.34653792927607	8.22126652940822	2.33316172769660
C	3.49315945318583	4.10884913872607	-1.08719574005913
C	2.16326348804300	4.27827884498595	-1.05686626263504
C	1.14873143972672	3.19190797903657	-1.25111827402443
O	0.81215780571521	2.63941310129956	-0.08158703795476
C	-0.27023541493279	1.63512583176390	-0.10916144244384
O	0.63778279139670	2.96421450358738	-2.33336868742062
C	4.07917510108484	2.75473428246826	-1.29464339388847
O	5.42199585643555	2.80652839912276	-1.33671109361928
C	6.12893917549468	1.52859838298518	-1.51302710536179
O	3.41532059815200	1.73747194177546	-1.42090419580148
C	-1.61669736455795	2.31529538879210	0.04880243180584
H	-0.03292172712884	0.98597806813008	0.73402888351557
H	-0.19012086795498	1.07985547503603	-1.04481030627731
H	-1.65083234103492	2.89570338111690	0.97555673587419
H	-2.39933799189989	1.55027863752412	0.08940861960654
H	-1.82340040483593	2.97663100762371	-0.79717450130944
C	6.37879569392423	0.87656561810527	-0.16568155647064
H	7.05641874559094	1.81785495366601	-2.00841121993624

H	5.52862141609061	0.89965971682040	-2.17274577319984
H	6.94989973094827	1.54357253026060	0.48673177907425
H	6.95765990405966	-0.04063282903146	-0.31724107155451
H	5.43641503296579	0.61547986544173	0.32345318472920

5.3.5 *3b*^{Me}

E = −3041.399925674273

C	3.69870517742494	6.40029686348000	0.67722749301750
C	2.35108116173161	6.58471030583555	0.68157415731006
P	1.32698275237884	6.05096047865052	-0.76056273539134
C	2.41809242647736	6.79746507709664	-2.02106786188037
C	3.76537943635303	6.60834297037754	-2.02000853995101
P	4.59187209880646	5.60279147881603	-0.70460420738980
N	4.41865710781721	7.24401378856339	-3.06311336033278
C	3.60256627089771	7.95769063197493	-3.92871051592945
S	1.94051708998708	7.79370245146300	-3.36408715520760
N	1.87047570033184	7.18634839566657	1.83347578816735
C	2.83105561127146	7.49990340094429	2.78352895186883
S	4.39912569391323	6.99586773530016	2.15316245464603
S	2.55952014282623	8.21899117209174	4.24290213746688
S	4.09563692588532	8.80828668519430	-5.25313971392033
C	5.86503620086989	7.20807617500669	-3.29317220809600
H	6.06217149814760	6.77317598278868	-4.27587143080810
H	6.32079239053359	6.60869363804150	-2.50411969299221
H	6.25504781415211	8.22863256158023	-3.28169658846716
C	0.46388107945697	7.50505249849493	2.09007484643200
H	0.13480754600025	6.98171219877402	2.99098443693841
H	-0.12058962493932	7.19236925629518	1.22394574228270
H	0.36457558413627	8.58000720897015	2.25851121642280
C	3.40858112824567	4.15848309393134	-0.86897272039886
C	2.08426397878186	4.35709646534866	-0.85003847503971
C	3.94287039049661	2.77136745467701	-1.00995291682598
O	5.28773348875795	2.79013913515988	-1.17399726687305
C	5.93655884301386	1.48577720687641	-1.31161586103009
O	3.26205741916899	1.76410084962777	-0.99404170738536
H	1.40989226559947	3.50504550350945	-0.92314891301440
C	6.28419457506559	0.91853529895524	0.05387969570262
H	6.82740069534554	1.70101100285074	-1.90479649010059
H	5.26325161849983	0.82796711089683	-1.86572345080714
H	6.92101442617710	1.61175962754045	0.61119767523471
H	6.82585939711634	-0.02515382055806	-0.07189741526735
H	5.37753168927151	0.72049011577825	0.63134463161876

5.3.6 *3c*^{Me}

E = −2931.297334350897

C	3.70702219643299	6.49697857969386	0.77987887684780
C	2.35016966379971	6.56599819061521	0.71074179668685
P	1.45956634725176	5.87918097883869	-0.74808377332178
C	2.54264035755058	6.67456516490892	-1.98259956129317
C	3.89922326001221	6.60045019101753	-1.91348117508322
P	4.70968277553927	5.70471488176377	-0.52262179736309

N	4.54763562393467	7.22166590695072	-2.97079850848976
C	3.71753874291261	7.79851367091470	-3.90448408297803
S	2.05744684283328	7.54337410079473	-3.40499171293421
N	1.76329149086602	7.15807980875427	1.81931924034367
C	2.64337679005479	7.56838686057742	2.79427640180701
S	4.27135204148786	7.19023152647282	2.26802521650426
S	2.24457143363160	8.30781237843026	4.23495241838285
S	4.19432411776017	8.60990223734219	-5.28133933722688
C	6.00548998475346	7.28078124582051	-3.12974230481286
H	6.29171149618484	6.74139013458857	-4.03527466769263
H	6.46042245316985	6.82312769919319	-2.25132733999654
H	6.31118614839298	8.32476561686163	-3.22026489845098
C	0.31838427758848	7.35137074960430	1.98887349182506
H	-0.02200412432787	6.78019885057602	2.85528495796840
H	-0.17788553492761	7.00472036546615	1.08249726648168
H	0.11779485468507	8.41154283548858	2.15474278469446
C	3.67145333036691	4.14601208100345	-0.67460521357157
C	2.33488828199706	4.21616322564556	-0.73775824554057
C	1.37530807153810	3.05253877042054	-0.78716633204747
C	0.57939327006057	2.93119307528753	0.52462183038958
C	4.50865955943306	2.89178165025271	-0.73822965940705
C	5.28790536089920	2.81051955091829	-2.06306708909202
H	-0.14883779629332	2.11718700299158	0.45655179994718
H	0.03063040410713	3.85715838507952	0.73602143931520
H	1.25147442211289	2.73433038701287	1.36563241444107
H	1.91668958347918	2.12265903354516	-0.98375944913979
H	0.67589038257166	3.20463464770913	-1.61956791630049
H	5.21976577835392	2.89636065638493	0.09806707854657
H	3.87558589265465	2.00748272795526	-0.62157625846792
H	5.92736570877057	3.69191506445988	-2.19537591635123
H	4.59910290133189	2.75968685231624	-2.91204681493595
H	5.93000360902982	1.92447491434332	-2.07590495968443

5.3.7 *3d*^{Me}

E = −2773.758301717286

C	3.70933765876113	6.46636498417746	0.77315364261383
C	2.35267094511148	6.53502750713963	0.70703904466619
P	1.44224340770972	5.84610056048511	-0.74799599365384
C	2.53747732011220	6.64477695723922	-1.97848608894606
C	3.89382029777198	6.57012724722625	-1.91262183077404
P	4.72339615540964	5.66978628915102	-0.52631947655585
N	4.54051778195785	7.21876402087935	-2.95416095007834
C	3.70851516323251	7.82081163671214	-3.87056480755524
S	2.04945081636594	7.54777026523141	-3.37747714874922
N	1.77050960239101	7.15651680695497	1.80178124648095
C	2.65520481215464	7.59353407386135	2.76133026577630
S	4.28020628445936	7.19570628596866	2.24047182074818
S	2.26442552938056	8.37094957959136	4.18332218707475
S	4.18168862688945	8.67047770373050	-5.22451509030974
C	5.99795587286413	7.28839761800694	-3.11387523707117
H	6.28247207041911	6.78702955254362	-4.04137498041713
H	6.45730045678072	6.79631289039569	-2.25690998048386

H	6.30018461633156	8.33624300345111	-3.16293509424225
C	0.32688545640815	7.35861789981958	1.97340271570343
H	-0.00733742451295	6.82248920339522	2.86411218818982
H	-0.17711766325502	6.97667226783353	1.08591298823116
H	0.12923408872083	8.42492228070670	2.09879121164342
C	3.66704873294018	4.14295193900356	-0.67526192878832
C	2.33772604769341	4.21307716043694	-0.73562681251614
H	4.19835087093378	3.19386462865647	-0.68963568839100
H	1.71304524476863	3.32502387260222	-0.80140298029584

5.3.8 4a^{Me}

E = −3310.279597850461

C	3.71650953293307	6.78713568522110	1.13654875898511
C	2.37304145037515	6.93348756574842	0.95568995876229
P	1.48498522803804	5.97371823947029	-0.32324688005143
C	2.68270874406844	6.18582667302877	-1.65836773198102
C	4.02901907377427	6.05994149254451	-1.47879659321052
P	4.74085873254562	5.65474241774798	0.15493719192855
N	4.75292831926578	6.13480526325797	-2.65649903823400
C	4.00266462147790	6.30125409209554	-3.80799786740682
S	2.30767135234551	6.38458273221165	-3.34642660540197
N	1.77861456304402	7.80204894152742	1.86038462736034
C	2.63459967774447	8.37129844533124	2.78982469815124
S	4.25841181152412	7.75910959071844	2.47675440203341
S	2.21353190544575	9.44292915522944	3.97162410067751
S	4.59762404015524	6.40876282494790	-5.34562081330229
C	6.21140732655051	6.05679402196509	-2.74335667767709
H	6.48746742314403	5.24068798979432	-3.41450308426429
H	6.60372996628942	5.88383819987434	-1.74091281212484
H	6.59806734767942	6.99019380258973	-3.16013817207548
C	0.35698868559895	8.15540151868597	1.87179633250063
H	-0.07076619606930	7.89440180537028	2.84267679901006
H	-0.13727063633783	7.60762303308623	1.06834512312584
H	0.25352389404908	9.23361192951214	1.72765413480620
C	3.66022657952476	4.11537679987520	0.45985923834515
C	2.11643184211760	4.27587391235978	0.30841932560132
C	1.49647657586657	3.27048409737676	-0.64689785189784
O	0.52661818950218	2.56322889467109	-0.04042659773458
C	-0.13715944068819	1.56476688415008	-0.88355700146789
O	1.80995066923846	3.15718362553553	-1.81658130514184
C	4.19269591715867	2.91852876248835	-0.32945817635937
O	5.03869463330966	3.30634661912688	-1.30480684868924
C	5.52916727924934	2.27024921778168	-2.22295024372549
O	3.89136522031715	1.77133490497735	-0.07593174693073
H	3.84491431539964	3.87101427940931	1.51122309965715
H	1.64346877284291	4.16351682211739	1.28615190526778
C	-1.13260169376888	0.83621572430872	-0.00597070324223
H	0.63555614142529	0.90337475277148	-1.28399180762418
H	-0.61260041777294	2.09013207406777	-1.71683355786094
H	-0.62595026353786	0.33901228760682	0.82610335839135
H	-1.65177971302892	0.07624883785677	-0.59888494058608
H	-1.87800406373076	1.52706169797334	0.39884374512708

C	4.71226069579675	2.29897803157227	-3.50185818879571
H	5.46218223014162	1.31088633865978	-1.70680831359650
H	6.57600751749373	2.53346098610395	-2.38961467159747
H	3.66217727897944	2.08536074377254	-3.29086154551394
H	5.09912659486672	1.53940782640068	-4.19016842363597
H	4.77718827565538	3.27340045907769	-3.99442859960125

5.3.9 4a′^{Me}

E = −3310.284562313831

C	3.78875414632365	6.26740579569706	1.34522764700674
C	2.43883816551574	6.20960589621497	1.53369319650200
P	1.35618230759973	5.15836278795293	0.49517622648140
C	2.20522209884127	5.50065610456184	-1.07980716672385
C	3.55913591031783	5.40514057430886	-1.22327461869238
P	4.67413237070812	5.15477422803647	0.21060875861816
N	3.98189136230362	5.47810542389503	-2.54498166693646
C	2.97828742962311	5.62389843455241	-3.47348772742460
S	1.44170087636424	5.67394462736662	-2.62955421862033
N	1.98900667147919	7.03261462516505	2.55975336633213
C	2.96769715087080	7.75662450764307	3.20017364866544
S	4.51400951730948	7.37200719393024	2.47024871796066
S	2.74044637959813	8.82278573452100	4.45847744809494
S	3.16858127793529	5.74992243775881	-5.12256307886666
C	5.38429239405970	5.41051617224470	-2.97404991486304
H	5.51796611194165	4.54148608710495	-3.62137542877865
H	6.00856119602300	5.32461408127966	-2.08487838187716
H	5.63065336913835	6.31733738252514	-3.52978171921581
C	0.58493785008544	7.16071795414729	2.96842702090877
H	0.48285802492437	6.83992679866806	4.00738182992191
H	-0.01911263695744	6.53248162074886	2.31407776443003
H	0.28256980191590	8.20623288102295	2.88331238620920
C	3.81047768138143	3.58608965493683	0.91408330431942
C	2.29935429595171	3.49797472934282	0.72115121493342
C	1.95925491871285	2.67916604959036	-0.51820735987900
O	0.63189421660777	2.66862935306320	-0.72436187927029
C	0.15982424204132	1.98932342056598	-1.94281808301617
O	2.77215853417843	2.13229037035926	-1.24143682880940
C	4.29893558790545	3.52105028397956	2.35171048620935
O	3.29794471481419	3.44228576983907	3.24180769084565
C	3.66964806639306	3.38466075416620	4.66700525091170
O	5.48408114543314	3.55350514000015	2.64312671894501
H	1.83038020038789	3.02451781749187	1.58810161457417
C	-1.30611556826133	2.33009266144098	-2.09592080299910
H	0.33222433601794	0.91844187714756	-1.80994734885509
H	0.76427111380868	2.34960555472996	-2.77846495268416
H	-1.88091474586263	1.98824692649648	-1.23023423975761
H	-1.69557869911383	1.83266930930019	-2.98977972834719
H	-1.44466779779267	3.40916826917671	-2.21195986875536
C	3.75442598528107	4.78192077819696	5.24942574864593
H	4.61463294248460	2.84531280919865	4.74632740367986
H	2.86412272168719	2.80158395787367	5.11469028439389
H	4.55935087310166	5.35448276340390	4.78203323094631

H	3.96124157575678	4.70743145838092	6.32219061930221
H	2.81053227631367	5.31847541114460	5.11868936038296
H	4.28400706795048	2.76053799322818	0.37147701045105

E = −3310.287147905976

C	3.30414769007489	5.34684094383334	1.56695249845490
C	1.99457814768751	5.18716861464380	1.21844684585071
P	1.51718172139722	4.04814606773543	-0.14719314198913
C	2.74292788810558	4.65997633093405	-1.33981809257617
C	4.02682096209234	4.98823727584564	-1.01526662195648
P	4.69789566106601	4.61709524565545	0.65370039352940
N	4.75840802008331	5.49947578982782	-2.07360606280707
C	4.07792139871071	5.58237134028423	-3.26880593914197
S	2.44987137571232	4.98481325362612	-3.02573088584926
N	1.10850575516770	5.81934079445380	2.07702140876247
C	1.69205742996416	6.49666181016973	3.12565090550497
S	3.42954509310606	6.31406138066148	3.00715398129416
S	0.89026566987883	7.35735691957303	4.30429358825213
S	4.68969302954050	6.15624392417594	-4.70673591934860
C	6.14112829244352	5.97998612725327	-1.96438793994261
H	6.75118716938502	5.49662354764673	-2.72901974148647
H	6.50759602261065	5.73370415697422	-0.96822291502483
H	6.15854224682869	7.06048344016693	-2.12351314043600
C	-0.34850133206769	5.83310682607201	1.90005031044151
H	-0.82233465610031	5.49754884991784	2.82394758035771
H	-0.59634743418860	5.16820616381119	1.07311697249657
H	-0.67443379348496	6.85252695993827	1.68200197709115
C	4.06349706882646	2.81484996427431	0.59893402814513
C	2.54810729070743	2.62654778744989	0.61971159818322
C	2.03715531603367	2.41970987748055	2.03673155226744
O	0.69203252611434	2.40418009677455	2.06000509235590
C	0.06584516985488	2.24033106601287	3.38326627672834
O	2.73989371314537	2.29877281855627	3.02330706909099
C	4.67980346687179	2.08179493335139	-0.58548770020462
O	5.87488630755732	2.59799012341530	-0.92146751432834
C	6.58917464111048	1.93307267105499	-2.02968679080129
O	4.16292873671917	1.12991437429031	-1.14137243872118
C	-1.42775395396719	2.14999690965022	3.16089031866909
H	0.35098134321518	3.10327677219797	3.99137358395714
H	0.47676066206143	1.33538305069358	3.83582731683076
H	-1.81294315542559	3.05428458385060	2.68142933091417
H	-1.92346044069575	2.03581290737456	4.13003659441893
H	-1.67693377128343	1.28538871987625	2.53903200202343
C	6.04824218164099	2.36466654956786	-3.37996124292706
H	6.49826144828280	0.85606030796974	-1.87845710622022
H	7.62285618330522	2.24606833269396	-1.88116381044749
H	4.99473431114553	2.09622327851865	-3.48771424041902
H	6.61674963728430	1.85110386169193	-4.16250677921049
H	6.16102369744574	3.44074416365521	-3.53188145655279
H	2.29319576438751	1.73910715309087	0.02880835084650
H	4.47375817804889	2.35683814210785	1.50872696832437

5.3.10 ***4b***^{Me}

E = −3042.642963165599

C	3.38047288779625	6.35397705985676	1.45453965783342
C	2.01639758902056	6.35197423818025	1.41860765153566
P	1.09591051562254	5.20537547188247	0.32238741571121
C	2.14714563793890	5.43001760440287	-1.14308500179019
C	3.51016071256338	5.41460405566352	-1.09769825400742
P	4.40886439975931	5.22116943384419	0.48537325740294
N	4.10999228865353	5.49188860889714	-2.34883698287649
C	3.23899043940735	5.57043427742899	-3.41007013047067
S	1.60068023204958	5.54323078708276	-2.78912093029596
N	1.43860374368193	7.20727827216040	2.34674100711684
C	2.32644906335386	7.90171085540602	3.13613476561814
S	3.95345981727162	7.45438487282920	2.67261905907135
S	1.93530811800207	9.00003471981079	4.32783066930898
S	3.65436884347322	5.68833803006161	-5.02012950813185
C	5.56005667224438	5.50627732304840	-2.57453266727253
H	5.83525136325446	4.64917081100789	-3.19261812579511
H	6.05559316607553	5.45374127221592	-1.60515214568163
H	5.83144220525145	6.42761198314504	-3.09421208486629
C	-0.00715563050300	7.39765376453290	2.51055666059326
H	-0.29963512062447	7.08611355807992	3.51562757712206
H	-0.51565416536547	6.79270419817765	1.75996106652524
H	-0.24438614967363	8.45513510862198	2.37783260998136
C	3.48515210718233	3.60112982962662	0.96426978986279
C	1.94579390311925	3.64955599843892	0.96190975251041
H	1.55664536467097	2.83750493449757	0.34090455409427
C	4.09724418013657	3.15980344472953	2.28143788617300
O	3.47324621962431	3.72059620907144	3.33374730524490
C	4.02202484675966	3.42345972417763	4.66420453843306
O	5.06002960847968	2.41634197173527	2.36311218045313
H	1.55715173520672	3.51956074626152	1.97463154626107
C	5.12713058109501	4.40211608945020	5.01635541086384
H	4.37349150438351	2.38998185161445	4.66086460450723
H	3.16043334617675	3.52412762196882	5.32573367861232
H	5.96736918085626	4.30883029229652	4.32269185715858
H	5.48658163749043	4.18487312750059	6.02794975945473
H	4.75628644365261	5.43061199029794	4.99236449858138
H	3.84786771191250	2.90105686199618	0.20780007115695

E = −3042.643259272092

C	3.38739843135142	6.37785982897746	1.48271772474902
C	2.02947891229315	6.24811014473729	1.46848424290800
P	1.21643132247083	4.89654042850740	0.53683480627002
C	2.21490837531165	5.05488732437045	-0.97047232032600
C	3.57265024337137	5.17963216504643	-0.95845434575826
P	4.51002252582343	5.25823167097633	0.61043885477370
N	4.15063677953981	5.08122087045820	-2.21773664214908
C	3.27074479459978	4.85565670452717	-3.24891765122532
S	1.64856198944419	4.79169174703574	-2.59176376808303
N	1.37675724439079	7.17677075683239	2.26696117933579
C	2.19844604657948	8.05740328162270	2.93265311777741

S	3.86088286163829	7.68828797323470	2.52398880400309
S	1.70933037756845	9.28434455164729	3.94841248177001
S	3.66325472595447	4.68370663005793	-4.85988961861667
C	5.59065742749730	5.18685018128302	-2.47952653885932
H	5.95870763102874	4.23607070036286	-2.87155079927324
H	6.09023372243945	5.43071478745200	-1.54218762703124
H	5.76024914247605	5.96990073648476	-3.22084410395884
C	-0.08124203007448	7.26685885846704	2.41270682680480
H	-0.34714722350483	7.11317833243011	3.46044446691613
H	-0.53251743879926	6.49795015368896	1.78595458802587
H	-0.40962070885555	8.25976315801405	2.09891161504011
C	3.76741768381650	3.64734736837414	1.35197371550973
C	2.23312979804685	3.49951352910864	1.29620276207845
H	1.95404111405238	2.62271670883190	0.70625000944486
C	4.50707606828841	2.49691077252214	0.69411174916138
O	4.06249592540035	2.29728198300807	-0.56177658073937
C	4.69111233944827	1.22314536295178	-1.34234343325395
O	5.40702131158472	1.86578916150525	1.22069959108042
H	1.84043477257714	3.36705324652638	2.30798667169496
C	3.95141134140564	-0.08400731592155	-1.12858793983963
H	5.74011065263049	1.15887883953210	-1.04782256830749
H	4.61062268787153	1.57397309642106	-2.37247443215597
H	4.03141296468366	-0.41236179843069	-0.08846991317200
H	4.39200738143686	-0.85405538940118	-1.77055241002752
H	2.89471665198235	0.02280485147239	-1.39137859915994
H	4.10644257873033	3.68863277998529	2.38914337999309

5.3.11 ***4c***^{Me}

E = −2932.531129860856

C	3.69104506965233	6.81172943839874	1.21069067870489
C	2.36009164149645	6.93811252525257	0.94340475216826
P	1.60213109110284	6.10887571664334	-0.50781782416404
C	2.90916760900694	6.55764224996028	-1.68943436498547
C	4.23754552752792	6.41520484127878	-1.41757123427232
P	4.81511330045657	5.79189395518400	0.20784193835138
N	5.05841550868320	6.71609078329270	-2.49984890121976
C	4.40183109024995	7.08518040724029	-3.64892027239109
S	2.67845101949441	7.06102638865092	-3.33711020649075
N	1.67536022514761	7.69960135563725	1.88396807396841
C	2.44356432821455	8.18735217671279	2.91363460800945
S	4.09609029335419	7.65957205834170	2.67318961261680
S	1.91114125650499	9.13465700345923	4.17974754704652
S	5.11190485595883	7.50447102186886	-5.09869214705606
C	6.52439420448956	6.66687308760162	-2.46574932255164
H	6.87886585134936	5.95371515419573	-3.21301489017114
H	6.83004525940939	6.35933544670411	-1.46561459457480
H	6.92097264730440	7.65705999824933	-2.69978239913977
C	0.24020977190832	8.00050726963027	1.82073874217812
H	-0.24953511032442	7.60270500232978	2.71195392463976
H	-0.16395630169773	7.53601356158659	0.92144768751878
H	0.10333072164660	9.08332762055818	1.78800035508373
C	3.73444896354365	4.23181570520277	0.30010155615033

C	2.27096773230824	4.38830413831913	-0.15904334814473
H	2.10915230777720	3.85934811028208	-1.10453620214610
C	4.43383611222431	3.04050190392332	-0.38740888316655
C	4.77263031165051	3.27064280343920	-1.86433477919169
C	5.26621594079493	2.00851062448689	-2.58808123595418
H	3.73477634777058	4.05349064134308	1.38129525795914
H	1.59870484359366	3.94541482904349	0.58243547110244
C	4.17525851509745	0.94852913208754	-2.78097698631584
H	6.10870368158367	1.57828347933272	-2.03014387659082
H	5.65745036095783	2.30179918621909	-3.56996658982150
H	3.79367085901443	0.57949488371293	-1.82280777216421
H	4.56114201249573	0.08792228973970	-3.33763240372029
H	3.32911241904875	1.36259716028930	-3.34249773346961
H	3.89956953152965	3.67100900236507	-2.39795111103299
H	5.55535607114987	4.03797548881235	-1.92664864478337
H	5.35558935367516	2.80671054498393	0.15879660729572
H	3.77228477484810	2.17196301364030	-0.28135108927503

E = −2932.530440734876

C	3.80868027140768	6.94664955394053	1.08871709183471
C	2.44639949941691	6.90644706954460	1.07144382875729
P	1.53847092583337	5.72923713941286	0.00055020629302
C	2.55409928279305	5.96852092879057	-1.48563324565080
C	3.91732302734651	6.00759858168890	-1.46470059553293
P	4.84183445946396	5.81794020105592	0.10943756044221
N	4.48887015644613	6.11228355224328	-2.72702313971167
C	3.59680515612918	6.14994839592948	-3.77264137708286
S	1.97350172228034	6.05578404224613	-3.12293233811454
N	1.85494642964571	7.80157569138354	1.95640365010296
C	2.73150208403935	8.56283697517673	2.69199082986309
S	4.36547136847437	8.12704363869612	2.23673205080452
S	2.32538411371354	9.71948291778181	3.82359158179538
S	3.97967602968182	6.28047274440901	-5.39068047091678
C	5.93244894636970	6.19382272416410	-2.97952757181332
H	6.23810482497640	5.34463944717350	-3.59425071028299
H	6.44570322820839	6.17590750241818	-2.01827778125092
H	6.14881781387067	7.12108339800764	-3.51393541540818
C	0.40617449413601	7.96550739153214	2.12440385001117
H	0.13147105206727	7.70958927928513	3.14990138638727
H	-0.09301223125895	7.30305294240040	1.41733315271889
H	0.14050781285321	9.00640512496880	1.92950372745198
C	3.97742020278980	4.22900296591073	0.61980426064101
C	2.43319373125233	4.16937630175060	0.61836407767774
C	1.93524568993175	2.95472414894416	-0.19067377994727
C	0.42914585533007	2.69489729235272	-0.09592441553704
C	0.00117261623744	1.43123522568092	-0.85078839212462
H	2.08072614522270	4.08254191690700	1.65269238779475
C	-1.50257523053147	1.16072797316192	-0.73969496412405
H	0.56149578775289	0.57085454508546	-0.46065080650927
H	0.28064725104562	1.53309195260177	-1.90803859935636
H	-1.79883707806956	1.02822633698628	0.30767760886522
H	-1.78573755489720	0.25570712058539	-1.28797743992900
H	-2.08099433249547	1.99807251796073	-1.14777130420610

H	0.14417108221937	2.60546086196514	0.96187988195218
H	-0.12457179473570	3.55583991630048	-0.49401600926869
H	2.23176463759025	3.08420290268776	-1.24115669278352
H	2.47730317766514	2.07231659771094	0.17446283008201
H	4.36434418314609	4.00764729021549	1.61923433597748
H	4.37989516265132	3.47219489094318	-0.06234924990197

5.3.12 ***4d***^{Me}

E = −2775.003499378858

C	3.70752092956405	6.75456885362109	1.11898728420333
C	2.36339283767822	6.90299127836374	0.94312089422140
P	1.45603912876338	5.91151154047716	-0.30689359088156
C	2.66221002333240	6.13448882589756	-1.64809010194773
C	4.00774058328472	5.99533423120754	-1.47531695451624
P	4.71375626254168	5.57760785812831	0.16658058119108
N	4.73527952104968	6.13669084919575	-2.65106749593208
C	3.98635661982707	6.38785177186046	-3.77623838824471
S	2.29711493765042	6.44610780910886	-3.31941260019363
N	1.78432108165687	7.80344168712403	1.82964924299168
C	2.65148666481946	8.38298497542910	2.72524223077663
S	4.26040679863965	7.76080463423060	2.42477286568694
S	2.25711552800960	9.50369023488514	3.89622895548495
S	4.57358511438287	6.61458053993767	-5.32106199704885
C	6.19774822303069	6.04772246215063	-2.73709805165329
H	6.46792719147886	5.23787899345052	-3.41779119116318
H	6.58466929666068	5.85366088550124	-1.73686778623775
H	6.59116179608603	6.98979045255412	-3.12460403084727
C	0.35983785579343	8.15714731188034	1.83951190917607
H	-0.07134363635536	7.88605606805419	2.80540363328077
H	-0.13027509889111	7.61062797818497	1.03397515502764
H	0.25905838055428	9.23403781510427	1.68991210251947
C	3.61972067525546	4.07253023624888	0.45273700807850
C	2.09731002235383	4.24418237414951	0.28893748154733
H	1.70675233148457	3.52329778002614	-0.43528262597484
H	1.58409604869855	4.07076757015613	1.23936146784699
H	3.86083689348626	3.74486656136369	1.46830481588235
H	3.99958210196374	3.31505369590835	-0.23911258927399

5.3.13 ***4e***^{Me}

E = −2931.324999179873

C	3.69776124308760	6.67217923035932	1.14281167117446
C	2.36509324531606	6.86643723924779	0.92872872628271
P	1.48578877429042	5.97145324472558	-0.40587463351198
C	2.73551719489562	6.24725480359048	-1.69461380793065
C	4.07411750178782	6.08640790679978	-1.48558014246667
P	4.71291001645732	5.54635782724558	0.14684062511909
N	4.83877923017838	6.25965363030806	-2.63305814128523
C	4.12796896939669	6.55638699463280	-3.77220287397109
S	2.42648532699591	6.62216391854105	-3.36469654867503
N	1.77274833962082	7.71612920788222	1.85567813676760
C	2.61734952012236	8.20841565495381	2.82205733972167

S	4.22258449376866	7.57030298999073	2.53700114832787
S	2.20197188950649	9.25062624003073	4.05690795006292
S	4.76521434886421	6.82494584717761	-5.28992199581012
C	6.30205633995217	6.15310842412999	-2.67605208046567
H	6.58439994602414	5.33395879756796	-3.34085870709923
H	6.65682827054246	5.96370495088785	-1.66308001045841
H	6.71555661604188	7.08757888205081	-3.06035410173493
C	0.35635086988859	8.10043781262266	1.83969924126218
H	-0.12120073970284	7.75543836285031	2.75921878506739
H	-0.10952359791499	7.63808734264370	0.96960406938957
H	0.28342524499118	9.18829547076604	1.78258168884253
C	3.59728068821542	4.01964633401105	0.24917802358584
C	2.06511675938862	4.24649415839192	0.12208464661505
C	1.40932074866748	3.22186711484190	-0.82614973599909
C	4.11026347882344	3.01101088229525	-0.79475303377013
H	3.80877142710101	3.63249998244364	1.25297974464929
H	1.61558729210392	4.13429095522070	1.11532517204836
C	3.40866422101839	1.65010714870649	-0.65076759491874
H	5.19457495837583	2.88832563938337	-0.69336353520458
H	3.92999014231165	3.41476488169882	-1.79806615738137
C	1.87648176840227	1.80529150793435	-0.46969065520045
H	3.83373638801609	1.11437186068761	0.20505138456116
H	3.62680450585425	1.05191616213139	-1.54213082922785
H	1.59796929281442	1.60476381118134	0.57195357940125
H	1.34427654546581	1.07367107170216	-1.08632768009385
H	1.66536491531487	3.45252152524261	-1.86819170893061
H	0.32078158241556	3.30210730092251	-0.73956086044330

5.3.14 ***4f***^{Me}

E = −2932.530912773049

C	3.72160487045439	6.61192284898036	1.25221616177810
C	2.40374081225230	6.83356200864951	0.98121251684486
P	1.61119053837933	6.12440813061026	-0.51537382028919
C	2.96121714823806	6.54738600556668	-1.65643253611567
C	4.26774893867409	6.28174256821402	-1.37611870128295
P	4.77707616912530	5.54575919013909	0.22366539343780
N	5.13230591563955	6.60905854958377	-2.41713889814768
C	4.52910774056177	7.11962374529251	-3.54080809544983
S	2.80195362004995	7.19907195253441	-3.25861969414235
N	1.75374761423430	7.57864518197680	1.95865481950218
C	2.53581319689476	7.95651127708672	3.02376985967923
S	4.15657511662793	7.34276922875249	2.76811899458205
S	2.04637953124376	8.86212345752949	4.33617601186608
S	5.29789312130248	7.60262424928306	-4.94001302326639
C	6.59037278285144	6.45399584377275	-2.36440885404077
H	6.90962661989874	5.76995262509171	-3.15363327378354
H	6.85361112071157	6.05927475290633	-1.38291508212472
H	7.05833381594760	7.42764027279755	-2.52383351296496
C	0.34193617840459	7.97523984636804	1.89619658707312
H	-0.18470399662110	7.56352474537437	2.75950677669024
H	-0.07833165896283	7.58615302840414	0.96894311793287
H	0.27554227824620	9.06493210902866	1.92003255782368

C	3.58166479685894	4.04076574544735	0.26061632725858
C	2.16056355597707	4.34538028752523	-0.26879627763696
H	2.01176294565581	3.90755445234751	-1.26139271510992
C	4.21659074859824	2.88446075059862	-0.55159888177870
C	4.56722437223476	3.19240629714192	-2.00876907977552
H	1.42045660673065	3.89039476032154	0.39855904451150
H	5.12105813536515	2.54697060833452	-0.03449020182480
H	3.50285941823426	2.05081241867187	-0.51405765306031
H	4.86119272193888	2.27319541453069	-2.52490199464259
H	5.41215032606679	3.88546978557943	-2.07674913379698
H	3.72507611299783	3.63061023151324	-2.55499434674561
C	3.45327819879251	3.61815763528843	1.75105327415681
C	4.75767474860455	3.44501871522006	2.53444670627827
H	2.89945871656658	2.66977646915786	1.75147643233496
H	2.81662673917726	4.34714490377050	2.26502418109851
H	5.43253193768872	2.72957522069495	2.05510190818162
H	4.53552438586161	3.07723905429833	3.54118071587892
H	5.29820781569621	4.39224249001521	2.64277934527004