Electronic Supplementary Information (ESI)

A cavity-shaped *cis*-chelating P,N ligand for highly selective nickel-catalysed ethylene dimerisation

Yang Li,[a] Katrin Pelzer,[a] Damien Sechet,[b] Geordie Creste,[a] Dominique Matt,[b] Pierre Braunstein,*[a] Dominique Armspach*[a]

[a] Equipe Confinement Moléculaire et Catalyse, Institut de Chimie de Strasbourg, UMR 7177 CNRS, Université de Strasbourg, 4, rue Blaise Pascal, CS 90032, 67081 Strasbourg Cedex, France,
[b] Laboratoire de Chimie Inorganique Moléculaire et Catalyse, Institut de Chimie de Strasbourg, UMR 7177 CNRS, Université de Strasbourg, 4, rue Blaise Pascal, CS 90032, 67081 Strasbourg cedex, France,

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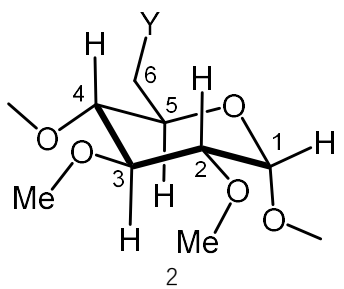
Experimental Details

1. General methods

All reactions and manipulations were carried out under an inert atmosphere (nitrogen or argon) using standard Schlenk techniques. All glassware was stored in the oven prior to use under an inert atmosphere of gas (Argon). All commercial reagents were used as supplied unless otherwise stated. Solvents were dried by conventional methods and distilled immediately prior to use. Deuterated solvents were passed through a 5 cm-thick alumina column and stored under nitrogen over molecular sieves (4 Å). Column chromatography was performed on silica gel 60 (particle size 40-63 µm, 230-240 mesh). Routine ^{1}H, $^{31}P\{^{1}H\}$ and $^{13}C\{^{1}H\}$ NMR spectra were recorded on Bruker FT instruments (AVANCE 300, 400, 500, 600 spectrometers) at room temperature unless otherwise stated. ^{1}H NMR spectral data were referenced to residual protiated solvents (δ = 7.26 ppm for $CDCl_3$, 7.15 ppm for C_6D_6 and 5.32 ppm for CD_2Cl_2), $^{13}C\{^{1}H\}$ chemical shifts are reported relative to deuterated solvents (δ = 77.16 ppm for $CDCl_3$, 128.02 ppm for C_6D_6 and 53.84 ppm for CD_2Cl_2) and the $^{31}P\{^{1}H\}$ NMR data are given relative to external H_3PO_4. Mass spectra were recorded on a Bruker MicroTOF spectrometer (ESI-TOF) using CH_2Cl_2, CH_3CN or CH_3OH as the solvent. Elemental analyses were performed by the Service de Microanalyse, Institut de Chimie UMR 7177, Strasbourg. Melting points were determined with a Buchi 535 capillary melting point apparatus. Dimesylate **5**[1], diethyl 2-amino-1-phenylphosphonate,[2] *N*,*N*-dimethyl-2-diethylphosphinoaniline[3-5] via 2-bromo-*N*,*N*-dimethylaniline[6] were prepared according to literature procedures. In this publication, the cyclodextrins are depicted as seen from the secondary face, the glucose units being ranged counterclockwise in the following order: A, B, C, D, E, F. The numbering of the atoms within a glucose unit is as follows:



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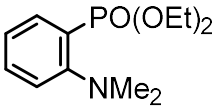
2. Synthesis and characterisation

Diethyl [2-(*N*,*N*-dimethylamino)phenyl]phosphonate (3)[7]



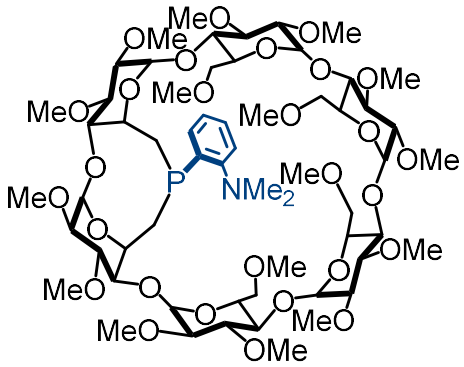
Diethyl 2-amino-1-phenylphosphonate[2] (530 mg, 2.31mmol), anhydrous K_2CO_3 (1.60 g, 11.56 mmol), methyl iodide (0.72 mL, 11.56 mmol) and dry DMF (5 mL) were placed in a 25 mL flask equipped with a condenser and stirred at 70 °C overnight. The reaction was cooled to room temperature before adding distilled H_2O (15 mL). The mixture was extracted with Et_2O (20 mL). The resulting aqueous layer was then further extracted with Et_2O (3 x 20 mL). The combined organic layers were washed with brine (3 x 15 mL), dried over $MgSO_4$ before being evaporated to dryness. The crude was then subjected to column chromatography (SiO_2; AcOEt/PE, 80/20, *v/v*) to afford **3** (510 mg, 86%) as yellow oil. R_f (SiO_2, AcOEt/PE , 90/10 , *v/v*) = 0.26; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.35 (t, ^3J = 7.1 Hz, 6H, OCH_2CH_3), 2.79 (s, 6H, NMe_2), 4.16 (m, 4H, OCH_2CH_3), 7.12 (m, 1H, aromatic H), 7.25 (m, 1H, aromatic H), 7.47 (m, 1H, aromatic H), 7.81 (m, 1H, aromatic H); $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$, 25°C): δ = 18 ppm. All spectral data are consistent with the literature values.[7]

2-(*N*,*N*-Dimethylamino)phenylphosphine (4)[8]

Pure Me_3SiCl (2.36 mL, 18.6 mmol) was added to a suspension of $LiAlH_4$ (71 mg, 18.6 mmol) in THF (20 mL) at −78 °C. The reaction mixture was allowed to reach room temperature and stirred for 2 h. A solution of phosphonate **3** (1.60 g, 6.2 mmol) in THF (6 mL) was then cannulated to the mixture at −30 °C and stirred for 1.5 h at 0 °C. The solvent was removed *in vacuo* and the residue was extracted with NaOH/Et_2O under argon to avoid phosphine oxidation. The organic layer was dried over $MgSO_4$. The solvent was finally removed under vacuum to afford primary phosphine **4** (0.56 g, 58%) as a colourless oil. The crude was used for the synthesis of **1** without further purification. R_f (SiO_2, AcOEt/PE, 70/30, *v/v*) = 0.95; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 2.73 (s, 6H, NMe_2), 3.91 (d,

2H, $^{1}J_{PH}$ = 204 Hz, PH_2), 6.98 (m, 1H, aromatic H), 7.12 (m, 1H, aromatic H), 7.27 (m, 1H, aromatic H), 7.48 (m, 1H, aromatic H); $^{31}P\{^{1}H\}$ NMR (161 MHz, $CDCl_3$, 25 °C): δ = −128 ppm. HRMS (ESI-TOF) for $C_8H_{12}NP$: *m/z* (%):154.0782 (100) $[M + H]^+$. All spectral data are consistent with the literature values.[8]

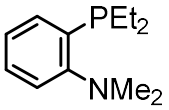
6^{A},6^{B}-Dideoxy-6^{A},6^{B}[(*R*)-2-(*N*,*N*-dimethylamino)phenylphosphinidene]-2^{A},2^{B},2^{C}, 2^{D},2^{E},2^{F},3^{A},3^{B},3^{C},3^{D},3^{E},3^{F}, 6^{C},6^{D},6^{E},6^{F}-hexadeca-O-methyl-α-cyclodextrin (1)



A solution of *n*-BuLi in hexane (1.6 M, 0.28 mL, 0.44 mmol) was added dropwise to a stirred solution of fully dried phosphine **4** (34 mg, 0.22 mmol) in 4 mL of THF at −78 °C. The mixture was then allowed to reach room temperature over a period of 1 h. The solution was cooled again to −78 °C and then added dropwise to a solution of fully dried dimesylate **5** (200 mg, 0.15 mmol) in THF (10 mL) via a cannula. The orange solution was stirred for 12 h at room temperature. The solvent was removed *in vacuo* and excess phosphide was protonated with MeOH (2 mL). The suspension was then evaporated to dryness to afford a colourless solid, which was subjected to chromatography over a short plug of silica (SiO_2; CH_2Cl_2/MeOH, 9/1, *v/v*). Finally, the filtrate was evaporated to dryness *in vacuo* and the resulting residue was subjected again to column chromatography (SiO_2; CH_2Cl_2/MeOH, 97:3, *v/v*) to afford pure **1** (122 mg, 63%) as a colourless solid. M.p. = 101-103 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ (assignment by COSY and HSQC) = 1.73 (m,1H, H-6a^{B}), 1.75 (m, 1H, H-6a^{A}), 2.68 (m, 1H, H-6b^{B}), 2.80 (s, 6H, NMe_2), 3.14 (m, 1H, H-6b^{A}), 3.23 (s, 3H, OMe), 3.24 (s, 3H, OMe), 3.38 (s, 6H, OMe), 3.46 (s, 3H, OMe), 3.47 (s, 3H, OMe), 3.48 (s, 3H, OMe), 3.49 (s, 6H, OMe), 3.50 (s, 3H, OMe), 3.60 (s, 3H, OMe), 3.63 (s, 6H, OMe), 3.64 (s, 3H, OMe), 3.65 (s, 3H, OMe), 3.67 (s, 3H, OMe), 3.11–3.90 (29H, H-2, H-3, H-4, H-5, H-6), 4.01 (m, 1H, H-5^{B}), 4.09 (dd, 1H, $^{2}J_{H\text{-}6a,\ H\text{-}6b}$ = 2.0 Hz, $^{2}J_{H6\text{-}H5}$ = 10.6 Hz, H-6), 4.30 (m, 1H, H-5^{A}), 4.96 (d, 1H, $^{3}J_{H1\text{-}H2}$ = 2.8 Hz, H-1), 4.99 (d, 1 H, $^{3}J_{H1\text{-}H2}$ = 2.9 Hz, H-1), 5.02 (d, 1H, $^{3}J_{H1\text{-}H2}$ = 4.0 Hz, H-1), 5.05 (d, 1H, $^{3}J_{H1\text{-}H2}$ = 4.2 Hz, H-1), 5.06-5.07 (2H, H-1), 7.01-7.44 (4H,

aromatic H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ (assignment by HSQC) = 27.38 (C-$6^{A\text{ or }B}$), 34.08 (C-$6^{A\text{ or }B}$), 46.10, 46.16 (-N(CH_3)$_2$), 57.58, 57.96 [x5], 58.95, 59.04, 59.07, 59.15, 61.77 [x3], 61.87, 62.05, 62.18 (OMe), 70.27, 71.02 (C-6), 71.05 (C-5), 71.28 (C-6), 71.32, 71.40, 71.46 (C-5), 71.56 (C-6), 72.90, 73.20 (C-5), 81.28 [x4], 81.43, 81.56 [x2], 81.66, 81.83 [x2], 82.14, 82.37 [x2], 82.52, 82.71, 83.47, 87.87, 89.18 (C-2, C-3, C-4), 97.51, 99.35, 100.01, 100.19, 100.28, 100.63 (C-1), 118.69, 123.65, 129.85, 133.48 (aromatic C), 135.12 (d, $^1J_{P,C}$ = 19.1 Hz, aromatic C), 157.27(d, $^2J_{P,C}$ = 12.2 Hz, aromatic C); ^{31}P{^{1}H} NMR (121 MHz , $CDCl_3$, 25 °C): δ = −28.4 ppm; elemental analysis (%) calcd for $C_{60}H_{100}NO_{28}P$•H_2O: C 54.09, H 7.72, N 1.05, found: C 54.13, H 7.64, N 0.97; MS (ESI-TOF) for $C_{60}H_{100}NO_{28}P$: *m/z* (%): 1314.63 (100) [*M* + H]$^+$.

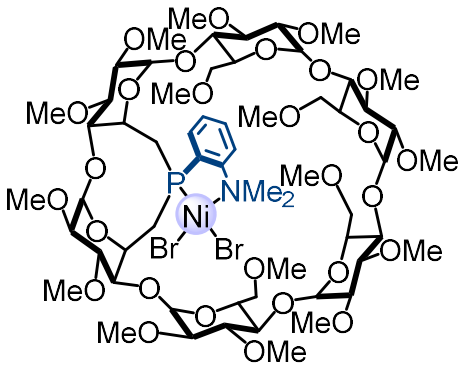
***N*,*N*-dimethyl-2-diethylphosphinoaniline (7)**[5]



A Schlenk tube filled with argon was charged with **(**2-bromo-N,N-dimethylaniline**)** (320 mg, 1.60 mmol) in THF (3 mL). The solution was cooled at -78 °C and *n*-BuLi (1.92 mmol, 1.2 eq.) was added dropwise. The mixture was allowed to rise slowly to room temperature. Et_2PCl (200 mg, 1.60 mmol) was then added to the mixture at 0 °C which was stirred overnight at room temperature. The solvent was removed *in vacuo*. The residue was suspended in DCM and filtered through Celite. Removal of the solvent under reduced pressure afforded the crude filtrate which was purified by column chromatography (SiO_2; PE/DCM, 50/50, *v/v*) to afford **10** as a pale yellow oil (135 mg, 40%). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) : δ = 0.98 (t, ^3J = 7.5 Hz, 3H, PCH_2CH_3), 1.03 (t, ^3J = 7.5 Hz, 3H, PCH_2CH_3), 1.69 (m, 4H, PCH_2CH_3), 2.75 (m, 6H, NMe_2), 7.09 (m, 1H, aromatic H), 7.14 (m, 1H, aromatic H), 7.25-7.34 (2H, aromatic H), ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 25 °C): δ = -25.05 ppm. HRMS (ESI-TOF) for $C_{12}H_{20}NP$: *m/z* (%): 210.1406 (100) [*M* + H]$^+$. All spectral data are consistent with the literature values.[5]

Dibromo-[{6^A,6^B-Dideoxy-6^A,6^B-[(*R*)-2-(*N*,*N*-dimethylamino)phenyl phosphinidene]-2^A,2^B,2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F,6^C,6^D,6^E,6^F-hexadeca-O-methyl

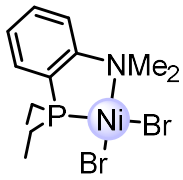
-α-cyclodextrin}-κ²P,N]nickel(II) (9)



To a solution of **1** (271.5 mg, 0.21 mmol) in CH_2Cl_2 (10 mL) was added dropwise a solution of [$NiBr_2$(DME)] (73 mg, 0.21 mmol) in CH_2Cl_2. The reaction mixture was stirred for 2 h at room temperature. The solution was evaporated to dryness under reduced pressure. The resulting violet residue was redissolved with benzene and then filtered through a pad of Celite. The filtrate was evaporated *in vacuo* to afford **9** as a violet solid (205 mg, 64.7%). A crystalline material was obtained by slow diffusion of *n*-pentane into a benzene solution of **9**. ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C): δ (assignment by COSY and HSQC) = 2.96-4.13 (27H, H-2, H-3, H-4, H-5^{C,D,E,F}, H-6), 3.38 (s, 3H, OMe), 3.39 (s, 3H, OMe), 3.44 (s, 3H, OMe), 3.45(s, 6H, OMe), 3.45 (s, 3H, OMe), 3.46 (s, 3H, OMe), 3.50 (s, 3H, OMe), 3.53 (s, 3H, OMe), 3.55 (s, 3H, OMe), 3.56 (s, 3H, OMe), 3.56 (s, 3H, OMe), 3.57 (s, 3H, OMe), 3.58 (s, 3H, OMe), 3.59 (s, 3H, OMe), 3.61 (s, 3H, OMe), 4.36 (m, 2H, H-5$^{A\text{ or }B}$, H-6), 4.47 (d, 1H, J = 10.9 Hz, H-6), 4.95 (1H, $^3J_{H1\text{-}H2}$ = 3.4 Hz, H-1), 4.98 (2H, H-1, H-5$^{B\text{ or }A}$), 4.99-5.03 (2H, H-1), 5.02 (m, 1H, H-6), 5.09-5.12 (m, 2H, H-1), 7.29-7.66 (4H, aromatic H), signal for NMe_2 is too broad to be identified; ^{13}C NMR (126 MHz, CD_2Cl_2, 25°C): δ (assignment by HSQC) = 57.62, 57.65, 57.78, 57.78, 57.79, 57.98, 58.97, 58.98, 59.26, 61.26, 61.53, 61.69, 61.80, 61.83, 62.12, 62.34 (OMe), 67.29, 68.85 (br, C-5^{A,B}), 70.65, 71.01, 71.11, 71.33 (C-5^{C,D,E,F}), 72.18, 72.55, 72.75, 73.39 (C-6^{C,D,E,F}), 80.79, 81.65, 81.69, 81.78, 81.88 [x2], 82.01, 82.14 [x2], 82.38, 82.53, 82.67, 82.73, 82.86, 83.02, 83.53, 88.58, 90.32 (C-2, C-3, C-4), 98.48, 99.92, 99.96, 100.31, 100.42, 101.67 (C-1), 121.75 (br), 128.69, 130.90 (br), 134.24 (aromatic C), C-6^{A,B}, NMe_2 and two quaternary aromatic carbons could not be identified because of signal broadness; ^{31}P{^{1}H} NMR (243 MHz, CD_2Cl_2, -60 °C): δ = 10.40 ppm; elemental analysis (%) calcd for

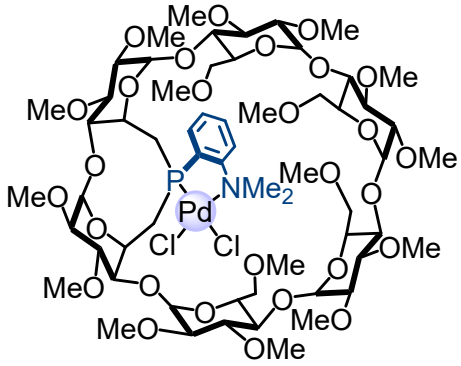
$C_{60}H_{100}Br_2NO_{28}PNi$•0.25 C_5H_{12}: C 47.43, H 6.69, N 0.90, found: C 47.26, H 6.88, N 0.98; MS (ESI-TOF) for $C_{60}H_{100}Br_2NO_{28}PNi$: *m/z* (%): 1452.47 (100) [*M* - Br]$^+$.

Dibromo[(*N*,*N*-dimethyl-2-diethylphosphinoaniline)-κ^{2}P,N]nickel(II) (10)



Solid $NiBr_2$ (124 mg, 0.57 mmol) was added to a solution of **7** (120 mg, 0.57 mmol) in CH_2Cl_2 (16 mL) under argon. The reaction mixture was stirred for 22 h at room temperature and filtered through a Celite pad under argon. The filtrate was concentrated to 3-4 mL *in vacuum* and 30 mL Et_2O was added to precipitate a dark red solid. The supernatant was removed with a syringe. The solid was washed with Et_2O and dried under reduced pressure to afford **10** as a dark red solid (180 mg, 74%). A crystalline material was obtained by slow diffusion of *n*-hexane into a dichloromethane solution of **10**. ^{1}H NMR (600 MHz, CD_2Cl_2, -60 °C): δ = 1.44–1.35 (m, 6H, PCH_2CH_3), 1.64 (dt, ^3J = 15.3, 7.7 Hz, 2H, PCH_2CH_3), 2.35 (dt, ^3J = 15.1, 7.8 Hz, 2H, PCH_2CH_3), 3.13 (s, 6H, NMe_2), 7.41 (m, 3H, aromatic-H), 7.55 (m, 1H, aromatic-H); ^{31}P{^{1}H} NMR (243 MHz, CD_2Cl_2, -60 °C): δ = 41.4 ppm; elemental analysis (%) calcd for $C_{12}H_{20}Br_2NNiP$: C 33.69, H 4.71, N 3.27, found: C 33.02, H 4.68, N 3.21; HRMS (ESI-TOF): *m/z* (%): 347.9846 (100) [*M* – Br]$^+$.

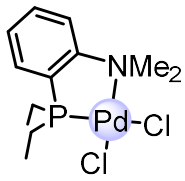
Dichloro[{6^A,6^B-Dideoxy-6^A,6^B-[(*R*)-2-(*N*,*N*-dimethylaminophenyl)phos phinidene]-2^A,2^B,2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F,6^C,6^D,6^E,6^F-hexadeca-O-methyl-α-cyclodextrin})-κ^{2}P,N]palladium(II) (8)



A solution of [$PdCl_2$(COD)] (108 mg, 0.38 mmol) in CH_2Cl_2 (4 mL) was added dropwise to a solution of **1** (500 mg, 0.38 mmol) in CH_2Cl_2 (4 mL) The reaction mixture was stirred for 2 h at room temperature and then evaporated to dryness under reduced pressure. The resulting yellow residue was subjected to column chromatography (SiO_2, CH_2Cl_2/MeOH, 97/3, *v/v*) to

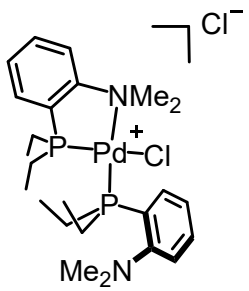
afford pure **8** (465 mg, 82%) as a yellow solid. A crystalline material was obtained by slow diffusion of *n*-pentane into a butanone solution of **8**. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ (assignment by COSY and HSQC) = 2.14 (m, 2H, H-6$^{A\text{ or }B}$), 3.06 (dd, 1H, $^{3}J_{H2\text{-}H3}$ = 10.1 Hz, $^{3}J_{H2\text{-}H1}$ = 2.9 Hz, H-2), 3.11–3.19 (4H, H-2), 3.21 (1H, H-6$^{A\text{ or }B}$), 3.26 (dd, 1H, $^{3}J_{H2\text{-}H3}$ = 9.3 Hz, $^{3}J_{H2\text{-}H1}$ = 4.2 Hz, H-2), 3.37 (s, 3H, OMe), 3.41 (s, 3H, OMe), 3.43 (s, 6H, NMe_2), 3.44 (s, 6H, OMe), 3.44 (s, 3H, OMe), 3.45 (s, 3H, OMe), 3.46 (s, 6H, OMe), 3.50 (s, 3H, OMe), 3.55 (s, 3H, OMe), 3.58 (s, 3H, OMe), 3.60 (s, 3H, OMe), 3.61 (s, 3H, OMe), 3.63 (s, 3H, OMe), 3.65 (s, 3H, OMe), 3.67 (s, 3H, OMe), 3.35–3.85 (15H, H-3, H-4, H-6), 3.87–3.95 (3H, H-5, H-6), 3.98 (d, 1H, *J* = 11.4 Hz, H-6), 4.15 (d, 1H, *J* = 11.1 Hz, H-6), 4.18–4.28 (4H, H-5, H-6), 4.56 (m, 1H H-5$^{A\text{ or }B}$, H-6 4.59 (m, 1H, H-5$^{A\text{ or }B}$), 4.93 (d, 1H, *J* = 3.1 Hz, H-1), 5.03 (d, 1H, *J* = 2.6 Hz, H-1), 5.06 (2H, H-1), 5.08 (2H, H-1), 5.19 (m, 1H, H-5$^{A\text{ or }B}$), 7.51–7.68 (4H, aromatic H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ (assignment by HSQC) = 31.62 (d, $^{1}J_{C6\text{-}P}$ = 32.6 Hz, C-6$^{A\text{ or }B}$), 41.15 (d, $^{1}J_{C6\text{-}P}$ = 28.0 Hz, C-6$^{A\text{ or }B}$), 55.21, 55.48, 57.42, 57.53, 57.68 (OMe), 57.79, 57.82 (NMe_2), 57.90, 59.13 [x2], 59.31, 59.43, 61.78, 61.84, 61.95 [x2], 62.27, 62.55 (OMe), 65.69 (d, $^{2}J_{C5\text{-}P}$ = 6.1 Hz, C-5$^{A\text{ or }B}$), 67.35 (C-5$^{A\text{ or }B}$), 70.02, 70.64, 70.82, 71.01 (C-5), 71.46, 72.03, 72.28, 72.97 (C-6), 80.03, 81.09, 81.13, 81.29, 81.44, 81.52, 81.67, 81.98, 82.07 [x2], 82.28 [x3], 82.55, 82.59, 82.62, 87.96, 90.07 (C-2, C-3, C-4), 98.14, 99.68, 99.99, 100.11, 100.65, 101.32 (C-1), 122.00 (d, $^{2}J_{P,C}$ = 11.7 Hz, aromatic C), 130.89 (d, $^{3}J_{P,C}$ = 6.6 Hz, aromatic C), 131.52 (aromatic C), 131.60 (d, $^{1}J_{P,C}$ = 47.1 Hz, aromatic C), 134.60 (aromatic C), 159.32 (d, $^{2}J_{P,C}$ = 16.2 Hz, aromatic C); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 25 °C): δ = 32.5 ppm; elemental analysis (%) calcd for $C_{60}H_{100}Cl_2NO_{28}PPd$•0.15 CH_2Cl_2: C 48.02, H 6.72, N 0.93, found: C 47.71, H 6.82, N 0.94; MS (ESI-TOF) for $C_{60}H_{100}Cl_2NO_{28}PPd$: *m/z* (%): 1456.49 (100) $[M - Cl]^+$.

Dichloro[(*N*,*N*-dimethyl-2-diethylphosphinoaniline)-κ^{2}P,N]palladium(II) (11)



A solution of $[PdCl_2(PhCN)_2]$ (126 mg, 0.31 mmol) was added to a solution of **7** (66 mg, 0.31 mmol) in CH_2Cl_2 (8 mL). The mixture was stirred at room temperature for 20 h and then filtered through Celite. The filtrate was concentrated under reduced pressure and after removal of the solvent under reduced pressure, a yellow solid was obtained which was subjected to column chromatography (SiO_2; CH_2Cl_2/MeOH, 98:2→90:10, *v/v*) to afford two fractions. The first one contained **11** (69 mg, 58%) and the second one **12** (7 mg, 11%). Recrystallisation of **11** was performed by slow diffusion of *n*-pentane into a dichloromethane solution of **11** to afford a yellow crystalline solid (59 mg, 48%). ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C) : δ = 1.17 (t, ^3J = 7.5 Hz, 3H, PCH_2CH_3), 1.22 (t, ^3J = 7.5 Hz, 3H, PCH_2CH_3), 1.87 (m, 2H, PCH_2CH_3), 2.46 (m, 2H, PCH_2CH_3), 3,42 (s, 6H, NMe_2), 7.58-7.46 (2H, aromatic H), 7.63 (m, 1H, aromatic H), 7.70 (m, 1H, aromatic H). ^{13}C NMR (126 MHz, CD_2Cl_2, 25 °C, assignments from HMQC and HMBC): 8.84 (d, $^2J_{P,C}$ = 1.3 Hz, PCH_2CH_3), 20.78 (d, $^1J_{P,C}$ = 36.5 Hz, PCH_2CH_3), 55.50 (d, $^3J_{P,C}$ = 1.0 Hz, NMe_2), 122.57 (d, $^2J_{P,C}$ = 11.7 Hz, aromatic C), 126.48 (d, $^1J_{P,C}$ = 41.3 Hz, aromatic C), 130.68 (d, $^3J_{P,C}$ = 6.5 Hz, aromatic C), 130.80 (aromatic C), 134.94 (d, $^3J_{P,C}$ = 2.3 Hz, aromatic C), 162.41 (d, $^2J_{P,C}$ = 14.7 Hz, aromatic C); ^{31}P{^{1}H} NMR (121 MHz, CD_2Cl_2, 25 °C): δ = 62.1 ppm. elemental analysis (%) calcd for $C_{12}H_{20}NPPdCl_2$: C 37.28, H 5.21, N 3.62, found: C 37.26, H 5.24, N 3.46; HRMS (ESI-TOF) for $C_{12}H_{20}Cl_2NPPd$: *m/z* (%): 350.0038 $[M - Cl]^+$.

[Chloro[*N*,*N*-dimethyl-2-diethylphosphinoaniline)-κ^2-P,N][*N*,*N*-dimethyl-2-diethylphosphinoaniline)-κ'-P]palladium(II) chloride (12)



The above procedure was used to prepare the cationic palladium complex **12** from $[PdCl_2(PhCN)_2]$ (73 mg, 0.18 mmol) and **7** (76 mg , 0.36 mmol, 2 equiv.) in CH_2Cl_2 (12 mL). Again two fractions were collected. The first one contained **11** (20 mg, 28 %) and the second one **12** (77 mg, 72%). Yellow single crystals of **12** were obtained by slow diffusion of *n*-pentane into a dichloromethane solution. ^{1}H NMR (500

MHz, $CDCl_3$, 25°C) : δ = 0.95 (br t, 3H, ^3J = 7.5 Hz, PCH_2CH_3), 0.99 (br t, 3H, ^3J = 7.5 Hz, PCH_2CH_3), 1.15 (br t, 3H, ^3J = 7.5 Hz, PCH_2CH_3), 1.19 (br t, 3H, ^3J = 7.5 Hz, PCH_2CH_3), 2.32-2.57 (m, 6H, PCH_2CH_3), 2.76 (s, 6H, NMe_2), 3.09-3.41 (8H, NMe_2, PCH_2CH_3), 7.36 (m, 1H, aromatic H), 7.42-7.50 (2H, aromatic H), 7.55-7.70 (4H, aromatic H), 8.35 (m, 1H, aromatic H); ^{13}C NMR (126 MHz, CD_2Cl_2, 25°C, assignments from HMQC and HMBC): 9.12, 9.41 (PCH_2CH_3), 18.79 (d, $^1J_{P,C}$ = 32.3 Hz, PCH_2CH_3), 21.68 (d, $^1J_{P,C}$ = 31.5 Hz, PCH_2CH_3), 47.12, 53.31 (NMe_2), 121.65, 124.41, 126.74, 127.61, 128.10, 131.33, 131.94, 133.15, 133.29, 134.46, 156.54, 158.96 (aromatic C). $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2, 25°C): δ = 56 (d, $^2J_{PP}$ = 13.1 Hz), 21.9 (d, $^2J_{PP}$ = 13.3 Hz) ppm; HRMS (ESI-TOF) for $C_{24}H_{40}Cl_2N_2P_2Pd$: *m/z* (%): 561.1334 $[M - Cl]^+$. A VT NMR experiment in $CDCl_3$ shows that line broadening occurs upon increasing the temperature from 273 K to 323 K with the two phosphorus signals beginning to merge at 323 K. Possibly, this fluxional behaviour is in keeping with the slow coordination and decoordination of the weak nitrogen donor atoms at the NMR time scale (see drawing below).

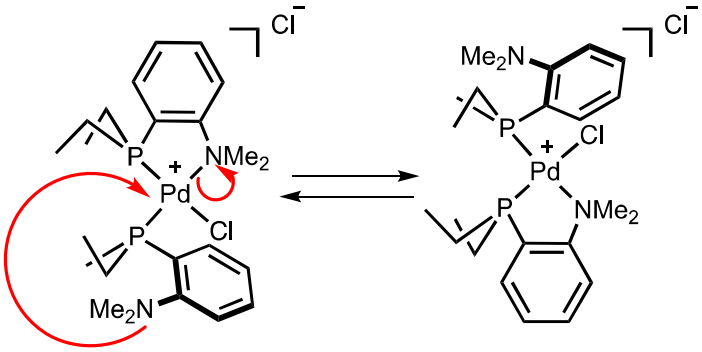
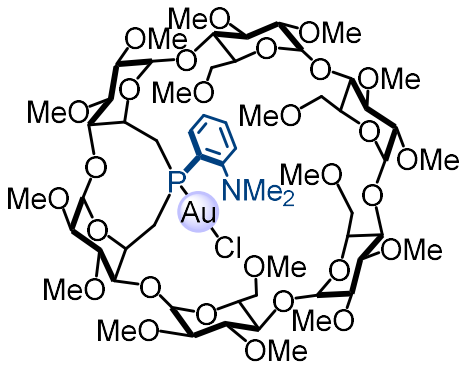


Figure S1. Possible coordination and decoordination processes taking place in **12**

Chloro[{6^A,6^B-Dideoxy-6^A,6^B-[(*R*)-2-(*N*,*N*-dimethylaminophenyl)phosphinidene]-2^A,2^B,2^C,2^D,2^E,2^F, 3^A,3^B,3^C,3^D,3^E,3^F, 6^C,6^D,6^E,6^F-hexadeca-O-methyl-α-cyclodextrin}-κP]gold(I) (13)



A solution of [AuCl(tht)] (42.2 mg, 0.13 mmol) in CH_2Cl_2 (4 mL) was added dropwise to a solution of **1** (173 mg, 0.13 mmol) in CH_2Cl_2 (4 mL). The reaction mixture was stirred for 3 h at room temperature. The solution was evaporated to dryness under reduced pressure and the resulting pale-yellow residue was subjected to column chromatography (SiO_2, CH_2Cl_2/MeOH, 97/3, *v/v*) to afford **13** (83.7 mg, 41%) as a pale-yellow solid. A crystalline material was obtained by slow diffusion of *n*-pentane into a benzene solution of **13**. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ (assignment by COSY) = 2.17-2.30 (2H, H-6$^{A, B}$), 2.73 (s, 6H, NMe_2), 3.25 (m, 1H, H-4$^{A \text{ or } B}$), 3.39 (s, 6H, OMe), 3.40 (s, 3H, OMe), 3.43 (s,3H, OMe), 3.45(s, 3H ,OMe), 3,48 (s,3H, OMe), 3.49 (s, 6H, OMe), 3.52 (s, 3H, OMe), 3.54 (m, 1H, H-6$^{A \text{ or } B}$), 3.57(m, 1H, H-6$^{A \text{ or } B}$), 3.59 (m, 1H, H-3$^{A \text{ or } B}$), 3.61 (s, 3H, OMe), 3.64 (s, 6H, OMe), 3.66 (s, 6H, OMe), 3.66 (m, 1H, H-3$^{A \text{ or } B}$), 3.70 (s, 3H, OMe), 3.71 (s, 3H, OMe), 3.13-3.85 (27H, H-2, H-3, H-4, H-5, H-6), 4.10 (m, 1H, H-5$^{A \text{ or } B}$), 4.56 (m, 1H, H-5$^{A \text{ or } B}$), 4.96 (d, 1H, $^3J_{H1\text{-}H2}$ = 3.2 Hz, H-1), 5.02 (d, 1H, $^3J_{H1\text{-}H2}$ = 4.3 Hz, H-1), 5.05 (d, 1H, $^3J_{H1\text{-}H2}$ = 2.9 Hz, H-1), 5.09 (d, 1H, $^3J_{H1\text{-}H2}$ = 3.2 Hz, H-1), 5.11 (m, 2H, H-1), 7.30-7.72 (4H, aromatic H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$, 25˚C): δ (assignment by HSQC) = 30.12 (C-6$^{A \text{ or } B}$) $^1J_{P,C}$ = 34.0 Hz (d, $^1J_{P,C}$ = 37.8 Hz, C-6$^{A \text{ or } B}$), 35.76 (d, $^1J_{P,C}$ = 34.0 Hz, C-6$^{A \text{ or } B}$), 47.39 (-NMe_2), 57.57, 57.60, 57.78, 58.00, 58.06, 58.18, 59.22 [x2], 59.30, 59.49, 61.70, 61.83, 61.90, 62.08, 62.16, 62.77 (OMe), 64.67, 70.88 [x2], 71.15, 71.45, 71.70, 71.75, 71.87, 72.87, 73.08 (C-5, C-6^{C,D,E,F}), 80.31, 81.22, 81.26, 81.43, 81.51, 81.63, 81.65, 81.89, 81.98, 82.07, 82.22, 82.24, 82.33, 82.47, 82.81, 82.89, 87.04, 89.66 (C-2, C-3, C-4), 97.88, 99.83, 100.05 100.16, 100.94, 101.12 (C-1), 124.99 (d, $^3J_{P,C}$ = 6.0 Hz, aromatic C), 126.72 (d, $^2J_{P,C}$ = 11.2 Hz, aromatic C), 128.69 (d, $^1J_{P,C}$ = 65.8 Hz, aromatic C), 133.52 (d, $^2J_{P,C}$ = 11.8 Hz, aromatic C), 133.66 (d, $^4J_{P,C}$ = 2.1 Hz, aromatic C), 158.56 (d, $^3J_{P,C}$ = 5.1 Hz, aromatic C) ppm; ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 25 ˚C): δ = 19.21 (s) ppm; elemental analysis (%) calcd for

$C_{60}H_{100}NO_{28}PAuCl$•0.4 CH_2Cl_2: C 45.89, H 6.43, N 0.89, found: C 45.78, H 6.53, N 0.85; MS (ESI-TOF) for $C_{60}H_{100}NO_{28}PAuCl$: *m/z* (%): 1568.54 (100) $[M + Na]^+$.

3. Procedure for ethylene oligomerisation reactions

The catalytic reactions were performed in a magnetically stirred (1200 rmp) 145 mL stainless steel autoclave. A 125 mL glass container was used to avoid corrosion of the autoclave walls. The precatalyst solution was prepared by dissolving 1 x 10^{-5} mol of the complex in toluene. This solution was injected into the reactor under an ethylene flux, followed by the cocatalyst solution (400 equiv. for MMAO-12 in toluene). After injection of the catalyst and cocatalyst solutions under a constant low flow of ethylene, which is considered as the t_0 time, the reactor was immediately pressurised to 10 bar of ethylene. The 10 bar working pressure was maintained through a continuous feed of ethylene from a bottle placed on a balance to allow monitoring of the ethylene uptake. The reaction mixture was stirred for the given reaction time. At the end of each test, a dry ice bath was used to rapidly cool the reactor. When the inner temperature reached 0 °C, the ice bath was removed, allowing the temperature to slowing rise to 18 °C. The gaseous phase was then transferred into a 10 L polyethylene tank filled with water. An aliquot of this gaseous phase was transferred into a Schlenk flask, previously evacuated, for GC analysis. The amount of ethylene consumed was thus determined by differential weighting of the bottle (accuracy of the scale: 0.01g). To this amount of ethylene, the remaining ethylene (calculated using the GC analysis) in the gaseous phase was subtracted. Although this method is of limited accuracy, it was used throughout and it gave satisfactory reproducibility. The reaction mixture in the reactor was quenched *in situ* by the addition of ethanol (5 mL), transferred into a Schlenk flask, and separated from the metal complexes by trap-to-trap evaporation into a second Schlenk flask previously immersed in liquid nitrogen in order to avoid loss of product for GC analysis. Each catalytic test was performed at least twice to ensure the reproducibility of the results.

4. NMR and mass spectra

NMR spectra of all compounds were recorded in $CDCl_3$ at 25 °C except stated otherwise.

Diethyl (2-(*N*,*N*-dimethylamino)phenyl)phosphonate (3)

^{1}H NMR spectrum
$^{31}P\{^{1}H\}$ NMR spectrum

2-(*N*,*N*-Dimethylamino)phenylphosphine (4)

^{1}H NMR spectrum
$^{31}P\{^{1}H\}$ NMR spectrum
Full High Resolution Mass Spectrum
Partial High Resolution Mass Spectrum

6^{A},6^{B}-Dideoxy-6^{A},6^{B}[(*R*)-2-(*N*,*N*-dimethylamino)phenylphosphinidene]-2^{A},2^{B},2^{C}, 2^{D},2^{E},2^{F},3^{A},3^{B},3^{C},3^{D},3^{E},3^{F},6^{C},6^{D},6^{E},6^{F}-hexadeca-O-methyl-α-cyclodextrin (1)

^{1}H NMR spectrum
$^{31}P\{^{1}H\}$ NMR spectrum
^{13}C NMR spectrum
DEPT 135 spectrum
$^{1}H/^{13}C$ edited HSQC spectrum
$^{1}H/^{1}H$ COSY spectrum
$^{1}H/^{1}H$ TOCSY spectrum
$^{1}H/^{1}H$ ROESY spectrum
Full Mass Spectrum
Partial Mass Spectrum

2-(*N*,*N*-Dimethylamino)diethylphosphine (7)

^{1}H NMR spectrum
$^{31}P\{^{1}H\}$ NMR spectrum
$^{13}C\{^{1}H\}$ NMR spectrum
DEPT 135 spectrum
$^{1}H/^{13}C$ edited HSQC spectrum
$^{1}H/^{13}C$ HMBC spectrum
Full Mass Spectrum
Partial Mass Spectrum

Dibromo[{6^{A},6^{B}-Dideoxy-6^{A},6^{B}-[(*R*)-2-(*N*,*N*-dimethylamino)phenyl

phosphinindene]-2^{A},2^{B},2^{C},2^{D},2^{E},2^{F},3^{A},3^{B},3^{C},3^{D},3^{E},3^{F},6^{C},6^{D},6^{E},6^{F},-hexadeca-O-methyl-α-cyclodextrin}-κ^{2}P,N]nickel(II) (9)

^{1}H NMR spectrum
^{31}P{^{1}H} NMR spectrum
^{13}C NMR spectrum
DEPT 135 spectrum
^{1}H/^{13}C edited HSQC spectrum
^{1}H/^{1}H COSY spectrum
^{1}H/^{1}H TOCSY spectrum
^{1}H/^{1}H ROESY spectrum
Full Mass Spectrum
Partial Mass Spectrum

Dibromo[(*N*,*N*-dimethyl-2-diethylphosphinoaniline)-κ^{2}P,N]nickel(II) (10)

^{1}H NMR spectrum
^{31}P{^{1}H} NMR spectrum
Full High Resolution Mass Spectrum
Partial High Resolution Mass Spectrum

Dichloro[{6^{A},6^{B}-Dideoxy-6^{A},6^{B}-[(*R*)-2-(*N*,*N*-dimethylainophenyl)phosphinidene]-2^{A},2^{B},2^{C},2^{D},2^{E},2^{F},3^{A},3^{B},3^{C},3^{D},3^{E},3^{F},6^{C},6^{D},6^{E},6^{F}-hexadeca-O-methyl-α-cyclodextrin}-κ^{2}P,N]palladium(II) (8)

^{1}H NMR spectrum
^{31}P{^{1}H} NMR spectrum
^{13}C NMR spectrum
DEPT 135 spectrum
^{1}H/^{13}C edited HSQC spectrum
^{1}H/^{1}H COSY spectrum
^{1}H/^{1}H TOCSY spectrum
^{1}H/^{1}H ROESY spectrum
Full Mass Spectrum
Partial Mass Spectrum

Dichloro[(*N*,*N*-dimethyl-2-diethylphosphinoaniline)-κ^{2}P,N]palladium(II) (11)

^{1}H NMR spectrum
^{31}P{^{1}H} NMR spectrum
^{13}C NMR spectrum
DEPT 135 spectrum
^{1}H/^{13}C edited HSQC spectrum
^{1}H/^{1}H COSY spectrum
^{1}H/^{13}C HMBC spectrum

Full High Resolution Mass Spectrum
Partial High Resolution Mass Spectrum

[Chloro[(*N*,*N*-dimethyl-2-diethylphosphinoaniline)-κ^2-P,N][(*N*,*N*-dimethyl-2-diethylphosphinoaniline)-κ'-P]palladium(II) chloride (12)

^{1}H NMR spectrum
^{31}P{^{1}H} NMR spectrum
^{13}C NMR spectrum
DEPT 135 spectrum
^{1}H/^{1}H COSY spectrum
^{1}H/^{13}C edited HSQC spectrum
^{1}H/^{13}C HMBC spectrum
^{1}H VT NMR spectrum
^{31}P VT NMR spectrum
Full High Resolution Mass Spectrum
Partial High Resolution Mass Spectrum

Chloro[{6^A,6^B-Dideoxy-6^A,6^B-[(*R*)-2-(*N*,*N*-dimethylaminophenyl)phosphinidene]-2^A,2^B,2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F,6^C,6^D,6^E,6^F,-hexadeca-O-methyl-α-cyclodextrin}-κP]gold(I) (13)

^{1}H NMR spectrum
^{31}P{^{1}H} NMR spectrum
^{13}C NMR spectrum
DEPT 135 spectrum
^{1}H/^{13}C edited HSQC spectrum
^{1}H/^{1}H COSY spectrum
^{1}H/^{1}H TOCSY spectrum
^{1}H/^{1}H ROESY spectrum
Full Mass Spectrum
Partial Mass Spectrum

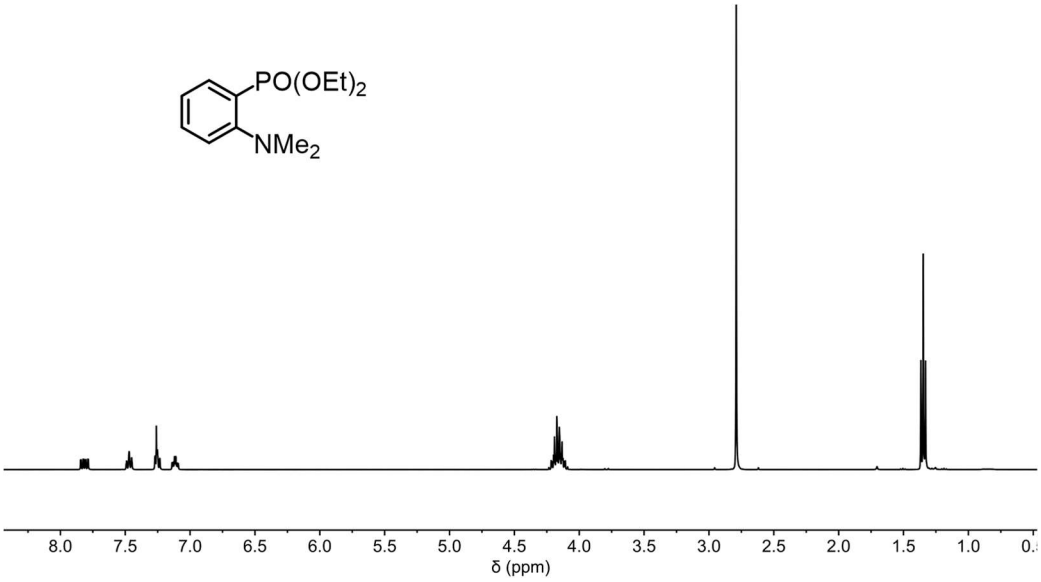


Figure S2. ^{1}H NMR spectrum of **3** in $CDCl_3$

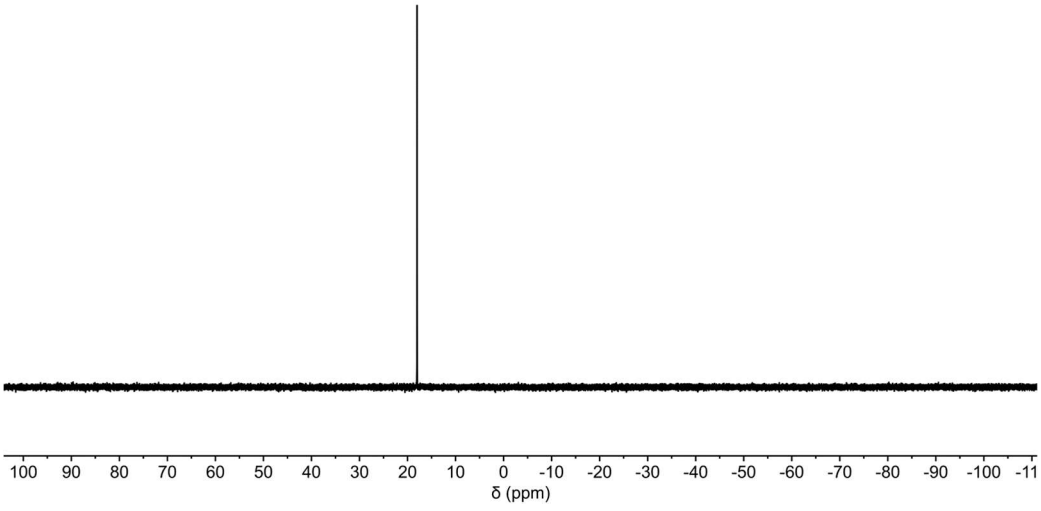


Figure S3. ^{31}P NMR spectrum of **3** in $CDCl_3$

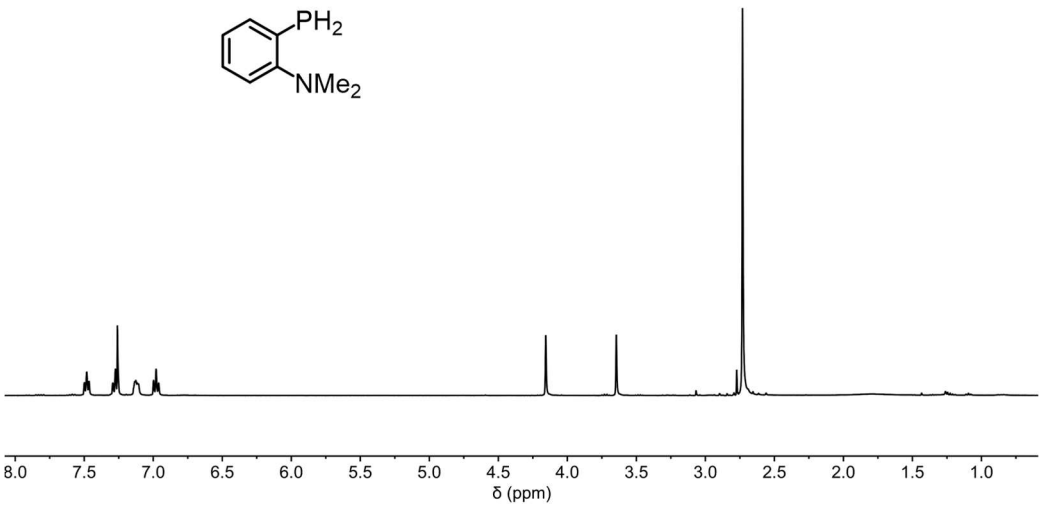


Figure S4. ^{1}H NMR spectrum of **4** in $CDCl_3$

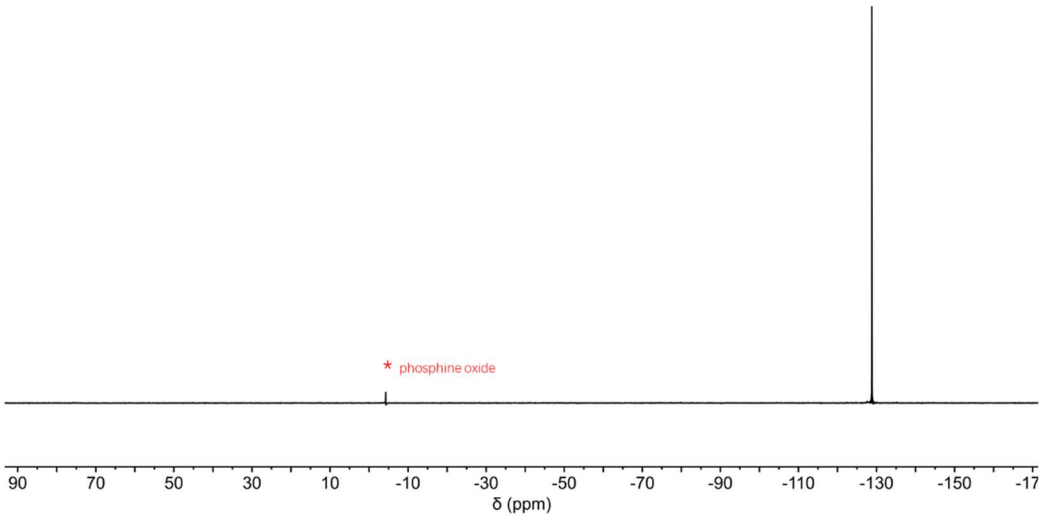


Figure S5. ^{31}P NMR spectrum of **4** in $CDCl_3$

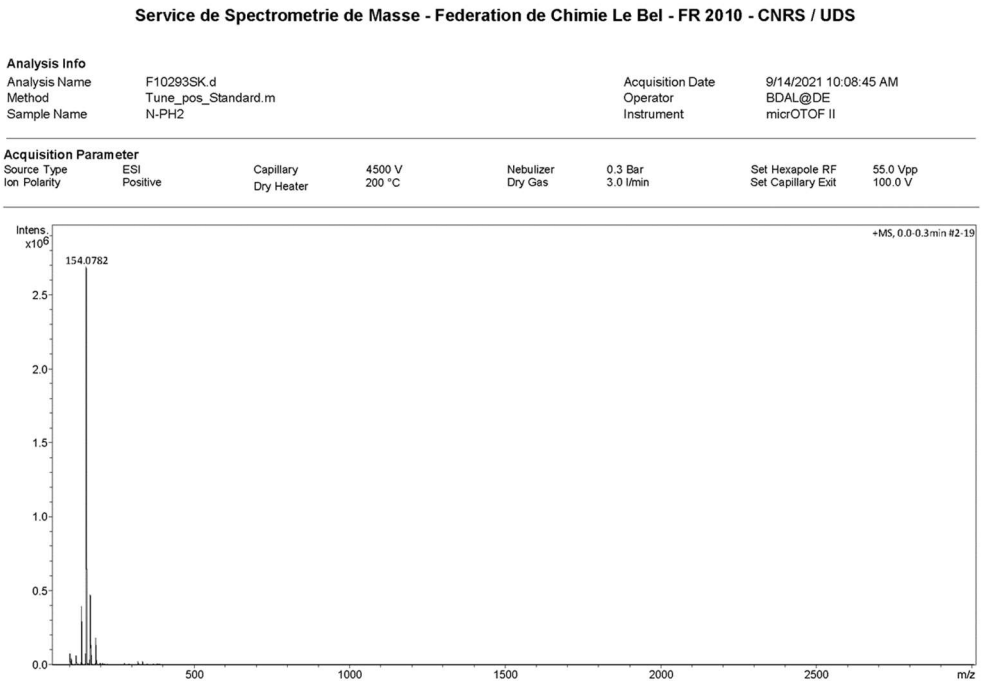


Figure S6. Full High Resolution Mass Spectrum of **4**

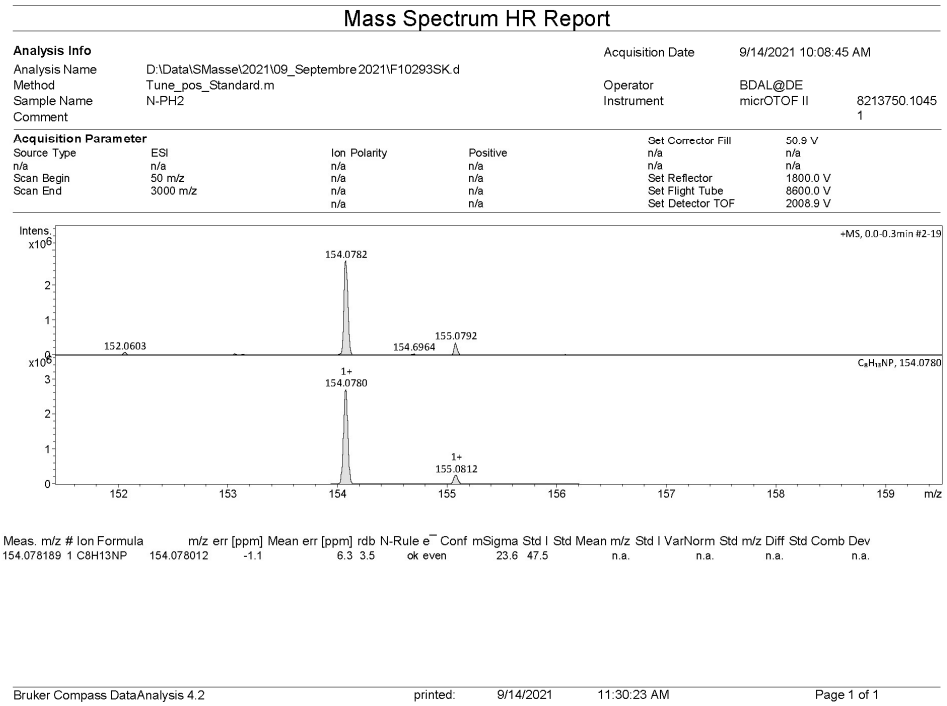


Figure S7. Partial High Resolution Mass Spectrum of **4**

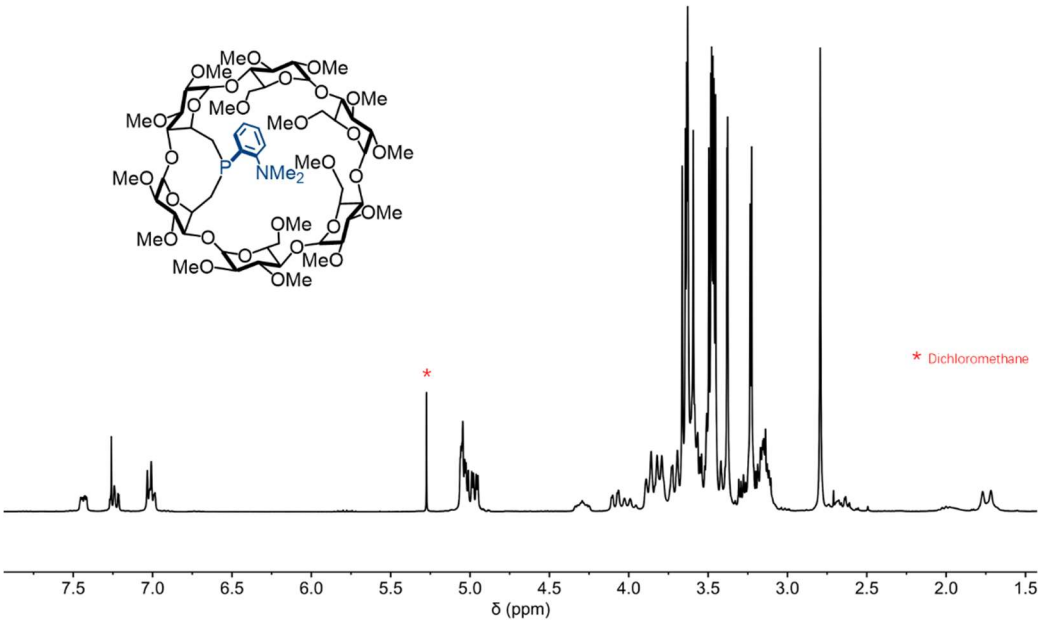


Figure S8. ^{1}H NMR spectrum of **1** in $CDCl_3$

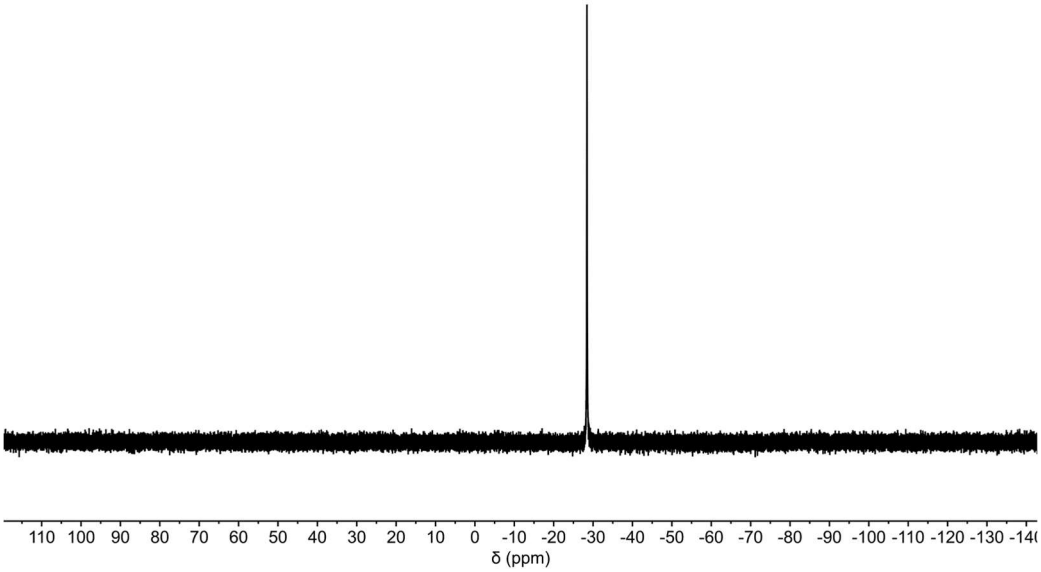


Figure S9. ^{31}P NMR spectrum of **1** in $CDCl_3$

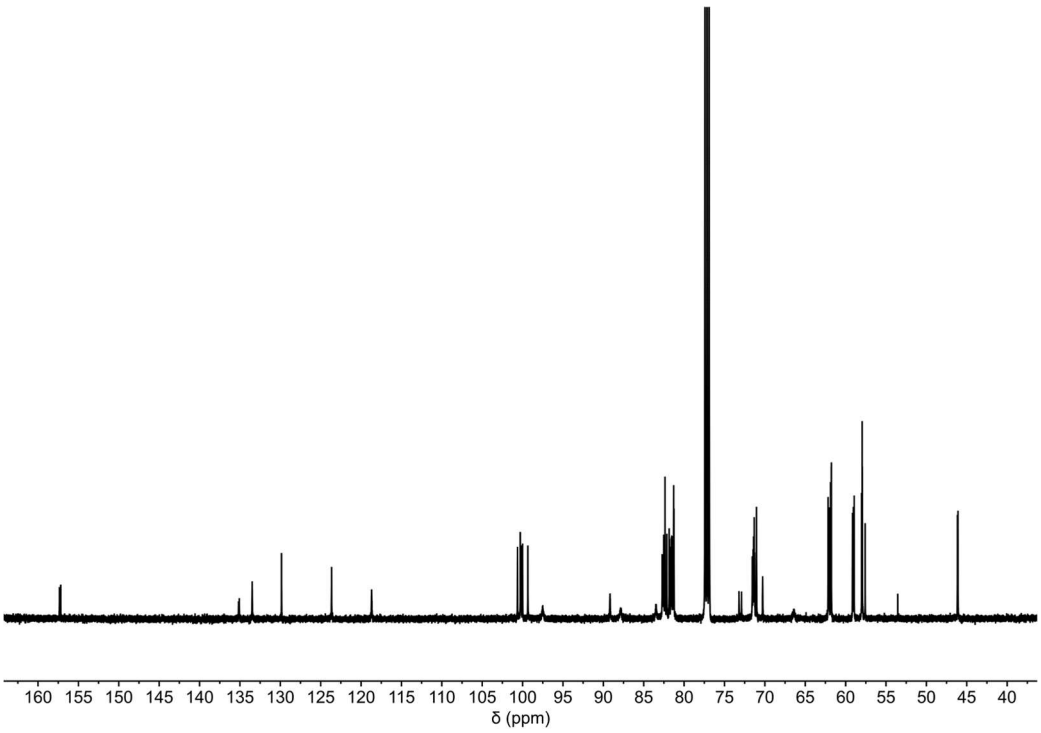


Figure S10. ^{13}C NMR spectrum of **1** in $CDCl_3$

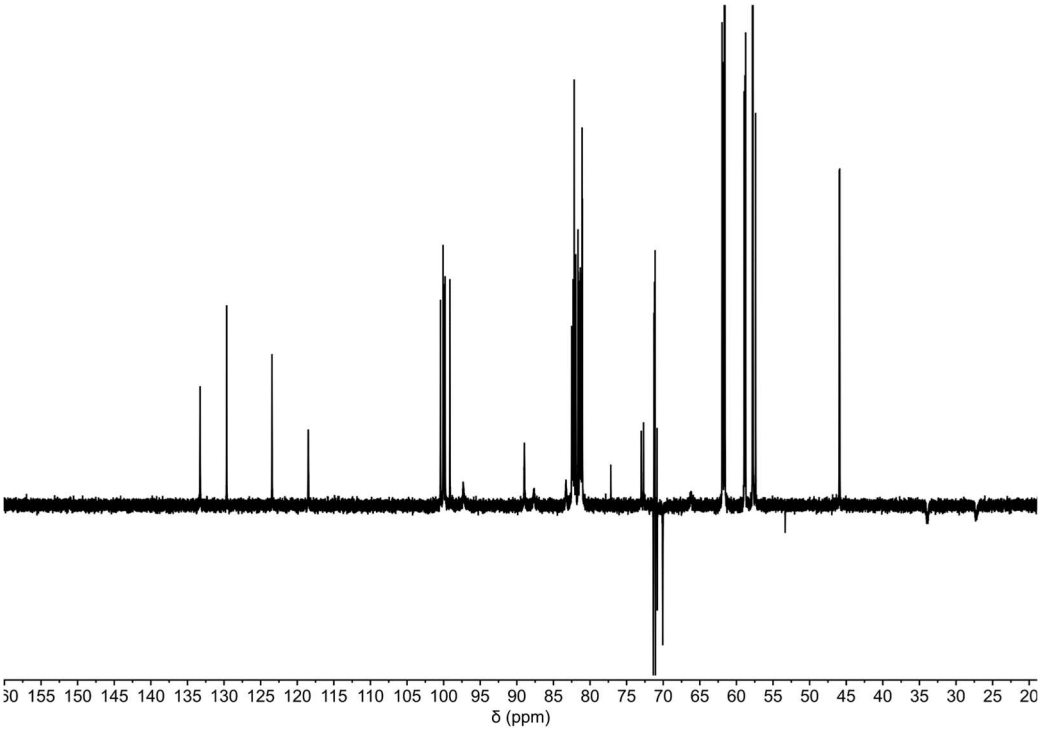


Figure S11. DEPT 135 spectrum of **1** in $CDCl_3$

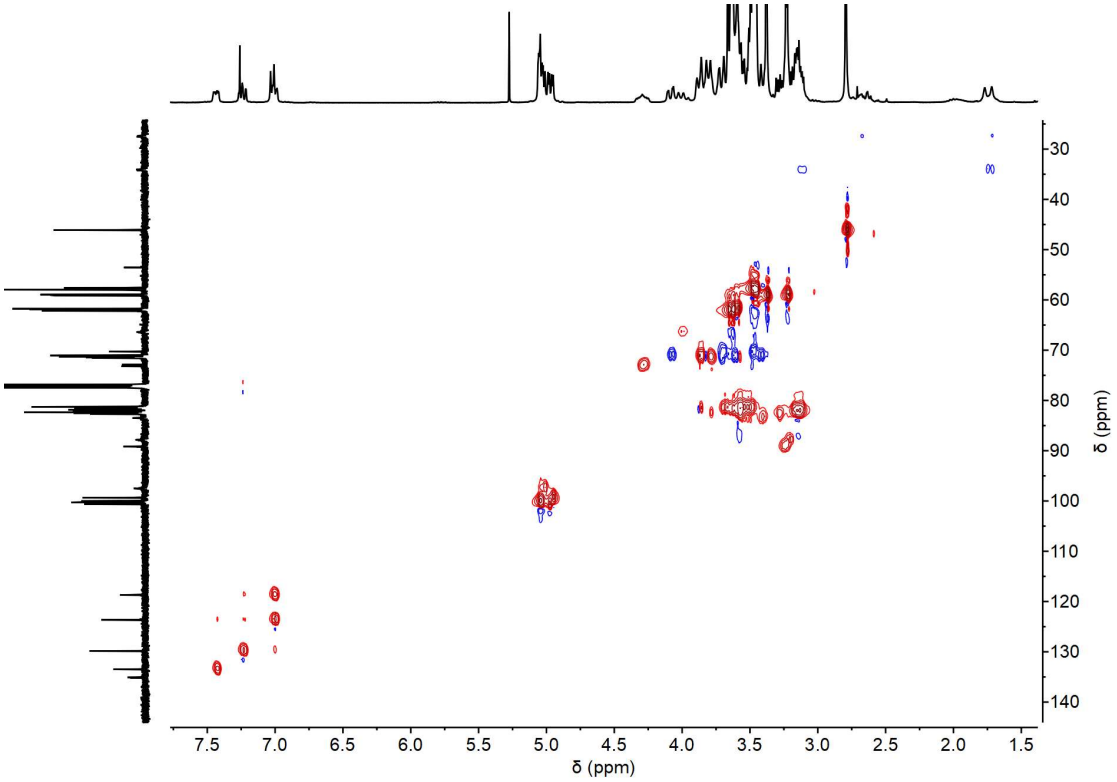


Figure S12. $^{1}H/^{13}C$ edited HSQC spectrum of **1** in $CDCl_3$

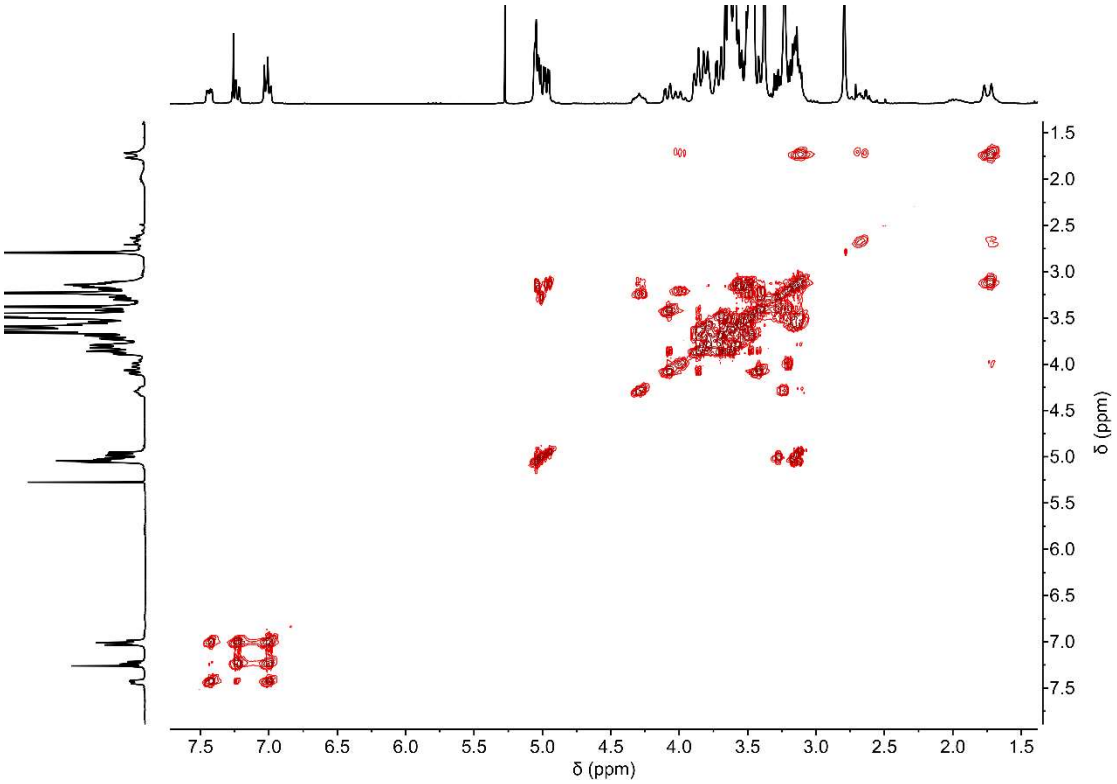


Figure S13. $^{1}H/^{1}H$ COSY spectrum of **1** in $CDCl_3$

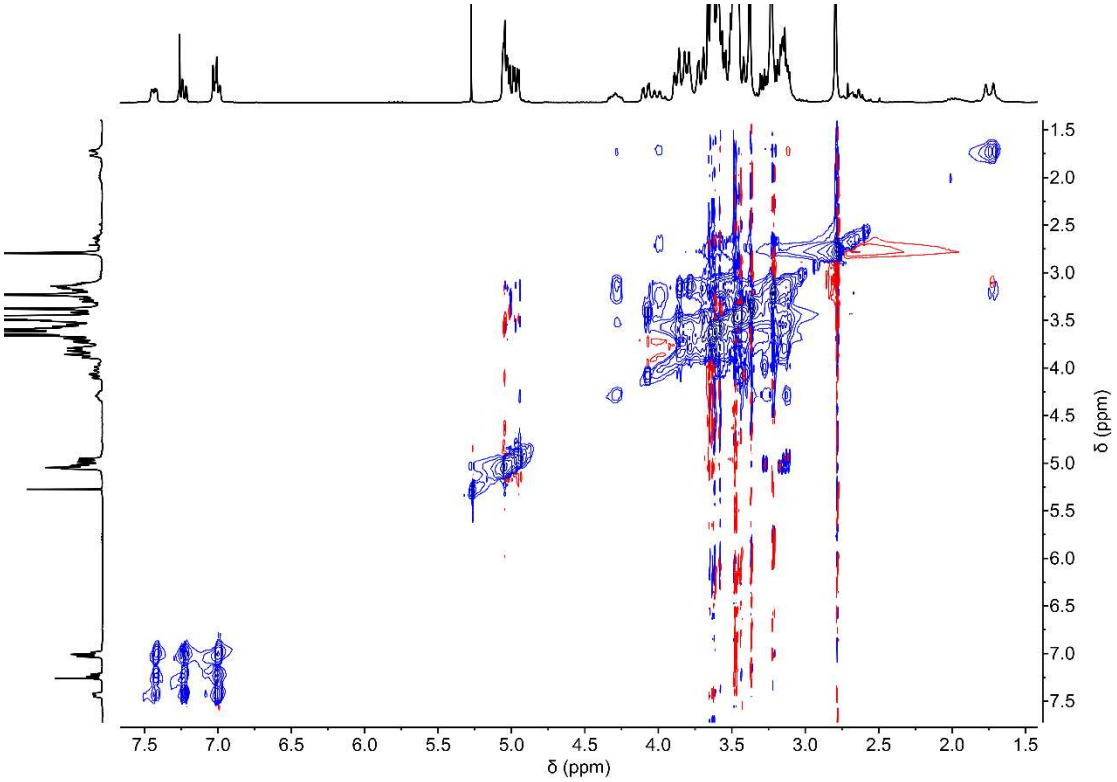


Figure S14. $^{1}H/^{1}H$ TOCSY spectrum of **1** in $CDCl_3$

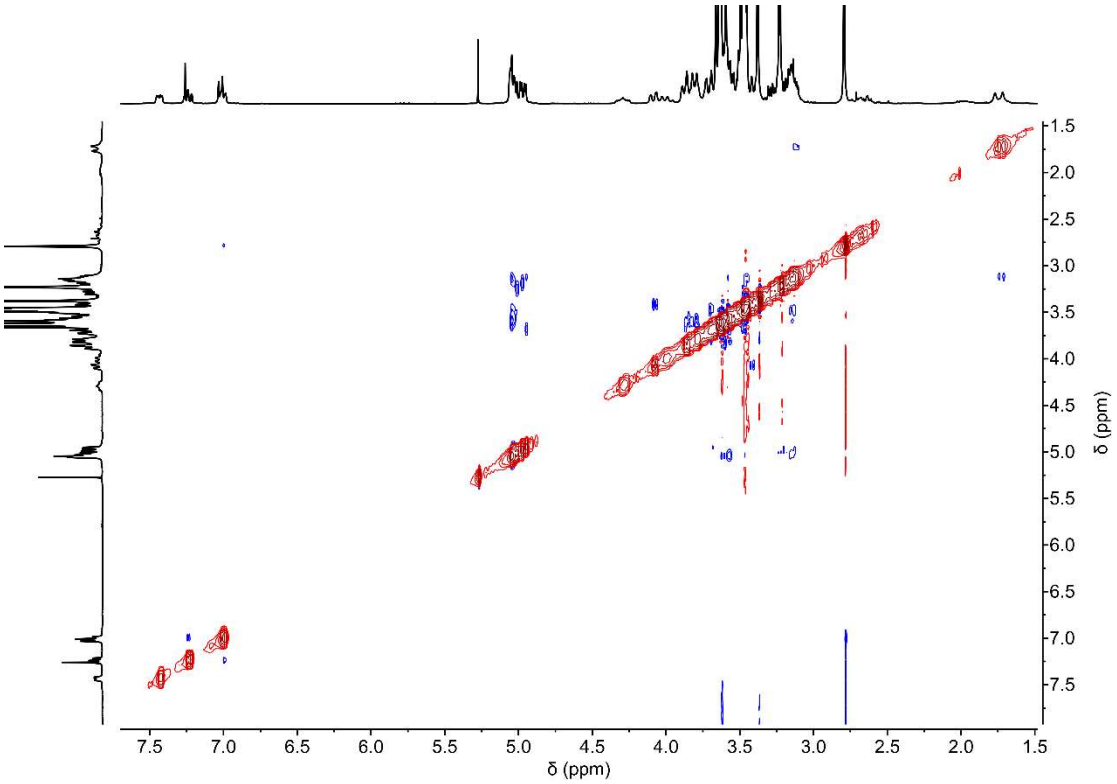


Figure S15. $^{1}H/^{1}H$ ROESY spectrum of **1** in $CDCl_3$

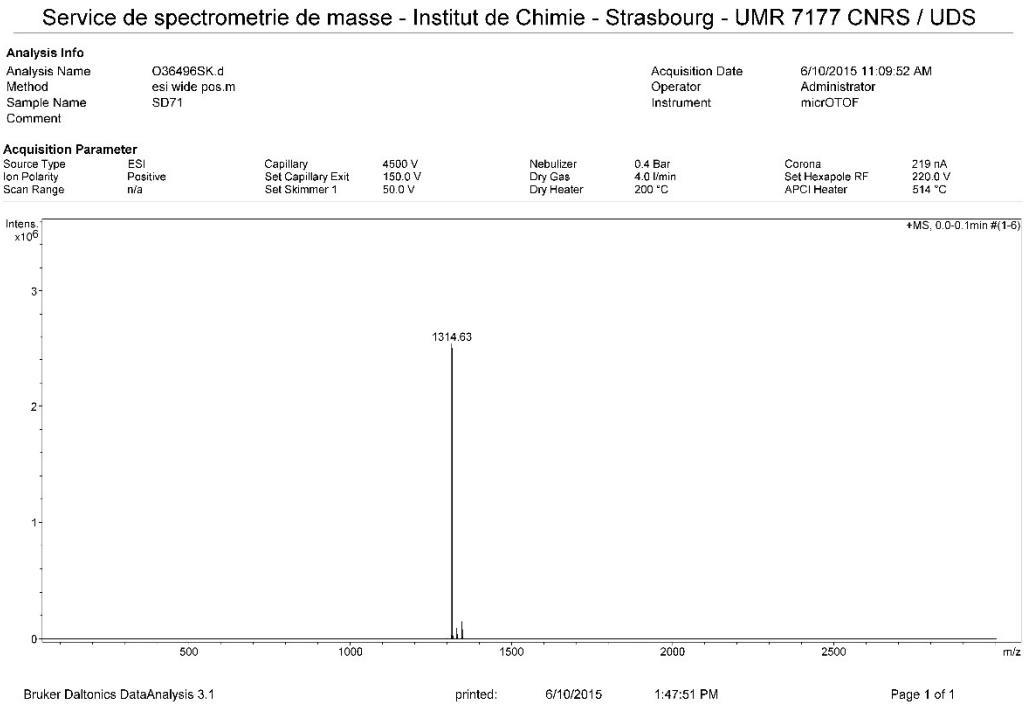


Figure S16. Full Mass Spectrum of **1**

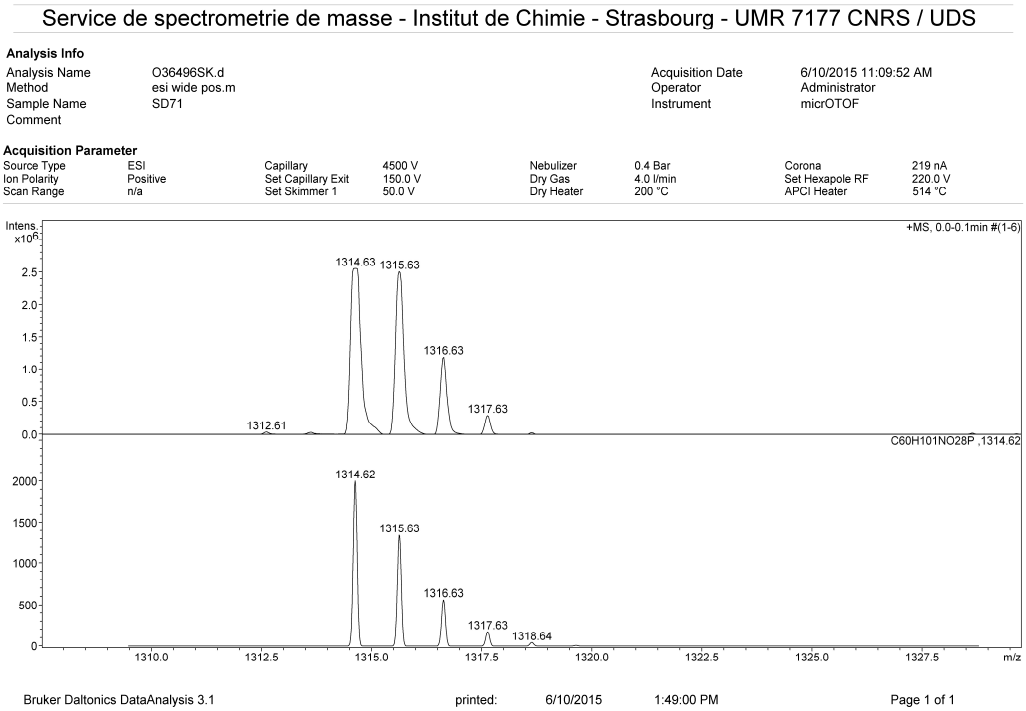


Figure S17. Partial Mass Spectrum of **1**

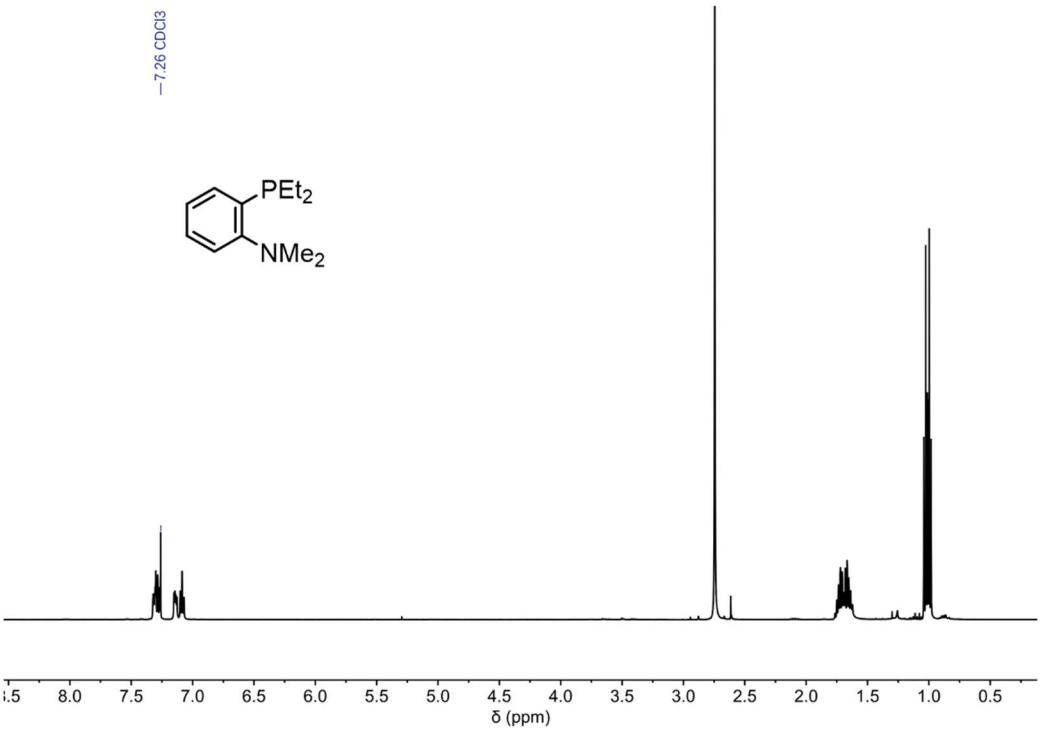


Figure S18. ^{1}H NMR spectrum of **7** in $CDCl_3$

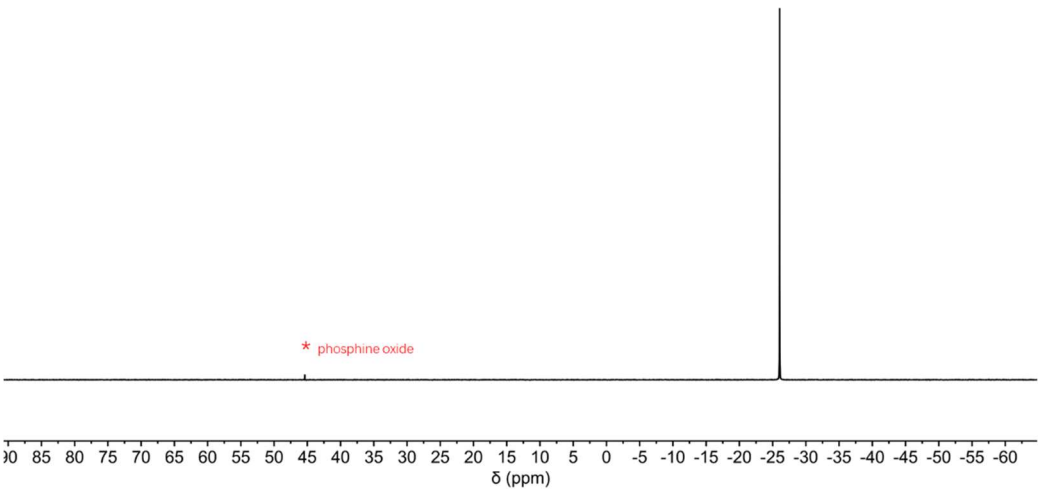


Figure S19. ^{31}P NMR spectrum of **7** in $CDCl_3$

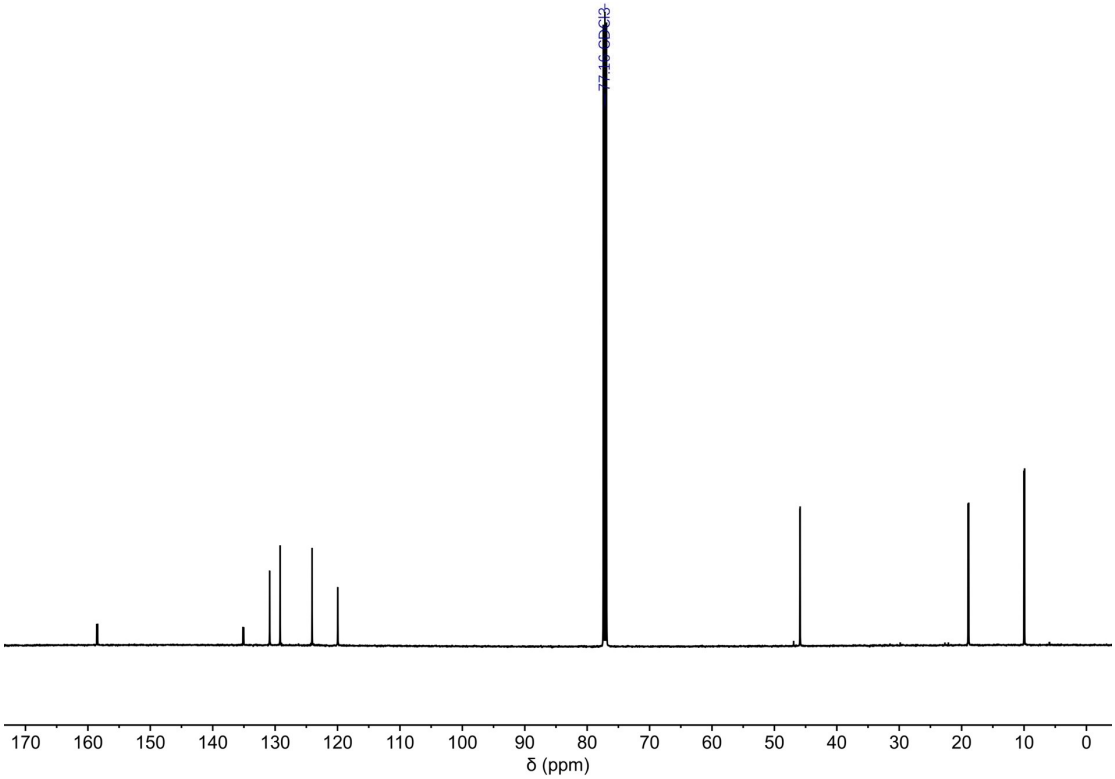


Figure S20. ^{13}C NMR spectrum of **7** in $CDCl_3$

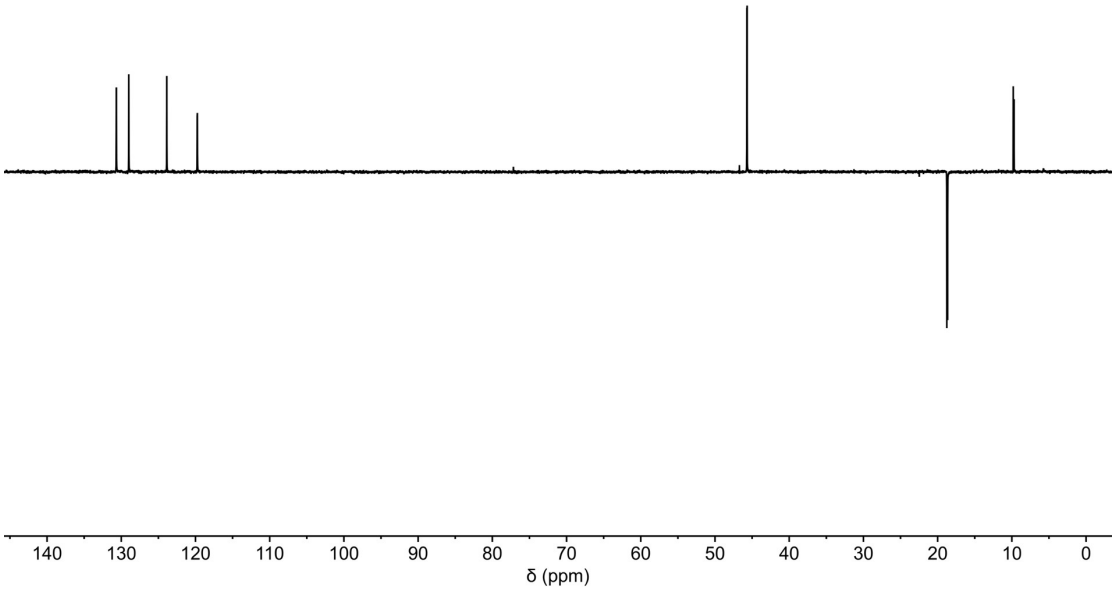


Figure S21. DEPT 135 spectrum of **7** in $CDCl_3$

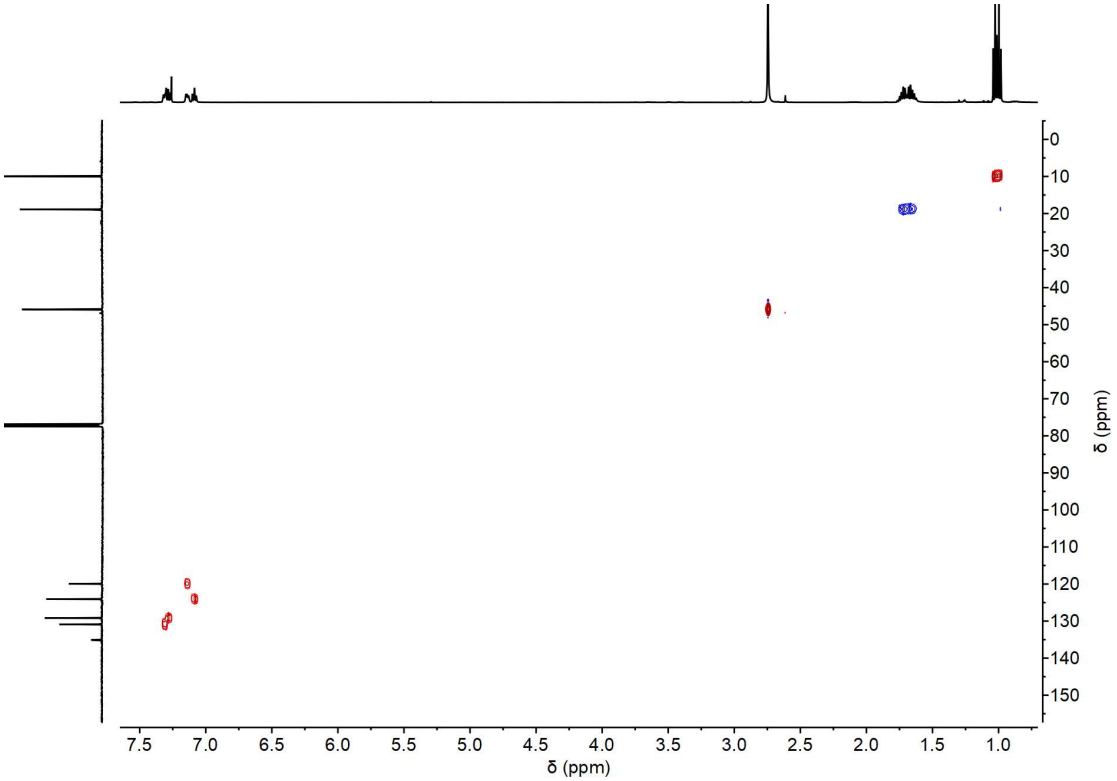


Figure S22. $^{1}H/^{13}C$ edited HSQC spectrum of **7** in $CDCl_3$

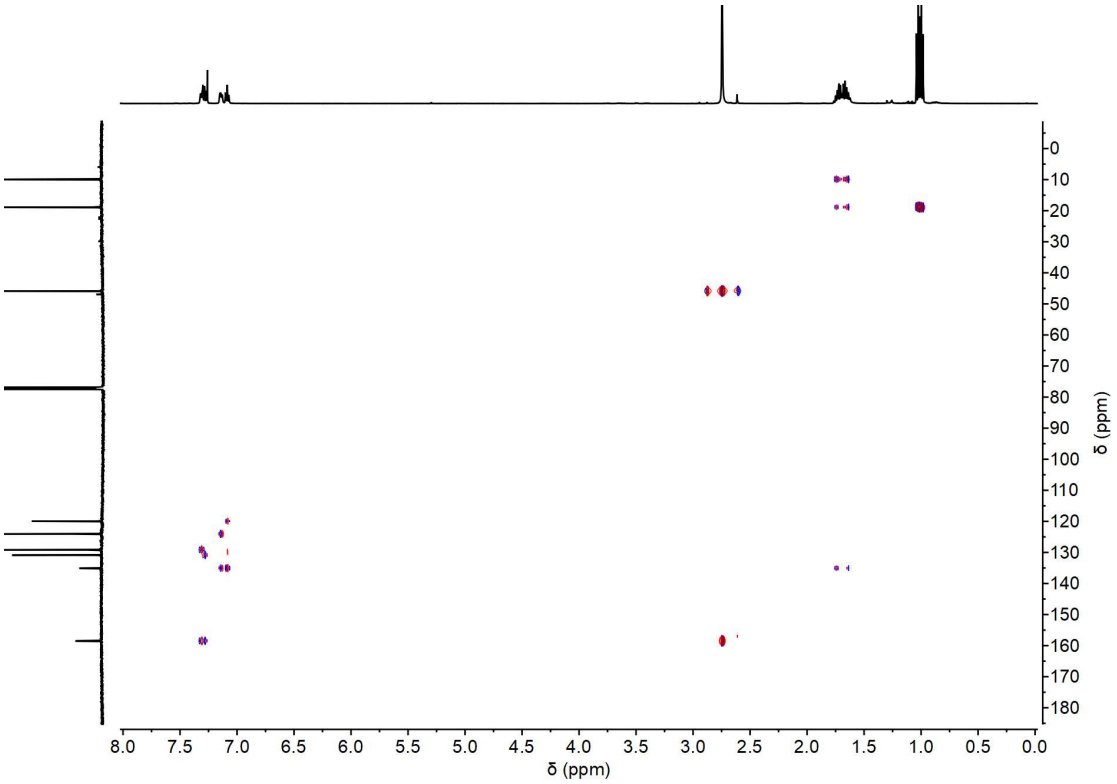


Figure S23. $^{1}H/^{13}C$ HMBC spectrum of **7** in $CDCl_3$

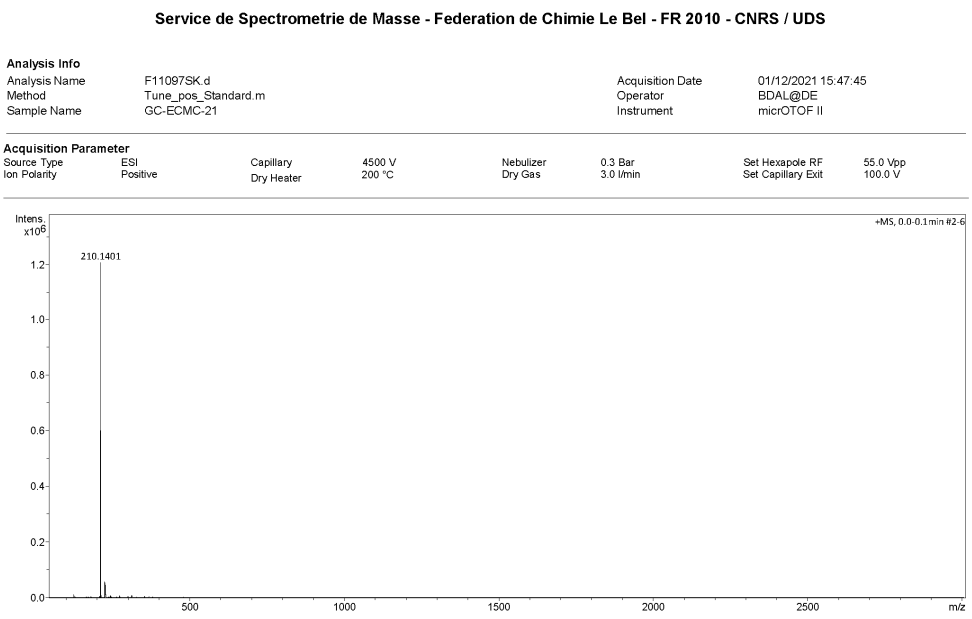


Figure S24. Full Mass Spectrum of **7**

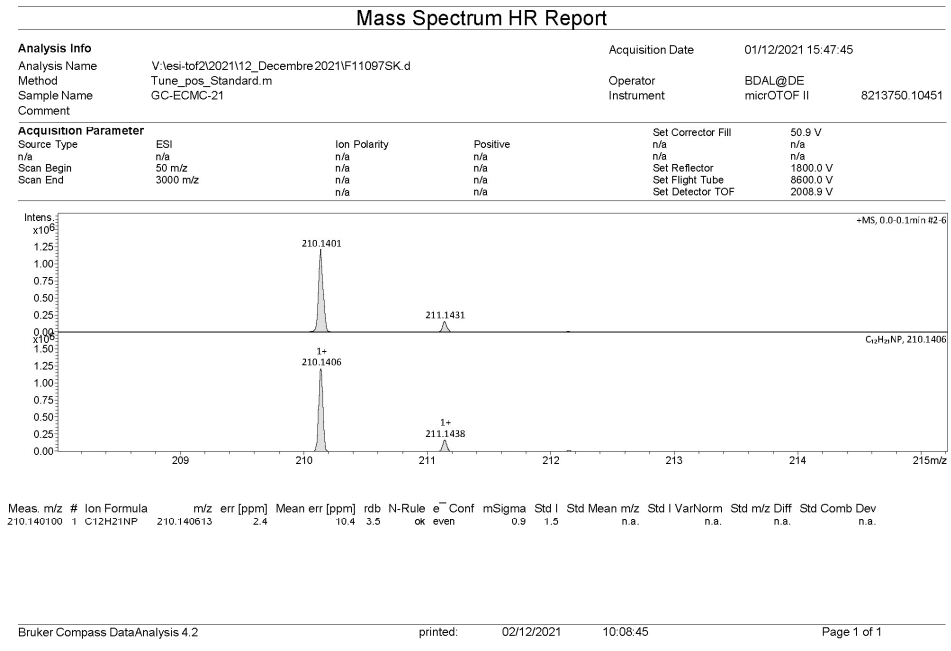


Figure S25. Partial Mass Spectrum of **7**

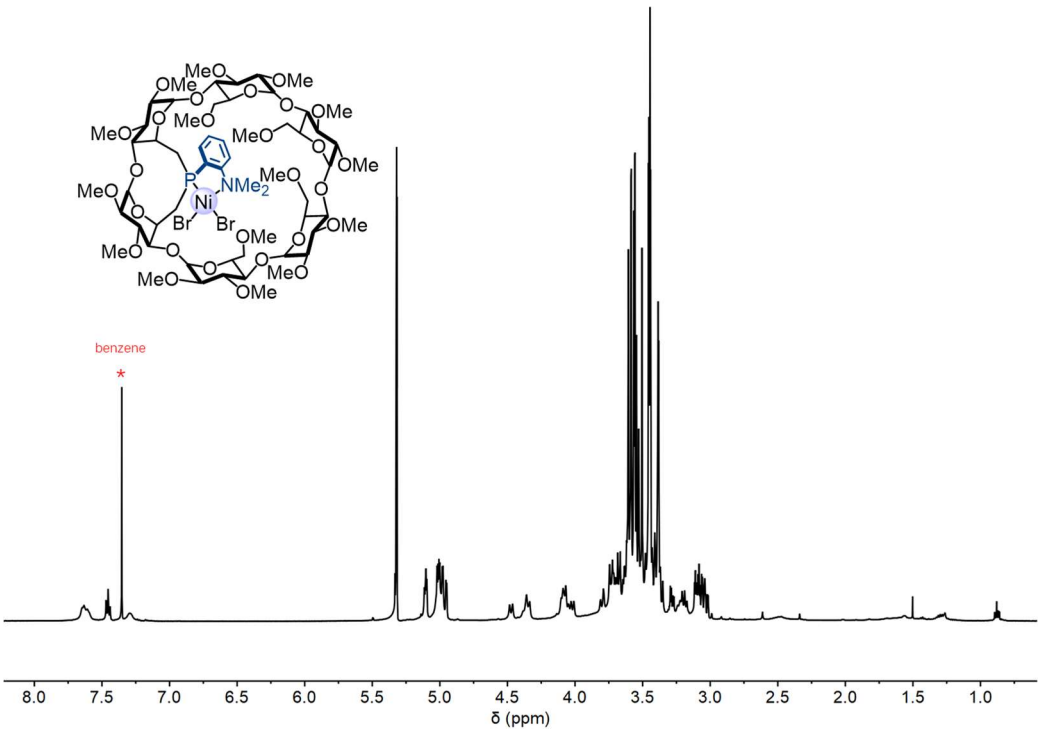


Figure S26. ^{1}H NMR spectrum of **9** in CD_2Cl_2

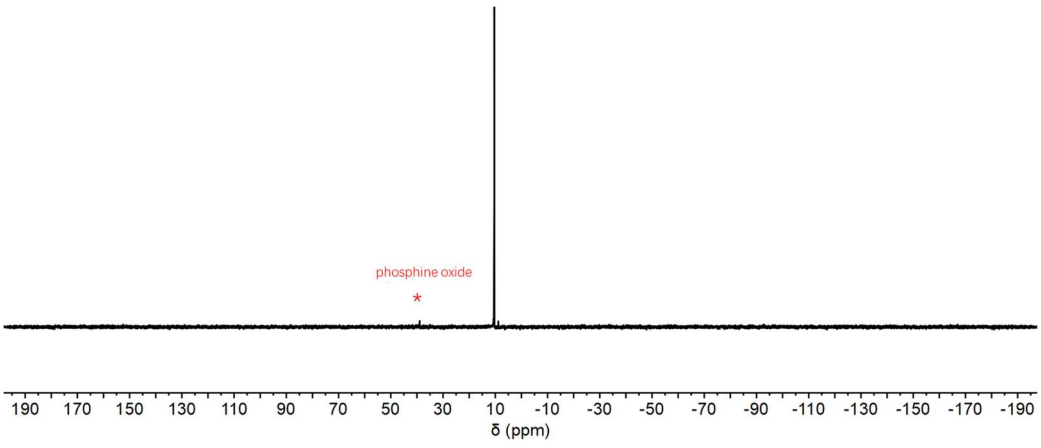


Figure S27. ^{31}P NMR spectrum of **9** in CD_2Cl_2 (-60°C)

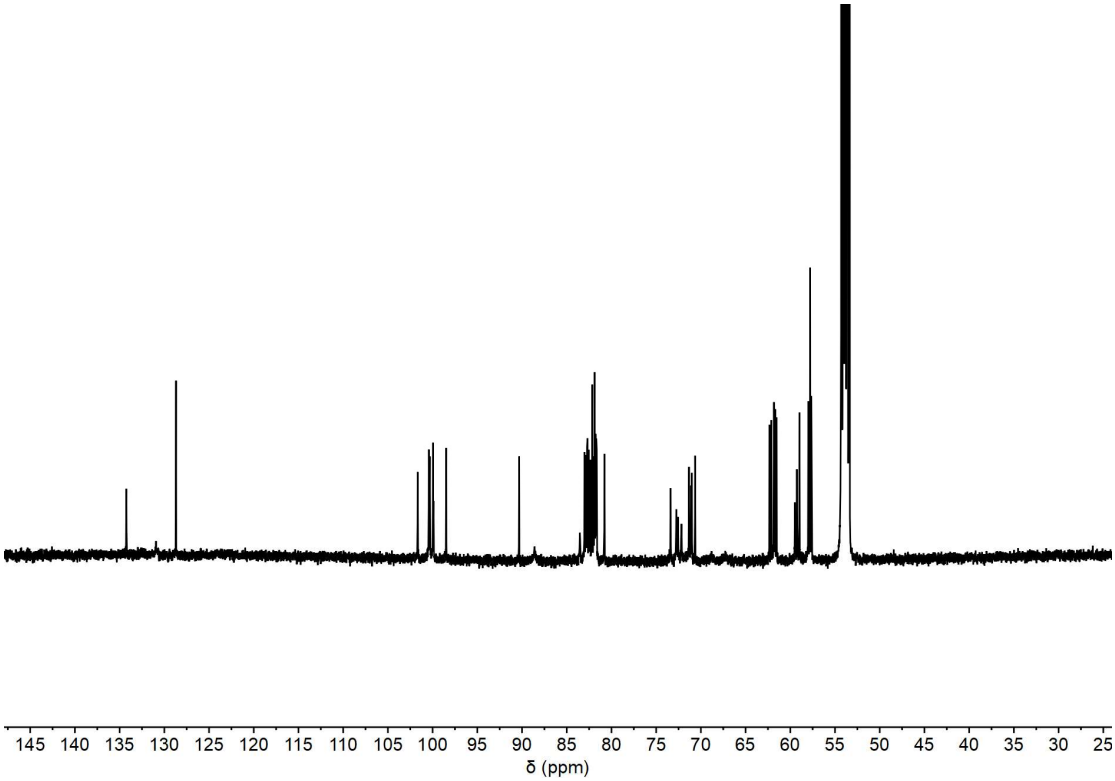


Figure S28. ^{13}C NMR spectrum of **9** in CD_2Cl_2

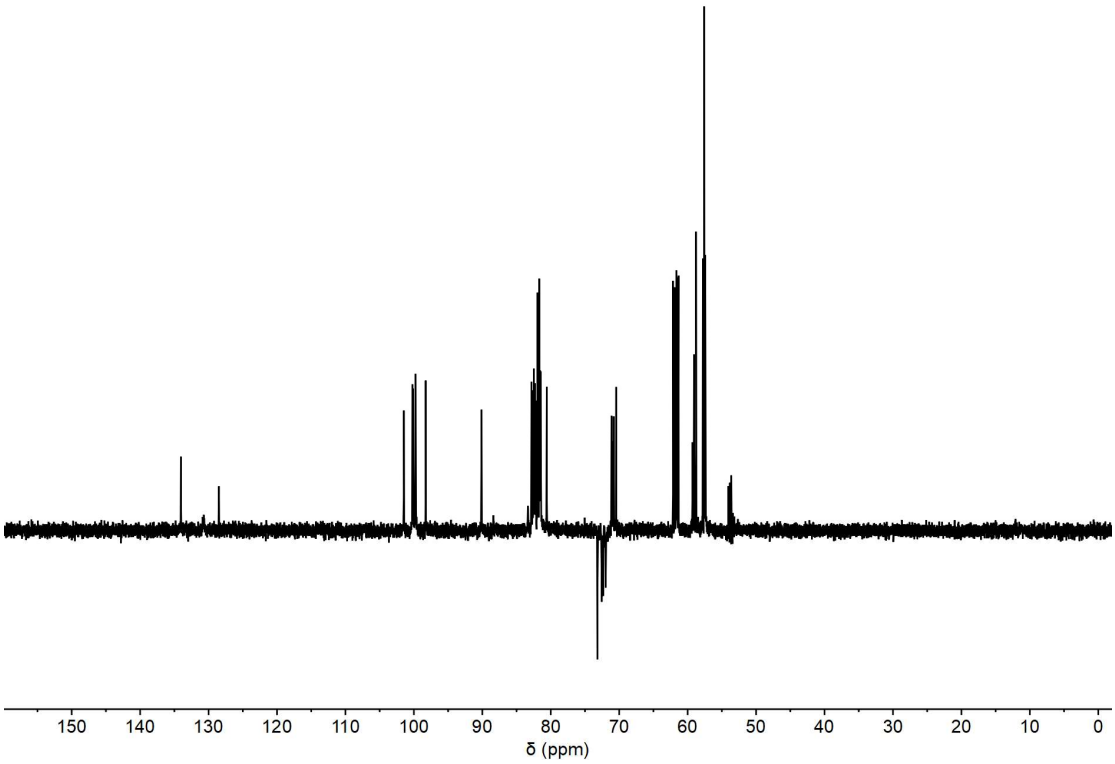


Figure S29. DEPT 135 spectrum of **9** in CD_2Cl_2

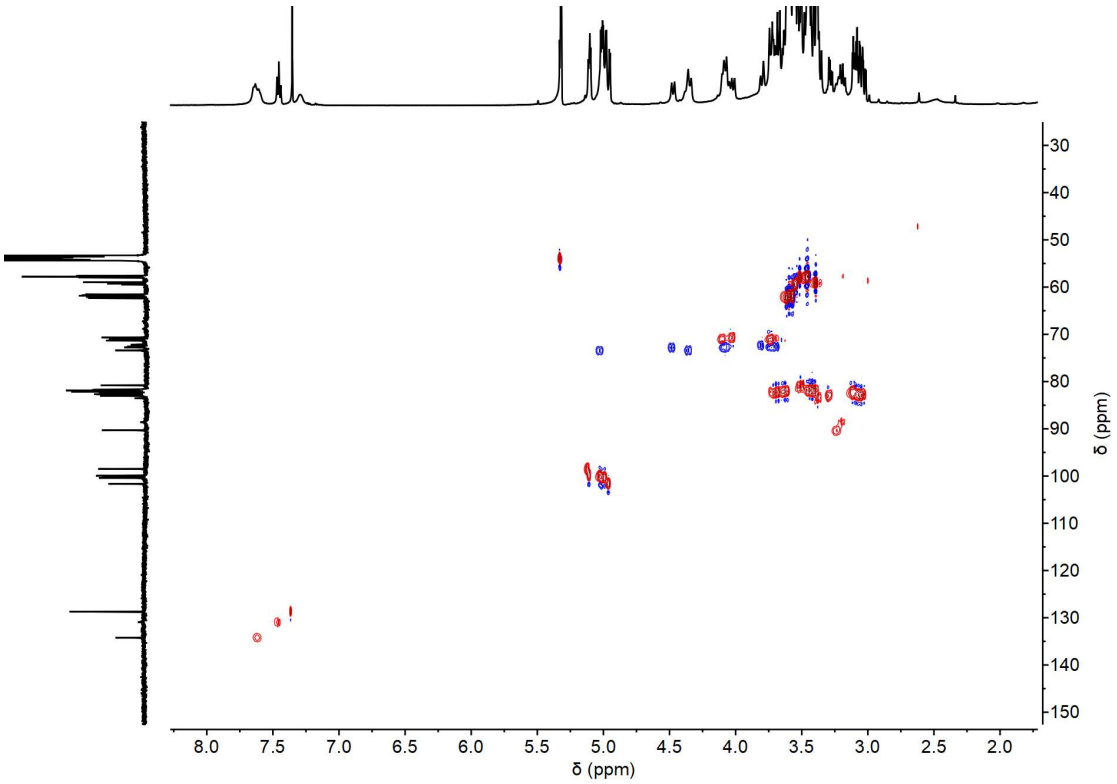


Figure S30. $^{1}H/^{13}C$ edited HSQC spectrum of **9** in CD_2Cl_2

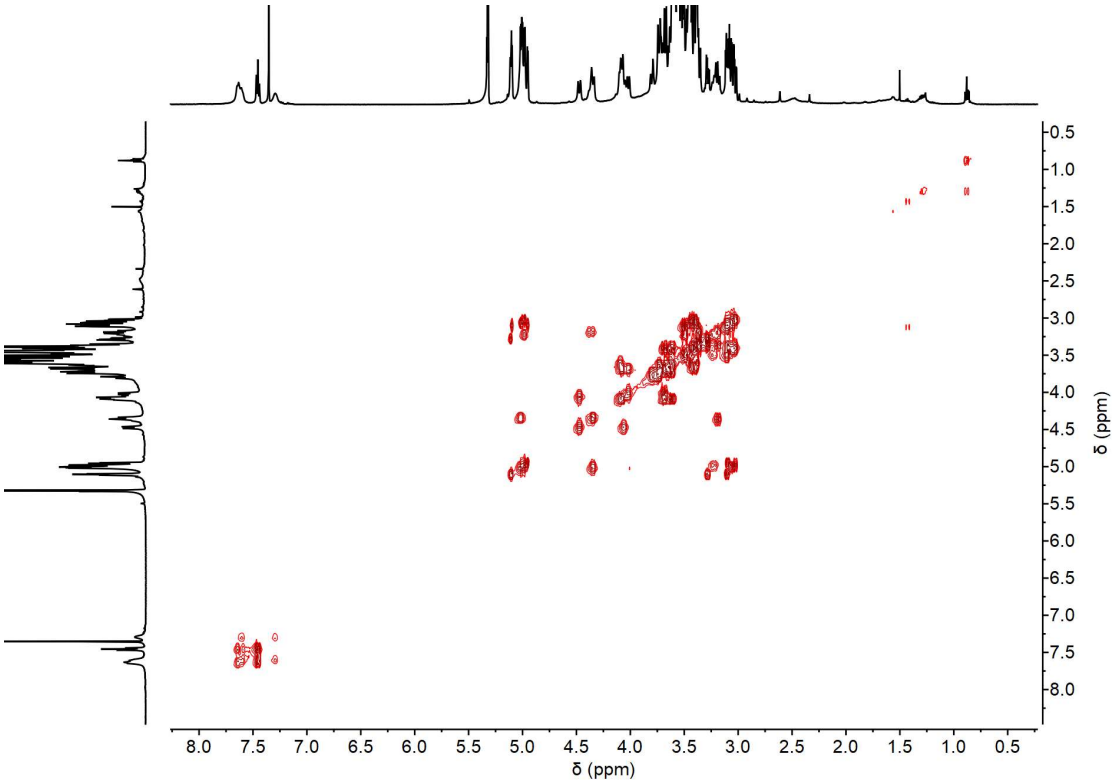


Figure S31. $^{1}H/^{1}H$ COSY spectrum of **9** in CD_2Cl_2

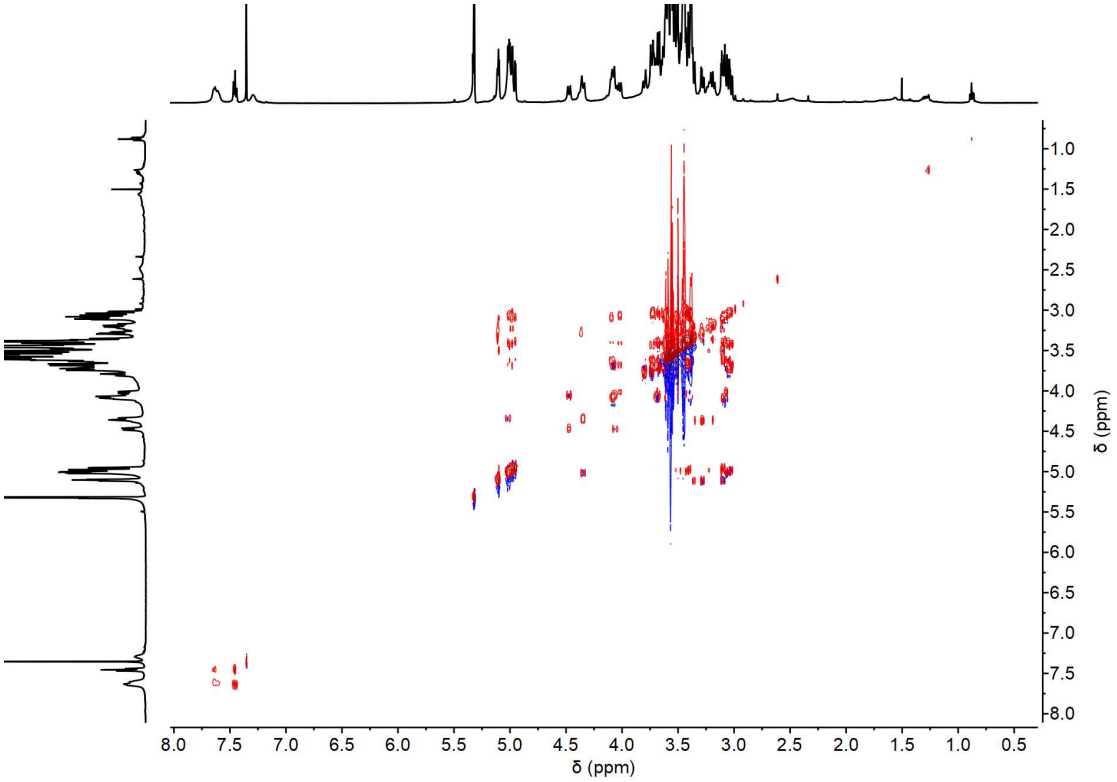


Figure S32. $^{1}H/^{1}H$ TOCSY spectrum of **9** in CD_2Cl_2

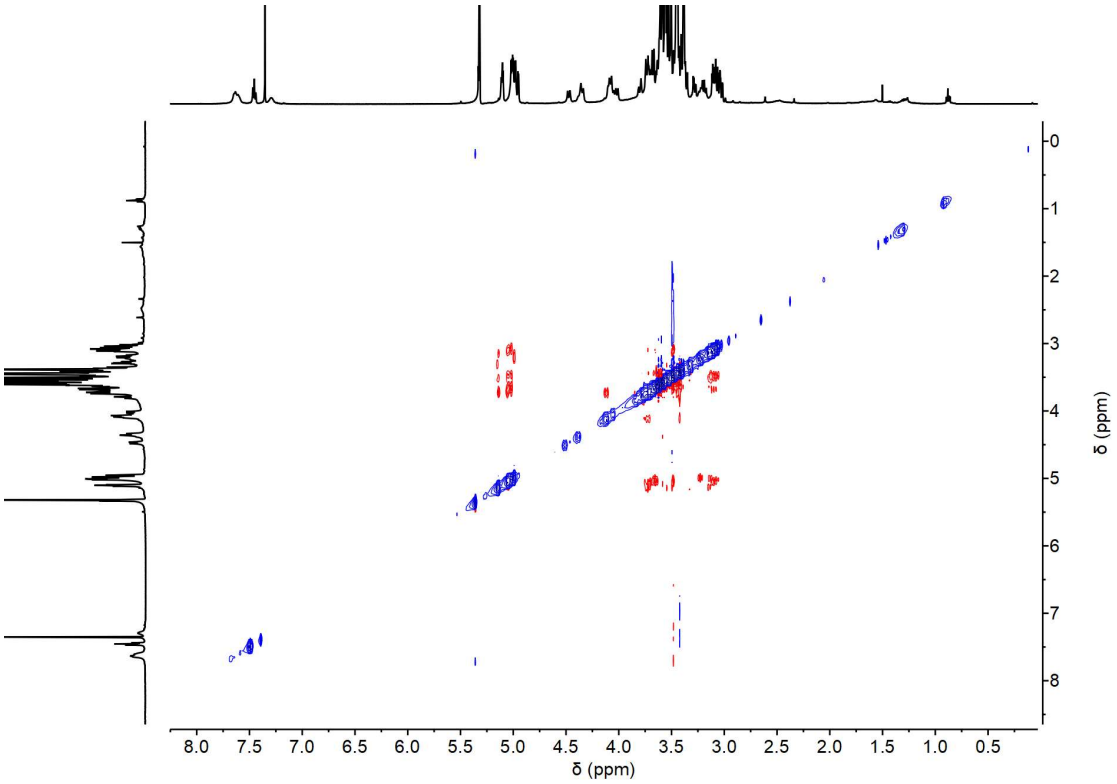


Figure S33. $^{1}H/^{1}H$ ROESY spectrum of **9** in CD_2Cl_2

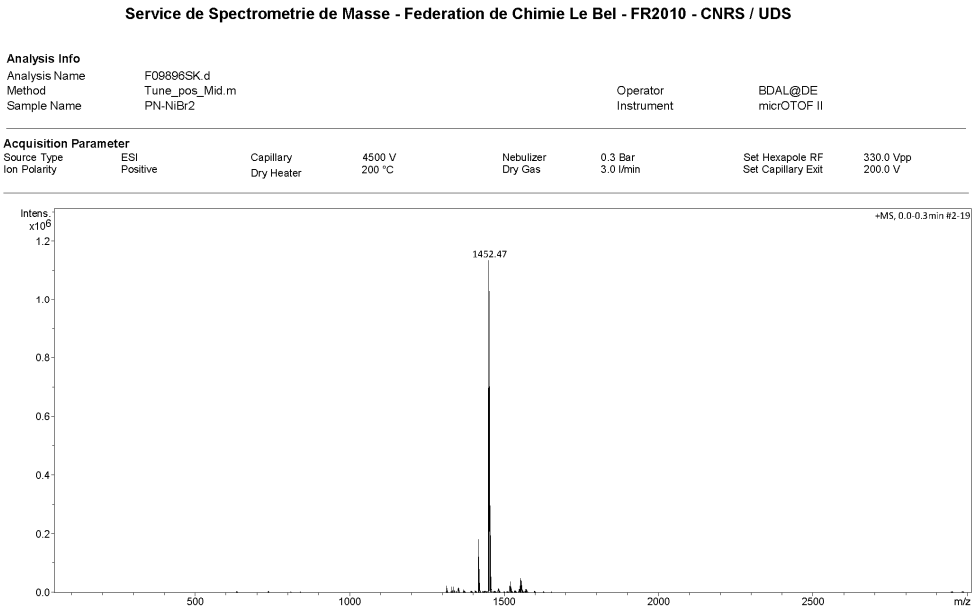


Figure S34. Full Mass Spectrum of **9**

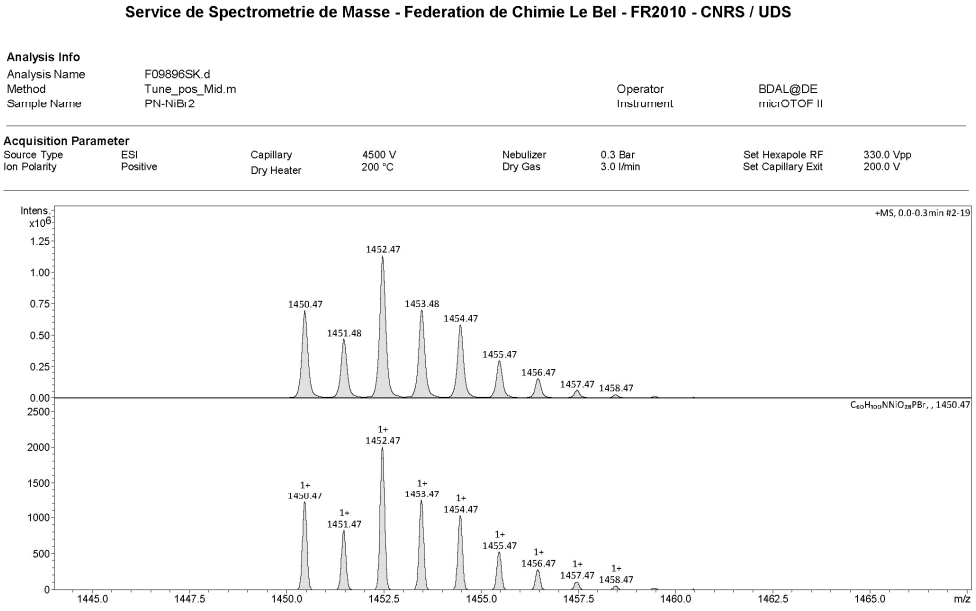


Figure S35. Partial Mass Spectrum of **9**

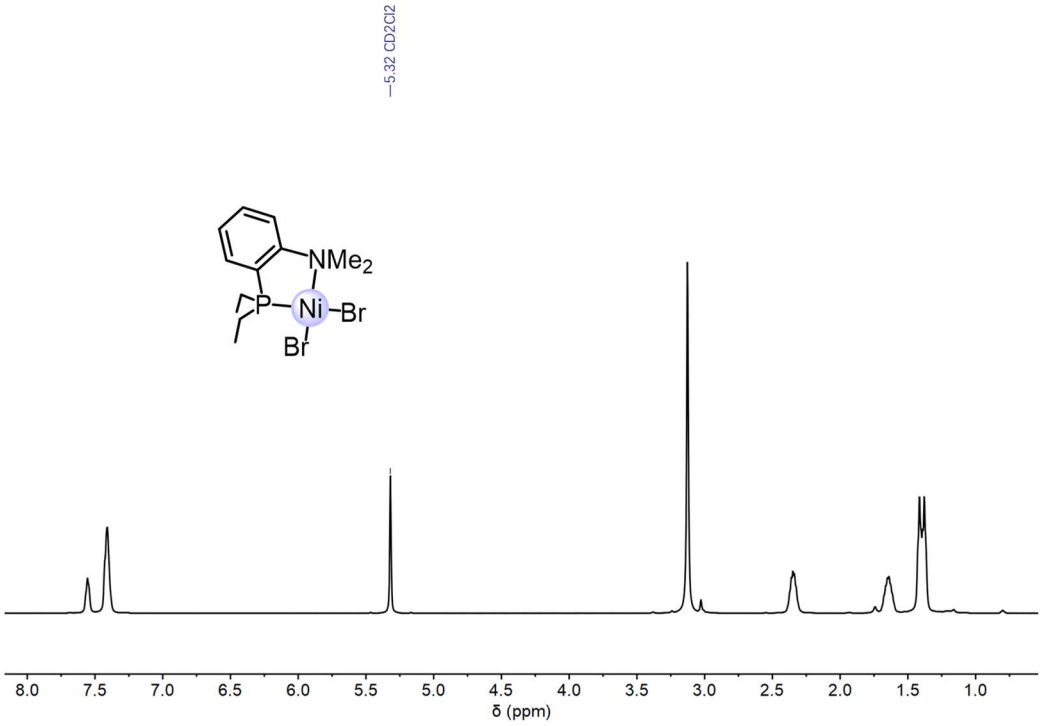


Figure S36. ^{1}H NMR spectrum of **10** in CD_2Cl_2 (-60°C)

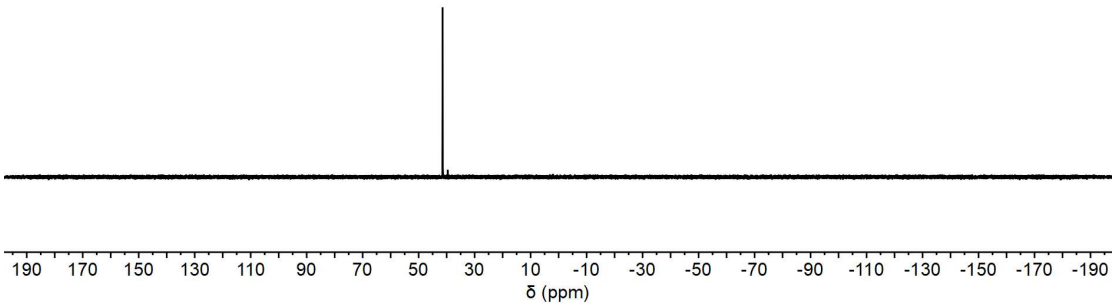


Figure S37. ^{31}P NMR spectrum of **10** in CD_2Cl_2 (-60°C)

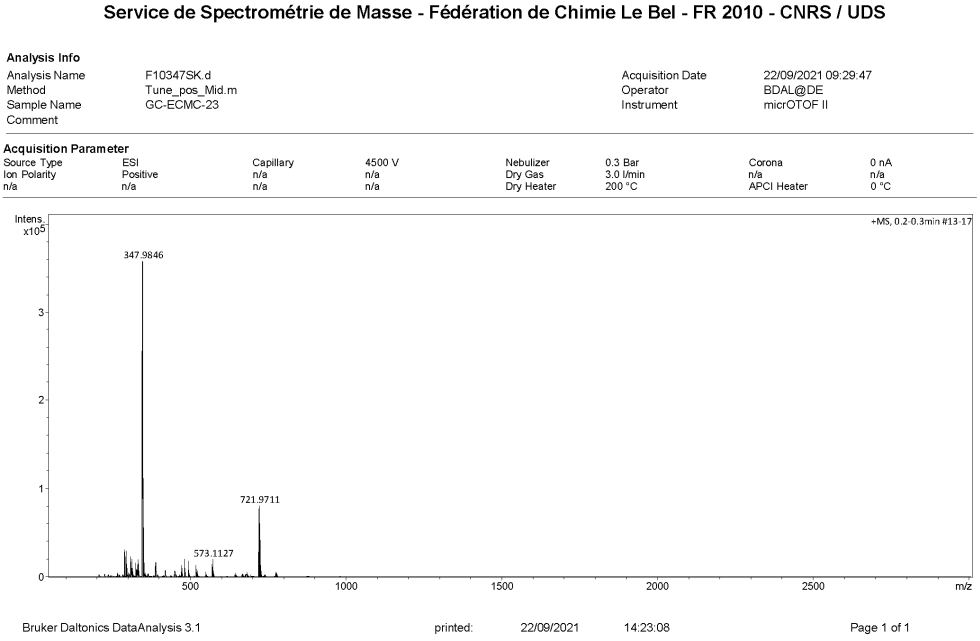


Figure S38. Full High Resolution Mass Spectra of **10**

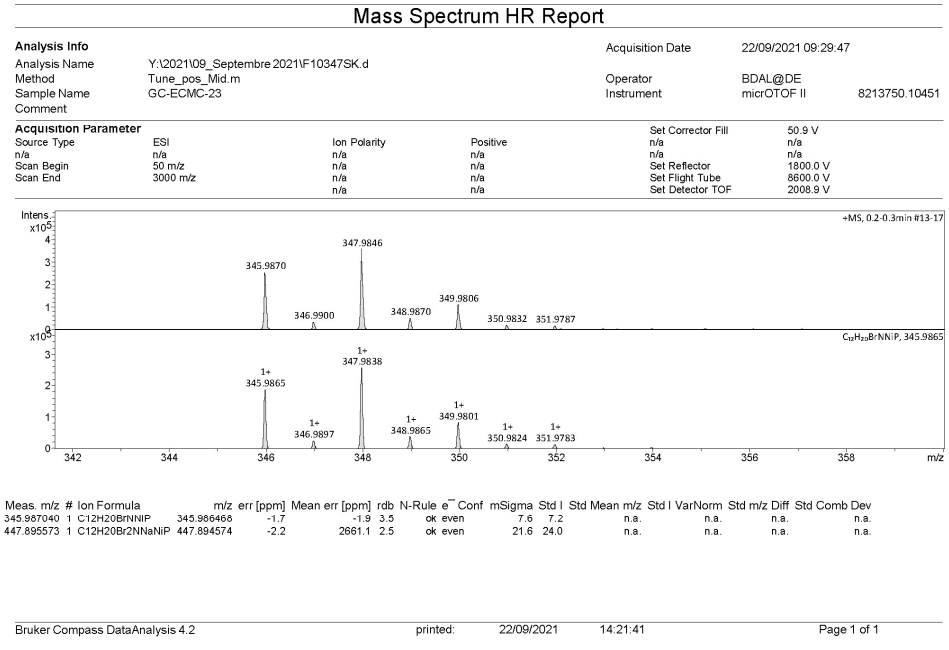


Figure S39. Partial High Resolution Mass Spectra of **10**

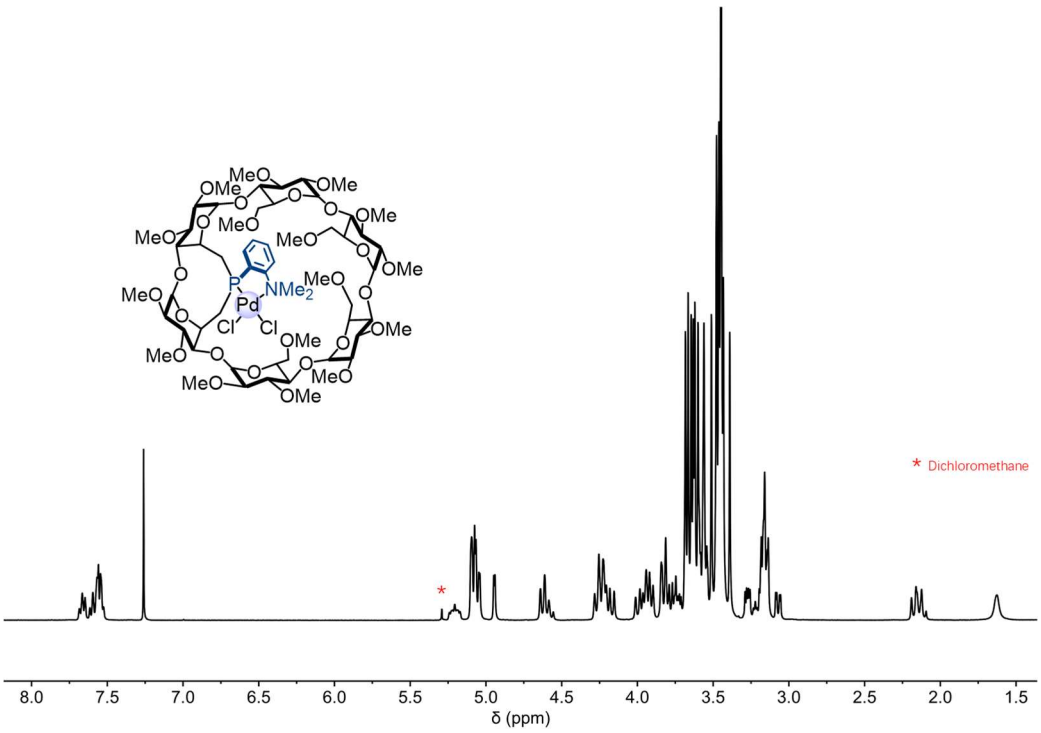


Figure S40. ^{1}H NMR spectrum of **8** in $CDCl_3$

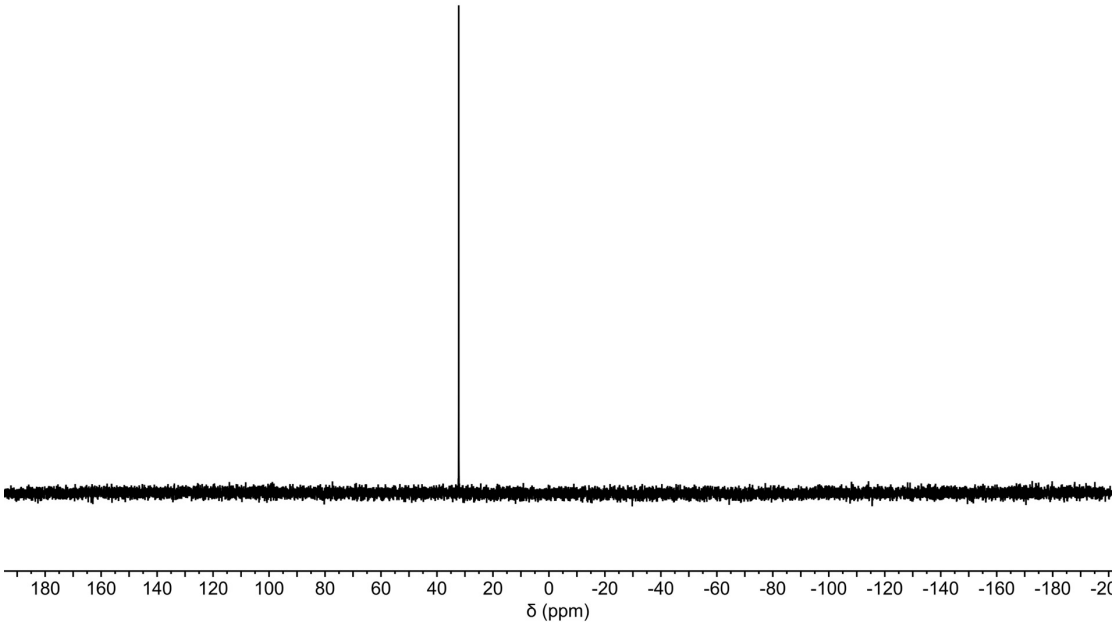


Figure S41. ^{31}P NMR spectrum of **8** in $CDCl_3$

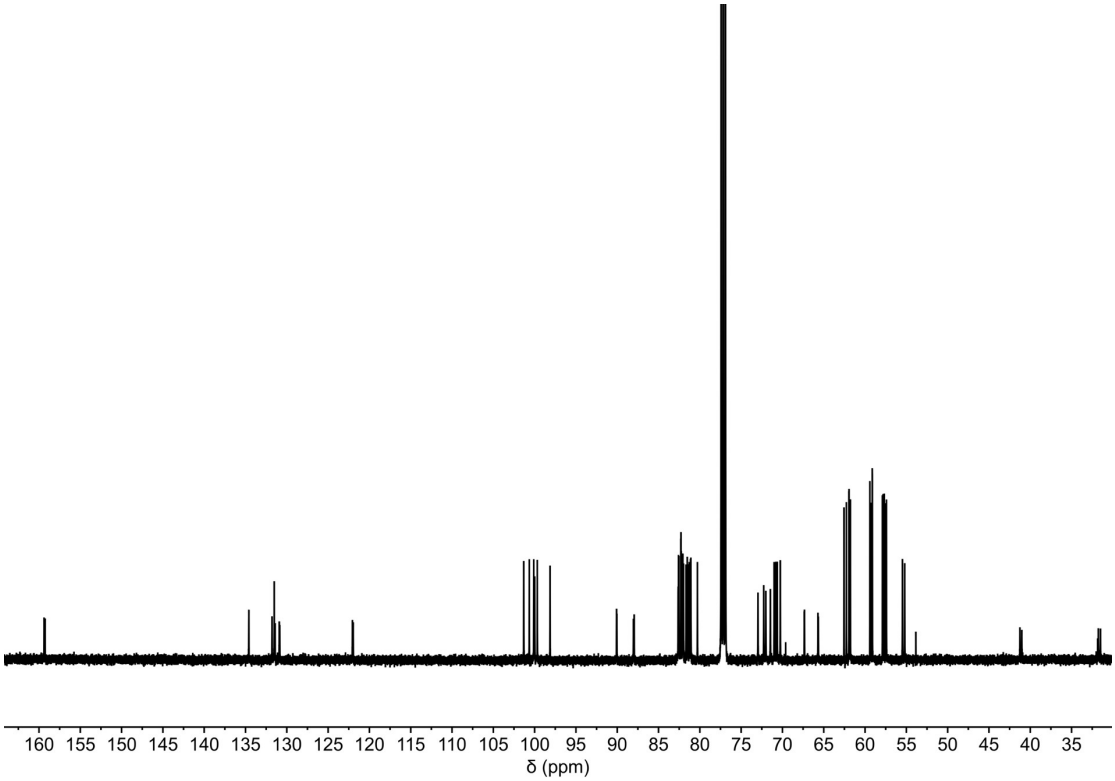


Figure S42. ^{13}C NMR spectrum of **8** in $CDCl_3$

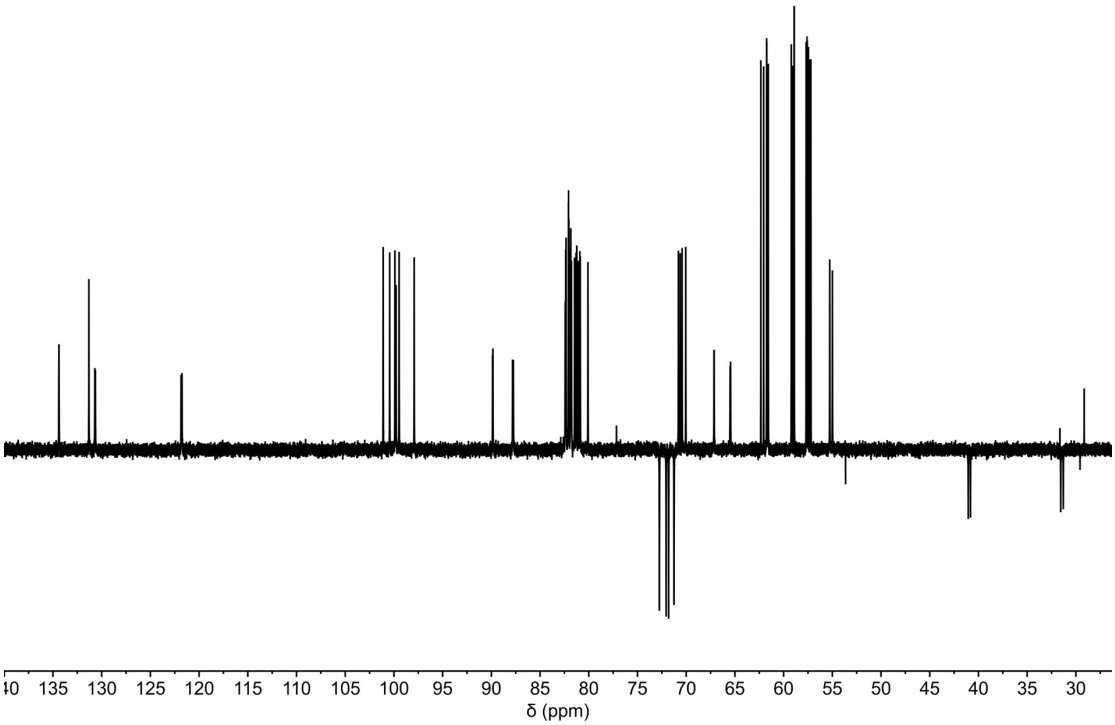


Figure S43. DEPT 135 spectrum of **8** in $CDCl_3$

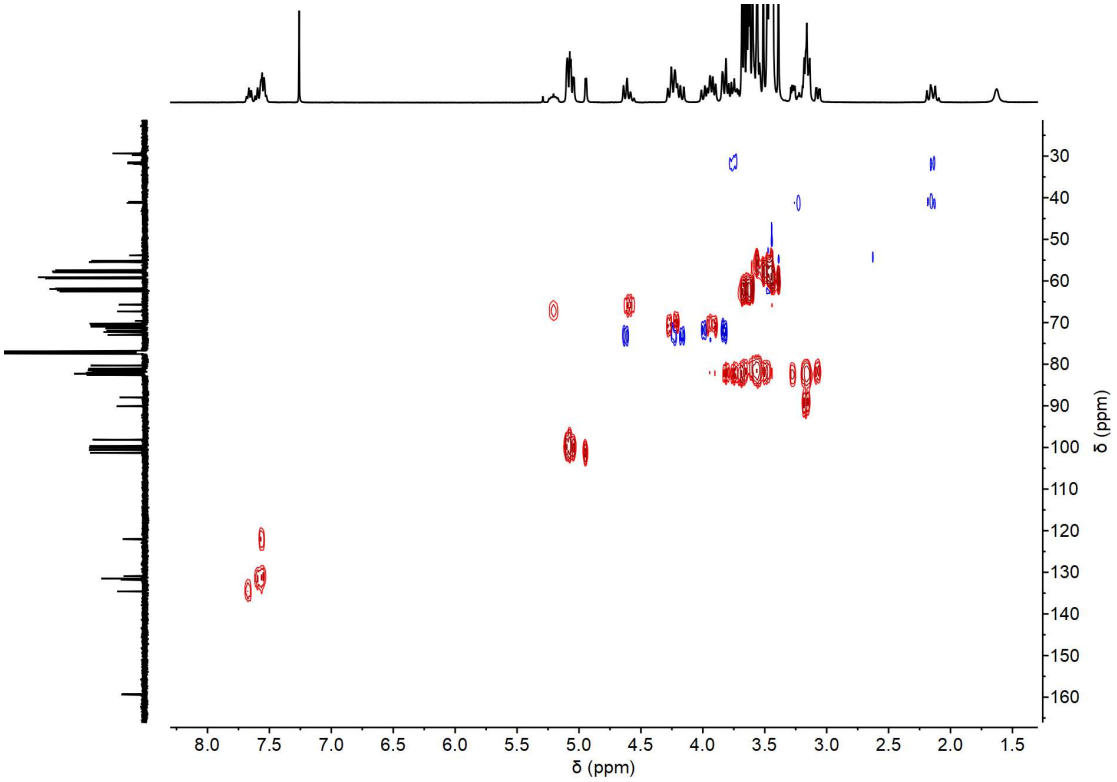


Figure S44. $^{1}H/^{13}C$ edited HSQC spectrum of **8** in $CDCl_3$

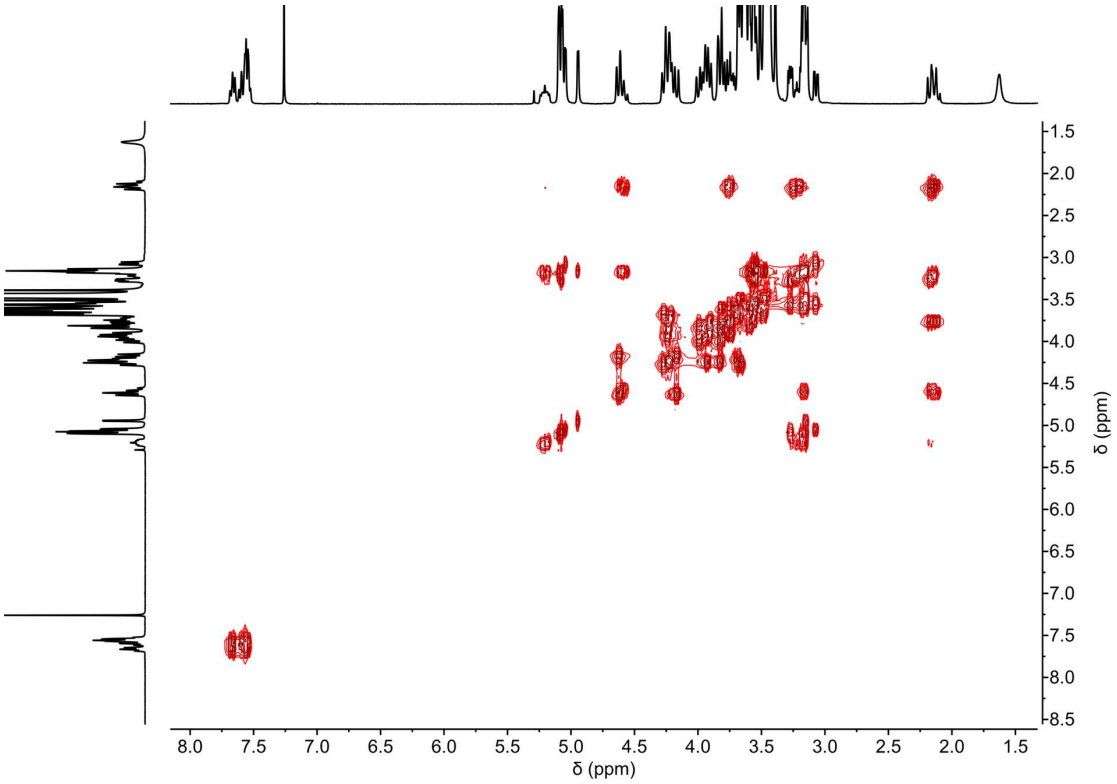


Figure S45. $^{1}H/^{1}H$ COSY spectrum of **8** in $CDCl_3$

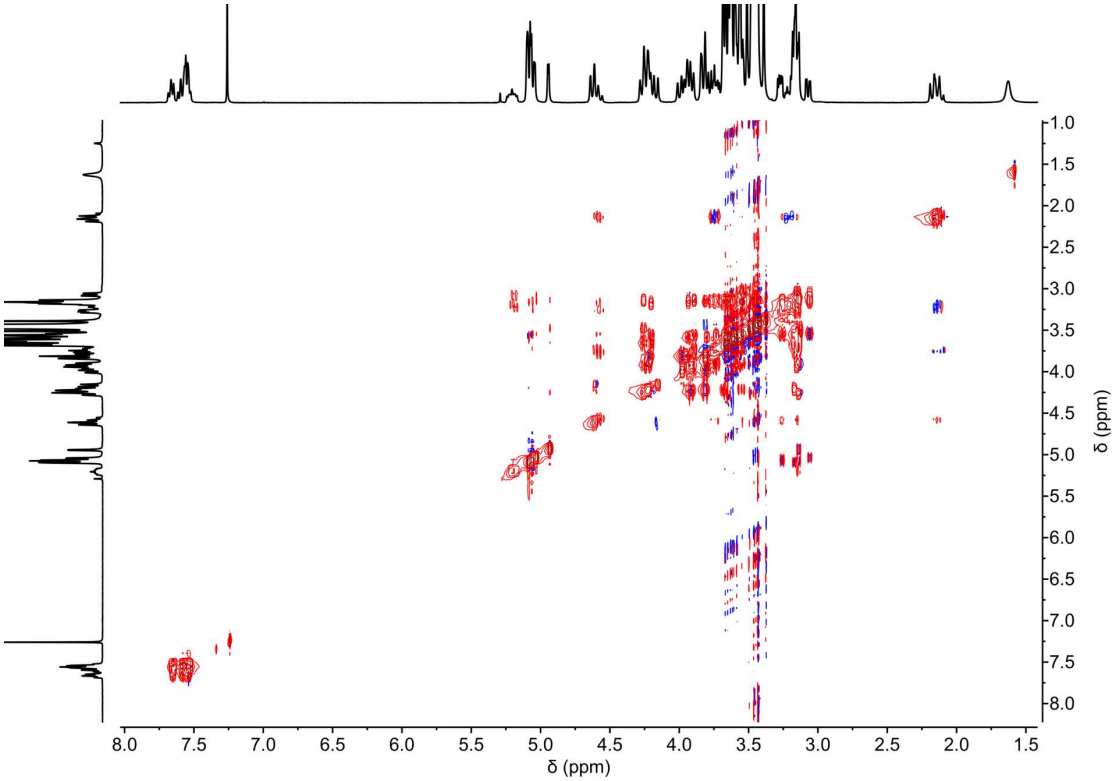


Figure S46. $^{1}H/^{1}H$ TOCSY spectrum of **8** in $CDCl_3$

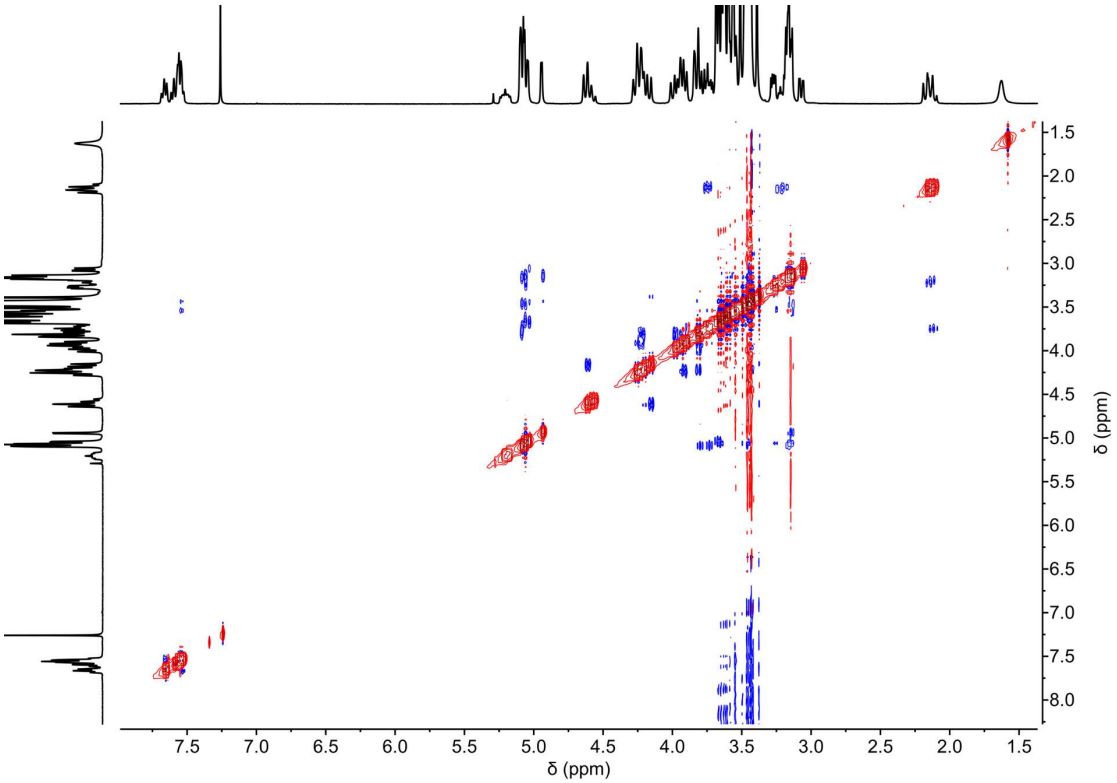


Figure S47. $^{1}H/^{1}H$ ROESY spectrum of **8** in $CDCl_3$

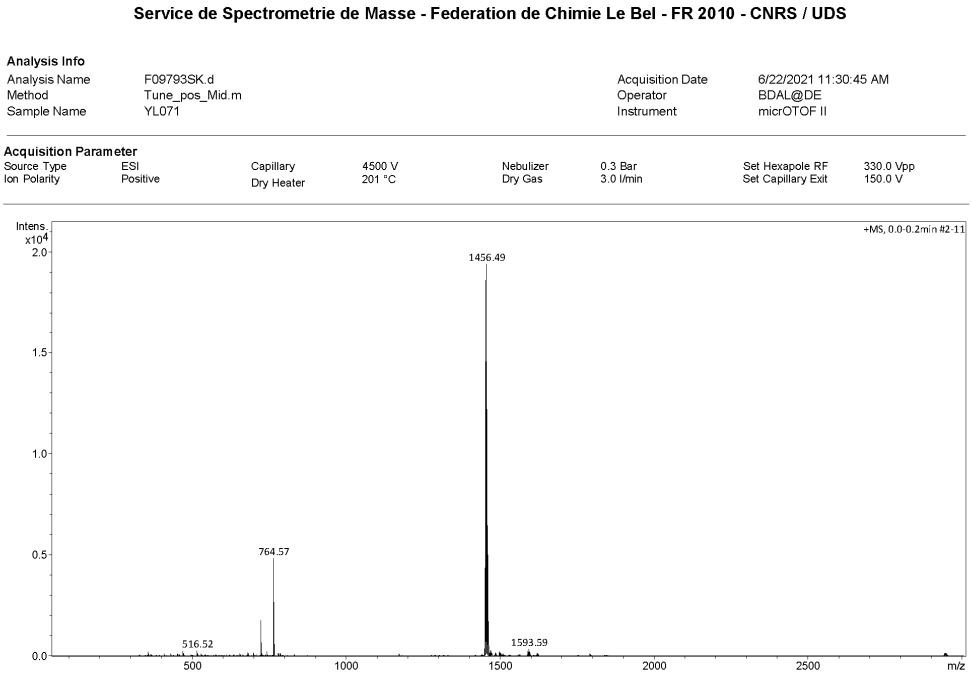


Figure S48. Full Mass Spectrum of **8**

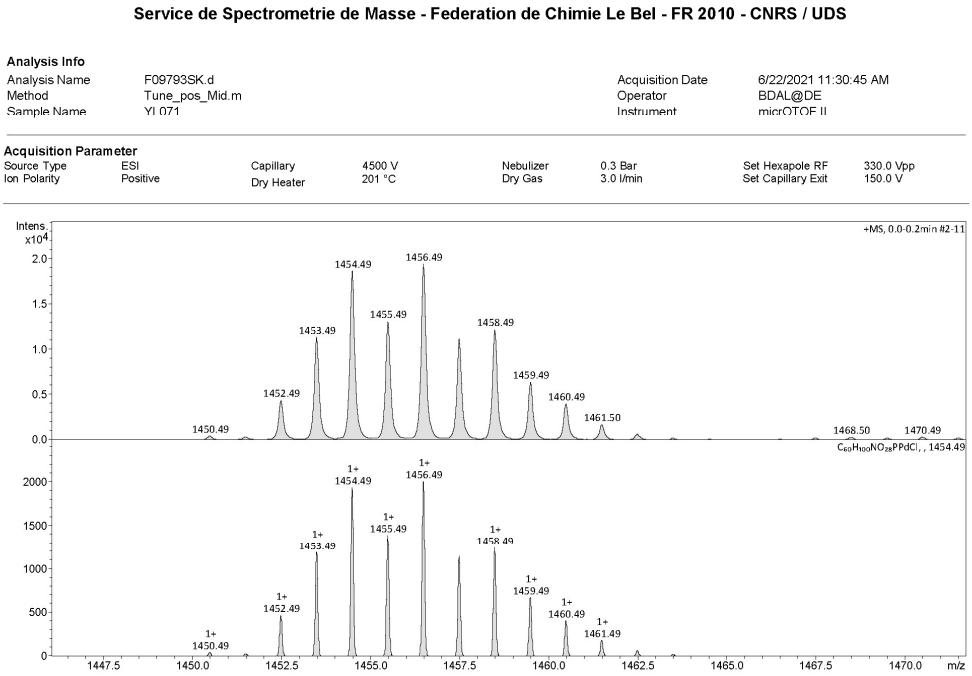


Figure S49. Partial Mass Spectrum of **8**

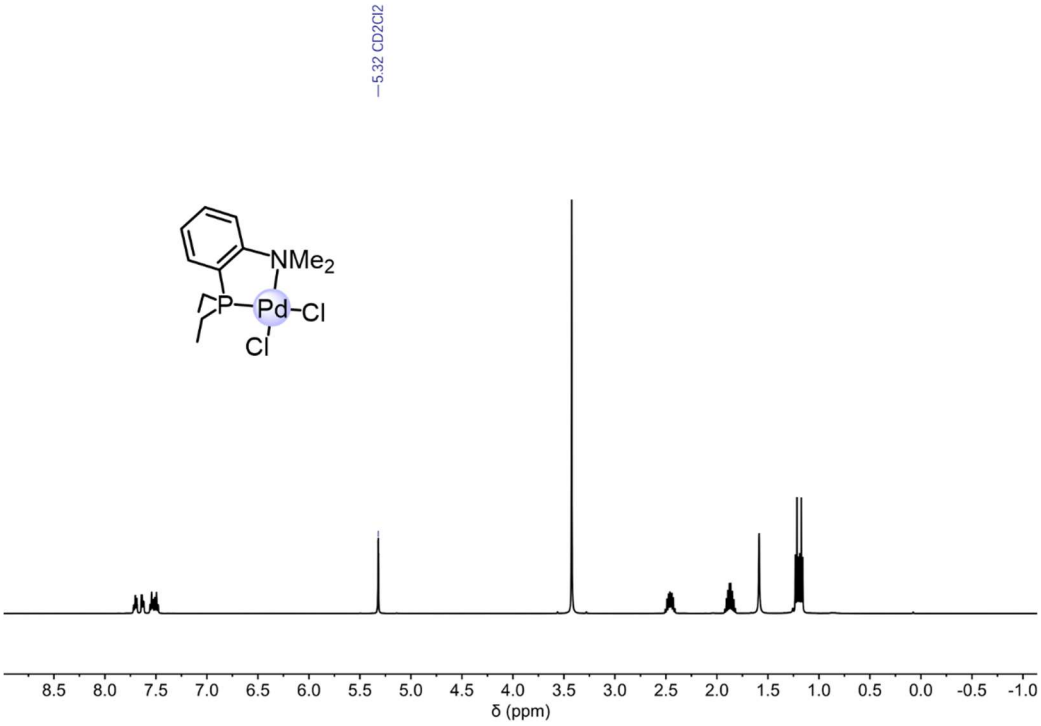


Figure S50. ^{1}H NMR spectrum of **11** in CD_2Cl_2

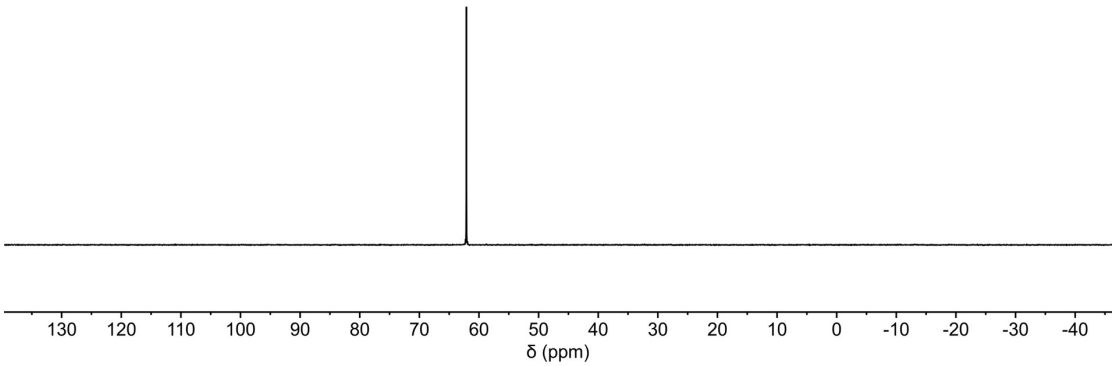


Figure S51. ^{31}P NMR spectrum of **11** in CD_2Cl_2

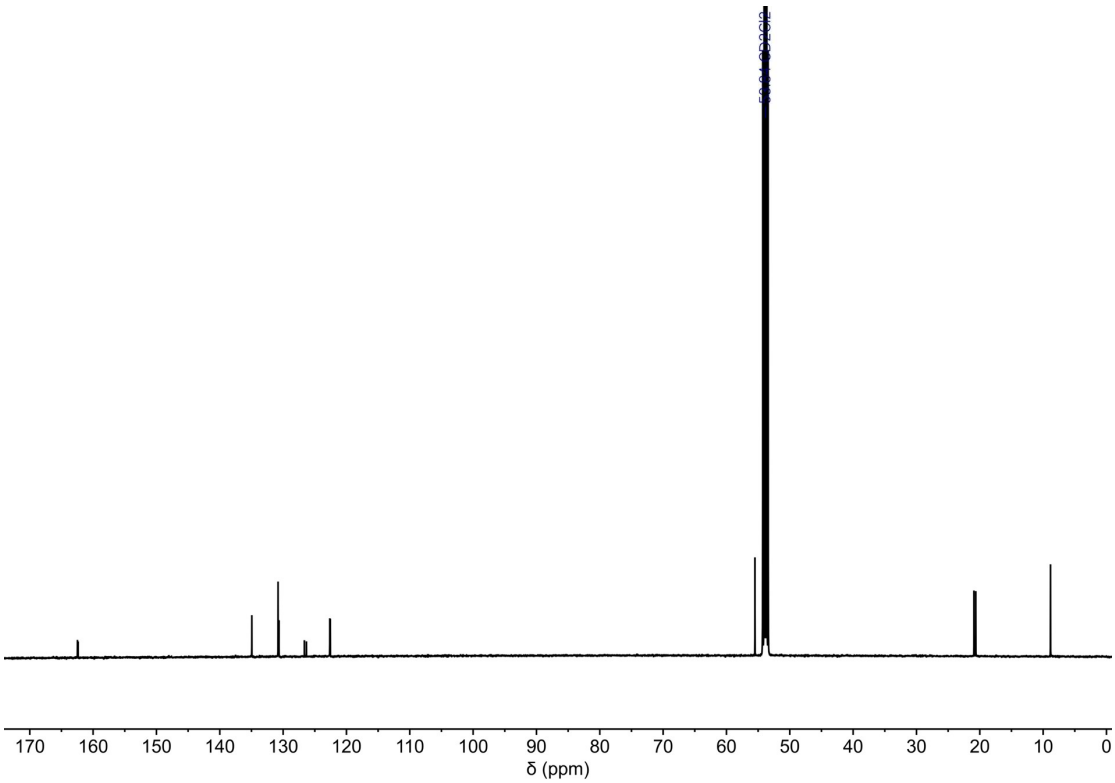


Figure S52. ^{13}C NMR spectrum of **11** in CD_2Cl_2

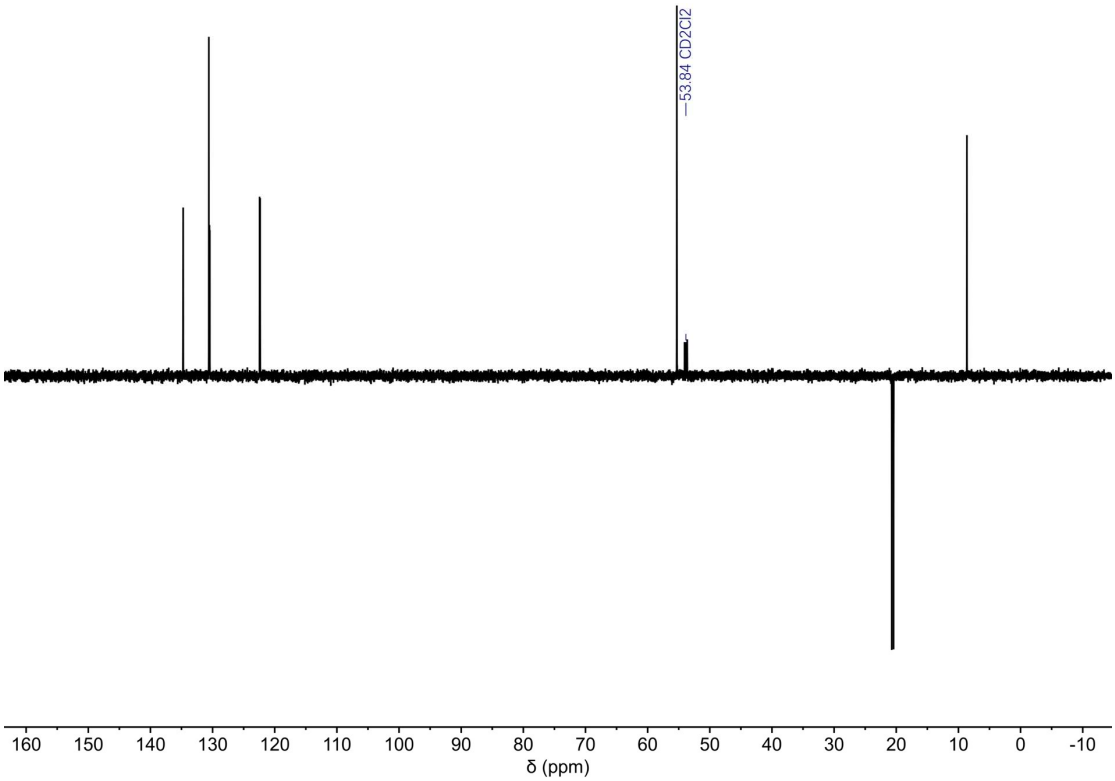


Figure S53. DEPT 135 spectrum of **11** in CD_2Cl_2

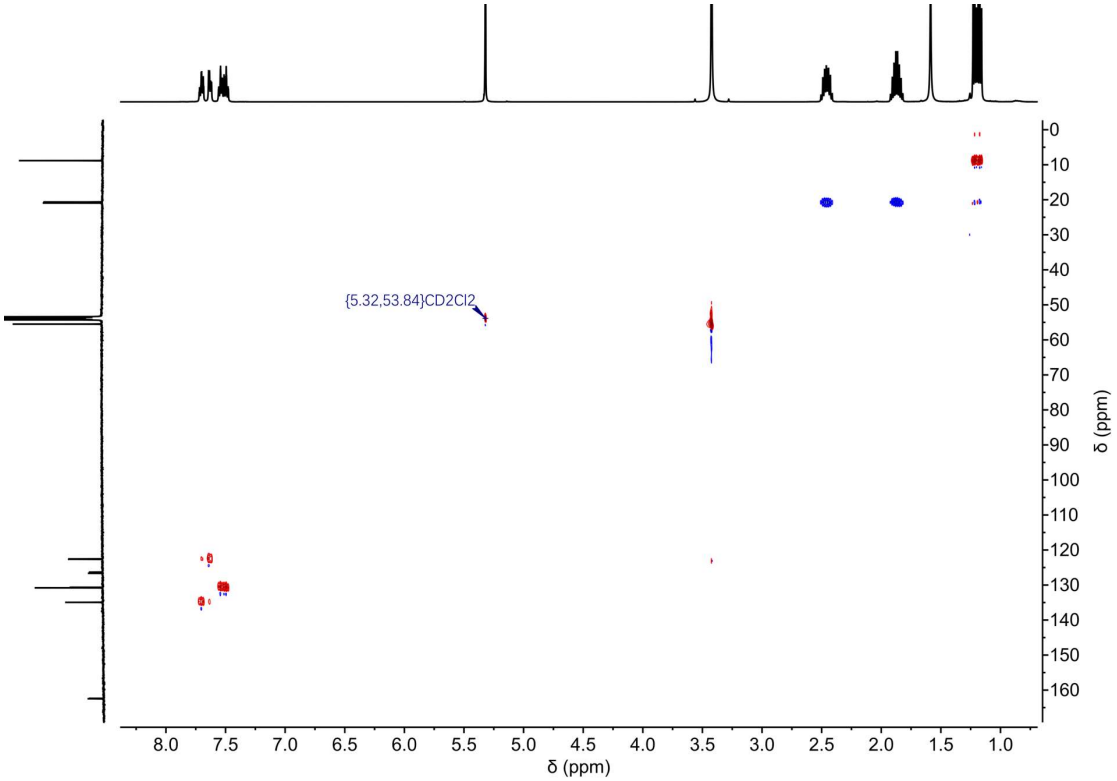


Figure S54. $^{1}H/^{13}C$ edited HSQC spectrum of **11** in CD_2Cl_2

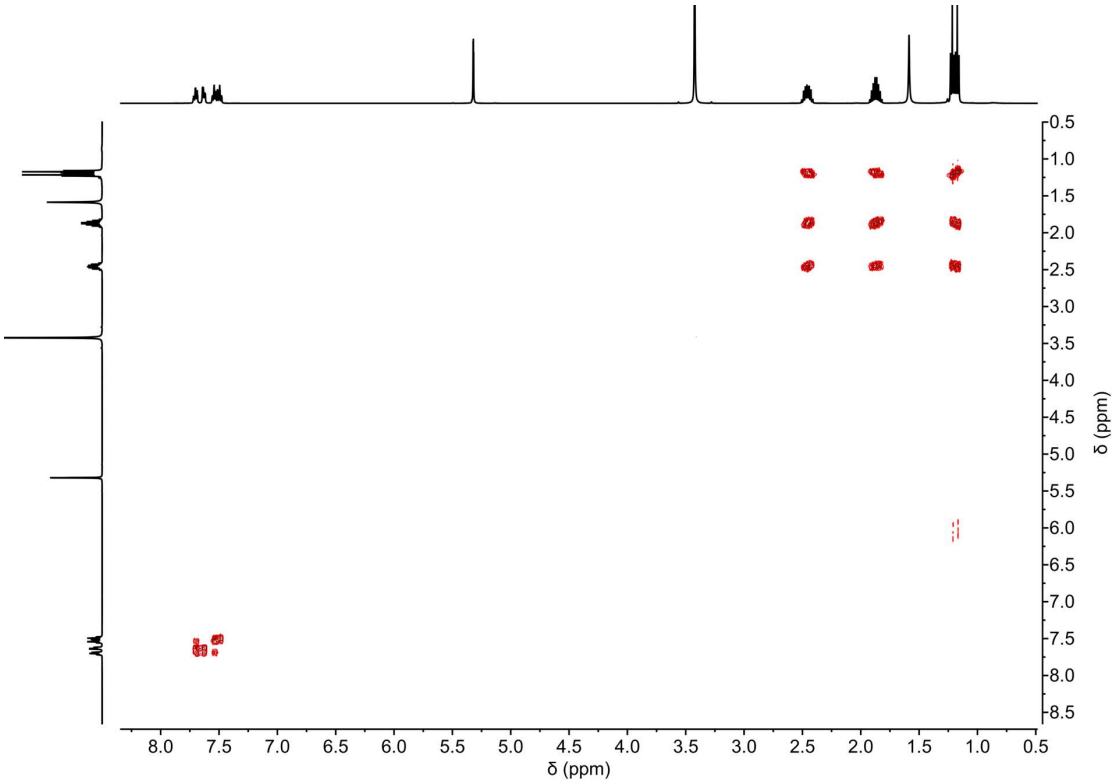


Figure S55. $^{1}H/^{1}H$ COSY spectrum of **11** in CD_2Cl_2

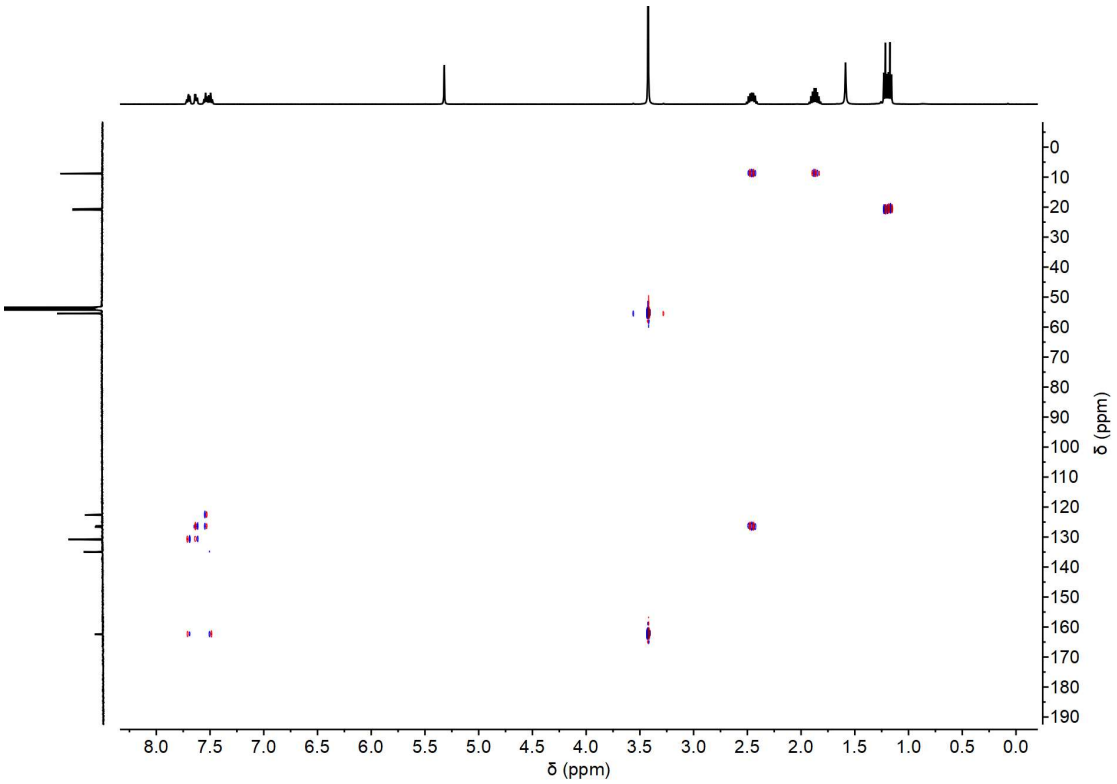


Figure S56. $^{1}H/^{13}C$ HMBC spectrum of **11** in CD_2Cl_2

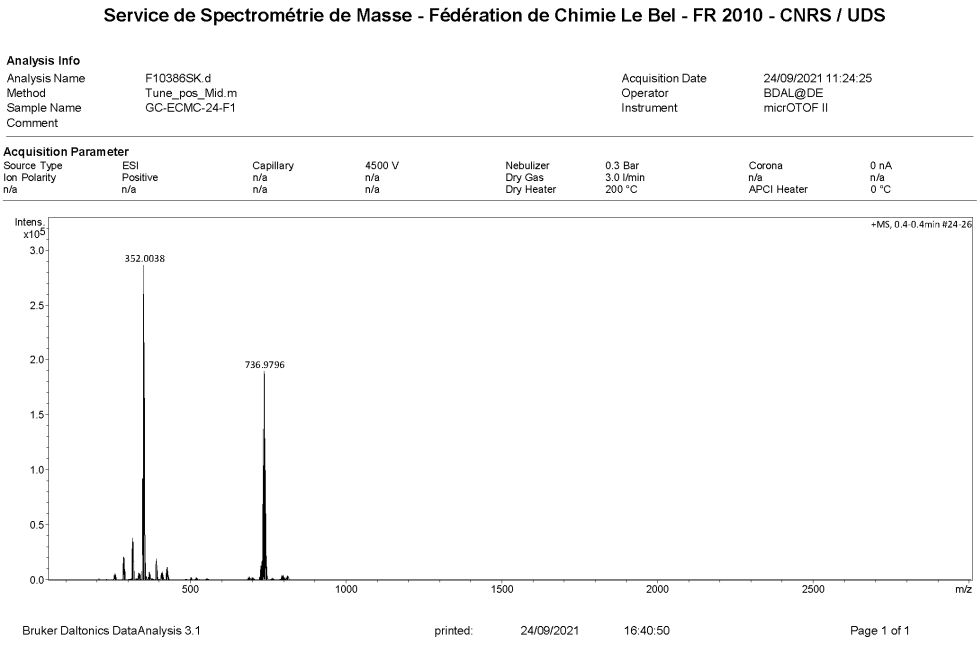


Figure S57. Full High Resolution Mass Spectrum of **11**

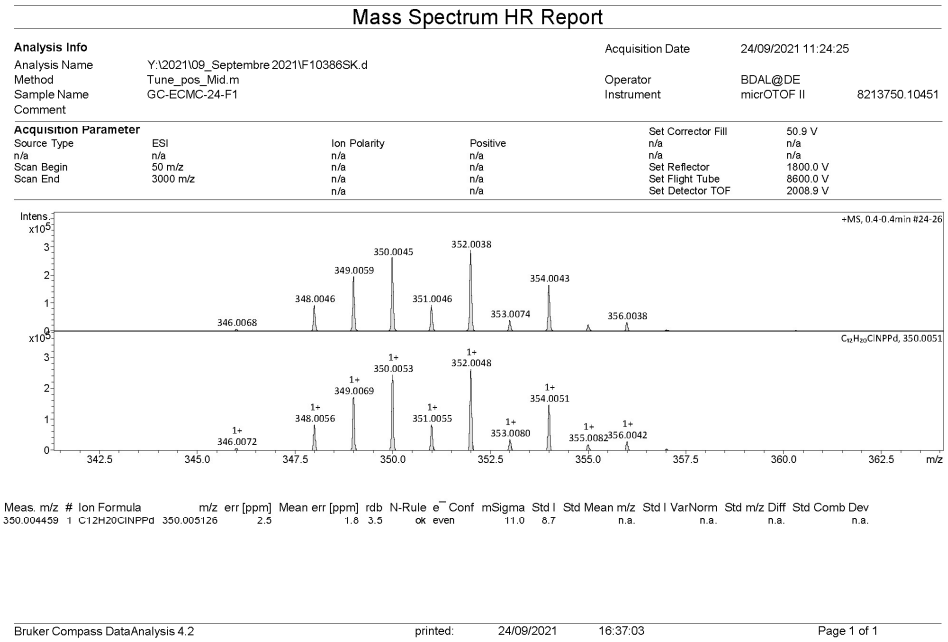


Figure S58. Partial High Resolution Mass Spectrum of **11**

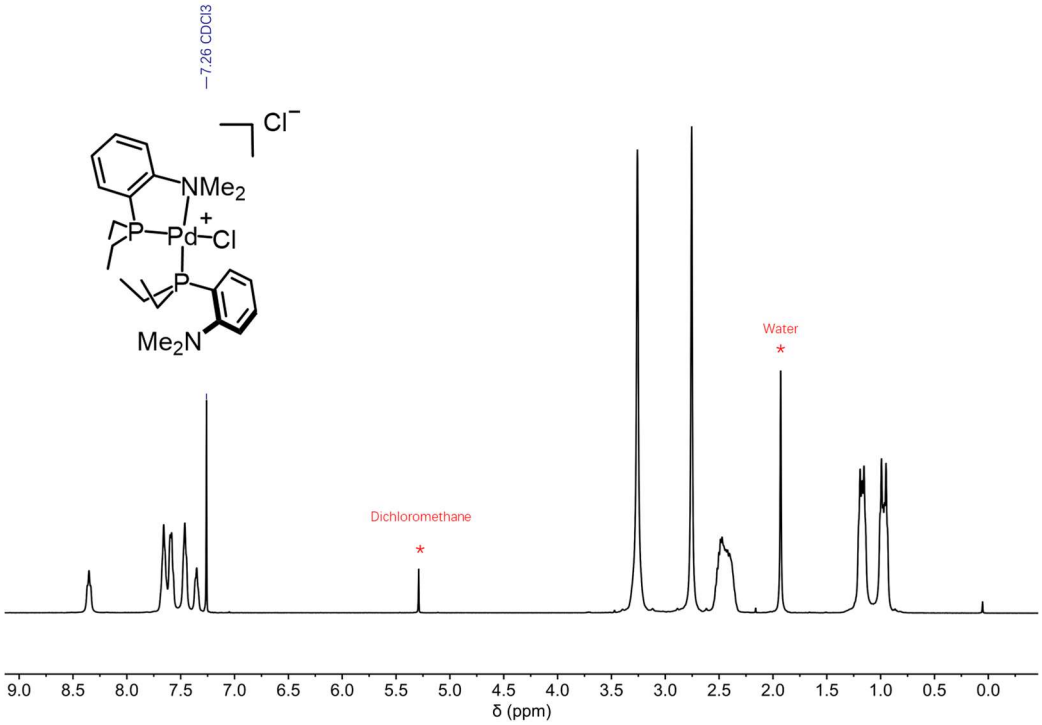


Figure S59. ^{1}H NMR spectrum of **12** in $CDCl_3$

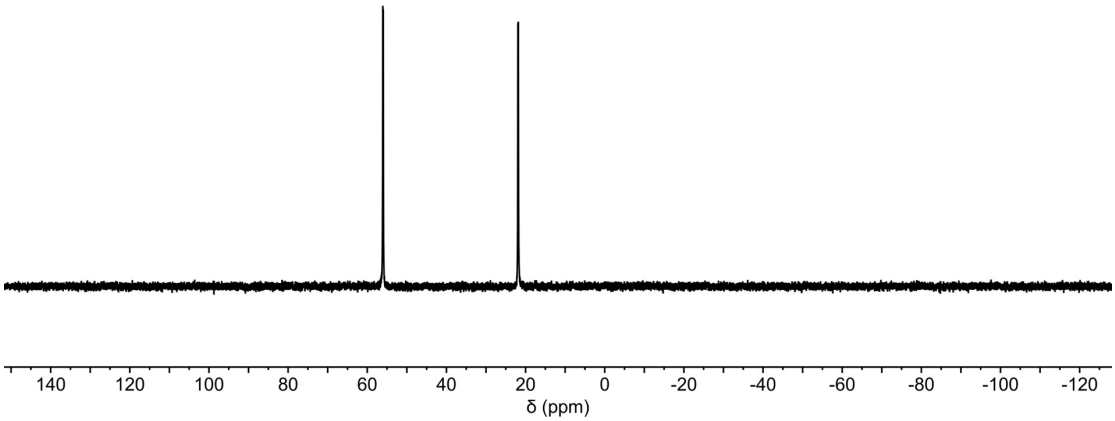


Figure S60. $^{31}P\{^{1}H\}$ NMR spectrum of **12** in $CDCl_3$

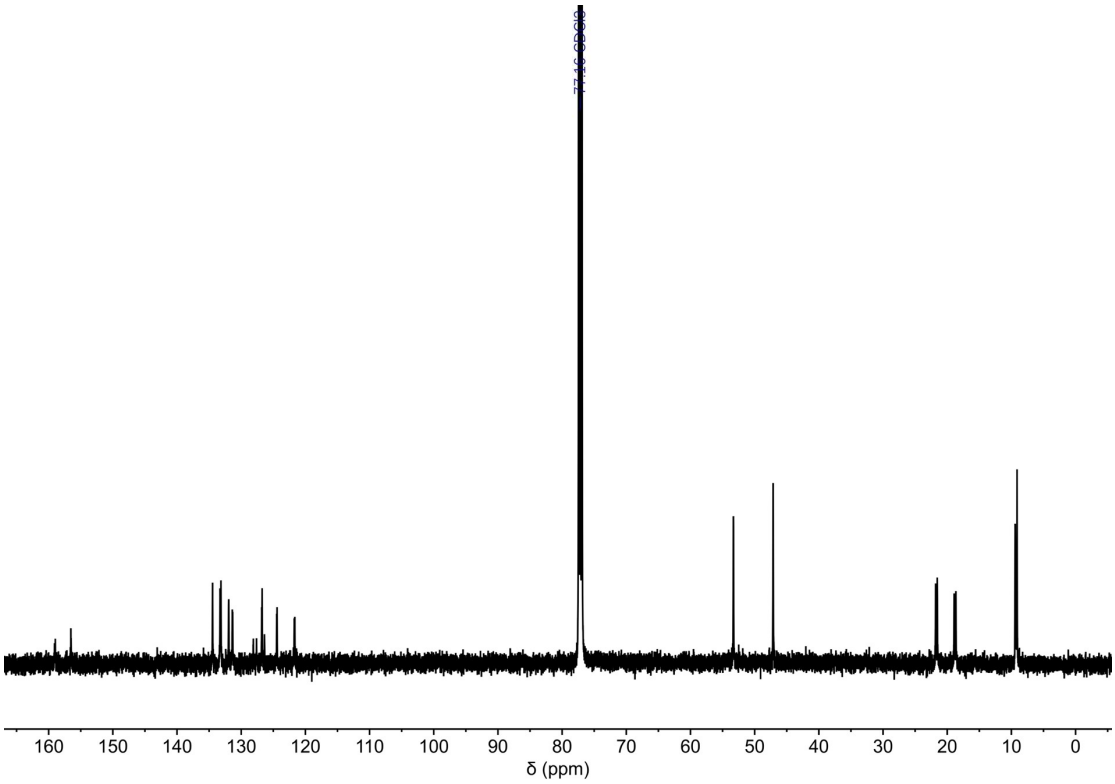


Figure S61. ^{13}C NMR spectrum of **12** in $CDCl_3$

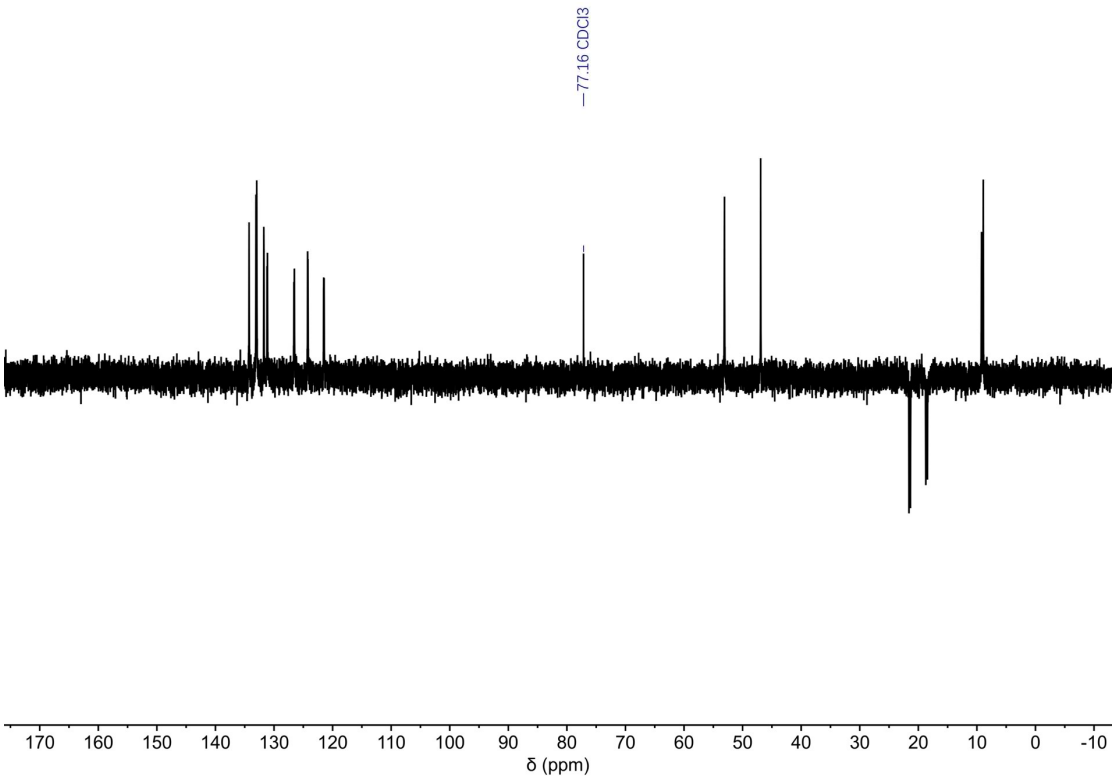


Figure S62. DEPT 135 spectrum of **12** in $CDCl_3$

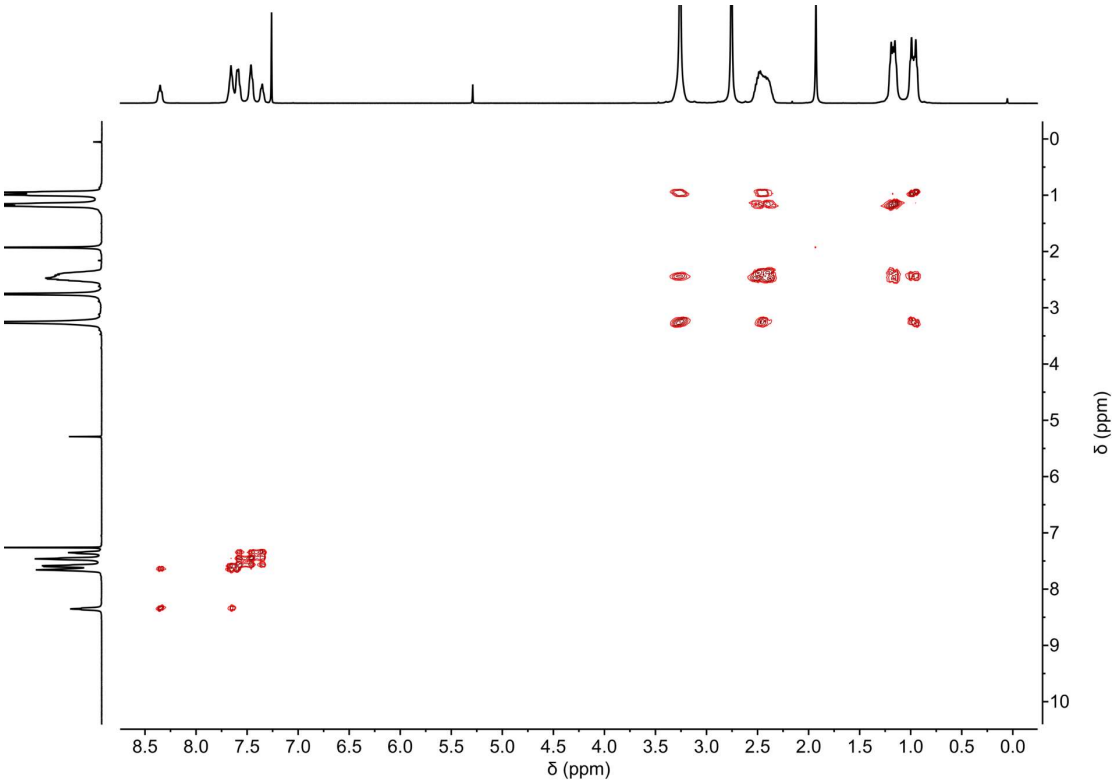


Figure S63. $^{1}H/^{1}H$ COSY spectrum of **12** in $CDCl_3$

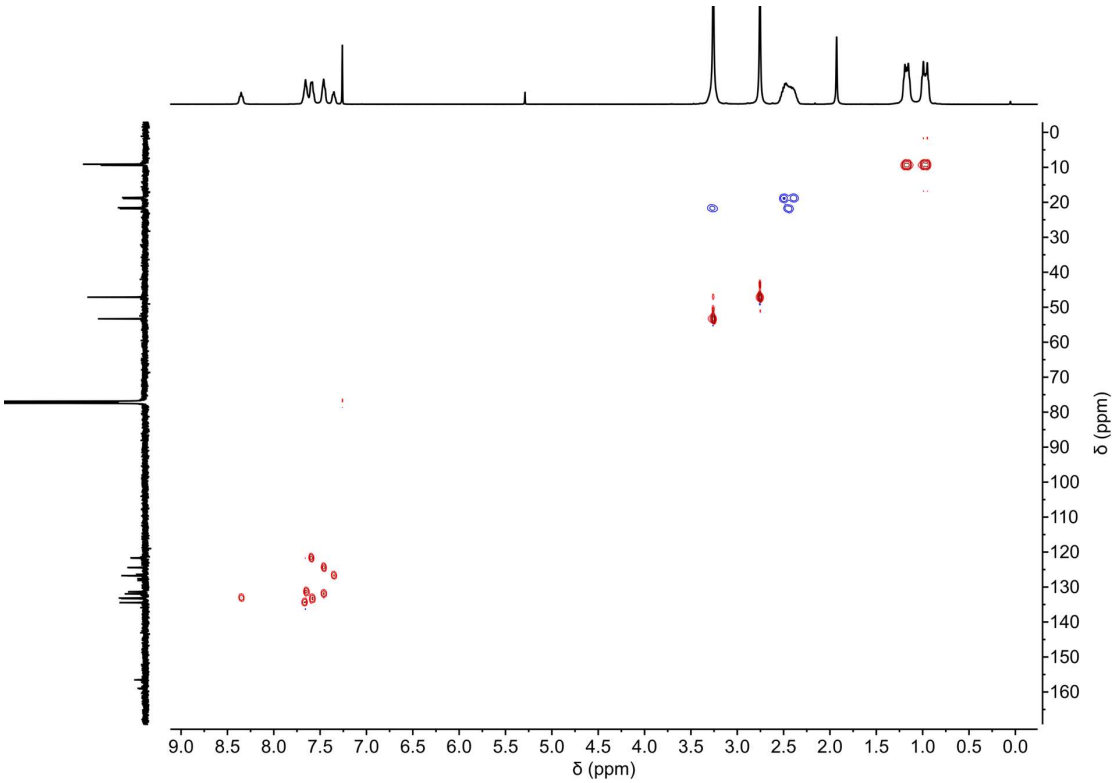


Figure S64. $^{1}H/^{13}C$ edited HSQC spectrum of **12** in $CDCl_3$

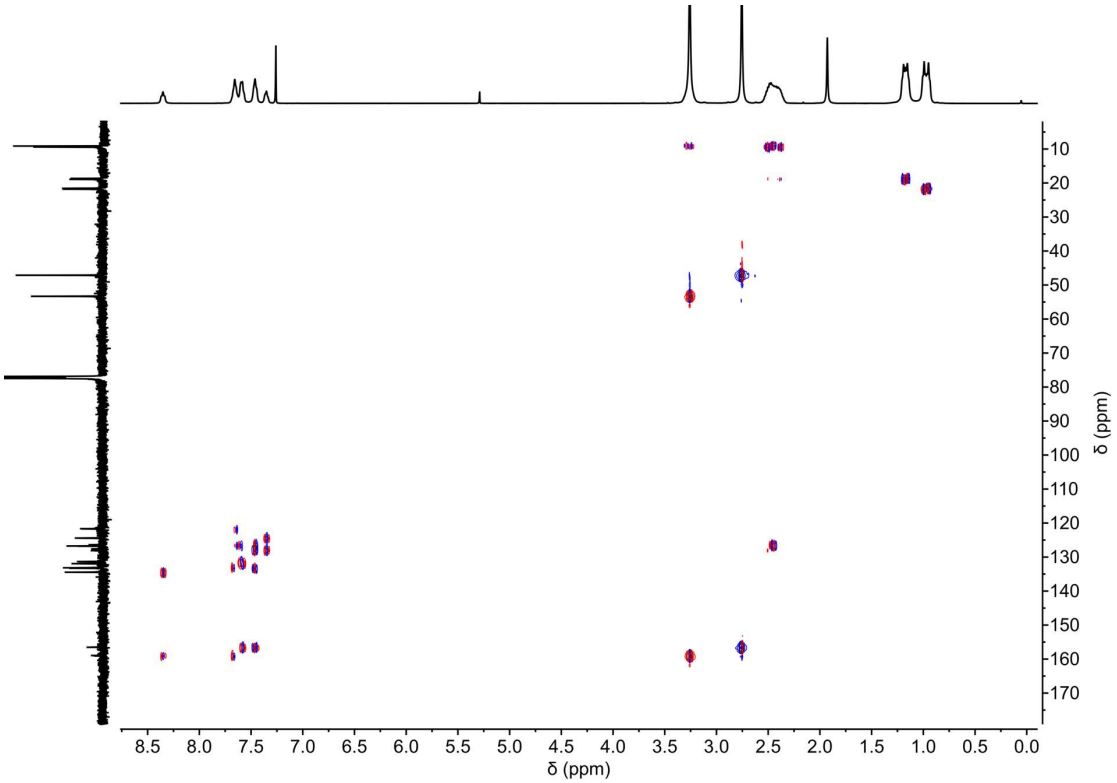


Figure S65. $^{1}H/^{13}C$ HMBC spectrum of **12** in $CDCl_3$

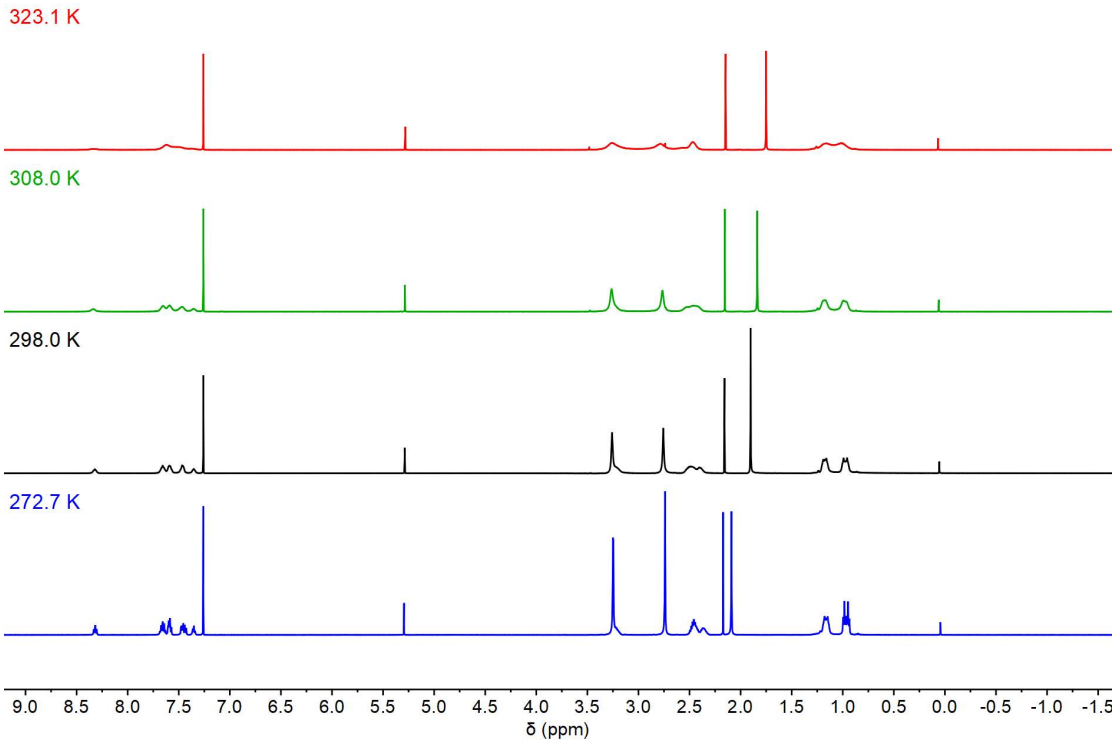


Figure S66. ^{1}H VT NMR spectrum of **12** in $CDCl_3$

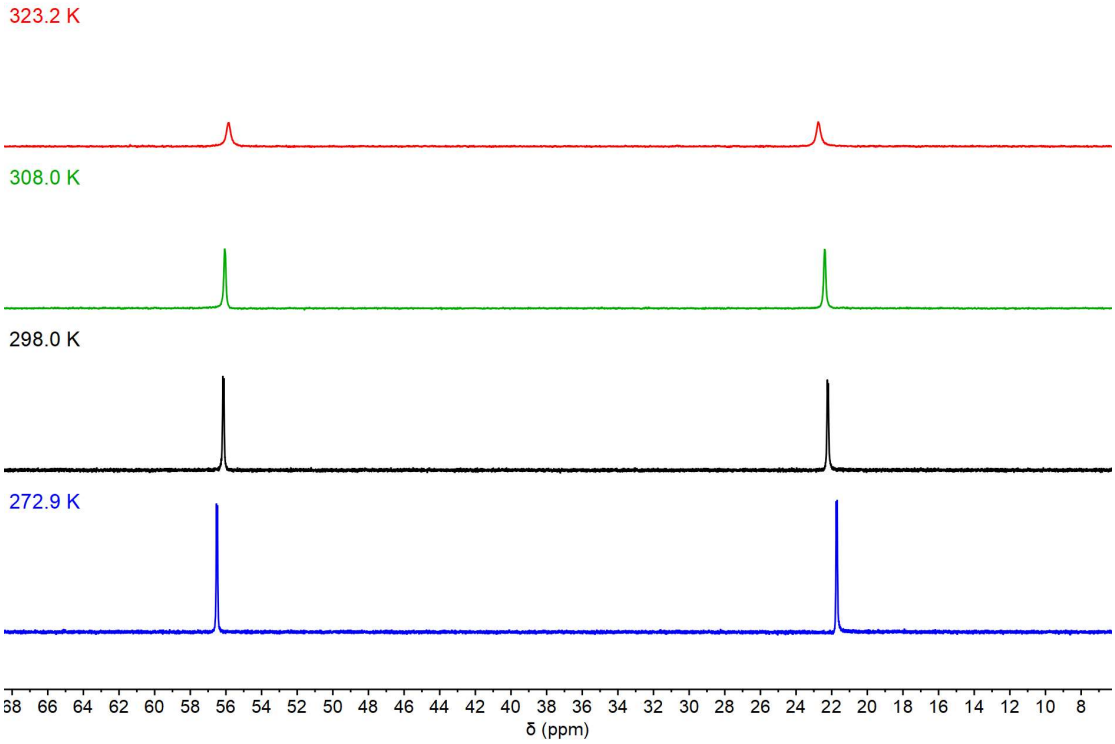


Figure S67. ^{31}P VT NMR spectrum of **12** in $CDCl_3$

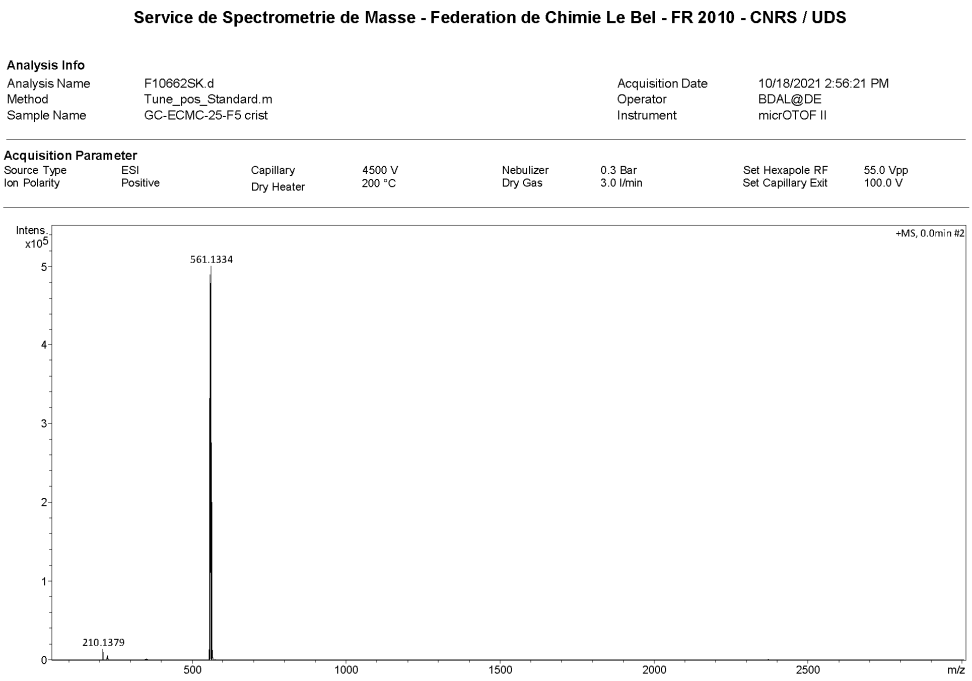


Figure S68. Full High Resolution Mass Spectrum of **12** in $CDCl_3$

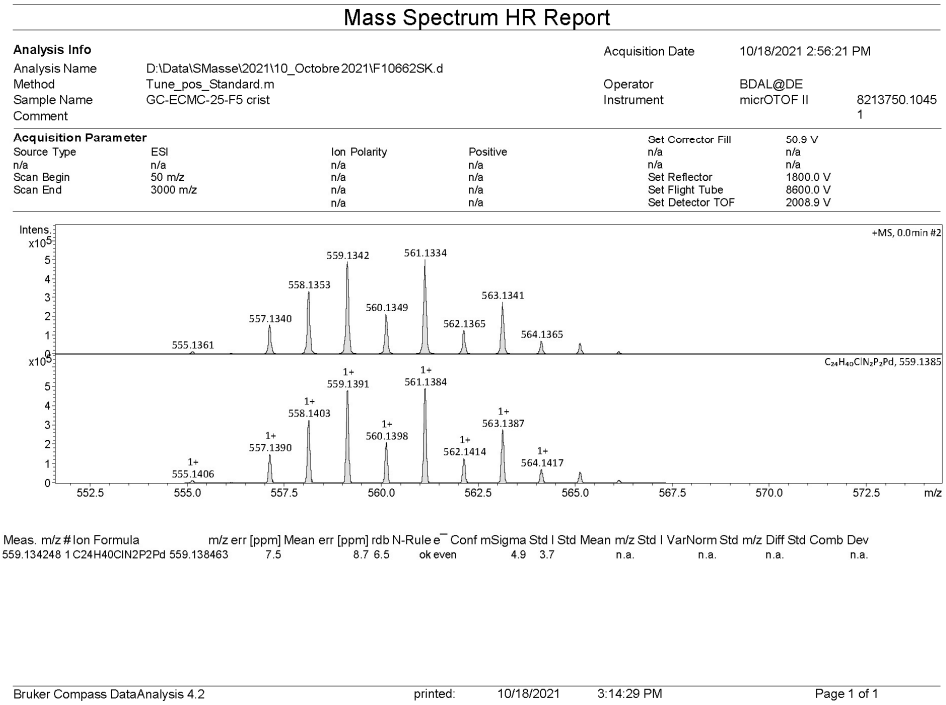


Figure S69. Partial High Resolution Mass Spectrum of **12** in $CDCl_3$

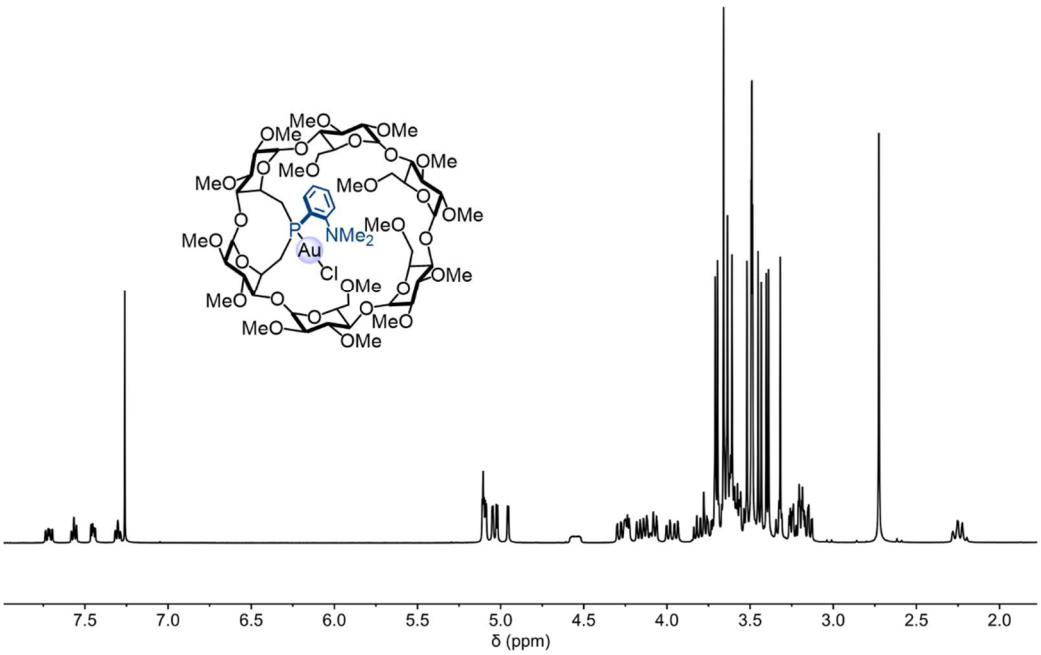


Figure S70. ^{1}H NMR spectrum of **13** in $CDCl_3$

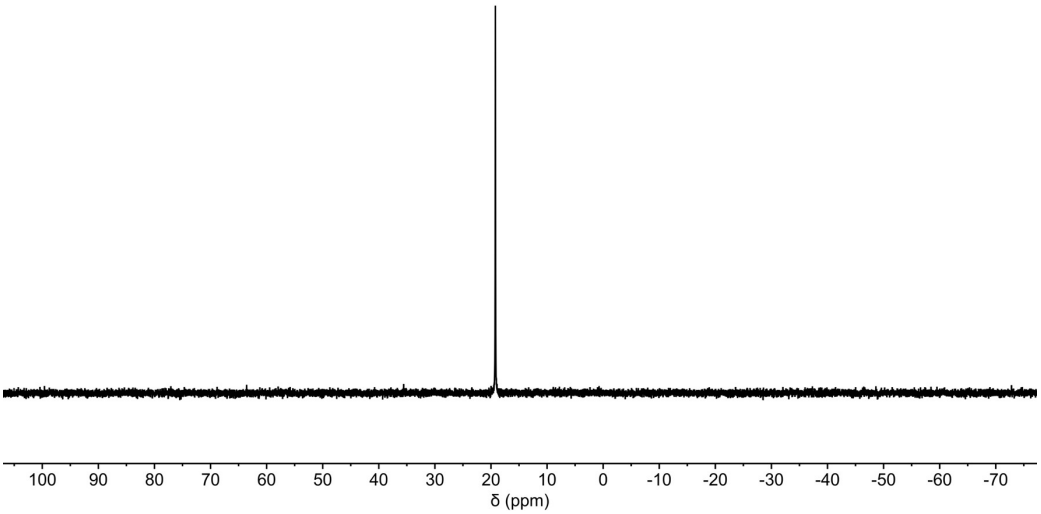


Figure S71. ^{31}P NMR spectrum of **13** in $CDCl_3$

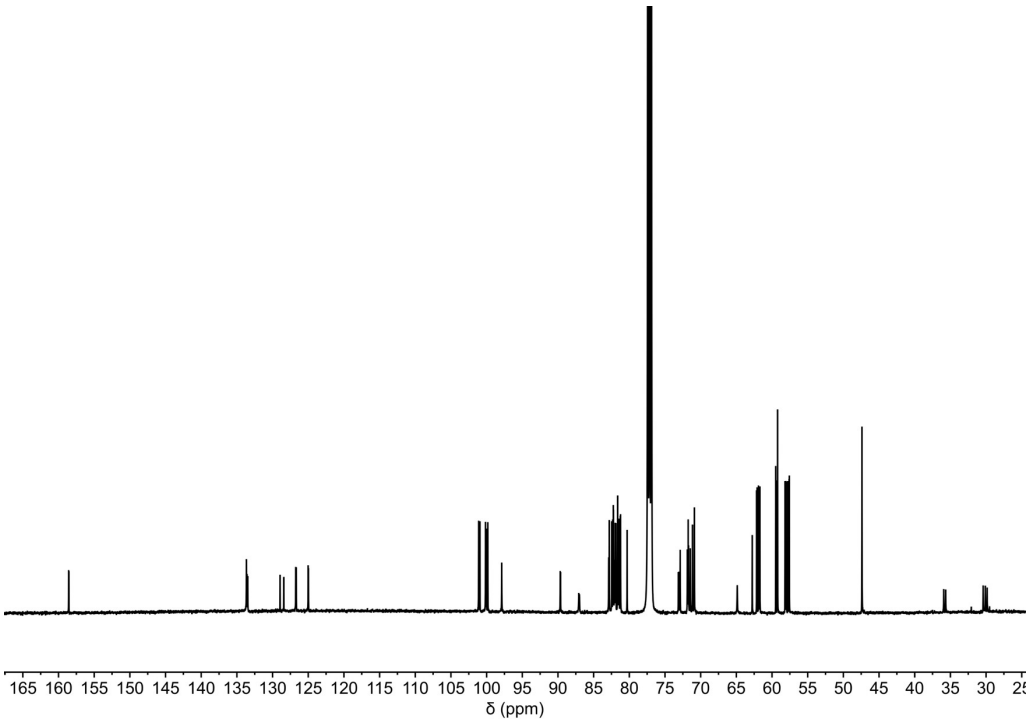


Figure S72. ^{13}C NMR spectrum of **13** in $CDCl_3$

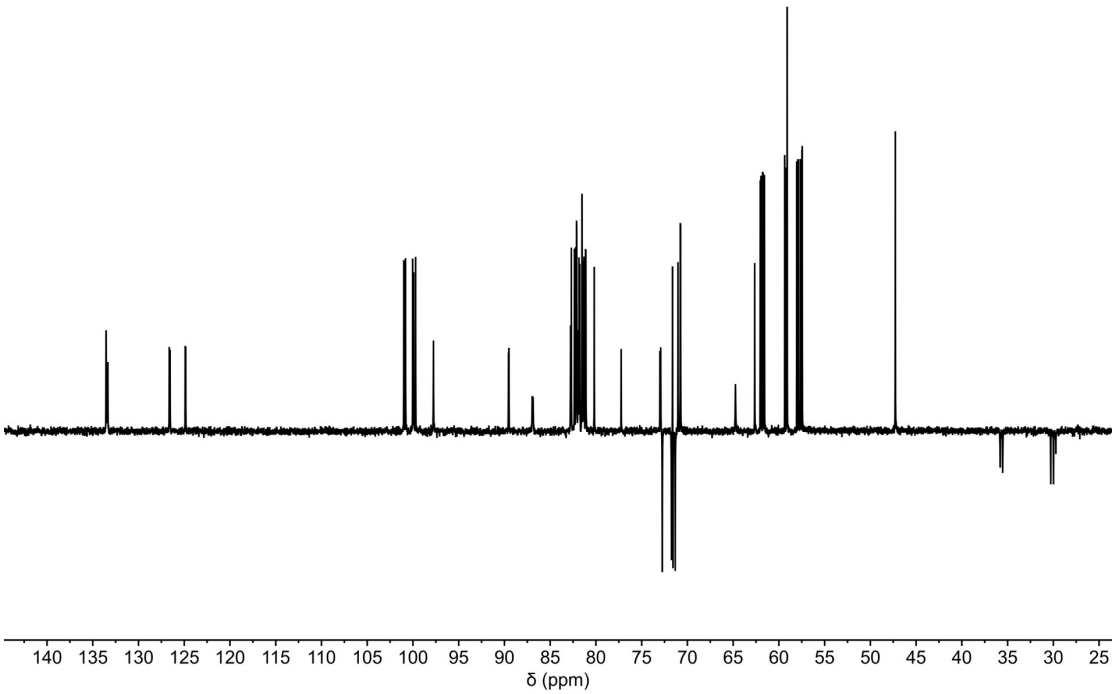


Figure S73. DEPT 135 spectrum of **13** in $CDCl_3$

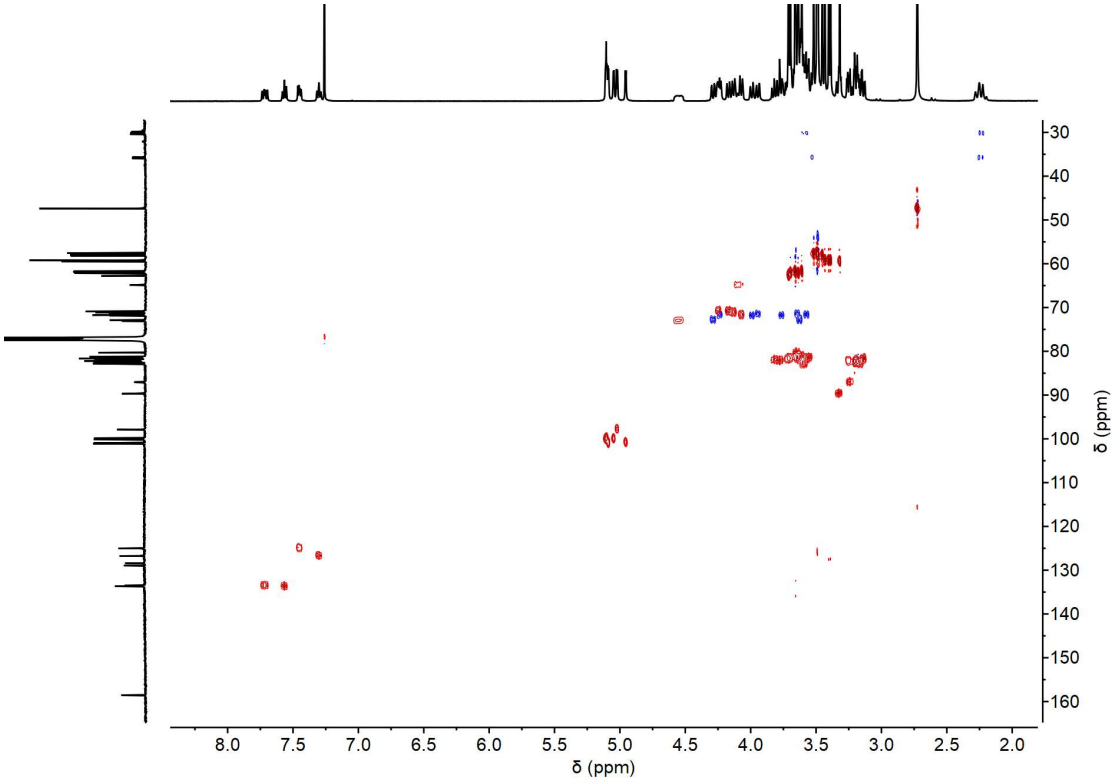


Figure S74. $^{1}H/^{13}C$ edited HSQC spectrum of **13** in $CDCl_3$

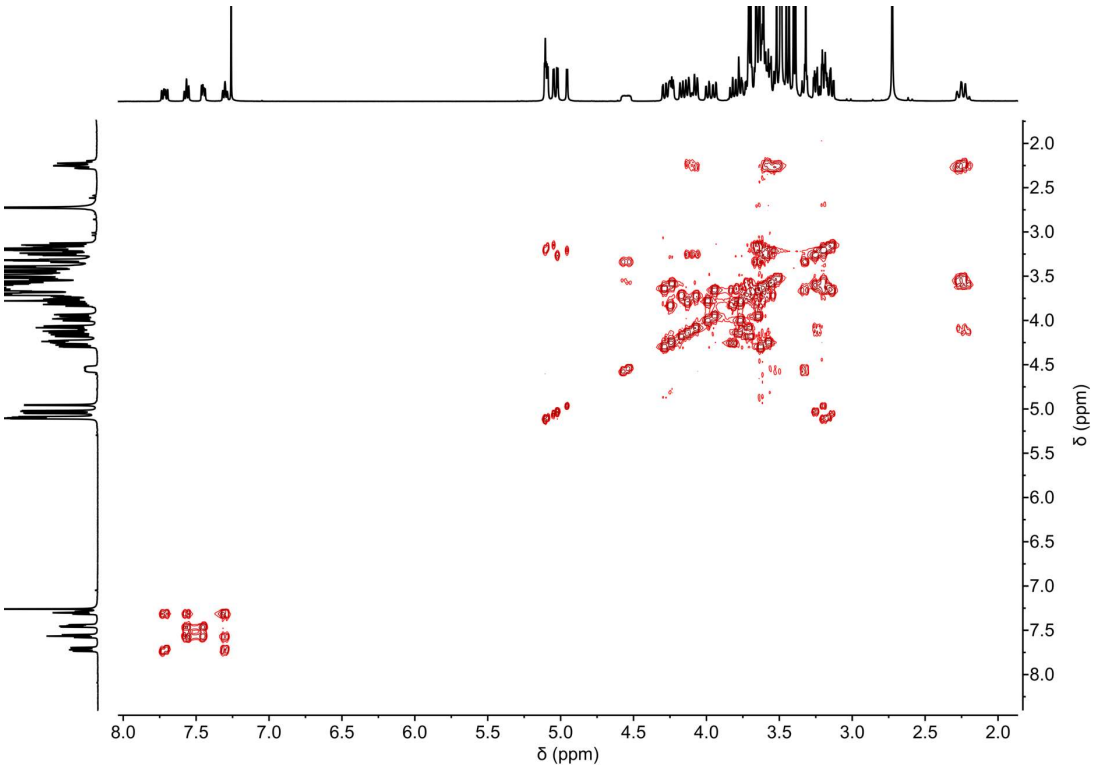


Figure S75. $^{1}H/^{1}H$ COSY spectrum of **13** in $CDCl_3$

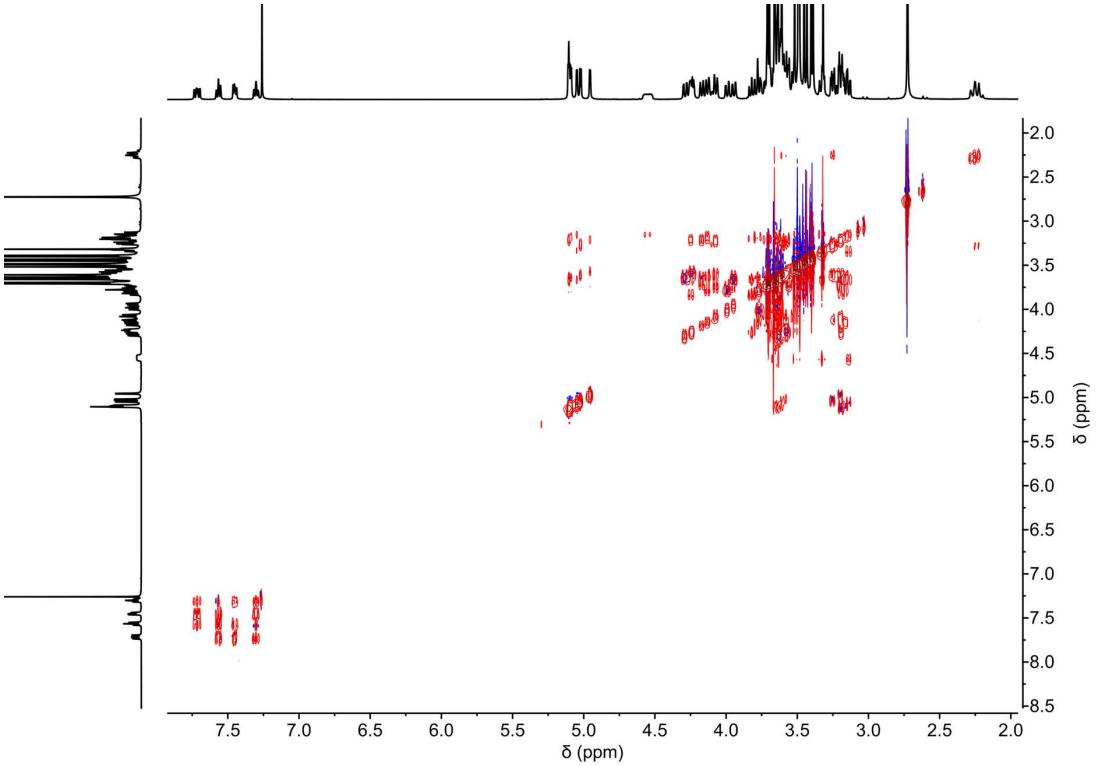


Figure S76. $^{1}H/^{1}H$ TOCSY spectrum of **13** in $CDCl_3$

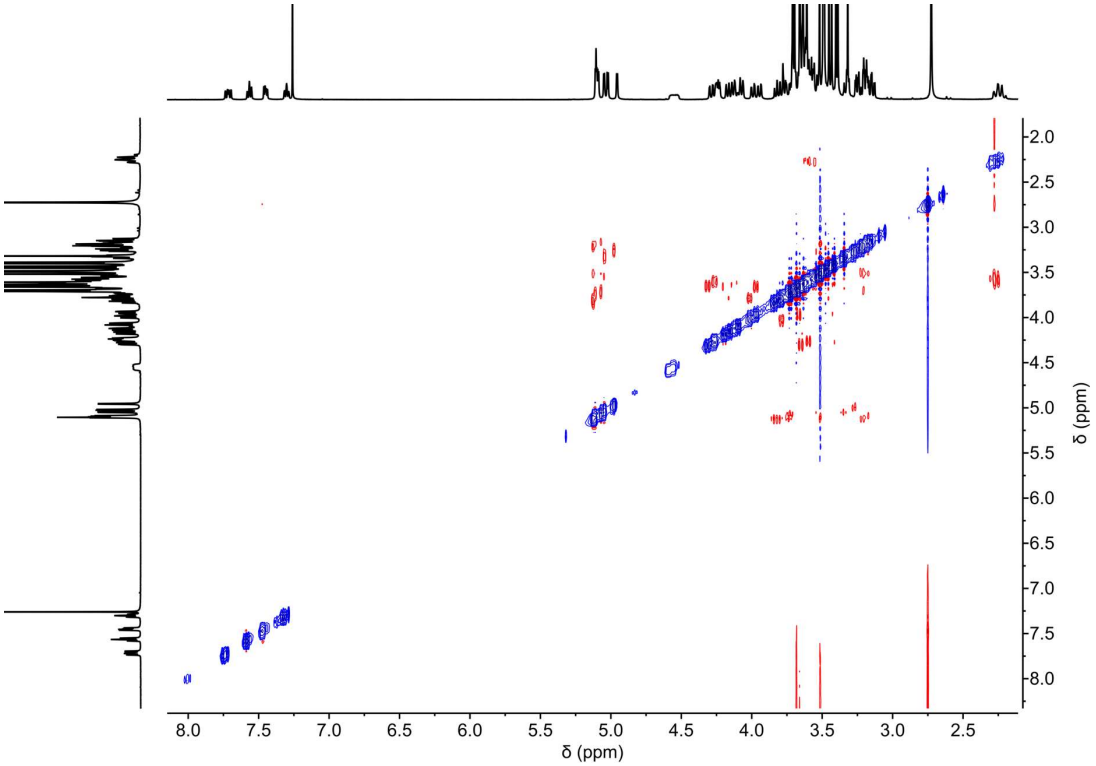


Figure S77. $^{1}H/^{1}H$ ROESY spectrum of **13** in $CDCl_3$

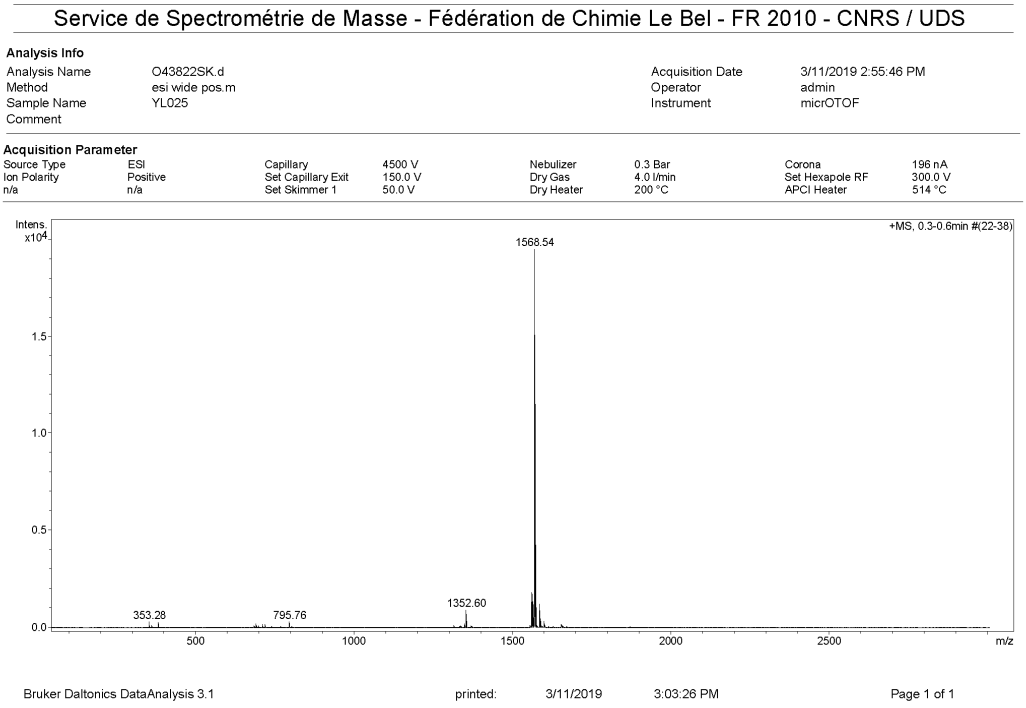


Figure S78. Full Mass Spectrum of **13**

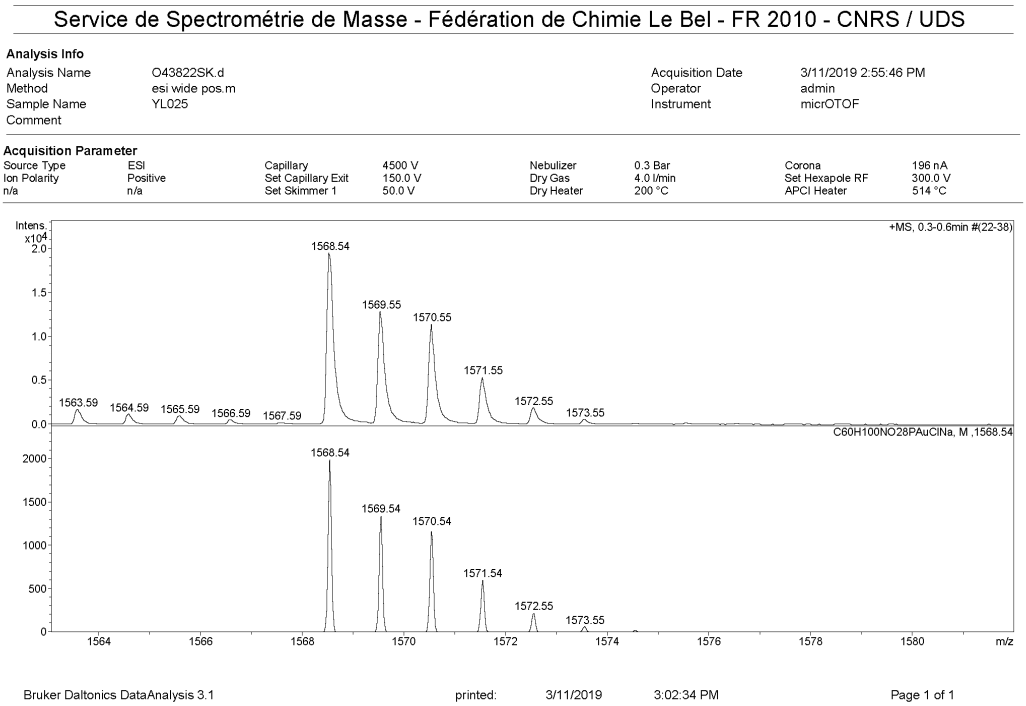
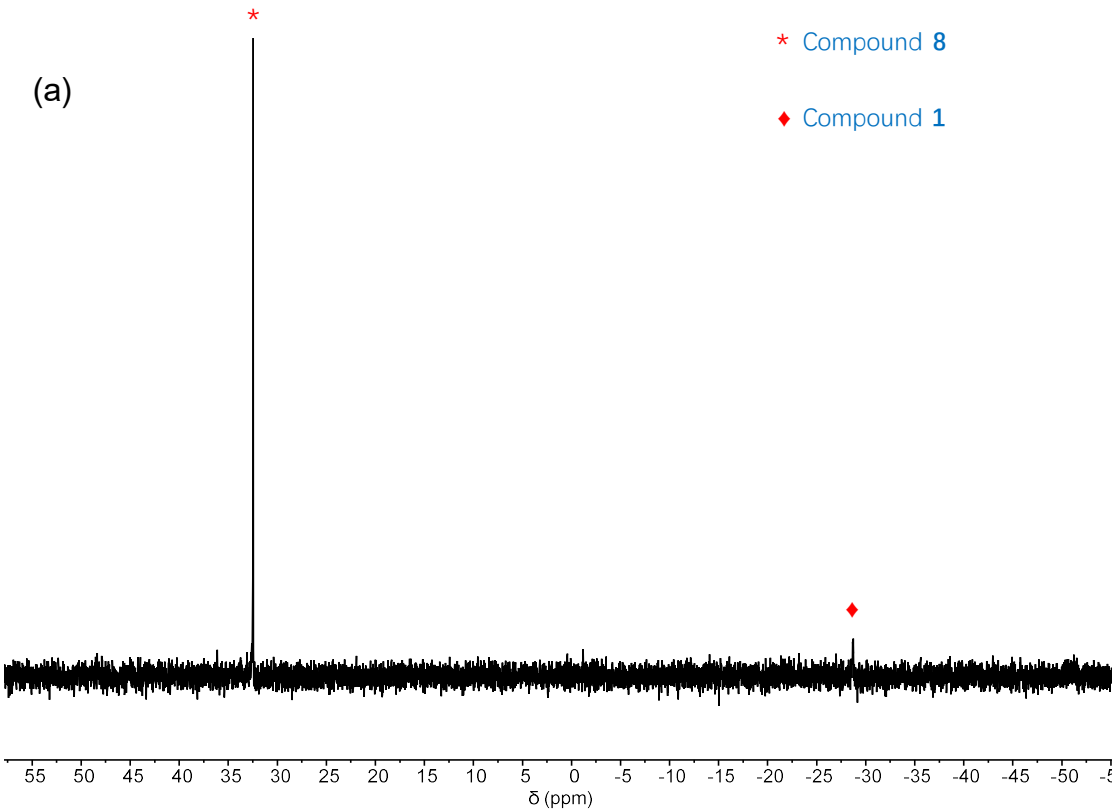
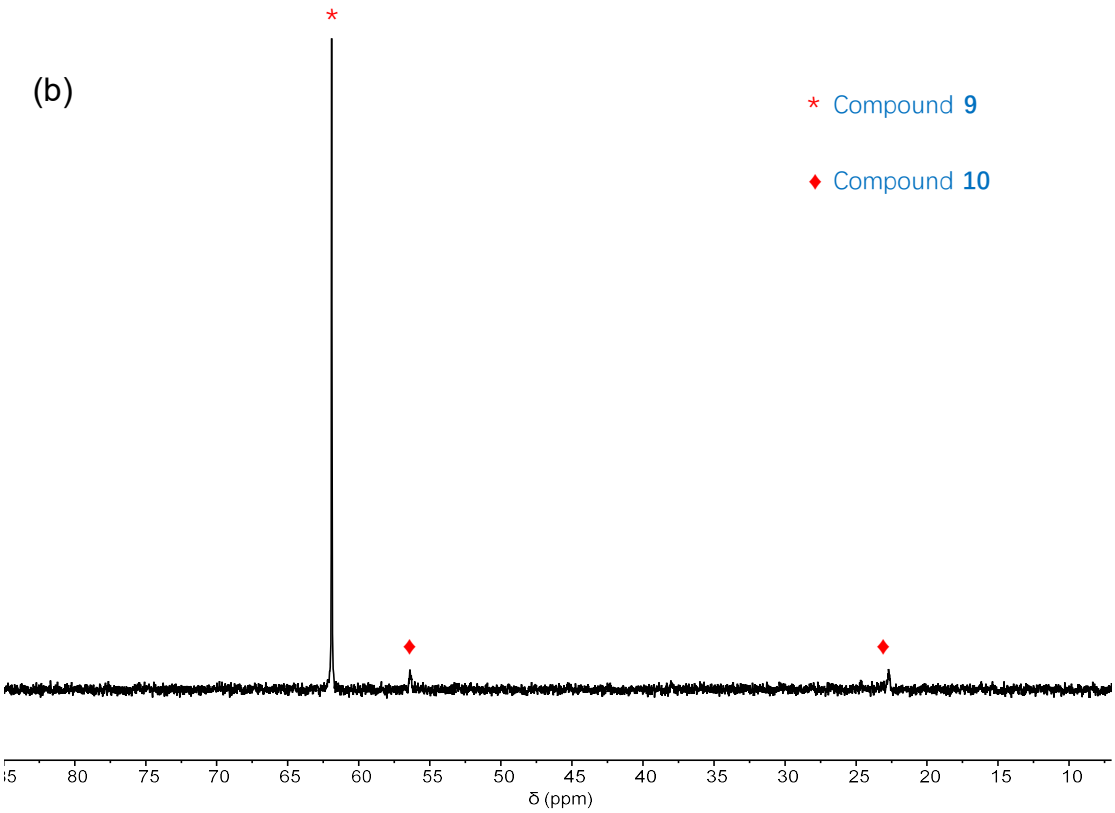


Figure S79. Partial Mass Spectrum of **13**


(a)
* Compound 8
♦ Compound 1
55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50
δ (ppm)


(b)
* Compound 9
♦ Compound 10
80 75 70 65 60 55 50 45 40 35 30 25 20 15 10
δ (ppm)

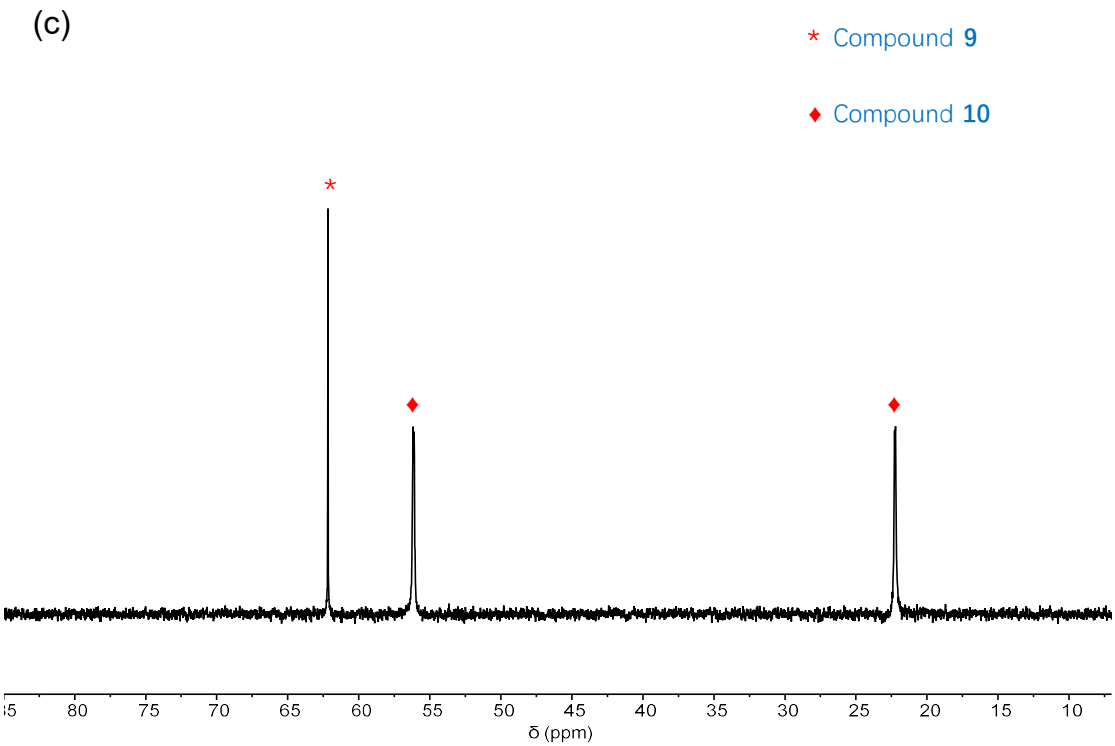


Figure S80. ^{31}P NMR spectra of crude complex **8** in the presence of excess ligand **1** (1.2 equiv) **(a)** and crude mixtures of complexes **11**/**12** respectively with a 1:1 **(b)** and a 1:2 **(c)** metal/ligand ratio.

5. Crystal structure analyses

Compound **8**: Crystal suitable for X-ray crystal-structure analysis of **8** was obtained as described in the synthetic procedures. Data were collected at 173(2) K on a Bruker APEX-II Duo KappaCCD diffractometer (Mo-Kα radiation, λ = 0.71073 Å). The structure was solved by direct methods (SHELXS-2013) and refined against F2 using the SHELXL-2014 software.[9] The non-hydrogen atoms were refined anisotropically, using weighted full-matrix least-squares on F2. The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. Residual electronic density is due to the presence of a butanone molecule, the contribution of which has been taken out by the SQUEEZE procedure in the final refinement.[10] The compound crystallizes with another butanone molecule in the monoclinic $P2_1$ space group, which is chiral. The Flack parameter is -0.009(11). The crystallographic data are reported in table S1.

Compounds **9**, **10**, **11**, **12**, **13**: Crystals suitable for X-ray crystal-structure analysis of **9**, **10**, **11**, **12**, **13** were obtained as described in the synthetic procedures. Data were collected at 120(2) K on a Bruker PHOTON-III CPAD (Mo-Kα radiation, λ = 0.71073 Å or Cu-Kα radiation, λ =1.54178 Å). The structures were solved by direct methods (SHELXT-2014) and refined against F2 using the SHELXL-2014 software.[9] The non-hydrogen atoms were refined anisotropically, using weighted full-matrix least-squares on F2. The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The crystallographic data are reported in table S2, S3, S4, S5, S6.

Compound **9**: The Ni complex co-crystallizes with two molecules of benzene, (one of which is located inside the cavity) and with half a molecule of benzene disordered with half a molecule of pentane. One methyl group (C57) is disordered over two positions. The compound crystallizes in the tetragonal $P4_12_12$ space group, which is chiral. The Flack parameter is 0.016(2).

Compound **10**: Although achiral, the Ni complex has crystallized in the triclinic $P1$ chiral space group hence a Flack parameter of 0.014(3). This is due to the presence of a pair of

Ni complexes in the asymmetric unit, which when taken together are chiral. Each unit cell contains only one of the two possible enantiomeric dimers.

Compound **11**: A pair of Pd complexes co-crystallizes with 4 $CHCl_3$ solvent molecules.

Compound **12**: A pair of cationic Pd complexes co-crystallizes with 4 water molecules which form a hydrogen bond network with the chloride counter-anions. This compound has crystallized in the non-centrosymmetric orthorhombic *P*na2_1 space group.

Compound **13**: The Au complex co-crystallizes with a benzene molecule located in the CD cavity. A SQUEEZE procedure has been used to eliminate residual density due to one and a half disordered additional benzene molecules.[10] The compound crystallizes in the monoclinic *C*2 space group, which is chiral. The Flack parameter is 0.171(4), which deviates from zero. This happens because the structure contains significant anomalous scatterers. The absolute configuration was established based on the known absolute configuration of the CD.

Table S1. Crystallographic and structure refinement data for **9** (CCDC 2163663)

Crystal Data	
Crystal size/mm^3	0.3 x 0.2 x 0.15
Empirical formula	$2(C_{60}H_{100}NNiO_{28}PNiBr_2)\bullet5(C_6H_6)\bullet C_5H_{12}$
Formula Weight	3528.49
Crystal system	tetragonal
Space group	$P4_12_12$
Temperature/K	120(2)
Unit cell parameters	
a/Å	17.8671(6)
b/Å	17.8671(6)
c/Å	53.805(2)
α/°	90
β/°	90
γ/°	90
V/Å^3	17176.2(14)
Z	4
$D_{(calc)}$ g/cm^3	1.364
F (000)	7440.0
μ/mm^{-1}	1.252

Data Processing and Reduction	
2θ range for data collection/°	3.79 to 55.792
Index ranges	$-23 \leq h \leq 23$, $-23 \leq k \leq 23$, $-70 \leq l \leq 68$
Reflections collected	277051
Independent reflections	20499 [R_{int} = 0.0618, R_{sigma} = 0.0391]
Data / restraints / parameters	20499/0/919
Goodness-of-fit on F^2	1.040
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0515, wR_2 = 0.1343
R indices (all data)	R_1 = 0.0741, wR_2 = 0.1474
Largest diff. peak and hole/eÅ^{-3}	0.80/-0.81
Flack parameter	0.016(2)

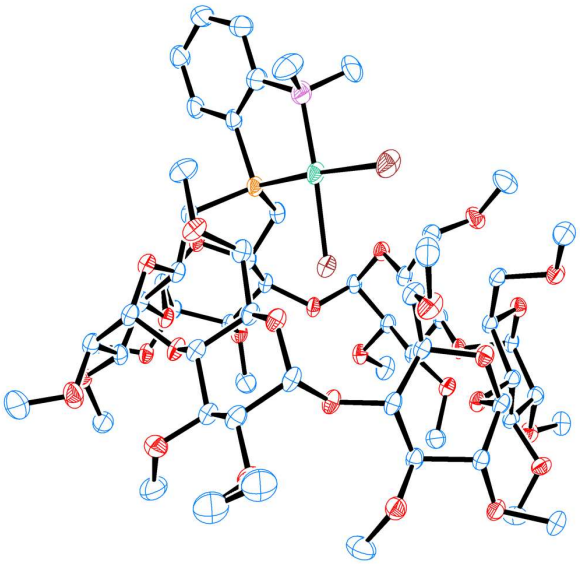


Figure S81. Crystal structure of **9** with H atoms and solvent molecules omitted for clarity

Table S2. Crystallographic and structure refinement data for **10** (CCDC 2163657)

Crystal Data	
Crystal size/mm^3	0.18 x 0.15 x 0.12
Empirical formula	$C_{12}H_{20}NPNiBr_2$
Formula Weight	427.79
Crystal system	triclinic
Space group	*P*1
Temperature/K	120(2)
Unit cell parameters	
a/Å	7.2760(3)
b/Å	8.6431(3)
c/Å	13.5955(5)
α/°	83.1970(10)
β/°	84.0140(10)
γ/°	71.1770(10)
V/Å^3	801.57(5)
Z	2
$D_{(calc)}$ g/cm^3	1.772
F (000)	424.0
μ/mm^{-1}	6.275

Data Processing and Reduction	
2θ range for data collection/°	5 to 55.84
Index ranges	$-9 \leq h \leq 9, -11 \leq k \leq 11, -17 \leq l \leq 17$
Reflections collected	54711
Independent reflections	7331 [R_{int} = 0.0369, R_{sigma} = 0.0276]
Data / restraints / parameters	7331/3/315
Goodness-of-fit on F^2	1.077
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0182, wR_2 = 0.0362
R indices (all data)	R_1 = 0.0203, wR_2 = 0.0376
Largest diff. peak and hole/eÅ^{-3}	0.54/-0.72
Flack parameter	0.014(3)

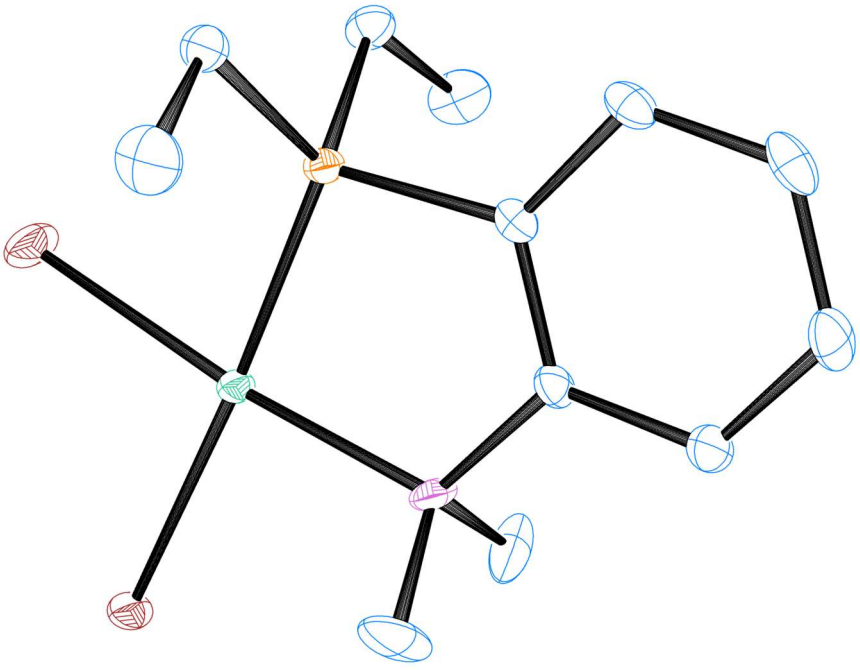


Figure S82. Crystal structure of **10** with H atoms and solvent molecules omitted for clarity

Table S3. Crystallographic and structure refinement data for **8** (CCDC 2163655)

Crystal Data	
Crystal size/mm^3	0.25 x 0.12 x 0.1
Empirical formula	$C_{60}H_{100}NO_{28}PCl_2Pd•C_4H_8O$
Formula Weight	1563.78
Crystal system	monoclinic
Space group	$P2_1$
Temperature/K	173(2)
Unit cell parameters	
a/Å	14.9237(6)
b/Å	17.5343(7)
c/Å	15.7250(6)
α/°	90
β/°	101.0630(10)
γ/°	90
V/Å^3	4038.4(3)
Z	2
$D_{(calc)}$ g/cm^3	1.286
F (000)	1652.0
μ/mm^{-1}	0.391

Data Processing and Reduction	
2θ range for data collection/°	3.446 to 56.042
Index ranges	$-19 \leq h \leq 19$, $-20 \leq k \leq 23$, $-20 \leq l \leq 20$
Reflections collected	39896
Independent reflections	18579 [R_{int} = 0.0509, R_{sigma} = 0.0849]
Data / restraints / parameters	18579/2/897
Goodness-of-fit on F^2	0.955
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0478, wR_2 = 0.0893
R indices (all data)	R_1 = 0.0810, wR_2 = 0.0978
Largest diff. peak and hole/eÅ^{-3}	0.53/-0.64
Flack parameter	0.002(11)

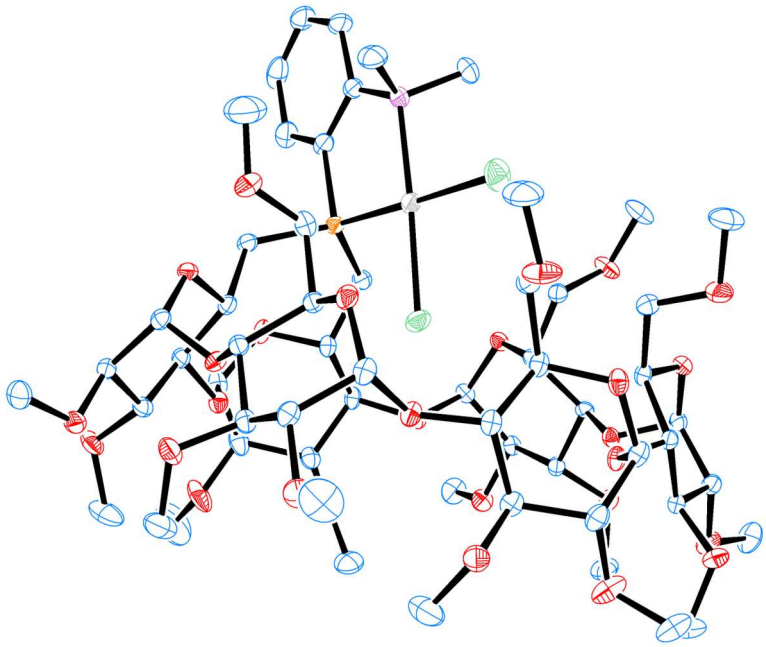


Figure S83. Crystal structure of **8** with H atoms and solvent molecules omitted for clarity

Table S4. Crystallographic and structure refinement data for **11** (CCDC 2163751)

Crystal Data	
Crystal size/mm^3	0.15 x 0.1 x 0.08
Empirical formula	$C_{12}H_{20}NPPdCl_2$•2($CHCl_3$)
Formula Weight	625.29
Crystal system	monoclinic
Space group	$P2_1/c$
Temperature/K	120(2)
Unit cell parameters	
a/Å	17.0385(7)
b/Å	8.8900(3)
c/Å	32.4365(14)
α/°	90
β/°	92.933(2)
γ/°	90
V/Å^3	4906.8(3)
Z	8
$D_{(calc)}$ g/cm^3	1.693
F (000)	2480.0
μ/mm^{-1}	1.694

Data Processing and Reduction	
2θ range for data collection/°	4.752 to 58.102
Index ranges	$-23 \leq h \leq 23$, $-12 \leq k \leq 11$, $-44 \leq l \leq 44$
Reflections collected	145578
Independent reflections	13078 [R_{int} = 0.1059, R_{sigma} = 0.0475]
Data / restraints / parameters	13078/0/459
Goodness-of-fit on F^2	1.060
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0423, wR_2 = 0.0784
R indices (all data)	R_1 = 0.0712, wR_2 = 0.0920
Largest diff. peak and hole/eÅ^{-3}	1.28/-1.04

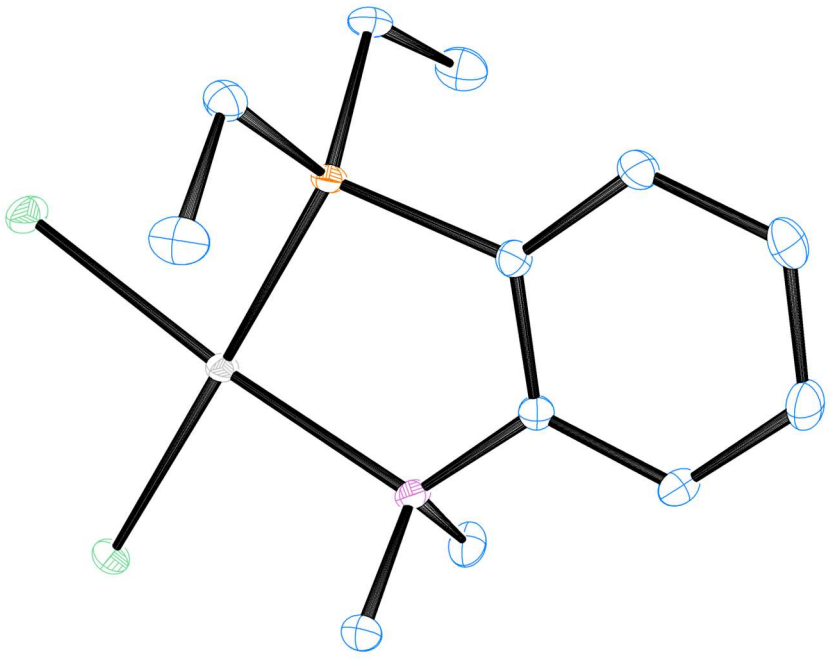


Figure S84. Crystal structure of **11** with H atoms and solvent molecules omitted for clarity

Table S5. Crystallographic and structure refinement data for **12** (CCDC 2163658)

Crystal Data	
Crystal size/mm^3	0.14 x 0.12 x 0.1
Empirical formula	$C_{24}H_{40}N_2P_2PdCl_2$•2(H_2O)
Formula Weight	631.85
Crystal system	orthorhombic
Space group	*P*na2$_1$
Temperature/K	120(2)
Unit cell parameters	
a/Å	13.1872(4)
b/Å	11.4097(3)
c/Å	38.4881(11)
α/°	90
β/°	90
γ/°	90
V/Å^3	5791.0(3)
Z	8
$D_{(calc)}$ g/cm^3	1.449
F (000)	2624.0
μ/mm^{-1}	0.959

Data Processing and Reduction	
2θ range for data collection/°	4.234 to 56.032
Index ranges	$-17 \leq h \leq 17$, $-15 \leq k \leq 15$, $-50 \leq l \leq 50$
Reflections collected	94671
Independent reflections	13931 [R_{int} = 0.0609, R_{sigma} = 0.0429]
Data / restraints / parameters	13931/1/611
Goodness-of-fit on F^2	1.069
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0350, wR_2 = 0.0719
R indices (all data)	R_1 = 0.0464, wR_2 = 0.0783
Largest diff. peak and hole/eÅ^{-3}	2.45/-0.64

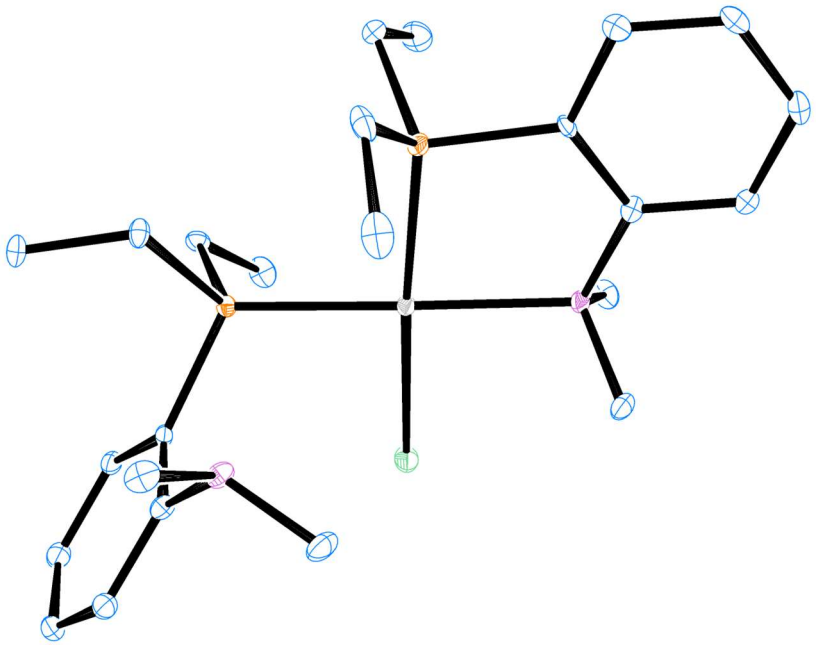


Figure S85 Crystal structure of **12** with H atoms and solvent molecules omitted for clarity

Table S6. Crystallographic and structure refinement data for **13** (CCDC 2163666)

Crystal Data	
Crystal size/mm^3	0.35 x 0.2 x 0.15
Empirical formula	$C_{60}H_{100}NO_{28}PAuCl•C_6H_6$
Formula Weight	1624.90
Crystal system	monoclinic
Space group	*C*2
Temperature/K	120(2)
Unit cell parameters	
a/Å	38.308(6)
b/Å	14.1787(6)
c/Å	15.4860(2)
α/°	90
β/°	93.007(2)
γ/°	90
V/Å^3	8399.7(8)
Z	4
$D_{(calc)}$ g/cm^3	1.285
F (000)	3376.0
μ/mm^{-1}	4.367

Data Processing and Reduction	
2θ range for data collection/°	4.62 to 134.642
Index ranges	$-45 \leq h \leq 45$, $-16 \leq k \leq 16$, $-18 \leq l \leq 18$
Reflections collected	108770
Independent reflections	14764 [R_{int} = 0.0684, R_{sigma} = 0.0434]
Data / restraints / parameters	14764/0/902
Goodness-of-fit on F^2	1.154
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0409, wR_2 = 0.0969
R indices (all data)	R_1 = 0.0419, wR_2 = 0.0980
Largest diff. peak and hole/eÅ^{-3}	1.31/-0.81
Flack parameter	0.147(8)

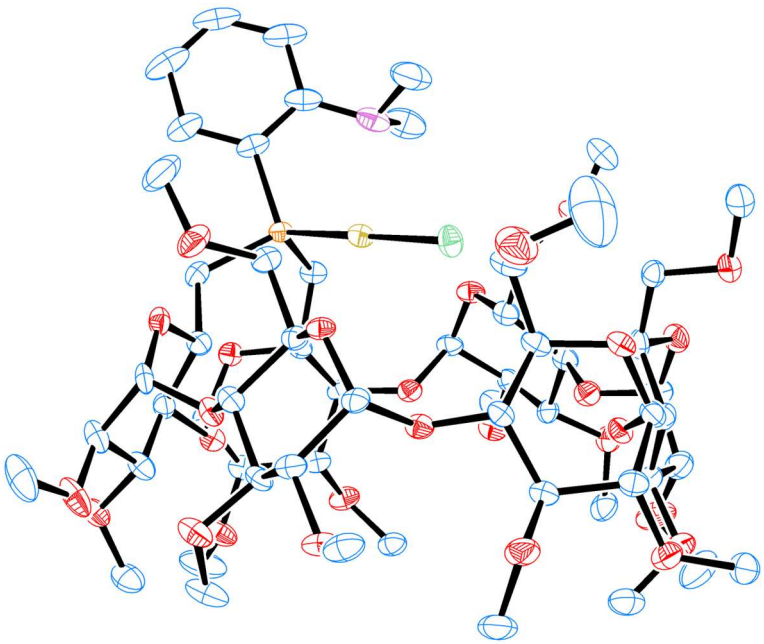


Figure S86. Crystal structure of **13** with H atoms and solvent molecules omitted for clarity

6. UV-visible spectra

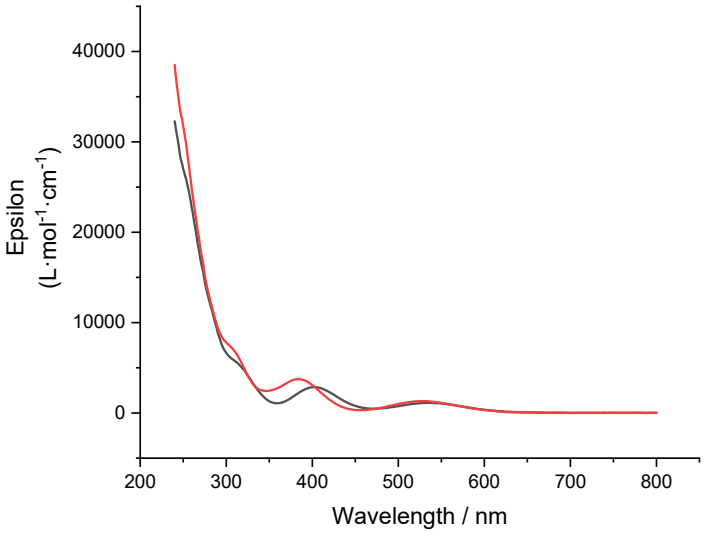


Figure S87. UV-vis spectra (CH_2Cl_2, 25°C) of cavity-shaped Ni complex **9** (black) and cavity-free Ni complex **10** (red). The UV-vis spectra feature a shoulder at 290-350 nm and two absorption maxima at 401, 536 nm for **9** and 384, 528 nm for **10**.

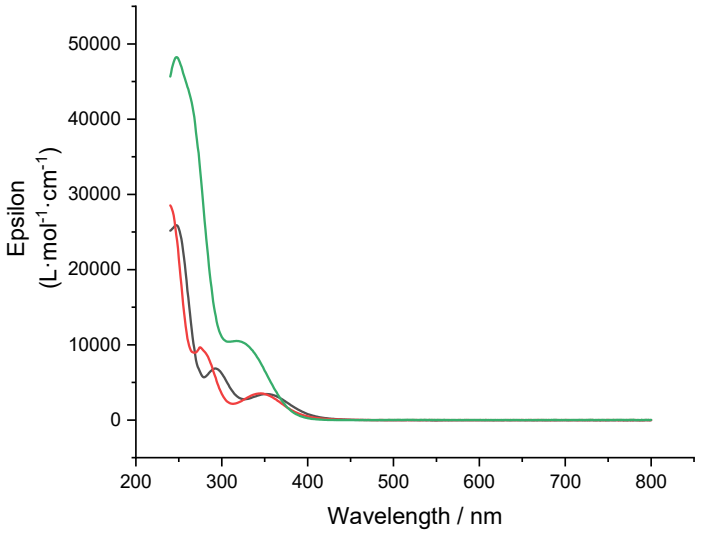


Figure S88. UV-vis spectra (CH_2Cl_2, 25°C) of cavity-shaped Pd complex **8** (black) and cavity-free complexes **11** (red) and **12** (green). The UV-vis spectra feature two absorption maxima at 293, 351 nm for **8** and 275, 345 nm for **11**. The spectrum of **12** shows a broad band between 300-330 nm.

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