Supporting Information

Access to ligand-stabilized PH-containing phosphenium complexes

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1 General methods

All reactions were performed under 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® R3-15S) at ca. 100 °C, removing moisture with silica gel, phosphorus pentoxide desiccant with indicator (Sicapent®) and calcium chloride). Glassware, spatulae, cannulae as well as filter papers were dried in a compartment dryer at 110 °C for at least one hour. Additionally, the glassware was heated with a heat gun (up to 550 °C) under active vacuum (<0.02 mbar) and filled with argon three times. Sterile syringes were purged with argon three times before use. The solvents were dried by standard procedures[1] by refluxing over proper desiccants under an argon atmosphere (*n*-pentane 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) for several days and distilled before use. Alternatively, diethyl ether and toluene were dried using an MBraun SPS-800 solvent purification system. For filtration stainless steel cannulae (Ø = 1 mm and 2 mm) with Whatman® glass microfiber filters (grade GF/B) were used if not stated otherwise. After use, devices made of stainless steel were cleaned with acetone, water and diluted hydrochloric acid and glassware by storage in a concentrated solution of potassium hydroxide in isopropanol for at least two days and in diluted hydrochloric acid for one day. Afterwards, the glassware was washed with water and soap, acetone and petroleum ether 40/65. All joints were greased with OKS 1112 grease or with PTFE paste (Carl Roth). Vacuum was applied by a rotary vane pump (vacuubrand RZ6) enabling pressures $<10^{-2}$ mbar.

NMR spectra were recorded on a Bruker Avance I 300 MHz, Bruker Avance I 400 MHz, Bruker Avance I 500 MHz or Bruker Avance III HD Ascend 500 MHz spectrometer at the NMR department of the University of Bonn and subsequently analysed by the program *Mestrenova 14.2*. The calibration of the ^{1}H and ^{13}C NMR spectra was done via the solvent residual signals relative to tetramethylsilane (<1% in $CDCl_3$) (C_6D_6: $\delta(^{1}H)$ = 7.16 ppm and $\delta(^{13}C)$ = 128.06 ppm, CD_2Cl_2: $\delta(^{1}H)$ = 5.32 ppm and $\delta(^{13}C)$ = 53.84 ppm).[2] ^{11}B NMR spectra were measured relative to $BF_3{\cdot}OEt_2$ in $CDCl_3$ as external reference by using the ^{2}H frequency of the deuterated solvent (lock frequency) and the frequency ratio value $\Xi(^{11}B)$ = 32.083974%, ^{19}F NMR spectra relative to $CFCl_3$ using the ^{2}H frequency of the deuterated solvent (lock frequency) and the frequency ratio value $\Xi(^{19}F)$ = 94.094011%, ^{27}Al NMR spectra relative to 1.1 M $Al(NO_3)_3$ in D_2O using the ^{2}H frequency of the deuterated solvent (lock frequency) and the frequency ratio value $\Xi(^{27}Al)$ = 26.056859%, ^{31}P NMR spectra relative to 85% H_3PO_4 in water using the ^{2}H frequency of the deuterated solvent (lock frequency) and the frequency ratio value $\Xi(^{31}P)$ = 40.480742%, and ^{15}N NMR spectra via ge-2D NMR ^{1}H,^{15}N HMBC experiments relative to liquid ammonia by using the ^{2}H frequency of the deuterated solvent (lock frequency) and the frequency ratio value $\Xi(^{15}N)$ = 10.132912%.[3] To obtain the ^{15}N NMR chemical shifts relative to CH_3NO_2, 380.5 ppm were

subtracted.[4] All lock frequencies were calibrated internally against the ^{1}H signals of solutions of tetramethylsilane with a volume fraction of $\Phi \leq 1\%$ in the corresponding deuterated solvent. The used deuterated solvents were purified by distillation over proper desiccants (C_6D_6 over a potassium mirror and CD_2Cl_2 over CaH_2), trap-to-trap recondensation and degassing by three freeze-pump-thaw cycles. The purified solvent was stored over 3 Å or 4 Å molecular sieves. The chemical shift (δ) is given in parts per million (ppm) and the coupling constant ($^{n}J_{X,Y}$) in Hertz (Hz) as absolute values neglecting the sign where *n* is the number of bonds between the coupling nuclei X and Y. For assigning the multiplicity following abbreviations were used: s = singlet, d = doublet, q = quartet, dq = doublet of quartets, qd = quartet of doublets, q* = quartet (intensities 1:1:1:1), qq* = quartet of quartets (intensities 1:1:1:1), sept = septet, m = multiplet, sat = satellites and br = broad. For ^{1}H NMR spectra additionally, the number of nuclei is given accordingly which is determined via integration. The ^{1}H and ^{13}C NMR signals of compounds were assigned by a combination of COSY, HSQC, HMQC and HMBC experiments to unequivocally assign protons and carbon resonances if necessary. All measurements were performed at ambient temperature (298 K) if not stated otherwise.

Mass spectra using electron impact ionisation (EI) were recorded on a Thermo Finnigan MAT 95 XL sector field instrument using an ionization energy of 70 eV. The calibration and referencing were done using perfluorokerosene (PFK). Liquid injection field desorption ionisation (LIFDI) measurements were performed on a Thermo Finnigan MAT 90 sector field instrument equipped with a LIFDI ion source (Linden CMS). The samples were dissolved in toluene. Electrospray ionisation (ESI) measurements were performed on a Thermo Fisher Scientific Orbitrap XL spectrometer with an HPLC autosampler using acetonitrile or dichloromethane as solvents. Solutions of highly air-sensitive compounds for LIFDI and ESI measurements were prepared in a glovebox using dried, recondensed and degassed solvents. Only selected data are given for detected ions. The peaks are given in mass-to-charge ratio (*m/z*) while only the isotopomer with the highest relative abundance is represented. Additionally, the relative intensities of the peaks are given in parentheses and the proposed molecule fragments are in square brackets if not stated otherwise. High-resolution mass spectra (HRMS) that were obtained using ESI were recorded in a single measurement and, hence, no standard deviations for ESI HRMS were obtained.

ATR-IR spectra of solids were recorded in the spectral range of 4000–400 cm^{-1} on a Bruker Alpha FTIR spectrometer with a single-reflection ATR measurement attachment (Platinum-ATR Diamond) or a Shimadzu IRSpirit FTIR spectrometer with a single-reflection ATR measurement attachment (QATR-S) in a glovebox at ambient temperature. For apodization, the Happ-Genzel function was used. All analyses were performed using the programs *EZ OMNIC 7.3* of Fisher Scientific, *OPUS* of Bruker and *LabSolutions IR 2.26* of Shimadzu. Only selected wavenumbers of the absorption bands are given using

reciprocal centimetres (cm^{-1}). The intensities of the bands are marked as strong (s), medium (m) or weak (w).

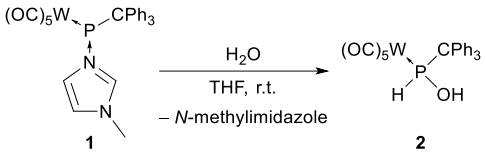
Elemental analyses were performed on an Elementar Vario Micro analysis device in quadruplicate or triplicate for each sample. All samples were prepared and weighed up in tin or silver sample containers using a micro-analytical balance in a glovebox. The mean C, H, N and S values are given for each compound. Due to instrumental problems and the air sensitivity of several compounds, some values fall outside the recommended error of ±0.4%.

Melting points were measured using an SRS DigiMelt device or a Büchi melting point determination device according to Dr. Tottoli. The samples were flame-sealed in a glass capillary (Ø = 0.1 mm) *in vacuo* (<0.02 mbar) and heated quickly (ca. 5 K/min) for a rough determination of the melting point or decomposition temperature. Afterwards, a heating rate of approximately 2 K/min was used until the sample melted or decomposed. The thermally treated samples were cooled to ambient temperature and studied by ^{1}H and/or ^{31}P NMR spectroscopy to confirm whether decomposition had occurred. No internal or external temperature corrections were performed.

Single crystal X-ray diffraction analyses were performed on a Bruker D8 Venture diffractometer, an STOE IPDS-2T diffractometer or an STOE STADIVARI diffractometer, equipped with a low-temperature device (Bruker Kryoflex, Oxford Cryostream 700 series or Oxford Cryostream 800 series) at 100(2) K or 123(2) K by using graphite monochromated Mo-K_α radiation (λ = 0.71073 Å) or Cu-K_α radiation (λ = 1.54186 Å). Intensities were measured by fine-slicing Φ and ω scans and corrected background, polarization and Lorentz effects. A semi-empirical absorption correction was applied for the data sets following Blessing's method.[5] The structure was solved by direct methods and refined anisotropically by the least-squares procedure implemented in the ShelX program system.[6] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included isotropically refined using a riding model at the bound carbon atoms. The program *Olex2 1.5*[7] of *OlexSys* was used for analyses and the ellipsoid representations of the molecular structures with the probability level set to 50%. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. 2302946 (**2**), 2302947 (**10a**), 2302948 (**10a-Cr**), 2302949 (**11a**), 2302950 (**11b**), 2302951 (**11c**), 2302952 (**12**) and 2302953 (**12-Cr**) which can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

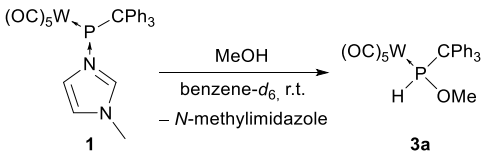
2 Experimental procedures and characterisation

Synthesis of complex 2



0.07 mL (3.87 mmol, 20.8 eq.) of water was added to a solution of 0.127 g (0.19 mmol, 1.0 eq.) of complex **1**[8] in 2.0 mL of THF at ambient temperature. The solution was stirred for 3 h at ambient temperature. Afterwards, all volatiles were removed *in vacuo* at ambient temperature within 5 minutes and the obtained yellow sticky solid was further dried for 30 minutes. The crude product was purified via column chromatography (SiO_2, Ø = 1 cm, h = 10 cm) using a 1:9 *n*-pentane/diethyl ether mixture at ambient temperature. Yield: 0.095 g (0.15 mmol, 83%). Mp 181 °C (dec.). Elemental analysis calcd (%) for $C_{24}H_{17}O_6PW$: C 46.78, H 2.78; found: C 47.30, H 3.05. IR (ATR Diamond): ν_{max} / cm^{-1} = 1924 (s) (CO), 1944 (m) (CO), 1993 (m) (CO), 2076 (m) (CO). ^{1}H NMR (500.04 MHz, CD_2Cl_2, 298 K): δ / ppm = 7.93 (d_{sat}, $^1J_{P,H}$ = 340 Hz, $^2J_{W,H}$ = 7 Hz, 1H; P*H*), 7.43–7.38 (m, 9H; CPh_3), 7.29–7.27 (m, 6H; CPh_3), 3.79 (d, $^2J_{P,H}$ = 5 Hz, 1H; PO*H*). ^{13}C{^{1}H} NMR (125.75 MHz, CD_2Cl_2, 298 K): δ / ppm = 199.3 (d_{sat}, $^2J_{P,C}$ = 31 Hz, $^1J_{W,C}$ = 143 Hz; *trans*-*C*O), 196.3 (d_{sat}, $^2J_{P,C}$ = 7 Hz, $^1J_{W,C}$ = 126 Hz; *cis*-*C*O), 141.7 (s; *ipso*-*C*), 130.4 (d, $J_{P,C}$ = 6 Hz; Ph), 129.4 (s; Ph), 128.3 (d, $J_{P,C}$ = 2 Hz; Ph). ^{31}P{^{1}H} NMR (202.44 MHz, CD_2Cl_2, 298 K): δ / ppm = 100.7 (s_{sat}, $^1J_{W,P}$ = 279 Hz). ^{31}P NMR (202.44 MHz, CD_2Cl_2, 298 K): δ / ppm = 100.7 (d_{sat}, $^1J_{P,H}$ = 341 Hz, $^1J_{W,P}$ = 279 Hz). MS (EI, 70 eV, selected data): *m/z* (%) = 616.0 (21) $[M]^+$, 476.0 (45) $[M-5CO]^+$, 243.3 (100) $[CPh_3]^+$. MS (ESI neg., selected data): *m/z* (%) = 615.021 (100) $[M-H]^-$, 1231.051 (42) $[2M-H]^-$. MS (ESI pos., selected data): *m/z* (%) = 243.117 (100) $[CPh_3]^+$. HRMS (ESI neg.): *m/z* calcd for $[C_{24}H_{16}O_6PW]^-$: 615.0202; found: 615.0209.

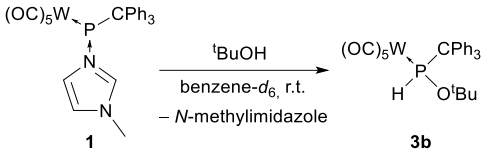
Generation of complex 3a



0.01 mL (0.25 mmol, 12.9 eq.) of methanol was added to a solution of 0.013 g (0.02 mmol, 1.0 eq.) of complex **1**[8] in 0.5 mL of benzene-d_6. The reaction mixture was shaken thoroughly for 30 seconds and then kept for 16 h at ambient temperature to obtain a yellow solution. The obtained analytical data were in accordance with the literature.[9] Yield: 97% (^{31}P NMR integration) (Lit.:[9] 76%). ^{1}H NMR (300.13 MHz, C_6D_6, 298 K): δ / ppm = 7.68 (d, $^1J_{P,H}$ = 343 Hz, 1H; P*H*), 7.28–7.24 (m, 6H; CPh_3), 7.12–7.04 (m, 9H; CPh_3), 2.75 (d, $^3J_{P,H}$ = 12 Hz, 3H; POC*H*$_3$). ^{31}P{^{1}H} NMR (121.51 MHz, C_6D_6, 298 K): δ / ppm

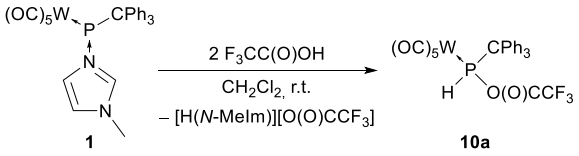
= 127.2 (s_{sat}, $^{1}J_{W,P}$ = 274 Hz). ^{31}P NMR (121.51 MHz, C_6D_6, 298 K): δ / ppm = 127.2 (dq_{sat}, $^{1}J_{P,H}$ = 343 Hz, $^{3}J_{P,H}$ = 13 Hz, $^{1}J_{W,P}$ = 274 Hz).

Generation of complex 3b



0.01 mL (0.11 mmol, 3.9 eq.) of *tert*-butanol was added to a solution of 0.018 g (0.03 mmol, 1.0 eq.) of complex **1**[8] in 0.5 mL of benzene-d_6. The reaction mixture was shaken thoroughly for 30 seconds and then kept for 14 days at ambient temperature to obtain a yellow solution. The obtained analytical data were in accordance with similar alkoxyphosphane complexes in the literature.[9] Yield: 77% (^{31}P NMR integration). ^{1}H NMR (400.13 MHz, C_6D_6, 298 K): δ / ppm = 7.79 (d, $^{1}J_{P,H}$ = 322 Hz, 1H; P*H*), 7.39–7.36 (m, 6H; CPh_3), 7.12–6.94 (m, 9H; CPh_3), 0.83 (d, $^{4}J_{P,H}$ = 1 Hz, 9H; POC(CH_3)$_3$). ^{31}P{^{1}H} NMR (162.00 MHz, C_6D_6, 298 K): δ / ppm = 97.4 (s_{sat}, $^{1}J_{W,P}$ = 283 Hz). ^{31}P NMR (162.00 MHz, C_6D_6, 298 K): δ / ppm = 97.4 (d_{sat}, $^{1}J_{P,H}$ = 322 Hz, $^{1}J_{W,P}$ = 283 Hz).

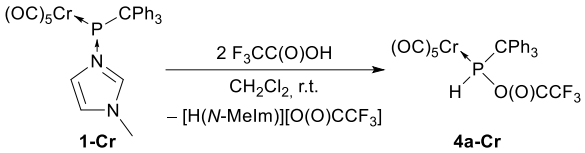
Synthesis of complex 10a



0.10 mL (1.30 mmol, 5.5 eq.) of trifluoroacetic acid was added dropwise to a solution of 0.16 g (0.2 mmol, 1.0 eq.) of complex **1**[8] in 30 mL of dichloromethane and the solution was stirred for 20.5 h at ambient temperature. Afterwards, all volatiles were removed *in vacuo* at ambient temperature within 30 minutes and the obtained pale yellow solid was further dried for 15 minutes. The product was extracted using three times 10 mL of *n*-pentane at ambient temperature via a filter cannular (Ø = 1 mm) with a glass microfibre filter paper. All volatiles of the extract were removed *in vacuo* at ambient temperature. The obtained colourless solid was further dried for 2 h. Yield: 0.131 g (0.18 mmol, 78%). Mp 158 °C (dec.). Elemental analysis calcd (%) for $C_{26}H_{16}O_7F_3PW$: C 43.85, H 2.26; found: C 44.83, H 2.65. IR (ATR Diamond): ν_{max} / cm^{-1} = 1930 (s) (CO), 1960 (s) (CO), 1999 (w) (CO), 2079 (m) (CO). ^{1}H NMR (500.04 MHz, C_6D_6, 298 K): δ / ppm = 8.42 (d_{sat}, $^{1}J_{P,H}$ = 362 Hz, $^{2}J_{W,H}$ = 7 Hz, 1H; P*H*), 7.23–7.12 (m, 6H; CPh_3), 7.05–6.99 (m, 9H; CPh_3). ^{13}C{^{1}H} NMR (125.52 MHz, C_6D_6, 298 K): δ / ppm = 197.1 (d, $^{2}J_{P,C}$ = 34 Hz; *trans*-*C*O), 194.7 (d_{sat}, $^{2}J_{P,C}$ = 7 Hz, $^{1}J_{W,C}$ = 126 Hz; *cis*-*C*O), 153.7 (qd, $^{2}J_{F,C}$ = 45 Hz, $^{2}J_{P,C}$ = 12 Hz; OO*C*CF_3), 140.2 (br s; *ipso*-*C*), 130.4 (br s; Ph), 129.1 (s; Ph), 128.5 (s; Ph), 114.7 (q, $^{1}J_{F,C}$ = 287 Hz; OOC*C*F_3), 65.2 (d, $^{1}J_{P,C}$ = 16 Hz; *C*Ph_3). ^{19}F{^{1}H} NMR (469.65 MHz, C_6D_6, 298 K): δ / ppm = −75.4 (s). ^{31}P{^{1}H}

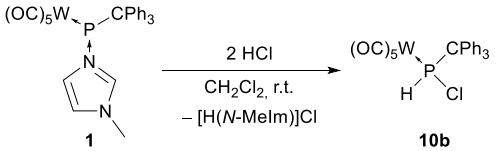
NMR (202.44 MHz, C_6D_6, 298 K): δ / ppm = 112.1 (s_{sat}, $^1J_{W,P}$ = 285 Hz). ^{31}P NMR (202.44 MHz, C_6D_6, 298 K): δ / ppm = 112.1 (d_{sat}, $^1J_{P,H}$ = 362 Hz, $^1J_{W,P}$ = 285 Hz). MS (LIFDI, selected data): *m/z* (%) = 712.2 (100) $[M]^+$, 243.2 (50) $[CPh_3]^+$.

Synthesis of complex 10a-Cr



0.11 mL (1.43 mmol, 5.9 eq.) of trifluoroacetic acid was added dropwise to a solution of 0.133 g (0.24 mmol, 1.0 eq.) of complex **1-Cr**[8] in 10 mL of dichloromethane and the solution was stirred for 3.5 h at ambient temperature. Afterwards, all volatiles were removed *in vacuo* at ambient temperature within 7 minutes and the obtained pale yellow solid was further dried for 50 minutes. The product was extracted using six times 3 mL of *n*-pentane at ambient temperature via a filter cannula (Ø = 1 mm) with a glass microfibre filter paper. All volatiles of the extract were removed *in vacuo* at ambient temperature. The obtained colourless solid was further dried for 1 h. Yield: 0.136 g (0.23 mmol, 96%). Mp 160 °C (dec.). Elemental analysis calcd (%) for $C_{26}H_{16}O_7F_3PCr$: C 53.81, H 2.78; found: C 54.26, H 2.95. IR (ATR Diamond): ν_{max} / cm^{-1} = 1944 (s) (CO), 1956 (s) (CO), 2003 (w) (CO), 2075 (m) (CO). ^{1}H NMR (400.13 MHz, C_6D_6, 298 K): δ / ppm = 8.19 (d, $^1J_{P,H}$ = 350 Hz, 1H; P*H*), 7.20–7.11 (m, 6H; CPh_3), 7.06–6.97 (m, 9H; CPh_3). ^{13}C{^{1}H} NMR (100.63 MHz, C_6D_6, 298 K): δ / ppm = 219.1 (d, $^2J_{P,C}$ = 2 Hz; *trans*-*C*O), 214.3 (d, $^2J_{P,C}$ = 13 Hz; *cis*-*C*O), 153.7 (qd, $^2J_{F,C}$ = 45 Hz, $^2J_{P,C}$ = 13 Hz; OO*C*CF_3), 140.3 (br s; *ipso*-*C*), 130.3 (br s; Ph), 129.1 (s; Ph), 128.5 (s; Ph), 114.6 (q, $^1J_{F,C}$ = 287 Hz; OOC*C*F_3), 66.9 (d, $^1J_{P,C}$ = 10 Hz; *C*Ph_3). ^{19}F NMR (470.51 MHz, C_6D_6, 298 K): δ / ppm = −75.5 (s). ^{31}P{^{1}H} NMR (162.00 MHz, C_6D_6, 298 K): δ / ppm = 164.8 (s). ^{31}P NMR (162.00 MHz, C_6D_6, 298 K): δ / ppm = 164.8 (d, $^1J_{P,H}$ = 350 Hz). MS (LIFDI, selected data): *m/z* (%) = 580.1 (100) $[M]^+$, 243.2 (5) $[CPh_3]^+$. MS (ESI neg., selected data): *m/z* (%) = 578.993 (21) $[M–H]^-$. HRMS (ESI neg.): *m/z* calcd for $[C_{26}H_{15}O_7F_3PCr]^-$: 578.9921; found: 578.9930.

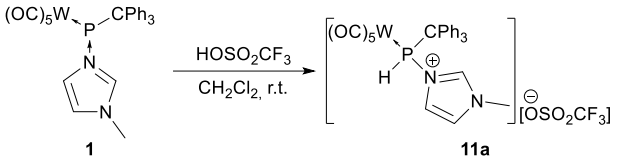
Synthesis of complex 10b



0.16 mL (0.32 mmol, 2.5 eq.) of a hydrogen chloride solution (c = 2 M in diethyl ether) was added to a solution of 0.086 g (0.13 mmol, 1.0 eq.) of complex **1**[8] in 8.0 mL of dichloromethane and the formed pale yellow suspension was stirred for 1 hour at ambient temperature. Afterwards, all volatiles were removed *in vacuo* at ambient temperature within 10 minutes and the obtained pale yellow solid was

further dried for 10 minutes. The product was extracted using three times 5.0 mL of diethyl ether at ambient temperature via a filter cannula (Ø = 1 mm) with a glass microfibre filter paper. All volatiles of the extract were removed *in vacuo* at ambient temperature. The obtained colourless solid was further dried for 30 minutes at ambient temperature. The obtained analytical data were in accordance with the literature.[11] Yield: 0.081 g (0.13 mmol, 100%) (Lit.:[11] 53%). $^{31}P\{^{1}H\}$ NMR (121.51 MHz, CH_2Cl_2, 298 K): δ / ppm = 71.2 (s_{sat}, $^{1}J_{W,P}$ = 271 Hz). ^{31}P NMR (121.51 MHz, CH_2Cl_2, 298 K): δ / ppm = 71.2 (d_{sat}, $^{1}J_{P,H}$ = 345 Hz, $^{1}J_{W,P}$ = 271 Hz).

Synthesis of complex 11a

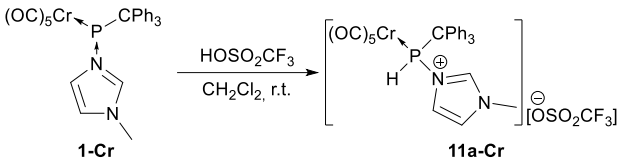


1 11a

0.02 mL (0.23 mmol, 1.1 eq.) of trifluoromethanesulfonic acid was added dropwise to a solution of 0.145 g (0.21 mmol, 1.0 eq.) of complex **1**[8] in 10 mL of dichloromethane and the solution was stirred for 1.5 h at ambient temperature. Afterwards, 10 mL of *n*-pentane were added to the reaction solution forming a colourless suspension. After additional stirring for 1 minute, the solid transformed to a yellow oil. All volatiles were removed *in vacuo* at ambient temperature within 15 minutes and the obtained pale yellow solid was further dried for 2 h. After the addition of 10 mL of diethyl ether the solid formed a yellow oil. The mixture was stirred for 10 minutes obtaining a pale yellow suspension. The supernatant was filtered off using a filter cannula (Ø = 1 mm) with a Whatman® 595 filter paper. The pale yellow solid residue was washed two times using 10 mL of diethyl ether and three times using 10 mL of *n*-pentane at ambient temperature. The obtained colourless solid was dried for 19 h *in vacuo* at ambient temperature. Yield: 0.153 g (0.18 mmol, 86%). Mp 142 °C (dec.). Elemental analysis calcd (%) for $C_{29}H_{22}N_2O_8F_3PSW$: C 41.95, H 2.67, N 3.37, S 3.86; found: C 42.13, H 2.83, N 3.42, S 3.92. IR (ATR Diamond): ν_{max} / cm^{-1} = 1932 (s) (CO), 1940 (m) (CO), 2001 (w) (CO), 2081 (m) (CO). ^{1}H NMR (500.04 MHz, CD_2Cl_2, 298 K): δ / ppm = 9.41 (d, $^{1}J_{P,H}$ = 373 Hz, 1H; P*H*), 9.12 (s, 1H; Im-*H*), 7.46–7.36 (m, 15H; CPh_3), 7.30 (br s, 1H; Im-*H*), 6.48–6.46 (m, 1H; Im-*H*), 3.87 (s, 3H; CH_3). $^{13}C\{^{1}H\}$ NMR (125.75 MHz, CD_2Cl_2, 298 K): δ / ppm = 196.5 (d_{sat}, $^{2}J_{P,C}$ = 35 Hz, $^{1}J_{W,C}$ = 143 Hz; *trans*-*C*O), 194.5 (d_{sat}, $^{2}J_{P,C}$ = 6 Hz, $^{1}J_{W,C}$ = 127 Hz; *cis*-*C*O), 141.2 (s; Im), 139.8 (br s; *ipso*-*C*), 130.4 (br s; Ph), 129.7 (s; Ph), 129.0 (s; Ph), 125.3 (s; Im), 125.2 (s; Im), 121.1 (q, $^{1}J_{F,C}$ = 320 Hz; *C*F_3), 64.7 (d, $^{1}J_{P,C}$ = 8 Hz; *C*Ph_3), 37.1 (s; *C*H_3). $^{15}N\{^{1}H\}$ NMR (50.68 MHz, CD_2Cl_2, 298 K): δ / ppm = −200.3 (s; *N*-P), −205.0 (s; *N*-CH_3). ^{19}F NMR (470.51 MHz, CD_2Cl_2, 298 K): δ / ppm = −79.0 (s). $^{31}P\{^{1}H\}$ NMR (202.44 MHz, CD_2Cl_2, 298 K): δ / ppm = 65.5 (s_{sat}, $^{1}J_{W,P}$ = 278 Hz). ^{31}P NMR (202.44 MHz, CD_2Cl_2, 298 K): δ / ppm = 65.5 (d_{sat}, $^{1}J_{P,H}$ = 373 Hz, $^{1}J_{W,P}$ = 278 Hz). MS (ESI pos., selected data): *m/z* (%) = 681.076 (100) $[W(CO)_5\{P(CPh_3)(H)(N\text{-MeIm})\}]^+$, 243.117 (11) $[CPh_3]^+$. MS (ESI

neg., selected data): *m/z* (%) = 149.0 (100) $[OSO_2CF_3]^-$. HRMS (ESI pos.): *m/z* calcd for $[C_{28}H_{22}N_2O_5PW]^+$: 681.0775; found: 681.0774.

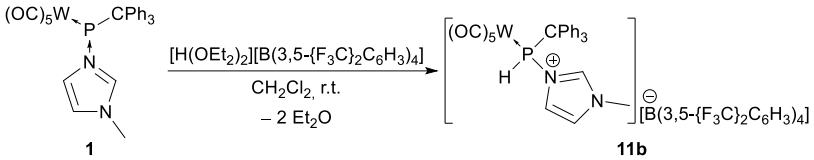
Synthesis of complex 11a-Cr



1-Cr **11a-Cr**

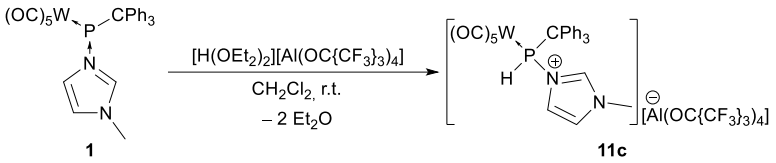
0.03 mL (0.34 mmol, 1.2 eq.) of trifluoromethanesulfonic acid was added dropwise to a solution of 0.161 g (0.29 mmol, 1.0 eq.) of complex **1-Cr**[8] in 10 mL of dichloromethane and the solution was stirred for 2 h at ambient temperature. Afterwards, 26 mL of *n*-pentane were added to the reaction solution forming a colourless suspension. After additional stirring for 1 minute, the solid transformed to a yellow oil. All volatiles were removed *in vacuo* at ambient temperature within 8 minutes and the obtained colourless and blue-green solids were further dried for 1.5 h. After the addition of 10 mL of diethyl ether, the solids formed a yellow oil. The mixture was stirred for 20 minutes obtaining a pale yellow suspension. The supernatant was filtered off using a filter cannula (Ø = 1 mm) with a Whatman® 595 filter paper. The pale yellow solid residue was washed two times using 10 mL of diethyl ether and four times using 10 mL of *n*-pentane at ambient temperature. The obtained pale yellow solid was dried for 16.5 h *in vacuo* at ambient temperature. Yield: 0.181 g (0.26 mmol, 88%). Mp 144 °C (dec.). Elemental analysis calcd (%) for $C_{29}H_{22}N_2O_8F_3PSCr$: C 49.86, H 3.17, N 4.01, S 4.59; found: C 49.53, H 3.21, N 4.07, S 4.60. IR (ATR Diamond): ν_{max} / cm^{-1} = 1941 (s) (CO), 1972 (m) (CO), 2001 (w) (CO), 2076 (m) (CO). ^{1}H NMR (500.04 MHz, CD_2Cl_2, 298 K): δ / ppm = 9.11 (s, 1H; Im-*H*), 8.94 (d, $^1J_{P,H}$ = 362 Hz, 1H; P*H*), 7.47–7.40 (m, 9H; CPh_3), 7.34–7.32 (m, 7H; CPh_3 & Im-*H*), 6.49 (s, 1H; Im-*H*), 3.87 (s, 3H; CH_3). ^{13}C{^{1}H} NMR (125.75 MHz, CD_2Cl_2, 298 K): δ / ppm = 218.8 (d, $^2J_{P,C}$ = 1 Hz; *trans*-*C*O), 214.0 (d, $^2J_{P,C}$ = 12 Hz; *cis*-*C*O), 141.2 (d, $^2J_{P,C}$ = 4 Hz; Im), 139.9 (br s; *ipso*-*C*), 130.3 (br s; Ph), 129.7 (s; Ph), 129.1 (s; Ph), 125.5 (d, $^3J_{P,C}$ = 2 Hz; Im), 124.9 (d, $^2J_{P,C}$ = 5 Hz; Im), 121.3 (q, $^1J_{F,C}$ = 321 Hz; *C*F_3), 66.0 (d, $^1J_{P,C}$ = 3 Hz; *C*Ph_3), 37.1 (s; *C*H_3). ^{15}N{^{1}H} NMR (50.68 MHz, CD_2Cl_2, 298 K): δ / ppm = −200.3 (s; *N*-P), −205.8 (s; *N*-CH_3). ^{19}F NMR (470.51 MHz, CD_2Cl_2, 298 K): δ / ppm = −78.9 (s). ^{31}P{^{1}H} NMR (202.44 MHz, CD_2Cl_2, 298 K): δ / ppm = 116.4 (s). ^{31}P NMR (202.44 MHz, CD_2Cl_2, 298 K): δ / ppm = 116.4 (d, $^1J_{P,H}$ = 362 Hz). MS (ESI pos., selected data): *m/z* (%) = 549.071 (100) $[Cr(CO)_5\{P(CPh_3)(H)(N\text{-MeIm})\}]^+$, 357.155 (3) $[P(CPh_3)(H)(N\text{-MeIm})]^+$, 243.119 (51) $[CPh_3]^+$. MS (ESI neg., selected data): *m/z* (%) = 149.1 (100) $[OSO_2CF_3]^-$. HRMS (ESI pos.): *m/z* calcd for $[C_{28}H_{22}N_2O_5PCr]^+$: 549.0666; found: 549.0676.

Synthesis of complex 11b



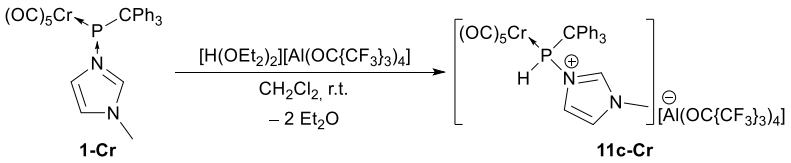
A solution of 0.1225 g (0.18 mmol, 1.0 eq.) of complex **1**[8] and 0.1847 g (0.18 mmol, 1.0 eq.) of $[H(OEt_2)_2][B(3,5\text{-}\{F_3C\}_2C_6H_3)_4]$[12] in 10 mL of dichloromethane was stirred for 1.5 h at ambient temperature. Afterwards, 60 mL of *n*-pentane were added to the reaction solution forming a colourless suspension with brown oil. The supernatant was filtered off using a filter cannula (Ø = 1 mm) with a Whatman® 595 filter paper. The pale brown residue was washed once with 5.0 mL of *n*-pentane at −40 °C. The obtained pale yellow solid was dried for 3.5 h *in vacuo* at ambient temperature. Yield: 0.251 g (0.16 mmol, 90%). Mp 84 °C (dec.). Elemental analysis calcd (%) for $C_{60}H_{34}BN_2O_5F_{24}PW$: C 46.66, H 2.22, N 1.81; found: C 46.86, H 2.56, N 1.93. IR (ATR Diamond): ν_{max} / cm^{-1} = 1949 (s) (CO), 1963 (m) (CO), 2001 (w) (CO), 2086 (m) (CO). ^{1}H NMR (500.04 MHz, CD_2Cl_2, 298 K): δ / ppm = 8.84 (d, $^1J_{P,H}$ = 353 Hz, 1H; P*H*), 7.75–7.73 (m, 8H; *ortho*-C*H*^{BArF}), 7.57 (s, 4H; *para*-C*H*^{BArF}), 7.48–7.44 (m, 9H; CPh_3), 7.28–7.23 (m, 7H; CPh_3 & Im-*H*), 7.19–7.17 (m, 1H; Im-*H*), 7.08 (br s, 1H; Im-*H*), 3.76 (s, 3H; CH_3). ^{11}B{^{1}H} NMR (160.43 MHz, CD_2Cl_2, 298 K): δ / ppm = −6.6 (s). ^{13}C{^{1}H} NMR (125.75 MHz, CD_2Cl_2, 298 K): δ / ppm = 195.1 (d_{sat}, $^2J_{P,C}$ = 36 Hz, $^1J_{W,C}$ = 141 Hz; *trans*-*C*O), 194.3 (d_{sat}, $^2J_{P,C}$ = 6 Hz, $^1J_{W,C}$ = 127 Hz; *cis*-*C*O), 162.2 (q*, $^1J_{C,B}$ = 50 Hz; *ipso*-*C*^{BArF}), 139.4 (br s; *ipso*-*C*^{Ph}), 138.3 (s; Im), 135.2 (s; *ortho*-*C*^{BArF}), 130.3 (br s; Ph), 130.1 (s; Ph), 129.8 (d, $J_{P,C}$ = 2 Hz; Ph), 129.3 (qq*, $^2J_{F,C}$ = 32 Hz, $^3J_{C,B}$ = 3 Hz; *meta*-*C*^{BArF}), 126.4 (s; Im), 125.2 (d, $J_{P,C}$ = 2 Hz; Im), 125.0 (q, $^1J_{F,C}$ = 272 Hz; *C*F_3), 117.9 (sept, $^3J_{F,C}$ = 4 Hz; *para*-*C*^{BArF}), 65.5 (d, $^1J_{P,C}$ = 7 Hz; *C*Ph_3), 37.7 (s; *C*H_3). ^{15}N{^{1}H} NMR (50.68 MHz, CD_2Cl_2, 298 K): δ / ppm = −194.6 (s; *N*-P), −203.1 (s; *N*-CH_3). ^{19}F NMR (470.51 MHz, CD_2Cl_2, 298 K): δ / ppm = −62.8 (s). ^{31}P{^{1}H} NMR (202.44 MHz, CD_2Cl_2, 298 K): δ / ppm = 77.7 (s_{sat}, $^1J_{W,P}$ = 284 Hz). ^{31}P NMR (202.44 MHz, CD_2Cl_2, 298 K): δ / ppm = 77.7 (d_{sat}, $^1J_{P,H}$ = 353 Hz, $^1J_{W,P}$ = 284 Hz). MS (ESI pos., selected data): *m/z* (%) = 681.084 (8) $[W(CO)_5\{P(CPh_3)(H)(N\text{-MeIm})\}]^+$, 599.030 (29) $[W(CO)_5\{P(CPh_3)H\}]^+$, 571.035 (11) $[W(CO)_4\{P(CPh_3)H\}]^+$, 543.040 (35) $[W(CO)_3\{P(CPh_3)H\}]^+$, 515.044 (100) $[W(CO)_2\{P(CPh_3)H\}]^+$, 487.050 (12) $[W(CO)\{P(CPh_3)H\}]^+$, 459.054 (23) $[W\{P(CPh_3)H\}]$, 357.156 (24) $[P(CPh_3)(H)(N\text{-MeIm})\}]^+$. MS (ESI neg., selected data): *m/z* (%) = 863.064 (100) $[B(3,5\text{-}\{F_3C\}_2C_6H_3)_4]^-$. HRMS (ESI pos.): *m/z* calcd for $[C_{28}H_{22}N_2O_5PW]^+$: 681.0775; found: 681.0775.

Synthesis of complex 11c



A solution of 0.109 g (0.16 mmol, 1.0 eq.) of complex **1**[8] and 0.178 g (0.16 mmol, 1.0 eq.) of $[H(OEt_2)_2][Al(OC\{CF_3\}_3)_4]$[13] in 16 mL of dichloromethane was stirred for 3 h at ambient temperature. Afterwards, 80 mL of *n*-pentane were added to the reaction solution forming a pale yellow suspension. The supernatant was filtered off using a filter cannula (Ø = 2 mm) with a glass microfibre filter paper. The pale yellow residue was washed three times using 11 mL of a 10:1 *n*-pentane/dichloromethane mixture and two times using 5 mL of *n*-pentane at ambient temperature. The obtained colourless solid was dried for 14 h *in vacuo* at ambient temperature. Yield: 0.234 g (0.14 mmol, 89%). Mp 160 °C (dec.). Elemental analysis calcd (%) for $C_{44}H_{22}N_2O_9F_{36}AlPW$: C 32.06, H 1.35, N 1.70; found: C 31.32, H 1.56, N 1.73. IR (ATR Diamond): ν_{max} / cm^{-1} = 1949 (s) (CO), 1963 (m) (CO), 2009 (w) (CO), 2085 (m) (CO). ^1H NMR (400.13 MHz, CD_2Cl_2, 298 K): δ / ppm = 8.84 (d, $^1J_{P,H}$ = 353 Hz, 1H; P*H*), 7.49–7.48 (m, 9H; CPh_3), 7.29–7.25 (m, 7H; CPh_3 & Im-*H*), 7.20–7.19 (m, 1H; Im-*H*), 7.08 (br s, 1H; Im-*H*), 3.81 (s, 3H; CH_3). $^{13}C\{^1H\}$ NMR (100.63 MHz, CD_2Cl_2, 298 K): δ / ppm = 195.1 (d, $^2J_{P,C}$ = 36 Hz; *trans*-*C*O), 194.3 (d, $^2J_{P,C}$ = 6 Hz; *cis*-*C*O), 139.3 (br s; *ispo*-*C*), 138.3 (s; Im), 130.3 (br d, $J_{P,C}$ = 9 Hz; Ph), 130.1 (s; Ph), 129.8 (d, $J_{P,C}$ = 2 Hz; Ph), 126.4 (s; Im), 126.0 (s; *C*$(CF_3)_3$), 125.2 (d, $J_{P,C}$ = 2 Hz; Im), 121.7 (q, $^1J_{F,C}$ = 293 Hz; *C*F_3), 65.5 (d, $^1J_{P,C}$ = 7 Hz; *C*Ph_3), 37.8 (s; *C*H_3). $^{15}N\{^1H\}$ NMR (50.68 MHz, CD_2Cl_2, 298 K): δ / ppm = −195.7 (s; *N*-P), −204.2 (s; *N*-CH_3). ^{19}F NMR (470.51 MHz, CD_2Cl_2, 298 K): δ / ppm = −75.7 (s). $^{27}Al\{^1H\}$ NMR (78.20 MHz, CD_2Cl_2, 298 K): δ / ppm = 34.7 (s). $^{31}P\{^1H\}$ NMR (162.00 MHz, CD_2Cl_2, 298 K): δ / ppm = 77.8 (s_{sat}, $^1J_{W,P}$ = 284 Hz). ^{31}P NMR (162.00 MHz, CD_2Cl_2, 298 K): δ / ppm = 77.8 (d_{sat}, $^1J_{P,H}$ = 354 Hz, $^1J_{W,P}$ = 284 Hz). MS (ESI pos., selected data): *m/z* (%) = 681.077 (<1) $[W(CO)_5\{P(CPh_3)(H)(N\text{-MeIm})\}]^+$, 243.116 (100) $[CPh_3]^+$. MS (ESI neg., selected data): *m/z* (%) = 966.907 (100) $[Al(OC\{CF_3\}_3)_4]^-$. HRMS (ESI pos.): *m/z* calcd for $[C_{28}H_{22}N_2O_5PW]^+$: 681.0775; found: 681.0782.

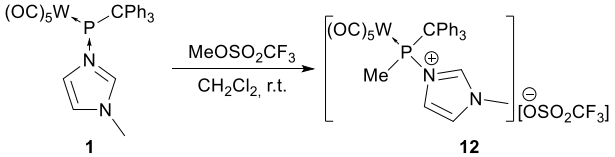
Synthesis of complex 11c-Cr



1-Cr **11c-Cr**

A solution of 0.167 g (0.30 mmol, 1.0 eq.) of complex **1-Cr**[8] and 0.339 g (0.30 mmol, 1.0 eq.) of $[H(OEt_2)_2][Al(OC\{CF_3\}_3)_4]$[13] in 16 mL of dichloromethane was stirred for 3 h at ambient temperature. Afterwards, 100 mL of *n*-pentane were added to the reaction solution forming a yellow suspension. The supernatant was filtered off using a filter cannula (Ø = 2 mm) with a Whatman® 595 filter paper. The pale yellow residue was washed three times using 11 mL of a 10:1 *n*-pentane/dichloromethane mixture and three times using 10 mL of *n*-pentane at ambient temperature. The obtained pale yellow solid was dried for 19 h *in vacuo* at ambient temperature. Yield: 0.44 g (0.29 mmol, 96%). Mp 151 °C (dec.). Elemental analysis calcd (%) for $C_{44}H_{22}N_2O_9F_{36}AlPCr$: C 34.85, H 1.46, N 1.85; found: C 33.50, H 1.52, N 1.84. IR (ATR Diamond): ν_{max} / cm^{-1} = 1953 (s) (CO), 1969 (s) (CO), 2014 (w) (CO), 2079 (m) (CO). ^1H NMR (500.04 MHz, CD_2Cl_2, 298 K): δ / ppm = 8.34 (d, $^1J_{P,H}$ = 341 Hz, 1H; P*H*), 7.50–7.49 (m, 9H; CPh_3), 7.28 (m, 1H; Im-*H*), 7.26–7.18 (m, 6H; CPh_3), 7.20–7.19 (m, 1H; Im-*H*), 7.03 (br s, 1H; Im-*H*), 3.80 (s, 3H; C*H*$_3$). $^{13}C\{^1H\}$ NMR (125.75 MHz, CD_2Cl_2, 298 K): δ / ppm = 217.4 (s; *trans*-*C*O), 213.8 (d, $^2J_{P,C}$ = 11 Hz; *cis*-*C*O), 139.5 (br s; *ipso*-*C*), 138.2 (d, $^2J_{P,C}$ = 5 Hz; Im), 130.2–129.9 (m; Ph); 126.3 (d, $J_{P,C}$ = 5 Hz; Im), 125.3 (s; Im), 121.7 (q, $^1J_{F,C}$ = 293 Hz; *C*F_3), 67.0 (d, $^1J_{P,C}$ = 2 Hz; *C*Ph_3), 37.7 (d, $^4J_{P,C}$ = 1 Hz; *C*H_3). $^{15}N\{^1H\}$ NMR (50.68 MHz, CD_2Cl_2, 298 K): δ / ppm = −195.7 (s; *N*-P), −204.2 (s; *N*-CH_3). ^{19}F NMR (470.51 MHz, CD_2Cl_2, 298 K): δ / ppm = −75.7 (s). $^{27}Al\{^1H\}$ NMR (130.29 MHz, CD_2Cl_2, 298 K): δ / ppm = 34.6 (s). $^{31}P\{^1H\}$ NMR (202.44 MHz, CD_2Cl_2, 298 K): δ / ppm = 132.0 (s). ^{31}P NMR (202.44 MHz, CD_2Cl_2, 298 K): δ / ppm = 132.0 (d, $^1J_{P,H}$ = 342 Hz). MS (ESI pos., selected data): *m/z* (%) = 549.067 (36) $[Cr(CO)_5\{P(CPh_3)(H)(N\text{-MeIm})\}]^+$. MS (ESI neg., selected data): *m/z* (%) = 966.9 (100) $[Al(OC\{CF_3\}_3)_4]^-$. HRMS (ESI pos.): *m/z* calcd for $[C_{28}H_{22}N_2O_5PCr]^+$: 549.0666; found: 549.0669.

Synthesis of complex 12

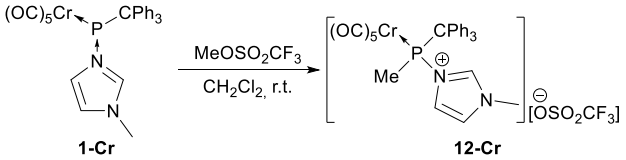


1 **12**

0.02 mL (0.18 mmol, 1.1 eq.) of methyl trifluoromethanesulfonate was added to a solution of 0.111 g (0.16 mmol, 1.0 eq.) of complex **1**[8] in 10 mL of dichloromethane at ambient temperature. The solution was stirred for 3 h at ambient temperature. After addition of 40 mL of *n*-pentane the formed colourless suspension was stirred for 2 h. The supernatant was filtered off using a filter cannula (Ø = 2 mm) with

a Whatman® 595 filter paper and the colourless solid residue was washed three times with 4.0 mL of *n*-pentane. The solid was dried for 14 h *in vacuo* at ambient temperature. The product was isolated by recrystallization in 20 mL of a 1:1 diethylether/THF mixture at −40 °C. After the supernatant was filtered off using a filter cannula (Ø = 2 mm) with a Whatman® 595 filter paper and washing the colourless solid three times with 3 mL of *n*-pentane at −40 °C. The product was dried for 75 minutes at ambient temperature. Yield: 0.078 g (0.09 mmol, 56%). Mp 155 °C (dec.). Elemental analysis calcd (%) for $C_{30}H_{24}N_2O_8F_3PSW$: C 42.67, H 2.87, N 3.32, S 3.80; found: C 41.74, H 2.92, N 3.35, S 4.32. IR (ATR Diamond): ν_{max} / cm^{-1} = 1927 (s) (CO), 1995 (w) (CO), 2079 (m) (CO). ^{1}H NMR (500.04 MHz, CD_2Cl_2, 298 K): δ / ppm = 8.71 (s, 1H; Im-*H*), 7.70–7.57 (m, 2H; CPh_3), 7.54–7.35 (m, 9H; CPh_3), 7.35–7.27 (m, 2H; CPh_3), 7.25 (s, 1H; Im-*H*), 6.98–6.69 (m, 1H; Im-*H*), 6.65–6.55 (m, 2H; CPh_3), 3.96 (s, 3H; N-CH_3), 2.53 (d, $^2J_{P,H}$ = 1 Hz, 3H; P-CH_3). ^{13}C{^{1}H} NMR (125.75 MHz, CD_2Cl_2, 298 K): δ / ppm = 197.1 (d, $^2J_{P,C}$ = 34 Hz; *trans*-*C*O), 196.0 (d_{sat}, $^2J_{P,C}$ = 6 Hz, $^1J_{W,C}$ = 127 Hz; *cis*-*C*O), 141.2 (br s; *ipso*-*C*), 139.9 (d, $J_{P,C}$ = 1 Hz; Im), 139.6 (br s; *ipso*-*C*), 137.3 (br s; *ipso*-*C*), 131.8–131.4 (m; Ph), 130.1–129.6 (m; Ph), 125.3 (d, $J_{P,C}$ = 5 Hz; Im), 125.1 (d, $J_{P,C}$ = 3 Hz; Im), 121.2 (q, $^1J_{F,C}$ = 320 Hz; *C*F_3), 68.1 (d, $^1J_{P,C}$ = 2 Hz; *C*Ph_3), 37.5 (s; N-*C*H_3), 26.1 (d, $^1J_{P,C}$ = 20 Hz; P-*C*H_3). ^{15}N{^{1}H} NMR (50.68 MHz, CD_2Cl_2, 298 K): δ / ppm = −191.4 (s; *N*-P), −202.4 (s; *N*-CH_3). ^{19}F NMR (470.51 MHz, CD_2Cl_2, 298 K): δ / ppm = −79.0 (s). ^{31}P{^{1}H} NMR (202.44 MHz, CD_2Cl_2, 298 K): δ / ppm = 116.4 (s_{sat}, $^1J_{W,P}$ = 274 Hz). ^{31}P NMR (121.51 MHz, CD_2Cl_2, 298 K): δ / ppm = 116.4 (s_{sat}, $^1J_{W,P}$ = 274 Hz). MS (ESI pos., selected data): *m/z* (%) = 695.092 (4) $[W(CO)_5\{P(CPh_3)(Me)(N\text{-MeIm})\}]^+$, 613.039 (3) $[W(CO)_5\{P(CPh_3)Me\}]^+$, 585.044 (1) $[W(CO)_4\{P(CPh_3)Me]^+$, 529.054 (1) $[W(CO)_2\{P(CPh_3)Me\}]^+$, 501.059 (1) $[W(CO)\{P(CPh_3)Me\}]^+$, 371.166 (12) $[P(CPh_3)(Me)(N\text{-MeIm})]^+$, 289.113 (44) $[P(CPh_3)Me]^+$, 243.116 (100) $[CPh_3]^+$. MS (ESI neg., selected data): *m/z* (%) = 148.9 (100) $[OSO_2CF_3]^-$. HRMS (ESI pos.): *m/z* calcd for $[C_{29}H_{24}N_2O_5PW]^+$: 695.0928; found: 695.0921.

Synthesis of complex 12-Cr



1-Cr **12-Cr**

0.04 mL (0.37 mmol, 1.2 eq.) of methyl trifluoromethanesulfonate was added to a solution of 0.171 g (0.31 mmol, 1.0 eq.) of complex **1-Cr**[8] in 16 mL of dichloromethane at ambient temperature. The solution was stirred for 80 minutes in a glovebox. Afterwards, all volatiles were removed *in vacuo* at ambient temperature. The obtained yellow solid was redissolved in 15 mL of dichloromethane. After addition of 50 mL of *n*-pentane the formed yellow suspension was stirred for 3 minutes. The supernatant was filtered off using a filter cannula (Ø = 2 mm) with a Whatman® 595 filter paper and the pale yellow solid residue was washed three times with 5.0 mL of *n*-pentane. The product was dried

for 2.5 h *in vacuo* at ambient temperature. Yield: 0.194 g (0.27 mmol, 87%). Mp 142 °C (dec.). Elemental analysis calcd (%) for $C_{30}H_{24}N_2O_8F_3PSCr$: C 50.57, H 3.40, N 3.93, S 4.50; found: C 47.04, H 3.46, N 3.60, S 4.31. IR (ATR Diamond): ν_{max} / cm^{-1} = 1934 (s) (CO), 1981 (m) (CO), 2001 (w) (CO), 2073 (m) (CO). ^{1}H NMR (500.04 MHz, CD_2Cl_2, 298 K): δ / ppm = 8.66 (s, 1H; Im-*H*), 7.67–7.63 (m, 2H; CPh_3), 7.56–7.45 (m, 6H; CPh_3), 7.45–7.33 (m, 3H; CPh_3), 7.28 (s, 1H; Im-*H*), 7.26–7.17 (m, 2H; CPh_3), 6.58 (s, 1H; Im-*H*), 6.56–6.45 (m, 2H; CPh_3), 3.97 (s, 3H; N-CH_3), 2.28 (s, 3H; P-CH_3). ^{13}C{^{1}H} NMR (125.75 MHz, CD_2Cl_2, 298 K): δ / ppm = 219.3 (d, $^2J_{P,C}$ = 2 Hz; *trans*-*C*O), 214.8 (d, $^2J_{P,C}$ = 11 Hz; *cis*-*C*O), 141.1 (br s; *ipso*-*C*), 139.8 (d, $J_{P,C}$ = 2 Hz; Im), 139.5 (br s; *ipso*-*C*), 137.8 (br s; *ispo*-*C*), 131.7–131.3 (m; Ph), 130.0–129.5 (m; Ph), 125.4 (d, $J_{P,C}$ = 2 Hz; Im), 124.9 (d, $J_{P,C}$ = 4 Hz; Im), 121.4 (br q, $^1J_{F,C}$ = 324 Hz; *C*F_3), 69.7 (d, $^1J_{P,C}$ = 2 Hz; *C*Ph_3), 37.5 (s; N-*C*H_3), 24.8 (d, $^1J_{P,C}$ = 16 Hz; P-*C*H_3). ^{15}N{^{1}H} NMR (50.68 MHz, CD_2Cl_2, 298 K): δ / ppm = −191.4 (s; *N*-P), −203.1 (s; *N*-CH_3). ^{19}F NMR (470.51 MHz, CD_2Cl_2, 298 K): δ / ppm = −78.8 (s). ^{31}P{^{1}H} NMR (202.44 MHz, CD_2Cl_2, 298 K): δ / ppm = 165.1 (s). ^{31}P NMR (202.44 MHz, CD_2Cl_2, 298 K): δ / ppm = 165.1 (s). MS (ESI pos., selected data): *m/z* (%) = 563.082 (12) $[Cr(CO)_5\{P(CPh_3)(Me)(N\text{-MeIm})\}]^+$, 481.029 (7) $[Cr(CO)_5\{P(CPh_3)Me\}]^+$, 425.039 (1) $[Cr(CO)_3\{P(CPh_3)Me\}]^+$, 397.044 (8) $[Cr(CO)_2\{P(CPh_3)Me\}]^+$, 382.081 (4) $[Cr(CO)_2(PCPh_3)]^+$, 371.167 (100) $[P(CPh_3)(Me)(N\text{-MeIm})\}]^+$, 289.114 (64) $[P(CPh_3)Me]^+$, 243.117 (26) $[CPh_3]^+$, 237.983 (1) $[Cr(CO)_5(PMe)]^+$. MS (ESI neg., selected data): *m/z* (%) = 149.0 (100) $[OSO_2CF_3]^-$. HRMS (ESI pos.): *m/z* calcd for $[C_{29}H_{24}N_2O_5PCr]^+$: 563.0825; found: 563.0820.

3 NMR spectra

Compound 2

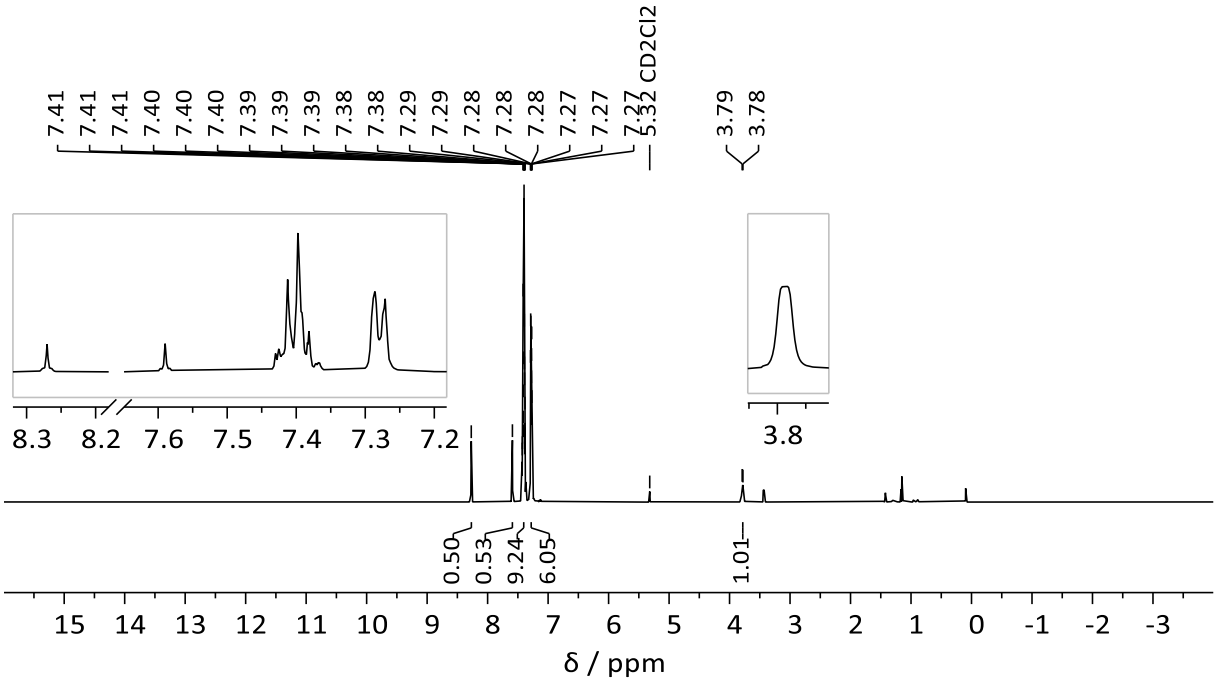


Fig. S1 ^{1}H NMR spectrum (500.04 MHz, CD_2Cl_2, 298 K) of compound **2**.

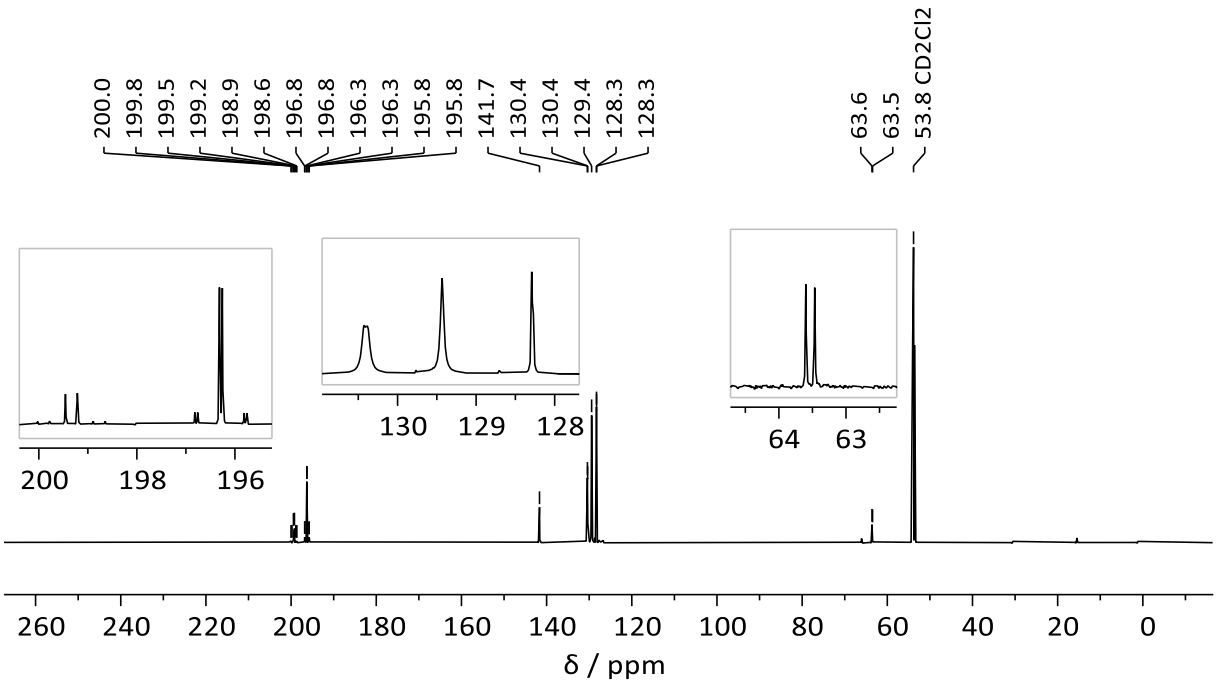


Fig. S2 $^{13}C\{^{1}H\}$ NMR spectrum (125.75 MHz, CD_2Cl_2, 298 K) of compound **2**.

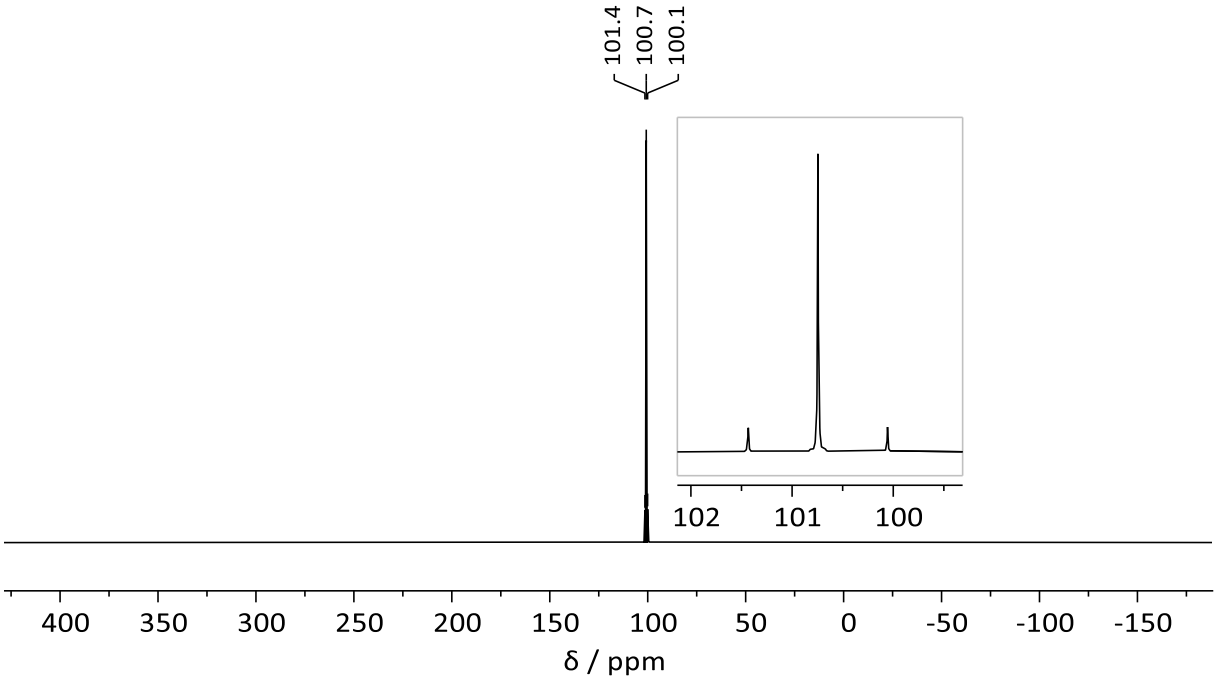


Fig. S3 $^{31}P\{^{1}H\}$ NMR spectrum (202.44 MHz, CD_2Cl_2, 298 K) of compound **2**.

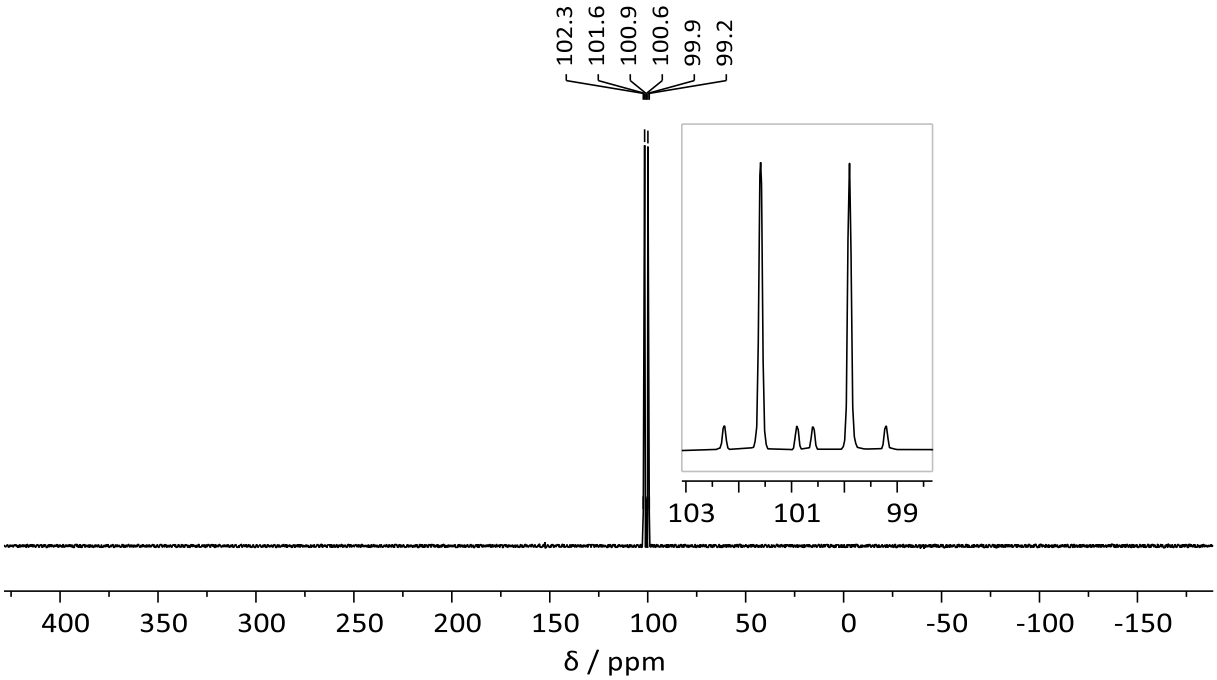


Fig. S4 ^{31}P NMR spectrum (202.44 MHz, CD_2Cl_2, 298 K) of compound **2**.

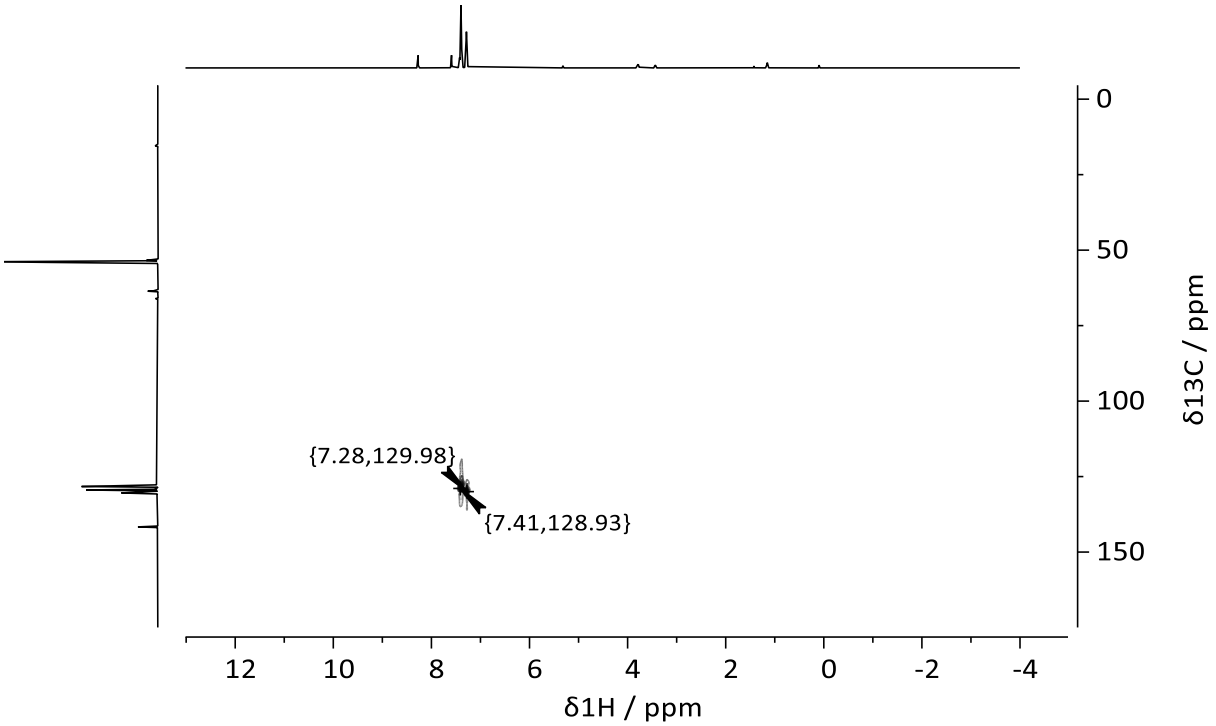


Fig. S5 $^{1}H,^{13}C$ HSQC NMR spectrum (500.04 MHz, 125.75 MHz, CD_2Cl_2, 298 K) of compound **2**.

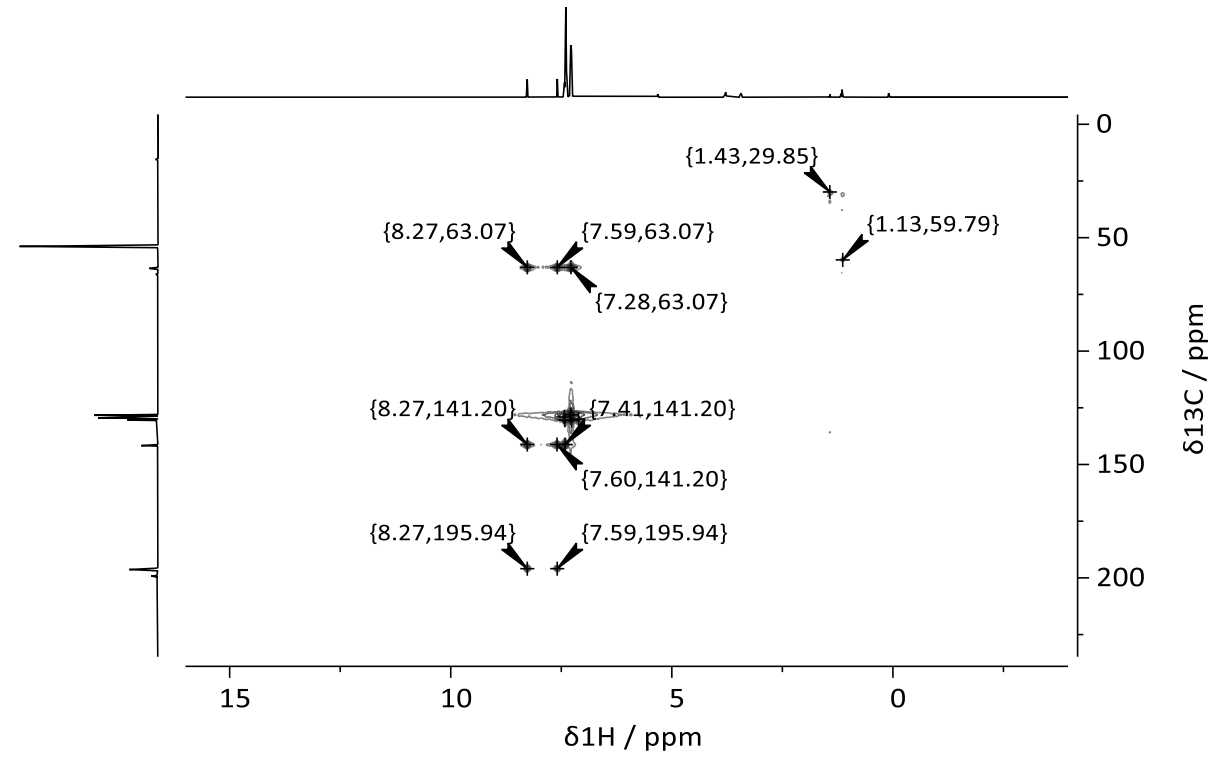


Fig. S6 $^{1}H,^{13}C$ HMBC NMR spectrum (500.04 MHz, 125.75 MHz, CD_2Cl_2, 298 K) of compound **2**.

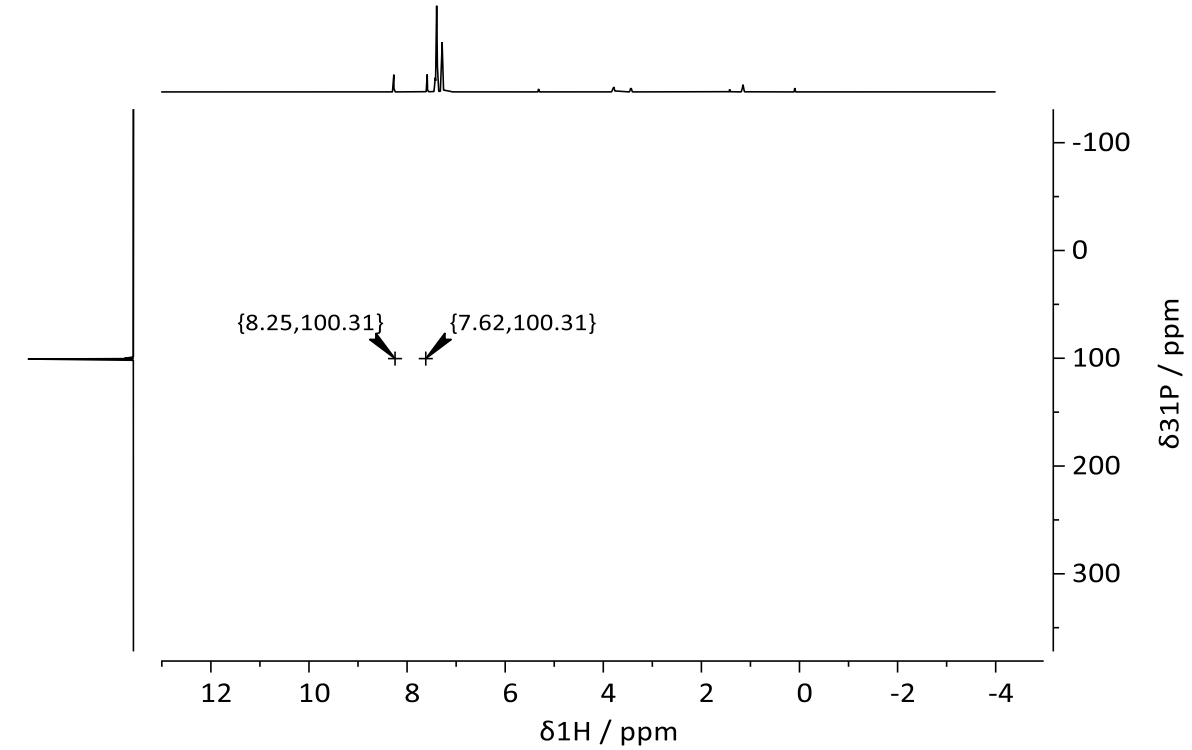


Fig. S7 $^{1}H,^{31}P$ HMQC NMR spectrum (500.04 MHz, 202.44 MHz, CD_2Cl_2, 298 K) of compound **2**.

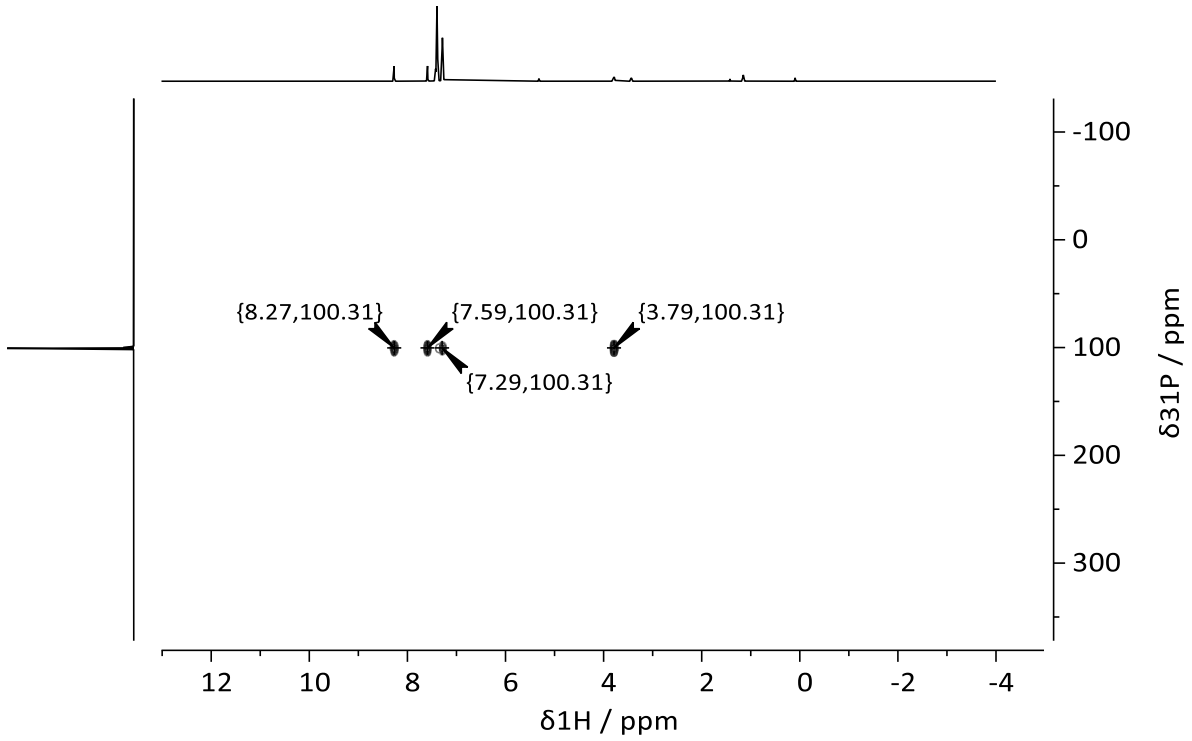


Fig. S8 $^{1}H,^{31}P$ HMBC NMR spectrum (500.04 MHz, 202.44 MHz, CD_2Cl_2, 298 K) of compound **2**.

Compound 3a

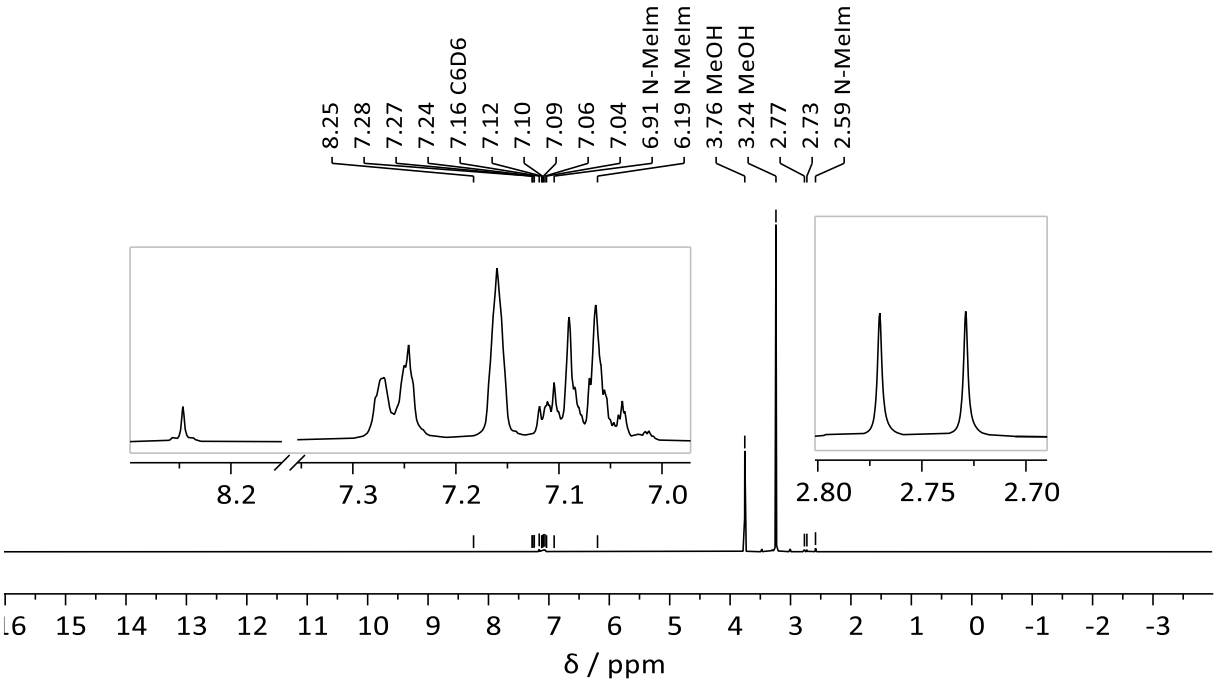


Fig. S9 ^{1}H NMR spectrum (300.13 MHz, C_6D_6, 298 K) of the reaction mixture of compound **1** with methanol to form compound **3a**.

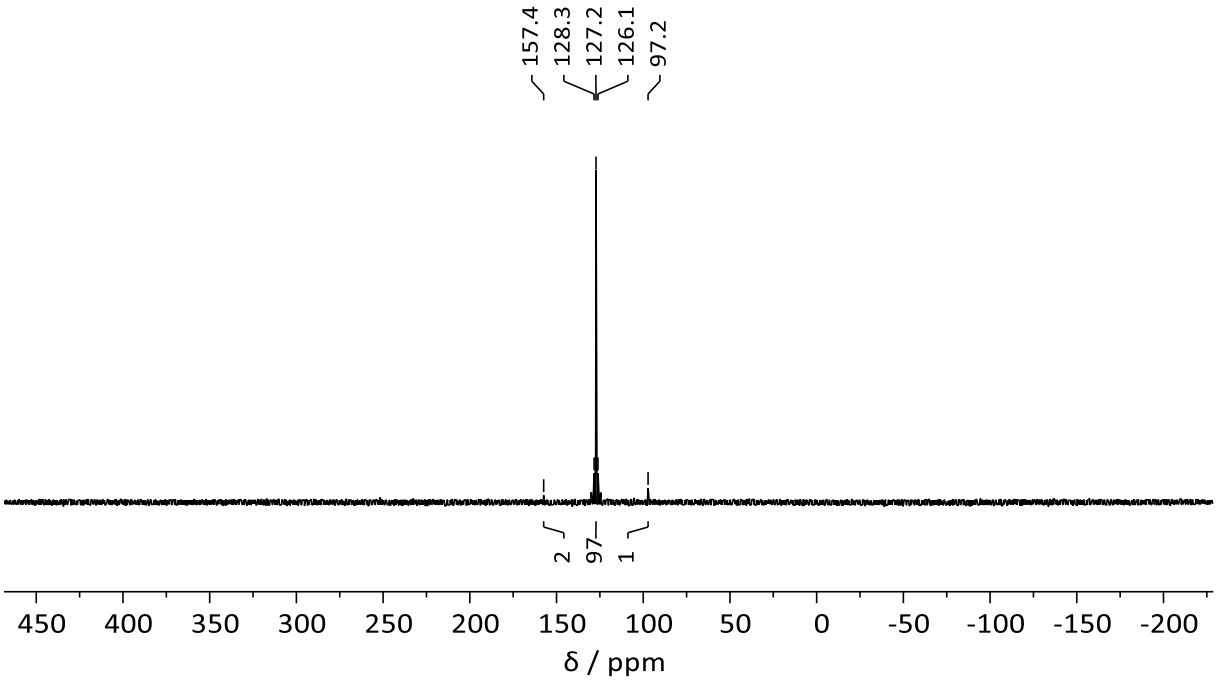


Fig. S10 $^{31}P\{^{1}H\}$ NMR spectrum (121.51 MHz, C_6D_6, 298 K) of the reaction mixture of compound **1** with methanol to form compound **3a**.

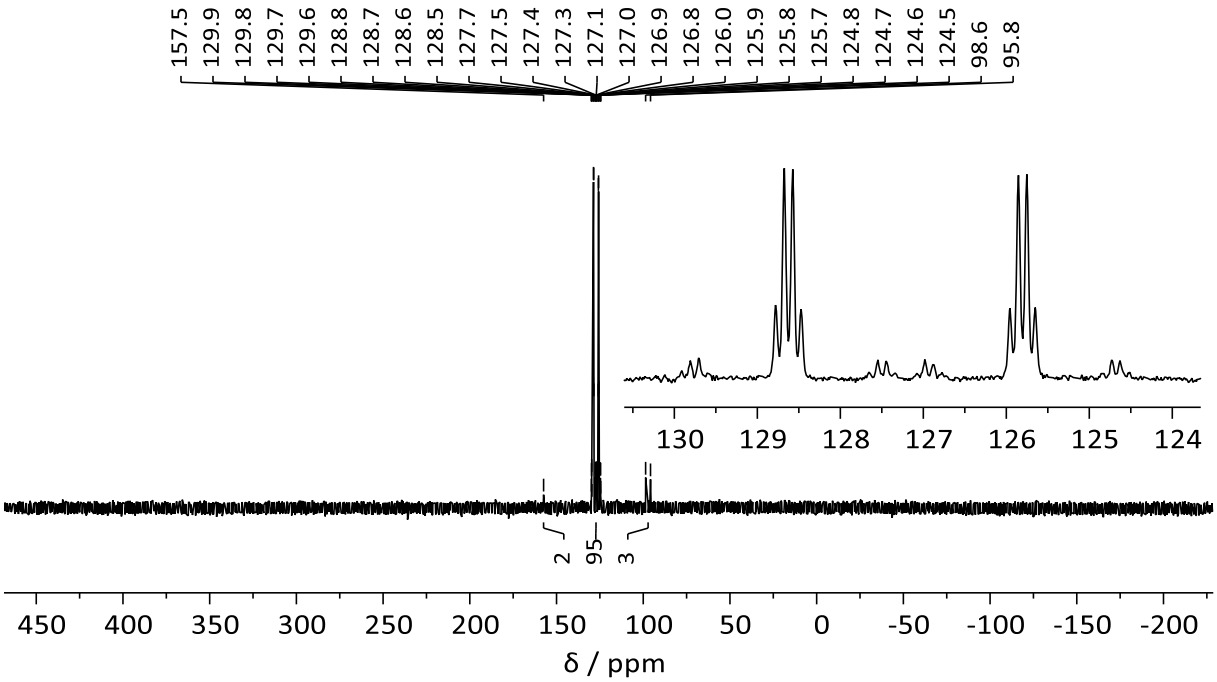


Fig. S11 ^{31}P NMR spectrum (121.51 MHz, C_6D_6, 298 K) of the reaction mixture of compound **1** with methanol to form compound **3a**.

Compound 3b

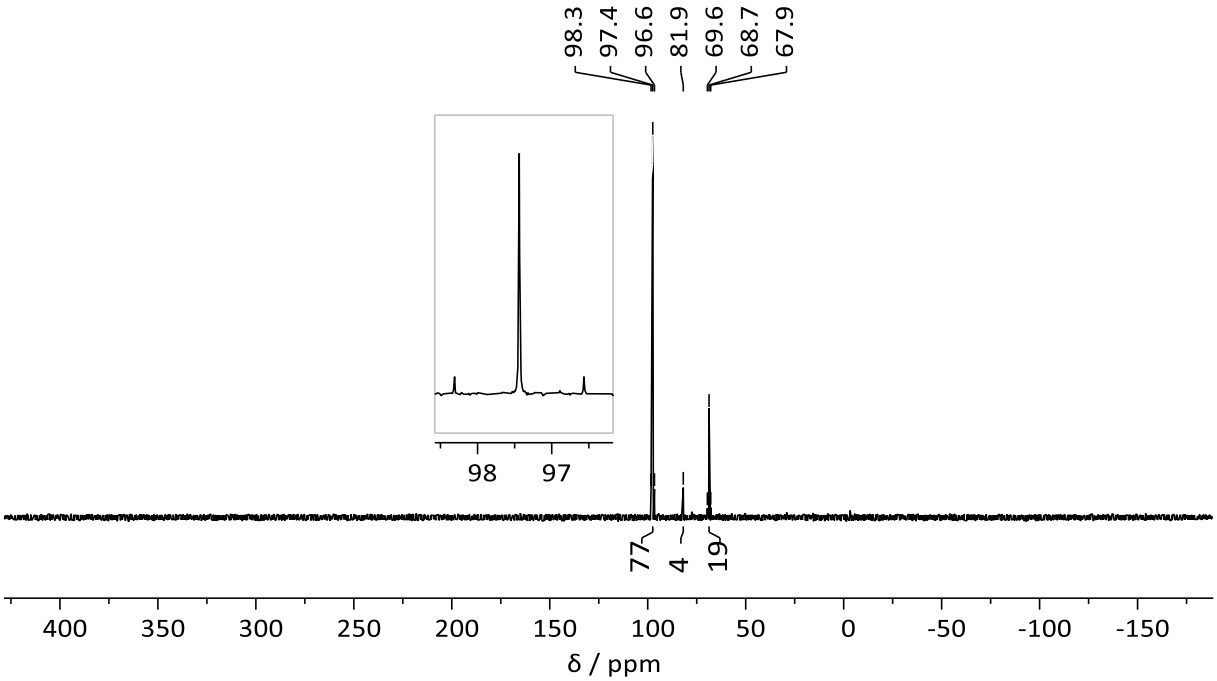


Fig. S12 $^{31}P\{^1H\}$ NMR spectrum (162.00 MHz, C_6D_6, 298 K) of the reaction mixture of compound **1** with *tert*-butanol to form compound **3b**.

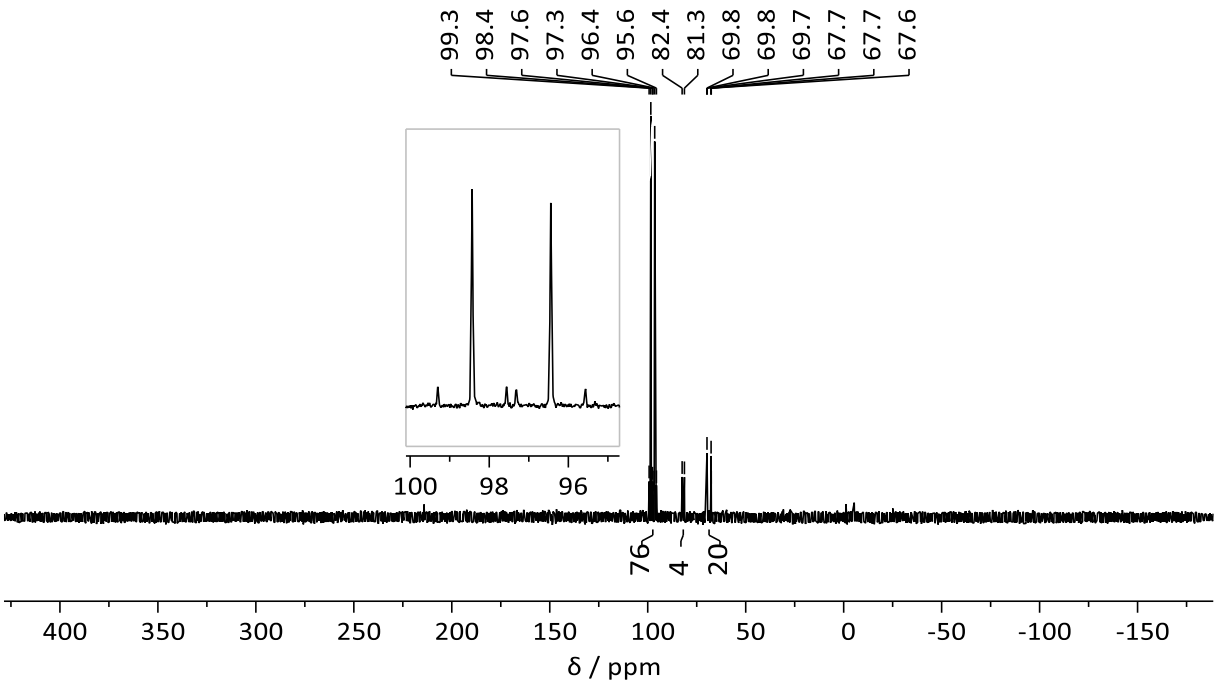


Fig. S13 ^{31}P NMR spectrum (162.00 MHz, C_6D_6, 298 K) of the reaction mixture of compound **1** with *tert*-butanol to form compound **3b**.

Compound 10a

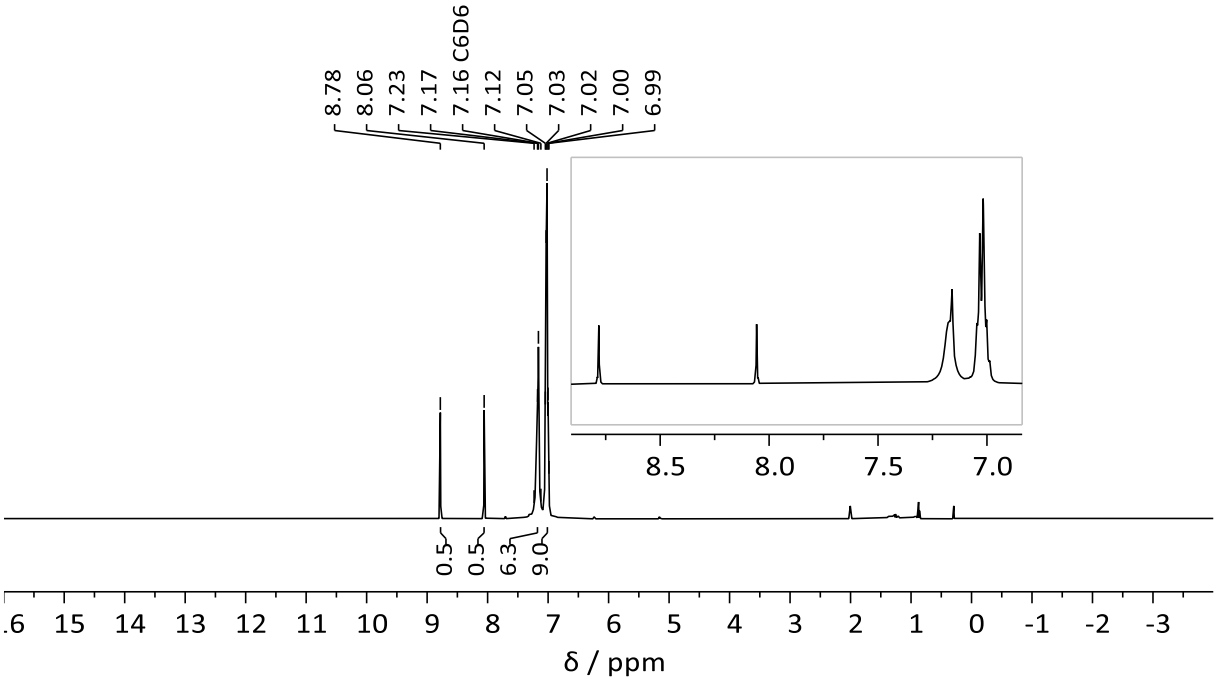


Fig. S14 ^{1}H NMR spectrum (500.04 MHz, C_6D_6, 298 K) of compound **10a**.

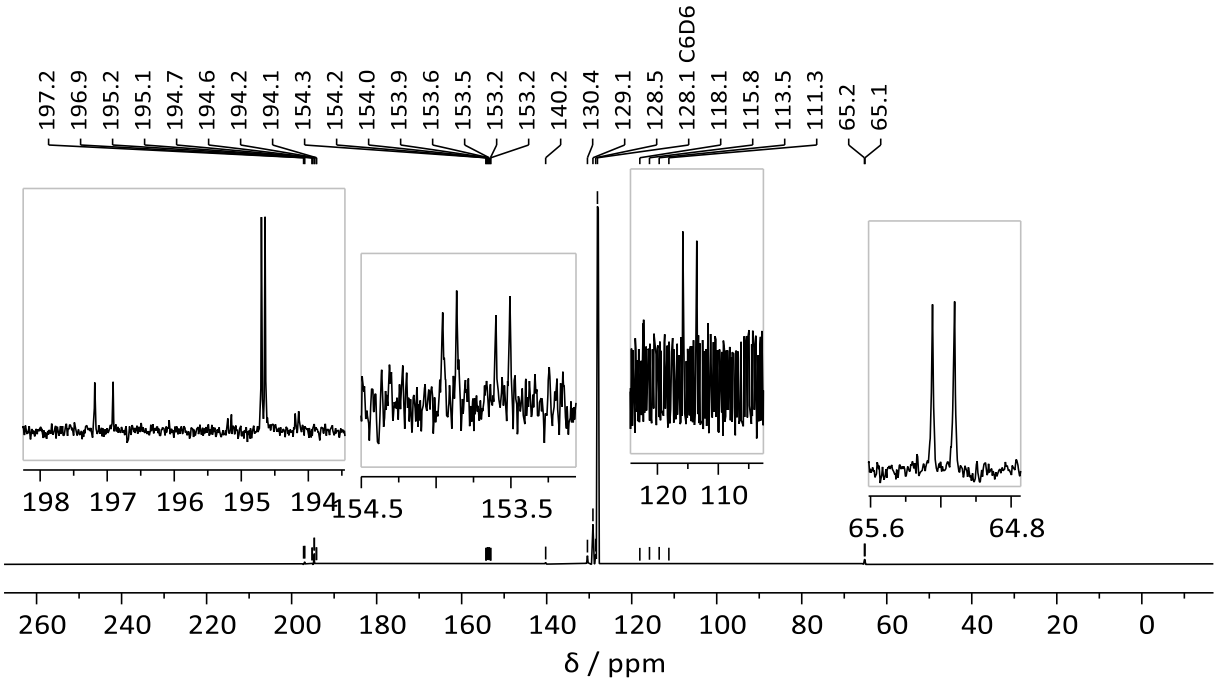


Fig. S15 $^{13}C\{^{1}H\}$ NMR spectrum (125.52 MHz, C_6D_6, 298 K) of compound **10a**.

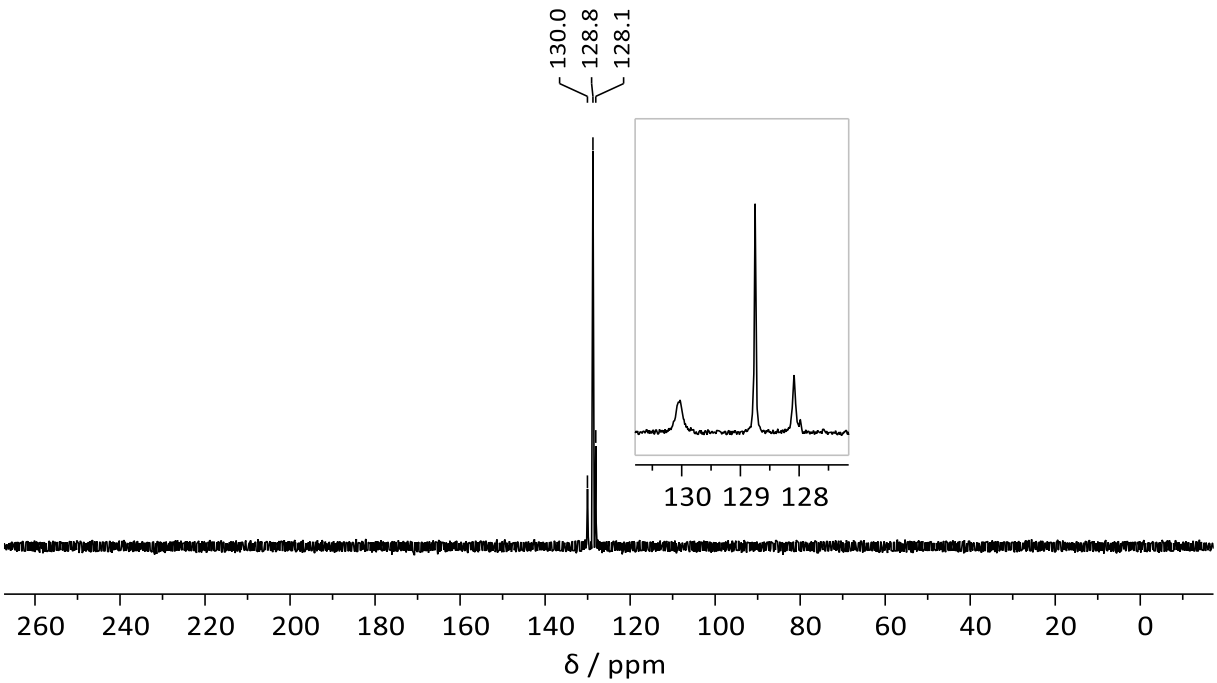


Fig. S16 $^{13}C\{^{1}H\}$ DEPT90 NMR spectrum (125.52 MHz, C_6D_6, 298 K) of compound **10a**.

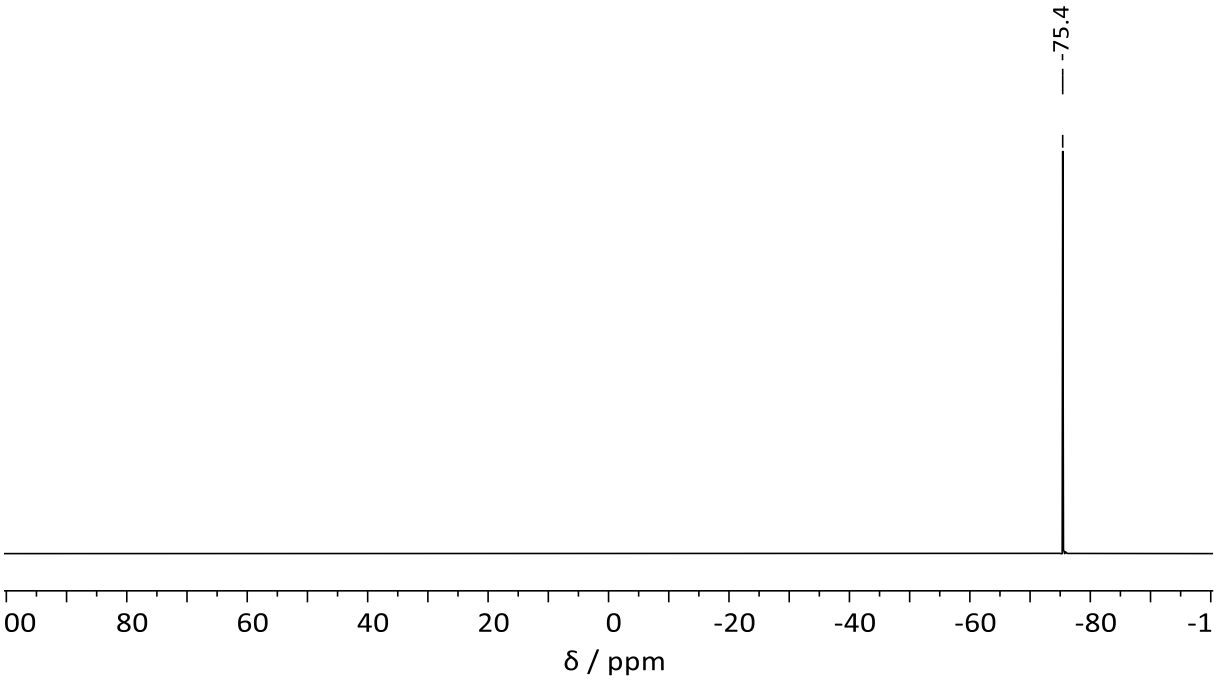


Fig. S17 $^{19}F\{^{1}H\}$ NMR spectrum (469.65 MHz, C_6D_6, 298 K) of compound **10a**.

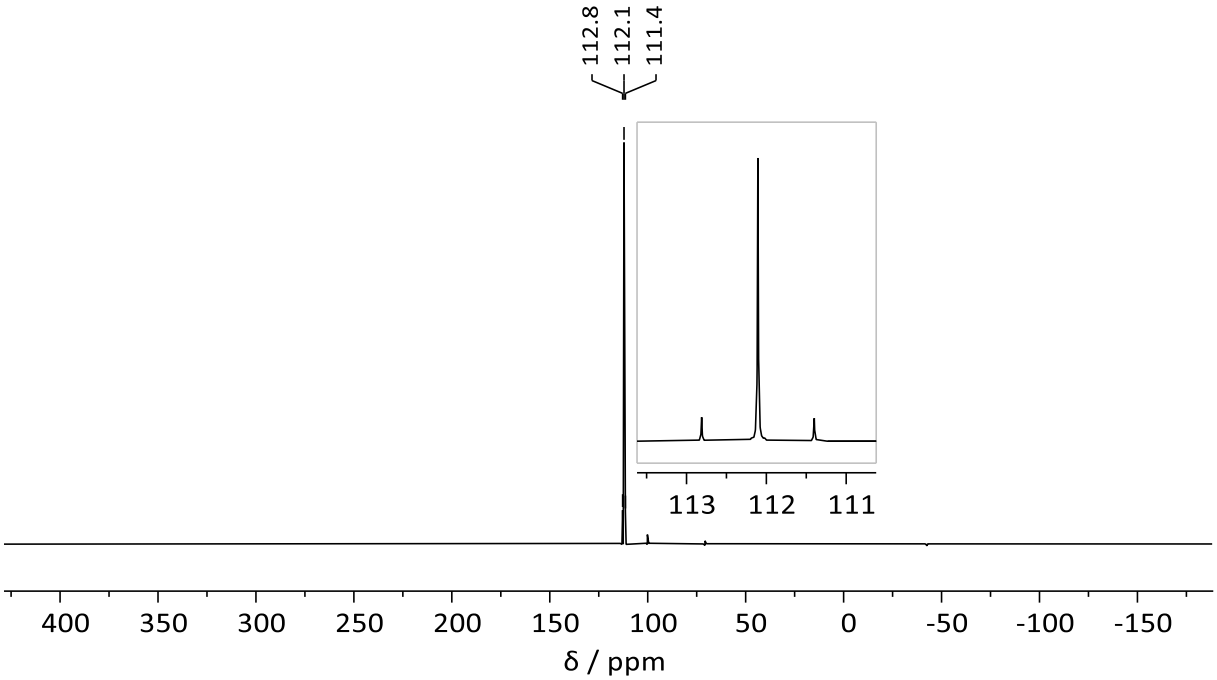


Fig. S18 $^{31}P\{^{1}H\}$ NMR spectrum (202.44 MHz, C_6D_6, 298 K) of compound **10a**.

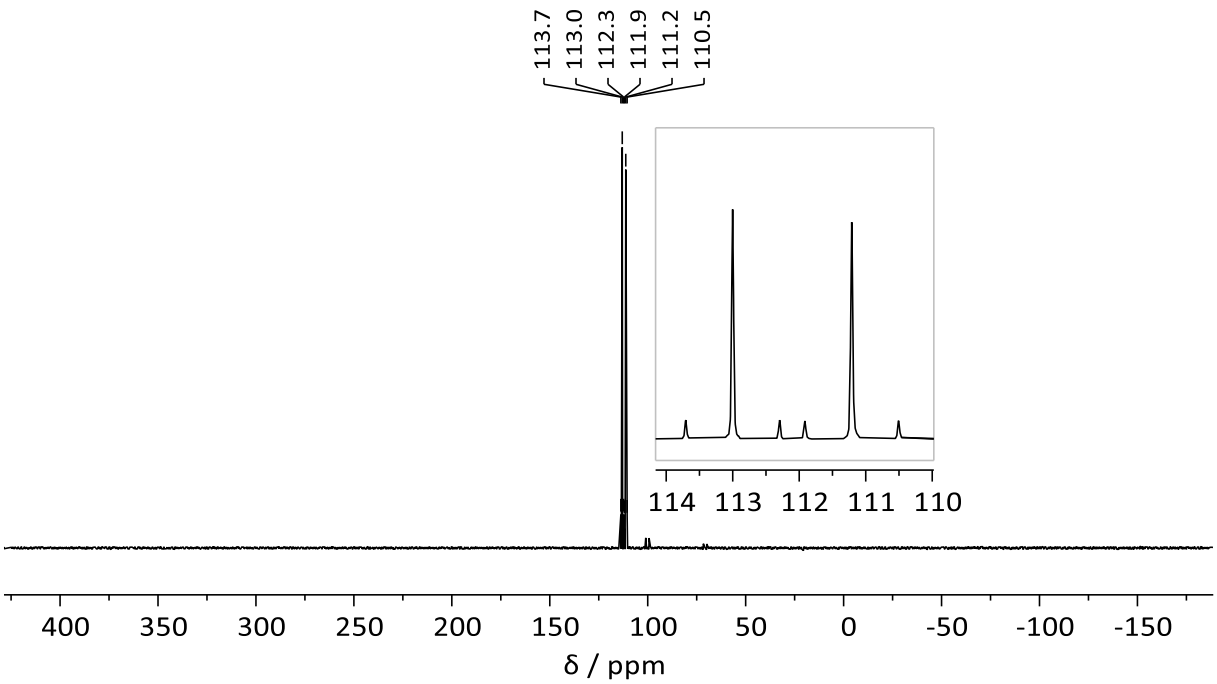


Fig. S19 ^{31}P NMR spectrum (202.44 MHz, C_6D_6, 298 K) of compound **10a**.

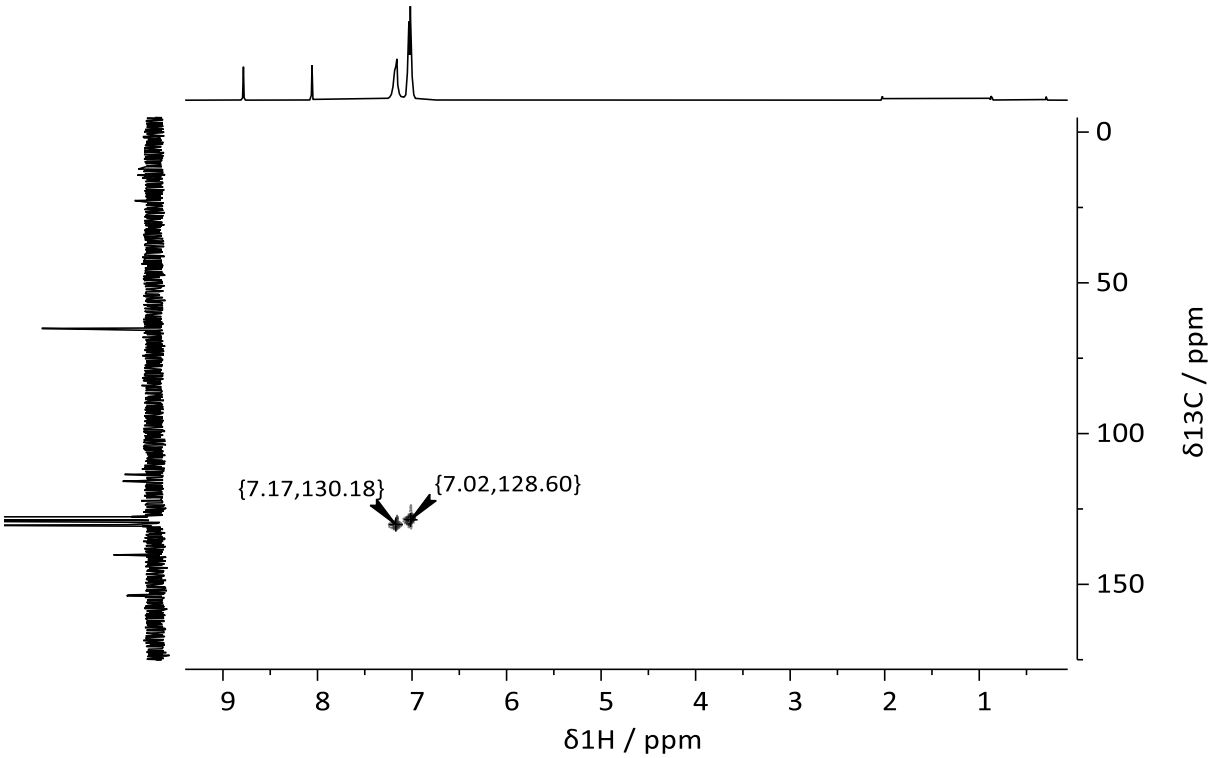


Fig. S20 ^{1}H,^{13}C HSQC NMR spectrum (499.13 MHz, 125.52 MHz, C_6D_6, 298 K) of compound **10a**.

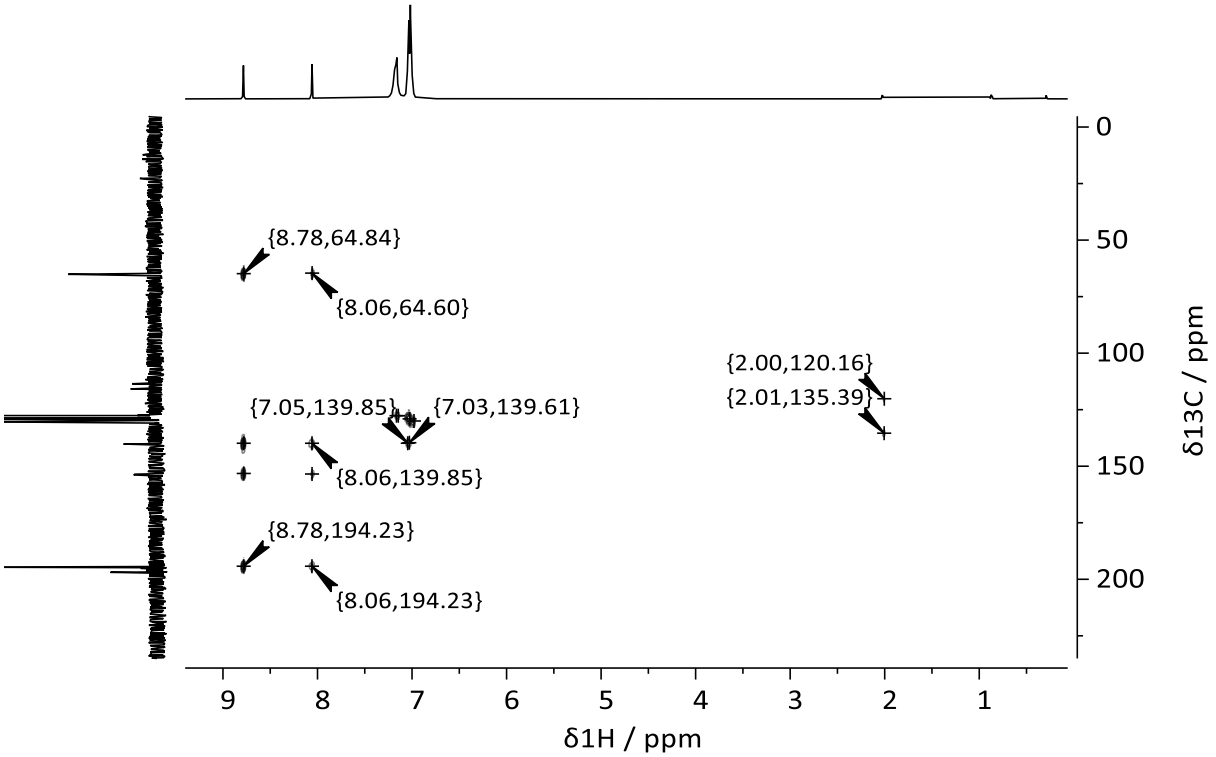


Fig. S21 $^{1}H,^{13}C$ HMBC NMR spectrum (499.13 MHz, 125.52 MHz, C_6D_6, 298 K) of compound **10a**.

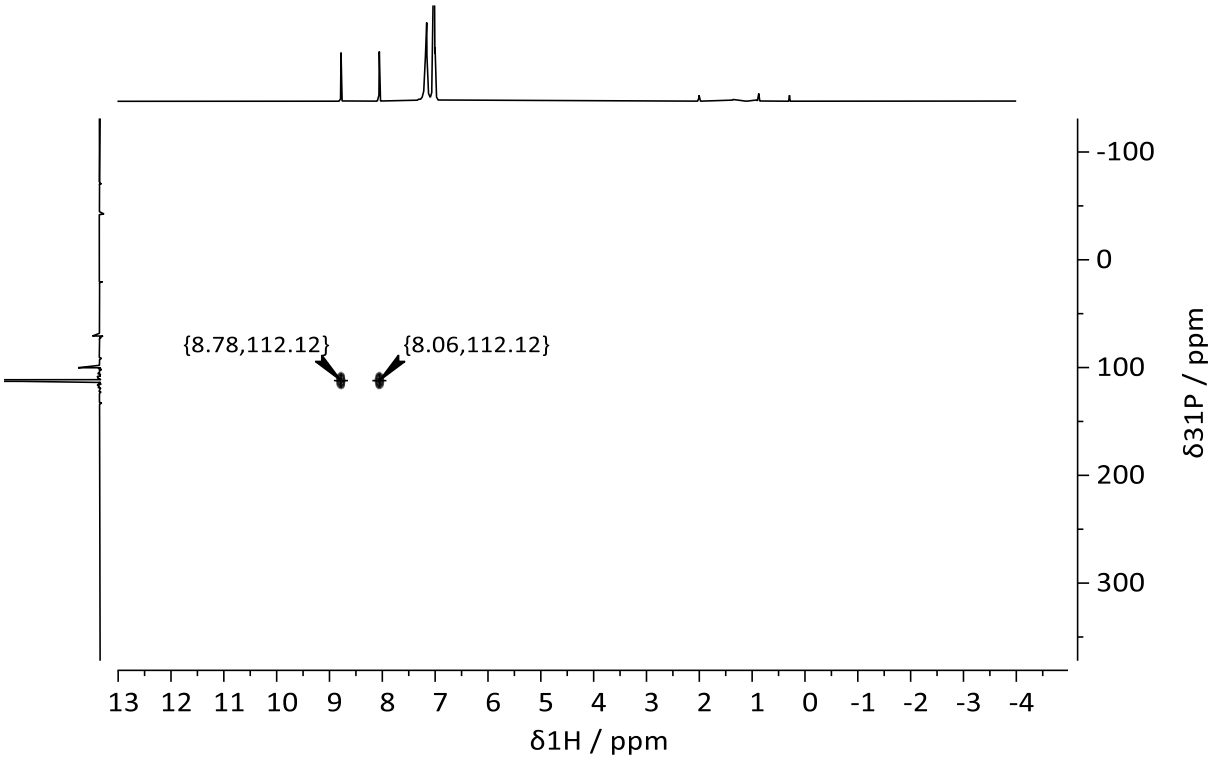


Fig. S22 $^{1}H,^{31}P$ HMBC NMR spectrum (500.04 MHz, 202.44 MHz, C_6D_6, 298 K) of compound **10a**.

Compound 10a-Cr

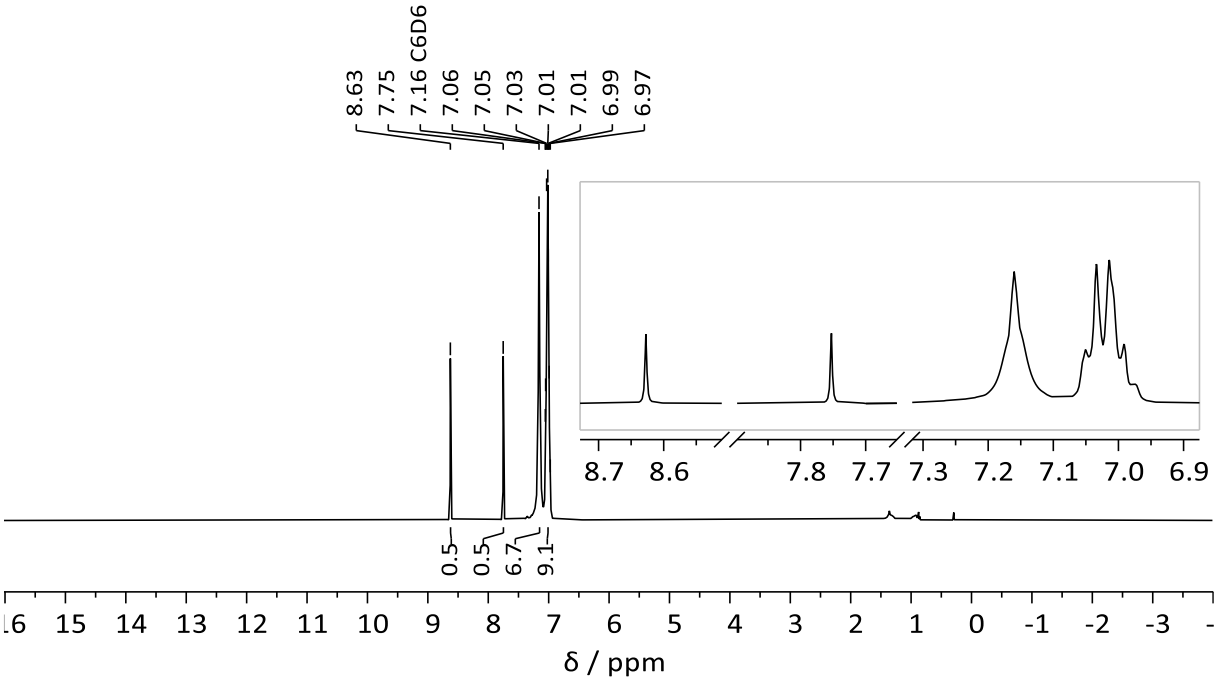


Fig. S23 ^{1}H NMR spectrum (400.13 MHz, C_6D_6, 298 K) of compound **10a-Cr**.

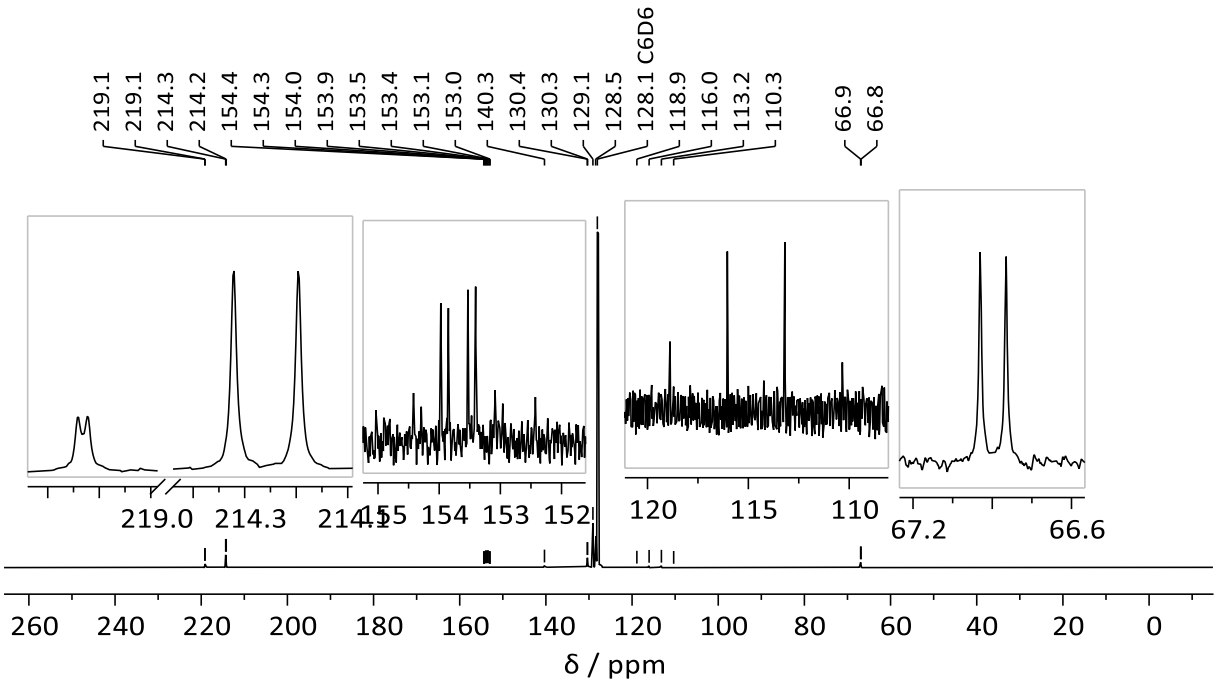


Fig. S24 $^{13}C\{^{1}H\}$ NMR spectrum (100.63 MHz, C_6D_6, 298 K) of compound **10a-Cr**.

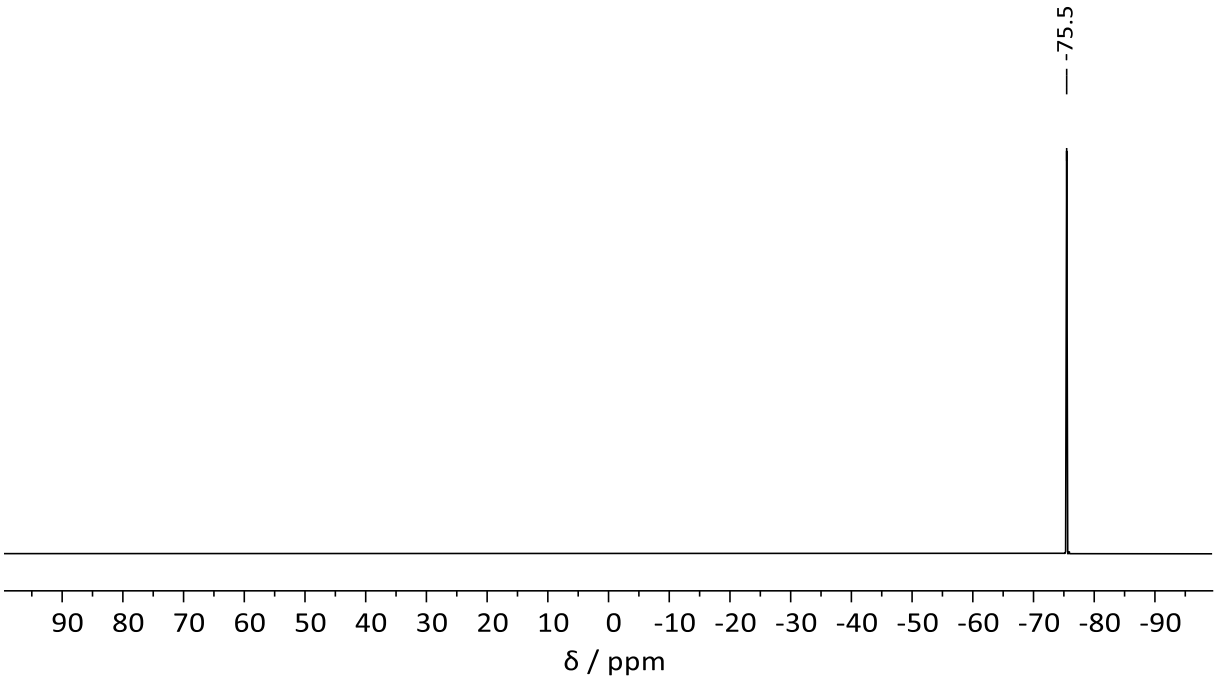


Fig. S25 ^{19}F NMR spectrum (470.51 MHz, C_6D_6, 298 K) of compound **10a-Cr**.

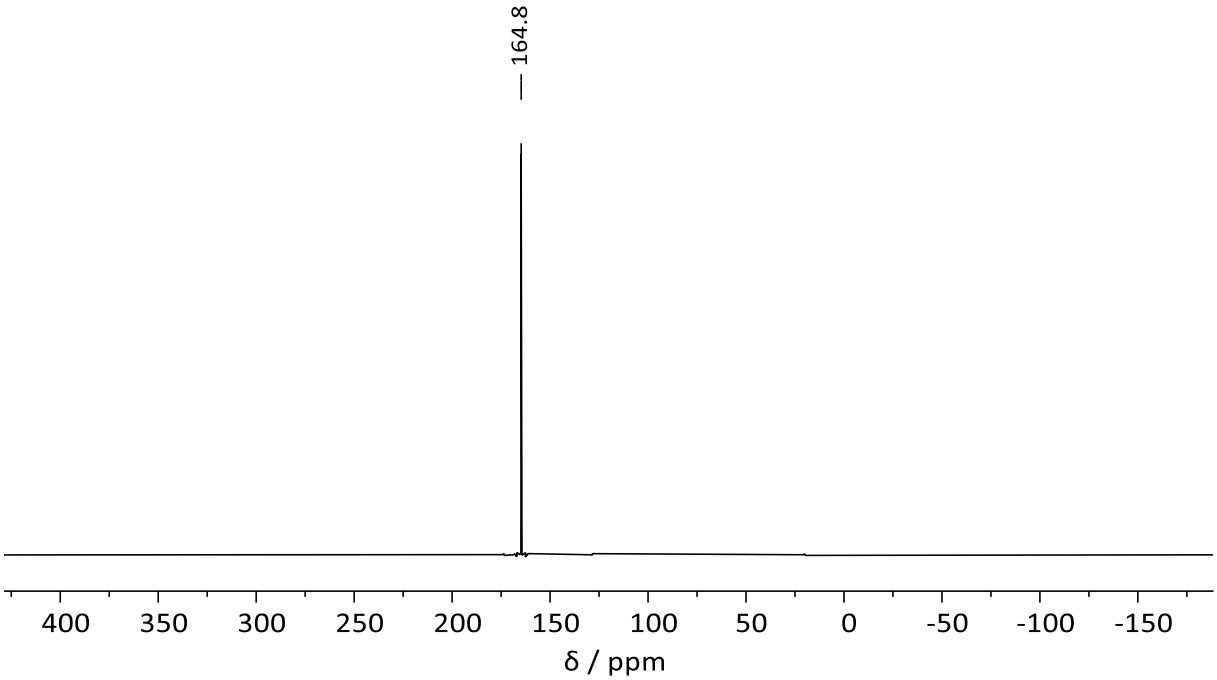


Fig. S26 $^{31}P\{^1H\}$ NMR spectrum (162.00 MHz, C_6D_6, 298 K) of compound **10a-Cr**.

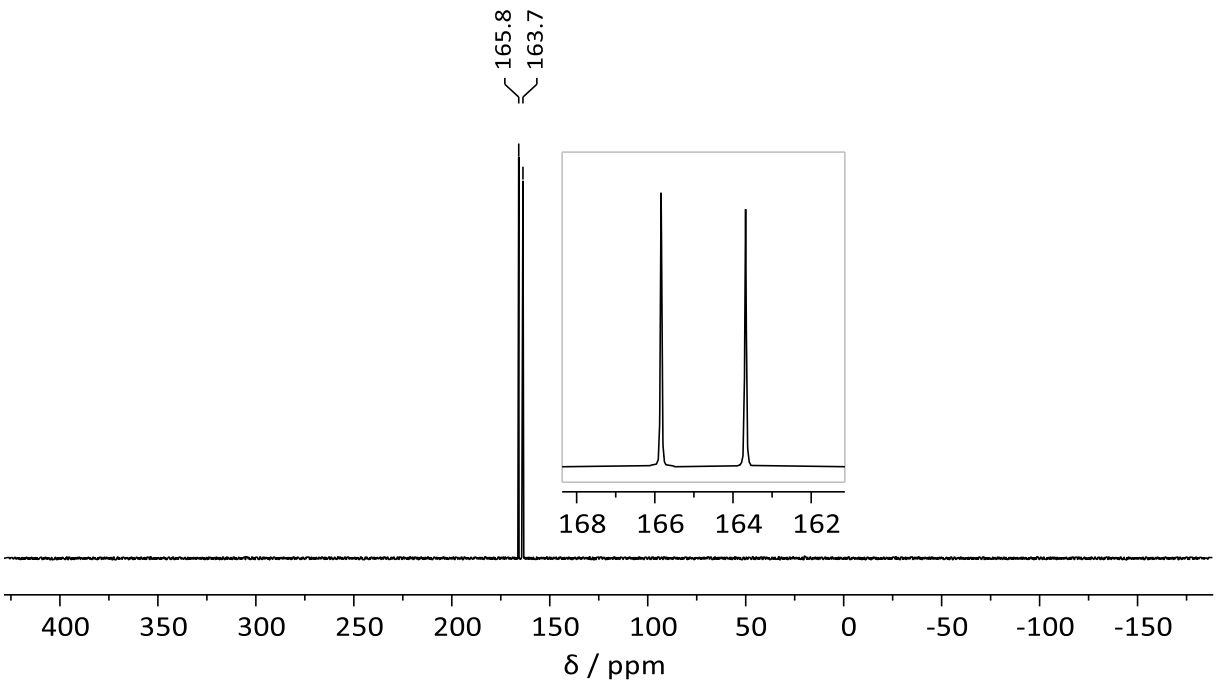


Fig. S27 ^{31}P NMR spectrum (162.00 MHz, C_6D_6, 298 K) of compound **10a-Cr**.

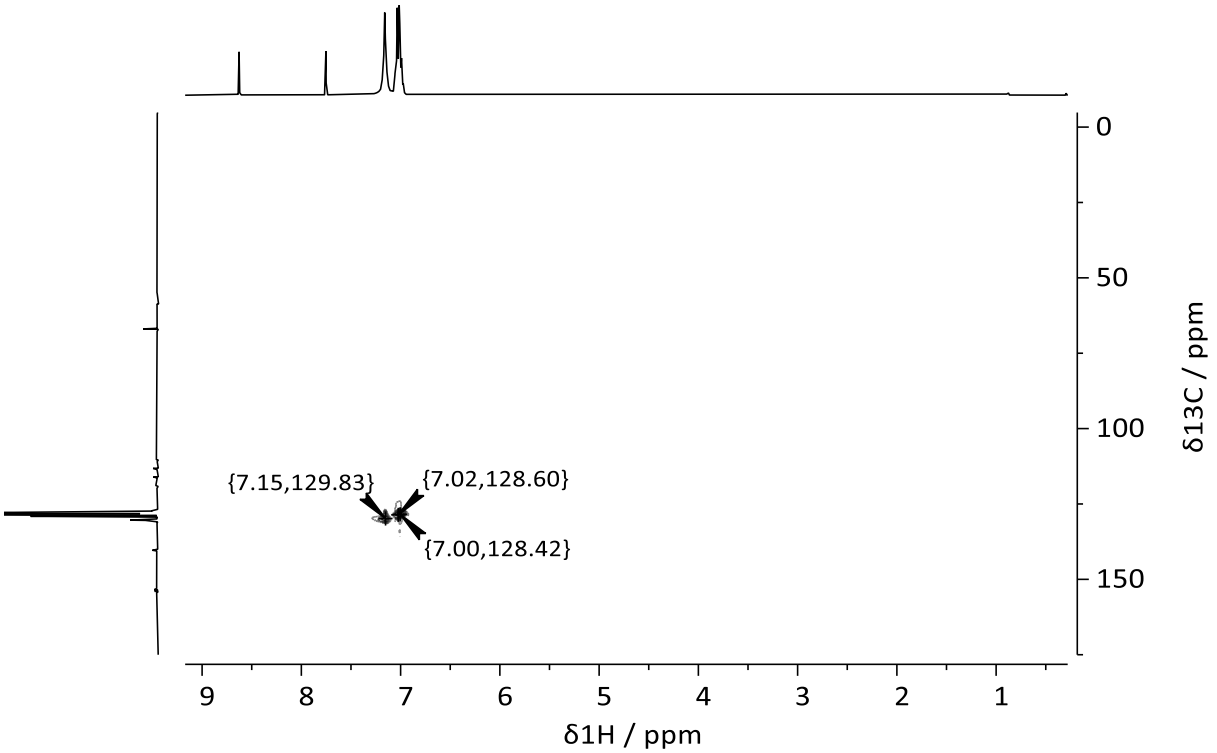


Fig. S28 ^{1}H,^{13}C HSQC NMR spectrum (400.13 MHz, 100.62 MHz, C_6D_6, 298 K) of compound **10a-Cr**.

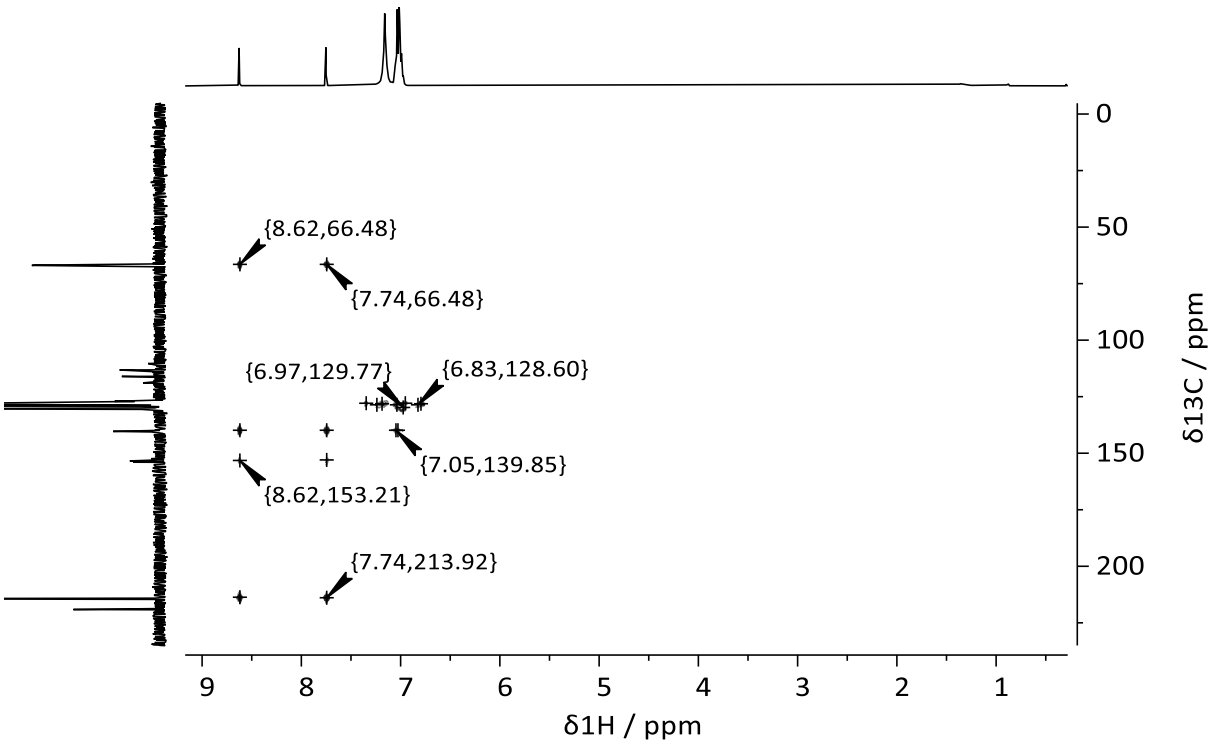


Fig. S29 $^{1}H,^{13}C$ HMBC NMR spectrum (400.13 MHz, 100.62 MHz, C_6D_6, 298 K) of compound **10a-Cr**.

Compound 10b

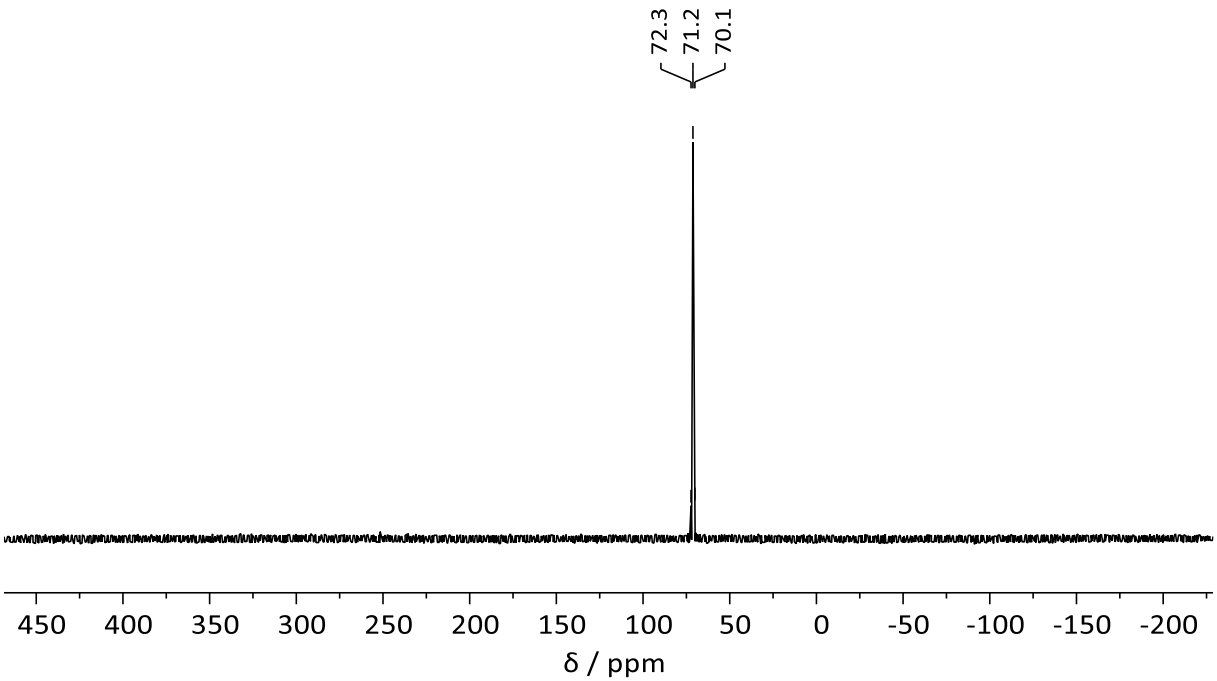


Fig. S30 $^{31}P\{^{1}H\}$ NMR spectrum (121.51 MHz, CH_2Cl_2, 298 K) of compound **10b**.

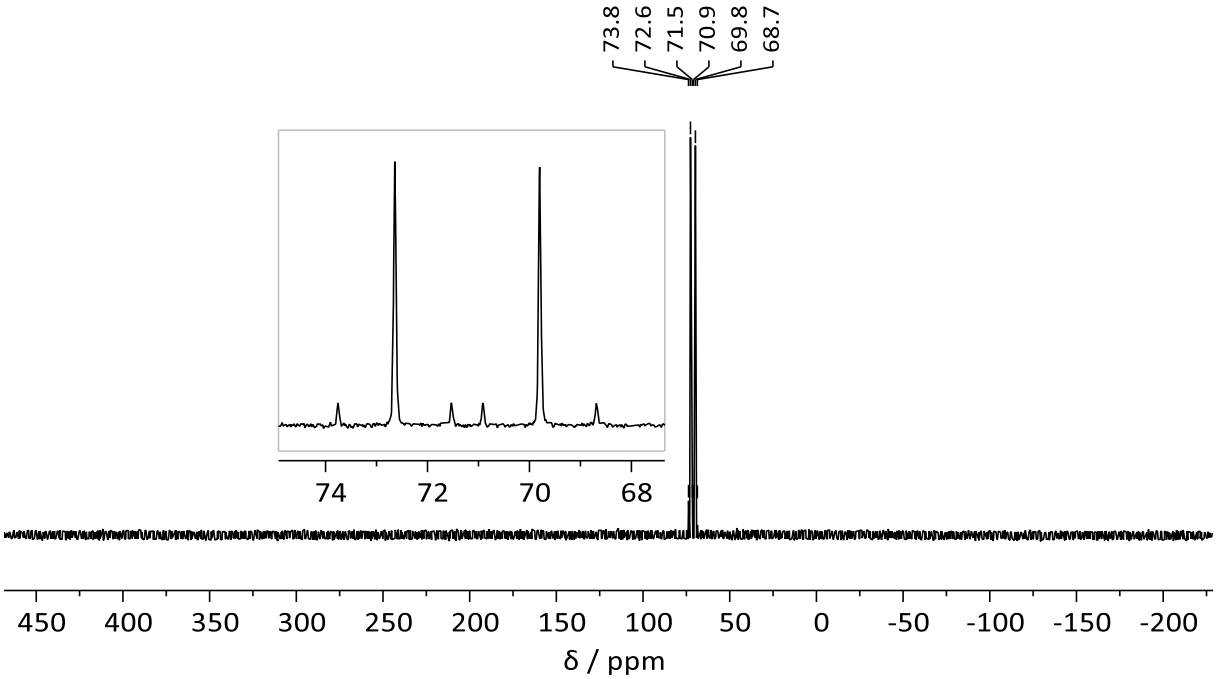


Fig. S31 ^{31}P NMR spectrum (121.51 MHz, CH_2Cl_2, 298 K) of compound **10b**.

Compound 11a

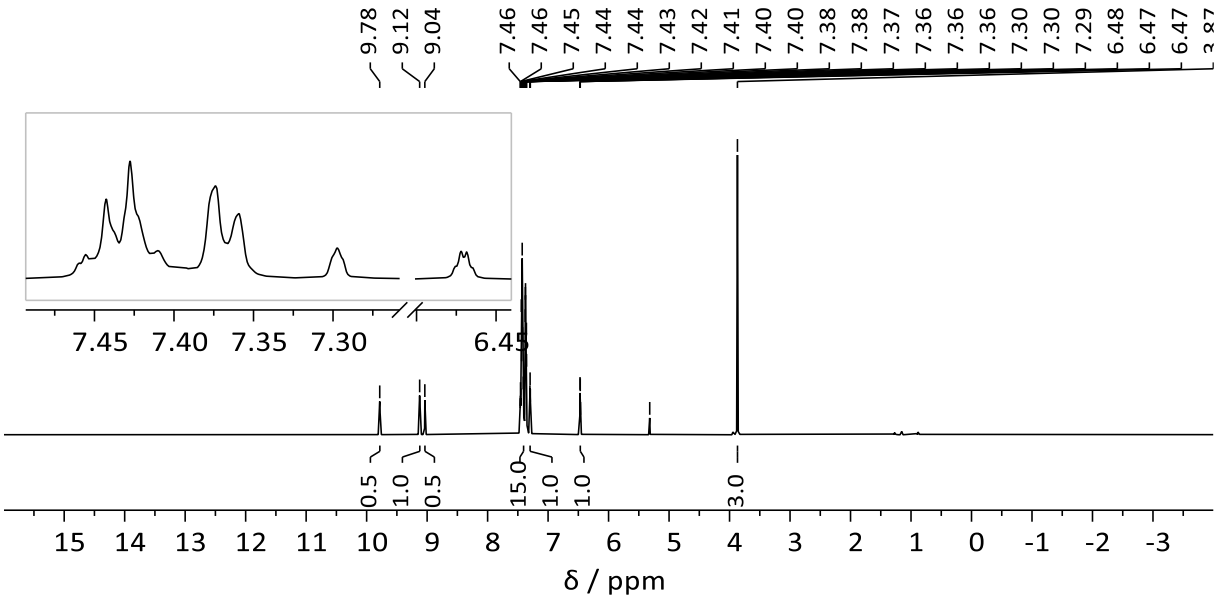


Fig. S32 ^{1}H NMR spectrum (500.04 MHz, CD_2Cl_2, 298 K) of compound **11a**.

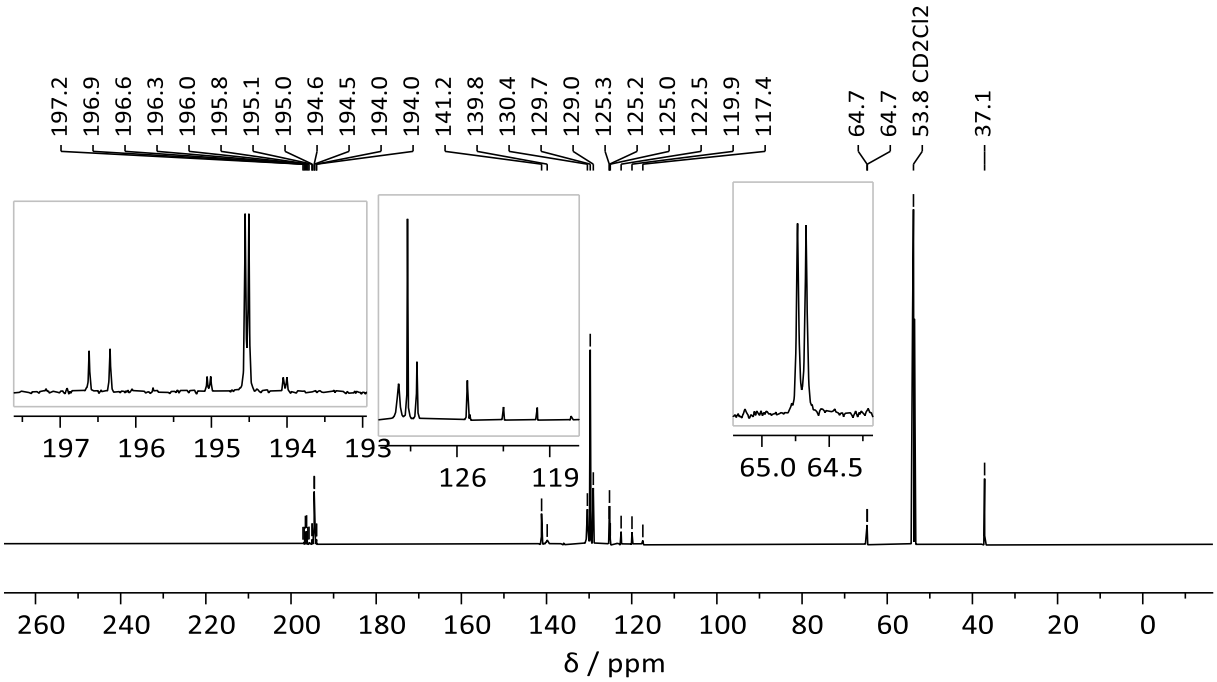


Fig. S33 $^{13}C\{^{1}H\}$ NMR spectrum (125.75 MHz, CD_2Cl_2, 298 K) of compound **11a**.

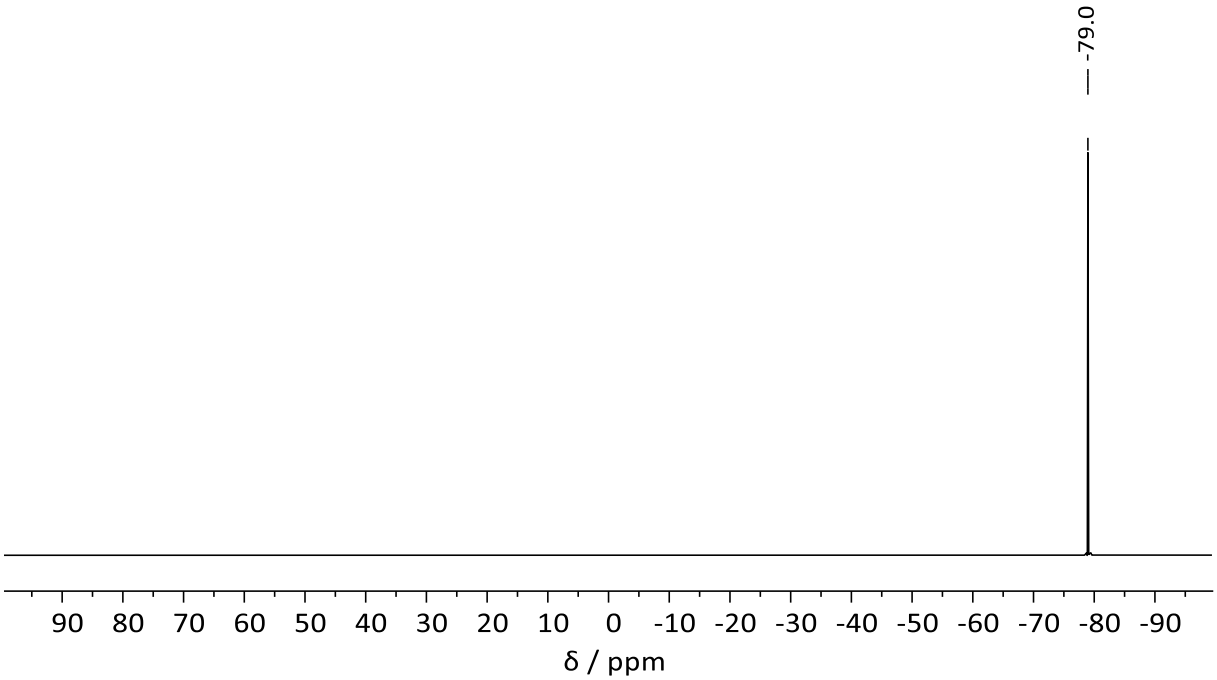


Fig. S34 ^{19}F NMR spectrum (470.51 MHz, CD_2Cl_2, 298 K) of compound **11a**.

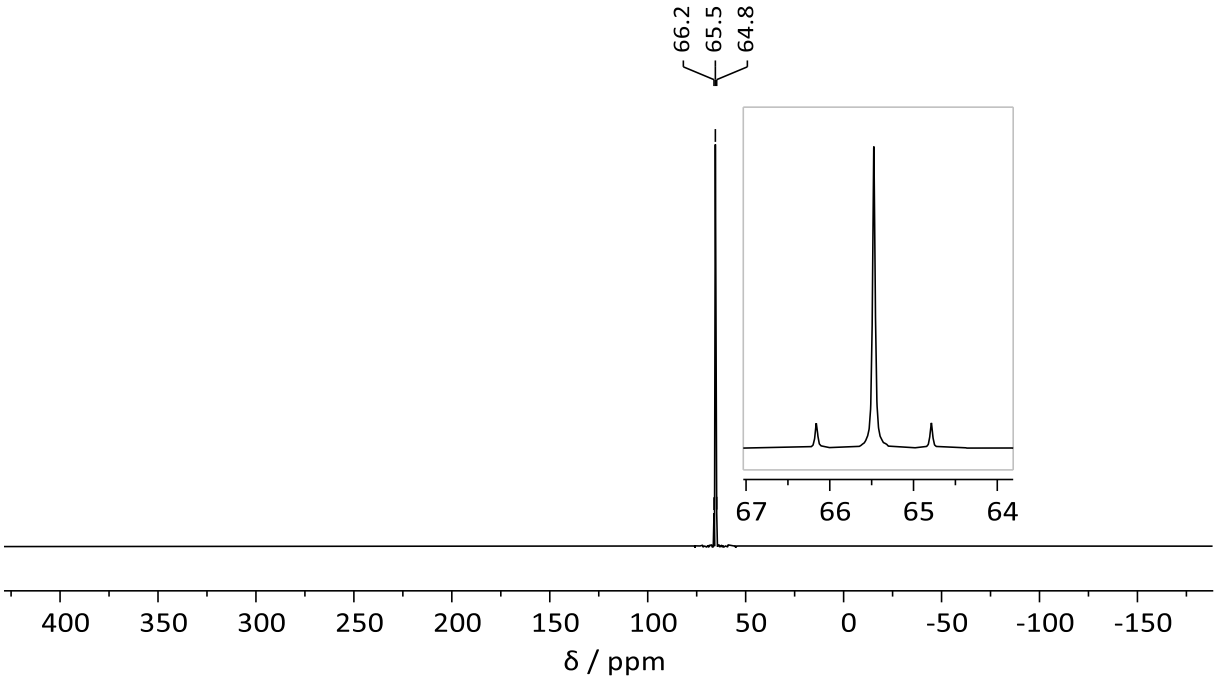


Fig. S35 $^{31}P\{^{1}H\}$ NMR spectrum (202.44 MHz, CD_2Cl_2, 298 K) of compound **11a**.

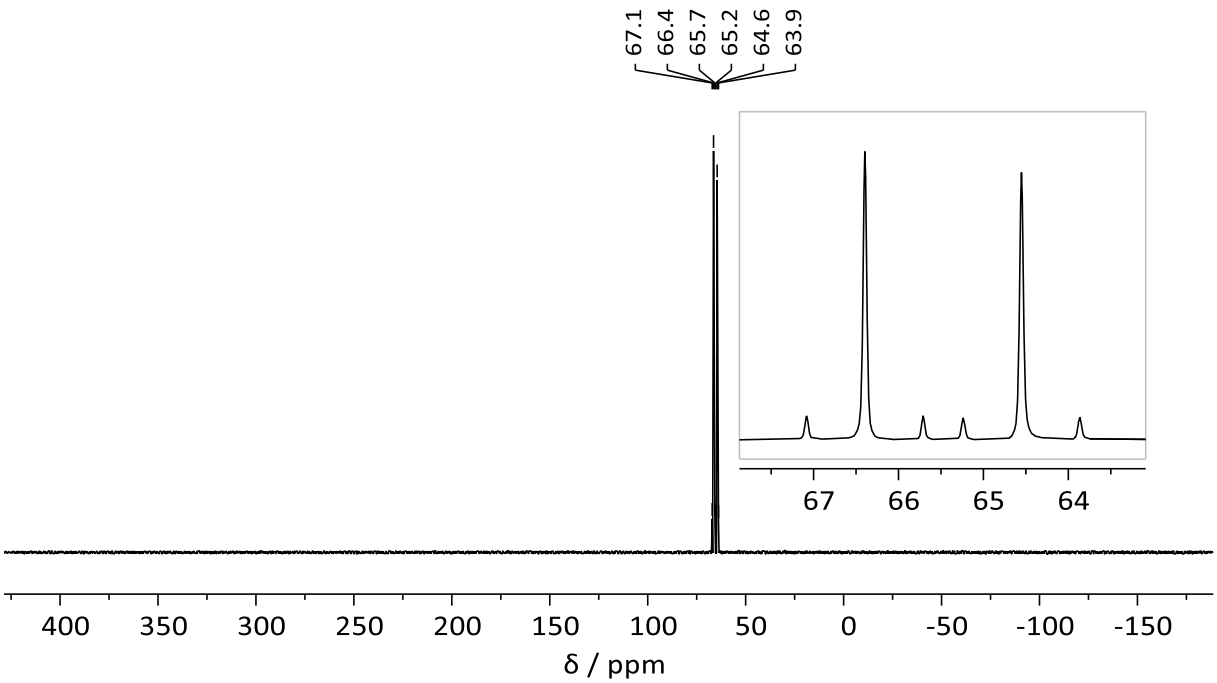


Fig. S36 ^{31}P NMR spectrum (202.44 MHz, CD_2Cl_2, 298 K) of compound **11a**.

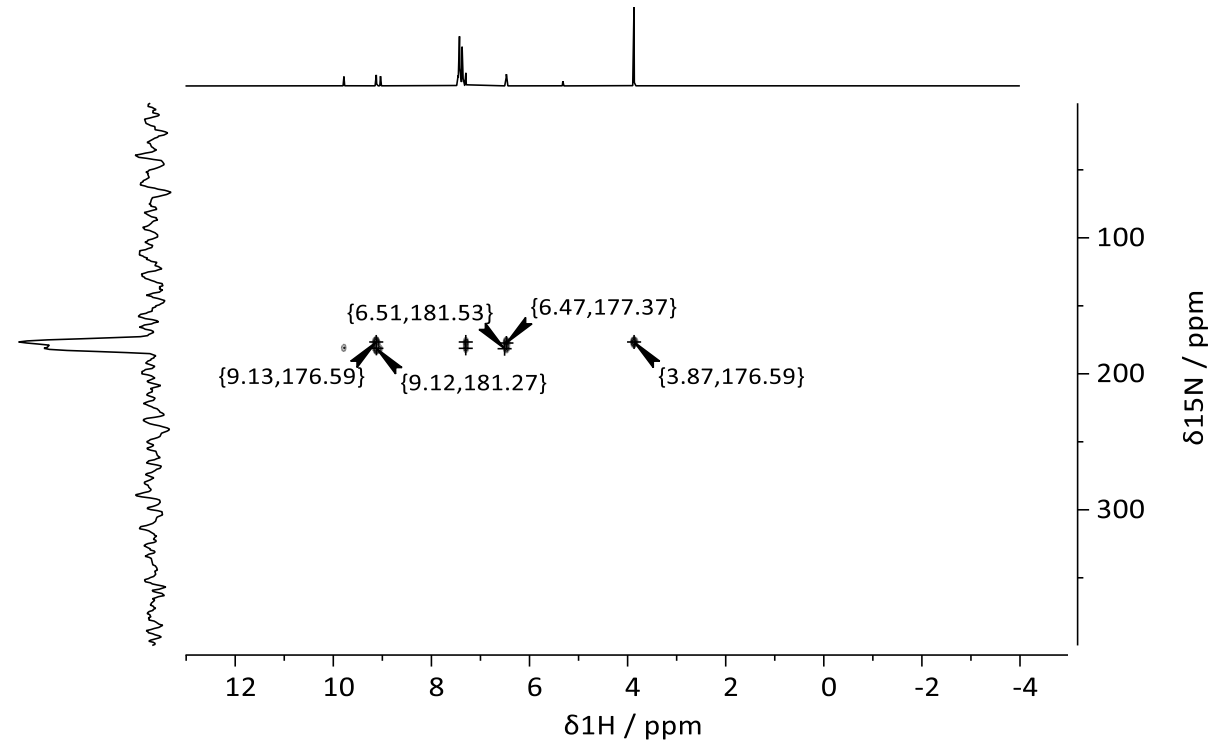


Fig. S37 $^{1}H,^{15}N$ HMBC NMR spectrum (500.04 MHz, 50.68 MHz, CD_2Cl_2, 298 K) of compound **11a**.

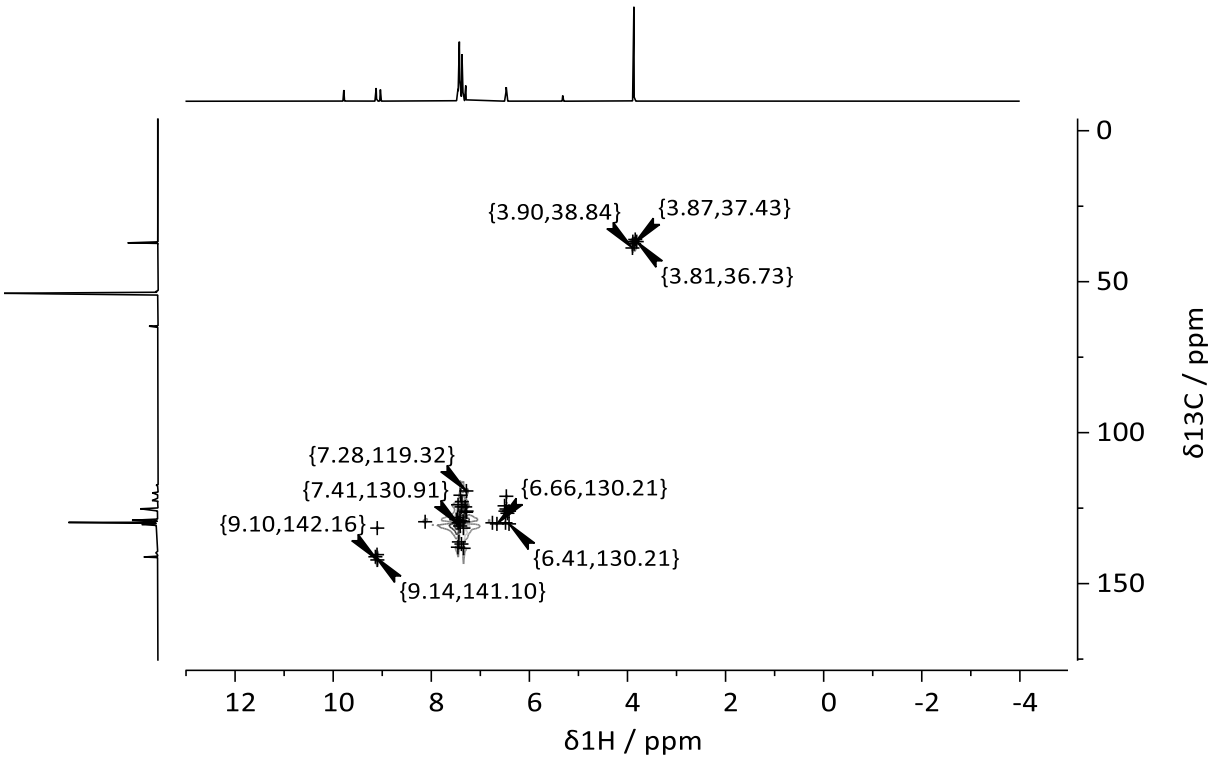


Fig. S38 $^{1}H,^{13}C$ HSQC NMR spectrum (500.04 MHz, 125.75 MHz, CD_2Cl_2, 298 K) of compound **11a**.

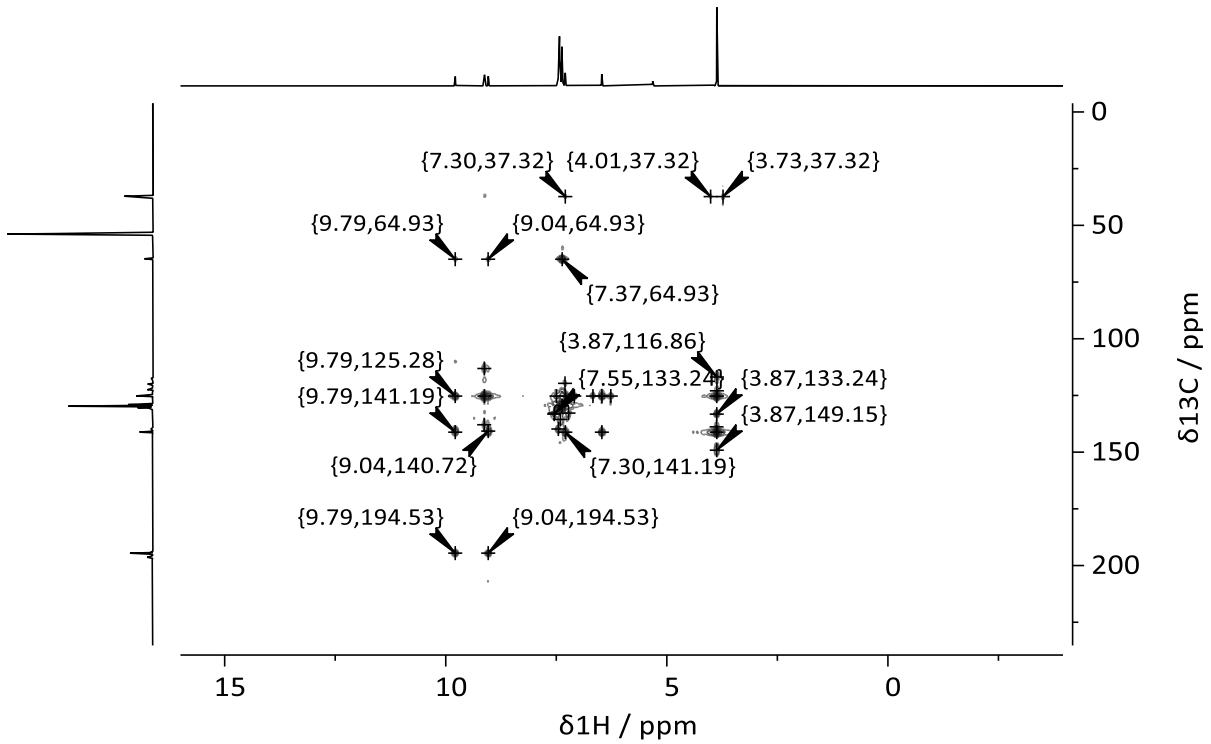


Fig. S39 $^{1}H,^{13}C$ HMBC NMR spectrum (500.04 MHz, 125.75 MHz, CD_2Cl_2, 298 K) of compound **11a**.

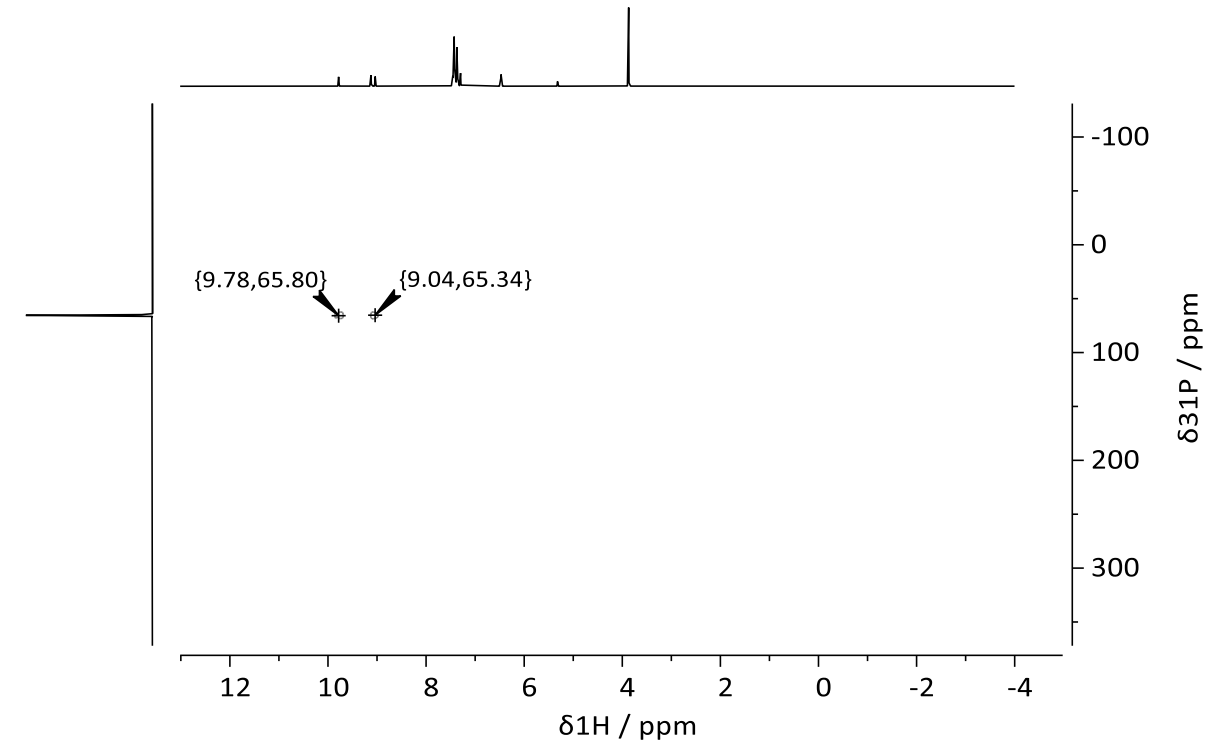


Fig. S40 $^{1}H,^{31}P$ HMQC NMR spectrum (500.04 MHz, 202.44 MHz, CD_2Cl_2, 298 K) of compound **11a**.

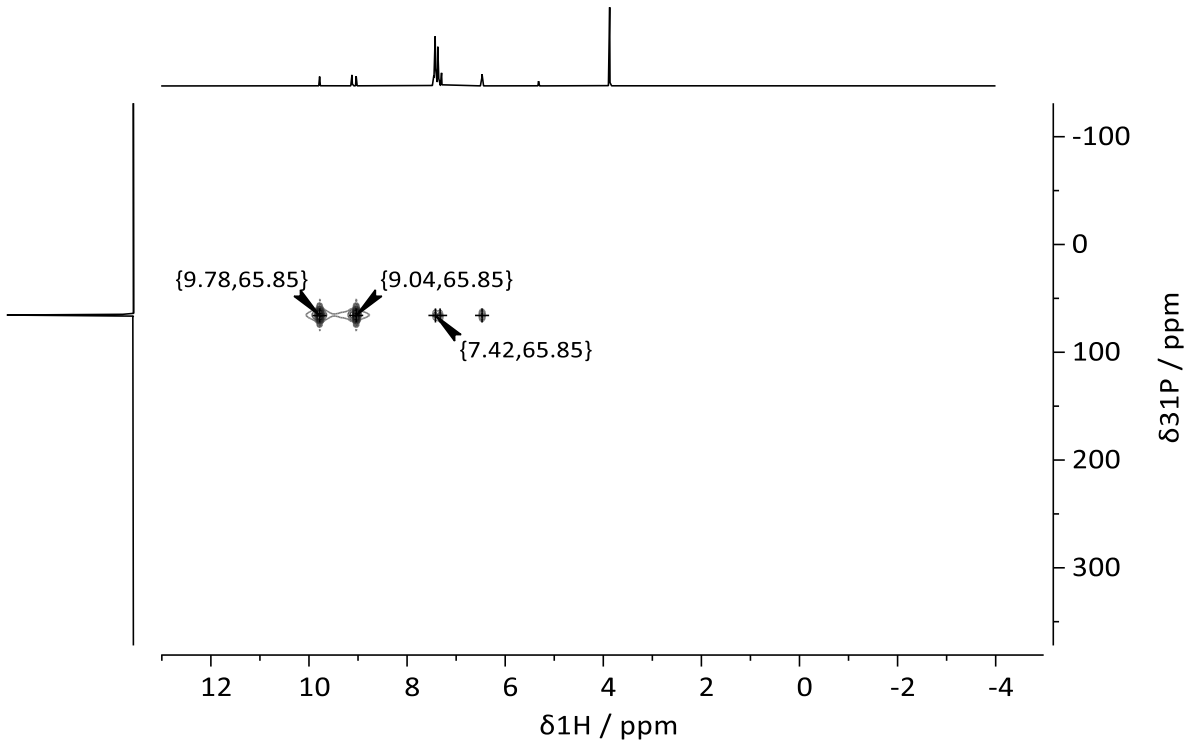


Fig. S41 $^{1}H,^{31}P$ HMBC NMR spectrum (500.04 MHz, 202.44 MHz, CD_2Cl_2, 298 K) of compound **11a**.

Compound 11a-Cr

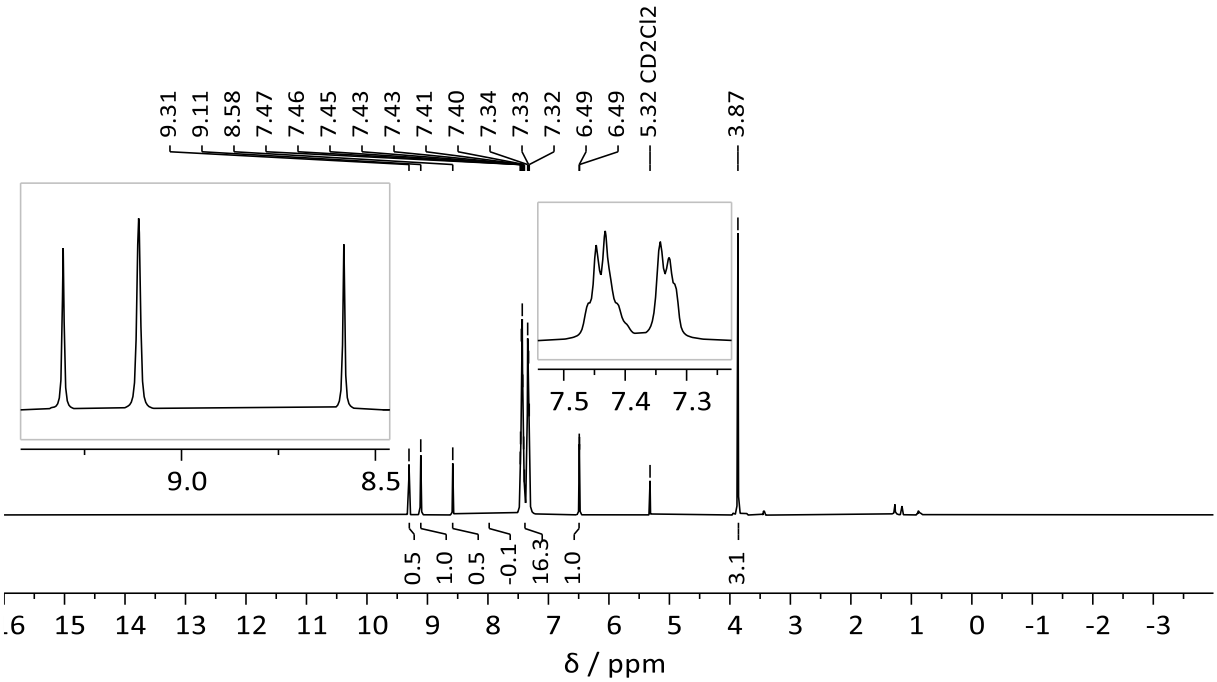


Fig. S42 ^{1}H NMR spectrum (500.04 MHz, CD_2Cl_2, 298 K) of compound **11a-Cr**.

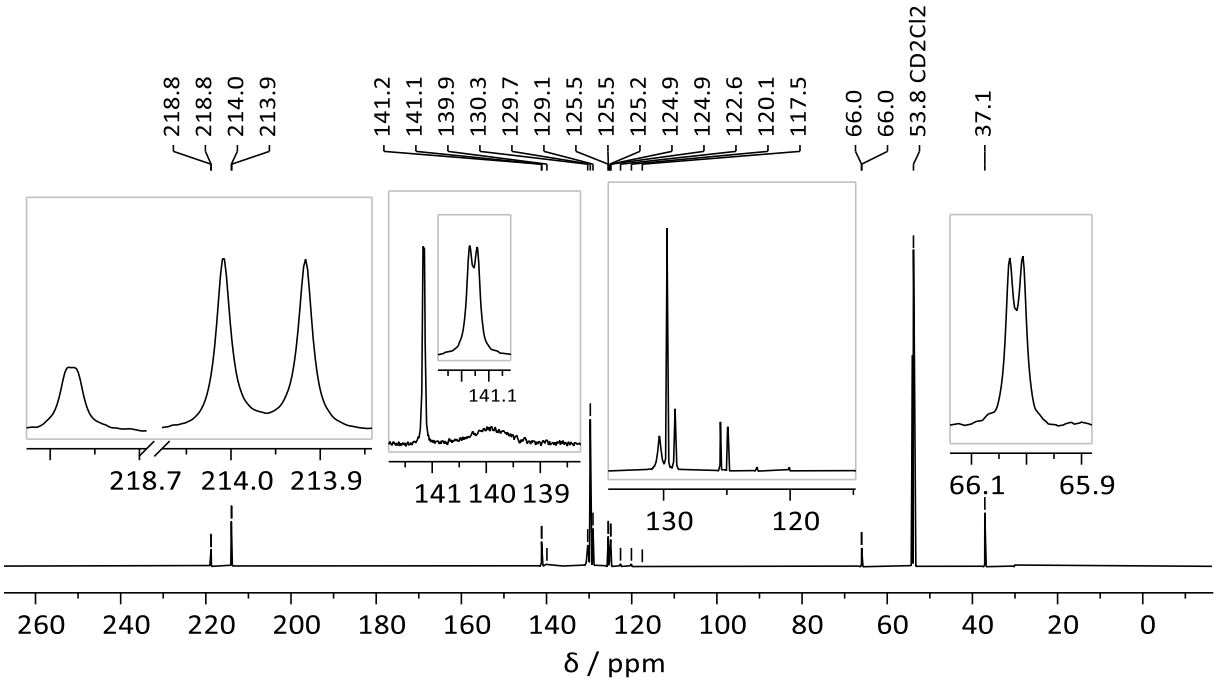


Fig. S43 $^{13}C\{^{1}H\}$ NMR spectrum (125.75 MHz, CD_2Cl_2, 298 K) of compound **11a-Cr**.

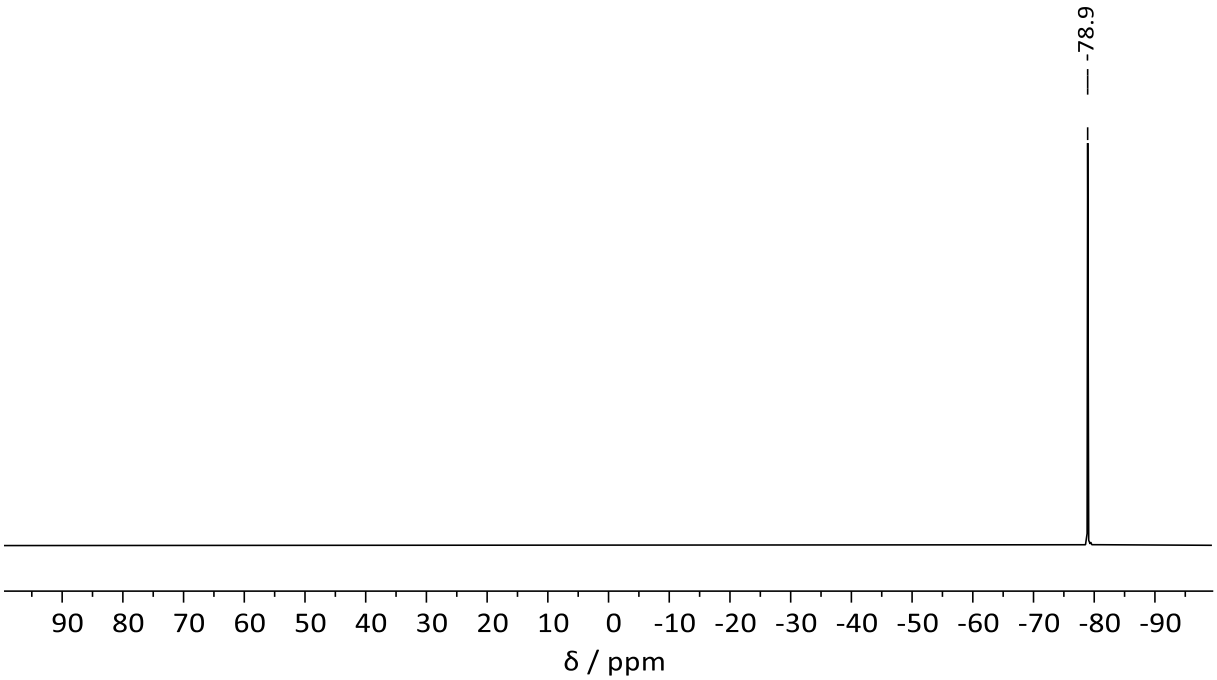


Fig. S44 ^{19}F NMR spectrum (470.51 MHz, CD_2Cl_2, 298 K) of compound **11a-Cr**.

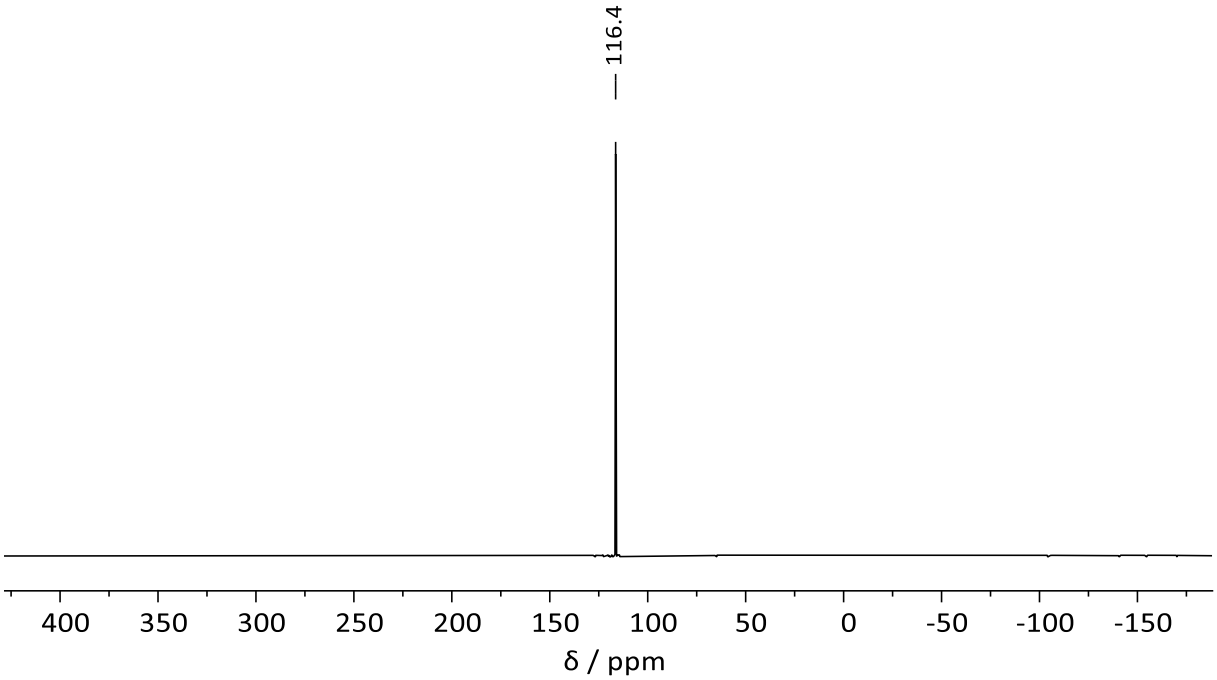


Fig. S45 $^{31}P\{^{1}H\}$ NMR spectrum (202.44 MHz, CD_2Cl_2, 298 K) of compound **11a-Cr**.

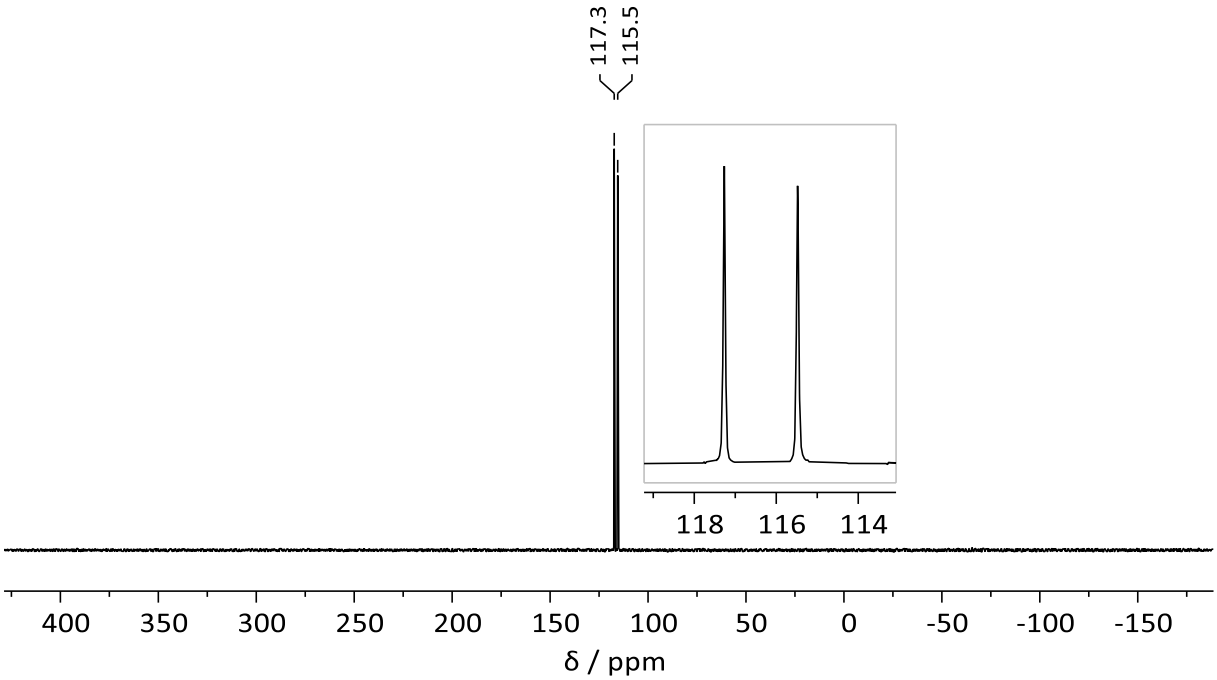


Fig. S46 ^{31}P NMR spectrum (202.44 MHz, CD_2Cl_2, 298 K) of compound **11a-Cr**.

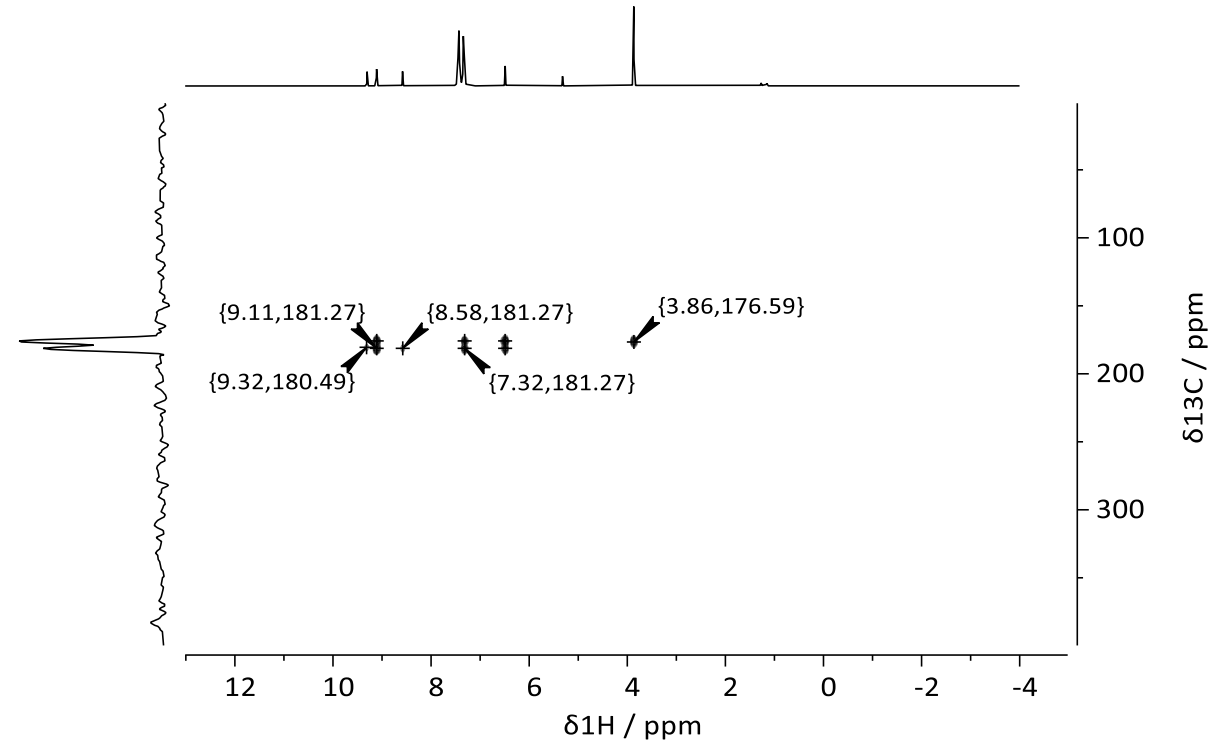


Fig. S47 $^{1}H,^{15}N$ HMBC NMR spectrum (500.04 MHz, 50.68 MHz, CD_2Cl_2, 298 K) of compound **11a-Cr**.

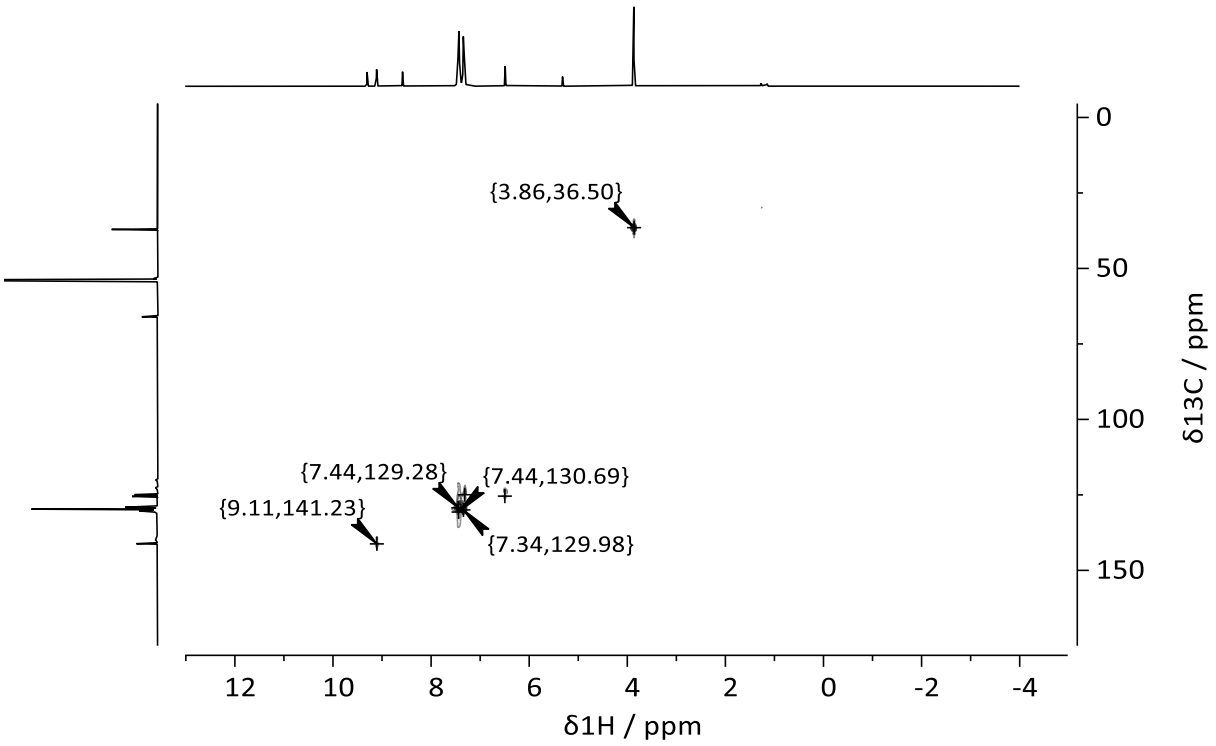


Fig. S48 $^{1}H,^{13}C$ HSQC NMR spectrum (500.04 MHz, 125.75 MHz, CD_2Cl_2, 298 K) of compound **11a-Cr**.

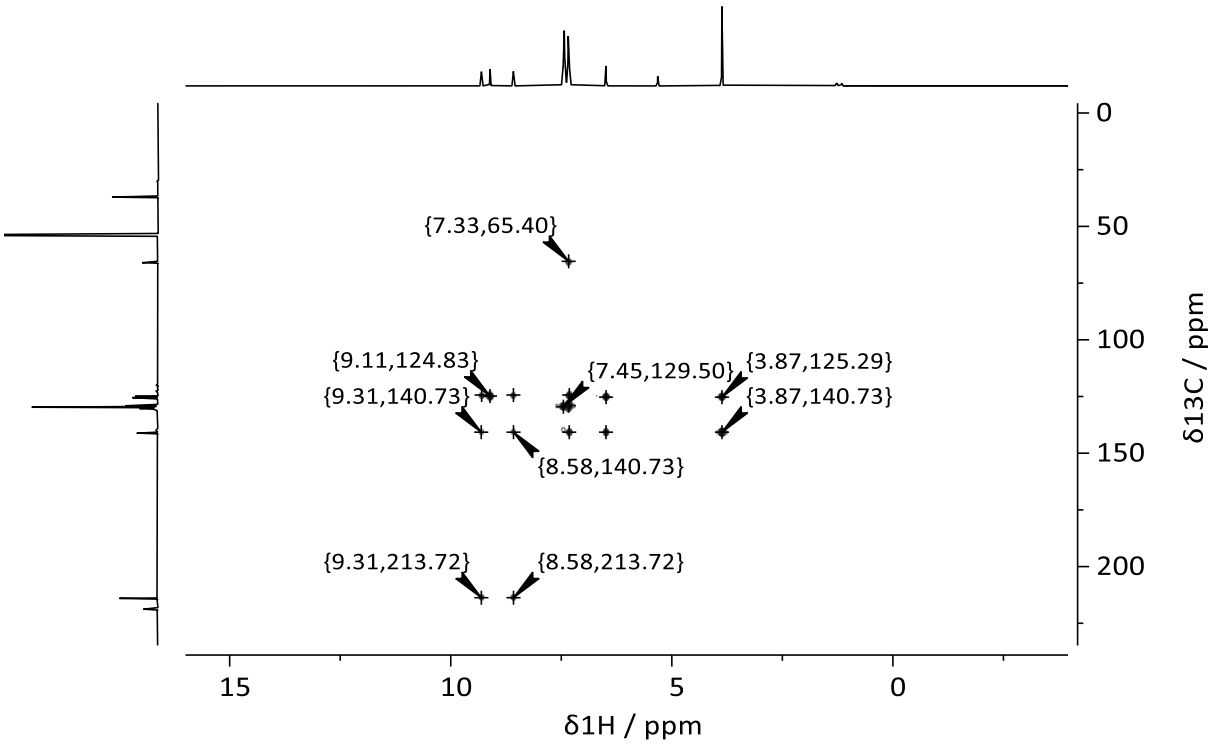


Fig. S49 $^{1}H,^{13}C$ HMBC NMR spectrum (500.04 MHz, 125.75 MHz, CD_2Cl_2, 298 K) of compound **11a-Cr**.

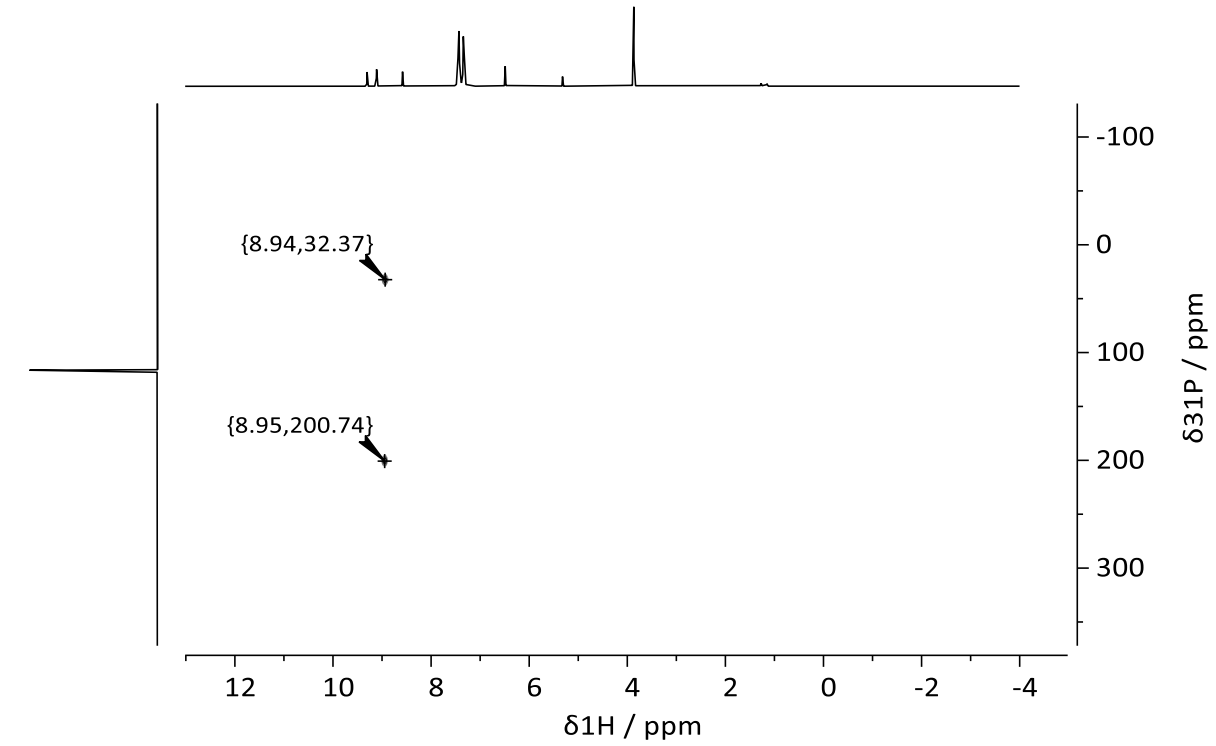


Fig. S50 $^{1}H,^{31}P$ HMQC NMR spectrum (500.04 MHz, 202.44 MHz, CD_2Cl_2, 298 K) of compound **11a-Cr**.

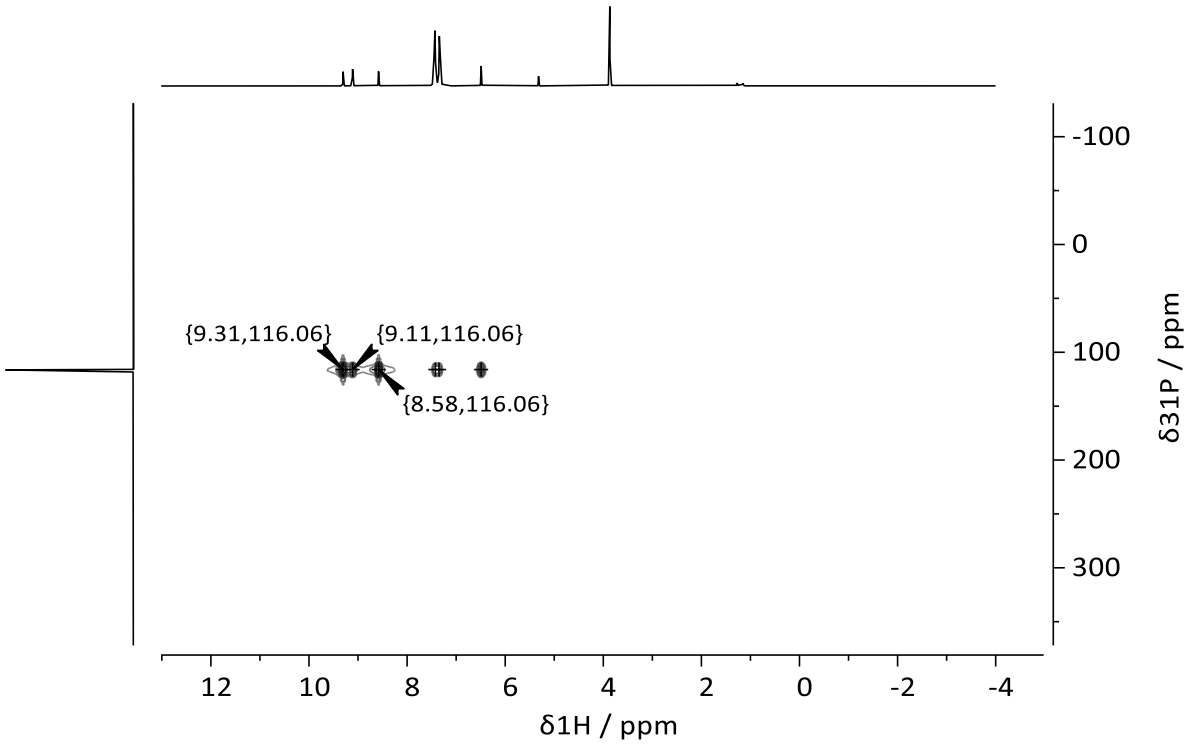


Fig. S51 $^{1}H,^{31}P$ HMBC NMR spectrum (500.04 MHz, 202.44 MHz, CD_2Cl_2, 298 K) of compound **11a-Cr**.

Compound 11b

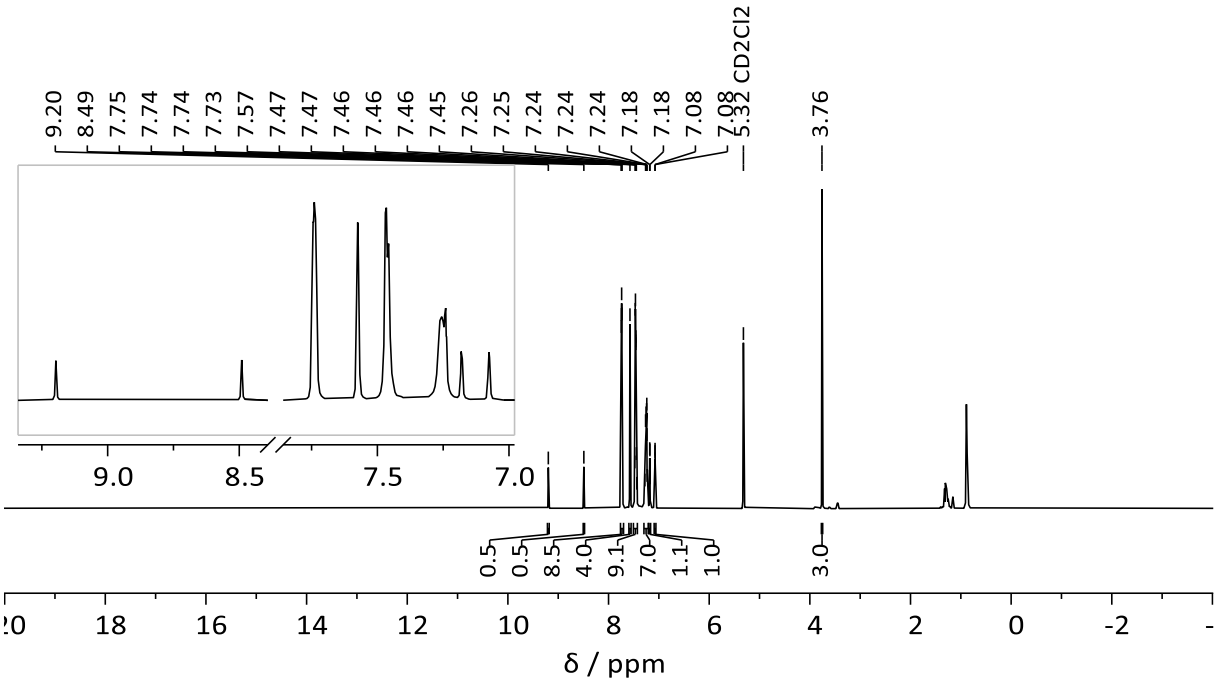


Fig. S52 ^{1}H NMR spectrum (500.04 MHz, CD_2Cl_2, 298 K) of compound **11b**.

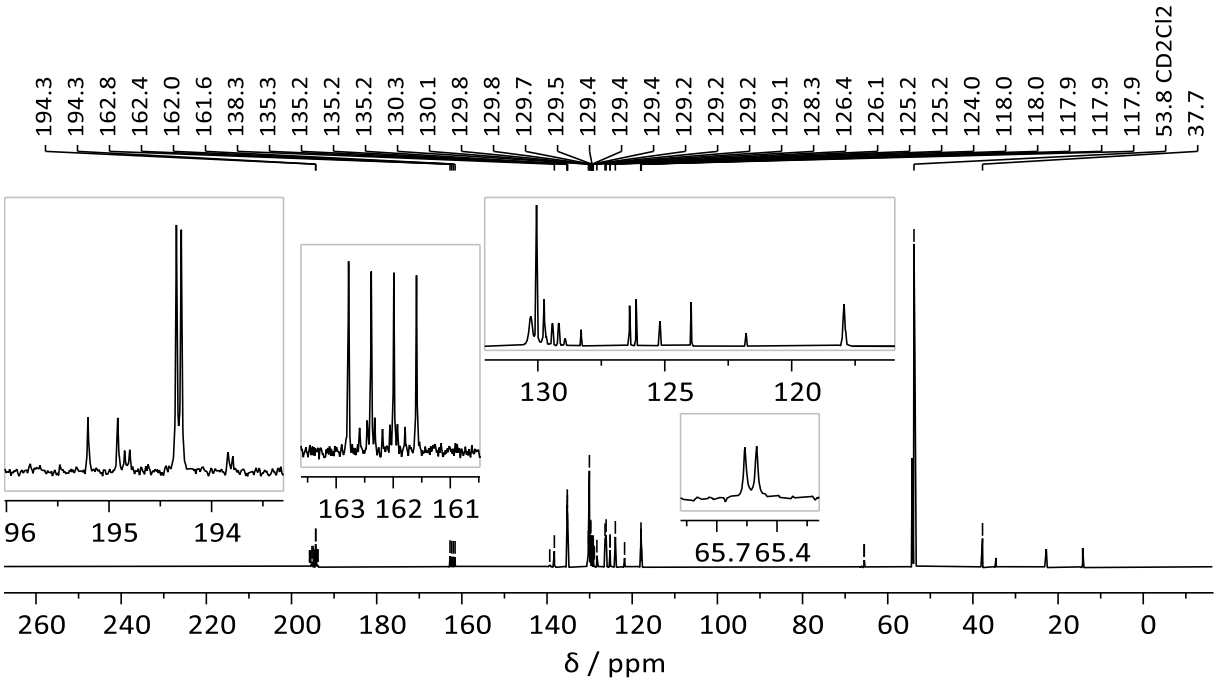


Fig. S53 $^{13}C\{^{1}H\}$ NMR spectrum (125.75 MHz, CD_2Cl_2, 298 K) of compound **11b**.

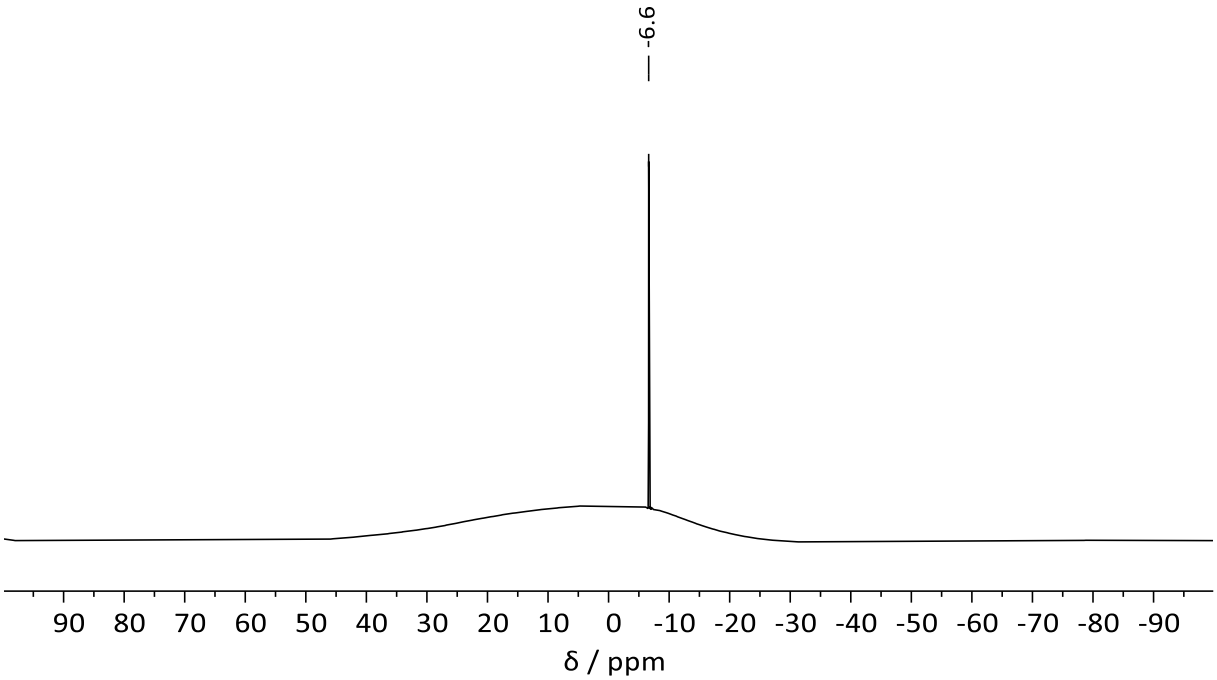


Fig. S54 $^{11}B\{^{1}H\}$ NMR spectrum (160.43 MHz, CD_2Cl_2, 298 K) of compound **11b**.

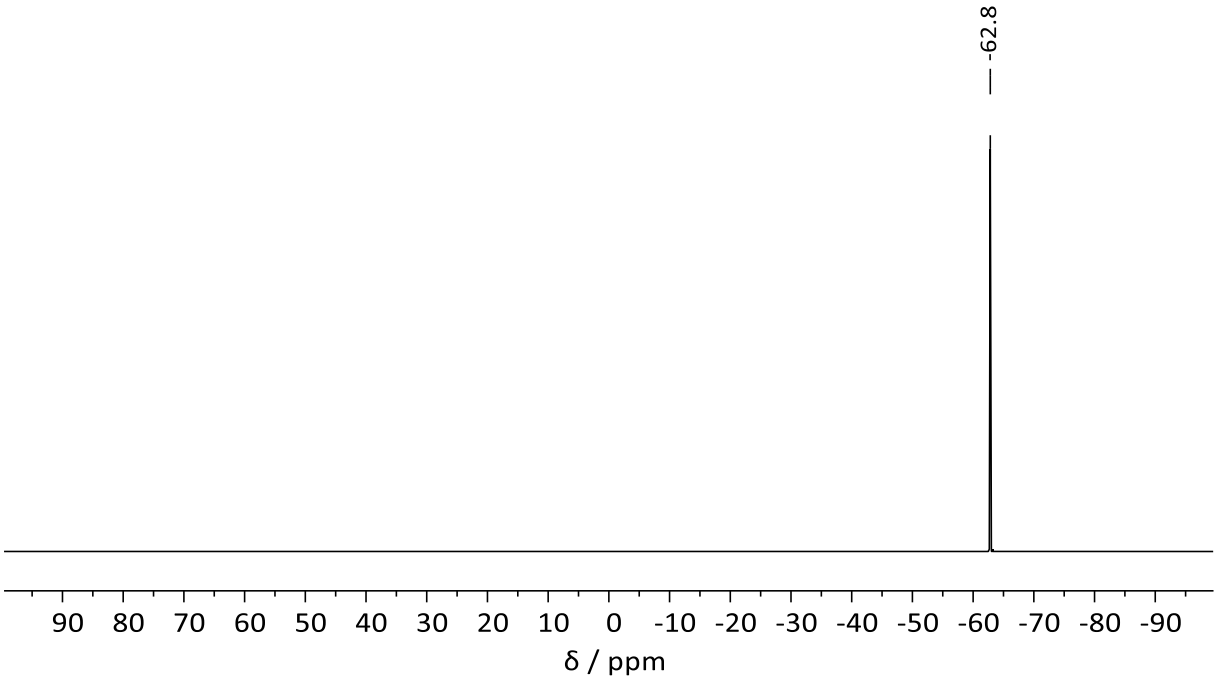


Fig. S55 ^{19}F NMR spectrum (470.51 MHz, CD_2Cl_2, 298 K) of compound **11b**.

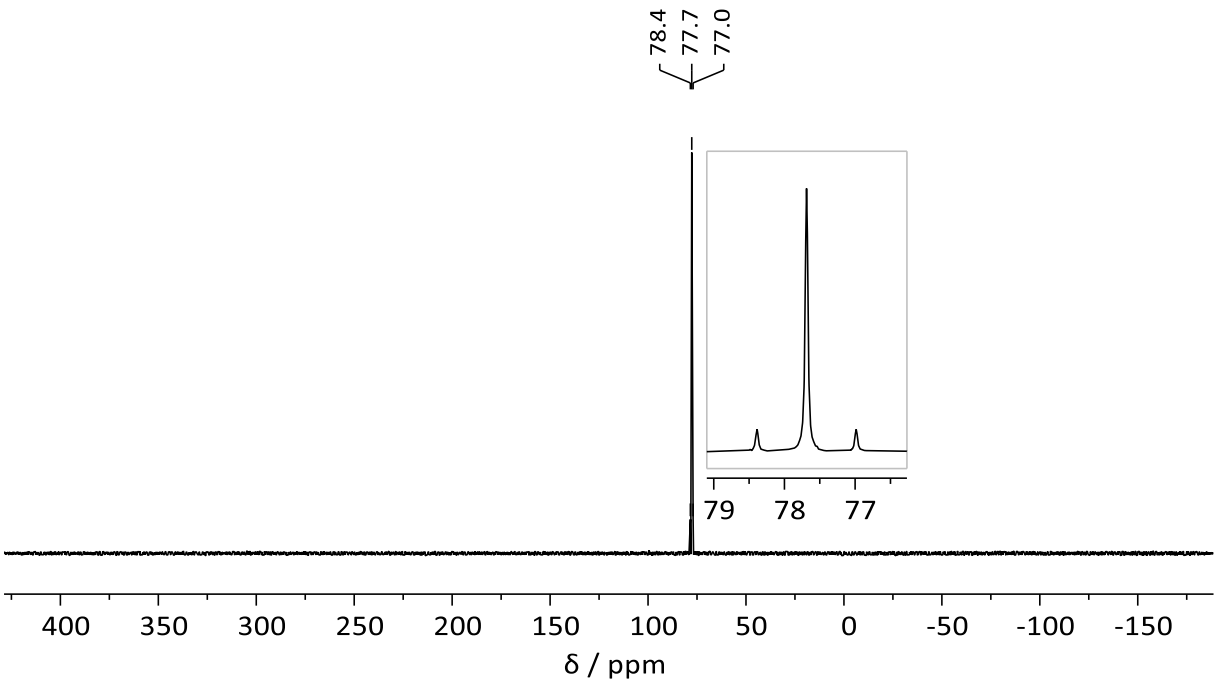


Fig. S56 $^{31}P\{^1H\}$ NMR spectrum (202.44 MHz, CD_2Cl_2, 298 K) of compound **11b**.

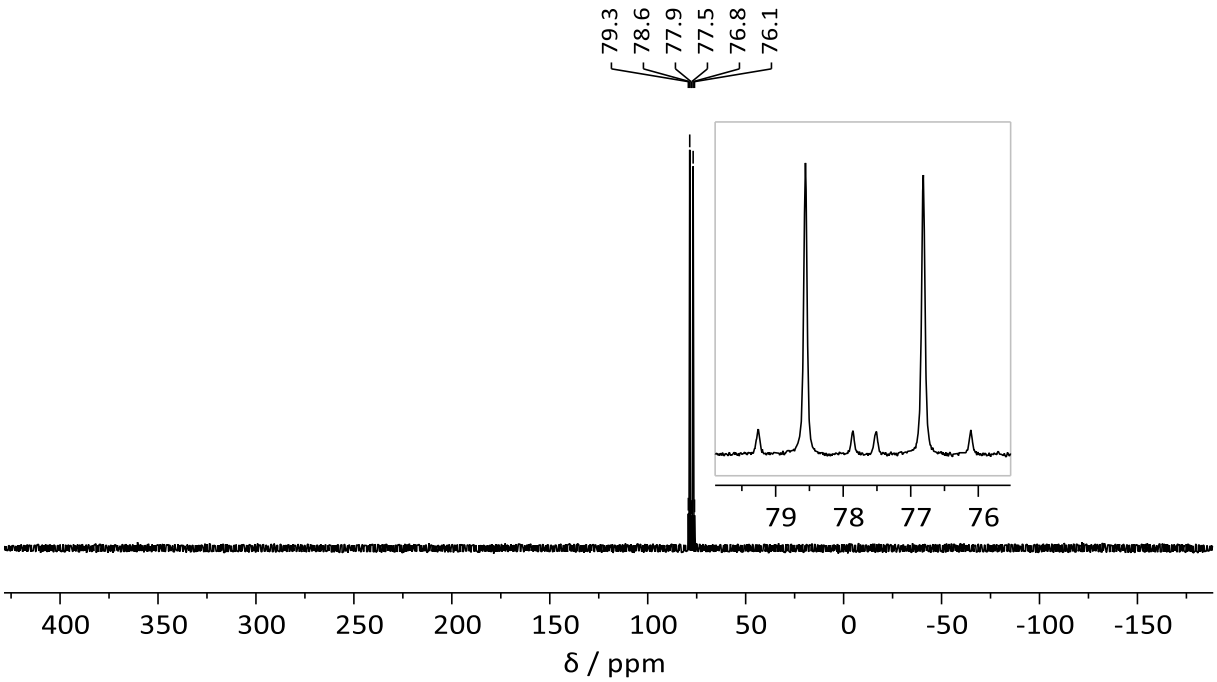


Fig. S57 ^{31}P NMR spectrum (202.44 MHz, CD_2Cl_2, 298 K) of compound **11b**.

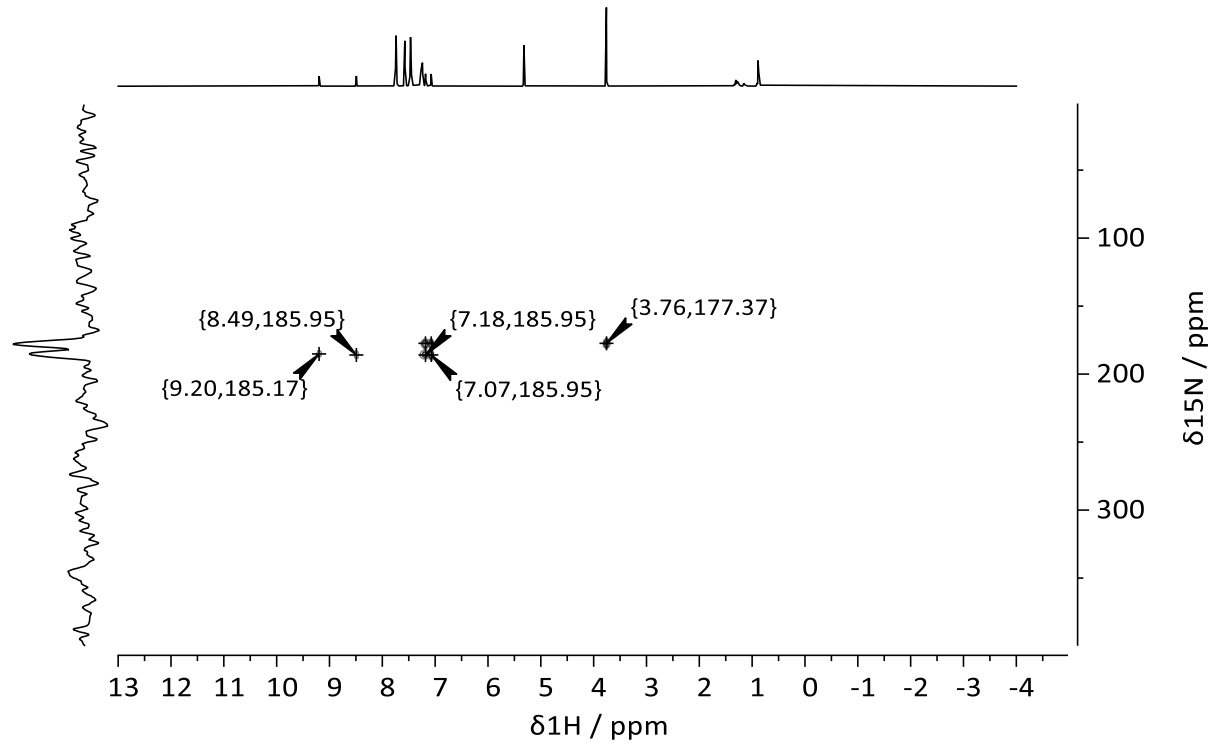


Fig. S58 ^{1}H,^{15}N HMBC NMR spectrum (500.04 MHz, 50.68 MHz, CD_2Cl_2, 298 K) of compound **11b**.

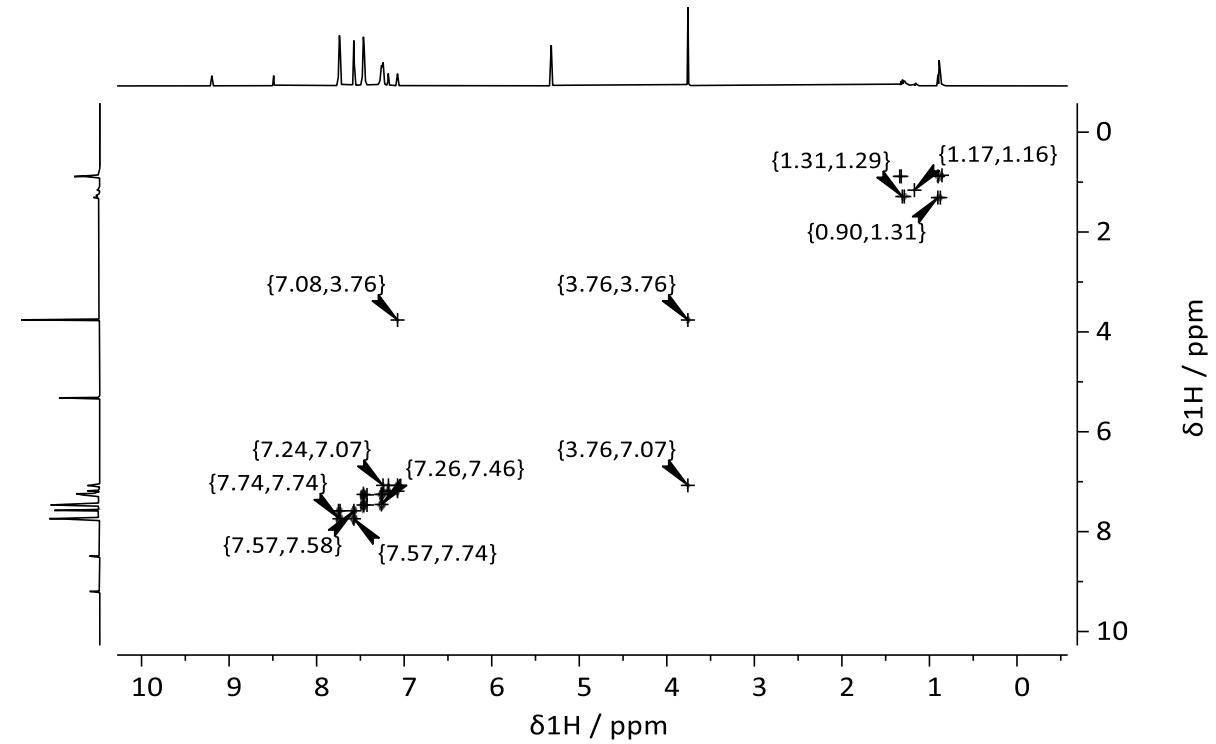


Fig. S59 $^{1}H,^{1}H$ COSY NMR spectrum (500.04 MHz, 500.04 MHz, CD_2Cl_2, 298 K) of compound **11b**.

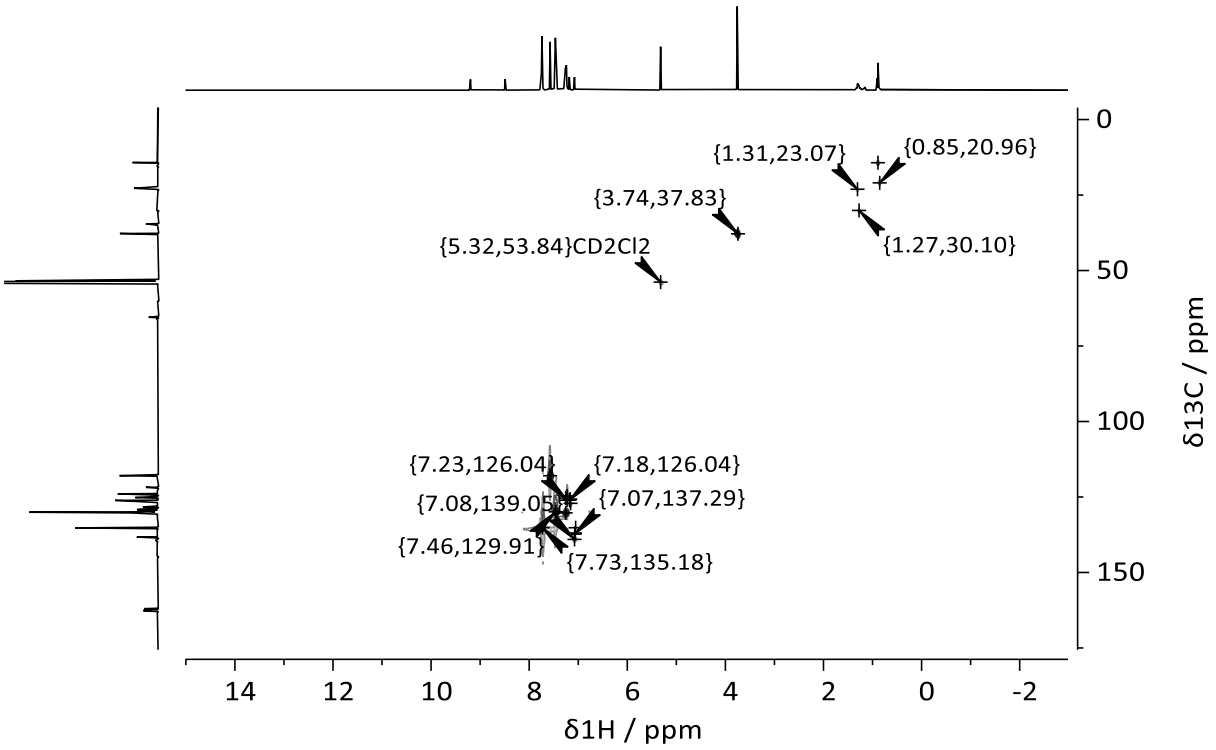


Fig. S60 $^{1}H,^{13}C$ HSQC NMR spectrum (500.04 MHz, 125.75 MHz, CD_2Cl_2, 298 K) of compound **11b**.

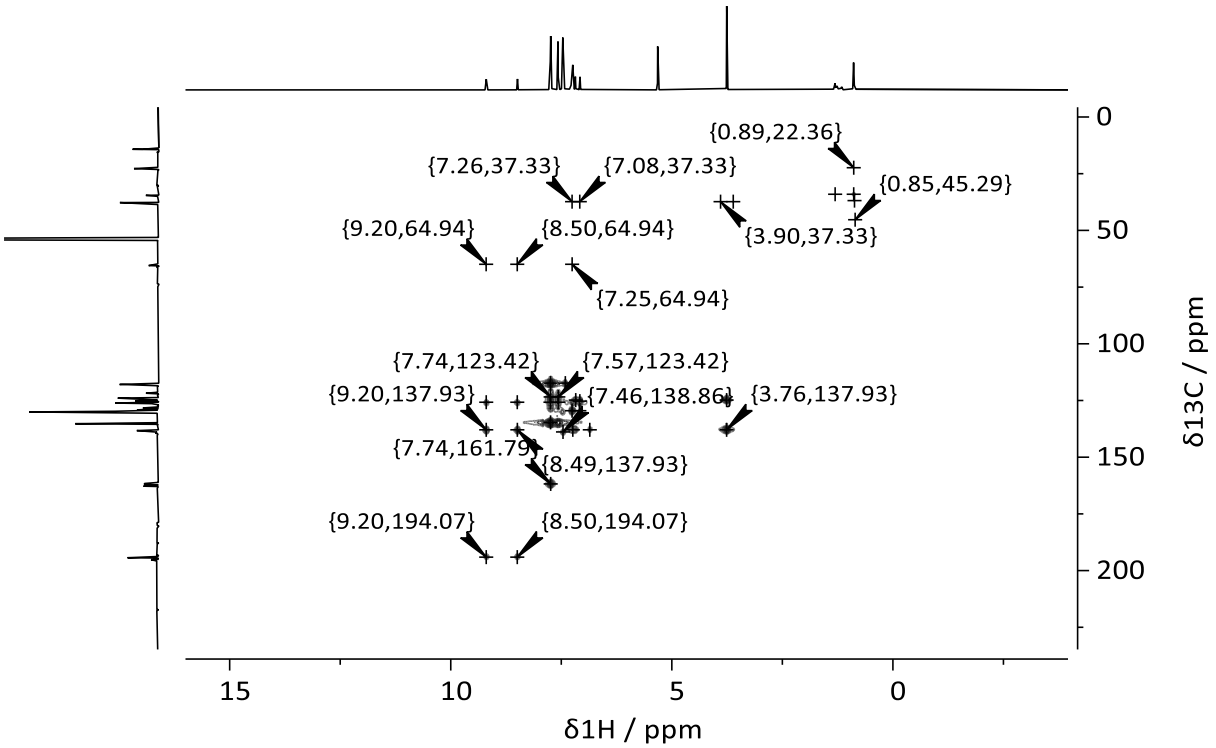


Fig. S61 $^{1}H,^{13}C$ HMBC NMR spectrum (500.04 MHz, 125.75 MHz, CD_2Cl_2, 298 K) of compound **11b**.

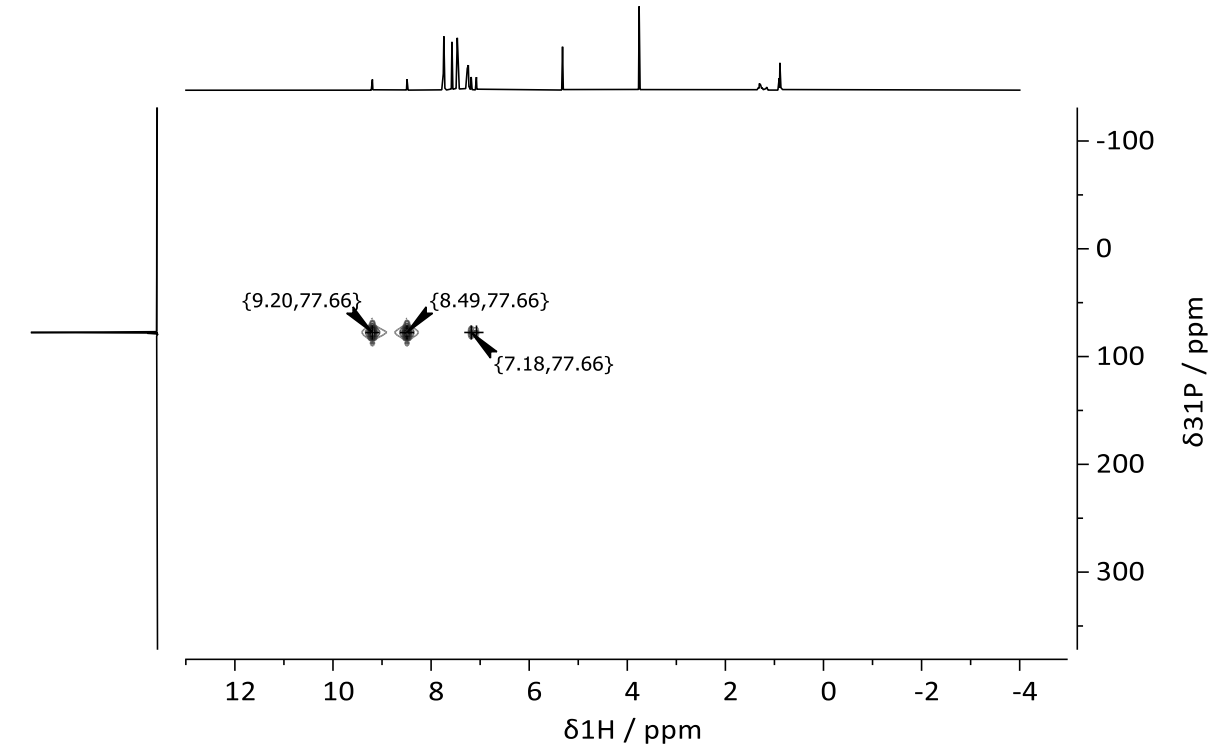


Fig. S62 $^{1}H,^{31}P$ HMBC NMR spectrum (500.04 MHz, 202.44 MHz, CD_2Cl_2, 298 K) of compound **11b**.

Compound 11c

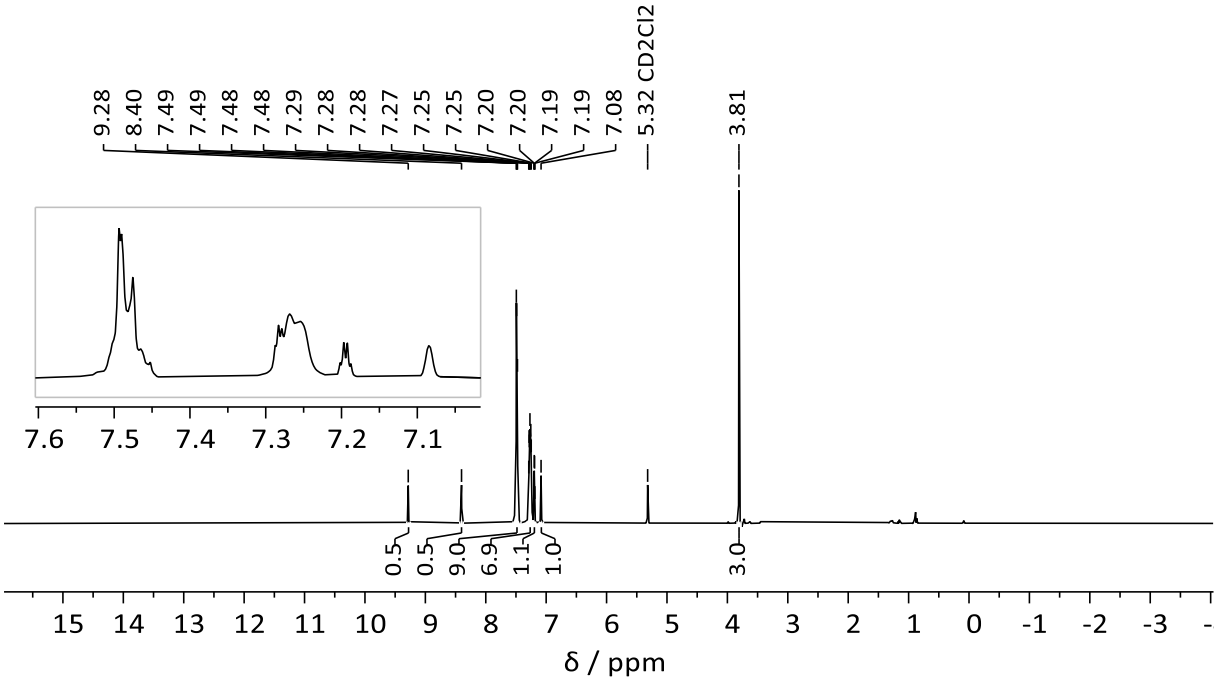


Fig. S63 ^{1}H NMR spectrum (400.13 MHz, CD_2Cl_2, 298 K) of compound **11c**.

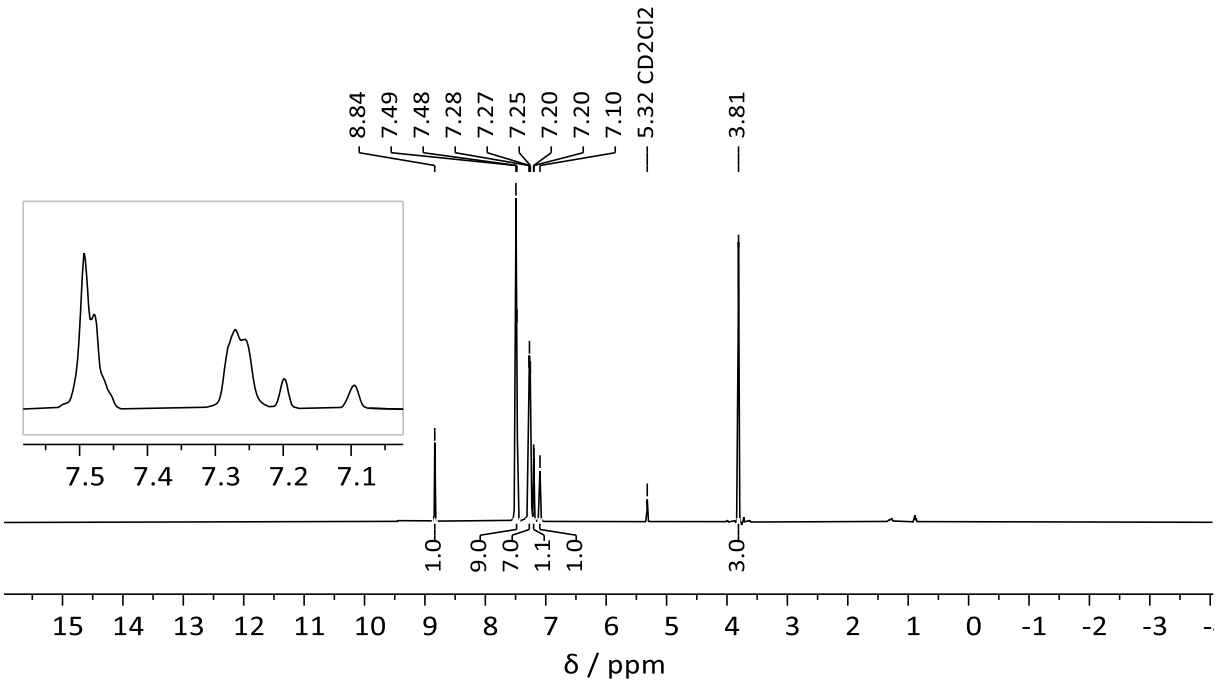


Fig. S64 ^{1}H{^{31}P} NMR spectrum (400.13 MHz, CD_2Cl_2, 298 K) of compound **11c**.

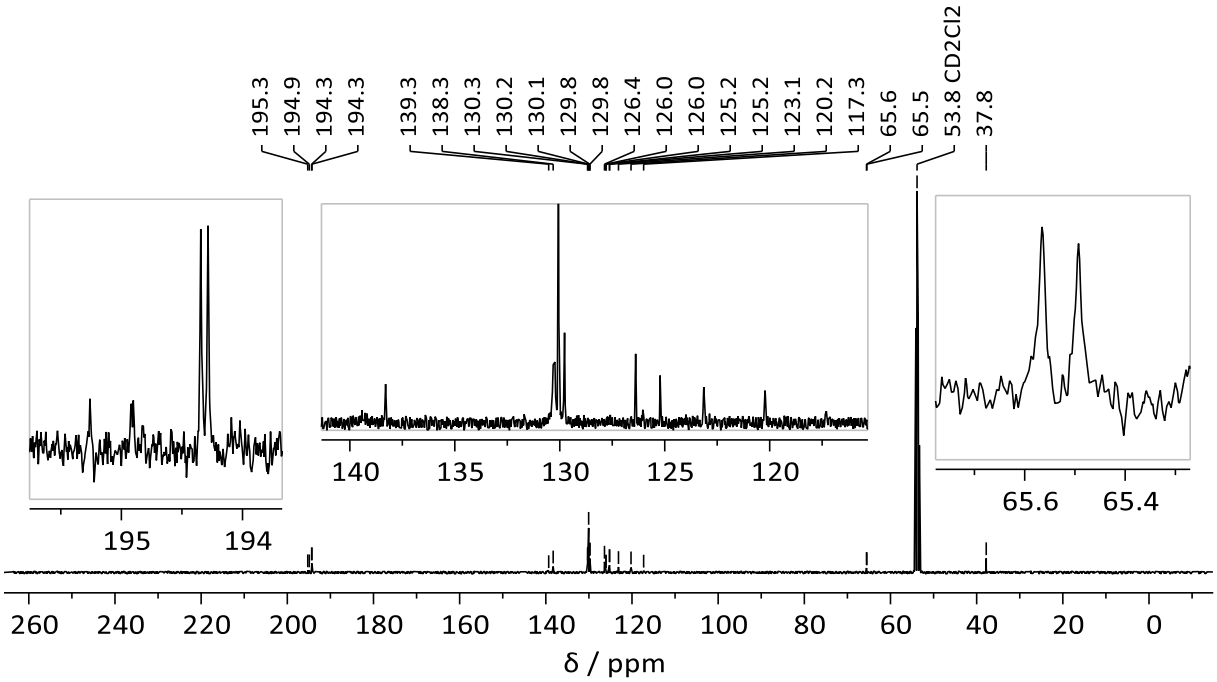


Fig. S65 $^{13}C\{^{1}H\}$ NMR spectrum (100.63 MHz, CD_2Cl_2, 298 K) of compound **11c**.

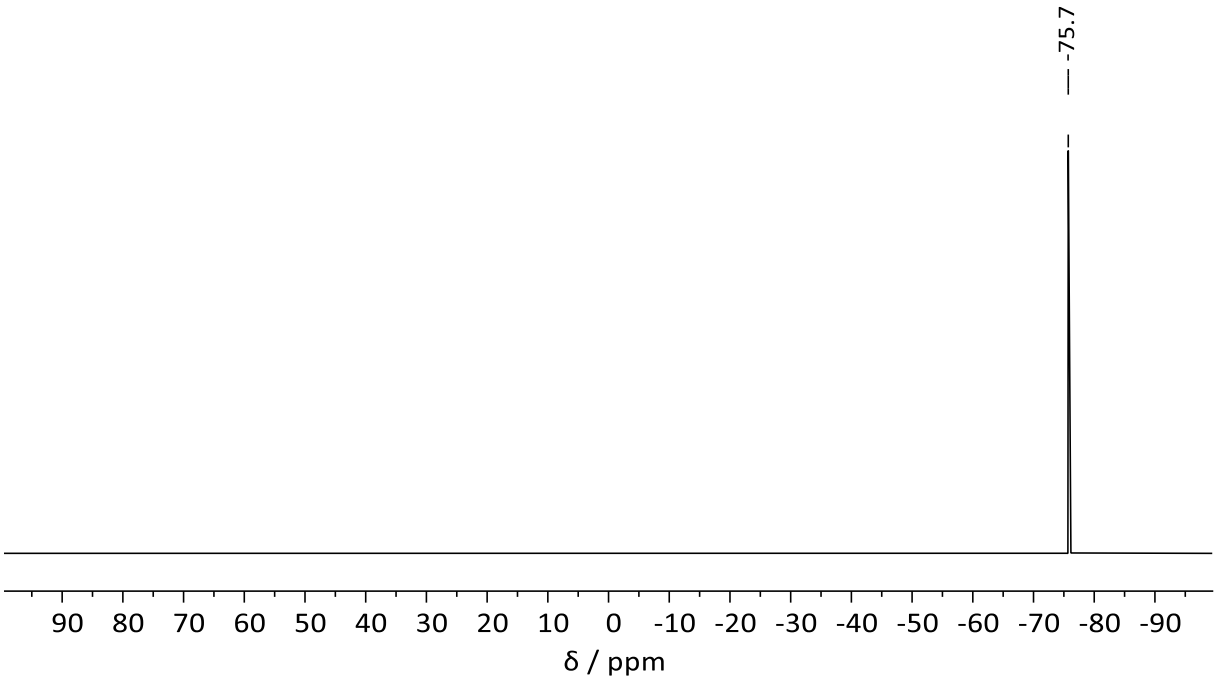


Fig. S66 ^{19}F NMR spectrum (470.51 MHz, CD_2Cl_2, 298 K) of compound **11c**.

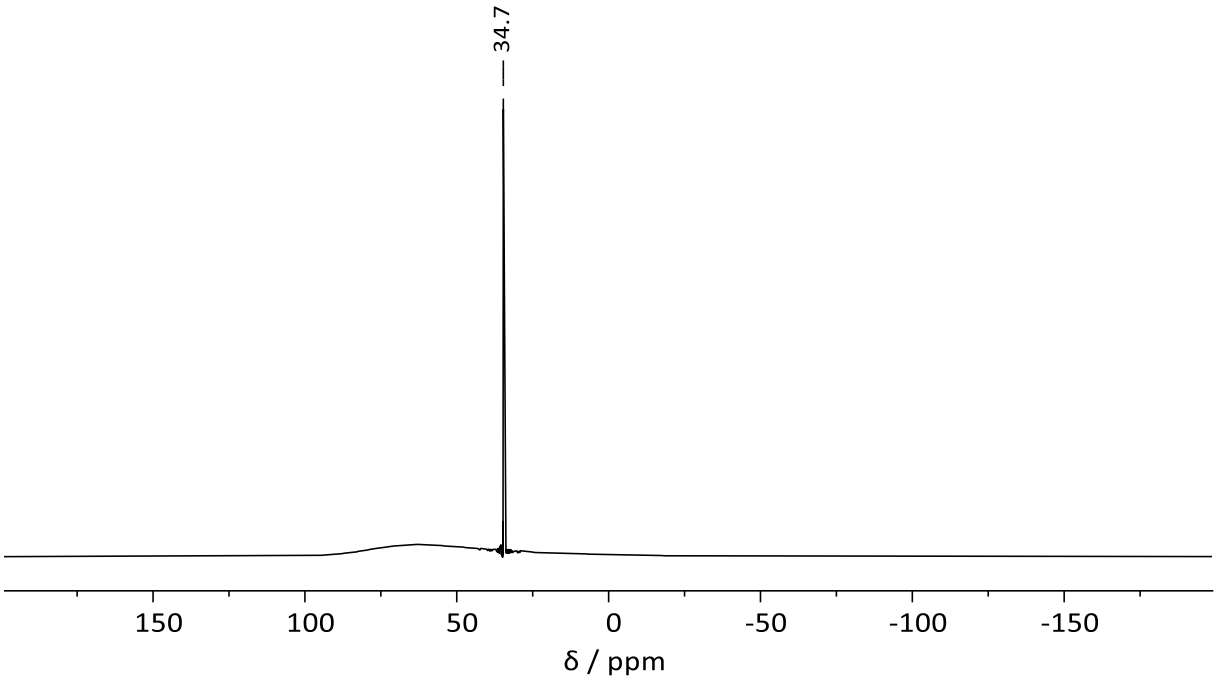


Fig. S67 $^{27}Al\{^{1}H\}$ NMR spectrum (78.20 MHz, CD_2Cl_2, 298 K) of compound **11c**.

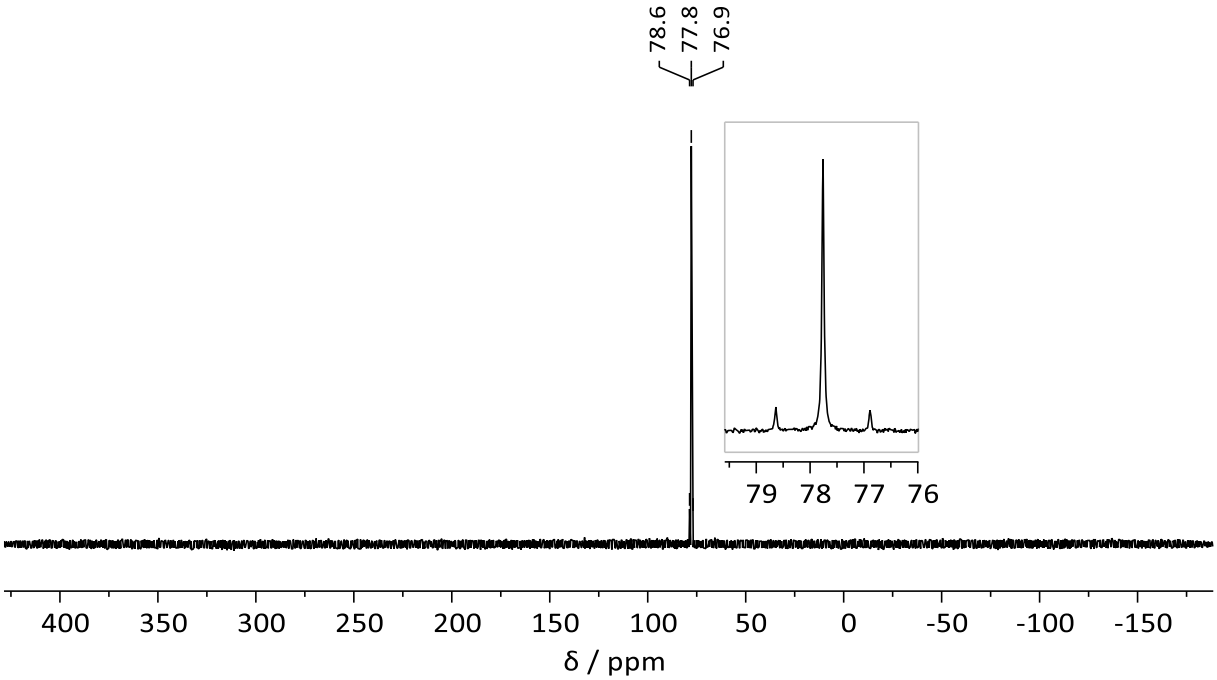


Fig. S68 $^{31}P\{^{1}H\}$ NMR spectrum (162.00 MHz, CD_2Cl_2, 298 K) of compound **11c**.

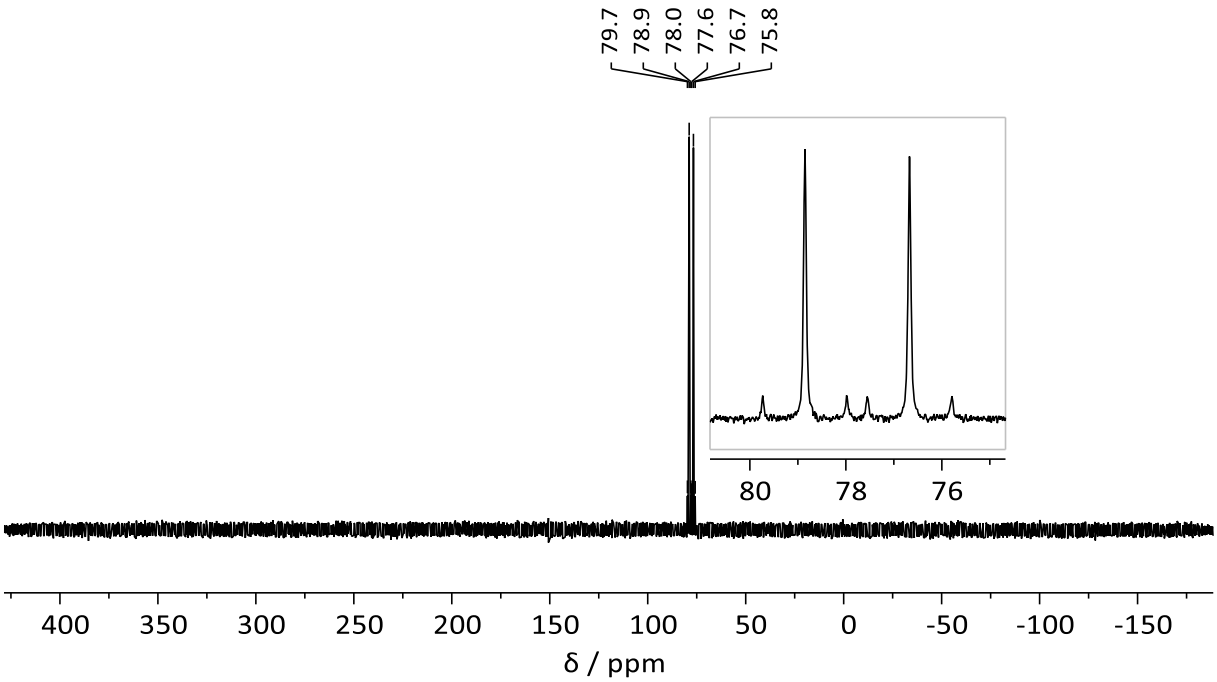


Fig. S69 ^{31}P NMR spectrum (162.00 MHz, CD_2Cl_2, 298 K) of compound **11c**.

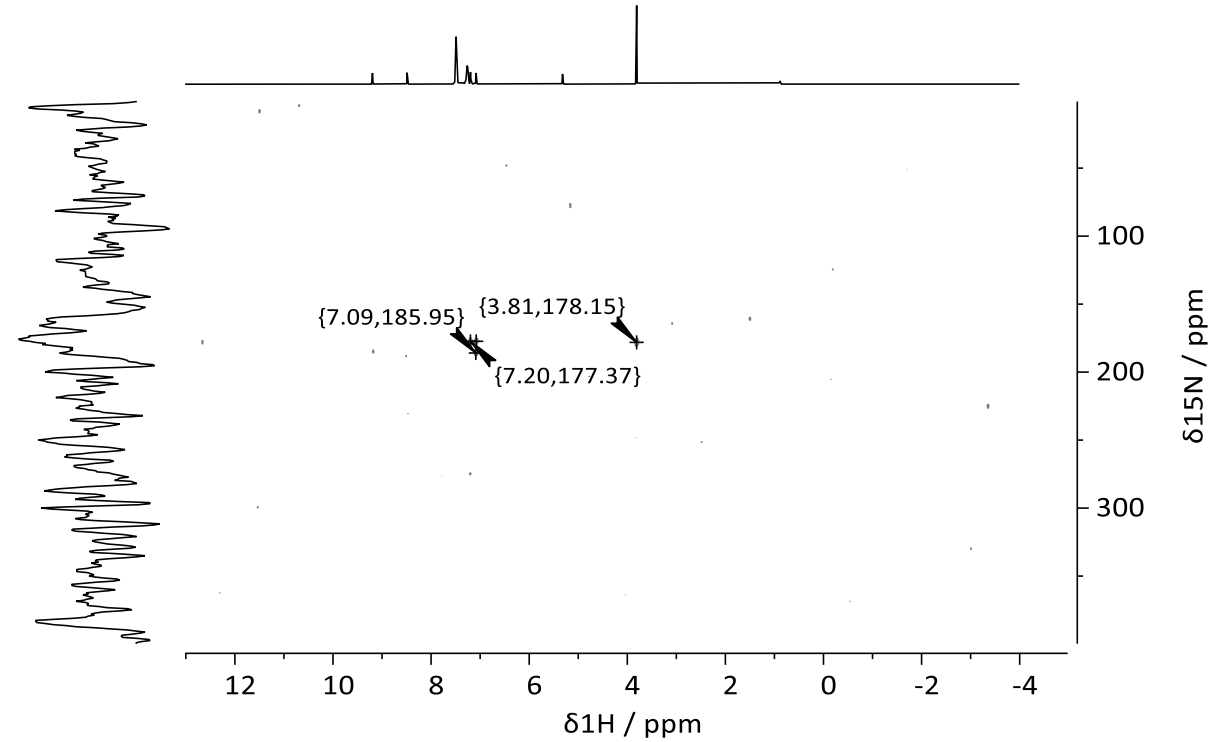


Fig. S70 ^{1}H,^{15}N HMBC NMR spectrum (500.04 MHz, 50.68 MHz, CD_2Cl_2, 298 K) of compound **11c**.

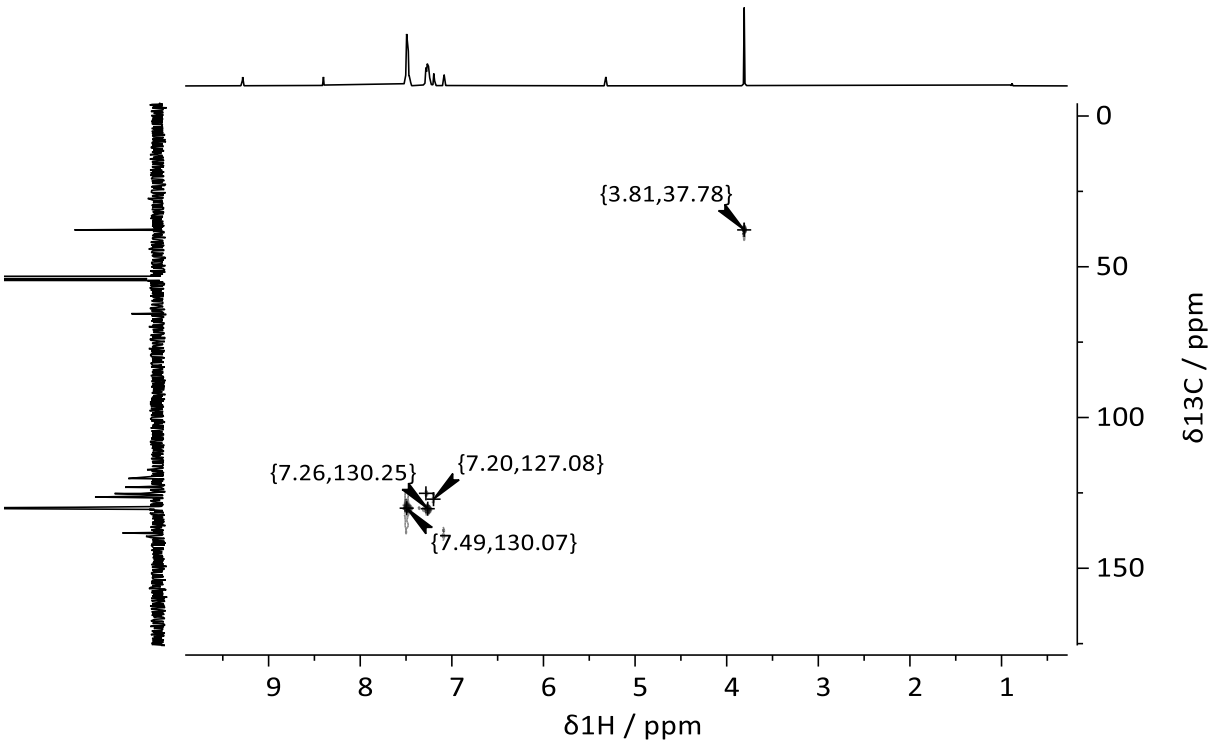


Fig. S71 $^{1}H,^{13}C$ HSQC NMR spectrum (400.13 MHz, 100.62 MHz, CD_2Cl_2, 298 K) of compound **11c**.

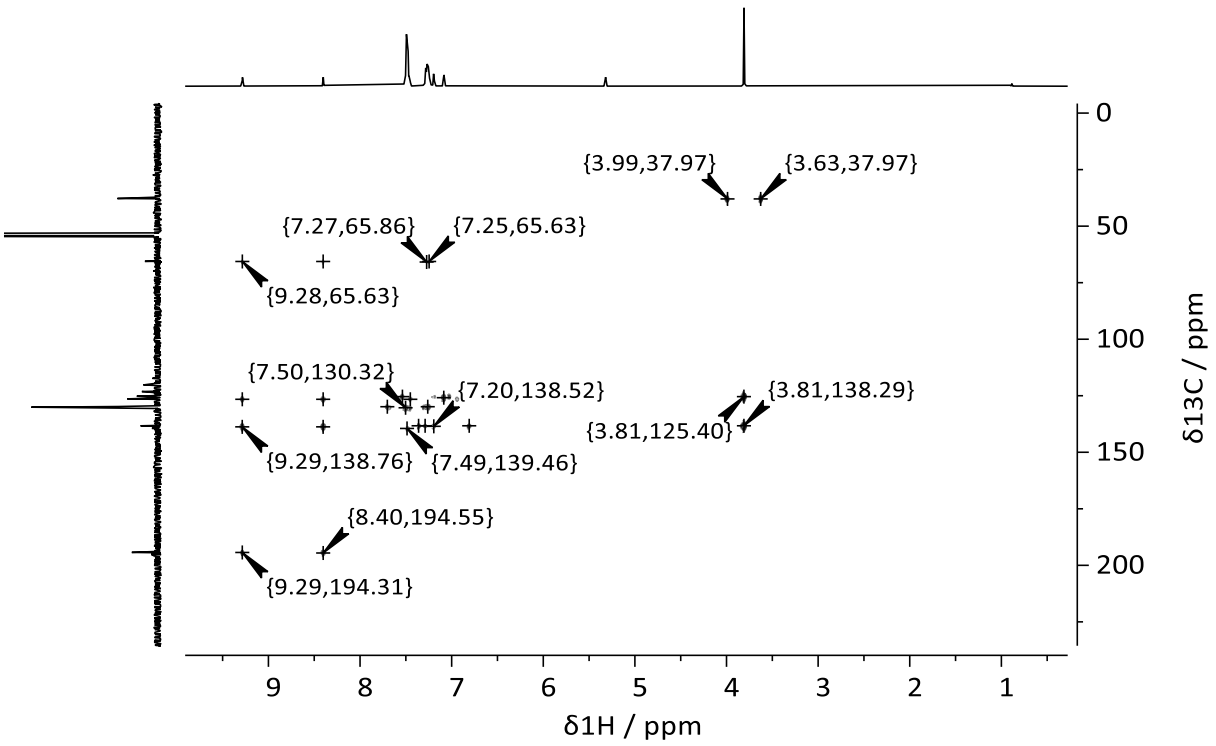


Fig. S72 $^{1}H,^{13}C$ HMBC NMR spectrum (400.13 MHz, 100.62 MHz, CD_2Cl_2, 298 K) of compound **11c**.

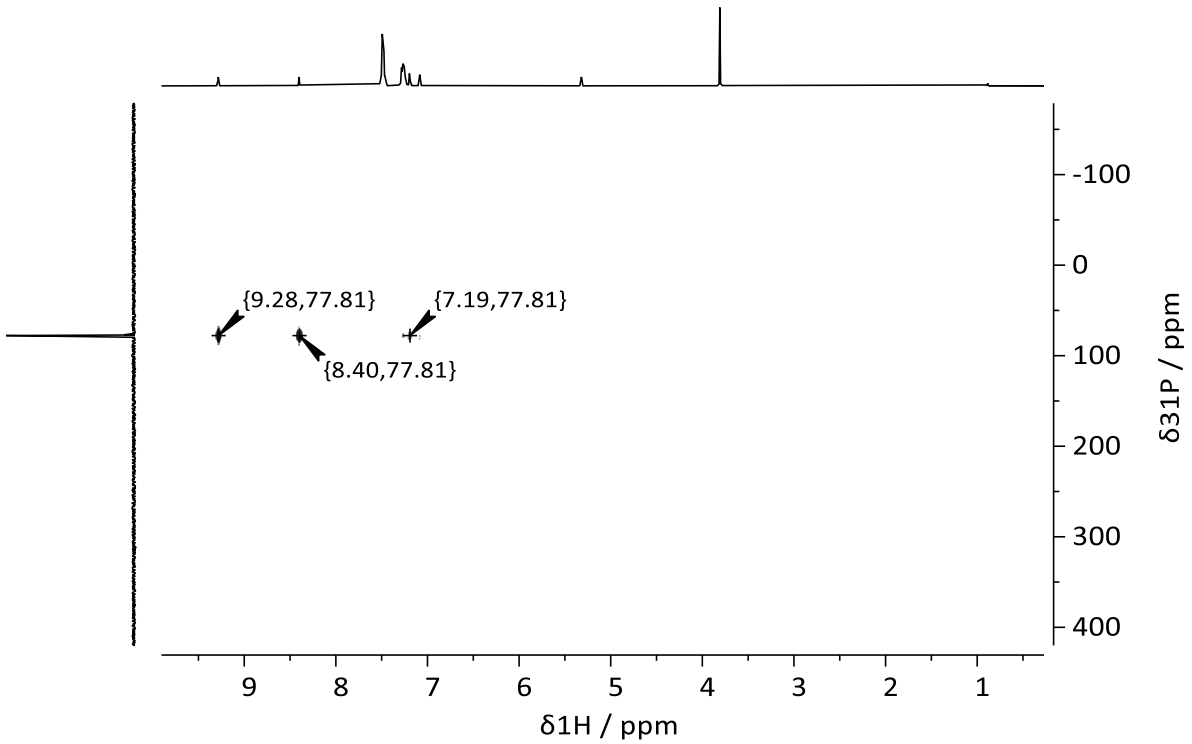


Fig. S73 $^{1}H,^{31}P$ HMBC NMR spectrum (400.13 MHz, 162.00 MHz, CD_2Cl_2, 298 K) of compound **11c**.

Decomposition of compound 11c in THF-d_8

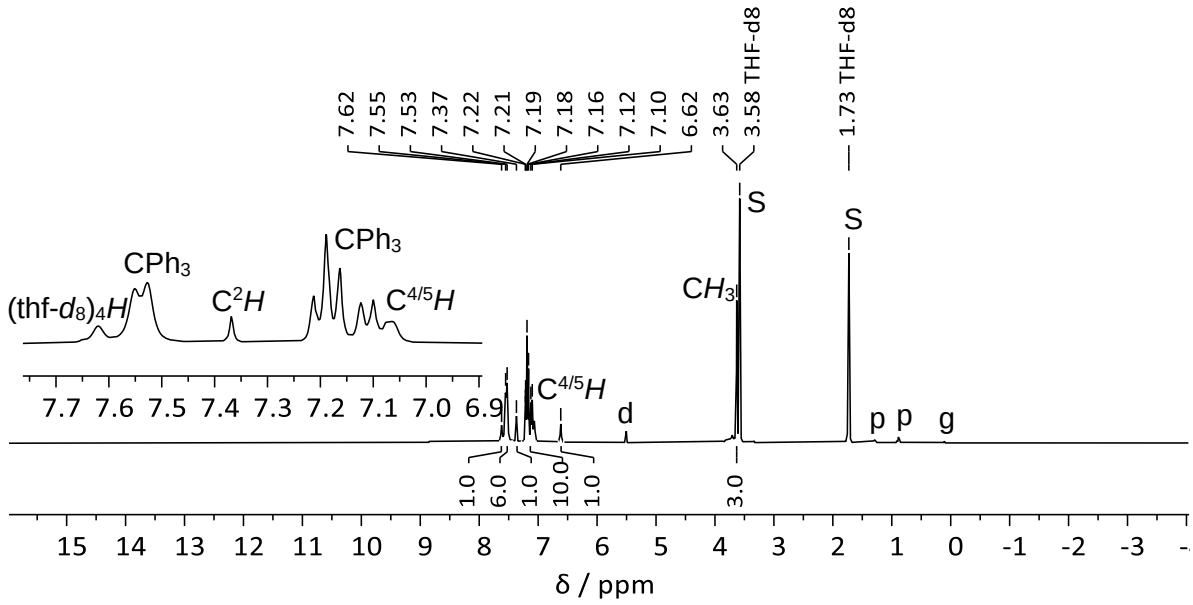


Fig. S74 ^{1}H NMR spectrum (300.13 MHz, THF-d_8, 298 K) of the decomposition mixture of compound **11c** in THF-d_8. The resonances of traces of dichloromethane are marked with a "d", of *n*-pentane with a "p" and of grease with a "g". The residual resonance signals of the deuterated solvent are marked with an "S".

Compound 11c-Cr

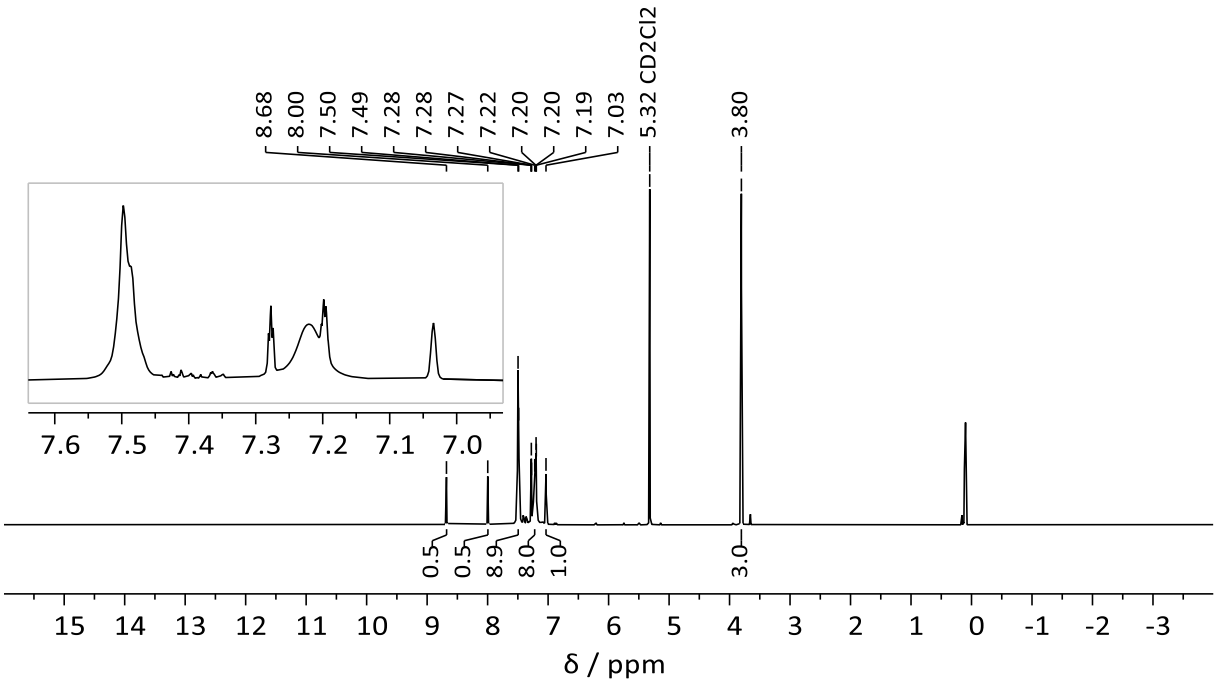


Fig. S75 ^{1}H NMR spectrum (500.04 MHz, CD_2Cl_2, 298 K) of compound **11c-Cr**.

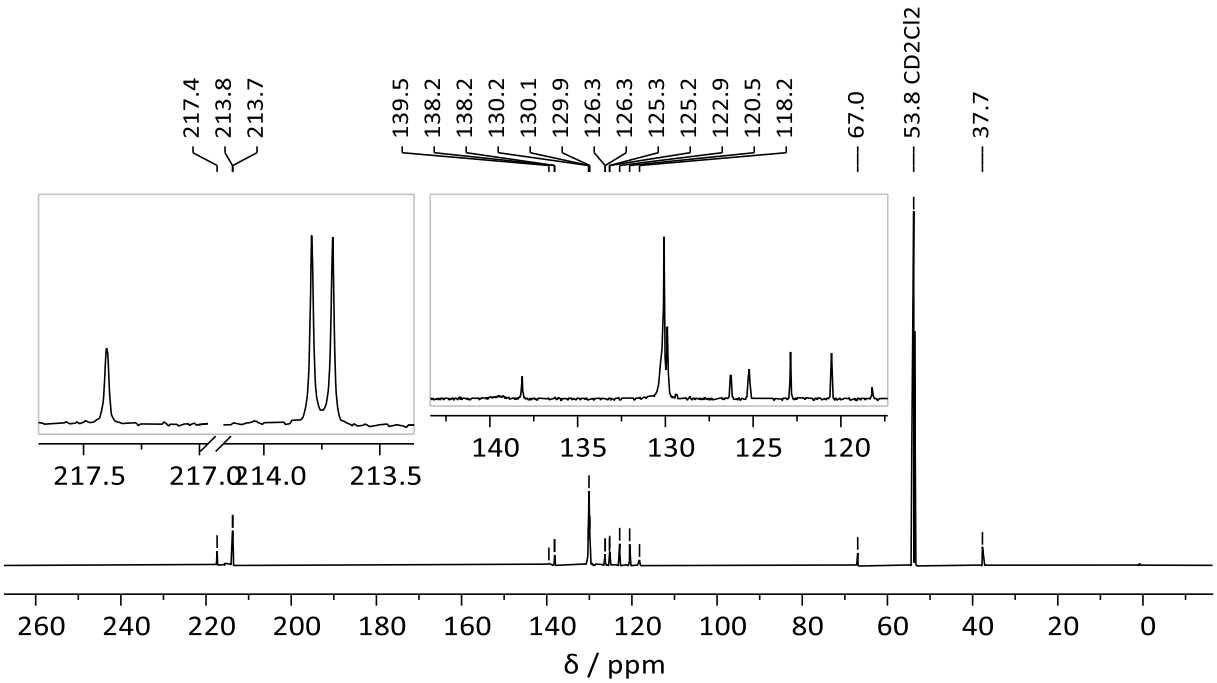


Fig. S76 $^{13}C\{^{1}H\}$ NMR spectrum (125.75 MHz, CD_2Cl_2, 298 K) of compound **11c-Cr**.

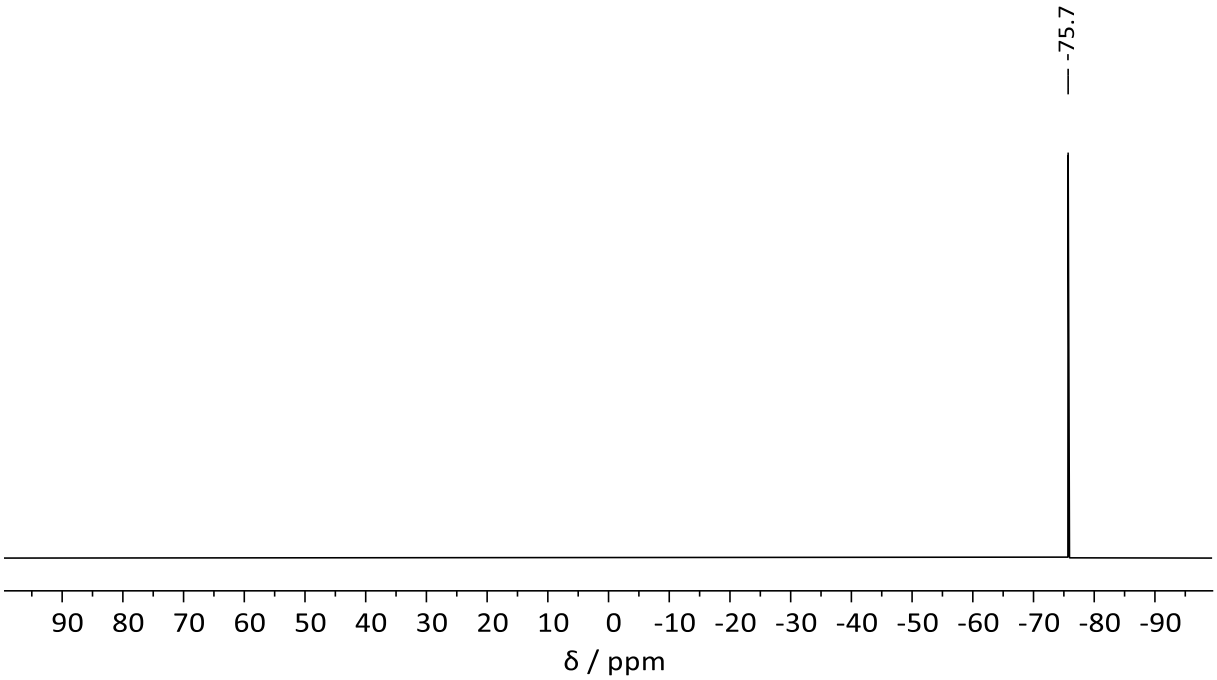


Fig. S77 ^{19}F NMR spectrum (470.51 MHz, CD_2Cl_2, 298 K) of compound **11c-Cr**.

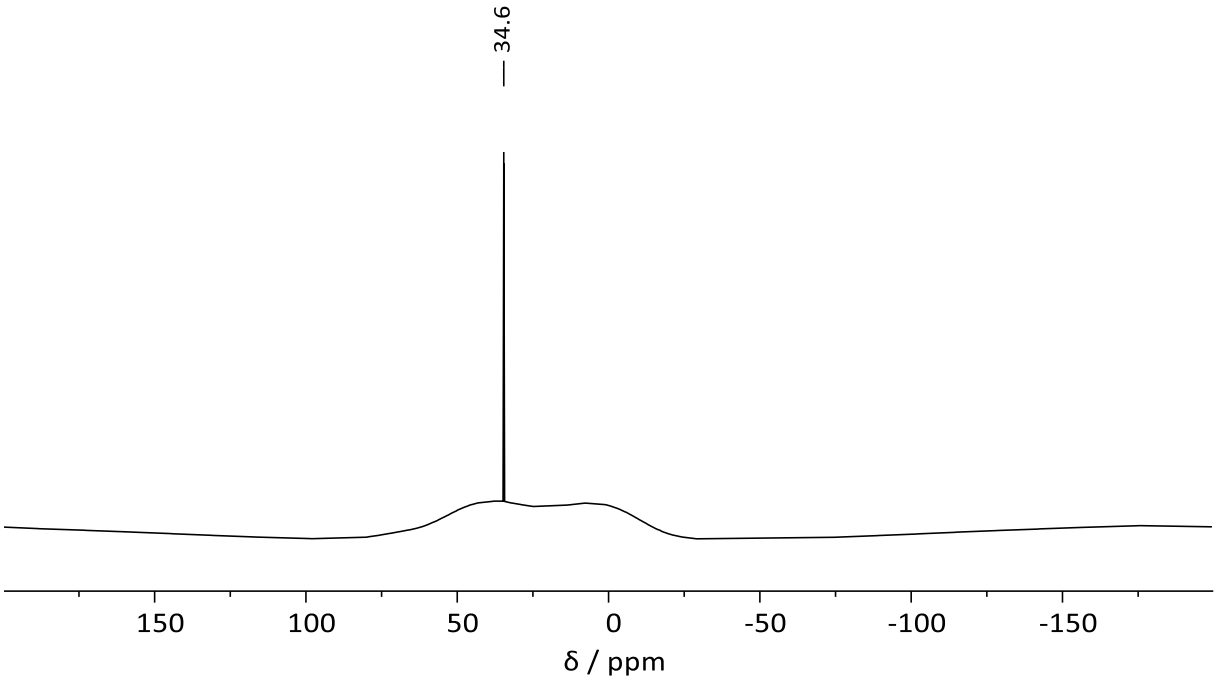


Fig. S78 $^{27}Al\{^1H\}$ NMR spectrum (130.29 MHz, CD_2Cl_2, 298 K) of compound **11c-Cr**.

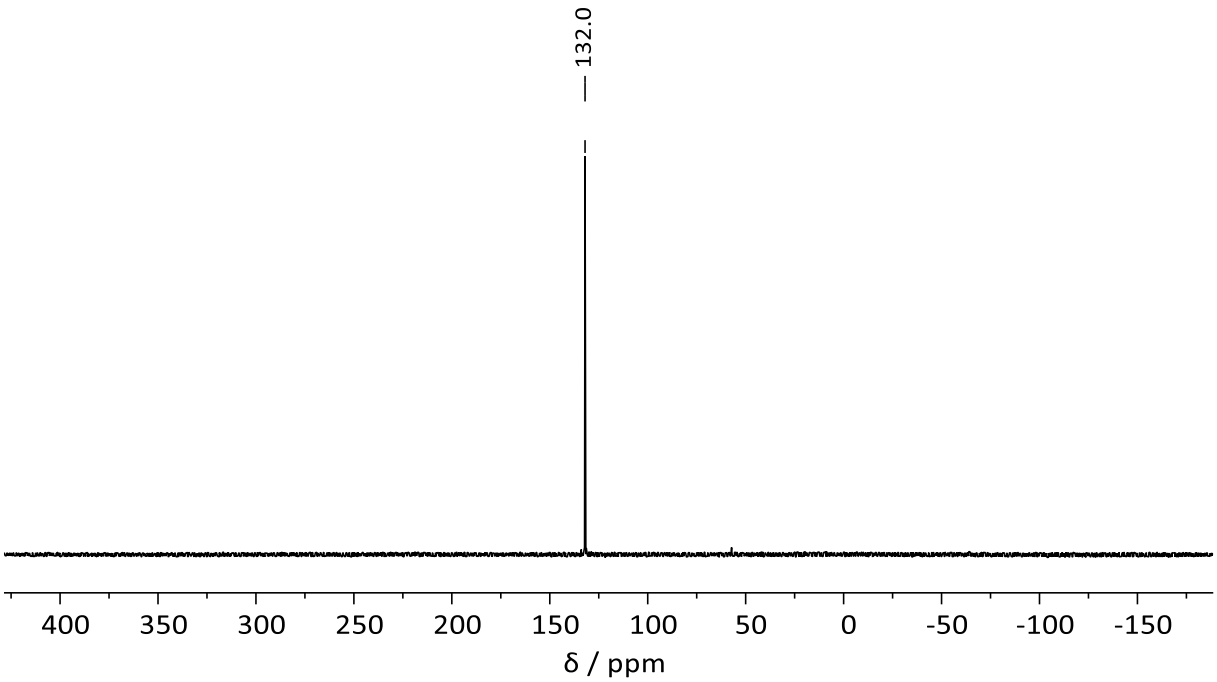


Fig. S79 $^{31}P\{^{1}H\}$ NMR spectrum (202.44 MHz, CD_2Cl_2, 298 K) of compound **11c-Cr**.

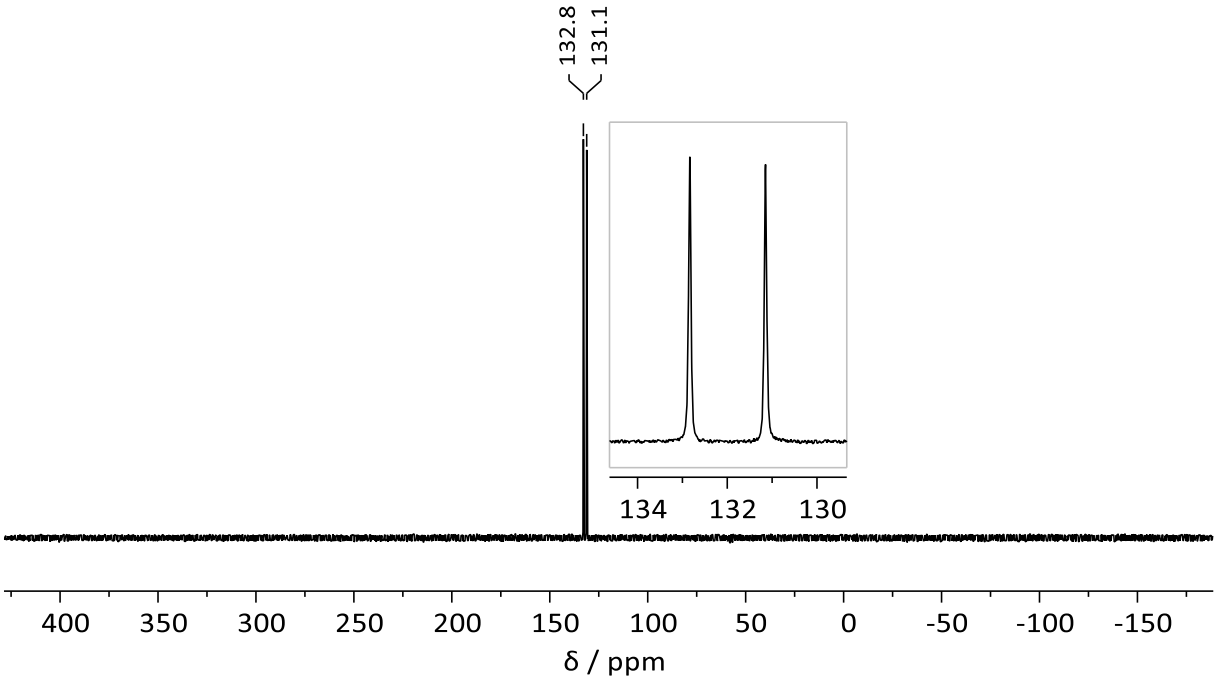


Fig. S80 ^{31}P NMR spectrum (202.44 MHz, CD_2Cl_2, 298 K) of compound **11c-Cr**.

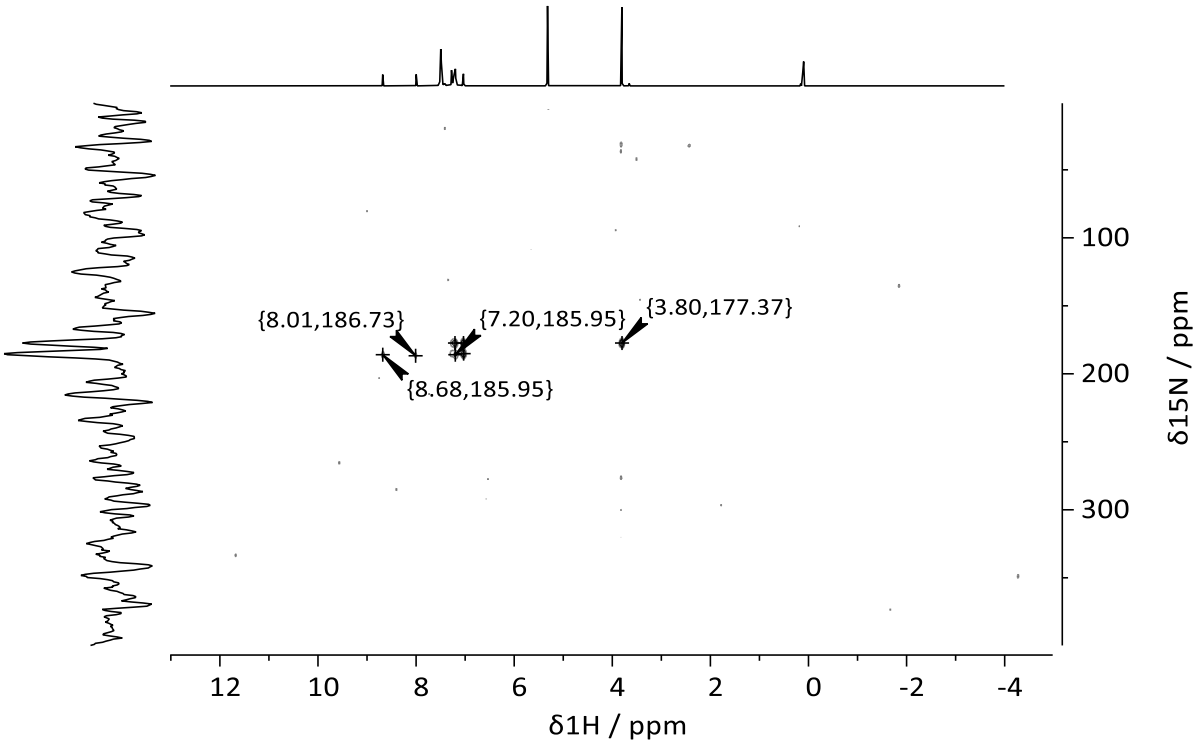


Fig. S81 $^{1}H,^{15}N$ HMBC NMR spectrum (500.04 MHz, 50.68 MHz, CD_2Cl_2, 298 K) of compound **11c-Cr**.

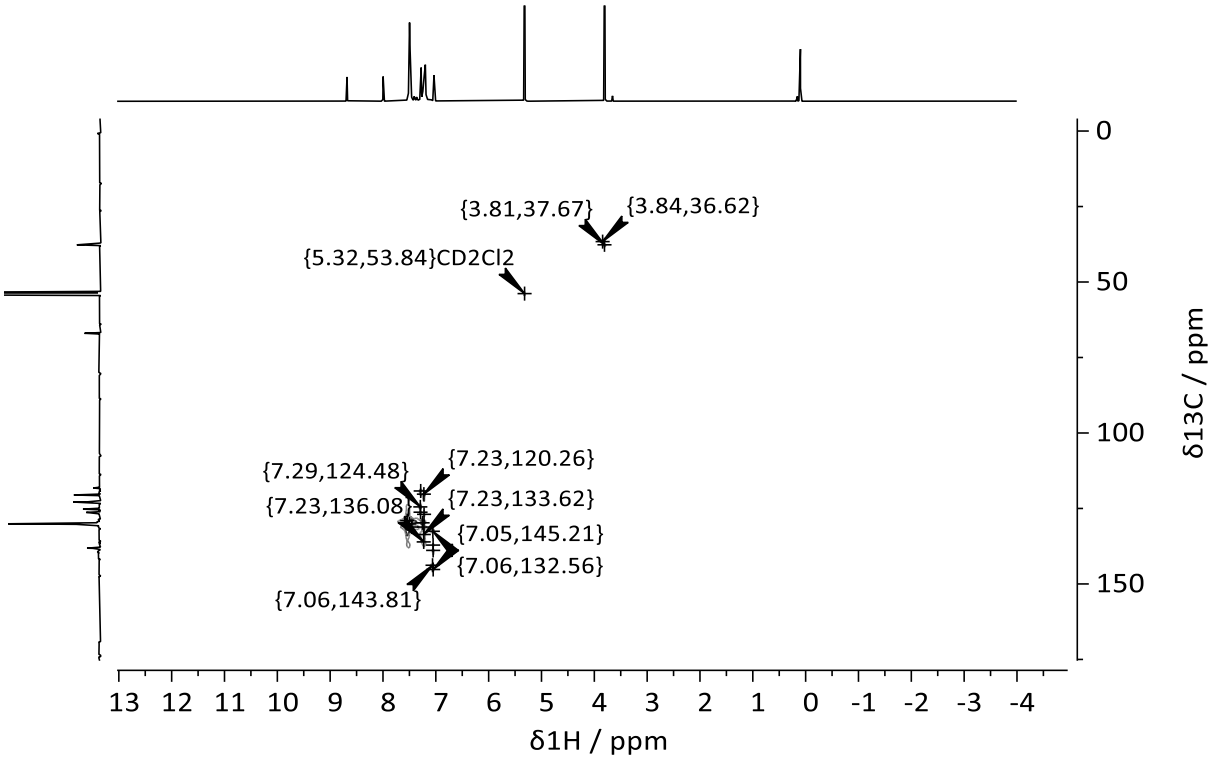


Fig. S82 $^{1}H,^{13}C$ HSQC NMR spectrum (500.04 MHz, 125.75 MHz, CD_2Cl_2, 298 K) of compound **11c-Cr**.

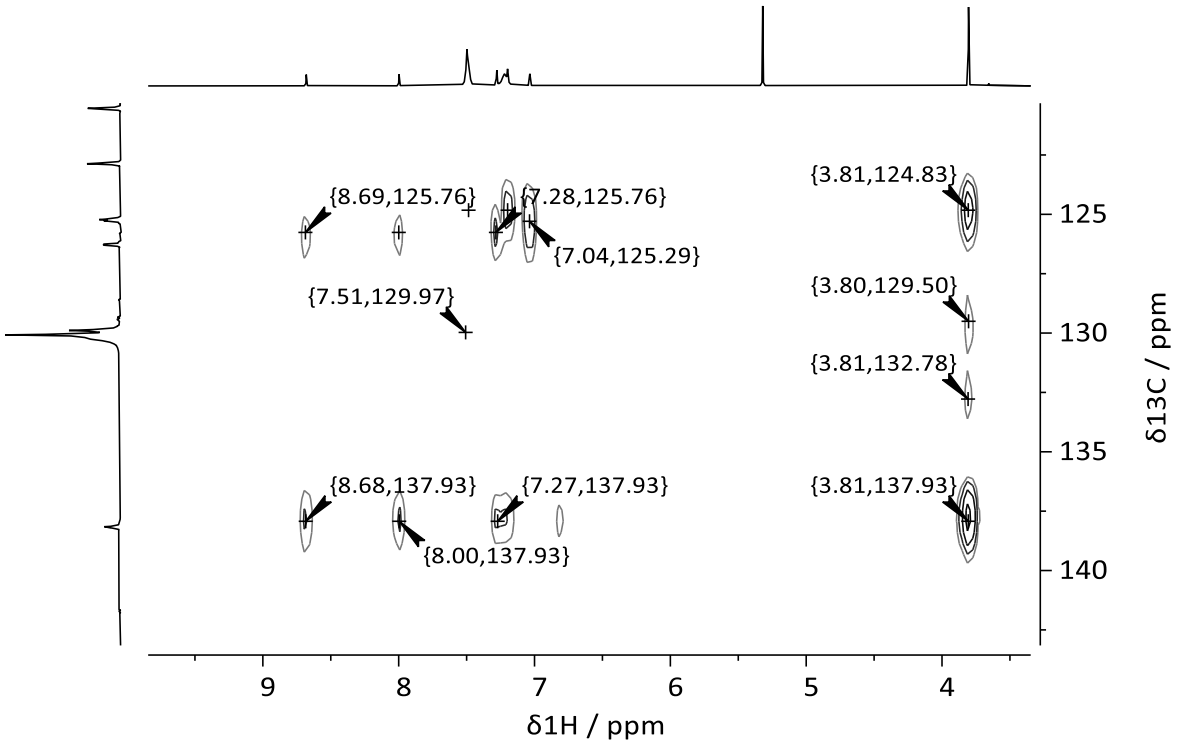


Fig. S83 $^{1}H,^{13}C$ HMBC NMR spectrum (500.04 MHz, 125.75 MHz, CD_2Cl_2, 298 K) of compound **11c-Cr**.

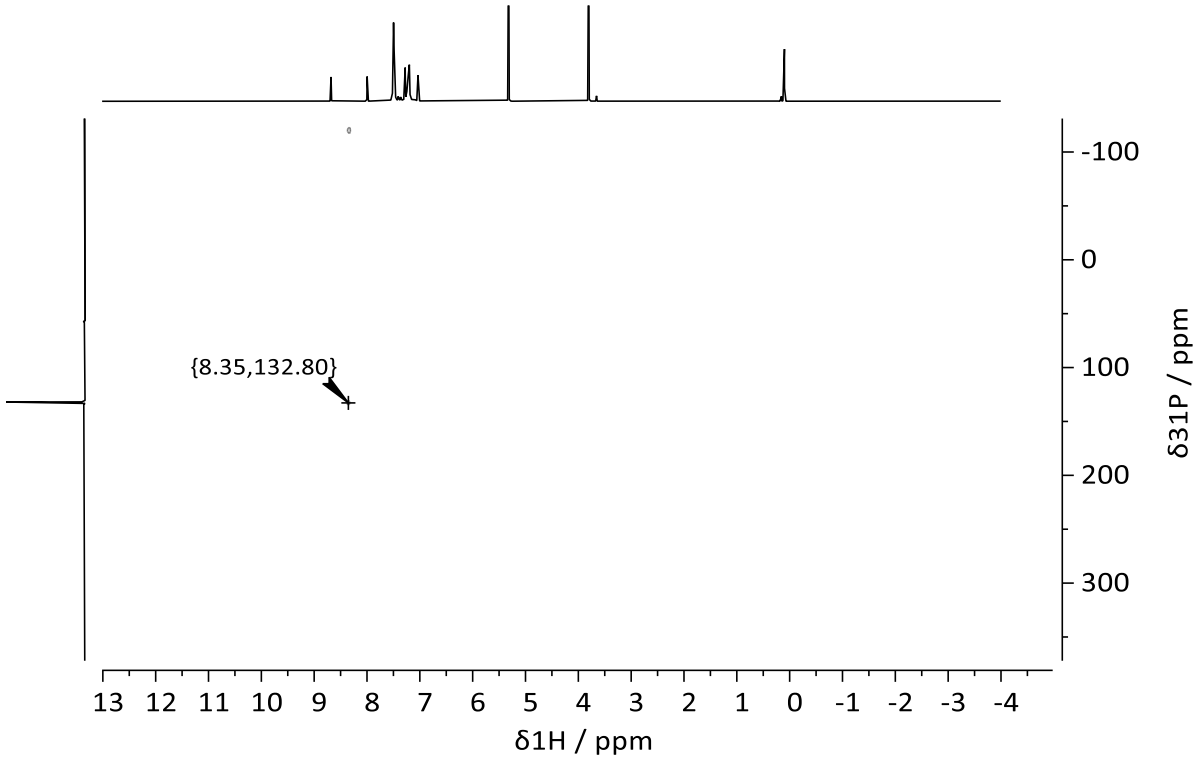


Fig. S84 $^{1}H,^{31}P$ HMQC NMR spectrum (500.04 MHz, 202.44 MHz, CD_2Cl_2, 298 K) of compound **11c-Cr**.

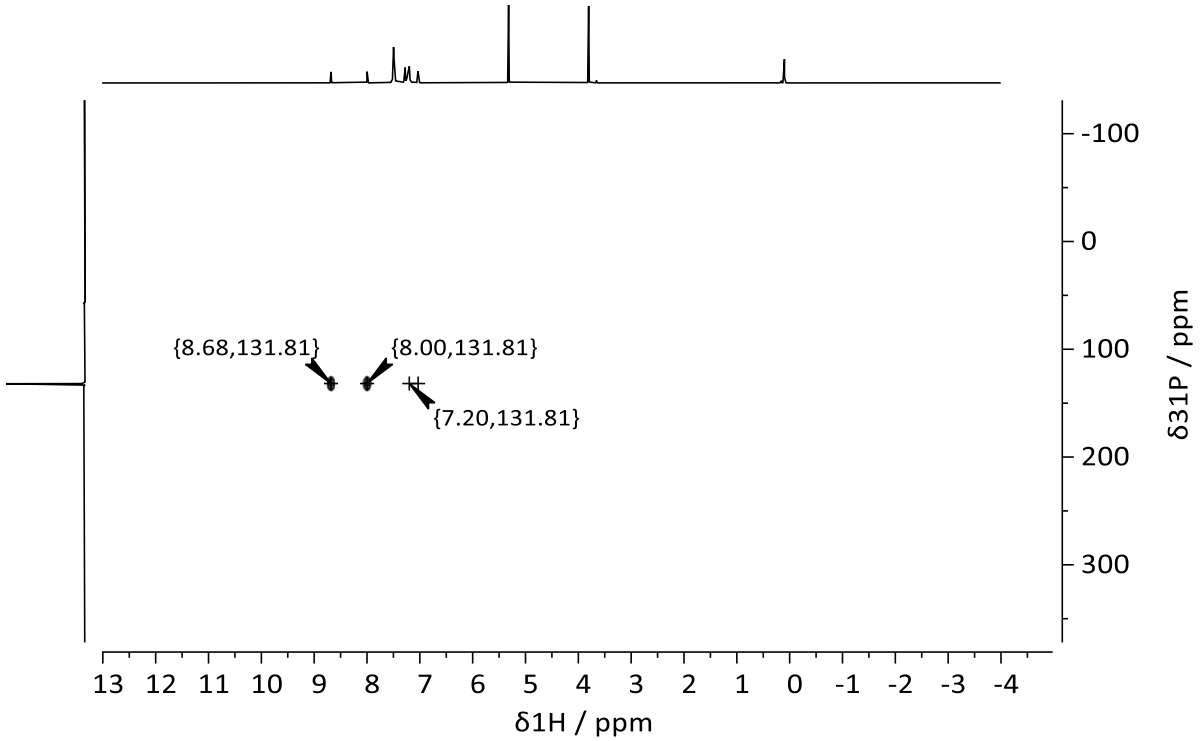


Fig. S85 $^{1}H,^{31}P$ HMBC NMR spectrum (500.04 MHz, 202.44 MHz, CD_2Cl_2, 298 K) of compound **11c-Cr**.

Compound 12

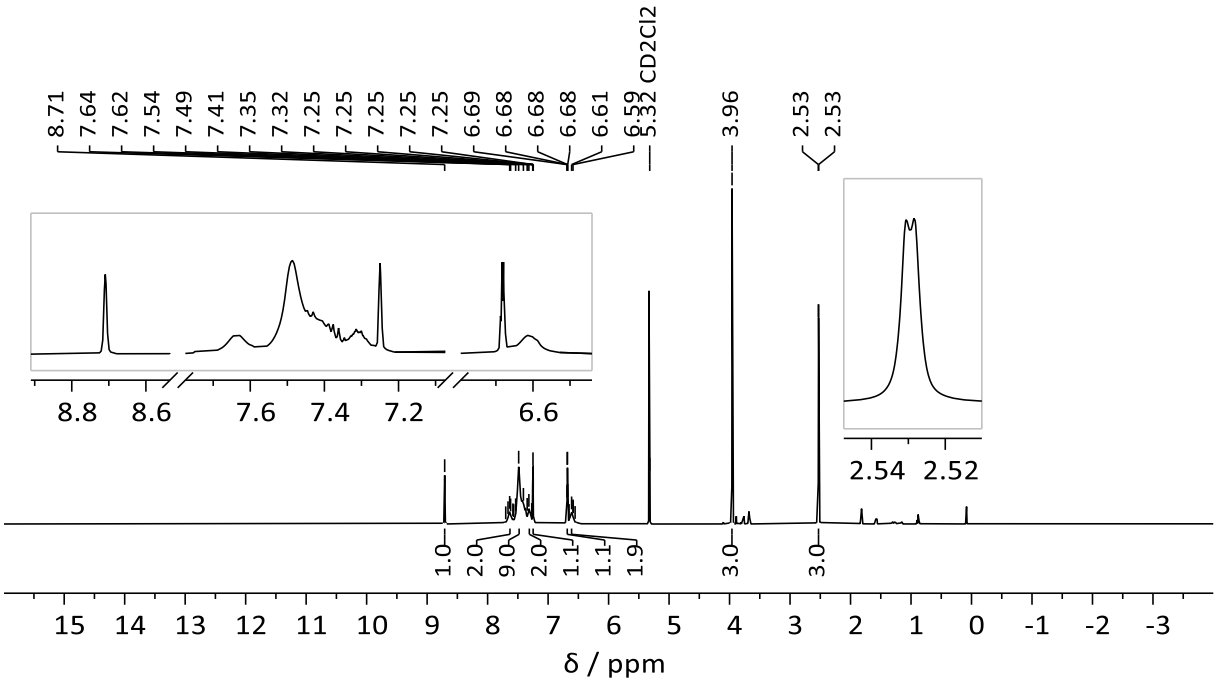


Fig. S86 ^{1}H NMR spectrum (500.04 MHz, CD_2Cl_2, 298 K) of compound **12**.

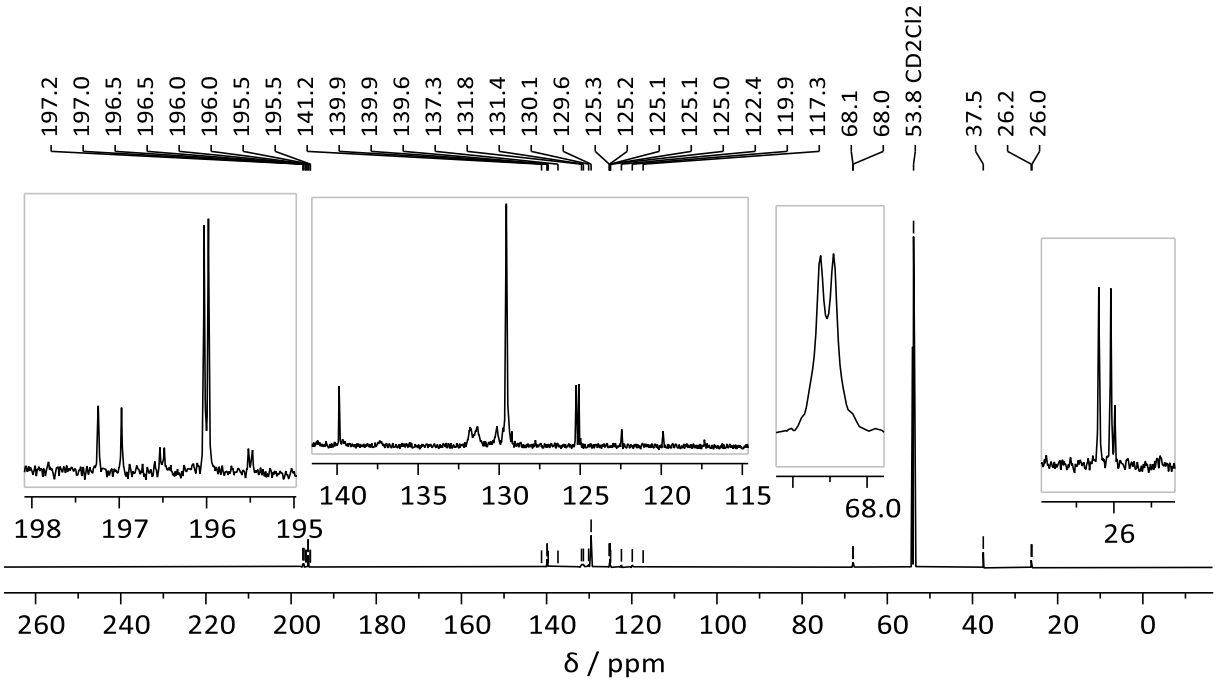


Fig. S87 $^{13}C\{^{1}H\}$ NMR spectrum (125.75 MHz, CD_2Cl_2, 298 K) of compound **12**.

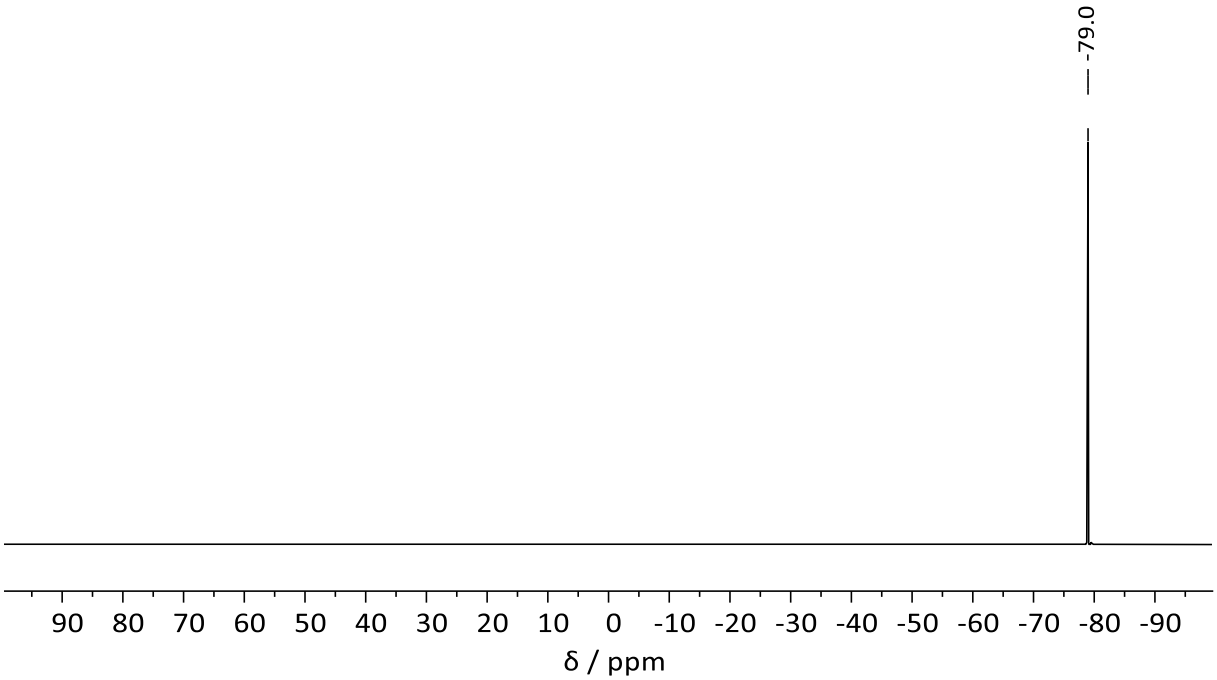


Fig. S88 ^{19}F NMR spectrum (470.51 MHz, CD_2Cl_2, 298 K) of compound **12**.

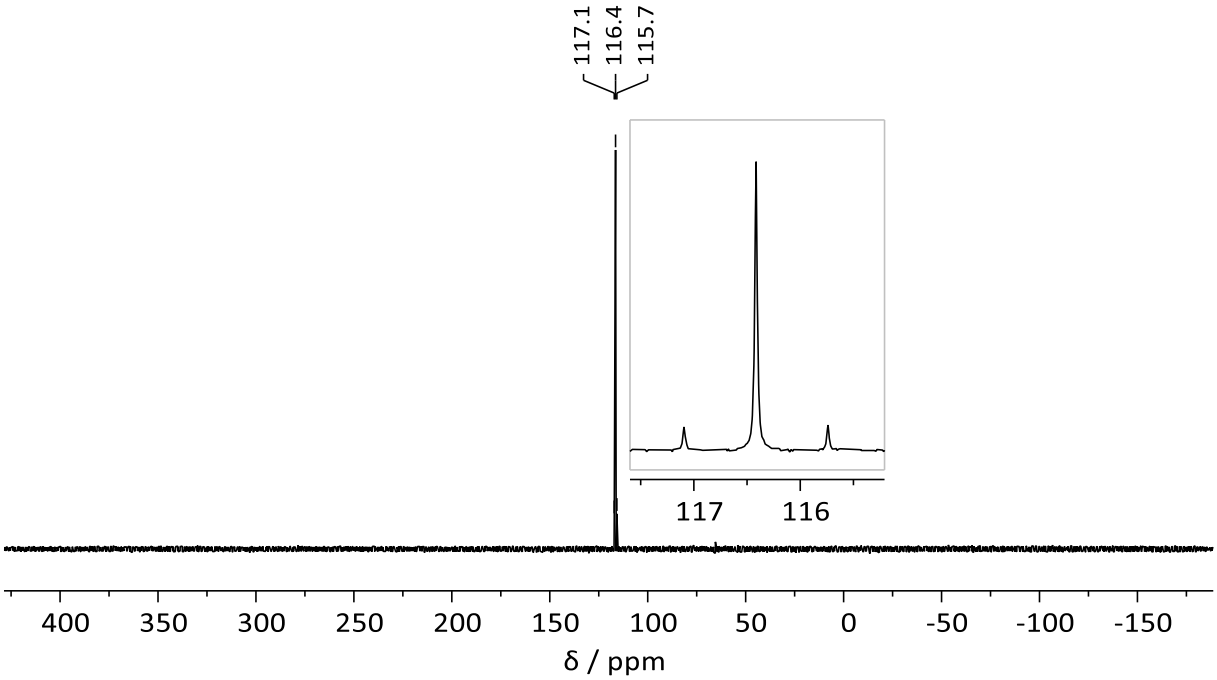


Fig. S89 $^{31}P\{^{1}H\}$ NMR spectrum (202.44 MHz, CD_2Cl_2, 298 K) of compound **12**.

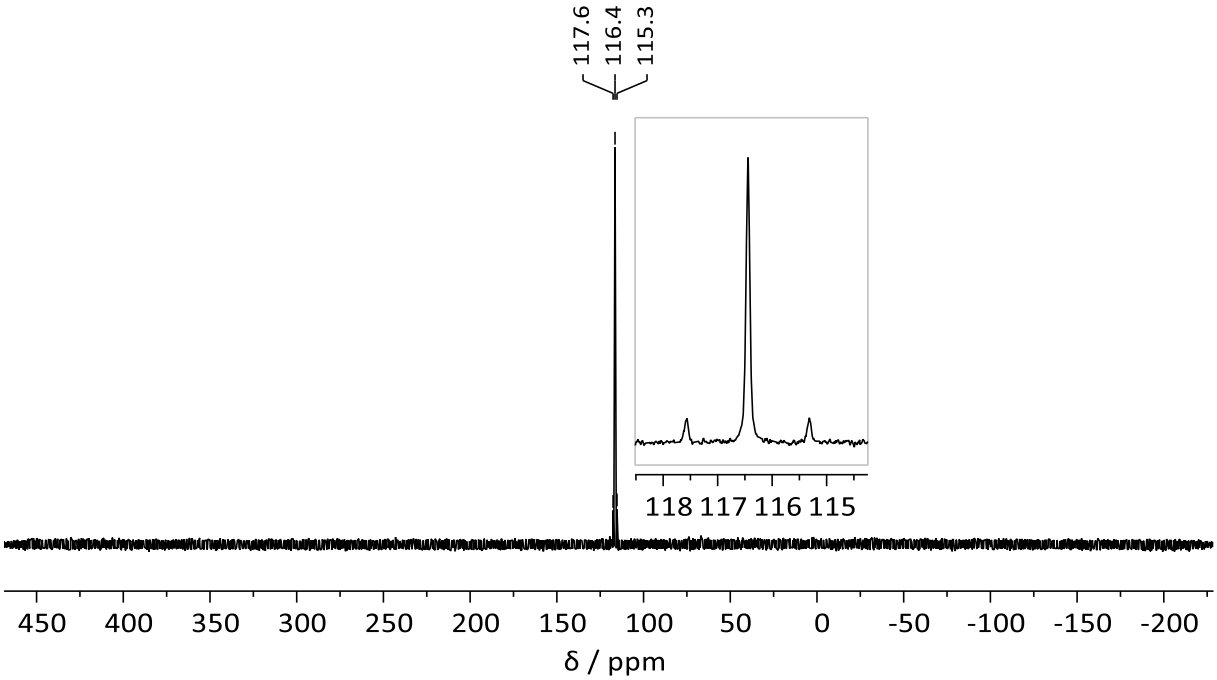


Fig. S90 ^{31}P NMR spectrum (121.51 MHz, CD_2Cl_2, 299 K) of compound **12**.

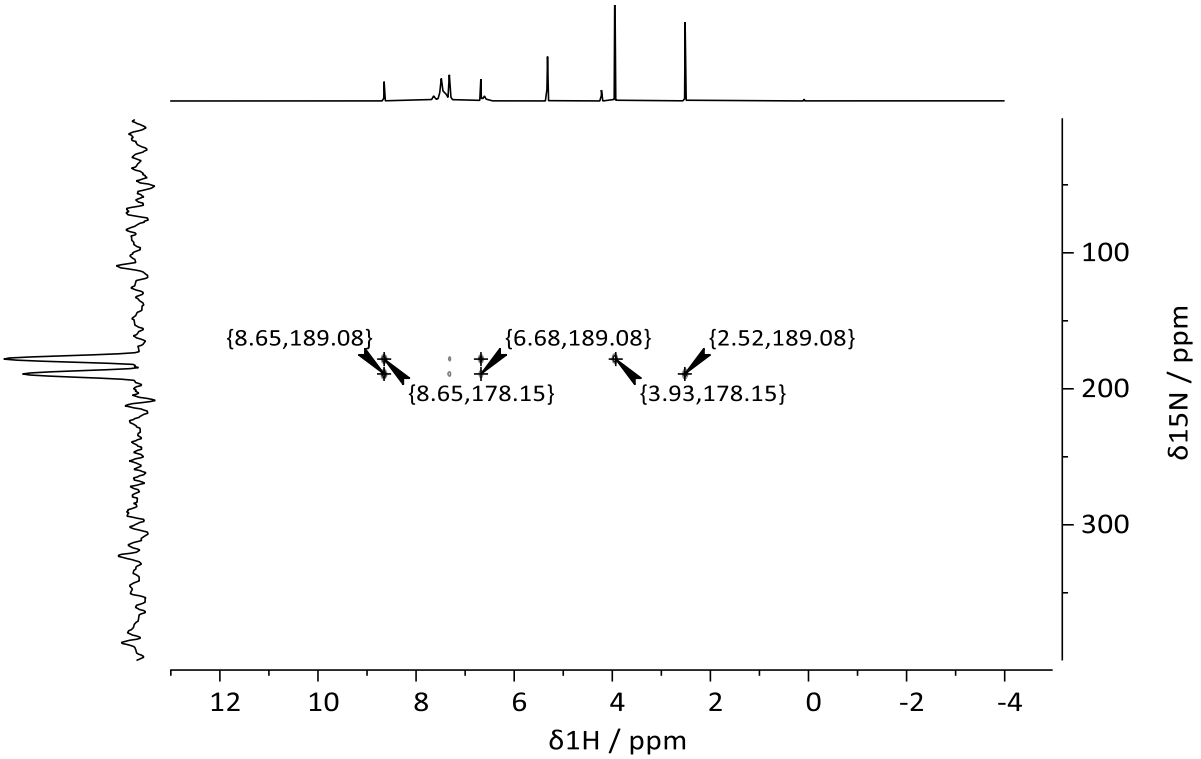


Fig. S91 $^{1}H,^{15}N$ HMBC NMR spectrum (500.04 MHz, 50.68 MHz, CD_2Cl_2, 298 K) of compound **12**.

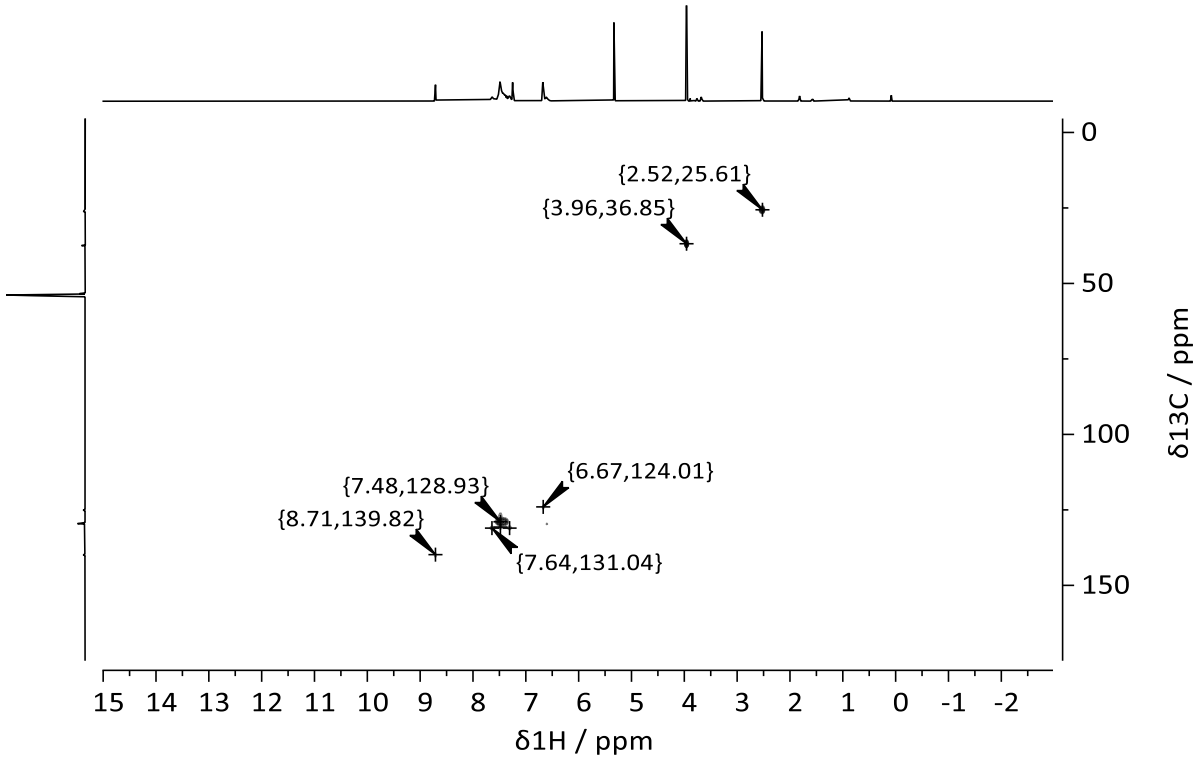


Fig. S92 $^{1}H,^{13}C$ HSQC NMR spectrum (500.04 MHz, 125.75 MHz, CD_2Cl_2, 298 K) of compound **12**.

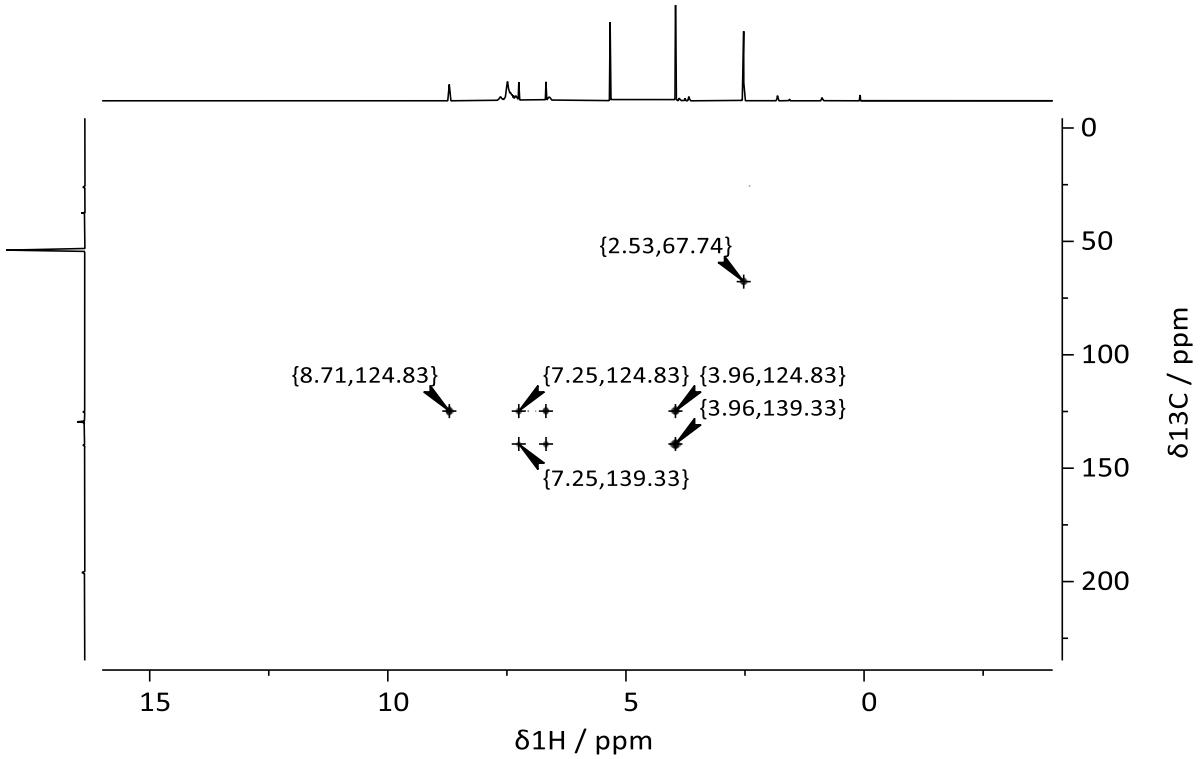


Fig. S93 $^{1}H,^{13}C$ HMBC NMR spectrum (500.04 MHz, 125.75 MHz, CD_2Cl_2, 298 K) of compound **12**.

Compound 12-Cr

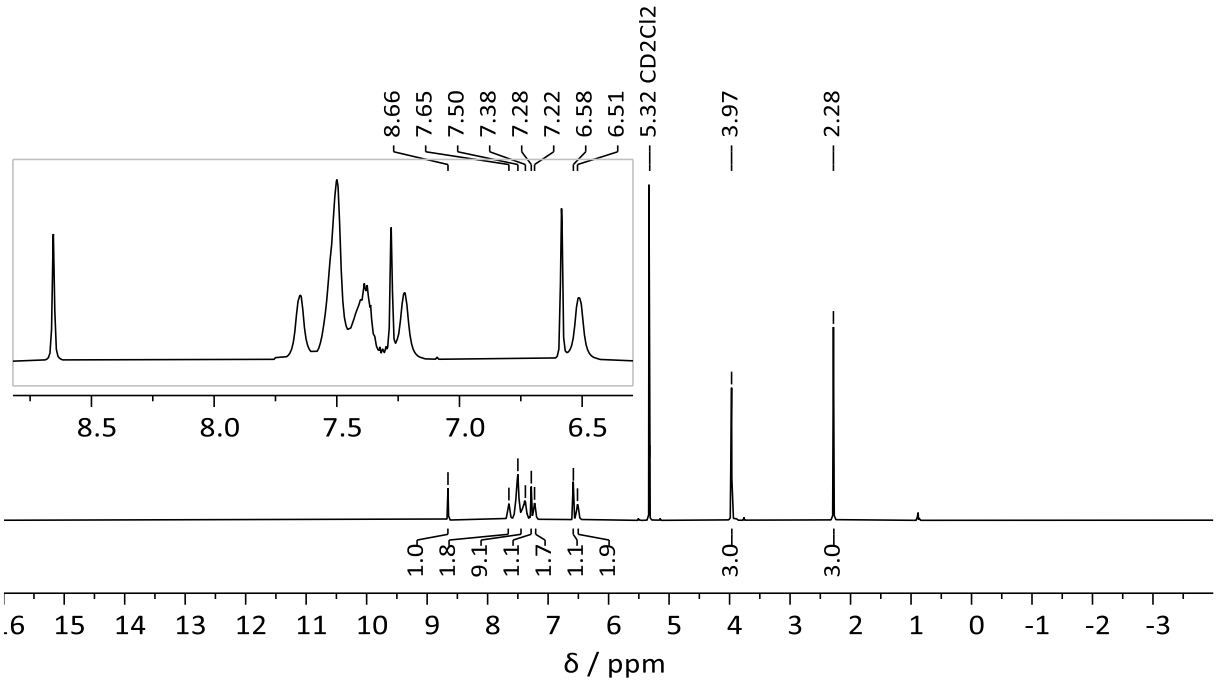


Fig. S94 ^{1}H NMR spectrum (500.04 MHz, CD_2Cl_2, 298 K) of compound **12-Cr**.

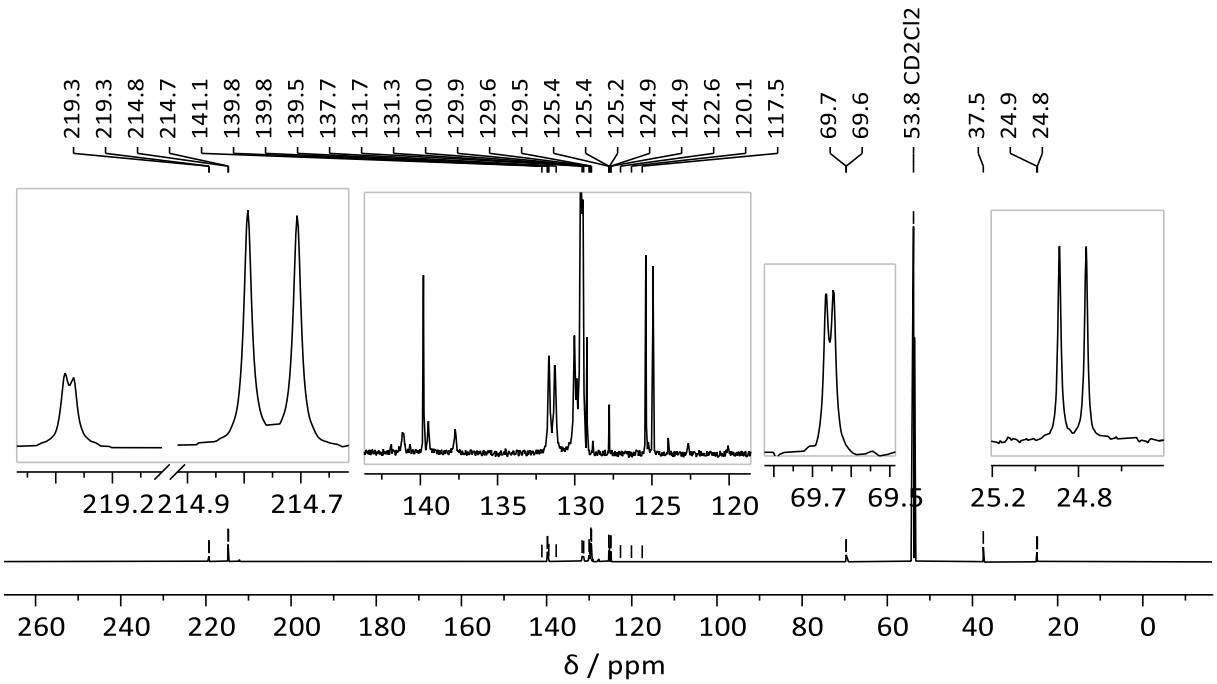


Fig. S95 $^{13}C\{^{1}H\}$ NMR spectrum (125.75 MHz, CD_2Cl_2, 298 K) of compound **12-Cr**.

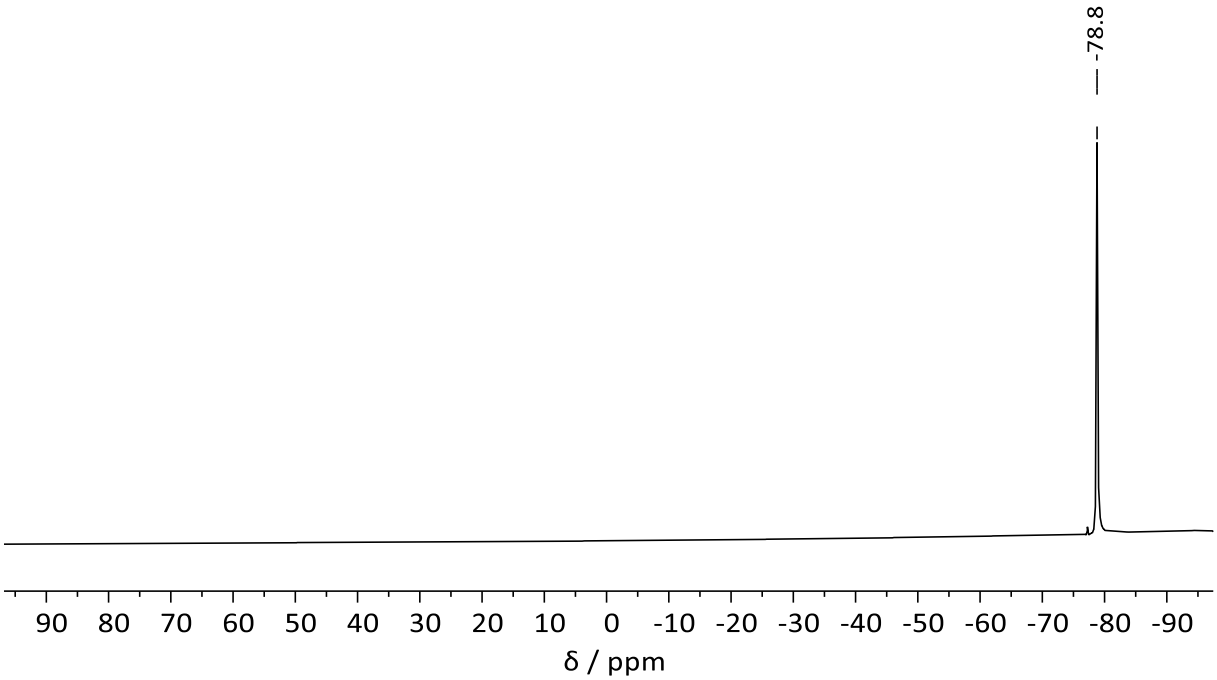


Fig. S96 ^{19}F NMR spectrum (470.51 MHz, CD_2Cl_2, 298 K) of compound **12-Cr**.

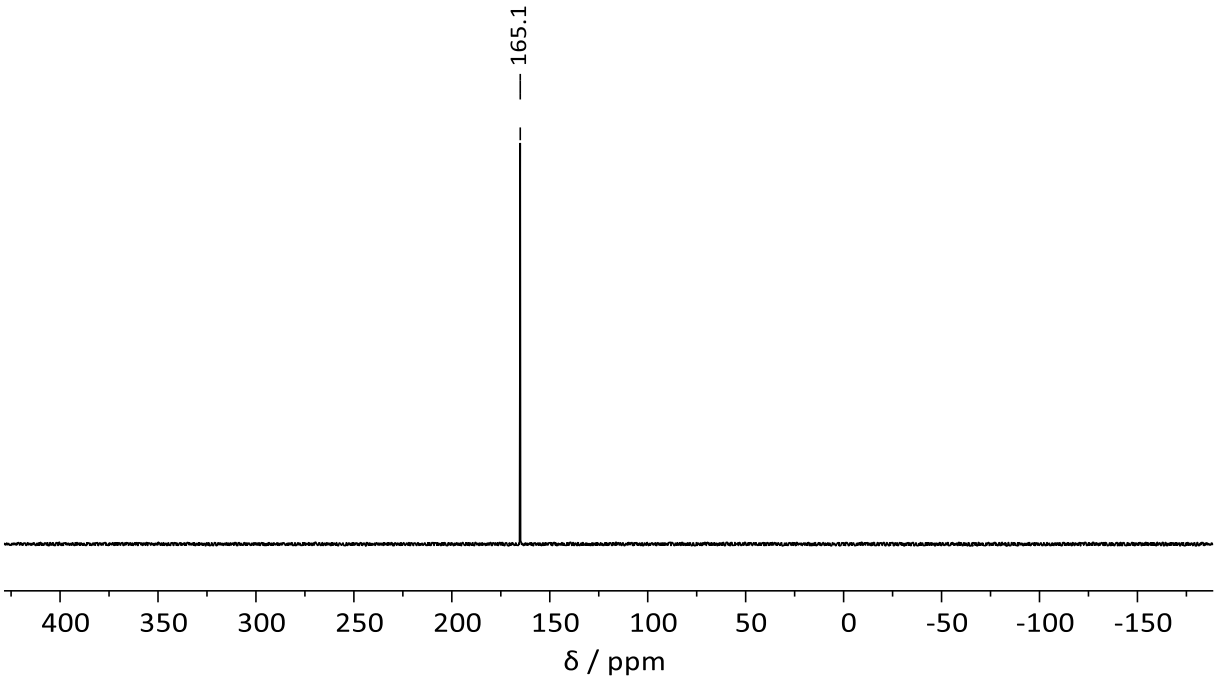


Fig. S97 $^{31}P\{^{1}H\}$ NMR spectrum (202.44 MHz, CD_2Cl_2, 298 K) of compound **12-Cr**.

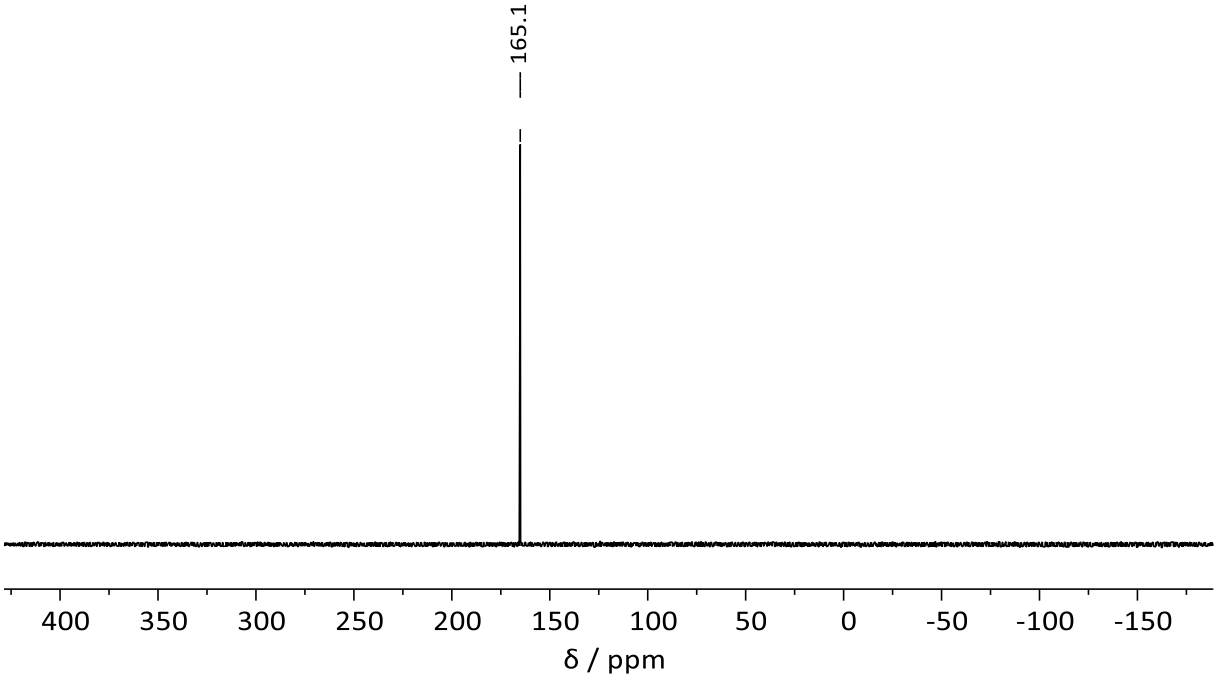


Fig. S98 ^{31}P NMR spectrum (202.44 MHz, CD_2Cl_2, 298 K) of compound **12-Cr**.

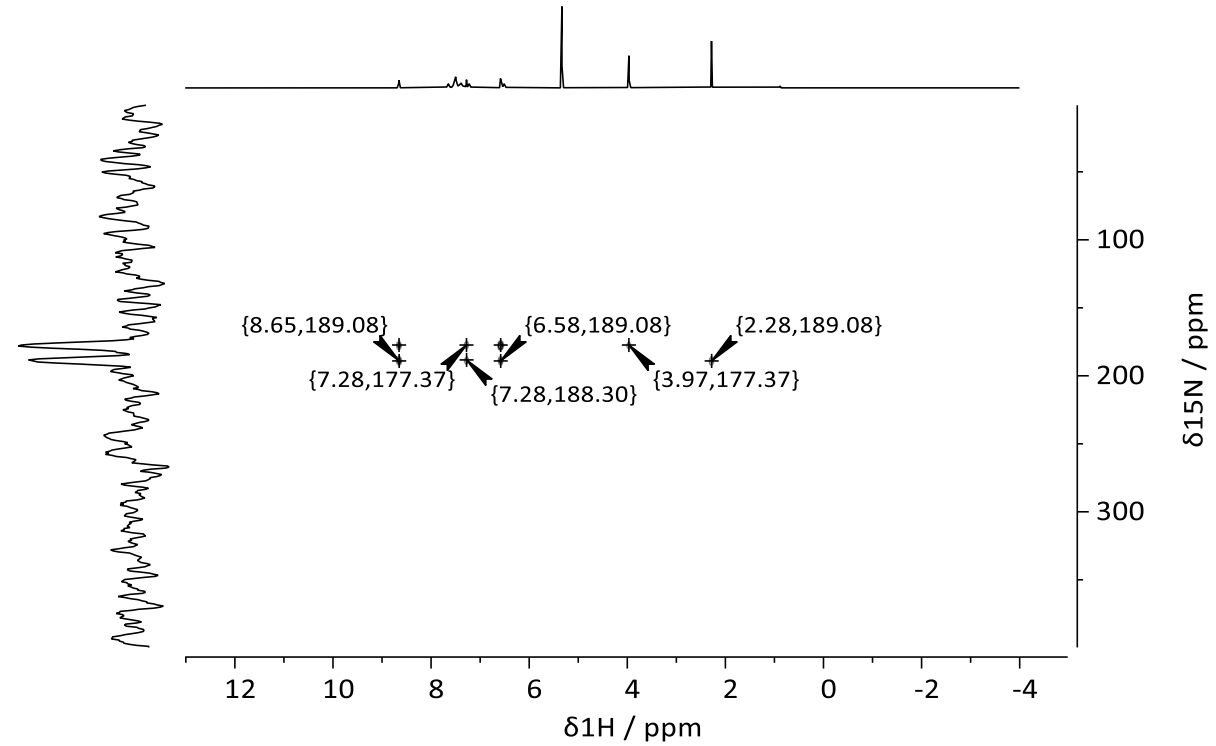


Fig. S99 $^{1}H,^{15}N$ HMBC NMR spectrum (500.04 MHz, 50.68 MHz, CD_2Cl_2, 298 K) of compound **12-Cr**.

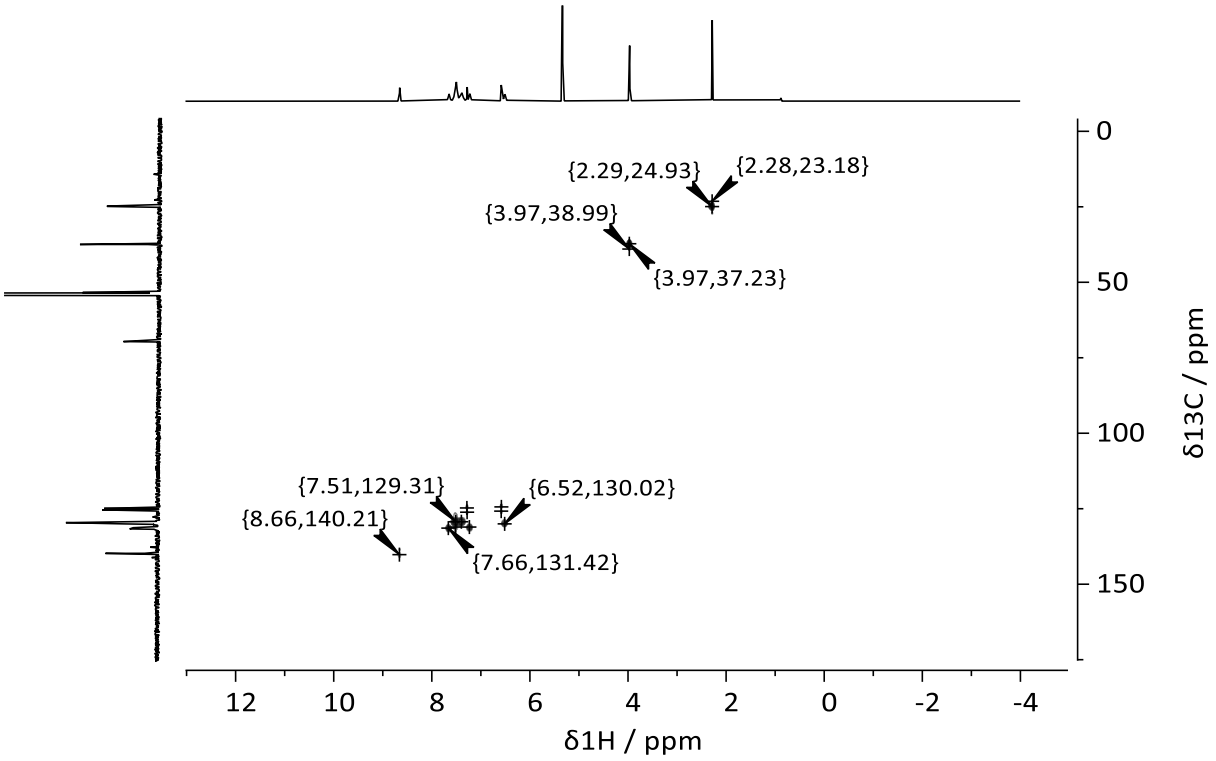


Fig. S100 $^{1}H,^{13}C$ HSQC NMR spectrum (500.04 MHz, 125.75 MHz, CD_2Cl_2, 298 K) of compound **12-Cr**.

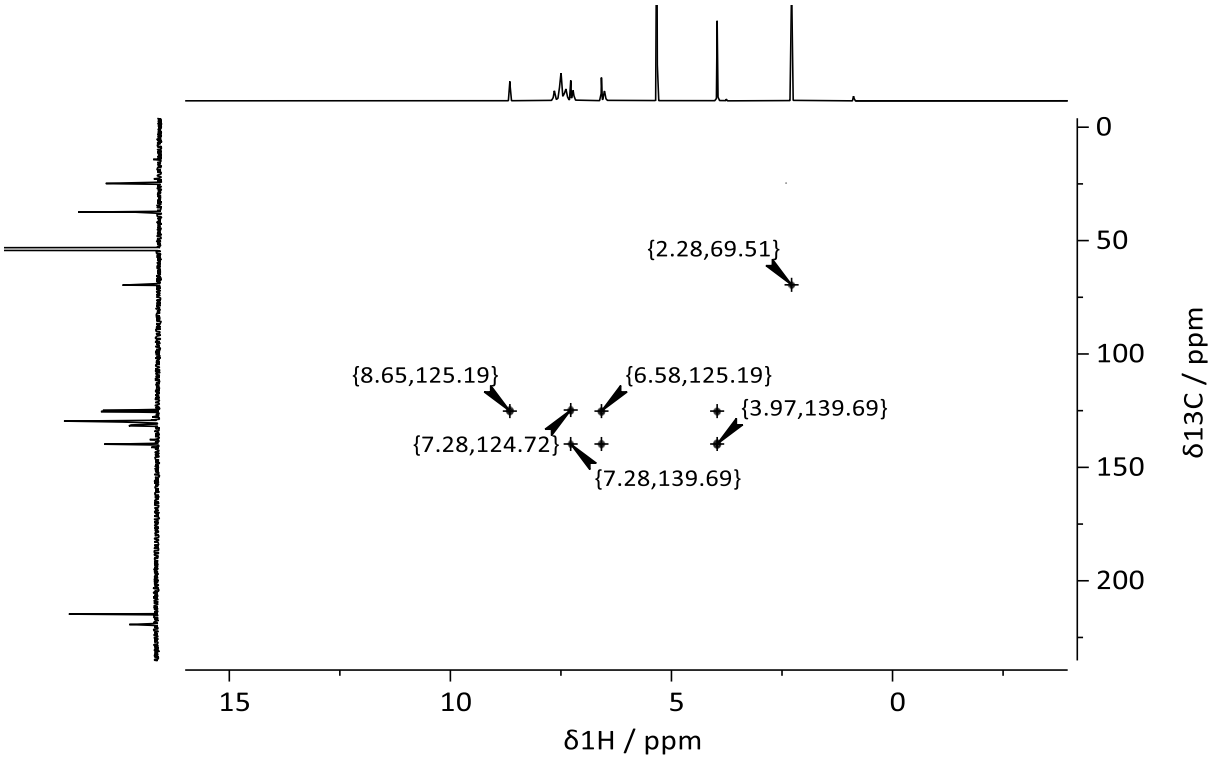


Fig. S101 $^{1}H,^{13}C$ HMBC NMR spectrum (500.04 MHz, 125.75 MHz, CD_2Cl_2, 298 K) of compound **12-Cr**.

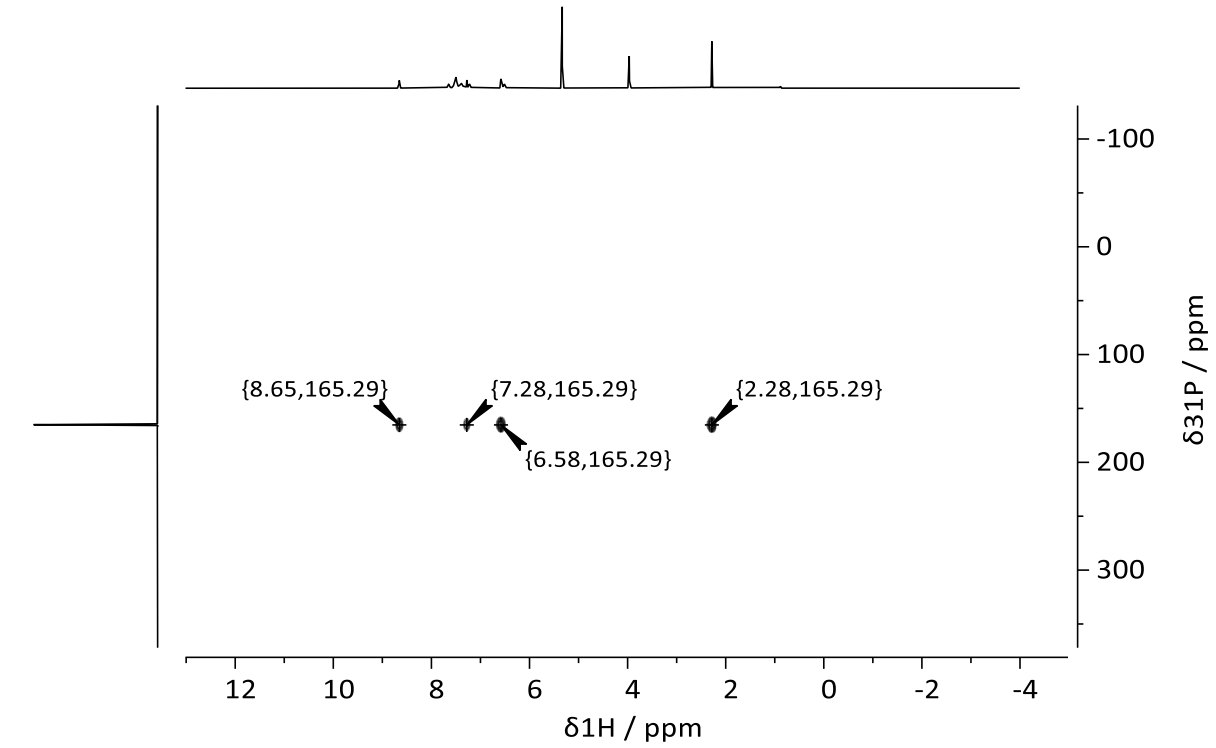


Fig. S102 $^{1}H,^{31}P$ HMBC NMR spectrum (500.04 MHz, 202.44 MHz, CD_2Cl_2, 298 K) of compound **12-Cr**.

4 X-ray diffraction studies

Compound 2

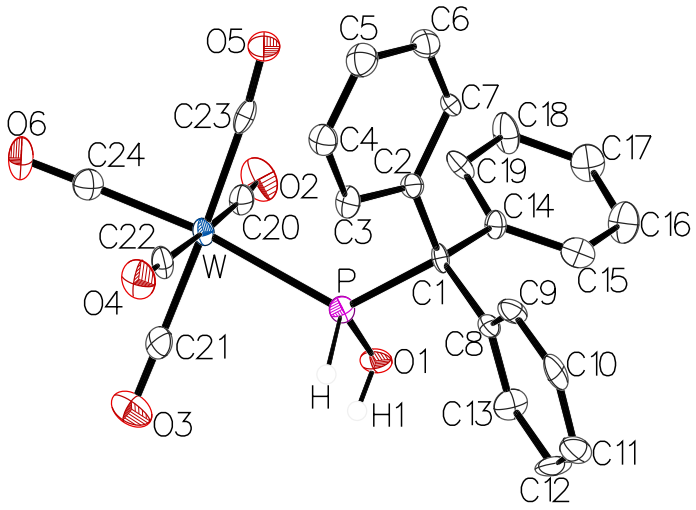


Fig. S103 Molecular structures of **2** in the single crystal lattice at 100(2) K. Thermal ellipsoids are set at 50% probability level. Hydrogen atoms and solvent molecules were omitted for clarity except for those bound to phosphorus and oxygen atoms. Suitable single crystals were obtained as clear colourless blocks by slow evaporation of a solution of 95 mg of **2** in 30 mL of a 1:1 *n*-pentane/diethyl ether mixture at 5 °C. CCDC-2302946.

Table S1 Crystal data and structure refinements for **2**.

Identification code	GSTR738, DB-403 // GXraymo_6721_0m_4
Crystal habitus	clear colourless block
Device type	Bruker D8 Venture
Empirical formula	$C_{52}H_{42}O_{13}P_2W_2$
Moiety formula	2 ($C_{24}H_{17}O_6PW$), C_4H_8O
Formula weight / g/mol	1304.49
T / K	100.0
Crystal system	triclinic
Space group	$P\bar{1}$
a / Å	9.3995(9)
b / Å	11.6790(10)
c / Å	12.0501(11)
α / °	97.985(3)
β / °	91.166(4)
γ / °	109.171(3)
V / Å^3	1234.3(2)
Z	1
ρ_{calc} / g/cm^3	1.755
μ / mm^{-1}	4.786
F(000)	636.0
Crystal size / mm^3	0.4 × 0.24 × 0.2
Absorption correction	empirical
Min. and max. transmission	0.588614 and 0.745472

Radiation	Mo-K_α (λ = 0.71073 Å)
2Θ range for data collection / °	3.736 to 52
Completeness to Θ	0.969
Index ranges	$-11 \le h \le 11$, $-14 \le k \le 14$, $0 \le l \le 14$
Reflections collected	4891
Independent reflections	4891 (R_σ = 0.0860)
Data / restraints / parameters	4891 / 117 / 342
Goodness-of-fit on F^2	1.110
Final R indexes ($I \ge 2\sigma(I)$)	R_1 = 0.0565, ωR_2 = 0.1230
Final R indexes (all data)	R_1 = 0.0745, ωR_2 = 0.1317
Largest diff. peak and hole / e/Å^3	2.06 and −2.81

Table S2 Bond lengths for **2**.

Atom	Atom	Length / Å	Atom	Atom	Length / Å
W	P	2.527(3)	C5	C6	1.390(16)
W	C20	2.053(12)	C6	C7	1.385(15)
W	C21	1.986(12)	C8	C9	1.401(14)
W	C22	2.032(11)	C8	C13	1.383(15)
W	C23	2.017(12)	C9	C10	1.393(15)
W	C24	1.991(11)	C10	C11	1.371(17)
P	O1	1.575(8)	C11	C12	1.404(16)
P	C1	1.919(10)	C12	C13	1.395(15)
O2	C20	1.135(13)	C14	C15	1.386(15)
O3	C21	1.184(14)	C14	C19	1.394(15)
O4	C22	1.154(13)	C15	C16	1.390(16)
O5	C23	1.172(13)	C16	C17	1.387(17)
O6	C24	1.150(13)	C17	C18	1.378(17)
C1	C2	1.521(14)	C18	C19	1.398(15)
C1	C8	1.538(14)	O7	C25	1.361(13)
C1	C14	1.565(14)	O7	C28	1.396(14)
C2	C3	1.405(13)	C25	C26	1.465(13)
C2	C7	1.410(14)	C26	C27	1.474(13)
C3	C4	1.366(15)	C27	C28	1.458(13)
C4	C5	1.391(16)			

Table S3 Bond angles for **2**.

Atom	Atom	Atom	Angle / °	Atom	Atom	Atom	Angle / °
C20	W	P	91.5(3)	C6	C5	C4	117.8(11)
C21	W	P	86.3(3)	C7	C6	C5	121.6(11)
C21	W	C20	90.7(4)	C6	C7	C2	119.8(10)
C21	W	C22	89.2(4)	C9	C8	C1	120.9(9)
C21	W	C23	177.3(5)	C13	C8	C1	122.5(9)
C21	W	C24	87.0(5)	C13	C8	C9	116.6(10)
C22	W	P	90.1(3)	C10	C9	C8	122.2(11)
C22	W	C20	178.4(4)	C11	C10	C9	120.5(10)
C23	W	P	96.0(3)	C10	C11	C12	118.5(10)
C23	W	C20	88.0(4)	C13	C12	C11	120.4(11)
C23	W	C22	92.1(4)	C8	C13	C12	121.8(10)
C24	W	P	173.1(3)	C15	C14	C1	122.6(9)
C24	W	C20	90.1(4)	C15	C14	C19	118.1(10)
C24	W	C22	88.4(4)	C19	C14	C1	119.3(9)
C24	W	C23	90.7(4)	C14	C15	C16	120.6(11)
O1	P	W	113.8(3)	C17	C16	C15	120.2(11)
O1	P	C1	105.8(4)	C18	C17	C16	120.6(11)
C1	P	W	124.1(3)	C17	C18	C19	118.4(11)
C2	C1	P	109.2(6)	C14	C19	C18	122.1(11)
C2	C1	C8	110.2(8)	O2	C20	W	176.6(10)
C2	C1	C14	111.9(9)	O3	C21	W	178.6(9)
C8	C1	P	109.0(7)	O4	C22	W	179.3(9)
C8	C1	C14	111.0(8)	O5	C23	W	174.4(8)
C14	C1	P	105.3(6)	O6	C24	W	178.9(11)
C3	C2	C1	118.8(9)	C25	O7	C28	109.0(13)
C3	C2	C7	118.3(10)	O7	C25	C26	112.0(11)
C7	C2	C1	122.8(9)	C25	C26	C27	103.0(10)
C4	C3	C2	120.5(10)	C28	C27	C26	107.6(10)
C3	C4	C5	122.0(10)	O7	C28	C27	108.3(12)

Table S4 Torsion angles for **2**.

A	B	C	D	Angle / °	A	B	C	D	Angle / °
P	C1	C2	C3	50.3(11)	C8	C1	C14	C15	−1.7(14)
P	C1	C2	C7	−133.5(9)	C8	C1	C14	C19	177.2(9)
P	C1	C8	C9	−129.0(9)	C8	C9	C10	C11	−1.5(17)
P	C1	C8	C13	49.9(12)	C9	C8	C13	C12	0.2(17)
P	C1	C14	C15	−119.6(10)	C9	C10	C11	C12	1.8(17)
P	C1	C14	C19	59.3(11)	C10	C11	C12	C13	−1.1(18)
C1	C2	C3	C4	177.2(9)	C11	C12	C13	C8	0.1(18)
C1	C2	C7	C6	−176.0(9)	C13	C8	C9	C10	0.5(16)
C1	C8	C9	C10	179.4(9)	C14	C1	C2	C3	166.5(9)
C1	C8	C13	C12	−178.7(10)	C14	C1	C2	C7	−17.3(13)
C1	C14	C15	C16	178.8(10)	C14	C1	C8	C9	115.4(11)
C1	C14	C19	C18	−179.7(10)	C14	C1	C8	C13	−65.8(13)
C2	C1	C8	C9	−9.1(13)	C14	C15	C16	C17	0.7(18)
C2	C1	C8	C13	169.7(10)	C15	C14	C19	C18	−0.7(17)
C2	C1	C14	C15	121.9(11)	C15	C16	C17	C18	0(2)
C2	C1	C14	C19	−59.2(12)	C16	C17	C18	C19	−0.4(19)
C2	C3	C4	C5	−2.2(17)	C17	C18	C19	C14	1.0(18)
C3	C2	C7	C6	0.2(15)	C19	C14	C15	C16	−0.1(17)
C3	C4	C5	C6	2.4(17)	O7	C25	C26	C27	1(2)
C4	C5	C6	C7	−1.3(17)	C25	O7	C28	C27	1(2)
C5	C6	C7	C2	0.0(16)	C25	C26	C27	C28	−1(2)
C7	C2	C3	C4	0.8(15)	C26	C27	C28	O7	0(2)
C8	C1	C2	C3	−69.5(11)	C28	O7	C25	C26	−1(2)
C8	C1	C2	C7	106.8(11)					

Compound 10a

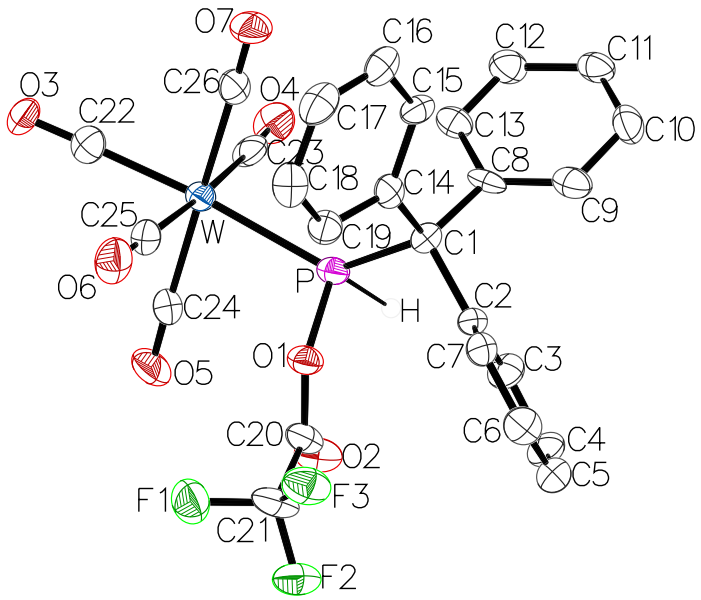


Fig. S104 Molecular structures of **10a** in the single crystal lattice at 123(2) K. Thermal ellipsoids are set at 50% probability level. Hydrogen atoms were omitted for clarity except for those bound to phosphorus atoms. Suitable single crystals were obtained as clear colourless blocks by slow evaporation of a solution of 2.2 mg of **10a** in 0.2 mL of *n*-pentane at ambient temperature in a glovebox. CCDC-2302947.

Table S5 Crystal data and structure refinements for **10a**.

Identification code	GSTR777, DB-550 // GXray6912
Crystal habitus	clear colourless block
Device type	STOE IPDS2T
Empirical formula	$C_{26}H_{16}F_3O_7PW$
Moiety formula	$C_{26}H_{16}F_3O_7PW$
Formula weight / g/mol	712.21
T / K	123(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a / Å	11.7247(3)
b / Å	11.0478(4)
c / Å	19.5690(5)
α / °	90
β / °	95.179(2)
γ / °	90
V / Å^3	2524.47(13)
Z	4
ρ_{calc} / g/cm^3	1.874
μ / mm^{-1}	4.706
F(000)	1376.0
Crystal size / mm^3	0.12 × 0.11 × 0.08
Absorption correction	multi-scan
Min. and max. transmission	0.0215 and 0.9140

Radiation	Mo-K_α (λ = 0.71073 Å)
2Θ range for data collection / °	5.076 to 50.5
Completeness to Θ	0.956
Index ranges	−13 ≤ *h* ≤ 14, −13 ≤ *k* ≤ 13, −23 ≤ *l* ≤ 23
Reflections collected	18095
Independent reflections	4366 (R_{int} = 0.1136, R_σ = 0.0689)
Data / restraints / parameters	4366 / 1 / 347
Goodness-of-fit on F^2	1.064
Final *R* indexes ($I \geq 2\sigma(I)$)	R_1 = 0.0731, ωR_2 = 0.1711
Final *R* indexes (all data)	R_1 = 0.0923, ωR_2 = 0.2016
Largest diff. peak and hole / e/Å^3	2.73 and −1.74

Table S6 Bond lengths for **10a**.

Atom	Atom	Length / Å	Atom	Atom	Length / Å
W	P	2.452(3)	C1	C14	1.503(18)
W	C22	2.001(14)	C2	C3	1.393(19)
W	C23	2.054(14)	C2	C7	1.403(18)
W	C24	2.070(14)	C3	C4	1.42(2)
W	C25	2.043(16)	C4	C5	1.38(2)
W	C26	2.064(13)	C5	C6	1.38(2)
P	O1	1.695(9)	C6	C7	1.40(2)
P	C1	1.915(12)	C8	C9	1.37(2)
F1	C21	1.34(2)	C8	C13	1.402(19)
F2	C21	1.296(18)	C9	C10	1.427(18)
F3	C21	1.339(17)	C10	C11	1.39(2)
O1	C20	1.349(16)	C11	C12	1.41(2)
O2	C20	1.170(17)	C12	C13	1.377(18)
O3	C22	1.143(17)	C14	C15	1.408(17)
O4	C23	1.132(17)	C14	C19	1.403(18)
O5	C24	1.118(17)	C15	C16	1.390(19)
O6	C25	1.125(18)	C16	C17	1.36(2)
O7	C26	1.110(16)	C17	C18	1.38(2)
C1	C2	1.551(17)	C18	C19	1.38(2)
C1	C8	1.553(15)	C20	C21	1.515(18)

Table S7 Bond angles for **10a**.

Atom	Atom	Atom	Angle / °	Atom	Atom	Atom	Angle / °
C22	W	P	175.5(4)	C6	C7	C2	121.0(13)
C22	W	C23	89.5(5)	C9	C8	C1	119.0(11)
C22	W	C24	90.4(6)	C9	C8	C13	120.1(11)
C22	W	C25	87.4(5)	C13	C8	C1	120.5(12)
C22	W	C26	90.0(5)	C8	C9	C10	120.1(13)
C23	W	P	92.0(4)	C11	C10	C9	119.8(13)
C23	W	C24	88.4(5)	C10	C11	C12	119.0(12)
C23	W	C26	91.6(5)	C13	C12	C11	120.8(13)
C24	W	P	85.3(4)	C12	C13	C8	120.2(13)
C25	W	P	91.2(4)	C15	C14	C1	121.9(11)
C25	W	C23	176.8(5)	C19	C14	C1	121.6(11)
C25	W	C24	92.3(5)	C19	C14	C15	116.5(13)
C25	W	C26	87.7(5)	C16	C15	C14	121.6(13)
C26	W	P	94.2(4)	C17	C16	C15	119.3(13)
C26	W	C24	179.5(5)	C16	C17	C18	122.0(14)
O1	P	W	106.6(3)	C17	C18	C19	118.5(14)
O1	P	C1	97.5(5)	C18	C19	C14	122.1(13)
C1	P	W	130.6(4)	O1	C20	C21	109.8(12)
C20	O1	P	124.0(9)	O2	C20	O1	126.1(12)
C2	C1	P	105.8(8)	O2	C20	C21	124.0(12)
C2	C1	C8	109.3(10)	F1	C21	C20	110.4(12)
C8	C1	P	108.2(8)	F2	C21	F1	107.3(11)
C14	C1	P	107.0(8)	F2	C21	F3	109.0(12)
C14	C1	C2	113.9(10)	F2	C21	C20	111.3(14)
C14	C1	C8	112.2(9)	F3	C21	F1	106.5(13)
C3	C2	C1	118.3(12)	F3	C21	C20	112.1(11)
C3	C2	C7	118.9(12)	O3	C22	W	178.8(12)
C7	C2	C1	122.8(11)	O4	C23	W	176.6(12)
C2	C3	C4	119.3(13)	O5	C24	W	178.8(13)
C5	C4	C3	120.6(13)	O6	C25	W	177.6(13)
C6	C5	C4	120.6(14)	O7	C26	W	178.7(13)
C5	C6	C7	119.5(14)				

Table S8 Torsion angles for **10a**.

A	B	C	D	Angle / °	A	B	C	D	Angle / °
W	P	O1	C20	102.8(10)	C2	C3	C4	C5	−2(2)
P	O1	C20	O2	−4(2)	C3	C2	C7	C6	−0.7(18)
P	O1	C20	C21	−179.2(9)	C3	C4	C5	C6	0(2)
P	C1	C2	C3	60.1(13)	C4	C5	C6	C7	1(2)
P	C1	C2	C7	−119.6(11)	C5	C6	C7	C2	−1(2)
P	C1	C8	C9	−148.7(10)	C7	C2	C3	C4	1.8(19)
P	C1	C8	C13	38.1(13)	C8	C1	C2	C3	−56.2(14)
P	C1	C14	C15	−126.6(11)	C8	C1	C2	C7	124.1(12)
P	C1	C14	C19	53.7(14)	C8	C1	C14	C15	−8.0(16)
O1	C20	C21	F1	79.9(14)	C8	C1	C14	C19	172.3(12)
O1	C20	C21	F2	−161.1(12)	C8	C9	C10	C11	−1(2)
O1	C20	C21	F3	−38.7(18)	C9	C8	C13	C12	0.9(19)
O2	C20	C21	F1	−95.6(19)	C9	C10	C11	C12	2(2)
O2	C20	C21	F2	23(2)	C10	C11	C12	C13	−1(2)
O2	C20	C21	F3	145.8(15)	C11	C12	C13	C8	−1(2)
C1	P	O1	C20	−120.7(11)	C13	C8	C9	C10	0.1(19)
C1	C2	C3	C4	−177.9(12)	C14	C1	C2	C3	177.4(11)
C1	C2	C7	C6	179.0(12)	C14	C1	C2	C7	−2.3(16)
C1	C8	C9	C10	−173.2(12)	C14	C1	C8	C9	93.4(14)
C1	C8	C13	C12	174.1(12)	C14	C1	C8	C13	−79.8(14)
C1	C14	C15	C16	178.8(12)	C14	C15	C16	C17	1(2)
C1	C14	C19	C18	−179.6(12)	C15	C14	C19	C18	1(2)
C2	C1	C8	C9	−33.9(15)	C15	C16	C17	C18	1(2)
C2	C1	C8	C13	152.8(11)	C16	C17	C18	C19	−2(2)
C2	C1	C14	C15	116.8(12)	C17	C18	C19	C14	1(2)
C2	C1	C14	C19	−62.9(15)	C19	C14	C15	C16	−1.5(18)

Compound 10a-Cr

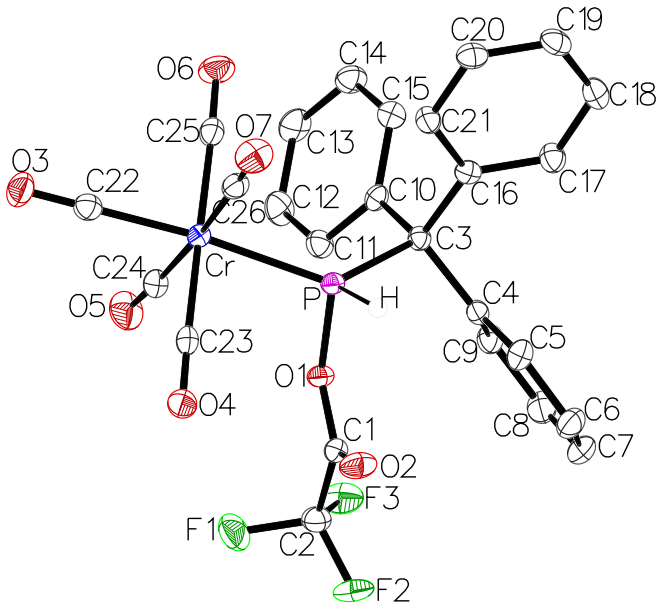


Fig. S105 Molecular structures of **10a-Cr** in the single crystal lattice at 123(2) K. Thermal ellipsoids are set at 50% probability level. Hydrogen atoms were omitted for clarity except for those bound to phosphorus atoms. Suitable single crystals were obtained as clear colourless blocks by slow evaporation of a solution of 1.9 mg of **10a-Cr** in 0.6 mL of *n*-pentane at ambient temperature in a glovebox. CCDC-2302948.

Table S9 Crystal data and structure refinements for **10a-Cr**.

Identification code	GSTR770, DB-557 // GXray6913
Crystal habitus	clear colourless plate
Device type	STOE IPDS-2T
Empirical formula	$C_{26}H_{16}CrF_3O_7P$
Moiety formula	$C_{26}H_{16}CrF_3O_7P$
Formula weight / g/mol	580.36
T / K	123(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a / Å	11.7074(11)
b / Å	10.9879(9)
c / Å	19.4438(23)
α / °	90.00
β / °	95.019(8)
γ / °	90.00
V / Å^3	2491.7(4)
Z	4
ρ_{calc} / g/cm^3	1.547
μ / mm^{-1}	0.17
F(000)	1176.0
Crystal size / mm^3	0.3 × 0.25 × 0.14
Absorption correction	integration

Min. and max. transmission	0.8377 and 0.9602
Radiation	Mo-K_α (λ = 0.71073 Å)
2Θ range for data collection / °	4.206 to 55.992
Completeness to Θ	0.990
Index ranges	$-15 \le h \le 12$, $-14 \le k \le 13$, $-24 \le l \le 25$
Reflections collected	12331
Independent reflections	13501 (R_{int} = 0.0396, R_σ = 0.0468)
Data / restraints / parameters	13501 / 0 / 346
Goodness-of-fit on F^2	1.013
Final R indexes ($I \ge 2\sigma(I)$)	R_1 = 0.0296, ωR_2 = 0.0776
Final R indexes (all data)	R_1 = 0.0433, ωR_2 = 0.0814
Largest diff. peak and hole / e/Å^3	0.39 and −0.50

Table S10 Bond lengths for **10a-Cr**.

Atom	Atom	Length / Å	Atom	Atom	Length / Å
Cr	P	2.3224(5)	C3	C10	1.543(2)
Cr	C22	1.8880(17)	C3	C16	1.5394(19)
Cr	C23	1.9096(17)	C4	C5	1.401(2)
Cr	C24	1.9071(17)	C4	C9	1.393(2)
Cr	C25	1.9158(17)	C5	C6	1.388(2)
Cr	C26	1.9115(16)	C6	C7	1.391(2)
P	O1	1.7017(10)	C7	C8	1.378(3)
P	C3	1.9148(16)	C8	C9	1.395(2)
F1	C2	1.3311(19)	C10	C11	1.400(2)
F2	C2	1.3259(19)	C10	C15	1.392(2)
F3	C2	1.3385(19)	C11	C12	1.385(2)
O1	C1	1.3280(18)	C12	C13	1.392(3)
O2	C1	1.1958(19)	C13	C14	1.381(2)
O3	C22	1.143(2)	C14	C15	1.390(2)
O4	C23	1.143(2)	C16	C17	1.397(2)
O5	C24	1.1388(19)	C16	C21	1.397(2)
O6	C25	1.140(2)	C17	C18	1.389(2)
O7	C26	1.1378(19)	C18	C19	1.393(2)
C1	C2	1.536(2)	C19	C20	1.383(2)
C3	C4	1.548(2)	C20	C21	1.393(2)

Table S11 Bond angles for **10a-Cr**.

Atom	Atom	Atom	Angle / °	Atom	Atom	Atom	Angle / °
C22	Cr	P	174.95(5)	C16	C3	C4	110.18(12)
C22	Cr	C23	90.45(7)	C16	C3	C10	110.43(12)
C22	Cr	C24	87.59(7)	C5	C4	C3	119.15(13)
C22	Cr	C25	90.37(7)	C9	C4	C3	122.72(14)
C22	Cr	C26	88.88(7)	C9	C4	C5	118.13(14)

C23	Cr	P	84.68(5)	C6	C5	C4	121.21(15)
C23	Cr	C25	178.85(7)	C5	C6	C7	119.95(16)
C23	Cr	C26	89.25(7)	C8	C7	C6	119.37(15)
C24	Cr	P	91.10(5)	C7	C8	C9	120.91(15)
C24	Cr	C23	90.88(7)	C4	C9	C8	120.40(15)
C24	Cr	C25	88.36(7)	C11	C10	C3	120.07(13)
C24	Cr	C26	176.46(7)	C15	C10	C3	121.96(13)
C25	Cr	P	94.47(5)	C15	C10	C11	117.96(14)
C26	Cr	P	92.43(5)	C12	C11	C10	121.05(15)
C26	Cr	C25	91.56(7)	C11	C12	C13	120.36(16)
O1	P	Cr	106.46(4)	C14	C13	C12	119.03(15)
O1	P	C3	97.56(6)	C13	C14	C15	120.73(16)
C3	P	Cr	131.96(5)	C14	C15	C10	120.87(15)
C1	O1	P	124.16(9)	C17	C16	C3	119.58(13)
O1	C1	C2	109.26(12)	C17	C16	C21	118.30(13)
O2	C1	O1	127.93(14)	C21	C16	C3	121.86(14)
O2	C1	C2	122.74(14)	C18	C17	C16	120.82(14)
F1	C2	F3	107.63(14)	C17	C18	C19	120.32(16)
F1	C2	C1	109.83(13)	C20	C19	C18	119.44(14)
F2	C2	F1	108.75(13)	C19	C20	C21	120.32(14)
F2	C2	F3	108.41(13)	C20	C21	C16	120.80(15)
F2	C2	C1	110.39(13)	O3	C22	Cr	178.80(14)
F3	C2	C1	111.75(13)	O4	C23	Cr	178.32(15)
C4	C3	P	106.61(10)	O5	C24	Cr	176.75(15)
C10	C3	P	107.29(10)	O6	C25	Cr	177.71(14)
C10	C3	C4	113.57(12)	O7	C26	Cr	177.31(15)
C16	C3	P	108.54(10)				

Compound 11a

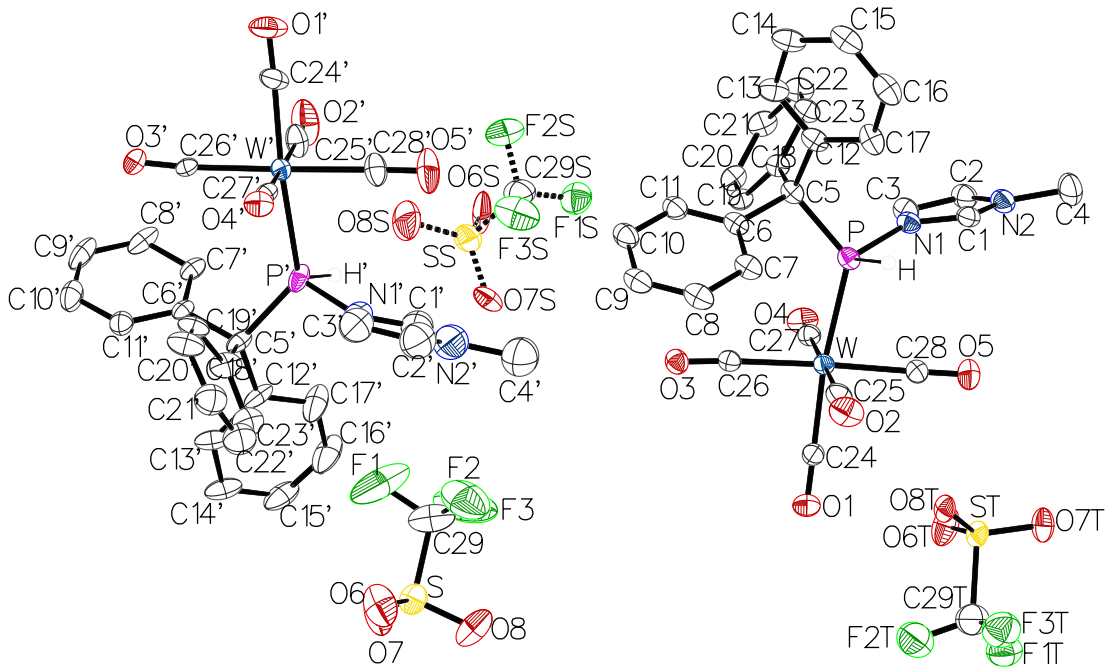


Fig. S106 Molecular structures of **11a** in the single crystal lattice at 100(2) K. Thermal ellipsoids are set at 50% probability level. Solvent molecules and hydrogen atoms were omitted for clarity except for those bound to phosphorus atoms. Suitable single crystals were obtained as clear colourless blocks by vapour diffusion of *n*-pentane into a concentrated solution of **11a** in dichloromethane at −40 °C in a glovebox. CCDC-2302949.

Table S12 Crystal data and structure refinements for **11a**.

Identification code	GSTR794, DB-571-2 // GXraymo_7115f
Crystal habitus	clear colourless block
Device type	Bruker D8 Venture
Empirical formula	$C_{30.25}H_{25}F_3N_2O_8PSW$
Moiety formula	$C_{28}H_{22}N_2O_5PW$, CF_3O_3S, 0.25 (C_5H_{12})
Formula weight / g/mol	848.40
T / K	100.0
Crystal system	monoclinic
Space group	*C*2/*c*
a / Å	54.221(3)
b / Å	8.9542(5)
c / Å	32.5364(19)
α / °	90
β / °	125.097(2)
γ / °	90
V / Å^3	12924.5(13)
Z	16
ρ_{calc} / g/cm^3	1.744
μ / mm^{-1}	3.758
F(000)	6664.0
Crystal size / mm^3	0.24 × 0.08 × 0.06

Absorption correction	multi-scan
Min. and max. transmission	0.5844 and 0.7464
Radiation	Mo-K_α (λ = 0.71073 Å)
2Θ range for data collection / °	3.672 to 58.5
Completeness to Θ	0.999
Index ranges	$-74 \le h \le 74$, $-12 \le k \le 12$, $-44 \le l \le 43$
Reflections collected	145150
Independent reflections	17600 (R_{int} = 0.0551, R_σ = 0.0319)
Data / restraints / parameters	17600 / 942 / 940
Goodness-of-fit on F^2	1.035
Final R indexes ($I \ge 2\sigma(I)$)	R_1 = 0.0452, ωR_2 = 0.1066
Final R indexes (all data)	R_1 = 0.0510, ωR_2 = 0.1104
Largest diff. peak and hole / e/Å^3	2.91 and −1.68

Table S13 Bond lengths for **11a**.

Atom	Atom	Length / Å	Atom	Atom	Length / Å
W	P	2.4815(12)	N1'	C1'	1.372(9)
W	C24	2.018(5)	N1'	C3'	1.423(9)
W	C25	2.051(5)	N2'	C1'	1.363(10)
W	C26	2.055(5)	N2'	C2'	1.291(11)
W	C27	2.046(5)	N2'	C4'	1.529(11)
W	C28	2.039(5)	C2'	C3'	1.382(11)
P	N1	1.776(4)	C5'	C6'	1.530(6)
P	C5	1.894(5)	C5'	C12'	1.547(6)
O1	C24	1.147(6)	C5'	C18'	1.538(7)
O2	C25	1.136(6)	C6'	C7'	1.394(6)
O3	C26	1.140(6)	C6'	C11'	1.394(7)
O4	C27	1.140(6)	C7'	C8'	1.387(6)
O5	C28	1.143(6)	C8'	C9'	1.373(9)
N1	C1	1.334(6)	C9'	C10'	1.391(9)
N1	C3	1.398(6)	C10'	C11'	1.386(7)
N2	C1	1.322(6)	C12'	C13'	1.395(8)
N2	C2	1.386(7)	C12'	C17'	1.366(8)
N2	C4	1.460(7)	C13'	C14'	1.386(7)
C2	C3	1.346(7)	C14'	C15'	1.372(9)
C5	C6	1.540(6)	C15'	C16'	1.359(10)
C5	C12	1.545(6)	C16'	C17'	1.420(8)
C5	C18	1.537(6)	C18'	C19'	1.394(7)
C6	C7	1.399(7)	C18'	C23'	1.388(8)
C6	C11	1.378(7)	C19'	C20'	1.389(7)
C7	C8	1.399(7)	C20'	C21'	1.376(9)
C8	C9	1.371(8)	C21'	C22'	1.340(10)
C9	C10	1.391(8)	C22'	C23'	1.409(9)
C10	C11	1.400(7)	S	O6	1.446(5)

C12	C13	1.393(7)	S	O7	1.426(5)
C12	C17	1.390(7)	S	O8	1.433(5)
C13	C14	1.395(7)	S	C29	1.775(8)
C14	C15	1.395(8)	F1	C29	1.330(11)
C15	C16	1.382(9)	F2	C29	1.349(11)
C16	C17	1.405(7)	F3	C29	1.322(11)
C18	C19	1.397(6)	SS	O6S	1.435(8)
C18	C23	1.402(6)	SS	O7S	1.394(9)
C19	C20	1.394(6)	SS	O8S	1.455(8)
C20	C21	1.390(7)	SS	C29S	1.806(11)
C21	C22	1.392(7)	F1S	C29S	1.275(12)
C22	C23	1.393(6)	F2S	C29S	1.326(11)
W'	P'	2.4947(13)	F3S	C29S	1.337(12)
W'	C24'	2.002(5)	ST	O6T	1.442(9)
W'	C25'	2.041(5)	ST	O7T	1.417(8)
W'	C26'	2.044(4)	ST	O8T	1.441(7)
W'	C27'	2.065(5)	ST	C29T	1.859(12)
W'	C28'	2.052(5)	F1T	C29T	1.334(12)
P'	N1'	1.776(5)	F2T	C29T	1.297(13)
P'	C5'	1.889(5)	F3T	C29T	1.350(13)
O1'	C24'	1.144(6)	C30	C31	1.5191(10)
O2'	C25'	1.135(7)	C31	C32	1.5200(10)
O3'	C26'	1.138(5)	C32	C33	1.5204(10)
O4'	C27'	1.129(6)	C33	C34	1.5201(10)
O5'	C28'	1.135(7)			

Table S14 Bond angles for **11a**.

Atom	Atom	Atom	Angle / ˚	Atom	Atom	Atom	Angle / ˚
C24	W	P	172.72(14)	C3'	N1'	P'	125.3(5)
C24	W	C25	88.8(2)	C1'	N2'	C4'	116.9(7)
C24	W	C26	88.69(18)	C2'	N2'	C1'	112.7(7)
C24	W	C27	90.23(18)	C2'	N2'	C4'	130.4(8)
C24	W	C28	88.73(19)	N2'	C1'	N1'	103.5(6)
C25	W	P	86.12(14)	N2'	C2'	C3'	110.5(8)
C25	W	C26	89.52(19)	C2'	C3'	N1'	102.4(7)
C26	W	P	96.43(13)	C6'	C5'	P'	105.7(3)
C27	W	P	94.85(13)	C6'	C5'	C12'	106.4(3)
C27	W	C25	178.9(2)	C6'	C5'	C18'	113.6(4)
C27	W	C26	90.87(18)	C12'	C5'	P'	116.3(4)
C28	W	P	86.22(15)	C18'	C5'	P'	103.4(3)
C28	W	C25	91.2(2)	C18'	C5'	C12'	111.6(4)
C28	W	C26	177.29(19)	C7'	C6'	C5'	119.3(4)
C28	W	C27	88.3(2)	C11'	C6'	C5'	122.2(4)
N1	P	W	110.94(14)	C11'	C6'	C7'	118.4(4)
N1	P	C5	103.78(19)	C8'	C7'	C6'	121.0(5)

C5	P	W	127.57(15)	C9'	C8'	C7'	120.3(5)
C1	N1	P	124.9(3)	C8'	C9'	C10'	119.3(5)
C1	N1	C3	107.9(4)	C11'	C10'	C9'	120.8(5)
C3	N1	P	125.4(3)	C10'	C11'	C6'	120.2(5)
C1	N2	C2	109.0(4)	C13'	C12'	C5'	116.5(5)
C1	N2	C4	125.7(5)	C17'	C12'	C5'	125.6(5)
C2	N2	C4	125.3(5)	C17'	C12'	C13'	117.8(5)
N2	C1	N1	109.0(5)	C14'	C13'	C12'	121.5(6)
C3	C2	N2	107.0(5)	C15'	C14'	C13'	120.0(6)
C2	C3	N1	107.1(5)	C16'	C15'	C14'	119.8(5)
C6	C5	P	104.6(3)	C15'	C16'	C17'	120.3(7)
C6	C5	C12	106.3(4)	C12'	C17'	C16'	120.6(7)
C12	C5	P	117.2(3)	C19'	C18'	C5'	119.5(5)
C18	C5	P	103.6(3)	C23'	C18'	C5'	123.1(5)
C18	C5	C6	114.5(4)	C23'	C18'	C19'	117.3(5)
C18	C5	C12	110.8(4)	C20'	C19'	C18'	120.7(5)
C7	C6	C5	118.4(4)	C21'	C20'	C19'	120.3(6)
C11	C6	C5	122.4(4)	C22'	C21'	C20'	120.5(7)
C11	C6	C7	119.1(4)	C21'	C22'	C23'	119.9(7)
C6	C7	C8	120.3(5)	C18'	C23'	C22'	121.2(6)
C9	C8	C7	120.4(5)	O1'	C24'	W'	177.6(5)
C8	C9	C10	119.4(5)	O2'	C25'	W'	177.1(6)
C9	C10	C11	120.5(5)	O3'	C26'	W'	175.4(4)
C6	C11	C10	120.2(5)	O4'	C27'	W'	177.0(4)
C13	C12	C5	116.4(4)	O5'	C28'	W'	178.6(6)
C17	C12	C5	125.0(5)	O6	S	C29	104.6(4)
C17	C12	C13	118.6(5)	O7	S	O6	117.4(3)
C12	C13	C14	121.5(5)	O7	S	O8	113.8(3)
C15	C14	C13	119.6(6)	O7	S	C29	103.0(4)
C16	C15	C14	119.1(5)	O8	S	O6	113.1(3)
C15	C16	C17	121.1(5)	O8	S	C29	102.5(4)
C12	C17	C16	120.0(5)	F1	C29	S	110.9(8)
C19	C18	C5	120.8(4)	F1	C29	F2	106.6(8)
C19	C18	C23	118.5(4)	F2	C29	S	110.8(6)
C23	C18	C5	120.3(4)	F3	C29	S	111.8(6)
C20	C19	C18	120.4(4)	F3	C29	F1	109.4(8)
C21	C20	C19	121.0(5)	F3	C29	F2	107.1(9)
C20	C21	C22	118.8(5)	O6S	SS	O8S	114.0(5)
C21	C22	C23	120.6(5)	O6S	SS	C29S	100.5(5)
C22	C23	C18	120.7(5)	O7S	SS	O6S	117.9(5)
O1	C24	W	179.3(4)	O7S	SS	O8S	116.6(5)
O2	C25	W	178.8(7)	O7S	SS	C29S	101.8(8)
O3	C26	W	176.6(4)	O8S	SS	C29S	102.0(6)
O4	C27	W	177.5(4)	F1S	C29S	SS	110.4(7)
O5	C28	W	177.6(5)	F1S	C29S	F2S	108.3(9)
C24'	W'	P'	173.81(17)	F1S	C29S	F3S	107.3(10)

C24'	W'	C25'	88.5(2)	F2S	C29S	SS	111.4(8)
C24'	W'	C26'	87.3(2)	F2S	C29S	F3S	109.6(9)
C24'	W'	C27'	88.8(2)	F3S	C29S	SS	109.7(8)
C24'	W'	C28'	91.9(2)	O6T	ST	C29T	104.4(6)
C25'	W'	P'	86.61(18)	O7T	ST	O6T	115.4(5)
C25'	W'	C26'	89.44(19)	O7T	ST	O8T	116.3(6)
C25'	W'	C27'	177.2(2)	O7T	ST	C29T	101.2(5)
C25'	W'	C28'	89.7(2)	O8T	ST	O6T	114.8(5)
C26'	W'	P'	96.50(12)	O8T	ST	C29T	101.7(5)
C26'	W'	C27'	91.40(17)	F1T	C29T	ST	109.6(8)
C26'	W'	C28'	178.8(2)	F1T	C29T	F3T	107.4(8)
C27'	W'	P'	95.98(13)	F2T	C29T	ST	112.7(9)
C28'	W'	P'	84.25(17)	F2T	C29T	F1T	110.5(9)
C28'	W'	C27'	89.4(2)	F2T	C29T	F3T	109.5(9)
N1'	P'	W'	110.87(17)	F3T	C29T	ST	107.0(8)
N1'	P'	C5'	103.1(2)	C30	C31	C32	113.45(11)
C5'	P'	W'	127.84(15)	C31	C32	C33	113.30(11)
C1'	N1'	P'	122.2(5)	C32	C33	C34	113.32(11)
C1'	N1'	C3'	110.9(6)				

Table S15 Torsion angles for **11a**.

A	B	C	D	Angle / ˚	A	B	C	D	Angle / ˚
W	P	N1	C1	−104.3(4)	N1'	P'	C5'	C18'	53.1(4)
W	P	N1	C3	58.9(4)	N2'	C2'	C3'	N1'	−1.9(9)
W	P	C5	C6	43.1(3)	C1'	N1'	C3'	C2'	1.1(8)
W	P	C5	C12	160.4(2)	C1'	N2'	C2'	C3'	2.1(10)
W	P	C5	C18	−77.2(3)	C2'	N2'	C1'	N1'	−1.3(8)
P	N1	C1	N2	165.9(3)	C3'	N1'	C1'	N2'	0.0(8)
P	N1	C3	C2	−166.5(4)	C4'	N2'	C1'	N1'	−179.7(6)
P	C5	C6	C7	45.6(5)	C4'	N2'	C2'	C3'	−179.8(8)
P	C5	C6	C11	−138.5(4)	C5'	P'	N1'	C1'	113.9(5)
P	C5	C12	C13	177.6(3)	C5'	P'	N1'	C3'	−81.8(6)
P	C5	C12	C17	−4.0(6)	C5'	C6'	C7'	C8'	178.2(4)
P	C5	C18	C19	71.1(5)	C5'	C6'	C11'	C10'	−176.1(4)
P	C5	C18	C23	−101.4(4)	C5'	C12'	C13'	C14'	177.0(5)
N1	P	C5	C6	173.8(3)	C5'	C12'	C17'	C16'	−177.6(6)
N1	P	C5	C12	−68.8(3)	C5'	C18'	C19'	C20'	−174.1(5)
N1	P	C5	C18	53.5(3)	C5'	C18'	C23'	C22'	174.0(6)
N2	C2	C3	N1	1.3(6)	C6'	C5'	C12'	C13'	−56.3(6)
C1	N1	C3	C2	−1.0(6)	C6'	C5'	C12'	C17'	120.9(6)
C1	N2	C2	C3	−1.1(6)	C6'	C5'	C18'	C19'	−44.3(6)
C2	N2	C1	N1	0.4(6)	C6'	C5'	C18'	C23'	139.9(5)
C3	N1	C1	N2	0.3(5)	C6'	C7'	C8'	C9'	−2.4(7)
C4	N2	C1	N1	178.8(5)	C7'	C6'	C11'	C10'	−0.4(7)
C4	N2	C2	C3	−179.5(5)	C7'	C8'	C9'	C10'	0.4(8)

C5	P	N1	C1	115.7(4)	C8'	C9'	C10'	C11'	1.5(8)
C5	P	N1	C3	−81.2(4)	C9'	C10'	C11'	C6'	−1.5(8)
C5	C6	C7	C8	179.5(4)	C11'	C6'	C7'	C8'	2.4(6)
C5	C6	C11	C10	−176.8(4)	C12'	C5'	C6'	C7'	−77.9(5)
C5	C12	C13	C14	179.7(4)	C12'	C5'	C6'	C11'	97.7(5)
C5	C12	C17	C16	−179.5(4)	C12'	C5'	C18'	C19'	−164.6(5)
C5	C18	C19	C20	−173.4(4)	C12'	C5'	C18'	C23'	19.7(7)
C5	C18	C23	C22	173.4(5)	C12'	C13'	C14'	C15'	1.4(8)
C6	C5	C12	C13	−66.0(5)	C13'	C12'	C17'	C16'	−0.3(10)
C6	C5	C12	C17	112.5(5)	C13'	C14'	C15'	C16'	−1.4(9)
C6	C5	C18	C19	−42.1(6)	C14'	C15'	C16'	C17'	0.6(12)
C6	C5	C18	C23	145.3(4)	C15'	C16'	C17'	C12'	0.3(13)
C6	C7	C8	C9	−3.3(7)	C17'	C12'	C13'	C14'	−0.4(8)
C7	C6	C11	C10	−0.9(7)	C18'	C5'	C6'	C7'	158.9(4)
C7	C8	C9	C10	0.5(7)	C18'	C5'	C6'	C11'	−25.5(6)
C8	C9	C10	C11	2.1(8)	C18'	C5'	C12'	C13'	68.1(6)
C9	C10	C11	C6	−1.9(8)	C18'	C5'	C12'	C17'	−114.6(7)
C11	C6	C7	C8	3.5(7)	C18'	C19'	C20'	C21'	0.6(9)
C12	C5	C6	C7	−79.0(5)	C19'	C18'	C23'	C22'	−1.9(9)
C12	C5	C6	C11	96.9(5)	C19'	C20'	C21'	C22'	−3.3(10)
C12	C5	C18	C19	−162.4(4)	C20'	C21'	C22'	C23'	3.4(11)
C12	C5	C18	C23	25.0(6)	C21'	C22'	C23'	C18'	−0.7(10)
C12	C13	C14	C15	−0.2(8)	C23'	C18'	C19'	C20'	1.9(8)
C13	C12	C17	C16	−1.1(7)	O6	S	C29	F1	−61.1(8)
C13	C14	C15	C16	−0.9(8)	O6	S	C29	F2	57.2(8)
C14	C15	C16	C17	1.0(8)	O6	S	C29	F3	176.6(7)
C15	C16	C17	C12	0.0(8)	O7	S	C29	F1	62.2(8)
C17	C12	C13	C14	1.2(7)	O7	S	C29	F2	−179.5(6)
C18	C5	C6	C7	158.2(4)	O7	S	C29	F3	−60.2(8)
C18	C5	C6	C11	−25.9(6)	O8	S	C29	F1	−179.3(7)
C18	C5	C12	C13	59.1(5)	O8	S	C29	F2	−61.1(7)
C18	C5	C12	C17	−122.5(5)	O8	S	C29	F3	58.3(8)
C18	C19	C20	C21	0.8(7)	O6S	SS	C29S	F1S	−57.1(9)
C19	C18	C23	C22	0.7(7)	O6S	SS	C29S	F2S	63.3(9)
C19	C20	C21	C22	−0.9(8)	O6S	SS	C29S	F3S	−175.1(8)
C20	C21	C22	C23	1.0(8)	O7S	SS	C29S	F1S	64.6(9)
C21	C22	C23	C18	−0.8(8)	O7S	SS	C29S	F2S	−175.0(8)
C23	C18	C19	C20	−0.7(7)	O7S	SS	C29S	F3S	−53.4(9)
W'	P'	N1'	C1'	−106.4(5)	O8S	SS	C29S	F1S	−174.6(8)
W'	P'	N1'	C3'	57.9(6)	O8S	SS	C29S	F2S	−54.2(9)
W'	P'	C5'	C6'	42.6(4)	O8S	SS	C29S	F3S	67.3(9)
W'	P'	C5'	C12'	160.3(3)	O6T	ST	C29T	F1T	64.3(9)
W'	P'	C5'	C18'	−77.0(3)	O6T	ST	C29T	F2T	−59.2(9)
P'	N1'	C1'	N2'	166.3(4)	O6T	ST	C29T	F3T	−179.6(7)
P'	N1'	C3'	C2'	−164.7(5)	O7T	ST	C29T	F1T	−55.9(9)
P'	C5'	C6'	C7'	46.3(5)	O7T	ST	C29T	F2T	−179.4(8)

P'	C5'	C6'	C11'	−138.1(4)	O7T	ST	C29T	F3T	60.2(8)
P'	C5'	C12'	C13'	−173.6(4)	O8T	ST	C29T	F1T	−176.1(7)
P'	C5'	C12'	C17'	3.6(7)	O8T	ST	C29T	F2T	60.4(9)
P'	C5'	C18'	C19'	69.7(5)	O8T	ST	C29T	F3T	−60.0(8)
P'	C5'	C18'	C23'	−106.1(5)	C30	C31	C32	C33	−161.6(12)
N1'	P'	C5'	C6'	172.7(3)	C31	C32	C33	C34	−142.1(11)
N1'	P'	C5'	C12'	−69.6(4)					

Compound 11b

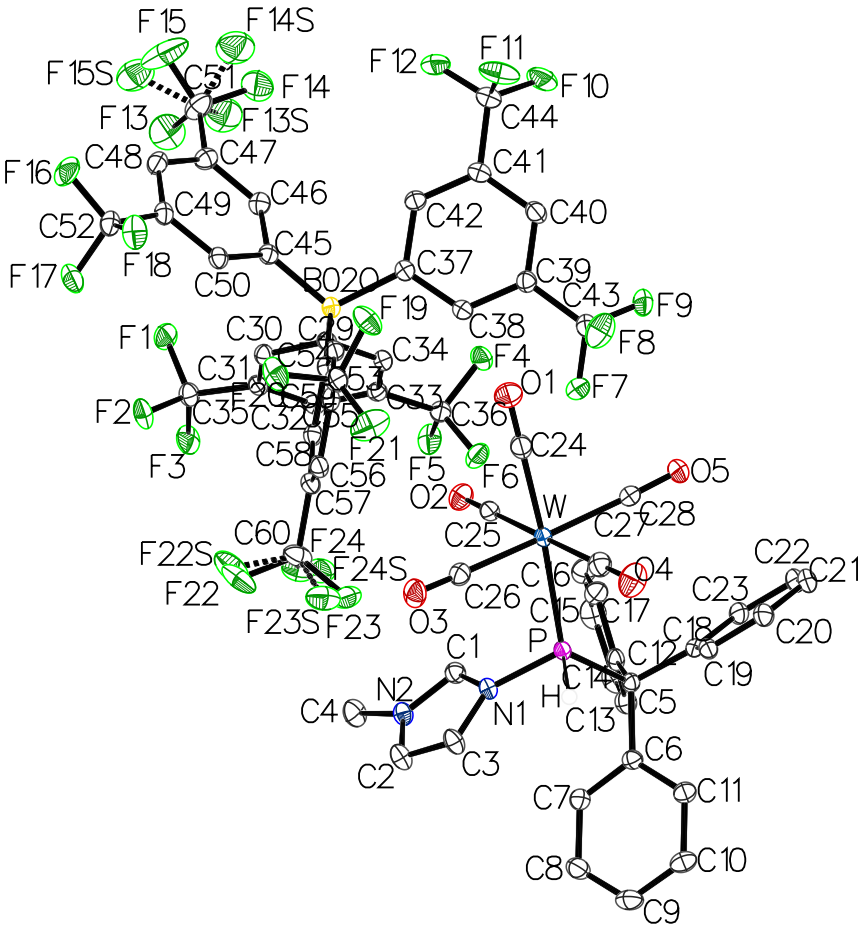


Fig. S107 Molecular structures of **11b** in the single crystal lattice at 100(2) K. Thermal ellipsoids are set at 50% probability level. Solvent molecules and hydrogen atoms were omitted for clarity except for those bound to phosphorus atoms. Suitable single crystals were obtained as clear colourless plates by vapour diffusion of *n*-pentane into a concentrated solution of **11b** in dichloromethane at −40 °C in a glovebox. CCDC-2302950.

Table S16 Crystal data and structure refinements for **11b**.

Identification code	GSTR796, DB-604 // GXraymo_7138v
Crystal habitus	clear colourless plate
Device type	Bruker D8 Venture
Empirical formula	$C_{61}H_{36}BCl_2F_{24}N_2O_5PW$
Moiety formula	$C_{28}H_{22}N_2O_5PW$, CH_2Cl_2, $C_{32}H_{12}BF_{24}$
Formula weight / g/mol	1629.45
T / K	100.0

Crystal system	triclinic
Space group	$P\bar{1}$
a / Å	11.3237(5)
b / Å	14.0365(6)
c / Å	20.5226(7)
α / °	98.0490(10)
β / °	104.5540(10)
γ / °	94.751(2)
V / Å^3	3102.4(2)
Z	2
ρ_{calc} / g/cm^3	1.744
μ / mm^{-1}	2.097
F(000)	1600.0
Crystal size / mm^3	0.22 × 0.18 × 0.1
Absorption correction	multi-scan
Min. and max. transmission	0.6329 and 0.7461
Radiation	Mo-K$_\alpha$ (λ = 0.71073 Å)
2Θ range for data collection / °	3.884 to 55.998
Completeness to Θ	0.995
Index ranges	−14 ≤ h ≤ 14, −18 ≤ k ≤ 18, −27 ≤ l ≤ 27
Reflections collected	89491
Independent reflections	14911 (R_{int} = 0.0233, R_σ = 0.0189)
Data / restraints / parameters	14911 / 126 / 944
Goodness-of-fit on F^2	1.059
Final R indexes ($I \geq 2\sigma(I)$)	R_1 = 0.0188, ωR_2 = 0.0470
Final R indexes (all data)	R_1 = 0.0192, ωR_2 = 0.0473
Largest diff. peak and hole / e/Å^3	1.17 and −0.71

Table S17 Bond lengths for **11b**.

Atom	Atom	Length / Å	Atom	Atom	Length / Å
W	P	2.4611(4)	F13	C51	1.350(3)
W	C24	2.0189(18)	F13S	C51	1.262(11)
W	C25	2.0411(18)	F14	C51	1.322(3)
W	C26	2.0532(17)	F14S	C51	1.407(12)
W	C27	2.0571(18)	F15	C51	1.305(3)
W	C28	2.0499(17)	F15S	C51	1.402(12)
P	N1	1.7773(14)	F16	C52	1.344(2)
P	C5	1.9239(16)	F17	C52	1.347(2)
O1	C24	1.141(2)	F18	C52	1.336(2)
O2	C25	1.142(2)	F19	C59	1.344(2)
O3	C26	1.135(2)	F20	C59	1.340(2)
O4	C27	1.136(2)	F21	C59	1.337(2)
O5	C28	1.135(2)	F22	C60	1.333(4)
N1	C1	1.341(2)	F22S	C60	1.336(7)

N1	C3	1.390(2)	F23	C60	1.386(3)
N2	C1	1.326(2)	F23S	C60	1.305(5)
N2	C2	1.380(2)	F24	C60	1.306(4)
N2	C4	1.469(2)	F24S	C60	1.402(7)
C2	C3	1.350(2)	C29	C30	1.406(2)
C5	C6	1.540(2)	C29	C34	1.397(2)
C5	C12	1.535(2)	C29	B02O	1.646(2)
C5	C18	1.539(2)	C30	C31	1.391(2)
C6	C7	1.404(2)	C31	C32	1.389(2)
C6	C11	1.396(2)	C31	C35	1.496(2)
C7	C8	1.388(2)	C32	C33	1.388(2)
C8	C9	1.391(3)	C33	C34	1.395(2)
C9	C10	1.386(3)	C33	C36	1.495(2)
C10	C11	1.394(2)	C37	C38	1.406(2)
C12	C13	1.395(2)	C37	C42	1.404(2)
C12	C17	1.400(2)	C37	B02O	1.649(2)
C13	C14	1.398(2)	C38	C39	1.391(2)
C14	C15	1.383(3)	C39	C40	1.391(2)
C15	C16	1.385(3)	C39	C43	1.502(2)
C16	C17	1.393(2)	C40	C41	1.390(2)
C18	C19	1.399(2)	C41	C42	1.391(2)
C18	C23	1.396(2)	C41	C44	1.501(2)
C19	C20	1.391(2)	C45	C46	1.409(2)
C20	C21	1.391(2)	C45	C50	1.399(2)
C21	C22	1.383(3)	C45	B02O	1.639(2)
C22	C23	1.394(2)	C46	C47	1.387(2)
Cl1	C61	1.756(2)	C47	C48	1.390(2)
Cl2	C61	1.811(3)	C47	C51	1.499(2)
Cl2S	C61	1.649(4)	C48	C49	1.383(2)
F1	C35	1.3557(19)	C49	C50	1.399(2)
F2	C35	1.3333(19)	C49	C52	1.498(2)
F3	C35	1.346(2)	C53	C54	1.408(2)
F4	C36	1.3515(18)	C53	C58	1.398(2)
F5	C36	1.3365(19)	C53	B02O	1.641(2)
F6	C36	1.3429(19)	C54	C55	1.391(2)
F7	C43	1.336(2)	C55	C56	1.391(2)
F8	C43	1.342(2)	C55	C59	1.493(2)
F9	C43	1.337(2)	C56	C57	1.386(2)
F10	C44	1.336(2)	C57	C58	1.395(2)
F11	C44	1.346(2)	C57	C60	1.495(2)
F12	C44	1.331(2)			

Table S18 Bond angles for **11b**.

Atom	Atom	Atom	Angle / ˚	Atom	Atom	Atom	Angle / ˚
C24	W	P	175.92(5)	C42	C37	C38	115.62(14)

C24	W	C25	89.46(7)	C42	C37	B02O	124.54(14)
C24	W	C26	87.50(7)	C39	C38	C37	122.34(14)
C24	W	C27	91.99(7)	C38	C39	C43	120.23(14)
C24	W	C28	88.56(7)	C40	C39	C38	121.06(15)
C25	W	P	90.50(5)	C40	C39	C43	118.67(14)
C25	W	C26	93.23(6)	C41	C40	C39	117.50(15)
C25	W	C27	177.82(7)	C40	C41	C42	121.49(15)
C25	W	C28	92.00(7)	C40	C41	C44	117.80(15)
C26	W	P	88.43(5)	C42	C41	C44	120.68(15)
C26	W	C27	88.46(7)	C41	C42	C37	121.97(15)
C27	W	P	88.17(5)	F7	C43	F8	106.27(15)
C28	W	P	95.52(5)	F7	C43	F9	106.78(15)
C28	W	C26	173.42(7)	F7	C43	C39	112.62(14)
C28	W	C27	86.41(7)	F8	C43	C39	111.84(15)
N1	P	W	113.30(5)	F9	C43	F8	106.11(14)
N1	P	C5	102.46(7)	F9	C43	C39	112.75(14)
C5	P	W	130.29(5)	F10	C44	F11	106.07(15)
C1	N1	P	127.59(11)	F10	C44	C41	112.31(15)
C1	N1	C3	107.73(13)	F11	C44	C41	111.48(15)
C3	N1	P	124.68(11)	F12	C44	F10	107.16(15)
C1	N2	C2	108.85(14)	F12	C44	F11	106.05(16)
C1	N2	C4	125.66(15)	F12	C44	C41	113.30(15)
C2	N2	C4	125.49(14)	C46	C45	B02O	119.96(14)
N2	C1	N1	108.94(14)	C50	C45	C46	115.77(14)
C3	C2	N2	107.12(14)	C50	C45	B02O	124.13(14)
C2	C3	N1	107.35(15)	C47	C46	C45	122.20(15)
C6	C5	P	106.51(10)	C46	C47	C48	120.92(15)
C12	C5	P	110.44(10)	C46	C47	C51	119.93(15)
C12	C5	C6	112.87(13)	C48	C47	C51	119.12(15)
C12	C5	C18	111.16(12)	C49	C48	C47	118.11(15)
C18	C5	P	102.01(10)	C48	C49	C50	120.99(15)
C18	C5	C6	113.18(12)	C48	C49	C52	120.11(15)
C7	C6	C5	120.60(14)	C50	C49	C52	118.82(15)
C11	C6	C5	121.70(14)	C45	C50	C49	121.98(15)
C11	C6	C7	117.68(14)	F13	C51	C47	110.90(17)
C8	C7	C6	121.27(16)	F13S	C51	F14S	96.0(7)
C7	C8	C9	120.18(16)	F13S	C51	F15S	113.7(7)
C10	C9	C8	119.30(16)	F13S	C51	C47	121.4(5)
C9	C10	C11	120.46(16)	F14	C51	F13	103.25(17)
C10	C11	C6	121.00(16)	F14	C51	C47	112.85(16)
C13	C12	C5	121.53(14)	F14S	C51	C47	111.9(5)
C13	C12	C17	118.24(15)	F15	C51	F13	107.7(2)
C17	C12	C5	120.05(15)	F15	C51	F14	108.6(2)
C12	C13	C14	120.48(16)	F15	C51	C47	113.04(17)
C15	C14	C13	120.57(17)	F15S	C51	F14S	95.5(7)
C14	C15	C16	119.58(17)	F15S	C51	C47	113.4(5)

C15	C16	C17	120.13(17)	F16	C52	F17	106.06(13)
C16	C17	C12	120.95(17)	F16	C52	C49	112.54(14)
C19	C18	C5	120.23(13)	F17	C52	C49	112.04(14)
C23	C18	C5	121.60(14)	F18	C52	F16	107.09(14)
C23	C18	C19	118.15(15)	F18	C52	F17	105.65(14)
C20	C19	C18	121.32(15)	F18	C52	C49	112.94(13)
C21	C20	C19	119.74(16)	C54	C53	B02O	119.65(13)
C22	C21	C20	119.59(16)	C58	C53	C54	115.96(14)
C21	C22	C23	120.71(16)	C58	C53	B02O	124.39(14)
C22	C23	C18	120.47(16)	C55	C54	C53	122.22(14)
O1	C24	W	178.51(17)	C54	C55	C59	120.97(15)
O2	C25	W	178.37(15)	C56	C55	C54	120.74(15)
O3	C26	W	176.56(16)	C56	C55	C59	118.21(14)
O4	C27	W	178.25(16)	C57	C56	C55	117.97(15)
O5	C28	W	175.77(16)	C56	C57	C58	121.28(15)
Cl1	C61	Cl2	108.03(16)	C56	C57	C60	118.06(15)
Cl2S	C61	Cl1	119.7(2)	C58	C57	C60	120.66(15)
C30	C29	B02O	120.51(13)	C57	C58	C53	121.82(15)
C34	C29	C30	115.53(14)	F19	C59	C55	113.10(14)
C34	C29	B02O	123.91(13)	F20	C59	F19	105.89(14)
C31	C30	C29	122.30(14)	F20	C59	C55	111.88(14)
C30	C31	C35	118.70(14)	F21	C59	F19	106.44(14)
C32	C31	C30	121.20(14)	F21	C59	F20	105.95(14)
C32	C31	C35	120.04(14)	F21	C59	C55	113.02(14)
C33	C32	C31	117.47(14)	F22	C60	F23	106.4(2)
C32	C33	C34	121.23(14)	F22	C60	C57	113.8(2)
C32	C33	C36	120.78(14)	F22S	C60	F24S	107.1(4)
C34	C33	C36	117.99(14)	F22S	C60	C57	109.5(3)
C33	C34	C29	122.27(14)	F23	C60	C57	111.27(17)
F1	C35	C31	111.67(13)	F23S	C60	F22S	104.7(3)
F2	C35	F1	105.88(13)	F23S	C60	F24S	110.5(4)
F2	C35	F3	107.22(13)	F23S	C60	C57	113.8(2)
F2	C35	C31	113.47(13)	F24	C60	F22	104.9(2)
F3	C35	F1	105.18(13)	F24	C60	F23	104.4(2)
F3	C35	C31	112.83(14)	F24	C60	C57	115.3(2)
F4	C36	C33	111.94(13)	F24S	C60	C57	110.8(3)
F5	C36	F4	106.30(13)	C29	B02O	C37	109.71(12)
F5	C36	F6	106.78(13)	C45	B02O	C29	107.09(12)
F5	C36	C33	113.31(13)	C45	B02O	C37	112.21(13)
F6	C36	F4	105.35(13)	C45	B02O	C53	110.96(12)
F6	C36	C33	112.59(13)	C53	B02O	C29	109.59(12)
C38	C37	B02O	119.82(13)	C53	B02O	C37	107.28(12)

Compound 11c

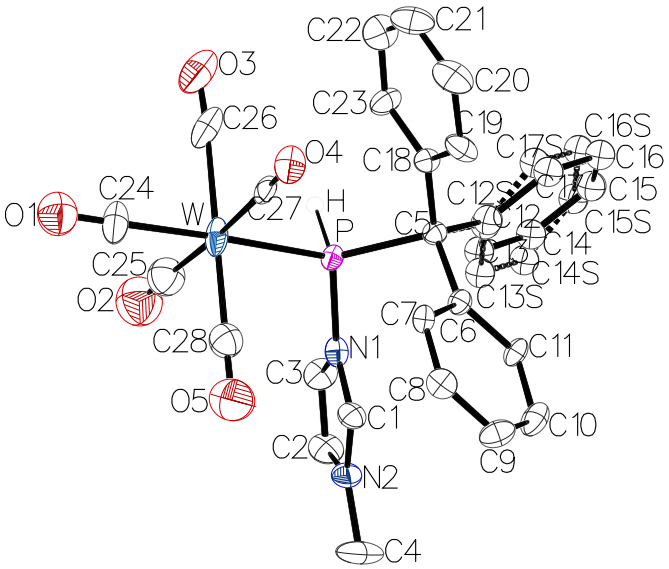


Fig. S108 Molecular structures of **11c** in the single crystal lattice at 100(2) K. Thermal ellipsoids are set at 50% probability level. Hydrogen atoms and the squeezed misordered $[Al(OC\{CF_3\}_3)_4]^-$ anion were omitted for clarity except for those bound to phosphorus atoms. Suitable single crystals were obtained as clear colourless blocks by vapour diffusion of *n*-pentane into a concentrated solution of **11c** in dichloromethane at −40 °C in a glovebox. CCDC-2302951.

Table S19 Crystal data and structure refinements for **11c**.

Identification code	GSTR789, DB-568 // GXraymo_7046f
Crystal habitus	clear colourless block
Device type	Bruker D8 Venture
Empirical formula	$C_{28}H_{22}N_2O_5PW$
Moiety formula	$C_{28}H_{22}N_2O_5PW$
Formula weight / g/mol	681.29
T / K	100.0
Crystal system	monoclinic
Space group	$P2_1/n$
a / Å	9.9563(5)
b / Å	34.958(2)
c / Å	16.3809(13)
α / °	90
β / °	97.490(2)
γ / °	90
V / Å^3	5652.8(6)
Z	4
ρ_{calc} / g/cm^3	0.801
μ / mm^{-1}	2.091
F(000)	1322.0
Crystal size / mm^3	0.12 × 0.09 × 0.05
Absorption correction	multi-scan
Min. and max. transmission	0.6491 and 0.7461

Radiation	Mo-K_α (λ = 0.71073 Å)
2Θ range for data collection / °	4.288 to 55.998
Completeness to Θ	0.998
Index ranges	−12 ≤ *h* ≤ 13, −46 ≤ *k* ≤ 46, −21 ≤ *l* ≤ 21
Reflections collected	137230
Independent reflections	13629 (R_{int} = 0.0502, R_σ = 0.0241)
Data / restraints / parameters	13629 / 268 / 369
Goodness-of-fit on F^2	1.032
Final *R* indexes ($I \geq 2\sigma(I)$)	R_1 = 0.0824, ωR_2 = 0.2406
Final *R* indexes (all data)	R_1 = 0.0870, ωR_2 = 0.2447
Largest diff. peak and hole / e/Å^3	2.27 and −1.88

Table S20 Bond lengths for **11c**.

Atom	Atom	Length / Å	Atom	Atom	Length / Å
W	P	2.4643(17)	C6	C11	1.398(9)
W	C24	2.023(9)	C7	C8	1.382(10)
W	C25	2.012(11)	C8	C9	1.399(11)
W	C26	2.113(10)	C9	C10	1.388(12)
W	C27	2.051(8)	C10	C11	1.422(11)
W	C28	2.013(10)	C12	C17	1.3900
P	N1	1.784(6)	C12	C13	1.3900
P	C5	1.923(7)	C17	C16	1.3900
O1	C24	1.153(12)	C16	C15	1.3900
O2	C25	1.158(14)	C15	C14	1.3900
O3	C26	1.083(12)	C14	C13	1.3900
O4	C27	1.145(10)	C16S	C15S	1.3900
O5	C28	1.166(13)	C16S	C17S	1.3900
N1	C1	1.352(9)	C15S	C14S	1.3900
N1	C3	1.398(9)	C14S	C13S	1.3900
N2	C1	1.331(9)	C13S	C12S	1.3900
N2	C2	1.409(11)	C12S	C17S	1.3900
N2	C4	1.451(11)	C18	C19	1.373(10)
C2	C3	1.325(11)	C18	C23	1.413(9)
C5	C6	1.555(9)	C19	C20	1.409(12)
C5	C12	1.534(10)	C20	C21	1.355(14)
C5	C12S	1.586(10)	C21	C22	1.334(13)
C5	C18	1.501(9)	C22	C23	1.411(12)
C6	C7	1.409(9)			

Table S21 Bond angles for **11c**.

Atom	Atom	Atom	Angle / ˚	Atom	Atom	Atom	Angle / ˚
C24	W	P	174.0(3)	C11	C6	C5	121.6(6)
C24	W	C26	89.7(4)	C11	C6	C7	117.7(6)
C24	W	C27	87.4(3)	C8	C7	C6	120.9(6)
C25	W	P	82.5(3)	C7	C8	C9	120.7(7)
C25	W	C24	91.5(4)	C10	C9	C8	120.4(7)
C25	W	C26	87.5(4)	C9	C10	C11	118.2(7)
C25	W	C27	176.5(4)	C6	C11	C10	122.0(6)
C25	W	C28	93.0(4)	C17	C12	C5	114.6(7)
C26	W	P	89.3(2)	C17	C12	C13	120.0
C27	W	P	98.6(2)	C13	C12	C5	125.4(7)
C27	W	C26	89.2(3)	C12	C17	C16	120.0
C28	W	P	90.9(3)	C15	C16	C17	120.0
C28	W	C24	90.1(4)	C16	C15	C14	120.0
C28	W	C26	179.5(4)	C15	C14	C13	120.0
C28	W	C27	90.3(4)	C14	C13	C12	120.0
N1	P	W	111.5(2)	C15S	C16S	C17S	120.0
N1	P	C5	105.2(3)	C14S	C15S	C16S	120.0
C5	P	W	127.4(2)	C15S	C14S	C13S	120.0
C1	N1	P	127.0(5)	C12S	C13S	C14S	120.0
C1	N1	C3	106.8(6)	C13S	C12S	C5	122.9(7)
C3	N1	P	126.1(5)	C13S	C12S	C17S	120.0
C1	N2	C2	108.0(6)	C17S	C12S	C5	117.1(7)
C1	N2	C4	123.9(7)	C12S	C17S	C16S	120.0
C2	N2	C4	128.2(7)	C19	C18	C5	123.5(6)
N2	C1	N1	109.4(6)	C19	C18	C23	119.6(7)
C3	C2	N2	107.0(7)	C23	C18	C5	116.8(6)
C2	C3	N1	108.9(7)	C18	C19	C20	119.4(8)
C6	C5	P	103.5(4)	C21	C20	C19	121.4(8)
C6	C5	C12S	111.4(6)	C22	C21	C20	119.3(8)
C12	C5	P	114.3(6)	C21	C22	C23	122.8(9)
C12	C5	C6	111.5(7)	C22	C23	C18	117.5(7)
C12S	C5	P	110.0(6)	O1	C24	W	179.0(10)
C18	C5	P	103.9(4)	O2	C25	W	177.7(10)
C18	C5	C6	114.4(5)	O3	C26	W	176.3(9)
C18	C5	C12	109.0(6)	O4	C27	W	177.1(7)
C18	C5	C12S	112.9(6)	O5	C28	W	178.0(9)
C7	C6	C5	120.6(6)				

Compound 12

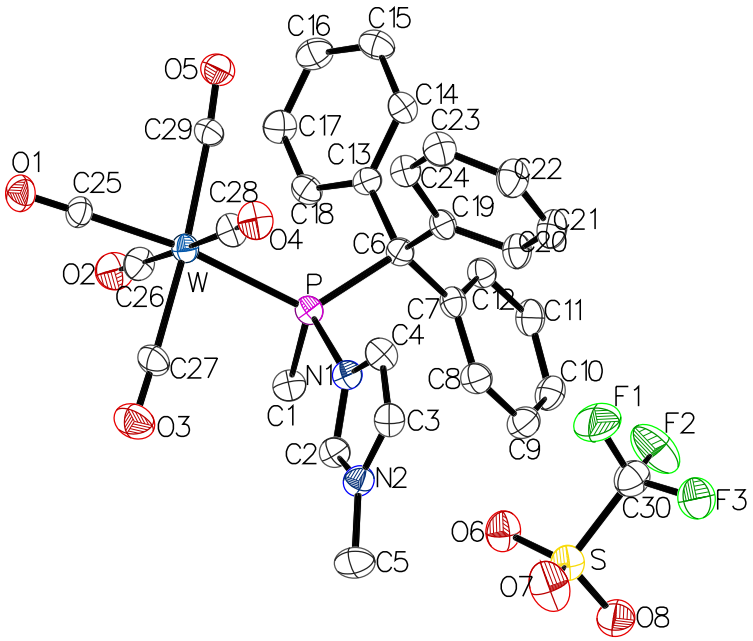


Fig. S109 Molecular structures of **12** in the single crystal lattice at 123(2) K. Thermal ellipsoids are set at 50% probability level. Hydrogen atoms and solvent molecules were omitted for clarity. Suitable single crystals were obtained as clear colourless blocks by vapour diffusion of *n*-pentane into a concentrated solution of **12** in dichloromethane at −40 °C in a glovebox. CCDC-2302952.

Table S22 Crystal data and structure refinements for **12**.

Identification code	GSTR763, DB-519 // GXray6876
Crystal habitus	clear colourless block
Device type	STOE IPDS-2T
Empirical formula	$C_{31}H_{26}Cl_2F_3N_2O_8PSW$
Moiety formula	$C_{29}H_{24}N_2O_5PW$, CF_3O_3S, CH_2Cl_2
Formula weight / g/mol	929.32
T / K	123(2)
Crystal system	triclinic
Space group	$P\bar{1}$
a / Å	9.1342(3)
b / Å	10.5960(4)
c / Å	18.7994(6)
α / °	87.804(3)
β / °	79.701(3)
γ / °	77.720(3)
V / Å^3	1749.24(11)
Z	2
ρ_{calc} / g/cm^3	1.764
μ / mm^{-1}	3.627
F(000)	912.0
Crystal size / mm^3	0.12 × 0.09 × 0.06
Absorption correction	multi-scan
Min. and max. transmission	0.0000 and 0.0000

Radiation	Mo-K_α (λ = 0.71073 Å)
2Θ range for data collection / °	3.934 to 56
Completeness to Θ	0.999
Index ranges	$-12 \le h \le 12$, $-13 \le k \le 13$, $-24 \le l \le 24$
Reflections collected	44205
Independent reflections	44205 (R_{int} = 0.0711, R_σ = 0.0591)
Data / restraints / parameters	44205 / 0 / 448
Goodness-of-fit on F^2	0.991
Final R indexes ($I \ge 2\sigma(I)$)	R_1 = 0.0586, ωR_2 = 0.1512
Final R indexes (all data)	R_1 = 0.0771, ωR_2 = 0.1631
Largest diff. peak and hole / e/Å^3	1.45 and −2.11

Table S23 Bond lengths for **12**.

Atom	Atom	Length / Å	Atom	Atom	Length / Å
W	P	2.4996(19)	C8	C9	1.375(10)
W	C25	2.022(7)	C9	C10	1.388(11)
W	C26	2.050(7)	C10	C11	1.382(11)
W	C27	2.046(8)	C11	C12	1.388(10)
W	C28	2.068(7)	C13	C14	1.395(10)
W	C29	2.083(7)	C13	C18	1.391(10)
P	N1	1.801(6)	C14	C15	1.388(10)
P	C1	1.837(7)	C15	C16	1.387(11)
P	C6	1.947(7)	C16	C17	1.383(11)
O1	C25	1.117(9)	C17	C18	1.389(10)
O2	C26	1.128(9)	C19	C20	1.385(10)
O3	C27	1.119(10)	C19	C24	1.407(10)
O4	C28	1.120(9)	C20	C21	1.395(11)
O5	C29	1.108(9)	C21	C22	1.392(11)
N1	C2	1.335(9)	C22	C23	1.383(11)
N1	C4	1.389(9)	C23	C24	1.387(10)
N2	C2	1.321(9)	S	O6	1.437(6)
N2	C3	1.380(10)	S	O7	1.432(7)
N2	C5	1.457(10)	S	O8	1.447(7)
C3	C4	1.344(11)	S	C30	1.824(10)
C6	C7	1.538(9)	F1	C30	1.315(10)
C6	C13	1.544(9)	F2	C30	1.324(11)
C6	C19	1.542(9)	F3	C30	1.334(10)
C7	C8	1.406(10)	Cl1	C31	1.766(12)
C7	C12	1.394(10)	Cl2	C31	1.748(13)

Table S24 Bond angles for **12**.

Atom	Atom	Atom	Angle / °	Atom	Atom	Atom	Angle / °
C25	W	P	172.7(2)	C9	C8	C7	120.6(7)
C25	W	C26	89.6(3)	C8	C9	C10	120.9(7)
C25	W	C27	88.3(3)	C11	C10	C9	119.3(7)
C25	W	C28	90.0(3)	C10	C11	C12	120.1(7)
C25	W	C29	88.0(3)	C11	C12	C7	121.1(7)
C26	W	P	88.2(2)	C14	C13	C6	120.3(6)
C26	W	C28	178.8(3)	C18	C13	C6	121.7(6)
C26	W	C29	88.3(3)	C18	C13	C14	117.7(6)
C27	W	P	84.8(2)	C15	C14	C13	120.8(7)
C27	W	C26	90.2(3)	C16	C15	C14	120.6(7)
C27	W	C28	91.0(3)	C17	C16	C15	119.2(7)
C27	W	C29	176.0(3)	C16	C17	C18	119.9(7)
C28	W	P	92.3(2)	C17	C18	C13	121.7(7)
C28	W	C29	90.5(3)	C20	C19	C6	122.8(6)
C29	W	P	98.9(2)	C20	C19	C24	118.3(7)
N1	P	W	109.4(2)	C24	C19	C6	118.9(6)
N1	P	C1	97.1(3)	C19	C20	C21	121.0(7)
N1	P	C6	104.6(3)	C22	C21	C20	119.9(7)
C1	P	W	111.5(3)	C23	C22	C21	119.9(7)
C1	P	C6	106.3(3)	C22	C23	C24	120.1(7)
C6	P	W	124.3(2)	C23	C24	C19	120.8(7)
C2	N1	P	124.6(5)	O1	C25	W	178.7(7)
C2	N1	C4	107.0(6)	O2	C26	W	178.6(7)
C4	N1	P	127.4(5)	O3	C27	W	177.9(8)
C2	N2	C3	108.2(6)	O4	C28	W	178.7(7)
C2	N2	C5	126.2(7)	O5	C29	W	176.2(7)
C3	N2	C5	125.7(7)	O6	S	O8	114.4(4)
N2	C2	N1	110.0(7)	O6	S	C30	103.4(4)
C4	C3	N2	107.2(7)	O7	S	O6	115.5(4)
C3	C4	N1	107.7(7)	O7	S	O8	114.4(5)
C7	C6	P	111.7(5)	O7	S	C30	103.3(4)
C7	C6	C13	110.6(6)	O8	S	C30	103.6(4)
C7	C6	C19	111.8(6)	F1	C30	S	111.7(7)
C13	C6	P	106.0(5)	F1	C30	F2	108.1(8)
C19	C6	P	105.3(5)	F1	C30	F3	107.0(7)
C19	C6	C13	111.1(6)	F2	C30	S	111.6(6)
C8	C7	C6	121.6(6)	F2	C30	F3	107.2(8)
C12	C7	C6	120.5(6)	F3	C30	S	111.1(6)
C12	C7	C8	117.9(7)	Cl2	C31	Cl1	112.0(6)

Table S25 Torsion angles for **12**.

A	B	C	D	Angle / °	A	B	C	D	Angle / °
W	P	N1	C2	96.0(6)	C8	C9	C10	C11	1.4(12)
W	P	N1	C4	−71.1(7)	C9	C10	C11	C12	−2.1(12)
P	N1	C2	N2	−169.2(5)	C10	C11	C12	C7	0.5(11)
P	N1	C4	C3	169.8(5)	C12	C7	C8	C9	−2.4(11)
P	C6	C7	C8	−48.2(8)	C13	C6	C7	C8	−166.0(7)
P	C6	C7	C12	133.9(6)	C13	C6	C7	C12	16.1(9)
P	C6	C13	C14	140.5(6)	C13	C6	C19	C20	−131.3(7)
P	C6	C13	C18	−45.3(8)	C13	C6	C19	C24	49.1(9)
P	C6	C19	C20	114.3(7)	C13	C14	C15	C16	0.4(12)
P	C6	C19	C24	−65.2(7)	C14	C13	C18	C17	−2.7(11)
N2	C3	C4	N1	−1.4(9)	C14	C15	C16	C17	−1.4(12)
C1	P	N1	C2	−19.8(7)	C15	C16	C17	C18	0.4(12)
C1	P	N1	C4	173.1(7)	C16	C17	C18	C13	1.7(12)
C2	N1	C4	C3	0.8(9)	C18	C13	C14	C15	1.6(11)
C2	N2	C3	C4	1.5(9)	C19	C6	C7	C8	69.6(8)
C3	N2	C2	N1	−1.0(9)	C19	C6	C7	C12	−108.3(7)
C4	N1	C2	N2	0.1(8)	C19	C6	C13	C14	26.5(9)
C5	N2	C2	N1	180.0(7)	C19	C6	C13	C18	−159.3(6)
C5	N2	C3	C4	−179.5(7)	C19	C20	C21	C22	−1.1(13)
C6	P	N1	C2	−128.8(6)	C20	C19	C24	C23	−4.0(11)
C6	P	N1	C4	64.1(7)	C20	C21	C22	C23	−1.1(14)
C6	C7	C8	C9	179.7(7)	C21	C22	C23	C24	0.6(13)
C6	C7	C12	C11	179.6(6)	C22	C23	C24	C19	2.0(12)
C6	C13	C14	C15	176.0(7)	C24	C19	C20	C21	3.6(12)
C6	C13	C18	C17	−177.0(7)	O6	S	C30	F1	61.5(7)
C6	C19	C20	C21	−176.0(7)	O6	S	C30	F2	−59.5(7)
C6	C19	C24	C23	175.5(7)	O6	S	C30	F3	−179.1(6)
C7	C6	C13	C14	−98.2(8)	O7	S	C30	F1	−59.2(7)
C7	C6	C13	C18	75.9(8)	O7	S	C30	F2	179.8(7)
C7	C6	C19	C20	−7.2(10)	O7	S	C30	F3	60.2(7)
C7	C6	C19	C24	173.2(6)	O8	S	C30	F1	−178.8(7)
C7	C8	C9	C10	0.8(12)	O8	S	C30	F2	60.1(7)
C8	C7	C12	C11	1.7(11)	O8	S	C30	F3	−59.5(7)

Compound 12-Cr

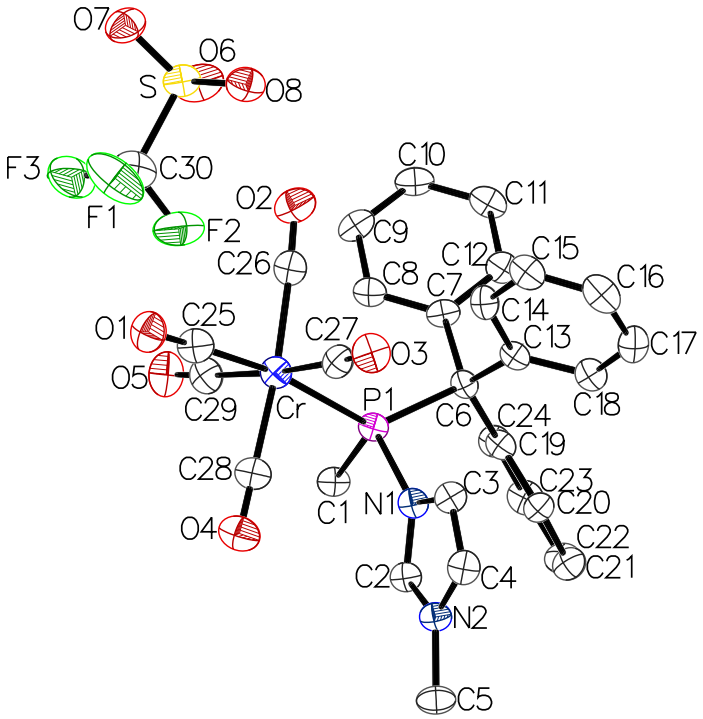


Fig. S110 Molecular structures of **12-Cr** in the single crystal lattice at 100(2) K. Thermal ellipsoids are set at 50% probability level. Hydrogen atoms and solvent molecules were omitted for clarity. Suitable single crystals were obtained as clear colourless needles by liquid-liquid diffusion of 0.3 mL of *n*-pentane layered on top of a solution of 1.7 mg of **12-Cr** in 0.3 mL of dichloromethane at −40 °C in a glovebox. CCDC-2302953.

Table S26 Crystal data and structure refinements for **12-Cr**.

Identification code	GSTR773, DB-558 // GXray6925
Crystal habitus	clear colourless needle
Device type	Stadivari
Empirical formula	$C_{31}H_{26}Cl_2CrF_3N_2O_8PS$
Moiety formula	$C_{29}H_{24}CrN_2O_5P$, CH_2Cl_2, CF_3O_3S
Formula weight / g/mol	797.47
T / K	100
Crystal system	triclinic
Space group	$P\bar{1}$
a / Å	8.5285(6)
b / Å	12.2121(9)
c / Å	17.7662(12)
α / °	69.997(5)
β / °	78.901(5)
γ / °	79.928(6)
V / Å^3	1694.3(2)
Z	2
ρ_{calc} / g/cm^3	1.563
μ / mm^{-1}	5.868
F(000)	812.0

Crystal size / mm^3	0.2 × 0.077 × 0.01
Absorption correction	multi-scan
Min. and max. transmission	0.4156 and 0.9570
Radiation	Cu-K_α (λ = 1.54186 Å)
2Θ range for data collection / °	7.758 to 135.496
Completeness to Θ	0.990
Index ranges	$-10 \le h \le 5$, $-14 \le k \le 14$, $-20 \le l \le 21$
Reflections collected	36949
Independent reflections	6088 (R_{int} = 0.0948, R_σ = 0.0538)
Data / restraints / parameters	6088 / 0 / 444
Goodness-of-fit on F^2	1.032
Final R indexes ($I \ge 2\sigma(I)$)	R_1 = 0.0714, ωR_2 = 0.1777
Final R indexes (all data)	R_1 = 0.1047, ωR_2 = 0.2061
Largest diff. peak and hole / e/$Å^3$	0.72 and −0.62

Table S27 Bond lengths for **12-Cr**.

Atom	Atom	Length / Å	Atom	Atom	Length / Å
Cr	P1	2.4024(15)	C8	C9	1.402(7)
Cr	C25	1.875(6)	C9	C10	1.360(8)
Cr	C26	1.909(6)	C10	C11	1.381(8)
Cr	C27	1.915(6)	C11	C12	1.389(7)
Cr	C28	1.891(6)	C13	C14	1.388(7)
Cr	C29	1.935(6)	C13	C18	1.393(8)
P1	N1	1.778(4)	C14	C15	1.398(7)
P1	C1	1.828(5)	C15	C16	1.374(9)
P1	C6	1.935(5)	C16	C17	1.375(8)
O1	C25	1.138(7)	C17	C18	1.390(8)
O2	C26	1.134(7)	C19	C20	1.403(7)
O3	C27	1.140(7)	C19	C24	1.409(7)
O4	C28	1.133(7)	C20	C21	1.390(7)
O5	C29	1.098(7)	C21	C22	1.391(8)
N1	C2	1.338(7)	C22	C23	1.378(8)
N1	C3	1.392(6)	C23	C24	1.389(8)
N2	C2	1.328(7)	Cl1	C31	1.736(7)
N2	C4	1.375(7)	Cl2	C31	1.762(8)
N2	C5	1.472(7)	S	O6	1.439(4)
C3	C4	1.339(8)	S	O7	1.442(4)
C6	C7	1.551(7)	S	O8	1.430(4)
C6	C13	1.552(7)	S	C30	1.814(7)
C6	C19	1.531(7)	F1	C30	1.335(8)
C7	C8	1.385(8)	F2	C30	1.335(8)
C7	C12	1.392(7)	F3	C30	1.324(8)

Table S28 Bond angles for **12-Cr**.

Atom	Atom	Atom	Angle / °	Atom	Atom	Atom	Angle / °
C25	Cr	P1	170.99(19)	C7	C8	C9	120.2(5)
C25	Cr	C26	89.1(2)	C10	C9	C8	121.1(5)
C25	Cr	C27	85.4(2)	C9	C10	C11	119.6(5)
C25	Cr	C28	85.7(2)	C10	C11	C12	119.8(5)
C25	Cr	C29	89.3(2)	C11	C12	C7	121.4(5)
C26	Cr	P1	99.85(17)	C14	C13	C6	117.9(4)
C26	Cr	C27	90.1(2)	C14	C13	C18	117.9(5)
C26	Cr	C29	86.9(2)	C18	C13	C6	124.0(4)
C27	Cr	P1	95.43(17)	C13	C14	C15	121.4(5)
C27	Cr	C29	173.9(2)	C16	C15	C14	119.5(5)
C28	Cr	P1	85.30(17)	C15	C16	C17	119.9(5)
C28	Cr	C26	174.7(2)	C16	C17	C18	120.7(5)
C28	Cr	C27	90.8(2)	C17	C18	C13	120.5(5)
C28	Cr	C29	91.6(2)	C20	C19	C6	121.8(4)
C29	Cr	P1	90.31(17)	C20	C19	C24	117.4(5)
N1	P1	Cr	106.91(14)	C24	C19	C6	120.7(5)
N1	P1	C1	98.3(2)	C21	C20	C19	121.7(5)
N1	P1	C6	99.9(2)	C20	C21	C22	119.6(5)
C1	P1	Cr	111.61(18)	C23	C22	C21	119.8(5)
C1	P1	C6	103.2(2)	C22	C23	C24	120.9(5)
C6	P1	Cr	131.59(16)	C23	C24	C19	120.6(5)
C2	N1	P1	126.7(4)	O1	C25	Cr	176.4(5)
C2	N1	C3	106.9(4)	O2	C26	Cr	176.8(5)
C3	N1	P1	126.1(4)	O3	C27	Cr	175.8(5)
C2	N2	C4	108.7(4)	O4	C28	Cr	177.9(5)
C2	N2	C5	124.5(5)	O5	C29	Cr	176.9(6)
C4	N2	C5	126.8(4)	Cl1	C31	Cl2	112.1(4)
N2	C2	N1	109.3(4)	O6	S	O7	113.6(3)
C4	C3	N1	108.1(5)	O6	S	C30	103.2(3)
C3	C4	N2	107.1(5)	O7	S	C30	103.3(3)
C7	C6	P1	109.0(3)	O8	S	O6	116.0(3)
C7	C6	C13	106.2(4)	O8	S	O7	115.1(3)
C13	C6	P1	108.1(3)	O8	S	C30	103.1(3)
C19	C6	P1	107.6(3)	F1	C30	S	111.5(4)
C19	C6	C7	110.9(4)	F2	C30	S	111.6(5)
C19	C6	C13	114.8(4)	F2	C30	F1	106.3(6)
C8	C7	C6	124.5(4)	F3	C30	S	112.7(5)
C8	C7	C12	117.9(5)	F3	C30	F1	107.1(6)
C12	C7	C6	117.5(5)	F3	C30	F2	107.3(5)

Table S29 Torsion angles for **12-Cr**.

A	B	C	D	Angle / °	A	B	C	D	Angle / °
Cr	P1	N1	C2	109.8(4)	C8	C9	C10	C11	-0.3(8)
Cr	P1	N1	C3	-62.1(4)	C9	C10	C11	C12	-0.5(8)
P1	N1	C2	N2	-172.3(3)	C10	C11	C12	C7	0.3(8)
P1	N1	C3	C4	172.4(4)	C12	C7	C8	C9	-1.4(7)
P1	C6	C7	C8	-9.5(6)	C13	C6	C7	C8	-125.8(5)
P1	C6	C7	C12	169.9(4)	C13	C6	C7	C12	53.6(5)
P1	C6	C13	C14	-57.7(5)	C13	C6	C19	C20	46.5(6)
P1	C6	C13	C18	128.5(4)	C13	C6	C19	C24	-136.2(5)
P1	C6	C19	C20	-73.9(5)	C13	C14	C15	C16	2.0(8)
P1	C6	C19	C24	103.4(5)	C14	C13	C18	C17	3.6(7)
N1	C3	C4	N2	0.5(6)	C14	C15	C16	C17	0.6(8)
C1	P1	N1	C2	-5.9(5)	C15	C16	C17	C18	-1.0(8)
C1	P1	N1	C3	-177.8(4)	C16	C17	C18	C13	-1.1(8)
C2	N1	C3	C4	-0.8(6)	C18	C13	C14	C15	-4.0(7)
C2	N2	C4	C3	0.0(6)	C19	C6	C7	C8	108.8(5)
C3	N1	C2	N2	0.9(6)	C19	C6	C7	C12	-71.8(6)
C4	N2	C2	N1	-0.6(6)	C19	C6	C13	C14	-177.8(4)
C5	N2	C2	N1	178.5(5)	C19	C6	C13	C18	8.3(7)
C5	N2	C4	C3	-179.0(5)	C19	C20	C21	C22	0.6(8)
C6	P1	N1	C2	-111.0(4)	C20	C19	C24	C23	-0.4(8)
C6	P1	N1	C3	77.1(4)	C20	C21	C22	C23	-0.9(9)
C6	C7	C8	C9	178.0(4)	C21	C22	C23	C24	0.5(9)
C6	C7	C12	C11	-178.8(5)	C22	C23	C24	C19	0.2(9)
C6	C13	C14	C15	-178.2(4)	C24	C19	C20	C21	0.0(8)
C6	C13	C18	C17	177.4(5)	O6	S	C30	F1	179.1(5)
C6	C19	C20	C21	177.4(5)	O6	S	C30	F2	60.4(5)
C6	C19	C24	C23	-177.8(5)	O6	S	C30	F3	-60.4(6)
C7	C6	C13	C14	59.2(5)	O7	S	C30	F1	-62.3(6)
C7	C6	C13	C18	-114.6(5)	O7	S	C30	F2	179.0(4)
C7	C6	C19	C20	166.9(5)	O7	S	C30	F3	58.2(6)
C7	C6	C19	C24	-15.8(7)	O8	S	C30	F1	57.9(6)
C7	C8	C9	C10	1.2(8)	O8	S	C30	F2	-60.8(5)
C8	C7	C12	C11	0.6(7)	O8	S	C30	F3	178.4(5)

5 Computational Details

Quantum chemical calculations were performed with the ORCA electronic structure program package.[14] All geometry optimizations were run in redundant internal coordinates with tight convergence criteria, using Grimme's fast PBEh-3c composite functional[15] which makes use of the atom-pairwise dispersion correction with the Becke-Johnson damping scheme (D3BJ)[16,17] and geometrical counterpoise gCP correction.[18] For W atoms the ecp-46 effective core potential (ECP) was used[19,20] to take into account scalar relativistic effects in the DFT calculations. Harmonic frequency calculations verified the nature of the computed species as minima structures, featuring nonnegative eigenvalues. From these geometries, all reported electronic data were obtained using the double-hybrid-meta-GGA functional PWPB95[21,22] with Grimme's D3 correction (PWPB95-D3) and the def2-QZVPP[23] basis set. Solvent effects (toluene) were included using the Conductor-like Polarizable Continuum Model (CPCM).[24,25] Data of the Laplacian of the electron density along the P-ligand bond path were obtained using Multiwfn.[26]

6 Calculated structures

Cartesian coordinates (in Å) and energies (in hartrees) for all computed species. Geometries, zero-point energy correction (ZPE) and Gibbs energy correction (G_{corr}) at the optimization level (*vide supra*), whereas electronic energies are computed at the CPCM(toluene)/PWPB95-D3/def2-QZVPP(ecp) level. When explicitly stated, geometries and energy calculations were obtained in the gas phase, including the thermal vibrational correction (TVC) to energy and the total entropy term T·S, at 298K.

1'

E = -1398.38964048 au
ZPE = 0.27476237 au
G_{corr} = 0.22262073 au

P	-0.604425	0.578718	0.388630
C	-0.242225	0.427138	2.235749
C	0.508387	-0.903929	2.347287
H	0.772611	-1.096422	3.390251
H	-0.099614	-1.739687	1.997300
H	1.437534	-0.906497	1.776275
C	0.607855	1.540728	2.835522
H	0.116555	2.513158	2.778010
H	0.799686	1.343434	3.894746
H	1.572424	1.623028	2.336133
C	-1.556701	0.309742	3.008355
H	-1.355186	0.041813	4.049368
H	-2.113176	1.248676	3.024110
H	-2.204380	-0.461436	2.587158
N	-1.863785	1.919548	0.455733
C	-3.120334	1.688165	0.116333
N	-3.821058	2.815287	0.183065
C	-2.976872	3.817447	0.587914
C	-1.755645	3.254433	0.752580
C	-5.226412	2.966323	-0.136008
H	-5.346940	3.653022	-0.970192
H	-5.765434	3.345953	0.728313
H	-5.636546	1.999672	-0.412053
H	-3.511405	0.727429	-0.173935
H	-3.308526	4.833495	0.715138
H	-0.827649	3.707162	1.047611
W	1.294886	1.543566	-1.113949
C	2.618676	2.175811	-2.477573
O	3.368051	2.545517	-3.268252
C	1.628036	3.232822	-0.013062
O	1.845657	4.189050	0.581067
C	2.817518	0.625763	-0.084871
O	3.695058	0.139391	0.464369
C	0.998965	-0.181410	-2.206817
O	0.843779	-1.134725	-2.814799
C	-0.222589	2.480797	-2.123081
O	-1.082069	3.004651	-2.668490

1' (gas phase)

E = -1398.37555568 au
ZPE = 0.27562876 au
TVC = 0.02296481au
T·*S* = 49.89 kcal/mol
G_{corr} = 0.22286675 au

P	-0.612736	0.551615	0.443918
C	-0.211577	0.401561	2.282109
C	0.553954	-0.923513	2.365545
H	0.828844	-1.130741	3.402859
H	-0.047623	-1.759825	2.006313
H	1.478485	-0.905579	1.787840
C	0.644044	1.515389	2.873415
H	0.138354	2.481936	2.856070
H	0.877397	1.301531	3.920952
H	1.587883	1.623510	2.341356
C	-1.508287	0.264851	3.080686
H	-1.285982	-0.000143	4.118199
H	-2.078702	1.195394	3.107185
H	-2.151435	-0.515221	2.669742
N	-1.867929	1.915710	0.537166
C	-3.093630	1.711529	0.097714
N	-3.783961	2.850564	0.124140
C	-2.956258	3.831171	0.609122

C	-1.761628	3.243220	0.860121
C	-5.147265	3.032805	-0.322569
H	-5.178302	3.715431	-1.169018
H	-5.759976	3.427766	0.484739
H	-5.555700	2.075337	-0.633121
H	-3.467193	0.759200	-0.239589
H	-3.276617	4.852461	0.721670
H	-0.848516	3.675028	1.225046
W	1.218283	1.544617	-1.108776
C	2.491922	2.209190	-2.516354
O	3.206450	2.595997	-3.326068
C	1.534770	3.243323	-0.021755
O	1.728708	4.205324	0.571787
C	2.791672	0.662371	-0.116345
O	3.687454	0.193445	0.415590
C	0.935932	-0.190924	-2.195513
O	0.787029	-1.145500	-2.800894
C	-0.353077	2.434025	-2.067355
O	-1.260083	2.924782	-2.567991

MeOH

E = -115.70940250 au
ZPE = 0.05271417 au
G_{corr} = 0.02999481 au

C	-0.033383	-0.013677	-0.007631
H	-0.008240	0.015405	1.087744
H	0.998017	-0.033417	-0.358318
H	-0.481903	0.923631	-0.356361
O	-0.679583	-1.155325	-0.513626
H	-1.589299	-1.145119	-0.209132

1'·MeOH

E = -1514.11134701 au
ZPE = 0.32959465 au
G_{corr} = 0.27100276 au

P	-0.084759	-0.044580	-0.011318
C	-0.065662	-0.079022	1.872512
C	1.424179	-0.154177	2.221026
H	1.550583	-0.176776	3.306233
H	1.888475	-1.053549	1.813034
H	1.982701	0.706585	1.851754
C	-0.688194	1.140201	2.542486
H	-1.752630	1.234030	2.321654
H	-0.593683	1.064338	3.629832
H	-0.199439	2.063359	2.232888
C	-0.749148	-1.351509	2.373431
H	-0.591660	-1.458304	3.450204
H	-1.828128	-1.333968	2.210378
H	-0.347267	-2.244279	1.890538
N	-1.860594	-0.416273	-0.293427
C	-2.256796	-1.573721	-0.802094
N	-3.576789	-1.568989	-0.945137
C	-4.052963	-0.359232	-0.507635
C	-2.977595	0.358743	-0.104828
C	-4.375072	-2.649710	-1.488473
H	-4.885174	-2.318699	-2.389633
H	-5.107692	-2.975799	-0.754569
H	-3.725434	-3.483871	-1.735174
H	-1.597600	-2.390276	-1.062050
H	-5.100158	-0.111394	-0.525397
H	-2.930119	1.355498	0.291685
W	0.351757	2.223096	-1.197799
C	0.734800	3.828049	-2.335585
O	0.943853	4.743294	-2.999054
C	-1.110425	3.273711	-0.228184
O	-1.911325	3.898409	0.302526
C	1.693059	2.914343	0.196681
O	2.439303	3.338865	0.951773
C	1.877790	1.205001	-2.140212
O	2.731893	0.655980	-2.661626
C	-1.003603	1.543719	-2.578985
O	-1.765504	1.149545	-3.336181
O	0.551570	-2.952900	-1.446179
H	0.622033	-2.161360	-0.878526
C	0.821751	-2.537642	-2.763190
H	1.865111	-2.237599	-2.906153
H	0.622347	-3.373307	-3.434249
H	0.192031	-1.697160	-3.082010

(**1'**·MeOH→**4'**·MeOH)‡

E = -1514.07134412 au
ZPE = 0.32134012 au

G_{corr} = 0.26472170 au
ν = -1067.67 cm^{-1}

P	-0.176047	0.100759	-0.028816
C	-0.034746	-0.103109	1.820302
C	1.471388	-0.185599	2.085826
H	1.645565	-0.294510	3.158414
H	1.922301	-1.046118	1.588701
H	2.005648	0.708254	1.763371
C	-0.645029	1.080281	2.562810
H	-1.718182	1.167529	2.382888
H	-0.507975	0.953917	3.639460
H	-0.178557	2.024328	2.280261
C	-0.695455	-1.408581	2.260278
H	-0.486293	-1.579608	3.318932
H	-1.779786	-1.381540	2.147248
H	-0.315040	-2.267177	1.705058
N	-1.870651	-0.380446	-0.340644
C	-2.146165	-1.602511	-0.822674
N	-3.465153	-1.665695	-0.974576
C	-4.043210	-0.477236	-0.587735
C	-3.037765	0.333428	-0.191505
C	-4.183131	-2.811647	-1.492327
H	-4.701027	-2.547452	-2.411613
H	-4.905899	-3.164821	-0.760297
H	-3.472038	-3.604804	-1.700685
H	-1.167275	-2.346061	-1.008905
H	-5.105326	-0.307136	-0.630087
H	-3.071729	1.343415	0.175412
W	0.362545	2.275867	-1.221904
C	0.768160	3.902465	-2.338518
O	0.989746	4.822662	-2.984280
C	-1.133219	3.307008	-0.275005
O	-1.951955	3.908280	0.250896
C	1.670395	2.974193	0.202093
O	2.397456	3.405442	0.969857
C	1.916596	1.274262	-2.141702
O	2.785045	0.739472	-2.650054
C	-0.951213	1.627396	-2.669190
O	-1.683724	1.271085	-3.467952
O	0.151859	-2.638983	-1.116734
H	0.306211	-1.250970	-0.539971
C	0.474056	-2.559727	-2.465661
H	0.772152	-3.531819	-2.882545
H	-0.365616	-2.201166	-3.091677
H	1.308905	-1.870655	-2.665781

4'·MeOH

E = -1514.09455275 au
ZPE = 0.32712476 au
G_{corr} = 0.27036209 au

P	-0.242603	0.190004	0.056139
C	-0.064348	-0.041468	1.893500
C	1.441795	-0.072662	2.164463
H	1.611717	-0.186621	3.236832
H	1.927351	-0.912581	1.664689
H	1.946557	0.842186	1.855426
C	-0.718494	1.124651	2.628561
H	-1.793643	1.173774	2.446519
H	-0.579340	1.003720	3.704785
H	-0.282513	2.083852	2.346765
C	-0.689368	-1.367394	2.321948
H	-0.478383	-1.536226	3.380291
H	-1.772186	-1.372060	2.199757
H	-0.283300	-2.211930	1.763326
N	-1.853141	-0.377419	-0.302364
C	-2.087390	-1.631396	-0.779243
N	-3.419166	-1.657550	-0.933006
C	-4.015952	-0.468300	-0.568532
C	-3.024598	0.350449	-0.171329
C	-4.141112	-2.800656	-1.444373
H	-4.658437	-2.547008	-2.368236
H	-4.869951	-3.152381	-0.715975
H	-3.428369	-3.594607	-1.643957
H	-0.664206	-2.802643	-1.216293
H	-5.078331	-0.300782	-0.623836
H	-3.067633	1.365287	0.183047
W	0.337814	2.312943	-1.170134
C	0.775018	3.911361	-2.325479
O	1.018359	4.807778	-2.993238
C	-1.168398	3.377021	-0.271326
O	-1.991707	3.992028	0.228311
C	1.627489	3.046052	0.252770
O	2.344519	3.499080	1.016842
C	1.893610	1.271195	-2.039783
O	2.757734	0.701137	-2.515144
C	-0.959663	1.651143	-2.631729
O	-1.677170	1.297304	-3.442951
O	0.172790	-3.229944	-1.517131
H	0.421023	-0.965932	-0.387846
C	0.408860	-2.786746	-2.823070
H	-0.332166	-3.152016	-3.546474
H	0.427270	-1.690806	-2.912982

H	1.385482	-3.149167	-3.148573

(**4'**·MeOH→**5'**)‡

E = -1514.05891731 au
ZPE = 0.32325338 au
G_{corr} = 0.26768839 au
ν = -983.86 cm^{-1}

P	-0.221182	-0.035599	0.536159
C	-0.369754	0.355075	2.356689
C	0.977599	1.000846	2.709115
H	1.007232	1.178143	3.786117
H	1.825703	0.357902	2.464691
H	1.120501	1.959152	2.213408
C	-1.487490	1.360737	2.627230
H	-2.485148	0.957620	2.461277
H	-1.438341	1.676847	3.671147
H	-1.388253	2.253618	2.011817
C	-0.514812	-0.909684	3.206669
H	-0.528219	-0.630816	4.262490
H	-1.423217	-1.476539	3.015689
H	0.328582	-1.584992	3.057887
N	-1.753546	-0.841614	0.083157
C	-1.930910	-1.199791	-1.203211
N	-3.144151	-1.743200	-1.272579
C	-3.751952	-1.736664	-0.040149
C	-2.877269	-1.173192	0.816827
C	-3.745184	-2.256537	-2.486438
H	-4.711754	-1.785921	-2.650638
H	-3.875795	-3.334500	-2.419640
H	-3.097436	-2.026645	-3.326323
H	-1.072962	-1.019169	-2.212056
H	-4.745382	-2.116814	0.125816
H	-2.993881	-0.979432	1.865376
W	0.580511	1.610661	-1.165262
C	1.297119	2.802945	-2.621209
O	1.706882	3.478754	-3.451447
C	0.141580	3.245420	-0.085279
O	-0.073601	4.207881	0.511440
C	2.447301	1.586539	-0.326086
O	3.495044	1.614789	0.133952
C	1.245775	-0.116067	-2.352461
O	2.162355	-0.734089	-2.695352
C	-1.276463	1.736192	-2.039061
O	-2.312170	1.865007	-2.506691
O	-0.274579	-0.879421	-3.138607
H	0.560285	-1.203902	0.659980
C	-0.101395	-2.101317	-3.793308
H	0.958261	-2.368877	-3.876365
H	-0.593871	-2.925437	-3.254925
H	-0.510191	-2.075243	-4.808878

5'

E = -1514.08433379 au
ZPE = 0.32973716 au
G_{corr} = 0.27484782 au

P	-0.242624	-0.020335	0.560483
C	-0.381942	0.369678	2.381001
C	0.974051	1.021885	2.694217
H	1.021990	1.225306	3.766008
H	1.816304	0.370703	2.450448
H	1.110436	1.965513	2.169341
C	-1.493513	1.381637	2.649482
H	-2.494292	0.976964	2.501302
H	-1.433119	1.716796	3.686810
H	-1.396796	2.261590	2.013999
C	-0.505048	-0.880687	3.253913
H	-0.474711	-0.587401	4.305421
H	-1.425317	-1.442706	3.110585
H	0.325471	-1.566309	3.081922
N	-1.829458	-0.850907	0.150035
C	-2.100622	-1.174632	-1.111379
N	-3.300928	-1.724963	-1.177844
C	-3.838605	-1.755384	0.082263
C	-2.917777	-1.213357	0.911327
C	-3.946526	-2.187006	-2.392860
H	-4.850303	-1.610392	-2.571122
H	-4.194265	-3.240984	-2.300987
H	-3.268609	-2.051061	-3.229873
H	-1.449634	-1.014858	-1.959753
H	-4.820807	-2.145780	0.284580
H	-2.980016	-1.055668	1.970145
W	0.477793	1.531154	-1.183587
C	1.173679	2.514434	-2.800813
O	1.568799	3.045549	-3.737839
C	0.205405	3.233807	-0.157585

O	0.065240	4.220303	0.429767
C	2.406756	1.424344	-0.470116
O	3.478902	1.402497	-0.073467
C	0.959355	-0.402354	-2.259343
O	1.823143	-1.208382	-1.979937
C	-1.406003	1.742005	-1.922155
O	-2.474279	1.891275	-2.322883
O	0.171346	-0.683903	-3.365672
H	0.500383	-1.215340	0.667430
C	0.489800	-1.850218	-4.115335
H	1.504542	-1.817846	-4.514971
H	0.385274	-2.767148	-3.530205
H	-0.211639	-1.880320	-4.947302

5'$^{conf\text{-}eq}$

E = -1514.09195872 au
ZPE = 0.32986161 au
G_{corr} = 0.27608133 au

P	0.061153	0.155070	0.045103
C	1.896746	-0.157408	-0.009327
C	2.505932	1.227066	-0.257415
H	3.590778	1.132564	-0.338594
H	2.147700	1.675985	-1.186539
H	2.293372	1.919774	0.556594
C	2.395108	-0.715206	1.321379
H	2.051563	-1.736284	1.494315
H	3.486729	-0.745258	1.316116
H	2.086574	-0.101180	2.166780
C	2.263703	-1.098562	-1.153879
H	3.350085	-1.194914	-1.213477
H	1.860338	-2.102096	-1.011570
H	1.916470	-0.723871	-2.118491
N	-0.578539	-1.534010	0.003173
C	-1.262180	-2.061362	-1.001362
N	-1.758399	-3.229237	-0.625695
C	-1.392740	-3.459185	0.678961
C	-0.661735	-2.392870	1.073554
C	-2.583026	-4.102352	-1.438959
H	-3.558296	-4.223820	-0.974904
H	-2.104198	-5.072335	-1.544302
H	-2.712002	-3.659337	-2.421491
H	-1.406642	-1.609714	-1.966832
H	-1.685418	-4.346653	1.212158
H	-0.208807	-2.179908	2.025365
W	-1.136902	1.662559	1.548656
C	-2.331207	2.951012	2.539724
O	-3.011283	3.688694	3.095810
C	0.404097	2.075894	2.761215
O	1.291656	2.317229	3.464520
C	-0.617204	3.198447	0.298125
O	-0.332820	4.067543	-0.393729
C	-2.827905	1.117215	0.132388
O	-2.809423	0.317152	-0.795422
C	-1.777496	0.188873	2.809444
O	-2.154524	-0.621725	3.530543
O	-3.997344	1.773652	0.363517
H	-0.140716	0.362372	-1.333620
C	-5.100443	1.488835	-0.484968
H	-4.895294	1.730629	-1.529857
H	-5.409587	0.442791	-0.429539
H	-5.920331	2.113429	-0.136519

5'$^{conf\text{-}ax}$

E = -1514.08701026 au
ZPE = 0.32942042 au
G_{corr} = 0.27355776 au

P	-0.189557	0.107669	0.214513
C	-0.444822	-0.151939	2.044337
C	0.244531	-1.418667	2.543568
H	0.171107	-1.463817	3.632337
H	-0.217197	-2.327511	2.155964
H	1.307076	-1.434842	2.291627
C	0.192817	1.071444	2.711903
H	-0.253212	2.008442	2.384348
H	0.050339	0.998888	3.792072
H	1.265246	1.129125	2.521016
C	-1.940845	-0.199425	2.342864
H	-2.097098	-0.257941	3.422076
H	-2.456502	0.688562	1.977425
H	-2.422890	-1.072535	1.898951
N	-0.400955	-1.598310	-0.395332
C	0.574192	-2.442084	-0.702013
N	0.053018	-3.543751	-1.221795
C	-1.311473	-3.404550	-1.251036
C	-1.593745	-2.183252	-0.740252
C	0.797207	-4.689819	-1.710797

H	0.620567	-4.815438	-2.775787
H	0.485327	-5.584934	-1.179420
H	1.857237	-4.527015	-1.543092
H	1.627039	-2.260023	-0.565396
H	-1.960758	-4.170365	-1.638167
H	-2.539643	-1.685562	-0.620433
W	-1.287249	1.725196	-1.224355
C	-1.892276	3.118375	-2.560263
O	-2.209795	3.903738	-3.331770
C	-3.120683	0.935890	-1.065272
O	-4.179239	0.474990	-0.952857
C	-1.728034	3.049153	0.280427
O	-1.997709	3.807006	1.096319
C	0.782608	2.634034	-1.333730
O	1.417021	2.982518	-2.306228
C	-0.819378	0.485567	-2.774548
O	-0.561081	-0.234455	-3.631396
O	1.381042	2.785360	-0.097056
H	1.217477	-0.001405	0.184878
C	2.685478	3.344456	-0.064290
H	3.414167	2.739739	-0.609186
H	2.715008	4.356911	-0.471521
H	2.976124	3.382343	0.984435

(**5'** →**3a'**+NMeIm)$^{‡\ ax}$

E = -1514.07684953 au
ZPE = 0.32893493 au
G_{corr} = 0.27425757 au
ν = -174.25 cm^{-1}

P	-0.108038	-0.058232	-0.112891
C	-0.251659	-0.093310	1.789057
C	1.121262	0.364619	2.285173
H	1.193781	0.217724	3.365540
H	1.941193	-0.197708	1.829714
H	1.287723	1.423004	2.087897
C	-1.326328	0.828324	2.355652
H	-2.334596	0.461086	2.159026
H	-1.222673	0.892537	3.441832
H	-1.252715	1.843070	1.967283
C	-0.500294	-1.520795	2.277836
H	-0.468635	-1.553852	3.369875
H	-1.479756	-1.901795	1.981808
H	0.258359	-2.217882	1.914049
N	-1.805643	-0.630728	-0.388020
C	-2.186742	-1.858030	-0.696770
N	-3.497596	-1.872157	-0.897776
C	-3.977608	-0.600342	-0.714786
C	-2.914031	0.174908	-0.395973
C	-4.289324	-3.031768	-1.260256
H	-4.792738	-2.851943	-2.206521
H	-5.026147	-3.235149	-0.487466
H	-3.636718	-3.892938	-1.365346
H	-1.541849	-2.715575	-0.782886
H	-5.018218	-0.353426	-0.831396
H	-2.862593	1.228268	-0.183810
W	0.595789	2.141871	-1.210832
C	1.236503	3.710492	-2.267102
O	1.608226	4.610337	-2.879057
C	-0.090359	3.430293	0.176875
O	-0.455478	4.216185	0.936777
C	2.430936	2.109238	-0.296513
O	3.472675	2.131427	0.176526
C	1.353782	0.794878	-2.708024
O	2.006405	0.384387	-3.556871
C	-1.167946	2.232324	-2.255070
O	-2.131919	2.308828	-2.866892
O	-0.001860	-0.693597	-2.237343
H	0.644975	-1.251762	-0.096174
C	0.442495	-1.958103	-2.535085
H	-0.351275	-2.621839	-2.922555
H	1.233523	-1.960428	-3.302088
H	0.886950	-2.484938	-1.661967

(**5'** →**3a'**+NMeIm)$^{‡\ eq}$

E = -1514.06552477 au
ZPE = 0.32733680au
G_{corr} = 0.27303963 au
ν = -234.64 cm^{-1}

P	-0.562359	0.366893	0.049338
C	1.285288	0.085675	-0.333455
C	1.876011	1.494122	-0.423443
H	2.898484	1.444278	-0.805680
H	1.312668	2.143595	-1.099264
H	1.915740	1.976266	0.552634

C	2.035141	-0.708097	0.730892
H	1.755709	-1.762626	0.737271
H	3.109117	-0.669968	0.531371
H	1.882404	-0.309882	1.732902
C	1.448917	-0.604183	-1.688261
H	2.507413	-0.659596	-1.955034
H	1.073025	-1.629286	-1.686141
H	0.944436	-0.060002	-2.490234
N	-0.965444	-1.399598	0.084887
C	-1.537133	-2.101119	-0.878387
N	-1.742220	-3.340985	-0.454618
C	-1.287444	-3.438623	0.835766
C	-0.801963	-2.219588	1.170547
C	-2.351418	-4.410906	-1.220798
H	-3.231855	-4.779743	-0.701220
H	-1.641045	-5.222335	-1.356693
H	-2.648595	-4.031172	-2.193446
H	-1.806114	-1.731633	-1.852993
H	-1.351803	-4.350272	1.403415
H	-0.364736	-1.876105	2.091490
W	-1.153669	1.756741	2.112742
C	-1.842990	2.897784	3.599316
O	-2.244508	3.556580	4.452057
C	0.468168	1.366137	3.241390
O	1.373741	1.184544	3.930841
C	-0.245062	3.431951	1.356412
O	0.234053	4.398543	0.974677
C	-2.893283	2.204690	0.928543
O	-3.799994	2.772716	0.516200
C	-2.177797	0.176211	2.927567
O	-2.771482	-0.676793	3.406261
O	-2.775471	0.433973	-0.135972
H	-0.803178	0.734246	-1.291909
C	-3.340111	0.502698	-1.385442
H	-3.872324	-0.420459	-1.677505
H	-4.080667	1.313913	-1.472952
H	-2.600105	0.700913	-2.192129

3a'

E = -1248.65846312 au
ZPE = 0.22416631 au
G_{corr} = 0.17459735au

P	0.866477	-0.222563	0.042102
C	0.321953	-0.264392	1.811211
C	1.087087	0.841750	2.538727
H	0.825375	0.825561	3.598534
H	2.168794	0.707124	2.469743
H	0.846714	1.835029	2.160298
C	-1.184512	-0.023619	1.889390
H	-1.747930	-0.818075	1.400260
H	-1.494528	0.005560	2.936055
H	-1.478067	0.923363	1.437050
C	0.670577	-1.621152	2.425572
H	0.376348	-1.628153	3.477518
H	0.151190	-2.441362	1.932463
H	1.742464	-1.821551	2.383624
W	0.774698	1.845488	-1.385568
C	0.799824	3.455360	-2.612093
O	0.823547	4.358932	-3.313523
C	-0.371969	2.953166	-0.084934
O	-1.000776	3.620498	0.595292
C	2.470801	2.503615	-0.427150
O	3.407574	2.866241	0.114325
C	1.940718	0.868357	-2.768718
O	2.597083	0.360472	-3.552541
C	-0.957516	1.162985	-2.269052
O	-1.924202	0.792958	-2.747708
O	0.086194	-1.550947	-0.525054
H	2.192308	-0.702404	0.204975
C	0.458189	-2.097134	-1.776502
H	1.520055	-2.359424	-1.805633
H	-0.125115	-3.004266	-1.920493
H	0.243603	-1.416629	-2.603433

6'

E = -1132.85770290 au
ZPE = 0.16863624 au
G_{corr} = 0.12191948 au

P	-0.429242	0.458832	0.368451
C	-0.126783	0.347998	2.210441
C	0.521462	-1.037235	2.375627
H	0.622840	-1.256176	3.442265
H	-0.082877	-1.835058	1.938266
H	1.517723	-1.085103	1.934891
C	0.755456	1.424022	2.826241
H	0.313869	2.414933	2.716202

H	0.874079	1.240404	3.897720
H	1.752482	1.446677	2.389918
C	-1.494417	0.347846	2.901790
H	-1.371532	0.184059	3.975953
H	-2.010745	1.300772	2.772916
H	-2.143284	-0.437336	2.512788
W	1.216096	1.489499	-1.030650
C	2.500379	2.321350	-2.445922
O	3.204803	2.774789	-3.215728
C	1.352063	3.229457	0.085633
O	1.444188	4.196382	0.677767
C	2.833272	0.755361	0.022608
O	3.739862	0.358185	0.586182
C	1.134810	-0.226534	-2.189376
O	1.089641	-1.162267	-2.833935
C	-0.384518	2.231723	-2.114606
O	-1.259348	2.632841	-2.720762

N-MeIm

E = -265.47223160 au
ZPE = 0.10229563 au
G_{corr} = 0.07362241 au

N	-0.595149	-1.164843	-0.637517
C	-1.065054	-0.515103	-1.668488
N	-1.884150	-1.279441	-2.423737
C	-1.937513	-2.507300	-1.826656
C	-1.134438	-2.413767	-0.725808
C	-2.567497	-0.878841	-3.629057
H	-3.645717	-0.974895	-3.513057
H	-2.247992	-1.483945	-4.475915
H	-2.335778	0.161604	-3.842262
H	-0.848768	0.512307	-1.921830
H	-2.525342	-3.316786	-2.226023
H	-0.919825	-3.179914	0.002783

7'

E = -1248.59012068 au
ZPE = 0.22531538 au
G_{corr} = 0.17516343 au

P	0.069764	0.029225	0.200825
C	0.178448	0.054084	2.073031
C	1.588489	0.029889	2.648575
H	1.551416	0.064467	3.741218
H	2.124709	-0.879955	2.374071
H	2.179594	0.880957	2.313882
C	-0.527460	1.363500	2.445623
H	-1.553069	1.394919	2.071886
H	-0.573123	1.455108	3.533496
H	-0.006767	2.244658	2.070942
C	-0.632383	-1.112324	2.644665
H	-0.705074	-1.016574	3.731561
H	-1.647369	-1.132717	2.244714
H	-0.165972	-2.077367	2.441542
W	1.816943	1.419071	-1.064182
C	3.048127	2.495631	-2.244797
O	3.748858	3.099406	-2.922722
C	2.064725	2.858689	0.388417
O	2.242713	3.686782	1.154035
C	3.425528	0.419536	-0.281514
O	4.338400	-0.117315	0.152831
C	1.634628	0.075441	-2.600886
O	1.549026	-0.656777	-3.476553
C	0.190032	2.465332	-1.785746
O	-0.705644	3.048845	-2.181895
O	0.819568	-1.732257	0.027460
C	0.010429	-2.728662	-0.632776
H	-0.177959	-2.449427	-1.667447
H	0.531896	-3.681436	-0.580802
H	-0.925800	-2.782631	-0.087941
H	1.709097	-1.695286	-0.352455

(**7'**→**3a'**)‡

E = -1248.55269867 au
ZPE = 0.22029633 au
G_{corr} = 0.17062555 au
ν = -1707.76 cm^{-1}

P	-0.243225	-0.326630	-0.003997
C	-0.086984	-0.027991	1.831182
C	1.376839	-0.084897	2.273005
H	1.448129	0.216546	3.320906

H	1.794663	-1.087334	2.194790
H	2.001721	0.594539	1.691070
C	-0.604283	1.398232	2.044909
H	-1.644202	1.525320	1.747863
H	-0.538934	1.648308	3.106115
H	-0.007735	2.131341	1.498281
C	-0.909953	-1.038139	2.624639
H	-0.813241	-0.837672	3.694592
H	-1.969795	-0.993062	2.377716
H	-0.567267	-2.058907	2.449782
W	-2.518885	-0.549043	-1.071007
C	-4.292643	-0.670893	-2.029818
O	-5.294857	-0.746127	-2.577423
C	-2.249163	1.373645	-1.765304
O	-2.105278	2.439641	-2.142617
C	-1.668647	-1.275024	-2.796437
O	-1.258981	-1.660848	-3.789765
C	-2.769233	-2.440284	-0.295417
O	-2.921509	-3.479043	0.151167
C	-3.584394	0.190233	0.525612
O	-4.253409	0.588288	1.360642
O	0.856560	-1.862081	-0.021716
C	0.736020	-2.806463	-1.078422
H	0.874845	-2.342627	-2.056900
H	1.514303	-3.554397	-0.935824
H	-0.237658	-3.293161	-1.048891
H	1.212692	-0.746970	-0.418272

(**7'**→**3a'**)‡·MeOH

E = -1364.30489212 au
ZPE = 0.27711982 au
G_{corr} = 0.22362663 au
ν = -314.21 cm^{-1}

P	0.264441	-0.102767	-0.268680
C	-0.145610	-0.220298	1.559718
C	1.082922	-0.312860	2.460855
H	0.782087	-0.310267	3.512616
H	1.648849	-1.229424	2.290383
H	1.760491	0.526433	2.310506
C	-0.918868	1.065534	1.865723
H	-1.833551	1.136093	1.274371
H	-1.202294	1.085292	2.921005
H	-0.330965	1.963554	1.675065
C	-1.060564	-1.416715	1.818285
H	-1.365781	-1.431368	2.868123
H	-1.970549	-1.363066	1.217079
H	-0.569271	-2.367102	1.609229
W	2.167927	1.469854	-0.994507
C	3.551664	2.703121	-1.769178
O	4.344779	3.399938	-2.222080
C	2.077893	2.715764	0.635095
O	2.074506	3.445905	1.515293
C	3.619264	0.391458	-0.024113
O	4.438268	-0.182503	0.531030
C	2.334059	0.313003	-2.682767
O	2.436785	-0.304242	-3.640143
C	0.656507	2.549069	-1.879558
O	-0.191054	3.143952	-2.361168
O	0.629924	-1.780522	-0.657781
C	1.893030	-2.408549	-0.519356
H	2.255380	-2.337638	0.505331
H	1.771069	-3.462117	-0.770337
H	2.636740	-1.975239	-1.188189
H	-0.371156	-2.010124	-1.622348
O	-1.247430	-1.653253	-2.115823
H	-1.209596	-0.746301	-1.585087
C	-2.421957	-2.426833	-1.797993
H	-2.571694	-2.484105	-0.721251
H	-3.274733	-1.949450	-2.270360
H	-2.283626	-3.422214	-2.208879

(**7'**→**3a'**)‡·(MeOH)$_2$

E = -1480.04011201 au
ZPE = 0.33230475 au
G_{corr} = 0.27407983 au
ν = -119.95 cm^{-1}

P	-0.041845	0.055083	-0.024508
C	-0.016309	0.011570	1.856503
C	1.381899	-0.026133	2.467945
H	1.318570	-0.034847	3.560313
H	1.942869	-0.911433	2.168025
H	1.968077	0.846191	2.181357
C	-0.719673	1.304158	2.281999
H	-1.758198	1.328036	1.946620

H	-0.719919	1.388328	3.371816
H	-0.226330	2.195920	1.893019
C	-0.832853	-1.178793	2.360649
H	-0.944227	-1.118445	3.446746
H	-1.836195	-1.196060	1.930187
H	-0.360058	-2.135948	2.139798
W	1.779316	1.438057	-1.230426
C	3.039934	2.517089	-2.359156
O	3.761061	3.125458	-3.015981
C	1.890252	2.890346	0.217358
O	1.983897	3.723063	0.995887
C	3.367896	0.492765	-0.338055
O	4.275703	-0.001583	0.152664
C	1.691029	0.016954	-2.705525
O	1.635316	-0.769405	-3.535734
C	0.170652	2.413706	-2.059273
O	-0.728373	2.955135	-2.510815
O	0.125751	-1.632590	-0.436517
C	1.312104	-2.388840	-0.271781
H	1.487700	-2.631342	0.777404
H	1.203224	-3.320445	-0.827831
H	2.178696	-1.854834	-0.659908
H	-1.049647	-2.157596	-1.050791
O	-1.962624	-2.330288	-1.533950
H	-2.525039	-1.380648	-1.382503
C	-1.742965	-2.596997	-2.928936
H	-2.711017	-2.705918	-3.409685
H	-1.185170	-1.791357	-3.405044
H	-1.190843	-3.528704	-3.021534
O	-2.939181	-0.166946	-1.139369
H	-2.078403	0.179951	-0.720357
C	-4.017759	-0.037880	-0.216890
H	-4.892295	-0.522879	-0.644185
H	-3.789342	-0.502208	0.744829
H	-4.244697	1.015507	-0.057102

(**7'**→**8'**)‡

E = -1248.55952114 au
ZPE = 0.21795860 au
G_{corr} = 0.16830392 au
ν = -1490.54 cm^{-1}

P	-0.043024	-0.005575	0.315068
C	0.181712	0.061283	2.172779
C	1.621390	0.012089	2.664909
H	1.641253	0.000672	3.758117
H	2.138124	-0.883997	2.320266
H	2.193775	0.880257	2.339971
C	-0.503044	1.354042	2.623442
H	-1.549198	1.388301	2.313757
H	-0.480573	1.419252	3.713732
H	-0.013295	2.248917	2.241144
C	-0.599788	-1.129993	2.739646
H	-0.618079	-1.064691	3.830552
H	-1.635507	-1.140306	2.394577
H	-0.141919	-2.083581	2.478163
W	1.830927	1.217798	-1.082780
C	3.056419	2.369295	-2.231462
O	3.753256	3.001320	-2.877617
C	1.859693	2.759777	0.300487
O	1.937481	3.650161	1.005366
C	3.502060	0.429466	-0.176937
O	4.446089	0.010404	0.305828
C	1.944567	-0.122395	-2.634774
O	2.035737	-0.823239	-3.530325
C	0.146044	2.027013	-1.977472
O	-0.781809	2.463344	-2.469041
O	0.685783	-1.641892	0.070000
C	-0.060078	-2.505738	-0.777146
H	-0.184649	-2.085293	-1.778683
H	0.477408	-3.449196	-0.854342
H	-1.050077	-2.681289	-0.351979
H	1.411093	-0.653396	-0.466188

8'

E = -1248.61478663 au
ZPE = 0.22244975 au
G_{corr} = 0.17206367 au

P	0.038395	-0.124372	0.502718
C	0.355558	-0.229750	2.339906
C	1.571464	-1.082837	2.684608
H	1.713349	-1.103795	3.767969
H	1.457807	-2.112051	2.346179
H	2.485241	-0.680455	2.242178
C	0.559683	1.209064	2.812195
H	-0.292655	1.847917	2.572787

H	0.686434	1.223833	3.896623
H	1.454397	1.660770	2.378057
C	-0.908439	-0.817263	2.971525
H	-0.796621	-0.846828	4.057570
H	-1.791832	-0.217385	2.746127
H	-1.094308	-1.836566	2.631967
W	1.841170	1.387231	-1.157608
C	2.678744	2.551431	-2.535159
O	3.178017	3.218391	-3.322385
C	0.856373	3.019461	-0.367353
O	0.320152	3.933366	0.049976
C	3.457697	1.774411	0.065916
O	4.369138	2.013360	0.706090
C	2.826155	-0.241402	-1.954389
O	3.381169	-1.124642	-2.411183
C	0.267702	1.081813	-2.458845
O	-0.587530	0.946607	-3.198624
O	0.127716	-1.718109	0.092969
C	-0.492998	-2.127147	-1.114428
H	0.139604	-1.914109	-1.979821
H	-0.643540	-3.203819	-1.058588
H	-1.463208	-1.646066	-1.265139
H	1.506933	0.181751	0.337219

(**8'**→**3a'**)‡

E = -1248.61160839 au
ZPE = 0.22202724 au
G_{corr} = 0.17204787 au
ν = -198.68 cm^{-1}

P	0.374096	-0.219164	0.511605
C	0.403630	-0.271472	2.373881
C	1.437989	-1.260976	2.901964
H	1.415694	-1.269390	3.994642
H	1.241785	-2.276800	2.560386
H	2.448877	-0.988898	2.593581
C	0.739985	1.148515	2.825071
H	0.001326	1.875927	2.484538
H	0.758977	1.187950	3.916175
H	1.722622	1.471877	2.474465
C	-0.998083	-0.661044	2.844352
H	-1.032156	-0.666012	3.936016
H	-1.754166	0.041759	2.491183
H	-1.275308	-1.659029	2.503027
W	1.817526	1.435791	-1.225502
C	2.508423	2.669898	-2.594127
O	2.909489	3.389836	-3.394913
C	0.762000	2.993230	-0.375056
O	0.188140	3.870075	0.070401
C	3.443323	1.920021	-0.054897
O	4.363073	2.227897	0.544601
C	2.887237	-0.095682	-2.100821
O	3.493567	-0.913839	-2.611689
C	0.222861	1.052087	-2.483558
O	-0.643796	0.882318	-3.202132
O	0.290895	-1.814612	0.106546
C	-0.442192	-2.162836	-1.056915
H	0.126849	-1.954496	-1.966329
H	-0.635131	-3.233318	-1.012635
H	-1.399311	-1.637934	-1.116459
H	1.823550	-0.058868	0.441654

9'

E = -1514.09934687 au
ZPE = 0.32940096 au
G_{corr} = 0.27259477 au

P	-0.348444	-0.416903	0.892400
C	-0.051839	0.459881	2.537806
C	1.456587	0.320263	2.768794
H	1.742762	0.817489	3.699898
H	1.755384	-0.726454	2.841562
H	2.043706	0.776468	1.970185
C	-0.428344	1.937922	2.596239
H	-1.489020	2.105255	2.409929
H	-0.203087	2.350013	3.585493
H	0.128904	2.522768	1.865424
C	-0.782326	-0.299934	3.646754
H	-0.477065	0.084654	4.624520
H	-1.865451	-0.191908	3.582493
H	-0.551633	-1.366349	3.622736
N	-1.972270	-2.914005	-0.568069
C	-2.878566	-3.385003	-1.400763
N	-2.311324	-4.300048	-2.177237
C	-0.987824	-4.406228	-1.827716
C	-0.778161	-3.527526	-0.816672
C	-2.970381	-5.051167	-3.227929

H	-2.938472	-6.113820	-3.001676
H	-2.476755	-4.865585	-4.178241
H	-4.006073	-4.733882	-3.300233
H	-3.908601	-3.077058	-1.454974
H	-0.315216	-5.082538	-2.325347
H	0.109174	-3.271533	-0.264045
W	0.044402	1.028072	-1.266160
C	0.414583	1.934912	-3.009963
O	0.618486	2.453736	-4.018411
C	-1.211395	2.543810	-0.682916
O	-1.902470	3.404266	-0.378567
C	1.630447	2.060077	-0.458906
O	2.521750	2.660772	-0.066838
C	1.298908	-0.525086	-1.735446
O	1.986498	-1.406885	-1.979669
C	-1.499413	0.042098	-2.162063
O	-2.353834	-0.508509	-2.698682
O	-2.042144	-0.826960	0.994814
H	-2.104594	-2.106773	0.113416
C	-3.088412	0.116111	0.918933
H	-4.037726	-0.424544	0.922361
H	-3.084694	0.789313	1.777998
H	-3.036895	0.719004	0.010266

(**9'**→**3a'**)‡

E = -1514.09756515 au
ZPE = 0.32924041 au
G_{corr} = 0.27317594 au
ν = -128.33 cm^{-1}

P	-0.450363	-0.431237	0.955659
C	-0.121397	0.507452	2.560778
C	1.387612	0.373113	2.783293
H	1.684400	0.899639	3.694822
H	1.685251	-0.671484	2.887632
H	1.967449	0.800497	1.963622
C	-0.499495	1.986527	2.565246
H	-1.566148	2.140964	2.402801
H	-0.248856	2.441718	3.529307
H	0.033037	2.541831	1.794404
C	-0.849135	-0.204526	3.702573
H	-0.548029	0.224302	4.663165
H	-1.932215	-0.103991	3.627433
H	-0.614224	-1.270198	3.726496
N	-1.483364	-3.173046	-0.431501
C	-2.581168	-3.402986	-1.123678
N	-2.269697	-4.175652	-2.154016
C	-0.919789	-4.428602	-2.120151
C	-0.425807	-3.787700	-1.033327
C	-3.187301	-4.628542	-3.182192
H	-3.154001	-5.712130	-3.255137
H	-2.915231	-4.187681	-4.137686
H	-4.195477	-4.320710	-2.923295
H	-3.560697	-3.019944	-0.896022
H	-0.430149	-5.029821	-2.865826
H	0.575739	-3.712255	-0.649760
W	0.016108	0.904546	-1.259038
C	0.401406	1.732563	-3.037896
O	0.610124	2.204898	-4.068287
C	-1.327492	2.385197	-0.784681
O	-2.059531	3.227211	-0.530137
C	1.525575	2.056021	-0.465393
O	2.378921	2.717325	-0.086565
C	1.367925	-0.598107	-1.580134
O	2.115448	-1.451946	-1.738048
C	-1.431458	-0.215359	-2.153671
O	-2.222736	-0.849190	-2.697535
O	-2.123581	-0.813819	1.069826
H	-1.425355	-2.520348	0.356677
C	-3.161253	0.108030	0.858637
H	-4.112246	-0.402973	1.030172
H	-3.114226	0.957554	1.544747
H	-3.169414	0.501049	-0.161820

11'$^{+}$

E = -1398.833880229162 au
ZPE = 0.28567851 au
G_{corr} = 0.23326223 au

P	-0.156627	0.253301	0.045125
C	-0.021979	-0.010242	1.881917
C	1.483935	-0.011822	2.166910
H	1.638844	-0.131470	3.240406
H	1.996254	-0.836738	1.669289
H	1.973492	0.917109	1.877571
C	-0.707286	1.140683	2.613088
H	-1.781298	1.175107	2.421335
H	-0.579218	1.012068	3.689091
H	-0.281586	2.108606	2.348025

C	-0.623487	-1.350672	2.295708
H	-0.415389	-1.520398	3.353578
H	-1.707105	-1.378437	2.178139
H	-0.189611	-2.188004	1.745718
N	-1.793157	-0.401280	-0.312923
C	-2.066949	-1.626020	-0.754550
N	-3.371376	-1.741378	-0.931557
C	-3.966966	-0.554220	-0.588882
C	-2.979745	0.286622	-0.205261
C	-4.064165	-2.921588	-1.425403
H	-4.572731	-2.682387	-2.355185
H	-4.786297	-3.255437	-0.685642
H	-3.342560	-3.712129	-1.604388
H	-1.343448	-2.400439	-0.948945
H	-5.030902	-0.403344	-0.650607
H	-3.037105	1.308939	0.123409
W	0.294170	2.358262	-1.174533
C	0.670979	4.005450	-2.314871
O	0.878104	4.916738	-2.964611
C	-1.194286	3.391235	-0.203124
O	-2.013022	3.979099	0.330749
C	1.636005	3.093131	0.214796
O	2.374627	3.540548	0.955910
C	1.833486	1.374576	-2.143480
O	2.681074	0.832289	-2.673406
C	-1.038775	1.721670	-2.607544
O	-1.783430	1.366353	-3.393740
H	0.506197	-0.905117	-0.406117

11'$^{+}$ (gas phase)

E = -1398.78584020 au
ZPE = 0.28656344 au
TVC = 0.02314551 au
T·*S* = 50.10 kcal/mol
G_{corr} = 0.23364027 au

P	-0.145022	0.265848	0.067673
C	-0.003174	-0.003480	1.904973
C	1.505505	0.008434	2.179963
H	1.671090	-0.117204	3.251164
H	2.026129	-0.808047	1.676534
H	1.984068	0.944116	1.894826
C	-0.690973	1.142086	2.642910
H	-1.769288	1.160005	2.474554
H	-0.541416	1.024622	3.717308
H	-0.286652	2.115002	2.363953
C	-0.589411	-1.349288	2.323041
H	-0.378323	-1.519079	3.380154
H	-1.673124	-1.390410	2.209584
H	-0.147337	-2.184299	1.775485
N	-1.802290	-0.402773	-0.272492
C	-2.077655	-1.601870	-0.771449
N	-3.384159	-1.709789	-0.960439
C	-3.976065	-0.537212	-0.566126
C	-2.986003	0.281587	-0.141129
C	-4.078088	-2.862311	-1.515751
H	-4.574247	-2.582389	-2.441497
H	-4.811073	-3.229973	-0.802446
H	-3.361723	-3.651310	-1.723815
H	-1.354331	-2.368004	-0.997265
H	-5.039010	-0.377208	-0.625423
H	-3.039305	1.290492	0.227806
W	0.282683	2.325175	-1.180043
C	0.640789	3.966734	-2.362775
O	0.832708	4.864143	-3.029060
C	-1.224622	3.354534	-0.233867
O	-2.059477	3.926619	0.290646
C	1.611450	3.109800	0.204769
O	2.336956	3.573702	0.945420
C	1.845519	1.350135	-2.131135
O	2.699636	0.807605	-2.646129
C	-1.036291	1.629786	-2.595360
O	-1.780534	1.221085	-3.355591
H	0.491727	-0.916200	-0.372976

12'$^{+}$

E = -1438.148890300190 au
ZPE = 0.31567536 au
G_{corr} = 0.26249370 au

P	0.057756	-0.088093	-0.021954
C	-0.017632	-0.030015	1.846892
C	1.436727	-0.034715	2.331402
H	1.447990	0.144406	3.407644
H	1.928823	-0.991651	2.158181
H	2.042791	0.747456	1.873781
C	-0.702843	1.265447	2.277343
H	-1.738452	1.326527	1.939080

H	-0.722555	1.313531	3.367418
H	-0.173770	2.149429	1.923060
C	-0.759241	-1.228375	2.435827
H	-0.669175	-1.194383	3.523034
H	-1.825250	-1.214668	2.207353
H	-0.346268	-2.186738	2.118057
N	-1.593879	-0.719197	-0.402612
C	-1.941206	-1.979041	-0.654310
N	-3.241842	-2.036365	-0.882904
C	-3.762501	-0.773229	-0.770602
C	-2.732781	0.050768	-0.473358
C	-3.996412	-3.234252	-1.216791
H	-4.445034	-3.120178	-2.199712
H	-4.772861	-3.393839	-0.473868
H	-3.327580	-4.088871	-1.225132
H	-1.280330	-2.828001	-0.681412
H	-4.807918	-0.563445	-0.917377
H	-2.731037	1.114536	-0.320920
W	0.605034	1.883351	-1.463219
C	1.062581	3.388063	-2.750854
O	1.314230	4.223292	-3.483801
C	-0.905920	3.062235	-0.721633
O	-1.729190	3.749121	-0.331423
C	1.885752	2.737520	-0.086615
O	2.598475	3.242477	0.643653
C	2.190358	0.827134	-2.257607
O	3.074168	0.270897	-2.710903
C	-0.653222	1.088409	-2.882983
O	-1.354563	0.641542	-3.663003
C	1.019389	-1.593361	-0.387980
H	2.069591	-1.352108	-0.229903
H	0.776909	-2.446735	0.244194
H	0.907999	-1.864747	-1.437343

Me_3P (gas phase)

E = -461.01963096 au
ZPE = 0.11637485 au
TVC = 0.00368700 au
T·*S* = 22.97 kcal/mol
G_{corr} = 0.08723634 au

P	0.340562	-0.370282	1.459911
C	1.510166	0.860827	0.727155
H	1.710699	1.655514	1.445791
H	2.462044	0.379801	0.501939
H	1.126231	1.312907	-0.189557
C	0.006414	-1.391668	-0.045343
H	-0.796892	-2.099946	0.157672
H	-0.275932	-0.787765	-0.910062
H	0.892181	-1.971767	-0.304337
C	-1.199116	0.654353	1.468569
H	-1.117740	1.440105	2.219666
H	-1.400705	1.120136	0.501846
H	-2.055005	0.035588	1.738321

Me_3PH^+ (gas phase)

E = -461.39490788 au
ZPE = 0.12699682 au
TVC = 0.00393930 au
T·*S* = 23.35 kcal/mol
G_{corr} = 0.09749620 au

H	-0.694694	0.845274	-1.672224
P	-1.594506	0.355874	-2.624374
C	-0.830506	-1.057908	-3.432327
H	-1.507306	-1.465174	-4.182996
H	0.096236	-0.759846	-3.920962
H	-0.606892	-1.835717	-2.703309
C	-1.921758	1.673001	-3.804780
H	-2.621919	1.324175	-4.563414
H	-2.353786	2.535859	-3.299524
H	-0.998836	1.980614	-4.294723
C	-3.099204	-0.128350	-1.766073
H	-3.824652	-0.515379	-2.481168
H	-2.883668	-0.903161	-1.031452
H	-3.535222	0.728048	-1.253308

$Me_2C=O$ (gas phase)

E = -193.11191615 au
ZPE = 0.08620305 au

TVC = 0.00163032 au
T·*S* = 20.20 kcal/mol
G_{corr} = 0.05941754 au

O	-0.000000	-0.000000	0.012673		H	1.317000	0.874854	2.674783
C	0.000000	0.000001	1.215752		C	-1.276647	0.000000	2.022743
C	1.276647	0.000000	2.022743		H	-2.149108	-0.000001	1.373900
H	2.149108	-0.000001	1.373900		H	-1.317000	0.874854	2.674783
H	1.316998	-0.874854	2.674783		H	-1.316998	-0.874854	2.674783

$Me_2C{=}O^+$ (gas phase)

E = -193.43536593 au
ZPE = 0.09883981 au
TVC = 0.00179692 au
T·*S* = 20.44 kcal/mol
G_{corr} = 0.07184320 au

O	-0.032405	-0.000000	0.036767		C	-1.271581	0.000000	2.002590
C	0.017261	-0.000000	1.300921		H	-2.121603	0.000000	1.325848
C	1.293496	0.000000	2.033834		H	-1.322669	0.870368	2.663088
H	2.178427	0.000000	1.399404		H	-1.322669	-0.870368	2.663088
H	1.327801	-0.870643	2.694549		H	0.831237	-0.000000	-0.413795
H	1.327801	0.870643	2.694549					

$CF_3SO_3^-$ (gas phase)

E = -961.60030040 au
ZPE = 0.02865669 au
TVC = 0.00418988 au
T·*S* = 25.00 kcal/mol
G_{corr} = -0.00322414 au

S	-1.326753	-4.066363	-1.425040		C	-2.467967	-4.596488	-0.064765
O	-0.044765	-3.967928	-0.730759		F	-3.726944	-4.749521	-0.498030
O	-1.917714	-2.798088	-1.846276		F	-2.505968	-3.703500	0.933879
O	-1.448579	-5.168660	-2.376519		F	-2.096563	-5.766434	0.473185

CF_3SO_3H (gas phase)

E = -962.08976692 au
ZPE = 0.04061674 au
TVC = 0.00471738 au
T·*S* = 25.55 kcal/mol
G_{corr} = 0.00838957 au

H	-1.525185	-2.034779	-1.388237		C	-2.490053	-4.621136	-0.034651
S	-1.298656	-4.173940	-1.370087		F	-3.701418	-4.767044	-0.532629
O	-0.033439	-3.926216	-0.734200		F	-2.501853	-3.665628	0.882894
O	-1.944802	-2.785494	-1.833374		F	-2.093581	-5.753698	0.514310
O	-1.495158	-5.104759	-2.437546					

AcO^- (gas phase)

E = -228.49541650 au
ZPE = 0.04998790 au
TVC = 0.00157678 au

TS = 20.37 kcal/mol
G_{corr} = 0.02288110 au

O	0.997982	-2.622347	2.870146	H	0.408811	-5.186353	3.212745
C	-0.025305	-3.174581	2.429592	H	-0.664249	-4.253998	4.232837
O	-0.766908	-2.838007	1.492668	H	-1.292099	-4.983471	2.745149
C	-0.428932	-4.483343	3.188861				

HOAc (gas phase)

E = -229.06404609 au
ZPE = 0.06400766 au
TVC = 0.00164075 au
T·S = 20.21 kcal/mol
G_{corr} = 0.03721520au

C	0.006157	-0.000002	0.004040	H	-2.107707	0.000001	-0.285208
O	-0.006480	0.000000	1.202445	H	-1.201902	0.876485	-1.533610
O	1.138919	0.000000	-0.711241	H	-1.201904	-0.876485	-1.533611
C	-1.203042	-0.000000	-0.885289	H	1.883140	0.000001	-0.095186

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