Cyclopalladation of a ferrocene acylphosphine and the reactivity of the C-H activated products

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Supporting Information

Contents

EXPERIMENTAL

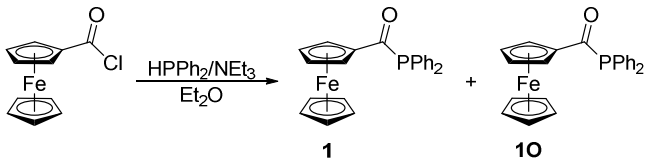
Materials and methods

Many reactions were performed in air. When appropriate, however, the syntheses were conducted under argon or nitrogen using standard Schlenk techniques. Ferrocenecarboxylic acid[1] and (diphenylphosphino)acetic acid[2] were prepared according to procedures reported in the literature. Sodium acetate was fused and stored under KOH. Other chemicals were purchased from commercial suppliers (Sigma-Aldrich and TCI) and used as received. Anhydrous diethyl ether, dichloromethane and tetrahydrofuran, employed in syntheses, were obtained from a PureSolv MD5 solvent purification system (Innovative Technology, USA). Triethylamine and toluene were distilled from sodium metal and stored under argon. Chloroform and acetonitrile were distilled from calcium hydride and stored under argon. Solvents utilised for the work-up, chromatography and crystallisations were used without additional purification (Lach-Ner, p. a. grade).

NMR spectra were acquired at 25°C on a Varian Unity Inova 400 spectrometer operating at 400, 101, 162 and 376 MHz for ^{1}H, ^{13}C, ^{31}P and ^{19}F respectively. In some cases, ^{13}C NMR spectra were recorded on a Bruker Avance III 600 spectrometer at 151 MHz. Chemical shifts (δ in ppm) are given relative to internal $SiMe_4$ (^{1}H and ^{13}C), to external 85% H_3PO_4 (^{31}P) and to external neat $CFCl_3$ (^{19}F). FTIR spectra were recorded on a Thermo Nicolet 6700 FT-IR spectrometer over the 400-4000 cm^{-1} range. Electrospray ionisation mass spectra were recorded on a Compact QTOF-MS spectrometer (Bruker Daltonics). Elemental analyses were performed on a PE 2400 Series II CHNS/O Elemental Analyser (Perkin Elmer). The amount of residual solvent was confirmed by NMR analysis.

Electrochemical measurements were performed using a μAUTOLAB III instrument (Eco Chemie, Netherlands) at room temperature and a Metrohm three-electrode cell equipped with a glassy carbon disc (2 mm diameter) working electrode, a platinum sheet auxiliary electrode, and a Ag/AgCl (3 M KCl) reference electrode. The samples were dissolved in anhydrous dichloromethane to give a 1 mM solution of the analyte and 0.1 M $Bu_4N[PF_6]$ (Fluka, puriss. for electrochemistry) as the supporting electrolyte. The solutions were deaerated with argon before the measurements and then kept under an argon blanket. Decamethylferrocene (Alfa-Aesar) was added as an internal standard for the final scans, and the redox potentials were converted into the ferrocene/ferrocenium scale by subtracting 0.548 V.[3]

Syntheses



1 1O

Synthesis of acylphosphine 1 and phosphine oxide 1O. The starting acyl chloride was prepared by following the literature method.[4] Specifically, ferrocenecarboxylic acid (11.50 g, 50.0 mmol) was suspended in dry dichloromethane (300 mL) and oxalyl chloride (9.93 ml, 115 mmol, 2.3 eq.) was introduced dropwise. The solid acid gradually dissolved, and the mixture turned deep red. The resulting solution was stirred at room temperature for 1 h and evaporated under vacuum. To remove residual oxalyl chloride, the dark red oily residue was dissolved in dry diethyl ether (100 ml), and the solution was evaporated, leaving ferrocenecarbonyl chloride as a red polycrystalline solid, which was redissolved in dry diethyl ether (150 mL), and the solution was cooled on ice.

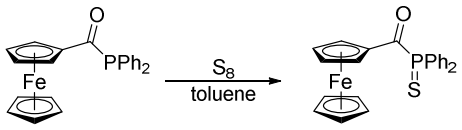
In a separate flask, diphenylphosphine (8.9 ml, 50 mmol) was mixed with anhydrous diethyl ether (150 mL), triethylamine (7.0 ml, 50 mmol) was added, and the solution was cooled on ice. To this solution, a freshly prepared solution of ferrocenecarbonyl chloride was introduced *via* a cannula, whereupon a white solid separated (triethylammonium chloride). After completing the addition, the mixture was stirred at 0°C for 30 min and then at room temperature for another 4 h. The suspension was filtered, the filter cake was washed in diethyl ether, and the combined filtrates were evaporated with chromatographic silica gel (ca. 120 mL). The crude pre-adsorbed product was transferred onto a silica gel column packed in hexane-ethyl acetate (8:1). Elution with the same solvent mixture removed acylphosphine **1** as a red tailing band. Subsequent evaporation and drying under vacuum afforded pure phosphine as a microcrystalline red solid. The following, deep purple band was eluted with hexane-ethyl acetate (1:1), leaving phosphine oxide **1O** as dark purple oily solid after evaporation (840 mg, 4%).

Phosphine **1** was further crystallised from hot ethyl acetate (150 ml) and hexane (500 ml). The red crystals, which separated upon cooling the solution slowly down to 4 °C, were filtered off, washed with pentane and dried under vacuum to give the first batch of analytically pure **1** (12.02 g, 60% yield). The mother liquor was evaporated, and the crystallisation repeated to afford another 4.57 g of the product. Combined yield of **1**: 16.59 g (83%), deep red crystalline solid. The crystals that were used for structure determination were obtained by recrystallisation of a small sample from ethyl acetate-hexane. Crystals of **1O** were grown by liquid-phase diffusion of hexane into an ethyl acetate solution. Crystals of **1O** were conveniently obtained by

dissolving the oil residue from the chromatography in diethyl ether and allowing the solution to spontaneously crystallise.

Analytical data for 1. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.22 (s, 5 H, C_5H_5), 4.47 (td, *J*' = 2.0 Hz, 1.1 Hz, 2 H, C_5H_4), 4.76-4.78 (m, 2 H, C_5H_4), 7.35-7.39 (m, 6 H, PPh_2), 7.44-7.49 (m, 4 H, PPh_2). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 69.80 (d, J_{PC} = 6 Hz, CH of C_5H_4), 70.45 (C_5H_5), 72.43 (d, J_{PC} = 2 Hz, CH of C_5H_4), 82.69 (d, $^{2}J_{PC}$ = 40 Hz, C^{ipso} of C_5H_4), 128.57 (d, J_{PC} = 8 Hz, CH of PPh_2), 129.32 (CH^{para} of PPh_2), 133.96 (d, $^{1}J_{PC}$ = 8 Hz, C^{ipso} of PPh_2), 134.72 (d, J_{PC} = 19 Hz, CH of PPh_2), 213.31 (d, $^{1}J_{PC}$ = 34 Hz, CO). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ 11.0 (s). IR (DRIFTS, KBr): ν_{max} 3082 w, 3056 w, 1773 w, 1643 w, 1609 s (ν_{CO}), 1567 w, 1475 w, 1435 s, 1409 w, 1395 w, 1369 w, 1348 w, 1336 w, 1307 w, 1242 s, 1184 w, 1104 m, 1097 m, 1071 w, 1050 m, 1027 m, 1001 m, 948 w, 871 w, 841 m, 820 s, 807 w, 755 m, 703 s, 694 m, 586 w, 556 m, 513 s, 502 s, 491 m, 484 m, 460 m, 433 m, 421 m cm^{-1}. ESI-MS: *m/z* 421 ([M + Na]$^{+}$), 437 ([M + K]$^{+}$). Anal. Calc. for $C_{23}H_{19}FeOP$ (398.2): C 69.37, H 4.81%. Found: C 69.22, H 4.83%.

Analytical data for 1O. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.04 (s, 5 H, C_5H_5), 4.74 (td, *J*' = 2.0 Hz, 0.8 Hz, 2 H, C_5H_4), 5.43 (t, *J*' = 2.0 Hz, 2 H, C_5H_4), 7.47-7.58 (m, 6 H, PPh_2), 7.96-8.03 (m, 4 H, PPh_2). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 70.57 (C_5H_5), 71.00 (br s, CH of C_5H_4), 74.41 (CH of C_5H_4), 79.95 (d, $^{2}J_{PC}$ = 53 Hz, C^{ipso} of C_5H_4), 128.52 (d, J_{PC} = 12 Hz, CH of PPh_2), 131.05 (d, $^{1}J_{PC}$ = 96 Hz, C^{ipso} of PPh_2), 131.68 (d, J_{PC} = 9 Hz, CH of PPh_2), 132.19 (d, $^{4}J_{PC}$ = 3 Hz, CH^{para} of PPh_2), 207.82 (d, $^{1}J_{PC}$ = 85 Hz, CO). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ 16.4 (s). IR (DRIFTS, KBr): ν_{max} 3118 w, 3073 w, 1607 s (ν_{CO}), 1588 w, 1571 w, 1484 w, 1439 m, 1436 m, 1411 w, 1399 w, 1375 w, 1330 w, 1264 m, 1217 w, 1188 m, 1159 w, 1115 m, 1051 m, 1031 w, 1003 w, 956 w, 845 w, 835 m, 753 m, 734 m, 701 m, 696 m, 583 m, 547 s, 500 m, 487 m, 479 s, 458 m, 424 m cm^{-1}. ESI-MS: *m/z* 437 ([M + Na]$^{+}$). Anal. Calc. for $C_{23}H_{19}FeO_2P$ (414.2): C 66.69, H 4.62%. Found: C 66.55, H 4.67%.

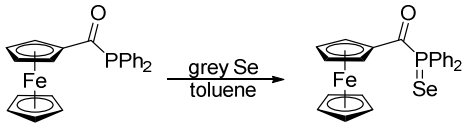


1 **1S**

Synthesis of phosphine sulfide 1S. Phosphine **1** (50.0 mg, 0.125 mmol) and sulfur (4.8 mg, 0.15 mmol) were dissolved in dry toluene (15 mL), and the mixture was heated at reflux for 3 hours. The reaction mixture was filtered through a short silica gel column, eluting with dichloromethane (black layer remains on the top of the column). A single purple band was collected and evaporated. The residue was taken up with warm dichloromethane (4 mL), and the solution was mixed with hot hexane (10 mL). After a slow cooling, dark purple crystals separated. These crystals were filtered off, washed with pentane and dried under vacuum. Yield of **1S**: 40 mg (74%), dark purple crystals. The crystals used for structure determination were selected directly from the preparative batch. Note: a shorter reaction time (2 h) results in

incomplete conversion, while extended refluxing (6 h) lowers the yield due to partial decomposition.

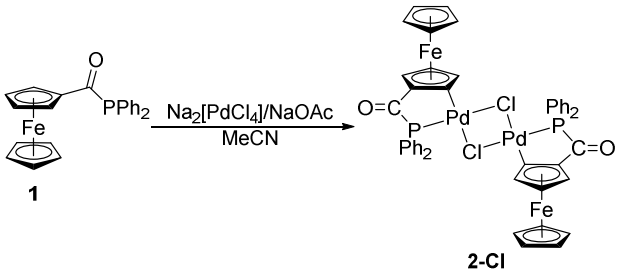
^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.22 (s, 5 H, C_5H_5), 4.62-4.64 (m, 2 H, C_5H_4), 5.22-5.23 (m, 2 H, C_5H_4), 7.44-7.55 (m, 6 H, PPh_2), 7.85-7.92 (m, 4 H, PPh_2). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 71.25 (C_5H_5), 71.51 (d, J_{PC} = 2 Hz, CH of C_5H_4), 73.67 (CH of C_5H_4), 77.68 (d, $^{2}J_{PC}$ = 59 Hz, C^{ipso} of C_5H_4), 128.45 (d, J_{PC} = 12 Hz, CH of PPh_2), 130.79 (d, $^{1}J_{PC}$ = 78 Hz, C^{ipso} of PPh_2), 131.84 (d, $^{4}J_{PC}$ = 3 Hz, CH^{para} of PPh_2), 132.16 (d, J_{PC} = 10 Hz, CH of PPh_2), 204.12 (d, $^{1}J_{PC}$ = 61 Hz, CO). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ 36.8 (s). IR (DRIFTS, KBr): ν_{max} 3097 w, 3089 w, 3054 w, 1615 s (ν_{CO}), 1582 w, 1478 w, 1438 m, 1409 w, 1371 w, 1350 w, 1325 w, 1312 w, 1254 m, 1183 w, 1096 m, 1074 w, 1049 m, 1029 w, 1002 w, 946 w, 841 m, 835 m, 824 w, 785 w, 744 m, 729 m, 713 s, 696 m, 688 m, 649 w, 615 w, 572 w, 554 m, 523 s, 500 s, 488 m, 463 m, 448 w, 427 m cm^{-1}. ESI-MS: *m/z* 453 ([M + Na]$^{+}$). Anal. Calc. for $C_{23}H_{19}FeOPS$ (430.3): C 64.20, H 4.45%. Found: C 64.02, H 4.32%.



1 **1Se**

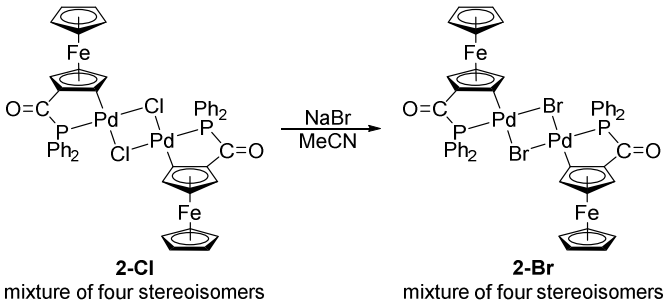
Synthesis of phosphine selenide 1Se. Phosphine **1** (80 mg, 0.20 mmol) and finely powdered grey selenium (16.6 mg, 0.21 mmol) were mixed in dry chloroform (10 mL), and the mixture was heated at gentle reflux overnight. The crude mixture was evaporated, and the solid residue was dissolved in little chloroform. The solution was filtered through a PTFE syringe filter (0.45 μm pore size), and the filtrate was layered with hexane. Crystallisation by liquid-phase diffusion over several weeks afforded dark purple crystals, which were filtered off, washed by pentane and dried in vacuum. Yield of **1Se**: 78 mg (82 %), dark purple crystals. Single crystals were selected directly from the preparative batch.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.26 (s, 5 H, C_5H_5), 4.60-4.62 (m, 2 H, C_5H_4), 5.16-5.18 (m, 2 H, C_5H_4), 7.44-7.54 (m, 6 H, PPh_2), 7.83-7.90 (m, 4 H, PPh_2).^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 71.52 (C_5H_5), 71.65 (d, J_{PC} = 2 Hz, CH of C_5H_4), 73.53 (CH of C_5H_4), 128.47 (d, J_{PC} = 12 Hz, CH of PPh_2), 129.51 (d, $^{1}J_{PC}$ = 69 Hz, C^{ipso} of PPh_2), 131.86 (d, $^{4}J_{PC}$ = 3 Hz, CH^{para} of PPh_2), 132.81 (d, J_{PC} = 10 Hz, CH of PPh_2), 201.92 (d, $^{1}J_{PC}$ = 49 Hz, CO). Signal due to C^{ipso} of C_5H_4 was overlapped by the solvent resonance. ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ 28.2 (s, with ^{77}Se satellites, $^{1}J_{SeP}$ = 749 Hz). IR (DRIFTS, KBr): ν_{max} 3100 w, 3087 w, 3074 w, 3051 w, 1641 m, 1615 s (ν_{CO}), 1583 m, 1573 w, 1478 m, 1438 s, 1411 m, 1396 w, 1371 m, 1350 w, 1323 m, 1311 m, 1254 s, 1210 w, 1182 m, 1164 w, 1107 m, 1096 m, 1073 w, 1048 m, 1029 m, 1002 m, 944 m, 869 w, 834 s, 821 m, 757 m, 743 m, 717 m, 705 m, 695 m, 687 m, 619 w, 589 m, 565 m, 529 m, 518 m, 498 s, 483 m, 460 m, 444 w, 425 m cm^{-1}. ESI-MS: *m/z* 501 ([M + Na]$^{+}$). Anal. Calc. for $C_{23}H_{19}FeOPSe$ (477.2): C 57.89, H 4.01%. Found: C 57.82, H 3.96%.



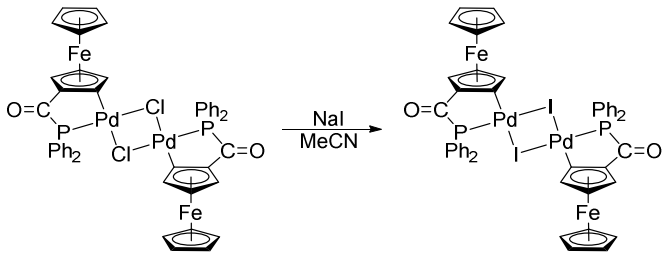
Palladation of 1. Compound **1** (398 mg, 1.00 mmol), sodium tetrachloropalladate(II) (294 mg, 1.00 mmol) and sodium acetate (123 mg, 1.50 mmol) were dissolved in dry acetonitrile (50 mL), and the resulting suspension was heated to 70 °C in a sealed Schlenk flask under argon for 3 hours. The reaction mixture was filtered, and the filtrate was evaporated under reduced pressure, leaving a dark red residue. This residue was dissolved in dichloromethane-methanol (50:1) and transferred onto a top of a short chromatographic column packed in the same solvent mixture. The first red tailing band was collected and evaporated to produce **2-Cl** as a deep red solid. Yield: 485 mg (90%, the typically yield is 70-90%). The crystal used for structure determination was obtained by liquid-liquid diffusion of hexane into an ethyl acetate solution of the complex. The compound is an inseparable mixture of four isomers. Crystals of the pure *meso* form, *trans*-R_p,S_p/S_p,R_p, can be obtained by crystallisation form ethyl acetate/hexane. However, the compound undergoes rapid isomerisation in solution.

Analytical data for the mixture of isomers. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.02 (s, C_5H_5), 4.13 (s, C_5H_5), 4.14 (s, C_5H_5), 4.15 (s, C_5H_5), 4.87 (br s, C_5H_3), 4.90-4.99 (m, C_5H_3), 5.20 (br s, C_5H_3), 5.40 (br s, C_5H_3), 7.18-7.25 (m, PPh_2), 7.32-7.92 (m, PPh_2), 8.18-8.44 (m, PPh_2). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ 50.5, 50.6, 51.09, 51.12 (4× s).IR (DRIFTS, KBr): ν_{max} 3054 w, 2952 w, 2922 w, 1738 m, 1682 m (ν_{CO}), 1666 m (ν_{CO}), 1652 s (ν_{CO}), 1647 s (ν_{CO}),1584 w, 1480 w, 1435 s, 1413 m, 1385 w, 1358 w, 1348 m, 1297 w, 1248 m, 1185 w, 1158 w, 1100 m, 1056 w, 1026 w, 999 w, 969 m, 825 m, 746 m, 719 w, 701 s, 690 m, 619 w, 610 w, 589 w, 531 m, 489 s, 458 m, 434 m cm^{-1}. ESI-MS: *m/z* 575 ([M/2 + Cl]$^-$). Anal. Calc. for $C_{46}H_{36}Cl_2Fe_2O_2P_2Pd_2$ (1078.2): C 51.24, H 3.37%. Found: C 51.09, H 3.28%.



Synthesis of 2-Br by halogen exchange. In air, dimer **2-Cl** (53.9 mg, 0.050 mmol) and sodium bromide (15.4 mg, 0.150 mmol) were dissolved in reagent-grade acetonitrile (10 mL), and the mixture was stirred for 1 h before evaporation. Solid residue was extracted with dichloromethane (5 mL), and the solution was washed with water (2× 5 mL), dried over anhydrous magnesium sulfate, filtered and evaporated. The dark red residue was dissolved in toluene, and the solution was layered with hexane in a test tube. Deep red crystals, which separated during several days, were isolated by suction, washed with pentane and dried under vacuum. Yield of **2-Br**: 50.6 mg (86%). The compound is a mixture of four stereoisomers. Crystals of the *meso* form can be obtained by recrystallisation from toluene/hexane. When dissolved, however, the same isomer mixture is obtained.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.00 (s, C_5H_5), 4.12 (s, C_5H_5), 4.14 (s, C_5H_5), 4.16 (s, C_5H_5), 4.84-4.88 (m, C_5H_3), 4.91-4.97 (m, C_5H_3), 5.21 (br d, J' = 1.4 Hz, C_5H_3), 5.23 (br d, J' = 1.5 Hz, C_5H_3), 5.45 (br s, C_5H_3), 7.13-7.66 (m, PPh_2), 7.69-7.83 (m, PPh_2), 8.15-8.22 (m, PPh_2), 8.22-8.29 (m, PPh_2), 8.31-8.39 (m, PPh_2). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ 51.9, 52.3, 52.7, 52.9 (4× s). IR (DRIFTS, KBr): ν_{max} 3054 w, 2952 w, 1737 m, 1679 m (ν_{CO}), 1667 m (ν_{CO}), 1652 s (ν_{CO}), 1645 s (ν_{CO}), 1584 w, 1481 w, 1435 m, 1413 m, 1385 w, 1358 w, 1348 m, 1394 w, 1248 m, 1186 w, 1153 w, 1099 m, 1058 w, 1026 w, 999 w, 967 m, 825 m, 746 m, 718 w, 701 s, 690 s, 619 w, 609 m, 596 m, 589 m, 530 s, 487 vs, 456 s, 433 m cm^{-1}. ESI-MS: *m/z* 663 ([M/2 + Br]$^-$). Anal. Calc. for $C_{46}H_{36}Br_2Fe_2O_2P_2Pd_2$·PhMe (1259.2): C 50.55, H 3.52%. Found: C 50.27, H 3.72%.



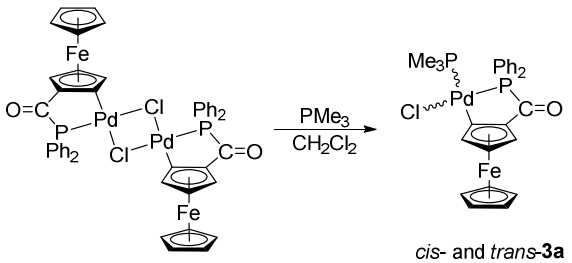
2-Cl
mixture of four stereoisomers

2-I
mixture of four stereoisomers

Synthesis of 2-I by halogen exchange. In air, dimer **2-Cl** (53.9 mg, 0.050 mmol) and sodium iodide (22.5 mg, 0.150 mmol) were dissolved in reagent-grade acetonitrile (10 mL). The mixture was stirred for 1 h and evaporated under vacuum. The solid residue was extracted with dichloromethane (5 mL), and the solution was washed with water (2× 5 mL), dried over anhydrous magnesium sulfate, filtered and evaporated. The dark red residue was dissolved in dichloromethane-methanol (50:1) and transferred to a short silica gel column packed in the same solvent mixture. The first red tailing band was collected, mixed with hexane and evaporated to give **2-I** as a dark red powdery solid. Yield: 58 mg (92 %). The compound is a mixture of four isomers. *Note*: evaporation with hexane leaves the product as an amorphous

solid rather than an oil, which is difficult to handle. The hexane remains present in the solid product.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.98 (s, C_5H_5), 4.09 (s, C_5H_5), 4.13 (s, C_5H_5), 4.18 (s, C_5H_5), 4.84 (vt, *J'* = 2.5 Hz, C_5H_3), 4.86 (vt, *J'* = 2.6 Hz, C_5H_3), 4.91-4.93 (m, C_5H_3), 4.93-4.97 (m, C_5H_3), 5.25 (dd, *J* = 2.4 Hz, 1.1 Hz, C_5H_3), 5.28 (dd, *J* = 2.4 Hz, 1.0 Hz, C_5H_3), 5.49 (dd, *J* = 2.3 Hz, 1.2 Hz, C_5H_3), 5.50 (vt, *J'* = 1.7 Hz, C_5H_3), 7.22-7.76 (m, PPh_2), 8.10-8.35 (m, PPh_2). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ 51.5, 52.1 , 52.3, 52.6 (4× s). IR (DRIFTS, KBr): ν_{max} 3054 w, 2953 w, 1676 m (ν_{CO}), 1666 s (ν_{CO}), 1654 s (ν_{CO}), 1643 s (ν_{CO}), 1481 w, 1435 s, 1411 m, 1386 w, 1358 w, 1347 w, 1286 w, 1247 m, 1186 w, 1152 w, 1098 m, 1061 w, 1026 w, 999 m, 964 m, 822 m, 742 m, 690 s, 607 m, 594 m, 556 w, 525 m, 486 s, 466 m, 448 w cm^{-1}. ESI-MS: *m/z* 757 ([M/2 + I]$^-$). Anal. Calc. for $C_{46}H_{36}Fe_2I_2O_2P_2Pd_2 \cdot C_6H_{14}$ (1347.2): C 46.36, H 3.74%. Found: C 46.52, H 3.67%.



2-Cl
mixture of four stereoisomers

cis- and *trans*-**3a**

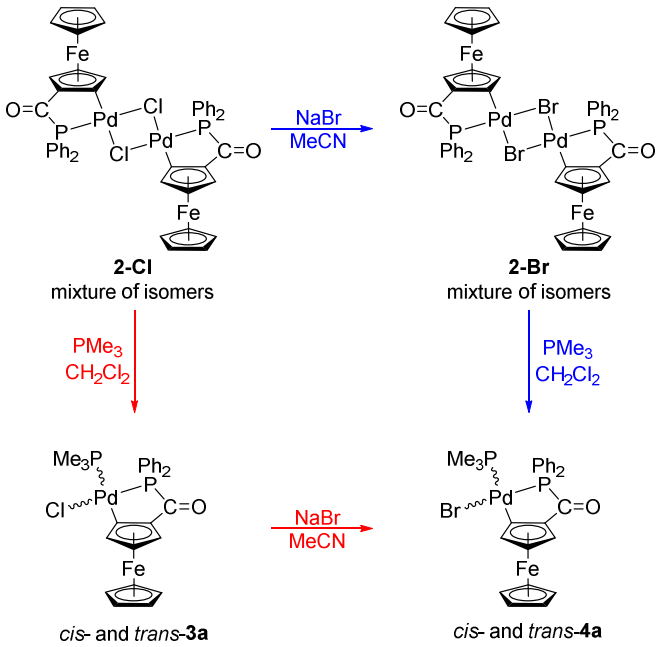
Synthesis of 3a. A trimethylphosphine solution (0.25 mL of 1 M in THF, 0.25 mmol) was added dropwise to a solution of complex **2-Cl** (107.8 mg, 0.10 mmol) in dry dichloromethane (10 mL). The mixture was stirred for 1 h and evaporated under vacuum. The crude product was purified by filtration through a short silica gel column using dichloromethane-methanol (50:1) as the eluent. A single red band was collected and evaporated, leaving pure **3a** as a dark red solid (100 mg, 82%). The compound is a mixture of *cis* and *trans* isomers. Crystallisation from ethyl acetate-hexane produces crystals of pure *cis*-**3a** (also used for structure determination), which gradually isomerises into an equilibrium mixture in solution (*cis*:*trans*-**3a** = 72:28 in $CDCl_3$).

Analytical data for cis-3a. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.20 (d, $^2J_{PH}$ = 8.9 Hz, 9 H, PMe_3), 3.91 (s, 5 H, C_5H_5), 4.94 (apparent p, *J'* = 1.2 Hz, 1 H, C_5H_3), 5.01 (apparent qd, *J'* = 2.4 Hz, 0.9 Hz, 1 H, C_5H_3), 5.72 (apparent p, *J'* = 1.2 Hz, 1 H, C_5H_3), 7.37-7.49 (m, 3 H, PPh_2), 7.60-7.68 (m, 5 H, PPh_2), 8.15-8.22 (m, 2 H, PPh_2). ^{13}C{^{1}H} NMR ($CDCl_3$, 151 MHz): δ 14.31 (d, $^1J_{PC}$ = 25 Hz, PMe_3), 66.46 (dd, J_{PC} = 19 Hz, 5 Hz, CH of C_5H_3), 70.36 (C_5H_5), 77.96 (d, J_{PC} = 9 Hz, CH of C_5H_3), 80.30 (dd, J_{PC} = 5 Hz, 1 Hz, CH of C_5H_3), 83.73 (dd, J_{PC} = 97 Hz, 3 Hz, C^{ipso}-CO of C_5H_3), 104.93 (dd, J_{PC} = 145 Hz, 7 Hz, C^{ipso}-Pd of C_5H_3), 126.73 (dd, J_{PC} = 43 Hz, 1 Hz, C^{ipso} of PPh_2), 128.94 (d, J_{PC} = 11 Hz, CH of PPh_2), 128.97 (d, J_{PC} = 10 Hz, CH of PPh_2), 130.02 (dd, J_{PC} = 42 Hz, 2 Hz, C^{ipso} of PPh_2), 131.33 (d, $^4J_{PC}$ = 3 Hz, CH^{para} of PPh_2), 132.42 (d, $^4J_{PC}$ = 3 Hz, CH^{para} of PPh_2), 132.91 (d, J_{PC} = 12 Hz, CH of PPh_2), 134.59 (dd, J_{PC} = 11 Hz, 1 Hz, CH of PPh_2), 207.28 (dd, J_{PC} = 34 Hz, 5 Hz, CO). ^{31}P{^{1}H} NMR ($CDCl_3$,

162 MHz): δ –19.9 (d, $^2J_{PP}$ = 34 Hz, PMe_3), 53.5 (d, $^2J_{PP}$ = 34 Hz, PPh_2). Anal. Calc. for $C_{26}H_{27}ClFeOP_2Pd$ (615.2): C 50.76, H 4.42%. Found: C 50.58, H 4.30%.

Analytical data for trans-3a. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.72 (dd, J_{PH} = 9.5 Hz, 2.6 Hz, 9 H, PMe_3), 3.93 (s, 5 H, C_5H_5), 4.61 (apparent dt, J' = 2.3 Hz, 1.0 Hz, 1 H, C_5H_3), 4.96 (apparent dt, J' = 2.6 Hz, 1.0 Hz, 1 H, C_5H_3), 7.32-7.37 (m, 3 H, PPh_2), 7.52-7.57 (m, 3 H, PPh_2), 7.72-7.79 (m, 2 H, PPh_2), 8.40-8.48 (m, 2 H, PPh_2). A signal due to C_5H_3 is obscured by the resonance of *cis*-**3a** (δ_H 4.93-4.96). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ –15.3 (d, $^2J_{PP}$ = 439 Hz, PMe_3), 37.9 (d, $^2J_{PP}$ = 439 Hz, PPh_2).

Data for isomer mixture. IR (DRIFTS, KBr): ν_{max} 3076 w, 2906 w, 1773 w, 1663 m (ν_{CO}), 1648 s (ν_{CO}), 1640 m (ν_{CO}), 1478 m, 1435 m, 1404 m, 1384 w, 1359 w, 1348 w, 1307 w, 1284 m, 1247 m, 1180 w, 1151 w, 1099 m, 1027 m, 1000 m, 953 s, 821 m, 752 m, 742 m, 719 w, 700 m, 692 m, 619 w, 614 w, 592 m, 525 m, 495 s, 486 s, 464 m, 455 w, 445 w, 427 w cm^{-1}. *Note:* the IR spectra of pure *cis*-**3a** and the mixture of isomers show no significant difference. ESI-MS: *m/z* 579 ($[M - Cl]^+$), 655 ($[M + K]^+$).



Synthesis of 4a. ***Route A.*** In air, complex **2-Cl** (53.9 mg, 0.050 mmol) and sodium bromide (15.4 mg, 0.15 mmol) were dissolved in acetonitrile (10 mL), and the mixture was stirred for 1 hour and evaporated under vacuum. The solid residue was extracted with dichloromethane (5 mL), and the solution was washed with water (5 mL), dried over magnesium sulfate and evaporated. Then, the reaction flask was flushed with argon, and the solid residue was dissolved in dry dichloromethane (10 mL), adding a solution of trimethylphosphine (0.13 mL of 1 M solution in THF, 0.13 mmol) dropwise. The resulting mixture was stirred 1 h and evaporated. The residue was purified by flash chromatography over silica gel with dichloromethane-methanol (50:1). A

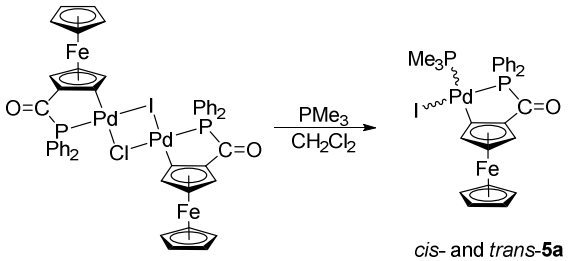
single dark red band was collected and evaporated to give *cis*/*trans*-**4a** as a dark red solid. In addition, the compound was crystallised by hexane (8 ml) diffusion into an ethyl-acetate solution of the complex (2 ml). Dark red crystals were isolated by suction, washed with pentane and dried under vacuum. Yield: 28 mg (36% over two steps). Crystallisation exclusively provides the *cis* isomer, which similarly isomerises in solution as the analogous chloro complex. The equilibrium *cis*:*trans*-**4a** ratio is 72:28 in $CDCl_3$.

Route B. In air, complex *cis*/*trans*-**3a** (30.8 mg, 0.05 mmol) and sodium bromide (7.7 mg, 0.075 mmol) were dissolved in acetonitrile (10 mL). The reaction mixture was stirred for 1 h and filtered through a PTFE syringe filter (0.45 µm pore size). The filtrate was evaporated, and the solid residue taken up with dichloromethane (5 mL). The extract was washed with water (5 mL), dried over anhydrous magnesium sulfate and evaporated. The crude product was crystalised as described above to give *cis*-**4a** as a dark red crystalline solid. Yield: 22 mg (yield 57%, 43% from **2-Cl**).

Analytical data for cis-4a. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.25 (d, $^{2}J_{PH}$ = 8.9 Hz, 9 H, PMe_3), 3.91 (s, 5 H, C_5H_5), 4.93 (apparent p, J' = 1.3 Hz, 1 H, C_5H_3), 5.00 (apparent qd, J' = 2.5 Hz, 0.9 Hz, 1 H, C_5H_3), 5.88 (apparent dt, J' = 2.4 Hz, 1.1 Hz, 1 H, C_5H_3), 7.37-7.49 (m, 3 H, PPh_2), 7.62-7.69 (m, 5 H, PPh_2), 8.14-8.21 (m, 2 H, PPh_2). ^{13}C{^{1}H} NMR ($CDCl_3$, 151 MHz): δ 15.25 (dd, J_{PC} = 26 Hz, 1 Hz, PMe_3), 66.51 (dd, J_{PC} = 19 Hz, 5 Hz, CH of C_5H_3), 70.40 (C_5H_5), 78.51 (d, J_{PC} = 9 Hz, CH of C_5H_3), 83.06 (dd, J_{PC} = 5 Hz, 2 Hz, CH of C_5H_3), 83.95 (d, J_{PC} = 95 Hz, C^{ipso}-CO of C_5H_3), 103.34 (dd, J_{PC} = 146 Hz, 6 Hz, C^{ipso}-Pd of C_5H_3), 126.76 (dd, J_{PC} = 42 Hz, 2 Hz, C^{ipso} of PPh_2), 128.95 (d, J_{PC} = 11 Hz, CH of PPh_2), 128.98 (d, J_{PC} = 10 Hz, CH of PPh_2), 129.90 (dd, J_{PC} = 41 Hz, 2 Hz, C^{ipso} of PPh_2), 131.34 (d, $^{4}J_{PC}$ = 3 Hz, CH^{para} of PPh_2), 132.41 (d, $^{4}J_{PC}$ = 3 Hz, CH^{para} of PPh_2), 132.96 (d, J_{PC} = 12 Hz, CH of PPh_2), 134.53 (dd, J_{PC} = 12 Hz, 1 Hz, CH of PPh_2), 207.38 (dd, J_{PC} = 33 Hz, 5 Hz, CO). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ –22.4 (d, $^{2}J_{PP}$ = 34 Hz, PMe_3), 52.2 (d, $^{2}J_{PP}$ = 34 Hz, PPh_2). Anal. Calc. for $C_{26}H_{27}BrFeOP_2Pd$ (659.6): C 47.34, H 4.13%. Found: C 47.46, H 3.85%.

Analytical data for trans-4a. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.76 (dd, J_{PH} = 9.4 Hz, 2.6 Hz, 9 H, PMe_3), 3.91 (s, 5 H, C_5H_5), 4.64-4.66 (m, 1 H, C_5H_3), 4.95-4.98 (m, 2 H, C_5H_3), 7.31-7.37 (m, 3 H, PPh_2), 7.51-7.57 (m, 3 H, PPh_2), 8.39-8.46 (m, 2 H, PPh_2). A signal due to the phenyl groups (2 H) overlaps with the signal of the *cis* isomer. ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ –17.6 (d, $^{2}J_{PP}$ = 440 Hz, PMe_3), 40.3 (d, $^{2}J_{PP}$ = 440 Hz, PPh_2).

Analytical data for the mixture of isomers. IR (DRIFTS, KBr): ν_{max} 3073 w, 3048 w, 2977 w, 2906 w, 1664 m (ν_{CO}), 1652 s (ν_{CO}), 1636 s (ν_{CO}), 1480 m, 1436 m, 1412 m, 1386 w, 1358 w, 1346 w, 1305 w, 1284 m, 1249 m, 1182 w, 1151 w, 1099 m, 1064 w, 1027 w, 1000 m, 957 s, 851 m, 825 m, 750 s, 744 s, 718 w, 695 s, 618 m, 591 m, 525 m, 488 s, 469 m, 444 m, 431 w cm^{-1}. *Note:* the IR spectrum of pure *cis*-**4a** and the isomer mixture do not practically differ. ESI-MS: *m/z* 503 ($[M – Br – PMe_3]^+$), 579 ($[M – Br]^+$), 661 ($[M + H]^+$); 663 ($[M – PMe_3 + Br]^-$).



2-I
mixture of isomers

cis- and *trans*-**5a**

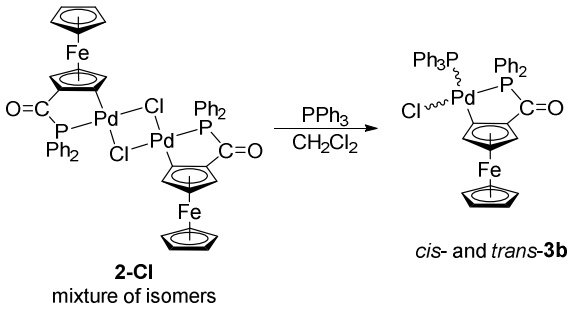
Synthesis of 5a. A solution of trimethylphosphine (0.13 mL of 1 M in THF, 0.13 mmol) was added dropwise to a dichloromethane solution of complex **2-I** (63.1 mg, 0.050 mmol in 10 mL) and the resulting mixture was stirred for 1 h and then evaporated. The crude product was purified by flash chromatography over silica gel, eluting with dichloromethane-methanol (50:1). A single dark red band was evaporated to give pure *cis*/*trans*-**5a** as a dark red solid (44 mg, 62%). The crystals that were used for X-ray analysis were grown by liquid-liquid diffusion of hexane into a solution of the complex in ethyl acetate. Such crystallisation exclusively provides the *cis* isomer, which isomerises in solution (*cis*:*trans*-**5a** = 68:32 in $CDCl_3$).

Analytical data for cis-5a. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.34 (d, $^2J_{PH}$ = 8.7 Hz, 9 H, PMe_3), 3.90 (s, 5 H, C_5H_5), 4.91 (apparent p, J' = 1.3 Hz, 1 H, C_5H_3), 4.97 (apparent qd, J' = 2.5 Hz, 1.0 Hz, 1 H, C_5H_3), 6.10 (apparent dt, J' = 2.3 Hz, 1.1 Hz, 1 H, C_5H_3), 7.38-7.50 (m, 3 H, PPh_2), 7.63-7.71 (m, 5 H, PPh_2), 8.14-8.21 (m, 2 H, PPh_2). ^{13}C{^{1}H} NMR ($CDCl_3$, 151 MHz): δ 17.18 (dd, J_{PC} = 27 Hz, 2 Hz, PMe_3), 66.53 (dd, J_{PC} = 19 Hz, 5 Hz, CH of C_5H_3), 70.48 (C_5H_5), 79.62 (d, J_{PC} = 8 Hz, CH of C_5H_3), 84.48 (dd, J_{PC} = 98 Hz, 3 Hz, C^{ipso}-CO of C_5H_3), 88.90 (dd, J_{PC} = 5 Hz, 2 Hz, CH of C_5H_3), 100.34 (dd, J_{PC} = 147 Hz, 6 Hz, C^{ipso}-Pd of C_5H_3), 126.77 (dd, J_{PC} = 40 Hz, 2 Hz, C^{ipso} of PPh_2), 128.97 (d, J_{PC} = 10 Hz, CH of PPh_2), 128.98 (d, J_{PC} = 11 Hz, CH of PPh_2), 129.92 (dd, J_{PC} = 39 Hz, 2 Hz, C^{ipso} of PPh_2), 131.28 (d, $^4J_{PC}$ = 3 Hz, CH^{para} of PPh_2), 132.37 (d, $^4J_{PC}$ = 3 Hz, CH^{para} of PPh_2), 132.93 (d, J_{PC} = 13 Hz, CH of PPh_2), 134.45 (dd, J_{PC} = 12 Hz, 1 Hz, CH of PPh_2), 207.70 (dd, J_{PC} = 32 Hz, 5 Hz, CO). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ –26.3 (d, $^2J_{PP}$ = 33 Hz, PMe_3), 47.2 (d, $^2J_{PP}$ = 33 Hz, PPh_2).

Analytical data for trans-5a. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.85 (dd, J_{PH} = 9.3 Hz, 2.6 Hz, 9 H, PMe_3), 3.88 (s, 5 H, C_5H_5), 4.71 (vt, J' = 1.6 Hz, 1 H, C_5H_3), 4.95-4.98 (m, 2 H, C_5H_3), 7.30-7.37 (m, 3 H, PPh_2), 7.52-7.60 (m, 5 H, PPh_2), 8.36-8.42 (m, 2 H, PPh_2). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ –21.1 (d, $^2J_{PP}$ = 440 Hz, PMe_3), 42.5 (d, $^2J_{PP}$ = 440 Hz, PPh_2).

Analytical data for the mixture of isomers. IR (DRIFTS, KBr): ν_{max} 3073 br w, 2969 w, 2905 w, 1664 m (ν_{CO}), 1648 m (ν_{CO}), 1637 s (ν_{CO}), 1481 w, 1436 m, 1411 m, 1359 w, 1347 w, 1307 w, 1284 m, 1247 m, 1220 w, 1184 w, 1149 w, 1098 m, 1060 w, 1026 m, 999 m, 955 s, 851 w, 836 m, 822 m, 747 s, 717 w, 692 s, 613 w, 591 m, 578 w, 522 m, 487 s, 468 m, 443 m, 430 w cm^{-1}. *Note:* The IR spectra of *cis*-**5a** and the isomer mixture do not show any substantial difference. ESI-MS:

m/z 579 ([M – I]$^+$), 707 ([M + H]$^+$). Anal. Calc. for $C_{26}H_{27}FeIOP_2Pd$ (706.6): C 44.19, H 3.85%. Found: C 44.22, H 3.85%.



2-Cl
mixture of isomers

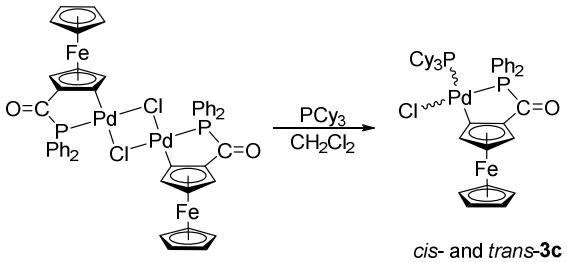
cis- and *trans*-**3b**

Synthesis of 3b. In air, complex **2-Cl** (107.8 mg, 0.10 mmol) and triphenylphosphine (57.7 mg, 0.22 mmol) were dissolved in dry dichloromethane (15 mL). The solution was stirred at room temperature for 1 h and evaporated. The crude product mixture was purified by flash chromatography over silica gel using dichloromethane-methanol (50:1) as the eluent. A single orange red band was evaporated to give pure *cis*/*trans*-**3b** as an orange red solid. Yield: 144 mg (87%). Crystallisation from ethyl acetate/hexane or from toluene/hexane provides pure *trans* isomer (the former method (ethyl acetate/hexane) typically leads to better yields; the crystal that was used for structure determination was grown from toluene/hexane). The compound immediately isomerises in a solution to give a 22:78 mixture of *cis*- and *trans*-**3b** (in $CDCl_3$).

Analytical data for cis-3b. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.00 (s, 5 H, C_5H_5), 4.93 (apparent p, *J'* = 1.3 Hz, 1 H, C_5H_3), 5.02 (apparent qd, *J'* = 2.4 Hz, 0.7 Hz, 1 H, C_5H_3), 5.95 (dt, *J'* = 2.4 Hz, 1.0 Hz, 1 H, C_5H_3), 7.10-7.16 (m, 2 H, PPh_2), 7.85-7.93 (m, 2 H, PPh_2). Other signals due to PPh_2 are obscured by the signals due to the major *trans* isomer. ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ 18.8 (d, $^2J_{PP}$ = 30 Hz, PPh_3), 53.9 (d, $^2J_{PP}$ = 30 Hz, PPh_2).

Analytical data for trans-3b. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.58 (s, 5 H, C_5H_5), 3.87 (apparent dt, *J'* = 2.5 Hz, 1.0 Hz, 1 H, C_5H_3), 4.55 (tdd, *J* = 2.5 Hz, 1.1 Hz, 0.6 Hz, 1 H, C_5H_3), 4.87 (dd, *J* = 2.6 Hz, 1.0 Hz, 1 H, C_5H_3), 7.16-7.22 (m, 2 H, PPh_2), 7.27-7.47 (m, 10 H, PPh), 7.52-7.57 (m, 3 H, PPh_3), 7.68-7.76 (m, 6 H, PPh), 7.78-7.85 (m, 2 H, PPh), 8.53-8.60 (m, 2 H, PPh_2). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ 29.0 (d, $^2J_{PP}$ = 414 Hz, PPh_3), 40.6 (d, $^2J_{PP}$ = 414 Hz, PPh_2).

Analytical data for the isomer mixture. ^{1}H NMR spectrum corroborates the presence of solvating AcOEt. IR (DRIFTS, KBr): ν_{max} 3053 w, 2987 w, 1736 m (ν_{CO}, AcOEt), 1641 s (ν_{CO}), 1481 m, 1436 s, 1408 m, 1390 w, 1372 w, 1312 w, 1275 w, 1244 m, 1185 w, 1154 w, 1096 m, 1045 m, 1028 m, 999 m, 967 w, 839 w, 826 m, 753 m, 744 m, 693 s, 618 w, 590 m, 523 m, 516 s, 508 s, 498 s, 486 s, 467 m, 453 m, 436 w, 427 w cm^{-1}. ESI-MS: *m/z* 765 ([M – Cl]$^+$). Anal. Calc. for $C_{41}H_{33}ClFeOP_2Pd \cdot 1.5AcOEt$ (933.5): C 60.47, H 4.86%. Found: C 60.08, H 4.77% (product crystallised from ethyl acetate/hexane)



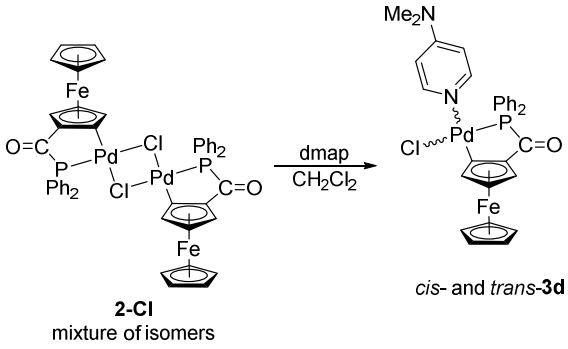
2-Cl
mixture of isomers

cis- and *trans*-**3c**

Synthesis of 3c. In air, compound **2-Cl** (53.9 mg, 0.05 mmol) and tricyclohexylphosphine (28.1 mg, 0.10 mmol) were dissolved in dry dichloromethane (5 mL), the solution was stirred for 1 h at room temperature and evaporated. The solid residue was dissolved in ethyl acetate (1.5 mL), and the solution was layered with hexane (7 mL). Dark red crystals, which separated during several days, were isolated by suction, washed in pentane and dried under vacuum. Yield: 38 mg (46%), dark red crystalline solid. Crystallisation produces pure *trans* isomer, which slowly isomerises in a solution to an equilibrium mixture of *cis*- and *trans*-**3c** in approximately 10:90 ratio (in $CDCl_3$). The spectra confirm the presence of ethyl acetate in the crystallised solid (^{1}H NMR: δ 1.26 (t, J = 7.2 Hz, 3 H), 2.04 (s, 3 H), 4.14 (q, J = 7.2 Hz, 3 H); IR: ν_{CO} 1737 cm^{-1}).

Analytical data for trans-3c. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.18-1.34 (m, 9 H, C_6H_{11}), 1.56-2.07 (m, 21 H, C_6H_{11}), 2.48-2.60 (m, 3 H, C_6H_{11}), 3.88 (s, 5 H, C_5H_5), 4.66 (vt, J' = 1.7 Hz, 1 H, C_5H_3), 4.92 (apparent d, J' = 1.4 Hz, 2 H, C_5H_3), 7.28-7.36 (m, 3 H, PPh_2), 7.54-7.68 (m, 5 H, PPh_2), 8.51-8.57 (m, 2 H, PPh_2). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 26.55 (C_6H_{11}), 27.68 (d, J_{PC} = 2 Hz, C_6H_{11}), 27.78 (d, J_{PC} = 2 Hz, C_6H_{11}), 30.25 (C_6H_{11}), 30.50 (C_6H_{11}), 32.91 (dd, J_{PC} = 15 Hz, 3 Hz, C_6H_{11}), 66.23 (d, J_{PC} = 17 Hz, CH of C_5H_3), 70.88 (C_5H_5), 75.91 (d, J_{PC} = 1 Hz, CH of C_5H_3), 80.32 (d, J_{PC} = 8 Hz, CH of C_5H_3), 88.20 (dd, J_{PC} = 87 Hz, 4 Hz, C^{ipso}-CO of C_5H_3), 95.26 (dd, J_{PC} = 5 Hz, 3 Hz, C^{ipso}-Pd of C_5H_3), 127.24 (dd, J_{PC} = 33 Hz, 8 Hz, C^{ipso} of PPh_2), 128.28 (d, J_{PC} = 10 Hz, CH of PPh_2), 128.46 (d, J_{PC} = 10 Hz, CH of PPh_2), 129.98 (d, $^4J_{PC}$ = 2 Hz, CH^{para} of PPh_2), 131.60 (d, $^4J_{PC}$ = 2 Hz, CH^{para} of PPh_2), 132.35 (dd, J_{PC} = 38 Hz, 2 Hz, C^{ipso} of PPh_2), 132.75 (dd, J_{PC} = 10 Hz, 2 Hz, CH of PPh_2), 135.27 (dd, J_{PC} = 10 Hz, 3 Hz, CH of PPh_2), 207.69 (dd, J_{PC} = 24 Hz, 1 Hz, CO). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ 32.6 (d, $^2J_{PP}$ = 397 Hz, PCy_3), 38.2 (d, $^2J_{PP}$ = 397 Hz, PPh_2). IR (DRIFTS, KBr): ν_{max} 3073 w, 3057 w, 2930 vs, 2852 m, 2845 m, 1739 w (ν_{CO}, AcOEt), 1639 m (ν_{CO}), 1571 w, 1482 w, 1445 m, 1436 m, 1417 m, 1393 w, 1362 w, 1350 w, 1326 w, 1299 w, 1270 w, 1248 m, 1191 w, 1183 w, 1175 w, 1145 w, 1129 w, 1102 m, 1051 w, 1030 m, 1004 m, 966 w, 916 w, 899 m, 886 w, 850 m, 830 m, 823 m, 753 m, 742 m, 720 w, 691 m, 619 m, 591 m, 581 w, 523 m, 508 m, 486 s, 467 m, 443 m, 431 m cm^{-1}. ESI-MS: *m/z* 783 ([M – Cl]$^+$). Anal. Calc. for $C_{41}H_{51}ClFeOP_2Pd$ (819.5): C 60.09, H 6.27%. Found: C 59.97, H 6.20%.

Analytical data for cis-3c. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.25 (s, 5 H, C_5H_5), 4.88-4.90 (m, 1 H, C_5H_3), 4.94-4.97 (m, 1 H, C_5H_3), 6.02-6.04 (m, 1 H, C_5H_3); only diagnostic signals. ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ 23.6 (d, $^2J_{PP}$ = 28 Hz, PCy_3), 55.2 (d, $^2J_{PP}$ = 28 Hz, PPh_2).



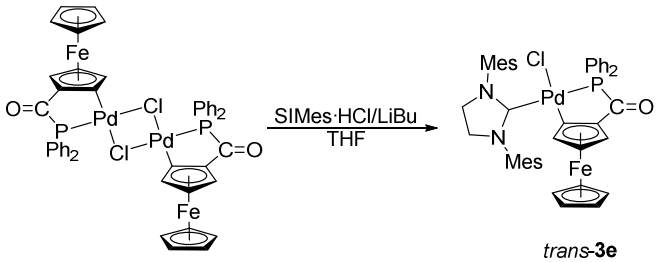
2-Cl
mixture of isomers

cis- and *trans*-**3d**

Synthesis of 3d. In air, complex **2-Cl** (27.0 mg, 0.025 mmol) and 4-(*N,N*-dimethyl-amino)pyridine (dmap; 6.2 mg, 0.050 mmol) were dissolved in dry dichloromethane (5 mL). The solution was stirred for 1 h and evaporated under vacuum. The solid residue was dissolved in chloroform, and the solution was layered with hexane. The resulting dark red crystals were filtered off, washed with pentane and dried under vacuum. Yield: 30 mg (89%). Crystals suitable for X-ray diffraction analysis were obtained by liquid-liquid diffusion of hexane into a solution of the complex in ethyl acetate. Crystallisation provides the pure *trans* isomer, which rapidly isomerises (*cis*:*trans* = 13:87 in $CDCl_3$).

Analytical data of trans-3d. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.10 (s, 6 H, NMe_2), 3.98 (s, 5 H, C_5H_5), 4.17 (dd, *J'* = 2.4 Hz, 1.0 Hz, 1 H, C_5H_3), 4.77 (td, *J'* = 2.5 Hz, 0.7 Hz, 1 H, C_5H_3), 4.92 (dd, *J'* = 2.6 Hz, 1.0 Hz, 1 H, C_5H_3), 6.59-6.63 (m, 2 H, CH of C_5H_4N), 7.33-7.40 (m, 3 H, PPh_2), 7.53-7.58 (m, 3 H, PPh_2), 7.88-7.96 (m, 2 H, PPh_2), 8.48-8.58 (m, 2 H of C_5H_4N and 2 H of PPh_2). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 39.29 (NMe_2), 65.97 (d, J_{PC} = 18 Hz, CH of C_5H_3), 70.48 (C_5H_5), 75.86 (CH of C_5H_3), 77.84 (CH of C_5H_3), 85.54 (d, $^{2}J_{PC}$ = 91 Hz, C^{ipso}-CO of C_5H_3), 96.87 (d, $^{3}J_{PC}$ = 6 Hz, C^{ipso}-Pd of C_5H_3), 107.14 (d, $^{3}J_{PC}$ = 2 Hz, CH of dmap), 127.97 (d, $^{1}J_{PC}$ = 44 Hz, C^{ipso} of PPh_2), 128.47 (d, J_{PC} = 10 Hz, CH of PPh_2), 128.55 (d, J_{PC} = 11 Hz, CH of PPh_2), 130.20 (d, $^{1}J_{PC}$ = 43 Hz, C^{ipso} of PPh_2), 130.72 (d, $^{4}J_{PC}$ = 3 Hz, CH^{para} of PPh_2), 131.55 (d, $^{4}J_{PC}$ = 3 Hz, CH^{para} of PPh_2), 133.40 (d, J_{PC} = 11 Hz, CH of PPh_2), 134.58 (d, J_{PC} = 11 Hz, CH of PPh_2), 150.91 (CH of dmap), 154.60 (C^{ipso}-N of dmap), 208.21 (d, $^{1}J_{PC}$ = 34 Hz, CO). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ 47.4 (PPh_2). IR (DRIFTS, KBr): ν_{max} 3052 w, 2922 w, 1682 w, 1667 m (ν_{CO}), 1651 m (ν_{CO}), 1644 s (ν_{CO}), 1635 s (ν_{CO}), 1615 s (ν_{CO}), 1541 m, 1480 m, 1443 m, 1434 m, 1411 m, 1392 m, 1361 w, 1350 m, 1289 w, 1249 m, 1226 m, 1187 w, 1152 w, 1107 w, 1095 m, 1074 m, 1066 m, 1019 m, 1006 w, 969 w, 951 w, 837 m, 826 m, 815 m, 762 m ,746 m, 715 w, 703 m, 690 m, 619 w, 609 m, 598 m, 577 w, 530 m, 491 m, 456 m, 439 m cm^{-1}. ESI-MS: *m/z* 625 ($[M - Cl]^+$). Anal. Calc. for $C_{30}H_{28}ClFeN_2OPPd$ (661.2): C 54.49, H 4.27, N 4.24%. Found: C 54.30, H 4.34, N 3.91%.

Analytical data for cis-3d. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.95 (s, 6 H, NMe_2), 4.07 (s, 5 H, C_5H_5), 4.95 (dd, *J'* = 2.6 Hz, 1.1 Hz, 1 H, C_5H_3), 5.00 (td, *J'* = 2.5 Hz, 0.8 Hz, 1 H, C_5H_3), 5.79 (dd, *J'* = 2.4 Hz, 1.1 Hz, 1 H, C_5H_3), 6.28-6.31 (m, 2 H, CH of C_5H_4N), the signal due to aromatic protons overlaps with those of the major isomer. ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ 48.7.



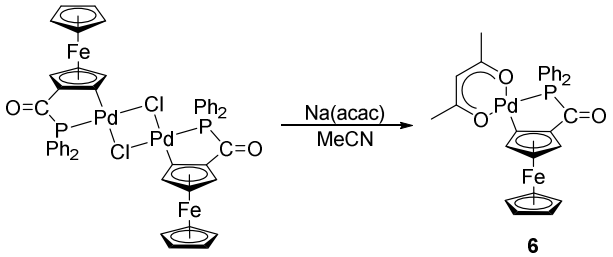
2-Cl
mixture of isomers

trans-**3e**

Synthesis of 3e. 1,3-Bis(2,4,6-trimethylphenyl)imidazolinium chloride (42.0 mg, 0.12 mmol) was dissolved in anhydrous THF (5 mL) under argon in a dry Schlenk flask, and the solution was cooled in a dry ice/ethanol bath to ca. –78 °C. *n*-Butyllithium (0.07 ml of 1.6 M in hexane, 0.11 mmol) was added dropwise, and the mixture was stirred with continuous cooling for 30 minutes. Subsequently, a solution of **2-Cl** (53.9 mg, 0.050 mmol) in dry THF (5 mL) was added, continuously stirring for 90 min at room temperature. The reaction mixture was concentrated under vacuum, leaving a red oily residue, which was purified by column chromatography over silica gel using dichloromethane-methanol (50:1) as the eluent. The first, pale red band was discarded, and the second main red band was collected and evaporated to give pure **3e** as a red solid (60 mg, 71%). The compound is obtained as pure *trans* isomer, which is stable in solution. The crystals that were used for structure determination were obtained from liquid-phase diffusion of hexane into a solution of the complex in toluene.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.02 (s, 3 H, Me of Mes), 2.29 (s, 3 H, Me of Mes), 2.31 (s, 3 H, Me of Mes), 2.52 (s, 3 H, Me of Mes), 2.67 (s, 3 H, Me of Mes), 2.89 (s, 3 H, Me of Mes), 3.42 (s, 5 H, C_5H_5), 3.86-4.13 (m, 4 H, CH_2 of imidazoline), 4.41 (dd, *J'* = 2.3 Hz, 1.1 Hz, 1 H, C_5H_3), 4.69 (dd, *J'* = 2.6 Hz, 1.1 Hz, 1 H, C_5H_3), 4.74 (td, *J'* = 2.4 Hz, 1.1 Hz, 1 H, C_5H_3), 6.69 (dq, *J* = 2.1 Hz, 0.6 Hz, 1 H, CH of Mes), 6.89 (dq, *J* = 2.1 Hz, 0.6 Hz, 1 H, CH of Mes), 7.06 (dq, *J* = 2.1 Hz, 0.6 Hz, 1 H, CH of Mes), 7.07-7.28 (m, 5 H of PPh_2 1 H of Mes), 7.42-7.47 (m, 3 H, PPh_2), 8.35-8.41 (m, 2 H, PPh_2). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 19.29 (Me of Mes), 19.41 (Me of Mes), 19.97 (Me of Mes), 20.96 (Me of Mes), 21.07 (Me of Mes), 21.19 (Me of Mes), 51.22 (d, J_{PC} = 4 Hz, CH_2 of imidazoline), 52.55 (d, J_{PC} = 5 Hz, CH_2 of imidazoline), 64.95 (d, J_{PC} = 17 Hz, CH of C_5H_3), 70.47 (C_5H_5), 75.40 (CH of C_5H_3), 82.18 (d, J_{PC} = 1 Hz, CH of C_5H_3), 86.62 (d, J_{PC} = 90 Hz, C^{ipso}-CO of C_5H_3), 93.98 (d, J_{PC} = 7 Hz, C^{ipso}-Pd of C_5H_3), 127.77 (d, J_{PC} = 11 Hz, CH of PPh_2), ca. 127.90 (C^{ipso} of PPh_2; only a half of a doublet is observed), 128.30 (d, J_{PC} = 9 Hz, CH of PPh_2), 128.79 (CH of Mes), 129.03 (CH of Mes), 129.63 (d, $^{4}J_{PC}$ = 3 Hz, CH^{para} of PPh_2), 129.64 (CH of Mes), 130.36 (CH of Mes), 131.09 (d, $^{4}J_{PC}$ = 2 Hz, CH^{para} of PPh_2), 131.10 (d, J_{PC} = 40 Hz, C^{ipso} of PPh_2), 133.29 (d, J_{PC} = 12 Hz, CH of PPh_2), 134.42 (C^{ipso}-Me of Mes), 134.58 (d, J_{PC} = 10 Hz, CH of PPh_2), 135.49 (C^{ipso}-Me of Mes), 136.28 (C^{ipso}-N of Mes), 136.31 (C^{ipso}-N of Mes), 137.42 (C^{ipso}-Me of Mes), 137.85 (C^{ipso}-Me of Mes), 138.03 (C^{ipso}-Me of Mes), 138.18 (C^{ipso}-Me of Mes), 208.11 (d, $^{1}J_{PC}$ = 27 Hz, CO), 210.05 (d, $^{1}J_{PC}$ = 143 Hz, $C^{carbene}$-Pd of imidazoline). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ 36.7 (PPh_2). IR (DRIFTS,

KBr): ν_{max} 2953 w, 2918 br w, 1636 s (ν_{CO}), 1482 m, 1436 m, 1422 m, 1290 w, 1264 s, 1182 w, 1157 w, 1100 m, 1026 m, 1000 w, 963 w, 888 w, 852 m, 822 m, 750 m, 744 m, 699 m, 690 m, 623 w, 590 w, 578 w, 564 w, 525 m, 489 s, 466 m, 452 w, 430 w cm^{-1}. ESI-MS: *m/z* 809 ([M – Cl]$^+$). Anal. Calc. for $C_{44}H_{44}ClFeN_2OPPd \cdot 0.4PhMe$ (882.4): C 63.70, H 5.39, N 3.17%. Found: C 63.53, H 5.05, N 3.12%. The presence and amount of toluene in the crystalline sample was confirmed by NMR spectra, showing a signal at δ_H 2.35 (s, Me of toluene).



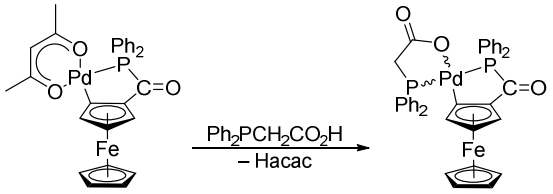
2-Cl
mixture of isomers

6

Synthesis of 6. In air, complex **2-Cl** (108 mg, 0.10 mmol) and sodium acetylacetonate monohydrate (35 mg, 0.25 mmol) were dissolved in 30 mL of reagent-grade acetonitrile, and the solution was stirred at room temperature for 1 h. The reaction mixture was filtered and evaporated, leaving a waxy red residue, which was filtered through a short silica gel column using dichloromethane-methanol (50:1) as the eluent. The filtrate was evaporated, and the oily residue was dissolved in diethyl ether and layered with hexane. Crystallisation rapidly produced red crystals, which were isolated by suction, washed with pentane and dried under vacuum. Yield of **6**: 90 mg (75%), red crystalline solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.99 (s, 3 H, Me of acac), 2.13 (s, 3 H, Me of acac), 4.01 (s, 5 H, C_5H_5), 4.92-4.93 (m, 1 H, C_5H_3), 4.94 (td, *J'* = 2.6 Hz, 0.6 Hz, 1 H, C_5H_3), 5.43-5.45 (m, 1 H, C_5H_3), 5.45 (s, 1 H, CH of acac), 7.32-7.42 (m, 3 H, PPh_2), 7.51-7.58 (m, 3 H, PPh_2), 7.82-7.88 (m, 2 H, PPh_2), 8.32-8.39 (m, 2 H, PPh_2). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 28.03 (d, $^4J_{PC}$ = 6 Hz, Me of acac), 28.15 (Me of acac), 65.89 (d, J_{PC} = 18 Hz, CH of C_5H_3), 70.67 (C_5H_5), 75.76 (CH of C_5H_3), 76.06 (CH of C_5H_3), 85.06 (d, $^2J_{PC}$ = 92 Hz, C^{ipso}-CO of C_5H_3), 95.24 (d, $^2J_{PC}$ = 14 Hz, C^{ipso}-Pd of C_5H_3), 99.60 (CH of acac), 128.56 (d, J_{PC} = 11 Hz, CH of PPh_2), 128.67 (d, J_{PC} = 10 Hz, CH of PPh_2), 128.97 (d, J_{PC} = 42 Hz, C^{ipso} of PPh_2), 130.44 (d, J_{PC} = 41 Hz, C^{ipso} of PPh_2), 130.82 (d, $^4J_{PC}$ = 3 Hz, CH^{para} of PPh_2), 131.55 (d, $^4J_{PC}$ = 3 Hz, CH^{para} of PPh_2), 133.06 (d, J_{PC} = 12 Hz, CH of PPh_2), 133.53 (d, J_{PC} = 11 Hz, CH of PPh_2), 187.07 (2×CO of acac; confirmed by 2D spectra), 205.89 (d, $^1J_{PC}$ = 38 Hz, CO-PPh_2). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ 42.5 (s). IR (DRIFTS, KBr): ν_{max} 3074 w, 2967 w, 1683 w (ν_{CO}), 1667 m (ν_{CO}), 1651 s (ν_{CO}), 1645 s (ν_{CO}), 1581 s (acac, ν_{CO}), 1519 s (acac, ν_{CO}), 1482 w, 1436 m, 1403 m, 1383 s, 1310 w, 1293 w, 1264 m, 1250 m, 1201 w, 1191 w, 1153 w, 1105 m, 1058 w, 1021 m, 964 m, 934 w, 858 w, 821 m, 771 m, 750 m, 746 m, 718 w, 701 m, 693 m, 658 w, 594 m,

530 m, 499 m, 485 m, 463 m, 456 m, 439 m cm^{-1}. ESI-MS: *m/z* 625 ($[M + Na]^+$). Anal. Calc. for $C_{28}H_{25}FeO_3PPd$ (602.7): C 55.80, H 4.18%. Found: C 55.75, H 3.91%.

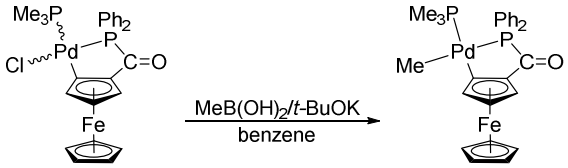


6 **7**

Synthesis of 7. In air, complex **6** (30 mg, 0.050 mmol) and (diphenylphosphino)acetic acid (12 mg, 0.050 mmol) were dissolved in dry dichloromethane (10 mL), and the solution was stirred at room temperature for 1 h and then evaporated under vacuum. The residue was purified by flash chromatography over silica gel with dichloromethane-methanol (20:1). The main red band was collected and evaporated, leaving pure **7** as a red solid. Yield: 35 mg (95%). The crystals that were used for X-ray diffraction analysis were obtained from hexane/ethyl acetate. Complex **7** crystallises as pure *trans* isomer. In solution, however, complex **7** slowly isomerises to a mixture of *cis* and *trans* isomers (*cis:trans* = 15:85 in $CDCl_3$).

Analytical data for trans-7. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.51 (dd, *J* = 10.4 Hz, 1.2 Hz, 1 H, CH_2), 3.55 (dd, *J* = 11.4 Hz, 2.3 Hz, 1 H, CH_2), 3.62 (s, 5 H, C_5H_5), 4.09 (dt, *J*' = 2.4 Hz, 1.1 Hz, 1 H, C_5H_3), 4.72 (tdd, *J* = 2.5 Hz, 1.3 Hz, 0.8 Hz, 1 H, C_5H_3), 4.89 (dd, *J*' = 2.7 Hz, 1.0 Hz, 1 H, C_5H_3), 7.34-7.62 (m, 12 H, PPh_2), 7.76-7.90 (m, 6 H, PPh_2), 8.35-8.42 (m, 2 H, PPh_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 151 MHz): δ 39.03 (d, $^1J_{PC}$ = 28 Hz, CH_2PPh_2), 66.07 (d, J_{PC} = 17 Hz, CH of C_5H_3), 70.56 (C_5H_5), 82.84 (dd, J_{PC} = 19 Hz, 2 Hz, CH of C_5H_3), 87.33 (d, $^2J_{PC}$ = 93 Hz, C^{ipso}-CO of C_5H_3), 90.34 (d, $^2J_{PC}$ = 10 Hz, C^{ipso}-Pd of C_5H_3), 127.43 (dd, J_{PC} = 45 Hz, 3 Hz, C^{ipso} of PPh_2), 128.55 (dd, J_{PC} = 36 Hz, 5 Hz, C^{ipso} of PPh_2), 128.92 (d, J_{PC} = 11 Hz, CH of PPh_2), 129.01 (d, J_{PC} = 10 Hz, CH of PPh_2), 129.35 (CH of PPh_2), 129.42 (d, J_{PC} = 2 Hz, CH of PPh_2), 130.31 (dd, J_{PC} = 36 Hz, 3 Hz, C^{ipso} of PPh_2), 130.97 (dd, J_{PC} = 9 Hz, 3 Hz, CH of PPh_2), 131.75 (d, $^4J_{PC}$ = 1 Hz, CH^{para} of PPh_2), 131.83 (CH^{para} of PPh_2), 131.84 (d, $^4J_{PC}$ = 2 Hz, CH^{para} of PPh_2), 132.10 (d, $^4J_{PC}$ = 3 Hz, CH^{para} of PPh_2), 132.27 (dd, J_{PC} = 41 Hz, 3 Hz, C^{ipso} of PPh_2), 133.08 (dd, J_{PC} = 12 Hz, 2 Hz, CH of PPh_2), 133.93 (dd, J_{PC} = 12 Hz, 2 Hz, CH of PPh_2), 135.04 (dd, J_{PC} = 14 Hz, 2 Hz, CH of PPh_2), 178.75 (dd, J_{PC} = 15 Hz, 4 Hz, CH_2COOPd), 205.66 (d, $^1J_{PC}$ = 29 Hz, CO-PPh_2). A signal due to one CH of C_5H_3 overlaps with the solvent resonance. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ 10.3 (d, $^2J_{PP}$ = 376 Hz, CH_2PPh_2), 34.0 (d, $^2J_{PP}$ = 376 Hz, $COPPh_2$). IR (DRIFTS, KBr): ν_{max} 3056 br w, 1735 w, 1644 s (ν_{CO}), 1640 s (ν_{CO}), 1634 vs (ν_{CO}), 1571 w, 1484 w, 1437 m, 1412 m, 1389 w, 1286 m, 1250 m, 1188 m, 1156 w, 1104 m, 1029 w, 1024 w, 999 m, 968 w, 902 m, 840 m, 821 m, 755 m, 745 m, 714 w, 701 m, 695 m, 621 w, 592 m, 580 w, 526 m, 509 m, 493 m, 457 m, 442 w, 436 w cm^{-1}. ESI-MS: *m/z* 747 ($[M + H]^+$), 769 ($[M + Na]^+$). Anal. Calc. for $C_{37}H_{30}FeO_3P_2Pd$ (746.8): C 59.50, H 4.05%. Found: C 59.26, H 3.88%.

Analytical data for cis-7. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.06 (s, 5 H, C_5H_5), 4.97-5.00 (m, 1 H, C_5H_3), 5.03-5.06 (m, 1 H, C_5H_3), 5.69-5.72 (m, 1 H, C_5H_3); only diagnostic signals. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz): δ 4.7 (d, $^{2}J_{PP}$ = 22 Hz, CH_2PPh_2), 54.6 (d, $^{2}J_{PP}$ = 22 Hz, $COPPh_2$).



cis- and *trans*-**3a** *cis*-**8a**

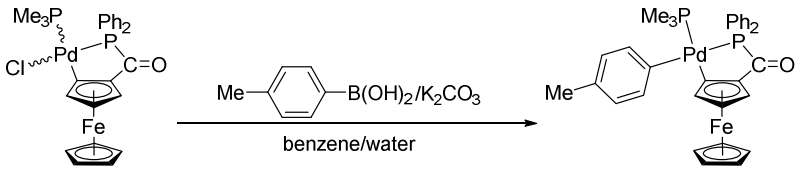
Synthesis of 8a. In air, methylboronic acid (15 mg, 0.25 mmol, 5 equiv.) and potassium *tert*-butoxide (22 mg, 0.20 mmol, 4 equiv.) were dissolved in reagent-grade benzene (5 mL), and the mixture stirred at room temperature for 1 hour. Subsequently, solid **3a** (31 mg, 0.050 mmol) was added, and the resulting mixture was stirred for another 24 h. Then, the reaction mixture was filtered through a PTFE syringe (0.45 μm pore size) and evaporated. The solid residue was extracted with diethyl ether and filtered again through the syringe filter to remove boronate residua. The filtrate was concentrated and cooled to 4 °C in a fridge. Purple crystals, which separated, were isolated by suction, washed with cold pentane and dried under vacuum. Yield of **8a**: 11 mg (37%). Crystals suitable for X-ray analysis were obtained by cooling a hexane solution of the complex. Crystallisation exclusively provides the *cis* isomer, which slowly isomerises and converts back to the starting complex **3a** in a chloroform solution.

Note: the compound decomposes on silica gel and alumina and, therefore, cannot be purified by chromatography. The rather low yield of **8a** is due to the high solubility of this compound in diethyl ether and pentane. The attempt to synthesize **8a** through the reaction of **3a** with methylboronic acid and K_2CO_3 in benzene/water at room temperature (*i.e.*, by applying the conditions used to prepare the aryl complexes mentioned below) afforded less than 5% of the product. The reaction of **3a** with 2 equiv. of $MeB(OH)_2$ and 1.8 equiv. KO*t*-Bu in benzene for 3 h resulted in only 24% conversion, as shown by NMR analysis. Hence, the amounts of reagents were increased and the reaction time was extended to achieve full conversion.

Analytical data for cis-8a. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.68 (dd, J_{PH} = 8.5 Hz, 6.6 Hz, 3 H, Me-Pd), 1.21 (d, $^{2}J_{PH}$ = 7.8 Hz, 9 H, PMe_3), 3.83 (s, 5 H, C_5H_5), 4.92-4.95 (m, 2 H, C_5H_3), 5.12 (dt, J' = 2.2 Hz, 1.3 Hz, 1 H, C_5H_3), 7.28-7.35 (m, 3 H, PPh_2), 7.45-7.52 (m, 2 H, PPh_2), 7.53-7.58 (m, 3 H, PPh_2), 8.02-8.09 (m, 2 H, PPh_2). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz): δ 1.00 (dd, J_{PC} = 93 Hz, 10 Hz, Me-Pd), 15.81 (dd, J_{PC} = 24 Hz, 3 Hz, PMe_3), 67.66 (dd, J_{PC} = 14 Hz, 5 Hz, CH of C_5H_3), 69.46 (C_5H_5), 77.56 (d, J_{PC} = 7 Hz, CH of C_5H_3), 88.08 (dd, J_{PC} = 87 Hz, 3 Hz, C^{ipso}-CO of C_5H_3), 102.73 (dd, J_{PC} = 135 Hz, 15 Hz, C^{ipso}-Pd of C_5H_3), 128.49 (d, J_{PC} = 9 Hz, CH of PPh_2), 128.54 (d, J_{PC} = 9 Hz, CH of PPh_2), 129.67 (d, $^{4}J_{PC}$ = 2 Hz, CH^{para} of PPh_2), 130.22 (d, $^{1}J_{PC}$ = 26 Hz, C^{ipso} of PPh_2), 131.14 (d, $^{4}J_{PC}$ = 2 Hz, CH^{para} of PPh_2), 132.77 (d, J_{PC} = 13 Hz, CH of PPh_2), 133.11 (d, $^{1}J_{PC}$ = 27 Hz, C^{ipso} of PPh_2), 134.75

(d, J_{PC} = 13 Hz, CH of PPh_2), 212.59 (dd, J_{PC} = 21 Hz, 7 Hz, CO).One signal CH of C_5H_3 was overlapped by $CDCl_3$. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ –18.6 (d, $^2J_{PP}$ = 26 Hz, PMe_3), 38.1 (d, $^2J_{PP}$ = 26 Hz, PPh_2). IR (DRIFTS, KBr): ν_{max} 3051 w, 2972 w, 2904 w, 1661 w (ν_{CO}), 1646 m (ν_{CO}), 1628 s (ν_{CO}), 1482 w, 1436 m, 1432 m, 1421 w, 1413 w, 1403 m, 1386 w, 1360 w, 1348 w, 1316 w, 1284 w, 1246 m, 1180 w, 1147 w, 1134 w, 1106 w, 1098 m, 1059 w, 1024 w, 1009 w, 998 w, 956 s, 854 w, 822 m, 755 m, 746 m, 735 m, 706 m, 698 m, 676 w, 620 w, 590 m, 519 w, 500 m, 489 m, 472 m, 434 m cm^{-1}. ESI-MS: *m/z* 594 (M^+), 617 ($[M + Na]^+$). Anal. Calc. for $C_{27}H_{30}FeOP_2Pd$ (594.7): C 54.53, H 5.08%. Found: C 54.38, H 4.86%.

Analytical data for trans-8a. ^1H NMR ($CDCl_3$, 400 MHz): δ –0.13 (dd, J_{PH} = 7.4 Hz, 4.9 Hz, 3 H, Me-Pd), 1.63 (dd, J_{PH} = 8.5, 2.3 Hz, 9 H, PMe_3), 3.78 (s, 5 H, C_5H_5); only diagnostic signals are given. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ –13.8 (d, $^2J_{PP}$ = 435 Hz, PMe_3), 46.3 (d, $^2J_{PP}$ = 435 Hz, PPh_2).

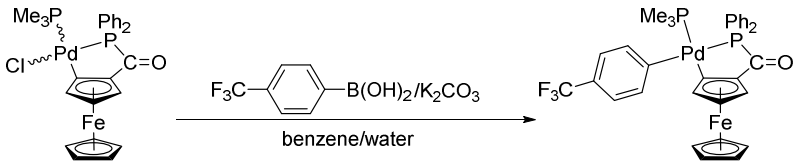


cis- and *trans*-**3a** *cis*-**8b**

Synthesis of 8b. In air, complex **3a** (62 mg, 0.10 mmol), 4-tolylboronic acid (21 mg, 0.15 mmol, 1.5 equiv.) and potassium carbonate (28 mg, 0.20 mmol, 2 equiv.) were mixed in benzene/water (1:1, 6 mL each), and the reaction mixture was stirred at room temperature for 1 h. The organic layer was separated, dried over anhydrous magnesium sulfate and evaporated. The glassy residue was dissolved in hexane-ethyl acetate (3:1) and filtered through a short silica gel column, eluting with the same solvent mixture. The main purple band was collected and evaporated to afford *cis*-**8b** as violet solid. Yield 50 mg (75%). Crystals suitable for X-ray diffraction analysis were obtained from hexane/ ethyl acetate. The compound is isolated as the *cis* isomer and does not isomerise or decompose in a chloroform solution, even after 30 hours.

^1H NMR ($CDCl_3$, 400 MHz): δ 1.05 (d, $^2J_{PH}$ = 8.1 Hz, 9 H, PMe_3), 2.32 (s, *Me*-C_6H_4), 3.84 (s, 5 H, C_5H_5), 3.89 (apparent p, *J'* = 1.1 Hz, 1 H, C_5H_3), 4.72 (apparent p, *J'* = 2.2 Hz, 1 H, C_5H_3), 4.85 (apparent p, *J'* = 1.2 Hz, 1 H, C_5H_3), 6.96 (br d, *J* = 7.5 Hz, 1 H, C_6H_4), 7.03 (br d, *J* = 7.5 Hz, 1 H, C_6H_4), 7.32-7.42 (m, 2 H of PPh_2 and 2H of C_6H_4), 7.52-7.63 (m, 6 H, PPh_2), 8.13-8.19 (m, 2 H, PPh_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 15.80 (dd, J_{PC} = 25 Hz, 3 Hz, PMe_3), 21.10 (*Me*-C_6H_4), 66.80 (dd, J_{PC} = 14 Hz, 5 Hz, CH of C_5H_3), 69.40 (C_5H_5), 78.17 (d, J_{PC} = 7 Hz, CH of C_5H_3), 82.61 (d, J_{PC} = 2 Hz, CH of C_5H_3), 87.68 (dd, J_{PC} = 88 Hz, 4 Hz, C^{ipso}-CO of C_5H_3), 103.75 (dd, J_{PC} = 130 Hz, 15 Hz, C^{ipso}-Pd of C_5H_3), 127.40 (dd, J_{PC} = 7 Hz, 2 Hz, CH of C_6H_4), 127.90 (dd, J_{PC} = 7 Hz, 2 Hz, CH of C_6H_4), 128.57 (d, J_{PC} = 9 Hz, CH of PPh_2), 128.62 (d, J_{PC} = 9 Hz, CH of PPh_2), 129.65 (d, $J_{PC} \approx$ 28 Hz, C^{ipso} of PPh_2), 129.79 (d, $^4J_{PC}$ = 2 Hz, CH^{para} of PPh_2), 130.86 (br s, C^{ipso}-Me of C_6H_4), 131.33 (d, $^4J_{PC}$

= 2 Hz, CH^{para} of PPh_2), 132.71 (d, J_{PC} = 13 Hz, CH of PPh_2), 132.85 (d, J_{PC} = 28 Hz, C^{ipso} of PPh_2), 134.88 (d, J_{PC} = 13 Hz, CH of PPh_2), 135.97 (dd, J_{PC} = 4 Hz, 2 Hz, CH of C_6H_4), 137.10 (apparent t, J_{PC} = 3 Hz, CH of C_6H_4), 163.16 (dd, J_{PC} = 115 Hz, 16 Hz, C^{ipso}-Pd of C_6H_4), 212.09 (dd, J_{PC} = 22 Hz, 6 Hz, CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ –22.0 (d, $^2J_{PP}$ = 26 Hz, PMe_3), 39.4 (d, $^2J_{PP}$ = 26 Hz, PPh_2). IR (DRIFTS, KBr): ν_{max} 2993 w, 2905 w, 1660w (ν_{CO}), 1644 m (ν_{CO}), 1633 s (ν_{CO}), 1479 m, 1435 m, 1417 w, 1398 m, 1384 w, 1355 w, 1347 w, 1306 w, 1285 m, 1242 m, 1148 w, 1105 w, 1093 m, 1054 w, 1049 w, 1026 w, 1015 w, 999 w, 951 s, 848 w, 837 w, 823 m, 811 m, 799 m, 750 m, 713 w, 698 s, 618 w, 598 w, 580 w, 523 w, 499 s, 487 m, 461 m, 439 w cm^{-1}. ESI-MS: *m/z* 670 (M^+). Anal. Calc. for $C_{33}H_{34}FeOP_2Pd$ (670.84): C 59.08, H 5.11%. Found: C 58.87, H 5.11%.

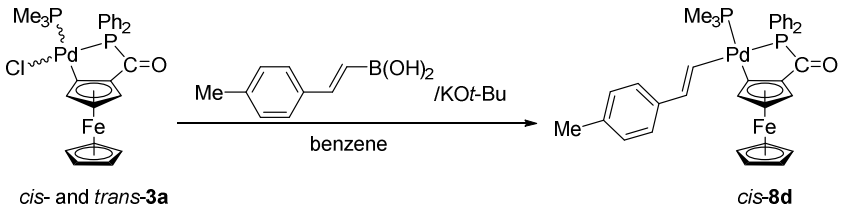


cis- and *trans*-**3a** *cis*-**8c**

Synthesis of 8c. In air, complex **3a** (31 mg, 0.050 mmol), 4-(trifluoromethyl)phenyl-boronic acid (15 mg, 0.075 mmol, 1.5 equiv.) and potassium carbonate (14 mg, 0.10 mmol, 2 equiv.) were dissolved in a mixture of benzene and water (3 mL each), and the resulting mixture was stirred at room temperature for 2 h. The organic phase was separated, dried over magnesium sulfate and evaporated. The glassy residue was purified by flash chromatography over silica gel using hexane-ethyl acetate (5:1). The main purple band was collected and evaporated to give *cis*-**8c** as violet solid. Yield: 25 mg (69%). The compound is obtained as pure *cis* isomer, which does not isomerise or decompose in chloroform solution, even after 24 hours. *Note*: shorter reaction times result in incomplete consumption of the starting material (80% after 1 h).

^1H NMR ($CDCl_3$, 400 MHz): δ 1.03 (d, $^2J_{PH}$ = 8.1 Hz, 9 H, PMe_3), 3.77 (d of vt, *J'* = 2.3 Hz, 1.2 Hz, 1 H, C_5H_3), 3.84 (s, 5 H, C_5H_5), 4.74 (d of vt, *J'* = 4.2 Hz, 2.3 Hz, 1 H, C_5H_3), 4.87 (apparent p, *J'* = 1.2 Hz, 1 H, C_5H_3), 7.32-7.42 (m, 3 H of PPh_2 and 2 H of C_6H_4), 7.52-7.66 (m, 5 H, PPh_2), 7.66-7.72 (m, 1 H, C_6H_4), 7.80-7.85 (m, 1 H, C_6H_4), 8.12-8.19 (m, 2 H, PPh_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 15.66 (dd, J_{PC} = 26 Hz, 3 Hz, PMe_3), 66.94 (dd, J_{PC} = 15 Hz, 4 Hz, CH of C_5H_3), 69.46 (C_5H_5), 78.16 (d, J_{PC} = 7 Hz, CH of C_5H_3), 82.19 (d, J_{PC} = 2 Hz, CH of C_5H_3), 87.41 (dd, J_{PC} = 87 Hz, 3 Hz, *C*^{ipso}-CO of C_5H_3), 102.67 (dd, J_{PC} = 127 Hz, 14 Hz, *C*^{ipso}-Pd of C_5H_3), 122.26 (dqd, *J* = 7 Hz, 3 Hz, 1 Hz, CH of C_6H_4), 122.80 (dqd, *J* = 7 Hz, 4 Hz, 2 Hz, CH of C_6H_4), 124.46 (q, $^2J_{FC}$ = 31 Hz, *C*^{ipso}-CF_3 of C_6H_4), 125.43 (q, $^1J_{FC}$ = 271 Hz, CF_3), 128.70 (d, J_{PC} = 9 Hz, CH of PPh_2), 128.74 (d, J_{PC} = 10 Hz, CH of PPh_2), 129.09 (d, J_{PC} = 29 Hz, C^{ipso} of PPh_2), 130.04 (d, $^4J_{PC}$ = 2 Hz, CH^{para} of PPh_2), 131.58 (d, $^4J_{PC}$ = 2 Hz, CH^{para} of PPh_2), 132.37 (d, J_{PC} = 30 Hz, C^{ipso} of PPh_2), 132.66 (d, J_{PC} = 13 Hz, CH of PPh_2), 134.85 (d, J_{PC} = 13 Hz, CH of PPh_2), 136.13 (dd, J_{PC} = 4 Hz, 2 Hz, CH of C_6H_4), 137.88 (dd, J_{PC} = 3 Hz, 2 Hz, CH of C_6H_4), 175.78 (dd, J_{PC} = 114 Hz, 15 Hz, C^{ipso}-Pd of C_6H_4), 211.44 (dd, J_{PC} = 22 Hz, 6 Hz,

CO). $^{19}F\{^1H\}$ NMR ($CDCl_3$, 376 MHz): δ –61.74 (s, CF_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ –22.5 (dq, J = 27 Hz, 2 Hz, PMe_3), 39.9 (d, $^2J_{PP}$ = 27 Hz, PPh_2). IR (DRIFTS, KBr): ν_{max} 3076 w, 3059 w, 2908 w, 1632 s (ν_{CO}), 1583 m, 1481 w, 1437 m, 1402 m, 1385 m, 1359 w, 1347 w, 1323 s, 1286 w, 1245 w, 1182 w, 1152 m, 1107 s, 1094 m, 1071 s, 1026 w, 1011 m, 952 m, 848 w, 821 m, 748 m, 732 m, 716 w, 692 m, 675 w, 618 w, 589 m, 518 w, 490 m, 466 m, 452 w, 442 w, 429 w cm^{-1}. ESI-MS: *m/*: 725 ($[M + H]^+$). Anal. Calc. for $C_{33}H_{31}F_3FeOP_2Pd$ (724.81): C 54.68, H 4.31%. Found: C 54.60, H 4.09%.



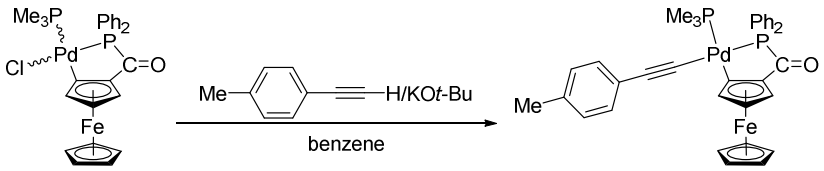
cis- and *trans*-**3a** *cis*-**8d**

Synthesis of 8d. In air, *trans*-2-(4-methylphenyl)vinylboronic acid (42 mg, 0.25 mmol, 5 equiv.) and potassium *tert*-butoxide (22 mg, 0.20 mmol, 4 equiv.) were dissolved in reagent-grade benzene (5 mL), and the mixture was stirred at room temperature for 1 h. Solid **3a** (31 mg, 0.050 mmol) was added, continuously stirring for another 2 h. The mixture was then mixed with little Celite and filtered through a PTFE syringe filter. The filtrate was evaporated with Celite. The preadsorbed crude product was washed successively with diethyl ether (15 mL) and with dichloromethane (10 mL). The ethereal washing was concentrated under reduced pressure (to ca. 1 mL) and added dropwise into warm hexane (10 mL). Purple crystals, which separated overnight, were isolated by suction, washed with pentane and dried under vacuum, providing another 5.7 mg of the complex. The dichloromethane washing containing most of the product was evaporated to give 17 mg of pure product. Combined yield of *cis*-**8d**: 22.7 mg (65%). The crystals used for structure determination were selected from the preparative batch (diethyl ether/hexane). The compound is obtained as pure *cis* isomer, which decomposes in $CDCl_3$, regenerating the starting complex **3a** (about 85% of **3a** is formed within 24 h).

Note: the analogous reaction of **3a** with 1.5 equiv. of boronic acid and 2 equiv. of K_2CO_3 in benzene/water resulted in 60% conversion after 1 or 3 h. Attempts to isolate the product from the reaction mixture were unsuccessful because the styryl complex **8d** decomposes on silica gel and is similarly soluble as the starting material **3a**. Increasing the amounts of reagents to 5 equiv. (both the boronic acid and the base) increased the conversion only to 83%.

^1H NMR ($CDCl_3$, 400 MHz): δ 1.21 (d, $^2J_{PH}$ = 8.1 Hz, 9 H, PMe_3), 2.35 (s, 3 H, *Me*-C_6H_4), 3.89 (s, 5 H, C_5H_5), 4.85 (qd, J' = 2.3 Hz, 1.7 Hz, 1 H, C_5H_3), 4.91 (apparent p, J' = 1.2 Hz, 1 H, C_5H_3), 4.97 (apparent p, J' = 1.2 Hz, 1 H, C_5H_3), 6.78 (ddd, J = 17.4 Hz, 9.4 Hz, 1.9 Hz, 1 H, CH=), 7.14 (br s, 1 H, CH of C_6H_4), 7.16 (br s, 1 H, CH of C_6H_4), 7.32-7.37 (m, 3 H of PPh_2, 2 H of CH of C_6H_4), 7.49-7.61 (m, 5 H, PPh_2), 8.07-8.12 (m, 2 H, PPh_2), 8.24 (ddd, J = 17.4 Hz, 7.5 Hz, 5.7 Hz, 1 H, CH=). $^{31}P\{^1H\}$

NMR ($CDCl_3$, 162 MHz): δ –21.2 (d, $^2J_{PP}$ = 26 Hz, PMe_3), 39.5 (d, $^2J_{PP}$ = 26 Hz, PPh_2). IR (DRIFTS, KBr): ν_{max} 3092 w, 3047 w, 2966 w, 2952 w, 2916 w, 1662 w (ν_{CO}), 1633 s (ν_{CO}), 1548 w, 1507 w, 1482 w, 1436 m, 1419 m, 1403 m, 1383 w, 1358 w, 1347 w, 1305 w, 1284 w, 1271 w, 1246 m, 1181 w, 1155 w, 1147 w, 1099 m, 1050 w, 1023 w, 999 w, 974 m, 951 s, 851 w, 839 m, 824 m, 815 m, 770 w, 749 m, 734 w, 719 w, 695 m, 619 w, 590 m, 578 w, 519 m, 500 s, 487 m, 469 m, 442 m, 432 w cm^{-1}. ESI-MS: *m/z* 696 (M^+). Anal. Calc. for $C_{35}H_{36}FeOP_2Pd$ (696.9): C 60.32, H 5.21%. Found: C 60.04, H 5.09%.



cis- and *trans*-**3a** *cis*-**8e**

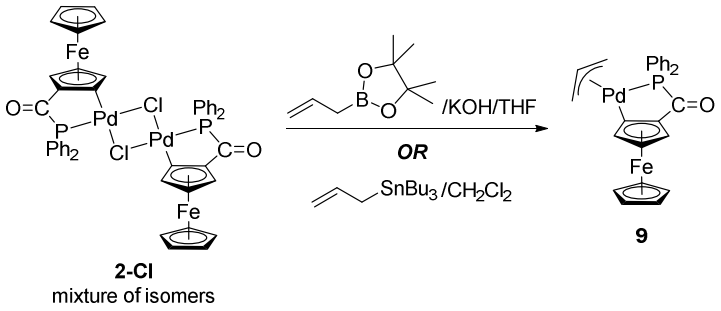
Synthesis of 8e. In air, 4-ethynyltoluene (13 μL, 0.10 mmol, 2 equiv.) and potassium *tert*-butoxide (6.7 mg, 0.060 mmol, 1.2 equiv.) were mixed in reagent-grade benzene (2 mL), and the mixture was stirred at room temperature for 1 h. Complex **3a** (31 mg, 0.050 mmol) was added, and the resulting mixture was stirred for another 2 h. After this period, the reaction mixture was diluted with benzene (3 mL) and water (5 mL), vigorously stirring for 2 min. Then, the benzene layer was separated, dried over magnesium sulfate, and evaporated (*Note:* NMR analysis showed traces of starting material and approximately 95% product purity). The solid residue was taken up with dichloromethane (about 0.5 mL) and added into warm hexane (10 mL). The mixture was slowly cooled to 4 °C, and the separated, dark purple crystals were filtered off, washed with cold pentane and dried under vacuum. Yield of *cis*-**8e**: 13.7 mg (40%), red solid.

Crystallisation produces pure *cis*-**8e**, while *trans*-**8e** concentrates in the mother liquor. Chromatography over silica gel cannot be used to separate the isomers due to partial decomposition. The *cis* isomer slowly isomerises and decomposes in a chloroform solution. As shown by ^{31}P NMR,the sample dissolved in standard $CDCl_3$ contained *cis*-**8e** (84%), *trans*-**8e** (10%) and **3a** (6%) after 30 h; *cis*-**8e** (64%), *trans*-**8e** (22%) and **3a** (14%) after 4 days, and *cis*-**8e** (40%), *trans*-**8e** (18%) and **3a** (41%) after 14 days (see Figures S5 and S6).

Analytical data for cis-8e. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.34 (d, $^2J_{HP}$ = 8.8 Hz, 9 H, PMe_3), 2.34 (s, 3 H, *Me*-C_6H_4), 3.88 (s, 5 H, C_5H_5), 4.93 (apparent p, *J'* = 1.3 Hz, 1 H, C_5H_3), 5.00 (apparent p, *J'* = 2.2 Hz, 1 H, C_5H_3), 5.61 (dq, *J'* = 1.6 Hz, 1.1 Hz, 1 H, C_5H_3), 7.07 (br s, 1 H, CH of C_6H_4), 7.09 (br s, 1 H, CH of C_6H_4), 7.32-7.42 (m, 3 H of PPh_2, 2 H of CH of C_6H_4), 7.48-7.55 (m, 2 H, PPh_2), 7.59-7.63 (m, 3 H, PPh_2), 8.09-8.15 (m, 2 H, PPh_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 16.33 (dd, J_{PC} = 27 Hz, 2 Hz, PMe_3), 21.34 (*Me*-C_6H_4), 66.52 (dd, J_{PC} = 17 Hz, 5 Hz, CH of C_5H_3), 70.02 (C_5H_5), 78.42 (d, J_{PC} = 8 Hz, CH of C_5H_3), 83.90 (d, J_{PC} = 4 Hz, CH of C_5H_3), 85.82 (dd, J_{PC} = 92 Hz, 3 Hz, C^{ipso}-CO of C_5H_3), 100.92 (dd, J_{PC} = 137 Hz, 12 Hz, C^{ipso}-Pd of C_5H_3), 108.67 (d, $^3J_{PC}$ = 30 Hz, ≡*C*-C_6H_4), 113.55 (dd, J_{PC}

= 140 Hz, 27 Hz, ≡*C*-Pd), 125.04 (apparent t, J_{PC} = 2 Hz, C^{ipso}-C≡ of C_6H_4), 128.04 (d, J_{PC} = 36 Hz, C^{ipso} of PPh_2), 128.69 (CH of C_6H_4), 128.74 (d, J_{PC} = 10 Hz, CH of PPh_2), 128.80 (d, J_{PC} = 10 Hz, CH of PPh_2), 130.49 (d, $^4J_{PC}$ = 2 Hz, CH^{para} of PPh_2), 131.17 (br s, CH of C_6H_4), 131.36 (dd, J_{PC} = 37 Hz, 2 Hz, C^{ipso} of PPh_2), 131.86 (d, $^4J_{PC}$ = 2 Hz, CH^{para} of PPh_2), 132.76 (d, J_{PC} = 13 Hz, CH of PPh_2), 134.77 (d, J_{PC} = 13 Hz, CH of PPh_2), 135.11 (C^{ipso}-Me of C_6H_4), 209.73 (dd, J_{PC} = 27 Hz, 5 Hz, CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ –20.4 (d, $^2J_{PP}$ = 29 Hz, PMe_3), 45.8 (d, $^2J_{PP}$ = 29 Hz, PPh_2). IR (DRIFTS, KBr): ν_{max} 3072 w, 3014 w, 2986 w, 2902 w, 2100 m ($\nu_{C\equiv C}$), 1625 m (ν_{CO}), 1586 w, 1505 m, 1477 w, 1435 w, 1423 m, 1398 m, 1361 w, 1349 w, 1304 w, 1282 w, 1246 m, 1213 w, 1183 w, 1155 w, 1106 w, 1097 m, 1026 w, 1000 m, 962 s, 957 s, 907 w, 857 m, 836 m, 818 s, 745 m, 716 w, 696 s, 621 w, 590 m, 581 w, 524 s, 501 m, 490 s, 462 m, 453 m, 443 w, 429 m cm^{-1}. ESI-MS: *m/z* 579 ($[M - C\equiv C–C_6H_4Me]^+$). Anal. Calc. for $C_{35}H_{34}FeOP_2Pd$·0.2Hexane (712.1): C 61.06, H 5.21%. Found: C 61.01, H 5.26%.

Analytical data for trans-8e. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.81 (dd, $^2J_{HP}$ = 9.5 Hz, 2.5 Hz, 9 H, PMe_3), 2.27 (s, 3 H, *Me*-C_6H_4), 3.86 (s, 5 H, C_5H_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ –15.5 (d, $^2J_{PP}$ = 430 Hz, PMe_3), 40.8 (d, $^2J_{PP}$ = 430 Hz, PPh_2).



Synthesis of 9. ***Method A.*** In air, dry THF (2 mL) and allylboronic acid pinacol ester (11.6 µl, 0.060 mmol) were added successively to finely ground KOH (6.7 mg, 0.12 mmol) in a small reaction flask. After stirring for 15 min, **2-Cl** (32 mg, 0.030 mmol) was added into the mixture using dry THF (3 mL). The resulting mixture was stirred for 4 h, filtered through a PTFE syringe filter and evaporated. The solid residue was dissolved in diethyl ether (5 mL) and washed with 10% KF in 10 % aqueous ammonia (2× 5 mL). The organic layer was separated, dried over anhydrous magnesium sulfate and evaporated. The residue was dissolved in hot hexane (5 ml) and cooled slowly down to –18 °C. Purple crystals formed during several days were isolated by suction, washed with cold pentane and dried under vacuum. Yield of **9**: 10 mg (31%), purple crystalline solid. The compound is a mixture of isomers differing in the orientation of the allyl moiety with respect to the rest of molecule.

Method B. Complex **2-Cl** (27 mg, 0.025 mmol) and allyltributylstannane (17 mg, 0.050 mmol, 2 equiv.) were dissolved in dry dichloromethane (5 mL), and the solution was stirred at room temperature for 8 h. Tetrabutylammonium fluoride (0.10 ml of 1 M solution in THF, 0.10 mmol,

4 eq.) was added, and the mixture was stirred for another 30 minutes before evaporating. The oily residue was diluted with diethyl ether (5 mL) and washed with 10% KF in 10% aqueous ammonia (2× 5 mL; *Note:* a white solid separated in aqueous phase). The organic layer was dried over $MgSO_4$ and evaporated. The crude product was crystallised by dissolving it in hot hexane (5 mL) and slowly cooling the solution to –18 °C. The resulting purple crystals were isolated by suction, washed with cold pentane and dried under vacuum. Yield of **9**: 9.2 mg (34 %). The compound contains traces of tributylstannyl compounds. *Note:* the yield of **9** is low due to problems in removing residual organotin compounds. Because the compound decomposes on silica gel, crystallisation remains the only efficient purification method. Attempts to prepare **9** by reacting **2-Cl** with allyl magnesium bromide only led to **4a** (*via* halogen exchange).

Analytical data for the major isomer. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.79 (d, *J* = 13.5 Hz, 1 H, CH of C_3H_5), 3.14 (ddq, *J* = 13.2 Hz, 9.6 Hz, 1.1 Hz, 1 H, CH of C_3H_5), 3.86 (s, 5 H, C_5H_5), 4.08-4.28 (m, 2 H, C_3H_5), 4.91-4.93 (m, 1 H, C_5H_3), 4.96-4.99 (m, 2 H, C_5H_3), 5.35 (tt, *J* = 13.3 Hz, 7.4 Hz, 1 H, CH of C_3H_5), 7.26-7.35 (m, 3 H, PPh_2), 7.48-7.58 (m, 5 H, PPh_2), 8.10-8.16 (m, 2 H, PPh_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ 46.6 (s).

Analytical data for minor isomer. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.55 (d, *J* = 13.6 Hz, 1 H, CH of C_3H_5), 3.21 (ddq, *J* = 13.3 Hz, 9.3 Hz, 1.1 Hz, 1 H, CH of C_3H_5), 3.77 (s, 5 H, C_5H_5), 4.08-4.27 (m, 2 H, C_3H_5), 4.89-4.99 (m, 3 H, C_5H_3), 5.46 (tt, *J* = 13.4 Hz, 7.5 Hz, 1 H, CH of C_3H_5), 7.26-7.35 (m, 3 H, PPh_2), 7.48-7.58 (m, 3 H, PPh_2), 7.60-7.66 (m, 2 H, PPh_2), 7.95-8.06 (m, 2 H, PPh_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ 45.9 (s).

Analytical data for the mixture of isomers. IR (DRIFTS, KBr): ν_{max} 3077 w, 3065 w, 2963 w, 1647 s (ν_{CO}), 1636 s (ν_{CO}), 1584 w, 1479 w, 1435 s, 1402 m, 1385 w, 1358 w, 1347 w, 1307 w, 1242 m, 1184 w, 1158 w, 1149 w, 1100 m, 1071 w, 1024 w, 999 m, 969 w, 959 w, 857 w, 837 w, 822 m, 749 m, 718 w, 700 s, 691 m, 619 w, 611 w, 587 m, 527 m, 490 s, 459 m, 430 m cm^{-1}. ESI-MS analyses did not provide any consistent results. Anal. Calc. for $C_{26}H_{23}FeOPPd$ (544.7): C 57.33, H 4.26%. Found: C 57.69, H 4.45%.

X-Ray crystallography

Diffraction data were collected on a Bruker D8 VENTURE Kappa Duo diffractometer equipped with a PHOTON detector and a Cryostream Cooler (Oxford Cryosystems), using Mo Kα radiation (λ = 0.71073 Å). The structures were solved using direct methods (SHELXT-2014[5]) and subsequently refined by full-matrix least-squares routine based on F^2 (SHELXL-2014 or 2017[6]). The nonhydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in their theoretical positions with their U_{iso}(H) assigned to a multiple of U_{eq}(C) (1.2-times for CH and CH_2 hydrogens, 1.5-times for methyl groups).

The solvent molecules in the structures of **2-Cl**·AcOEt and **2-Br**·PhMe were disordered around the crystallographic inversion centers and could not be satisfactorily included in the structure model. Therefore, their contribution to the overall scattering was numerically eliminated using PLATON SQUEEZE.[7] In both cases, the count of "removed" electrons (51 and 47) matched the expected values (48 and 50, respectively). In the case of *trans*-**3b**·PhMe, four disordered molecules of toluene per the unit cell were treated similarly (monoclinic space group $P2_1/n$, $Z = 4$, 216 electrons removed, 200 electrons expected). Lastly, the phenyl rings and trimethylphosphine ligand in the structure of *cis*-**8e** were disordered and had to be modelled over two positions with a refined 58:42 ratio (displacement parameters were kept the same for the pairs of analogous atoms in this case). A similar approach was applied to the disordered η^3-allyl ligand in the structure of **9**. The refined occupancies were 57:43.

Relevant crystallographic data and refinement parameters are presented in Table S1. All geometric data and structural diagrams were obtained using a recent version of the PLATON program.[8] The numerical values were rounded to one decimal place with respect to the respective estimated standard deviations (ESDs).

Complete crystallographic data were deposited with the Cambridge Crystallographic Data Centre and can be obtained free of charge at www.ccdc.cam.ac.uk/data_request/cif or on request, or by email at data_request@ccdc.cam.ac.uk or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033. Deposition numbers are quoted in Table S1.

Table S1 Selected crystallographic data and structure refinement parameters[a]

Compound	**1**	**1O**	**1S**	**1Se**
Formula	$C_{23}H_{19}FeOP$	$C_{23}H_{19}FeO_2P$	$C_{23}H_{19}FeOPS$	$C_{23}H_{19}FeOPSe$
M	398.20	414.20	430.26	477.16
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)
T [K]	150(2)	150(2)	120(2)	150(2)
a [Å]	9.6059(3)	9.7147(3)	9.4321(4)	9.5729(6)
b [Å]	12.8591(4)	8.3983(2)	24.1340(8)	24.366(2)
c [Å]	14.7624(5)	22.3979(7)	9.3836(3)	9.3510(6)
α [°]				
β [°]	93.313(1)	91.870(1)	116.498(1)	116.444(2)
γ [°]				
V [Å]^3	1820.5(1)	1826.40(9)	1911.6(1)	1952.9(2)
Z	4	4	4	4
μ(Mo Kα) [mm^{-1}]	0.925	0.929	0.992	2.728
Diffrns collected	26493	34300	19713	66100
Independent diffrns	4190	4184	4383	4469
Observed[a] diffrns	3777	3987	4052	4294
R_{int}[b] [%]	2.76	1.97	2.20	2.66
No. of parameters	235	244	244	244
R[b] obsd diffrns [%]	2.54	2.49	2.63	2.15
R, wR[b] all data [%]	2.98, 6.70	2.65, 6.45	2.96, 6.31	2.26, 5.12
Δρ [e Å^{-3}]	0.269, –0.418	0.336, –0.445	0.344, –0.357	0.368, –0.425
CCDC no.	2063464	2063465	2063466	2063467

[a] Diffractions with $I > 2\sigma(I)$. [b] Definitions: $R_{int} = \Sigma \left| F_o^2 - F_o^2(\text{mean}) \right| / \Sigma F_o^2$, where F_o^2(mean) is the average intensity of symmetry-equivalent diffractions. $R = \Sigma \left| \left| F_o \right| - \left| F_c \right| \right| / \Sigma \left| F_o \right|$, $wR = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma w(F_o^2)^2]^{1/2}$.

Table S1 continued

Compound	**2-Cl**·AcOEt	**2-Br**·PhMe	*cis*-**3a**·½AcOEt	*cis*-**4a**
Formula	$C_{50}H_{44}Cl_2Fe_2O_4P_2Pd$	$C_{53}H_{44}Br_2Fe_2O_2P_2Pd$	$C_{28}H_{31}ClFeO_2P_2Pd$	$C_{26}H_{27}BrFeOP_2Pd$
M	1166.19	1259.14	659.17	659.57
Crystal system	triclinic	triclinic	triclinic	monoclinic
Space group	*P*–1 (no. 2)	*P*–1 (no. 2)	*P*–1 (no. 2)	$P2_1/c$ (no. 14)
T [K]	120(2)	120(2)	120(2)	125(2)
a [Å]	8.5435(7)	8.6520(4)	9.7769(5)	14.3362(3)
b [Å]	9.9630(9)	9.9950(4)	12.7459(7)	18.9960(4)
c [Å]	14.303(1)	14.4343(6)	12.9436(7)	19.3060(4)
α [°]	108.712(3)	108.735(2)	111.318(2)	
β [°]	92.984(3)	95.248(2)	111.032(2)	104.219(1)
γ [°]	98.230(3)	97.272(2)	94.681(2)	
V [Å]^3	1135.0(2)	1160.93(9)	1360.2(1)	5096.5(2)
Z	1	1	2	8
μ(Mo Kα) [mm^{-1}]	1.640	3.206	1.434	2.985
Diffrns collected	22234	25301	24431	114697
Independent diffrns	5205	5317	6246	11702
Observed[a] diffrns	4575	4872	5896	10757
R_{int}[b] [%]	2.76	2.06	1.82	2.90
No. of parameters	253	253	347	583
R[b] obsd diffrns [%]	3.04	3.35	1.85	2.31
R, *wR*[b] all data [%]	3.70, 8.10	3.74, 8.61	2.02, 4.75	2.62, 5.93
Δρ [e Å^{-3}]	0.822, –1.192	1.806, –1.852	0.875, –0.400	1.480, –0.565
CCDC no.	2063468	2063469	2063470	2063471

Table S1 continued

Compound	*cis*-**5a**·½AcOEt	*trans*-**3b**·PhMe	*trans*-**3c**	*trans*-**3d**
Formula	$C_{28}H_{31}FeIO_2P_2Pd$	$C_{48}H_{41}ClFeOP_2Pd$	$C_{41}H_{51}ClFeOP_2Pd$	$C_{30}H_{28}ClFeN_2OPPd$
M	750.62	893.45	819.45	661.21
Crystal system	triclinic	monoclinic	triclinic	monoclinic
Space group	*P*–1 (no. 2)	$P2_1/n$ (no. 14)	*P*–1 (no. 2)	$P2_1/c$ (no. 14)
T [K]	120(2)	150(2)	120(2)	150(2)
a [Å]	9.7609(3)	17.1059(7)	10.4131(5)	15.5171(5)
b [Å]	9.8375(3)	10.5682(4)	13.2889(6)	16.0612(5)
c [Å]	15.1599(4)	23.8749(8)	13.9654(6)	10.5449(4)
α [°]	91.105(1)		98.020(2)	
β [°]	101.835(1)	106.820(1)	96.468(2)	96.740(1)
γ [°]	102.583(1)		103.875(2)	
V [Å]^3	1387.41(7)	4131.4(3)	1836.2(2)	2609.9(2)
Z	2	4	2	4
μ(Mo Kα) [mm^{-1}]	2.423	0.964	1.077	1.436
Diffrns collected	30143	90024	35664	53085
Independent diffrns	6336	12066	8469	5974
Observed[a] diffrns	6186	9912	7547	5772
R_{int}[b] [%]	1.73	4.32	2.62	1.88
No. of parameters	334	424	425	336
R[b] obsd diffrns [%]	1.51	2.80	2.17	2.32
R, *wR*[b] all data [%]	1.56, 3.62	4.16, 6.25	2.74, 5.22	2.40, 6.18
Δρ [e Å^{-3}]	0.711, –0.673	0.408, –0.664	0.454, –0.595	1.189, –0.403
CCDC no.	2063472	2063473	2063474	2063475

Table S1 continued

Compound	*trans*-**3e**·½PhMe	**6**	*trans*-**7**	*cis*-**8a**
Formula	$C_{47.5}H_{48}ClFeN_2OPPd$	$C_{28}H_{25}FeO_3PPd$	$C_{37}H_{30}FeO_3P_2Pd$	$C_{27}H_{30}FeOP_2Pd$
M	891.55	602.70	746.80	594.70
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	Cc (no. 9)	$P2_1/c$ (no. 14)
T [K]	120(2)	120(2)	120(2)	170(2)
a [Å]	18.0418(4)	11.161(2)	8.9972(4)	9.7651(4)
b [Å]	10.4741(3)	12.745(2)	38.285(2)	19.2606(7)
c [Å]	21.5596(4)	17.603(3)	9.9331(4)	14.2575(6)
α [°]				
β [°]	90.629(1)	104.674(6)	116.703(1)	108.071(2)
γ [°]				
V [Å]^3	4073.9(2)	2422.4(7)	3056.6(2)	2549.3(2)
Z	4	4	4	4
μ(Mo Kα) [mm^{-1}]	0.941	1.436	1.205	1.417
Diffrns collected	40502	36797	60869	133992
Independent diffrns	9190	5578	6933	5862
Observed[a] diffrns	7530	4981	6911	5691
R_{int}[b] [%]	5.58	5.55	2.12	2.87
No. of parameters	518	309	397	293
R[b] obsd diffrns [%]	3.39	3.66	1.64	1.87
R, *wR*[b] all data [%]	4.84, 7.03	4.23, 10.32	1.65, 4.11	1.94, 4.61
Δρ [e Å^{-3}]	0.460, –0.407	0.756, –1.654	0.382, –0.346	0.547, –0.349
CCDC no.	2063476	2063477	2063478	2063479

Table S1 continued

Compound	*cis*-**8b**	*cis*-**8d**	*cis*-**8e**	**9**
Formula	$C_{33}H_{34}FeOP_2Pd$	$C_{35}H_{36}FeOP_2Pd$	$C_{35}H_{34}FeOP_2Pd$	$C_{26}H_{23}FeOPPd$
M	670.79	696.83	694.81	544.66
Crystal system	monoclinic	monoclinic	triclinic	triclinic
Space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
T [K]	120(2)	120(2)	120(2)	150(2)
a [Å]	10.9479(4)	8.5031(3)	10.2842(5)	8.5645(2)
b [Å]	19.3440(7)	28.5338(9)	10.2936(6)	9.8056(3
c [Å]	13.8498(5)	13.2495(5)	15.968(1)	13.6065(4)
α [°]			97.438(3)	103.482(1)
β [°]	96.491(1)	105.104(1)	99.402(3)	101.283(1)
γ [°]			111.776(2)	95.979(1)
V [Å]^3	2914.3(2)	3103.6(2)	1515.0(2)	1076.19(5)
Z	4	4	2	2
μ(Mo Kα) [mm^{-1}]	1.249	1.176	1.205	1.599
Diffrns collected	32842	39118	69746	40266
Independent diffrns	6676	7108	6966	4937
Observed[a] diffrns	6139	6476	6398	4655
R_{int}[b] [%]	2.27	3.52	2.44	2.88
No. of parameters	347	365	435	299
R[b] obsd diffrns [%]	2.22	4.99	2.83	2.04
R, *wR*[b] all data [%]	2.57, 5.31	5.55, 11.42	3.18, 6.63	2.23, 4.95
Δρ [e Å^{-3}]	0.741, –0.542	2.450, –1.179	1.124, –1.421	0.545, –0.394
CCDC no.	2063480	2063481	2063482	2063483

STABILITY TESTS

A sample of **1** (0.1 mmol) was dissolved in a 1:1 mixture of the two solvents (5 mL), and the mixture was stirred for 72 h in air (in a closed vial) before evaporating under vacuum. In the case of the water/THF mixture, the reaction mixture was partitioned between ethyl acetate and brine, the organic phase was concentrated, and the residue analysed by ^{31}P NMR spectroscopy.

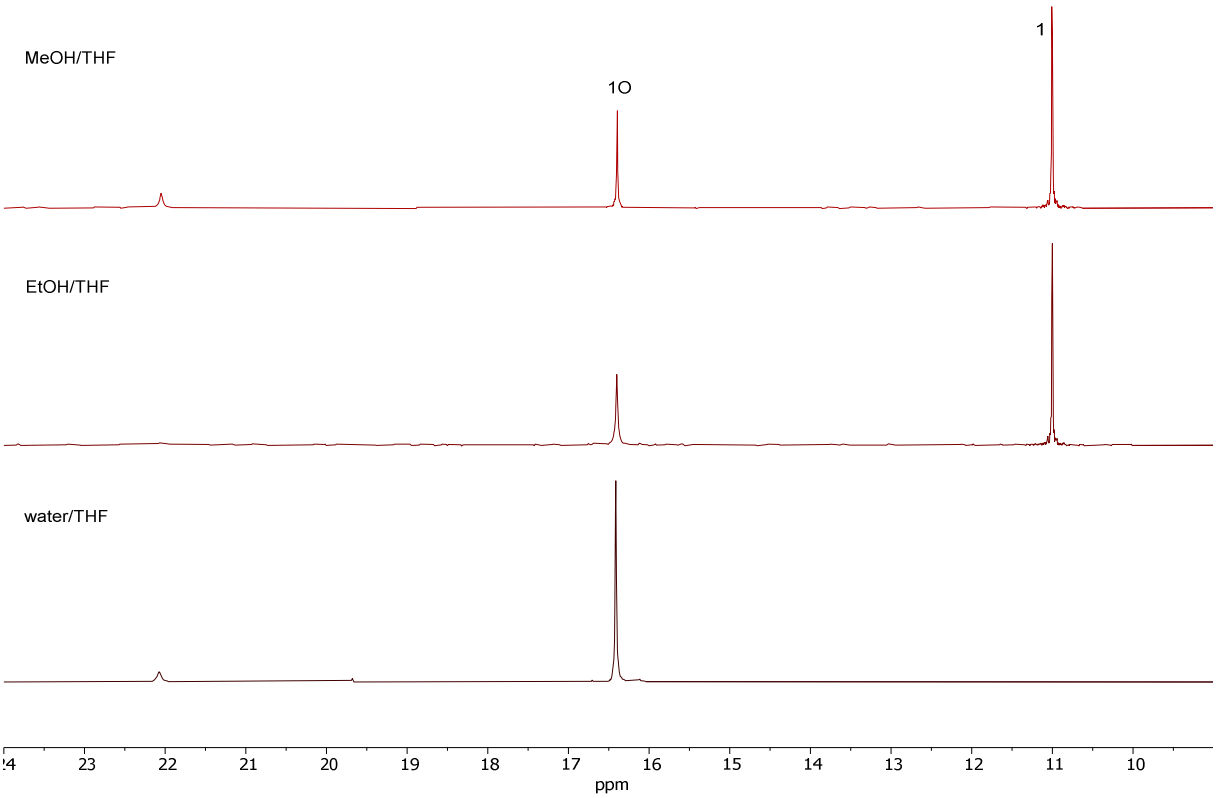


Figure S1 ^{31}P{^{1}H} NMR spectra ($CDCl_3$, 400 MHz) of the reaction mixtures obtained after stirring **1** in the given solvent mixture (1:1) for 72 h (the signal at $\delta_P \approx 22$ is assigned to diphenylphosphine oxide[9])

^{31}P NMR SPECTRA AND STEREOISOMERS OF COMPLEXES 2-X

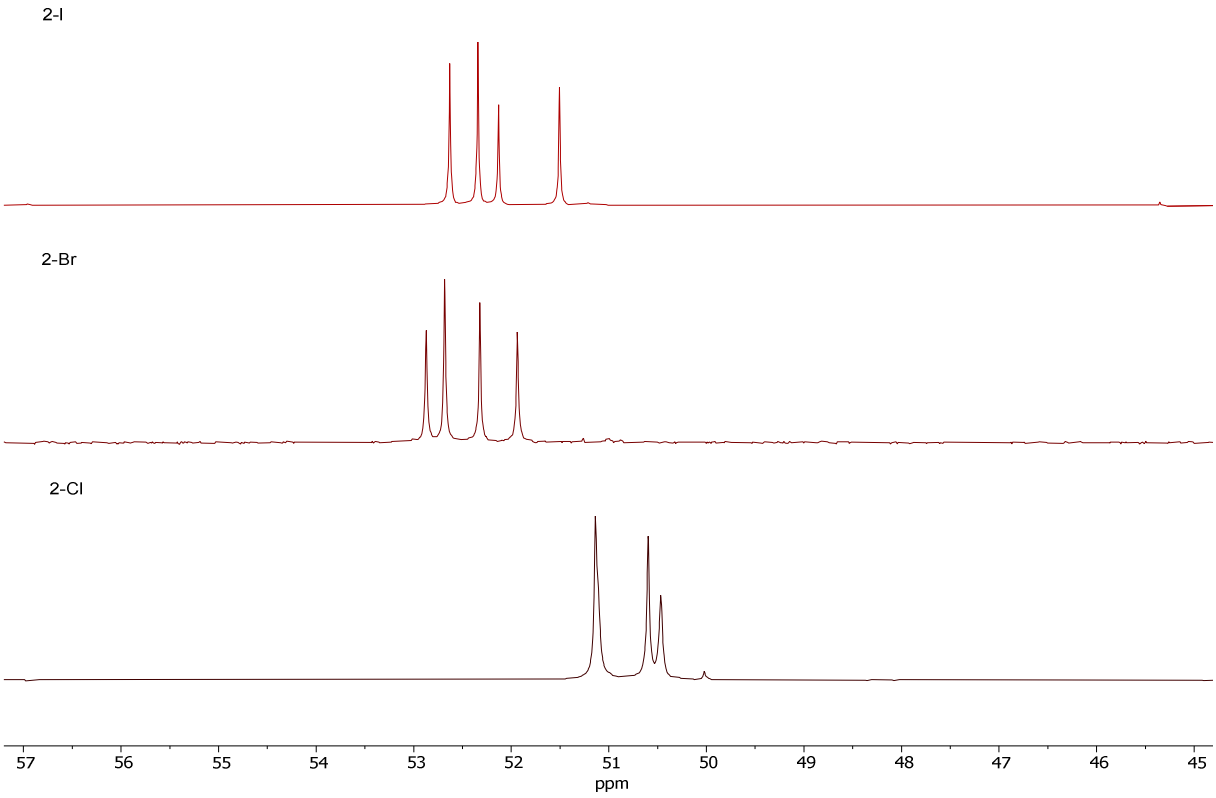


Figure S2 ^{31}P{^{1}H} NMR spectra (162 MHz, $CDCl_3$) of dipalladium complexes **2-Cl**, **2-Br** and **2-I**

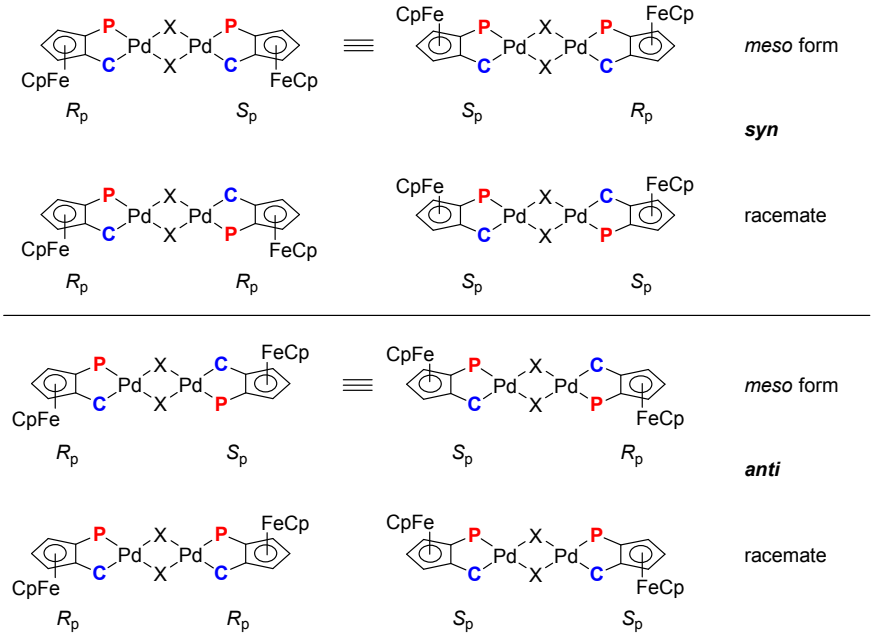


Figure S3 Stereoisomers of **2-X**

KINETIC PROFILES FOR ISOMERISATION OF *cis*-**8e**

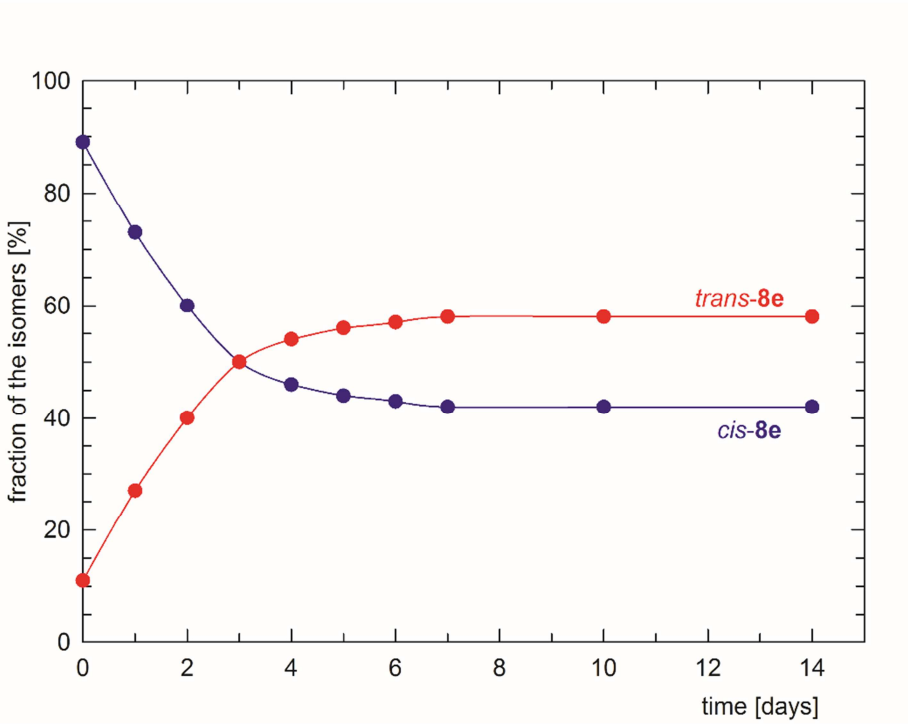


Figure S4 Kinetic profiles of the isomerisation of *cis*-**8e** in C_6D_6 (data from NMR spectroscopy)

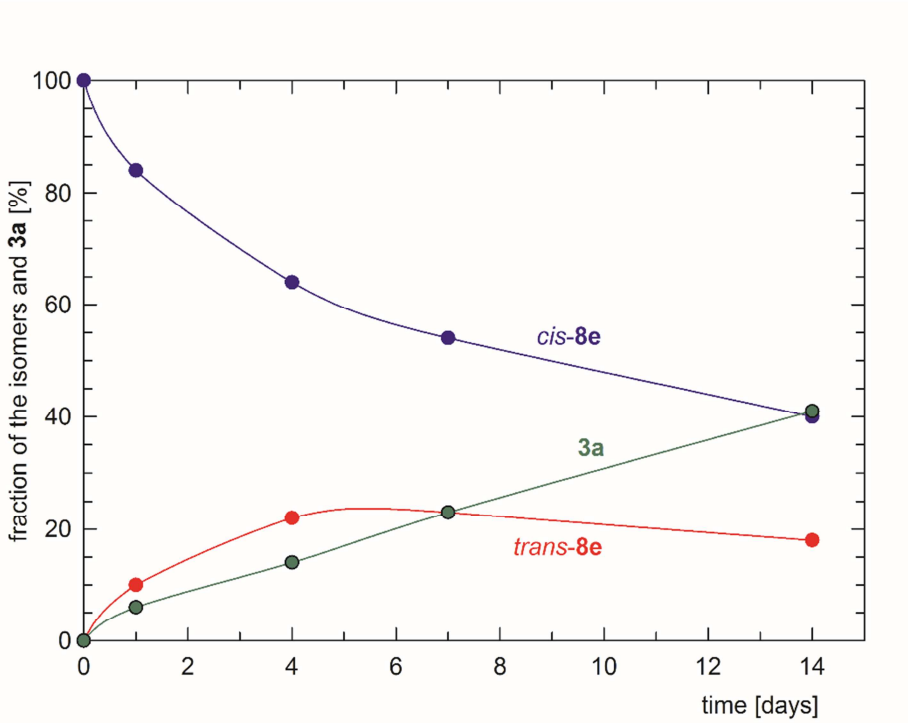


Figure S5 Kinetic profiles of the isomerisation of *cis*-**8e** in $CDCl_3$ (data from NMR spectroscopy)

ADDITIONAL STRUCTURAL PARAMETERS AND STRUCTURAL DIAGRAMS

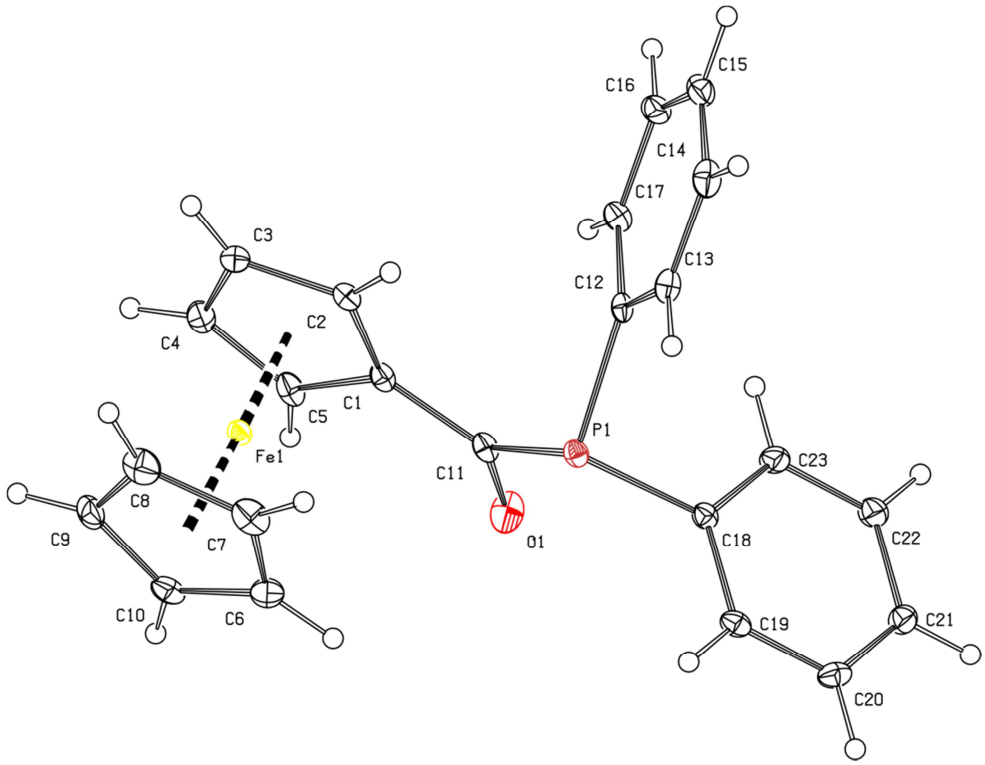


Figure S6 PLATON plot of the molecular structure of **1** (displacement ellipsoids are drawn at the 30% probability level)

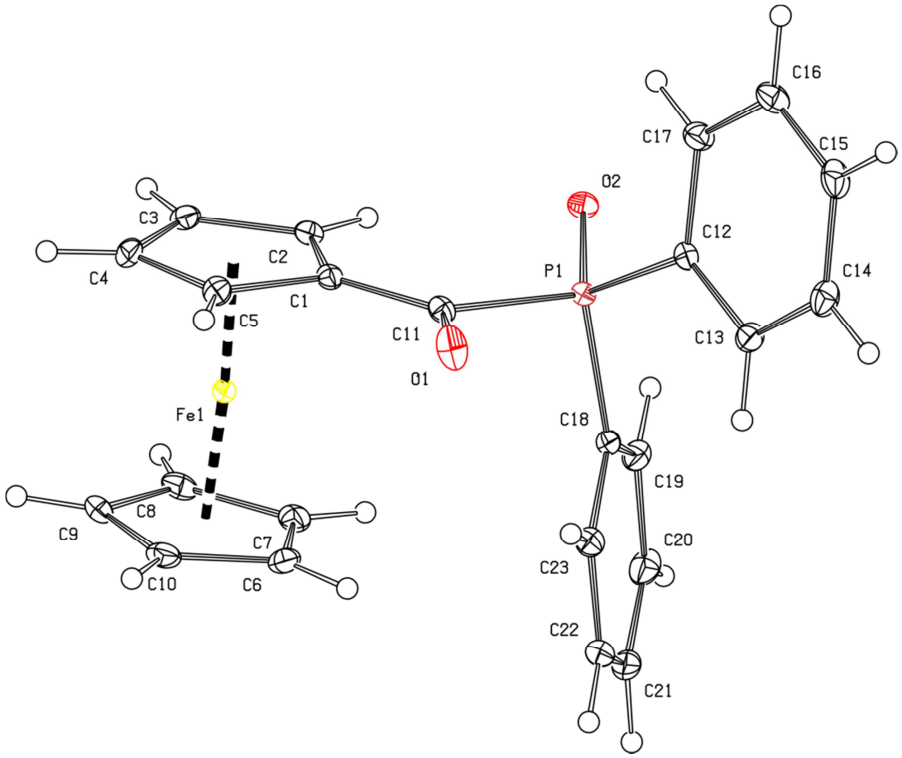


Figure S7 PLATON plot of the molecular structure of **1O** (displacement ellipsoids are drawn at the 30% probability level)

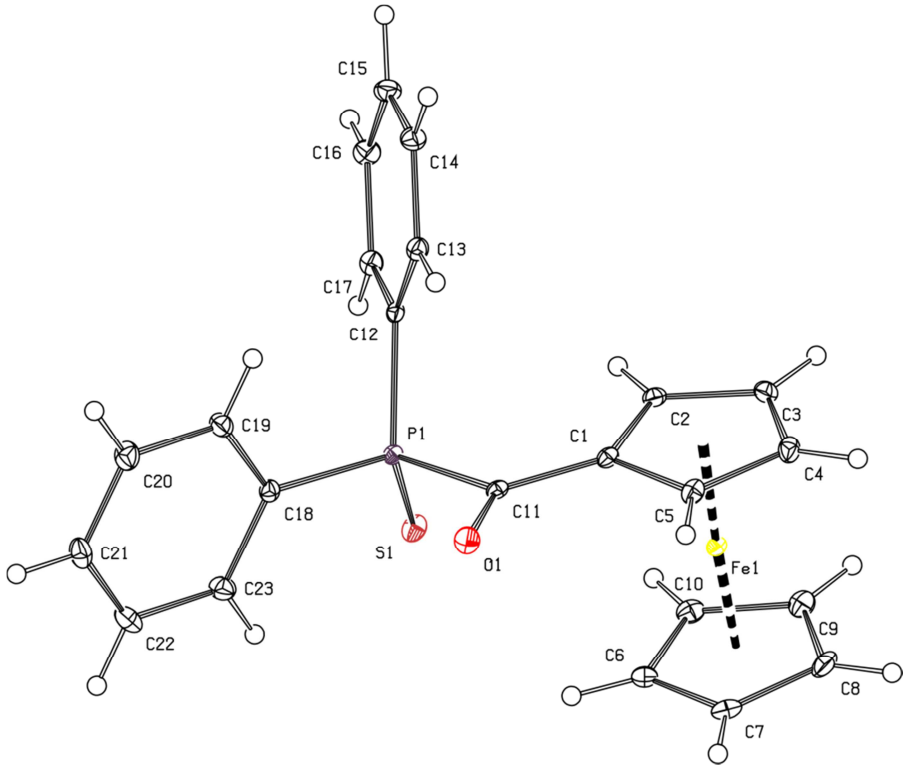


Figure S8 PLATON plot of the molecular structure of **1S** (displacement ellipsoids are drawn at the 30% probability level)

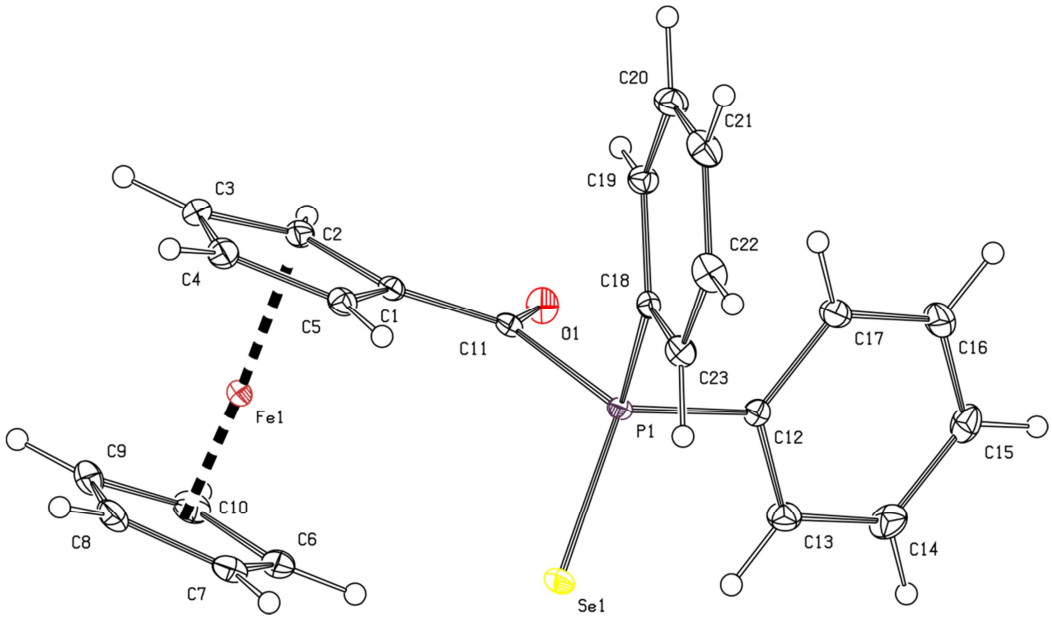


Figure S9 PLATON plot of the molecular structure of **1Se** (displacement ellipsoids are drawn at the 30% probability level)

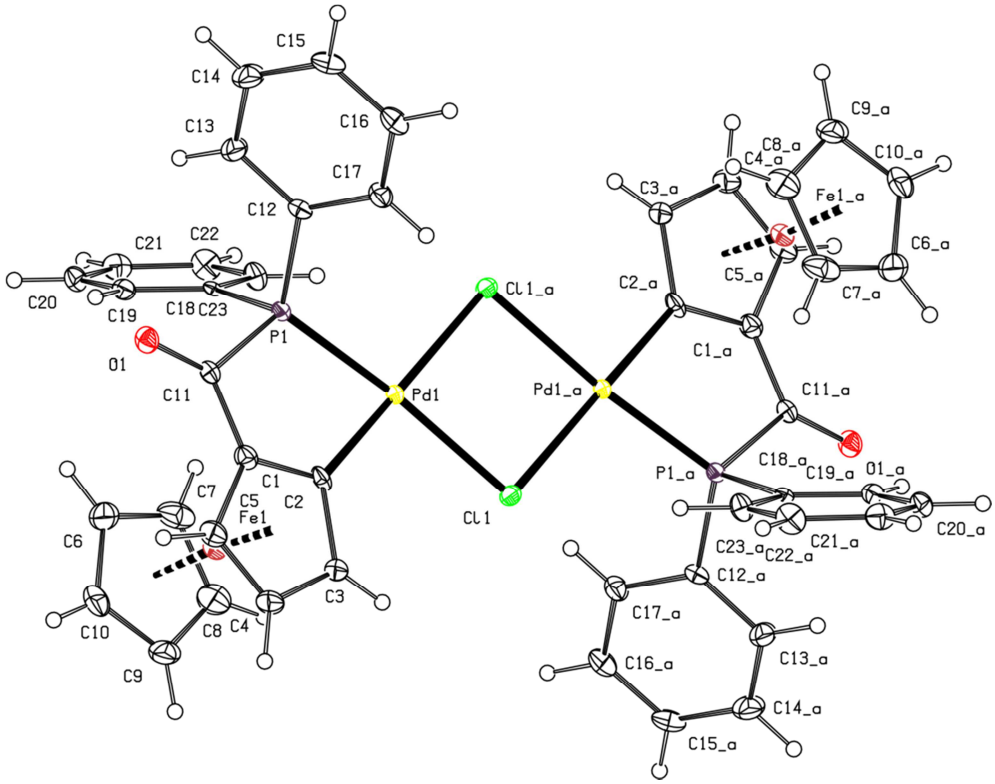


Figure S10 PLATON plot of the complex molecule in the structure of **2-Cl**·AcOEt (at the 30% probability level). The half of the molecule is generated by the inversion operation.

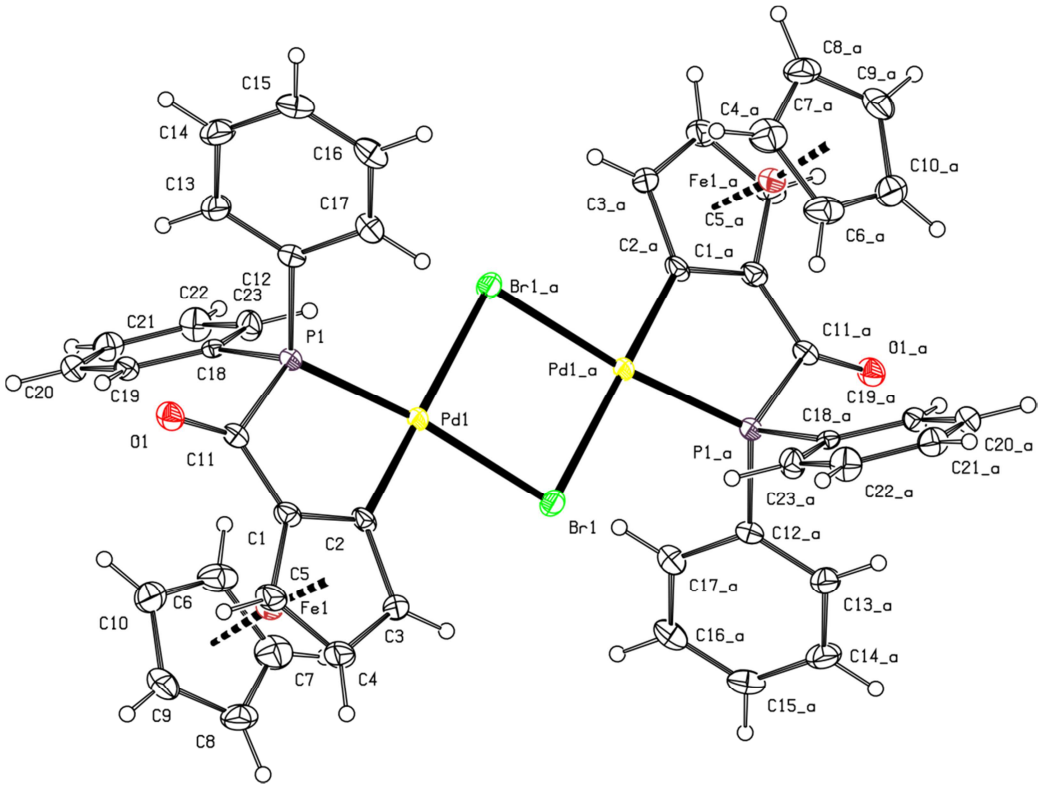


Figure S11 PLATON plot of the complex molecule in the structure of **2-Br**·PhMe (displacement ellipsoids are drawn at the 30% probability level). The half of the molecule is generated by the inversion operation.

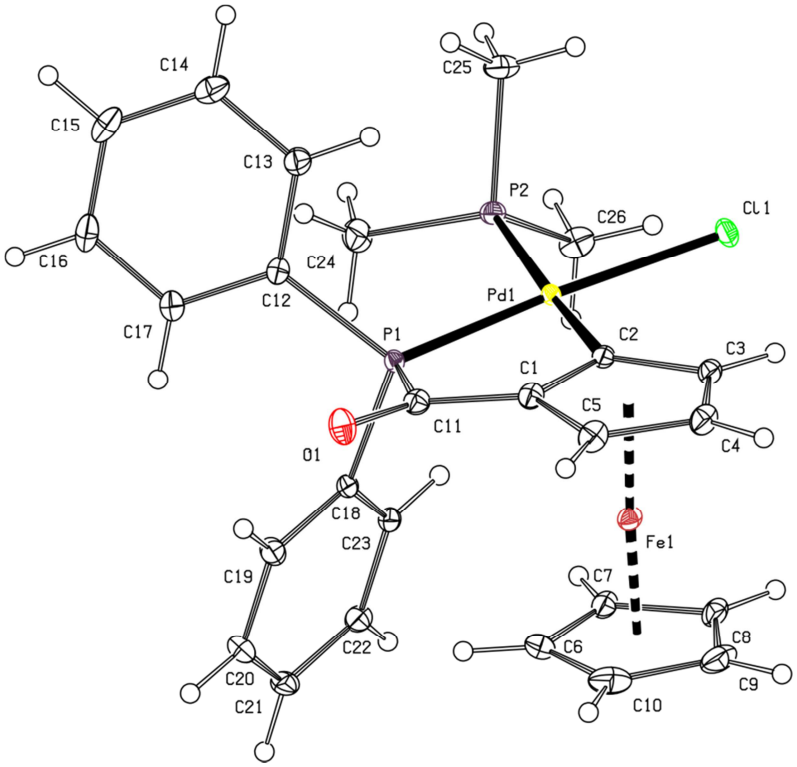


Figure S12 PLATON plot of the molecular structure of *cis*-**3a**·½AcOEt (displacement ellipsoids are drawn at the 30% probability level)

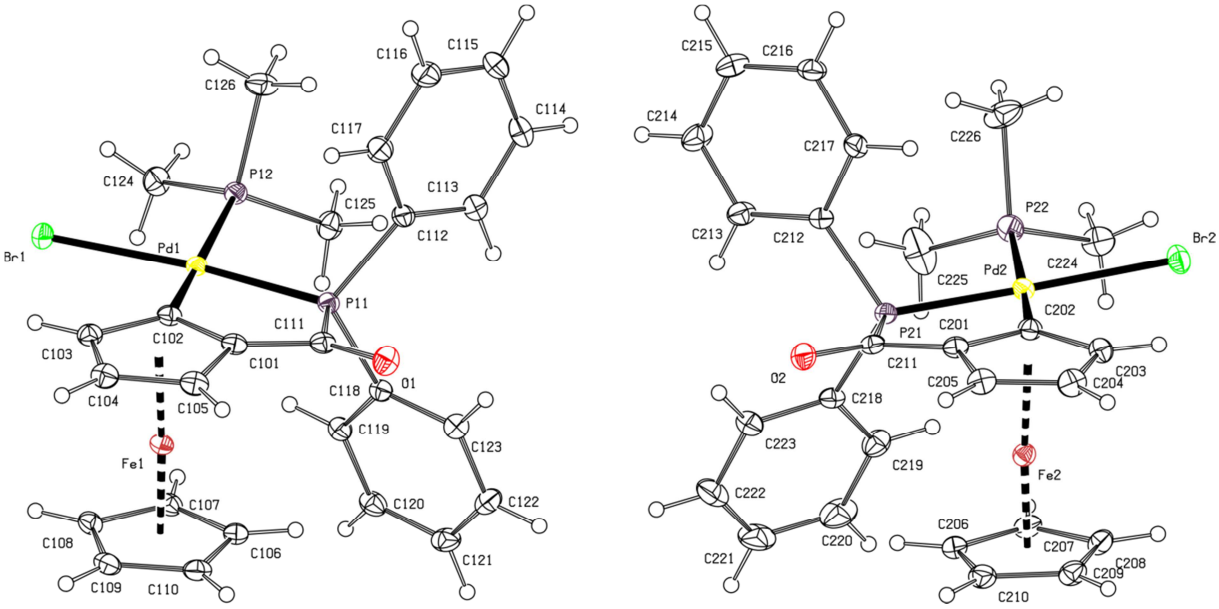


Figure S13 PLATON plot of the two crystallographically independent complex molecules in the structure of *cis*-**4a** (displacement ellipsoids are drawn at the 30% probability level)

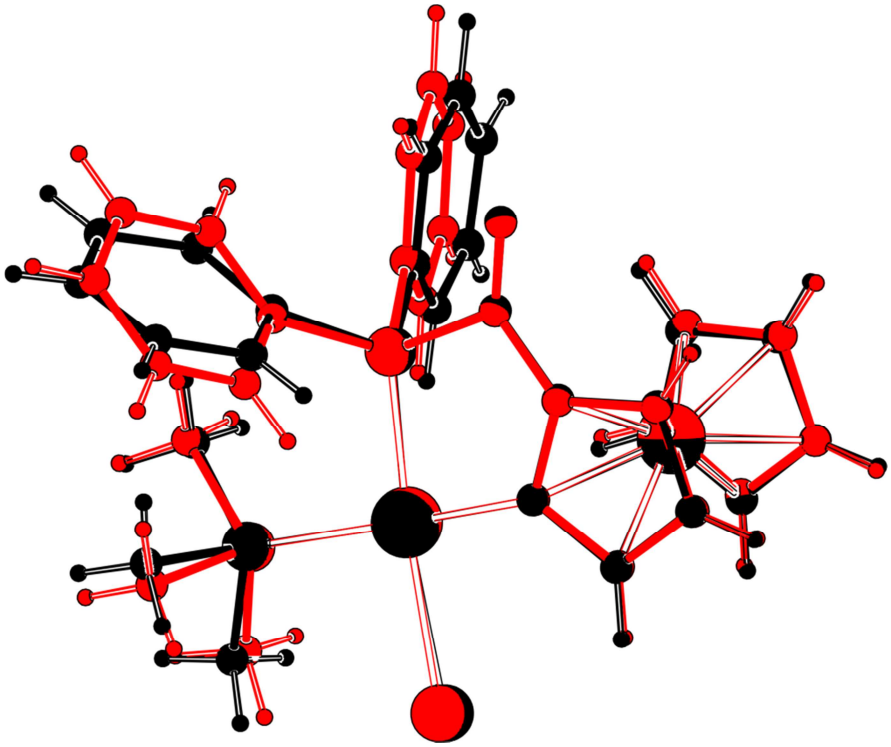


Figure S14 Overlap of the two structurally independent molecules in the structure of **4a**. Inverted molecule 2 (in red) was fitted onto molecule 1.

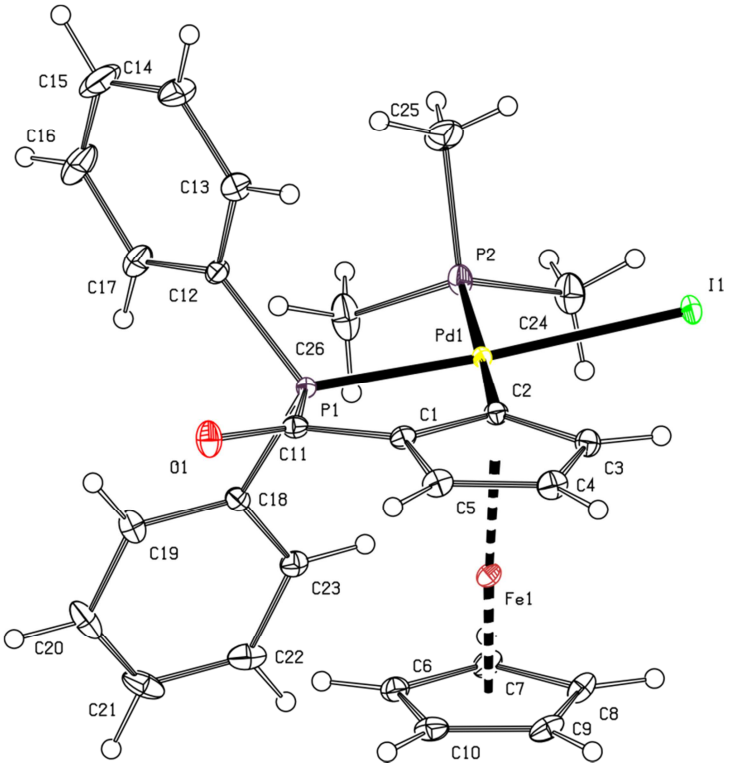


Figure S15 PLATON plot of the complex molecule in the structure of *cis*-**5a**·½AcOEt (displacement ellipsoids are drawn at the 30% probability level)

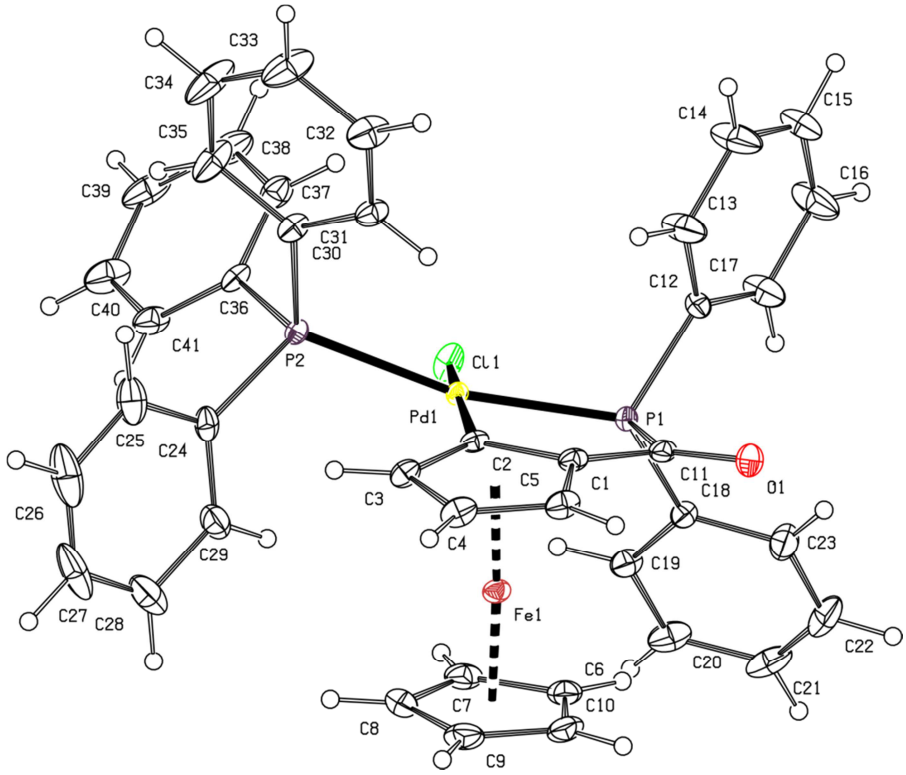


Figure S16 PLATON plot of the complex molecule in the structure of *trans*-**3b**·PhMe (displacement ellipsoids are drawn at the 30% probability level)

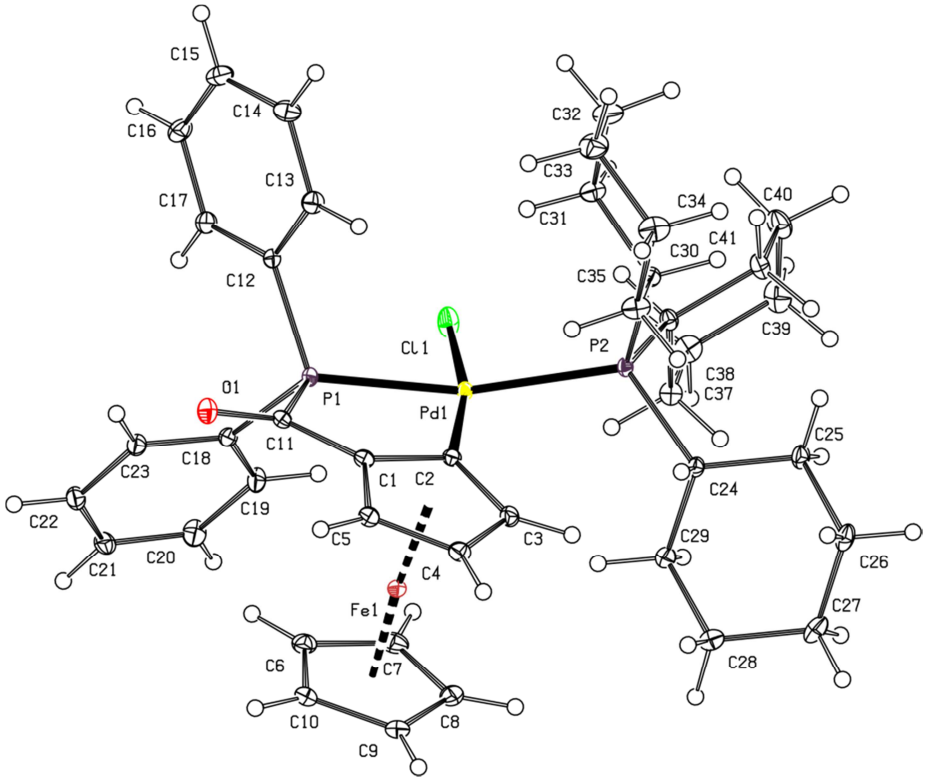


Figure S17 PLATON plot of the molecular structure of *trans*-**3c** (displacement ellipsoids are drawn at the 30% probability level)

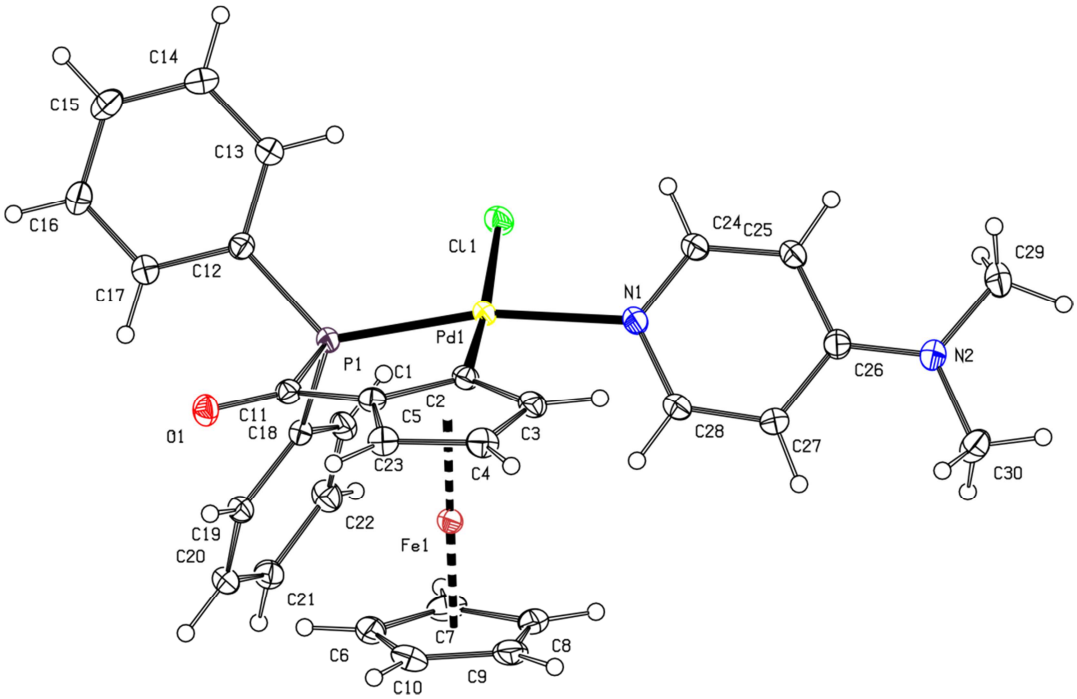


Figure S18 PLATON plot of the molecular structure of *trans*-**3d** (displacement ellipsoids are drawn at the 30% probability level)

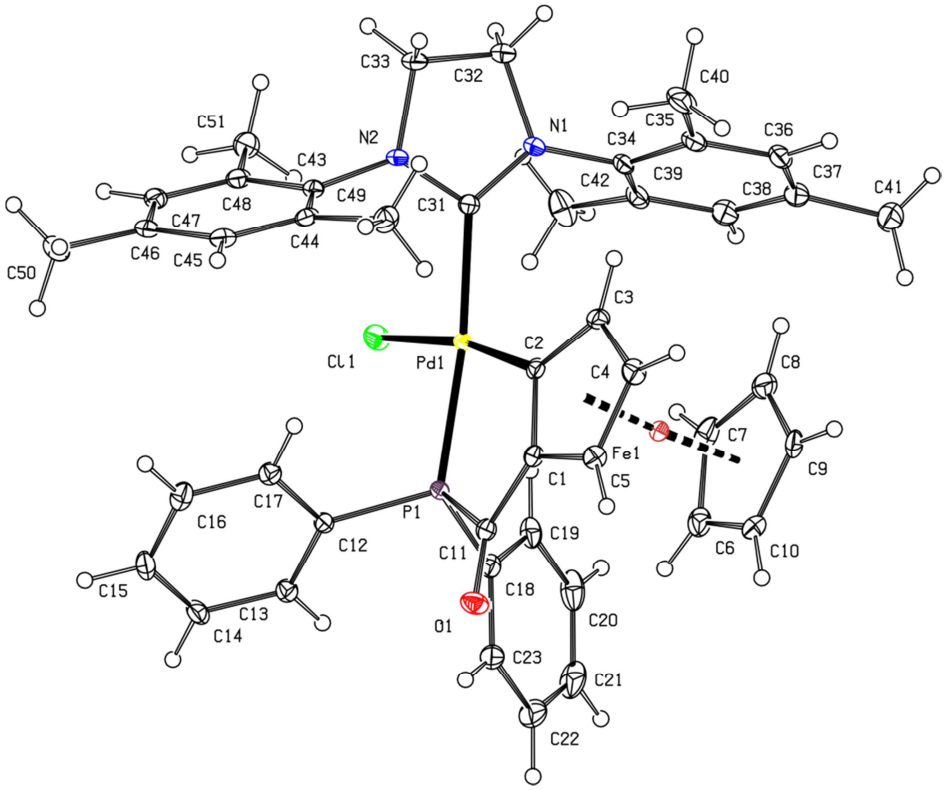


Figure S19 PLATON plot of the complex molecule in the structure of *trans*-**3e**·½PhMe (displacement ellipsoids are drawn at the 30% probability level)

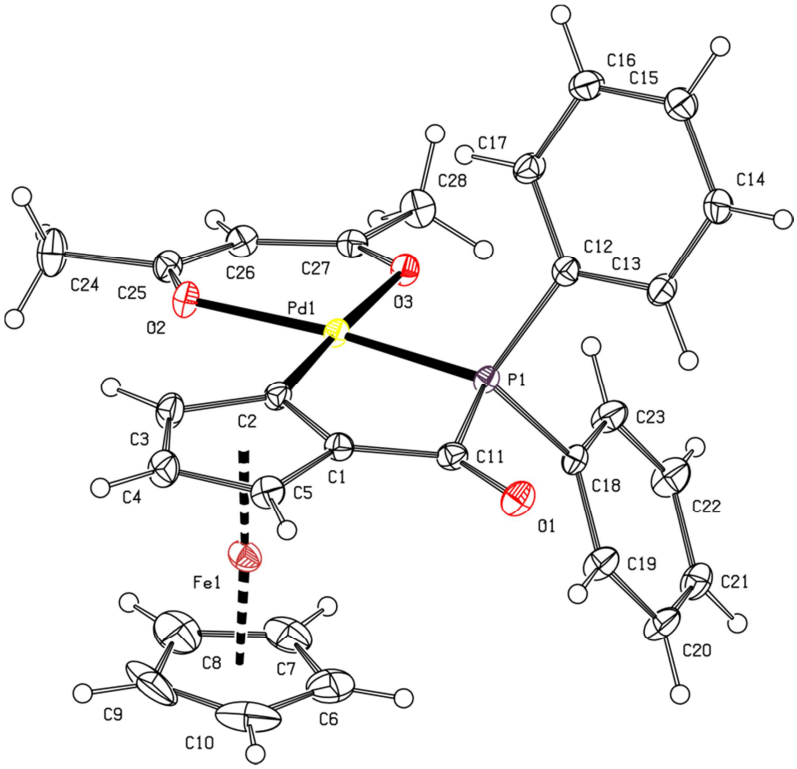


Figure S20 PLATON plot of the molecular structure of **6** (displacement ellipsoids are drawn at the 30% probability level)

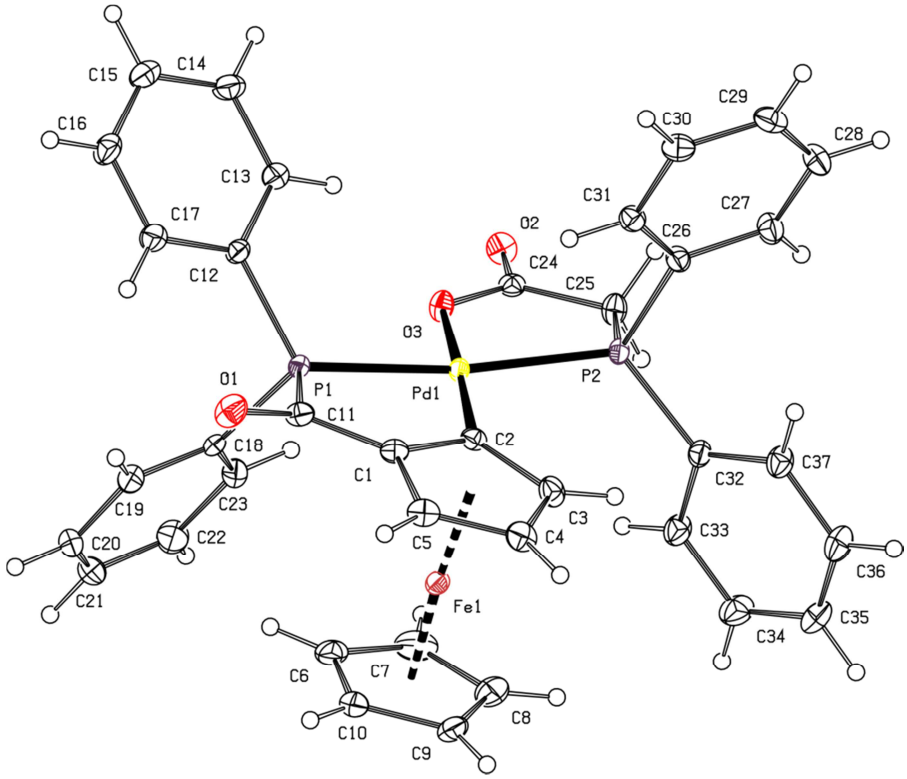


Figure S21 PLATON plot of the molecular structure of *trans*-**7** (displacement ellipsoids are drawn at the 30% probability level)

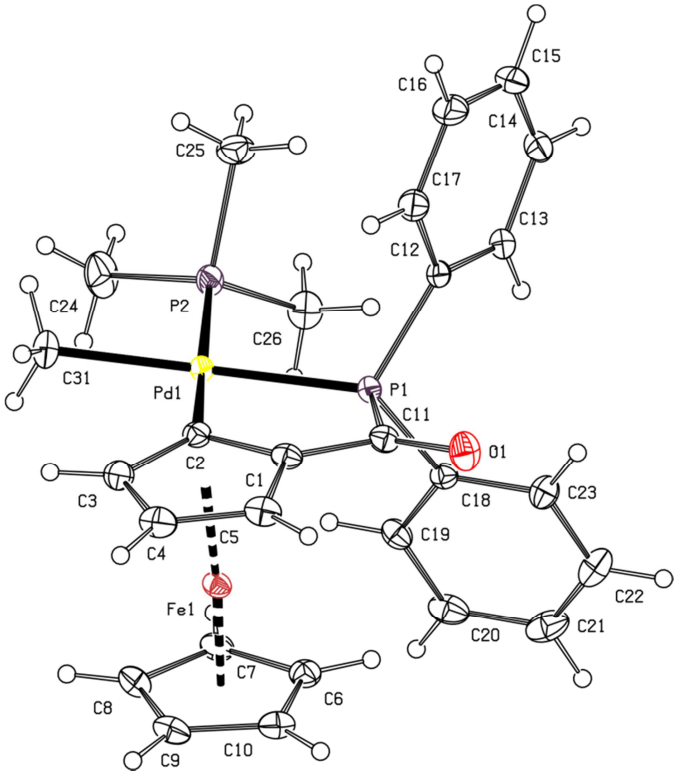


Figure S22 PLATON plot of the molecular structure of *cis*-**8a** (displacement ellipsoids are drawn at the 30% probability level)

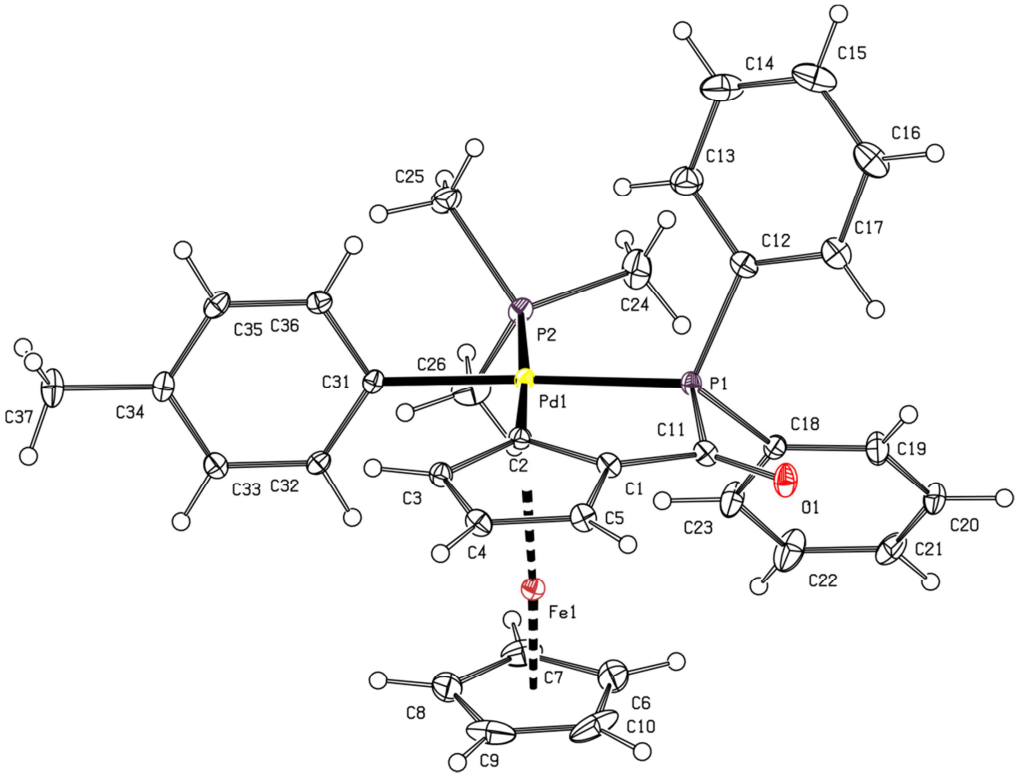


Figure S23 PLATON plot of the molecular structure of *cis*-**8b** (displacement ellipsoids are drawn at the 30% probability level)

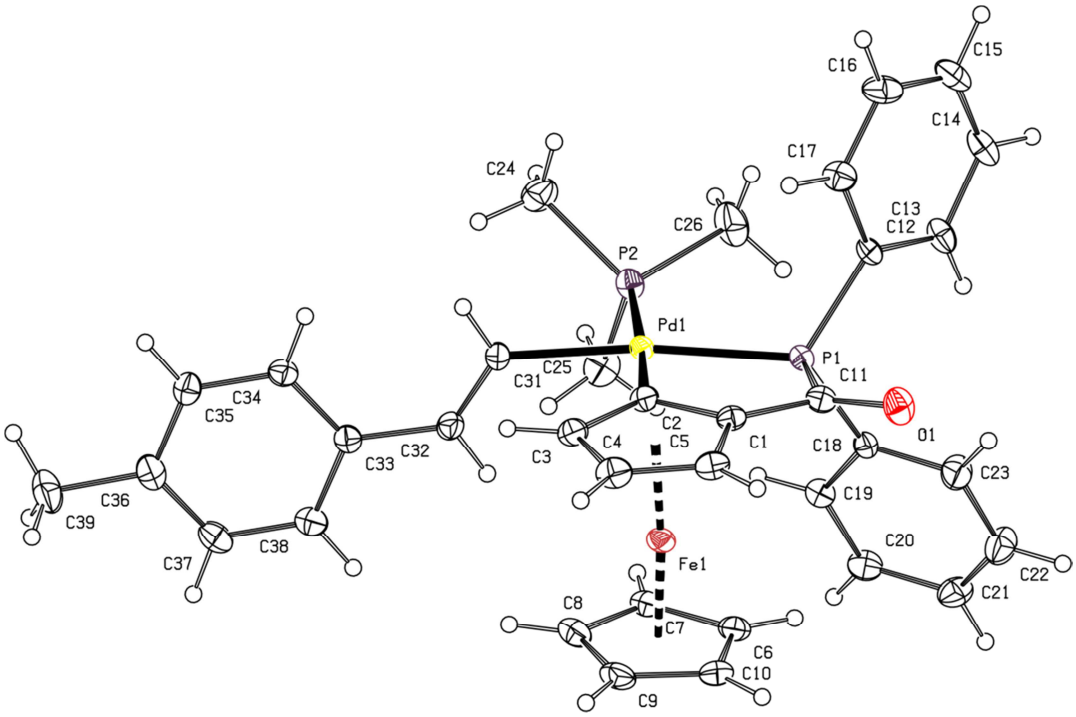


Figure S24 PLATON plot of the molecular structure of *cis*-**8d** (displacement ellipsoids are drawn at the 30% probability level)

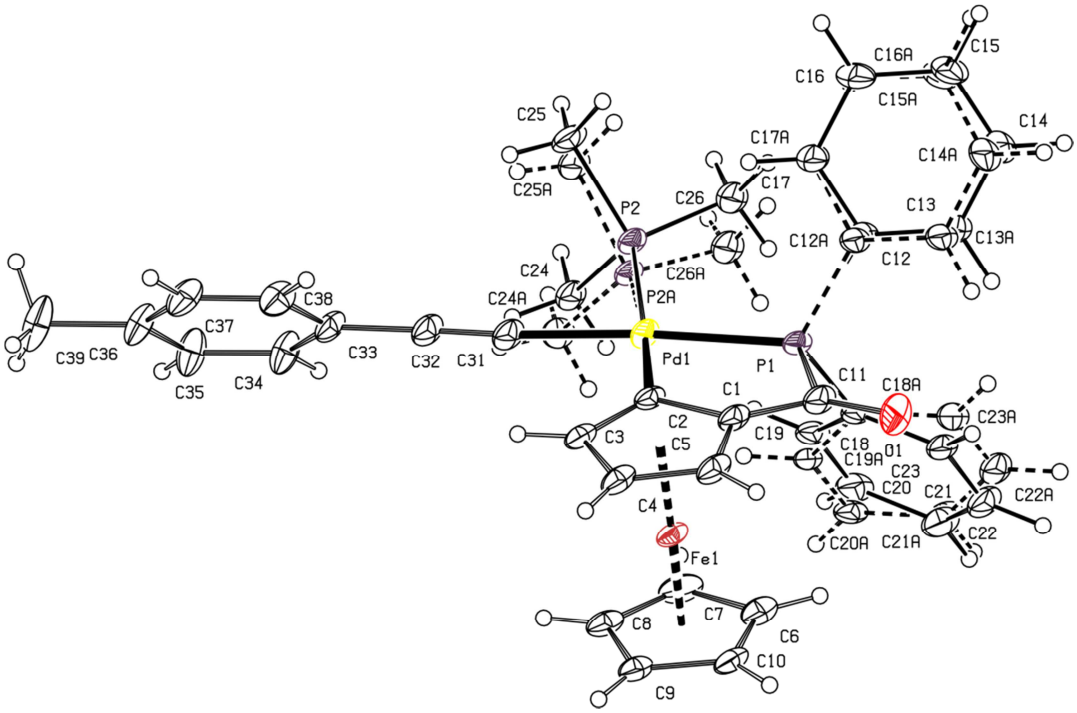


Figure S25 PLATON plot of the molecular structure of *cis*-**8e** showing both positions of the disordered PPh_2 and PMe_3 units (displacement ellipsoids are drawn at the 30% probability level)

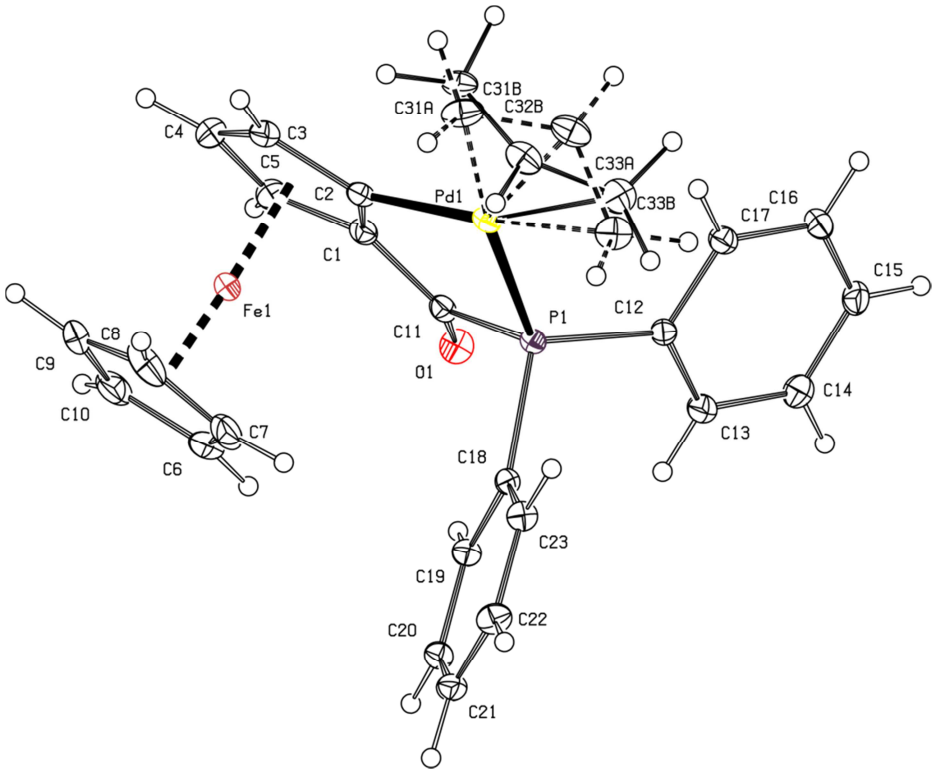


Figure S26 PLATON plot of the molecular structure of **9** showing both orientations of the disordered allyl moiety (displacement ellipsoids are drawn at the 30% probability level)

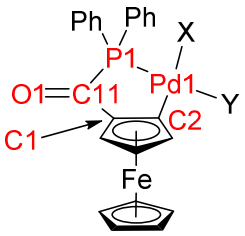
Table S2 Parameters of the orthometallated ligand **1** in the Pd(II) complexes (in Å and deg)

Parameter[a]	**2-Cl**·AcOEt	**2-Br**·PhMe	*cis*-**3a**·½AcOEt	*cis*-**4a**[b]	*cis*-**5a**·½AcOEt
Pd1-P1	2.2070(8)	2.2114(9)	2.2206(5)	2.2290(7)/2.2221(7)	2.2417(4)
Pd1-C2	1.996(3)	2.003(3)	2.041(2)	2.047(2)/2.045(2)	2.059(2)
P1-Pd1-C2	80.78(8)	81.1(1)	81.83(5)	81.18(7)/81.49(7)	81.90(4)
P1-C11	1.893(3)	1.890(3)	1.911(2)	1.900(2)/1.899(2)	1.904(2)
O1-C11	1.215(3)	1.213(4)	1.219(2)	1.215(3)/1.215(3)	1.210(2)
C1-C11	1.439(4)	1.445(5)	1.443(3)	1.436(3)/1.439(3)	1.442(2)
P1-C11-C1	107.5(2)	107.3(2)	108.0(1)	107.5(2)/108.1(2)	108.4(1)
P1-C11-C1-C2	–1.0(3)	–0.3(4)	3.7(2)	–1.7(2)/–1.0(2)	2.9(2)
Pd1-C2-C1-C11	11.7(4)	11.3(5)	6.0(2)	–3.1(3)/5.3(3)	3.0(2)
tilt	4.6(2)	4.4(3)	1.4(1)	1.2(1)/3.9(1)	2.4(1)

Parameter	*trans*-**3b**·PhMe	*trans*-**3c**	*trans*-**3d**	*trans*-**3e**·½PhMe
Pd1-P1	2.2824(6)	2.2728(5)	2.2250(5)	2.2619(7)
Pd1-C2	2.020(2)	2.032(2)	2.001(2)	2.009(3)
P1-Pd1-C2	82.94(5)	83.63(5)	82.48(5)	82.86(8)
P1-C11	1.883(2)	1.887(2)	1.897(2)	1.887(3)
O1-C11	1.220(2)	1.222(2)	1.216(2)	1.220(3)
C1-C11	1.445(2)	1.447(2)	1.443(3)	1.445(4)
P1-C11-C1	109.1(1)	108.7(1)	107.7(1)	108.0(2)
P1-C11-C1-C2	–2.0(2)	4.0(2)	–4.7(2)	3.0(3)
Pd1-C2-C1-C11	–4.0(2)	4.3(2)	10.9(2)	6.5(3)
tilt	4.7(1)	4.5(1)	6.1(1)	3.7(2)

Parameter	**6**	*trans*-**7**	**9**
Pd1-P1	2.1999(9)	2.3083(9)	2.2625(5)
Pd1-C2	1.976(3)	2.002(3)	2.040(2)
P1-Pd1-C2	81.6(1)	82.75(9)	83.16(5)
P1-C11	1.892(3)	1.887(3)	1.900(2)
O1-C11	1.215(4)	1.214(4)	1.219(2)
C1-C11	1.444(4)	1.442(4)	1.448(3)
P1-C11-C1	106.7(2)	108.6(2)	109.3(1)
P1-C11-C1-C2	6.9(3)	7.0(3)	–1.3(2)
Pd1-C2-C1-C11	–2.5(4)	0.2(4)	14.5(2)
tilt	3.4(3)	5.0(2)	5.0(1)

Labelling scheme



Parameter	*cis*-**8a**	*cis*-**8b**	*cis*-**8d**	*cis*-**8e**
Pd1-P1	2.2883(5)	2.2923(5)	2.297(1)	2.2658(7)
Pd1-C2	2.055(2)	2.061(2)	2.056(4)	2.042(2)
P1-Pd1-C2	82.59(5)	81.77(5)	82.3(1)	81.78(7)
P1-C11	1.900(2)	1.892(2)	1.899(4)	1.899(3)
O1-C11	1.215(2)	1.220(2)	1.219(5)	1.223(3)
C1-C11	1.445(2)	1.449(2)	1.442(5)	1.438(4)
P1-C11-C1	109.1(1)	108.5(1)	109.0(3)	108.6(2)
P1-C11-C1-C2	–1.6(2)	8.5(2)	–4.3(5)	4.2(3)
Pd1-C2-C1-C11	–3.8(2)	–1.4(2)	2.1(5)	–6.1(4)
tilt	3.5(1)	2.3(1)	4.6(3)	0.3(2)

[a] Tilt is the dihedral angles of the least-squares cyclopentadienyl planes. [b] Parameters of two crystallographically independent molecules.

DFT CALCULATIONS

Theoretical calculations were performed using the Gaussian 16 program package.[10] The reported energies correspond to Gibbs free energies obtained after full geometry optimisations (starting from atomic coordinates determined by X-ray diffraction analysis where possible) using PBE0[11] density functional combined with the Stuttgart effective core potential[12] for iodine and for the transition metal atoms (Fe, Pd) and the def2-TZVP[13] basis set for the remaining elements (C, H, O, P, Cl, Br) with added Grimme's D3 dispersion correction.[14] The solvent effects were approximated using the polarised continuum model (PCM).[15] Orbital composition analysis based on natural atomic orbitals (NAO)[16] was performed using the Multiwfn software package (version 3.7).[17] Molecular orbitals were visualised using the Avogadro programme.[18] Cartesian coordinates of all DFT optimised structures are available in ESI as *mol2* files.

Table S3 Dipole moments μ (*D*) calculated for the isomers of the palladium complexes **3a**-**5a**

Complex	μ (*D*)	Complex	μ (*D*)
cis-**3a**	6.696	*trans*-**3a**	4.268
cis-**4a**	6.884	*trans*-**4a**	4.380
cis-**5a**	7.261	*trans*-**5a**	4.673

Table S4 Comparison of selected bond distances determined by X-ray diffraction analysis and calculated by DFT at the PBE0/def2-TZVP:sdd(Pd,Fe,I)-D3 level of theory

Complex	**Bond**	**Exp. (Å)**	**Calc. (Å)**	**Complex**	**Bond**	**Calc. (Å)**
***cis*-3a**	Pd–C	2.041(2)	2.034	***trans*-3a**	Pd–C	2.019
	Pd–PPh_2	2.2206(5)	2.219		Pd–PPh_2	2.299
	Pd–PMe_3	2.3368(5)	2.332		Pd–PMe_3	2.313
	Pd–Cl	2.3647(5)	2.358		Pd–Cl	2.376
***cis*-4a**	Pd–C	2.046(2)	2.042	***trans*-4a**	Pd–C	2.025
	Pd–PPh_2	2.2256(7)	2.224		Pd–PPh_2	2.299
	Pd–PMe_3	2.3419(8)	2.336		Pd–PMe_3	2.315
	Pd–Br	2.492(5)	2.491		Pd–Br	2.510
***cis*-5a**	Pd–C	2.059(2)	2.052	***trans*-5a**	Pd–C	2.033
	Pd–PPh_2	2.2417(4)	2.229		Pd–PPh_2	2.296
	Pd–PMe_3	2.3448(5)	2.342		Pd–PMe_3	2.317
	Pd–I	2.6543(3)	2.701		Pd–I	2.716

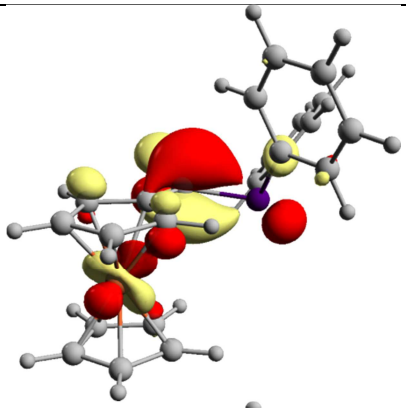
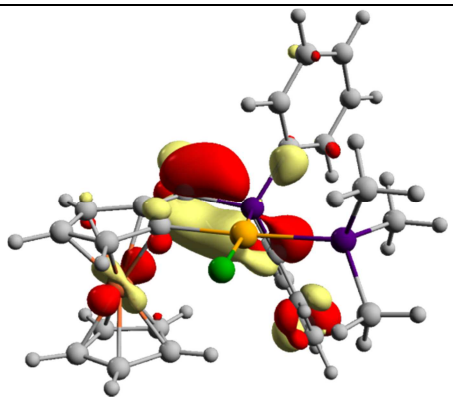
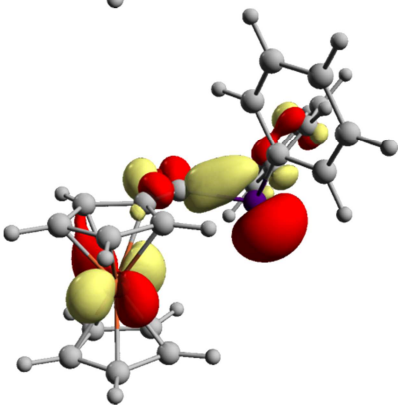
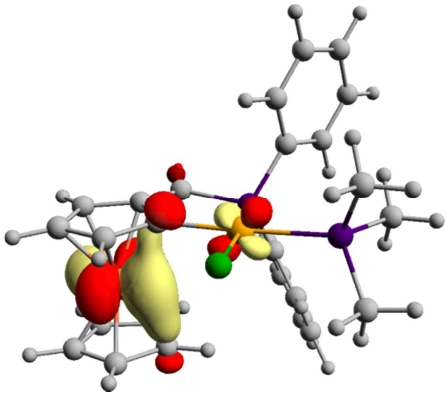
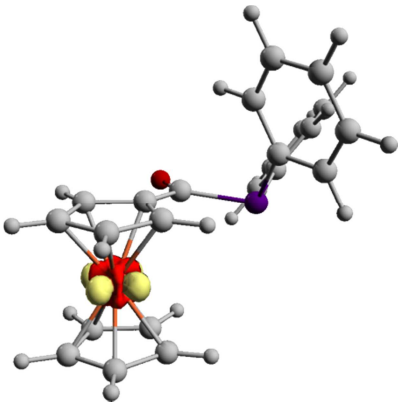
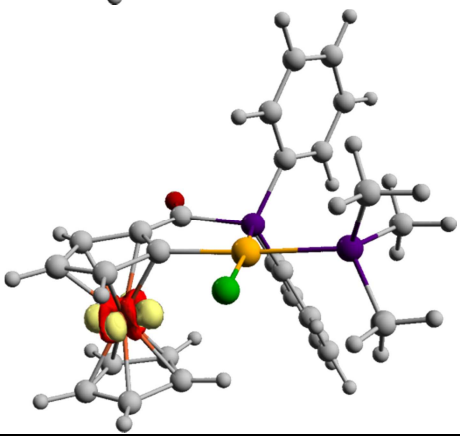
M	**1**	*cis*-**3a**
LUMO		
HOMO		
$\rho(M) - \rho(M^+)$		

Figure S27 Frontier orbitals (contour maps with isosurfaces at ±0.05 a.u) and electron density difference maps $\rho(M) - \rho(M^+)$ at the geometry of M (isosurfaces at ±0.02 a.u.) for compounds **1** and *cis*-**3a**. Note: molecular orbital analysis revealed that the HOMO of ligand **1** is mainly contributed from the iron 3d orbitals (≈51%), with a smaller contribution from phosphorus (≈16%, 3p) and oxygen (≈7%, 2p). The contribution of iron 3d orbitals to HOMO of *cis*-**3a** is even larger (≈77%), with only minor involvement of orbitals at palladium (≈4%, 4d) and ferrocene carbon atoms (≈13%, 2p).

COPIES OF THE NMR SPECTRA

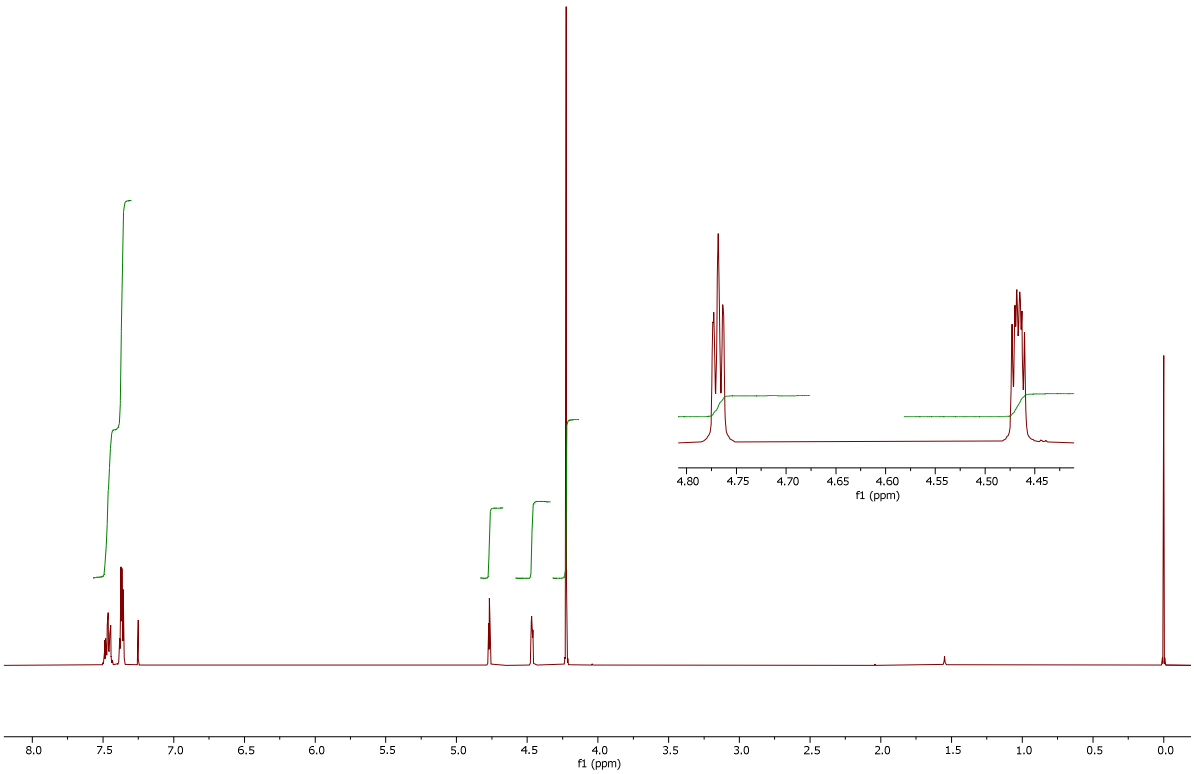


Figure S28 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **1**

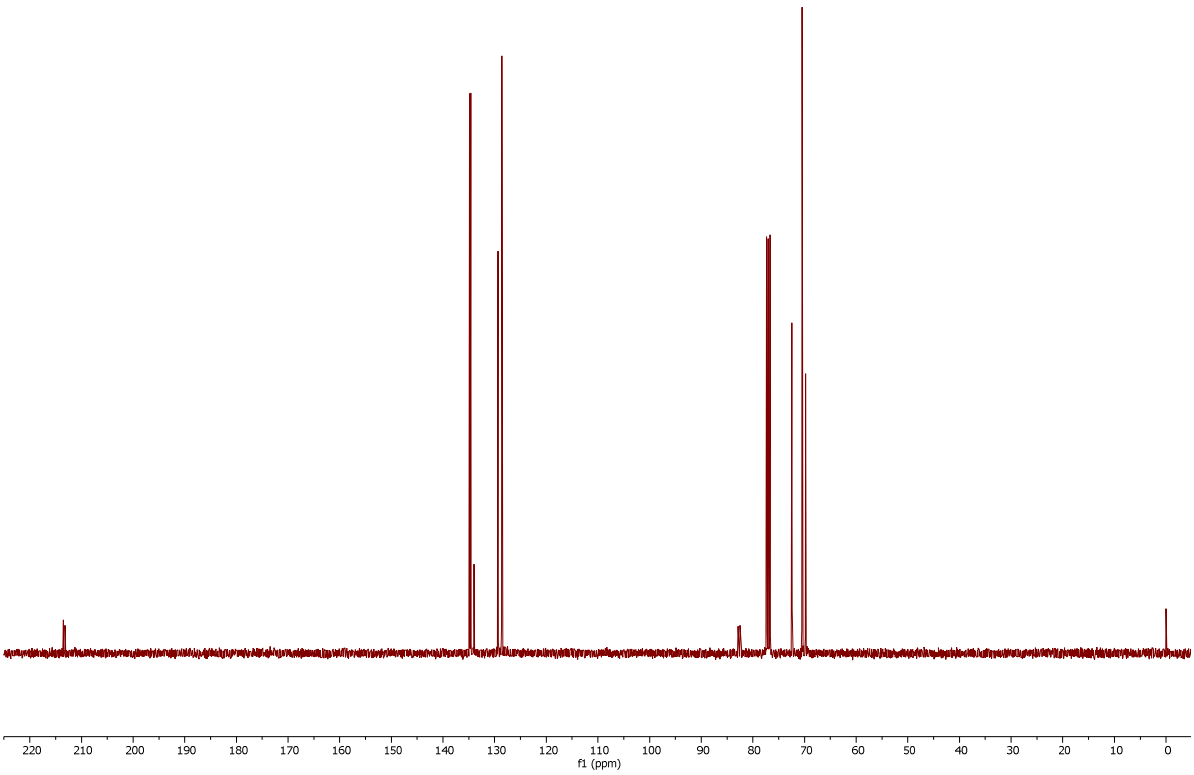


Figure S29 $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 101 MHz) of **1**

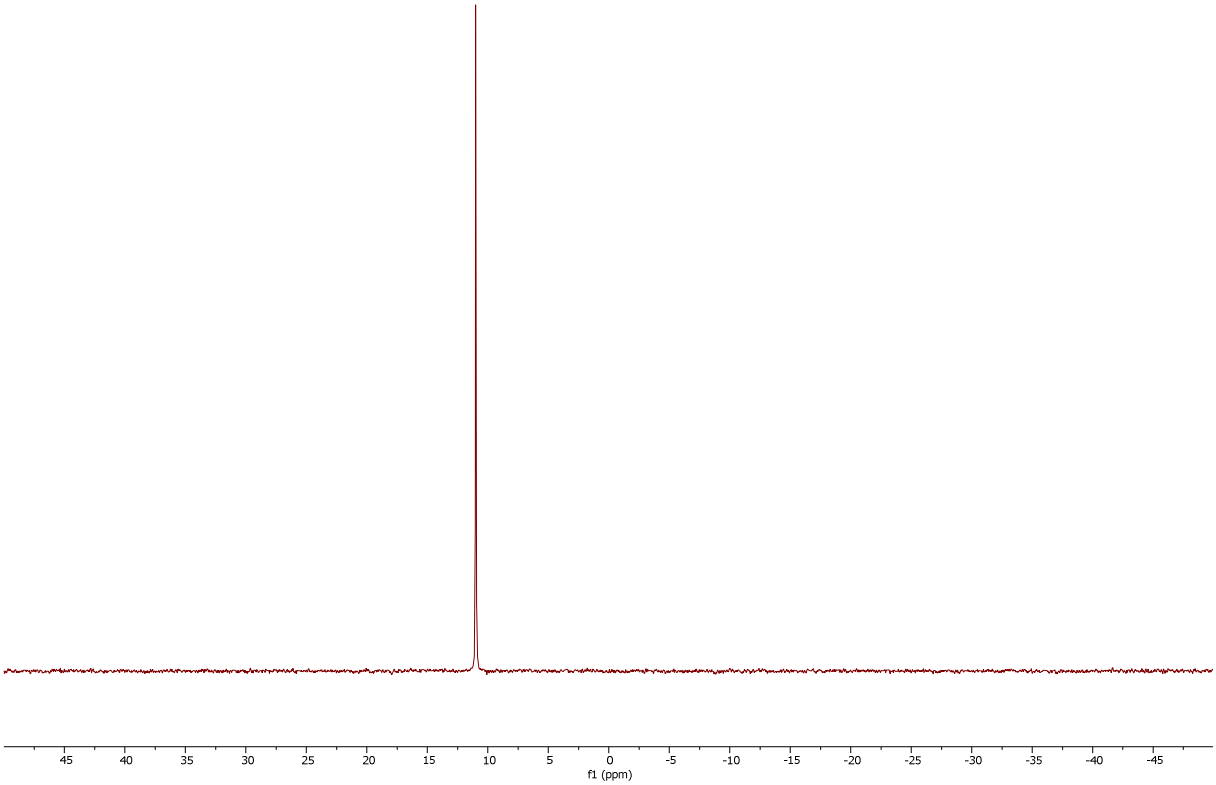


Figure S30 $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$, 162 MHz) of **1**

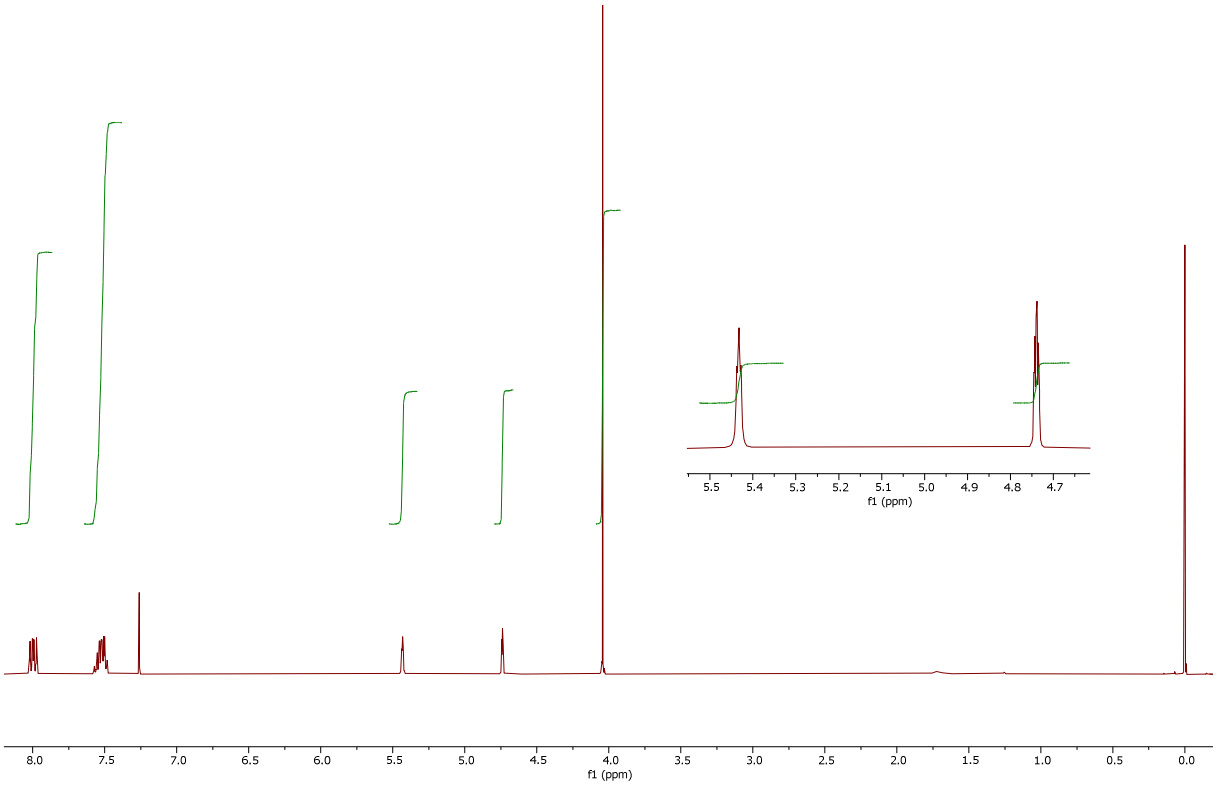


Figure S31 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **1O**

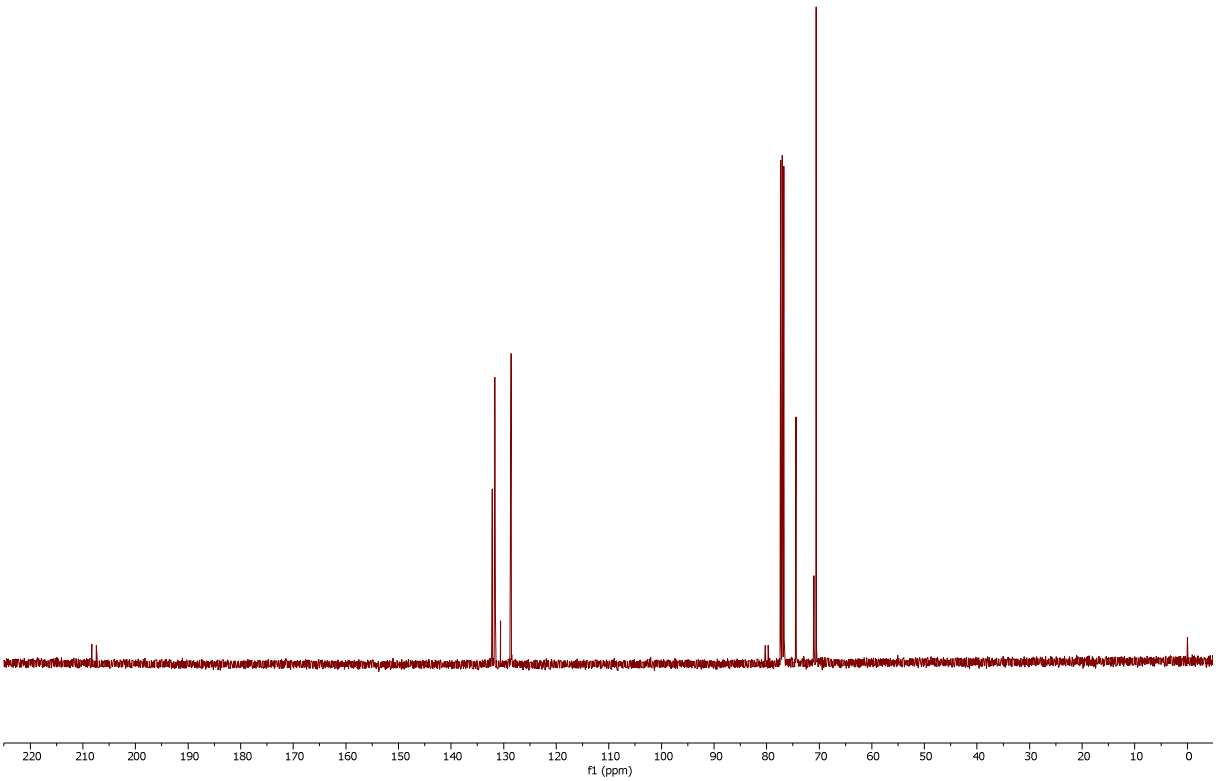


Figure S32 $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 101 MHz) of **1O**

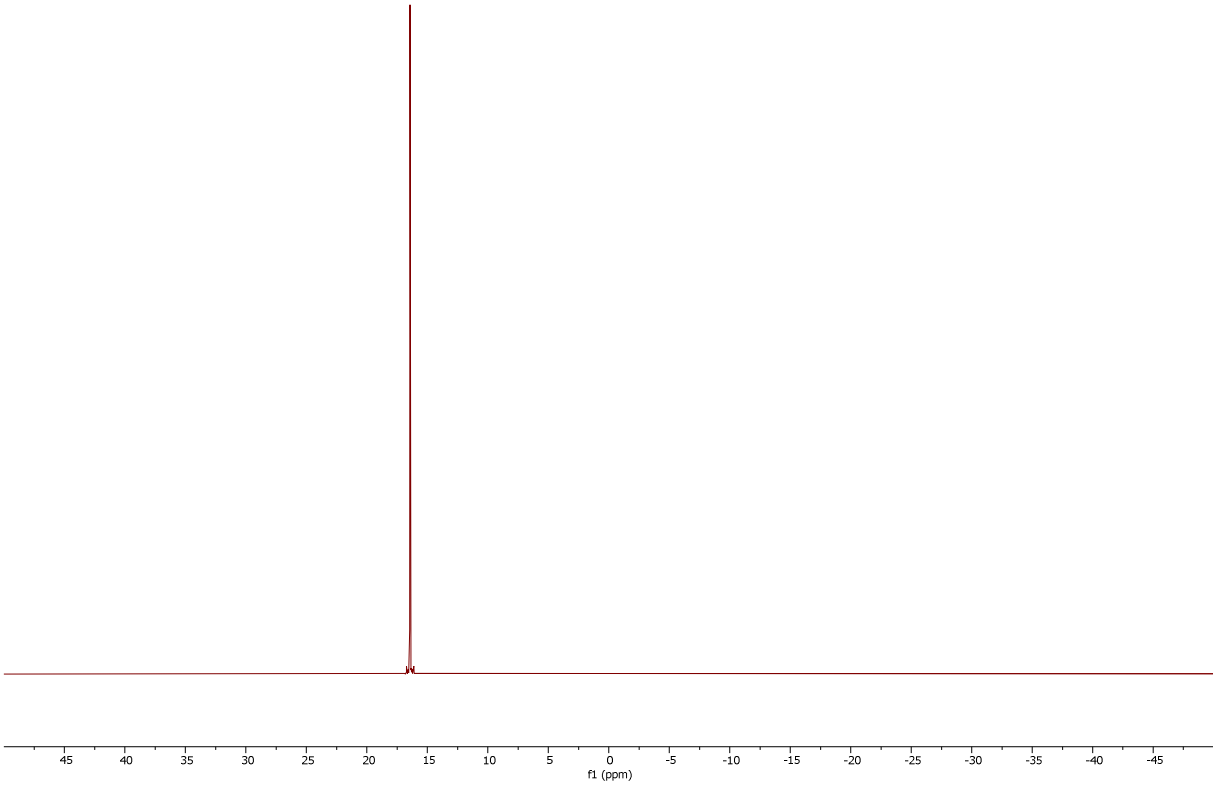


Figure S33 $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$, 162 MHz) of **1O**

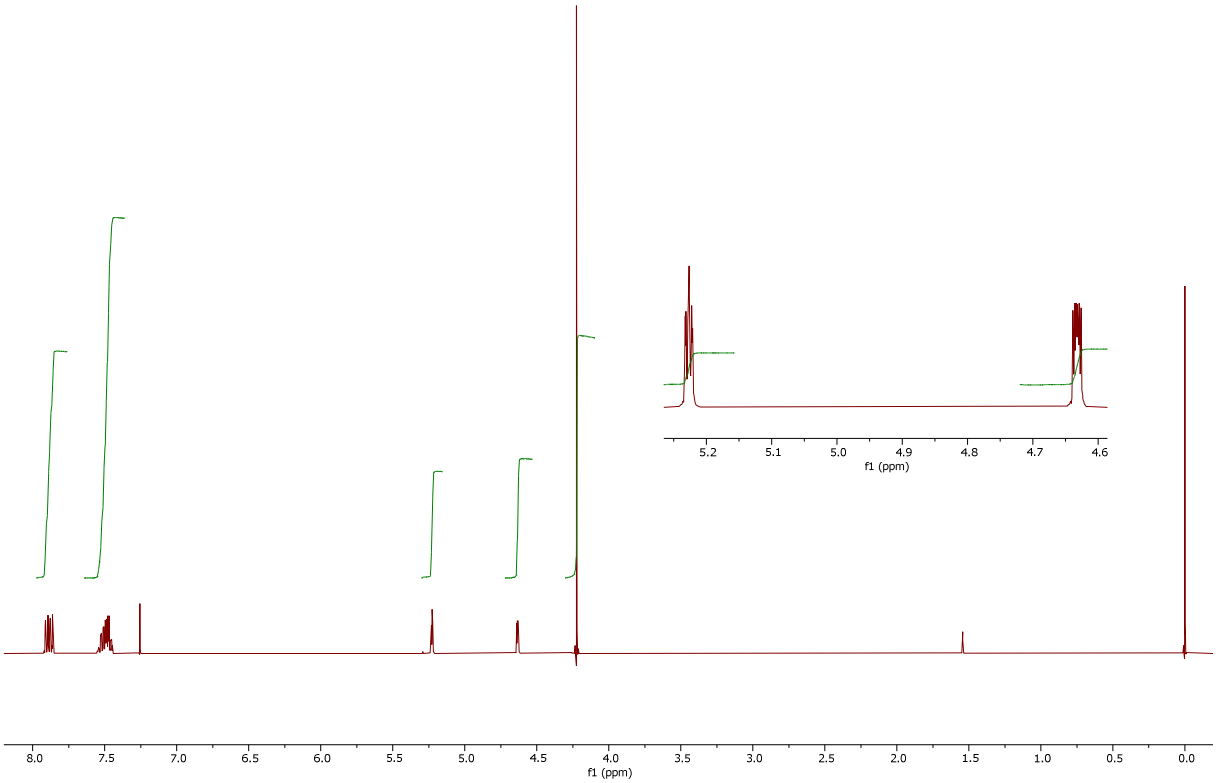


Figure S34 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **1S**

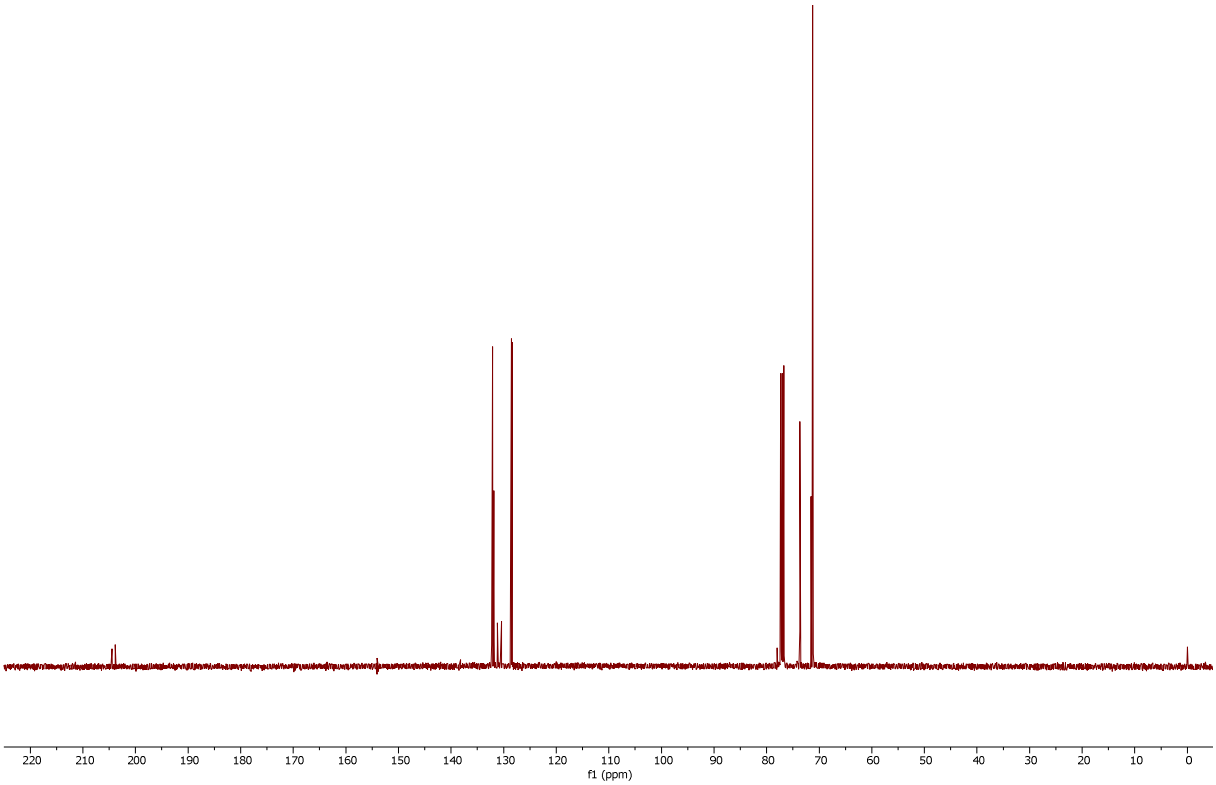


Figure S35 $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 101 MHz) of **1S**

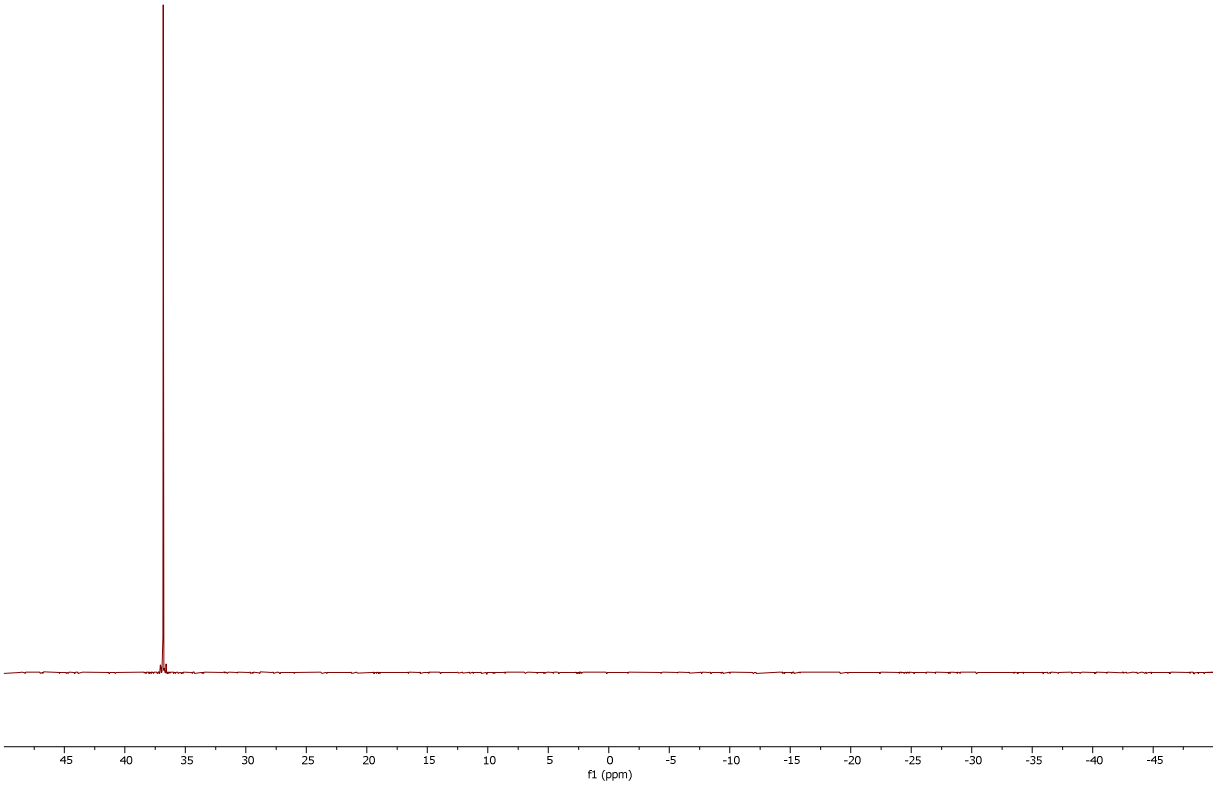


Figure S36 $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$, 162 MHz) of **1S**

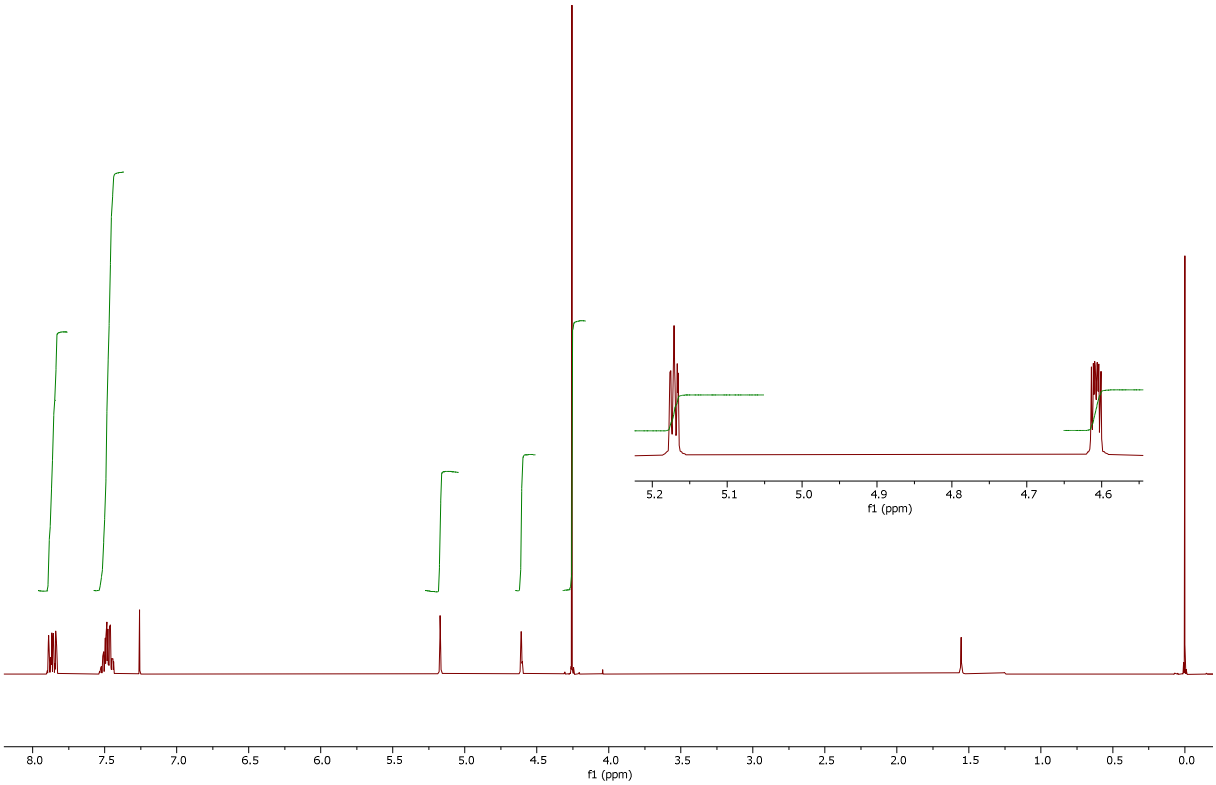


Figure S37 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **1Se**

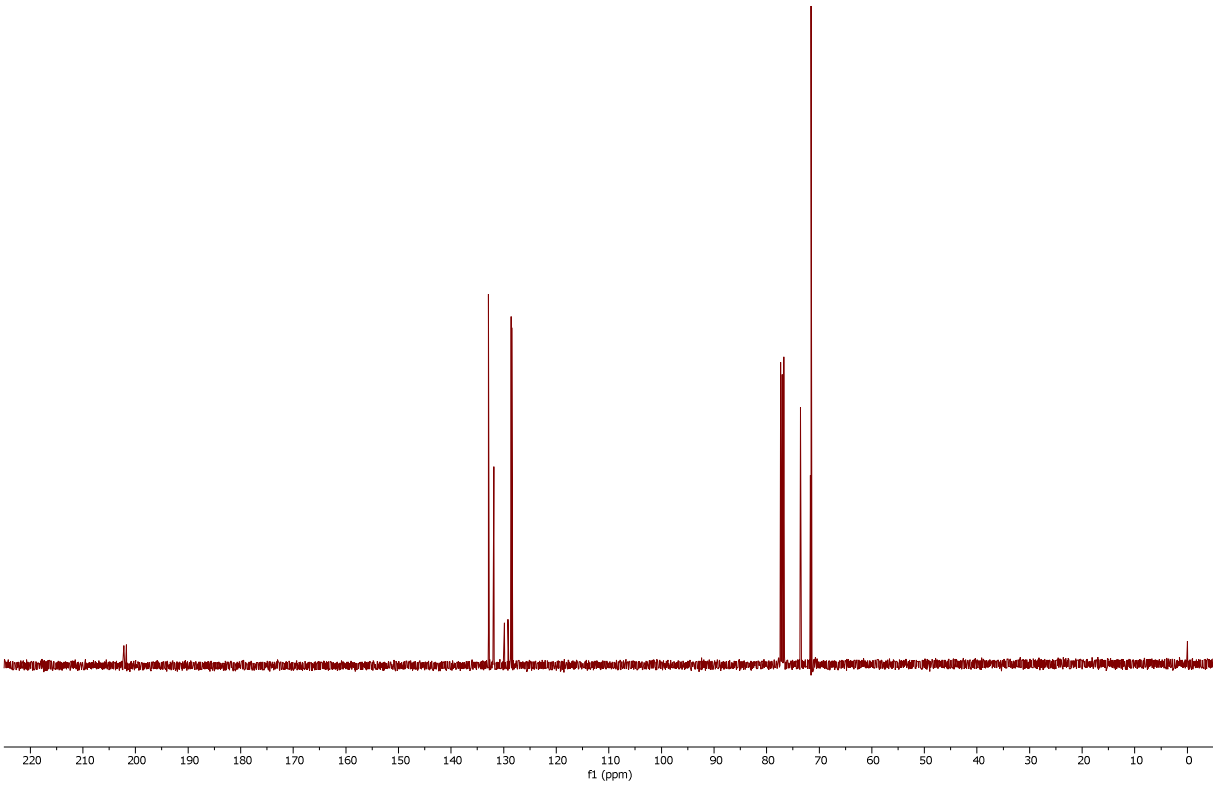


Figure S38 $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 101 MHz) of **1Se**

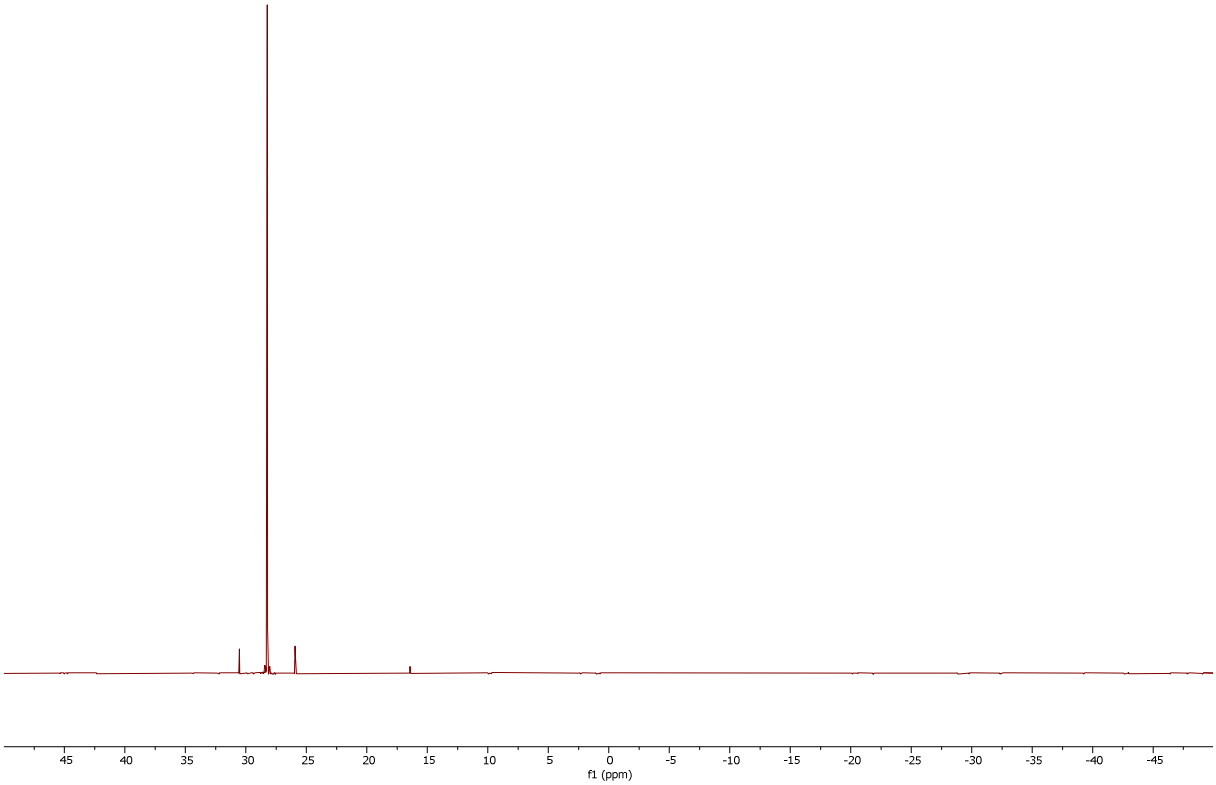


Figure S39 $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$, 162 MHz) of **1Se**

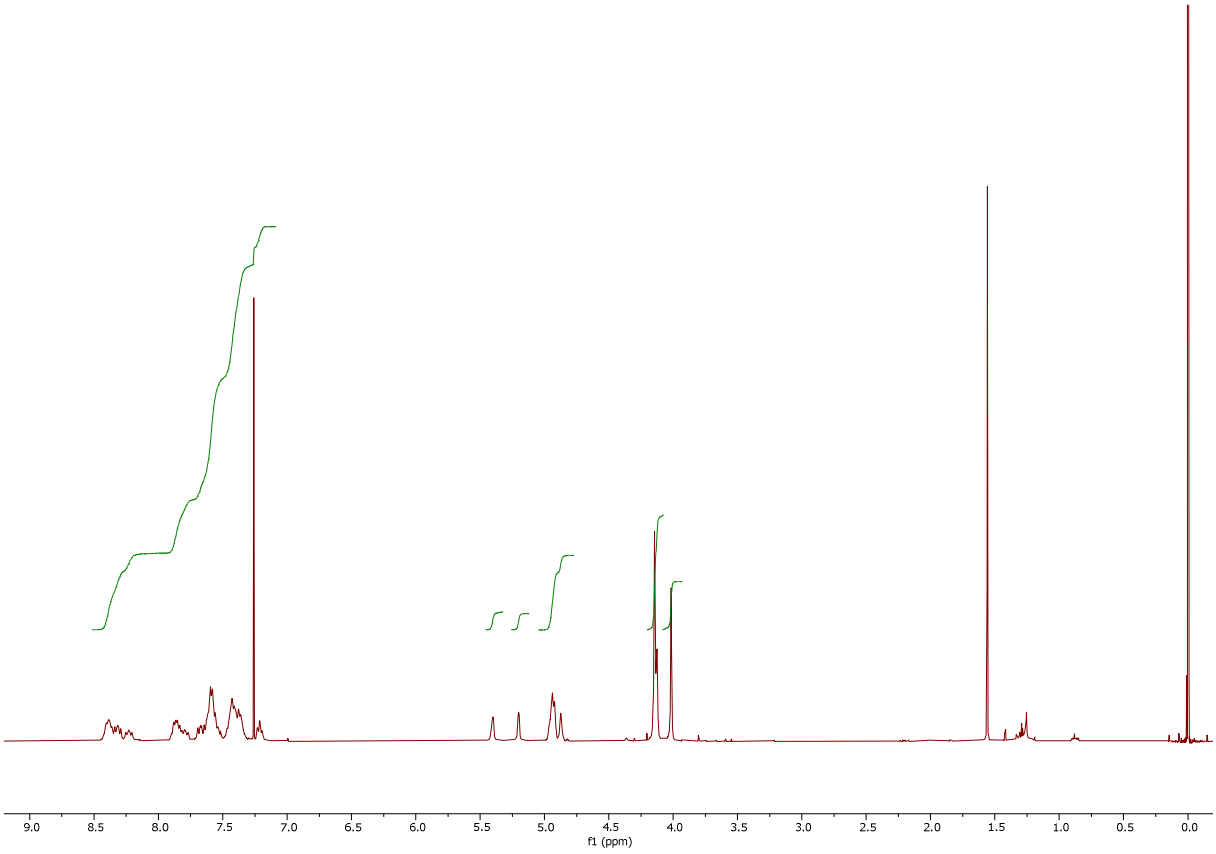


Figure S40 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **2-Cl** (mixture of isomers)

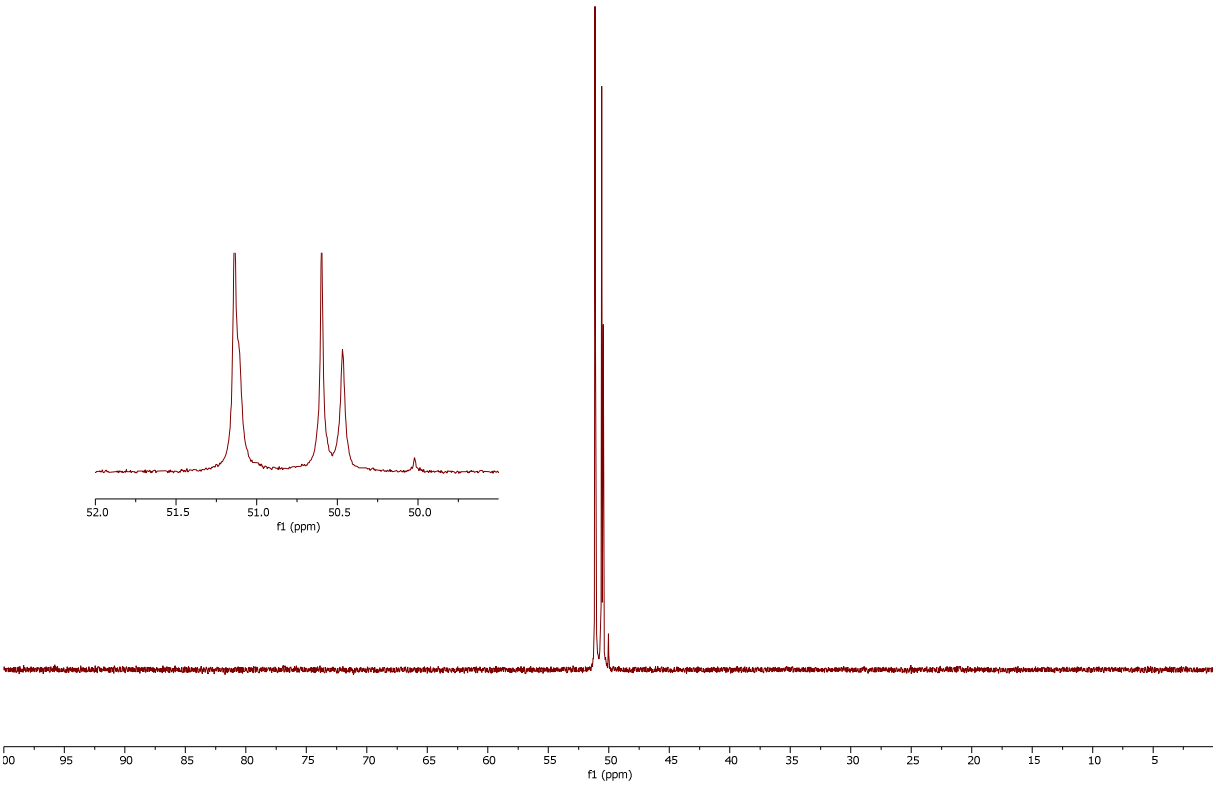


Figure S41 $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$, 162 MHz) of **2-Cl** (mixture of isomers)

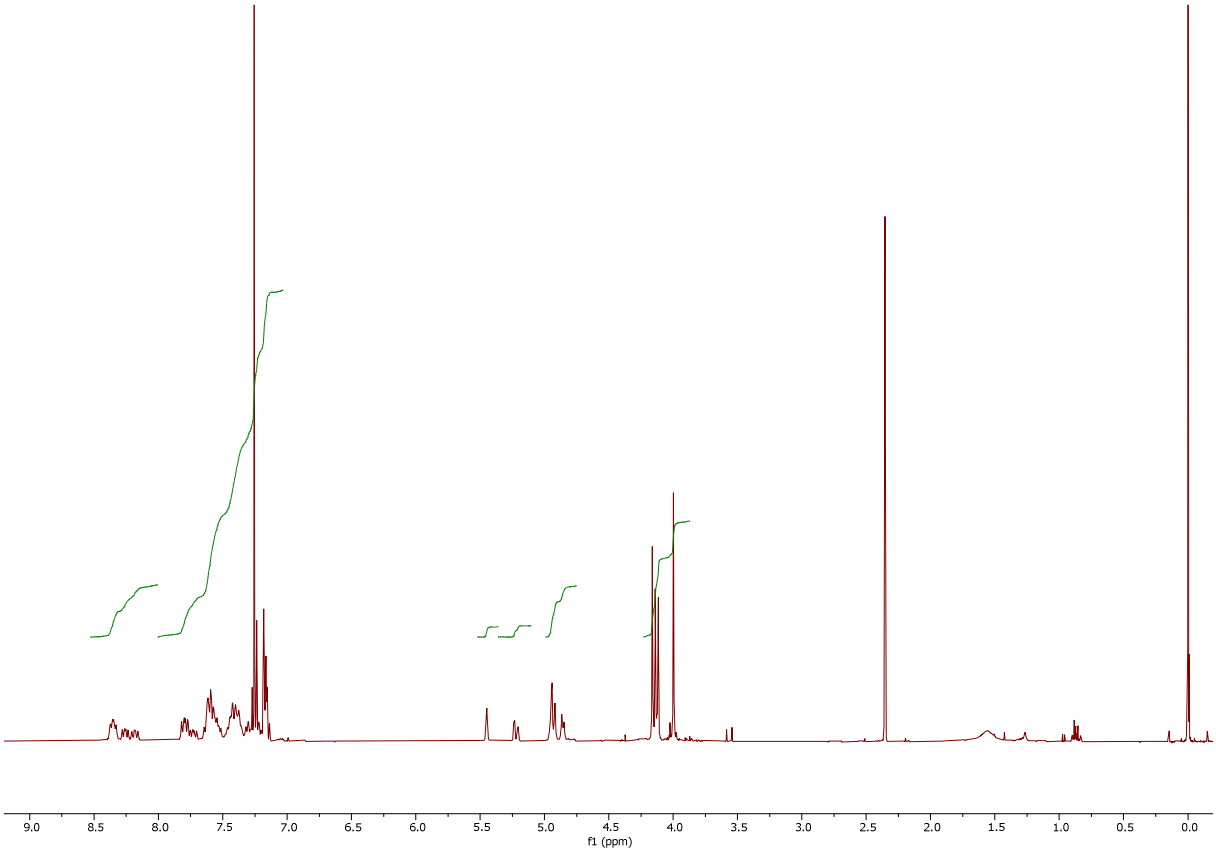


Figure S42 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **2-Br** (mixture of isomers)

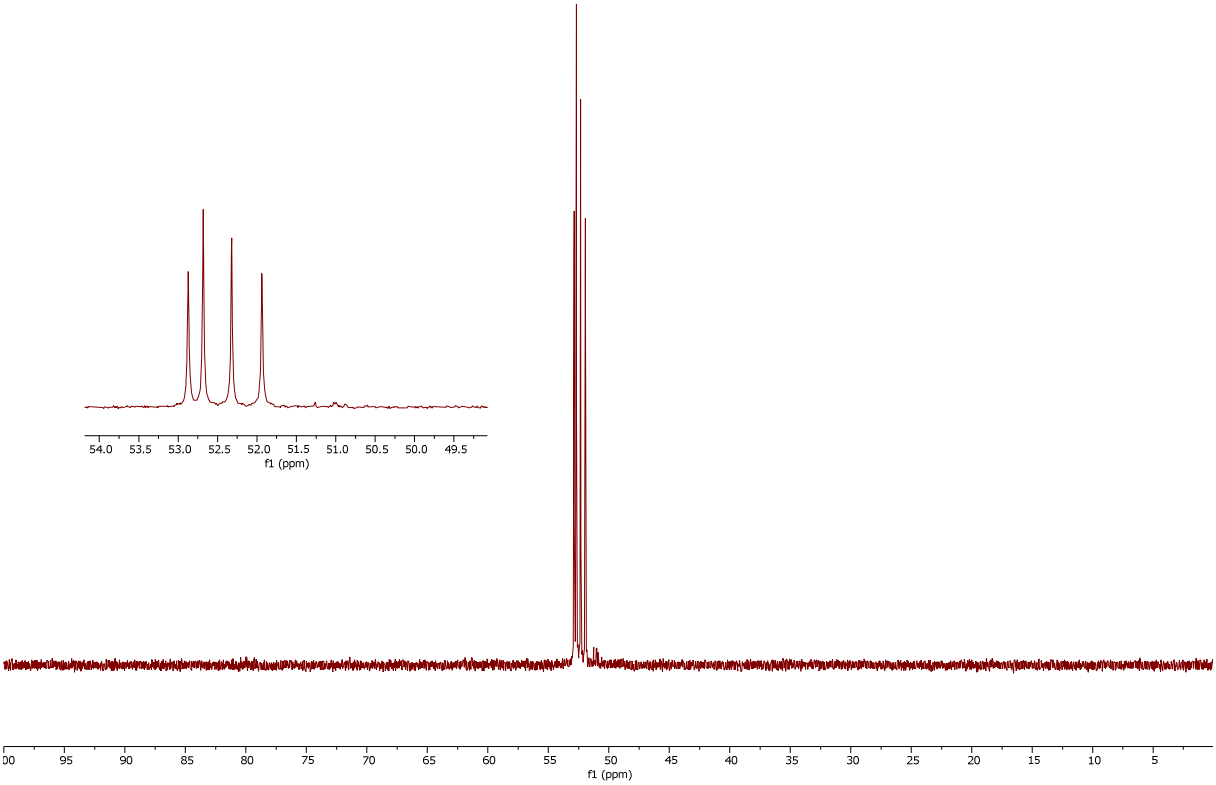


Figure S43 $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$, 162 MHz) of **2-Br** (mixture of isomers)

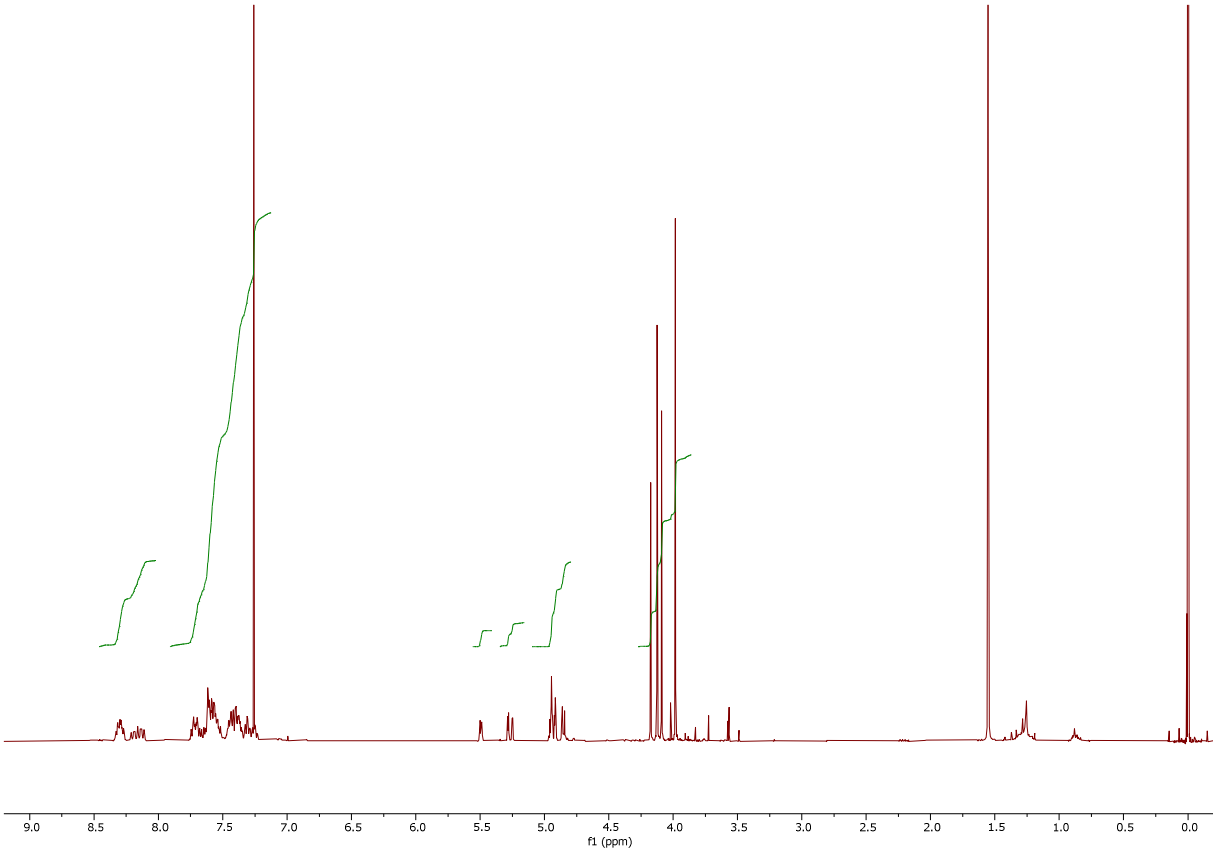


Figure S44 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **2-I** (mixture of isomers)

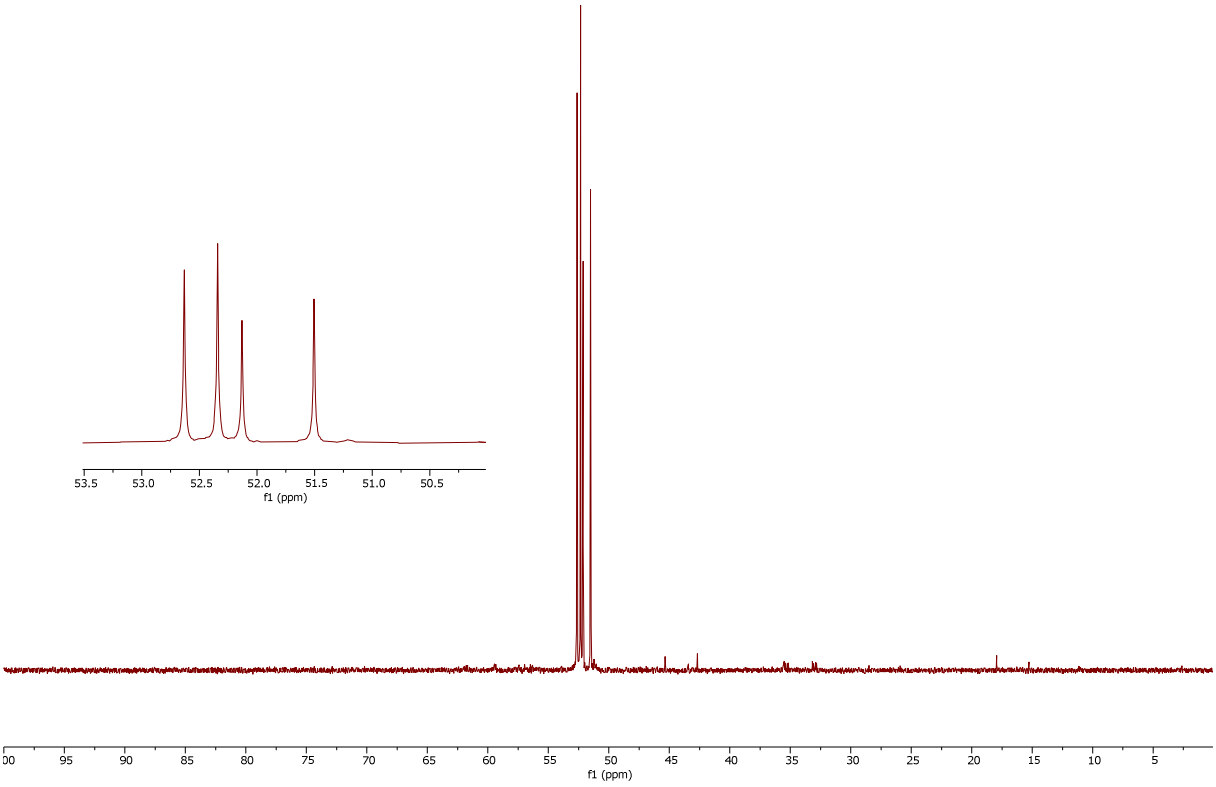


Figure S45 $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$, 162 MHz) of **2-I** (mixture of isomers)

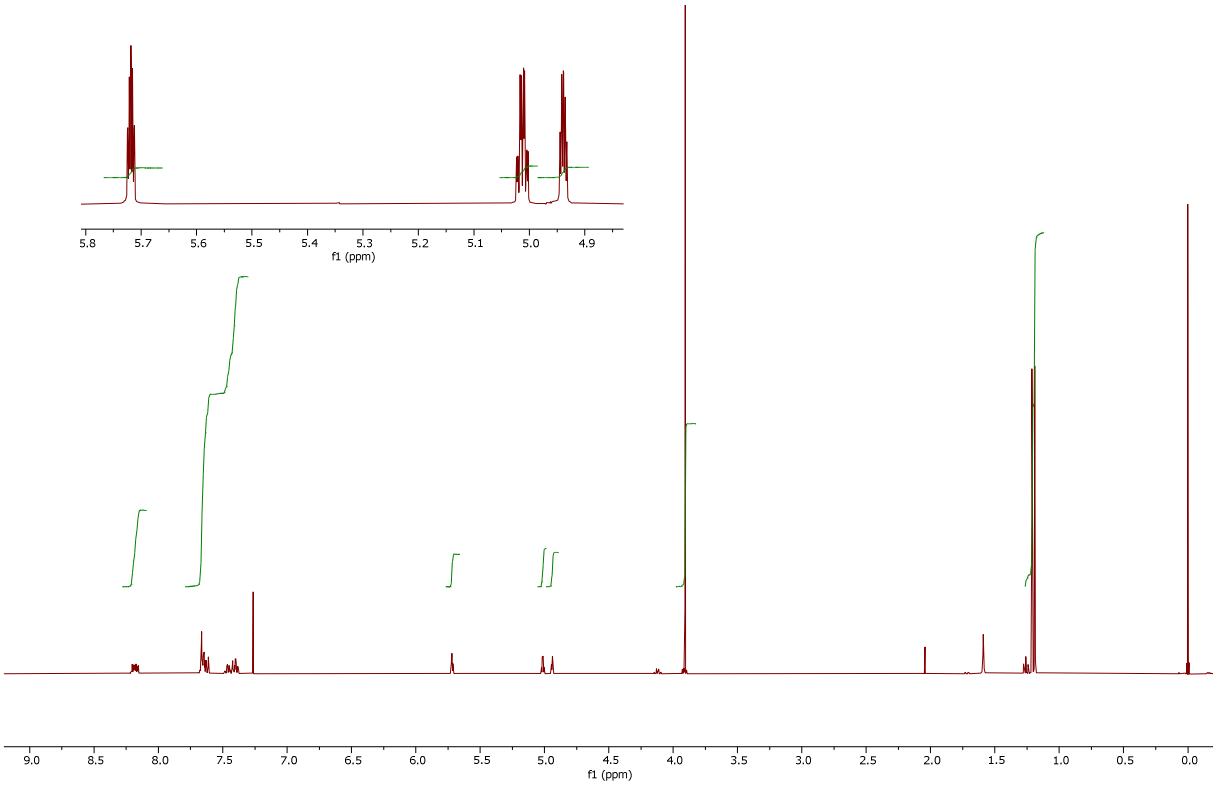


Figure S46 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of *cis*-**3a**

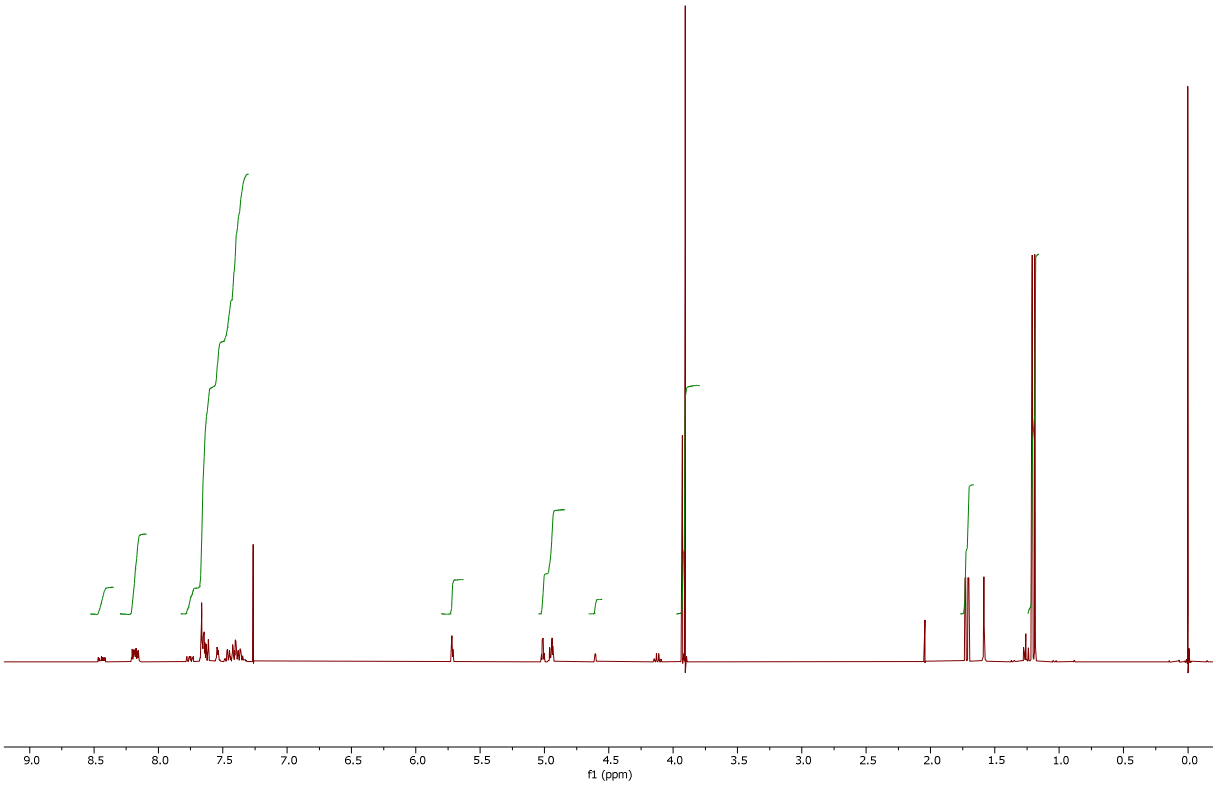


Figure S47 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of *cis*- and *trans*-**3a** (aged sample)

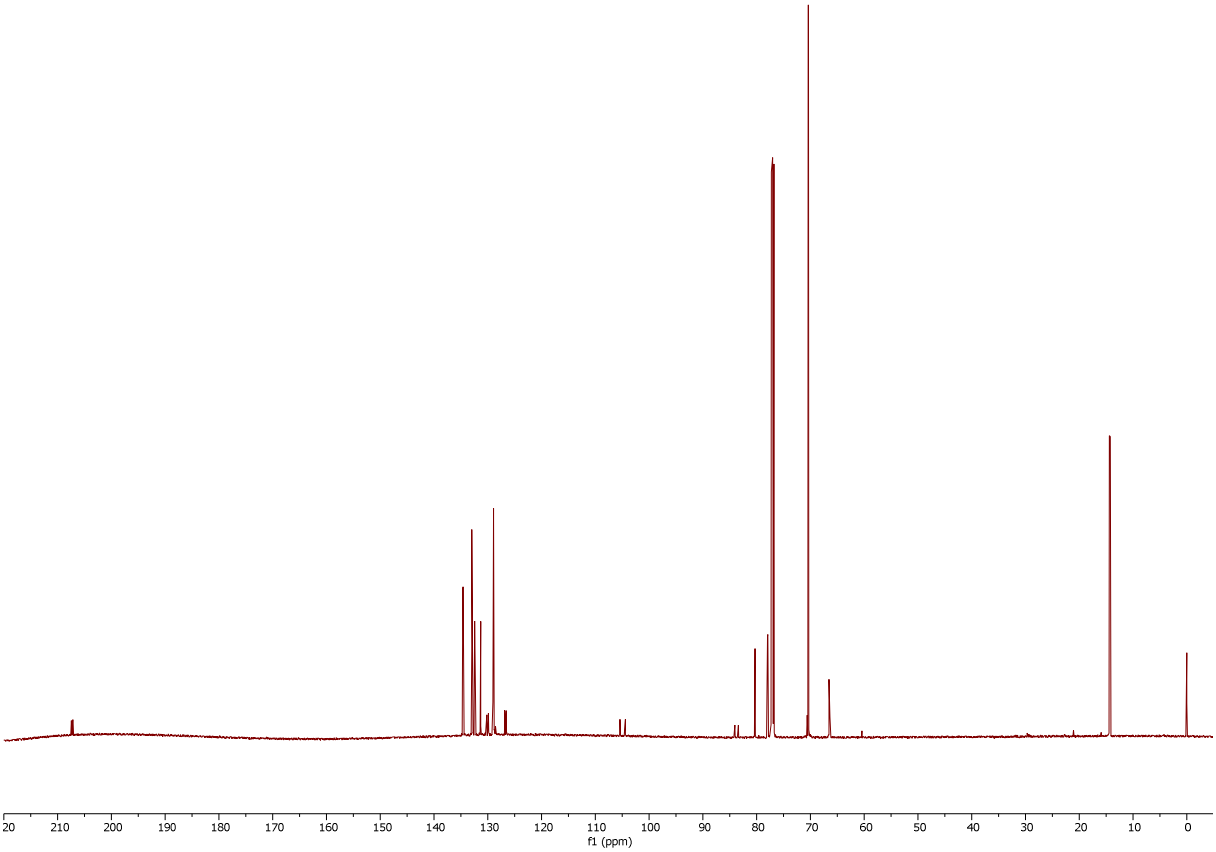


Figure S48 $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 151 MHz) of *cis*-**3a**

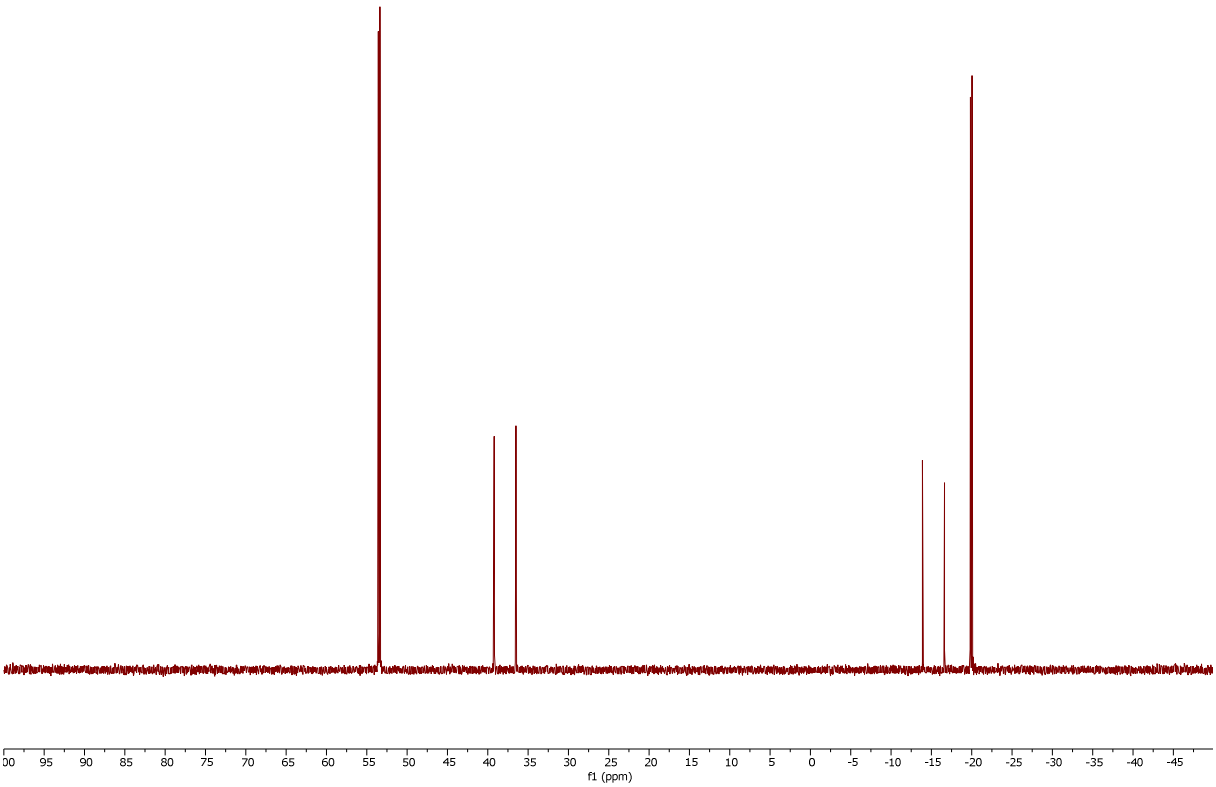


Figure S49 $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$, 162 MHz) of **3a** (mixture of isomers)

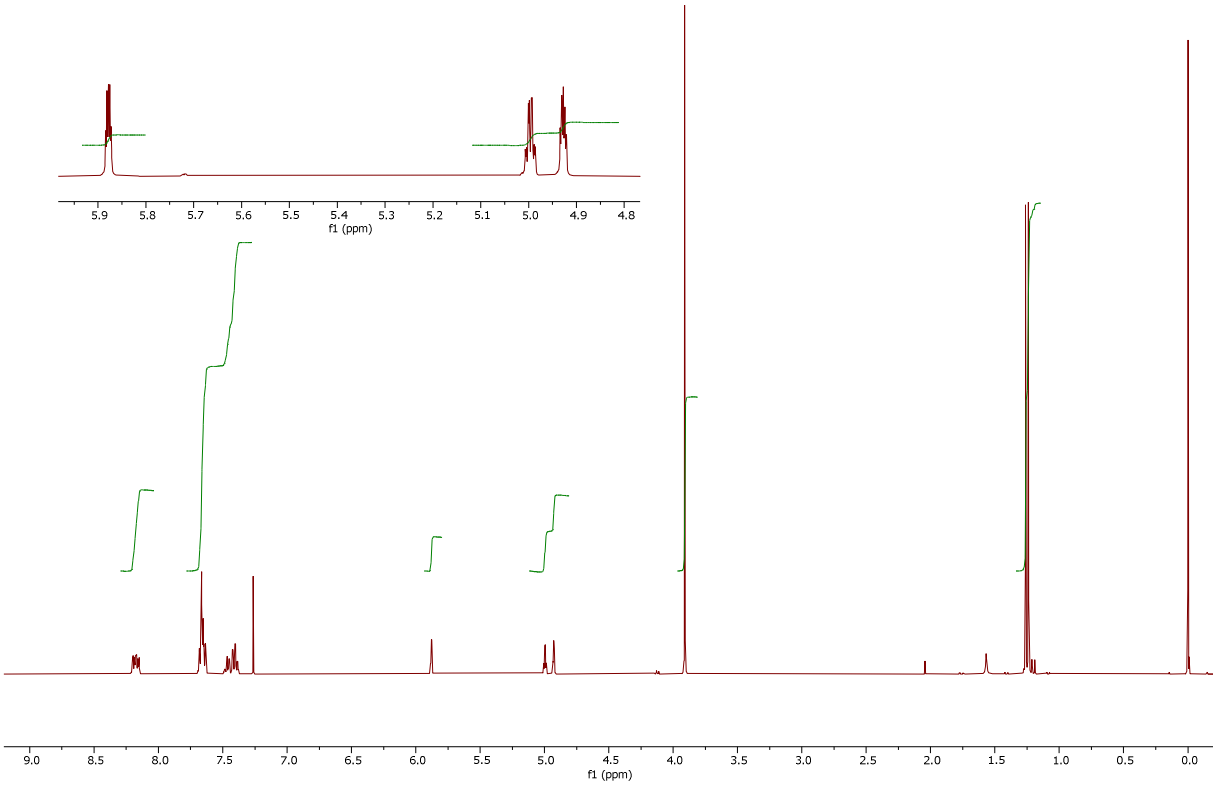


Figure S50 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of *cis*-**4a**

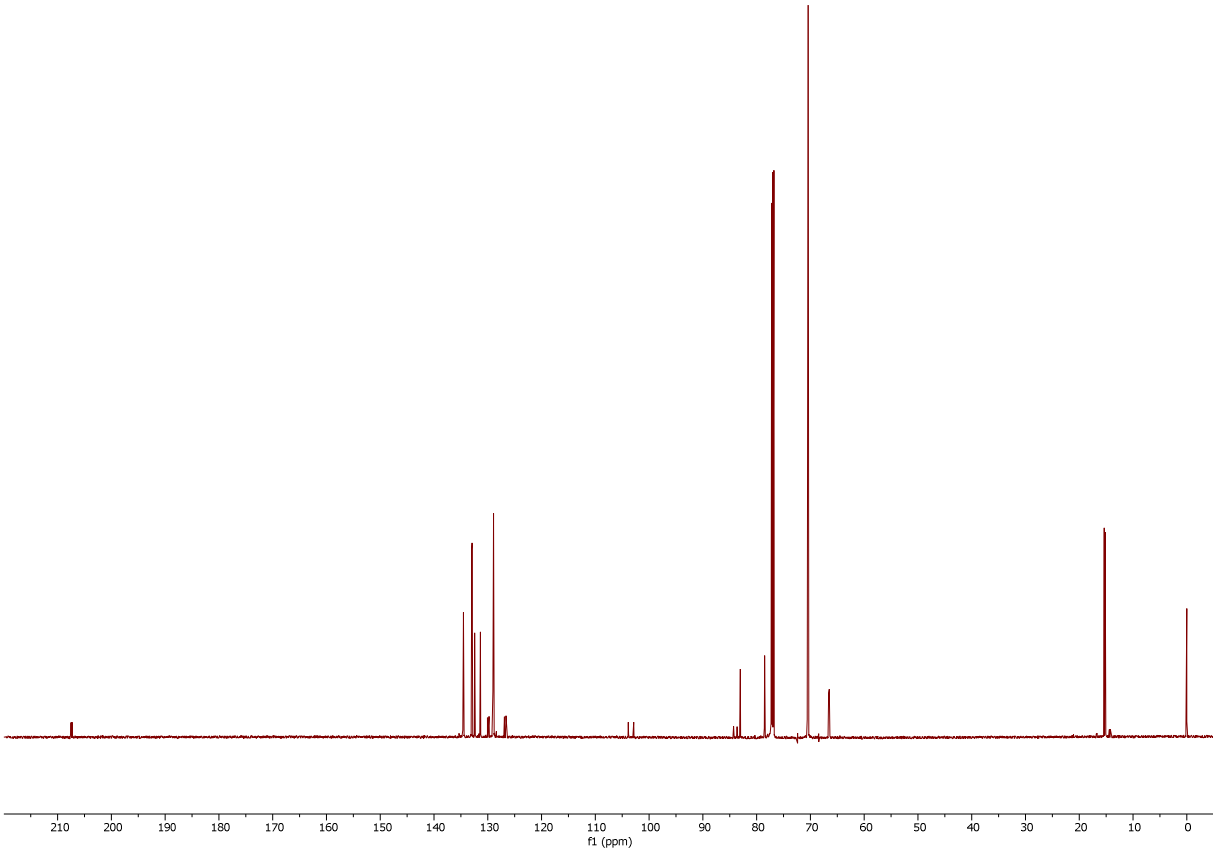


Figure S51 $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 151 MHz) of *cis*-**4a**

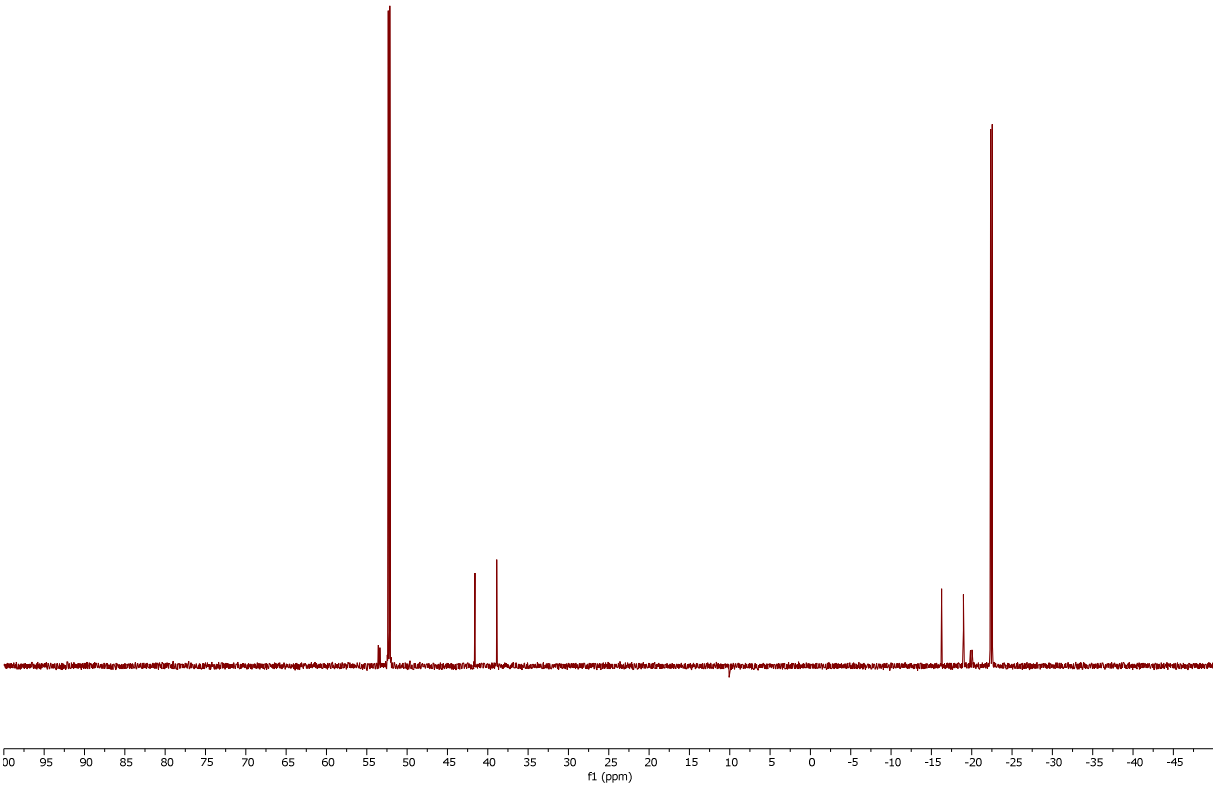


Figure S52 $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$, 162 MHz) of **4a** (isomer mixture)

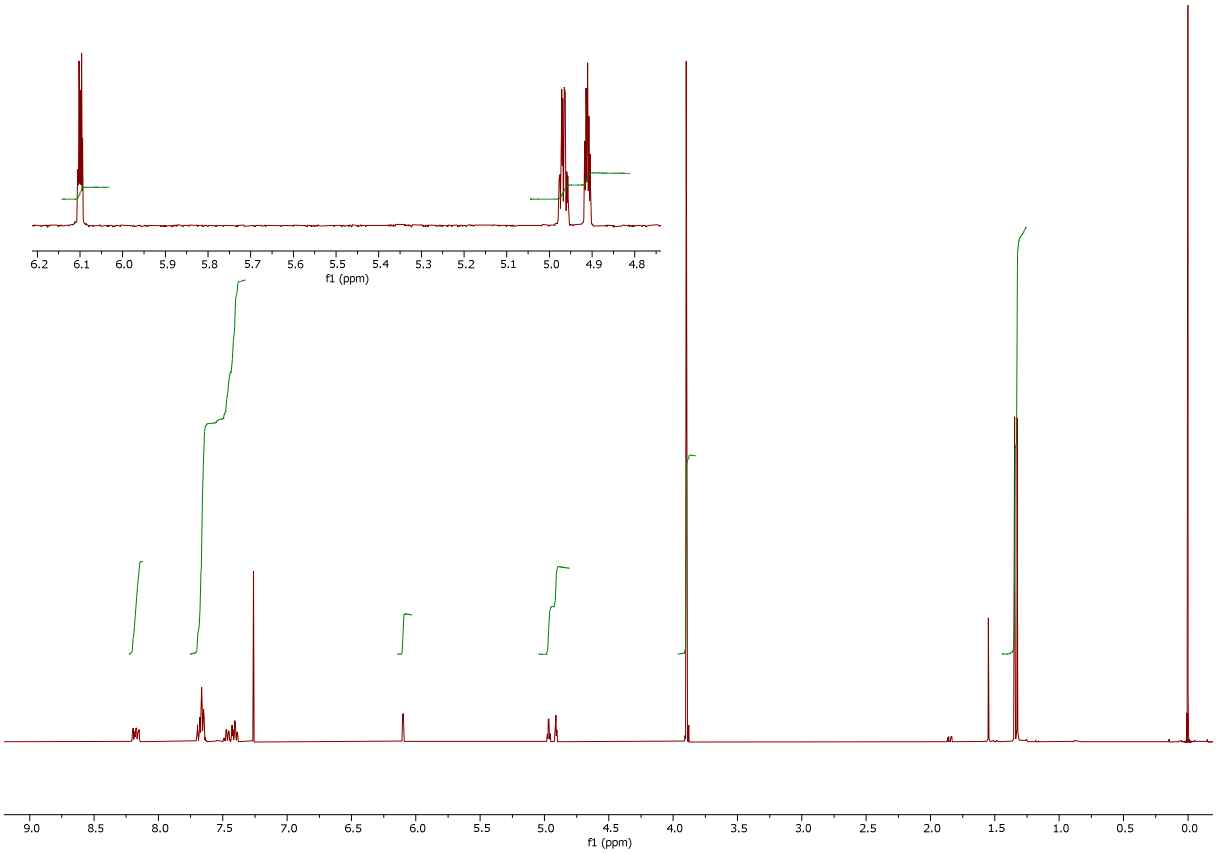


Figure S53 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of *cis*-**5a**

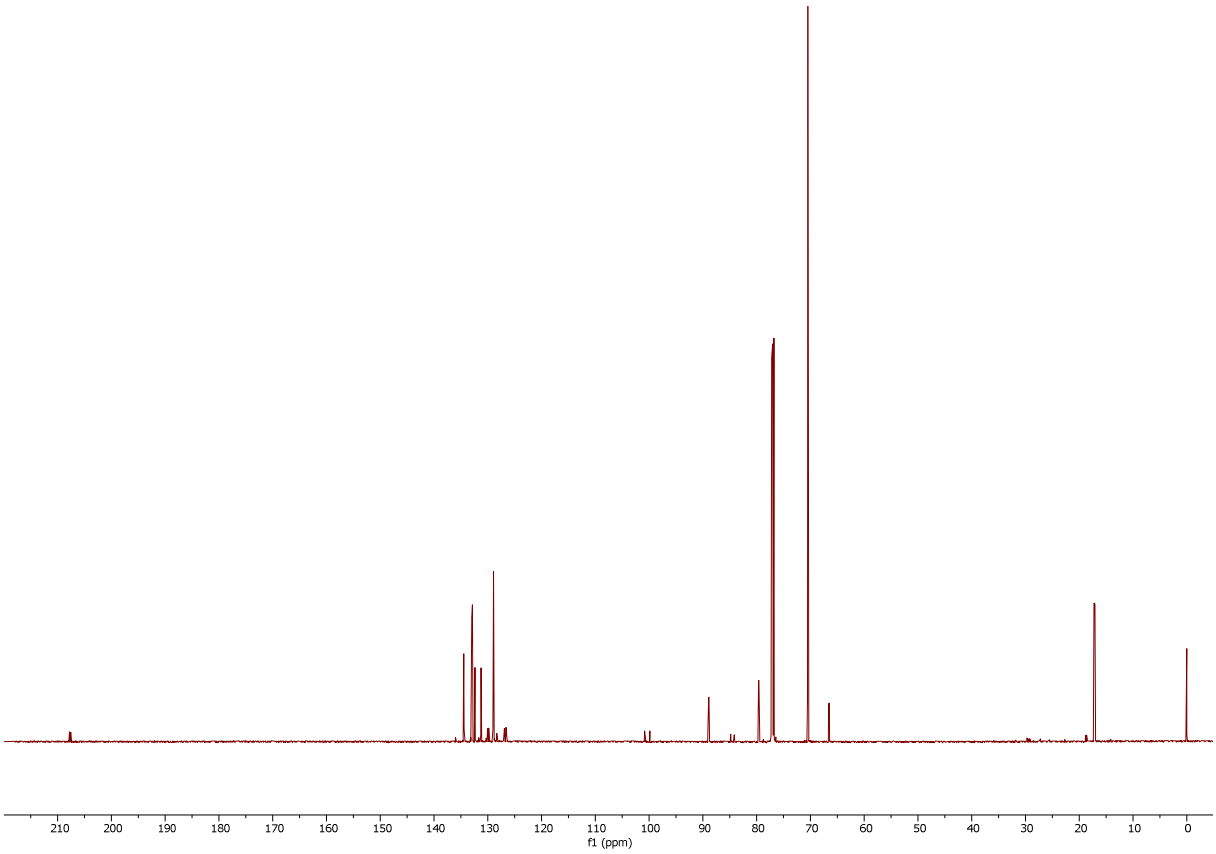


Figure S54 $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 151 MHz) of *cis*-**5a**

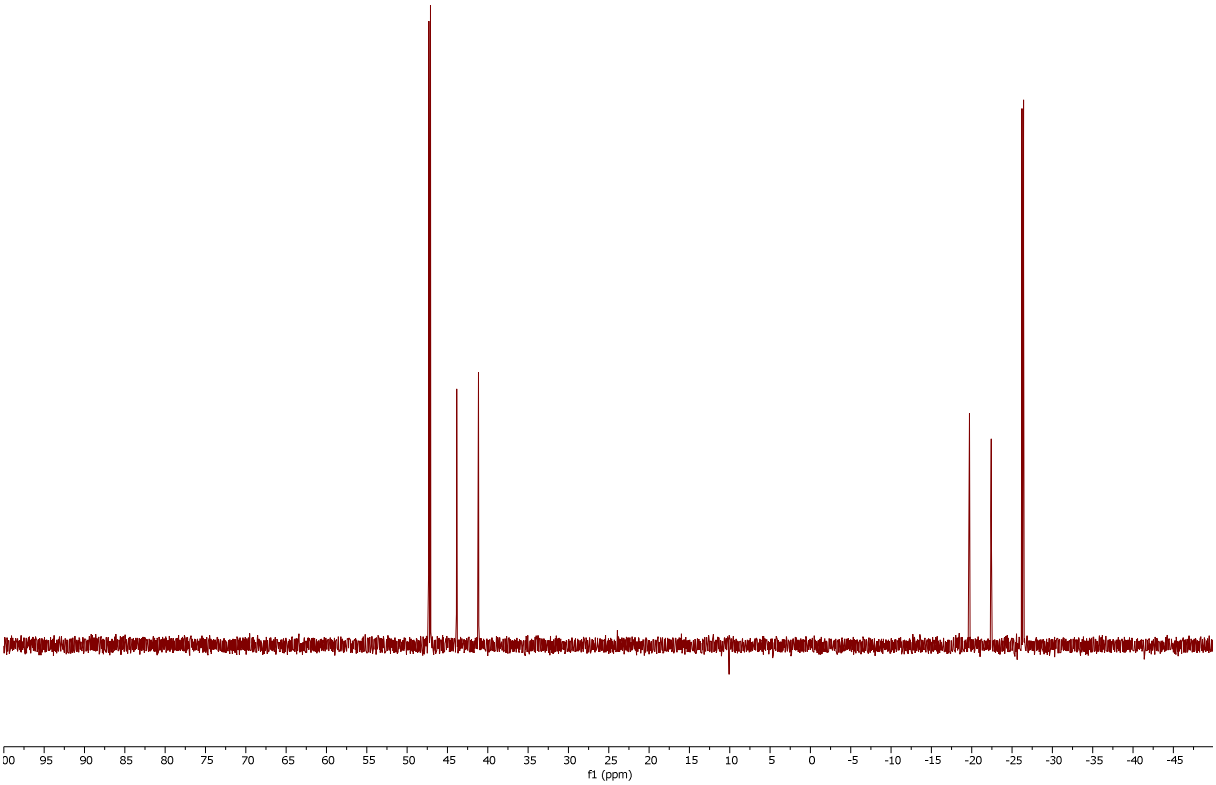


Figure S55 $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$, 162 MHz) of **5a** (mixture of isomers)

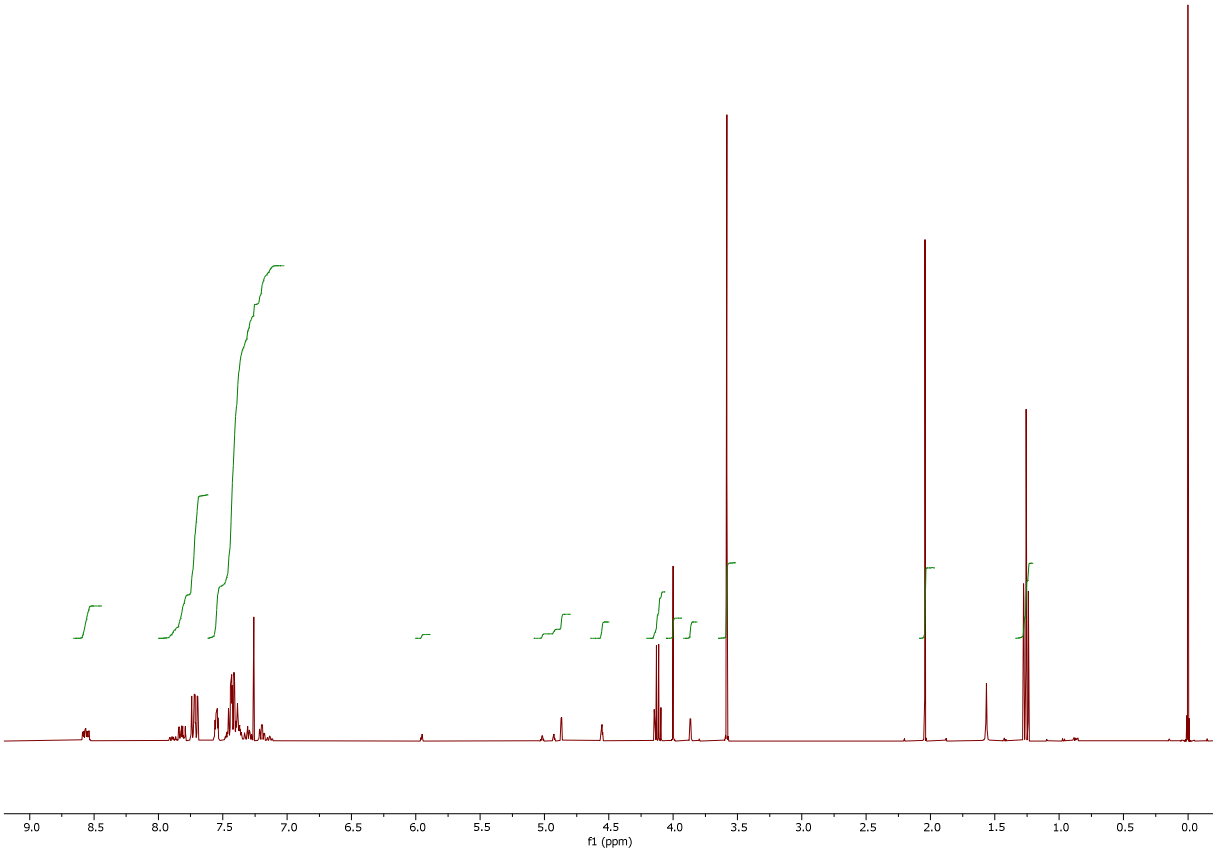


Figure S56 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3b** (isomer mixture; *Note*: the sample contained AcOEt)

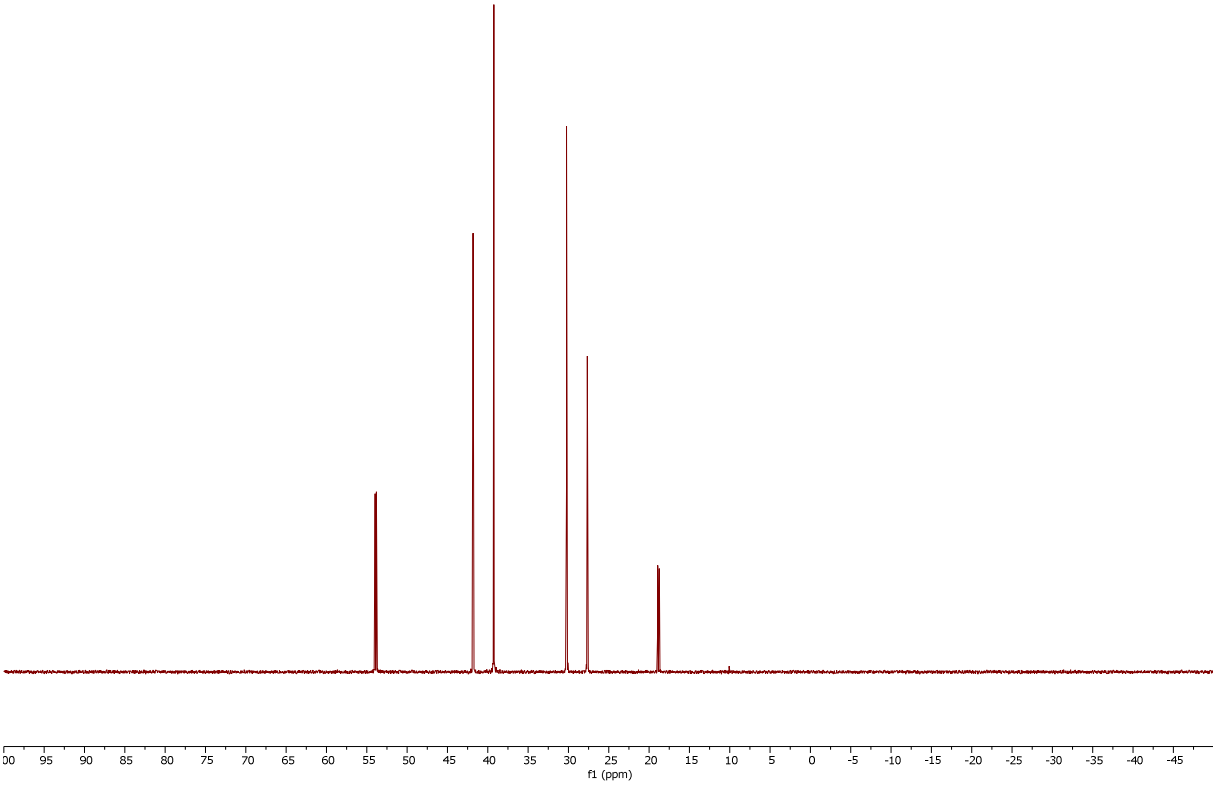


Figure S57 $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$, 162 MHz) of **3b** (isomer mixture)

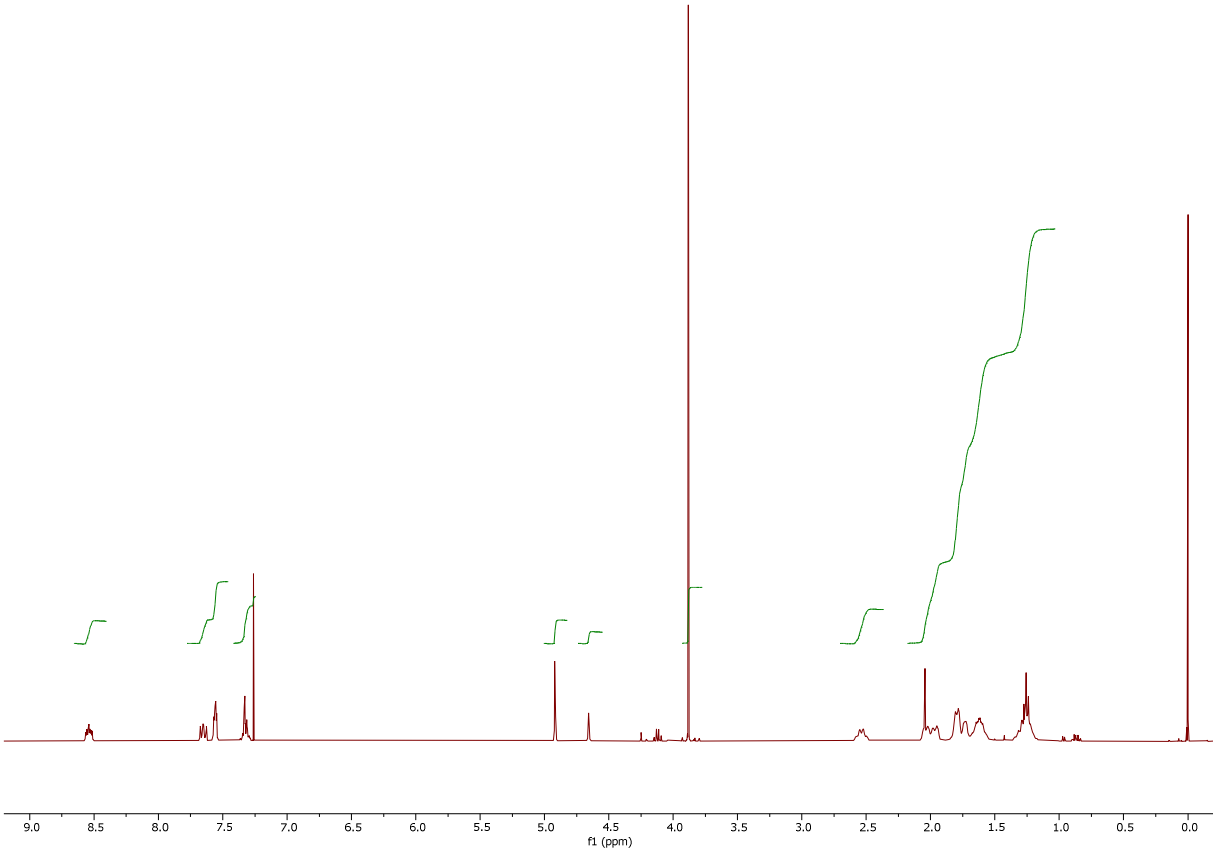


Figure S58 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of *trans*-**3c**

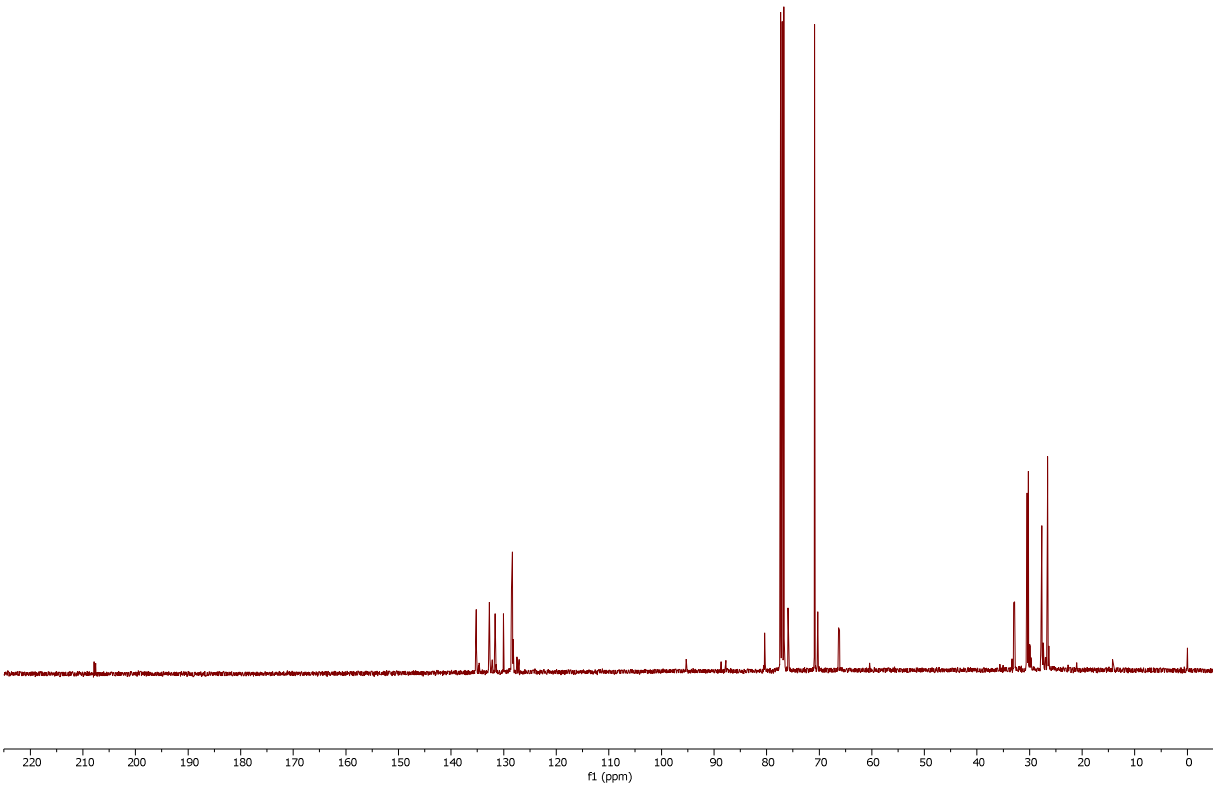


Figure S59 $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 101 MHz) of **3c** (isomer mixture)

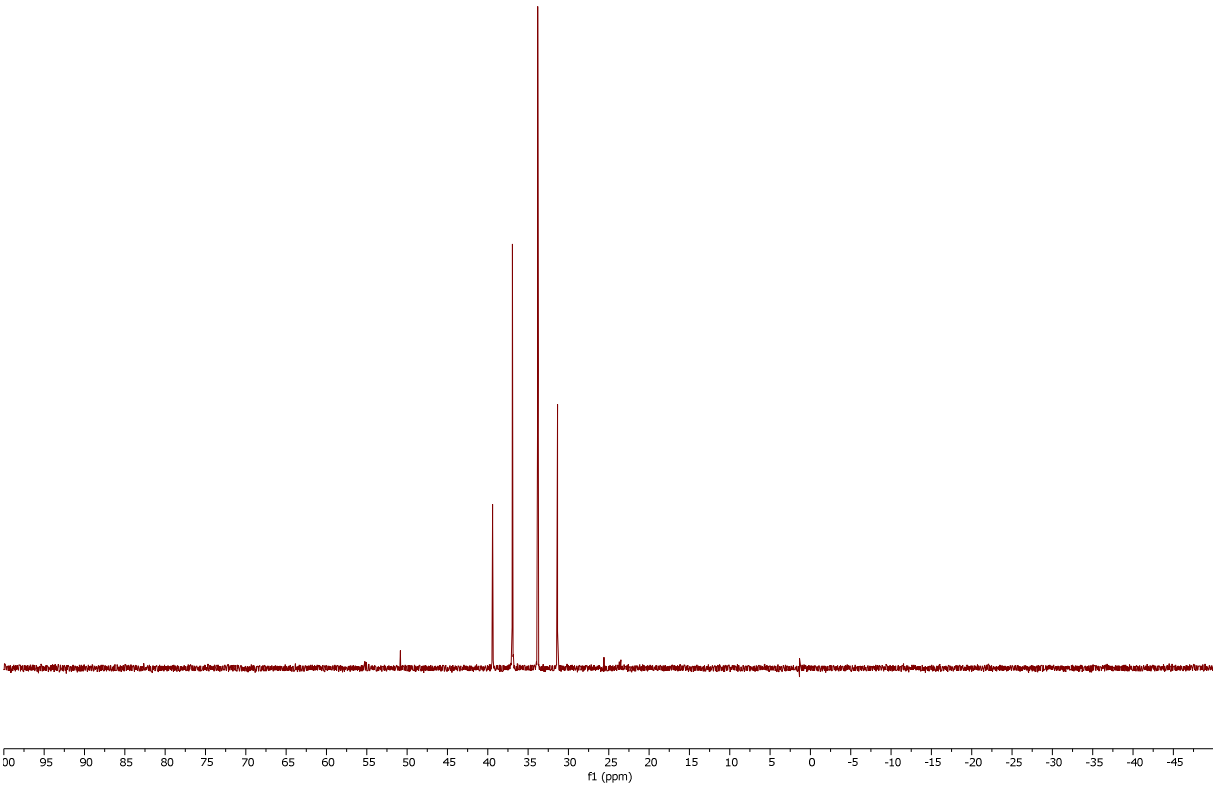


Figure S60 $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$, 162 MHz) of *trans*-**3c**

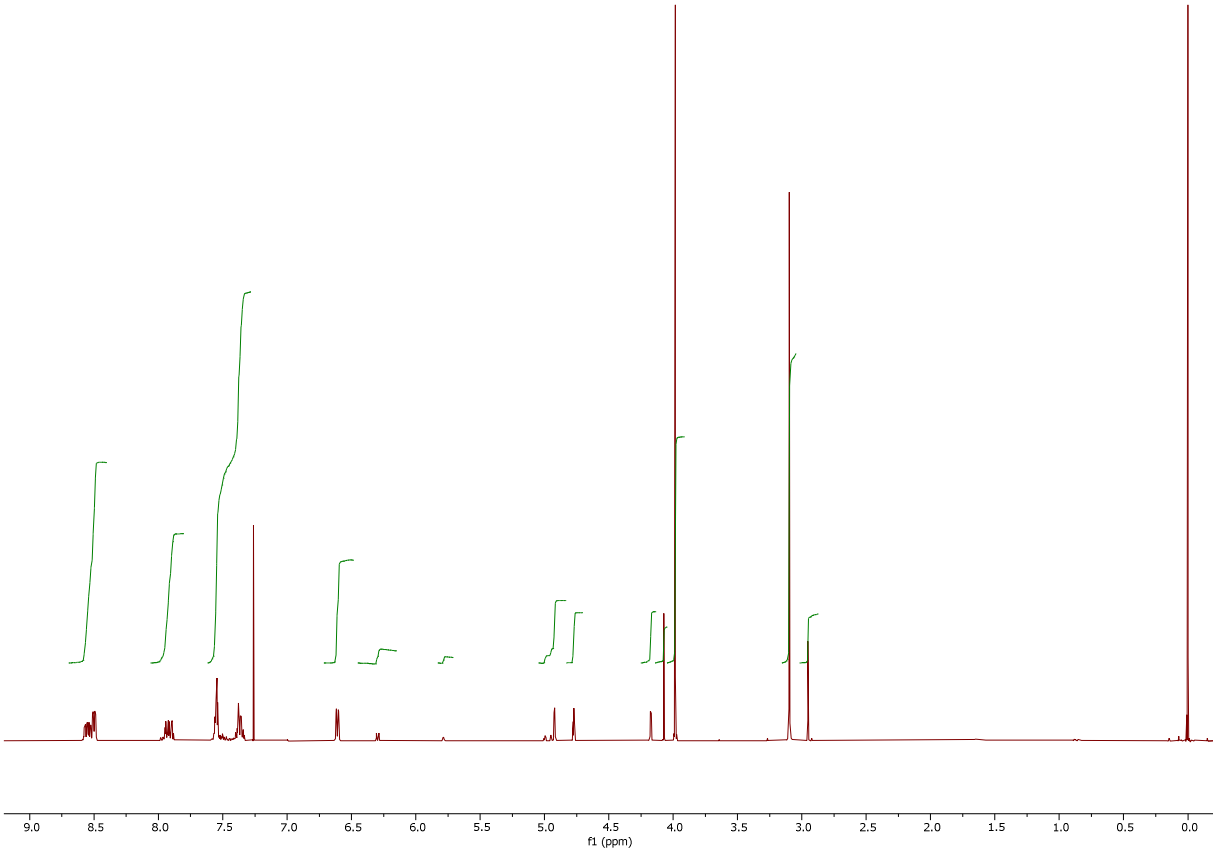


Figure S61 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3d** (isomer mixture)

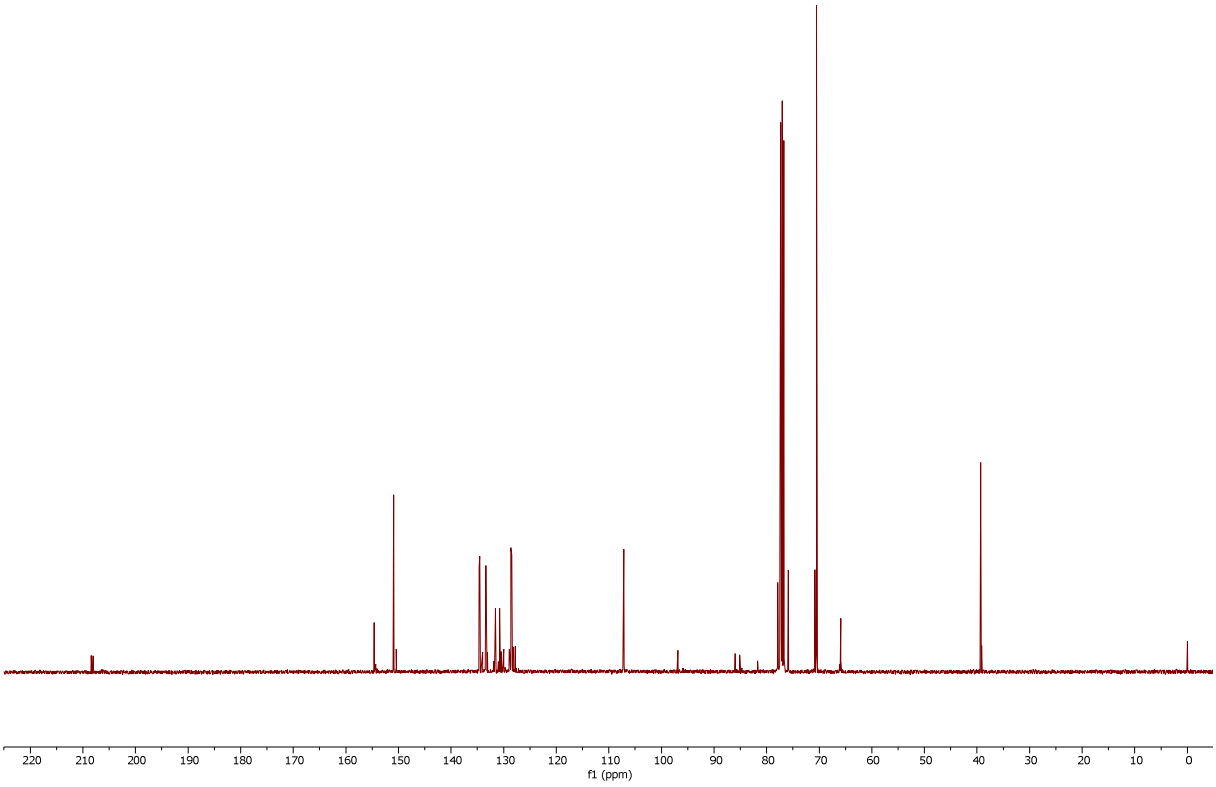


Figure 62 $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 101 MHz) of **3d** (isomer mixture)

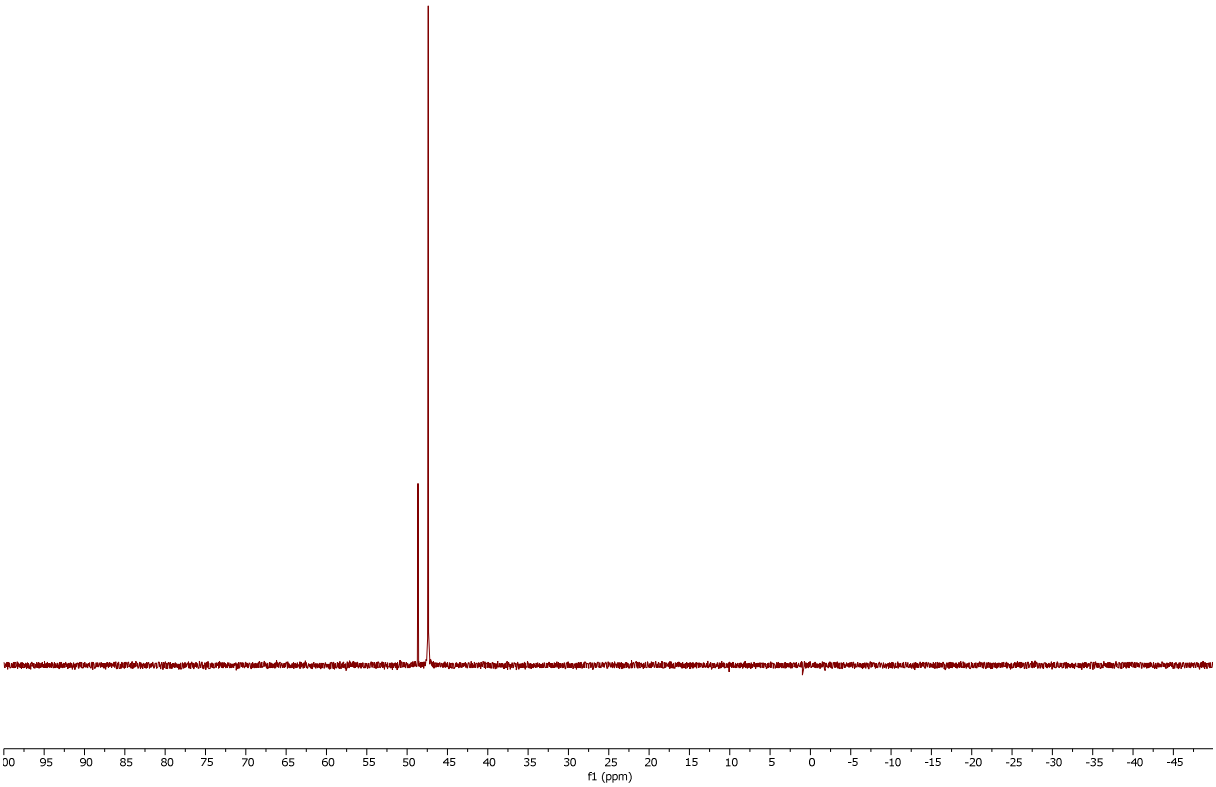


Figure S63 $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$, 162 MHz) of **3d** (isomer mixture)

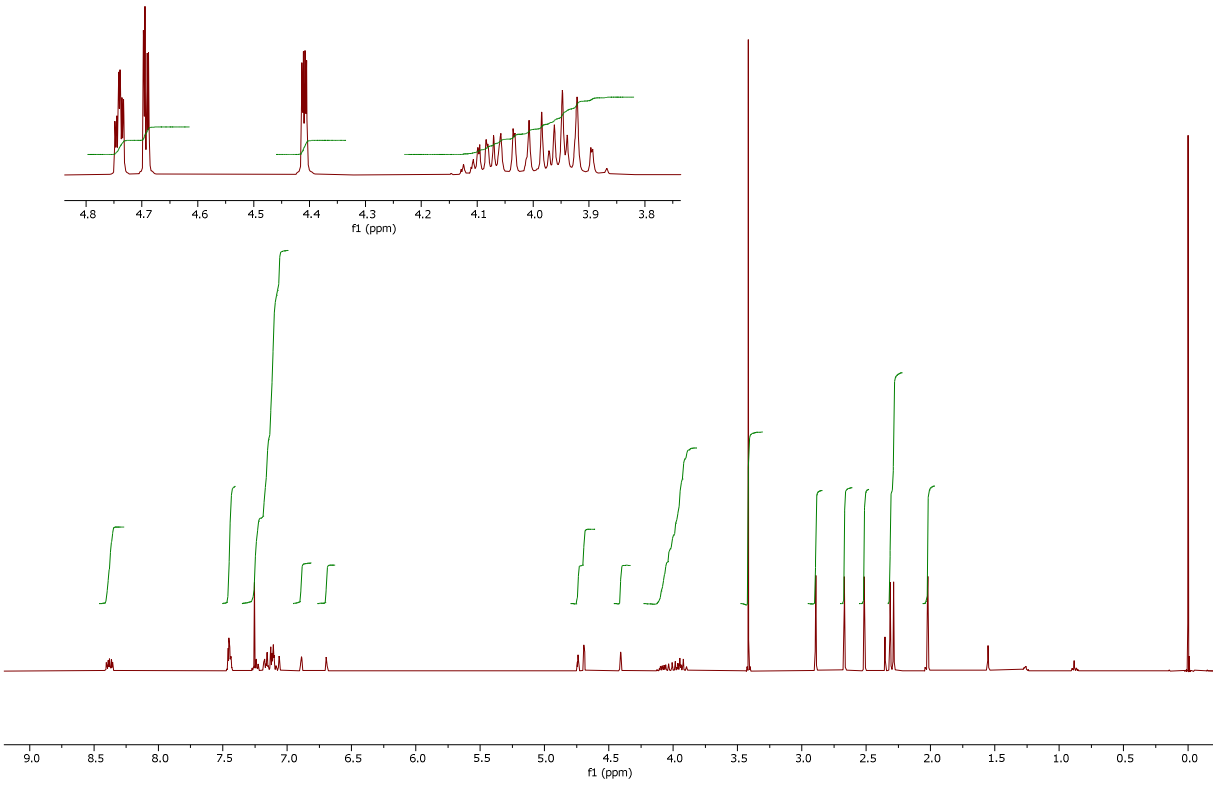


Figure S64 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of *trans*-**3e**

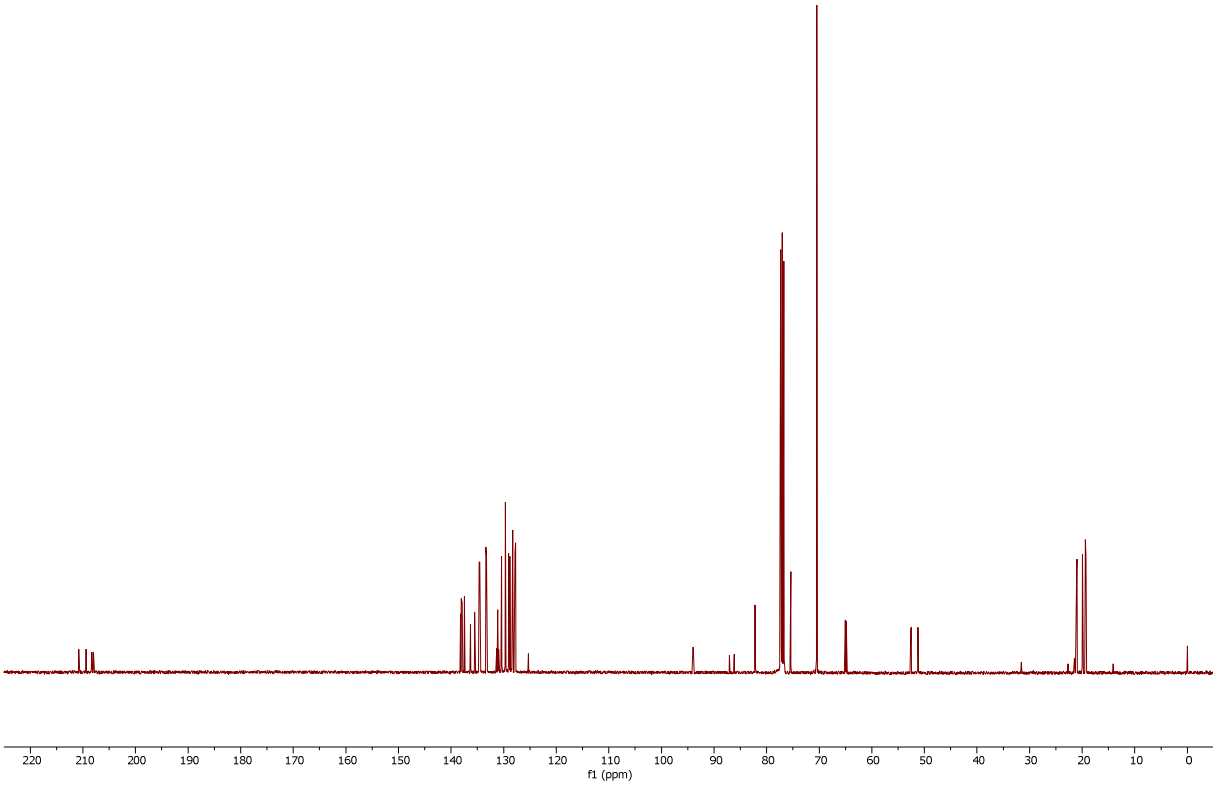


Figure S65 $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 101 MHz) of *trans*-**3e**

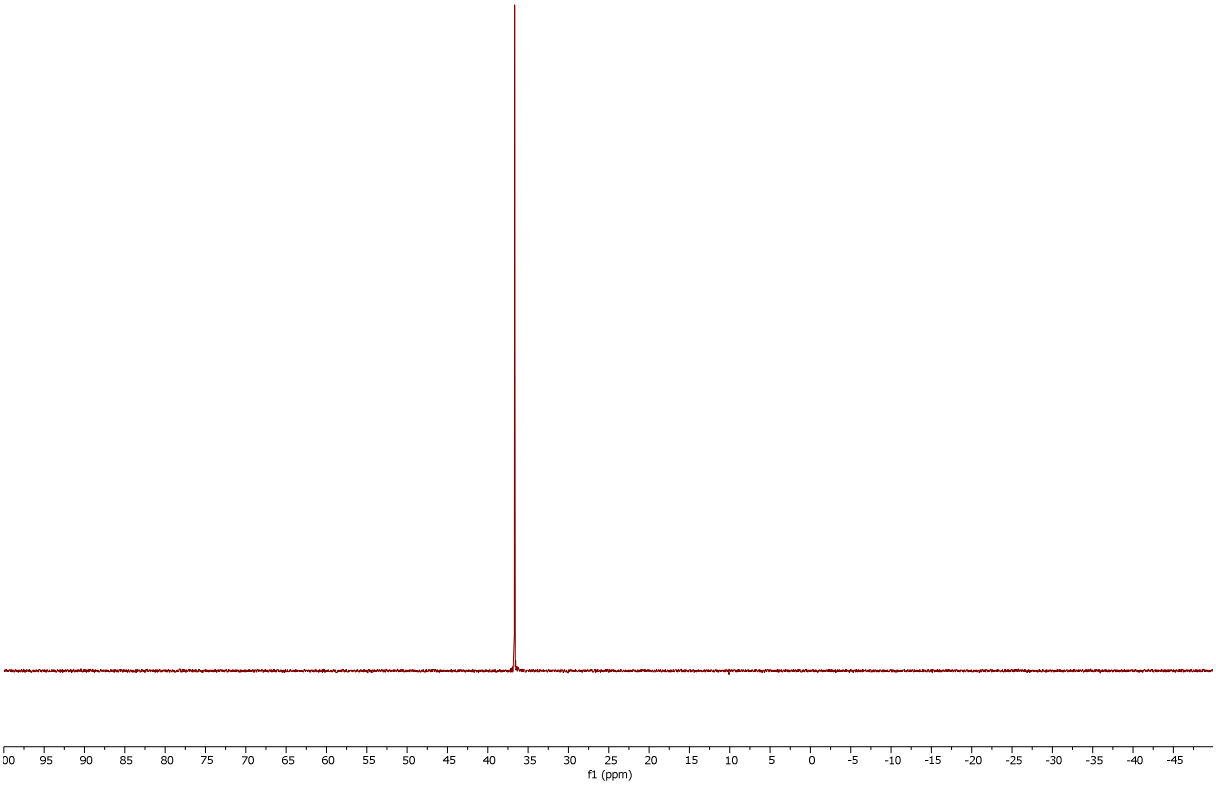


Figure S66 $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$, 162 MHz) of *trans*-**3e**

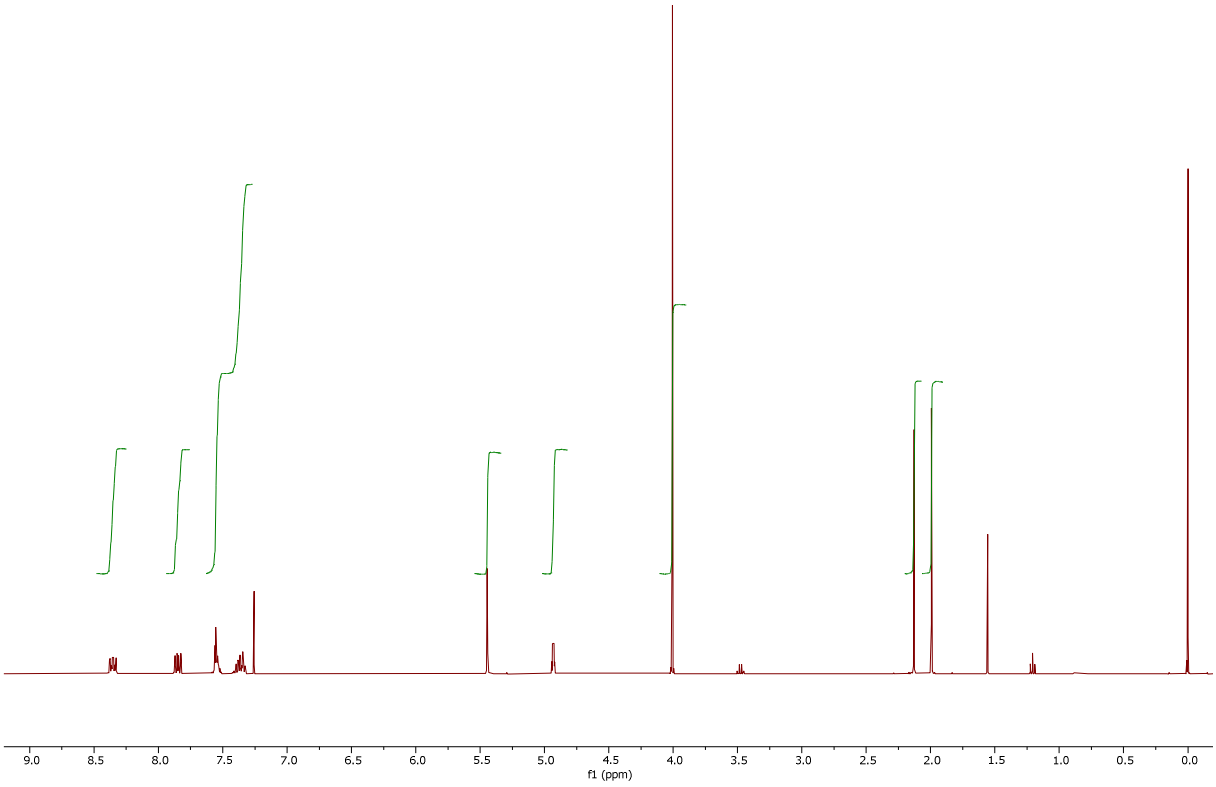


Figure S67 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **6**

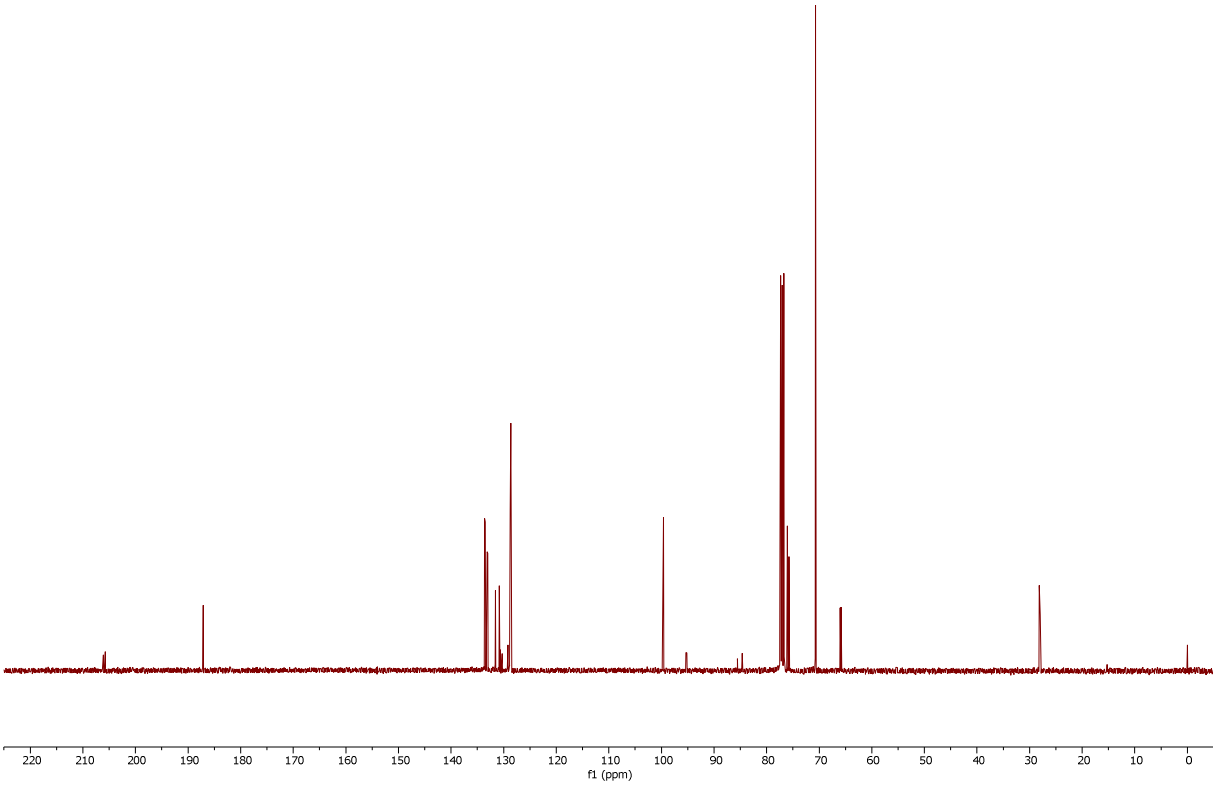


Figure S68 $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 101 MHz) of **6**

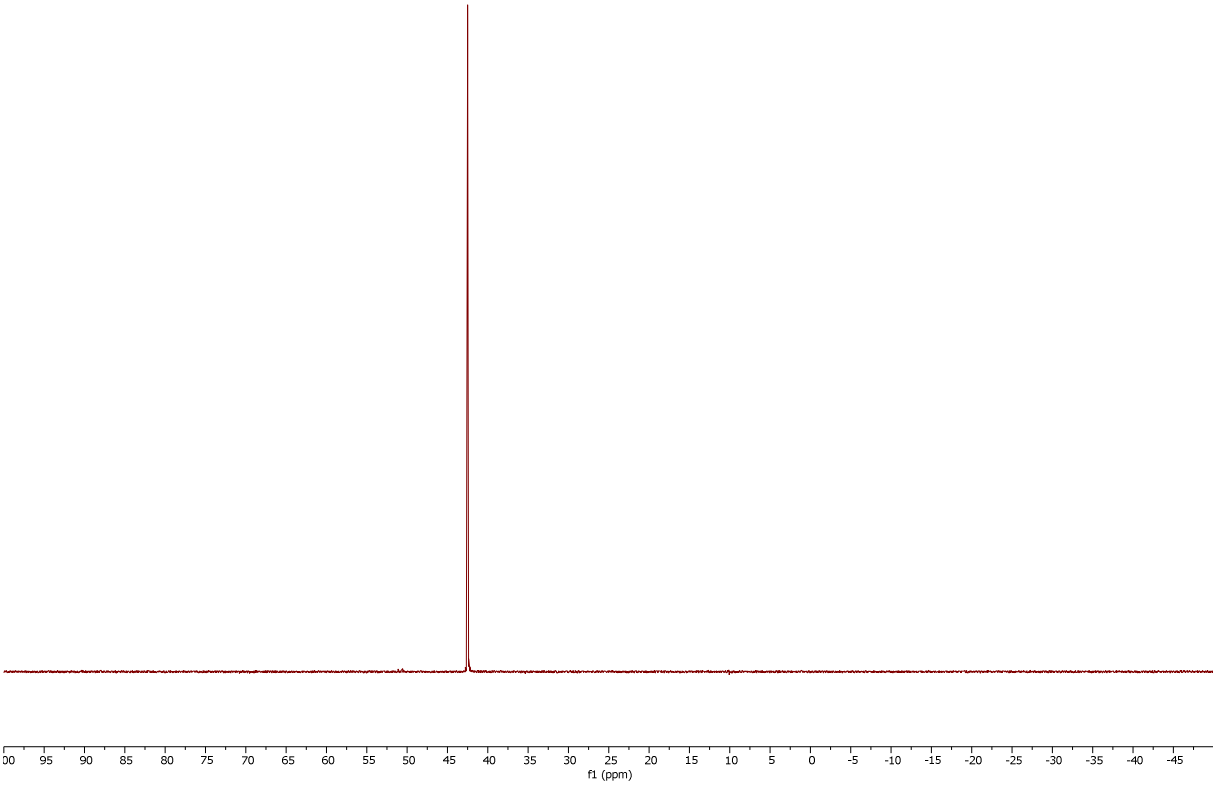


Figure S69 $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$, 162 MHz) of **6**

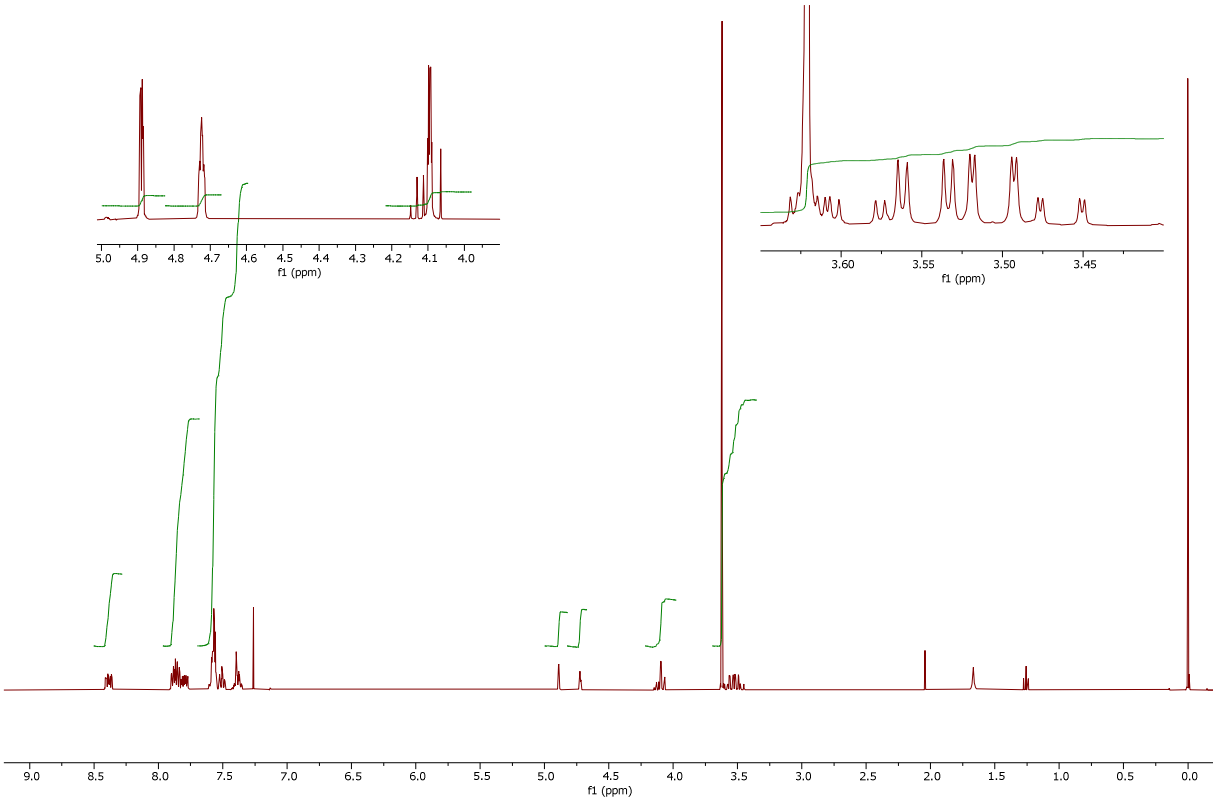


Figure S70 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of *trans*-**7**

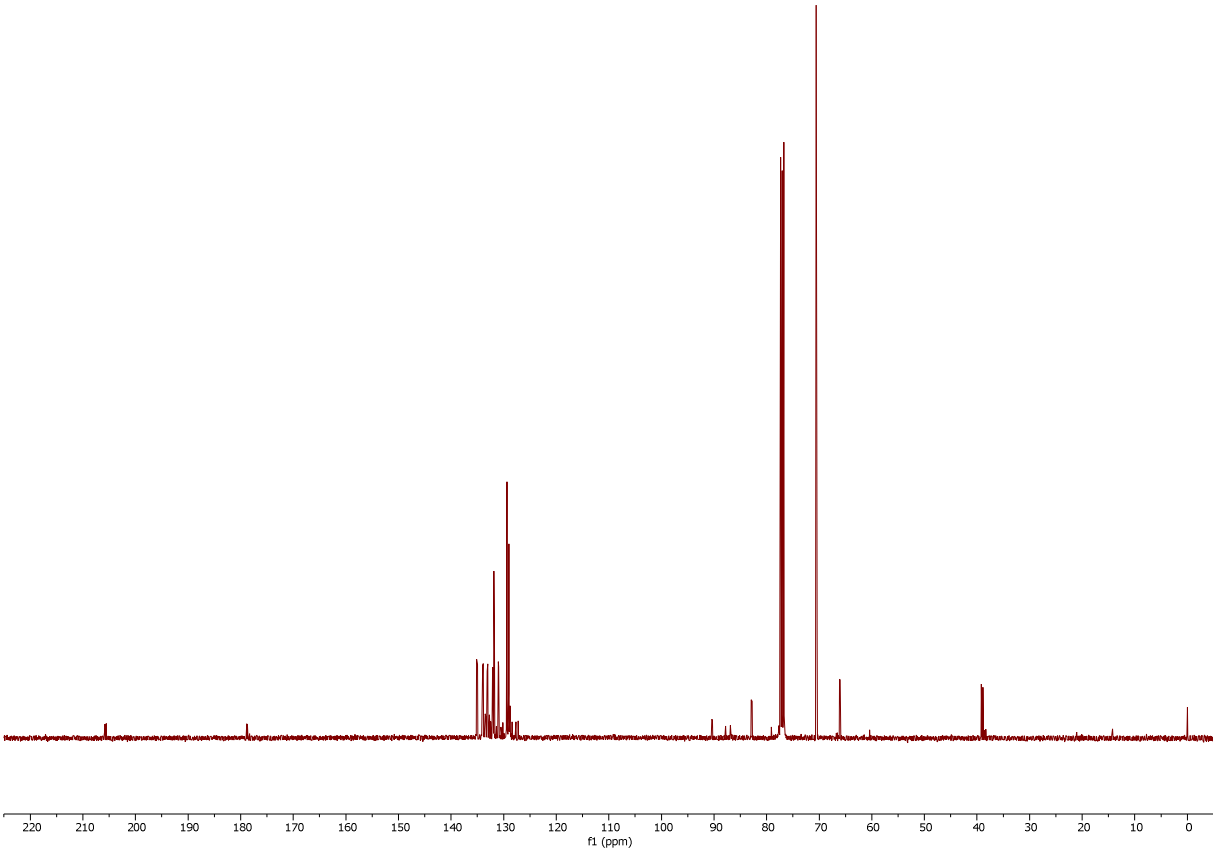


Figure S71 $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 101 MHz) of **7** (isomer mixture)

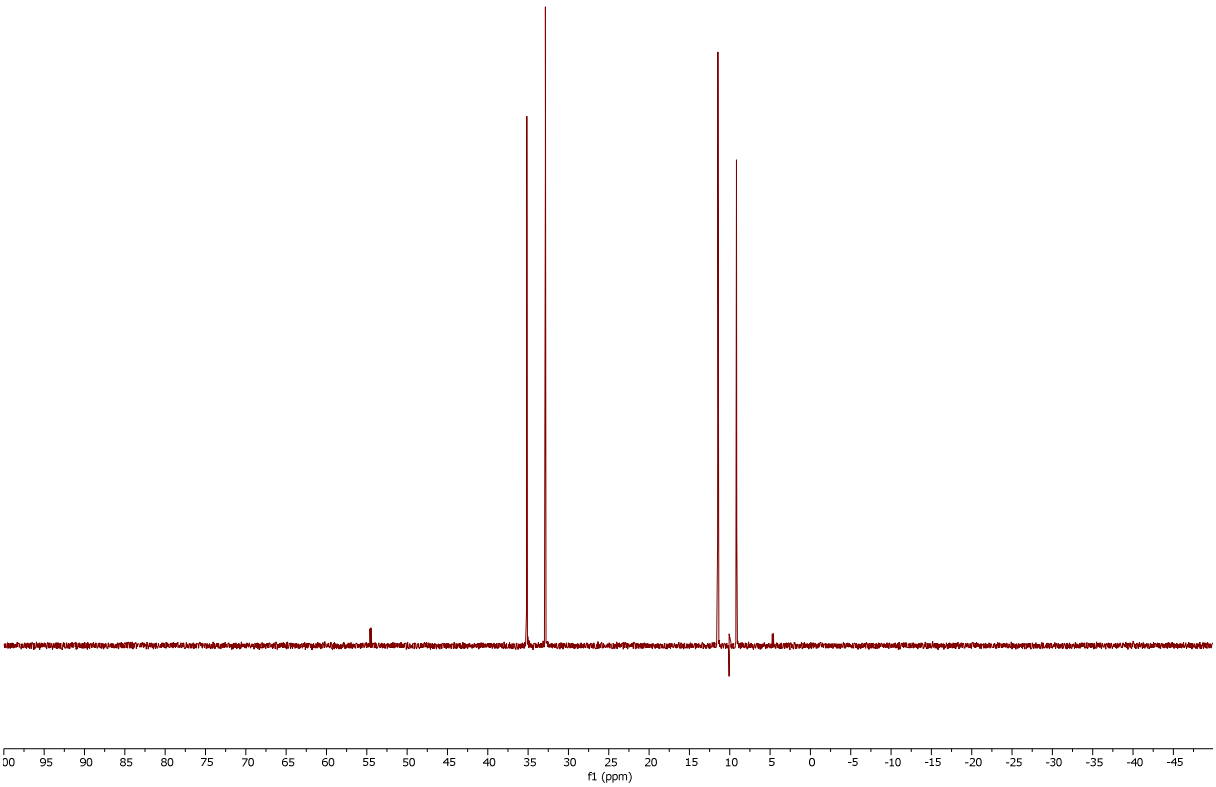


Figure S72 $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$, 162 MHz) of *trans*-**7** (minor signals are due to *cis* -**7**)

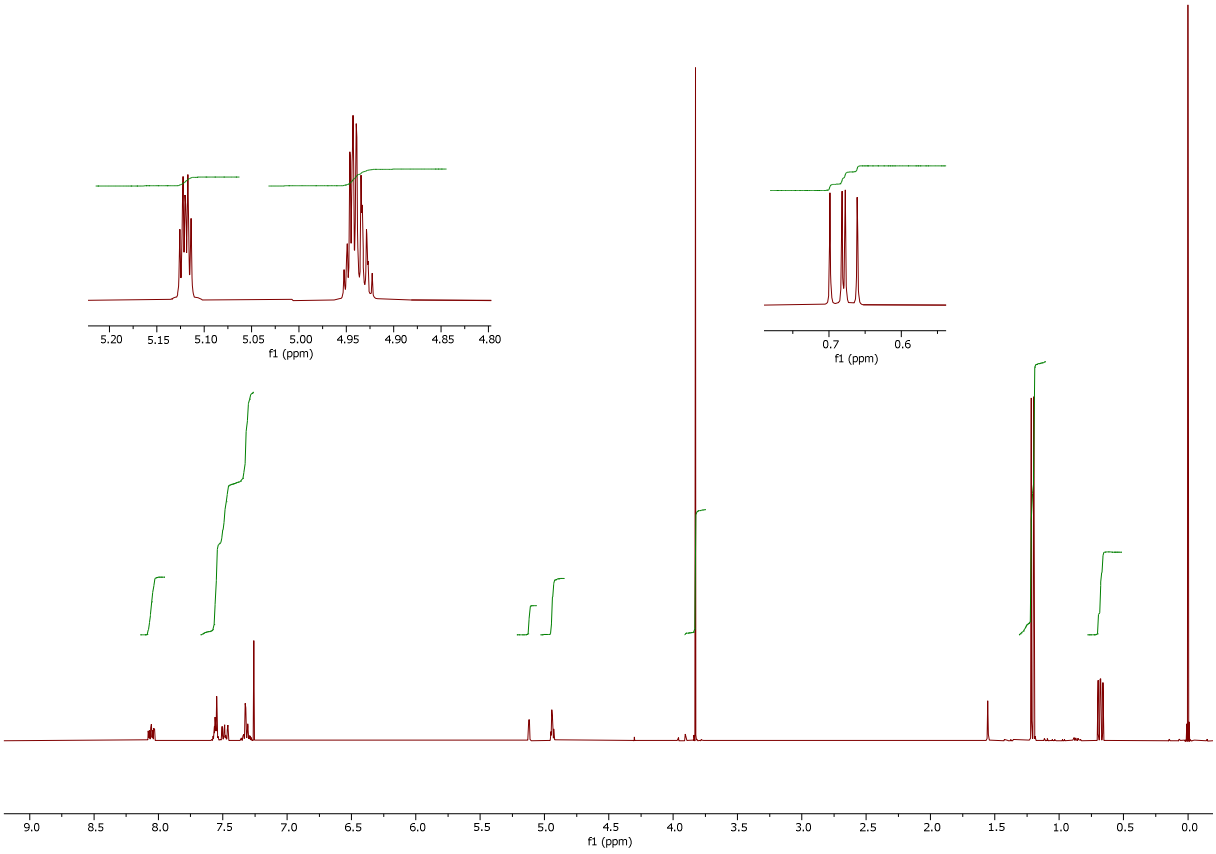


Figure S73 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of *cis*-**8a**

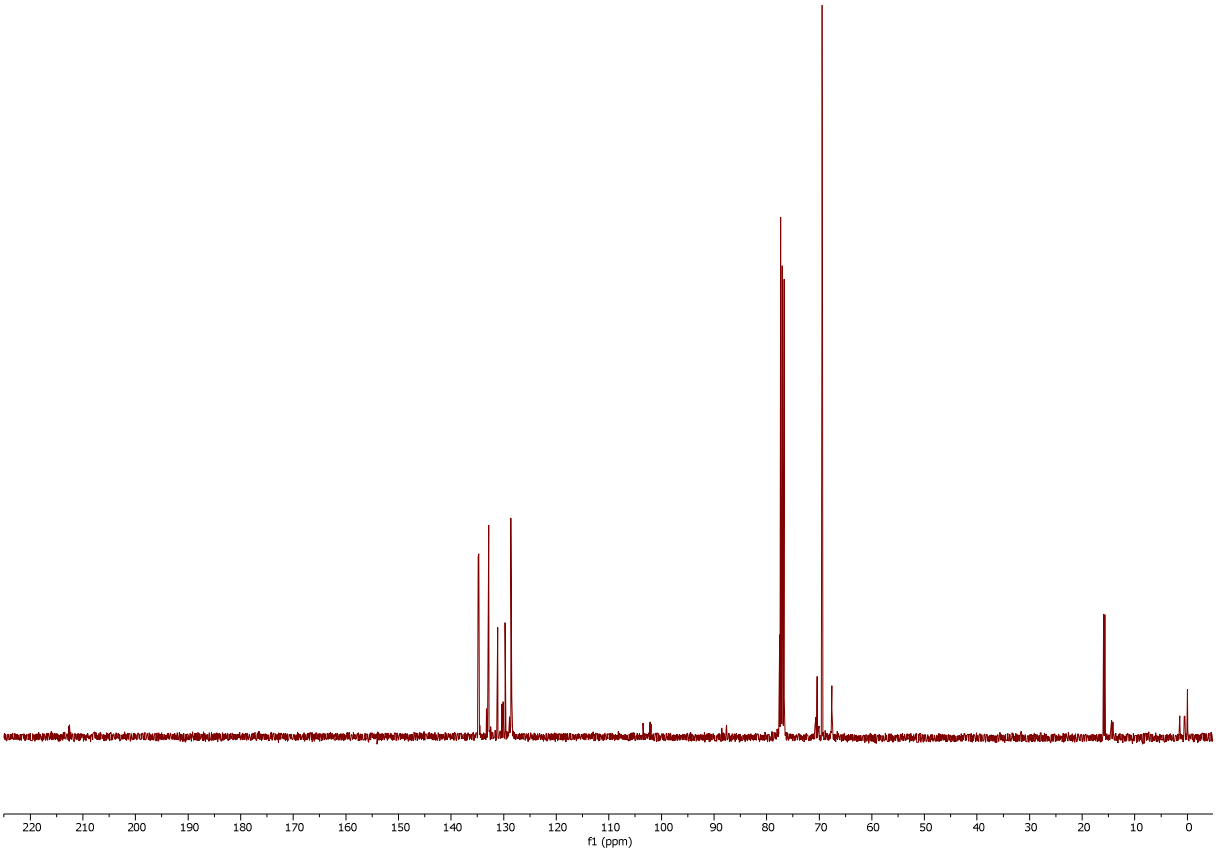


Figure S74 $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 101 MHz) of *cis*-**8a**

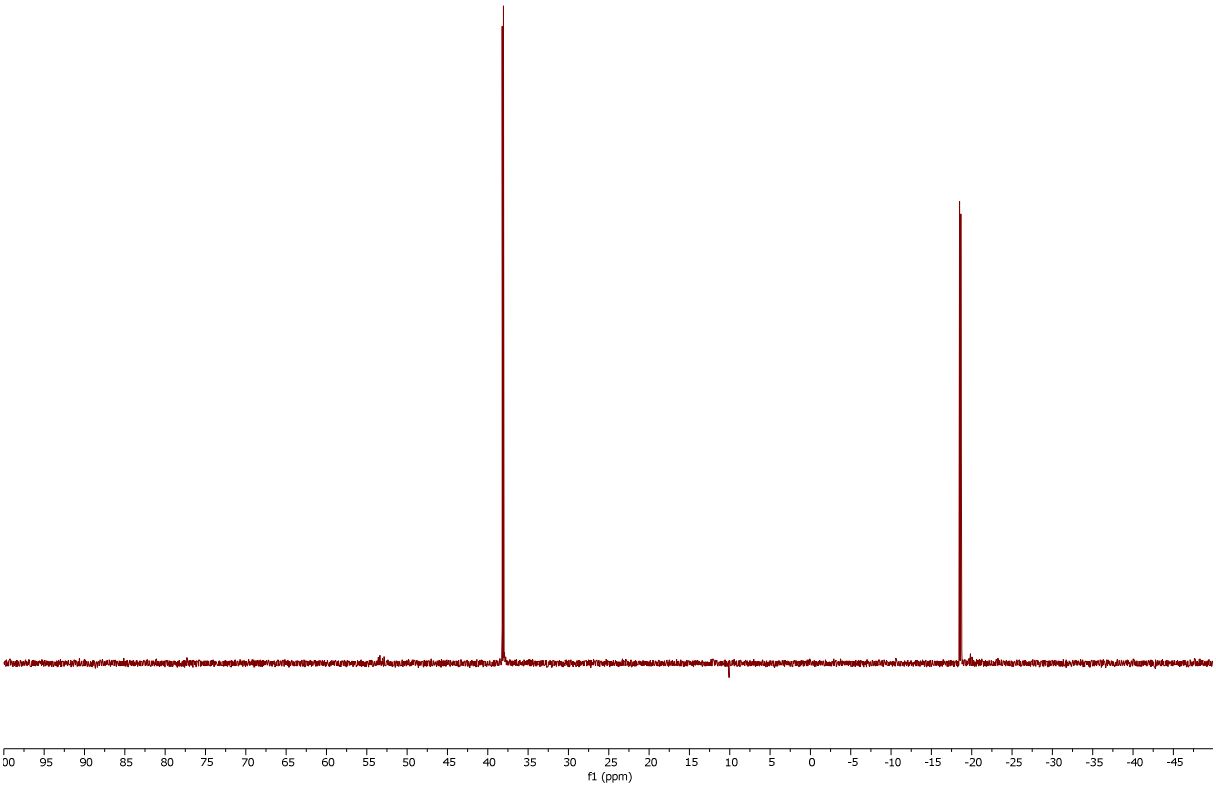


Figure S75 $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$, 162 MHz) of *cis*-**8a**

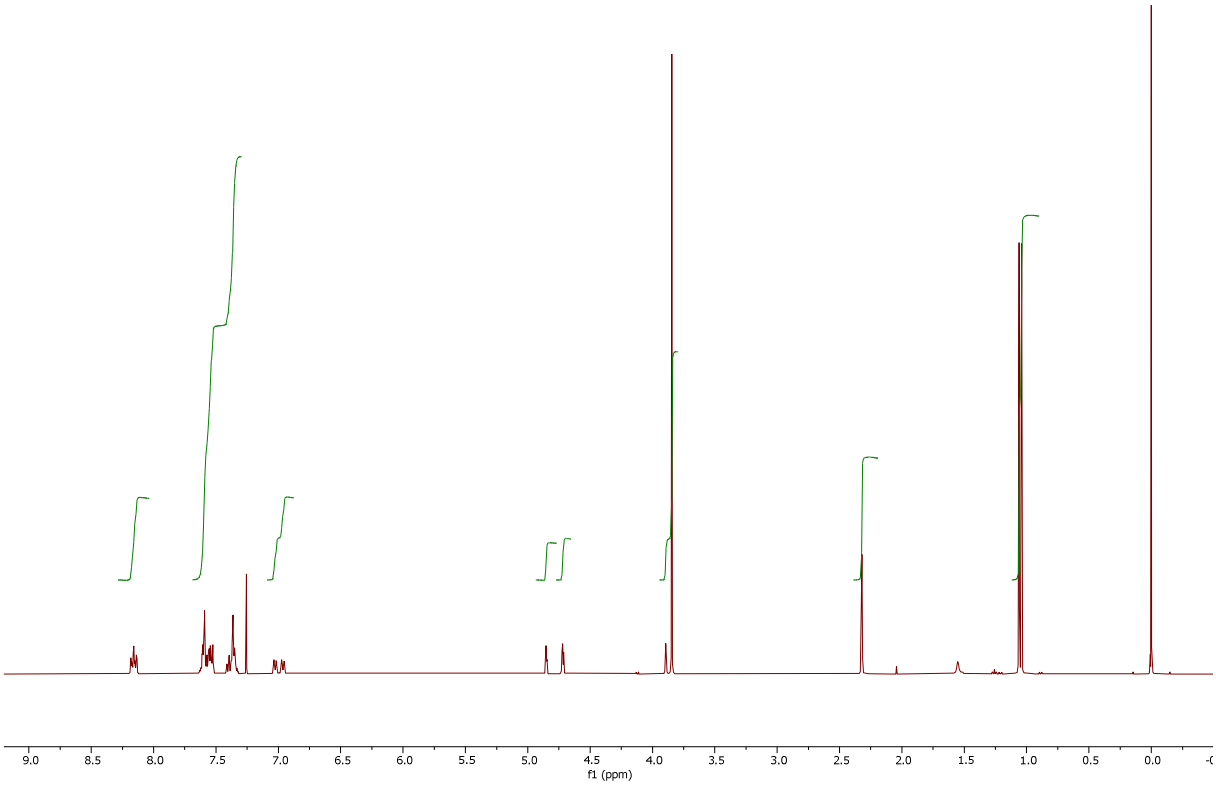


Figure S76 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of *cis*-**8b**

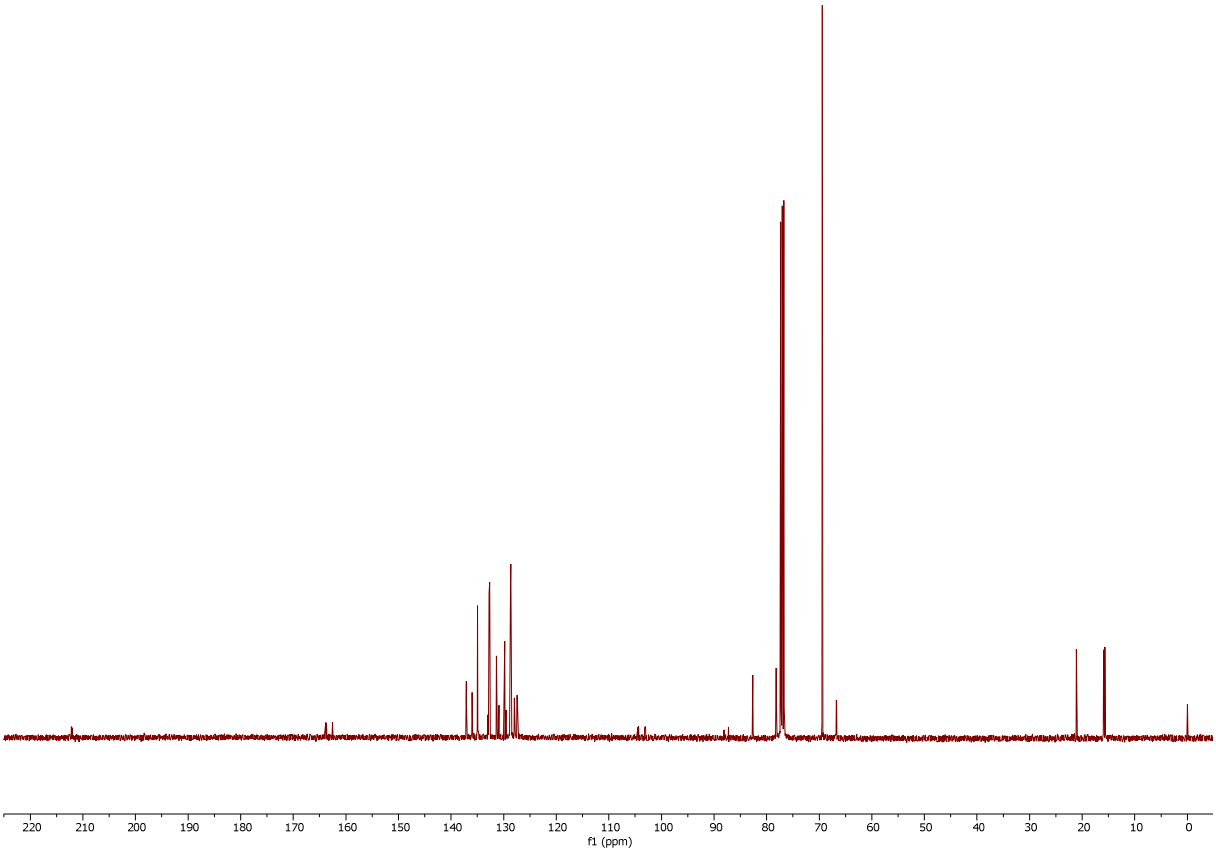


Figure S77 $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 101 MHz) of *cis*-**8b**

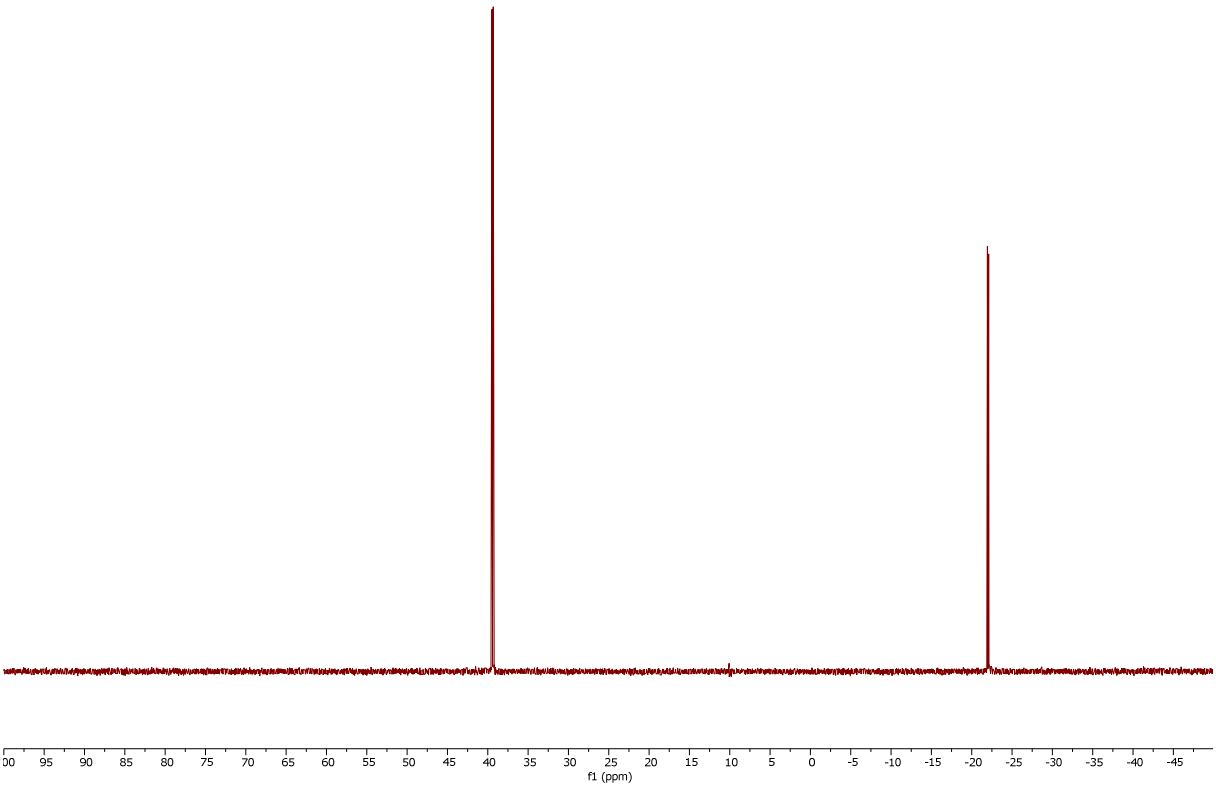


Figure S78 $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$, 162 MHz) of *cis*-**8b**

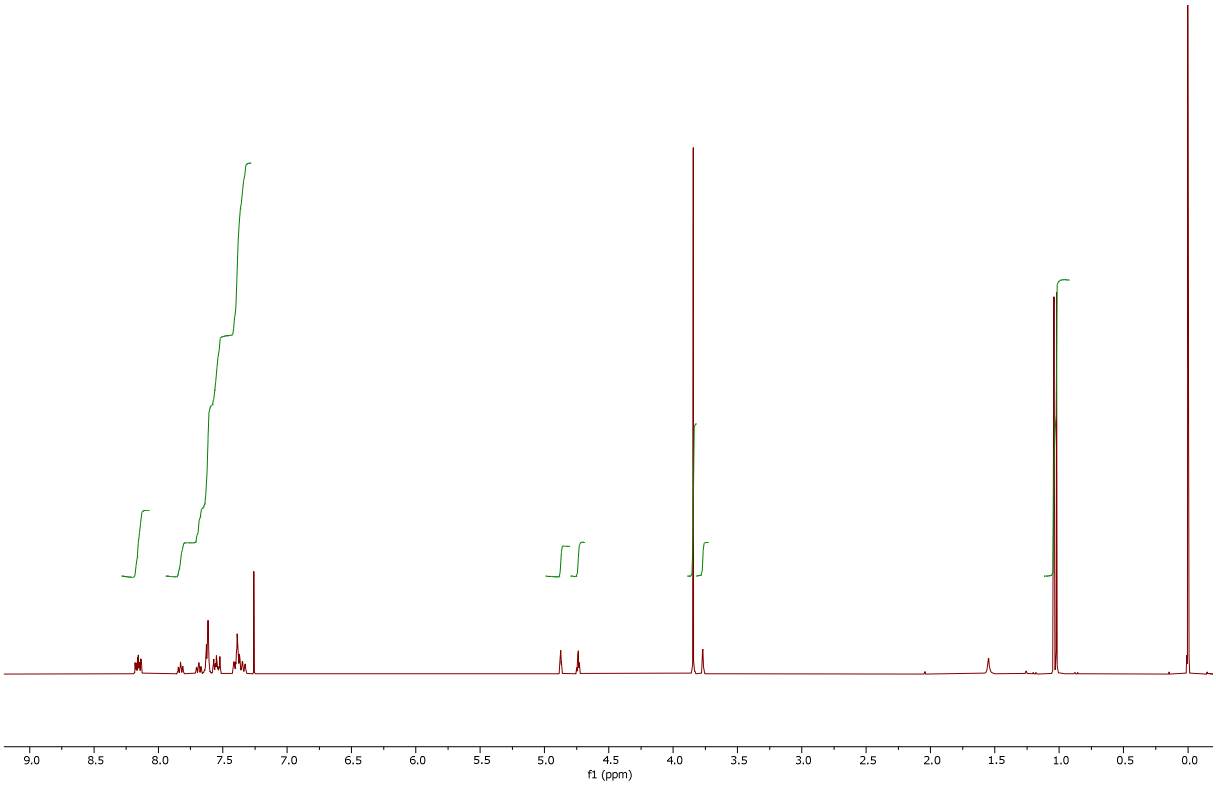


Figure S79 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of *cis*-**8c**

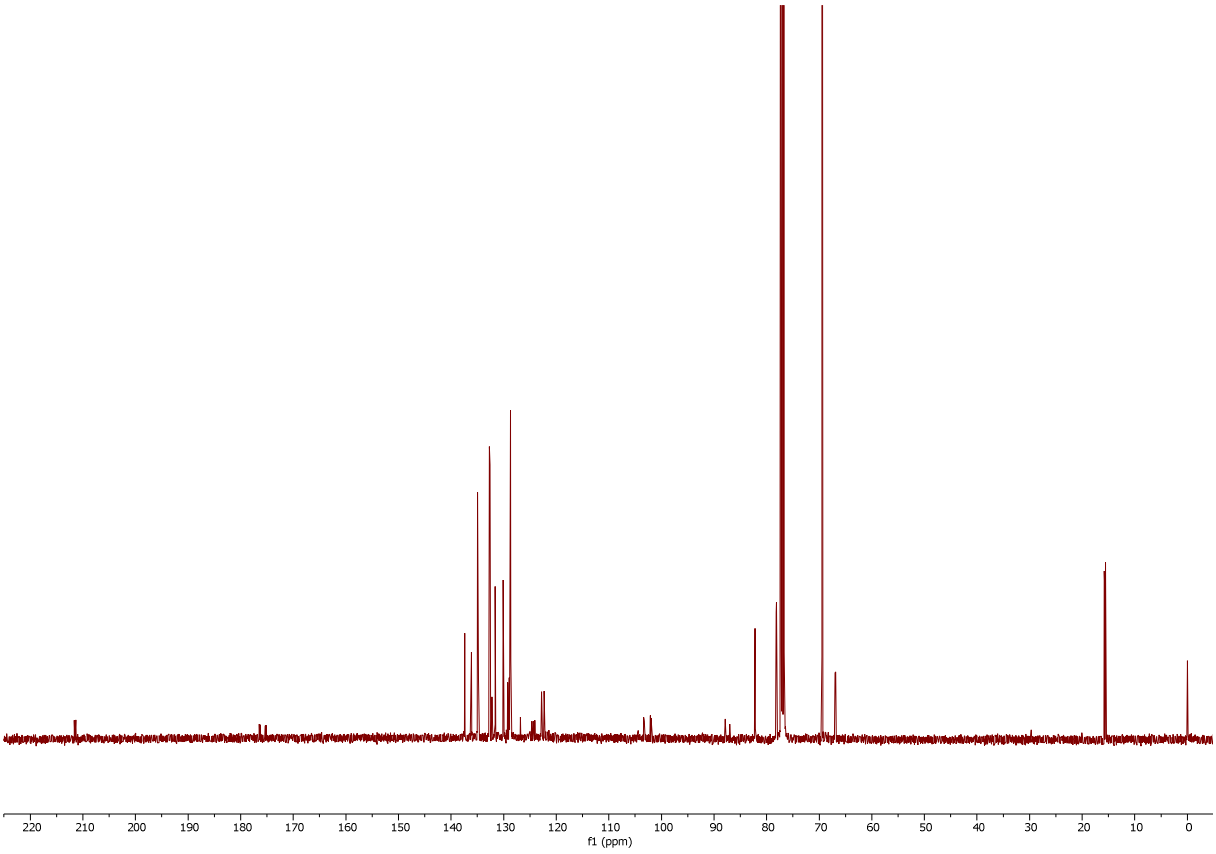


Figure S80 $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 101 MHz) of *cis*-**8c**

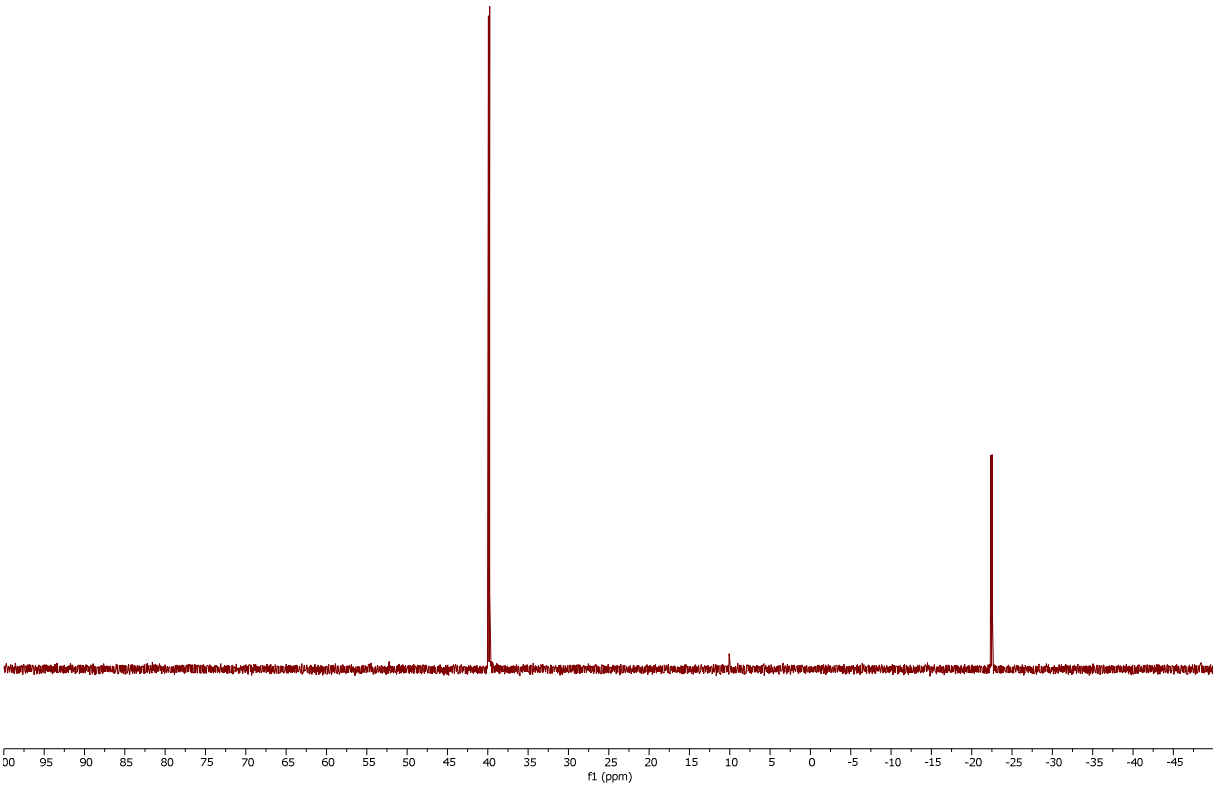


Figure S81 $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$, 162 MHz) of *cis*-**8c**

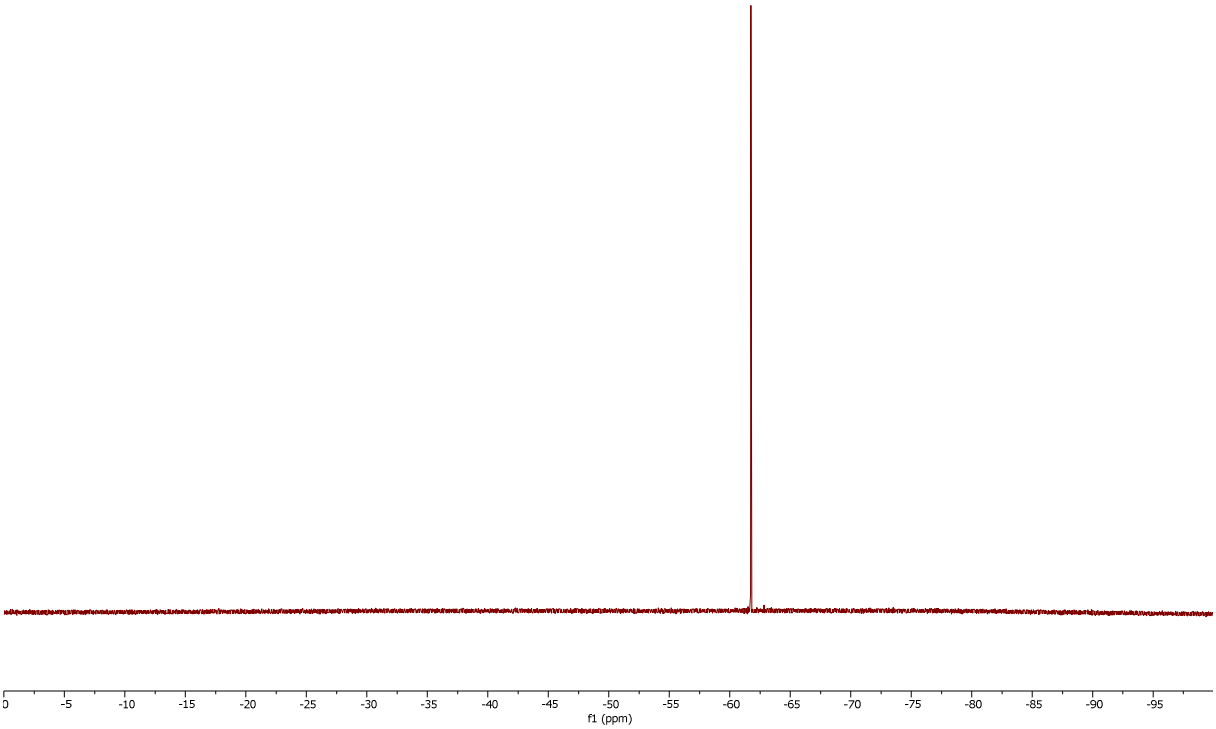


Figure S82 ^{19}F NMR spectrum ($CDCl_3$, 376 MHz) of *cis*-**8c**

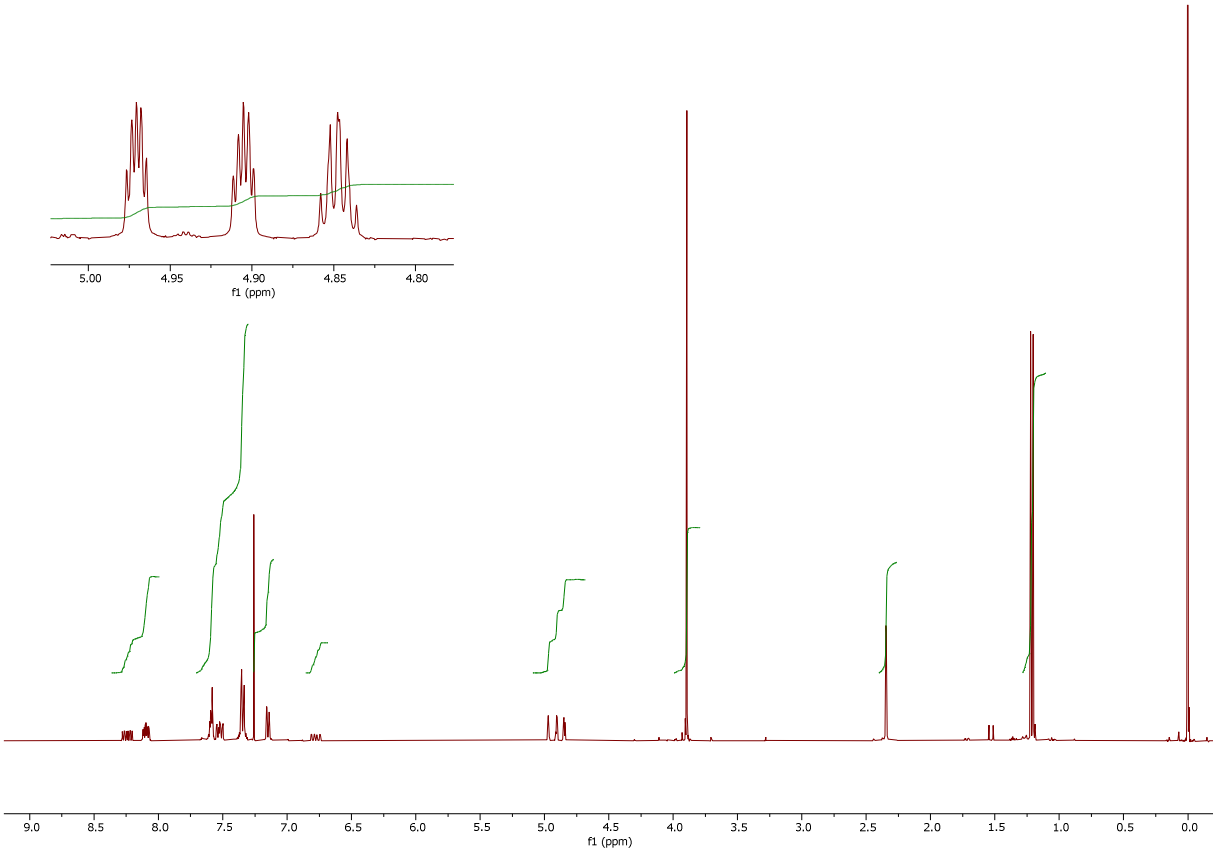


Figure S83 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of *cis*-**8d**

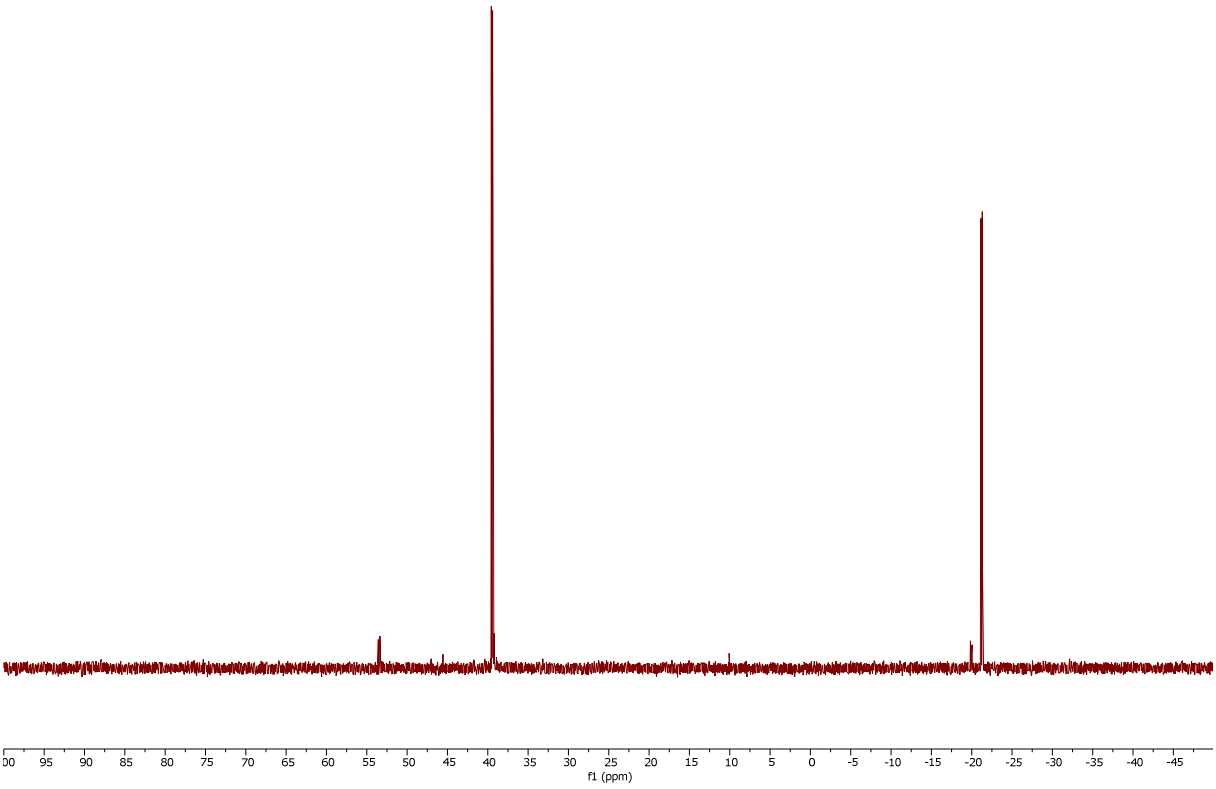


Figure S84 $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$, 162 MHz) of *cis*-**8d**

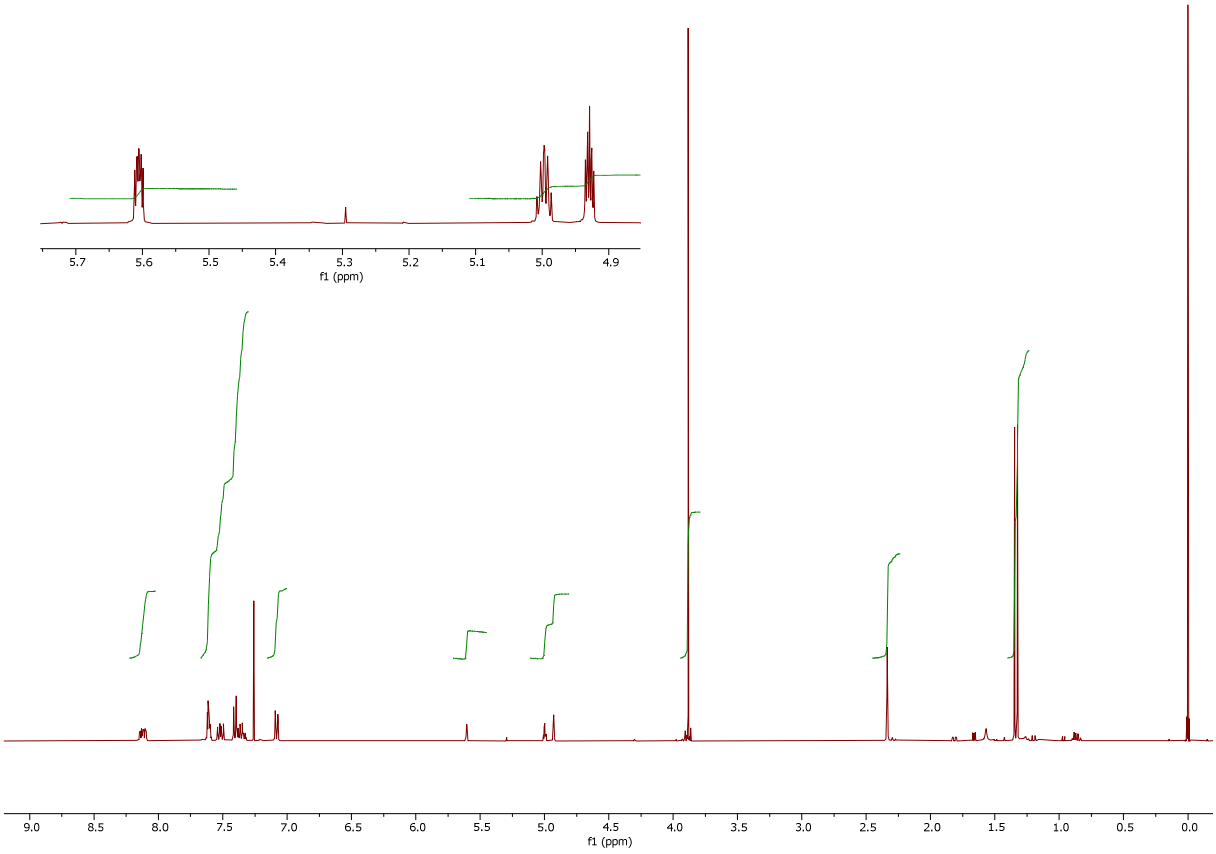


Figure 85 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of *cis*-**8e**

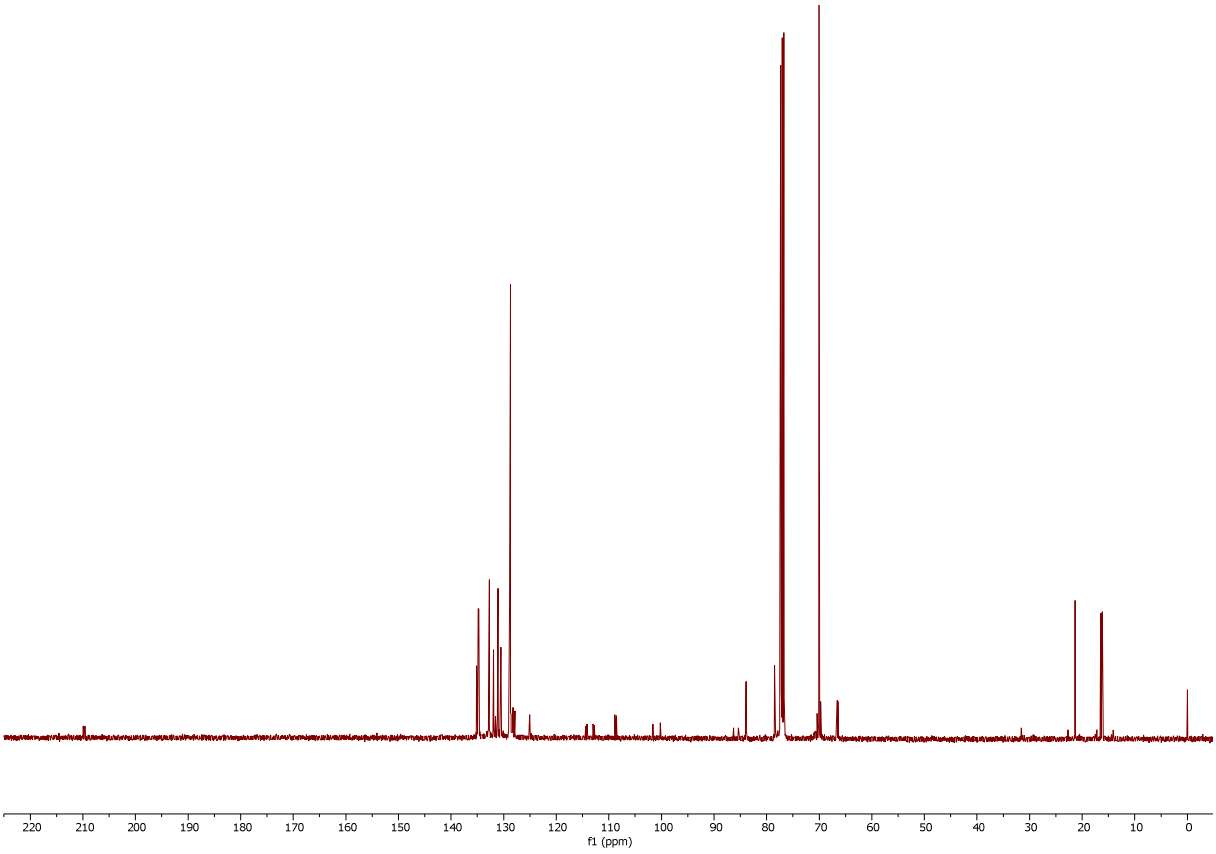


Figure S86 $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 101 MHz) of *cis*-**8e**

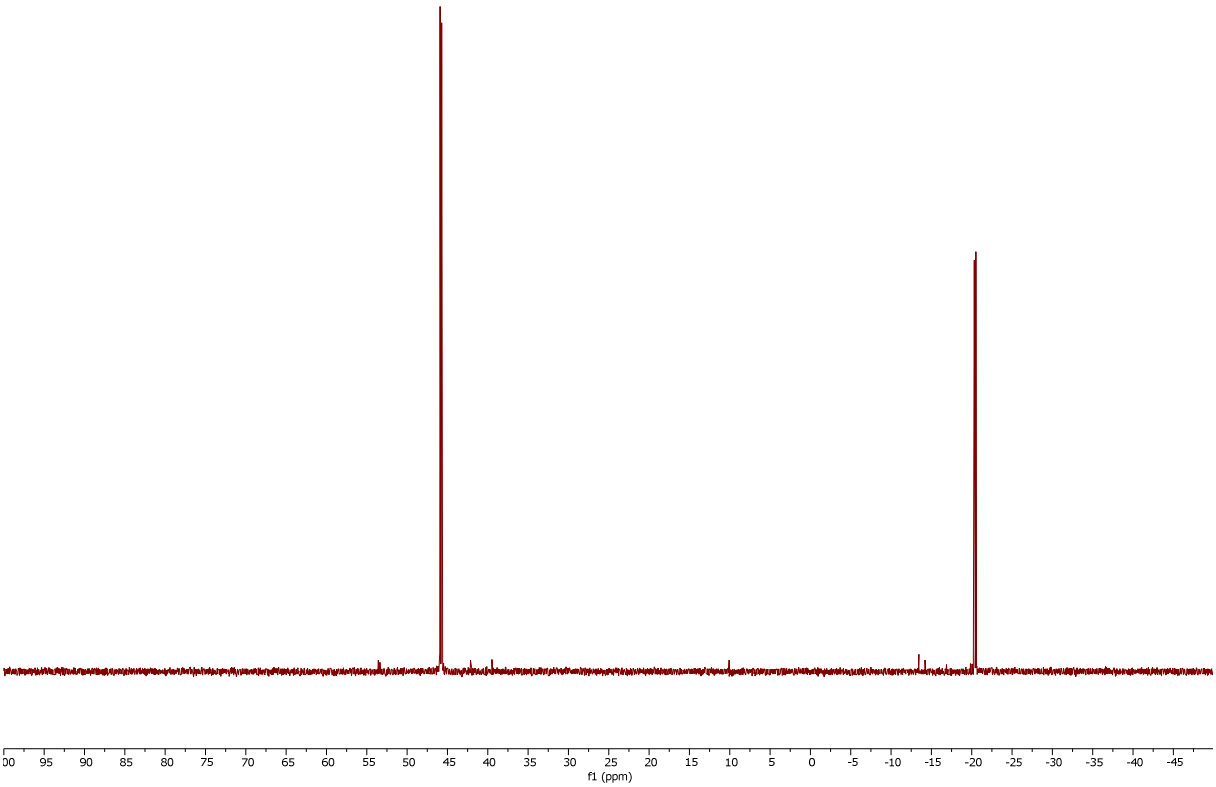


Figure S87 $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$, 162 MHz) of *cis*-**8e**

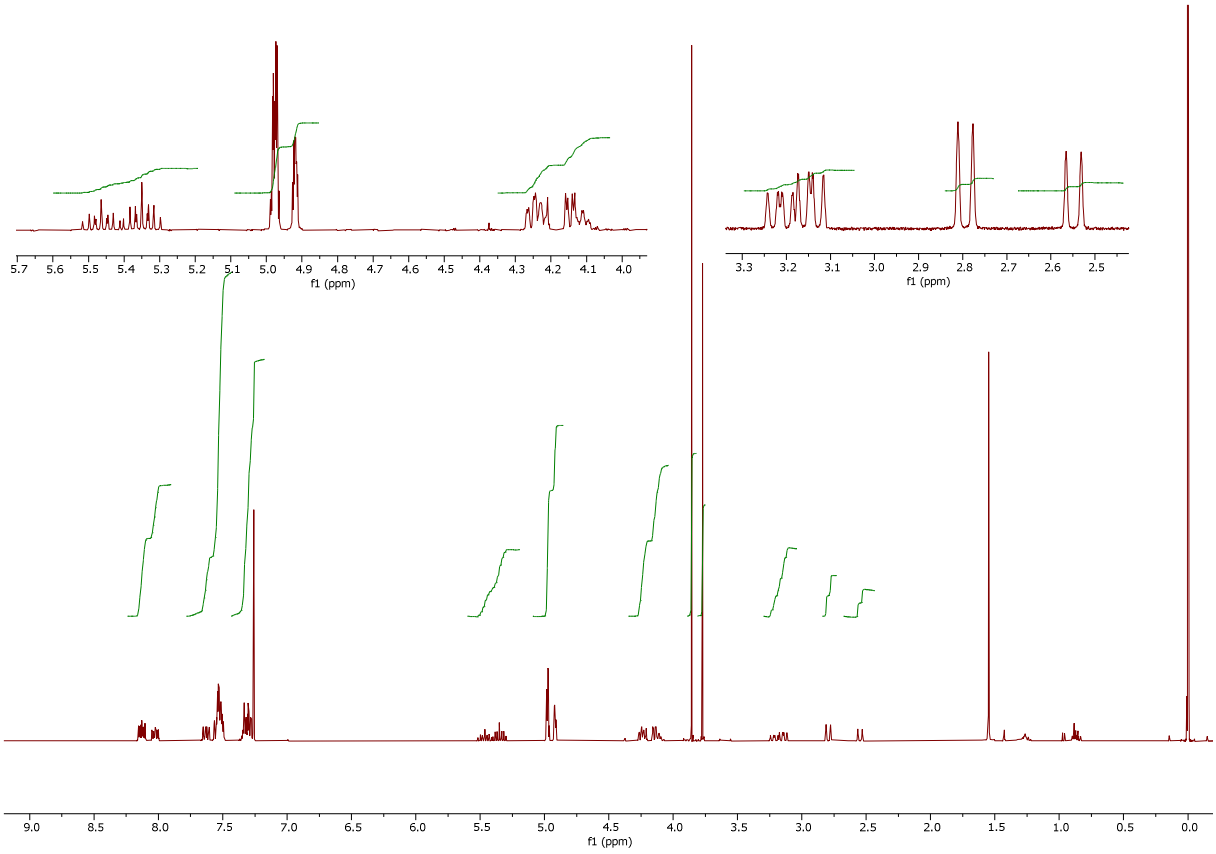


Figure S88 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **9** (mixture of isomers)

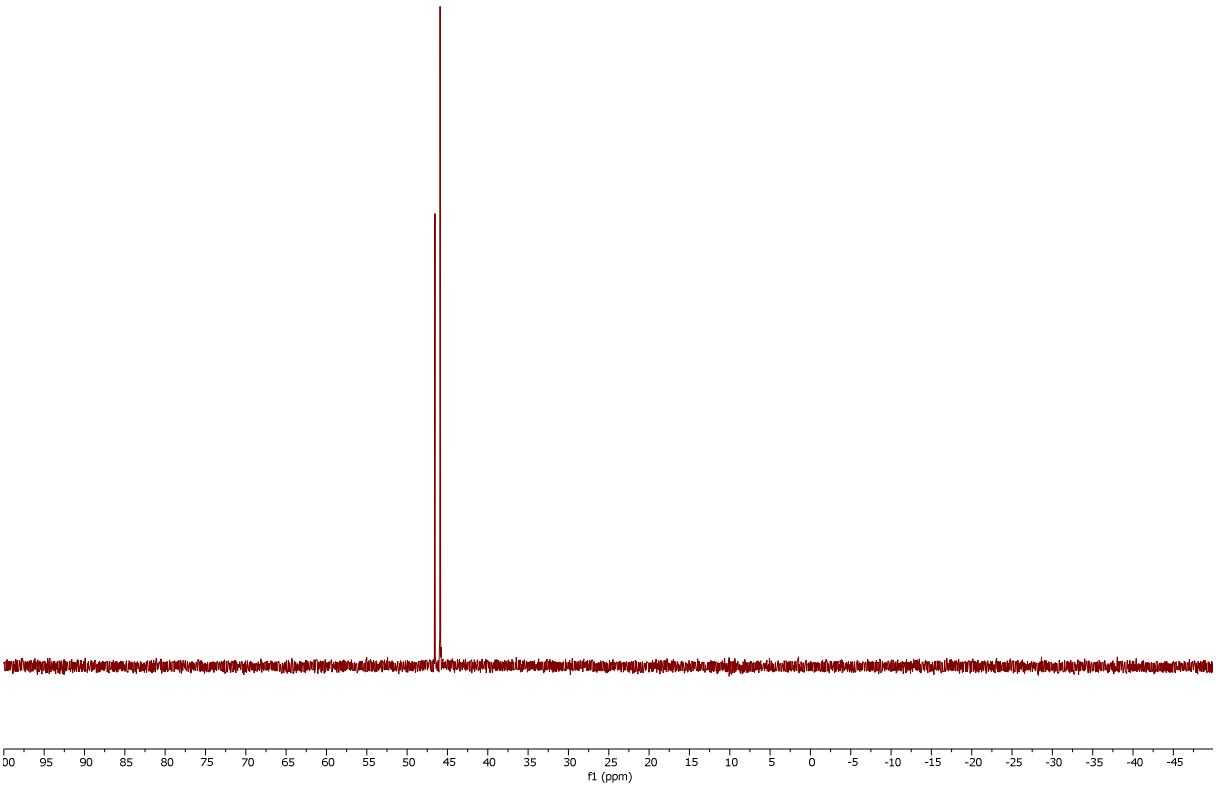


Figure S89 $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$, 162 MHz) of **9** (mixture of isomers)

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