Supporting Information

for

Synthesis and reactivity of Pd(II) imidoyl complexes obtained by insertion of isocyanoferrocene into the Pd-C bonds of orthopalladated precursors

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Contents

Experimental

Materials and methods

Unless stated otherwise, the syntheses were performed under an inert atmosphere (argon or dinitrogen) using standard Schlenk techniques and oven-dried glassware. Complex $[(L^{SC})PdCl]_2$[1] and isocyanoferrocene[2] were prepared according to the literature procedures. Other chemicals were purchased from commercial vendors (Sigma–Aldrich and TCI) and used as received. Anhydrous dichloromethane and methanol used during syntheses were obtained from a PureSolv MD5 solvent purification system (Innovative Technology, USA). Solvents utilised for work-up and crystallisations were used without additional purification (Lach-Ner, Czech Republic, p.a. grade).

NMR spectra were recorded at 25°C on a Varian Unity Inova 400 spectrometer operating at 400, 101 and 162 MHz for ^{1}H, ^{13}C and ^{31}P, respectively. Chemical shifts (δ in ppm) are given relative to internal $SiMe_4$ (^{1}H and ^{13}C) and external 85% aqueous H_3PO_4 (^{31}P). FTIR spectra were recorded over the 400-4000 cm^{-1} range on a Thermo Nicolet 6700 spectrometer. Electrospray ionisation mass spectra were acquired 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 with an μAUTOLAB III instrument (Eco Chemie, The Netherlands) at room temperature and a three-electrode cell equipped with a glassy carbon disc (2 mm diameter) working electrode, a platinum sheet auxiliary electrode, and an Ag/AgCl (3 M KCl) reference electrode. The samples were dissolved in anhydrous dichloromethane to give a solution containing 1 mM of the analyte and 0.1 M $Bu_4N[PF_6]$ (Sigma–Aldrich, puriss. for electrochemistry). The solutions were deaerated by bubbling with argon before the measurement and then maintained under an argon blanket. Decamethylferrocene (Alfa-Aesar) was added as an internal standard for the final scans, and the determined redox potentials were converted into the ferrocene/ferrocenium scale by subtracting 0.548 V.[3]

Syntheses

Synthesis of 1a. A solution of triphenylphosphine (105 mg, 0.40 mmol) in dichloromethane (5 mL) was added to $[(L^{NC})PdCl]_2$ (113 mg, 0.20 mmol) suspended in the same solvent (5 mL). The solid rapidly dissolved to give a clear yellowish solution, which was stirred for 1 h and then precipitated by adding into pentane. The precipitate was filtered off and dried under vacuum to give **1a** as a yellowish solid. The mother liquor was evaporated and the residue crystallised from hot methanol. The separated solid was filtered off and dried under vacuum. The combined yield of **1a** was 221 mg (95%).

^{1}H NMR (399.95 MHz, $CDCl_3$): δ 2.85 (d, $^{4}J_{PH}$ = 2.6 Hz, 6H, NMe_2), 4.07 (d, $^{4}J_{PH}$ = 2.2 Hz, 2H, NCH_2), 6.29-6.40 (m, 2H, C_6H_4), 6.81 (td, J_{HH} = 7.2, 1.3 Hz, 1H, C_6H_4), 7.00 (dd, J_{HH} = 7.4, 1.3 Hz, 1H, C_6H_4), 7.31-7.44 (m, 9H, PPh_3), 7.68-7.76 (m, 6H, PPh_3). ^{13}C{^{1}H} NMR (100.58 MHz, $CDCl_3$): δ 50.53 (d, $^{3}J_{PC}$ = 3 Hz, NMe_2), 73.23 (d, $^{3}J_{PC}$ = 3 Hz, NCH_2), 122.31 (s, CH C_6H_4), 123.78 (s, CH C_6H_4), 124.87 (d, J_{PC} = 6 Hz, CH C_6H_4), 127.98 (d, $^{3}J_{PC}$ = 11 Hz, CH^{meta} PPh_3), 130.47 (d, $^{4}J_{PC}$ = 3 Hz, CH^{para} PPh_3), 131.38 (d, $^{1}J_{PC}$ = 50 Hz, C^{ipso} PPh_3), 135.28 (d, $^{2}J_{PC}$ = 12 Hz, CH^{ortho} PPh_3), 137.86 (d, J_{PC} = 11 Hz, CH C_6H_4), 148.45 (d, J_{PC} = 2 Hz, C^{ipso}-C C_6H_4), 150.74 (s, C^{ipso}-Pd). ^{31}P{^{1}H} NMR (161.90 MHz, $CDCl_3$): δ 43.0 (s). ESI+ MS: *m/z* 502 ($[M - Cl]^+$). IR (DRIFTS, KBr): ν_{max} 3052 w, 3008 w, 1579 w, 1479 w, 1466 w, 1452 m, 1435 m, 1311 w, 1290 w, 1181 w, 1097 m, 1072 w, 1047 w, 1020 w, 997 w, 974 w, 933 w, 867 w, 846 m, 748 s, 702 s, 695 s, 535 s, 514 s, 495 m, 459 w, 436 w, 427 w cm^{-1}. The NMR data match those in the literature.[4]

Synthesis of 1b. A solution of trimethylphosphine (0.44 mL of 1M in THF, ca. 0.44 mmol) was added to a dichloromethane suspension of $[(L^{NC})PdCl]_2$ (110 mg, 0.20 mmol in 5 mL) and the mixture was stirred for 30 min. The resulting clear solution was concentrated under reduced pressure and the crude product was three times redissolved in chloroform and evaporated to remove THF. The crude product was purified by chromatography over silica gel using dichloromethane/methanol (75:1) as the eluent. The first light yellow band was collected and evaporated, affording **1b** as a light yellow solid. Yield: 134 mg (95%)

^{1}H NMR (399.95 MHz, $CDCl_3$): δ 1.64 (d, $^{2}J_{PH}$ = 10.7 Hz, 9H, PMe_3), 2.70 (d, $^{4}J_{PH}$ = 2.8 Hz, 6H, NMe_2), 3.92 (d, $^{4}J_{PH}$ = 2.4 Hz, 2H, NCH_2), 6.94-7.10 (m, 4H, C_6H_4). ^{13}C{^{1}H} NMR (100.58 MHz, $CDCl_3$): δ 16.63 (d, $^{1}J_{PC}$ = 33 Hz, PMe_3), 50.05 (d, $^{3}J_{PC}$ = 3 Hz, NMe_2), 72.60 (d, $^{3}J_{PC}$ = 4 Hz, NCH_2), 123.08 (s, CH C_6H_4), 124.24 (s, CH C_6H_4), 125.73 (d, J_{PC} = 6 Hz, CH C_6H_4), 135.47 (d, J_{PC} = 11 Hz, CH C_6H_4), 148.80 (d, J_{PC} = 2 Hz, C^{ipso}-C C_6H_4), 151.23 (d, J_{PC} = 4 Hz, C^{ipso}-Pd). ^{31}P{^{1}H} NMR (161.90 MHz, $CDCl_3$): δ −2.9 (s). ESI+ MS: *m/z* 316 ($[M - Cl]^+$). IR (DRIFTS, KBr): ν_{max} 3054 w, 3043 w, 3006 w, 2976 w, 2909 m, 2857 w, 2835 w, 2800 w, 2788 w, 1577 w, 1456 m, 1449 s, 1435 m, 1410 m, 1356 w, 1307 w, 1291 m, 1284 m, 1263 w, 1247 w, 1181 w, 1139 w, 1105 w, 1049 w, 1019 w, 993 m, 959 s, 935 s, 871 s, 849 s, 760 s, 752 s, 738 m, 715 w, 683 w, 656 w, 614 w, 516 w, 487 w, 437 w cm^{-1}. Anal. Calc. for $C_{12}H_{21}ClNPPd$ (352.15): C 40.93, H 6.01, N 3.98%. Found: C 41.18, H 6.00, N 3.62%.

Synthesis of 2a. A solution of triphenylphosphine (105 mg, 0.40 mmol) in dichloromethane (5 mL) was added to a solution of $[(L^{SC})PdCl]_2$ (112 mg, 0.2 mmol) in the same solvent (5 mL). The resulting clear yellowish solution was stirred for 1 h and evaporated, leaving pure **2a** as a yellowish solid in quantitative yield.

^{1}H NMR (399.95 MHz, $CDCl_3$): δ 2.70 (br s, 3H, SMe), 4.24 (br s, 2H, SCH_2), 6.33 (dt, *J* = 7.6, 1.7 Hz, 1H, C_6H_4), 6.45-6.52 (br m, 1H, C_6H_4), 6.76 (td, J_{HH} = 7.4, 1.2 Hz, 1H, C_6H_4), 7.04 (dd, *J* = 7.5, 1.6 Hz, 1H, C_6H_4), 7.31-7.38 (m, 6H, PPh_3), 7.39-7.45 (m, 3H PPh_3), 7.65-7.72 (m, 6H, PPh_3). ^{13}C{^{1}H} NMR (100.58 MHz, $CDCl_3$): δ 21.32 (s, SMe), 48.35 (s, SCH_2), 123.93 (s, 2×CH C_6H_4), 125.56 (d, J_{PC}

= 5 Hz, CH C_6H_4), 128.13 (d, $^3J_{PC}$ = 11 Hz, CH^{meta} PPh_3), 130.56 (d, $^4J_{PC}$ = 2 Hz, CH^{para} PPh_3), 130.73 (d, $^1J_{PC}$ = 47 Hz, C^{ipso} PPh_3), 135.26 (d, $^2J_{PC}$ = 12 Hz, CH^{ortho} PPh_3), 139.71 (d, J_{PC} = 12 Hz, CH C_6H_4), 148.51 (s, C^{ipso}-C C_6H_4), 151.86 (s, C^{ipso}-Pd). $^{31}P\{^1H\}$ NMR (161.90 MHz, $CDCl_3$): δ 37.5 (s). ESI+ MS: *m/z* 505 ($[M - Cl]^+$). IR (DRIFTS, KBr): ν_{max} 3051 w, 3004 w, 2987 w, 2918 w, 1574 w, 1481 m, 1435 s, 1313 w, 1290 w, 1185 w, 1159 w, 1096 m, 1072 w, 1020 w, 998 w 967 w, 850 w, 741 s, 703 s, 693 s, 650 w, 619 w, 529 vs, 511 s, 496 m, 437 w cm^{-1}. Anal. Calc. for $C_{26}H_{24}ClPPdS$ (541.38): C 57.68, H 4.47%. Found: C 57.30, H 4.11%.

Synthesis of 2b. A solution of trimethylphosphine (0.4 mL of 1M in THF, ca. 0.4 mmol) was added to a dichloromethane solution of $[(L^{SC})PdCl]_2$ (112 mg, 0.20 mmol in 5 mL), and the mixture was stirred for 40 min. The resulting clear solution was concentrated under reduced pressure and the residue was three times redissolved in chloroform and evaporated to remove THF. According to NMR analysis, the product was essentially pure and was therefore used directly in the following step. Yield: 138 mg (95%), yellowish solid.

^1H NMR (399.95 MHz, $CDCl_3$): δ 1.62 (d, $^2J_{PH}$ = 10.6 Hz, 9H, PMe_3), 2.55 (d, $^3J_{PH}$ = 4.0 Hz, 3H, SMe), 4.12 (br s, 2H, SCH_2), 6.93-7.01 (m, 2H, C_6H_4), 7.07-7.18 (m, 2H, C_6H_4). $^{13}C\{^1H\}$ NMR (100.58 MHz, $CDCl_3$): δ 15.81 (d, $^1J_{PC}$ = 31 Hz, PMe_3), 20.41 (d, $^3J_{PC}$ = 2 Hz, SMe), 47.85 (d, $^3J_{PC}$ = 1 Hz, SCH_2), 124.35 (s, CH C_6H_4), 124.70 (s, CH C_6H_4), 126.28 (d, J_{PC} = 6 Hz, CH C_6H_4), 137.69 (d, J_{PC} = 13 Hz, CH C_6H_4), 148.96 (s, J_{PC} = 2 Hz, C^{ipso}-C C_6H_4), 152.17 (s, C^{ipso}-Pd). $^{31}P\{^1H\}$ NMR (161.90 MHz, $CDCl_3$): δ −5.8 (s). ESI+ MS: *m/z* 319 ($[M - Cl]^+$). IR (DRIFTS, KBr): ν_{max} 3048 w, 3016 w, 2975 w, 2915 w, 2901 w, 1570 w, 1445 m, 1434 m, 1418 m, 1317 w, 1306 w, 1284 m, 1259 w, 1152 w, 1129 w, 1101 w, 1044 w, 1023 w, 962 s, 952 vs, 938 m, 872 w, 856 w, 807 w, 765 s, 743 m 716 w, 698 w, 680 w, 651 w, 572 w, 503 w, 445 m cm^{-1}. Anal. Calc. for $C_{11}H_{18}ClPPdS$ (355.17): C 37.20, H 5.11%. Found: C 36.93, H 4.86%.

Synthesis of *trans*-3. Complex *trans*-**3** was prepared similarly using trimethylphosphine (0.8 mL of 1M in THF, ca. 0.8 mmol), $[(L^{SC})PdCl]_2$ (112 mg, 0.20 mmol) and 5 mL of the solvent. The mixture was stirred for 3 h and worked up as described above, leaving **3** as a colourless solid in quantitative yield (172.5 mg). Crystals used for structure determination were grown from chloroform/hexane.

^1H NMR (399.95 MHz, $CDCl_3$): δ 1.20 (apparent t, *J* = 3.4 Hz, 18H, PMe_3), 2.16 (s, 3H, SMe), 3.96 (s, 2H, SCH_2), 6.87-6.94 (m, 2H, C_6H_4), 7.08-7.14 (m, 1H, C_6H_4), 7.24-7.30 (m, 1H, C_6H_4). $^{13}C\{^1H\}$ NMR (100.58 MHz, $CDCl_3$): δ 13.78 (apparent t, *J* = 15 Hz, PMe_3), 16.37 (s, SMe), 44.20 (apparent t, *J* = 2 Hz, SCH_2), 122.76 (s, CH C_6H_4), 126.14 (s, CH C_6H_4), 128.82 (s, CH C_6H_4), 135.53 (apparent t, *J* = 5 Hz, CH C_6H_4), 140.82 (apparent t, *J* = 4 Hz, C^{ipso}-C C_6H_4), 154.33 (apparent t, *J* = 6 Hz, C^{ipso}-Pd). $^{31}P\{^1H\}$ NMR (161.90 MHz, $CDCl_3$): δ −14.9 (s). ESI+ MS: *m/z* 319 ($[M - Cl - PMe_3]^+$). IR (DRIFTS, KBr): ν_{max} 3038 w, 2983 w, 2964 w, 2904 m, 2809 w, 2019 w, 1956 w, 1915 w, 1571 m, 1556 w, 1453 m, 1431 m, 1419 m, 1320 m, 1299 w, 1283 m, 1242 w, 1194 w, 1159 w, 1142 w,

1097 w, 1045 m, 1030 m, 1013 w, 954 s, 876 w, 856 m, 813 w, 775 m, 742 s, 719 w, 696 w, 673 m, 649 w, 578 w, 509 w, 447 w cm^{-1}. Anal. Calc. for $C_{14}H_{27}ClP_2PdS$ (431.25): C 38.99, H 6.31%. Found: C 38.88, H 6.31%.

Synthesis of 4a. Complex **1a** (54 mg, 0.10 mmol) was dissolved in dichloromethane (3 mL) and the solution was added to isocyanoferrocene dissolved in the same solvent (21 mg, 0.10 mmol in 3 mL). The resulting mixture was stirred for 30 min, during which time the initially light orange mixture turned deep orange. Then, the reaction mixture was evaporated under reduced pressure and the solid residue was purified by chromatography over silica gel, eluting with dichloromethane/methanol (10:1). The first orange band containing the product was collected and evaporated, leaving **4a** as an orange solid. Yield: 58 mg (77%). Crystals used for structure determination were grown from ethyl acetate/hexane.

^{1}H NMR (399.95 MHz, $CDCl_3$): δ 2.84 (d, $^4J_{PH}$ = 1.7 Hz, 3H, NMe_2), 3.06 (dd, $^2J_{HH}$ = 11.6 Hz, $^4J_{PH}$ = 4.6 Hz, 1H, NCH_2), 3.21 (d, $^4J_{PH}$ = 2.0 Hz, 3H, NMe_2), 3.71 (d, $^2J_{HH}$ = 11.6 Hz, 1H, NCH_2), 3.95 (vt, J' = 1.9 Hz, 2H, C_5H_4), 4.13 (s, 5H, C_5H_5), 4.37 (vq, J' = 1.8 Hz, 1H, C_5H_4), 5.73 (br d, J = 7.2 Hz, 1H, C_6H_4), 6.40 (m, 1H, C_5H_4), 7.08 (td, J = 7.3, 1.9 Hz, 1H, C_6H_4), 7.13-7.20 (m, 2H, C_6H_4), 7.23-7.29 (m, 6H, PPh_3), 7.34-7.47 (m, 9H, PPh_3). ^{13}C{^{1}H} NMR (100.58 MHz, $CDCl_3$): δ 48.60 (d, $^3J_{PC}$ = 2 Hz, NMe_2), 50.96 (d, $^3J_{PC}$ = 2 Hz, NMe_2), 61.89 (d, J_{PC} = 2 Hz, CH C_5H_4), 65.72 (d, $^3J_{PC}$ = 2 Hz, NCH_2), 66.21 (s, CH C_5H_4), 66.90 (s, CH C_5H_4), 69.11 (s, C_5H_5), 69.67 (s, CH C_5H_4), 104.70 (d, J_{PC} = 6 Hz, C^{ipso}-N C_5H_4), 121.90 (s, CH C_6H_4), 126.35 (s, CH C_6H_4), 127.83 (d, $^3J_{PC}$ = 11 Hz, CH^{meta} PPh_3), 128.94 (s, CH C_6H_4), 129.36 (s, CH C_6H_4), 130.31 (d, $^4J_{PC}$ = 2 Hz, CH^{para} PPh_3), 131.26 (d, $^1J_{PC}$ = 49 Hz, C^{ipso} PPh_3), 131.72 (s, C^{ipso}-C C_6H_4), 134.69 (d, $^2J_{PC}$ = 12 Hz, CH^{ortho} PPh_3), 144.02 (d, J_{PC} = 8 Hz, C^{ipso}-C C_6H_4), 190.27 (d, J_{PC} = 2 Hz, C^{ipso}-Pd). ^{31}P{^{1}H} NMR (161.90 MHz, $CDCl_3$): δ 26.5 (s). ESI+ MS: *m/z* 748 ($[M - H]^+$), 713 ($[M - Cl]^+$). IR (DRIFTS, KBr): ν_{max} 3061 w, 3014 vw, 2879 w, 1745 w, 1606 m, 1596 m, 1571 w, 1480 w, 1434 m, 1398 w, 1333 w, 1238 w, 1213 w, 1203 w, 1183 w, 1156 w 1105 w, 1094 m, 1029 w, 1019 w, 999 w, 989 w, 962 w, 926 w, 889 m, 882 m, 839 m, 817 m, 809 w, 760 s, 751 m, 739 s, 710 s, 694 vs, 655 w, 636 w, 599 w, 571 w, 530 vs, 507 s, 495 s, 454 w, 435 w cm^{-1}. Anal. Calc. for $C_{38}H_{36}ClFeN_2PPd$ (749.40): C 60.90, H 4.84, N 3.74%. Found: C 60.53, H 4.92, N 3.48%.

Synthesis of 4b. Complex **4b** was prepared similarly starting from **1b** (44.0 mg, 0.125 mmol) and isocyanoferrocene (26.4 mg, 0.125 mmol) in 9 mL of dichloromethane. Isolation as described above produced the target compound as an orange solid. Yield: 60 mg (85%). X-ray quality crystals were grown from ethyl acetate/hexane.

^{1}H NMR (399.95 MHz, $CDCl_3$): δ 1.19 (d, $^2J_{PH}$ = 11.0 Hz, 9H, PMe_3), 2.71 (d, $^4J_{PH}$ = 1.9 Hz, 3H, NMe_2), 3.04 (dd, $^2J_{HH}$ = 11.7 Hz, $^4J_{PH}$ = 4.7 Hz, 1H, NCH_2), 3.07 (d, $^4J_{PH}$ = 2.0 Hz, 3H, NMe_2), 3.67 (d, $^2J_{HH}$ = 11.7 Hz, 1H, NCH_2), 4.20 (s, 5H, C_5H_5), 4.18-4.22 (m, 1H, C_5H_4; obscured by the signal due to C_5H_5), 4.27 (td, J' = 2.6, 1.5 Hz, 1H, C_5H_4), 4.67 (dt, J' = 2.6, 1.4 Hz, 1H, C_5H_4), 6.15 (dq, J' = 2.6, 1.3 Hz, 1H, C_5H_4), 7.02 (dd, J = 7.4, 1.2 Hz, 1H, C_6H_4), 7.16 (br d, J = 6.8 Hz, 1H, C_6H_4), 7.23 (td, J = 7.5,

1.3 Hz, 1H, C_6H_4), 7.35 (td, *J* = 7.4, 1.2 Hz, 1H, C_6H_4). $^{13}C\{^1H\}$ NMR (100.58 MHz, $CDCl_3$): δ 16.43 (d, $^1J_{PC}$ = 32 Hz, PMe_3), 48.14 (d, $^3J_{PC}$ = 2 Hz, NMe_2), 51.19 (d, $^3J_{PC}$ = 2 Hz, NMe_2), 60.42 (d, J_{PC} = 3 Hz, CH C_5H_4), 65.69 (d, $^3J_{PC}$ = 2 Hz, NCH_2), 66.11 (s, CH C_5H_4), 67.36 (s, CH C_5H_4), 69.35 (s, C_5H_5), 69.57 (s, CH C_5H_4), 106.82 (d, J_{PC} = 6 Hz, C^{ipso}-N C_5H_4), 121.36 (s, CH C_6H_4), 126.44 (s, CH C_6H_4), 129.48 (s, CH C_6H_4), 129.68 (s, CH C_6H_4), 132.10 (s, C^{ipso}-C C_6H_4), 145.11 (d, $^3J_{PC}$ = 8 Hz, C^{ipso}-C C_6H_4), 191.70 (d, $^2J_{PC}$ = 3 Hz, C^{ipso}-Pd). $^{31}P\{^1H\}$ NMR (161.90 MHz, $CDCl_3$): δ –4.2 (s). ESI+ MS: *m/z* 527 ($[M - Cl]^+$). IR (DRIFTS, KBr): ν_{max} 3096 w, 3068 w, 3026 w, 3012 w, 2993 w, 2977 w, 2956 w, 2932 w, 2911 w, 2887 w, 2864 w, 2831 w, 1736 w, 1586 s, 1479 m, 1470 m, 1460 m, 1452 m, 1436 m, 1424 m, 1420 w, 1409 w, 1399 w, 1363 w, 1333 w, 1302 w, 1282 m, 1235 w, 1209 m, 1181 w, 1104 m, 1028 m, 1018 m, 1001 s, 968 s, 950 s, 931 m, 895 m, 880 m, 862 m, 841 m, 818 m, 804 m, 763 m, 739 s, 712 w, 683 w, 660 w, 635 w, 610 w, 595 w, 571 m, 528 w, 501 s, 495 s, 461 w, 439 w cm^{-1}. Anal. Calc. for $C_{23}H_{30}ClFeN_2PPd$ (563.19): C 49.05, H 5.37, N 4.95%. Found: C 49.21, H 5.07, N 4.87%.

Synthesis of 5a. A solution of complex **2a** (54 mg, 0.10 mmol) in dichloromethane (7 mL) was added to isocyanoferrocene (21 mg, 0.10 mmol) dissolved in the same solvent (3 mL) and the mixture was stirred for 30 min, whereupon its colour changed from light orange to orange brown. Then, all volatiles were removed under reduced pressure and the crude product was purified by chromatography over silica gel using dichloromethane/methanol (20:1) as the eluent. The first orange band was collected and evaporated to give **5a** as a brown solid. Yield: 64 mg, 85%. Crystals used for X-ray diffraction analysis were obtained from ethyl acetate/hexane.

^1H NMR (399.95 MHz, $CDCl_3$): δ 2.68 (d, $^4J_{PH}$ = 1.9 Hz, 3H, SMe), 3.44 (br d, $^2J_{HH} \approx$ 13.2 Hz, 1H, SCH_2), 3.57 (d, $^2J_{HH}$ = 13.2 Hz, 1H, SCH_2), 3.94 (td, *J* = 2.6, 1.4 Hz, 1H, C_5H_4), 3.99 (td, *J* = 2.6, 1.3 Hz, 1H, C_5H_4), 4.15 (s, 5H, C_5H_5), 4.40 (dt, *J* = 2.4, 1.4 Hz , 1H, C_5H_4), 5.72 (br d, *J* = 7.1 Hz, 1H, C_6H_4), 6.33 (br s, 1H, C_5H_4), 7.01-7.06 (m, 1H, C_6H_4), 7.10-7.17 (m, 2H, C_6H_4), 7.25-7.32 (m, 6H, PPh_3), 7.35-7.45 (m, 9H, PPh_3). $^{13}C\{^1H\}$ NMR (100.58 MHz, $CDCl_3$): δ 20.26 (s, SMe), 36.31 (s, SCH_2), 61.00 (d, J_{PC} = 1 Hz, CH C_5H_4), 66.36 (s, CH C_5H_4), 67.17 (s, CH C_5H_4), 69.13 (s, C_5H_5), 69.53 (s, CH C_5H_4), 104.25 (d, J_{PC} = 4 Hz, C^{ipso}-N C_5H_4), 123.29 (s, CH C_6H_4), 126.13 (s, CH C_6H_4), 128.07 (d, $^3J_{PC}$ = 11 Hz, CH^{meta} PPh_3), 128.84 (s, CH C_6H_4), 129.37 (s, CH C_6H_4), 130.50 (d, $^4J_{PC}$ = 3 Hz, CH^{para} PPh_3), 130.77 (d, $^1J_{PC}$ = 47 Hz, C^{ipso} PPh_3), 131.91 (br s, C^{ipso}-C C_6H_4), 134.63 (d, $^2J_{PC}$ = 12 Hz, CH^{ortho} PPh_3), 143.16 (d, J_{PC} = 7 Hz, C^{ipso}-C C_6H_4), 187.37 (d, *J* = 2 Hz, C^{ipso}-Pd). $^{31}P\{^1H\}$ NMR (161.90 MHz, $CDCl_3$): δ 24.3 (s). ESI+ MS: *m/z* 716 ($[M - Cl]^+$). IR (DRIFTS, KBr): ν_{max} 3088 w, 3076 w, 3057 w, 3004 w, 2926 w, 1135 w, 1633 w, 1604 m, 1572 w, 1479 w, 1435 m, 1411 w, 1374 w, 1332 w, 1314 w, 1278 w, 1242 w, 1211 w, 1188 w, 1176 w, 1159 w, 1143 w, 1105 m, 1094 m, 1071 w, 1048 w, 1026 w, 999 w, 969 w, 930 w, 894 w, 870 w, 860 w, 829 w, 818 m, 810 m, 698 s, 670 w, 655 w, 628 w, 603 w, 574 w, 564 s, 529 s, 511 s, 494 m, 456 w, 438 w, 425 w cm^{-1}. Anal. Calc. for $C_{37}H_{33}ClFeNPPdS$ (752.42): C 59.06, H 4.42, N 1.86%. Found: C 59.25, H 4.71, N 2.03%.

Synthesis of 5b. Complex **5b** was prepared analogously from **2b** (44.4 mg, 0.125 mmol) and isocyanoferrocene (26.4 mg, 0.125 mmol) in 9 mL of dichloromethane. The crude product was purified by chromatography over silica gel using dichloromethane/methanol (10:1) as the eluent. Yield: 64 mg (90%), orange solid. Crystal used for structure determination was obtained from ethyl acetate/hexane.

^{1}H NMR (399.95 MHz, $CDCl_3$): δ 1.25 (d, $^{2}J_{PH}$ = 10.9 Hz, 9H, PMe_3), 2.57 (br s, 3H, SMe), 3.45 (br d, $^{3}J_{HH}$ ≈ 13 Hz, 1H, SCH_2), 3.54 (d, $^{2}J_{HH}$ = 13.2 Hz, SCH_2), 4.20 (s, 5H, C_5H_5), 4.20 (dt, *J* = 2.5, 1.2 Hz, C_5H_4; partly obscured by the C_5H_5 signal), 4.27 (dt, *J* = 2.6, 1.4 Hz 1H, C_5H_4), 4.65 (td, *J* = 2.6, 1.4 Hz, 1H, C_5H_4), 6.10 (br s, 1H, C_5H_4), 7.01 (br d, *J* = 7.4 Hz, 1H, C_6H_4), 7.14-7.23 (m, 2H, C_6H_4), 7.29-7.36 (m, 1H, C_6H_4). ^{13}C{^{1}H} NMR (100.58 MHz, $CDCl_3$): δ 15.80 (d, $^{1}J_{PC}$ = 31 Hz, PMe_3), 19.28 (br s, SMe), 36.07 (s, SCH_2), 59.54 (d, J_{PC} = 2 Hz, CH C_5H_4), 66.31 (s, CH C_5H_4), 67.43 (s, CH C_5H_4), 69.36 (s, C_5H_5), 69.60 (s, CH C_5H_4), 106.14 (d, J_{PC} = 6 Hz, C^{ipso}-N C_5H_4), 122.91 (s, CH C_6H_4), 126.25 (s, CH C_6H_4), 129.17 (s, CH C_6H_4), 129.92 (s, CH C_6H_4), 132.17 (br s, C^{ipso}-C C_6H_4), 144.21 (br s, C^{ipso}-C C_6H_4), 188.64 (d, *J* = 2 Hz, C^{ipso}-Pd). ^{31}P{^{1}H} NMR (161.90 MHz, $CDCl_3$): δ −7.2 (s). ESI+ MS: *m/z* 530 ($[M - Cl]^+$). IR (DRIFTS, KBr): ν_{max} 3089 w, 3065 m, 2917 w, 1732 w, 1596 s, 1476 m, 1453 w, 1428 m, 1416 m, 1332 w, 1315 w, 1286 m, 1280 m, 1243 w, 1211 m, 1179 m, 1155 w, 1105 w, 1036 w, 1023 w, 1003 w, 989 w, 957 m, 931 vs, 893 s, 863 m, 855 s, 818 s, 759 s, 739 m, 706 s, 676 m, 657 w, 626 m, 576 w, 508 s, 501 s, 482 m, 474 m, 444 w, 433 w cm^{-1}. Anal. Calc. for $C_{22}H_{27}ClFeNPPdS$ (566.21): C 46.67, H 4.81, N 2.47%. Found: C 46.49, H 4.56, N 2.16%.

Synthesis of 6a. An oven-dried reaction flask equipped with a gas inlet and a stirring bar was charged with complex **4a** (37.5 mg, 0.050 mmol), flushed with argon and sealed with a rubber septum. The solid complex was dissolved in dry dichloromethane (5 mL) and solid $[Me_3O][BF_4]$ (8.1 mg, 0.055 mmol) was added at once against an argon flow, whereupon the colour of the mixture changed gradually from orange to red. After stirring for 22 h, the reaction mixture was evaporated and the residue was purified by chromatography on a silica gel column using dichloromethane/methanol (20:1) as the eluent. The second (main) band was collected and evaporated, leaving **6a** as a red solid (34 mg, 80%). Crystals used for diffraction analysis were obtained from ethyl acetate/hexane.

^{1}H NMR (399.95 MHz, CD_2Cl_2): δ 2.80 (d, $^{4}J_{PH}$ = 2.4 Hz, 3H, NMe_2), 3.20 (d, $^{4}J_{PH}$ = 2.8 Hz, 3H, NMe_2), 3.37 (dd, $^{2}J_{HH}$ = 12.4, $^{4}J_{PH}$ = 6.5 Hz, 1H, NCH_2), 3.41 (s, 3H, CH_3-N), 3.44 (d, $^{2}J_{HH}$ = 12.4 Hz, 1H, NCH_2), 4.31 (td, *J* = 2.7, 1.3 Hz, 1H, CH C_5H_4), 4.39 (s, 5H, C_5H_5), 4.43 (td, *J* =2.7, 1.1 Hz, 1H, CH C_5H_4), 4.53 (dt, *J* = 2.7, 1.3 Hz, 1H, CH C_5H_4), 5.79 (d, *J* = 7.5 Hz, 1H, C_6H_4), 6.88 (dq, *J* = 2.5, 1.2 Hz, 1H, C_5H_4), 7.31-7.58 (m, 18H, PPh_3 + 3CH of C_6H_4). ^{13}C{^{1}H} NMR (100.58 MHz, CD_2Cl_2): δ 47.65 (s, CH_3-N), 49.22 (d, $^{3}J_{PC}$ = 3 Hz, NMe_2), 51.66 (d, $^{3}J_{PC}$ = 3 Hz, NMe_2), 64.63 (d, J_{PC} = 4 Hz, CH C_5H_4), 66.15 (s, CH C_5H_4), 66.42 (d, $^{3}J_{PC}$ = 3 Hz, NCH_2), 68.91 (s, CH C_5H_4), 70.21 (s, CH C_5H_4), 71.12 (s, C_5H_5), 103.46 (s, C^{ipso}-N C_5H_4), 121.12 (s, CH C_6H_4), 128.81 (d, $^{1}J_{PC}$ = 54 Hz, C^{ipso} PPh_3), 129.03 (d, $^{3}J_{PC}$ =11 Hz,

CH^{meta} PPh_3), 129.82 (s, C^{ipso}-C C_6H_4), 130.31 (CH C_6H_4), 130.50 (CH C_6H_4), 131.52 (CH C_6H_4), 132.28 (d, $^4J_{PC}$ = 3 Hz, CH^{para} PPh_3), 134.53 (d, $^2J_{PC}$ = 11 Hz, CH^{ortho} PPh_3), 139.42 (d, J_{PC} = 2 Hz, C^{ipso}-C C_6H_4), 227.46 (d, J = 2 Hz, C^{ipso}-Pd). $^{31}P\{^1H\}$ NMR (161.90 MHz, CD_2Cl_2): δ 25.1 (s). ESI+ MS: *m/z* 763 ([M – BF_4]$^+$). IR (DRIFTS, KBr): ν_{max} 3116 w, 3077 w, 3057 w, 3035 w, 2971 w, 2917 w, 2890 w, 2865 w, 2838 w, 1557 w, 1482 m, 1471 m, 1455 m, 1436 s, 1404 w, 1378 w, 1356 w, 1316 w, 1283 w, 1261 w, 1238 w, 1215 w, 1189 w, 1163 w, 1142 w, 1097 s, 1054 s, 1038 s, 1002 s, 984 m, 960 w, 902 w, 877 w, 838 m, 821 w, 755 s, 716 m, 707 s, 700 s, 694 s, 665 m, 532 s, 511 s, 497 m, 461 m, 428 w cm^{-1}. Anal. Calc. for $C_{39}H_{39}BClF_4FeN_2PPd$ (851.24): C 55.03, H 4.62, N 3.29%. Found: C 54.61, H 4.75, N 3.04%.

Synthesis of 6b. Compound **6b** was obtained similarly from **4b** (56.3 mg, 0.10 mmol) and $[Me_3O][BF_4]$ (22.2 mg, 0.15 mmol) in dichloromethane (7.5 mL). Isolation as above afforded the complex as a red solid. Yield: 56 mg (84%). Crystals used for structure determination were obtained from chloroform/ethyl acetate.

^1H NMR (399.95 MHz, CD_2Cl_2): δ 1.25 (d, $^2J_{PH}$ = 12.0 Hz, 9H, PMe_3), 2.66 (d, $^4J_{PH}$ = 2.5 Hz, 3H, NMe_2), 3.04 (d, $^4J_{PH}$ = 2.7 Hz, 3H, NMe_2), 3.29 (dd, $^2J_{HH}$ = 12.4 Hz, $^4J_{PH}$ = 6.4 Hz, 1H, NCH_2), 3.43 (d, $^2J_{HH}$ = 12.4 Hz, 1H, NCH_2), 3.95 (s, 3H, CH_3-N), 4.45 (s, 5H, C_5H_5), 4.60 (td, J = 2.7, 1.4 Hz, 1H, C_5H_4), 4.65 (td, J = 2.7, 1.3 Hz, 1H, C_5H_4), 5.01 (dt, J = 2.8, 1.4 Hz, 1H, C_5H_4), 6.49 (dq, J = 2.6, 1.3 Hz, 1H, C_5H_4), 7.19 (br d, J = 7.5 Hz, 1H, C_6H_4), 7.44 (br d, J = 7.4 Hz, 1H, C_6H_4), 7.50 (td, J = 7.5, 1.2 Hz Hz, 1H, C_6H_4), 7.62 (td, J = 7.5, 1.3 Hz, 1H, C_6H_4). $^{13}C\{^1H\}$ NMR (100.58 MHz, CD_2Cl_2): δ 15.85 (d, $^1J_{PC}$ = 37 Hz, PMe_3), 48.31 (s, CH_3-N), 48.60 (d, $^3J_{PC}$ = 3 Hz, NMe_2), 51.71 (d, $^3J_{PC}$ = 3 Hz, NMe_2), 64.92 (d, J_{PC} = 5 Hz, CH C_5H_4), 66.26 (s, CH C_5H_4), 66.32 (d, $^3J_{PC}$ = 3 Hz, NCH_2), 68.41 (s, CH C_5H_4), 70.64 (s, CH C_5H_4), 71.17 (s, C_5H_5), 105.07 (d, J_{PC} = 2 Hz, C^{ipso}-N C_5H_4), 121.42 (s, CH C_6H_4), 130.07 (s, C^{ipso}-C C_6H_4), 130.20 (s, CH C_6H_4), 130.91 (s, CH C_6H_4), 131.52 (s, CH C_6H_4), 139.98 (d, J_{PC} = 2 Hz, C^{ipso}-C C_6H_4), 229.53 (d, J_{PC} = 2 Hz, C^{ipso}-Pd). $^{31}P\{^1H\}$ NMR (161.90 MHz, CD_2Cl_2): δ –0.2 (s). ESI+ MS: *m/z* 577 ([M – BF_4]$^+$). IR (DRIFTS, KBr): ν_{max} 3009 w, 2976 w, 2911 w, 1644 w, 1553 w, 1472 w, 1455 w, 1414 w, 1359 w, 1287 m, 1261 w, 1216 w, 1142 m, 1107 s, 1062 s, 1036 s, 1004 m, 961 s, 901 w, 860 w, 842 m, 770 m, 738 m, 717 w, 678 w, 665 w, 639 w, 624 w, 612 w, 598 w, 521 m, 498 m, 484 m, 458 m, 447 m, 432 w. Anal. Calc. for $C_{24}H_{33}BClF_4FeN_2PPd$ (665.04): C 43.35, H 5.00, N 4.21%. Found: C 43.60, H 4.81, N 3.89%.

Synthesis of 7a. Complex **7a** was similarly prepared and isolated starting from **5a** (37.6 mg, 0.050 mmol) and $[Me_3O][BF_4]$ (8.1 mg, 0.055 mmol) in 5 mL of dichloromethane. Yield: 32 mg (75%), red solid. X-ray quality crystals were grown from ethyl acetate/hexane.

^1H NMR (399.95 MHz, CD_2Cl_2): δ 2.66 (br s, 3H, SMe), 3.30 (d, $^2J_{HH}$ = 14.2 Hz, 1H, SCH_2), 3.47 (d, J_{PH} = 0.5 Hz, 3H, CH_3-N), 3.82 (very br s, 1H, SCH_2), 4.29 (td, J = 2.8, 1.4 Hz, 1H, C_5H_4), 4.39 (s, 5H, C_5H_5), 4.43-4.46 (m, 1H, C_5H_4), 4.55 (dt, J = 2.8, 1.4 Hz, 1H, C_5H_4), 5.62 (br d, J_{HH} = 7.5 Hz, 1H, C_6H_4), 6.65 (br s, 1H, C_5H_4), 7.28-7.59 (m, 18H, PPh_3 and 3×CH of C_6H_4). $^{13}C\{^1H\}$ NMR (100.58 MHz,

CD_2Cl_2): δ 20.87 (br s, 3H, SMe), 36.87 (br s, SCH_2), 48.00 (s, CH_3-N), 63.98 (d, J_{PC} = 3 Hz, CH C_5H_4), 65.72 (s, CH C_5H_4), 68.97 (s, CH C_5H_4), 70.29 (s, CH C_5H_4), 71.17 (s, C_5H_5), 103.62 (s, C^{ipso}-N C_5H_4), 121.60 (s, CH C_6H_4), 128.44 (d, $^1J_{PC}$ = 53 Hz, C^{ipso} PPh_3), 129.21 (d, $^3J_{PC}$ = 11 Hz, CH^{meta} PPh_3), 129.94 (s, CH C_6H_4), 130.10 (s, CH C_6H_4), 132.03 (s, CH C_6H_4), 132.41 (d, $^4J_{PC}$ = 3 Hz, CH^{para} PPh_3), 134.51 (d, $^2J_{PC}$ = 11 Hz, CH^{ortho} PPh_3), 138.66 (s, *C*^{ipso}-C C_6H_4), 226.88 (d, J_{PC} = 2 Hz, C^{ipso}-Pd). One signal due to C_6H_4 was not found. $^{31}P\{^1H\}$ NMR (161.90 MHz, CD_2Cl_2): δ 24.8 (s). ESI+ MS: *m/z* 768 ([M – BF_4]$^+$). IR (DRIFTS, KBr): ν_{max} 3058 w, 2924 w, 2854 w, 1553 w, 1482 w, 1436 m, 1414 w, 1314 w, 1283 w, 1262 w, 1244 w, 1209 w, 1187 w, 1162 w, 1096 s, 1058 s, 1001 m, 898 w, 826 w, 751 m, 709 s, 694 s, 662 w, 529 s, 509 s, 495 s, 463 m, 429 w cm^{-1}. Anal. Calc. for $C_{38}H_{36}BClF_4FeNPdS$ (854.26): C 53.43, H 4.25, N 1.64%. Found: C 53.87, H 4.57, N 1.45%.

Synthesis of 7b. An analogous reaction of **5b** (56.6 mg, 0.10 mmol) with $[Me_3O][BF_4]$ (22.2 mg, 0.15 mmol) in 7.5 mL of dichloromethane and purification as described above produced **7b** as a red solid. Yield: 60 mg (90%). Crystals suitable for structure determination were grown from chloroform/ethyl acetate

^1H NMR (399.95 MHz, CD_2Cl_2): δ 1.30 (d, $^2J_{PH}$ = 12.0 Hz, 9H, PMe_3), 2.53 (br s, 3H, SMe), 3.30 (d, $^2J_{HH}$ = 14.2 Hz, 1H, SCH_2), 3.76 (very br s, 1H, SCH_2), 3.94 (s, 3H, CH_3-N), 4.44 (s, 5H, C_5H_5), 4.58 (td, *J* = 2.7, 1.4 Hz, 1H, C_5H_4), 4.62 (td, *J* = 2.7, 1.3 Hz, 1H, C_5H_4), 4.99 (m, 1H, C_5H_4), 6.25 (m, 1H, CH C_5H_4), 7.16 (d, *J* = 7.5 Hz, 1H, C_6H_4), 7.43-7.49 (m, 2H, C_6H_4), 7.56-7.62 (m, 1H, C_6H_4). $^{13}C\{^1H\}$ NMR (100.58 MHz, CD_2Cl_2): δ 15.23 (d, $^1J_{PC}$ = 35 Hz, PMe_3), 19.83 (br s, SMe), 36.66 (br s, SCH_2), 48.69 (s, CH_3-N), 64.40 (d, J_{PC} = 3 Hz, CH C_5H_4), 66.07 (s, CH C_5H_4), 68.45 (s, CH C_5H_4), 70.51 (s, CH C_5H_4), 71.21 (s, C_5H_5), 105.21 (d, J_{PC} = 2 Hz, C^{ipso}-N C_5H_4), 122.16 (s, CH C_6H_4), 129.90 (s, CH C_6H_4), 130.62 (s, CH C_6H_4), 131.92 (s, CH C_6H_4), 139.22 (s, *C*^{ipso}-C C_6H_4), 229.08 (s, C^{ipso}-Pd). One signal due to C_6H_4 was not found. $^{31}P\{^1H\}$ NMR (161.90 MHz, CD_2Cl_2): δ –1.5 (s). ESI+ MS: *m/z* 582 ([M – BF_4]$^+$). IR (DRIFTS, KBr): ν_{max} 3112 w, 3064 w, 3007 w, 2916 w, 1560 m, 1475 w, 1450 w, 1417 m, 1295 m, 1285 m, 1261 m, 1242 w, 1207 w, 1105 s, 1078 s, 1058 s, 1035 s, 990 m, 958 s, 905 m, 897 m, 871 m, 822 m, 799 w, 772 m, 766 m, 753 m, 711 m, 679 m, 666 m, 572 w, 520 m, 503 m, 485 m, 463 m, 450 m cm^{-1}. Anal. Calc. for $C_{23}H_{30}BClF_4FeNPPdS{\cdot}0.2CH_2Cl_2$ (685.04): C 40.67, H 4.48, N 2.05%. Found: C 40.75, H 4.34, N 1.93%.

Synthesis of 8. Method A. Complex [AuCl(PPh_3)] (20.0 mg, 0.040 mmol) was dissolved in dichloromethane (1.0 mL) and added to Ag[BF_4] (7.8 mg, 0.040 mmol) dissolved in MeOH (1.0 mL). The mixture was stirred for 30 min and filtered through a PTFE syringe filter (0.45 μm porosity) to remove a white precipitate (AgCl). The filtrate was added to solid **6a** (30.0 mg, 0.040 mmol) and the reaction mixture was stirred for 16 hours and evaporated under vacuum. The solid residue was taken up with dichloromethane:methanol (50:1) and transferred onto the top of a short silica gel column. Elution with the same solvent mixture first removed a red band containing unidentified phosphine and palladium-containing side products, which were discarded. The

following purple band was collected and evaporated, leaving **8** as a purple amorphous solid (9.0 mg, 52%). The product was crystallised from chloroform/hexane to give deep purple crystals, which were decanted, washed with pentane, and dried under vacuum (yield: 3.9 mg, 23%).

^{1}H NMR (399.95 MHz, $CDCl_3$): δ 3.47 (s, 6H, NMe_2), 4.29 (s, 5H, C_5H_5), 4.41 (vt, *J´* = 1.8 Hz, 2H, C_5H_4), 4.55 (vt, *J´* = 1.8 Hz, 2H, C_5H_4), 5.11 (s, 2H, NCH_2), 7.38-7.43 (m, 1H, C_6H_4), 7.57 (dt, *J* = 7.8, 0.9 Hz, 1H, C_6H_4), 7.69 (td, *J* = 7.6, 1.1 Hz, 1H, C_6H_4), 8.02 d, *J* = 8.1 Hz, 1H, C_6H_4). ^{13}C{^{1}H} NMR (100.58 MHz, $CDCl_3$): δ 52.38 (s, NMe_2), 64.28 (s, CH C_5H_4), 66.31 (s, NCH_2), 67.93 (s, CH C_5H_4), 70.46 (s, C_5H_5), 97.8 (*C*^{ipso}-N C_5H_4, identified in ^{13}C HMBC spectrum), 121.86 (*C*^{ipso}-C C_6H_4, identified in HMBC spectrum), 125.29 (s, CH C_6H_4), 126.32 (s, CH C_6H_4), 129.81 (s, CH C_6H_4), 135.21 (s, CH C_6H_4), 138.27 (s, *C*^{ipso}-CH_2 C_6H_4), 156.01 (s, *C*^{ipso}-NMe_2). ESI+ MS: *m/z* 345 ($[M - BF_4]^+$). IR (DRIFTS, KBr): ν_{max} 3081 br w, 2926 w, 2855 w, 1690 w, 1604 w, 1590 w, 1466 m, 1438 m, 1410 w, 1311 w, 1289 w, 1267 w, 1182 w, 1163 w, 1058 br s, 1004 m, 947 w, 861 w, 824 m, 777 m, 752 m, 724 m, 696 m, 663 w, 616 w, 541 s, 521 m, 498 s, 472 m cm^{-1}. Analysis Calc. for $C_{20}H_{21}N_2BF_4Fe \cdot 0.1CHCl_3$ (443.98): C 54.38, H 4.79, N 6.31%. Found: C 54.51, H 4.47, N 5.76%.

Method B. Solid $Ag[BF_4]$ (4.9 mg, 0.025 mmol) and **6a** (18.7 mg, 0.025 mmol) were dissolved in $CDCl_3$ (1.0 mL) and the solution was stirred for 1 h. The resulting suspension was filtered through a PTFE syringe filter, adding Celite and the filtrate was analysed by NMR spectroscopy, which revealed an 87% conversion of starting material into **8**. The solution was evaporated and the residue was purified by chromatography as described above to give **8** in 70% yield (7.6 mg).

Method C. Solid $NH_4[BF_4]$ (2.0 mg, 0.019 mmol, 1.5 equiv.) and **6a** (9.4 mg, 0.0125 mmol) were dissolved in a mixture of CH_2Cl_2 and MeOH (1.0 mL each). The solution was stirred for 48 h and evaporated under vacuum. The solid residue was dissolved in $CDCl_3$ (0.7 mL) and analysed by NMR spectroscopy. The yield of **8** was 26% (conversion ≈40%). *Note*: a similar reaction with $NH_4[BF_4]$ in pure dichloromethane was probably hampered by the poor solubility of the inorganic salt. After 24 h, it resulted in approximately 20% conversion of the starting material but the signals due to **8** were not observed.

X-ray crystallography

Full-sphere diffraction data ($\pm h \pm k \pm l$, θ_{max} = 26-30°) were collected on Bruker APEX-II CCD (**4a**, **5a**, and **6a**·$CHCl_3$) or a Bruker D8 VENTURE Kappa Duo diffractometer (other compounds), equipped with a Cryostream Cooler (Oxford Cryosystems) at 120 or 150 K. Mo Kα radiation (λ = 0.71073 Å) was used in all cases. The structures were solved by direct methods (SHELXT-2014[5]) and subsequently refined by a full-matrix least-squares routine based on F^2 (SHELXL-2017[6]). All nonhydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were included in their theoretical positions and refined as riding atoms with their U_{iso}(H) set to a multiple of U_{eq}(C) of their bonding carbon atom (1.2 times for CH and CH_2 groups and 1.5 times for methyl groups). The OH hydrogens in the structure of **4b**·$0.35H_2O$ were identified on the electron density map and refined similarly. The location of the hydrogen atoms was facilitated because two water molecules, viz. the molecule and its image generated by crystallographic inversion, form hydrogen brides towards imine nitrogen in a centrosymmetric pair of molecules 2 in the structure (see Figure S4). In addition, the unsubstituted cyclopentadienyl ring in molecule 2 was disordered and had to be refined over two positions mutually rotated along the axis of the ferrocene core. The refined occupancies were 53:47.

The thioether group (SMe) in the structure of **5a** was also disordered and was refined over two, closely separated positions in a 74:26 ratio. A different type of disorder of the SMe group was observed in **7b**, where pendant thiomethyl moiety was refined over two positions (83:17) representing approximately mirror images with respect to the coordination plane, thereby corresponding to different stereoisomers (S_S and R_S).

All geometric parameters and structural diagrams were obtained using the PLATON program.[7] Relevant crystallographic data and structure refinement parameters are presented in Table S1. The numerical values were rounded to one decimal place with respect to their estimated standard deviations (ESDs).

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

Compound	**3**	**4a**
Formula	$C_{14}H_{27}ClP_2PdS$	$C_{38}H_{36}ClFeN_2PPd$
M	431.20	749.36
Crystal system	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)
Space group	monoclinic	monoclinic
T [K]	120(2)	150(2)
a [Å]	16.2283(9)	21.4864(7)
b [Å]	10.6693(5)	15.0931(5)
c [Å]	11.2552(6)	10.2377(3)
α [°]	90	90
β [°]	100.130(2)	103.377(1)
γ [°]	90	90
V [Å]^3	1918.4(2)	3230.0(2)
Z	4	4
F(000)	880	1528
μ(Mo Kα) [mm^{-1}]	1.369	1.169
Diffrns collected	20426	32457
Independent diffrns	4388	7429
Observed[a] diffrns	4313	5915
R_{int}[b] [%]	1.79	4.42
No. of parameters	180	399
R[b] obsd diffrns [%]	1.69	3.33
R, *wR*[b] all data [%]	1.72, 4.26	5.02, 7.12
Δρ [e Å^{-3}]	0.535, –0.542	0.754, –0.556

[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	**4b**·0.35H_2O	**5a**
Formula	$C_{23}H_{30}ClFeN_2PPd$·0.35H_2O	$C_{37}H_{33}ClFeNPPdS$
M	569.60	752.37
Crystal system	*P*–1 (no. 2)	$P2_1/c$ (no. 14)
Space group	triclinic	monoclinic
T [K]	150(2)	120(2)
a [Å]	10.3488(5)	21.183(1)
b [Å]	13.7820(7)	15.1442(9)
c [Å]	17.1619(9)	10.0918(6)
α [°]	101.004(2)	90
β [°]	95.440(2)	102.060(2)
γ [°]	96.566(2)	90
V [Å]^3	2369.9(2)	3165.9(3)
Z	4	4
F(000)	1158	1528
μ(Mo Kα) [mm^{-1}]	1.565	1.255
Diffrns collected	46893	118331
Independent diffrns	10857	9256
Observed[a] diffrns	10235	8826
R_{int}[b] [%]	1.99	0.97
No. of parameters	535	398
R[b] obsd diffrns [%]	2.08	2.03
R, *wR*[b] all data [%]	2.25, 5.10	2.18, 4.95
Δρ [e Å^{-3}]	0.618, –0.794	0.646, –0.535

Table S1 continued

Compound	**5b**	**6a**·$CHCl_3$
Formula	$C_{22}H_{27}ClFeNPPdS$	$C_{39}H_{39}BClF_4FeN_2PPd·CHCl_3$
M	566.17	970.57
Crystal system	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)
Space group	monoclinic	monoclinic
T [K]	150(2)	150(2)
a [Å]	8.9162(5)	19.1161(7)
b [Å]	17.4114(9)	11.5322(4)
c [Å]	15.0731(7)	20.5774(8)
α [°]	90	90
β [°]	104.774(2)	116.782(1)
γ [°]	90	90
V [Å]^3	2262.6(2)	4049.7(3)
Z	4	4
F(000)	1144	1960
μ(Mo Kα) [mm^{-1}]	1.725	1.157
Diffrns collected	18721	29932
Independent diffrns	4427	9295
Observed[a] diffrns	4165	7464
R_{int}[b] [%]	1.67	4.06
No. of parameters	257	490
R[b] obsd diffrns [%]	2.22	3.56
R, *wR*[b] all data [%]	2.41, 5.45	4.96, 9.03
Δρ [e Å^{-3}]	1.763, –0.464	1.613, –1.145

Table S1 continued

Compound	**6b**	**7a**
Formula	$C_{24}H_{33}BClF_4FeN_2PPd$	$C_{38}H_{36}BClF_4FeNPPdS$
M	665.00	854.22
Crystal system	$P2_1/c$ (no. 14)	*Pbca* (no. 61)
Space group	monoclinic	orthorombic
T [K]	120(2)	120(2)
a [Å]	14.8935(4)	18.3903(7)
b [Å]	10.3396(3)	17.3243(9)
c [Å]	17.0483(5)	21.845(1)
α [°]	90	90
β [°]	95.193(1)	90
γ [°]	90	90
V [Å]^3	2614.5(1)	6959.9(6)
Z	4	8
F(000)	1344	3456
μ(Mo Kα) [mm^{-1}]	1.451	1.168
Diffrns collected	28290	55408
Independent diffrns	5991	7985
Observed[a] diffrns	5705	5675
R_{int}[b] [%]	1.67	6.04
No. of parameters	322	444
R[b] obsd diffrns [%]	2.29	4.16
R, *wR*[b] all data [%]	2.43, 6.10	6.71, 11.95
Δρ [e Å^{-3}]	1.554, –0.686	1.408, –1.070

Table S1 continued

Compound	**7b**	**8**
Formula	$C_{23}H_{30}BClF_4FeNPPdS$	$C_{20}H_{21}BF_4FeN_2$
M	668.02	432.05
Crystal system	$P2_1/c$ (no. 14)	$C2/c$ (no. 15)
Space group	monoclinic	monoclinic
T [K]	120(2)	120(2)
a [Å]	14.7586(6)	36.1427(7)
b [Å]	10.3653(4)	7.3110(2)
c [Å]	17.0751(6)	14.5300(4)
α [°]	90	90
β [°]	97.684(1)	101.740(1)
γ [°]	90	90
V [Å]^3	2588.7(2)	3759.1(2)
Z	4	8
F(000)	1344	1776
μ(Mo Kα) [mm^{-1}]	1.543	0.848
Diffrns collected	60275	30940
Independent diffrns	5951	4317
Observed[a] diffrns	5683	4049
R_{int}[b] [%]	4.47	2.21
No. of parameters	332	255
R[b] obsd diffrns [%]	4.49	3.19
R, *wR*[b] all data [%]	4.66, 10.50	3.39, 8.26
Δρ [e Å^{-3}]	1.735, –1.477	0.696, –0.503

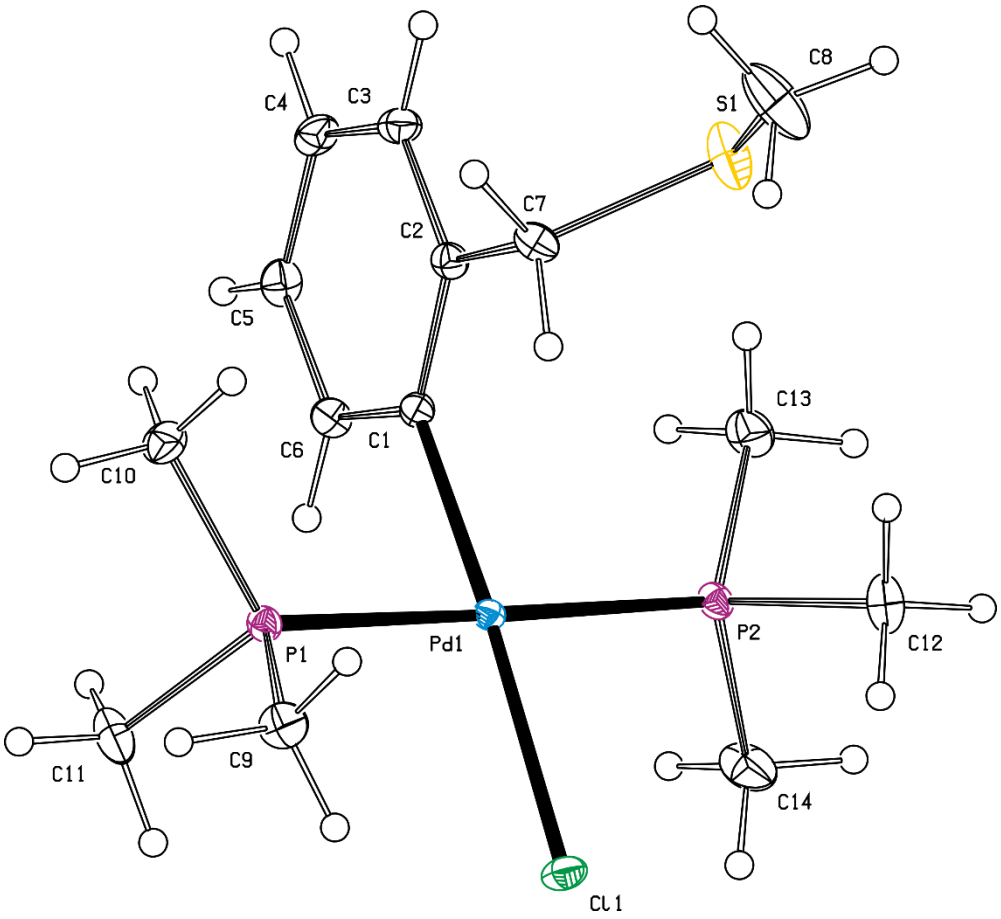


Figure S1 PLATON plot of the molecular structure of *trans*-**3**. Displacement ellipsoids enclose the 30% probability level. Selected distances and angles (in Å and deg): Pd1-P1 2.3033(5), Pd1-P2 2.3023(5), Pd1-Cl1 2.3925(4), Pd1-C1 2.009(1), P1-Pd1-Cl1 91.40(1), P1-Pd1-C1 89.87(4), P2-Pd1-Cl1 89.25(1) and P1-Pd1-C1 89.60(4).

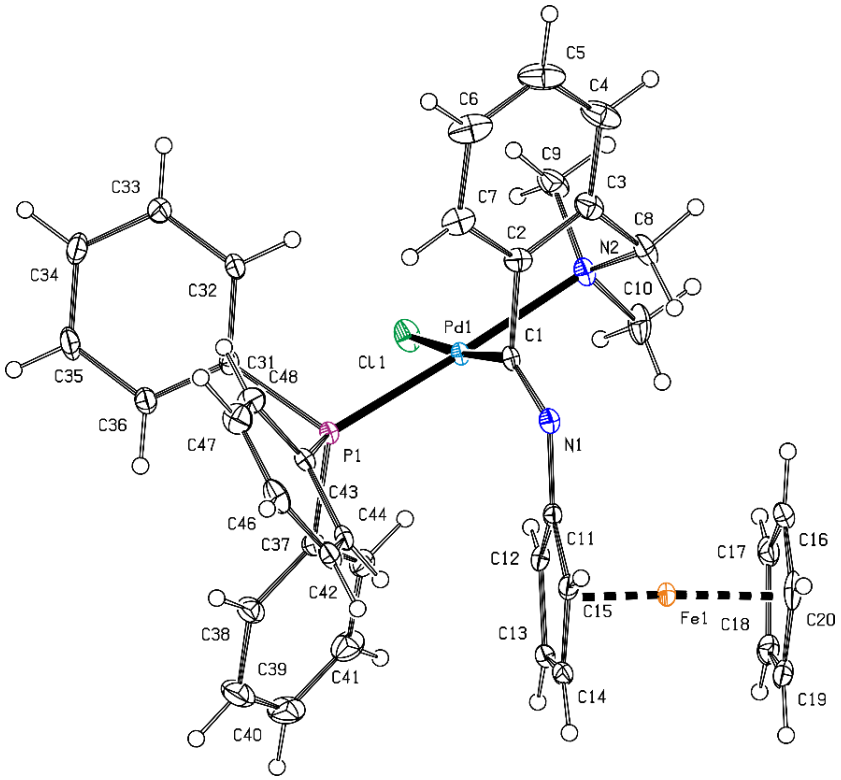


Figure S2 PLATON plot of the molecular structure of **4a** showing displacement ellipsoids at the 30% probability level

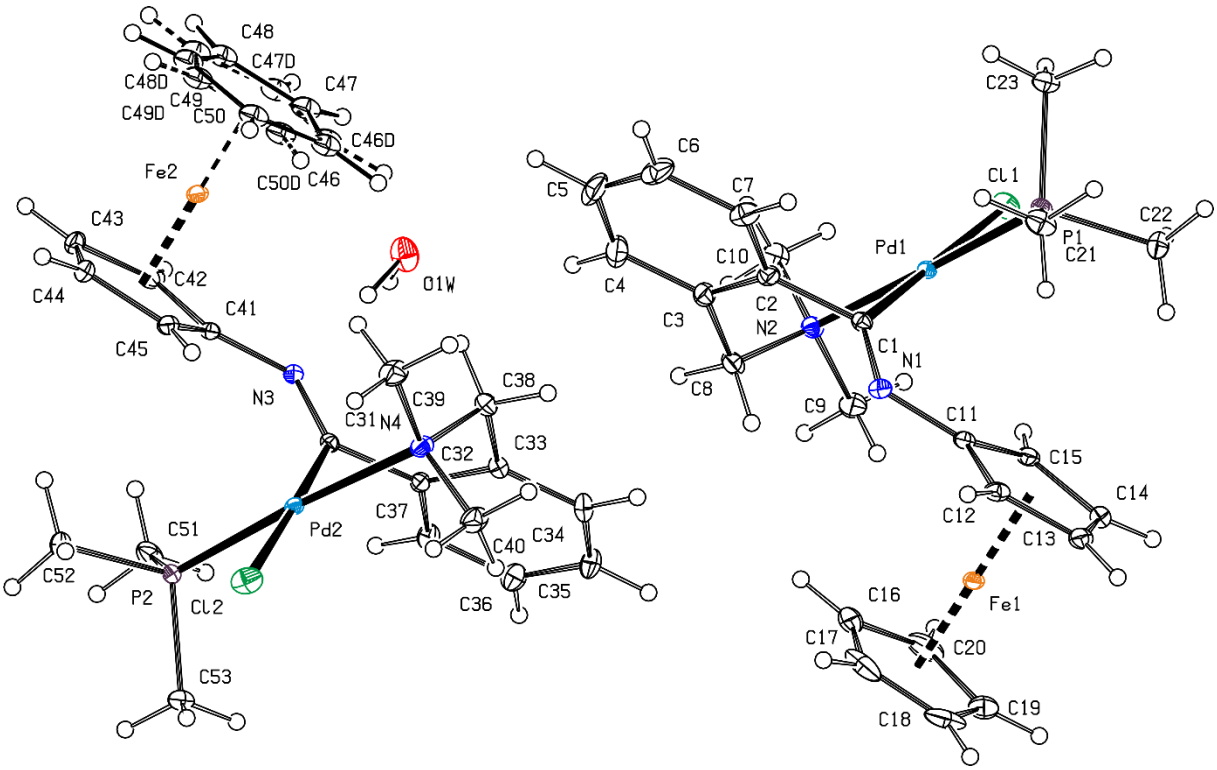


Figure S3 PLATON plot of the molecular structure of **4b**·0.35H_2O showing displacement ellipsoids at the 30% probability level

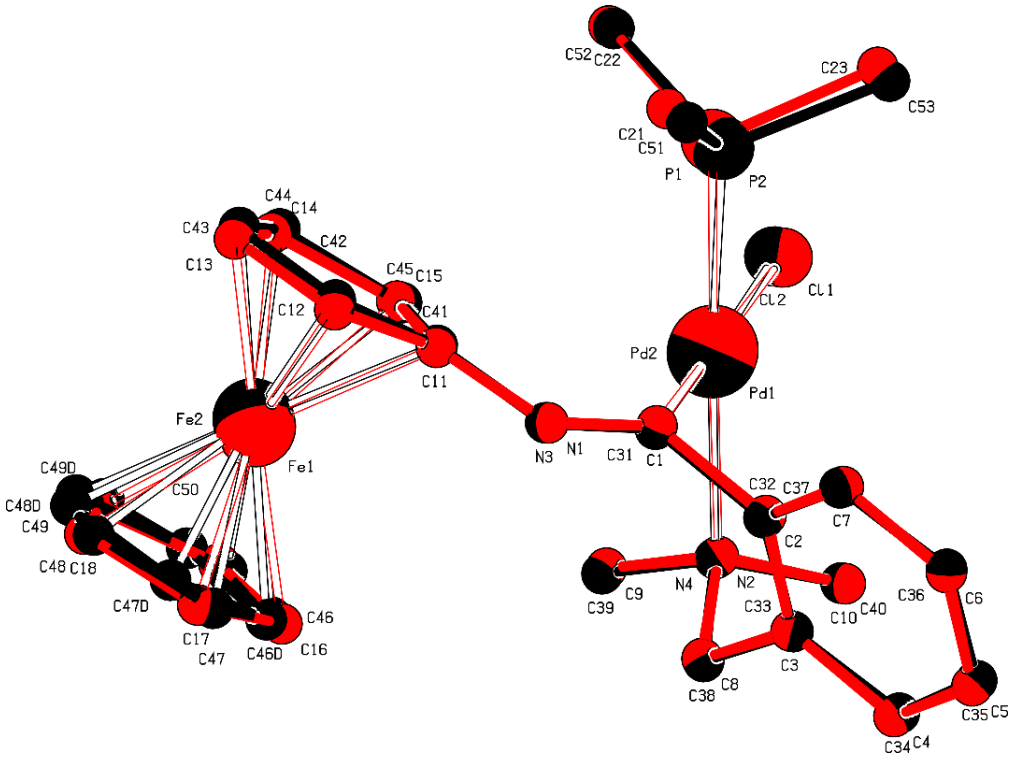


Figure S4 Least-squares overlap of the two crystallographically independent complex molecules in the structure of **4b**·0.35H_2O

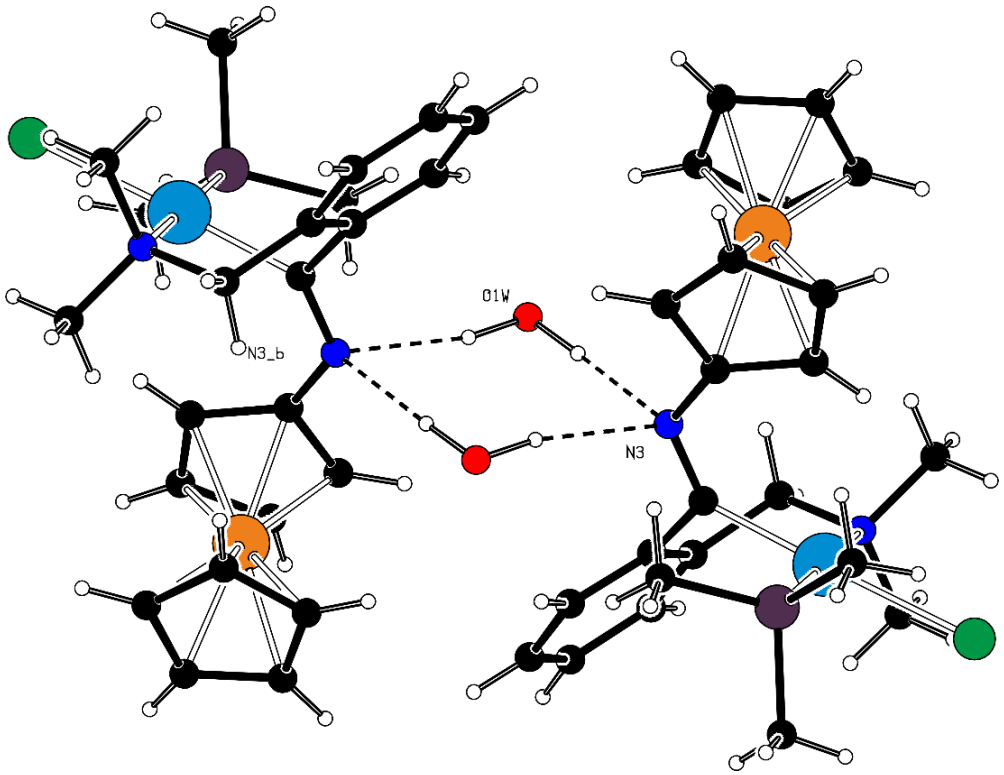


Figure S5 Hydrogen bond interactions in the structure of **4b**·0.35H_2O (for clarity, only one orientation of the disordered cyclopentadienyl ring is shown). Hydrogen bond parameters: O1W-H1W···N3 = 2.921(2) Å, angle at H1W = 177°; O1W-H2W···N3′ = 2.998(2) Å, angle at H2W = 167°.

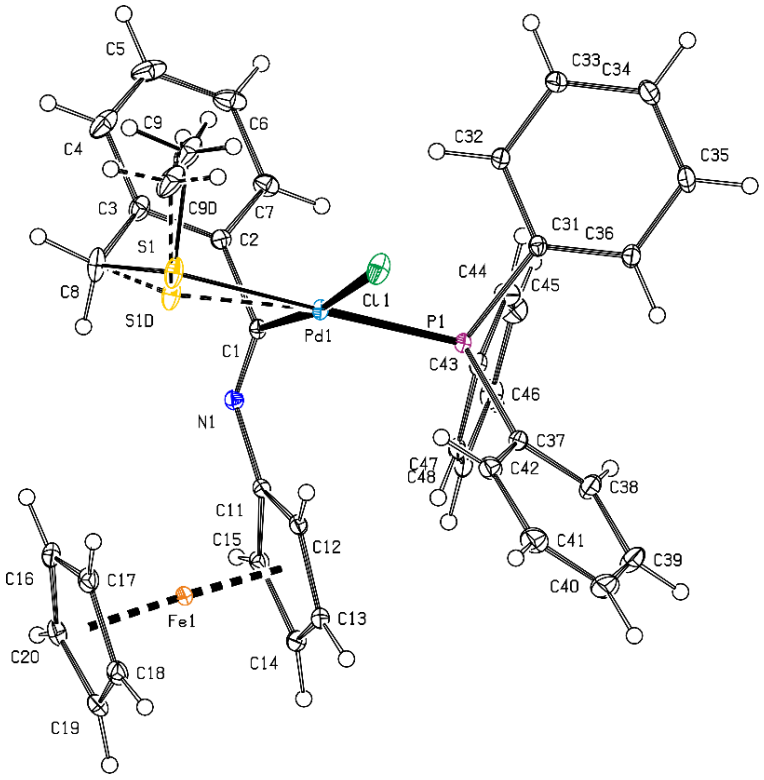


Figure S6 PLATON plot of the molecular structure of **5a** showing displacement ellipsoids at the 30% probability level

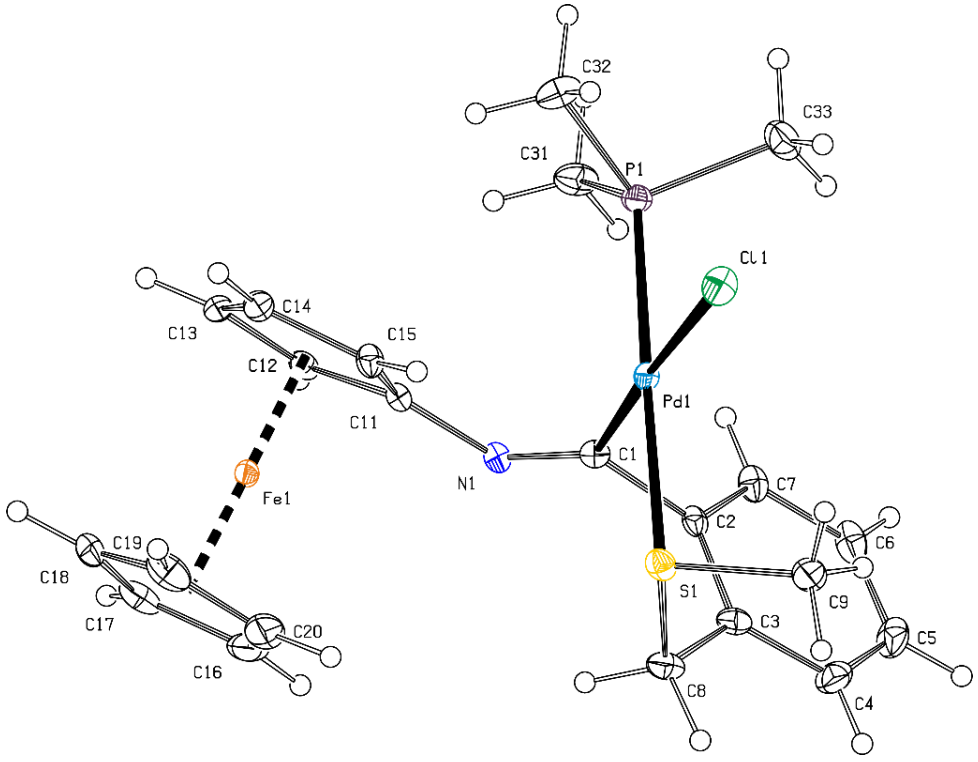


Figure S7 PLATON plot of the molecular structure of **5b** showing displacement ellipsoids at the 30% probability level

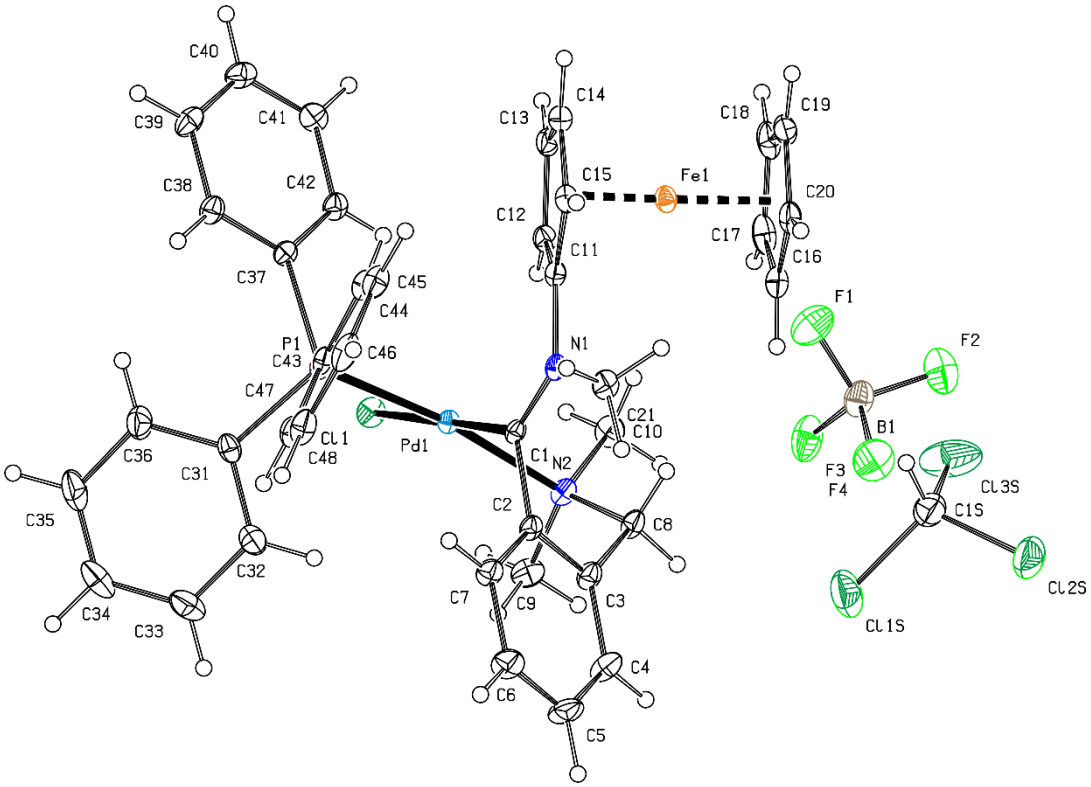


Figure S8 PLATON plot of the molecular structure of **6a**·$CHCl_3$ showing displacement ellipsoids at the 30% probability level

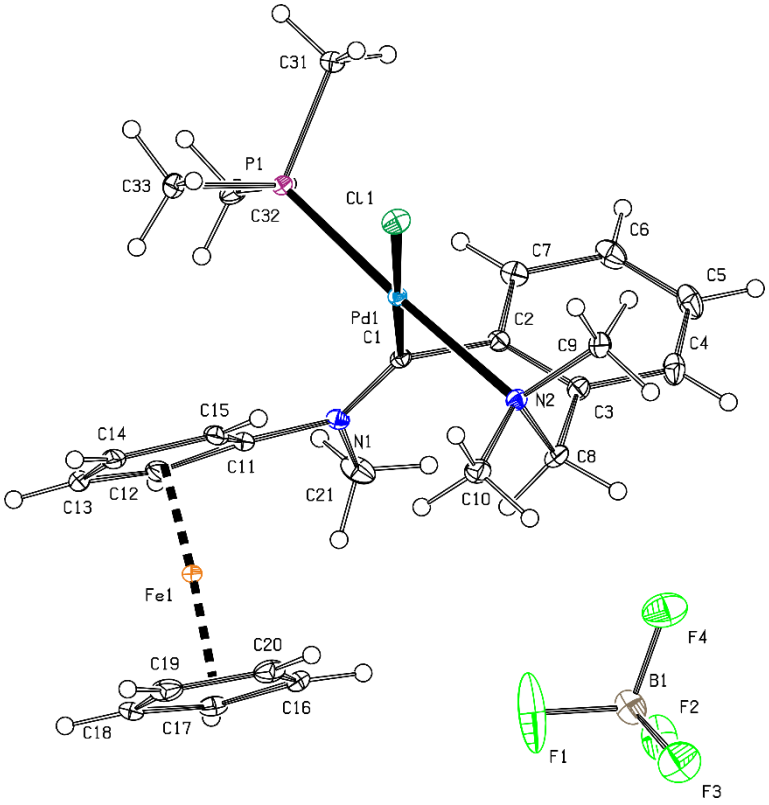


Figure S9 PLATON plot of the molecular structure of **6b** showing displacement ellipsoids at the 30% probability level

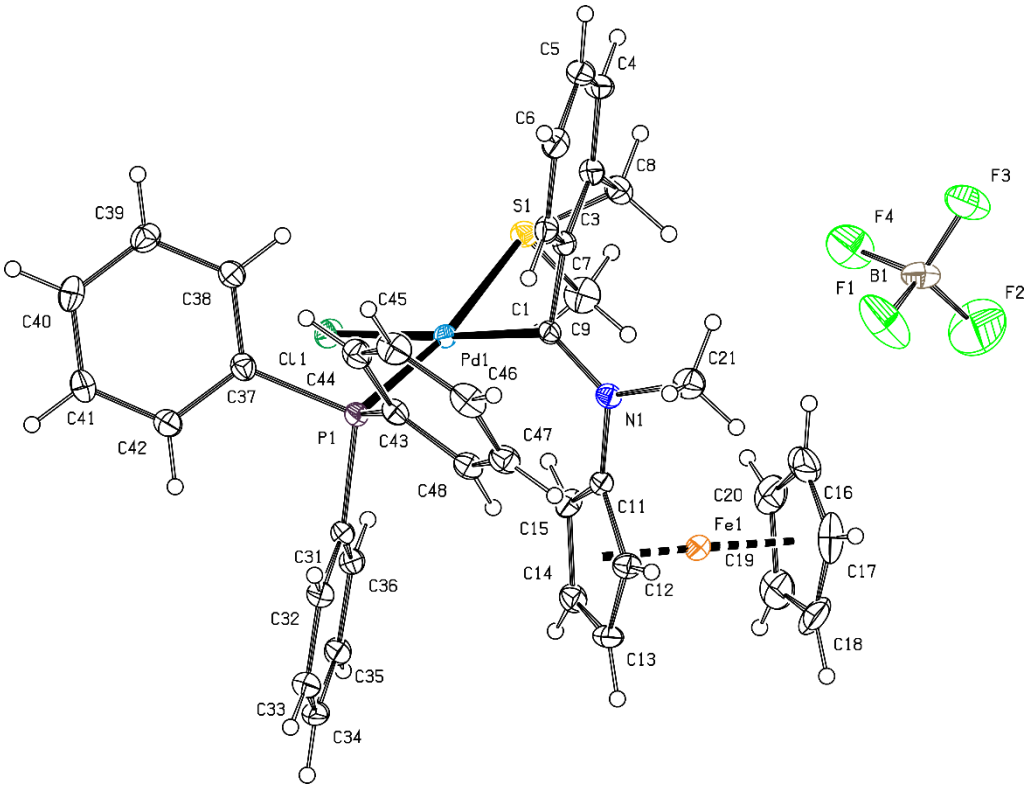


Figure S10 PLATON plot of the molecular structure of **7a** showing displacement ellipsoids at the 30% probability level

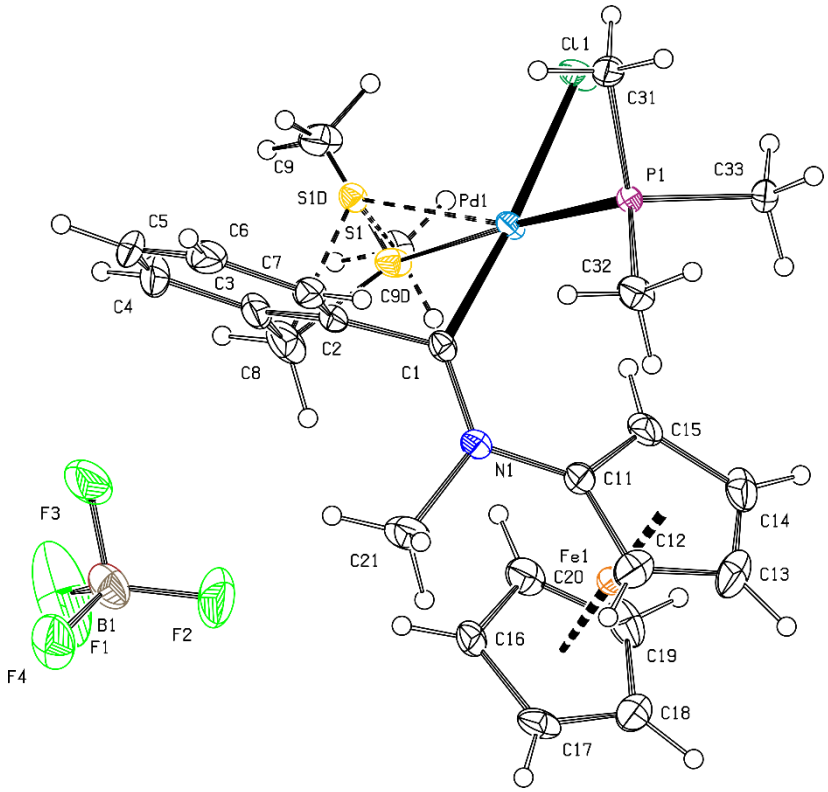


Figure S11 PLATON plot of the molecular structure of **7b** showing displacement ellipsoids at the 30% probability level

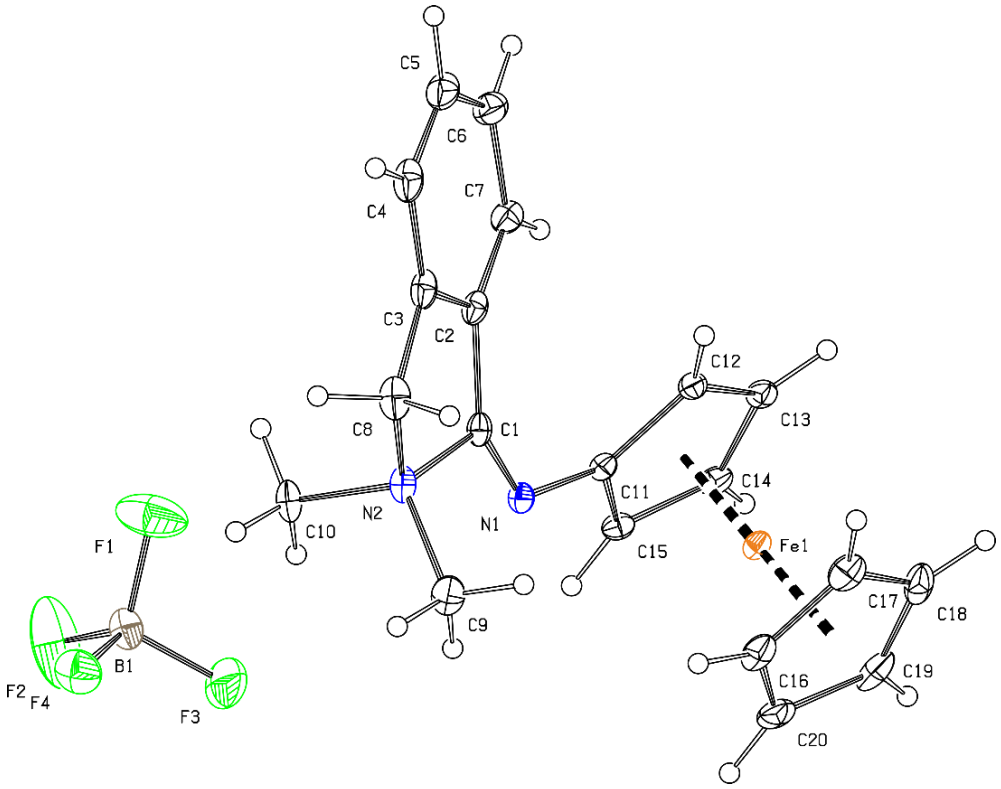


Figure S12 PLATON plot of the molecular structure of **8** showing displacement ellipsoids at the 30% probability level

Cyclic voltammograms for 4-7

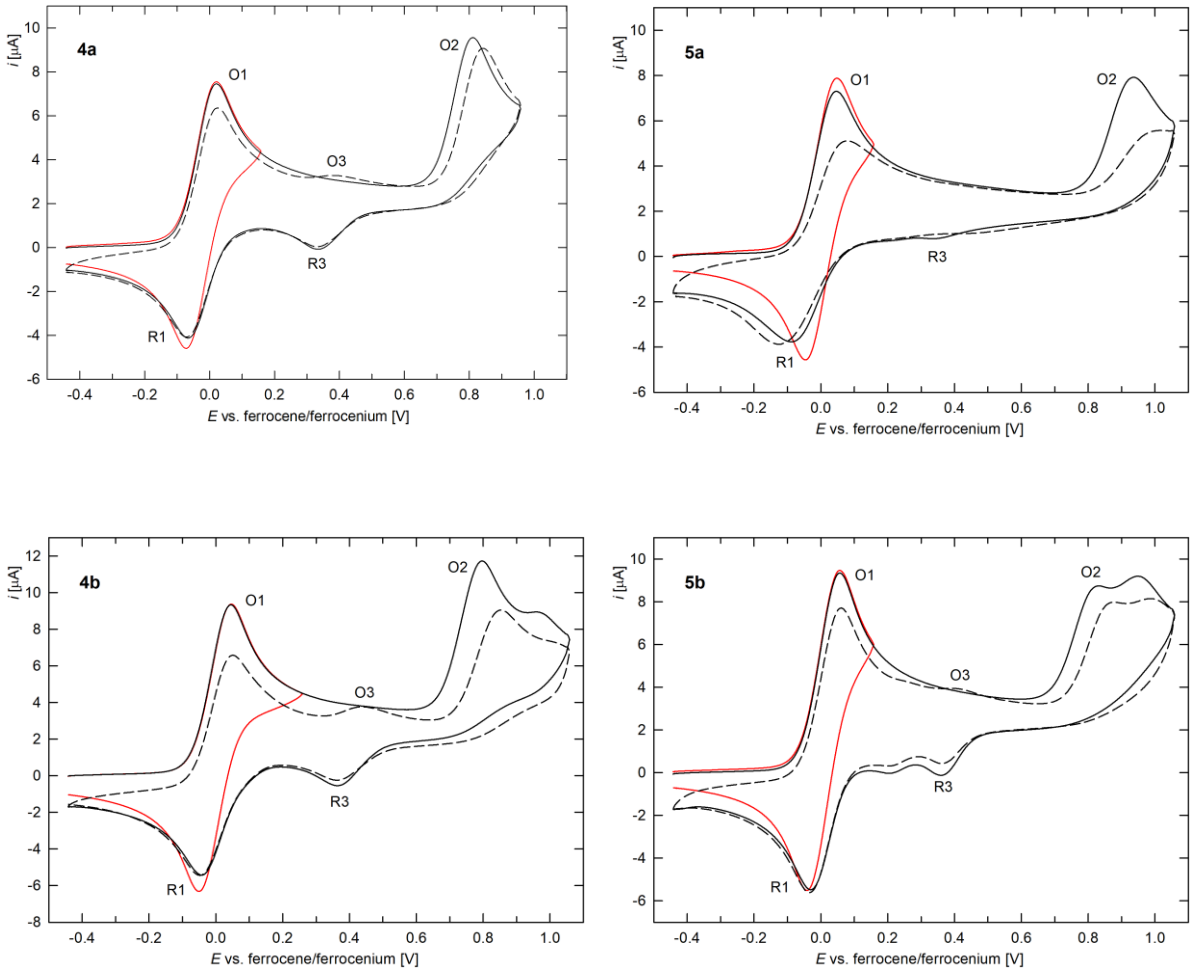


Figure S13 Cyclic voltammograms of the imidoyl complexes **4** and **5** recorded at a glassy carbon electrode in dichloromethane containing $Bu_4N[PF_6]$ as the supporting electrolyte and 100 mV s^{-1} scan rate. The second scan are shown by dashed lines.

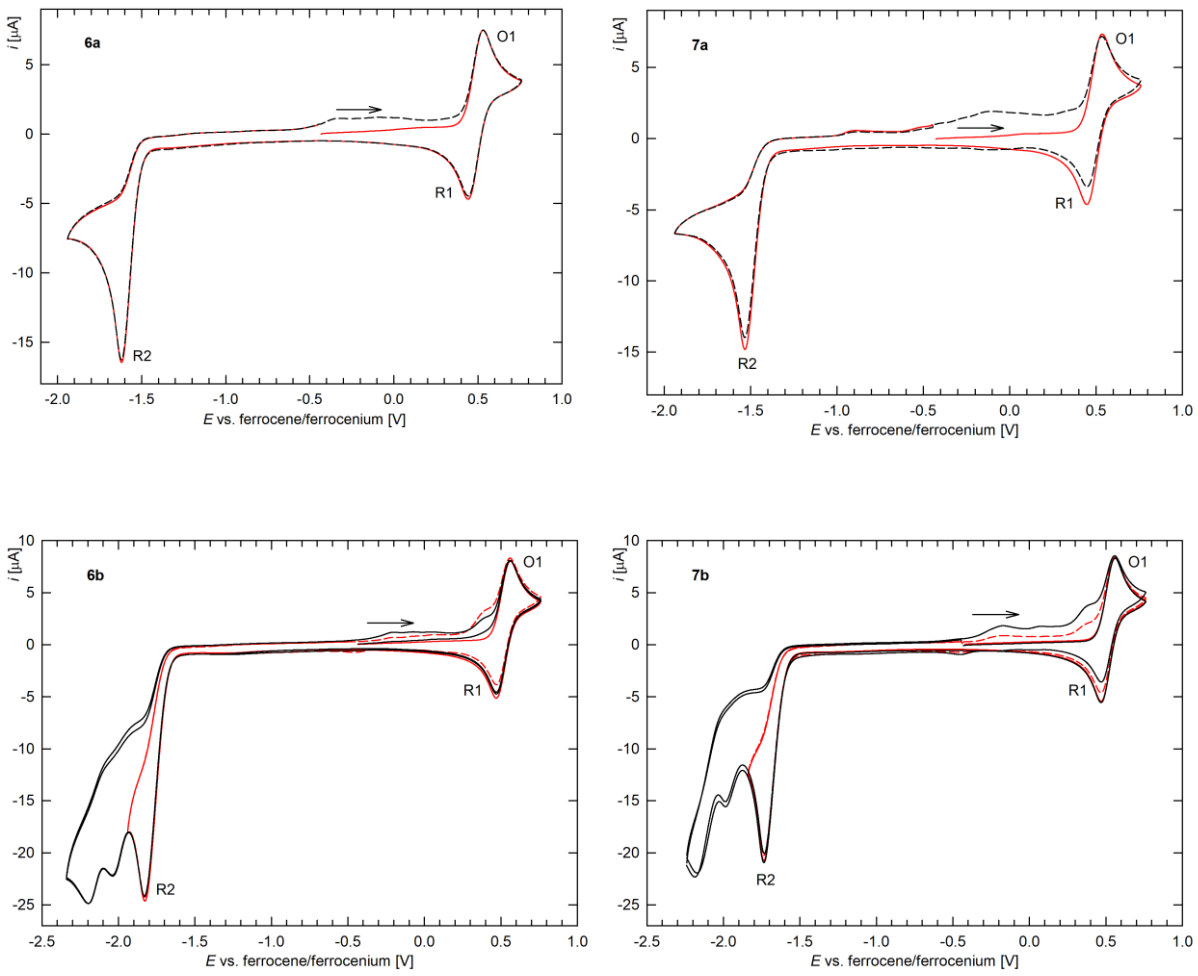


Figure S14 Cyclic voltammograms of the carbene complexes **6** and **7** recorded at a glassy carbon electrode in dichloromethane containing $Bu_4N[PF_6]$ as the supporting electrolyte and 100 mV s^{-1} scan rate. The second scans are shown by dashed lines and initial scan directions are indicated by arrows.

DFT calculations

Theoretical calculations were performed using the Gaussian 16 program package.[8] If available, the geometry optimizations were started from atomic coordinates determined by X-ray diffraction analysis. All the calculations were done using B3LYP[9] density functional in conjunction with the def2-TZVPP[10] basis set with added Grimme's D3 dispersion correction with Becke-Johnson damping.[11] Stuttgart effective core potential[12] was used for palladium. Orbital composition analysis based on the Natural Atomic Orbitals (NAO)[13] was performed using the Multiwfn software package (version 3.8).[14] Molecular orbitals were visualized using the Avogadro programme.[15] Intrinsic bond orbital (IBO) analysis and visualization of the obtained orbitals were performed using the IboView software.[16]

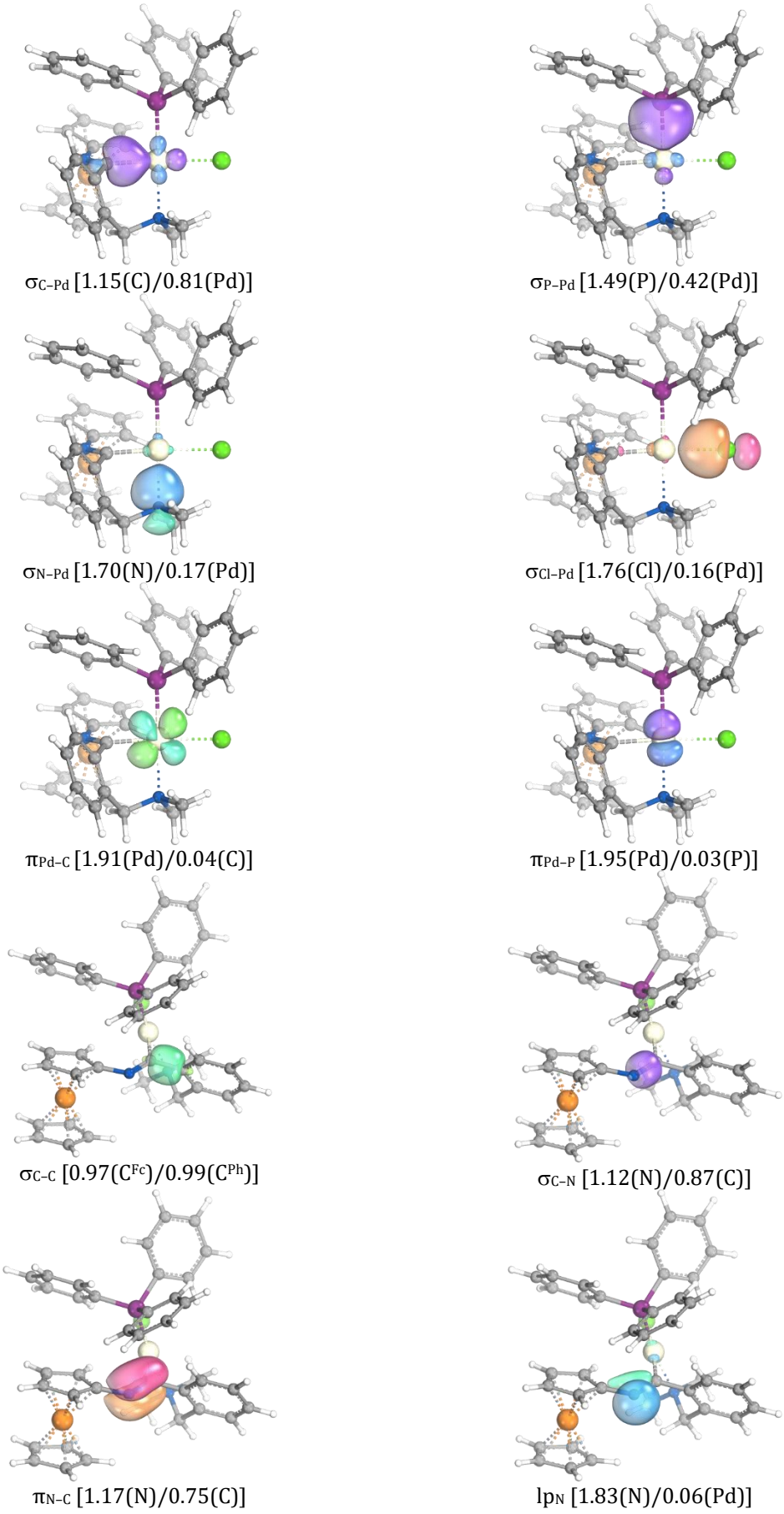
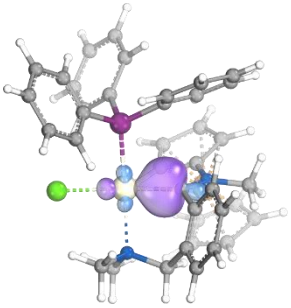
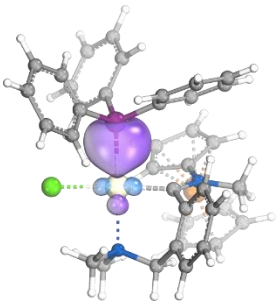


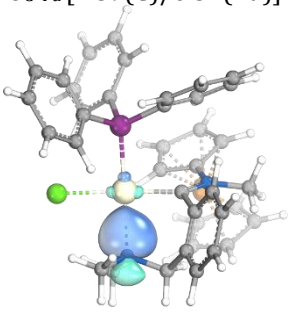
Figure 15 Selected intrinsic bond orbitals (IBOs) of **4a** (values in parentheses indicate the fraction of σ and π bonding electrons assigned to the individual atoms; lp = lone electron pair)



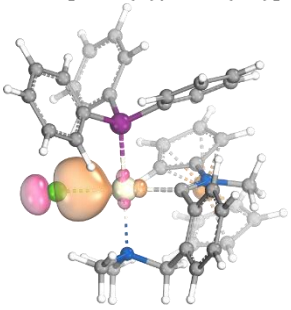
σ_{C-Pd} [1.39(C)/0.52(Pd)]



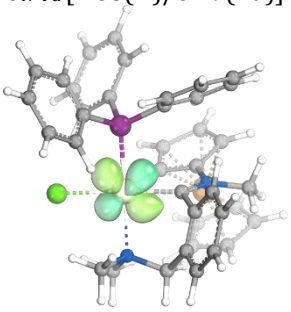
σ_{P-Pd} [1.39(P)/0.55(Pd)]



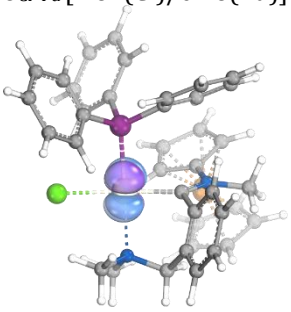
σ_{N-Pd} [1.68(N)/0.19(Pd)]



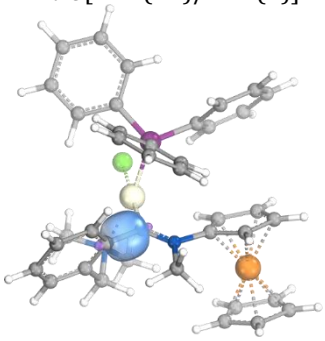
σ_{Cl-Pd} [1.67(Cl)/0.26(Pd)]



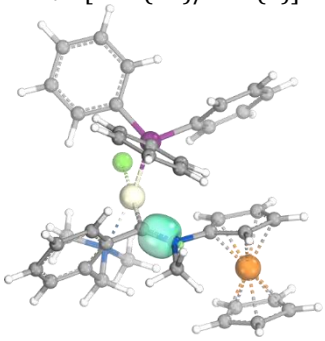
π_{Pd-C} [1.88(Pd)/0.07(C)]



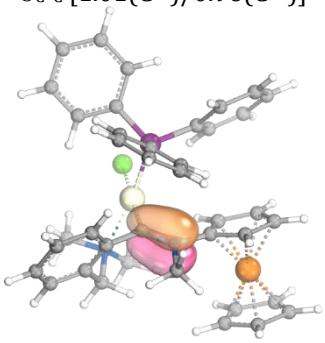
π_{Pd-P} [1.96(Pd)/0.02(P)]



σ_{C-C} [1.01(C^{Fc})/0.96(C^{Ph})]



σ_{C-N} [1.17(N)/0.82(C)]



π_{N-C} [1.37(N)/0.56(C)]

Figure 16 Selected intrinsic bond orbitals (IBOs) of **6a** (values in parentheses indicate the fraction of σ and π bonding electrons assigned to the individual atoms)

Copies of the NMR and MS spectra

(Note: solvent signals in the NMR spectra are denoted by an asterisk.)

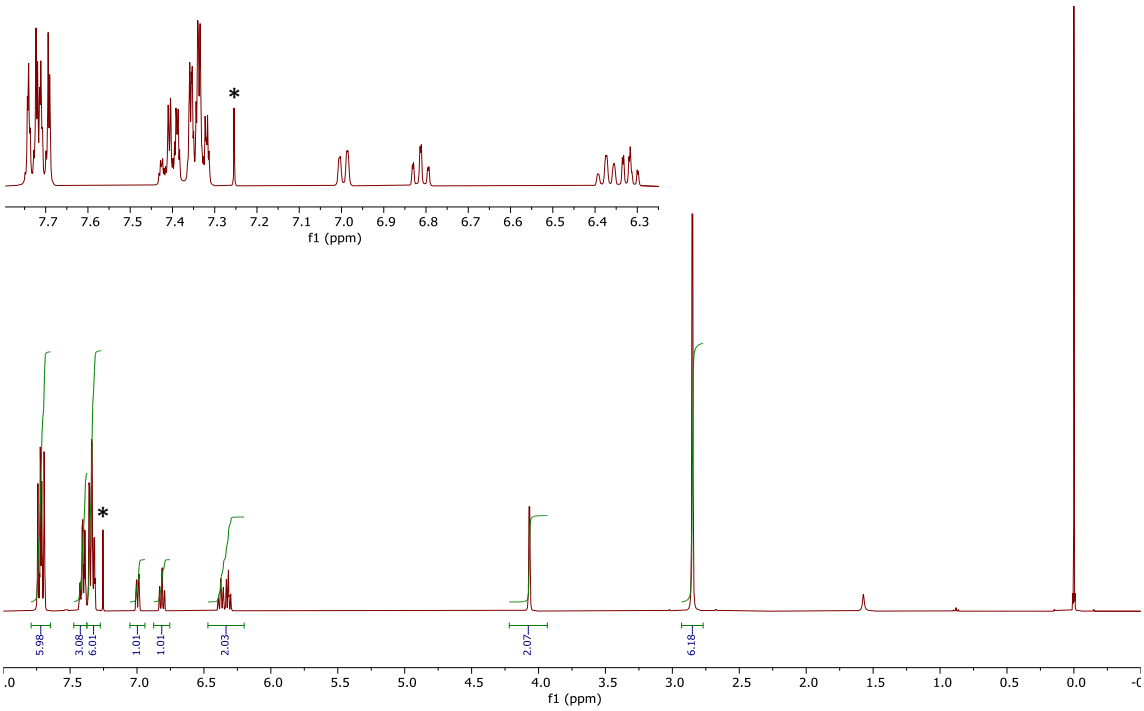


Figure S17 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1a**

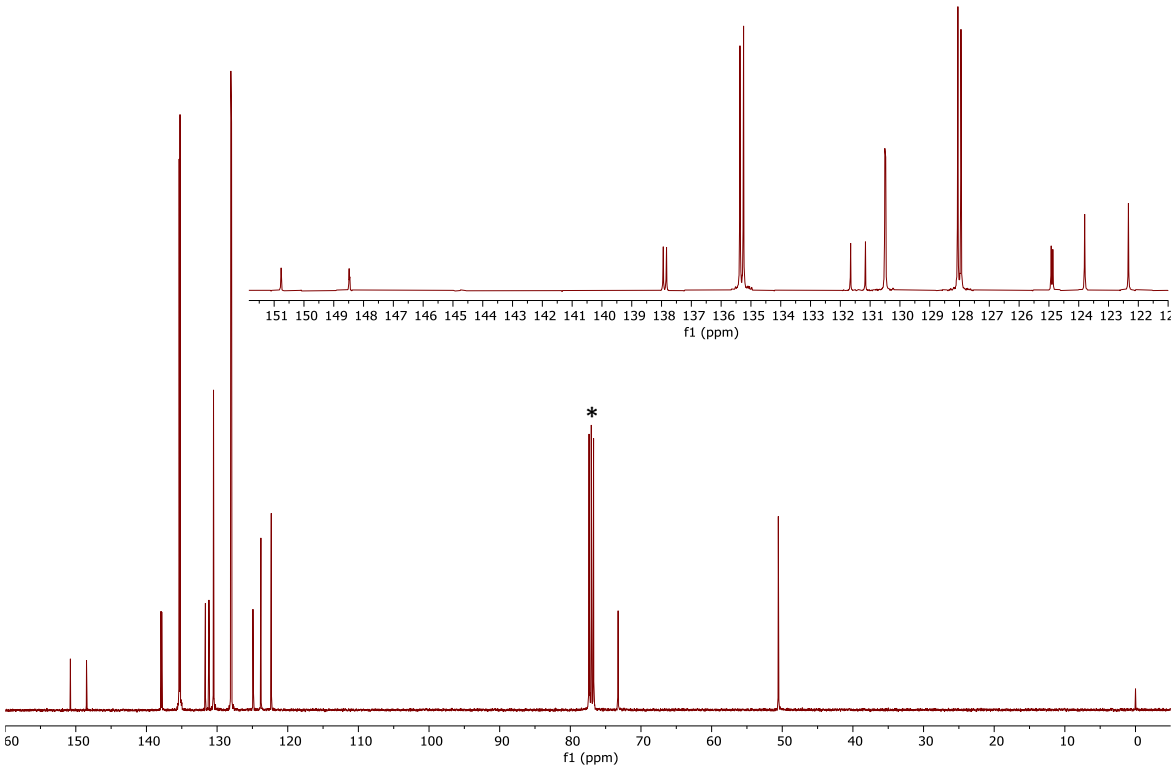


Figure S18 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **1a**

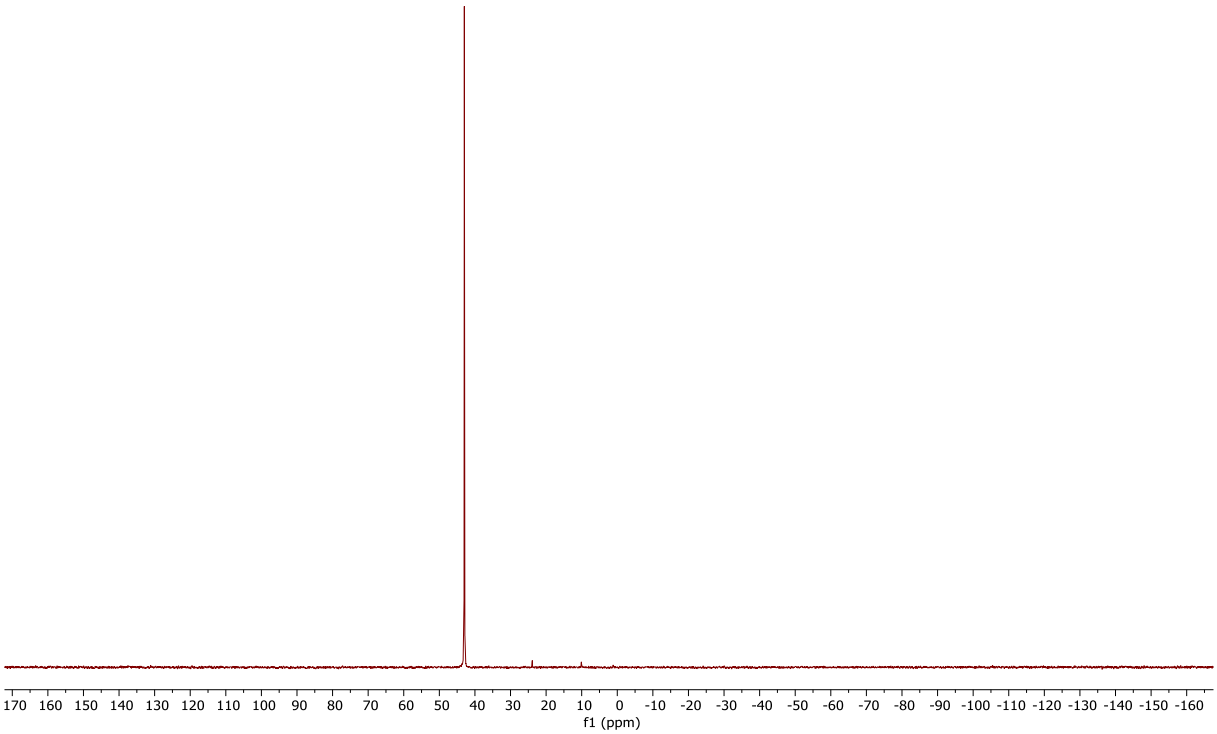


Figure S19 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of **1a**

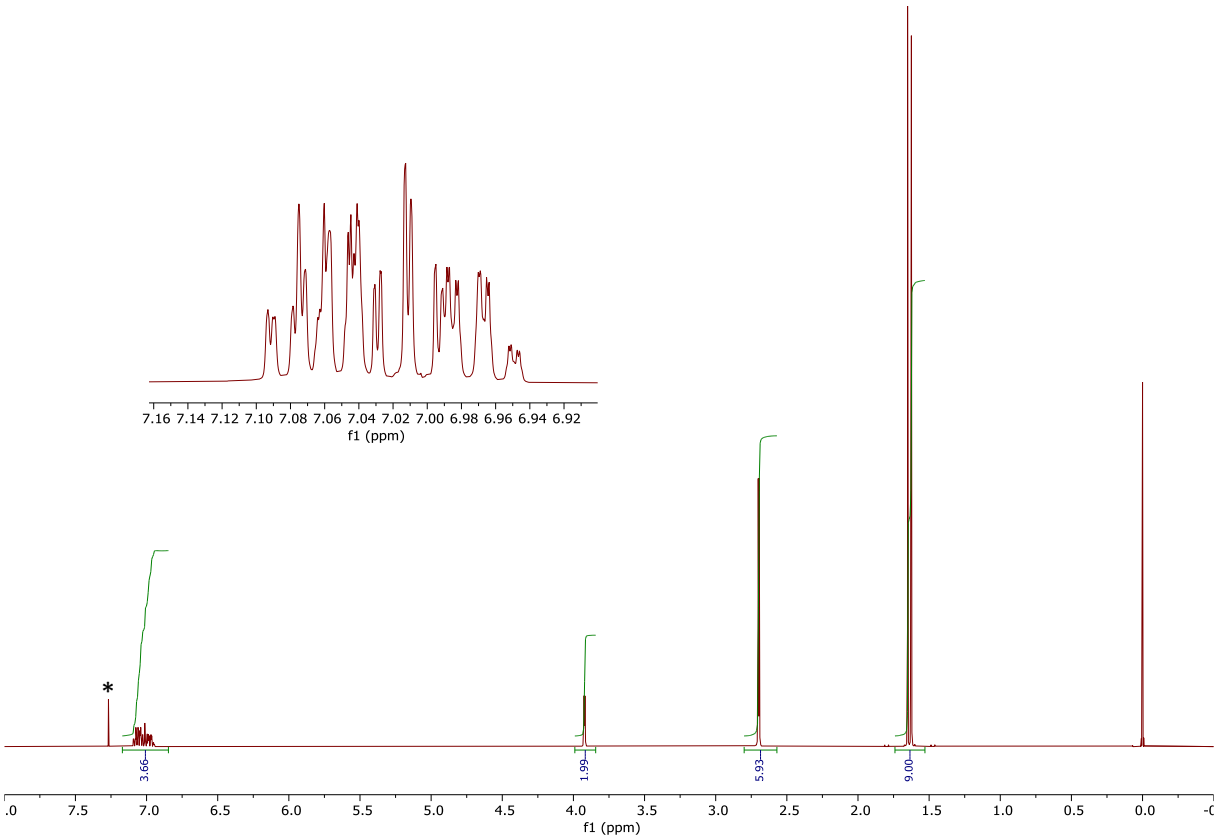


Figure S20 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1b**

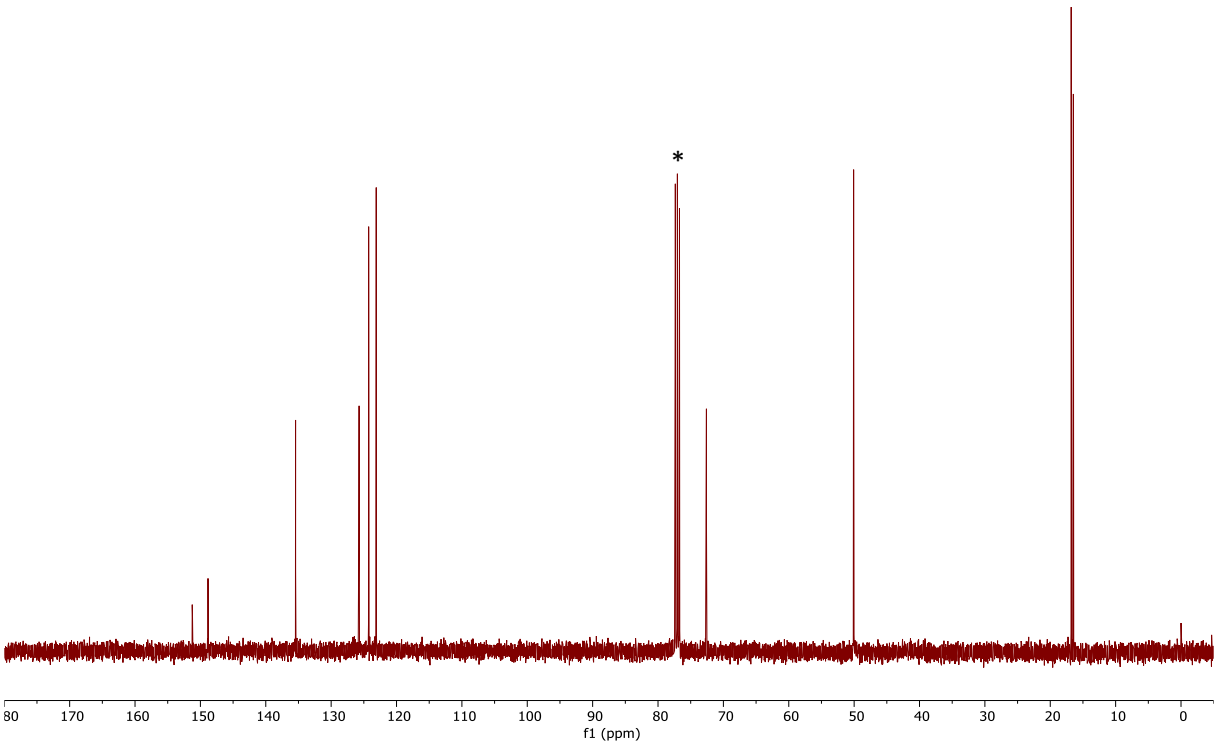


Figure S21 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **1b**

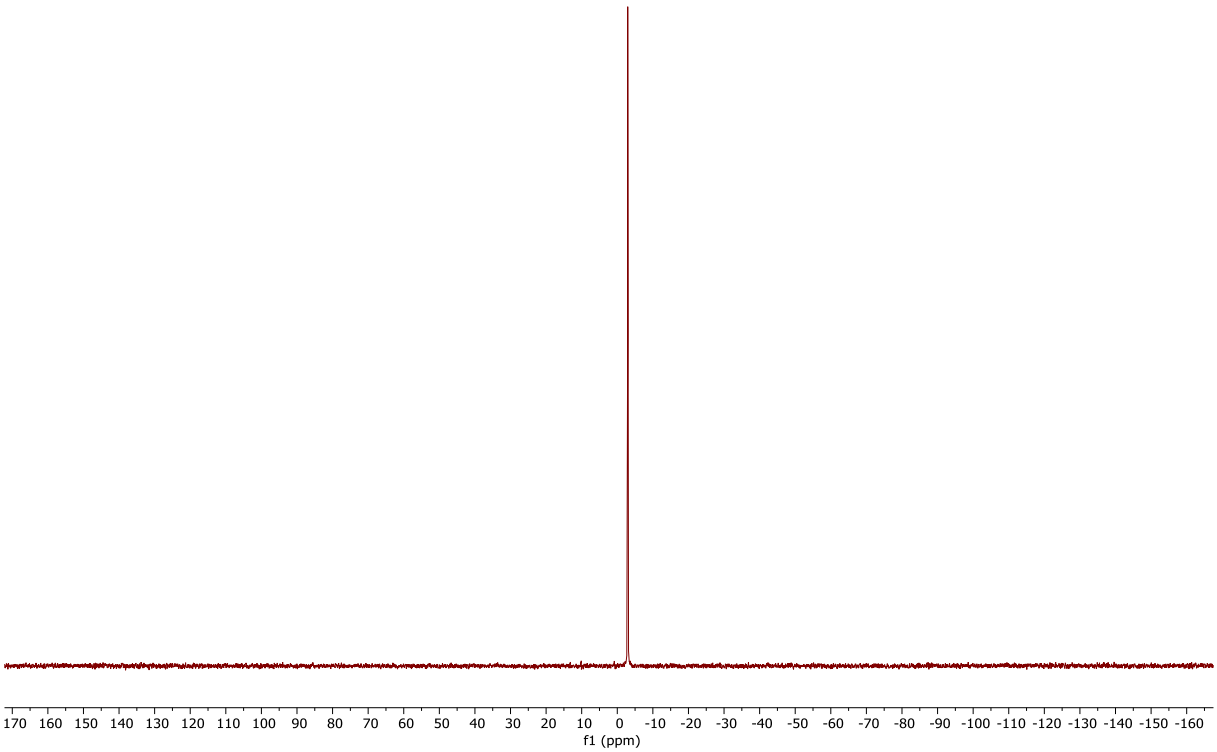


Figure S22 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of **1b**

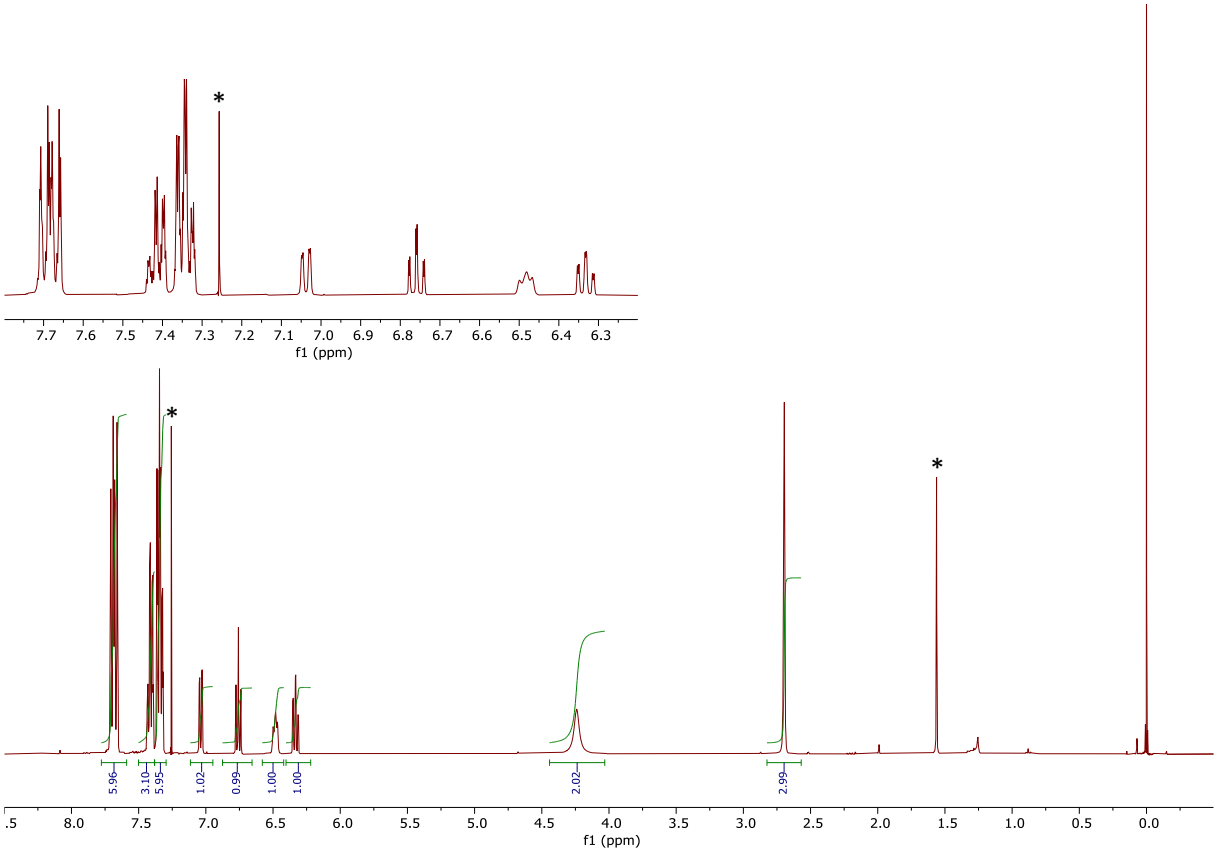


Figure S23 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2a**

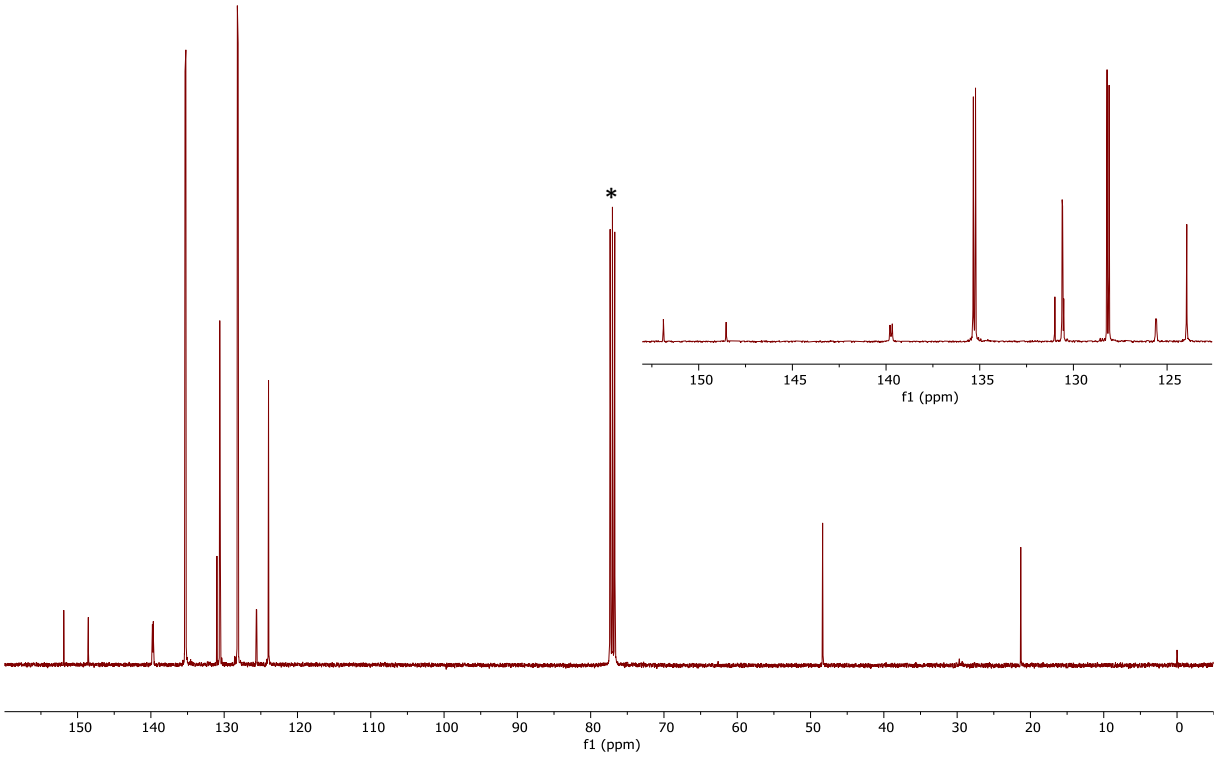


Figure S24 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **2a**

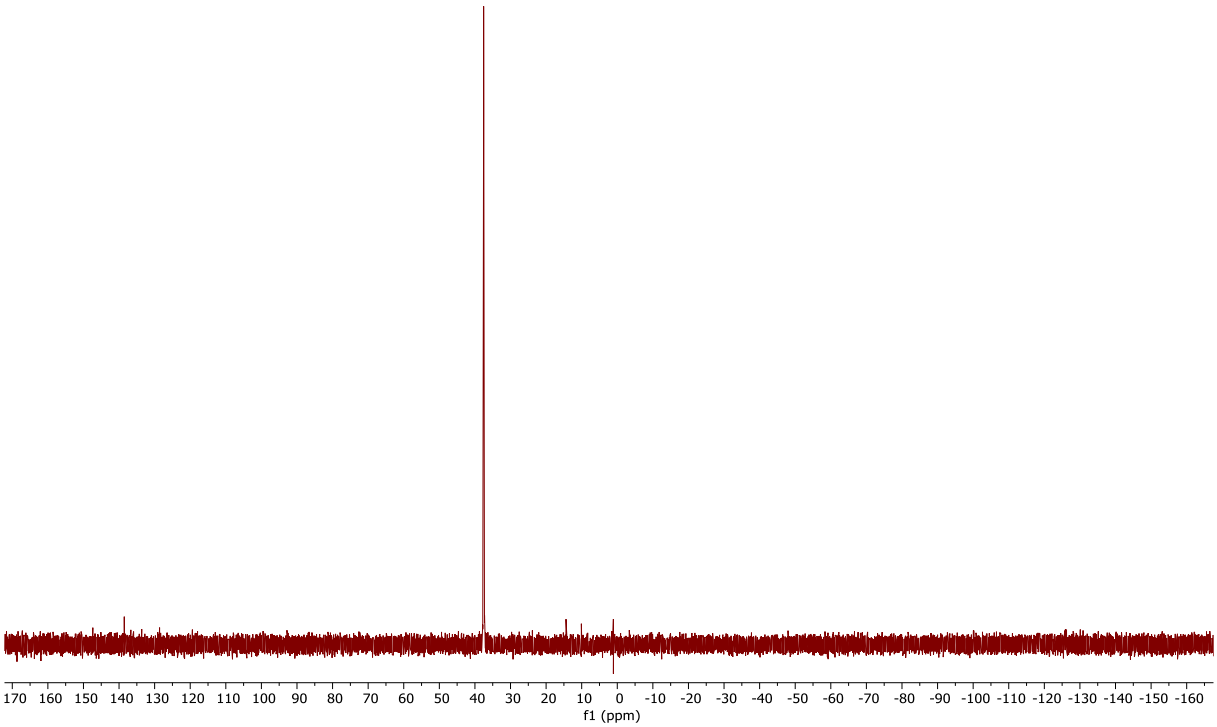


Figure S25 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of **2a**

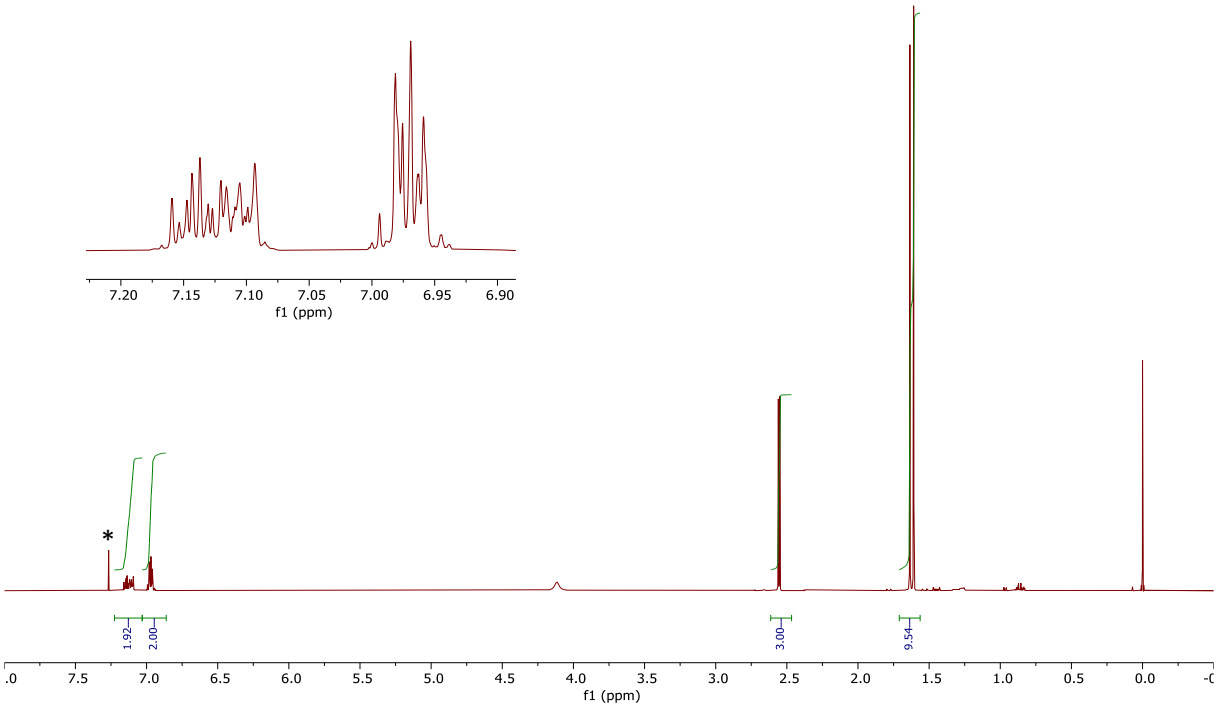


Figure S26 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2b**

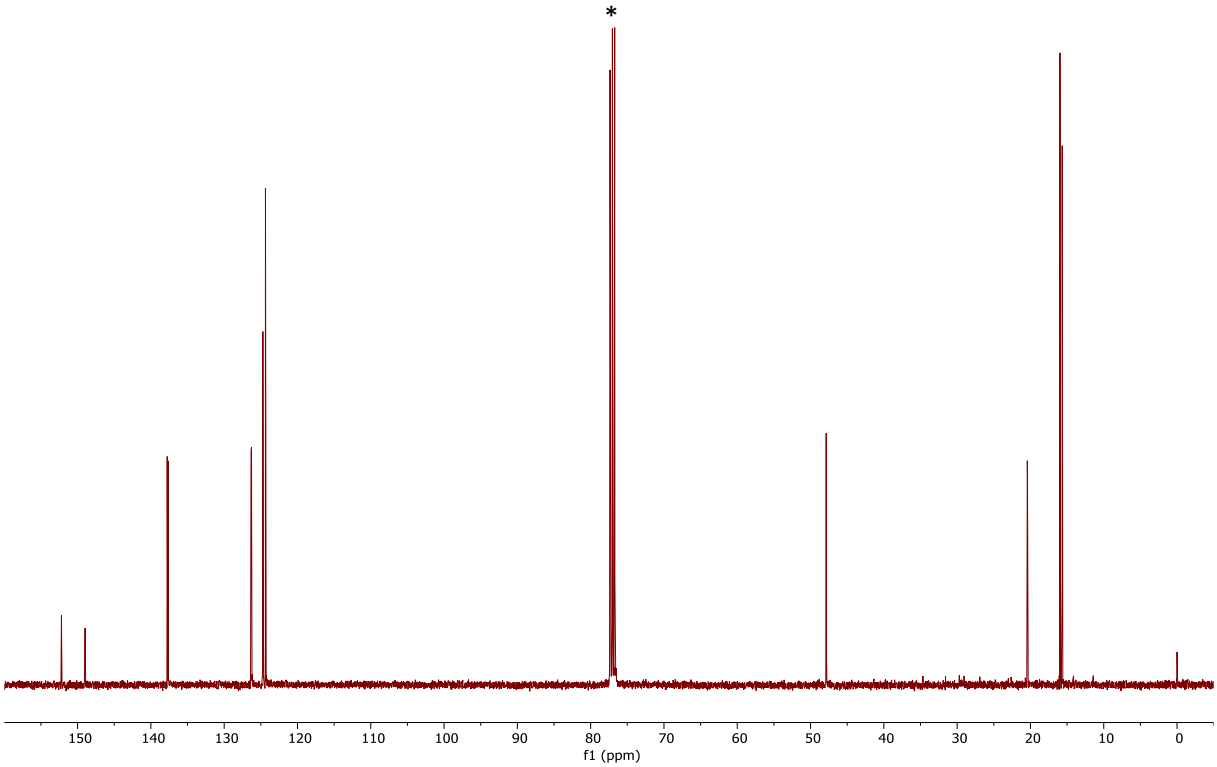


Figure S27 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **2b**

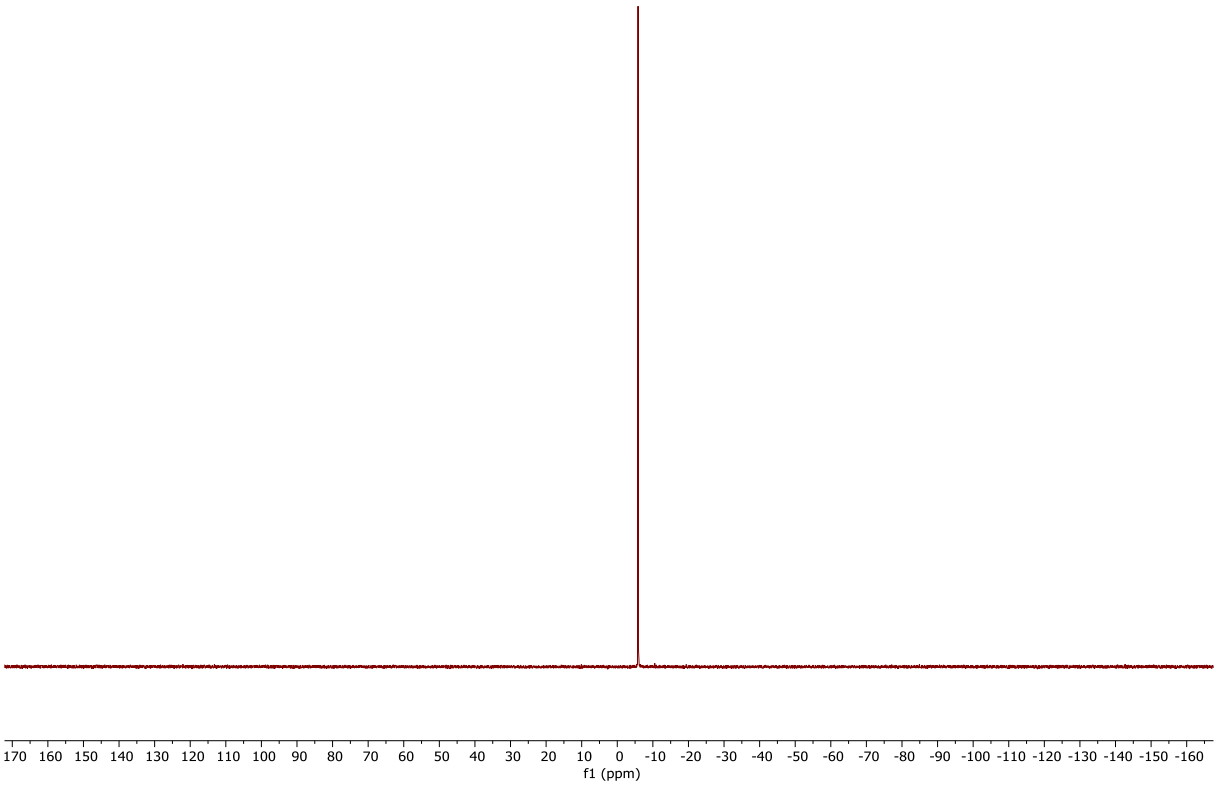


Figure S28 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of **2b**

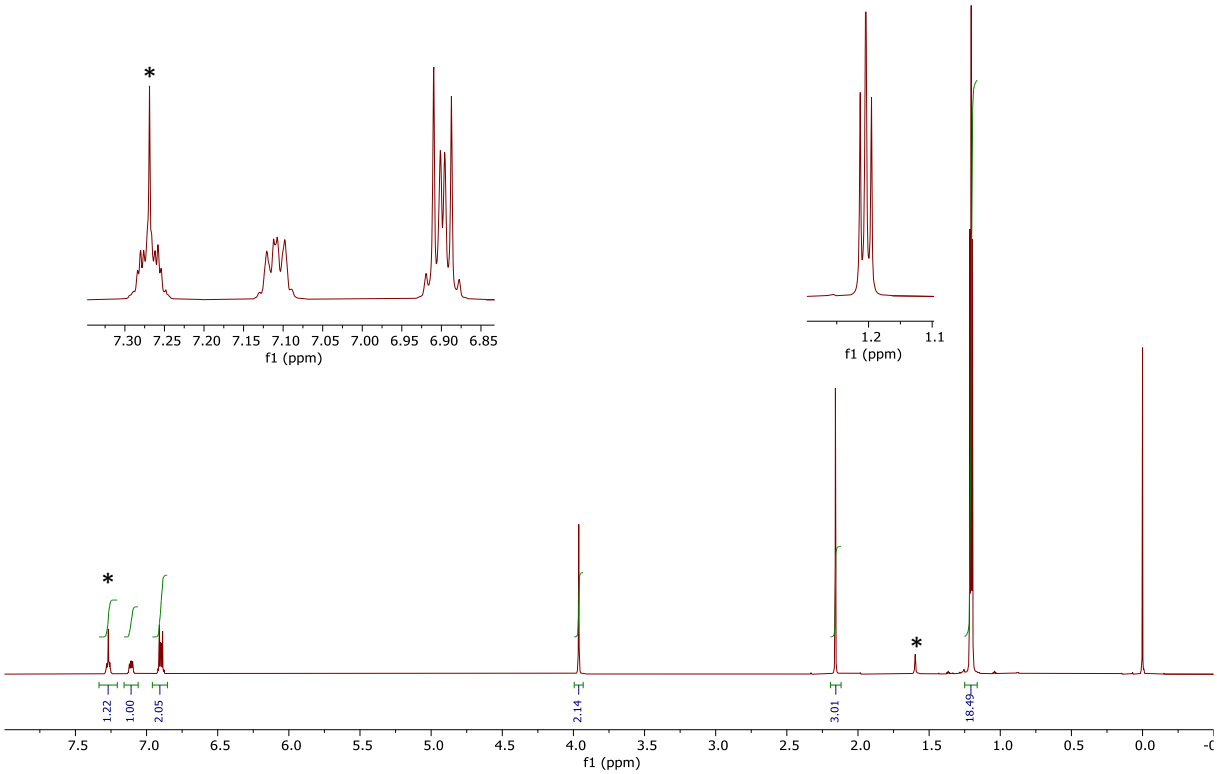


Figure S29 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of *trans*-**3**

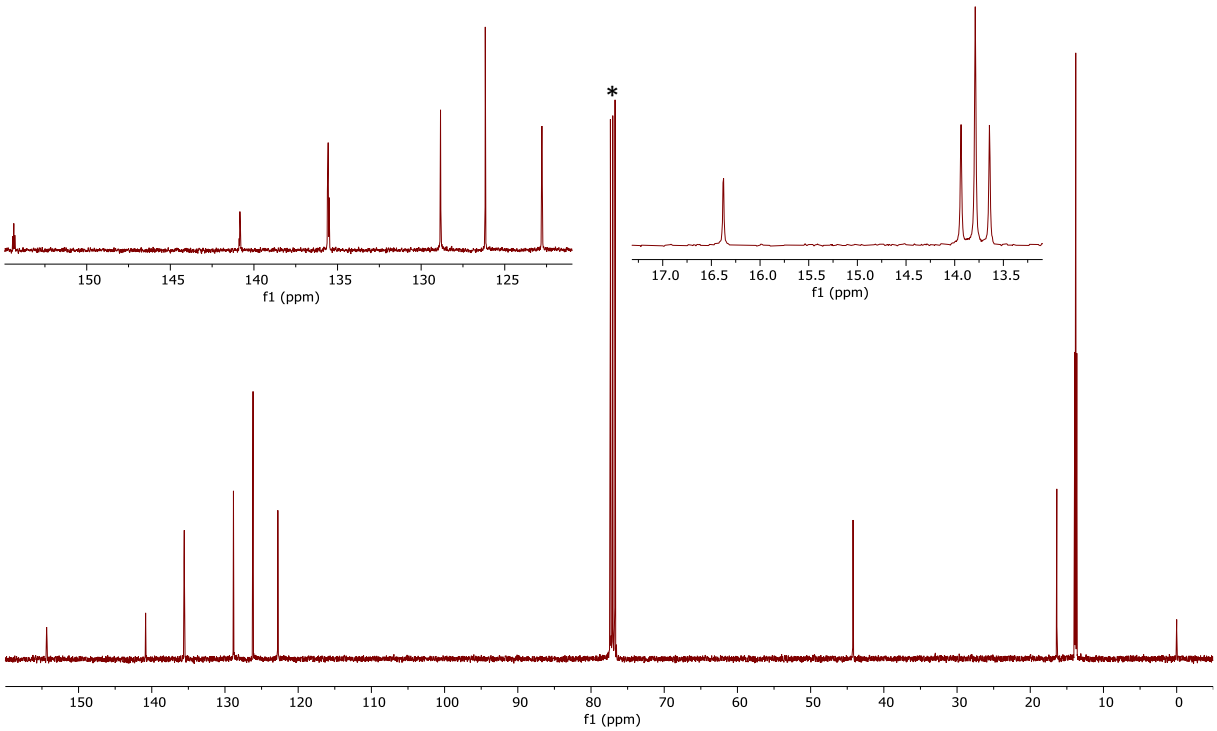


Figure S30 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of *trans*-**3**

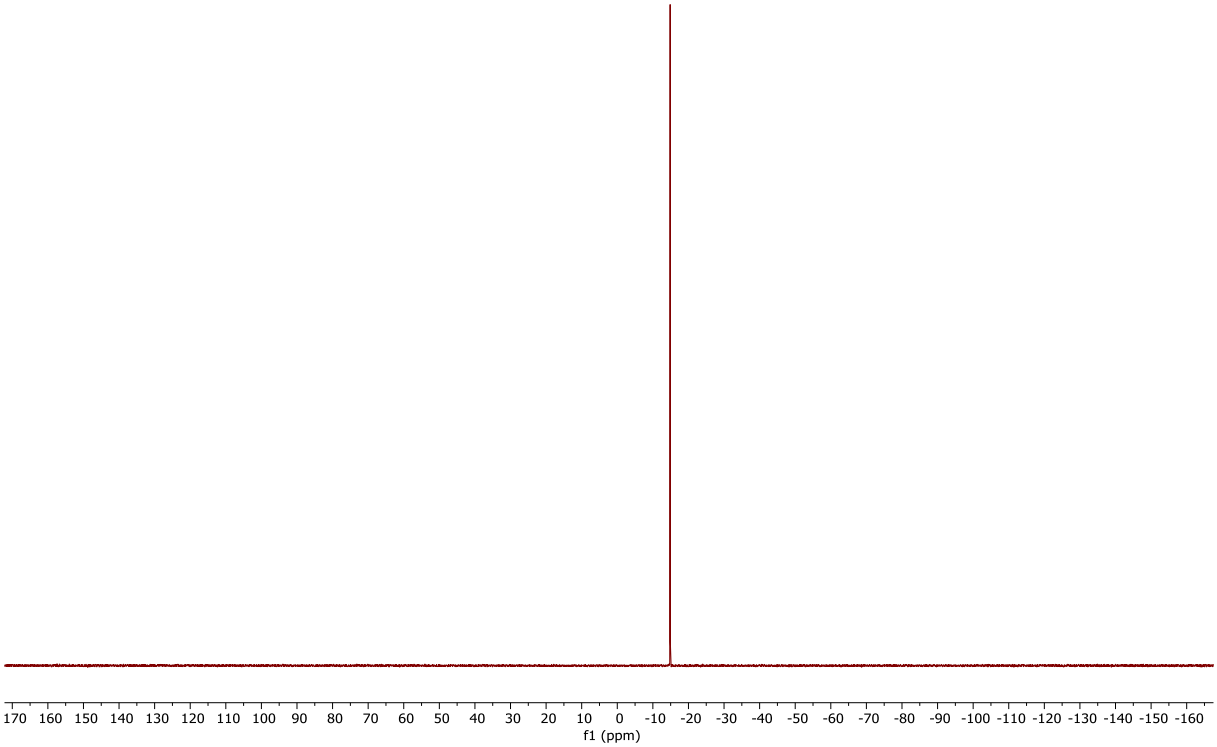


Figure S31 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of *trans*-**3**

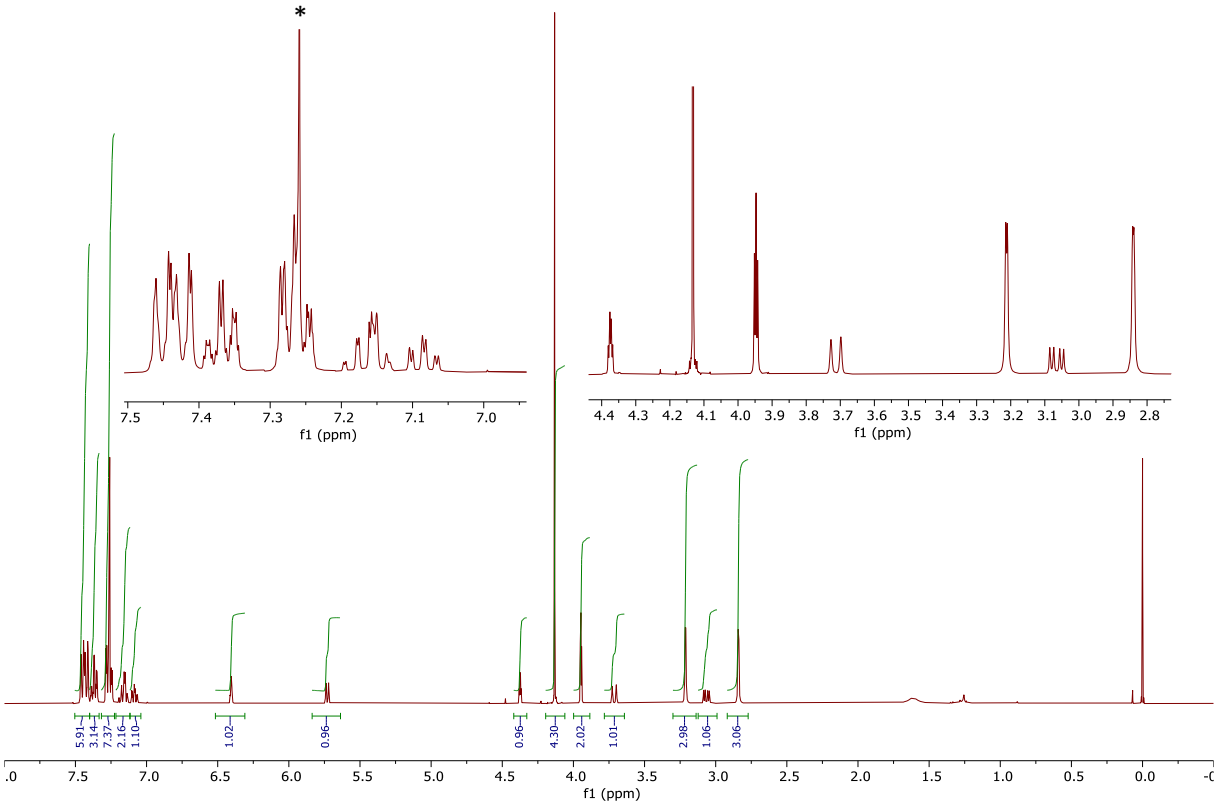


Figure S32 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4a**

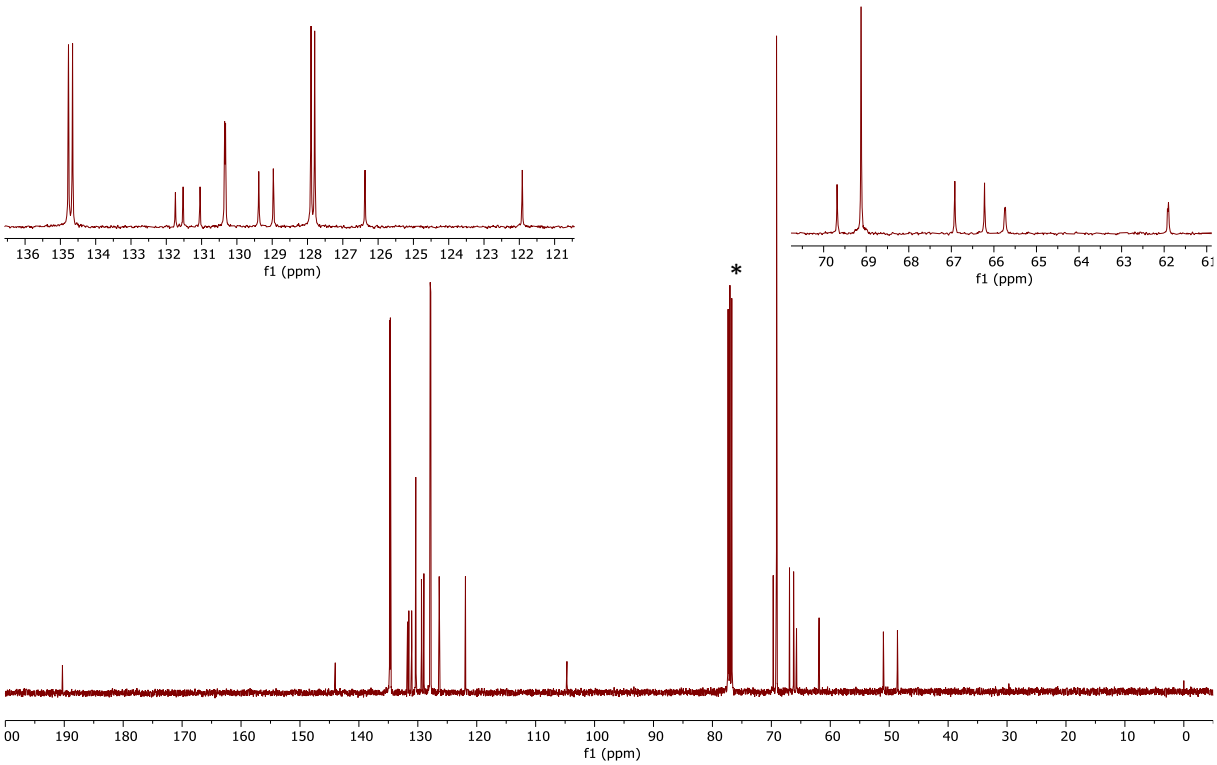


Figure S33 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **4a**

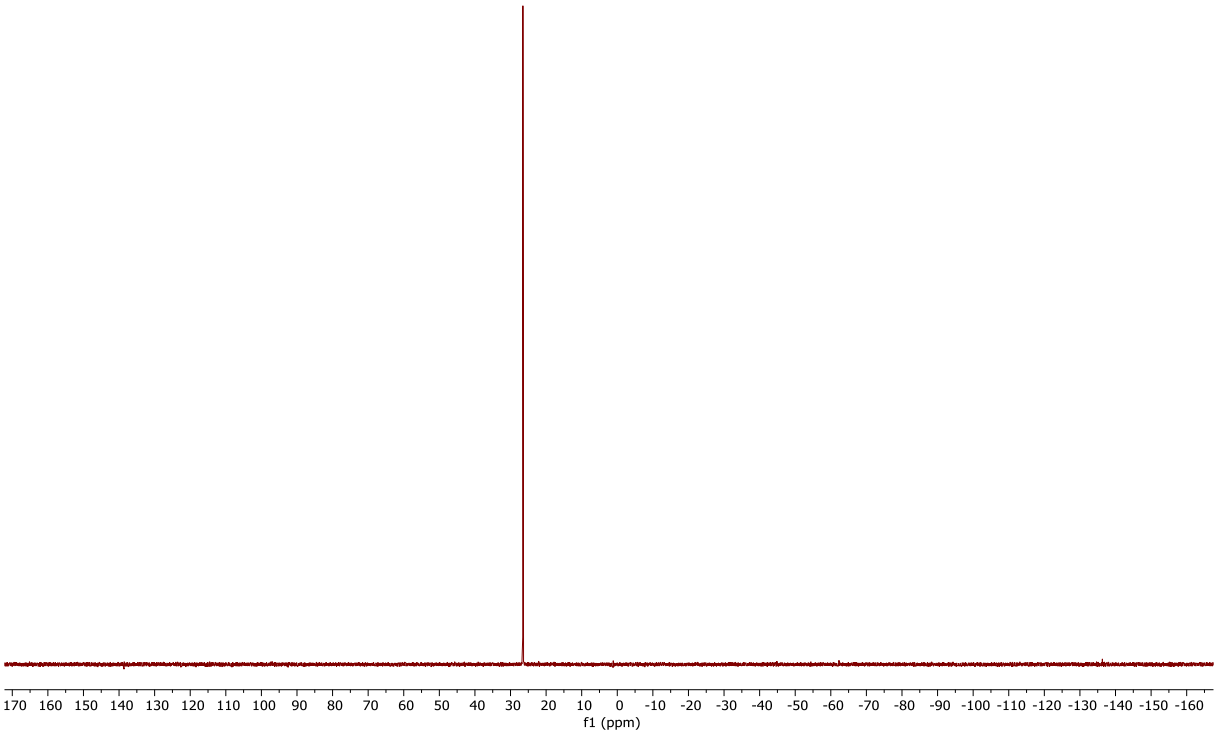


Figure S34 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of **4a**

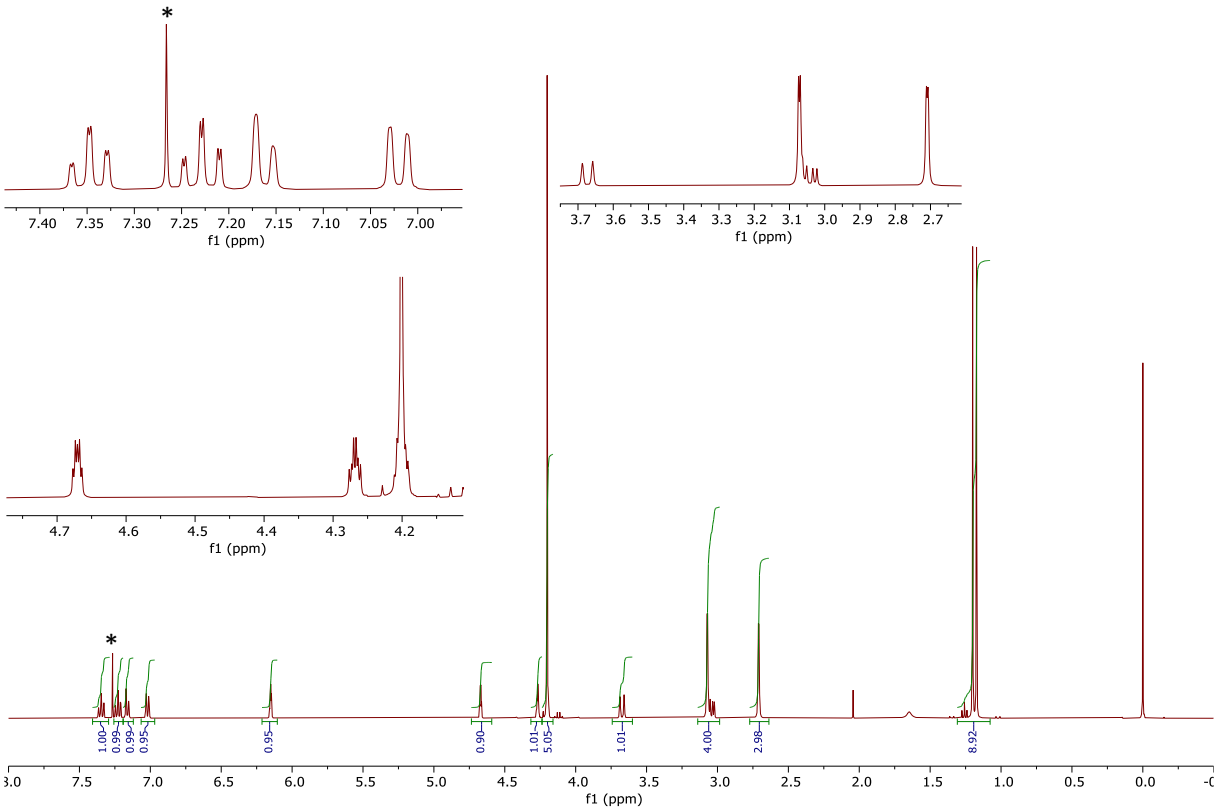


Figure S35 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4b**

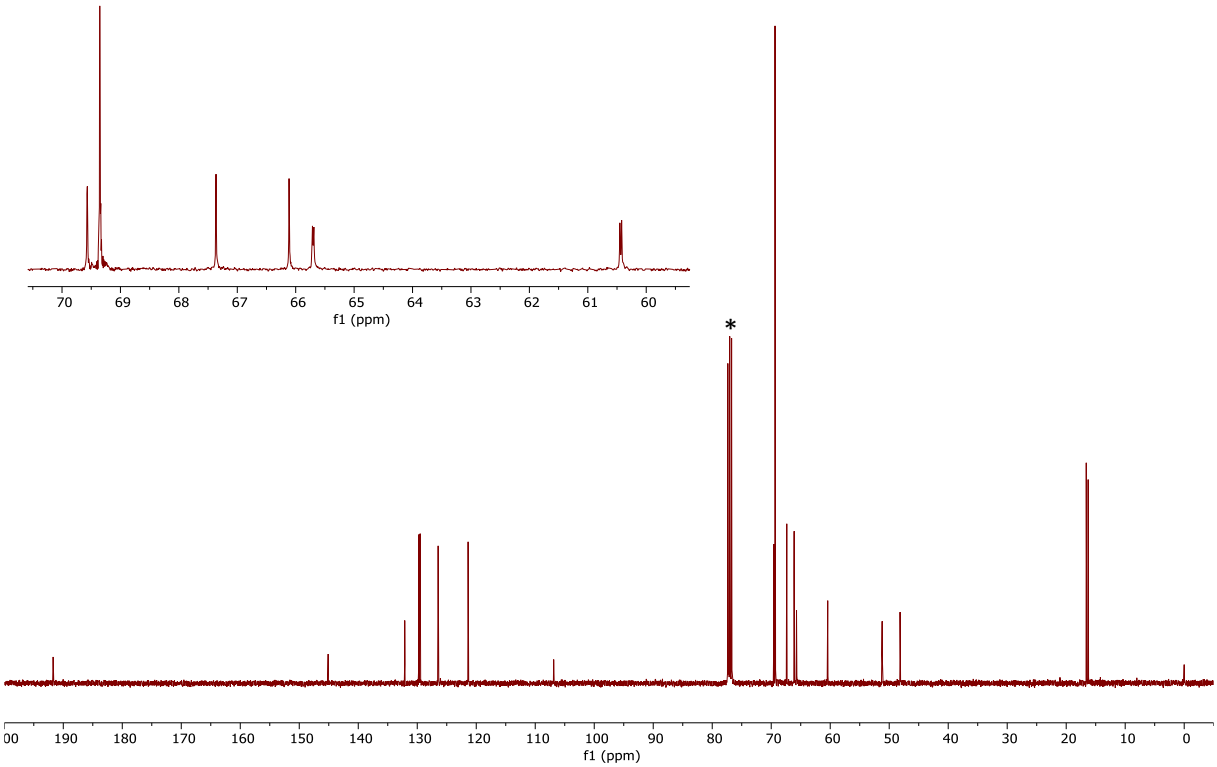


Figure S36 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **4b**

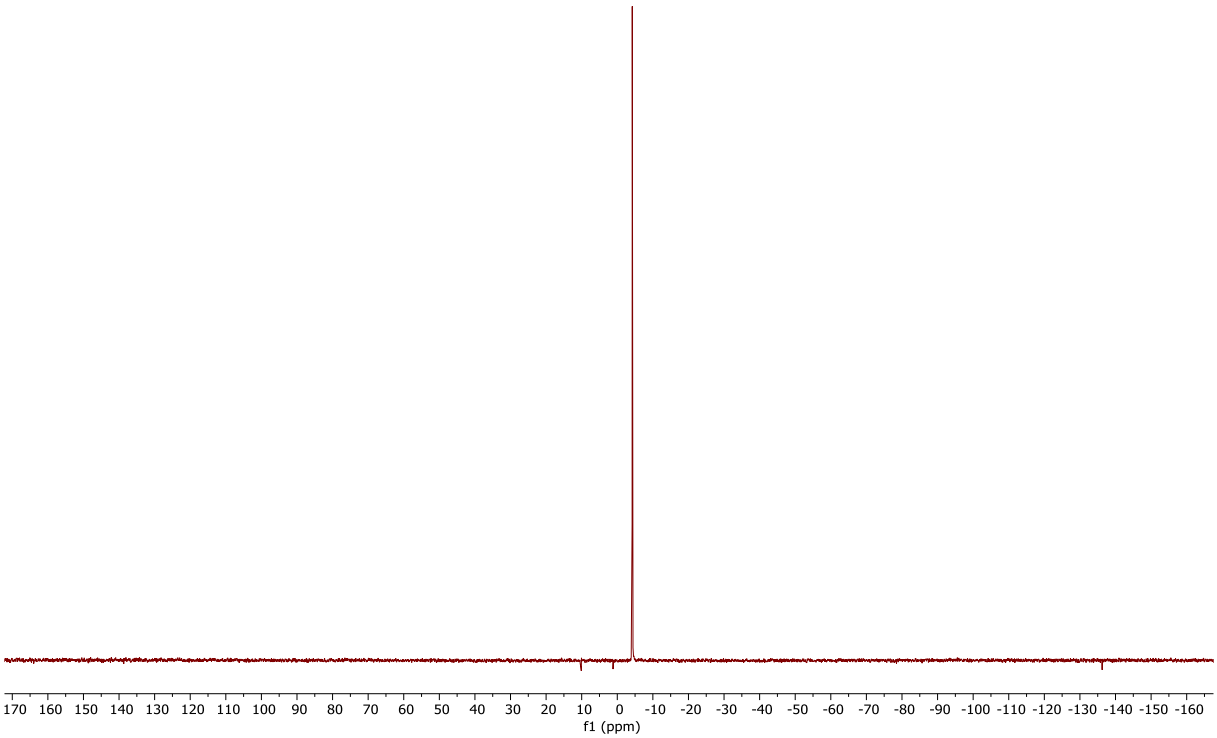


Figure S37 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of **4b**

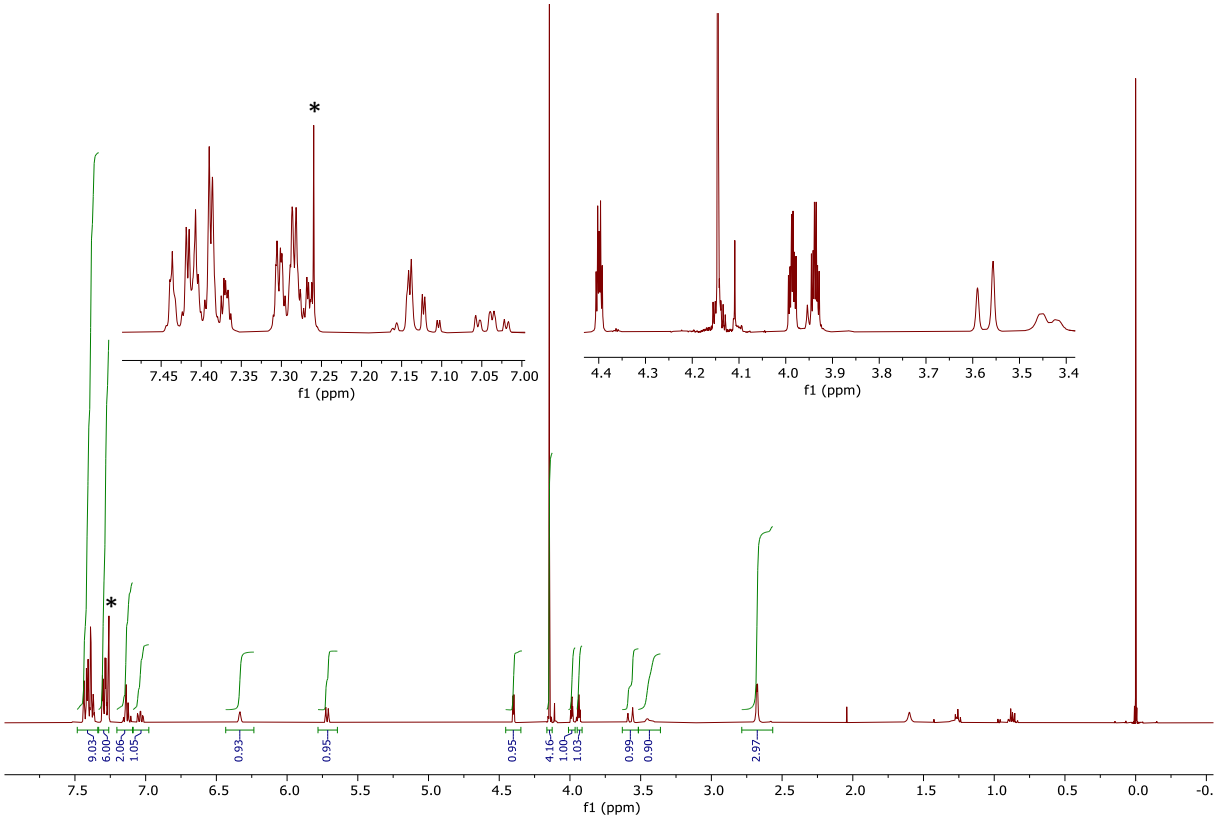


Figure S38 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5a**

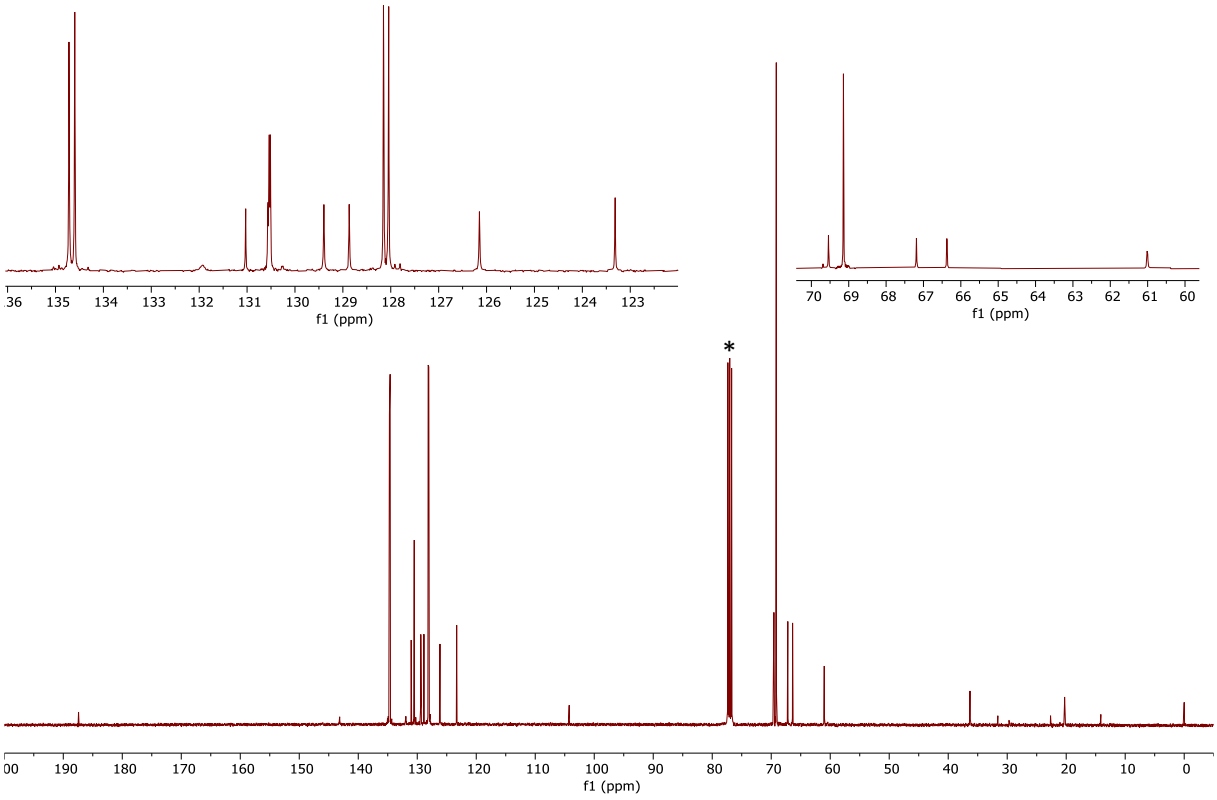


Figure S39 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **5a**

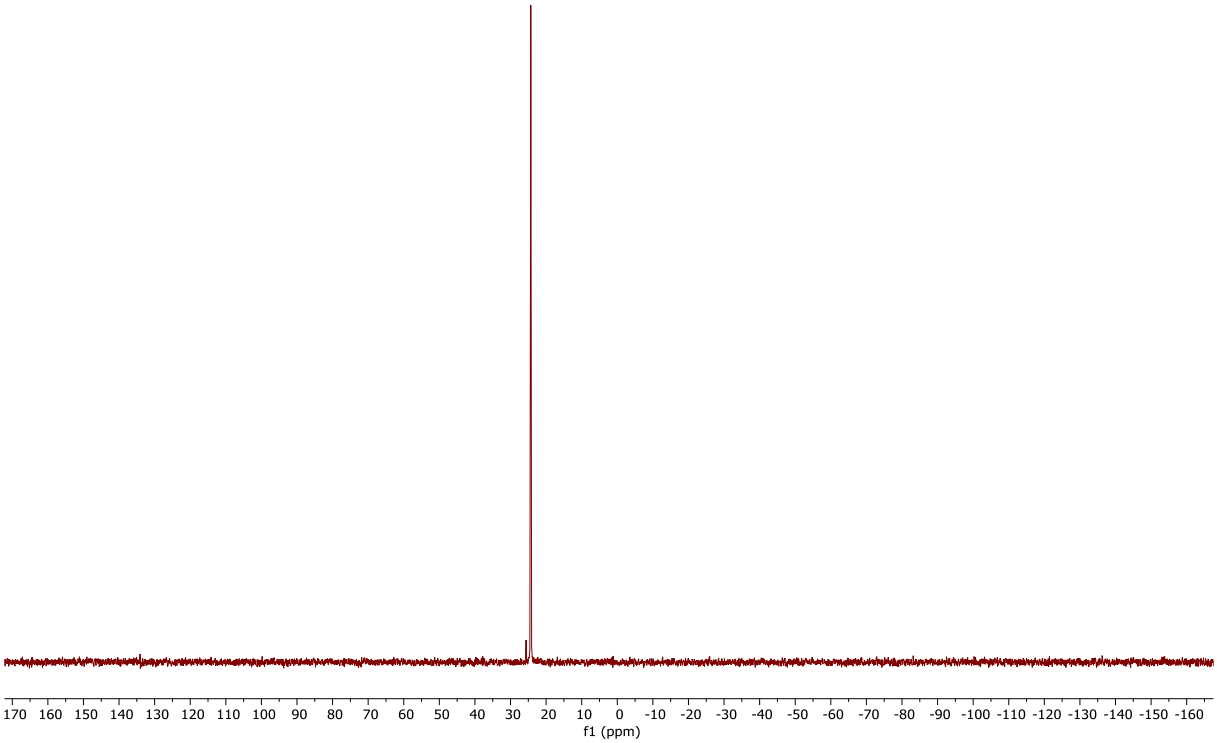


Figure S40 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of **5a**

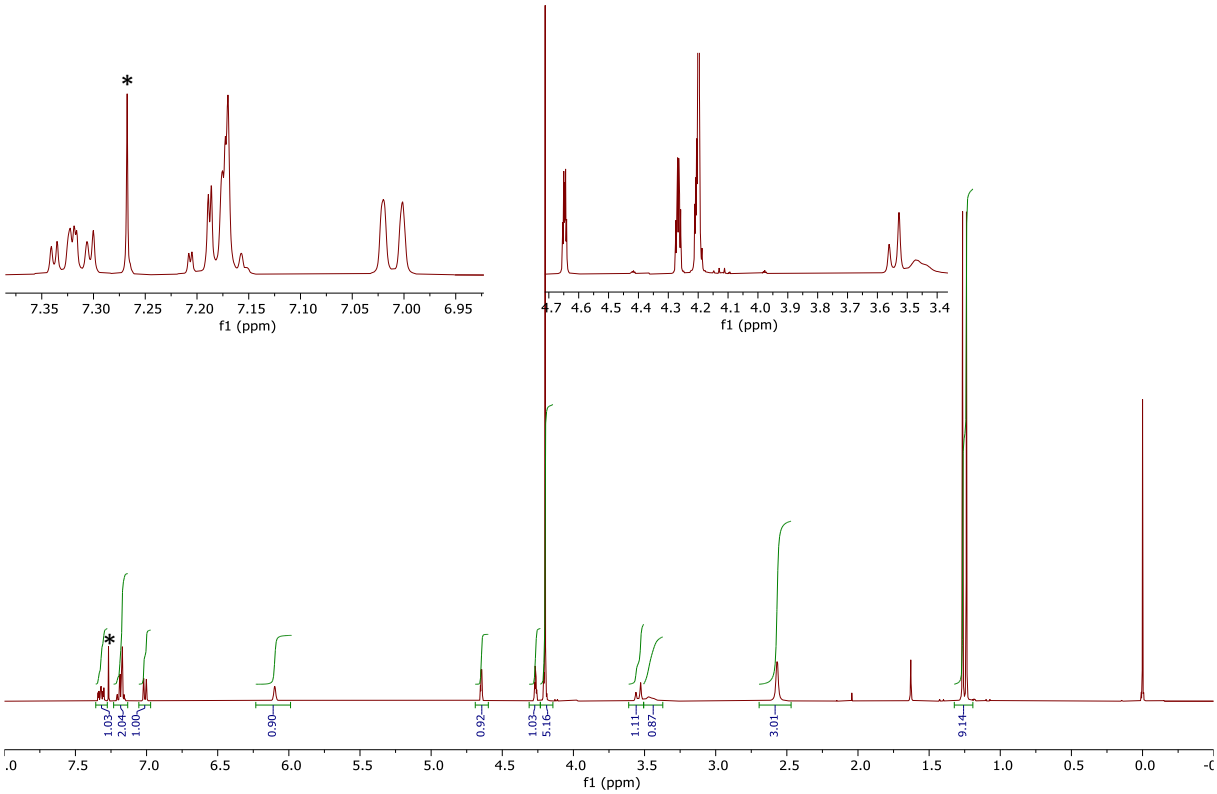


Figure S41 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5b**

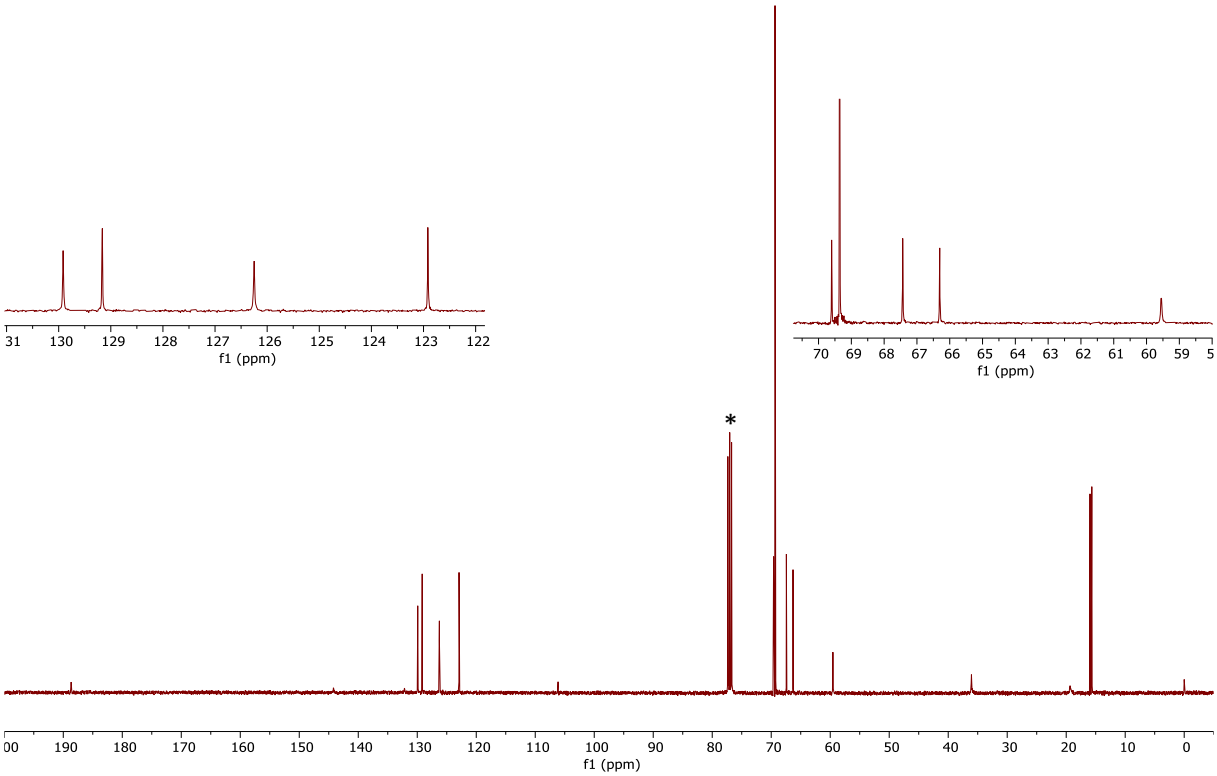


Figure S42 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **5b**

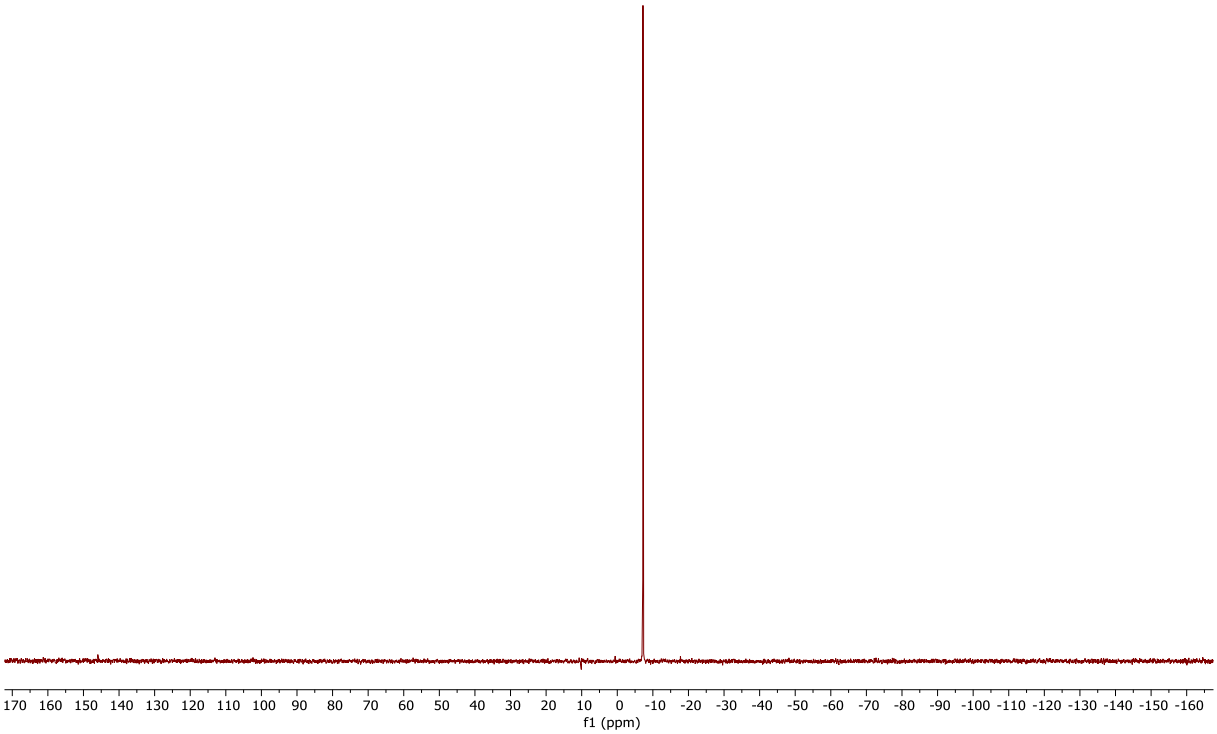


Figure S43 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of **5b**

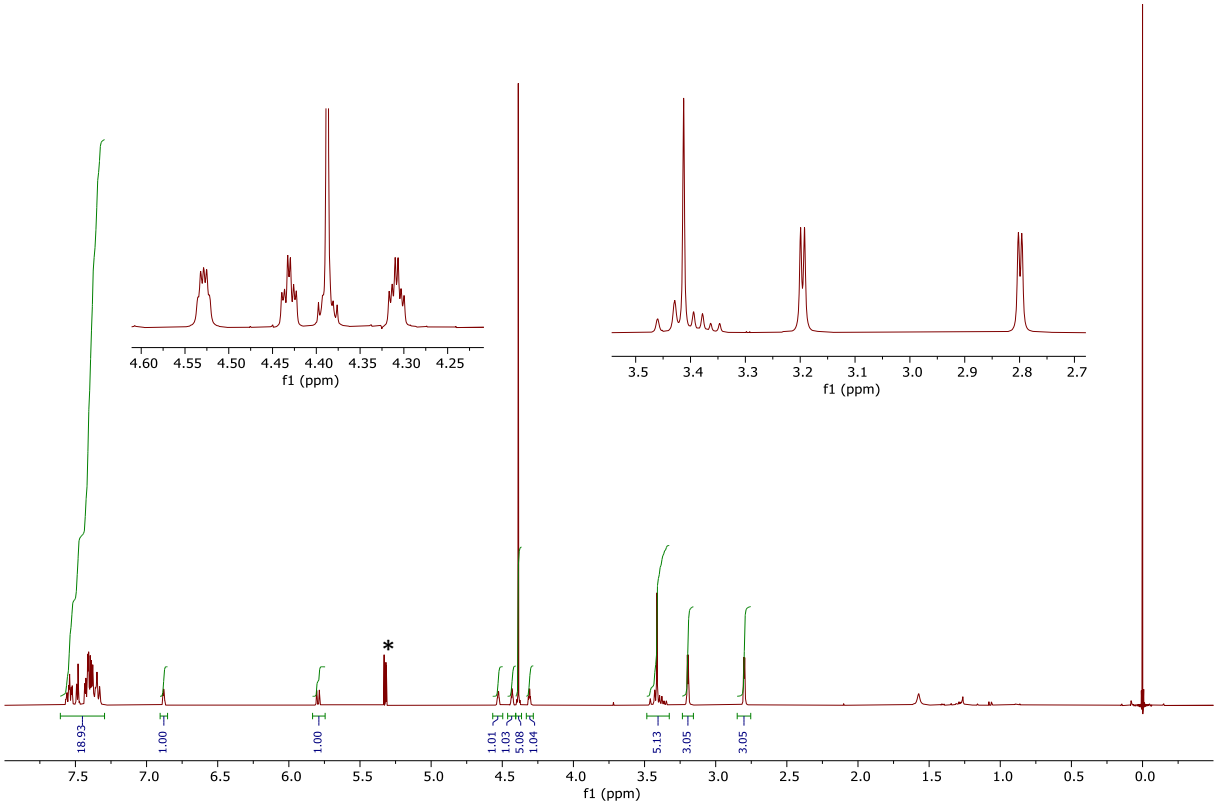


Figure S44 ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of **6a**

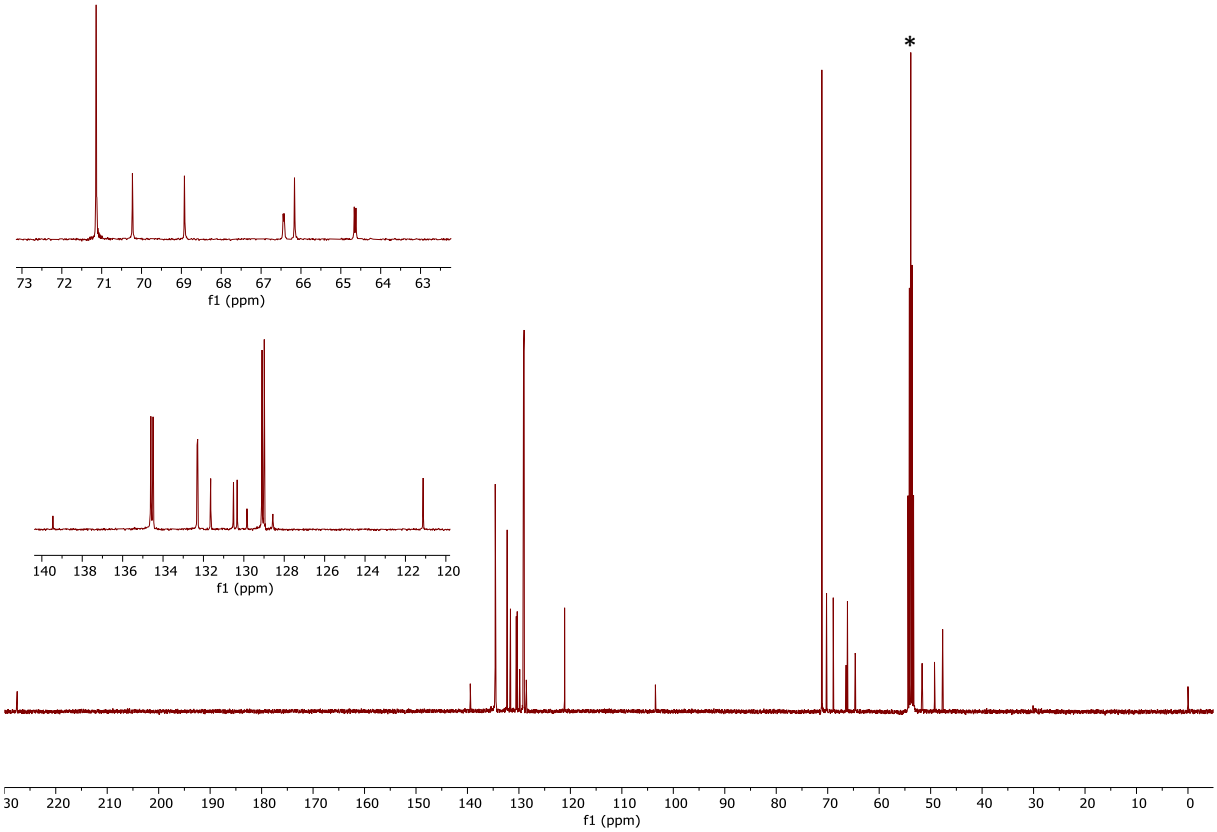


Figure S45 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, CD_2Cl_2) of **6a**

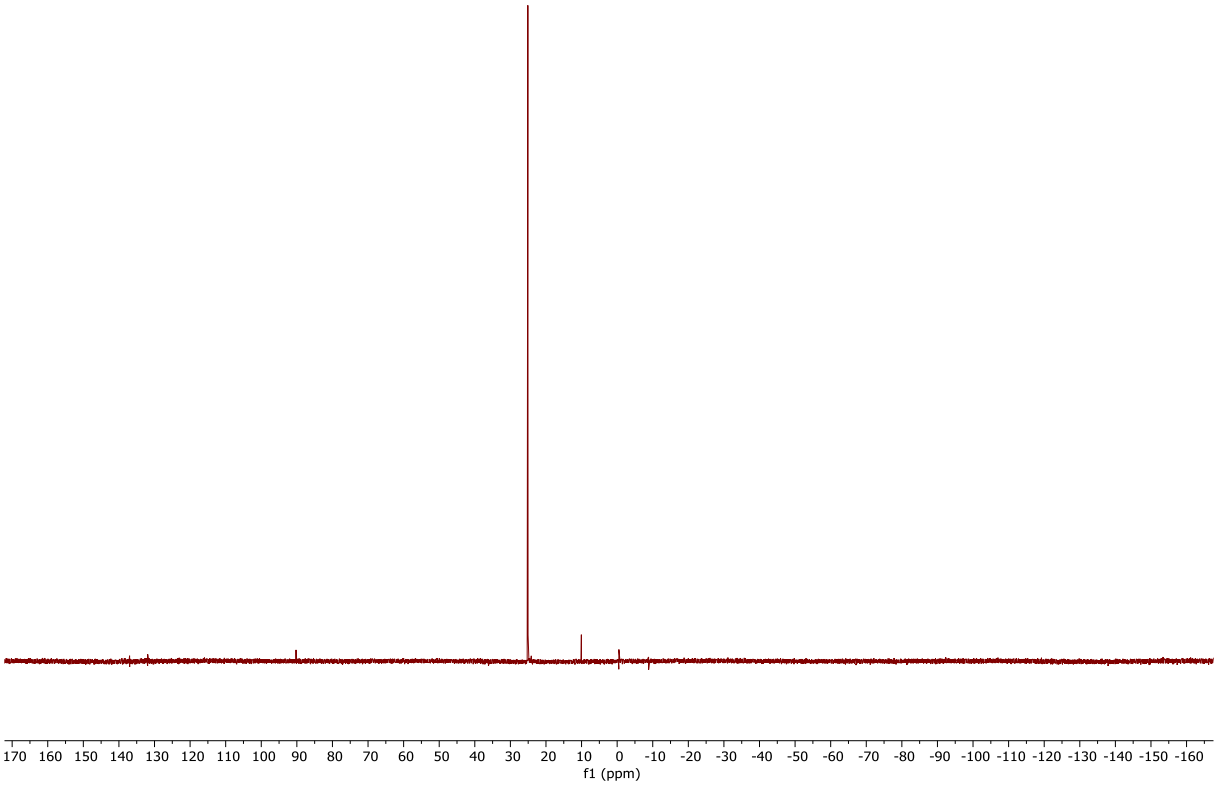


Figure S46 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, CD_2Cl_2) of **6a**

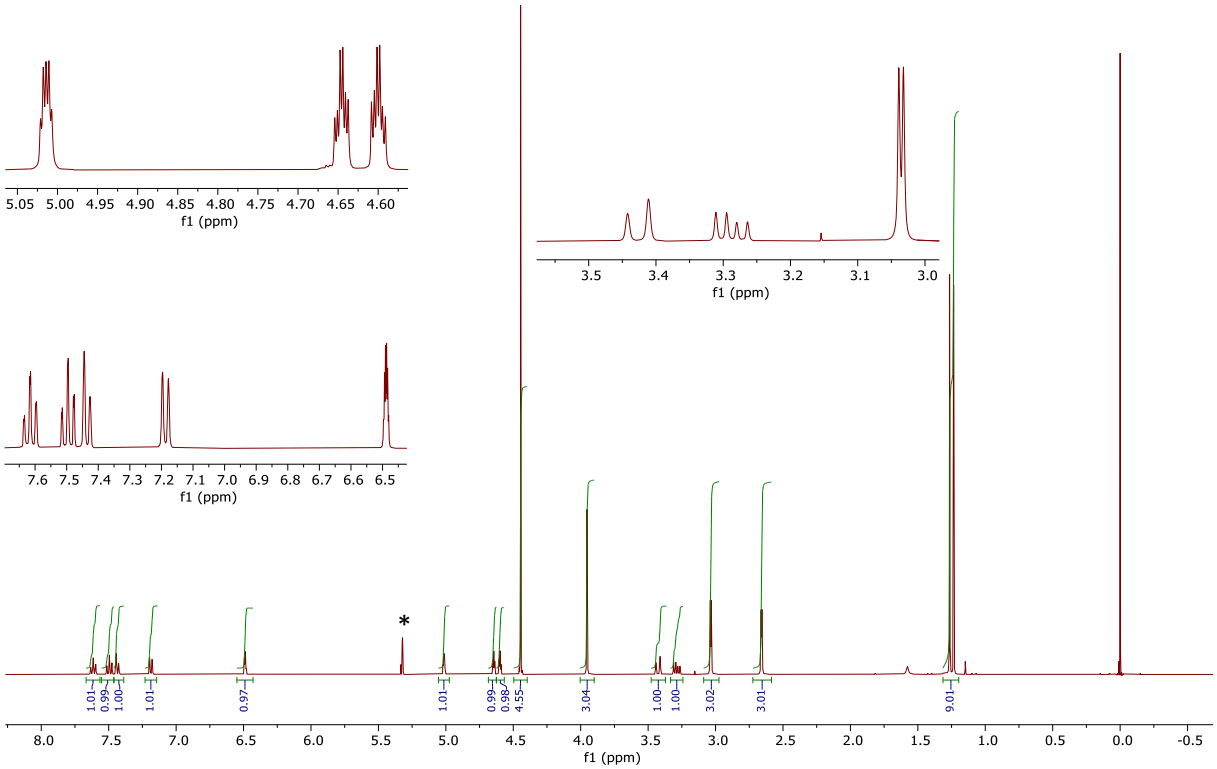


Figure S47 ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of **6b**

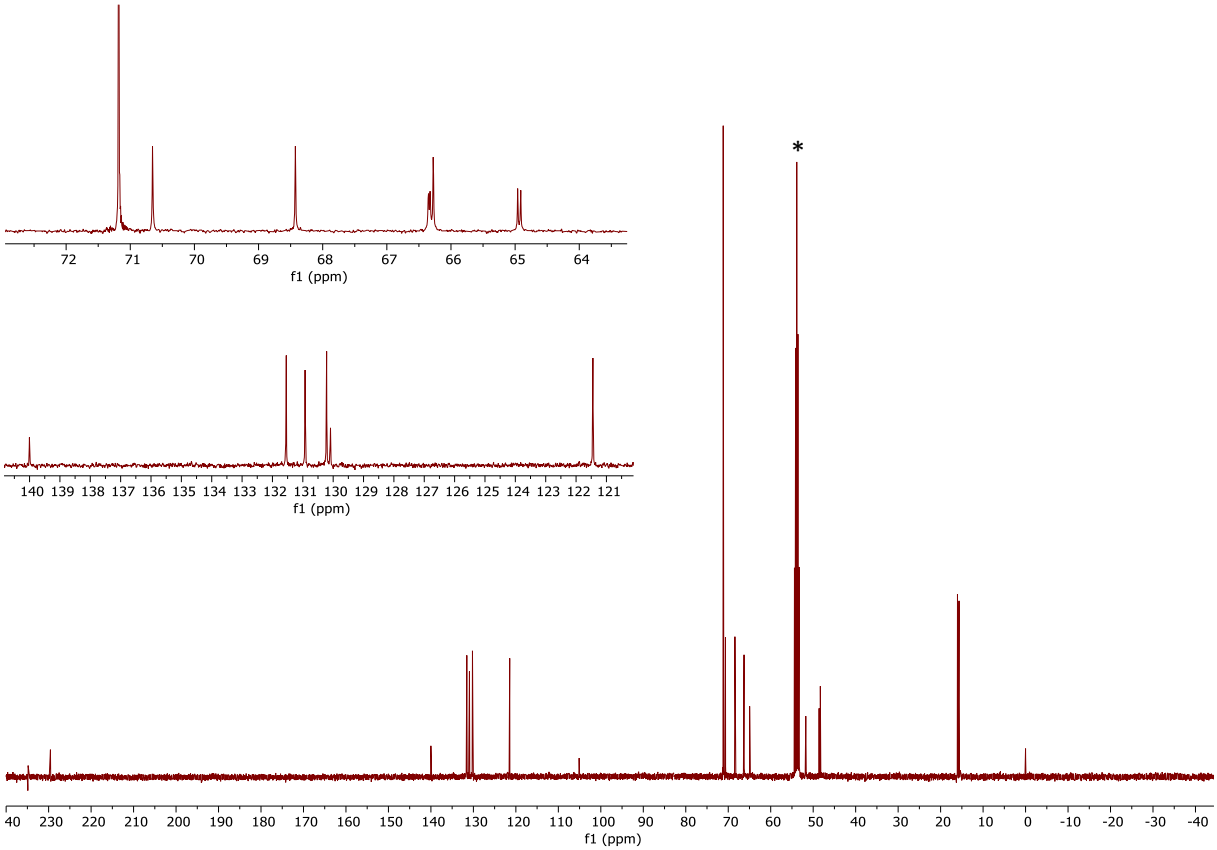


Figure S48 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, CD_2Cl_2) of **6b**

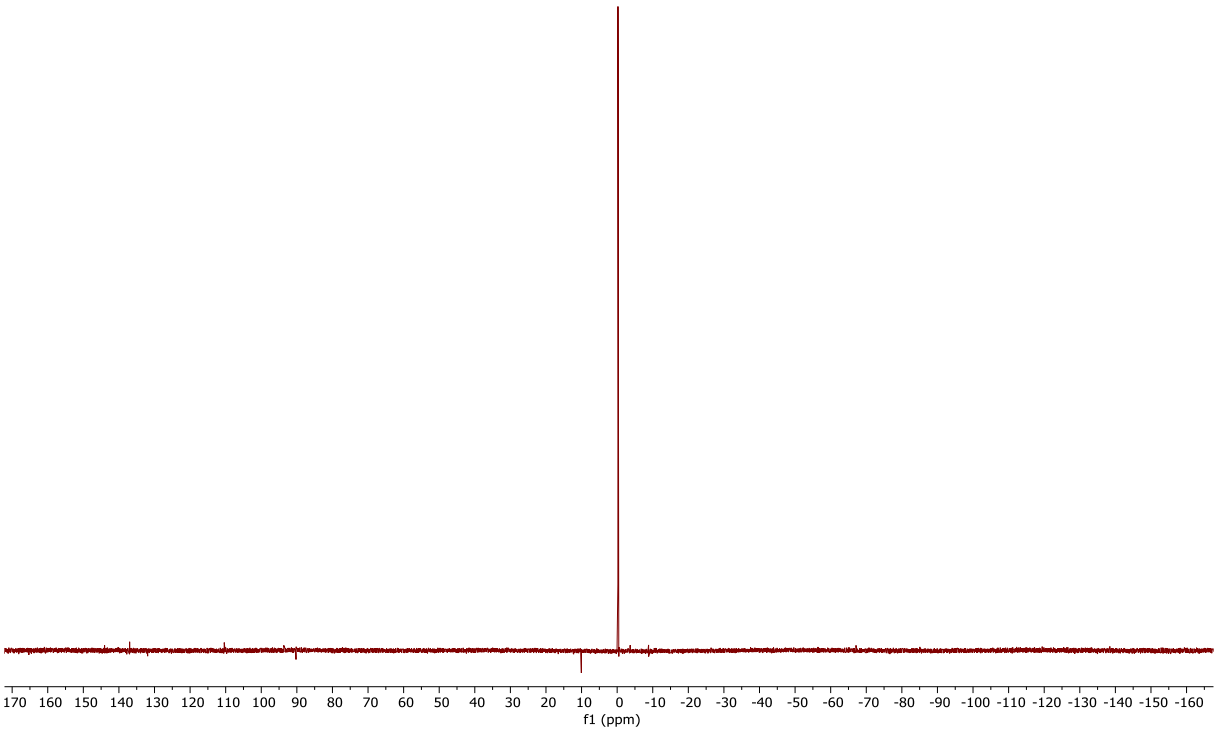


Figure S49 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, CD_2Cl_2) of **6b**

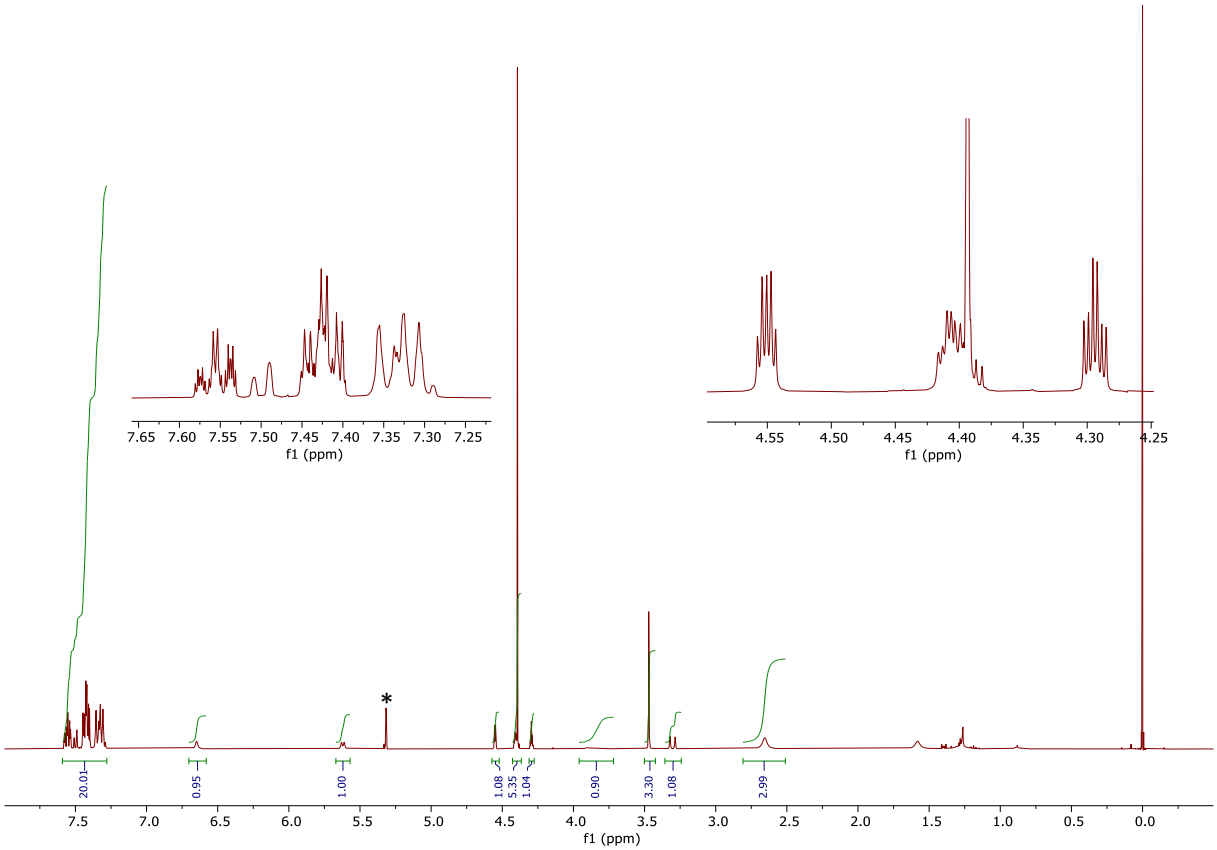


Figure S50 ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of **7a**

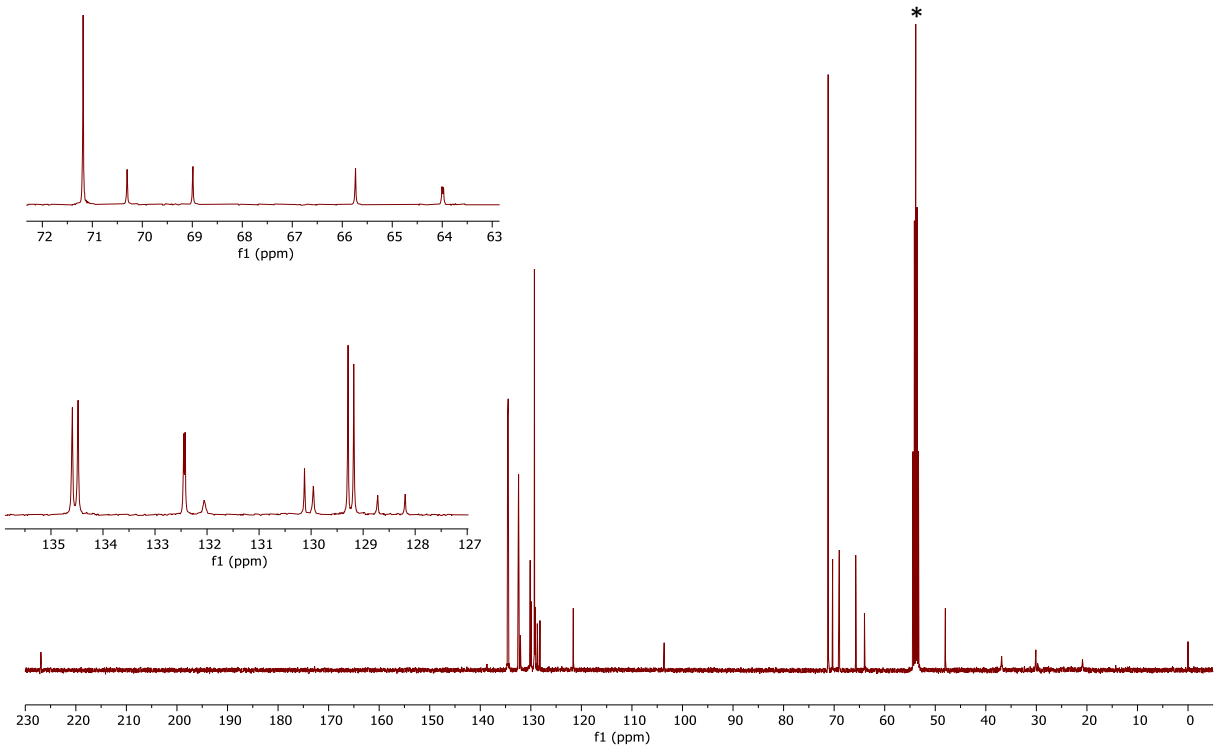


Figure S51 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, CD_2Cl_2) of **7a**

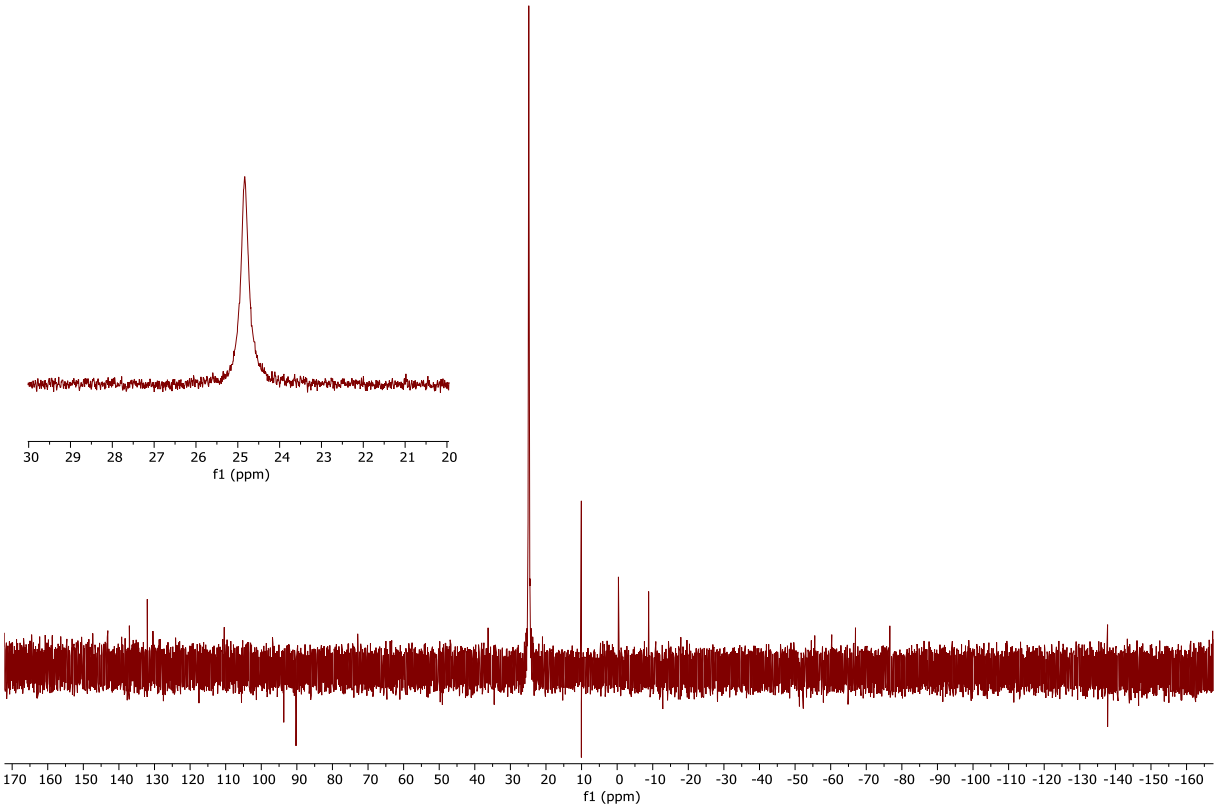


Figure S52 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, CD_2Cl_2) of **7a** (the sharp "signals" are spikes)

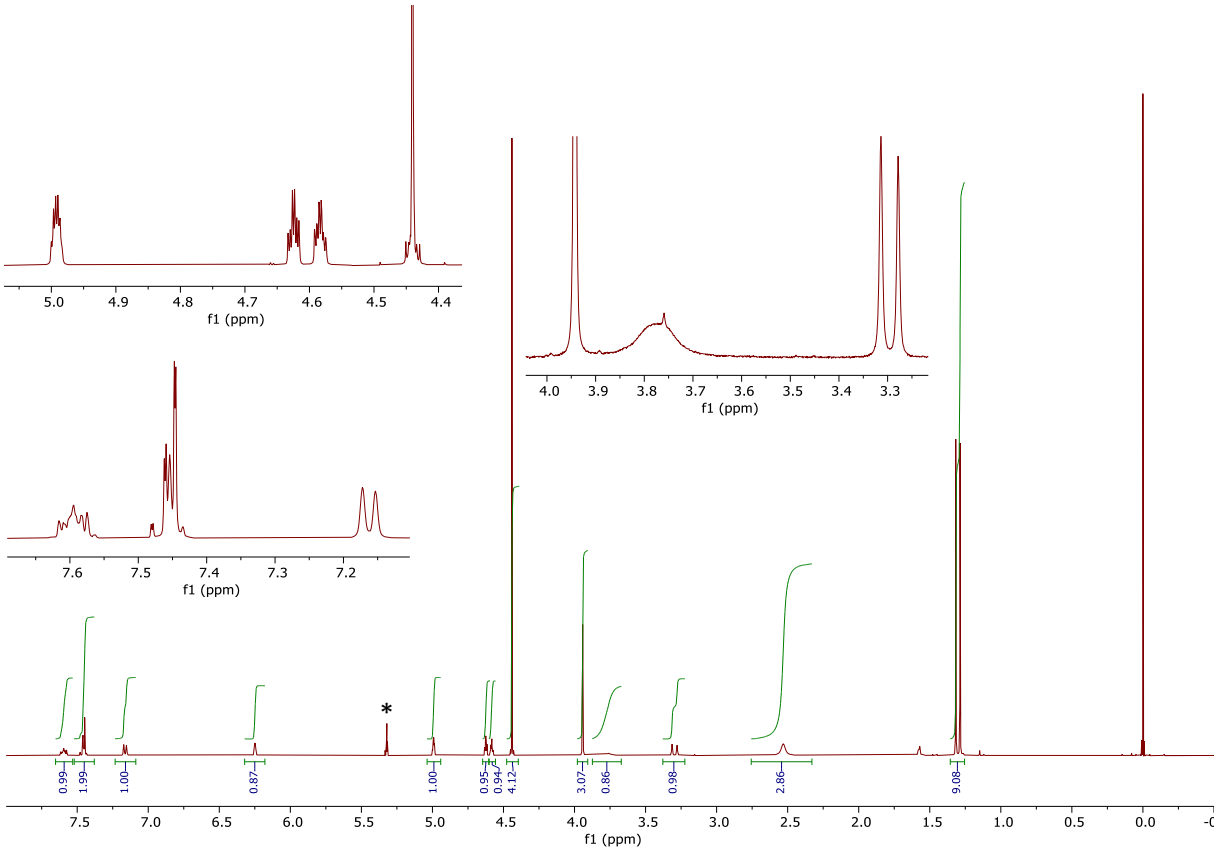


Figure S53 ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of **7b**

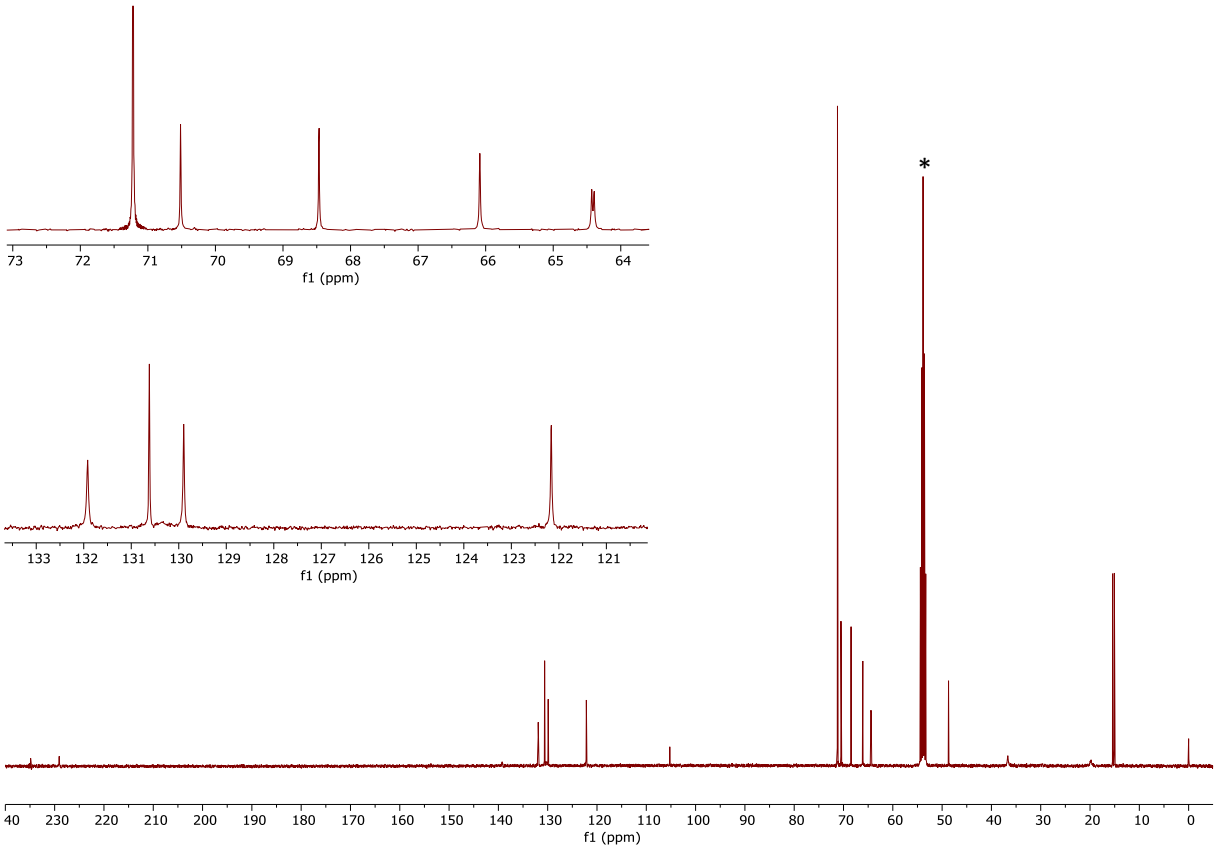


Figure S54 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, CD_2Cl_2) of **7b**

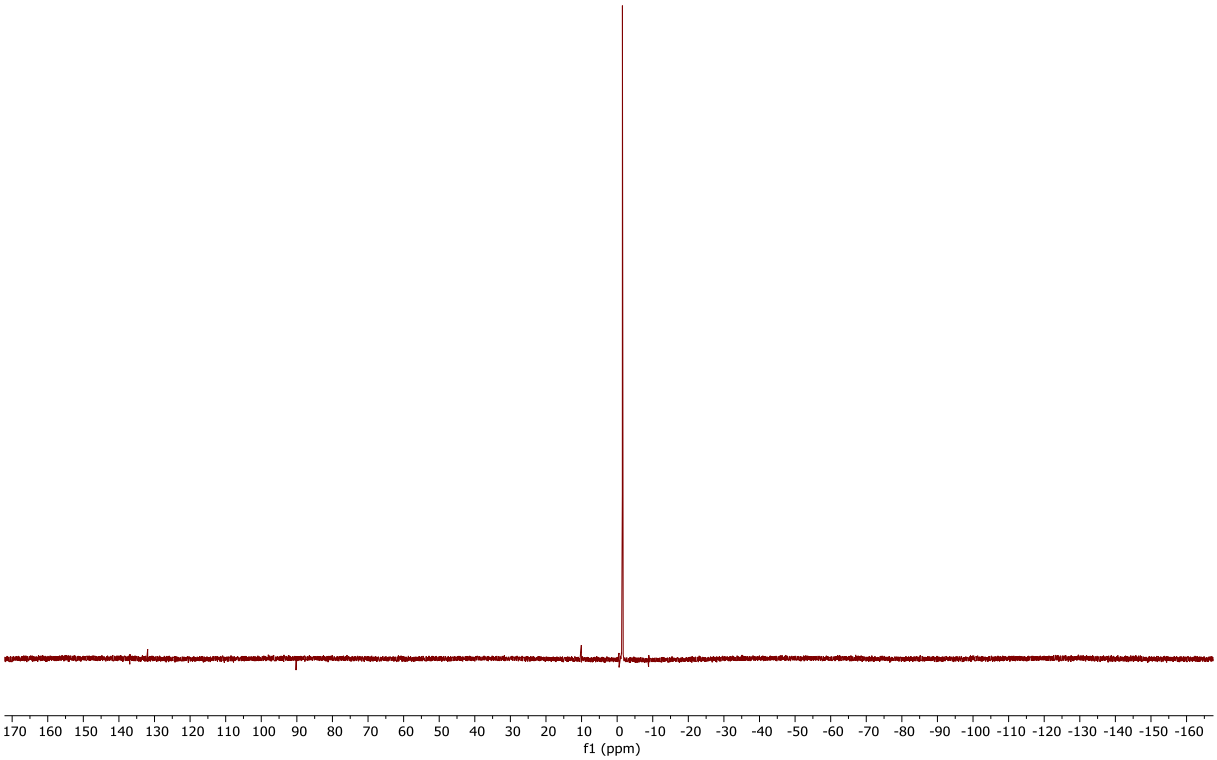


Figure S55 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, CD_2Cl_2) of **7b**

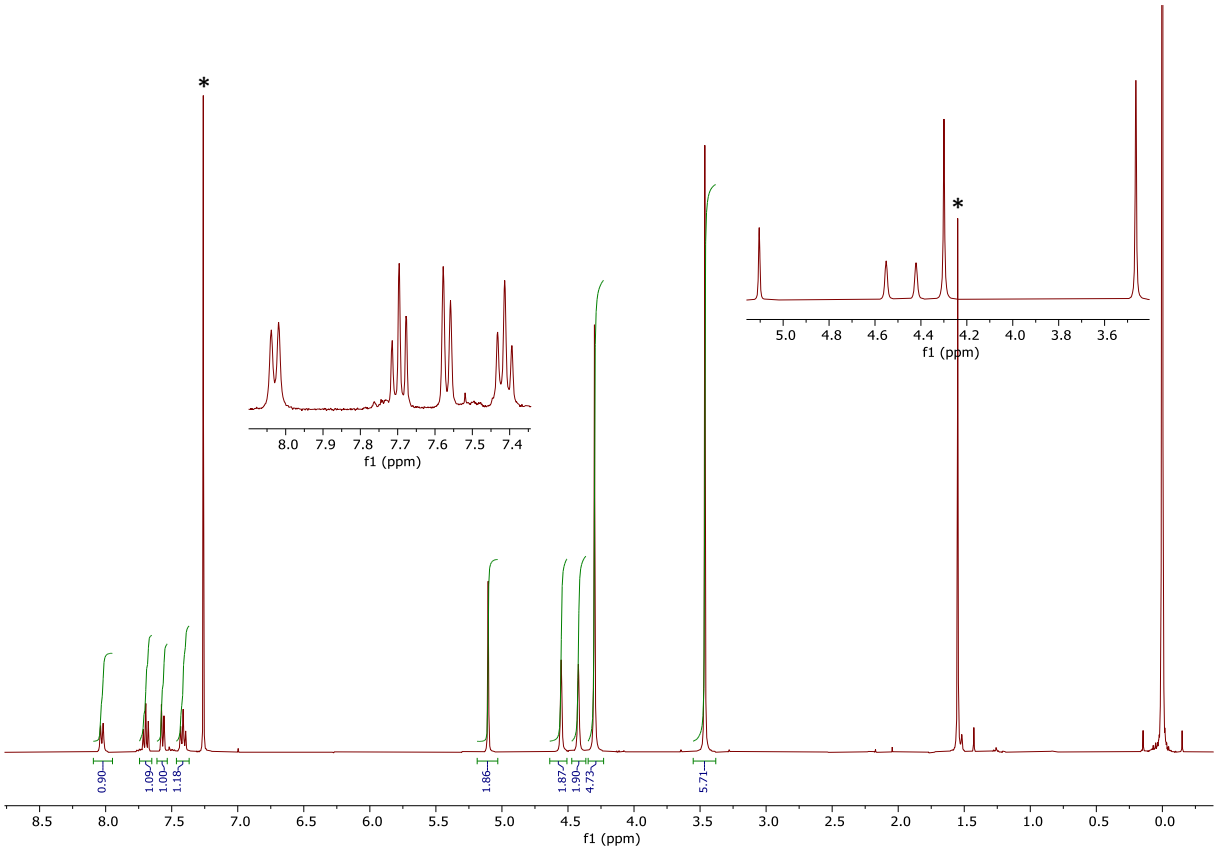


Figure S56 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **8**

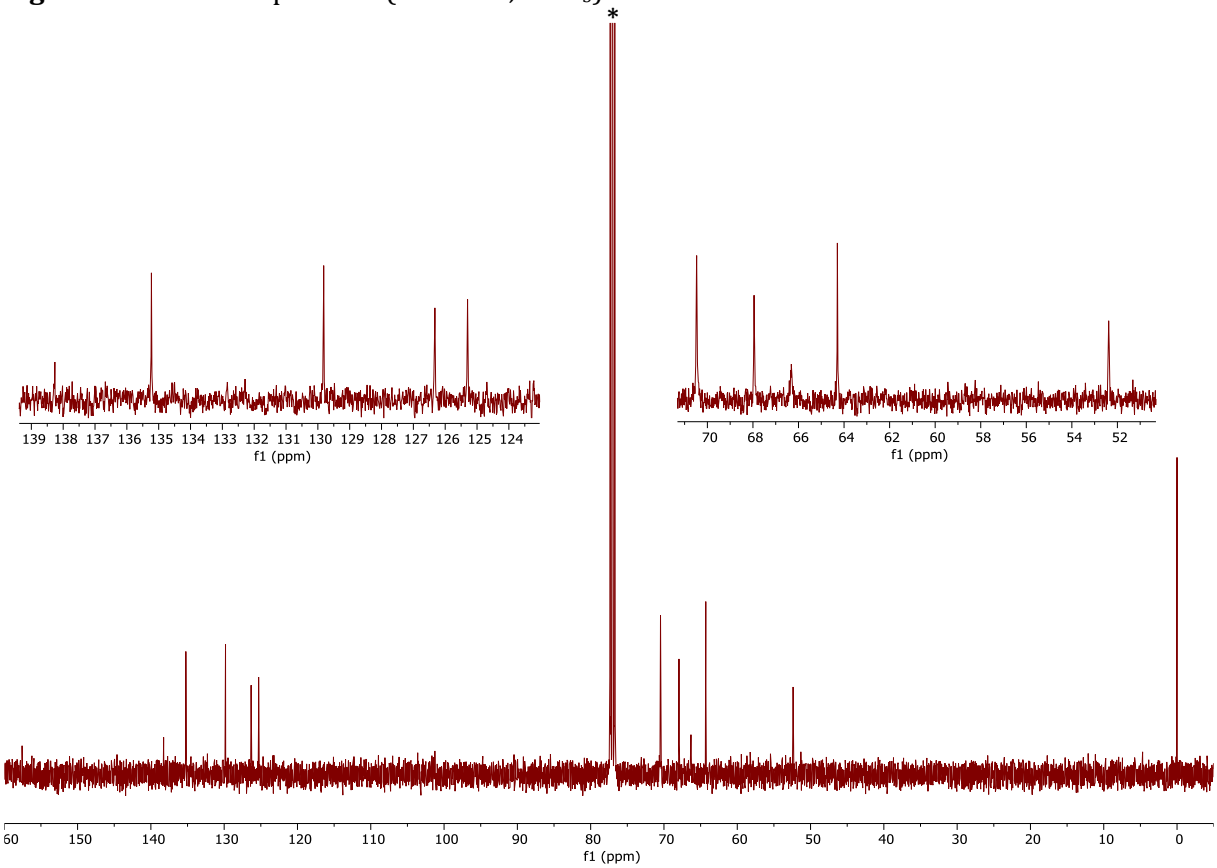


Figure S57 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **8**

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